A Computational Triage Approach into the Synthesis of Novel Difluorocyclopentenes and Fluorinated Heptadienes using Thermal Rearrangements

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Supporting Information

General Experimental

NMR spectra were recorded on Bruker DPX-400, AV-500 Avance-II+ 600 spectrometers. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded using the deuterated solvent as the lock and the residual solvent as the internal reference. The multiplicities of the spectroscopic data are presented in the following manner: s = singlet, d = doublet, dd = double doublet, ddd = doublet of double doublets, etc up to ddddd, dt = doublet of triplets, ddt = doublet of double triplet, dddt = doublet of double double triplet, dq = doublet of quartet; t = triplet, td = triple doublet; tt = triple triplet, q = quartet, ABq = AB system quartet, m = multiplet and br. = broad. Unless stated otherwise, all couplings refer to ^{3}J homocouplings. All ^{1}H spectra are fully assigned as much as possible. Relevant 2D-NMR spectra are supplied to confirm assignment.

IR spectra were recorded on a Shimadzu IRAffinity-1 FT-IR Spectrophotometer using a MIRacle™ Single Reflection Horizontal ATR Accessory.

GC/MS spectra were obtained on an Agilent 7890A GC System fitted with a DB5-type column (30 m × 0.25 µm) running a 40–320 °C temperature program, ramp rate 20 °C min^{-1} with helium carrier gas flow at 1 cm^{3} min^{-1}. Chemical ionisation (CI) (methane) mass spectra were recorded on an Agilent Technologies 5975C mass spectrometer.

HRMS measurements were obtained from a Waters GCT Premier MS (CI-MS), Fiinigan MAT 95 XP (EI-MS and/or APCI-MS) or Thermo Scientific LTQ Orbitrap XL via Advion TriVersa NanoMate infusion (NSI-ES) spectrometers (EPSRC National Mass Spectrometry Service Centre, Swansea).

Melting points were recorded on a Griffin melting point apparatus and are uncorrected.

Thin layer chromatography was performed on pre-coated aluminium-backed silica gel plates (E.Merck, A.G.Darmstadt, Germany. Silica gel 60 F254, thickness 0.2 mm). Visualisation was achieved using potassium permanganate or UV detection at 254 nm. Column chromatography was performed on silica gel (Zeochem, Zeoprep 60 HYD, 40-63 µm) using a Büchi Sepacore system. Hexane was distilled before chromatography.

Preparative HPLC was performed using Grace Reveleris PREP purification system with a Kromasil 100-10-C18 column (L = 250 mm, ID = 200 mm). Compound was loaded in a minimum volume of 1:1 DMSO:MeOH in a 5 mL sample loop. Flow rates varied depending on separation (5-30 ml/min) and peaks determined using ELSD and UV detection.

Commercial furfural (black) was percolated through a pad of alumina to afford an orange solution which was used immediately in reactions. 2-Formyl-pyrrole-1-carboxylic acid tert-butyl ester **12f** was synthesised from NaH and Boc anhydride using conditions described by Carreira and co-workers.[S1] 2-thiazolyl-carboxaldehyde **12g** was synthesised from thiazole, BuLi and DMF using conditions described by Glorius and co-workers.[S2] Due to the volatility of the aldehyde, crude product was used directly in subsequent Wittig olefinations.

Diglyme was distilled from CaH_2 (60 °C/23 mbar) and stored under nitrogen over CaH_2. Trimethylsilyl chloride was distilled from CaH_2 (60 °C/430 mbar) and stored under nitrogen over CaH_2 in the refrigerator. Methyl 2,2-difluoro-2-(fluorosulfonyl)acetate (MDFA) and trimethylsilyl 2,2-difluoro-2-(fluorosulfonyl)acetate (TFDA) were purchased from Fluorochem and stored under a headspace of nitrogen.Potassium iodide (Sigma Aldrich) and magnesium sulfate ($MgSO_4$, VWR Chemicals) were dried in the oven (150 °C) before use. DCM (for tandem oxidation/olefination, acetylation and cyclopropanation reactions) and toluene (for reduction reactions) were dried using a PureSolv system from Innovative Technology, Inc..

All other chemicals were purchased from Sigma Aldrich, Apollo Scientific, Alfa Aesar, or Fluorochem and used as received.

Computational Methodology

Structures were built in Spartan’10 using previously published compounds as models and geometry optimisation calculations were carried out for all closed shell compounds. For known diradical compounds unrestricted methodology was invoked using the keywords MIX and SCF=UNRESTRICTED, with CONVERGE deprecated. In cases where SCF convergence was difficult, the keyword NODIIS was used. All calculations were performed *in vacuo*. Spartan’10 was run on a Dell Precision T7500 (2 x Intel E5530 processors, four cores each, 2.40 GHz) with 24 GB RAM Debian GNU/Linux 5.

The calculation methods used in Spartan have been documented in: Y. Shao, L.F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S.T. Brown, A.T.B. Gilbert, L.V. Slipchenko, S.V. Levchenko, D.P. O’Neill, R.A. DiStasio Jr., R.C. Lochan, T. Wang, G.J.O. Beran, N.A. Besley, J.M. Herbert, C.Y. Lin, T. Van Voorhis, S.H. Chien, A. Sodt, R.P. Steele, V.A. Rassolov, P.E. Maslen, P.P. Korambath, R.D. Adamson, B. Austin, J. Baker, E.F.C. Byrd, H. Dachsel, R.J. Doerksen, A. Dreuw, B.D. Dunietz, A.D. Dutoi, T.R. Furlani, S.R. Gwaltney, A. Heyden, S. Hirata, C-P. Hsu, G. Kedziora, R.Z. Khalliulin, P. Klunzinger, A.M. Lee, M.S. Lee, W.Z. Liang, I. Lotan, N. Nair, B. Peters, E.I. Proynov, P.A. Pieniazek, Y.M. Rhee,J. Ritchie, E. Rosta, C.D. Sherrill, A.C. Simmonett, J.E. Subotnik, H.L. Woodcock III, W. Zhang, A.T. Bell, A.K. Chakraborty, D.M. Chipman, F.J. Keil, A.Warshel, W.J. Hehre, H.F. Schaefer, J. Kong, A.I. Krylov, P.M.W. Gill and M. Head-Gordon, *Phys. Chem. Chem. Phys*., **2006**, *8*, 3172.

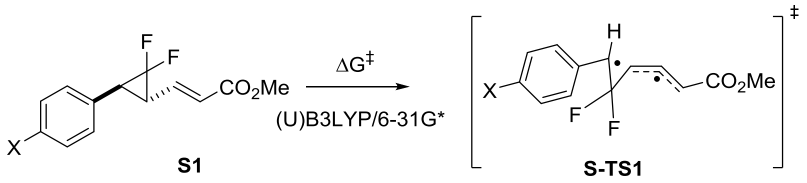
Full reference for the Gaussian09 programme: Gaussian 09, Revision A.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

Hammett Plot Data

The lower activation energy calculated for the more electron rich phenyl-substituted **9f** (-2.3 kcal mol^{-1}) prompted further investigations into the electronic effects of phenyl ring substitution. The VCPR activation energies for a range of precursors with electron-donating and -withdrawing groups were assessed (**Table S1**), focusing solely on *para*-substituents, since these show the greatest effects for resonance stabilisation of benzylic radicals. Substrates containing electron-donating groups were predicted to undergo faster rearrangement (**Table S1**, Entries 1-6) than unsubstituted **9j** (**Table S1**, Entry 7), whereas substrates bearing electron-withdrawing groups only showed a modest increase in activation energy (**Table S1**, Entries 8-12). The Hammett plot[S3] (**Figure S1**) constructed from this data gave an extremely low ρ value of 0.05 and supported a radical mechanism. A variety of free radical substituent constants ($\sigma^{\bullet}$) have been reported in the literature[S4-7] but only those reported by Creary and co-workers ($\sigma_C^{\bullet}$) are applicable to the more commonly used substituents.[S8] Our calculated activation energies correlated poorly when $\sigma_C^{\bullet}$ constants were used ($R^2 = 0.4259$) but still gave a ρ value close to zero (**Figure S1**). The relatively small increases in activation barriers, suggest that even substrates bearing electron-deficient phenyl rings should undergo VCPR at or close to 100 °C.

Both Hammett plots were generated using Excel from calculated free energies of activation ((U)B3LYP/6-31G*, gas phase, 298 K, kcal mol^{-1}) manipulated into $\log(\Delta G^{\ddagger}(X)/\Delta G^{\ddagger}(H))$ values and literature σ values[S3] (**Figure S1**) or $\sigma^{\bullet}$ values[S8] (**Table S1** and **Figure S2**). Graphs were generated on Excel and a straight line fitted using the trendline function for **Figure S1** and **Figure S2**.

Table S1: Calculated free energies of activation (298 K) and $\sigma^{\bullet}$ data used to generate Hammett Plot in **Figure S1**.



VCP	X	$\Delta G^{\ddagger}$	$\Delta\Delta G^{\ddagger}$	log (ΔG(X)/ΔG (X=H))	σ^{S3}	$\sigma^{\bullet}$ ref. S8
a	$N(Me)_2$	21.2	-4.1	-0.056	-0.83	0.9
b	NH_2	21.9	-3.4	-0.042	-0.66	0.7
c	OH	23.5	-1.8	-0.011	-0.37	0.26
d	OMe	23.3	-2.0	-0.015	-0.27	0.27
e	NHC(O)Me	23.7	-1.6	-0.007	-0.17	0.34
f	Me	24.5	-0.8	-0.072	0	0.16
9j	H	25.3	0	0.000	*0*	-
i	Cl	25.3	0	0.021	0.23	0.11
j	Br	25.4	0.1	0.023	0.23	0.11
k	CF_3	25.4	0.1	0.023	0.54	0.05
l	CN	25.6	0.3	0.026	0.66	0.47
m	NO_2	25.9	0.6	0.031	0.78	0.57

[a] $\Delta\Delta G^{\ddagger}_{B3LYP} = (\Delta G^{\ddagger}_{B3LYP}$ **S1x**$)-(\Delta G^{\ddagger}_{B3LYP}$ **9j**$)$

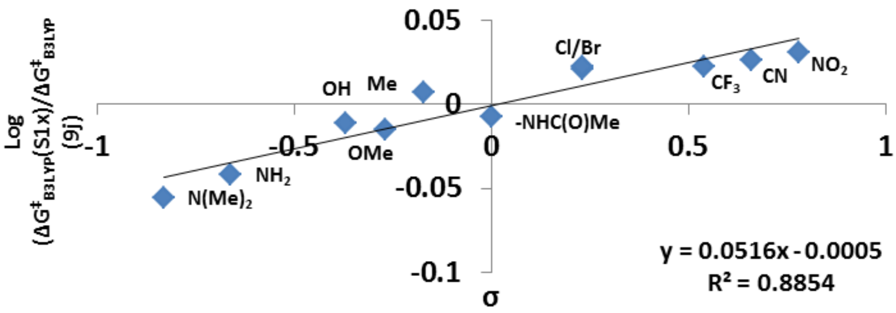


Figure S1: Hammett plot generated from calculated free energies of activation and σ values.

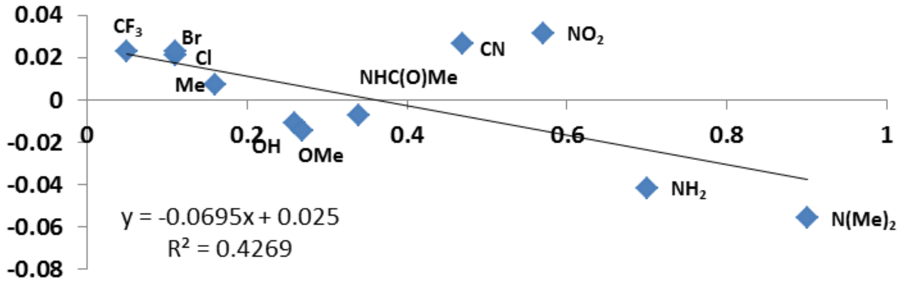
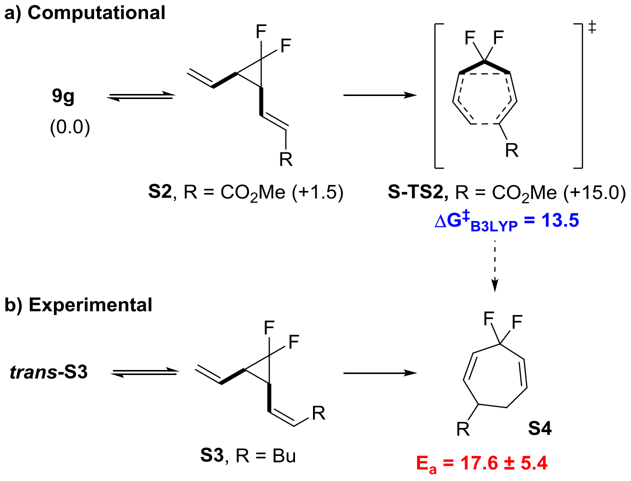


Figure S2: Hammett plot generated from calculated free energies of activation and $\sigma^{\bullet}$ values.

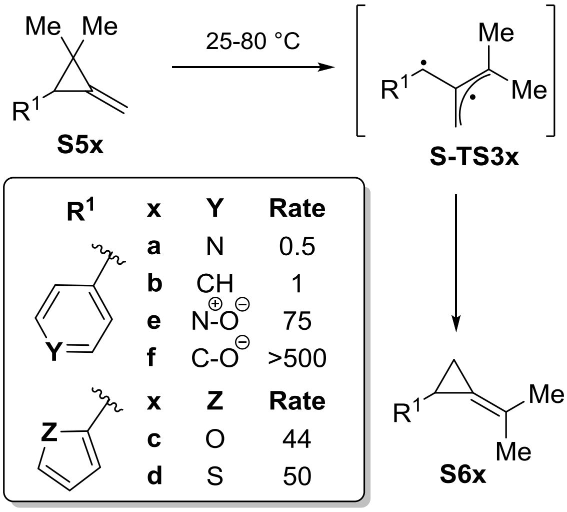
Radical Stabilising Effects

As our prime goal was to lower VCPR reaction temperatures, our screening was directed towards vinyl, (hetero)aryl and alkynyl substituents because the most effective mechanism for radical stabilisation is delocalisation through adjacent π-systems.[S9,10] The lower activation energy observed for **9g** (ethenyl, 24.5 kcal mol^{-1}) compared with **9j** (phenyl, 25.3 kcal mol^{-1}) and **9l** (ethynyl, 25.9 kcal mol^{-1}) showed good correlation with the increased radical stabilisation energy reported for these substituents (calculated as 17.6, 14.6 and 14.5 kcal mol^{-1}, respectively).[S10] The higher activation energy observed for **9p** (cyano, 29.3 kcal mol^{-1}) can be rationalised by a decreased radical stabilisation energy (7.9 kcal mol^{-1}),[S10] which arises from the higher electronegativity of the nitrogen atom. These calculations suggested that *bis*-vinyl VCP-**9g** has the potential to rearrange at temperatures lower than 100 °C, but electronic structure calculations predicted that *cis*-isomer **S2** would favour divinylcyclopropane rearrangement via **S-TS2** ($\Delta G^{\ddagger}_{B3LYP}$ = 13.5 kcal mol^{-1}, VCPR vs [3,3] difference of 11.5 kcal mol^{-1}, **Scheme S1a**). Erbes and Boland showed experimentally that a similar dialkenyl-substituted *gem*-difluorocyclopropane (**S3**) exclusively favoured the [3,3]-pathway through to heptadiene **S4** (**Scheme S1b**).[S11] Dialkenyl-**9g** was omitted from any subsequent synthetic investigations due to the unlikelihood of selective VCPR.



Scheme S1: a) Predicted lower energy [3,3]-pathway for bis-vinyldifluorocyclopropane **S2** (free energies are relative to **9h**). b) Experimental example of preferential divinylcyclopropane rearrangement from bis-vinyl-difluorocyclopropane **S3** to difluoroheptadiene **S4**[S11] (experimental activation energy (E_a) is derived from an Arrhenius determination of reported kinetic data[S11]).

Of the heteroaromatic substituents examined, only the 2- and 4-pyridyl species gave higher VCPR barriers compared with **9j** (**9o**, +2.9 kcal/mol^{-1} and **9m**, +1.1 kcal mol^{-1}); the nitrogen atom cannot help stabilise radicals in these cases. Creary and co-workers reported similar results during investigations into the radical rearrangement of methylenecyclopropane **S5** to isopropylidenecyclopropane **S6** (**Scheme S2**).[S8,12]

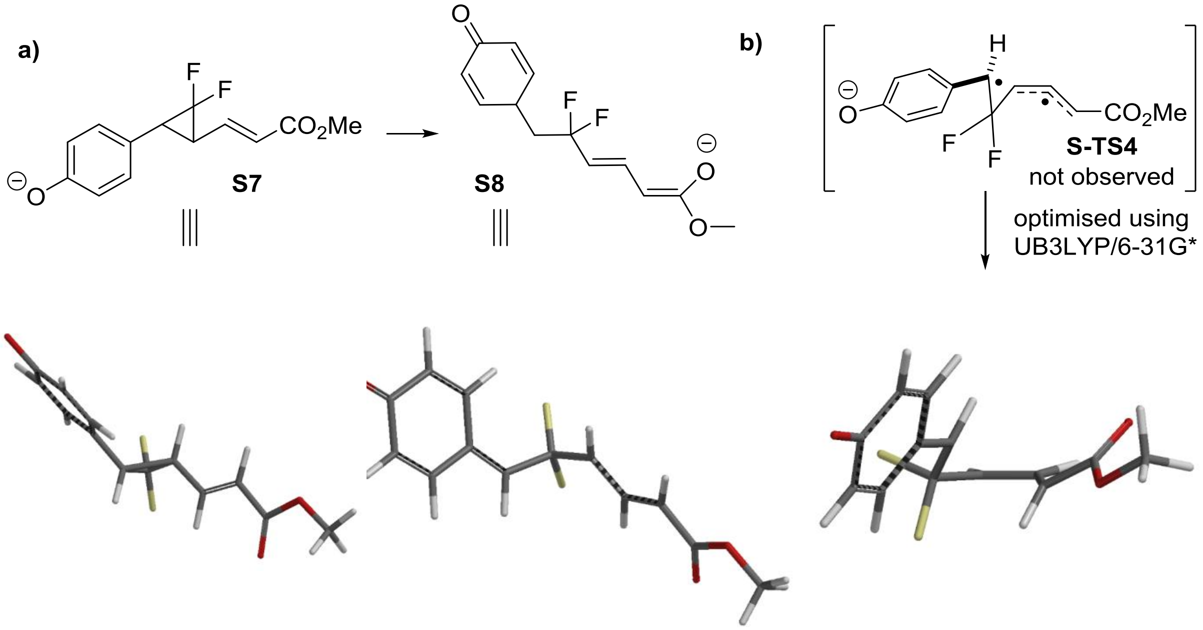


Scheme S2: Substituent group radical stability determined from the rate of rearrangement of **S5** to **S6**.[S8]

They reported higher rearrangement rates when heterocycles **S5c-e** and phenolate **S5f** were present. These substituents were dubbed “super radical stabilisers”. Unfortunately all computational attempts at incorporating the most strongly-activating 4-phenoxide substituent into a VCPR failed; a diradicaloid transition state could not be obtained. Ring opening occurred via a donor-acceptor mechanism when the rearrangement precursor was optimised[S13,14] (*vida infra*).

Computational Searches Involving Phenolate S7

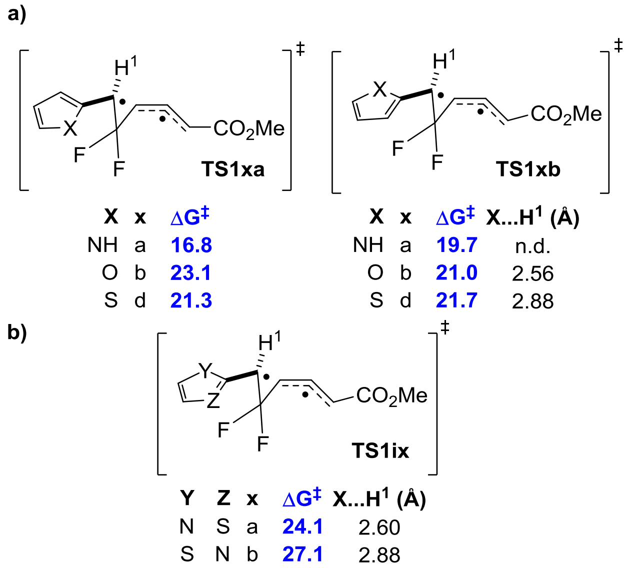
Intermediate VCP **S7** and transition state **S-TS4** were built from previously optimised structure of phenyl VCP **9j** and **TS1j** and optimised using B3LYP/6-31G* or UB3LYP/6-31G*, respectively (Spartan'10, gas phase, 298 K, multiplicity = 1). It was observed that closed shell intermediate **S7** optimised to ring opened cyclopropane intermediate **S8** (Scheme **S3a**); desired VCP **S7** was never observed after optimisation. An optimised transition state structure could be obtained from **S-TS4** (ν_i = i107 cm^{-1}) but the lack of diradical character (S^2 = 0.0001) suggested that the process had a donor-acceptor mechanism rather than VCPR (Scheme **S3b**).



Scheme S3: Failed attempts at obtaining optimised structures for a) intermediate **S7** and b) transition state **STS4**. The resulting structures strongly suggest the process proceeds *via* a donor-acceptor mechanism.

Regioselectivity with Heteroarene Precursors

When, the heteroarenes were embedded in our VCPR system, the calculated activation energies (for **9b-9d**) were consistently lower (ranging from -5.3 to -4.2 kcal mol^{-1} lower) than for phenyl **9j**. Two regioisomeric transition-states exist for the unsymmetrical species; the 2-pyrrolyl and 2-thiophenyl species favoured **TS1a** whilst the 2-furyl favoured **TS1b** (**Figure S3a**).



X	x	ΔG‡
NH	a	**16.8**
O	b	**23.1**
S	d	**21.3**

X	x	ΔG‡	X...H^1 (Å)
NH	a	**19.7**	n.d.
O	b	**21.0**	2.56
S	d	**21.7**	2.88

Y	Z	x	ΔG‡	X...H^1 (Å)
N	S	a	**24.1**	2.60
S	N	b	**27.1**	2.88

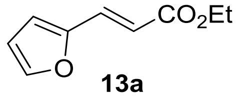
Figure S3: Two alternative VCPR transition states available for difluoro-VCP substituted with heteroarenes (ΔG‡ energies calculated on Spartan'10, (U)B3LYP/6-31G*, 298 K, gas phase, energies quoted in kcal mol^{-1}).

We propose that the lower energies observed for **TS1bb** compared with **S-TS1ba** arose from a complementary polar interaction between the δ$^+$ proton (H^1) and the oxygen atom in the furan ring (calculated distances are within the sum of the Van der Waals radii used in Spartan'10). The absence of additional stabilisation observed in **S-TS1cb** over **S-TS1ca** can be attributed to lower strength S…H interactions. This was consistent with calculated activation energies for thiazolyl **TS1i**, favouring the stronger N…H interaction over S…H (**Figure S3b**).[S15] Furthermore, 2-pyrrolyl **9a** favoured **S-TS1xa** due to an unfavourable N-H…H interaction in **S-TS1ab.** The extra stabilisation experience by furyl **9b** over thiophenyl **XXc** offered some explanation as to why our calculated rearrangement rates were ordered differently from those reported by Creary and co-workers. Our lowest calculated activation energy was observed with 2-pyrrolyl **9a** (-8.5 kcal mol^{-1}), a substituent which to our knowledge has not previously been reported as a strong radical stabiliser.

Synthetic Procedures

General Procedure A: Synthesis of Alkenoates from Commercial Aldehydes

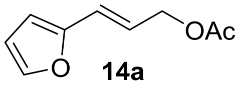
Preparation of ethyl 3-(2′-furyl) prop-2*E*-enoate (13a)



13a

(Carbethoxmethylene)triphenylphosphorane (3.7 g, 10.4 mmol) was added to a solution of furfural **12a** (0.79 mL, 9.5 mmol) in anhydrous DCM (50 mL) and the reaction mixture stirred at room temperature under nitrogen for 7 hours. An aliquot was taken and TLC confirmed full conversion of aldehyde. The reaction mixture was concentrated under reduced pressure and column chromatography on silica gel (1:9 Et_2O in hexane) afforded alkenoate **13a** (1.36 g, 82%) as a yellow oil. R_f = 0.31 (1:4 Et_2O in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 1.8 Hz; Ar*H*, 1H), 7.45 (d, *J* = 15.8 Hz, ArC*H*=CH, 1H), 6.62 (d, *J* = 3.4 Hz, Ar*H*, 1H), 6.48 (dd, *J* = 3.4, 1.8 Hz, Ar*H*, 1H), 6.33 (d, *J* = 15.8 Hz, ArCH=C*H*, 1H), 4.26 (q, *J* = 7.1 Hz, OCH_2CH_3, 2H), 1.34 ppm (t, *J* = 7.1 Hz, OCH_2CH_3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 150.5, 144.1, 130.4, 115.5, 114.0, 111.7, 59.9, 13.8 ppm; $\bar{\nu}$/(film) = 2361, 2342, 1703, 1638, 1302, 1258, 1207, 1159, 1017 cm^{-1}; MS (CI): m/z (%): 195 (12) $[M+C_2H_5]^+$, 167 (100) $[M+H]^+$, 139 (61), 121 (80) $[M-OEt]^+$; t_R (GC) = 9.62 minutes. The data was in agreement with that reported by Lebel and Davi.[S16]

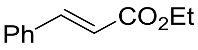
Preparation of (*E*)-3-(furan-2-yl)allyl acetate (14a)



14a

Diisobutylaluminium hydride (14.0 mL of a 1.1 M solution in cyclohexane, 15.0 mmol)) was added dropwise to a solution of ester **13a** (1.12 g, 5.0 mmol) in anhydrous toluene (40 mL) under nitrogen at 0 °C for 10 minutes. The reaction mixture was allowed to warm to room temperature and stirred for a further 8 hours, cooled to 0 °C and quenched by dropwise addition of H_2O (1 mL), 0.1 M aqueous NaOH (1 mL) and H_2O (1 mL) in that order. $MgSO_4$ was added to quenched mixture until the solid was free flowing and the mixture was left overnight at room temperature (17 h). The resulting white emulsion was washed with EtOAc (3 x 50 mL) and the organic extracts were combined and concentrated under reduced pressure. ^{1}H NMR spectrum confirmed full conversion to the corresponding alcohol (603 mg, 97%) which was directly acetylated without further purification. Acetic anhydride (0.78 ml, 8.3 mmol) was added dropwise to a solution of crude alcohol (860 g, 6.9 mmol) and pyridine (0.67 ml, 8.3 mmol) in DCM (7 mL) under nitrogen and the reaction mixture was heated to 45 °C for 5 hours. The TLC of the reaction mixture showed complete consumption of alcohol. H_2O (20 mL) was added to the reaction mixture and the organic layer separated. The aqueous layer was extracted with DCM (2 x 10 mL) and the organic layer and extracts were combined and backwashed with HCl (2 x 20 mL of a 1 M aqueous solution), NaOH (3 x 20 mL of a 10 M aqueous solution) and aqueous NaCl (20 mL) in that order. The resulting organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. Any remaining pyridine in the resulting oil was removed by co-evaporation with toluene (2 x 25 mL) to afford acetate **14a** as a colourless oil (950 g, 83%). R_f = 0.43 (1:4 Et_2O in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, J = 1.8 Hz, ArH, 1H), 6.49 (dt, J = 15.8 Hz, ^4J = 1.3 Hz, ArCH=CHCH$_2$, 1H), 6.40 (dd, J = 3.5, 1.8 Hz, ArH, 1H), 6.30 (d, J = 3.4 Hz, ArH, 1H), 6.23 (dt, J = 15.8, 6.5 Hz, CH=CHCH$_2$, 1H), 4.72 (dd, J = 6.4 Hz, ^4J = 1.3 Hz, CH_2OAc, 2H), 2.12 ppm (s, COCH_3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 151.3, 141.9, 121.6, 121.2, 110.9, 108.4, 64.1, 20.5 ppm; $\bar{\nu}$/(film) = 2359, 1734, 1377, 1360, 1223, 1013 cm^{-1}; MS (CI): m/z (%): 166 (5) [M], 123 (8) [M-COMe]$^+$, 107 (100) [M-OAc]$^+$, 61 (75); t_R (GC) = 10.26 minutes. The data were in agreement with those reported by Iwasaki and co-workers.[S17]

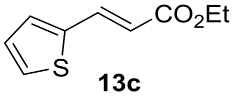
Preparation of cinnamyl acetate (13b)



13b

Ester **13b** was prepared from benzaldehyde **12b** (1.06 ml, 10 mmol), (carbethoxmethylene)triphenylphosphorane (3.83 g, 11.0 mmol) and DCM (20 ml) according to General Procedure A. Column chromatography on silica gel (1:4 Et_2O in hexane) afforded ester **13b** as a yellow oil (930 mg, 87%). ^{1}H NMR data was consistent with a commercial sample.

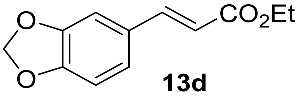
Preparation of ethyl 3-(2'-thiophenyl)-prop-2*E*-enoate (13c)



13c

Ester **13c** was prepared from thiophene-2-carbaldehyde **12c** (0.92 ml, 10 mmol), (carbethoxmethylene)triphenylphosphorane (4.6 g, 11.2 mmol) and DCM (30 ml) over 20 hours according to General Procedure A. Column chromatography on silica gel (1:4 Et_2O in hexane) afforded ester **13c** as a yellow oil (1.79 g, 98%). R_f = 0.31 (1:1 Et_2O in hexane); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 15.7 Hz, ArC*H*=CH, 1H), 7.39 (d, *J* = 5.1 Hz, Ar*H*, 1H), 7.27 (d, *J* = 3.6 Hz, Ar*H*, 1H), 7.07 (dd, *J* = 5.1, 3.6 Hz, Ar*H*, 1H), 6.26 (d, *J* = 15.7 Hz, ArCH=C*H*, 1H), 4.27 (q, *J* = 7.0 Hz, OCH_2CH_3, 2H), 1.35 ppm (t, *J* = 7.0 Hz, OCH_2CH_3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.4, 139.1, 136.5, 130.3, 127.8, 127.6, 116.5, 60.0, 13.8 ppm; $\bar{\nu}$/(film) = 2358, 2342, 1703, 1624, 1369, 1304, 1202, 1159,1042 cm^{-1}; MS (CI): m/z (%): 211 (13) $[M+C_2H_5]^+$, 183 (100) $[M+H]^+$, 137 (80) $[M-OEt]^+$; t_R (GC) = 11.85 minutes. The data was in agreement with that reported by Lebel and Davi.[S16]

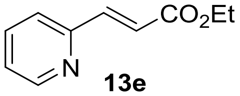
Preparation of ethyl 3-(5'-benzo[*d*][1,3]dioxolyl)-prop-2*E*-enoate (13d)



13d

Ester **13d** was prepared from benzo[*d*][1,3]dioxole-5-carbaldehyde **12d** (1.39 g, 6.3 mmol), (carbethoxmethylene)triphenylphosphorane (3.47 g, 8.4 mmol) and DCM (30 ml) over 18 hours according to General Procedure A. Column chromatography on silica gel (1:4 Et_2O in hexane) afforded ester **13d** as a white solid (1.88 g, 98%). m.p. = 63-65 °C (obtained from powdered solid isolated after chromatography); R_f = 0.38 (1:4 Et_2O in hexane); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 15.9 Hz, ArC*H*=CH, 1H), 7.06 (d, ^4J = 1.6 Hz, Ar*H*, 1H), 7.03 (dd, *J* = 8.1, ^4J = 1.6 Hz, Ar*H*, 1H), 6.83 (d, *J* = 8.1 Hz, Ar*H*, 1H), 6.29 (d, *J* = 15.9 Hz, ArCH=C*H*, 1H), 6.03 (s, O_2CH_2, 2H), 4.28 (q, *J* = 7.1 Hz, OCH_2CH_3, 2H), 1.35 ppm (t, *J* = 7.1 Hz, OCH_2CH_3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7, 149.1, 147.8, 143.8, 128.4, 123.9, 115.7, 108.1, 106.0, 101.1, 59.9, 13.9 ppm; $\bar{\nu}$/(film) = 2359, 2342, 1701, 1632, 1489, 1445, 1236, 1163 cm^{-1}; MS (CI): m/z (%): 249 (19) $[M+C_2H_5]^+$, 221 (95) $[M+H]^+$, 193 (12), 175 (100) $[M-OEt]^+$, 147 (10) $[M-CO_2Et]^+$; t_R (GC) = 13.91 minutes. The data was in agreement with that reported by Lebel and Davi.[S16]

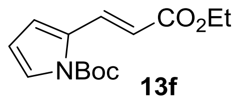
Preparation of ethyl 3-(2’-pyridyl)-prop-2*E*-enoate (13e)



13e

Ester **13e** was prepared from picolinaldehyde **12e** (0.57 ml, 6 mmol), (carbethoxmethylene)triphenylphosphorane (2.7 g, 6.6 mmol) and DCM (25 ml) according to General Procedure A. Column chromatography on silica gel (1:1 Et$_2$O in hexane) afforded ester **13e** as a yellow oil (930 mg, 87%). R_f = 0.34 (1:1 Et$_2$O in hexane); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.66 (br. d, *J* = 4.7 Hz, Ar*H*, 1H), 7.72 (td, *J* = 7.8 Hz, ^4J = 1.9 Hz, Ar*H*, 1H), 7.70 (d, *J* = 15.7 Hz, ArC*H*=CH, 1H), 7.44 (dt, *J* = 7.8 Hz, ^4J = 1.0 *Hz*, Ar*H*, 1H), 7.27 (ddd, *J* = 7.8, 4.7 Hz, ^4J = 1.0 Hz, Ar*H*, 1H), 6.93 (d, *J* = 15.7 Hz, ArCH=C*H*, 1H), 4.29 (q, *J* = 7.14 Hz, OC*H*$_2$CH$_3$, 2H), 1.35 ppm (t, *J* = 7.14 Hz, OCH$_2$C*H*$_3$, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 166.3, 152.5, 149.6, 142.8, 136.2, 123.7, 123.6, 122.0, 60.2, 13.8 ppm; $\bar{\nu}$/(film) = 2981, 2359, 2342, 1717, 1201, 1167 cm^{-1}; MS (CI): m/z (%): 218 (5) [M+C$_3$H$_5$]$^+$, 206 (10) [M+C$_2$H$_5$]$^+$, 178 (100) [M+H]$^+$, 150 (15), 132 (20) [M-OEt]$^+$; t$_R$ (GC) = 12.10 minutes. The data was in agreement with that reported by Lebel and Davi.[S16]

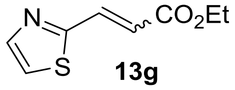
Preparation of ethyl 3-(2’-pyrrolyl-1-carboxylic acid *tert*-butyl ester)-prop-2*E*-enoate (13f)



13f

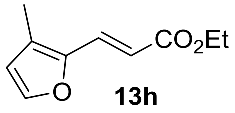
Ester (**13f**) was prepared from aldehyde **12f** (3.9 g, 20 mmol), (carbethoxmethylene)triphenylphosphorane (9.25 g, 26 mmol) and DCM (125 ml) according to General Procedure A. Column chromatography (1:19 Et$_2$O in hexane to 1:4 Et$_2$O in hexane) afforded alkenoate **13f** as a yellow oil (3.4 g, 60%). R_f = 0.40 (1:4 Et$_2$O in hexane); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.30 (d, *J* = 15.9 Hz, ArC*H*=CH, 1H), 7.42 (br. dd, *J* = 3.6 Hz, ^4J = 1.6 Hz, Ar*H*, 1H), 6.72-6.70 (m, Ar*H*, 1H), 6.23 (t, *J* = 3.6 Hz, Ar*H*, 1H), 6.22 (d, *J* = 15.9 Hz, CH=C*H*CO$_2$Et, 1H), 4.26 (q, *J* = 7.1 Hz, OC*H*$_2$CH$_3$, 2H), 1.65 (s, OC(C*H*$_3$)$_3$, 9H), 1.3 ppm (t, *J* = 7.1 Hz, OCH$_2$C*H*$_3$, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 166.6, 148.5, 134.4, 130.6, 124.3, 116.1, 114.3, 110.9, 84.4, 59.8, 27.5, 13.9 ppm; $\bar{\nu}$/(film) = 2976, 1742, 1705, 1621, 1316, 1299, 1245, 1158, 1117 cm^{-1}; MS (CI): m/z (%): 194 (12) [M+ C$_2$H$_5$-Pyrroyl-N-Boc]$^+$, 166 (50) [M-Pyrroyl-N-Boc]$^+$, 120 (100); t$_R$ (GC) = 12.58 minutes. The data was in agreement with that reported by Jeffrey and co-workers.[S18]

Preparation of ethyl 3-(2'-thiazolyl)-prop-2*E*-enoate (13g)


13g

Aldehyde **12g** was synthesised from thiazole (1.75 mL, 25 mmol), DMF (3.9 mL, 20 mmol), BuLi (14.3 mL of a 2.1 M in THF, 30 mmol) in THF (100 mL) according to Glorius and co-workers[S2] as a yellow oil. ^{1}H NMR confirmed full conversion to aldehyde. Ester **13f** was prepared from crude aldehyde **12g** (assumed 25 mmol), (carbethoxmethylene)triphenylphosphorane (9.75 g, 27 mmol) and DCM (150 ml) according to general procedure A. Column chromatography (7:20 Et_2O in hexane) afforded ester **13f** as a yellow oil (3.38 g, 74%) with a 4:1 mixture of alkene isomers (*E*-isomer major). **Data for Mixture:** R_f = 0.20 (1:4 Et_2O in hexane); $\bar{\nu}$/(film) = 2978, 1708, 1630, 1468, 1480, 1299, 1266, 1175 1030 cm^{-1}; HRMS (FTMS): calcd. for $C_8H_{10}O_2N_1S_1$, 184.0423 $[M+H]^+$ found 184.0427. **Data for *E*-13f**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 3.3 Hz, Ar*H*, 1H), 7.82 (d, *J* = 15.9 Hz, ArC*H*=CH, 1H), 7.45 (d, *J* =3.3 Hz, Ar*H*, 1H), 6.77 (d, *J* = 15.9 Hz, CH=C*H*CO_2Et, 1H), 4.31 (q, *J* = 7.3 Hz, OC$H_2$$CH_3$, 2H), 1.36 ppm (t, *J* = 7.3 Hz, CH_2CH_3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.3, 162.9, 144.2, 135.2, 122.5, 120.8, 60.3, 13.7 ppm; MS (CI): m/z (%): 224 (17), $[M+C_3H_5]^+$, 212 (25) $[M+C_2H_5]^+$, 184 (100) $[M+H]^+$, 156 (42), 138 (59) [M-OEt]; t_R (GC) = 11.83 minutes. **Data for *Z*-13f**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 3.3 Hz, Ar*H*, 1H), 7.57 (dd, *J* = 3.3 Hz, ^5J = 1.0 Hz, Ar*H*, 1H), 7.37 (dd, *J* = 12.7 Hz, ^5J = 1.0 Hz, ArC*H*=CH, 1H), 6.15 (d, *J* = 12.7 Hz, CH=C*H*CO_2Et, 1H), 4.32 (q, *J* = 7.2 Hz, OC$H_2$$H_3$, 2H), 1.37 ppm (t, *J* = 7.2 Hz, $CH_2$$H_3$, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.3, 160.2, 142.6, 136.4, 123.7, 118.9, 60.2, 13.6 ppm; MS (CI): m/z (%):224 (11), $[M+C_3H_5]^+$, 212 (18) $[M+C_2H_5]^+$, 184 (100) $[M+H]^+$, 156 (20), 138 (97) [M-OEt]; 112 (14); t_R (GC) = 11.59 minutes.

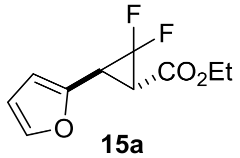
Preparation of ethyl 3-(2'-furyl-3-methyl)-prop-2*E*-enoate (13h)


13h

Diisobutylaluminium hydride (50 mL of a 0.9 M solution in cyclohexane, 45 mmol)) was added dropwise to a solution of methyl 3-methyl-2-furoate (2.04 g, 14.6 mmol) in anhydrous toluene (120 mL) under nitrogen at -78 °C for 5 minutes. The reaction mixture was allowed to warm to room temperature and stirred for a further 8 hours, cooled to -78 °C and quenched with aqueous potassium sodium tartrate tetrahydrate (sat. Rochelle salt, 40 mL) and EtOAc (50 mL). The resulting organic layer was separated and collected. The aqueous layer was extracted further with EtOAc (50 mL x 6) and the separated extracts combined with the original organic layer, dried ($MgSO_4$) and concentrated under reduced pressure to afford (3-methylfuran-2-yl)methanol as a yellow oil (1.33 g 81%). ^{1}H NMR confirmed full conversion to desired alcohol which was used without further purification. *Bis*(acetoxy)iodobenzene (BAIB, 4.18 g, 13 mmol) was added to a solution of (3-methylfuran-2-yl)methanol (1.33 g, 11.8 mmol), TEMPO (184 mg, 1.18 mmol), in anhydrous DCM (90 mL) and the reaction mixture was stirred at room temperature under nitrogen for 4 hours. The ^{1}H NMR spectrum of a reaction aliquot showed complete conversion to corresponding aldehyde **12h**. (Carbethoxmethylene)triphenylphosphorane (5.2 g, 15 mmol) was then added and the reaction mixture stirred for 17 hours. ^{1}H NMR of a reaction aliquot showed complete consumption of aldehyde. The resulting orange solution was concentrated under reduced pressure and column chromatography on silica gel (2:25 Et_2O in hexane) afforded alkenoate **13h** as a yellow oil (1.26 g, 45%). R_f = 0.44 (1:10 Et_2O in hexane); $\bar{\nu}$/(film) = 2976, 1703, 1632, 1299, 1253, 1164 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 15.5 Hz, Ar*CH*=CH, 1H), 7.40 (dq, *J* = 1.6 Hz, ^4J = 0.5 Hz, Ar*H*, 1H), 6.34 (d, *J* = 1.6 Hz, Ar*H*, 1H), 6.26 (d, *J* = 15.5 Hz, CH=C*H*CO_2Et, 1H), 4.27 (q, *J* = 7.1 Hz, OCH_2H_3, 2H), 2.18 (s, ArCH_3, 3H), 1.35 ppm (t, *J* = 7.1 Hz, CH_2CH_3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 146.6, 143.4, 128.5, 125.1, 114.1, 113.5, 59.7, 13.8, 9.7 ppm; MS (CI): m/z (%): 209 (18), $[M+C_2H_5]^+$, 181 (100), $[M+H]^+$, 153 (12), 135 (72), [M-OEt]; HRMS (NSI): calcd. for $C_{10}H_{13}O_3$, 181.0859 $[M+H]^+$ found 184.0857; t_R (GC) = 11.43 minutes.

General Procedure B: Difluorocyclopropanation of Alkenoates **13** with MDFA

Preparation of ethyl (1S*,3S*)-2,2-difluoro-3-(fur-2-yl)cyclopropane-1-carboxylate (15a)

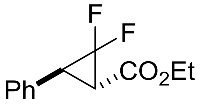


15a

An oven dried two-necked round bottom flask containing potassium iodide (1.87 g, 11.2 mmol) was sealed with a SubaSeal, and the salt was stirred and lightly flame dried under an atmosphere of argon. A low boiling point water condenser with a gas outlet connected to an argon/vacuum manifold was fitted to the reaction flask and the atmosphere was purged three times. Alkenoate **13a** (1.48 g, 8.9 mmol) followed by diglyme (1.43 mL) were added and the yellow suspension purged with argon/vacuum once and then heated to 120 °C. Once the reaction temperature had been reached, TMSCl (2.9 mL, 22.3 mmol) and MDFA (2.9 mL, 22.3 mmol) were added dropwise in that order. After 4 hours, the black reaction mixture was allowed to cool to room temperature and the reaction mixture was quenched with aqueous NH_4Cl (10 mL) and diethyl ether (10 mL) was added. The organic layer was separated and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The original organic layer and the extracts were combined, dried ($MgSO_4$) and concentrated under reduced pressure to remove volatile materials. The ^{1}H NMR spectrum of the resulting brown oil confirmed 66% conversion to difluorocyclopropyl **15a**. Column chromoatography on silica gel (1:20 Et_2O in hexane) afforded difluorocyclopropyl **15a** as a yellow oil (760 mg, 40%) and recovered starting alkenoate **13a** (340 mg, 23%). R_f = 0.4 (1:19 Et_2O in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (dd, J = 2.0 Hz, ^{4}J = 0.8 Hz, Ar*H*, 1H), 6.38 (dd, J = 3.4, 2.0 Hz, Ar*H*, 1H), 6.29 (dd, J = 3.4 Hz, ^{4}J = 0.8 Hz, Ar*H*, 1H), 4.28 (q, J = 7.1 Hz, $\mathrm{OC}H_2\mathrm{CH}_3$, 2H), 3.48 (ddd, $J_{\mathrm{H\text{-}F}}$ = 12.3 Hz, J = 7.7 Hz, $^{4}J_{\mathrm{H\text{-}F}}$ = 1.8 Hz, $\mathrm{ArC}H\mathrm{CF}_2$, 1H), 2.79 (dd, $J_{\mathrm{H\text{-}F}}$ = 13.4 Hz, J = 7.7 Hz, $\mathrm{CF_2C}H\mathrm{CO_2Et}$, 1H), 1.34 ppm (t, J = 7.2 Hz, $\mathrm{OCH_2C}H_3$, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.5, 145.1, 142.6, 110.6, 108.8 (dd, $^{1}J_{\mathrm{C\text{-}F}}$ = 294.6, 289.7 Hz) 108.4, 61.9, 32.1 (t, $^{2}J_{\mathrm{C\text{-}F}}$ = 10.9 Hz), 26.7 (dd, $^{2}J_{\mathrm{C\text{-}F}}$ = 13.3, 8.9 Hz) 14.1 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -133.1 (dd, ^{2}J = 151.7 Hz, $J_{\mathrm{F\text{-}H}}$ = 13.4 Hz, 1F), -135.1 ppm (dd, ^{2}J = 152.8 Hz, $J_{\mathrm{F\text{-}H}}$ = 12.2 Hz, 1F); $\tilde{\nu}$/(film) = 2986, 2932, 2359, 2342, 1736, 1447, 1331, 1290, 1153, 1009 cm^{-1}; MS (CI): *m/z* (%): 257 (4) $[M+C_3H_5]^+$, 245 (9) $[M+C_2H_5]^+$, 217 (45) $[M+H]^+$, 197 (100) $[M-F]^+$, 189 (58), 171 (42) [M-

OEt]$^+$, 169 (70) [(M+H)-F-Et]$^+$, 143 (20), 125 (16); t_R (GC) = 9.49 minutes; HRMS (APCI): calcd for $C_{10}H_{11}F_2O_3$, 217.0668 [M+H]$^+$ found 217.0671.

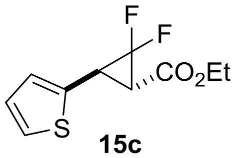
Preparation of ethyl (1S*,3S*)-2,2-difluoro-3-phenylcyclopropane-1-carboxylate (15b)



15b

The preparation of ester **15b** was attempted from alkenoate **13b** (0.67 mL, 4.03 mmol), MDFA (2.6 mL, 10 mmol), TMSCl (2.6 mL, 10 mmol), potassium iodide (1.87 g, 11.2 mmol) and diglyme (1.4 mL) according to General Procedure B with a total reaction time of 24 hours. The resulting ^{1}H NMR of the crude reaction mixture after work up confirmed incomplete conversion of **13b** (28% conv. to **15b**). The reaction was repeated using commercial ethyl cinnamate (**13b**) according to general procedure B on twice the scale. The resulting ^{1}H spectrum of the resulting brown oil confirmed incomplete conversion of **13b** (29% conv. to **15b**).

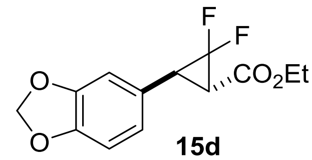
Preparation of ethyl (1S*,3R*)-2,2-difluoro-3-(thiophen-2-yl)cyclopropane-1-carboxylate (15c)



15c

Ester **15c** was prepared from alkenoate **13c** (1.45 mg, 8 mmol), MDFA (2.6 mL, 20 mmol), TMSCl (2.6 mL, 20 mmol), potassium iodide (3.68 g, 22.6 mmol) and diglyme (1.3 mL) according to general procedure B with a reaction time of 4 hours. ^{1}H NMR of the resulting crude product showed 77% conversion to desired ester **15c**. Column chromatography on silca gel (1:19 Et_2O in hexane) afforded ester **15c** as a yellow oil (1.32 g, 71%) and recovered alkenoate **13c** (310 mg, 21%). R_f = 0.42 (1:24 Et_2O in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26 (dd, J = 3.3, 3.1 Hz, ArH, 1H), 7.00 (d, J = 3.3 Hz, ArH, 1H), 7.00 (d, J = 3.1 Hz, ArH, 1H), 4.27 (q, J = 7.2 Hz, OCH_2CH_3, 2H), 3.63 (ddd, $J_{H\text{-}F}$ = 13.1, 2.3 Hz, J = 7.7 Hz, ArCH, 1H), 2.67 (dd, $J_{H\text{-}F}$ = 13.6, J = 7.7 Hz, CHCO$_2$Et, 1H), 1.33 ppm (t, J = 7.2 Hz, OCH_2CH_3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 133.3, 127.0, 126.7, 125.4, 110.4 (dd, $^1J_{C\text{-}F}$ = 296.8, 290.3 Hz), 61.9, 34.5 ($^2J_{C-F}$ = 10.9 Hz), 28.6 (dd, $^2J_{C-F}$ = 13.0, 9.2 Hz), 14.1 ppm; ^{19}F NMR (376 MHz, CDCl$_3$): δ = -132.8 (ddd, $^2J_{F-F}$ = 151.7 Hz, J_{F-H} = 13.6, 2.4 Hz, 1F), -134.2 ppm (dd, $^2J_{F-F}$ = 151.2 Hz, J_{F-H} = 13.3 Hz, 1F); $\bar{\nu}$/(film) = 2965, 2359, 2342, 1732, 1466, 1431, 1325, 1285, 1215, 1152, 1009 cm^{-1}; MS (CI): *m/z* (%): 261 (7) [M+C$_2$H$_5$]$^+$, 233 (33) [M+H]$^+$, 213 (100) [M-F]$^+$, 205 (43), 187 (36), 185 (66) [M-(F+Et)]$^+$, 159 (16), 139 (18); HRMS (APCI): calcd for $C_{10}H_{14}F_2O_2S_1N_1$, 250.0708 [M+NH$_4$]$^+$ found 250.0706; t$_R$ (GC) = 11.15 minutes.

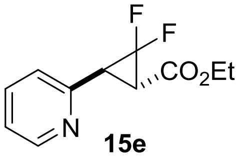
Preparation of ethyl (1S*,3S*)-3-(benzo[d][1,3]dioxol-5-yl)-2,2-difluorocyclopropane-1-carboxylate (15d)



15d

Ester **15d** was prepared from alkenoate **13d** (1.66 g, 7.5 mmol), MDFA (2.4 mL, 18.5 mmol), TMSCl (2.4 mL, 18.5 mmol), potassium iodide (3.45 g, 20.7 mmol) and diglyme (1.2 mL) according to general procedure B. ^{1}H NMR of the resulting crude product showed 50% conversion to desired ester **15d**. Column chromatography on silca gel (1:9 Et$_2$O in hexane) afforded ester **15d** as a yellow oil (880 mg, 43%) and recovered alkenoate **13d** (700 mg, 42%). R$_f$ = 0.59 (1:4 Et$_2$O in hexane); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 6.82-6.73 (m, Ar*H*, 3H), 6.00 (s, OC*H$_2$*O, 2H), 4.28 (q, *J* = 7.2 Hz, OC*H$_2$*CH$_3$, 2H), 3.44 (ddd, J_{H-F} = 13.2, 2.9 Hz, *J* = 7.9 Hz, ArC*H*, 1H), 2.65 (dd, J_{H-F} = 13.2 Hz, *J* = 7.9 Hz, C*H*CO$_2$Et, 1H), 1.34 (t, *J* = 7.2 Hz, OCH$_2$C*H$_3$*, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 165.8, 147.5, 146.9, 124.1, 121.3, 110.2 (t, $^1J_{C-F}$ = 294.2, 287.2 Hz), 107.9 (represents 2 carbons), 100.8, 61.3, 32.4 (dd, $^2J_{C-F}$ = 11.2, 8.8 Hz), 32.0 (t, $^2J_{C-F}$ = 11.1 Hz) 13.6 ppm; ^{19}F NMR (376 MHz, CDCl$_3$): δ = -133.1 (dd, $^2J_{F-F}$ = 151.9 Hz, J_{F-H} = 13.6 Hz, 1F), -134.1 (ddd, $^2J_{F-F}$ = 151.3 Hz, J_{F-H} = 13.5, 2.7 Hz, 1F), $\bar{\nu}$/(film) = 2359, 2342, 1732, 1506, 1466, 1449, 1290, 1242, 1213,1152, 1038, 1013, 989 cm^{-1}; MS (CI): *m/z* (%): 299 (19) [M+C$_2$H$_5$]$^+$, 271 (44) [M+H]$^+$, 251 (94) [M-F]$^+$, 223 (75) [(M+H)-F-OEt]$^+$, 206 (24), 197 (26) [M-CO$_2$Et]$^+$, 177 (100); HRMS (APCI): calcd for $C_{13}H_{13}F_2O_4$, 271.0776 [M+H]$^+$ found 271.0776; t$_R$ (GC) = 13.50 minutes.

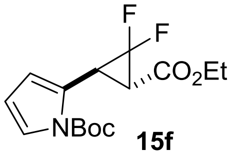
Preparation of ethyl (1S*,3S*)-2,2-difluoro-3-(pyridin-2-yl)cyclopropane-1-carboxylate (15e)



15e

The preparation of ester **15e** was attempted from alkenoate **13e** (400 mg, 2.3 mmol), MDFA (0.74 mL, 5.7 mmol), TMSCl (0.74 mL, 5.7 mmol), potassium iodide (1.1 g, 6.6 mmol) and diglyme (0.45 mL) according to general procedure B with a total reaction time of 4 hours. The resulting ^{1}H NMR of the resulting crude black solid showed diglyme and diethyl ether with trace amounts of alkenoate **13e**. The desired product **15e** was not observed (0% conversion).

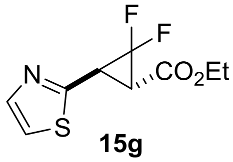
Preparation of ethyl (1S*,3S*)-2,2-difluoro-3-(2′-pyrrolyl-1-carboxylic acid *tert*-butyl ester)cyclopropane-1-carboxylate (15f)



15f

Ester **15f** was prepared from alkenoate **13f** (2.12 g, 8 mmol), MDFA (2.6 mL, 20 mmol), TMSCl (2.6 mL, 20 mmol), potassium iodide (3.74 g, 22.4 mmol) and diglyme (1.6 mL) according to general procedure B. ^{1}H NMR of the resulting crude product showed 92% conversion to desired product. Column chromatography on silica gel (1:20 Et$_2$O in hexane) afforded ester **15f** as a yellow oil (1.37 g, 54%) and recovered alkenoate **13f** (140 mg, 7%). R_f = 0.35 (1:4 Et$_2$O in hexane); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.29 (ddd, J = 3.3 Hz, ^4J = 1.7 Hz, ^5J = 0.7 Hz, ArH, 1H), 6.17-6.15 (br. m, ArH, 1H), 6.14 (t, J = 3.4 Hz, ArH, 1H), 4.28 (ABq, J = 7.4 Hz, ^2J = 3.1 Hz, OCH_aH_bCH$_3$, 2H), 3.73 (br. dd, $J_{\text{H-F}}$ = 12.8 Hz, J = 7.8 Hz, ArCH, 1H), 2.63 (dd, J = 13.4 Hz, J = 7.8 Hz, HCCO$_2$Et, 1H), 1.63 (s, C(CH_3)$_3$, 9H), 1.34 (t, J = 7.2 Hz, CH$_2$CH_3, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 165.7, 148.4, 124.0, 122.1, 112.9, 110.3 (dd, $^1J_{\text{C-F}}$ = 297.3, 287.2 Hz), 109.6, 84.1, 61.1, 31.7 (t, $^2J_{\text{C-F}}$ = 10.9 Hz), 27.6 (t, $^2J_{\text{C-F}}$ = 12.9, 8.0 Hz), 27.5, 13.7 ppm; ^{19}F NMR (376 MHz, CDCl$_3$): δ = -133.4 (dd, ^2J = 149.8 Hz, $J_{\text{F-H}}$ = 12.8 Hz, CF_aF$_b$, 1F), -134.9 ppm (dd, ^2J = 149.8 Hz, $J_{\text{F-H}}$ = 13.4 Hz, CF_aF$_b$, 1F); $\bar{\nu}$/(film) = 2980, 1742, 1459, 1325, 1158, 1128 cm^{-1}; MS (CI): *m/z* (%): 224 (17) [M-(F+CO_2Et)+H]$^+$, 196 (100) [M-(F+Boc)+H]$^+$, 168 (29), 150 (72) [M-(*N*-Boc-pyrrolyl)+H]$^+$; HRMS (APCI): calcd for $C_{15}H_{23}F_2N_2O_4$, 333.1620 [M+NH_4]$^+$ found 333.1623; t_R (GC) = 12.07 minutes.

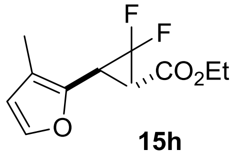
Preparation of ethyl (1S*,3S*)-2,2-difluoro-3-(2′-thiazolyl)cyclopropane-1-carboxylate (15g)



15g

The preparation of ester **15g** was attempted from alkenoate **13g** (1.18 g, 6.4 mmol), MDFA (2.1 mL, 16.2 mmol), TMSCl (2.1 mL, 16.2 mmol), potassium iodide (3.0 g, 18 mmol) and diglyme (1.28 mL) according to general procedure B with a total reaction time of 4 hours. The resulting ^{1}H NMR of the resulting crude black solid showed diglyme and diethyl ether the desired product **15g** was not observed (0% conversion).

Preparation of ethyl (1S*,3S*)-2,2-difluoro-3-(2′-furyl-3-methyl) cyclopropane-1-carboxylate (15h)



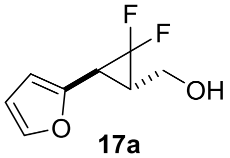
15h

Ester **15h** was prepared from alkenoate **13h** (721 mg, 4.0 mmol), MDFA (1.3 mL, 10 mmol), TMSCl (1.3 mL, 10 mmol), potassium iodide (1.84 g, 12 mmol) and diglyme (0.7 mL) according to general procedure B. ^{1}H NMR of the resulting crude product showed 80% conversion to desired product. Column chromatography on silica gel (1:20 Et_2O in hexane) afforded ester **15h** as a yellow oil (417 mg, 45%) and recovered alkenoate **13h** (136 mg, 19%). R_f = 0.56 (1:4 Et_2O in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 1.8 Hz, Ar*H*, 1H), 6.23 (d, *J* = 1.8 Hz, Ar*H*, 1H), 4.26 (q, *J* = 7.1 Hz, OC*H*$_2$CH$_3$, 2H), 3.67 (ddd, $J_{H\text{-}F}$ = 12.2, 2.3 Hz, *J* = 7.7 Hz, ArC*H*, 1H), 2.92 (dd, $J_{H\text{-}F}$ = 13.5 Hz, *J* = 7.7 Hz, *H*CCO$_2$Et, 1H), 2.05 (s, ArC*H*$_3$, 3H), 1.33 ppm (t, *J* = 7.1 Hz, CH$_2$C*H*$_3$, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9, 141.4, 139.8, 119.0, 113.4, 110.1 (t, $^1J_{C\text{-}F}$ = 294.1, 287.4 Hz), 61.9, 30.8 (t, $J_{C\text{-}F}$ = 11.0 Hz), 25.5 (dd, $J_{C\text{-}F}$ = 13.5, 9.5 Hz), 14.1, 9.6 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -132.8 (ddd, ^2J = 150.5 Hz, $J_{F\text{-}H}$ =

13.5, 2.3 Hz, C*F$_a$*F$_b$, 1F), -131.5 ppm (dd, ^2J = 150.5 Hz, $J_{F\text{-}H}$ = 12.2 Hz, CF$_a$*F$_b$*, 1F); $\bar{\nu}$/(film) = 2985, 1738, 1454, 1329, 1290, 1208, 1154, 1091, 1013, 989 cm^{-1}; MS (CI): *m/z* (%): 259 (6) $[M+C_2H_5]^+$, 231 (25) $[M+H]^+$, 211 (100) $[M-F]^+$, 203 (23), 185 (25) $[M-OEt]^+$, 183 (28); HRMS (APCI): calcd for $C_{11}H_{11}F_2O_3$, 229.0671 $[M-H]^+$ found 229.0676; t_R (GC) = 10.61 minutes.

General Procedure C: Reduction of Difluorocyclopropyl Ethyl Esters

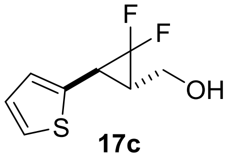
Preparation of ethyl ((1S*,3S*)-2,2-difluoro-3-(furan-2-yl)cyclopropyl)methanol (17a)



17a

Diisobutylaluminium hydride (24 ml of a 1.1 M solution in cyclohexane, 23.7 mmol) was added dropwise to a solution of ester **15a** (1.71 g, 7.9 mmol) in anhydrous toluene (70 mL) under nitrogen at -78 °C over 10 minutes. The reaction mixture was allowed to warm to room temperature and stirred for a further 8 hours, then cooled to 0 °C and quenched by dropwise addition of H_2O (2 mL), 0.1 M aqueous NaOH (2 mL) and H_2O (2 mL) in that order. $MgSO_4$ was added to the quenched mixture until the solid was free flowing and the mixture was left overnight at room temperature (14-17 h). The resulting white emulsion was washed with EtOAc (4 x 50 mL) and the organic extracts were combined and concentrated under reduced pressure to afford alcohol **17a** as a pale yellow oil (1.3 g, 94%). R_f = 0.19 (1:2 Et_2O in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (dd, *J* = 1.9 Hz, ^4J = 0.8 Hz, Ar*H*, 1H), 6.38 (dd, *J* = 3.3, 1.9 Hz, Ar*H*, 1H), 6.21 (br. d, *J* = 3.3 Hz, Ar*H*, 1H), 3.99-3.91 (br. m, C*H$_a$*H$_b$OH, 1H), 3.90-3.83 (br. m, CH$_a$*H$_b$*OH, 1H), 2.64 (dd, $J_{H\text{-}F}$ = 13.1 Hz, *J* = 7.3 Hz, ArC*H*, 1H), 2.32-2.23 (m, C*H*CH$_2$O, 1H), 1.62 ppm (br. s, CH$_2$O*H*, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.6, 141.6, 112.1 (t, $^1J_{C\text{-}F}$ = 289.0 Hz), 110.1, 106.9, 58.6 (d, $J_{C\text{-}F}$ = 5.9 Hz), 30.4 (t, $^2J_{C\text{-}F}$ = 9.5 Hz), 24.2 ppm (dd, $^2J_{C\text{-}F}$ = 13.6, 10.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -135.5 (ddd, ^2J = 158.7 Hz, $J_{F\text{-}H}$ = 13.6, 2.0 Hz, 1F), -138.3 ppm (dd, ^2J = 158.8 Hz, $J_{F\text{-}H}$ = 13.1 Hz, 1F); $\bar{\nu}$/(film) = 2926, 2359, 2342, 1458, 1263, 1167, 1009, 736 cm^{-1}; MS (CI): *m/z* (%): 175 (13) $[M+H]^+$, 157 (100) $[M-OH]^+$, 139 (13), 127 (12), 109 (18); HRMS (TOF): calcd for $C_8H_8O_2F_2$, 174.0492 [M] found 174.0496; t_R (GC) = 9.39 minutes.

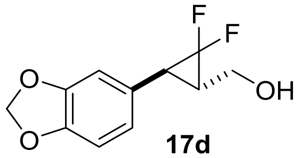
Preparation of ((1S*,3R*)-2,2-difluoro-3-(thiophen-2-yl)cyclopropyl)methanol (17c)



17c

Alcohol **17c** was prepared from ester **15c** (272 mg, 0.85 mmol), DIBAL (2.3ml of a 1.1 M solution in cyclohexane, 2.55 mmol) and DCM (6 mL) according to general procedure B. ^{1}H NMR of the result crude reaction mixture confirmed 83% conversion. Column chromatography on silica gel (2:3 Et_2O in hexane) afforded alcohol **17c** as a yellow oil (81 mg, 50%). R_f = 0.19 (1:2 Et_2O in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (dd, J = 5.2, ^{4}J = 1.3 Hz, ArH, 1H), 6.99 (dd, J = 5.2, 3.6 Hz, ArH, 1H), 6.95 (br. d, J = 3.6 Hz, ArH, 1H), 3.94 (dddd, ^{2}J = 12.1 Hz, J = 6.6, 1.1 Hz, $^{4}J_{H\text{-}F}$ = 2.7 Hz, CH_aH_bOH, 1H), 3.84 (ddd, ^{2}J = 12.1 Hz, J = 7.8, 1.6 Hz, CH_aH_bOH, 1H), 2.77 (dd, $J_{H\text{-}F}$ = 13.6 Hz, J = 7.3 Hz, ArCH, 1H), 2.33 (br. s, CH_2OH, 1H), 2.17 ppm (ddddd, $J_{H\text{-}F}$ = 13.4 Hz, J = 7.8, 7.4, 6.6 Hz, ^{4}J = 0.9 Hz, C$H$$CH_2OH$, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.1, 126.5, 125.4, 124.2, 112.7 (t, $^{1}J_{C\text{-}F}$ = 290.1 Hz), 58.7 (d, $J_{C\text{-}F}$ = 5.7 Hz), 32.9 (t, $^{2}J_{C\text{-}F}$ = 9.6 Hz), 26.1 ppm (dd, $^{2}J_{C\text{-}F}$ = 12.5, 11.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -135.4 (ddd, ^{2}J = 158.0 Hz, $J_{F\text{-}H}$ = 13.5 Hz, $^{4}J_{F\text{-}H}$ = 2.7 Hz, 1F), -137.5 ppm (dd, ^{2}J = 158.0 Hz, $J_{F\text{-}H}$ = 13.5 Hz, 1F); $\bar{\nu}$/(film) = 3324, 2930, 2885, 1472, 1435, 1245, 1080, 1037, 1007 cm^{-1}; MS (CI): m/z (%): 219 (6) $[M+C_2H_5]^+$, 191 (26) $[M+H]^+$, 173 (100) $[M-OH]^+$, 153 (42) $[M-F_2]^+$, 123 (22); HRMS (ASAP): calcd for $C_8H_7F_2S_1$, 173.0231 $[M-H_2O+H]^+$ found 173.0229; t_R (GC) = 10.51 minutes.

Preparation of ((1S*,3R*)-2,2-difluoro-3-(benzo[d][1,3]dioxol-5-yl)cyclopropyl)methanol (17d)

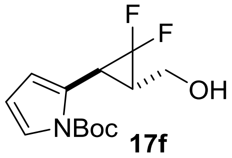


17d

Alcohol **17d** was prepared from ester **15d** (550 mg, 2 mmol), DIBAL (1.0 M in cyclohexane, 6.0 mL, 6 mmol) and toluene (30 mL) according to general procedure C. Column chromatography on silica gel (1:1 Et_2O in hexane) afforded desired alcohol **17d** as a colourless oil (342 mg, 75%). R_f = 0.35 (1:1 Et_2O in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ =

6.80-6.72 (m, Ar*H*, 3H), 5.97 (s, OC*H₂*O, 2H), 3.95-3.83 (m, CHC*H₂*OH, 2H), 2.57 (ddd, $J_{H\text{-}F}$ = 11.2 Hz, *J* = 7.6 Hz, ^4J = 3.3 Hz, ArC*H,* 1H), 2.12 (ddddd, $J_{H\text{-}F}$ = 11.2 Hz, *J* = 7.6, 7.5, 7.1 Hz, ^4J = 3.3 Hz, C*H*CH$_2$OH, 1H), 1.92 ppm (br. s, CH$_2$OH, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 147.3, 146.4, 126.1, 121.1, 113.1 (t, $^1J_{C\text{-}F}$ = 289.1 Hz), 108.0, 107.8, 100.6, 59.1 (d, $J_{C\text{-}F}$ = 4.3 Hz), 30.8 (t, $^2J_{C\text{-}F}$ = 9.1 Hz), 30.7 ppm (t, $^2J_{C\text{-}F}$ = 11.1 Hz); ^{19}F NMR (376 MHz, CDCl$_3$): δ = -136.5 (ddd, ^2J = 158.2 Hz, $J_{F\text{-}H}$ = 10.8 Hz, $^4J_{F\text{-}H}$ = 4.2 Hz, CHCF_aF$_b$CHCH$_2$, 1F), -136.6 ppm (ddt, ^2J = 157.8 Hz, $J_{F\text{-}H}$ = 10.8 Hz, $^4J_{F\text{-}H}$ = 3.7 Hz, CHCF$_a$$F_b$CHCH$_2$, 1F). Reported chemical shifts are representative of an AB system; $\bar{\nu}$/(film) = 3292, 1495, 1476, 1437, 1236, 1167, 1036, 1011, 930 cm^{-1}; MS (CI): *m/z* (%): 269 (2) [M+C$_3$H$_5$]$^+$, 257 (10) [M+C$_2$H$_5$]$^+$, 229 (32) [M+H]$^+$, 211 (100) [M-OH]$^+$, 191 (90) [(M+H)-F$_2$]$^+$, 181 (48), 161 (74), 131 (26); HRMS (APCI): calcd for C$_{11}$H$_{11}$F$_2$O$_3$, 229.0671 [M+H]$^+$ found 229.0668; t$_R$ (GC) = 12.96 minutes.

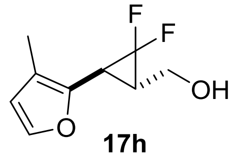
Preparation of ((1S*,3R*)-2,2-difluoro-3-(2'-pyrrolyl-1-carboxylic acid *tert*-butyl ester)methanol (17f)



17f

Alcohol **17f** was prepared from ester **15f** (600 mg, 1.9 mmol), DIBAL (1.0 M in cyclohexane, 5.7 mL, 5.7 mmol) and toluene (40 mL) according to general procedure C. Column chromatography on silica gel (1:1 Et$_2$O in hexane) afforded desired alcohol **17f** as a pale yellow oil (30 mg, 6%). R$_f$ = 0.32 (1:1 Et$_2$O in hexane); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.23 (ddd, *J* = 3.4 Hz, ^4J = 1.8 Hz, ^5J = 0.8 Hz, Ar*H*, 1H), 6.25 (m, Ar*H*, 1H), 6.14 (t, *J* = 3.4 Hz, Ar*H*, 1H), 3.98 (ddd, ^2J = 12.0 Hz, *J* = 5.7, 1.8 Hz, CHCH_aH$_b$OH, 1H), 3.74 (dt, ^2J = 11.9 Hz, *J* = 1.8 Hz, CHCH$_a$$H_b$OH, 1H), 2.96 (br. s, O*H*, 1H), 2.86 (dd, $^3J_{H\text{-}F}$ = 15.3 Hz, *J* = 7.3 Hz, ArC*H*, 1H), 1.99 (m, C*H*CH$_2$OH, 1H), 1.63 ppm (s, OC(CH_3)$_3$, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 149.3, 126.5, 121.2, 113.3 (dd, $^1J_{C\text{-}F}$ = 290.3, 287.3 Hz), 112.3 (d, $^4J_{C\text{-}F}$ = 3,3 Hz), 110.0, 84.2, 59.0 (d, $J_{C\text{-}F}$ = 4.4 Hz), 32.9 (t, $^2J_{C\text{-}F}$ = 9.3 Hz), 23.5, 23.3 ppm (dd, $^2J_{C\text{-}F}$ = 13.0, 9.6 Hz); ^{19}F NMR (376 MHz, CDCl$_3$): δ = -132.6 (dd, ^2J = 160.0 Hz, $J_{F\text{-}H}$ = 13.6 Hz, CF_aF$_b$, 1F), -134.7 ppm (dd, ^2J = 159.0 Hz, $J_{F\text{-}H}$ = 15.1 Hz, CF$_a$$F_b$, 1F); $\bar{\nu}$/(film) = 3443, 2982, 2835, 1740, 1478, 1405, 1372, 1323, 1260, 1164, 1128 cm^{-1}; MS (CI): *m/z* (%): 180 (23), 152 (100); t$_R$ (GC) = 10.12 minutes. Due to lack of m/z consistent with product accurate mass analysis was not attempted.

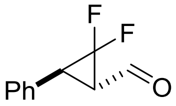
Preparation of ((1S*,3R*)-2,2-difluoro-3-(2'-furyl-3-methyl)cyclopropyl)methanol (17h)



17h

Alcohol **17h** was prepared from ester **15h** (234 mg, 1.0 mmol), DIBAL (1.0 M in cyclohexane, 3.0 mL, 3.0 mmol) and toluene (6.2 mL) according to general procedure C to afford desired alcohol **17h** as a pale yellow oil (160 mg, 84%). $R_f = 0.21$ (1:1 Et_2O in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, J = 1.8 Hz, Ar*H*, 1H), 6.22 (d, J = 1.8 Hz, Ar*H*, 1H), 3.97-3.84 (br. m., CHCH_2OH, 2H), 2.52 (dd, $J_{\text{H-F}}$ = 12.7, J = 7.3 Hz, ArC*H*, 1H), 2.40 (ddddd, $J_{\text{H-F}}$ = 13.9, 2.0 Hz, J = 7.6, 7.3, 6.4 Hz), 2.04 (s, ArCH_3, 3H), 1.62 ppm (br. s, O*H*, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.5, 141.0, 118.2, 113.3, 113.0 (t, $^1J_{\text{C-F}}$ = 289.0 Hz), 59.1 (d, $J_{\text{C-F}}$ = 5.6 Hz), 29.5 (t, $^2J_{\text{C-F}}$ = 9.5 Hz), 23.4 (dd, $^2J_{\text{C-F}}$ = 13.4, 10.8 Hz), 9.6 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -134.8 (ddd, ^2J = 157.3 Hz, $J_{\text{F-H}}$ = 13.9, 2.2 Hz, CF_aF$_b$, 1F), -138.4 ppm (dd, ^2J = 157.3 Hz, $J_{\text{F-H}}$ = 12.7 Hz, CF$_a$$F_b$, 1F); $\bar{\nu}$/(film) = 3333, 2928, 2887, 1632, 1455, 1271, 1180, 1041, 1013 cm^{-1}; MS (CI): *m/z* (%): 189 (9) [M+H]$^+$, 171 (100) [M-OH]$^+$, 153 (16), 121 (14); HRMS (APCI): calcd for $C_9H_9F_2O_1$, 171.0616 [M-H_2O+H]$^+$ found 171.0615; t_R (GC) = 9.99 minutes.

Preparation of (1S*,3S*)-2,2-difluoro-3-phenylcyclopropane-1-carbaldehyde (18b)



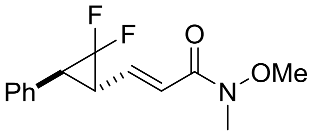
18b

BAIB (3.0 g, 9.3 mmol) was added to a solution of ((1S*,3S*)-2,2-difluoro-3-phenylcyclopropyl)methanol (**17b**) (1.58 g, 8.6 mmol) and TEMPO (133 mg, 0.9 mmol) in anhydrous DCM (45 mL) and the reaction mixture was stirred at room temperature under nitrogen for 6 hours. The ^{1}H NMR spectrum showed complete conversion to aldehyde **18b**. Kugelrohr distillation (50 °C, 20 mbar) removed iodobenzene side product then (60 °C, 0.1 mbar) afforded aldehyde **18b** as a pale yellow oil (1.17 g, 75%). R_f = 0.26 (1:4 Et_2O in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.51 (dd, J = 4.4 Hz, ^4J = 2.0 Hz, C(O)*H*, 1H), 7.42-7.34 (m, Ar*H*, 3H), 7.29-7.27 (m, Ar*H*, 2H), 3.63 (ddd, $J_{\text{H-F}}$ = 14.8 Hz, J = 7.6 Hz, ^4J = 2.1 Hz, ArC*H*, 1H), 2.97 (ddd, $J_{\text{H-F}}$ = 12.8 Hz, J = 7.5, 4.4 Hz, C*H*C(O)H, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =

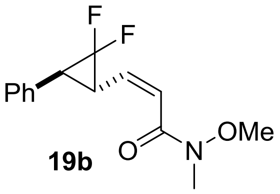
191.8 (d, $J_{C\text{-}F}$ = 3.9 Hz), 130.0, 128.4, 127.8, 127.6, 111.0 (t, $^2J_{C\text{-}F}$ = 291.3 Hz), 40.3 (t, $J_{C\text{-}F}$ = 40.4 Hz), 32.8 ppm (dd, $J_{C\text{-}F}$ 12.1, 8.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -129.4 (dd, ^2J = 158.0 Hz, $J_{F\text{-}H}$ = 15.0 Hz, 1F), -133.4 ppm (dd, ^2J = 157.9 Hz, $J_{F\text{-}H}$ = 12.9 Hz, 1F); $\bar{\nu}$/(film) = 1738, 1634, 1059, 980 cm^{-1}; MS (CI): *m/z* (%): 183 (11) $[M+H]^+$, 163 (73) $[M-F]^+$, 135 (100) [(M+H)-F-CO], 115 (24) [(M+H)-F_2-CO]; HRMS (APCI): calcd for $C_{10}H_9F_2O$, 183.0616 $[M+H]^+$ found 183.0615; t_R (GC) = 10.03 minutes.

General Procedure D: Tandem Oxidation/Olefination of Difluorocyclopropyl Alcohols

Preparation of (*E*)-3-((1R*,3S*)-2,2-difluoro-3-phenylcyclopropyl)-N-methoxy-N-methylacrylamide (19a) and (*Z*)-3-((1R*,3S*)-2,2-difluoro-3-phenylcyclopropyl)-N-methoxy-N-methylacrylamide (19b)



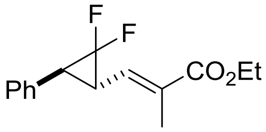
19a



19b

Bis(acetoxy)iodobenzene (BAIB, 304 mg, 0.92 mmol) was added to a solution of alcohol **17b** (148 mg, 0.8 mmol) and TEMPO (12 mg, 0.08 mmol) in anhydrous DCM (3.2 mL) and the reaction mixture was stirred at room temperature under nitrogen for 6 hours. The ^{1}H NMR spectrum showed complete conversion to the corresponding aldehyde. *N*-methoxy-*N*-methyl(triphenylphosphoranylidene)acetamide (378 mg, 1.04 mmol) was then added, and the reaction mixture stirred for 16 hours until the ^{1}H or ^{19}F NMR spectrum showed complete conversion. The resulting orange solution was concentrated under reduced pressure and column chromatography on silica gel (1:1 to 3:2 diethyl ether in hexane) afforded **19a** (157 mg, 74%) as a pale yellow solid and **19b** (25 mg, 9%) as a yellow oil. Data for **19a**: m.p. = 52-55 °C (chloroform/pentane); R_f = 0.14 (1:1 Et_2O in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39-7.31 (m, Ar*H*, 3H), 7.30-7.25 (m, Ar*H*, 2H), 6.82 (dd, *J* = 15.6, 9.6 Hz, CHC*H*=CH, 1H), 6.69 (d, *J* = 15.4 Hz, CH=C*H*CO, 1H), 3.74 (s, OC*H₃*, 3H), 3.28 (s, NC*H₃*, 3H), 2.91 (dd, $J_{H\text{-}F}$ = 14.6 Hz, *J* = 7.1 Hz, ArC*H*CF_2CH, 1H), 2.70 ppm (ddd, $J_{H\text{-}F}$ = 13.1 Hz, *J* = 9.6, 7.2 Hz, C*H*CH, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.3, 138.5 (d, $^4J_{C\text{-}F}$ = 4.8 Hz), 132.1, 128.2, 127.4, 127.1, 120.6, 112.9 (t, $^1J_{C\text{-}F}$ = 292.7 Hz), 61.3, 35.6 (dd, $J_{C\text{-}F}$ = 11.2, 9.0 Hz), 33.8 (t, $J_{C\text{-}F}$ = 11.5), 31.9 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -130.5 (dd, ^2J = 156.1 Hz, $J_{F\text{-}H}$ = 14.1 Hz, 1F), -135.7 ppm (dd, ^2J = 156.0 Hz, J_{F-H} = 13.5 Hz, 1F); $\bar{\nu}$/(film) = 1661, 1630, 1383, 1273, 1152, 986 cm^{-1}; MS (CI): *m/z* (%): 288 (8) [(M-F)+C_3H_5]$^+$, 276 (9) [(M-F)+C_2H_5]$^+$, 248 (100) [M-F]$^+$; HRMS (APCI): calcd for $C_{14}H_{16}F_2NO_2$, 268.1144 [M+H]$^+$ found 268.1145; t_R (GC) = 11.30 minutes. Data for **19b**: R_f = 0.33 (1:1 Et_2O in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.34 (m, Ar*H*, 4H), 7.32-7.27 (m, Ar*H*, 1H), 6.53 (d, *J* = 11.4 Hz, CH=C*H*CO, 1H), 5.95 (dddd, *J* = 11.4, 10.1 Hz, $^4J_{H-F}$ = 1.4, 1.3 Hz, CHC*H*=CH, 1H), 4.29 (br. ddd, J_{H-F} = 14.0 Hz, *J* = 10.1, 7.2 Hz, CHCH=C*H*, 1H), 3.74 (s, OC*H₃*, 3H), 3.27 (s, NC*H₃*, 3H), 2.81 (dd, J_{H-F} = 14.9 Hz, *J* = 7.2 Hz, ArC*H*CF$_2$CH, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.2 (d, $^5J_{C-F}$ = 3.7 Hz), 133.3 (d, $^4J_{C-F}$ = 6.0 Hz), 131.8, 128.1, 127.7, 126.9, 119.0, 113.7 (t, $^1J_{C-F}$ = 291.3 Hz), 61.3, 36.1 (dd, ^2J = 11.5, 8.9 Hz), 31.5, 29.8 ppm (dd, ^2J = 13.2, 9.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -132.6 (dd, ^2J = 153.9 Hz, J_{F-H} = 14.8 Hz, 1F), -136.3 ppm (dd, ^2J = 153.8 Hz, J_{F-H} = 14.0 Hz, 1F); $\bar{\nu}$/(film) = 2982, 2360, 2343, 1656, 1627, 1425, 1354, 1252, 1169, 1001 cm^{-1}; MS (CI): *m/z* (%): 296 (12) [M+C_2H_5]$^+$, 268 (52) [M+H]$^+$, 248 (100) [M-F]$^+$, 217 (8) [M-(F-OMe)], 187 (8); HRMS (APCI): calcd for $C_{14}H_{16}F_2NO_2$, 268.1144 [M+H]$^+$ found 268.1145; t_R (GC) = 13.37 minutes.

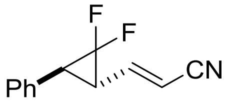
Preparation of ethyl (*E*)-3-((1R*,3S*)-2,2-difluoro-3-phenylcyclopropyl)-2-methylacrylate (20a)



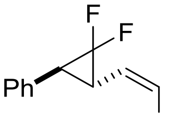
20a

Ester **20a** was prepared from alcohol **17b** (340 mg, 1.47 mmol), TEMPO (26 mg, 0.47 mmol), BAIB (512 mg, 1.62 mmol), (carbethoxyethylidene)triphenylphosphorane (692 mg, 1.9 mmol) and anhydrous DCM (10 mL) according to general procedure D with an oxidation time of 4 hours and an olefination time of 17 hours. Column chromatography on silca gel (1:19 Et_2O in hexane) afford ester **20a** as a yellow oil (290 mg, 74%); R_f = 0.47 (1:4 Et_2O in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39-7.30 (m, Ar*H*, 3H), 7.29-7.25 (m, Ar*H*, 2H), 6.59 (ddd, *J* = 9.7 Hz, $^4J_{H-F}$ = 3.0 Hz, ^4J = 1.5 Hz, C*H*=CCH$_3$, 1H), 4.25 (q, *J* = 7.2 Hz, OC*H₂*CH$_3$, 2H), 2.86 (dd, J_{H-F} = 14.9 Hz, *J* = 7.2 Hz, ArC*H*CF$_2$CH, 1H), 2.70 (ddd, J_{H-F} = 13.3 Hz, *J* = 9.7, 7.3 Hz, C*H*CH=CH$_3$, 1H), 2.00 (d, ^4J = 1.2 Hz, CH=C(C*H₃*), 3H), 1.34 ppm (t, *J* = 7.2 Hz, OCH$_2$C*H₃*, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 133.4 (d, $^4J_{C-F}$ = 4.9 Hz) 132.6, 130.8, 128.7, 127.9, 127.6, 113.8 (t, $^1J_{C-F}$ = 292.5 Hz), 60.8, 36.2 (dd, $^2J_{C-F}$ = 11.8, 9.6 Hz), 31.2 (t, $^2J_{C-F}$ = 11.2 Hz), 14.3, 13.1 ppm; ^{19}F NMR (376 MHz, CDCl$_3$): δ = -130.73 (dd, ^2J = 154.4 Hz, $J_{F\text{-}H}$ = 14.6 Hz, 1F), -135.5 (dd, ^2J = 154.8 Hz, $J_{F\text{-}H}$ = 13.5 Hz, 1F); $\bar{\nu}$/(film) = 2984, 2359, 2342, 1705, 1441, 1259 cm^{-1}; MS (CI): *m/z* (%): 275 (8) [(M-F)+C$_2$H$_5$]$^+$, 247 (100), [M-F]$^+$, 219 (11), [(M+H)-F-Et], 201 (20), 173 (39); HRMS (APCI): calcd for $C_{15}H_{17}F_2O_2$, 267.1191 [M+H]$^+$ found 267.1192; t$_R$ (GC) = 12.46 minutes.

Preparation of ethyl (*E*)-3-((1R*,3S*)-2,2-difluoro-3-phenylcyclopropyl)acrylonitrile (21a) and (*Z*)-3-((1R*,3S*)-2,2-difluoro-3-phenylcyclopropyl)acrylonitrile (21b) mixture



21a

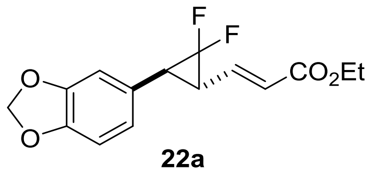


21b

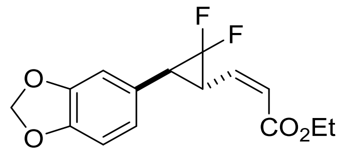
(Triphenylphosphoranylidene)acetonitrile (536 mg, 1.8 mmol) was added to a colourless solution of aldehyde **18b** (250 mg, 1.37 mmol) in anhydrous DCM (6 mL) at room temperature under nitrogen. The resulting yellow reaction mixture changed to a red solution after being stirred for 2.5 hours. The reaction mixture was concentrated under reduced pressure and the resulting ^{1}H NMR of crude product confirmed complete conversion of **18b**. Column chromatography on silca gel (1:4 Et$_2$O in hexane) afforded a 3:2 diastereoisomeric mixture of cyano-**21a** and **21b** (237 mg, 84%). Mixed data for **21a** and **21b**: R$_f$ = 0.29 (1:4 Et$_2$O in hexane); HRMS (APCI): calcd for $C_{12}H_{10}F_2N$, 206.0776 [M+H]$^+$ found 206.0774; $\bar{\nu}$/(film) = 3291, 2912, 1495, 1476, 1437, 1236, 1167, 1103, 1036, 1011, 930 cm^{-1}; Extracted data for **21a**: ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.42-7.24 (m, Ar*H*, 5H), 6.53 (ddt, *J* = 16.3, 9.6 Hz, $^4J_{H\text{-}F}$ = 1.3 Hz, C*H*=CHCN, 1H), 5.60 (d, *J* = 16.4 Hz, CH=C*H*CN, 1H), 3.00-2.93 (m, ArC*H*, 1H), 2.65 ppm (ddd, $J_{H\text{-}F}$ = 12.3 Hz, *J* = 9.6, 7.2 Hz, C*H*CH=CH, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 146.9 (d, $^4J_{C\text{-}F}$ = 4.9 Hz), 131.5, 128.9, 128.1, 127.9, 116.8, 112.8 (t, $^1J_{C\text{-}F}$ = 293.6 Hz), 101.8, 36.4 (dd, $^2J_{C\text{-}F}$ = 11.9, 9.6 Hz), 34.2 ppm (t, $^2J_{C\text{-}F}$ = 11.6 Hz); ^{19}F NMR (376 MHz, CDCl$_3$): δ = -129.9 (dd, ^2J = 158.1 Hz, $J_{F\text{-}H}$ = 15.3 Hz, 1F), -135.5 ppm (dd, ^2J = 158.1 Hz, $J_{F\text{-}H}$ = 12.10 Hz, 1F); MS (CI): *m/z* (%): 246 (11) [M+C$_3$H$_5$]$^+$, 234 (23) [M+C$_2$H$_5$]$^+$, 206 (94) [M+H]$^+$, 186 (100) [M-F]$^+$; t$_R$ (GC) = 11.45 minutes. Extracted data for **21b**: ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.42-7.24 (m, Ar*H*, 5H), 6.32 (ddt, *J* = 11.0, 9.8 Hz, $^4J_{H\text{-}F}$ = 1.1 Hz, CHC*H*=CHCN, 1H), 5.55 (d, *J* = 11.1 Hz, CH=C*H*CN, 1H), 3.09 (ddd, $J_{H\text{-}F}$ = 12.3 Hz, *J* = 9.8, 6.9 Hz, C*H*CH=, 1H), 3.00-2.93 ppm (m, ArC*H*, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 146.2 (d, $^4J_{C\text{-}F}$ =

5.4 Hz), 131.2, 128.9, 128.1, 127.9, 115.8, 112.8 (t, $^{1}J_{C\text{-}F}$ = 293.1 Hz), 101.4, 36.6 (d, $^{2}J_{C\text{-}F}$ = 11.8, 9.22), 33.1 ppm (d, $^{2}J_{C\text{-}F}$ = 13.3, 10.4); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -130.0 (dd, ^{2}J = 156.9, $J_{H\text{-}F}$ = 15.0 Hz, 1F), -135.8 ppm (dd, ^{2}J = 156.9, $J_{H\text{-}F}$ = 12.2 Hz, 1F); MS (CI): *m/z* (%): 246 (6) $[M+C_3H_5]^+$, 234 (15) $[M+C_2H_5]^+$, 206 (22) $[M+H]^+$, 186 (100) $[M-F]^+$; t_R (GC) = 11.86 minutes.

Preparation of ethyl (*E*)-3-((1R*,3S*)-3-(benzo[d][1,3]dioxol-5-yl)-2,2-difluorocyclopropyl)acrylate (22a) and of ethyl (*Z*)-3-((1R*,3S*)-3-(benzo[d][1,3]dioxol-5-yl)-2,2-difluorocyclopropyl)acrylate (22b)



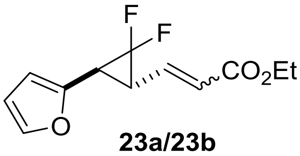
22a



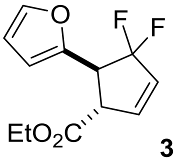
22b

Ester **22a** was prepared from alcohol **17d** (36.5 mg, 0.16 mmol), TEMPO (3.7 mg, 0.02 mmol), BAIB (57 mg, 0.18 mmol), (ethoxycarbonylmethylene)triphenylphosphorane (85 mg, 0.21 mmol) and anhydrous DCM (2 mL) according to General Procedure D with an oxidation time of 4 hours and an olefination time of 4 hours. Column chromatography on silica gel (1:9 diethyl ether in hexane) afforded **22a** (23.5 mg, 50%) and a mixture of **22a** and **22b** (10 mg, 21%) as pale yellow oils. Data for **22a**: R_f = 0.25 (1:4 Et_2O in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.81-6.72 (m, Ar*H*, 3H), 6.77 (dd, *J* = 15.3, 8.9 Hz, C*H*=CHCO$_2$Et, 1H), 6.08 (d, *J* = 15.5 Hz, CH=C*H*CO$_2$Et, 1H), 5.98 (s, OC*H$_2$*O, 2H), 4.23 (q, *J* = 7.1 Hz, OC*H$_2$*CH$_3$, 2H), 2.84 ($J_{H\text{-}F}$ = 14.7 Hz, *J* = 7.1 Hz, ArC*H*, 1H), 2.54 (ddd, $J_{H\text{-}F}$ = 13.0 Hz, *J* = 8.9, 7.1 Hz, C*H*CH=CH, 1H), 1.33 (t, *J* = 7.1 Hz, OCH$_2$C*H$_3$*, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.2, 147.5, 146.7, 139.8 (d, $J_{C\text{-}F}$ = 4.7 Hz), 125.2, 123.1, 121.2, 112.7 (t, $^{1}J_{C\text{-}F}$ = 292.4 Hz), 107.9, 107.7, 100.8, 60.1, 35.2 (dd, $^{2}J_{C\text{-}F}$ = 12.1, 9.3 Hz), 33.4 (t, $^{2}J_{C\text{-}F}$ = 11.7 Hz), 13.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -130.6 (dd, ^{2}J = 156.5 Hz, $J_{F\text{-}H}$ = 14.7 Hz, 1F), -135.5 (dd, ^{2}J = 156.2 Hz, $J_{F\text{-}H}$ = 13.0 Hz, 1F); $\bar{\nu}$/(film) = 2924, 2359, 2342, 1715, 1505, 1493, 1445, 1256, 1188 1165, 1096, 1038, 1018, 789 cm^{-1}; MS (CI): m/z (%): 325 (4) $[M+C_2H_5]^+$, 305 (9) $[(M-F)+C_2H_5]^+$, 277 (100) $[M-F]^+$, 259 (11) $[M-F_2]^+$, 231 (44), 203 (24), 175 (5); HRMS (APCI): calcd for $C_{15}H_{18}F_2O_4N$, 314.1198 $[M+NH_4]^+$ found 314.1199; t_R (GC) = 14.30 minutes. Extracted Data for **22b**: R_f = 0.40 (1:4 Et_2O in hexane); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -132.5 (dd, ^{2}J = 154.4 Hz, $J_{F\text{-}H}$ = 14.8 Hz, 1F), -136.1 (dd, ^{2}J = 153.6 Hz, $J_{F\text{-}H}$ = 13.5 Hz, 1F).

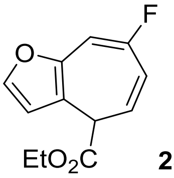
Attempted preparation of ethyl (*E*)-3-((1R*,3S*)-2,2-difluoro-3-(furan-2-yl)cyclopropyl)acrylate (23a/23b)



23a/23b



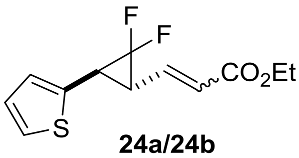
30a



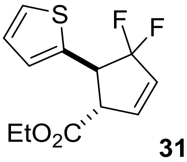
28a

The synthesis of ester **23a** was attempted from alcohol **17a** (1.33 g, 7.6 mmol), BAIB (2.67 mg, 8.36 mmol), TEMPO (60 mg, 1.52 mmol), (ethoxycarbonylmethylene)-triphenylphosphorane (5.3 g, 9.8 mmol) and DCM (30 mL) according to general procedure D with an oxidation time of 3 h and olefination time of 16 h. The ^{19}F NMR of the resulting crude reaction mixture confirmed complete consumption of **17a**. Column chromatography on silica gel (1:19 Et_2O in hexane) afforded a set of fractions containing rearrangement product **28a** with trace amounts of difluorocyclopentene **30a** (1.06 g, 80%) as a pale yellow oil. Further purification attempts failed as isolated compounds showed signs of decomposition (solution turned black). No evidence of ester **23** was observed during the reaction and initial purification, consistent with rearrangement occurring at room temperature. ^{1}H and ^{19}F NMR spectra are consistent with heptadiene **28a** and show similarities with the corresponding thiophene based product (**29a**) which was fully characterised (*vide infra*). Extracted data for **28a**: R_f = 0.38 (1:4 Et_2O in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, J = 2.0 Hz, Ar*H*, 1H), 6.57 (dddd, $J_{H\text{-}F}$ = 15.2 Hz, ^4J = 2.0 Hz, ^5J = 0.7, 0.5 Hz, C-C*H*=CF, 1H), 6.28 (dd, J = 2.0 Hz, ^4J = 0.6 Hz, Ar*H*, 1H), 6.17 (dddd, $J_{H\text{-}F}$ = 11.5 Hz, J = 10.7 Hz, ^4J = 2.0 Hz, 0.5 Hz, (F)CC*H*=CH, 1H), 5.89 (ddd, J = 10.7, 7.2 Hz, $^4J_{H\text{-}F}$ = 4.1 Hz, ^5J = 0.5 Hz), 4.23 (ABq, J = 7.4 Hz, ^2J = 1.4 Hz, $OCH_aH_bCH_3$, 2H), 4.18 (br. d, J = 7.5 Hz, C(*H*)CO_2Et, 1H), 1.29 ppm (t, J = 7.2 Hz, CH_2CH_3, 3H); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -105.67 ppm (ddd, $J_{F\text{-}H}$ = 15.2, 11.5 Hz, $^4J_{F\text{-}H}$ = 4.2 Hz).

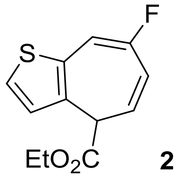
Attempted preparation of ethyl (*E*)-3-((1R*,3S*)-2,2-difluoro-3-(thiophen-2-yl)cyclopropyl)acrylate (24a/24b)



24a/24b



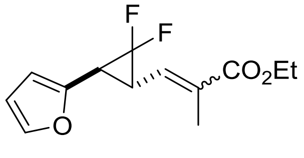
31a



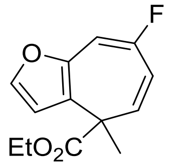
29a

The synthesis of ester **24a** was attempted from alcohol **17c** (684 mg, 3.6 mmol), BAIB (1.26 g, 3.96 mmol), TEMPO (28 mg, 0.72 mmol), (ethoxycarbonylmethylene)-triphenylphosphorane (1.64 g, 4.68 mmol) and DCM (15 mL) according to general procedure D with an oxidation time of 3 h and an olefination time of 16 h. The ^{1}H NMR spectrum of the crude reaction mixture confirmed complete consumption of **17c**. Column chromatography on silica gel (1:19 Et_2O in hexane) afforded a set of fractions containing **24b** (12 mg), a mixture of rearrangement products and alkenoate **24a** (420 mg) and a mixture of rearrangement products **29a** and **31a** (212 mg). A solution of crude product containing **24a** in $CDCl_3$ (1 mL) and **24b** in $CDCl_3$ (1 mL) were heated at 40 °C and 50 °C, respectively for 17 h. ^{1}H and ^{19}F NMR showed complete consumption of VCP-precursors. Product samples containing a clean mixture of **29a** and **31a** were combined and concentrated under reduced pressure to afford a brown oil (488 mg). HPLC purification on a Kromasil C18 cartridge (2:5 to 1:1 gradient of MeCN containing 0.1% ammonia solution in 10 mM ammonium bicarbonate for 10 minutes then 1:1 to 9.9:10 of the same eluent for 30 minutes) afforded clean heptadiene **29a** (112 mg, 14%) as an orange oil and a brown oil containing a mixture of **29a** and dilfuorocyclopentene **31a** (24 mg, 1:1 by ^{1}H NMR, the latter characterised by the distinctive ^{19}F NMR signals). Data for **29a**: $R_f = 0.42$ (1:4 Et_2O in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.38 (d, J = 5.2 Hz, Ar*H*, 1H), 6.80 (dd, $J_{\text{H-F}}$ = 15.6 Hz, ^{4}J = 1.7 Hz, C-C*H*=CF, 1H), 6.77 (d, J = 5.24 Hz, Ar*H*, 1H), 6.21 (dddd, J = 10.9 Hz, $J_{\text{H-F}}$ = 7.3 Hz, ^{4}J = 1.7, 0.8 Hz, CHCH=C*H*-CF, 1H), 6.01 (ddd, J = 10.9, 7.0 Hz, $^{4}J_{\text{H-F}}$ = 4.6 Hz, CH-C*H*=CH, 1H), 4.29 (ABq, J = 7.2 Hz, ^{2}J = 1.4 Hz, $OCH_aH_bCH_3$, 2H), 3.98 (d, J = 7.0 Hz, C(*H*)CO_2Et, 1H), 1.32 ppm (t, J = 7.2 Hz, CH_2CH_3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.6, 158.8 (d, $^{1}J_{\text{C-F}}$ = 246 Hz), 132.3 (d, $J_{\text{C-F}}$ = 14.9 Hz), 129.7, 126.8 (d, $^{5}J_{\text{C-F}}$ = 3.1 Hz), 125.8 (d, $J_{\text{C-F}}$ = 13.0 Hz), 125.5, 120.5 (d, $^{2}J_{\text{C-F}}$ = 35.2 Hz), 106.1 (d, $^{2}J_{\text{C-F}}$ = 31.4 Hz), 60.9, 44.7, 13.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -103.4 ppm (ddd, $J_{\text{F-H}}$ = 15.6, 7.3 Hz, $^{4}J_{\text{F-H}}$ = 4.6 Hz); $\bar{\nu}$/(film) = 2980, 2937, 1733, 1632, 1444, 1402, 1370, 1333, 1308, 1186, 1137 cm^{-1}; MS (CI): *m/z* (%): 239 (41) [M+H]$^+$, 219 (35) [M-F]$^+$, 193 (25) [M-OEt]$^+$, 165 (100) [M-CO$_2$Et]$^+$, 147 (9); HRMS (APCI): calcd for $C_{12}H_{12}FSO_2$, 239.0542 [M+H]$^+$ found 239.0548; t$_R$ (GC) = 12.91 minutes. Extracted data for **31a**: ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.31 (dd, *J* = 5.1 Hz, ^4J = 1.3 Hz, Ar*H*, 1H), 7.09-7.07 (br m, containing d *J* = 3.7 Hz, Ar*H*, 1H), 7.04 (dd, *J* = 5.1, 3.7 Hz, Ar*H*, 1H), 6.46 (dt, *J* = 6.0, 1.9 Hz, ^4J = 1.9 Hz, CF$_2$-CH=C*H*, 1H), 6.10 (dd, *J* = 6.0 Hz, ^4J = 2.7 Hz, CF$_2$-C*H*=CH, 1H), 4.34-4.24 (m, under peak for **29a**, ArC*H*, 1H), 4.21 (q, *J* = 7.2 Hz, OC*H$_2$*CH$_3$, 2H), 3.94-3.88 (m, C*H*CO$_2$Et, 1H), 1.28 ppm (t, *J* = 7.2 Hz, CH$_2$C*H$_3$*, 3H); ^{19}F NMR (376 MHz, CDCl$_3$): δ = -92.4 (ddd, ^2J = 250.5 Hz, $J_{F\text{-}H}$ = 14.8 Hz, $^4J_{F\text{-}H}$ = 7.6 Hz, CF_aF$_b$, 1F), -93.7 ppm (ddd, ^2J = 250.5 Hz, $J_{F\text{-}H}$ = 14.6 Hz, $^4J_{F\text{-}H}$ = 5.4 Hz, CF$_a$$F_b$, 1F); MS (CI): *m/z* (%): 267 (7) [M-F+C$_2$H$_5$]$^+$, 239 (100) [M-F]$^+$, 221 (8) [M-F$_2$+H]$^+$, 193 (25), 165 (12); t$_R$ (GC) = 12.11 minutes.

Attempted preparation of ethyl (*E*)-3-((1R*,3S*)-2,2-difluoro-3-(furan-2-yl)cyclopropyl)acrylate (25a/25b)



25a/25b

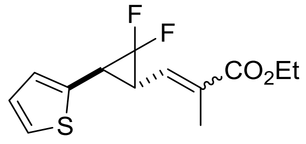


28b

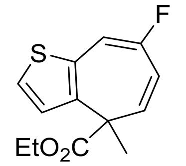
The synthesis of ester **25a** was attempted from alcohol **17a** (52 mg, 0.3 mmol), BAIB (106 mg, 0.33 mmol), TEMPO (5 mg, 0.03 mmol), (carbethoxyethylidene)triphenylphosphorane (142 mg, 0.39 mmol) and DCM (2 mL) according to general procedure D with an oxidation time of 3 h and an olefination time of 14 h. The ^{1}H NMR spectrum of the crude reaction mixture confirmed complete consumption of **17a**, forming cycloheptadiene **28b** exclusively. The crude reaction mixture was transferred onto a pad of silica (10 g) in a sinter funnel which had been conditioned with hexane. The pad was eluted with 0:1 to 1:9 Et$_2$O in hexane to afford cycloheptadiene **28b** as a pale yellow oil (34 mg, 48%). R$_f$ = 0.41(1:4 Et$_2$O in hexane); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.53 (d, *J* = 2.0 Hz, Ar*H*, 1H), 6.57 (dddd, $J_{H\text{-}F}$ = 14.9 Hz, ^4J = 2.0, 0.7 Hz, ^5J = 0.6 Hz, C-C*H*=CF, 1H), 6.28 (dd, *J* = 2.0 Hz, ^4J = 0.7 Hz, Ar*H*, 1H), 6.14 (ddd, *J* = 11.7 Hz, $J_{H\text{-}F}$ = 10.3 Hz, ^4J = 2.0 Hz, C(F)-C*H*=CH, 1H), 5.76 (dd, *J* = 11.7 Hz, $^4J_{H\text{-}F}$ = 4.2 Hz, C(F)-CH=C*H*, 1H), 4.18 (q, *J* = 7.2 Hz, OC*H$_2$*CH$_3$, 2H), 1.64 (s, C*H$_3$*, 3H), 1.25 ppm (t, *J* = 7.2 Hz, CH$_2$C*H$_3$*, 3H); ^{13}C NMR (150 MHz, CDCl$_3$): δ = 173.9, 157.8 (d, $^1J_{C\text{-}F}$ = 241.0 Hz), 146.2 (d,

$^4J_{C\text{-}F}$ = 15.9 Hz), 144.4 (d, $^5J_{C\text{-}F}$ = 4.1 Hz), 133.2 (d, $J_{C\text{-}F}$ = 13.1 Hz), 120.5 (d, $^2J_{C\text{-}F}$ = 37.7 Hz), 120.3 (d, $J_{C\text{-}F}$ = 3.9 Hz), 109.9, 102.5 (d, $J_{C\text{-}F}$ =33.7 Hz), 61.4, 44.9, 24.0, 14.1 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -107.05 (ddd, $J_{F\text{-}H}$ = 14.9, 10.3 Hz, $^4J_{F\text{-}H}$ = 4.2 Hz); $\bar{\nu}$/(film) =2980, 2934, 1794, 1731, 1641, 1459, 1405, 1376, 1251, 1216, 1149, 1108, 1017 cm^{-1}; MS (CI): *m/z* (%): 237 (33) $[M+H]^+$, 217 (30) $[M-F]^+$, 191 (15) $[M-OEt]^+$, 189 (13) $[M-(F+Et)+H]^+$, 163 (100) $[M-CO_2Et]^+$, 145 (8) $[M-(CO_2Et+F)+H]^+$; HRMS (APCI): calcd for $C_{13}H_{17}F_1N_1O_3$, 254.1187 $[M+NH_4]^+$ found 254.1189; t_R (GC) = 12.05 minutes.

Attempted preparation of ethyl (*E*)-3-((1R*,3S*)-2,2-difluoro-3-(thiophen-2-yl)cyclopropyl)acrylate (26a/26b)



26a/26b

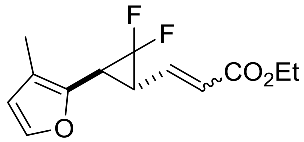


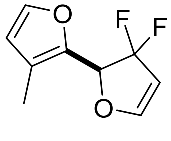
29b

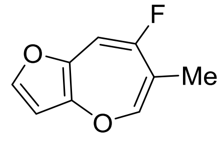
The synthesis of ester **26a** was attempted from alcohol **17c** (93 mg, 0.48 mmol), BAIB (171 mg, 0.53 mmol), TEMPO (7.5 mg, 0.05 mmol), (carbethoxyethylidene)triphenylphosphorane (226 mg, 0.62 mmol) and DCM (3.2 mL) according to general procedure D with an oxidation time of 3 h and an olefination time of 14 h. The ^{1}H NMR spectrum of the crude reaction mixture confirmed complete consumption of **17c**, forming cycloheptadiene **29b** exclusively. The crude reaction mixture was transferred onto a pad of silica (10 g) in a sinter funnel which had been conditioned with hexane. The pad was eluted with 0:1 to 1:9 Et_2O in hexane to afford cycloheptadiene **29b** as a pale yellow oil (66 mg, 55%). R_f = 0.39 (1:4 Et_2O in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 5.4 Hz, Ar*H*, 1H), 6.88 (d, *J* = 5.4 Hz, Ar*H*, 1H), 6.76 (dd, $J_{H\text{-}F}$ = 15.4 Hz, ^4J = 2.0 Hz, C-C*H*=CF, 1H), 6.24 (ddd, *J* = 11.1 Hz, $J_{H\text{-}F}$ = 8.2 Hz, ^4J = 2.0 Hz, CF-C*H*=CH, 1H), 5.80 (dd, *J* = 11.1 Hz, $^4J_{H\text{-}F}$ = 4.6 Hz, CF-CH=C*H*, 1H), 4.14 (q, *J* = 7.2 Hz, OCH_2CH_3, 2H), 1.79 (s, C-CH_3, 3H), 1.20 ppm (t, *J* = 7.2 Hz, CH_2CH_3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.8, 158.2 (d, $^1J_{C\text{-}F}$ = 244.5 Hz), 135.4 (d, $^4J_{C\text{-}F}$ = 2.0 Hz), 132.9 (d, $J_{C\text{-}F}$ = 13.1 Hz), 132.0 (d, $J_{C\text{-}F}$ = 13.5 Hz), 126.4 (d, $^5J_{C\text{-}F}$ = 3.3 Hz), 125.3, 120.0 (d, $^2J_{C\text{-}F}$ = 36.0 Hz), 105.9 (d, $^2J_{C\text{-}F}$ = 31.3 Hz), 60.8, 47.6, 23.3, 13.6 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -106.10 (ddd, $J_{F\text{-}H}$ = 15.4, 8.2 Hz, $^4J_{F\text{-}H}$ = 4.6 Hz); $\bar{\nu}$/(film) = 2980, 2937, 1733, 1632, 1444, 1402, 1370, 1333, 1308, 1186, 1137 cm^{-1}; MS (CI): *m/z* (%): 253 (31) $[M+H]^+$, 233 (53) $[M-F]^+$, 207 (19) $[M-OEt]^+$, 179

(100) [M-CO_2Et]$^+$, 161 (8) [M-(CO_2Et+F)+H]$^+$; HRMS (APCI): calcd for $C_{13}H_{14}F_1S_1O_2$, 253.0693 [M+H]$^+$ found 253.0696; t_R (GC) = 13.17 minutes.

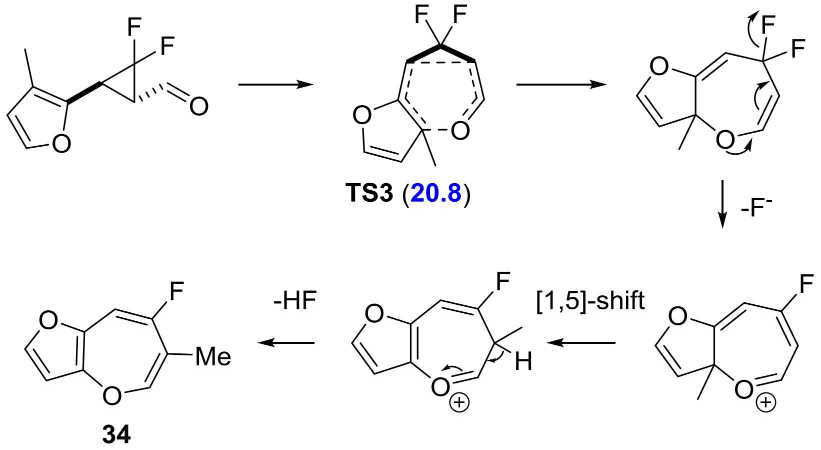
Attempted preparation of ethyl (*E*)-3-((1R*,3S*)-2,2-difluoro-3-(2'-furyl-3-methyl)cyclopropyl)acrylate (S9a/S9b)


S9a/S9b


33


34

The synthesis of ester **S9a** was attempted from alcohol **17h** (71 mg, 0.38 mmol), BAIB (144 mg, 0.45 mmol), TEMPO (11 mg, 0.08 mmol), (carbethoxyethylidene)triphenylphosphorane (183 mg, 0.53 mmol) and DCM (3 mL) according to general procedure D with an oxidation time of 6 h and an olefination time of 16 h. Crude ^{1}H and ^{19}F NMR after oxidation suggested rearrangement had occurred before addition of phosphorane. The reaction mixture was concentrated under reduced pressure and crude ^{1}H and ^{19}F NMR showed no new formation of rearrangement products. Attempted chromoatographic purification on silica gel (0:1 to 1:4 Et_2O in hexane) failed to isolated desired rearrangement products either due to product volatility or decomposition on silica. ^{19}F NMR of crude products showed strong similarities to 3,3-difluoro-4,5-dihydrofurans reported by Hammond and Arimitsu (^{19}F NMR: δ = -84.6 (ddd, J = 248.0, 23.1, 19.8 Hz, 1F) -87.2 ppm (ddd, J = 248.0, 13.2, 13.2 Hz, 1F))[S19] and benzoheptadiene compounds reported previously by ourselves (^{19}F NMR: δ = -100.7 ppm (dt, $J_{F\text{-}H}$ = 18.2, 5.2 Hz, $^4J_{F\text{-}H}$ = 5.2 Hz, 1F).[S20] Due to these similarities the crude products were tentatively assigned as dihydrofuran **33** and ether **34** (1:2.5 ratio respectively by ^{19}F NMR); the doublet of doublet observed for the latter suggest the methyl group underwent [1,5]-shift during the re-aromatisation of the furan (**Scheme S4**).

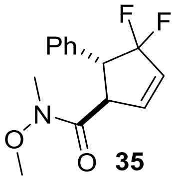


Scheme S4: Proposed mechanism rearrangement of **18h** to **34** through rearrangements ($\Delta G^{\ddagger}$ value (**blue**) quoted in kcal mol^{-1})

Data for **33**: ^{19}F NMR (376 MHz, CDCl$_3$): δ = -81.9 (dd, ^2J = 248.0 Hz, $J_{F\text{-}H}$ = 20.0 Hz, 1F), -89.3 ppm (dt, ^2J = 248.0 Hz, $J_{F\text{-}H}$ = 13.8 Hz, 1F). Data for **34**: ^{19}F NMR (376 MHz, CDCl$_3$): δ = -99.4 ppm (dd, $J_{F\text{-}H}$ = 34.0 Hz, $^4J_{F\text{-}H}$ = 18.5 Hz).

General Procedure E: Thermal Rearrangement of Vinyl Difluorocyclopropanes

Preparation of (1R*,5R*)-4,4-difluoro-N-methoxy-N-methyl-5-phenylcyclopent-2-ene-1-carboxamide (35)



35

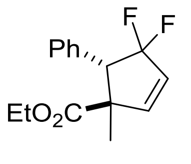
A solution of **19a** (7.0 mg, 0.026 mmol) in toluene (0.3 mL) was heated to 95 °C in a sealed microwave vial for 17 hours in a DrySyn block. After cooling and venting the vial, ^{19}F NMR confirmed complete consumption of **19a**. The reaction mixture was transferred to a round bottom flask using DCM (5 mL) and concentrated under reduced pressure to afford difluorocyclopentene **35** (6.8 mg, 97%) as a yellow oil. R$_f$ = 0.36 (1:1 Et$_2$O in hexane); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.40-7.31 (m, Ar*H*, 5H), 6.40 (dt, J = 6.0, 1.6 Hz, $J_{H\text{-}F}$ = 1.6 Hz, =C*H*CHCO, 1H), 6.10 (dd, J = 6.0 Hz, ^4J = 2.5 Hz, CF$_2$C*H*=CH, 1H), 4.34 (dddd, $^4J_{H\text{-}F}$ = 8.9, 5.2 Hz, J = 6.7, 1.6 Hz, COC*H*, 1H), 4.11 (ddd, $J_{H\text{-}F}$ = 16.1, 15.4 Hz, J = 6.7 Hz, PhC*H*, 1H), 3.49 (s, OC*H*$_3$, 3H), 3.20 ppm (s, OC*H*$_3$, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 170.5, 139.1 (t, $J_{C\text{-}F}$ = 10.0 Hz), 134.1, 129.6 (t, $^1J_{C\text{-}F}$ = 254.7 Hz), 128.9, 128.3 (dd, $^2J_{C\text{-}F}$ = 30.1, 25.2 Hz), 128.0, 127.3, 60.9, 53.2 (t,

$^{2}J_{C\text{-}F}$ = 24.5 Hz), 51.4 (d, $J_{C\text{-}F}$ = 5.3 Hz), 31.9 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -90.2 (ddd, ^{2}J = 251.0 Hz, $J_{F\text{-}H}$ = 16.1, $^{4}J_{H\text{-}F}$ = 8.9 Hz, 1F), -92.0 ppm (ddd, ^{2}J = 251.1 Hz, $J_{F\text{-}H}$ = 15.4, $^{4}J_{H\text{-}F}$ = 5.2 Hz, 1F); $\bar{\nu}$/(film) = 2963, 2940, 2361, 2342, 1661, 1456, 1418, 1387, 1364, 1350, 1169, 1051, 1034, 1026, 1093 cm^{-1}; MS (CI): *m/z* (%): 296 (19) [(M+H)-F]$^+$, 276 (26) [(M+H)-F]$^+$, 248 (100) [M-F]$^+$, 218 (10) [(M+H)-OMe-F]$^+$, 187 (16), 161 (6); HRMS (APCI): calcd for $C_{14}H_{15}F_2NO_2Na$, 290.0963 [M+Na]$^+$ found 290.0964; t_R (GC) = 12.97 minutes.

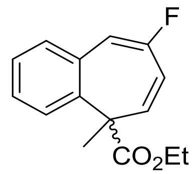
Thermolysis of (*Z*)-3-((1R*,3S*)-2,2-difluoro-3-phenylcyclopropyl)-N-methoxy-N-methylacrylamide (19b)

A solution of **19b** (126 mg, 0.47 mmol) in Ph_2O (0.5 mL) was heated at 165 °C for 17 h according to General Procedure E. The crude reaction mixture was loaded onto a silica pad (10 g) conditioned with hexane. Ph_2O was eluted with hexane then crude products were eluted with Et_2O, collected and concentrated under reduced pressure to afford a brown oil (53 mg). ^{1}H and ^{19}F NMR confirmed full consumption of alkenoate **19b**. Column chromatography on silica gel (1:9 to 2:5 EtOAc in hexane) was used to separated two major unknown products as yellow oils; unknown **S10a** (13 mg) and unknown **S10b** (7 mg). Lack of distinctive Weinreb amide signals in the ^{1}H NMR suggests decomposition had occurred. Data for **S10a**: R_f = 0.21 (1:1 Et_2O in hexane); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -100.41 (d, $J_{F\text{-}H}$ = 15.9 Hz). Data for **S10b**: R_f = 0.39 (1:1 Et_2O in hexane); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -87.39 (s).

Attempted preparation of ethyl (1R*,5S*)-4,4-difluoro-1-methyl-5-phenylcyclopent-2-ene-1-carboxylate (36)



36

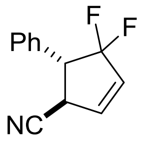


41

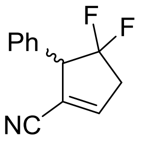
A solution of **20** (100 mg, 0.37 mmol) in Ph_2O (0.45 mL) was heated at 155 °C for 17 h according to General Procedure E. The crude reaction mixture was loaded onto a silica pad (16 g) conditioned with hexane. Ph_2O was eluted with hexane then crude products were eluted with Et_2O, collected and concentrated under reduced pressure to afford crude reaction mixture as a brown oil (100 mg). ^{1}H and ^{19}F NMR confirmed full consumption of alkenoate **20**. Column chromatography on silica gel (0:1 to 1:19 EtOAc in hexane) was used to separated two major unknown products as yellow oils; unknown **S11a** (8 mg) and unknown **S11b** (29 mg). Product assignment could not be determined due to complexity in ^{1}H NMR spectra. However, the major ^{19}F NMR signal for **S11b** was consistent with previously observed benzoheptadiene compounds and tentatively assigned as benzoheptadiene **41**. No evidence for VCPR rearrangement to difluorocyclopentene **36**.

Data for **S11a**: R_f = 0.18 (1:19 EtOAc in hexane); ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -103.67 (minor peak, dd, $J_{\text{F-H}}$ = 12.0, 7.5 Hz), -110.58 ppm (major peak, s). Data for **S11b**: R_f = 0.28 (1:19 EtOAc in hexane); ^{19}F NMR ($CDCl_3$, 376 MHz): δ = -95.84 (minor peak, dd, $J_{\text{F-H}}$ = 32.9, 15.0 Hz), -104.43 ppm (major peak, dt, $J_{\text{F-H}}$ = 17.8, 5.4 Hz, $^{4}J_{\text{F-H}}$ = 5.4 Hz).

Preparation of (1R*,5R*)-4,4-difluoro-5-phenylcyclopent-2-ene-1-carbonitrile (37) and 4,4-difluoro-5-phenylcyclopent-1-ene-1-carbonitrile (43)



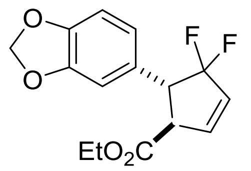
37



43

A solution of mixture **21a**/**21b** (100 mg, 0.48 mmol) in Ph_2O (1.0 mL) was heated to 90 °C in a sealed microwave vial for 17 hours in a DrySyn block. After cooling and venting, the resulting ^{19}F NMR spectrum confirmed full conversion of **21a**. The microwave vial was resealed and heated to 160 °C for 17 hours in a DrySyn block. After cooling and venting, the resulting ^{19}F NMR spectrum confirmed full consumption of **21b**. The crude reaction mixture was transferred onto a pad of silica (15 g) in a sinter funnel which has been conditioned with hexane. Ph_2O was eluted using hexane and then crude product fractions were eluted using Et_2O, collected and concentrated under reduced pressure to afford a red oil (106 mg). Column chromatography on silica gel (0:1 to 1:9 Et_2O in hexane) afforded a mixture difluorocyclopentenes **37** and **43** (6:1 ratio by ^{1}H NMR) as a yellow oil (44.7 mg, 48%). Data for mixture of **37** and **43**: R_f = 0.21 (1:9 Et_2O in hexane); $\bar{\nu}$/(film) = 3091, 3069, 3036, 2915, 2249, 2229, 1502, 1457, 1349, 1178 cm^{-1}; HRMS (APCI): calcd for $C_{12}H_8F_2N$, 204.0625 [M-H] found 204.0634; Data for **37**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47-7.40 (m, Ar*H*, 3H), 7.35-7.32 (m, Ar*H*, 2H), 6.45 (dt, *J* = 6.0, 1.9 Hz, $^{4}J_{\text{H-F}}$ = 1.3 Hz, C(F_2)CH=C*H*, 1H) 6.26 (dd, *J* = 6.0 Hz, $J_{\text{H-F}}$ = 2.6 Hz, C(F_2)-C*H*=CH, 1H), 3.99 (dddd, *J* = 7.6, 2.0 Hz, $^{4}J_{\text{H-F}}$ = 9.6, 5.0 Hz, C(*H*)CN, 1H), 3.90 ppm (ddd, J = 7.6 Hz, $J_{\text{H-F}}$ = 14.6, 13.7 Hz, ArC*H*, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 134.8 (t, $J_{\text{C-F}}$ = 10.0 Hz), 131.0, 130.4 (dd, $^{2}J_{\text{C-F}}$ = 30.1, 24.1 Hz), 128.5, 128.4 (represents 2 carbon atoms), 127.4 (t, $^{1}J_{\text{C-F}}$ = 246.7 Hz), 117.3 (d, $^{4}J_{\text{C-F}}$ = 5.2 Hz), 5.4 (t, $^{2}J_{\text{C-F}}$ = 25.4 Hz), 38.3 ppm (d, $J_{\text{C-F}}$ = 6.4 Hz); ^{19}F NMR (376 MHz, CDCl$_3$): δ = -90.98 (ddd, ^{2}J = 255.6 Hz, $J_{\text{F-H}}$ = 14.9 Hz, $^{4}J_{\text{F-H}}$ = 9.6 Hz, CF_aF$_b$, 1F), -93.00 ppm (ddd, ^{2}J = 255.6 Hz, $J_{\text{F-H}}$ = 13.7 Hz, $^{4}J_{\text{F-H}}$ = 14.6 Hz, CF$_a$$F_b$, 1F); MS (CI): *m/z* (%): 246 (10) [M+C$_3$H$_5$]$^+$, 234 (20) [M+C$_2$H$_5$]$^+$, 206 (77) [M+H]$^+$, 186 (100) [M-F]$^+$; t$_R$ (GC) = 11.31 minutes. Data for **47**: ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.47-7.40 (m, Ar*H*, 3H), 7.24-7.22 (m, Ar*H*, 2H), 6.87 (dtt, J = 5.0 Hz, $^{4}J_{\text{H-F}}$ = 2.6 Hz, ^{4}J = 2.2 Hz, CF$_2$-CH$_2$-C*H*=, 1H), 4.36 (dddt, $J_{\text{H-F}}$ = 18.0, 7.9 Hz, ^{4}J = 2.2, 1.4 Hz, ArC*H*, 1H), 3.17-3.09 (m, CF$_2$-CH_2-CH=,2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 143.9 (t, $J_{\text{C-F}}$ = 4.1 Hz), 129.9, 128.3, 128.2 (represents 2 carbon atoms), 127.1 (t, $^{1}J_{\text{C-F}}$ = 255.1 Hz), 115.9 (dd, $J_{\text{C-F}}$ = 6.7, 2.8 Hz), 114.1, 58.7 (dd, $^{2}J_{\text{C-F}}$ = 26.7, 25.4 Hz), 41.9 ppm (dd, $J_{\text{C-F}}$ = 28.9, 28.3 Hz); ^{19}F NMR (376 MHz, CDCl$_3$): δ = (-90.62)-(-91.40) (m, CF_aF$_b$, underneath ^{19}F signal for major product **37**), (-98.05)-(-98.76) ppm (m, containing d, ^{2}J = 233.1 Hz, CF$_a$$F_b$); MS (CI): *m/z* (%): 246 (7) [M+C$_3$H$_5$]$^+$, 234 (17) [M+C$_2$H$_5$]$^+$, 206 (100) [M+H]$^+$, 186 (35) [M-F]$^+$; t$_R$ (GC) = 11.50 minutes.

Preparation of ethyl (1R,5R)-5-(benzo[d][1,3]dioxol-5-yl)-4,4-difluorocyclopent-2-ene-1-carboxylate (39) and ethyl 8-fluoro-5H-cyclohepta[4,5]benzo[1,2-d][1,3]dioxole-5-carboxylate (44)



39

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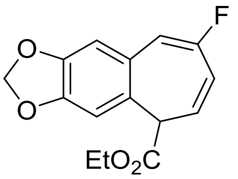
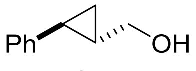


44

A solution of **22a** (445 mg, 0.07 mmol) in a toluene (7.5 mL) was heated to 70 °C for 17 h according the General Procedure E. ^{1}H and ^{19}F NMR showed full consumption of **22a** to a mixture of difluorocyclopentene **39** and benzoheptadiene **44** (42:58 respectively, relative ratio by ^{19}F NMR). HPLC purification on a Kromasil C18 cartridge (3:10 to 9.9:10 gradient of MeCN containing 0.1% ammonia solution in 10 mM ammonium bicarbonate) afford clean fluoroheptadiene **44** (45 mg, 11%) as a white solid and dilfuorocyclopentene **39** (82 mg, 18%). Note: poor yield could be due to partial solubility of crude reaction mixture in loading solvent for HPLC purification (1:1 DMSO/MeOH). Data for **39**: R$_f$ = 0.35 (1:4 Et$_2$O in hexane);

^{1}H NMR (400 MHz, CDCl$_3$): δ = 6.81 (s, Ar*H*, 3H), 6.48 (ddd, *J* = 6.0 Hz, $J_{\text{H-F}}$ = 1.7 Hz, ^{4}J = 1.7 Hz, CF$_2$-C*H*=CH, 1H), 6.07 (dd, *J* = 6.0, 2.5 Hz, CH=C*H*, 1H), 5.98 (s, O$_2$C*H*$_2$, 2H), 4.19 (q, *J* = 7.0 Hz, OC*H*$_2$CH$_3$, 2H), 3.95-3.82 (m, ArC*H* and *H*CCO$_2$Et, 2H), 1.26 ppm (t, *J* = 7.0 Hz, CH$_2$C*H*$_3$, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 170.2 (d, $^{4}J_{\text{C-F}}$ = 2.7 Hz), 147.3, 146.8, 138.4 (t, $J_{\text{C-F}}$ = 10.4 Hz), 129.0 (t, $^{1}J_{\text{C-F}}$ = 245.7 Hz), 128.4 (dd, $^{2}J_{\text{C-F}}$ = 30.8, 24.5 Hz), 127.2, 122.3, 108.8, 107.7, 100.6, 61.0, 54.2 (d, $J_{\text{C-F}}$ = 5.8 Hz), 53.1 (t, $^{2}J_{\text{C-F}}$ = 24.0 Hz), 13.6 ppm; ^{19}F NMR (376 MHz, CDCl$_3$): δ = -90.21 (ddd, ^{2}J = 252.5 Hz, $J_{\text{F-H}}$ = 16.4, $^{4}J_{\text{F-H}}$ = 8.6 Hz, C*F$_a$*F$_b$, 1F), -93.07 ppm (ddd, ^{2}J = 252.5 Hz, $J_{\text{F-H}}$ = 14.1, $^{4}J_{\text{F-H}}$ = 5.1 Hz, CF$_a$*F$_b$*, 1F); $\bar{\nu}$/(film) = 2982, 2904, 1614, 1731, 1506, 1493, 1446, 1245, 1167, 1018 cm^{-1}; MS (CI): *m/z* (%): 277 (100) [M-F]$^+$, 231 (16), 203 (15), 175 (4) [M-C$_7$O$_2$H$_5$]$^+$; HRMS (APCI): calcd for C$_{15}$H$_{14}$FO$_4$, 277.0876 [M-F] found 277.0905; t$_R$ (GC) = 14.09 minutes. Data for **44**: m.p. = 118-120 °C (chloroform/pentane); R$_f$ = 0.40 (1:4 Et$_2$O in hexane); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 6.82 (s, Ar*H*, 1H), 6.80 (d, $J_{\text{H-F}}$ = 18.1 Hz, C-C*H*=CF, 1H), 6.59 (s, Ar*H*, 1H), 6.22-6.14 (m, representing CF-C*H*=CH and C(H)-C*H*=CH, 2H), 6.01 (d, ^{2}J = 1.4 Hz, OC*H$_a$*H$_b$O, 1H), 5.98 (d, ^{2}J = 1.4 Hz, OCH$_a$*H$_b$*O, 1H), 4.30 (ABq, *J* = 7.2 Hz, ^{2}J = 1.9 Hz, OC*H$_a$H$_b$*CH$_3$, 2H), 3.69 (d, *J* = 5.2 Hz, *H*CCO$_2$Et, 1H), 1.31 ppm (t, *J* = 7.2 Hz, CH$_2$C*H*$_3$, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 171.0, 158.6 (d, $^{2}J_{\text{C-F}}$ = 245.5 Hz), 148.6, 146.1, 127.7 (d, $J_{\text{C-F}}$ = 12.5 Hz), 126.0 (d, $J_{\text{C-F}}$ = 11.4 Hz), 125.8, 119.3 (d, $^{2}J_{\text{C-F}}$ = 35.1 Hz), 113.0 (d, $^{2}J_{\text{C-F}}$ = 27.9 Hz), 107.0 (d, $^{5}J_{\text{C-F}}$ = 3.8 Hz), 105.1, 101.1, 60.9, 48.9, 13.7 ppm; ^{19}F NMR (376 MHz, CDCl$_3$): δ = -102.97 ppm (ddd, $J_{\text{F-H}}$ = 18.1, 4.8 Hz, $^{4}J_{\text{C-F}}$ = 4.8 Hz); $\bar{\nu}$/(film) = 2982, 2904, 1733, 1645, 1506, 1485, 1374, 1333, 1305, 1238, 1193 cm^{-1}; MS (CI): *m/z* (%): 305 (11) [M+C$_2$H$_5$]$^+$, 277 (65) [M+H]$^+$, 257 (41) [M+H]$^+$, 231 (100) [M-OEt]$^+$, 203 (40) [M-CO$_2$Et]$^+$, 57 (80); HRMS (ASAP+): calcd for C$_{15}$H$_{14}$FO$_4$, 277.0876 [M+H]$^+$ found 277.0884; t$_R$ (GC) = 14.97 minutes.

Preparation of ((1S*,2S*)-2-phenylcyclopropyl)methanol (S12)

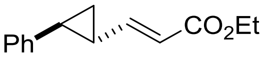


S12

Diiodomethane (1 ml, 12.5 mmol) was added dropwise to a solution of diethylzinc (6.25 mL of a 1 M solution in hexane, 6.25 mmol) in DCM (2 mL) at 0 °C over a period of 5 minutes and stirred for 20 minutes under nitrogen. A solution of cinnamyl alcohol (335 mg, 1.25 mmol) in DCM (1.5 mL) was added dropwise and the reaction mixture and stirred for 2.5 hours at 0 °C. The reaction mixture was quenched with saturated aqueous NH$_4$Cl (10 ml) and

EtOAc (10 ml). The organic layer was separated and the aqueous layer extracted further with EtOAc (3 x 10 ml). The original organic layer and extracts were combined, dried ($MgSO_4$) and concentrated under reduced pressure to remove volatile organic solvent. Column chromatography on silica gel (2:3 EtOAc in hexane) afforded alcohol **S12** as a yellow oil (93 mg, 52%). R_f = 0.23 (1:1 Et_2O in hexane); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.29-7.26 (m, Ar*H*, 2H), 7.17 (tt, *J* = 7.3 Hz, ^4J = 1.2 Hz, Ar*H*, 1H), 7.10-7.08 (m, Ar*H*, 2H), 3.64 (dd, ^2J = 11.3 Hz, *J* = 6.8 Hz, CH_aH_bOH, 1H), 3.62 (dd, ^2J = 11.3 Hz, *J* = 6.8 Hz, CH_aH_bOH, 1H), 1.84 (td, *J* = 9.8, 4.9 Hz, PhC*H*, 1H), 1.78 (br. s, O*H*, 1H), 1.50-1.44 (m, $CH_2CH(CH_2)CH$, 1H), 1.00-0.92 ppm (m, CH_2, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.5, 128.4, 125.9, 125.7, 66.5, 25.3, 21.3, 13.8 ppm; $\bar{\nu}$/(film) = 3333, 3026, 3003, 2361, 2342, 1605, 1497, 1018, 743, 696 cm^{-1}; MS (CI): *m/z* (%): 159 (14) $[(M+H)-OH]^+$, 131 (100) $[M-OH]^+$; 117 (29), 91 (28); t_R (GC) = 11.10 minutes. Data was in agreement with those reported by Charette and co-workers.[S21]

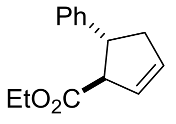
Preparation of ethyl (*E*)-3-((1R*,2S*)-2-phenylcyclopropyl)acrylate (47)



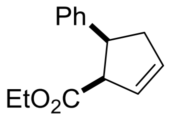
47

Ester **47** was prepared from alcohol **S12** (100 mg, 0.67 mmol), TEMPO (10 mg, 0.067 mmol), BAIB (237 mg, 0.74 mmol), (carbethoxyethylidene)triphenylphosphorane (303 mg, 0.87 mmol) and anhydrous DCM (1 mL) according to general procedure D with an oxidation time of 3.5 hours and an olefination time of 20 hours. Column chromatography on silica gel (1:9 Et_2O in hexane) afforded ester **47** as a colourless oil (100 mg, 67%). R_f = 0.42 (1:4 Et_2O in hexane); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.28 (m, Ar*H*, 2H), 7.21 (tt, *J* = 7.3 Hz, ^4J = 1.3 Hz, Ar*H*, 1H), 7.12-7.09 (m, Ar*H*, 2H), 6.62 (dd, *J* = 15.5, 9.9 Hz, CHC*H*=CH, 1H), 5.92 (d, *J* = 15.5 Hz, CH=C*H*, 1H), 4.21 (q, *J* = 7.2 Hz, OCH_2CH_3, 2H), 2.20 (ddd, *J* = 9.5, 6.2, 4.3 Hz, PhC*H*, 1H), 1.84 (dddd, *J* = 9.9, 8.4, 5.4, 4.1 Hz, $CH_2CHCH=CH$, 1H), 1.47 (ddd, ^2J = 8.5, *J* = 6.6, 5.2 Hz, $CHCH_aH_bCH$, 1H), 1.36-1.30 ppm (m, (incld. 1.31 ppm, t, *J* = 7.2 Hz, OCH_2CH_3, 3H), 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.2, 151.0, 140.3, 128.0, 125.7, 125.4, 118.4, 59.6, 26.4, 26.2, 17.2, 13.8 ppm; $\bar{\nu}$/(film) = 2980, 2359, 2342, 1709, 1643, 1256, 1175, 1036 cm^{-1}; MS (CI): *m/z* (%): 245 (6) $[M+C_2H_5]^+$, 217 (56) $[M+H]^+$, 171 (50) $[M-OEt]^+$, 143 (100) $[M-CO_2Et]^+$, HRMS (APCI): calcd for $C_{14}H_{17}O_2$, 217.1223 $[M+H]^+$ found 217.1224; t_R (GC) = 13.57 minutes.

Preparation of ethyl (1R*,5R*)-5-phenylcyclopent-2-ene-1-carboxylate (38a) and ethyl (1R*,5S*)-5-phenylcyclopent-2-ene-1-carboxylate (38b)



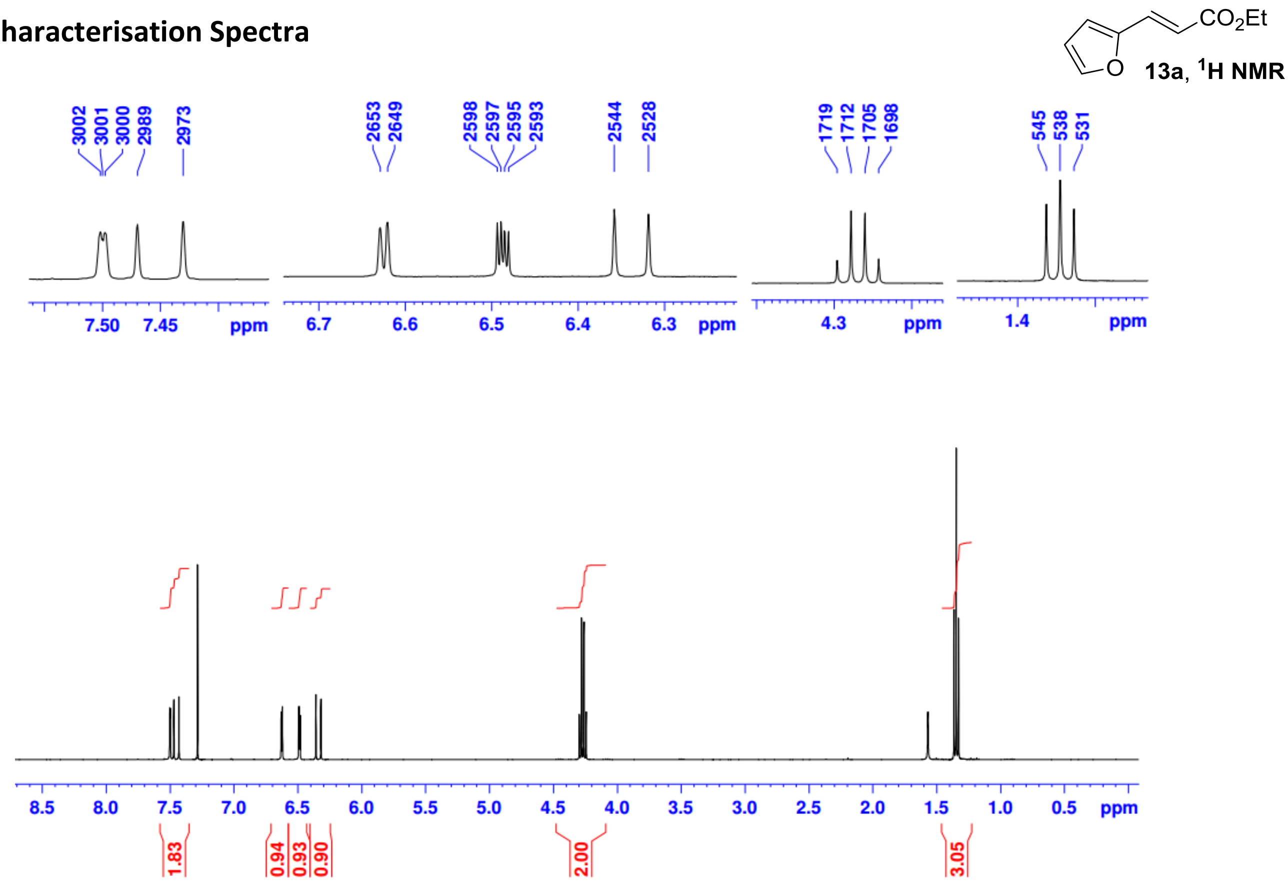
38a



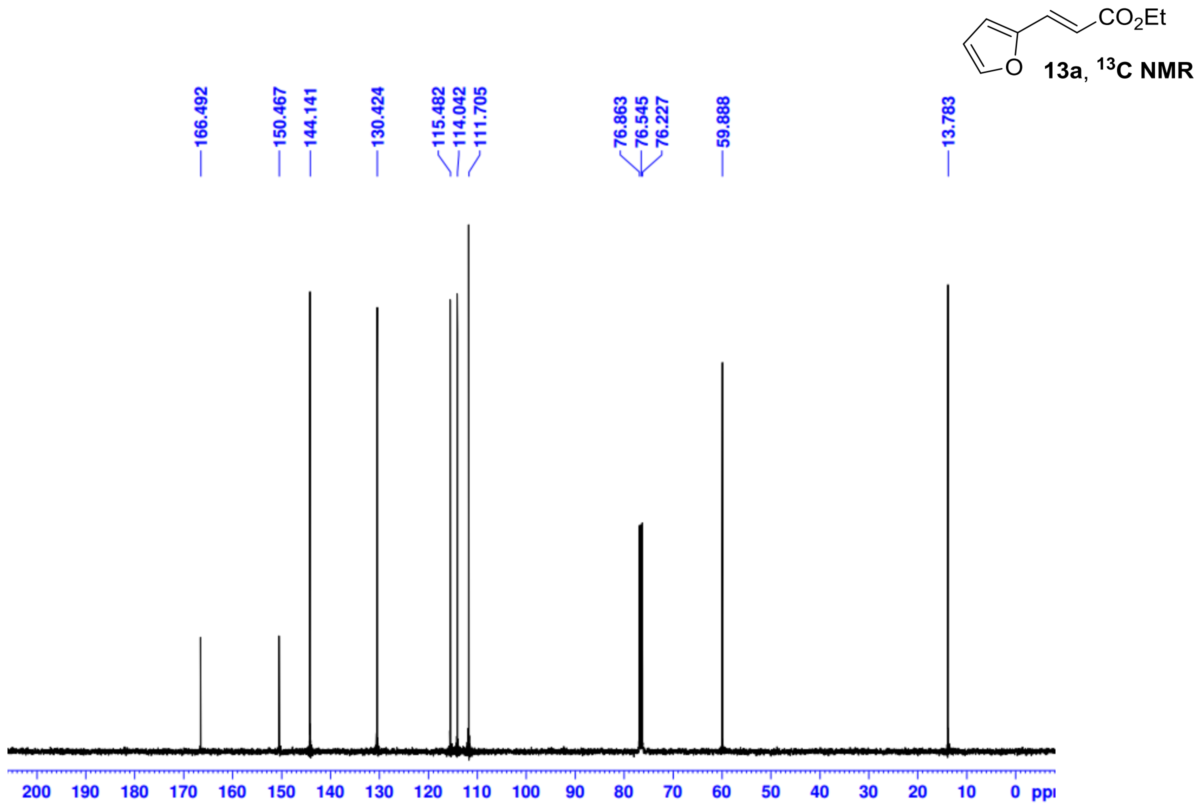
38b

A solution of **47a** (100 mg, 0.46 mmol) in a Ph_2O (0.5 mL) was heated to 220 °C for 17 h according the General Procedure E. The crude reaction mixture was transferred onto a pad of silica (10 g) in a sinter funnel which has been conditioned with hexane. Ph_2O was eluted using hexane and then crude product fractions were eluted using Et_2O, collected and concentrated under reduced pressure to afford an orange oil (80 mg). Column chromatography on silica gel (0:1 to 1:9 Et_2O in hexane) afforded a *trans*-**38a** (40 mg, 40%) and *cis*-**38b** (22 mg, 22%, compound started to decompose slowly after isolation to an unknown side product) as pale yellow oils. Data for *trans*-**38a**: R_f = 0.65 (1:4 Et_2O in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35-7.27 (m, Ar*H*, 3H), 7.25-7.21 (m, Ar*H*, 2H), 5.96 (ddt, *J* = 5.7, 2.5 Hz, ^4J = 2.3 Hz, $CH_2CH{=}C\mathit{H}$, 1H), 5.79 (ddt, *J* = 5.7, 2.4 Hz, ^4J = 2.2 Hz, $CH_2C\mathit{H}{=}CH$, 1H), 4.17 (q, *J* = 7.2 Hz, $OC\mathit{H_2}CH_3$, 2H), 3.83 (dt, *J* = 9.2, 6.6 Hz, ArC*H*, 1H), 3.67 (dddd, *J* = 9.2, 2.5 Hz, ^4J = 2.5, 2.2 Hz, $\mathit{H}CCO_2Et$, 1H), 3.00 (ddddd, ^2J = 16.9 Hz, *J* = 9.2, 2.4 Hz, ^4J = 2.6, 2.3 Hz, -$C\mathit{H_a}H_b$-, 1H), 2.56 (ddddd, ^2J = 16.9 Hz, *J* = 6.6, 2.4 Hz, ^4J = 2.6, 2.3 Hz, -$C\mathit{H_a}H_b$-, 1H), 1.27 ppm (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.6, 145.0, 132.2, 128.1, 127.7, 126.6, 125.9, 60.2, 59.0, 45.8, 41.1, 13.7 ppm; $\bar{\nu}$/(film) = 3060, 3029, 2980, 2932, 2906, 2854, 1731, 1495, 1457, 1245, 1176 cm^{-1}; MS (CI): *m/z* (%): 245 (2) $[M+C_2H_5]^+$, 217 (8) $[M+H]^+$, 171 (19) $[M\text{-}OEt]^+$, 143 (100) $[M\text{-}CO_2Et]^+$, HRMS (APCI): calcd for $C_{14}H_{17}O_2$, 217.1228 $[M+H]^+$ found 217.1229; t_R (GC) = 12.44 minutes. Data *cis*-**38b**: R_f = 0.52 (1:4 Et_2O in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27-7.28 (m, Ar*H*, 4H), 7.22-7.17 (m, Ar*H*, 1H), 6.15 (ddt, *J* = 5.7, 2.2 Hz, ^4J = 2.1 Hz, $CH_2CH{=}C\mathit{H}$, 1H), 5.85 (ddt, *J* = 5.7, 2.3 Hz, ^4J = 1.9 Hz, $CH_2C\mathit{H}{=}CH$, 1H), 3.93 (dddt, *J* = 9.1, 2.1 Hz, ^4J = 2.0, 1.9 Hz, $\mathit{H}CCO_2Et$, 1H), 3.85 (dt, *J* = 9.1, 7.2 Hz, ArC*H*, 1H), 3.78-3.61 (m, $OC\mathit{H_a}\mathit{H_b}CH_3$, 2H); 2.83 (dddd, *J* = 7.2, 2.3 Hz, ^4J = 2.2, 1.9 Hz, CH-$C\mathit{H_2}$-CH=CH-, 2H), 0.85 ppm (t, *J* = 7.0 Hz, CH_2CH_3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.2, 141.5, 133.8, 128.0, 127.5, 127.4, 126.0, 59.6, 55.9, 46.3, 38.4, 13.2 ppm; $\bar{\nu}$/(film) = 3060, 3029, 2980, 2932, 2904, 1729, 1495, 1457, 1370, 1178 cm^{-1}; MS (CI): *m/z* (%): 245 (5) $[M+C_2H_5]^+$, 217 (14) $[M+H]^+$, 171 (20) $[M\text{-}OEt]^+$, 143 (100) $[M\text{-}CO_2Et]^+$; HRMS (TOF): calcd for $C_{14}H_{17}O_2$, 216.1150 [M] found 216.1155; t_R (GC) = 12.28 minutes.

