Supporting Information for

Designed iron catalysts for allylic C−H functionalization of propylene and simple terminal olefins

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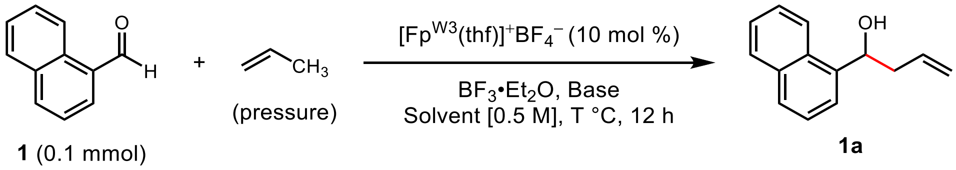
General Information

General Reagent Information: Anhydrous tetrahydrofuran (THF, Acros, AcroSeal packaging), toluene (Aldrich, Sure/Seal packaging), trifluorotoluene (Frontier Scientific, J&KSeal packaging), *p*-xylene (Acros, AcroSeal packaging) and 1,2-dichloroethane (DCE, Aldrich, Sure/Seal packaging) were obtained from commercial suppliers and were deoxygenated by sparging with nitrogen, transferred into an argon-filled glovebox, and used without further purification. Other dry solvents were obtained by distillation and storage over 3Å or 4Å molecular sieves. Propylene was purchased from Sigma Aldrich (CAS: 115-07-1, ≥99% purity). Boron trifluoride etherate was purchased from Sigma Aldrich. 2,2,6,6-Tetramethylpiperidine (TMPH) was purchased from Chem-Impex Int'l. Inc. and was redistilled and obtained as a pale yellow liquid before use. Silver tetrafluoroborate was purchased from Strem and was stored in the glovebox protected from light. (*Note:* Silver tetrafluoroborate used for catalyst synthesis should be a white free-flowing solid. The use of greyish discolored $AgBF_4$ resulted in catalyst of inferior reactivity.) All other reagents were purchased from TCI, Acros, Alfa Aesar, Sigma Aldrich or Combi-Blocks and were used as received. Compounds were purified by flash column chromatography using SiliCycle *SiliaFlash® F60* silica gel, unless otherwise indicated.

General Analytical Information: New compounds were characterized by ^{1}H NMR, ^{13}C NMR, HRMS, and, where appropriate, other analytical techniques as indicated. Copies of the ^{1}H NMR and ^{13}C NMR spectra can be found at the end of the Supporting Information. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on Bruker 300 MHz, 400 MHz or 500 MHz instruments. All ^{1}H NMR data are reported in δ units, parts per million (ppm), and were measured relative to the residual proton signal in the deuterated solvent at 7.26 ppm ($CDCl_3$) or 1.94 ppm (CD_3CN). All ^{13}C NMR spectra are ^{1}H decoupled and reported in ppm relative to the solvent signal at 77.16 ppm ($CDCl_3$) or 1.32/118.26 ppm (CD_3CN). Unless otherwise stated, 2,4-dinitrotoluene was used as the internal standard for yields determined by ^{1}H NMR. High resolution mass spectra were obtained on a Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS instrument (ESI) or Waters Micromass GCT Premier instrument (EI). Thin-layer chromatography (TLC) was performed on Silicycle 250 µm (analytical) or 1000 µm (preparative) silica gel plates. Compounds were visualized by irradiation with UV light, or by staining with iodine/silica gel, potassium permanganate, or phosphomolybdic acid (PMA). Yields refer to isolated compounds, unless otherwise indicated.

Optimization of reaction conditions

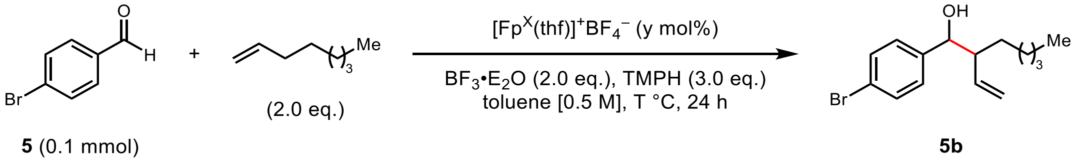
1. Conditions of propylene functionalization



Entry	Pressure (atm)	Base	Acid/base	Solvent	Temperature (°C)	Yield (%)[a]
1	8	*sym*-collidine	2.5/3	Toluene	80	0
2	8	2,6-lutidine	2.5/3	Toluene	80	0
3	8	TMPH	1.5/2	Toluene	80	37
4	8	TMPH	2.5/3	Toluene	80	84
5	8	TMPH	2.5/2	Toluene	80	48
6	8	TMPH	2/4	Toluene	80	78
7	**8**	**TMPH**	**2/2**	**Toluene**	**80**	**87**
8	8	TMPH	2/2	$PhCF_3$	80	80
9	8	TMPH	2/2	DCE	80	76
10	8	TMPH	2/2	*p*-xylene	80	81
11	8	TMPH	2/2	Toluene	60	85
12	8	TMPH	2/2	Toluene	100	49
13	1	TMPH	2/2	Toluene	80	64
14	5	TMPH	2/2	Toluene	80	79

[a]Yields were determined by ^{1}H NMR using 2,4-dinitrotoluene as the internal standard.

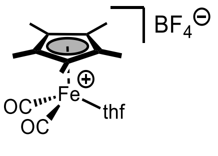
2. Conditions of allylic functionalization of higher olefins



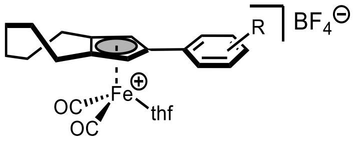
Entry	Iron catalyst	Catalyst loading	Temperature (°C)	Yield (%)[a]	d.r.
1	$Fp^*(thf)BF_4$	10 mol %	80	36	2.0:1
2	$Fp^*(thf)BF_4$	10 mol %	45	6	1.7:1
3	$Fp^{W3}(thf)BF_4$	5 mol %	50	90	4.0:1
4	$Fp^{W3}(thf)BF_4$	5 mol %	45	95	4.3:1
5	$Fp^{W3}(thf)BF_4$	5 mol %	42	79	4.6:1
6	$Fp^{W2}(thf)BF_4$	5 mol %	45	16	4.1:1
7	$Fp^{W5}(thf)BF_4$	5 mol %	45	95	4.8:1
8	$Fp^{W6}(thf)BF_4$	5 mol %	45	95	3.4:1

[a]Yields were determined by ^{1}H NMR using 2,4-dinitrotoluene as the internal standard.

Catalysts listed in the tables



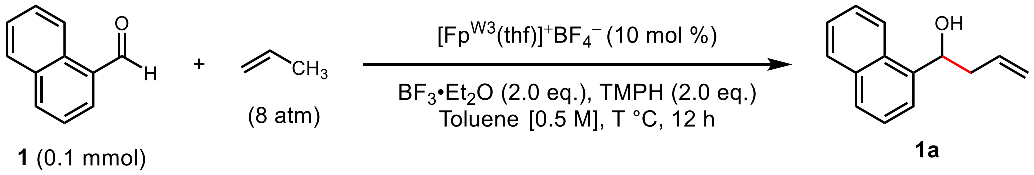
Fp*(thf)BF$_4$



Fp^X(thf)BF$_4$

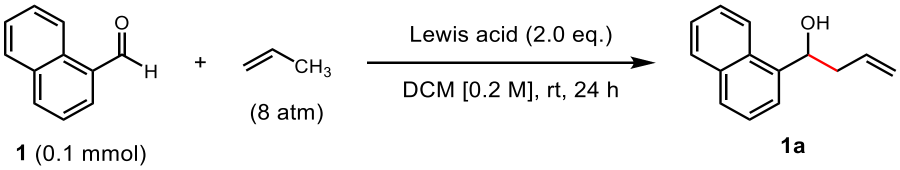
Fp^{W2}: R = H
Fp^{W3}: R = 4-OMe
Fp^{W5}: R = 3,5-2Me, 4-OMe
Fp^{W6}: R = 2-Me, 4-OMe

3. Control experiments



Entry	Catalyst	BF$_3$·Et$_2$O	TMPH	Temperature (℃)	Yield
1		✓	✓	80	N.P.
2		✓	✓	22	N.P.
3		✓		80	N.P.
4	✓			80	N.P.
5	✓	✓		80	N.P.
6		✓		80	N.P.

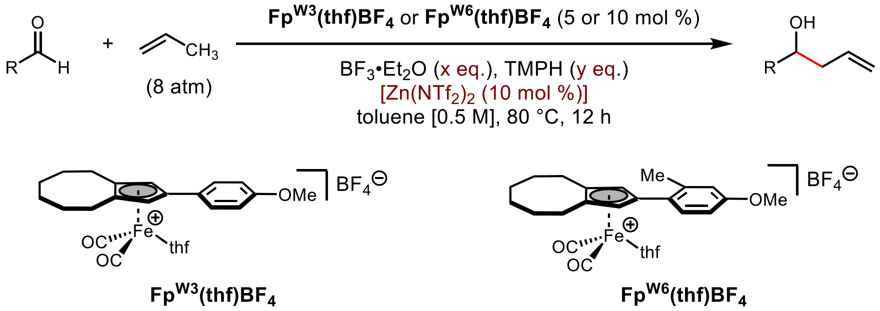
4. Testing possibility for the ene reaction



Entry	Lewis acid	yield
1	BF$_3$·Et$_2$O	N.P.
2	AlCl$_3$	N.P.

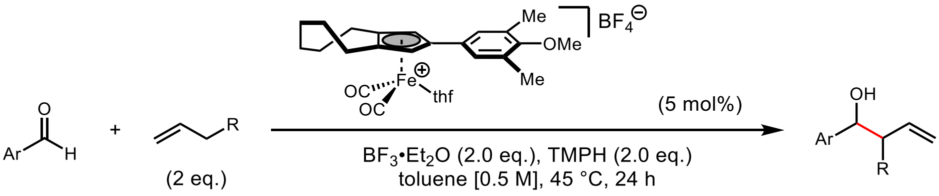
Note for experiments 3 and 4: Given the presence of Lewis acid, we wondered if our product could be generated through an ene reaction pathway, since double bond migration would not be apparent in the case of propylene as a substrate. This possibility was ruled out by a series of control experiments showing that the reaction could not occur in the absence of either the catalyst or the base. When the substrates were subjected to the conditions of classical ene reactions, no detectable amount of product was observed, indicating that the homoallylic alcohol products obtained from propylene by our approach are not easily accessible by the ene reaction. Thus, the role of iron catalyst is indispensable in this allylic functionalization process.

General procedure A for functionalization of allylic C−H bonds

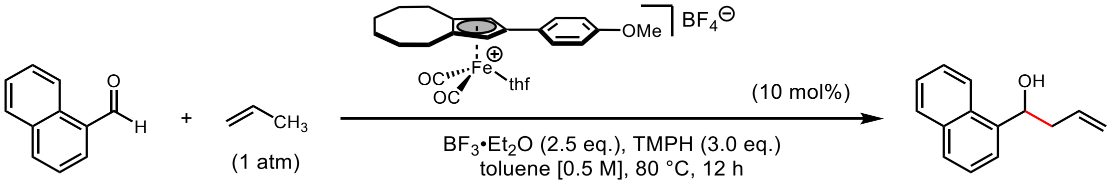


Conditions A1: To an oven-dried pressure tube (102 mm × 13 mm, Ace glass, part# 8648-61) charged with a magnetic stir bar, $Fp^{W3}(thf)BF_4$ (5.2 mg or 10.4 mg, 5 or 10 mol %) or $Fp^{W6}(thf)BF_4$ (10.8 mg, 10 mol %), aldehyde (0.2 mmol, 1.0 equiv), dry toluene (0.4 mL), BF_3•Et_2O (49 µL, 0.4 mmol, 2.0 equiv), TMPH (68 µL, 0.4 mmol, 2.0 equiv) were added in succession in an argon-filled glovebox. The tube was capped with a PTFE bushing with plunger valve (#7 Ace-Thred) and was cooled in liquid nitrogen. After the whole reaction mixture was frozen, the tube was placed under vacuum. Propylene (27 mL, 5.5 equiv, 8 atm at 80 °C, initial pressure) was condensed into the vacuum tube through the plunger valve, then the tube was resealed and taken out of liquid nitrogen. Details of introducing propylene gas are elaborated on page S76. After warming up to room temperature, the tube was heated at 80 °C for 12 h with vigorous stirring. The crude mixture was concentrated *in vacuo* and purified by flash column chromatography on silica gel to obtain the desired products.

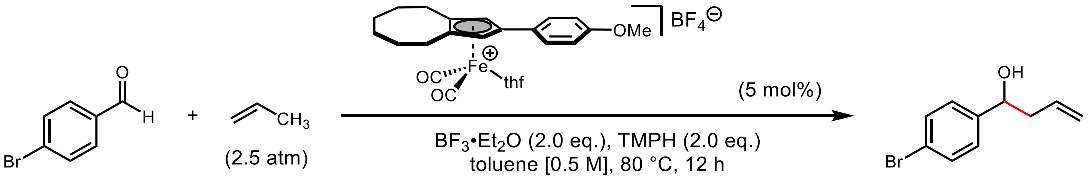
Conditions A2: To an oven-dried pressure tube (102 mm × 13 mm, Ace glass, part# 8648-61) charged with a magnetic stir bar, $Fp^{W3}(thf)BF_4$ (10.4 mg, 10 mol %), aldehyde (0.2 mmol, 1.0 equiv), $Zn(NTf_2)_2$ (12.5 mg, 0.02 mmol, 10 mol %), dry toluene (0.4 mL), BF_3•Et_2O (49 µL, 0.4 mmol, 2.0 equiv), TMPH (101 µL, 0.6 mmol, 3.0 equiv) were added in succession in an argon-filled glovebox. The tube was capped with a PTFE bushing with plunger valve (#7 Ace-Thred) and was cooled in liquid nitrogen. After the whole reaction mixture was frozen, the tube was placed under vacuum. Propylene (27 mL, 5.5 equiv, 8 atm at 80 °C, initial pressure) was condensed into the vacuum tube through the plunger valve, then the tube was resealed and taken out of liquid nitrogen. Details of introducing propylene gas are elaborated on page S76. After warming up to room temperature, the tube was heated at 80 °C for 12 h with vigorous stirring. The crude mixture was concentrated *in vacuo* and purified by flash column chromatography on silica gel to obtain the desired products.



Conditions A3: To a flame-dried reaction tube (100 mm × 13 mm, Fisherbrand, part# 14-959-35C) charged with a magnetic stir bar, $Fp^{W5}(thf)BF_4$ (5.5 mg, 5 mol %), aldehyde (0.2 mmol, 1.0 equiv), alkene (0.4 mmol, 2.0 equiv), dry toluene (0.4 mL), BF_3•Et_2O (49 µL, 0.4 mmol, 2.0 equiv), TMPH (101 µL, 0.6 mmol, 3.0 equiv) were added in succession in an argon-filled glovebox. The tube was capped with a Teflon/silicone septum (Thermo/National part# C4015-66A) screw cap and placed in an oil bath preheated at 45 °C with vigorous stirring. (Temperature must be controlled steadily at 45 °C during the course of the reaction.) After 24 h, the tube was allowed to cool to room temperature. The crude mixture was concentrated *in vacuo* and purified by flash column chromatography on silica gel to obtain the desired products.



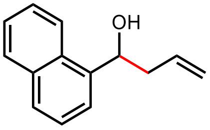
Conditions A4 (Scheme 3a−Initial results): To an oven-dried Schlenk flask (10 mL, Synthware, item# F490010) charged with a magnetic stir bar, $Fp^{W3}(thf)BF_4$ (10.4 mg, 10 mol %), 1-naphthaldehyde (31 mg, 0.2 mmol, 1.0 equiv), dry toluene (0.4 mL), $BF_3•Et_2O$ (62 µL, 0.5 mmol, 2.5 equiv), TMPH (101 µL, 0.6 mmol, 3.0 equiv) were added in succession in an argon-filled glovebox. The flask was sealed with a knob and was cooled in liquid nitrogen. After the whole reaction mixture was frozen, the flask was placed under vacuum for 10 min. The flask was resealed under vacuum and a balloon of propylene gas was attached to the side arm. The liquid nitrogen was removed and the knob was opened to allow propylene to fill the flask. After warming up to room temperature, the flask was heated at 80 °C for 12 h with vigorous stirring. The yield (4%) was determined by crude NMR using 2,4-dinitrotoluene as the internal standard.



Conditions A5 (Scheme 4a−Large-scale reaction): To an oven-dried Schlenk flask (100 mL, Chemglass, item# AF-0094-02) charged with a magnetic stir bar, $Fp^{W3}(thf)BF_4$ (79 mg, 5 mol %), 4-bromobenzaldehyde (555 mg, 3.0 mmol, 1.0 equiv), dry toluene (6 mL), $BF_3•Et_2O$ (740 µL, 6.0 mmol, 2.0 equiv), TMPH (1.0 mL, 6.0 mmol, 2.0 equiv) were added in succession in an argon-filled glovebox. The flask was sealed with a knob and was cooled in liquid nitrogen. After the whole reaction mixture was frozen, the flask was placed under vacuum for 10 min. Then propylene gas (207 mL, 2.9 equiv, 2.5 atm at 80 °C, initial pressure) was condensed into the flask through the side arm from a plastic syringe. The liquid nitrogen was removed and the flask was resealed. After warming up to room temperature, the flask was heated at 80 °C for 12 h with vigorous stirring. The crude mixture was concentrated *in vacuo* and purified by flash column chromatography on silica gel to obtain the desired product in 76% yield.

Characterization data for products

1. 1-(Naphthalen-1-yl)but-3-en-1-ol (1a, wrh-04-87A, 90B-C)



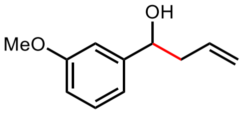
Compound **1a** was prepared as a pale yellow oil (33 mg, 83% yield, eluent: 10:1 hexanes/EtOAc) from 1-naphthaldehyde using Fp^{W3}(thf)BF_4 (10 mol %) according to general procedure A1.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 − 8.04 (m, 1H), 7.94 − 7.85 (m, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 7.1 Hz, 1H), 7.59 − 7.43 (m, 3H), 6.03 − 5.85 (m, 1H), 5.53 (dd, *J* = 8.1, 3.9 Hz, 1H), 5.31 − 5.13 (m, 2H), 2.85 − 2.71 (m, 1H), 2.69 − 2.52 (m, 1H), 2.27 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 134.9, 133.9, 130.4, 129.1, 128.1, 126.2, 125.63, 125.56, 123.1, 122.1, 118.5, 70.1, 42.1.

HRMS (APCI) calcd for $C_{14}H_{13}$ $[M{-}OH]^+$: 181.1012, found: 181.1010.

2. 1-(3-Methoxyphenyl)but-3-en-1-ol (2a, wrh-04-97A)



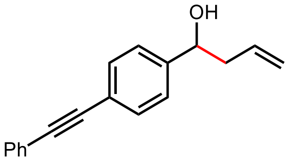
Compound **2a** was prepared as a pale yellow oil (30 mg, 82% yield, eluent: 10:1 → 5:1 hexanes/EtOAc) from 3-methoxybenzaldehyde using Fp^{W3}(thf)BF_4 (5 mol %) according to general procedure A1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 − 7.12 (m, 1H), 6.92 − 6.80 (m, 2H), 6.74 (d, *J* = 8.2 Hz, 1H), 5.82 − 5.65 (m, 1H), 5.17 − 5.00 (m, 2H), 4.70 − 4.57 (m, 1H), 3.73 (s, 3H), 2.50 − 2.34 (m, 2H), 2.08 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 145.7, 134.6, 129.5, 118.5, 118.2, 113.1, 111.4, 73.3, 55.3, 43.9.

HRMS (ESI) calcd for $C_{11}H_{15}O_2$ $[M+H]^+$: 179.1067, found: 179.1067.

3. 1-(4-(Phenylethynyl)phenyl)but-3-en-1-ol (3a, wrh-04-163A)



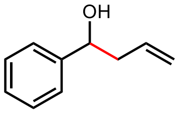
Compound **3a** was prepared as a pale yellow oil (44 mg, 87% yield, eluent: 15:1 → 10:1 hexanes/EtOAc) from 4-(phenylethynyl)benzaldehyde using Fp^{W3}(thf)BF_4 (10 mol %) according to general procedure A1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 − 7.50 (m, 4H), 7.40 − 7.30 (m, 5H), 5.86 − 5.74 (m, 1H), 5.22 − 5.12 (m, 2H), 4.75 (dd, *J* = 7.7, 5.1 Hz, 1H), 2.58 − 2.44 (m, 2H), 2.12 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 134.2, 131.8, 131.7, 128.5, 128.4, 126.0, 123.4, 122.5, 118.9, 89.5, 89.4, 73.1, 43.9.

HRMS (ESI) calcd for $C_{18}H_{15}$ $[M{-}OH]^+$: 231.1168, found: 231.1164.

4. 1-Phenylbut-3-en-1-ol (4a, wrh-05-36)

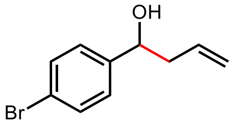


Compound **4a** was prepared as a pale yellow oil (23 mg, 77% yield, eluent: 15:1 → 10:1 hexanes/EtOAc) from benzaldehyde using $Fp^{W3}(thf)BF_4$ (10 mol %) according to general procedure A1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 − 7.15 (m, 5H), 5.80 − 5.65 (m, 1H), 5.15 − 5.00 (m, 2H), 4.65 (dd, *J* = 7.2, 5.6 Hz, 1H), 2.51 − 2.35 (m, 2H), 2.04 (s, 1H).

^{1}H NMR data were in agreement with the literature.[1]

5. 1-(4-Bromophenyl)but-3-en-1-ol. (5a, wrh-04-61A, wrh-04-12D)



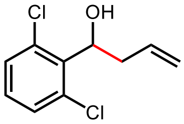
Compound **5a** was prepared as a pale yellow oil (38 mg, 84% yield, eluent: 8:1 hexanes/EtOAc) from 4-bromobenzaldehyde using $Fp^{W3}(thf)BF_4$ (5 mol %) according to general procedure A1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 5.89 − 5.69 (m, 1H), 5.29 − 5.06 (m, 2H), 4.80 − 4.63 (m, 1H), 2.59 − 2.37 (m, 2H), 2.02 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 134.0, 131.6, 127.7, 121.4, 119.0, 72.7, 43.9.

HRMS (ESI) calcd for $C_{10}H_{10}Br$ $[M{-}OH]^+$: 208.9960, found: 208.9961.

6. 1-(2,6-Dichlorophenyl)but-3-en-1-ol (6a, wrh-04-93A)



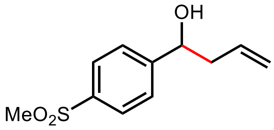
Compound **6a** was prepared as a pale yellow oil (40 mg, 91% yield, eluent: 20:1 hexanes/EtOAc) from 2,6-dichlorobenzaldehyde using $Fp^{W3}(thf)BF_4$ (5 mol %) according to general procedure A1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 8.0 Hz, 1H), 5.90 − 5.77 (m, 1H), 5.55 − 5.44 (m, 1H), 5.13 (d, *J* = 17.1 Hz, 1H), 5.09 (d, *J* = 10.1 Hz, 1H), 2.91 (d, *J* = 9.7 Hz, 1H), 2.89 − 2.80 (m, 1H), 2.74 − 2.63 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 137.4, 134.4, 133.9, 129.5, 129.0, 118.2, 71.5, 40.1.

HRMS (ESI) calcd for $C_{10}H_9Cl_2$ $[M{-}OH]^+$: 199.0076, found: 199.0078.

7. 1-(4-(Methylsulfonyl)phenyl)but-3-en-1-ol (7a, wrh-04-116A)



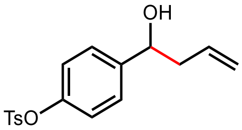
Compound **7a** was prepared as a pale yellow oil (35 mg, 79% yield, eluent: 1.5:1 hexanes/EtOAc) from 4-(methylsulfonyl)benzaldehyde using $Fp^{W3}(thf)BF_4$ (10 mol %) according to general procedure A1.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 5.90 − 5.68 (m, 1H), 5.28 − 5.11 (m, 2H), 4.85 (dd, *J* = 7.9, 4.6 Hz, 1H), 3.05 (s, 3H), 2.63 − 2.38 (m, 2H), 2.21 (br s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 150.4, 139.4, 133.5, 127.6, 126.9, 119.4, 72.4, 44.6, 44.0.

HRMS (ESI) calcd for $C_{11}H_{15}O_3S$ $[M+H]^+$: 227.0736, found: 227.0741.

8. 4-(1-Hydroxybut-3-en-1-yl)phenyl 4-methylbenzenesulfonate (8a, wrh-04-98A)



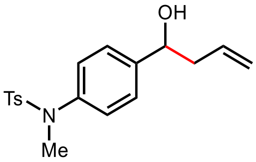
Compound **8a** was prepared as a pale yellow oil (57 mg, 89% yield, eluent: 4:1 → 3:1 hexanes/EtOAc) from 4-formylphenyl 4-methylbenzenesulfonate using $Fp^{W3}(thf)BF_4$ (10 mol %) according to general procedure A1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.21 (dd, *J* = 17.9, 8.1 Hz, 4H), 6.87 (d, *J* = 8.4 Hz, 2H), 5.76 − 5.60 (m, 1H), 5.14 − 4.99 (m, 2H), 4.69 − 4.57 (m, 1H), 2.46 − 2.28 (m, 5H), 2.13 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.9, 145.5, 142.9, 134.0, 132.4, 129.9, 128.6, 127.1, 122.4, 119.0, 72.5, 44.0, 21.8.

HRMS (ESI) calcd for $C_{17}H_{19}O_4S$ $[M+H]^+$: 319.0999, found: 319.0989.

9. *N*-(4-(1-Hydroxybut-3-en-1-yl)phenyl)-*N*,4-dimethylbenzenesulfonamide (9a, wrh-04-96A)



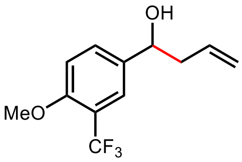
Compound **9a** was prepared as a pale yellow oil (46 mg, 70% yield, eluent: 3:1 → 2:1 hexanes/EtOAc) from *N*-(4-formylphenyl)-*N*,4-dimethylbenzenesulfonamide according to general procedure A2.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.1 Hz, 2H), 7.29 − 7.10 (m, 4H), 6.99 (d, *J* = 8.4 Hz, 2H), 5.82 − 5.61(m, 1H), 5.20 − 4.99 (m, 2H), 4.73 − 4.58 (m, 1H), 3.07 (s, 3H), 2.51 − 2.36 (m, 2H), 2.34 (s, 3H), 2.15 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 143.0, 140.8, 134.3, 133.6, 129.4, 128.1, 126.6, 126.4, 118.8, 72.7, 44.0, 38.2, 21.6.

HRMS (ESI) calcd for $C_{18}H_{22}O_3NS$ $[M+H]^+$: 332.1315, found: 332.1307.

10. 1-(4-Methoxy-3-(trifluoromethyl)phenyl)but-3-en-1-ol (10a, wrh-04-95A)



Compound **10a** was prepared as a pale yellow oil (34 mg, 69% yield, eluent: 5:1 → 3:1 hexanes/EtOAc) from 4-methoxy-3-(trifluoromethyl)benzaldehyde according to general procedure A2.

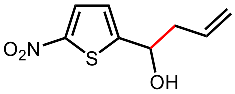
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 1H), 5.84 − 5.72 (m, 1H), 5.23 − 5.12 (m, 2H), 4.78 − 4.67 (m, 1H), 3.90 (s, 3H), 2.58 − 2.41 (m, 2H), 2.12 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 157.0, 135.7, 134.1, 130.8, 124.9 (q, *J* = 5.2 Hz), 123.8 (q, *J* = 270 Hz), 119.1, 119.1 − 118.4 (q, *J* = 31.2 Hz), 112.1, 72.5, 56.2, 44.0.

^{19}F NMR (471 MHz, $CDCl_3$) δ −62.39.

HRMS (APCI) calcd for $C_{12}H_{12}F_3O$ $[M-OH]^+$: 229.0835, found: 229.0833.

11. 1-(5-Nitrothiophen-2-yl)but-3-en-1-ol (11a, wrh-04-120A)



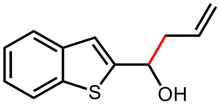
Compound **11a** was prepared as a brown oil (32 mg, 80% yield, eluent: 3:1 hexanes/EtOAc) from 5-nitrothiophene-2-carbaldehyde using $\mathrm{Fp^{W3}(thf)BF_4}$ (10 mol %) according to general procedure A1.

^{1}**H NMR** (300 MHz, $\mathrm{CDCl_3}$) δ 7.80 (d, *J* = 4.2 Hz, 1H), 6.90 (dd, *J* = 4.2, 0.8 Hz, 1H), 5.90 – 5.71 (m, 1H), 5.33 – 5.17 (m, 2H), 5.05 – 4.94 (m, 1H), 2.75 – 2.43 (m, 3H).

^{13}**C NMR** (75 MHz, $\mathrm{CDCl_3}$) δ 157.1, 150.7, 132.3, 128.7, 122.5, 120.6, 69.4, 43.7.

HRMS (ESI) calcd for $\mathrm{C_8H_{10}O_3NS}$ $[\mathrm{M+H}]^+$: 200.0376, found: 200.0371.

12. 1-(Benzo[*b*]thiophen-2-yl)but-3-en-1-ol (12a, wrh-04-158B)



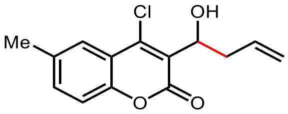
Compound **12a** was prepared as a pale yellow oil (21 mg, 52% yield, eluent: 20:1 → 10:1 hexanes/EtOAc) from benzo[*b*]thiophene-2-carbaldehyde according to general procedure A2.

^{1}**H NMR** (400 MHz, $\mathrm{CDCl_3}$) δ 7.85 – 7.79 (m, 1H), 7.75 – 7.69 (m, 1H), 7.38 – 7.27 (m, 2H), 7.20 (s, 1H), 5.86 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.27 – 5.15 (m, 2H), 5.07 (t, *J* = 6.3 Hz, 1H), 2.76 – 2.62 (m, 2H), 2.29 (s, 1H).

^{13}**C NMR** (100 MHz, $\mathrm{CDCl_3}$) δ 148.5, 139.6, 139.5, 133.6, 124.4, 124.3, 123.6, 122.6, 120.3, 119.3, 70.0, 43.6.

HRMS (ESI) calcd for $\mathrm{C_{12}H_{11}S}$ $[\mathrm{M{-}OH}]^+$: 187.0576, found: 187.0566.

13. 4-Chloro-3-(1-hydroxybut-3-en-1-yl)-6-methyl-2*H*-chromen-2-one (13a, wrh-04-152A)



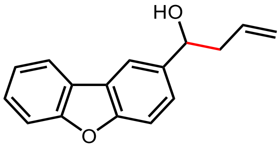
Compound **13a** was prepared as a pale yellow oil (43 mg, 81% yield, eluent: 6:1 hexanes/EtOAc) from 4-chloro-6-methyl-2-oxo-2*H*-chromene-3-carbaldehyde using $\mathrm{Fp^{W3}(thf)BF_4}$ (10 mol %) according to general procedure A1.

^{1}**H NMR** (500 MHz, $\mathrm{CDCl_3}$) δ 7.68 (s, 1H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 5.91 – 5.79 (m, 1H), 5.19 – 5.02 (m, 3H), 4.13 (d, *J* = 11.8 Hz, 1H), 2.74 (dt, *J* = 14.2, 7.2 Hz, 1H), 2.59 (dt, *J* = 13.9, 6.9 Hz, 1H), 2.44 (s, 3H).

^{13}**C NMR** (125 MHz, $\mathrm{CDCl_3}$, rotamers observed) δ 160.3, 149.8, 145.3, 135.2, 133.9, 133.5, 126.4, 125.8, 118.2, 117.9, 116.6, 70.7/70.6*, 40.71/40.68*, 21.1.

HRMS (ESI) calcd for $\mathrm{C_{14}H_{14}O_3Cl}$ $[\mathrm{M+H}]^+$: 265.0626, found: 265.0615.

14. 1-(Dibenzo[*b*,*d*]furan-2-yl)but-3-en-1-ol (14a, wrh-04-125B)



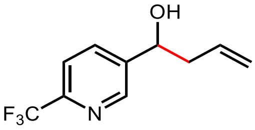
Compound **14a** was prepared as a pale yellow oil (23 mg, 48% yield, eluent: 15:1 → 10:1 hexanes/EtOAc) from dibenzo[*b*,*d*]furan-2-carbaldehyde according to general procedure A2.

^{1}**H NMR** (500 MHz, $\mathrm{CDCl_3}$) δ 7.97 (d, *J* = 1.2 Hz, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.63 – 7.50 (m, 2H), 7.50 – 7.41 (m, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 5.85 (ddt, *J* = 17.1, 10.1, 7.1 Hz, 1H), 5.26 − 5.12 (m, 2H), 4.96 − 4.86 (m, 1H), 2.68 − 2.54 (m, 2H), 2.20 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 156.7, 155.8, 138.7, 134.5, 127.3, 125.3, 124.4, 124.3, 122.9, 120.8, 118.7, 118.1, 111.8, 111.6, 73.5, 44.5.

HRMS (ESI) calcd for $C_{16}H_{13}O$ [M−OH]$^+$: 221.0961, found: 221.0959.

15. 1-(6-(Trifluoromethyl)pyridin-3-yl)but-3-en-1-ol (15a, wrh-04-107B)



Compound **15a** was prepared as a yellow oil (40 mg, 91% yield, eluent: 4:1 → 3:1 hexanes/EtOAc) from 6-(trifluoromethyl)nicotinaldehyde using Fp^{W3}(thf)BF_4 (10 mol %) according to general procedure A1. 80% yield was obtained using 5 mol % of catalyst.

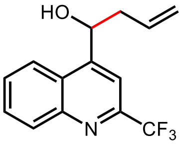
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 5.90 − 5.67 (m, 1H), 5.29 − 5.11 (m, 2H), 4.95 − 4.80 (m, 1H), 2.67 (s, 1H), 2.62 − 2.41 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 147.3 (q, *J* = 34 Hz), 142.6, 135.0, 133.0, 121.7 (q, *J* = 272 Hz), 120.3 (q, *J* = 3.0 Hz), 120.0, 70.5, 43.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ −67.75.

HRMS (ESI) calcd for $C_{10}H_{11}ONF_3$ [M+H]$^+$: 218.0787, found: 218.0788.

16. 1-(2-(Trifluoromethyl)quinolin-4-yl)but-3-en-1-ol (16a, wrh-04-140A)



Compound **16a** was prepared as a pale yellow oil (50 mg, 93% yield, eluent: 5:1 hexanes/EtOAc) from 2-(trifluoromethyl)quinoline-4-carbaldehyde using Fp^{W3}(thf)BF_4 (10 mol %) according to general procedure A1.

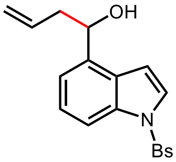
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.98 (s, 1H), 7.86 − 7.79 (m, 1H), 7.73 − 7.66 (m, 1H), 5.97 − 5.86 (m, 1H), 5.58 (dd, *J* = 8.6, 3.6 Hz, 1H), 5.32 − 5.22 (m, 2H), 2.84 − 2.75 (m, 1H), 2.58 − 2.47 (m, 1H), 2.39 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 148.1 (q, *J* = 34.5 Hz), 147.4, 133.4, 131.3, 130.4, 128.7, 126.0, 122.8, 121.7 (q, *J* = 276 Hz), 120.0, 113.5 (q, *J* = 2.5 Hz), 68.9, 43.1.

^{19}F NMR (470 MHz, $CDCl_3$) δ −67.58.

HRMS (ESI) calcd for $C_{14}H_{13}ONF_3$ [M+H]$^+$: 268.0944, found: 268.0941.

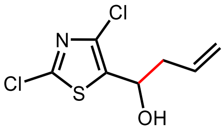
17. 1-(1-((4-Bromophenyl)sulfonyl)-1*H*-indol-4-yl)but-3-en-1-ol (17a, wrh-04-101B)



Compound **17a** was prepared as a pale yellow oil (52 mg, 64% yield, eluent: 5:1 → 3:1 hexanes/EtOAc) from 1-((4-bromophenyl)sulfonyl)-1*H*-indole-4-carbaldehyde according to general procedure A2.

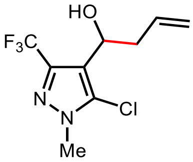
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.81 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.54 − 7.40 (m, 3H), 7.31 − 7.13 (m, 2H), 6.79 (d, *J* = 3.3 Hz, 1H), 5.80 − 5.64 (m, 1H), 5.16 − 5.00 (m, 2H), 4.93 (t, *J* = 6.1 Hz, 1H), 2.48 (t, *J* = 6.6 Hz, 2H), 2.12 (s, 1H).
^{13}C NMR (100 MHz, CDCl$_3$) δ 137.2, 136.9, 135.1, 134.4, 132.7, 129.3, 128.34, 128.31, 126.1, 125.0, 120.6, 118.6, 112.8, 108.3, 72.0, 43.0.
HRMS (ESI) calcd for $C_{18}H_{15}O_3NBrS$ $[M-H]^+$: 403.9951, found: 403.9941.

18. 1-(2,4-Dichlorothiazol-5-yl)but-3-en-1-ol (18a, wrh-04-159A)



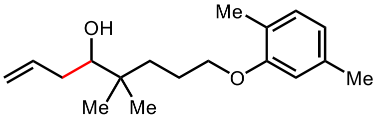
Compound **18a** was prepared as a pale yellow oil (34 mg, 76% yield, eluent: 15:1 → 10:1 hexanes/EtOAc) from 2,4-dichlorothiazole-5-carbaldehyde using Fp^{W3}(thf)BF_4 (10 mol %) according to general procedure A1.
^{1}H NMR (500 MHz, CDCl$_3$) δ 5.90 − 5.75 (m, 1H), 5.30 − 5.15 (m, 2H), 5.11 − 5.00 (m, 1H), 2.70 − 2.43 (m, 3H).
^{13}C NMR (125 MHz, CDCl$_3$) δ 150.7, 137.3, 132.4, 132.3, 120.4, 67.0, 42.5.
HRMS (ESI) calcd for $C_7H_8ONCl_2S$ $[M+H]^+$: 223.9698, found: 223.9688.

19. 1-(5-Chloro-1-methyl-3-(trifluoromethyl)-1*H*-pyrazol-4-yl)but-3-en-1-ol (19a, wrh-04-154B)



Compound **19a** was prepared as a pale yellow oil (45 mg, 88% yield, eluent: 6:1 hexanes/EtOAc) from 5-chloro-1-methyl-3-(trifluoromethyl)-1*H*-pyrazole-4-carbaldehyde using Fp^{W3}(thf)BF_4 (10 mol %) according to general procedure A1.
^{1}H NMR (500 MHz, CDCl$_3$) δ 5.76 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.20 − 5.10 (m, 2H), 4.89 − 4.83 (m, 1H), 3.87 (s, 3H), 2.71 − 2.61 (m, 1H), 2.58 − 2.48 (m, 1H), 2.17 (s, 1H).
^{13}C NMR (125 MHz, CDCl$_3$) δ 138.8 (q, *J* = 37.8 Hz), 133.6, 127.5, 121.1 (q, *J* = 268 Hz), 119.0, 118.7, 65.1, 41.4, 37.0.
^{19}F NMR (470 MHz, CDCl$_3$) δ −60.49.
HRMS (ESI) calcd for $C_9H_{11}ON_2ClF_3$ $[M+H]^+$: 255.0506, found: 255.0504.

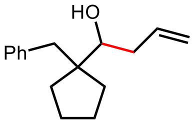
20. 8-(2,5-Dimethylphenoxy)-5,5-dimethyloct-1-en-4-ol (20a, wrh-04-107A)



Compound **20a** was prepared as a pale yellow oil (43 mg, 78% yield, eluent: 30:1 → 20:1 hexanes/EtOAc) from 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanal (**20**) using Fp^{W3}(thf)BF_4 (10 mol %) according to general procedure A1.
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.02 (d, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 6.64 (s, 1H), 5.96 − 5.80 (m, 1H), 5.25 − 5.09 (m, 2H), 3.94 (t, *J* = 6.1 Hz, 2H), 3.39 (d, *J* = 10.5 Hz, 1H), 2.40 (dd, *J* = 13.8, 4.4 Hz, 1H), 2.32 (s, 3H), 2.20 (s, 3H), 2.11 − 1.97 (m, 1H), 1.92 − 1.71 (m, 2H), 1.65 (s, 1H), 1.61 − 1.50 (m, 1H), 1.49 − 1.36 (m, 1H), 0.95 (d, *J* = 6.5 Hz, 6H).

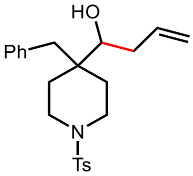
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 136.63, 136.57, 130.4, 123.7, 120.8, 118.1, 112.1, 68.7, 37.0, 36.4, 35.3, 24.1, 23.11, 23.09, 21.5, 15.9.
HRMS (ESI) calcd for $C_{18}H_{29}O_2$ $[M+H]^+$: 277.2162, found: 277.2161.

21. 1-(1-Benzylcyclopentyl)but-3-en-1-ol (21a, wrh-04-125A)



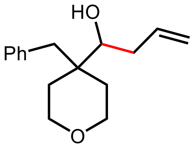
Compound **21a** was prepared as a pale yellow oil (40 mg, 86% yield, eluent: 60:1 → 50:1 hexanes/EtOAc) from 1-benzylcyclopentane-1-carbaldehyde (**21**) according to general procedure A2.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 − 7.09 (m, 5H), 5.83 − 5.71 (m, 1H), 5.14 − 5.03 (m, 2H), 3.39 (d, *J* = 10.4 Hz, 1H), 2.81 (d, *J* = 13.2 Hz, 1H), 2.51 (d, *J* = 13.3 Hz, 1H), 2.42 − 2.31 (m, 1H), 2.10 − 1.97 (m, 1H), 1.67 − 1.32 (m, 9H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 139.6, 136.5, 130.9, 128.0, 126.0, 118.1, 75.0, 50.7, 42.0, 37.3, 33.4, 33.2, 25.7, 25.6.
HRMS (ESI) calcd for $C_{16}H_{21}$ $[M-OH]^+$: 213.1638, found: 213.1633.

22. 1-(4-Benzyl-1-tosylpiperidin-4-yl)but-3-en-1-ol (22a, wrh-04-146A)



Compound **22a** was prepared as a pale yellow oil (60 mg, 76% yield, eluent: 5:1 → 4:1 hexanes/EtOAc) from 4-benzyl-1-tosylpiperidine-4-carbaldehyde (**22**) according to general procedure A2.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.28 − 7.17 (m, 3H), 7.06 (d, *J* = 7.1 Hz, 2H), 5.77 − 5.66 (m, 1H), 5.19 − 5.10 (m, 2H), 3.40 − 3.28 (m, 3H), 3.00 − 2.89 (m, 2H), 2.77 (d, *J* = 13.6 Hz, 1H), 2.55 (d, *J* = 13.6 Hz, 1H), 2.45 (s, 3H), 2.33 (dd, *J* = 13.5, 4.2 Hz, 1H), 2.02 (dt, *J* = 13.7, 9.9 Hz, 1H), 1.82 − 1.71 (m, 2H), 1.67 − 1.48 (m, 2H), 1.46 − 1.36 (m, 1H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 137.6, 135.7, 133.6, 130.9, 129.8, 128.2, 127.8, 126.5, 119.1, 71.7, 42.01, 41.97, 38.7, 37.4, 35.8, 29.5, 29.0, 21.7.
HRMS (ESI) calcd for $C_{23}H_{30}O_3NS$ $[M+H]^+$: 400.1941, found: 400.1936.

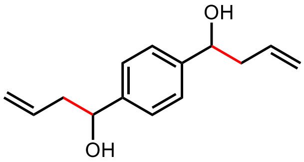
23. 1-(4-Benzyltetrahydro-2*H*-pyran-4-yl)but-3-en-1-ol (23a, wrh-04-156B, 04-184A-C)



Compound **23a** was prepared as a pale yellow oil (44 mg, 88% yield, eluent: 4:1 → 3:1 hexanes/EtOAc) from 4-benzyltetrahydro-2*H*-pyran-4-carbaldehyde (**23**) using $Fp^{W3}(thf)BF_4$ (10 mol %), $BF_3•Et_2O$ (74 µL, 0.6 mmol, 3.0 equiv), TMPH (101 µL, 0.6 mmol, 3.0 equiv) according to general procedure A1.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 − 7.05 (m, 5H), 5.74 (dtd, *J* = 14.6, 9.0, 5.6 Hz, 1H), 5.15 − 5.05 (m, 2H), 3.81 − 3.66 (m, 4H), 3.46 (d, *J* = 9.2 Hz, 1H), 2.92 (d, *J* = 13.6 Hz, 1H), 2.76 (d, *J* = 13.6 Hz, 1H), 2.35 (dd, *J* = 13.7, 4.4 Hz, 1H), 2.02 (dt, *J* = 13.7, 9.9 Hz, 1H), 1.72 − 1.58 (m, 3H), 1.47 − 1.35 (m, 1H), 1.32 − 1.20 (m, 1H).

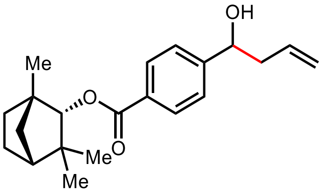
^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 136.1, 131.1, 128.1, 126.3, 118.7, 72.4, 63.72, 63.66, 38.7, 37.5, 35.8, 30.3, 30.0.
HRMS (ESI) calcd for $C_{16}H_{23}O_2$ $[M+H]^+$: 247.1693, found: 247.1685.

24. 1,1'-(1,4-Phenylene)bis(but-3-en-1-ol) (24a, wrh-04-160C)



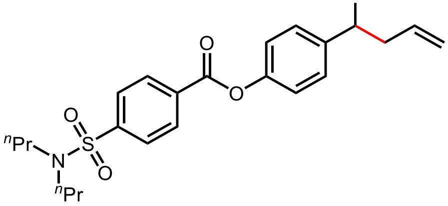
Compound **24a** was prepared as a waxy solid (11 mg, 52% yield, eluent: 3:1 → 2:1 hexanes/EtOAc) from terephthalaldehyde according to general procedure A2. The reaction was performed on 0.1 mmol scale, with the stoichiometries of the catalyst and reagents doubled.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (s, 4H), 5.87 − 5.74 (m, 2H), 5.23 − 5.09 (m, 4H), 4.78 − 4.69 (m, 2H), 2.57 − 2.44 (m, 4H), 2.06 (s, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 134.5, 126.1, 118.6, 73.21/73.18* (diastereomer observed), 44.0.
HRMS (ESI) calcd for $C_{14}H_{15}$ $[M-2OH-H]^+$: 183.1168, found: 183.1165.

25. 1,3,3-Trimethylbicyclo[2.2.1]heptan-2-yl 4-(1-hydroxybut-3-en-1-yl)benzoate (25a, wrh-04-121A)



Compound **25a** was prepared as a pale yellow oil (59 mg, 90% yield, eluent: 7:1 → 6:1 hexanes/EtOAc) from 1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl 4-formylbenzoate (**25**) using $Fp^{W3}(thf)BF_4$ (5 mol %) according to general procedure A1.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 5.86 − 5.74 (m, 1H), 5.24 − 5.11 (m, 2H), 4.85 − 4.77 (m, 1H), 4.61 (s, 1H), 2.62 − 2.41 (m, 2H), 2.21 (d, *J* = 2.8 Hz, 1H), 1.99 − 1.87 (m, 1H), 1.85 − 1.72 (m, 2H), 1.71 − 1.61 (m, 1H), 1.57 − 1.47 (m, 1H), 1.29 − 1.19 (m, 2H), 1.18 (s, 3H), 1.11 (s, 3H), 0.84 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 149.0, 134.0, 130.0, 129.8, 125.9, 119.1, 86.8, 72.9, 48.8, 48.6, 43.9, 41.6, 40.0, 29.9, 27.0, 26.1, 20.4, 19.6.
HRMS (ESI) calcd for $C_{21}H_{29}O_3$ $[M+H]^+$: 329.2111, found: 329.2101.

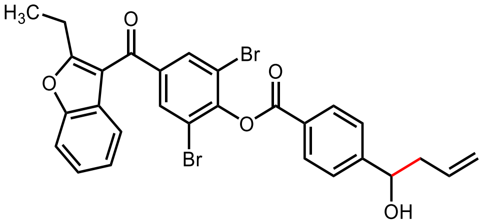
26. 4-(1-Hydroxybut-3-en-1-yl)phenyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (26a, wrh-04-107C)



Compound **26a** was prepared as a pale yellow oil (63 mg, 74% yield, eluent: 4:1 → 3:1 hexanes/EtOAc) from 4-formylphenyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (**26**) according to general procedure A2.

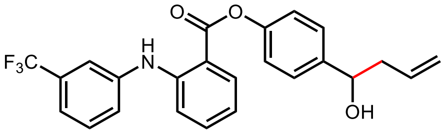
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.1 Hz, 2H), 7.94 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 5.91 − 5.75 (m, 1H), 5.25 − 5.10 (m, 2H), 4.84 − 4.73 (m, 1H), 3.12 (t, *J* = 8.0 Hz, 4H), 2.61 − 2.42 (m, 2H), 2.18 (s, 1H), 1.62 − 1.46 (m, 4H), 0.88 (t, *J* = 7.3 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 150.0, 145.0, 142.1, 134.3, 132.9, 130.9, 127.3, 127.2, 121.5, 118.9, 72.1, 50.1, 44.0, 22.1, 11.3.
HRMS (ESI) calcd for $C_{23}H_{30}O_5NS$ $[M+H]^+$: 432.1839, found: 432.1831.

27. 2,6-Dibromo-4-(2-ethylbenzofuran-3-carbonyl)phenyl 4-(1-hydroxybut-3-en-1-yl)benzoate (27a, wrh-04-187B)



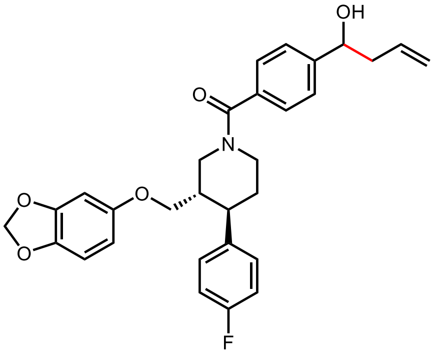
Compound **27a** was prepared as a pale yellow oil (48 mg, 40% yield, eluent: 5:1 hexanes/EtOAc) from 2,6-dibromo-4-(2-ethylbenzofuran-3-carbonyl)phenyl 4-formylbenzoate (**27**) using $Fp^{W6}(thf)BF_4$ (10 mol %) according to general procedure A1.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.3 Hz, 2H), 8.07 (s, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.48 − 7.43 (m, 1H), 7.36 − 7.30 (m, 1H), 7.29 − 7.24 (m, 1H), 5.90 − 5.78 (m, 1H), 5.26 − 5.17 (m, 2H), 4.87 (dd, *J* = 8.0, 4.6 Hz, 1H), 2.94 (q, *J* = 7.5 Hz, 2H), 2.65 − 2.56 (m, 1H), 2.55 − 2.46 (m, 1H), 2.26 (s, 1H), 1.38 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 188.1, 167.5, 162.6, 153.9, 150.8, 150.0, 139.1, 133.8, 133.2, 130.9, 127.2, 126.4, 126.3, 124.9, 124.2, 121.2, 119.4, 118.6, 115.4, 111.3, 72.8, 44.0, 22.2, 12.3.
HRMS (ESI) calcd for $C_{28}H_{23}O_5Br_2$ $[M+H]^+$: 596.9907, found: 596.9909.

28. 4-(1-Hydroxybut-3-en-1-yl)phenyl 2-((3-(trifluoromethyl)phenyl)amino) benzoate (28a, wrh-05-11)



Compound **28a** was prepared as a pale yellow oil (32 mg, 37% yield, eluent: CH_2Cl_2) from 4-formylphenyl 2-((3-(trifluoromethyl)phenyl)amino)benzoate (**28**) using $Fp^{W6}(thf)BF_4$ (10 mol %) according to general procedure A1.
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.25 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.53 − 7.29 (m, 8H), 7.20 (d, *J* = 8.5 Hz, 2H), 6.91 (t, *J* = 7.6 Hz, 1H), 5.90 − 5.79 (m, 1H), 5.24 − 5.13 (m, 2H), 4.79 (dd, *J* = 7.9, 5.0 Hz, 1H), 2.62 − 2.46 (m, 2H), 2.05 (s, 1H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 150.0, 147.7, 141.9, 141.4, 135.3, 134.4, 132.4, 132.0 (q, *J* = 32.1 Hz), 130.1, 127.2, 124.9, 124.0 (q, *J* = 271 Hz), 121.9, 120.0 (q, *J* = 3.8 Hz), 118.8, 118.5, 118.4 (q, *J* = 3.8 Hz), 114.4, 111.9, 72.9, 44.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ −62.82.
HRMS (ESI) calcd for $C_{24}H_{21}O_3NF_3$ $[M+H]^+$: 428.1468, found: 428.1455.

29. ((3*S*,4*R*)-3-((Benzo[*d*][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)piperidin-1-yl)(4-(1-hydroxybut-3-en-1-yl)phenyl)methanone (29a, wrh-04-172A, 176A)



Compound **29a** was prepared as a pale yellow oil (60 mg, 59% yield, eluent: 1:1.2 → 1:1.3 hexanes/EtOAc) from 4-((3*S*,4*R*)-3-((benzo[*d*][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)piperidine-1-carbonyl)benzaldehyde (**29**) according to general procedure A2.

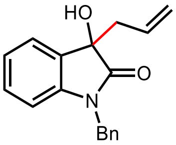
^{1}H NMR (400 MHz, $CDCl_3$, rotamers observed) δ 7.48 − 7.37 (m, 4H), 7.16 (dd, *J* = 8.3, 5.5 Hz, 2H), 6.99 (t, *J* = 8.4 Hz, 2H), 6.61 (br s, 1H), 6.39 (br s, 0.5H), 6.16 (br s, 1H), 5.99 (br s, 0.5H), 5.92 − 5.74 (m, 3H), 5.23 − 5.12 (m, 2H), 5.09 − 4.82 (br m, 1H), 4.82 − 4.72 (m, 1H), 4.11 (br s, 0.5H), 3.90 (br s, 0.5H), 3.78 − 3.30 (m, 2H), 3.26 − 2.63 (m, 3H), 2.60 − 2.40 (m, 2H), 2.29 (s, 1H), 2.17 − 1.68 (br m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 162.9, 160.5, 154.2, 153.7, 148.2, 146.0, 141.8, 138.6, 134.9, 134.3, 128.9, 128.8, 127.2, 126.0, 118.6, 115.8, 115.5, 107.9, 105.6, 101.2, 98.1, 72.8, 68.4, 51.2, 48.3, 45.6, 44.2, 43.9, 42.8, 42.0, 34.6, 33.7. (Complexity of the spectrum is due to the presence of rotamers and C−F coupling. C−F coupling constants could not be unambiguously determined.)

^{19}F NMR (376 MHz, $CDCl_3$, rotamers observed) δ −115.7, −115.8.

HRMS (ESI) calcd for $C_{30}H_{31}O_5NF$ $[M+H]^+$: 504.2181, found: 504.2166.

30. 3-Allyl-1-benzyl-3-hydroxyindolin-2-one (30a, wrh-05-2B)



Compound **30a** was prepared as a brown solid (53 mg, 95% yield, eluent: 3:1 hexanes/EtOAc) from 1-benzylindoline-2,3-dione using $Fp^{W3}(thf)BF_4$ (10 mol %) and DCE as solvent according to general procedure A1.

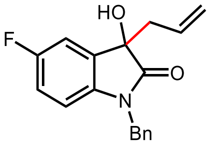
m.p. = 146 − 147 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.1 Hz, 1H), 7.36 − 7.23 (m, 5H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.70 (d, *J* = 7.7 Hz, 1H), 5.72 − 5.55 (m, 1H), 5.12 (dd, *J* = 25.7, 13.6 Hz, 2H), 5.02 (d, *J* = 15.7 Hz, 1H), 4.73 (d, *J* = 15.7 Hz, 1H), 3.36 (s, 1H), 2.88 − 2.77 (m, 1H), 2.76 − 2.66 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.2, 142.6, 135.5, 130.7, 129.8, 129.7, 128.9, 127.8, 127.4, 124.3, 123.2, 120.6, 109.6, 76.1, 43.9, 43.1.

HRMS (ESI) calcd for $C_{18}H_{18}O_2N$ $[M+H]^+$: 280.1332, found: 280.1336.

31. 3-Allyl-1-benzyl-5-fluoro-3-hydroxyindolin-2-one (31a, wrh-04-191B)



Compound **31a** was prepared as a brown solid (43 mg, 72% yield, eluent: 3:1 hexanes/EtOAc) from 1-benzyl-5-fluoroindoline-2,3-dione using $Fp^{W3}(thf)BF_4$ (10 mol %) and DCE as solvent according to general procedure A1.

m.p. = 126 − 127 °C.

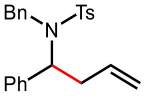
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 − 7.19 (m, 5H), 7.15 (dd, *J* = 7.5, 2.1 Hz, 1H), 6.88 (td, *J* = 8.9, 2.2 Hz, 1H), 6.59 (dd, *J* = 8.5, 3.9 Hz, 1H), 5.67 − 5.53 (m, 1H), 5.12 (dd, *J* = 19.4, 13.8 Hz, 2H), 5.00 (d, *J* = 15.7 Hz, 1H), 4.70 (d, *J* = 15.7 Hz, 1H), 4.04 − 3.81 (m, 1H), 2.87 − 2.76 (m, 1H), 2.76 − 2.65 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.1, 159.6 (d, *J* = 242 Hz), 138.3, 135.2, 131.6 (d, *J* = 7.9 Hz), 130.2, 128.9, 127.9, 127.4, 121.0, 115.9 (d, *J* = 23.6 Hz), 112.5 (d, *J* = 24.9 Hz), 110.3 (d, *J* = 8.0 Hz), 76.4, 44.1, 43.1.

^{19}F NMR (470 MHz, $CDCl_3$) δ −119.6.

HRMS (ESI) calcd for $C_{18}H_{17}O_2NF$ $[M+H]^+$: 298.1238, found: 298.1234.

32. *N*-Benzyl-4-methyl-*N*-(1-phenylbut-3-en-1-yl)benzenesulfonamide (32a, wrh-04-111A)



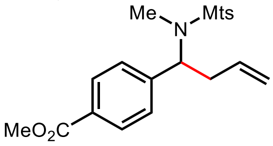
Compound **32a** was prepared as a pale yellow oil (73 mg, 93% yield, eluent: 10:1 hexanes/EtOAc) from *N*-benzyl-*N*-((benzyloxy)(phenyl)methyl)-4-methylbenzene sulfonamide using $Fp^{W3}(thf)BF_4$ (10 mol %) and DCE as solvent according to general procedure A1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.14 − 6.98 (m, 8H), 6.95 − 6.83 (m, 2H), 5.55 − 5.39 (m, 1H), 4.97 (dd, *J* = 9.0, 6.5 Hz, 1H), 4.90 − 4.74 (m, 2H), 4.40 (d, *J* = 15.8 Hz, 1H), 3.86 (d, *J* = 15.8 Hz, 1H), 2.55 − 2.36 (m, 2H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 138.5, 137.8, 137.2, 134.8, 129.6, 129.0, 128.4, 128.3, 128.2, 128.0, 127.41, 127.39, 117.5, 61.3, 48.3, 36.9, 21.6.

HRMS (ESI) calcd for $C_{24}H_{26}O_2NS$ $[M+H]^+$: 392.1679, found: 392.1684.

33. Methyl 4-(1-((*N*,2,4,6-tetramethylphenyl)sulfonamido)but-3-en-1-yl)benzoate (33a, wrh-04-111B)



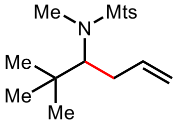
Compound **33a** was prepared as a pale yellow oil (69 mg, 86% yield, eluent: 10:1 → 8:1 hexanes/EtOAc) from methyl 4-(methoxy((*N*,2,4,6-tetramethylphenyl)sulfonamido) methyl)benzoate using $Fp^{W3}(thf)BF_4$ (10 mol %) and DCE as solvent according to general procedure A1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 6.95 (s, 2H), 5.64 − 5.47 (m, 1H), 5.05 (dd, *J* = 17.1, 1.1 Hz, 1H), 4.96 (d, *J* = 10.2 Hz, 1H), 4.88 (dd, *J* = 9.5, 6.0 Hz, 1H), 3.89 (s, 3H), 2.93 − 2.79 (m, 1H), 2.78 − 2.67 (m, 1H), 2.64 (s, 3H), 2.56 (s, 6H), 2.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 142.7, 142.6, 140.4, 134.0, 133.2, 132.1, 129.8, 129.7, 128.5, 118.1, 58.7, 52.2, 34.7, 28.3, 23.1, 21.0.

HRMS (ESI) calcd for $C_{22}H_{28}O_4NS$ $[M+H]^+$: 402.1734, found: 402.1734.

34. *N*-(2,2-Dimethylhex-5-en-3-yl)-*N*,2,4,6-tetramethylbenzenesulfonamide (34a, wrh-05-9A)



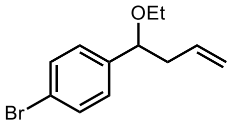
Compound **34a** was prepared as a pale yellow oil (60 mg, 92% yield, eluent: 50:1 hexanes/EtOAc) from methyl *N*-(1-methoxy-2,2-dimethylpropyl)-*N*,2,4,6-tetramethylbenzenesulfonamide using $Fp^{W3}(thf)BF_4$ (10 mol %) and DCE as solvent according to general procedure A1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.91 (s, 2H), 5.57 − 5.43 (m, 1H), 4.97 (d, *J* = 16.9 Hz, 1H), 4.80 (d, *J* = 10.0 Hz, 1H), 3.61 − 3.52 (m, 1H), 2.85 (s, 3H), 2.62 (s, 6H), 2.42 − 2.30 (m, 2H), 2.28 (s, 3H), 0.91 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 141.8, 139.6, 136.6, 134.6, 132.1, 116.3, 64.9, 36.6, 33.0, 30.7, 28.6, 24.2, 21.0.

HRMS (ESI) calcd for $C_{18}H_{30}O_2NS$ $[M+H]^+$: 324.1992, found: 324.1987.

35. 1-Bromo-4-(1-ethoxybut-3-en-1-yl)benzene (35a, WRH-05-123A)



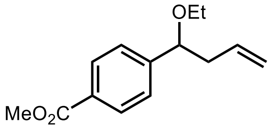
Compound **35a** was prepared as a pale yellow oil (18 mg, 35% yield, gradient elution from 8:1 to 4:1 hexanes/CH_2Cl_2) from 4-bromobenzaldehyde diethyl acetal using $Fp^{W3}(thf)BF_4$ (10 mol %) at 100 °C according to general procedure A1.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 5.66 (ddt, *J* = 17.2, 10.3, 7.0 Hz, 1H), 5.00 − 4.89 (m, 2H), 4.15 (t, *J* = 6.7 Hz, 1H), 3.34 − 3.21 (m, 2H), 2.52 − 2.42 (m, 1H), 2.34 − 2.23 (m, 1H), 1.09 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 141.7, 134.6, 131.6, 128.5, 121.3, 117.2, 81.3, 64.4, 42.6, 15.4.

HRMS (ESI) calcd for $C_{10}H_{10}Br$ $[M-C_2H_5O]^+$: 208.9960, found: 208.9967.

36. Methyl 4-(1-ethoxybut-3-en-1-yl)benzoate (36a, WRH-05-121C)



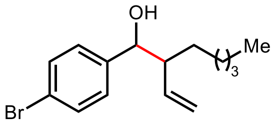
Compound **36a** was prepared as a pale yellow oil (26 mg, 55% yield, eluent: 40:1 hexanes/EtOAc) from methyl 4-(diethoxymethyl)benzoate (**36**) using $Fp^{W3}(thf)BF_4$ (10 mol %) at 100 °C according to general procedure A1.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 5.83 − 5.65 (m, 1H), 5.07 − 4.93 (m, 2H), 4.32 (t, *J* = 6.6 Hz, 1H), 3.91 (s, 3H), 3.36 (qd, *J* = 7.0, 1.6 Hz, 2H), 2.63 − 2.48 (m, 1H), 2.44 − 2.31 (m, 1H), 1.18 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 148.0, 134.5, 129.8, 129.5, 126.7, 117.3, 81.5, 64.6, 52.2, 42.6, 15.4.

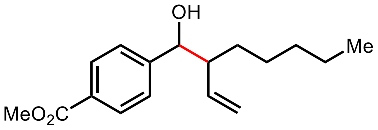
HRMS (ESI) calcd for $C_{14}H_{19}O_3$ $[M+H]^+$: 235.1329, found: 235.1336.

37. 1-(4-Bromophenyl)-2-vinylheptan-1-ol (5b, wrh-04-176C)



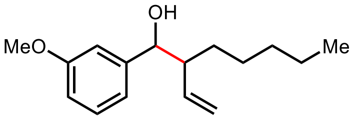
Compound **5b** was prepared as a pale yellow oil (55 mg, 93% yield, 4.8:1 d.r., eluent: 30:1 → 20:1 hexanes/EtOAc) from 1-octene according to general procedure A3.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 − 7.40 (m, 2H), 7.20/7.14* (d, *J* = 8.3 Hz, 2H), 5.62/5.47* (dt, *J* = 17.3, 9.7 Hz, 1H), 5.29 − 5.23/5.13 − 5.05* (m, 1H), 5.18/5.01* (d, *J* = 17.2 Hz, 1H), 4.59*/4.35 (d, *J* = 5.7 Hz*/7.7 Hz, 1H), 2.43 − 2.31*/2.27 − 2.18 (m, 1H), 2.00 (s, 1H), 1.56 − 1.06 (m, 8H), 0.92 − 0.79 (m, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 141.69/141.65*, 139.1/138.3*, 131.5/131.2*, 128.8/128.6*, 121.5/121.3*, 119.3/117.9*, 76.4*/76.2, 53.0/51.5*, 32.0*/31.8, 30.5/29.6*, 27.05*/27.00, 22.71*/22.66, 14.19*/14.15.
HRMS (ESI) calcd for $C_{15}H_{20}Br$ $[M-OH]^+$: 279.0743, found: 279.0738.

38. Methyl 4-(1-hydroxy-2-vinylheptyl)benzoate (6b, wrh-05-95A)



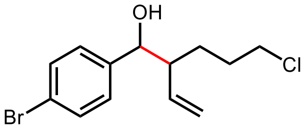
Compound **6b** was prepared as a pale yellow oil (52 mg, 94% yield, 4.6:1 d.r., eluent: 15:1 → 10:1 hexanes/EtOAc) from methyl 4-formylbenzoate according to general procedure A3.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 − 7.94 (m, 2H), 7.39/7.34* (d, *J* = 8.2 Hz, 2H), 5.63/5.49* (dt, *J* = 17.2, 9.7 Hz, 1H), 5.24/5.07* (dd, *J* = 10.2, 1.5 Hz, 1H), 5.15/5.00* (d, *J* = 17.2 Hz, 1H), 4.72 − 4.64*/4.47 (m*/d, *J* = 7.2 Hz, 1H), 3.90 (s, 3H), 2.45 − 2.17 (m, 2H), 1.56 − 1.06 (m, 8H), 0.90 − 0.78 (m, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 148.0/147.9*, 138.8/138.4*, 129.7*/129.6, 129.4*/129.3, 127.0/126.8*, 119.2/117.8*, 76.7*/76.3, 52.8/52.2*, 51.6, 31.9*/31.8, 30.5/29.5*, 27.03*/26.97, 22.7*/22.6, 14.15*/14.10.
HRMS (ESI) calcd for $C_{17}H_{25}O_3$ $[M+H]^+$: 277.1798, found: 277.1804.

39. 1-(3-Methoxyphenyl)-2-vinylheptan-1-ol (7b, wrh-05-95B)



Compound **7b** was prepared as a pale yellow oil (46 mg, 93% yield, 3.6:1 d.r., eluent: 10:1 hexanes/EtOAc) from 3-methoxybenzaldehyde according to general procedure A3.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 − 7.19 (m, 1H), 6.92 − 6.76 (m, 3H), 5.71 − 5.60/5.58 − 5.47* (m, 1H), 5.24/5.07* (dd, *J* = 10.3, 1.7 Hz, 1H), 5.18/5.01* (dd, *J* = 17.2, 1.5 Hz, 1H), 4.58*/4.37 (d, *J* = 5.5 Hz*/7.7 Hz, 1H), 3.81/3.80* (s, 3H), 2.44 − 2.34*/2.33 − 2.25 (m, 1H), 2.23/2.13* (s, 1H), 1.61 − 1.07 (m, 8H), 0.89 − 0.80 (m, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7/159.6*, 144.5*/144.4, 139.5/138.8*, 129.3/129.1*, 119.5/119.3*, 118.7/117.2*, 113.2/112.8*, 112.6, 77.0*/76.8, 55.3, 52.7/51.5*, 32.0*/31.8, 30.5/29.6*, 27.1*/27.0, 22.7*/22.6, 14.2*/14.1.
HRMS (ESI) calcd for $C_{16}H_{23}O$ $[M-OH]^+$: 231.1743, found: 231.1750.

40. 1-(4-Bromophenyl)-5-chloro-2-vinylpentan-1-ol (5c, wyd-6-170)



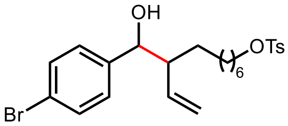
Compound **5c** was prepared as a pale yellow oil (53 mg, 86% yield, 3.7:1 d.r., eluent: 15:1 hexanes/EtOAc) from 1-(4-bromophenyl)-5-chloro-2-vinylpentan-1-ol according to general procedure A3.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 − 7.41 (m, 2H), 7.19/7.15* (d, *J* = 7.7 Hz, 2H), 5.68 − 5.56/5.54 − 5.42* (m, 1H), 5.28/5.10* (d, *J* = 10.2 Hz, 1H), 5.18/5.00* (d, *J* = 17.1 Hz, 1H), 4.57*/4.40 (d, *J* = 5.8 Hz*/7.3 Hz, 1H), 3.55 − 3.36 (m, 2H), 2.41 − 2.30 (m, 0.8H), 2.29 − 2.21 (m, 0.2H), 2.08 (s, 1H), 1.88 − 1.55 (m, 3H), 1.40 − 1.29 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 141.5*/141.3, 138.2/137.7*, 131.5/131.3*, 128.7/128.5*, 121.7/121.5*, 119.8/118.4*, 76.4*/76.2, 52.3/51.0*, 45.1*/44.9, 30.51*/30.47, 27.7/27.0*.

HRMS (ESI) calcd for $C_{13}H_{15}BrCl$ [M−OH]$^+$: 285.0040, found: 285.0027.

41. 8-((4-Bromophenyl)(hydroxy)methyl)dec-9-en-1-yl 4-methylbenzenesulfonate (5d, wyd-6-167)



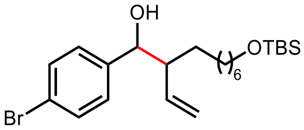
Compound **5d** was prepared as a pale yellow oil (94 mg, 95% yield, 3.4:1 d.r., eluent: 5:1 hexanes/EtOAc) from dec-9-en-1-yl 4-methylbenzenesulfonate according to general procedure A3.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.48 − 7.40 (m, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.19/7.13* (d, *J* = 8.3 Hz, 2H), 5.60/5.46* (dt, *J* = 17.2, 9.8 Hz, 1H), 5.27 − 5.21/5.10 − 5.03* (m, 1H), 5.15/4.98* (d, *J* = 17.1 Hz, 1H), 4.56*/4.35 (d, *J* = 5.8 Hz*/7.6 Hz, 1H), 4.04 − 3.94 (m, 2H), 2.44 (s, 3H), 2.37 − 2.28*/2.24 − 2.16 (m, 1H), 2.09 (s, 1H), 1.65 − 1.54 (m, 2H), 1.54 − 1.44 (m, 1H), 1.34 − 1.01 (m, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 141.70*/141.66, 138.9/138.3*, 133.3, 131.4/131.2*, 129.9, 128.8/128.5*, 128.0, 121.5/121.2*, 119.3/117.8*, 76.4*/76.1, 70.8*/70.7, 52.9/51.4*, 30.4/29.5*, 29.4*/29.2, 28.90, 28.88, 27.14*/27.12, 25.4*/25.3, 21.7.

HRMS (ESI) calcd for $C_{24}H_{30}O_3BrS$ [M−OH]$^+$: 477.1093, found: 477.1104.

42. 1-(4-Bromophenyl)-9-((tert-butyldimethylsilyl)oxy)-2-vinylnonan-1-ol (5e, wyd-6-180)



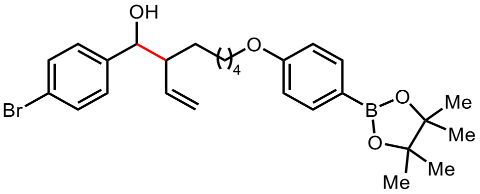
Compound **5e** was prepared as a pale yellow oil (82 mg, 90% yield, 4.3:1 d.r., eluent: 20:1 hexanes/EtOAc) from *tert*-butyl(dec-9-en-1-yloxy)dimethylsilane according to general procedure A3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 − 7.40 (m, 2H), 7.19/7.14* (d, *J* = 8.2 Hz, 2H), 5.68 − 5.55/5.53 − 5.39* (m, 1H), 5.25/5.08* (d, *J* = 10.1 Hz, 1H), 5.17/5.00* (d, *J* = 17.2 Hz, 1H), 4.57*/4.34 (d, *J* = 5.1 Hz*/7.7 Hz, 1H), 3.62 − 3.53 (m, 2H), 2.44 − 2.02 (m, 2H), 1.57 − 1.40 (m, 3H), 1.38 − 1.06 (m, 9H), 0.89 (s, 9H), 0.04 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 139.1/138.3*, 131.4/131.2*, 128.8/128.6*, 121.5/121.3*, 119.4/117.9*, 76.4*/76.2, 63.4, 53.0/51.5*, 33.0, 30.5/29.72*, 29.66*/29.54, 29.47*/29.4, 27.32*/27.27, 26.1, 25.9*/25.8, 18.5, −5.1.

HRMS (ESI) calcd for $C_{23}H_{38}OBrSi$ [M−OH]$^+$: 437.1870, found: 437.1861.

43. 1-(4-Bromophenyl)-7-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy) -2-vinylheptan-1-ol (5f, wyd-6-171)



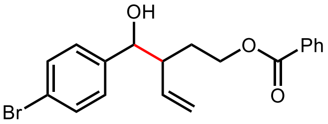
Compound **5f** was prepared as a pale yellow oil (88 mg, 85% yield, 4.0:1 d.r., eluent: 7:1 hexanes/EtOAc) from 4,4,5,5-tetramethyl-2-(4-(oct-7-en-1-yloxy)phenyl)-1,3,2-dioxaborolane (**f**) according to general procedure A3.

^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.77 − 7.70 (m, 2H), 7.49 − 7.41 (m, 2H), 7.19/7.14* (d, *J* = 8.3 Hz, 2H), 6.91 − 6.82 (m, 2H), 5.67 − 5.57/5.54 − 5.40* (m, 1H), 5.26/5.08* (dd, *J* = 10.2, 1.6 Hz, 1H), 5.21 − 5.14/5.04 − 4.97* (m, 1H), 4.58*/4.36 (d, *J* = 5.7 Hz*/7.7 Hz, 1H), 4.01 − 3.87 (m, 2H), 2.42 − 2.32 (m, 0.8H), 2.29 − 2.19 (m, 0.2H), 2.07 (s, 1H), 1.82 − 1.63 (m, 2H), 1.62 − 1.51 (m, 1H), 1.50 − 1.36 (m, 3H), 1.33 (s, 12H), 1.28 − 1.16 (m, 2H).

^{13}**C NMR** (125 MHz, $CDCl_3$) δ 161.81*/161.77, 141.65*/141.60, 138.9/138.2*, 136.6, 131.5/131.2*, 128.8/128.6*, 121.6/121.3*, 119.4, 118.0, 113.98*/113.96, 83.6, 76.4*/76.2, 67.74*/67.67, 52.9/51.4*, 30.4/29.5*, 29.21*/29.16, 27.10*/27.07, 26.1*/26.0, 25.0.

HRMS (ESI) calcd for $C_{27}H_{35}O_3BBr$ $[M-OH]^+$: 497.1857, found: 497.1832.

44. 3-((4-Bromophenyl)(hydroxy)methyl)pent-4-en-1-yl benzoate (5g, wyd-6-152-2)



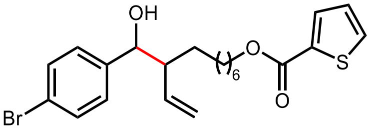
Compound **5g** was prepared as a pale yellow oil (69 mg, 92% yield, 3.4:1 d.r., eluent: 10:1 hexanes/EtOAc) from pent-4-en-1-yl benzoate according to general procedure A3.

^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.02 − 7.91 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.50 − 7.37 (m, 4H), 7.24 − 7.12 (m, 2H), 5.77 − 5.53 (m, 1H), 5.29/5.14* (d, *J* = 10.2 Hz, 1H), 5.20/5.07* (d, *J* = 17.1 Hz, 1H), 4.66*/4.49 (d, *J* = 4.4 Hz*/7.2 Hz, 1H), 4.40 − 4.28 (m, 1H), 4.27 − 4.13 (m, 1H), 2.65 − 2.54*/2.54 − 2.45 (m, 1H), 2.37 − 2.15 (m, 1H), 2.14 − 2.01 (m, 1H), 1.81 − 1.60 (m, 1H).

^{13}**C NMR** (125 MHz, $CDCl_3$) δ 166.7*/166.6, 141.4*/141.2, 137.4/137.2*, 133.1/133.0*, 131.6/131.4*, 130.4*/130.3, 129.65*/129.63, 128.7/128.5*, 128.5/128.4*, 121.8/121.5*, 120.1/118.6*, 76.3*/76.0, 63.2*/63.0, 49.6/48.3*, 29.6/28.5*.

HRMS (ESI) calcd for $C_{19}H_{18}O_2Br$ $[M-OH]^+$: 357.0485, found: 357.0492.

45. 8-((4-Bromophenyl)(hydroxy)methyl)dec-9-en-1-yl thiophene-2-carboxylate (5h, wyd-6-168)



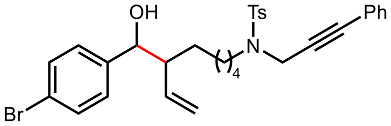
Compound **5h** was prepared as a pale yellow oil (86 mg, 95% yield, 4.3:1 d.r., eluent: 8:1 hexanes/EtOAc) from dec-9-en-1-yl thiophene-2-carboxylate according to general procedure A3.

^{1}**H NMR** (500 MHz, CDCl$_3$) δ 7.81 − 7.76 (m, 1H), 7.54 (d, *J* = 4.9 Hz, 1H), 7.49 − 7.41 (m, 2H), 7.19/7.14* (d, *J* = 8.3 Hz, 2H), 7.11 − 7.07 (m, 1H), 5.66 − 5.56/5.52 − 5.41* (m, 1H), 5.25/5.07* (d, *J* = 10.2 Hz, 1H), 5.16/4.99* (d, *J* = 17.1 Hz, 1H), 4.57*/4.35 (d, *J* = 5.6 Hz*/7.7 Hz, 1H), 4.31 − 4.22 (m, 2H), 2.40 − 2.30 (m, 0.8H), 2.26 − 2.18 (m, 0.2H), 2.09 (s, 1H), 1.78 − 1.64 (m, 2H), 1.56 − 1.46 (m, 1H), 1.45 − 1.04 (m, 9H).

^{13}**C NMR** (125 MHz, CDCl$_3$) δ 162.5, 141.7, 139.0/138.3*, 134.2, 133.4, 132.3, 131.4/131.2*, 128.8/128.6*, 127.8, 121.5/121.2*, 119.3/117.9*, 76.4*/76.1, 65.4*/65.3, 52.9/51.5*, 30.4/29.5*, 29.5*/29.4, 29.2*/29.1, 28.8*/28.7, 27.23*/27.19, 26.0*/25.9.

HRMS (ESI) calcd for $C_{22}H_{26}O_3BrS$ [M−H]$^+$: 449.0780, found: 449.0813.

46. *N*-(6-((4-Bromophenyl)(hydroxy)methyl)oct-7-en-1-yl)-4-methyl-*N*-(3-phenyl prop-2-yn-1-yl)benzenesulfonamide (5i, wyd-6-178)



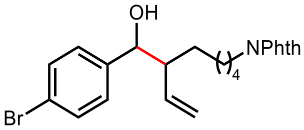
Compound **5i** was prepared as a pale yellow oil (88 mg, 76% yield, 3.5:1 d.r., eluent: 6:1 hexanes/EtOAc) from 4-methyl-*N*-(oct-7-en-1-yl)-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (**i**) using Fp^{W5}(thf)BF$_4$ (10 mol %) according to general procedure A3.

^{1}**H NMR** (500 MHz, CDCl$_3$) δ 7.79 − 7.69 (m, 2H), 7.49 − 7.40 (m, 2H), 7.32 − 7.16 (m, 6H), 7.13 (d, *J* = 8.3 Hz, 1H), 7.08 − 7.00 (m, 2H), 5.60*/5.45 (dt, *J* = 17.2, 9.8 Hz, 1H), 5.24*/5.06 (dd, *J* = 10.2, 1.5 Hz, 1H), 5.15*/4.98 (d, *J* = 17.1 Hz, 1H), 4.56/4.35* (d, *J* = 5.7 Hz/7.5 Hz*, 1H), 4.30/4.28* (s, 2H), 3.26 − 3.14 (m, 2H), 2.38 − 1.99 (m, 5H), 1.65 − 1.44 (m, 3H), 1.42 − 1.09 (m, 5H).

^{13}**C NMR** (125 MHz, CDCl$_3$, mixture of diastereomers) δ 143.4, 141.7, 138.8, 138.2, 136.1, 131.6, 131.5, 131.2, 129.6, 128.8, 128.6, 128.5, 128.2, 127.9, 122.3, 121.3, 119.4, 117.9, 85.6, 81.9, 76.4, 76.1, 52.8, 51.4, 46.4, 37.1, 30.3, 29.5, 27.5, 26.9, 26.6, 26.5, 21.5.

HRMS (ESI) calcd for $C_{31}H_{33}O_2NBrS$ [M−OH]$^+$: 562.1410, found: 562.1395.

47. 2-(6-((4-Bromophenyl)(hydroxy)methyl)oct-7-en-1-yl)isoindoline-1,3-dione (5j, wyd-6-163)



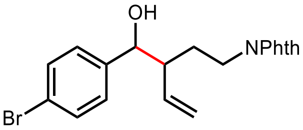
Compound **5j** was prepared as a pale yellow oil (81 mg, 92% yield, 4.6:1 d.r., eluent: 5:1 hexanes/EtOAc) from 2-(oct-7-en-1-yl)isoindoline-1,3-dione (**j**) according to general procedure A3.

^{1}**H NMR** (500 MHz, CDCl$_3$) δ 7.85 − 7.78 (m, 2H), 7.74 − 7.66 (m, 2H), 7.46 − 7.38 (m, 2H), 7.20 − 7.15/7.15 − 7.08* (m, 2H), 5.64 − 5.53/5.50 − 5.38* (m, 1H), 5.22/5.04* (d, *J* = 10.1 Hz/10.3 Hz*, 1H), 5.13/4.96* (d, *J* = 17.1 Hz/17.2 Hz*, 1H), 4.54*/4.34 (d, *J* = 4.1 Hz*/7.4 Hz, 1H), 3.68 − 3.57 (m, 2H), 2.40 − 2.15 (m, 2H), 1.69 − 1.45 (m, 3H), 1.44 − 1.04 (m, 5H).