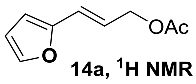
Characterisation Spectra



13a, ^{1}H NMR



13a, ^{13}C NMR



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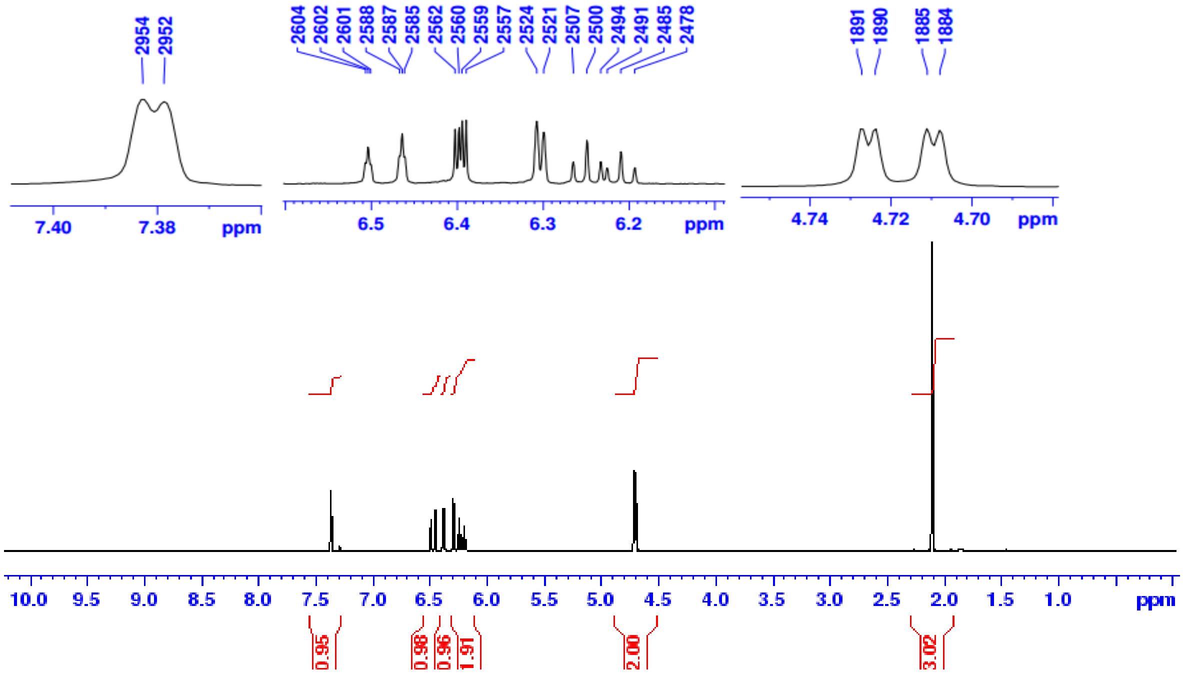
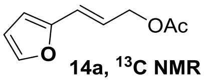
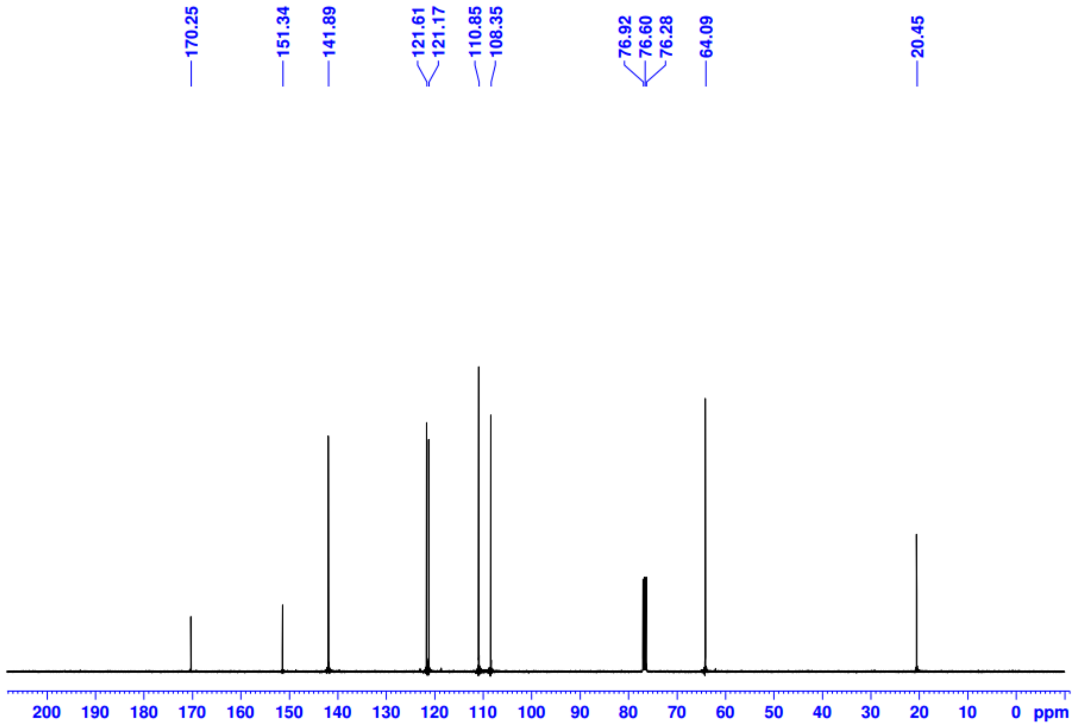
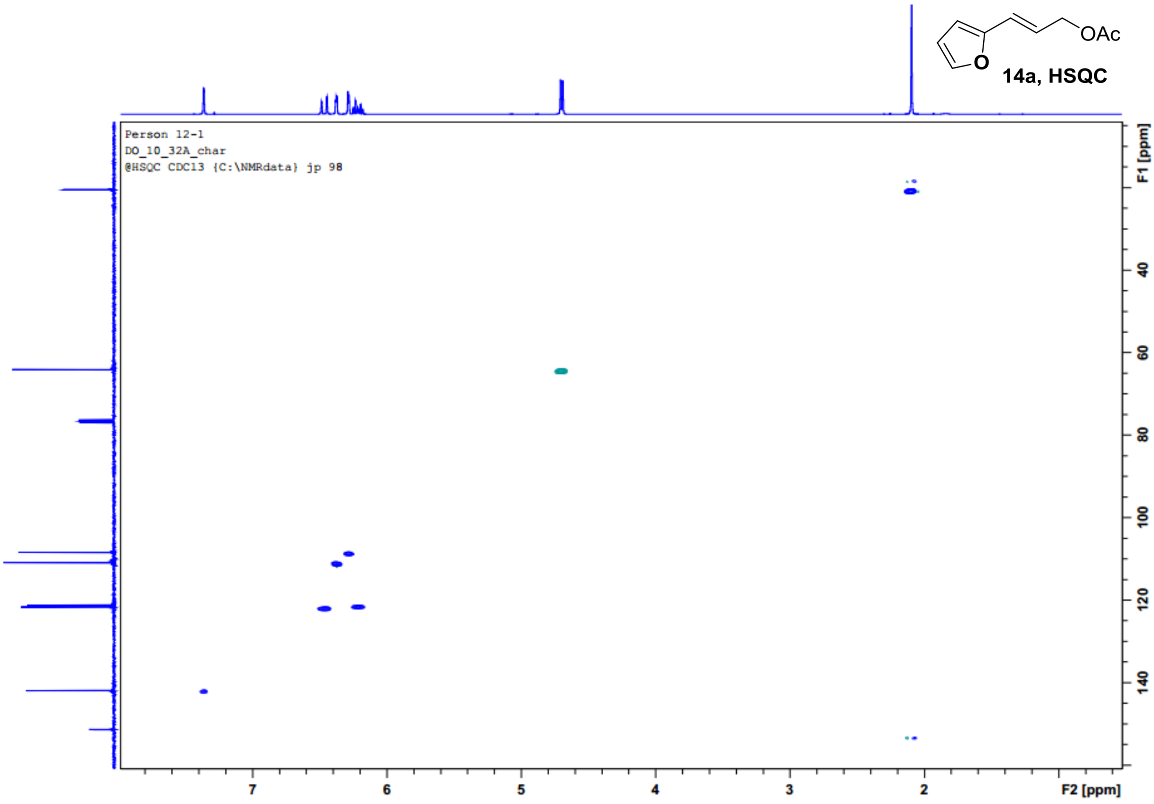




14a, ^{13}C NMR

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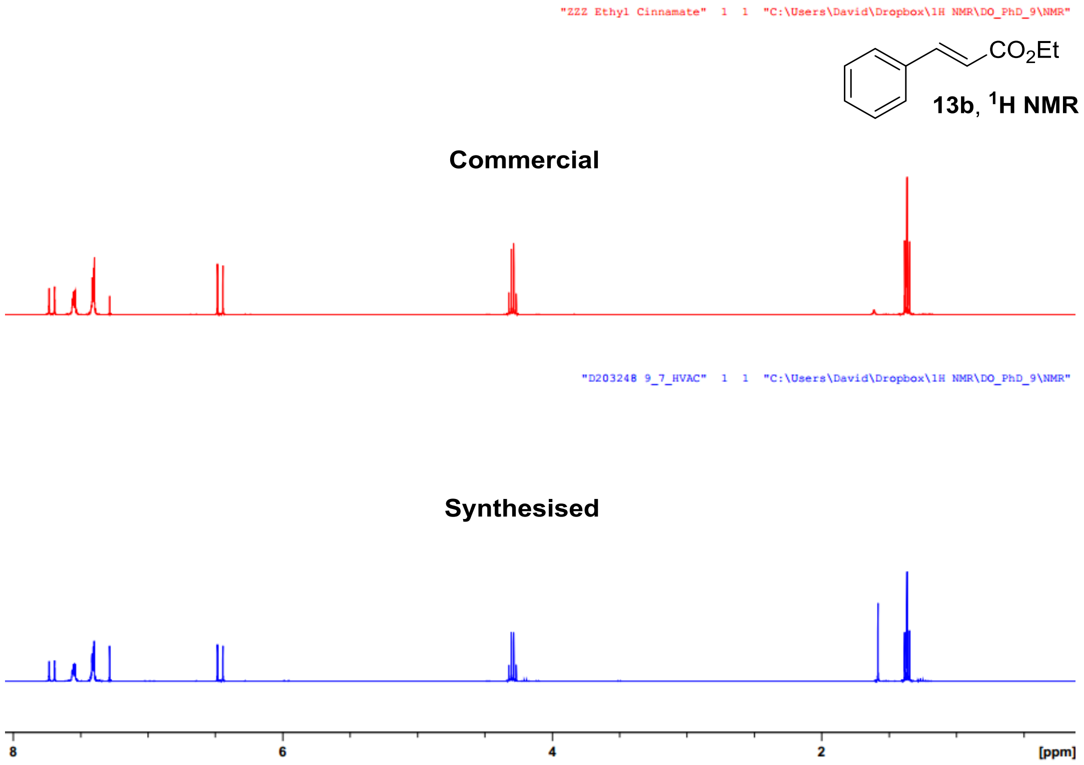
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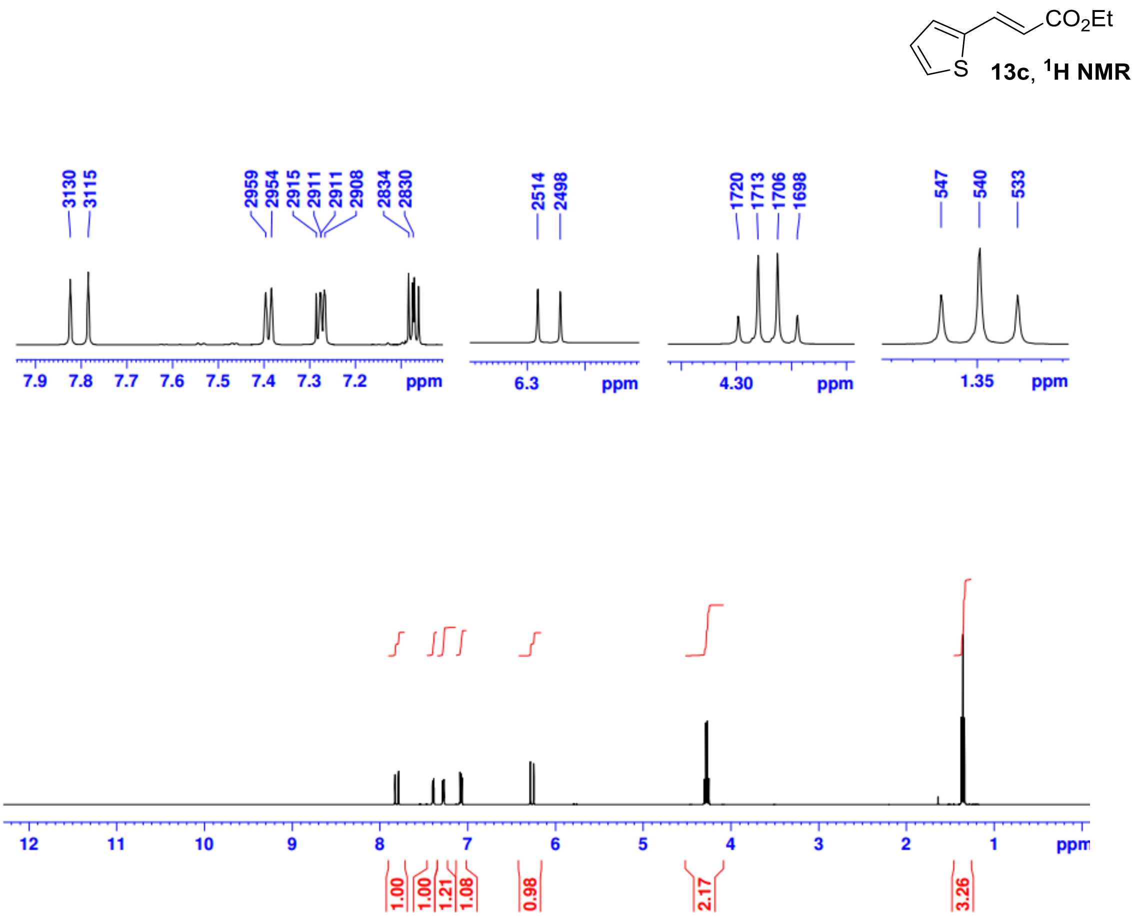
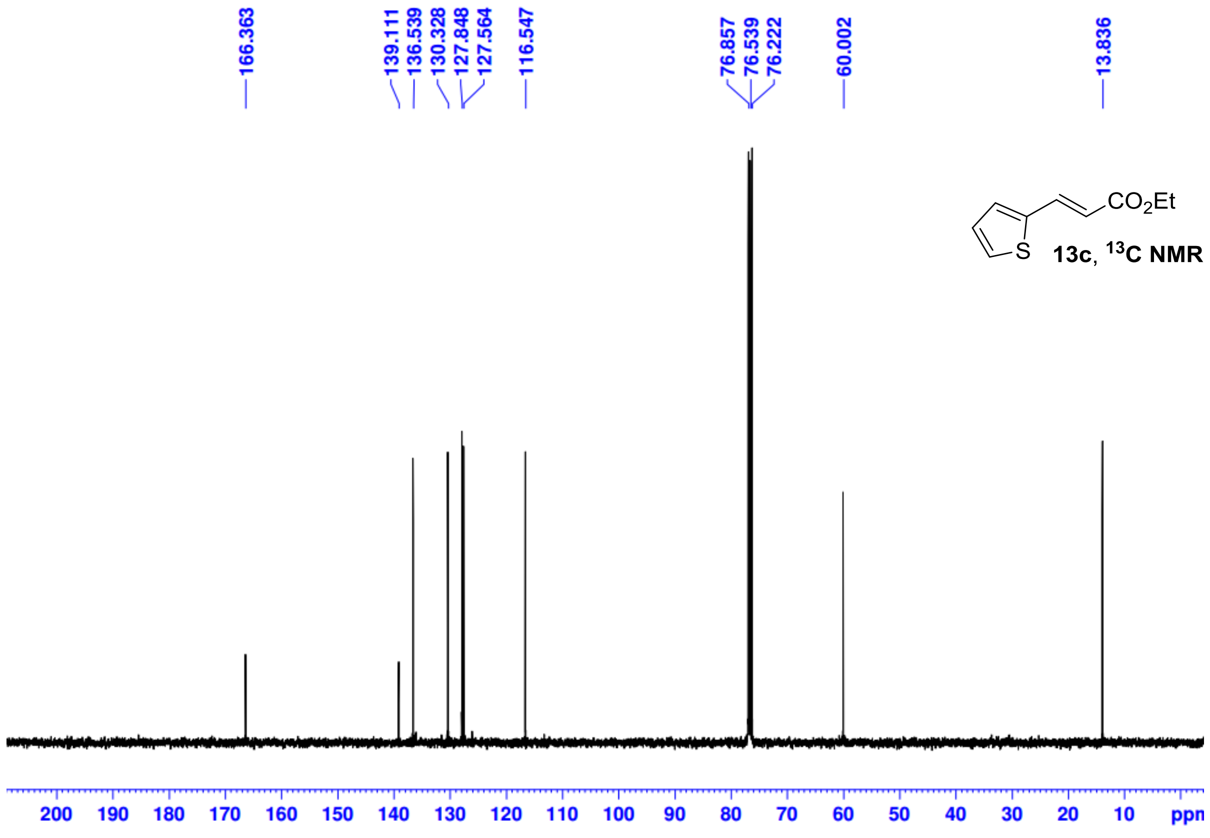
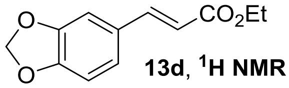


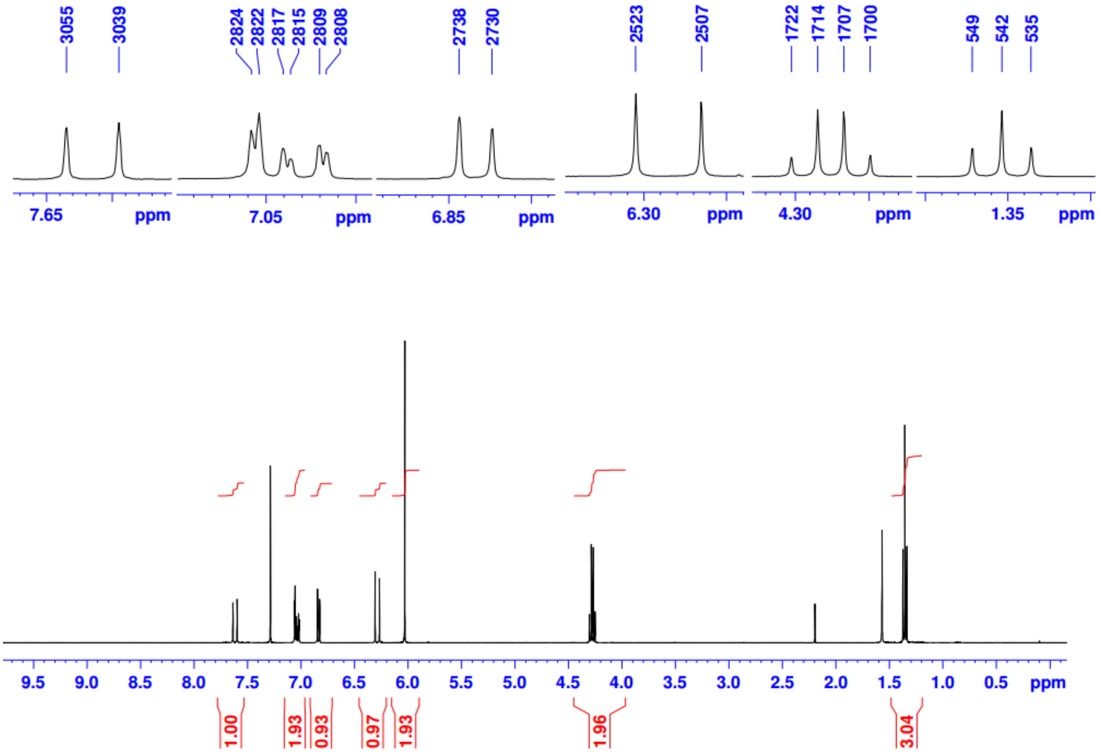
13c, ^{1}H NMR

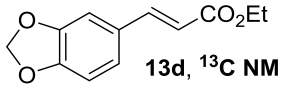


13c, ^{13}C NMR

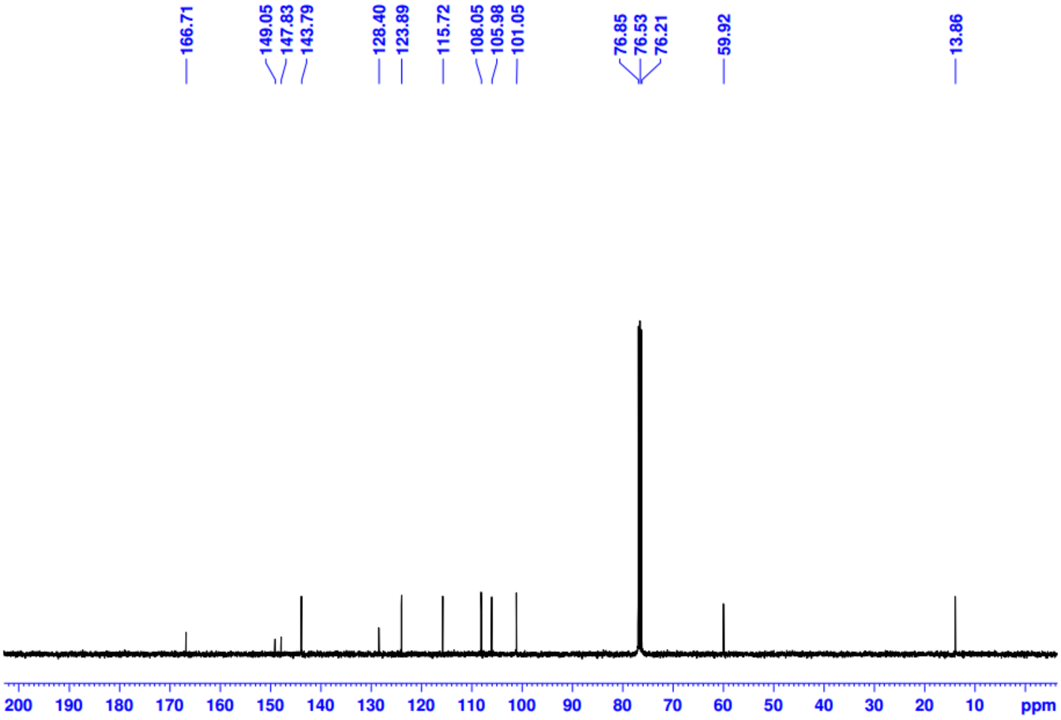


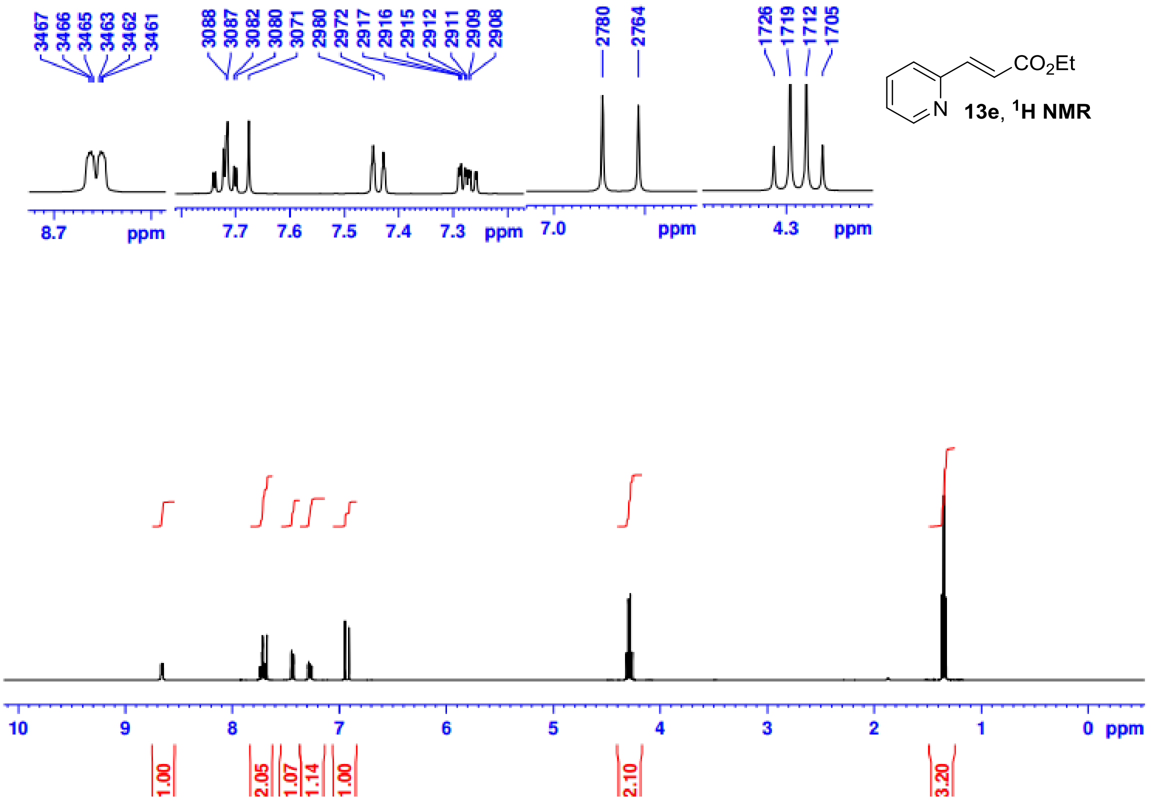
13d, **^{1}H NMR**





13d, **^{13}C NMR**

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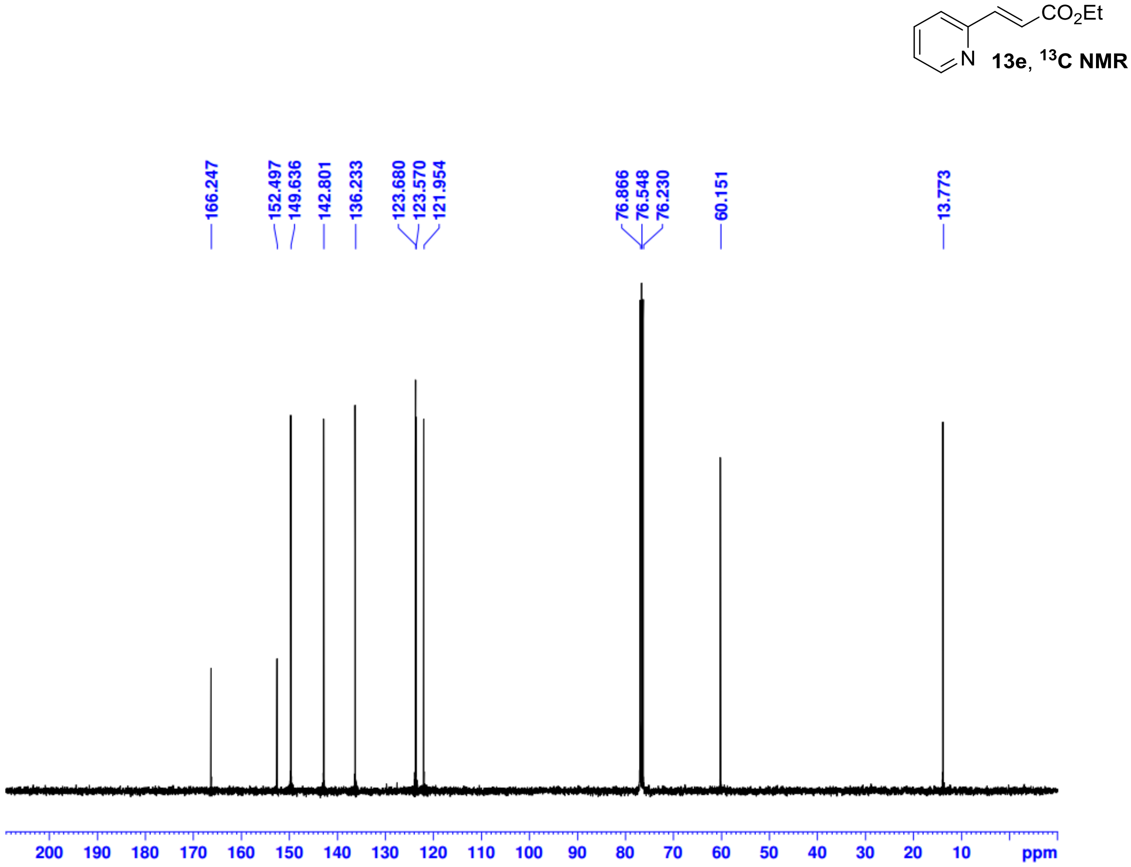
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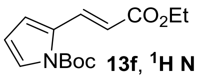

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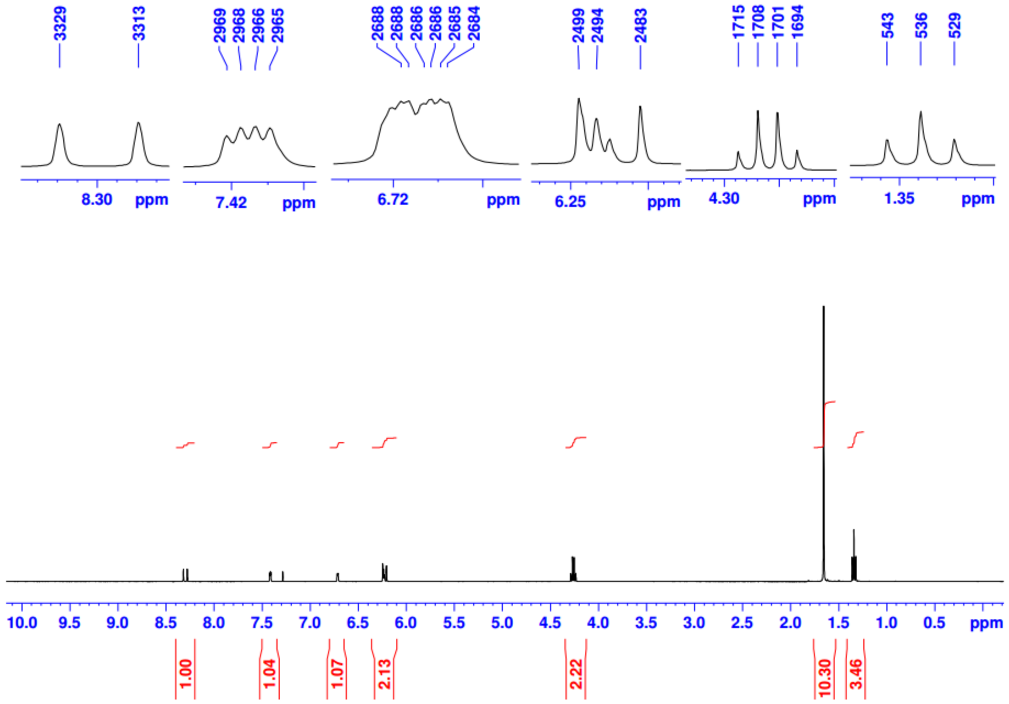

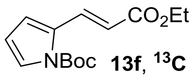

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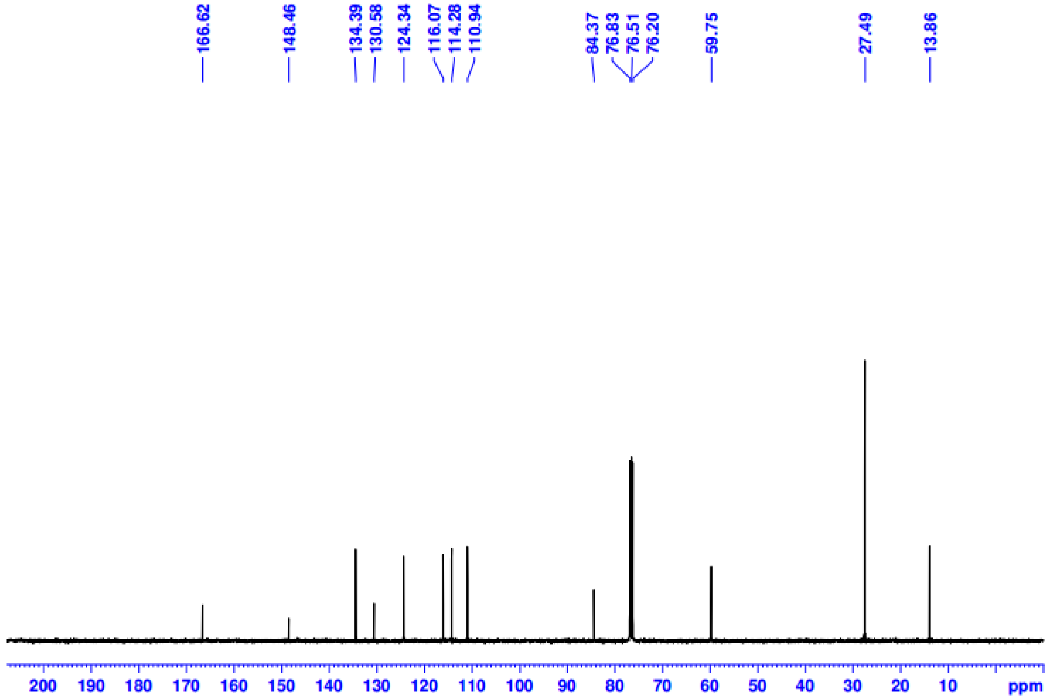

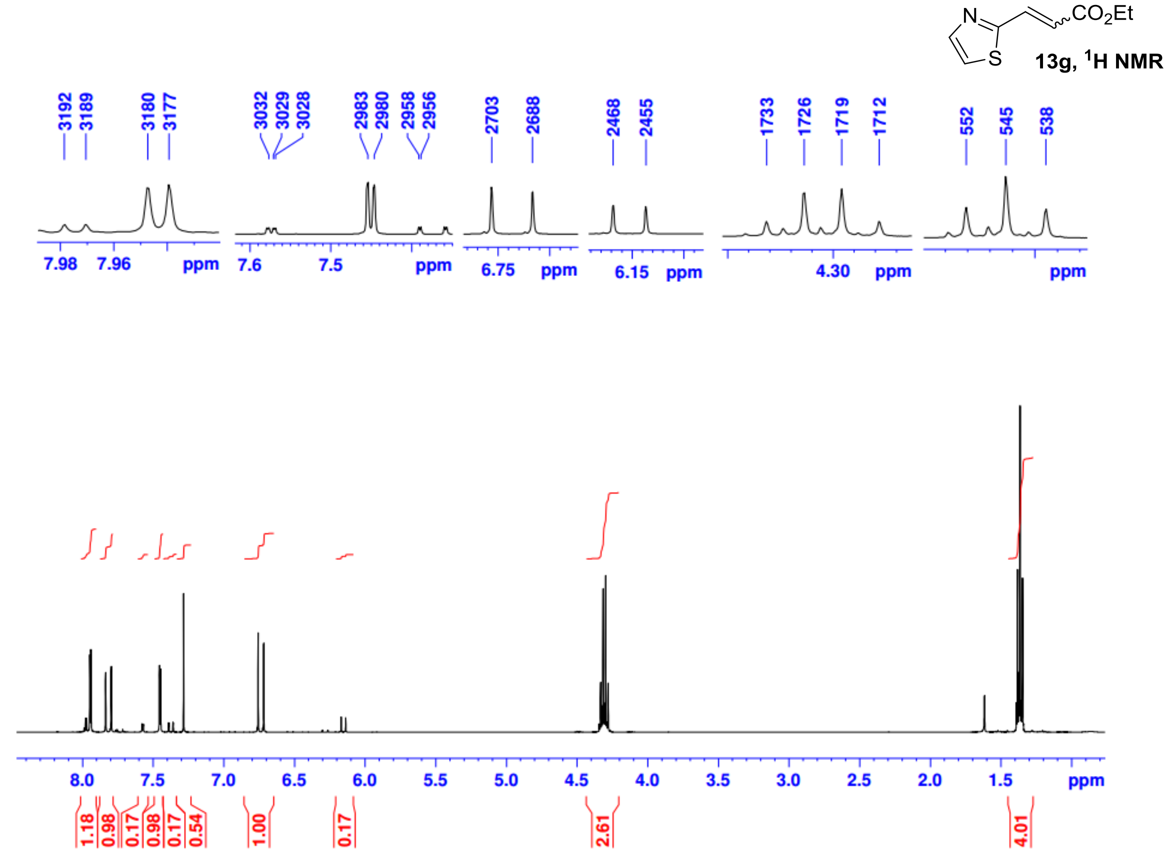
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CO$_2$Et
13g, ^{1}H NMR
3192
3189
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3177
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2958
2956
2703
2688
2468
2455
1733
1726
1719
1712
552
545
538
7.98
7.96
ppm
7.6
7.5
ppm
6.75
ppm
6.15
ppm
4.30
ppm
ppm
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7.5
7.0
6.5
6.0
5.5
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4.0
3.5
3.0
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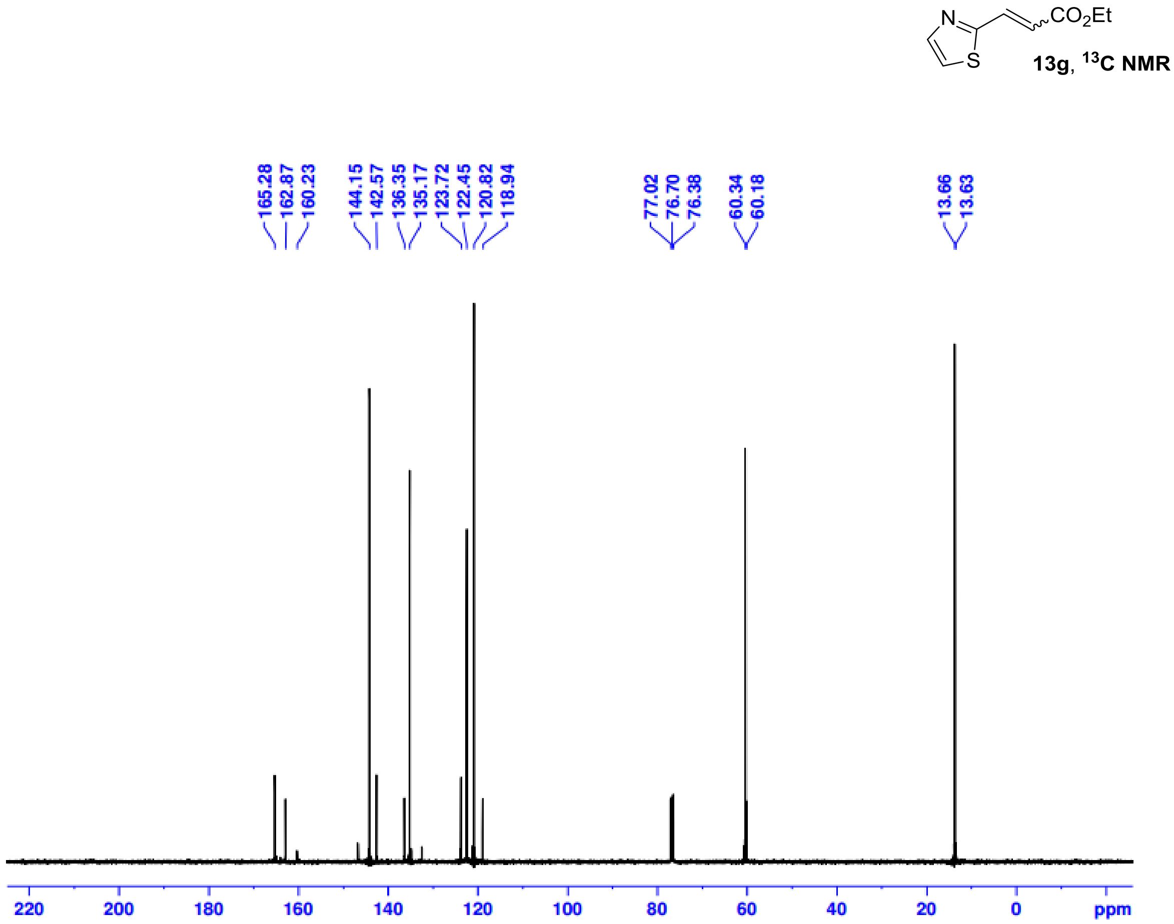
N
S
CO$_2$Et
13g, ^{13}C NMR
165.28
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123.72
122.45
120.82
118.94
77.02
76.70
76.38
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13.63
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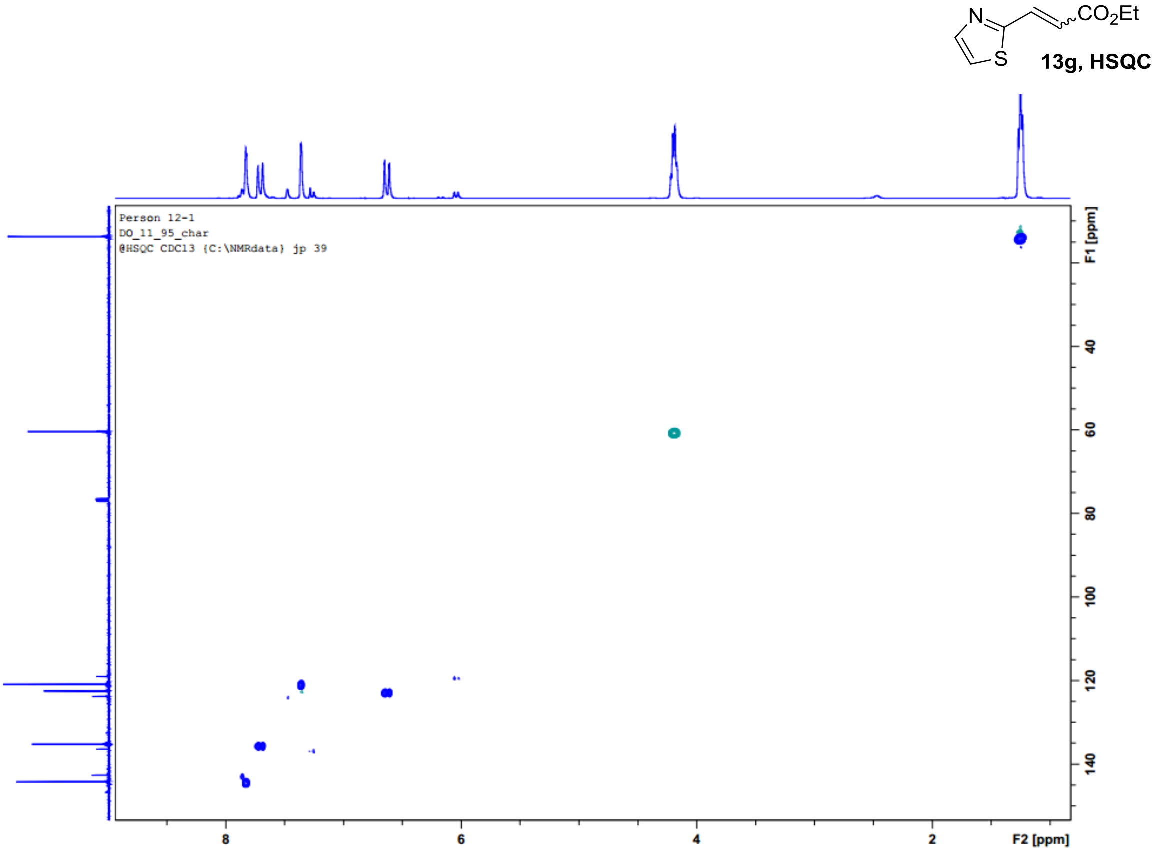
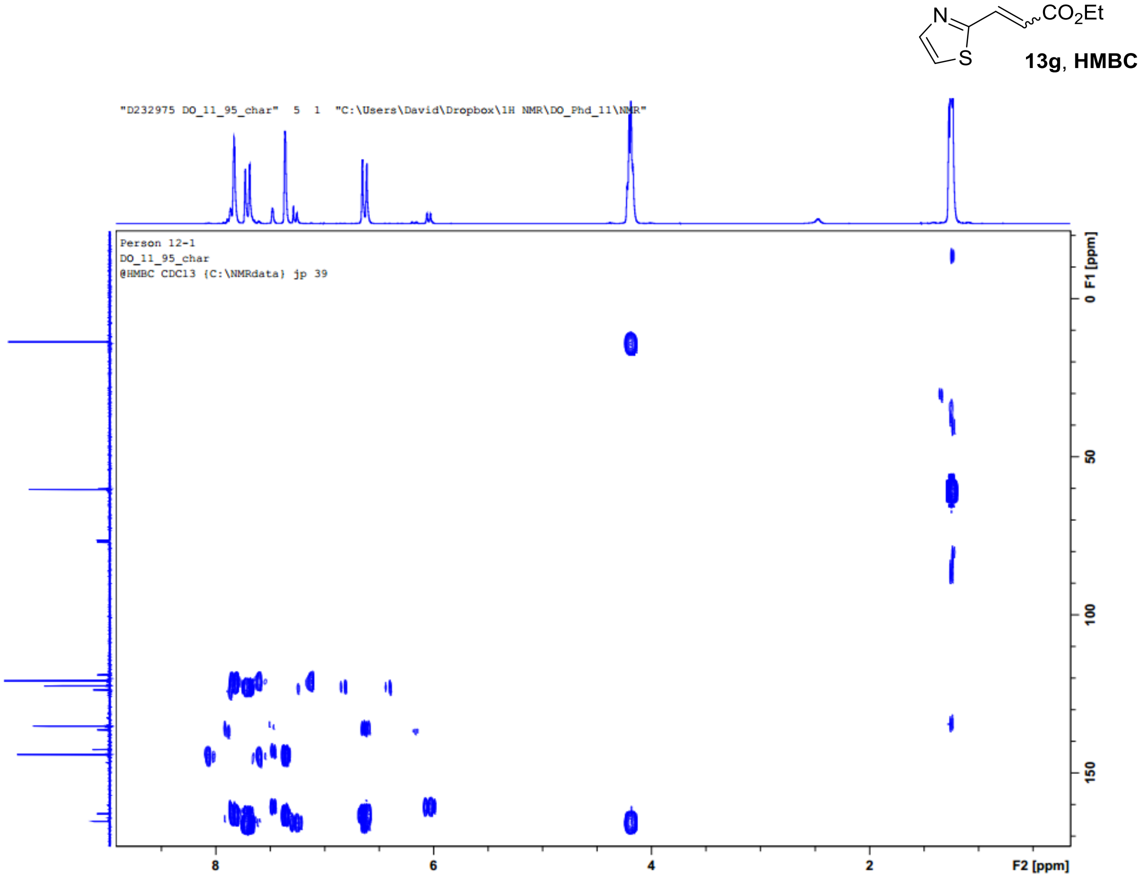
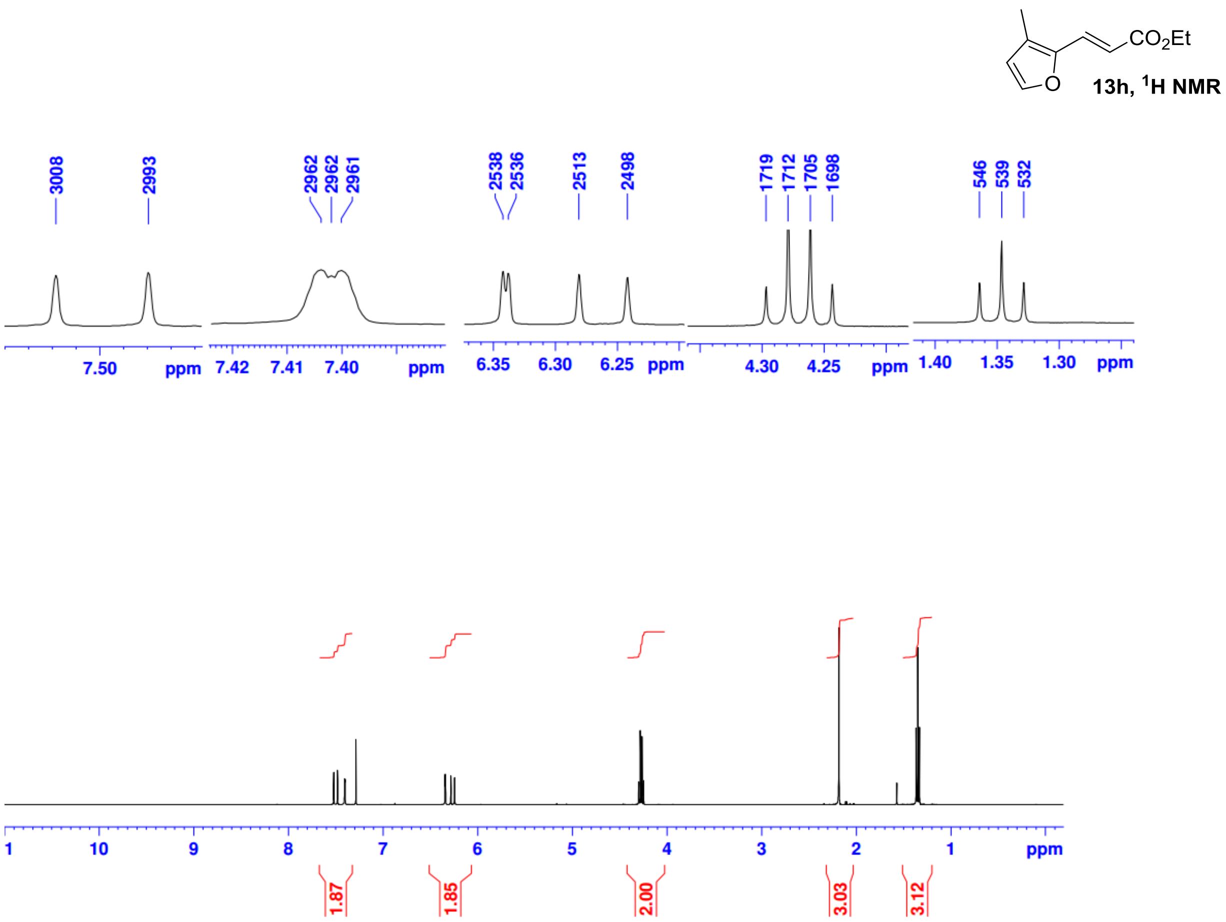
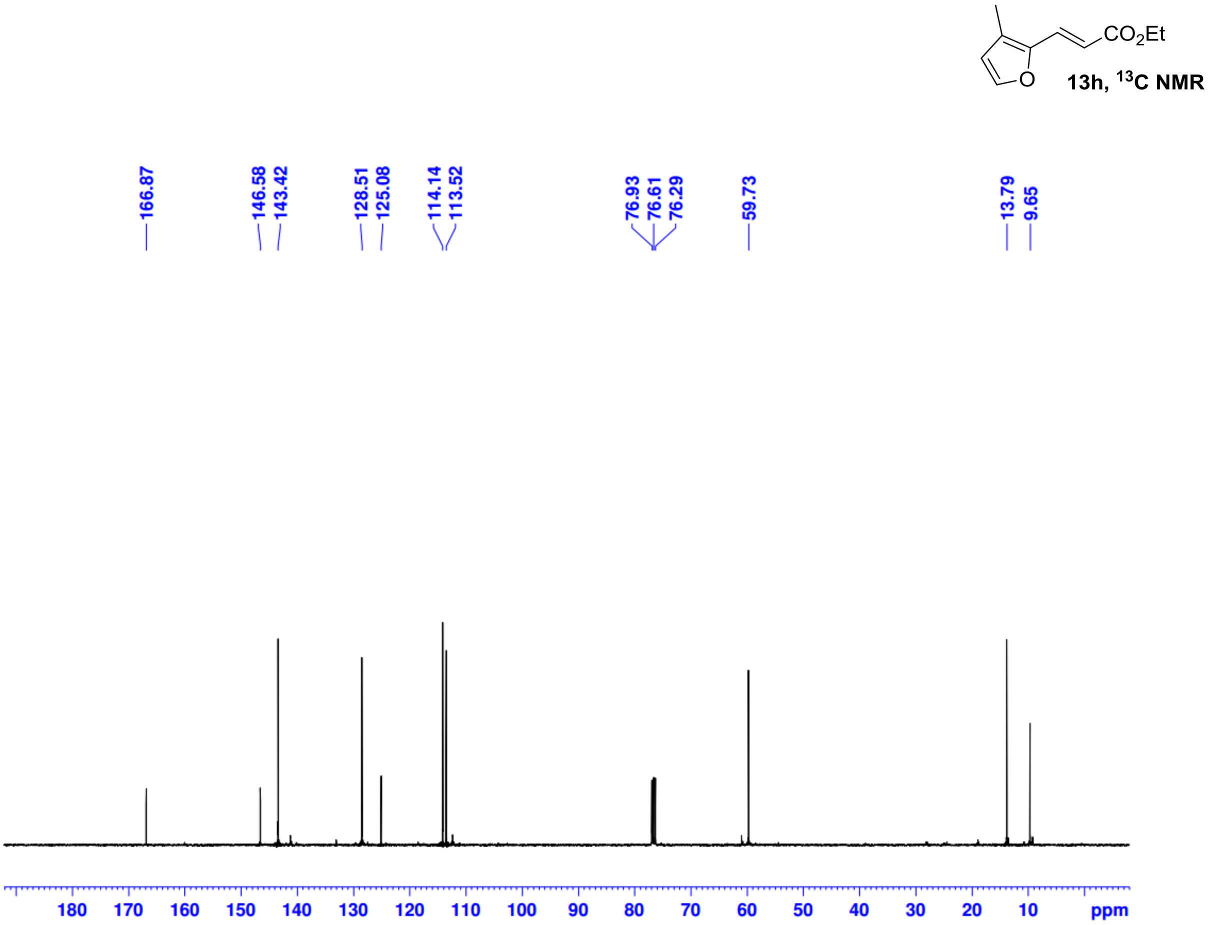


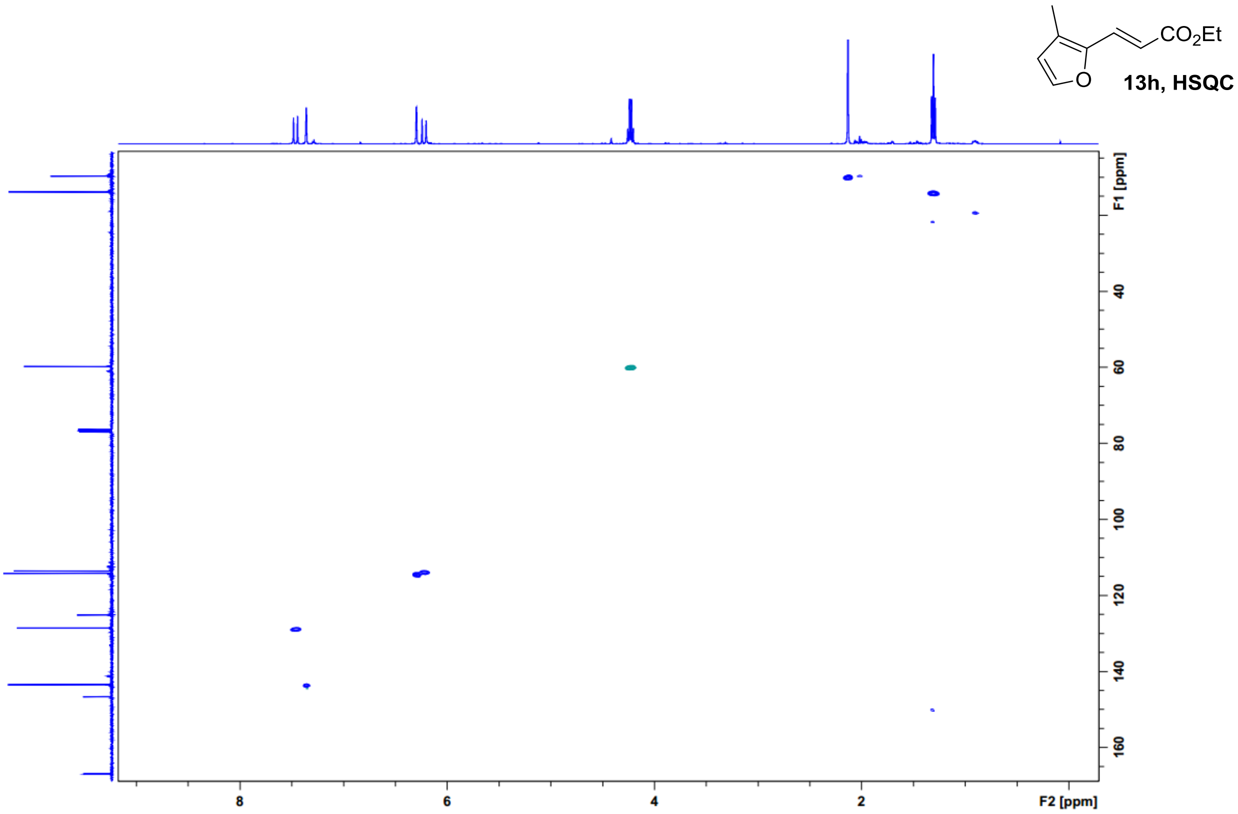
13g, HSQC



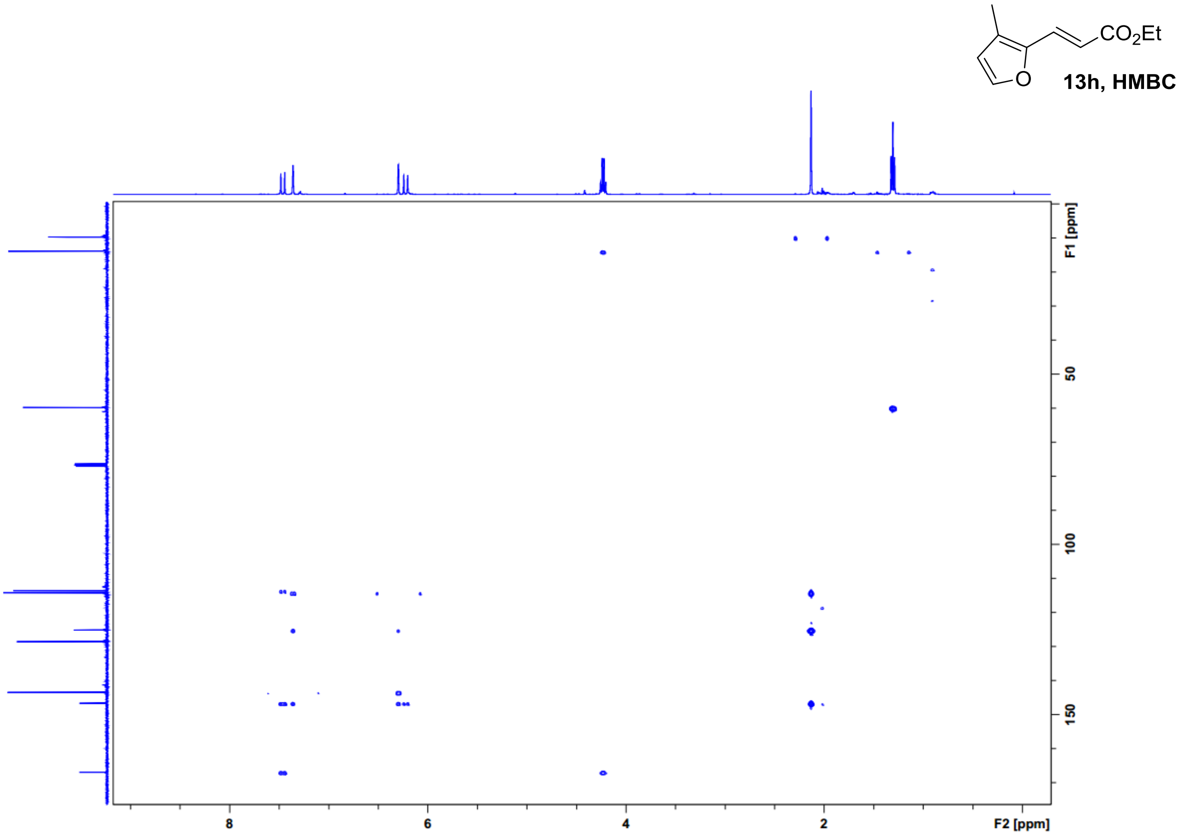
13g, HMBC


13h, ^{1}H NMR


13h, ^{13}C NMR



13h, HSQC



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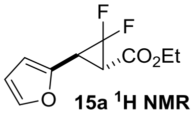
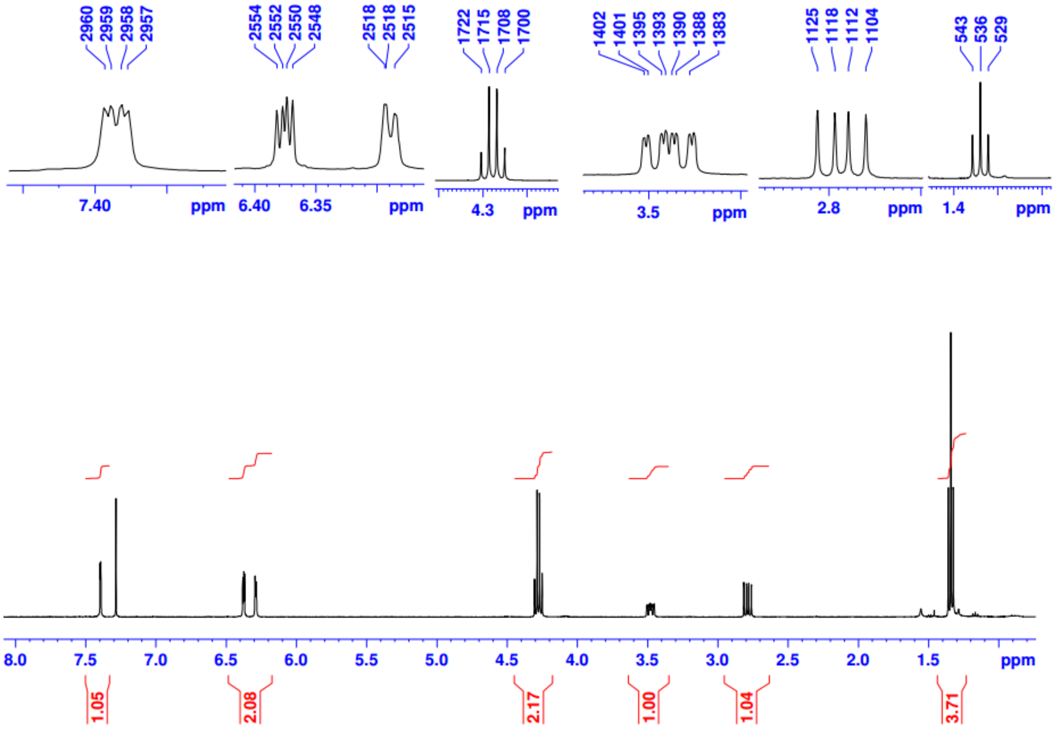
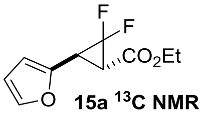


15a ^{1}H NMR





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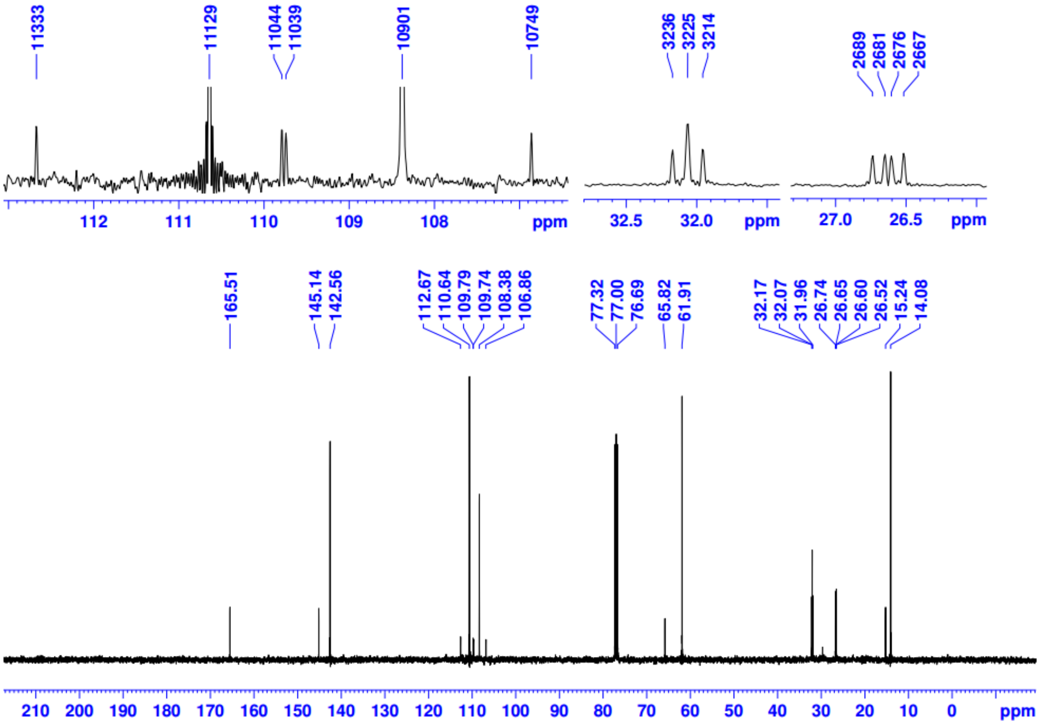
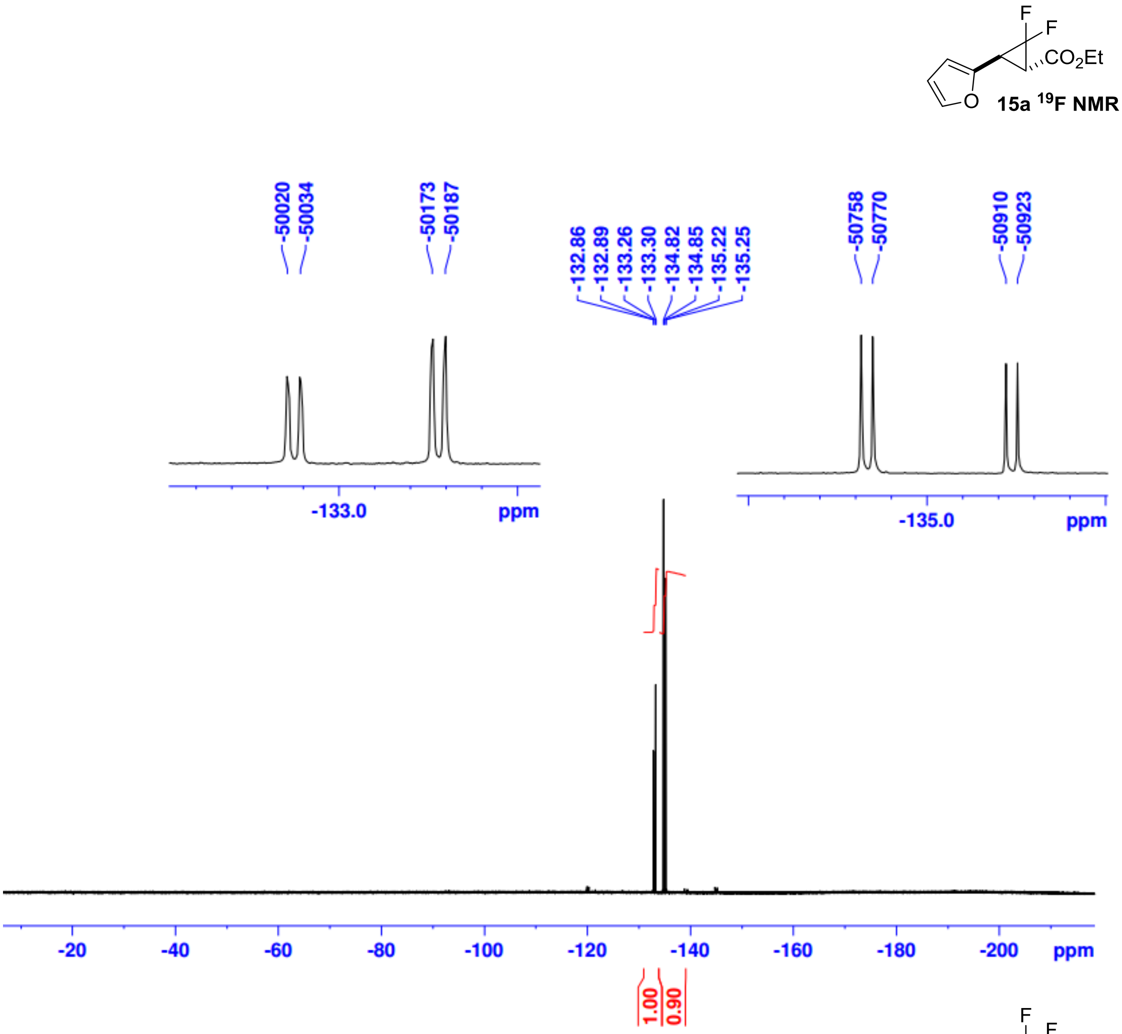
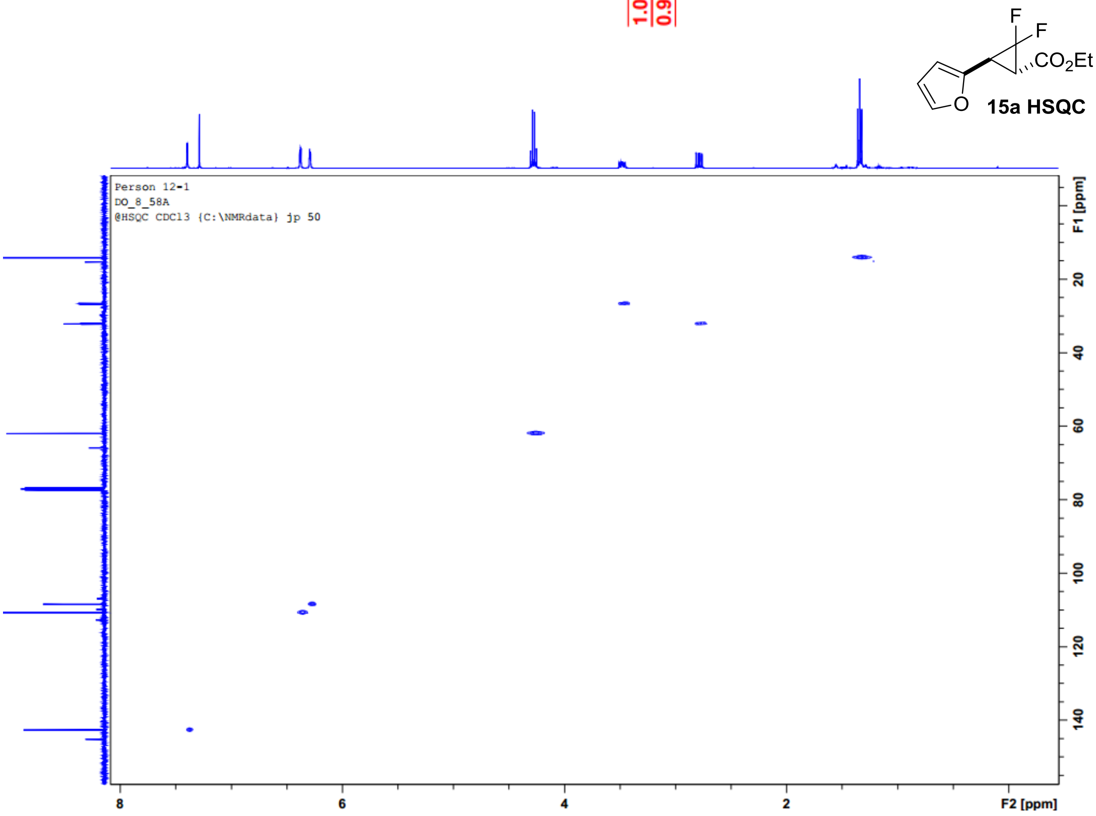
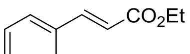
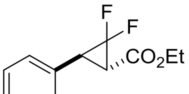



15a ^{19}F NMR


15a HSQC

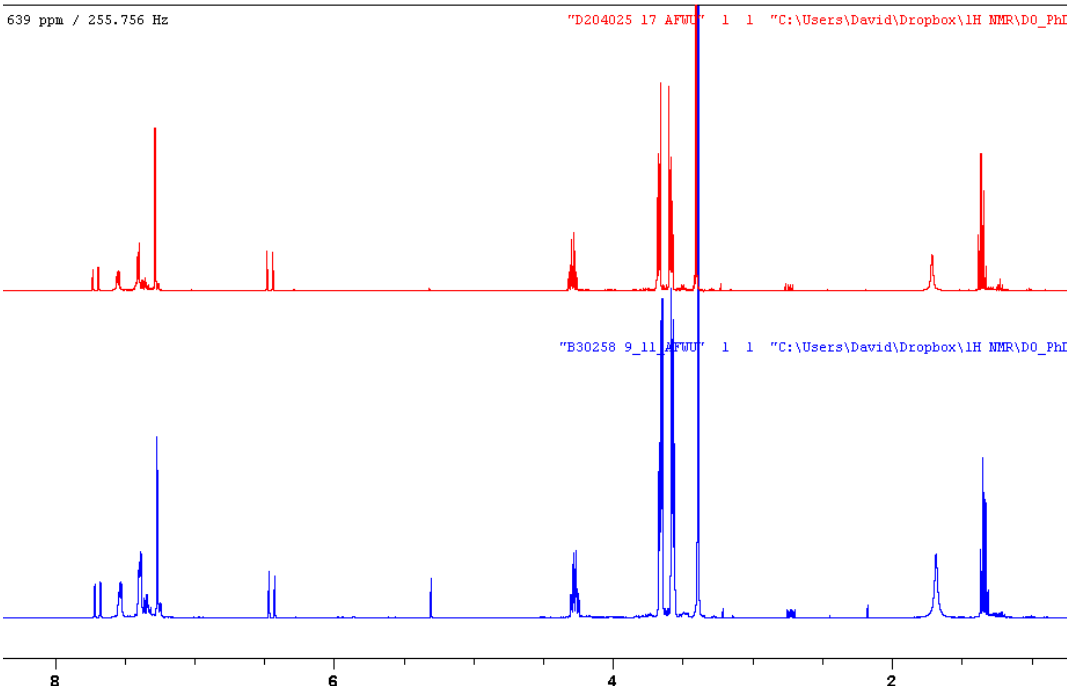


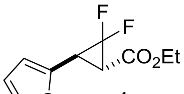
13b



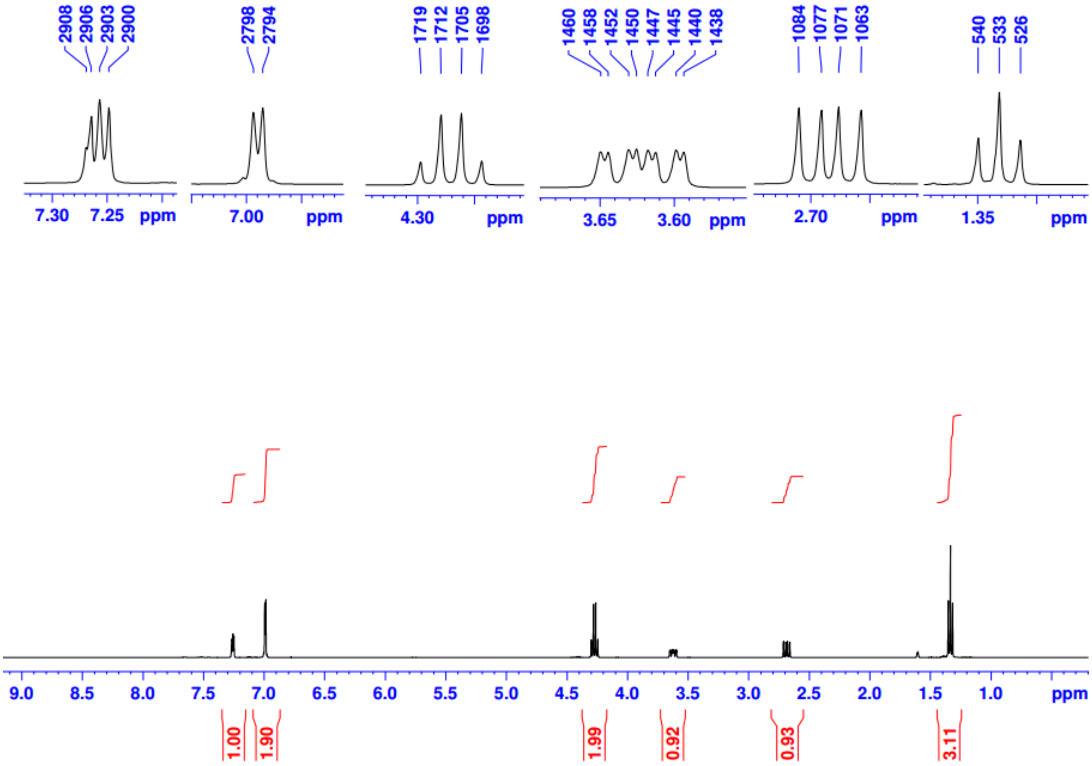
15b

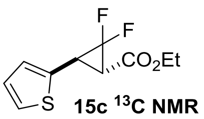
^{1}H crude spectra from incomplete difluorocyclopropanation of 13b.



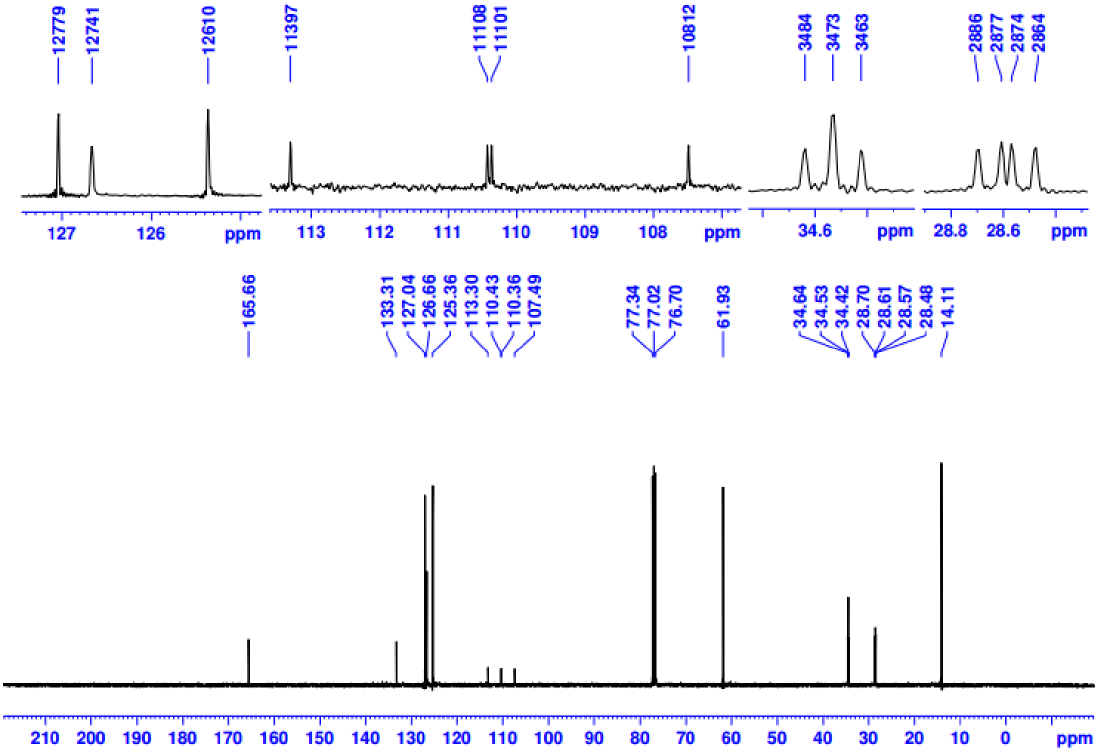


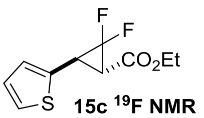
15c, ^{1}H NMR



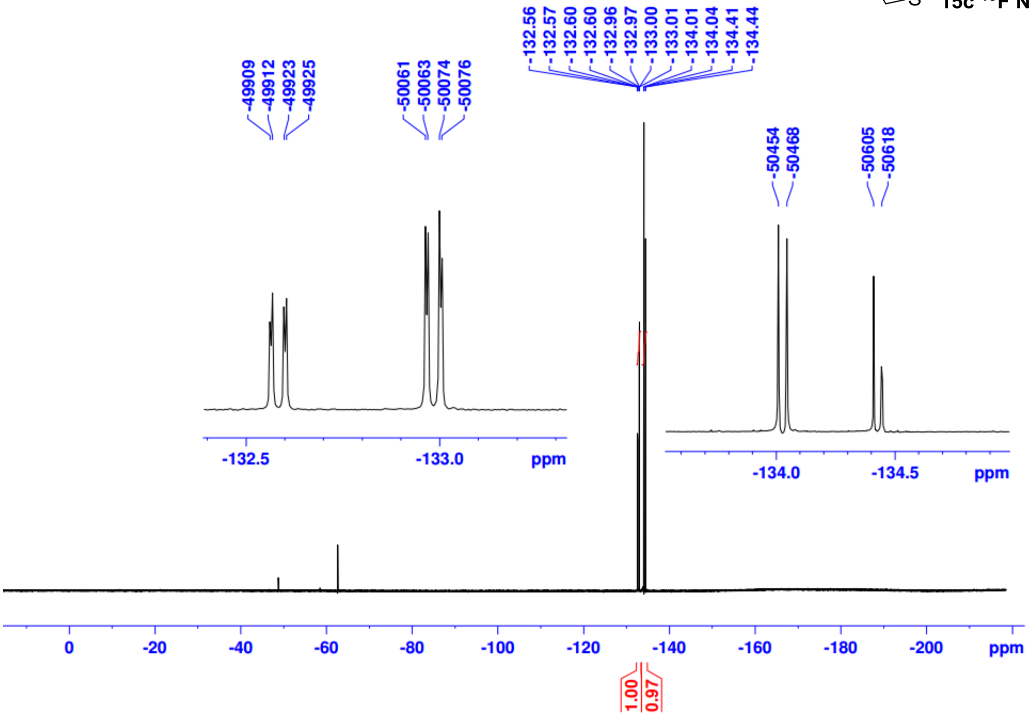


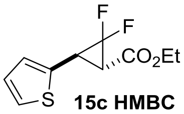
15c ^{13}C NMR



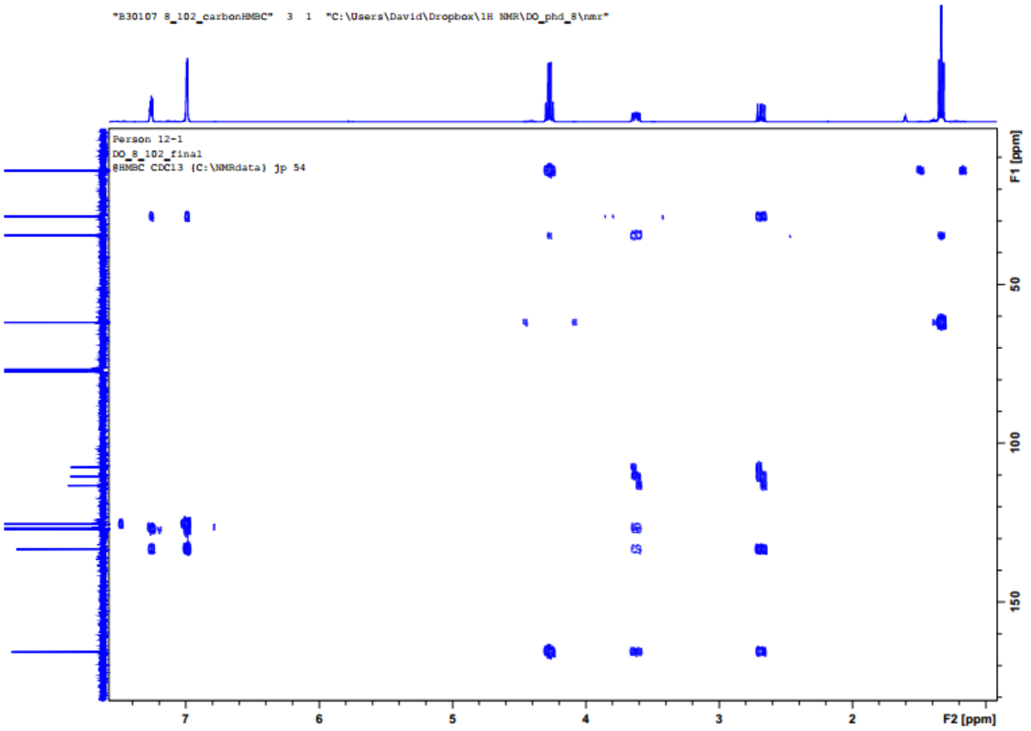


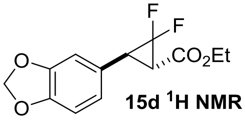
15c ^{19}F NMR



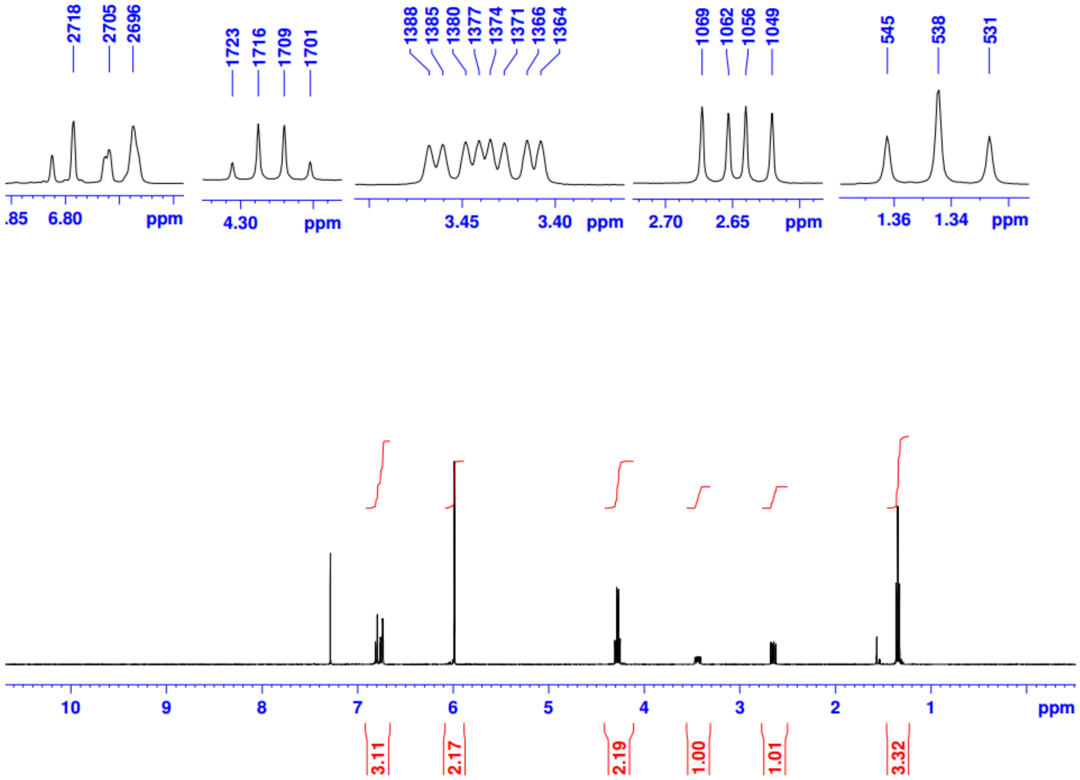


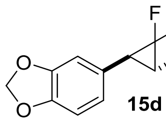
15c HMBC



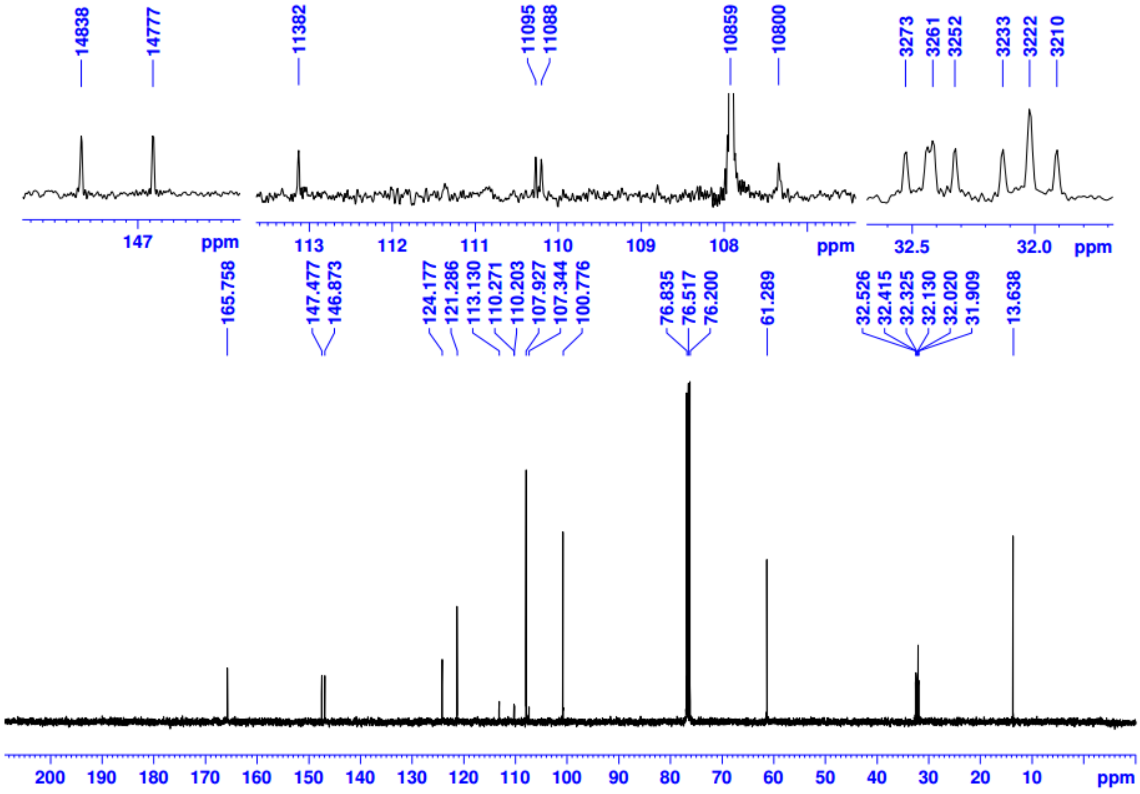


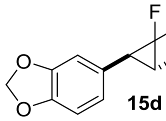
15d ^{1}H NMR



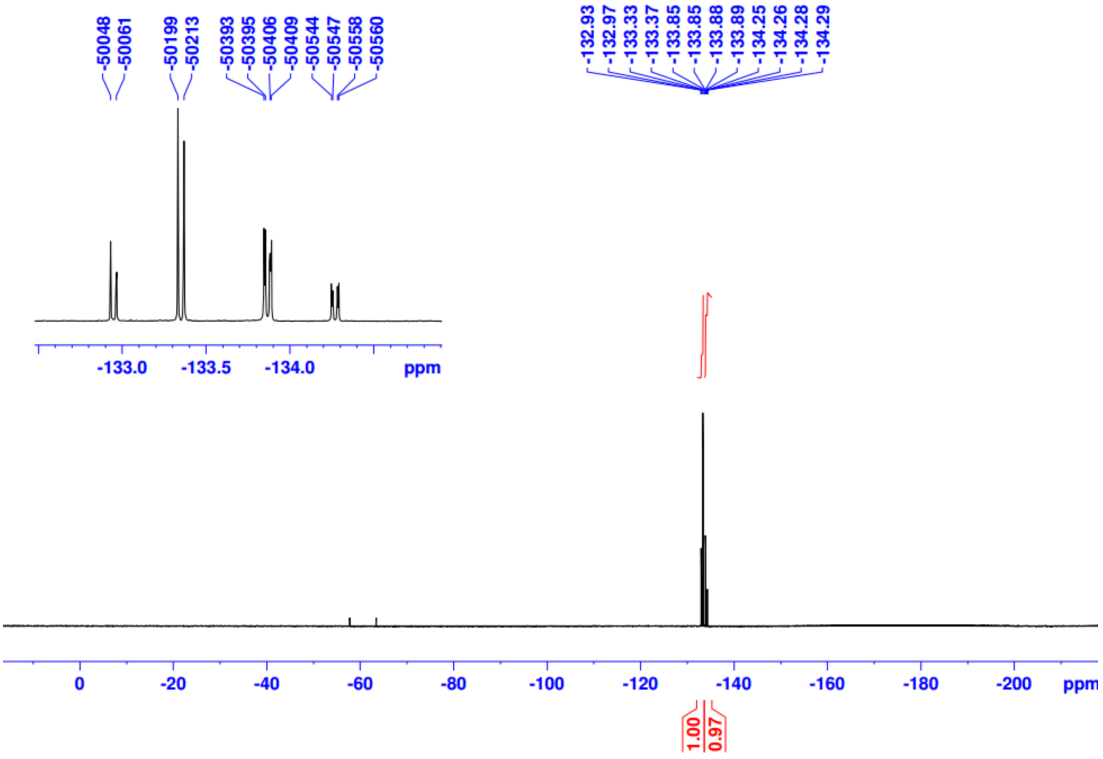


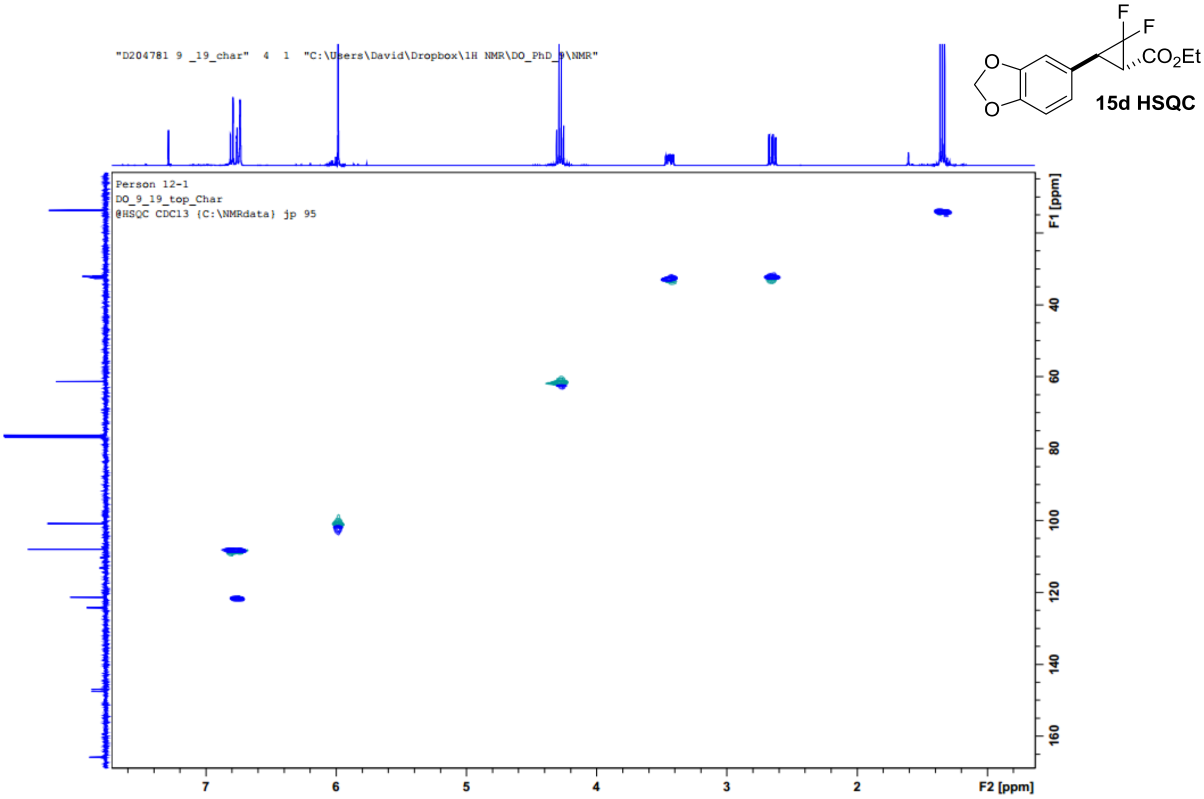
15d ^{13}C NMR



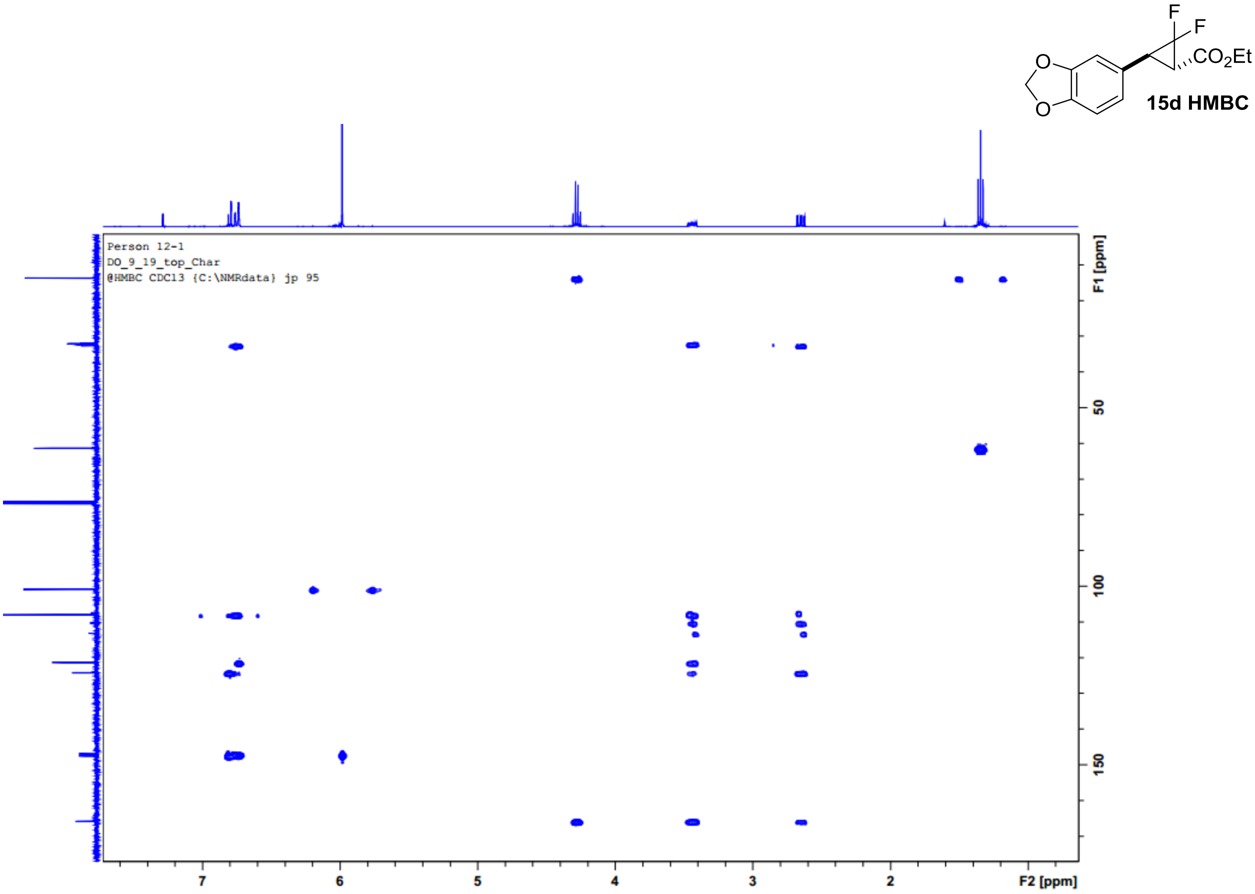


15d ^{19}F NMR

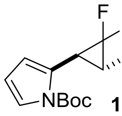




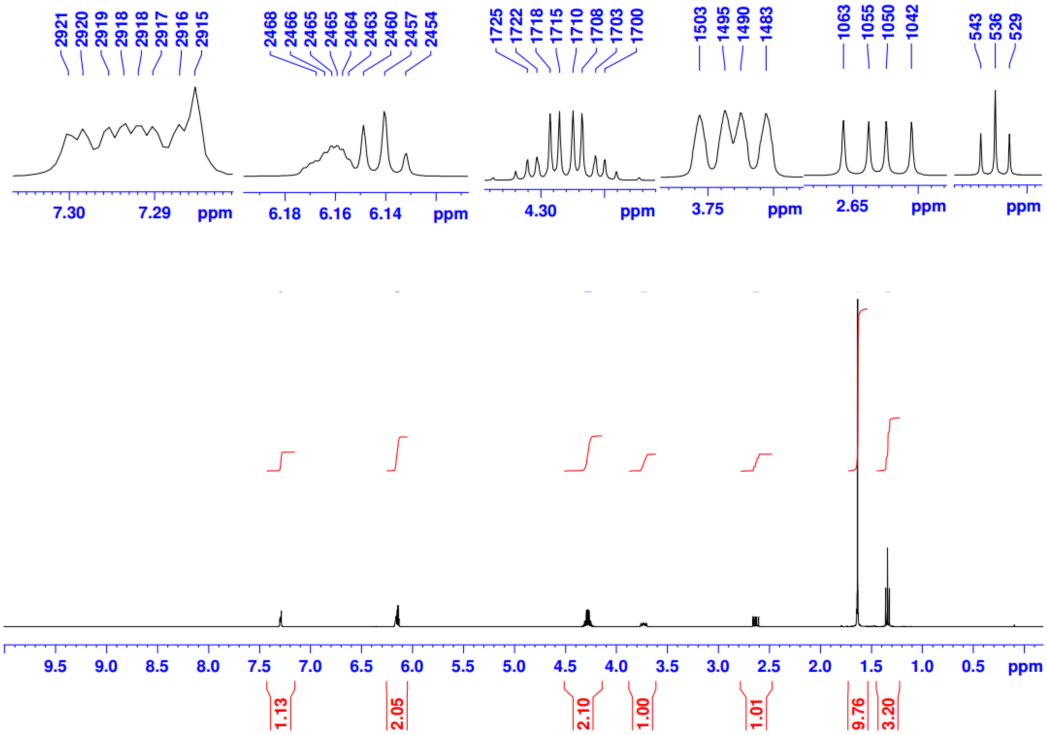
15d HSQC

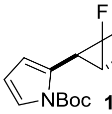


15d HMBC

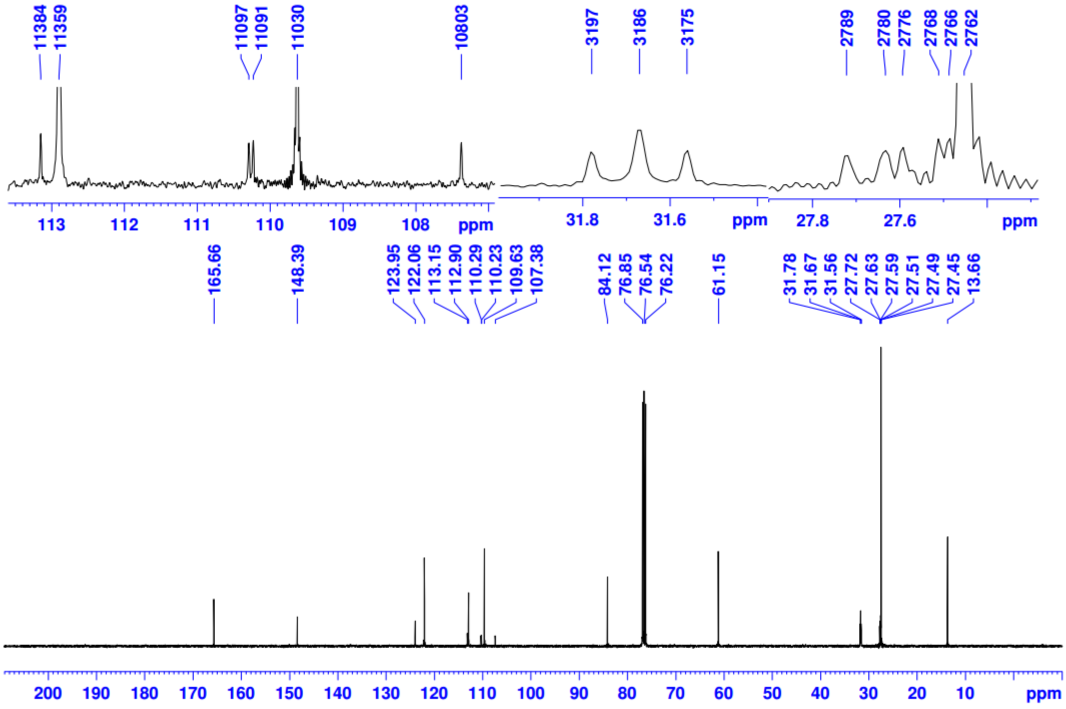


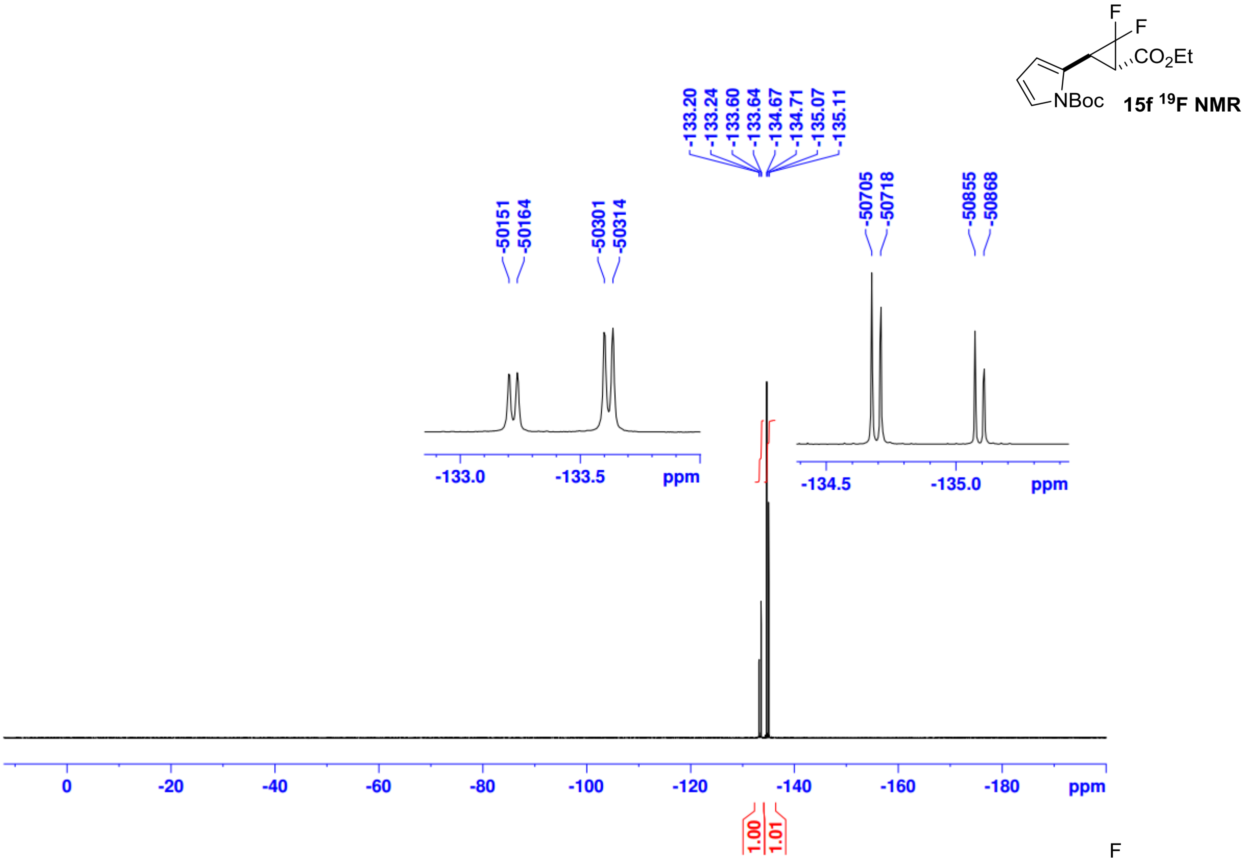
15f ^{1}H NMR

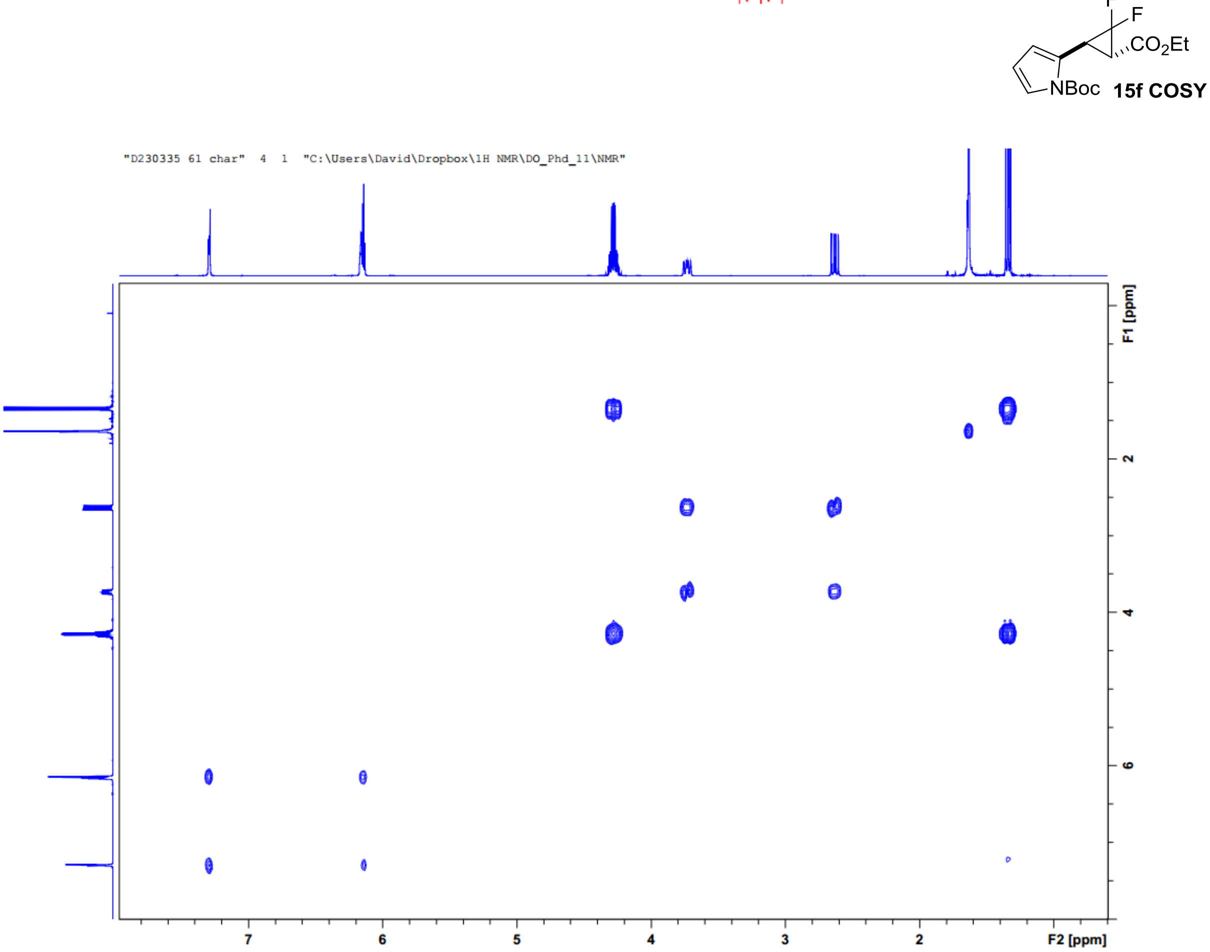


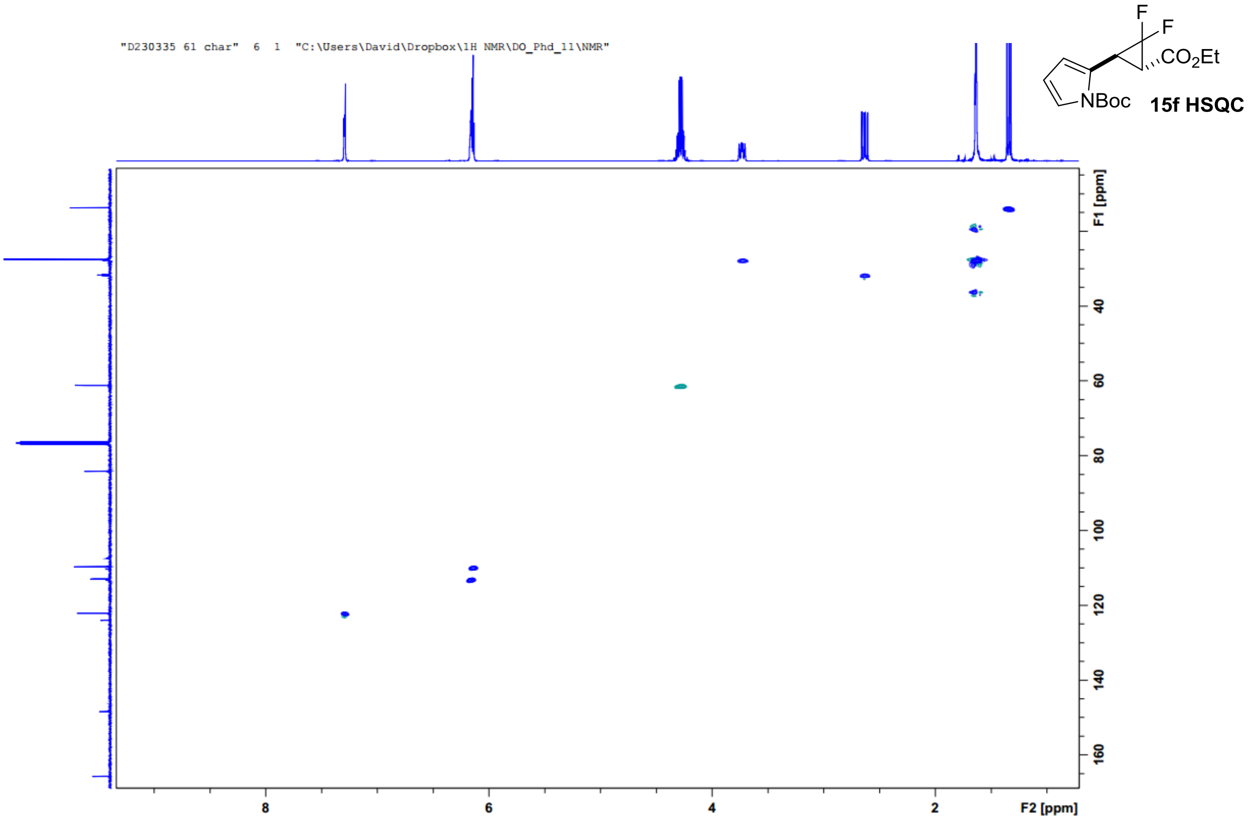


15f ^{13}C NMR




15f ^{19}F NMR


15f COSY



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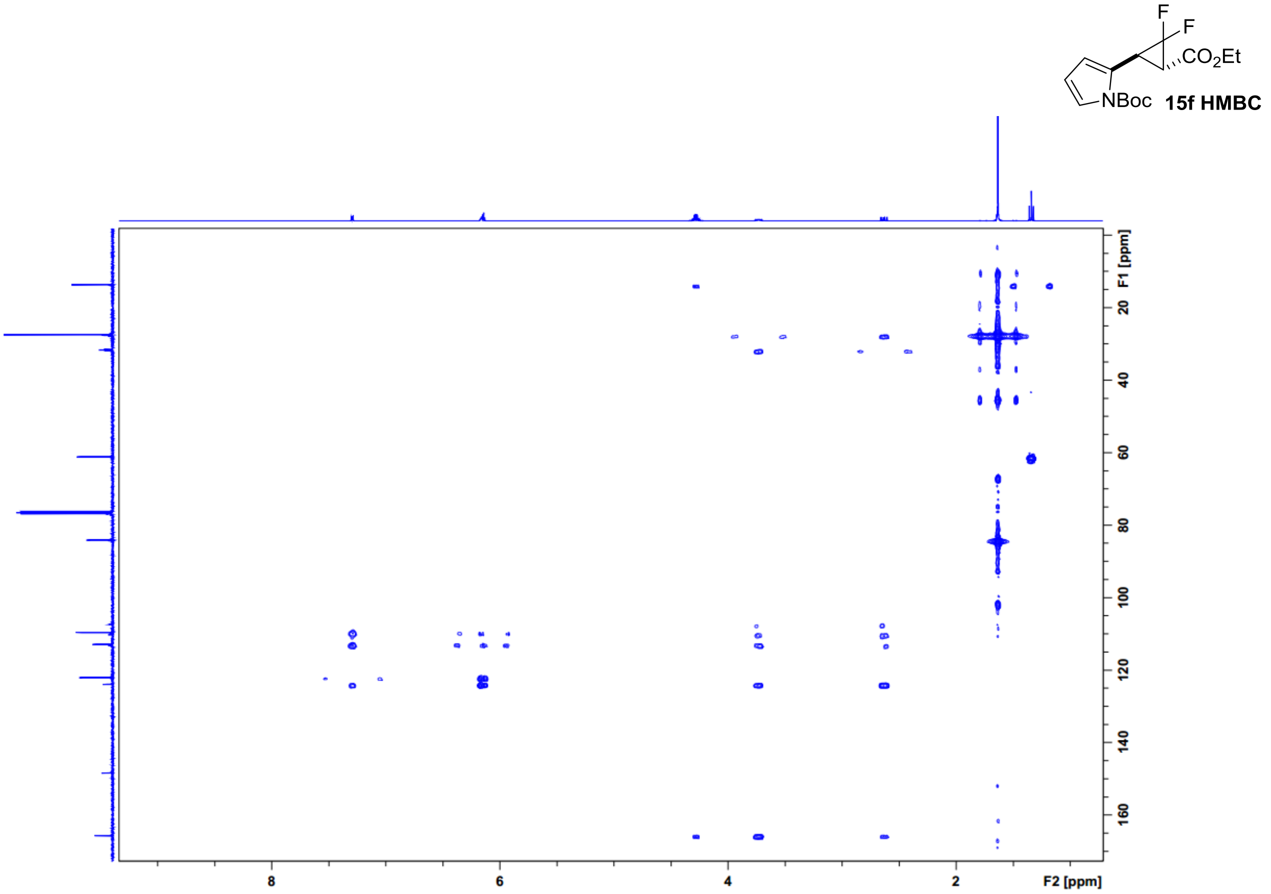

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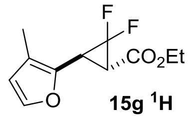
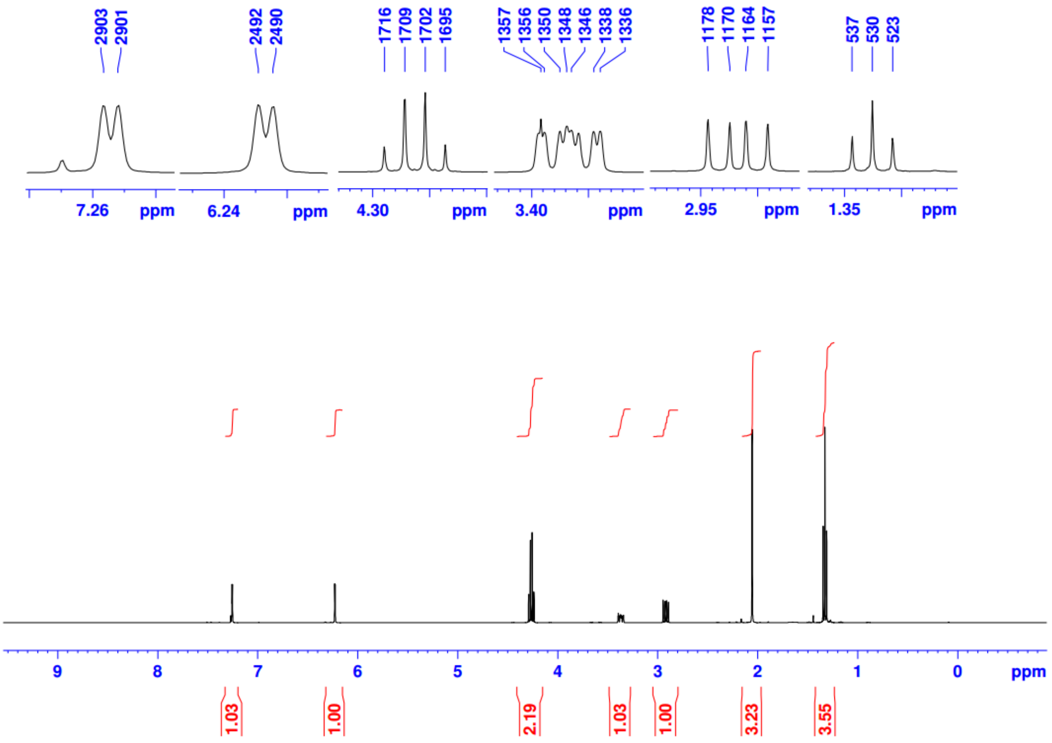
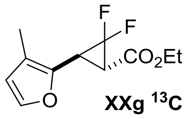
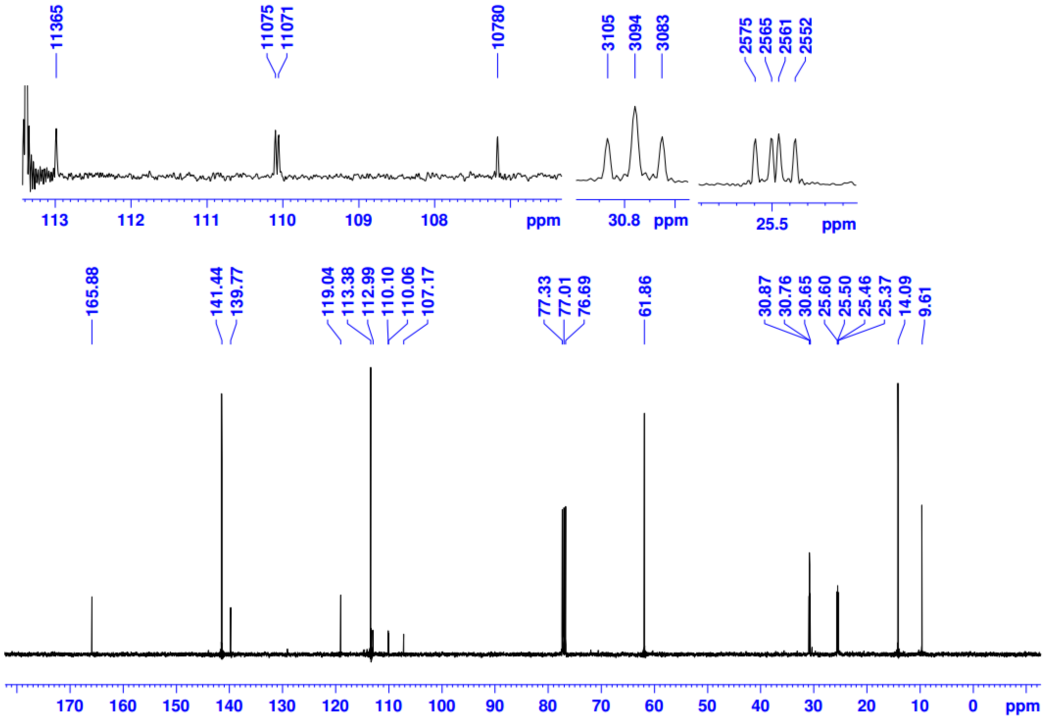


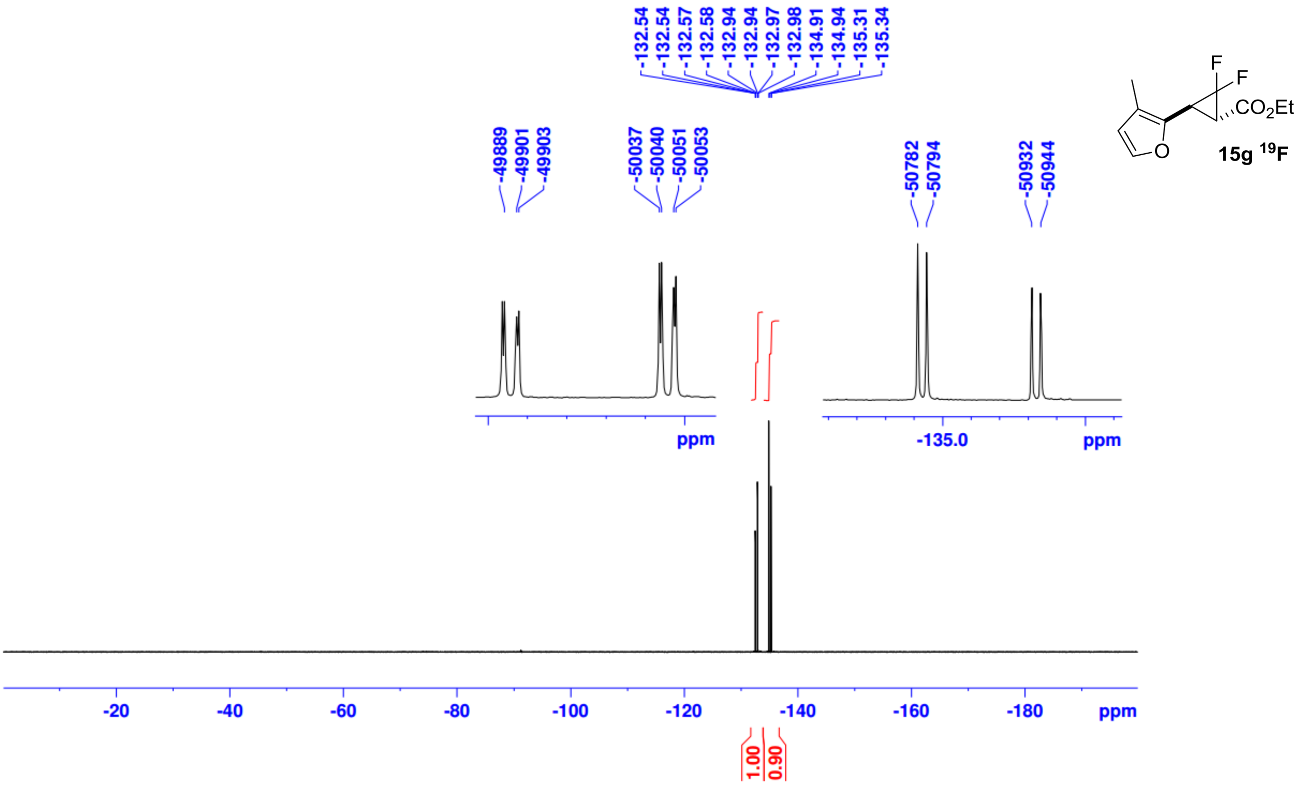
15g ^{1}H



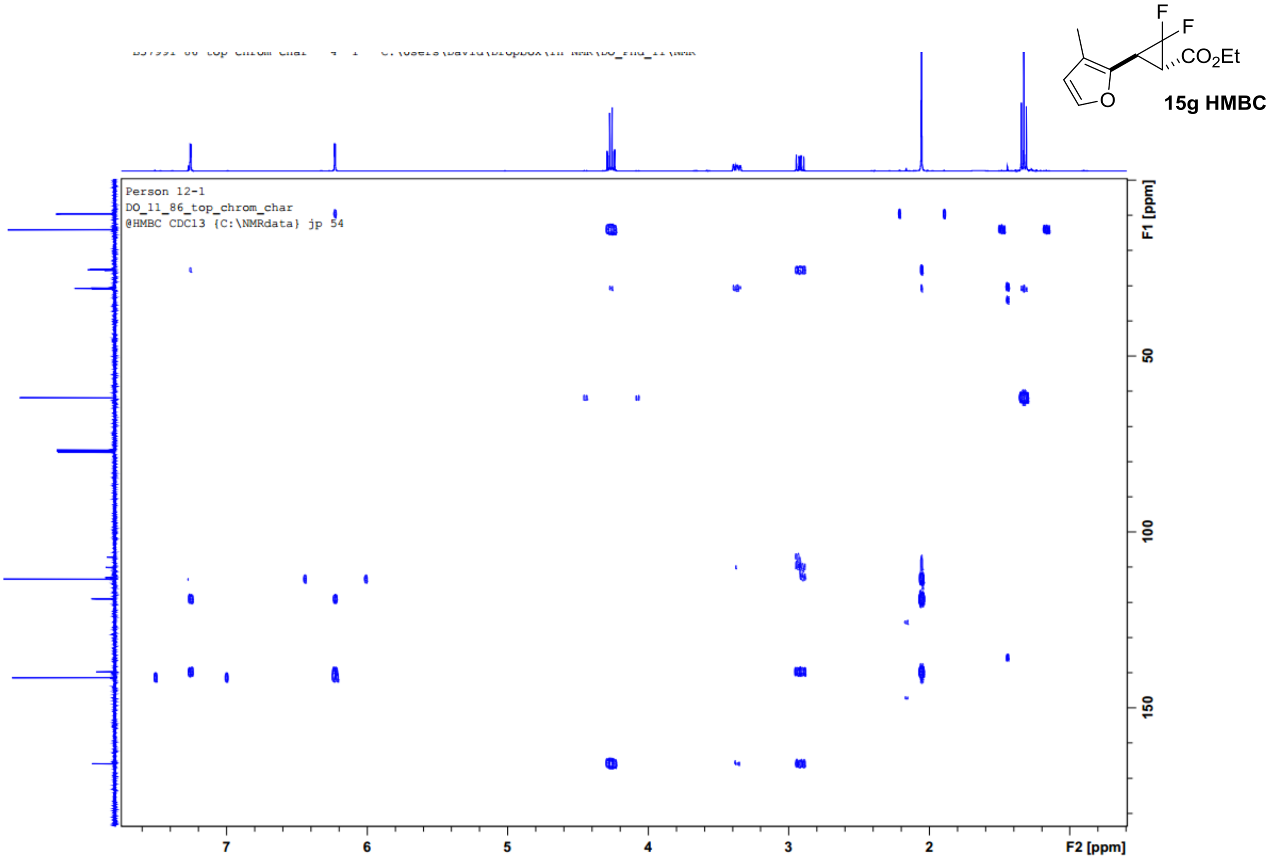


XXg ^{13}C





15g ^{19}F



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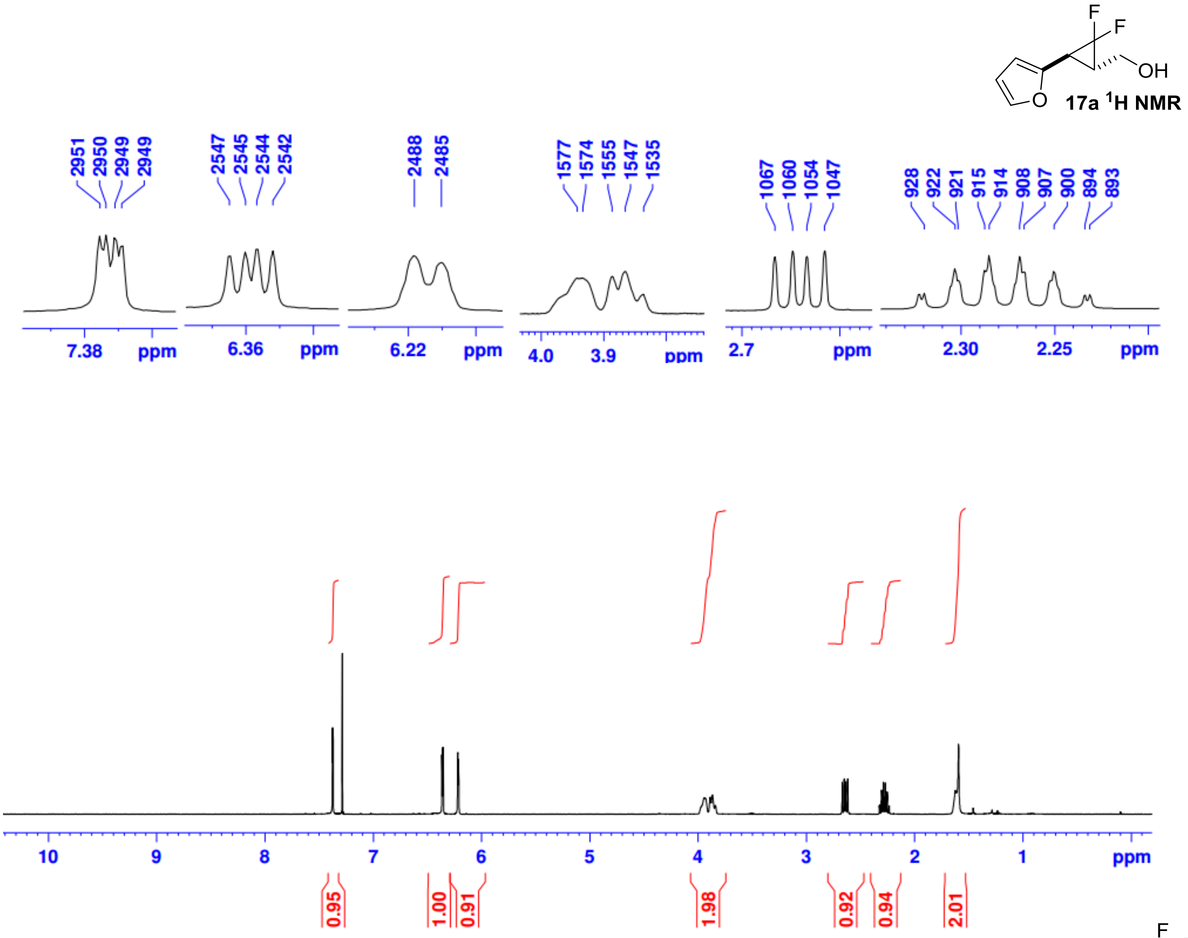
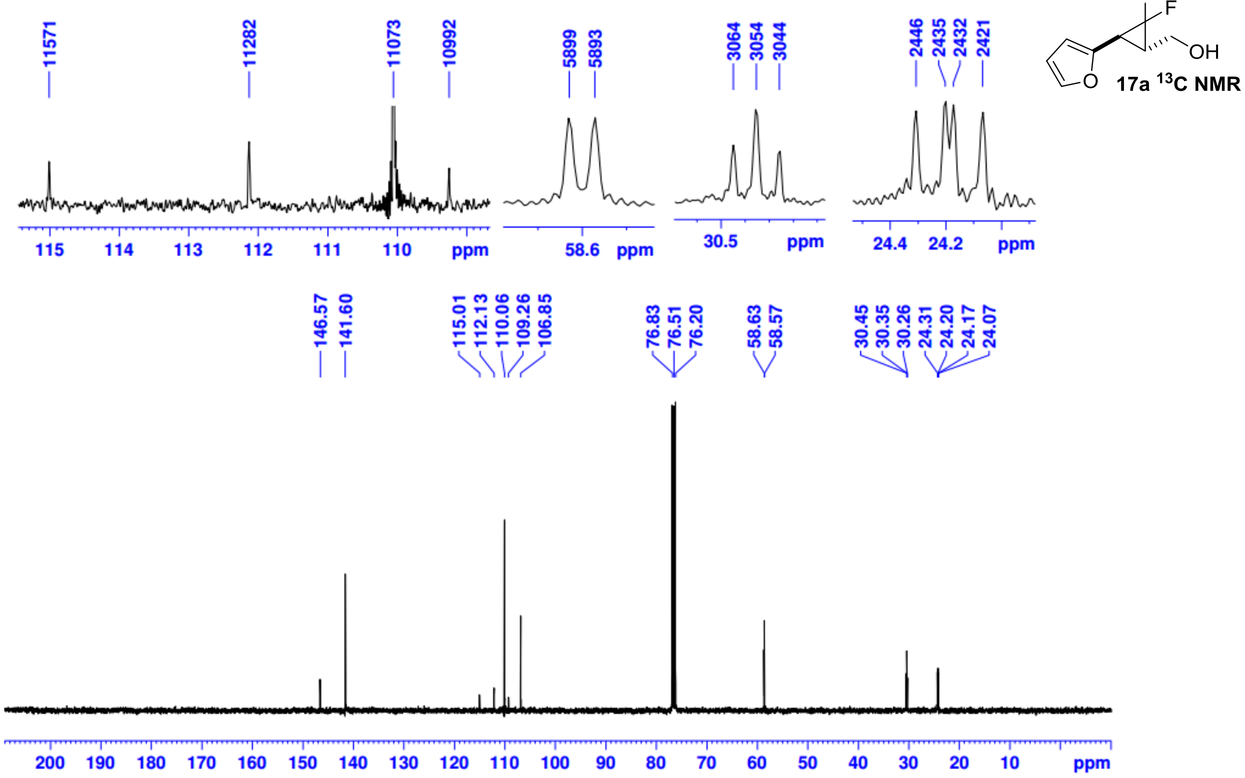
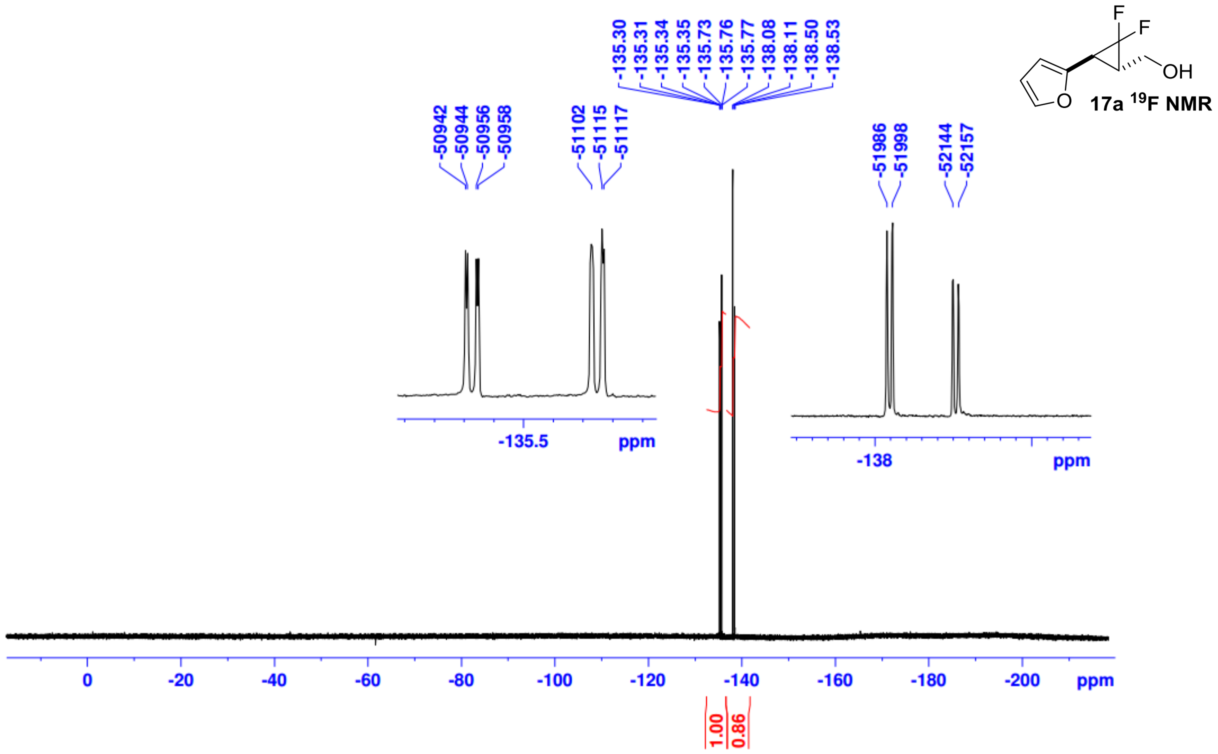


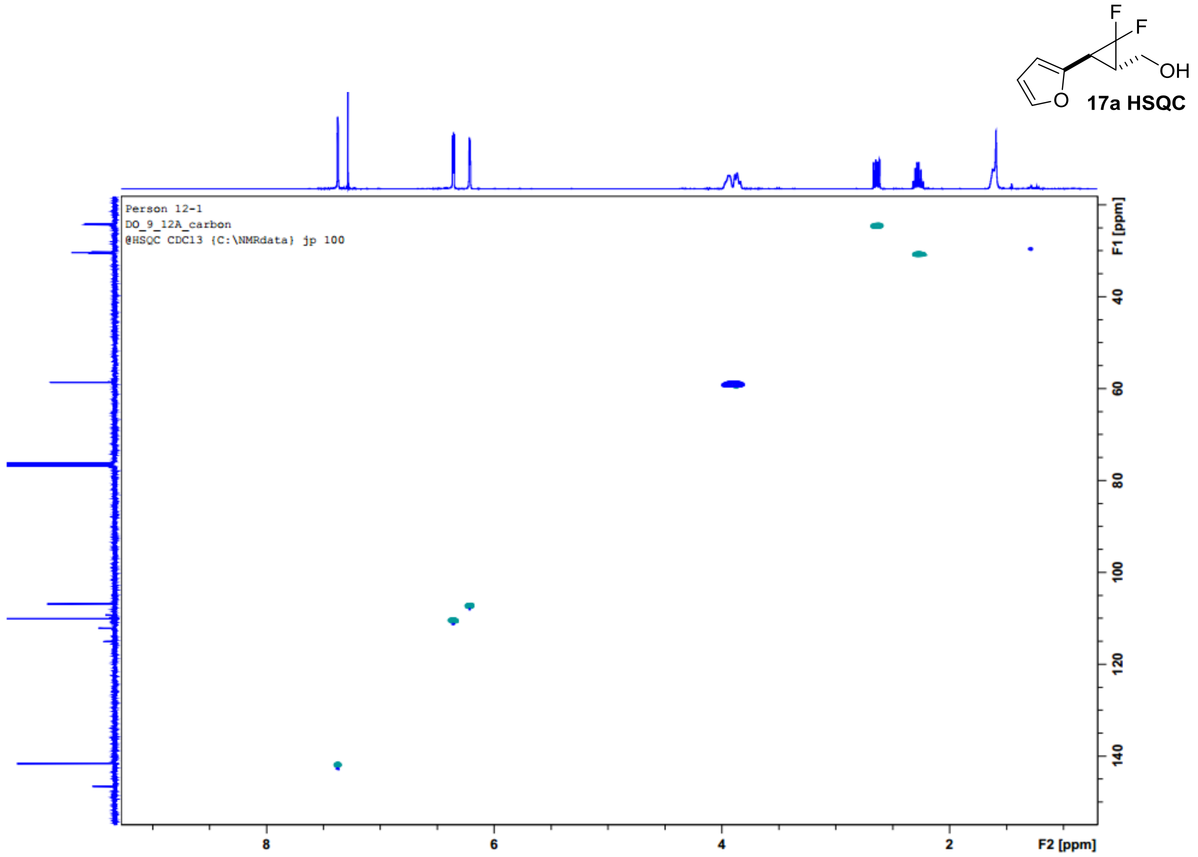
17a ¹H NMR



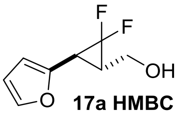
17a ¹³C NMR



17a ^{19}F NMR



17a HSQC



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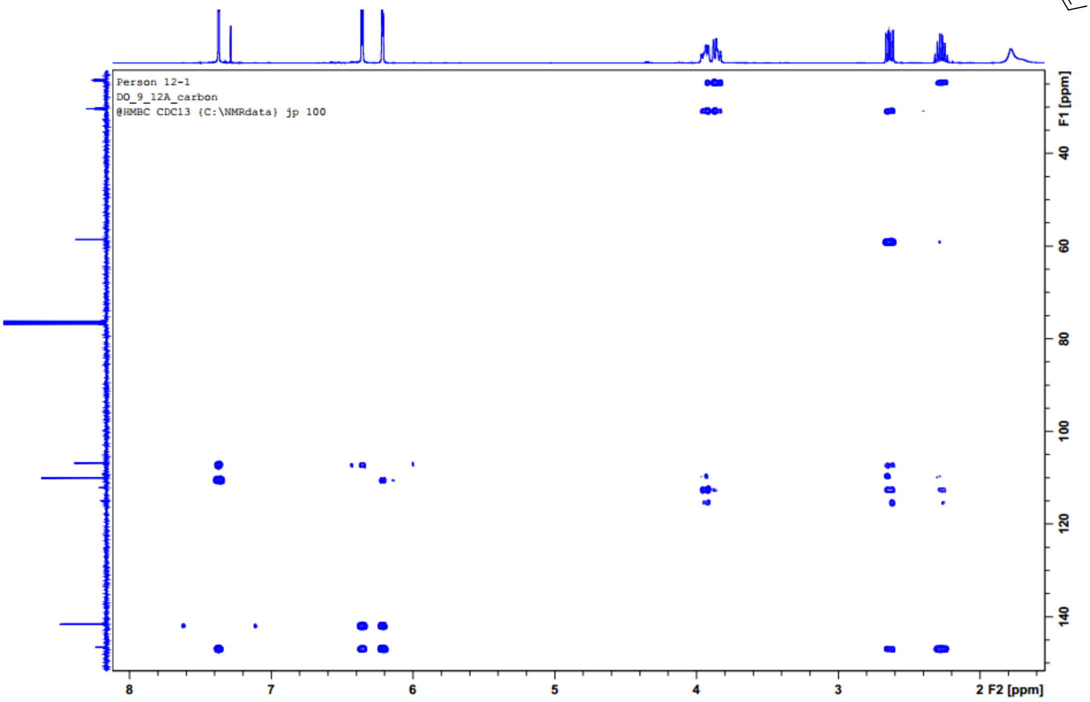
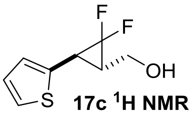
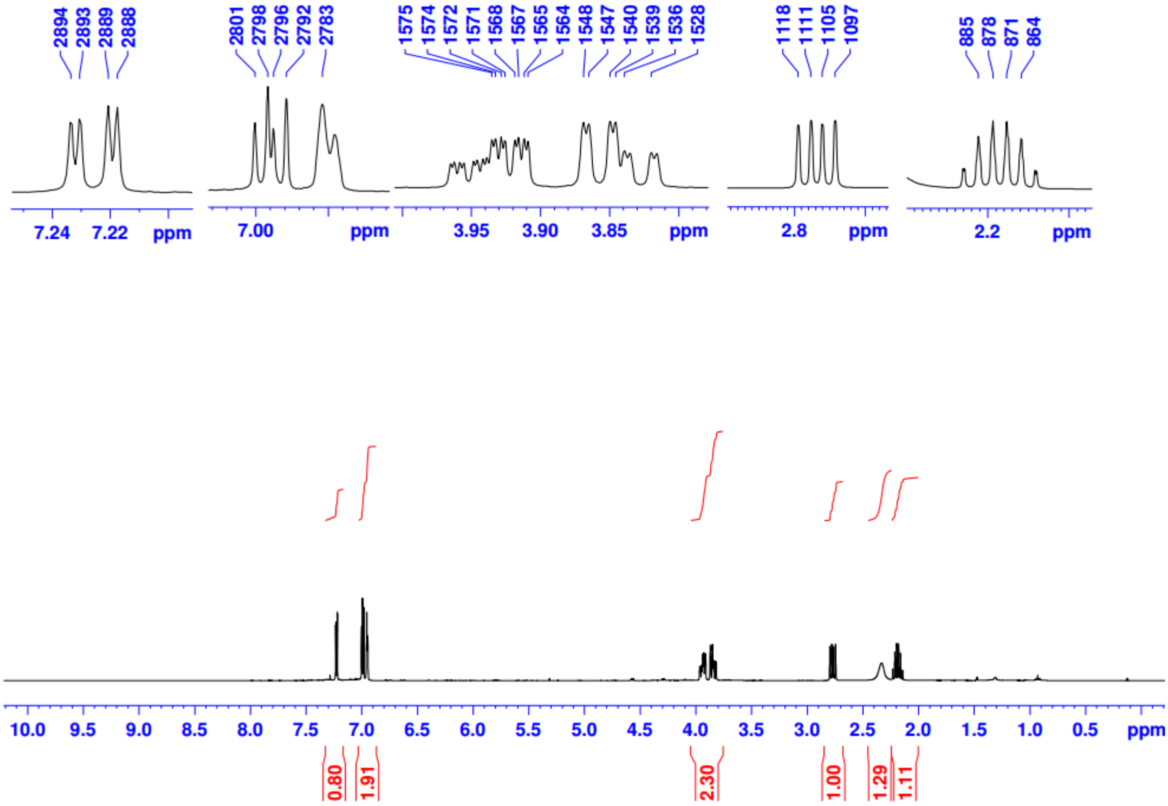
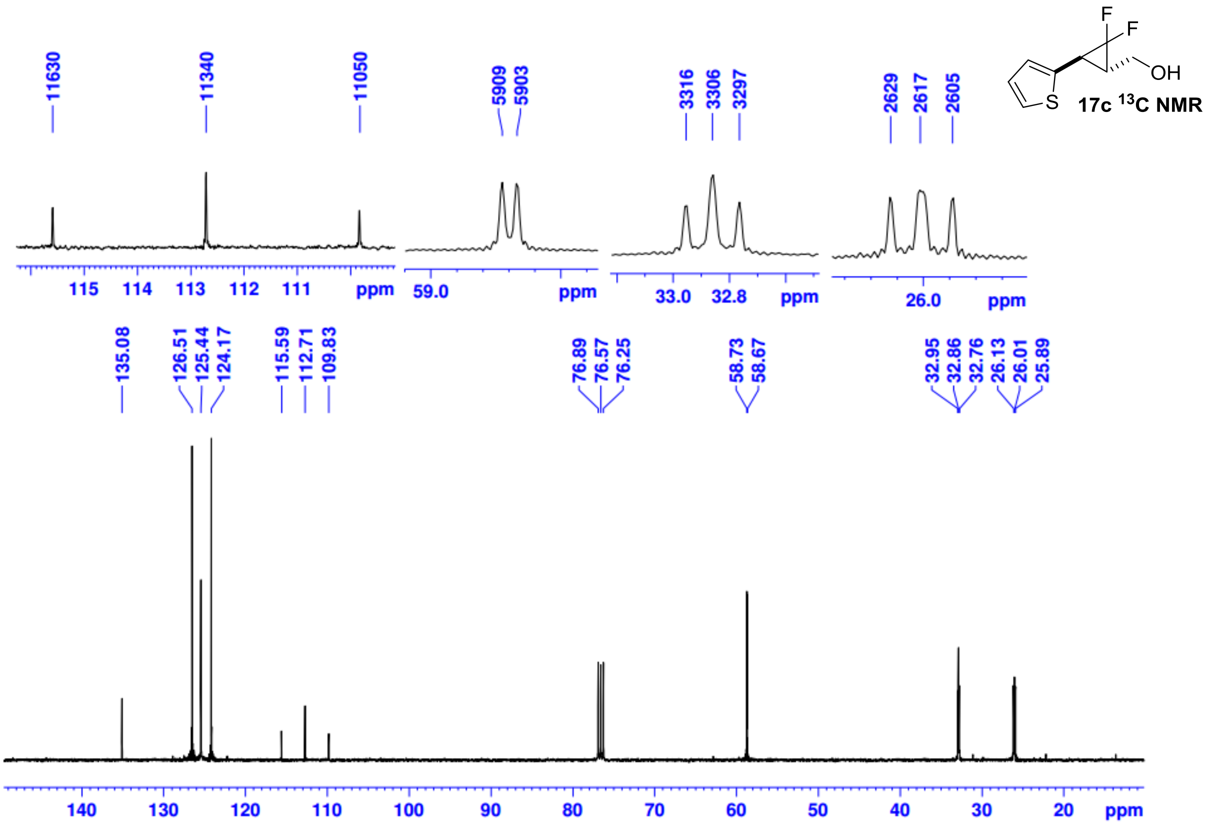
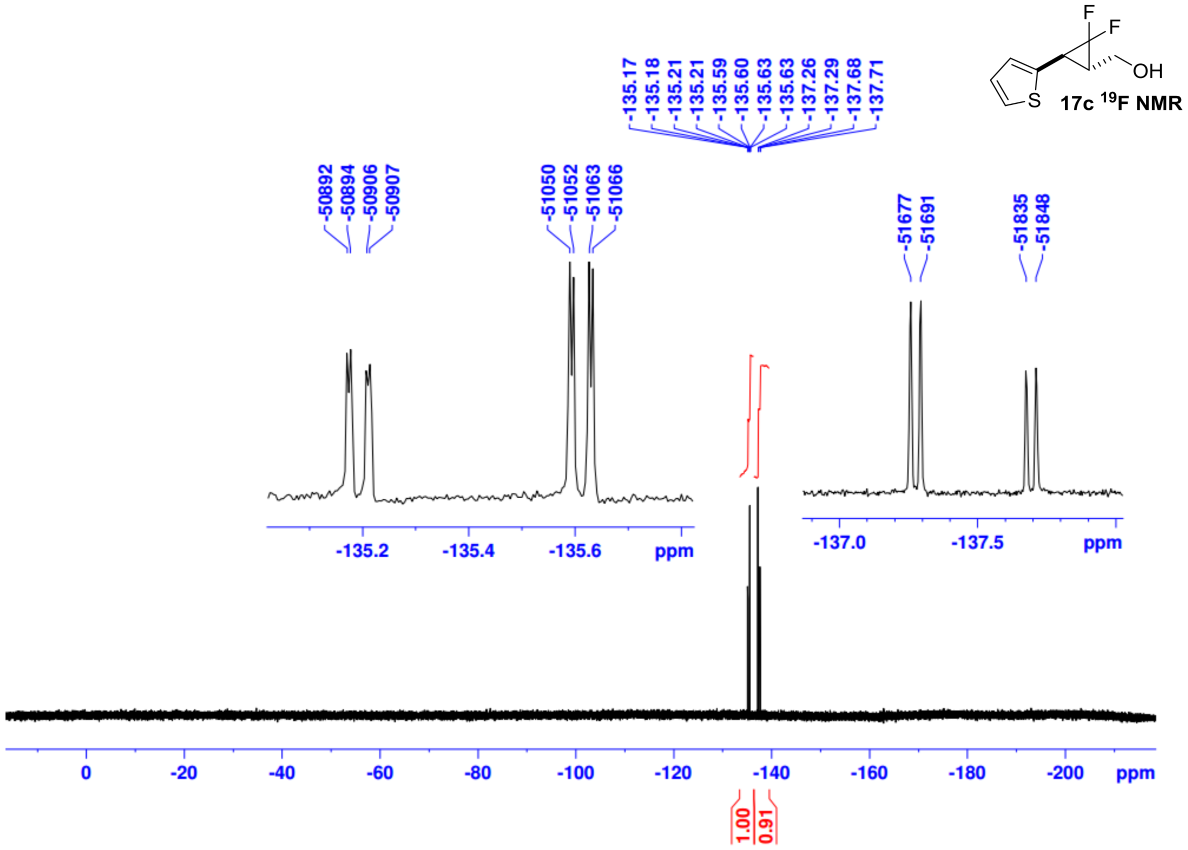


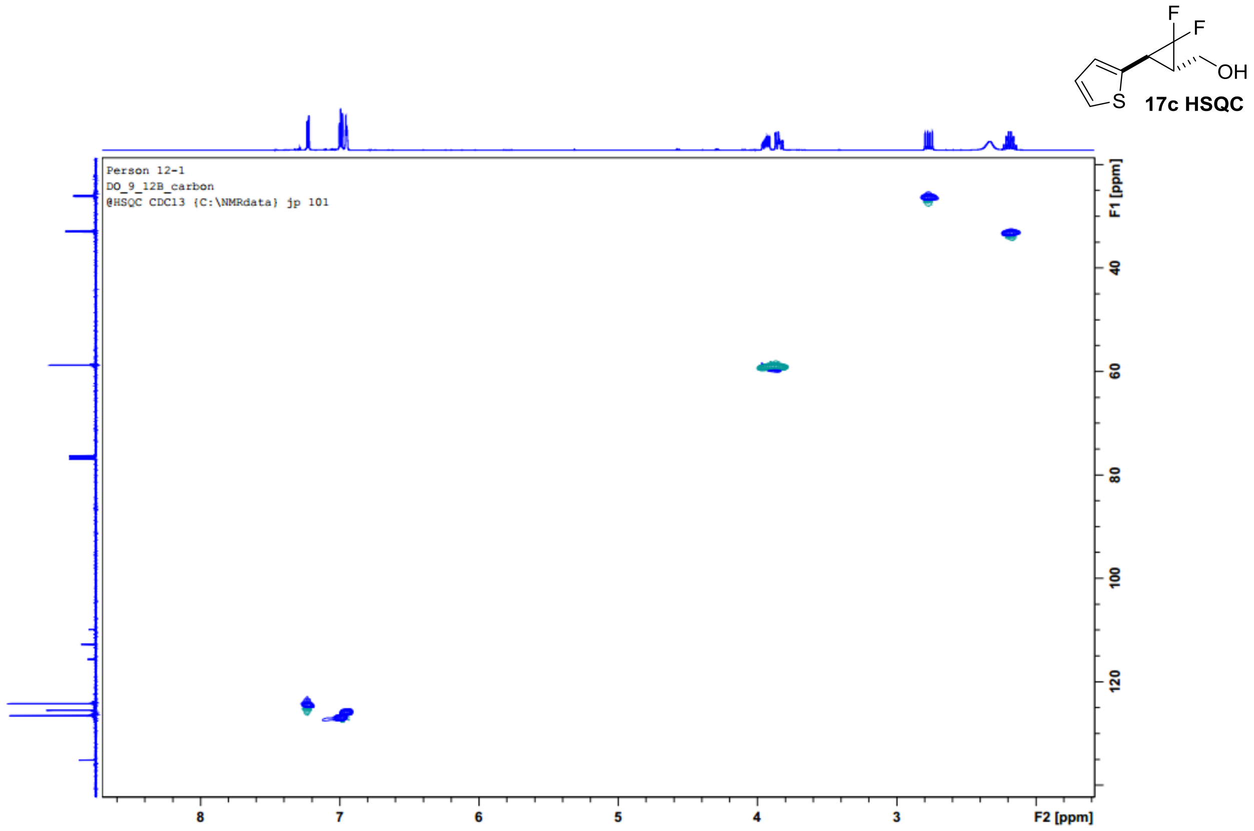


17c ^{1}H NMR

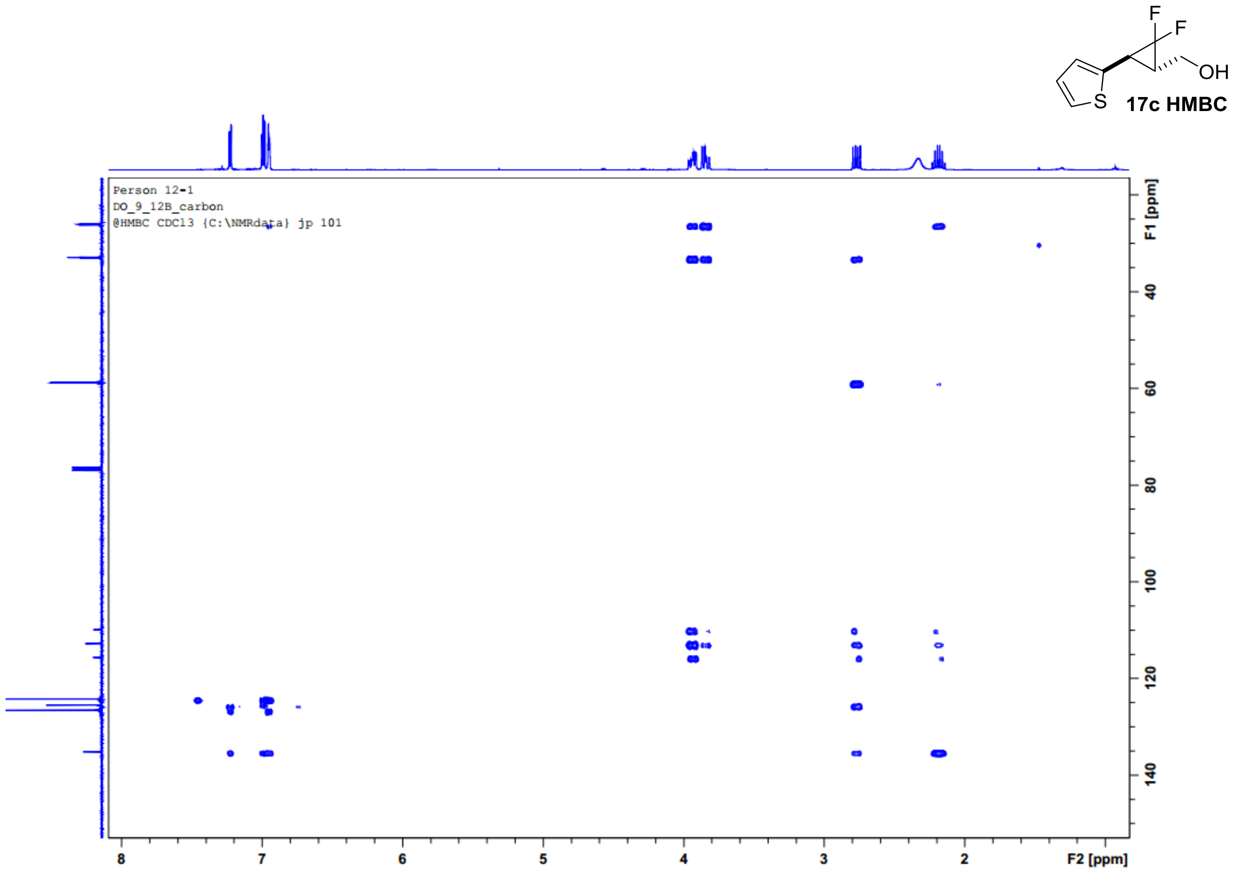



17c ^{13}C NMR

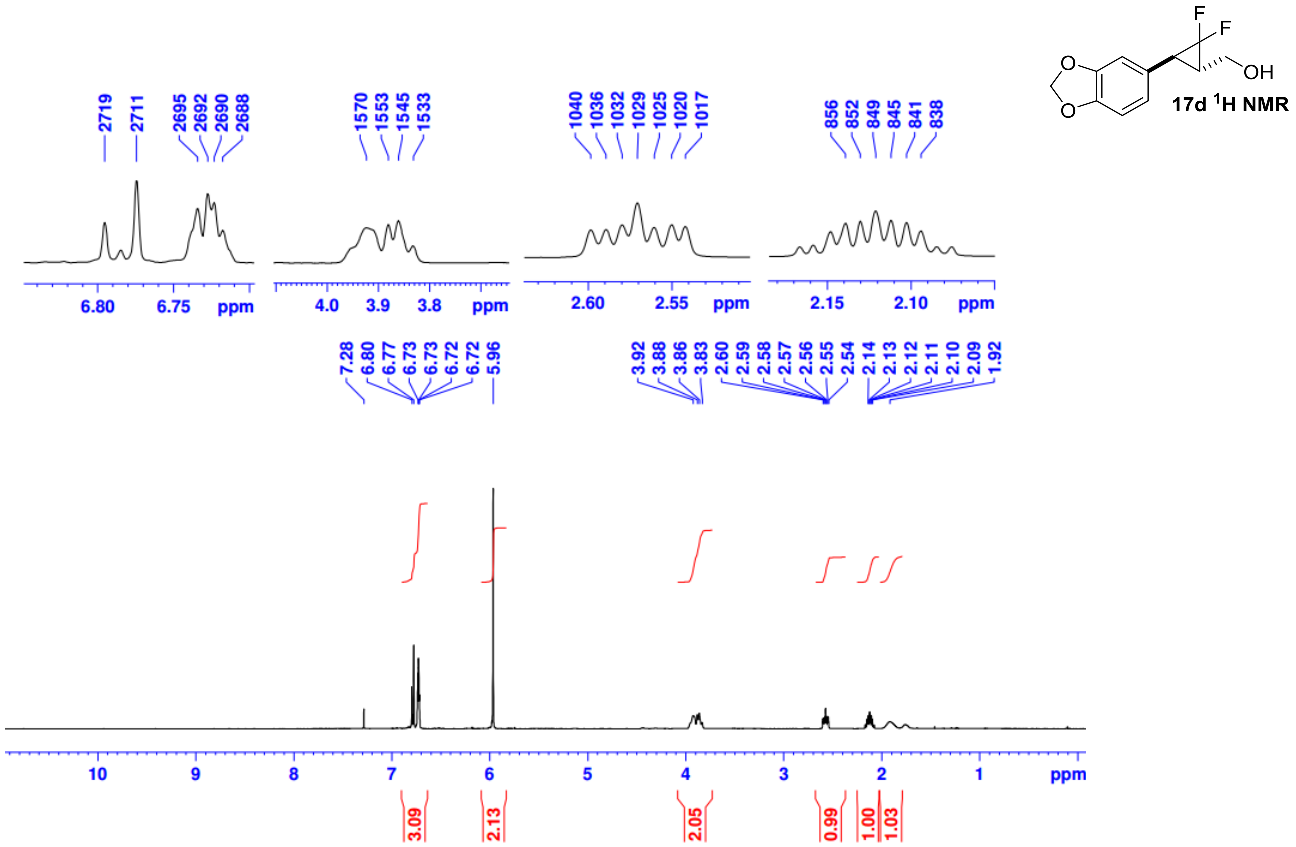

17c ^{19}F NMR



17c HSQC



17c HMBC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F
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O
OH
17d ¹H NMR
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1553
1545
1533
4.0
3.9
3.8
ppm
1040
1036
1032
1029
1025
1020
1017
2.60
2.55
ppm
856
852
849
845
841
838
2.15
2.10
ppm
7.28
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6.72
6.72
5.96
3.92
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3.86
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2.58
2.57
2.56
2.55
2.54
2.14
2.13
2.12
2.11
2.10
2.09
1.92
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0.99
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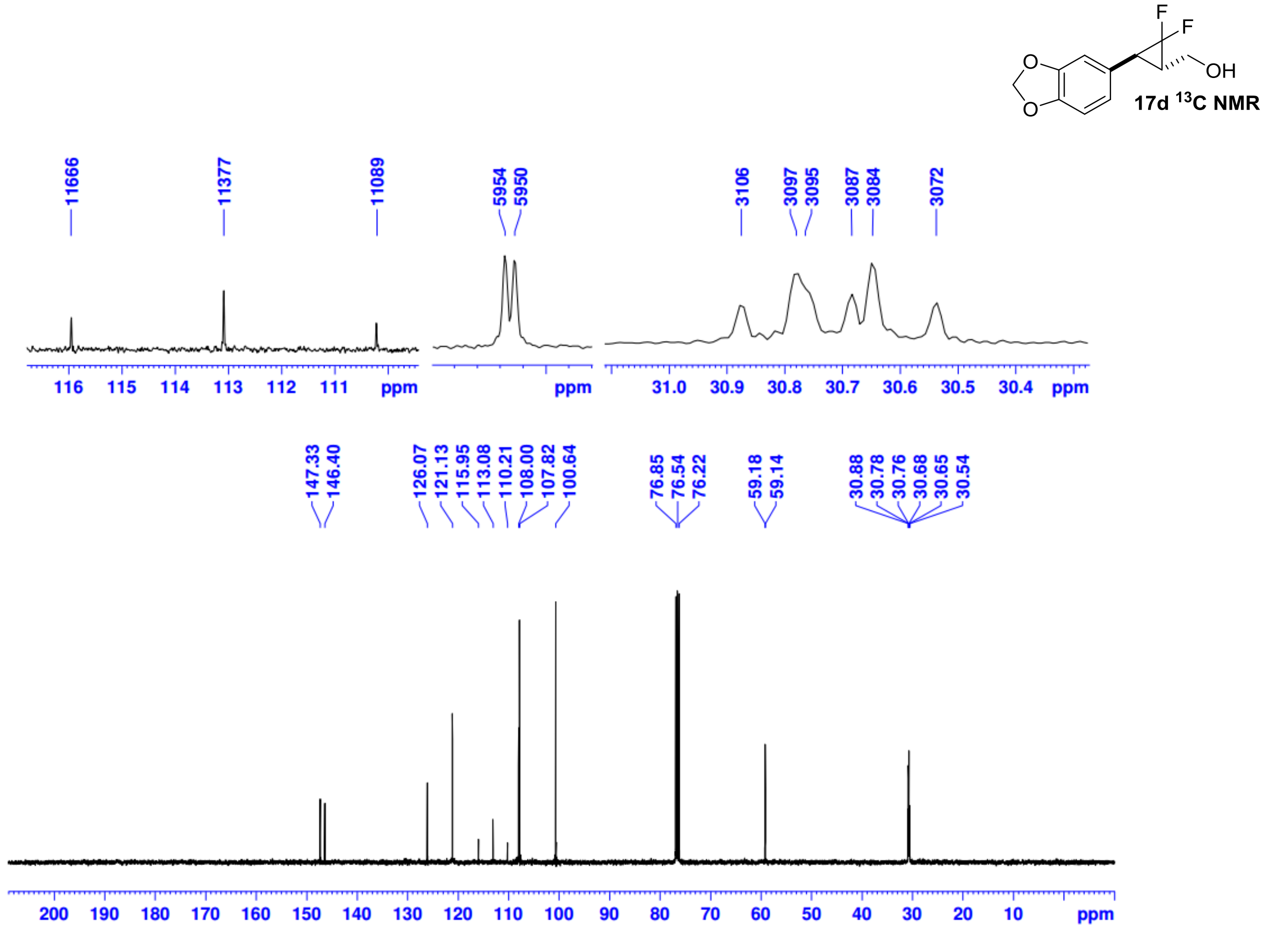
1.03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ppm
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3095
3087
3084
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30.9
30.8
30.7
30.6
30.5
30.4
ppm
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115.95
113.08
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108.00
107.82
100.64
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76.54
76.22
59.18
59.14
30.88
30.78
30.76
30.68
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30.54
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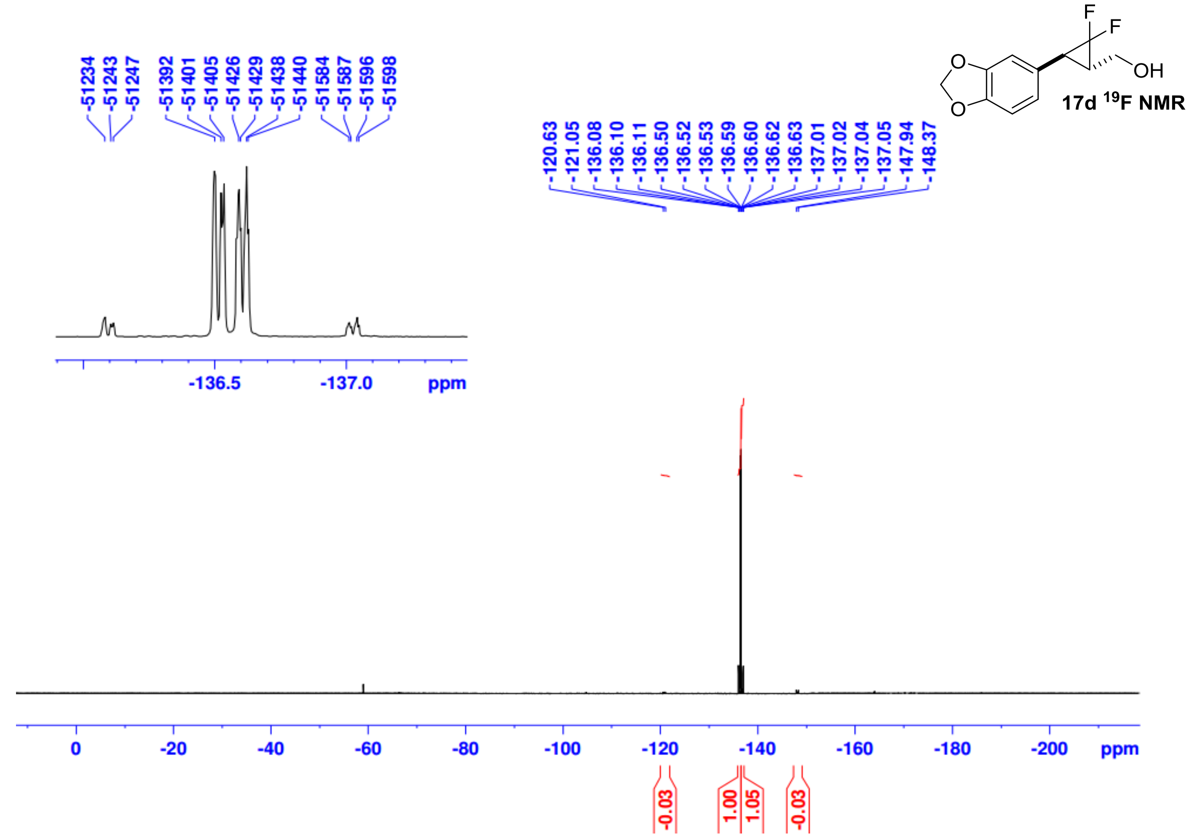
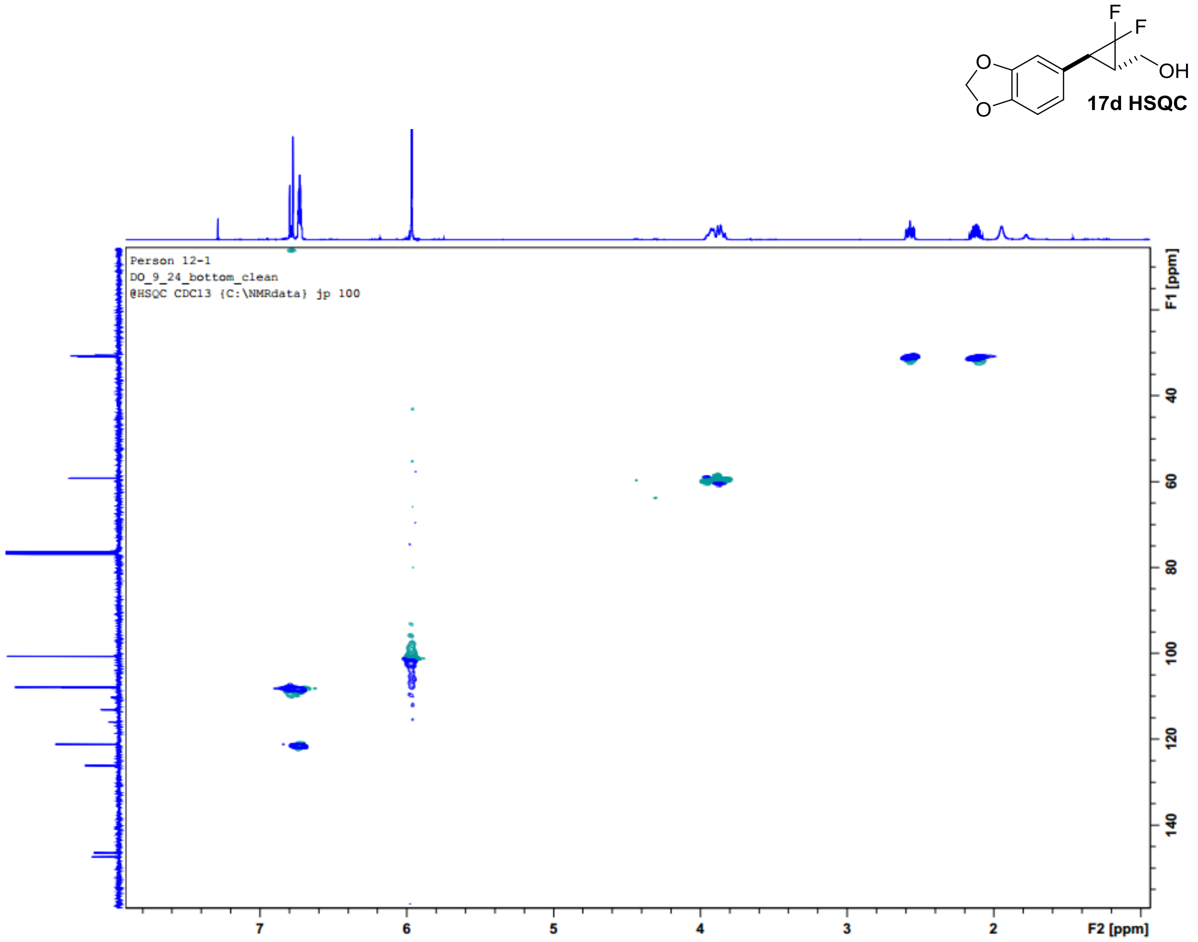
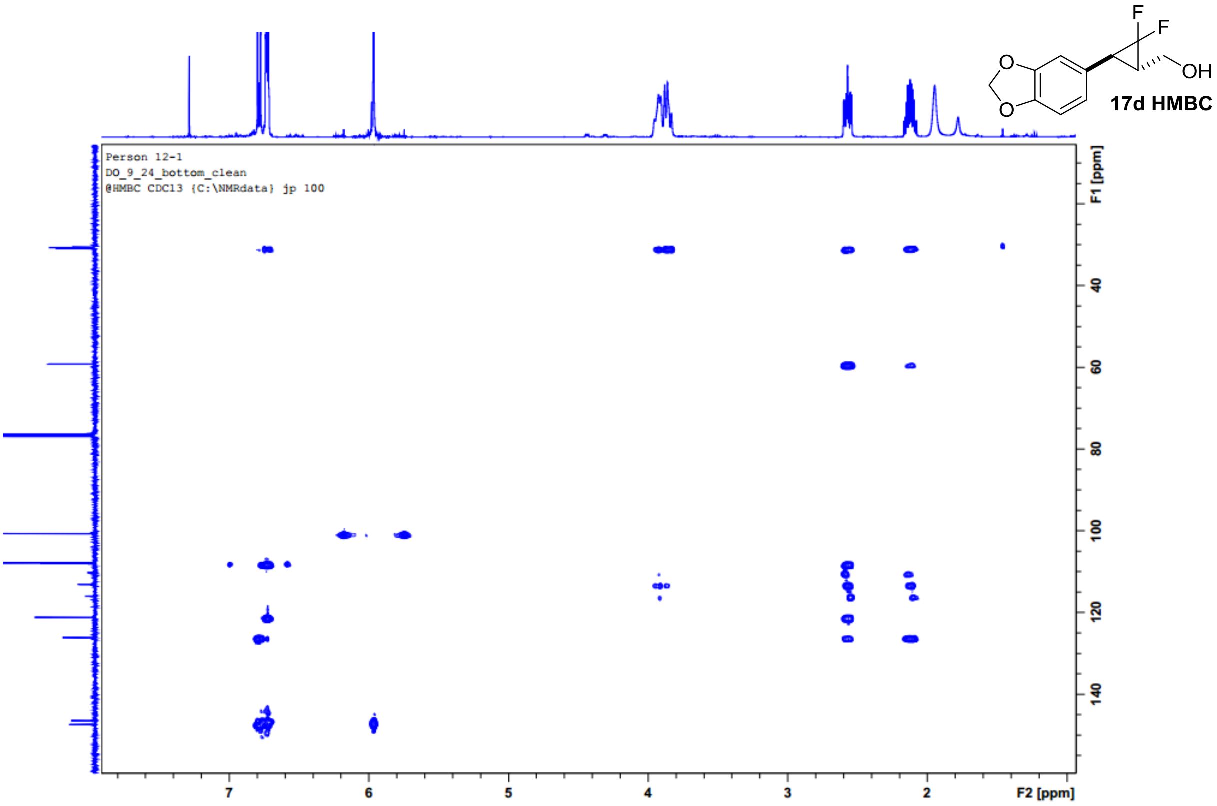
ppm



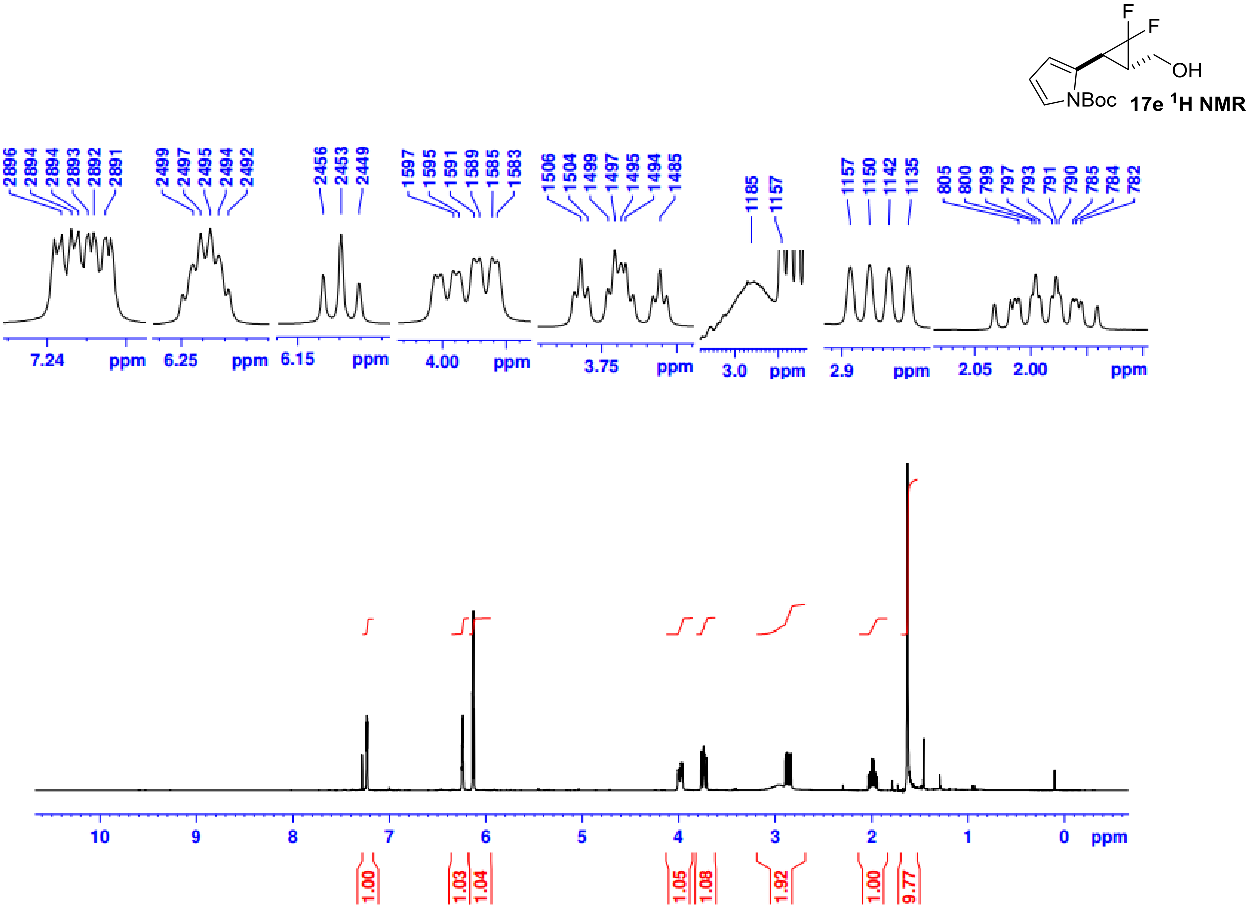
17d ^{19}F NMR



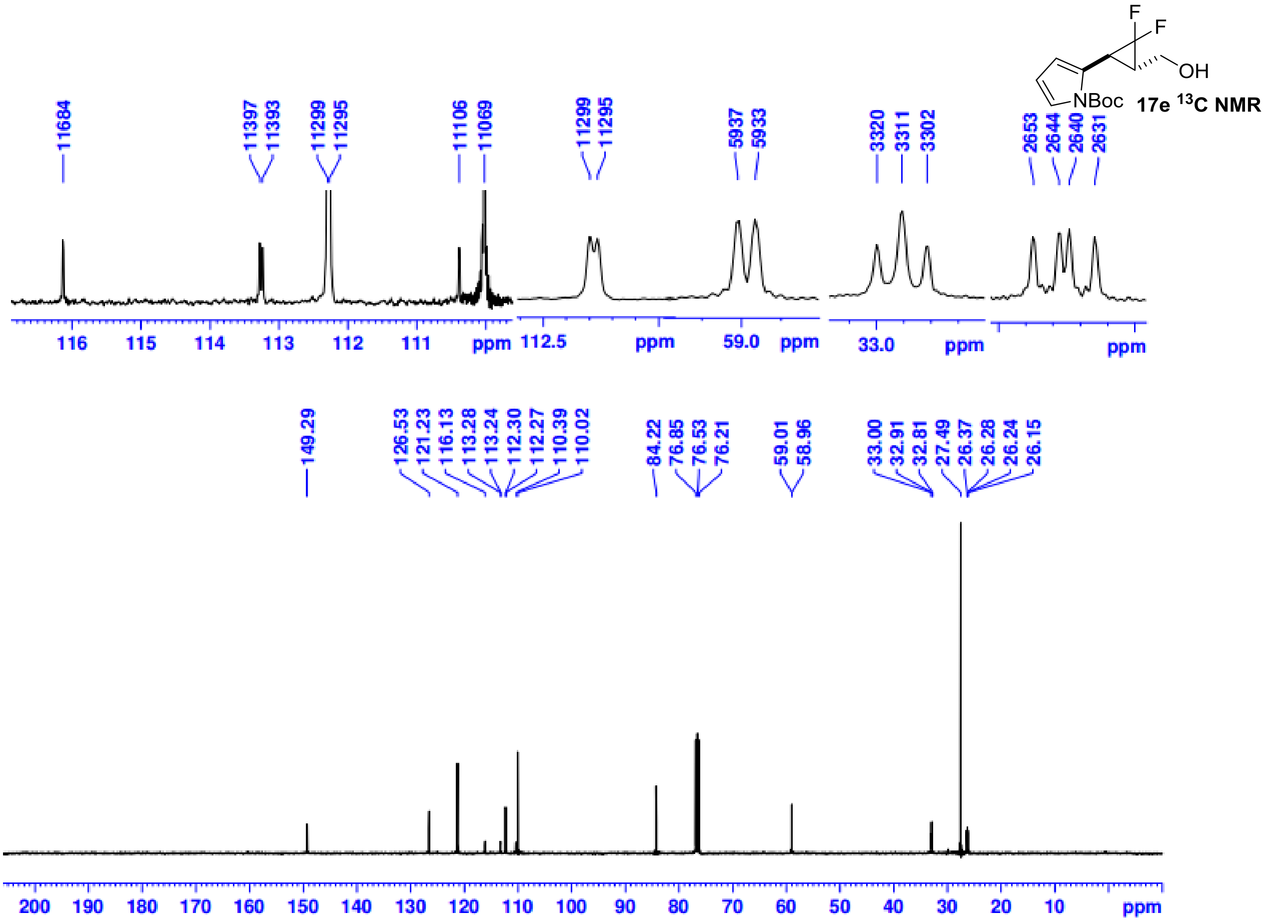
17d HSQC



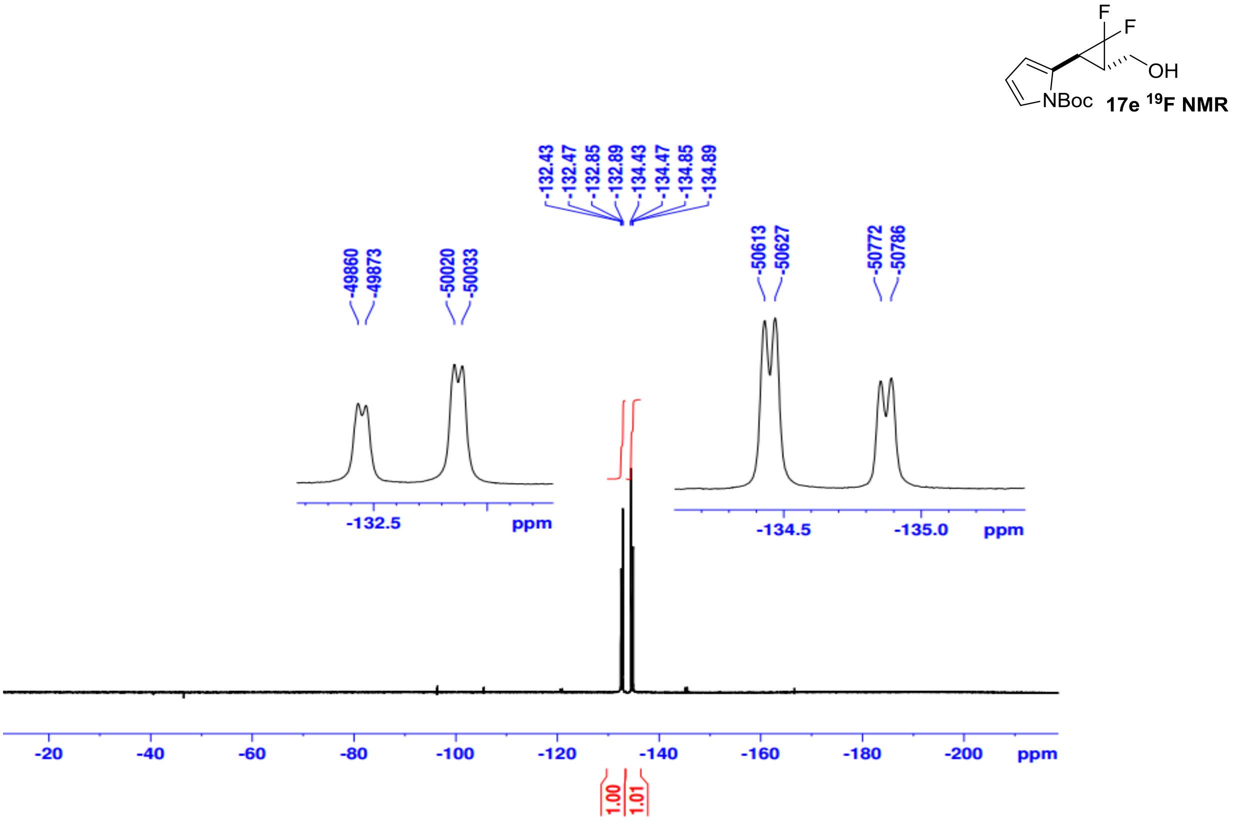
17d HMBC



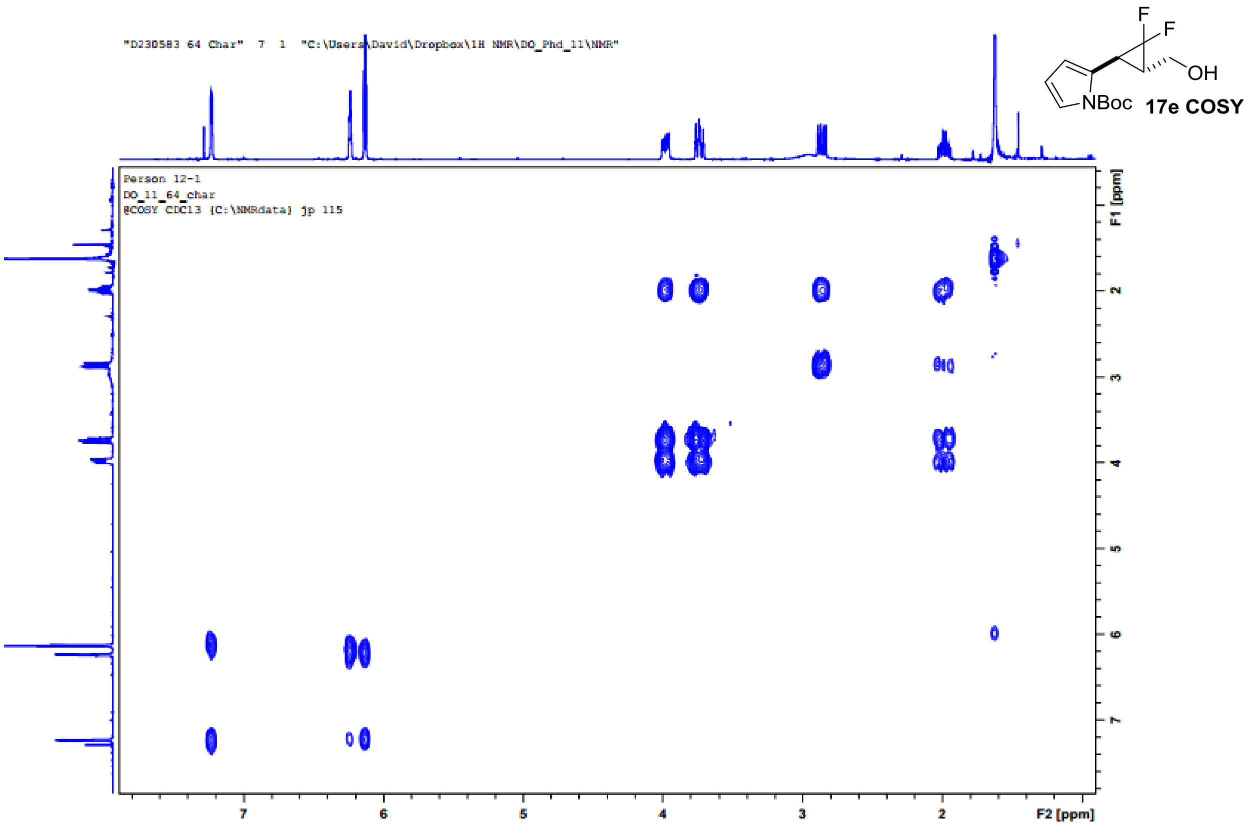
17e ^{1}H NMR



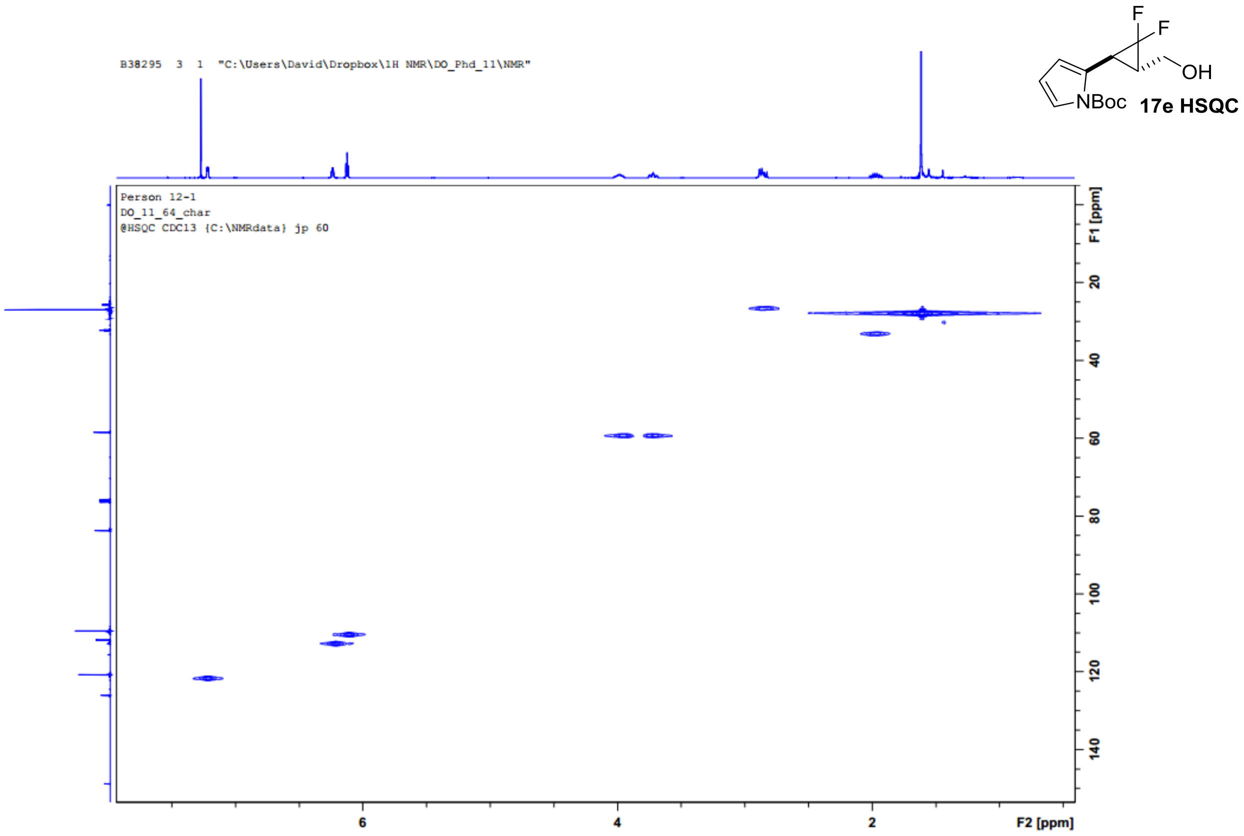
17e ^{13}C NMR



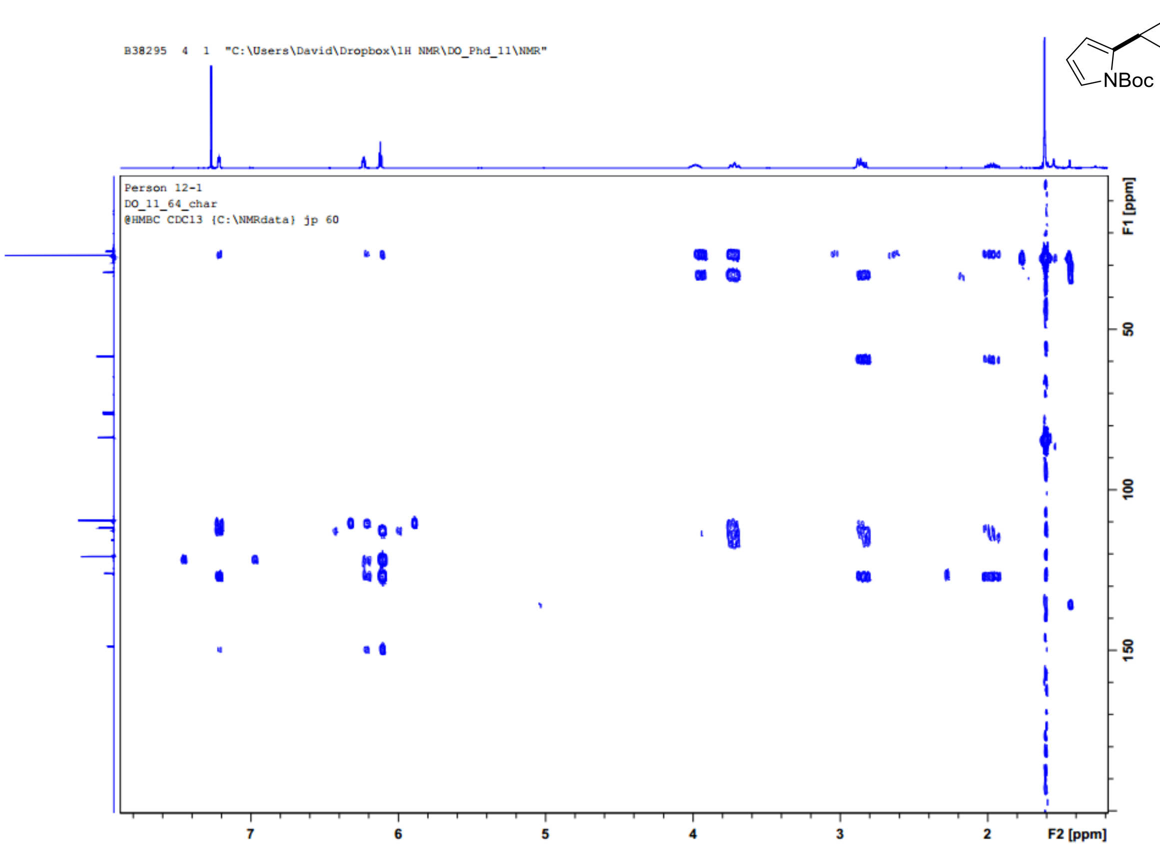
17e ^{19}F NMR



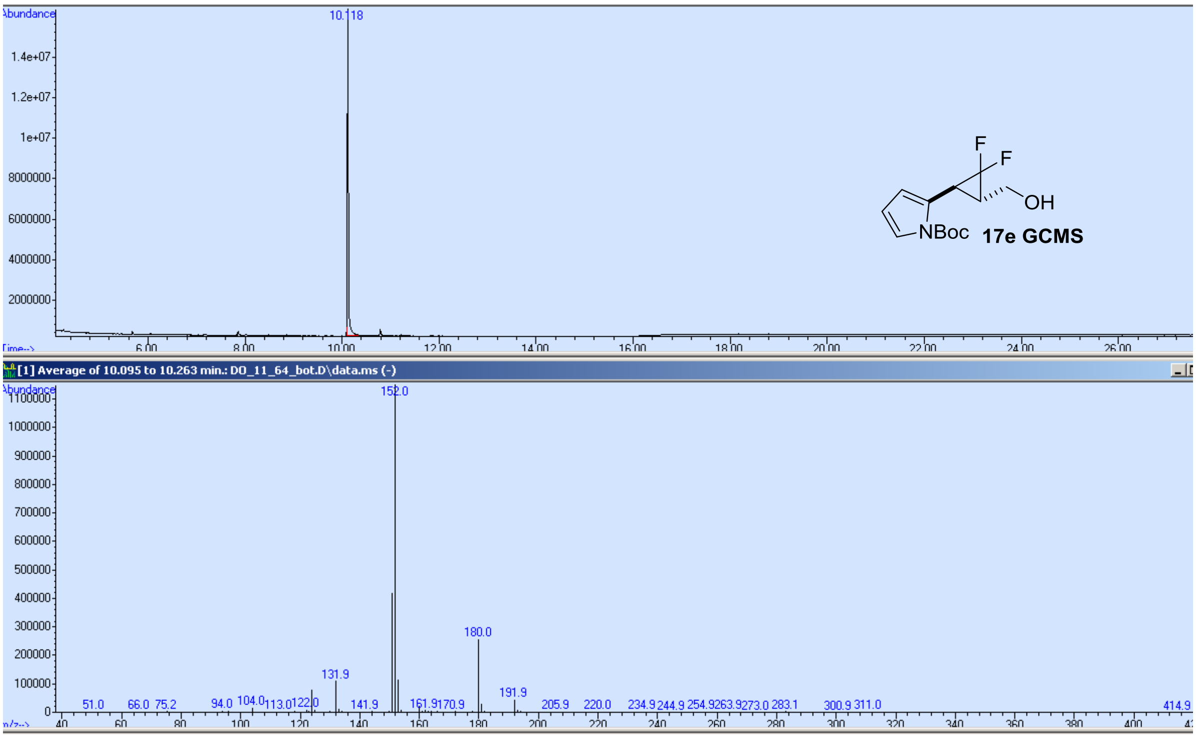
17e COSY



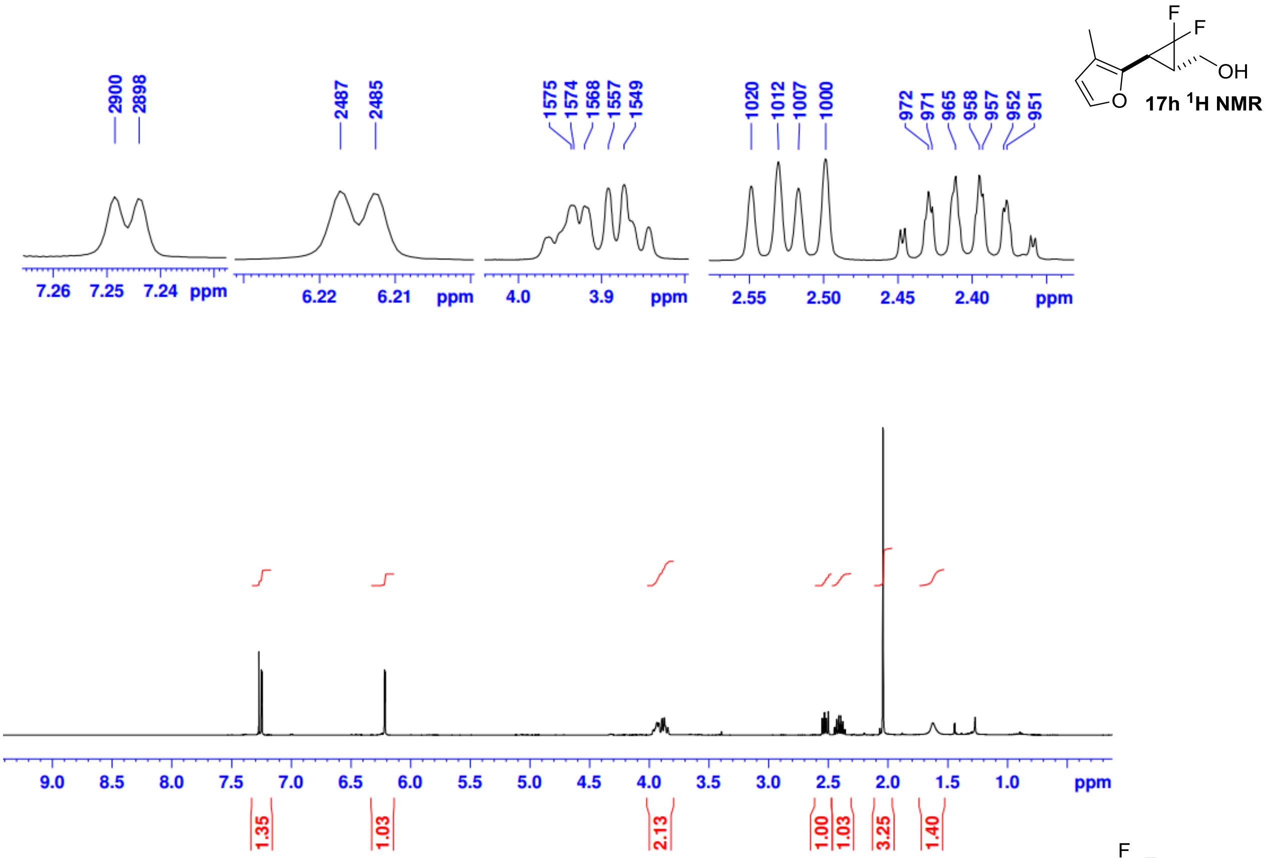
17e HSQC



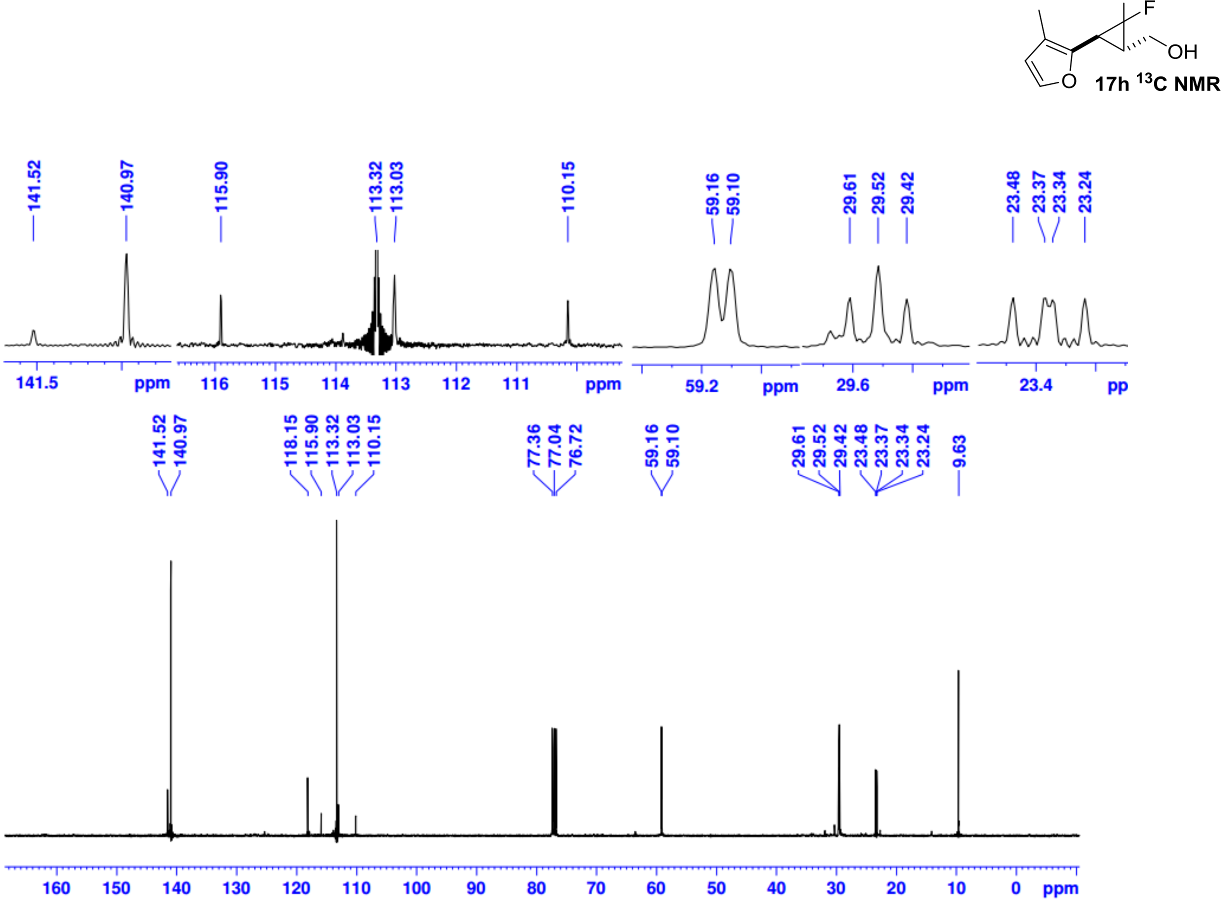
17e HMBC



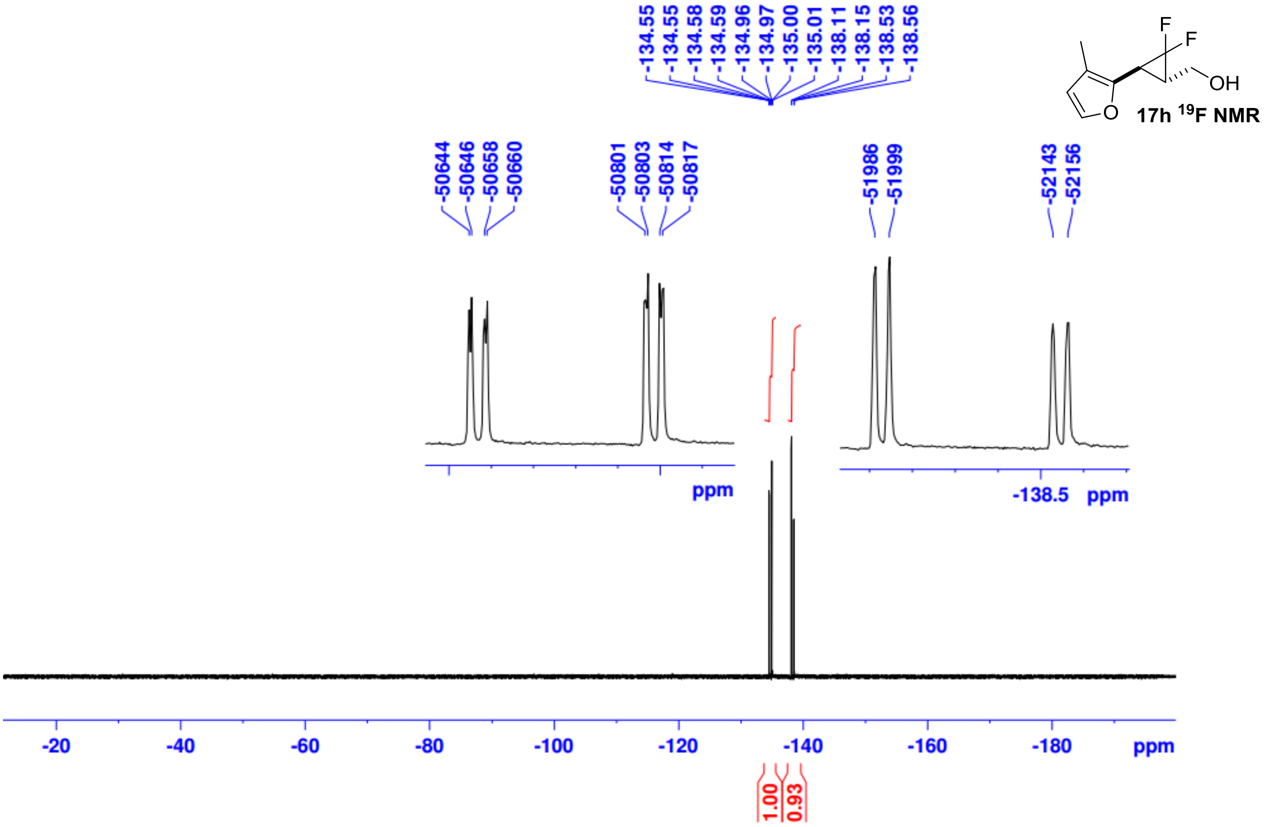
17e GCMS



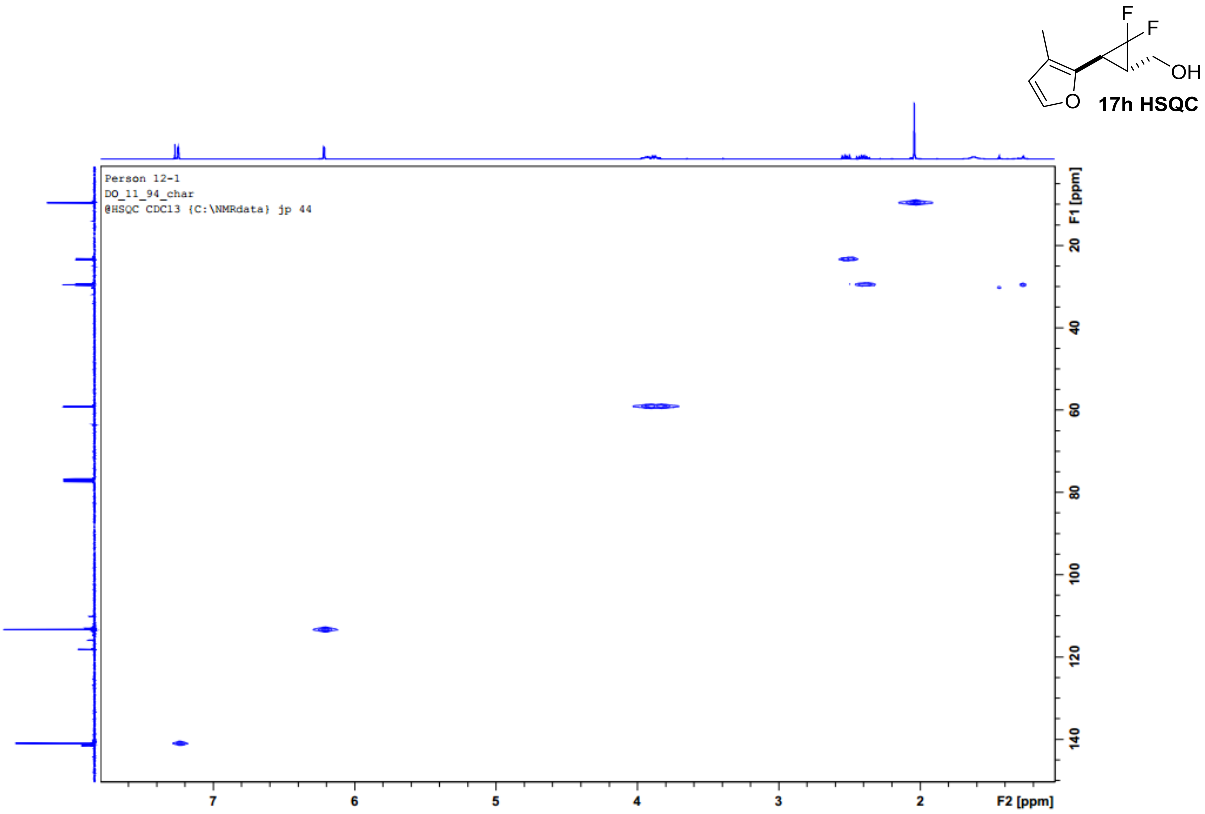
17h ^{1}H NMR



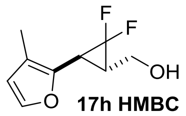
17h ^{13}C NMR



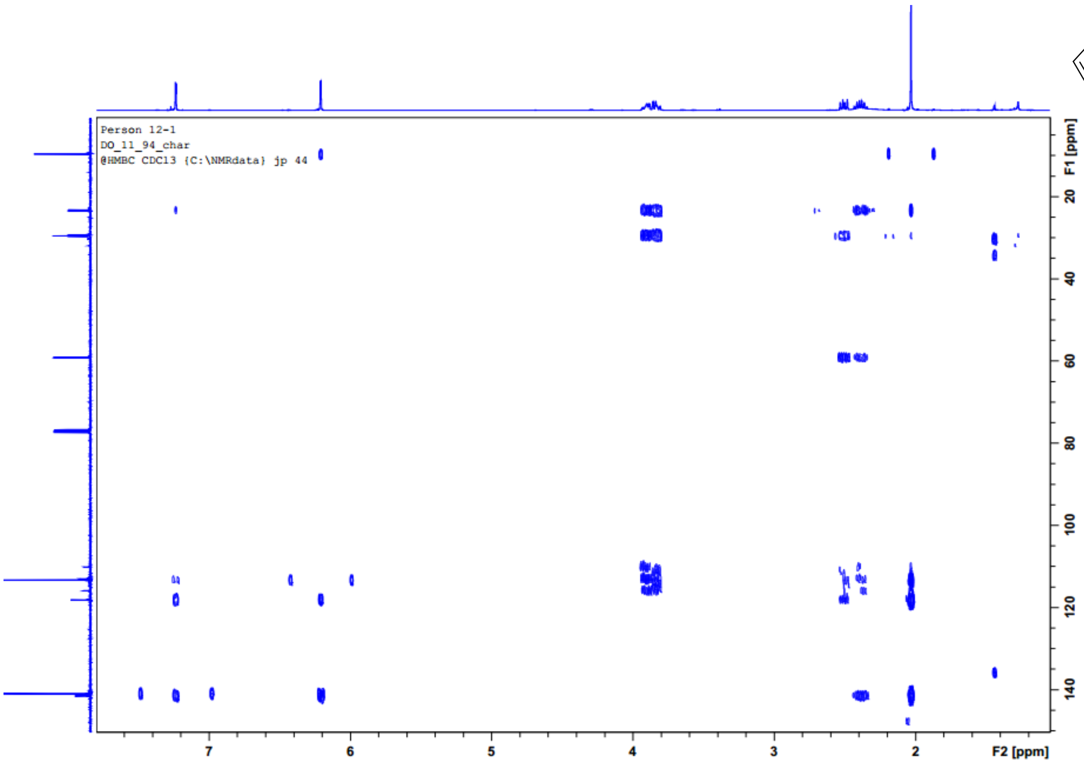
17h ^{19}F NMR

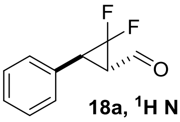


17h HSQC

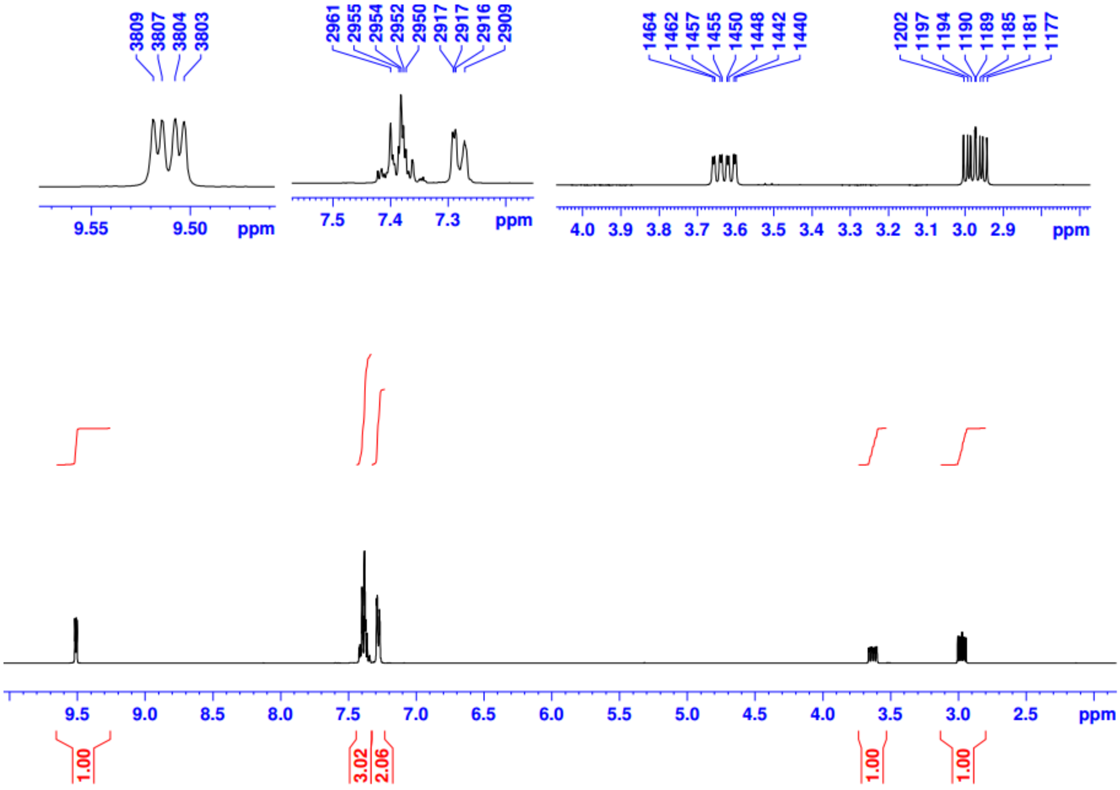


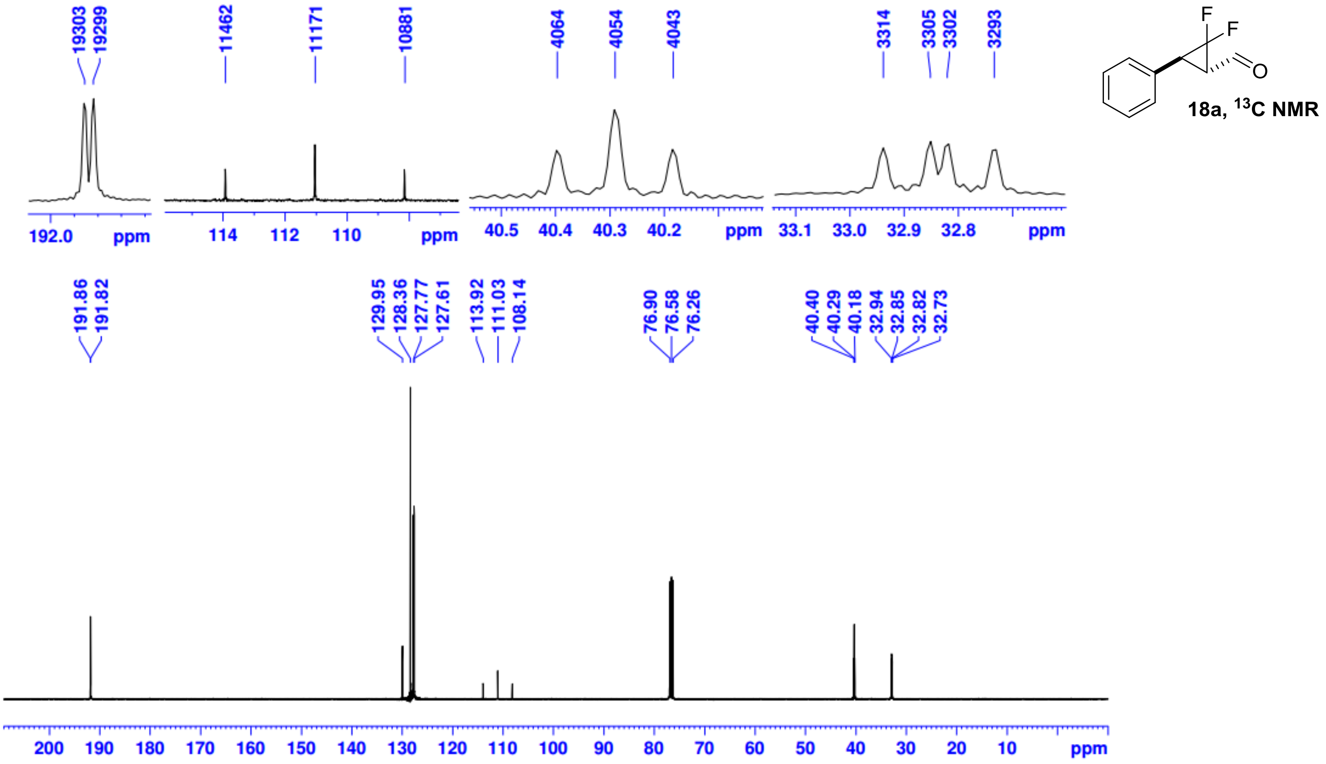
17h HMBC

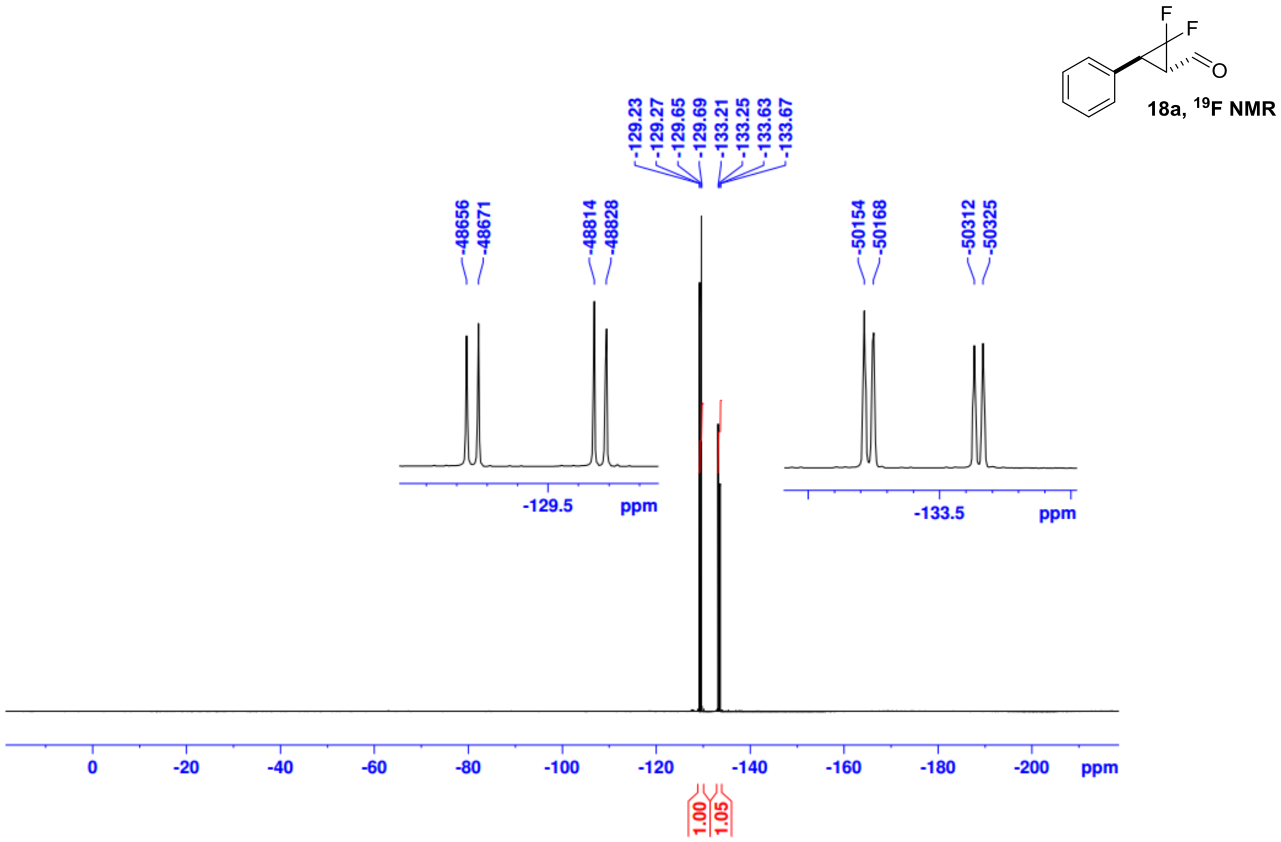


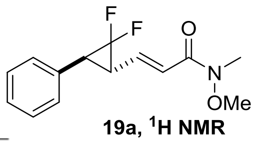


18a, ^{1}H NMR

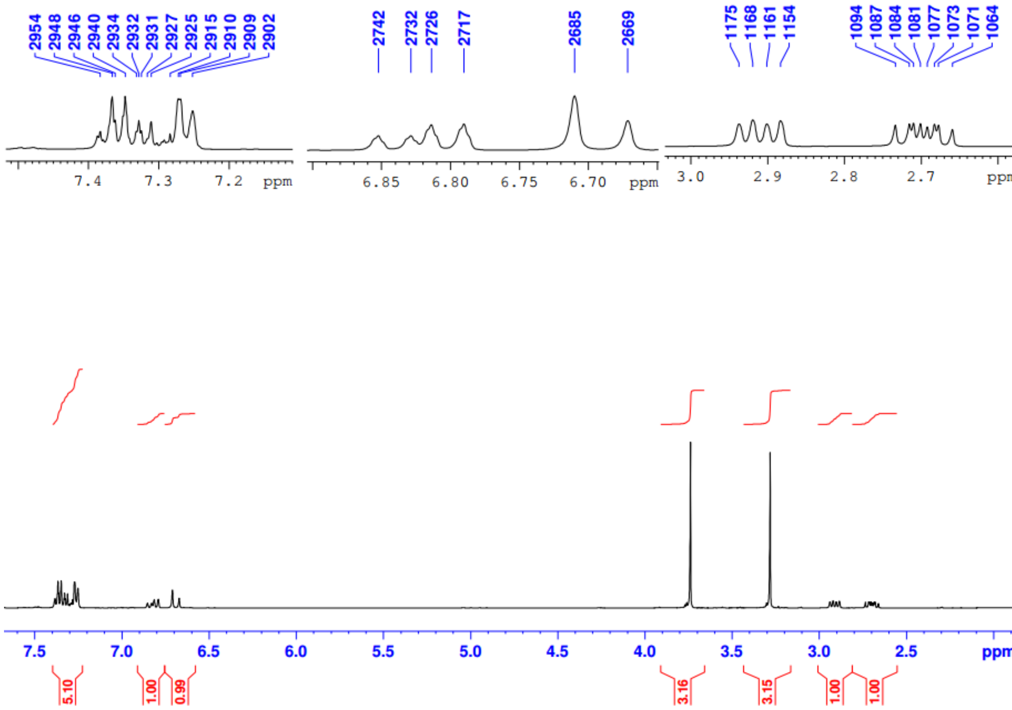


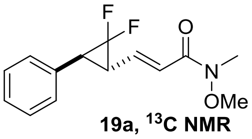

18a, ^{13}C NMR


18a, ^{19}F NMR

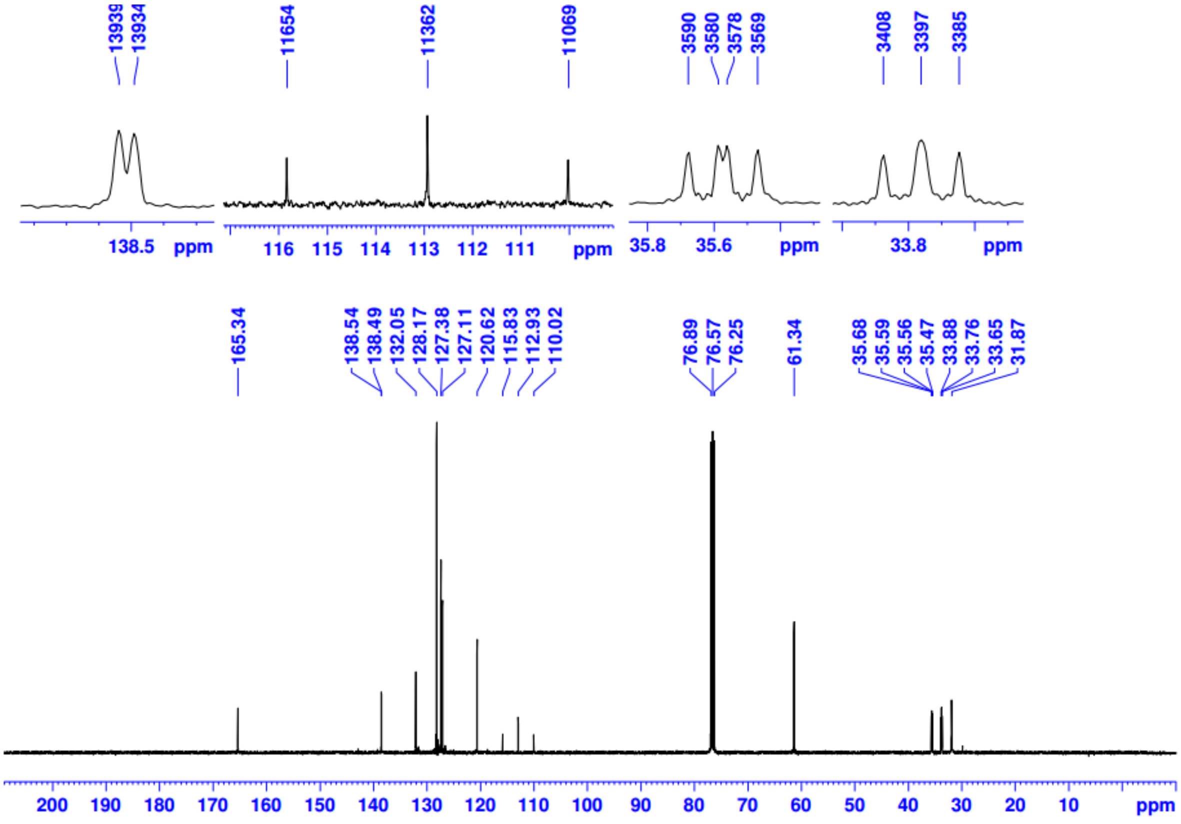


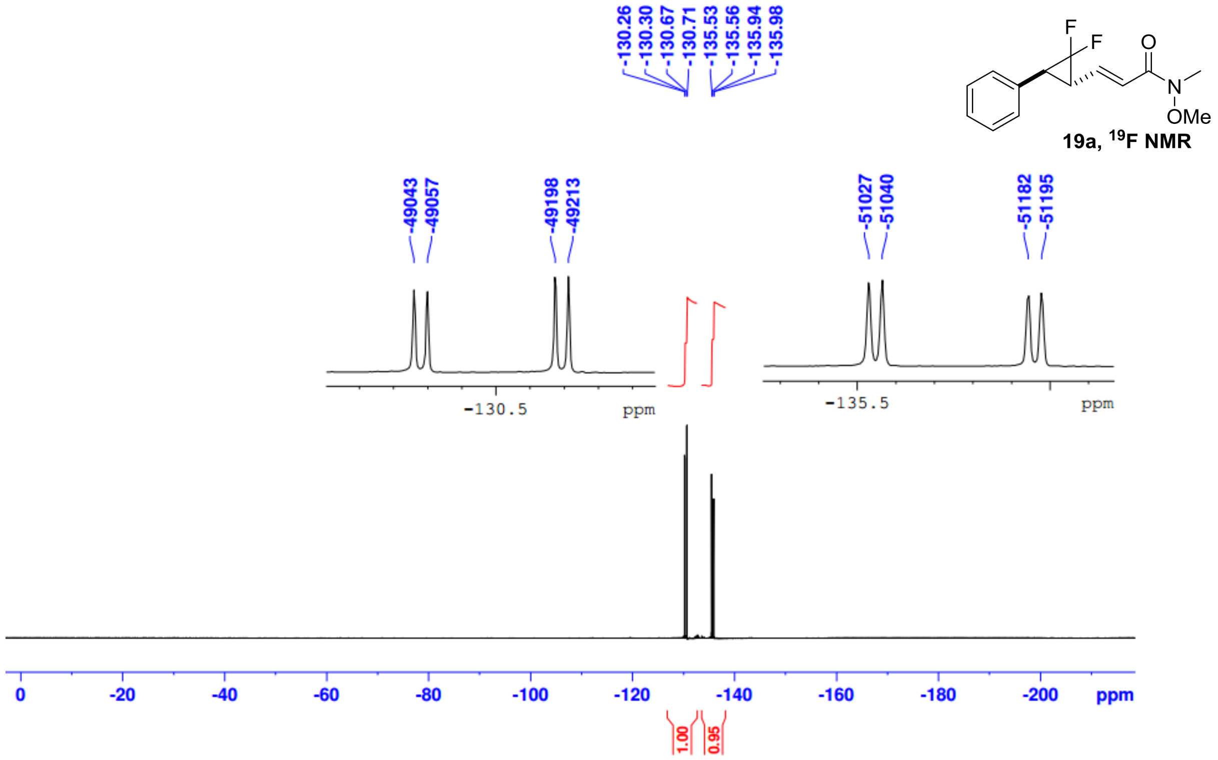
19a, ^{1}H NMR

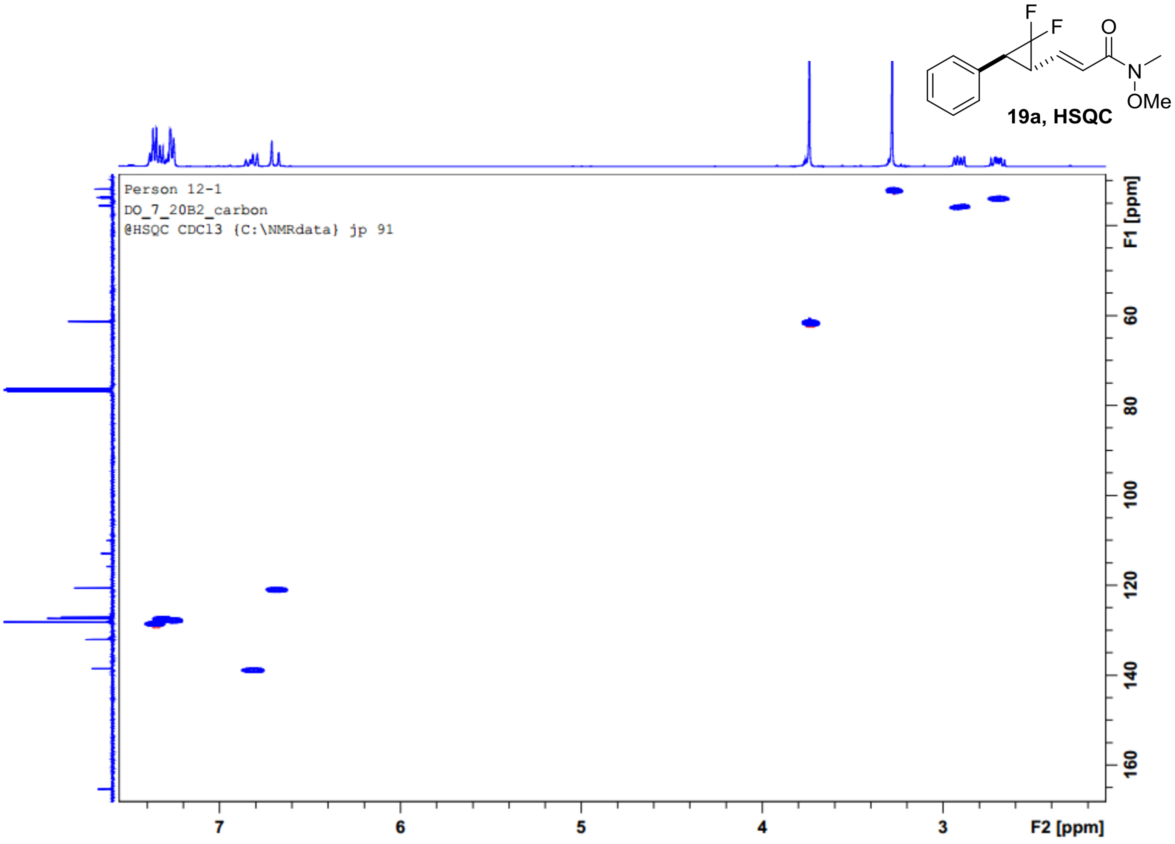


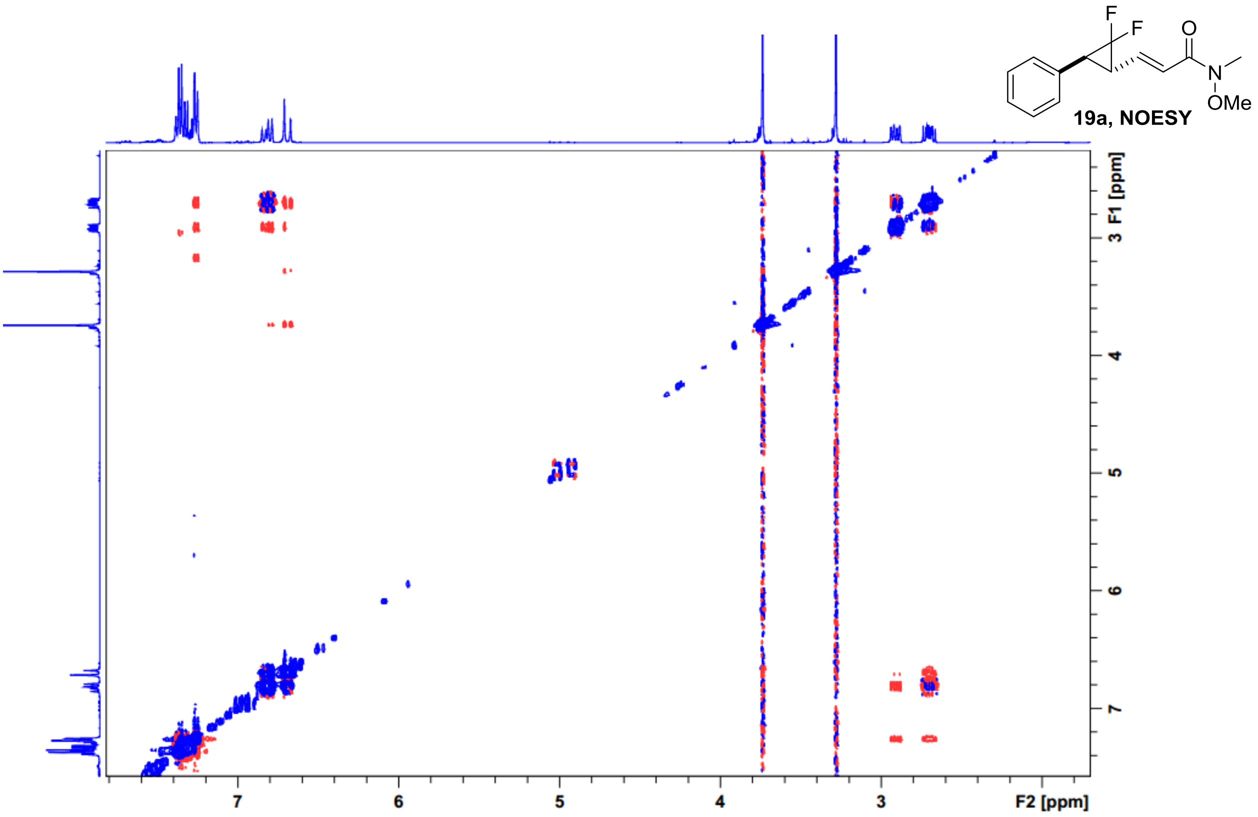


19a, ^{13}C NMR

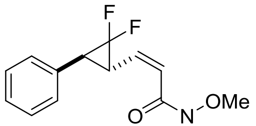



19a, ^{19}F NMR

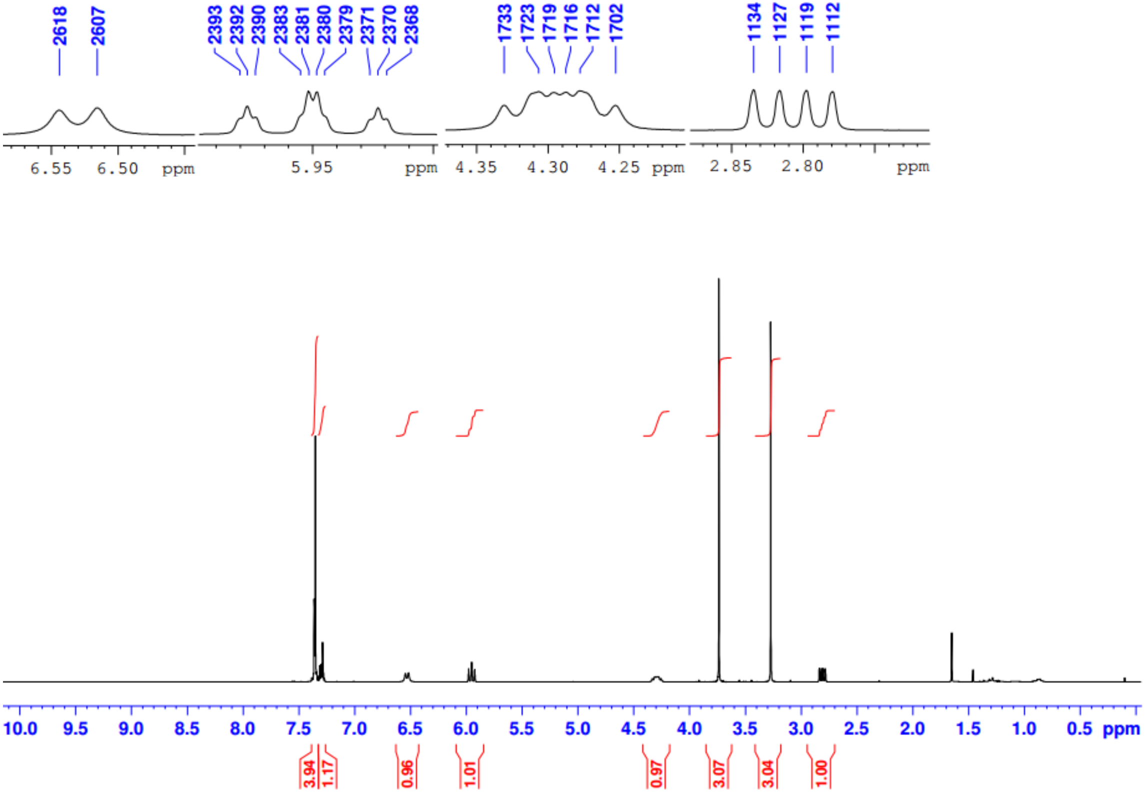

19a, HSQC

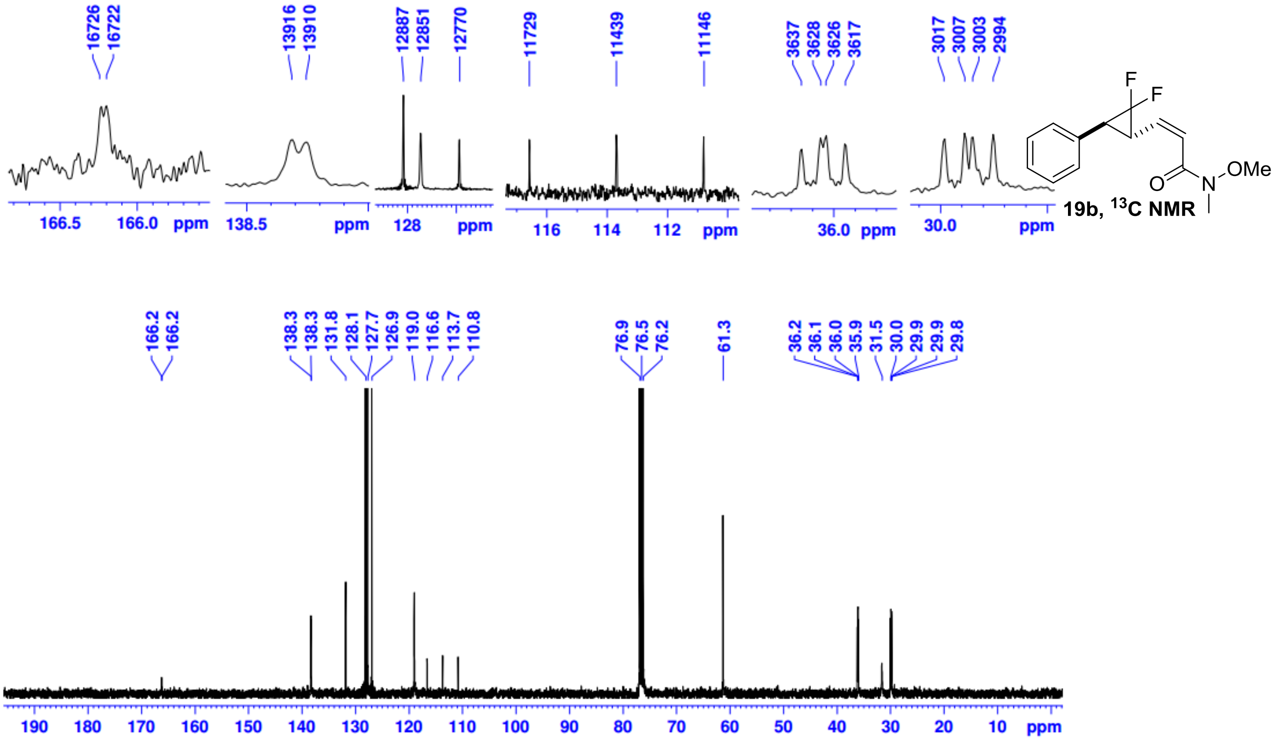


19a, NOESY

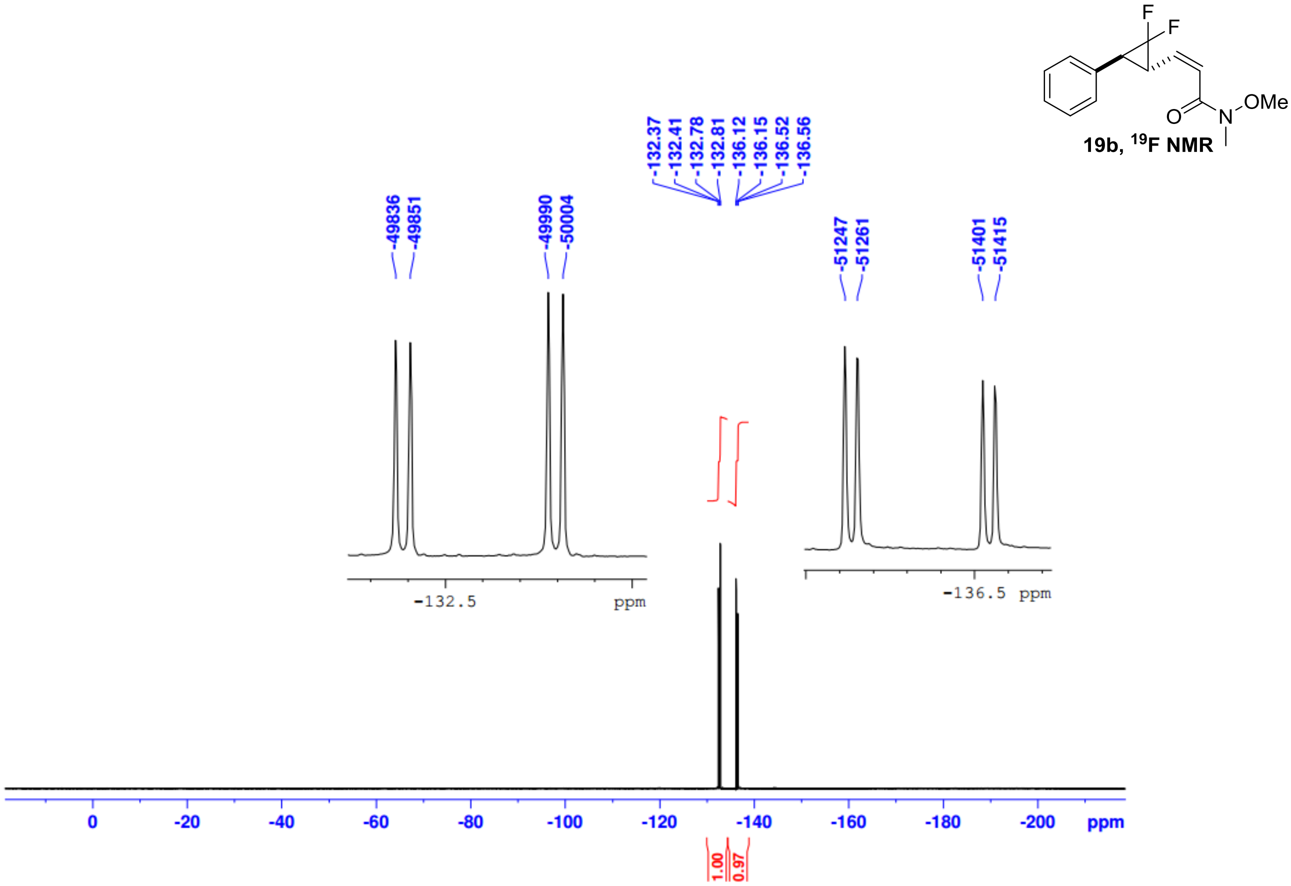


19b, ^{1}H NMR

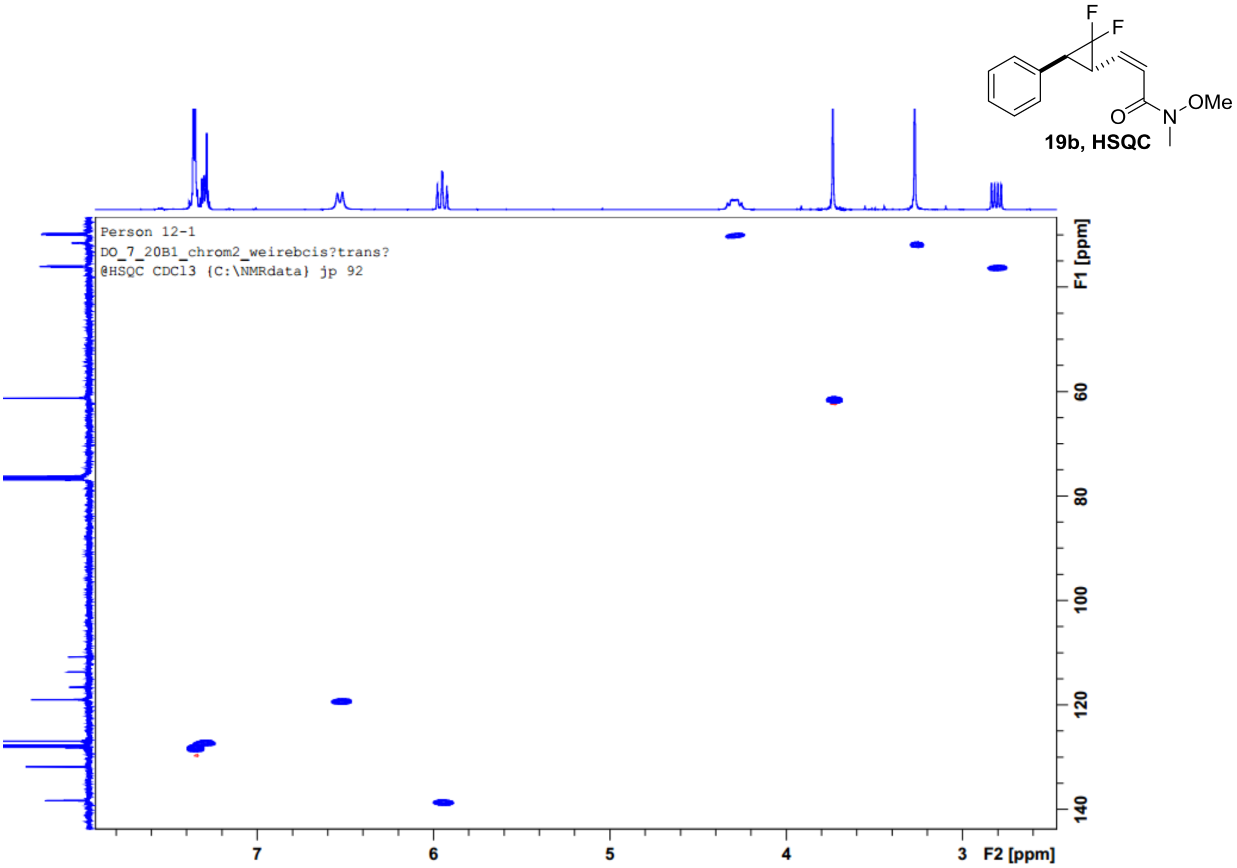


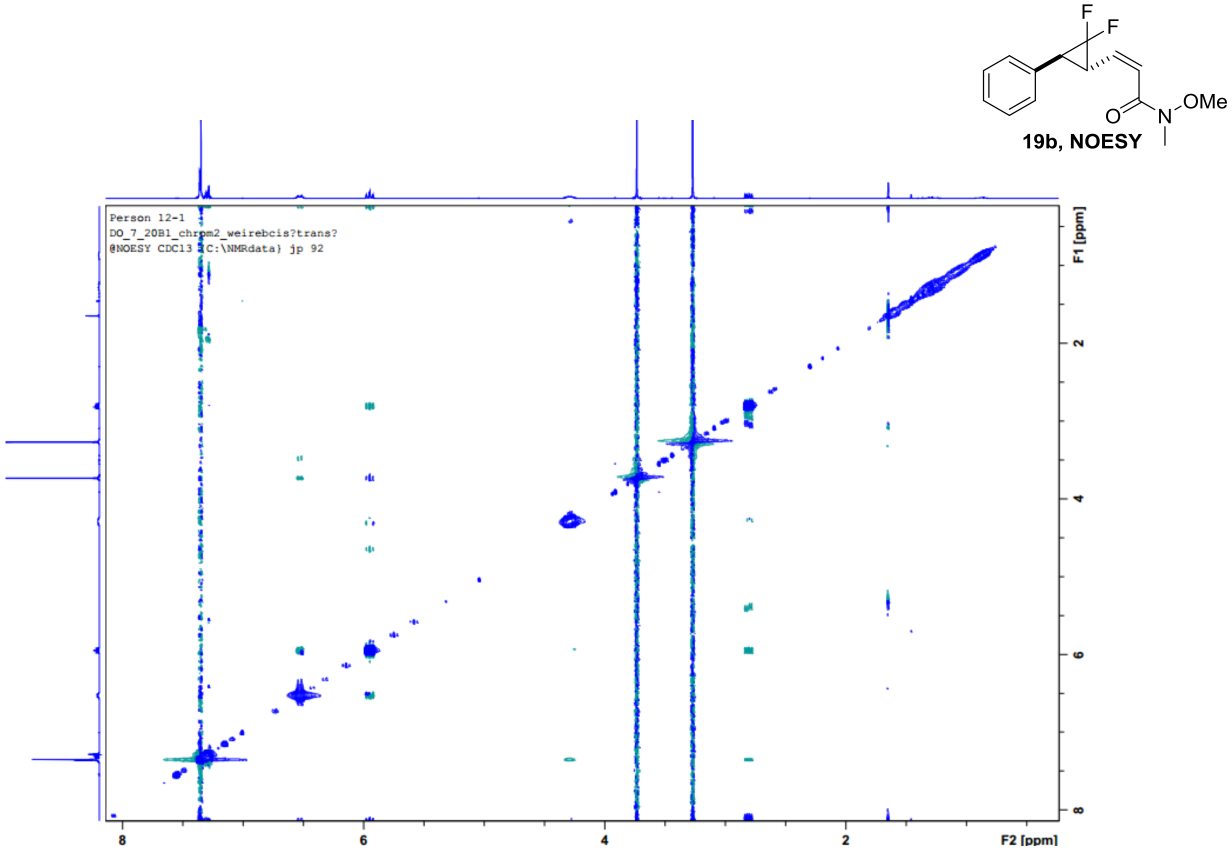


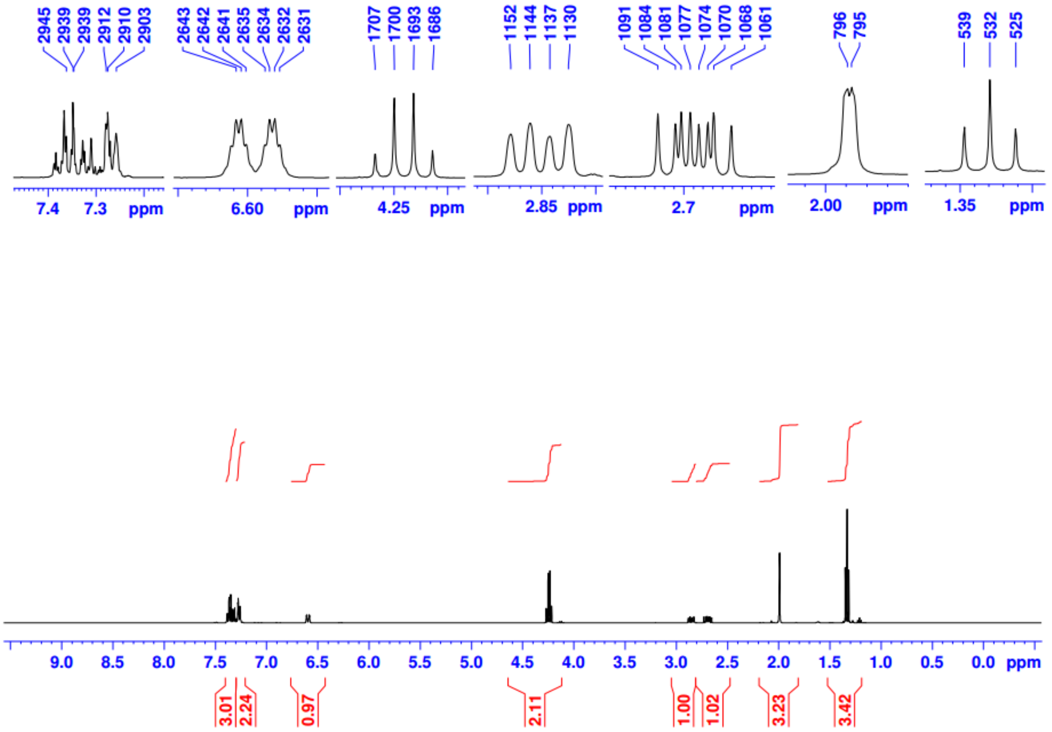
19b, ^{13}C NMR

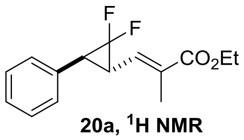


19b, ^{19}F NMR

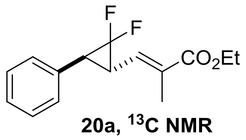

19b, HSQC


19b, NOESY

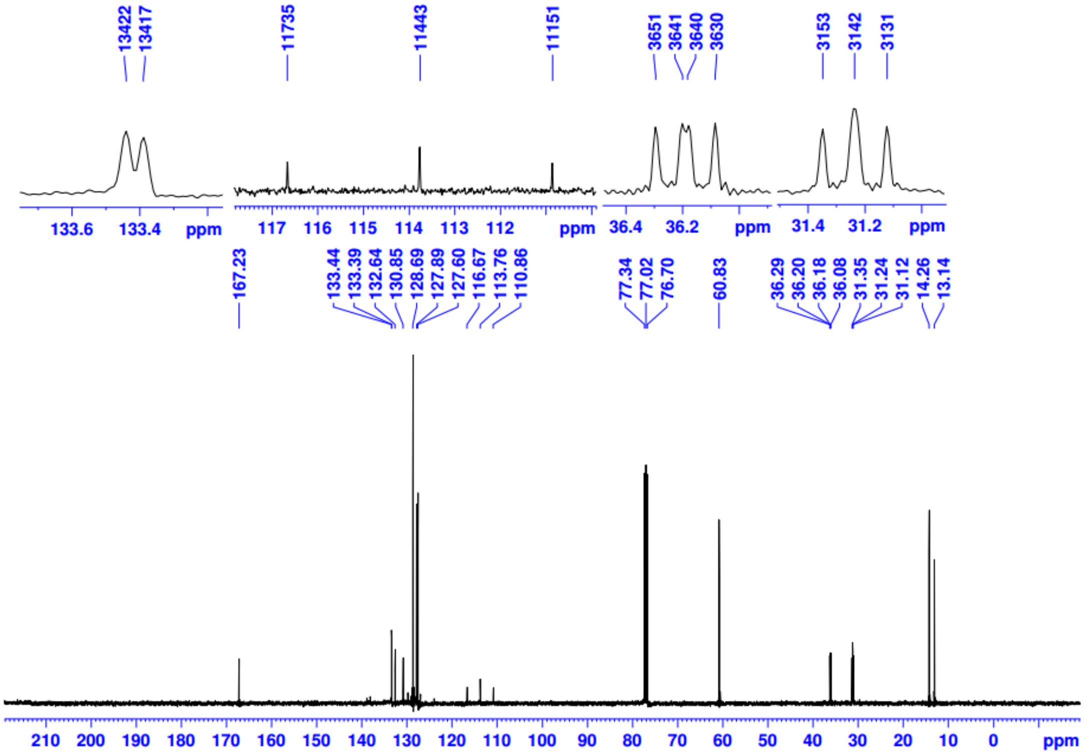


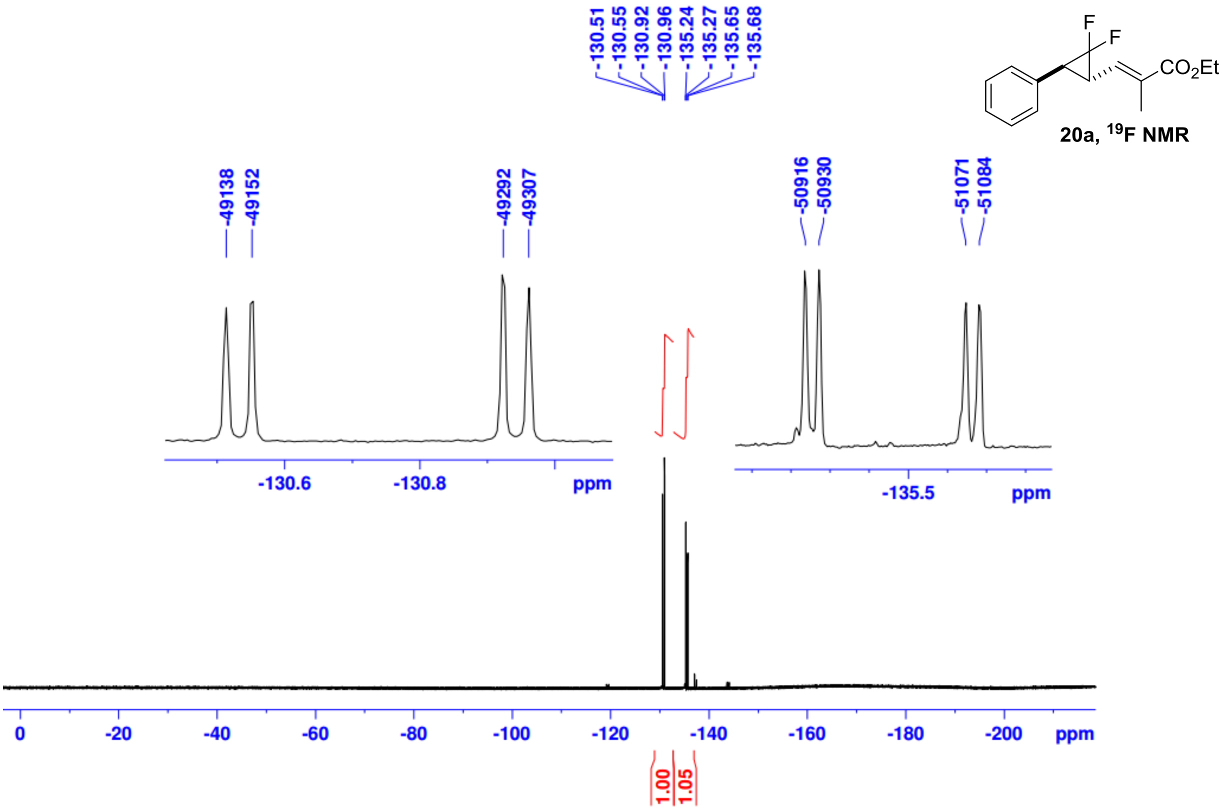


20a, ^1H NMR

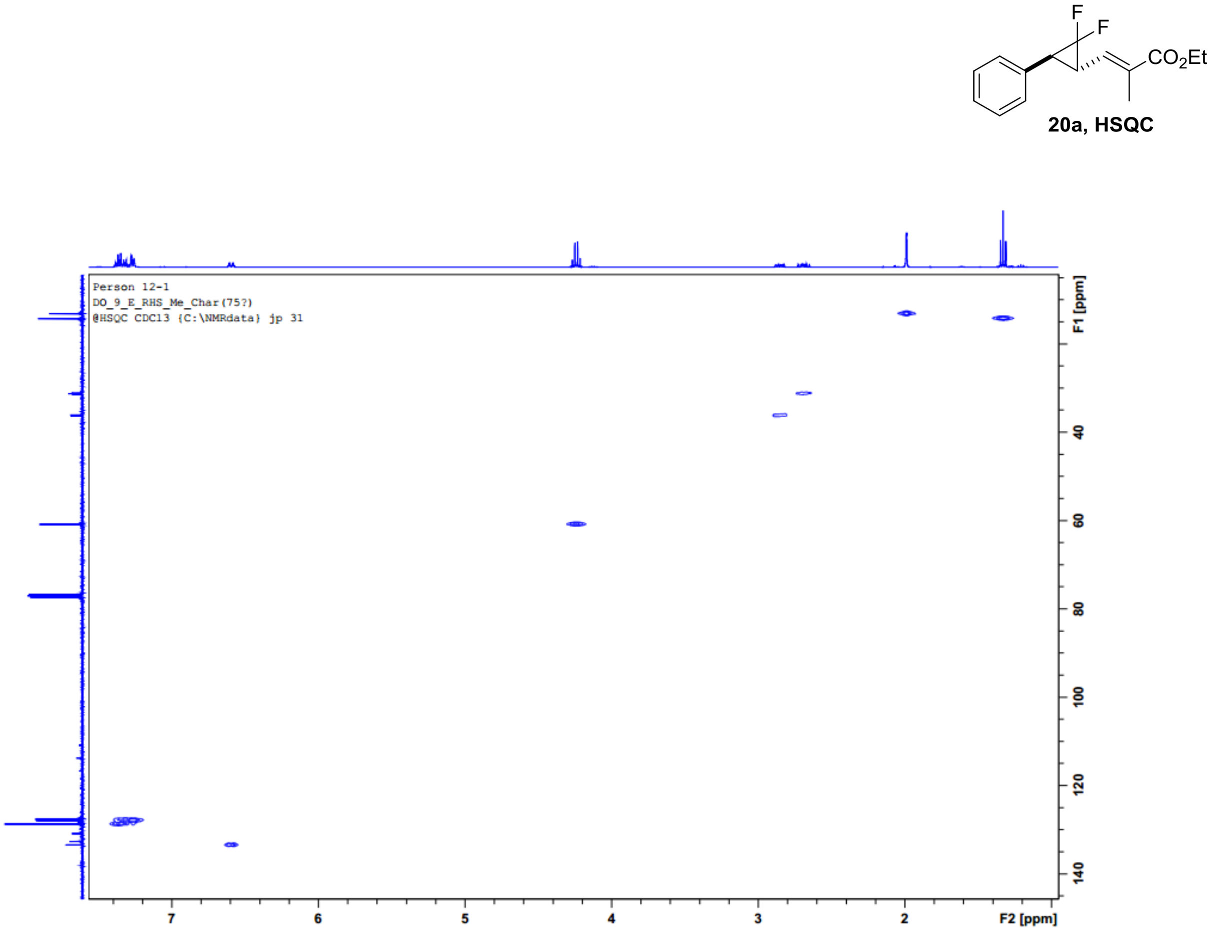


20a, ^{13}C NMR



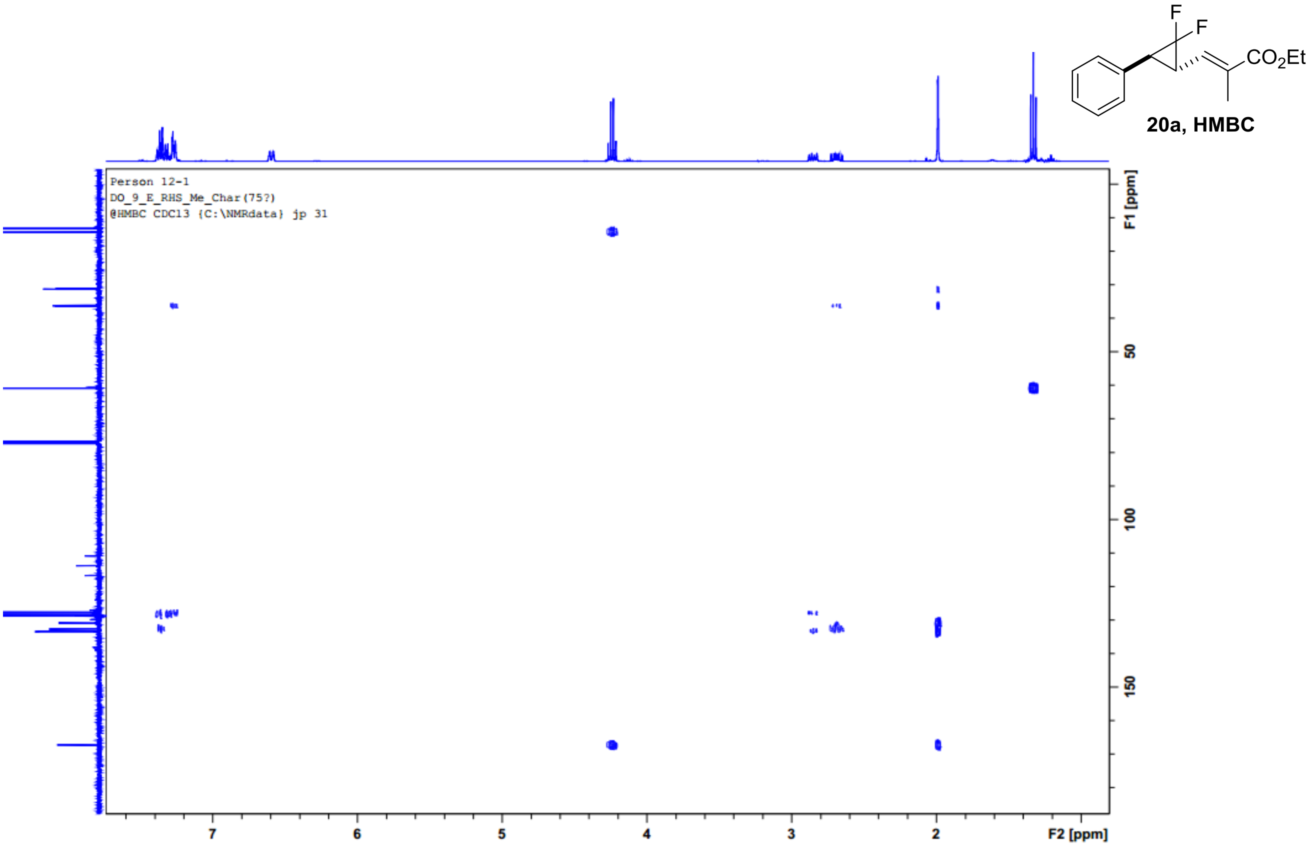


20a, ^{19}F NMR

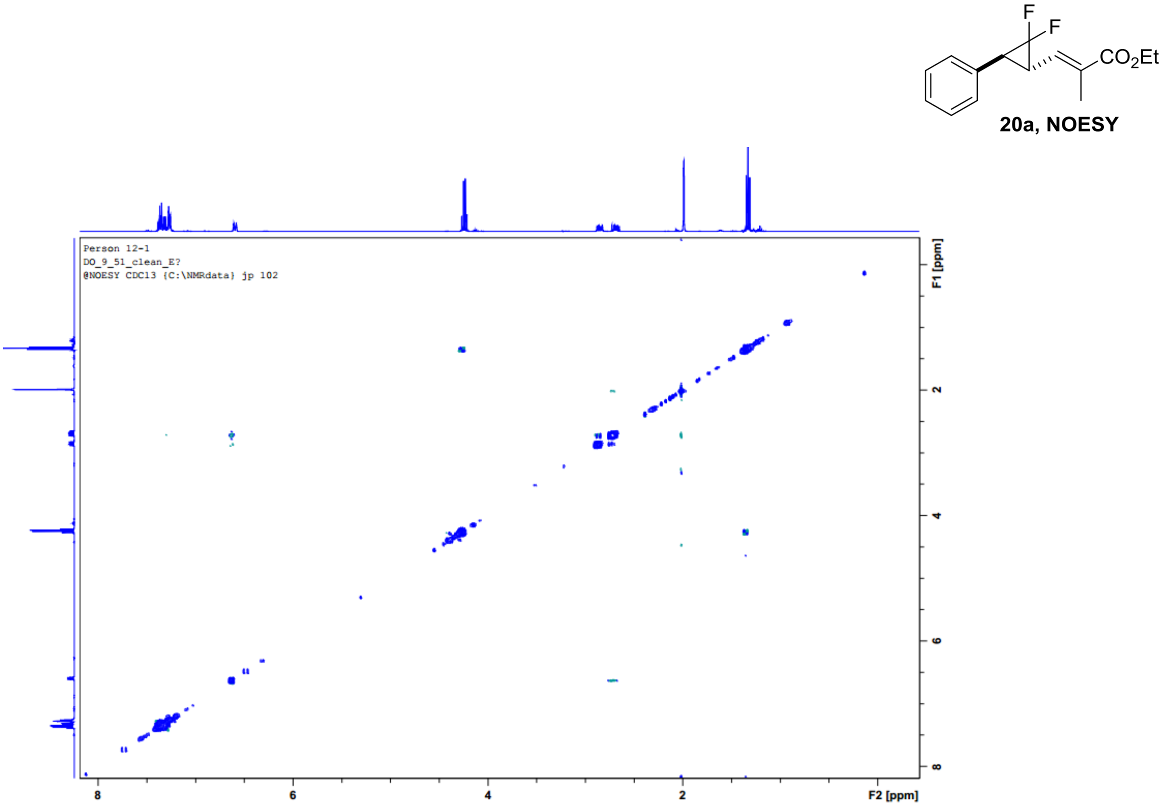


20a, HSQC

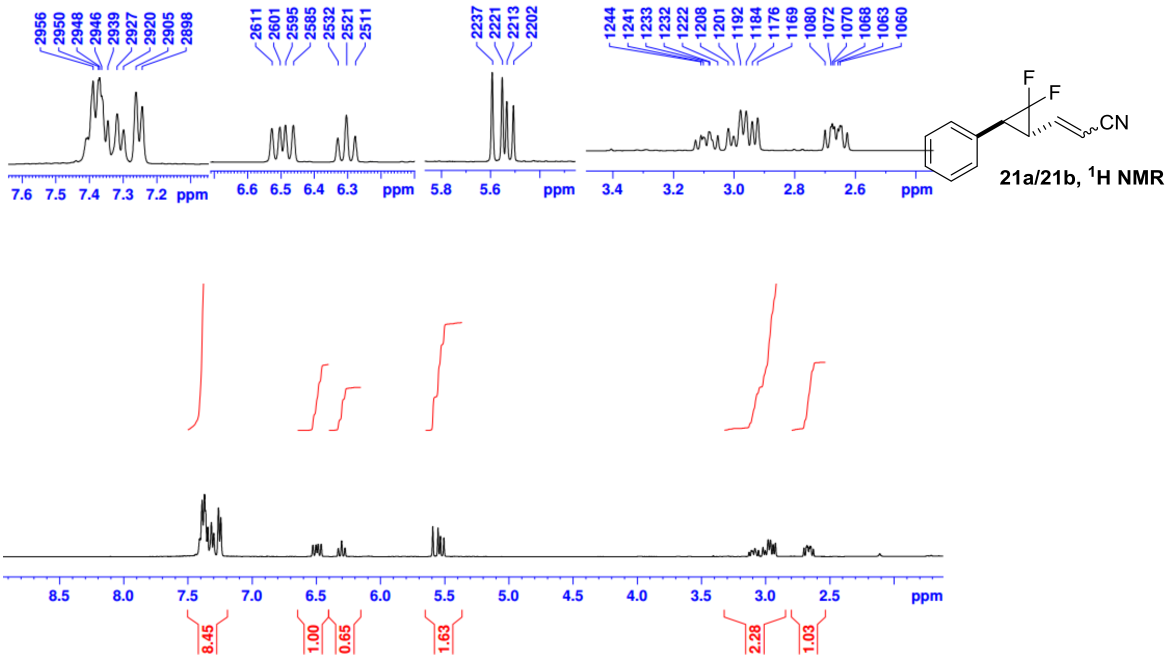
C



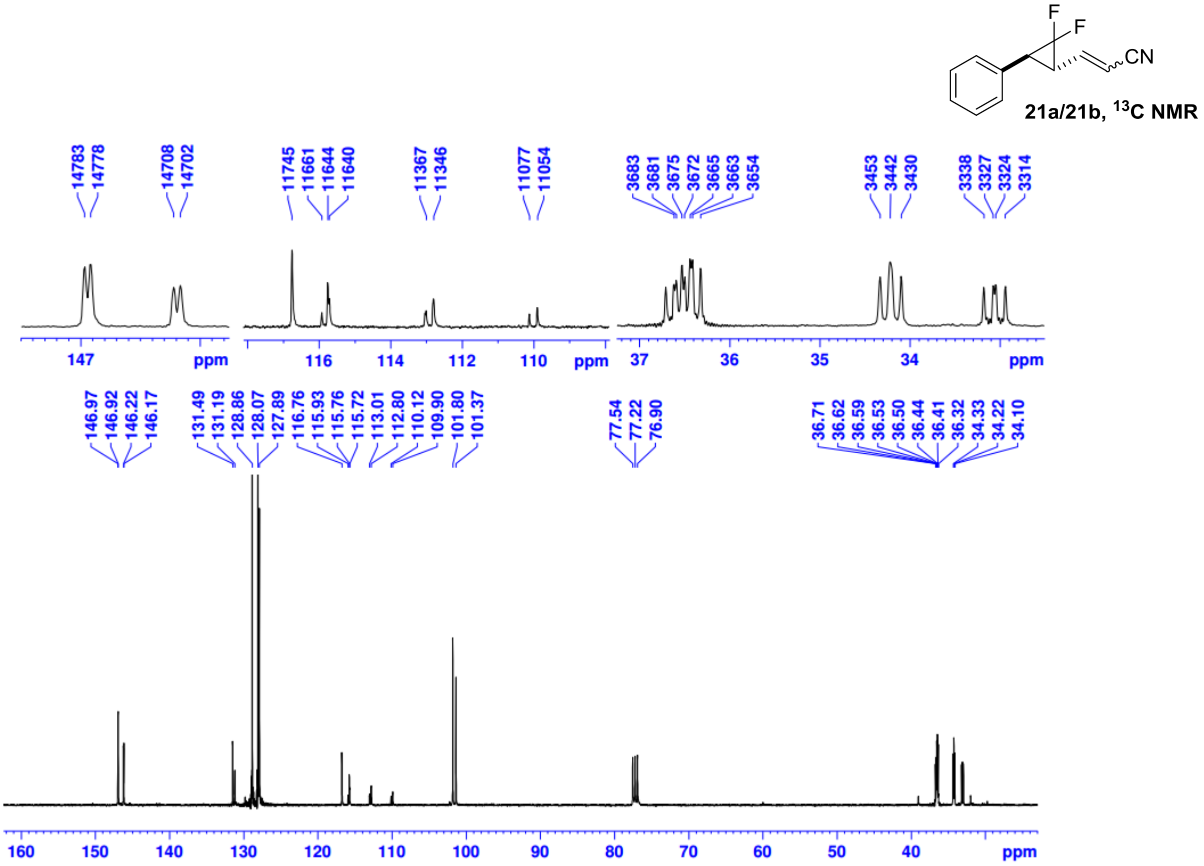
20a, HMBC



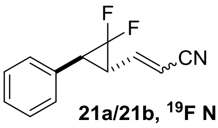
20a, NOESY



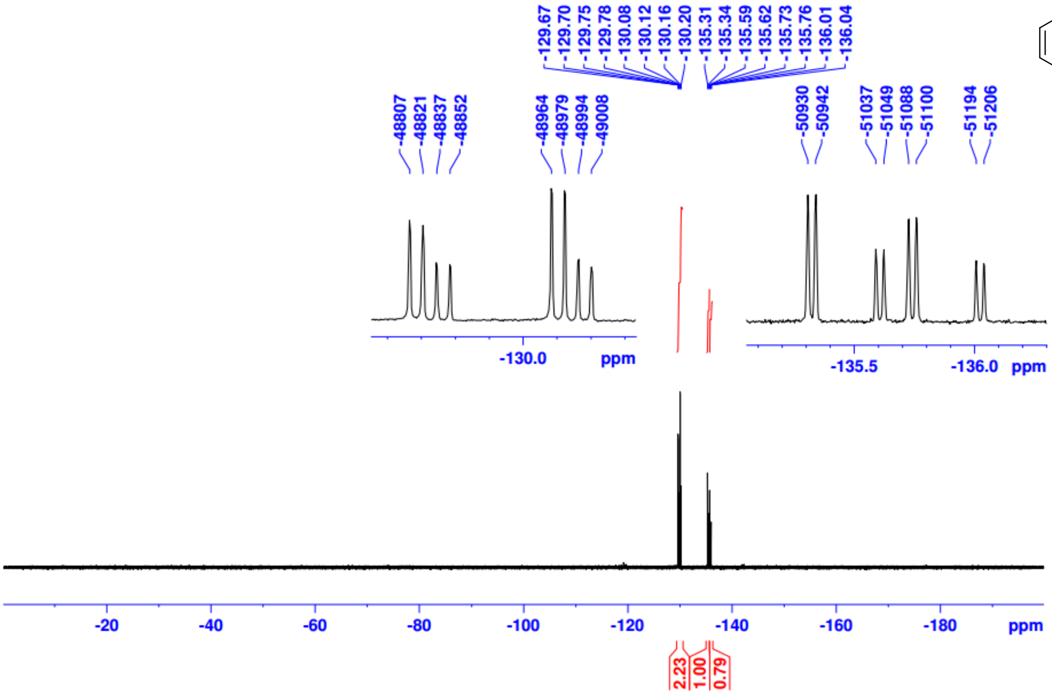
21a/21b, ^{1}H NMR

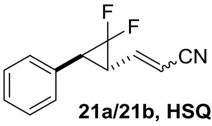


21a/21b, ^{13}C NMR

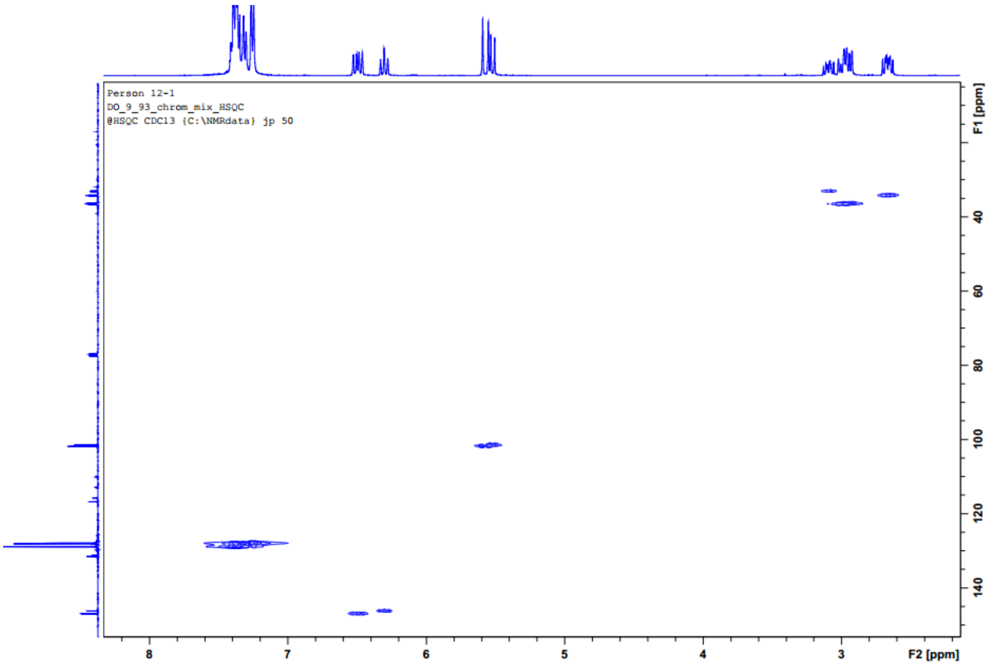


21a/21b, ^{19}F NMR





21a/21b, HSQC



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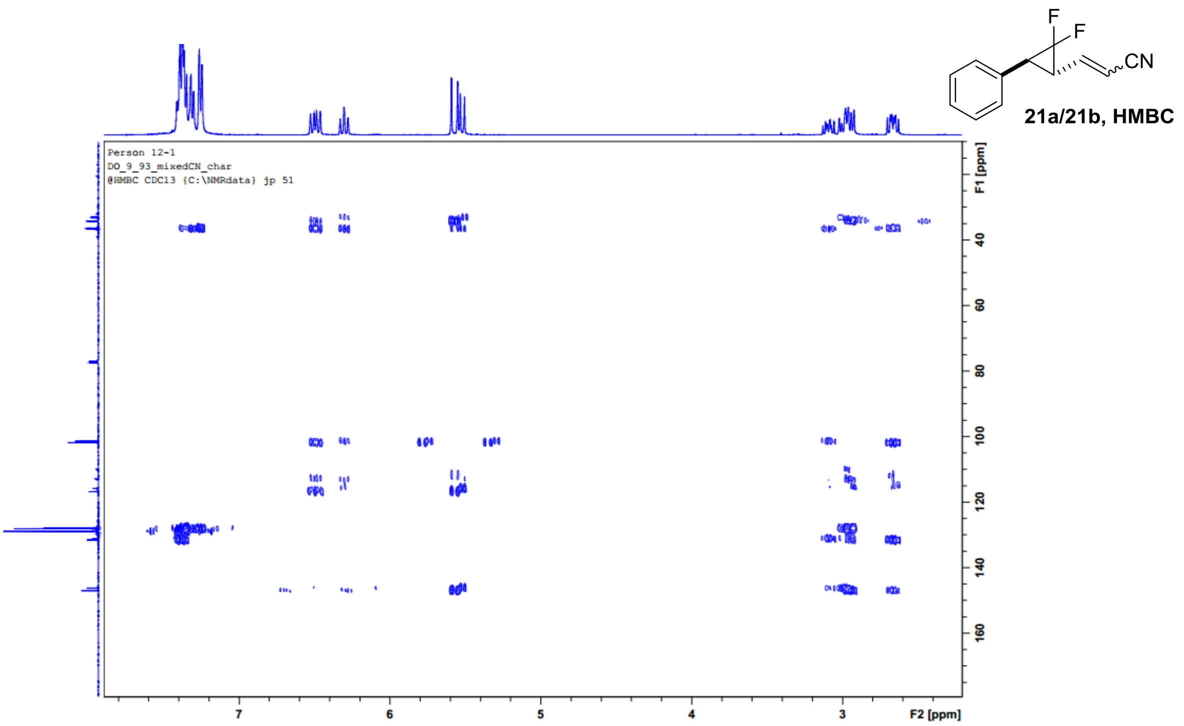
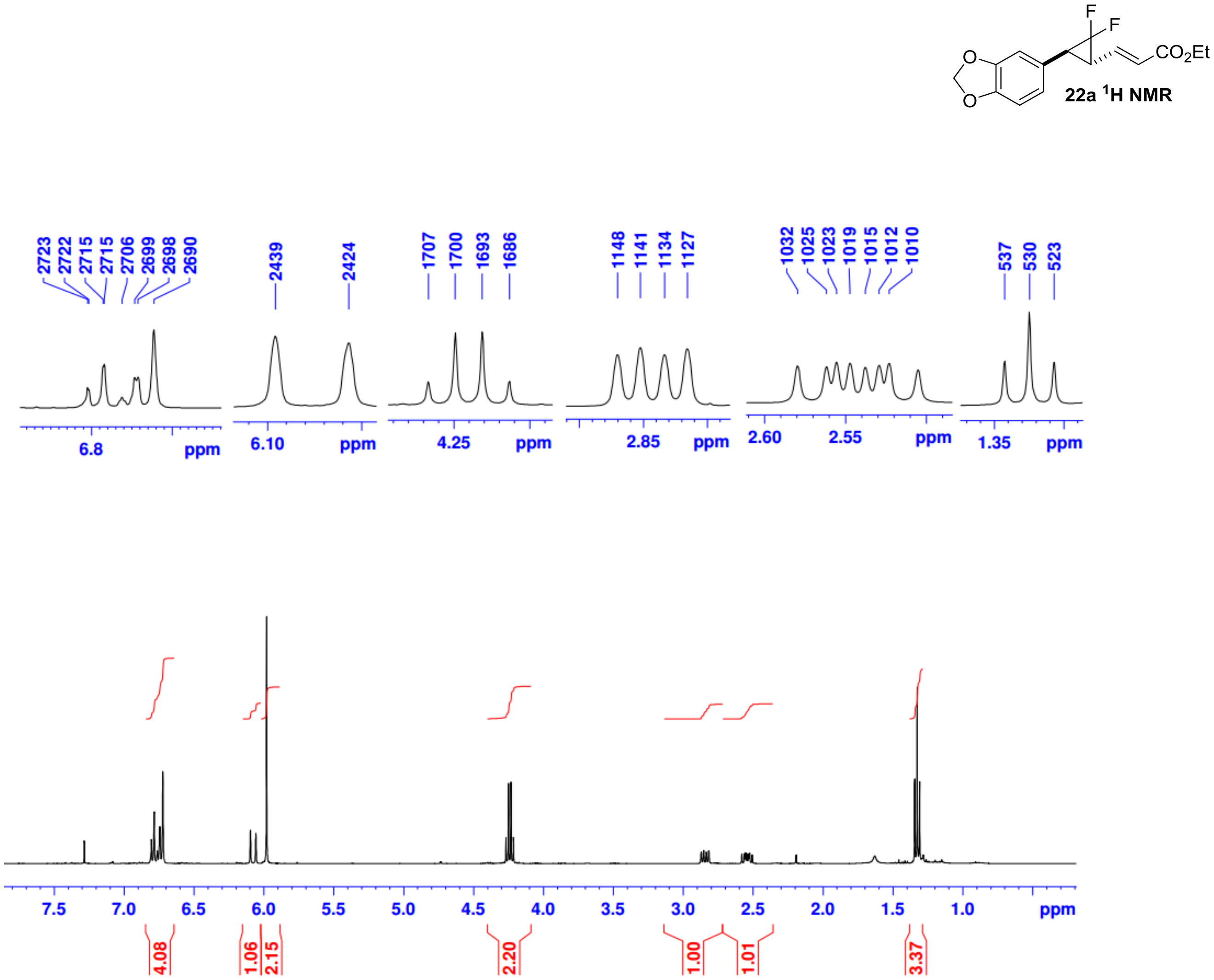
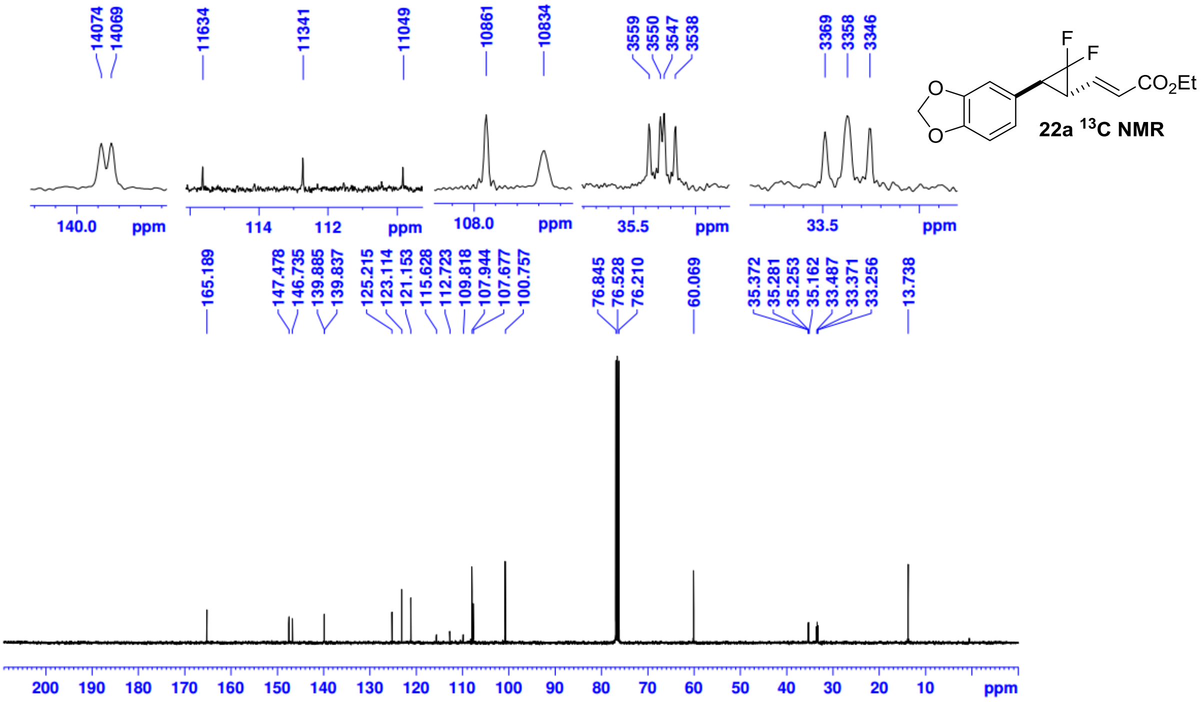


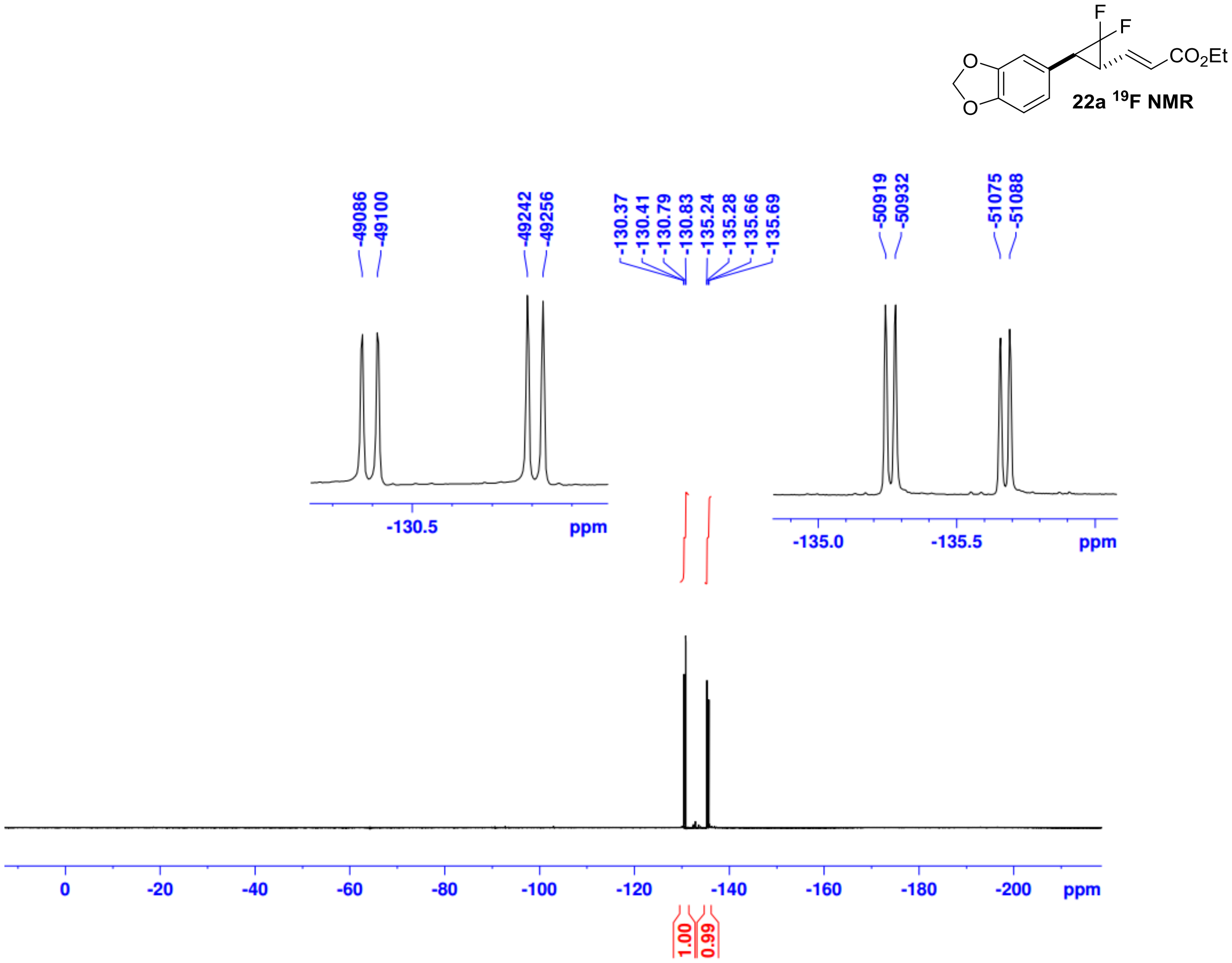
21a/21b, HMBC



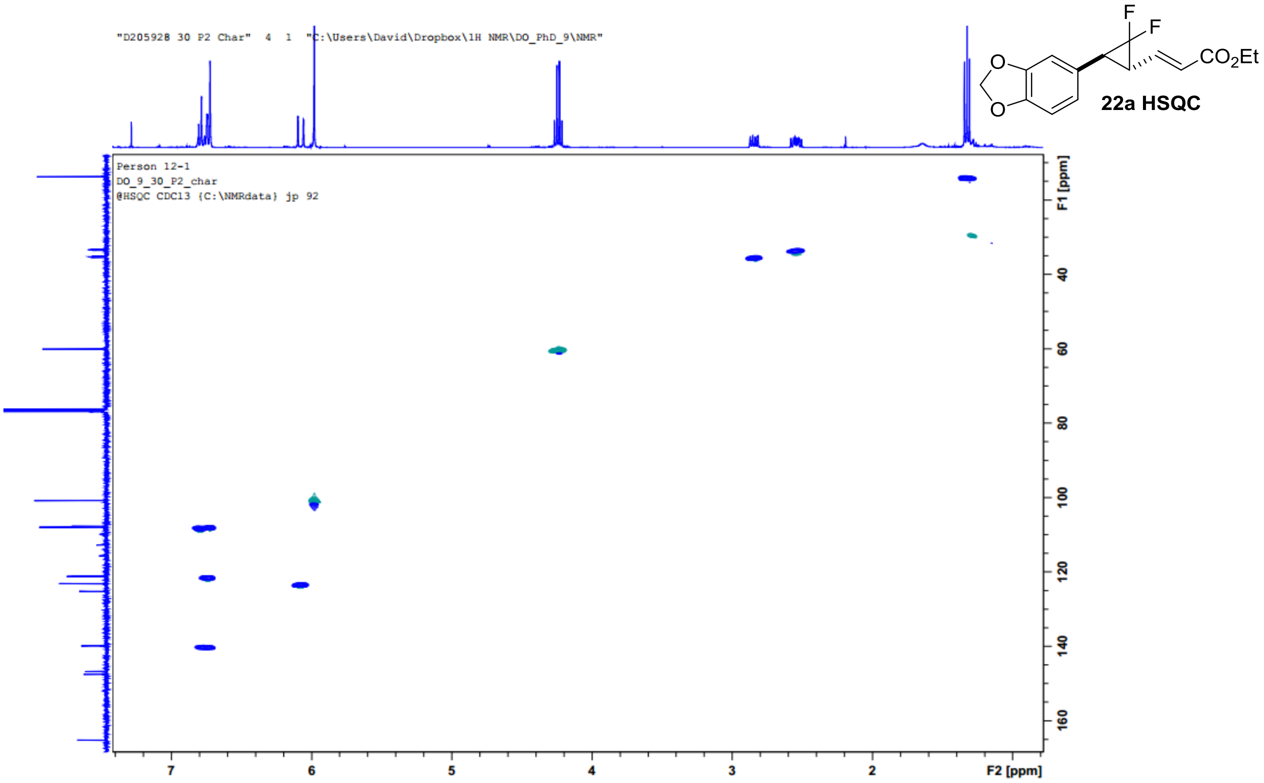
22a ^{1}H NMR



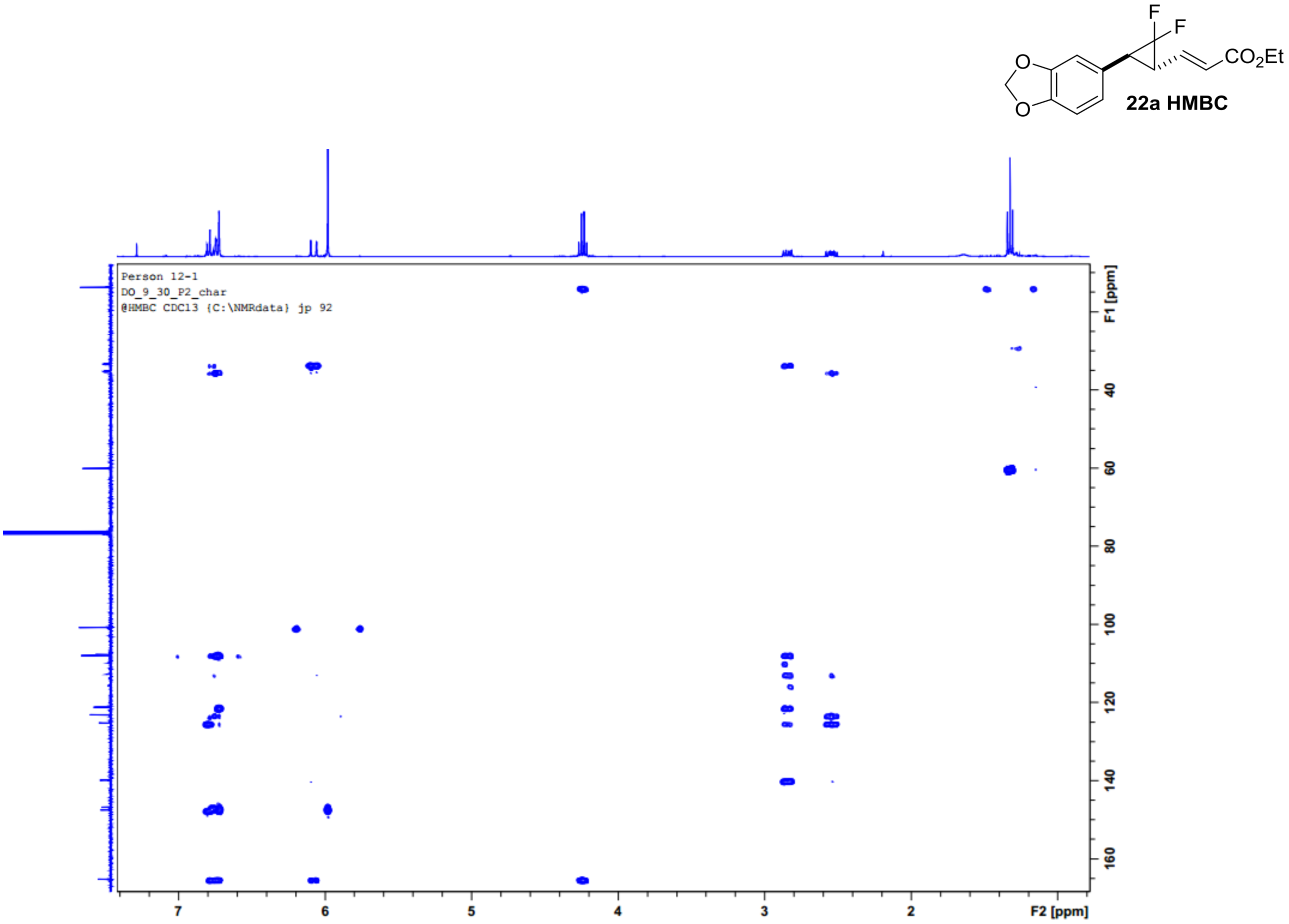
22a ^{13}C NMR



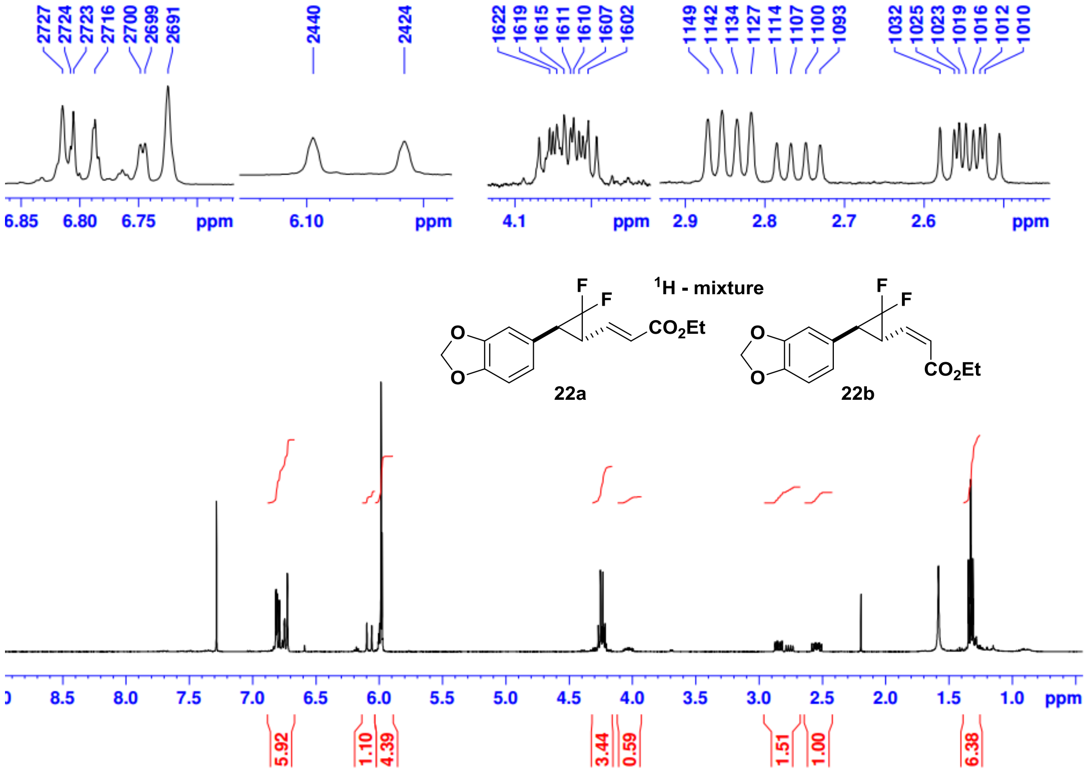
22a ^{19}F NMR



22a HSQC



22a HMBC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1023
1019
1016
1012
1010
6.85
6.80
6.75
ppm
6.10
ppm
4.1
ppm
2.9
2.8
2.7
2.6
ppm
^{1}H - mixture
F
F
O
O
CO_2Et
22a
F
F
O
O
CO_2Et
22b
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
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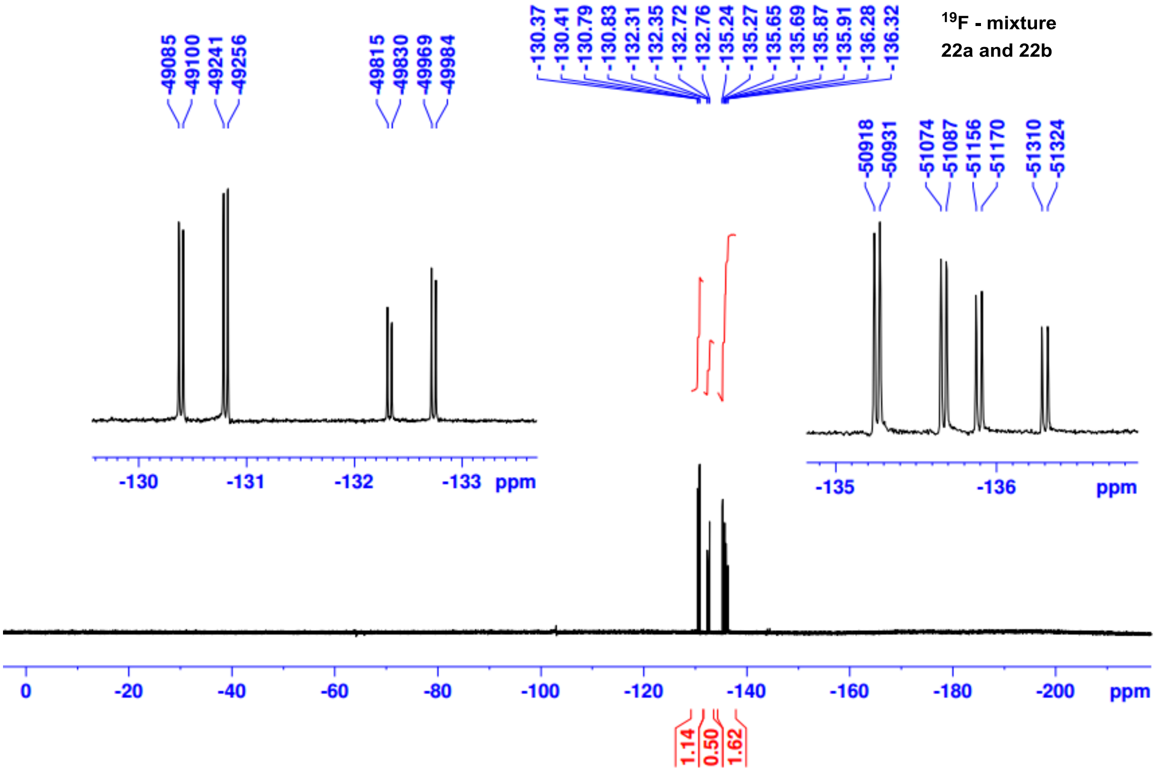
^{19}F - mixture
22a and 22b
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-135.27
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-132
-133
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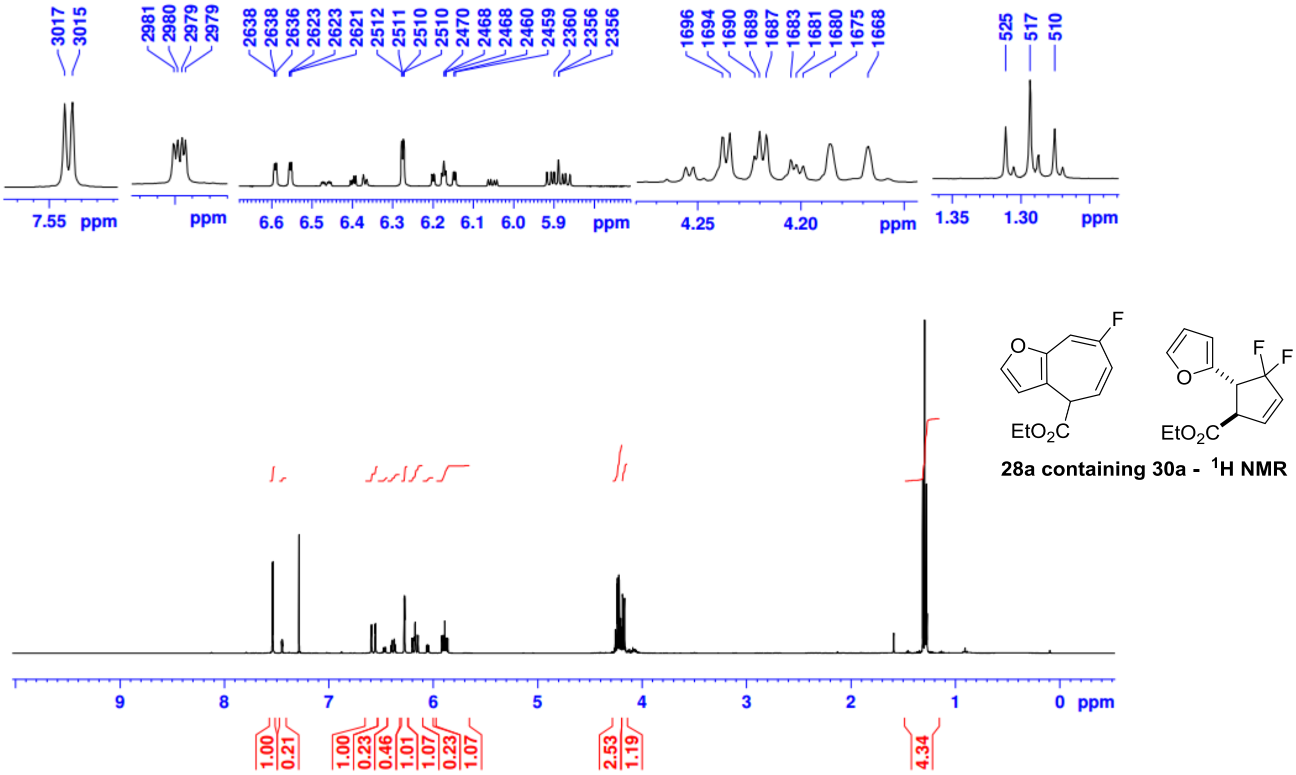
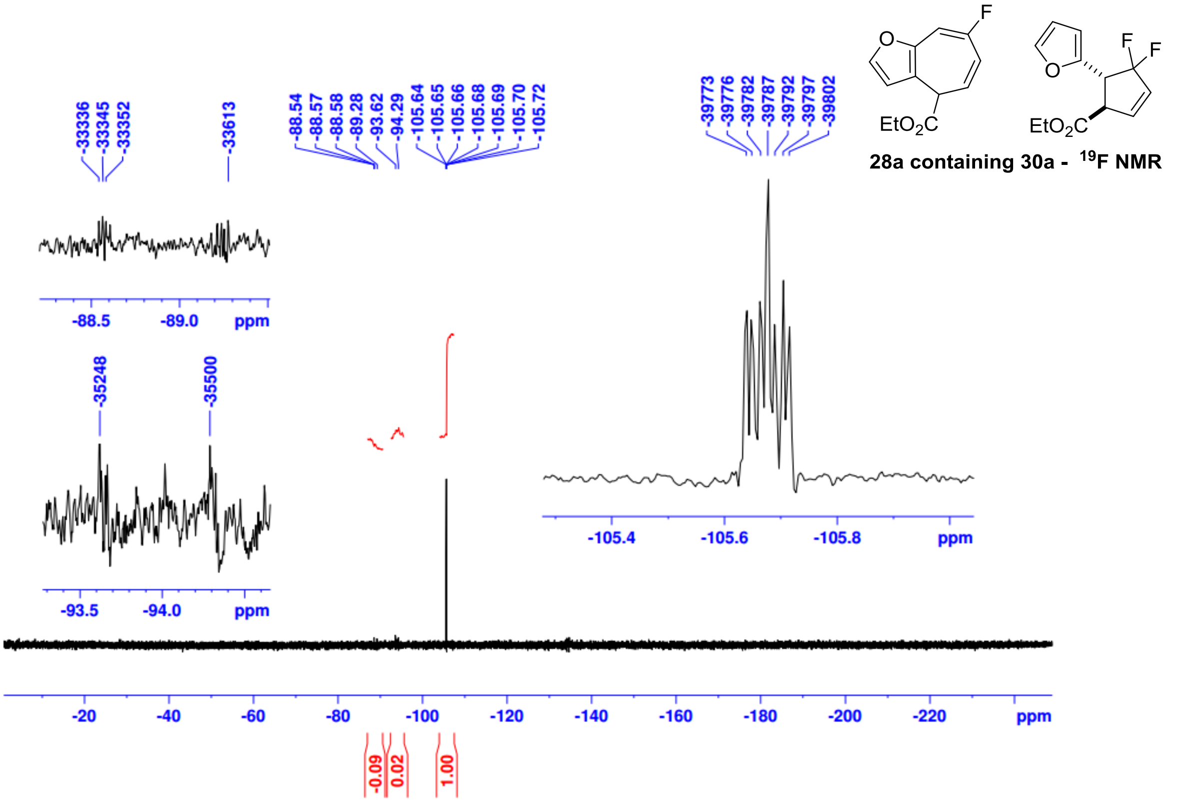
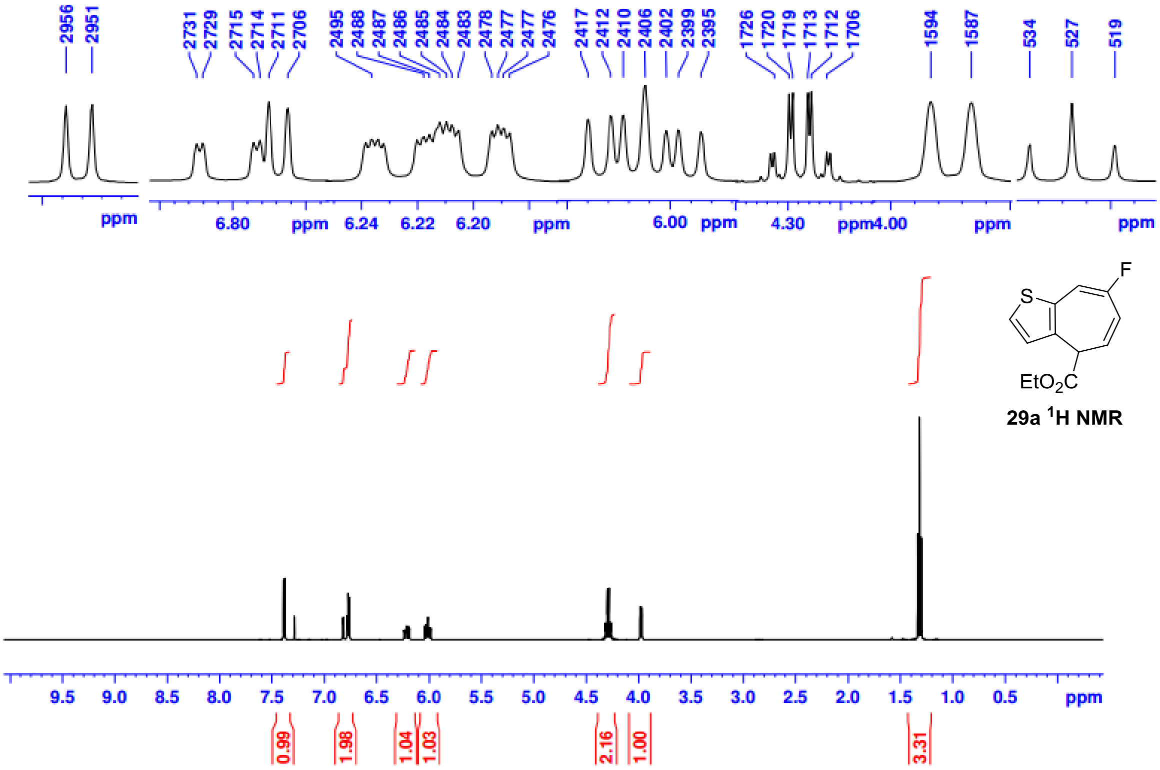
1.62