^{13}**C NMR** (125 MHz, CDCl$_3$) δ 168.60*/168.58, 141.7, 138.8/138.2*, 134.0, 132.2, 131.4/131.2*, 128.8/128.6*, 123.3, 121.5/121.2*, 119.3/117.9*, 76.3*/76.2, 52.7/51.4*, 38.1*/38.0, 30.3/29.4*, 28.53*/28.47, 26.9, 26.8*/26.7.

HRMS (ESI) calcd for $C_{23}H_{23}O_3NBr$ [M−H]$^+$: 440.0856, found: 440.0885.

48. 2-(3-((4-Bromophenyl)(hydroxy)methyl)pent-4-en-1-yl)isoindoline-1,3-dione (5k, wyd-6-147-4)



Compound **5k** was prepared as a white solid (76 mg, 95% yield, 3.9:1 d.r., eluent: 5:1 hexanes/EtOAc) from 2-(pent-4-en-1-yl)isoindoline-1,3-dione (**k**) according to general procedure A3.

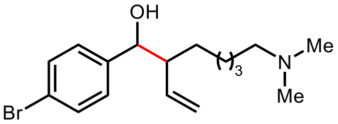
m.p. = 92 − 94 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 − 7.76 (m, 2H), 7.74 − 7.66 (m, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.18 − 7.09 (m, 2H), 5.73 − 5.63/5.63 − 5.53* (m, 1H), 5.30 − 5.18/5.16 − 5.07* (m, 2H), 4.59*/4.47 (d, *J* = 5.9 Hz*/8.9 Hz, 1H), 3.73 − 3.54 (m, 2H), 2.49 − 2.41*/2.40 − 2.32 (m, 1H), 2.17 (s, 1H), 2.01 − 1.91 (m, 1H), 1.68 − 1.56 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.5*/168.4, 141.2*/141.0, 137.4/137.1*, 134.05/134.03*, 132.2*/132.1, 131.5/131.3*, 128.6/128.4*, 123.3, 121.7/121.5*, 119.9/118.7*, 76.2*/75.7, 50.3/49.1*, 36.5*/36.4, 29.2/28.5*.

HRMS (ESI) calcd for $C_{20}H_{17}O_2NBr$ $[M{-}OH]^+$: 382.0437, found: 382.0446.

49. 1-(4-Bromophenyl)-7-(dimethylamino)-2-vinylheptan-1-ol (5l, WRH-06-31)



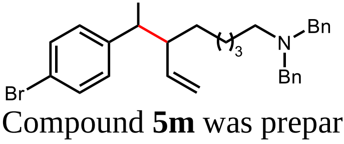
Compound **5l** was prepared as a pale yellow oil (46 mg, 68% yield, 2.6:1 d.r.) from *N*,*N*-dimethyloct-7-en-1-amine (**l**, 47 mg, 0.3 mmol, 1.5 equiv) using $Fp^{W5}(thf)BF_4$ (10 mol %) and $BF_3{\bullet}Et_2O$ (74 µL, 0.6 mmol, 3.0 equiv) according to general procedure A3. The compound was purified by column chromatography (eluent: 1.5:1:0.25 hexanes/EtOAc/Et_3N) followed by fast filtration through a pad of silica gel with EtOAc.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.41 (m, 2H), 7.19/7.14* (d, *J* = 8.4 Hz, 2H), 5.66 – 5.54/5.53 – 5.41* (m, 1H), 5.26/5.07* (dd, *J* = 10.2, 1.6 Hz, 1H), 5.17/4.98* (dd, *J* = 17.1, 1.5 Hz, 1H), 4.56*/4.35 (d, *J* = 5.8 Hz*/7.7 Hz, 1H), 2.87 – 2.74 (m, 2H), 2.55*/2.53 (s, 6H), 2.38 – 2.02 (m, 2H), 1.67 – 1.47 (m, 3H), 1.43 – 1.05 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7*/141.5, 138.7/138.1*, 131.5/131.3*, 128.8/128.5*, 121.6/121.3*, 119.6/118.1*, 76.4*/76.1, 58.5, 52.8, 51.4, 43.9, 30.1/29.1*, 27.1, 26.9, 22.4*/22.3. (mixture of diastereomers)

HRMS (ESI) calcd for $C_{17}H_{27}ONBr$ $[M+H]^+$: 340.1271, found: 340.1278.

50. 1-(4-Bromophenyl)-7-(dibenzylamino)-2-vinylheptan-1-ol (5m, wrh-06-46B)



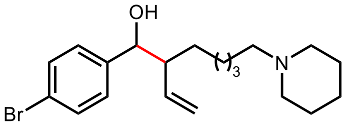
Compound **5m** was prepared as a pale yellow oil (62 mg, 63% yield, 3.7:1 d.r., eluent: 10:1 → 6:1 hexanes/EtOAc) from *N*,*N*-dibenzyloct-7-en-1-amine (**m**) using $Fp^{W5}(thf)BF_4$ (10 mol %) according to general procedure A3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.39 (m, 2H), 7.38 – 7.03 (m, 12H), 5.63 – 5.51/5.48 – 5.35* (m, 1H), 5.23/5.05* (d, *J* = 10.3 Hz, 1H), 5.13/4.96* (d, *J* = 17.2 Hz, 1H), 4.55*/4.32 (d, *J* = 5.5 Hz*/7.7 Hz, 1H), 3.52*/3.50 (s, 4H), 2.43 – 2.11 (m, 3H), 2.08 – 1.88 (m, 1H), 1.54 – 1.32 (m, 2H), 1.31 – 0.97 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 140.1, 138.9/138.3*, 131.4/131.2*, 128.9, 128.8/128.5*, 128.2, 126.8, 121.5/121.2*, 119.3/117.8*, 76.3*/76.1, 58.4, 53.4*/53.3, 52.8/51.4*, 30.4/29.5*, 27.2*/27.06, 27.15*/27.0, 26.9.

HRMS (ESI) calcd for $C_{29}H_{35}ONBr$ $[M+H]^+$: 492.1896, found: 492.1910.

51. 1-(4-bromophenyl)-7-(piperidin-1-yl)-2-vinylheptan-1-ol (5n, wrh-06-47A)



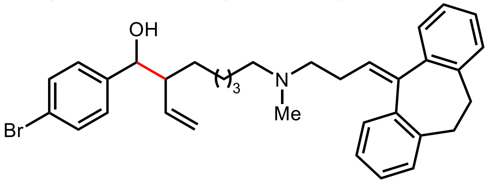
Compound **5n** was prepared as a pale yellow oil (46 mg, 60% yield, 2.7:1 d.r.) from *1*-(oct-7-en-1-yl)piperidine (**n**, 59 mg, 0.3 mmol, 1.5 equiv) using $Fp^{W5}(thf)BF_4$ (10 mol %) and $BF_3{\bullet}Et_2O$ (74 µL, 0.6 mmol, 3.0 equiv) according to general procedure A3. The compound was first purified by fast column chromatography (eluent: 2:1 hexanes/EtOAc). The product obtained was dissolved in EtOAc (10 mL) and was washed with 2 M NaOH (2 × 5 mL) and brine (1 × 5 mL) to remove the coordinated BF_3. The organic layer was dried over magnesium sulfate and concentrated in vacuo. The resulting mixture was purified again by column chromatography (eluent: 10:1:0.1 hexanes/EtOAc/Et_3N) to afford the pure product **5n**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.37 (m, 2H), 7.19/7.14* (d, *J* = 8.3 Hz, 2H), 5.60/5.46* (dt, *J* = 17.2, 9.8 Hz, 1H), 5.24/5.06* (dd, *J* = 10.2, 1.6 Hz, 1H), 5.15/4.97* (dd, *J* = 17.2, 1.2 Hz, 1H), 4.56*/4.35 (d, *J* = 5.7 Hz/7.6 Hz, 1H), 2.48 – 2.29 (m, 4H), 2.29 – 2.14 (m, 3H), 1.66 – 1.64 (m, 4H), 1.53 – 1.37 (m, 4H), 1.35 – 1.05 (m, 7H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1*/141.9, 139.0/138.5*, 131.4/131.1*, 128.8/128.6*, 121.4/121.1*, 119.1/117.6*, 76.3*/76.0, 59.43*/59.40, 54.5, 52.8/51.5*, 30.3/29.5*, 27.7*/27.5, 27.2*/27.1, 26.49*/26.46, 25.71/25.67*, 24.4.

HRMS (ESI) calcd for $C_{20}H_{31}ONBr$ $[M+H]^+$: 380.1584, found: 380.1594.

52. 1-(4-Bromophenyl)-7-((3-(10,11-dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-ylidene)propyl)(methyl)amino)-2-vinylheptan-1-ol (5o, wrh-06-50B)

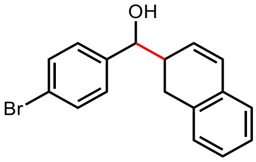


Compound **5o** was prepared as a pale yellow oil (62 mg, 55% yield, 2.8:1 d.r.) from *N*-(3-(10,11-dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-ylidene)propyl)-*N*-methyloct-7-en-1-amine (**o**, 112 mg, 0.3 mmol, 1.5 equiv) using $Fp^{W5}(thf)BF_4$ (10 mol %) and $BF_3{\bullet}Et_2O$ (74 µL, 0.6 mmol, 3.0 equiv) according to general procedure A3. The compound was first purified by fast column chromatography (eluent: 2:1 hexanes/EtOAc). The product obtained was dissolved in EtOAc (10 mL) and was washed with 2 M NaOH (2 × 5 mL) and brine (1 × 5 mL) to remove the coordinated BF_3. The organic layer was dried over magnesium sulfate and concentrated in vacuo to obtain the pure product **5o**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.39 (m, 2H), 7.30 – 7.08 (m, 9H), 7.06 – 6.99 (m, 1H), 5.90 – 5.76 (m, 1H), 5.59/5.45* (dt, *J* = 17.2, 9.8 Hz, 1H), 5.24/5.06* (dd, *J* = 10.2, 1.5 Hz, 1H), 5.14/4.97* (dd, *J* = 17.2, 1.1 Hz, 1H), 4.53*/4.33 (d, *J* = 5.7

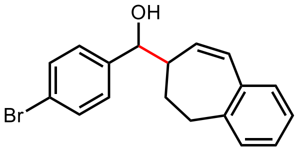
Hz*/7.6 Hz, 1H), 3.52 – 3.20 (m, 2H), 3.07 – 2.85 (m, 1H), 2.84 – 2.65 (m, 1H), 2.52 – 2.36 (m, 2H), 2.36 – 2.17 (m, 5H), 2.13*/2.10 (s, 3H), 1.55 – 1.44 (m, 1H), 1.41 – 1.03 (m, 8H).
^{13}**C NMR** (100 MHz, $CDCl_3$) δ 143.81*/143.77, 142.0, 141.8/141.3*, 140.1, 139.4, 138.9/138.4*, 137.1, 131.3/131.1*, 130.1, 129.2/129.1*, 128.8/128.7*, 128.6, 128.2, 128.1, 127.5, 127.1, 126.1, 125.8, 121.4/121.1*, 119.0/117.6*, 76.3*/76.0, 57.3, 57.2/57.1*, 52.7/51.5*, 41.9, 33.9, 32.1, 30.4/29.5*, 27.5*/27.4, 27.2, 26.93/26.89*, 26.8.
HRMS (ESI) calcd for $C_{34}H_{41}ONBr$ $[M+H]^+$: 558.2366, found: 558.2375.

53. (4-Bromophenyl)(1,2-dihydronaphthalen-2-yl)methanol (5p, wyd-6-193-2)



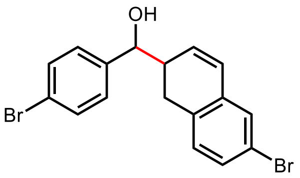
Compound **5p** was prepared as a pale yellow oil (51 mg, 81% yield, 1.3:1 d.r., eluent: 10:1 hexanes/EtOAc) from 1,2-dihydronaphthalene according to general procedure A3.
^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.53 − 7.45 (m, 2H), 7.24 − 6.96 (m, 6H), 6.59/6.50* (dd, *J* = 9.7, 1.4 Hz, 1H), 6.16/5.56* (dd, *J* = 9.7, 3.9 Hz/4.3 Hz*, 1H), 4.60 − 4.50 (m, 1H), 3.02 (dd, *J* = 15.8, 8.3 Hz, 0.6H), 2.90 (dd, *J* = 15.8, 6.8 Hz, 0.6H), 2.79 − 2.68 (m, 1H), 2.68 − 2.60 (m, 0.4H), 2.53 (dd, *J* = 15.5, 9.2 Hz, 0.4H), 2.03 (s, 1H).
^{13}**C NMR** (100 MHz, $CDCl_3$) δ 142.0/141.9*, 134.3*/134.1, 133.8/133.6*, 131.7/131.6*, 129.5*/129.2, 128.9/128.7*, 128.5/128.3*, 127.9, 127.6*/127.5, 126.8/126.7*, 126.21/126.19*, 121.8/121.6*, 76.6/75.1*, 41.6*/41.5, 30.9/29.4*.
HRMS (ESI) calcd for $C_{17}H_{14}OBr$ $[M-H]^+$: 313.0223, found: 313.0216.

54. (4-Bromophenyl)(6,7-dihydro-5*H*-benzo[7]annulen-7-yl)methanol (5q, wyd-6-193-1)



Compound **5q** was prepared as a pale yellow oil (50 mg, 76% yield, 2.0:1 d.r., eluent: 10:1 hexanes/EtOAc) from 6,7-dihydro-5*H*-benzo[7]annulene (**q**) according to general procedure A3.
^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.25 − 7.05 (m, 6H), 6.60 − 6.48 (m, 1H), 5.97/5.70* (dd, *J* = 12.2, 3.6 Hz, 1H), 4.74*/4.62 (d, *J* = 5.6 Hz*/6.2 Hz, 1H), 2.92 − 2.70 (m, 3H), 2.10 − 1.69 (m, 3H).
^{13}**C NMR** (100 MHz, $CDCl_3$) δ 142.4/142.0*, 141.7*/141.6, 136.0/135.5*, 132.20, 132.18, 131.9, 131.6, 131.5, 131.1, 131.0, 130.8, 129.0*/128.9, 128.2*/128.0, 127.2*/127.1, 126.23/126.20*, 121.5/121.4*, 77.0/76.3*, 49.8*/49.1, 33.7/33.5*, 31.9/27.9*. (mixture of diastereomers)
HRMS (ESI) calcd for $C_{18}H_{16}OBr$ $[M-H]^+$: 327.0379, found: 327.0379.

55. (6-Bromo-1,2-dihydronaphthalen-2-yl)(4-bromophenyl)methanol (5r, wyd-6-197-2)



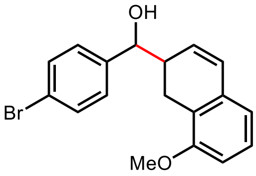
Compound **5r** was prepared as a pale yellow oil (68 mg, 86% yield, 1.0:1 d.r., eluent: 10:1 hexanes/EtOAc) from 6-bromo-1,2-dihydronaphthalene (**r**) according to general procedure A3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 − 7.36 (m, 2H), 7.22 − 7.06 (m, 4H), 6.91*/6.77 (d, *J* = 8.0 Hz*/7.9 Hz, 1H), 6.42*/6.34 (dd, *J* = 9.7, 1.4 Hz*/1.3 Hz, 1H), 6.14*/5.53 (dd, *J* = 9.7, 3.9 Hz*/4.3 Hz, 1H), 4.45 (t, *J* = 8.2 Hz, 1H), 2.89*/2.75 (dd, *J* = 15.8, 8.1 Hz*/6.8 Hz, 1H), 2.70 − 2.59 (m, 1H), 2.49*/2.38 (dd, *J* = 15.8, 6.8 Hz*/9.4 Hz, 1H), 1.92 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8*/141.7, 135.7*/135.5, 133.1*/132.9, 131.8*/131.6, 130.6, 130.3, 130.2, 130.1, 129.8, 129.4, 128.9, 128.5, 128.3, 128.2, 128.0, 121.9*/121.8, 120.2*/120.1, 76.5*/74.9, 41.41*/41.37, 30.3*/28.8. (mixture of diastereomers)

HRMS (ESI) calcd for $C_{18}H_{15}O_3Br_2$ $[M+HCOO]^+$: 436.9382, found: 436.9396.

56. (4-Bromophenyl)(8-methoxy-1,2-dihydronaphthalen-2-yl)methanol (5s, wyd-6-198)



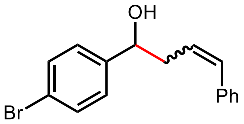
Compound **5s** was prepared as a pale yellow oil (57 mg, 83% yield, 1.7:1 d.r., eluent: 10:1 → 8:1 hexanes/EtOAc) from 1,2-dihydro-8-methoxynaphthalene (**s**) according to general procedure A3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 − 7.43 (m, 2H), 7.24 − 7.17 (m, 2H), 7.17 − 7.08 (m, 1H), 6.81 − 6.65 (m, 2H), 6.55/6.46* (dd, *J* = 9.7, 1.4 Hz/1.7 Hz*, 1H), 6.10/5.58* (dd, *J* = 9.7, 3.7 Hz/4.3 Hz*, 1H), 4.58/4.53* (d, *J* = 6.5 Hz/7.5 Hz*, 1H), 3.82*/3.79 (s, 3H), 3.01 (dd, *J* = 16.6, 8.2 Hz, 0.6H), 2.89 (dd, *J* = 16.6, 7.3 Hz, 0.6H), 2.79 − 2.67 (m, 1.4H), 2.64 − 2.53 (m, 0.4H), 2.11 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7*/156.3, 142.0/141.9*, 134.6/134.5*, 131.52/131.49*, 129.30*/129.26, 128.8/128.63*, 128.60/128.2*, 127.0/126.9*, 121.8, 121.6, 119.2, 110.3*/110.1, 76.7/75.5*, 55.6*/55.5, 41.13*/41.11, 23.1/21.7*.

HRMS (ESI) calcd for $C_{18}H_{16}O_2Br$ $[M-H]^+$: 343.0328, found: 343.0329.

57. 1-(4-Bromophenyl)-4-phenylbut-3-en-1-ol (5t, wrh-05-124A)



Compound **5t** was prepared as a pale yellow solid (50 mg, 82% yield, 1:2.2 *Z*/*E*, eluent: 15:1 → 8:1 hexanes/EtOAc) from *cis*-β-methylstyrene according to general procedure A3.

m.p. = 103 − 105 °C.

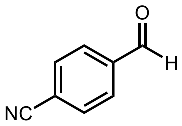
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 − 7.43 (m, 2H), 7.37 − 7.18 (m, 7H), 6.58*/6.49 (d, *J* = 11.7 Hz*/15.9 Hz, 1H), 6.19 − 6.11/5.67* (m/dt*, *J* = 11.7, 7.3 Hz, 1H), 4.80 − 4.73 (m, 1H), 2.90 − 2.55 (m, 2H), 2.10/2.00* (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, mixture of *Z* and *E* isomers) δ 143.0, 137.2, 134.0, 132.3*/131.7, 128.8, 128.7, 128.4, 127.8, 127.7, 127.6, 127.3, 127.1, 126.3/125.4*, 121.6*/121.5, 73.7*/73.2, 43.2/38.3*.

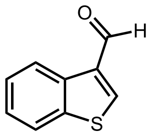
HRMS (ESI) calcd for $C_{16}H_{14}Br$ $[M-OH]^+$: 285.0273, found: 285.0280.

Unsuccessful substrates

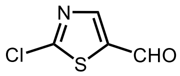
The substrates listed below were tried in propylene functionalization reactions with no product or low yields.



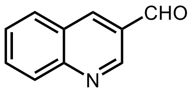
N.P.



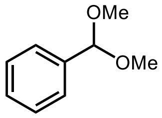
13% NMR yield



N.P.



13% NMR yield



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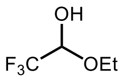

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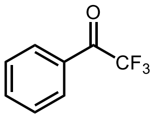

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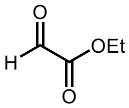

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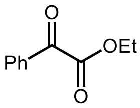

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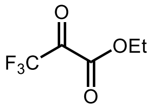

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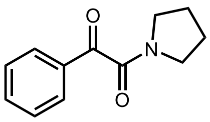

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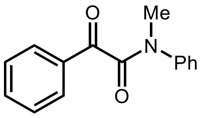

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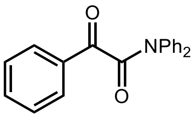

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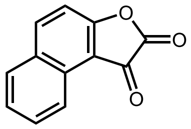
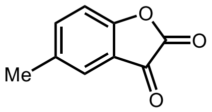


15% NMR yield



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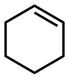
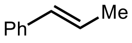


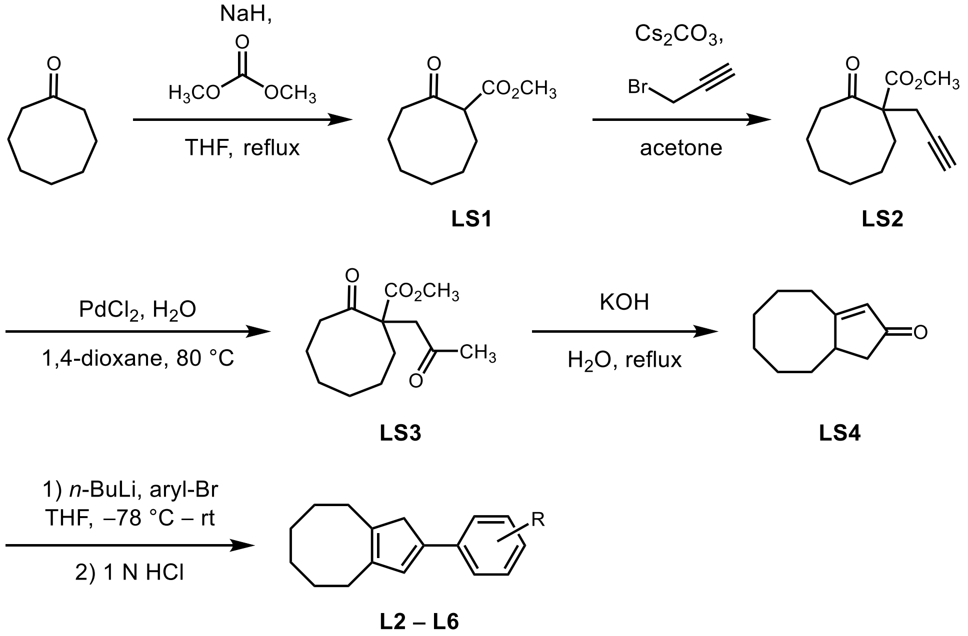
trace



N.P.

Synthesis and characterization data of iron complexes

Synthesis of ligands (L2−L6)



A 500 mL three-necked round bottom flask was fitted with a reflux condenser and a 125 mL pressure-equalizing dropping funnel containing cyclooctanone (12.6 g, 100 mmol, 1.0 equiv) and 100 mL of anhydrous THF. The reaction vessel was charged with NaH (8.00 g, 200 mmol, 2.0 equiv, 60% oil dispersion), dimethyl carbonate (17 mL, 200 mmol, 2.0 equiv) and 100 mL of dry THF under a flow of nitrogen. The flask was placed in an oil bath preheated at 76 °C. The ketone solution was added slowly to the flask at reflux with stirring. After the addition was completed, the reaction mixture was heated at reflux for 6 h. Then the mixture was cooled to room temperature, quenched by adding 1 N HCl solution dropwise at 0 °C until no bubbles were formed, and extracted with EtOAc (2 × 200 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed by rotary evaporation. The crude product **LS1** was used in the next step without purification.

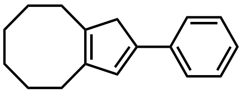
Propargyl bromide (17 mL, 200 mmol, 2.0 equiv) was added to the solution of compound **LS1** obtained in the last step and Cs_2CO_3 (47.9 g, 150 mmol, 1.5 equiv) in 250 mL of acetone, previously dried over magnesium sulfate for 2 h. The reaction mixture was stirred at room temperature overnight. Solid material was removed by vacuum filtration, and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography (gradient elution from 50:1 to 10:1 hexanes/EtOAc) to obtain compound **LS2** as a pale yellow liquid (22.2 g, 100% yield). ^1H NMR data were in agreement with the literature.[2]

A 500 mL round bottom flask was charged with $PdCl_2$ (355 mg, 2.0 mmol, 2 mol %), compound **LS2** (22.2 g, 100 mmol, 1.0 equiv), water (5 mL, 50 mg/mmol) and 250 mL of 1,4-dioxane under a flow of nitrogen. The reaction mixture was heated at 80 °C for 3 h. After the reaction was complete, the flask was allowed to cool to room temperature. The crude residue was purified by column chromatography (gradient elution from 50:1 to 3:1) to afford compound **LS3** as a yellow oil (24.0 g, 100% yield). ^1H NMR data were in agreement with the literature.[3]

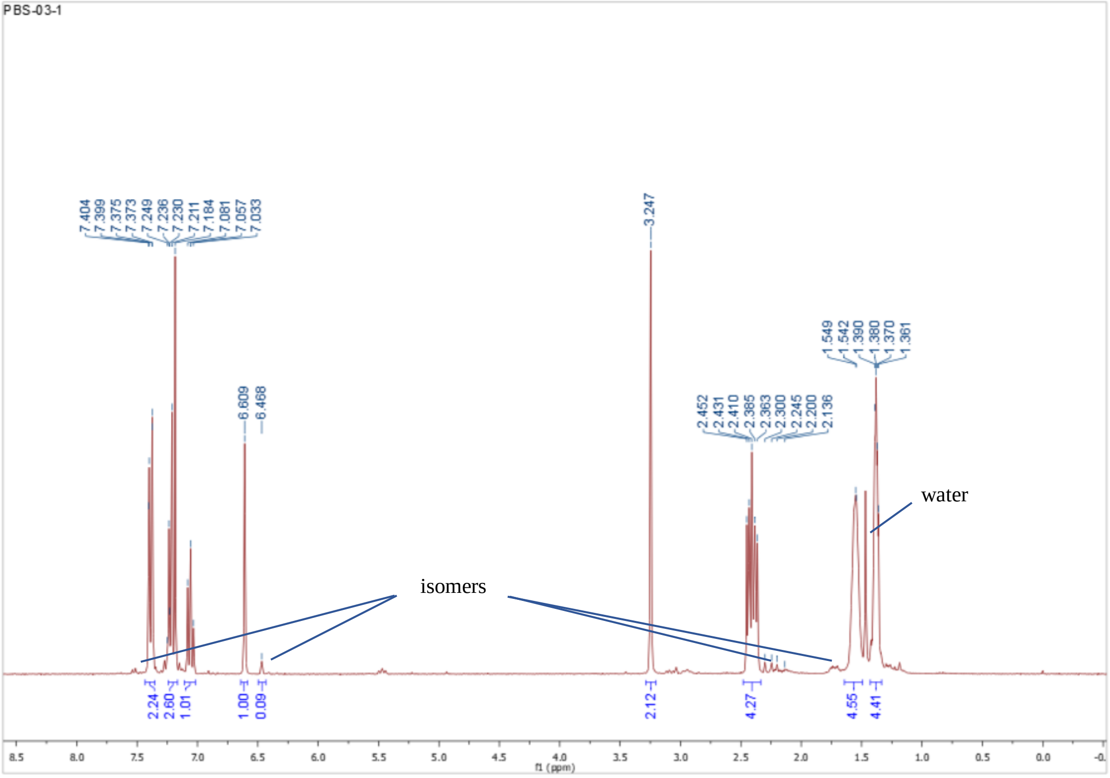
Compound **LS4** was synthesized according to literature procedure.[3]

n-BuLi (2.2 mL, 5.5 mmol, 1.1 equiv, 2.5 M in hexanes) was added dropwise to the solution of aryl bromide (1.1 equiv, 0.3 M) in anhydrous THF at −78 °C under nitrogen. The reaction mixture was stirred at −78 °C for 1 h, then compound **LS4** (821 mg, 5.0 mmol, 1.0 equiv) was added dropwise. The mixture was gradually warmed to room temperature and was stirred overnight. After completion, aqueous HCl (1 M, 10 mL) was added to the reaction mixture with vigorous stirring for 10 min. Then the resulting mixture was transferred to a separatory funnel and extracted with EtOAc (4 × 20 mL). The combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. Purification by column chromatography afforded ligands **L2**−**L6** as a mixture of cyclopentadiene isomers, which were used in the next step without further purification.

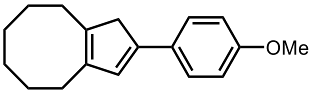
2-Phenyl-4,5,6,7,8,9-hexahydro-1*H*-cyclopenta[8]annulene (L2, PBS-03-1)



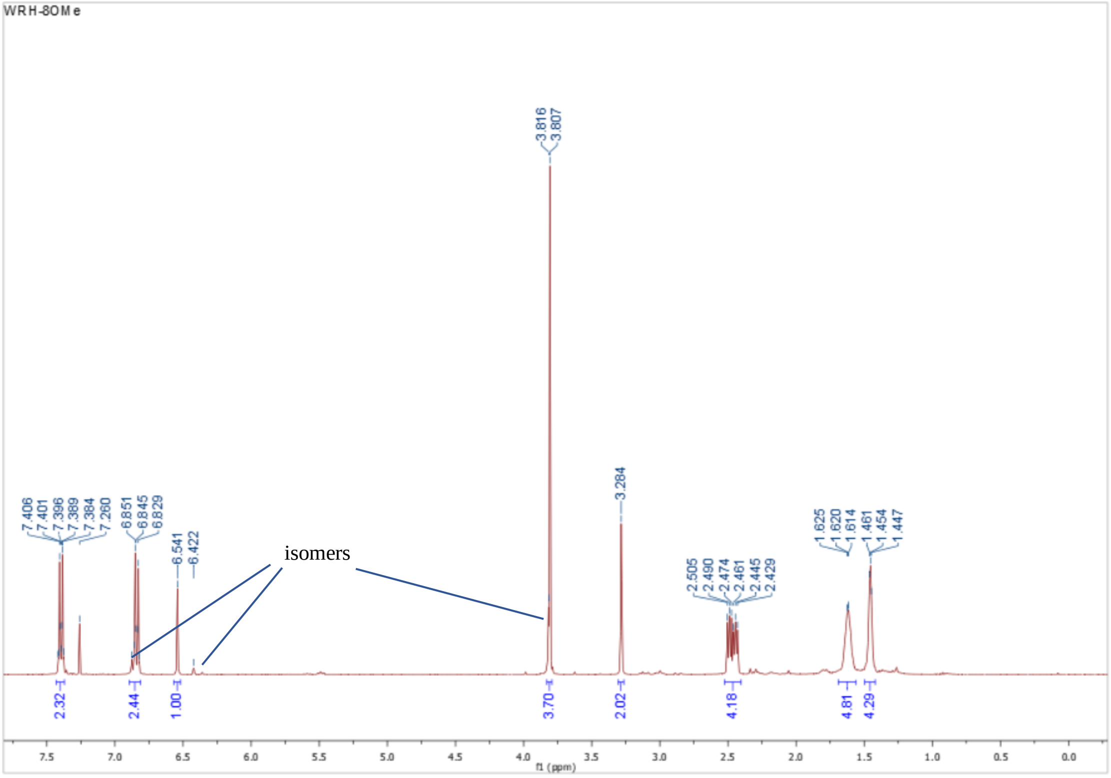
This compound was prepared as a pale yellow solid (954 mg, 85% yield, eluent: hexanes) using bromobenzene as the aryl bromide in the last step.

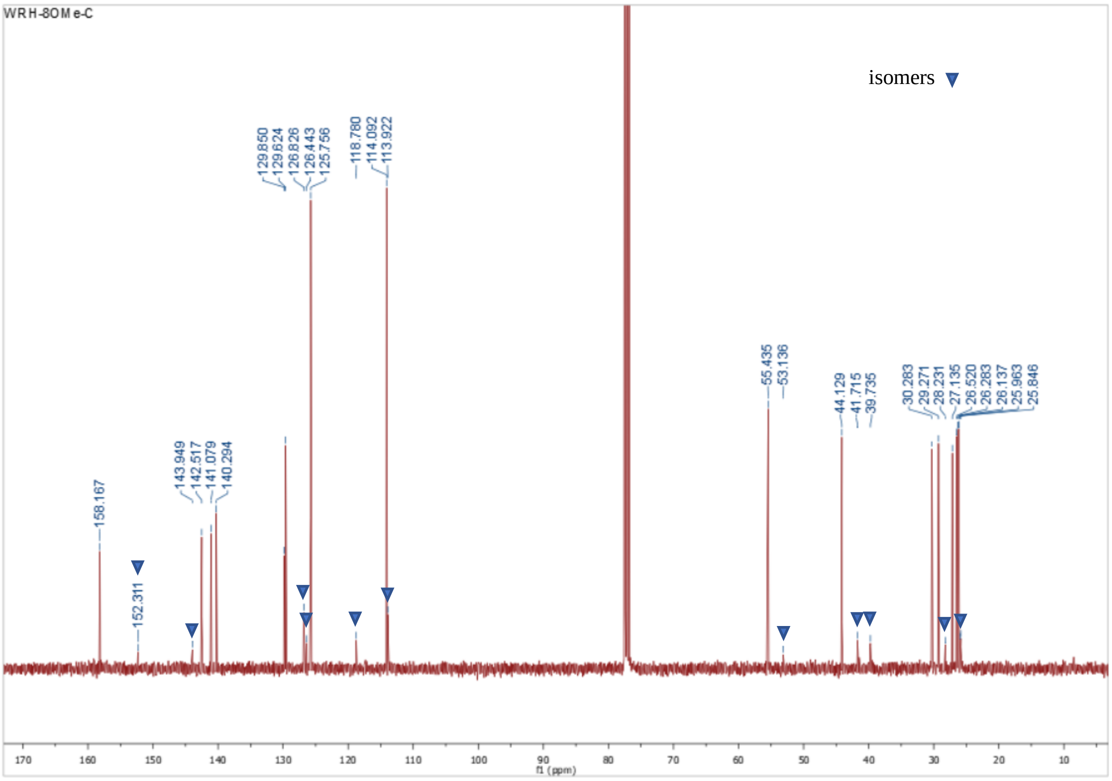


2-(4-Methoxyphenyl)-4,5,6,7,8,9-hexahydro-1*H*-cyclopenta[8]annulene (L3, wrh-8OMe)

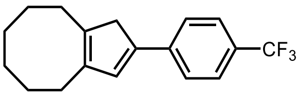


This compound was prepared as a pale yellow solid (866 mg, 68% yield, eluent: 100:1 hexanes/EtOAc) using 4-bromoanisole as the aryl bromide in the last step.

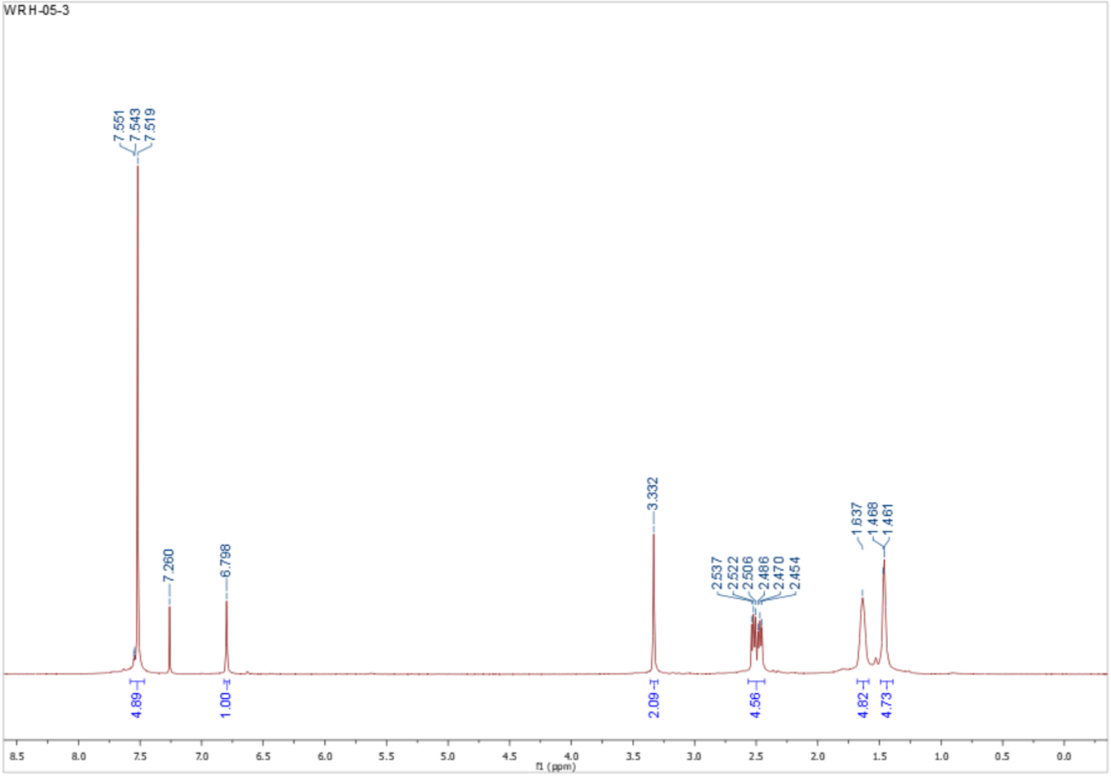


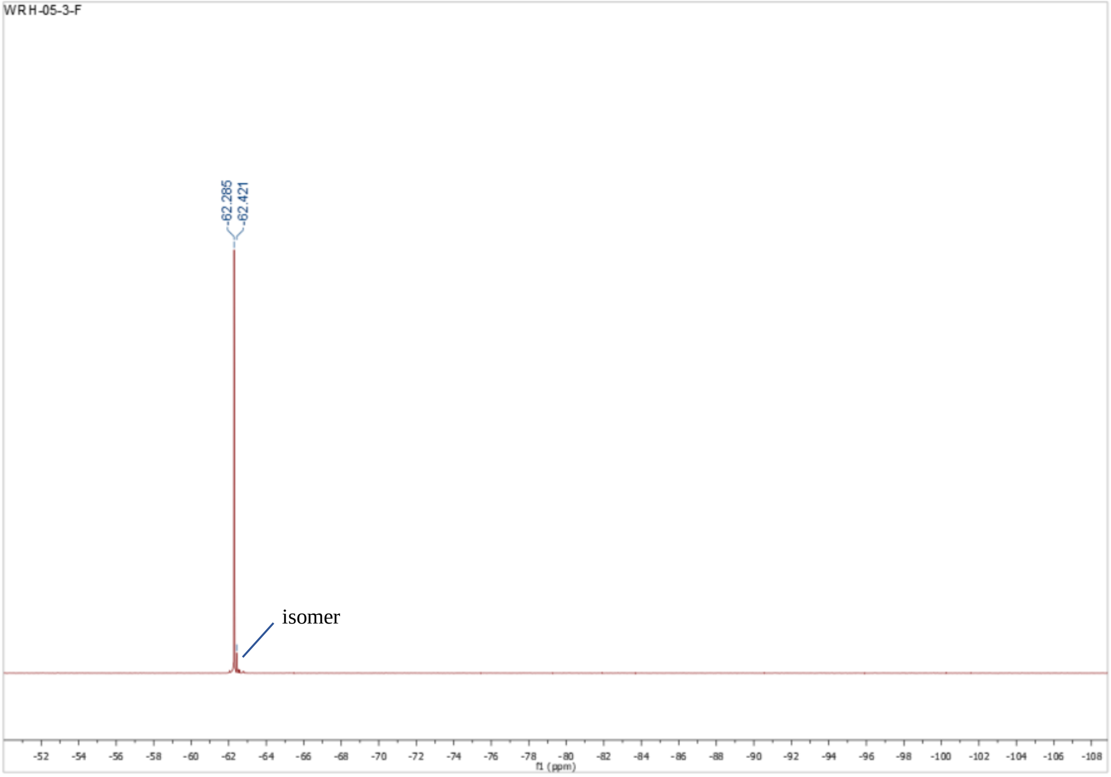


2-(4-(Trifluoromethyl)phenyl)-4,5,6,7,8,9-hexahydro-1*H*-cyclopenta[8]annulene (L4, wrh-05-3)

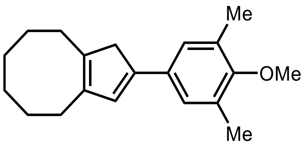


This compound was prepared as a pale yellow solid (1.01 g, 69% yield, eluent: hexanes) using 4-bromobenzotrifluoride as the aryl bromide in the last step.

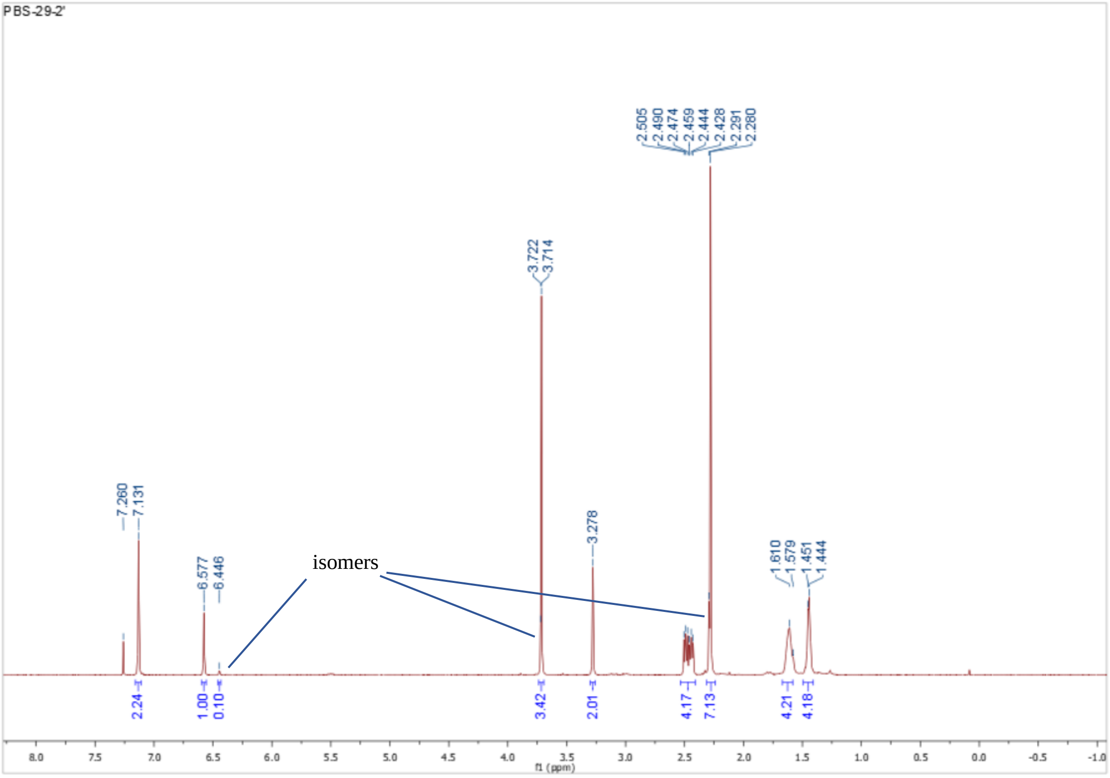


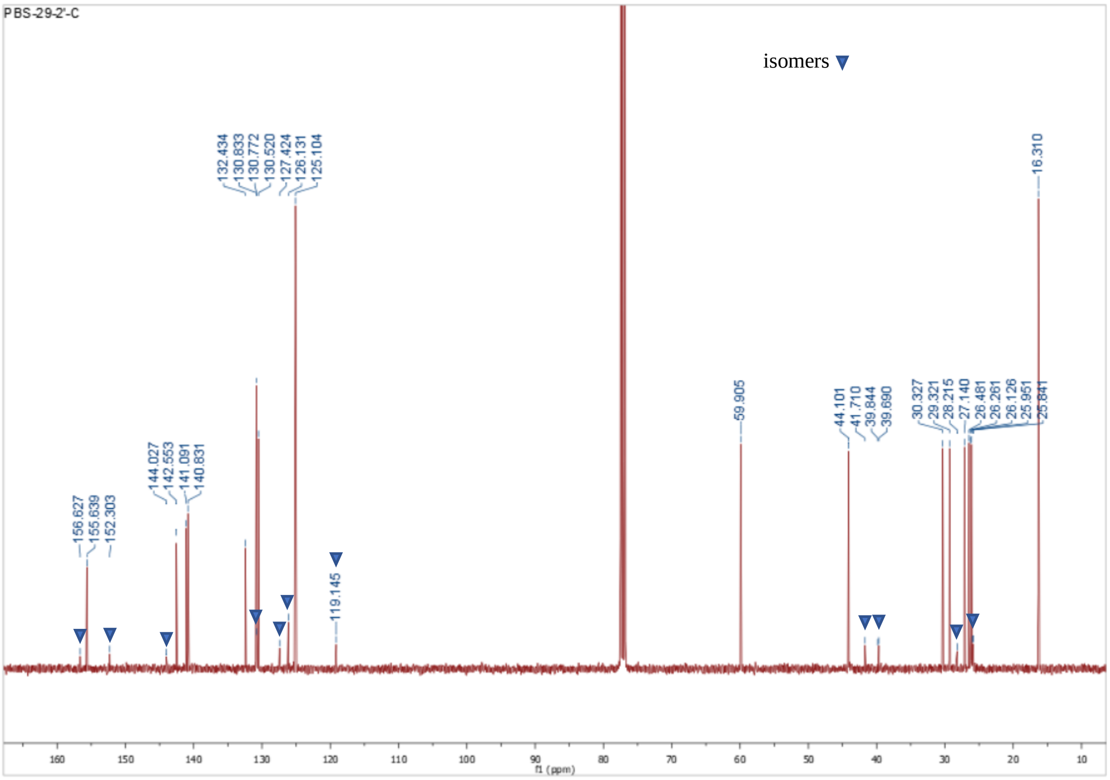


2-(4-Methoxy-3,5-dimethylphenyl)-4,5,6,7,8,9-hexahydro-1*H*-cyclopenta[8]annulene (L5, PBS-29-2)

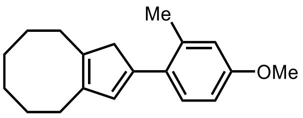


This compound was prepared as a yellow oil (1.11 g, 79% yield, eluent: 80:1 hexanes/EtOAc) using 4-bromo-2,6-dimethylanisole as the aryl bromide in the last step.

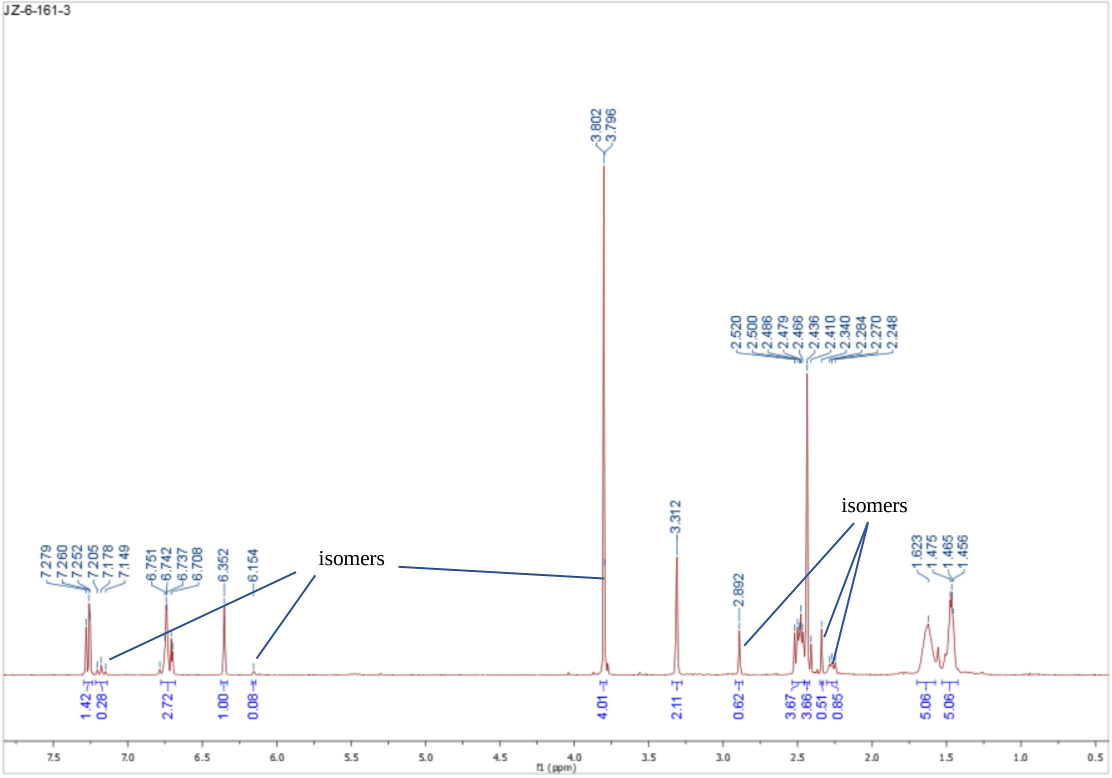




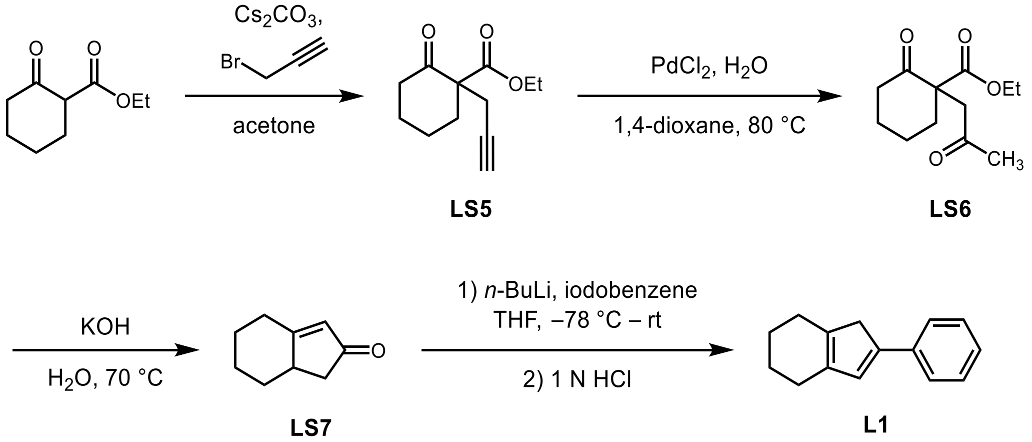
2-(4-Methoxy-2-methylphenyl)-4,5,6,7,8,9-hexahydro-1*H*-cyclopenta[8]annulene (L6, JZ-6-161-3)



This compound was prepared as a pale yellow solid (844 mg, 63% yield, eluent: 50:1 hexanes/EtOAc) using 4-bromo-3-methylanisole as the aryl bromide in the last step.



Synthesis of ligand L1



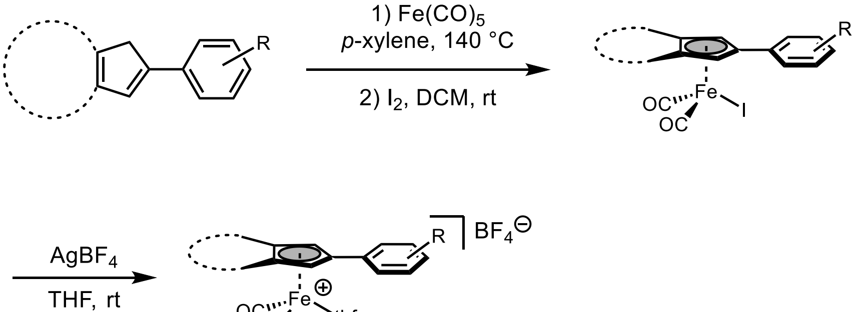
Propargyl bromide (8.5 mL, 100 mmol, 2.0 equiv) was added to the solution of ethyl 2-oxocyclohexanecarboxylate (7.9 mL, 50 mmol, 1.0 equiv) and Cs_2CO_3 (24.4 g, 75 mmol, 1.5 equiv) in 150 mL of acetone, previously dried over magnesium sulfate for 2 h. The reaction mixture was stirred at room temperature overnight. Solid material was removed by vacuum filtration, and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography (gradient elution from 40:1 to 10:1 hexanes/EtOAc) to obtain compound **LS5** as a colorless liquid (8.54 g, 82% yield). ^{1}H NMR data were in agreement with the literature.[4]

A 250 mL round bottom flask was charged with $PdCl_2$ (145 mg, 0.8 mmol, 2 mol %), compound **LS5** (8.54 g, 41 mmol 1.0 equiv), water (2.0 mL, 50 mg/mmol) and 120 mL of 1,4-dioxane under a flow of nitrogen. The reaction mixture was heated at 80 °C for 3 h. After the reaction was complete, the flask was allowed to cool to room temperature. The crude residue was purified by column chromatography (5:1 → 3:1 hexanes/EtOAc) to afford compound **LS6** as a yellow oil (9.00 g, 97% yield). ^1H NMR data were in agreement with the literature.[2]

A 500 mL round bottom flask was charged with compound **LS6** (2.26 g, 10 mmol), 15% aqueous KOH solution (25 mL, 2.5 mL/mmol) and 200 mL of water (20 mL/mmol). The reaction mixture was heated at 70 °C for 2 h. After cooling to room temperature, the mixture was extracted with CH_2Cl_2 (4 × 200 mL). The combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. The mixture was purified by column chromatography (5:1 hexanes/EtOAc) to give compound **LS7** as a pale yellow liquid (1.18 g, 87% yield). ^1H NMR data were in agreement with the literature.[3]

n-BuLi (2.2 mL, 5.5 mmol, 1.1 equiv, 2.5 M in hexanes) was added dropwise to the solution of bromobenzene (0.58 mL, 5.5 mmol, 1.1 equiv, 0.3 M) in anhydrous THF at −78 °C under nitrogen. The reaction mixture was stirred at −78 °C for 1 h, then compound **LS7** (681 mg, 5.0 mmol, 1.0 equiv) was added dropwise. The mixture was gradually warmed to room temperature and was stirred overnight. After completion, aqueous HCl (1 M, 10 mL) was added to the reaction mixture with vigorous stirring for 5 min. The resulting mixture was transferred to a separatory funnel and extracted with EtOAc (4 × 20 mL). The combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. Purification by column chromatography (hexanes) afforded ligand **L1** as a white crystalline solid (745 mg, 76% yield). ^1H NMR data were in agreement with the literature.[5]

Synthesis of iron complexes



A solution of ligand (2.4–3.7 mmol, 1.0 equiv, 0.5 M) and pentacarbonyliron(0) (3.0 equiv) in *p*-xylene was thoroughly deoxygenated and heated at reflux under nitrogen for 20 h. Then the mixture was cooled to room temperature, the solvent was removed by rotary evaporation. The residue was dissolved in CH_2Cl_2 (0.2 M) and was treated with iodine (1.0 equiv). After stirring at room temperature for 2 h, the mixture was filtered through a pad of celite to remove insoluble solid material. The filtrate was washed with saturated Na_2SO_3 solution (5 × 5 mL). The organic layer was dried over magnesium sulfate and concentrated *in vacuo*. Column chromatography on silica gel or recrystallization afforded the iron-iodide complex.

A flame-dried flask was charged with iron-iodide complex (0.5 or 1.0 mmol, 1.0 equiv, 0.2 M), $AgBF_4$ (1.0 equiv) and anhydrous THF in an argon-filled glovebox.

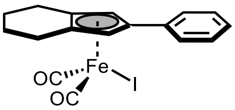
The reaction mixture was stirred at room temperature for 6 h. After completion, the solvent was removed by rotary evaporation. The residue was dissolved in dry CH_2Cl_2 (10 mL) and filtered through a pad of celite to remove silver iodide. The catalysts were obtained with two methods depending on the feasibility of recrystallization.

Method A: The filtrate was concentrated until approximately 1 mL of CH_2Cl_2 remained, then dry diethyl ether (10 mL) was added until large amounts of crystalline material were precipitated. The crystals were collected by vacuum filtration, washed with dry diethyl ether, and dried *in vacuo* for 10 min.

Method B: The solvent of the filtrate was removed under reduced pressure. Dry diethyl ether (5 mL) was added to wash the residue and was decanted. This step was repeated five times. The residual solvent was removed *in vacuo* for 30 min. Work-up and purification before drying under vacuum should be carried out as quickly as possible, preferably within 15 min.

Characterization data for $Cp^xFe(CO)_2I$ complexes

$Cp^{W1}Fe(CO)_2I$ (ZJ-6-84-3)



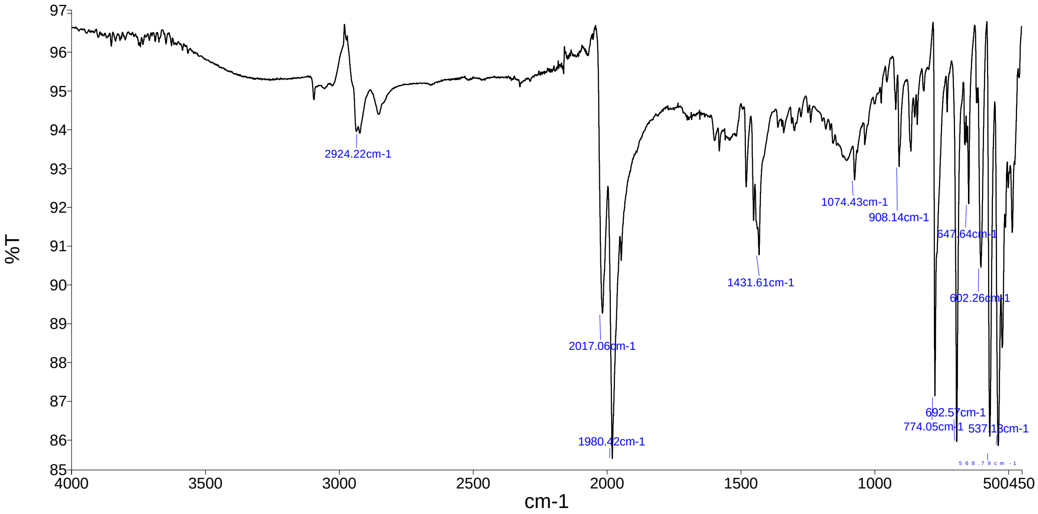
This compound was synthesized on the scale of 3.7 mmol. Product was purified by recrystallization using CH_2Cl_2 (2 mL) and hexanes (10 mL) to afford a dark brown solid (940 mg, 58% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 − 7.31 (m, 5H), 4.95 (s, 2H), 3.04 − 2.72 (m, 2H), 2.71 − 2.41 (m, 2H), 2.10 − 1.65 (m, 4H).

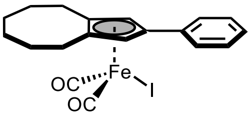
^{13}C NMR (75 MHz, $CDCl_3$) δ 214.4, 130.9, 129.5, 129.1, 126.7, 104.1, 100.7, 76.1, 23.1, 22.2.

HRMS (ESI) calcd for $C_{17}H_{16}O_2FeI$ $[M+H]^+$: 434.9539, found: 434.9530.

IR (ATR, neat): ṽ(CO) = 2017, 1980 cm^{-1}.



$Cp^{W2}Fe(CO)_2I$ (wrh-8Ph)



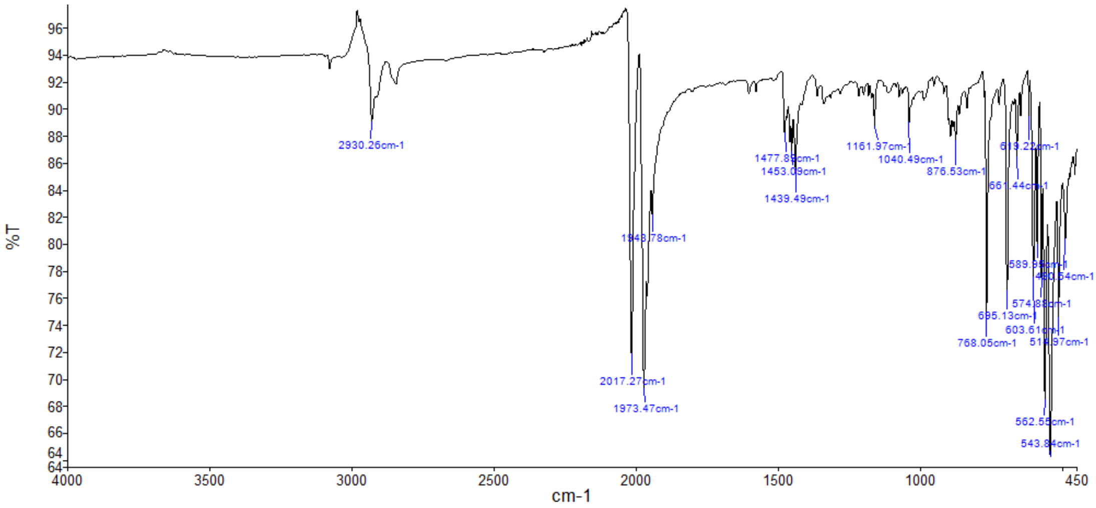
This compound was synthesized on the scale of 3.4 mmol. Purification by column chromatography (50:1 → 20:1 hexanes/EtOAc) afforded the product as a black solid (1.0 g, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.45 (m, 2H), 7.45 – 7.30 (m, 3H), 5.16 (s, 2H), 2.70 – 2.40 (m, 4H), 2.04 – 1.82 (m, 2H), 1.69 – 1.34 (m, 6H).

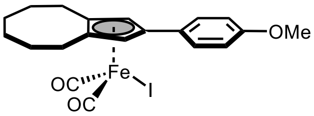
^{13}C NMR (100 MHz, $CDCl_3$) δ 214.0, 130.8, 129.3, 129.1, 126.5, 104.1, 96.8, 81.5, 31.8, 26.1, 25.8.

HRMS (ESI) calcd for $C_{19}H_{19}O_2FeI$ $[M]^+$: 461.9774, found: 461.9778.

IR (ATR, neat): ṽ(CO) = 2017, 1973 cm^{-1}.



$Cp^{W3}Fe(CO)_2I$ (wrh-8OMe-I)



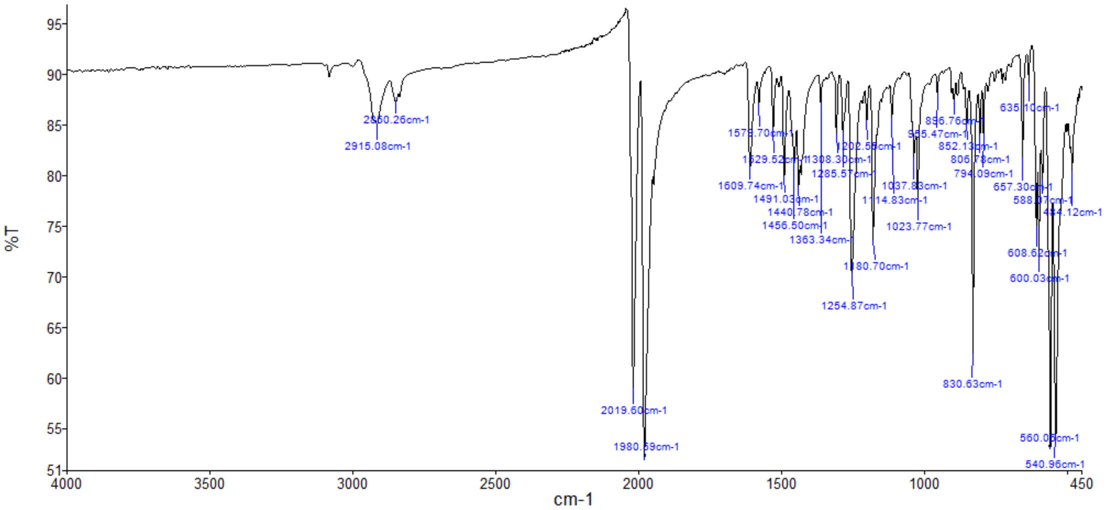
This compound was synthesized on the scale of 3.4 mmol. Purification by column chromatography (gradient elution from 50:1 to 8:1 hexanes/EtOAc) afforded the product as a brown solid (1.0 g, 62% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 5.07 (s, 2H), 3.84 (s, 3H), 2.63 – 2.47 (m, 4H), 1.92 (s, 2H), 1.61 – 1.37 (m, 6H).

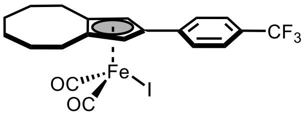
^{13}C NMR (100 MHz, $CDCl_3$) δ 214.1, 160.5, 127.9, 122.6, 114.5, 103.8, 98.7, 80.2, 55.5, 31.8, 26.1, 25.8.

HRMS (ESI) calcd for $C_{20}H_{21}O_3FeI$ $[M]^+$: 491.9879, found: 491.9883.

IR (ATR, neat): ṽ(CO) = 2020, 1981 cm^{-1}.



$Cp^{W4}Fe(CO)_2I$ (wrh-05-7)



This compound was synthesized on the scale of 2.4 mmol. Purification by column chromatography (60:1 → 50:1 hexanes/EtOAc) afforded the product as a black oil (664 mg, 52% yield).

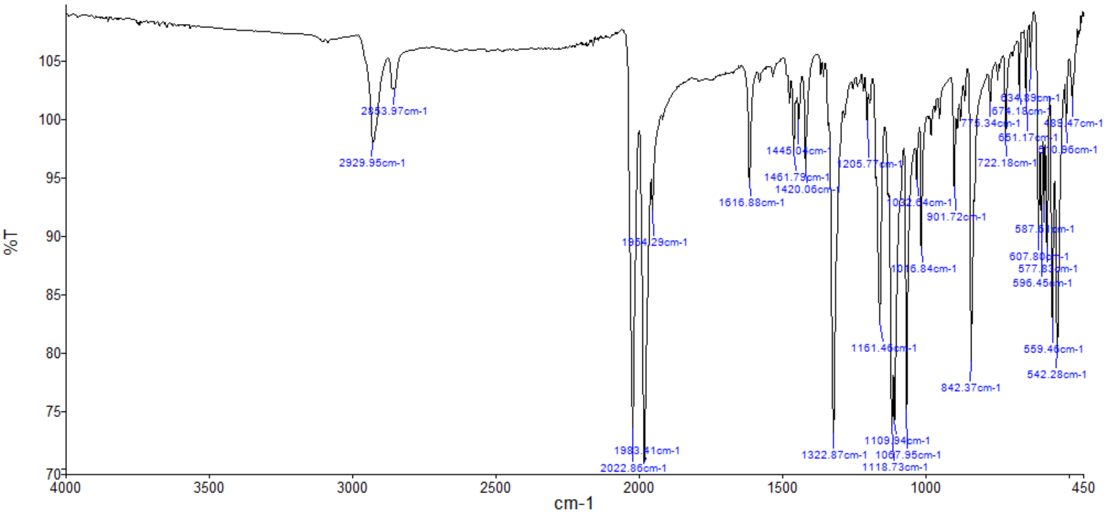
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (q, *J* = 8.3 Hz, 4H), 5.24 (s, 2H), 2.69 – 2.40 (m, 4H), 2.05 – 1.83 (m, 2H), 1.66 – 1.35 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 213.7, 135.1, 130.7 (q, *J* = 32.6 Hz), 126.7, 126.0 (q, *J* = 3.4 Hz), 124.0 (q, *J* = 271 Hz), 103.8, 93.7, 83.3, 31.7, 25.8, 25.7.

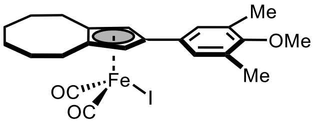
^{19}F NMR (282 MHz, $CDCl_3$) δ −62.80.

HRMS (ESI) calcd for $C_{20}H_{19}F_3O_2FeI$ $[M{-}H]^+$: 528.9569, found: 528.9587.

IR (ATR, neat): ṽ(CO) = 2023, 1983 cm^{-1}.



$Cp^{W5}Fe(CO)_2I$ (wrh-04-180-2)



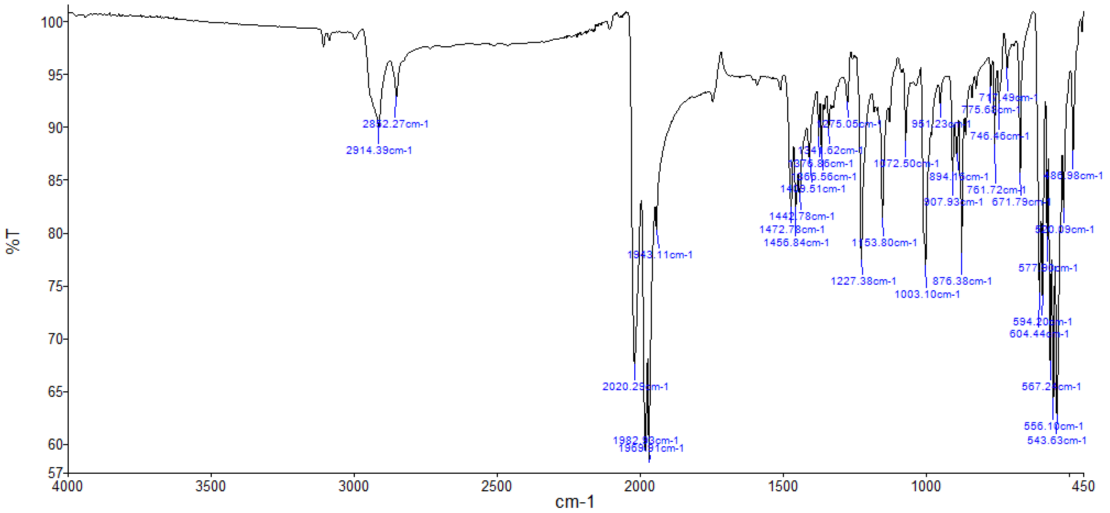
This compound was synthesized on the scale of 3.0 mmol. Purification by column chromatography (80:1 → 50:1 hexanes/EtOAc) afforded the product as a black solid (920 mg, 59% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (s, 2H), 5.07 (s, 2H), 3.73 (s, 3H), 2.74 – 2.42 (m, 4H), 2.30 (s, 6H), 2.02 – 1.79 (m, 2H), 1.68 – 1.33 (m, 6H).

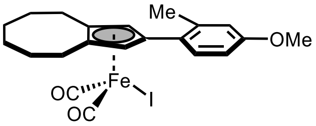
^{13}C NMR (100 MHz, $CDCl_3$) δ 214.2, 158.1, 131.7, 127.1, 125.7, 104.1, 97.8, 80.6, 60.0, 31.9, 26.1, 25.8, 16.4.

HRMS (ESI) calcd for $C_{22}H_{25}O_3FeI$ $[M]^+$: 520.0192, found: 520.0203.

IR (ATR, neat): ṽ(CO) = 2020, 1983, 1969 cm^{-1}.



Cp^{W6}Fe(CO)$_2$I (JZ-6-163-1)



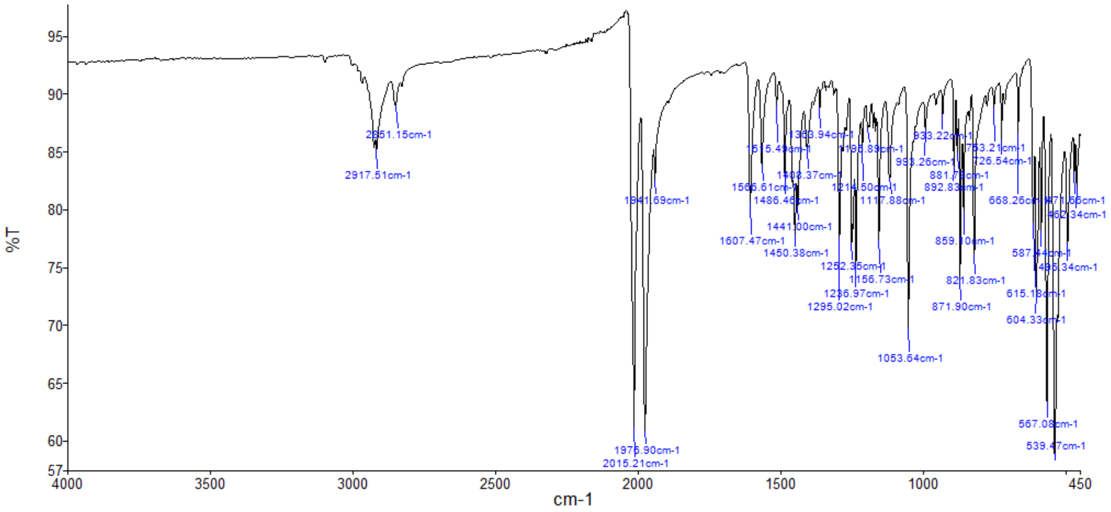
This compound was synthesized on the scale of 3.0 mmol. Purification by column chromatography (30:1 → 20:1 hexanes/EtOAc) afforded the product as a black solid (1.1 g, 71% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.5 Hz, 1H), 6.84 – 6.70 (m, 2H), 4.90 (s, 2H), 3.82 (s, 3H), 2.65 – 2.48 (m, 4H), 2.41 (s, 3H), 2.00 – 1.85 (m, 2H), 1.61 – 1.38 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 214.2, 159.8, 138.1, 131.6, 122.1, 116.7, 111.8, 103.5, 100.7, 83.8, 55.4, 31.9, 25.94, 25.86, 22.0.

HRMS (ESI) calcd for $C_{21}H_{23}O_3FeI$ $[M]^+$: 506.0036, found: 506.0048.

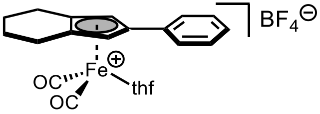
IR (ATR, neat): ṽ(CO) = 2015, 1977 cm^{-1}.



Characterization data for Fp^X(thf)BF_4 complexes

Based on literature and our previous experience[6-7], clean NMR spectra of iron-thf complexes cannot be obtained due to the formation of water complexes and solvated species in chlorine-containing deuterated solvents. Therefore, all the NMR characterization data of the catalysts were obtained in acetonitrile-*d*$_3$. The actual species observed in the spectra are the iron-CD_3CN complexes, along with free THF liberated from the iron-thf complexes. The peaks of complexed CD_3CN are not observed in the ^{13}C NMR spectra due to rapid exchange with the solvent. Based on the ratio of the iron complex to free THF molecule, the purity of the iron catalysts is within the range of 86−100%. The impurities are most likely iron-H_2O complexes generated during work-up.

Fp^{W1}(thf)BF_4 (wrh-05-6Ph)



This compound was synthesized on the scale of 0.5 mmol. Purification using method B afforded the product as a sticky dark red solid (207 mg, 89% yield).

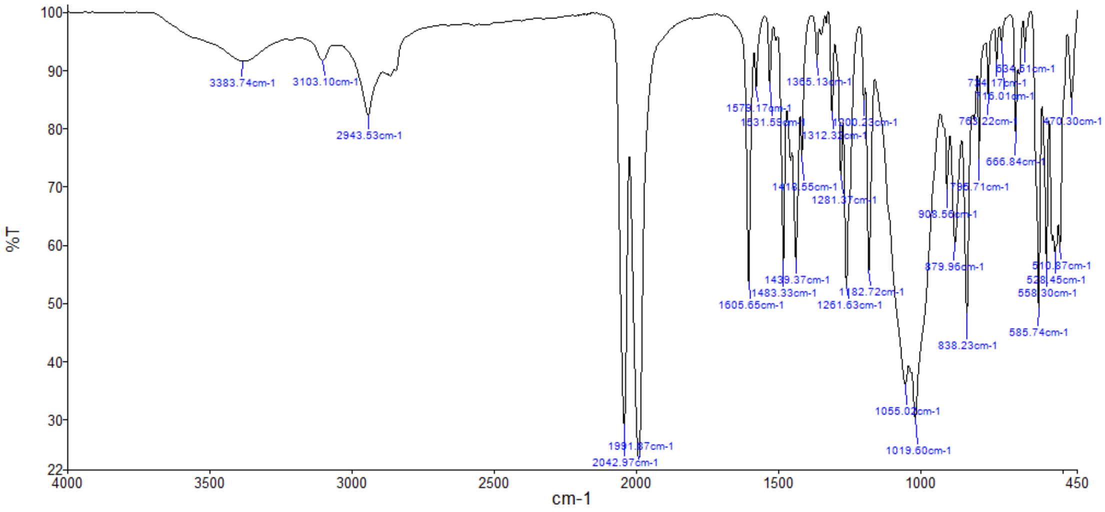
^{1}H NMR (400 MHz, CD_3CN) δ 7.64 – 7.59 (m, 2H), 7.55 – 7.45 (m, 3H), 5.68 (s, 2H), 3.68 – 3.60 (m, 4H), 2.47 – 2.30 (m, 4H), 1.83 – 1.78 (m, 4H), 1.77 – 1.63 (m, 4H).

^{13}C NMR (100 MHz, CD_3CN) δ 210.5, 131.7, 130.2, 129.5, 128.4, 110.0, 107.0, 75.8, 68.2, 26.1, 22.7, 22.1.

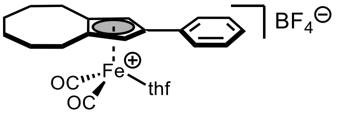
^{19}F NMR (376 MHz, CD_3CN) δ −151.6.

HRMS (ESI) calcd for $C_{17}H_{15}O_2Fe$ $[M-C_4H_8O-BF_4]^+$: 307.0416, found: 307.0410.

IR (ATR, neat): ṽ(CO) = 2043, 1992 cm^{-1}.



Fp^{W2}(thf)BF$_4$ (wrh-05-Ph)



This compound was synthesized on the scale of 0.5 mmol. Purification using method A afforded the product as a red solid (173 mg, 70% yield).

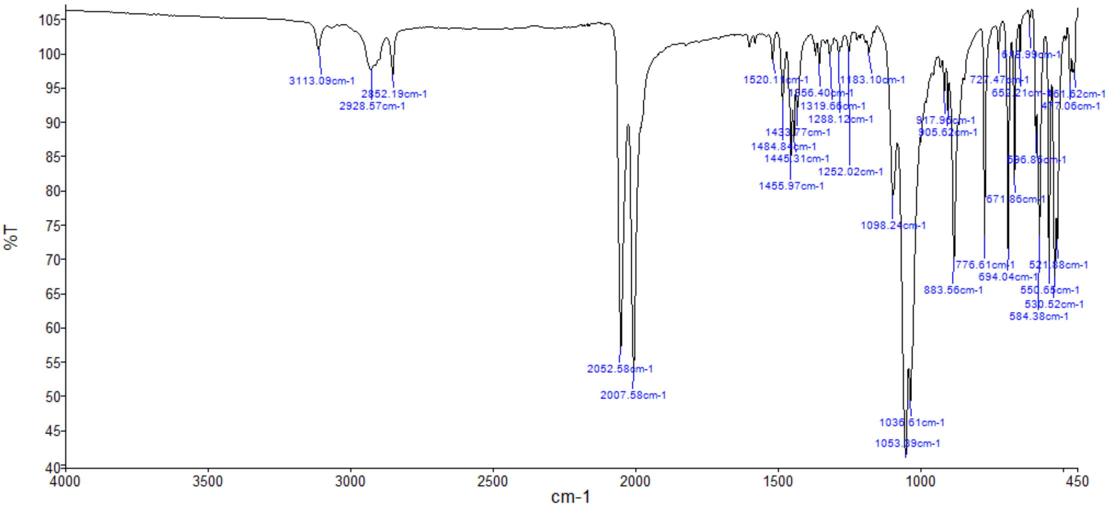
^{1}H NMR (400 MHz, CD_3CN) δ 7.67 – 7.59 (m, 2H), 7.56 – 7.44 (m, 3H), 5.87 (s, 2H), 3.69 – 3.59 (m, 4H), 2.49 (dt, *J* = 13.8, 3.8 Hz, 2H), 2.32 – 2.20 (m, 2H), 1.97 – 1.85 (m, 2H), 1.84 – 1.73 (m, 4H), 1.64 – 1.32 (m, 6H).

^{13}C NMR (100 MHz, CD_3CN) δ 210.3, 131.6, 130.3, 129.6, 128.5, 109.3, 106.9, 80.5, 68.2, 31.2, 26.2, 26.1, 25.4.

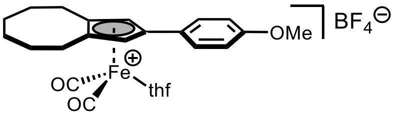
^{19}F NMR (376 MHz, CD_3CN) δ −151.7.

HRMS (ESI) calcd for $C_{21}H_{22}O_2NFe$ $[M{-}C_4H_8O{-}BF_4{+}C_2H_3N]^+$: 376.0994, found: 376.0996.

IR (ATR, neat): ṽ(CO) = 2053, 2008 cm^{-1}.



Fp^{W3}(thf)BF$_4$ (wrh-05-OMe)



This compound was synthesized on the scale of 1.0 mmol. Purification using method B afforded the product as a red solid (498 mg, 95% yield).

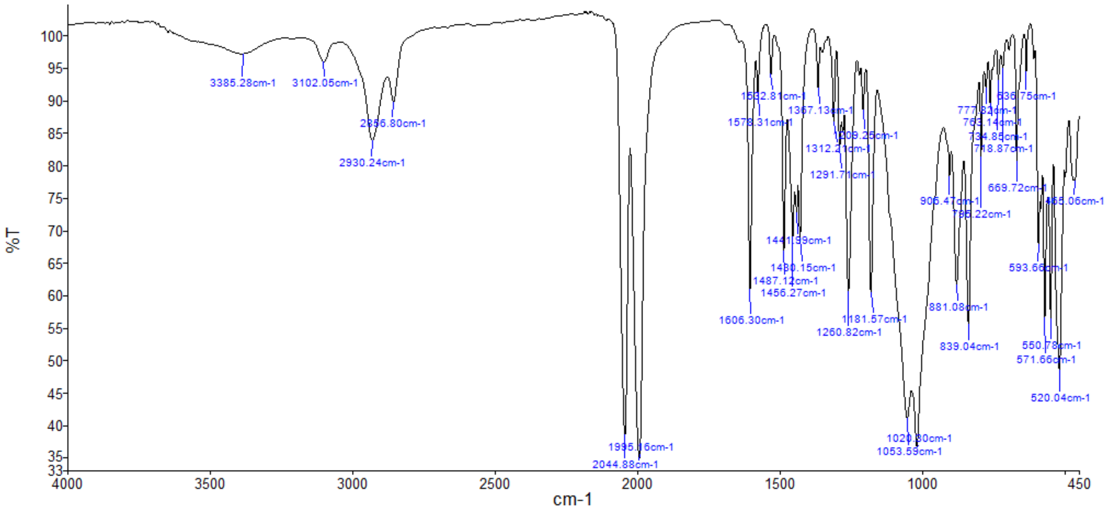
^{1}H NMR (400 MHz, CD_3CN) δ 7.62 − 7.55 (m, 2H), 7.05 − 6.99 (m, 2H), 5.78 (s, 2H), 3.84 (s, 3H), 3.68 − 3.60 (m, 4H), 2.46 (dt, *J* = 13.8, 3.9 Hz, 2H), 2.27 − 2.20 (m, 2H), 1.92 − 1.84 (m, 2H), 1.84 − 1.76 (m, 4H), 1.61 − 1.32 (m, 6H).

^{13}C NMR (100 MHz, CD_3CN) δ 210.5, 162.8, 130.3, 121.1, 115.7, 113.0, 106.2, 78.9, 68.2, 56.2, 31.2, 26.1, 26.0, 25.4.

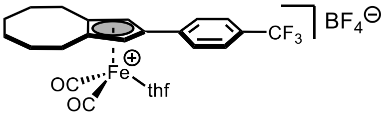
^{19}F NMR (376 MHz, CD_3CN) δ −151.6.

HRMS (ESI) calcd for $C_{22}H_{24}O_3NFe$ $[M{-}C_4H_8O{-}BF_4{+}C_2H_3N]^+$: 406.1100, found: 406.1104.

IR (ATR, neat): ṽ(CO) = 2045, 1995 cm^{-1}.



Fp^{W4}Fe(thf)BF$_4$ (wrh-05-8CF3)



This compound was synthesized on the scale of 0.5 mmol. Purification using method A afforded the product as a red solid (211 mg, 75% yield).