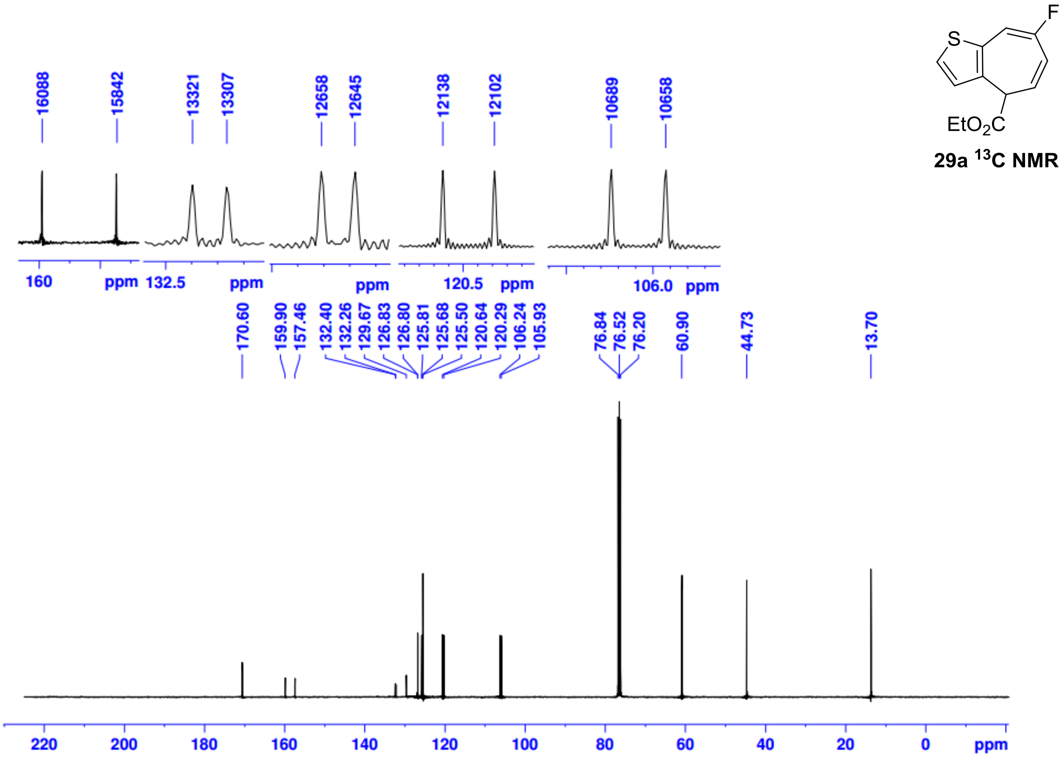
28a containing 30a - ^{1}H NMR



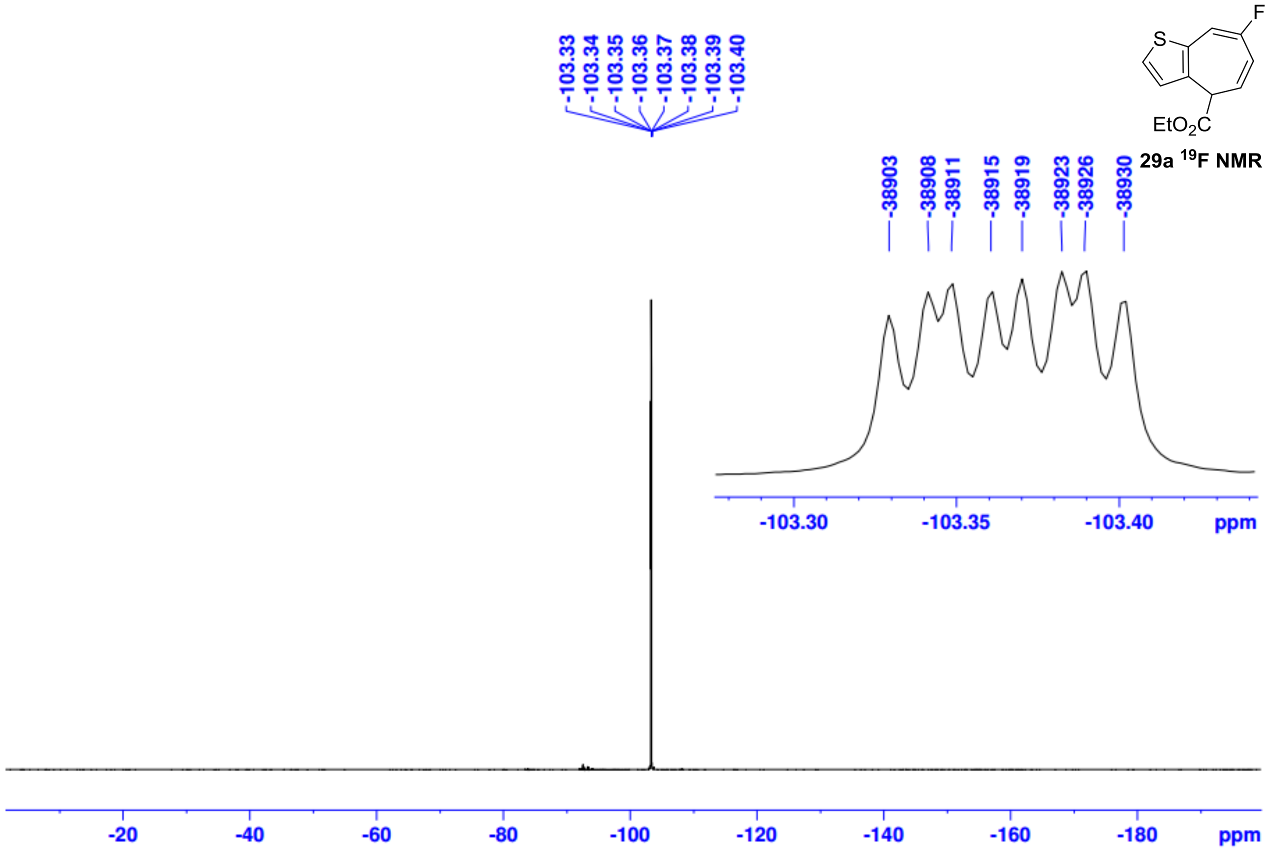
28a containing 30a - ^{19}F NMR



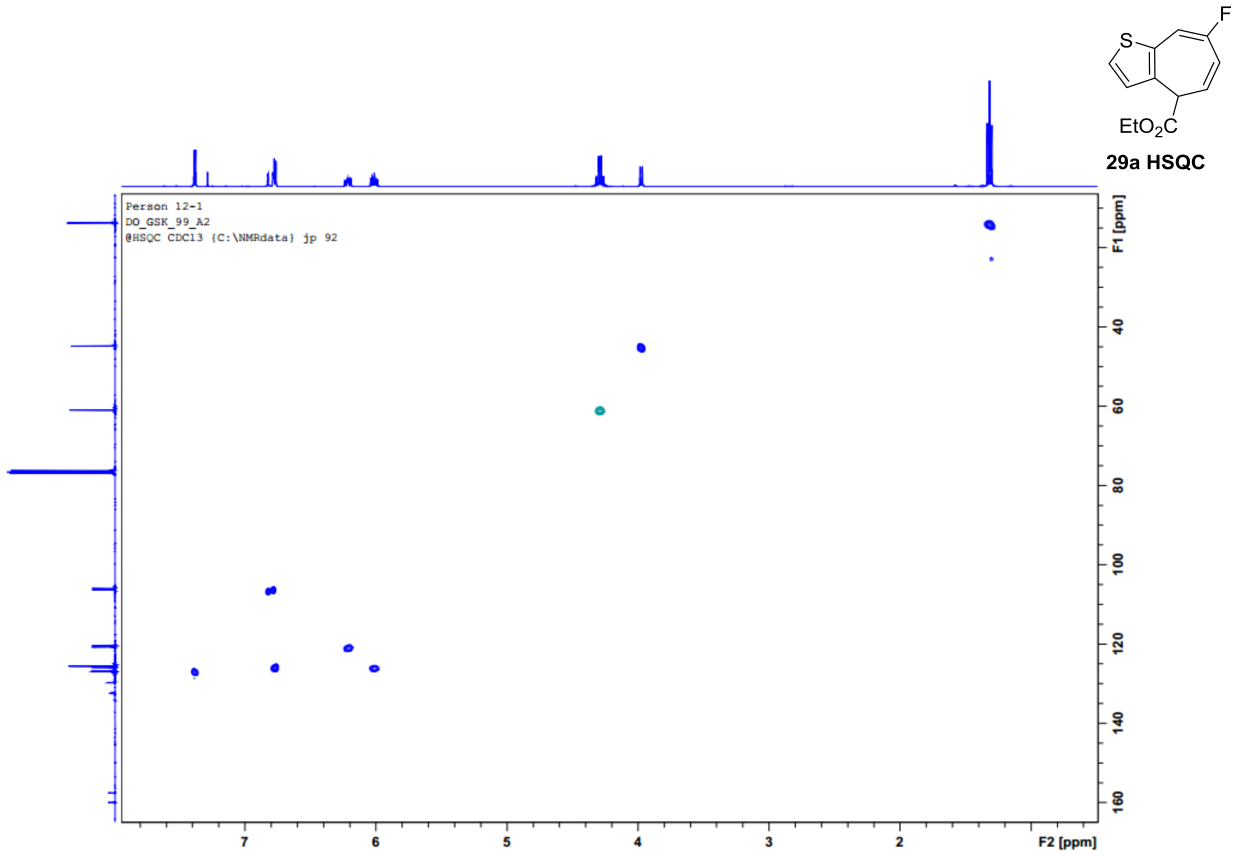
29a ^{1}H NMR



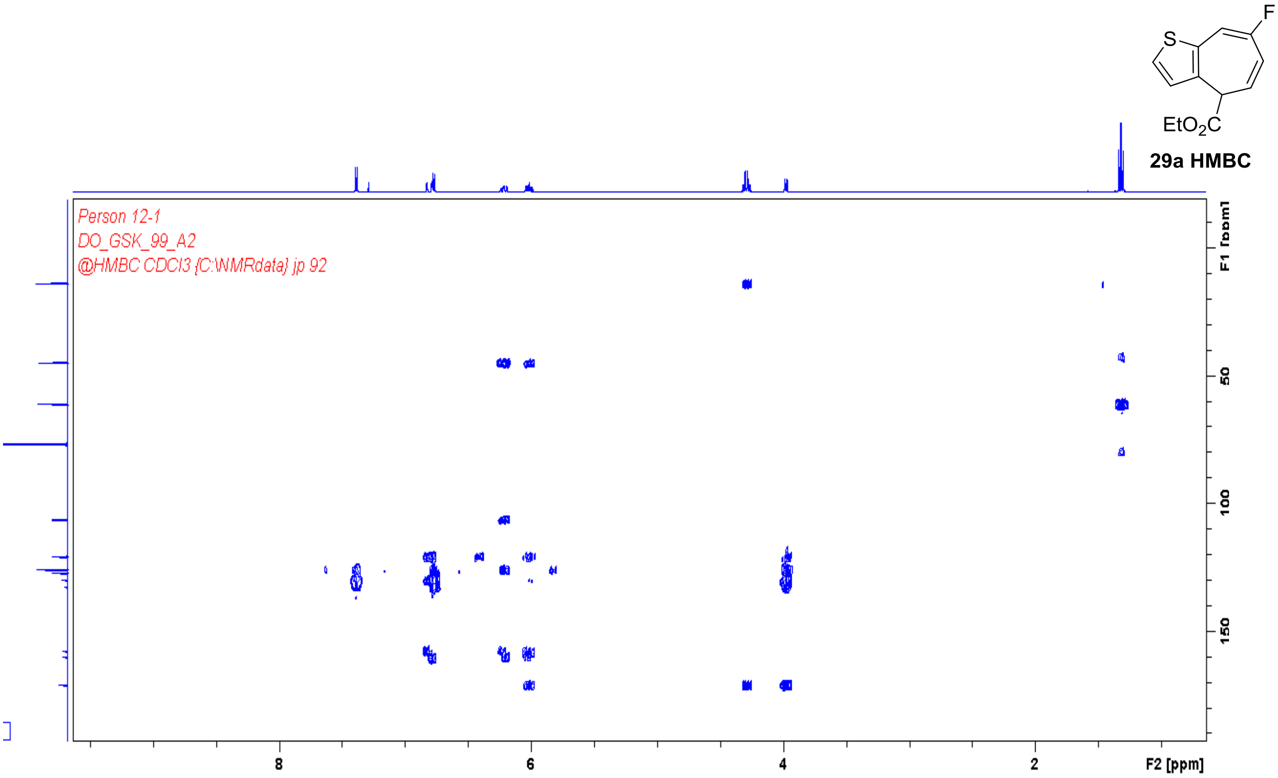
29a ^{13}C NMR



29a ^{19}F NMR

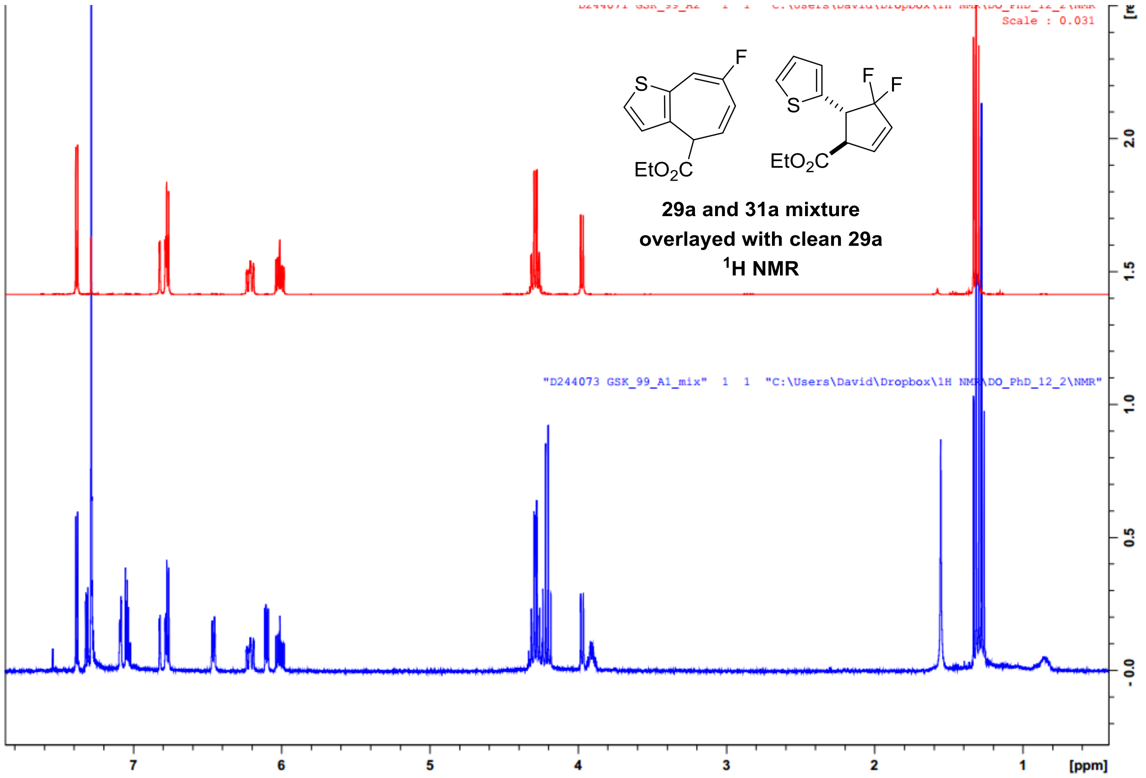


29a HSQC

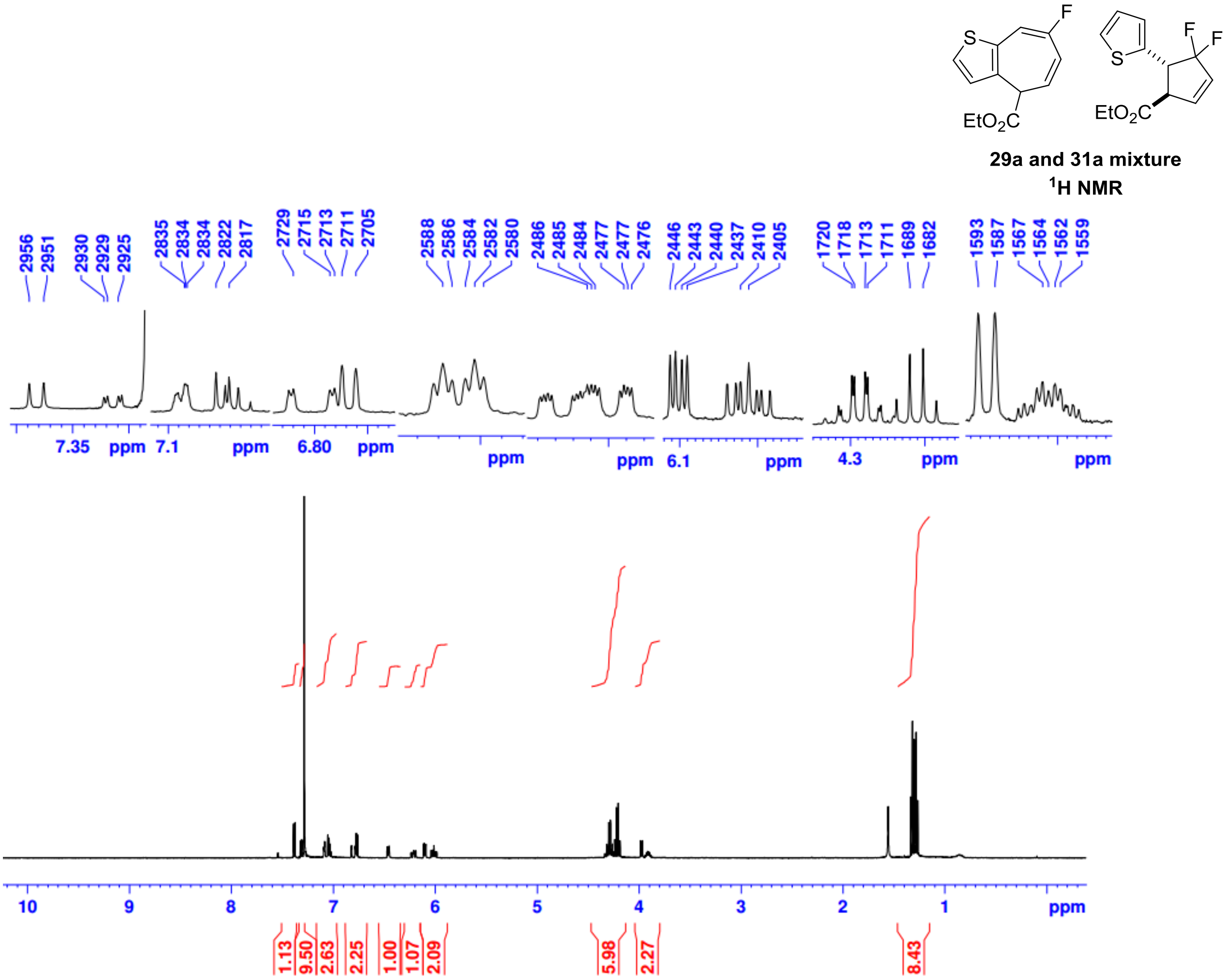


29a HMBC

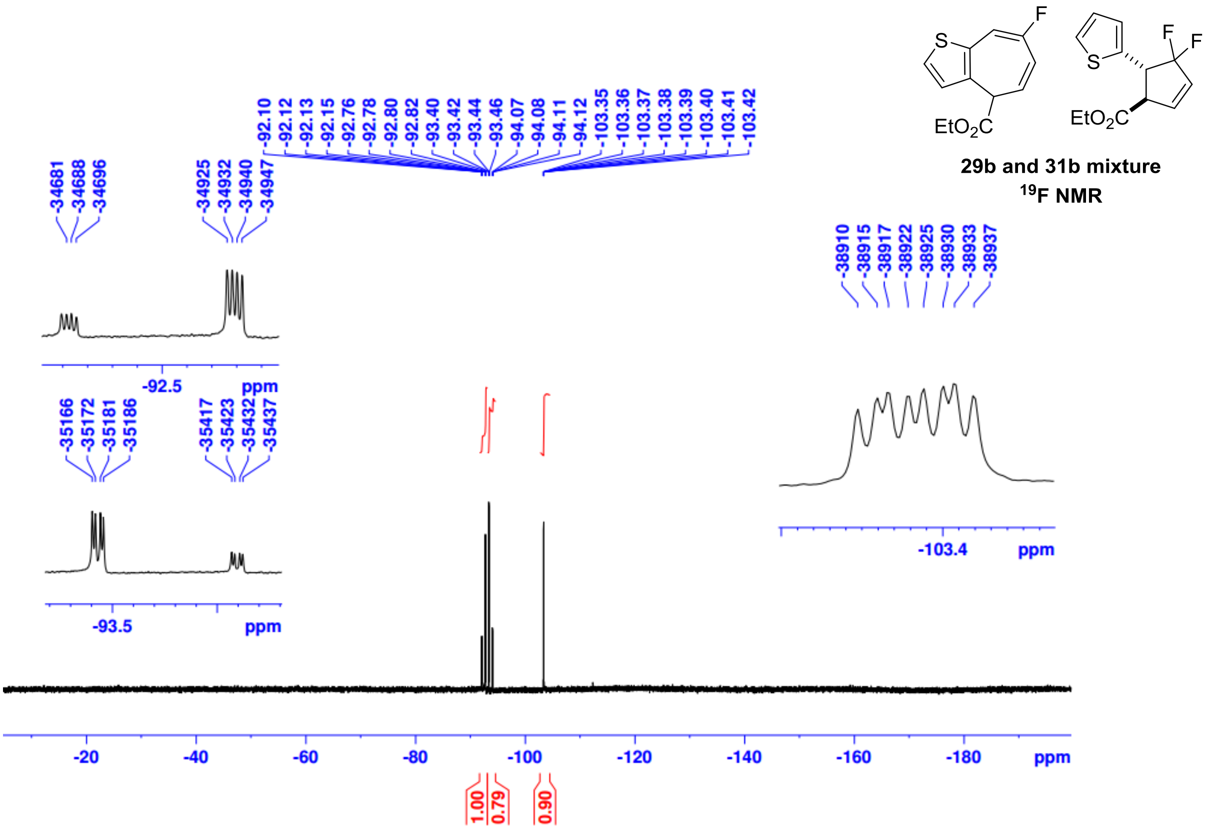
29a HMBC (expanded)

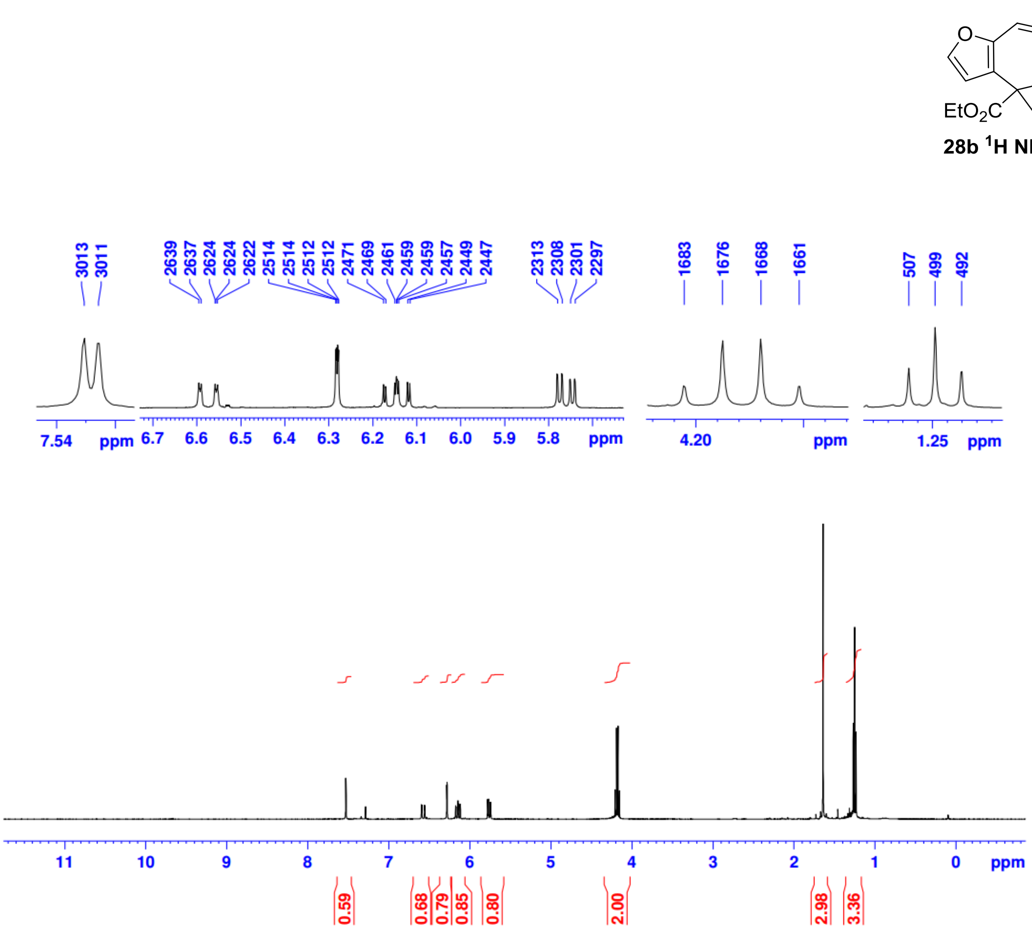


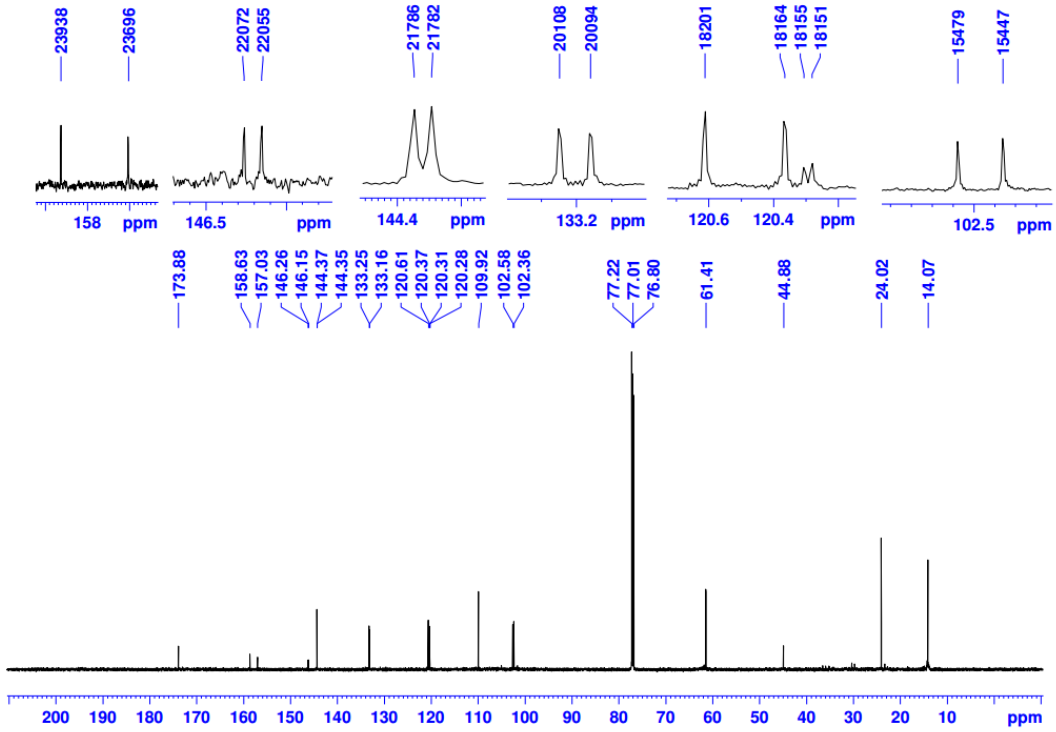
29a and 31a mixture overlayed with clean 29a ^{1}H NMR

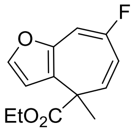


29a and 31a mixture ^{1}H NMR

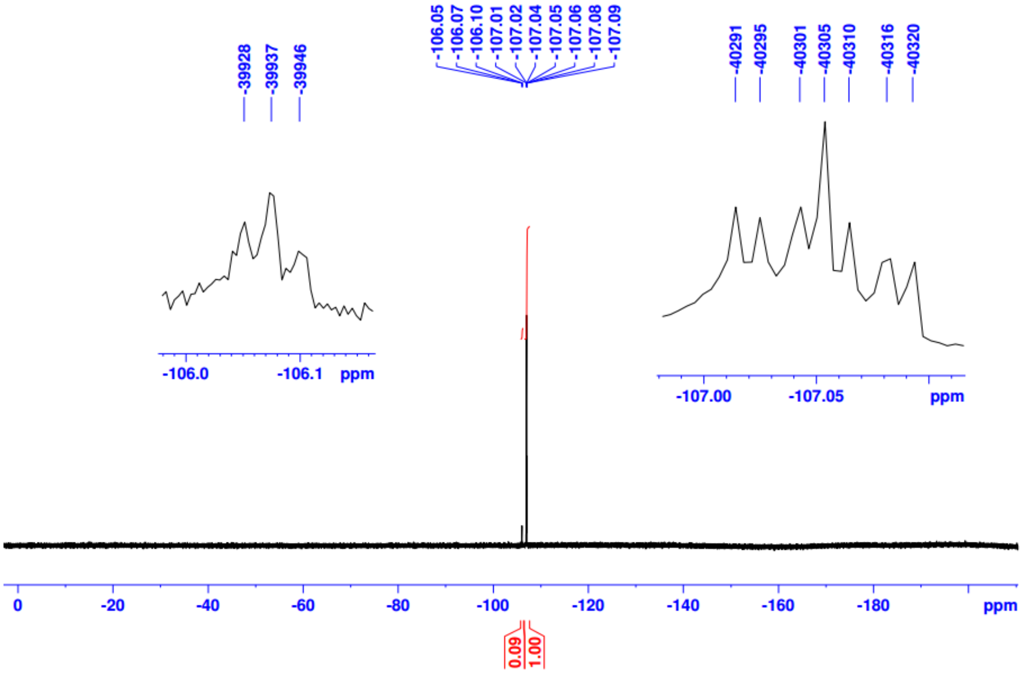

29b and 31b mixture
^{19}F NMR

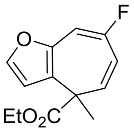

28b ^{1}H NMR



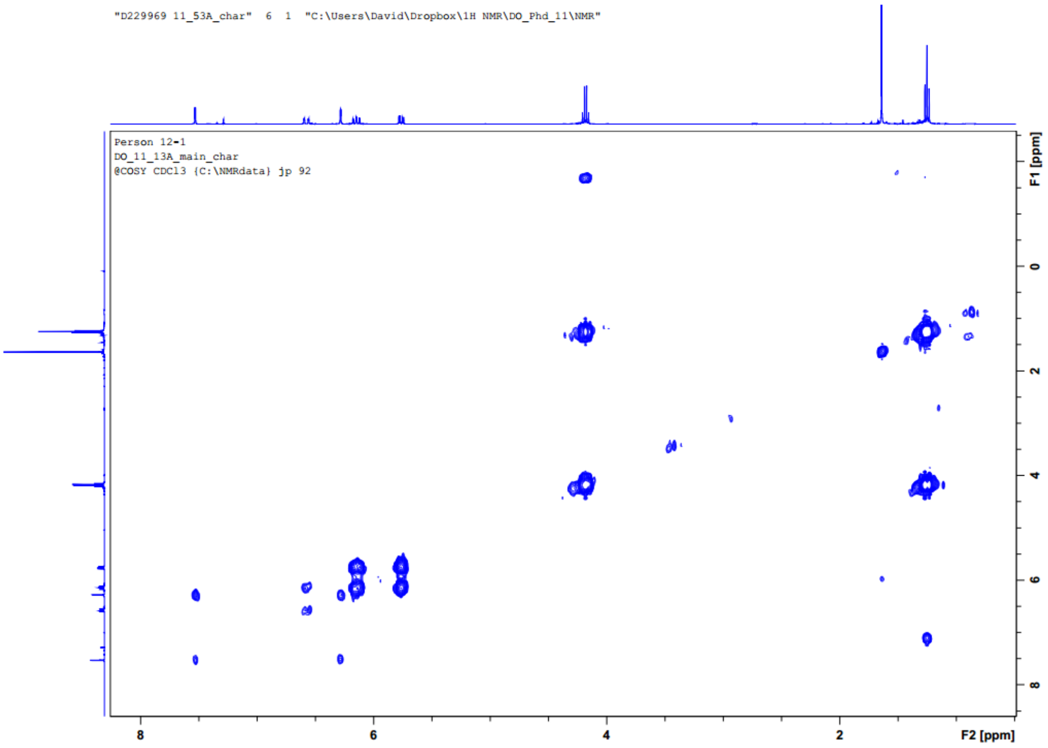


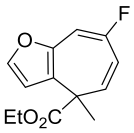
28b ^{13}C NMR



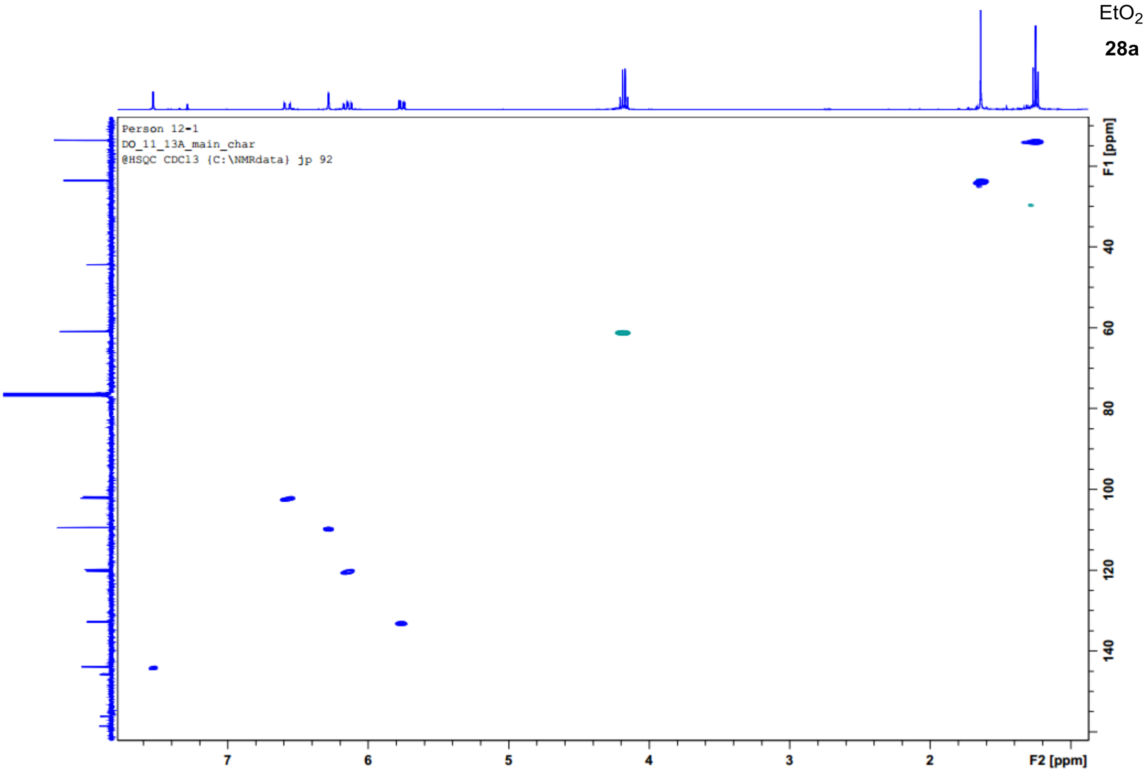


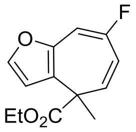
28b ^{19}F NMR



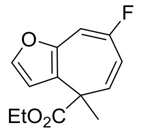


28a COSY

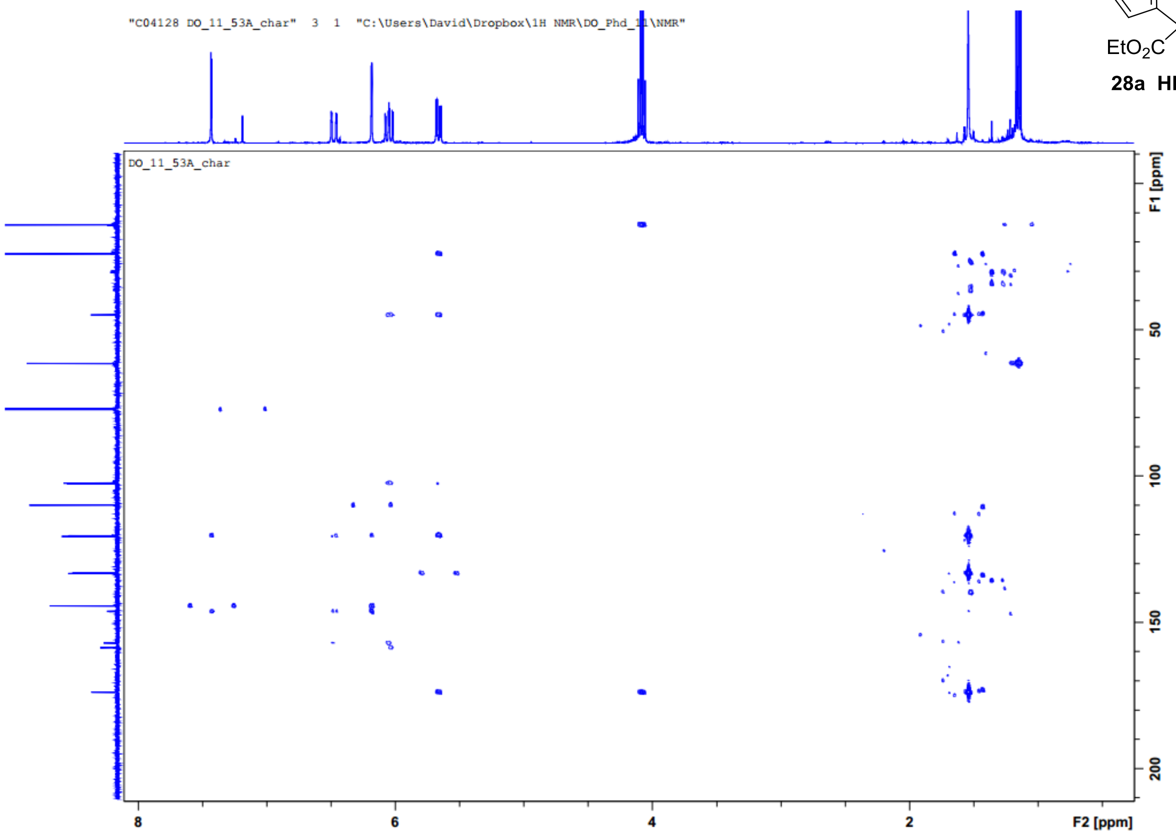


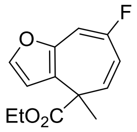


28a HSQC

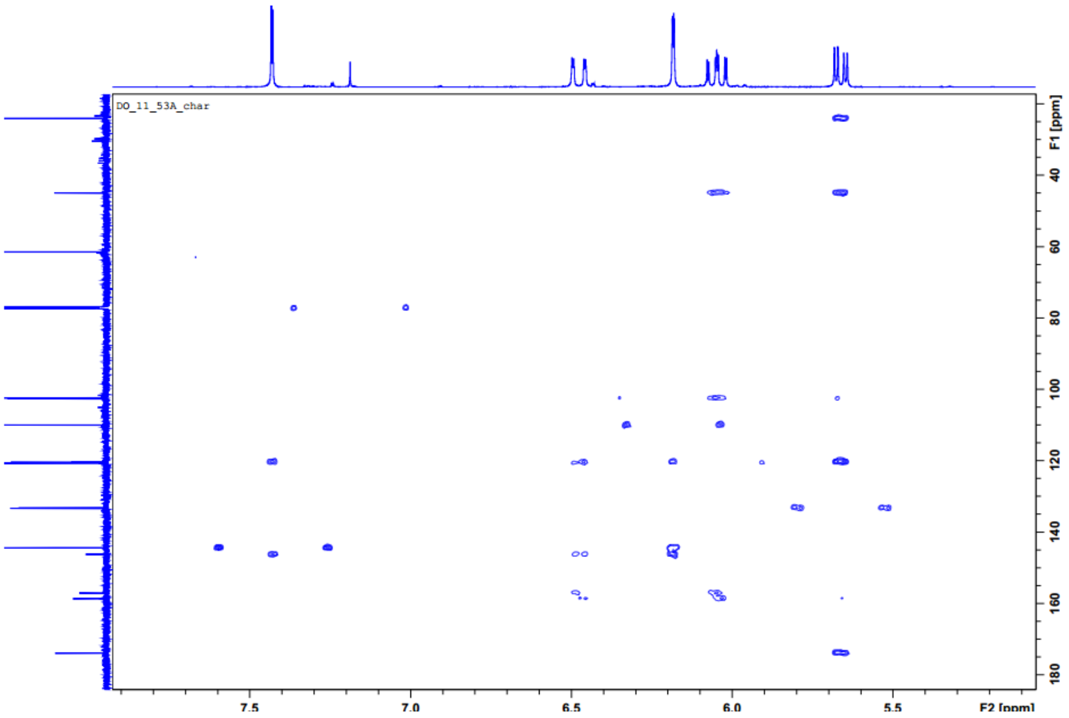


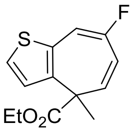
28a HMBC



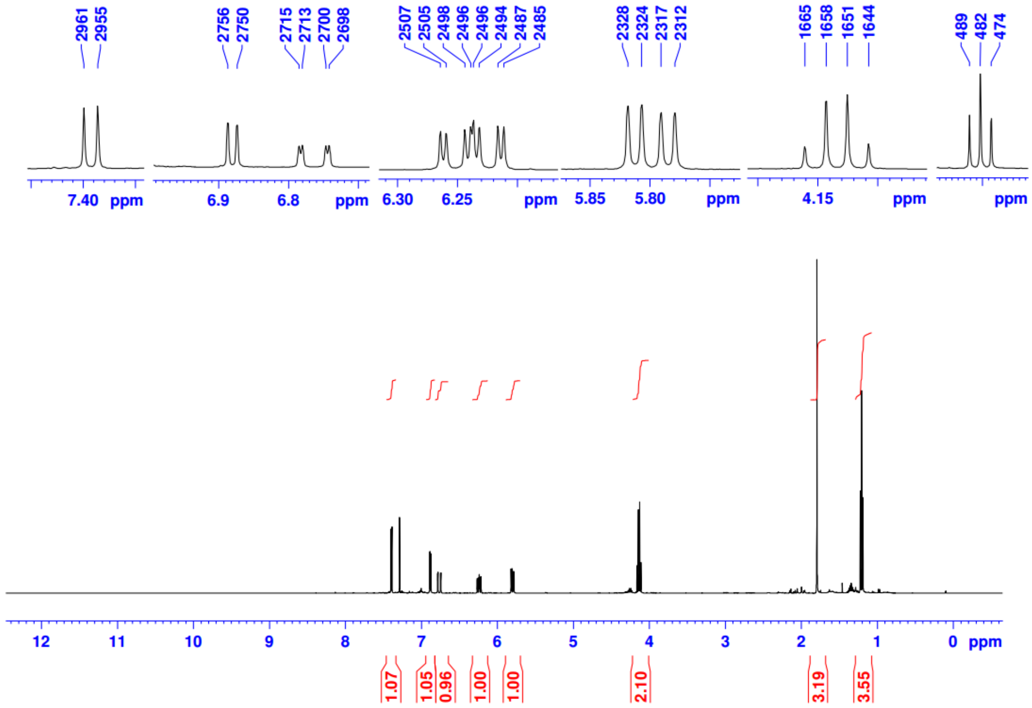


28a HMBC
(expanded)

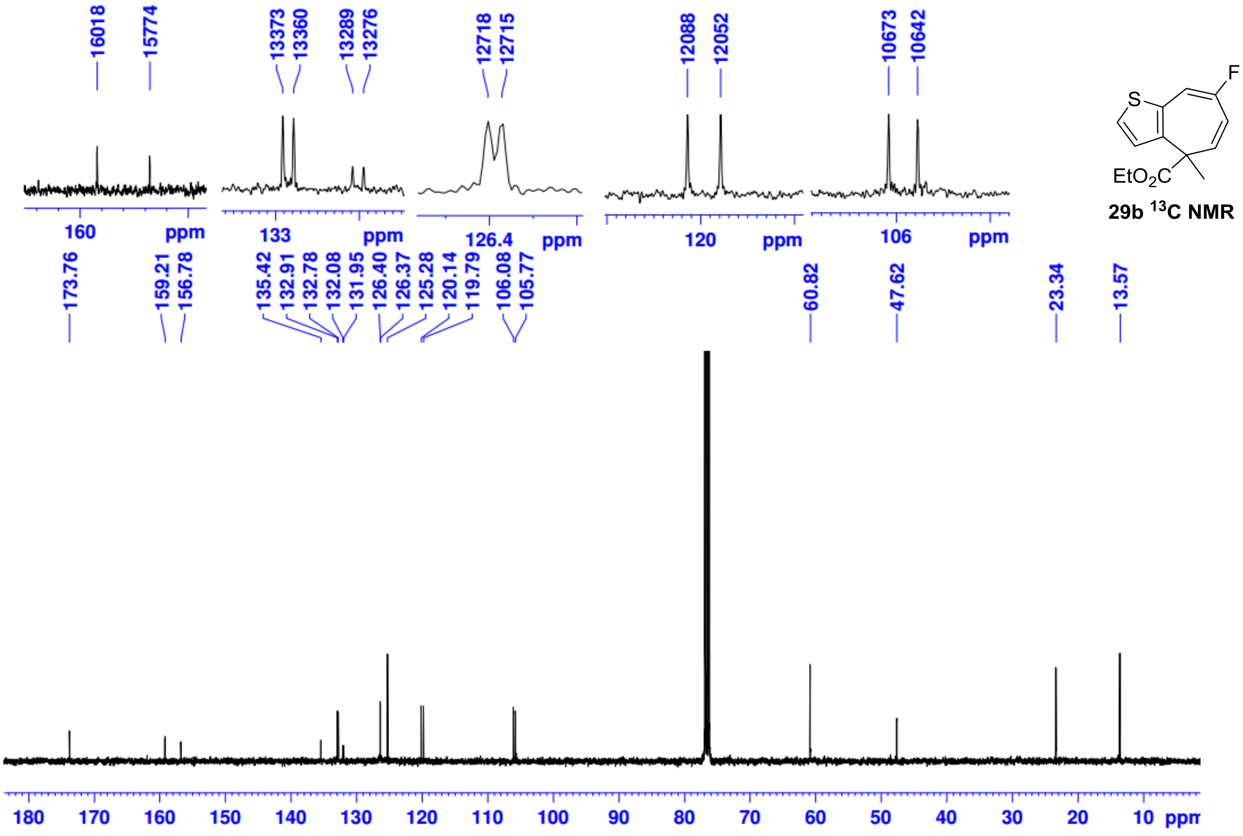


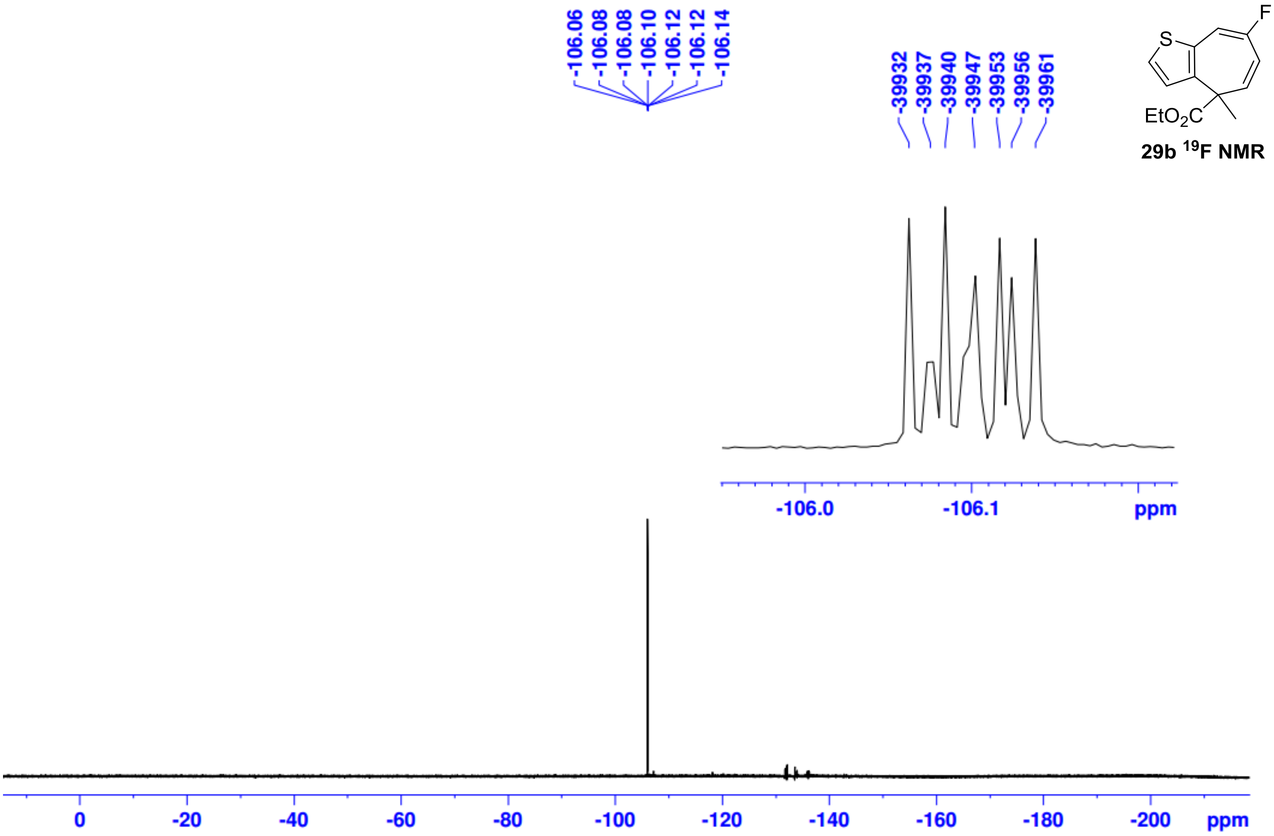


29b ^{1}H NMR

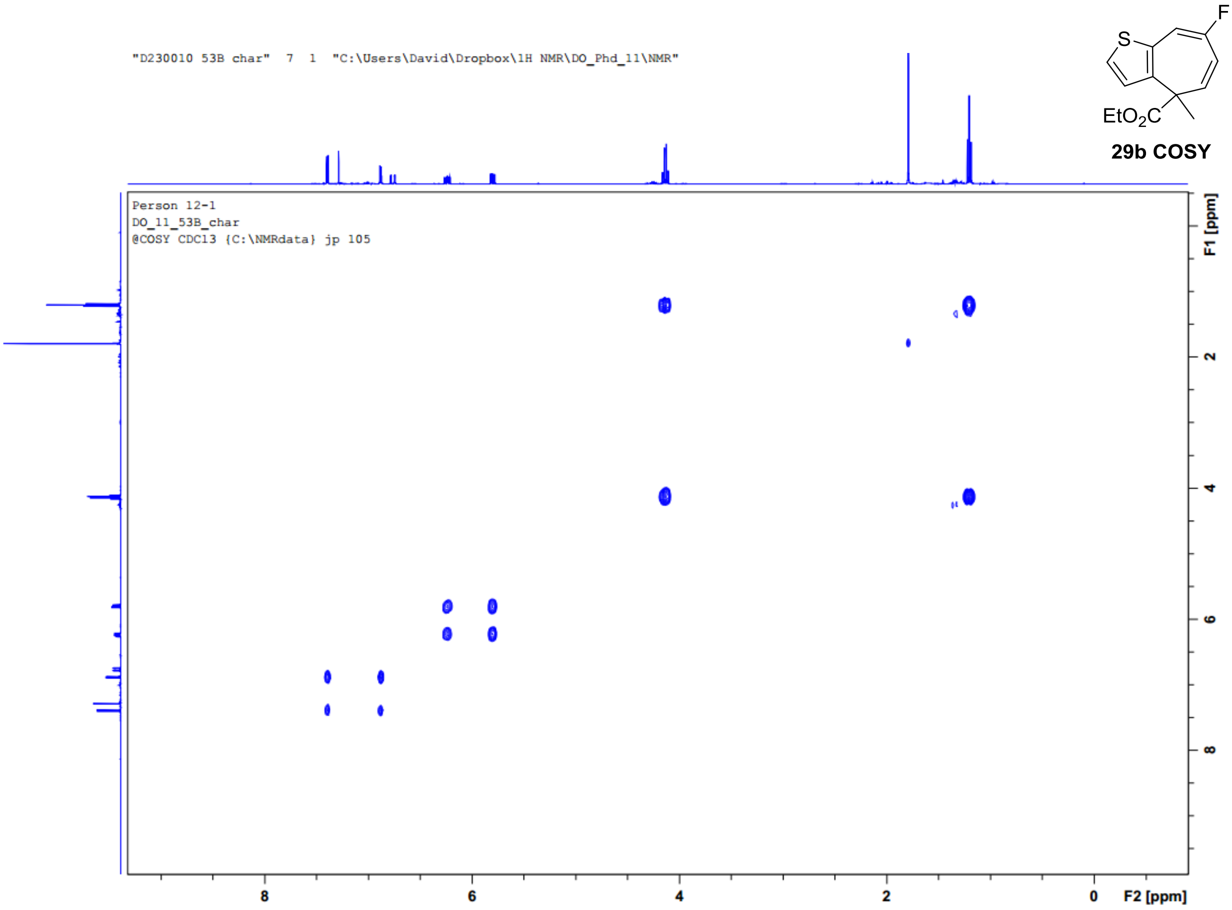


29b ^{13}C NMR

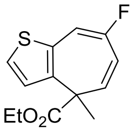




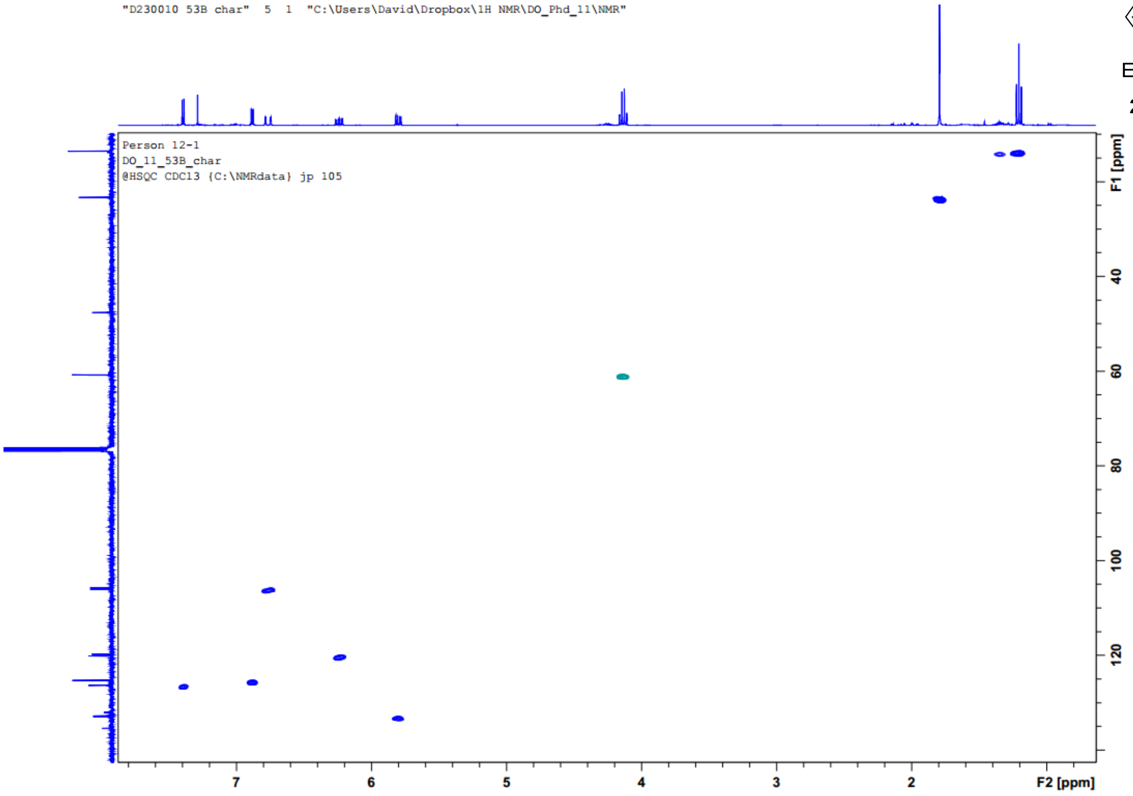
29b ^{19}F NMR

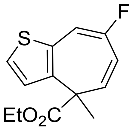


29b COSY

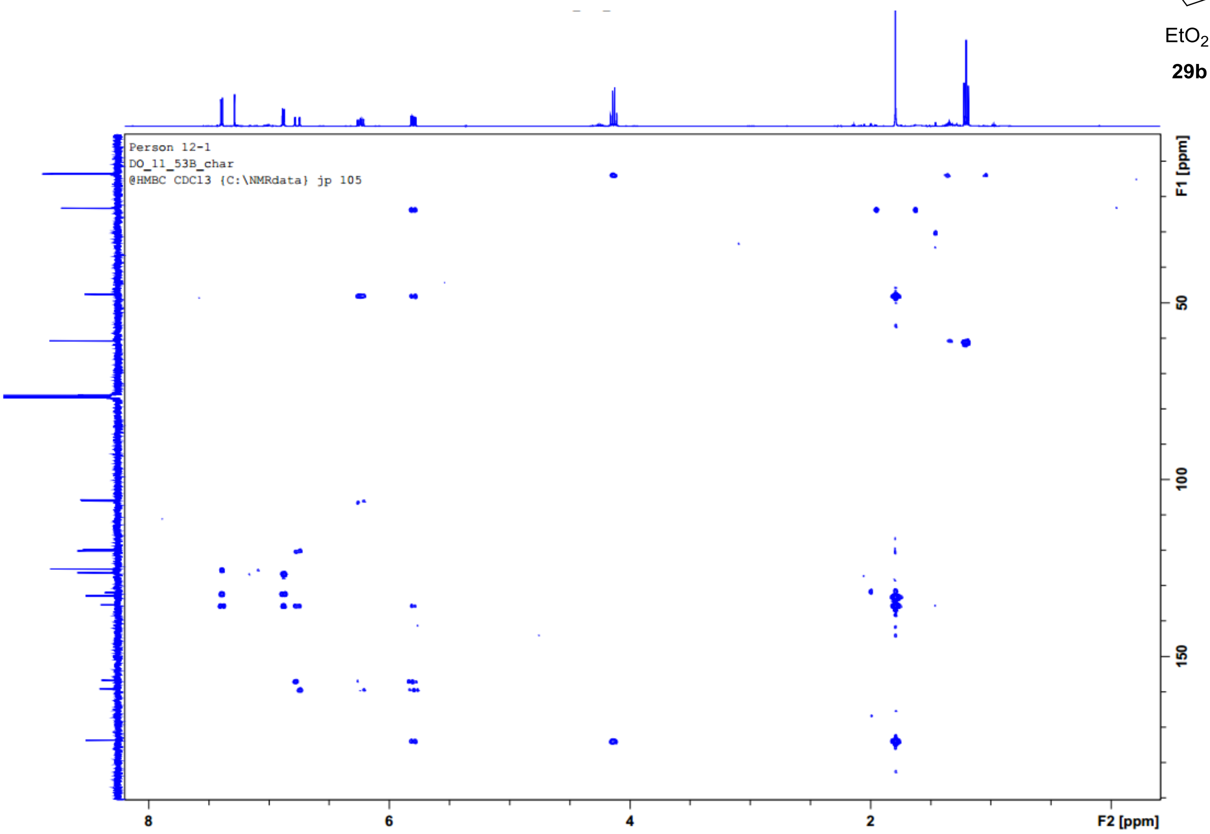


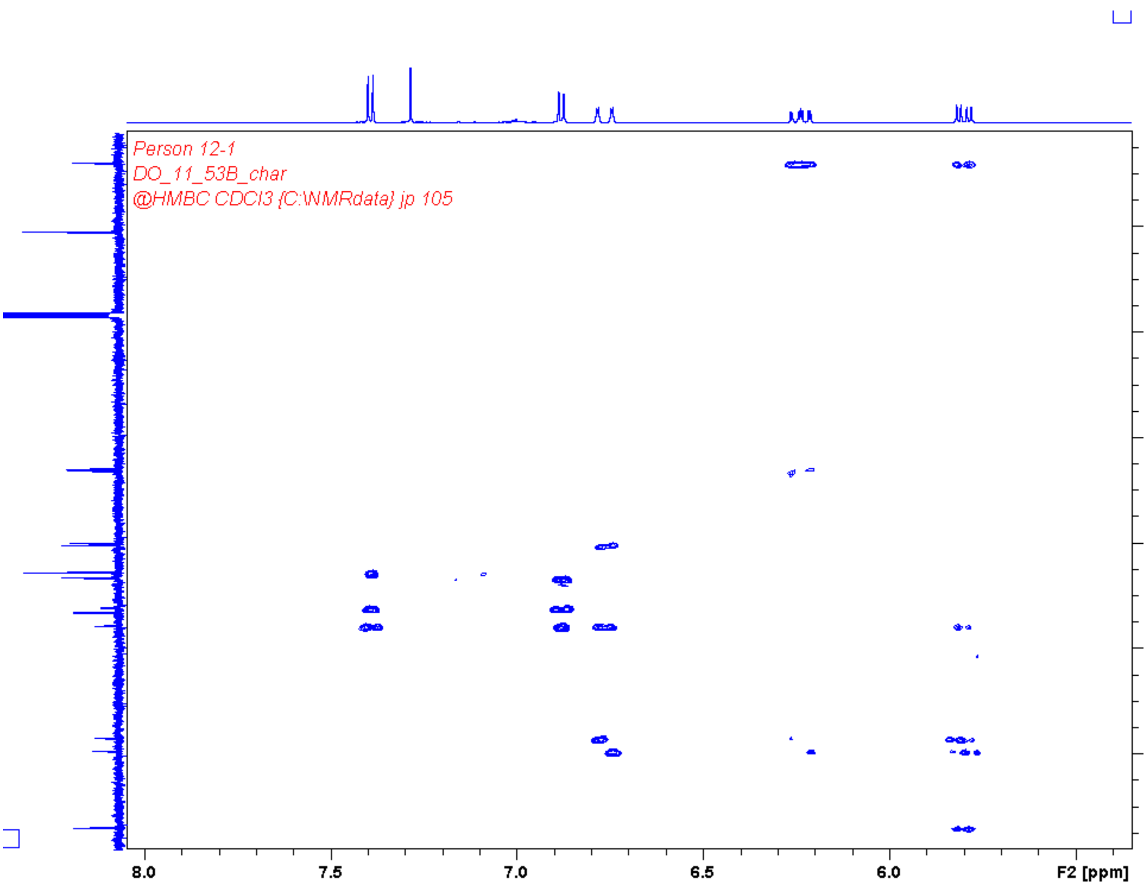
29b HSQC

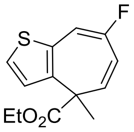




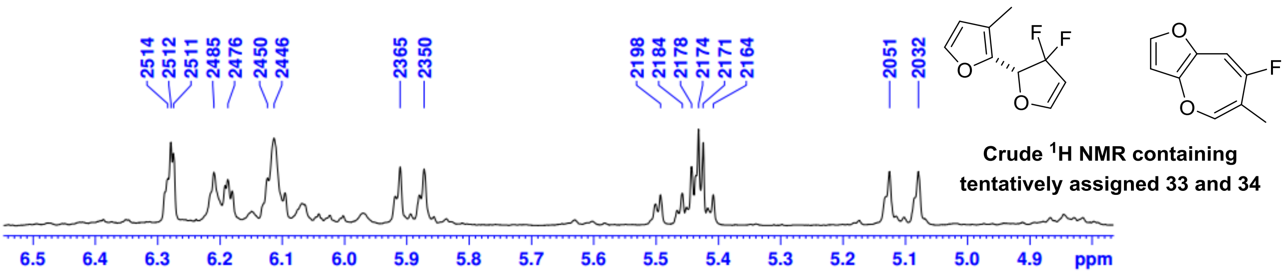
29b HMBC



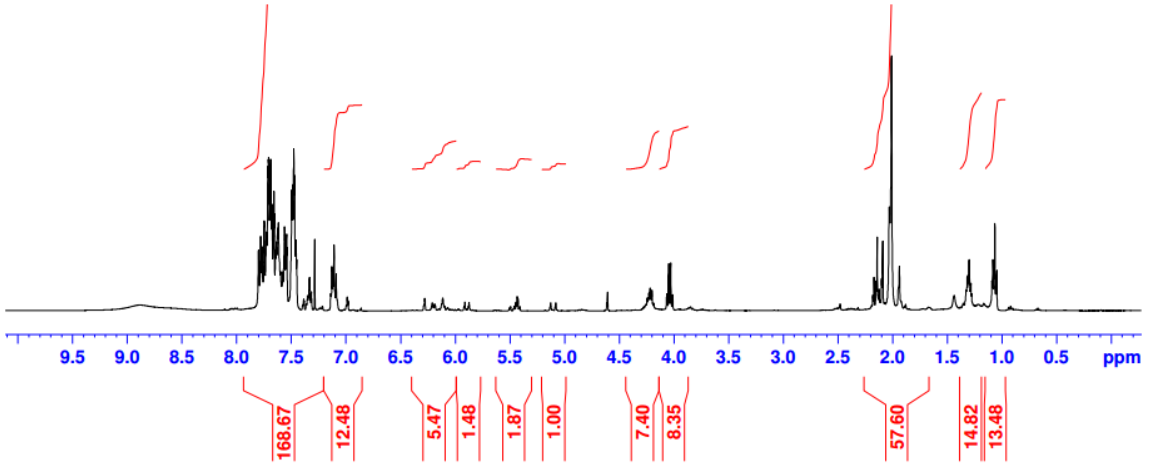


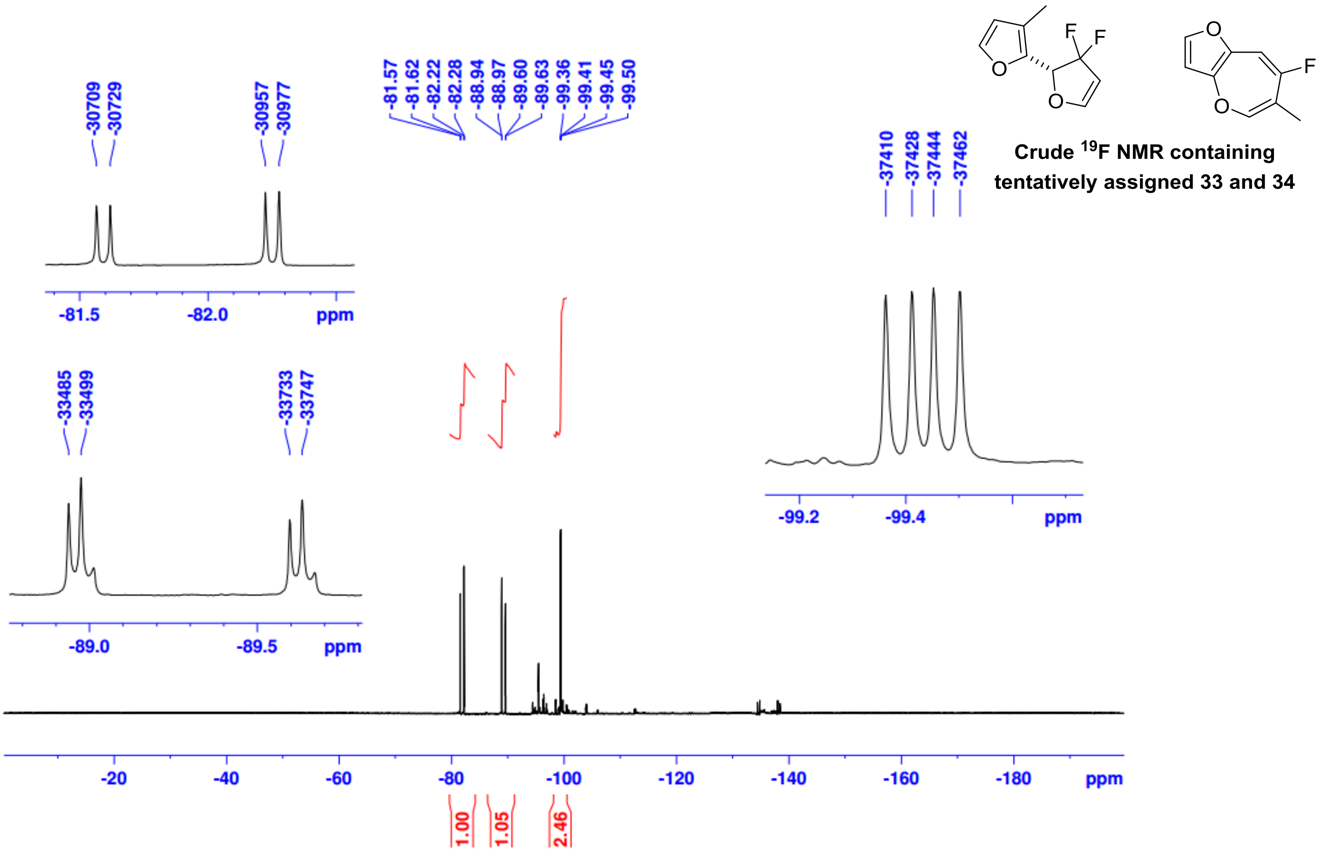


29b HMBC (expanded)

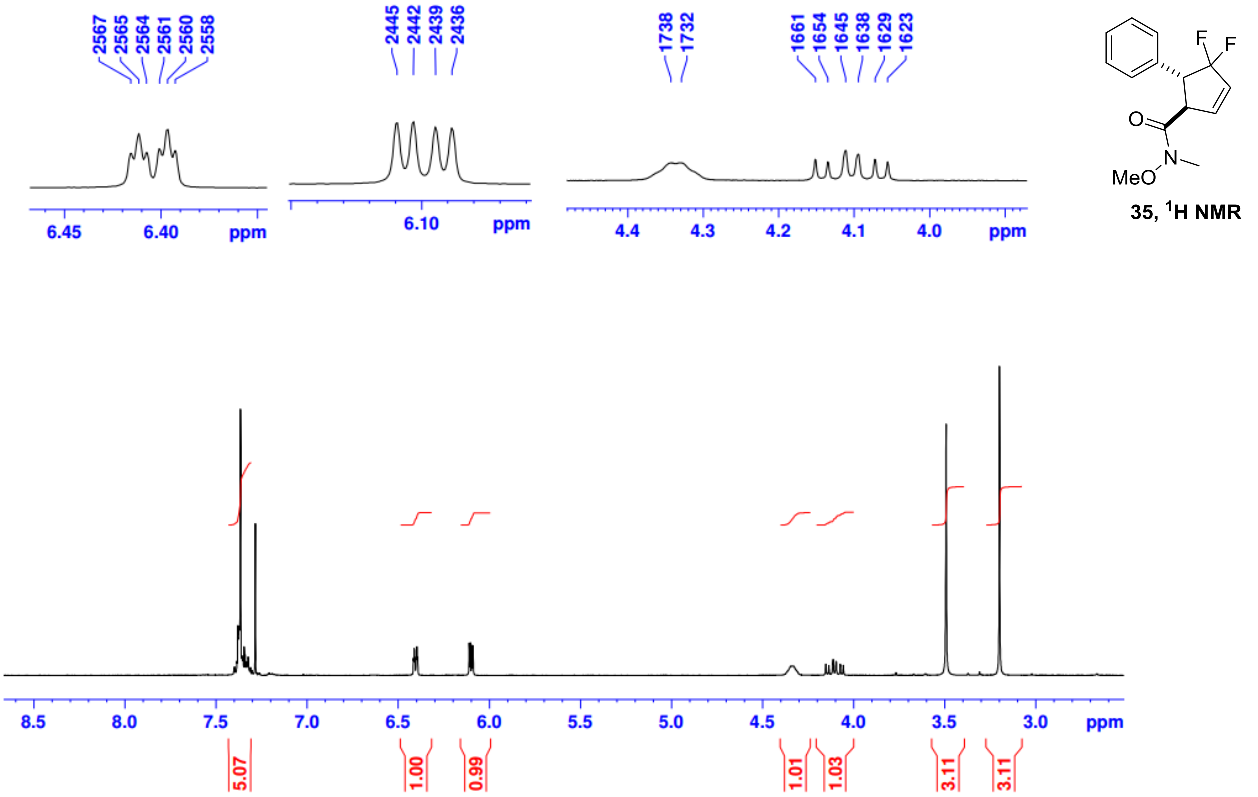


Crude ^{1}H NMR containing tentatively assigned 33 and 34

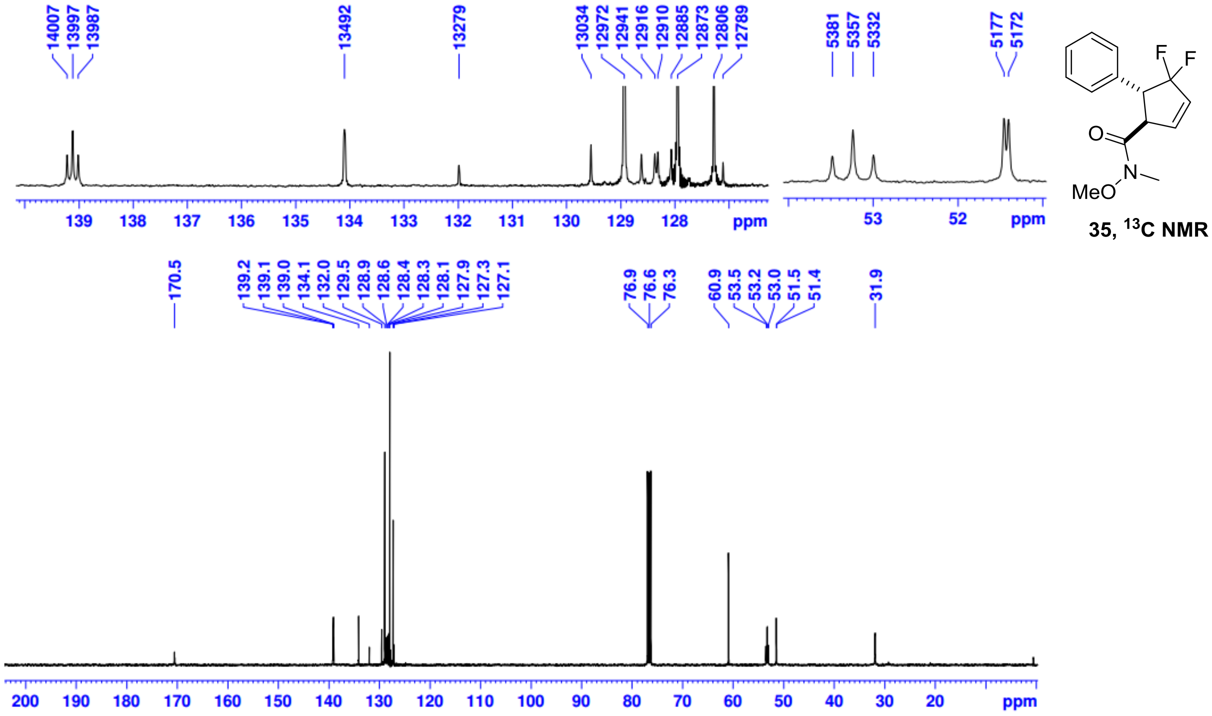




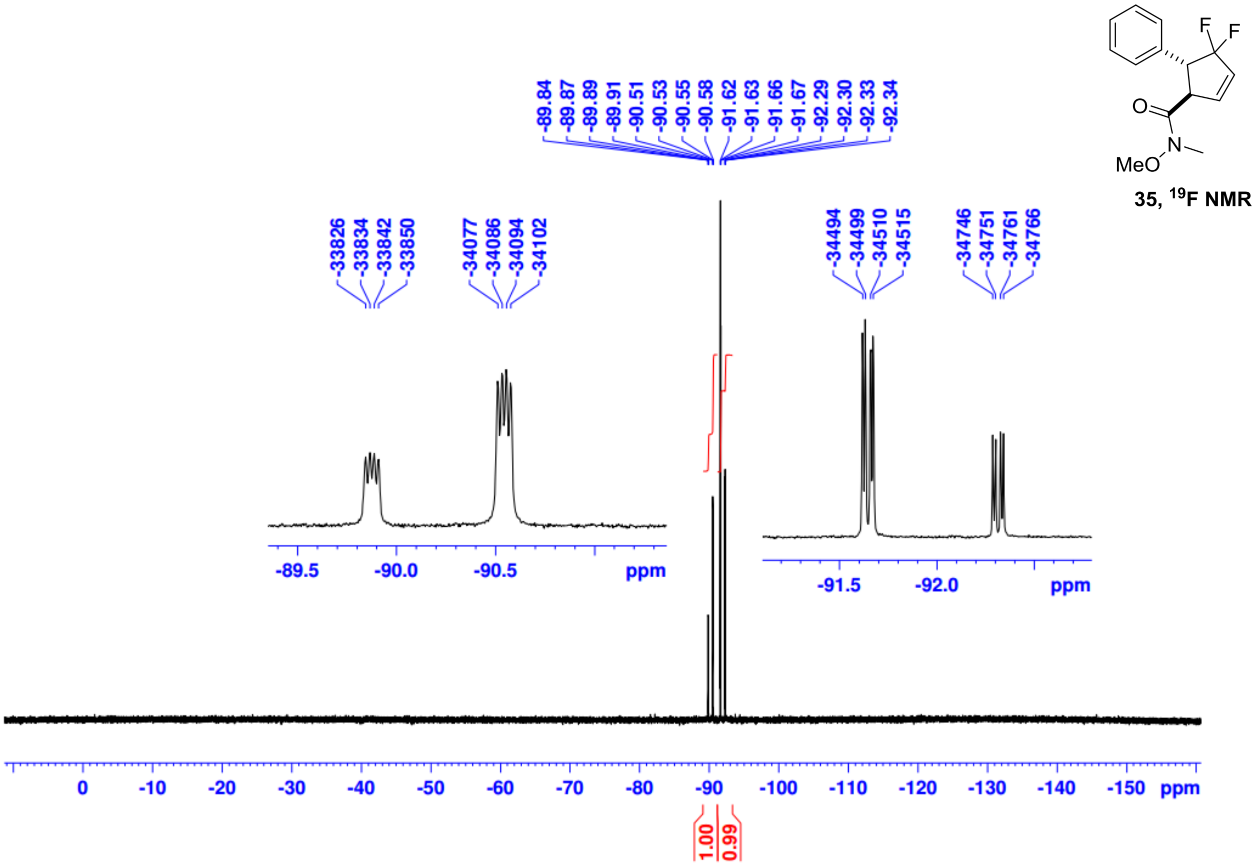
Crude ^{19}F NMR containing tentatively assigned 33 and 34



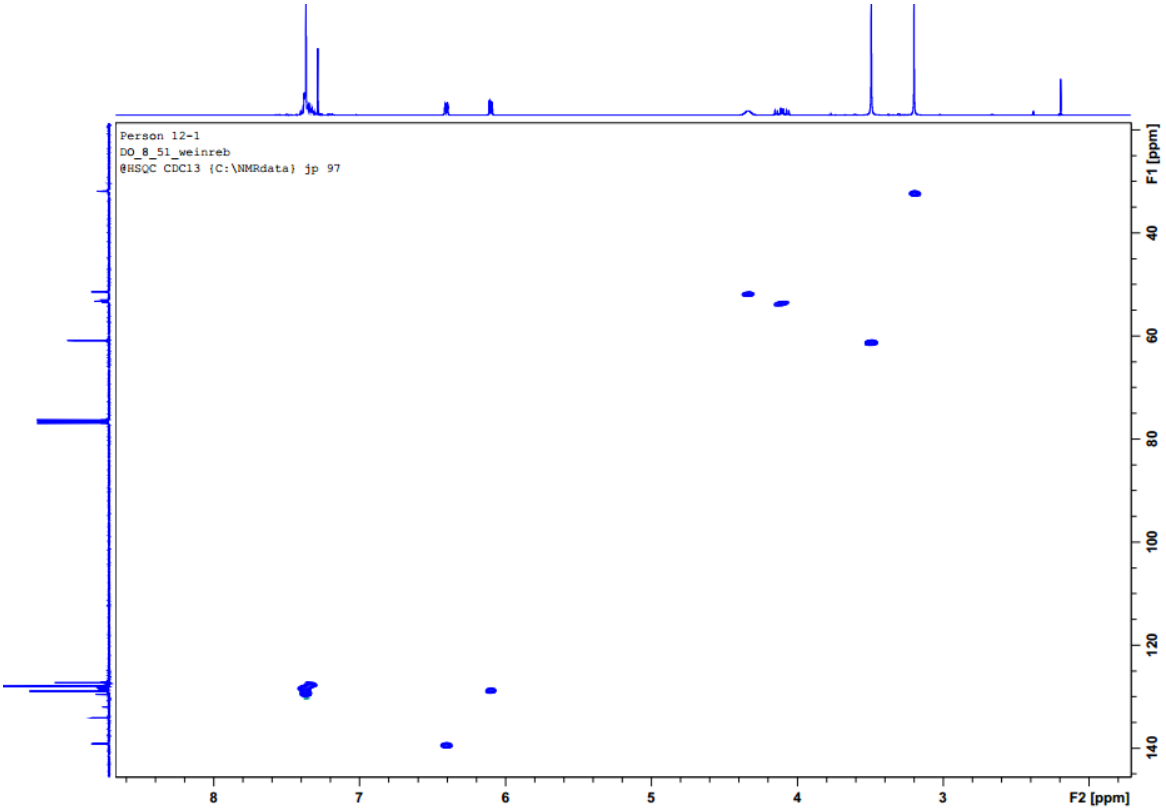
35, ^{1}H NMR

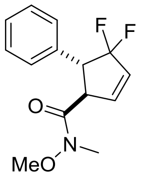


35, ^{13}C NMR

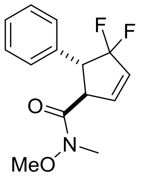


35, ^{19}F NMR

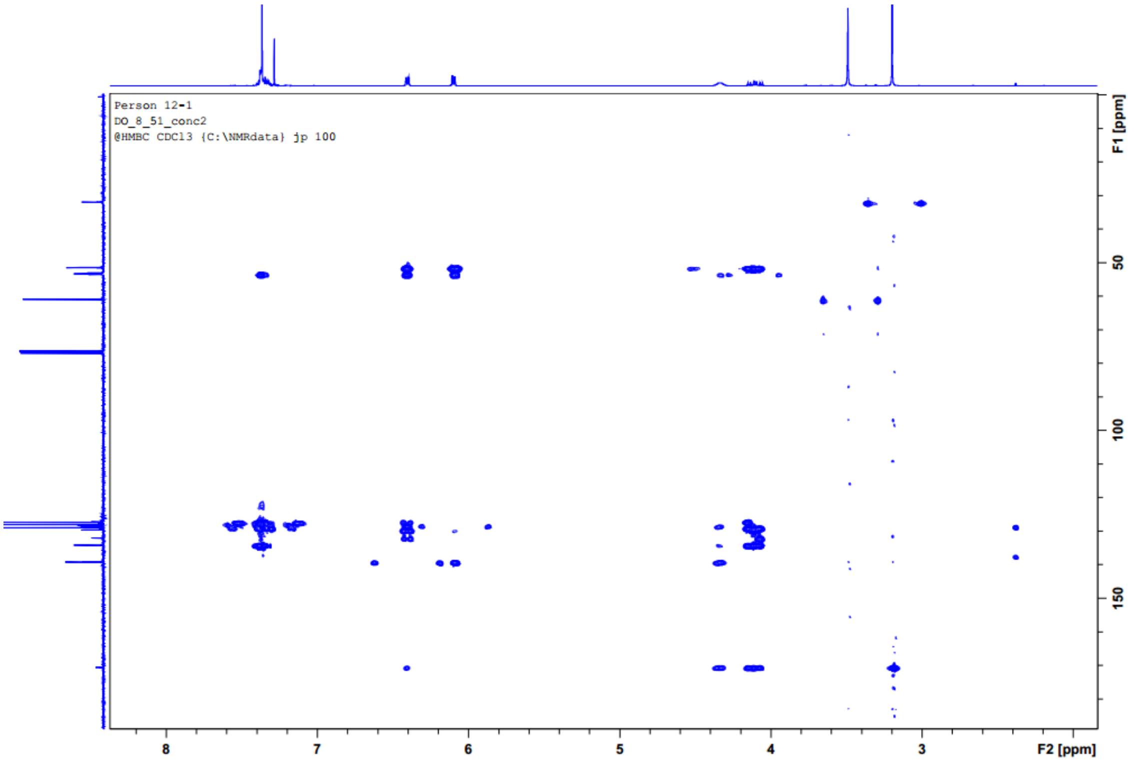


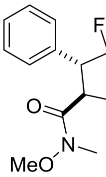


35, HSQC

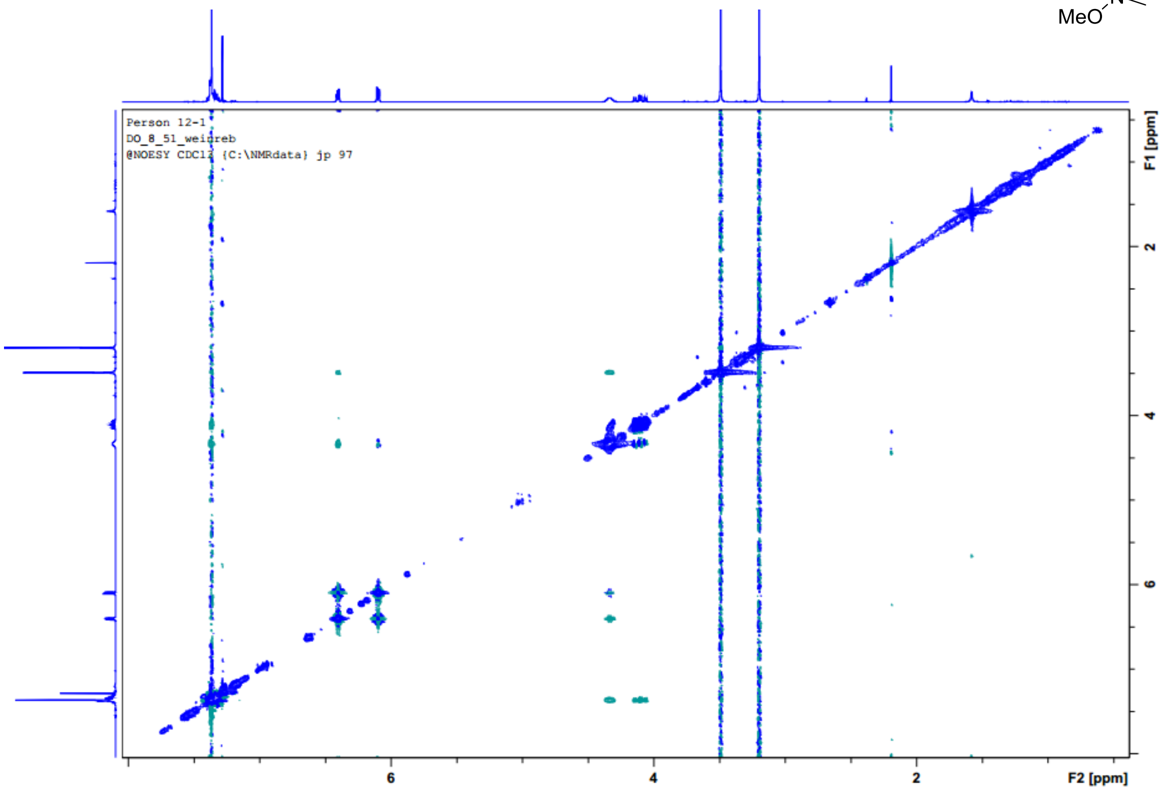


35, HMBC

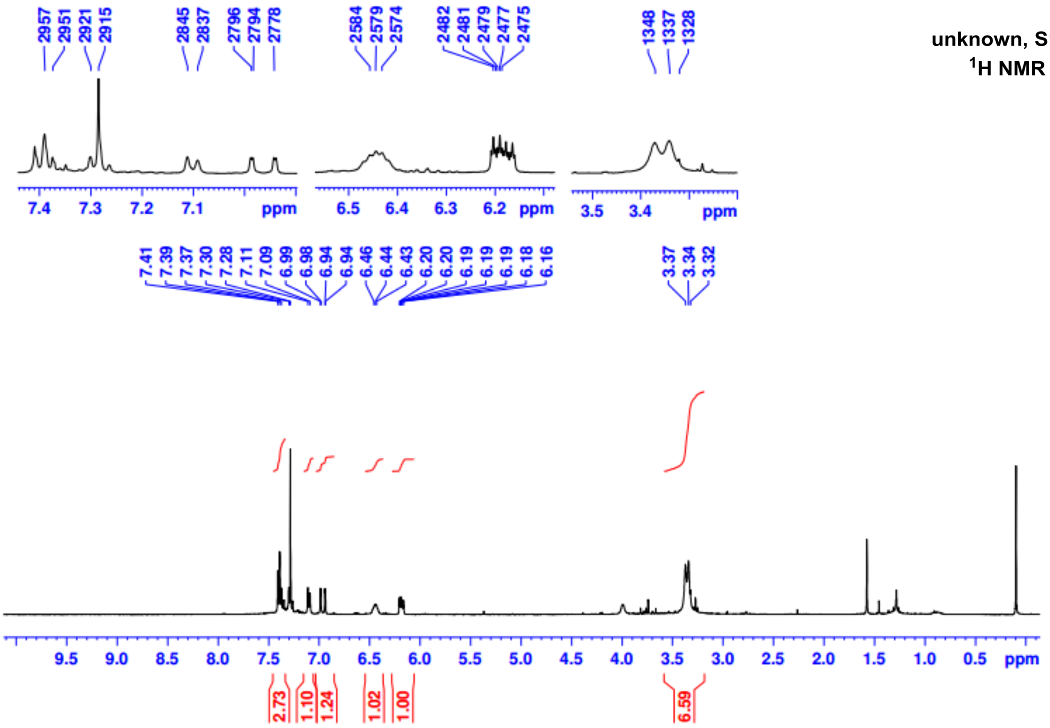


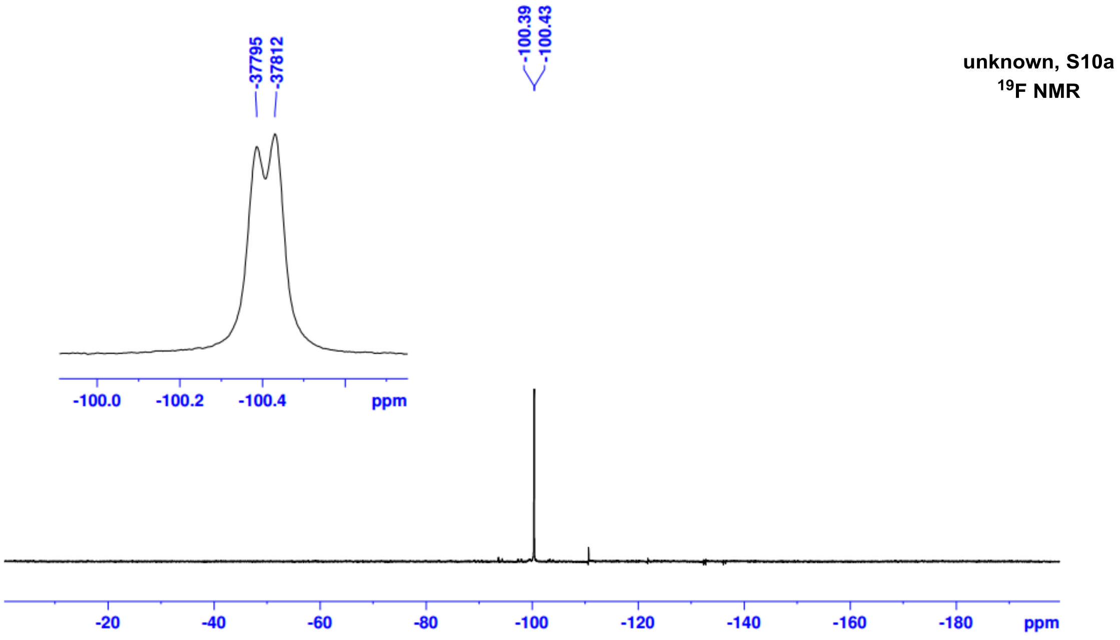


35, NOESY

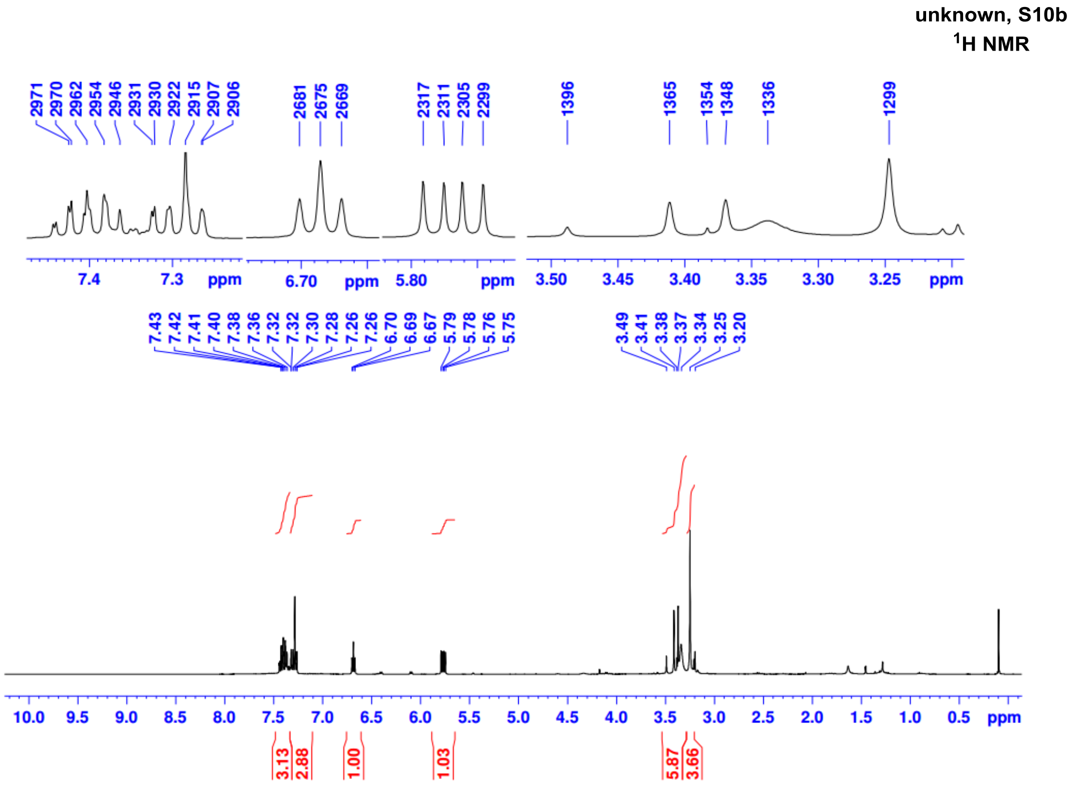


unknown, S10a
^{1}H NMR




unknown, S10a

^{19}F NMR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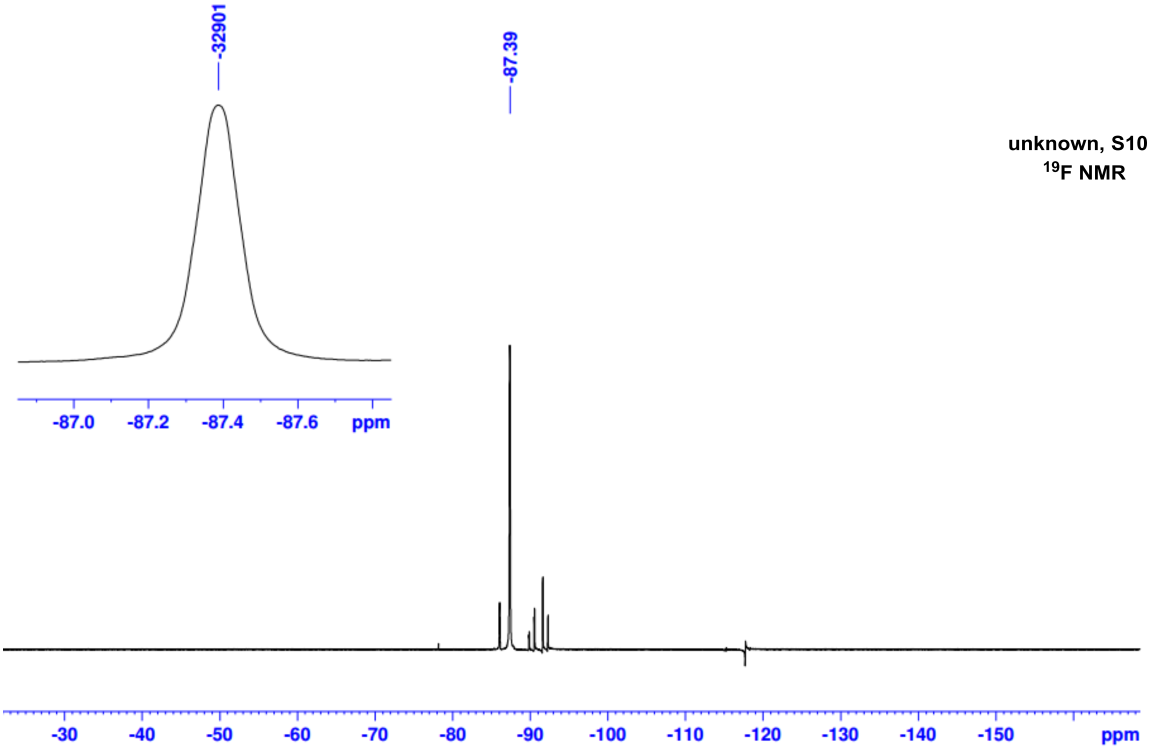
^{1}H NMR



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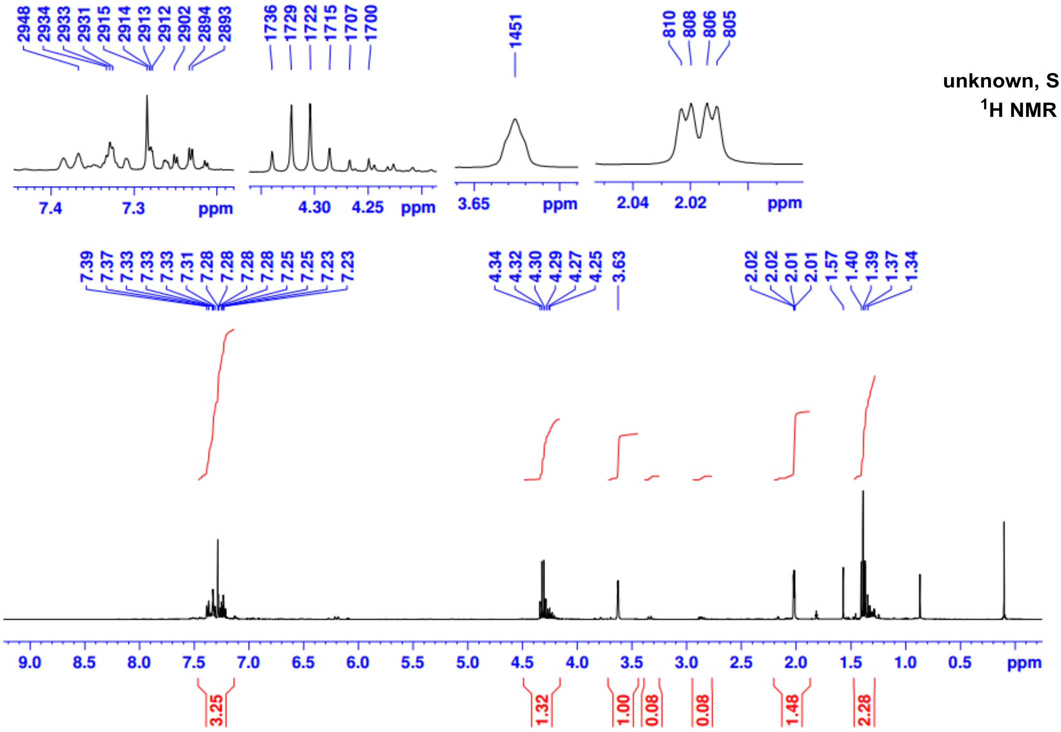
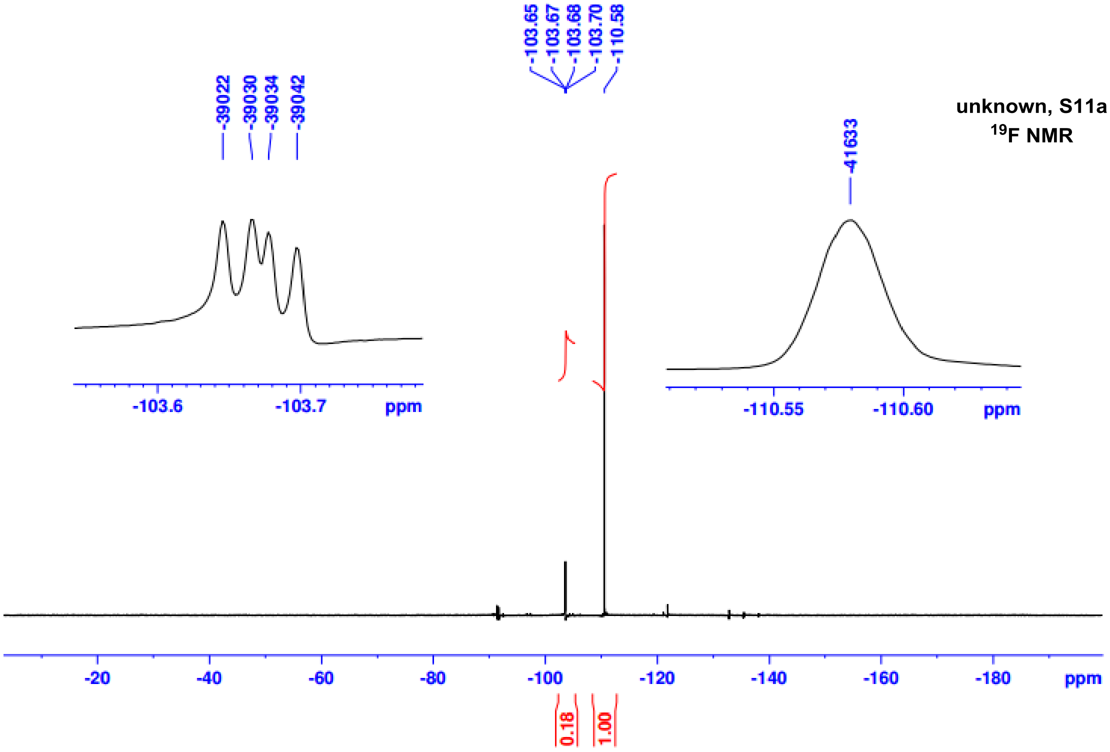


unknown, S11a
^{1}H NMR

unknown, S11a
^{19}F NMR



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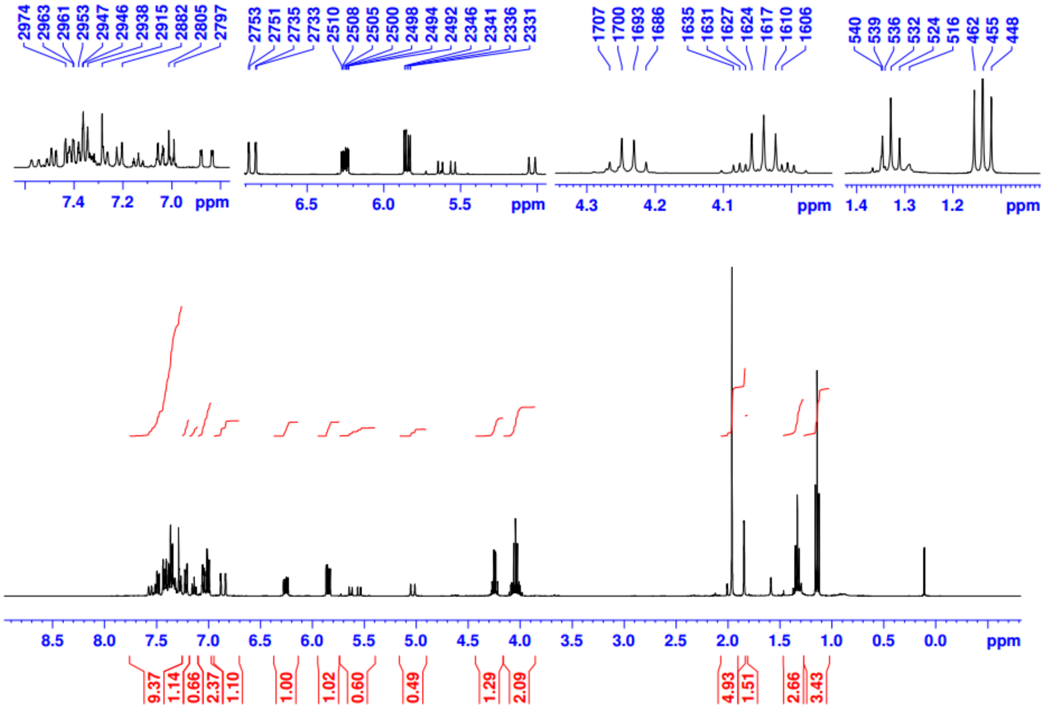
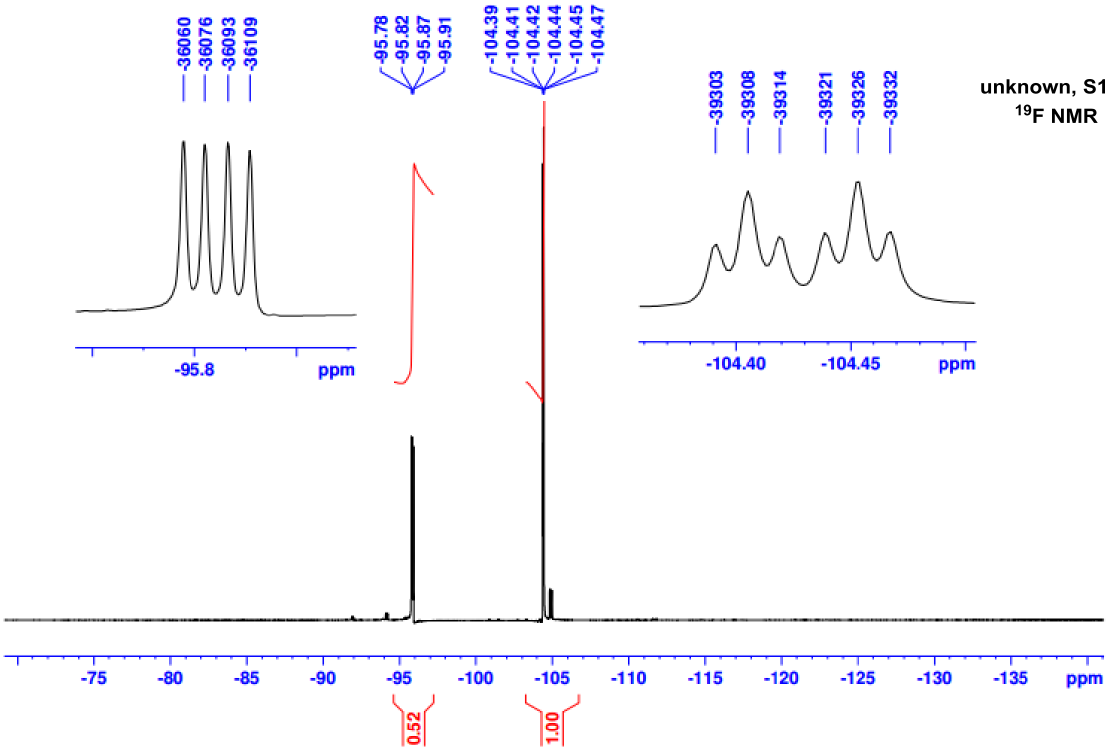
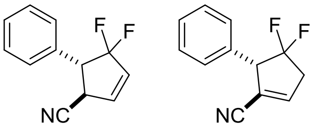
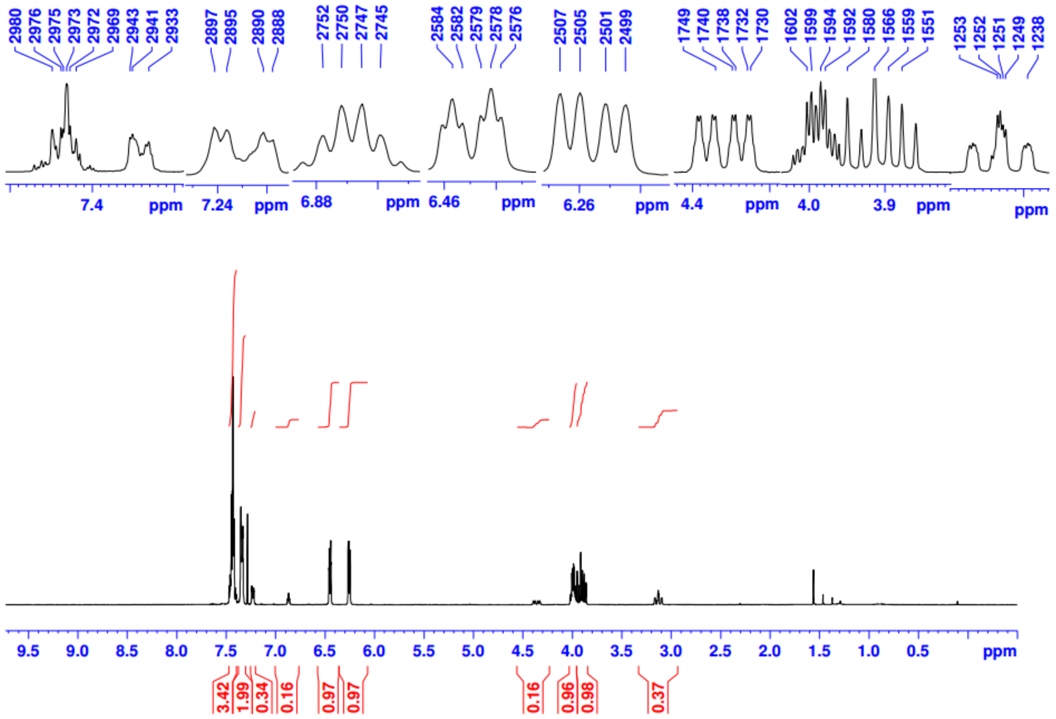


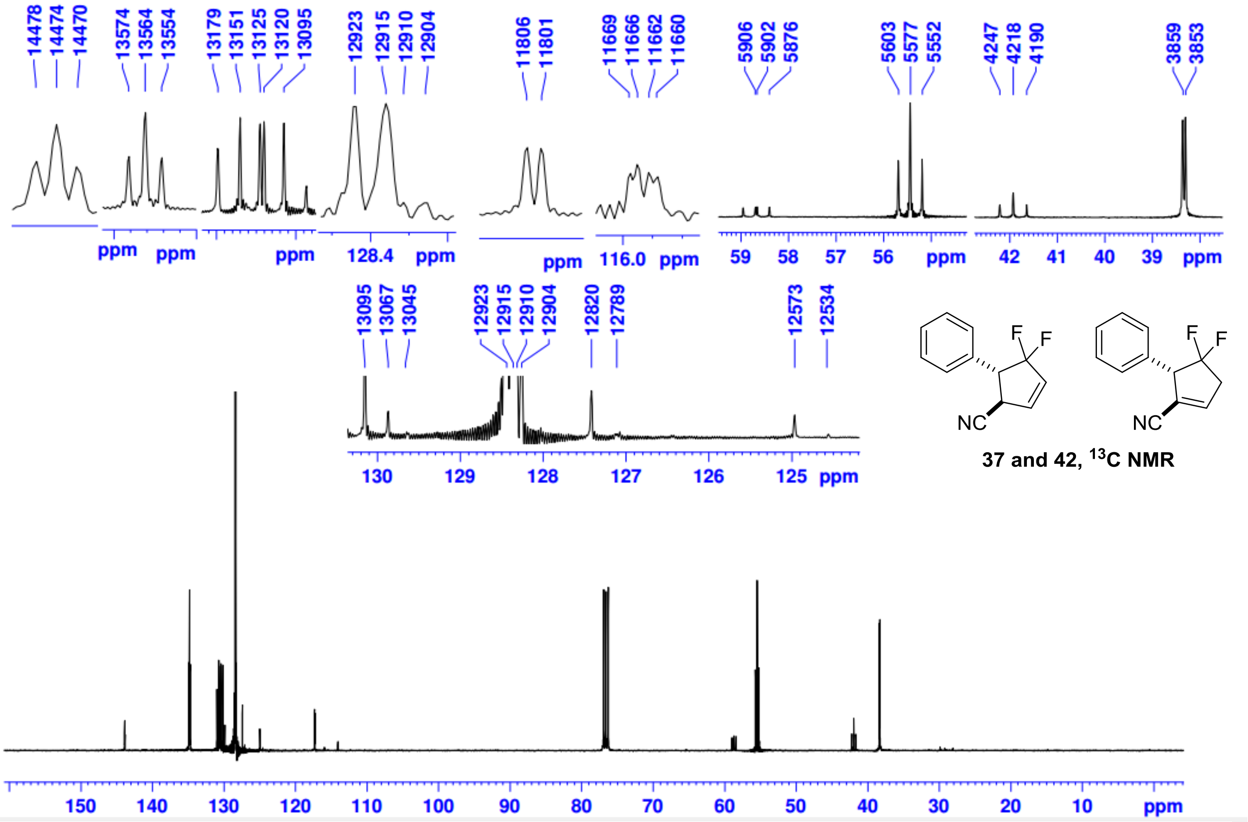
unknown, S11b
^{19}F NMR



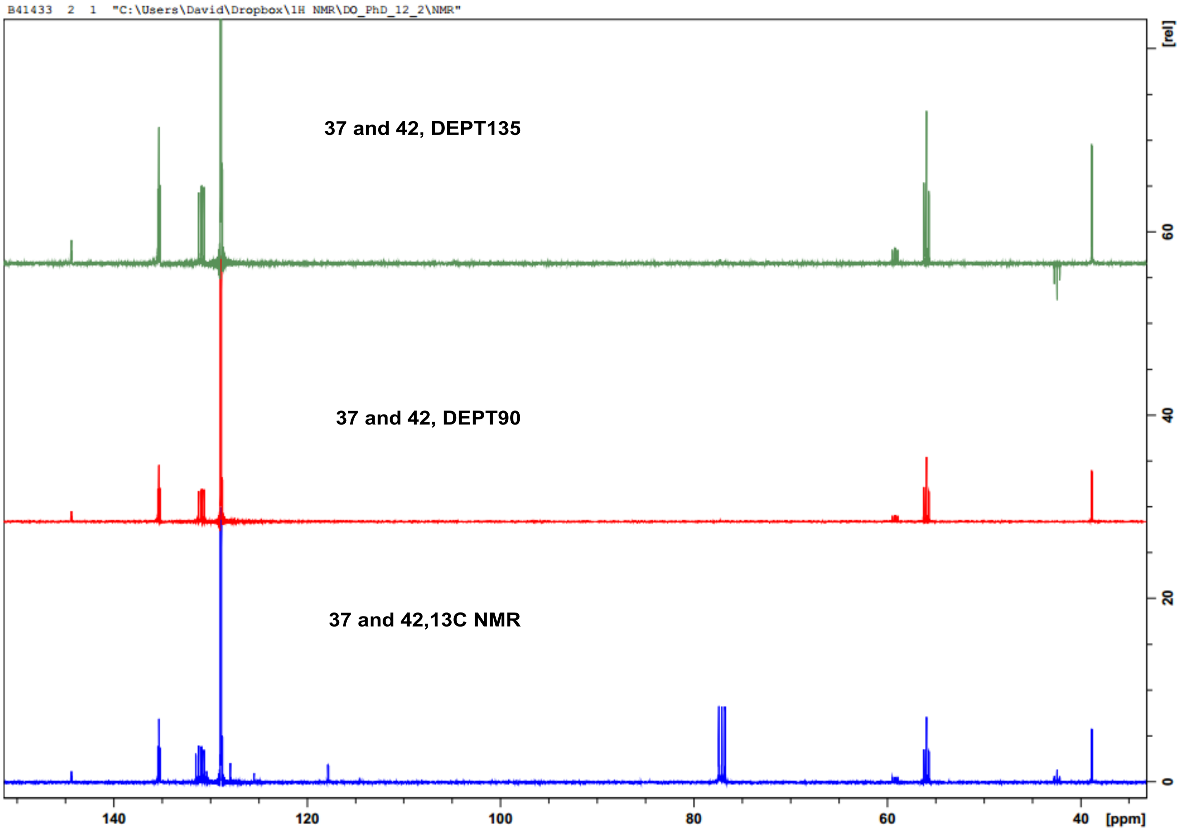


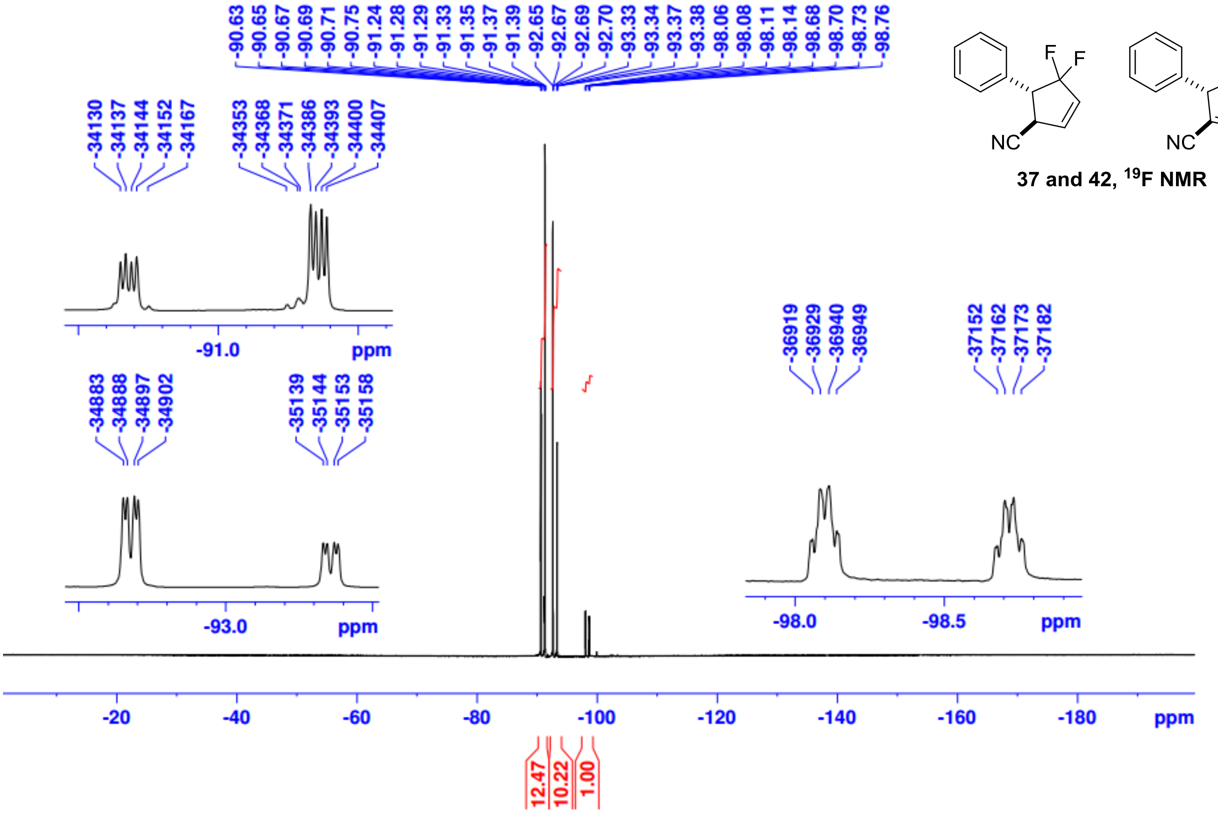
37 and 42, ^{1}H NMR



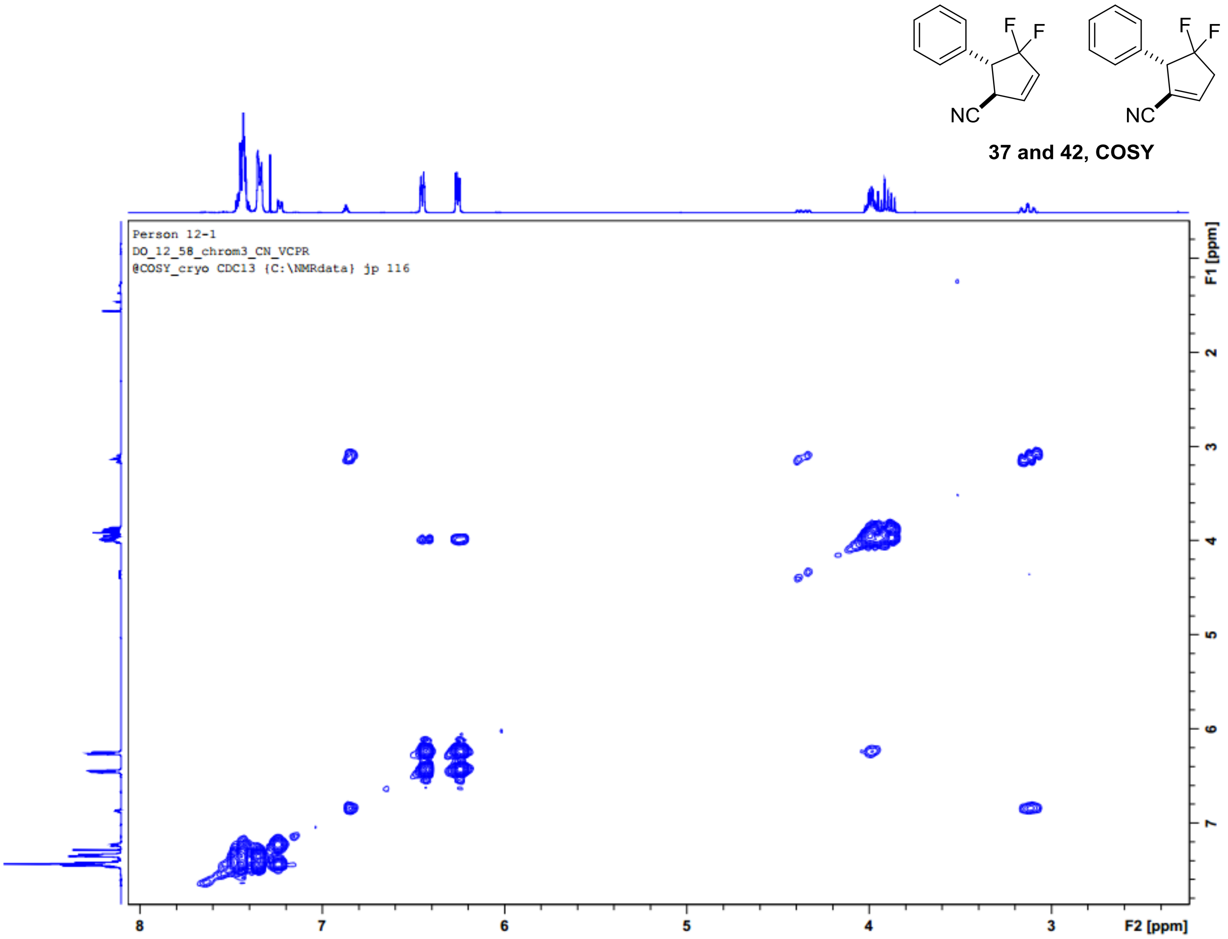


37 and 42, ^{13}C NMR

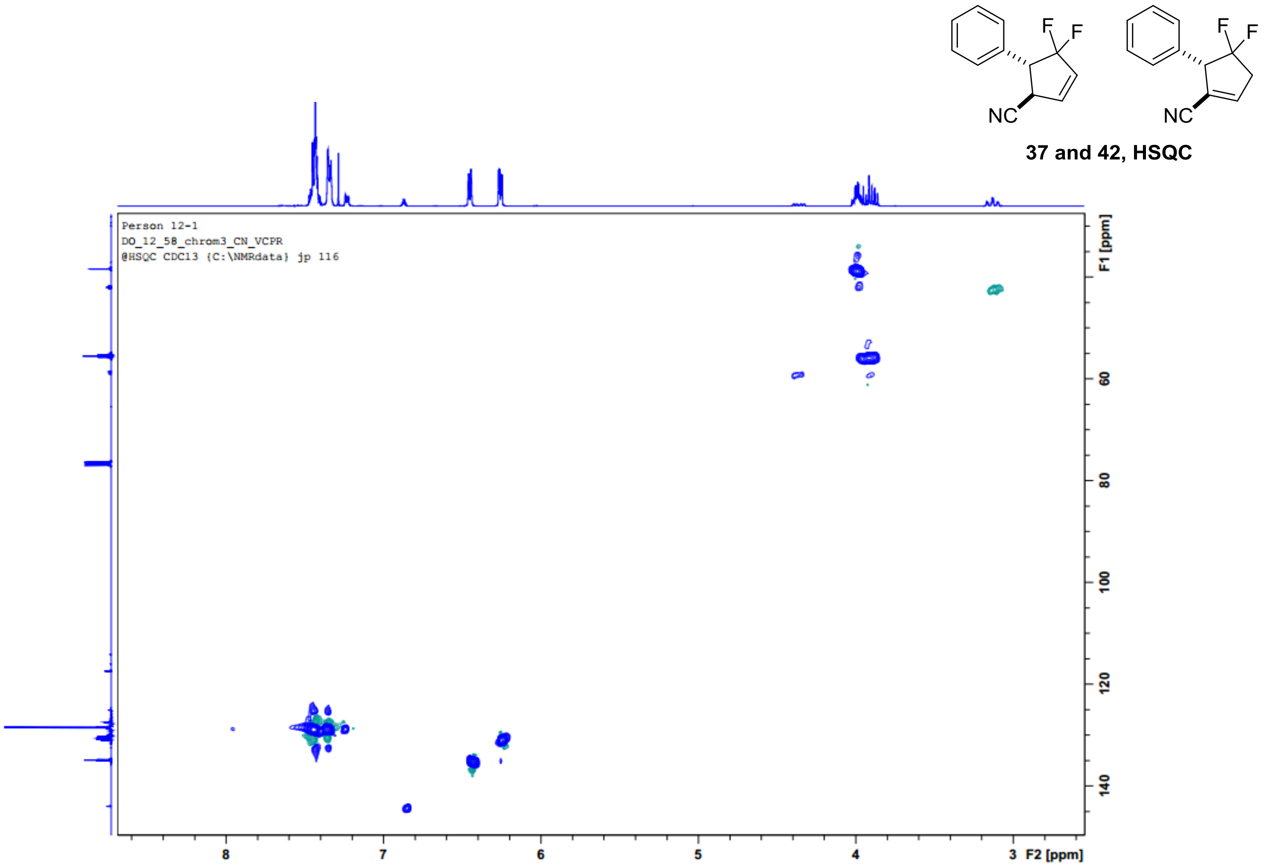




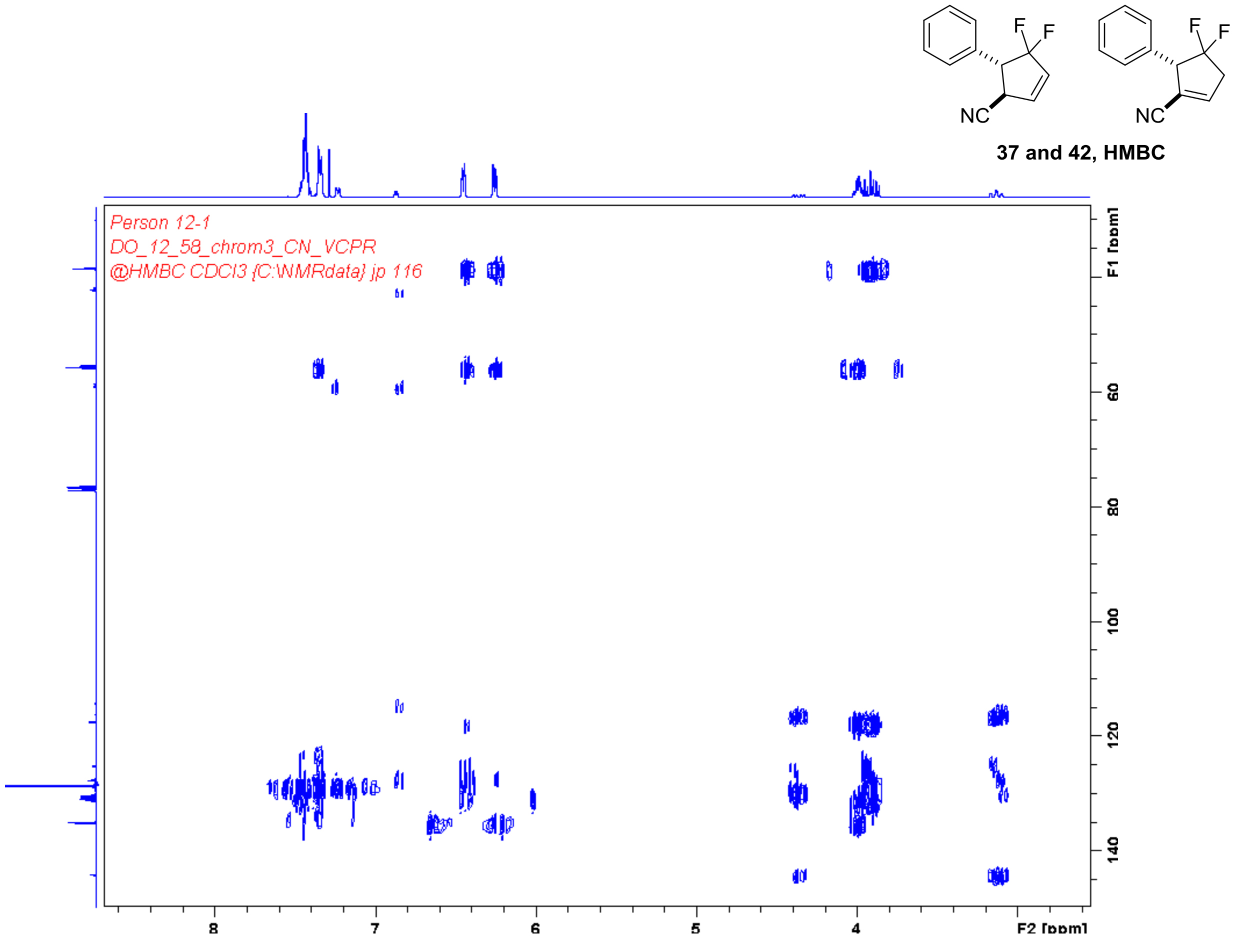
37 and 42, ^{19}F NMR



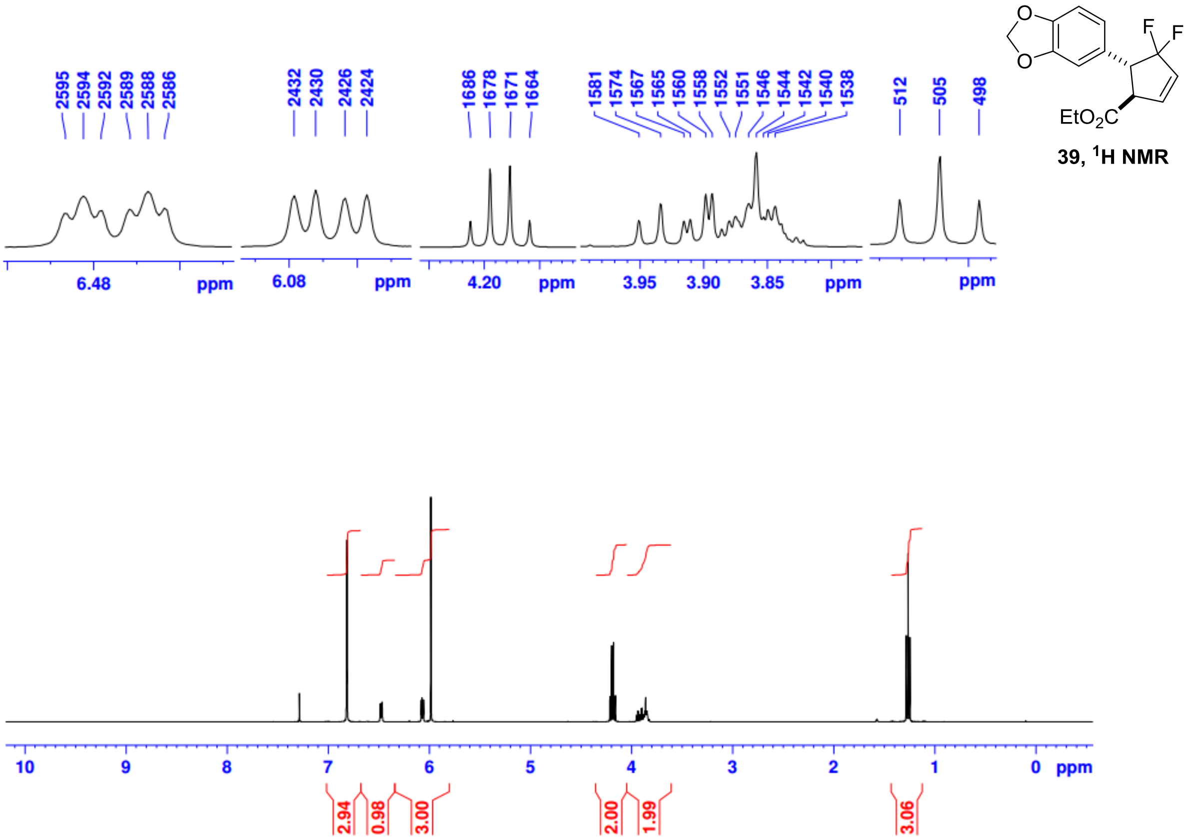
37 and 42, COSY



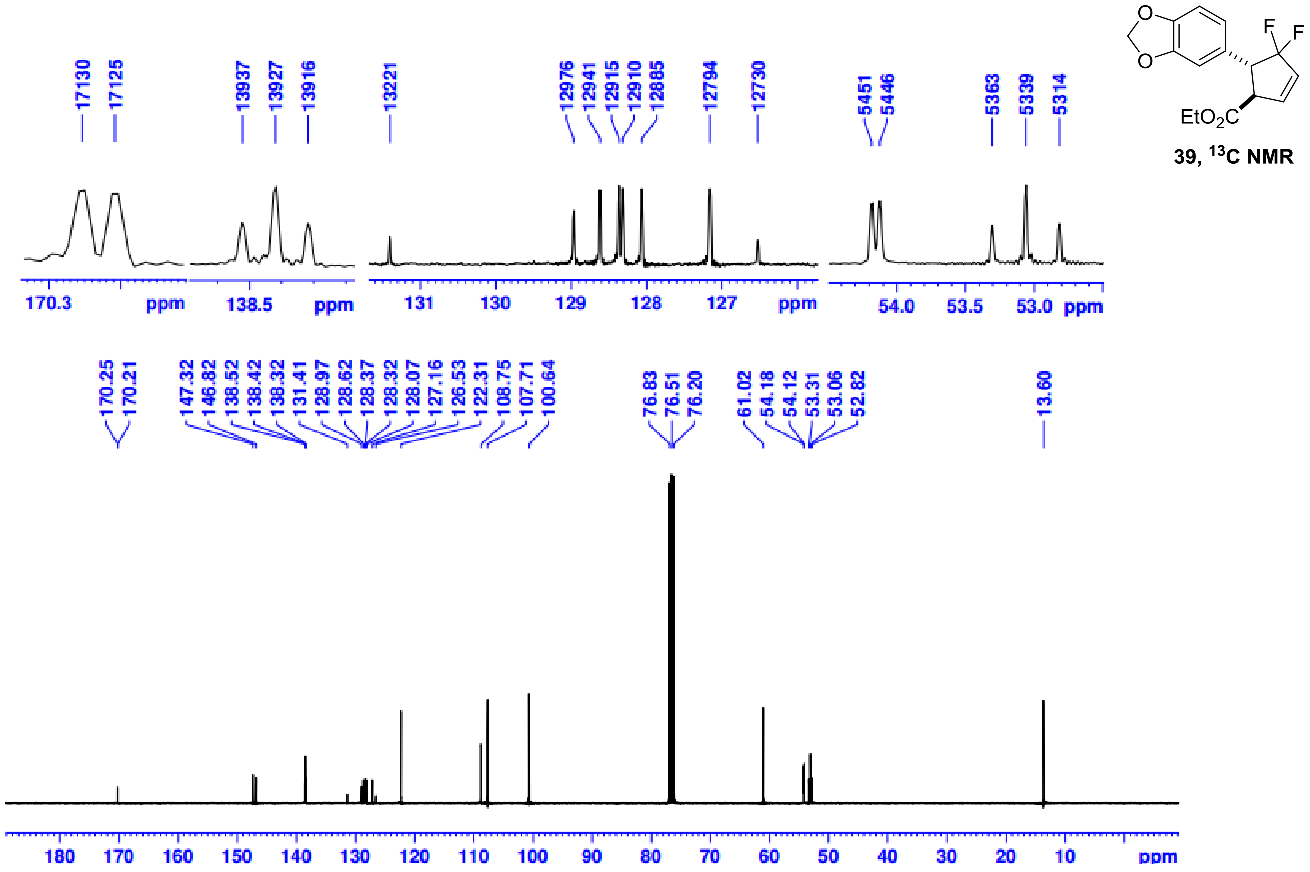
37 and 42, HSQC



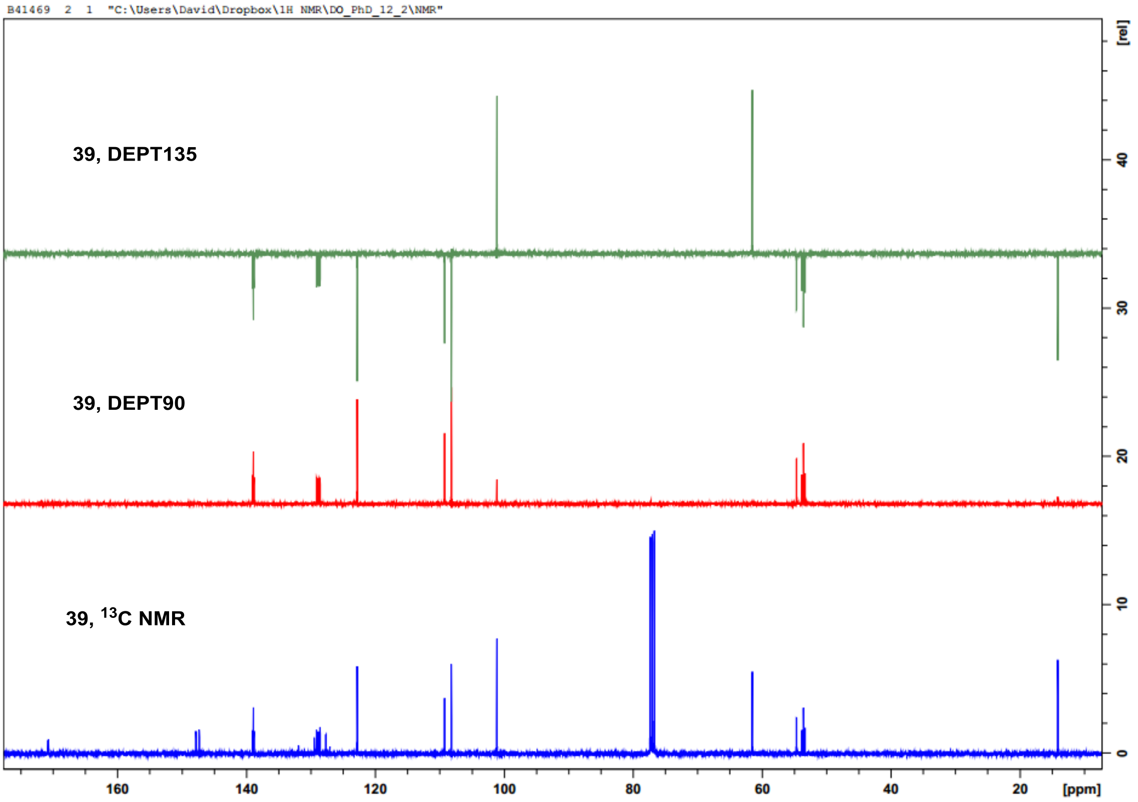
37 and 42, HMBC



39, ^{1}H NMR



39, ^{13}C NMR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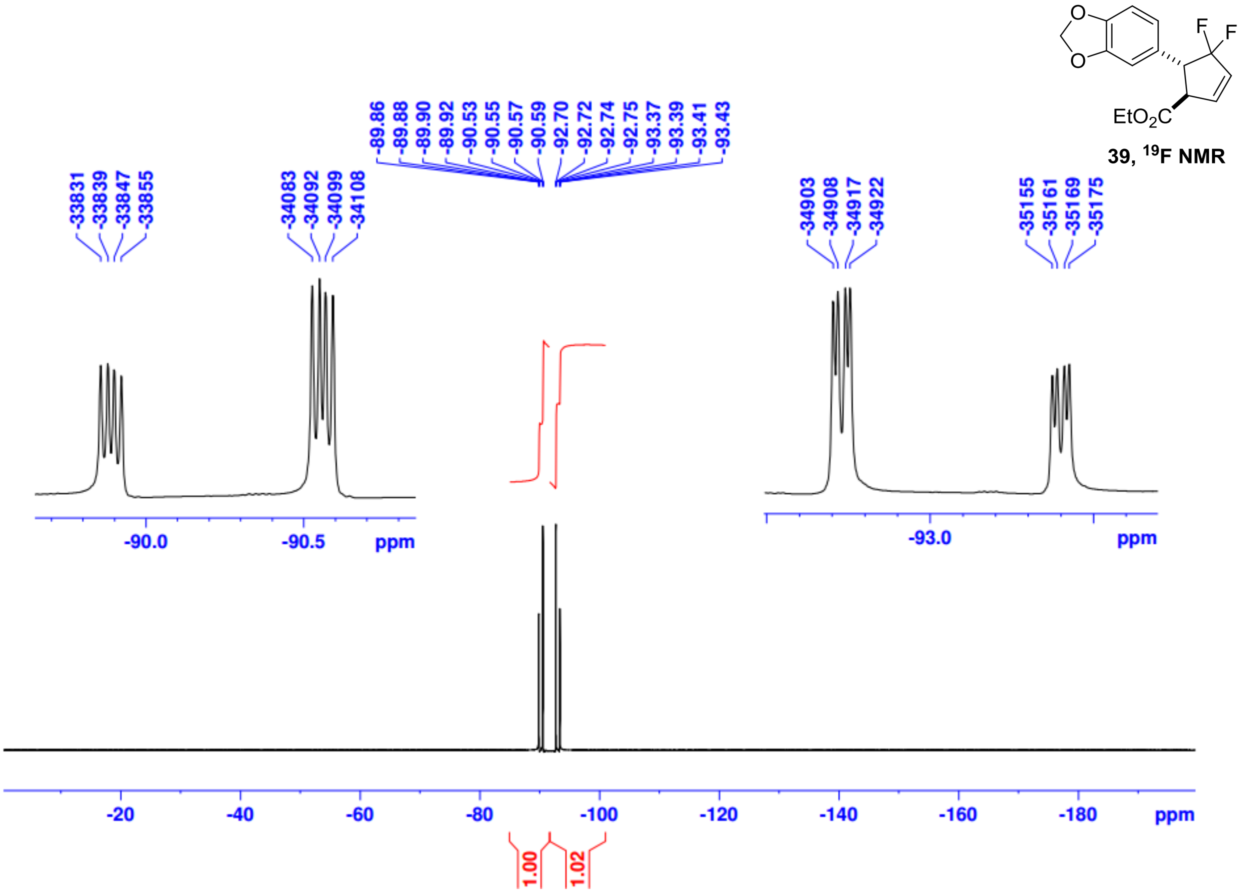
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39, 19F NMR
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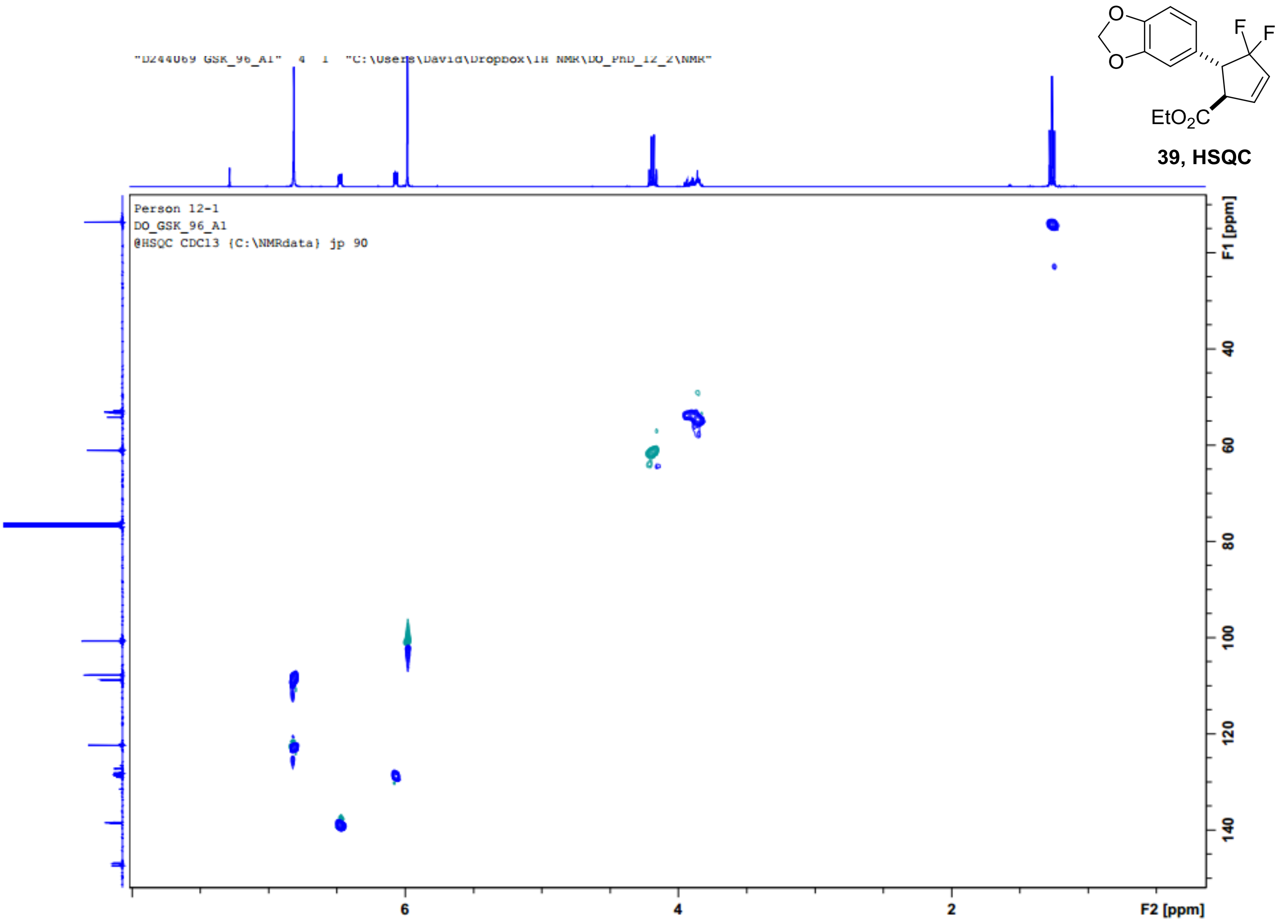
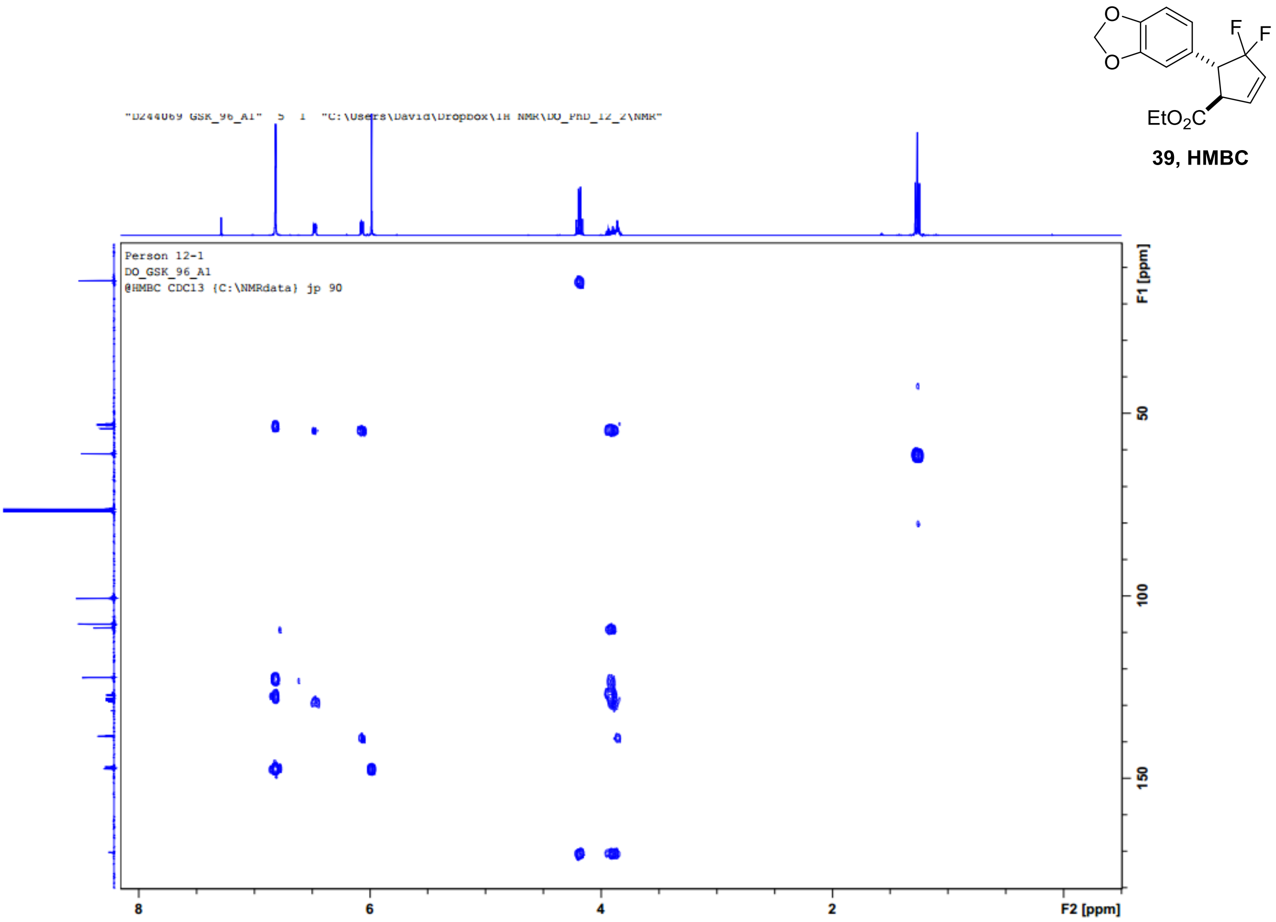
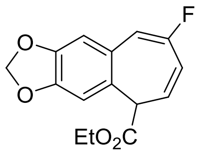
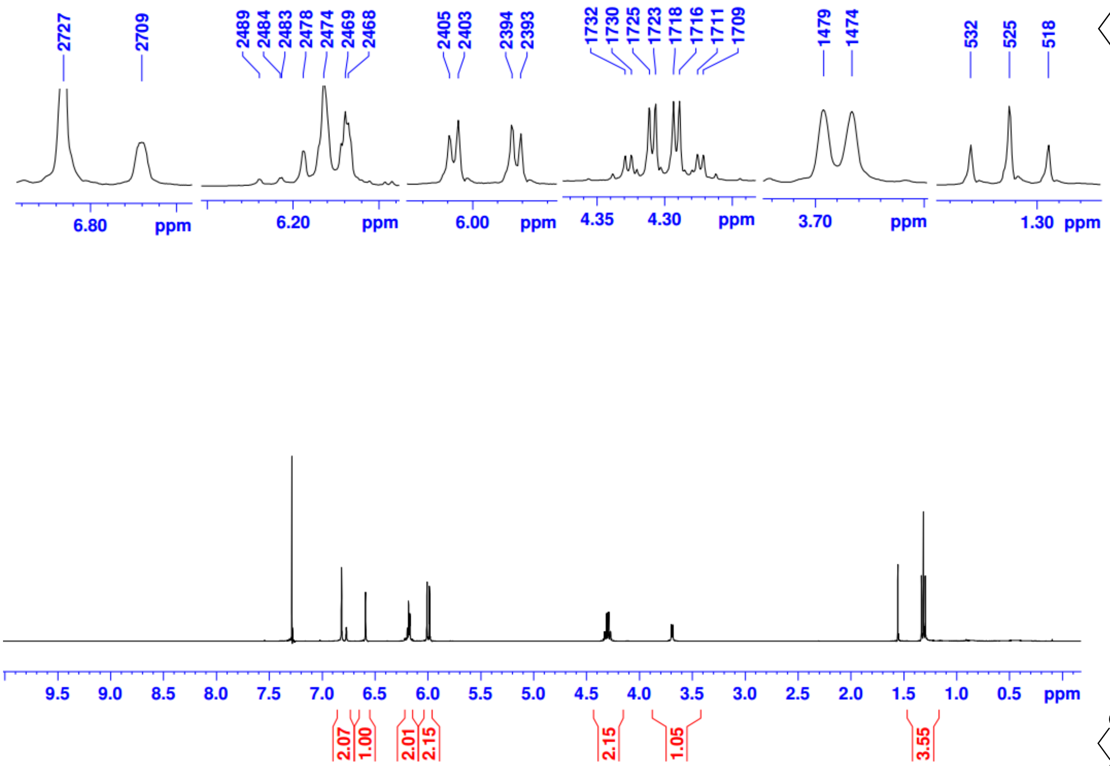


39, HSQC

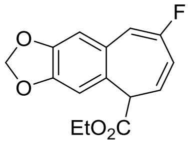


39, HMBC

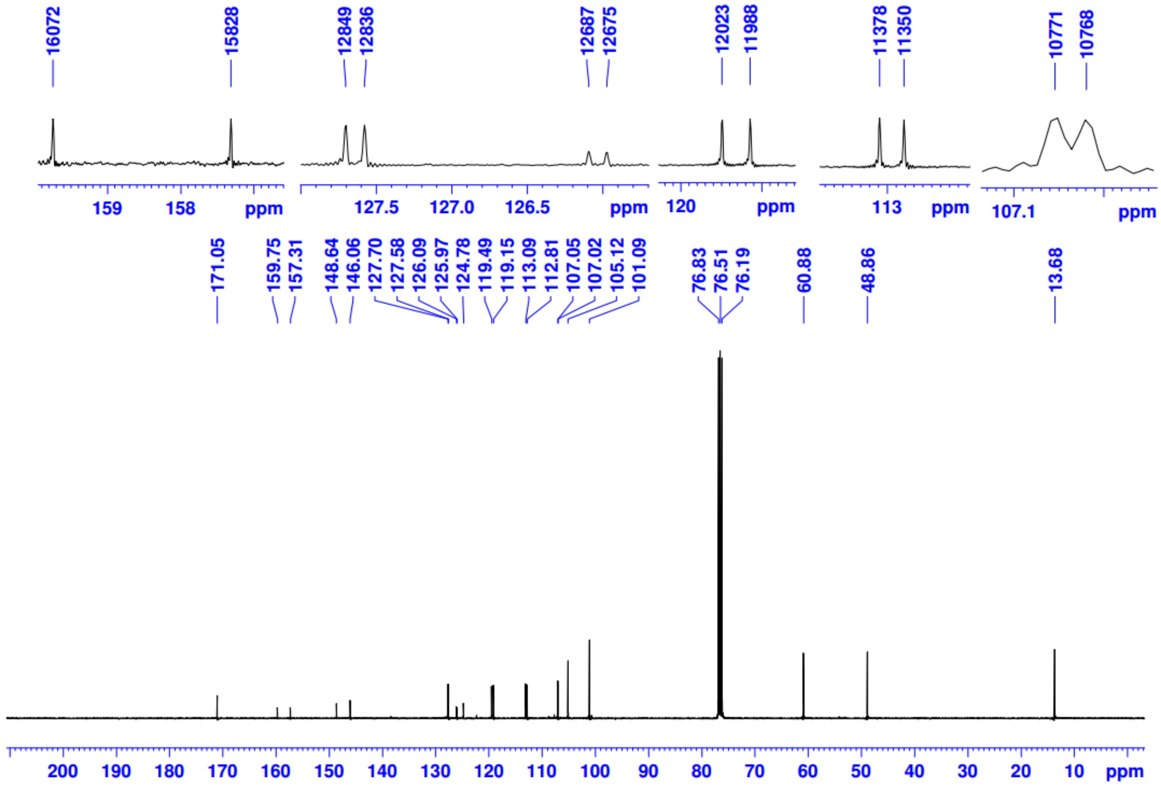


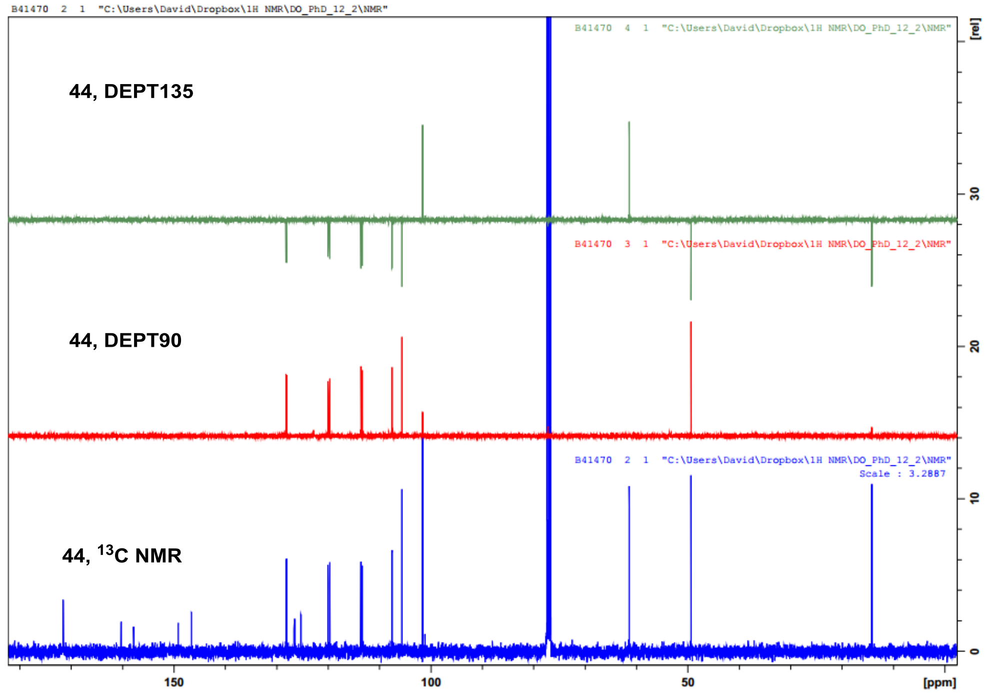


44, ^{1}H NMR



44, ^{13}C NMR

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44, DEPT135
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44, DEPT90
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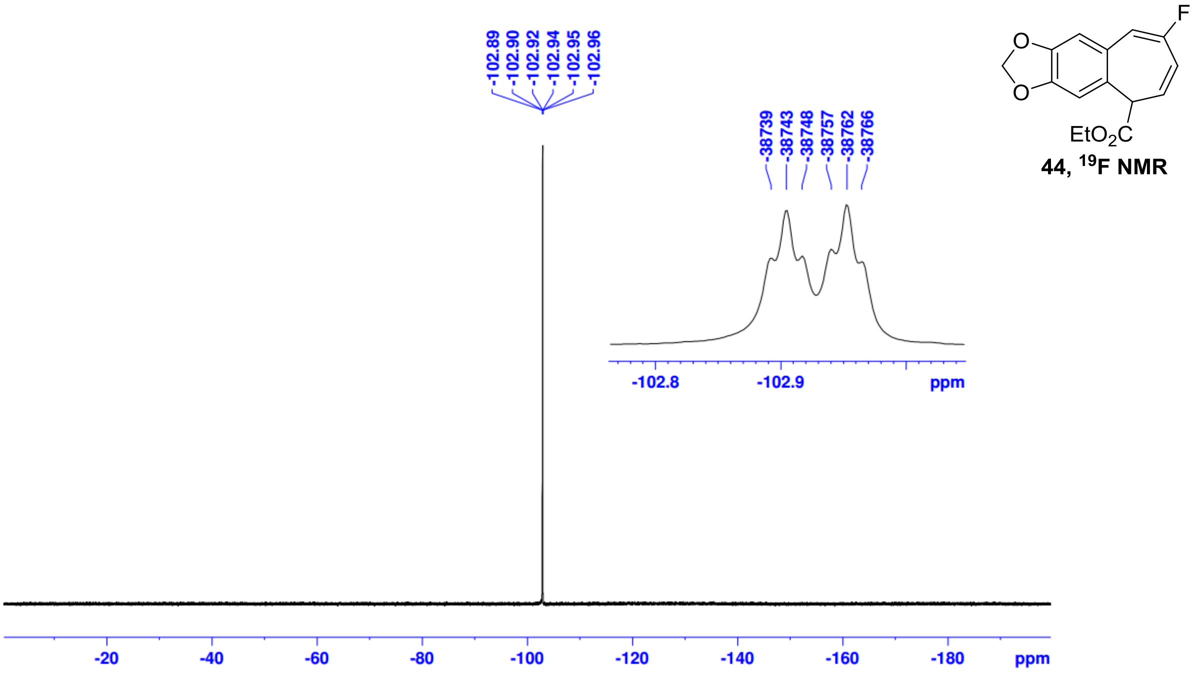
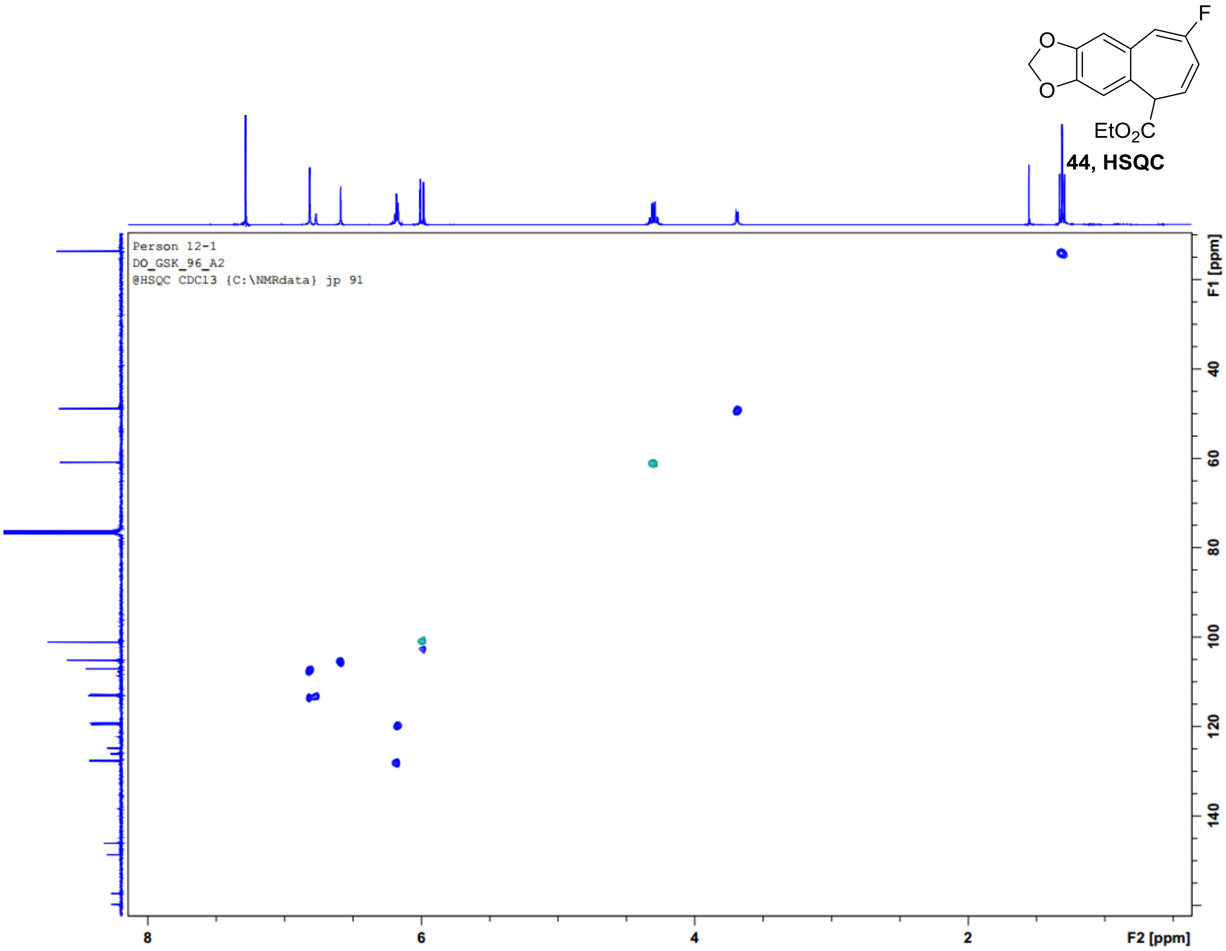
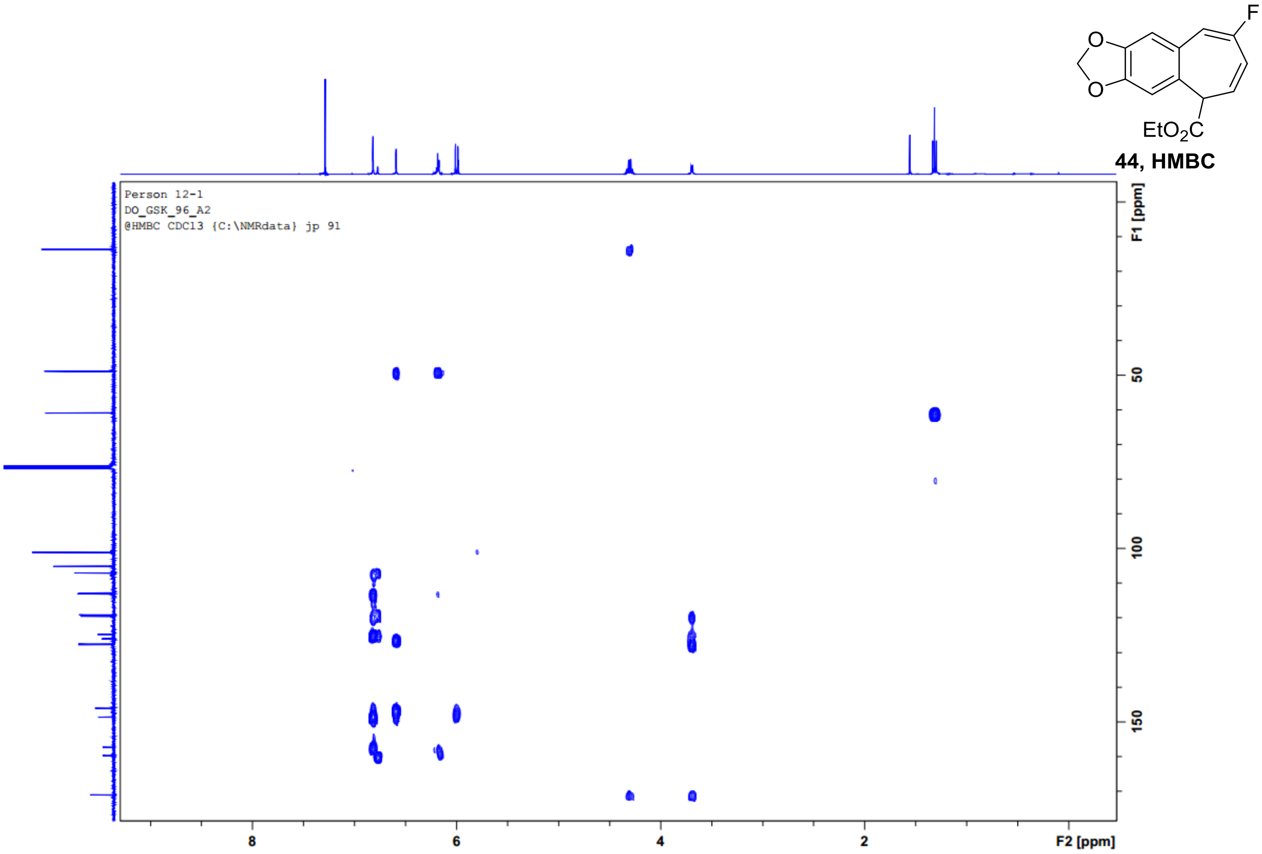
44, ^{13}C NMR
150
100
50
[ppm]
[rel]
30
20
10
0

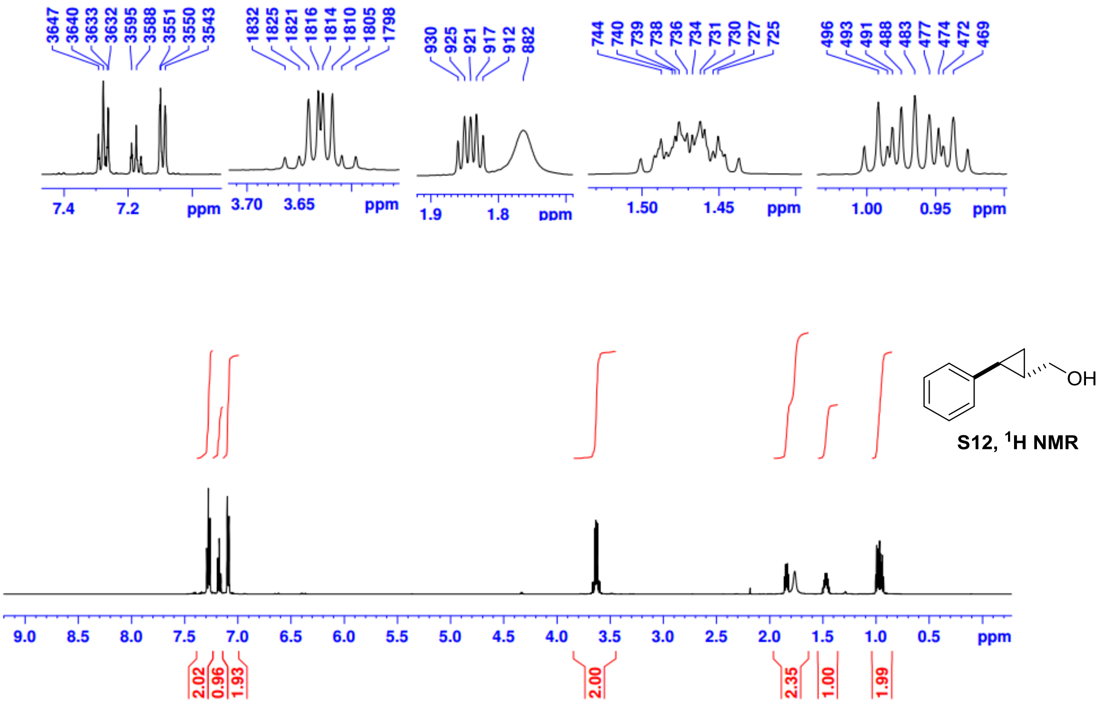

-102.89
-102.90
-102.92
-102.94
-102.95
-102.96
-38739
-38743
-38748
-38757
-38762
-38766
-102.8
-102.9
ppm
F
O
O
EtO$_2$C
44, ^{19}F NMR
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm



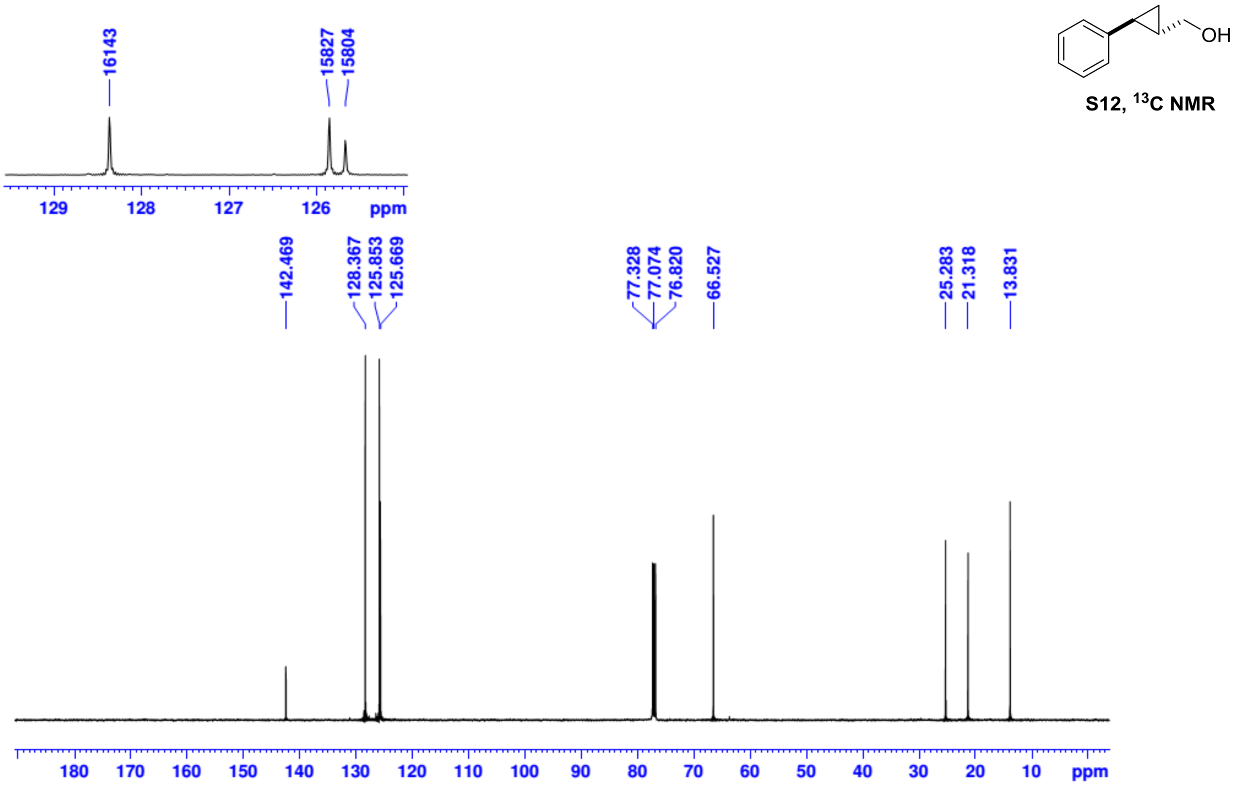
44, HSQC



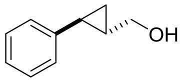
44, HMBC



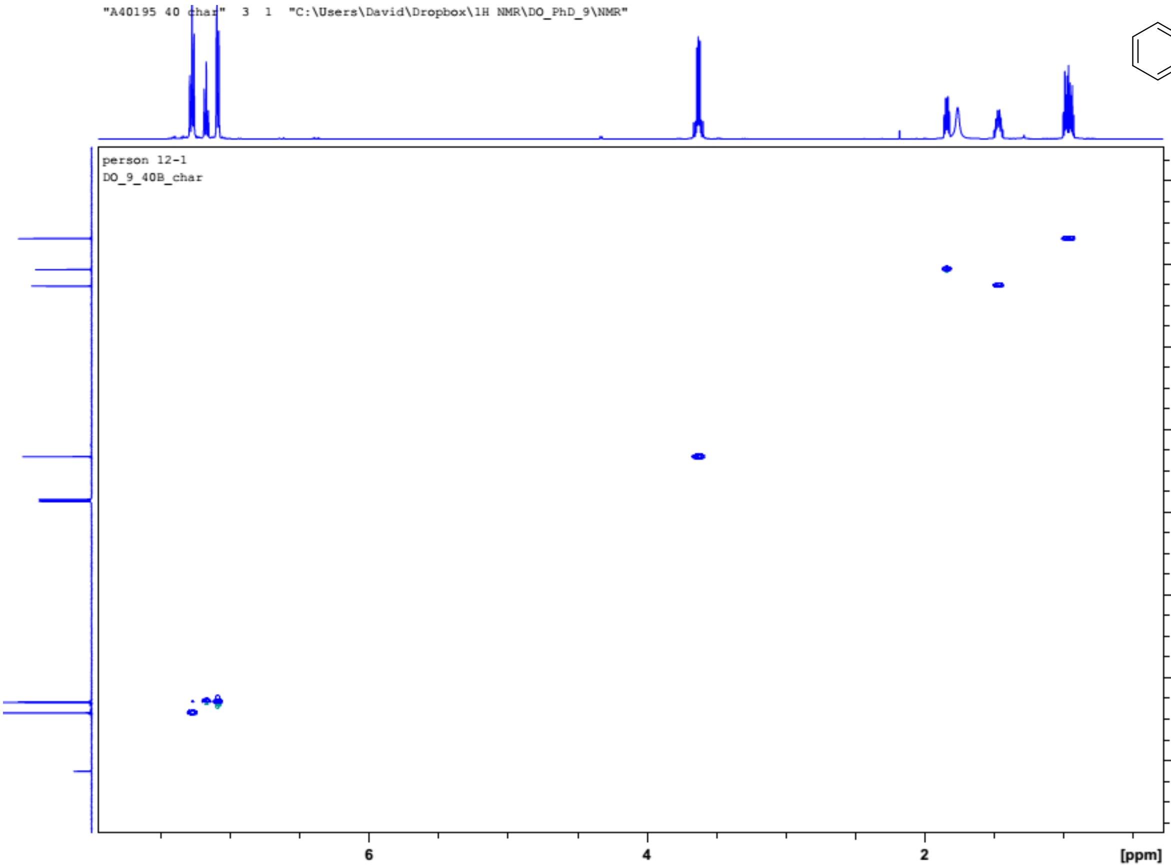
S12, ^{1}H NMR

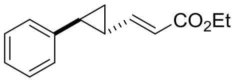


S12, ^{13}C NMR

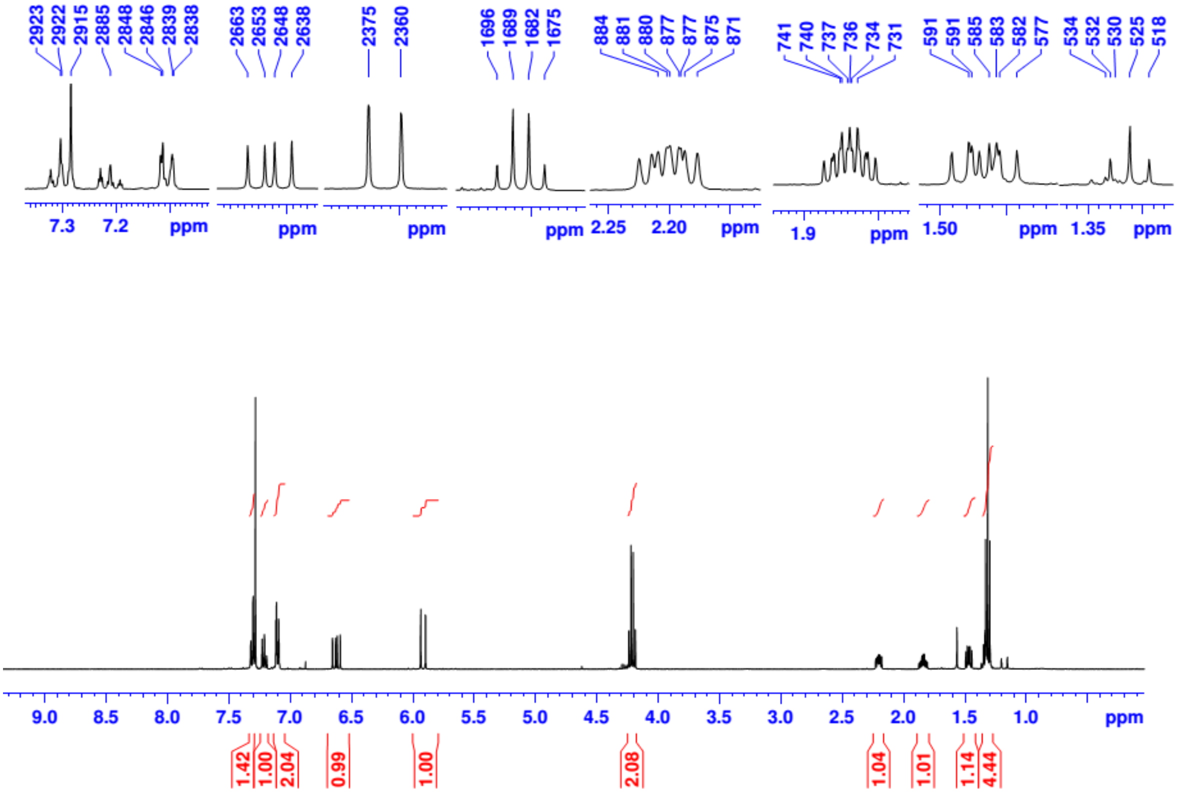


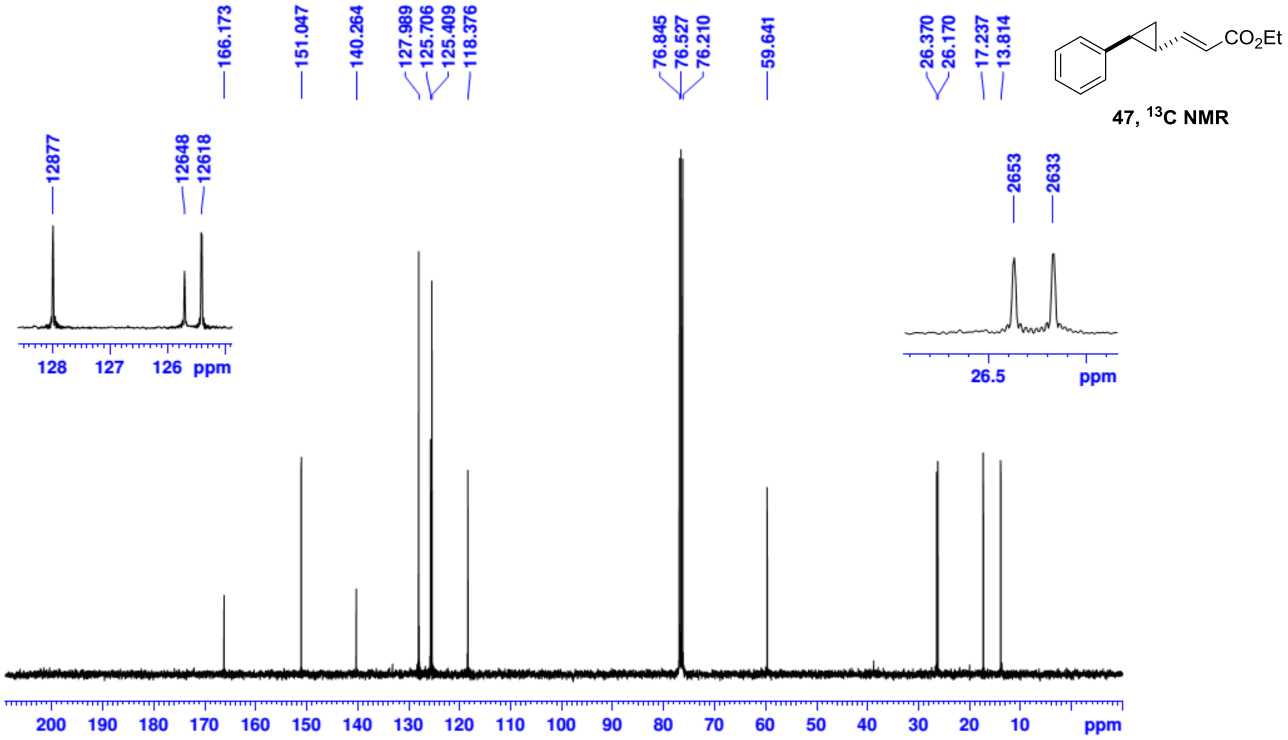
S12, HSQC



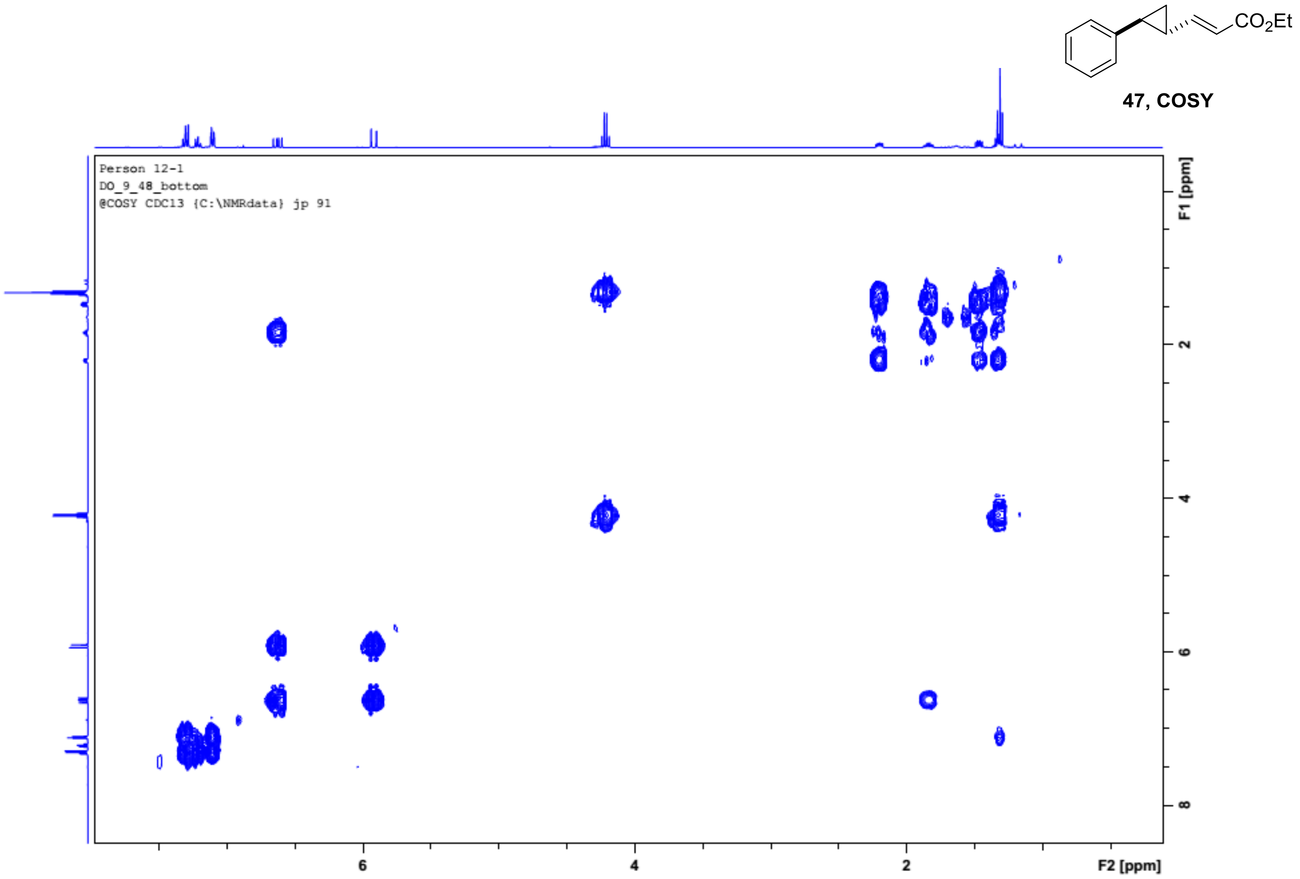


47, ^{1}H NMR

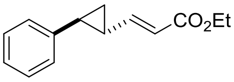




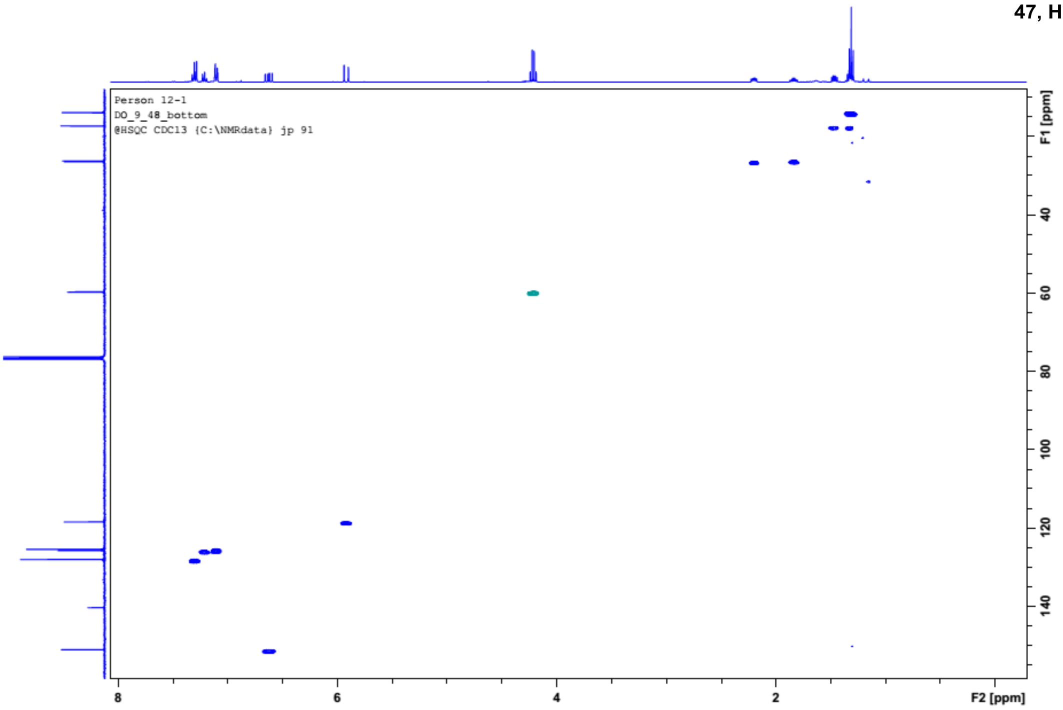
47, ^{13}C NMR

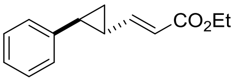


47, COSY

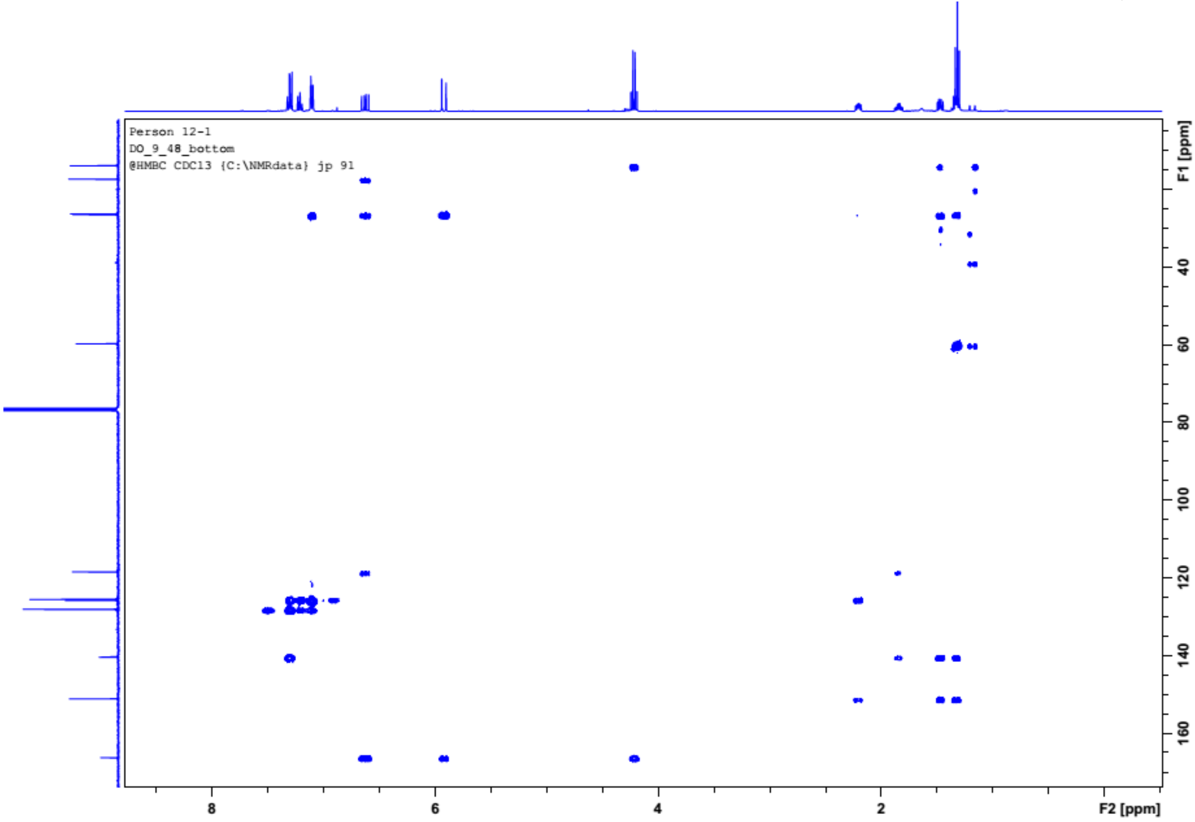


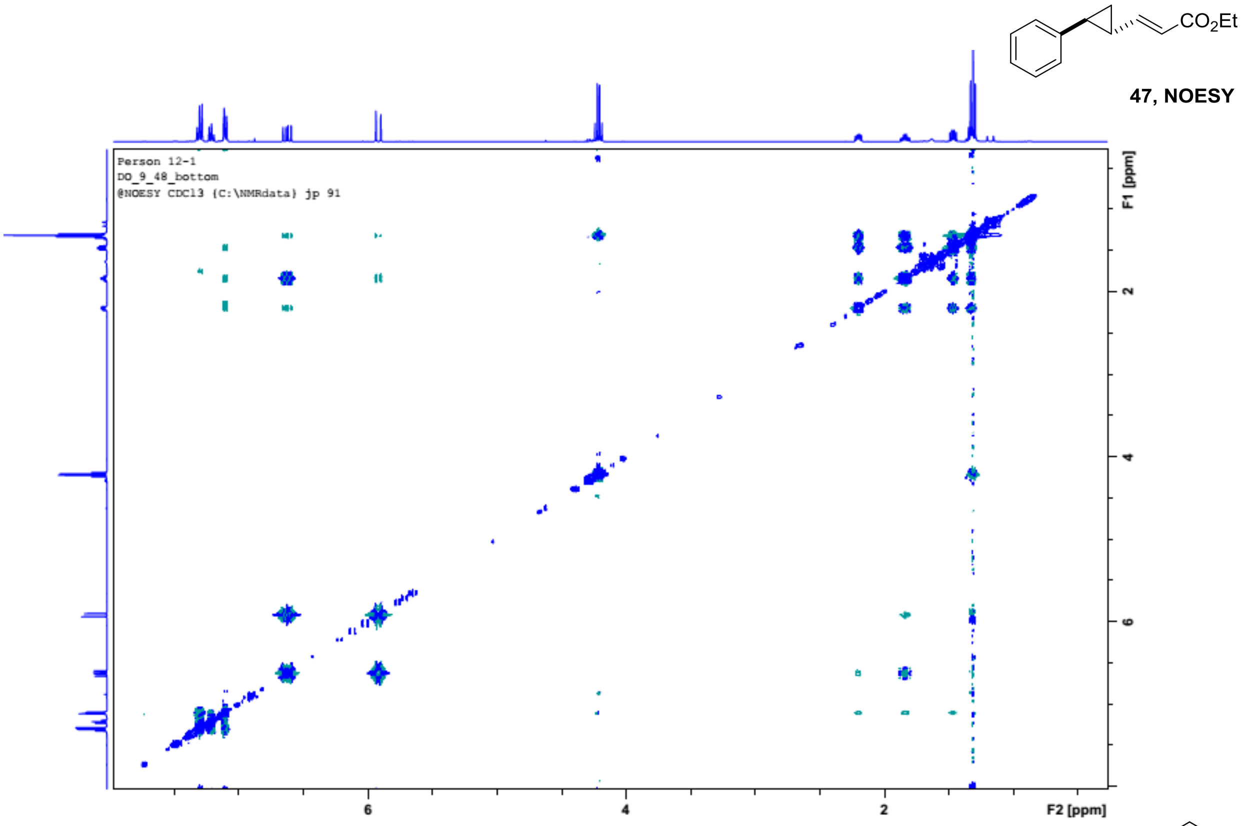
47, HSQC



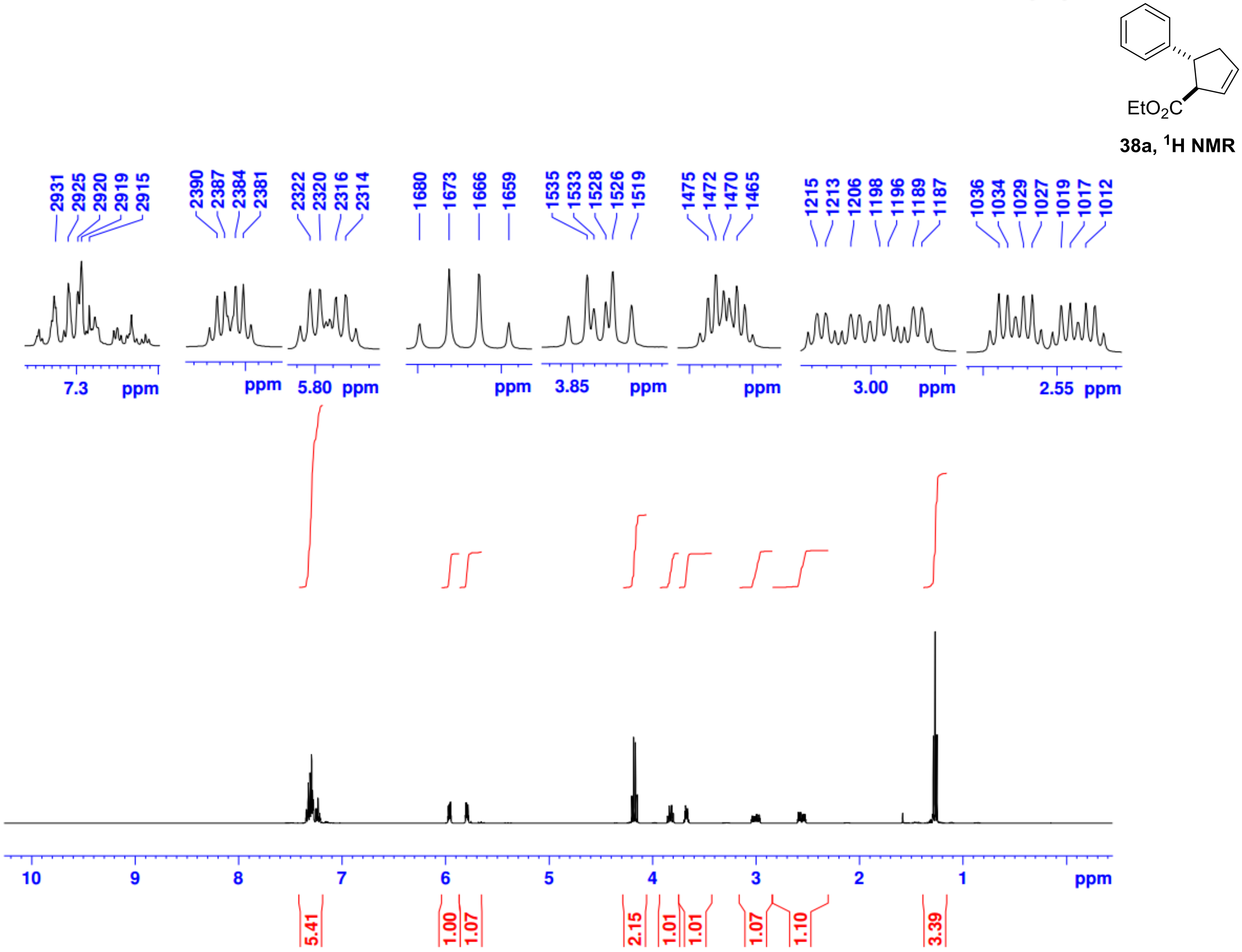


47, HMBC

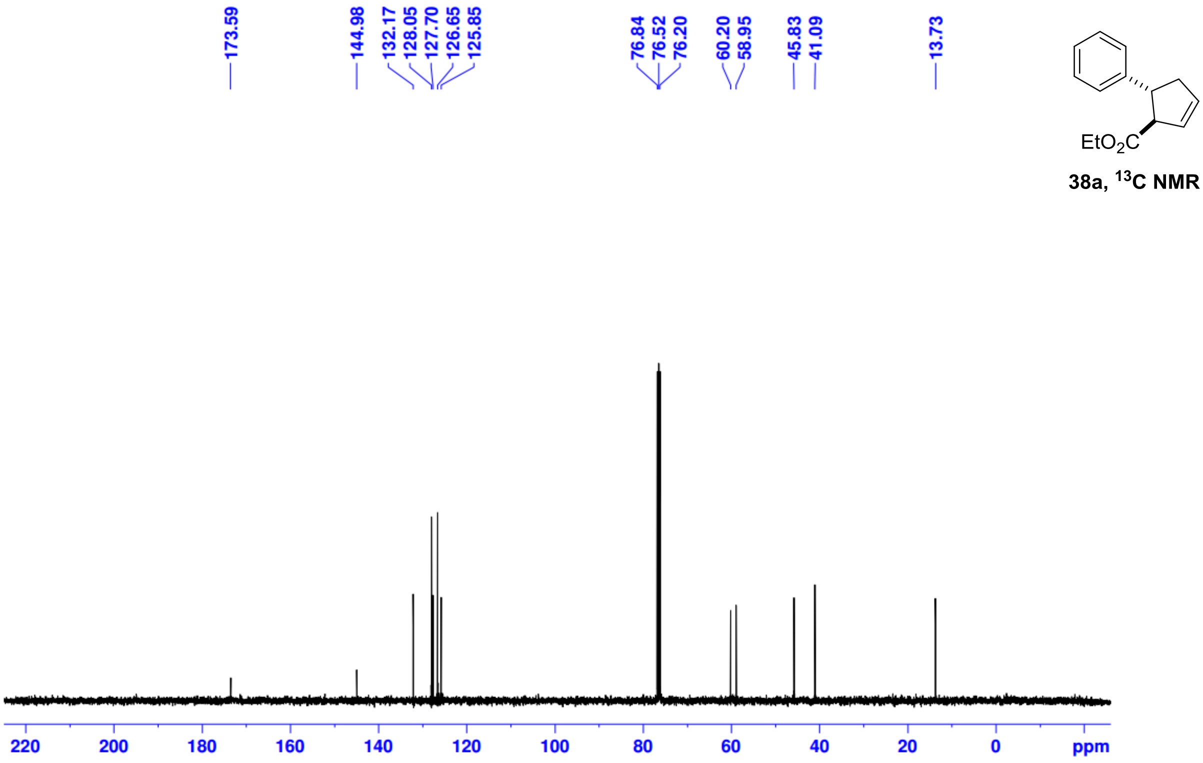




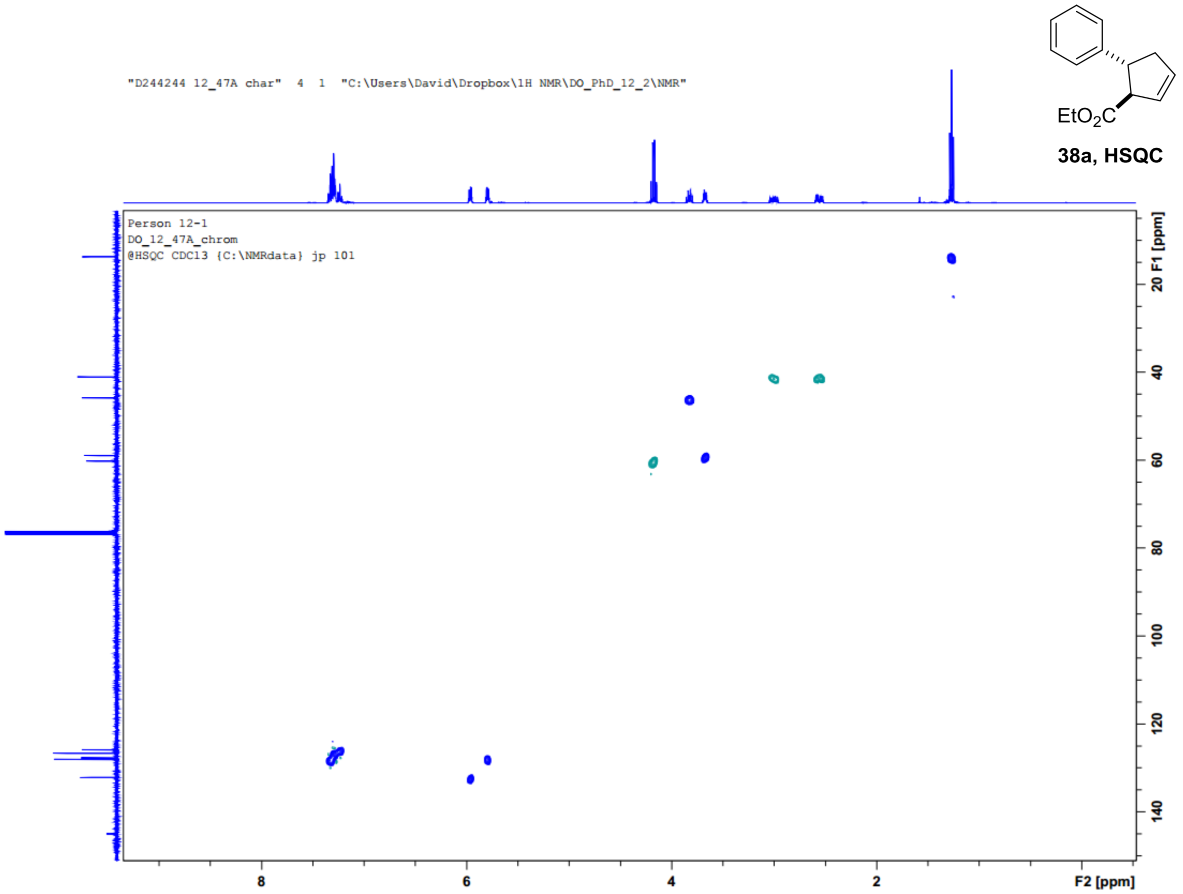
47, NOESY



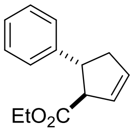
38a, ^{1}H NMR



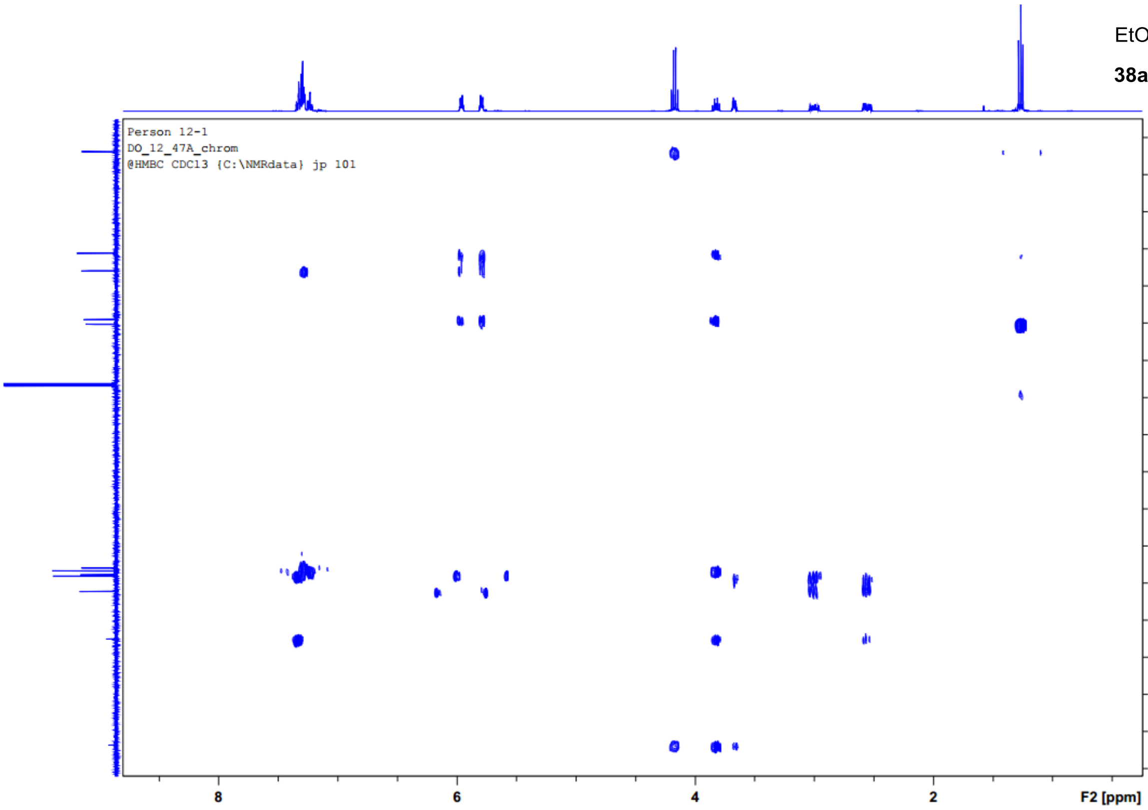
38a, ^{13}C NMR

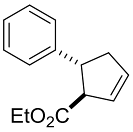


38a, HSQC

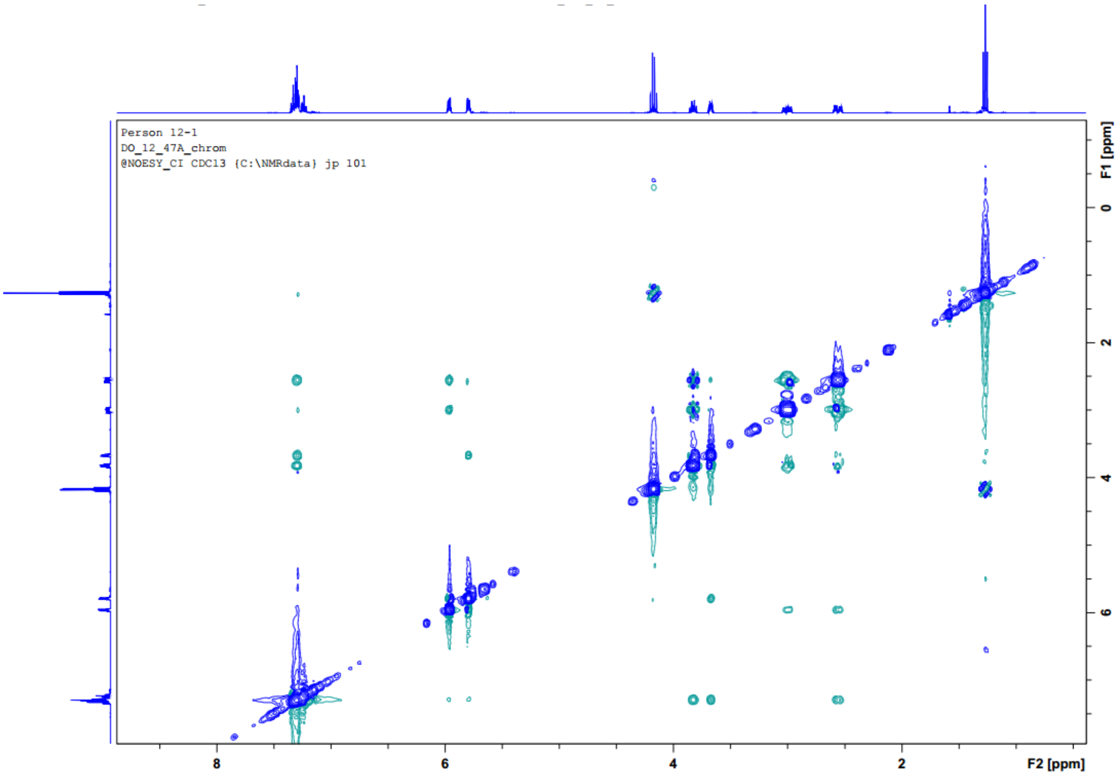


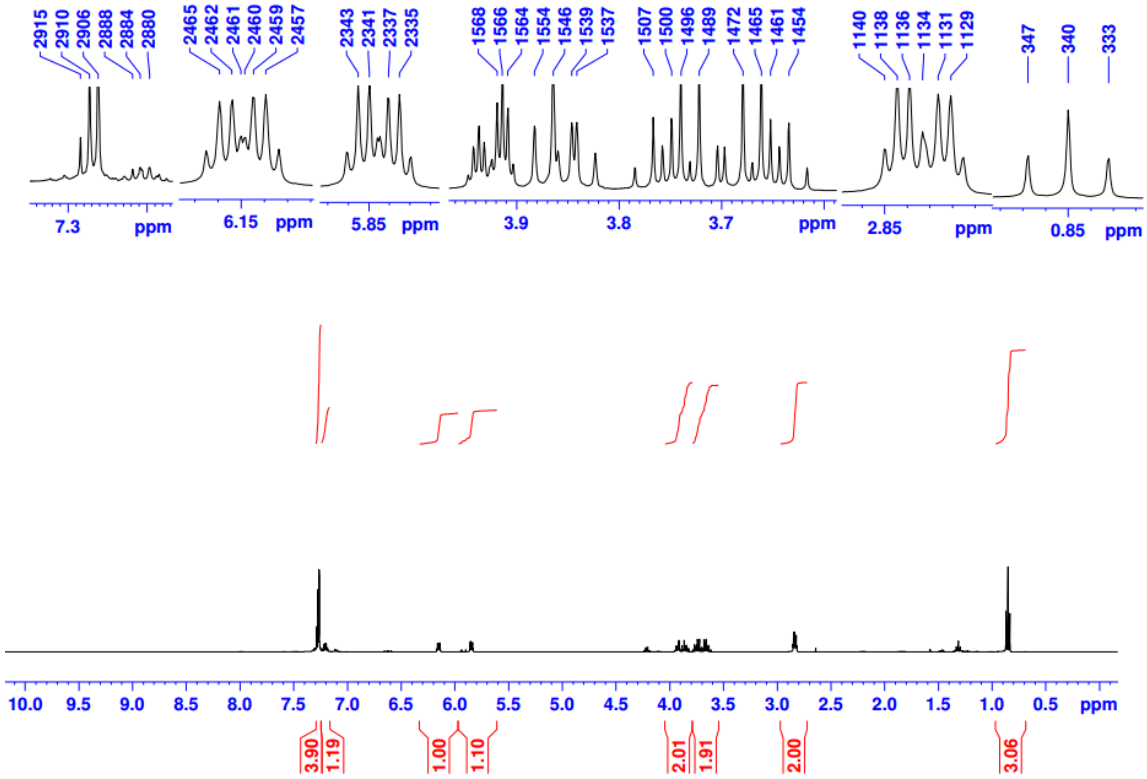
38a, HMBC

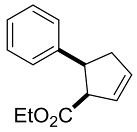




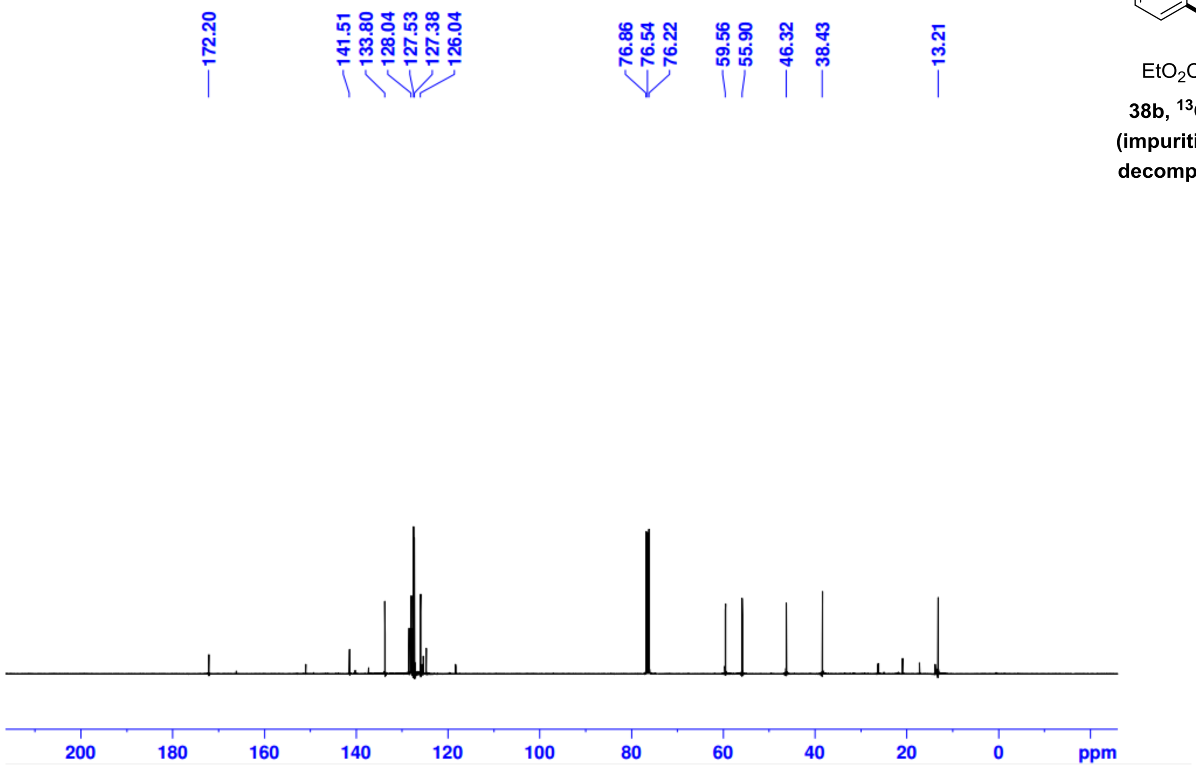
38a, NOESY
no Et-Ar through
space interactions
***trans*-relationship**

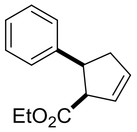




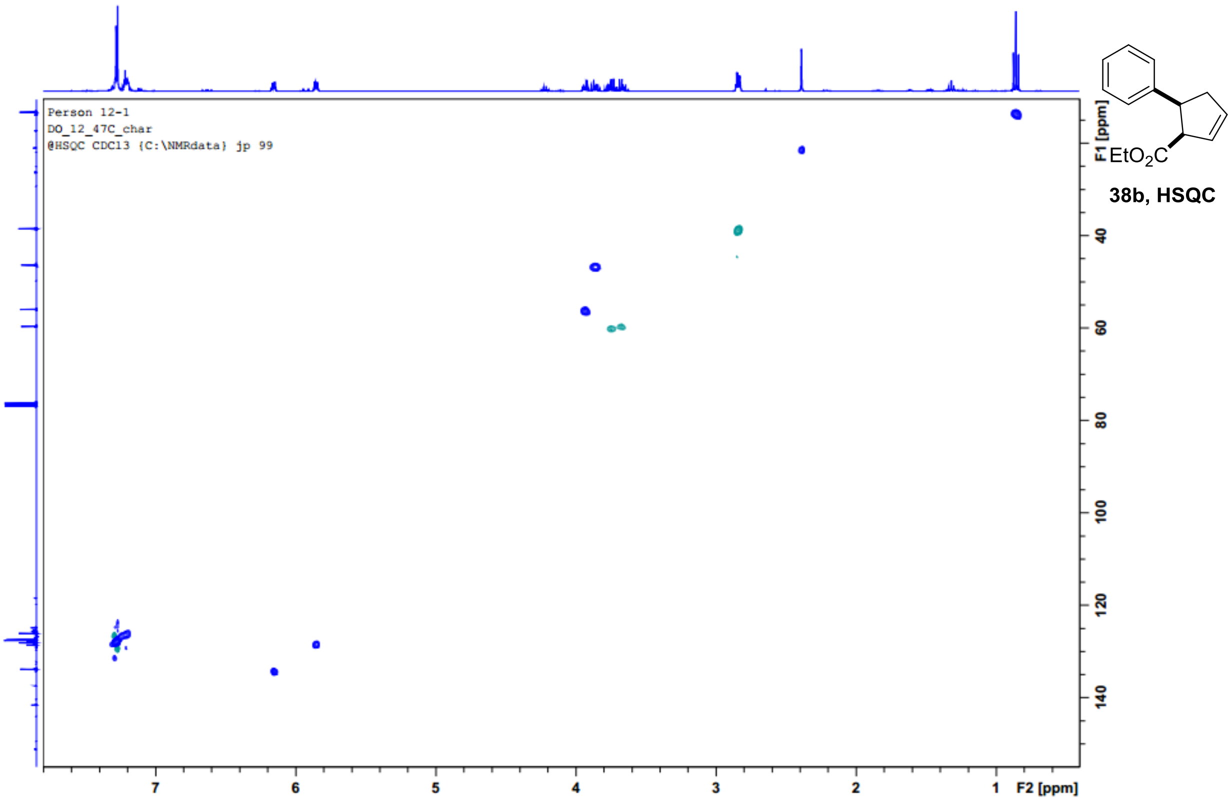


38b, ^{1}H NMR

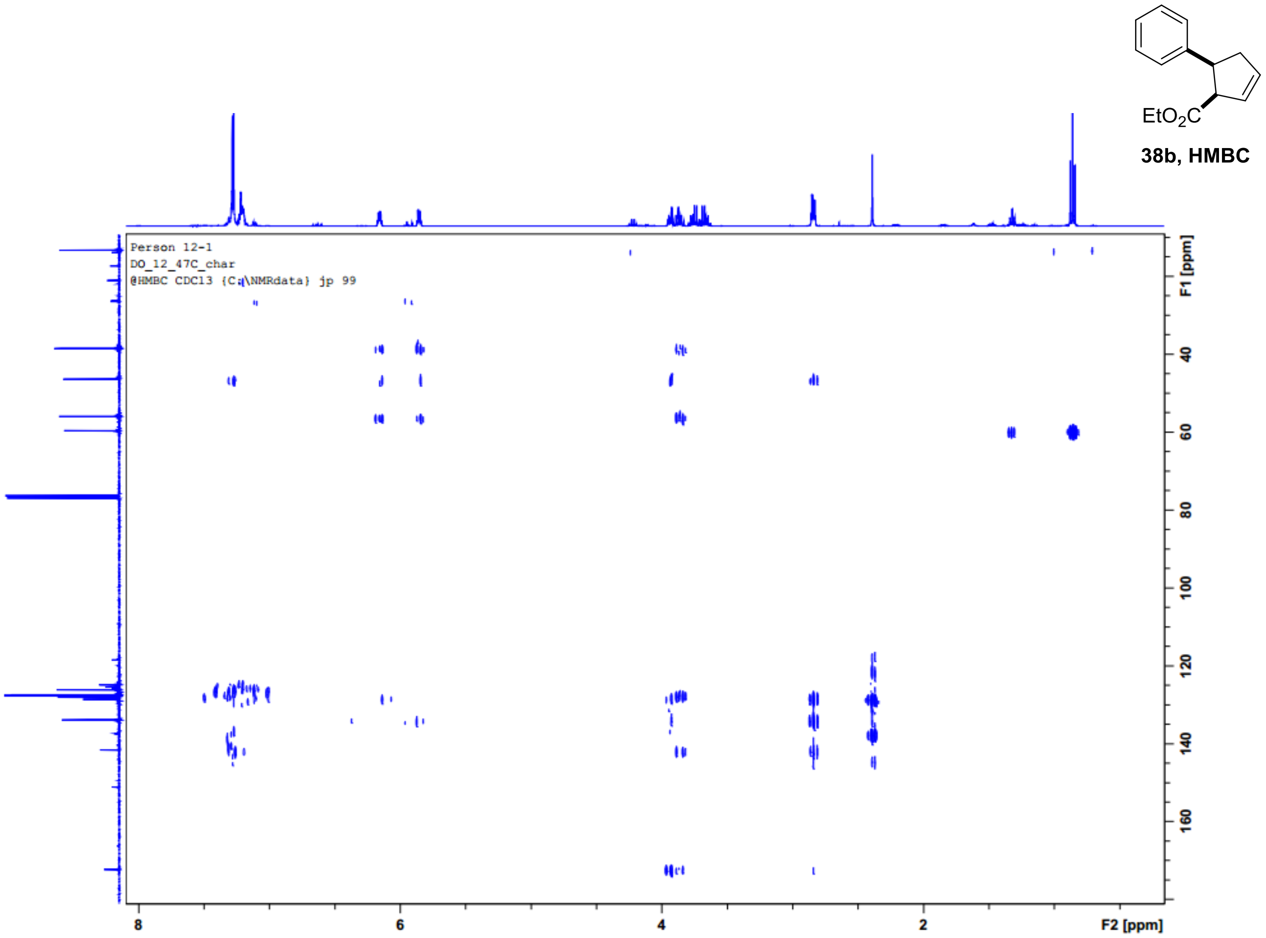




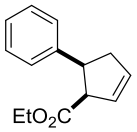
38b, ^{13}C NMR (impurities from decomposition)



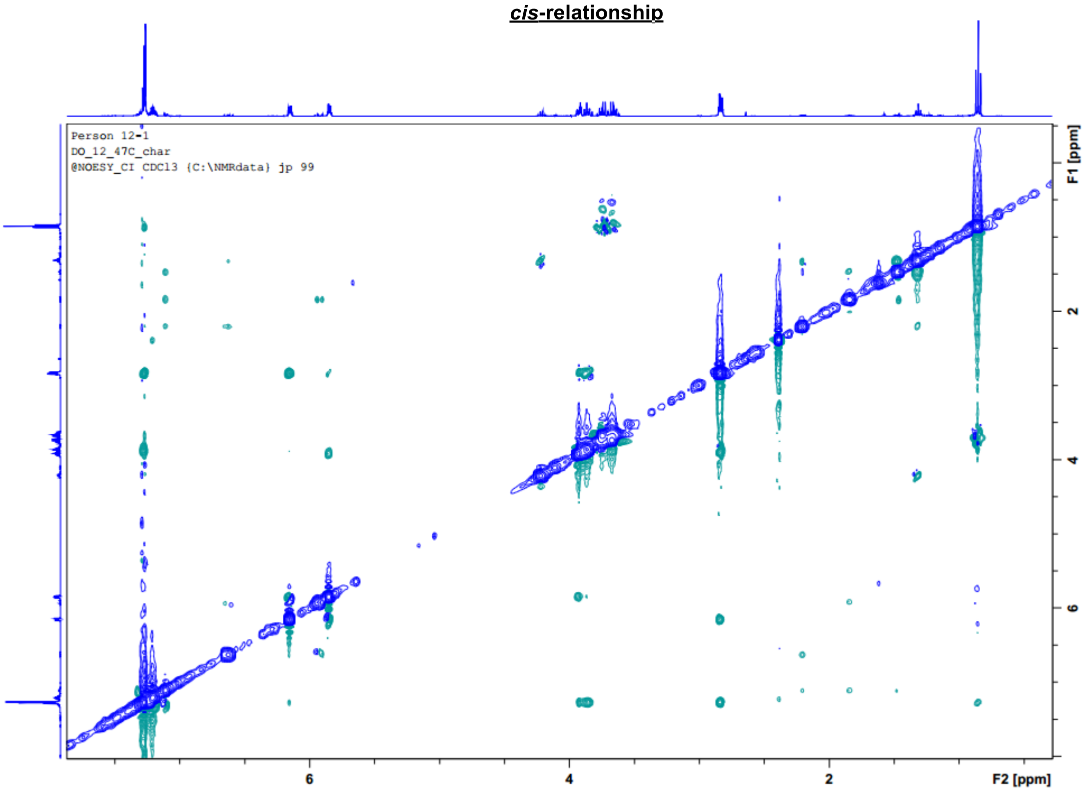
38b, HSQC



38b, HMBC



38b, NOESY
observed Et-Ar through
space interactions
<u>*cis*-relationship</u>



Decomposition Evidence for Furyl Vinyl Acetate 14a

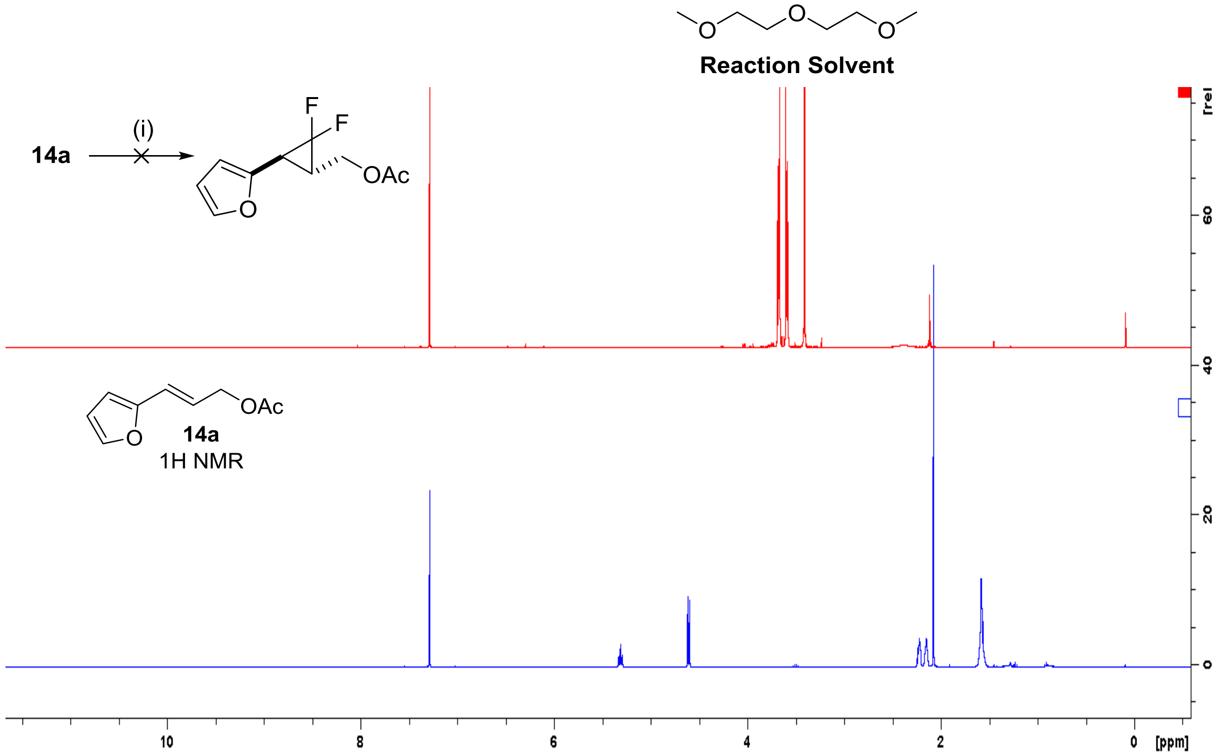


Figure S4: Overlay of ^{1}H NMR spectra representing 2-furyl vinyl acetate **14a** (bottom) and the resulting crude mixture from the failed difluorocyclopropanation. Conditions: (i) MDFA (2.5 eq.), TMSCl (2.5 eq.), KI (2.8 eq.), digylme (1.17 eq.), 120 °C, 24 h.

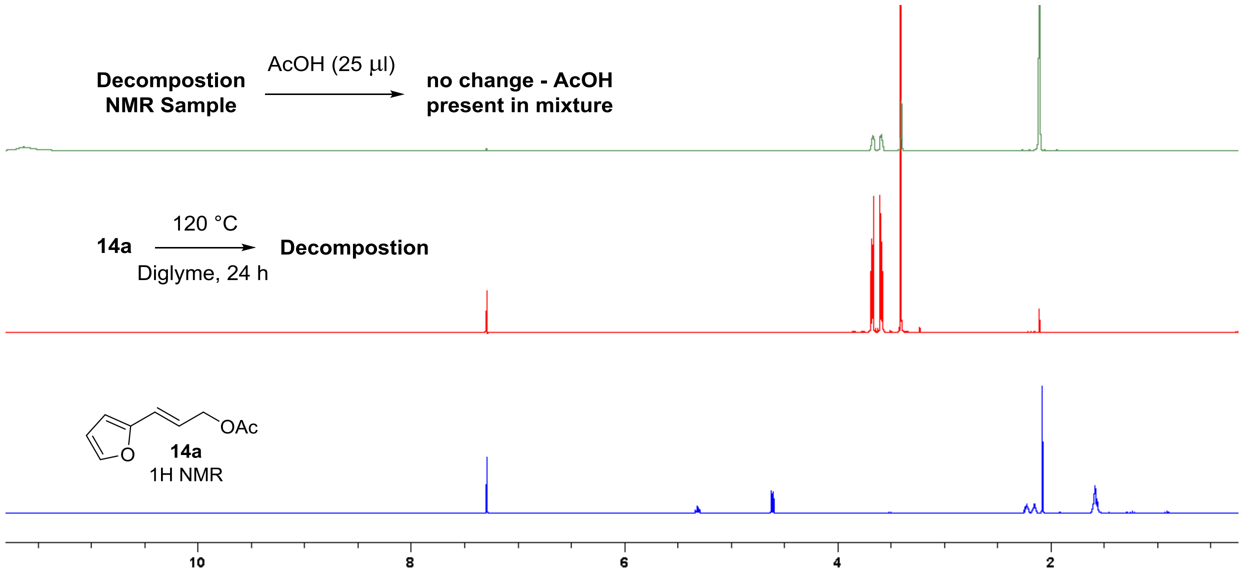
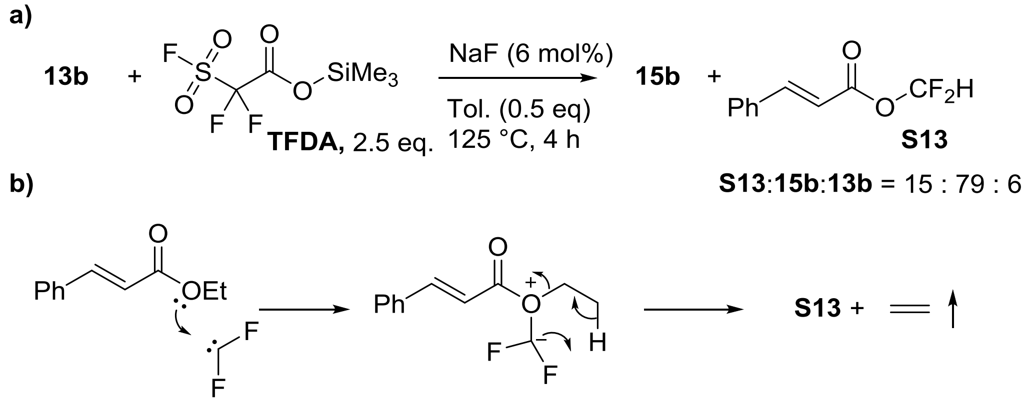


Figure S5: Overlay of ^{1}H NMR spectra representing 2-furyl vinyl acetate **14a** (bottom), resulting mixture after heating **14a** at 120 °C for 24 hours (middle) and spiking the middle NMR sample with 25 µl of AcOH which showed no change suggesting that the AcOH was the only visible side product from the decomposition experiment (top).

Difluorocyclopropanation of Ethyl Cinnamate

Both synthesised and commercial ethyl cinnamate **13b** gave similarly low conversion after difluorocyclopropanation (28% and 29%, respectively) so we were confident that there were no side products from the previous olefination step which were responsible for the poor conversion (**Table 3**, Entries 2-3). Again, slightly higher conversions could be obtained by decreasing the reaction time to 4 hours (**Table 3**, Entry 4, 37% conversion) but **15b** could not be separated from **13b** using either chromatography or distillation. Under the same conditions, cinnamyl acetate (**14b**) had given 100% conversion to the desired difluorocyclopropane.[S20] The dramatic reactivity difference between **14b** and **13b** can be attributed to increased electron-deficiency of the alkene in **13b**. Selectivity experiments carried out by Dolbier and co-workers showed that difluorocarbene addition to a 1:1 mixture of butyl acrylate and 1-octene favoured the latter at 120 °C (product ratio of 1:3.3), consistent with the lower reactivity observed for **13b**.[S22] Other literature methods[S23,24] using commercial reagents were previously unsuccessful when used for the difluorocyclopropanation of cinnamyl acetate (**14b**)[S20] and were therefore not investigated for these less reactive alkenoates.

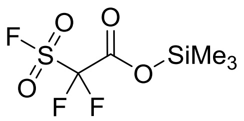
Dolbier and co-workers reported more success in the synthesis of **15b** using alternative MDFA conditions (64%, ^{19}F NMR conversion);[S25] we were able to replicate their results (69% ^{1}H NMR conversion) but felt that the longer reaction time of 48 hours would be detrimental to the product recovery of the more reactive alkenoates. Higher conversion of 81% was achieved for this substrate by the same group using trimethylsilyl 2,2-difluoro-2-(fluorosulfonyl)acetate (TFDA) as the difluorocarbene precursor but it is unclear if this is an isolated or NMR yield.[S22] This reagent is less practical than others since it is prone to hydrolysis; purification is necessary before every reaction. We observed similar conversion with TFDA (79%, determined by ^{1}H NMR) but the isolation of synthetically useful quantities of **15b** proved difficult due to the presence of starting alkenoate **13b** and the previously unreported difluoromethyl ester side product **S13** (**Scheme S4a**, see below for a full discussion on difluorocyclopropanation of **13b** with TFDA). We currently do not have a reason for the formation of **S13** but it is proposed to proceed via a mechanism similar to that of the difluoromethylation of acids reported by Wu and Chen[S26] and driven by the elimination of ethene (**Scheme S4a**).



Scheme 5: a) Difluorocyclopropanation of **13b** using TFDA (ratios determined by ^{1}H NMR). b) Proposed mechanism for the formation of side product **S13**.

Reported difluorocyclopropanation methodologies are generally screened against a set of simple alkene substrates but reactivity issues are rarely discussed. We have used alkenoates **13a** and **13b** to assess the most reactive procedures in the literature and highlighted the synthetic limitations for electron deficient olefins. For this study, the main purpose of the synthetic investigations was to obtain a range of substituted cyclopropane precursors in order to test computational predictions. No further screening of conditions was carried out, but recent synthetic advances with metal-mediated difluorocyclopropanation reported by Ichikawa and co-worker, look to be a more promising method for the synthesis of difluorocyclopropyl esters **15b**.[S27]

Preparation of trimethylsilyl 2,2-difluoro-2-(fluorosulfonyl)acetate (S14)



S14

A mixture of chlorotrimethylsilane (4.9 mL, 38.8 mmol) and commercial trimethylsilyl 2,2-difluoro-2-(fluorosulfonyl)acetate (TFDA, **S14**, 1 mL, 9.7 mmol, 80% purity determined by ^{19}F NMR) was refluxed (110 °C) for 1 hour under an atmosphere of argon. The reaction mixture was cooled to room temperature and the water condenser was replaced with an oven dried distillation apparatus and the glassware cooled under an atmosphere of argon. Excess TMSCl was removed (90 °C, 600 mbar) and the residual **S14** was stored under argon at room temperature. The ^{19}F NMR spectrum of the residue confirmed reagent purity at > 95% and **S14** used immediately for a difluorocyclopropanation reaction. ^{19}F NMR (376 MHz, CDCl$_3$): δ = -41.2 (dd, *J* = 4.6, 4.2 Hz, *F*SO$_2$CF$_2$, 1F), -103.1 ppm (d, *J* = 4.4 Hz, FSO$_2$C*F*$_2$, 2F). The data was in agreement with that reported by Tian and co-workers.[S28]

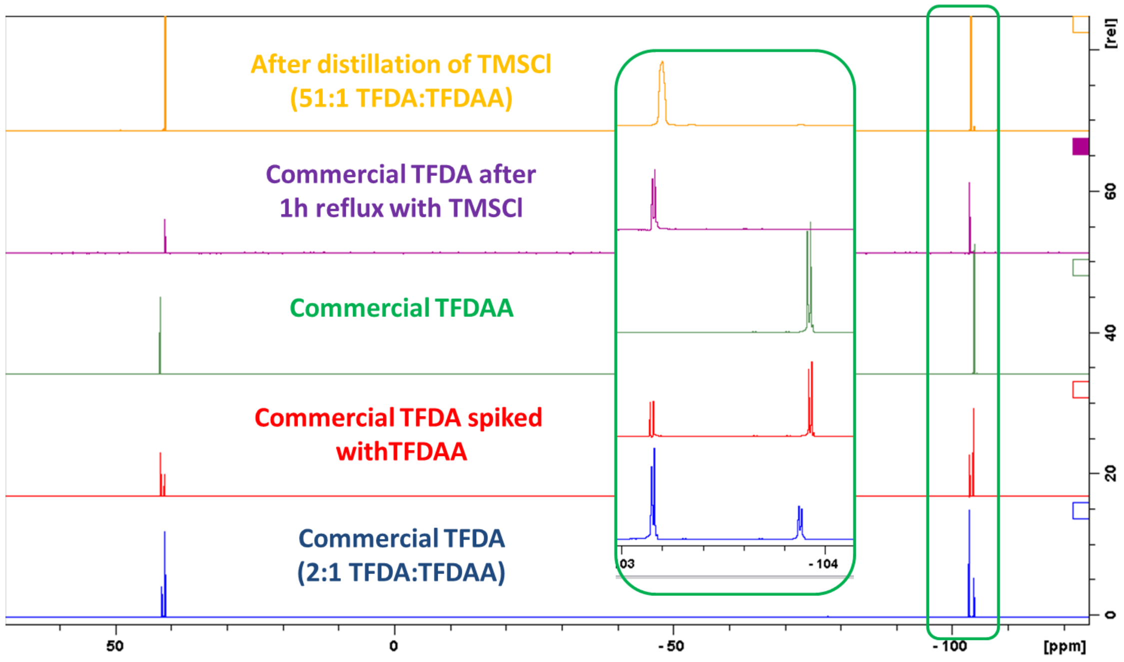


Figure S6: ^{19}F NMR analysis of the synthesis and purification of TFDA.

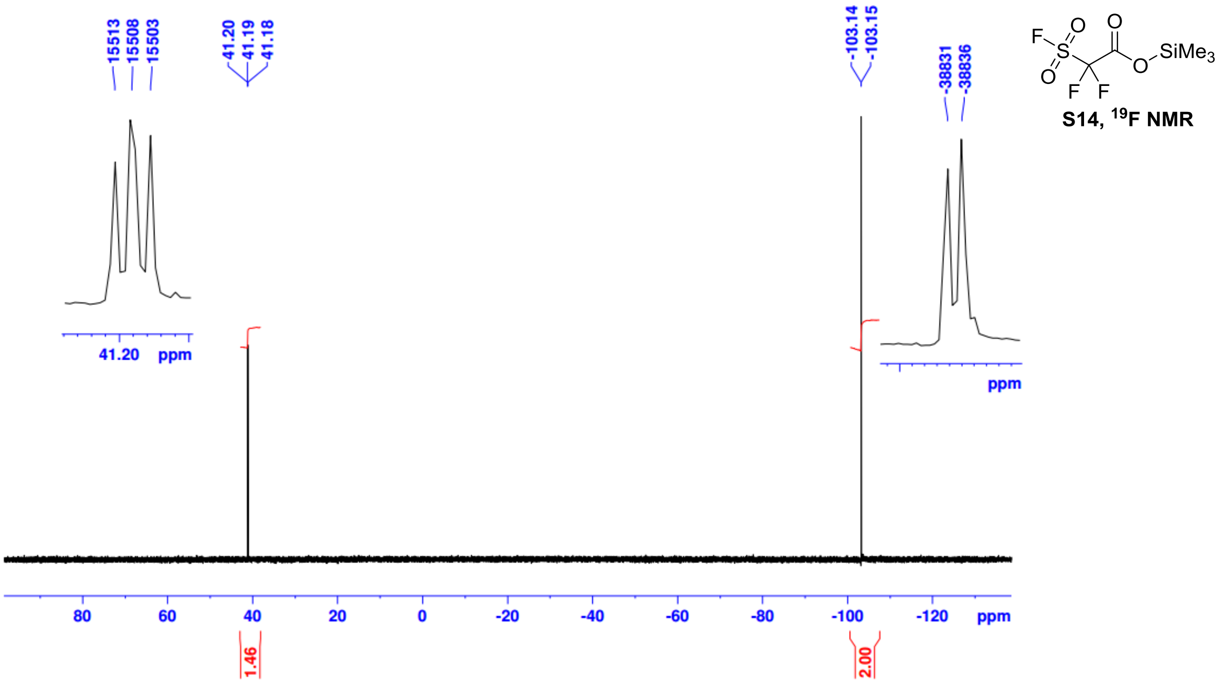
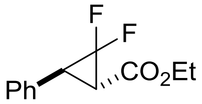


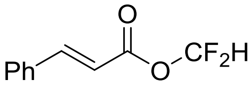
Figure S7: ^{19}F NMR for clean TFDA used in difluorocyclopropanation reaction.

Attempted difluorocyclopropanation of ethyl cinnamate with TFDA



15b

+



S13

An oven dried two-necked round bottom flask containing sodium fluoride (7 mg, 0.17 mmol) was sealed with a SubaSeal, and the salt was stirred and lightly flame dried under an atmosphere of argon. A low boiling point water condenser with a gas outlet connected to an argon/vacuum manifold was attached to the reaction flask and the atmosphere was purged three times. Ethyl cinnamate (0.48 mL, 2.84 mmol) followed by toluene (0.15 mL, 1.42 mmol) were added and the colourless suspension was heated to 125 °C. Once the reaction temperature had been reached, freshly distilled TFDA (1.4 mL, 7.1 mmol) was added dropwise over a period of 3 hours using a syringe pump. The mixture was stirred for a further 1 hour (total reaction time of 4 hours). The reaction mixture was cooled to room temperature and the reaction mixture was quenched with addition of water (10 mL) and diethyl ether (10 mL). The organic layer was separated and the aqueous layer was extracted with diethyl ether (4 x 10 mL). The original organic layer and the extracts were combined, dried ($MgSO_4$) and concentrated under reduced pressure to remove volatile materials. The ^1H NMR spectrum of the crude reaction mixture was used to determine the ratio of **13b**, **15b** and **S13**.

A similar crude reaction mixture was purified by column chromatography on silica gel (1:19 to 1:9 Et_2O in hexane) and a mixture of **S13** and **13b** (4:1 ratio determined by NMR) was isolated.

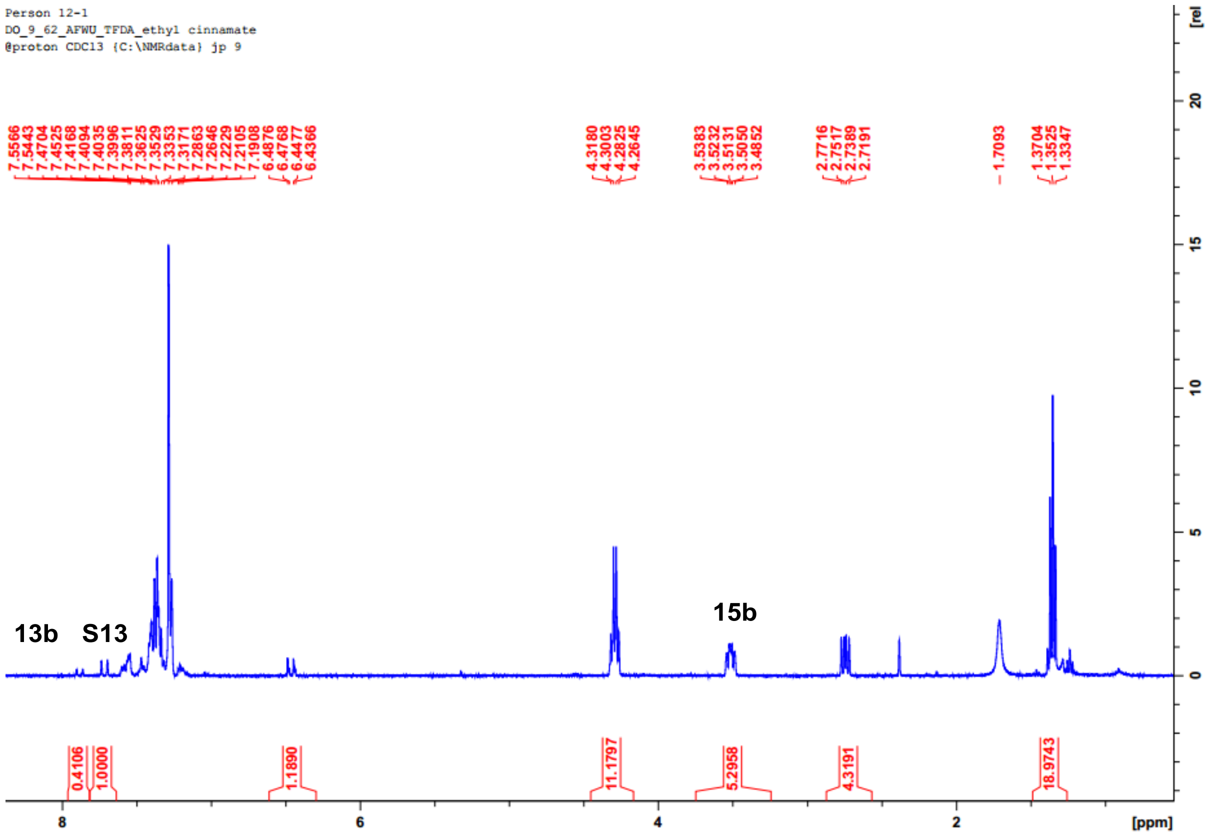
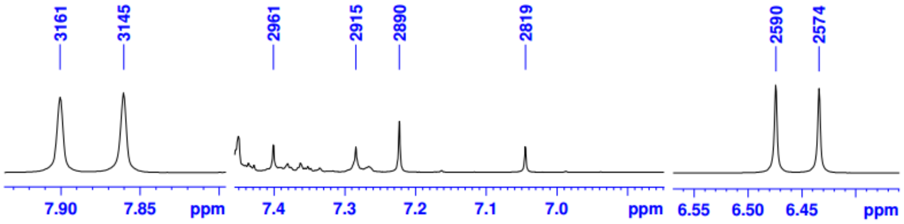
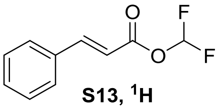


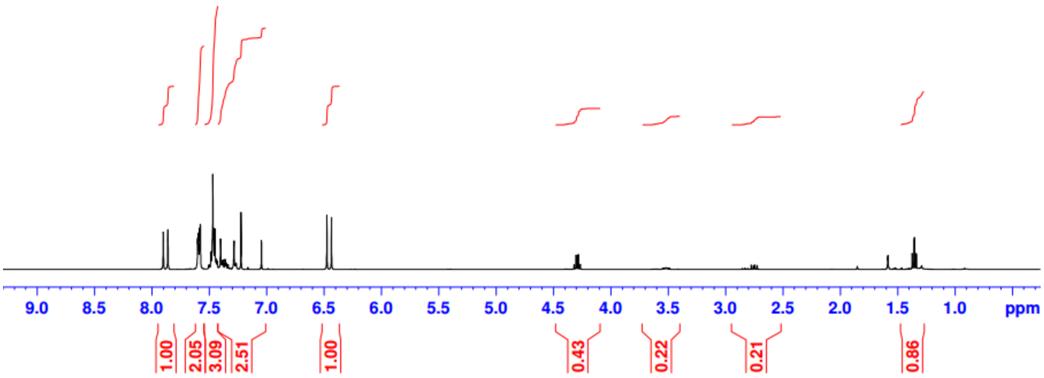
Figure S8: Crude ^{1}H NMR used to relative conversion ratio from TFDA difluorocyclopropanation.

Extracted data for **S13**: R_f = 0.26 (1:4 Et_2O in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, J = 16.0 Hz, ArC*H*=CH, 1H), 7.60-7.58 (m, Ar*H*, 3H), 7.49-7.43 (m, Ar*H*, 2H), 7.22 (t, $^2J_{H\text{-}F}$ = 71.2 Hz, CF_2*H*, 1H), 6.56 ppm (d, J = 16.0 Hz, CH=C*H*CO, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.8 (t, $J_{C\text{-}F}$ = 3.4 Hz), 149.2, 133.6, 131.6, 129.2, 128.8, 115.1, 112.8 ppm (t, $^1J_{C\text{-}F}$ = 257.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -91.4 ppm (d, $^2J_{F\text{-}H}$ = 71.2 Hz); $\bar{\nu}$/(film) = 1738, 1634, 1059, 980 cm^{-1}; MS (CI): *m*/*z* (%): 227 (4) $[M+C_2H_5]^+$, 199 (47) $[M+H]^+$, 157 (6), 131 (100) $[M-OCF_2H]^+$; t_R (GC) = 10.45 minutes.

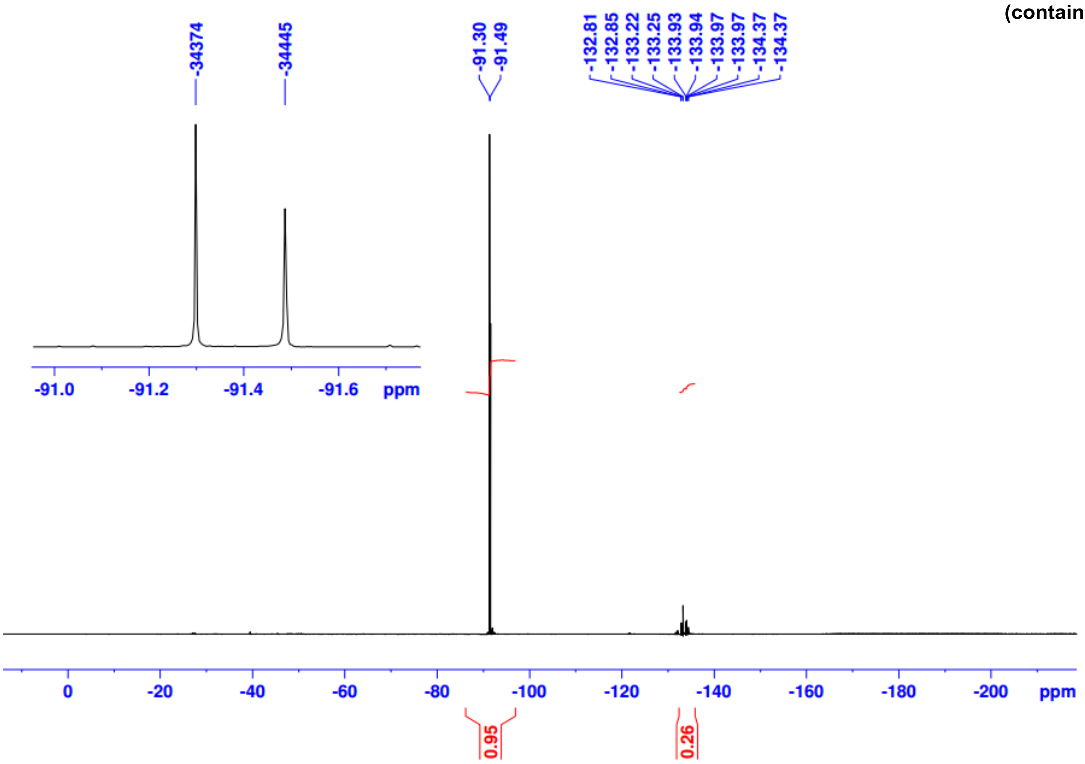


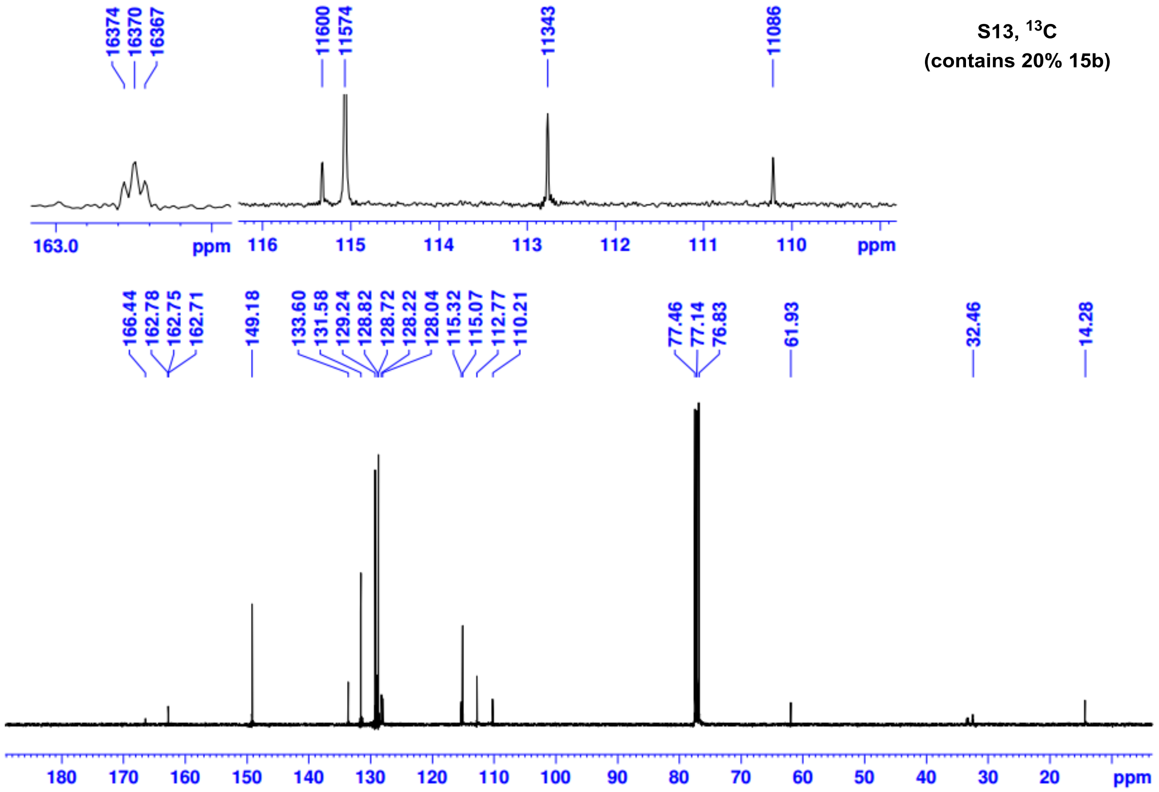


S13, ^{1}H
(contains 20% 15b)

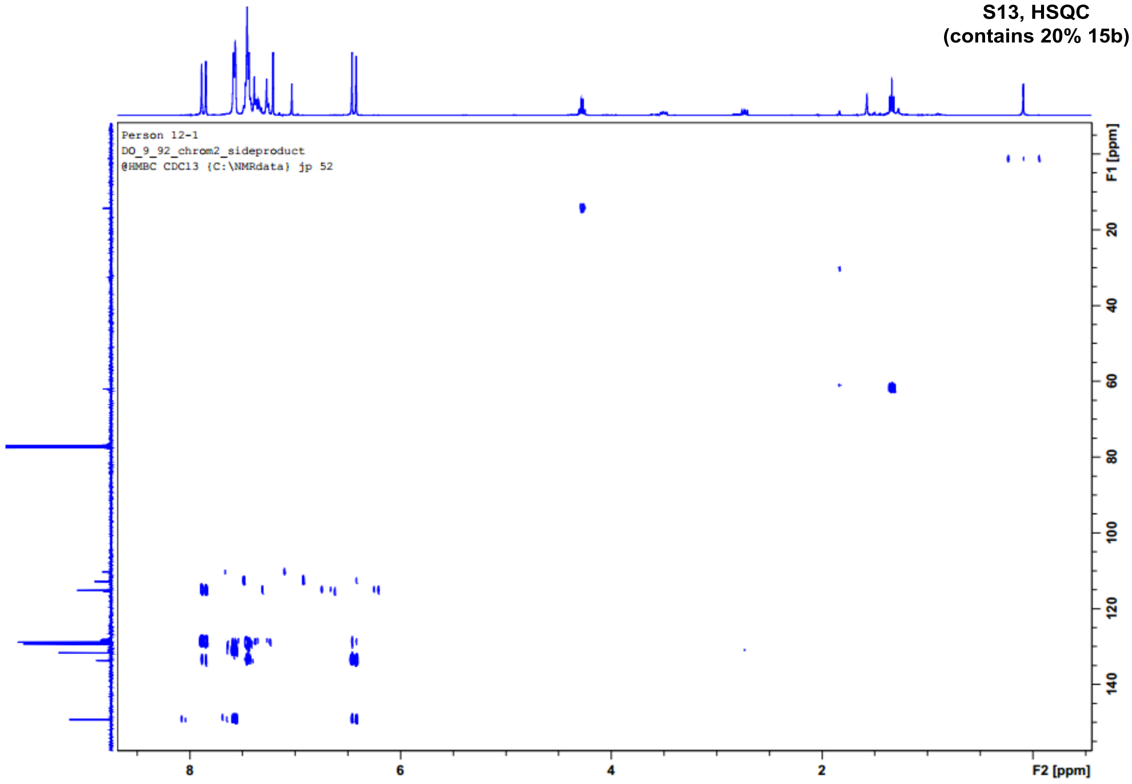


S13, ^{19}F
(contains 20% 15b)



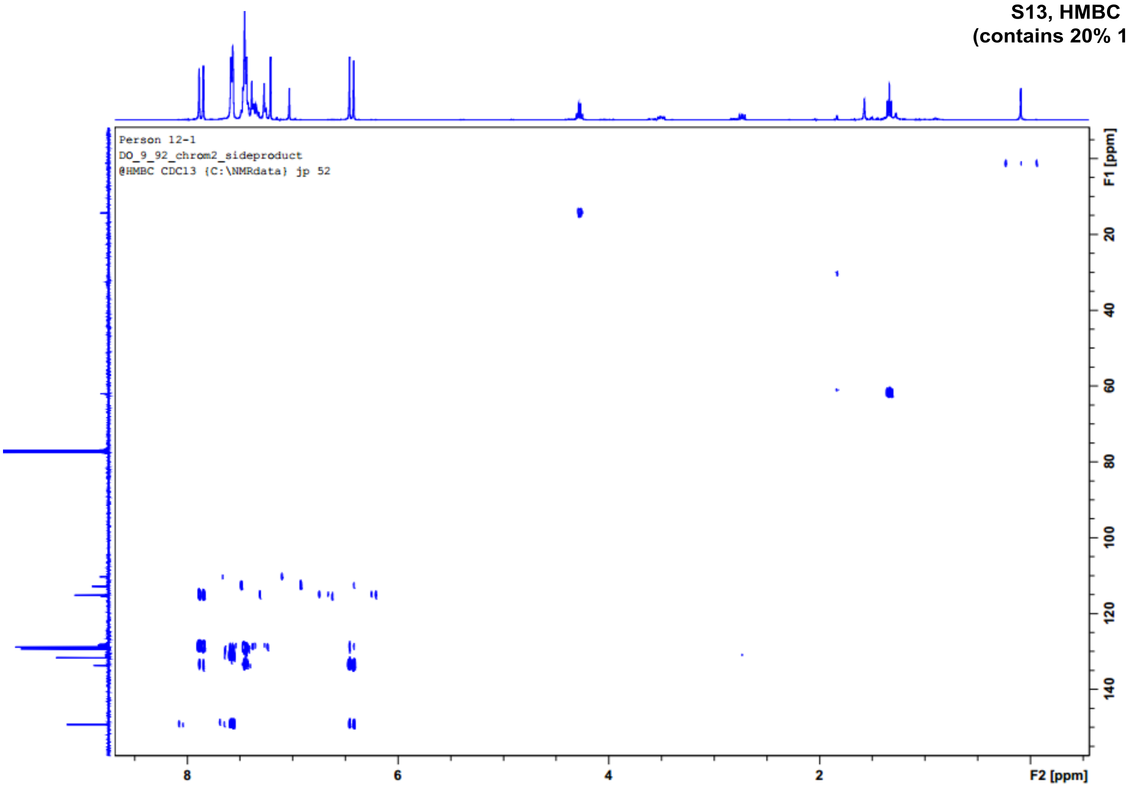


S13, ^{13}C
(contains 20% 15b)



S13, HSQC
(contains 20% 15b)

S13, HMBC
(contains 20% 15b)



Evidence of Difluorocarbene-Digylme Reaction

An oven dried two-necked round bottom flask containing sodium chlorodifluoroacetate (275 mg, 1.8 mmol) was sealed with a SubaSeal, and the salt lightly flame dried under vacuum. The atmosphere was replaced with nitrogen and the flask allowed to cool to room temperature. A low boiling point water condenser with a gas outlet connected to an argon/vacuum manifold was attached to the reaction flask and the atmosphere was purged three times. Diglyme (1 mL) was added and a reaction aliquot (< 0.1 mL) was taken and analysed by ^{19}F NMR. The saturated mixture was heated to 180 °C and reaction aliquot taken at different time points and analysed by ^{19}F NMR (see **Figure S9**).

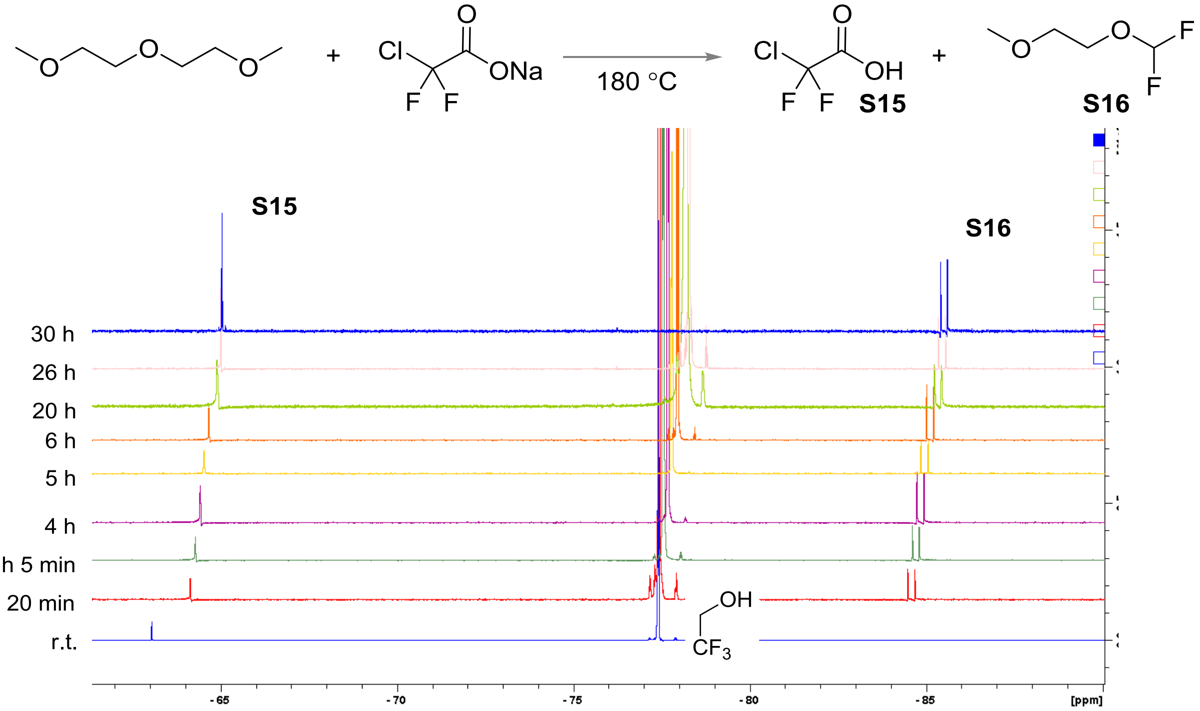
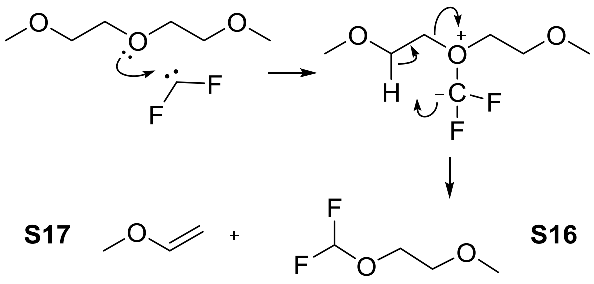


Figure S9: ^{19}F NMR (CDCl$_3$, 400 MHz) spectrum of reaction time-points showing difluorocarbene generated from sodium chlorodifluoroacetate reacting with diglmye (horizontal offset = 0.15 ppm, trifluoroethanol used as external reference).

The observed ^{19}F NMR experimental data for the proposed side product **S16** (-84.6 ppm, d, $^{2}J_{F\text{-}H}$ = 74.6 Hz) is extremely similar to 1,1-difluoro-3-(2-methoxyethoxy)propane reported by Rozen and co-workers[S29] (-84.6 ppm, d, $^{2}J_{F\text{-}H}$ = 75.0 Hz). Houk *et. al*. previously performed low level theoretical calculations (MP2/3-21G) showing that the attack by water on difluorocarbene resulted in a stabilisation of 9.7 kcal mol^{-1} compared with the separate species, concluding that the ether stabilisation was greater than that seen with alkenes.[S30]

This side product was common when less reactive alkenoates underwent difluorocyclopropanation attempts with MDFA and thought to proceed via the attack by solvent on difluorocarbene followed by elimination of vinyl ether **S17** (**Scheme S5**).



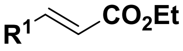
Scheme S6: Proposed mechanism for the reaction between diglyme and difluorocarbene.

Trend in Difluorocyclopropanation Conversion and Calculated HOMO Energies

The HOMO energy for a reactive species is generally considered to give a good representation of the compounds' nucleophilicity, but only a weak trend was observed between the reactivity of the alkenoates (determined by percentage conversion) and the HOMO energies of **13a-c**, **13f** and **13h** (R^2 = 0.8287, see Supporting Information for details). This model only assessed the reactivity of the olefin and did not take into consideration the alternative trapping reactions difluorocarbene can undergo; difluoromethylation of carboxylic acids, ketones, alcohols, thiols, heterocyclic amines and hydrophosphine oxides have all been reported.[S31-35] Compounds which reacted slowly under the difluorocyclopropanation conditions contained common side products which were attributed to difluorocarbene reacting with the reaction solvent diglyme.

Aryl alkenoates were built *de novo* using Spartan'10 software and HOMO energies obtained after geometry optimisiation using B3LYP/6-31G* methodology (gas phase, 298 K, orbitals and energies selected). Minimum energy structures were confirmed by a lack of imaginary frequency. HOMO energies are listed in **Table S2** alongside observed conversions.

Table S2: Difluorocyclopropanation conversion and calculated HOMO energies for (hetero)aromatic alkenoates.

 **R^1 =**	**Percentage Conversion (%)**	**HOMO Energy (eV)**
2-Pyridyl	0	-6.70
2-Thiazolyl	0	-6.47
Piperonyl	50	-5.68
Phenyl	37	-6.36
2-Furyl	66	-5.96
2-Thiophenyl	77	-6.10
3-Methyl-2-furyl	80	-5.84
2-*N*Boc-Pyrroyl	92	-5.68

Both 2-pyridyl and 2-thiazoyl failed to show any reactivity and this could be due to their low calculated HOMO energies of -6.70 eV and -6.47 eV, respectively. However, the moderate conversion observed with piperonyl **13d** is not consistent with its higher HOMO energy of -5.68 eV, suggesting that alternative side reactions occur with these substituents. The remaining compounds show a slight trend relating percentage conversion with calculated HOMO energy but the data is not sufficient to make prediction on whether substrates will successfully undergo difluorocyclopropanation.

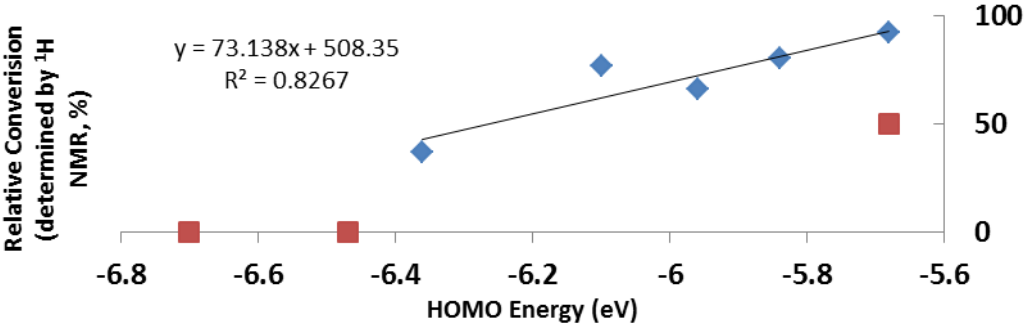
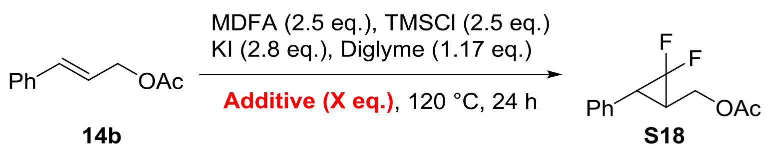


Figure S10: Plot of % conversion in difluorocyclopropanation reaction against calculated HOMO energies (eV) (data represented in Table SXX). ◆ = substrates which show slight trend, ■= substrates which do not fit the trend.

Difluorocyclopropanation Functional Group Tolerance: Additive Experiment

We found that an indication of functional group tolerance was to measure the effects of heterocycles as additives in the previously successful difluorocyclopropanation of cinnamyl acetate **14b** (**Table S3,** Entry 1).[S20]

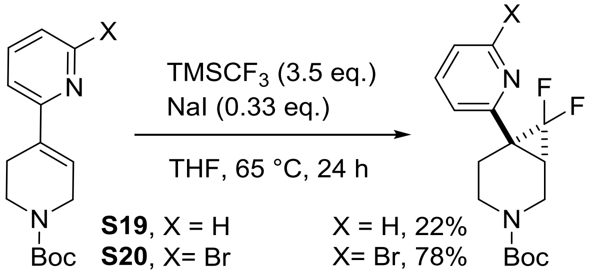
Table S3: Effect of Heterocyclic Additives on the Difluorocyclopropanation of Cinnamyl Acetate **14b**.



Entry[a]	Additive	Equivalents	Conversion to S18 (%)[b]
1[c]	none	n.a.	100
2	Pyridine	1.0	0
3	Pyridine	0.5	4
4[c]	Pyridine	0.1	85
5	Thiazole	0.5	34
6	Pyridine-N-oxide	0.5	14
7	N-Boc-pyrrole	0.5	88
8	Methyl-3-methyl-2-furoate	0.5	100
9	1,3-Benodioxole	0.5	50

[a] All reactions run on an 8 mmol scale with respect to **14b** unless otherwise stated. [b] Determined by 1H NMR. [c] 16 mmol scale.

We observed that 1.0 and 0.5 equivalents of pyridine completely hindered the trapping of difluorocarbene with **14b** (**Table S3**, Entries 2-3); even small quantities of the heterocycle (10 mol%) lowered the conversion to **S18** by 15% (**Table S3**, Entry 4). Addition of thiazole to the reaction had a smaller effect, but a low 34% conversion confirmed that both of these heterocycles do suppress the difluorocarbene-alkene reaction (**Table S3**, Entry 5). DeNinno and co-workers reported similar issues when the difluorocyclopropanation of **S19** gave a poor 22% yield, but shielding the pyridine nitrogen using *ortho*-bromo substitution gave a highly improved 78% yield from **S20** (**Scheme S6**).[S36]



Scheme 7: Increased difluorocyclopropanation yields by blocking aromatic nitrogen atom.[S36]

We hoped that blocking the nitrogen atom directly via the N-oxide would help the difluorocyclopropanation reaction in a similar way and potentially give access to a more reactive VCPR precursor. However, since a poor 14% conversion to **15b** was observed when pyridine-N-oxide was used as an additive, no further synthetic investigations were carried out (**Table S3**, Entry 6). Heterocycles which were tolerated during the difluorocyclopropanation of alkenoate **13**, gave higher 88-100% conversions to **15b** when used as additives (**Table S3**, Entries 7-8). This experimental approach of assessing functional group tolerance was a more effective way to prioritising the synthesis of heteroaromatic olefins and can be used to assess which substrates will be tolerated during difluorocyclopropanation without competing side reactions.

Methodology: An oven dried two-necked round bottom flask containing potassium iodide (3.68 g, 22.2 mmol) was sealed with a SubaSeal, and the salt was stirred and lightly flame dried under an atmosphere of argon. A low boiling point water condenser with a gas outlet connected to an argon/vacuum manifold was attached and the reaction flask and the atmosphere were purged three times. Cinnamyl acetate **14b** (1.34 mL, 8.0 mmol) followed by a solution of **additive (X eq.)** in diglyme (1.3 mL) were added and the resulting suspension was heated to 120 °C. Once the reaction temperature had been reached, TMSCl (2.6 mL, 19.7 mmol) and MDFA (2.6 mL, 19.7 mmol) were added dropwise in that order. After 5 hours, the reaction mixture had evaporated to dryness and a further portion of diglyme (1.3 mL) was added. The mixture was stirred for a further 19 hours (total reaction time of 24 hours). The resulting brown solution was cooled to room temperature and the reaction mixture was quenched with aqueous NaCl (10 mL) and diethyl ether (10 mL) was added. The organic layer was separated and the aqueous layer was extracted with diethyl ether (2 x 10 mL). The original organic layer and the extracts were combined, dried ($MgSO_4$) and concentrated under reduced pressure to remove volatiles. The ^1H NMR spectrum of the resulting brown oil was used to determine conversion of **13b** to difluorocyclopropyl **15b** and the results highlighted in **Table S3**.

Crude Spectra for Low Temperature Rearrangement Precursors

Spectra below highlight the results of oxidation/Wittig chemistry on highly reactive heteroaromatic substituents.

- Furyl Alcohol **17a** with (ethoxycarbonylmethylene)triphenylphosphorane

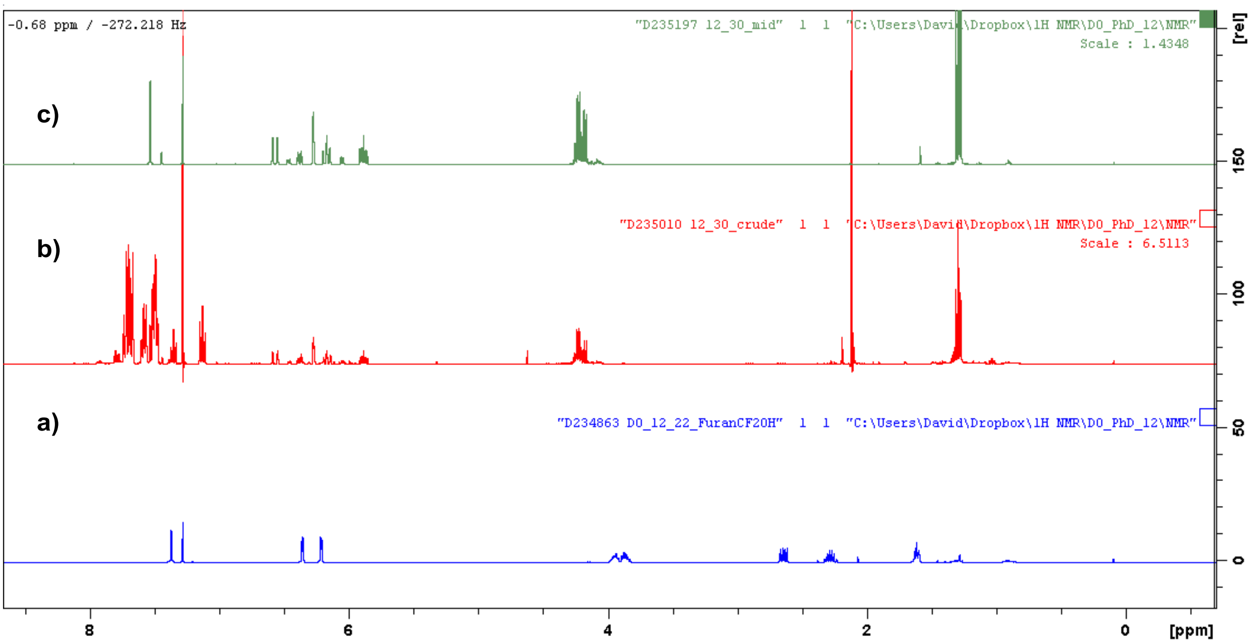


Figure S11: a) Isolated ^{1}H NMR for alcohol **17a** b) Crude ^{1}H NMR after oxidation/Wittig reaction showing no evidence of peaks relating to cyclopropane proton atoms. c) ^{1}H NMR of main fraction isolated from first purification on silica.

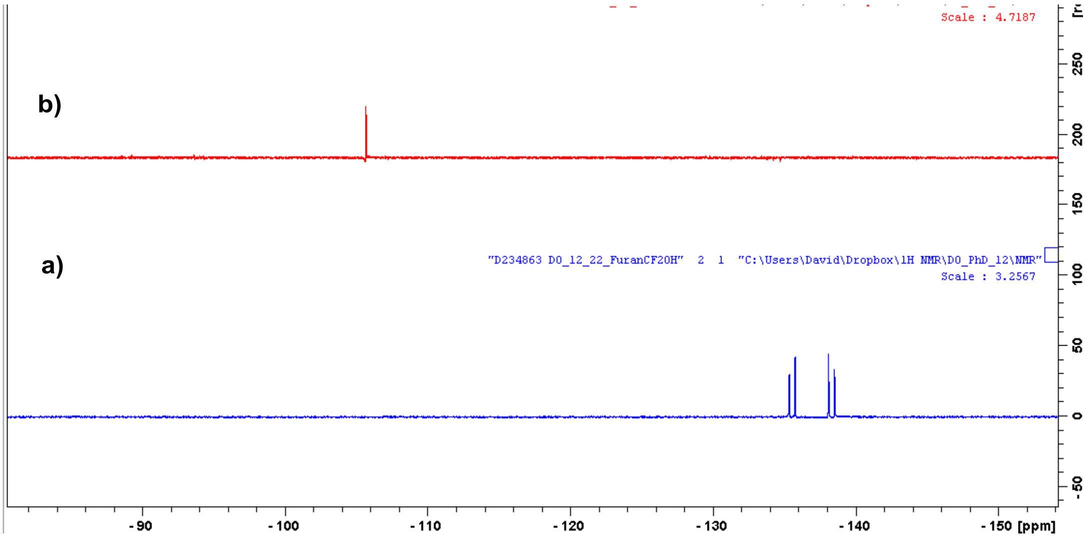
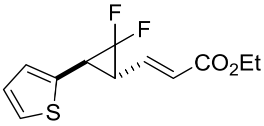
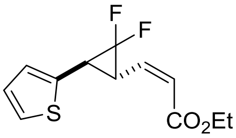


Figure S12: a) Isolated ^{19}F NMR for furyl alcohol **17a** b) ^{19}F NMR of main fraction isolated from first purification after oxidation/Wittig.

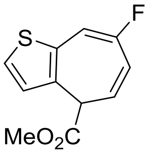
- Thiophenyl alcohol **17c** with (ethoxycarbonylmethylene)triphenylphosphorane



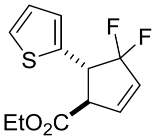
I



II



III



IV

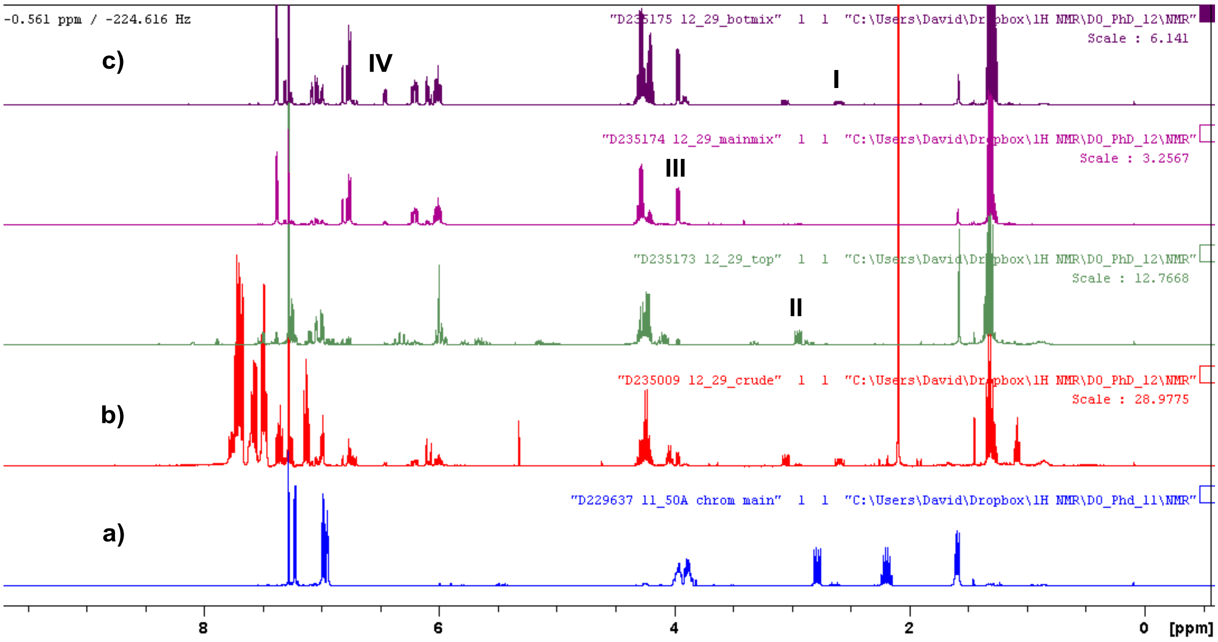


Figure S13: a) ^{1}H NMR of isolated thiophenyl alcohol **17c**. b) Crude ^{1}H NMR after oxidation/Wittig reaction. c) Three different fractions isolated after first purification on silca. (Assignment of crude spectra based on previous knowledge on *E*/Z cyclopropane isomers and ^{19}F NMR data for products which was confirmed on isolation of products).

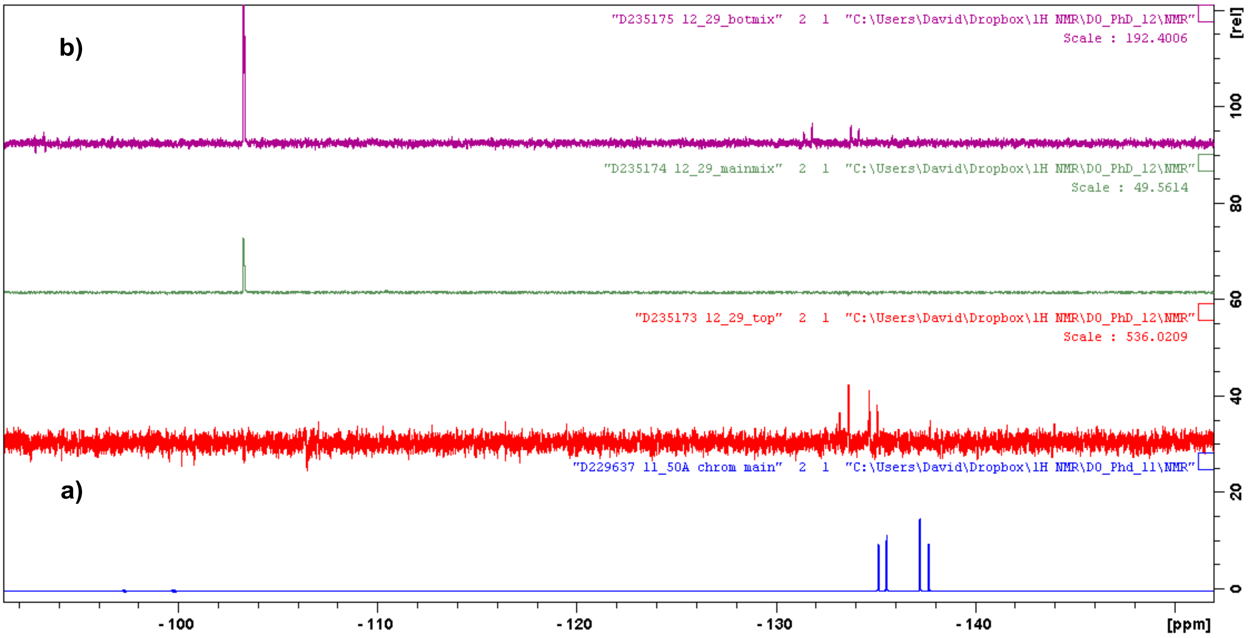


Figure S14: a) Crude ^{19}F NMR for isolated thiophenyl alcohol **17c**. b) ^{19}F NMR for isolated fractions highlighted in **Figure S13** from first purification on silica.

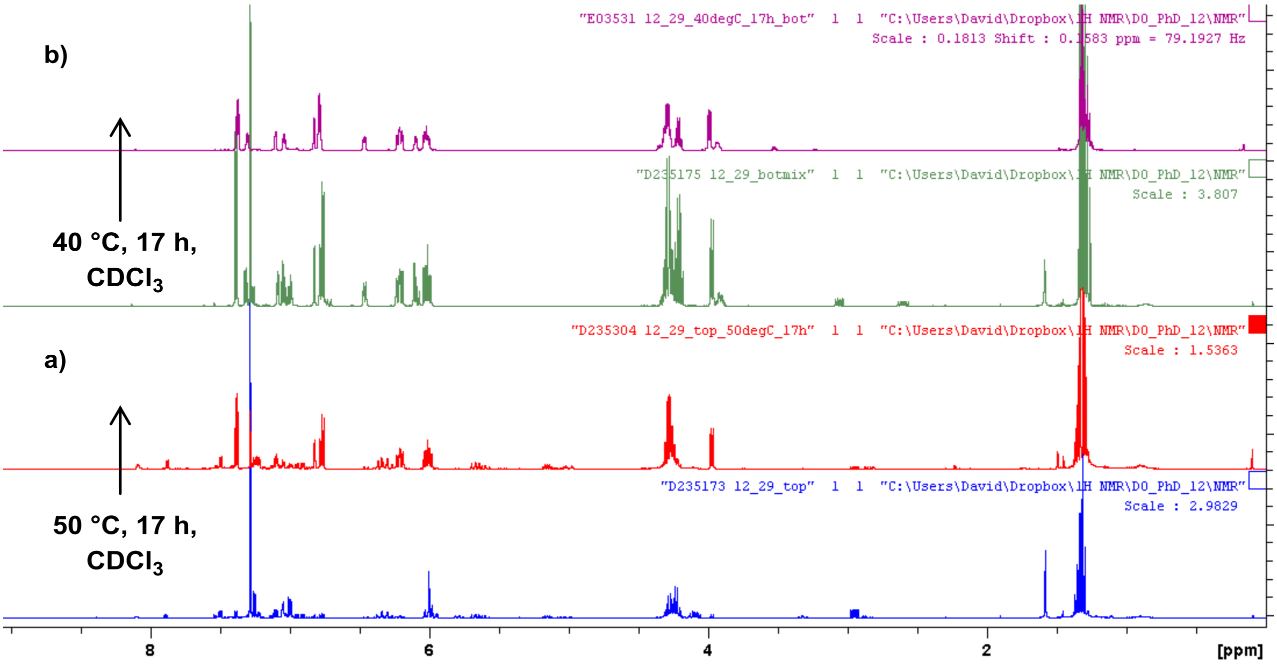


Figure S15: a) Thermolysis of < 10 mg sample containing *Z*-thiophenyl **24b** at 50 °C for 17 hours resulting in full conversion to heptadiene **29a** alongside other side products. b) Thermolysis of 420 mg sample containing *E*-thiophenyl **24a** at 40 °C for 17 hours resulting in full conversion to a mixture of VCPR and [3,3] product.

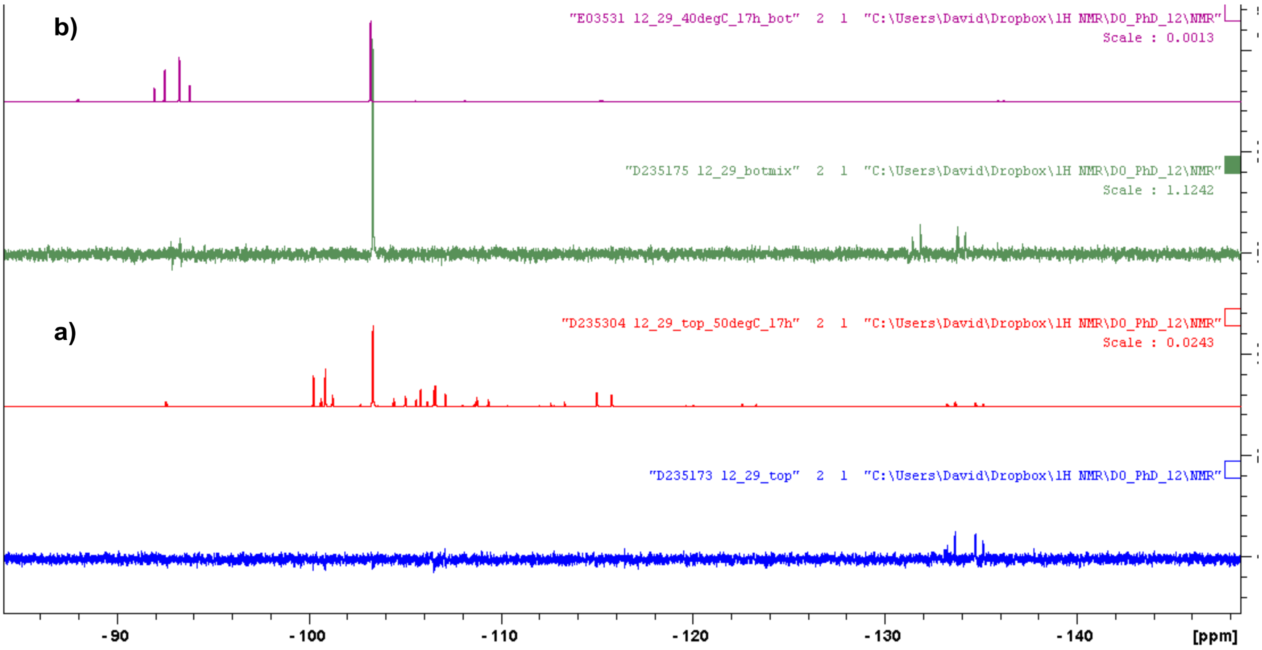


Figure S16: Corresponding ^{19}F NMR for ^{1}H NMR discussed in **Figure S15**.

- Furyl alcohol **17a** with (carbethoxyethylidene)triphenylphosphorane

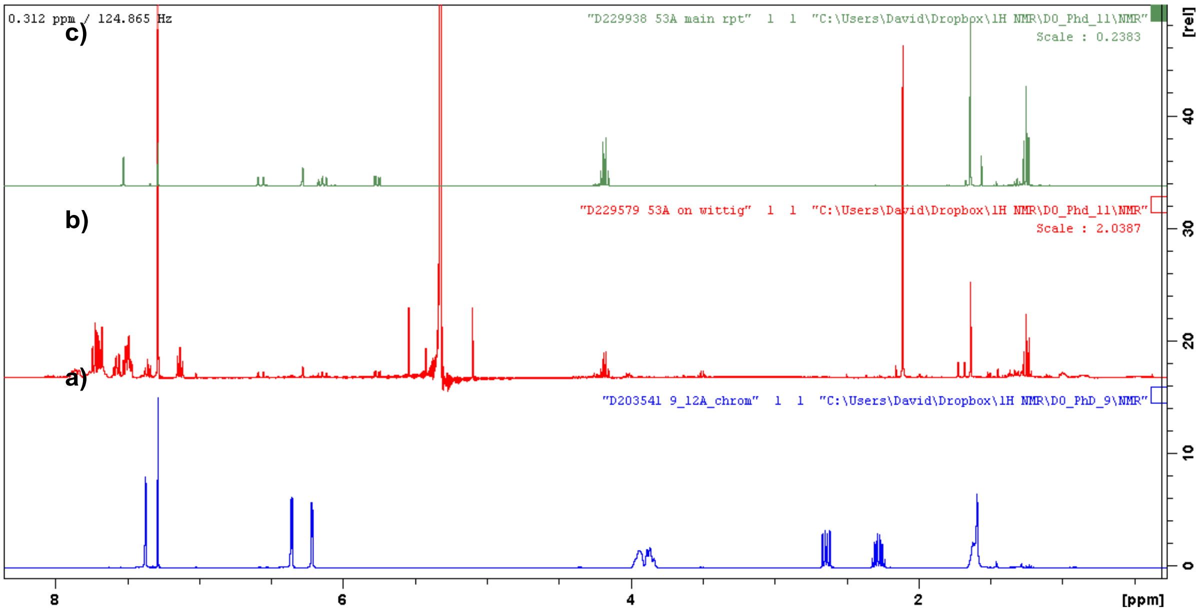


Figure S17: a) ^{1}H NMR of isolated furyl alcohol **17a**. b) Crude ^{1}H NMR after oxidation/Wittig with (carbethoxyethylidene)triphenylphosphorane c) ^{1}H NMR after 1st purification on silica.

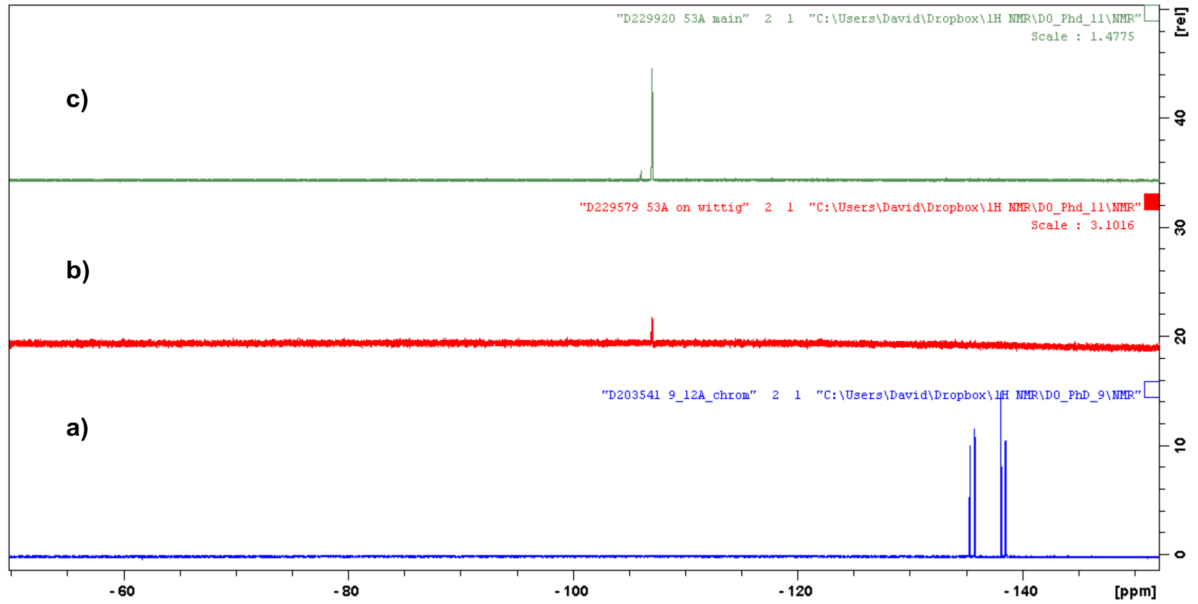


Figure S18: a) ^{19}F NMR for isolated furyl alcohol **17a** b) Crude ^{19}F NMR after oxidation/Wittig with (carbethoxyethylidene)triphenylphosphorane c) ^{19}F NMR after 1st purification on silica.

- Thiophenyl alcohol **17c** with (carbethoxyethylidene)triphenylphosphorane

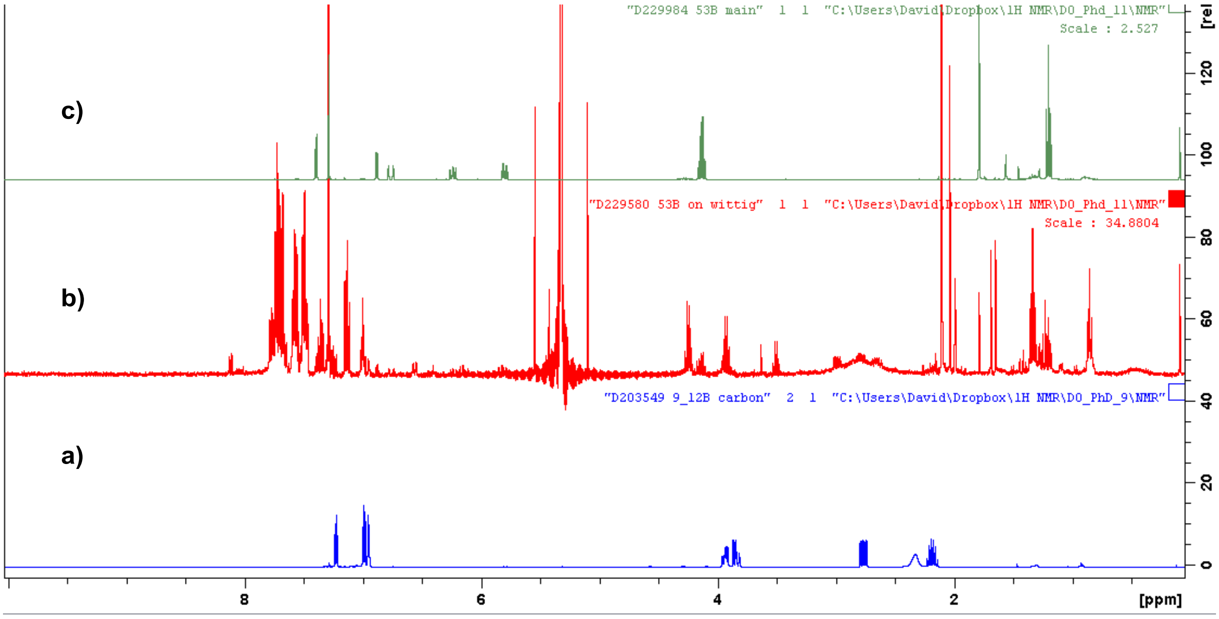


Figure S19: a) ^{1}H NMR for isolated thiophenyl alcohol **17c** b) Crude ^{1}H NMR after oxidation/Wittig with (carbethoxyethylidene)triphenylphosphorane c) ^{1}H NMR after 1st purification on silica.

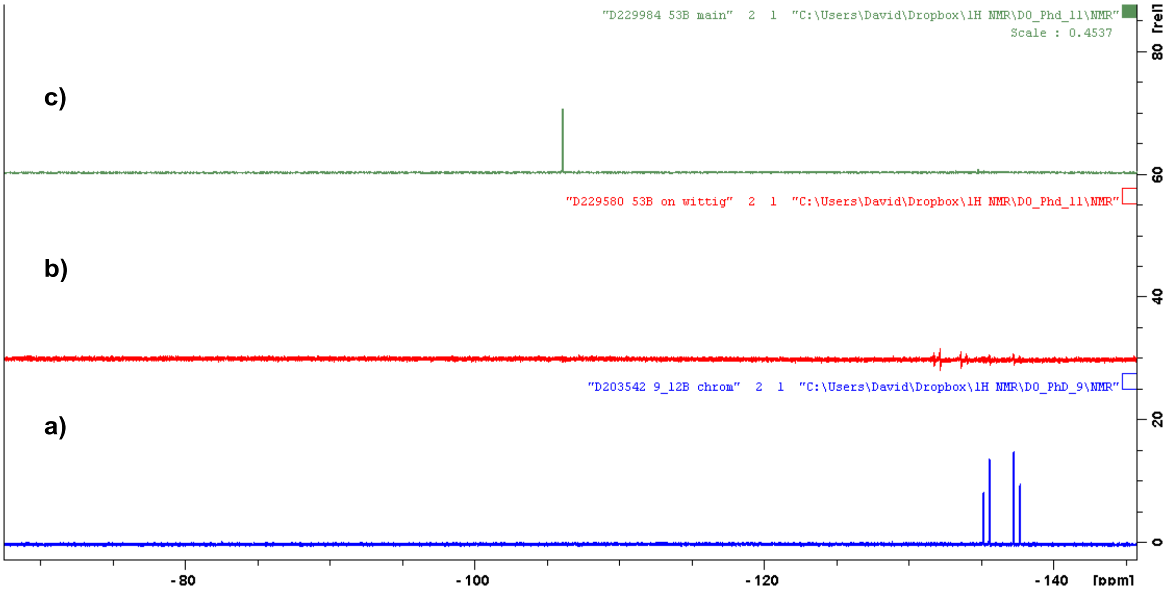


Figure S20: a) ^{19}F NMR for isolated thiophenyl alcohol **17c** b) Crude ^{19}F NMR after oxidation/Wittig with (carbethoxyethylidene)triphenylphosphorane c) ^{19}F NMR after 1st purification on silica.

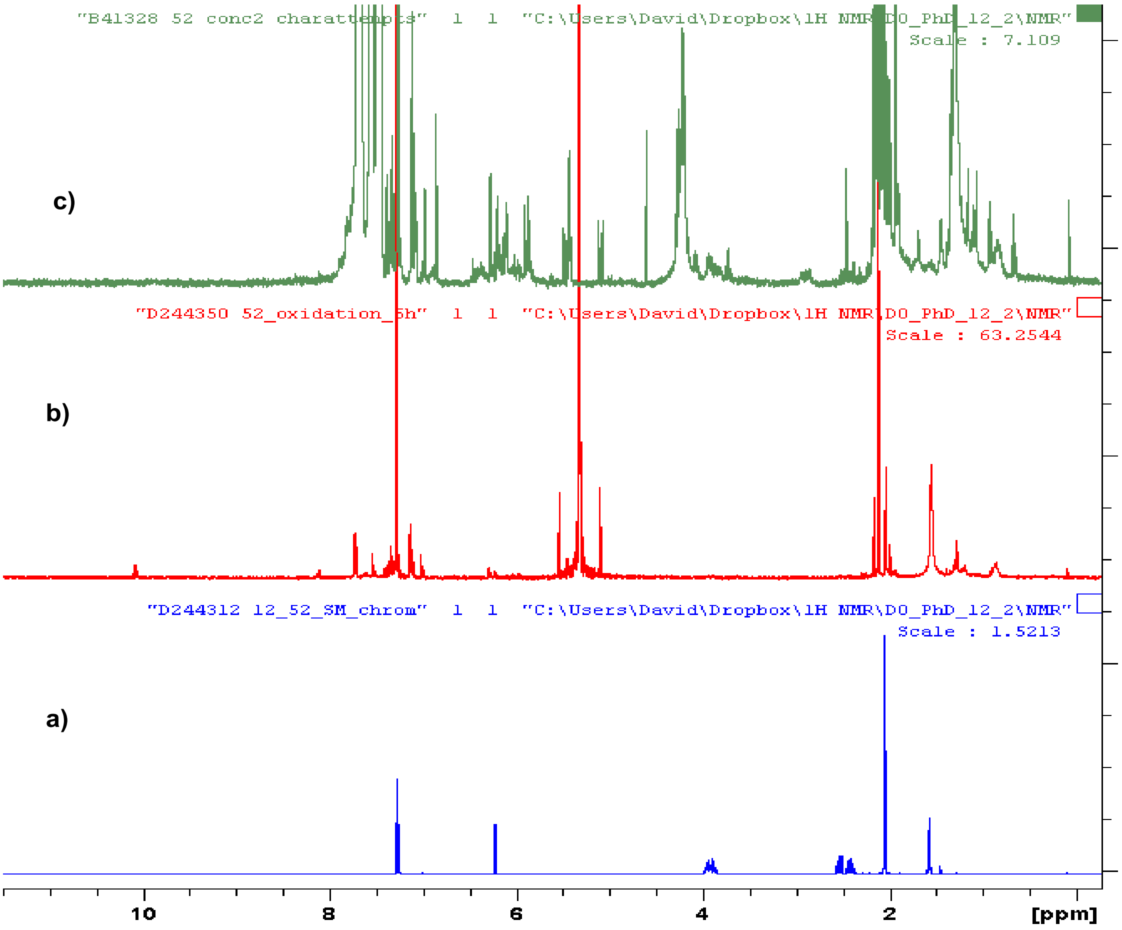


Figure S21: ^{1}H NMR for isolated 3-methyl-furyl alcohol **17h** b) Crude ^{1}H NMR after oxidation with (ethoxycarbonylmethylene)triphenylphosphorane c) ^{1}H NMR after olefination and concentration of reaction mixture.

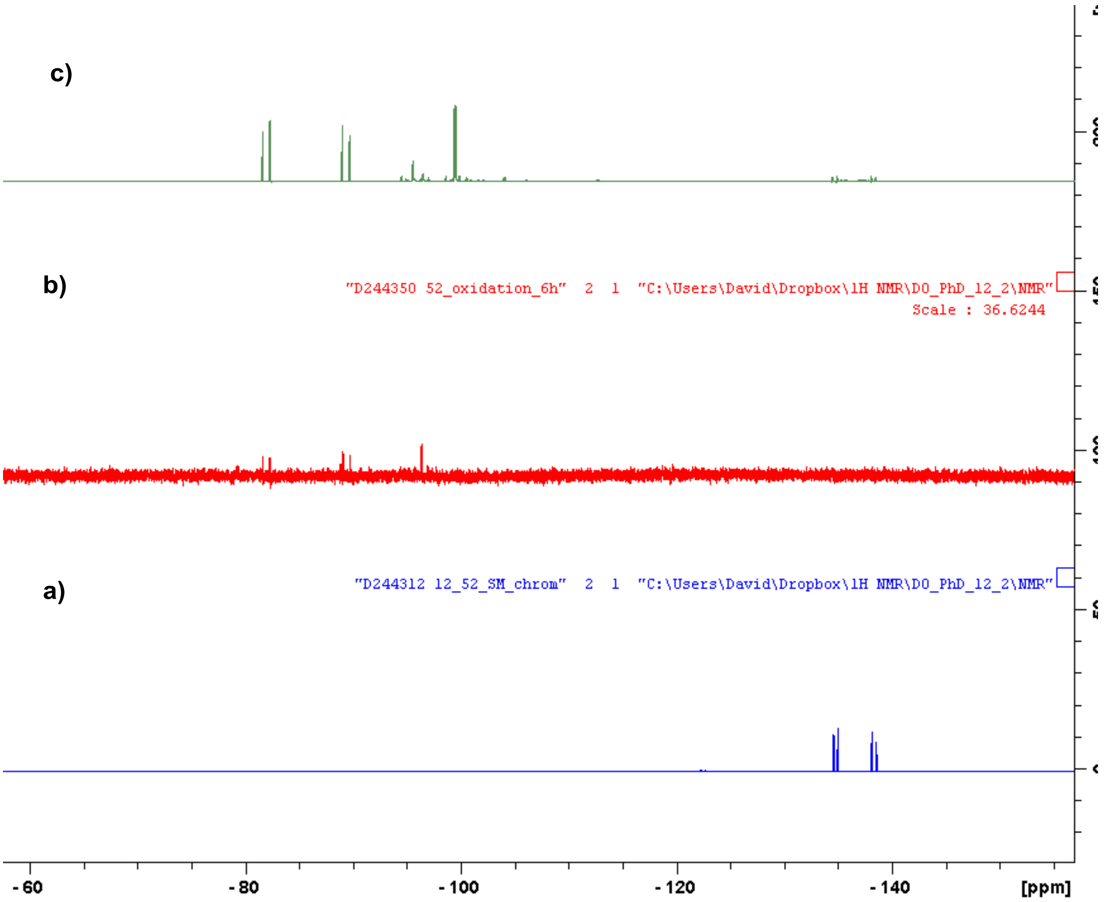


Figure S22: ^{19}F NMR for isolated 3-methyl-furyl alcohol **17h** b) Crude ^{19}F NMR after oxidation with (ethoxycarbonylmethylene)triphenylphosphorane c) ^{19}F NMR after olefination and concentration of reaction mixture.

Rearrangement of Isolated VCP – Crude Spectra

- **(*E*)-Weinreb Amide 19a**

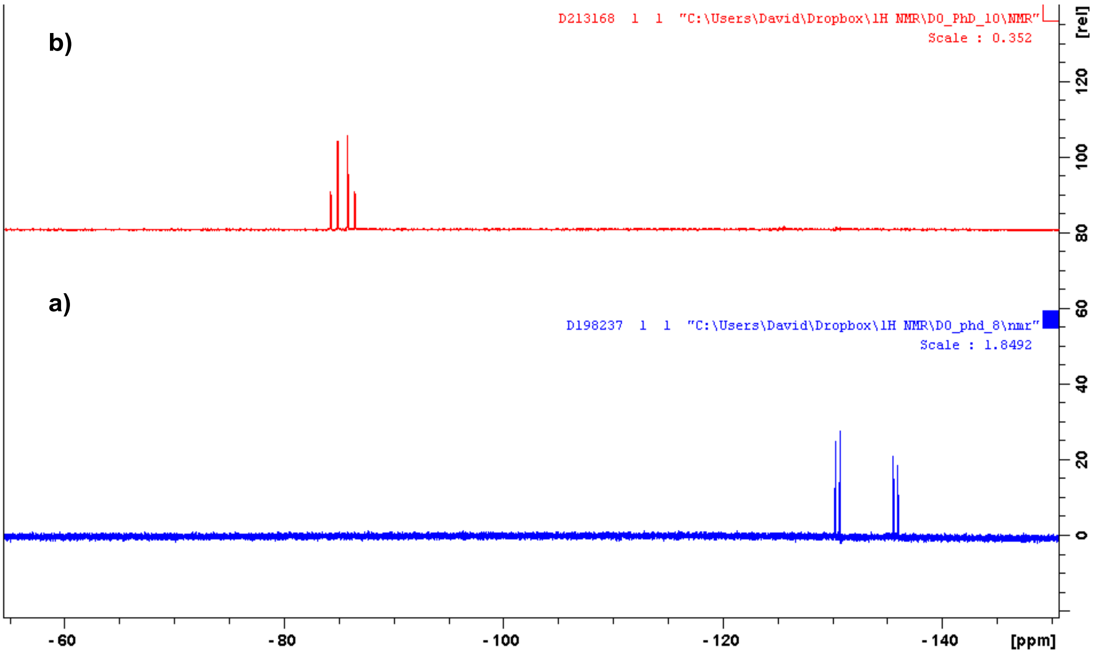


Figure S23: a) ^{19}F NMR of isolated *E*-Weinreb amide VCP **19a**. b) Crude ^{19}F NMR for rearrangement of **19a** at 95 °C for 17 hours.

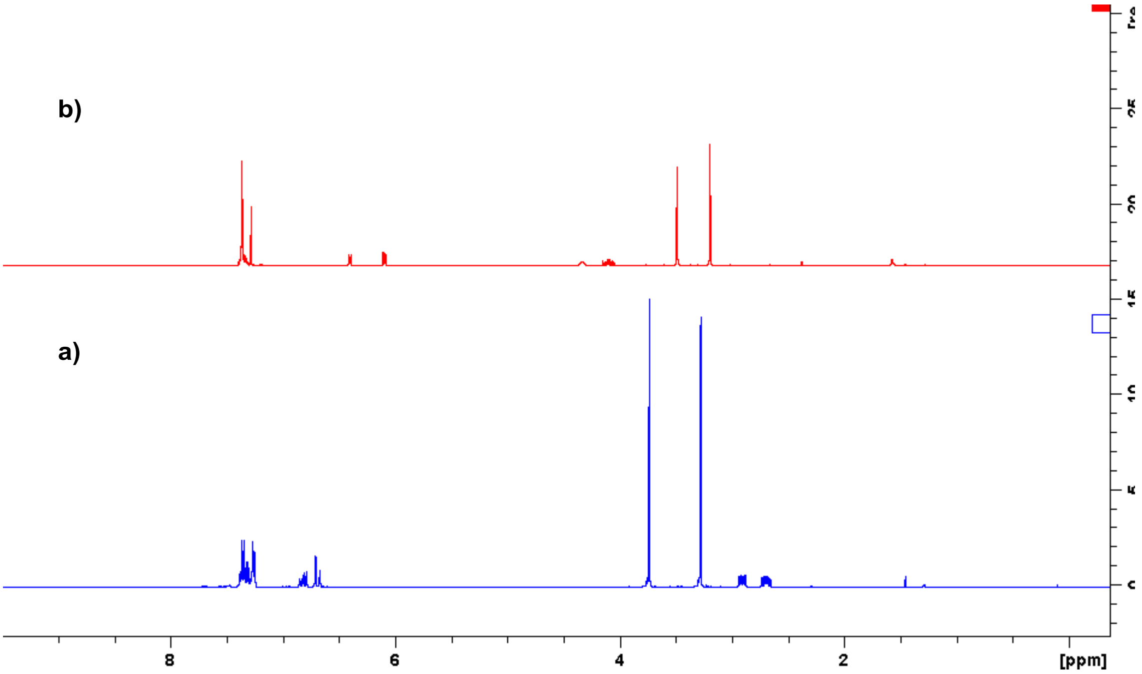


Figure S24: a) ^{1}H NMR of isolated *E*-Weinreb amide VCP **19a**. b) Crude ^{1}H NMR for rearrangement of **19a** at 95 °C for 17 hours.