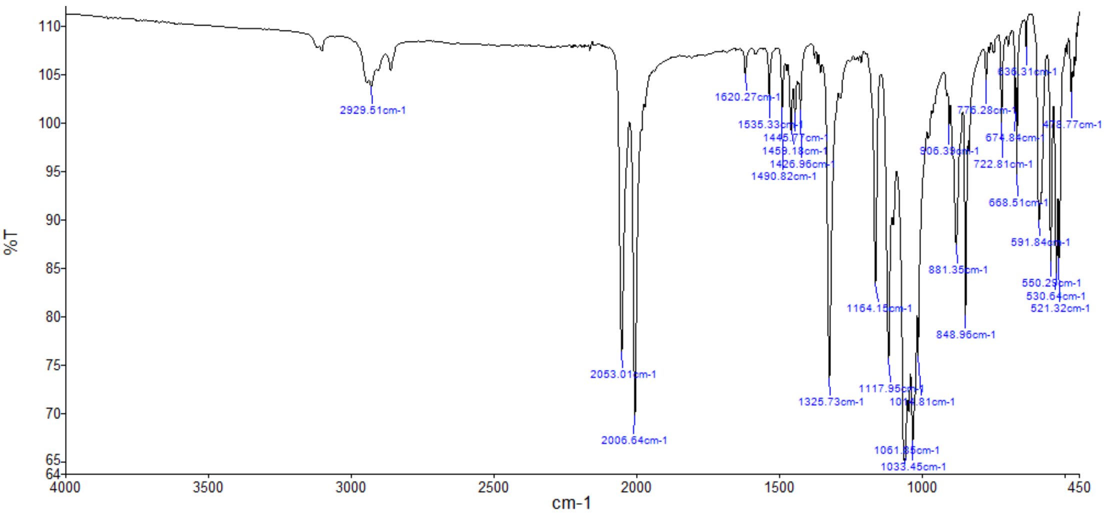
^{1}H NMR (400 MHz, CD_3CN) δ 7.79 (s, 4H), 5.94 (s, 2H), 3.68 − 3.59 (m, 4H), 2.50 (dt, *J* = 13.9, 3.9 Hz, 2H), 2.36 − 2.25 (m, 2H), 1.97 − 1.86 (m, 2H), 1.84 − 1.75 (m, 4H), 1.63 − 1.33 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 134.4 (q, *J* = 1.2 Hz), 132.0 (q, *J* = 32.5 Hz), 128.9, 127.1 (q, *J* = 3.9 Hz), 125.0 (q, *J* = 270 Hz), 107.4, 104.1, 82.2, 68.2, 31.2, 26.2, 26.0, 25.3.

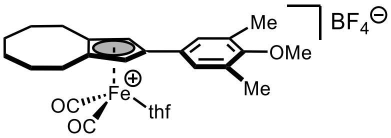
^{19}F NMR (376 MHz, CD_3CN) δ −63.52, −151.7.

HRMS (ESI) calcd for $C_{22}H_{21}O_2NF_3Fe$ $[M{-}C_4H_8O{-}BF_4{+}C_2H_3N]^+$: 444.0868, found: 444.0870.

IR (ATR, neat): ṽ(CO) = 2053, 2007 cm^{-1}.



Fp^{W5}(thf)BF$_4$ (wrh-05-2MeOMe)



This compound was synthesized on the scale of 1.0 mmol. Purification using method A afforded the product as a red solid (464 mg, 84% yield).

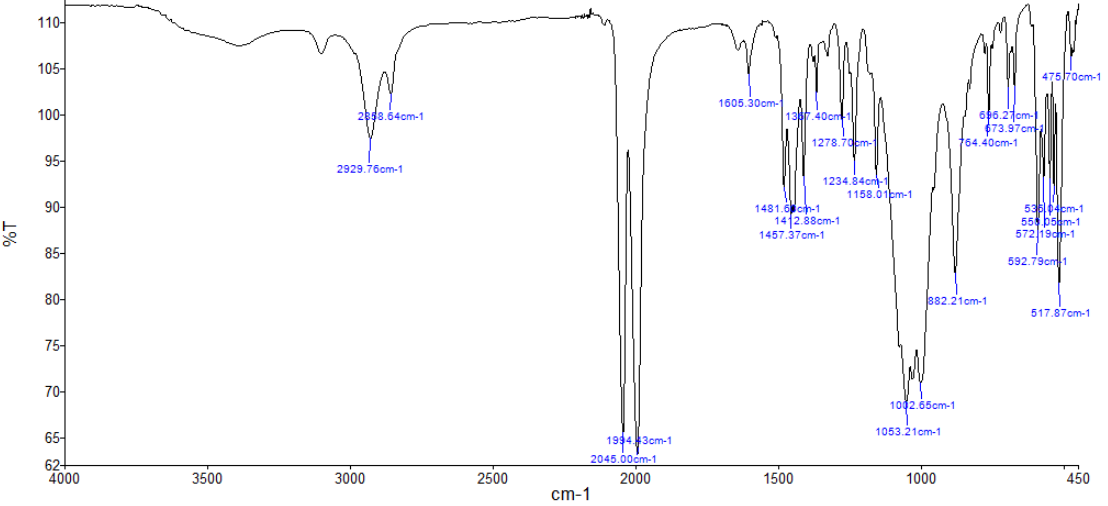
^{1}H NMR (400 MHz, CD$_3$CN) δ 7.34 (s, 2H), 5.79 (s, 2H), 3.71 (d, *J* = 4.8 Hz, 3H), 3.68 – 3.60 (m, 4H), 2.46 (dt, *J* = 13.8, 3.8 Hz, 2H), 2.30 (s, 6H), 2.27 – 2.18 (m, 2H), 1.93 – 1.84 (m, 2H), 1.84 – 1.75 (m, 4H), 1.61 – 1.30 (m, 6H).

^{13}C NMR (100 MHz, CD$_3$CN) δ 210.5, 160.3, 133.1, 129.3, 124.5, 111.6, 106.4, 79.8, 68.2, 60.2, 31.2, 26.2, 26.0, 25.4, 16.2.

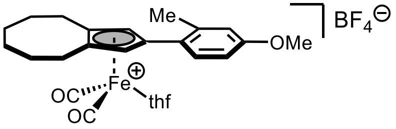
^{19}F NMR (376 MHz, CD$_3$CN) δ −151.6.

HRMS (ESI) calcd for $C_{24}H_{28}O_3NFe$ $[M{-}C_4H_8O{-}BF_4{+}C_2H_3N]^+$: 434.1413, found: 434.1419.

IR (ATR, neat): ṽ(CO) = 2045, 1994 cm^{-1}.



Fp^{W6}Fe(thf)BF$_4$ (wrh-05-8MeOMe)



This compound was synthesized on the scale of 1.0 mmol. Purification using method B afforded the product as a dark red solid (484 mg, 90% yield).

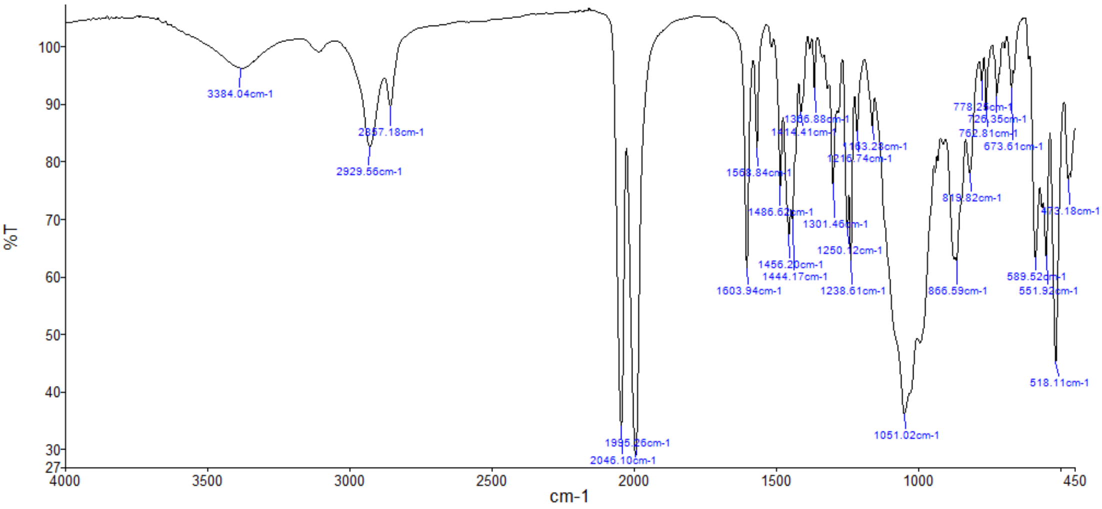
^{1}H NMR (400 MHz, CD_3CN) δ 7.52 − 7.46 (m, 1H), 6.89 − 6.83 (m, 2H), 5.64 (s, 2H), 3.81 (s, 3H), 3.68 – 3.60 (m, 4H), 2.52 – 2.44 (m, 5H), 2.32 – 2.21 (m, 2H), 1.93 – 1.86 (m, 2H), 1.84 – 1.76 (m, 4H), 1.63 – 1.45 (m, 4H), 1.45 – 1.33 (m, 2H).

^{13}C NMR (100 MHz, CD_3CN) δ 210.6, 161.9, 140.6, 134.8, 132.8, 120.4, 112.9, 112.8, 106.4, 82.2, 68.2, 56.0, 31.1, 26.2, 26.0, 25.2, 22.3.

^{19}F NMR (376 MHz, CD_3CN) δ −151.6.

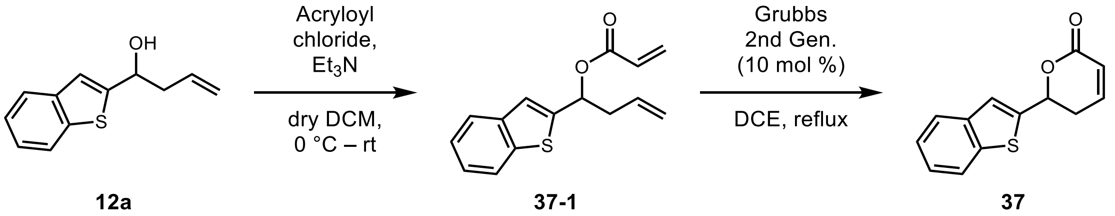
HRMS (ESI) calcd for $C_{23}H_{26}O_3NFe$ $[M{-}C_4H_8O{-}BF_4{+}C_2H_3N]^+$: 420.1257, found: 420.1259.

IR (ATR, neat): ṽ(CO) = 2046, 1995 cm^{-1}.



Synthetic applications of the products

Synthesis of 6-(benzo[*b*]thiophen-2-yl)-5,6-dihydro-*2H*-pyran-2-one (37, PBS-54B)



A flame-dried 10 mL round bottom flask was charged with compound **12a** (204 mg, 1.0 mmol, 1.0 equiv) and CH_2Cl_2 (2 mL), and was cooled to 0 °C. To the resulting mixture were added triethylamine (0.36 mL, 2.5 mmol, 2.5 equiv) and acryloyl chloride (0.12 mL, 1.5 mmol, 1.5 equiv) in succession dropwise. The reaction mixture was allowed to warm to room temperature overnight, filtered through magnesium sulfate and purified by column chromatography (40:1 hexanes/EtOAc) to afford the acrylate product **37-1** as a colorless oil (165 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 − 7.77 (m, 1H), 7.76 − 7.70 (m, 1H), 7.37 − 7.27 (m, 3H), 6.46 (dd, *J* = 17.3, 1.3 Hz, 1H), 6.24 (t, *J* = 6.9 Hz, 1H), 6.15 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.87 (dd, *J* = 10.4, 1.3 Hz, 1H), 5.78 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.21 − 5.06 (m, 2H), 2.89 − 2.72 (m, 2H). (**PBS-54A**)

^{1}H NMR data were in agreement with the literature.[8]

A degassed solution of compound **37-1** (165 mg, 0.6 mmol, 1.0 equiv) in anhydrous DCE (6.4 mL) was added to a flamed-dried two-neck 50 mL round bottom flask fitted with a reflux condenser. The mixture was heated to the point of reflux, and a degassed solution of Grubbs Catalyst 2nd Generation (54 mg, 10 mol %) in 6.4 mL of anhydrous DCE was added dropwise. The reaction mixture was stirred at reflux for 10 h, and was allowed to cool to room temperature. The mixture was concentrated *in vacuo* and purified by column chromatography (3:1 → 1:1 hexanes/EtOAc) to afford product **37** as a light brown solid (128 mg, 87% yield).

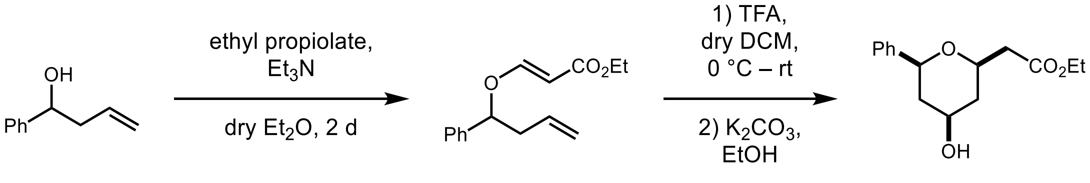
m.p. = 129 − 130 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 − 7.80 (m, 1H), 7.76 (m, 1H), 7.41 − 7.31 (m, 3H), 6.97 (ddd, *J* = 9.6, 5.3, 3.1 Hz, 1H), 6.15 (d, *J* = 9.9 Hz, 1H), 5.79 (dd, *J* = 10.0, 4.9 Hz, 1H), 2.92 − 2.76 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 144.3, 141.8, 139.7, 139.4, 125.5, 124.8, 124.0, 122.6, 122.4, 122.0, 75.6, 31.4.

HRMS (ESI) calcd for $C_{13}H_9O_2S$ $[M-H]^+$: 229.0318, found: 229.0327.

Synthesis of ethyl 2-(-4-hydroxy-6-phenyltetrahydro-*2H*-pyran-2-yl)acetate (38, CZZ-54)



This compound was synthesized according to a modified literature procedure.[9]

A flame-dried 25 mL round bottom flask was charged with ethyl propiolate (114 mg, 1.1 mmol, 1.1 equiv), dry diethyl ether (4 mL) and triethylamine (0.24 mL, 1.7 mmol, 1.7 equiv) under nitrogen. The resulting mixture was stirred at room temperature for 15 min and compound **4a** (148 mg, 1.0 mmol, 1.0 equiv) was added dropwise. After stirring for 2 days, the mixture was concentrated *in vacuo* and purified by column chromatography (30:1 hexanes/EtOAc) to afford the product **38-1** as a colorless oil (234 mg, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 12.5 Hz, 1H), 7.41 − 7.23 (m, 5H), 5.73 (ddt, J = 17.3, 10.4, 6.9 Hz, 1H), 5.22 (d, J = 12.5 Hz, 1H), 5.14 − 5.04 (m, 2H), 4.89 (dd, J = 7.6, 5.7 Hz, 1H), 4.17 − 4.04 (m, 2H), 2.75 − 2.65 (m, 1H), 2.59 − 2.50 (m, 1H), 1.22 (t, J = 7.1 Hz, 3H). (**czz-40**)

^{1}H NMR data were in agreement with the literature.[9]

A flame-dried 50 mL round bottom flask was charged with compound **38-1** (183 mg, 0.7 mmol, 1.0 equiv) and dry CH_2Cl_2 (8.3 mL) under nitrogen. The reaction mixture was cooled to 0 °C, and trifluoroacetic acid (0.57 mL, 7.4 mmol, 10 equiv) was added dropwise to the stirred solution. After 15 min, the reaction mixture was allowed to warm to room temperature and stirred for another 30 min. Then the reaction mixture was carefully poured into a saturated aqueous solution of Na_2CO_3 (50 mL) and crushed ice, and was added 10 mL of CH_2Cl_2. The resulting mixture was stirred vigorously for 10 min, and was extracted with CH_2Cl_2 (3 × 80 mL). The combined organic layers were dried over magnesium sulfate, concentrated *in vacuo* and used directly for the next step.

A 50 mL round bottom flask containing extracts from the last step was charged with potassium carbonate (51 mg, 0.4 mmol, 0.5 equiv) and ethanol (8.3 mL). The resulting mixture was stirred at room temperature for 19 h. Then the mixture was diluted with 5 mL of water and 5 mL of brine, and was subsequently extracted with EtOAc (3 × 20 mL). The combined organic layers were dried over magnesium sulfate, concentrated *in vacuo* and purified by column chromatography (2:1 hexanes/EtOAc) to afford the product **38** as a colorless oil (102 mg, 52% yield).

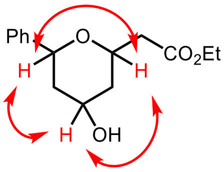
^{1}H NMR (400 MHz, C_6D_6) δ 7.29 (d, J = 7.2 Hz, 2H), 7.20 − 7.13 (m, 2H), 7.11 − 7.05 (m, 1H), 4.11 (dd, J = 11.5, 1.9 Hz, 1H), 3.97 − 3.81 (m, 3H), 3.50 − 3.39 (m, 1H), 2.62 (dd, J = 15.3, 7.5 Hz, 1H), 2.27 (dd, J = 15.3, 5.5 Hz, 1H), 1.83 (ddt, J = 12.4, 4.3, 2.0 Hz, 1H), 1.77 (ddt, J = 6.5, 4.1, 1.9 Hz, 1H), 1.27 (dd, J = 23.6, 11.4 Hz, 1H), 1.14 − 1.03 (m, 1H), 0.95 − 0.89 (m, 4H).

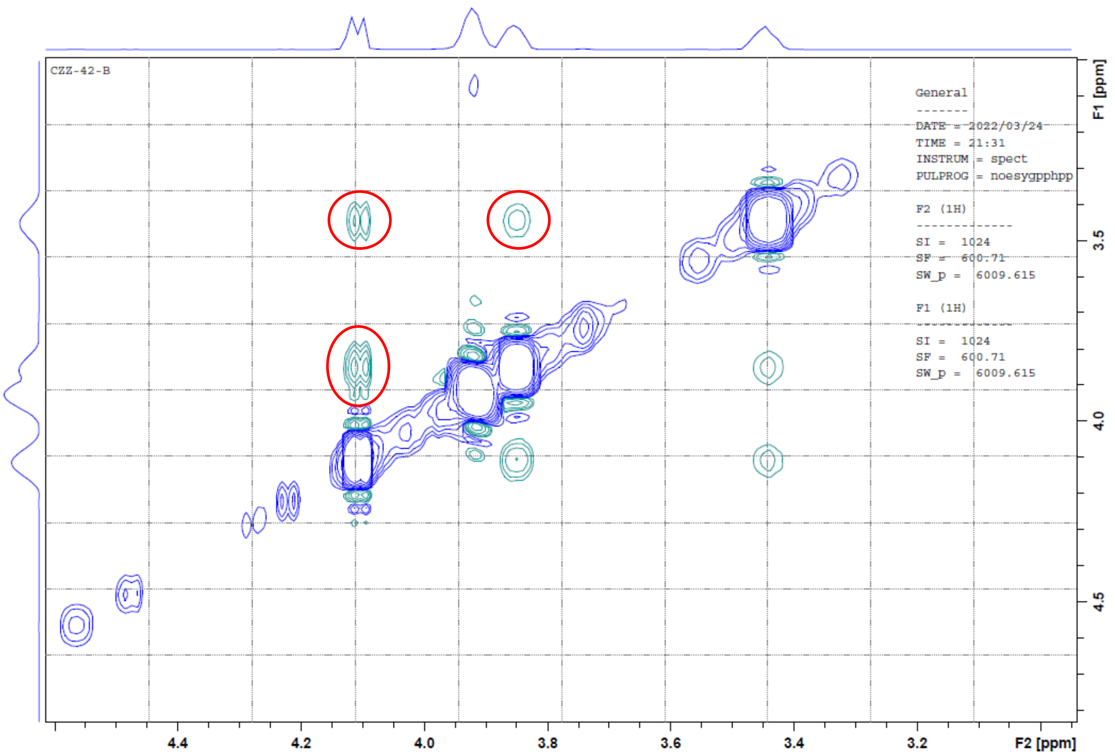
^{13}C NMR (100 MHz, C_6D_6) δ 170.9, 143.1, 128.7, 127.7, 126.4, 77.9, 73.0, 68.2, 60.6, 43.7, 41.7, 41.0, 14.5.

HRMS (ESI) calcd for $C_{15}H_{21}O_4$ $[M+H]^+$: 265.1434, found: 265.1435.

^{1}H NMR data were in agreement with the literature.[9]

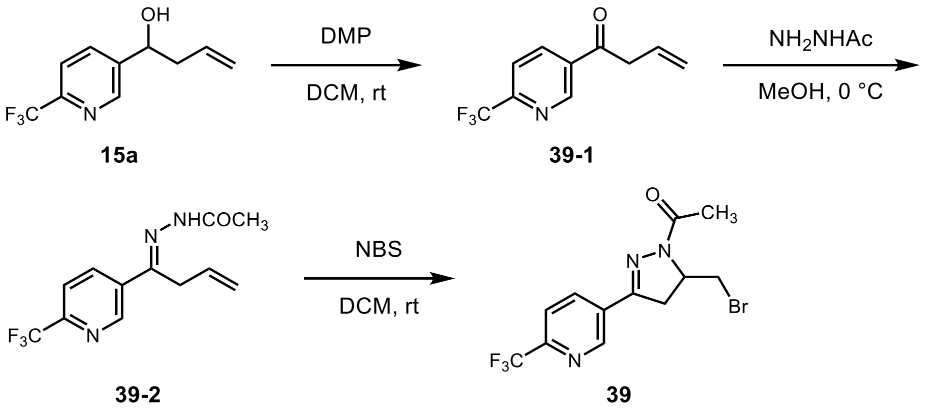
The relative configuration of **38** was assigned via the 2D NOESY correlation illustrated below:





The correlations between each of the three protons indicate a syn relationship among the three substituents on the THP ring.

Synthesis of 1-(5-(bromomethyl)-3-(6-(trifluoromethyl)pyridin-3-yl)-4,5-dihydro-1*H*-pyrazol-1-yl)ethan-1-one (39, czz-53')



A flame-dried 25 mL round bottom flask was charged with Dess-Martin periodinane (723 mg, 1.7 mmol, 1.3 equiv), compound **15a** (285 mg, 1.3 mmol, 1.0 equiv) and anhydrous CH_2Cl_2 (8 mL). The reaction was monitored by thin layer chromatography until completion. Then the reaction mixture was quenched with water (2 mL), stirred vigorously at room temperature for 30 min and extracted with CH_2Cl_2 (5 × 10 mL). The combined organic layers were dried over magnesium sulfate, concentrated *in vacuo* and purified by column chromatography (10:1 hexanes/EtOAc) to afford the product **39-1** as a pale yellow solid (200 mg, 71% yield). (PBS-59A)

m.p. = 44 − 46 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.25 (d, *J* = 1.5 Hz, 1H), 8.41 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 6.05 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.34 − 5.23 (m, 2H), 3.80 (dt, *J* = 6.7, 1.3 Hz, 2H).

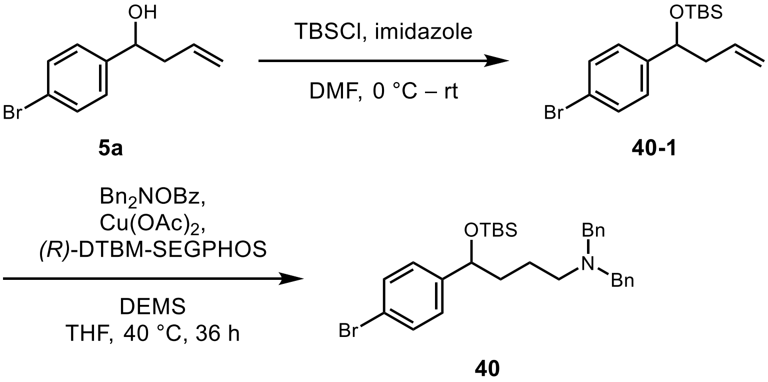
^{13}C NMR (125 MHz, $CDCl_3$) δ 195.7, 151.4 (q, *J* = 35.1 Hz), 150.0, 137.4, 133.9, 129.6, 121.2 (q, *J* = 273 Hz), 120.7 (q, *J* = 2.7 Hz), 120.1, 44.1.
^{19}F NMR (470 MHz, $CDCl_3$) δ −68.29.
HRMS (ESI) calcd for $C_{10}H_9ONF_3$ $[M+H]^+$: 216.0631, found: 216.0624.

A flame-dried 10 mL round bottom flask was charged with compound **39-1** (200 mg, 0.9 mmol, 1.0 equiv) and methanol (1 mL). The resulting mixture was cooled to 0 °C and was added acethydrazide (103 mg, 1.4 mmol, 1.5 equiv). The mixture was stirred at 0 °C and monitored by thin layer chromatography until completion. The solvent was removed under reduced pressure, and the residue was diluted with water (5 mL) and extracted with EtOAc (5 × 10 mL). The combined organic layers were dried over magnesium sulfate, concentrated *in vacuo* and purified by column chromatography (1.5:1 hexanes/EtOAc) to yield the product **39-2** as a white solid (127 mg, 52% yield). (czz-56)
m.p. = 144 − 145 °C
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.34 (s, 1H), 9.08 (s, 1H), 8.17 (d, *J* = 7.7 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 5.97 − 5.81 (m, 1H), 5.24 (d, *J* = 10.1 Hz, 1H), 5.13 (d, *J* = 17.3 Hz, 1H), 3.60 − 3.42 (m, 2H), 2.39 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 174.1, 148.2 (q, *J* = 34.7 Hz), 148.0, 143.8, 135.8, 134.7, 129.1, 121.6 (q, *J* = 272 Hz), 120.30 (q, *J* = 2.6 Hz), 118.9, 30.9, 20.7.
^{19}F NMR (470 MHz, $CDCl_3$) δ −67.98.
HRMS (ESI) calcd for $C_{12}H_{13}ON_3F_3$ $[M+H]^+$: 272.1005, found: 272.0996.

This step was performed according to literature procedure.[10]

A flame-dried 25 mL round bottom flask was charged with compound **39-2** (132 mg, 0.5 mmol, 1.0 equiv), NBS (105 mg, 0.6 mmol, 1.2 equiv) and dry CH_2Cl_2 (5 mL). The reaction mixture was stirred at room temperature and monitored by thin layer chromatography until completion. The mixture was concentrated *in vacuo* and purified by column chromatography (2:1 hexanes/EtOAc) to afford the dihydropyrazole product **39** as a colorless oil (102 mg, 60% yield). (czz-53)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.21 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 4.96 (dtd, *J* = 7.9, 5.7, 2.6 Hz, 1H), 3.86 (dd, *J* = 10.4, 6.1 Hz, 1H), 3.70 (dd, *J* = 10.5, 2.6 Hz, 1H), 3.49 (dd, *J* = 17.9, 11.5 Hz, 1H), 3.24 (dd, *J* = 17.9, 5.2 Hz, 1H), 2.40 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 150.0, 149.0 (q, *J* = 35.1 Hz), 147.9, 134.9, 130.0, 121.4 (q, *J* = 273 Hz), 120.5 (q, *J* = 2.7 Hz), 57.4, 37.6, 34.1, 22.0.
^{19}F NMR (470 MHz, $CDCl_3$) δ −68.03.
HRMS (ESI) calcd for $C_{12}H_{12}ON_3BrF_3$ $[M+H]^+$: 350.0110, found: 350.0099.

Synthesis of *N,N*-dibenzyl-4-(4-bromophenyl)-4-((*tert*-butyldimethylsilyl)oxy) butane-1-amine (40, PBS-63)



A 10 mL round bottom flask was charged with compound **5a** (227 mg, 1.0 mmol, 1.0 equiv) and DMF (1 mL), and was cooled to 0 °C. To the mixture were added imidazole (204 mg, 3.0 mmol, 3 equiv) and the solution of TBSCl (301 mg, 2.0 mmol, 2.0 equiv) in DMF (0.5 mL) dropwise (1 mL/min). The mixture was stirred at 0 °C for 10 min and was allowed to warm to room temperature. After stirring for 1 h, the mixture was quenched with saturated NH_4Cl solution and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over magnesium sulfate, concentrated *in vacuo* and purified by column chromatography (100% hexanes) to afford the product **40-1** as a colorless liquid (326 mg, 95% yield). (PBS-62B)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 5.74 (ddt, *J* = 17.4, 10.4, 7.1 Hz, 1H), 5.04 − 4.95 (m, 2H), 4.65 (dd, *J* = 6.7, 5.6 Hz, 1H), 2.46 − 2.31 (m, 2H), 0.88 (s, 9H), 0.03 (s, 3H), −0.12 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.3, 134.8, 131.3, 127.8, 120.8, 117.4, 74.6, 45.5, 26.0, 18.4, −4.5, −4.7.

HRMS (ESI) calcd for $C_{10}H_{10}Br$ $[M{-}OTBS]^+$: 208.9960, found: 208.9959.

This step was performed according to literature procedure.[11]

In an argon-filled glovebox, a flame-dried screw-cap reaction tube was charged with $Cu(OAc)_2$ (3.6 mg, 0.02 mmol, 2 mol %), (*R*)-DTBM-SEGPHOS (26 mg, 0.022 mmol, 2.2 mol %) and dry THF (1 mL). The mixture was stirred at room temperature for 15 min. Diethoxymethylsilane (DEMS) (0.32 mL, 2.0 mmol, 2.0 equiv) was added to the mixture. After stirring for 10 min, the solution was added to another screw-cap reaction tube charged with compound **40-1** (341 mg, 1.0 mmol, 1.0 equiv) and (dibenzylamino) benzoate (381 mg, 1.2 mmol, 1.2 equiv). The resulting mixture was stirred at 40 °C for 24 h. After cooling to room temperature, the reaction mixture was quenched with saturated Na_2CO_3 solution (2 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over magnesium sulfate, concentrated *in vacuo* and purified via column chromatography (150:1 hexanes/EtOAc) to afford the product **40** as a colorless oil (348 mg, 65% yield).

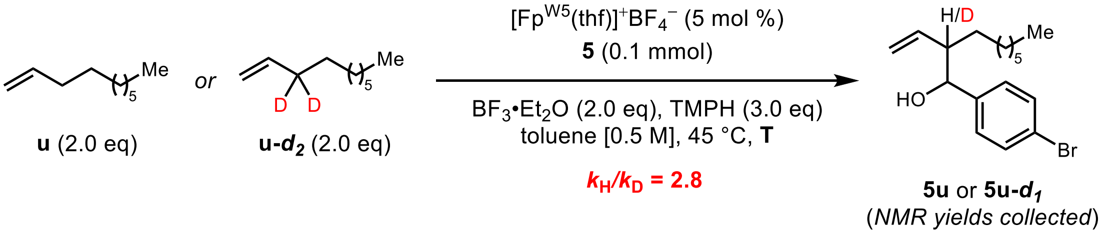
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.35 − 7.27 (m, 8H), 7.25 − 7.20 (m, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 4.50 (dd, *J* = 6.4, 5.4 Hz, 1H), 3.54 (d, *J* = 13.6 Hz, 2H), 3.48 (d, *J* = 13.6 Hz, 2H), 2.43 − 2.33 (m, 2H), 1.68 − 1.41 (m, 4H), 0.86 (s, 9H), −0.03 (s, 3H), −0.18 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 140.1, 131.2, 128.9, 128.3, 127.8, 126.9, 120.6, 74.2, 58.6, 53.4, 38.3, 26.1, 22.9, 18.3, −4.5, −4.8.

HRMS (ESI) calcd for $C_{30}H_{41}ONBrSi$ $[M+H]^+$: 538.2135, found: 538.2119.

Kinetic isotope effect experiments

1. Independent KIE results

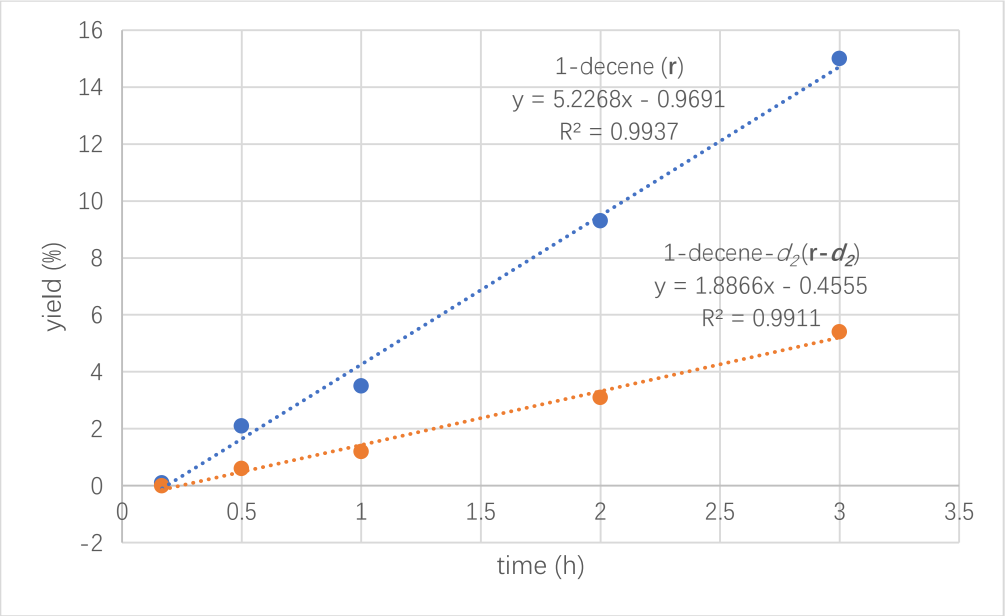


To a flame-dried reaction tube charged with a magnetic stir bar, $Fp^{W5}(thf)BF_4$ (2.8 mg, 5 mol %), aldehyde **5** (18 mg, 0.1 mmol, 1.0 equiv), alkene **u** (38 µL, 0.2 mmol, 2.0 equiv) or **u-*d*$_2$** (28 mg, 0.2 mmol, 2.0 equiv), dry toluene (0.2 mL), BF_3•Et_2O (25 µL, 0.2 mmol, 2.0 equiv), TMPH (51 µL, 0.3 mmol, 3.0 equiv) were added in succession in an argon-filled glovebox. The tube was sealed and placed in an oil bath preheated at 45 °C with vigorous stirring. Reactions were stopped at corresponding times within 0 min to 3 h. Yields were determined by ^{1}H NMR using 2,4-dinitrotoluene as the internal standard (Table S1). Each reaction was conducted twice, and average yields of two runs were used for the calculation of the KIE value (Chart S1).

Table S1. Original data for independent kinetic experiments (yields).

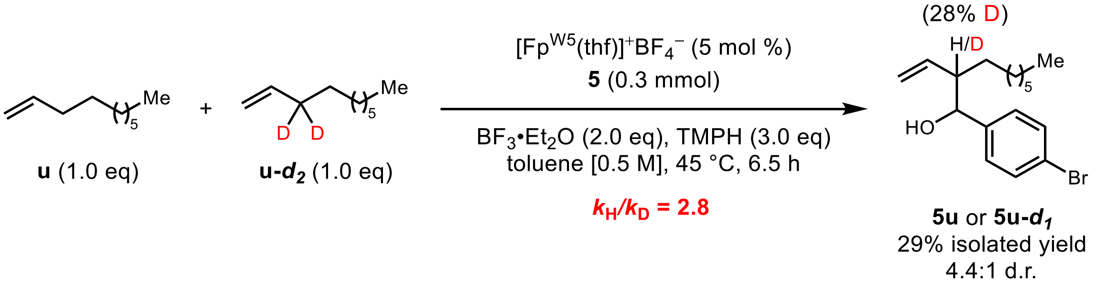
	10 min		30 min		1 h		2 h		3 h	
	Run#1	Run#2	Run#1	Run#2	Run#1	Run#2	Run#1	Run#2	Run#1	Run#2
1-decene (**u**)	0	0.2%	2.6%	1.5%	3.7%	3.3%	9.1%	9.5%	16%	15%
1-decene-*d*$_2$ (**u-*d*$_2$**)	0	0	0.8%	0.4%	1.1%	1.4%	2.9%	3.3%	5.6%	5.2%

Chart S1. Initial rates with **u** and **u-*d*$_2$**.



k_H/k_D = 5.2268/1.8866 = 2.8

2. Competition KIE results



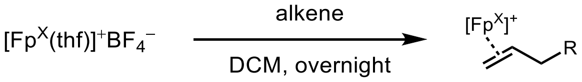
To a flame-dried reaction tube charged with a magnetic stir bar, $\mathrm{Fp}^{\mathrm{W5}}(\mathrm{thf})\mathrm{BF}_4$ (8.4 mg, 5 mol %), aldehyde **5** (55 mg, 0.3 mmol, 1.0 equiv), alkene **u** (42 mg, 0.3 mmol, 1.0 equiv) or **u-*d*$_2$** (43 mg, 0.3 mmol, 1.0 equiv), dry toluene (0.6 mL), $BF_3•Et_2O$ (74 μL, 0.6 mmol, 2.0 equiv), TMPH (152 μL, 0.9 mmol, 3.0 equiv) were added in succession in an argon-filled glovebox. The tube was sealed and placed in an oil bath preheated at 45 °C with vigorous stirring. After 6.5 h, the tube was allowed to cool to room temperature. The crude mixture was concentrated *in vacuo* and purified by flash column chromatography on silica gel to obtain a mixture of **5u** and **5u-*d*$_1$**. The percentage of deuterium in the product was determined based on the area of the deuterated peak over that of the mixture peak. Considering the ratio between the amounts of the two products changes gradually over the course of the reaction, the KIE value was calculated using the following equation:

$$\mathrm{KIE}=\frac{k_{\mathrm{H}}}{k_{\mathrm{D}}}=\frac{\ln(1-\mathrm{F_H})}{\ln(1-\mathrm{F_D})}$$

$\mathrm{F_H}$ and $\mathrm{F_D}$ refer to the fraction of conversions for species **u** and **u-*d*$_2$**, respectively.

Stoichiometric experiments

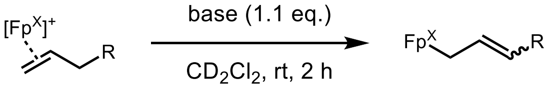
1. Synthesis of Fp^X-alkene complexes



Gaseous alkenes: To an oven-dried pressure tube (102 mm × 13 mm, Ace glass, part# 8648-61) charged with a magnetic stir bar, Fp^X(thf)BF$_4$ (0.05 mmol, 1.0 equiv) and dry CH_2Cl_2 (0.5 mL) were added in succession in an argon-filled glovebox. The tube was capped with a PTFE bushing with plunger valve (#7 Ace-Thred) and was taken out of the glovebox cooled in liquid nitrogen. After the whole mixture was frozen, the tube was placed under vacuum. Propylene or 1-butene (10 mL, 8.0 equiv) was condensed into the vacuum tube through the plunger valve, then the tube was resealed and taken out of liquid nitrogen. The mixture was stirred at room temperature overnight. The Fp^X-alkene complexes were obtained as yellow oils or solids by removing the solvent under reduced pressure and were used in the deprotonation reactions without further purification.

1-Hexene: To an oven-dried reaction tube charged with a magnetic stir bar, Fp^X(thf)BF$_4$ (0.05 mmol, 1.0 equiv), dry CH_2Cl_2 (0.5 mL) and 1-hexene (12 µL, 0.1 mmol, 2.0 equiv) were added in succession in an argon-filled glovebox. The tube was capped and taken out of the glovebox. The mixture was stirred at room temperature overnight. The Fp^X-alkene complexes were obtained as yellow oils or solids by removing the solvent under reduced pressure and were used in the deprotonation reactions without further purification.

2. Deprotonation of Fp^X-alkene complexes



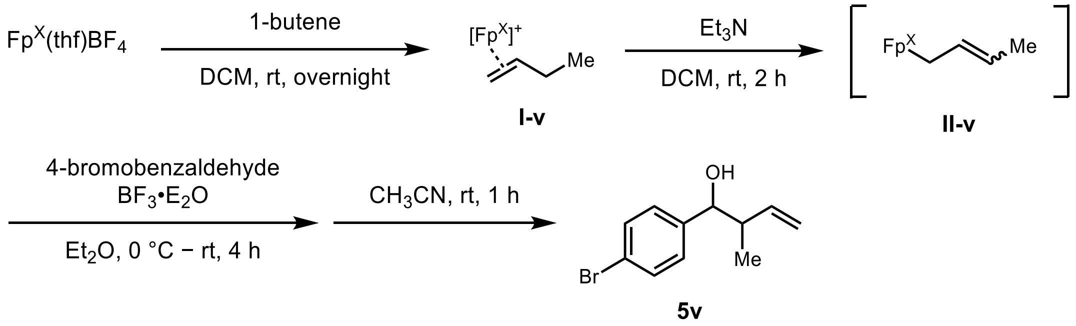
To a 4 mL dram vial, the Fp^X-alkene complex, CD_2Cl_2 (0.5 mL) and Et_3N (7.7 µL, 0.055 mmol, 1.1 equiv) or TMPH (9.4 µL, 0.055 mmol, 1.1 equiv) were added in succession. The mixture was stirred at room temperature for 2 h. The yields were determined by ^{1}H NMR using 1,3-bis(trifluoromethyl)benzene as the internal standard (Table S2).

Table S2. Results of stoichiometric deprotonation experiments.

		Fp*	**Fp^{W3}**
Propylene	Et_3N	N.P.	P. 28% SM. 35%
	TMPH	P. 1% SM. 16% free alkene 4%	P. 28% SM. 15%
1-Butene	Et_3N	P. 32% 1.3:1 *Z*/*E* isomers SM. 22% free alkene 7%	P. 66% 1.5:1 *Z*/*E* isomers SM. 14%

	TMPH	P. 24% 1:2.1 *Z*/*E* isomers SM. 14% free alkene 14%	P. 67% 1:1.6 *Z*/*E* isomers
1-Hexene	Et_3N	P. 26% SM. 21% free alkene 33%	P. 58% 1.0:1 *Z*/*E* isomers
	TMPH	N.P. SM. 18% free alkene 43%	P. 30% 1:1.4 *Z*/*E* isomers SM. 21%

3. Additional stoichiometric experiments



Compound **I-v** was synthesized according to the abovementioned procedure. Fp*(1-butene)BF_4 was prepared on 0.2 mmol scale, Fp^{W3}(1-butene)BF_4 was prepared on 0.1 mmol scale.

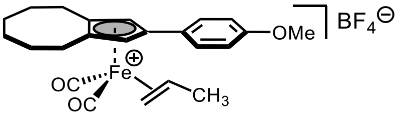
Compound **I-v** was transferred to a 4 mL dram vial, CH_2Cl_2 (1 mL) and Et_3N (1.1 equiv) were added. After stirring at room temperature for 2 h, the solvent was removed under reduced pressure. The mixture was dissolved in diethyl ether and compound **II-v** was obtained by filtering the solution through a pipet column containing neutral aluminum oxide. After removing the solvent *in vacuo*, the product was immediately subjected to the next step. (Note: The allyliron species is heat sensitive.)

A flame-dried 10 mL round bottom flask was charged with 4-bromobenzaldehyde (Fp*: 18.5 mg, 0.1 mmol, 0.5 equiv; Fp^{W3}: 15.0 mg, 0.08 mmol, 0.8 equiv), BF_3•Et_2O (1.5 equiv) and dry diethyl ether (1 mL). The mixture was stirred at 0 °C for 10 min. Compound **II-v** was dissolved in 0.5 mL of dry diethyl ether and the resulting solution was added to the mixture dropwise over 3 min at 0 °C. The mixture was stirred at 0 °C for 1 h and was gradually warmed up to room temperature. After stirring for 3 h, the mixture was concentrated under reduced pressure and redissolved in 1 mL of acetonitrile. The resulting mixture was stirred at room temperature for 1 h. The yield of **5v** over three steps from Fp^X(thf)BF_4 was determined by ^{1}H NMR using 2,4-dinitrotoluene as the internal standard. Diagnostic peaks are in agreement with those of the known compound **5v** reported in the literature.[12]

Characterization data for Fp^X-alkene complexes

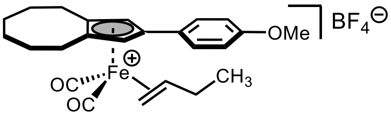
The ^{13}C NMR data for the Fp^{W3}-alkene complexes are ambiguous and therefore only spectra are included. Fp*-alkene complexes are impure and presumably contain solvated species. Peaks that are assigned to the desired products are reported.

Fp^{W3}(propene)BF$_4$ (wrh-05-125A)



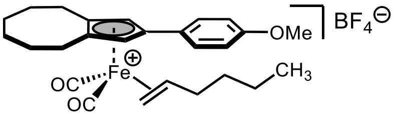
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.59 − 7.55 (m, 2H), 7.04 − 7.00 (m, 2H), 5.93 (d, *J* = 2.0 Hz, 1H), 5.79 (d, *J* = 1.9 Hz, 1H), 4.23 − 4.13 (m, 1H), 3.86 (s, 3H), 3.22 (d, *J* = 14.6 Hz, 1H), 3.03 (d, *J* = 8.1 Hz, 1H), 2.81 (ddt, *J* = 27.4, 13.7, 3.9 Hz, 2H), 2.49 (qd, *J* = 13.3, 4.6 Hz, 2H), 2.08 − 1.98 (m, 2H), 1.74 − 1.33 (complex multiplet).
^{19}F NMR (470 MHz, CD_2Cl_2) δ −149.6.
HRMS (ESI) calcd for $C_{20}H_{21}O_3Fe$ $[M{-}BF_4{-}C_3H_6]^+$: 365.0835, found: 365.0846.

Fp^{W3}(1-butene)BF$_4$ (wrh-05-70-1, 05-125B)



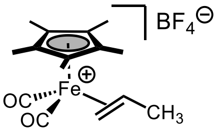
^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.58 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 5.92 (s, 1H), 5.83 (s, 1H), 4.29 − 4.13 (m, 1H), 3.86 (s, 3H), 3.21 (d, *J* = 14.6 Hz, 1H), 2.99 (d, *J* = 8.0 Hz, 1H), 2.89 − 2.71 (m, 2H), 2.59 − 2.40 (m, 2H), 2.39 − 2.26 (m, 1H), 2.11 − 1.29 (complex multiplet), 0.97 (t, *J* = 7.2 Hz, 3H).
^{19}F NMR (282 MHz, CD_2Cl_2) δ −151.4.
HRMS (ESI) calcd for $C_{24}H_{29}O_3Fe$ $[M{-}BF_4]^+$: 421.1461, found: 421.1470.

Fp^{W3}(1-hexene)BF$_4$ (wrh-05-125C)



^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.57 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 5.90 (d, *J* = 1.7 Hz, 1H), 5.81 (d, *J* = 1.7 Hz, 1H), 4.19 − 4.09 (m, 1H), 3.86 (s, 3H), 3.19 (d, *J* = 14.6 Hz, 1H), 3.04 (d, *J* = 8.1 Hz, 1H), 2.85 − 2.74 (m, 2H), 2.55 − 2.43 (m, 2H), 2.38 − 2.29 (m, 1H), 2.08 − 1.98 (m, 2H), 1.92 − 1.12 (complex multiplet), 0.84 (t, *J* = 7.2 Hz, 3H).
^{19}F NMR (470 MHz, CD_2Cl_2) δ −151.5.
HRMS (ESI) calcd for $C_{26}H_{33}O_3Fe$ $[M{-}BF_4]^+$: 449.1774, found: 449.1783.

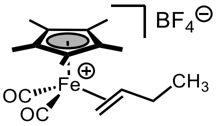
Fp*(propene)BF$_4$ (wrh-05-125D)



^{1}H NMR (500 MHz, CD_2Cl_2) δ 4.12 − 4.00 (m, 1H), 3.23 (d, *J* = 14.4 Hz, 1H), 2.95 (d, *J* = 8.1 Hz, 1H), 1.92 (s, 15H), 1.78 − 1.72 (complex multiplet).
^{13}C NMR (100 MHz, CD_2Cl_2) δ 212.6, 212.2, 102.0, 98.1, 84.4, 21.9, 9.5.
^{19}F NMR (470 MHz, CD_2Cl_2) δ −152.4.

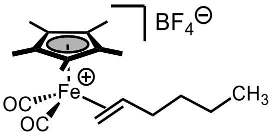
HRMS (ESI) calcd for $C_{15}H_{21}O_2Fe$ $[M-BF_4]^+$: 289.0885, found: 289.0896.

Fp*(1-butene)BF₄ (wrh-Fp', wrh-05-73-2B)



^{1}H NMR (300 MHz, CD_2Cl_2) δ 4.12 − 3.92 (m, 1H), 3.20 (d, *J* = 14.4 Hz, 1H), 2.89 (d, *J* = 8.1 Hz, 1H), 2.43 − 2.25 (m, 1H), 1.90 (s, 15H), 1.54 − 1.34 (m, 1H), 1.12 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, CD_2Cl_2) δ 212.6, 212.3, 102.2, 98.1, 90.3, 30.1, 16.6, 9.5, 9.3.
^{19}F NMR (282 MHz, CD_2Cl_2) δ −152.1.
HRMS (ESI) calcd for $C_{16}H_{23}O_2Fe$ $[M-BF_4]^+$: 303.1042, found: 303.1043.

Fp*(1-hexene)BF₄ (wrh-05-125E)

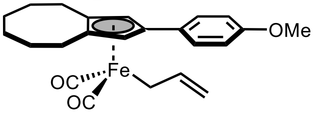


^{1}H NMR (500 MHz, CD_2Cl_2) δ 4.00 − 3.89 (m, 1H), 3.18 (d, *J* = 14.4 Hz, 1H), 2.91 (d, *J* = 8.1 Hz, 1H), 2.40 − 2.28 (m, 1H), 1.92 (s, 15H), 1.72 − 1.22 (complex multiplet), 0.93 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, CD_2Cl_2) δ 212.5, 212.3, 102.1, 98.1, 88.3, 36.8, 35.1, 22.6, 13.8, 9.5, 9.3.
^{19}F NMR (470 MHz, CD_2Cl_2) δ −152.5.
HRMS (ESI) calcd for $C_{18}H_{27}O_2Fe$ $[M-BF_4]^+$: 331.1355, found: 331.1366.

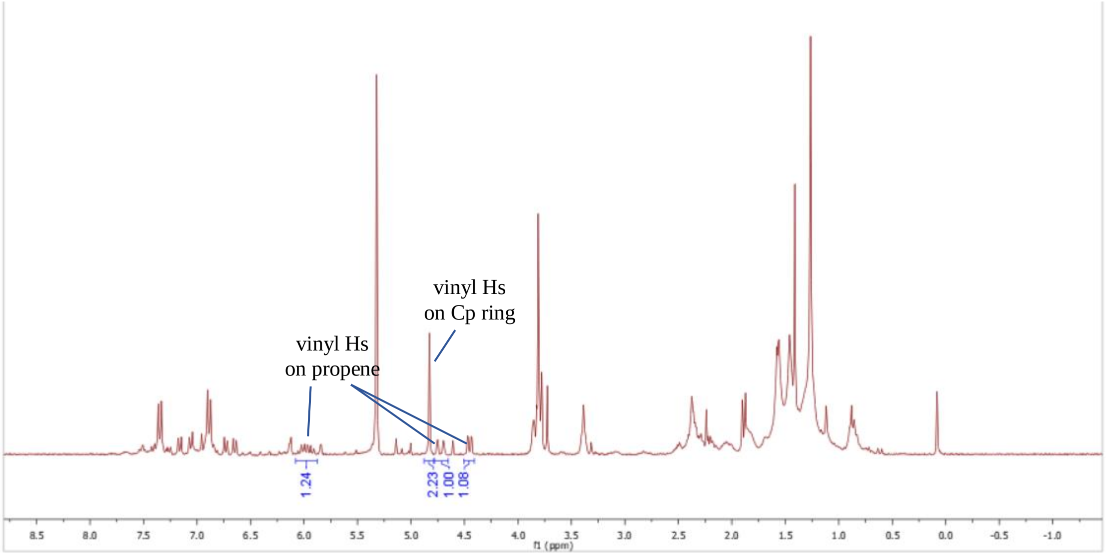
Characterization data for allyliron species

The allyliron species decomposed gradually within one hour under air. Purification of these compounds is challenging because they are unstable on the silica gel and their oily nature renders recrystallization impossible. NMR spectra of the crude products are reported.

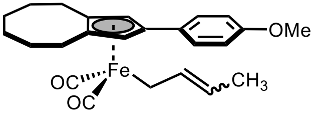
(II-a-Fp^{W3}, WRH-05-40A)



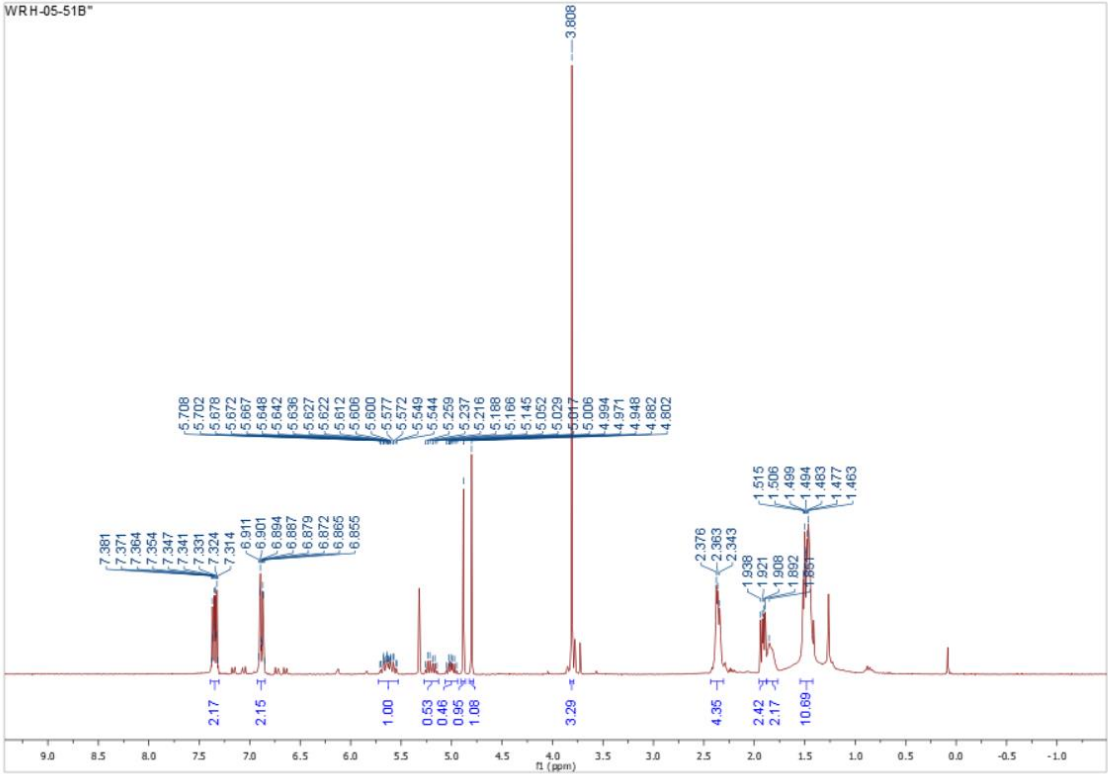
This compound was obtained by filtering the solution of the reaction mixture through a plug of celite.



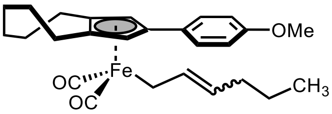
(II-s-Fp^{W3}, WRH-05-51B)



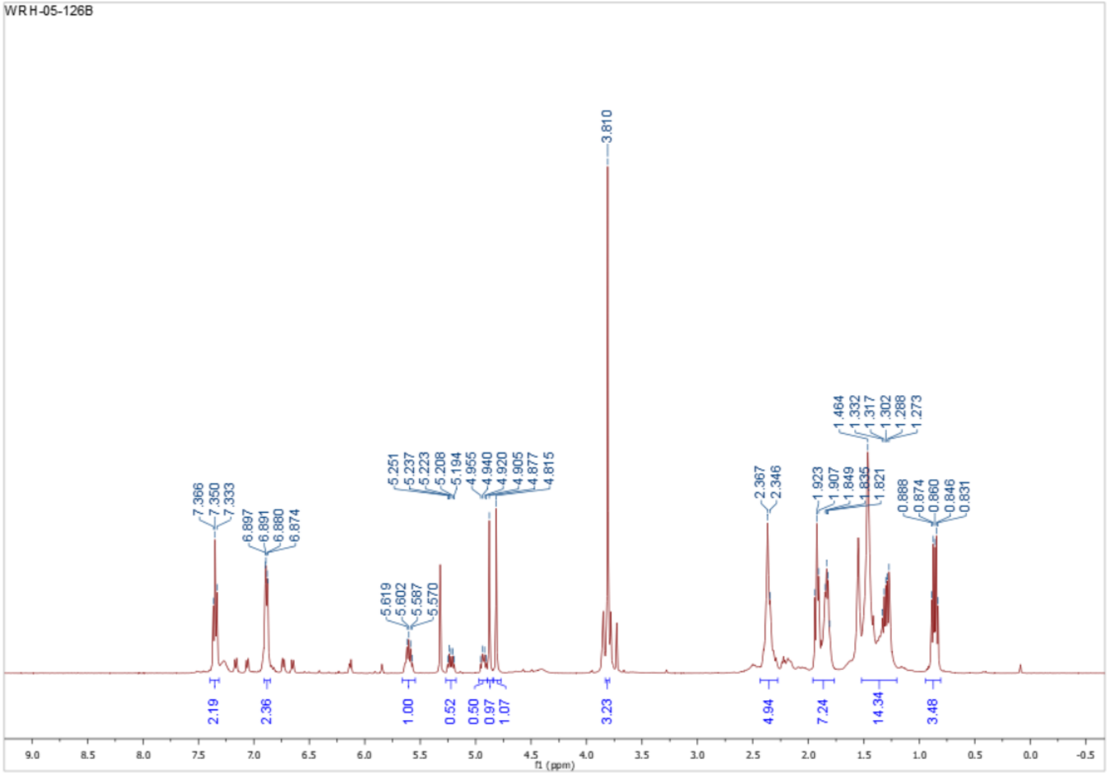
^{1}**H NMR** (300 MHz, CD$_2$Cl$_2$) δ 7.39 − 7.30 (m, 2H), 6.92 − 6.85 (m, 2H), 5.73 − 5.53 (m, 1H), 5.20 (dq, *J* = 12.9, 6.4 Hz, 0.5H), 5.06 − 4.93 (m, 0.5H), 4.88 (s, 1H), 4.80 (s, 1H), 3.81 (s, 3H), 2.43 − 2.30 (m, 4H), 1.95 − 1.88 (m, 2H), 1.88 − 1.76 (m, 2H), 1.55 − 1.42 (complex multiplet).



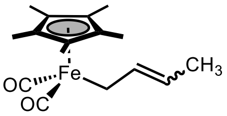
(II-t-Fp^{W3}, wrh-05-126B)

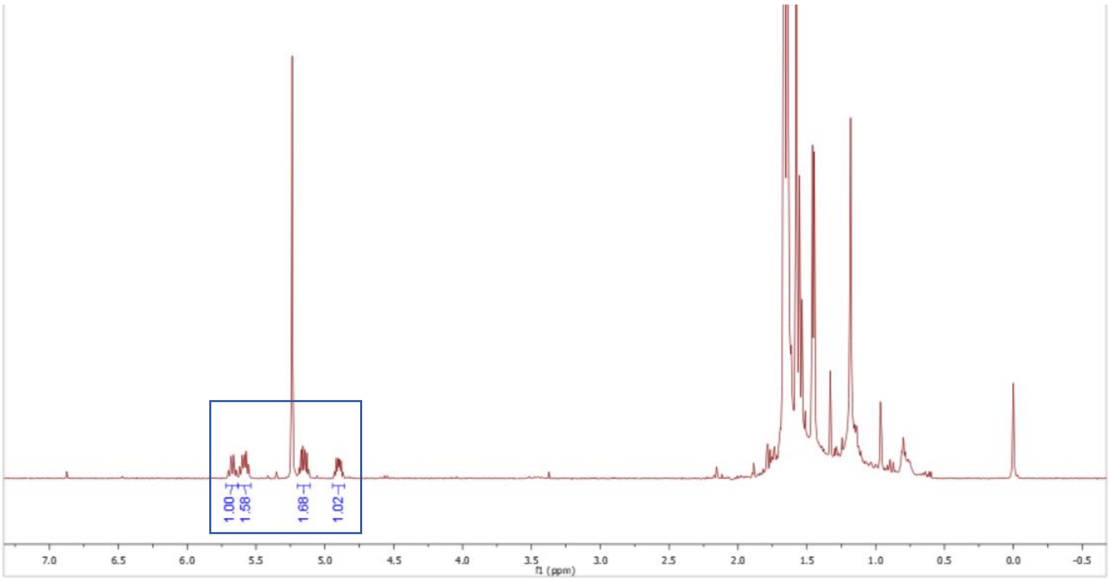


^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.35 (t, *J* = 8.3 Hz, 2H), 6.89 (dd, *J* = 8.7, 2.9 Hz, 2H), 5.66 − 5.55 (m, 1H), 5.27 − 5.18 (m, 0.5H), 4.97 − 4.90 (m, 0.5H), 4.88 (s, 1H), 4.81 (s, 1H), 3.81 (s, 3H), 2.36 (d, *J* = 10.9 Hz, 5H), 1.96 − 1.76 (m, 7H), 1.52 − 1.21 (complex multiplet), 0.86 (dt, *J* = 14.4, 7.3 Hz, 3H).

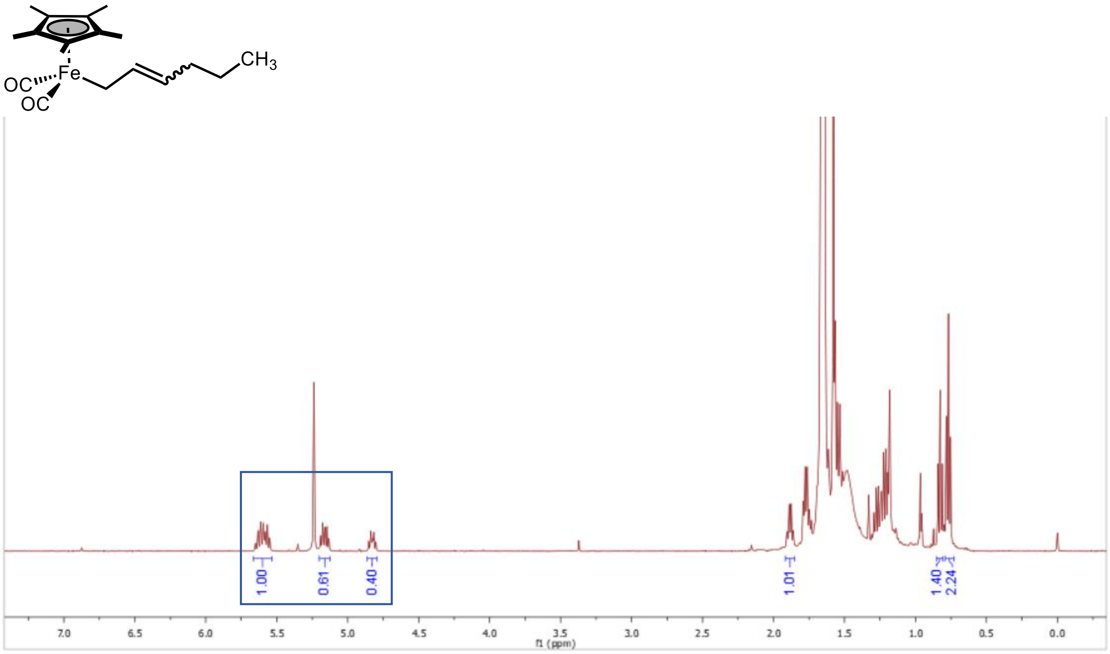


(**II-s-Fp***, wrh-05-84-2)





(**II-t-Fp***, wrh-05-126C)


CH3
Fe
OC
OC
1.00
0.61
0.40
1.01
1.40
2.24
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

DFT calculations

1. Computational Details

All density functional theory (DFT) calculations were carried out using Gaussian 16.[13] Conformational search was carried out using the CREST program[14] with the GFN2-xTB method.[15] The CREST conformational search was performed using the generalized Born model with solvent accessible surface (GBSA) in toluene solvent. An energy windows of 9.0 kcal/mol and an RMSD threshold of 0.75 Å was used. In the CREST/GFN2-xTB conformer search of transition state structures, forming and breaking bonds were constrained to the corresponding distances obtained from the DFT-optimized structures. Low-energy conformers from CREST/GFN2-xTB were then reoptimized using DFT. DFT geometry optimizations were performed in the gas phase using the dispersion-corrected B3LYP[16]-D3(BJ) functional, which includes Grimme's DFT-D3 dispersion correction[17] with Becke-Johnson (BJ) damping.[18] A mixed basis set of SDD[19] for Fe and 6-31G(d) for other atoms was used in geometry optimizations. Vibrational frequency calculations were performed for all the stationary points to confirm if each optimized structure is a minimum or a transition state structure. Single point energies were calculated using the M06 functional[20] with a mixed basis set of SDD for Fe and 6-311+G(d,p) for other atoms. Solvation energy corrections were calculated in single point energy calculations with the SMD continuum solvation model.[21] In the deprotonation step, solvation energies were calculated in both dichloromethane (Figure 1c) and toluene (Figure S6). In all other calculations, toluene was used as the solvent. Only the lowest energy conformers from the DFT calculations were reported in the main text. Selected higher energy conformers are discussed in the Supporting Information (*vide infra*). We have considered both the singlet and triplet spin states of the Fe complexes. The wavefunction stability of Fe complexes was confirmed by using the "stable=opt" keyword in Gaussian. The triplet spin state of complexes **41** and **43** is 11.9 and 16.3 kcal/mol less stable than corresponding closed-shell singlet complexes, respectively. Therefore, only the more stable singlet spin state is reported in this computational study.

DLPNO-CCSD(T)[22] calculations were carried out using ORCA 5.0.[23] DLPNO-CCSD(T) single point energy calculations were performed with the def2-TZVP basis set and def2-TZVP/C auxiliary basis set using the B3LYP-D3-optimized geometries. In the HF step, RIJCOSX approximations[24] with the def2/J auxiliary basis set was used. The SMD solvation model and toluene solvent were used in the DLPNO-CCSD(T) single point energy calculations.

The reported Gibbs free energies and enthalpies include thermal corrections at 298.15 K calculated at the B3LYP-D3(BJ)/SDD–6-31G(d) level (*i.e.*, the same level as geometry optimization). Gibbs free energies in Figure 1a contain concentration corrections to 1 mol/L and translational-entropy corrections.[25] GoodVibes 3.0.2[26] was used to compute Gibbs free energies with Grimme's quasi-harmonic oscillator approximation.[27]

Images of 3D molecular structures were generated using CYLview.[28]

2. Additional Computational Results

C–H Deprotonation Pathway Leading to *cis*-allyliron Intermediate

We computed the deprotonation pathway leading to *cis*-allyliron intermediate **43'** (Figure S1). The C–H deprotonation transition state leading to **43'** (**TS1'**) is 0.3 kcal/mol less stable than the deprotonation transition state leading to the trans isomer (**TS1**). The small energy difference between **TS1** and **TS1'** indicate that the cis-deprotonation pathway is competing. From the *cis*-allyliron intermediate **43'**, the aldehyde addition favors the same diastereomeric product as in the *trans*-deprotonation pathway discussed in Figure 1 in the main text. T-shaped π/π interactions between the Ph group on the benzaldehyde substrate and the *p*-OMe phenyl group on the ligand were observed in both **cis-TS2** and **cis-TS2'**, which demonstrates the importance of the π/π interactions with the ligand in confining the substrate orientation in the transition states. The more favorable transition state **cis-TS2** ($\Delta G^‡$ = 20.9 kcal/mol) is stabilized by C–H···F interactions between the sp^2 C–H bond on the ligand and the F atom on the BF_3•aldehyde complex. The C–H···F interaction with the ligand was not observed in the less favorable **cis-TS2'** ($\Delta G^‡$ = 22.0 kcal/mol), in which the BF_3 moiety points away from the Cp ligand.

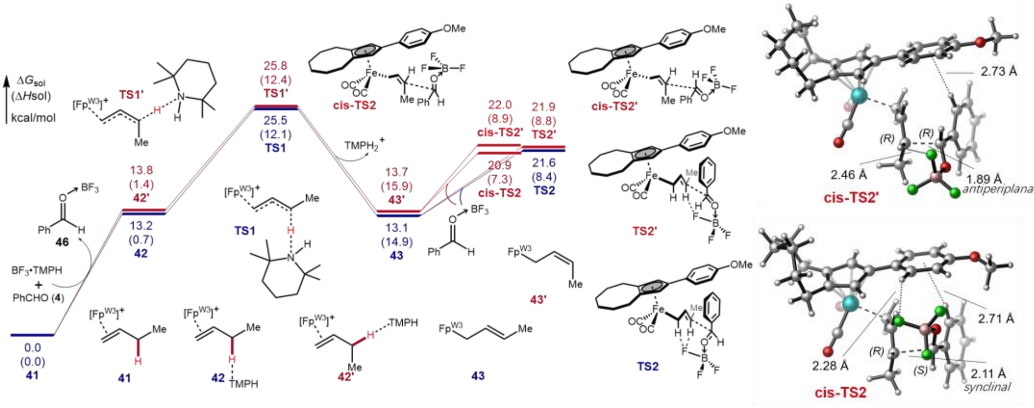


Figure S1. Reaction energy profile of the competing pathways involving *cis*-allyliron intermediate **43'**.

Benchmark of Computational Methods for Diastereoselectivity Prediction

The relative Gibbs free energies between the diastereoselectivity-determining aldehyde addition transition states (**TS2** and **TS2'**) were computed using three level of theories. In addition to the reaction between 1-butene and benzaldehyde (Figure 1), the transition states in the reactions between 1-octene and *para*-bromobenzaldehyde and between 1-butene and *para*-bromobenzaldehyde were also computed. These calculations indicated that **TS2** is more favorable than **TS2'** regardless of the computational methods and substrates used in the calculations. The DLPNO-CCSD(T) calculations provided better agreement with the experimentally observed diastereoselectivity compared to the Gibbs free energy differences computed using M06 and ωB97X-D methods.

Table S1. Computed Gibbs free energy difference ($\Delta\Delta G^{\ddagger}$) between diastereoselectivity-determining aldehyde addition transition states (**TS2** and **TS2'**) using three different levels of theories.[a]

Reaction	**Method**[b] M06/ 6-311+G(d,p)–SDD[a]	 ωB97X-D/ def2-TZVPP	 DLPNO-CCSD(T)/ def2-TZVP
1-butene + PhCHO	0.3	0.3	0.9
1-octene + *p*-BrPhCHO	0.3	0.3	0.6
1-butene + *p*-BrPhCHO	0.3	0.3	0.7

[a] All energies are in kcal/mol. [b] Method for single point energy calculations. The SMD(toluene) solvent model was used in all single point energy calculations. Geometry optimizations were performed at the B3LYP-D3(BJ)/SDD–6-31G(d) level for all calculations.

Conformers of Aldehyde Addition Transition States

Select higher energy conformers of the aldehyde addition transition states **TS2** and **TS2'** are shown in Figures S2–S3. Both conformers of the *p*-OCH_3 group were considered (*e.g.*, **TS2**/**TS2-1** and **TS2'**/**TS2'-1**). The *p*-OCH_3 conformation has a relatively small impact on the TS energy. Rotamers about the forming C–C bond were also considered. In these rotamers, such as **TS2-2** and **TS2-3**, the lack of π/π interaction between the ligand and the benzaldehyde Ph group leads to their higher energies compared to **TS2**. Similarly, several conformers of **TS2'** that lack π/π interactions (*e.g.*, **TS2'-2** and **TS2'-3**) were located and are higher in energy than **TS2'**. **TS2** and **TS2'** are the most stable conformers of the transition states.

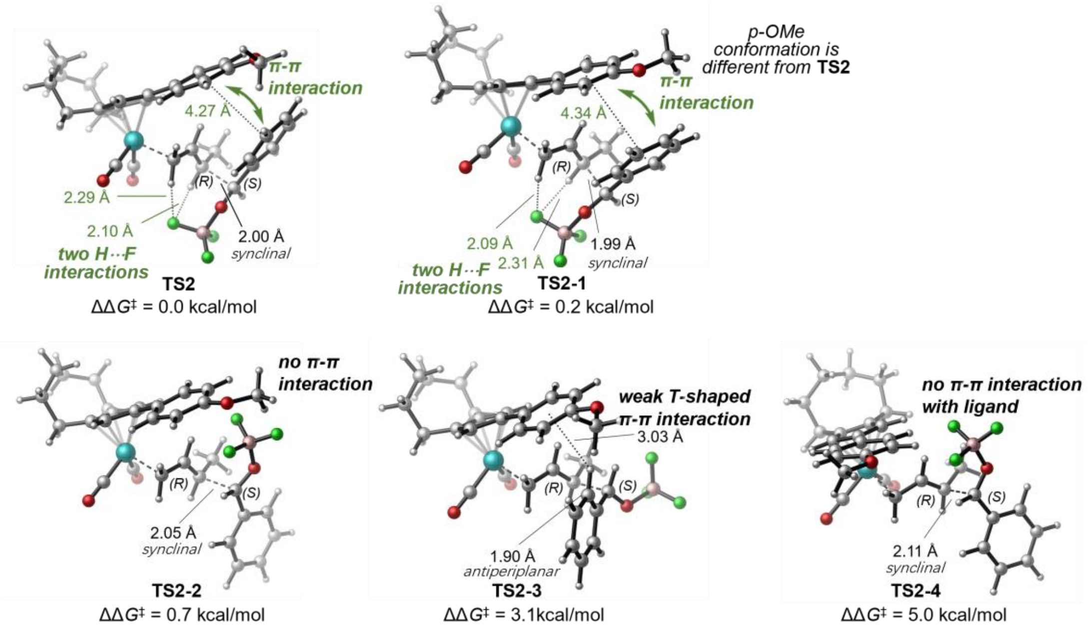


Figure S2. Select conformers of **TS2**.

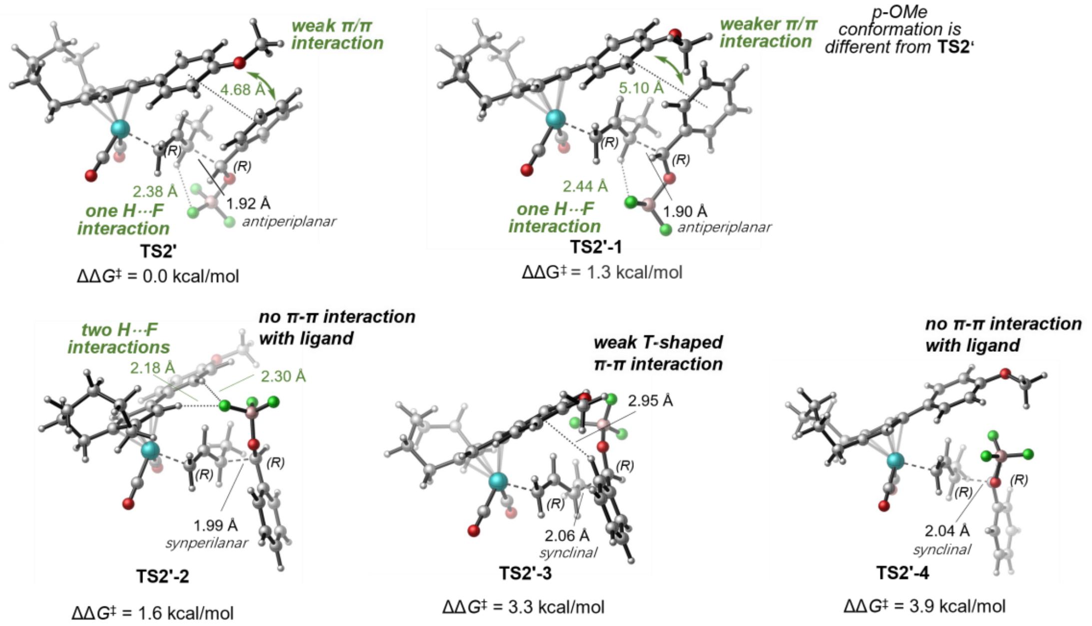


Figure S3. Select conformers of **TS2'**.

Ligand–Substrate Dispersion Energies

Dispersion energies between the Cp^{W3} ligand on the Fp^{W3} catalyst and the BF$_3$-coordinated benzaldehyde in transition states **TS2** and **TS2'** were calculated using Grimme's DFT-D3 program using HF as the reference "functional". The complexes of the Cp^{W3} ligand and the BF$_3$-coordinated benzaldehyde substrate were taken from the optimized geometries of **TS2** and **TS2'** by removing other atoms (*i.e.*, the Fe, CO ligands, and the allyl group). Because the HF method can be considered "dispersion-free", the D3 dispersion correction to HF describes the overall dispersion energy for each fragment. The dispersion energy of the ligand–substrate complex minus the sum of dispersion energies of the two fragments was calculated as the dispersion interaction energy (ΔE_{disp}) between the two fragments.

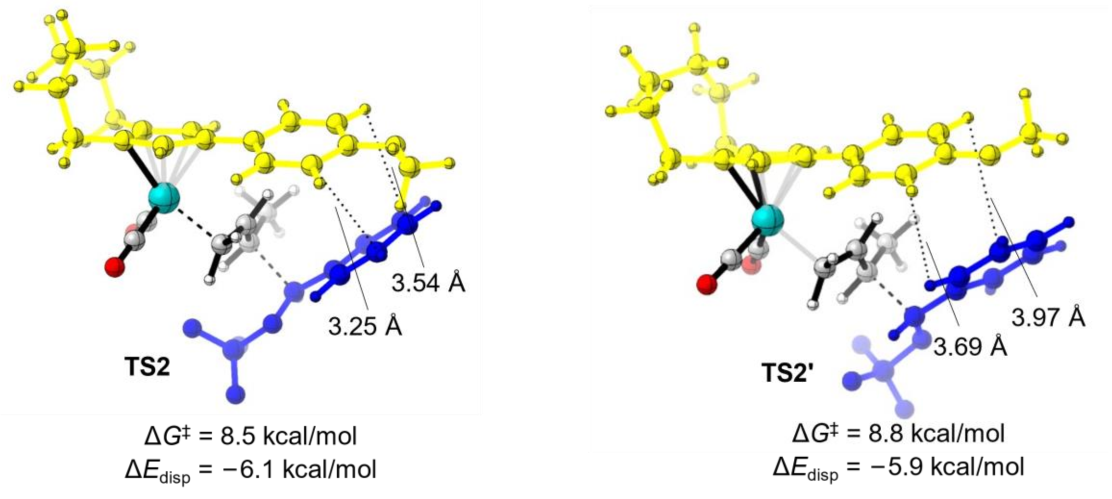


Figure S4. Dispersion interaction energy between ligand and benzaldehyde in **TS2** and **TS2'**.

NPA Charge Calculations

The computed NPA charges (Figure S5) show that the α and γ H atoms in **TS2** and **TS2'** are both positively charged (0.23~0.26), whereas the F atom on the carbonyl-coordinated BF_3 group is negatively charged (−0.57~−0.58). The H atoms in **TS2** and **TS2'** are slightly more positively charged than those in the allyl Fe intermediate **43** and the C(*sp*^{2})–H and C(*sp*^{3})–H in butene. These results suggest relatively strong H…F interactions in **TS2** and **TS2'**.

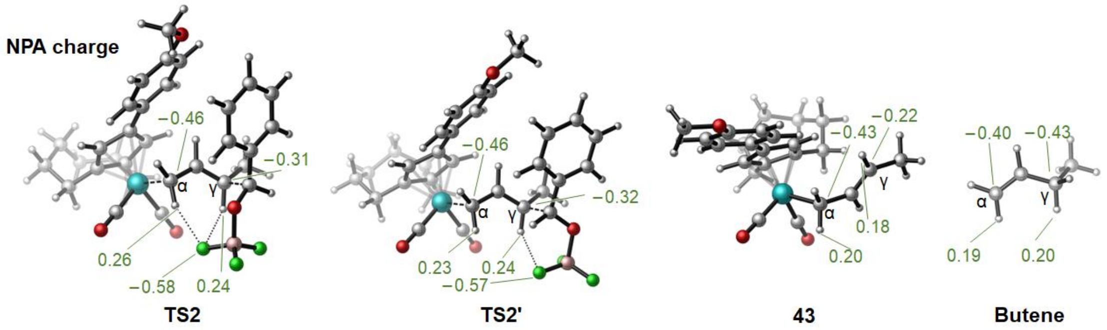


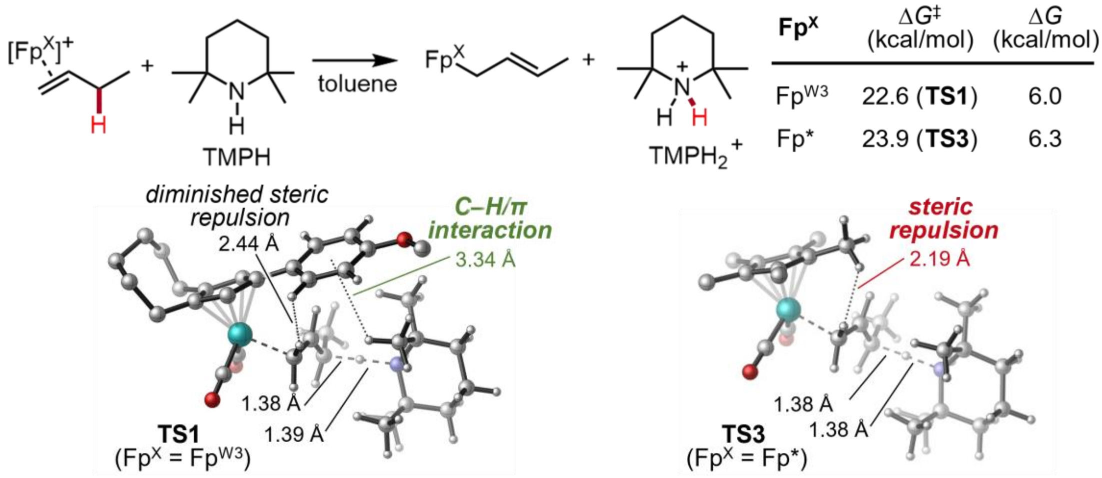
Figure S5. Computed NPA charges of select H and F atoms of **TS2**, **TS2'**, the allyl iron intermediate **43**, and butene.

Driving Force of the Overall Reaction

In the computed reaction energy profile (Figure 1 in the main text), the aldehyde addition leads to zwitterionic complexes **44** and **44'**, which subsequently undergo ligand exchange to liberate the ionic allylic functionalization products (**45**, **45'**). This process is facilitated by hydrogen-bonding in **45** and **45'** between tetramethylpiperidinium (TMPH$_2^+$) and the anionic alkoxytrifluoroborate moiety,[29] which upon work-up give the neutral homoallylic alcohol products. The hydrogen bonding in **45** and **45'** was found to provide an important thermodynamic driving force to the overall reaction, as the reaction of 1-butene and benzaldehyde to form the major homoallylic alcohol as a neutral species is endergonic by 7.9 kcal/mol, rendering the overall reaction thermodynamically unfavorable in the absence of stoichiometric amounts of Lewis acid and base to stabilize the ammonium alkoxytrifluoroborate product.

C–H Deprotonation Pathways Computed in Toluene

The C–H deprotonation in toluene (Figure S6) is more endergonic and requires higher activation barriers than in the more polar CH_2Cl_2 solvent (Figure 1c). The same ligand effects were observed in toluene solvent. The deprotonation with the Fp^{W3} catalyst requires a 1.3 kcal/mol lower activation barrier than that with the Fp* catalyst (Figure S6).