- **(*Z*)-Weinreb Amide (19b)**

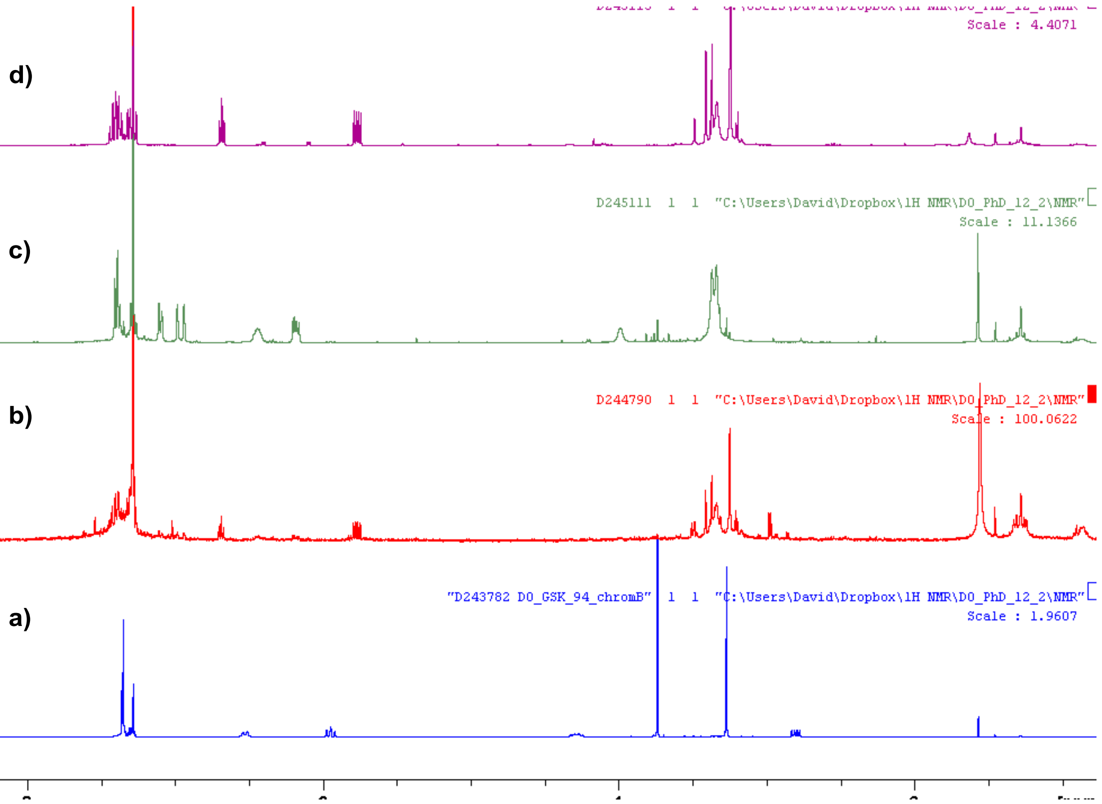


Figure S25: a) ^{1}H NMR of isolated *Z*Weinreb amide VCP **19b**. b) Crude ^{1}H NMR of **19b** after rearrangement at 165 °C for 17 hours (silica pad used to remove Ph$_2$O solvent c) and d) ^{1}H NMR of isolated products after chromatography.

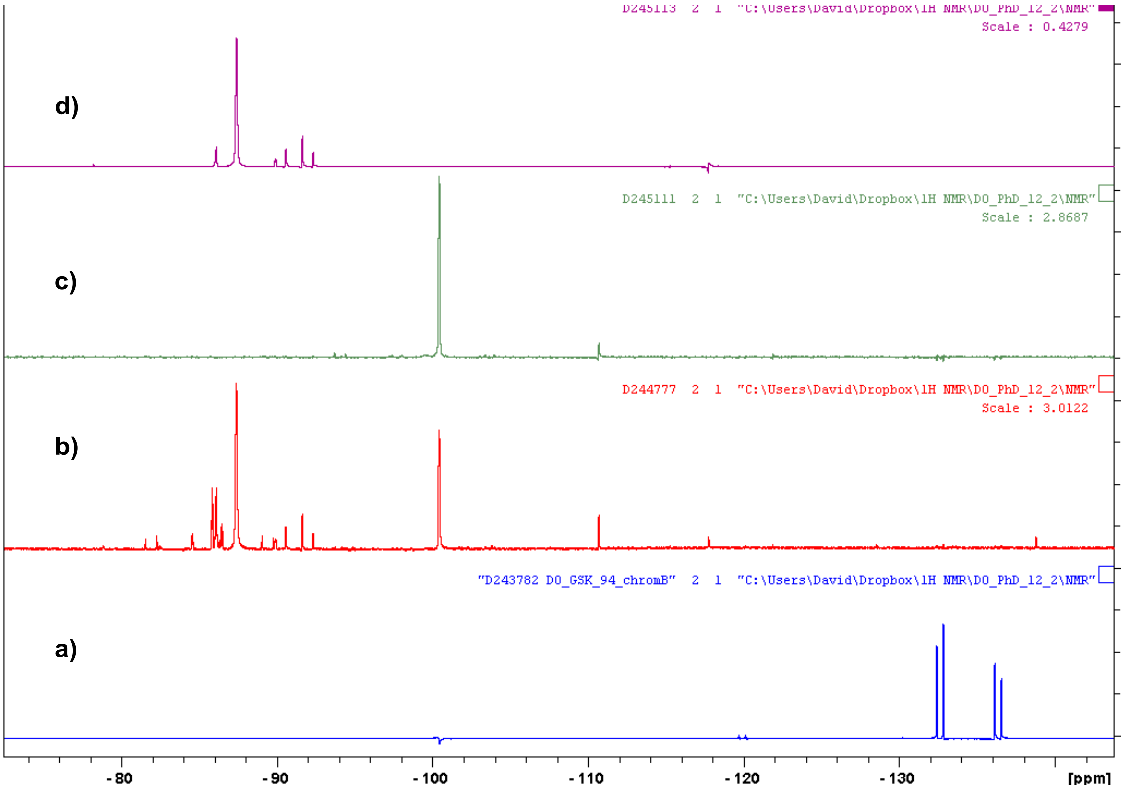


Figure S26: a) ^{19}F NMR of isolated *Z*-Weinreb amide VCP **19b**. b) Crude ^{19}F NMR of **19b** after rearrangement at 165 °C for 17 hours (silica pad used to remove Ph_2O solvent. c) and d) ^{19}F NMR of isolated products after chromatography.

- **α-Methyl Ester (20a)**

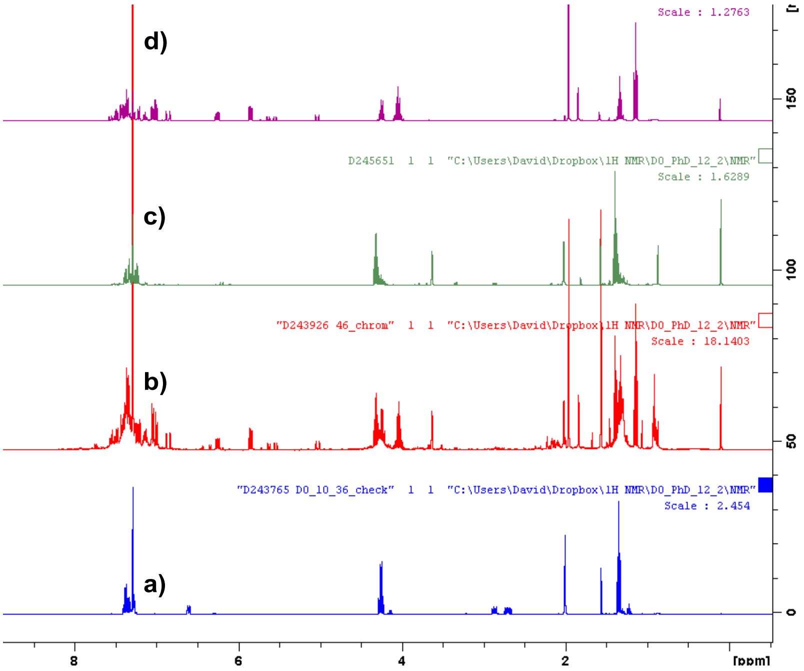


Figure S27: a) ^{1}H NMR of isolated alkenoate **20a** b) Crude ^{1}H NMR of **20a** after rearrangement at 155 °C for 17 hours (silica pad used to remove Ph_2O solvent). c) and d) ^{1}H NMR of isolated products after chromatography.

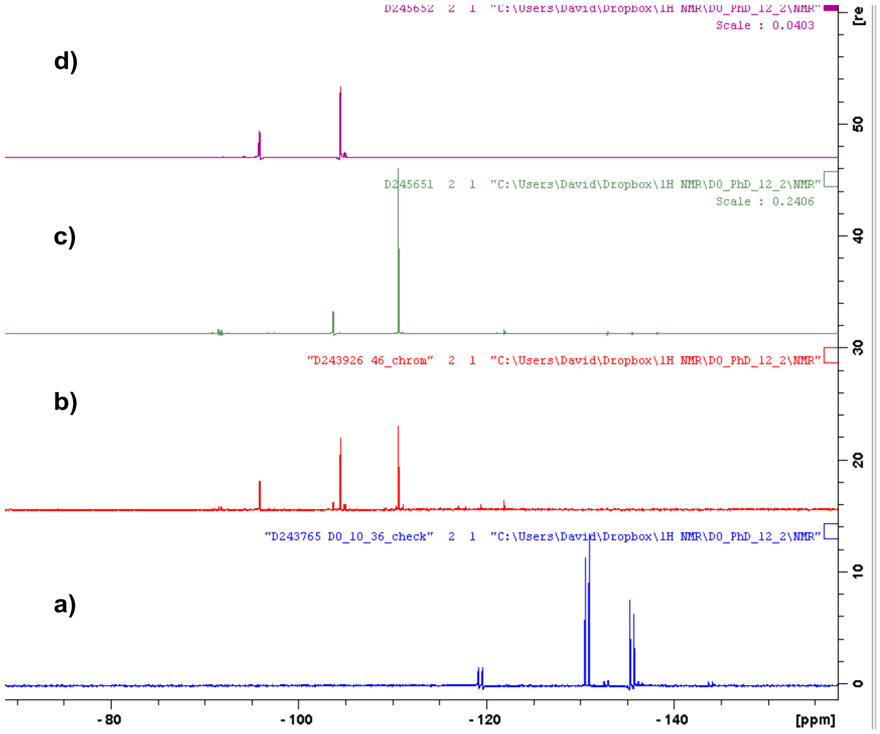


Figure S28: a) ^{19}F NMR of isolated alkenoate **20a**. b) Crude ^{19}F NMR of **20a** after rearrangement at 155 °C for 17 hours (silica pad used to remove Ph_2O solvent). c) and d) ^{19}F NMR of unknown products after chromatography.

- ***E*/*Z*-Cyano VCP mixture (21a/21b)**

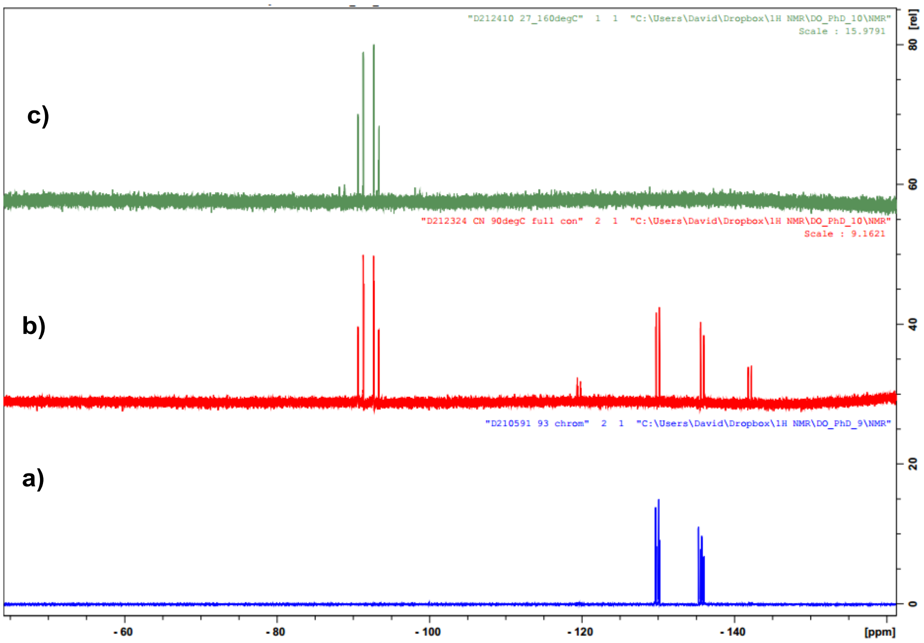


Figure S29: a) ^{19}F NMR spectra of **21a/21b** mixture. b) ^{19}F NMR spectra for the rearrangement of **21a/21b** at 90 °C for 17 h resulting in full conversion of **21a** to difluorocyclopentene **37** and only cyclopropane stereoisomeration of **21b** to **42**. c) ^{19}F NMR spectra after the rearrangement of crude mixture in b) at 160 °C for 17 h.

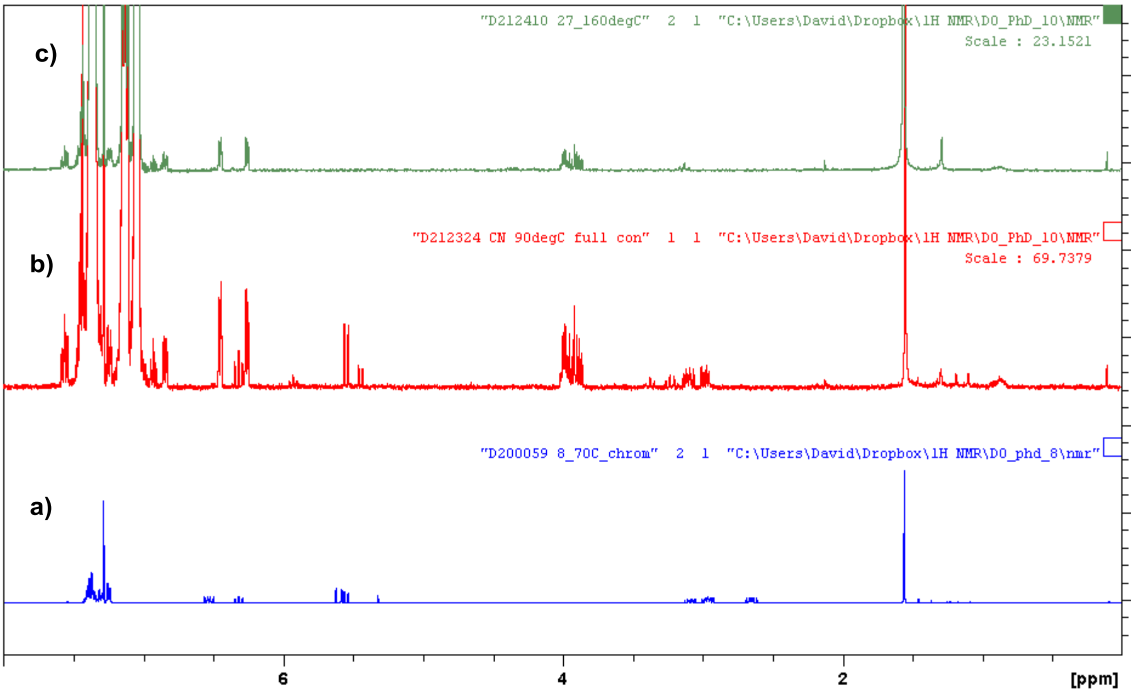


Figure S30: Corresponding ^{1}H spectra for mixtures in **Figure 29.**

- **Piperonyl 22a**

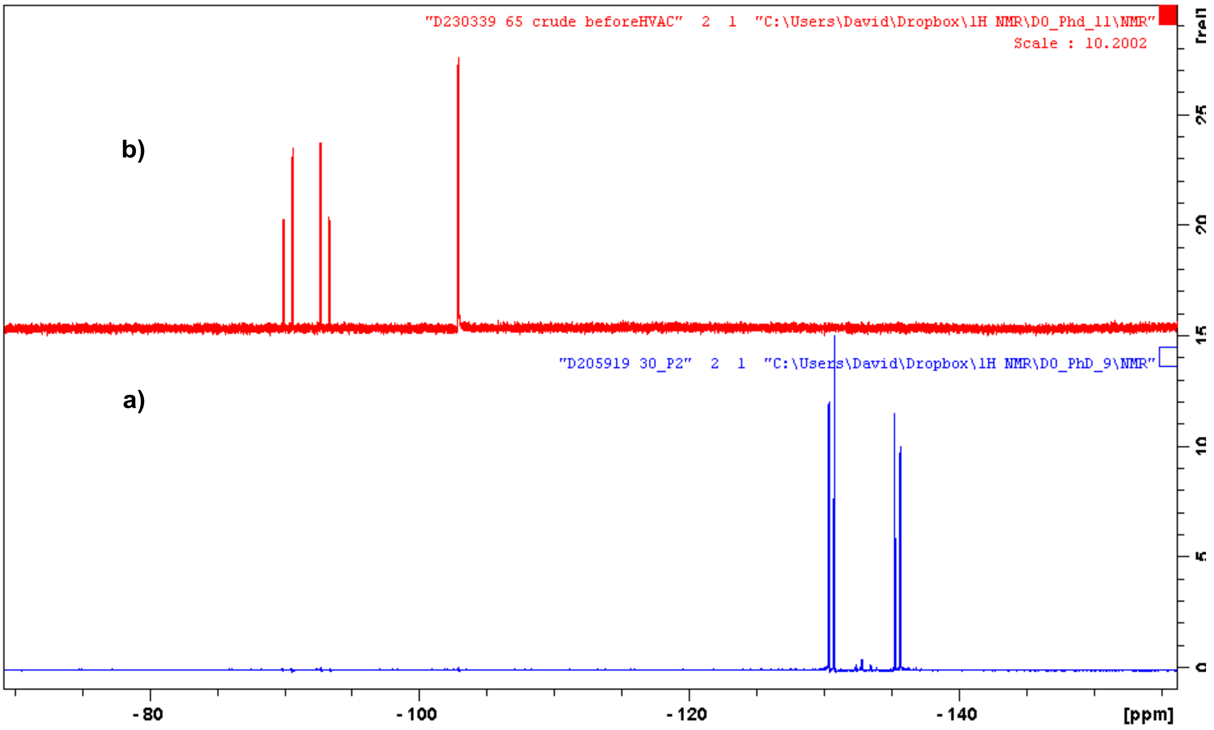


Figure S31: a) ^{19}F NMR of isolated piperonyl VCP **22a**. b) ^{19}F NMR of crude reaction mixture after rearrangement at 70 °C for 17 h.

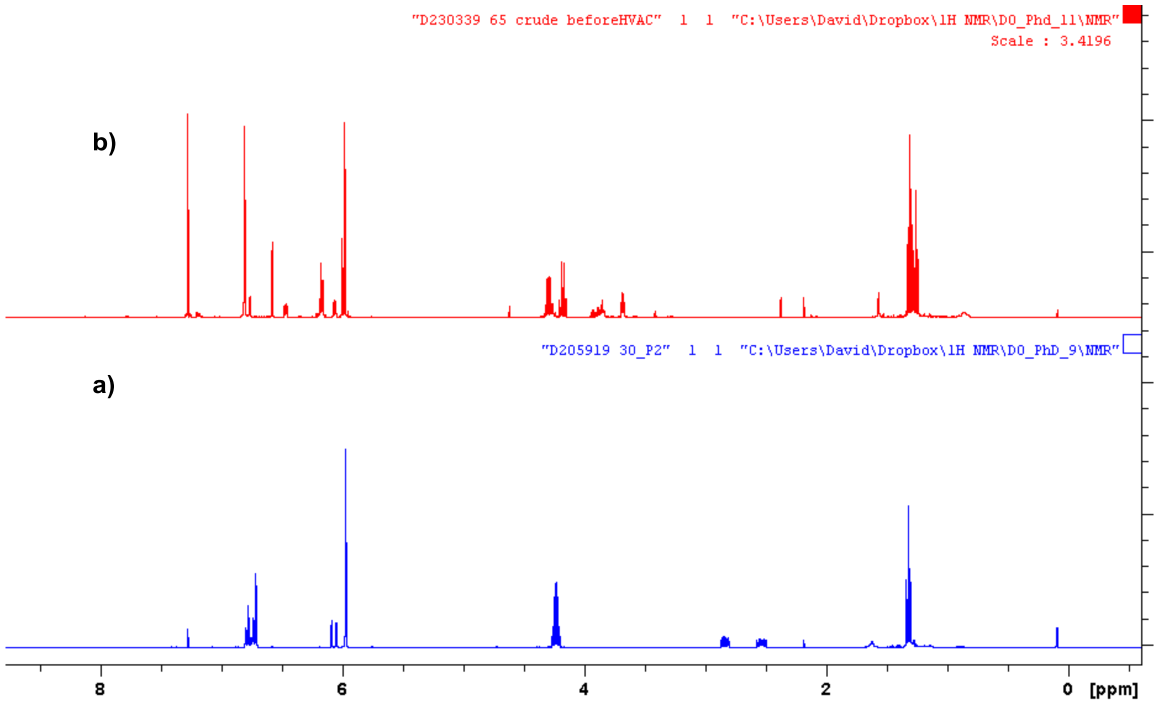


Figure S32: Corresponding ^{1}H NMR spectra for ^{19}F NMR discussed in **Figure S31**.

- **Non-fluorinated 47**

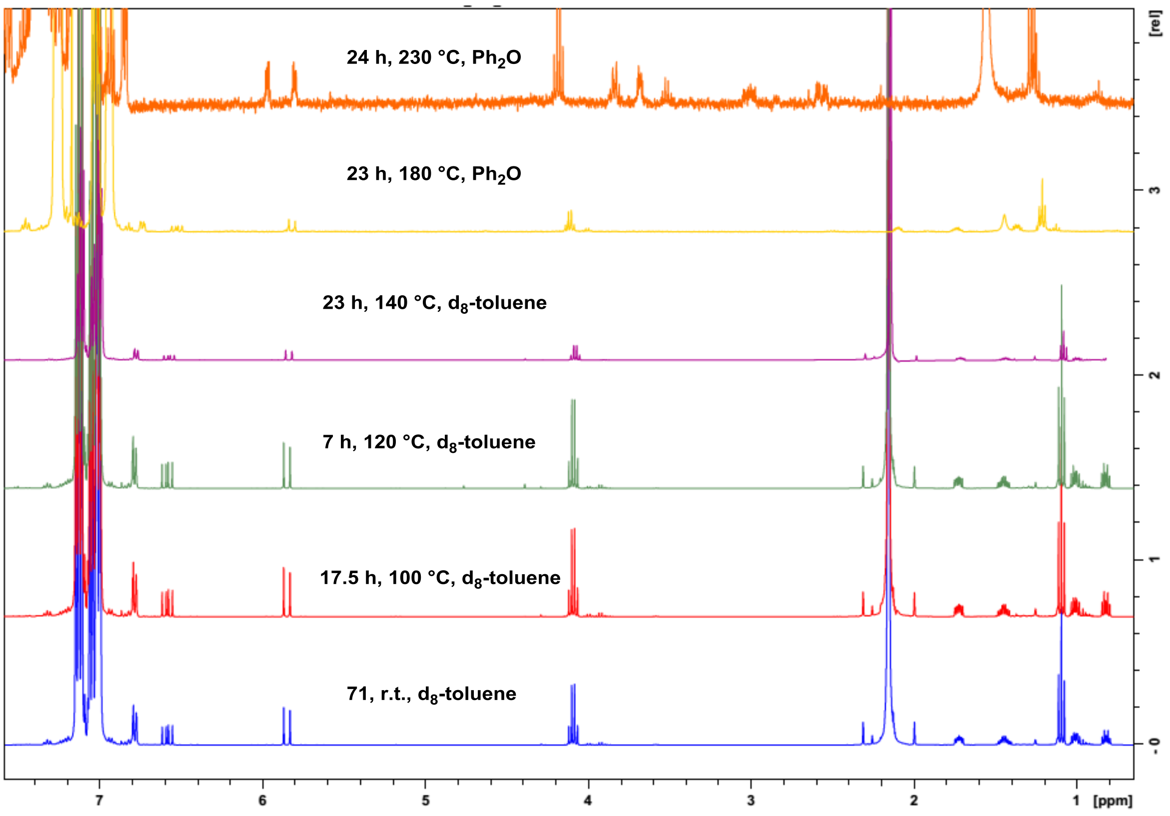


Figure S33: Rearrangement temperature screening show temperatures > 180 °C are required for the rearrangement of non-fluorinated VCP **47**.

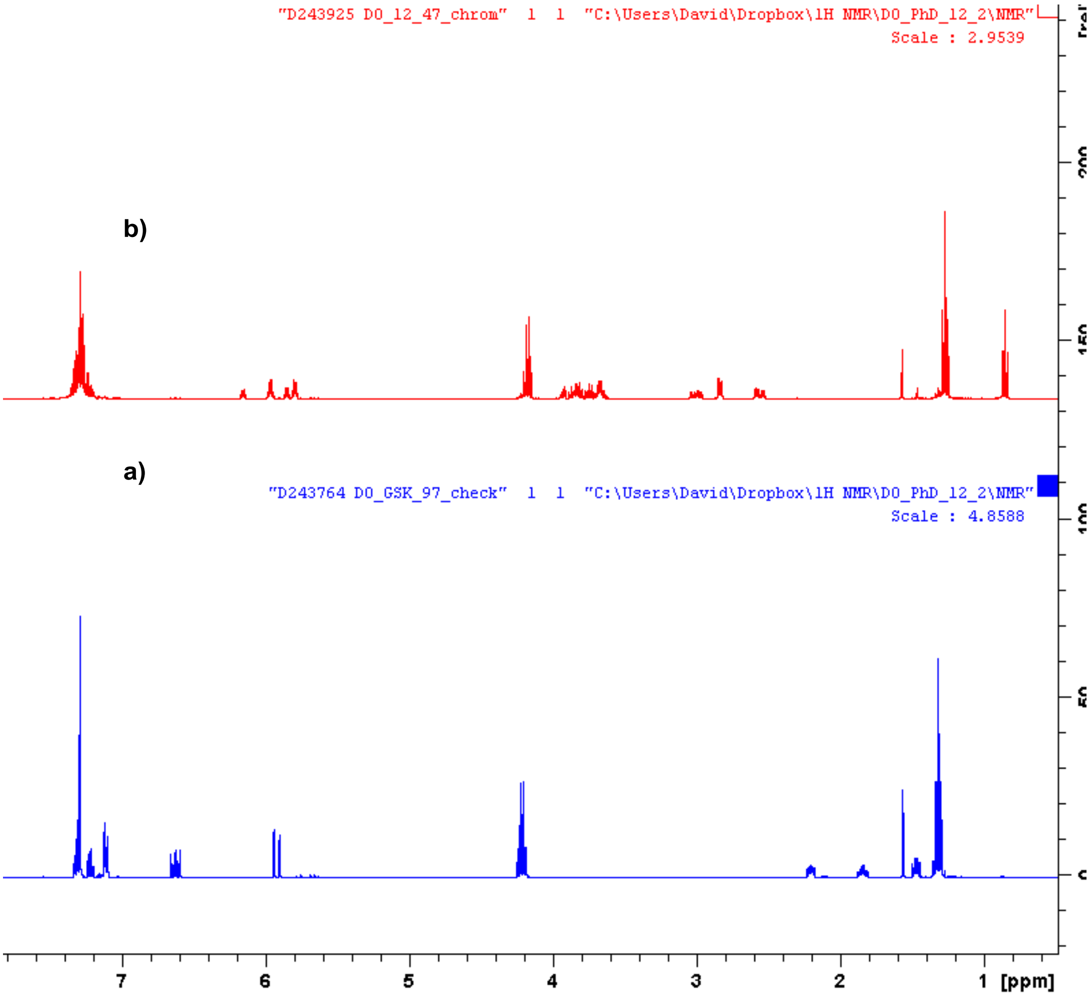


Figure S34: a) 1H NMR for isolated alkenoate **47** b) Crude ^{1}H NMR for the rearrangement of isolated non-fluorinated **47** at 210 °C for 17 h (after removal of Ph_2O solvent).

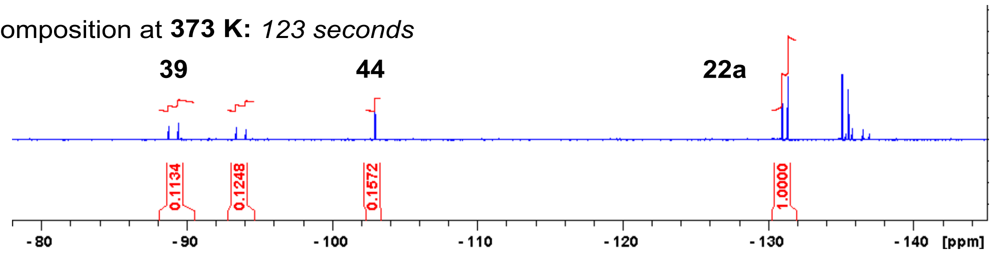
Piperonyl 22a Rearrangement: Kinetic Modelling

VT ^{19}F NMR Procedure for Piperonyl 22a

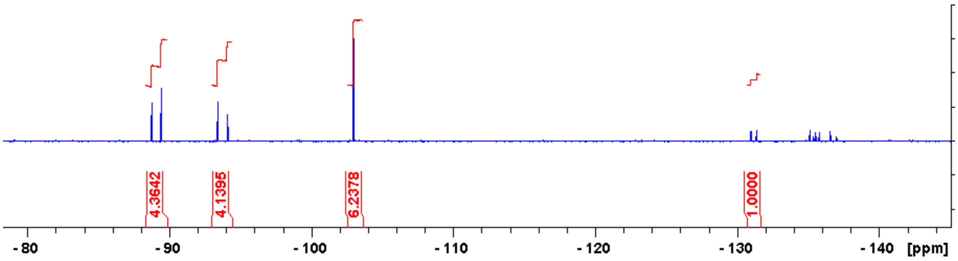
^{19}F NMR spectra were acquired on a Brüker AV400 instrument equipped with a QNP-z probe and a temperature control unit. Data was collected at 376 MHz using 8 scans per data point. Settings for spectra acquisition were as follows: NS = 8 scans; D1 = 1.5 s; SW = 199.77 ppm and O1P = -100 ppm. The samples were held at reaction temperature for the duration of the experiment: 343, 353, 363 and 373 K for Arrhenius plots with **22a**. d8-Toluene was purchased from and Sigma Aldrich and used as received. A solution of VCPR precursor (typically 0.13-0.15 M) was made up in a clean, dry NMR tube and the tube was capped. The tube was inserted into the magnet and the instrument's internal temperature was set to the desired reaction temperature and allowed to equilibrate (approx. 2 minutes heating time). The sample was then analysed at appropriate intervals using a Brüker Topspin automated script, *multi_zgvd2b*. Samples were automatically shimmed using *topshim* between acquisitions. In order to obtain sufficient data points for kinetic analysis; the above procedure was altered slightly for rearrangements at temperatures of 363 and 373 K. Reactions at both temperatures used *noshim* to cancel any shimming between spectra acquisition, allowing time points to be taken every 40 or 25 seconds (respectively) instead of 60 seconds with shimming between samples. A sacrificial sample was used to shim the reaction mixture at 373 K. This was ejected and replaced with a fresh sample which was locked and followed at 25 second intervals (*multi_zgvd2b*) after solvent locking. This procedure allowed the first time point to be taken after 50 seconds instead of 180 seconds. Relative percentages were determined by averaging the manual integration for each compound on the resulting spectra using proprietary software.

Example Spectra:

22a decomposition at **373 K:** *123 seconds*



22a decomposition at **373 K:** *867 seconds*



Raw Kinetic Data for Piperonyl 22a

^{19}F NMR integration data for the VCPR of ***22a*** *in d8-toluene (0.13 M) heated at 343 K (AV400, QNP-z probe); 8 scans, D1= 1.5 s, TE = 343 K.*

Time	Average Integrations			Relative Percentage		
(s)	SM	VCPR	3,3	SM	VCPR	3,3
0	1.00	0.03	0.01	96.4	3.1	0.5
360	1.00	0.05	0.02	93.7	4.6	1.7
480	1.00	0.07	0.04	90.0	6.3	3.7
720	1.00	0.07	0.06	88.5	6.2	5.3
960	1.00	0.11	0.09	83.5	9.1	7.5
1200	1.00	0.11	0.09	83.0	9.3	7.7
1440	1.00	0.14	0.15	77.2	10.9	11.9
1680	1.00	0.16	0.17	74.9	12.2	12.8
1920	1.00	0.19	0.20	71.8	14.0	14.2
2160	1.00	0.22	0.22	69.5	15.0	15.6
2400	1.00	0.25	0.27	66.0	16.4	17.5
2640	1.00	0.28	0.30	63.2	17.7	19.1
2880	1.00	0.28	0.31	63.0	17.5	19.5
3120	1.00	0.32	0.36	59.6	19.0	21.4
3360	1.00	0.34	0.36	58.7	20.1	21.2
3600	1.00	0.40	0.44	54.4	21.6	24.0
3840	1.00	0.38	0.45	54.4	20.9	24.7
4080	1.00	0.46	0.52	50.7	23.1	26.2
4320	1.00	0.45	0.51	50.9	22.9	26.2
4560	1.00	0.50	0.55	48.8	24.2	27.0
4800	1.00	0.57	0.68	44.5	25.2	30.3
5040	1.00	0.60	0.70	43.5	26.1	30.4
5280	1.00	0.62	0.72	42.8	26.4	30.7
5520	1.00	0.62	0.77	41.9	26.1	32.1
5760	1.00	0.69	0.79	40.2	27.9	31.9
6000	1.00	0.76	0.83	38.5	29.5	32.0
6240	1.00	0.78	0.95	36.6	28.5	34.8
6480	1.00	0.82	0.99	35.7	29.1	35.2
6720	1.00	0.88	1.02	34.5	30.5	35.0
6960	1.00	0.90	1.08	33.6	30.3	36.1
7200	1.00	0.99	1.15	31.8	31.7	36.5
7440	1.00	1.02	1.23	30.8	31.3	37.9
7680	1.00	1.09	1.32	29.3	32.0	38.8
7920	1.00	1.15	1.38	28.4	32.6	39.0
8160	1.00	1.22	1.51	26.8	32.6	40.6
8400	*1.00*	*1.26*	*1.45*	*27.0*	*34.0*	*39.1*

Time	Average Integrations			Relative Percentage		
(s)	SM	VCPR	3,3	SM	VCPR	3,3
8640	1.00	1.27	1.56	26.1	33.2	40.6
8880	1.00	1.44	1.77	23.8	34.2	42.0
9120	1.00	1.54	1.84	22.8	35.2	42.0
9360	1.00	1.50	1.83	23.1	34.6	42.3
9600	1.00	1.66	1.96	21.6	35.9	42.5
9840	1.00	1.77	2.12	20.4	36.2	43.3
10080	1.00	1.81	2.20	19.9	36.1	43.9
10320	1.00	1.83	2.10	20.3	37.1	42.6
10560	1.00	1.89	2.37	19.0	36.0	45.0
10800	1.00	1.93	2.43	18.6	36.0	45.4
11280	1.00	2.09	2.60	17.6	36.7	45.7
63960	0.00	0.97	1.26	0.0	43.6	56.4

^{19}F NMR integration data for the VCPR of ***22a*** *in d8-toluene (0.13 M) heated at 353 K (AV400, QNP-z probe); 8 scans, D1= 1.0 s, TE = 353 K.*

Time	**Average Integrations**			**Relative Percentage**		
(s)	**SM**	**VCPR**	**3,3**	**SM**	**VCPR**	**3,3**
0	1.00	0.04	0.02	94.0	3.9	2.2
240	1.00	0.06	0.05	90.1	5.8	4.1
420	1.00	0.12	0.06	84.4	10.2	5.4
600	1.00	0.18	0.18	73.8	13.1	13.2
780	1.00	0.23	0.24	67.6	15.8	16.5
960	1.00	0.27	0.31	63.2	17.1	19.7
1140	1.00	0.33	0.38	58.3	19.5	22.1
1320	1.00	0.43	0.49	52.1	22.3	25.6
1500	1.00	0.47	0.57	49.1	22.9	28.1
1680	1.00	0.55	0.65	45.6	25.0	29.4
1860	1.00	0.59	0.75	42.7	25.3	32.0
2040	1.00	0.73	0.89	38.2	27.9	33.8
2220	1.00	0.81	1.03	35.2	28.4	36.4
2400	1.00	0.94	1.15	32.3	30.5	37.2
2580	1.00	1.00	1.32	30.1	30.2	39.7
2760	1.00	1.20	1.55	26.7	32.1	41.3
2940	1.00	1.21	1.55	26.6	32.2	41.2
3120	1.00	1.40	1.78	23.9	33.5	42.6
3300	1.00	1.48	1.91	22.8	33.7	43.6
3480	1.00	1.71	2.24	20.2	34.6	45.2
3660	1.00	2.01	2.64	17.7	35.6	46.7
3840	1.00	2.03	2.59	17.8	36.1	46.1
4020	1.00	2.27	2.91	16.2	36.7	47.1
4200	1.00	2.85	3.80	13.1	37.3	49.6
4380	1.00	2.75	3.64	13.5	37.2	49.3
4560	1.00	3.23	4.31	11.7	37.8	50.5
4740	1.00	3.32	4.34	11.5	38.3	50.2
4920	1.00	4.35	5.59	9.1	39.8	51.1
5100	1.00	4.13	5.38	9.5	39.3	51.2
5280	1.00	4.26	5.65	9.2	39.1	51.8
5460	1.00	5.00	6.58	7.9	39.8	52.3
5640	1.00	4.81	6.06	8.4	40.5	51.1
5820	1.00	6.21	8.21	6.5	40.3	53.2
6000	1.00	6.75	8.85	6.0	40.7	53.3
6180	1.00	8.11	10.43	5.1	41.5	53.4
6360	1.00	5.79	7.55	7.0	40.4	52.7
6540	1.00	9.03	12.02	4.5	41.0	54.5
6720	1.00	9.71	12.64	4.3	41.6	54.1
6900	1.00	10.78	14.33	3.8	41.3	54.9
7080	1.00	9.40	12.23	4.4	41.5	54.0
7260	1.00	10.10	12.74	4.2	42.4	53.4
7440	1.00	12.65	16.46	3.3	42.0	54.7
7620	1.00	12.47	16.40	3.3	41.7	54.9
15120	*0.00*	*1.01*	*1.61*	*0.0*	*38.4*	*61.6*

^{19}F NMR integration data for the VCPR of ***22a*** *in d8-toluene (0.13 M) heated at 363 K (AV400, QNP-z probe); 8 scans, D1= 1.0 s, TE = 363 K.*

Time	**Average Integrations**			**Relative Percentage**		
(s)	**SM**	**VCPR**	**3,3**	**SM**	**VCPR**	**3,3**
0	1.00	0.03	0.02	95.0	2.8	2.1
120	1.00	0.11	0.10	82.8	8.8	8.4
160	1.00	0.12	0.13	80.0	9.9	10.0
190	1.00	0.15	0.15	77.2	11.4	11.4
210	1.00	0.17	0.19	73.2	12.8	14.0
245	1.00	0.18	0.22	71.4	13.1	15.5
275	1.00	0.22	0.27	67.2	14.6	18.2
305	1.00	0.23	0.30	65.7	14.9	19.4
335	1.00	0.26	0.31	63.4	16.7	19.9
365	1.00	0.30	0.34	61.0	18.1	20.9
395	1.00	0.32	0.37	59.2	18.8	22.0
425	1.00	0.36	0.43	55.9	20.1	24.1
455	1.00	0.36	0.47	54.4	19.8	25.7
485	1.00	0.43	0.51	51.8	22.1	26.2
515	1.00	0.43	0.55	50.6	21.7	27.7
545	1.00	0.44	0.55	50.3	21.9	27.8
575	1.00	0.48	0.63	47.3	22.8	29.8
605	1.00	0.52	0.66	45.7	24.0	30.3
635	1.00	0.54	0.71	44.5	23.9	31.6
665	1.00	0.59	0.80	42.0	24.6	33.4
695	1.00	0.64	0.83	40.5	25.9	33.6
725	1.00	0.69	0.85	39.3	27.1	33.6
755	1.00	0.70	0.92	38.2	26.8	35.0
785	1.00	0.73	0.98	36.9	26.8	36.3
815	1.00	0.77	1.06	35.3	27.1	37.5
845	1.00	0.86	1.13	33.5	28.8	37.7
875	1.00	0.86	1.15	33.2	28.6	38.2
905	1.00	0.93	1.23	31.7	29.4	39.0
935	1.00	0.96	1.28	30.8	29.8	39.4
965	1.00	1.02	1.35	29.7	30.3	40.0
995	1.00	1.09	1.47	28.0	30.7	41.3
1025	1.00	1.16	1.64	26.3	30.5	43.2
1055	1.00	1.18	1.65	26.1	30.8	43.1
1085	1.00	1.30	1.72	24.9	32.4	42.7
1115	1.00	1.27	1.75	24.9	31.6	43.5
1145	1.00	1.41	1.91	23.2	32.6	44.2
1175	1.00	1.38	1.88	23.5	32.4	44.1
1205	1.00	1.56	2.07	21.6	33.7	44.7
1235	1.00	1.78	2.43	19.2	34.2	46.7
1265	1.00	1.72	2.35	19.7	34.0	46.3
1295	1.00	1.69	2.41	19.6	33.1	47.3
1325	1.00	1.87	2.51	18.6	34.8	46.6
1355	1.00	1.86	2.60	18.3	34.1	47.6
1385	1.00	1.95	2.65	17.9	34.8	47.3
1415	1.00	2.48	3.36	14.6	36.2	49.1
1445	1.00	2.31	3.18	15.4	35.6	49.0
1475	1.00	2.65	3.57	13.9	36.6	49.5
1505	1.00	2.31	3.08	15.6	36.1	48.2
1535	1.00	2.70	3.55	13.8	37.2	49.0
1565	1.00	2.65	3.68	13.6	36.2	50.2
1595	1.00	3.04	4.27	12.0	36.5	51.4
1625	1.00	3.07	4.41	11.8	36.2	52.0
1655	1.00	2.96	4.16	12.3	36.5	51.2
1685	1.00	3.04	4.26	12.1	36.6	51.3
1715	1.00	3.22	4.44	11.6	37.2	51.3
1745	1.00	4.05	5.63	9.4	37.9	52.7
1775	1.00	3.50	4.64	10.9	38.3	50.8
1805	1.00	3.63	4.95	10.4	37.9	51.7
1835	1.00	4.26	5.99	8.9	37.9	53.2
1865	1.00	4.10	5.49	9.4	38.7	51.8
1895	1.00	4.71	6.66	8.1	38.1	53.9
1925	1.00	5.27	7.43	7.3	38.4	54.3
1955	1.00	4.75	6.31	8.3	39.4	52.3
1985	1.00	5.47	7.64	7.1	38.8	54.1
2015	1.00	4.68	6.58	8.2	38.2	53.7
2045	1.00	4.82	6.57	8.1	38.9	53.0
2075	1.00	6.13	8.45	6.4	39.4	54.2
2105	1.00	5.63	7.83	6.9	38.9	54.2
2135	1.00	5.74	8.28	6.7	38.2	55.1
2165	1.00	6.95	9.38	5.8	40.1	54.1
2315	1.00	12.12	16.74	3.3	40.6	56.1
2465	1.00	11.96	16.63	3.4	40.4	56.2
2525	1.00	10.33	14.72	3.8	39.6	56.5
2585	1.00	10.78	15.52	3.7	39.5	56.9
2645	1.00	14.73	21.04	2.7	40.0	57.2
6360	*1.00*	*55.62*	*98.61*	*0.6*	*35.8*	*63.5*

^{19}F NMR integration data for the VCPR of ***22a*** *in d8-toluene (0.15 M) heated at 373 K (AV400, QNP-z probe); 8 scans, D1= 1.0 s, TE = 373 K.*

Time	Average Integrations			Relative Percentage		
(s)	SM	VCPR	3,3	SM	VCPR	3,3
51	1.00	0.07	0.04	90.6	6.1	3.4
75	1.00	0.08	0.04	90.0	6.8	3.3
99	1.00	0.10	0.11	82.6	7.9	9.5
123	1.00	0.12	0.16	78.4	9.3	12.3
147	1.00	0.18	0.22	71.1	13.1	15.8
171	1.00	0.24	0.29	65.2	15.9	18.9
195	1.00	0.28	0.35	61.6	17.0	21.4
219	1.00	0.32	0.42	57.2	18.6	24.2
243	1.00	0.35	0.52	53.4	18.9	27.6
267	1.00	0.43	0.58	49.7	21.3	29.0
291	1.00	0.51	0.68	45.7	23.2	31.1
315	1.00	0.56	0.77	42.8	24.2	33.0
339	1.00	0.61	0.85	40.5	24.9	34.6
363	1.00	0.66	0.95	38.3	25.2	36.5
387	1.00	0.76	1.08	35.2	26.7	38.1
411	1.00	0.85	1.23	32.5	27.6	39.9
435	1.00	0.93	1.36	30.4	28.4	41.2
459	1.00	0.99	1.41	29.4	29.1	41.4
483	1.00	1.10	1.57	27.2	30.0	42.8
507	1.00	1.22	1.83	24.7	30.2	45.1
531	1.00	1.34	1.88	23.7	31.7	44.6
555	1.00	1.52	2.20	21.2	32.2	46.6
579	1.00	1.59	2.34	20.3	32.3	47.5
603	1.00	1.76	2.58	18.7	33.0	48.3
627	1.00	1.97	2.92	17.0	33.4	49.6
651	1.00	2.21	3.16	15.7	34.7	49.7
675	1.00	2.13	3.13	16.0	34.0	50.0
699	1.00	2.43	3.56	14.3	34.8	50.9
723	1.00	2.70	3.87	13.2	35.6	51.2
747	1.00	2.88	4.15	12.4	35.8	51.7
771	1.00	2.98	4.32	12.0	35.9	52.1
795	1.00	3.59	5.19	10.2	36.7	53.1
819	1.00	3.78	5.38	9.8	37.2	53.0
843	1.00	3.36	4.88	10.8	36.3	52.8
867	1.00	4.25	6.24	8.7	37.0	54.3
891	1.00	5.13	7.42	7.4	37.9	54.7
915	1.00	6.12	8.78	6.3	38.5	55.2
939	1.00	5.47	7.85	7.0	38.2	54.8
963	1.00	6.99	10.23	5.5	38.4	56.2
987	1.00	6.75	9.82	5.7	38.4	55.9
1011	1.00	7.67	10.89	5.1	39.2	55.7
1035	1.00	6.99	10.21	5.5	38.4	56.1
1059	1.00	6.96	9.74	5.6	39.3	55.0
1083	1.00	8.89	12.55	4.5	39.6	55.9
1107	1.00	10.62	14.97	3.8	39.9	56.3
1131	1.00	9.79	14.16	4.0	39.2	56.8
1155	1.00	14.57	21.05	2.7	39.8	57.5
1179	1.00	12.66	17.92	3.2	40.1	56.7
1203	1.00	16.53	23.12	2.5	40.7	56.9
1227	1.00	16.37	22.65	2.5	40.9	56.6
1251	1.00	16.80	23.88	2.4	40.3	57.3
1275	1.00	23.06	33.48	1.7	40.1	58.2
1299	1.00	20.64	28.65	2.0	41.0	57.0
1323	1.00	41.69	61.14	1.0	40.2	58.9
1347	1.00	22.65	32.25	1.8	40.5	57.7
1371	1.00	29.39	42.34	1.4	40.4	58.2
1395	1.00	28.58	40.41	1.4	40.8	57.7
1419	1.00	39.00	56.55	1.0	40.4	58.6
1443	1.00	38.19	54.13	1.1	40.9	58.0
1467	1.00	34.78	50.50	1.2	40.3	58.5
1635	*1.00*	*382.68*	*547.06*	*0.1*	*41.1*	*58.8*

Rearrangement Reaction Profiles for 22a (343-373 K)

The reaction profile (relative percentage conversion vs time) was plotted using the NMR data above on Excel.

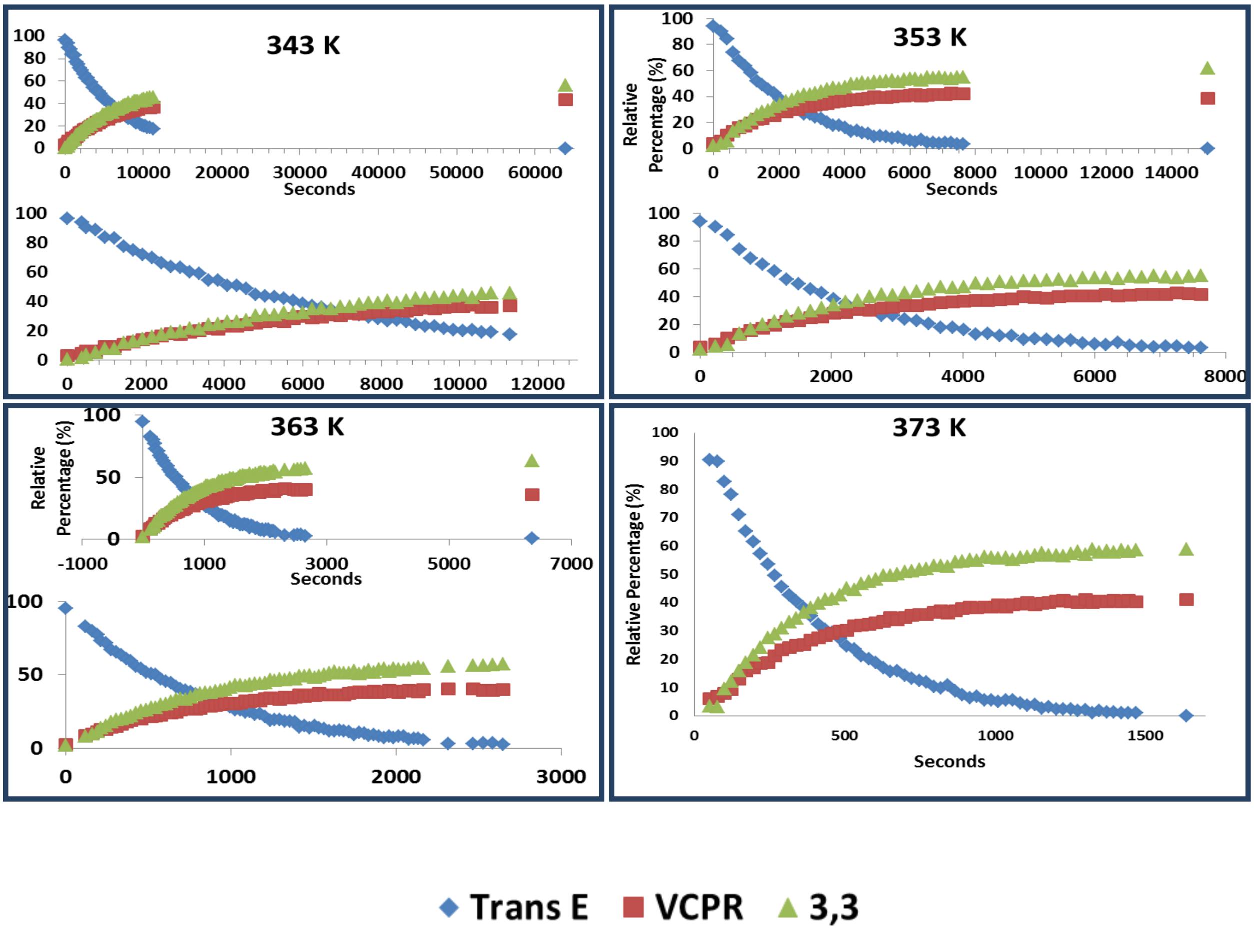


Figure S35: Reaction profiles for the rearrangement of **22a** at 343-373 K.

NMR Simulations

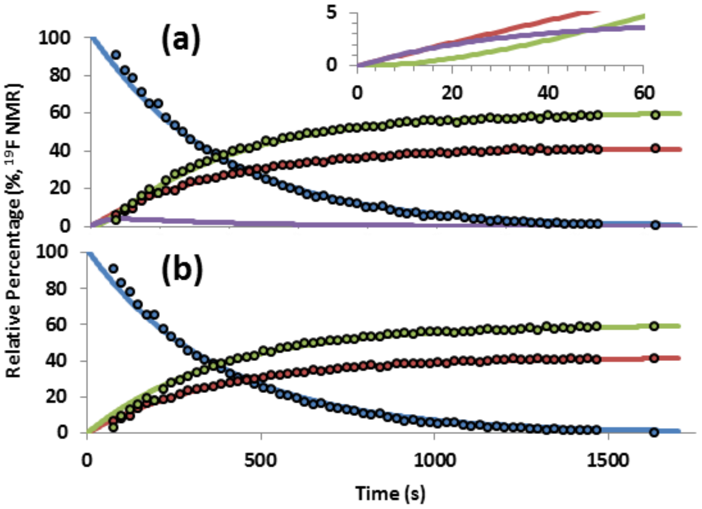
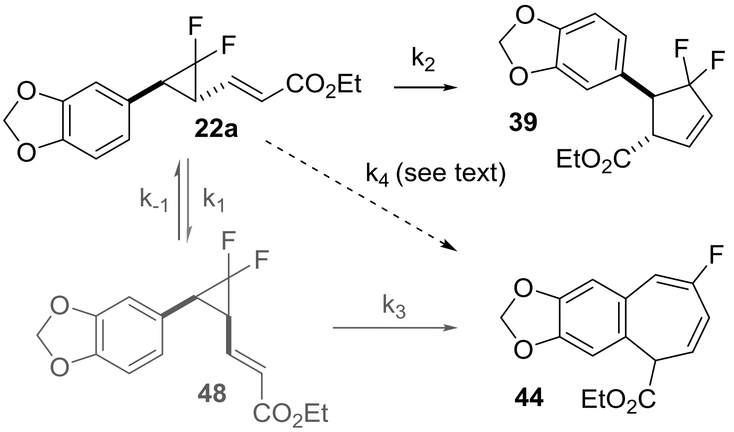


Figure S36: Experimental (points) and simulated (lines) concentration/time profile for thermolysis (373 K) of **22a**; a) simulation Model A takes into account *cis*-**48**; insert shows the first simulated 30 seconds of the rearrangement b) Model B utilising a steady state approximation for cis-**48** (**blue** = *trans*-**22a**, **green** = **44**, **red** = **39**, **purple** = *cis*-**48**).

The experimental concentration/time profile could be simulated successfully as far as experimental end points using numerical integration software[S37] based on two kinetic models expressed in **Scheme S7**.



Scheme S8: Kinetic models used in the simulation of parallel VCPR and [3,3]-pathways.

Model A used successfully with phenyl **1a**, takes into account the equilibrium set up between *cis*-**48** and *trans*-**22a** due to cyclopropane stereoisomerisation and the subsequent first order rearrangement through to diene **44** and cyclopentene **39**, respectively. Simulated data using this model showed formation of cis-**48**, rising to a maximum at about 3% in the reaction mixture after 30 seconds before slowly decaying (**Figure S36a**). These values are below the lower limit of experimental detection and explain why **48** was not observed. Deconvolution of rate constants predicted that rearrangement of **22a** should be selective for the [3,3]-pathway, with a rate approximately 40 times faster than VCPR (**Table S4**). This does not match experimental findings and may be due to an overestimation in rates involving *cis*-**XX** due to the lack of experimental data points to fit profiles to.

This issue was resolved by treating both rearrangement pathways as first order with respect to *trans*-**22a** (Model B), k_4 represents an overall rate for the conversion of **22a** to **48** and incorporates the cyclopropane stereoisomerisation and [3,3]-rearrangement rates associated with **48**. Again, simulated data showed good correlation with experimental values (**Figure S36b**) and this time the rate constants favoured the [3,3] pathway only slightly (1.5 times faster than VCPR), consistent with experimental conversions of 59% and 41% to diene **44** and cyclopentene **39**, respectively. Furthermore, the much higher rate for VCPR from **22a** (11.5×10^{-4} s^{-1}) than from phenyl **1a** (1.6×10^{-4} s^{-1}), matched the predicted differences in calculated activation energies.

Table S4: Rate Constants extracted from reaction simulations.

Rate	**Model**	
(10^{-4} s^{-1})	**A**	**B**
k_2	11.2	11.1
K_1	21.8	-
k_{-1}	153.2	-
k_3	439.4	-
k_4	-	15.8
k_3/k_2	39.2	-
k_4/k_2	-	1.4

Simulation Procedure: The NMR concentration/time data obtained for **22a** (including a measured endpoint) was imported into Berkeley Madonna software[S37] from text files and simulated using the two methods discussed below:

```
Model A

STARTTIME = 0
STOPTIME=43200
DT = 0.05

A0=100 {start concentration of trans cyclopropane}
Init A=A0
B0=0 {start concentration of cis cyclopropane}
Init B=B0
C0=0 {start concentration of cyclopentene}
Init C=C0
D0=0 {start concentration of benzoheptadiene}
Init D=D0

k1=0.0001 {k1 is isomerisation to cis}
k_1=0.0001 {k_1 is isomerisation to trans}
k2=0.0001 {k2 is the VCPR}
k3=0.0001 {k3 is the 3,3}

d/dt (A)=-k1*A-k2*A+k_1*B
d/dt (B)=-k_1*B-k3*B+k1*A
d/dt (C)=k2*A
d/dt (D)=k3*B

LIMIT A>=0
LIMIT B>=0
LIMIT C>=0
LIMIT D>=0
```

The extracted rate data (343-373 K) from Model A was not consistent with experimental observation of VCPR and [3,3] pathways having similar rates (**Table S5**).

Table S5: Rate data based on Model A.

Temp (K)	k_1 (10^{-4} s^{-1})	k_{-1} (10^{-4} s^{-1})	k_2 (10^{-4} s^{-1})	k_3 (10^{-4} s^{-1})
343	5.243	440.186	0.734	88.296
353	2.667	0.193	2.028	114.035
363	11.061	165.75	5.466	357.913
373	21.794	153.183	11.246	439.420

Model B

```
STARTTIME = 0
STOPTIME=43200
DT = 0.05

A0=100 {start concentration of trans cyclopropane}
Init A=A0
C0=0 {start concentration of cyclopentene}
Init C=C0
D0=0 {start concentration of benzoheptadiene}
Init D=D0

k2=0.0001 {k2 is the VCPR}
k4=0.0001 {k3 is the 3,3}

d/dt (A)=- -k2*A-k4*A
d/dt (C)=k2*A
d/dt (D)=k4*A

LIMIT A>=0
LIMIT C>=0
LIMIT D>=0
```

The rate data extracted from **Model B** matched experimental results more closely, giving similar rate values for VCPR and [3,3]-rearrangement pathways (**Table S6**).

Table S6: Rate data extracted from Model B.

Temp (K)	k_2 (10^{-4} s^{-1})	k_4 (10^{-4} s^{-1})
343	0.7338	0.8725
353	2.0242	2.6320
363	5.4558	7.4840
373	11.0977	15.7878

Arrhenius Plot for Piperonyl 22a

Rate data from **Table S4** was changed into the desired Arrhenius parameters (**Table S7**).

Table S7: Arrhenius Data

Temperature (K)	1/T	k_2 (10^{-4} s^{-1})	Ln k_2	k_4 (10^{-4} s^{-1})	Ln k_4
344.1	0.002906132	0.7338	-9.51986	0.8725	-9.34673
354.2	0.002823264	2.0242	-8.50517	2.632	-8.2426
364.2	0.002745744	5.4558	-7.51366	7.484	-7.19757
374.2	0.002672368	11.0977	-6.8036	15.7878	-6.4511

From Arrhenius equation **1**, a plot of Ln k_2 or Ln k_4 vs 1/T was generated on Excel and a line fitted using the trendline function (**Figure S37**). The equation of the line was calculated using the *LINEST* statistical function and the gradient used to calculate E_a. The errors in the values were estimated by plotting two lines which would result from the maximum errors (± 5%) in the outermost points and averaging the gradient to determine the E_a.

$$\ln \mathrm{k} = \frac{-E_a}{\mathrm{R}}\frac{1}{\mathrm{T}} + \ln \mathrm{A} \qquad (\mathbf{1})$$

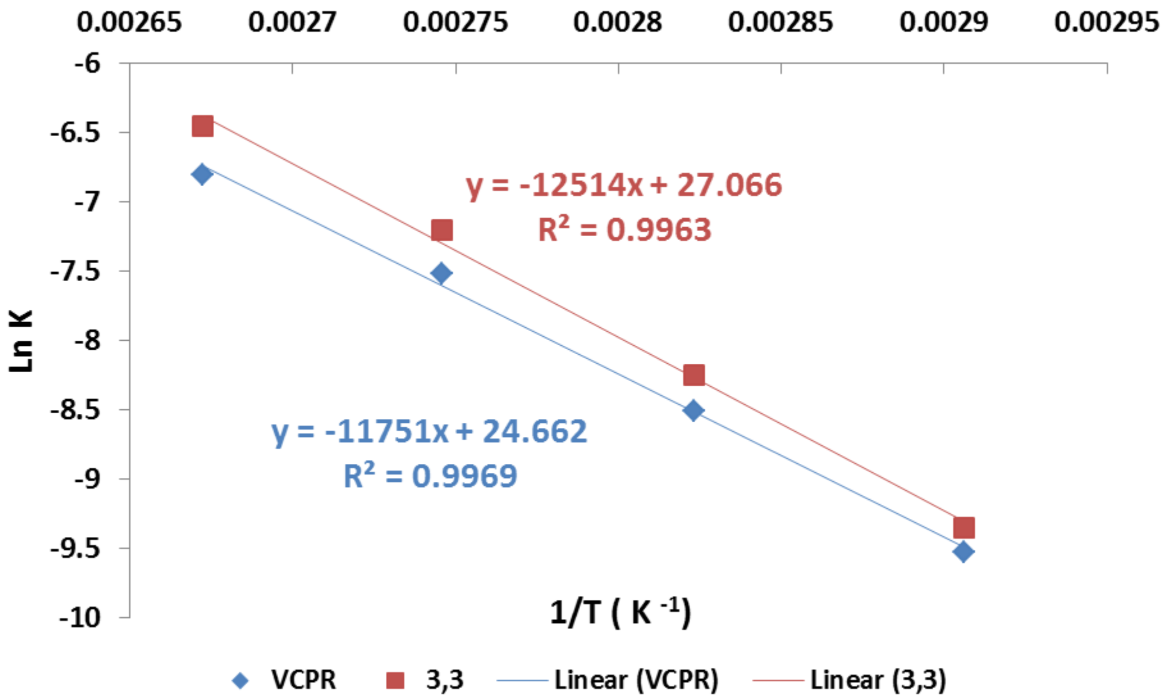


Figure S37: Combined Arrhenius Plots for VCPR and [3,3]-rearrangement of **22a.**

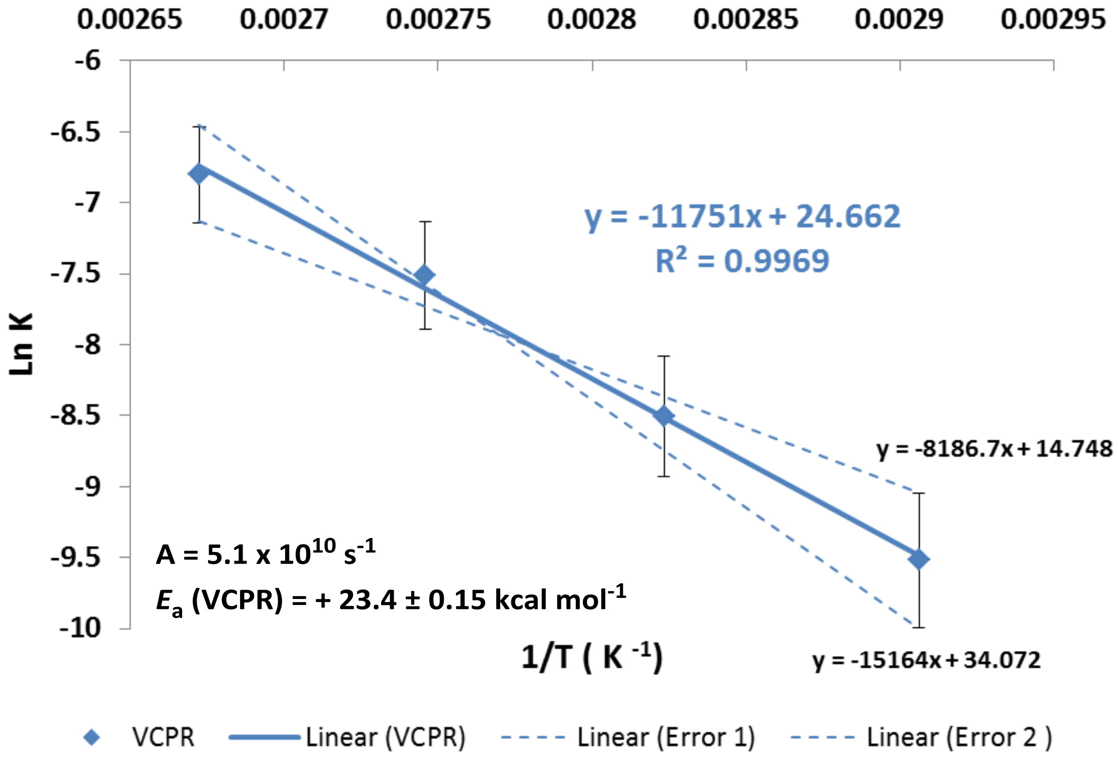


Figure S38: Arrhenius plot for VCPR of **22a** with error estimations.

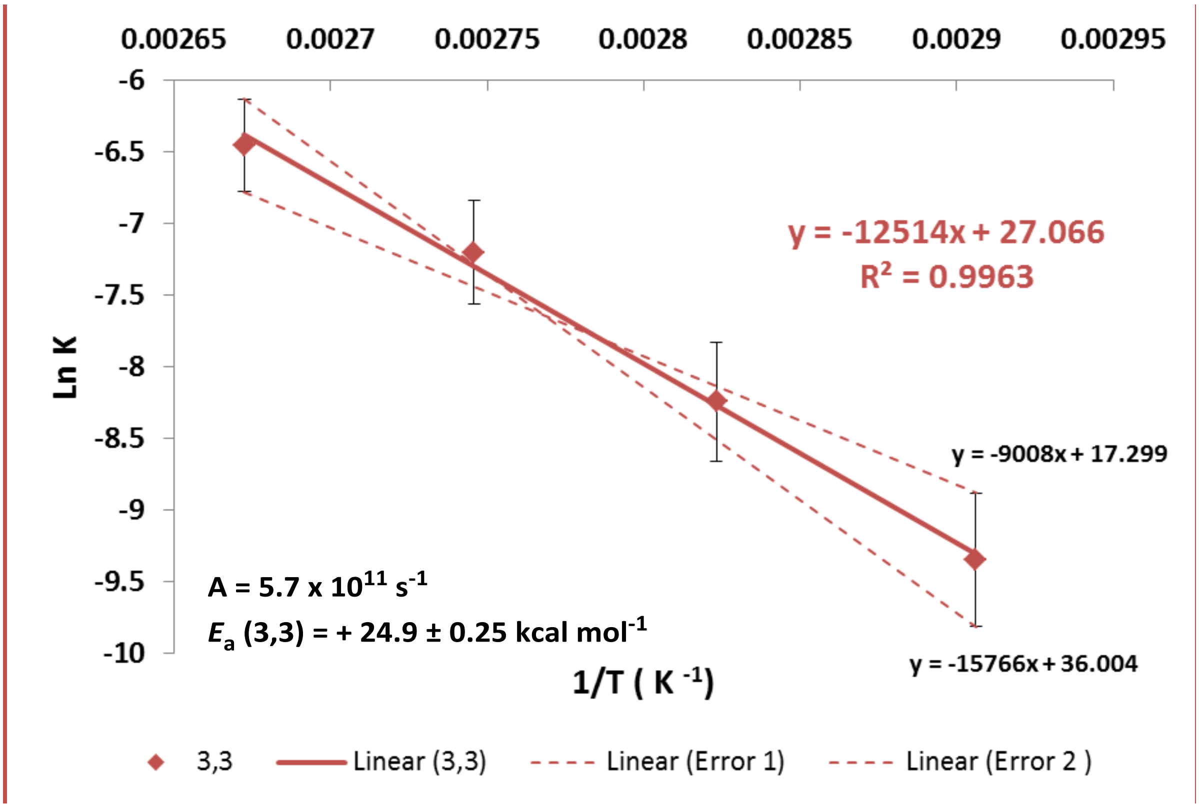


Figure S39: Arrhenius plot for [3,3]-rearrangement of **22a** with error estimations.

Identification the Most Appropriate Method for Electronic Structure Calculations

In order to assess the accuracy of the electronic structure calculations efficiently, all experimental activation energies were recalculated to 298 K using the Arrhenius data and methods described by Maskill.[S38] We previously reported that for VCPRs, changes to the basis set either had detrimental effects (with UB3LYP, UM06-2X and UB97-D functionals) or gave slightly more accurate values of $\Delta G^{\ddagger}$ when the diffuse function was introduced (6-31+G*) with the UM05-2X functional. Increasing polarisation and diffuse functions (6-31+G**) gave no improvement in the agreement between experimental and calculated values for a benchmarking set of VCPRs; these trends were also followed for piperonyl **22a** (see S182 for more details). Initial methodology screening was carried out using Spartan'10 software due to the ease of local implementation. All activation energies were then recalculated in Gaussian'09, since the software dealt with the open shell singlet character of the VCPR better giving $<S^2>$ values closer to 0.75, some additional valuable methods were available, and the energies obtained would then be more comparable with the literature. Investigating the barrier height for the rearrangement of VCP **9f** to **TS1f** (models representing piperonyl **22a**), gave results comparable to those observed with phenyl **9j**. The M05-2X functional[S39] with the 6-31+G* basis set still proved to be the most accurate methodology, with a $\Delta\Delta G^{\ddagger}$ = 0.2 kcal mol^{-1} (**Figure S40**). Truhlar and co-workers reported that the M06-2X functional, with a similar HF-exchange (56% for M05-2X and 58% M06-2X), was slightly more accurate overall in assessing kinetic parameters than M05-2X.[S40] However in our new system (VCP-**9f**) this was not the case, with a higher (4.5 kcal mol^{-1}) overestimation by the M06-2X functional with the same basis set.

During the review of the manuscript of our previous publication, it was suggested that the different amounts of HF-exchange used in each method could have some role in determining the accuracy of the calculated free energies of activation for the VCPR. The M06 functional, with a lower HF-exchange of 27%, gave the closest agreement with experimental values when the 6-31G* basis set was used ($\Delta\Delta G^{\ddagger}$ = 0.7 kcal mol^{-1}). Electronic structure calculations using M05/6-31G* methodology were less accurate ($\Delta\Delta G^{\ddagger}$ = 2.6 kcal mol^{-1}), even though this functional has a similar HF-exchange value (28%) to the M06 functional. However, we observed little difference between the M05-2X and M06 functionals when the VCPR barrier heights were calculated with Gaussian'09 for piperonyl **9f**, simple precursor **8a** and phenyl **9j**. Furthermore, for the VCPR of non-fluoro **8b**, M06/6-

31+G* calculations were only within 1.6 kcal mol^{-1} (underestimate) whereas M05-2X/6-31+G* methods gave ΔΔG‡ values within 0.8 kcal mol^{-1} (overestimate, see S183 for more details).

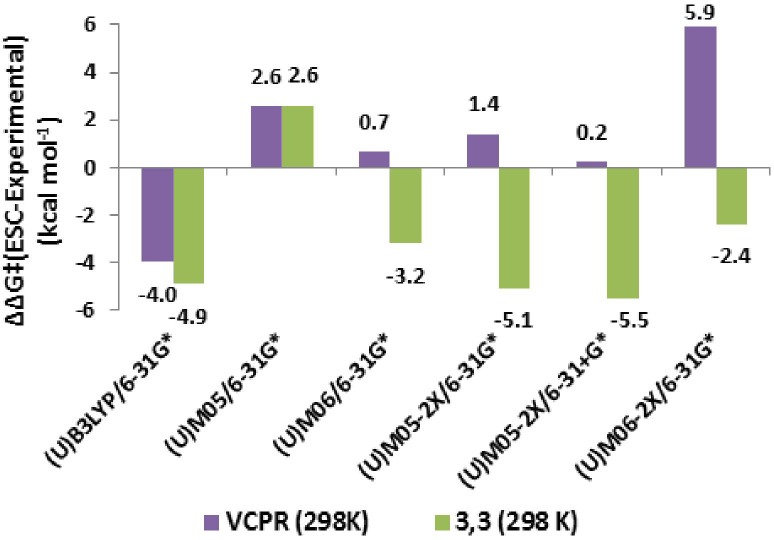


Figure S40: Differences between experimental ΔG‡ (298 K, re-calculated from activation parameters) and ΔG‡ from electronic structure calculations (298 K, gas phase, Spartan'10) plotted as ΔΔG‡ (ΔG‡(ESC)-ΔG‡(experimental), kcal mol^{-1}) for the VCPR and [3,3]-rearrangement of VCP **9f** and **48**, respectively. Expected error associated with calculated data is ± 0.5 kcal mol^{-1}.

Other DFT methods either underestimated experimental barrier heights when 20% HF-exchange was used (B3LYP), or overestimated (+1.8 kcal mol^{-1}) when a hybrid exchange-correlation was used with 19% HF-exchange at short range and 65% at long range (CAM-B3LYP,[S41] (**Figure S41**)). These results suggest that HF-exchange alone does not determine the accuracy of VCPR activation energies.

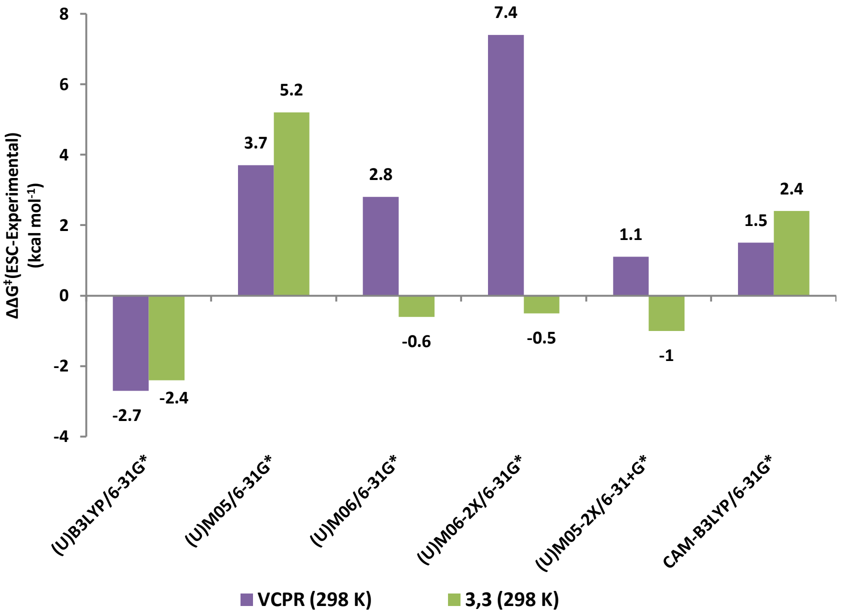


Figure S41: Differences between experimental ΔG‡ (298 K, re-calculated from activation parameters) and ΔG‡ from electronic structure calculations (298 K, gas phase, Gaussian'09) plotted as ΔΔG‡ (ΔG‡(ESC)-ΔG‡(experimental), kcal mol^{-1}) for the VCPR and [3,3]-rearrangement of VCP **9f** and **48**, respectively. Expected error associated with calculated data is ± 0.5 kcal mol^{-1}.

One difference which was observed between phenyl and piperonyl substituents was the change in dipole moment calculated from precursor to transition state; **9j** showed a slight decrease in calculated polarity during VCPR and [3,3]-rearrangement (change in dipole = -0.39 and -0.22 Debyes, respectively) whereas **9f** showed a slight increase (change in dipole = +1.2 and +0.95 Debyes, respectively, UB3LYP/6-31G*, Gaussian'09, gas phase, 298 K). The calculated activation energies for the two rearrangement pathways from 9f were assessed using M05-2X/6-31+G* method with different solvation parameters which had varying dielectric constants (range of ε = 2.37-35.7), but only a slight decrease in barrier height for the [3,3]-rearrangement in acetonitrile compared with gas phase was predicted (ΔG‡Gas-ΔG‡MeCN = -0.9 kcal mol^{-1}). Maas reported that the experimental rate for the [3,3]-rearrangement of non-fluorinated 1-aryl-2-vinylcyclopropanes was more than 8 times faster in acetonitrile than benzene, but VCPR rates were not affected by reaction solvent.[S42] VCP **22a** showed no significant change in rearrangement outcome when heated in either [D3]acetonitrile (52% (**44**([3,3]) and 48% (**39**(VCPR)) conversion, determined by ^{19}F NMR) or [D8]toluene (58% (**44**([3,3]) and 42% (**39**(VCPR)) conversion, determined by ^{19}F NMR).

Therefore, no solvation methods were applied and all electronic structure calculations were carried out in the gas phase (see S184 for more details).

Previously, only a concerted closed-shell transition state was investigated for the [3,3]-rearrangement of *cis*-**1b**. This was consistent with Özkan and Zora's study[S43] of the divinylcyclopropane rearrangement; despite running spin-unrestricted calculations, no low energy diradical or triplet intermediates or transition states were found. We used our previously optimised triplet intermediate of ring opened phenyl VCP **9j** as a starting point to search for alternative triplet or open shell singlet pathways for the [3,3]-rearrangement ((U)B3LYP/6-31G* (gas phase, 298 K), Spartan'10). Two triplet transition states connected the alkenoate radical with alternative *ortho*-carbon centred radicals on the aromatic ring; both had uncompetitive calculated activation energies of 53.6 kcal mol^{-1} and 59.2 kcal mol^{-1}. Only one of these optimised as a diradical, but had a much higher barrier for rearrangement (37.8 kcal mol^{-1}) than the closed shell pathway (27.8 kcal mol^{-1}). For subsequent computational methodology screening, the [3,3]-rearrangement was treated using closed shell methodology (see S187 for more details).

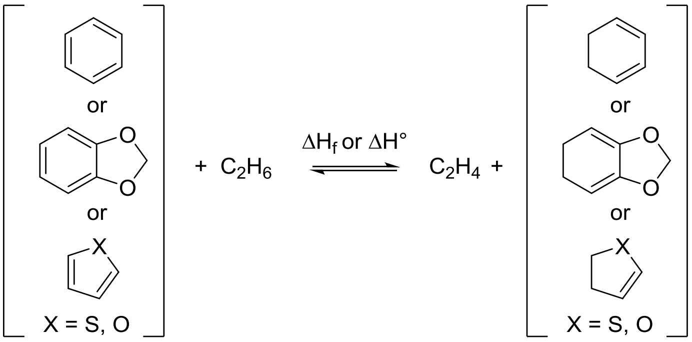
Irrespective of the basis set used, the M05-2X functional was found to be the least accurate of those examined for calculating the free energy of activation of **48** to **TS6a** (6-31G*, $\Delta\Delta G^{\ddagger}$ = - 5.1 kcal mol^{-1} and 6-31+G*, $\Delta\Delta G^{\ddagger}$ = -5.5 kcal mol^{-1}). Instead, the M06-2X/6-31G* combination was found to be the best at predicting barrier height with a $\Delta\Delta G^{\ddagger}$ = -2.4 kcal mol^{-1} (**Figure S40**). This is opposite to what was observed for the VCPR and gives a strong indication of the functionals' differing abilities in dealing with open shell singlet character or the loss of aromaticity at transition states. The (U)B3LYP/6-31G* method gave a similar underestimation in barrier height for both pathways ($\Delta\Delta G^{\ddagger}$ values were within error of ± 0.9 kcal mol^{-1}) but (U)M05/6-31G* gave exactly the same overestimate of 2.6 kcal mol^{-1}. If required, these two combinations of functions and basis sets provide a universal method for assessing both rearrangement pathways in Spartan'10.

Electronic structure calculations for VCP **9f** which were carried out in Gaussian'09 dealt with the open shell singlet character of the VCPR better (S^2 value closer to 0.75) than Spartan'10, resulting in more accurate barrier heights; M05/6-31G* was the key exception, with higher $\Delta\Delta G^{\ddagger}$ values for both VCPR and [3,3]-pathways (+3.7 kcal mol^{-1} and +5.2 kcal mol^{-1}, respectively). DFT methodology using B3LYP/6-31G* still gave consistent underestimation in barrier height for both pathways; $\Delta\Delta G^{\ddagger}$ values were within 0.3 kcal mol^{-1} of each other

(**Figure S41**). Of the Minnesota functionals, the M06-2X/6-31G* method remained the most accurate for the [3,3]-rearrangement ($\Delta\Delta G^{\ddagger}$ = -0.5 kcal mol^{-1}) and M05-2X/6-31+G* for the VCPR ($\Delta\Delta G^{\ddagger}$ = +1.1 kcal mol^{-1}).

We looked to explore the effectiveness of the B3LYP/6-31G* and M06-2X/6-31G* calculations of barrier heights for divinylcyclopropane[S11,S44] and heteroarene-vinylcyclopropane rearrangements[S45] reported in the literature but the reported experimental errors were so big that it made it impossible to distinguish between accurate and inaccurate calculated barriers (see S189 for more details).

An absolutely critical event in the [3,3]-rearrangement is the temporary disruption of aromaticity; the enthalpic consequences of this event must be handled well if any method is to provide realistic free energies of activation. The isodesmic reactions represented in **Scheme S9** were used to assess how well the B3LYP and M06-2X methods dealt with this temporary dearomatisation in the transition state.



Scheme S9: Isodesmic reactions used to model the disruption of aromaticity.

We therefore benchmarked the DFT calculations against well-known thermochemical recipes using these isodesmic reactions. There was little difference between the calculated heats of formation for either T1[S46] or G3(MP2)[S47] thermochemical recipes (within computational error of ±0.5 kcal mol^{-1}), but when compared with experimental values,[S48,S49] T1 was more accurate for ethane and ethylene whereas G3(MP2) was slightly more accurate for aromatic compounds (**Figure S42**).

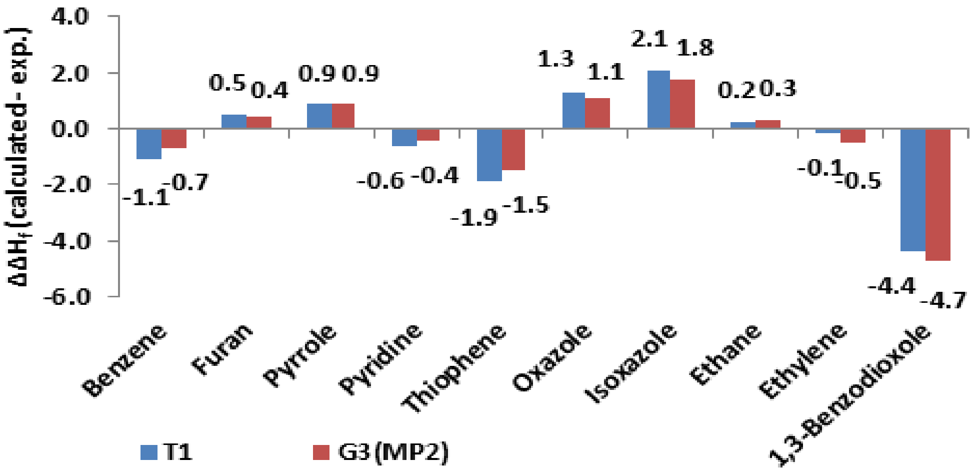


Figure S40: Differences between calculated and experimental heats of formation (Spartan'10, values in kcal mol^{-1}).

The average error associated with the calculated heats of formation for benzene, furan, pyrrole, pyridine, thiophene, oxazole and isoxaxole were ± 1.21 kcal mol^{-1} and ± 0.95 kcal mol^{-1} for T1 and G3(MP2), respectively. Calculated data for 1,3-benzodioxole had an underestimation greater than 4.0 kcal mol^{-1} for both methods when compared with experimental values.[S50]

The G3(MP2) values were used to assess the accuracy of the calculated enthalpy change for the dearomatisation of benzene, benzodioxole, furan and thiophene using either B3LYP/6-31G* or M06-2X/6-31G* methodology (**Figure S43**, see S193, S194 for more details). The B3LYP method had an average overprediction in enthalpy of 5.3 kcal mol^{-1} for benzene, furan, thiophene and 1,3-benzodioxole, and M06-2X consistently over-estimated the enthalpic cost of dearomatisation, ranging from 3.6 kcal mol^{-1} to 6.4 kcal mol^{-1} (total average error of 4.8 kcal mol^{-1}).

This thermochemical analysis suggests that the two most desirable methods for assessing the [3,3]-rearrangement do not deal with the loss of aromaticity at the transition state well. This is important since M06-2X/6-31G* calculations were perceived to be the most accurate, but are likely to over-predict the free energy ($\Delta G^{\ddagger}$) for rearrangements involving benzene, furan, thiophene and 1,3-benzodioxole.

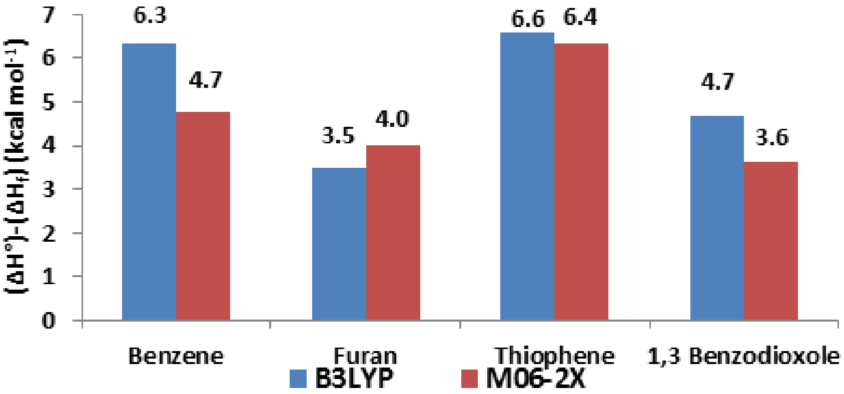


Figure S43: Difference in change in enthalpy (ΔH°) calculated using B3LYP or M06-2X (6-31G*) methods and G3(MP2) heats of formation (ΔHf) for the isodesmic reactions represented in Scheme 10 (gas phase, 298 K, Spartan'10, units are in kcal mol^{-1}).

Basis Set Effect on 9f VCPR Activation Energies

M05-2X functional was the most accurate method for calculating the free energies of activation for the VCPR of phenyl-**9j** and piperonyl-**9f**. No benefit was found from increased basis sets higher than 6-31+G* for **9f** consistent with our previous studies[S20] (**Table S8** and **Figure S44**).

Table S8: Basis Set Effect on Accuracy of Calculated VCPR Free Energies of Activation for **9f**

Functional	Basis Set	$\Delta G^{\ddagger[a]}$	$\Delta\Delta G^{\ddagger[b]}$
M05-2X	6-31G*	29.80	2.80
M05-2X	6-31+G*	28.10	1.10
M05-2X	6-311G*	30.30	3.30
M05-2X	6-311+G**	28.30	1.30

[a] Gaussian'09, gas phase, 298 K. [b] Difference in calculated free energy of activation $\Delta G^{\ddagger}$ and calculated activation energy (E_a); $\Delta\Delta G^{\ddagger} = (\Delta G)-(E_a)$. All units are in kcal mol^{-1}.

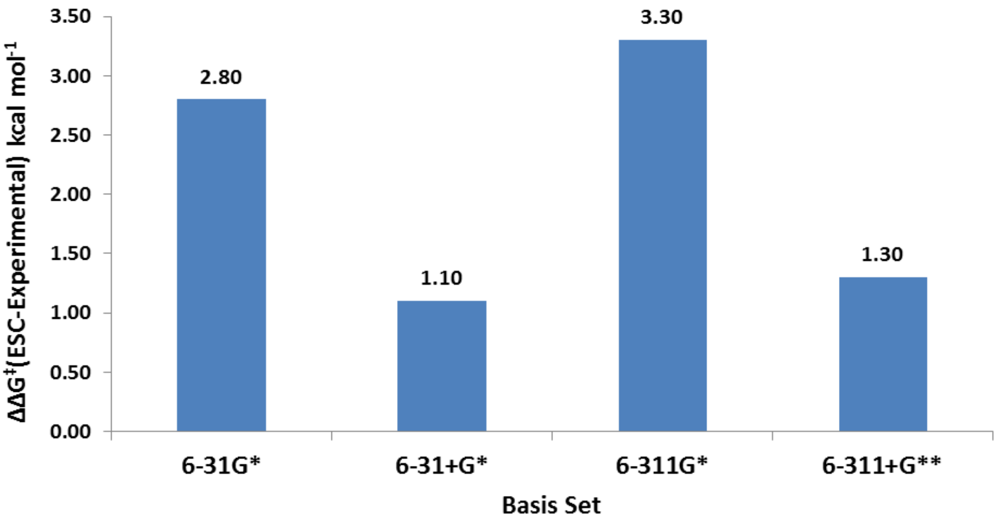


Figure S41: Comparison of $\Delta\Delta G^{\ddagger}$ values and basis set effects (Gaussian'09, M05-2X, gas phase, 298 K, Energies quoted in kcal mol^{-1}).

Method Screening for VCPR

The calculated activation energies for the VCPR of simple VCP **8b** and difluoro-VCPs, phenyl **9j** and piperonyl **9f**, were assessed showing that the M05-2X/6-31+G* method was the most accurate for all three compounds (**Table S9** and **Figure S45**).

Table S9: Methodology Screening for VCPR

Method	**$\Delta\Delta G^{\ddagger}$ (ESC – Exerimental, kcal mol^{-1})[a]**		
	8b [b]	**9j**[c]	**9f**[d]
UB3LYP/6-31G*	-2.3	-2	-2.7
UCAM-B3LYP/6-31G*	-	-	1.5
UM05/6-31G*	2.0	3.3	3.7
UM06/6-31G*	1.4	2.4	2.8
UM05-2X/6-31G*	1.6	2.5	2.8
UM05-2X/6-31+G*	0.8	1.2	1.1
UM06/6-31+G*	-1.6	-	-

[a] Gaussian'09, gas phase, 298 K. [b] Experimental activation energy corrected to 298 K from literature data.[S51] [c] Experimental data reported in previous publication.[S20] [d] This work.

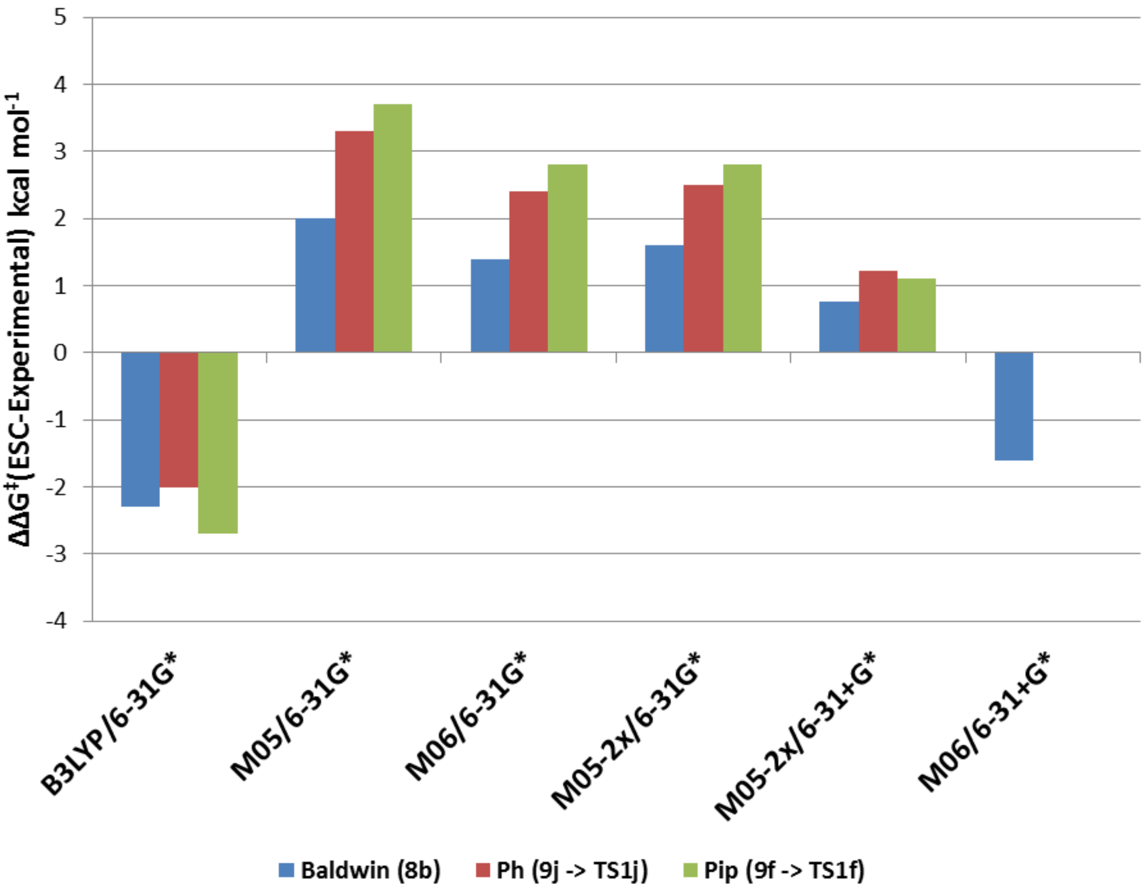


Figure S42: Computational methodology screening for VCPR.

Assessment of Solvent Effects

The difference in dipole between the VCPR and aromatic-vinylcyclopropane rearrangement transition states for the rearrangement of piperonyl-VCP precursors (*trans*-**9f** and *cis*-**9f**, respectively) was used to assess the potential effect solvent would have on electronic structure calculations (**Table S10**).

Table S10: Solvation Effect on VCPR and [3,3]-Rearrangement Dipole Moments

Solvent	**Solvent Properties**		**Difference in Dipole Moment (Debyes)**[c]	
	Dielectric Constant[a]	**Dipole Moment (Debyes)**[b]	**9f -> TS1f**	**48 -> TS6a**
Gas Phase (n.a.)	n.a.	n.a.	0.11	0.74
Toluene	2.37	0.36	0.30	0.74
Diphenyl Ether	3.73	1.30	0.63	0.73

1-Pentanol	15.13	1.70	0.50	1.06
Acetonitrile	35.70	3.92	0.53	1.06

[a] Data reported in Gaussian'09 user's reference.[S52] [b] Data reported by National Institute of Standards and Technology (NIST).[S53] [c] Gaussian'09, (U)M05-2X/6-31+G*, 298 K, solvation parameterised using Self-Consistent Reaction Field (SCRF)[S54] using the Conductor-like Polarisable Continuum Model (CPCM).[S55]

Due to the slightly higher dipole moment for the [3,3]-pathway, more polar solvents (1-pentanol, acetonitrile) gave lower $\Delta G^{\ddagger}$ values compared with gas phase or less polar solvents (toluene, diphenyl ether); approximately 1.0 kcal mol^{-1} lower energy barrier (**Table S11** and **Figure S46**).

Table S11: Solvent Effect on Rearrangement Free Energies of Activation ($\Delta G^{\ddagger}$)

Solvation	**$\Delta G^{\ddagger}$ ((U)M05-2X/6-31+G*, 298 K, Gaussian'09)**		
	VCPR	**[3,3]**	**$\Delta\Delta G^{\ddagger}$ ($\Delta G^{\ddagger}_{VCPR}$-$\Delta G^{\ddagger}_{[3,3]}$)**
Gas Phase	28.1	25.3	2.8
Toluene	28.2	25.5	2.7
Diphenylether	28.3	25.7	2.6
1-Pentanol	28.5	24.4	4.1
Acetonitrile	28.6	24.4	4.2

All units are in kcal mol^{-1}.

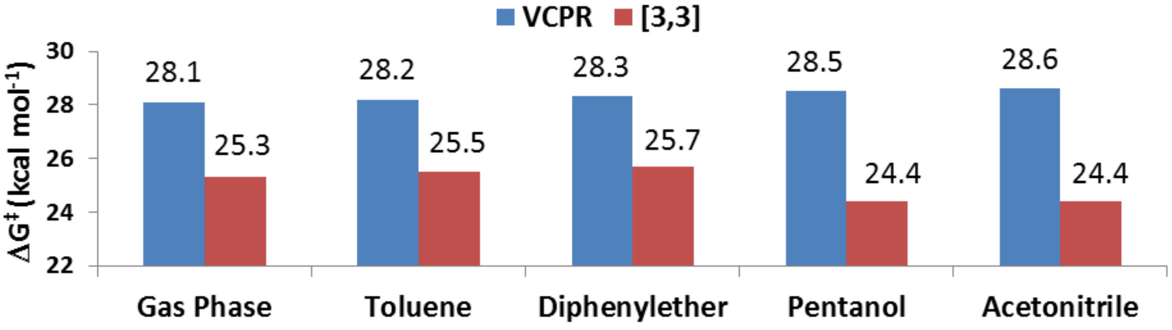


Figure S43: Solvent effect on calculated $\Delta G^{\ddagger}$ values for the VCPR of **9f** and [3,3]-rerrangement of **48**.

The effect of solvent was also investigated experimentally: A solution of piperonyl-**22a** (19.3 mg, 0.33 mmol) in 0.44 M [D3]acetonitrile (0.75 mL) or [D8]toluene (0.75 mL) was heated in an oil bath at 70 °C for 17 hours. Crude ^{19}F NMR analysis of the resulting mixture was used to determine relative conversion of rearrangement products (**Table S12**), showing little difference in reaction selectivity between solvents (**Figure S47**).

Table S12: Solvent Effect on Thermal Rearrangement of **22a**.

Solvent	**Average ^{19}F NMR Integration**		**Relative Percentage (%)[a]**	
	VCPR (39)	**[3,3] (44)**	**VCPR (39)**	**[3,3] (44)**
[D3]acetonitrile	0.9584	1.0281	48	52
[D6]toluene	0.9744	1.3721	42	58

[a] Assumed NMR integration error of ± 5 %.

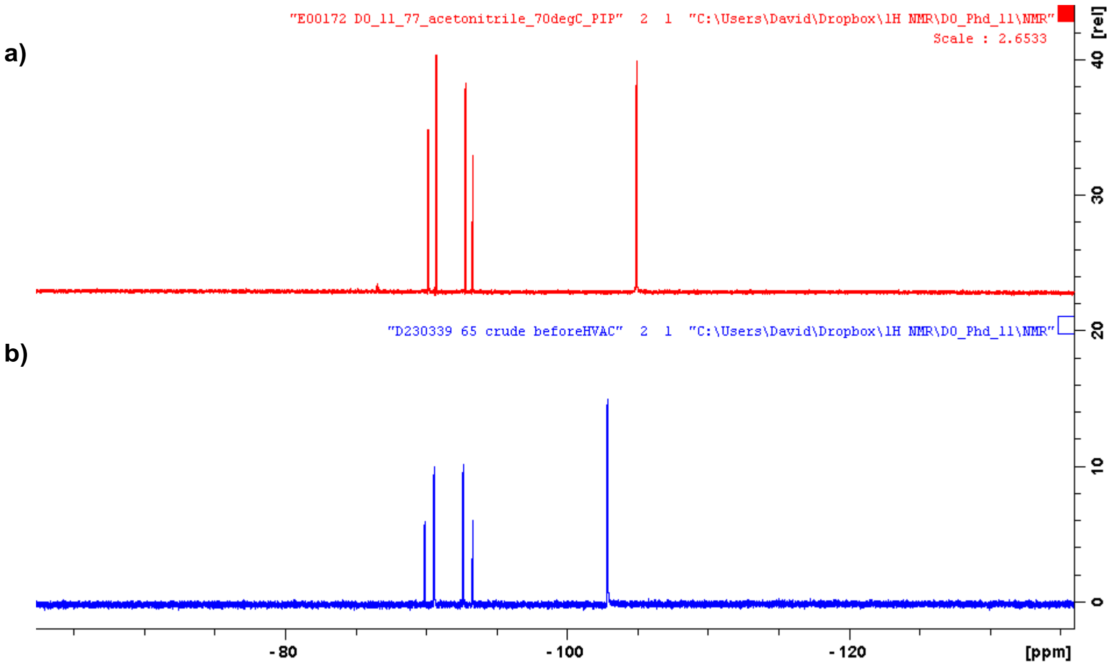


Figure S44: Crude ^{19}F NMR for thermal rearrangement of **22a** in a)[D3]acetonitrile and b) [D8]toluene.

Investigations into Alternative [3,3]-Diradical/Triplet Pathways

Attempts to use transition state **S-TS5** as a starting point to investigate triplet or diradicaloid possibilities failed when all calculations resulted in closed shell compounds ($S^2 = 0$). Instead, our previously reported *transoid* triplet intermediate **S21** was used as a starting point with atom constraints set up between alkenoate carbon and aryl C5 or C2, giving rise to *transoid* and *cisoid* structures, respectively (**Figure S42**). Molecules were manipulated in Spartan’10 to bring reaction centres within approx. 3.0 Å. Energy profiles were examined by bringing the reaction centres closer together along the constraint (3.073 Å to 1.073 Å, over 15 steps) using low level molecular mechanics (UAM1, multiplicity = 3, no MIX keyword used). Higher energy species with imaginary frequencies were examined without constraints and afforded three triplet transition states for the [3,3]-rearrangement, *transoid* **S-TS6** and *cisoid* **S-TS7a** and **S-TS7b**. These were further optimised using (U)B3LYP/6-31G* methodology with the <S2> values used to determine multiplicity of the transition state; values of 0 = closed shell, close to 0.75 = diradical and 2.0 = triplet. For triplet calculations the multiplicity was set to 3 and diradical calculations required the additional keyword MIX. For the *transoid* system (**STS-7a**) all three multiplicities gave much higher free energies of activation ($\Delta G^{\ddagger}$ = 37.8-53.6 kcal mol^{-1}) with respect to the previously optimised closed-shell **S-TS5** ($\Delta G^{\ddagger}$ = 27.8 kcal mol^{-1}). Only a triplet transition state optimised from *cisoid* **S-TS7a** ($\Delta G^{\ddagger}$ = 59.2 kcal mol^{-1}). Alternative *cisoid* **S-TS7b** optimised as a closed shell transition state ($\Delta G^{\ddagger}$ = 25.7 kcal mol^{-1}), the diradical calculations resulted a similar closed shell transition state (<S2> = 0). This newly found closed-shell **S-TS7b** and **S-TS5** were further optimised in Gaussian'09 and gave the same $\Delta G^{\ddagger}$ value of 23.9 kcal mol^{-1}. These investigations confirmed that the *cisoid*-closed shell **S-TS5** is the lowest energy pathway for aromatic-vinylcyclopropane rearrangements.

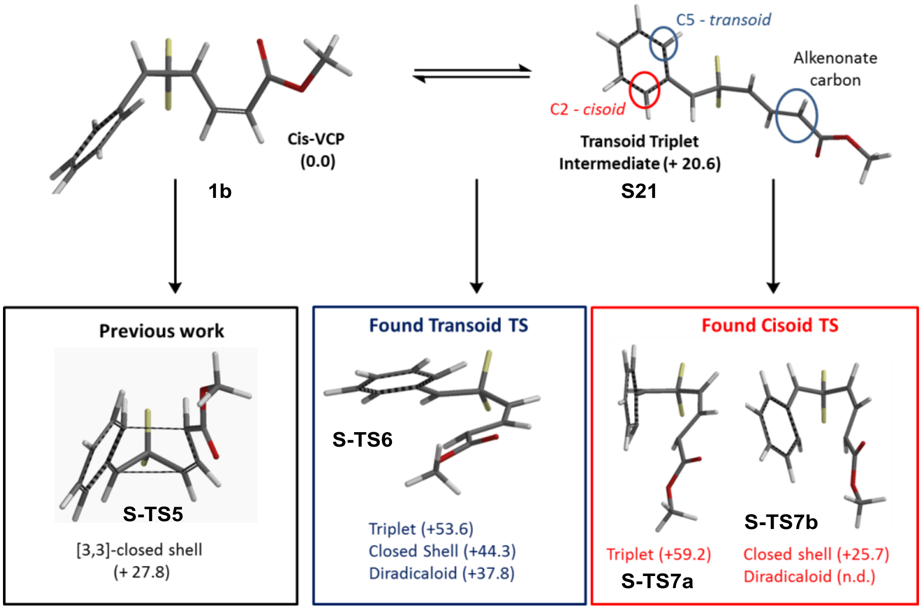


Figure S45: Closed-shell, diradical and triplet transition states for [3,3]-rearrangement (units in kcal mol^{-1}).

Arrhenius Plot for divinyl-difluorocyclopropane S3

The kinetic data reported by Erbes and Boland[S11] for the rearrangement of divinyl-**S3** was altered into Arrhenius parameters in Excel (**Table S13**) and plotted as described above. The resulting Arrhenius plot (**Figure S49**) and errors (**Figure S50**) gave an experimental E_a value for the divinylcyclopropane rearrangements as (24.0 ± 0.17) kcal mol^{-1}; within error of reported value of 23.8 kcal mol^{-1}. The pre-exponential factor (A) was calculated as 7.4 x 10^{16} s^{-1}. These values were used to recalculated the activation energy at 298 K.

Table S13: Kinetic Data used to generate Arrhenius Plot in **Figure S49**.

T (K)	1/T	k (x 10^{-5}) s^{-1}	ln k
298	0.003356	0.75	-0.2877
313	0.003195	4.94	1.5974
323	0.003096	14.9	2.7014
333	0.003003	47.8	3.8670
343	0.002915	152.0	5.0239

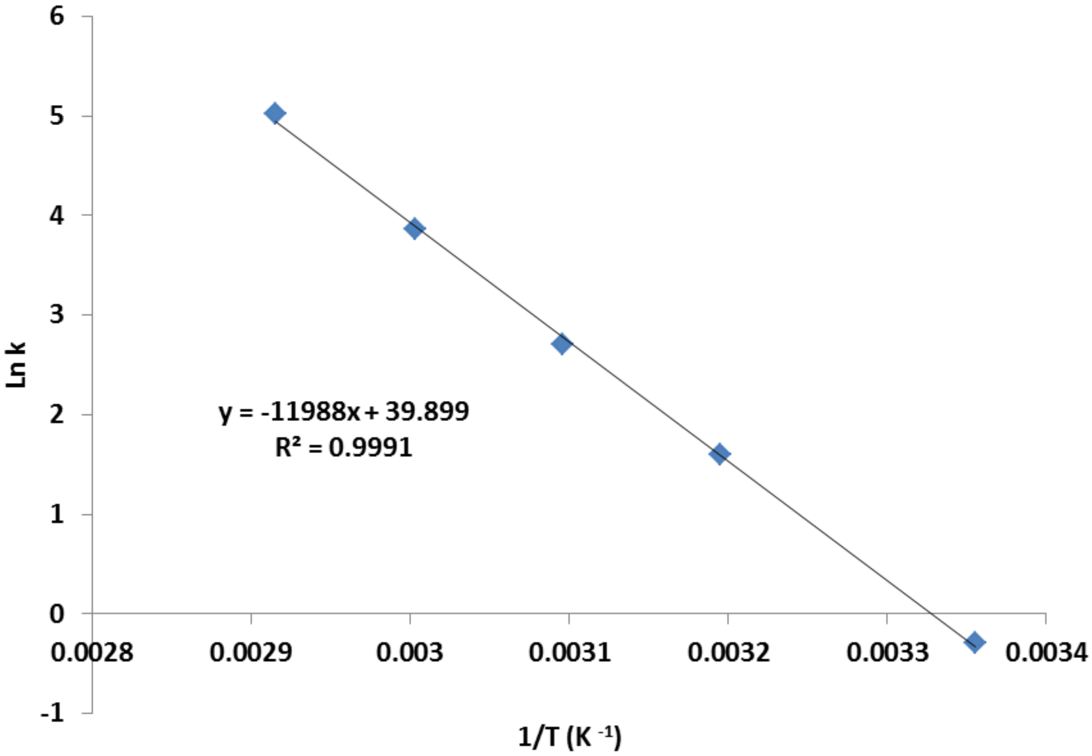


Figure S46: Arrhenius plot from literature kinetic data for the [3,3]-rearrangement of **S3**.

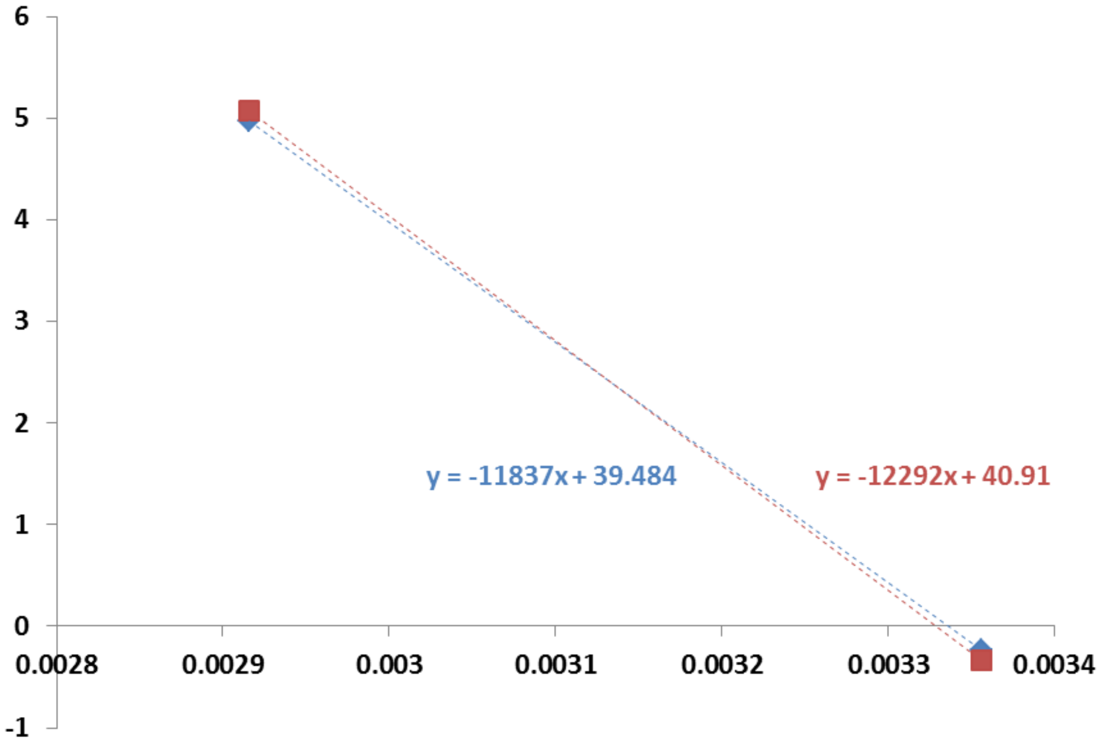


Figure S50: Error associated with Arrhenius plot in **Figure S49.**

[3,3]-Sigmatropic Computational Methodology Screening

We looked to explore the effectiveness of the B3LYP/6-31G* and M06-2X/6-31G* calculations of barrier heights ($\Delta G^{\ddagger}_{B3LYP}$ and $\Delta G^{\ddagger}_{M062X}$, respectively) for divinylcyclopropane[S11,44,45] and heteroaromatic-vinylcyclopropane rearrangements[S46] reported in the literature (**Figure S51**).

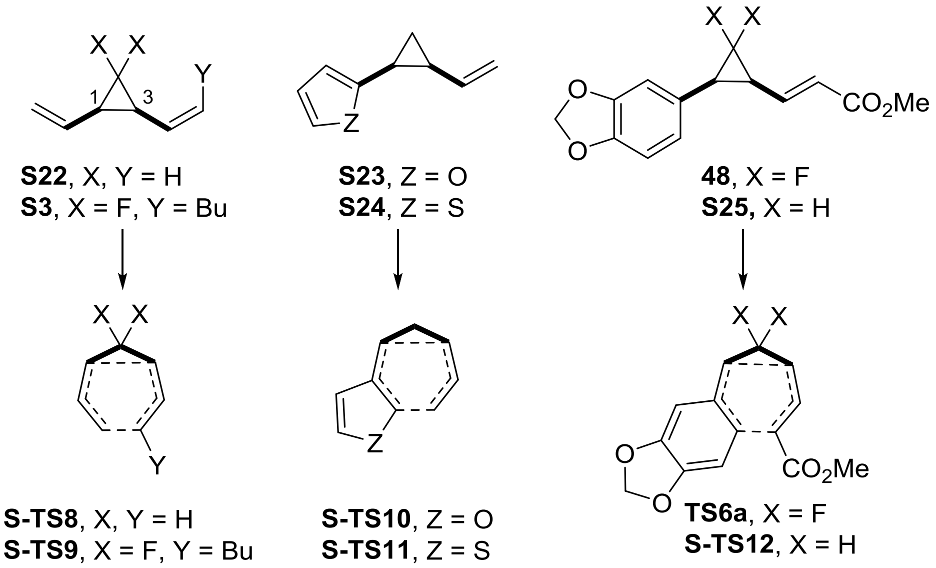


Figure S51: [3,3]-precursors and their corresponding transition states examined with electronic structure calculations.

Little difference was observed for the calculated $\Delta G^{\ddagger}$ values for the divinylcyclopropane rearrangement of di-VCP **S22** and fluorinated **S3** using the DFT method ($\Delta G^{\ddagger}_{\text{B3LYP}}$ difference of 0.4 kcal mol^{-1}) but the Minnesota method gave a $\Delta G^{\ddagger}_{\text{M06-2X}}$ difference of 4.6 kcal mol^{-1} between systems (**Table S14**). The latter was more consistent with the distal bond of *gem*-difluorocyclopropane being weaker than the corresponding non-fluorinated system.[S56]

Due to the disruption of aromaticity in **S-TS10** and **S-TS11**, the aromatic-vinylcyclopropane rearrangement of furyl-**S23** and thiophenyl-**S24** showed higher $\Delta G^{\ddagger}$ values of approximately 4.0 kcal mol^{-1} (B3LYP) or 10.0 kcal mol^{-1} (M06-2X) than **S22**; this was less significant for piperonyl **48** (2.8 kcal mol^{-1} (B3LYP) and 6.1 kcal mol^{-1} (M06-2X)). In our system, the difluorocyclopropyl ring has a beneficial effect on the [3,3]-rearrangement, with $\Delta G^{\ddagger}$ values approximately 8 kcal mol^{-1} lower than the corresponding non-fluorinated **S25** ($\Delta\Delta G^{\ddagger}_{\text{B3LYP}}$ = 31.8 kcal mol^{-1} and $\Delta\Delta G^{\ddagger}_{\text{M06-2X}}$ = 33.2 kcal mol^{-1}).

Table S14: Barriers for [3,3]-rearrangement from electronic structure calculations (ESC) and recalculated experimental Arrhenius data.

Computational Methodology	**Barriers for [3,3]-Rearrangement ($\Delta G^{\ddagger}$, kcal mol^{-1}, gas phase, 298 K)**					
	S22 -> S-TS8	**S3 -> S-TS9**	**S23-> S-TS10**	**S24 -> S-TS11**	**48 -> TS6a**	**S25 -> S-TS12**
B3LYP/6-31G*	21.1	21.6	26.1	26.2	23.9	31.8
M06-2X/6-31G*	23.5	19.2	29.7	29.8	25.6	33.2
Experimental[a]	*21.0*	*17.6*	*25.7*	*27.0*	*26.3*	*n.d.*
(error)	*(± 3.8)*	*(± 5.9)*	*(± 3.0)*	*(± 2.6)*	*(± 1.9)*	

[a] All experimental values were recalculated to 298 K to allow comparison with ESC. Arrhenius determination of kinetic data for substrate **S3** provided an experimental $\Delta G^{\ddagger}$ which was recalculated to 298 K using methods described by Maskill.[S38] Calculated values of $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ were used for precursors **S23** and **S24** to recalculated $\Delta G^{\ddagger}$ values to 298 K.

It was promising that the majority of calculated free energies of activation were within experimental error, but the size of the errors made it difficult to assess the most accurate method for the [3,3]-rearrangement fully (**Figure S52**). The B3LYP/6-31G* was the most accurate for the divinylcyclopropane rearrangement with a $\Delta\Delta G^{\ddagger}$ value of +0.1 kcal mol^{-1}, comparable with Özkan and Zoras' DFT studies ($\Delta\Delta G^{\ddagger}$ = -0.3 kcal mol^{-1}).[S43] In contrast, the M06-2X/6-31G* calculations gave the best results with difluoro-**S3** (($\Delta\Delta G^{\ddagger}$ = +1.6 kcal mol^{-1}) but the extremely large error associated the experimental free energy of activation (± 5.9 kcal mol^{-1}) made it difficult for an effective comparison between methods.

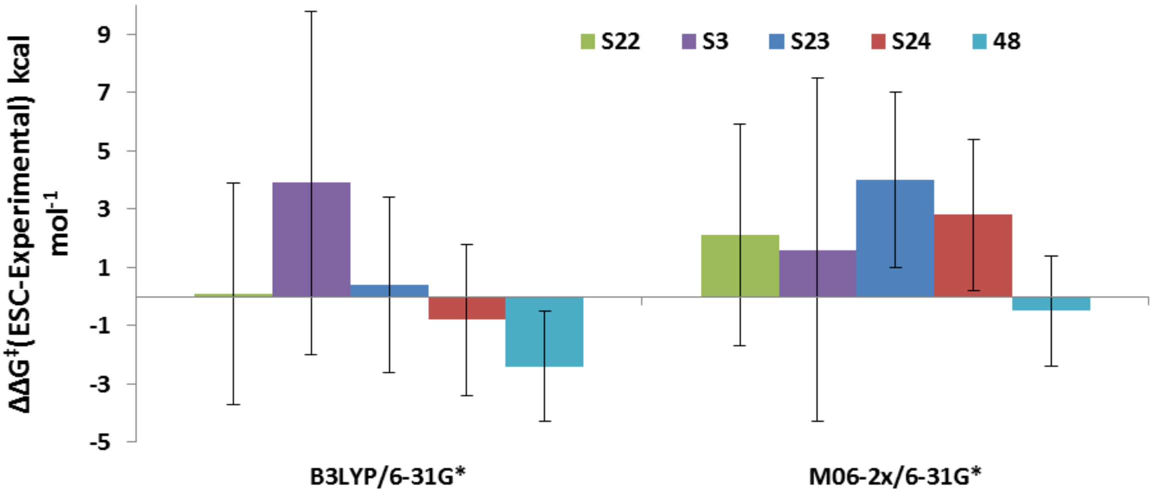


Figure S52: Differences between experimental ΔG‡ (298 K) and ΔG‡ from electronic structure calculations (298 K), plotted as ΔΔG‡ (ΔG‡ (ESC) - ΔG‡(experimental), Gaussian'09, kcal mol^{-1}). Expected error associated with calculated data is ± 0.5 kcal mol^{-1}. Error bars represent error associated with experimental data (see **Table S12** for values).

For the aromatic-vinylcyclopropane rearrangement, the closest agreement with experimental values was observed with B3LYP/6-31G* for hetereoaromatic substituents **S23** and **S24** (ΔΔG‡ values were within 0.8 kcal mol^{-1}) but M06-2X/6-31G* was favoured for piperonyl **48** ((ΔΔG‡ values were within 0.7 kcal mol^{-1}).

Error Associated with T1 and G3(MP2) Calculations

All aromatics examined experimental were built *de novo* on Spartan'10 and minimised using low level molecular mechanics then the heat of formation calculated using the T1 and G3(MP2) thermochemical recipe. The calculated heat of formation ($\Delta H_f°$, **Table 13**) were compared with experimental values to determine the error associated with the calculations (**Figure S53**).

Table S15: Experimental and Calculated Heats of Formation

Compound	**Heat of Formation ($\Delta H_f°$, 298 K, kcal mol^{-1})**				
	Experimental[a]	**T1**	**$\Delta\Delta H_f°$[b]**	**G3(MP2)**	**$\Delta\Delta H_f°$[b]**
Benzene	19.8	18.7	-1.1	19.1	-0.7
1,3-Benzodixoane	-34.1[c]	-38.5	-4.4	-38.8	-4.7
Furan	-8.2	-7.7	0.5	-7.8	0.4
Pyrrole	25.9	26.8	0.9	26.7	0.8
Pyridine	33.6	33.0	-0.6	33.2	-0.4
Thiophene	27.5[d]	25.6	-1.9	26.0	-1.5
Oxazole	-3.7	-2.4	1.3	-2.6	1.1
Isoxazole	18.8	20.9	2.1	20.5	1.8
Ethane	-20.2	-20.0	0.2	-19.9	0.3
Ethylene	12.5	12.4	-0.1	12.0	-0.5

[a] All values reported by Domalski unless otherwise stated.[S48] [b] $\Delta\Delta H_f° = (\Delta H_f°$ calculated) - ($\Delta H_f°$ experimental). [c] Value reported by Cohen.[S50] [d] Value reported by Hubbard and co-workers.[S49]

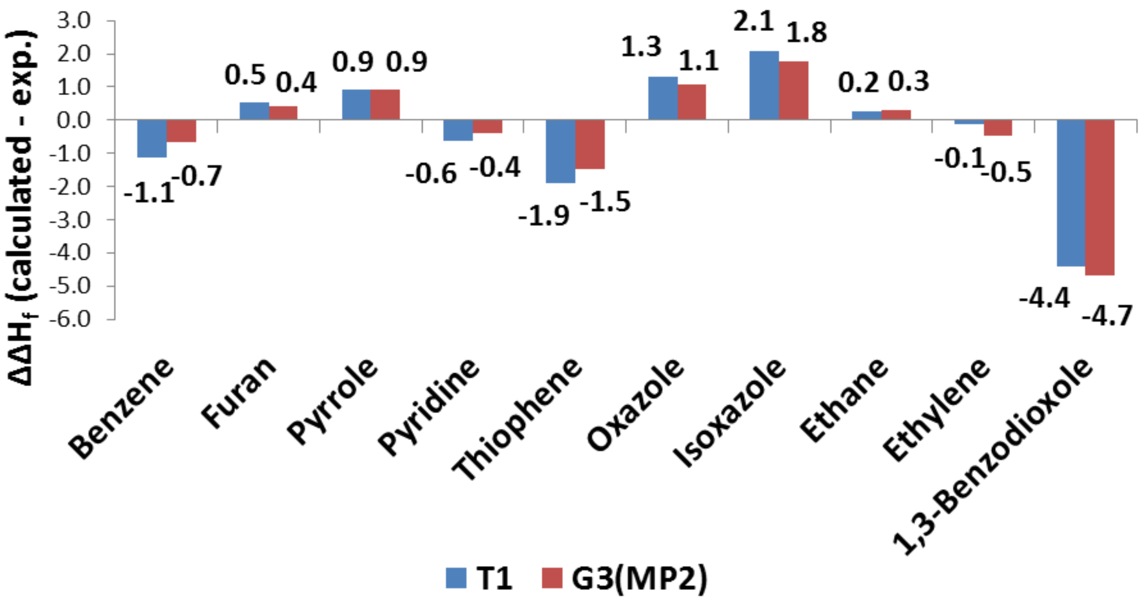


Figure S47: Difference in calculated and experimental heats of formation.

Raw Data for Isodesmic Reactions

The enthalpic change (ΔH°, B3LYP/6-31G* and M06-2X/6-31G*) and heat of formation (ΔH_f, T1 and G3(MP2) for the isodesmic reactions depicted in **Scheme 10** were calculated on Spartan'10 using the method described above.

Raw data for benzene, 1,3-benzodioxole, furan and thiophene are displayed in **Tables S16-S19**.

Table S16: Raw energy values based on isodesmic reaction with benzene.

Method	benzene	Ethane	Total	reduced	Ethene	Total	ΔH_f or ΔH°
T1 (kJ mol^{-1})	78.22	-83.67	-5.45	106.59	51.70	158.29	163.74
G3(MP2) (kJ mol^{-1})	80.017	-83.366	-3.35	106.35	50.35	156.71	160.054
B3LYP (a.u.)	-232.14	-79.75	-311.89	-233.29	-78.53	-311.82	0.071055
M062x (a.u.)	-232.03	-79.72	-311.75	-233.17	-78.50	-311.68	0.069946

Table S17: Raw energy values based on isodesmic reaction with 1,3-benzodioxole.

Method	benzodioxole	Ethane	Total	reduced	Ethene	Total	ΔHf or ΔH°
T1 (kJ mol^{-1})	-161.11	-83.67	-244.78	-136.07	51.70	-84.37	160.41
G3(MP2) (kJ mol^{-1})	-162.45	-83.37	-245.82	-138.56	50.35	-88.21	157.609
B3LYP (a.u.)	-420.65	-79.75	-500.40	-421.81	-78.53	-500.34	0.0675978
M062x (a.u.)	-420.48	-79.69	-500.17	-421.63	-78.48	-500.11	0.0659189

Table S18: Raw energy values based on isodesmic reaction with thiophene.

Method	thiophene	Ethane	Total	reduced	Ethene	Total	ΔH_f or ΔH°
T1 (kJ mol^{-1})	107.11	-83.67	51.70	76.24	51.70	127.94	76.24
G3(MP2) (kJ mol^{-1})	108.91	-83.37	50.35	79.29	50.35	129.64	79.285
B3LYP (a.u.)	-552.93	-79.75	-632.68	-554.11	-78.53	-632.64	0.040688
M062x (a.u.)	-552.82	-79.72	-632.54	-553.99	-78.51	-632.50	0.041781

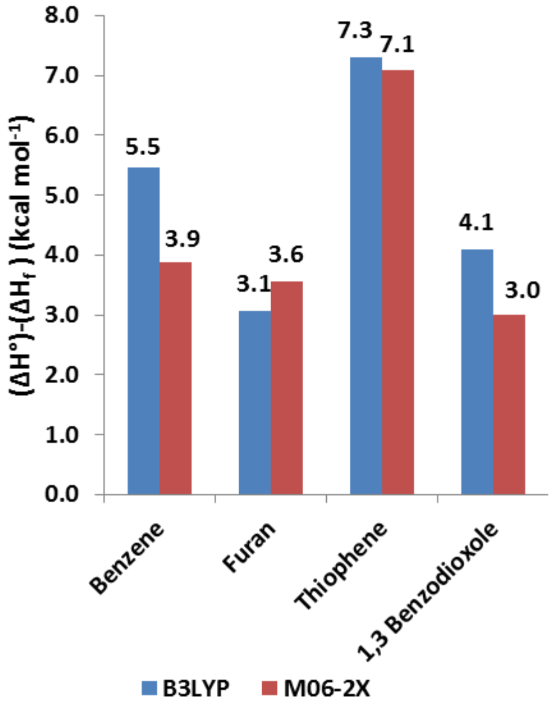
Table S19: Raw energy values based on isodesmic reaction with furan.

Method	furan	Ethane	Total	reduced	Ethene	Total	ΔH_f or ΔH°
T1 (kJ mol^{-1})	-32.24	-83.67	-115.91	-73.30	51.70	-21.60	94.31
G3(MP2) (kJ mol^{-1})	-32.73	-83.37	-116.10	-73.96	50.35	-23.61	92.486
B3LYP (a.u.)	-229.95	-79.75	-309.70	-231.12	-78.53	-309.68	0.0408578
M062x (a.u.)	-229.85	-79.72	-309.57	-231.02	-78.51	-309.52	0.0430657

All raw values were converted into kcal mol^{-1} for comparison (**Table S20**). Differences between ΔH_f and ΔH° values were used to assess how well the DFT and Minnesota functionals dealt with the loss of aromaticity in the isodesmic reaction (**Figures S50** and **S51**).

Table S20: Compiled Heats of Formation (ΔH_f) and Enthalpies (ΔH°) for Isodesmic Reaction (all energies are in kcal mol^{-1}).

Method		benzene	furan	thiophene	1,3-benzodioxole
ΔH_f	T1	39.1	38.3	22.5	18.2
	G3(MP2)	38.3	37.7	22.1	18.9
ΔH°	B3LYP	44.6	42.4	25.6	25.5
	M062X	43.0	41.3	26.1	25.3



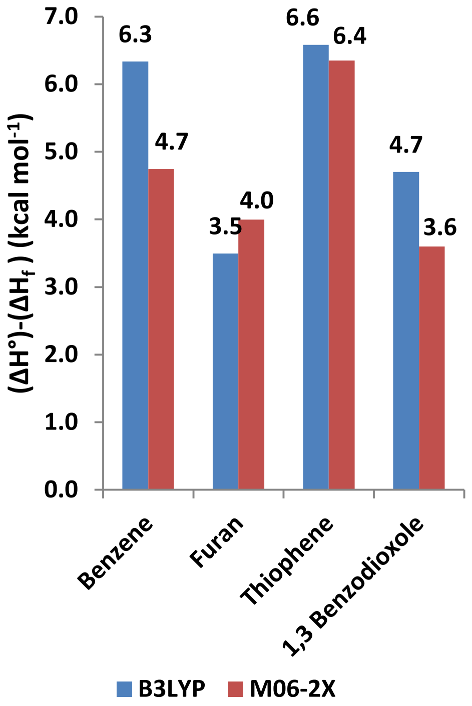


Figure S48: T1 differences between calculated ΔH° and ΔH_f .

Figure S55: G3(MP2) differences between calculated ΔH° and ΔH_f .

Free Energy Values for Computational Predictions

Table S21: Calculated free energies of activation ($\Delta G^{\ddagger}$) for VCPR and [3,3]-rearrangement.

VCP	Calculated $\Delta G^{\ddagger}$ (Gaussian'09, gas phase, 298 K, kcal mol^{-1})							
	(U)B3LYP[a]		Corrected		UM052X[b]	M062X[a]	Corrected	
	VCPR	[3,3]	VCPR[c]	[3,3] [d]	VCPR	[3,3]	VCPR[e]	[3,3] [f]
1a	26.6	27.8	29.3	30.2	29.8	29.5	28.6	30.0
47	35.1	35.5	37.8	37.9	38.1	36.5	36.9	37.0
22a	24.3	23.9	27.0	26.3	28.1	27.0	26.9	27.8
20a	30.6	33.9	33.3	36.3	32.7	35.0	31.5	35.5
23a	22.1	17.5	24.8	19.9	25.7	20.7	24.5	21.2
25a	25.3	24.2	28.0	26.6	32.7	26.1	26.7	26.6
27a	22.5	21.8	25.2	24.2	26.2	24.2	25.0	24.7
27a	26.3	32.6	29.0	35.0	30.4	33.0	29.2	33.5
24a	22.5	18.5	25.2	20.9	26.0	21.2	24.8	21.7
26a	25.7	25.0	28.4	27.4	29.2	27.5	28.0	28.0
19a	26.2	33.3	28.9	35.7	28.0	35.6	27.6	36.1
21a	24.7	27.9	27.4	30.3	28.8	30.8	27.6	31.3
21b	29.7	32.7	32.4	35.1	34.0	36.7	32.8	37.2

[a] Using 6-31G* basis set. [b] Using 6-31+G* basis set. [c] $\Delta G^{\ddagger}$ + 2.7 kcal mol^{-1} (UB3LYP/6-31G*) [d] Calculated $\Delta G^{\ddagger}$ + 2.4 kcal mol^{-1} (B3LYP/6-31G*) [e] Calculated $\Delta G^{\ddagger}$ - 1.2 kcal mol^{-1} (UM05-2X/6-31+G*) [f] Calculated $\Delta G^{\ddagger}$ + 0.5 kcal mol^{-1} (M06-2X/6-31G*). All intermediates and transition states are for conformationally simpler Me ester.

VCPR Temperature Predictions

Table S22 represents the data used to generate temperature prediction graphs for M05-2x/6-31+G* and B3LYP/6-31+G* methods (**Figure 12** and **Figure S56**, respectively).

Table S22: Temperature and $\Delta G^{\ddagger}$ data for prediction graphs.

VCP	Opt. Reaction Temp.		VCPR $\Delta G^{\ddagger}$	
	°C	K	B3LYP/6-31G*	M05-2X/6-31+G*
22a	70	343	27.0	26.9
21a	90	363	27.4	27.6
19a	95	368	28.9	28.0
1a	100	373	29.3	28.6
21b	160	433	32.4	32.8
47	220	493	37.8	36.9

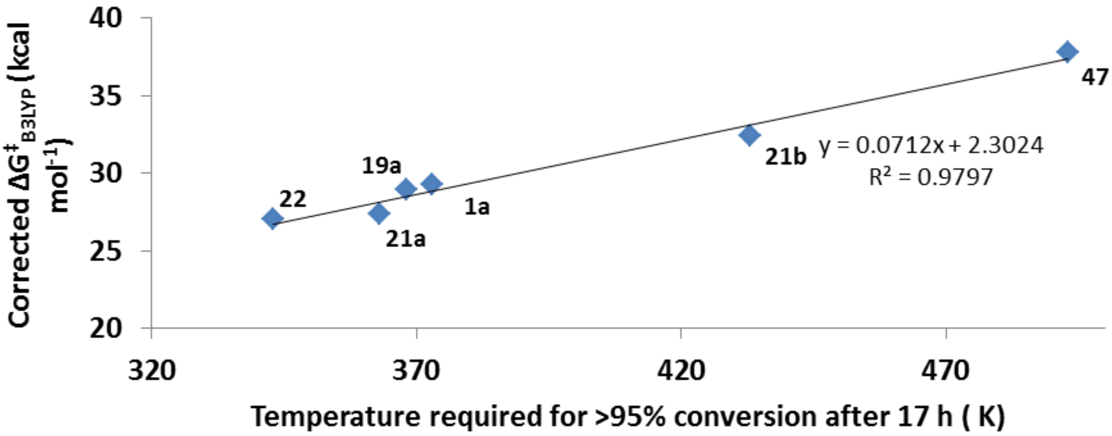


Figure S56: Trend between corrected $\Delta G^{\ddagger}$ values for VCPR (UB3LYP/6-31G*) and rearrangement temperature.

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Cartesian Coordinates

Cartesian Coordinates used in electronic structure calculations – Spartan'10 structures (Gaussian'09 energy values provided if obtained). All energies are in a.u..

Triage: Cyclopropane Substitution

Pyyrole SM (9a)

```
G = -830.0446014 a.u.
vi = none

Cartesian Coordinates (Angstroms)
      Atom             X             Y             Z
    ---------    ------------- ------------- -------------
  1 C   C1           1.7222269     1.2445885    -0.9729440
  2 C   C2           0.6041819     1.6925847    -0.1197857
  3 C   C3           0.9304149     0.1385579    -0.3669379
  4 H   H3          -0.2634018     2.0265621    -0.6880495
  5 H   H6           1.3972895    -0.3352988     0.4928236
  6 C   C10          0.0096991    -0.6684673    -1.1704285
  7 H   H11         -0.3761963    -0.2280125    -2.0883867
  8 C   C11         -0.4005248    -1.9064327    -0.8511647
  9 H   H12         -0.0564018    -2.4218961     0.0407895
 10 C   C12         -1.3494274    -2.6233645    -1.7272019
 11 O   O1          -1.8337068    -2.1932897    -2.7572939
 12 O   O2          -1.6283020    -3.8532978    -1.2286266
 13 C   C13         -2.5405183    -4.6357388    -2.0122175
 14 H   H5          -3.4923969    -4.1115587    -2.1331000
 15 H   H13         -2.6804404    -5.5652310    -1.4591559
 16 H   H14         -2.1218863    -4.8377263    -3.0022856
 17 F   F1           1.6247087     1.4521976    -2.3073350
 18 F   F2           3.0024035     1.4205751    -0.5768409
 19 C   C4           0.7970878     2.2851547     1.2148360
 20 C   C5           1.8863411     2.8913793     1.8170170
 21 C   C6           1.4964665     3.2807468     3.1275918
 22 C   C7           0.1816452     2.9031882     3.2976489
 23 H   H1           2.8510224     3.0395555     1.3549197
 24 H   H8           2.1102781     3.7860042     3.8606918
 25 H   H9          -0.4878149     3.0144079     4.1384141
 26 N   N1          -0.2348714     2.3028757     2.1350296
 27 H   H2          -1.1478764     1.9019360     1.9819925
```

Pyyrole TS2 (TS1aa)

```
G = -830.419263
vi =  i78
S^2 = 0.457

                Cartesian Coordinates (Angstroms)
      Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C           -0.9297737     2.5748429     0.6568401
```

```
  2  C   C2           -1.9194433     1.6312626     0.6608880
  3  C   C3           -1.6411990     0.2517920     0.7737971
  4  C   C4            0.4710368     2.1238864     0.5119996
  5  C   C5            0.6265790     1.0214606    -0.4882548
  6  H   H            -1.1171696     3.6410222     0.7171927
  7  H   H7           -2.9595671     1.9256767     0.5328070
  8  H   H8           -0.7662823    -0.1029137     1.3009722
  9  H   H12          -0.1240240     0.9537771    -1.2623941
 10  F   F1            1.2877910     3.1931977     0.1719855
 11  F   F2            1.0287529     1.6979289     1.7555366
 12  C   C11          -2.6538475    -0.7310434     0.3954601
 13  O   O1           -3.7440986    -0.4774870    -0.0947453
 14  O   O2           -2.2384745    -2.0004546     0.6602510
 15  C   C12          -3.1717980    -3.0280382     0.3079669
 16  H   H1           -4.1123292    -2.9029289     0.8523623
 17  H   H9           -2.6929097    -3.9684920     0.5846646
 18  H   H10          -3.3842153    -3.0079672    -0.7652038
 19  C   C1            1.8411946     0.3622857    -0.6905360
 20  C   C6            2.2631551    -0.4716555    -1.7562523
 21  C   C7            3.5614344    -0.9103603    -1.4767628
 22  C   C8            3.9309200    -0.3557429    -0.2484364
 23  H   H3            1.6666996    -0.7030954    -2.6285180
 24  H   H5            4.1791181    -1.5561366    -2.0853420
 25  H   H11           4.8492544    -0.4533396     0.3134152
 26  N   N1            2.9011554     0.3967289     0.2113611
 27  H   H6            2.8480404     0.8957936     1.0889455
```

pyyrole_higher_energyTS2 (TS1ab)

```
G = -830.414696
iv = i86
S^2 = 0.5102

 Cartesian Coordinates (Angstroms)
      Atom             X             Y             Z
   ---------    ------------- ------------- -------------

  1  C   C            -0.6158183     2.7256632     0.6820107
  2  C   C2           -1.5971922     2.1028680    -0.0343527
  3  C   C3           -1.6947996     0.6924256    -0.0975346
  4  C   C4            0.4992112     1.9015225     1.2220471
  5  C   C5            0.9748909     0.8813229     0.2312319
  6  H   H            -0.5893481     3.7953210     0.8584969
  7  H   H7           -2.3084203     2.6842247    -0.6185155
  8  H   H8           -1.3530473     0.0711430     0.7187428
  9  H   H12           0.8034239     1.1175807    -0.8108546
 10  F   F1            1.5520191     2.7254997     1.5953164
 11  F   F2            0.1389744     1.2638429     2.4199903
 12  C   C11          -2.4700560     0.0560454    -1.1581920
 13  O   O1           -3.0479337     0.6343226    -2.0667899
 14  O   O2           -2.4755496    -1.3002263    -1.0228217
 15  C   C12          -3.2164866    -2.0059029    -2.0242332
 16  H   H1           -4.2783074    -1.7449992    -1.9780600
 17  H   H9           -3.0760518    -3.0653510    -1.8034635
 18  H   H10          -2.8431902    -1.7687789    -3.0250429
 19  C   C1            1.9005424    -0.1117304     0.5589328
```

```
 20  C   C6          2.3766330    -0.5907480     1.8048456
 21  C   C7          3.2738964    -1.6361421     1.5563537
 22  C   C8          3.3447797    -1.8097260     0.1746747
 23  H   H3          2.0712456    -0.1937930     2.7607488
 24  H   H5          3.8158363    -2.2172635     2.2895826
 25  H   H11         3.9124580    -2.5151602    -0.4157203
 26  N   N1          2.5264033    -0.8948515    -0.4121237
 27  H   H6          2.3758869    -0.7971094    -1.4052698
```

Furan trans-SM (9b)

```
Spartan'10: G = -850.314059 vi = none
Gaussian'09: B3LYP/6-31G*, G =-850.319618 vi = none
Gaussian'09: M05-2X/6-31G*, G = -850.262612, vi = none

                    Cartesian Coordinates (Angstroms)
       Atom              X             Y             Z
    ---------     ------------- ------------- -------------

  1  C   C1          1.5992207     1.3955614    -0.9776466
  2  C   C2          0.5194974     1.8052430    -0.0580500
  3  C   C3          0.8775038     0.2658666    -0.3303277
  4  H   H3         -0.4002896     2.1204185    -0.5444083
  5  H   H6          1.4087112    -0.1989848     0.4965651
  6  C   C10        -0.0692639    -0.5633929    -1.0807464
  7  H   H11        -0.5451553    -0.1204950    -1.9541452
  8  C   C11        -0.3946896    -1.8258644    -0.7635527
  9  H   H12         0.0391353    -2.3439339     0.0867471
 10  C   C12        -1.3721319    -2.5700978    -1.5853767
 11  O   O1         -1.9604997    -2.1384533    -2.5585899
 12  O   O2         -1.5371983    -3.8286142    -1.1099537
 13  C   C13        -2.4677534    -4.6398049    -1.8414309
 14  H   H5         -3.4717553    -4.2079556    -1.7983632
 15  H   H13        -2.4506879    -5.6161272    -1.3558111
 16  H   H14        -2.1651118    -4.7245612    -2.8886582
 17  F   F1          1.4275165     1.6056448    -2.3021574
 18  F   F2          2.8925579     1.6160802    -0.6434690
 19  C   C4          0.7705242     2.3994701     1.2599089
 20  C   C5          1.8869409     2.7841676     1.9494628
 21  C   C6          1.4335592     3.2644071     3.2204022
 22  C   C7          0.0786439     3.1404409     3.2120022
 23  H   H1          2.9039660     2.7376631     1.5907183
 24  H   H8          2.0403843     3.6562081     4.0247172
 25  H   H9         -0.6983851     3.3741271     3.9236340
 26  O   O3         -0.3452394     2.6129866     2.0285292
```

Furan TS2 (TS1bb)

```
Spartan'10: G = -850.28681, vi = i125, S^2 = 0.5808
Gaussian'09: B3LYP/6-31G*, G = -850.284463, vi = i137, S^2 = 0.57
Gaussian'09: M05-2X/6-31G*, G = -850.221609, vi = i163, S^2 = 0.75

                    Cartesian Coordinates (Angstroms)
       Atom              X             Y             Z
    ---------     ------------- ------------- -------------
```

```
   1  C   C             -0.8561031      2.7015691      0.3283079
   2  C   C2            -1.8381630      1.8024358      0.0383813
   3  C   C3            -1.6444484      0.4102119      0.2272503
   4  C   C4             0.5072269      2.1790487      0.6288748
   5  C   C5             0.8856784      1.0394530     -0.2712286
   6  H   H             -0.9995893      3.7763684      0.3174435
   7  H   H7            -2.7826728      2.1292823     -0.3926797
   8  H   H8            -1.0099284      0.0361089      1.0187846
   9  H   H12            0.4705459      1.0412851     -1.2696769
  10  F   F1             1.4360242      3.2007638      0.5162551
  11  F   F2             0.6134274      1.7738239      1.9674583
  12  C   C11           -2.4989795     -0.5525386     -0.4685442
  13  O   O1            -3.3684446     -0.2715912     -1.2784601
  14  O   O2            -2.2061722     -1.8278254     -0.1011751
  15  C   C12           -2.9862758     -2.8407750     -0.7484711
  16  H   H1            -4.0493679     -2.7126694     -0.5253266
  17  H   H9            -2.6237993     -3.7896870     -0.3511872
  18  H   H10           -2.8484901     -2.8009163     -1.8330240
  19  C   C1             2.0038465      0.2433660     -0.0273076
  20  C   C6             2.8291747      0.0348828      1.0837613
  21  C   C7             3.7855008     -0.9333375      0.7106043
  22  C   C8             3.4978427     -1.2782298     -0.5873676
  23  H   H3             2.7222504      0.5366346      2.0329496
  24  H   H5             4.5837052     -1.3373896      1.3175395
  25  H   H11            3.9437590     -1.9756074     -1.2810134
  26  O   O3             2.4334523     -0.5846670     -1.0521485
```

furan_higher_energyTS2 (TS1ba)

```
G = -850.277257
iv = i117
S^2 = 0.600

Cartesian Coordinates (Angstroms)
       Atom            X              Y              Z
    ---------    -------------- -------------- --------------

   1  C   C             -0.9502546      2.6495991      0.6501376
   2  C   C2            -1.8908863      1.6636452      0.6340407
   3  C   C3            -1.5252413      0.2997528      0.7679050
   4  C   C4             0.4866883      2.2452973      0.5815975
   5  C   C5             0.6994623      1.1466886     -0.4230640
   6  H   H             -1.1843317      3.7083129      0.6705550
   7  H   H7            -2.9410498      1.8946944      0.4667669
   8  H   H8            -0.6672285      0.0082292      1.3580427
   9  H   H12            0.0014180      1.1086166     -1.2480338
  10  F   F1             1.2635235      3.3417125      0.2455922
  11  F   F2             0.9578758      1.8500449      1.8288746
  12  C   C11           -2.4336857     -0.7569674      0.3243831
  13  O   O1            -3.5074436     -0.5836509     -0.2312859
  14  O   O2            -1.9309470     -1.9884494      0.6061859
  15  C   C12           -2.7538814     -3.0880991      0.1987920
  16  H   H1            -3.7287557     -3.0463091      0.6926392
  17  H   H9            -2.2124283     -3.9867342      0.4969680
```

```
 18 H  H10          -2.9090023    -3.0753115    -0.8840734
 19 C  C1            1.8920642     0.4419550    -0.5879881
 20 C  C6            2.3133656    -0.4200912    -1.6085995
 21 C  C7            3.5834925    -0.9104235    -1.2387796
 22 C  C8            3.8752209    -0.3326880    -0.0273526
 23 H  H3            1.7534328    -0.6493108    -2.5047380
 24 H  H5            4.2111886    -1.5983851    -1.7876640
 25 H  H11           4.7235775    -0.4012302     0.6371705
 26 O  O3            2.8738262     0.4791018     0.3819280
```

para-Pyridine-N-oxide SM (9c)

```
G = -943.714388
vi = none
```

```
              Cartesian Coordinates (Angstroms)
     Atom             X             Y             Z
   ---------    ------------- ------------- -------------

  1 C  C1            1.3089641     1.2878086    -1.4497207
  2 C  C2            0.3057078     1.5125208    -0.3822889
  3 C  C3            0.7951372     0.0499645    -0.8058908
  4 H  H3           -0.6826092     1.7431318    -0.7723904
  5 H  H6            1.4675209    -0.4016004    -0.0798213
  6 C  C10          -0.1475861    -0.8399612    -1.4924370
  7 H  H11          -0.7435160    -0.4144786    -2.2979791
  8 C  C11          -0.3306841    -2.1327832    -1.1854696
  9 H  H12           0.2308402    -2.6289737    -0.3990166
 10 C  C12          -1.3267131    -2.9400203    -1.9226782
 11 O  O1           -2.0384947    -2.5410180    -2.8245489
 12 O  O2           -1.3530146    -4.2104131    -1.4542092
 13 C  C13          -2.2945397    -5.0801688    -2.1008460
 14 H  H5           -3.3109551    -4.6904395    -1.9982644
 15 H  H13          -2.1988666    -6.0424089    -1.5969908
 16 H  H14          -2.0596651    -5.1776157    -3.1644068
 17 F  F1            0.9485834     1.5578329    -2.7241156
 18 F  F2            2.6047735     1.6327810    -1.2590384
 19 C  C4            0.5748704     2.0527265     0.9723227
 20 N  N1            0.9519961     3.0708098     3.5869269
 21 C  C6           -0.4849677     2.5780627     1.7269249
 22 C  C7            1.8381277     2.0634026     1.5880374
 23 C  C8            2.0043379     2.5628860     2.8639135
 24 C  C9           -0.2895778     3.0730703     3.0006694
 25 H  H2           -1.4913534     2.6050752     1.3191932
 26 H  H1            2.7153381     1.6911372     1.0725650
 27 H  H4            2.9491794     2.6021993     3.3891100
 28 H  H7           -1.0668534     3.4896658     3.6269169
 29 O  O3            1.1240199     3.5268064     4.7635328
```

para-pyridine-N-oxide TS2 (TS1c)

```
G = -943.680817
vi= i173
S^2 = 0.6244
```

```
 Cartesian Coordinates (Angstroms)
     Atom             X             Y             Z
```

```
   ---------     ------------- ------------- -------------

  1 C   C            -0.7442934     2.9911665    -0.6529612
  2 C   C2           -1.8633238     2.2189125    -0.6559668
  3 C   C3           -1.8768379     0.9614702     0.0125223
  4 C   C4            0.5056189     2.3730776    -0.1201484
  5 C   C5            0.6538498     0.9460111    -0.5710700
  6 H   H            -0.6970805     4.0005318    -1.0464526
  7 H   H7           -2.7503323     2.5120346    -1.2138959
  8 H   H8           -1.3399625     0.8184490     0.9404952
  9 H   H12           0.2045073     0.7258017    -1.5310947
 10 F   F1            1.6088236     3.1107358    -0.5101945
 11 F   F2            0.5285161     2.4437114     1.2816101
 12 C   C1            1.6190072     0.0436571    -0.0843508
 13 N   N1            3.5077418    -1.8693317     0.8212471
 14 C   C7            1.8384409    -1.1962806    -0.7581019
 15 C   C8            2.4134554     0.2521798     1.0854579
 16 C   C9            3.3234735    -0.6801557     1.5006845
 17 C   C10           2.7505123    -2.1100167    -0.3093180
 18 H   H2            1.2716721    -1.4303514    -1.6542811
 19 H   H6            2.3060988     1.1634289     1.6585467
 20 H   H5            3.9580480    -0.5786565     2.3711521
 21 H   H3            2.9607491    -3.0624405    -0.7773622
 22 C   C11          -2.8422352    -0.0682516    -0.3784039
 23 O   O1           -3.6244498     0.0175318    -1.3119035
 24 O   O2           -2.7589742    -1.1547562     0.4310049
 25 C   C12          -3.6624428    -2.2222009     0.1130110
 26 H   H1           -4.7003788    -1.8921776     0.2148756
 27 H   H9           -3.4417473    -3.0160126     0.8275249
 28 H   H10          -3.5038444    -2.5707545    -0.9116447
 29 O   O3            4.3553882    -2.7273136     1.2290179
```

2-thiophene SM (9d)

```
Spartan'10: G = -1173.29592, vi = none
Gaussian'09: B3LYP/6-31G*, G = -1173.30199, vi = none
Gaussian'09: M05-2X/6-31G*, G = -1173.23053, vi = none
```

```
 Cartesian Coordinates (Angstroms)
      Atom            X             Y             Z
   ---------     ------------- ------------- -------------

  1 C   C1            1.6447102     1.2814457    -0.9375890
  2 C   C2            0.5212287     1.7458593    -0.0943692
  3 C   C3            0.8411195     0.1957362    -0.3104794
  4 H   H3           -0.3426689     2.0754370    -0.6688474
  5 H   H6            1.3040248    -0.2653453     0.5585792
  6 C   C10          -0.0785972    -0.6272681    -1.1025299
  7 H   H11          -0.4640952    -0.2034661    -2.0283529
  8 C   C11          -0.4802431    -1.8616494    -0.7637583
  9 H   H12          -0.1388546    -2.3582980     0.1397290
 10 C   C12          -1.4198937    -2.6011787    -1.6329982
 11 O   O1           -1.8957629    -2.1937891    -2.6757460
 12 O   O2           -1.6963244    -3.8212538    -1.1117456
 13 C   C13          -2.6006195    -4.6235892    -1.8848499
 14 H   H5           -3.5553537    -4.1076858    -2.0178802
```

```
 15  H   H13          -2.7364164    -5.5439176    -1.3157681
 16  H   H14          -2.1767881    -4.8399854    -2.8695951
 17  F   F1            1.5518602     1.4680768    -2.2742731
 18  F   F2            2.9262425     1.4561124    -0.5411711
 19  C   C4            0.7023730     2.3602625     1.2372566
 20  C   C5            1.8035834     2.9777018     1.7761645
 21  C   C6            1.5918459     3.4496041     3.1064879
 22  C   C7            0.3333226     3.1878326     3.5700286
 23  H   H1            2.7340315     3.0937873     1.2348702
 24  H   H8            2.3477142     3.9664063     3.6878268
 25  H   H9           -0.0945008     3.4371092     4.5318277
 26  S   S1           -0.6219377     2.3520552     2.3871829
```

2-thiophene TS2 (TS1da)

```
Spartan'10: G = -1173.261131, vi = i131, S^2 = 0.5683
Gaussian'09: B3LYP/6-31G*, G = --1173.266174, vi = i334, S^2 = 0.58
Gaussian'09: M05-2X/6-31G*, G = -1173.189048, vi = i147, S^2 = 0.76
```

```
 Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

   1  C   C           -0.7210256    -0.3769473    -2.7513915
   2  C   C2          -1.6633130    -0.7878751    -1.8574746
   3  C   C3          -1.6425208    -0.3469323    -0.5084804
   4  C   C4           0.4568673     0.3730574    -2.2301141
   5  C   C5           0.9604340    -0.2059585    -0.9352110
   6  H   H           -0.7617934    -0.5913906    -3.8136378
   7  H   H7          -2.4261631    -1.5096041    -2.1435472
   8  H   H8          -1.2822483     0.6385526    -0.2471795
   9  H   H12          0.7937751    -1.2673813    -0.8066724
  10  F   F1           1.4705438     0.3718068    -3.1716569
  11  F   F2           0.1531733     1.7304276    -2.0604202
  12  C   C11         -2.3398484    -1.1152447     0.5241681
  13  O   O1          -2.9346804    -2.1662237     0.3423726
  14  O   O2          -2.2429288    -0.5139217     1.7384721
  15  C   C12         -2.8807106    -1.2132354     2.8149511
  16  H   H1          -3.9557208    -1.3034663     2.6345635
  17  H   H9          -2.6914657    -0.6153949     3.7074120
  18  H   H10         -2.4588123    -2.2161999     2.9276998
  19  C   C1           1.9188089     0.4334481    -0.1364692
  20  C   C6           2.3884821     1.7569630    -0.1691832
  21  C   C7           3.3512113     2.0350217     0.8188765
  22  C   C8           3.6266421     0.9527961     1.6286792
  23  H   H3           2.0271893     2.4727681    -0.8952321
  24  H   H5           3.8264599     3.0018556     0.9428367
  25  H   H11          4.3129625     0.9081502     2.4642703
  26  S   S1           2.7146815    -0.4450712     1.1823680
```

2_thiophene_higher_energyTS2 (TS1db)

```
G = -1173.26196
iv = i122
S^2 = 0.601
```

```
Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C            -0.9278013     0.7602316    -2.6901911
  2 C   C2           -1.8672172     0.7618182    -1.7032288
  3 C   C3           -1.5086288     0.8413210    -0.3336491
  4 C   C4            0.5043701     0.6104751    -2.3065949
  5 C   C5            0.7012026    -0.3701149    -1.1866012
  6 H   H            -1.1656141     0.8285247    -3.7460605
  7 H   H7           -2.9232110     0.6526694    -1.9433104
  8 H   H8           -0.6295369     1.3839016    -0.0131775
  9 H   H12           0.0016210    -1.1964024    -1.1568814
 10 F   F1            1.2424323     0.2099791    -3.4085654
 11 F   F2            1.0677132     1.8421132    -1.9497644
 12 C   C11          -2.4546584     0.4124461     0.6970248
 13 O   O1           -3.5602301    -0.0629061     0.4887400
 14 O   O2           -1.9502468     0.6069819     1.9438422
 15 C   C12          -2.8142156     0.2091798     3.0160398
 16 H   H1           -3.7451809     0.7831206     2.9953433
 17 H   H9           -2.2589454     0.4135549     3.9324871
 18 H   H10          -3.0572818    -0.8549834     2.9429923
 19 C   C1            1.8878436    -0.5154771    -0.4587369
 20 C   C6            2.2076707    -1.5955701     0.3831959
 21 C   C7            3.4563134    -1.4720247     1.0164381
 22 C   C8            4.1089268    -0.3048071     0.6769360
 23 H   H3            1.5361313    -2.4380247     0.5102434
 24 H   H5            3.8686245    -2.2100946     1.6953957
 25 H   H11           5.0800204     0.0300601     1.0180010
 26 S   S1            3.1998985     0.6740277    -0.4199186
```

pyrrole_N_Boc – SM (9e)

```
G = -1176.15618
iv = none
```

```
Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C1            2.7535104     0.5329447    -2.5439534
  2 C   C2            1.9022163     0.9879434    -1.4270432
  3 C   C3            1.8744042    -0.5181088    -1.9545018
  4 H   H3            1.0240211     1.5436471    -1.7384084
  5 H   H6            2.3889501    -1.2127350    -1.2950455
  6 C   C10           0.6922396    -1.0140414    -2.6636953
  7 H   H11           0.2033785    -0.3375816    -3.3618949
  8 C   C11           0.1738953    -2.2418222    -2.5067290
  9 H   H12           0.6086345    -2.9725220    -1.8307627
 10 C   C12          -1.0270908    -2.6493021    -3.2620710
 11 O   O1           -1.6401087    -1.9646035    -4.0590672
 12 O   O2           -1.3777460    -3.9235125    -2.9510128
 13 C   C13          -2.5355171    -4.4200730    -3.6359457
 14 H   H5           -3.4124388    -3.8079976    -3.4065128
 15 H   H13          -2.6754402    -5.4400731    -3.2758182
 16 H   H14          -2.3762980    -4.4132677    -4.7179344
```

```
 17  F   F1           2.4675232      0.9968779     -3.7830902
 18  F   F2           4.0957545      0.4116881     -2.4057509
 19  C   C4           2.4334821      1.2902387     -0.0860095
 20  C   C5           3.7232841      1.5276603      0.3230500
 21  C   C6           3.7171782      1.7451030      1.7362044
 22  C   C7           2.4272226      1.6350730      2.1677360
 23  H   H1           4.5820521      1.5408932     -0.3309699
 24  H   H8           4.5748523      1.9620229      2.3583141
 25  H   H9           1.9875509      1.7354041      3.1455720
 26  N   N1           1.6202058      1.3551326      1.0643105
 27  C   C8           0.2226284      1.1991010      1.0943728
 28  O   O3          -0.2133437      1.2468479      2.3591224
 29  C   C9          -1.6575265      1.1251508      2.6728774
 30  C   C14         -2.4290862      2.2782238      2.0251443
 31  H   H4          -2.0009948      3.2405094      2.3261956
 32  H   H15         -3.4707766      2.2507602      2.3630633
 33  H   H16         -2.4136606      2.2073436      0.9367034
 34  C   C15         -1.6721970      1.2482366      4.1979027
 35  H   H7          -1.2663801      2.2142387      4.5152625
 36  H   H17         -1.0770148      0.4526265      4.6573822
 37  H   H18         -2.7006075      1.1669068      4.5639643
 38  C   C16         -2.1679553     -0.2495484      2.2317861
 39  H   H10         -2.1369785     -0.3572100      1.1464935
 40  H   H19         -3.2033431     -0.3743943      2.5670994
 41  H   H20         -1.5664571     -1.0443221      2.6862017
 42  O   O4          -0.4520227      1.0465409      0.0974583
```

pyyrole_N_boc_TS2 (TS1e)

```
G = -1176.11077
iv = i75
S^2 = 0.7190

  Cartesian Coordinates (Angstroms)
      Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1  C   C           -2.2966442      2.5038283     -0.7522378
  2  C   C2          -3.2202595      1.5004654     -0.6686955
  3  C   C3          -2.8998157      0.1253002     -0.6486436
  4  C   C4          -0.8707789      2.2304137     -1.0897300
  5  C   C5          -0.6665939      1.0255474     -1.9622623
  6  H   H           -2.5642692      3.5472360     -0.6166446
  7  H   H7          -4.2782632      1.7570888     -0.6453204
  8  H   H8          -1.9495060     -0.2386669     -0.2794002
  9  H   H12         -1.3323635      1.0127471     -2.8182339
 10  F   F1          -0.3734540      3.3374628     -1.7833582
 11  F   F2          -0.0802355      2.1913624      0.0547077
 12  C   C11         -3.9457174     -0.8595544     -0.9329093
 13  O   O1          -5.1044351     -0.6039567     -1.2244142
 14  O   O2          -3.4698166     -2.1283518     -0.8295764
 15  C   C12         -4.4254535     -3.1600249     -1.0993711
 16  H   H1          -5.2735717     -3.0933775     -0.4117197
 17  H   H9          -3.8909565     -4.1003850     -0.9574250
 18  H   H10         -4.7998331     -3.0837324     -2.1247538
 19  C   C1           0.5248792      0.2999435     -2.1256533
```

```
 20  C   C6             1.0440565    -0.2010755    -3.3344732
 21  C   C7             2.3342710    -0.7117037    -3.0941433
 22  C   C8             2.5993629    -0.5513321    -1.7497834
 23  H   H3             0.5450331    -0.1125159    -4.2904793
 24  H   H5             3.0099156    -1.1422242    -3.8205963
 25  H   H11            3.4492929    -0.8463660    -1.1545859
 26  N   N1             1.5064027     0.0499485    -1.1450145
 27  C   C9             1.2605679    -0.0765626     0.2545129
 28  O   O3             2.3872856     0.1841217     0.9151857
 29  C   C10            2.4358210     0.1211324     2.3991176
 30  C   C13            1.4208616     1.1040404     2.9897361
 31  H   H13            1.5380529     2.0922187     2.5332578
 32  H   H14            0.3958318     0.7679561     2.8300664
 33  H   H15            1.5985712     1.1988611     4.0666651
 34  C   C14            3.8672117     0.5723141     2.6929274
 35  H   H4             4.0324401     1.5918928     2.3313039
 36  H   H16            4.5916532    -0.0899223     2.2080669
 37  H   H17            4.0478971     0.5521972     3.7724520
 38  C   C15            2.2028363    -1.3203461     2.8572202
 39  H   H6             1.1937030    -1.6568408     2.6118931
 40  H   H18            2.9281275    -1.9949784     2.3889698
 41  H   H19            2.3344957    -1.3817917     3.9430077
 42  O   O4             0.1933966    -0.4123696     0.7103349
```

piperanal_SM (9f)

```
Spartan'10: G = -1041.02196, iv = none
Gaussian'09: B3LYP/6-31G*, G = -1041.030057, iv = none
Gaussian'09: M05-2X/6-31G*, G = -1040.961182, iv = none

 Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

  1  H   H1             0.3173526     1.8117346    -0.4860782
  2  C   C1             0.0796698     1.9703530     0.5619833
  3  C   C4            -0.5139337     2.3341161     3.2187058
  4  C   C2             0.2084874     0.9017002     1.4568499
  5  C   C6            -0.3484961     3.2417645     0.9790992
  6  C   C5            -0.6383061     3.3915793     2.3211549
  7  C   C3            -0.0958245     1.0796197     2.8250814
  8  H   H6            -0.4515198     4.0668061     0.2827391
  9  H   H3            -0.0162481     0.2654692     3.5352692
 10  C   C7             0.7180325    -0.4153577     0.9594682
 11  C   C8             0.1449534    -1.7162582     1.3582272
 12  C   C9            -0.1583847    -1.2780583    -0.0372637
 13  H   H2             1.7827390    -0.4632471     0.7318922
 14  H   H9            -1.1646025    -0.8901221    -0.1771914
 15  F   F1            -0.8678092    -1.7730911     2.2531620
 16  F   F2             0.9806161    -2.7644429     1.5466580
 17  C   C10            0.4727736    -1.9279483    -1.1918646
 18  H   H8             1.4598095    -2.3639054    -1.0472524
 19  C   C11           -0.0808889    -2.0200610    -2.4103728
 20  H   H10           -1.0656251    -1.6194806    -2.6329824
 21  C   C12            0.6434521    -2.6904227    -3.5104695
 22  O   O1             1.7572372    -3.1745849    -3.4406949
```

```
 23  O   O2            -0.1053900    -2.6999901    -4.6407824
 24  C   C13            0.5090769    -3.3295069    -5.7742877
 25  H   H7            -0.2243694    -3.2656527    -6.5788836
 26  H   H11            0.7479377    -4.3733616    -5.5532355
 27  H   H12            1.4297941    -2.8084978    -6.0514828
 28  O   O3            -0.8886457     2.7475398     4.4747810
 29  C   C14           -1.1176431     4.1571614     4.3678767
 30  H   H13           -0.3195540     4.6995025     4.8933865
 31  H   H14           -2.0979599     4.3997452     4.7885223
 32  O   O4            -1.0967313     4.5068976     2.9779849
```

piperanal_TS2 (TS1f)

```
Spartan'10: G = -1040.98527, iv = i123, S^2 = 0.4875
Gaussian'09: B3LYP/6-31G*, G = -1040.991312, iv = i123 S^2 = 0.49
Gaussian'09: M05-2X/6-31G*, G = -1040.916448, iv = i154, S^2 = 0.70
```

```
 Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1  C   C             -1.9415125     2.8459054    -0.1145085
  2  C   C2            -2.8968928     1.8980800     0.1045137
  3  C   C3            -2.5560611     0.6313994     0.6442402
  4  C   C4            -0.5213291     2.4249366     0.0232476
  5  C   C5            -0.2785848     1.0938538    -0.6265670
  6  H   H             -2.1537181     3.8659395    -0.4147181
  7  H   H7            -3.9327982     2.0688843    -0.1819285
  8  H   H8            -1.7420745     0.5235062     1.3476045
  9  H   H12           -0.9914780     0.8153500    -1.3903371
 10  F   F1             0.3209903     3.3806811    -0.5228531
 11  F   F2            -0.1367627     2.3813647     1.3763306
 12  C   C1             0.9674345     0.4091213    -0.6132428
 13  C   C6             3.3393187    -1.0419376    -0.7024803
 14  C   C7             1.1304562    -0.7070957    -1.4805967
 15  C   C8             2.0508659     0.7887275     0.2442712
 16  C   C9             3.2035145     0.0544406     0.1585045
 17  C   C10            2.3096788    -1.4497963    -1.5357170
 18  H   H2             0.3006140    -0.9867083    -2.1230616
 19  H   H6             1.9583437     1.6244971     0.9238368
 20  H   H3             2.4233575    -2.3001809    -2.1987607
 21  C   C11           -3.4612854    -0.5051960     0.4740267
 22  O   O1            -4.5012178    -0.4946765    -0.1664901
 23  O   O2            -3.0011475    -1.6060197     1.1264093
 24  C   C12           -3.8252873    -2.7716733     1.0064332
 25  H   H1            -4.8175953    -2.5900216     1.4297484
 26  H   H9            -3.3098968    -3.5550517     1.5638819
 27  H   H10           -3.9401814    -3.0590914    -0.0429790
 28  C   C16            5.2862127    -0.7515467     0.3636972
 29  H   H16            5.6638544    -1.3654739     1.1871797
 30  H   H17            6.1072607    -0.2495450    -0.1631722
 31  O   O3             4.5775514    -1.5919137    -0.5642076
 32  O   O4             4.3683699     0.2192409     0.8676951
```

Vinyl_SM (9g)

```
G = -698.896923
iv = none

Cartesian Coordinates (Angstroms)
       Atom             X              Y              Z
    ---------    -------------- -------------- --------------


   1  C   C1          1.9355502      1.7969259     -0.3459348
   2  C   C2          0.8307819      2.1575483      0.5704414
   3  C   C3          1.1920029      0.6392453      0.2183687
   4  H   H3         -0.0759566      2.5122382      0.0862674
   5  H   H6          1.6963533      0.1125771      1.0252585
   6  C   C10         0.2552858     -0.1365557     -0.6009850
   7  H   H11        -0.1543285      0.3425355     -1.4885605
   8  C   C11        -0.1335964     -1.3913708     -0.3282800
   9  H   H12         0.2329983     -1.9394131      0.5347714
  10  C   C12        -1.0945064     -2.0825309     -1.2131158
  11  O   O1         -1.5953320     -1.6208579     -2.2209946
  12  O   O2         -1.3607729     -3.3286259     -0.7502454
  13  C   C13        -2.2872051     -4.0875934     -1.5403591
  14  H   H5         -3.2430000     -3.5630588     -1.6222382
  15  H   H13        -2.4121995     -5.0357462     -1.0162391
  16  H   H14        -1.8896012     -4.2541816     -2.5455875
  17  F   F1          1.8126274      2.0764637     -1.6634147
  18  F   F2          3.2135469      1.9930861      0.0537993
  19  C   C4          1.0896415      2.6534012      1.9367450
  20  H   H2          2.0583814      2.3967857      2.3621727
  21  C   C5          0.2219098      3.3789314      2.6464829
  22  H   H1          0.4602017      3.7221319      3.6487135
  23  H   H4         -0.7527828      3.6580640      2.2529337
```

Vinyl_TS2 LHS (TS1g)

```
G = -698.857875
iv = i198
S^2 = 0.6714

Cartesian Coordinates (Angstroms)
       Atom             X              Y              Z
    ---------    -------------- -------------- --------------


   1  C   C           0.1652595      2.6452115     -0.3143155
   2  C   C2         -0.9584813      1.8809569     -0.3019228
   3  C   C3         -0.9637138      0.5905294      0.2988038
   4  C   C4          1.4504042      2.0089192      0.1090996
   5  C   C5          1.5736222      0.5798217     -0.3410965
   6  H   H           0.1907607      3.6766667     -0.6489816
   7  H   H7         -1.8694255      2.2159214     -0.7940528
   8  H   H8         -0.3786445      0.3846912      1.1849748
   9  H   H12         1.1669910      0.3487995     -1.3194338
  10  F   F1          2.5134097      2.7425610     -0.3921617
  11  F   F2          1.6046460      2.0673940      1.4925765
  12  C   C11        -1.9729073     -0.3973458     -0.0922705
  13  O   O1         -2.8112126     -0.2389039     -0.9652907
```

```
 14 O   O2          -1.8623287    -1.5331343     0.6422082
 15 C   C12         -2.8063532    -2.5626474     0.3167219
 16 H   H1          -3.8302743    -2.2111786     0.4741522
 17 H   H9          -2.5784639    -3.3924022     0.9872065
 18 H   H10         -2.6972065    -2.8709552    -0.7274202
 19 C   C1           2.4851927    -0.3044672     0.2691289
 20 H   H3           2.9377797     0.0188533     1.2042950
 21 C   C6           2.7966479    -1.5403617    -0.2250625
 22 H   H2           3.4848028    -2.2007601     0.2926869
 23 H   H4           2.3594953    -1.9081690    -1.1498455
```

3-thiophene_SM (9h)

```
G = -1173.29649
iv = none

 Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

   1 C   C1           1.4442820     1.5404046    -1.0097879
   2 C   C2           0.3927582     1.8764466    -0.0237970
   3 C   C3           0.8288766     0.3719452    -0.3204143
   4 H   H3          -0.5607177     2.1328018    -0.4786628
   5 H   H6           1.4362987    -0.0670530     0.4676500
   6 C   C10         -0.1107572    -0.5159186    -1.0134407
   7 H   H11         -0.6603421    -0.1039428    -1.8581155
   8 C   C11         -0.3435135    -1.7926382    -0.6731372
   9 H   H12          0.1711044    -2.2773250     0.1516008
  10 C   C12         -1.3258436    -2.5989270    -1.4276396
  11 O   O1          -1.9984877    -2.2113527    -2.3641198
  12 O   O2          -1.3897156    -3.8597859    -0.9339553
  13 C   C13         -2.3181495    -4.7285856    -1.5989953
  14 H   H5          -3.3350508    -4.3325827    -1.5279792
  15 H   H13         -2.2432837    -5.6872218    -1.0845376
  16 H   H14         -2.0553539    -4.8368853    -2.6549552
  17 F   F1           1.1825558     1.7359006    -2.3226269
  18 F   F2           2.7405856     1.8349551    -0.7532548
  19 C   C4           0.6386102     2.4940989     1.3012228
  20 C   C5           1.8650771     2.4391855     2.0495963
  21 C   C6           1.7847172     3.0813387     3.2512183
  22 S   S1           0.2168841     3.7791875     3.5053528
  23 C   C8          -0.3357356     3.1901481     1.9737064
  24 H   H1           2.7672056     1.9564327     1.6953535
  25 H   H8           2.5584428     3.1962145     3.9983072
  26 H   H15         -1.3504474     3.3831587     1.6514110
```

2-thiophene TS2 alt (TS1h)

```
G = -1173.25727
iv = i114
S^2 = 0.5844

Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------
```

```
  1 C   C              -0.3331252     2.7439182    -0.5242953
  2 C   C2             -1.4517833     1.9650401    -0.5727216
  3 C   C3             -1.5103739     0.7180630     0.0976444
  4 C   C4              0.9029740     2.1508129     0.0594263
  5 C   C5              1.1146943     0.7374396    -0.3968356
  6 H   H              -0.2825728     3.7530236    -0.9182330
  7 H   H7             -2.3112866     2.2592107    -1.1717697
  8 H   H8             -0.9585452     0.5456332     1.0118178
  9 H   H12             0.6711376     0.4815216    -1.3498593
 10 F   F1              2.0021802     2.9255137    -0.2725910
 11 F   F2              0.8715525     2.1990947     1.4621430
 12 C   C11            -2.5122966    -0.2777141    -0.2889431
 13 O   O1             -3.3033639    -0.1635621    -1.2119161
 14 O   O2             -2.4575935    -1.3702203     0.5160657
 15 C   C12            -3.3994409    -2.4043657     0.2026418
 16 H   H1             -4.4248487    -2.0408846     0.3169501
 17 H   H9             -3.1984520    -3.2090659     0.9108671
 18 H   H10            -3.2635384    -2.7531014    -0.8251504
 19 C   C1              2.1319687    -0.1093191     0.1123631
 20 C   C6              2.5032706    -1.3622827    -0.5148334
 21 C   C7              3.4928028    -2.0212654     0.1397115
 22 S   S1              4.0211354    -1.1473099     1.5576573
 23 C   C9              2.8912283     0.1141277     1.2640703
 24 H   H3              2.0309517    -1.7285710    -1.4201138
 25 H   H5              3.9542148    -2.9658622    -0.1152083
 26 H   H14             2.8191103     0.9601255     1.9311122
```

2-thiazole SM (9i)

```
G = -1189.35451
iv = none

 Cartesian Coordinates (Angstroms)
      Atom             X             Y             Z
   ---------    ------------- ------------- -------------

  1 C   C1              1.4013058     1.6826903    -0.9862793
  2 C   C2              0.3481207     1.9349898     0.0400251
  3 C   C3              0.8159698     0.4777131    -0.3397660
  4 H   H6              1.4365614     0.0346426     0.4351354
  5 C   C10            -0.1119487    -0.4004681    -1.0663144
  6 H   H11            -0.6646054     0.0283623    -1.9004368
  7 C   C11            -0.3216483    -1.6902861    -0.7672656
  8 H   H12             0.1965106    -2.1904600     0.0457575
  9 C   C12            -1.2854305    -2.4901029    -1.5544828
 10 O   O1             -1.9512959    -2.0857909    -2.4883978
 11 O   O2             -1.3389844    -3.7630262    -1.0940432
 12 C   C13            -2.2476632    -4.6264585    -1.7931289
 13 H   H5             -3.2687791    -4.2396457    -1.7340227
 14 H   H13            -2.1742931    -5.5940744    -1.2957037
 15 H   H14            -1.9635389    -4.7121801    -2.8456385
 16 F   F1              1.0897515     1.9454442    -2.2761353
 17 F   F2              2.6798604     2.0163755    -0.7391868
 18 C   C4              0.6871187     2.4484393     1.3825995
 19 N   N1              1.5569002     1.9082761     2.1889631
```

```
 20 C   C7            0.9016926     3.7544921     3.4403495
 21 H   H9            0.8278894     4.4632764     4.2532685
 22 S   S1           -0.0542307     3.9215840     2.0031029
 23 H   H3           -0.6141778     2.2362664    -0.3652607
 24 C   C6            1.6824389     2.6395753     3.3463609
 25 H   H7            2.3724759     2.3003654     4.1105000
```

2-thiazole TS2 (TS1ia)

```
G = -1189.31604
iv = i158
S^2 = 0.6401

Cartesian Coordinates (Angstroms)
         Atom              X             Y             Z
     ---------     ------------- ------------- -------------

  1 C   C            -0.8624600     0.6458233    -2.6809721
  2 C   C2           -1.7945142     0.6484678    -1.6885283
  3 C   C3           -1.4196477     0.7346465    -0.3224604
  4 C   C4            0.5731559     0.5015687    -2.2988314
  5 C   C5            0.7688284    -0.4679819    -1.1699536
  6 H   H            -1.1050971     0.7031453    -3.7364239
  7 H   H7           -2.8520204     0.5322726    -1.9168489
  8 H   H8           -0.5487926     1.2963848    -0.0125430
  9 H   H12           0.1063398    -1.3231256    -1.1382335
 10 F   F1            1.3102300     0.0940487    -3.3953137
 11 F   F2            1.1248412     1.7403949    -1.9531783
 12 C   C11          -2.3513200     0.2959998     0.7223360
 13 O   O1           -3.4476576    -0.2001740     0.5203581
 14 O   O2           -1.8421206     0.5130008     1.9592936
 15 C   C12          -2.6828069     0.0961690     3.0445494
 16 H   H1           -3.6349998     0.6336831     3.0225873
 17 H   H9           -2.1283804     0.3339141     3.9529242
 18 H   H10          -2.8823985    -0.9775536     2.9854094
 19 C   C1            1.9504425    -0.5849422    -0.4186831
 20 N   N1            2.1984549    -1.6348782     0.3707388
 21 C   C8            4.1034809    -0.3580502     0.7303876
 22 H   H11           5.0684951    -0.0693435     1.1245010
 23 S   S1            3.2435322     0.6444020    -0.3730350
 24 C   C7            3.3860264    -1.5066663     1.0000569
 25 H   H4            3.7183885    -2.2912055     1.6718630
```

thiazole_higher_energyTS2 (TS1ib)

```
G = -1189.31128
iv = i172
S^2 = 0.6211

Cartesian Coordinates (Angstroms)
         Atom              X             Y             Z
     ---------     ------------- ------------- -------------

  1 C   C            -0.9124198     0.5660171    -2.6688343
  2 C   C2           -1.8409100     0.5476441    -1.6746237
  3 C   C3           -1.4526669     0.6770132    -0.3132767
```

```
  4  C   C4            0.5318908      0.5151246     -2.2727045
  5  C   C5            0.7450768     -0.4716982     -1.1503779
  6  H   H            -1.1557524      0.5780877     -3.7256670
  7  H   H7           -2.8933373      0.3752347     -1.8897007
  8  H   H8           -0.6112304      1.2936434     -0.0270815
  9  H   H12           0.0711162     -1.3178375     -1.1388929
 10  F   F1            1.2984462      0.1460785     -3.3609117
 11  F   F2            0.9821656      1.7714234     -1.9150056
 12  C   C11          -2.3479460      0.2107881      0.7509096
 13  O   O1           -3.4172720     -0.3501472      0.5736335
 14  O   O2           -1.8381305      0.4805843      1.9781156
 15  C   C12          -2.6495697      0.0533101      3.0811159
 16  H   H1           -3.6204748      0.5563684      3.0622352
 17  H   H9           -2.0932806      0.3274638      3.9780292
 18  H   H10          -2.8124816     -1.0275786      3.0439963
 19  C   C1            1.9449539     -0.5742326     -0.4236465
 20  N   N1            2.9420037      0.3050315     -0.3933605
 21  C   C8            3.7444018     -1.3024687      1.0843730
 22  H   H11           4.4074900     -1.7902521      1.7856196
 23  S   S1            2.2310906     -1.9904853      0.6387774
 24  C   C7            3.9330111     -0.1008447      0.4304792
 25  H   H4            4.8138256      0.5217320      0.5467991
```

Ph LHS SM (control compound) (9j)

```
Spartan'10: G = -852.507737, iv = none
Gaussian'09: B3LYP/6-31G*, G = -852.513911, iv = none
Gaussian'09: M05-2X/6-31G*, G = -852.454583, iv = none

Cartesian Coordinates (Angstroms)
      Atom             X             Y             Z
   ---------    ------------- ------------- -------------

  1  H   H1           -0.7342992      2.1292350     -0.6038797
  2  C   C1           -0.6896550      2.5456381      0.3996721
  3  C   C4           -0.5788215      3.6046272      2.9736287
  4  C   C2            0.1528229      1.9539030      1.3524642
  5  C   C6           -1.4665871      3.6544153      0.7292205
  6  C   C5           -1.4135141      4.1868572      2.0197807
  7  C   C3            0.2019187      2.4950669      2.6438137
  8  H   H6           -2.1142921      4.1021150     -0.0198156
  9  H   H5           -2.0191435      5.0512131      2.2786045
 10  H   H3            0.8466623      2.0454541      3.3913082
 11  H   H4           -0.5318796      4.0135924      3.9793780
 12  C   C7            1.0044769      0.7904903      0.9510633
 13  C   C8            1.3092637     -0.3611739      1.8231770
 14  C   C9            0.3451828     -0.6317107      0.7160262
 15  H   H9           -0.6950119     -0.6814867      1.0296629
 16  F   F1            0.8550859     -0.4026367      3.0973066
 17  F   F2            2.5471373     -0.9057421      1.7618348
 18  C   C10           0.7256057     -1.4333489     -0.4525928
 19  H   H8            1.7776668     -1.4516307     -0.7317858
 20  C   C11          -0.1366627     -2.1405728     -1.1983779
 21  H   H10          -1.1996782     -2.1775237     -0.9780074
 22  C   C12           0.3401656     -2.9115132     -2.3652549
 23  O   O1            1.4898785     -2.9767628     -2.7568938
```

```
 24  O   O2          -0.6913356    -3.5547476    -2.9657551
 25  C   C13         -0.3365797    -4.3399461    -4.1129601
 26  H   H7           0.3705291    -5.1270044    -3.8365732
 27  H   H11          0.1186948    -3.7122448    -4.8840365
 28  H   H12         -1.2707537    -4.7727264    -4.4725849
 29  H   H2           1.7931229     1.0081637     0.2315763
```

Ph_LHS_TS2 (TS1j)

```
Spartan'10: G = -852.467491, iv = i124, S^2 = 0.5609
Gaussian'09: B3LYP/6-31G*, G = -852.471539, iv = i139, S^2 = 0.72
Gaussian'09: M05-2X/6-31G*, G = -852.407064, iv = i150 S^2 = 0.73
```

```
 Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1  C   C           -0.7938224     2.9281295    -0.4973567
  2  C   C2          -1.9169588     2.1548519    -0.5208385
  3  C   C3          -1.9447433     0.8899069     0.1188859
  4  C   C4           0.4554569     2.3058113     0.0257641
  5  C   C5           0.6396500     0.9126099    -0.5034969
  6  H   H           -0.7489920     3.9452945    -0.8705278
  7  H   H7          -2.7990824     2.4628835    -1.0784486
  8  H   H8          -1.3634344     0.6999835     1.0109197
  9  H   H12          0.1318702     0.7046588    -1.4362973
 10  F   F1           1.5526349     3.0842611    -0.3012959
 11  F   F2           0.4548498     2.2993475     1.4302410
 12  C   C1           1.6981159     0.0337646    -0.1244960
 13  C   C6           3.7528699    -1.7843479     0.5356695
 14  C   C7           1.9221078    -1.1367612    -0.8981062
 15  C   C8           2.5370955     0.2579721     1.0002180
 16  C   C9           3.5497938    -0.6376134     1.3129267
 17  C   C10          2.9311417    -2.0302287    -0.5711578
 18  H   H2           1.2868288    -1.3240531    -1.7604162
 19  H   H6           2.3799547     1.1370129     1.6122318
 20  H   H5           4.1864329    -0.4470045     2.1726196
 21  H   H3           3.0852933    -2.9185318    -1.1775979
 22  H   H4           4.5447429    -2.4828045     0.7915831
 23  C   C11         -2.9550719    -0.1019472    -0.2577349
 24  O   O1          -3.7794569     0.0322524    -1.1481949
 25  O   O2          -2.8655294    -1.2148241     0.5148987
 26  C   C12         -3.8127241    -2.2457971     0.2059573
 27  H   H1          -4.8355106    -1.8867747     0.3524122
 28  H   H9          -3.5920855    -3.0635919     0.8932747
 29  H   H10         -3.7014272    -2.5744602    -0.8316365
```

bis_Ph_SM (9k)

```
G = -1083.47906
iv = none
```

```
 Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------
```

```
  1 C   C1          2.1401892    -0.0956954    -0.5030615
  2 C   C2          1.0084305     0.6541421     0.1013241
  3 C   C3          1.0969993    -0.9312616     0.1653649
  4 H   H6          1.3824353    -1.3078350     1.1445602
  5 C   C4          1.2610998     1.3842374     1.3998916
  6 C   C5          1.6621778     2.8368121     3.7687618
  7 C   C6          0.5771414     1.0383205     2.5708181
  8 C   C7          2.1514488     2.4655458     1.4290384
  9 C   C8          2.3510230     3.1865204     2.6055784
 10 C   C9          0.7744797     1.7603828     3.7486637
 11 H   H4         -0.1128299     0.1982990     2.5605250
 12 H   H7          2.6904649     2.7407226     0.5268287
 13 H   H8          3.0475027     4.0206999     2.6144128
 14 H   H9          0.2348075     1.4804399     4.6494368
 15 C   C10         0.1997949    -1.7833133    -0.6270916
 16 H   H11        -0.0529765    -1.4603042    -1.6341065
 17 C   C11        -0.3192736    -2.9411307    -0.1905993
 18 H   H12        -0.1109823    -3.3375552     0.7992122
 19 C   C12        -1.2026816    -3.7385484    -1.0670984
 20 O   O1         -1.5445314    -3.4423954    -2.1960226
 21 O   O2         -1.5992964    -4.8756654    -0.4422651
 22 C   C13        -2.4590919    -5.7243013    -1.2159658
 23 H   H5         -3.3938217    -5.2092327    -1.4552872
 24 H   H13        -2.6519025    -6.5966411    -0.5904149
 25 H   H14        -1.9711465    -6.0186838    -2.1489851
 26 F   F1          2.2560587    -0.1617158    -1.8507333
 27 F   F2          3.3716170    -0.0205447     0.0501528
 28 H   H16         1.8186444     3.3988195     4.6855521
 29 C   C14        -0.0221504     1.2954522    -0.7972292
 30 C   C15        -1.9532314     2.5840539    -2.3773674
 31 C   C16        -1.3881705     1.1209839    -0.5374988
 32 C   C17         0.3650011     2.1252734    -1.8574405
 33 C   C18        -0.5955412     2.7651048    -2.6420020
 34 C   C19        -2.3475632     1.7589318    -1.3221684
 35 H   H2         -1.7000848     0.4771947     0.2803560
 36 H   H1          1.4189827     2.2629083    -2.0781994
 37 H   H3         -0.2800252     3.4018179    -3.4642146
 38 H   H10        -3.4028383     1.6083512    -1.1113529
 39 H   H15        -2.7001597     3.0798098    -2.9913732
```

bis_Ph_TS2 (TS1k)

```
G = -1083.43796
iv = i170
S^2 = 0.5387

 Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C          -0.4905029     2.9644064     0.2699805
  2 C   C2         -1.6739456     2.3000484     0.1811172
  3 C   C3         -1.8234284     0.9930522     0.7115034
  4 C   C4          0.7007691     2.2204344     0.7848070
  5 C   C5          0.8020209     0.7758907     0.2922367
  6 H   H          -0.3628539     4.0113164     0.0158601
```

```
  7  H   H7              -2.5148493     2.7325649    -0.3574474
  8  H   H8              -1.3254011     0.6920489     1.6207777
  9  F   F1               1.8636038     2.8958172     0.4238450
 10  F   F2               0.7094526     2.2676910     2.1728991
 11  C   C1               1.4274022    -0.2471139     1.1415429
 12  C   C6               2.6632180    -2.2619875     2.7066499
 13  C   C7               2.3919579    -1.1262335     0.5910474
 14  C   C8               1.1150697    -0.4092438     2.5134199
 15  C   C9               1.7196106    -1.4031744     3.2752391
 16  C   C10              2.9998396    -2.1130276     1.3598395
 17  H   H2               2.6831985    -1.0061205    -0.4461451
 18  H   H6               0.3847455     0.2361774     2.9804870
 19  H   H5               1.4477300    -1.5099628     4.3216431
 20  H   H3               3.7451214    -2.7611627     0.9068595
 21  H   H4               3.1324323    -3.0357165     3.3080647
 22  C   C11             -2.8669953     0.1051841     0.2041829
 23  O   O1              -3.6526536     0.3696869    -0.6919707
 24  O   O2              -2.8577312    -1.0884394     0.8590324
 25  C   C12             -3.8453877    -2.0292641     0.4217172
 26  H   H1              -4.8524776    -1.6265121     0.5631762
 27  H   H9              -3.6987149    -2.9175849     1.0380379
 28  H   H10             -3.7106018    -2.2706167    -0.6369425
 29  C   C13              0.7059762     0.5609448    -1.1515914
 30  C   C14              0.4088753     0.1093913    -3.9293928
 31  C   C15              0.9236744     1.5965010    -2.0893611
 32  C   C16              0.3436510    -0.7135608    -1.6564080
 33  C   C17              0.1940066    -0.9325095    -3.0176990
 34  C   C18              0.7744233     1.3681896    -3.4571869
 35  H   H11              1.2584263     2.5672437    -1.7492165
 36  H   H12              0.1380548    -1.5165279    -0.9558351
 37  H   H13             -0.1056006    -1.9144923    -3.3740211
 38  H   H14              0.9565966     2.1808425    -4.1552514
 39  H   H15              0.2912871    -0.0641812    -4.9954973
```

alkynyl_LHS_SM (9l)

```
G = -697.662199
iv = none
```

```
   Cartesian Coordinates (Angstroms)
        Atom                X             Y             Z
    ---------     ------------- ------------- -------------

  1  C   C1               2.0424676     1.9684931    -0.1391170
  2  C   C2               0.8725035     2.4962424     0.6162951
  3  C   C3               1.1493632     0.9340715     0.4498497
  4  H   H3               0.0609649     2.8669018    -0.0070648
  5  H   H6               1.5244582     0.4683830     1.3570881
  6  C   C10              0.2426017     0.1419043    -0.3899421
  7  H   H11             -0.0646980     0.5667251    -1.3437475
  8  C   C11             -0.2303187    -1.0678896    -0.0571690
  9  H   H12              0.0360504    -1.5606142     0.8732704
 10  C   C12             -1.1469251    -1.7848967    -0.9704422
 11  O   O1              -1.5497743    -1.3718325    -2.0409954
 12  O   O2              -1.4935214    -2.9877721    -0.4535502
 13  C   C13             -2.3834903    -3.7677120    -1.2660675
```

```
 14 H   H5           -3.3175284    -3.2268389    -1.4405158
 15 H   H13          -2.5682923    -4.6831435    -0.7031171
 16 H   H14          -1.9222194    -3.9957741    -2.2309570
 17 F   F1            2.0512871     2.1302983    -1.4803672
 18 F   F2            3.2825906     2.1200466     0.3600670
 19 C   C4            1.0217110     3.0973457     1.9084994
 20 H   H1            1.2541083     4.0534359     3.9587574
 21 C   C5            1.1386614     3.6026259     2.9992259
```

alkynyl_LHS_TS2 (TS1l)

```
G = -697.620962
iv = i184
S^2 = 0.6758

Cartesian Coordinates (Angstroms)
      Atom            X             Y             Z
   ---------    ------------- ------------- -------------

  1 C   C             0.4165731     2.5068791    -0.3637114
  2 C   C2           -0.6902111     1.7284846    -0.5113690
  3 C   C3           -0.7689538     0.4441358     0.0901598
  4 C   C4            1.6325214     1.8895419     0.2525525
  5 C   C5            1.8367364     0.4685151    -0.2135836
  6 H   H             0.4814311     3.5345224    -0.7045805
  7 H   H7           -1.5231515     2.0493445    -1.1332736
  8 H   H8           -0.2830066     0.2352376     1.0335260
  9 H   H12           1.5620280     0.2510525    -1.2394046
 10 F   F1            2.7448939     2.6456606    -0.0628903
 11 F   F2            1.5608009     1.9131080     1.6360459
 12 C   C11          -1.7408621    -0.5420694    -0.3985955
 13 O   O1           -2.5033990    -0.3717384    -1.3355925
 14 O   O2           -1.6893955    -1.6811234     0.3336227
 15 C   C12          -2.6113098    -2.7077900    -0.0591668
 16 H   H1           -3.6404973    -2.3981585     0.1488279
 17 H   H9           -2.3494573    -3.5814320     0.5392686
 18 H   H10          -2.5162890    -2.9258022    -1.1264765
 19 C   C1            2.6781292    -0.3978923     0.4613271
 20 H   H2            4.0143079    -1.8713020     1.5919161
 21 C   C6            3.3891107    -1.1891739     1.0613974
```

4-pyridine_LHS_SM (9m)

```
G = -868.554947
iv = none

Cartesian Coordinates (Angstroms)
      Atom            X             Y             Z
   ---------    ------------- ------------- -------------

  1 C   C1            1.7379906     1.0533701    -1.0125123
  2 C   C2            0.5948548     1.5544215    -0.2227780
  3 C   C3            0.8612826     0.0062370    -0.4070529
  4 H   H3           -0.2344211     1.9188458    -0.8277523
  5 H   H6            1.2755361    -0.4729380     0.4771572
  6 C   C10          -0.0500743    -0.7951991    -1.2344074
```

7	H	H11	-0.3979950	-0.3587991	-2.1691355
8	C	C11	-0.4826418	-2.0238238	-0.9158956
9	H	H12	-0.1760631	-2.5312450	-0.0058114
10	C	C12	-1.4082921	-2.7431426	-1.8178865
11	O	O1	-1.8477926	-2.3196153	-2.8698685
12	O	O2	-1.7178395	-3.9617345	-1.3139346
13	C	C13	-2.6120458	-4.7454915	-2.1180937
14	H	H5	-3.5544664	-4.2138221	-2.2744602
15	H	H13	-2.7778343	-5.6670627	-1.5592395
16	H	H14	-2.1631492	-4.9616572	-3.0915960
17	F	F1	1.7223381	1.2232993	-2.3539189
18	F	F2	3.0003533	1.1868913	-0.5460287
19	C	C4	0.7315355	2.1769759	1.1301111
20	N	N1	0.9105237	3.3755852	3.6778867
21	C	C6	-0.1933435	1.8824315	2.1393948
22	C	C7	1.7489586	3.0877968	1.4319480
23	C	C8	1.7909243	3.6507591	2.7088508
24	C	C9	-0.0613028	2.5028302	3.3802346
25	H	H2	-1.0006241	1.1775720	1.9604804
26	H	H1	2.4979879	3.3500452	0.6929301
27	H	H4	2.5765237	4.3602219	2.9639503
28	H	H7	-0.7709234	2.2872482	4.1774282

4-pyridine_LHS_TS2 (TS1m)

G = -868.512852
iv = i151
S^2 = 0.5934

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C	0.3070064	2.7970608	-0.9446703
2	C	C2	-0.8702346	2.2484882	-1.3570235
3	C	C3	-1.4285757	1.1354692	-0.6765308
4	C	C4	1.0819644	2.0509262	0.0900012
5	C	C5	1.1037370	0.5761160	-0.1992953
6	H	H	0.7280987	3.7102181	-1.3504719
7	H	H7	-1.3808928	2.6113983	-2.2462561
8	H	H8	-1.2991936	1.0085770	0.3895858
9	H	H12	0.9892222	0.3102938	-1.2422746
10	F	F1	2.3744958	2.5344481	0.1628290
11	F	F2	0.5526452	2.2904937	1.3649280
12	C	C1	1.6724039	-0.4116988	0.6680910
13	N	N1	2.7702392	-2.4577611	2.2998445
14	C	C7	1.9062917	-1.7183103	0.1748682
15	C	C8	2.0121818	-0.1793825	2.0237279
16	C	C9	2.5517642	-1.2197246	2.7707856
17	C	C10	2.4457148	-2.6822852	1.0166428
18	H	H2	1.6680436	-1.9635620	-0.8566372
19	H	H6	1.8552203	0.7934610	2.4703350
20	H	H5	2.8223384	-1.0542993	3.8121624
21	H	H3	2.6310239	-3.6892368	0.6468259
22	C	C11	-2.4292836	0.2928172	-1.3442906
23	O	O1	-2.7867842	0.4153052	-2.5041783
24	O	O2	-2.9178859	-0.6490733	-0.5024576
25	C	C12	-3.9064488	-1.5218351	-1.0694465
26	H	H1	-4.7684266	-0.9486601	-1.4213600
27	H	H9	-4.1964768	-2.1977280	-0.2648775
28	H	H10	-3.4881892	-2.0815155	-1.9108571

2-pyridine_SM (9n)

G = -868.560284
iv = none

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	2.1000029	0.5055043	-0.6965333
2	C	C2	0.9184896	1.2927387	-0.2508197
3	C	C3	0.9201405	-0.2843109	-0.2566169
4	H	H3	0.3655689	1.7584852	-1.0628600
5	H	H6	1.0020918	-0.6850727	0.7505895
6	C	C10	0.0820217	-1.0040781	-1.2242092
7	H	H11	0.0715084	-0.6434600	-2.2512806
8	C	C11	-0.6680193	-2.0749420	-0.9252445

9	H	H12	-0.7026792	-2.4985163	0.0742806
10	C	C12	-1.4832540	-2.7315458	-1.9687958
11	O	O1	-1.5706412	-2.3850279	-3.1315743
12	O	O2	-2.1432411	-3.7999312	-1.4572169
13	C	C13	-2.9636894	-4.5145889	-2.3923749
14	H	H5	-3.7374900	-3.8605552	-2.8038684
15	H	H13	-3.4129366	-5.3306347	-1.8252458
16	H	H14	-2.3588262	-4.9055369	-3.2152852
17	F	F1	2.4062756	0.5330426	-2.0166253
18	F	F2	3.2294763	0.4892063	0.0356387
19	C	C4	0.8835237	2.0151828	1.0526041
20	C	C5	0.4862175	4.0200942	2.3217539
21	C	C6	1.2149747	1.9755476	3.3252197
22	C	C7	0.8534596	3.3152944	3.4674928
23	C	C9	0.5011632	3.3634083	1.0942391
24	H	H1	0.1920557	5.0644380	2.3820080
25	H	H10	1.5038450	1.3864459	4.1940646
26	H	H7	0.8566146	3.7858904	4.4457855
27	H	H4	0.2238540	3.8813328	0.1805933
28	N	N1	1.2294931	1.3315891	2.1542812

2-pyridine_LHS_TS2 (TS1n)

G = -868.515403
iv = i143
S^2 = 0.6016

Cartesian Coordinates (Angstroms)

Atom			X	Y	Z
1	C	C	-1.3374758	2.5356748	-1.0093448
2	C	C2	-2.2782936	1.6088466	-0.6708224
3	C	C3	-1.9635131	0.5397633	0.2053482
4	C	C4	0.0726353	2.2614527	-0.6057535
5	C	C5	0.4434383	0.8277131	-0.8440428
6	H	H	-1.5466778	3.4307520	-1.5847047
7	H	H7	-3.2738083	1.6322947	-1.1088727
8	H	H8	-1.2360491	0.6601069	0.9961678
9	H	H12	-0.1008181	0.3085738	-1.6207575
10	F	F1	0.9380644	3.0934627	-1.2933938
11	F	F2	0.2717235	2.6027654	0.7419510
12	C	C11	-2.8012772	-0.6650313	0.2258161
13	O	O1	-3.7626787	-0.8645502	-0.4984173
14	O	O2	-2.3748274	-1.5432864	1.1655528
15	C	C12	-3.1247583	-2.7633846	1.2453564
16	H	H1	-4.1702767	-2.5577539	1.4924223
17	H	H9	-2.6510838	-3.3472613	2.0353189
18	H	H10	-3.0865709	-3.3018428	0.2938812
19	C	C1	1.6820642	0.2233836	-0.4512118
20	C	C6	3.0429579	-1.6244868	-0.6922048
21	C	C7	3.7697283	0.1398279	0.7639039
22	C	C8	4.0071794	-1.1069262	0.1855604
23	C	C9	2.5956014	0.8152813	0.4550249
24	H	H6	3.1965203	-2.5964725	-1.1593318
25	H	H2	4.4882175	0.5785235	1.4508757

```
  26  H   H11           2.3721687     1.7800871     0.8912999
  27  H   H15           4.9094911    -1.6702421     0.4031932
  28  N   N1            1.9183188    -0.9972714    -1.0128147
```

mestial_LHS_SM (9o)

```
G = -931.084973
iv = none

 Cartesian Coordinates (Angstroms)
       Atom             X              Y              Z
    ---------    -------------- -------------- --------------

   1  C   C1            0.1004469     2.2220900     0.6645602
   2  C   C4            0.6179998     2.7845380     3.3602783
   3  C   C2            0.4412212     1.1795836     1.5534176
   4  C   C6           -0.0085121     3.5271508     1.1593174
   5  C   C5            0.2335058     3.8095278     2.5001810
   6  C   C3            0.7356289     1.4666546     2.9061109
   7  H   H6           -0.2769598     4.3290486     0.4757904
   8  C   C7            0.5808699    -0.2319649     1.0555541
   9  C   C8           -0.1705426    -1.3846140     1.6029641
  10  C   C9           -0.5552311    -0.9555791     0.2298027
  11  H   H2            1.5767018    -0.5169806     0.7105993
  12  H   H9           -1.4941709    -0.4095453     0.1875632
  13  F   F1           -1.0798392    -1.2110464     2.5911733
  14  F   F2            0.4777548    -2.5599177     1.7786826
  15  C   C10          -0.1959880    -1.7500721    -0.9518852
  16  H   H8            0.6860607    -2.3846041    -0.8834668
  17  C   C11          -0.8754358    -1.7385575    -2.1084376
  18  H   H10          -1.7676427    -1.1355409    -2.2504491
  19  C   C12          -0.4247943    -2.5601502    -3.2515758
  20  O   O1            0.5476472    -3.2903961    -3.2670891
  21  O   O2           -1.2497147    -2.3917060    -4.3140848
  22  C   C13          -0.9012200    -3.1455892    -5.4840422
  23  H   H7           -1.6573250    -2.8967817    -6.2294611
  24  H   H11          -0.9114799    -4.2176582    -5.2686542
  25  H   H12           0.0948902    -2.8669536    -5.8391450
  26  H   H13           0.8410760     3.0050004     4.4012792
  27  H   H14           0.1448661     4.8280735     2.8688423
  28  C   C14           1.2027439     0.3953000     3.8685409
  29  H   H3            2.0048709    -0.2166351     3.4392861
  30  H   H4            0.3904854    -0.2853752     4.1410036
  31  H   H5            1.5858001     0.8469728     4.7884605
  32  C   C15          -0.1261934     1.9824906    -0.8125576
  33  H   H1            0.6219677     1.3088903    -1.2428746
  34  H   H15          -0.0814835     2.9275316    -1.3626110
  35  H   H16          -1.1080042     1.5368148    -1.0170736
```

mestial_LHS_TS2 (TS1o)

```
G = -931.03943
iv = i163
S^2 = 0.4019

Cartesian Coordinates (Angstroms)
       Atom             X              Y              Z
    ---------    ------------- ------------- -------------

   1 C   C            -0.9096073     2.9999154    -0.6912791
   2 C   C2           -2.0360516     2.2377163    -0.7378677
   3 C   C3           -2.1135924     1.0215839    -0.0058768
   4 C   C4            0.2750223     2.4204254     0.0037197
   5 C   C5            0.4715012     0.9822567    -0.3974421
   6 H   H            -0.8218177     3.9896965    -1.1255369
   7 H   H7           -2.8733542     2.5030118    -1.3800533
   8 H   H8           -1.6394225     0.9189243     0.9604468
   9 H   H12          -0.0225180     0.7726982    -1.3310704
  10 F   F1            1.4016049     3.1758374    -0.2977579
  11 F   F2            0.1212585     2.5546778     1.3887792
  12 C   C1            1.4217506    -0.0048547     0.0215955
  13 C   C6            3.1264852    -2.1716909     0.6879449
  14 C   C7            1.3363574    -1.2694638    -0.6749484
  15 C   C8            2.4113891     0.1340256     1.0593259
  16 C   C9            3.2330401    -0.9551468     1.3562590
  17 C   C10           2.1784890    -2.3184261    -0.3231740
  18 H   H5            3.9816581    -0.8398030     2.1353523
  19 H   H3            2.0933610    -3.2653645    -0.8495429
  20 H   H4            3.7819432    -2.9982625     0.9491787
  21 C   C11          -3.1018826     0.0086805    -0.3848636
  22 O   O1           -3.8836344     0.0960370    -1.3186036
  23 O   O2           -3.0497525    -1.0689426     0.4432732
  24 C   C12          -3.9932816    -2.1074128     0.1491285
  25 H   H1           -5.0179906    -1.7422433     0.2652941
  26 H   H9           -3.7880318    -2.9023816     0.8670705
  27 H   H10          -3.8644584    -2.4699381    -0.8747308
  28 C   C13           0.3217102    -1.5138343    -1.7672206
  29 H   H2            0.4539469    -0.8378948    -2.6220265
  30 H   H11          -0.7036854    -1.3781792    -1.4022584
  31 H   H13           0.4101087    -2.5361182    -2.1452878
  32 C   C14           2.6522116     1.3956379     1.8523865
  33 H   H6            3.5569560     1.2846271     2.4567706
  34 H   H14           1.8176205     1.6153149     2.5241571
  35 H   H15           2.7726663     2.2688901     1.2088587
```

CN_LHS_SM (9p)

G = -713.768678
iv = none

Cartesian Coordinates (Angstroms)

Atom			X	Y	Z
1	C	C1	2.1105281	2.1676364	0.0607816
2	C	C2	0.9282908	2.6973176	0.8055329
3	C	C3	1.2084693	1.1411205	0.6469596
4	H	H3	0.1174426	3.0867177	0.1951720
5	H	H6	1.5781365	0.6749817	1.5564852
6	C	C10	0.2994338	0.3482683	-0.1952820
7	H	H11	-0.0074648	0.7713752	-1.1498698
8	C	C11	-0.1680119	-0.8609948	0.1413430
9	H	H12	0.0980057	-1.3501675	1.0737703
10	C	C12	-1.0836522	-1.5834987	-0.7736110
11	O	O1	-1.4813821	-1.1690509	-1.8448390
12	O	O2	-1.4294060	-2.7821559	-0.2538465
13	C	C13	-2.3207190	-3.5670072	-1.0628304
14	H	H5	-3.2547926	-3.0265207	-1.2372134
15	H	H13	-2.5037297	-4.4796588	-0.4953127
16	H	H14	-1.8592968	-3.7978324	-2.0267518
17	F	F1	2.1283668	2.3361226	-1.2752149
18	F	F2	3.3385408	2.3297532	0.5788564
19	C	C4	1.0853552	3.2951414	2.1015202
20	N	N1	1.2158852	3.7684526	3.1543505

CN_TS2_LHS (TS1p)

G = -713.721964
iv = i155
S^2 = 0.7284

Cartesian Coordinates (Angstroms)

Atom			X	Y	Z
1	C	C	0.6241679	2.4031406	-0.2738745
2	C	C2	-0.4805786	1.6202633	-0.4326921
3	C	C3	-0.5716376	0.3395870	0.1665526
4	C	C4	1.8411921	1.7973544	0.3558040
5	C	C5	2.0667465	0.3810862	-0.1131399
6	H	H	0.6878658	3.4299286	-0.6174105
7	H	H7	-1.3048091	1.9405880	-1.0662309
8	H	H8	-0.0794007	0.1167471	1.1042300
9	H	H12	1.8288848	0.1377578	-1.1414734
10	F	F1	2.9471866	2.5617131	0.0595204
11	F	F2	1.7442745	1.8038173	1.7346643
12	C	C11	-1.5489598	-0.6406201	-0.3373632
13	O	O1	-2.2846036	-0.4580160	-1.2919570
14	O	O2	-1.5247731	-1.7723946	0.3978188
15	C	C12	-2.4409557	-2.7978593	-0.0199103
16	H	H1	-3.4727192	-2.4461302	0.0688983

```
 17 H   H9             -2.2617445    -3.6389979     0.6500185
 18 H   H10            -2.2500442    -3.0821967    -1.0583823
 19 C   C1              2.9068816    -0.4760555     0.6003823
 20 N   N1              3.5730261    -1.2197129     1.2145449
```

bis_Me_SM (9q)

```
G = -700.111308
iv = none

 Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

   1 C   C1             2.0731041     1.4329992    -0.0574773
   2 C   C2             0.9105710     2.0532084     0.6154089
   3 C   C3             1.0819624     0.4757247     0.5293786
   4 H   H6             1.3885151     0.0266553     1.4718288
   5 C   C10            0.2298959    -0.3588462    -0.3263205
   6 H   H11           -0.0043230    -0.0017723    -1.3264940
   7 C   C11           -0.2750917    -1.5474524     0.0392841
   8 H   H12           -0.0818387    -1.9863458     1.0138698
   9 C   C12           -1.1201020    -2.3171720    -0.8962823
  10 O   O1            -1.4474721    -1.9684929    -2.0150925
  11 O   O2            -1.5010940    -3.4947810    -0.3414644
  12 C   C13           -2.3270747    -4.3210829    -1.1737455
  13 H   H5            -3.2622960    -3.8090614    -1.4171567
  14 H   H13           -2.5237829    -5.2216600    -0.5908583
  15 H   H14           -1.8096520    -4.5700095    -2.1043086
  16 F   F1             2.1749089     1.5080913    -1.4073872
  17 F   F2             3.3089790     1.5151021     0.4929244
  18 C   C4             1.1196354     2.6538467     1.9943286
  19 H   H2             1.3688246     3.7187737     1.9119609
  20 H   H1             1.9340872     2.1627737     2.5336219
  21 H   H4             0.2046912     2.5670947     2.5917509
  22 C   C5            -0.1555183     2.7305982    -0.2274199
  23 H   H3             0.0607406     3.8027064    -0.3054149
  24 H   H7            -1.1418916     2.6190904     0.2369124
  25 H   H8            -0.2057783     2.3300117    -1.2418472
```

bis_Me_TS2 (TS1q)

```
G = -700.060667
iv = i100
S^2 = 0.7900

Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

   1 C   C              0.1237299     2.3869725    -0.1597606
   2 C   C2            -1.0083310     1.6232422    -0.1860150
   3 C   C3            -1.0802427     0.3424862     0.4046702
   4 C   C4             1.4031081     1.8012226     0.3541250
   5 C   C5             1.6811928     0.3858892    -0.0908040
   6 H   H              0.1467319     3.4180567    -0.4968980
```

```
   7 H   H7             -1.8932190      1.9779903     -0.7108761
   8 H   H8             -0.4412332      0.0606467      1.2306433
   9 F   F1              2.4620626      2.6105992     -0.0533107
  10 F   F2              1.4223842      1.8616800      1.7422396
  11 C   C11            -2.1665313     -0.5719112      0.0454378
  12 O   O1             -3.0467581     -0.3398684     -0.7678811
  13 O   O2             -2.0779041     -1.7366836      0.7382398
  14 C   C12            -3.0991150     -2.6990411      0.4427816
  15 H   H1             -4.0897223     -2.2910524      0.6629351
  16 H   H9             -2.8872352     -3.5573064      1.0817029
  17 H   H10            -3.0645781     -2.9878448     -0.6119782
  18 C   C1              2.5335867     -0.4762974      0.7855487
  19 H   H2              3.6034920     -0.2525135      0.6302659
  20 H   H3              2.3934697     -1.5349386      0.5393255
  21 H   H4              2.3220170     -0.3237354      1.8460327
  22 C   C6              1.6772984      0.1237909     -1.5629317
  23 H   H5              2.6195015      0.4789808     -2.0145781
  24 H   H6              0.8634720      0.6478645     -2.0733145
  25 H   H11             1.6028234     -0.9482291     -1.7756002
```

spiro_Cy_SM (9r)

```
G = -816.783222
iv = none

Cartesian Coordinates (Angstroms)
       Atom             X              Y              Z
    ---------    ------------- ------------- -------------

   1 C   C7              0.8338418      0.2700360      1.6681000
   2 C   C8              1.3019352     -1.0963801      1.9585323
   3 C   C9              0.1199460     -1.0099642      1.0427021
   4 H   H9             -0.8364595     -1.2368433      1.5094591
   5 F   F1              1.1361577     -1.6278679      3.1952081
   6 F   F2              2.4865374     -1.5127188      1.4443376
   7 C   C10             0.2327149     -1.3458225     -0.3817849
   8 H   H8              1.2117319     -1.2760414     -0.8494771
   9 C   C11            -0.7940576     -1.7382254     -1.1529121
  10 H   H10            -1.8033911     -1.8477723     -0.7663437
  11 C   C12            -0.5809612     -2.0369866     -2.5837731
  12 O   O1              0.4763905     -1.9589756     -3.1808004
  13 C   C1              0.0253239      1.0203924      2.7196751
  14 C   C3              1.6510379      1.1890916      0.7694728
  15 C   C5             -0.0685140      3.0189961      1.1530655
  16 C   C4              0.7469214      2.2428305      0.1069988
  17 C   C6             -0.8763674      2.0762243      2.0588939
  18 H   H6              2.4012181      1.6924191      1.3970295
  19 H   H1              0.6167925      3.6165654      1.7724597
  20 H   H3              0.0654169      1.7409366     -0.5935039
  21 H   H4             -1.6452781      1.5663157      1.4610916
  22 H   H13            -0.5610714      0.3219513      3.3257121
  23 H   H14             2.2108182      0.6259676      0.0173195
  24 H   H15            -0.7402863      3.7301518      0.6567296
  25 H   H16             1.3571245      2.9335692     -0.4875397
  26 H   H17            -1.4061865      2.6472244      2.8313489
  27 H   H19             0.7275683      1.5149340      3.4072191
```

```
 28  O   O2           -1.7431661    -2.4142474    -3.1732278
 29  C   C2           -1.6457089    -2.7183003    -4.5716870
 30  H   H2           -0.9410616    -3.5372764    -4.7398430
 31  H   H5           -1.3079479    -1.8430298    -5.1339370
 32  H   H7           -2.6510199    -3.0071538    -4.8805256
```

spiro_Cy_TS2 (TS1r)

```
G = -816.731056
iv = i97
S^2 = 0.7478

Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
   ---------    ------------- ------------- -------------

  1  C   C            -0.9106382     0.1385209    -2.4198357
  2  C   C2           -2.0066762     0.0588373    -1.6096145
  3  C   C3           -2.0468213     0.6448966    -0.3245854
  4  C   C4            0.3617085     0.7027390    -1.8766115
  5  C   C5            0.7101923     0.2673726    -0.4763650
  6  H   H            -0.9127853    -0.1936752    -3.4526047
  7  H   H7           -2.8809086    -0.5071742    -1.9252811
  8  H   H8           -1.4417739     1.5058868    -0.0739070
  9  F   F1            1.4122950     0.3522255    -2.7348973
 10  F   F2            0.3253288     2.0931194    -1.9280441
 11  C   C11          -3.0625295     0.2215394     0.6410615
 12  O   O1           -3.9253566    -0.6174316     0.4373100
 13  O   O2           -2.9288840     0.8840187     1.8196481
 14  C   C12          -3.8809944     0.5254657     2.8300970
 15  H   H1           -4.8911736     0.8195024     2.5290081
 16  H   H9           -3.5784079     1.0691925     3.7260809
 17  H   H10          -3.8678857    -0.5531413     3.0093056
 18  C   C1            0.7278114    -1.1969004    -0.1483625
 19  C   C6            3.1970845    -0.9642782     0.4242527
 20  C   C7            1.6949869     1.0935451     0.2973150
 21  C   C8            3.1336164     0.5342591     0.0967162
 22  C   C10           2.1569301    -1.7667288    -0.3710193
 23  H   H6            3.0191287    -1.1074851     1.5005324
 24  H   H2            1.4469283     1.0280261     1.3671402
 25  H   H3            3.4328635     0.7002145    -0.9452832
 26  H   H4            2.3923188    -1.7226277    -1.4412872
 27  H   H5           -0.0026178    -1.7533951    -0.7426260
 28  H   H12           4.2045241    -1.3485397     0.2199300
 29  H   H13           1.6477085     2.1463858     0.0092794
 30  H   H14           3.8312146     1.0989149     0.7277639
 31  H   H16           2.1753025    -2.8235721    -0.0765909
 32  H   H17           0.4675095    -1.3297124     0.9114743
```

Me_LHS_SM (9s)

```
G = -660.822287
iv = none

Cartesian Coordinates (Angstroms)
      Atom            X             Y             Z
    ---------    ------------- ------------- -------------

  1  C   C1           2.0231665     1.8219797    -0.1009084
  2  C   C2           0.8591224     2.3957932     0.5973220
  3  C   C3           1.0653756     0.8373953     0.4948820
  4  H   H3           0.0828452     2.7793574    -0.0623670
  5  H   H6           1.4065548     0.3683184     1.4155768
  6  C   C10          0.1794920     0.0384012    -0.3610723
  7  H   H11         -0.1057450     0.4597875    -1.3234845
  8  C   C11         -0.3015600    -1.1721524    -0.0405860
  9  H   H12         -0.0568987    -1.6648328     0.8959144
 10  C   C12         -1.1930632    -1.8907679    -0.9742955
 11  O   O1          -1.5745636    -1.4815698    -2.0545686
 12  O   O2          -1.5477945    -3.0970966    -0.4663047
 13  C   C13         -2.4130947    -3.8792491    -1.3015377
 14  H   H5          -3.3460342    -3.3437464    -1.4979605
 15  H   H13         -2.6068929    -4.7973238    -0.7456777
 16  H   H14         -1.9280348    -4.1029442    -2.2558562
 17  F   F1           2.1083142     1.9187173    -1.4481460
 18  F   F2           3.2560764     1.9357782     0.4474883
 19  C   C4           0.9961342     3.0828046     1.9380245
 20  H   H2           1.1842622     4.1541589     1.8037964
 21  H   H1           1.8310465     2.6675779     2.5100867
 22  H   H4           0.0812917     2.9696133     2.5296743
```

Me_LHS_TS2 (TS1s)

```
G = -660.768319
iv = i131
S^2 = 0.6779

Cartesian Coordinates (Angstroms)
      Atom            X             Y             Z
    ---------    ------------- ------------- -------------

  1  C   C            0.3085323     2.3948690    -0.3713510
  2  C   C2          -0.8130753     1.6163945    -0.4309390
  3  C   C3          -0.8733321     0.3534257     0.2006025
  4  C   C4           1.5557584     1.7871013     0.1739419
  5  C   C5           1.7883266     0.4037325    -0.3426420
  6  H   H            0.3500821     3.4137669    -0.7408256
  7  H   H7          -1.6791382     1.9321921    -1.0087759
  8  H   H8          -0.2831662     0.1347899     1.0804898
  9  H   H12          1.3603866     0.1697550    -1.3099371
 10  F   F1           2.6477364     2.5869476    -0.1376405
 11  F   F2           1.5407328     1.7597005     1.5709135
 12  C   C11         -1.9181127    -0.6061449    -0.1751014
 13  O   O1          -2.7455039    -0.4375735    -1.0556302
 14  O   O2          -1.8572819    -1.7243077     0.5904331
```

```
 15  C   C12          -2.8504334    -2.7170042     0.2970293
 16  H   H1           -3.8548958    -2.3160435     0.4598089
 17  H   H9           -2.6521582    -3.5419732     0.9820799
 18  H   H10          -2.7687977    -3.0501926    -0.7414680
 19  C   C1            2.9503630    -0.3851851     0.1507666
 20  H   H2            3.8623132    -0.1334861    -0.4167327
 21  H   H3            2.7802482    -1.4597707     0.0183974
 22  H   H4            3.1514158    -0.1809937     1.2065809
```

Cyclohexane_LHS_SM (9t)

```
G = -856.068176
iv = none

Cartesian Coordinates (Angstroms)
      Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1  C   C1            1.8132546    -0.1254555    -1.2431369
  2  C   C2            0.6689606     0.5838044    -0.6484235
  3  C   C3            0.7976203    -0.9827691    -0.5514934
  4  H   H6            1.0980521    -1.3510941     0.4276266
  5  C   C10          -0.0974759    -1.8420595    -1.3358473
  6  H   H11          -0.3637252    -1.5051304    -2.3363689
  7  C   C11          -0.6038909    -3.0121600    -0.9186998
  8  H   H12          -0.3800074    -3.4297584     0.0586900
  9  C   C12          -1.4888097    -3.7946546    -1.8059083
 10  O   O1           -1.8576938    -3.4646708    -2.9173734
 11  O   O2           -1.8499558    -4.9621632    -1.2174127
 12  C   C13          -2.7011198    -5.8031835    -2.0087260
 13  H   H5           -3.6432313    -5.2952692    -2.2332015
 14  H   H13          -2.8796215    -6.6930651    -1.4039693
 15  H   H14          -2.2120140    -6.0690561    -2.9498777
 16  F   F1            1.9300157    -0.2036574    -2.5895176
 17  F   F2            3.0420992     0.0008356    -0.6833144
 18  H   H27          -0.0787439     0.9222028    -1.3654762
 19  C   C4            0.8320289     1.4467615     0.5901217
 20  C   C5            1.5341502     3.7458363     1.4385367
 21  C   C6           -0.3191983     2.4784660     2.6147853
 22  C   C7            0.2214645     3.8631329     2.2267911
 23  C   C8           -0.4816357     1.5709344     1.3856840
 24  C   C9            1.3760635     2.8396635     0.2090836
 25  H   H1            2.3145050     3.3312512     2.0936405
 26  H   H10           0.3738144     2.0058396     3.3264914
 27  H   H7           -0.5259304     4.3824974     1.6086663
 28  H   H2           -1.2592787     1.9886008     0.7282212
 29  H   H3            0.6841610     3.3106055    -0.5056947
 30  H   H4            1.5795893     0.9671361     1.2389613
 31  H   H8            1.8840046     4.7383857     1.1281029
 32  H   H9           -1.2801993     2.5756065     3.1353638
 33  H   H15           0.3682606     4.4789489     3.1231632
 34  H   H16          -0.8321850     0.5758432     1.6887860
 35  H   H17           2.3366723     2.7277945    -0.3082738
```

Cyclohexane_LHS_TS2 (TS1t)

```
G = -856.014022
iv = i85
S^2 = 0.6959

 Cartesian Coordinates (Angstroms)
       Atom             X              Y              Z
   ---------    -------------- -------------- --------------

  1 C   C            -1.1459943     3.1420549     -0.3807845
  2 C   C2           -2.3123754     2.4309537     -0.4431040
  3 C   C3           -2.4581901     1.1834592      0.2011743
  4 C   C4            0.0639459     2.4728074      0.1785269
  5 C   C5            0.2378422     1.0780749     -0.3265326
  6 H   H            -1.0443228     4.1549539     -0.7551947
  7 H   H7           -3.1534524     2.7964908     -1.0285193
  8 H   H8           -1.8743492     0.9306885      1.0759075
  9 H   H12          -0.1990978     0.8539743     -1.2939466
 10 F   F1            1.1937126     3.2292701     -0.1245203
 11 F   F2            0.0351417     2.4568309      1.5756810
 12 C   C11          -3.5671769     0.2930240     -0.1557100
 13 O   O1           -4.3893255     0.5049005     -1.0319125
 14 O   O2           -3.5758169    -0.8171822      0.6256282
 15 C   C12          -4.6388617    -1.7415579      0.3566904
 16 H   H1           -5.6111052    -1.2696221      0.5252804
 17 H   H9           -4.4906418    -2.5695469      1.0508394
 18 H   H10          -4.5931794    -2.0931125     -0.6779004
 19 C   C1            1.3281238     0.2014565      0.1880883
 20 C   C6            2.0361646    -2.2017771      0.6649187
 21 C   C7            3.7606359    -0.5154607     -0.1164017
 22 C   C8            3.3347840    -1.9902941     -0.1272322
 23 C   C9            2.6408840     0.4018975     -0.6276467
 24 C   C10           0.9096345    -1.2879287      0.1613144
 25 H   H6            2.2214743    -1.9930558      1.7287106
 26 H   H2            4.0288647    -0.2203249      0.9085850
 27 H   H3            3.1802209    -2.3140483     -1.1672855
 28 H   H11           2.4375610     0.1804705     -1.6856019
 29 H   H4            0.6471647    -1.5634168     -0.8713829
 30 H   H5            1.5382216     0.4850275      1.2284702
 31 H   H13           1.7187659    -3.2504677      0.6040024
 32 H   H14           4.6613020    -0.3721416     -0.7272798
 33 H   H15           4.1354506    -2.6202288      0.2804987
 34 H   H16           2.9425636     1.4522243     -0.5736873
 35 H   H17           0.0014311    -1.4283938      0.7603263
```

Nosub_SM (9u)

```
G = -621.530722
iv = none

Cartesian Coordinates (Angstroms)
       Atom             X              Y              Z
    ---------    -------------- -------------- --------------

   1 C   C1           2.2693226      2.2659885      0.0864734
   2 C   C2           1.1197603      2.9740186      0.6698508
   3 C   C3           1.2450634      1.4144417      0.7701306
   4 H   H6           1.5344577      1.0450348      1.7510014
   5 C   C10          0.3425391      0.5632196     -0.0173407
   6 H   H11          0.0778347      0.9032775     -1.0171279
   7 C   C11         -0.1726064     -0.6001362      0.4056053
   8 H   H12          0.0465146     -1.0118713      1.3865594
   9 C   C12         -1.0708885     -1.3795287     -0.4724605
  10 O   O1          -1.4275210     -1.0602966     -1.5906800
  11 O   O2          -1.4615842     -2.5255858      0.1371570
  12 C   C13         -2.3404688     -3.3567339     -0.6346471
  13 H   H5          -3.2668138     -2.8246330     -0.8690111
  14 H   H13         -2.5467023     -4.2262388     -0.0095105
  15 H   H14         -1.8609645     -3.6579635     -1.5697553
  16 F   F1           2.3857290      2.1922397     -1.2587838
  17 F   F2           3.4912239      2.3878929      0.6511892
  18 H   H19          1.2698913      3.5329598      1.5878548
  19 H   H27          0.3652130      3.3639145     -0.0065050
```

Nosub_TS2 (TS1u)

```
G = -621.573778, iv = i192, S^2 = 0.7541

 Cartesian Coordinates (Angstroms)
       Atom             X              Y              Z
    ---------    -------------- -------------- --------------

   1 C   C            0.7946670      2.3077343     -0.3275513
   2 C   C2          -0.3207882      1.5191922     -0.3512372
   3 C   C3          -0.3471353      0.2472733      0.2644960
   4 C   C4           2.0777544      1.7153433      0.1641641
   5 C   C5           2.2929621      0.3245173     -0.3214240
   6 H   H            0.8063598      3.3332337     -0.6810900
   7 H   H7          -1.2132158      1.8362782     -0.8866403
   8 H   H8           0.2852294      0.0174445      1.1119224
   9 H   H12          1.9390721      0.0455178     -1.3051098
  10 F   F1           3.1381612      2.5196024     -0.2259812
  11 F   F2           2.1241288      1.7200433      1.5552521
  12 C   C11         -1.3975823     -0.7187094     -0.0857327
  13 O   O1          -2.2725753     -0.5339239     -0.9149029
  14 O   O2          -1.2755861     -1.8575817      0.6374555
  15 C   C12         -2.2574039     -2.8663948      0.3575224
  16 H   H1          -3.2646088     -2.4873954      0.5511549
  17 H   H9          -2.0236528     -3.6957507      1.0256294
  18 H   H10         -2.1949143     -3.1843250     -0.6871621
  19 H   H14          3.1091280     -0.2420994      0.1192347
```

Traige: Alkene Substition

CN_E_RHS_SM (10a)

```
Spartan'10: G = -716.912803, iv = none
Gaussian'09: B3LYP/6-31G*, G = -716.917313, iv = none
Gaussian'09: M05-2X/6-31G*, G = -716.875782, iv = none

Cartesian Coordinates (Angstroms)
      Atom             X             Y             Z
   ---------    ------------- ------------- -------------

  1  C   C1           1.2099133    -0.0977419    -1.6065770
  2  C   C2           0.0590977     0.4469622    -0.8600824
  3  C   C3           0.2832058    -1.1118198    -1.0155466
  4  H   H3          -0.7357640     0.8262827    -1.5022389
  5  H   H6           0.6520854    -1.5923392    -0.1124772
  6  C   C4           0.1766691     1.0873485     0.4884279
  7  C   C5           0.3166115     2.3312581     2.9990340
  8  C   C6          -0.7584871     0.7817166     1.4871255
  9  C   C7           1.1837058     2.0222044     0.7609151
 10  C   C8           1.2518592     2.6400825     2.0107107
 11  C   C9          -0.6903124     1.3999595     2.7345575
 12  H   H4          -1.5401211     0.0543296     1.2818457
 13  H   H7           1.9166062     2.2596338    -0.0034322
 14  H   H8           2.0386332     3.3621794     2.2112263
 15  H   H9          -1.4215208     1.1546333     3.5000254
 16  H   H10          0.3715235     2.8128553     3.9715426
 17  C   C10         -0.6131026    -1.9007668    -1.8689807
 18  H   H11         -0.9056200    -1.4587226    -2.8188340
 19  C   C11         -1.0781109    -3.1203258    -1.5398247
 20  H   H12         -0.7980410    -3.5941554    -0.6016563
 21  F   F1           1.2349442     0.0471189    -2.9525554
 22  F   F2           2.4623054     0.0002929    -1.1107415
 23  C   C12         -1.9519651    -3.8639691    -2.3870171
 24  N   N1          -2.6641154    -4.4870174    -3.0654468
```

CN_E_RHS_TS2 (TS2a)

```
Spartan'10: G = -716.875779, iv = i139, S^2 = 0.5463
Gaussian'09: B3LYP/6-31G*, G = -716.878006, iv = i142, S^2 = 0.71
Gaussian'09: M05-2X/6-31G*, G = -716.822858, iv = i163, S^2 = 0.87

 Cartesian Coordinates (Angstroms)
      Atom             X             Y             Z
   ---------    ------------- ------------- -------------

  1  C   C           -2.0151459     2.2303766    -0.0973687
  2  C   C2          -2.9431550     1.3505820     0.3674799
  3  C   C3          -2.5398690     0.1873772     1.0918623
  4  C   C4          -0.5821229     1.8287807    -0.0075954
  5  C   C5          -0.3850858     0.4037320    -0.4380687
  6  H   H           -2.2614819     3.1842132    -0.5498818
  7  H   H7          -4.0012889     1.4983995     0.1605929
  8  H   H8          -1.6636352     0.2188718     1.7271340
  9  H   H12         -1.1535598     0.0087404    -1.0894109
```

```
 10  F   F1           0.2022057     2.6699625    -0.7739606
 11  F   F2          -0.1019806     2.0131870     1.2992351
 12  C   C1           0.8586417    -0.2923927    -0.3976390
 13  C   C6           3.2581461    -1.7749134    -0.3738577
 14  C   C7           0.9563986    -1.5448774    -1.0627802
 15  C   C8           2.0071669     0.1905469     0.2877517
 16  C   C9           3.1855331    -0.5420531     0.2868369
 17  C   C10          2.1357579    -2.2738553    -1.0474285
 18  H   H2           0.0850569    -1.9299378    -1.5868042
 19  H   H6           1.9565916     1.1379754     0.8093028
 20  H   H5           4.0568926    -0.1560074     0.8089601
 21  H   H3           2.1878759    -3.2298883    -1.5607497
 22  H   H4           4.1834916    -2.3440671    -0.3629747
 23  C   C11         -3.3726726    -0.9440476     1.2101815
 24  N   N1          -4.0537612    -1.8907052     1.2991830
```

Weinreb_Amide_RHS_SM (10b)

```
Spartan'10: G = -947.067954, iv = none
Gaussian'09: B3LYP/6-31G*, G = -947.076299, iv = none
Gaussian'09: M05-2X/6-31G*, G = -947.020971, iv = none
```

```
 Cartesian Coordinates (Angstroms)
       Atom              X              Y              Z
   ---------    -------------- -------------- --------------

  1  C   C1          -1.4670215    -1.8630042    -0.2979475
  2  C   C2          -1.7954595    -0.7553857     0.6210089
  3  C   C3          -0.5077807    -0.7195424    -0.3017992
  4  H   H3          -1.5563263    -0.9723070     1.6617199
  5  H   H6          -0.6081401    -0.0550275    -1.1571230
  6  C   C4          -2.9022014     0.2271570     0.4004430
  7  C   C5          -4.9645210     2.1066034     0.0780893
  8  C   C6          -2.7137389     1.5659107     0.7746769
  9  C   C7          -4.1376207    -0.1588032    -0.1355554
 10  C   C8          -5.1610036     0.7773159    -0.2962337
 11  C   C9          -3.7364277     2.4990068     0.6162029
 12  H   H4          -1.7569553     1.8733261     1.1900092
 13  H   H7          -4.2953475    -1.1902837    -0.4317271
 14  H   H8          -6.1137281     0.4635579    -0.7144940
 15  H   H9          -3.5747818     3.5324214     0.9112700
 16  H   H10         -5.7625886     2.8333963    -0.0472600
 17  C   C10          0.8266066    -0.8336070     0.2998313
 18  H   H11          0.9617074    -1.5572226     1.1015221
 19  C   C11          1.8856003    -0.0975559    -0.0705567
 20  H   H12          1.8128700     0.6439152    -0.8574601
 21  C   C12          3.1819019    -0.2851643     0.6277332
 22  O   O1           3.3361624    -1.0633959     1.5655795
 23  N   N1           4.2673549     0.4261932     0.1278718
 24  C   C13          5.4661468     0.6116434     0.9286587
 25  H   H5           5.5681329    -0.2635093     1.5695692
 26  H   H13          5.3895370     1.5154256     1.5463922
 27  H   H14          6.3395043     0.6949450     0.2750625
 28  F   F1          -1.0729595    -3.0457522     0.2301305
 29  F   F2          -2.2134450    -2.0857404    -1.4061244
 30  O   O2           3.9800488     1.5460992    -0.6824481
```

31	C	C14	4.4328597	1.3118606	-2.0186236
32	H	H2	4.2195193	2.2375591	-2.5596953
33	H	H1	3.8943077	0.4753809	-2.4795787
34	H	H15	5.5107114	1.1111478	-2.0471366

Weinreb_amide_RHS_TS2 (TS2b)

Spartan'10: G = -947.029070, iv = i127, S^2 = 0.5635
Gaussian'09: B3LYP/6-31G*, G = -947.034526, iv = i142, S^2 = 0.55
Gaussian'09: M05-2X/6-31G*, G = -716.829881, iv = i163, S^2 = 0.87

Cartesian Coordinates (Angstroms)

Atom			X	Y	Z
1	C	C	-0.3708103	3.2467077	-0.7831259
2	C	C2	-1.5345291	2.5375201	-0.8136579
3	C	C3	-1.6370972	1.2810981	-0.1615410
4	C	C4	0.8362767	2.5577318	-0.2460828
5	C	C5	0.9440416	1.1547946	-0.7683250
6	H	H	-0.2640747	4.2559235	-1.1654640
7	H	H7	-2.3928187	2.8872876	-1.3828514
8	H	H8	-1.0886985	1.0873996	0.7477209
9	H	H12	0.4333421	0.9712623	-1.7046199
10	F	F1	1.9794635	3.2721405	-0.5629116
11	F	F2	0.8234439	2.5560476	1.1595635
12	C	C1	1.9584378	0.2243082	-0.3835976
13	C	C6	3.9199424	-1.6910241	0.2942364
14	C	C7	2.1243885	-0.9626358	-1.1474145
15	C	C8	2.8072229	0.4142519	0.7398366
16	C	C9	3.7737304	-0.5287123	1.0609754
17	C	C10	3.0871008	-1.9039211	-0.8110489
18	H	H2	1.4847797	-1.1228519	-2.0121957
19	H	H6	2.6945236	1.3061860	1.3428490
20	H	H5	4.4196154	-0.3619704	1.9188608
21	H	H3	3.1977030	-2.8027072	-1.4116446
22	H	H4	4.6764064	-2.4256027	0.5560373
23	C	C11	-2.7109407	0.3574663	-0.5597123
24	O	O1	-3.4753177	0.5889965	-1.4986722
25	N	N1	-2.7996676	-0.8457652	0.1359310
26	O	O2	-2.1985384	-0.8783023	1.4133387
27	C	C12	-4.0180133	-1.6373118	0.0779455
28	H	H9	-3.7798796	-2.6879591	0.2658295
29	H	H10	-4.4370453	-1.5272446	-0.9217100
30	H	H11	-4.7482652	-1.2934599	0.8216190
31	C	C13	-1.1294124	-1.8306027	1.4283861
32	H	H1	-0.7534186	-1.8191473	2.4549569
33	H	H13	-0.3318626	-1.5429230	0.7352616
34	H	H14	-1.4900290	-2.8369809	1.1812269

AllylAlcohol_RHS_E_SM (10c)

```
G = -739.155508
iv = none

  Cartesian Coordinates (Angstroms)
       Atom             X              Y              Z
    ---------     -------------  -------------  -------------

  1  C   C1          0.2555785      2.1890182      0.4890142
  2  C   C4         -0.0090838      2.6009899      3.2310042
  3  C   C2          0.3676012      1.0972270      1.3622191
  4  C   C6          0.0168255      3.4717008      0.9799304
  5  C   C5         -0.1172528      3.6810733      2.3545178
  6  C   C3          0.2336460      1.3170931      2.7394558
  7  H   H6         -0.0667795      4.3074216      0.2899720
  8  C   C7          0.6624323     -0.2635615      0.8118213
  9  C   C8          0.0034628     -1.4998679      1.2885984
 10  C   C9         -0.4096150     -1.0224052     -0.0598878
 11  H   H2          1.6825928     -0.4228790      0.4619987
 12  H   H9         -1.3779573     -0.5256805     -0.0738933
 13  F   F1         -0.8920404     -1.4510192      2.3058011
 14  F   F2          0.7442514     -2.6307156      1.3926437
 15  C   C10        -0.0144213     -1.7308339     -1.2938316
 16  C   C11        -0.7356426     -1.7174309     -2.4181920
 17  H   H10        -1.6777015     -1.1702959     -2.4622000
 18  H   H13        -0.1140383      2.7552384      4.3017809
 19  H   H14        -0.3054297      4.6800810      2.7388050
 20  H   H17         0.3109915      0.4797849      3.4253868
 21  H   H3          0.3540560      2.0251906     -0.5814957
 22  H   H12         0.9182520     -2.2882847     -1.2718986
 23  C   C12        -0.3541539     -2.4248015     -3.6850703
 24  H   H1         -0.3431852     -1.6949674     -4.5151730
 25  H   H4         -1.1372756     -3.1636898     -3.9344604
 26  O   O1          0.9111033     -3.0494862     -3.5340332
 27  H   H5          1.0937834     -3.5488993     -4.3428135
```

allylalcohol_RHS_E_TS2 (TS2c)

```
G = -739.115497
iv = i149
S^2 = 0.5638

Cartesian Coordinates (Angstroms)
       Atom             X              Y              Z
    ---------     -------------  -------------  -------------

  1  C   C          -0.9916180      2.5756204     -0.6751842
  2  C   C2         -2.1559361      1.8593542     -0.5635713
  3  C   C3         -2.2167936      0.7019090      0.2369574
  4  C   C4          0.2411986      1.9532219     -0.1246117
  5  C   C5          0.3251911      0.5046037     -0.4913438
  6  H   H          -0.9166136      3.5396422     -1.1658984
  7  H   H8         -1.5833461      0.6228962      1.1114011
  8  H   H12        -0.2252742      0.2257674     -1.3802903
  9  F   F1          1.3654598      2.6372691     -0.5628246
```

```
 10  F   F2            0.2941675     2.1103313     1.2790261
 11  C   C1            1.3651672    -0.3820207    -0.0641299
 12  C   C6            3.3555405    -2.2306219     0.7196571
 13  C   C7            1.5116549    -1.6321336    -0.7209743
 14  C   C8            2.2515829    -0.0921458     1.0071926
 15  C   C9            3.2304789    -1.0033181     1.3810741
 16  C   C10           2.4878426    -2.5398509    -0.3345601
 17  H   H2            0.8427593    -1.8714578    -1.5445940
 18  H   H6            2.1571432     0.8506500     1.5309215
 19  H   H5            3.9032527    -0.7590580     2.1991517
 20  H   H3            2.5795329    -3.4894655    -0.8552001
 21  H   H4            4.1215079    -2.9392671     1.0226611
 22  H   H14          -3.0327146     2.1343550    -1.1457768
 23  C   C11          -3.3073964    -0.3132689     0.1297800
 24  H   H1           -4.0085898    -0.1780739     0.9764311
 25  H   H7           -2.8726158    -1.3209940     0.2537061
 26  O   O1           -3.9795164    -0.1834506    -1.1147506
 27  H   H9           -4.7420651    -0.7804935    -1.1042495
```

Me_RHS_E_SM (10d)

```
G = -663.957928
iv = none

Cartesian Coordinates (Angstroms)
       Atom              X             Y             Z
    ---------    ------------- ------------- -------------

  1  C   C1            0.4009824     2.0386001     0.3731448
  2  C   C4           -0.0441784     2.4200530     3.0959599
  3  C   C2            0.3917446     0.9285029     1.2304266
  4  C   C6            0.1932558     3.3240719     0.8705544
  5  C   C5           -0.0312215     3.5181574     2.2355956
  6  C   C3            0.1679087     1.1329872     2.5983758
  7  H   H6            0.2045607     4.1739084     0.1930297
  8  C   C7            0.6594677    -0.4356104     0.6749485
  9  C   C8           -0.0604812    -1.6558925     1.1030610
 10  C   C9           -0.3990780    -1.1480238    -0.2537758
 11  H   H2            1.6880637    -0.6259657     0.3677942
 12  H   H9           -1.3489336    -0.6193858    -0.3044273
 13  F   F1           -0.9952085    -1.5969659     2.0833357
 14  F   F2            0.6411994    -2.8117864     1.2177540
 15  C   C10           0.0217734    -1.8588060    -1.4791923
 16  C   C11          -0.6265763    -1.7904779    -2.6471827
 17  H   H10          -1.5257926    -1.1758116    -2.7142843
 18  H   H13          -0.2193715     2.5626497     4.1591164
 19  H   H14          -0.1950732     4.5194536     2.6249715
 20  H   H17           0.1518618     0.2821452     3.2714201
 21  H   H3            0.5698026     1.8869875    -0.6903161
 22  H   H12           0.9179436    -2.4736188    -1.3967510
 23  C   C12          -0.2172187    -2.5078523    -3.9001855
 24  H   H1            0.6855317    -3.1076787    -3.7429439
 25  H   H4           -0.0183799    -1.8012469    -4.7175624
 26  H   H5           -1.0125826    -3.1783942    -4.2528668
```

Me_RHS_E_TS2 (TS2d)

```
G = -663.917301
iv = i184
S^2 = 0.5585

Cartesian Coordinates (Angstroms)
       Atom              X             Y             Z
    ---------    ------------- ------------- -------------

   1 C   C          -0.9151383     2.6513547    -0.7786512
   2 C   C2         -2.1077249     1.9853535    -0.8954940
   3 C   C3         -2.3582101     0.7899579    -0.1888719
   4 C   C4          0.1849905     1.9441886    -0.0714278
   5 C   C5          0.2556601     0.5076570    -0.4856083
   6 H   H          -0.7255362     3.6365584    -1.1899678
   7 H   H8         -1.8833208     0.6491853     0.7747308
   8 H   H12        -0.1358502     0.3017099    -1.4732521
   9 F   F1          1.3945439     2.5835277    -0.3012456
  10 F   F2          0.0234202     2.0493885     1.3265275
  11 C   C1          1.1528036    -0.4591358     0.0724220
  12 C   C6          2.8706507    -2.4587781     1.0962271
  13 C   C7          1.3491309    -1.6865482    -0.6134791
  14 C   C8          1.8458027    -0.2716662     1.2975662
  15 C   C9          2.6926693    -1.2560728     1.7896820
  16 C   C10         2.1907439    -2.6682562    -0.1092948
  17 H   H2          0.8298147    -1.8495212    -1.5553695
  18 H   H6          1.7092330     0.6511676     1.8469904
  19 H   H5          3.2177380    -1.0883929     2.7266783
  20 H   H3          2.3247423    -3.5980963    -0.6560184
  21 H   H4          3.5316207    -3.2251805     1.4915181
  22 H   H14        -2.8650800     2.3500191    -1.5911246
  23 C   C11        -3.4330427    -0.1819377    -0.5617517
  24 H   H1         -3.0292397    -1.2005583    -0.6427918
  25 H   H7         -3.9040764     0.0698443    -1.5176679
  26 H   H9         -4.2163453    -0.2257684     0.2096742
```

nosub_RHS_SM (10e)

```
G = -624.665083
iv = none

Cartesian Coordinates (Angstroms)
       Atom              X             Y             Z
    ---------    ------------- ------------- -------------

   1 H   H1         -0.7768006     1.0388829    -1.6047737
   2 C   C1         -0.7173554     1.4647263    -0.6059672
   3 C   C4         -0.5698059     2.5451006     1.9567121
   4 C   C2          0.1393784     0.8803837     0.3387670
   5 C   C6         -1.4888334     2.5770693    -0.2751774
   6 C   C5         -1.4173630     3.1205023     1.0098283
   7 C   C3          0.2059673     1.4328222     1.6246422
   8 H   H6         -2.1470385     3.0188171    -1.0187338
   9 H   H5         -2.0187004     3.9875695     1.2699744
  10 H   H3          0.8604990     0.9879185     2.3665809
```

```
 11 H  H4            -0.5091567     2.9619231     2.9586068
 12 C  C7             0.9869728    -0.2859276    -0.0643017
 13 C  C8             1.2810050    -1.4418712     0.8111093
 14 C  C9             0.3385846    -1.7037254    -0.3110794
 15 H  H9            -0.7064157    -1.7584663    -0.0129154
 16 F  F1             0.8141422    -1.4814324     2.0827236
 17 F  F2             2.5240203    -1.9833723     0.7679361
 18 C  C10            0.7298449    -2.5175481    -1.4803324
 19 H  H8             1.7922604    -2.5300748    -1.7195707
 20 C  C11           -0.1267143    -3.2164337    -2.2292022
 21 H  H10           -1.1933096    -3.2345539    -2.0164315
 22 H  H2             1.7888044    -0.0620621    -0.7678205
 23 H  H13            0.2100143    -3.8002475    -3.0805750
```

nosub_RHS_TS2 (TS2e)

```
G = -624.623111
iv = i300
S^2 = 0.5749

Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1 C  C             -1.7874470     2.4421631    -0.5045635
  2 C  C2            -2.9103076     1.6546177    -0.5179662
  3 C  C3            -2.9306507     0.4028033     0.1255955
  4 C  C4            -0.5366945     1.8213362     0.0097436
  5 C  C5            -0.3654349     0.4249353    -0.5081575
  6 H  H             -1.7528806     3.4631134    -0.8681306
  7 H  H7            -3.7853806     1.9730485    -1.0847020
  8 H  H8            -2.3409283     0.2191327     1.0131394
  9 H  H12           -0.8595597     0.2241621    -1.4499067
 10 F  F1             0.5605938     2.5993423    -0.3282603
 11 F  F2            -0.5231132     1.8293521     1.4181294
 12 C  C1             0.6996512    -0.4548601    -0.1310145
 13 C  C6             2.7580381    -2.2748292     0.5294732
 14 C  C7             0.9343812    -1.6177403    -0.9109320
 15 C  C8             1.5307144    -0.2392681     1.0000659
 16 C  C9             2.5445757    -1.1348745     1.3131165
 17 C  C10            1.9442125    -2.5118766    -0.5846335
 18 H  H2             0.3072605    -1.8002019    -1.7805825
 19 H  H6             1.3680550     0.6346591     1.6181396
 20 H  H5             3.1740740    -0.9480413     2.1792411
 21 H  H3             2.1048388    -3.3940255    -1.1988995
 22 H  H4             3.5500534    -2.9732849     0.7852097
 23 H  H11           -3.6840514    -0.3396633    -0.1241046
```

AllylAlcohol_RHS_Z_SM (10f)

```
G = -739.152680
iv = none

Cartesian Coordinates (Angstroms)
       Atom             X              Y              Z
    ---------    -------------  -------------  -------------

   1  C   C1          0.0851050      1.6761281      0.3841732
   2  C   C4          0.9694170      2.3216998      2.9514251
   3  C   C2          0.7293453      0.7021926      1.1574226
   4  C   C6         -0.1117169      2.9621284      0.8898064
   5  C   C5          0.3298641      3.2887861      2.1730192
   6  C   C3          1.1666918      1.0368216      2.4462655
   7  H   H6         -0.6130479      3.7100865      0.2806242
   8  C   C7          0.9817207     -0.6701300      0.6123821
   9  C   C8          0.3001452     -1.8728140      1.1463146
  10  C   C9         -0.1309859     -1.4173229     -0.2025879
  11  H   H2          1.9948860     -0.8646646      0.2592903
  12  H   H9         -1.0772748     -0.8910040     -0.2262031
  13  F   F1         -0.5547505     -1.7599330      2.1893523
  14  F   F2          1.0125521     -3.0239942      1.2656796
  15  C   C10         0.2344924     -2.1846184     -1.4139185
  16  C   C11        -0.2989358     -2.0996594     -2.6390618
  17  H   H10         0.1029440     -2.7637087     -3.4044095
  18  H   H13         1.3107232      2.5658500      3.9540720
  19  H   H14         0.1735724      4.2899330      2.5661627
  20  H   H17         1.6597545      0.2828651      3.0547075
  21  H   H3         -0.2702189      1.4158108     -0.6094971
  22  H   H12         1.0420510     -2.9017490     -1.2741580
  23  C   C12        -1.4035451     -1.2271609     -3.1634237
  24  H   H1         -2.2789188     -1.8620928     -3.3906656
  25  H   H4         -1.0748721     -0.8007048     -4.1272752
  26  O   O1         -1.7595442     -0.1917930     -2.2533476
  27  H   H5         -2.5194536      0.2790478     -2.6261489
```

Allylalochol_RHS_Z_TS2 (TS2f)

```
G = -739.107323
iv = i244
S^2 = 0.6641

Cartesian Coordinates (Angstroms)
       Atom             X              Y              Z
    ---------    -------------  -------------  -------------

   1  C   C          -2.1259931      2.0740105     -0.1662080
   2  C   C2         -2.5424791      1.5174060      1.0086412
   3  C   C15        -1.8016030      0.6027220      1.8031781
   4  C   C4         -0.9168276      1.5576179     -0.8649583
   5  C   C13        -0.7384488      0.0873205     -0.6639539
   6  H   H          -2.6797738      2.8649364     -0.6622078
   7  H   H8         -2.3837208     -0.0497596      2.4558284
   8  H   H12        -1.6672560     -0.4609286     -0.5726305
   9  F   F1         -1.0227259      1.8395517     -2.2240077
```

```
 10 F   F2            0.2272279     2.2801359    -0.4820522
 11 C   C1            0.4300140    -0.6726015    -0.9764675
 12 C   C6            2.6656667    -2.3058208    -1.5618602
 13 C   C7            0.3417808    -2.0913285    -0.9412475
 14 C   C8            1.6894536    -0.1010288    -1.3069829
 15 C   C9            2.7777544    -0.9110292    -1.6028171
 16 C   C10           1.4388181    -2.8908837    -1.2260127
 17 H   H2           -0.6111088    -2.5494343    -0.6868931
 18 H   H6            1.7894984     0.9759755    -1.3396011
 19 H   H5            3.7265815    -0.4526459    -1.8683576
 20 H   H3            1.3419452    -3.9726504    -1.1924436
 21 H   H4            3.5248236    -2.9305226    -1.7894764
 22 H   H14          -3.5589411     1.7394595     1.3403955
 23 C   C11          -0.3624922     0.6962153     2.2256699
 24 H   H1            0.1722012     1.4506196     1.6412898
 25 H   H7            0.1431767    -0.2710079     2.0799692
 26 O   O1           -0.3830862     1.0317742     3.6228611
 27 H   H9            0.5255144     0.9418970     3.9503449
```

Me_Z_RHS_SM (10g)

```
G = -664.955651
iv = none

Cartesian Coordinates (Angstroms)
      Atom              X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C1            0.6876844     1.8059308     0.2717546
  2 C   C4            0.2332772     2.1619593     2.9962718
  3 C   C2            0.6402783     0.6845481     1.1130431
  4 C   C6            0.5129610     3.0897137     0.7856787
  5 C   C5            0.2839789     3.2711096     2.1517316
  6 C   C3            0.4122952     0.8762936     2.4822057
  7 H   H6            0.5541235     3.9482377     0.1204040
  8 C   C7            0.8758488    -0.6774199     0.5386953
  9 C   C8            0.1402163    -1.8910747     0.9564978
 10 C   C9           -0.2033816    -1.3607236    -0.3908768
 11 H   H2            1.8972229    -0.8817126     0.2169921
 12 H   H9           -1.1441406    -0.8177792    -0.4139133
 13 F   F1           -0.7876269    -1.8294679     1.9434392
 14 F   F2            0.8237780    -3.0590947     1.0536399
 15 C   C10           0.2126043    -2.0669876    -1.6213846
 16 C   C11          -0.3788681    -2.0009782    -2.8219581
 17 H   H13           0.0549811     2.2947349     4.0601739
 18 H   H14           0.1465586     4.2711907     2.5541931
 19 H   H17           0.3680571     0.0172382     3.1433062
 20 H   H3            0.8611049     1.6644457    -0.7923559
 21 H   H5            0.0623687    -2.5931285    -3.6236434
 22 H   H12           1.0901639    -2.7021730    -1.5132039
 23 C   C12          -1.5928016    -1.2066712    -3.2116891
 24 H   H1           -1.3569106    -0.5121795    -4.0294335
 25 H   H4           -2.0052938    -0.6196340    -2.3862491
 26 H   H7           -2.3884795    -1.8663773    -3.5833190
```

Me_Z_RHS_TS2 (TS2g)

```
G = -663.908400
iv = i271
S^2 = 0.7108

 Cartesian Coordinates (Angstroms)
       Atom             X              Y              Z
    ---------    -------------- -------------- --------------

   1 C   C            -1.5504450     2.4776641    -0.6191524
   2 C   C2           -2.6238280     1.6386294    -0.6718734
   3 C   C3           -2.6681504     0.3067540    -0.1672499
   4 C   C4           -0.2008042     1.9546502    -0.2616217
   5 C   C5            0.0096776     0.5600419    -0.7584830
   6 H   H            -1.6142070     3.5236503    -0.9017007
   7 H   H12          -0.4798152     0.3547298    -1.7024576
   8 F   F1            0.7668653     2.7997959    -0.7985427
   9 F   F2            0.0214425     2.0575976     1.1224109
  10 C   C1            1.0293103    -0.3495120    -0.3479285
  11 C   C6            2.9841249    -2.2674036     0.3711957
  12 C   C7            1.2144525    -1.5409105    -1.1033773
  13 C   C8            1.8610609    -0.1597168     0.7899370
  14 C   C9            2.8220179    -1.1026679     1.1298415
  15 C   C10           2.1707081    -2.4804807    -0.7487619
  16 H   H2            0.5883137    -1.7070611    -1.9770387
  17 H   H6            1.7452761     0.7351629     1.3868514
  18 H   H5            3.4518718    -0.9319488     1.9991310
  19 H   H3            2.2898196    -3.3812381    -1.3451807
  20 H   H4            3.7347479    -3.0020007     0.6493852
  21 H   H7           -3.3665500    -0.3611418    -0.6760890
  22 H   H14          -3.5119600     1.9904034    -1.2035033
  23 C   C11          -2.2362635    -0.1744225     1.1888731
  24 H   H1           -1.5813535     0.5328307     1.6967027
  25 H   H8           -1.7263941    -1.1446348     1.1324948
  26 H   H9           -3.1299182    -0.3287709     1.8161379
```

CN_Z_RHS_SM (10h)

```
Spartan'10: G = -716.912699, iv = none
Gaussian'09: B3LYP/6-31G*, G =-716.917609, iv = none
Gaussian'09: M05-2X/6-31G*, G = -716.877091, iv = none

Cartesian Coordinates (Angstroms)
       Atom             X              Y              Z
    ---------    -------------- -------------- --------------

   1 C   C1            0.8179847     0.4610398    -1.8635220
   2 C   C2           -0.3416567     0.4689995    -0.9506254
   3 C   C3            0.4045255    -0.8718587    -1.3259301
   4 H   H3           -1.2995784     0.5872061    -1.4573460
   5 H   H6            1.0320986    -1.2635388    -0.5294869
   6 C   C4           -0.2651222     0.9957873     0.4498269
   7 C   C5           -0.1980338     2.0131451     3.0630712
   8 C   C6           -0.7499435     0.2341961     1.5211498
   9 C   C7            0.2576765     2.2709732     0.7012935
```

```
 10 C   C8             0.2898950     2.7763162     2.0014705
 11 C   C9            -0.7179257     0.7399927     2.8203014
 12 H   H4            -1.1462860    -0.7610274     1.3358170
 13 H   H7             0.6466198     2.8635872    -0.1213348
 14 H   H8             0.7007166     3.7655608     2.1843421
 15 H   H9            -1.0945771     0.1378479     3.6425950
 16 H   H10           -0.1699119     2.4064027     4.0757033
 17 C   C10           -0.2505385    -1.8537494    -2.1986835
 18 H   H11           -0.7665948    -1.4637915    -3.0729015
 19 C   C11           -0.2592490    -3.1874688    -2.0083162
 20 H   H12           -0.7683717    -3.8396237    -2.7121403
 21 F   F1             1.9994365     0.9831711    -1.4741208
 22 F   F2             0.6103896     0.7185857    -3.1784391
 23 C   C12            0.3781323    -3.8268640    -0.9027312
 24 N   N1             0.8903143    -4.3548891     0.0000069
```

CN_Z_RHS_TS2 (TS2h)

```
Spartan'10: G = -716.865358, iv = i141, S^2 = 0.6948
Gaussian'09: B3LYP/6-31G*, G = -716.870285, iv = i165, S^2 = 0.71
Gaussian'09: M05-2X/6-31G*, G = -716.822858, iv = i157, S^2 = 0.87

Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C             -1.6959458     2.4322037    -0.5853651
  2 C   C2            -2.8320034     1.6728406    -0.5751580
  3 C   C3            -2.9807398     0.3998630     0.0375008
  4 C   C4            -0.4175204     1.8559479    -0.1169702
  5 C   C5            -0.2444133     0.4520397    -0.6140125
  6 H   H             -1.6942970     3.4655487    -0.9128003
  7 H   H7            -3.6967941     2.0395279    -1.1290636
  8 H   H12           -0.8219802     0.2020451    -1.4936243
  9 F   F1             0.6514990     2.6240699    -0.5853241
 10 F   F2            -0.2852804     1.9416445     1.2749634
 11 C   C1             0.8219841    -0.4094148    -0.2537761
 12 C   C6             2.8634354    -2.2330723     0.4205645
 13 C   C7             1.0618240    -1.5728641    -1.0405546
 14 C   C8             1.6432015    -0.1977193     0.8914358
 15 C   C9             2.6488791    -1.0981051     1.2106711
 16 C   C10            2.0650588    -2.4670966    -0.7082571
 17 H   H2             0.4437234    -1.7493459    -1.9171956
 18 H   H6             1.4717272     0.6691657     1.5142291
 19 H   H5             3.2624894    -0.9291043     2.0913627
 20 H   H3             2.2336450    -3.3494409    -1.3192103
 21 H   H4             3.6455019    -2.9392286     0.6860434
 22 H   H9            -3.8222598    -0.2064568    -0.3046222
 23 C   C11           -2.3987703    -0.0760801     1.2324707
 24 N   N1            -1.9229643    -0.5269678     2.1966924
```

Me_CO2Et_RHS_SM (10i)

```
Spartan'10, G = -891.796469, iv = none
Gaussian'09: B3LYP/6-31G*, G = -891.805001, iv = none
Gaussian'09: M05-2X/6-31G*, G = -891.739337, iv = none

Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------


  1  H   H1          1.0446575     2.2529926     0.3038655
  2  C   C1          0.6803316     2.4282900     1.3133353
  3  C   C4         -0.2625032     2.8772000     3.8951227
  4  C   C2          0.2451012     1.3409889     2.0855825
  5  C   C6          0.6461051     3.7238963     1.8257449
  6  C   C5          0.1726455     3.9521526     3.1200901
  7  C   C3         -0.2258138     1.5785692     3.3836570
  8  H   H6          0.9875777     4.5551942     1.2146256
  9  H   H5          0.1441892     4.9618900     3.5207809
 10  H   H3         -0.5693807     0.7480578     3.9909839
 11  H   H4         -0.6314050     3.0461543     4.9033250
 12  C   C7          0.3355870    -0.0422941     1.5220763
 13  C   C8         -0.6565510    -1.1087543     1.7646985
 14  C   C9         -0.6767509    -0.5166698     0.3952902
 15  H   H2          1.3441159    -0.4219058     1.3611400
 16  H   H9         -1.4879302     0.1870095     0.2353990
 17  F   F1         -1.7181082    -0.8976478     2.5784862
 18  F   F2         -0.2105188    -2.3788247     1.9208703
 19  C   C10        -0.1732717    -1.2781974    -0.7575398
 20  H   H8          0.5383231    -2.0645695    -0.5233232
 21  C   C11        -0.5062844    -1.0987494    -2.0513345
 22  C   C12         0.0974987    -1.9667538    -3.1024499
 23  O   O1         -0.1662135    -1.8665359    -4.2864012
 24  O   O2          0.9733092    -2.8843421    -2.6229824
 25  C   C13         1.5644962    -3.7388047    -3.6115307
 26  H   H7          2.2118431    -4.4205317    -3.0585095
 27  H   H11         2.1468352    -3.1535082    -4.3286787
 28  H   H12         0.7938764    -4.2943522    -4.1526963
 29  C   C14        -1.4727345    -0.0764040    -2.5904011
 30  H   H10        -0.9791214     0.5663472    -3.3277598
 31  H   H13        -1.8904669     0.5564653    -1.8044602
 32  H   H14        -2.2994382    -0.5663625    -3.1170062
```

Me_CO2Et_RHS_TS2 (TS2i)

```
Spartan'10: G = -891.751323, iv = i100, S^2 = 0.7421
Gaussian'09: B3LYP/6-31G*, G = -891.756292, iv = i92, S^2 = 0.75
Gaussian'09: M05-2X/6-31G*, G = -891.68717, iv = i70, S^2 = 0.91

Cartesian Coordinates (Angstroms)
       Atom            X              Y              Z
    ---------    -------------- -------------- --------------

  1 C   C          -0.7492316     2.8416276    -0.6069933
  2 C   C2         -1.8256500     2.0339074    -0.4681444
  3 C   C3         -1.8311064     0.7379227     0.1677036
  4 C   C4          0.6373249     2.3487772    -0.3422518
  5 C   C5          0.8153452     0.9098674    -0.7192309
  6 H   H          -0.8360057     3.8517814    -0.9954873
  7 H   H7         -2.7673212     2.3486960    -0.9174200
  8 H   H12         0.2552825     0.6281755    -1.6035435
  9 F   F1          1.5256631     3.1226515    -1.0794369
 10 F   F2          1.0038965     2.6003383     0.9844375
 11 C   C1          1.8685020     0.0389292    -0.3180248
 12 C   C6          3.9090872    -1.7988735     0.3628609
 13 C   C7          2.0633196    -1.1621470    -1.0576450
 14 C   C8          2.7324120     0.2773956     0.7875127
 15 C   C9          3.7319599    -0.6297908     1.1116369
 16 C   C10         3.0667499    -2.0588718    -0.7258170
 17 H   H2          1.4142271    -1.3625323    -1.9066413
 18 H   H6          2.6102043     1.1790719     1.3722462
 19 H   H5          4.3820658    -0.4266731     1.9585224
 20 H   H3          3.2014201    -2.9617152    -1.3153402
 21 H   H4          4.6952357    -2.5015952     0.6247043
 22 C   C11        -2.7852724    -0.2244240    -0.4164488
 23 O   O1         -3.3895750    -0.0539514    -1.4651962
 24 O   O2         -2.9290712    -1.3403758     0.3432352
 25 C   C12        -3.8551082    -2.3092594    -0.1659952
 26 H   H1         -4.8430391    -1.8615727    -0.3058310
 27 H   H9         -3.8935191    -3.1006354     0.5838020
 28 H   H10        -3.5102835    -2.7061803    -1.1254549
 29 C   C13        -1.2696131     0.4568753     1.5383462
 30 H   H8         -0.6997947    -0.4782820     1.5628785
 31 H   H11        -2.0971278     0.3325175     2.2523740
 32 H   H13        -0.6309769     1.2683454     1.8846422
```

Other Synthesised VCP Precursors

Me Furan SM Trans (S9a)

```
G = -697.705753
iv = none

 Cartesian Coordinates (Angstroms)
      Atom            X             Y             Z
   ---------    ------------- ------------- -------------

   1 C   C7          0.1406689    -0.9956178     0.5964871
   2 C   C8          1.3872171    -1.1047379     1.3823601
   3 C   C9          0.4327958    -0.0392131     1.8146329
   4 H   H2         -0.5882604    -1.7749922     0.8259152
   5 H   H9          0.7063655     0.9810075     1.5644678
   6 F   F1          2.5620693    -0.7294608     0.8469569
   7 F   F2          1.5578818    -2.1889554     2.1726557
   8 C   C10        -0.3889264    -0.2021742     3.0432596
   9 H   H12        -0.6630748    -1.2485563     3.2963319
  10 O   O1         -0.7568556     0.7285319     3.7269647
  11 C   C1          0.1434540    -0.4465200    -0.7726300
  12 O   O2          0.9128662    -1.1269062    -1.6855271
  13 C   C3          0.7601324    -0.4932891    -2.8790145
  14 C   C4         -0.0823992     0.5655587    -2.7531779
  15 C   C5         -0.4971161     0.6019962    -1.3757939
  16 H   H6          1.3135119    -0.9125578    -3.7057550
  17 H   H8         -0.3834437     1.2479830    -3.5367193
  18 C   C2         -1.4470105     1.5859241    -0.7584351
  19 H   H1         -1.0728967     2.6131767    -0.8500036
  20 H   H3         -1.6130408     1.3840237     0.3032771
  21 H   H4         -2.4239387     1.5547792    -1.2562526
```

Me Furan SM cis (S9b)

```
G = -697.706140
iv = none

   Cartesian Coordinates (Angstroms)
      Atom            X             Y             Z
   ---------    ------------- ------------- -------------

   1 C   C7          0.7390908     0.3844384    -1.0657176
   2 C   C8          1.6688781    -0.7588474    -0.9599335
   3 C   C9          2.1938189     0.5450926    -0.4611973
   4 H   H9          2.9086128     1.0603466    -1.0954608
   5 F   F1          2.1952401    -1.2833724    -2.0859645
   6 F   F2          1.4154475    -1.7446922    -0.0696108
   7 C   C10         2.3730149     0.7819041     0.9998585
   8 H   H12         1.6535859     0.2669332     1.6659712
   9 O   O1          3.2535027     1.4874759     1.4429023
  10 C   C1         -0.4487462     0.5029065    -0.1991059
  11 O   O2         -0.6162882     1.7157256     0.4288353
  12 C   C3         -1.7758070     1.6365772     1.1365563
  13 C   C4         -2.3502310     0.4161752     0.9749909
  14 C   C5         -1.4901531    -0.3344543     0.0984126
```

```
  15  H   H6            -2.0449353     2.5206780     1.6946725
  16  H   H8            -3.2754549     0.0746172     1.4194284
  17  C   C2            -1.7172756    -1.7403138    -0.3741531
  18  H   H1            -1.6172550    -2.4576887     0.4494956
  19  H   H3            -1.0063412    -2.0322880    -1.1511297
  20  H   H4            -2.7278852    -1.8545588    -0.7834508
  21  H   H5             0.6691809     0.8133453    -2.0653994
```

Me Furan [3,3]-TS (TS3)

```
G = -697.672991
iv = i309
   Cartesian Coordinates (Angstroms)
       Atom              X             Y             Z
    ---------     ------------- ------------- -------------

   1  C   C1            -0.9655277    -0.1281625     0.5395914
   2  C   C2             0.3919177     0.1289556     0.9945501
   3  C   C5             0.2274272     0.8396342    -1.9004649
   4  H   H7             0.1609263     1.7533491    -2.5101504
   5  O   O1            -0.8684853     0.4606492    -1.3383232
   6  C   C3             1.4773684     0.2600752    -1.8088386
   7  C   C4             1.6018603    -0.1920409     0.4785488
   8  C   C11            1.8373657    -0.8215650    -0.8598650
   9  H   H2             2.3096381     0.7303558    -2.3220689
  10  H   H10            2.4830843     0.2571453     0.9257838
  11  F   F1             1.1678797    -2.0112550    -1.0464222
  12  F   F2             3.1739584    -1.1193241    -0.9750310
  13  O   O3             0.3647330     1.1247164     1.9796098
  14  C   C8            -0.9295091     1.5043356     2.1026746
  15  H   H12           -1.1124427     2.2748555     2.8394582
  16  C   C7            -1.7628534     0.8250046     1.2825503
  17  H   H11           -2.8371378     0.9257828     1.2236656
  18  C   C9            -1.5565897    -1.4572627     0.1605722
  19  H   H3            -0.8663429    -2.0669327    -0.4148454
  20  H   H4            -2.4636009    -1.2919639    -0.4275625
  21  H   H9            -1.8336694    -1.9963523     1.0765677
```

Me Furan VCPR Ts (use NODISS keyword) (TS4)

```
G = -697.665879
iv = i234
S^2 = 0.29

Cartesian Coordinates (Angstroms)
       Atom              X             Y             Z
    ---------     ------------- ------------- -------------

   1  C   C             -1.4362337     2.2538247    -1.3566871
   2  C   C2            -2.5135153     1.5219083    -1.8423498
   3  C   C4            -0.5217870     1.5210494    -0.4698253
   4  C   C5            -0.3577867     0.0914781    -0.9001564
   5  H   H             -1.2556072     3.2975305    -1.5802847
   6  H   H12           -0.6239173    -0.1605270    -1.9144912
   7  F   F1             0.7415242     2.1148315    -0.4410394
   8  F   F2            -0.9294237     1.5682960     0.8718760
```

```
  9  H   H14          -3.1555660     1.9765040    -2.6177622
 10  O   O1           -2.7358741     0.3260619    -1.4868078
 11  C   C1            0.3479232    -0.8708234    -0.1989309
 12  O   O2            0.4898193    -2.0924328    -0.8613604
 13  C   C6            1.1870195    -2.9027068    -0.0585477
 14  C   C7            1.5357917    -2.2711910     1.1116651
 15  C   C8            1.0070982    -0.9638114     1.0508234
 16  H   H5            1.3664614    -3.9011673    -0.4315501
 17  H   H7            2.1094802    -2.6960812     1.9238066
 18  C   C3            1.1627819     0.0895214     2.0983756
 19  H   H2            1.9011221    -0.2221925     2.8422719
 20  H   H3            0.2090776     0.2796994     2.6039992
 21  H   H4            1.4716117     1.0402281     1.6569753
```

Non-Fluoro-SM trans (47a)

```
Spartan'10: G = -654.027526, iv = none
Gaussian'09: B3LYP/6-31G*, G = -654.032624 , iv = none
Gaussian'09: M05-2X/6-31G*, G = -653.968582, iv = none

   Cartesian Coordinates (Angstroms)
       Atom              X             Y             Z
    ---------     ------------- ------------- -------------

  1  H   H1            2.4558148     1.9664977     1.3490937
  2  C   C1            1.5137206     2.2423943     1.8174568
  3  C   C4           -0.8907964     2.9604966     3.0162407
  4  C   C2            0.4921939     1.2865397     1.9171313
  5  C   C6            1.3395373     3.5362157     2.3087436
  6  C   C5            0.1349941     3.9019932     2.9103722
  7  C   C3           -0.7135294     1.6673011     2.5267193
  8  H   H6            2.1472528     4.2581074     2.2200627
  9  H   H5           -0.0036711     4.9091323     3.2937697
 10  H   H3           -1.5254456     0.9506187     2.6227930
 11  H   H4           -1.8335371     3.2322952     3.4841012
 12  C   C7            0.7180306    -0.0812305     1.3680533
 13  C   C8            0.0127924    -1.3021650     1.8856731
 14  C   C9           -0.3721006    -0.7724019     0.5197991
 15  H   H2            1.7317359    -0.2449302     1.0093980
 16  H   H9           -1.3118509    -0.2275742     0.4625525
 17  C   C10           0.0192075    -1.4923450    -0.6960636
 18  H   H8            0.9411453    -2.0733622    -0.6593643
 19  C   C11          -0.6623738    -1.4863038    -1.8532113
 20  H   H10          -1.5889776    -0.9328562    -1.9759883
 21  C   C12          -0.1648266    -2.2407264    -3.0192128
 22  O   O1            0.8483886    -2.9142415    -3.0597069
 23  O   O2           -0.9984269    -2.0894137    -4.0801680
 24  C   C13          -0.6046241    -2.7846876    -5.2704153
 25  H   H7           -1.3671695    -2.5496443    -6.0140814
 26  H   H11          -0.5623012    -3.8628738    -5.0915100
 27  H   H12           0.3786244    -2.4463030    -5.6097971
 28  H   H13          -0.7063055    -1.1776952     2.6905673
 29  H   H14           0.5724986    -2.2328375     1.9269918
```

Non-Fluoro-SM cis (47b)

```
Spartan'10: G = -654.024790, iv = none
Gaussian'09: B3LYP/6-31G*, -654.030414, iv = none
Gaussian'09: M06-2X/6-31G*, -653.744967, iv = none

 Cartesian Coordinates (Angstroms)
       Atom             X              Y              Z
    ---------    -------------- -------------- --------------

  1  H   H1          -0.2542662     2.2915662    -0.5021848
  2  C   C1           0.7344812     2.1645972    -0.0684421
  3  C   C4           3.2703973     1.8162921     1.0317255
  4  C   C2           0.8557636     1.5844524     1.2029998
  5  C   C6           1.8639337     2.5634010    -0.7812665
  6  C   C5           3.1369438     2.3904917    -0.2325234
  7  C   C3           2.1367416     1.4171786     1.7429408
  8  H   H6           1.7515622     3.0044603    -1.7682719
  9  H   H5           4.0179587     2.6984646    -0.7892128
 10  H   H3           2.2450075     0.9756370     2.7302087
 11  H   H4           4.2566489     1.6773723     1.4669251
 12  C   C7          -0.3721506     1.2032446     1.9764382
 13  C   C8          -0.4452043    -0.0400410     2.8065827
 14  C   C9          -1.2889387     0.0486890     1.5393170
 15  H   H9          -2.3527386     0.2234564     1.6844538
 16  C   C10         -0.9508286    -0.7867763     0.3807042
 17  H   H8           0.1013634    -1.0033740     0.2018760
 18  C   C11         -1.8446828    -1.3043687    -0.4777387
 19  H   H10         -2.9127551    -1.1332973    -0.3753246
 20  C   C12         -1.4011137    -2.1362181    -1.6124187
 21  O   O1          -0.2530060    -2.4438418    -1.8737535
 22  O   O2          -2.4635381    -2.5336285    -2.3607591
 23  C   C13         -2.1367419    -3.3489422    -3.4935561
 24  H   H7          -1.6065193    -4.2521592    -3.1792809
 25  H   H11         -1.5049799    -2.7981740    -4.1966114
 26  H   H12         -3.0903901    -3.6047972    -3.9573000
 27  H   H13         -0.9306797     2.0551654     2.3645298
 28  H   H2          -0.9651543    -0.0097442     3.7598570
 29  H   H14          0.4028861    -0.7191062     2.7800860
```

non-fluoro-VCPR TS trans (TS5a)

```
Spartan'10: -653.972598, iv = i236, S^2 = 0.7146
Gaussian'09: B3LYP/6-31G*, G = -653.976701, iv = i246, S^2 = 0.73
Gaussian'09: M05-2X/6-31+G*, G = -653.90781, iv = i262, S^2 = 0.84

Cartesian Coordinates (Angstroms)
       Atom             X              Y              Z
    ---------    -------------- -------------- --------------

  1  C   C           -0.8222470     3.0250060    -0.4539541
  2  C   C2          -1.9052459     2.2106773    -0.3804376
  3  C   C3          -1.7973923     0.8903636     0.1578220
  4  C   C4           0.5337323     2.4619301    -0.0897511
  5  C   C5           0.6885928     1.0683410    -0.6550086
  6  H   H           -0.9020935     4.0478346    -0.8109030
```

```
  7  H   H7          -2.8638439     2.5116103    -0.7984342
  8  H   H8          -1.1422527     0.6749249     0.9926968
  9  H   H12          0.2525740     0.9082878    -1.6370826
 10  C   C1           1.6275974     0.0969890    -0.1977950
 11  C   C6           3.4438317    -1.9011993     0.6552119
 12  C   C7           1.7957586    -1.1120289    -0.9276113
 13  C   C8           2.4099294     0.2652341     0.9762530
 14  C   C9           3.2978055    -0.7199932     1.3906673
 15  C   C10          2.6850935    -2.0892635    -0.5080156
 16  H   H2           1.2071244    -1.2629430    -1.8294584
 17  H   H6           2.3250788     1.1801860     1.5546033
 18  H   H5           3.8876218    -0.5662147     2.2907224
 19  H   H3           2.7948555    -3.0029020    -1.0863701
 20  H   H4           4.1438640    -2.6655275     0.9811905
 21  C   C11         -2.7745767    -0.1316268    -0.2028367
 22  O   O1          -3.6664012    -0.0019144    -1.0287858
 23  O   O2          -2.5783681    -1.2815095     0.5006099
 24  C   C12         -3.4934341    -2.3395480     0.1952483
 25  H   H1          -4.5241878    -2.0317324     0.3947253
 26  H   H9          -3.2103695    -3.1704373     0.8431085
 27  H   H10         -3.4145251    -2.6308234    -0.8566405
 28  H   H11          1.3311852     3.1187271    -0.4745862
 29  H   H13          0.6702929     2.4475518     1.0048117
```

non-fluoro-VCPR TS cis (TS5b)

```
Spartan'10:
G = -654.971681,
iv = i237,
S^2 = 0.7337

Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1  C   C            0.2453010     2.5048609     1.2953703
  2  C   C2          -0.8039811     1.7101068     1.6249380
  3  C   C3          -0.6682026     0.3122649     1.8687047
  4  C   C4           1.6121357     1.9196713     0.9916982
  5  C   C5           1.5785997     0.5091379     0.4474431
  6  H   H            0.1262525     3.5838445     1.2259920
  7  H   H7          -1.8111301     2.1230173     1.6485146
  8  H   H8           0.1915083    -0.0898749     2.3880552
  9  C   C11         -1.8097139    -0.5797378     1.6968693
 10  O   O1          -2.9124260    -0.2548200     1.2832605
 11  O   O2          -1.5012132    -1.8571654     2.0611001
 12  C   C12         -2.5659716    -2.8020317     1.9057740
 13  H   H1          -3.4406680    -2.5021625     2.4904006
 14  H   H9          -2.1715884    -3.7530990     2.2671430
 15  H   H10         -2.8605324    -2.8857106     0.8549572
 16  H   H11          2.1336028     2.5856755     0.2877626
 17  H   H13          2.2259734     1.9238677     1.9062310
 18  H   H16          2.0380922    -0.2751250     1.0425867
 19  C   C1           1.2934012     0.1999010    -0.9135336
 20  C   C6           0.6974007    -0.4795327    -3.5935287
 21  C   C7           0.8119491     1.1739275    -1.8285683
```

```
 22  C   C8             1.4690232     -1.1260625     -1.3953192
 23  C   C9             1.1765396     -1.4563796     -2.7094170
 24  C   C10            0.5172298      0.8326852     -3.1429608
 25  H   H2             0.6605875      2.1940342     -1.4909004
 26  H   H6             1.8339548     -1.8874860     -0.7099350
 27  H   H5             1.3199579     -2.4769201     -3.0548471
 28  H   H3             0.1450793      1.5932011     -3.8244866
 29  H   H4             0.4688384     -0.7400881     -4.6233044
```

non fluoro VCP- [3,3] TS (S-TS13)

```
Spartan'10 G = -653.971614, iv = i403
Gaussian'09: B3LYP/6-31G*, -653.973922, iv = i403
Gaussian'09: M06-2X/6-31G*, -653.686835, iv = i400
```

```
 Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
   ---------    ------------- ------------- -------------

  1  C   C1            -0.0894029     -0.6486226      0.8616396
  2  H   H3            -0.2343972     -1.7199948      0.7606184
  3  C   C2             1.2368519     -0.2540877      1.3416020
  4  C   C5             1.2386251     -0.1502183     -1.6576682
  5  H   H7             1.3283122      0.7889579     -2.1995328
  6  C   C6            -0.0737839     -0.5112904     -1.2033351
  7  H   H6            -0.3526574     -1.5564982     -1.2871950
  8  C   C7             1.3398635      0.9153519      2.1770254
  9  H   H4             2.3328995      1.2425020      2.4775117
 10  C   C8             0.2341933      1.6054176      2.5757404
 11  H   H9             0.3352882      2.4889856      3.1999974
 12  C   C9            -1.0757048      1.1624901      2.1900805
 13  H   H11           -1.9457203      1.6985261      2.5607054
 14  C   C10           -1.2329787      0.0613238      1.4049207
 15  H   H12           -2.2246786     -0.2981886      1.1479309
 16  C   C3             2.3703942     -0.8199918     -1.2934753
 17  C   C4             2.3739013     -0.8979018      0.8956232
 18  C   C11            2.3917636     -1.8913224     -0.2310380
 19  H   H2             3.3360345     -0.4478167     -1.6272447
 20  H   H10            3.3402224     -0.5319360      1.2370583
 21  C   C12           -1.1691115      0.4082697     -1.6053860
 22  O   O1            -1.0412943      1.5755153     -1.9183351
 23  O   O2            -2.3775113     -0.2147373     -1.5535430
 24  C   C13           -3.5017889      0.6153777     -1.8776802
 25  H   H1            -3.4106571      1.0103859     -2.8931257
 26  H   H5            -3.5750941      1.4536613     -1.1791992
 27  H   H8            -4.3774856     -0.0300456     -1.7958804
 28  H   H13            3.3004002     -2.4970704     -0.2515753
 29  H   H14            1.5235165     -2.5570425     -0.2562403
```

piperonyl cis SM (48)

```
Spartan'10: G = -1041.02078, iv = none
Gaussian'09: B3LYP/6-31G* G = -1041.028189, iv = none
Gaussian'09: M06-2X/6-31G* G = -1040.629122, iv = none

   Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C1          3.0423844    -0.2086799     0.8498853
  2 C   C2          1.9712958     0.6511022     1.3910393
  3 C   C3          1.8273286    -0.9333291     1.3301227
  4 H   H6          1.9311472    -1.4268921     2.2931801
  5 C   C10         0.9105989    -1.5575832     0.3680707
  6 H   H11         0.8299722    -1.1099408    -0.6198009
  7 C   C11         0.1704137    -2.6453405     0.6293754
  8 H   H12         0.1962986    -3.1500943     1.5910290
  9 C   C12        -0.7183097    -3.2114163    -0.4070501
 10 O   O1         -0.8667601    -2.7810948    -1.5347917
 11 O   O2         -1.3693752    -4.3033018     0.0663863
 12 C   C13        -2.2558576    -4.9350251    -0.8680243
 13 H   H5         -3.0221314    -4.2329708    -1.2081799
 14 H   H13        -2.7091715    -5.7665514    -0.3271395
 15 H   H14        -1.7017856    -5.2994578    -1.7376918
 16 F   F1          3.3167039    -0.2109170    -0.4764377
 17 F   F2          4.1926516    -0.3416594     1.5506246
 18 C   C4          1.1090415     1.5624446     0.5757094
 19 C   C5          0.8036928     3.1156355    -1.2954926
 20 C   C6         -0.9956292     2.6403948     0.2548302
 21 C   C7         -0.4946950     3.2982780    -0.8682452
 22 C   C9          1.6034720     2.2303373    -0.5494306
 23 H   H1          1.1902327     3.6322954    -2.1670758
 24 H   H4          2.6255347     2.0574505    -0.8640583
 25 C   C8         -0.2261551     1.7713216     0.9962538
 26 H   H2          2.1680653     0.9832609     2.4097456
 27 H   H3         -0.6311615     1.2628101     1.8648840
 28 O   O3         -2.2980178     3.0223465     0.4704360
 29 O   O4         -1.4650229     4.1142322    -1.3960229
 30 C   C14        -2.6615555     3.8075867    -0.6710824
 31 H   H7         -3.1330517     4.7362777    -0.3381130
 32 H   H10        -3.3401538     3.2284802    -1.3129356
```

piperonyl [3,3]-TS - actual product (TS6a)

```
Spartan'10: G = -1040.98573, iv = i345
Gaussian'09: B3LYP/6-31G* G = -1040.990095, iv = i346
Gaussian'09: M06-2X/6-31G* G = -1040.586048, iv = i403

Cartesian Coordinates (Angstroms)
       Atom              X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C1            0.0299913    -0.9765097     0.5447855
  2 H   H3           -0.0919916    -2.0411956     0.4137142
  3 C   C2            1.3614143    -0.5751782     1.0108108
  4 C   C5            1.3636871    -0.5111860    -2.0543037
  5 H   H7            1.4537369     0.4091006    -2.6287065
  6 C   C6            0.0517463    -0.8483121    -1.5978248
  7 H   H6           -0.2395078    -1.8891689    -1.6318160
  8 C   C7            1.4922535     0.5993397     1.8477715
  9 H   H4            2.4728296     0.9436762     2.1581912
 10 C   C8            0.3628135     1.2572276     2.2002409
 11 C   C9           -0.9392342     0.8221317     1.8038003
 12 C   C10          -1.1381880    -0.2826499     1.0474906
 13 H   H12          -2.1309181    -0.6337514     0.7940555
 14 C   C3            2.5066100    -1.1683158    -1.7020673
 15 C   C4            2.5020439    -1.2262617     0.5869547
 16 C   C11           2.5903161    -2.1494753    -0.5812988
 17 H   H2            3.4711995    -0.8224478    -2.0616157
 18 H   H10           3.4706018    -0.8816310     0.9385686
 19 C   C12          -1.0242132     0.1017440    -1.9670565
 20 O   O1           -0.8665404     1.2683970    -2.2727871
 21 O   O2           -2.2473210    -0.4856953    -1.8957493
 22 C   C13          -3.3538526     0.3761447    -2.2020706
 23 H   H1           -3.2688036     0.7645485    -3.2204452
 24 H   H5           -3.3906132     1.2179722    -1.5049668
 25 H   H8           -4.2456265    -0.2439745    -2.1027276
 26 F   F1            1.6195434    -3.1315895    -0.6096091
 27 F   F2            3.8003624    -2.7946598    -0.5875743
 28 O   O3           -1.8708063     1.6633345     2.3447234
 29 O   O4            0.2406542     2.3885294     2.9577602
 30 C   C14          -1.1582213     2.6450504     3.1015459
 31 H   H9           -1.3866334     3.6423907     2.7120647
 32 H   H13          -1.4373328     2.5624154     4.1581412
```

piperonyl [3,3] -TS - alternative regioisomer (TS6b)

```
Spartan'10: G = -1040.97722
iv = i380

Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C1           0.2385885    -0.7298865     0.7224743
  2 H   H3           0.0276832    -1.7842292     0.6037600
  3 C   C2           1.5951995    -0.4027051     1.2177965
  4 C   C5           1.4721330    -0.1108453    -1.8181119
  5 H   H7           1.5045379     0.8562664    -2.3158420
  6 C   C6           0.1974816    -0.5696510    -1.3534490
  7 H   H6           0.0086455    -1.6282209    -1.4642294
  8 C   C7           1.7716717     0.6741291     2.1666199
  9 H   H4           2.7859233     0.9105927     2.4746075
 10 C   C8           0.7251018     1.4116844     2.6504553
 11 H   H9           0.8673343     2.2246265     3.3541622
 12 C   C9          -0.5691163     1.0800378     2.1831251
 13 C   C10         -0.7933501     0.0582918     1.3159113
 14 C   C3           2.6474765    -0.7549716    -1.5599684
 15 C   C4           2.7220531    -1.0155180     0.7105452
 16 C   C11          2.7866601    -1.8315684    -0.5349616
 17 H   H2           3.5910266    -0.3508489    -1.9139038
 18 H   H10          3.6972904    -0.7160370     1.0845140
 19 C   C12         -0.9732522     0.2802463    -1.6932325
 20 O   O1          -0.9832406     1.4969908    -1.6931776
 21 O   O2          -2.0514151    -0.4793664    -1.9984359
 22 C   C13         -3.2456076     0.2469918    -2.3140927
 23 H   H1          -3.0876808     0.8904759    -3.1847093
 24 H   H5          -3.5544741     0.8660227    -1.4670107
 25 H   H8          -4.0017662    -0.5095511    -2.5281664
 26 F   F1           1.8295525    -2.8240916    -0.6069984
 27 F   F2           4.0040881    -2.4515217    -0.6373763
 28 O   O3          -2.1500850    -0.1133524     1.1274261
 29 O   O4          -1.7631087     1.6229029     2.6040112
 30 C   C14         -2.7287256     1.0660126     1.7046521
 31 H   H12         -2.9406554     1.7919193     0.9059492
 32 H   H14         -3.6299698     0.7951741     2.2576566
```

Isodesmic Compounds (Energies can be found in Table S16-S19)

```
Ethane

Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

   1 C   C1           0.0000001     0.0000000     0.7637754
   2 H   H2           1.0121266    -0.0000001     1.1565569
   3 H   H3          -0.5060633    -0.8765272     1.1565570
   4 H   H4          -0.5060631     0.8765274     1.1565570
   5 C   C2          -0.0000001     0.0000000    -0.7637754
   6 H   H1           0.5060631    -0.8765274    -1.1565570
   7 H   H5           0.5060633     0.8765272    -1.1565570
   8 H   H6          -1.0121266     0.0000001    -1.1565569
```

```
Ethene

Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

   1 C   C1           0.0000000     0.0000000     0.6585346
   2 H   H2           0.0000000     0.9144843     1.2256492
   3 H   H3           0.0000000    -0.9144843     1.2256492
   4 C   C2           0.0000000     0.0000000    -0.6585346
   5 H   H1           0.0000000    -0.9144843    -1.2256492
   6 H   H4           0.0000000     0.9144843    -1.2256492
```

```
Benzene

Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

   1 H   H1           0.0000000     0.0000000    -2.4836029
   2 C   C1           0.0000000    -0.0000001    -1.3965320
   3 C   C4           0.0000000    -0.0000001     1.3965320
   4 C   C2           0.0000000    -1.2095560    -0.6982739
   5 C   C6           0.0000000     1.2095560    -0.6982740
   6 C   C5           0.0000000     1.2095560     0.6982740
   7 C   C3           0.0000000    -1.2095560     0.6982739
   8 H   H2           0.0000000    -2.1508686    -1.2419479
   9 H   H6           0.0000000     2.1508686    -1.2419480
  10 H   H5           0.0000000     2.1508686     1.2419480
  11 H   H3           0.0000000    -2.1508686     1.2419480
  12 H   H4           0.0000000    -0.0000001     2.4836029
```

Benzene - reduced

```
Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

  1 H  H1             1.0881541    -0.5985062    -2.1761678
  2 C  C1             0.6434959    -0.2310204    -1.2671432
  3 C  C3             0.4539005     1.3985299     0.5292146
  4 C  C5            -0.6486740    -0.7877853     0.8245360
  5 C  C4            -0.3680277     0.6386557     1.2368443
  6 C  C6            -0.5413287    -0.9731704    -0.6936467
  7 C  C2             1.0859599     0.8801419    -0.6985849
  8 H  H10            0.0680039    -1.4397351     1.3250990
  9 H  H7            -0.8121612     1.0069181     2.1458111
 10 H  H11           -1.4473510    -0.6014106    -1.1733836
 11 H  H3             1.9051309     1.4317046    -1.1264837
 12 H  H5             0.6856329     2.4020851     0.8415236
 13 H  H9            -1.6321903    -1.0961221     1.1650105
 14 H  H12           -0.4805450    -2.0302851    -0.9326293
```

Furan

```
Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

  1 O  O1             0.0506086    -0.4485978    -1.2845127
  2 C  C2             1.0978809    -0.0928593    -0.5216394
  3 C  C3             0.6907284     0.3010616     0.6916180
  4 C  C4            -0.7447007     0.1773514     0.6782675
  5 C  C5            -1.0559874    -0.2784870    -0.5416720
  6 H  H3             2.0606797    -0.1735618    -0.9770217
  7 H  H5             1.3099502     0.6364801     1.4975195
  8 H  H7            -1.4269491     0.4006048     1.4720643
  9 H  H9            -1.9822107    -0.5219919    -1.0146236
```

Furan - reduced

```
Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

  1 O  O1             0.2823937    -0.4458870    -1.3684354
  2 C  C2             1.2687481     0.0829888    -0.6101449
  3 C  C3             0.9192139     0.4245706     0.6106088
  4 C  C4            -0.5396163     0.0842859     0.8071793
  5 C  C5            -0.9272401    -0.3714167    -0.6179478
  6 H  H3             2.2210539     0.1535510    -1.0962173
  7 H  H5             1.5638401     0.8469238     1.3544034
  8 H  H7            -1.1345112     0.9320998     1.1315137
  9 H  H8            -0.6786505    -0.7048947     1.5411980
 10 H  H9            -1.5783534     0.3422369    -1.1071110
 11 H  H10           -1.3968781    -1.3444585    -0.6450469
```

thiophene

```
Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

   1 S   S1           0.1167444    -0.7253040    -1.5997346
   2 C   C2           1.2671448    -0.1588718    -0.4449549
   3 C   C3           0.6707684     0.3240820     0.6597454
   4 C   C4          -0.7621015     0.2433484     0.5917821
   5 C   C5          -1.1936835    -0.2975247    -0.5616759
   6 H   H3           2.3162648    -0.2167911    -0.6518827
   7 H   H5           1.2070897     0.7252313     1.4987648
   8 H   H7          -1.4167593     0.5773933     1.3743115
   9 H   H9          -2.2054677    -0.4715633    -0.8663556
```

thiophene -reduced

```
Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

   1 S   S1           0.2381818    -0.1586916    -1.8476764
   2 C   C2           1.4343914     0.1554841    -0.5805729
   3 C   C3           0.9357534     0.2978303     0.6304529
   4 C   C4          -0.5698240     0.2147878     0.7144893
   5 C   C5          -1.0420275    -0.4756587    -0.5772318
   6 H   H3           2.4697948     0.2300008    -0.8513928
   7 H   H5           1.5396600     0.5097448     1.4940703
   8 H   H7          -0.9878734     1.2166165     0.7920098
   9 H   H8          -0.9060149    -0.3384097     1.5853369
  10 H   H9          -1.9954398    -0.1062750    -0.9266186
  11 H   H10         -1.1166018    -1.5454293    -0.4328669
```

piperonyl

```
Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

   1 H   H1          -2.4890973     0.0000000     0.7605630
   2 C   C1          -1.4155844     0.0000000     0.7735268
   3 C   C4           1.4155844     0.0000000     0.7735268
   4 C   C2          -0.6905232     0.0000000    -0.3841316
   5 C   C6          -0.6899151     0.0000000     1.9718652
   6 C   C5           0.6899151     0.0000000     1.9718652
   7 C   C3           0.6905232     0.0000000    -0.3841316
   8 H   H6          -1.2223019     0.0000000     2.9054279
   9 H   H5           1.2223019     0.0000000     2.9054279
  10 H   H4           2.4890973     0.0000000     0.7605630
  11 O   O1          -1.1369414     0.0000000    -1.6665113
  12 O   O2           1.1369414     0.0000000    -1.6665113
  13 C   C7           0.0000000     0.0000000    -2.4974534
  14 H   H3           0.0000000    -0.8891458    -3.1120134
  15 H   H8           0.0000000     0.8891458    -3.1120134
```

piperonyl reduced

```
Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

   1 H   H1          -2.5329374     0.0000000     0.4013201
   2 C   C1          -1.4590576     0.0000000     0.4432548
   3 C   C3           0.7815602     0.0000000     1.7990097
   4 C   C5           0.7299606     0.0000000    -0.6478620
   5 C   C4           1.4590576     0.0000000     0.4432548
   6 C   C6          -0.7299606     0.0000000    -0.6478620
   7 C   C2          -0.7815602     0.0000000     1.7990097
   8 H   H6           1.1341868     0.8637486     2.3556278
   9 H   H7           2.5329374     0.0000000     0.4013201
  10 H   H3          -1.1341868    -0.8637486     2.3556278
  11 H   H5           1.1341868    -0.8637486     2.3556278
  12 H   H4          -1.1341868     0.8637486     2.3556278
  13 O   O1           1.1332016     0.0000000    -1.9415502
  14 O   O2          -1.1332016     0.0000000    -1.9415502
  15 C   C7           0.0000000     0.0000000    -2.7666606
  16 H   H12          0.0000000     0.8882923    -3.3820978
  17 H   H13          0.0000000    -0.8882923    -3.3820978
```

pyrrole

```
Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

   1 C   C1          -0.4449852     1.0284683     0.3679170
   2 H   H2          -0.8752591     1.9155106     0.8102523
   3 C   C2           0.0893702     0.8040222    -0.8825847
   4 H   H4           0.1681822     1.5338806    -1.6771450
   5 N   N1          -0.3576710    -0.1471977     1.0761889
   6 H   H3          -0.6730776    -0.2771132     2.0246473
   7 C   C3           0.2239280    -1.1194084     0.2961859
   8 H   H6           0.3804864    -2.1188340     0.6759902
   9 C   C4           0.5125838    -0.5560907    -0.9280150
  10 H   H5           0.9764424    -1.0632377    -1.7634369
```

pyridine

```
Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

   1 H   H1           0.0000000    -0.0000007    -2.2824770
   2 C   C1           0.0000000    -0.0000003    -1.1955420
   3 N   N1           0.0000000     0.0000004     1.6106501
   4 C   C2           0.0000000    -1.1985966    -0.4833139
   5 C   C6           0.0000000     1.1985963    -0.4833146
   6 C   C5           0.0000000     1.1422376     0.9115526
   7 C   C3           0.0000000    -1.1422371     0.9115532
   8 H   H2           0.0000000    -2.1577589    -0.9929579
   9 H   H6           0.0000000     2.1577583    -0.9929590
```

```
 10 H  H5            0.0000000     2.0597701     1.4984036
 11 H  H3            0.0000000    -2.0597693     1.4984048
```

oxazole

```
Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

  1 N  N1           -0.2423485    -1.0732650    -0.6256410
  2 C  C2            0.9713989    -0.7097296    -0.3615412
  3 C  C5           -1.0233183    -0.0579885    -0.0804509
  4 H  H4            1.8940387    -1.2145675    -0.6086099
  5 H  H10          -2.1019922    -0.0783051    -0.1413901
  6 O  O1            1.0812771     0.4623778     0.3144037
  7 C  C1           -0.2161812     0.8710022     0.4885116
  8 H  H2           -0.3628746     1.8004756     1.0147178
```

isoxazole

```
Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

  1 N  N1           -1.3579729    -0.3166155     0.6680020
  2 O  O1           -0.9688970    -1.0478468    -0.4596005
  3 C  C1           -0.3749555     0.5260090     0.8839956
  4 H  H3           -0.4490582     1.2097088     1.7205650
  5 C  C2            0.2337272    -0.6094549    -0.8719390
  6 H  H4            0.6405663    -1.1029212    -1.7432137
  7 C  C3            0.6770494     0.3923385    -0.0660168
  8 H  H5            1.5995407     0.9487822    -0.1317926
```

Remaining Species for Computational Prediction

Ph cis SM (1b)

```
Spartan'10: G = -852.505870, iv = none
Gaussian'09: B3LYP/6-31G*, G = -852.511692, iv = none
Gaussian'09: M06-2X/6-31G*, G = -852.17197, iv = none

                          Cartesian Coordinates (Angstroms)
      Atom                 X               Y               Z
   ---------       ------------- ------------- -------------

   1  H   H1         -0.2566781      2.1773309     -0.5418559
   2  C   C1          0.7326203      2.1016848     -0.0979338
   3  C   C4          3.2705797      1.8884782      1.0330952
   4  C   C2          0.8683703      1.5838354      1.1975351
   5  C   C6          1.8530942      2.5100396     -0.8195723
   6  C   C5          3.1260344      2.4054202     -0.2547015
   7  C   C3          2.1488322      1.4797692      1.7561690
   8  H   H6          1.7326412      2.9064500     -1.8241942
   9  H   H5          3.9999792      2.7221862     -0.8173662
  10  H   H3          2.2673570      1.0735024      2.7558601
  11  H   H4          4.2579709      1.8001634      1.4782035
  12  C   C7         -0.3508853      1.2086657      1.9816477
  13  C   C8         -0.4570777     -0.0224345      2.7885630
  14  C   C9         -1.2947057      0.0093460      1.5504614
  15  H   H9         -2.3531250      0.1988810      1.7111959
  16  F   F1         -1.0722914      0.0238570      3.9930383
  17  F   F2          0.5874286     -0.8816675      2.8417710
  18  C   C10        -0.9504897     -0.8346112      0.3975477
  19  H   H8          0.0925116     -1.1108468      0.2613425
  20  C   C11        -1.8431113     -1.2883794     -0.4950921
  21  H   H10        -2.9028398     -1.0588657     -0.4270965
  22  C   C12        -1.4068747     -2.1361501     -1.6249384
  23  O   O1         -0.2668900     -2.4927457     -1.8526699
  24  O   O2         -2.4647872     -2.4769771     -2.4025691
  25  C   C13        -2.1481186     -3.3039233     -3.5313814
  26  H   H7         -1.6796913     -4.2367585     -3.2058806
  27  H   H11        -1.4645918     -2.7848208     -4.2092518
  28  H   H12        -3.0995277     -3.5034504     -4.0257970
  29  H   H13        -0.9257341      2.0420210      2.3838702
```

Ph [3,3] – TS

```
Spartan'10: G = -852.464912, iv = i379
Gaussian'09: B3LYP/6-31G*, G = -852.467339, iv = i380
Gaussian'09: M06-2X/6-31G*, G = -852.124968, iv = i450

Cartesian Coordinates (Angstroms)
      Atom                 X               Y               Z
   ---------       ------------- ------------- -------------

   1  C   C1         -0.1088780     -0.6432231      0.8863613
   2  H   H3         -0.2589437     -1.7075866      0.7739837
```

```
   3 C   C2             1.2220184    -0.2597465     1.3621125
   4 C   C5             1.2048982    -0.1785670    -1.6827749
   5 H   H7             1.2844671     0.7425621    -2.2565575
   6 C   C6            -0.1033175    -0.5238935    -1.2142480
   7 H   H6            -0.3862752    -1.5665343    -1.2643495
   8 C   C7             1.3310470     0.9008674     2.2111675
   9 H   H4             2.3241582     1.2134430     2.5246042
  10 C   C8             0.2299951     1.6063232     2.5951180
  11 H   H9             0.3384265     2.4867706     3.2225007
  12 C   C9            -1.0815962     1.1903990     2.1893254
  13 H   H11           -1.9465638     1.7409931     2.5492119
  14 C   C10           -1.2449905     0.0914736     1.4014086
  15 H   H12           -2.2377005    -0.2546742     1.1316479
  16 C   C3             2.3539553    -0.8303083    -1.3422934
  17 C   C4             2.3677107    -0.9013675     0.9378646
  18 C   C11            2.4527866    -1.8220421    -0.2319275
  19 H   H2             3.3133015    -0.4772245    -1.7088463
  20 H   H10            3.3345269    -0.5601096     1.2979552
  21 C   C12           -1.1878915     0.4137056    -1.6091269
  22 O   O1            -1.0362810     1.5742628    -1.9352174
  23 O   O2            -2.4035180    -0.1866668    -1.5458552
  24 C   C13           -3.5160485     0.6557767    -1.8841186
  25 H   H1            -3.4156713     1.0343754    -2.9050867
  26 H   H5            -3.5773554     1.5046847    -1.1970147
  27 H   H8            -4.4003348     0.0232509    -1.7948402
  28 F   F1             1.4839922    -2.8045753    -0.2568552
  29 F   F2             3.6640819    -2.4623688    -0.2541494
```

furan cis SM (cis-9b)

```
Spartan'10: G = -850.312391, iv = none
Gaussian'09: B3LYP/6-31G*, G = -850.318011, iv = none
Gaussian'09: M06-2X/6-31G*, G = -849.99051, iv = none

Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

   1 C   C1             2.4512641     1.3354068     0.2415934
   2 C   C2             1.3356127     1.7987431     1.0906077
   3 C   C3             1.6498298     0.2431782     0.8642397
   4 H   H6             2.1119688    -0.2326259     1.7254883
   5 C   C10            0.7489355    -0.5847449     0.0548152
   6 H   H11            0.2835022    -0.1279728    -0.8156985
   7 C   C11            0.4611098    -1.8668181     0.3233625
   8 H   H12            0.8845279    -2.3941822     1.1733777
   9 C   C12           -0.4570930    -2.6247006    -0.5533210
  10 O   O1            -1.0187351    -2.1938951    -1.5421198
  11 O   O2            -0.5986966    -3.8979997    -0.1092677
  12 C   C13           -1.4696957    -4.7237084    -0.8953584
  13 H   H5            -2.4872360    -4.3224924    -0.8919402
  14 H   H13           -1.4449165    -5.7075124    -0.4253723
  15 H   H14           -1.1173309    -4.7811726    -1.9288566
  16 F   F1             2.3876458     1.5065515    -1.1002996
  17 F   F2             3.7188171     1.5340913     0.6670521
```

18	C	C4	0.1324177	2.4429016	0.5472554
19	C	C5	-0.2167458	2.9711565	-0.6638453
20	C	C6	-1.5600181	3.4501561	-0.5266274
21	C	C7	-1.9288519	3.1814347	0.7548266
22	H	H1	0.4101903	3.0158134	-1.5416556
23	H	H8	-2.1620993	3.9312406	-1.2845736
24	H	H9	-2.8285917	3.3542179	1.3254461
25	O	O3	-0.9144789	2.5658491	1.4256099
26	H	H2	1.6286680	2.1270843	2.0852611

Furan 3,3 TS

Spartan'10: G = -850.287883, iv = none
Gaussian'09: B3LYP/6-31G*, G = -850.290209, iv = i284
Gaussian'09: M06-2X/6-31G*, G = -849.957473, iv = i332

			Cartesian Coordinates (Angstroms)		
	Atom		X	Y	Z
1	C	C1	-0.0686022	-0.6391635	1.1400999
2	H	H3	-0.3649563	-1.6315030	0.8437269
3	C	C2	1.2811173	-0.3378544	1.5213062
4	C	C5	1.1576922	0.3153033	-1.4749842
5	H	H7	1.1552839	1.3253536	-1.8803005
6	C	C6	-0.0969354	-0.2147826	-1.0919058
7	H	H6	-0.2642143	-1.2768469	-1.1819185
8	C	C3	2.3686760	-0.2873355	-1.2439468
9	C	C4	2.4762418	-0.7290840	0.9905851
10	C	C11	2.5722832	-1.4377316	-0.3188344
11	H	H2	3.2891460	0.2053055	-1.5429394
12	H	H10	3.4002144	-0.3149572	1.3784504
13	C	C12	-1.2884862	0.6414637	-1.2503270
14	O	O1	-1.2818295	1.8382432	-1.4710164
15	O	O2	-2.4318212	-0.0765206	-1.0850122
16	C	C13	-3.6464005	0.6748159	-1.2190799
17	H	H1	-3.7181560	1.1183212	-2.2162060
18	H	H5	-3.6912395	1.4756892	-0.4752773
19	H	H8	-4.4538401	-0.0415801	-1.0609347
20	F	F1	1.6519208	-2.4545275	-0.4594124
21	F	F2	3.8126397	-1.9929923	-0.4799666
22	O	O3	1.2640133	0.6728156	2.4716370
23	C	C8	-0.0472362	0.9682551	2.7083964
24	H	H12	-0.2145705	1.7366318	3.4495822
25	C	C7	-0.8906130	0.2167166	1.9638239
26	H	H11	-1.9703284	0.2459645	1.9844542

cis 2-thiophene (cis-9d)

```
Spartan;10: G = -1173.29413, iv = none
Gaussian'09: B3LYP/6-31G*, G = -1173.266174, iv = none
Gaussian'09: M06-2X/6-31G*, G = -1172.963766, iv = none

Cartesian Coordinates (Angstroms)
       Atom              X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C1           2.5255454     1.2442007     0.3046356
  2 C   C2           1.4092065     1.7127642     1.1546039
  3 C   C3           1.7042303     0.1577513     0.9110483
  4 H   H6           2.1492153    -0.3384332     1.7698751
  5 C   C10          0.7967803    -0.6445570     0.0819703
  6 H   H11          0.4006088    -0.1915052    -0.8237508
  7 C   C11          0.4227832    -1.8986507     0.3752741
  8 H   H12          0.7706948    -2.4181631     1.2634495
  9 C   C12         -0.4986782    -2.6301292    -0.5203969
 10 O   O1          -0.9591428    -2.2123635    -1.5654584
 11 O   O2          -0.7784609    -3.8584840    -0.0190998
 12 C   C13         -1.6709491    -4.6513349    -0.8149407
 13 H   H5          -2.6213165    -4.1310089    -0.9613722
 14 H   H13         -1.8205664    -5.5759300    -0.2562606
 15 H   H14         -1.2297810    -4.8612060    -1.7934949
 16 F   F1           2.4811110     1.4238483    -1.0366860
 17 F   F2           3.7919029     1.4207600     0.7448429
 18 C   C4           0.1974389     2.3794114     0.6317526
 19 C   C5          -0.0206193     2.9993977    -0.5735478
 20 C   C6          -1.3376590     3.5345359    -0.7029058
 21 C   C7          -2.1103877     3.3194067     0.4031767
 22 H   H1           0.7391033     3.0735412    -1.3415374
 23 H   H8          -1.6890187     4.0596242    -1.5843589
 24 H   H9          -3.1355766     3.6182392     0.5758638
 25 S   S1          -1.2434068     2.4495722     1.6278462
 26 H   H2           1.7269422     2.0187127     2.1494713
```

cis 2-thiophene TS

```
Spartan'10: G = -1173.26802, iv = i300
Gaussian'09: B3LYP/6-31G*, G = -1173.27068, iv = i292
Gaussian'09: M06-2X/6-31G*, G = -1172.930053, iv = i355

Cartesian Coordinates (Angstroms)
       Atom              X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C1           0.0363919    -0.6432743     1.1516885
  2 H   H3          -0.1761859    -1.6591940     0.8567293
  3 C   C2           1.3874465    -0.2999837     1.5137127
  4 C   C5           1.1733536     0.2907682    -1.4934262
  5 H   H7           1.1752585     1.2953169    -1.9124989
  6 C   C6          -0.0790655    -0.2116921    -1.0622572
  7 H   H6          -0.2724851    -1.2692479    -1.1547817
```

```
  8 C   C3           2.3786214    -0.3339823    -1.3002843
  9 C   C4           2.5468282    -0.7424851     0.9329581
 10 C   C11          2.5890941    -1.4767566    -0.3677304
 11 H   H2           3.2976792     0.1349339    -1.6388706
 12 H   H10          3.5118299    -0.3750983     1.2683835
 13 C   C12         -1.2579048     0.6675101    -1.2124209
 14 O   O1          -1.2307474     1.8606375    -1.4478607
 15 O   O2          -2.4125233    -0.0273033    -1.0305440
 16 C   C13         -3.6139604     0.7468960    -1.1609657
 17 H   H1          -3.6960384     1.1636488    -2.1688630
 18 H   H5          -3.6249968     1.5685421    -0.4391052
 19 H   H8          -4.4331588     0.0529329    -0.9673123
 20 F   F1           1.6536572    -2.4833370    -0.4711193
 21 F   F2           3.8170567    -2.0516754    -0.5559142
 22 S   S2           1.3849854     1.0245650     2.7059169
 23 C   C8          -0.3631965     1.0161350     2.7583118
 24 H   H12         -0.8724305     1.6934226     3.4324691
 25 C   C7          -0.9252665     0.1083666     1.9231062
 26 H   H11         -1.9942427    -0.0496457     1.8406781
```

alpha Me cis SM (*cis*-10i)

```
Spartan'10: G = -891.794682, iv = none
Gaussian'09: B3LYP/6-31G*, G = -891.802283, iv = none
Gaussian'09: M06-2X/6-31G*, G = -891.443545, iv = none

Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

  1 H   H1           1.0605970     2.2101135     0.9795402
  2 C   C1           1.4318218     1.3411226     1.5172655
  3 C   C4           2.3865025    -0.8862409     2.8887981
  4 C   C2           0.5185848     0.4461580     2.0944014
  5 C   C6           2.8045038     1.1268614     1.6258776
  6 C   C5           3.2865377     0.0103681     2.3130865
  7 C   C3           1.0111170    -0.6707822     2.7826651
  8 H   H6           3.4977073     1.8308283     1.1731001
  9 H   H5           4.3566476    -0.1582550     2.3986995
 10 H   H3           0.3185399    -1.3740829     3.2324462
 11 H   H4           2.7523580    -1.7575112     3.4255959
 12 C   C7          -0.9468513     0.7418941     2.0124806
 13 C   C8          -2.0024763    -0.2830311     1.8928866
 14 C   C9          -1.7848029     0.5524054     0.6736209
 15 H   H9          -2.5331798     1.3236271     0.5234112
 16 F   F1          -3.1525956    -0.1268753     2.5902310
 17 F   F2          -1.6724700    -1.5967678     1.8516777
 18 C   C10         -1.1539931    -0.0304295    -0.5213977
 19 H   H8          -0.4580820    -0.8435968    -0.3434813
 20 C   C11         -1.3639456     0.3454763    -1.7988830
 21 C   C12         -0.6574363    -0.3600092    -2.9068867
 22 O   O1          -0.8167572    -0.0880527    -4.0826858
 23 O   O2           0.1855185    -1.3350438    -2.4887181
 24 C   C13          0.8788792    -2.0320139    -3.5329248
 25 H   H7           1.5263014    -2.7480706    -3.0254650
```

```
  26  H   H11          1.4701051     -1.3364892     -4.1346099
  27  H   H12          0.1715048     -2.5502677     -4.1865157
  28  H   H13         -1.2694853      1.6294198      2.5548831
  29  C   C14         -2.2831145      1.4423181     -2.2707235
  30  H   H2          -1.7367054      2.1587340     -2.8934231
  31  H   H10         -2.7448759      1.9845092     -1.4427544
  32  H   H14         -3.0804549      1.0336839     -2.9021983
```

alpha Me [3,3] - TS

```
Spartan'10: G = -891.746085, iv = i364
Gaussian'09: B3LYP/6-31G*, G = -891.748315, iv = i353
Gaussian'09: M06-2X/6-31G*, G = -891.387733, iv = i436

Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------     -------------- -------------- --------------

   1  C   C1          -0.0100016     -0.5463738      1.0292330
   2  H   H3          -0.0273706     -1.6176378      0.8919358
   3  C   C2           1.2581965      0.0056784      1.4941897
   4  C   C5           1.2777056     -0.1356812     -1.5540668
   5  H   H7           1.3712153      0.7638974     -2.1600692
   6  C   C6          -0.0625493     -0.4626455     -1.1428007
   7  C   C7           1.2247206      1.2095288      2.2856223
   8  H   H4           2.1708031      1.6498380      2.5907106
   9  C   C8           0.0431027      1.7927875      2.6374625
  10  H   H9           0.0404109      2.7063545      3.2256452
  11  C   C9          -1.2045022      1.2028254      2.2521706
  12  H   H11         -2.1324069      1.6587688      2.5871540
  13  C   C10         -1.2272576      0.0556325      1.5131135
  14  H   H12         -2.1709460     -0.4165290      1.2572406
  15  C   C3           2.4490914     -0.7115405     -1.1506657
  16  C   C4           2.4742416     -0.5391727      1.1292349
  17  C   C11          2.6692876     -1.5584310      0.0591998
  18  H   H2           3.3809668     -0.3191597     -1.5489410
  19  H   H10          3.3945289     -0.0738765      1.4714696
  20  C   C12         -1.0180917      0.6571089     -1.4359339
  21  O   O1          -0.7001388      1.8127592     -1.6418218
  22  O   O2          -2.3096672      0.2444313     -1.4290949
  23  C   C13         -3.2803384      1.2756347     -1.6612080
  24  H   H1          -3.1226569      1.7401591     -2.6382425
  25  H   H5          -3.2131662      2.0462063     -0.8880948
  26  H   H8          -4.2502372      0.7774966     -1.6258174
  27  F   F1           1.8593515     -2.6707964      0.1829681
  28  F   F2           3.9592687     -2.0250141      0.0765105
  29  C   C14         -0.6043500     -1.8668552     -1.3905727
  30  H   H6           0.1631754     -2.6169170     -1.2093664
  31  H   H13         -0.9247594     -1.9509253     -2.4368304
  32  H   H14         -1.4776266     -2.0875518     -0.7703345
```