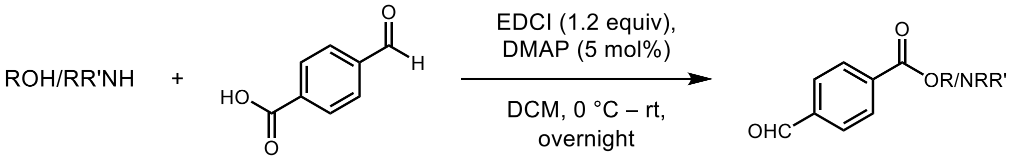


Fp^X	$\Delta G^‡$ (kcal/mol)	ΔG (kcal/mol)
Fp^{W3}	22.6 (**TS1**)	6.0
Fp*	23.9 (**TS3**)	6.3

Figure S6. Computed C–H deprotonation pathways in toluene.

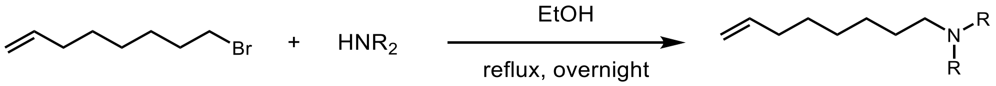
Procedures for substrate synthesis and characterization data

General procedure B1



Alcohol or amine (1.0 equiv, 0.2 M in CH_2Cl_2), 4-formylbenzoic acid (1.0 equiv) and DMAP (5 mol %) were dissolved in CH_2Cl_2, the resulting solution was cooled in ice bath. EDCI (1.2 equiv) was added to the solution at 0 °C. The mixture was stirred at room temperature overnight. Then the mixture was washed by water (3 × 10 mL). The organic layer was dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude residue was purified by column chromatography to afford the products.

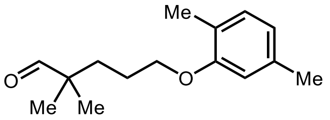
General procedure B2



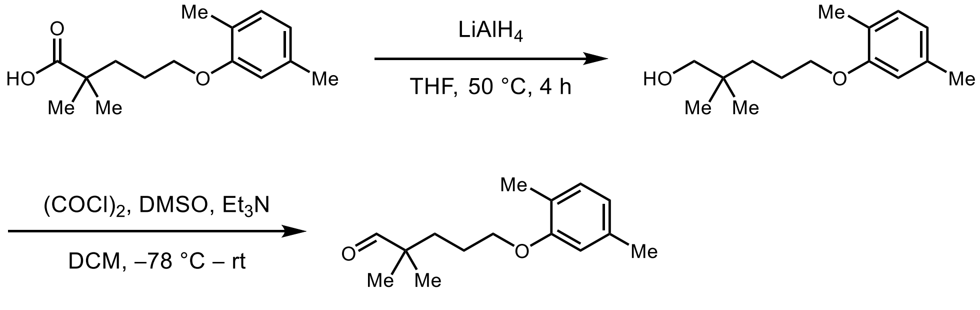
A 250 mL round bottom flask was charged with 8-bromo-1-octene (1.7 mL, 10 mmol, 1.0 equiv), amine (6.0 equiv) and ethanol (60 mL). The reaction mixture was heated at reflux overnight. After completion, the mixture was concentrated in vacuo and diluted with EtOAc (30 mL). The resulting mixture was washed with saturated Na_2CO_3 solution (3 × 10 mL). The organic layer was dried over magnesium sulfate and concentrated under reduced pressure. The crude residue was purified by column chromatography to afford the products.

Characterization data for substrates

5-(2,5-Dimethylphenoxy)-2,2-dimethylpentanal (20, PBS-23-2)



This compound was synthesized according to the following procedure.



The solution of gemfibrozil (1.25 g, 5.0 mmol, 1.0 equiv) in 20 mL of dry THF was added dropwise to the suspension of $LiAlH_4$ (949 mg, 25 mmol, 5.0 equiv) in 40 mL of dry THF at 0 °C. The mixture was stirred in a 50 °C oil bath for 4 hours. Then the mixture was quenched by slow addition of 10% NaOH solution at 0 °C until no bubbles were formed. The resulting white precipitates were filtered out through a pad of celite and washed with EtOAc. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography (5:1 hexanes/EtOAc) to afford the alcohol product as a pale yellow liquid (1.13 g, 96% yield).

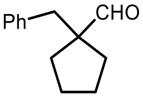
DMSO (1.0 mL, 14.4 mmol, 3.0 equiv) was added dropwise to the solution of oxalyl chloride (0.8 mL, 9.6 mmol, 2.0 equiv) in 25 mL of dry CH_2Cl_2 at −78 °C. After stirring at −78 °C for 15 min, the alcohol obtained from last step (1.13 g, 4.8 mmol, 1.0 equiv) was added. The mixture was stirred at −78 °C for another 15 min, then Et_3N (3.4 mL, 24.0 mmol, 5.0 equiv) was added. The mixture was gradually warmed to room temperature and was stirred overnight. After completion, the mixture was quenched with saturated aqueous solution of $NaHCO_3$ (15 mL), followed by extraction with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed under reduced pressure. Purification by column chromatography (60:1 → 50:1 hexanes/EtOAc) afforded the aldehyde product as a colorless liquid (979 mg, 87% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 6.61 (s, 1H), 3.93 (t, *J* = 5.8 Hz, 2H), 2.31 (s, 3H), 2.18 (s, 3H), 1.77 − 1.65 (m, 4H), 1.11 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 206.2, 157.0, 136.6, 130.4, 123.7, 120.9, 112.1, 67.9, 45.7, 33.7, 24.6, 21.52, 21.46, 15.9.

HRMS (ESI) calcd for $C_{15}H_{23}O_2$ $[M+H]^+$: 235.1693, found: 235.1690.

1-Benzylcyclopentane-1-carbaldehyde (21, PBS-24-2)



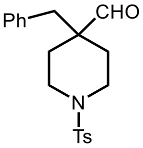
This compound was prepared following literature procedure.[30]

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.49 (s, 1H), 7.22 − 7.15 (m, 2H), 7.15 − 7.09 (m, 1H), 7.07 − 7.01 (m, 2H), 2.85 (s, 2H), 1.90 − 1.80 (m, 2H), 1.62 − 1.41 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 205.2, 138.0, 130.0, 128.4, 126.5, 59.3, 41.2, 32.4, 24.9.

HRMS (ESI) calcd for $C_{12}H_{15}$ $[M−CHO]^+$: 159.1168, found: 159.1166.

4-Benzyl-1-tosylpiperidine-4-carbaldehyde (22, wrh-04-138-1)



This compound was prepared from methyl 4-piperidinecarboxylate following literature procedure.[30]

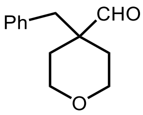
m.p. = 128 − 130 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.40 (s, 1H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.31 − 7.21 (m, 5H), 7.03 − 6.97 (m, 2H), 3.67 − 3.57 (m, 2H), 2.73 (s, 2H), 2.42 (s, 3H), 2.27 (td, *J* = 12.1, 2.1 Hz, 2H), 2.03 (d, *J* = 13.9 Hz, 2H), 1.72 (td, *J* = 13.5, 4.3 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 205.4, 143.8, 134.8, 133.1, 130.2, 129.9, 128.6, 127.7, 127.2, 48.9, 43.6, 43.5, 30.3, 21.7.

HRMS (ESI) calcd for $C_{20}H_{24}O_3NS$ $[M+H]^+$: 358.1471, found: 358.1468.

4-Benzyltetrahydro-2*H*-pyran-4-carbaldehyde (23, wrh-04-135-2)



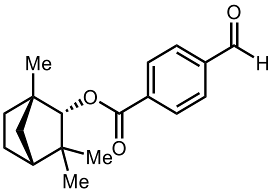
This compound was prepared from methyl tetrahydropyran-4-carboxylate following literature procedure.[30]

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.24 − 7.13 (m, 3H), 7.01 − 6.96 (m, 2H), 3.81 − 3.72 (m, 2H), 3.32 (td, *J* = 11.8, 2.5 Hz, 2H), 2.73 (s, 2H), 1.88 − 1.79 (m, 2H), 1.65 − 1.54 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 206.0, 135.3, 130.3, 128.5, 127.0, 64.9, 48.7, 43.8, 31.3.

HRMS (ESI) calcd for $C_{12}H_{15}O$ $[M{-}CHO]^+$: 175.1117, found: 175.1115.

1,3,3-Trimethylbicyclo[2.2.1]heptan-2-yl 4-formylbenzoate (25, wrh-04-118)



This compound was prepared from fenchyl alcohol (820 µL, 5.0 mmol, 1.0 equiv) according to general procedure B1. The compound was obtained as a white solid (942 mg, 66% yield, eluent: 60:1 hexanes/EtOAc).

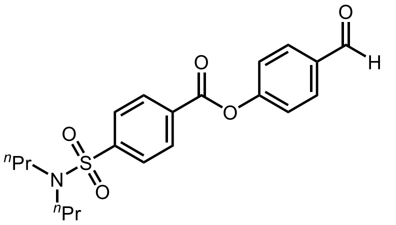
m.p. = 61 − 63 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.21 (d, *J* = 8.2 Hz, 2H), 7.96 (d, *J* = 8.4 Hz, 2H), 4.64 (d, *J* = 1.9 Hz, 1H), 1.96 − 1.88 (m, 1H), 1.83 − 1.75 (m, 2H), 1.70 − 1.62 (m, 1H), 1.58 − 1.48 (m, 1H), 1.29 − 1.21 (m, 2H), 1.19 (s, 3H), 1.11 (s, 3H), 0.84 (s, 3H).

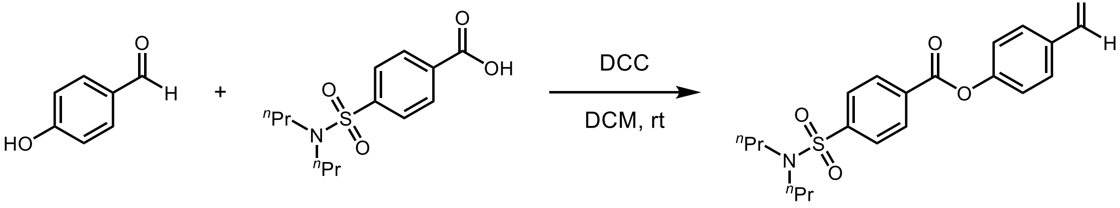
^{13}C NMR (125 MHz, $CDCl_3$) δ 191.8, 166.0, 139.2, 135.8, 130.2, 129.7, 87.6, 48.8, 48.5, 41.6, 40.0, 29.9, 27.0, 26.0, 20.4, 19.6.

HRMS (ESI) calcd for $C_{18}H_{23}O_3$ $[M+H]^+$: 287.1642, found: 287.1637.

4-Formylphenyl 4-(*N,N*-dipropylsulfamoyl)benzoate (26, PBS-22A)



This compound was synthesized according to the following procedure.

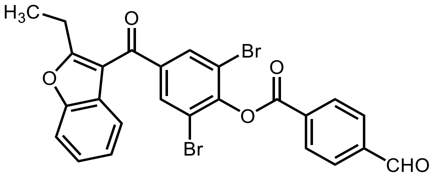


DCC (928 mg, 4.5 mmol, 1.5 equiv) was added to the solution of probenecid (856 mg, 3.0 mmol, 1.0 equiv) and 4-hydroxybenzaldehyde (440 mg, 3.6 mmol, 1.2 equiv) in 15 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature overnight. The crude mixture was recrystallized from hot ethanol (6 mL) to obtain the pure compound as a white solid (632 mg, 54% yield).

m.p. = 83 − 84 °C.

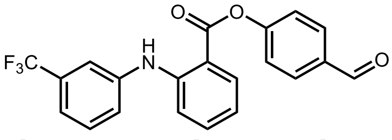
^{1}H NMR (500 MHz, $CDCl_3$) δ 10.04 (s, 1H), 8.33 (d, *J* = 8.5 Hz, 2H), 8.03 − 7.93 (m, 4H), 7.43 (d, *J* = 8.5 Hz, 2H), 3.20 − 3.09 (m, 4H), 1.63 − 1.52 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 190.9, 163.4, 155.4, 145.5, 134.5, 132.3, 131.5, 131.0, 127.4, 122.5, 50.1, 22.1, 11.3.
HRMS (ESI) calcd for $C_{20}H_{24}O_5NS$ $[M+H]^+$: 390.1370, found: 390.1370.

2,6-Dibromo-4-(2-ethylbenzofuran-3-carbonyl)phenyl 4-formylbenzoate (27, wrh-04-165A)

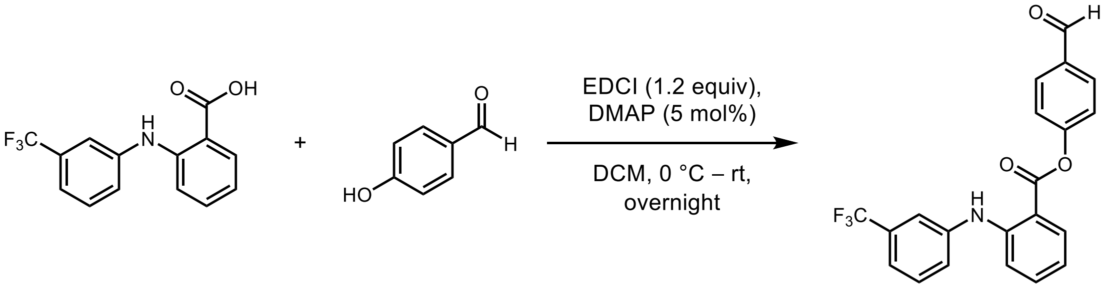


This compound was prepared from benzbromarone (1.27 g, 3.0 mmol) according to general procedure B1. The compound was obtained as a white solid (1.51 g, 90% yield, eluent: 30:1 → 20:1 hexanes/EtOAc).
m.p. = 128 − 129 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (s, 1H), 8.44 (d, *J* = 8.1 Hz, 2H), 8.13 − 8.03 (m, 4H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.37 − 7.22 (m, 2H), 2.95 (q, *J* = 7.5 Hz, 2H), 1.39 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 187.9, 167.6, 161.9, 153.9, 149.5, 140.2, 139.4, 133.3, 133.0, 131.3, 130.0, 126.4, 125.0, 124.2, 121.2, 118.3, 115.4, 111.4, 22.3, 12.4.
HRMS (ESI) calcd for $C_{25}H_{17}O_5Br_2$ $[M+H]^+$: 554.9437, found: 554.9432.

4-Formylphenyl 2-((3-(trifluoromethyl)phenyl)amino)benzoate (28, wrh-05-8)



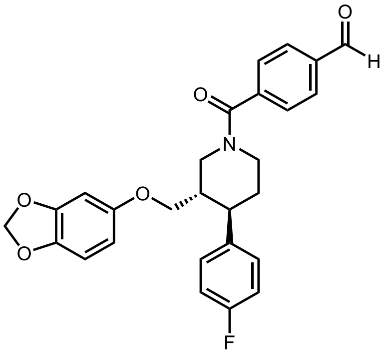
This compound was synthesized according to the following procedure.



Flufenamic acid (844 mg, 3.0 mmol, 1.0 equiv), 4-hydroxybenzaldehyde (366 mg, 3 mmol, 1.0 equiv) and DMAP (18 mg, 5 mol %) were dissolved in CH_2Cl_2 (15 mL), the resulting solution was cooled in ice bath. EDCI (690 mg, 3.6 mmol, 1.2 equiv) was added to the solution at 0 °C. The mixture was allowed to warm up to room temperature and stirred overnight. After completion, the mixture was washed with water (3 × 10 mL). The organic layer was dried over magnesium sulfate and the solvent was removed under reduced pressure. Purification by column chromatography afforded the product as a yellow solid (1.11 g, 96% yield, eluent: 5:1 hexanes/EtOAc).
m.p. = 75 − 76 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 9.45 (s, 1H), 8.23 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.03 − 7.96 (m, 2H), 7.53 − 7.38 (m, 6H), 7.33 (t, *J* = 8.2 Hz, 2H), 6.95 − 6.87 (m, 1H).

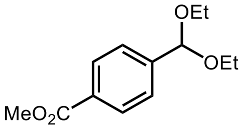
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 166.6, 155.5, 148.1, 141.1, 135.7, 134.3, 132.3, 132.1 (q, J = 32.3 Hz), 131.4, 130.2, 125.3, 124.0 (q, J = 271 Hz), 122.9, 120.4 (q, J = 3.9 Hz), 118.7 (q, J = 3.8 Hz), 118.5, 114.4, 111.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ −62.81.
HRMS (ESI) calcd for $C_{21}H_{15}O_3NF_3$ $[M+H]^+$: 386.0998, found: 386.1024.

4-((3*S*,4*R*)-3-((Benzo[*d*][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)piperidine-1-carbonyl)benzaldehyde (29, wrh-04-177)



This compound was prepared from paroxetine (494 mg, 1.5 mmol) according to general procedure B1. The compound was obtained as a white solid (607 mg, 88% yield, eluent: 30:1 → 20:1 CH_2Cl_2/EtOAc).
m.p. = 138 − 139 °C.
^{1}H NMR (500 MHz, $CDCl_3$, rotamers observed) δ 10.06 (s, 1H), 7.95 (s, 2H), 7.61 (s, 2H), 7.23 − 7.10 (m, 2H), 7.00 (s, 2H), 6.69 − 6.53 (m, 1H), 6.39 (s, 0.5H), 6.23 − 6.15 (m, 0.5H), 6.12 (s, 0.5H), 5.96 (d, J = 5.8 Hz, 0.5H), 5.88 (s, 2H), 4.96 (dd, J = 69.3, 9.9 Hz, 1H), 3.98 (d, J = 12.1 Hz, 0.5H), 3.78 (d, J = 9.8 Hz, 0.5H), 3.74 − 3.64 (m, 0.5H), 3.60 − 3.45 (m, 1H), 3.45 − 3.33 (m, 0.5H), 3.29 − 3.05 (m, 1H), 3.04 − 2.84 (m, 1.5H), 2.84 − 2.71 (m, 0.5H), 2.25 − 1.59 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 169.1, 163.0, 160.6, 154.3, 153.6, 148.3, 141.9, 138.3, 137.0, 130.0, 128.9, 127.7, 115.9, 115.7, 108.0, 105.7, 105.4, 101.3, 100.1, 98.1, 97.9, 68.6, 68.2, 51.0, 48.2, 45.6, 44.4, 43.9, 42.9, 42.0, 34.7, 33.6. (Spectrum is obscured by rotamers and C-F coupling peaks.)
^{19}F NMR (470 MHz, $CDCl_3$, rotamers observed) δ −115.5, −115.6.
HRMS (ESI) calcd for $C_{27}H_{25}O_5NF$ $[M+H]^+$: 462.1711, found: 462.1694.

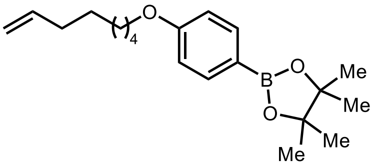
Methyl 4-(diethoxymethyl)benzoate (36, wrh-05-120B)



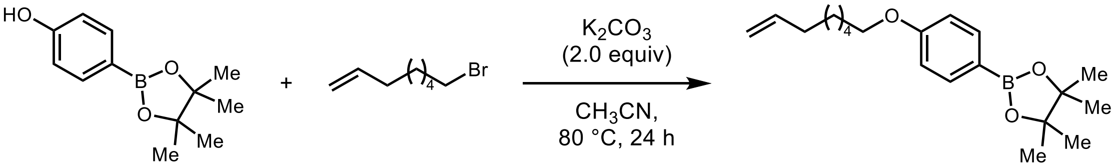
This compound was synthesized according to literature procedure.[31]

To a flame-dried 10 mL round bottom flask was added methyl 4-formylbenzoate (821 mg, 5.0 mmol, 1.0 equiv), $Cu(BF_4)_2 \cdot xH_2O$ (17 mg) and triethyl orthoformate (1.7 mL, 10 mmol, 2.0 equiv). After stirring at room temperature for 1 h, the mixture was quenched with saturated $NaHCO_3$ solution (2 mL) and extracted with EtOAc (1 × 5 mL). The organic layer was dried over magnesium sulfate, concentrated *in vacuo* and purified through a basified silica gel column (40:1:0.8 hexanes/EtOAc/Et_3N).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 5.54 (s, 1H), 3.91 (s, 3H), 3.68 − 3.47 (m, 4H), 1.23 (t, J = 6.9 Hz, 6H).
^{1}H NMR data were in agreement with the literature.[32]

(1*S*,2*S*)-1-(4-Bromophenyl)-7-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)-2-vinylheptan-1-ol (f, paul-1-69)



This compound was synthesized according to following procedure.



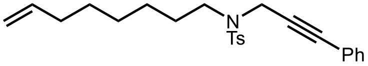
To a suspension of 4-hydroxyphenylboronic acid pinacol ester (1.10 g, 5.0 mmol, 1.0 equiv) and potassium carbonate (1.38 g, 10 mmol, 2.0 equiv) in acetonitrile (25 mL) was added 8-bromooct-1-ene (0.92 mL, 5.5 mmol, 1.1 equiv) at room temperature. The resulting mixture was stirred at 80 °C for 24 h. After completion, the mixture was quenched with water (10 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. The crude residue was purified by column chromatography to afford the product as a colorless oil. (1.02 g, 62% yield, eluent: 60:1 hexanes/EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 − 7.69 (m, 2H), 6.97 − 6.79 (m, 2H), 5.82 (ddt, *J* = 16.9, 10.0, 6.5 Hz, 1H), 5.05 − 4.90 (m, 2H), 3.98 (t, *J* = 6.5 Hz, 2H), 2.12 − 2.00 (m, 2H), 1.84 − 1.72 (m, 2H), 1.52 − 1.36 (m, 6H), 1.33 (s, 12H).

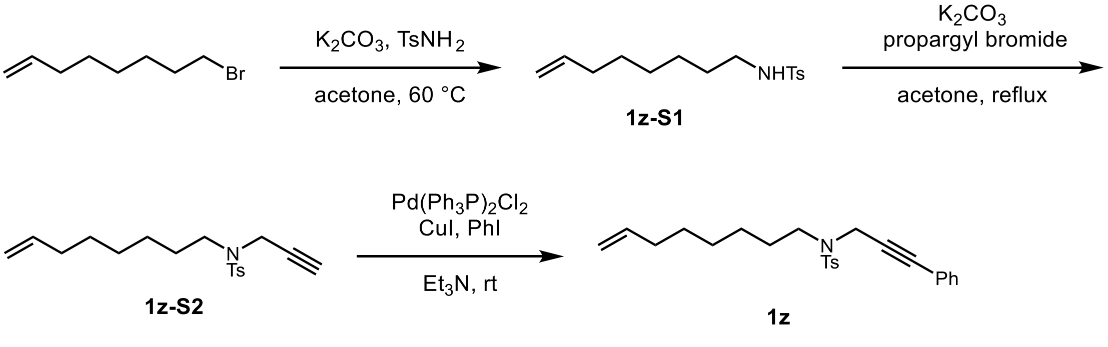
^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7, 139.0, 136.5, 114.3, 113.8, 83.5, 67.7, 33.7, 29.1, 28.82, 28.80, 25.9, 24.8.

HRMS (ESI) calcd for $C_{20}H_{32}O_3B$ $[M+H]^+$: 331.2439, found: 331.2441.

4-Methyl-*N*-(oct-7-en-1-yl)-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (i)



This compound was synthesized according to following procedure.



To the suspension of *p*-toluenesulfonamide (3.76 g, 22 mmol, 1.1 equiv) and potassium carbonate (5.56 g, 40 mmol, 2.0 equiv) in acetone (20 mL) was added 8-bromooct-1-ene (3.3 mL, 20 mmol, 1.0 equiv) at room temperature. The reaction mixture was stirred at 60 °C for 24 h. After completion, the reaction mixture was quenched with water (10 mL) and extracted with ethyl acetate (3 × 20 mL). The organic layer was washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. The crude residue was purified through a silica gel column to give compound **1z-S1** (4.43 g, 79% yield, eluent: 15:1) as a colorless oil.

To the suspension of compound **1z-S1** (1.40 g, 5.0 mmol, 1.0 equiv), potassium carbonate (1.38 g, 10 mmol, 2.0 equiv) in acetone (10 mL) was added propargyl bromide (0.45 mL, 6.0 mmol, 1.2 equiv) at room temperature. The reaction mixture was stirred at reflux for 24 h. After completion, the reaction mixture was quenched with water (5 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layers were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. The crude residue was purified through a silica gel column to give compound **1z-S2** (1.49 g, 94% yield, eluent: 30:1) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 − 7.69 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.80 (ddt, *J* = 17.0, 10.0, 6.5 Hz, 1H), 5.03 − 4.89 (m, 2H), 4.13 (d, *J* = 2.5 Hz, 2H), 3.21 − 3.14 (m, 2H), 2.42 (s, 3H), 2.06 − 2.01 (m, 2H), 2.00 (t, *J* = 2.5 Hz, 1H), 1.61 − 1.50 (m, 2H), 1.42 − 1.28 (m, 6H).

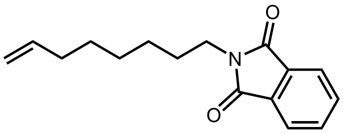
To a 25 mL round bottom flask equipped with a magnetic stirrer bar were added compound **1z-S2** (1.49 g, 4.7 mmol, 1.0 equiv), $Pd(Ph_3P)_2Cl_2$ (33 mg, 1 mol %), CuI (18 mg, 2 mol %), Et_3N (9 mL) and iodobenzene (0.57 mL, 5.2 mmol, 1.1 equiv). The reaction mixture was stirred at room temperature under nitrogen for 24 h. After completion, the reaction mixture was quenched with water (5 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layers were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. The crude residue was purified through a silica gel column to give product **1z** (1.83 g, 99% yield, eluent: 30:1) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 − 7.66 (m, 2H), 7.23 − 7.12 (m, 5H), 7.01 − 6.96 (m, 2H), 5.72 (ddt, *J* = 17.0, 10.0, 6.5 Hz, 1H), 4.95 − 4.83 (m, 2H), 4.26 (s, 2H), 3.17 (t, *J* = 7.5 Hz, 2H), 2.26 (s, 3H), 2.01 − 1.92 (m, 2H), 1.59 − 1.49 (m, 2H), 1.36 − 1.21 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.4, 139.1, 136.1, 131.6, 129.6, 128.5, 128.3, 127.9, 122.4, 114.4, 85.6, 82.0, 46.5, 37.1, 33.8, 28.9, 28.8, 27.6, 26.6, 21.5.

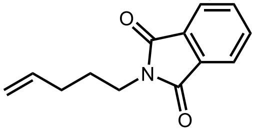
HRMS (ESI) calcd for $C_{24}H_{30}O_2NS$ $[M+H]^+$: 396.1992, found: 396.1982.

2-(Oct-7-en-1-yl)isoindoline-1,3-dione (j)



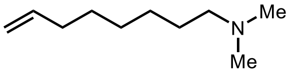
This compound was synthesized according to literature procedure.[33]

2-(Pent-4-en-1-yl)isoindoline-1,3-dione (k)



This compound was synthesized according to literature procedure.[33]

***N*,*N*-Dimethyloct-7-en-1-amine (l, CZZ-83)**

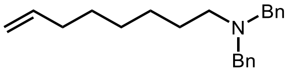


This compound was prepared from dimethylamine according to general procedure B2. The compound was obtained as a brown liquid (1.08 g, 70% yield, eluent: 40:1:4 DCM/MeOH/Et_3N).

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.04 – 4.85 (m, 2H), 2.27 – 2.16 (m, 8H), 2.03 (q, *J* = 6.6 Hz, 2H), 1.50 – 1.22 (m, 8H).

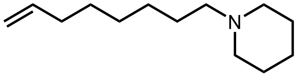
^{13}C NMR (75 MHz, $CDCl_3$) δ 139.3, 114.3, 60.1, 45.7, 33.9, 29.2, 29.0, 27.9, 27.5.
HRMS (ESI) calcd for $C_{10}H_{22}N$ $[M+H]^+$: 156.1747, found: 156.1746.

_N,N_-Dibenzyloct-7-en-1-amine (m, wrh-06-39-2)



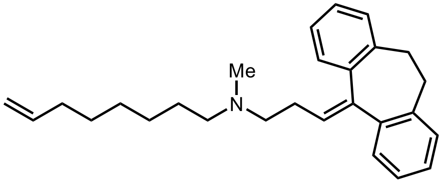
This compound was prepared from dibenzylamine according to general procedure B2. The compound was obtained as a yellow liquid (2.12 g, 69% yield, eluent: 100:1 hexanes/EtOAc).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 4H), 7.35 – 7.29 (m, 4H), 7.27 – 7.21 (m, 2H), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.04 – 4.91 (m, 2H), 3.56 (s, 4H), 2.45 – 2.38 (m, 2H), 2.02 (dd, *J* = 14.6, 7.0 Hz, 2H), 1.56 – 1.49 (m, 2H), 1.41 – 1.32 (m, 2H), 1.32 – 1.19 (m, 4H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2, 139.3, 128.9, 128.2, 126.8, 114.3, 58.4, 53.5, 33.9, 29.1, 29.1, 27.2, 27.1.
HRMS (ESI) calcd for $C_{22}H_{30}N$ $[M+H]^+$: 308.2373, found: 308.2379.

1-(Oct-7-en-1-yl)piperidine (n, wrh-06-39-1)

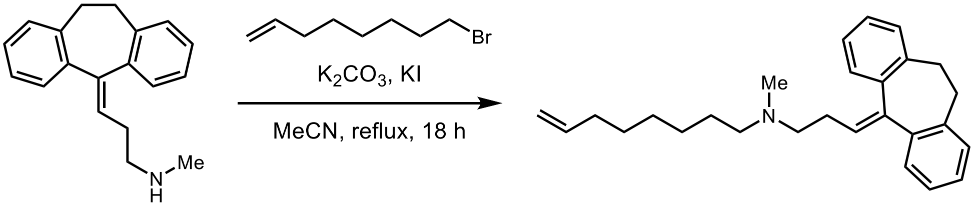


This compound was prepared from piperidine according to general procedure B2. The compound was obtained as a yellow liquid (1.73 g, 89% yield, eluent: 1:1:0.01 hexanes/EtOAc/Et_3N).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 4.95 (ddd, *J* = 13.6, 11.1, 1.3 Hz, 2H), 2.46 – 2.29 (m, 4H), 2.29 – 2.21 (m, 2H), 2.03 (q, *J* = 7.0 Hz, 2H), 1.63 – 1.53 (m, 4H), 1.52 – 1.18 (m, 10H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 139.3, 114.3, 59.8, 54.8, 33.9, 29.2, 29.0, 27.8, 27.1, 26.2, 24.7.
HRMS (ESI) calcd for $C_{13}H_{26}N$ $[M+H]^+$: 196.2060, found: 196.2061.

_N_-(3-(10,11-Dihydro-5_H_-dibenzo[_a,d_][7]annulen-5-ylidene)propyl)-_N_-methyloct-7-en-1-amine (o, wrh-06-49)



This compound was synthesized according to following procedure.



A 50 mL round bottom flask was charged with nortriptyline (1.32 g, 5.0 mmol, 1.0 equiv), 8-bromo-1-octene (0.84 mL, 5.0 mmol, 1.0 equiv), K_2CO_3 (898 mg, 6.5 mmol, 1.3 equiv), KI (83 mg, 0.5 mmol, 10 mol %) and acetonitrile (10 mL). The reaction mixture was heated to reflux for 18 h. After completion, the mixture was cooled to room temperature and filtered through a pad of Celite to remove the insoluble solid materials. The crude residue was purified through a silica gel column to give product

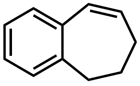
o (1.31 g, 70% yield, eluent: 10:1 → 2:1 hexanes/EtOAc with 1% Et_3N) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 1H), 7.22 – 7.08 (m, 6H), 7.05 – 6.99 (m, 1H), 5.89 – 5.73 (m, 2H), 5.04 – 4.88 (m, 2H), 3.51 – 3.20 (m, 2H), 3.08 – 2.86 (m, 1H), 2.86 – 2.66 (m, 1H), 2.48 – 2.37 (m, 2H), 2.33 – 2.18 (m, 4H), 2.14 (s, 3H), 2.08 – 1.98 (m, 2H), 1.51 – 1.17 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 141.5, 140.3, 139.4, 139.3, 137.2, 130.1, 129.8, 128.7, 128.4, 128.1, 127.5, 127.1, 126.1, 125.8, 114.3, 57.7, 57.5, 42.3, 33.93, 33.89, 32.2, 29.2, 29.0, 27.5, 27.44, 27.37.

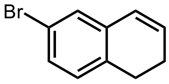
HRMS (ESI) calcd for $C_{27}H_{36}N$ $[M+H]^+$: 374.2842, found: 374.2849.

6,7-Dihydro-5*H*-benzo[7]annulene (q)



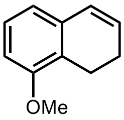
This compound was synthesized according to literature procedure.[34]

6-Bromo-1,2-dihydronaphthalene (r)



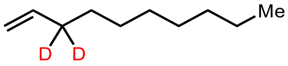
This compound was synthesized from 7-bromotetral-1-on according to literature procedure.[34]

8-Methoxy-1,2-dihydronaphthalene (s)

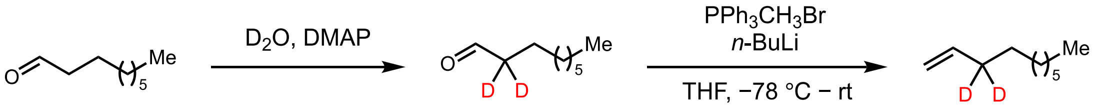


This compound was synthesized from 5-methoxy-1-tetralone according to literature procedure.[34]

Dec-1-ene-3,3-d_2 (u-d_2, CZZ-63)



This compound was synthesized according to the following procedure.



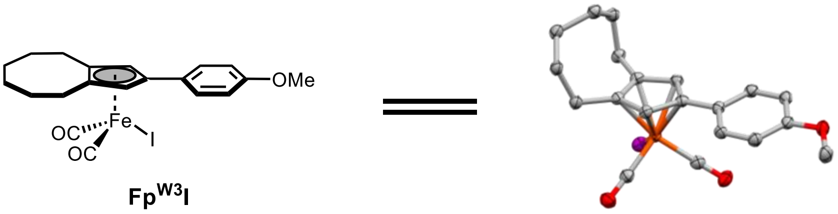
A 25 mL round bottom flask was charged with nonanal (8.6 mL, 50 mmol, 1.0 equiv), DMAP (611 mg, 5 mmol, 0.1 equiv) and D_2O (12.6 mL, 695 mmol, 14 equiv). The mixture was stirred at 100 °C for 2 h. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 (20 mL). The layers were separated and the organic layer was washed with 1 N HCl (2 × 10 mL), dried over magnesium sulfate and concentrated under reduced pressure at 0 °C. The residue was subjected to the same reaction conditions again to afford nonanal-d_2 with >95% D incorporation. The product was used in the next step without further purification.

n-BuLi (8.8 mL, 22 mmol, 1.1 equiv, 2.5 M in hexanes) was added dropwise over 5 min to the solution of PPh_3CH_3Br (8.57 g, 24 mmol, 1.2 equiv) in dry THF (80 mL). The mixture was stirred at −78 °C under nitrogen for 20 min, and was warmed up to room temperature and stirred for another 30 min. Then the mixture was cooled back to −78 °C, nonanal-d_2 (2.88 g, 20 mmol, 1.0 equiv) was added dropwise over 5 min.

The resulting mixture was allowed to gradually warm up to room temperature and was stirred overnight. After completion, the solid material was filtered out through celite and the filtrate was concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel to afford the desired product 1-decene-d_2 as a colorless liquid (846 mg, 30% yield, eluent: hexanes) with 97% D incorporation. (See ^{1}H NMR)

^{1}H NMR data were in agreement with the literature.[35]

X-ray structure of complex $Fp^{W3}I$ and product 5k



$Fp^{W3}I$

Datablock: Ruihan2_0ma_a

```
Bond precision:    C-C = 0.0030 A          Wavelength=1.54178

Cell:               a=11.6149(4)      b=11.0189(3)      c=29.5374(9)
                    alpha=90          beta=90           gamma=90
Temperature:        100 K

                  Calculated                    Reported
Volume            3780.3(2)                     3780.3(2)
Space group       P b c a                       P b c a
Hall group        -P 2ac 2ab                    -P 2ac 2ab
Moiety formula    C20 H21 Fe I O3               ?
Sum formula       C20 H21 Fe I O3               C20 H21 Fe I O3
Mr                492.12                        492.12
Dx,g cm-3         1.729                         1.729
Z                 8                             8
Mu (mm-1)         19.347                        19.347
F000              1952.0                        1952.0
F000'             1945.93
h,k,lmax          14,13,36                      14,13,36
Nref              3731                          3723
Tmin,Tmax         0.147,0.908                   0.170,0.450
Tmin'             0.025

Correction method= # Reported T Limits: Tmin=0.170 Tmax=0.450
AbsCorr = MULTI-SCAN

Data completeness= 0.998            Theta(max)= 72.162

                                                     wR2(reflections)=
R(reflections)= 0.0270( 3532)                        0.0783( 3723)

S = 0.980                  Npar= 310
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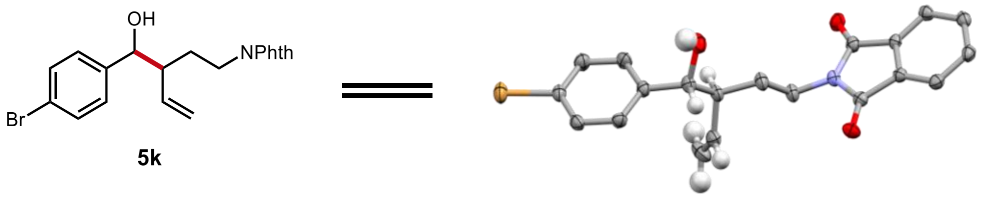
Deposit number: CCDC 2220935.



5k

Datablock: wyd61474_0m_a

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Bond precision:    C-C = 0.0030 A           Wavelength=1.54178

Cell:              a=27.947(3)     b=7.9597(7)          c=17.2671(14)
                   alpha=90        beta=112.486(5)      gamma=90
Temperature:       150 K

                  Calculated                  Reported
Volume            3549.0(6)                   3549.0(5)
Space group       C 2/c                       C 2/c
Hall group        -C 2yc                      -C 2yc
Moiety formula    C20 H18 Br N O3             ?
Sum formula       C20 H18 Br N O3             C20 H18 Br N O3
Mr                400.25                      400.26
Dx,g cm-3         1.498                       1.498
Z                 8                           8
Mu (mm-1)         3.312                       3.312
F000              1632.0                      1632.0
F000'             1630.72
h,k,lmax          34,9,21                     34,9,21
Nref              3388                        3315
Tmin,Tmax         0.652,0.767                 0.610,0.750
Tmin'             0.561

Correction method= # Reported T Limits: Tmin=0.610 Tmax=0.750
AbsCorr = MULTI-SCAN

Data completeness= 0.978            Theta(max)= 70.387

                                                         wR2(reflections)=
R(reflections)= 0.0309( 2958)                            0.1027( 3315)

S = 1.176                  Npar= 226
```

Pressure vessels and gas introducing procedure

The pressure vessels for propylene functionalization reactions were purchased from ACE glass company. The product (part # 8648-61) includes a pressure tube and a PTFE bushing with plunger valve that allows purging of the tube. The loosed bottom plunger has a hole inside, that when positioned in relation to O-Ring seal, will open the tube to the atmosphere (i.e., pull to close, push to open). The plunger has step-down extension that acts as a stopper in bushing (Figure S7).

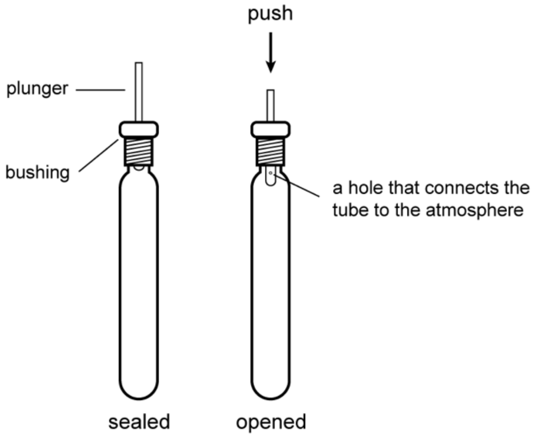


Figure S7. Working mode of the pressure tube.

In order to exchange the gas inside of the tube with propylene, the top of the plunger was wrapped with tapes and tightly equipped with a rubber septum. The plunger was pushed to open when the tube was placed under vacuum via a needle connected to the Schlenk line. After evacuating for 5 min, the needle was removed and propylene was immediately condensed into the tube from a plastic syringe. The plunger was pulled to close and the tube was allowed to warm to room temperature before heating up. (Figure S8)

Pressure tubes and bushings are individually fitted and should be carefully matched and tested for air-tightness before use.

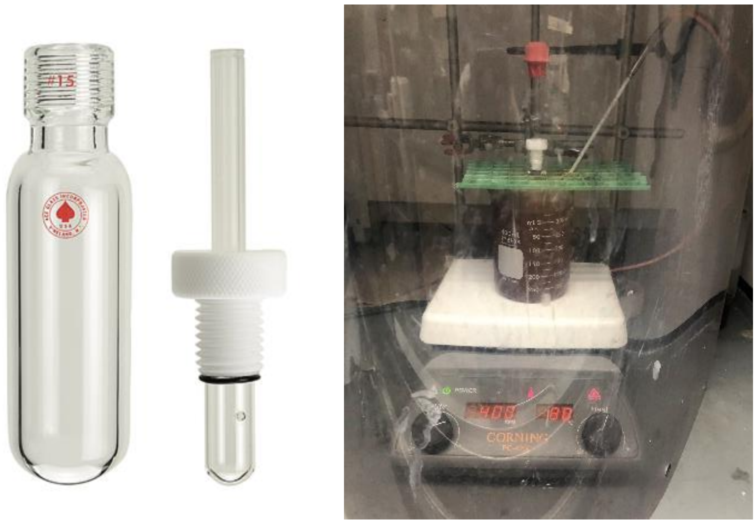


Figure S8. Pressure tube and reaction set-up.

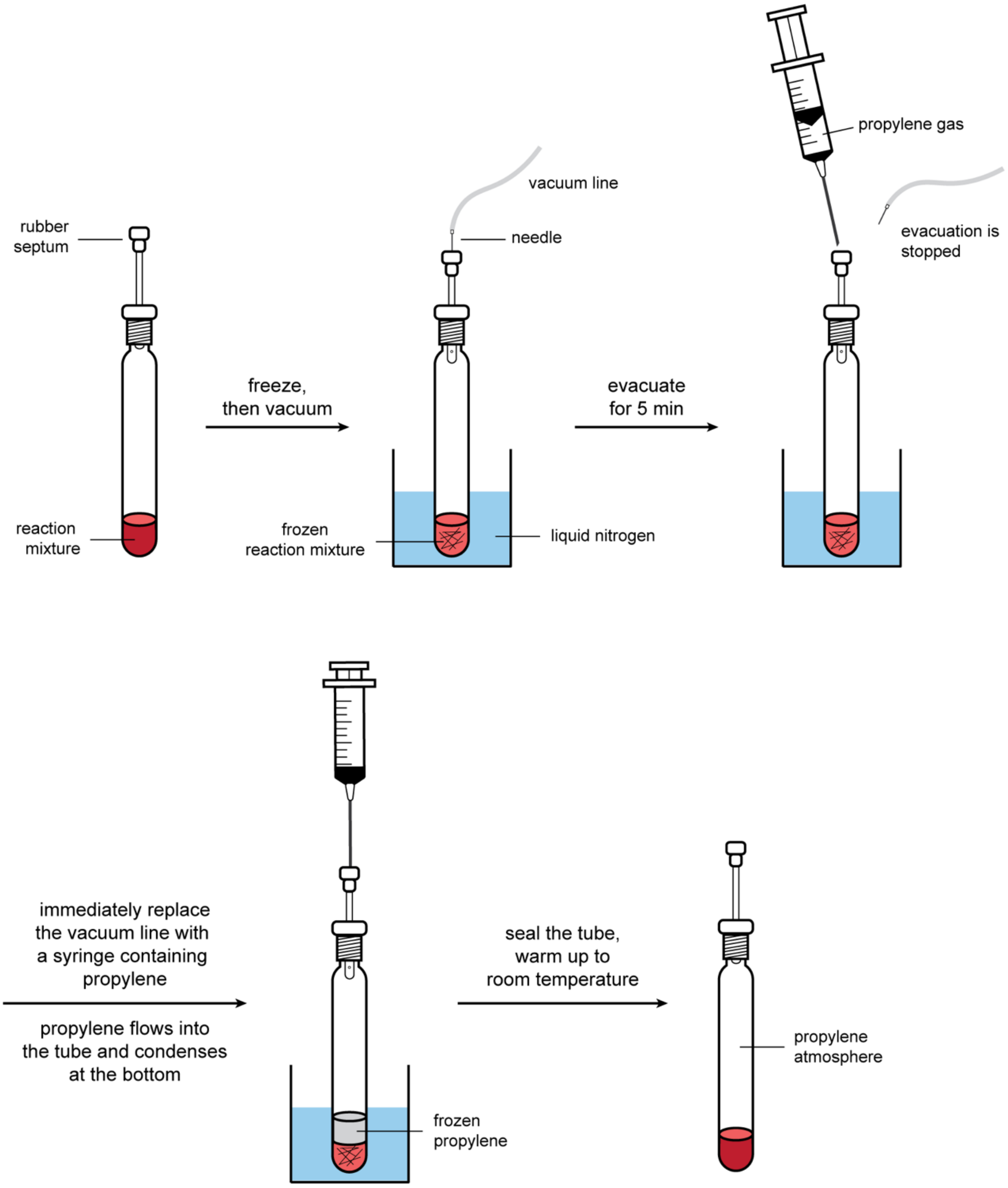


Figure S9. Gas introducing procedure.

References

1. Wang, L.; Wang, L.; Li, M.; Chong, Q.; Meng, F. Cobalt-Catalyzed Diastereo- and Enantioselective Reductive Allyl Additions to Aldehydes with Allylic Alcohol Derivatives via Allyl Radical Intermediates. *J. Am. Chem. Soc.* **2021**, *143*, 12755−12765.
2. Barabé, F.; Bétournay, G.; Bellavance, G.; Barriault, L. Gold-Catalyzed Synthesis of Carbon-Bridged Medium-Sized Rings. *Org. Lett.* **2009**, *11*, 4236−4238.
3. Polo, E.; Bellabarba, R. M.; Prini, G.; Traverso, O.; Green, M. L. H. Synthesis of ring-substituted bis-η^5-cyclopentadienyl derivatives of the Group IV elements containing the bicyclic ligands η^5-C_5H_3(1,2-CH_2–)n, n=4, 5, or 6. *J. Organomet. Chem.* **1999**, *577*, 211−218.
4. Shanmugam, P.; Srinivasan, R.; Rajagopalan, K. Synthesis of functionalised bicyclo[4.4.0] and spiro [5.4] compounds by tin-mediated radical cyclization. *Tetrahedron* **1997**, *53*, 11685−11692.
5. Asachenko, A. F.; Bush, A. A.; Smirnov, A. Y.; Morozov, O. S.; Dzhevakov, P. B.; Kim, S. Y.; Cho, M. S.; Lee, K. S.; Lee, Y. H.; Cho, K. J.; Lee, S. M.; Nechaev, M. S. New zirconocenes with 4,5,6,7-tetrahydroindene ligands. Synthesis and catalytic activity in the polymerization of ethylene and copolymerization of ethylene with hex-1-ene. *Russ. Chem. Bull.* **2016**, *65*, 1580−1585.
6. Akita, M.; Terada, M.; Tanaka, M.; Morooka, Y. Some additional aspects of versatile starting compounds for cationic organoiron complexes: molecular structure of the aqua complex [(η^5-C_5Me_4Et)Fe$(CO)_2(OH_2)$]BF_4 and solution behavior of the THF complex [(η^5-C_5R_5)Fe$(CO)_2$(THF)]BF_4. *J. Organomet. Chem.* **1996**, *510*, 255−261.
7. Wang, Y.; Scrivener, S. G.; Zuo, X. D.; Wang, R.; Palermo, P. N.; Murphy, E.; Durham, A. C.; Wang, Y. M. Iron-Catalyzed Contrasteric Functionalization of Allenic C(sp^2)−H Bonds: Synthesis of alpha-Aminoalkyl 1,1-Disubstituted Allenes. *J. Am. Chem. Soc.* **2021**, *143*, 14998−15004.
8. Büyükadalı, N. N.; Aslan, N.; Gümüş, S.; Gümüş, A. Stereoselective synthesis of benzofuran and benzothiophene substituted dihydropyran derivatives via ring closing metathesis. *Tetrahedron: Asymmetry* **2016**, *27*, 954−959.
9. Nortcliffe, A.; Milne, G. D. S.; Hamza, D.; Moody, C. J. Synthesis of 4-aminotetrahydropyran scaffolds for drug discovery. *Bioorg. Med. Chem.* **2017**, *25*, 2218−2225.
10. Hu, X.-Q.; Chen, J.-R.; Wei, Q.; Liu, F.-L.; Deng, Q.-H.; You-Quan, Z.; Xiao, W.-J. Efficient Synthesis of Dihydropyrazoles by Halocyclization of β,γ-Unsaturated Hydrazones. *Eur. J. Org. Chem.* **2014**, *2014*, 3082−3086.
11. Zhu, S.; Buchwald, S. L. Enantioselective CuH-catalyzed anti-Markovnikov hydroamination of 1,1-disubstituted alkenes. *J. Am. Chem. Soc.* **2014**, *136*, 15913−15916.
12. Zbieg, J. R.; Fukuzumi, T.; Krische, M. J. Iridium Catalyzed Hydro-hydroxyalkylation of Butadiene: Carbonyl Crotylation. *Adv. Synth. Catal.* **2010**, *352*, 2416−2420.
13. Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.;

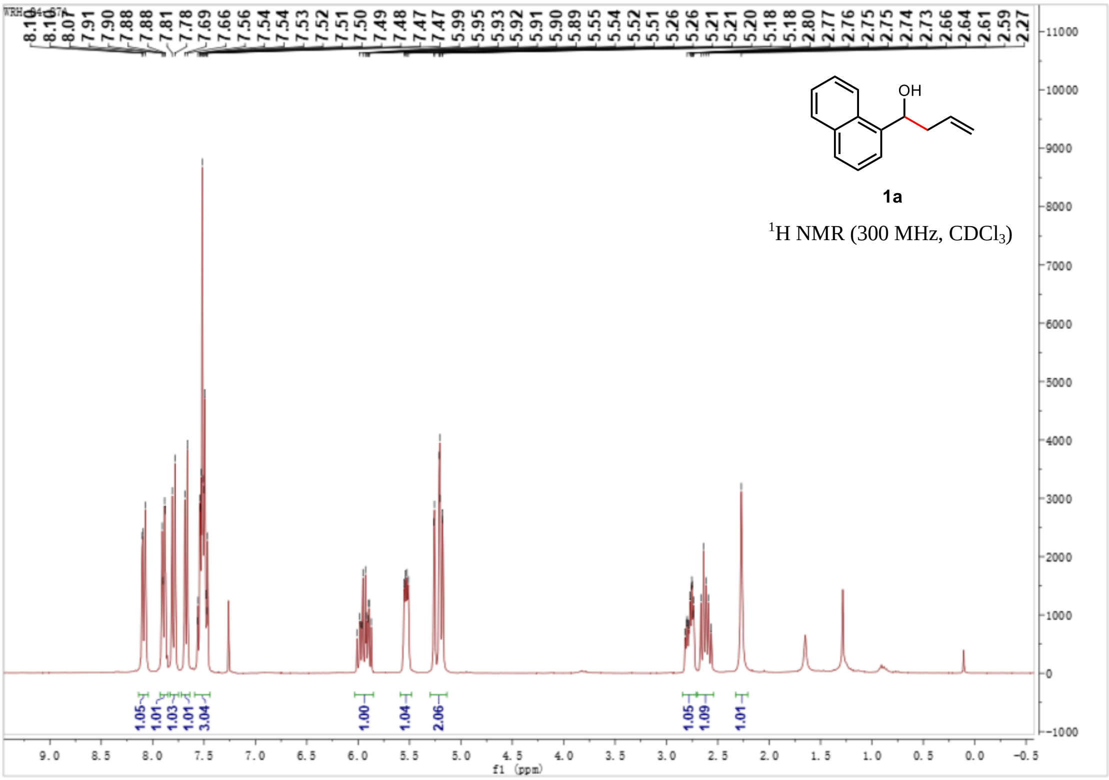
Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2016**.

14. Pracht, P.; Bohle, F.; Grimme, S. Automated Exploration of the Low-Energy Chemical Space with Fast Quantum Chemical Methods. *Phys. Chem. Chem. Phys.* **2020**, *22*, 7169−7192.
15. Bannwarth, C.; Ehlert, S.; Grimme, S. GFN2-xTB—an Accurate and Broadly Parametrized Self-Consistent Tight-Binding Quantum Chemical Method with Multipole Electrostatics and Density-Dependent Dispersion Contributions. *J. Chem. Theory Comput.* **2019**, *15*, 1652−1671.
16. (a) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phy. Rev. B* **1988**, *37*, 785−789. (b) Becke, A. D., Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648−5652.
17. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.
18. Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* **2011**, *32*, 1456−1465.
19. Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. Energy-adjusted ab initio pseudopotentials for the first row transition elements. *J. Chem. Phys.* **1987**, *86*, 866−872.
20. Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Functionals. *Theor. Chem. Acc.* **2008**, *120*, 215−241.
21. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009**, *113*, 6378−6396.
22. Guo, Y.; Riplinger, C.; Becker, U.; Liakos, D. G.; Minenkov, Y.; Cavallo, L.; Neese, F. An improved linear scaling perturbative triples correction for the domain based local pair-natural orbital based singles and doubles coupled cluster method DLPNO-CCSD(T). *J. Chem. Phys.* **2018**, *148,* 011101.
23. Neese, F. Software update: The ORCA program system, version 5.0. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2022**, *12,* e1606.
24. (a) Neese, F. An Improvement of the Resolution of the Identity Approximation for the Calculation of the Coulomb Matrix. *J. Comp. Chem.* **2003**, *24*, 1740−1747. (b) Neese, F.; Wennmohs, F.; Hansen, A.; Becker, U. Efficient, approximate and parallel Hartree-Fock and hybrid DFT calculations. A ‘chain-of-spheres’ algorithm for the Hartree-Fock exchange. *Chem. Phys.* **2009**, *356*, 98−109. (c)

Izsak, R.; Neese, F. An overlap fitted chain of spheres exchange method. *J. Chem. Phys.* **2011**, *135*,144105.

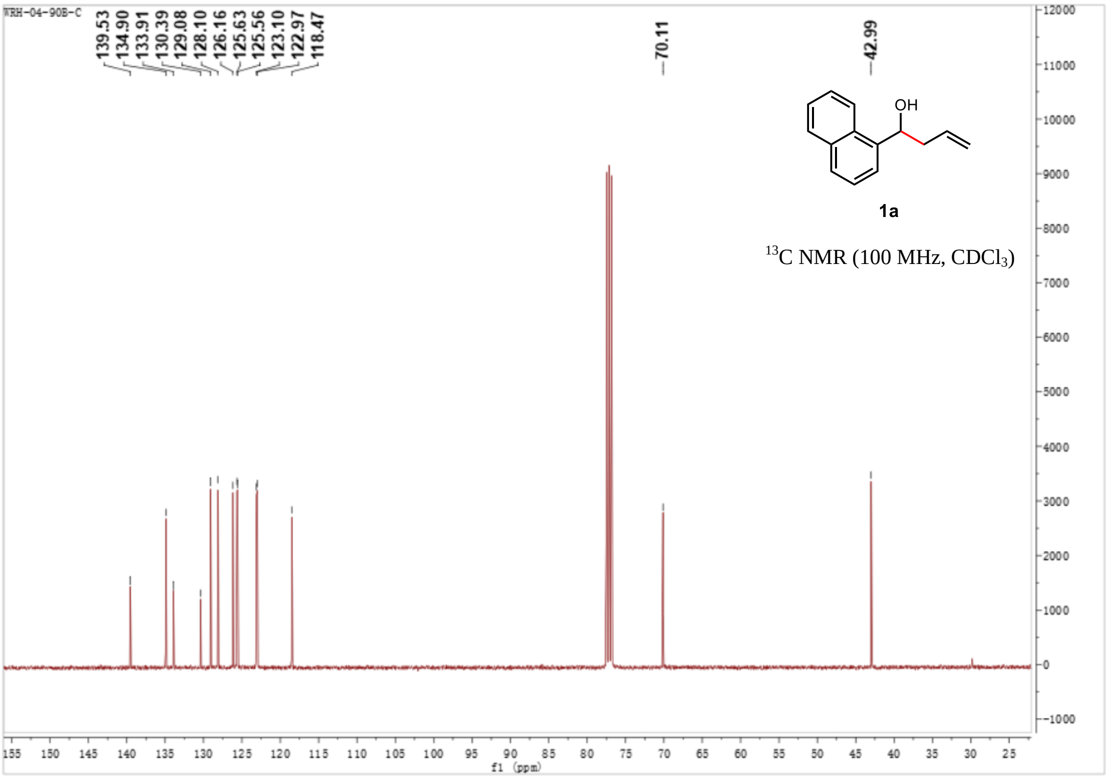
25. Mammen, M.; Shakhnovich, E. I.; Deutch, J. M.; Whitesides, G. M. *J. Org. Chem.* **1998**, *63*, 3821-3830.
26. Luchini, G.; Alegre-Requena, J. V.; Funes-Ardoiz, I.; Paton, R. S. F, GoodVibes: automated thermochemistry for heterogeneous computational chemistry data [version 1; peer review: 2 approved with reservations]. *F1000Research* **2020**, *9*, 291.
27. Grimme, S. Supramolecular Binding Thermodynamics by Dispersion-Corrected Density Functional Theory. *Chem. Eur. J.* **2012**, *18*, 9955−9964.
28. Legault, C. Y., CYLView 2.0. Université de Sherbrooke **2020**, http://www.cylview.org.
29. Crosthwaite, J. M.; Aki, S. N.; Maginn, E. J.; Brennecke, J. F. Liquid phase behavior of imidazolium-based ionic liquids with alcohols: effect of hydrogen bonding and non-polar interactions. *Fluid Phase Equilib.* **2005**, *228−229*, 303−309.
30. Li, B.; Lawrence, B.; Li, G.; Ge, H. Ligand-Controlled Direct gamma-C−H Arylation of Aldehydes. *Angew. Chem. Int. Ed*. **2020**, *59*, 3078−3082.
31. Kumar, R.; Chakraborti, A. K. Copper(II) tetrafluoroborate as a novel and highly efficient catalyst for acetal formation. *Tetrahedron Lett.* **2005**, *46,* 8319−8323.
32. Bognar, S.; van Gemmeren, M. Direct Synthesis of Unsymmetrical Dithioacetals. *Chem. Eur. J.* **2021**, *27,* 4859−4863.
33. Wang, Y.; Wang, L.; Chen, M.; Tu, Y.; Liu, Y.; Zhang, J. Palladium/Xu-Phos-catalyzed asymmetric carboamination towards isoxazolidines and pyrrolidines. *Chem. Sci.* **2021**, *12*, 8241−8245.
34. Singh, K.; Fennell, C. J.; Coutsias, E. A.; Latifi, R.; Hartson, S.; Weaver, J. D. Light Harvesting for Rapid and Selective Reactions: Click Chemistry with Strain-Loadable Alkenes. *Chem* **2018**, *4*, 124−137.
35. Ma, R.; White, M. C. C–H to C–N Cross-Coupling of Sulfonamides with Olefins. *J. Am. Chem. Soc.* **2018**, *140*, 3202−3205.

NMR spectra



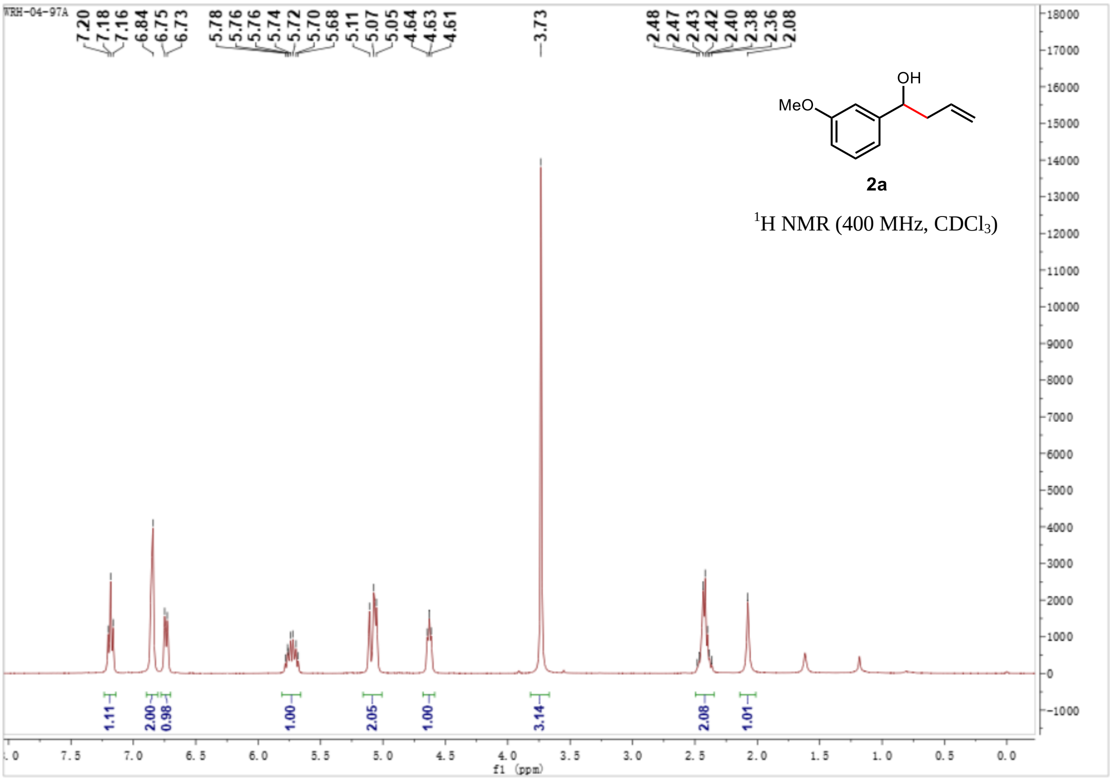
1a

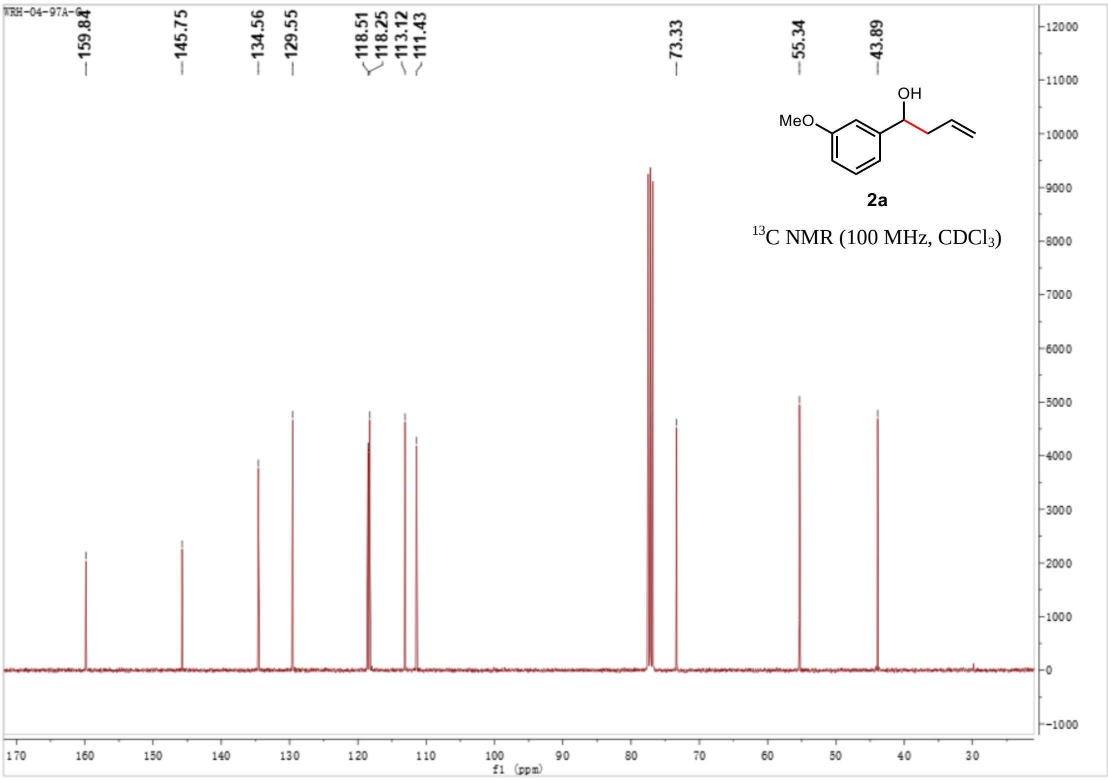
^{1}H NMR (300 MHz, CDCl$_3$)



1a

^{13}C NMR (100 MHz, CDCl$_3$)


WRH-04-97A
7.20
7.18
7.16
6.84
6.75
6.73
5.78
5.76
5.76
5.74
5.72
5.70
5.68
5.11
5.07
5.05
4.64
4.63
4.61
3.73
2.48
2.47
2.43
2.42
2.40
2.38
2.36
2.08
OH
MeO
2a
^{1}H NMR (400 MHz, CDCl$_3$)
1.11
2.00
0.98
1.00
2.05
1.00
3.14
2.08
1.01
f1 (ppm)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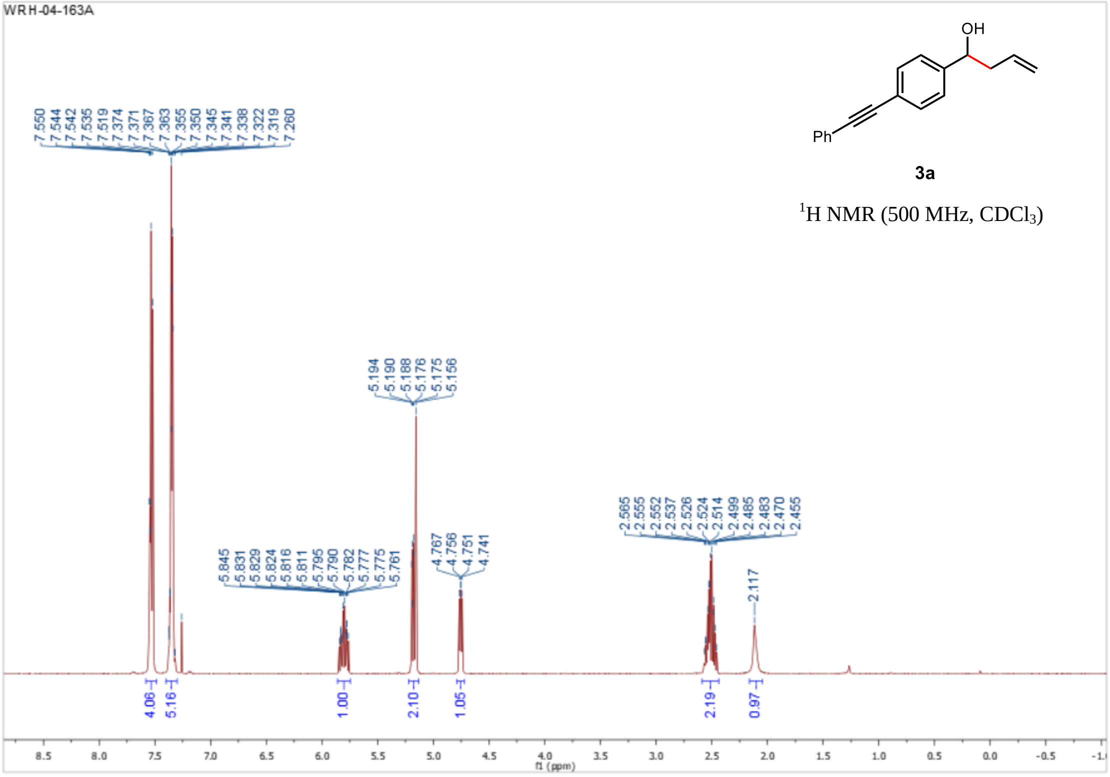
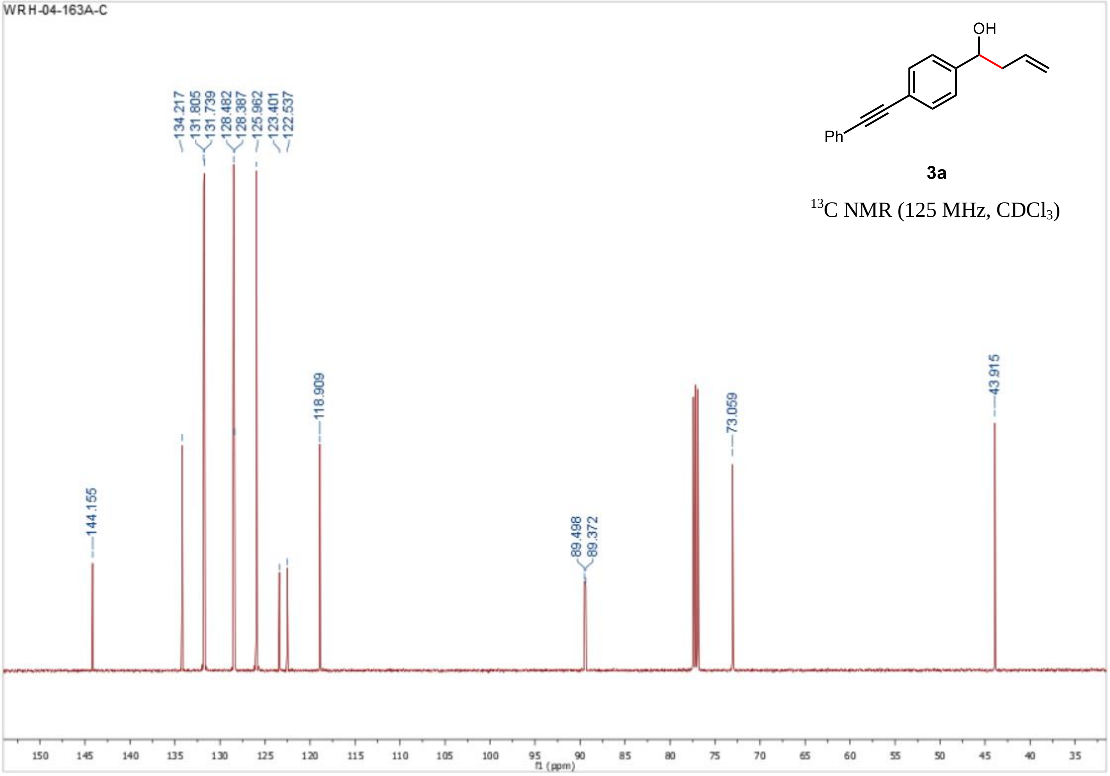
159.84
145.75
134.56
129.55
118.51
118.25
113.12
111.43
73.33
55.34
43.89
OH
MeO
2a
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)



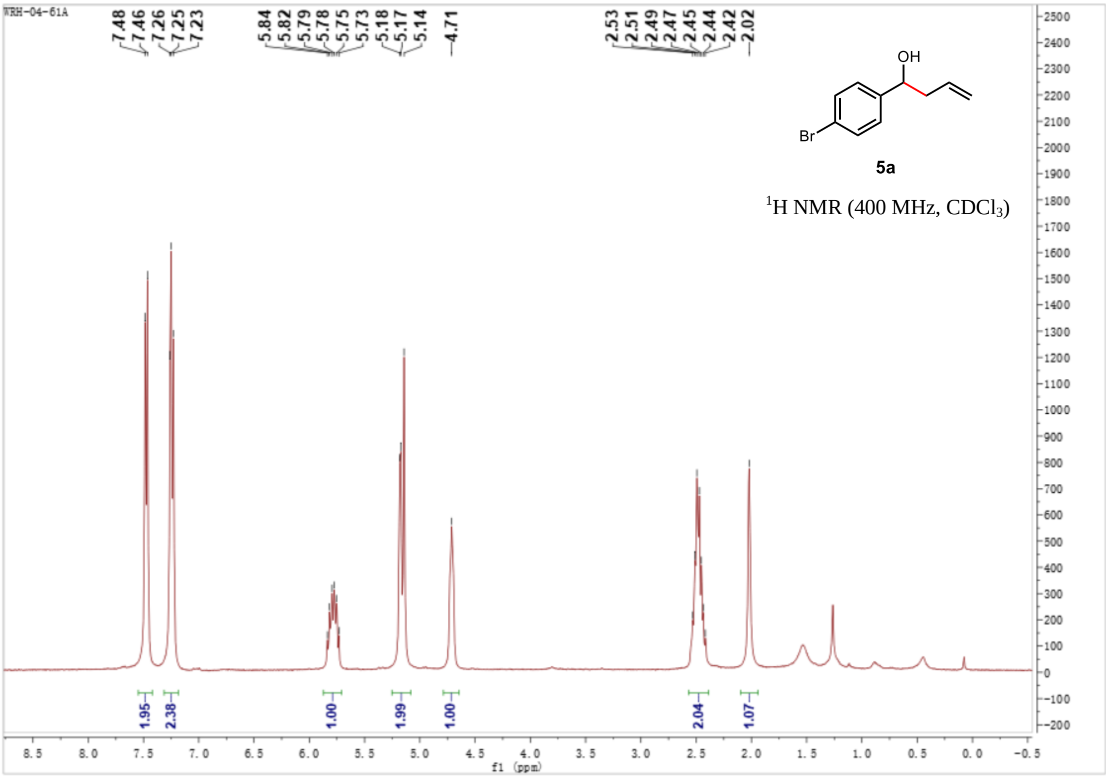
3a

^{1}H NMR (500 MHz, CDCl$_3$)



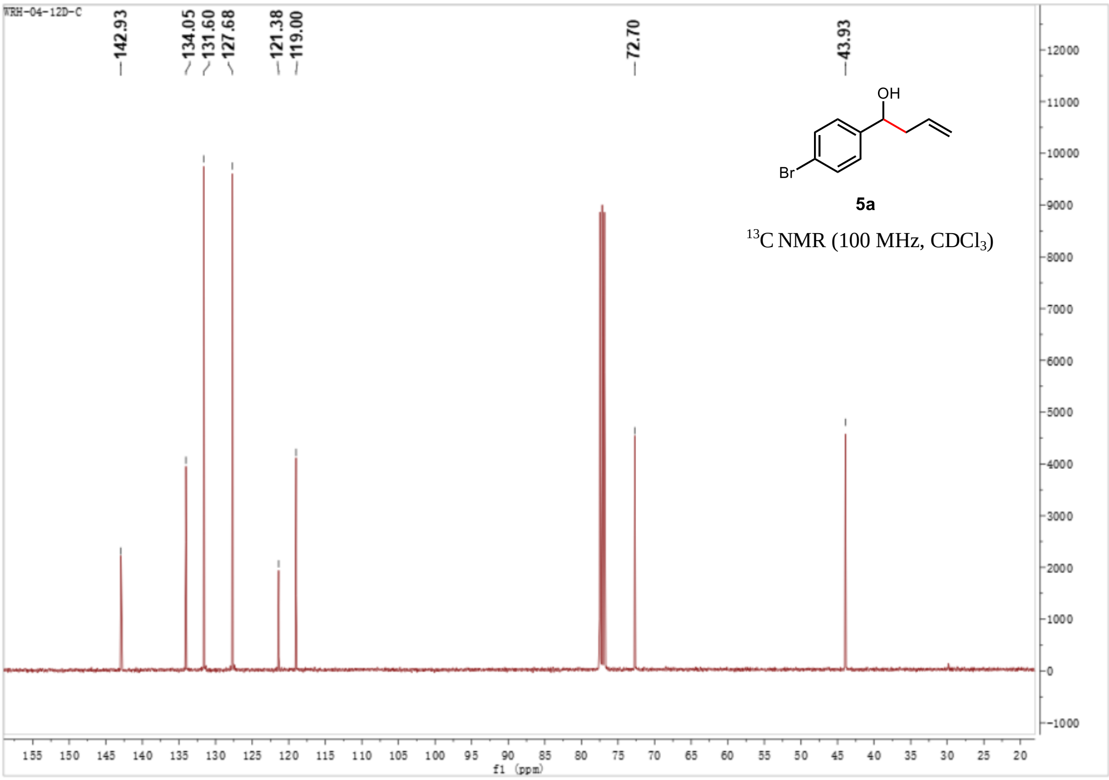
3a

^{13}C NMR (125 MHz, CDCl$_3$)



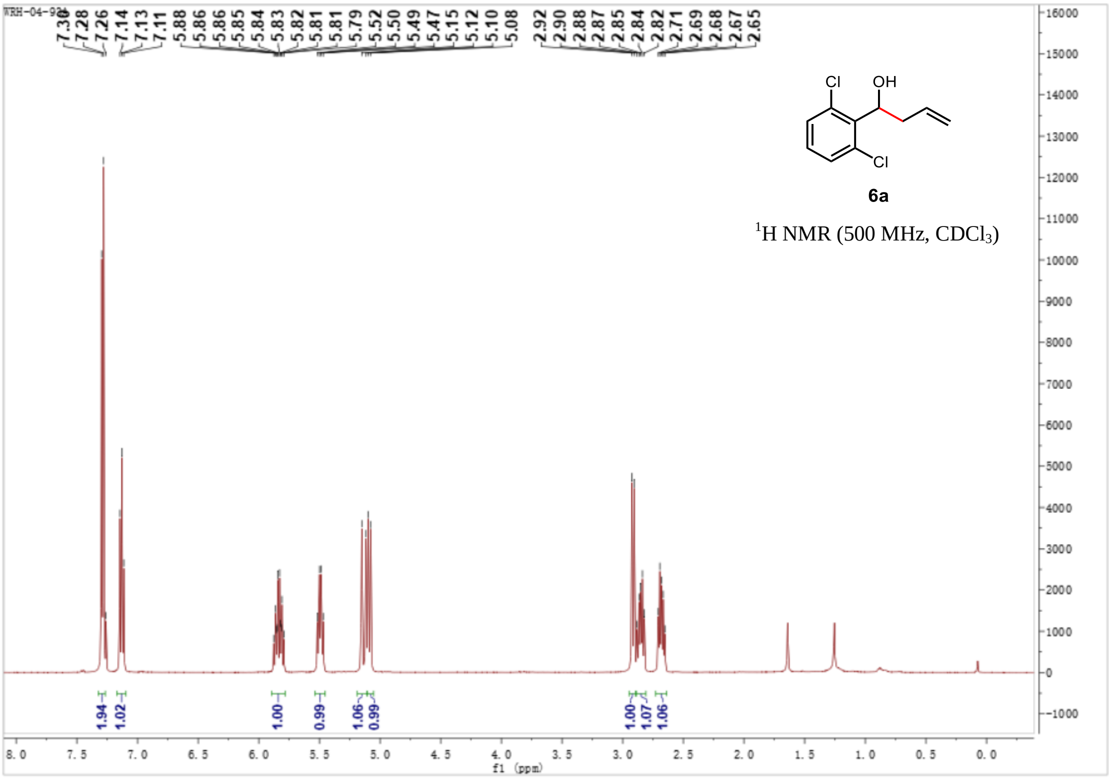
5a

^{1}H NMR (400 MHz, CDCl$_3$)



5a

^{13}C NMR (100 MHz, CDCl$_3$)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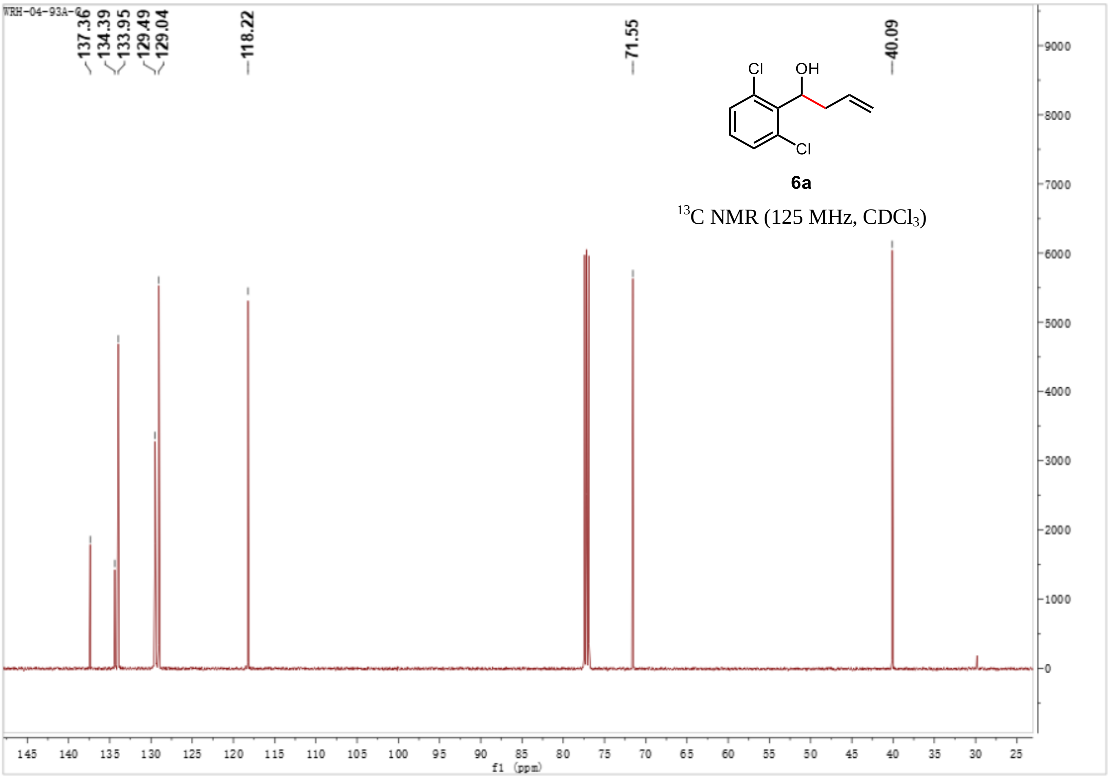
7.28
7.26
7.14
7.13
7.11
5.88
5.86
5.86
5.85
5.84
5.83
5.82
5.81
5.81
5.79
5.52
5.50
5.49
5.47
5.15
5.12
5.10
5.08
2.92
2.90
2.88
2.87
2.85
2.84
2.82
2.71
2.69
2.68
2.67
2.65
Cl
OH
Cl
6a
^{1}H NMR (500 MHz, CDCl$_3$)
1.94
1.02
1.00
0.99
1.06
0.99
1.00
1.07
1.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000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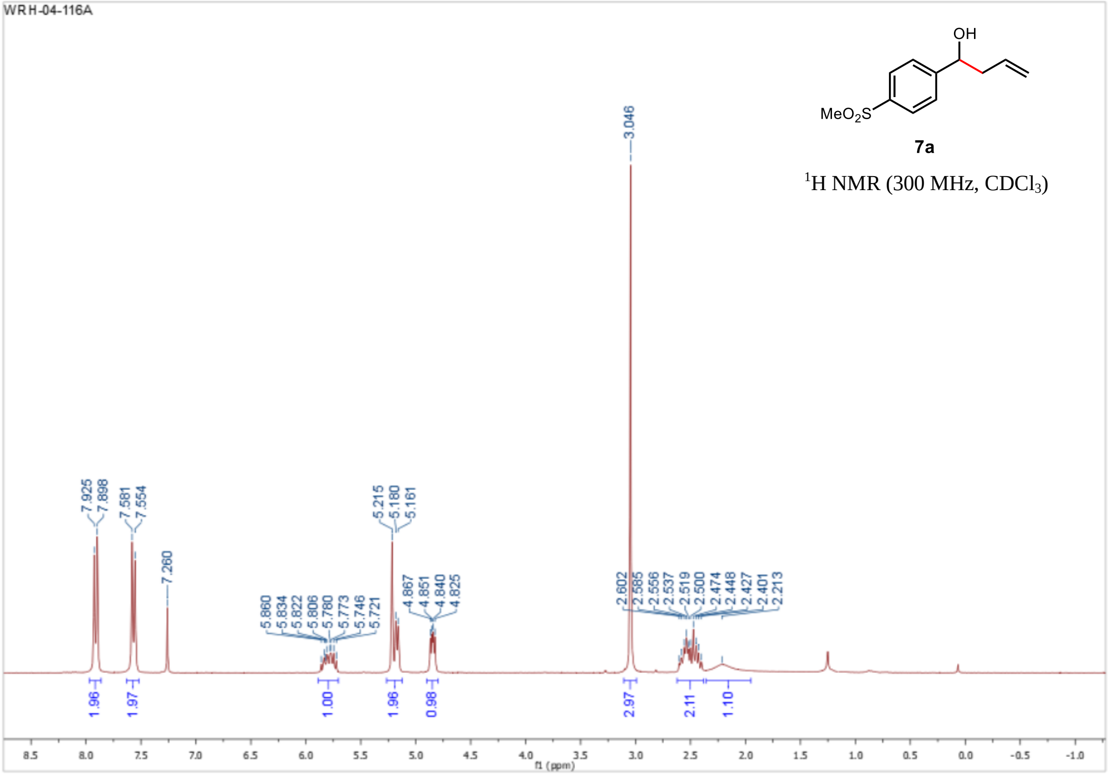
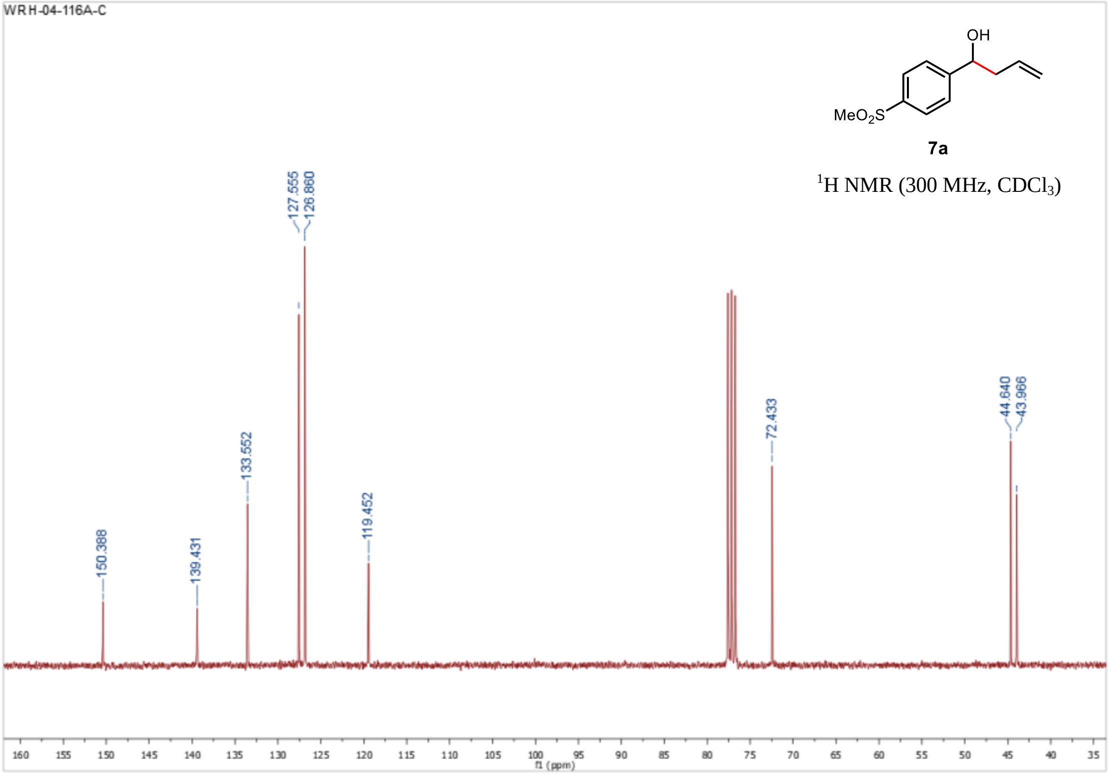
137.36
134.39
133.95
129.49
129.04
118.22
71.55
40.09
Cl
OH
Cl
6a
^{13}C NMR (125 MHz, CDCl$_3$)
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
f1 (ppm)
9000
8000
7000
6000
5000
4000
3000
2000
1000
0