Alpha-Me furan trans intermediate (25a)

```
Spartan'10: G = -889.603013, iv = none
Gaussian'09: B3LYP/6-31G*, G = -889.610117, iv = none
Gaussian'09: M05-2X/6-31+G*, G = -889.546801, iv = none


                    Cartesian Coordinates (Angstroms)
      Atom             X             Y             Z
   ---------    ------------- ------------- -------------

  1 C   C1          1.5534980     1.4511661    -0.8407189
  2 C   C2          0.4917211     1.7903833     0.1279921
  3 C   C3          0.9244027     0.2753336    -0.1820042
  4 H   H3         -0.4628635     2.0583940    -0.3175496
  5 H   H6          1.5218784    -0.1559734     0.6148856
  6 C   C10        -0.0116118    -0.5872870    -0.9142971
  7 H   H11        -0.4795535    -0.1381529    -1.7855085
  8 C   C11        -0.3444786    -1.8574102    -0.6079688
  9 C   C12        -1.3239442    -2.5939509    -1.4571208
 10 O   O1         -1.6466618    -3.7502884    -1.2574843
 11 O   O2         -1.8309451    -1.8576180    -2.4768333
 12 C   C13        -2.7730240    -2.5429624    -3.3135530
 13 H   H5         -2.2981176    -3.3916242    -3.8139591
 14 H   H13        -3.1050025    -1.8051376    -4.0450116
 15 H   H14        -3.6177249    -2.9086313    -2.7238128
 16 F   F1          1.3171784     1.6717582    -2.1548017
 17 F   F2          2.8454017     1.7427335    -0.5556694
 18 C   C4          0.7592403     2.3888452     1.4405016
 19 C   C5          1.8814512     2.7972985     2.1068452
 20 C   C6          1.4445417     3.2683479     3.3872879
 21 C   C7          0.0927241     3.1158777     3.4074928
 22 H   H1          2.8913403     2.7738015     1.7262248
 23 H   H8          2.0596539     3.6732968     4.1787556
 24 H   H9         -0.6741849     3.3331767     4.1351185
 25 O   O3         -0.3444406     2.5796988     2.2324140
 26 C   C8          0.1868351    -2.6638126     0.5478402
 27 H   H2          0.9275234    -2.1143936     1.1329438
 28 H   H4          0.6441148    -3.5929560     0.1908463
 29 H   H7         -0.6289523    -2.9599131     1.2171449
```

alpha Me Furan Cis (cis-25a)

```
Spartan'10: G = --889.601018, iv = none
Gaussian'09: B3LYP/6-31G*, G = -889.608862, iv = none
Gaussian'09: M06-2X/6-31G*, G = -889.261077, iv = none

Cartesian Coordinates (Angstroms)
      Atom             X             Y             Z
   ---------    ------------- ------------- -------------

  1 C   C1         -0.3974741    -2.6219144    -0.7714089
  2 C   C2         -0.7247780    -2.2690318     0.6247589
```

```
  3 C   C3            -1.1395947     -1.3394771     -0.6178839
  4 H   H6            -2.1994387     -1.4005129     -0.8440415
  5 C   C10           -0.4706465     -0.0488947     -0.8306487
  6 H   H11            0.5991262     -0.0217513     -0.6541930
  7 C   C11           -1.0889629      1.0876410     -1.2085464
  8 C   C12           -0.2992271      2.3444460     -1.3638573
  9 O   O1            -0.7798013      3.4150566     -1.6872710
 10 O   O2             1.0223717      2.1864956     -1.1093573
 11 C   C13            1.8179072      3.3713603     -1.2452303
 12 H   H5             1.7452196      3.7714566     -2.2602172
 13 H   H13            2.8408053      3.0620862     -1.0270429
 14 H   H14            1.4908954      4.1394187     -0.5386698
 15 F   F1             0.8932726     -2.5849295     -1.1823553
 16 F   F2            -1.0238371     -3.6754609     -1.3426948
 17 C   C8            -2.5694172      1.2172905     -1.4795333
 18 H   H2            -2.9498456      0.3755506     -2.0671873
 19 H   H4            -2.7689453      2.1413464     -2.0245422
 20 H   H7            -3.1435270      1.2566239     -0.5445140
 21 H   H12           -1.5836150     -2.7932609      1.0376843
 22 C   C4             0.2948733     -1.8679838      1.6026016
 23 C   C5             1.6595919     -1.9238444      1.6504779
 24 C   C6             2.0461629     -1.3645208      2.9116015
 25 C   C7             0.8917900     -1.0125971      3.5394103
 26 O   O3            -0.1860522     -1.3079138      2.7592418
 27 H   H8             2.3055975     -2.3206775      0.8820351
 28 H   H10            3.0502738     -1.2492973      3.2950736
 29 H   H15            0.6672747     -0.5667041      4.4963103
```

alpha Me Furan VCPR TS

```
Spartan'10: G = -889.565926, iv = i88, 0.7630
Gaussian'09: B3LYP/6-31G*, G = -889.569816, iv = i85, S^2 = 0.76
Gaussian'09: M05-2X/6-31+G*, G = -889.502352, iv = i56, S^2 = 0.9266

 Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
   ---------    ------------- ------------- -------------

  1 C   C             -0.4041129      2.5914948     -0.9599034
  2 C   C2            -1.4497983      1.7333183     -0.9510775
  3 C   C3            -1.5151473      0.4795265     -0.2387479
  4 C   C4             0.9435780      2.2099149     -0.4366464
  5 C   C5             1.2510123      0.7573553     -0.6097426
  6 H   H             -0.4729379      3.5694436     -1.4267338
  7 H   H7            -2.3116161      1.9696306     -1.5753268
  8 H   H12            0.9287033      0.3061349     -1.5389267
  9 F   F1             1.8954887      2.9697258     -1.1062616
 10 F   F2             1.0946380      2.5940510      0.9005045
 11 C   C11           -2.2979979     -0.5701880     -0.9151502
 12 O   O1            -2.7696087     -0.4709860     -2.0386564
 13 O   O2            -2.4406324     -1.6860087     -0.1536856
 14 C   C12           -3.1718374     -2.7532977     -0.7712530
 15 H   H1            -4.1968192     -2.4421135     -0.9921350
 16 H   H9            -3.1665562     -3.5696404     -0.0474465
 17 H   H10           -2.6905039     -3.0619753     -1.7032552
 18 C   C1             2.1664149      0.0632262      0.1719121
```

```
 19 C  C6          2.8457301    0.3285411    1.3714154
 20 C  C7          3.6296160   -0.8085007    1.6620184
 21 C  C8          3.3922828   -1.7109159    0.6550611
 22 H  H3          2.7687563    1.2442339    1.9361133
 23 H  H5          4.2858374   -0.9543082    2.5087800
 24 H  H11         3.7547219   -2.7086143    0.4573138
 25 O  O3          2.5168398   -1.2117084   -0.2505679
 26 C  C9         -1.1929891    0.3198419    1.2245581
 27 H  H2         -0.6549729   -0.6120974    1.4253217
 28 H  H4         -2.1297930    0.2662678    1.7999525
 29 H  H6         -0.6082963    1.1576479    1.6025651
```

alpha Me Furan [3,3] TS

```
Spartan'10: G = -889.572731, iv = i272
Gaussian'09: B3LYP/6-31G*, G = -889.570319, iv = i247
Gaussian'09: M06-2X/6-31G*, G = -889.219479, iv = i329

    Cartesian Coordinates (Angstroms)
       Atom              X             Y             Z
    ---------    ------------- ------------- -------------

  1 C  C1         -0.0507601   -0.4543224    1.0779417
  2 C  C2          1.3285473   -0.1922498    1.4254050
  3 C  C5          1.2591109    0.6796953   -1.4833306
  4 H  H7          1.2276939    1.7135085   -1.8212804
  5 C  C6          0.0194505    0.0856812   -1.1461993
  6 H  H6         -0.1045372   -0.9757655   -1.2924427
  7 C  C3          2.4871096    0.0990027   -1.2918649
  8 C  C4          2.5242029   -0.5775166    0.8877604
  9 C  C11         2.7170973   -1.1330789   -0.4856225
 10 H  H2          3.3934558    0.6452063   -1.5353547
 11 H  H10         3.4272686   -0.1629699    1.3237368
 12 C  C12        -1.1932294    0.9112987   -1.2931720
 13 O  O1         -1.2210239    2.1234481   -1.3997915
 14 O  O2         -2.3211897    0.1474670   -1.2620386
 15 C  C13        -3.5513839    0.8747359   -1.3868180
 16 H  H1         -3.5914586    1.4020560   -2.3439272
 17 H  H5         -3.6540328    1.6057142   -0.5796587
 18 H  H8         -4.3426300    0.1260135   -1.3300535
 19 F  F1          1.8935485   -2.1879088   -0.8149991
 20 F  F2          4.0033845   -1.5811108   -0.6317074
 21 O  O3          1.3742344    0.8415684    2.3582190
 22 C  C8          0.0889164    1.2342896    2.5778535
 23 H  H12        -0.0279724    2.0390440    3.2899567
 24 C  C7         -0.7988195    0.5208325    1.8549223
 25 H  H11        -1.8752294    0.6180992    1.8757905
 26 C  C9         -0.6351157   -1.8391381    0.8793952
 27 H  H3          0.0482415   -2.5028530    0.3522604
 28 H  H4         -1.5800524   -1.7834940    0.3308222
 29 H  H9         -0.8448273   -2.2772530    1.8641973
```

alpha Me thiophene trans INT

```
Spartan'10: G = -1212.58519, iv = none
Gaussian'09: B3LYP/6-31G*, G = -1212.592277, iv = none
Gaussian'09: M05-2X/6-31+G*, G = -1212.515989, iv = none

     Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C1           1.3238346     1.8053593    -1.0873313
  2 C   C2           0.3236245     2.0555461    -0.0261839
  3 C   C3           0.7947459     0.5774852    -0.4337566
  4 H   H3          -0.6629199     2.2910881    -0.4193521
  5 H   H6           1.4671961     0.1447690     0.3006432
  6 C   C10         -0.1521435    -0.2998764    -1.1306003
  7 H   H11         -0.7086025     0.1470115    -1.9516066
  8 C   C11         -0.4132408    -1.5938060    -0.8575352
  9 C   C12         -1.4436718    -2.2378082    -1.7276760
 10 O   O1          -2.0529892    -1.6948496    -2.6300681
 11 O   O2          -1.6367371    -3.5367477    -1.3911883
 12 C   C13         -2.6140969    -4.2329163    -2.1782058
 13 H   H5          -3.5922056    -3.7524431    -2.0896039
 14 H   H13         -2.6456048    -5.2463562    -1.7764506
 15 H   H14         -2.3212873    -4.2449945    -3.2316104
 16 F   F1           0.9666480     2.0709919    -2.3647945
 17 F   F2           2.6255702     2.1330297    -0.9051421
 18 C   C4           0.6368519     2.6075189     1.3066015
 19 C   C5           1.8186201     3.0845746     1.8198117
 20 C   C6           1.7098868     3.5215417     3.1739268
 21 C   C7           0.4500156     3.3767994     3.6831748
 22 H   H1           2.7336715     3.1321452     1.2437964
 23 H   H8           2.5379027     3.9365040     3.7385555
 24 H   H9           0.0885315     3.6356113     4.6692928
 25 S   S1          -0.6328297     2.6926397     2.5135808
 26 C   C8           0.2286312    -2.4216599     0.2250870
 27 H   H2           0.9683101    -1.8523869     0.7935081
 28 H   H4           0.7256047    -3.3028920    -0.1960225
 29 H   H7          -0.5233161    -2.7958786     0.9291498
```

alpha Me thiophene cis INT

```
Spartan'10: G = -1212.58342, iv = none
Gaussian'09: B3LYP/6-31G*, G = -1212.590736, iv = none
Gaussian'09: M06-2X/6-31G*, G = -1212.235623, iv = none

   Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C1          -0.3940924    -2.6141307    -0.8489641
  2 C   C2          -0.6969888    -2.3231410     0.5698131
  3 C   C3          -1.1912896    -1.3758097    -0.6243956
  4 H   H6          -2.2506758    -1.4802514    -0.8338615
  5 C   C10         -0.5785213    -0.0523812    -0.8104740
```

```
  6  H   H11          0.4985106    -0.0069438    -0.6890946
  7  C   C11         -1.2258589     1.0922481    -1.1062525
  8  C   C12         -0.4554745     2.3600827    -1.2657540
  9  O   O1          -0.9745590     3.4315331    -1.5179732
 10  O   O2           0.8816684     2.2138075    -1.1053489
 11  C   C13          1.6495322     3.4162353    -1.2480852
 12  H   H5           1.5244135     3.8375129    -2.2492658
 13  H   H13          2.6864147     3.1213705    -1.0834070
 14  H   H14          1.3404552     4.1617108    -0.5102149
 15  F   F1           0.8754880    -2.5058601    -1.3074883
 16  F   F2          -0.9959479    -3.6751708    -1.4339463
 17  C   C8          -2.7101438     1.2581473    -1.3035409
 18  H   H2          -3.2576160     0.3225437    -1.1691833
 19  H   H4          -2.9256928     1.6449311    -2.3055924
 20  H   H7          -3.1088181     1.9955476    -0.5985513
 21  H   H12         -1.5180544    -2.9178563     0.9655118
 22  C   C4           0.3183431    -1.8915918     1.5540113
 23  C   C5           1.6851787    -2.0166016     1.5284367
 24  C   C6           2.3232695    -1.4802018     2.6874215
 25  C   C7           1.4390497    -0.9528049     3.5858528
 26  S   S1          -0.1970221    -1.0952734     3.0276960
 27  H   H8           2.2159130    -2.4811604     0.7070238
 28  H   H10          3.3963745    -1.4948614     2.8431709
 29  H   H15          1.6461442    -0.4916305     4.5424558
```

alpha Me thiophene VCPR TS

```
Spartan'10: G = -1212.54641, iv = i83, S^2 = 0.7803
Gaussian'09: B3LYP/6-31G*, G = -1212.551391, iv = i86, S^2 = 0.58
Gaussian'09: M05-2X/6-31+G*, G = -1173.189048, iv = i147, S^2 = 0.76
```

```
     Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
   ---------    ------------- ------------- -------------

  1  C   C           -0.4286277     2.7001455    -0.9162575
  2  C   C2          -1.4696176     1.8359440    -0.9008575
  3  C   C3          -1.5298555     0.5868081    -0.1810509
  4  C   C4           0.9236504     2.3299843    -0.3973802
  5  C   C5           1.2423567     0.8764220    -0.5519030
  6  H   H           -0.5044532     3.6750544    -1.3882538
  7  H   H7          -2.3326688     2.0647375    -1.5261167
  8  H   H12          0.9100625     0.4291747    -1.4816979
  9  F   F1           1.8675989     3.0832268    -1.0833248
 10  F   F2           1.0843598     2.7255446     0.9334470
 11  C   C11         -2.3012032    -0.4732423    -0.8537228
 12  O   O1          -2.7566482    -0.3912181    -1.9855045
 13  O   O2          -2.4475340    -1.5807004    -0.0805073
 14  C   C12         -3.1677261    -2.6588455    -0.6922473
 15  H   H1          -4.1896634    -2.3530341    -0.9335474
 16  H   H9          -3.1724031    -3.4633918     0.0441862
 17  H   H10         -2.6722572    -2.9815926    -1.6123564
 18  C   C1           2.1479112     0.1502133     0.2188714
 19  C   C6           2.5984777    -1.1573475    -0.0604199
 20  C   C7           3.5003476    -1.6637240     0.8898238
 21  C   C8           3.7575592    -0.7702064     1.9093507
```

```
 22  H   H3            2.2685549     -1.6969482     -0.9416766
 23  H   H5            3.9518922     -2.6480383      0.8325259
 24  H   H11           4.4127766     -0.9097496      2.7593308
 25  S   S1            2.8858342      0.7148177      1.7306140
 26  C   C9           -1.1945736      0.4309267      1.2788112
 27  H   H2           -0.6295144     -0.4869083      1.4728387
 28  H   H4           -2.1251082      0.3495401      1.8604097
 29  H   H6           -0.6295277      1.2824074      1.6566148
```

alpha Me thiophene 3,3 TS

```
Spartan'10: G = -1212.54839, iv = i263
Gaussian'09: B3LYP/6-31G*, G = -1173.27068, iv = 292
Gaussian'09: M06-2X/6-31G*, G = -1172.930053, iv = i335

Cartesian Coordinates (Angstroms)
          Atom              X              Y              Z
   ---------    -------------- -------------- --------------


  1  C   C1            0.1457678     -0.4810391      1.3189222
  2  H   H3            0.1130342     -1.5256464      1.0528317
  3  C   C2            1.4068513      0.1148581      1.6544117
  4  C   C5            1.1974107      0.2862417     -1.4050061
  5  H   H7            1.1652146      1.2606365     -1.8906403
  6  C   C6           -0.0702641     -0.2276530     -1.0040764
  7  C   C3            2.4511871     -0.1973151     -1.1229512
  8  C   C4            2.6415093     -0.2034674      1.1489605
  9  C   C11           2.8414681     -1.1165508     -0.0159610
 10  H   H2            3.3075510      0.3408363     -1.5206281
 11  H   H10           3.5263145      0.3521231      1.4426269
 12  C   C12          -1.1599725      0.7907009     -1.0778121
 13  O   O1           -0.9961082      1.9873594     -1.2296738
 14  O   O2           -2.3904437      0.2366229     -0.9236220
 15  C   C13          -3.4816825      1.1680769     -0.9479221
 16  H   H1           -3.5329320      1.6767006     -1.9144631
 17  H   H5           -3.3642256      1.9185182     -0.1616101
 18  H   H8           -4.3799083      0.5719050     -0.7817891
 19  F   F1            2.1428866     -2.2998007      0.0822550
 20  F   F2            4.1653004     -1.4563063     -0.1251042
 21  S   S1            1.1568384      1.5248199      2.7115962
 22  C   C8           -0.5628487      1.2204223      2.7615546
 23  H   H12          -1.1944145      1.8597683      3.3654718
 24  C   C7           -0.9435487      0.1521811      2.0143278
 25  H   H11          -1.9682185     -0.1939008      1.9442078
 26  C   C9           -0.4705883     -1.6687664     -1.2745490
 27  H   H4            0.3836005     -2.3380882     -1.1976401
 28  H   H6           -0.8652987     -1.7402301     -2.2972913
 29  H   H9           -1.2644803     -2.0130071     -0.6064268
```

Weinreb cis E INT (29a)

```
Spartan'10: G = -947.065987, iv = none
Gaussian'09: B3LYP/6-31G*, G = -947.073972, iv = none
Gaussian'09: M06-2X/6-31G*, G = -946.691616, iv = none

Cartesian Coordinates (Angstroms)
       Atom              X             Y             Z
    ---------    ------------- ------------- -------------

   1 C   C1          -2.3342695    -1.5454125    -1.3511858
   2 C   C2          -2.7447096    -0.4462149    -0.4551097
   3 C   C3          -1.4273573    -0.3577660    -1.3337565
   4 H   H6          -1.5152749     0.2988081    -2.1960640
   5 C   C4          -2.6988380    -0.5252874     1.0397700
   6 C   C5          -2.6905013    -0.5938805     3.8467547
   7 C   C6          -2.2668534     0.5848170     1.7792730
   8 C   C7          -3.1259504    -1.6709614     1.7235669
   9 C   C8          -3.1207600    -1.7036023     3.1190950
  10 C   C9          -2.2629843     0.5521683     3.1726594
  11 H   H4          -1.9246668     1.4736453     1.2554516
  12 H   H7          -3.4552808    -2.5399206     1.1631142
  13 H   H8          -3.4517391    -2.6000725     3.6365206
  14 H   H9          -1.9215411     1.4191895     3.7317247
  15 H   H10         -2.6846636    -0.6219162     4.9330309
  16 C   C10         -0.0989138    -0.4383716    -0.7096473
  17 H   H11          0.0410455    -1.1351713     0.1130367
  18 C   C11          0.9532007     0.2940602    -1.1057679
  19 H   H12          0.8719660     1.0115473    -1.9139824
  20 C   C12          2.2567329     0.1334208    -0.4136725
  21 O   O1           2.4230121    -0.6104655     0.5490410
  22 N   N1           3.3366603     0.8264438    -0.9512772
  23 C   C13          4.5433780     1.0426835    -0.1707411
  24 H   H5           4.6505058     0.1942966     0.5044075
  25 H   H13          4.4740857     1.9710549     0.4103888
  26 H   H14          5.4103153     1.0977487    -0.8358071
  27 F   F1          -1.8898330    -2.7129702    -0.8300171
  28 F   F2          -3.0590584    -1.7918138    -2.4682801
  29 O   O2           3.0426753     1.9122541    -1.8046925
  30 C   C14          3.4748363     1.6169464    -3.1354056
  31 H   H2           3.2608473     2.5197991    -3.7136277
  32 H   H1           2.9239356     0.7653288    -3.5521093
  33 H   H15          4.5506512     1.4065694    -3.1695807
  34 H   H16         -3.5406528     0.1730448    -0.8671103
```

Weinreb [3,3] TS

```
Spartan'10: G = -947.017003, iv = i374
Gaussian'09: B3LYP/6-31G*, G = -947.020971, iv = i276
Gaussian'09: M06-2X/6-31G*, G = -946.63488, iv = i451

   Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
     ---------    ------------- ------------- -------------

   1  C   C1          -0.2914116    -0.5301221     1.3258970
   2  H   H3          -0.1490741    -1.5987044     1.2410897
   3  C   C2          -1.5992406    -0.1288100     1.8498740
   4  C   C5          -1.7065614    -0.0875395    -1.1823929
   5  H   H7          -1.7936212     0.8376777    -1.7473401
   6  C   C6          -0.3866717    -0.4669373    -0.7768860
   7  H   H6          -0.1859351    -1.5272410    -0.8212505
   8  C   C7          -1.6684294     1.0558448     2.6685345
   9  H   H4          -2.6462624     1.3782920     3.0177572
  10  C   C8          -0.5526258     1.7769196     2.9728796
  11  H   H9          -0.6332733     2.6798318     3.5717877
  12  C   C9           0.7381171     1.3485167     2.5196794
  13  H   H11          1.6188502     1.9132518     2.8122116
  14  C   C10          0.8642911     0.2210823     1.7668847
  15  H   H12          1.8503260    -0.1294780     1.4762307
  16  C   C3          -2.8492911    -0.7208373    -0.7866194
  17  C   C4          -2.7675325    -0.7699790     1.4889247
  18  C   C11         -2.9136347    -1.7018603     0.3353786
  19  H   H2          -3.8192515    -0.3540813    -1.1095863
  20  H   H10         -3.7145119    -0.4114708     1.8831897
  21  C   C12          0.6929765     0.4679799    -1.2320579
  22  O   O1           0.4761184     1.6632645    -1.3886650
  23  N   N1           1.9294753    -0.0828262    -1.5421181
  24  F   F1          -1.9577050    -2.6994676     0.2803596
  25  F   F2          -4.1312168    -2.3293136     0.3714625
  26  C   C13          2.4761775    -1.3675948    -1.1439412
  27  H   H1           3.2010075    -1.6879700    -1.8983552
  28  H   H5           1.6857440    -2.1163524    -1.0894241
  29  H   H8           2.9888294    -1.3077874    -0.1739330
  30  O   O2           2.9719230     0.8527016    -1.6718440
  31  C   C14          3.0387716     1.3529058    -3.0114028
  32  H   H13          3.1756382     0.5367688    -3.7324742
  33  H   H14          3.9163757     2.0046060    -3.0220940
  34  H   H15          2.1416286     1.9287295    -3.2517563
```

CN E cis (*cis*-10a)

```
Spartan'10: G = -716.911798, iv = none
Gaussian'09: B3LYP/6-31G*, G = -716.91601, iv = none
Gaussian'09: M06-2X/6-31G*, G = -716.635411, iv = none

 Cartesian Coordinates (Angstroms)
      Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C1          0.8384972    -0.0293373    -2.2221422
  2 C   C2         -0.3885136     0.3527766    -1.4965935
  3 C   C3          0.0569712    -1.1649306    -1.6406357
  4 H   H3         -1.2259717     0.5801881    -2.1550650
  5 C   C4         -0.4016202     1.0552264    -0.1737740
  6 C   C5         -0.5390172     2.4067366     2.2840982
  7 C   C6         -1.3816954     0.7197947     0.7719740
  8 C   C7          0.5083578     2.0774201     0.1262152
  9 C   C8          0.4386420     2.7474573     1.3492651
 10 C   C9         -1.4511456     1.3901265     1.9918145
 11 H   H4         -2.0912052    -0.0732301     0.5488670
 12 H   H7          1.2735488     2.3463932    -0.5943289
 13 H   H8          1.1521606     3.5368782     1.5694348
 14 H   H9         -2.2152386     1.1173901     2.7146395
 15 H   H10        -0.5905754     2.9289998     3.2354672
 16 C   C10         0.5670599    -1.9031929    -0.4780249
 17 H   H11         1.2154473    -1.3671086     0.2095548
 18 F   F1          0.8806104     0.1048032    -3.5664402
 19 F   F2          2.0528279     0.2561481    -1.6955350
 20 H   H2         -0.5309570    -1.7369171    -2.3540265
 21 C   C11         0.2694682    -3.1931334    -0.2351451
 22 H   H1         -0.3753362    -3.7579873    -0.9051597
 23 C   C12         0.7710893    -3.8997362     0.8981439
 24 N   N1          1.1665959    -4.4947655     1.8173967
```

CN E [3,3] TS

```
Spartan'10: G = -716.870471, iv = i381
Gaussian'09: B3LYP/6-31G*, G = -716.871513, iv = i384
Gaussian'09: M06-2X/6-31G*, G = -716.586383, iv = i459

 Cartesian Coordinates (Angstroms)
      Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C1         -0.8088086    -0.5052546     0.4670589
  2 H   H3         -0.9601465    -1.5672415     0.3333548
  3 C   C2          0.5041776    -0.1360068     1.0003515
  4 C   C5          0.6094299     0.0070984    -2.0576895
  5 H   H7          0.7322234     0.9241156    -2.6299300
  6 C   C6         -0.7219691    -0.3378939    -1.6323141
  7 H   H6         -0.9883166    -1.3847092    -1.7170743
  8 C   C7          0.5845518     1.0116801     1.8701791
  9 H   H4          1.5646116     1.3115768     2.2327551
 10 C   C8         -0.5278186     1.7231151     2.2079213
 11 H   H9         -0.4417853     2.5954906     2.8497921
```

```
  12  C   C9           -1.8226470      1.3286345      1.7312997
  13  H   H11          -2.6973987      1.8905458      2.0459019
  14  C   C10          -1.9604833      0.2386595      0.9266856
  15  H   H12          -2.9446696     -0.0819697      0.5984315
  16  C   C3            1.7357562     -0.6589915     -1.6744165
  17  C   C4            1.6614246     -0.7759015      0.6076258
  18  C   C11           1.7837623     -1.6715874     -0.5788014
  19  H   H2            2.7107493     -0.3107918     -2.0015767
  20  H   H10           2.6162454     -0.4503849      1.0114748
  21  F   F1            0.8069298     -2.6435541     -0.6632285
  22  F   F2            2.9879160     -2.3219049     -0.5697096
  23  C   C12          -1.7787176      0.5460953     -2.0362881
  24  N   N1           -2.6450171      1.2691801     -2.3218035
```

CN Z INT (*cis*-10h)

```
Spartan'10: G = -716.911953, iv = none
Gaussian'09: B3LYP/6-31G*, G = -716.916391, iv = none
Gaussian'09: M06-2X/6-31G*, G = --716.637087, iv = none

Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

   1  C   C1           -1.3052491      0.6534900     -1.7473256
   2  C   C2           -1.3174749     -0.1515324     -0.5107186
   3  C   C3           -0.4276179     -0.5571128     -1.7622719
   4  H   H3           -2.1888862     -0.7992368     -0.4249284
   5  C   C4           -0.7118527      0.2902570      0.7861344
   6  C   C5            0.3586852      1.0479699      3.2694727
   7  C   C6           -0.0334426     -0.6418633      1.5849899
   8  C   C7           -0.8476052      1.6066244      1.2466254
   9  C   C8           -0.3145495      1.9816313      2.4812757
  10  C   C9            0.4975196     -0.2667018      2.8179120
  11  H   H4            0.0793366     -1.6643518      1.2335346
  12  H   H7           -1.3672142      2.3390743      0.6376639
  13  H   H8           -0.4277317      3.0060297      2.8256598
  14  H   H9            1.0205771     -1.0003674      3.4254199
  15  H   H10           0.7729671      1.3412882      4.2302219
  16  C   C10           1.0319841     -0.4074183     -1.7078640
  17  H   H11           1.4187922      0.4888395     -1.2314107
  18  C   C11           1.9199131     -1.2914217     -2.2029974
  19  H   H12           2.9864701     -1.1004944     -2.1261998
  20  F   F1           -0.7198674      1.8760887     -1.7499297
  21  F   F2           -2.3991365      0.6706445     -2.5398610
  22  H   H2           -0.8069124     -1.4069014     -2.3229696
  23  C   C12           1.5417345     -2.5090008     -2.8455583
  24  N   N1            1.2395607     -3.5055343     -3.3668747
```

CN Z [3,3] TS

```
Spartan'10: G = -716.863331, iv = none
Gaussian'09: B3LYP/6-31G*, G = -716.864276, iv = i384
Gaussian'09: M06-2X/6-31G*, G = -716.578656, iv = i458
```

```
 Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
   ---------    ------------- ------------- -------------

  1 C   C1          -0.8423313    -0.3854496     0.4662477
  2 H   H3          -0.9858849    -1.4242021     0.2074645
  3 C   C2           0.4608799    -0.0289211     1.0064344
  4 C   C5           0.6213220     0.2719571    -2.0300150
  5 H   H7           0.8147920     1.2431589    -2.4844903
  6 C   C6          -0.7472213     0.0044337    -1.6969464
  7 H   H8          -1.4126024     0.8586842    -1.8178538
  8 C   C7           0.5317204     1.0873507     1.9133168
  9 H   H4           1.5069625     1.3804196     2.2941124
 10 C   C8          -0.5896368     1.7785552     2.2738744
 11 H   H9          -0.5117713     2.6244792     2.9512872
 12 C   C9          -1.8760834     1.3957891     1.7765733
 13 H   H11         -2.7567043     1.9402548     2.1060845
 14 C   C10         -1.9991775     0.3320961     0.9280028
 15 H   H12         -2.9767536     0.0045472     0.5842892
 16 C   C3           1.7198049    -0.4566810    -1.6635881
 17 C   C4           1.6261879    -0.6463821     0.5838551
 18 C   C11          1.7519420    -1.5222970    -0.6186132
 19 H   H2           2.7069898    -0.1011847    -1.9440974
 20 H   H10          2.5791735    -0.3257808     0.9957299
 21 F   F1           0.7885549    -2.4881404    -0.7296507
 22 F   F2           2.9645099    -2.1596987    -0.6208029
 23 C   C12         -1.3931786    -1.2146902    -2.0820448
 24 N   N1          -1.9814943    -2.1682982    -2.3991697
```

Literature Predictions

Erbes and Boland trans SM (trans-49)

Gaussian'09: B3LYP/6-31G*, G = -628.208979, iv = none

```
 Cartesian Coordinates (Angstroms)
       Atom             X              Y              Z
    ---------    -------------  -------------  -------------

  1  C   C1          2.1824440      2.4440161     -0.9529439
  2  C   C2          0.8731754      3.0361150     -0.5198276
  3  C   C3          1.0267060      1.5332680     -0.6077047
  4  H   H6          1.0998863      1.0140289      0.3462317
  5  C   C10         0.3221516      0.7643655     -1.6561767
  6  H   H11         0.2760916      1.2185969     -2.6460780
  7  C   C11        -0.2358471     -0.4350329     -1.4712997
  8  H   H15        -0.7345043     -0.9617367     -2.2797294
  9  C   C4          0.7568048      3.6565147      0.8060946
 10  C   C6          0.0066983      4.7264722      1.1004036
 11  H   H1         -0.5936315      5.2214553      0.3431933
 12  H   H13        -0.0211473      5.1271845      2.1088408
 13  H   H17         1.3404568      3.2048235      1.6081830
 14  F   F1          3.2781083      2.4714643     -0.1094657
 15  F   F2          2.4980711      2.5871280     -2.2918194
 16  C   C5         -0.2048685     -1.1384911     -0.1118337
 17  H   H3          0.8356307     -1.2967445      0.1939984
 18  H   H5         -0.7140301     -0.5163774      0.6331126
 19  C   C7         -0.9161152     -2.4899150     -0.2201975
 20  H   H4         -0.4069540     -3.1120293     -0.9651436
 21  H   H7         -1.9566144     -2.3316614     -0.5260294
 22  C   C8         -0.8851375     -3.1933728      1.1392687
 23  H   H8          0.1553615     -3.3516268      1.4451012
 24  H   H10        -1.3942988     -2.5712584      1.8842147
 25  C   C9         -1.5963850     -4.5447962      1.0309051
 26  H   H9         -1.0872241     -5.1669111      0.2859594
 27  H   H12        -2.6368840     -4.3865419      0.7250728
 28  H   H14        -1.5742096     -5.0483816      2.0041091
 29  H   H16         0.3062651      3.5394442     -1.2964399
```

Erbes and Boland cis SM (49)

Gaussian'09: B3LYP/6-31G*, G = -628.207323, iv = none

```
Cartesian Coordinates (Angstroms)
       Atom             X              Y              Z
    ---------    -------------  -------------  -------------

  1  C   C1          2.3048106      2.4092042     -0.5864680
  2  C   C2          1.0108544      3.0286131     -0.1099256
  3  C   C3          1.1490726      1.4984560     -0.2412288
  4  H   H6          1.2222529      0.9792168      0.7127076
  5  C   C10         0.4445181      0.7295535     -1.2897008
  6  H   H11         0.3984581      1.1837849     -2.2796021
  7  C   C11        -0.1134805     -0.4698449     -1.1048238
  8  H   H2          1.0063096      3.3831285      0.9192383
```

```
  9  H   H15         -0.6121377     -0.9965488     -1.9132536
 10  C   C4           0.1658656      3.8275133     -1.0234979
 11  C   C6          -0.5814338      4.8690025     -0.6480115
 12  H   H1          -0.6234135      5.2003890      0.3875069
 13  H   H13         -1.1781026      5.4289125     -1.3622669
 14  H   H17          0.1764772      3.5403149     -2.0750644
 15  F   F1           3.4004749      2.4366523      0.2570101
 16  F   F2           2.6204377      2.5523160     -1.9253435
 17  C   C5          -0.0825019     -1.1733032      0.2546422
 18  H   H3           0.9579973     -1.3315565      0.5604743
 19  H   H5          -0.5916635     -0.5511894      0.9995885
 20  C   C7          -0.7937486     -2.5247270      0.1462784
 21  H   H4          -0.2845874     -3.1468413     -0.5986678
 22  H   H7          -1.8342478     -2.3664734     -0.1595536
 23  C   C8          -0.7627709     -3.2281848      1.5057446
 24  H   H8           0.2777281     -3.3864388      1.8115770
 25  H   H10         -1.2719322     -2.6060704      2.2506905
 26  C   C9          -1.4740185     -4.5796082      1.3973810
 27  H   H9          -0.9648575     -5.2017231      0.6524352
 28  H   H12         -2.5145175     -4.4213540      1.0915487
 29  H   H14         -1.4518430     -5.0831936      2.3705850
```

Erbes and Boland VCPR TS

```
Gaussian'09: B3LYP/6-31G*, G = -628.163404, iv = i262, S^2 = 0.7753
```

```
 Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
   ---------    ------------- ------------- -------------

  1  C   C            0.1797769      2.4851927     -1.7655285
  2  C   C2          -0.9439639      1.7209381     -1.7531359
  3  C   C3          -0.9491965      0.4305106     -1.1524093
  4  C   C4           1.4649215      1.8489004     -1.3421135
  5  C   C5           1.5881396      0.4198029     -1.7923096
  6  H   H            0.2052781      3.5166479     -2.1001947
  7  H   H7          -1.8549081      2.0559026     -2.2452659
  8  H   H12          1.1815084      0.1887807     -2.7706469
  9  F   F1           2.5279271      2.5825422     -1.8433748
 10  F   F2           1.6191634      1.9073752      0.0413634
 11  C   C1           2.4997100     -0.4644860     -1.1820841
 12  H   H3           2.9522971     -0.1411655     -0.2469181
 13  C   C6           2.8111653     -1.7003805     -1.6762756
 14  H   H2           3.4993201     -2.3607789     -1.1585262
 15  H   H4           2.3740126     -2.0681877     -2.6010585
 16  H   H16         -1.7373684     -0.2135955     -1.5598184
 17  C   C7          -0.4063762     -0.1645800      0.0803931
 18  H   H1           0.3309212      0.4487369      0.5844297
 19  H   H5           0.0334044     -1.1397334     -0.1532436
 20  C   C8          -1.5525354     -0.3853769      1.0822626
 21  H   H8          -2.3197989     -1.0295050      0.6341871
 22  H   H9          -2.0358990      0.5747139      1.3037845
 23  C   C9          -1.0461147     -1.0194032      2.3778715
 24  H   H6          -0.2876426     -0.3746243      2.8368189
 25  H   H10         -0.5660855     -1.9803051      2.1590619
 26  C   C10         -2.1775044     -1.2408641      3.3689390
```

```
 27 H   H11          -1.7931010    -1.6945214     4.2878153
 28 H   H13          -2.9384534    -1.9088238     2.9528676
 29 H   H14          -2.6585977    -0.2937128     3.6331091
```

Erbes and Boland [3,3] TS

```
Gaussian'09: B3LYP/6-31G*, G = -628.172483, iv = i284

Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C1           -0.7635387     1.2387820     2.6379056
  2 H   H3           -0.9712143     0.1953323     2.4383484
  3 C   C2            0.5214959     1.6455185     2.9610528
  4 C   C5            0.5149436     1.7746469    -0.0281305
  5 H   H7            0.6413982     2.7611400    -0.4746427
  6 C   C6           -0.7712610     1.3484632     0.2653336
  7 C   C3            1.6749619     1.1534769     0.4440985
  8 C   C4            1.6800959     1.0703481     2.4308735
  9 C   C11           1.6956791    -0.0067176     1.3906396
 10 H   H2            2.6396795     1.5699725     0.1427050
 11 H   H10           2.6460830     1.4328050     2.7921912
 12 H   H17          -1.6195833     1.9563442    -0.0370334
 13 H   H1           -1.6149759     1.8093846     2.9985664
 14 H   H11           0.6397727     2.5236634     3.5908744
 15 F   F1            0.5830745    -0.8275205     1.3577380
 16 F   F2            2.8511190    -0.7659216     1.3551840
 17 C   C7           -1.2869475    -0.1133111    -0.2617409
 18 H   H5           -2.3310062     0.0417838    -0.5682532
 19 H   H6           -1.3322165    -0.8273506     0.5612621
 20 C   C8           -0.4980649    -0.6330584    -1.4586575
 21 H   H4            0.5484327    -0.7963460    -1.1815678
 22 H   H8           -0.5024572     0.1240830    -2.2517814
 23 C   C9           -1.0898539    -1.9387801    -1.9875949
 24 H   H12          -2.1338189    -1.7826954    -2.2833101
 25 H   H13          -1.0864397    -2.6963103    -1.1951802
 26 C   C10          -0.3067223    -2.4618498    -3.1811563
 27 H   H9            0.7352312    -2.6601956    -2.9103080
 28 H   H14          -0.3167139    -1.7397327    -4.0038203
 29 H   H15          -0.7471530    -3.3959545    -3.5435962
```

Gaich trans VCP SM (50)

```
Gaussian'09: B3LYP/6-31G*, G = -1145.573154, iv = none

Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C1            1.6197059    -0.8005199    -2.6549743
  2 C   C2            0.5016609    -0.3525236    -1.8018160
  3 C   C3            0.8278940    -1.9065505    -2.0489682
  4 H   H3           -0.3659227    -0.0185463    -2.3700799
  5 H   H6            1.2947686    -2.3804072    -1.1892069
  6 C   C10          -0.0928219    -2.7135757    -2.8524589
```

```
  7 H   H11         -0.4787172    -2.2731209    -3.7704171
  8 C   C11         -0.5030457    -3.9515410    -2.5331951
  9 H   H12         -0.1589228    -4.4670044    -1.6412409
 10 C   C4           0.6945669     0.2400464    -0.4671944
 11 C   C5           1.7838202     0.8462710     0.1349866
 12 C   C6           1.3939455     1.2356385     1.4455614
 13 C   C7           0.0791243     0.8580797     1.6156185
 14 H   H1           2.7485014     0.9944472    -0.3271107
 15 N   N1          -0.3373923     0.2577674     0.4529992
 16 H   H4           2.6578182    -0.6578100    -2.3337691
 17 H   H7           1.5407672    -0.6324651    -3.7351328
 18 H   H10         -1.1996851    -4.4813017    -3.1751735
 19 C   C8          -0.5815492     1.1320459     2.8351548
 20 C   C12          1.4364990     2.1607410     3.6885985
 21 C   C13          2.0869119     1.8917182     2.4846385
 22 C   C14          0.1140458     1.7824750     3.8598686
 23 H   H13          3.1242060     2.1867092     2.3504244
 24 H   H14         -0.3886491     1.9853945     4.8031395
 25 H   H16         -1.6118828     0.8380517     3.0161146
 26 H   H18          1.9693372     2.6622921     4.4922558
 27 S   S1          -2.0091027    -0.0544889     0.1539555
 28 O   O1          -2.1126963    -0.8254080    -1.0678739
 29 O   O2          -2.5459969    -0.5894233     1.3920482
 30 C   C9          -2.7561756     1.5265115    -0.1429219
 31 H   H2          -2.2740572     1.9858205    -1.0079086
 32 H   H5          -2.6400932     2.1531404     0.7424699
 33 H   H8          -3.8168623     1.3675366    -0.3483918
```

Gaich cis VCP SM (cis-50)

```
Gaussian'09: B3LYP/6-31G*, G = -1145.574428, iv = none

Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C1           0.5772912    -2.0168209    -2.6912849
  2 C   C2          -0.4755920    -1.4227026    -1.8065477
  3 C   C3           0.1486847    -0.6115404    -2.9341770
  4 H   H6          -0.5652451    -0.4887302    -3.7446853
  5 C   C10          1.0297737     0.5175099    -2.6283467
  6 H   H11          1.8128888     0.3591332    -1.8886099
  7 C   C11          0.9343620     1.7352010    -3.1859273
  8 H   H12          0.1886167     1.9741007    -3.9385868
  9 C   C4          -0.1797073    -1.0976278    -0.3127173
 10 C   C5           0.8118500    -1.6934701     0.4355737
 11 C   C6           0.7786294    -1.1265360     1.7382202
 12 C   C7          -0.2780851    -0.2076168     1.7758048
 13 H   H1           1.5091388    -2.4445218     0.0876724
 14 N   N1          -0.8679872    -0.2463571     0.5217833
 15 H   H4           0.3076245    -2.7846842    -3.4253706
 16 H   H7           1.5763829    -2.1850111    -2.3024834
 17 H   H10          1.6182629     2.5265533    -2.8958751
 18 C   C8          -0.5639331     0.5245644     2.9441336
 19 C   C12          1.2864664    -0.5905565     4.0494810
 20 C   C13          1.5661520    -1.3194300     2.8908299
```

```
 21 C  C14          0.2348618     0.3177570     4.0731321
 22 H  H13          2.3878390    -2.0303952     2.8816971
 23 H  H14          0.0211906     0.8691525     4.9865939
 24 H  H16         -1.3946649     1.2226822     3.0002371
 25 H  H18          1.8924320    -0.7413470     4.9396372
 26 S  S1          -2.1152702     0.8215448     0.0447368
 27 O  O1          -2.5640956     0.3965081    -1.2676831
 28 O  O2          -3.0458025     0.8515416     1.1593617
 29 C  C9          -1.3897601     2.4303800    -0.1089514
 30 H  H2          -0.5860389     2.3920360    -0.8420049
 31 H  H5          -1.0075041     2.7484702     0.8619686
 32 H  H8          -2.1659855     3.1214365    -0.4444398
 33 H  H9          -1.4827759    -1.8012238    -1.9731721
```

```
Gaich cis VCPR TS 50
Gaussian'09: B3LYP/6-31G*, G = -1145.512932, iv = i451, S^2 = 0.7540

 Cartesian Coordinates (Angstroms)
      Atom            X             Y             Z
   ---------    ------------- ------------- -------------

  1 C  C           -3.2306126     2.4446878     0.6697624
  2 C  C2          -4.2202822     1.5011075     0.6738103
  3 C  C3          -3.9420378     0.1216369     0.7867193
  4 C  C4          -1.8298021     1.9937313     0.5249219
  5 C  C5          -1.6742598     0.8913056    -0.4753325
  6 H  H           -3.4311433     3.5154477     0.6530915
  7 H  H7          -5.2604059     1.7955217     0.5457293
  8 H  H8          -3.0671211    -0.2330688     1.3138945
  9 H  H12         -2.4248628     0.8236220    -1.2494718
 10 C  C1          -0.4596443     0.2321306    -0.6776137
 11 C  C6          -0.2005191    -0.4626763    -1.8531098
 12 C  C7           1.1697130    -0.8601541    -1.8616532
 13 C  C8           1.7273980    -0.4742062    -0.6391548
 14 H  H3          -0.8602812    -0.6009484    -2.7062280
 15 N  N1           0.6809631     0.0224647     0.0816724
 16 H  H2          -1.4017182     1.6667809     1.4794185
 17 H  H4          -1.1848019     2.8381787     0.2564089
 18 H  H13         -4.7016903    -0.6156509     0.5029046
 19 C  C9           3.0889678    -0.6561729    -0.3579910
 20 C  C11          1.9799289    -1.4934810    -2.8204477
 21 C  C12          3.3318649    -1.6992840    -2.5376187
 22 C  C13          3.8768732    -1.2773033    -1.3304490
 23 H  H1           3.5714265    -0.3184691     0.5560382
 24 H  H14          1.5919290    -1.8166411    -3.7863838
 25 H  H15          3.9740948    -2.1817240    -3.2767897
 26 H  H17          4.9426785    -1.4328413    -1.1485794
 27 S  S1           0.5609192     0.0277857     1.7628150
 28 O  O1           0.7534589     1.4339937     2.0410944
 29 O  O2          -0.8212567    -0.4545720     1.8865347
 30 C  C10          1.7027156    -1.0271505     2.6098716
 31 H  H5           2.7004349    -0.5918645     2.5708941
 32 H  H6           1.6764925    -2.0178412     2.1536728
 33 H  H9           1.3805806    -1.0943451     3.6515687
```

Gaich cis [3,3] TS

```
Gaussian'09: B3LYP/6-31G*, G = -1145.535705, iv = i388

Cartesian Coordinates (Angstroms)
      Atom             X            Y            Z
   ---------    ------------- ------------- -------------

  1 C   C1          -0.5354495    -0.9954063    -0.6005013
  2 H   H3          -0.6066520    -2.0631530    -0.7723441
  3 C   C2           0.7837370    -0.5430534    -0.1823152
  4 C   C5           0.5332369    -0.1362140    -3.0944368
  5 H   H7           0.5127026     0.8715480    -3.5066809
  6 C   C6          -0.6930158    -0.6444662    -2.5707256
  7 H   H6          -0.9282083    -1.6827987    -2.7742534
  8 C   C3           1.7525154    -0.7429426    -2.9246180
  9 C   C4           1.9459117    -1.0599260    -0.7440129
 10 C   C11          1.9810344    -1.8681167    -1.9859001
 11 H   H2           2.6585646    -0.2828496    -3.3108351
 12 H   H10          2.9153312    -0.6781863    -0.4285817
 13 C   C9          -1.5088898    -0.2812568     0.1619200
 14 C   C8          -0.8226449     0.6792747     0.7617455
 15 N   N2           0.5383226     0.6398357     0.6569621
 16 H   H11         -1.5487914     0.0329326    -2.6707005
 17 H   H16          1.2454242    -2.6784578    -2.0445588
 18 H   H17          2.9656358    -2.3250472    -2.1375266
 19 C   C7          -2.9003677    -0.4601979     0.3202661
 20 C   C12         -1.5704315     1.6188409     1.5337430
 21 C   C13         -2.9562851     1.4943808     1.6866126
 22 C   C14         -3.6226375     0.4435674     1.0905411
 23 H   H1          -3.4073908    -1.2784191    -0.1831761
 24 H   H13         -1.0869852     2.4573567     2.0308196
 25 H   H14         -3.5021339     2.2237180     2.2799495
 26 H   H18         -4.6966160     0.3318542     1.2055523
 27 S   S1           1.6919267     1.3908105     1.6402702
 28 O   O1           2.9810173     1.1549805     1.0178166
 29 O   O2           1.2241193     2.7472334     1.8558173
 30 C   C10          1.6640816     0.5328646     3.1908993
 31 H   H4           2.4112996     0.9875830     3.8445906
 32 H   H5           1.9092720    -0.5166522     3.0180000
 33 H   H8           0.6723665     0.6303628     3.6356613
```

Sustmann VCP INT (51)

```
Gaussian'09: B3LYP/6-31G*, G = -888.147718, iv = none

Cartesian Coordinates (Angstroms)
      Atom             X            Y            Z
   ---------    ------------- ------------- -------------

  1 C   C1           2.3755578     0.2955231    -0.2584893
  2 C   C2           1.2437991     1.0453606     0.3458963
  3 C   C3           1.3323679    -0.5400432     0.4099371
  4 H   H6           1.6293956    -0.9742177     1.3626546
  5 C   C4           1.4964683     1.7754558     1.6444639
  6 C   C5           1.8975463     3.2280305     4.0133341
```

```
  7 C   C6            0.8125100     1.4295389     2.8153903
  8 C   C7            2.3868173     2.8567642     1.6736107
  9 C   C8            2.5863915     3.5777389     2.8501506
 10 C   C9            1.0098482     2.1516013     3.9932360
 11 H   H4            0.1036468     0.6053497     2.8103845
 12 H   H7            2.9165295     3.1509523     0.7712183
 13 H   H8            3.2746411     4.4187474     2.8602973
 14 H   H9            0.4670704     1.8787003     4.8943076
 15 C   C10           0.4351634    -1.3920948    -0.3825193
 16 H   H11           0.2058968    -1.0547255    -1.3920468
 17 C   C11          -0.0839051    -2.5499123     0.0539730
 18 H   H12           0.1640927    -2.9173582     1.0465816
 19 H   H16           2.0497456     3.7930719     4.9286282
 20 C   C14           0.2132182     1.6866706    -0.5526569
 21 C   C15          -1.7178629     2.9752724    -2.1327952
 22 C   C16          -1.1528020     1.5122024    -0.2929265
 23 C   C17           0.6003696     2.5164918    -1.6128682
 24 C   C18          -0.3601727     3.1563232    -2.3974298
 25 C   C19          -2.1121947     2.1501502    -1.0775961
 26 H   H2           -1.4740149     0.8847489     0.5348762
 27 H   H1            1.6540170     2.6825218    -1.8205484
 28 H   H3           -0.0491263     3.8026883    -3.2139870
 29 H   H10          -3.1683130     2.0104767    -0.8629331
 30 H   H15          -2.4648964     3.4766167    -2.7418699
 31 H   H17           3.3513352     0.3428039     0.2164551
 32 H   H18           2.4593056     0.2393659    -1.3395042
 33 C   C12          -0.9860671    -3.3988915    -0.7362677
 34 C   C13          -2.7262649    -5.0860924    -2.1560505
 35 C   C20          -1.9629416    -2.8637967    -1.5869450
 36 C   C21          -0.9080837    -4.7900142    -0.5908611
 37 C   C22          -1.7697516    -5.6296747    -1.3013609
 38 C   C23          -2.8248758    -3.7035835    -2.2971076
 39 H   H5           -2.0707841    -1.7874104    -1.6994879
 40 H   H13          -0.1679214    -5.2335634     0.0711705
 41 H   H14          -1.6932297    -6.7074940    -1.1856945
 42 H   H19          -3.5754602    -3.2756175    -2.9563243
 43 H   H20          -3.3970656    -5.7386774    -2.7082956
```

Sustmann VCPR TS

```
Gaussian'09: B3LYP/6-31G*, G = -888.098339, iv = i201, S^2 = 0.6849
```

```
 Cartesian Coordinates (Angstroms)
      Atom              X             Y             Z
   ---------    ------------- ------------- -------------

  1 C   C            -0.0269135     3.0322724     0.3651644
  2 C   C2           -1.2103563     2.3679144     0.2763010
  3 C   C3           -1.3598391     1.0609182     0.8066873
  4 C   C4            1.1643584     2.2883003     0.8799909
  5 C   C5            1.2656103     0.8437567     0.3874205
  6 H   H             0.1194959     4.0502385     0.0037539
  7 H   H7           -2.0512600     2.8004308    -0.2622636
  8 H   H8           -0.8618118     0.7599148     1.7159615
  9 C   C1            1.8909915    -0.1792479     1.2367267
 10 C   C6            3.1268072    -2.1941215     2.8018338
```

```
 11 C   C7          2.8555473   -1.0583675    0.6862312
 12 C   C8          1.5786590   -0.3413779    2.6086037
 13 C   C9          2.1831999   -1.3353085    3.3704229
 14 C   C10         3.4634290   -2.0451617    1.4550234
 15 H   H2          3.2210392   -0.9799177   -0.3384494
 16 H   H6          0.8868435    0.2999722    3.1447167
 17 H   H5          1.9531260   -1.4530058    4.4328034
 18 H   H3          4.2224089   -2.7040790    1.0248655
 19 H   H4          3.6127696   -2.9629314    3.4072836
 20 C   C13         1.1695655    0.6288107   -1.0564075
 21 C   C14         0.8724646    0.1772572   -3.8342089
 22 C   C15         1.3872637    1.6643669   -1.9941773
 23 C   C16         0.8072404   -0.6456949   -1.5612241
 24 C   C17         0.6575959   -0.8646435   -2.9225151
 25 C   C18         1.2380126    1.4360556   -3.3620031
 26 H   H11         1.8179670    2.6327972   -1.7364651
 27 H   H12         0.6492528   -1.5164453   -0.9209106
 28 H   H13         0.4119018   -1.8580422   -3.3112913
 29 H   H14         1.4735600    2.2149849   -4.0950196
 30 H   H15         0.7975208   -0.0117358   -4.9092232
 31 H   H16         1.1167981    2.3143977    1.9749587
 32 H   H17         2.0788858    2.8248769    0.5980375
 33 C   C11        -2.5255896    0.0640594    0.3526260
 34 C   C12        -4.4846969   -1.7852412   -0.3841672
 35 C   C19        -3.3685840    0.3320269   -0.7365100
 36 C   C20        -2.6731429   -1.1355713    1.0686093
 37 C   C21        -3.6530577   -2.0555931    0.6977398
 38 C   C22        -4.3461298   -0.5980304   -1.0985063
 39 H   H1         -3.3329778    1.2302020   -1.3474036
 40 H   H9         -2.0583888   -1.3923795    1.9312546
 41 H   H10        -3.7896071   -2.9892860    1.2506341
 42 H   H18        -5.0219184   -0.4118401   -1.9386429
 43 H   H19        -5.2580407   -2.5055313   -0.6682614
```

Sustmann [3,3] TS

Gaussian'09: B3LYP/6-31G*, G = -888.090641, iv = i385

```
Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C1         -1.2158865   -0.8522870    0.6734974
  2 H   H3         -1.3659523   -1.9166506    0.5611198
  3 C   C2          0.1150097   -0.4688105    1.1492486
  4 C   C5          0.0978896   -0.3876310   -1.8956387
  5 H   H7          0.1774585    0.5334981   -2.4694213
  6 C   C6         -1.2103261   -0.7329575   -1.4271119
  7 H   H6         -1.4932838   -1.7755982   -1.4772134
  8 C   C7          0.2240385    0.6918035    1.9983036
  9 H   H4          1.2171496    1.0043791    2.3117403
 10 C   C8         -0.8770135    1.3972592    2.3822541
 11 H   H9         -0.7685821    2.2777066    3.0096368
 12 C   C9         -2.1886048    0.9813351    1.9764615
 13 H   H11        -3.0535724    1.5319291    2.3363479
 14 C   C10        -2.3519991   -0.1175903    1.1885447
```

```
 15  H   H12          -3.3447091    -0.4637382     0.9187841
 16  C   C3            1.2469468    -1.0393722    -1.5551573
 17  C   C4            1.2607021    -1.1104314     0.7250007
 18  C   C11           1.3457780    -2.0311061    -0.4447914
 19  H   H2            2.2062929    -0.6862884    -1.9217102
 20  H   H13           0.5763900    -2.8114049    -0.4645882
 21  H   H14           2.3145953    -2.5432517    -0.4625649
 22  C   C14           2.6763274    -0.7228923     1.2349276
 23  C   C15           5.2516079    -0.0650837     2.1853548
 24  C   C16           3.2742115    -1.4487114     2.2797424
 25  C   C17           3.4072101     0.3442956     0.6815639
 26  C   C18           4.6813961     0.6713438     1.1505058
 27  C   C19           4.5482476    -1.1250240     2.7515672
 28  H   H10           2.7323243    -2.2771313     2.7313969
 29  H   H15           2.9668480     0.9359623    -0.1181157
 30  H   H16           5.2249259     1.5026153     0.7094284
 31  H   H17           4.9883312    -1.7004903     3.5615061
 32  H   H18           6.2423913     0.1887231     2.5524460
 33  C   C12          -2.3385948     0.1661957    -1.9295166
 34  C   C13          -4.4027784     1.7976193    -2.8176402
 35  C   C20          -2.2398596     1.5472552    -1.7738149
 36  C   C21          -3.4616944    -0.4095593    -2.5177089
 37  C   C22          -4.4965870     0.4116445    -2.9657211
 38  C   C23          -3.2759898     2.3659111    -2.2200140
 39  H   H1           -1.3679619     1.9698680    -1.2846959
 40  H   H5           -3.5283929    -1.4856102    -2.6323173
 41  H   H8           -5.3756705    -0.0270590    -3.4301205
 42  H   H19          -3.2076139     3.4431710    -2.0960297
 43  H   H20          -5.2109992     2.4361639    -3.1654863
```

Ichikawa VCP INT (52)

Gaussian'09: B3LYP/6-31G*, G = -1108.506583, iv = none

```
Cartesian Coordinates (Angstroms)
      Atom              X             Y             Z
   ---------    ------------- ------------- -------------

   1  C   C1            2.2910281     2.0104097    -1.1886598
   2  C   C2            1.1414659     2.7184398    -0.6052825
   3  C   C3            1.2667689     1.1588629    -0.5050026
   4  C   C10           0.3642447     0.3076408    -1.2924739
   5  H   H11           0.0800168     0.6873774    -2.2712185
   6  C   C11          -0.1509008    -0.8557149    -0.8695280
   7  H   H12           0.1025203    -1.2572522     0.1062422
   8  C   C4           -1.0821648    -1.6724113    -1.6593521
   9  C   C5           -2.8682629    -3.3006439    -3.0877385
  10  C   C6           -0.9100064    -1.8836438    -3.0334648
  11  C   C7           -2.1480908    -2.3047403    -1.0065605
  12  C   C8           -3.0403695    -3.1103883    -1.7182796
  13  C   C9           -1.8020244    -2.6901298    -3.7449847
  14  H   H3           -0.0731336    -1.4334427    -3.5615838
  15  H   H4           -2.2975245    -2.1679229     0.0620295
  16  H   H5           -3.8678956    -3.5900222    -1.2022587
  17  H   H7           -1.6594109    -2.8458606    -4.8111041
  18  H   H8           -3.5610375    -3.9289132    -3.6413769
```

```
 19 H   H9              1.3255102     3.3309280     0.2670203
 20 H   H10             0.3916141     3.1226335    -1.2753837
 21 O   O1              1.7880427     0.6696859     0.7730615
 22 Si  Si1             0.9911971     0.9088461     2.2335392
 23 C   C12             1.0619693    -0.6762027     3.2549177
 24 H   H13             2.1006089    -0.9713172     3.4299155
 25 H   H15             0.5540851    -1.4914534     2.7316314
 26 H   H16             0.5751629    -0.5302304     4.2235639
 27 C   C13            -0.8176967     1.3790454     2.0350855
 28 H   H6             -1.2795211     1.5279189     3.0159549
 29 H   H17            -1.3734971     0.5922526     1.5178984
 30 H   H18            -0.9244139     2.3079912     1.4682959
 31 C   C14             1.8461939     2.2653271     3.2230294
 32 H   H14             2.8988511     2.0148413     3.3836261
 33 H   H19             1.3676965     2.3868878     4.1992625
 34 H   H20             1.7962275     3.2212932     2.6945525
 35 F   F1              3.5239867     2.1531621    -0.5786402
 36 F   F2              2.3887598     1.9467462    -2.5667325
```

Ichikawa VCPR TS

Gaussian'09: B3LYP/6-31G* using scf=(qcverytight) and guess=(mix,always,densitymix) in input line, G = -1108.460735, iv = i109, S^2 = 0.79

```
Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C               1.9137391     1.1672811     0.4623618
  2 C   C2              0.7982840     0.3787391     0.4386759
  3 C   C3              0.7719369    -0.8931799     1.0544091
  4 C   C4              3.1968266     0.5748901     0.9540772
  5 C   C5              3.4120343    -0.8159359     0.4684891
  6 H   H               1.9254320     2.1927805     0.1088231
  7 H   H8              1.4043016    -1.1230086     1.9018355
  8 H   H12             3.0581443    -1.0949354    -0.5151967
  9 H   H4              4.2350300    -1.3872942     0.9128354
 10 O   O3             -0.3890101     0.7109659    -0.1542352
 11 Si  Si1            -0.7786309     2.1508656    -0.9389403
 12 C   C1             -0.6701825     3.5884769     0.2476550
 13 H   H7             -1.3026780     3.4129458     1.1232011
 14 H   H11            -1.0122807     4.5094809    -0.2345161
 15 H   H13             0.3508105     3.7575846     0.5985019
 16 C   C6              0.3729825     2.4152865    -2.3902891
 17 H   H5              0.3692404     1.5399622    -3.0469016
 18 H   H14             1.4026811     2.5957345    -2.0723966
 19 H   H15             0.0509264     3.2797206    -2.9791621
 20 C   C7             -2.5316834     2.0200185    -1.5819238
 21 H   H6             -3.2343665     1.8577902    -0.7591750
 22 H   H16            -2.6260887     1.1830513    -2.2802412
 23 H   H17            -2.8233725     2.9357156    -2.1047400
 24 C   C8             -0.3347065    -2.0859988     0.8493571
 25 C   C9             -2.1173226    -4.2323675     0.6236915
 26 C   C10            -1.3177024    -2.0818909    -0.1502703
 27 C   C11            -0.2485493    -3.1829850     1.7262542
```

```
 28  C   C12          -1.1408365     -4.2489898      1.6126115
 29  C   C13          -2.2062767     -3.1567098     -0.2549064
 30  H   H1           -1.4565368     -1.3088833     -0.8971375
 31  H   H9            0.4835660     -3.2459843      2.5313231
 32  H   H10          -1.0931269     -5.1014248      2.2961903
 33  H   H18          -2.9836290     -3.1763755     -1.0247698
 34  H   H19          -2.8191322     -5.0675515      0.5381456
 35  F   F1            4.2306300      1.3778540      0.6270610
 36  F   F2            3.1095464      0.5543711      2.3093024
```

Hammett Plot

p_NMe2_SM (S1a)

```
G = -986.405584
iv = none

Cartesian Coordinates (Angstroms)
      Atom              X              Y              Z
   ---------    ------------- ------------- -------------


  1  C   C1            1.5584825      0.1025224     -2.3886327
  2  C   C2            0.4103350      0.6021148     -1.6087786
  3  C   C3            0.6679862     -0.9553396     -1.8292907
  4  H   H3           -0.3986704      0.9730780     -2.2377576
  5  H   H6            1.0586619     -1.4515965     -0.9442274
  6  C   C4            0.5001002      1.1869267     -0.2380093
  7  C   C5            0.5732065      2.3190323      2.3824332
  8  C   C6           -0.5615688      1.0151570      0.6614430
  9  C   C7            1.6000107      1.9356895      0.1982475
 10  C   C8            1.6435293      2.4858832      1.4755522
 11  C   C9           -0.5345924      1.5585553      1.9391770
 12  H   H4           -1.4287926      0.4329341      0.3574701
 13  H   H7            2.4449454      2.0864268     -0.4648848
 14  H   H8            2.5221955      3.0502945      1.7635900
 15  H   H9           -1.3797019      1.3873351      2.5950487
 16  C   C10          -0.2340745     -1.7296817     -2.6860464
 17  H   H11          -0.5575400     -1.2745917     -3.6205935
 18  C   C11          -0.6941664     -2.9563111     -2.3925762
 19  H   H12          -0.4109535     -3.4788213     -1.4834960
 20  C   C12          -1.6147289     -3.6494885     -3.3153280
 21  O   O1           -2.0354075     -3.2116057     -4.3698009
 22  O   O2           -1.9500367     -4.8718127     -2.8302762
 23  C   C13          -2.8426018     -5.6310552     -3.6570646
 24  H   H5           -3.7770573     -5.0862991     -3.8173613
 25  H   H13          -3.0270436     -6.5595776     -3.1153547
 26  H   H14          -2.3854629     -5.8382771     -4.6289032
 27  F   F1            1.5632782      0.3054300     -3.7284662
 28  F   F2            2.8228242      0.2003465     -1.9124621
 29  N   N1            0.6028731      2.8829986      3.6510640
 30  C   C14           1.8395244      3.4710273      4.1367540
 31  H   H1            2.1484069      4.3141581      3.5067625
 32  H   H10           2.6710701      2.7489363      4.1695523
 33  H   H15           1.6805189      3.8558945      5.1459552
 34  C   C15          -0.4124265      2.5103263      4.6210870
 35  H   H2           -0.2419652      3.0633957      5.5468705
```

```
 36  H   H16          -0.4061960     1.4336214     4.8563569
 37  H   H17          -1.4149619     2.7723735     4.2619463
```

NMe2_TS2 (S-TS1a)

```
G = -986.371766
iv = i75
S^2 = 0.4500

                       Cartesian Coordinates (Angstroms)
       Atom              X             Y             Z
    ---------     ------------- ------------- -------------

  1  C   C            -1.7257165     3.6608005    -1.0708224
  2  C   C2           -2.8870564     2.9448482    -1.1483783
  3  C   C3           -3.0524220     1.7261259    -0.4506724
  4  C   C4           -0.5565938     3.0194769    -0.4159069
  5  C   C5           -0.3836554     1.5979954    -0.8610707
  6  H   H            -1.6022001     4.6557693    -1.4838963
  7  H   H7           -3.6991650     3.2728347    -1.7948143
  8  H   H8           -2.5315502     1.5364955     0.4779677
  9  H   H12          -0.8743979     1.3410869    -1.7900136
 10  F   F1            0.5982312     3.7432144    -0.6825366
 11  F   F2           -0.6580277     3.0804251     0.9893451
 12  C   C1            0.6067414     0.7159363    -0.3745757
 13  C   C6            2.5419146    -1.1846315     0.5589313
 14  C   C7            0.8259172    -0.5246276    -1.0369708
 15  C   C8            1.4021316     0.9650054     0.7809334
 16  C   C9            2.3374050     0.0555558     1.2252386
 17  C   C10           1.7498539    -1.4449934    -0.5932123
 18  H   H2            0.2369406    -0.7532016    -1.9219840
 19  H   H6            1.2651172     1.8922670     1.3235701
 20  H   H5            2.9141905     0.2991633     2.1095642
 21  H   H3            1.8633518    -2.3748420    -1.1375105
 22  C   C11          -4.0928551     0.7828418    -0.8453818
 23  O   O1           -4.8594126     0.9119027    -1.7888919
 24  O   O2           -4.1147561    -0.3020953    -0.0188599
 25  C   C12          -5.0906560    -1.2947775    -0.3485181
 26  H   H1           -6.1040563    -0.8931400    -0.2514844
 27  H   H9           -4.9354454    -2.1081869     0.3623164
 28  H   H10          -4.9537390    -1.6503536    -1.3741766
 29  N   N1            3.4629040    -2.0964084     1.0116655
 30  C   C13           3.6322520    -3.3693753     0.3261360
 31  H   H4            4.4017447    -3.9509484     0.8352652
 32  H   H13           3.9474534    -3.2280999    -0.7162523
 33  H   H14           2.7040599    -3.9568964     0.3266268
 34  C   C14           4.2471670    -1.8172132     2.2061765
 35  H   H11           4.9151404    -2.6574804     2.3998742
 36  H   H15           3.6075847    -1.6789864     3.0885939
 37  H   H16           4.8616043    -0.9154872     2.0837247
```

pNH2_SM (S1b)

```
G = -907.846024
iv = none

Cartesian Coordinates (Angstroms)
       Atom             X              Y              Z
    ---------    ------------- ------------- -------------

   1 C   C1           1.6851610     0.1319418    -1.5815304
   2 C   C2           0.6384108     0.9359312    -0.9216993
   3 C   C3           0.6730599    -0.6463225    -0.8066263
   4 H   H3          -0.1322477     1.2860880    -1.6088658
   5 H   H6           1.0203339    -0.9992078     0.1615377
   6 C   C4           0.8805428     1.7764293     0.2902526
   7 C   C5           1.2586871     3.4160653     2.5710386
   8 C   C6          -0.0743025     1.8211479     1.3164424
   9 C   C7           2.0281729     2.5685850     0.4268111
  10 C   C8           2.2176801     3.3742094     1.5456268
  11 C   C9           0.1049242     2.6230367     2.4372474
  12 H   H4          -0.9719102     1.2120028     1.2378336
  13 H   H7           2.7894641     2.5492299    -0.3465061
  14 H   H8           3.1164852     3.9816222     1.6268973
  15 H   H9          -0.6525406     2.6419044     3.2180763
  16 C   C10         -0.3479446    -1.4519089    -1.4842468
  17 H   H11         -0.6428478    -1.1489419    -2.4876272
  18 C   C11         -0.9455504    -2.5303317    -0.9540096
  19 H   H12         -0.7023801    -2.9010621     0.0376269
  20 C   C12         -1.9715553    -3.2674690    -1.7192850
  21 O   O1          -2.3657116    -2.9917879    -2.8367407
  22 O   O2          -2.4387865    -4.3209899    -1.0030180
  23 C   C13         -3.4418486    -5.1077992    -1.6601821
  24 H   H5          -4.2967329    -4.4869973    -1.9414600
  25 H   H13         -3.7395441    -5.8681781    -0.9370796
  26 H   H14         -3.0349725    -5.5754868    -2.5614979
  27 F   F1           1.6792664     0.0435328    -2.9332927
  28 F   F2           2.9618784     0.1596004    -1.1329688
  29 N   N1           1.4187425     4.2650383     3.6670814
  30 H   H2           0.9101470     3.9942771     4.4993782
  31 H   H1           2.3759190     4.5158404     3.8807859
```

pNH2_TS2 (S-TS1b)

```
G = -907.811148
iv = i93
S^2 = 0.4444

 Cartesian Coordinates (Angstroms)
       Atom             X              Y              Z
    ---------    ------------- ------------- -------------

   1 C   C           -1.0033632     3.1014530    -0.7660046
   2 C   C2          -2.1485900     2.3610330    -0.8316443
   3 C   C3          -2.2708494     1.1339810    -0.1359989
   4 C   C4           0.1839831     2.4738482    -0.1310559
   5 C   C5           0.3705269     1.0576570    -0.5915524
```

```
  6 H   H           -0.9033214     4.1003023    -1.1761130
  7 H   H7          -2.9780636     2.6709029    -1.4646857
  8 H   H8          -1.7499928     0.9640771     0.7962412
  9 H   H12         -0.1191565     0.8072066    -1.5228758
 10 F   F1           1.3244981     3.2147033    -0.4056469
 11 F   F2           0.0981061     2.5204954     1.2754407
 12 C   C1           1.3963136     0.1950264    -0.1345531
 13 C   C6           3.4137602    -1.6272165     0.7115376
 14 C   C7           1.6470497    -1.0214553    -0.8308863
 15 C   C8           2.2002934     0.4568797     1.0128273
 16 C   C9           3.1820342    -0.4235911     1.4158791
 17 C   C10          2.6207714    -1.9087996    -0.4239561
 18 H   H2           1.0484108    -1.2537662    -1.7080921
 19 H   H6           2.0335083     1.3660344     1.5770487
 20 H   H5           3.7873072    -0.1954740     2.2905431
 21 H   H3           2.7895711    -2.8287797    -0.9791327
 22 C   C11         -3.2961996     0.1690414    -0.5228418
 23 O   O1          -4.0604403     0.2788837    -1.4702046
 24 O   O2          -3.3086894    -0.9043195     0.3167099
 25 C   C12         -4.2820913    -1.9058321     0.0036247
 26 H   H1          -5.2961855    -1.5047171     0.0952275
 27 H   H9          -4.1241115    -2.7069217     0.7274931
 28 H   H10         -4.1449068    -2.2768805    -1.0163953
 29 N   N1           4.4201155    -2.4844004     1.0969438
 30 H   H4           4.7824353    -2.3941872     2.0359887
 31 H   H11          4.3872762    -3.4351844     0.7561341
```

pOH_SM (S1c)

```
G = -927.720966
iv = none

 Cartesian Coordinates (Angstroms)
       Atom             X            Y            Z
    ---------     ------------- ------------- -------------

  1 C   C1           1.7176635     0.7049715    -1.2705558
  2 C   C2           0.5244052     1.2429854    -0.5888208
  3 C   C3           0.8191476    -0.3143685    -0.6521193
  4 H   H3          -0.2658900     1.5445537    -1.2763492
  5 H   H6           1.1813468    -0.7248364     0.2875717
  6 C   C4           0.5664812     1.9608276     0.7219435
  7 C   C5           0.5510370     3.3453453     3.1697163
  8 C   C6          -0.4413795     1.7357997     1.6732258
  9 C   C7           1.5661187     2.8935809     1.0212313
 10 C   C8           1.5625457     3.5815466     2.2345678
 11 C   C9          -0.4569616     2.4159899     2.8847103
 12 H   H4          -1.2238110     1.0124494     1.4576288
 13 H   H7           2.3594454     3.0816508     0.3057250
 14 H   H8           2.3489012     4.3021003     2.4524849
 15 H   H9          -1.2354174     2.2422225     3.6207104
 16 C   C10         -0.0256227    -1.1835437    -1.4787692
 17 H   H11         -0.3308351    -0.8084850    -2.4543328
 18 C   C11         -0.4506697    -2.4033908    -1.1162162
 19 H   H12         -0.1849613    -2.8529013    -0.1637986
 20 C   C12         -1.3099918    -3.1921371    -2.0232351
```

21	O	O1	-1.7058173	-2.8384995	-3.1178977
22	O	O2	-1.6165460	-4.3919981	-1.4708236
23	C	C13	-2.4504622	-5.2374544	-2.2758548
24	H	H5	-3.4026611	-4.7454437	-2.4925444
25	H	H13	-2.6102318	-6.1404204	-1.6854493
26	H	H14	-1.9556246	-5.4785865	-3.2207919
27	F	F1	1.7827542	0.7845676	-2.6206418
28	F	F2	2.9518510	0.8833571	-0.7438053
29	O	O3	0.4915019	3.9861025	4.3747873
30	H	H15	1.2436836	4.5940145	4.4477026

pOH_TS2 (S-TS1c)

G = -927.683551
iv = i104
S^2 = 0.5058

Cartesian Coordinates (Angstroms)

Atom			X	Y	Z
1	C	C	-0.8343384	3.0005875	-0.7407077
2	C	C2	-1.9829047	2.2662349	-0.8020632
3	C	C3	-2.1042135	1.0372641	-0.1082562
4	C	C4	0.3542186	2.3643336	-0.1116000
5	C	C5	0.5256601	0.9448303	-0.5683545
6	H	H	-0.7301742	3.9984166	-1.1522788
7	H	H7	-2.8147603	2.5799453	-1.4296835
8	H	H8	-1.5836454	0.8652785	0.8238757
9	H	H12	0.0492697	0.7031459	-1.5090688
10	F	F1	1.4973858	3.0949055	-0.3957734
11	F	F2	0.2712326	2.4172782	1.2927841
12	C	C1	1.5376800	0.0644986	-0.0982657
13	C	C6	3.5070141	-1.7720166	0.7576334
14	C	C7	1.7747574	-1.1543337	-0.7946901
15	C	C8	2.3301349	0.3200217	1.0546892
16	C	C9	3.2991461	-0.5778997	1.4669917
17	C	C10	2.7337107	-2.0572561	-0.3797899
18	H	H2	1.1816258	-1.3754413	-1.6783337
19	H	H6	2.1723372	1.2324451	1.6157909
20	H	H5	3.8997598	-0.3626211	2.3492904
21	H	H3	2.9095243	-2.9851554	-0.9146080
22	C	C11	-3.1320862	0.0717056	-0.4974130
23	O	O1	-3.8953467	0.1895222	-1.4437008
24	O	O2	-3.1415021	-1.0023819	0.3367300
25	C	C12	-4.1134268	-2.0068523	0.0224721
26	H	H1	-5.1277049	-1.6073436	0.1168668
27	H	H9	-3.9514965	-2.8086909	0.7442256
28	H	H10	-3.9754656	-2.3741969	-0.9985851
29	O	O3	4.4384058	-2.6900073	1.1254616
30	H	H4	4.9052025	-2.3762166	1.9163605

pOMe_SM (S1d)

```
G = -966.999935
iv = none

Cartesian Coordinates (Angstroms)
      Atom            X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C1           1.5684705     0.2206178    -1.7265240
  2 C   C2           0.3767325     0.7586473    -1.0428449
  3 C   C3           0.6711354    -0.7986142    -1.1054805
  4 H   H3          -0.4146782     1.0603301    -1.7291412
  5 H   H6           1.0361460    -1.2083128    -0.1665828
  6 C   C4           0.4192798     1.4751382     0.2683520
  7 C   C5           0.3995578     2.8646981     2.7183402
  8 C   C6          -0.5826736     1.2374397     1.2250323
  9 C   C7           1.4069566     2.4176329     0.5652301
 10 C   C8           1.4062191     3.1116747     1.7788282
 11 C   C9          -0.5978226     1.9188432     2.4327813
 12 H   H4          -1.3580613     0.5051265     1.0139794
 13 H   H7           2.1951714     2.6143151    -0.1540665
 14 H   H8           2.1883617     3.8356514     1.9764159
 15 H   H9          -1.3698877     1.7390233     3.1742316
 16 C   C10         -0.1777455    -1.6675893    -1.9280107
 17 H   H11         -0.4818819    -1.2951250    -2.9049402
 18 C   C11         -0.6097880    -2.8832318    -1.5593780
 19 H   H12         -0.3457029    -3.3298459    -0.6051592
 20 C   C12         -1.4759922    -3.6705031    -2.4608967
 21 O   O1          -1.8727548    -3.3192847    -3.5560320
 22 O   O2          -1.7885307    -4.8663163    -1.9026053
 23 C   C13         -2.6297513    -5.7098323    -2.7019138
 24 H   H5          -3.5815062    -5.2147909    -2.9137000
 25 H   H13         -2.7893392    -6.6115801    -2.1095754
 26 H   H14         -2.1413615    -5.9538428    -3.6494661
 27 F   F1           1.6301616     0.2985041    -3.0770919
 28 F   F2           2.8034684     0.4007019    -1.2029834
 29 O   O3           0.2963876     3.4834113     3.9292099
 30 C   C14          1.2722343     4.4550219     4.2726559
 31 H   H2           2.2778950     4.0167761     4.3222211
 32 H   H1           0.9909234     4.8256908     5.2598928
 33 H   H10          1.2783764     5.2896248     3.5592219
```

pOMe_TS2 (S-TS1d)

```
G = -966.962804
iv = i120
S^2 = 0.4627

Cartesian Coordinates (Angstroms)
      Atom            X             Y             Z
    ---------   ------------- ------------- -------------

  1 C   C          -1.2853765    -0.9843654    -3.2298744
  2 C   C2         -2.4478855    -1.0570847    -2.5210862
  3 C   C3         -2.5969876    -0.3738806    -1.2876998
  4 C   C4         -0.1215990    -0.3415462    -2.5660629
  5 C   C5          0.0152474    -0.7873108    -1.1388865
  6 H   H          -1.1548866    -1.3895044    -4.2272081
  7 H   H7         -3.2700595    -1.6867161    -2.8552197
  8 H   H8         -2.0992402     0.5680364    -1.1019723
  9 H   H12        -0.4471057    -1.7370223    -0.9060560
 10 F   F1          1.0444644    -0.6188252    -3.2626443
 11 F   F2         -0.2163996     1.0621237    -2.6311444
 12 C   C1          1.0108366    -0.3040677    -0.2465697
 13 C   C6          2.9925752     0.5632996     1.5807666
 14 C   C7          1.2470701    -0.9924939     0.9779465
 15 C   C8          1.7997017     0.8480714    -0.5034394
 16 C   C9          2.7768615     1.2693620     0.3848445
 17 C   C10         2.2087428    -0.5715467     1.8713489
 18 H   H2          0.6540083    -1.8744149     1.2063193
 19 H   H6          1.6379786     1.4053597    -1.4172121
 20 H   H5          3.3622031     2.1496247     0.1452903
 21 H   H3          2.3890886    -1.0999616     2.8021740
 22 C   C11        -3.6490779    -0.7776127    -0.3544587
 23 O   O1         -4.4312068    -1.7000828    -0.5247839
 24 O   O2         -3.6601480     0.0151239     0.7508289
 25 C   C12        -4.6736312    -0.2900381     1.7162525
 26 H   H1         -5.6501013     0.0616953     1.3679974
 27 H   H9         -4.3875978     0.2408311     2.6251722
 28 H   H10        -4.7307654    -1.3660361     1.8947585
 29 O   O3          3.9193253     0.8926177     2.5124782
 30 C   C13         4.7696399     2.0076929     2.2673506
 31 H   H4          5.4324808     2.0698038     3.1316097
 32 H   H11         4.1950788     2.9381197     2.1803286
 33 H   H13         5.3667660     1.8607484     1.3588516
```

pNHCOMe_SM (S1e)

```
G = -1060.47329
iv = none

 Cartesian Coordinates (Angstroms)
      Atom            X             Y             Z
    ---------   ------------- ------------- -------------

  1 C   C1          1.1713988     0.1575743    -2.5063816
  2 C   C2          0.0746468     0.5360569    -1.5940816
  3 C   C3          0.4551586    -0.9803119    -1.8554379
```

4	H	H3	-0.8364244	0.8316940	-2.1138577
5	H	H6	0.9977653	-1.4393910	-1.0322157
6	C	C4	0.2848449	1.1340345	-0.2398241
7	C	C5	0.5967967	2.2851907	2.3182726
8	C	C6	-0.5347055	0.7412212	0.8278222
9	C	C7	1.2582649	2.1111000	-0.0000613
10	C	C8	1.4233990	2.6872720	1.2588706
11	C	C9	-0.3842648	1.3064663	2.0872504
12	H	H4	-1.2963958	-0.0181440	0.6698103
13	H	H7	1.9085981	2.4281561	-0.8084713
14	H	H8	2.1795727	3.4397135	1.4311937
15	H	H9	-1.0315881	0.9864734	2.9017992
16	C	C10	-0.4605186	-1.8381581	-2.6155977
17	H	H11	-0.9621526	-1.3995086	-3.4768142
18	C	C11	-0.7271914	-3.1200015	-2.3225197
19	H	H12	-0.2622053	-3.6350699	-1.4868079
20	C	C12	-1.6764426	-3.8919940	-3.1511922
21	O	O1	-2.2963893	-3.4692799	-4.1086108
22	O	O2	-1.7767426	-5.1674604	-2.7017280
23	C	C13	-2.6724119	-6.0064804	-3.4449387
24	H	H5	-3.6915473	-5.6111880	-3.4077610
25	H	H13	-2.6236443	-6.9849591	-2.9658000
26	H	H14	-2.3589465	-6.0737342	-4.4903650
27	F	F1	1.0067983	0.3562810	-3.8353220
28	F	F2	2.4596795	0.3884930	-2.1653710
29	N	N1	0.6944204	2.8088096	3.6232082
30	H	H2	0.0386330	2.4191320	4.2864124
31	C	C14	1.5413221	3.7860268	4.1073753
32	C	C15	1.3137490	4.1357926	5.5722271
33	H	H10	2.2809986	4.3566528	6.0286279
34	H	H15	0.8180166	3.3435332	6.1430953
35	H	H16	0.7007428	5.0424378	5.6345030
36	O	O3	2.3867645	4.3535694	3.4326912

pNHCOMe_TS2 (S-TS1e)

G = -1060.43552
iv = i111
S^2 = 0.5197

Cartesian Coordinates (Angstroms)

Atom			X	Y	Z
1	C	C	-1.6566376	3.6562397	-1.3429537
2	C	C2	-2.8091997	2.9353394	-1.4526862
3	C	C3	-2.9883888	1.7254383	-0.7364660
4	C	C4	-0.5135962	3.0231753	-0.6280485
5	C	C5	-0.3433739	1.5860810	-1.0289568
6	H	H	-1.5148126	4.6412060	-1.7738071
7	H	H7	-3.5988899	3.2442342	-2.1348052
8	H	H8	-2.5298791	1.5721052	0.2307956
9	H	H12	-0.7556016	1.3301491	-1.9960268
10	F	F1	0.6542942	3.7247365	-0.8777820
11	F	F2	-0.6747975	3.1267197	0.7632907
12	C	C1	0.6022874	0.6913855	-0.4611539

```
 13 C   C6             2.4405540    -1.1914785     0.6027409
 14 C   C7             0.8445679    -0.5530769    -1.1050284
 15 C   C8             1.3194300     0.9470487     0.7398929
 16 C   C9             2.2230487     0.0367430     1.2593855
 17 C   C10            1.7360915    -1.4694016    -0.5875130
 18 H   H2             0.3128024    -0.7833655    -2.0245305
 19 H   H6             1.1551133     1.8812405     1.2618904
 20 H   H5             2.7621316     0.2510878     2.1710956
 21 H   H3             1.8992264    -2.4146737    -1.1015990
 22 C   C11           -4.0012680     0.7610459    -1.1655510
 23 O   O1            -4.6951792     0.8583805    -2.1659369
 24 O   O2            -4.0858484    -0.2853448    -0.3010219
 25 C   C12           -5.0537372    -1.2823288    -0.6490319
 26 H   H1            -6.0577532    -0.8501166    -0.6890899
 27 H   H9            -4.9935350    -2.0375100     0.1359261
 28 H   H10           -4.8235019    -1.7226931    -1.6237780
 29 N   N1             3.3253262    -2.1722419     1.0681610
 30 H   H11            3.3779714    -3.0037897     0.4949480
 31 C   C13            4.1130617    -2.1734547     2.2098966
 32 O   O3             4.1640704    -1.2460722     3.0004609
 33 C   C14            4.8948472    -3.4621882     2.4184878
 34 H   H4             5.0617664    -4.0281969     1.4960790
 35 H   H13            4.3512309    -4.1022614     3.1235117
 36 H   H14            5.8581785    -3.2141621     2.8692043
```

pMe_SM (S1f)

```
G = -891.799548
iv = none

Cartesian Coordinates (Angstroms)
       Atom             X              Y             Z
    ---------    ------------- ------------- -------------

  1 C   C1             1.3804811     0.7111935    -1.7861492
  2 C   C2             0.2866776     1.1001233    -0.8747163
  3 C   C3             0.6545210    -0.4190597    -1.1326506
  4 H   H3            -0.6218868     1.4031422    -1.3943647
  5 H   H6             1.1922568    -0.8807027    -0.3076510
  6 C   C4             0.4999533     1.7001255     0.4795990
  7 C   C5             0.8180760     2.8514766     3.0485519
  8 C   C6            -0.3228548     1.3150779     1.5462997
  9 C   C7             1.4852563     2.6683170     0.7125421
 10 C   C8             1.6392027     3.2305764     1.9790346
 11 C   C9            -0.1651259     1.8825139     2.8089096
 12 H   H4            -1.0877670     0.5590569     1.3853688
 13 H   H7             2.1401209     2.9749506    -0.0963091
 14 H   H8             2.4142963     3.9768668     2.1390680
 15 H   H9            -0.8130135     1.5654741     3.6230621
 16 C   C10           -0.2649214    -1.2725938    -1.8936981
 17 H   H11           -0.7636714    -0.8315028    -2.7553215
 18 C   C11           -0.5361347    -2.5538572    -1.6025425
 19 H   H12           -0.0747847    -3.0711972    -0.7662466
 20 C   C12           -1.4852845    -3.3226127    -2.4346723
 21 O   O1            -2.1001038    -2.8977963    -3.3944603
 22 O   O2            -1.5911644    -4.5978163    -1.9858790
```

23	C	C13	-2.4873711	-5.4339559	-2.7316450
24	H	H5	-3.5055214	-5.0358820	-2.6967921
25	H	H13	-2.4426931	-6.4127267	-2.2526976
26	H	H14	-2.1715024	-5.5017247	-3.7763096
27	F	F1	1.2180697	0.9082906	-3.1158431
28	F	F2	2.6714102	0.9320561	-1.4462235
29	C	C14	0.9777194	3.4838681	4.4113072
30	H	H2	2.0336375	3.6363601	4.6612334
31	H	H1	0.5308679	2.8644512	5.1956799
32	H	H10	0.4912538	4.4675073	4.4535157

pMe_TS2 (S-TS1f)

G = -891.760479
iv = i127
S^2 = 0.5260

Cartesian Coordinates (Angstroms)

		Atom	X	Y	Z
1	C	C	-3.2411448	-1.2102549	-0.6227091
2	C	C2	-2.4874199	-2.3441240	-0.6934144
3	C	C3	-1.2165378	-2.4161221	-0.0674915
4	C	C4	-2.5935456	0.0064873	-0.0586121
5	C	C5	-1.1983952	0.1824275	-0.5854099
6	H	H	-4.2614524	-1.1355115	-0.9823186
7	H	H7	-2.8158369	-3.2012848	-1.2777478
8	H	H8	-1.0091756	-1.8761448	0.8464066
9	H	H12	-1.0032239	-0.2927791	-1.5377288
10	F	F1	-3.3510705	1.1303709	-0.3428770
11	F	F2	-2.5823967	-0.0427127	1.3458421
12	C	C1	-0.3037842	1.2109320	-0.1706401
13	C	C6	1.5609839	3.2326926	0.5674210
14	C	C7	0.8735575	1.4472643	-0.9302234
15	C	C8	-0.5101283	2.0163608	0.9806499
16	C	C9	0.4012146	3.0022437	1.3260025
17	C	C10	1.7792142	2.4286188	-0.5661451
18	H	H2	1.0593694	0.8395307	-1.8125398
19	H	H6	-1.3893384	1.8548016	1.5913664
20	H	H5	0.2168835	3.6080511	2.2102775
21	H	H3	2.6724990	2.5831353	-1.1672359
22	C	C11	-0.2498418	-3.4333873	-0.4866398
23	O	O1	-0.4115242	-4.2305043	-1.3975294
24	O	O2	0.8750528	-3.3888637	0.2741351
25	C	C12	1.8774345	-4.3551328	-0.0657145
26	H	H1	1.5029010	-5.3711438	0.0908148
27	H	H9	2.7184454	-4.1524296	0.5986839
28	H	H10	2.1789390	-4.2503344	-1.1117792
29	C	C13	2.5350013	4.3207831	0.9419171
30	H	H4	3.5725585	3.9931121	0.8114697
31	H	H11	2.4041978	4.6352923	1.9820438
32	H	H13	2.3965637	5.2086255	0.3097265

pCl_SM (S1i)

```
G = -1312.11478
iv = none

 Cartesian Coordinates (Angstroms)
       Atom              X              Y              Z
    ---------    ------------- ------------- -------------

   1 C   C1            1.0629383      1.4158113     -1.5049339
   2 C   C2            0.1398042      1.5398942     -0.3527260
   3 C   C3            0.6951483      0.1310238     -0.8500301
   4 H   H3           -0.8906327      1.7074024     -0.6573324
   5 H   H6            1.4579103     -0.2833529     -0.1946151
   6 C   C4            0.4782137      2.0756827      0.9941942
   7 C   C5            0.9765783      3.0761558      3.5642872
   8 C   C6           -0.5657112      2.5572507      1.7980247
   9 C   C7            1.7836200      2.1102276      1.5110443
  10 C   C8            2.0351636      2.6052449      2.7889840
  11 C   C9           -0.3281184      3.0574004      3.0764095
  12 H   H4           -1.5847155      2.5400634      1.4200373
  13 H   H7            2.6183172      1.7625201      0.9131847
  14 H   H8            3.0474087      2.6301134      3.1785618
  15 H   H9           -1.1452559      3.4269295      3.6864817
  16 C   C10          -0.2266630     -0.8184726     -1.4845070
  17 H   H11          -0.9308160     -0.4240651     -2.2149550
  18 C   C11          -0.2609302     -2.1326999     -1.2185126
  19 H   H12           0.4155811     -2.5990981     -0.5081290
  20 C   C12          -1.2386765     -3.0086821     -1.8988252
  21 O   O1           -2.0799745     -2.6502155     -2.7007146
  22 O   O2           -1.0788318     -4.2959737     -1.5072398
  23 C   C13          -1.9833911     -5.2345541     -2.1077452
  24 H   H5           -3.0166572     -5.0010274     -1.8356089
  25 H   H13          -1.6960144     -6.2107232     -1.7156897
  26 H   H14          -1.8922845     -5.2144020     -3.1970391
  27 F   F1            0.5750157      1.6800851     -2.7386468
  28 F   F2            2.3408549      1.8533815     -1.4198456
  29 Cl  Cl1           1.2921180      3.7040797      5.1758867
```

pCl_TS2 (S-TS1i)

```
G = -1312.07449
iv = i128
S^2 = 0.5583

Cartesian Coordinates (Angstroms)
       Atom              X              Y              Z
    ---------    ------------- ------------- -------------

   1 C   C            -0.7144027      2.9378750     -0.6746949
   2 C   C2           -1.8511631      2.1867377     -0.7221207
   3 C   C3           -1.9368194      0.9513782     -0.0304521
   4 C   C4            0.4928846      2.3128350     -0.0633652
   5 C   C5            0.6661820      0.8922119     -0.5199505
   6 H   H            -0.6282091      3.9366106     -1.0883615
   7 H   H7           -2.6978162      2.4866973     -1.3362765
```

```
  8 H   H8            -1.4114849     0.7924321     0.9016563
  9 H   H12            0.2049960     0.6564334    -1.4701264
 10 F   F1             1.6232164     3.0494124    -0.3706913
 11 F   F2             0.4255219     2.3689785     1.3382104
 12 C   C1             1.6791377     0.0074726    -0.0450402
 13 C   C6             3.6443348    -1.8165463     0.7981102
 14 C   C7             1.9135574    -1.2045907    -0.7476448
 15 C   C8             2.4683437     0.2617319     1.1090983
 16 C   C9             3.4425531    -0.6352618     1.5198311
 17 C   C10            2.8790198    -2.1090211    -0.3356613
 18 H   H2             1.3216660    -1.4240667    -1.6324540
 19 H   H6             2.3093340     1.1715125     1.6741328
 20 H   H5             4.0459134    -0.4291387     2.3977672
 21 H   H3             3.0491448    -3.0301417    -0.8828047
 22 C   C11           -2.9471157    -0.0383071    -0.4165050
 23 O   O1            -3.7156678     0.0695285    -1.3586056
 24 O   O2            -2.9270737    -1.1113717     0.4138963
 25 C   C12           -3.8792252    -2.1384886     0.1055527
 26 H   H1            -4.9007242    -1.7588757     0.2013831
 27 H   H9            -3.6978636    -2.9334902     0.8297628
 28 H   H10           -3.7348658    -2.5053594    -0.9146126
 29 Cl  Cl1            4.8766261    -2.9471882     1.3199661
```

pBr_TS2 (S1j)

```
G = -3425.80123
iv = none

 Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
   ---------    ------------- ------------- -------------

  1 C   C1             1.3562471     2.6029050     1.2666918
  2 C   C4            -0.6298350     2.8110397     3.2079051
  3 C   C2             0.7185734     1.4376814     1.7172858
  4 C   C6             1.0156669     3.8582232     1.7679532
  5 C   C5             0.0187999     3.9511614     2.7362616
  6 C   C3            -0.2767281     1.5624892     2.6997928
  7 H   H6             1.5175193     4.7487317     1.4057904
  8 C   C7             1.1124539     0.1354154     1.1133198
  9 C   C8             0.9466757    -1.1990873     1.7365377
 10 C   C9             0.0186687    -0.9076405     0.6097841
 11 H   H2             1.9701604     0.1879599     0.4468276
 12 H   H9            -0.9951829    -0.6472929     0.9066102
 13 F   F1             0.4393115    -1.3158115     2.9860755
 14 F   F2             1.9255881    -2.1146176     1.5561425
 15 C   C10            0.1900134    -1.5358200    -0.7050430
 16 H   H8             1.1912244    -1.8658255    -0.9766831
 17 C   C11           -0.7967142    -1.7231741    -1.5941015
 18 H   H10           -1.8237509    -1.4308560    -1.3952506
 19 C   C12           -0.5098685    -2.3537982    -2.9004189
 20 O   O1             0.5832979    -2.7182529    -3.2898171
 21 O   O2            -1.6438204    -2.4791110    -3.6311886
 22 C   C13           -1.4742752    -3.0839992    -4.9217103
 23 H   H7            -2.4696650    -3.1096851    -5.3663640
 24 H   H11           -1.0703997    -4.0951857    -4.8222437
```

```
 25 H  H12          -0.7925507    -2.4909454    -5.5376410
 26 H  H13          -1.4009261     2.8927997     3.9661981
 27 H  H3            2.1299839     2.5312127     0.5064749
 28 H  H1           -0.7762866     0.6814874     3.0855627
 29 Br Br1          -0.4741812     5.6699962     3.4252475
```

pBr_TS2 (S-TS1j)

```
G = -3425.76075
iv = i133
S^2 = 0.5546

Cartesian Coordinates (Angstroms)
      Atom             X             Y             Z
   ---------    ------------- ------------- -------------

  1 C  C            -0.8155237     2.9537288    -0.5005872
  2 C  C2           -1.9361827     2.1779372    -0.5224954
  3 C  C3           -1.9545462     0.9087785     0.1112560
  4 C  C4            0.4367717     2.3287633     0.0126214
  5 C  C5            0.6140255     0.9352300    -0.5191788
  6 H  H            -0.7736767     3.9729385    -0.8683150
  7 H  H7           -2.8226476     2.4857335    -1.0731278
  8 H  H8           -1.3765984     0.7210921     1.0060768
  9 H  H12           0.1141262     0.7341125    -1.4577151
 10 F  F1            1.5334149     3.1042878    -0.3197891
 11 F  F2            0.4451122     2.3186286     1.4168530
 12 C  C1            1.6689735     0.0538574    -0.1377762
 13 C  C6            3.7061034    -1.7621794     0.5299251
 14 C  C7            1.8972427    -1.1169033    -0.9086001
 15 C  C8            2.5045807     0.2725334     0.9903035
 16 C  C9            3.5144744    -0.6203524     1.3151728
 17 C  C10           2.8992134    -2.0179835    -0.5834434
 18 H  H2            1.2701520    -1.3074775    -1.7757957
 19 H  H6            2.3514741     1.1504878     1.6046668
 20 H  H5            4.1489201    -0.4387045     2.1760502
 21 H  H3            3.0594091    -2.9063750    -1.1843230
 22 C  C11          -2.9634732    -0.0861036    -0.2659838
 23 O  O1           -3.7881729     0.0484362    -1.1556234
 24 O  O2           -2.8700630    -1.1978847     0.5058995
 25 C  C12          -3.8159820    -2.2322315     0.2024378
 26 H  H1           -4.8390917    -1.8783145     0.3588484
 27 H  H9           -3.5853585    -3.0496220     0.8865239
 28 H  H10          -3.7123637    -2.5580693    -0.8366212
 29 Br Br1           5.0896863    -2.9943441     0.9927401
```

pCF3_SM (S1k)

```
G = -1189.54302
iv = none

Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1  C   C1           1.3905282     0.7055646    -1.7814656
  2  C   C2           0.2860935     1.0987292    -0.8829945
  3  C   C3           0.6555983    -0.4194453    -1.1289813
  4  H   H3          -0.6187309     1.4030623    -1.4078014
  5  H   H6           1.1862778    -0.8794566    -0.2982996
  6  C   C4           0.4892453     1.7050214     0.4698021
  7  C   C5           0.7850619     2.8541838     3.0090151
  8  C   C6          -0.3390294     1.3145880     1.5311086
  9  C   C7           1.4671871     2.6831757     0.6967647
 10  C   C8           1.6144269     3.2544324     1.9584724
 11  C   C9          -0.1953346     1.8829654     2.7939078
 12  H   H4          -1.1003497     0.5572787     1.3640782
 13  H   H7           2.1162669     2.9943651    -0.1141762
 14  H   H8           2.3696859     4.0159093     2.1260048
 15  H   H9          -0.8429598     1.5783240     3.6088363
 16  C   C10         -0.2602967    -1.2750697    -1.8940802
 17  H   H11         -0.7489088    -0.8381627    -2.7635918
 18  C   C11         -0.5380935    -2.5527254    -1.5965082
 19  H   H12         -0.0868739    -3.0667832    -0.7526672
 20  C   C12         -1.4830539    -3.3227510    -2.4344922
 21  O   O1          -2.0871486    -2.8970320    -3.4003378
 22  O   O2          -1.5959496    -4.5945813    -1.9822844
 23  C   C13         -2.4876238    -5.4324597    -2.7329928
 24  H   H5          -3.5059636    -5.0348042    -2.7029678
 25  H   H13         -2.4440293    -6.4107954    -2.2533911
 26  H   H14         -2.1657269    -5.4996729    -3.7757532
 27  F   F1           1.2442136     0.8987727    -3.1118325
 28  F   F2           2.6753105     0.9304317    -1.4225751
 29  C   C14          0.9962693     3.4407113     4.3786791
 30  F   F3           2.0580250     2.8770349     5.0005748
 31  F   F4           1.2410832     4.7691376     4.3188786
 32  F   F5          -0.0752004     3.2600513     5.1810706
```

pCF3_TS2 (S-TS1k)

```
G = -1189.50258
iv = i125
S^2 = 0.6218

 Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1  C   C           -3.2797245    -1.2121588    -0.6934350
  2  C   C2          -2.5116752    -2.3389138    -0.7257791
  3  C   C3          -1.2485162    -2.3795873    -0.0840931
  4  C   C4          -2.6572962     0.0335206    -0.1545598
```

```
  5 C   C5           -1.2544317     0.2152299    -0.6599795
  6 H   H            -4.2960100    -1.1609020    -1.0682988
  7 H   H7           -2.8238888    -3.2146668    -1.2915952
  8 H   H8           -1.0537595    -1.8003942     0.8086027
  9 H   H12          -1.0478156    -0.2542267    -1.6132811
 10 F   F1           -3.4240074     1.1344557    -0.4887828
 11 F   F2           -2.6735928     0.0180651     1.2469293
 12 C   C1           -0.3414879     1.2165497    -0.2128568
 13 C   C6            1.5803490     3.1115657     0.6072974
 14 C   C7            0.8566129     1.4185644    -0.9486864
 15 C   C8           -0.5428462     2.0040522     0.9524360
 16 C   C9            0.4027038     2.9375492     1.3464393
 17 C   C10           1.8018631     2.3468040    -0.5454231
 18 H   H2            1.0317660     0.8247198    -1.8418622
 19 H   H6           -1.4418121     1.8672061     1.5393060
 20 H   H5            0.2384953     3.5271246     2.2426382
 21 H   H3            2.7160970     2.4785463    -1.1145699
 22 C   C11          -0.2546706    -3.3889999    -0.4658764
 23 O   O1           -0.3981751    -4.2218233    -1.3459778
 24 O   O2            0.8666229    -3.2780076     0.2884928
 25 C   C12           1.9083338    -4.2149400    -0.0204087
 26 H   H1            1.5696190    -5.2398952     0.1571965
 27 H   H9            2.7348424    -3.9637807     0.6454817
 28 H   H10           2.2139805    -4.1210829    -1.0664875
 29 C   C13           2.5837831     4.1520212     1.0246198
 30 F   F3            3.8341185     3.8301821     0.6250771
 31 F   F4            2.6119925     4.3099328     2.3660114
 32 F   F5            2.2985296     5.3632898     0.4914248
```

pCN_SM (S1l)

```
G = -944.753991
iv = none

Cartesian Coordinates (Angstroms)
      Atom            X             Y             Z
   ---------    ------------- ------------- -------------

  1 C   C1            1.0319461     1.2778849    -1.6937737
  2 C   C2            0.0960445     1.4105239    -0.5500448
  3 C   C3            0.6562833    -0.0010430    -1.0350636
  4 H   H3           -0.9313648     1.5780907    -0.8640662
  5 H   H6            1.4120200    -0.4125834    -0.3698562
  6 C   C4            0.4258318     1.9500567     0.7956994
  7 C   C5            0.9120884     2.9620527     3.3793517
  8 C   C6           -0.6242761     2.4441046     1.5866669
  9 C   C7            1.7293305     1.9753284     1.3219641
 10 C   C8            1.9710244     2.4727423     2.5969470
 11 C   C9           -0.3928655     2.9454223     2.8618626
 12 H   H4           -1.6382702     2.4325100     1.1963269
 13 H   H7            2.5640968     1.6184703     0.7302804
 14 H   H8            2.9815089     2.4894410     2.9924417
 15 H   H9           -1.2149625     3.3233372     3.4609522
 16 C   C10          -0.2624683    -0.9535721    -1.6712338
 17 H   H11          -0.9582229    -0.5639595    -2.4121110
 18 C   C11          -0.3001821    -2.2650782    -1.3947489
```

```
  19  H   H12            0.3681632    -2.7265686    -0.6734562
  20  C   C12           -1.2719021    -3.1459489    -2.0797017
  21  O   O1            -2.1015530    -2.7909135    -2.8947798
  22  O   O2            -1.1196444    -4.4287818    -1.6745291
  23  C   C13           -2.0183944    -5.3721133    -2.2777354
  24  H   H5            -3.0547174    -5.1307052    -2.0252943
  25  H   H13           -1.7410356    -6.3439496    -1.8683700
  26  H   H14           -1.9089291    -5.3660210    -3.3654563
  27  F   F1             0.5541761     1.5386864    -2.9307855
  28  F   F2             2.3079413     1.7167013    -1.5969534
  29  C   C14            1.1623931     3.4751953     4.6940105
  30  N   N1             1.3659400     3.8906899     5.7614562
```

pCN_TS2 (S-TS1l)

```
G = -944.713152
iv = i137
S^2 = 0.6312
```

```
 Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------     ------------- ------------- -------------

   1  C   C             -3.1090839    -0.9324188    -0.6288647
   2  C   C2            -2.3299329    -2.0510375    -0.6568641
   3  C   C3            -1.0677673    -2.0729066    -0.0120571
   4  C   C4            -2.4941114     0.3212685    -0.0957804
   5  C   C5            -1.0923355     0.5099731    -0.6068847
   6  H   H             -4.1244855    -0.8900055    -1.0067117
   7  H   H7            -2.6301789    -2.9322518    -1.2195622
   8  H   H8            -0.8846812    -1.4899310     0.8805992
   9  H   H12           -0.8991695     0.0591984    -1.5725171
  10  F   F1            -3.2673527     1.4146714    -0.4344781
  11  F   F2            -2.5075325     0.3085765     1.3047115
  12  C   C1            -0.1713863     1.4984922    -0.1545684
  13  C   C6             1.7710068     3.3804744     0.6695429
  14  C   C7             1.0077671     1.7263356    -0.9176674
  15  C   C8            -0.3437069     2.2530012     1.0391001
  16  C   C9             0.6063549     3.1763799     1.4373984
  17  C   C10            1.9601638     2.6448086    -0.5183662
  18  H   H2             1.1573829     1.1623713    -1.8345869
  19  H   H6            -1.2283877     2.0984419     1.6431480
  20  H   H5             0.4639545     3.7456288     2.3504729
  21  H   H3             2.8537470     2.8065734    -1.1128248
  22  C   C11           -0.0618197    -3.0751446    -0.3826549
  23  O   O1            -0.1945299    -3.9142076    -1.2579497
  24  O   O2             1.0527218    -2.9477331     0.3771840
  25  C   C12            2.1026021    -3.8824063     0.0888101
  26  H   H1             1.7739496    -4.9044379     0.2965142
  27  H   H9             2.9289161    -3.6062448     0.7440922
  28  H   H10            2.4016408    -3.8142906    -0.9604735
  29  C   C13            2.7594867     4.3219007     1.0961977
  30  N   N1             3.5667676     5.0849199     1.4450410
```

pNO2_SM (S1m)

```
G = -1057.00885
iv = none

Cartesian Coordinates (Angstroms)
       Atom              X              Y              Z
    ---------    ------------- ------------- -------------

   1  C   C1           0.9606723      1.1812896     -1.8531310
   2  C   C2           0.0349246      1.3009843     -0.6988658
   3  C   C3           0.6076703     -0.1026353     -1.1926552
   4  H   H3          -0.9977203      1.4565647     -1.0014392
   5  H   H6           1.3756553     -0.5061260     -0.5366140
   6  C   C4           0.3728128      1.8414923      0.6438564
   7  C   C5           0.8678980      2.8424244      3.1975676
   8  C   C6          -0.6762743      2.3263099      1.4439078
   9  C   C7           1.6821014      1.8755084      1.1574627
  10  C   C8           1.9328487      2.3726145      2.4314691
  11  C   C9          -0.4396627      2.8281044      2.7184806
  12  H   H4          -1.6930405      2.3069563      1.0617016
  13  H   H7           2.5138430      1.5262153      0.5574401
  14  H   H8           2.9367882      2.4057915      2.8364874
  15  H   H9          -1.2428769      3.2030971      3.3406388
  16  C   C10         -0.3076445     -1.0649760     -1.8194009
  17  H   H11         -1.0183375     -0.6823453     -2.5496635
  18  C   C11         -0.3245048     -2.3775919     -1.5468055
  19  H   H12          0.3591994     -2.8329974     -0.8361436
  20  C   C12         -1.2937805     -3.2687425     -2.2226481
  21  O   O1          -2.1399540     -2.9205701     -3.0234733
  22  O   O2          -1.1171806     -4.5510993     -1.8270998
  23  C   C13         -2.0109161     -5.5043847     -2.4224850
  24  H   H5          -3.0469881     -5.2780942     -2.1555785
  25  H   H13         -1.7149043     -6.4738903     -2.0208165
  26  H   H14         -1.9155940     -5.4923632     -3.5114841
  27  F   F1           0.4660604      1.4392177     -3.0836845
  28  F   F2           2.2315837      1.6358706     -1.7681280
  29  N   N1           1.1310496      3.3684380      4.5444891
  30  O   O3           2.2963591      3.3664470      4.9414150
  31  O   O4           0.1699121      3.7784903      5.1952003
```

pNO2_TS2 (S-TS1m)

```
G = -1056.96757
iv = i146
S^2 = 0.6042

 Cartesian Coordinates (Angstroms)
       Atom              X              Y              Z
    ---------    ------------- ------------- -------------

   1  C   C           -1.0505402      3.1613109     -0.7618680
   2  C   C2          -2.1778288      2.3962176     -0.7922475
   3  C   C3          -2.2302077      1.1537247     -0.1084434
   4  C   C4           0.1781153      2.5460614     -0.1766937
   5  C   C5           0.3521525      1.1241184     -0.6346538
```

```
  6  H   H            -0.9837357     4.1629145    -1.1721862
  7  H   H7           -3.0406011     2.6876625    -1.3875016
  8  H   H8           -1.6896861     0.9984542     0.8158345
  9  H   H12          -0.1009347     0.8923349    -1.5900162
 10  F   F1            1.2940308     3.2870577    -0.5132652
 11  F   F2            0.1336866     2.6051720     1.2220645
 12  C   C1            1.3486363     0.2263447    -0.1484016
 13  C   C6            3.2565094    -1.6254149     0.7179857
 14  C   C7            1.5537745    -0.9991868    -0.8410035
 15  C   C8            2.1409860     0.4810842     1.0053119
 16  C   C9            3.0916634    -0.4325935     1.4277239
 17  C   C10           2.4929002    -1.9212115    -0.4151085
 18  H   H2            0.9577564    -1.2107602    -1.7245399
 19  H   H6            2.0011554     1.4019270     1.5562857
 20  H   H5            3.7062824    -0.2451737     2.2997809
 21  H   H3            2.6528627    -2.8563351    -0.9375804
 22  C   C11          -3.2254250     0.1435432    -0.4913149
 23  O   O1           -4.0094962     0.2502472    -1.4195601
 24  O   O2           -3.1620420    -0.9377572     0.3211888
 25  C   C12          -4.0918647    -1.9882898     0.0159936
 26  H   H1           -5.1206382    -1.6338762     0.1248956
 27  H   H9           -3.8819071    -2.7821657     0.7331040
 28  H   H10          -3.9474514    -2.3441567    -1.0078561
 29  N   N1            4.2574823    -2.5951503     1.1752864
 30  O   O3            4.9390762    -2.2930285     2.1558377
 31  O   O4            4.3552888    -3.6530746     0.5509473
```

Phenolate Computational Attempts

Phenolate Intermediate - before opt (S7)

```
Cartesian Coordinates (Angstroms)
      Atom             X             Y             Z
   ---------     ------------- ------------- -------------

  1  H   H1           -1.2586477     1.7626345    -0.6723651
  2  C   C1           -0.9593205     2.4202187     0.1371390
  3  C   C4           -0.2979218     4.1741696     2.1509685
  4  C   C2            0.2137577     2.1675758     0.8567993
  5  C   C6           -1.7765691     3.5228465     0.4322519
  6  C   C5           -1.4837140     4.4444830     1.4487606
  7  C   C3            0.5323914     3.0761858     1.8689170
  8  H   H6           -2.6812601     3.6767329    -0.1548029
  9  H   H3            1.4327505     2.9470927     2.4620282
 10  H   H4           -0.0103865     4.8530754     2.9532110
 11  C   C7            1.0948251     0.9939612     0.5158621
 12  C   C8            1.6506051     0.0771063     1.5469454
 13  C   C9            0.5283833    -0.4138679     0.7043742
 14  H   H9           -0.4263771    -0.5138067     1.2125096
 15  F   F1            1.4564273     0.2726912     2.8952971
 16  F   F2            2.9162592    -0.4510259     1.3985080
 17  C   C10           0.7675142    -1.4081322    -0.3507062
 18  H   H8            1.7384715    -1.3585969    -0.8450345
 19  C   C11          -0.1058439    -2.3552803    -0.7279450
 20  H   H10          -1.0813320    -2.4452598    -0.2647076
 21  C   C12           0.2326341    -3.3145459    -1.7973213
```

```
 22  O   O1          1.2898992    -3.3544446    -2.4044986
 23  O   O2         -0.8331080    -4.1340864    -1.9776217
 24  C   C13        -0.6385568    -5.1147946    -2.9957679
 25  H   H7          0.1956046    -5.7751339    -2.7383907
 26  H   H11        -0.4683390    -4.6343656    -3.9644557
 27  H   H12        -1.5482733    -5.7177461    -3.0641878
 28  H   H2          1.7504441     1.1589466    -0.3355664
 29  O   O3         -2.2303178     5.4433666     1.7097995
```

Phenolate Intermediate - after geometry optimisation (Total Charge = -1) (S8)

```
Spartan'10: G = -927.192975, iv = none

Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

  1  H   H1          1.2808579     3.0897020     0.6306506
  2  C   C1          0.7034081     2.9159564     1.5382962
  3  C   C4         -0.7906655     2.3886376     3.8520824
  4  C   C2          0.4615034     1.5430458     1.9214290
  5  C   C6          0.2458640     3.9704274     2.2653526
  6  C   C5         -0.5409795     3.7856705     3.4865468
  7  C   C3         -0.3177473     1.3411958     3.1233992
  8  H   H6          0.4449109     4.9963243     1.9647671
  9  H   H3         -0.5169180     0.3229192     3.4373228
 10  H   H4         -1.3749331     2.2249088     4.7547202
 11  C   C7          0.9940677     0.5293339     1.1434880
 12  C   C8          0.7754011    -0.9401199     1.1873830
 13  C   C9         -0.3501997    -1.1906383     0.2744310
 14  H   H2          1.5802893     0.8142811     0.2724571
 15  H   H9         -1.3228352    -0.8910906     0.6559472
 16  F   F1          0.5348639    -1.4046105     2.4809257
 17  F   F2          1.9329416    -1.5751813     0.7622446
 18  C   C10        -0.1909201    -1.6214304    -1.0372029
 19  H   H8          0.8233621    -1.8602679    -1.3499328
 20  C   C11        -1.1941300    -1.8064516    -1.9796295
 21  H   H10        -2.2305457    -1.5924159    -1.7330885
 22  C   C12        -0.9905567    -2.2883093    -3.3131497
 23  O   O1         -1.8563495    -2.4639529    -4.1707136
 24  O   O2          0.3441622    -2.5618713    -3.6054491
 25  C   C13         0.5736672    -3.0254089    -4.9252715
 26  H   H7          1.6529881    -3.1873279    -5.0035254
 27  H   H11         0.2512599    -2.2918886    -5.6739473
 28  H   H12         0.0402419    -3.9627018    -5.1235976
 29  O   O3         -0.9630088     4.7412646     4.1640642
```

Phenolate VCPR Transition State - before optimisation (S-TS4)

```
Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

  1  C   C          -0.6651935     2.9186490    -0.6746263
  2  C   C2         -1.8137598     2.1842964    -0.7359817
  3  C   C3         -1.9350686     0.9553256    -0.0421748
  4  C   C4          0.5233634     2.2823951    -0.0455186
  5  C   C5          0.6948050     0.8628918    -0.5022731
  6  H   H          -0.5610292     3.9164781    -1.0861974
  7  H   H7         -2.6456154     2.4980068    -1.3636021
  8  H   H8         -1.4145005     0.7833400     0.8899571
  9  H   H12         0.2184147     0.6212074    -1.4429874
 10  F   F1          1.6665307     3.0129670    -0.3296920
 11  F   F2          0.4403775     2.3353397     1.3588655
 12  C   C1          1.7068249    -0.0174399    -0.0321843
 13  C   C6          3.6761591    -1.8539552     0.8237148
 14  C   C7          1.9439024    -1.2362722    -0.7286087
 15  C   C8          2.4992798     0.2380831     1.1207706
 16  C   C9          3.4682911    -0.6598382     1.5330731
 17  C   C10         2.9028556    -2.1391946    -0.3137085
 18  H   H2          1.3507707    -1.4573798    -1.6122523
 19  H   H6          2.3414821     1.1505066     1.6818723
 20  H   H5          4.0689047    -0.4445596     2.4153719
 21  H   H3          3.0786691    -3.0670939    -0.8485266
 22  C   C11        -2.9629413    -0.0102329    -0.4313316
 23  O   O1         -3.7262018     0.1075837    -1.3776194
 24  O   O2         -2.9723572    -1.0843205     0.4028114
 25  C   C12        -3.9442819    -2.0887908     0.0885536
 26  H   H1         -4.9585600    -1.6892821     0.1829482
 27  H   H9         -3.7823516    -2.8906294     0.8103071
 28  H   H10        -3.8063206    -2.4561354    -0.9325037
 29  O   O3          4.6075507    -2.7719458     1.1915431
```

Phenolate VCPR Transition State - after optimisation (Total Charge = -1) (S-TS4)

```
Spartan'10: G = -927.176731, iv = i107, S^2 = 0.0001
```

```
Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

  1  C   C          -0.7028045     3.1038515    -0.7049473
  2  C   C2         -1.8062730     2.3228423    -0.6517956
  3  C   C3         -1.7138557     1.0591249     0.0372463
  4  C   C4          0.5346220     2.4555659    -0.2063623
  5  C   C5          0.5468191     0.9779598    -0.5446132
  6  H   H          -0.6564795     4.1166443    -1.0921863
  7  H   H7         -2.7285382     2.5909061    -1.1690556
  8  H   H8         -1.3345859     1.0349481     1.0507740
  9  H   H12         0.1757076     0.8044173    -1.5488622
 10  F   F1          1.6590641     3.0695692    -0.7550712
 11  F   F2          0.7014846     2.6522265     1.1777744
```

```
 12 C  C1           1.4400750     0.0208918    -0.0467964
 13 C  C6           3.2567048    -2.0801602     0.8438868
 14 C  C7           1.6307000    -1.1953743    -0.7939404
 15 C  C8           2.1821669     0.1323339     1.1826385
 16 C  C9           3.0387980    -0.8459548     1.5968119
 17 C  C10          2.4790717    -2.1830413    -0.3899775
 18 H  H2           1.0690408    -1.3098361    -1.7214063
 19 H  H6           2.0580032     1.0296004     1.7780306
 20 H  H5           3.5991611    -0.7413867     2.5237495
 21 H  H3           2.6118024    -3.0895804    -0.9767112
 22 C  C11         -2.5691403    -0.0267344    -0.3637043
 23 O  O1          -3.2566035    -0.0943725    -1.3823008
 24 O  O2          -2.5362285    -1.0691777     0.5430958
 25 C  C12         -3.2875790    -2.2130706     0.1628205
 26 H  H1          -4.3600864    -1.9901305     0.1056993
 27 H  H9          -3.1030485    -2.9638402     0.9357245
 28 H  H10         -2.9691897    -2.5938533    -0.8138878
 29 O  O3           4.0411914    -2.9743692     1.2233663
```

Cartesian Coordinates for Alkenoates

```
2-pyridyl

Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1 H  H1          -0.8129841     0.1160651     2.5439774
  2 C  C1          -0.4744235     1.0344220     2.0725097
  3 C  C4           0.3943767     3.2735988     0.7940912
  4 C  C2          -0.0405019     1.0174219     0.7369124
  5 C  C6          -0.4631111     2.2371419     2.7754328
  6 C  C5          -0.0197364     3.3864943     2.1263621
  7 N  N1           0.3892637     2.1317818     0.1089558
  8 H  H4           0.7478073     4.1512814     0.2545482
  9 C  C7          -0.0462173    -0.2423610    -0.0175247
 10 H  H7          -0.3962029    -1.1224421     0.5161015
 11 C  C8           0.3475029    -0.3625529    -1.2967223
 12 H  H8           0.7005955     0.5006879    -1.8504334
 13 C  C9           0.3445492    -1.6289205    -2.0555207
 14 O  O1          -0.1019638    -2.6869584    -1.3305635
 15 O  O2           0.7050368    -1.7230232    -3.2132418
 16 C  C10         -0.1160287    -3.9392129    -2.0292282
 17 H  H2           0.8925777    -4.2122539    -2.3520599
 18 H  H9          -0.7640376    -3.8835557    -2.9083329
 19 H  H10         -0.5000801    -4.6695127    -1.3157786
 20 H  H5          -0.7941878     2.2743412     3.8097505
 21 H  H14          0.0077656     4.3475572     2.6307644
```

2-thiazoyl

```
Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

   1 C   C1           -0.5454436     0.0226715     0.5437647
   2 H   H2           -1.5032974     0.5360423     0.5852073
   3 C   C2            0.2303064     0.1838704    -0.5432247
   4 H   H1            1.1980552    -0.2977856    -0.6521511
   5 C   C3           -0.2472724    -0.7859274     1.7085530
   6 N   N1           -1.0663557    -0.8859838     2.7293949
   7 C   C5           -0.5603522    -1.7087601     3.6968361
   8 C   C6            0.6653319    -2.2605474     3.4372234
   9 S   S1            1.2388862    -1.7305197     1.8953617
  10 H   H8           -1.1365473    -1.8812683     4.5989361
  11 H   H9            1.2465596    -2.9321230     4.0541349
  12 C   C7           -0.2190138     1.0410760    -1.6602688
  13 O   O2           -1.2669478     1.6552306    -1.7114256
  14 O   O3            0.7078642     1.0543694    -2.6485952
  15 C   C8            0.3693540     1.8522579    -3.7929022
  16 H   H3            1.2024448     1.7372158    -4.4868972
  17 H   H4            0.2476541     2.9011807    -3.5085135
  18 H   H6           -0.5612263     1.4990010    -4.2454338
```

piperonyl

```
Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

   1 H   H1           -0.3968724     1.5543129    -1.3560687
   2 C   C1           -0.2192789     1.5267201    -0.2859382
   3 C   C4            0.2450682     1.4866853     2.5233457
   4 C   C2            0.0211857     0.2990016     0.3837331
   5 C   C6           -0.2191316     2.6804777     0.4651621
   6 C   C5            0.0089855     2.6658740     1.8389725
   7 C   C3            0.2470043     0.3044367     1.7726828
   8 H   H3            0.4295927    -0.6324651     2.2881308
   9 H   H4            0.4213928     1.4824670     3.5934008
  10 C   C7            0.0240148    -0.9245584    -0.4176954
  11 H   H7           -0.1664618    -0.7832148    -1.4795257
  12 C   C8            0.2353728    -2.1861381     0.0068761
  13 H   H8            0.4339741    -2.4278969     1.0460958
  14 C   C9            0.2267218    -3.3702372    -0.8687748
  15 O   O1           -0.0136184    -3.0745762    -2.1734061
  16 O   O2            0.4168139    -4.5054560    -0.4720569
  17 C   C10          -0.0228284    -4.2012089    -3.0594418
  18 H   H2           -0.8102129    -4.9071183    -2.7801998
  19 H   H9            0.9393850    -4.7202783    -3.0349791
  20 H   H10          -0.2118046    -3.7914998    -4.0526112
  21 O   O3           -0.4233879     3.9719759     0.0435385
  22 O   O4           -0.0403356     3.9417654     2.3335158
  23 C   C11          -0.3280039     4.7920731     1.2135373
  24 H   H11           0.4857080     5.5156442     1.0892889
  25 H   H12          -1.2832833     5.3032144     1.3824176
```

Ethyl cinnamate

```
 Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

   1 H   H1          0.8094665     2.1829020    -1.8821796
   2 C   C1          0.6152364     2.3709243    -0.8290218
   3 C   C4          0.1166399     2.8516511     1.8674978
   4 C   C2          0.2366564     1.2981348    -0.0015361
   5 C   C6          0.7431351     3.6617944    -0.3205155
   6 C   C5          0.4946944     3.9069062     1.0304224
   7 C   C3         -0.0111336     1.5636824     1.3593274
   8 H   H6          1.0367395     4.4750189    -0.9786682
   9 H   H5          0.5939834     4.9120816     1.4309070
  10 H   H3         -0.3067116     0.7558034     2.0222448
  11 H   H4         -0.0787780     3.0361425     2.9204475
  12 C   C7          0.1191615    -0.0348170    -0.5930555
  13 C   C8         -0.2237237    -1.1829758     0.0195615
  14 H   H2          0.3360990    -0.1044686    -1.6583634
  15 H   H7         -0.4614193    -1.2461745     1.0765785
  16 C   C10        -0.2891713    -2.4409783    -0.7496115
  17 O   O1         -0.0614930    -2.5691224    -1.9382809
  18 O   O2         -0.6456391    -3.4745586     0.0550586
  19 C   C11        -0.7367231    -4.7496375    -0.5948518
  20 H   H8          0.2257049    -5.0290876    -1.0327061
  21 H   H11        -1.4897831    -4.7263014    -1.3877804
  22 H   H12        -1.0229413    -5.4569196     0.1845253
```

2-furyl

```
 Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

   1 C   C1         -0.5861778    -0.0457215     0.4069199
   2 H   H2         -1.6046844     0.3335817     0.3597083
   3 C   C2          0.2518868     0.2643737    -0.6030869
   4 H   H1          1.2811268    -0.0766997    -0.6246977
   5 C   C3         -0.2679092    -0.8368358     1.5595421
   6 C   C4         -1.0186753    -1.2156629     2.6482011
   7 C   C5         -0.1709988    -2.0004238     3.4831726
   8 C   C6          1.0370148    -2.0482303     2.8499015
   9 O   O1          1.0002162    -1.3521308     1.6850159
  10 H   H5         -2.0542990    -0.9572724     2.8216408
  11 H   H8         -0.4226338    -2.4661278     4.4255788
  12 H   H9          1.9809179    -2.5160889     3.0863099
  13 C   C7         -0.2240321     1.0933730    -1.7233965
  14 O   O2         -1.3455036     1.5517945    -1.8497766
  15 O   O3          0.7672365     1.2943735    -2.6288477
  16 C   C8          0.4033583     2.0961908    -3.7604271
  17 H   H3          1.2990927     2.1540682    -4.3800789
  18 H   H4          0.0919452     3.0950270    -3.4414956
  19 H   H6         -0.4178814     1.6324117    -4.3141840
```

2-thiophenyl

```
Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

   1 C   C1          -0.4535858    -0.0243428     0.3412620
   2 H   H2          -1.4645077     0.3808937     0.3148997
   3 C   C2           0.3535076     0.2789904    -0.6953413
   4 H   H1           1.3778722    -0.0748932    -0.7661434
   5 C   C3          -0.1423379    -0.8297731     1.4961240
   6 C   C4          -0.9971067    -1.1209763     2.5413079
   7 C   C5          -0.4150242    -1.9414346     3.5445300
   8 C   C6           0.8834163    -2.2741323     3.2616380
   9 S   S1           1.4183528    -1.5900039     1.7624876
  10 H   H5          -2.0159633    -0.7489986     2.5761987
  11 H   H8          -0.9355970    -2.2706286     4.4369541
  12 H   H9           1.5598762    -2.8829791     3.8468853
  13 C   C7          -0.1471378     1.1227217    -1.7944892
  14 O   O2          -1.2619570     1.6062332    -1.8750323
  15 O   O3           0.8116420     1.3030524    -2.7380140
  16 C   C8           0.4213655     2.1165398    -3.8527611
  17 H   H3           1.2929905     2.1560024    -4.5071847
  18 H   H4           0.1455531     3.1209030    -3.5190446
  19 H   H6          -0.4313588     1.6728258    -4.3742764
```

3-Me-2-furyl

```
 Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

   1 C   C1          -0.1800432     0.0010486    -0.0533776
   2 H   H2          -1.1985498    -0.0461630    -0.4326809
   3 C   C2           0.6580214    -1.0089582    -0.3634728
   4 H   H1           1.6872614    -1.0305690    -0.0223994
   5 C   C3           0.1382254     1.1536708     0.7377366
   6 C   C4          -0.6125407     2.2423298     1.1165637
   7 C   C5           0.2351358     3.0773013     1.9013247
   8 C   C6           1.4431494     2.4440302     1.9491312
   9 O   O1           1.4063508     1.2791446     1.2530316
  10 H   H8          -0.0164993     4.0197075     2.3670287
  11 H   H9           2.3870525     2.6804386     2.4169897
  12 C   C7           0.1821025    -2.1292679    -1.1924721
  13 O   O2          -0.9393690    -2.2556479    -1.6508937
  14 O   O3           1.1733711    -3.0347191    -1.3934727
  15 C   C8           0.8094929    -4.1662985    -2.1952900
  16 H   H3           1.7052273    -4.7859503    -2.2531674
  17 H   H4           0.4980798    -3.8473669    -3.1941262
  18 H   H6          -0.0117468    -4.7200553    -1.7315109
  19 C   C9          -2.0787718     2.4878848     0.7507357
  20 H   H5          -2.1312767     3.0980072    -0.1582252
  21 H   H7          -2.5773364     3.0137329     1.5730088
  22 H   H10         -2.5773364     1.5276999     0.5755379
```

```
N-Boc-2-pyrroyl

Cartesian Coordinates (Angstroms)
       Atom              X             Y             Z
    ---------     ------------- ------------- -------------

   1 C   C1          1.2835003     0.0246371    -0.8176050
   2 H   H2          0.4573820     0.6022074    -0.4253786
   3 C   C2          1.6434672     0.2773757    -2.0940092
   4 H   H1          2.4366695    -0.2564087    -2.6077389
   5 C   C3          1.9067766    -0.9304564     0.0646007
   6 C   C4          3.1300951    -1.5680919    -0.0617223
   7 C   C5          3.3727855    -2.3355217     1.1068869
   8 C   C6          2.3000683    -2.1602396     1.9417346
   9 N   N1          1.3927693    -1.3112357     1.3275764
  10 H   H5          3.7966605    -1.4526068    -0.9059462
  11 H   H8          4.2415600    -2.9448850     1.3147515
  12 H   H9          2.0707186    -2.5626340     2.9152865
  13 C   C7          0.9274185     1.3158813    -2.8498912
  14 O   O2          0.0024641     1.9983814    -2.4411995
  15 O   O3          1.4288196     1.4302126    -4.1074914
  16 C   C8          0.7931884     2.4165788    -4.9300804
  17 H   H3          1.3037365     2.3698145    -5.8929337
  18 H   H4          0.8961602     3.4127238    -4.4900456
  19 H   H6         -0.2711004     2.1941355    -5.0492187
  20 C   C9          0.1569124    -1.0315429     1.9667199
  21 O   O1         -0.0304055    -1.3261031     3.1276429
  22 O   O4         -0.7017898    -0.4573704     1.1277316
  23 C   C10        -2.0430104     0.0056071     1.5781028
  24 C   C11        -1.8692816     1.0950983     2.6378016
  25 H   H7         -1.3961684     0.7013709     3.5394425
  26 H   H12        -2.8524620     1.4962416     2.9074989
  27 H   H13        -1.2634745     1.9190589     2.2458376
  28 C   C12        -2.8591165    -1.1864860     2.0837571
  29 H   H10        -2.4441450    -1.5982818     3.0048652
  30 H   H14        -2.8916951    -1.9750289     1.3241647
  31 H   H15        -3.8873846    -0.8606490     2.2757576
  32 C   C13        -2.6408231     0.5700264     0.2877880
  33 H   H11        -2.0110335     1.3598982    -0.1330557
  34 H   H16        -3.6325881     0.9862970     0.4928455
  35 H   H17        -2.7466742    -0.2180043    -0.4644761
```

Baldwin VCP INT (8b)

H	1.442750	0.921698	-1.239800
C	1.174223	1.088619	-0.199764
C	-0.205397	1.594368	0.105723
C	0.151197	0.149790	0.419148
H	2.000646	1.417717	0.424305
H	-0.883108	1.775465	-0.724784
H	-0.338621	2.274416	0.942683
H	0.296804	-0.086999	1.471332
C	-0.430333	-0.944346	-0.387160
H	-0.576162	-0.721840	-1.446325
C	-0.778212	-2.146752	0.078483

```
H       -1.202504     -2.908299     -0.569397
H       -0.651283     -2.413837      1.125558

Baldwin VCPR TS

C       -0.215191      1.190052     -0.227090
C       -1.349112      0.421866     -0.217252
C       -1.386915     -0.875798      0.339664
C        1.093057      0.583636      0.232001
C        1.230186     -0.836001     -0.253629
H       -0.232714      2.211810     -0.596753
H       -2.244410      0.795796     -0.714968
H       -0.751599     -1.161244      1.168910
H        1.069204     -1.040072     -1.308078
H        1.867359     -1.532357      0.287554
H        1.931023      1.206053     -0.128602
H        1.174797      0.603886      1.332791
H       -2.185686     -1.567628      0.085453
```

[3,3]-Mechanism Searching

(S-TS6)

```
[3,3] Transoid Triplet Transition State
Spartan'10: G = -852.420461, iv = i613, S^2 = 2.0177
[3,3] Transoid Diradicaloid
Spartan'10: G = -852.445602, iv = i552, S^2 = 0.6134
[3,3] Transoid Closed Shell
Spartan'10: G = -852.435275, iv = i67

Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C             2.3374563     0.3330489    -2.1080915
  2 F   F             2.4256384    -0.9115264    -2.7529639
  3 F   F3            3.4032088     1.0617736    -2.6006786
  4 C   C4            2.5657165     0.1320971    -0.6505621
  5 H   H             3.5622940     0.3928016    -0.3080310
  6 C   C6            1.0789034     0.9809830    -2.6058204
  7 H   H7            1.1643354     1.2641873    -3.6525420
  8 C   C8           -0.0983823     1.1552714    -1.9821114
  9 H   H9           -0.9281032     1.5043633    -2.5947118
 10 C   C10          -0.4496947     0.8566367    -0.5843182
 11 H   H11           0.0756405     1.4190667     0.1825713
 12 C   C12          -1.9129894     0.7750143    -0.3343334
 13 O   O            -2.7518708     0.4856100    -1.1684378
 14 O   O14          -2.2070567     1.0142512     0.9659606
 15 C   C15          -3.5943332     0.8855277     1.3115032
 16 H   H16          -3.9494122    -0.1297150     1.1106489
 17 H   H17          -4.2020983     1.5907992     0.7377134
 18 H   H18          -3.6522700     1.1081487     2.3777128
 19 C   C19           1.6719391    -0.5048293     0.2540782
 20 C   C20          -0.0900694    -1.7376610     2.1226550
 21 C   C21           0.3209353    -0.9075669    -0.1755517
 22 C   C22           2.0237697    -0.6627839     1.5896103
 23 C   C23           1.1433487    -1.2623996     2.5352652
```

```
 24 C   C24           -0.4724439     -1.6238969      0.7762227
 25 H   H25            0.2363543     -1.2466427     -1.2060124
 26 H   H26            3.0008465     -0.3182240      1.9195639
 27 H   H27            1.4593765     -1.3631237      3.5690190
 28 H   H28           -1.4118475     -2.0562905      0.4427653
 29 H   H29           -0.7491923     -2.2349208      2.8288763
```

S-TS7a

```
[3,3] Cisoid Triplet Transition State
Spartan'10: G = -852.411611, iv = i538, S^2 = 2.0397

Cartesian Coordinates (Angstroms)
       Atom              X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C              1.6839700      1.4112607     -2.0466638
  2 F   F              2.5766738      1.4465241     -3.1009893
  3 F   F3             1.4296522      2.7520214     -1.7493923
  4 C   C4             2.3582761      0.7947560     -0.8570935
  5 H   H              3.2596855      1.2951852     -0.5073202
  6 C   C6             0.4237176      0.7233898     -2.4994167
  7 H   H7             0.4089928      0.4155717     -3.5405067
  8 C   C8            -0.6096278      0.4606696     -1.6793565
  9 H   H9            -1.4616330     -0.1043965     -2.0492272
 10 C   C10           -0.6553100      0.8631396     -0.2727040
 11 H   H11           -0.2399756      1.8467288     -0.0730032
 12 C   C12           -1.9414769      0.6218576      0.4290469
 13 O   O             -2.8204701     -0.1344267      0.0639202
 14 O   O14           -1.9994752      1.3246740      1.5906512
 15 C   C15           -3.1948822      1.1333352      2.3624714
 16 H   H16           -3.3078673      0.0836187      2.6482809
 17 H   H17           -4.0751618      1.4390237      1.7906988
 18 H   H18           -3.0761145      1.7608966      3.2465162
 19 C   C19            1.7705130     -0.3620541     -0.1613052
 20 C   C20            0.4476392     -2.5605370      1.0378059
 21 C   C21            2.0701335     -1.6586126     -0.5413184
 22 C   C22            0.6974892     -0.1188347      0.7983874
 23 C   C23            0.1260122     -1.2833207      1.4447133
 24 C   C24            1.4172969     -2.7631849      0.0394031
 25 H   H25            2.8258561     -1.8237732     -1.3048759
 26 H   H26            0.8222681      0.7481696      1.4468545
 27 H   H27           -0.5881718     -1.1257393      2.2476791
 28 H   H28            1.6790043     -3.7695293     -0.2736922
 29 H   H29           -0.0270143     -3.4164129      1.5104359
```

S-TS7b

```
[3,3] Cisoid Closed Shell Transition State
Spartan'10: G = -852.464842, iv = i385

Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C           1.8306612     1.5956508    -1.8575741
  2 F   F           2.6870122     2.1184195    -2.7906786
  3 F   F3          1.8069515     2.4827641    -0.7996484
  4 C   C4          2.2410148     0.2100367    -1.4905855
  5 H   H           2.8205396    -0.2931099    -2.2601120
  6 C   C6          0.4929078     1.3164800    -2.4574821
  7 H   H7          0.5094519     1.1703634    -3.5334670
  8 C   C8         -0.6102237     0.9738261    -1.7309582
  9 H   H9         -1.4344701     0.4807224    -2.2423811
 10 C   C10        -0.7132016     1.0783911    -0.3075953
 11 H   H11        -0.3784892     2.0027709     0.1423622
 12 C   C12        -1.9631461     0.5379098     0.2891657
 13 O   O          -2.7047621    -0.2721485    -0.2306949
 14 O   O14        -2.1783377     1.0574306     1.5250633
 15 C   C15        -3.3528503     0.5724078     2.1939135
 16 H   H16        -3.3040250    -0.5128555     2.3185646
 17 H   H17        -4.2514107     0.8221237     1.6232500
 18 H   H18        -3.3648593     1.0714663     3.1636692
 19 C   C19         1.7137344    -0.5284032    -0.4510369
 20 C   C20         0.5579043    -2.1472863     1.5830749
 21 C   C21         1.8689793    -1.9623226    -0.4539682
 22 C   C22         0.8996587     0.0751830     0.6064962
 23 C   C23         0.3968822    -0.7962414     1.6475472
 24 C   C24         1.3030441    -2.7412087     0.5104419
 25 H   H25         2.4373971    -2.4126343    -1.2642251
 26 H   H26         1.2378510     1.0456992     0.9401489
 27 H   H27        -0.1236510    -0.3391174     2.4835210
 28 H   H28         1.4204899    -3.8209299     0.4779126
 29 H   H29         0.1549463    -2.7853874     2.3652758
```

[3,3]-Methodology Screening

Divinyl Species VCP INT (S22)

```
Spartan'10: B3LYP/6-31G*, G = -272.648654, iv = none
Gaussian’09: B3LYP/6-31G*, G = -272.569679, iv = none
M06-2X/6-31G*,G = -272.431421, iv = none

Cartesian Coordinates (Angstroms)
       Atom            X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C1          1.6922994     0.1392844     0.1378774
  2 C   C2          0.3988567     0.7574908     0.6151673
  3 C   C3          0.5377290    -0.7716186     0.4834085
  4 H   H6          0.6119170    -1.2877553     1.4356786
  5 C   C10        -0.1664634    -1.5377762    -0.5636591
  6 H   H11        -0.2166977    -1.0847065    -1.5512695
```

```
  7 C   C11          -0.7243985    -2.7353400    -0.3801304
  8 H   H12          -0.7005566    -3.2348517     0.5837612
  9 H   H2            0.3943943     1.1086332     1.6424865
 10 H   H8            2.5494545     0.1604584     0.8004636
 11 H   H9            1.9359198     0.2523124    -0.9131092
 12 H   H15          -1.2222093    -3.2567650    -1.1892550
 13 C   C4           -0.4449305     1.5535815    -0.2977803
 14 C   C6           -1.1908461     2.5945287     0.0754445
 15 H   H1           -1.2316971     2.9258508     1.1086497
 16 H   H13          -1.7851697     3.1497837    -0.6406867
 17 H   H17          -0.4376017     1.2668891    -1.3470473
```

Divinyl Species [3,3]-TS (S-TS8)

```
Spartan'10: B3LYP/6-31G*, G = -272.536339, iv = i434
Gaussian'09: B3LYP/6-31G*, G = -272.53598, iv = i419
M06-2X/6-31G*,G = -272.394561, iv = i518
```

```
 Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C1           -1.3141431     0.0858792     1.1956138
  2 H   H3           -1.5218186    -0.9575706     0.9960566
  3 C   C2           -0.0291084     0.4926157     1.5187609
  4 C   C5           -0.0356607     0.6217441    -1.4704223
  5 H   H7            0.0907939     1.6082371    -1.9169345
  6 C   C6           -1.3218653     0.1955604    -1.1769583
  7 H   H6           -1.5372630    -0.8597391    -1.0695242
  8 C   C3            1.1243576     0.0005740    -0.9981933
  9 C   C4            1.1294915    -0.0825547     0.9885817
 10 C   C11           1.1450748    -1.1596204    -0.0516523
 11 H   H2            2.0898886     0.4141807    -1.2762521
 12 H   H10           2.0959052     0.3084491     1.2937960
 13 H   H17          -2.1701876     0.8034414    -1.4793252
 14 H   H21           0.2677384    -1.8068587    -0.0775966
 15 H   H22           2.0565693    -1.7585354    -0.0796222
 16 H   H1           -2.1655803     0.6564818     1.5562745
 17 H   H11           0.0958078     1.4377156     2.0473972
```

Furan basic alkene INT [3,3] (S23)

```
Spartan'10: B3LYP/6-31G*, G = -423.988081, iv = none
Gaussian'09: B3LYP/6-31G*, G = -423.990183, iv = none
M06-2X/6-31G*,G = -423.804524, iv = none
```

```
 Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C1            2.0211098    -0.2019559    -0.2878635
  2 C   C2            1.0455931     0.5679385     0.5563511
  3 C   C3            1.1811074    -0.9579600     0.7227411
  4 H   H6            1.6950687    -1.2655714     1.6311662
  5 C   C10           0.1137728    -1.8791687     0.2796023
  6 H   H11          -0.4504758    -1.5718682    -0.6005445
```

```
   7  C   C11          -0.1862803    -3.0316599     0.8841588
   8  H   H12           0.3516805    -3.3717411     1.7665564
   9  C   C4           -0.1463955     1.1835360    -0.0514472
  10  C   C5           -0.5099529     1.5057073    -1.3288209
  11  C   C6           -1.8161123     2.0934018    -1.2526201
  12  C   C7           -2.1512630     2.0926024     0.0654157
  13  H   H1            0.0865861     1.3586969    -2.2183691
  14  H   H8           -2.4149282     2.4695347    -2.0705875
  15  H   H9           -3.0151894     2.4311237     0.6170684
  16  O   O3           -1.1518294     1.5413520     0.8119593
  17  H   H2            1.4658002     1.1388947     1.3828715
  18  H   H3            3.0821058    -0.0798072    -0.0895872
  19  H   H4            1.7797895    -0.3460992    -1.3375905
  20  H   H7           -0.9801871    -3.6769564     0.5195397
```

Furan basic alkene TS [3,3] (S-TS10)

```
Spartan'10: B3LYP/6-31G*, G = -423.948929, iv = i375
Gaussian'09: B3LYP/6-31G*, G = -423.94862, iv = i364
M06-2X/6-31G*,G = -423.804524, iv = i501

Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

   1  C   C1           -1.0283397    -0.4010231     0.7571931
   2  H   H3           -1.3288846    -1.4018108     0.4822254
   3  C   C2            0.3149653    -0.0843233     1.1143534
   4  C   C5            0.1806775     0.5851929    -1.8049434
   5  H   H7            0.1886549     1.6298365    -2.1155432
   6  C   C6           -1.0478457    -0.0056010    -1.4914104
   7  H   H6           -1.1562864    -1.0802117    -1.5818701
   8  C   C3            1.4061193    -0.0015796    -1.5255067
   9  C   C4            1.5056262    -0.4561222     0.5381058
  10  C   C11           1.5647472    -1.2614028    -0.7289562
  11  H   H2            2.3179841     0.5447544    -1.7517164
  12  H   H10           2.4243494    -0.0184088     0.9139063
  13  O   O3            0.3046054     0.9591443     2.0340899
  14  C   C8           -1.0061254     1.2405430     2.2973044
  15  H   H12          -1.1694267     2.0232775     3.0244229
  16  C   C7           -1.8501102     0.4577518     1.5881914
  17  H   H11          -2.9302458     0.4734522     1.6347546
  18  H   H8           -1.9647426     0.5515984    -1.6637485
  19  H   H13           0.7543954    -1.9858727    -0.8430314
  20  H   H14           2.5198825    -1.7691948    -0.8778209
```

Thiophene basic alkene INT [3,3] (S24)

```
Spartan'10: B3LYP/6-31G*, G = -746.970146, iv = none
Gaussian'09: B3LYP/6-31G*, G = -746.972369, iv = none
M06-2X/6-31G*,G = -746.779248, iv = none
```

```
Cartesian Coordinates (Angstroms)
      Atom            X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C1          2.0342002    -0.2274222    -0.0893840
  2 C   C2          1.0083838     0.5175287     0.7205973
  3 C   C3          1.1438292    -1.0097873     0.8564552
  4 H   H6          1.6098827    -1.3407959     1.7825414
  5 C   C10         0.1071938    -1.9243166     0.3331753
  6 H   H11        -0.4024356    -1.6036092    -0.5748702
  7 C   C11        -0.2265279    -3.0867859     0.9001834
  8 H   H12         0.2573181    -3.4399102     1.8085163
  9 C   C4         -0.1614673     1.1537212     0.0676524
 10 C   C5         -0.3028157     1.5991983    -1.2219863
 11 C   C6         -1.5793267     2.1816071    -1.4925050
 12 C   C7         -2.4031674     2.1789389    -0.4026654
 13 H   H1          0.4935970     1.5255504    -1.9551030
 14 H   H8         -1.8643257     2.5889943    -2.4567860
 15 H   H9         -3.4137035     2.5570230    -0.3227241
 16 S   S1         -1.6333832     1.4513366     0.9735079
 17 H   H2          1.3955547     1.0633116     1.5801496
 18 H   H3          3.0826091    -0.1075179     0.1690450
 19 H   H4          1.8493969    -0.3496373    -1.1530430
 20 H   H7         -0.9948125    -3.7274275     0.4772432
```

Thiophene basic alkene TS [3,3] (S-TS11)

```
Spartan'10: B3LYP/6-31G*, G = -746.930649, iv = i388
Gaussian'09: B3LYP/6-31G*, G = -746.93057, iv = i390
M06-2X/6-31G*,G = -746.731749, iv = i513
```

```
 Cartesian Coordinates (Angstroms)
      Atom            X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C1         -0.9189548    -0.4240114     0.7504790
  2 H   H3         -1.1147122    -1.4402266     0.4318292
  3 C   C2          0.4086231    -0.0557975     1.1303085
  4 C   C5          0.2563491     0.6375349    -1.7780825
  5 H   H7          0.2835947     1.6895231    -2.0613975
  6 C   C6         -0.9818885     0.0654255    -1.4649227
  7 H   H6         -1.1223033    -1.0004326    -1.6017383
  8 C   C3          1.4714917     0.0183867    -1.5254622
  9 C   C4          1.5815088    -0.4486707     0.5176155
 10 C   C11         1.6126170    -1.2567297    -0.7494393
 11 H   H2          2.3922651     0.5471979    -1.7569661
 12 H   H10         2.5296780    -0.0491525     0.8658829
 13 S   S1          0.3554048     1.2920013     2.2966335
 14 C   C8         -1.3938788     1.2278275     2.3506109
 15 H   H12        -1.9282369     1.8907785     3.0194038
 16 C   C7         -1.9142747     0.2946522     1.5169151
 17 H   H11        -2.9785961     0.0998604     1.4329914
 18 H   H8         -1.8852902     0.6542682    -1.5999269
 19 H   H13         0.7880972    -1.9646036    -0.8631282
 20 H   H14         2.5585060    -1.7778317    -0.9116061
```

Non-fluoro Pip cis (S25)

Spartan'10: B3LYP/6-31G*, G = -842.539706, iv = none
Gaussian’09: B3LYP/6-31G*, G = -842.546027, iv = none
M06-2X/6-31G*,G = -842.201221, iv = none

```
Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C1          3.0422011    -0.2059109     0.8333341
  2 C   C2          1.9462495     0.6301462     1.4123946
  3 C   C3          1.7915637    -0.9034859     1.3561728
  4 H   H6          1.8915419    -1.4139110     2.3115219
  5 C   C10         0.8668632    -1.5315163     0.4062663
  6 H   H11         0.7192598    -1.0383017    -0.5535636
  7 C   C11         0.1896422    -2.6696412     0.6288198
  8 H   H12         0.2760755    -3.2240637     1.5592409
  9 C   C12        -0.7076642    -3.2212370    -0.4038901
 10 O   O1         -0.9249719    -2.7396061    -1.5003832
 11 O   O2         -1.2831356    -4.3747921     0.0257938
 12 C   C13        -2.1743954    -4.9936572    -0.9108810
 13 H   H5         -3.0200563    -4.3360514    -1.1326643
 14 H   H13        -2.5192305    -5.9092198    -0.4284011
 15 H   H14        -1.6551503    -5.2236293    -1.8455651
 16 C   C4          1.0978825     1.5520209     0.5894276
 17 C   C5          0.7952224     3.0268768    -1.3505680
 18 C   C6         -0.9677564     2.7108075     0.2779478
 19 C   C7         -0.4784712     3.2893029    -0.8931402
 20 C   C9          1.5781117     2.1438437    -0.5822917
 21 H   H1          1.1760331     3.4839111    -2.2574735
 22 H   H4          2.5895542     1.9257801    -0.9106321
 23 C   C8         -0.2120485     1.8458768     1.0381704
 24 H   H2          2.1242673     0.9867590     2.4267254
 25 H   H3         -0.6104691     1.3989510     1.9432289
 26 O   O3         -2.2450646     3.1618447     0.5151643
 27 O   O4         -1.4305404     4.1247672    -1.4279509
 28 C   C14        -2.6158043     3.8916840    -0.6597057
 29 H   H7         -3.0544472     4.8499658    -0.3687754
 30 H   H10        -3.3255377     3.2962697    -1.2517681
 31 H   H8          3.9619561    -0.3310041     1.3976659
 32 H   H9          3.1783192    -0.2027794    -0.2442203
```

Non-fluoro Pip cis [3,3] TS (S-TS12)

Spartan'10: B3LYP/6-31G*, G = -842.491477, iv = i374
Gaussian’09: B3LYP/6-31G*, G = -842.495343, iv = i369
M06-2X/6-31G*,G = -842.148309, iv = i487

```
 Cartesian Coordinates (Angstroms)
       Atom             X             Y             Z
    ---------    ------------- ------------- -------------

  1 C   C1          0.0520814    -0.9917968     0.5259498
  2 H   H3         -0.0680629    -2.0610640     0.3911571
  3 C   C2          1.3793483    -0.5890499     1.0005366
  4 C   C5          1.3946502    -0.4550237    -2.0184814
  5 H   H7          1.4907740     0.4909212    -2.5477833
  6 C   C6          0.0803486    -0.8195318    -1.5814762
```

7	H	H6	-0.2016633	-1.8639056	-1.6606524
8	C	C7	1.5052318	0.5844828	1.8403494
9	H	H4	2.4855943	0.9358776	2.1449348
10	C	C8	0.3724354	1.2214879	2.2165992
11	C	C9	-0.9278742	0.7683988	1.8341607
12	C	C10	-1.1222078	-0.3267477	1.0639775
13	H	H12	-2.1142224	-0.6851961	0.8171351
14	C	C3	2.5223390	-1.1324057	-1.6537495
15	C	C4	2.5117020	-1.2325879	0.5429250
16	C	C11	2.5316142	-2.2105191	-0.5981357
17	H	H2	3.4917592	-0.7607891	-1.9772189
18	H	H10	3.4793786	-0.8679440	0.8810774
19	C	C12	-1.0121538	0.1108352	-1.9457873
20	O	O1	-0.8861163	1.2902719	-2.2159820
21	O	O2	-2.2234775	-0.5100299	-1.9038794
22	C	C13	-3.3475585	0.3342121	-2.1883485
23	H	H1	-3.2619765	0.7689444	-3.1882166
24	H	H5	-3.4161761	1.1444830	-1.4567240
25	H	H8	-4.2243907	-0.3122520	-2.1268798
26	O	O3	-1.8664221	1.5764937	2.4190921
27	O	O4	0.2391522	2.3310099	3.0111647
28	C	C14	-1.1535291	2.6447480	3.0458727
29	H	H9	-1.3334033	3.5774634	2.4962941
30	H	H13	-1.4795959	2.7345598	4.0862811
31	H	H11	3.4385629	-2.8191869	-0.6170676
32	H	H14	1.6638581	-2.8761594	-0.6371249