WRH-04-116A
OH
MeO$_2$S
7a
^{1}H NMR (300 MHz, CDCl$_3$)
7.925
7.898
7.581
7.554
7.260
5.860
5.834
5.822
5.806
5.780
5.773
5.746
5.721
5.215
5.180
5.161
4.867
4.851
4.840
4.825
3.046
2.602
2.585
2.556
2.537
2.519
2.500
2.474
2.448
2.427
2.401
2.213
1.96
1.97
1.00
1.96
0.98
2.97
2.11
1.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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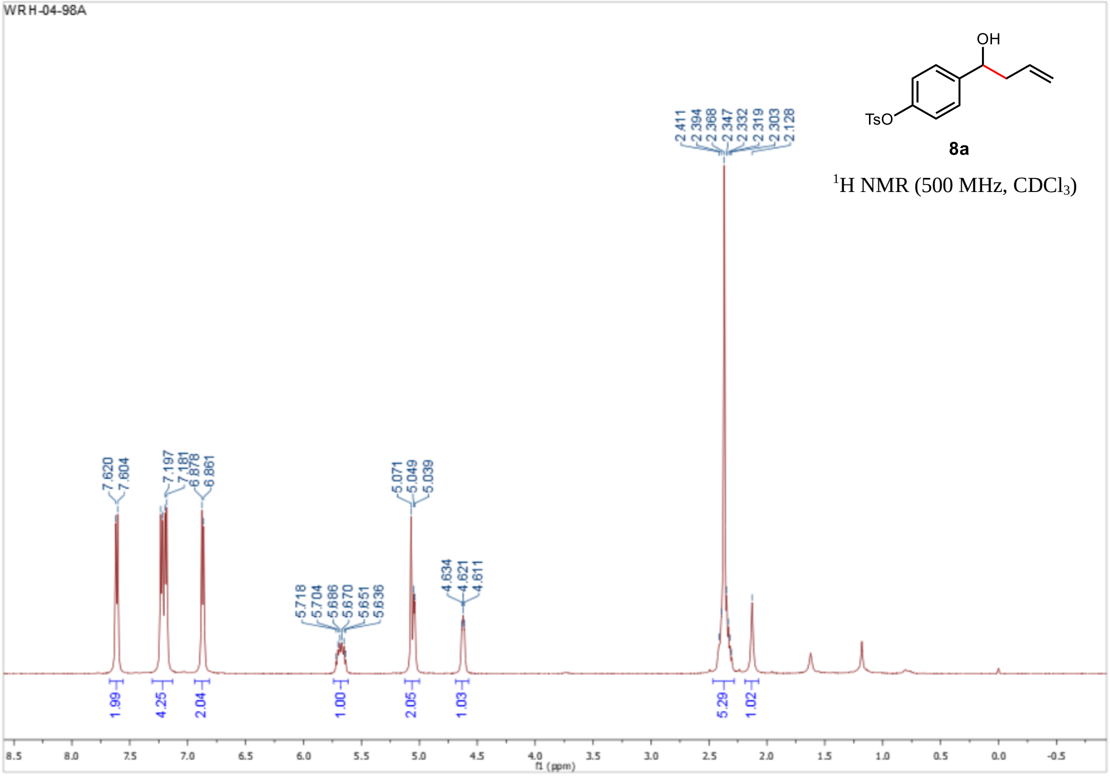
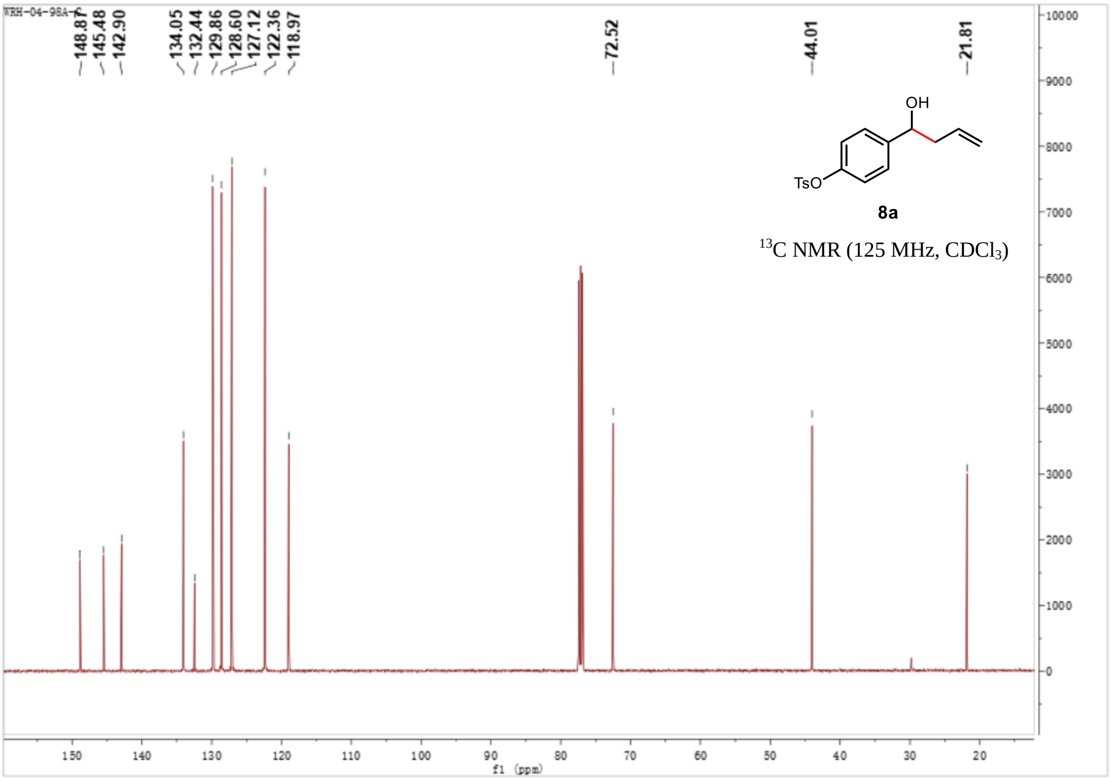
OH
MeO$_2$S
7a
^{1}H NMR (300 MHz, CDCl$_3$)
150.388
139.431
133.552
127.555
126.860
119.452
72.433
44.640
43.966
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
f1 (ppm)


WRH-04-98A
OH
TsO
8a
¹H NMR (500 MHz, CDCl₃)
7.620
7.604
7.197
7.181
6.878
6.861
5.718
5.704
5.686
5.670
5.651
5.636
5.071
5.049
5.039
4.634
4.621
4.611
2.411
2.394
2.368
2.347
2.332
2.319
2.303
2.128
1.99
4.25
2.04
1.00
2.05
1.03
5.29
1.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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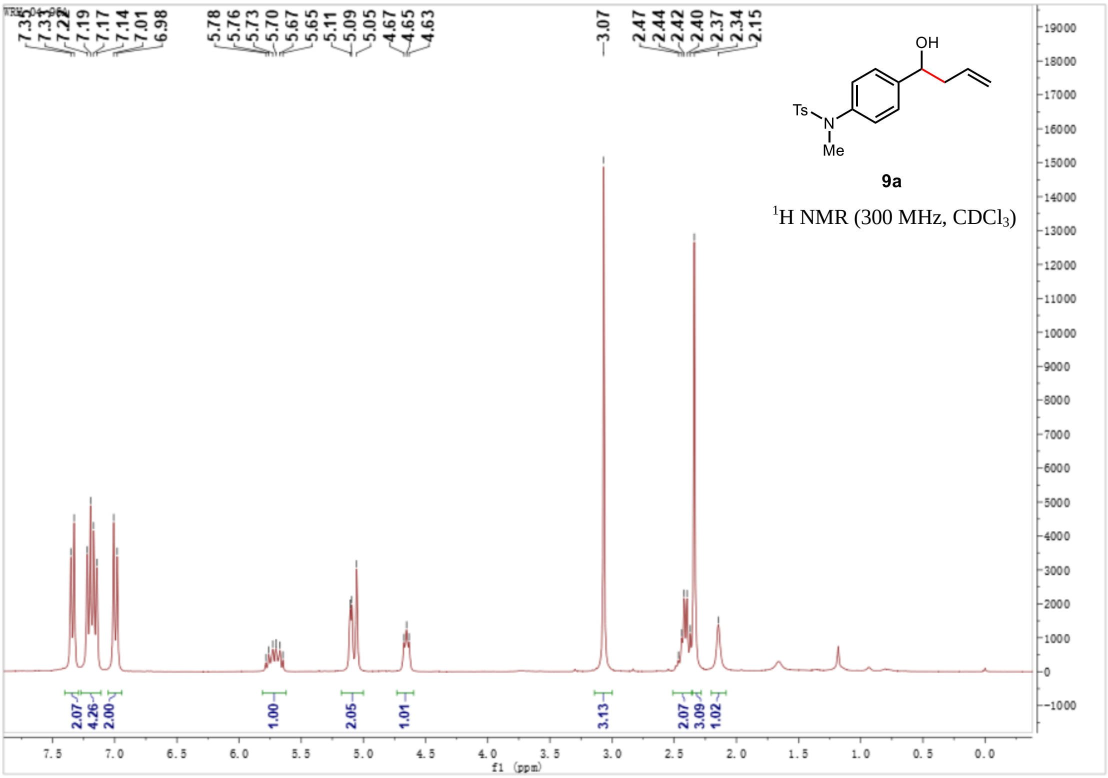
148.87
145.48
142.90
134.05
132.44
129.86
128.60
127.12
122.36
118.97
72.52
44.01
21.81
OH
TsO
8a
¹³C NMR (125 MHz, CDCl₃)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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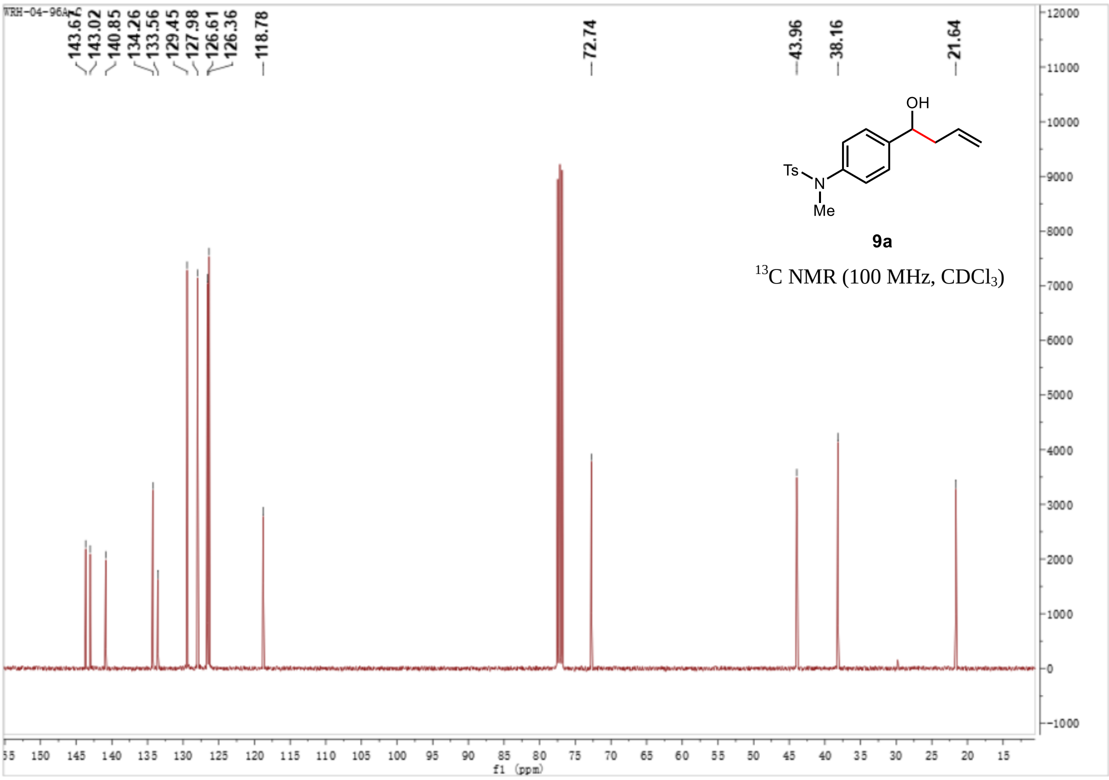
7.35
7.33
7.22
7.19
7.17
7.14
7.01
6.98
5.78
5.76
5.73
5.70
5.67
5.65
5.11
5.09
5.05
4.67
4.65
4.63
3.07
2.47
2.44
2.42
2.40
2.37
2.34
2.15
OH
Ts
N
Me
9a
¹H NMR (300 MHz, CDCl₃)
2.07
4.26
2.00
1.00
2.05
1.01
3.13
2.07
3.09
1.02
f1 (ppm)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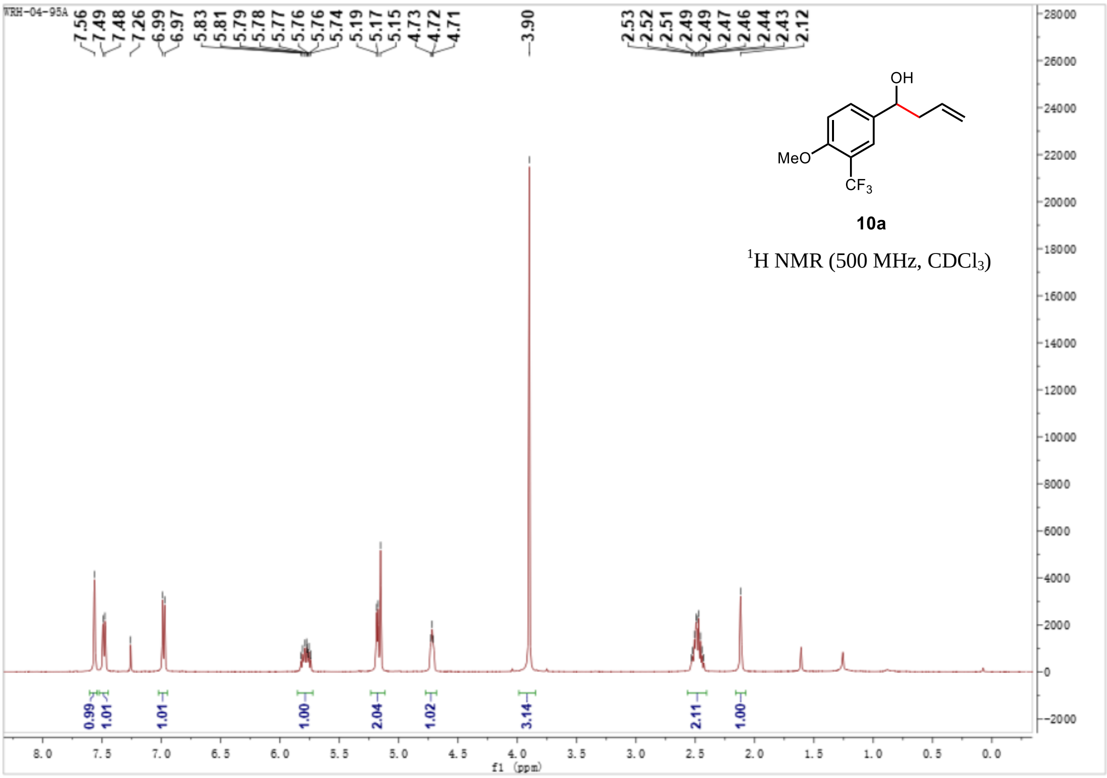
143.02
140.85
134.26
133.56
129.45
127.98
126.61
126.36
118.78
72.74
43.96
38.16
21.64
OH
Ts
N
Me
9a
¹³C NMR (100 MHz, CDCl₃)
f1 (ppm)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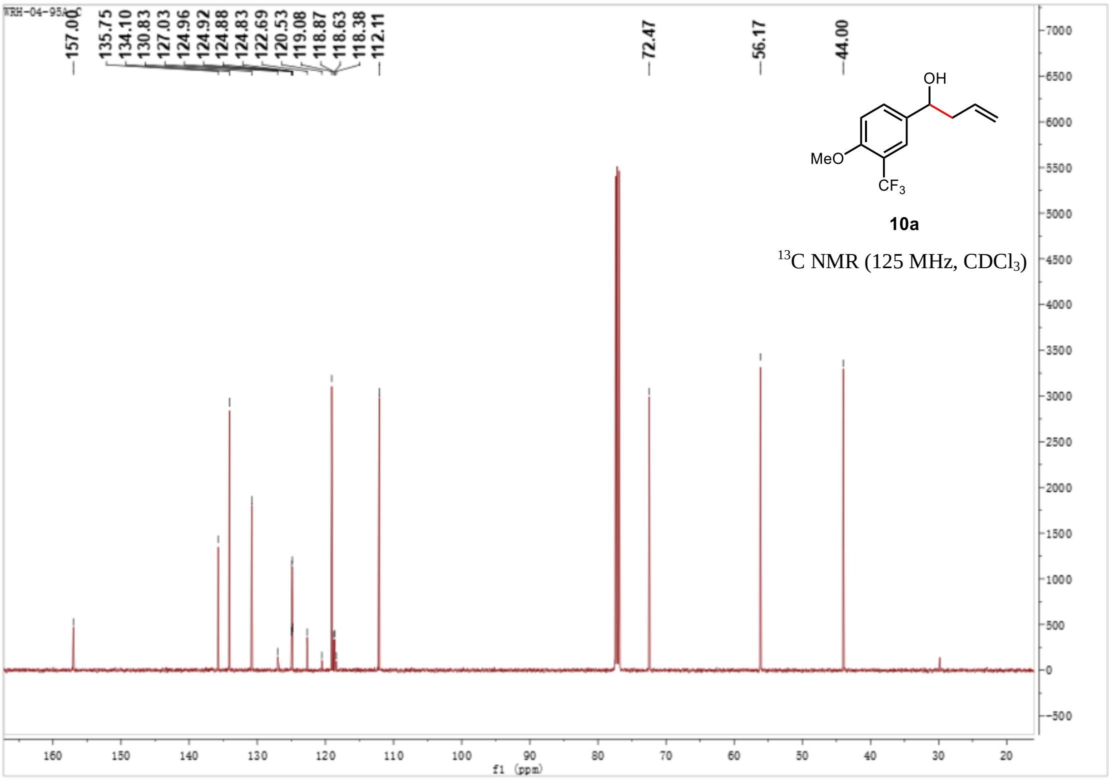
7.56
7.49
7.48
7.26
6.99
6.97
5.83
5.81
5.79
5.78
5.77
5.76
5.76
5.74
5.19
5.17
5.15
4.73
4.72
4.71
3.90
2.53
2.52
2.51
2.49
2.49
2.47
2.46
2.44
2.43
2.12
OH
MeO
CF3
10a
1H NMR (500 MHz, CDCl3)
0.99
1.01
1.01
1.00
2.04
1.02
3.14
2.11
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000


WRH-04-95A-C
157.00
135.75
134.10
130.83
127.03
124.96
124.92
124.88
124.83
122.69
120.53
119.08
118.87
118.63
118.38
112.11
72.47
56.17
44.00
OH
MeO
CF3
10a
13C NMR (125 MHz, CDCl3)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)
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6000
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5000
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3000
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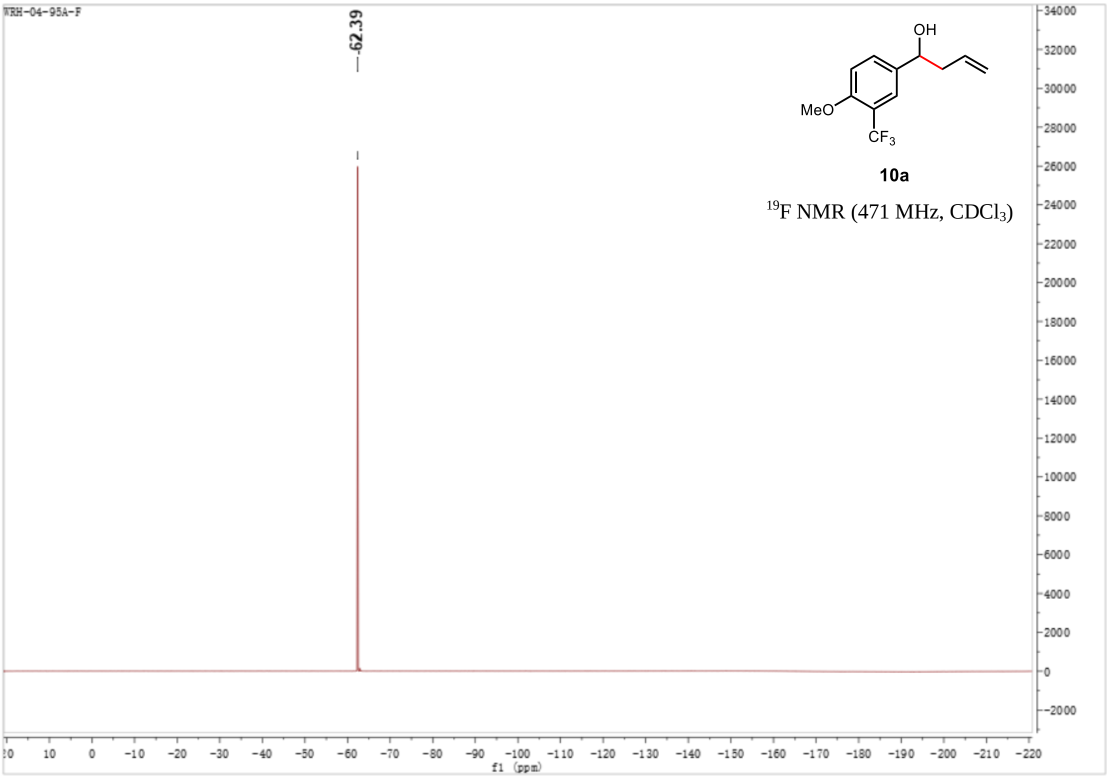
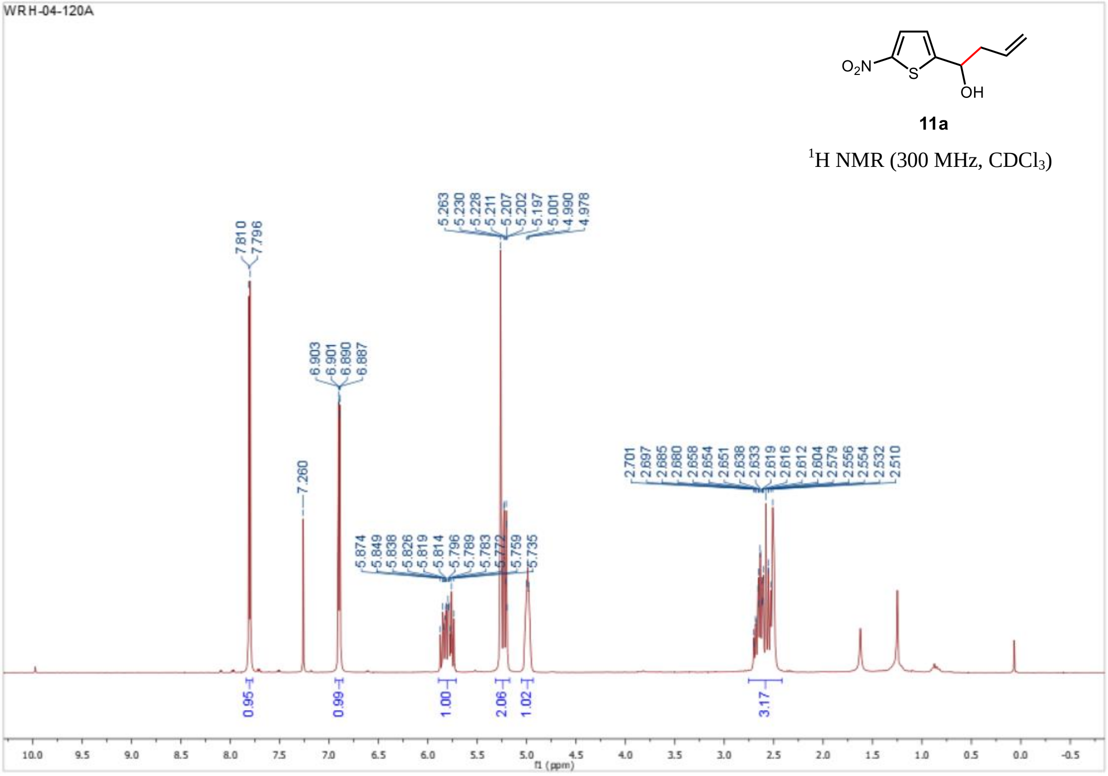
2000
1500
1000
500
0
-500



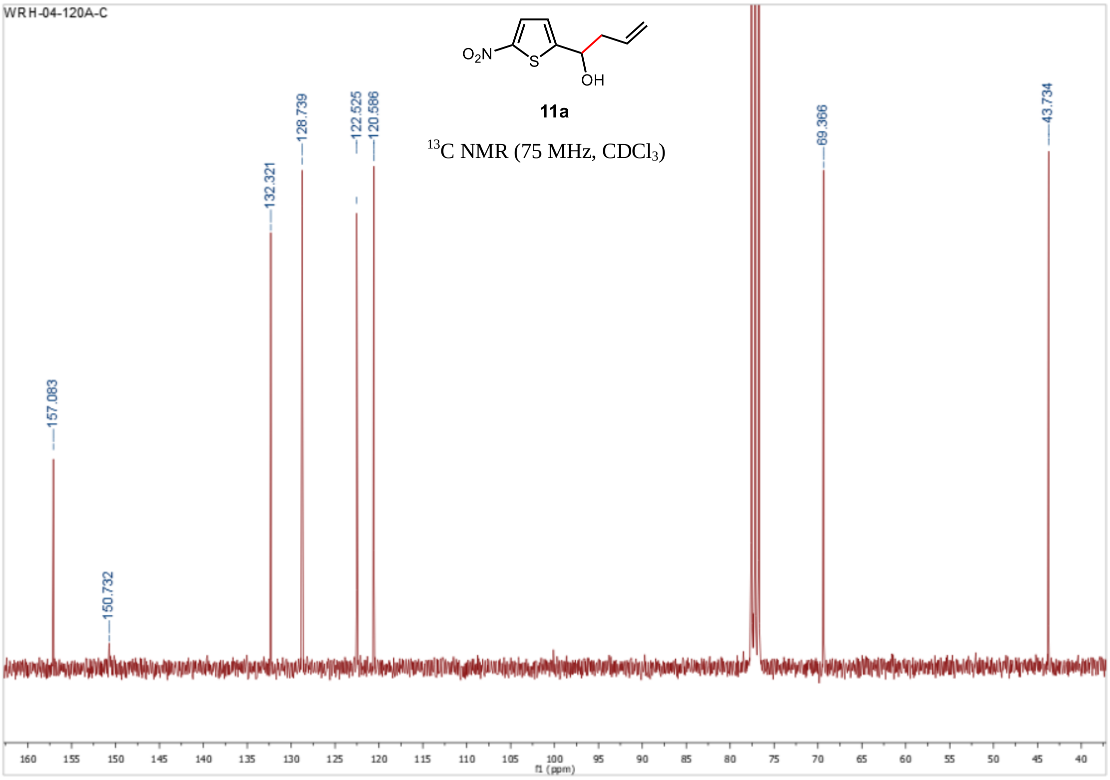
10a

^{19}F NMR (471 MHz, $CDCl_3$)



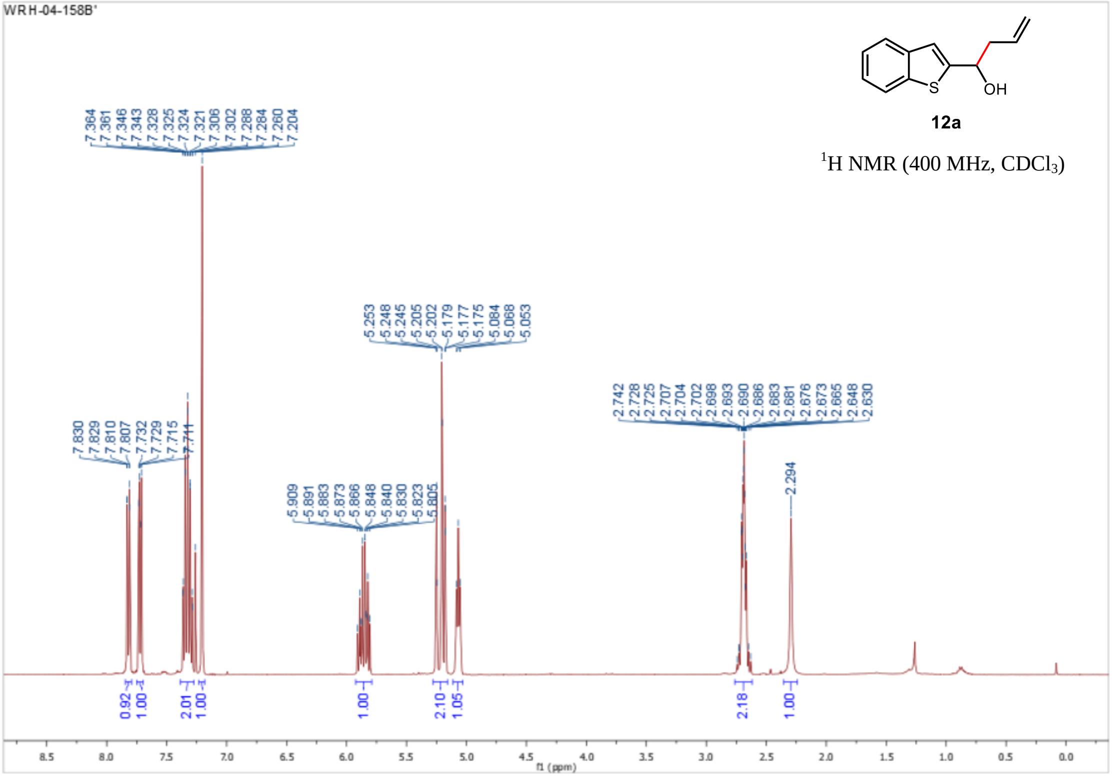
11a

^{1}H NMR (300 MHz, $CDCl_3$)



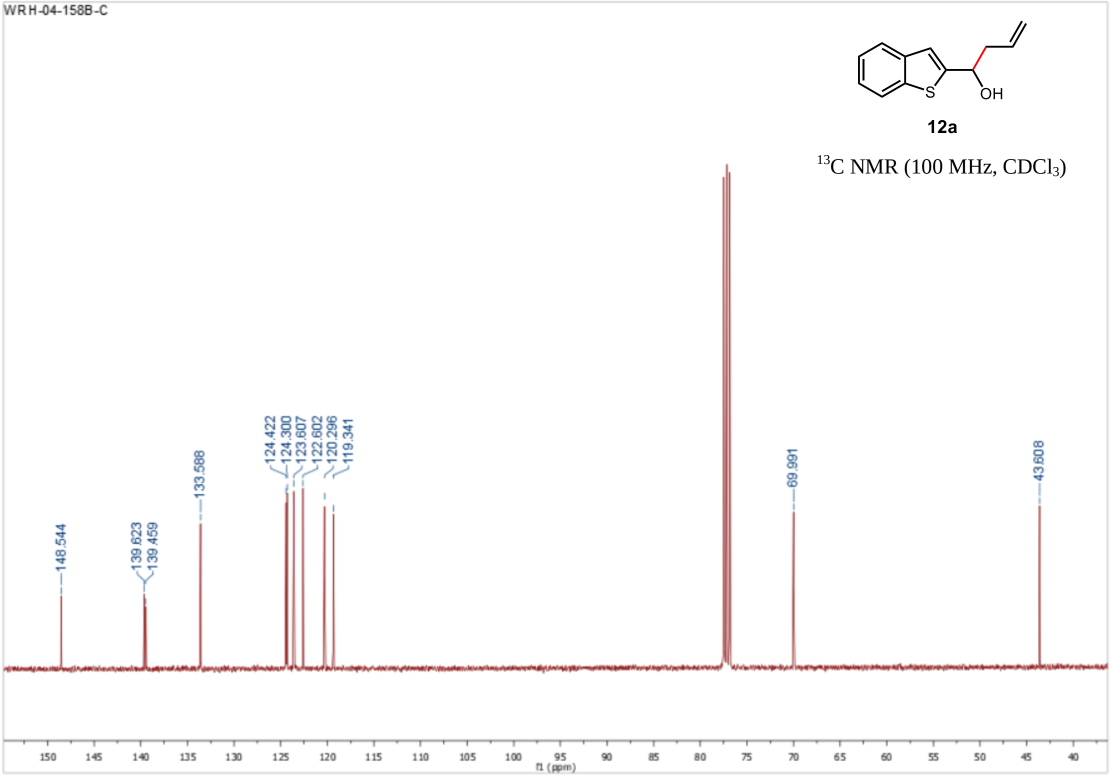
11a

^{13}C NMR (75 MHz, $CDCl_3$)



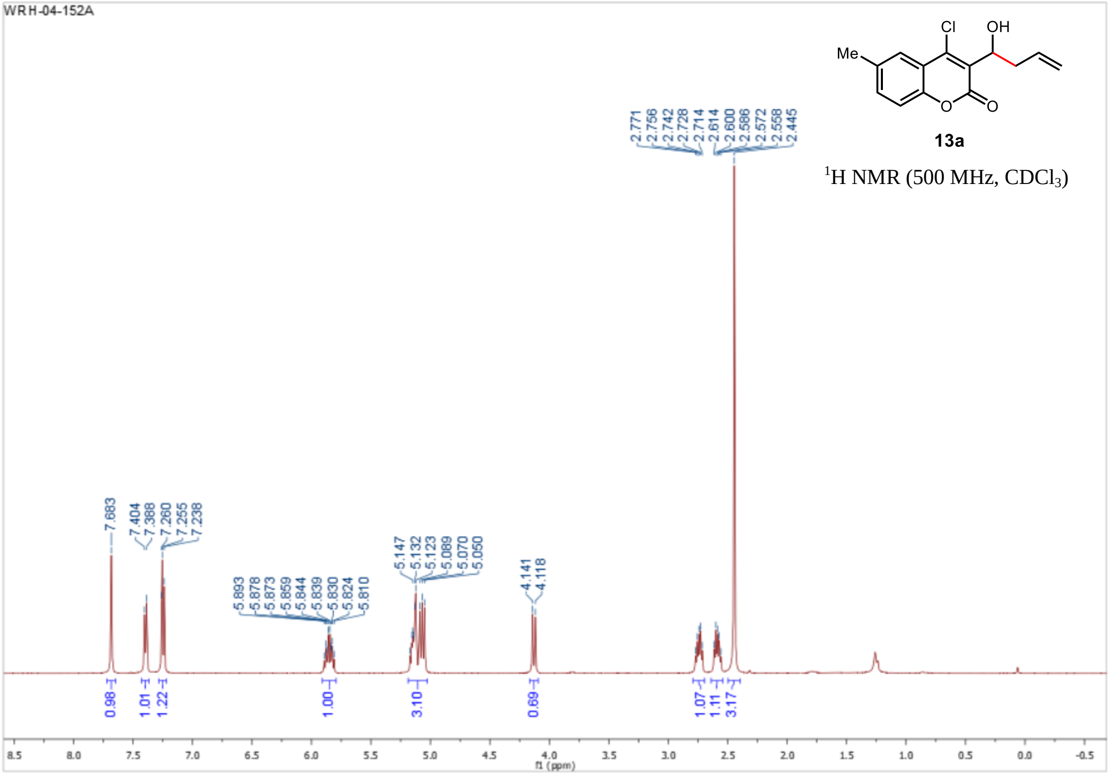
12a

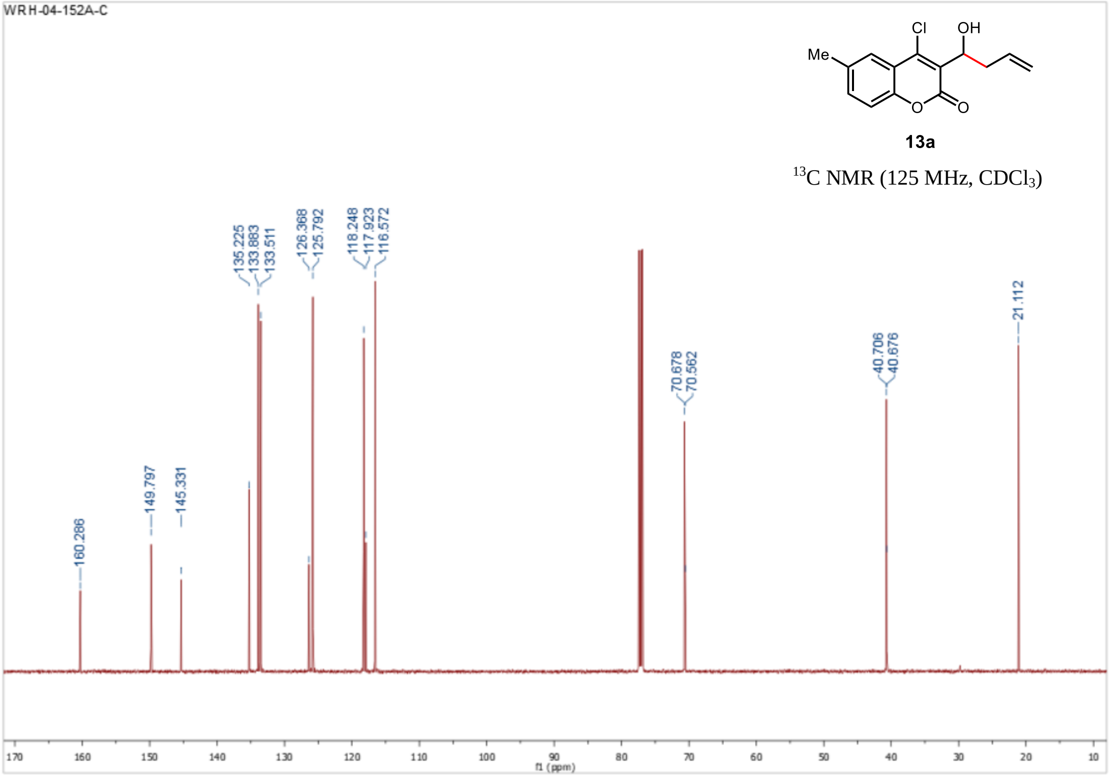
^{1}H NMR (400 MHz, CDCl$_3$)

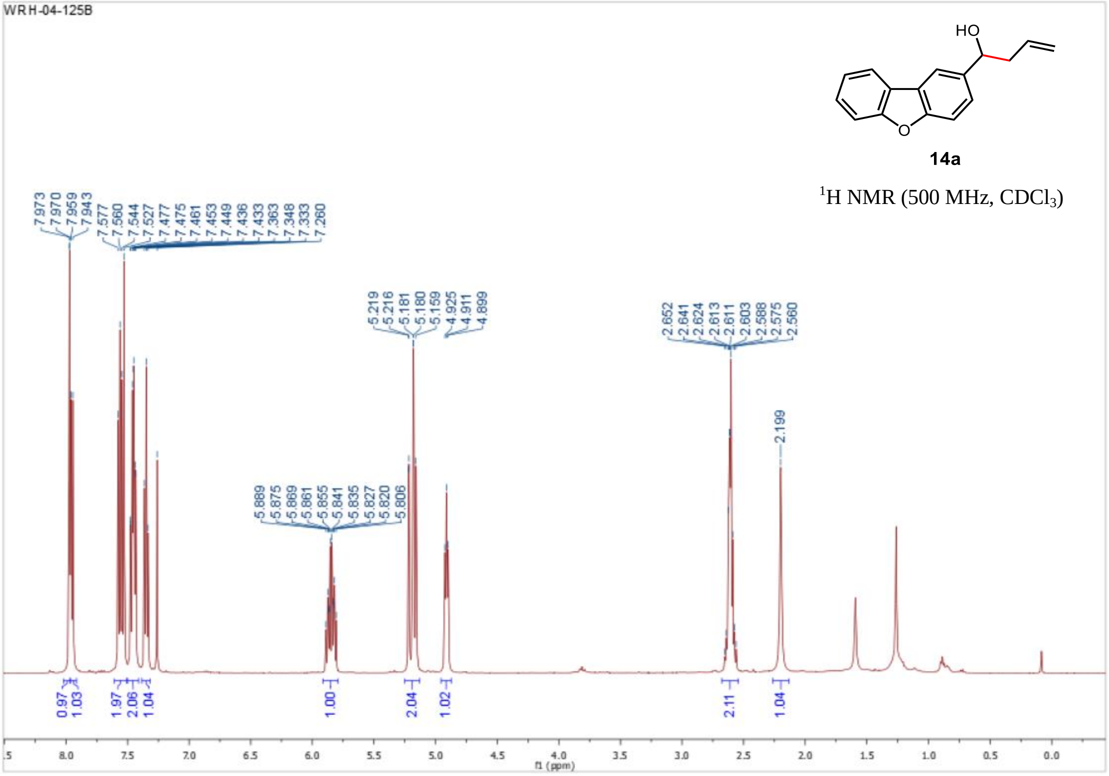


12a

^{13}C NMR (100 MHz, CDCl$_3$)

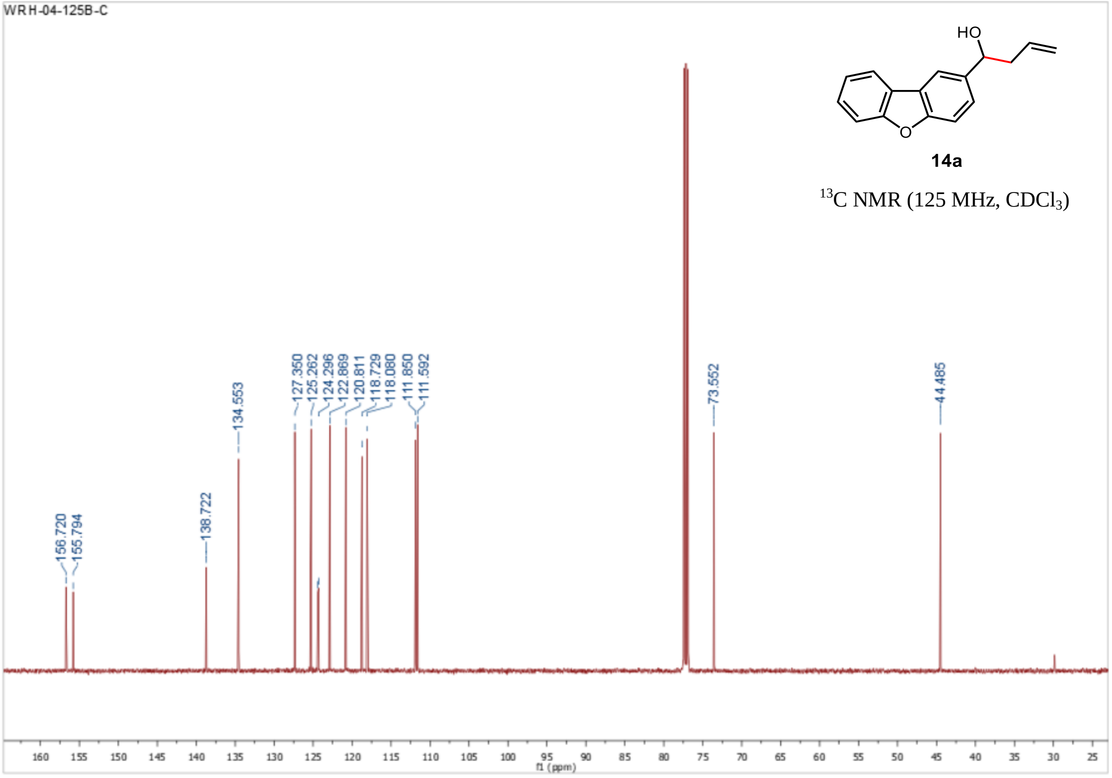

WRH-04-152A
Cl
OH
Me
O
O
13a
^{1}H NMR (500 MHz, CDCl$_3$)
7.683
7.404
7.388
7.260
7.255
7.238
5.893
5.878
5.873
5.859
5.844
5.839
5.830
5.824
5.810
5.147
5.132
5.123
5.089
5.070
5.050
4.141
4.118
2.771
2.756
2.742
2.728
2.714
2.614
2.600
2.586
2.572
2.558
2.445
0.98
1.01
1.22
1.00
3.10
0.69
1.07
1.11
3.17
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


WRH-04-152A-C
Cl
OH
Me
O
O
13a
^{13}C NMR (125 MHz, CDCl$_3$)
160.286
149.797
145.331
135.225
133.883
133.511
126.368
125.792
118.248
117.923
116.572
70.678
70.562
40.706
40.676
21.112
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



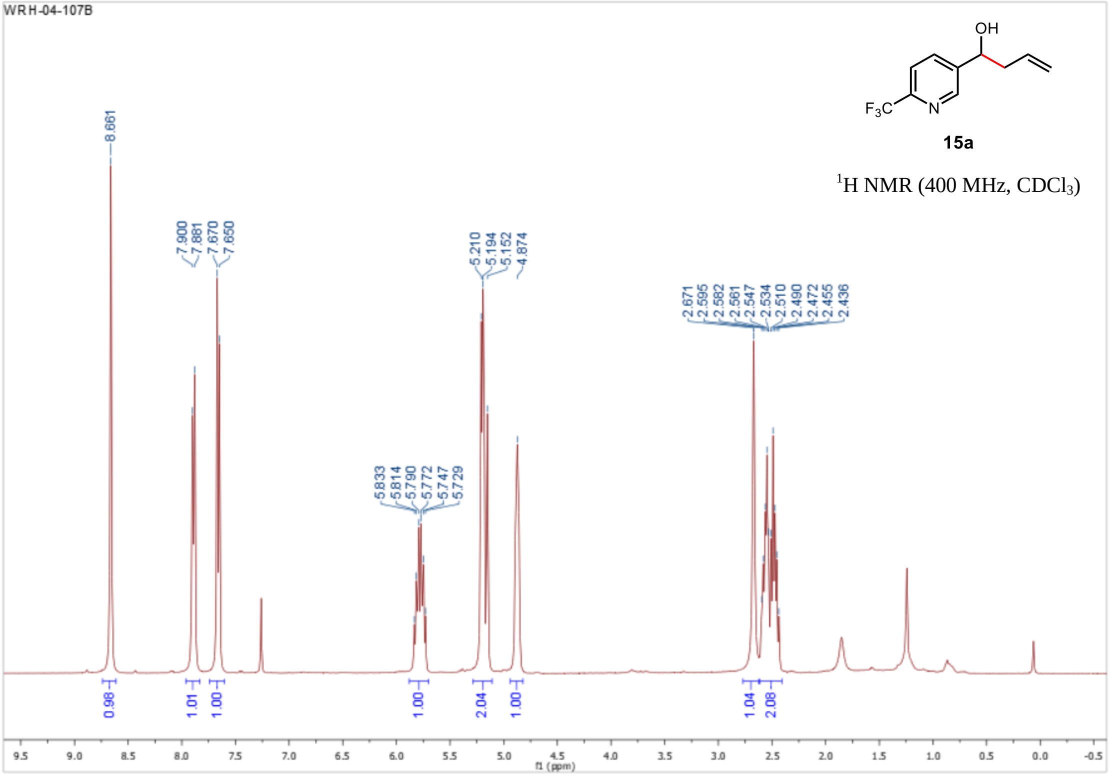
14a

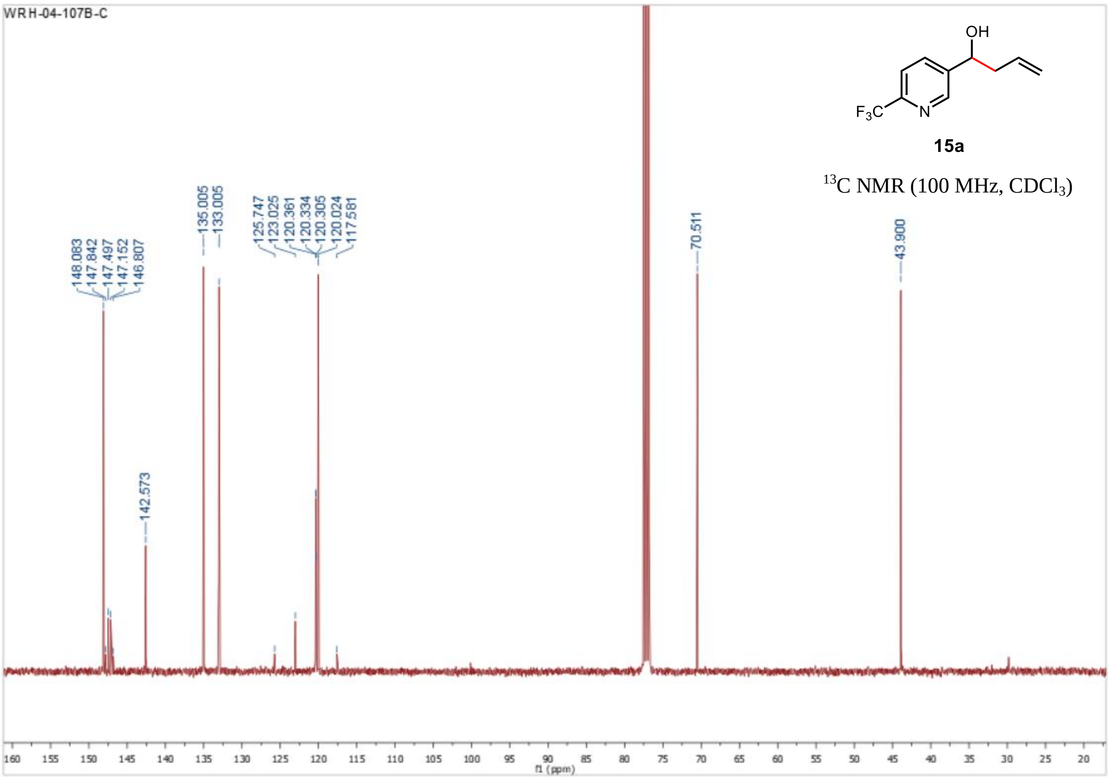
^{1}H NMR (500 MHz, $CDCl_3$)

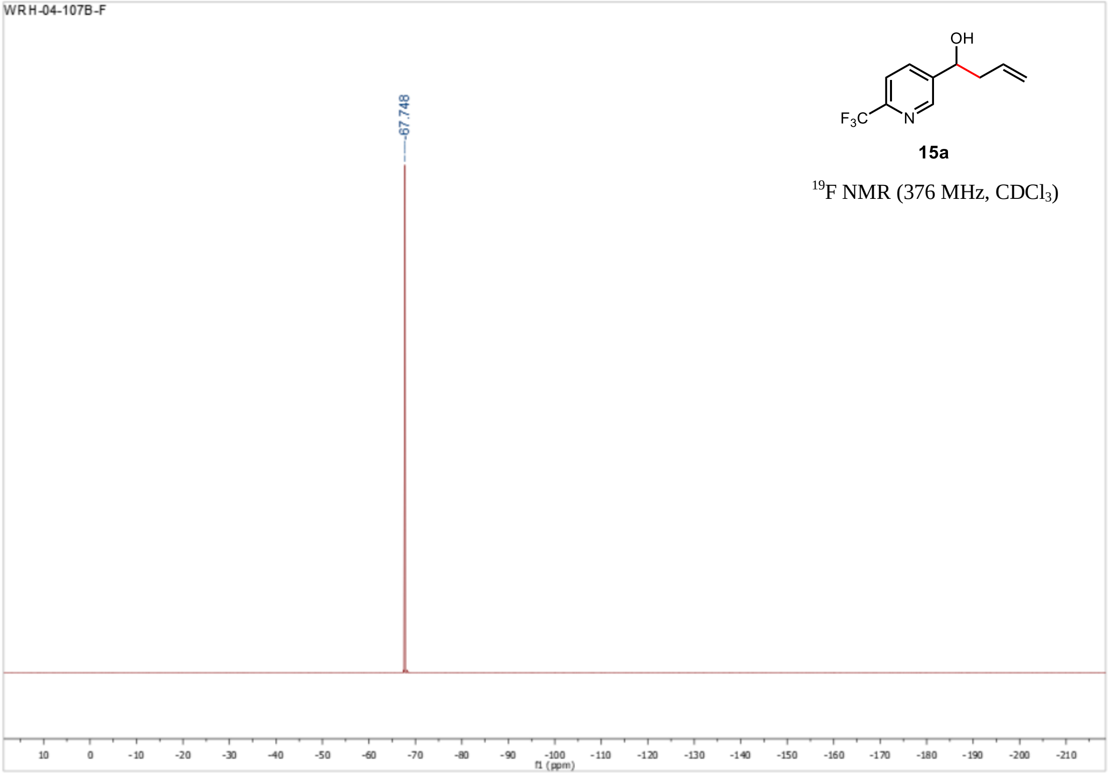


14a

^{13}C NMR (125 MHz, $CDCl_3$)

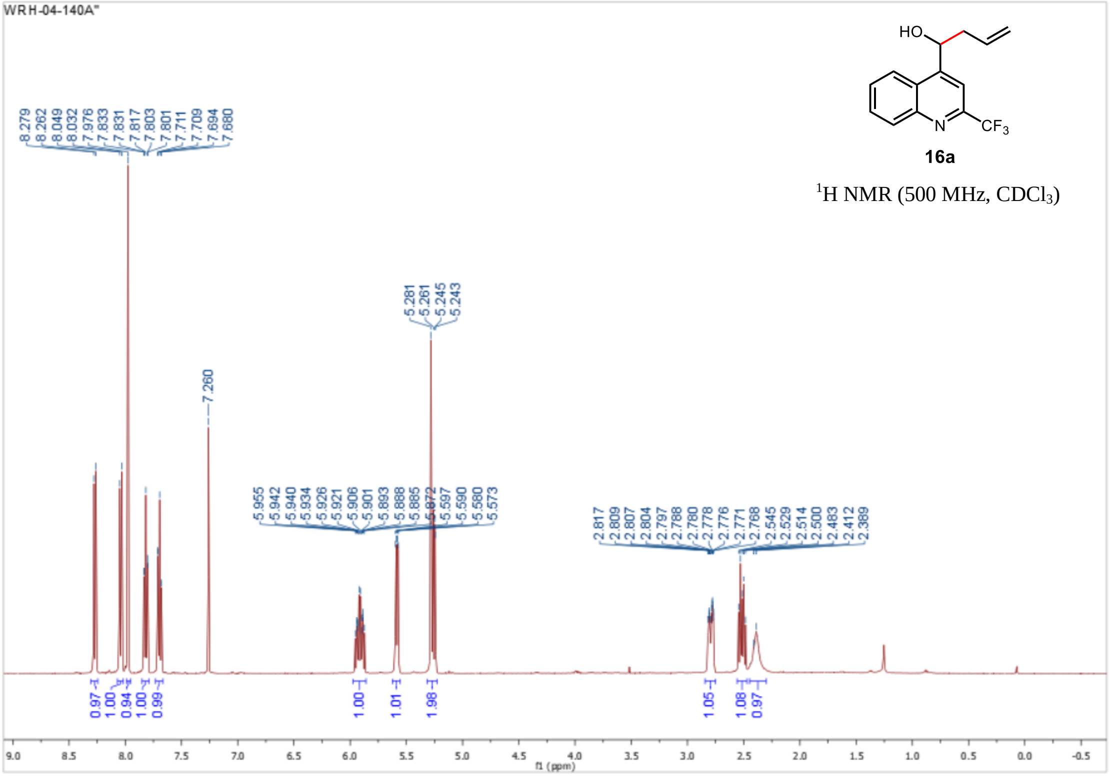

WRH-04-107B
OH
F3C
N
15a
1H NMR (400 MHz, CDCl3)
8.661
7.900
7.881
7.670
7.650
5.833
5.814
5.790
5.772
5.747
5.729
5.210
5.194
5.152
4.874
2.671
2.595
2.582
2.561
2.547
2.534
2.510
2.490
2.472
2.455
2.436
0.98
1.01
1.00
1.00
2.04
1.00
1.04
2.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


WRH-04-107B-C
OH
F3C
N
15a
13C NMR (100 MHz, CDCl3)
148.083
147.842
147.497
147.152
146.807
142.573
135.005
133.005
125.747
123.025
120.361
120.334
120.305
120.024
117.581
70.511
43.900
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)



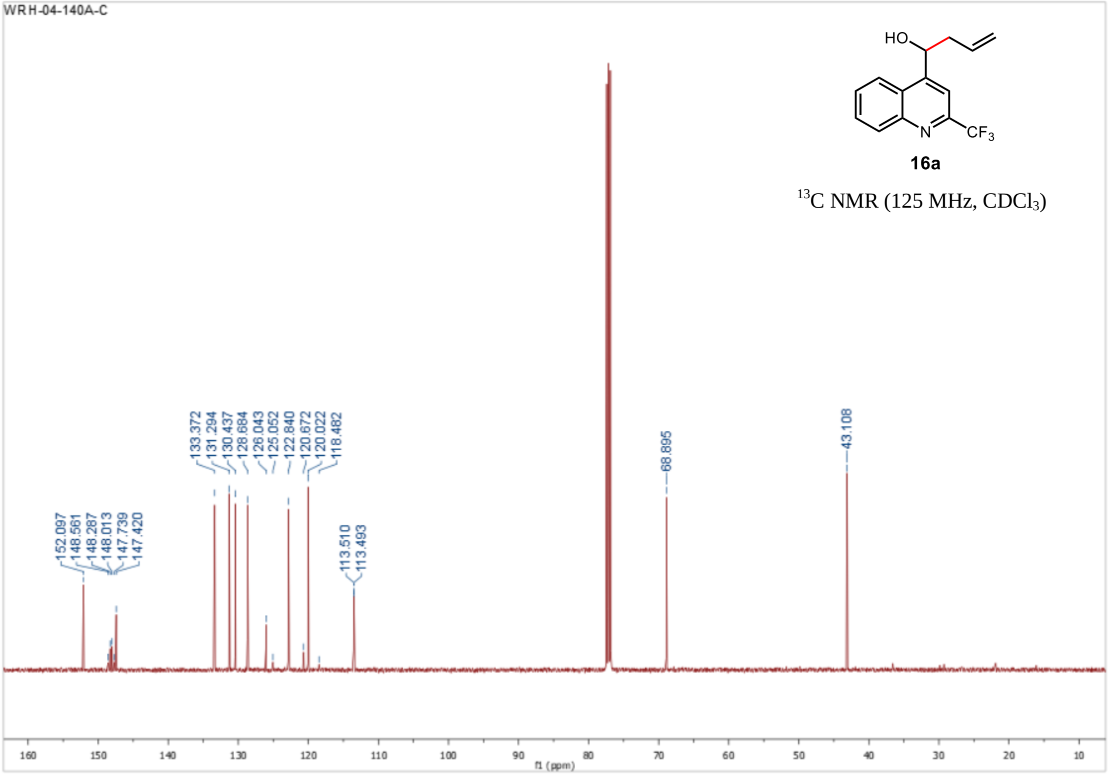
15a

^{19}F NMR (376 MHz, CDCl$_3$)



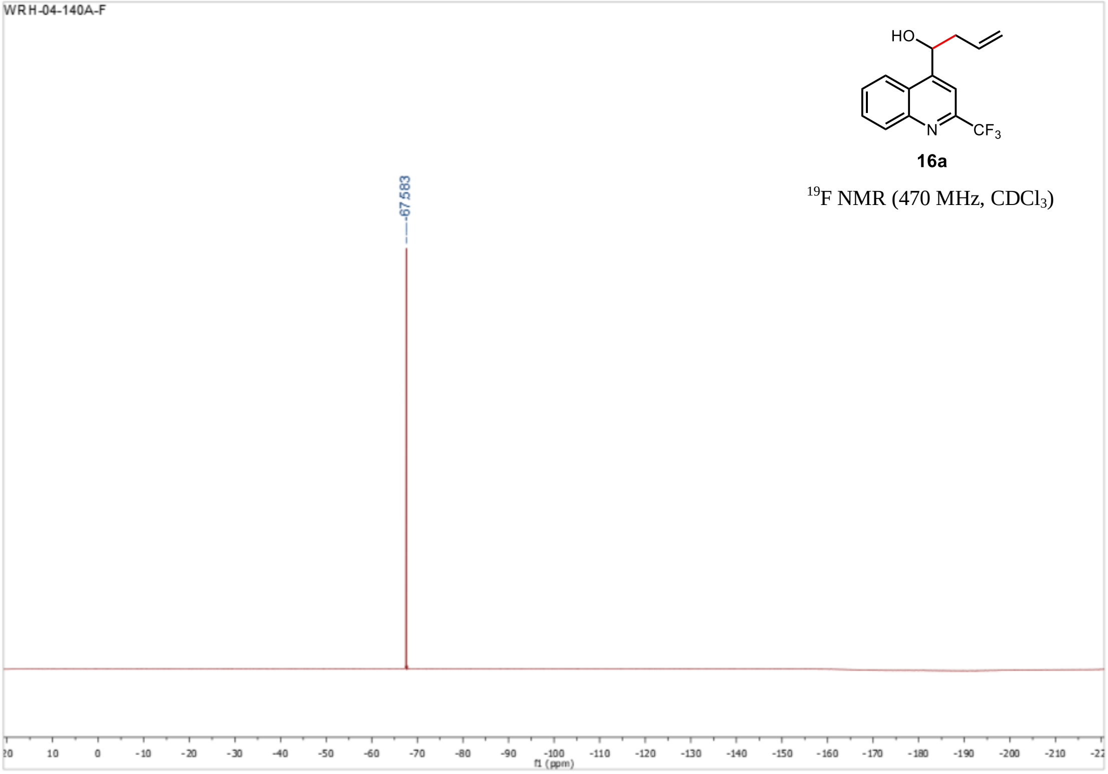
16a

^{1}H NMR (500 MHz, CDCl$_3$)



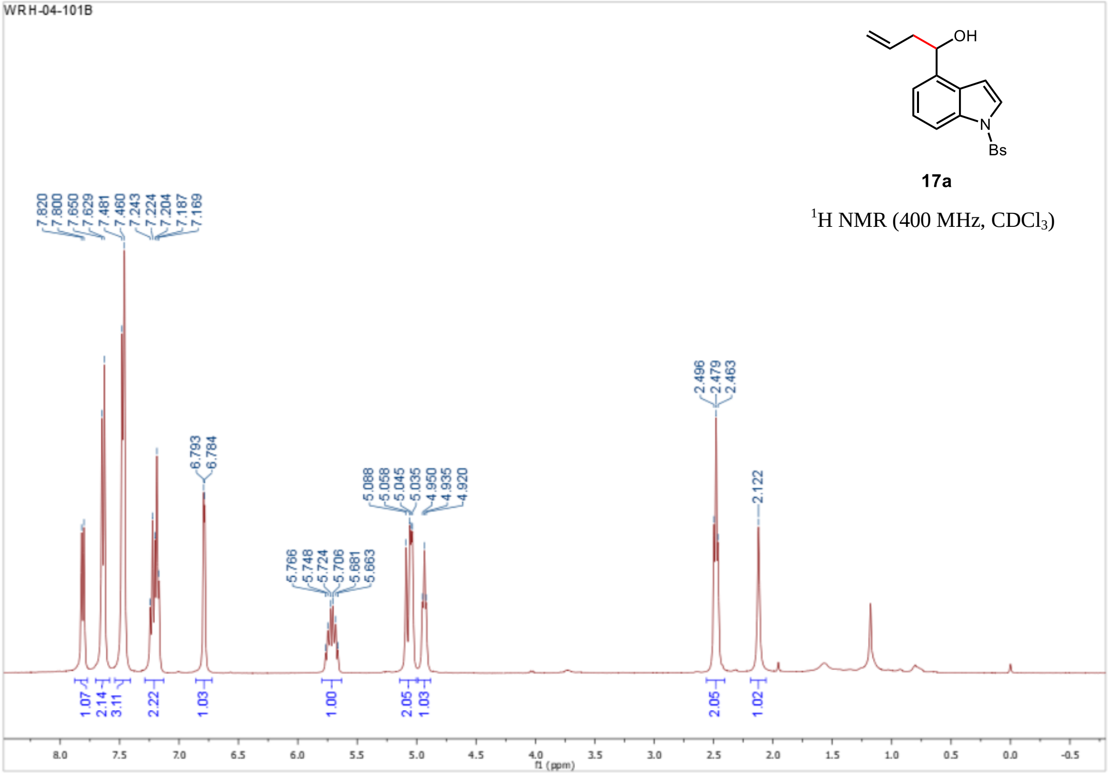
16a

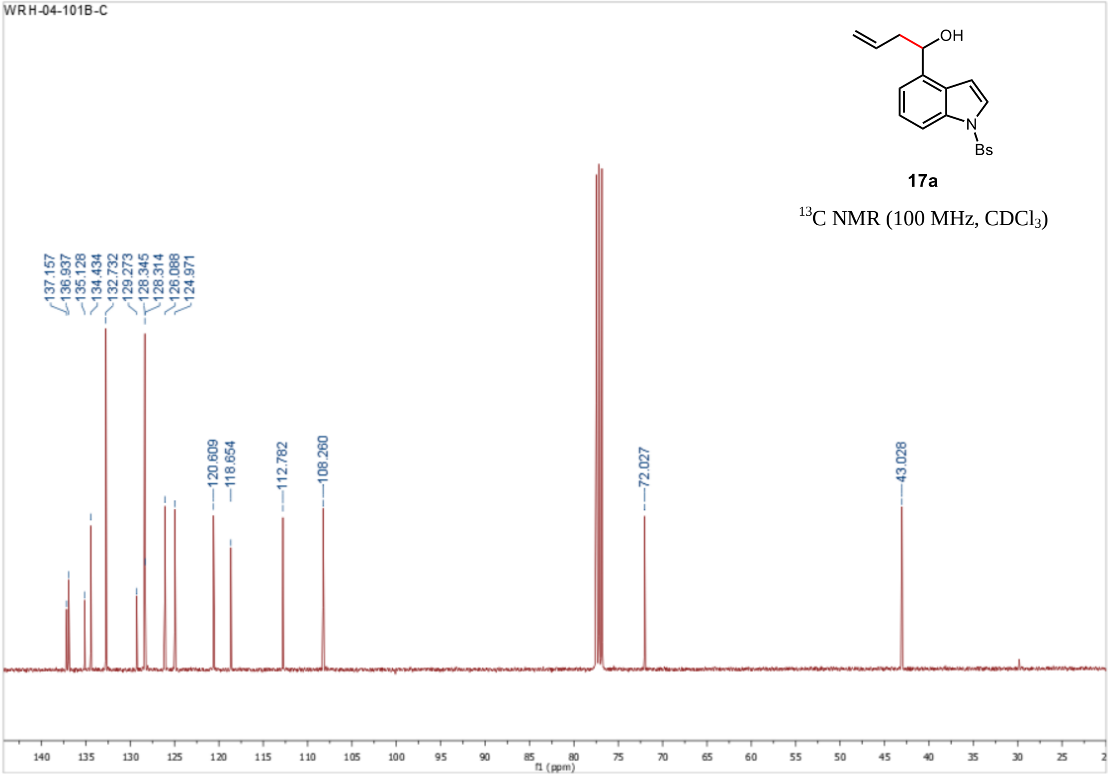
^{13}C NMR (125 MHz, CDCl$_3$)

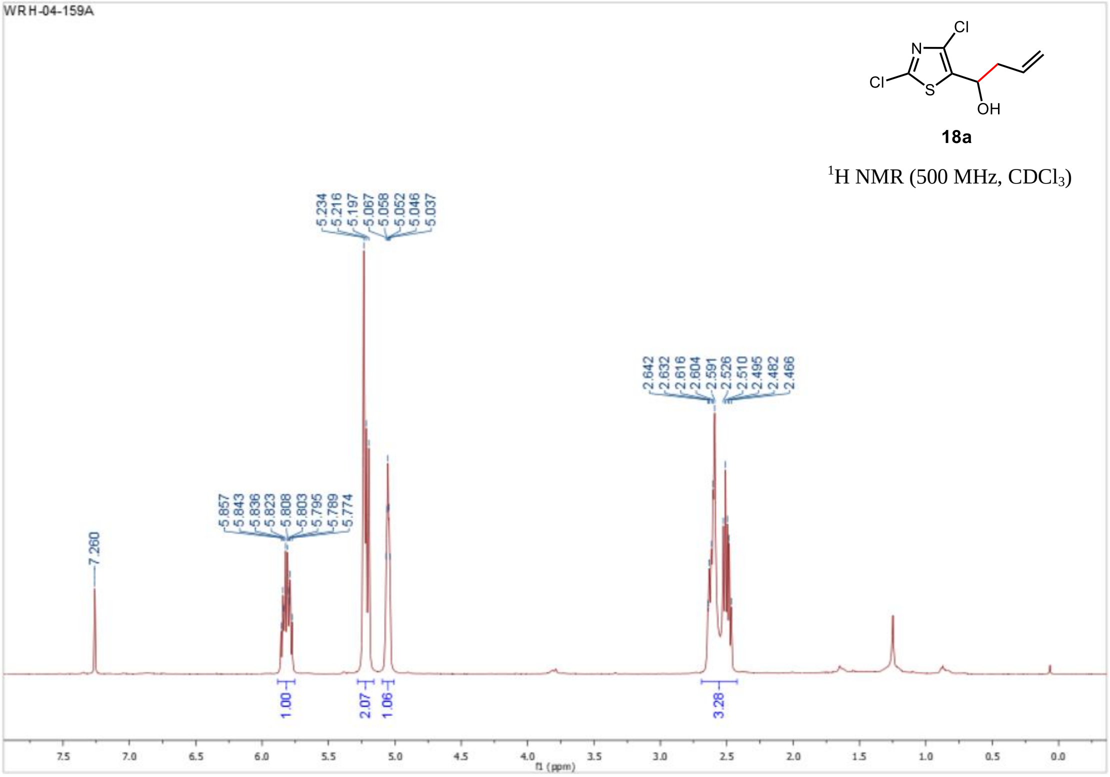


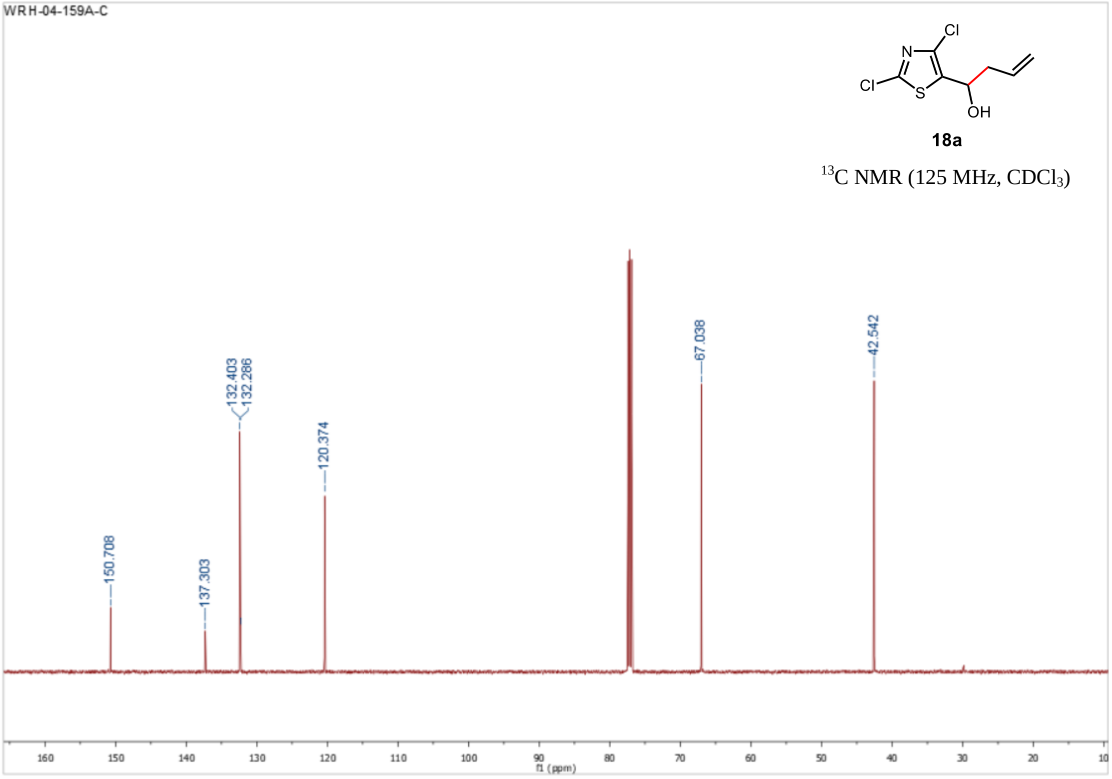
16a

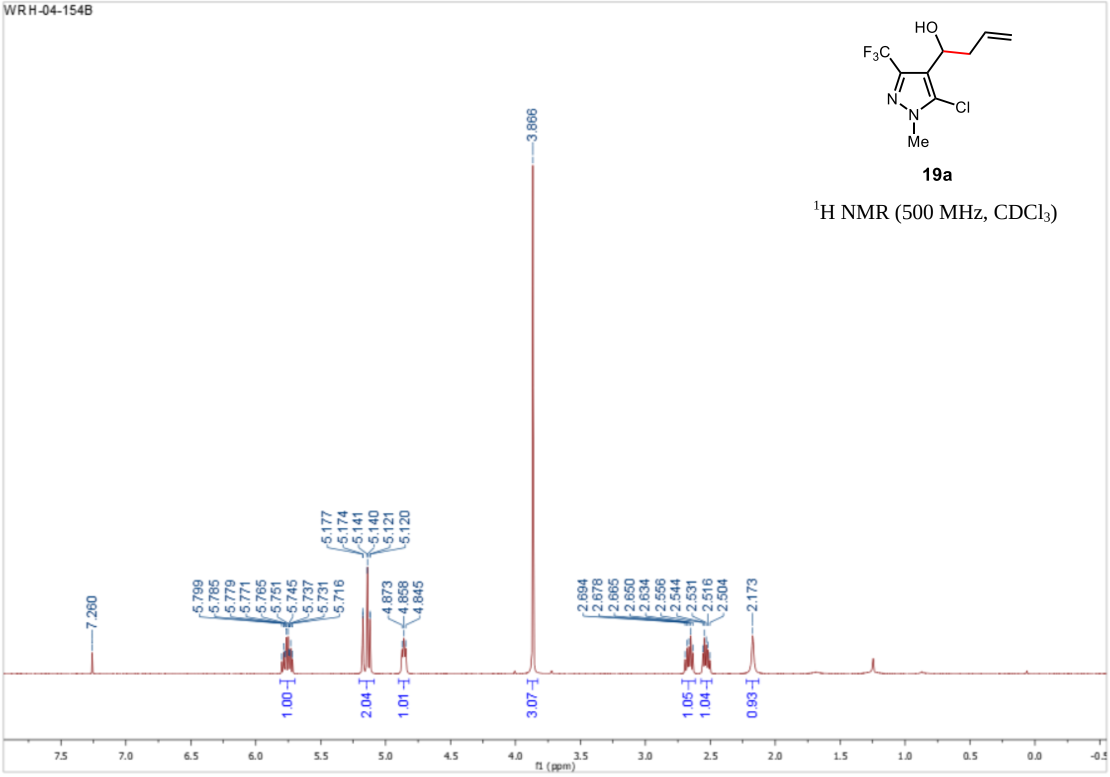
^{19}F NMR (470 MHz, CDCl$_3$)


WRH-04-101B
OH
N
Bs
17a
^{1}H NMR (400 MHz, CDCl$_3$)
7.820
7.800
7.650
7.629
7.481
7.460
7.243
7.224
7.204
7.187
7.169
6.793
6.784
5.766
5.748
5.724
5.706
5.681
5.663
5.088
5.058
5.045
5.035
4.950
4.935
4.920
2.496
2.479
2.463
2.122
1.07
2.14
3.11
2.22
1.03
1.00
2.05
1.03
2.05
1.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


WRH-04-101B-C
OH
N
Bs
17a
^{13}C NMR (100 MHz, CDCl$_3$)
137.157
136.937
135.128
134.434
132.732
129.273
128.345
128.314
126.088
124.971
120.609
118.654
112.782
108.260
72.027
43.028
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
f1 (ppm)

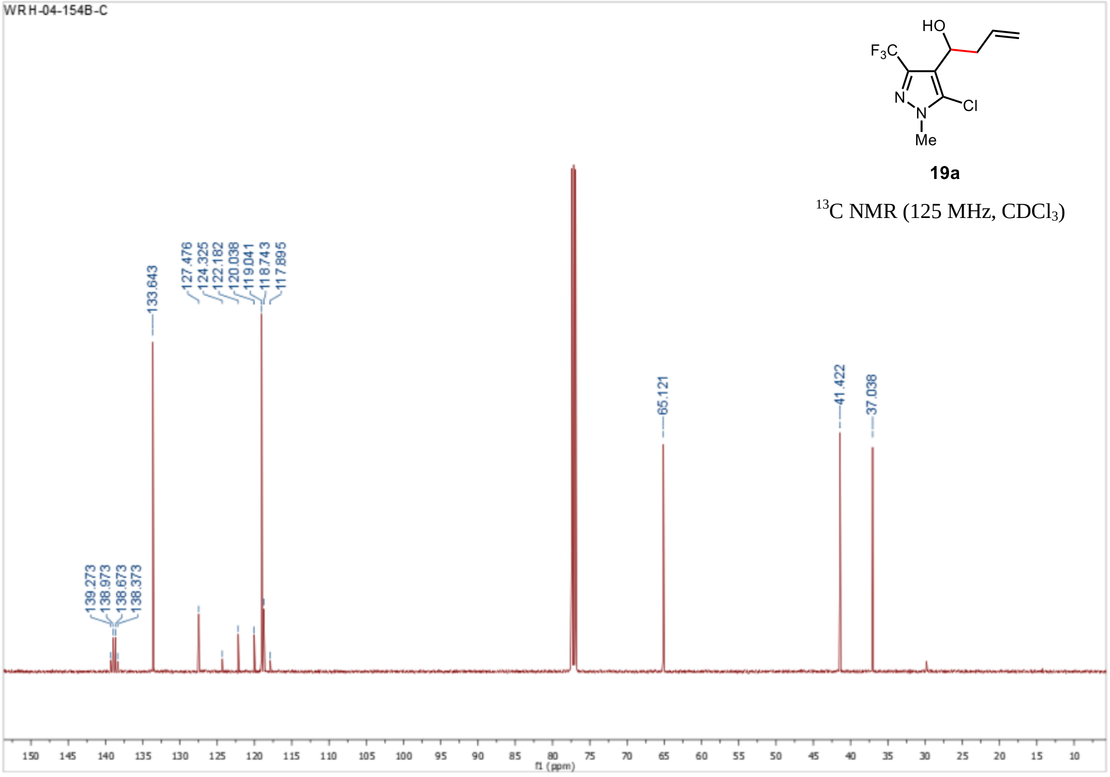

WRH-04-159A
Cl
N
Cl
S
OH
18a
^{1}H NMR (500 MHz, CDCl$_3$)
7.260
5.857
5.843
5.836
5.823
5.808
5.803
5.795
5.789
5.774
5.234
5.216
5.197
5.067
5.058
5.052
5.046
5.037
2.642
2.632
2.616
2.604
2.591
2.526
2.510
2.495
2.482
2.466
1.00
2.07
1.06
3.28
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


WRH-04-159A-C
Cl
N
Cl
S
OH
18a
^{13}C NMR (125 MHz, CDCl$_3$)
150.708
137.303
132.403
132.286
120.374
67.038
42.542
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



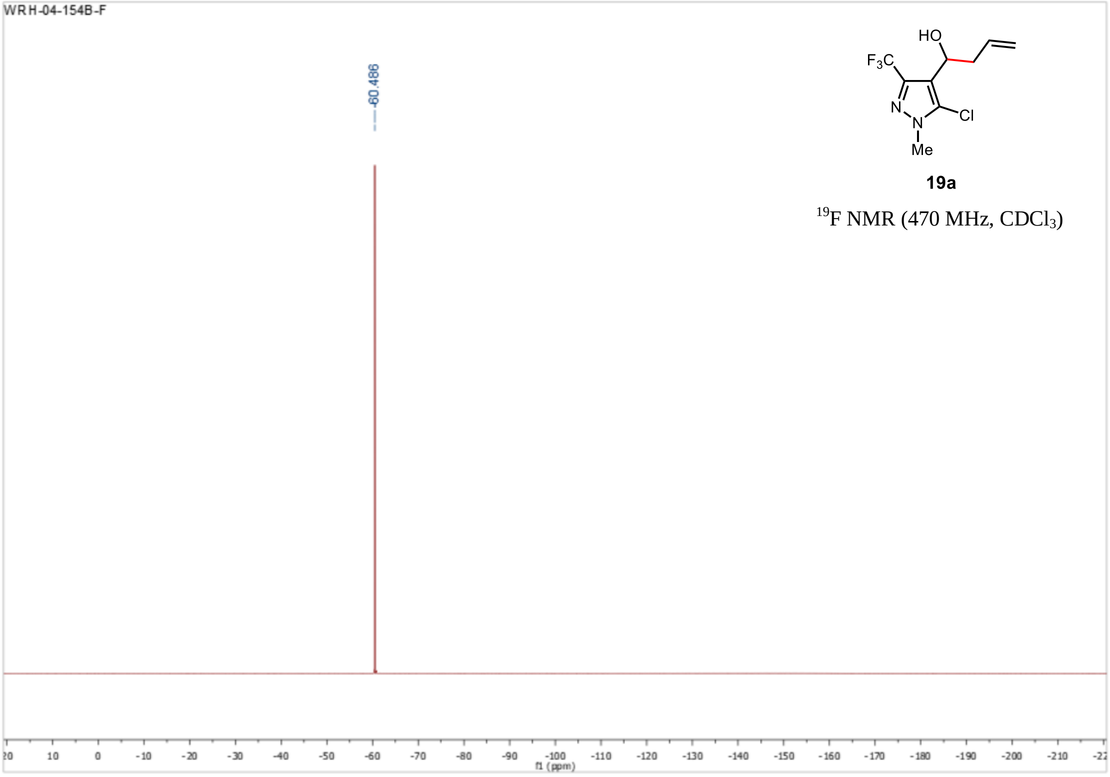
19a

^{1}H NMR (500 MHz, $CDCl_3$)



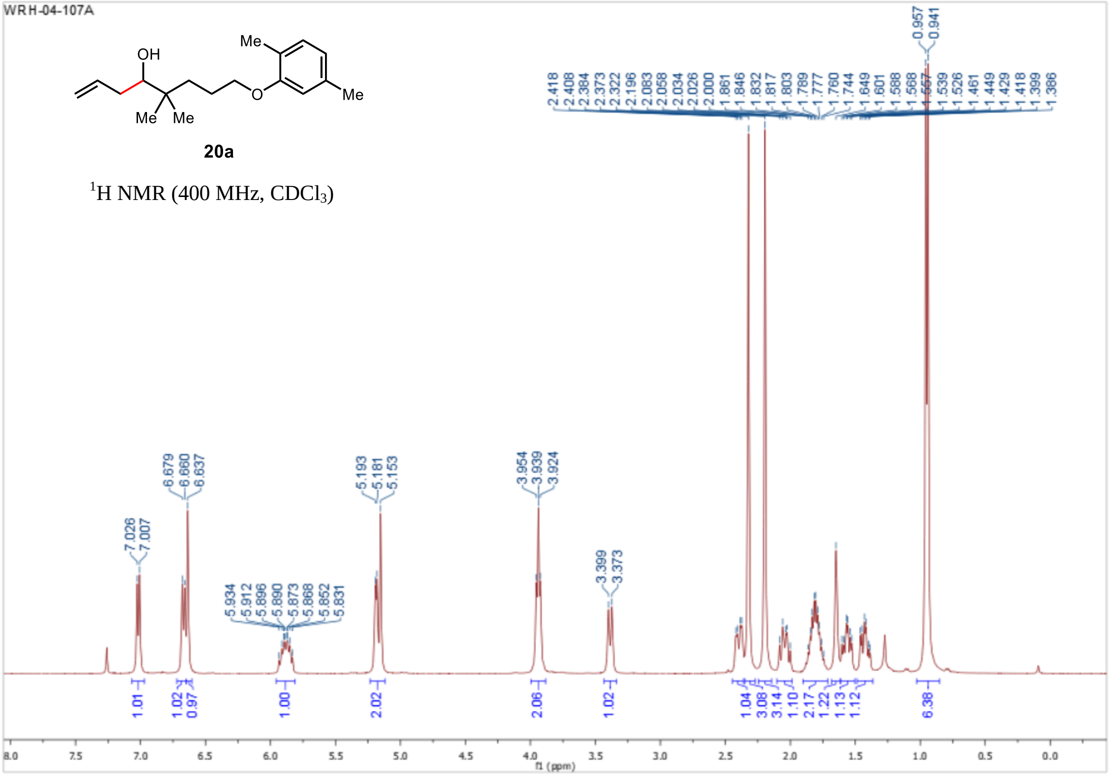
19a

^{13}C NMR (125 MHz, $CDCl_3$)



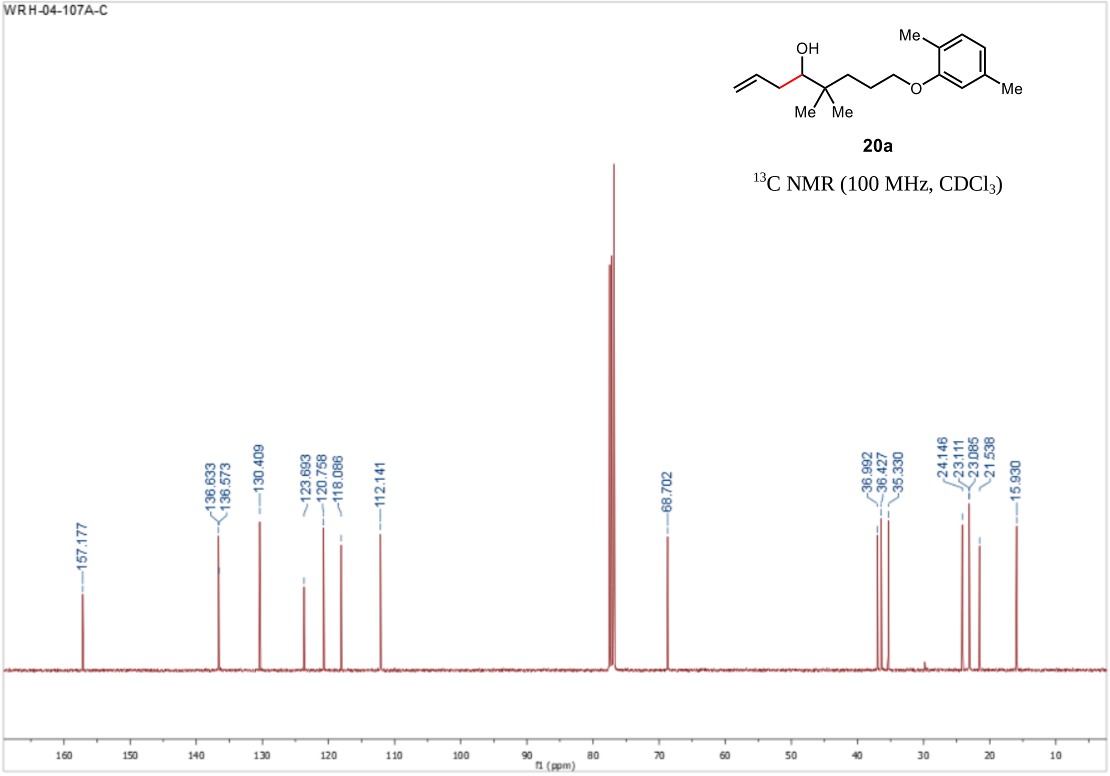
19a

^{19}F NMR (470 MHz, CDCl$_3$)



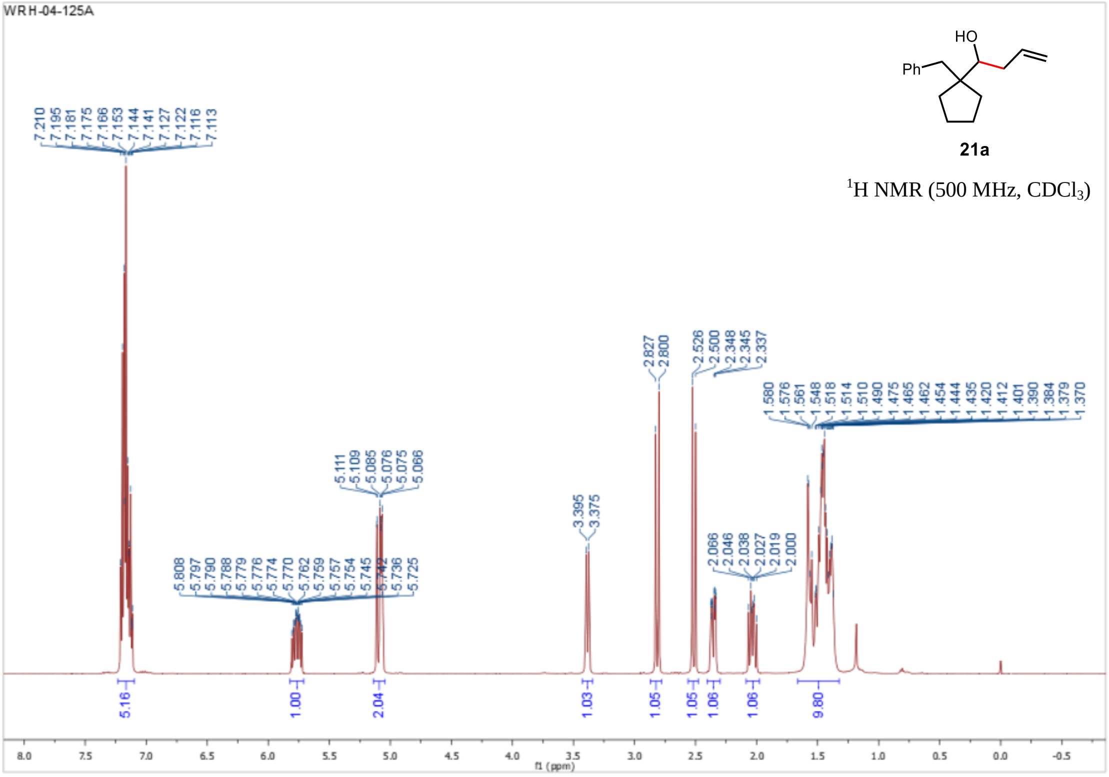
20a

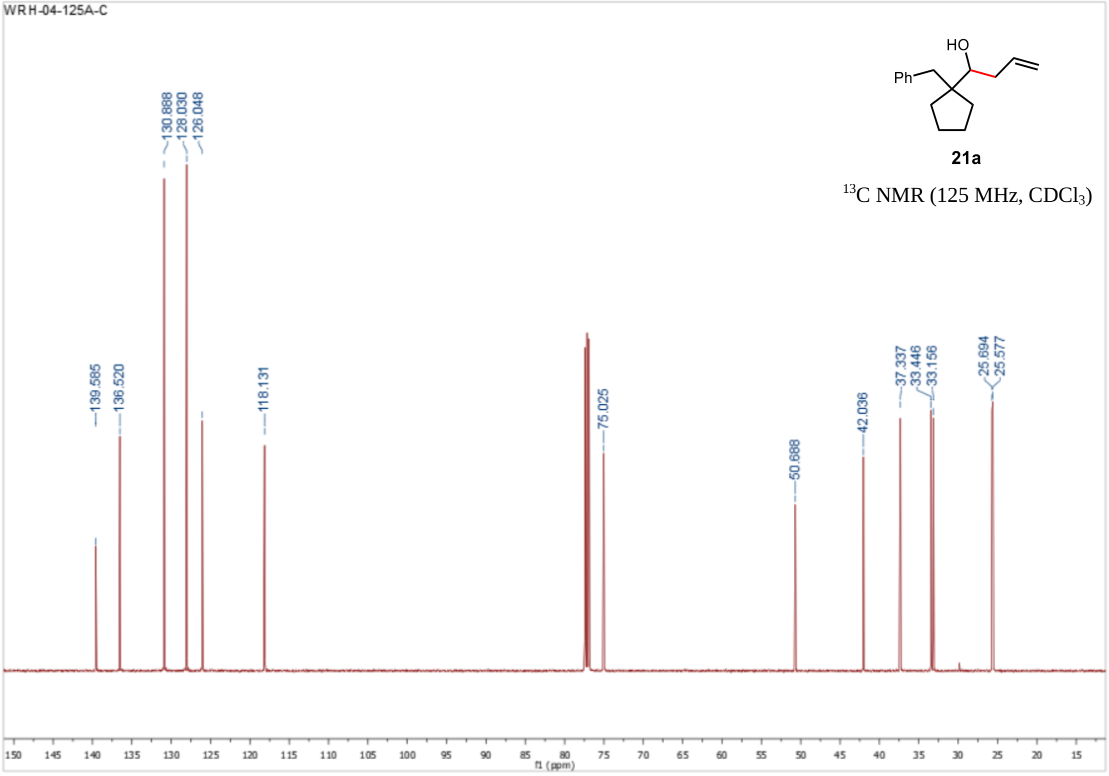
^{1}H NMR (400 MHz, CDCl$_3$)

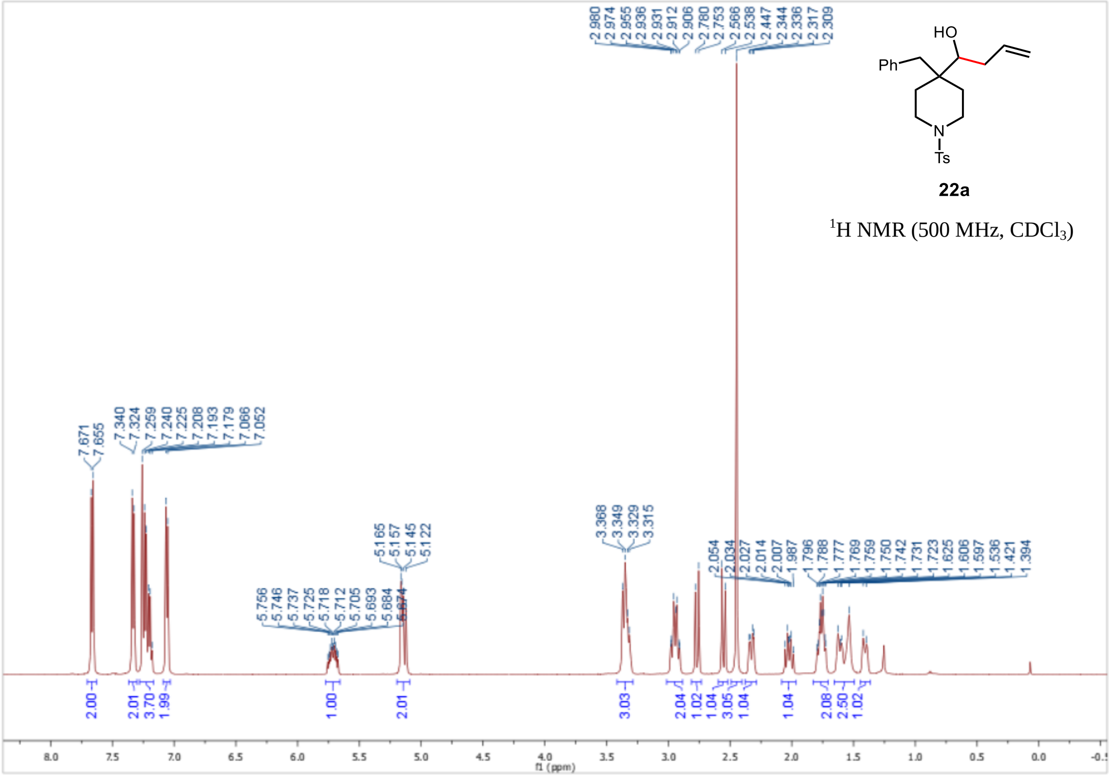


20a

^{13}C NMR (100 MHz, CDCl$_3$)

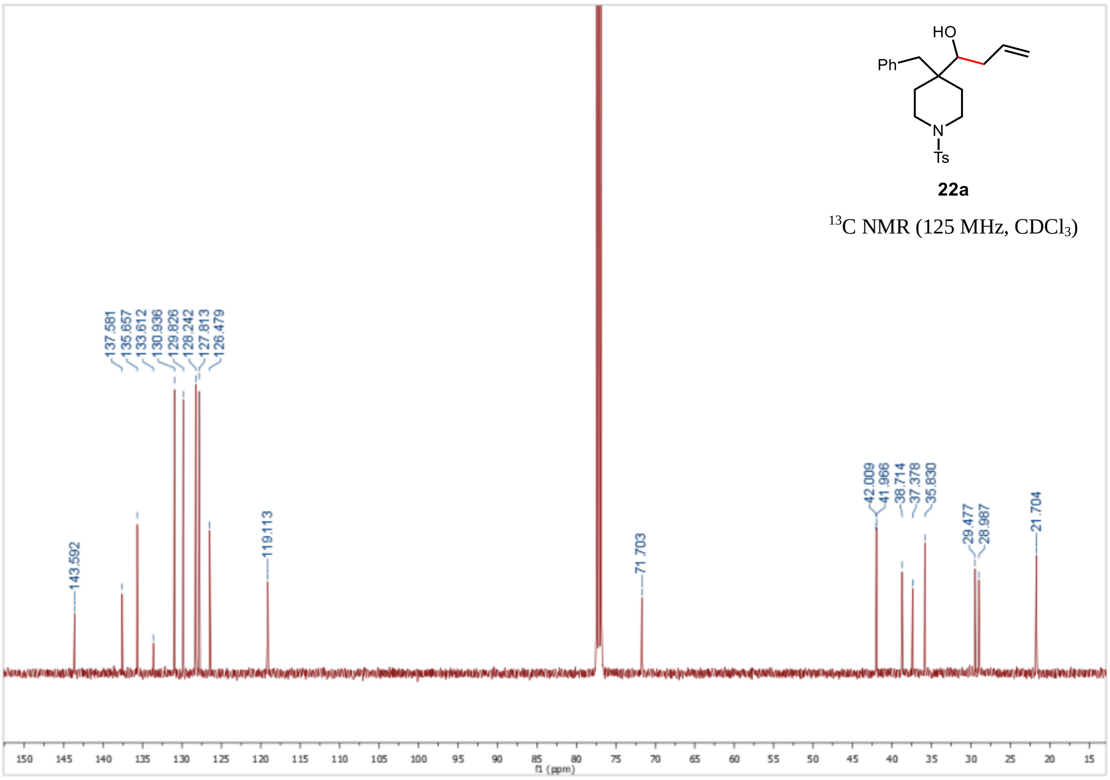

WRH-04-125A
HO
Ph
21a
^{1}H NMR (500 MHz, CDCl$_3$)
7.210 7.195 7.181 7.175 7.166 7.153 7.144 7.141 7.127 7.122 7.116 7.113
5.808 5.797 5.790 5.788 5.779 5.776 5.774 5.770 5.762 5.759 5.757 5.754 5.745 5.742 5.736 5.725
5.111 5.109 5.085 5.076 5.075 5.066
3.395 3.375
2.827 2.800
2.526 2.500 2.348 2.345 2.337
2.066 2.046 2.038 2.027 2.019 2.000
1.580 1.576 1.561 1.548 1.518 1.514 1.510 1.490 1.475 1.465 1.462 1.454 1.444 1.435 1.420 1.412 1.401 1.390 1.384 1.379 1.370
5.16
1.00
2.04
1.03
1.05
1.05
1.06
1.06
9.80
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


WRH-04-125A-C
HO
Ph
21a
^{13}C NMR (125 MHz, CDCl$_3$)
139.585
136.520
130.888
128.030
126.048
118.131
75.025
50.688
42.036
37.337
33.446
33.156
25.694
25.577
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)



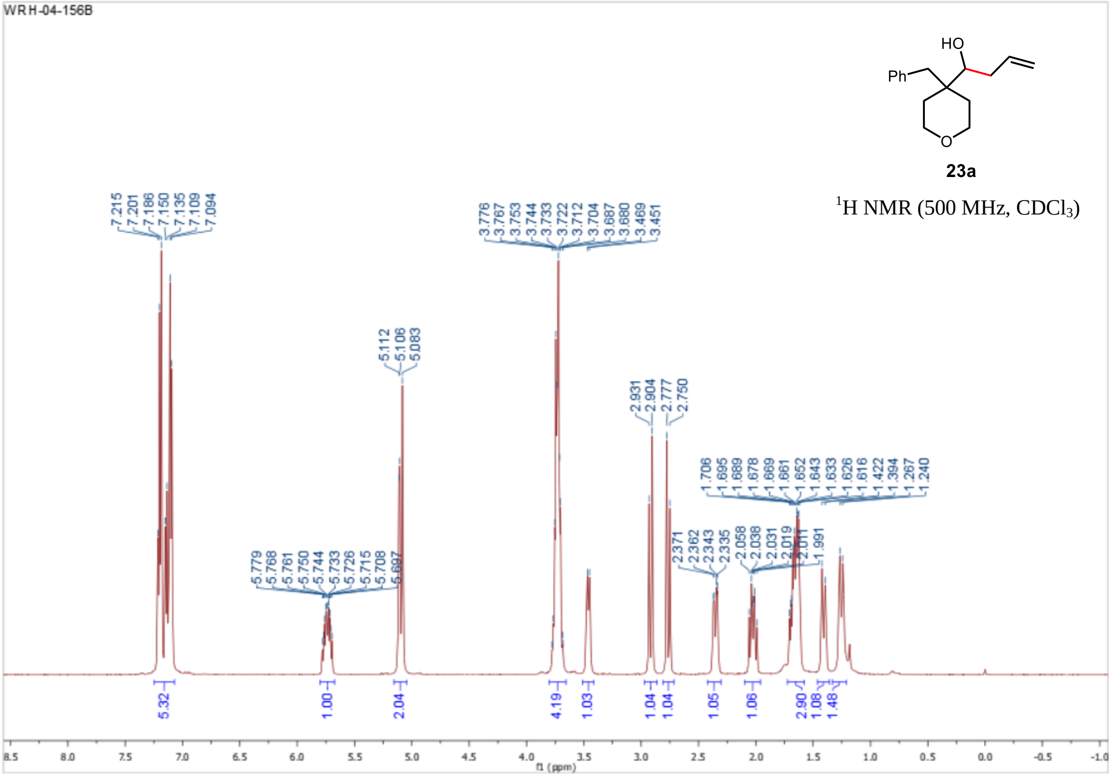
22a

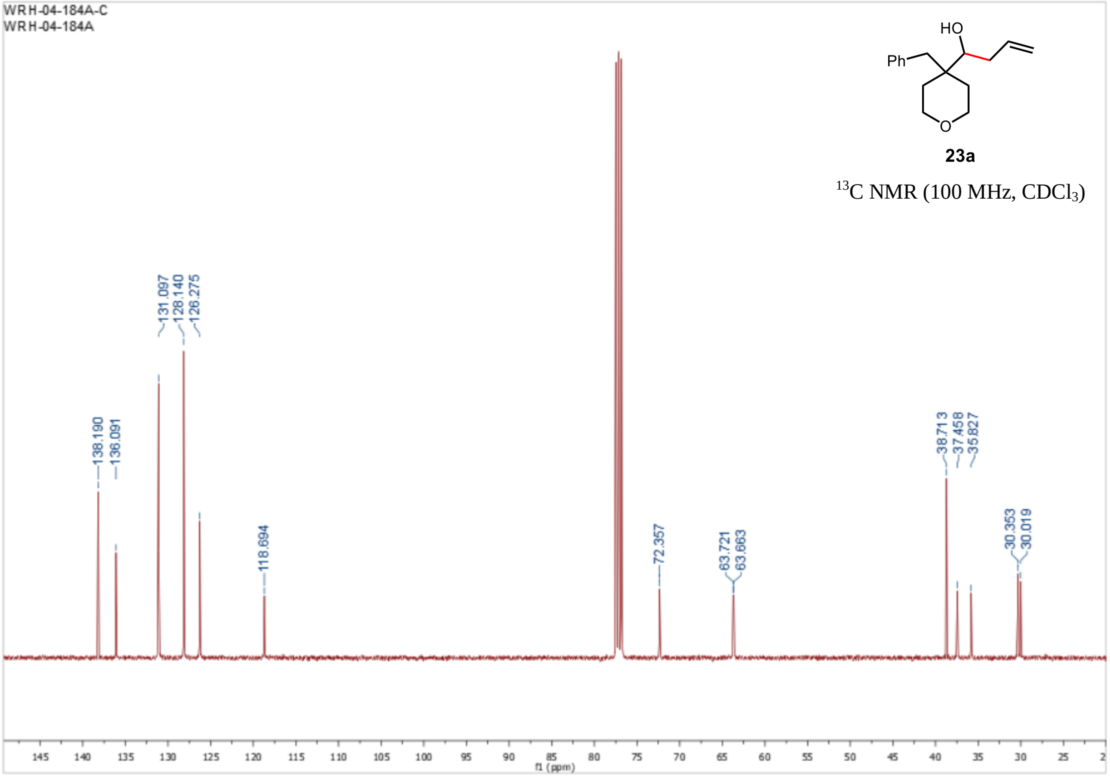
^{1}H NMR (500 MHz, CDCl$_3$)

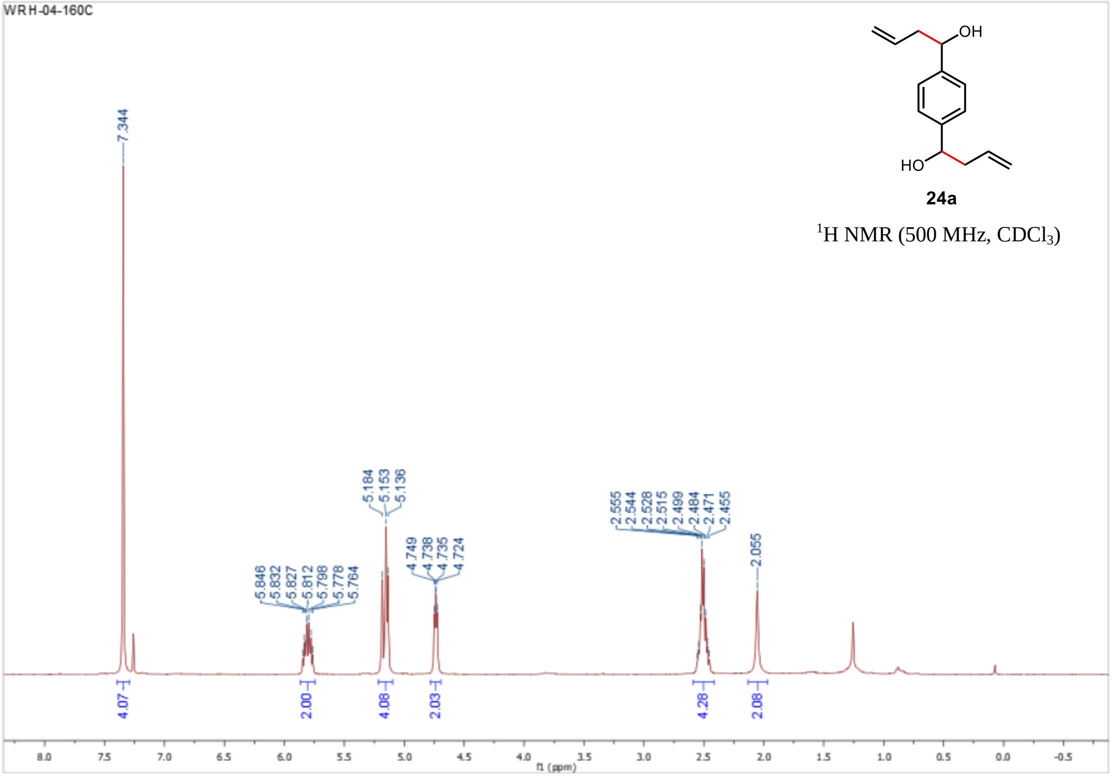


22a

^{13}C NMR (125 MHz, CDCl$_3$)

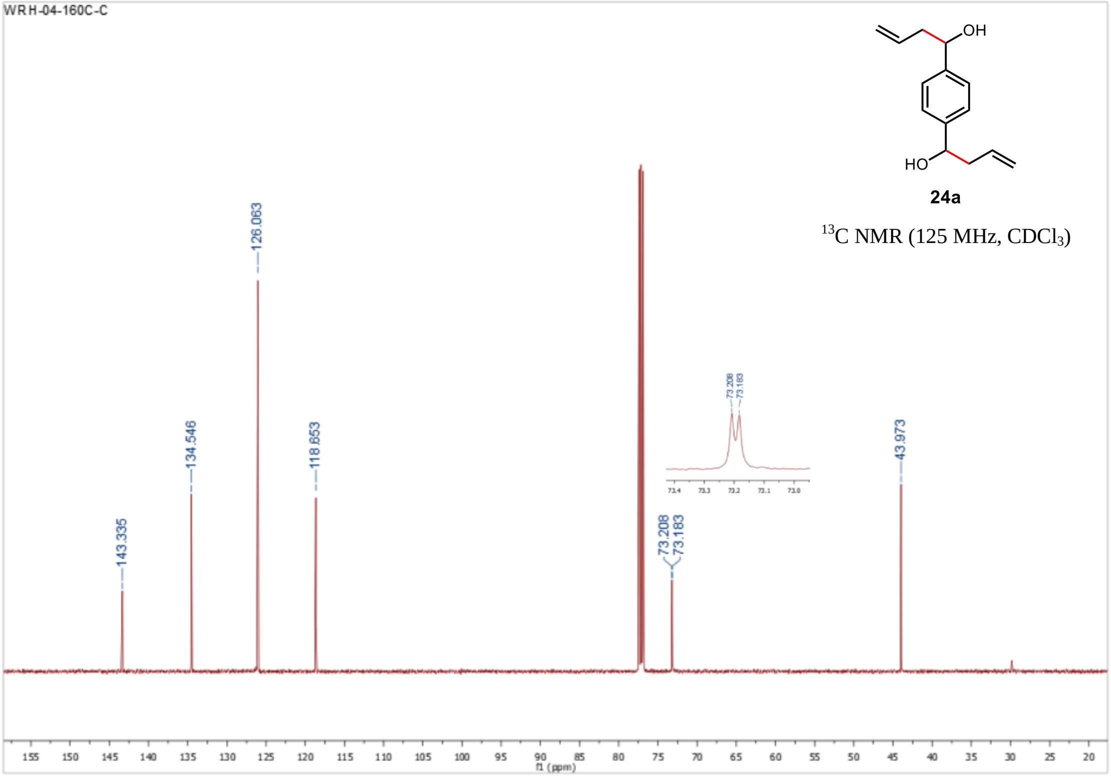

WRH-04-156B
HO
Ph
O
23a
^{1}H NMR (500 MHz, CDCl$_3$)
7.215
7.201
7.186
7.150
7.135
7.109
7.094
5.779
5.768
5.761
5.750
5.744
5.733
5.726
5.715
5.708
5.697
5.112
5.106
5.083
3.776
3.767
3.753
3.744
3.733
3.722
3.712
3.704
3.687
3.680
3.469
3.451
2.931
2.904
2.777
2.750
2.371
2.362
2.343
2.335
2.058
2.038
2.031
2.019
2.011
1.991
1.706
1.695
1.689
1.678
1.669
1.661
1.652
1.643
1.633
1.626
1.616
1.422
1.394
1.267
1.240
5.32
1.00
2.04
4.19
1.03
1.04
1.04
1.05
1.06
2.90
1.08
1.48
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


WRH-04-184A-C
WRH-04-184A
HO
Ph
O
23a
^{13}C NMR (100 MHz, CDCl$_3$)
138.190
136.091
131.097
128.140
126.275
118.694
72.357
63.721
63.663
38.713
37.458
35.827
30.353
30.019
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
2
f1 (ppm)



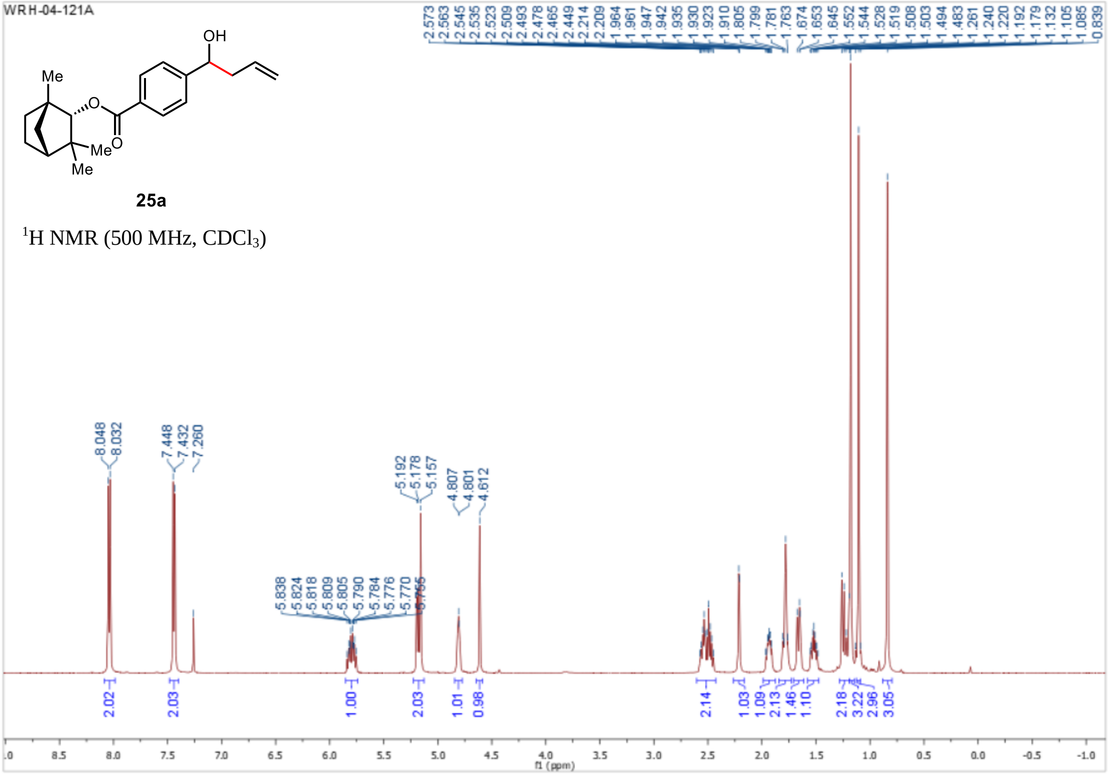
24a

^{1}H NMR (500 MHz, CDCl$_3$)



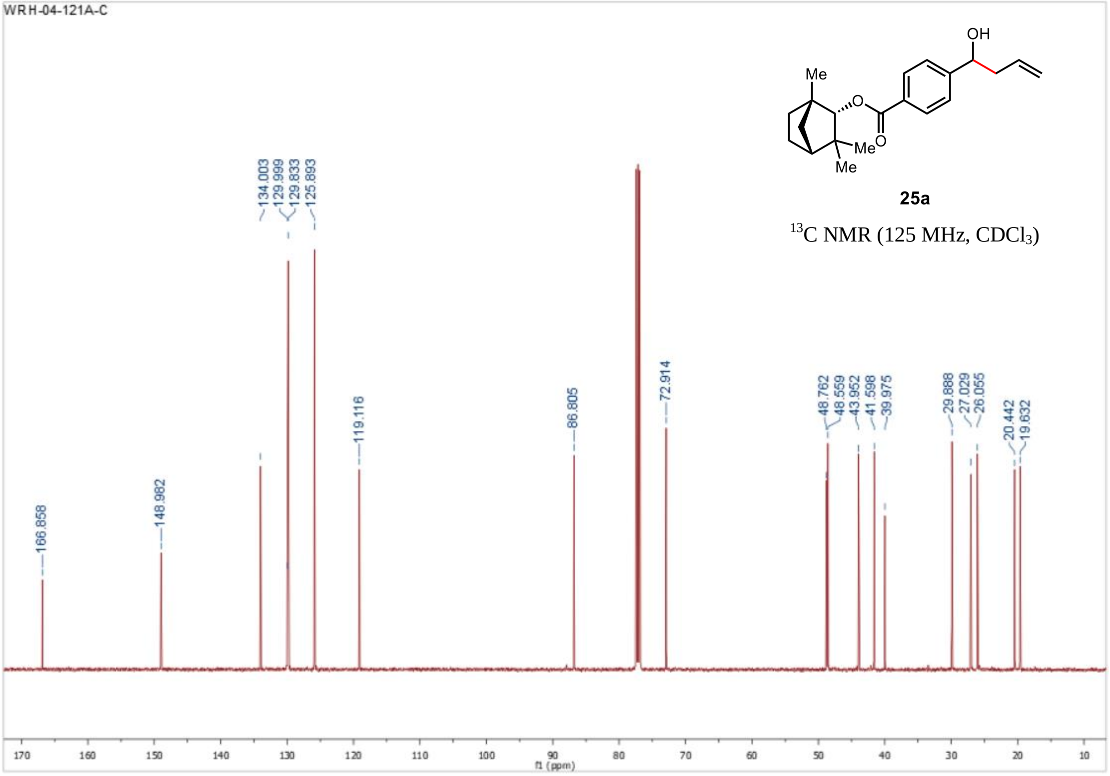
24a

^{13}C NMR (125 MHz, CDCl$_3$)



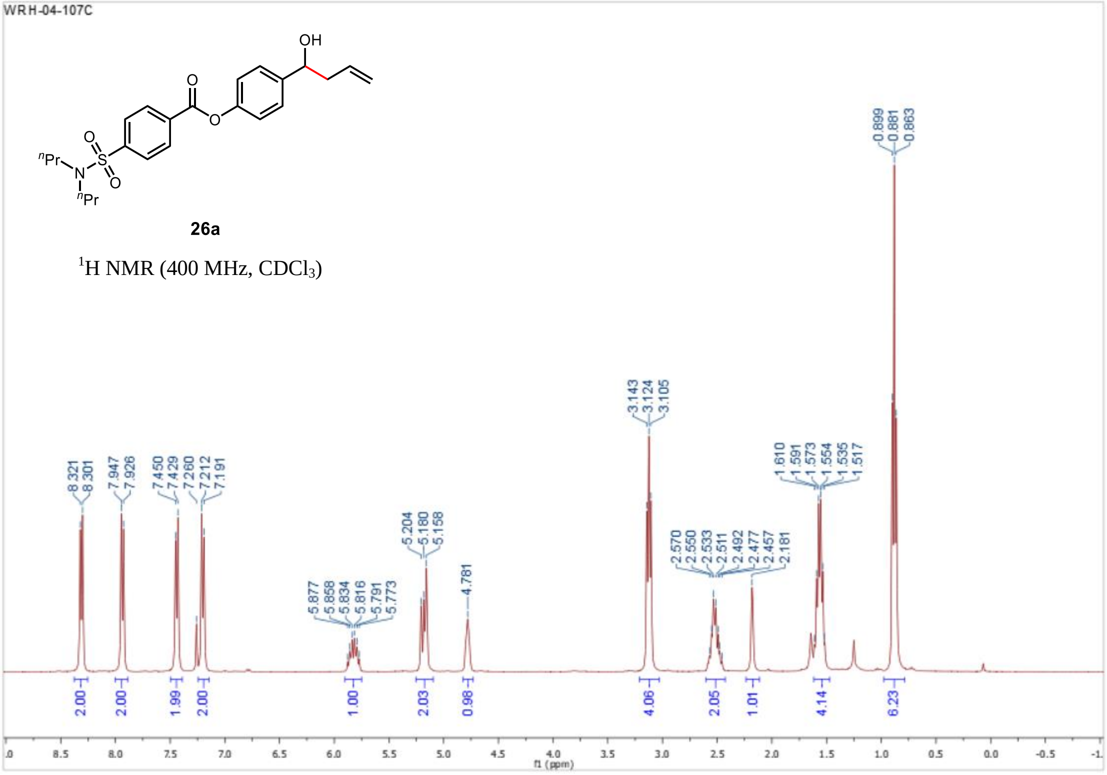
25a

^{1}H NMR (500 MHz, CDCl$_3$)



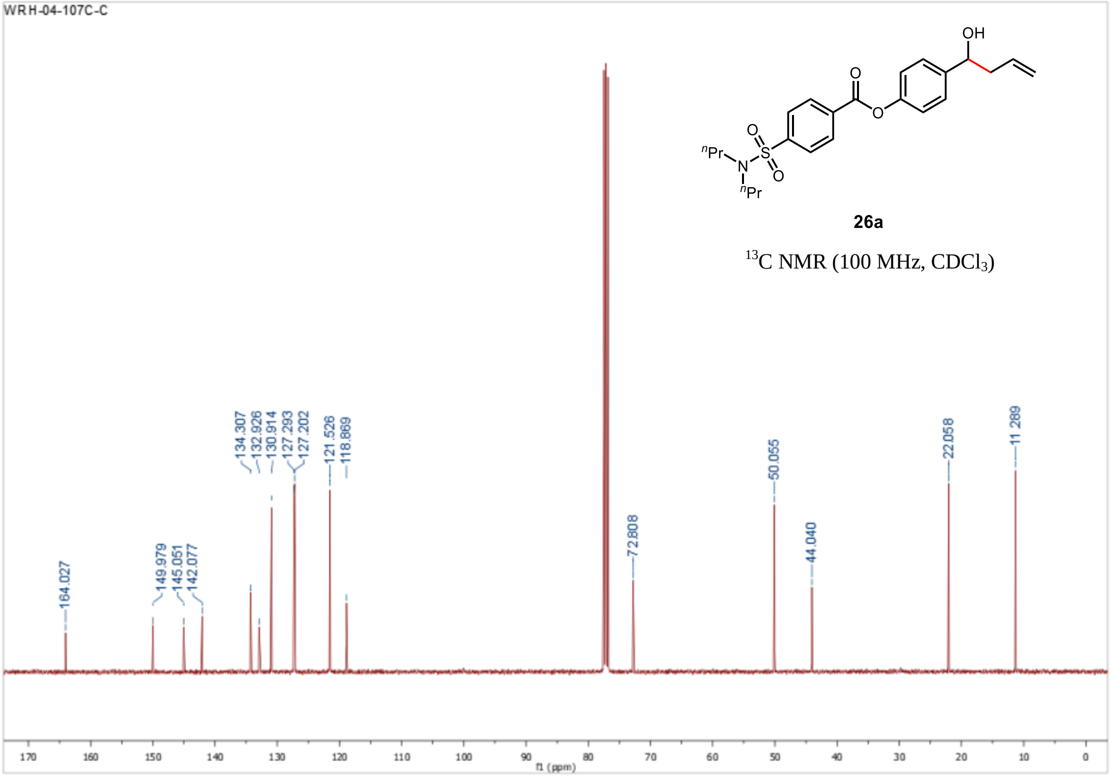
25a

^{13}C NMR (125 MHz, CDCl$_3$)



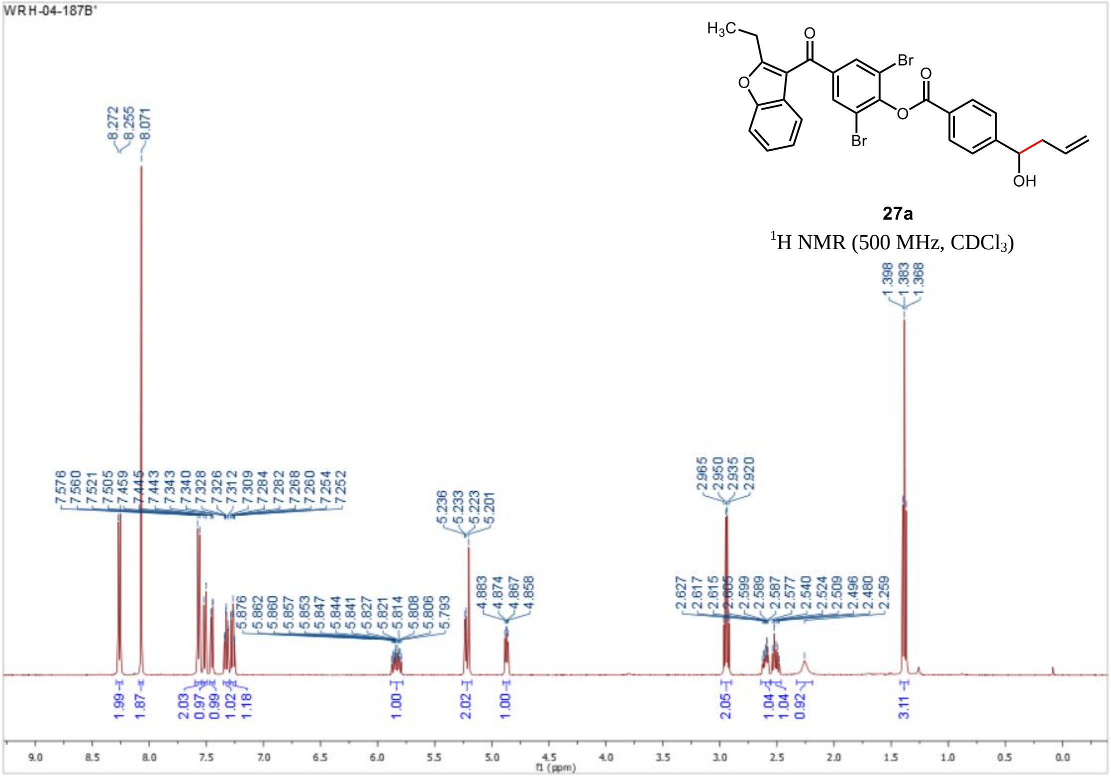
26a

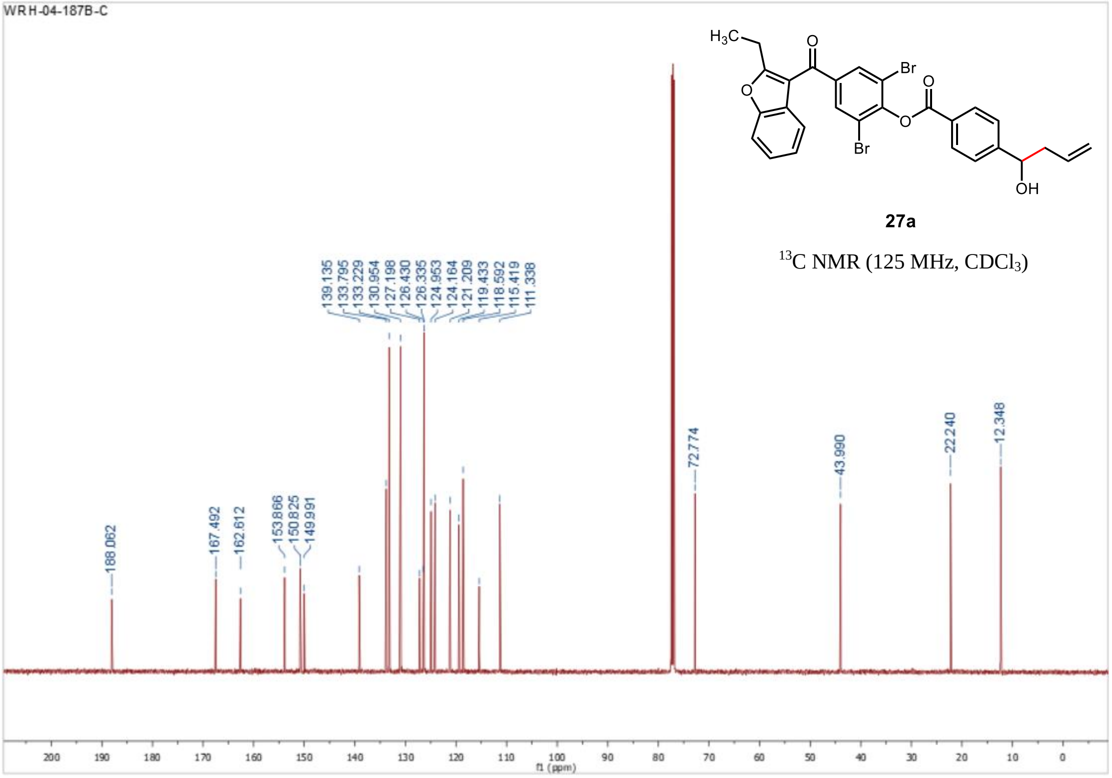
^{1}H NMR (400 MHz, CDCl$_3$)

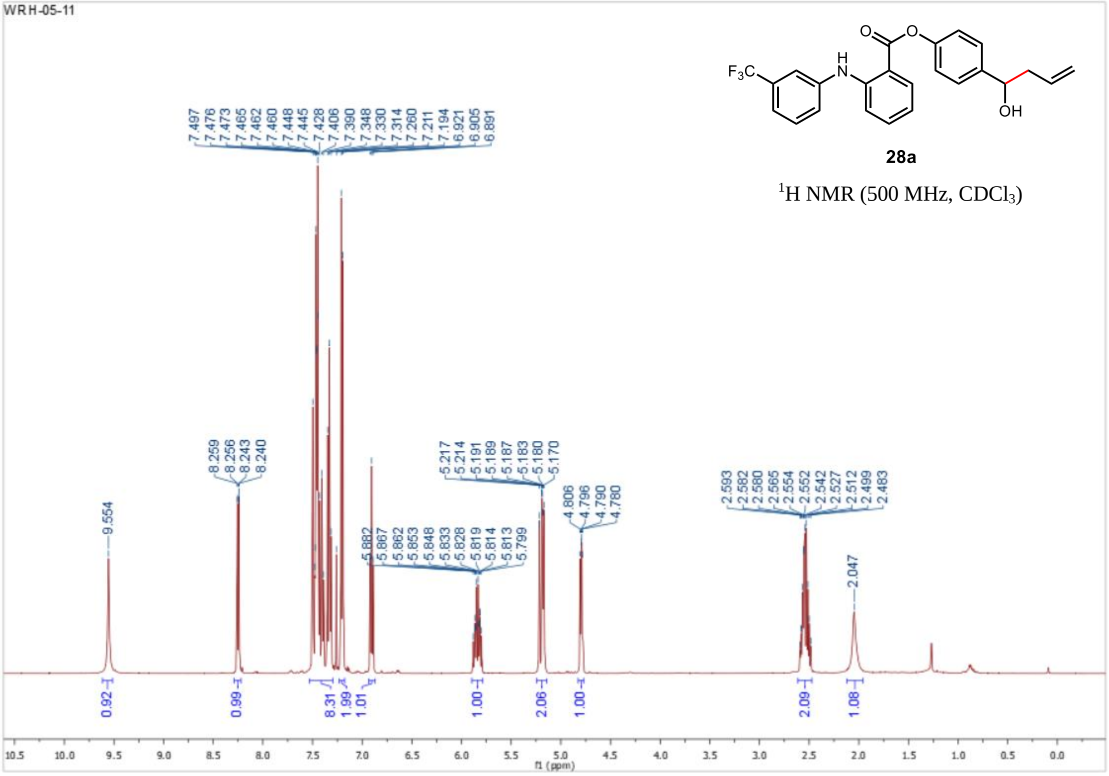


26a

^{13}C NMR (100 MHz, CDCl$_3$)

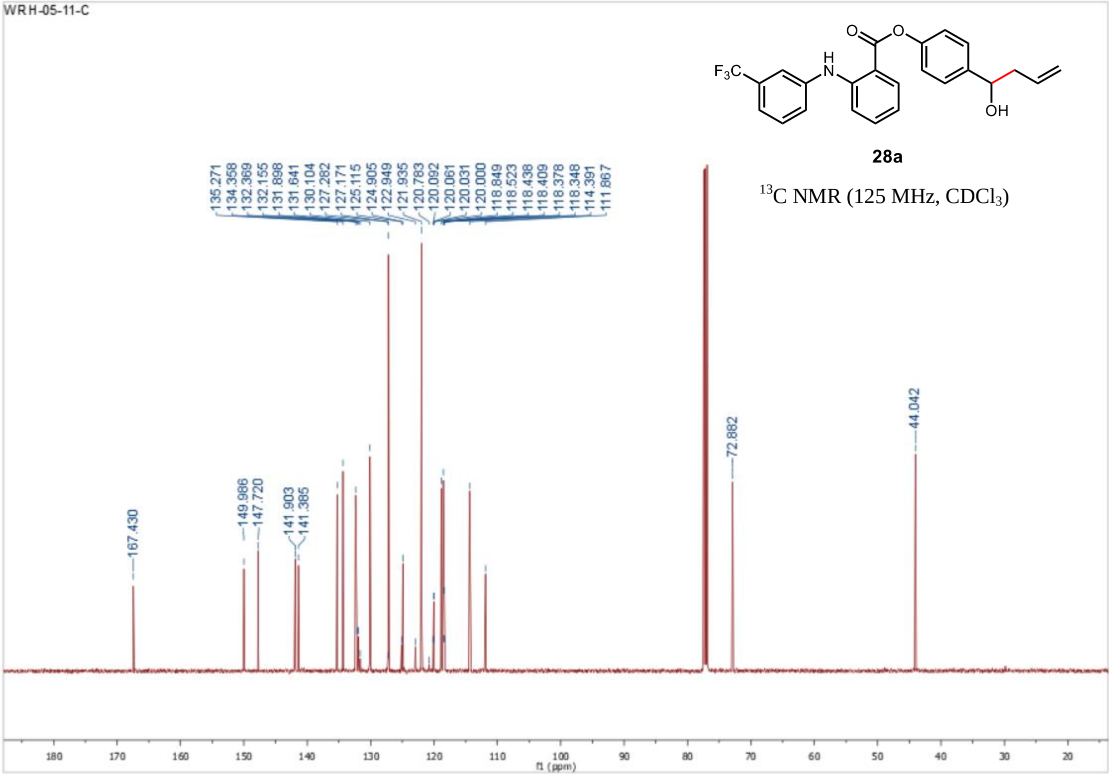

WRH-04-187B'
27a
^{1}H NMR (500 MHz, CDCl$_3$)
8.272 8.255 8.071
7.576 7.560 7.521 7.505 7.459 7.445 7.443 7.343 7.340 7.328 7.326 7.312 7.309 7.284 7.282 7.268 7.260 7.254 7.252
5.876 5.862 5.860 5.857 5.853 5.847 5.844 5.841 5.827 5.821 5.814 5.808 5.806 5.793
5.236 5.233 5.223 5.201
4.883 4.874 4.867 4.858
2.965 2.950 2.935 2.920
2.627 2.617 2.615 2.605 2.599 2.589 2.587 2.577 2.540 2.524 2.509 2.496 2.480 2.259
1.398 1.383 1.368
1.99 1.87 2.03 0.97 0.99 1.02 1.18 1.00 2.02 1.00 2.05 1.04 1.04 0.92 3.11
f1 (ppm)


WRH-04-187B-C
27a
^{13}C NMR (125 MHz, CDCl$_3$)
188.062
167.492 162.612
153.866 150.825 149.991
139.135 133.795 133.229 130.954 127.198 126.430 126.335 124.953 124.164 121.209 119.433 118.592 115.419 111.338
72.774
43.990
22.240
12.348
f1 (ppm)



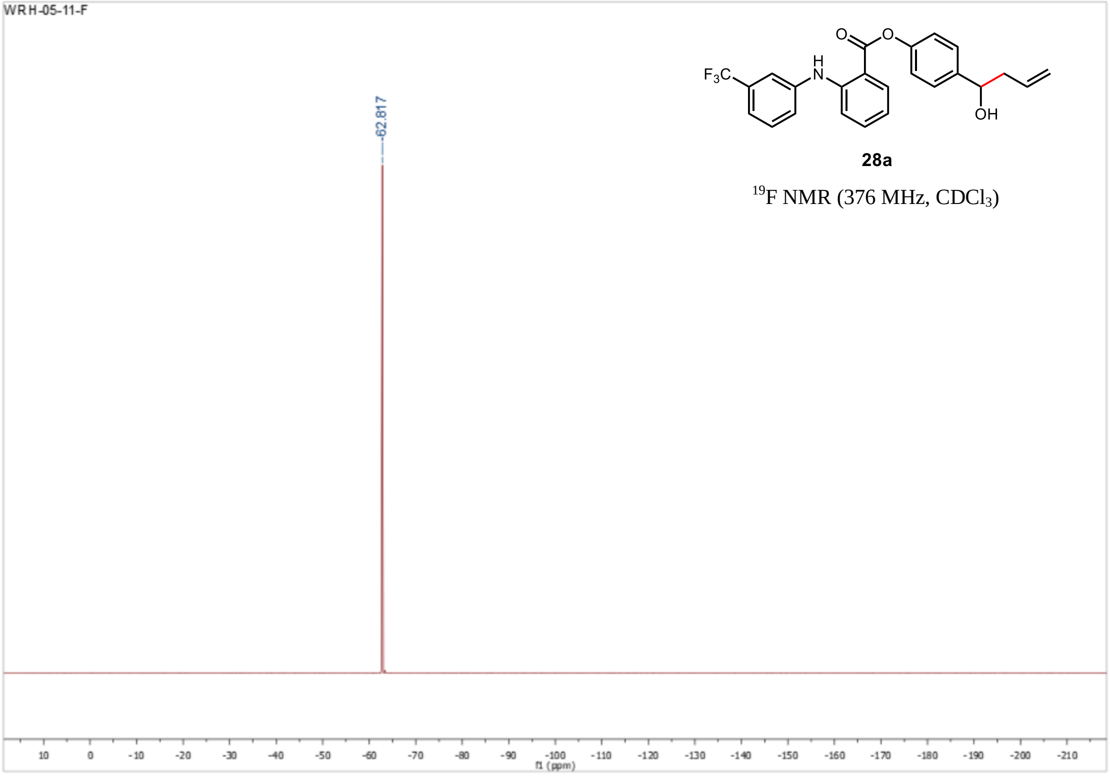
28a

^{1}H NMR (500 MHz, CDCl$_3$)



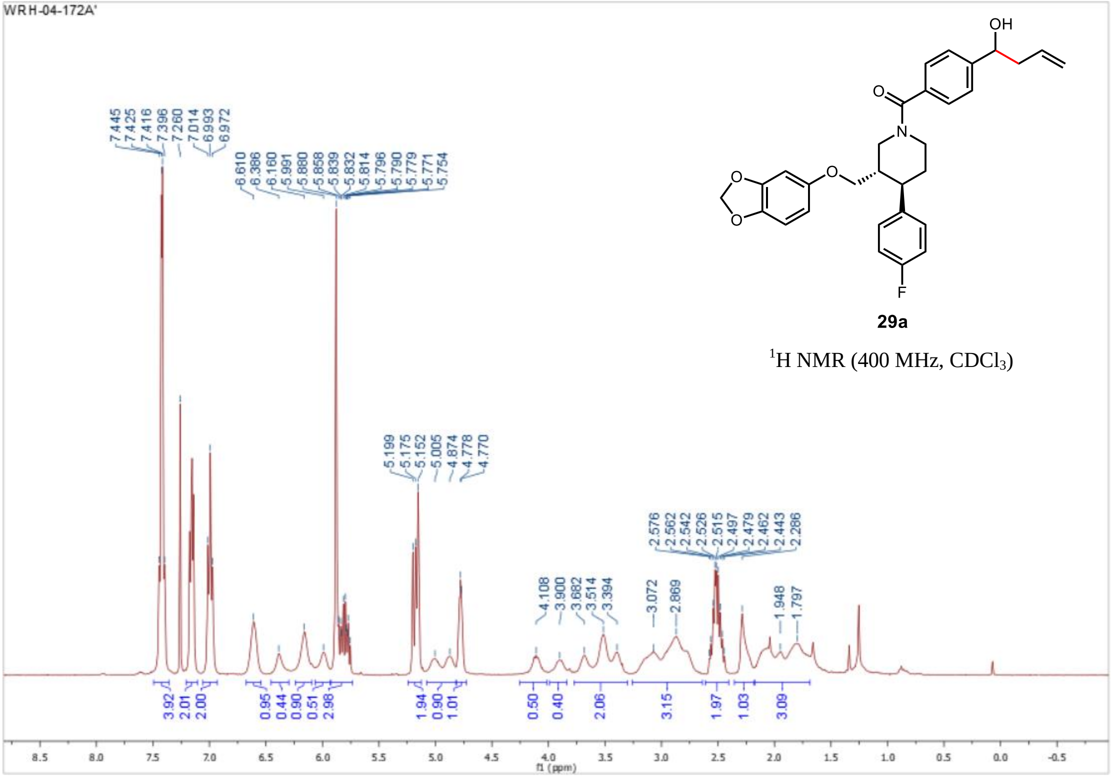
28a

^{13}C NMR (125 MHz, CDCl$_3$)



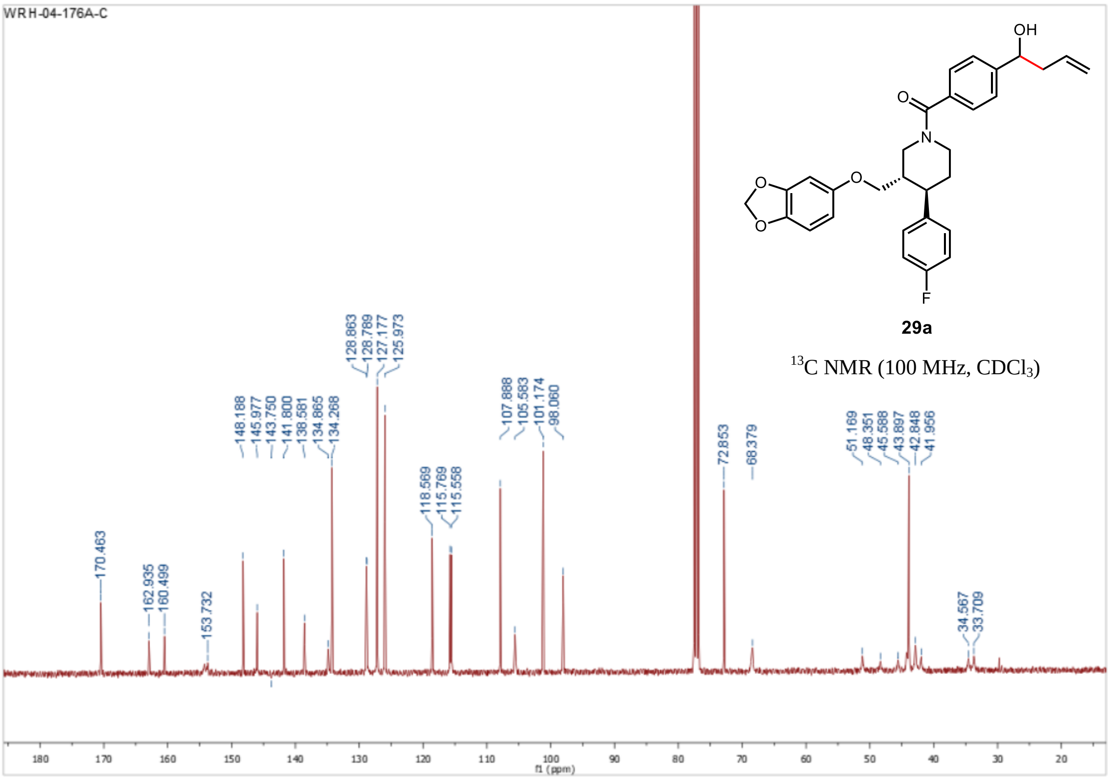
28a

^{19}F NMR (376 MHz, CDCl$_3$)



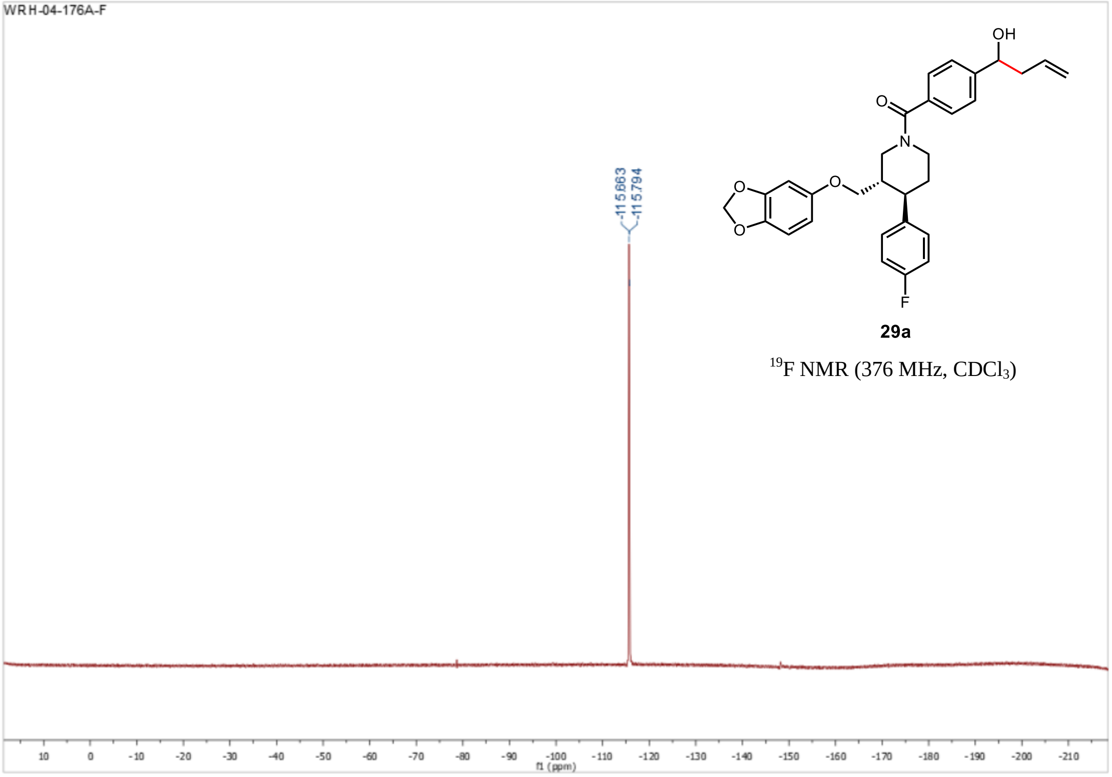
29a

^{1}H NMR (400 MHz, $CDCl_3$)



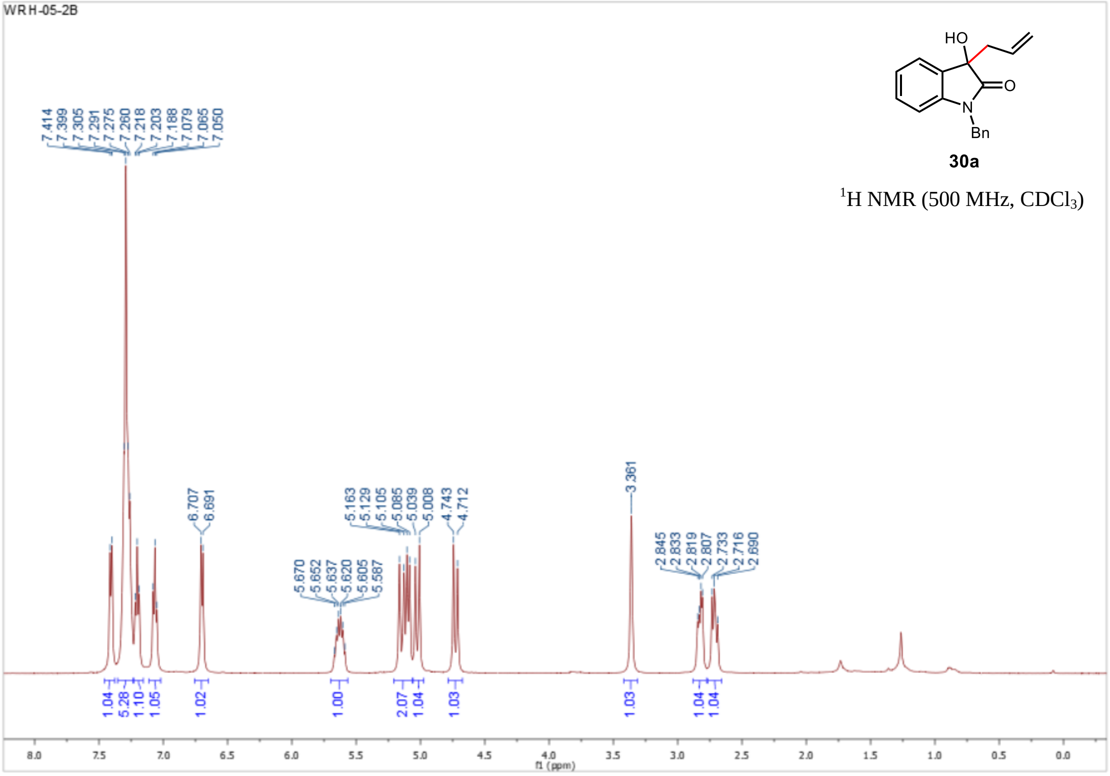
29a

^{13}C NMR (100 MHz, $CDCl_3$)



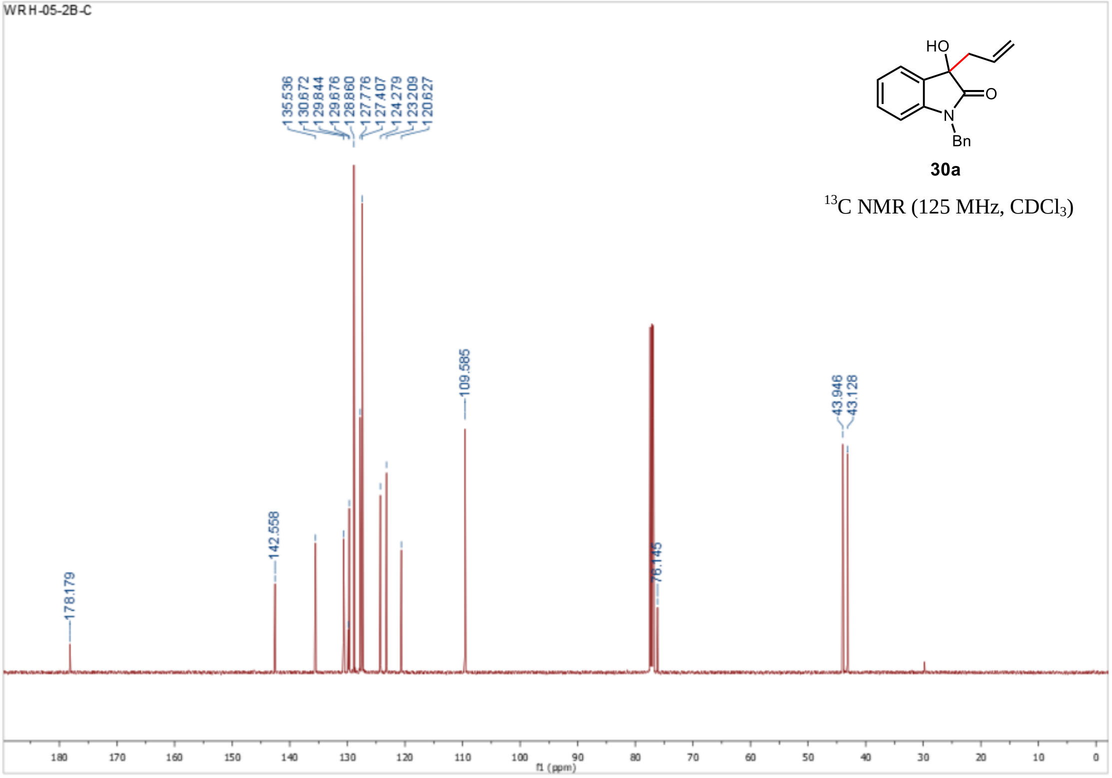
29a

^{19}F NMR (376 MHz, $CDCl_3$)



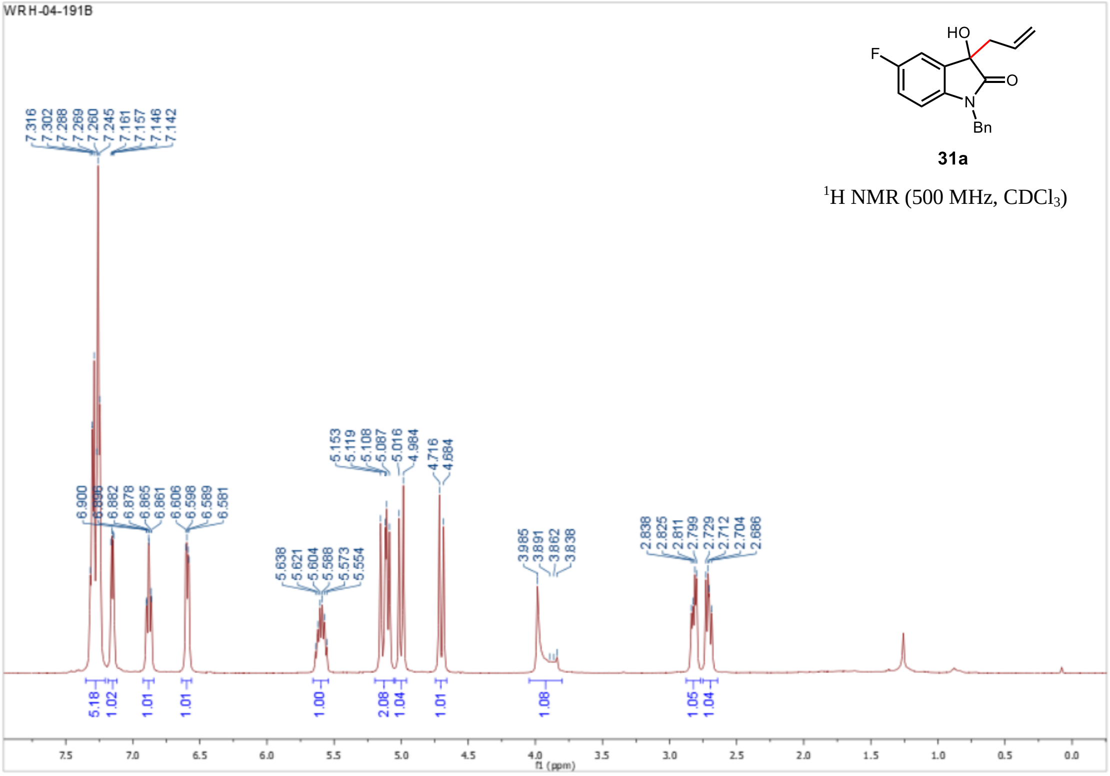
30a

^{1}H NMR (500 MHz, CDCl$_3$)



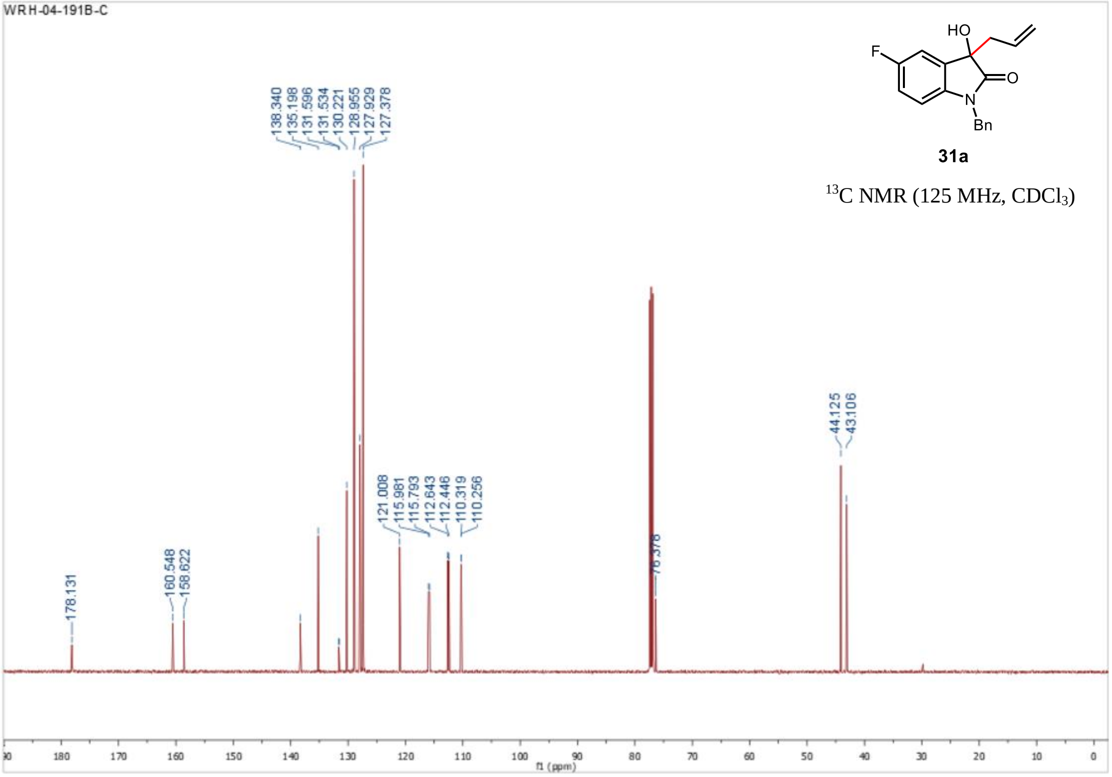
30a

^{13}C NMR (125 MHz, CDCl$_3$)



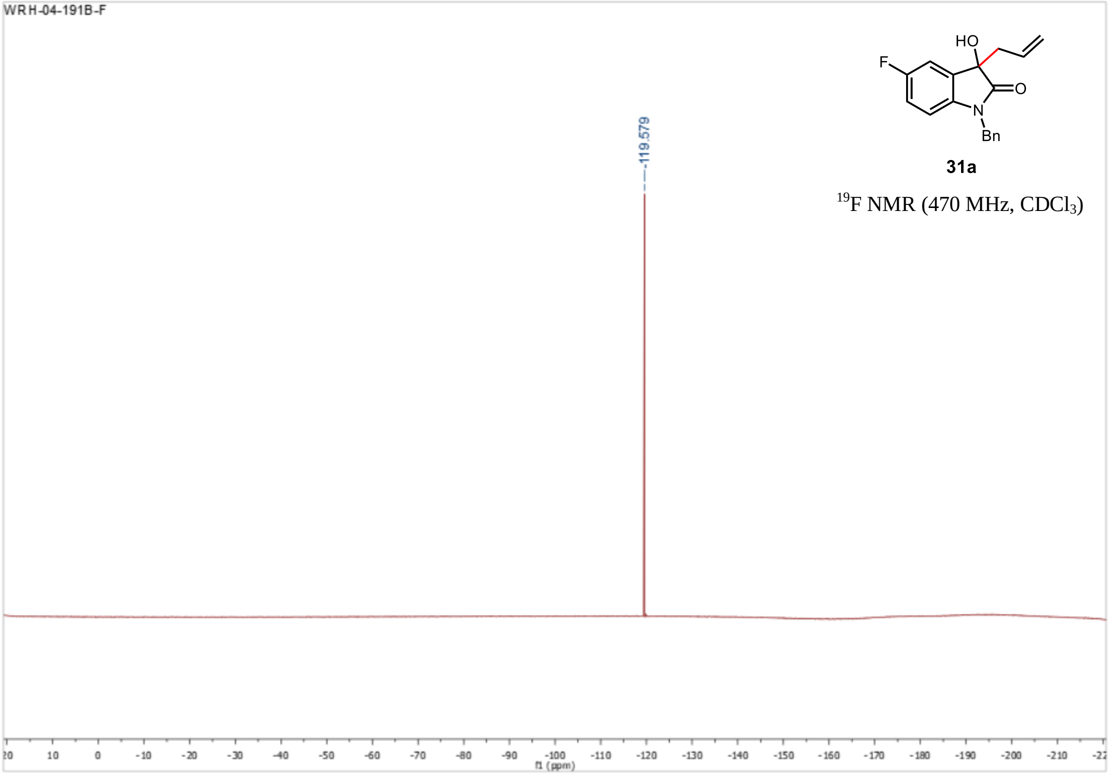
31a

^{1}H NMR (500 MHz, CDCl$_3$)



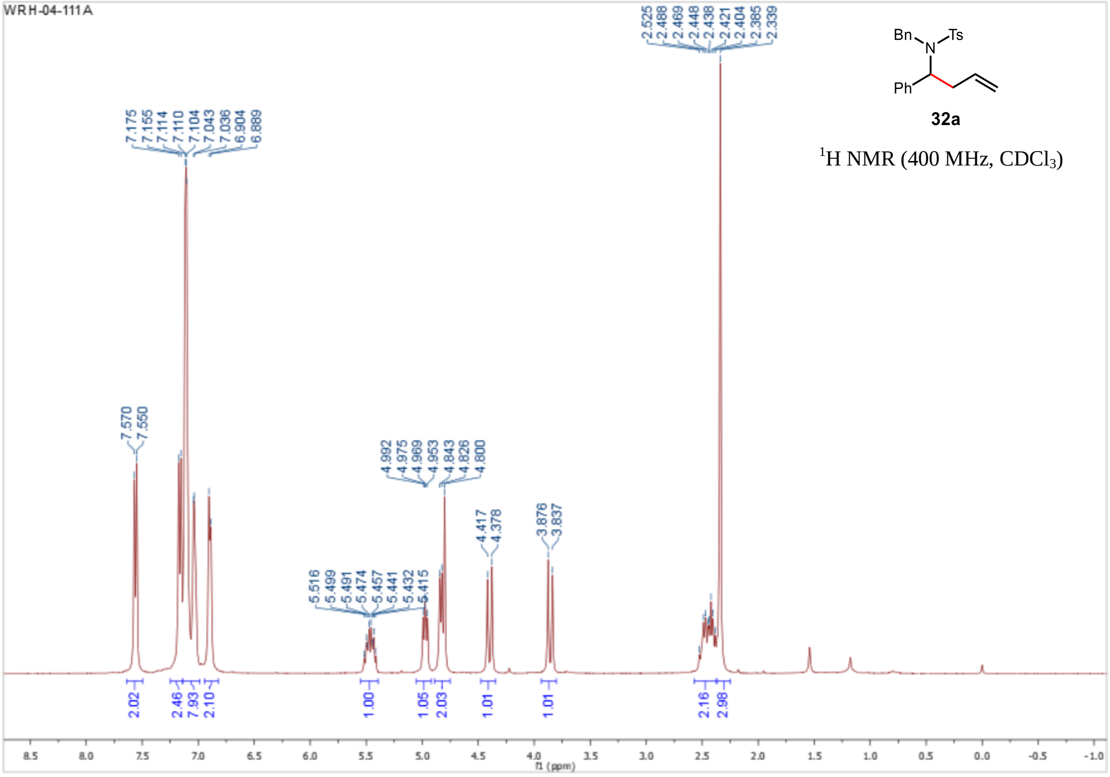
31a

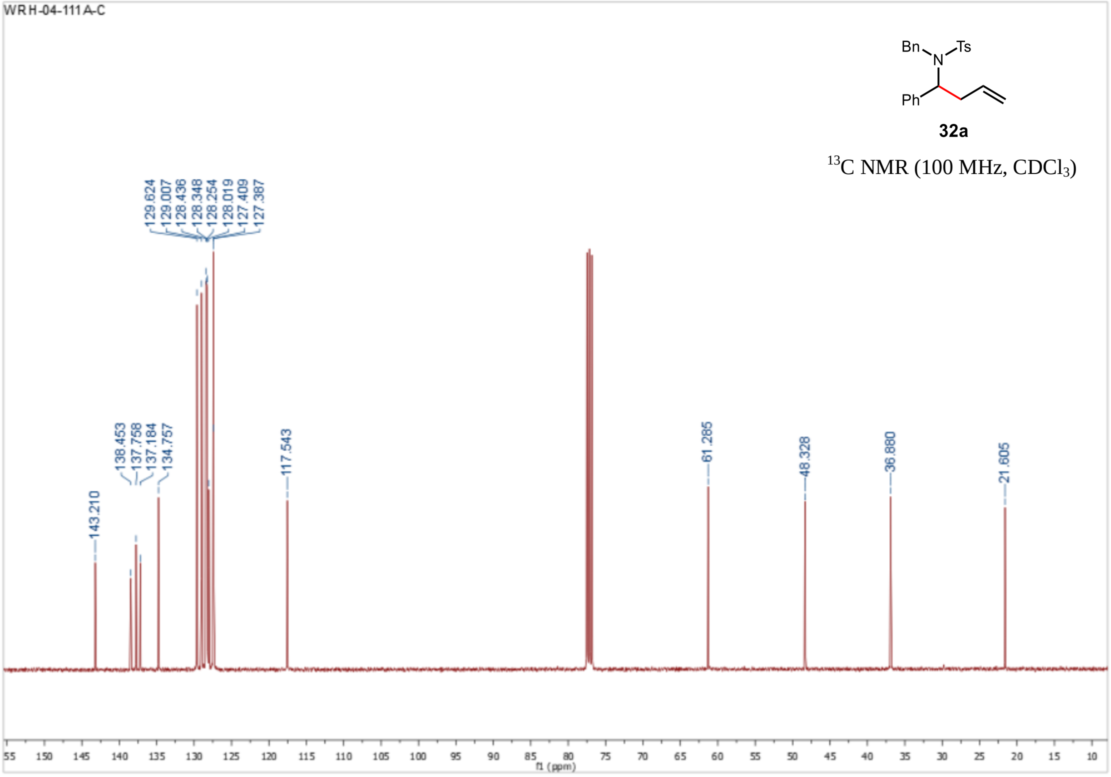
^{13}C NMR (125 MHz, CDCl$_3$)

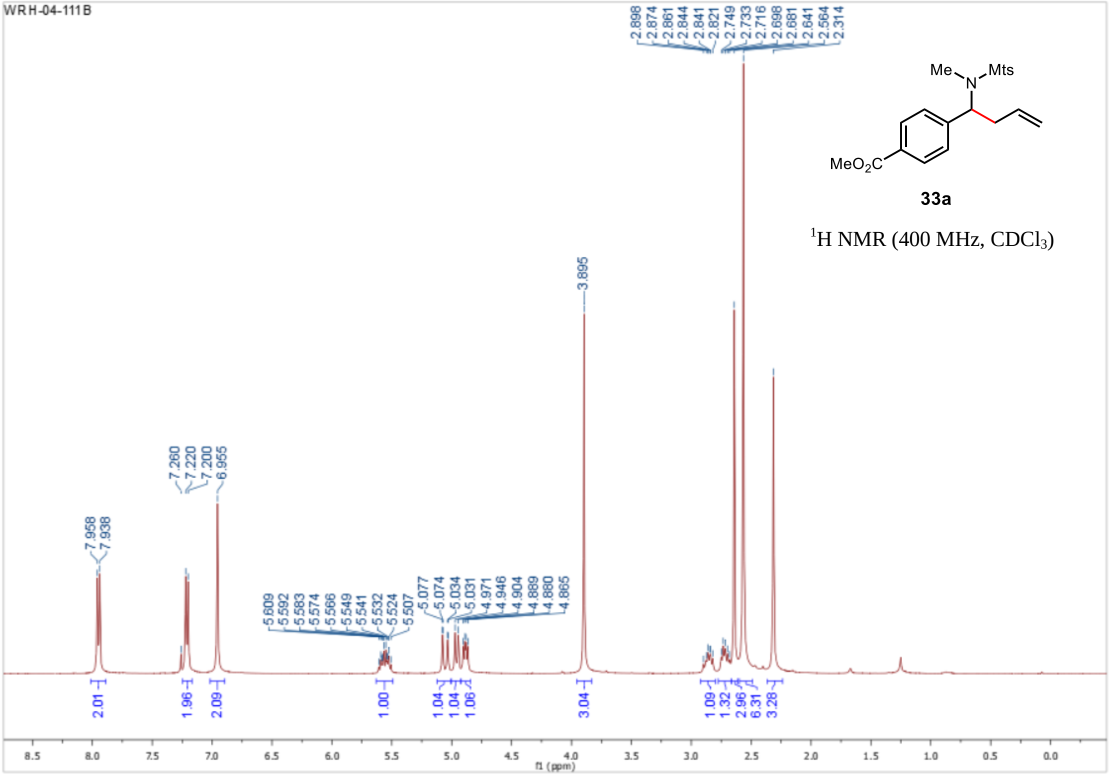


31a

^{19}F NMR (470 MHz, $CDCl_3$)

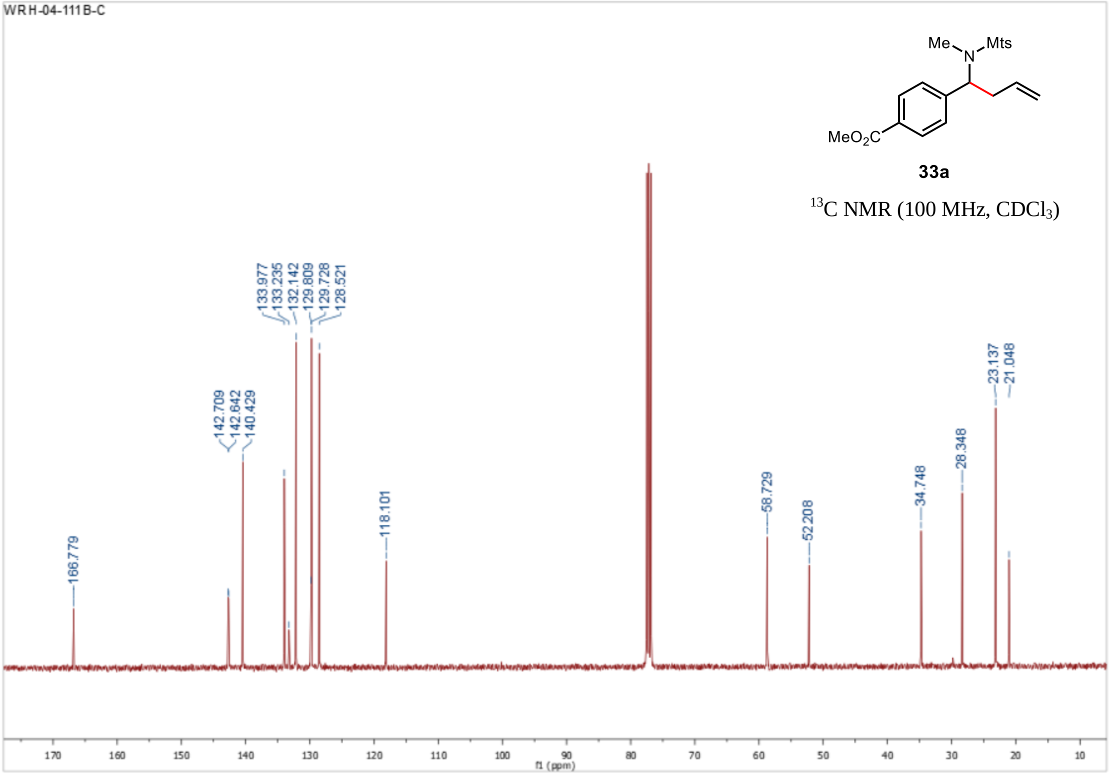

WRH-04-111A
Bn
N
Ts
Ph
32a
^{1}H NMR (400 MHz, CDCl$_3$)
7.570
7.550
7.175
7.155
7.114
7.110
7.104
7.043
7.036
6.904
6.889
5.516
5.499
5.491
5.474
5.457
5.441
5.432
5.415
4.992
4.975
4.969
4.953
4.843
4.826
4.800
4.417
4.378
3.876
3.837
2.525
2.488
2.469
2.448
2.438
2.421
2.404
2.385
2.339
2.02
2.46
7.93
2.10
1.00
1.05
2.03
1.01
1.01
2.16
2.98
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


WRH-04-111A-C
Bn
N
Ts
Ph
32a
^{13}C NMR (100 MHz, CDCl$_3$)
143.210
138.453
137.758
137.184
134.757
129.624
129.007
128.436
128.348
128.254
128.019
127.409
127.387
117.543
61.285
48.328
36.880
21.605
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)



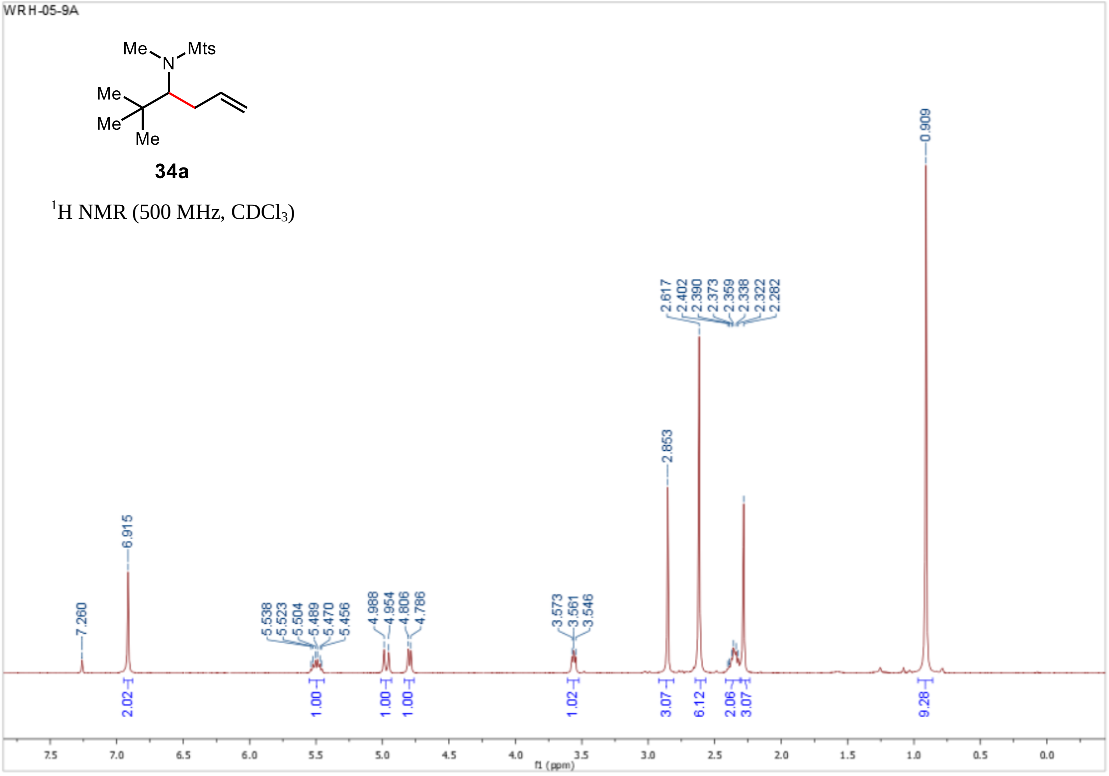
33a

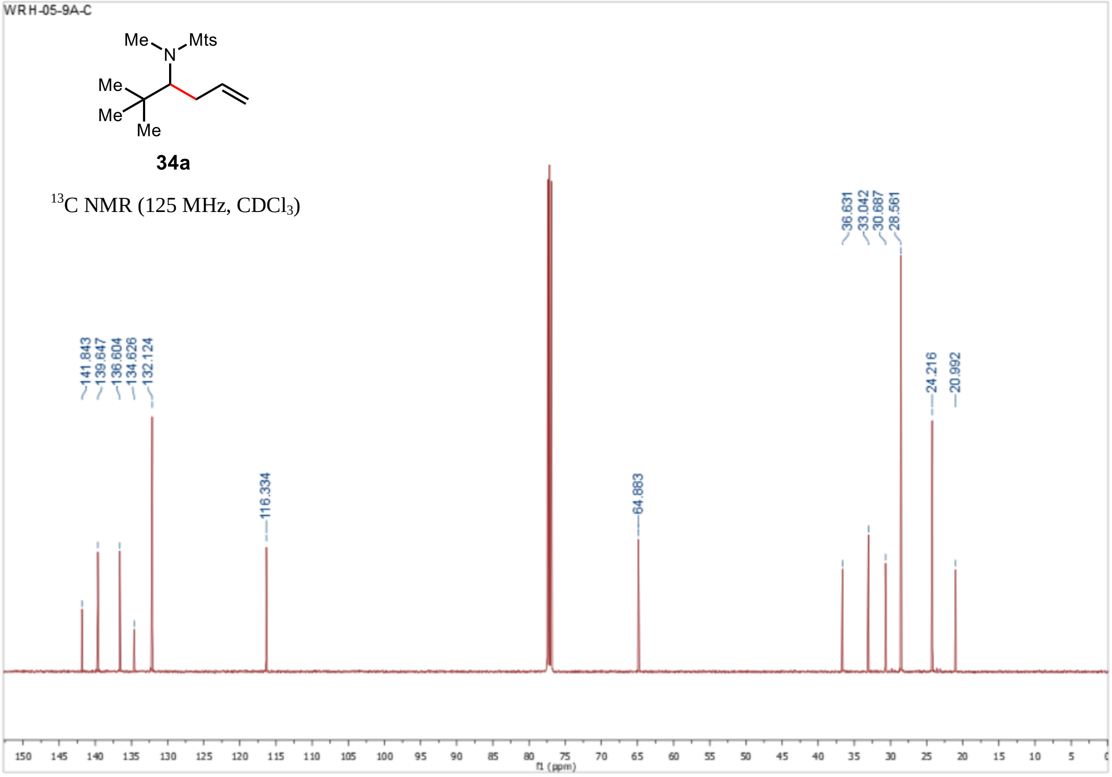
^{1}H NMR (400 MHz, CDCl$_3$)

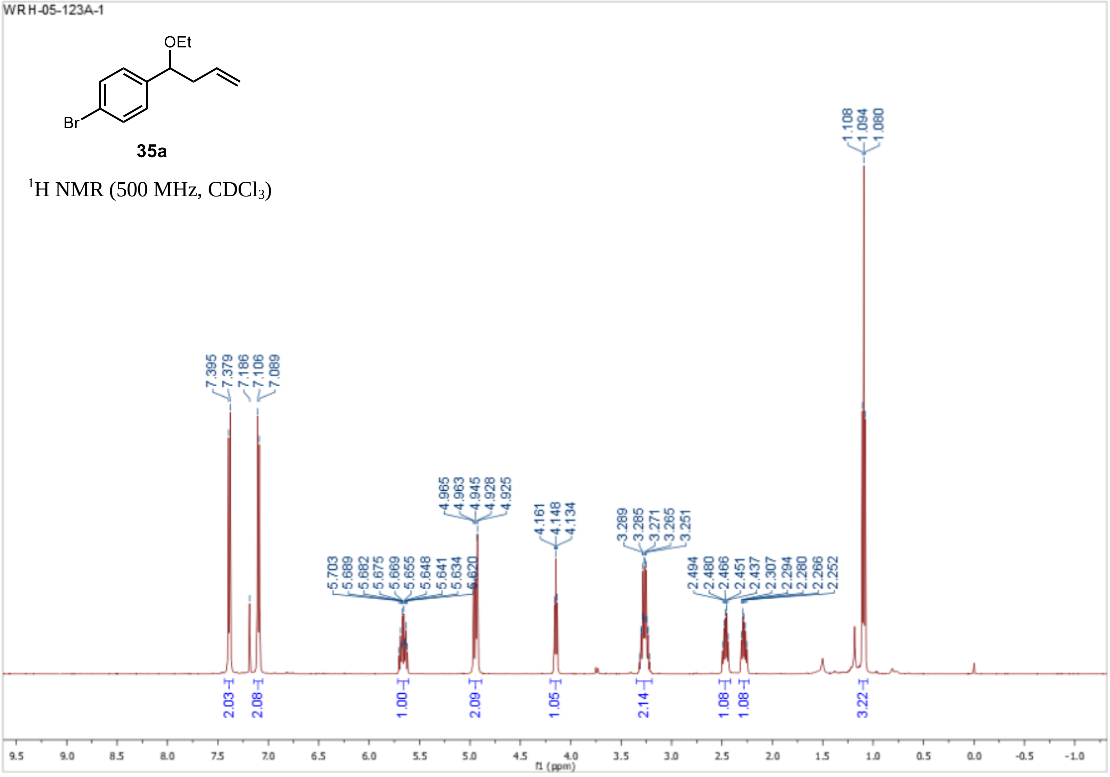


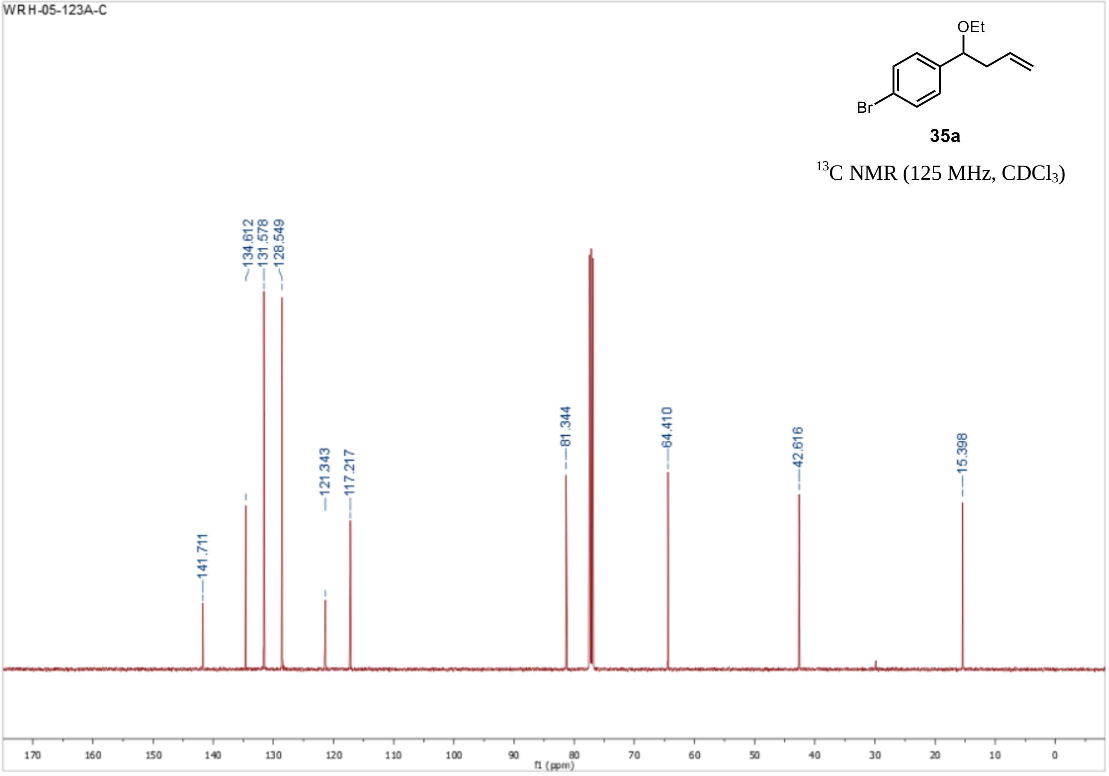
33a

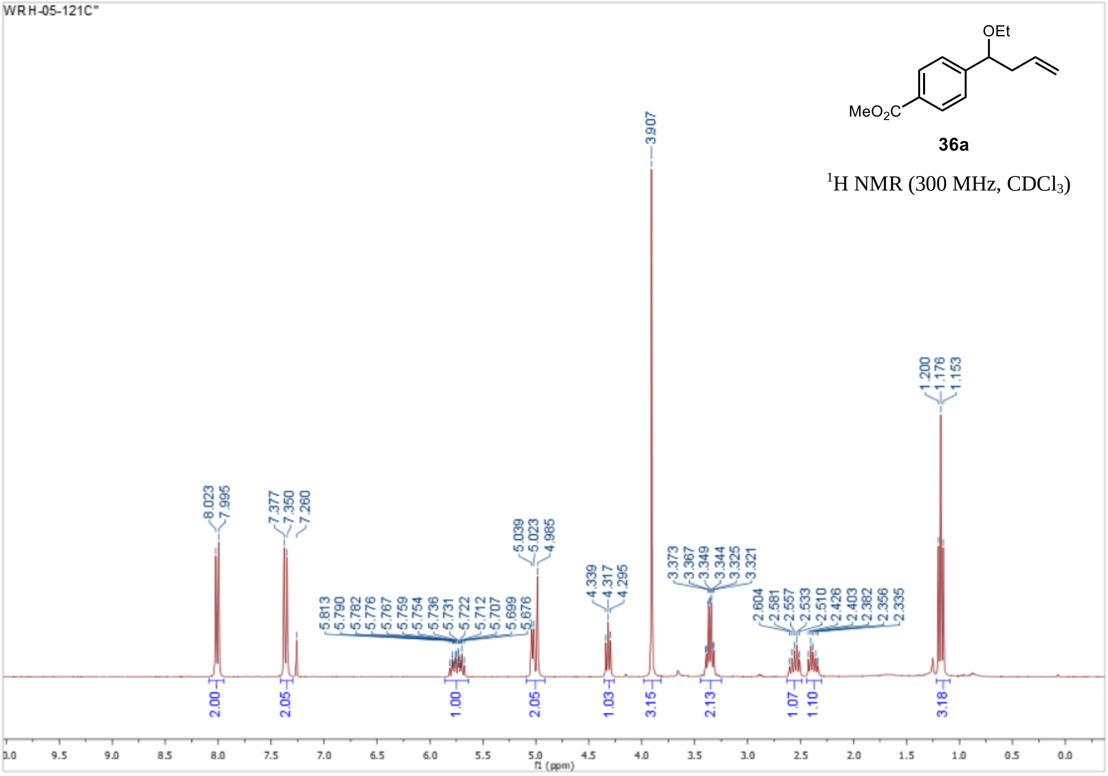
^{13}C NMR (100 MHz, CDCl$_3$)


WRH-05-9A
Me
N
Mts
Me
Me
Me
34a
1H NMR (500 MHz, CDCl3)
7.260
6.915
5.538
5.523
5.504
5.489
5.470
5.456
4.988
4.954
4.806
4.786
3.573
3.561
3.546
2.853
2.617
2.402
2.390
2.373
2.359
2.338
2.322
2.282
0.909
2.02
1.00
1.00
1.00
1.02
3.07
6.12
2.06
3.07
9.28
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


WRH-05-9A-C
Me
N
Mts
Me
Me
Me
34a
13C NMR (125 MHz, CDCl3)
141.843
139.647
136.604
134.626
132.124
116.334
64.883
36.631
33.042
30.687
28.561
24.216
20.992
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

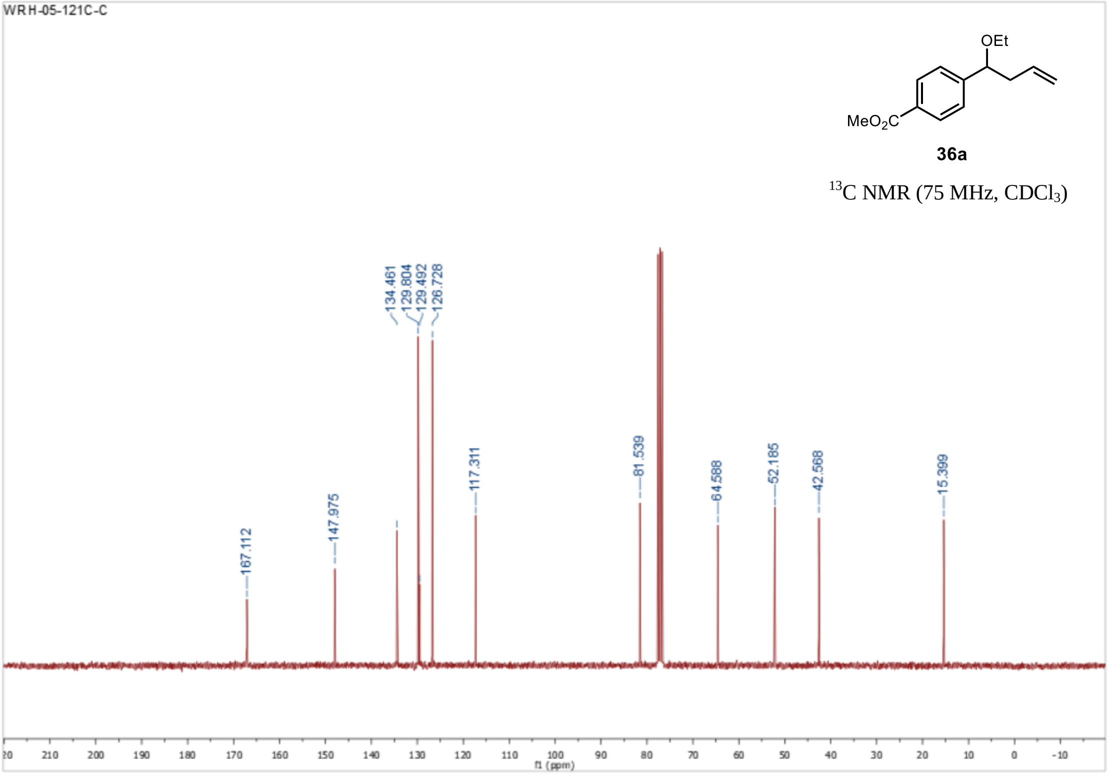

WRH-05-123A-1
OEt
Br
35a
^{1}H NMR (500 MHz, CDCl$_3$)
7.395 7.379 7.186 7.106 7.089
5.703 5.689 5.682 5.675 5.669 5.655 5.648 5.641 5.634 5.620
4.965 4.963 4.945 4.928 4.925
4.161 4.148 4.134
3.289 3.285 3.271 3.265 3.251
2.494 2.480 2.466 2.451 2.437 2.307 2.294 2.280 2.266 2.252
1.108 1.094 1.080
2.03 2.08 1.00 2.09 1.05 2.14 1.08 1.08 3.22
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


WRH-05-123A-C
OEt
Br
35a
^{13}C NMR (125 MHz, CDCl$_3$)
141.711
134.612 131.578 128.549
121.343 117.217
81.344
64.410
42.616
15.398
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



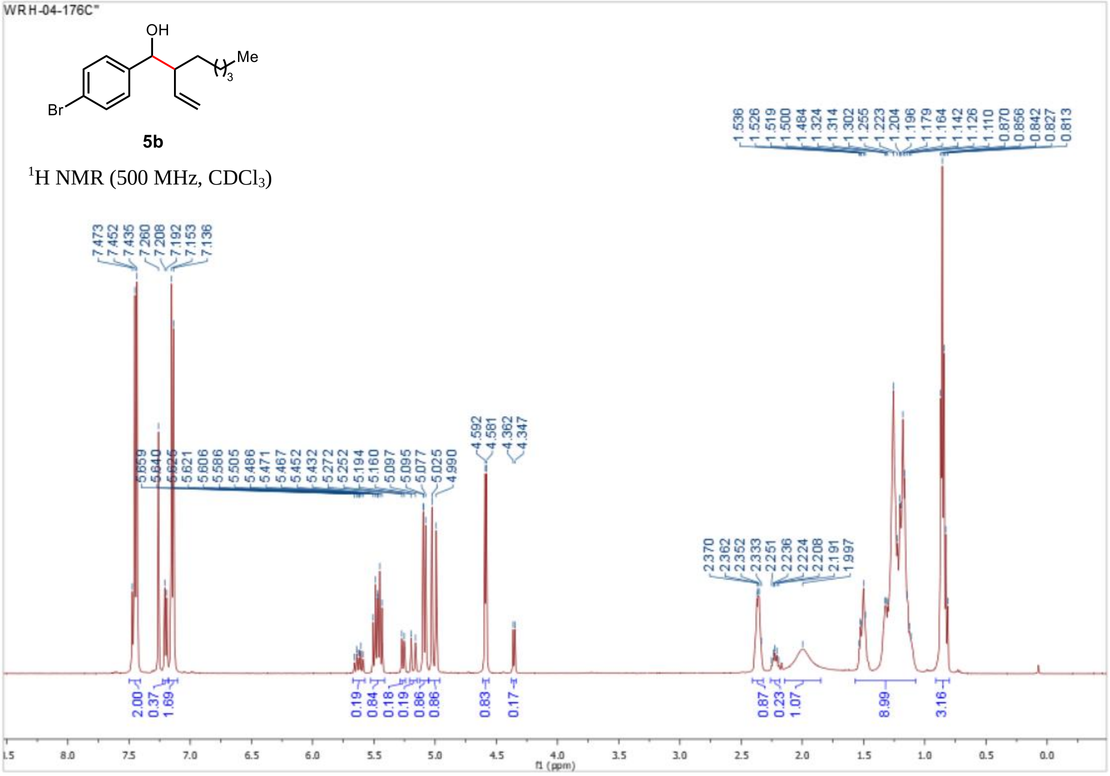
36a

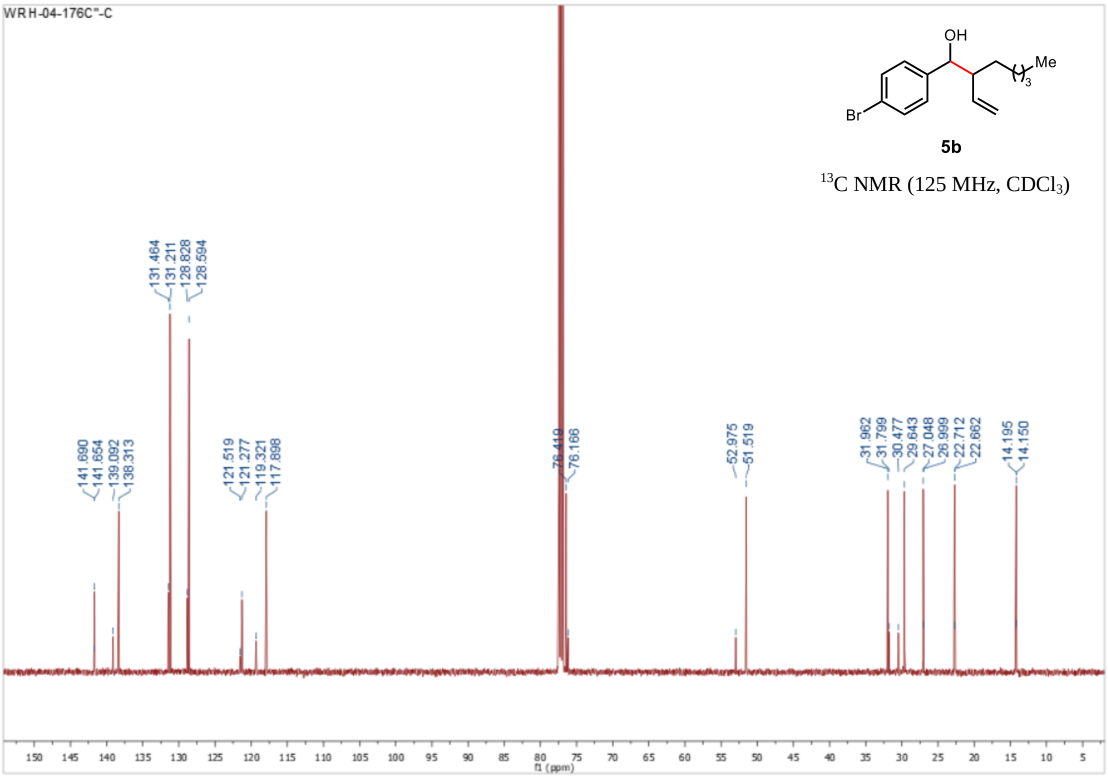
^{1}H NMR (300 MHz, CDCl$_3$)

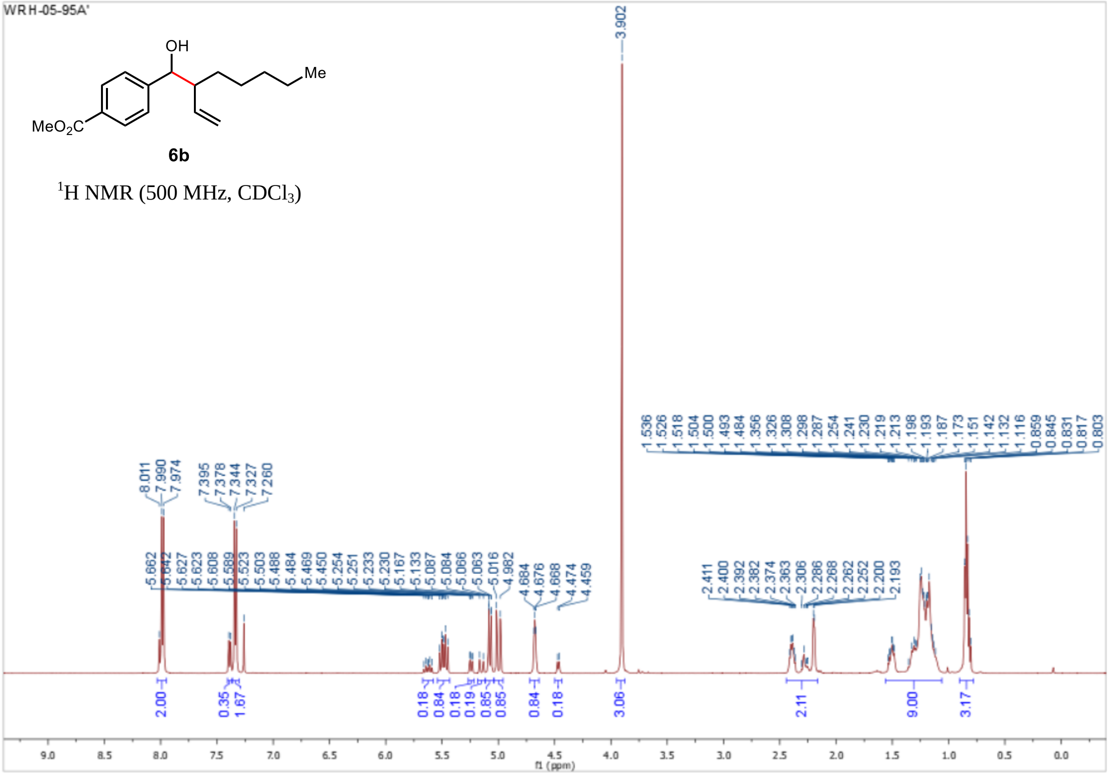


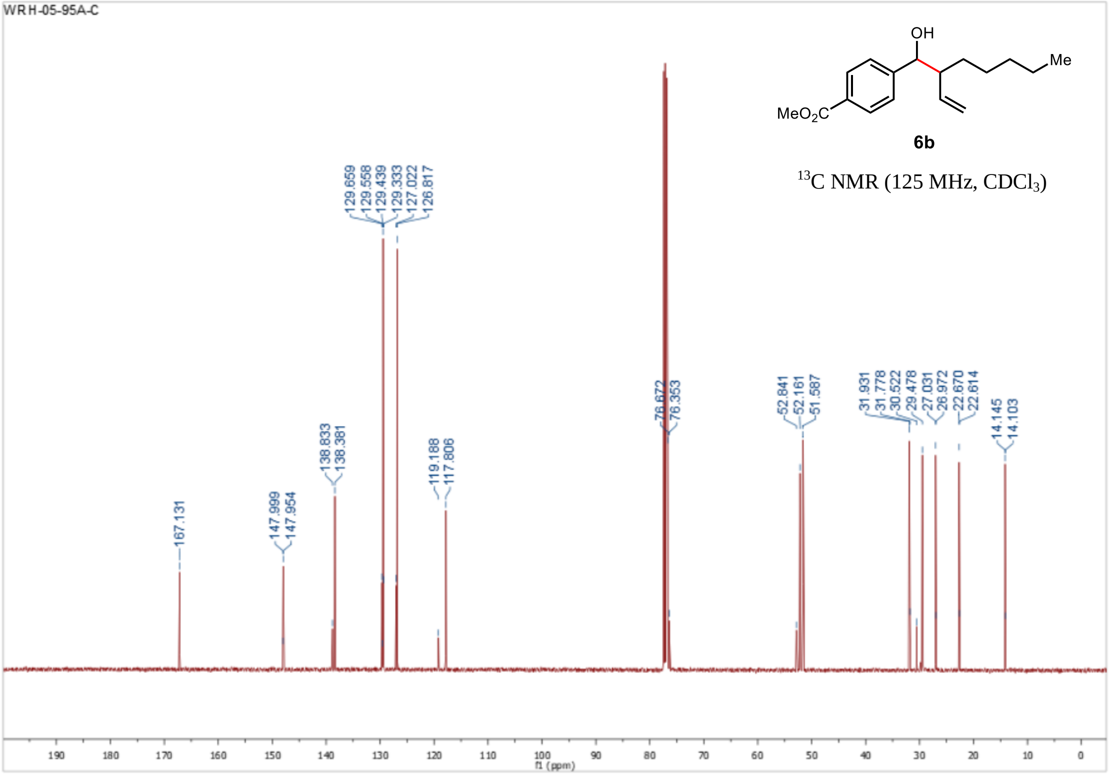
36a

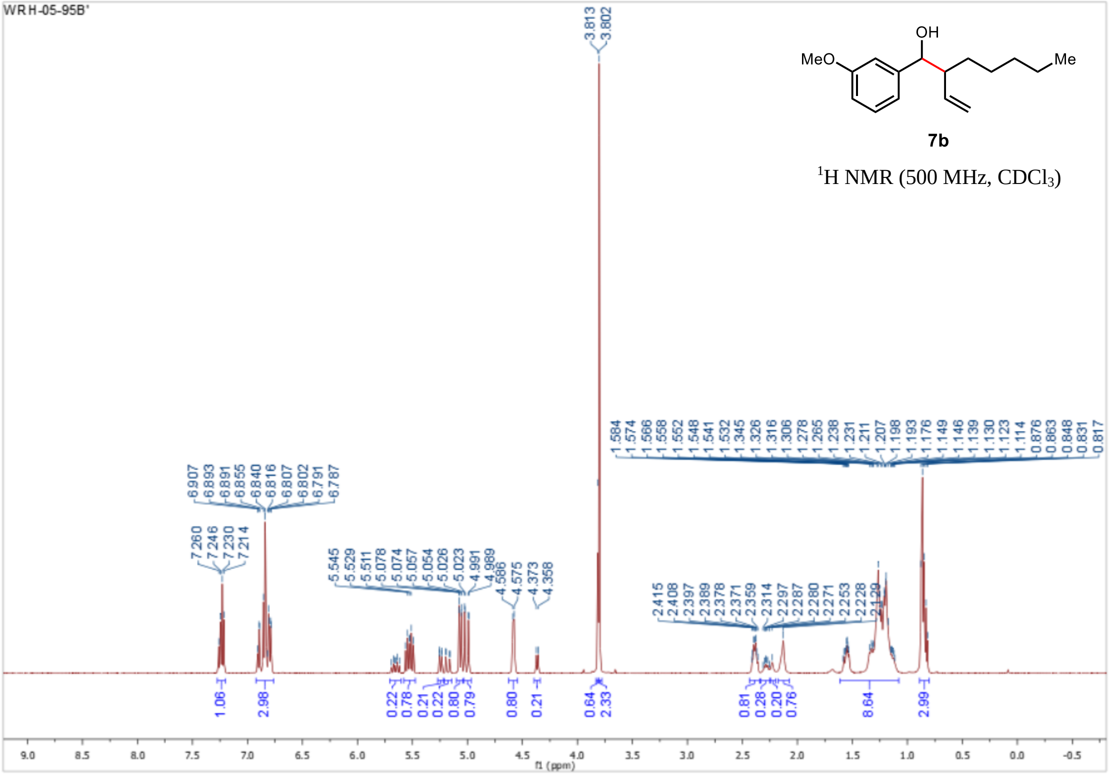
^{13}C NMR (75 MHz, CDCl$_3$)


WRH-04-176C"
OH
Me
3
Br
5b
^{1}H NMR (500 MHz, CDCl$_3$)
7.473
7.452
7.435
7.260
7.208
7.192
7.153
7.136
5.659
5.640
5.626
5.621
5.606
5.586
5.505
5.486
5.471
5.467
5.452
5.432
5.272
5.252
5.194
5.160
5.097
5.095
5.077
5.025
4.990
4.592
4.581
4.362
4.347
2.370
2.362
2.352
2.333
2.251
2.236
2.224
2.208
2.191
1.997
1.536
1.526
1.519
1.500
1.484
1.324
1.314
1.302
1.255
1.223
1.204
1.196
1.179
1.164
1.142
1.126
1.110
0.870
0.856
0.842
0.827
0.813
2.00
0.37
1.69
0.19
0.84
0.18
0.19
0.86
0.86
0.86
0.83
0.17
0.87
0.23
1.07
8.99
3.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


WRH-04-176C"-C
OH
Me
3
Br
5b
^{13}C NMR (125 MHz, CDCl$_3$)
141.690
141.654
139.092
138.313
131.464
131.211
128.828
128.594
121.519
121.277
119.321
117.898
76.419
76.166
52.975
51.519
31.962
31.799
30.477
29.643
27.048
26.999
22.712
22.662
14.195
14.150
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

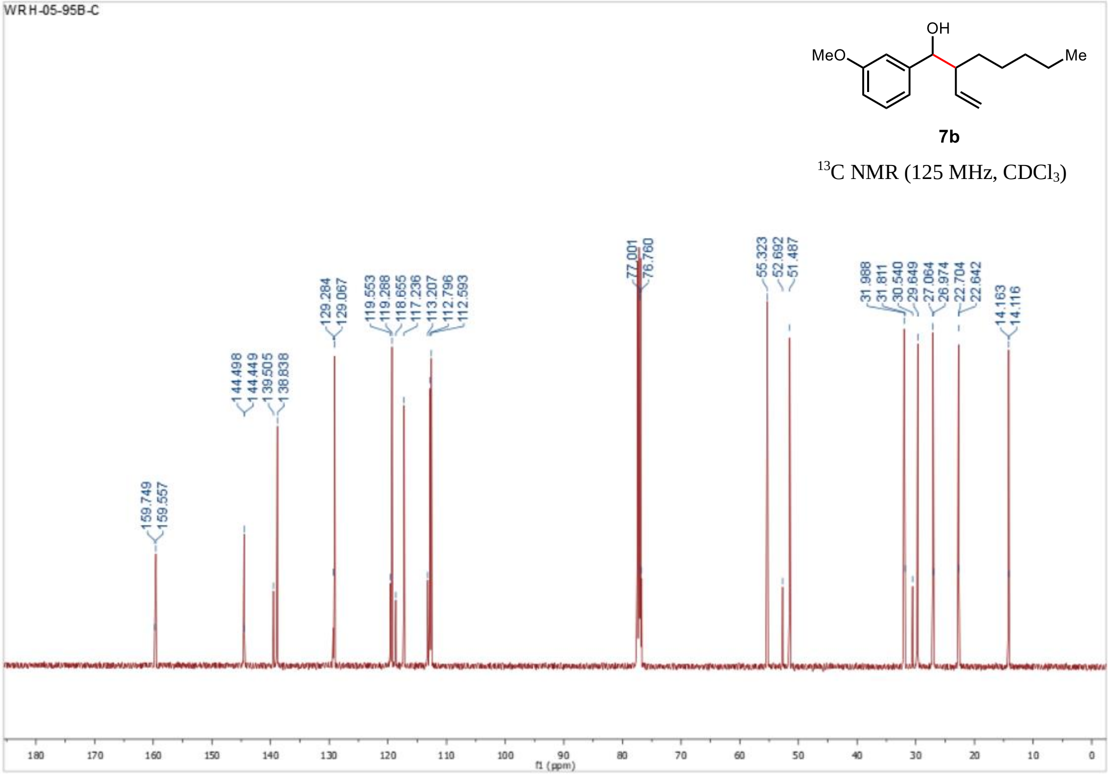

WRH-05-95A'
OH
Me
MeO$_2$C
6b
^{1}H NMR (500 MHz, CDCl$_3$)
8.011
7.990
7.974
7.395
7.378
7.344
7.327
7.260
5.662
5.642
5.627
5.623
5.608
5.589
5.523
5.503
5.488
5.484
5.469
5.450
5.254
5.251
5.233
5.230
5.167
5.133
5.087
5.084
5.066
5.063
5.016
4.982
4.684
4.676
4.668
4.474
4.459
3.902
2.411
2.400
2.392
2.382
2.374
2.363
2.306
2.286
2.268
2.262
2.252
2.200
2.193
1.536
1.526
1.518
1.504
1.500
1.493
1.484
1.356
1.326
1.308
1.298
1.287
1.254
1.241
1.230
1.219
1.213
1.198
1.193
1.187
1.173
1.151
1.142
1.132
1.116
0.859
0.845
0.831
0.817
0.803
2.00
0.35
1.67
0.18
0.84
0.18
0.19
0.85
0.85
0.84
0.18
3.06
2.11
9.00
3.17
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


WRH-05-95A-C
OH
Me
MeO$_2$C
6b
^{13}C NMR (125 MHz, CDCl$_3$)
167.131
147.999
147.954
138.833
138.381
129.659
129.558
129.439
129.333
127.022
126.817
119.188
117.806
76.672
76.353
52.841
52.161
51.587
31.931
31.778
30.522
29.478
27.031
26.972
22.670
22.614
14.145
14.103
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



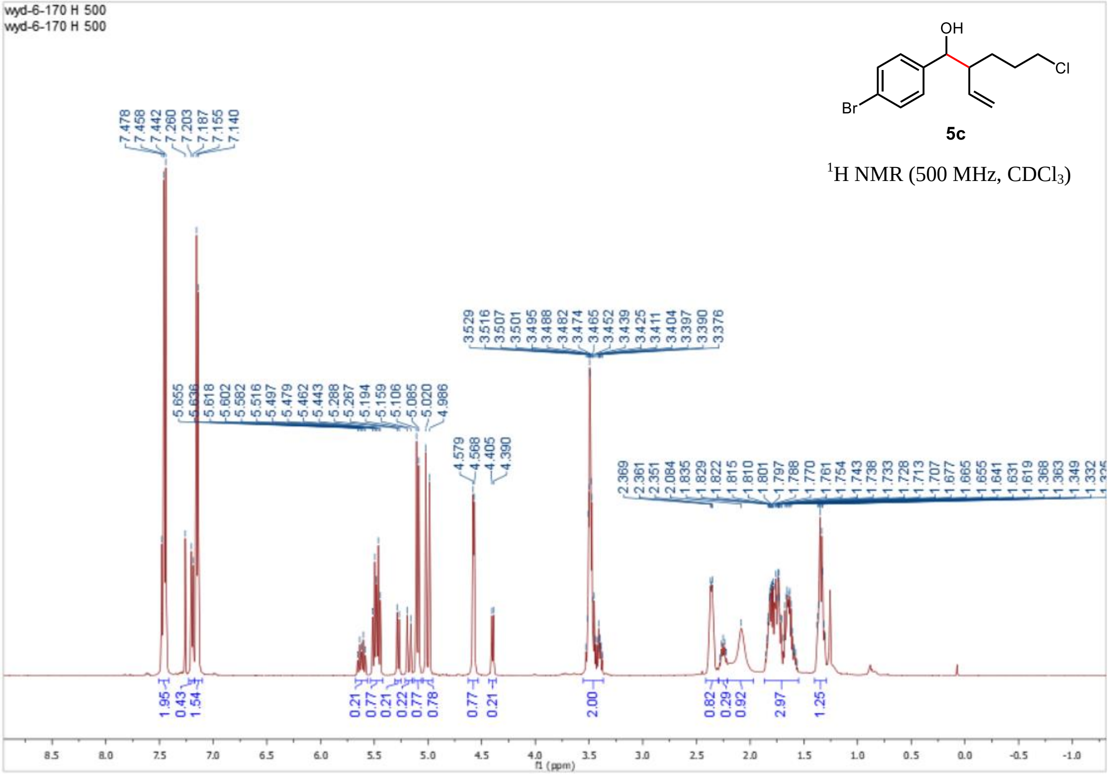
7b

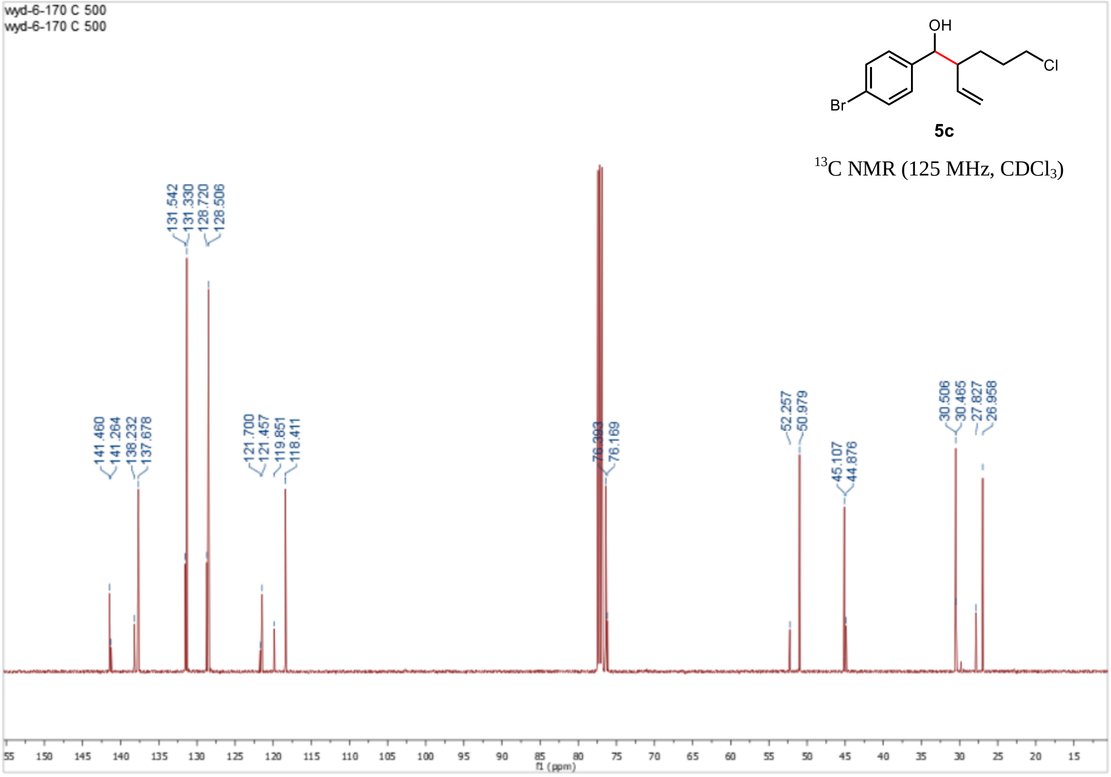
^{1}H NMR (500 MHz, CDCl$_3$)

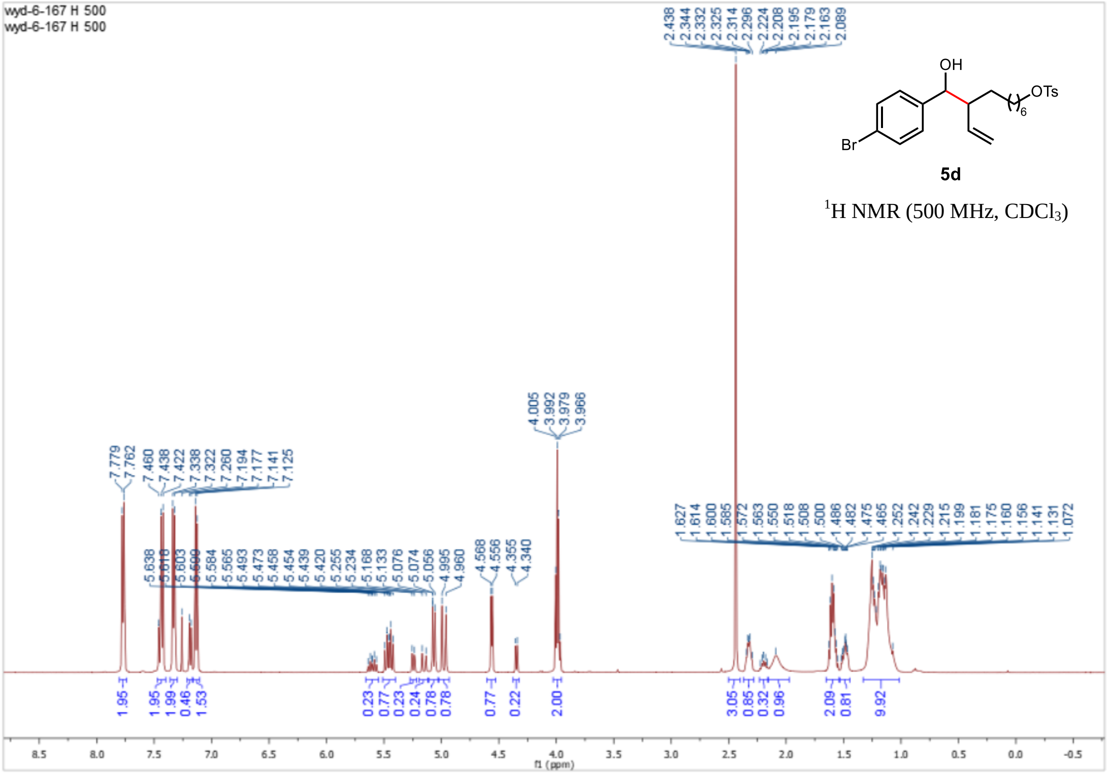


7b

^{13}C NMR (125 MHz, CDCl$_3$)

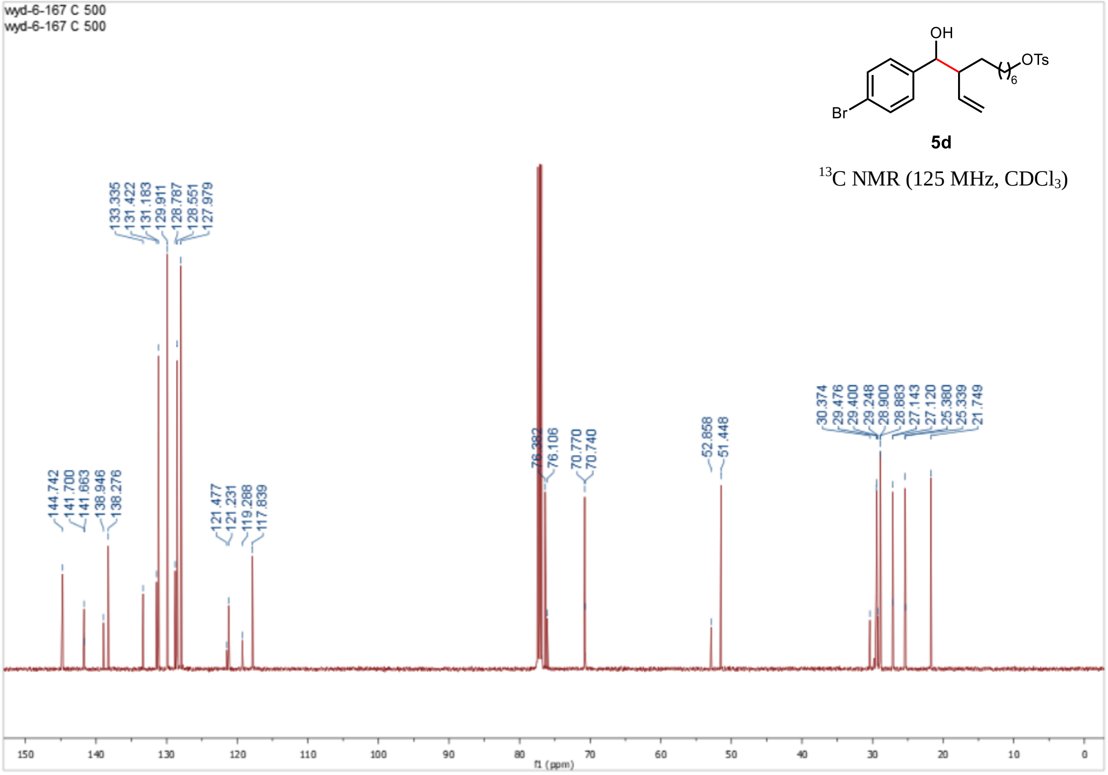

wyd-6-170 H 500
wyd-6-170 H 500
OH
Cl
Br
5c
^{1}H NMR (500 MHz, CDCl$_3$)
7.478
7.458
7.442
7.260
7.203
7.187
7.155
7.140
5.655
5.636
5.618
5.602
5.582
5.516
5.497
5.479
5.462
5.443
5.288
5.267
5.194
5.159
5.106
5.085
5.020
4.986
4.579
4.568
4.405
4.390
3.529
3.516
3.507
3.501
3.495
3.488
3.482
3.474
3.465
3.452
3.439
3.425
3.411
3.404
3.397
3.390
3.376
2.369
2.361
2.351
2.084
1.835
1.829
1.822
1.815
1.810
1.801
1.797
1.788
1.770
1.761
1.754
1.743
1.738
1.733
1.728
1.713
1.707
1.677
1.665
1.655
1.641
1.631
1.619
1.368
1.363
1.349
1.332
1.325
1.95
0.43
1.54
0.21
0.77
0.21
0.22
0.77
0.78
0.77
0.21
2.00
0.82
0.29
0.92
2.97
1.25
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


wyd-6-170 C 500
wyd-6-170 C 500
OH
Cl
Br
5c
^{13}C NMR (125 MHz, CDCl$_3$)
141.460
141.264
138.232
137.678
131.542
131.330
128.720
128.506
121.700
121.457
119.851
118.411
76.393
76.169
52.257
50.979
45.107
44.876
30.506
30.465
27.827
26.958
55
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
f1 (ppm)



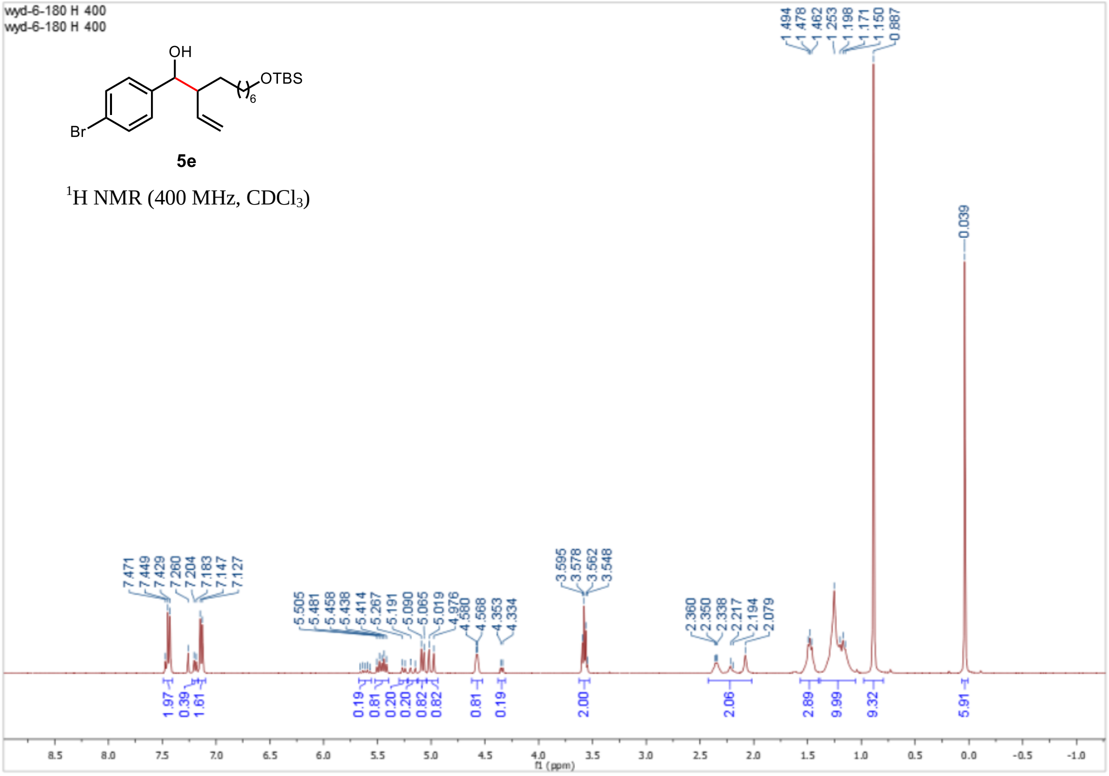
5d

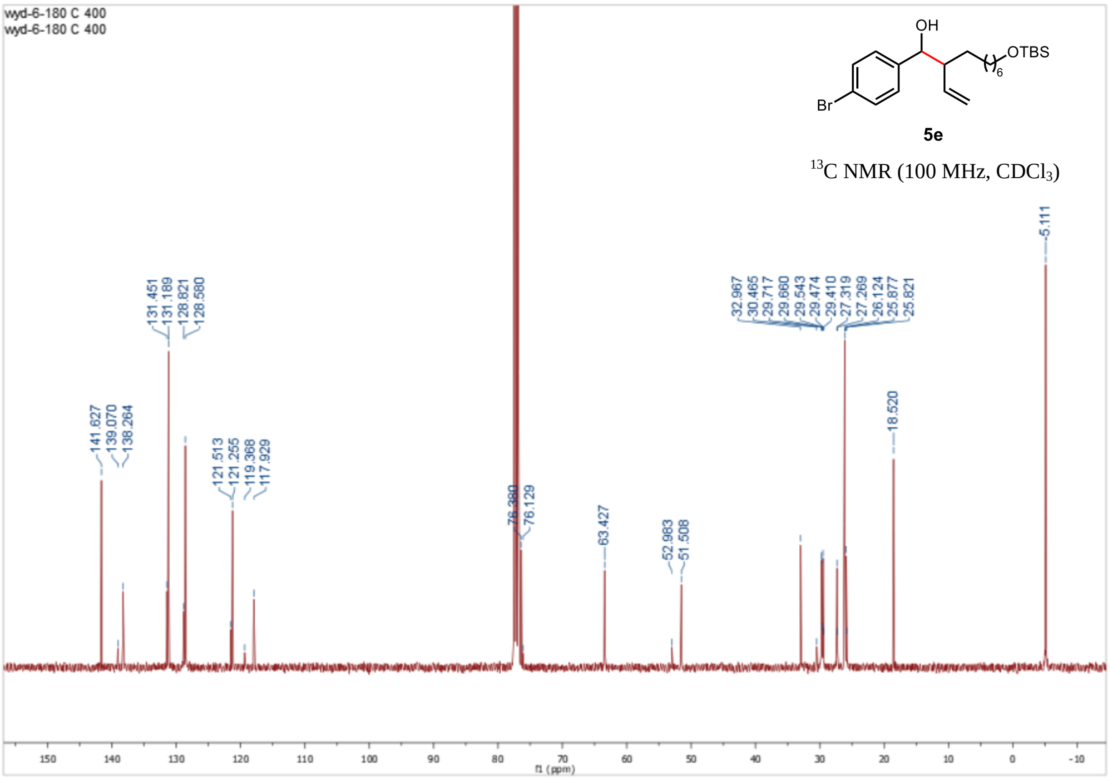
^{1}H NMR (500 MHz, CDCl$_3$)

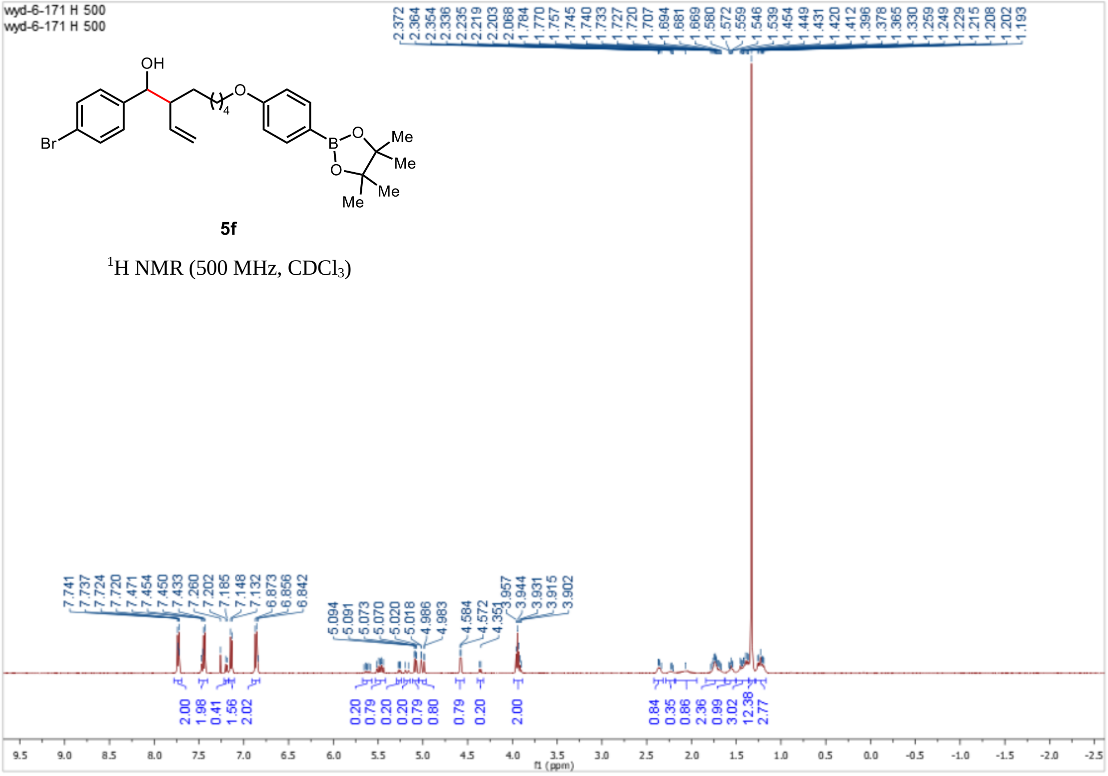


5d

^{13}C NMR (125 MHz, CDCl$_3$)

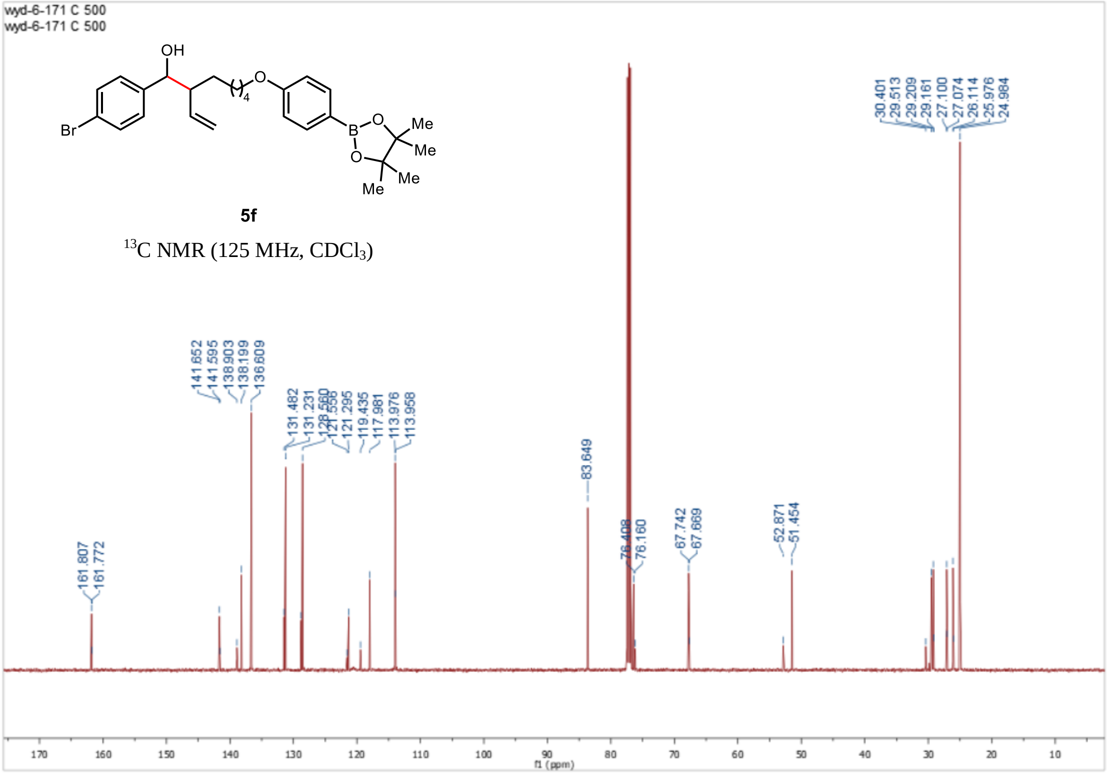

wyd-6-180 H 400
wyd-6-180 H 400
OH
OTBS
6
Br
5e
^{1}H NMR (400 MHz, CDCl$_3$)
7.471
7.449
7.429
7.260
7.204
7.183
7.147
7.127
5.505
5.481
5.458
5.438
5.414
5.267
5.191
5.090
5.065
5.019
4.976
4.580
4.568
4.353
4.334
3.595
3.578
3.562
3.548
2.360
2.350
2.338
2.217
2.194
2.079
1.494
1.478
1.462
1.253
1.198
1.171
1.150
0.887
0.039
1.97
0.39
1.61
0.19
0.81
0.20
0.20
0.82
0.82
0.82
0.81
0.19
2.00
2.06
2.89
9.99
9.32
5.91
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


wyd-6-180 C 400
wyd-6-180 C 400
OH
OTBS
6
Br
5e
^{13}C NMR (100 MHz, CDCl$_3$)
141.627
139.070
138.264
131.451
131.189
128.821
128.580
121.513
121.255
119.368
117.929
76.380
76.129
63.427
52.983
51.508
32.967
30.465
29.717
29.660
29.543
29.474
29.410
27.319
27.269
26.124
25.877
25.821
18.520
-5.111
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



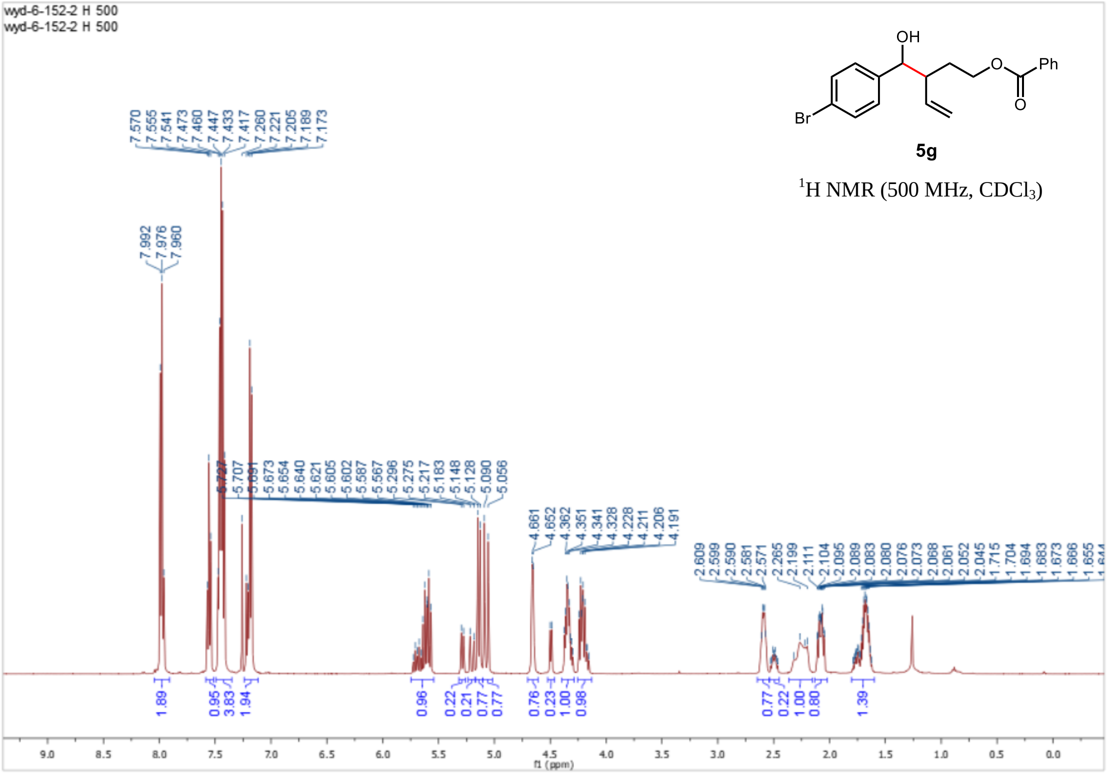
5f

^{1}H NMR (500 MHz, CDCl$_3$)



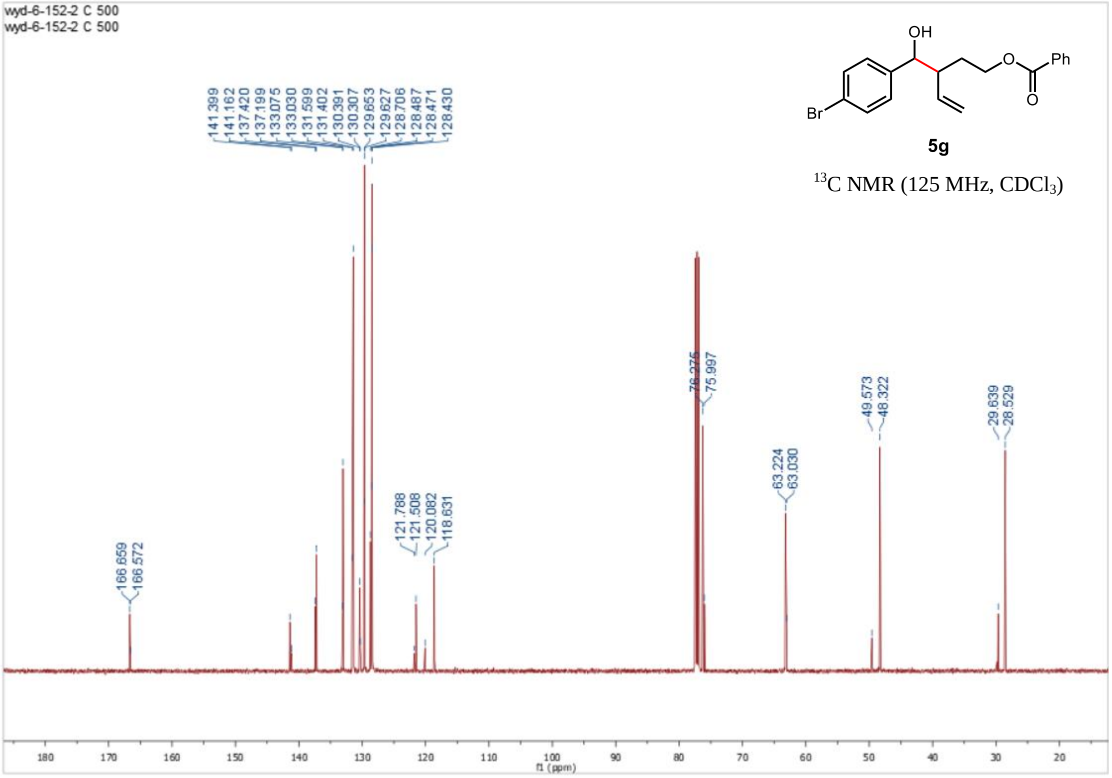
5f

^{13}C NMR (125 MHz, CDCl$_3$)



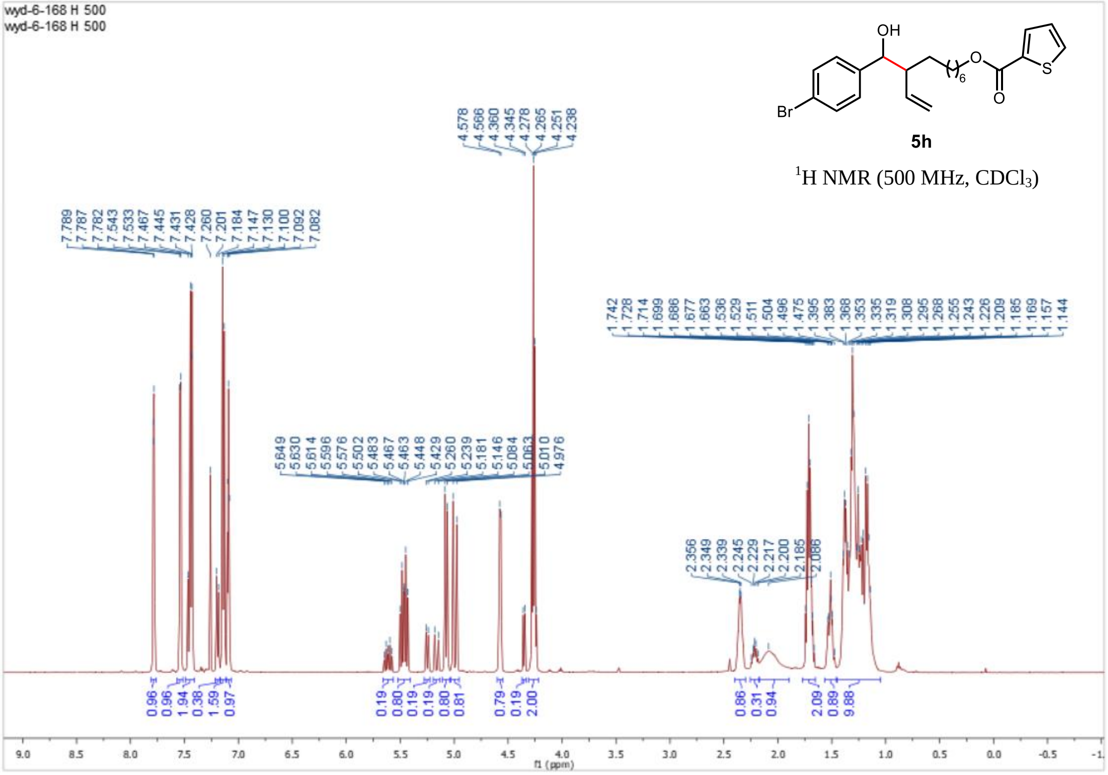
5g

^{1}H NMR (500 MHz, CDCl$_3$)



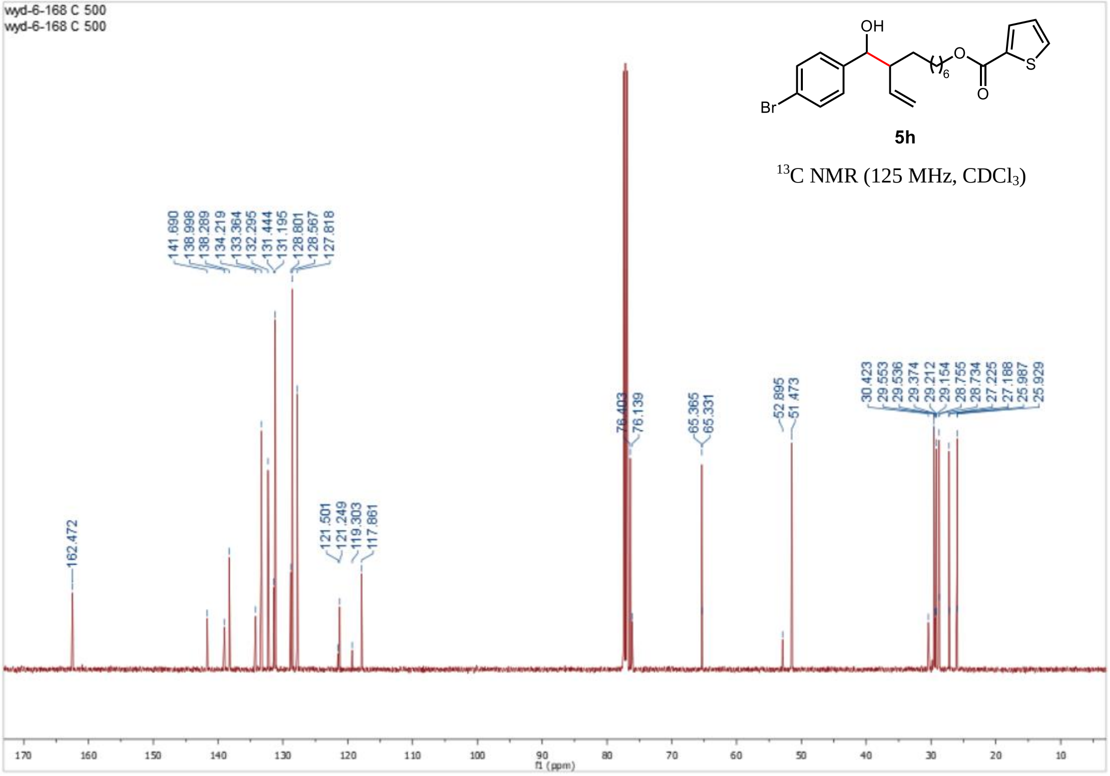
5g

^{13}C NMR (125 MHz, CDCl$_3$)



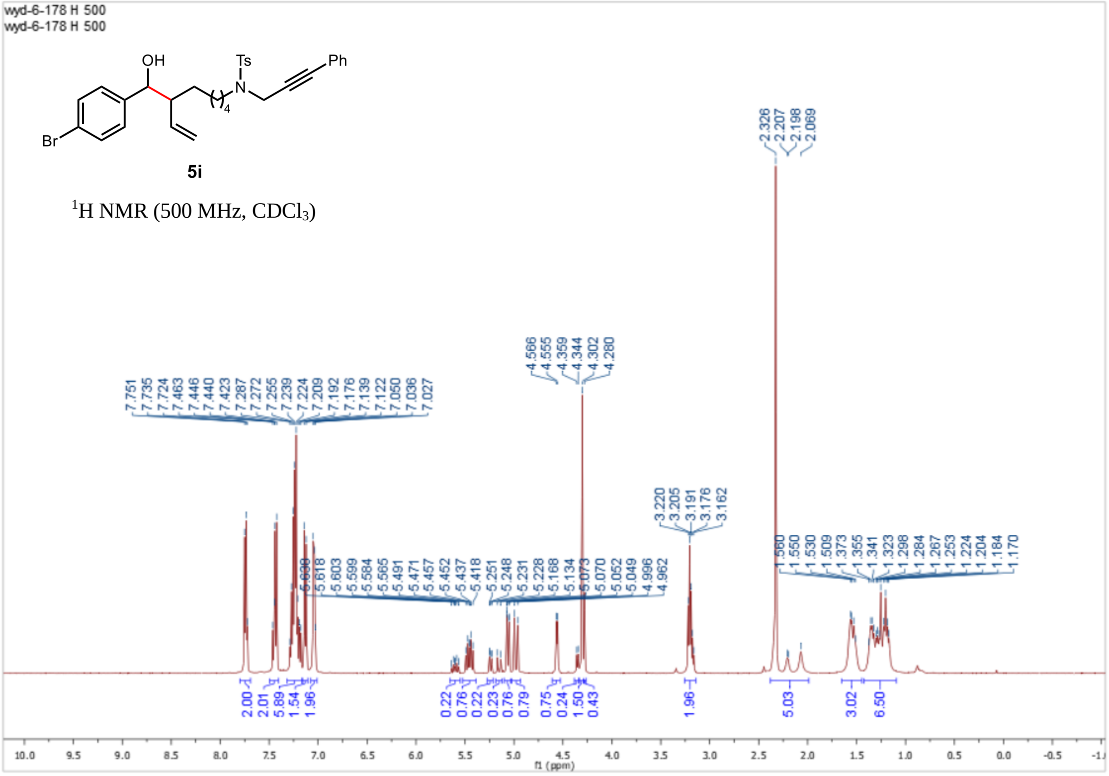
5h

^{1}H NMR (500 MHz, CDCl$_3$)



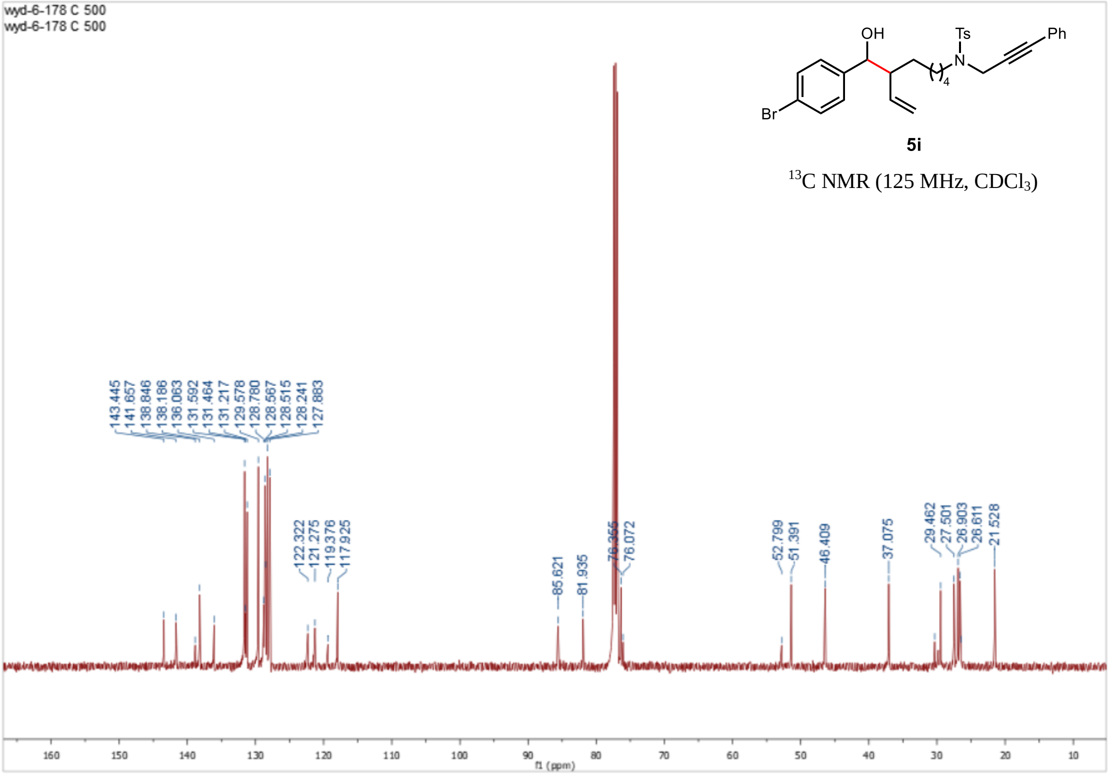
5h

^{13}C NMR (125 MHz, CDCl$_3$)



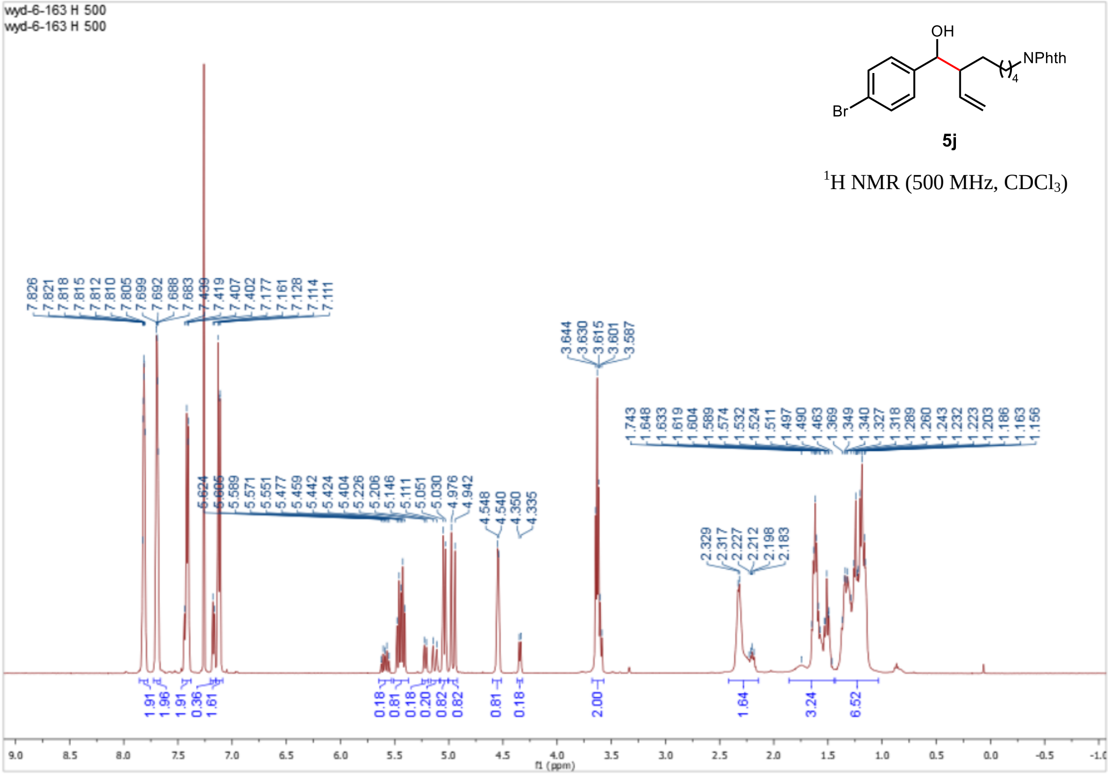
5i

^{1}H NMR (500 MHz, CDCl$_3$)



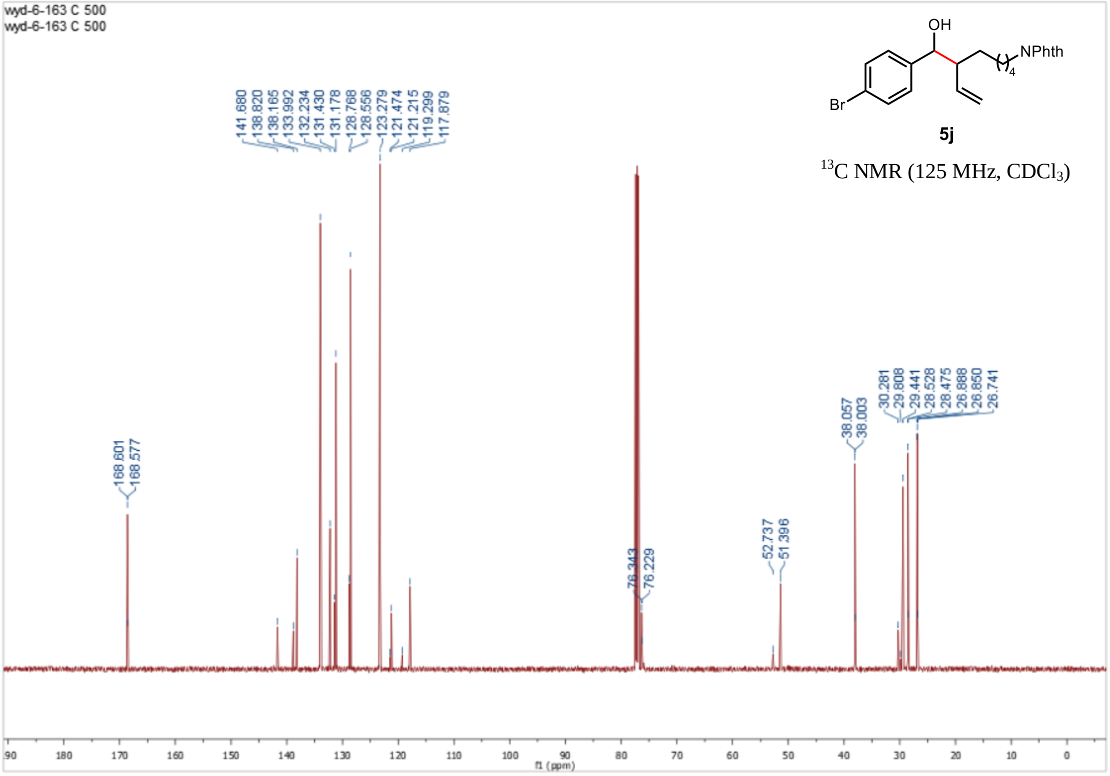
5i

^{13}C NMR (125 MHz, CDCl$_3$)



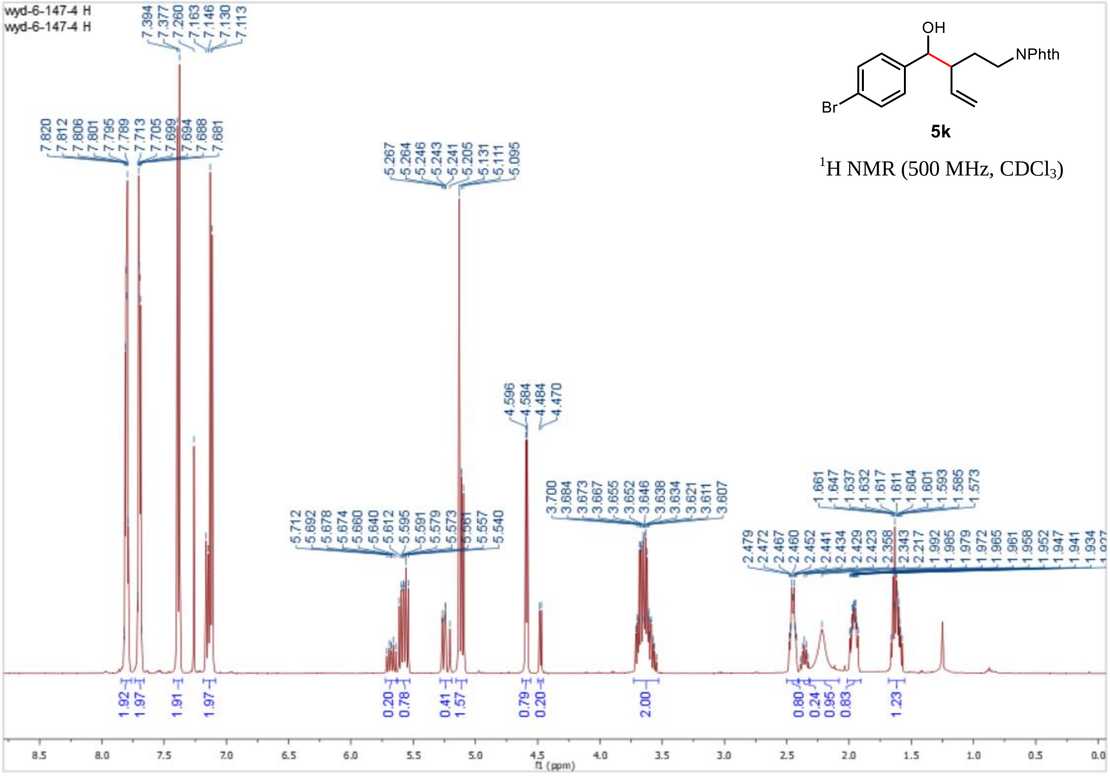
5j

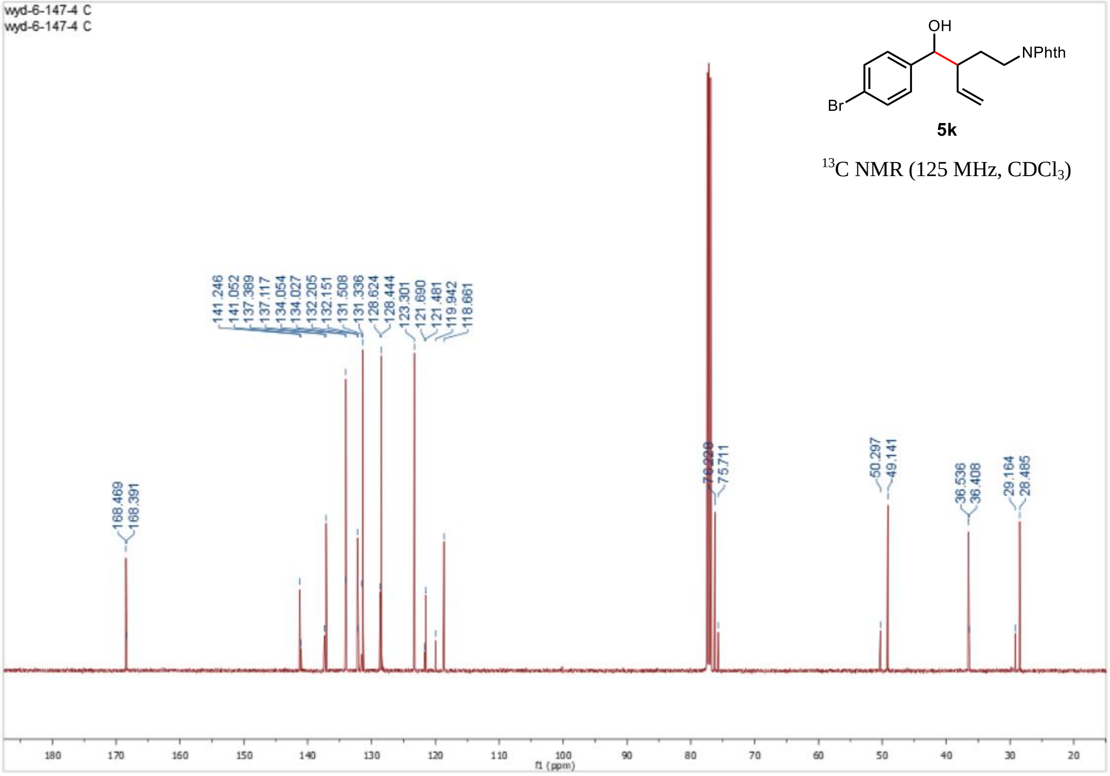
^{1}H NMR (500 MHz, CDCl$_3$)

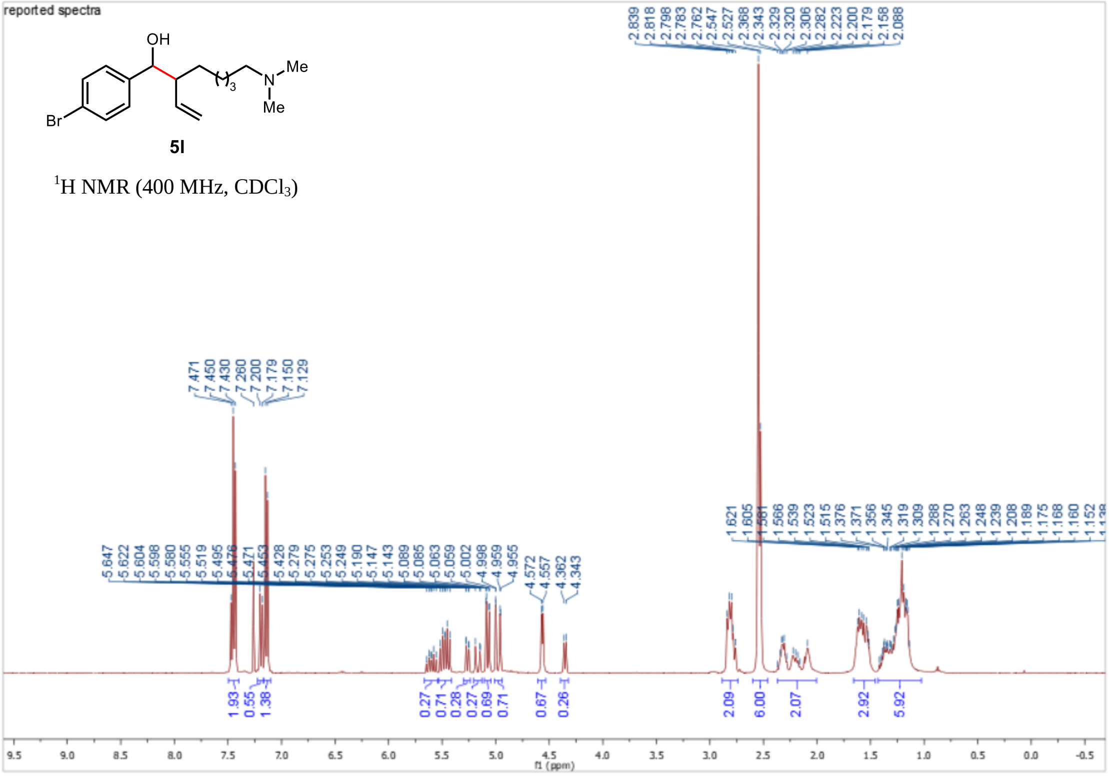


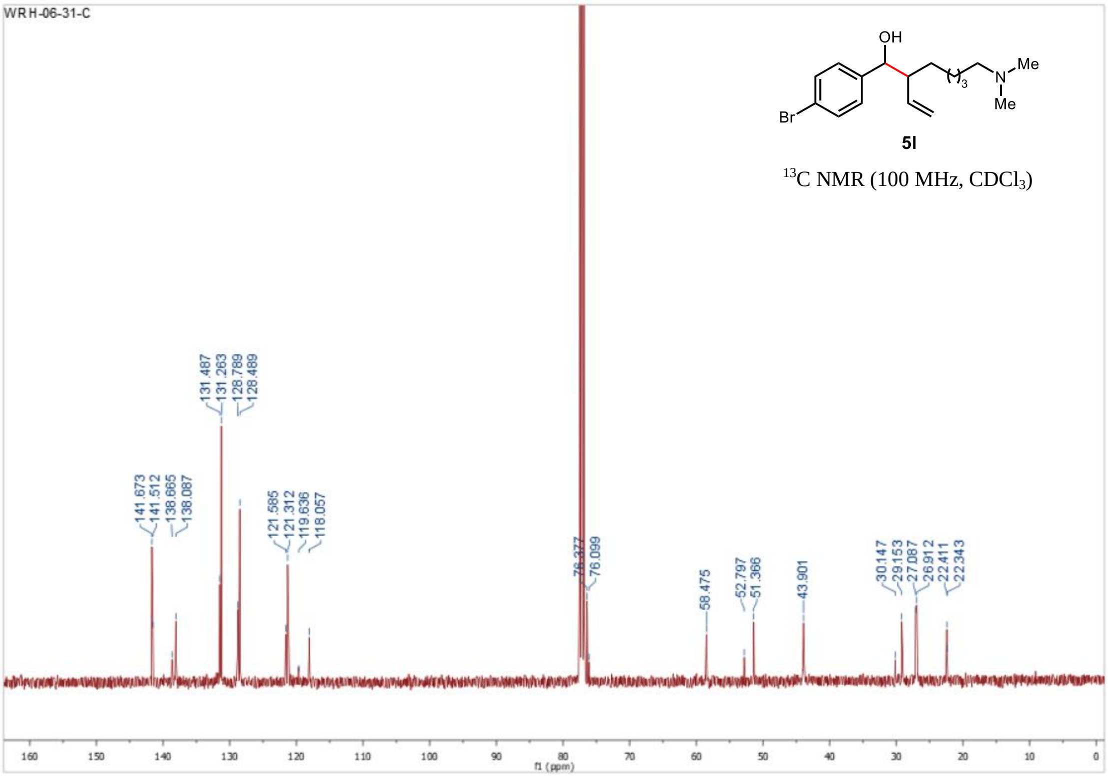
5j

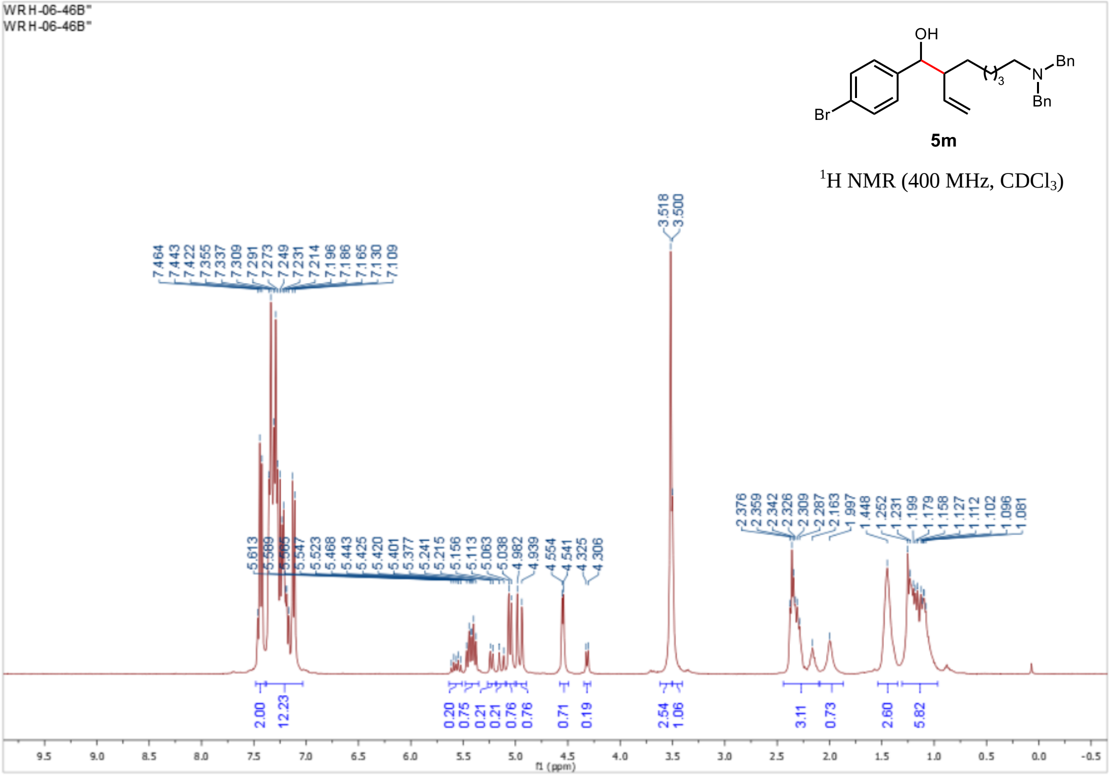
^{13}C NMR (125 MHz, CDCl$_3$)

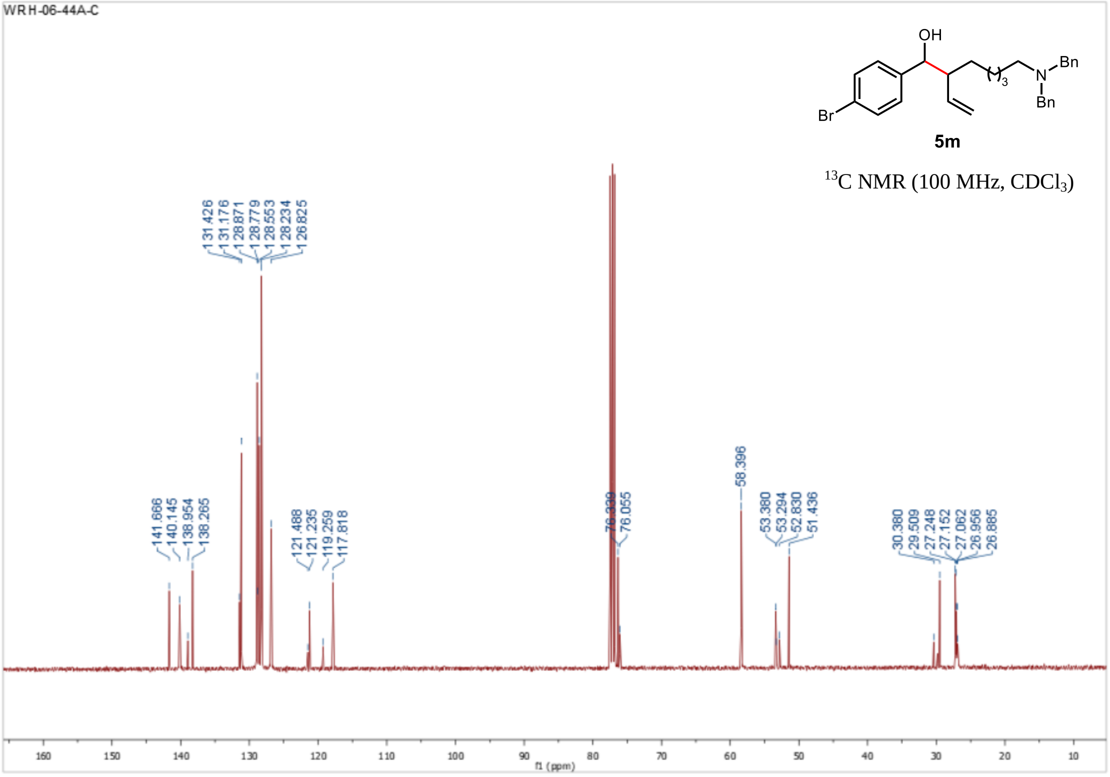

wyd-6-147-4 H
wyd-6-147-4 H
OH
NPhth
Br
5k
^{1}H NMR (500 MHz, CDCl$_3$)
7.394 7.377 7.260 7.163 7.146 7.130 7.113
7.820 7.812 7.806 7.801 7.795 7.789 7.713 7.705 7.699 7.694 7.688 7.681
5.267 5.264 5.246 5.243 5.241 5.205 5.131 5.111 5.095
4.596 4.584 4.484 4.470
5.712 5.692 5.678 5.674 5.660 5.640 5.612 5.595 5.591 5.579 5.573 5.561 5.557 5.540
3.700 3.684 3.673 3.667 3.655 3.652 3.646 3.638 3.634 3.621 3.611 3.607
1.661 1.647 1.637 1.632 1.617 1.611 1.604 1.601 1.593 1.585 1.573
2.479 2.472 2.467 2.460 2.452 2.441 2.434 2.429 2.423 2.358 2.343 2.217 1.992 1.985 1.979 1.972 1.965 1.961 1.958 1.952 1.947 1.941 1.934
1.92 1.97 1.91 1.97 0.20 0.78 0.41 1.57 0.79 0.20 2.00 0.80 0.24 0.95 0.83 1.23
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

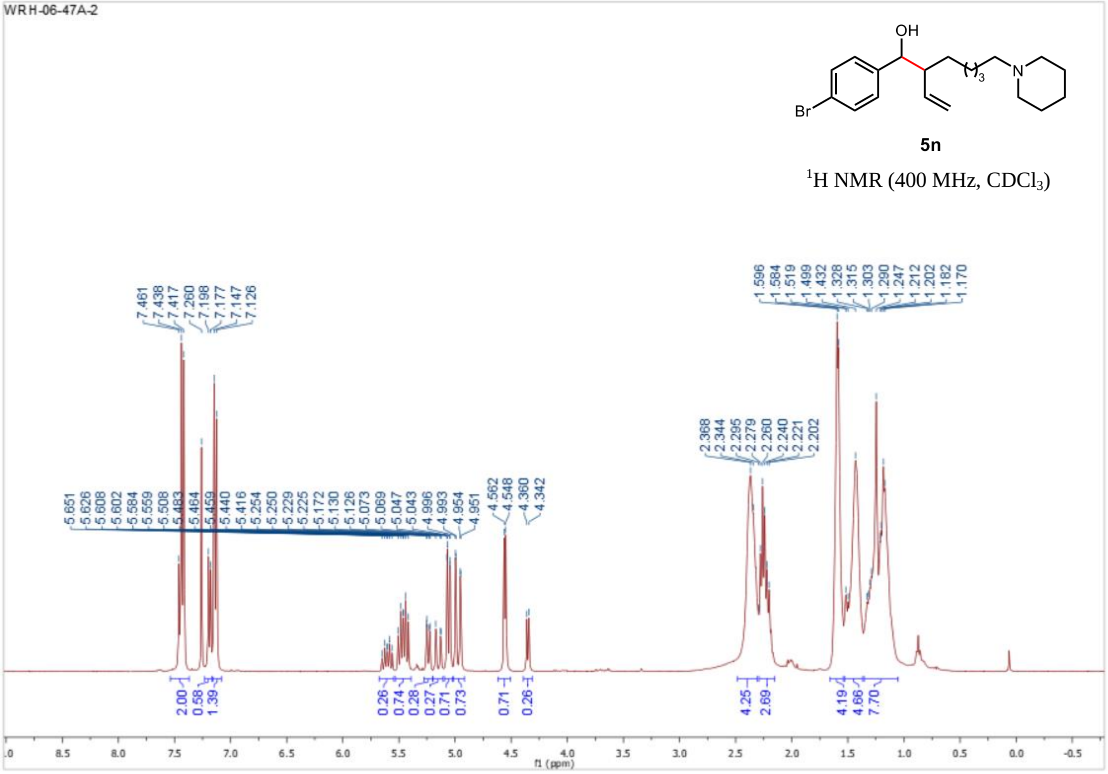

wyd-6-147-4 C
wyd-6-147-4 C
OH
NPhth
Br
5k
^{13}C NMR (125 MHz, CDCl$_3$)
141.246 141.052 137.389 137.117 134.054 134.027 132.205 132.151 131.508 131.336 128.624 128.444 123.301 121.690 121.481 119.942 118.661
168.469 168.391
76.229 75.711
50.297 49.141
36.536 36.408
29.164 28.485
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


reported spectra
OH
Br
Me
N
Me
3
5l
1H NMR (400 MHz, CDCl3)
7.471
7.450
7.430
7.260
7.200
7.179
7.150
7.129
5.647
5.622
5.604
5.598
5.580
5.555
5.519
5.495
5.476
5.471
5.453
5.428
5.279
5.275
5.253
5.249
5.190
5.147
5.143
5.089
5.085
5.063
5.059
5.002
4.998
4.959
4.955
4.572
4.557
4.362
4.343
2.839
2.818
2.798
2.783
2.762
2.547
2.527
2.368
2.343
2.329
2.320
2.306
2.282
2.223
2.200
2.179
2.158
2.088
1.621
1.605
1.581
1.566
1.539
1.523
1.515
1.376
1.371
1.356
1.345
1.319
1.309
1.288
1.270
1.263
1.248
1.239
1.208
1.189
1.175
1.168
1.160
1.152
1.93
0.55
1.38
0.27
0.71
0.28
0.27
0.69
0.71
0.67
0.26
2.09
6.00
2.07
2.92
5.92
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


WRH-06-31-C
OH
Br
Me
N
Me
3
5l
13C NMR (100 MHz, CDCl3)
141.673
141.512
138.665
138.087
131.487
131.263
128.789
128.489
121.585
121.312
119.636
118.057
76.377
76.099
58.475
52.797
51.366
43.901
30.147
29.153
27.087
26.912
22.411
22.343
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

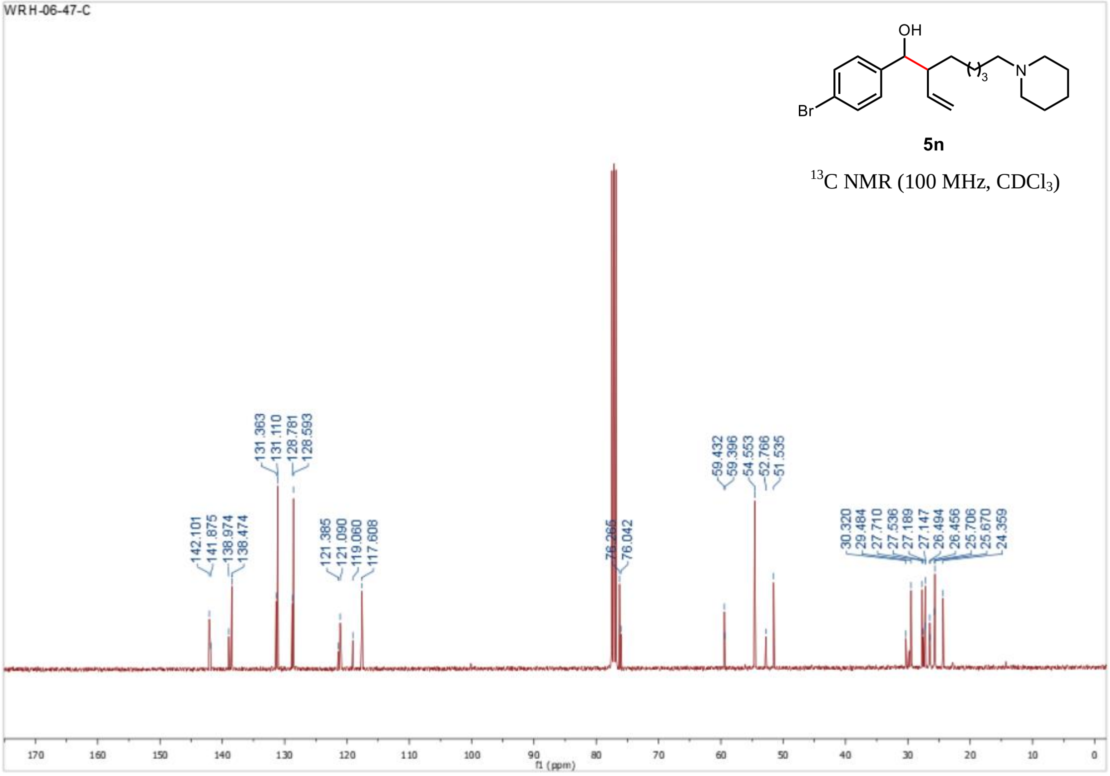

WRH-06-46B"
WRH-06-46B"
OH
Br
N
Bn
Bn
3
5m
^{1}H NMR (400 MHz, CDCl$_3$)
7.464
7.443
7.422
7.355
7.337
7.309
7.291
7.273
7.249
7.231
7.214
7.196
7.186
7.165
7.130
7.109
5.613
5.589
5.565
5.547
5.523
5.468
5.443
5.425
5.420
5.401
5.377
5.241
5.215
5.156
5.113
5.063
5.038
4.982
4.939
4.554
4.541
4.325
4.306
3.518
3.500
2.376
2.359
2.342
2.326
2.309
2.287
2.163
1.997
1.448
1.252
1.231
1.199
1.179
1.158
1.127
1.112
1.102
1.096
1.081
2.00
12.23
0.20
0.75
0.21
0.21
0.76
0.76
0.71
0.19
2.54
1.06
3.11
0.73
2.60
5.82
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


WRH-06-44A-C
OH
Br
N
Bn
Bn
3
5m
^{13}C NMR (100 MHz, CDCl$_3$)
141.666
140.145
138.954
138.265
131.426
131.176
128.871
128.779
128.553
128.234
126.825
121.488
121.235
119.259
117.818
76.339
76.055
58.396
53.380
53.294
52.830
51.436
30.380
29.509
27.248
27.152
27.062
26.956
26.885
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



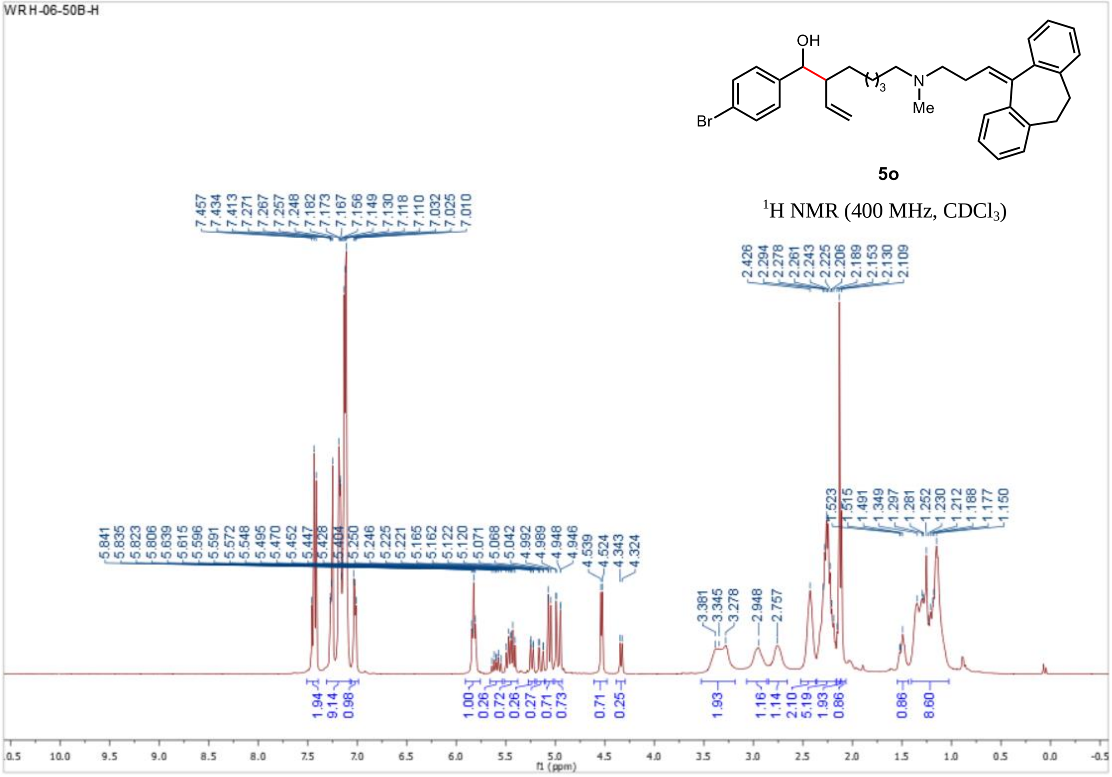
5n

^{1}H NMR (400 MHz, $CDCl_3$)



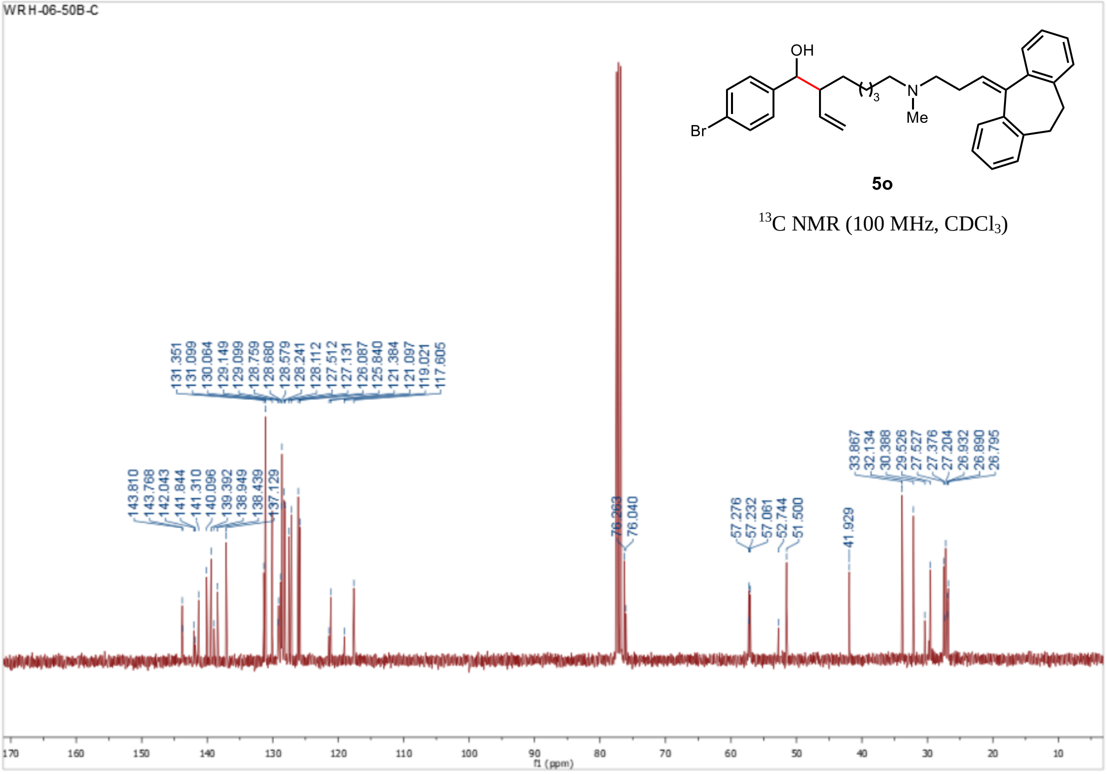
5n

^{13}C NMR (100 MHz, $CDCl_3$)



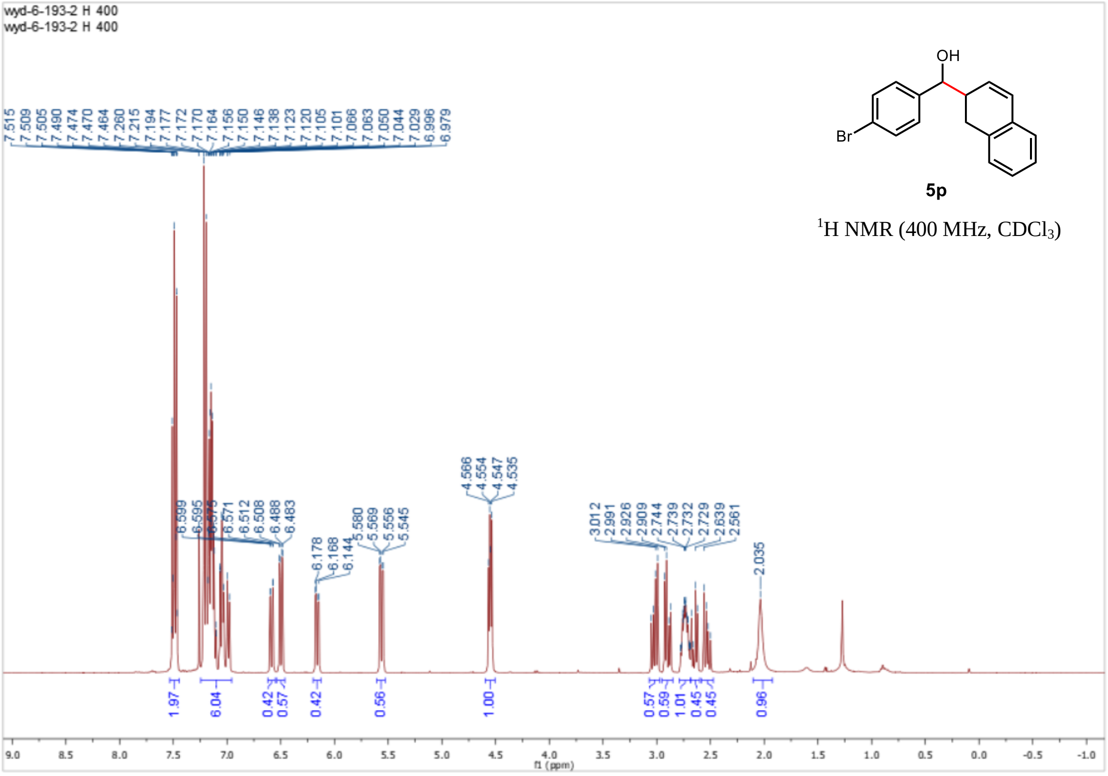
5o

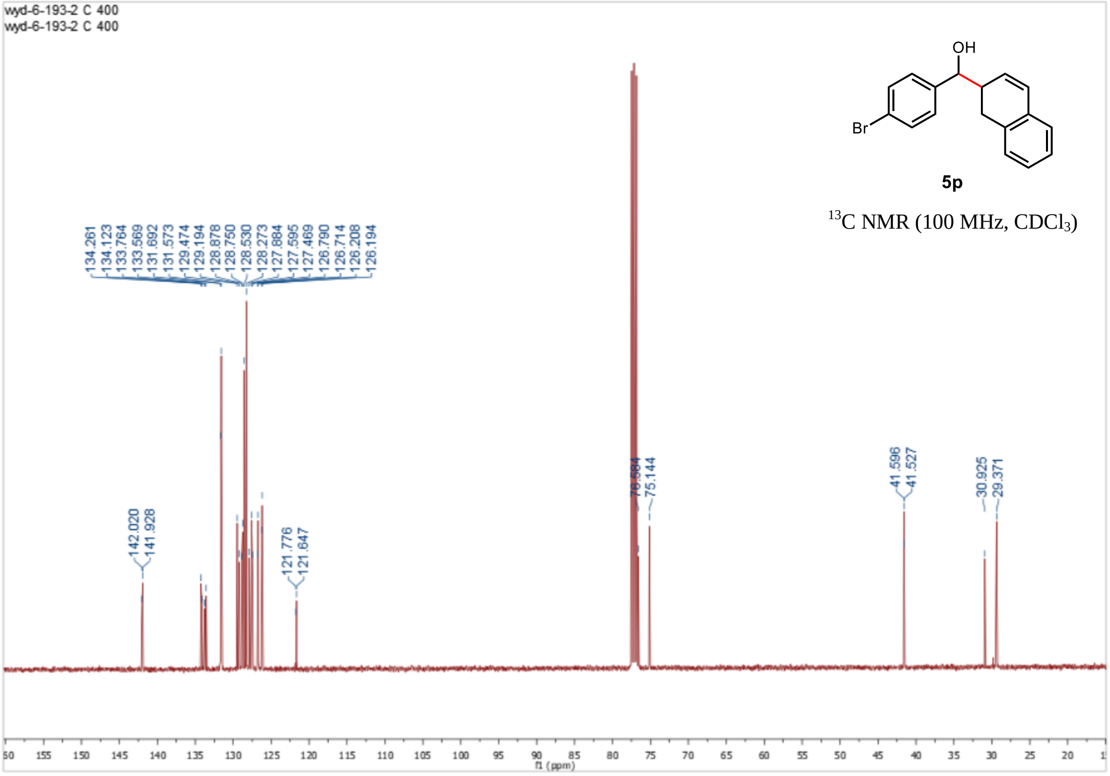
^{1}H NMR (400 MHz, CDCl$_3$)

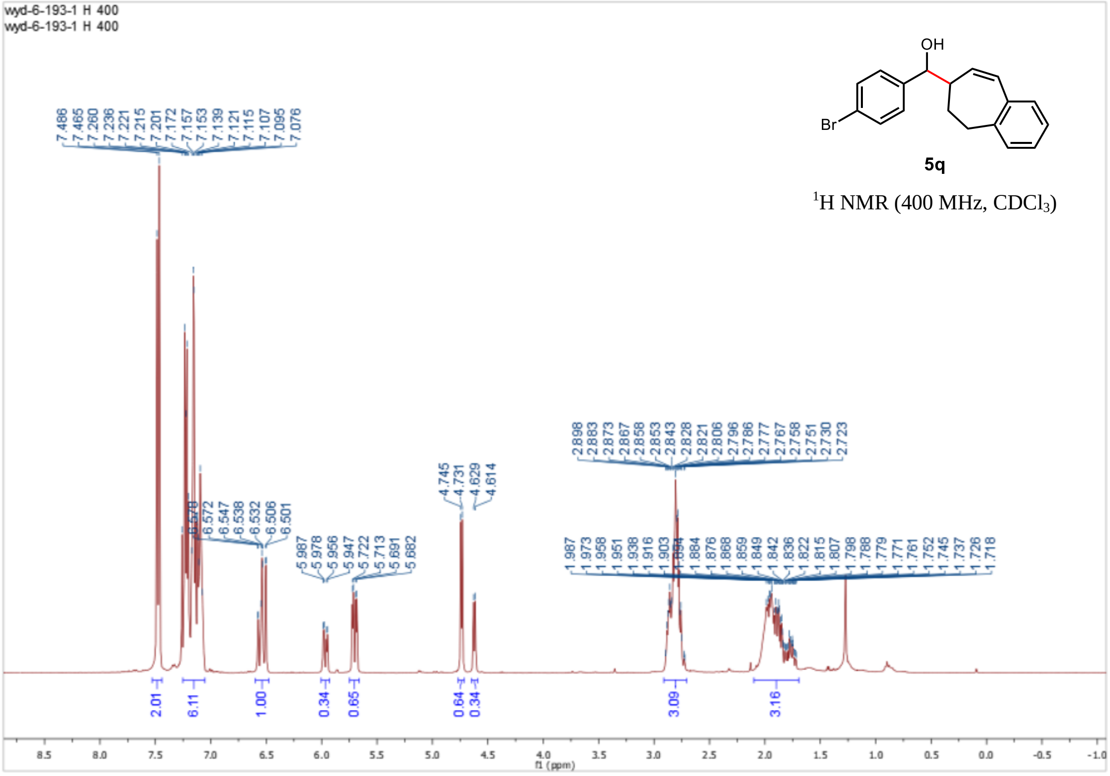


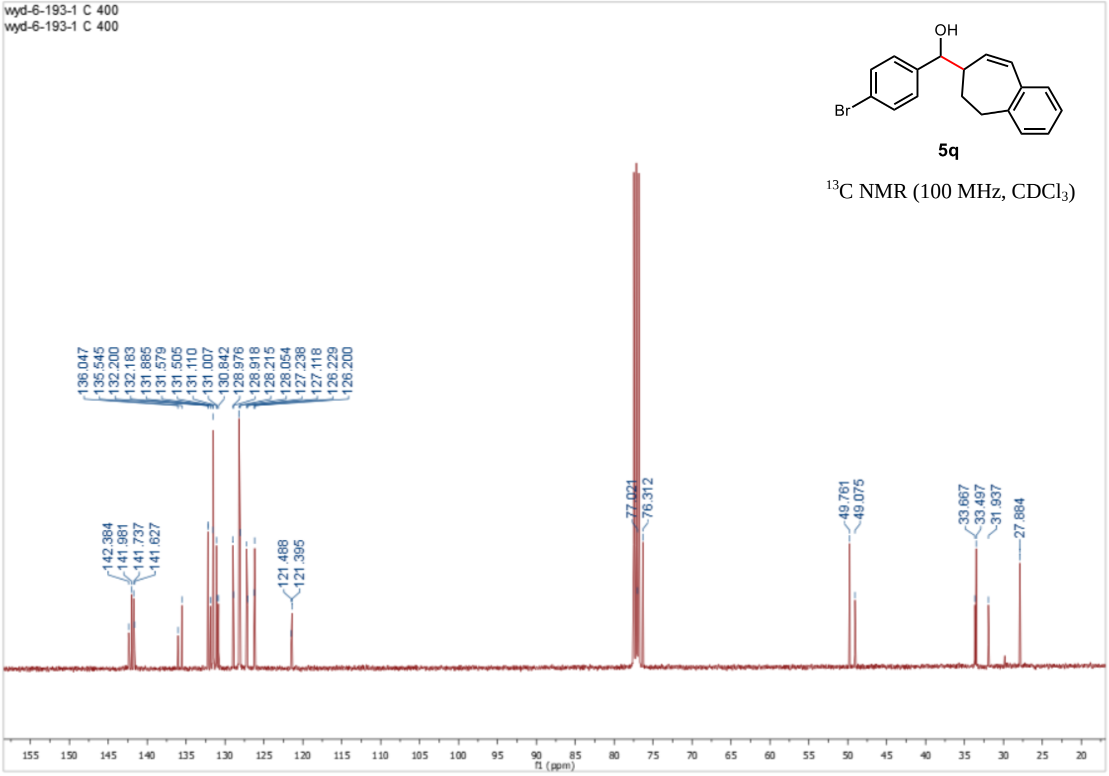
5o

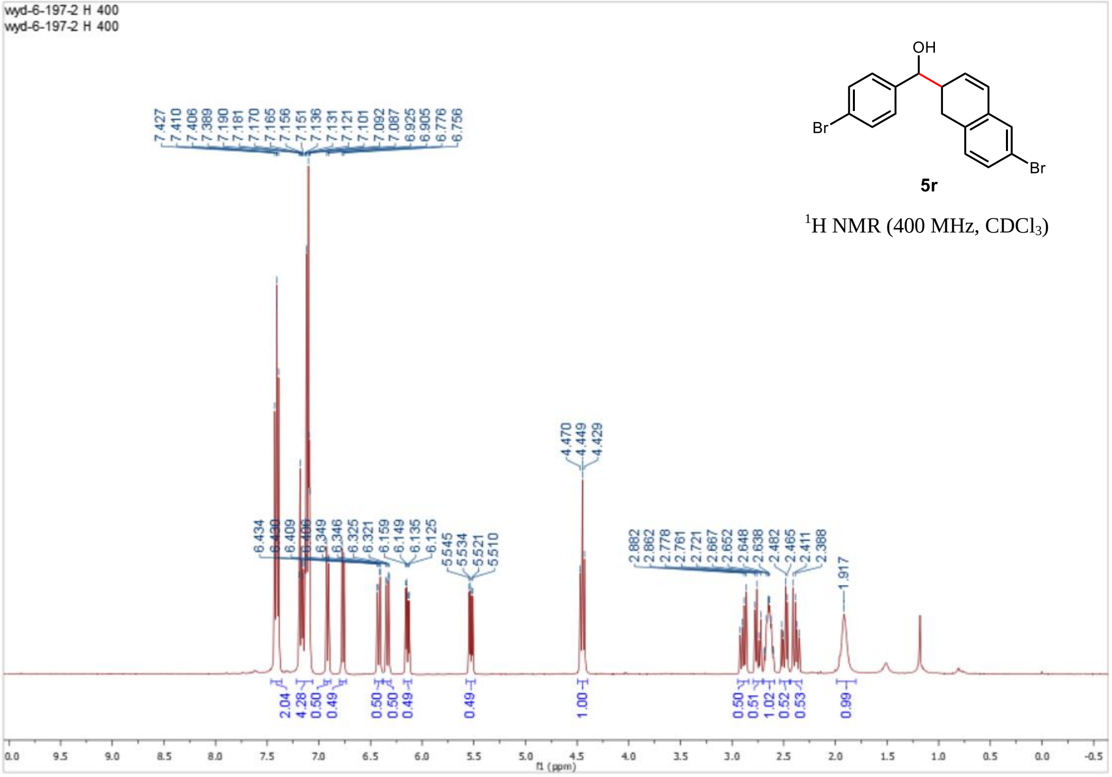
^{13}C NMR (100 MHz, CDCl$_3$)


wyd-6-193-2 H 400
wyd-6-193-2 H 400
OH
Br
5p
^{1}H NMR (400 MHz, CDCl$_3$)
7.515 7.509 7.505 7.490 7.474 7.470 7.464 7.260 7.215 7.194 7.177 7.172 7.170 7.164 7.156 7.150 7.146 7.138 7.123 7.120 7.105 7.101 7.066 7.063 7.050 7.044 7.029 6.996 6.979
6.599 6.595 6.578 6.571 6.512 6.508 6.488 6.483
6.178 6.168 6.144
5.580 5.569 5.556 5.545
4.566 4.554 4.547 4.535
3.012 2.991 2.926 2.909 2.744 2.739 2.732 2.729 2.639 2.561
2.035
1.97 6.04 0.42 0.57 0.42 0.56 1.00 0.57 0.59 1.01 0.45 0.45 0.96
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


wyd-6-193-2 C 400
wyd-6-193-2 C 400
OH
Br
5p
^{13}C NMR (100 MHz, CDCl$_3$)
134.261 134.123 133.764 133.569 131.692 131.573 129.474 129.194 128.878 128.750 128.530 128.273 127.884 127.595 127.469 126.790 126.714 126.208 126.194
142.020 141.928
121.776 121.647
76.584 75.144
41.596 41.527
30.925 29.371
60 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)

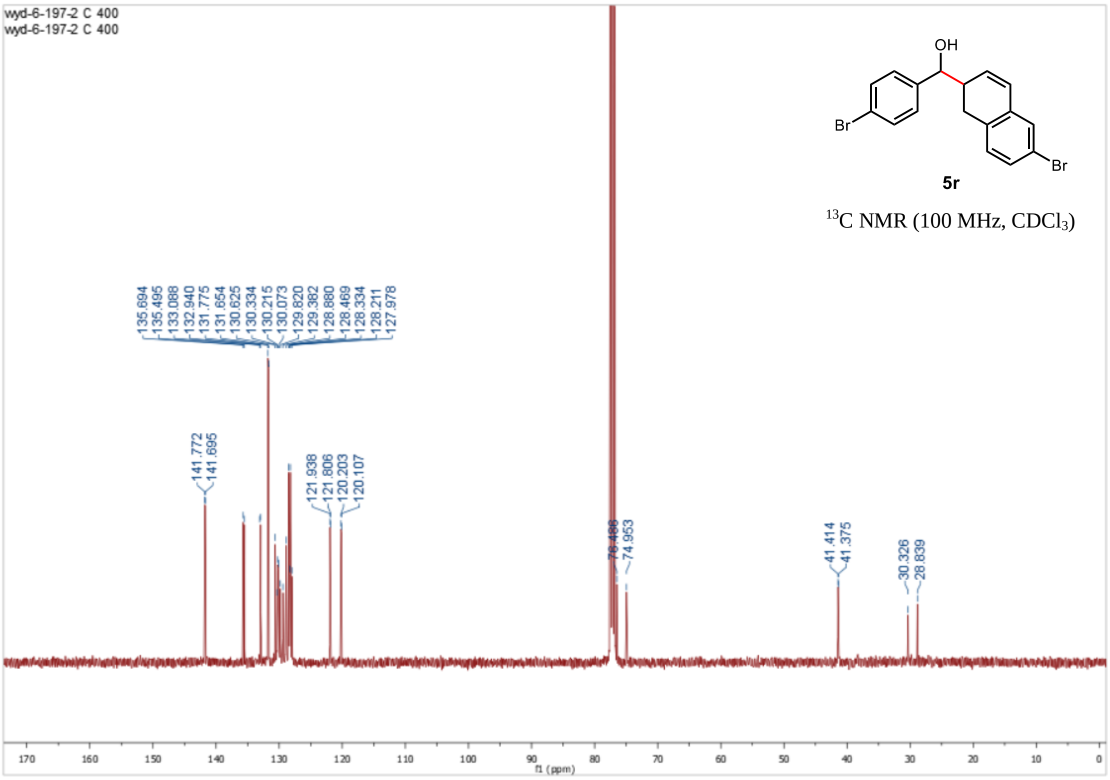

wyd-6-193-1 H 400
wyd-6-193-1 H 400
OH
Br
5q
^{1}H NMR (400 MHz, CDCl$_3$)
7.486
7.465
7.260
7.236
7.221
7.215
7.201
7.172
7.157
7.153
7.139
7.121
7.115
7.107
7.095
7.076
6.578
6.572
6.547
6.538
6.532
6.506
6.501
5.987
5.978
5.956
5.947
5.722
5.713
5.691
5.682
4.745
4.731
4.629
4.614
2.898
2.883
2.873
2.867
2.858
2.853
2.843
2.828
2.821
2.806
2.796
2.786
2.777
2.767
2.758
2.751
2.730
2.723
1.987
1.973
1.958
1.951
1.938
1.916
1.903
1.894
1.884
1.876
1.868
1.859
1.849
1.842
1.836
1.822
1.815
1.807
1.798
1.788
1.779
1.771
1.761
1.752
1.745
1.737
1.726
1.718
2.01
6.11
1.00
0.34
0.65
0.64
0.34
3.09
3.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


wyd-6-193-1 C 400
wyd-6-193-1 C 400
OH
Br
5q
^{13}C NMR (100 MHz, CDCl$_3$)
142.384
141.981
141.737
141.627
136.047
135.545
132.200
132.183
131.885
131.579
131.505
131.110
131.007
130.842
128.976
128.918
128.215
128.054
127.238
127.118
126.229
126.200
121.488
121.395
77.021
76.312
49.761
49.075
33.667
33.497
31.937
27.884
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
f1 (ppm)



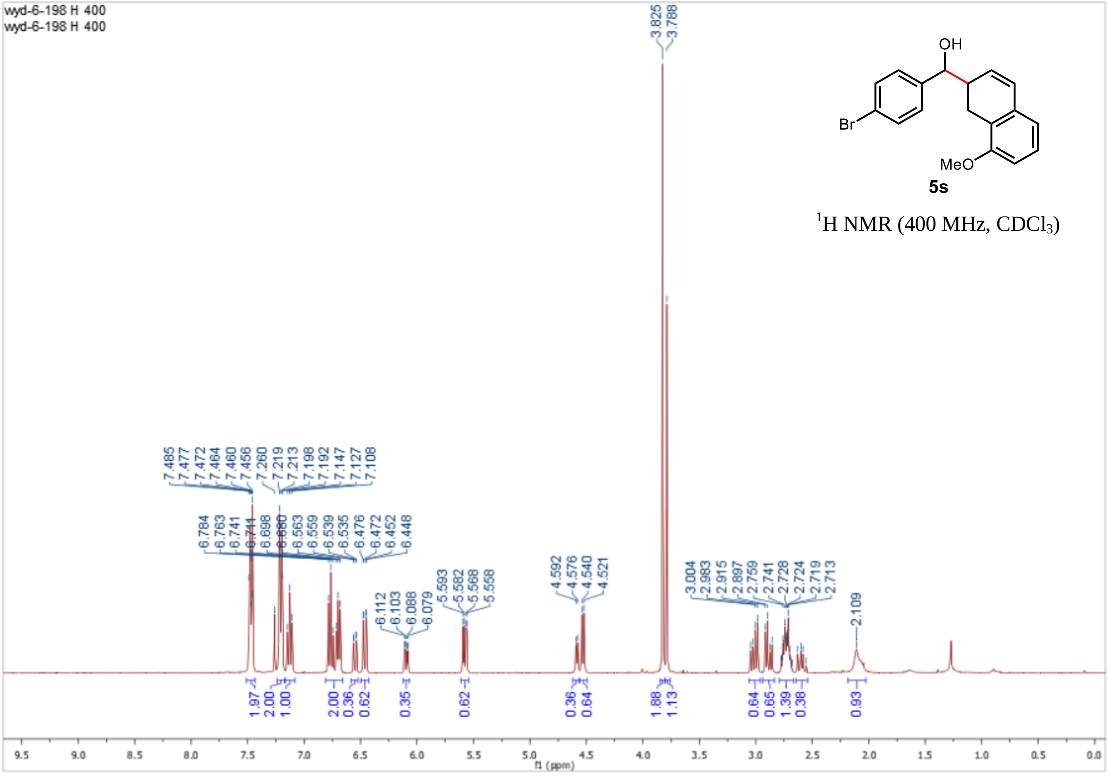
5r

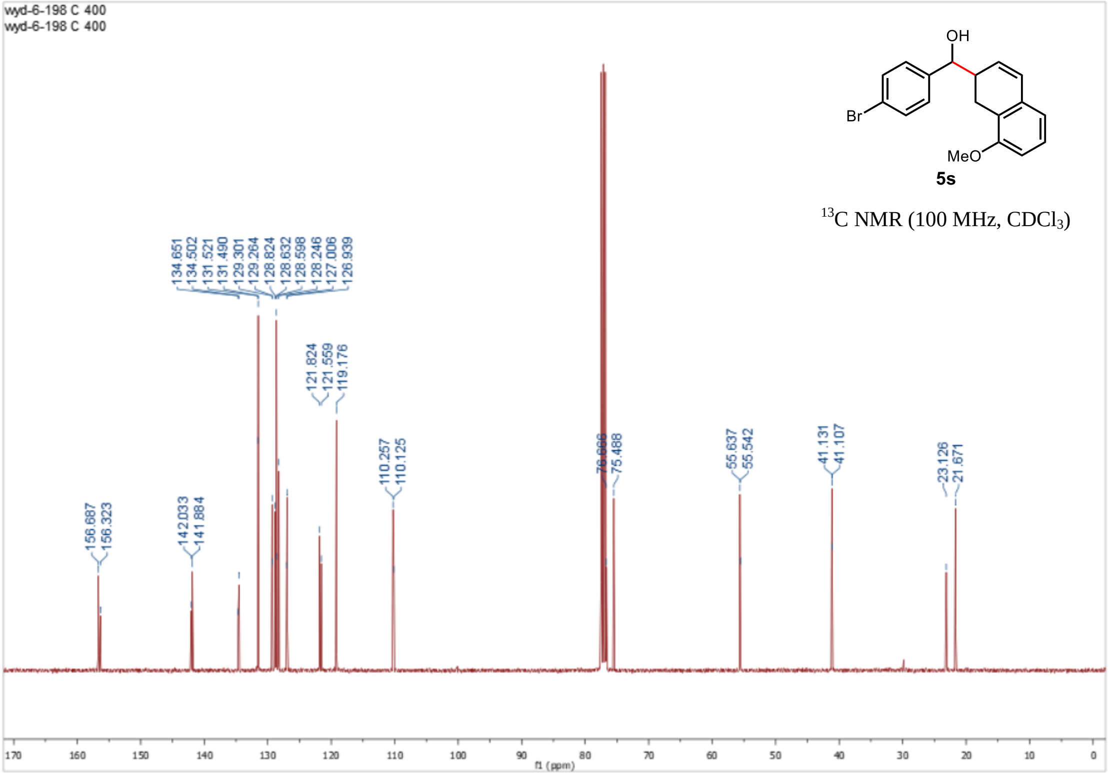
^{1}H NMR (400 MHz, CDCl$_3$)

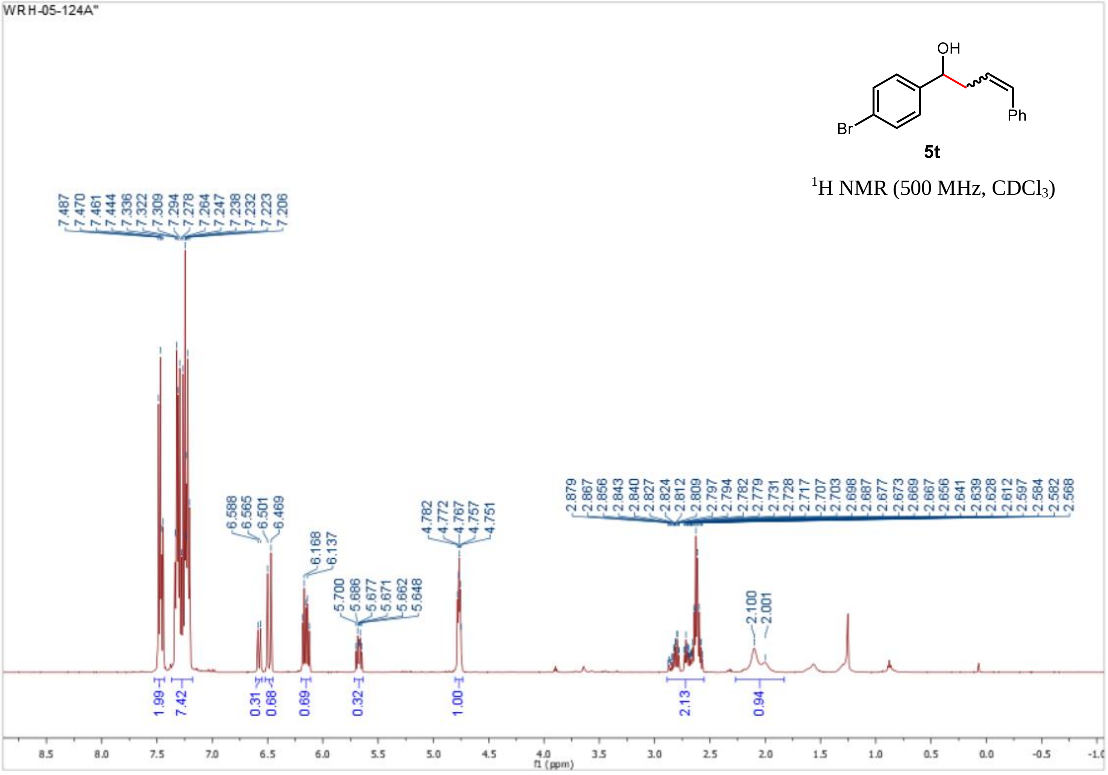


5r

^{13}C NMR (100 MHz, CDCl$_3$)

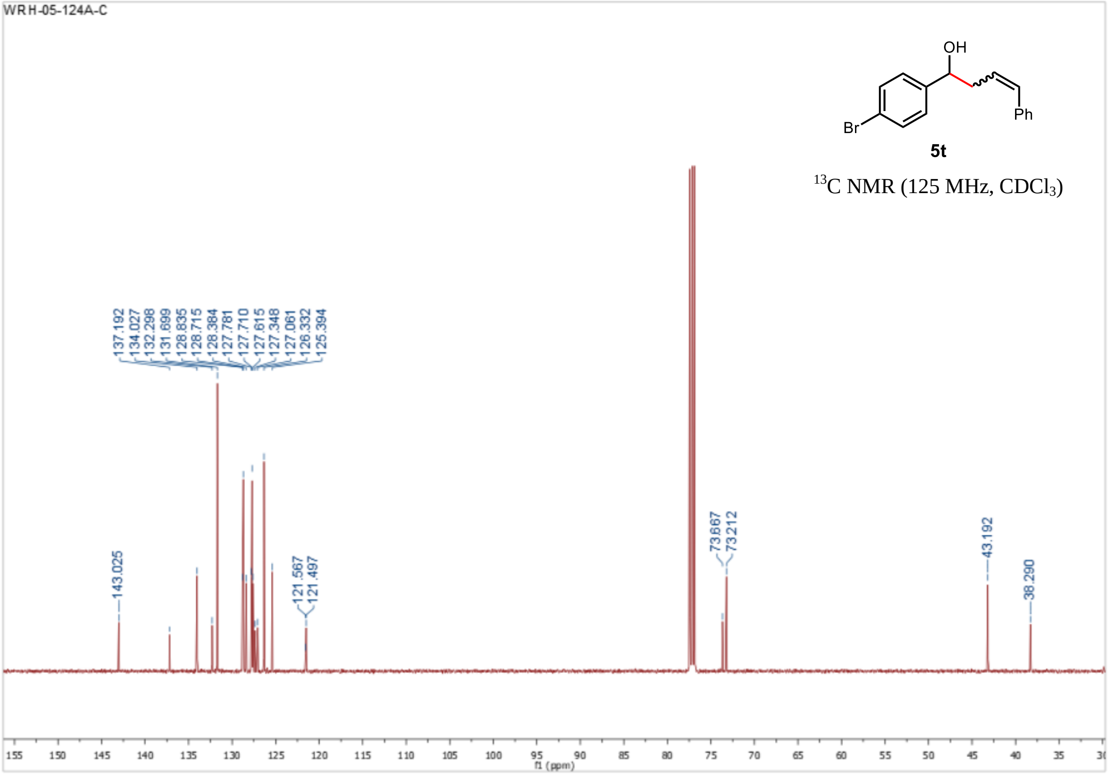

wyd-6-198 H 400
wyd-6-198 H 400
OH
Br
MeO
5s
^{1}H NMR (400 MHz, CDCl$_3$)
7.485
7.477
7.472
7.464
7.460
7.456
7.260
7.219
7.213
7.198
7.192
7.147
7.127
7.108
6.784
6.763
6.741
6.741
6.698
6.680
6.563
6.559
6.539
6.535
6.476
6.472
6.452
6.448
6.112
6.103
6.088
6.079
5.593
5.582
5.568
5.558
4.592
4.576
4.540
4.521
3.825
3.788
3.004
2.983
2.915
2.897
2.759
2.741
2.728
2.724
2.719
2.713
2.109
1.97
2.00
1.00
2.00
0.36
0.62
0.35
0.62
0.36
0.64
1.88
1.13
0.64
0.65
1.39
0.38
0.93
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


wyd-6-198 C 400
wyd-6-198 C 400
OH
Br
MeO
5s
^{13}C NMR (100 MHz, CDCl$_3$)
156.687
156.323
142.033
141.884
134.651
134.502
131.521
131.490
129.301
129.264
128.824
128.632
128.598
128.246
127.006
126.939
121.824
121.559
119.176
110.257
110.125
76.696
75.488
55.637
55.542
41.131
41.107
23.126
21.671
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



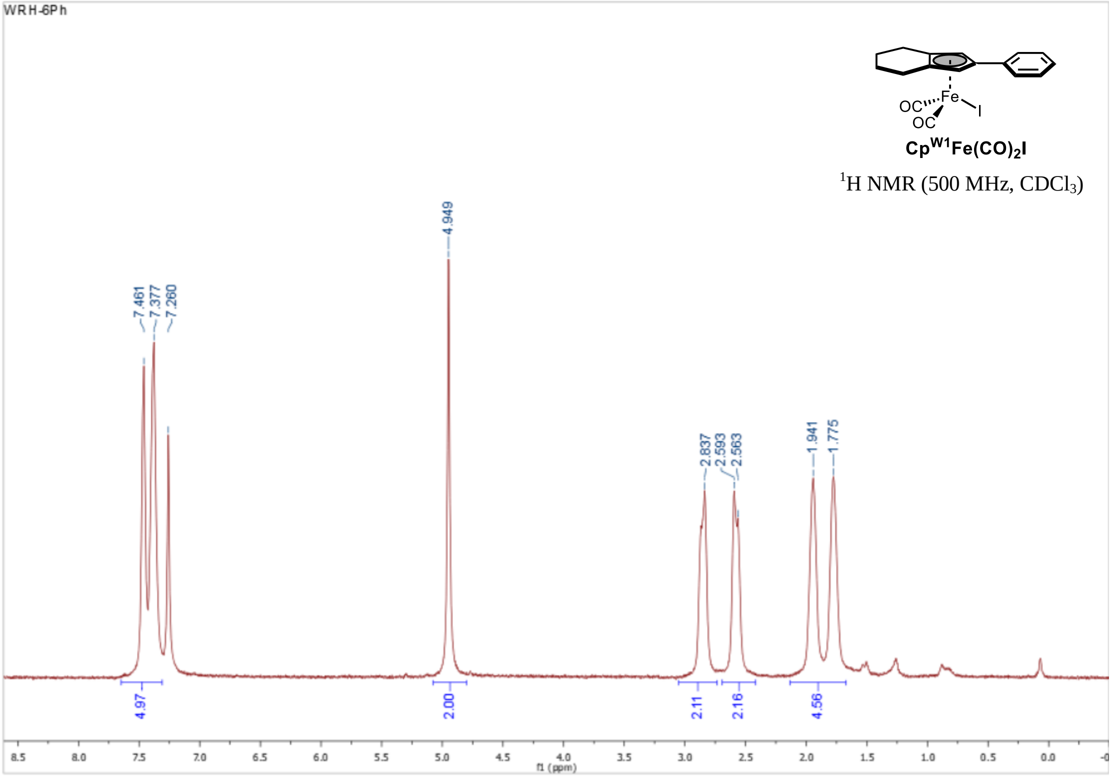
5t

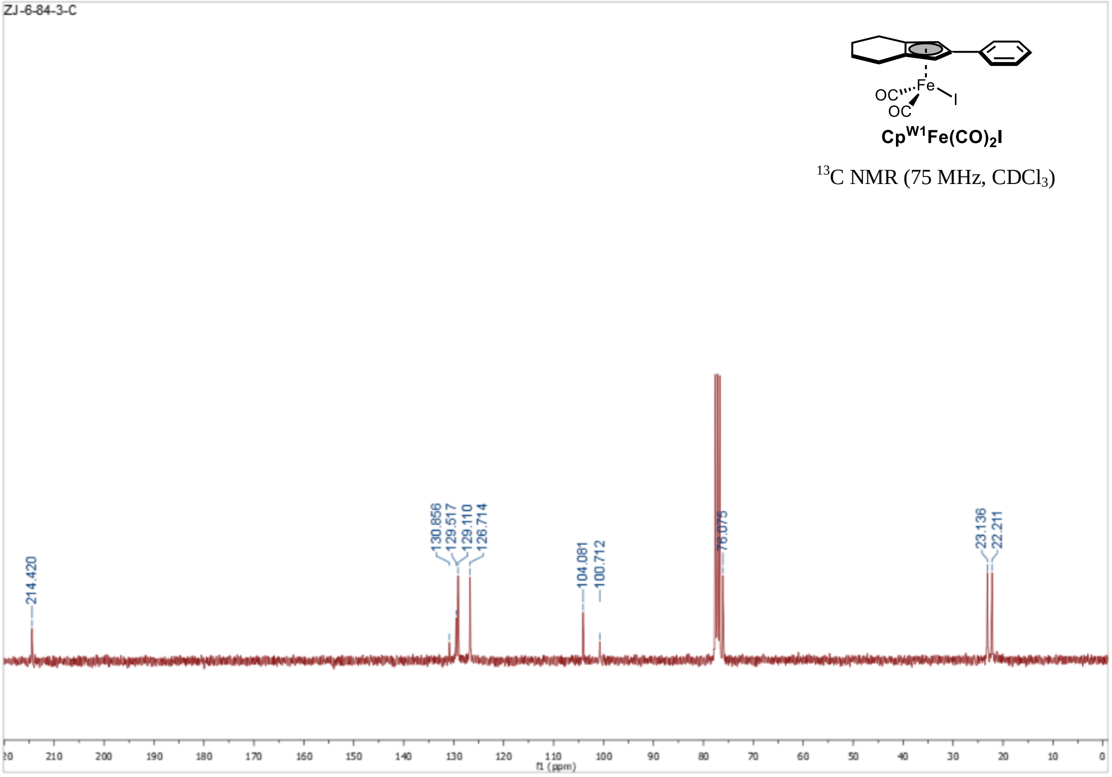
^{1}H NMR (500 MHz, CDCl$_3$)

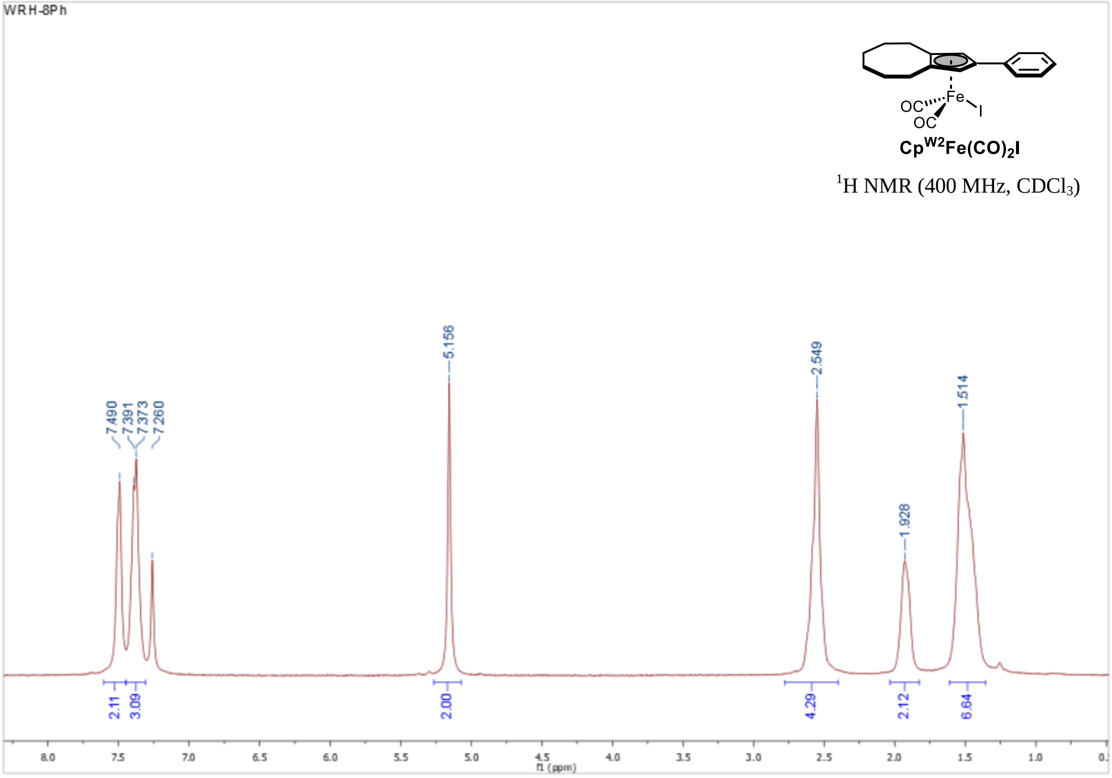


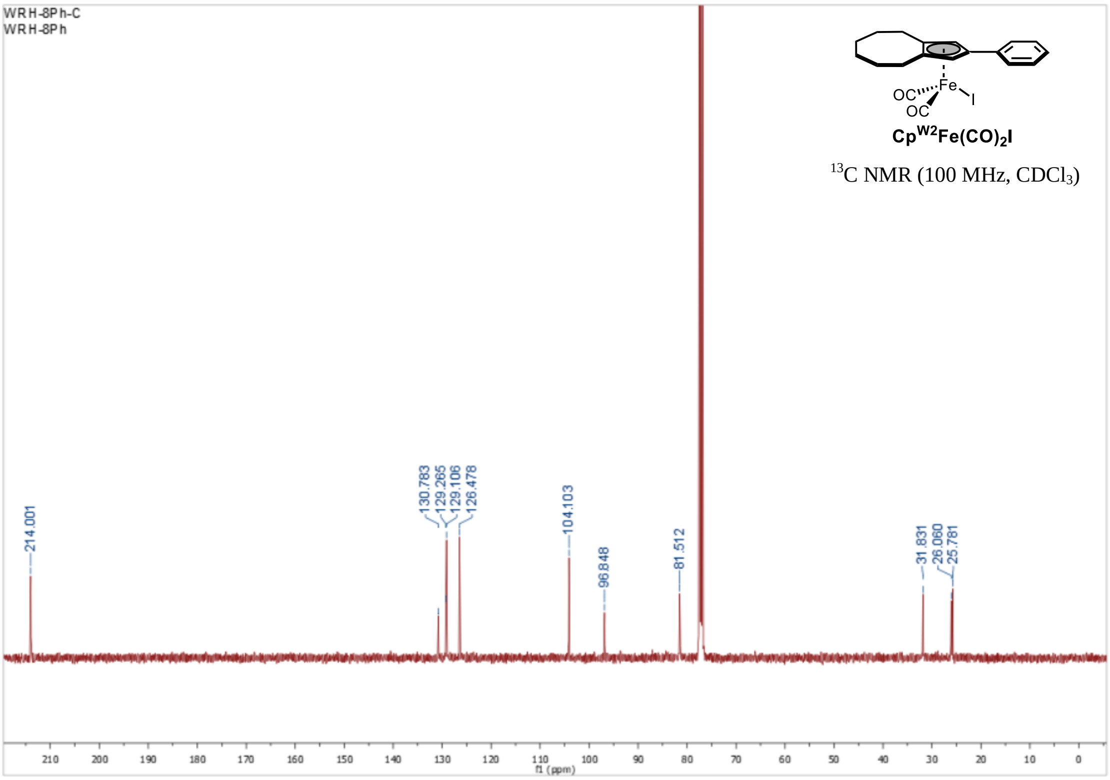
5t

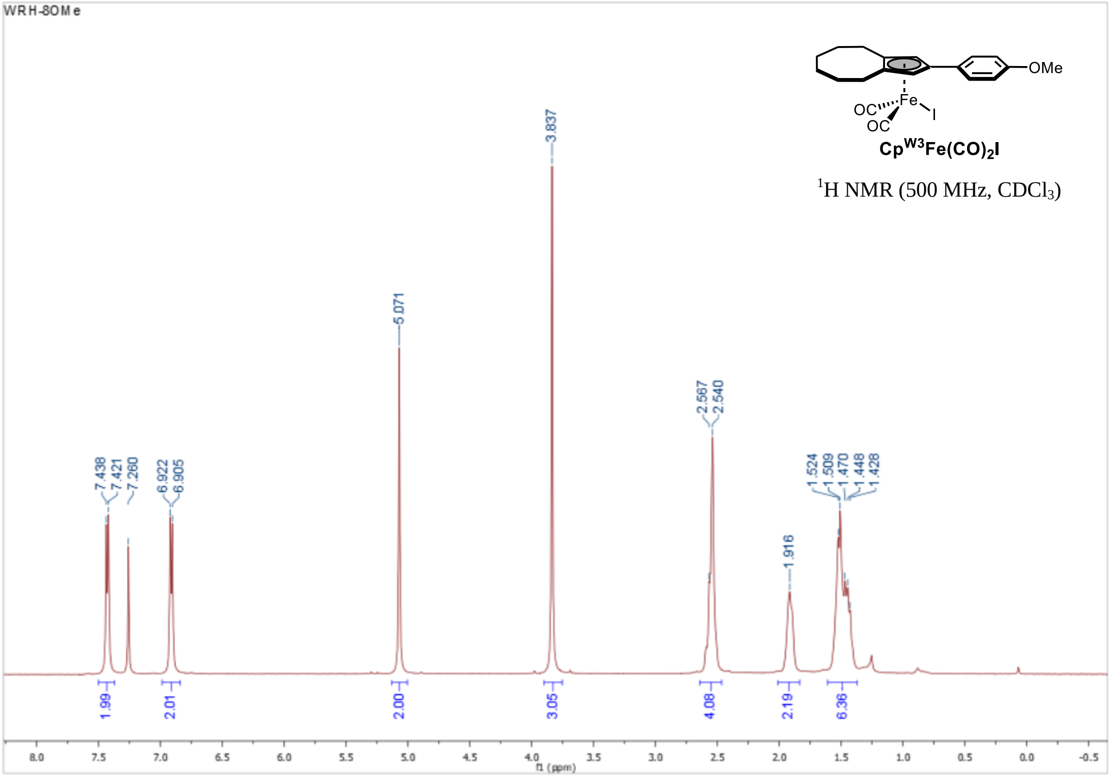
^{13}C NMR (125 MHz, CDCl$_3$)


WRH-6Ph
OC
OC
Fe
I
$Cp^{W1}Fe(CO)_2I$
^{1}H NMR (500 MHz, CDCl$_3$)
7.461
7.377
7.260
4.949
2.837
2.593
2.563
1.941
1.775
4.97
2.00
2.11
2.16
4.56
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


ZJ-6-84-3-C
OC
OC
Fe
I
$Cp^{W1}Fe(CO)_2I$
^{13}C NMR (75 MHz, CDCl$_3$)
214.420
130.856
129.517
129.110
126.714
104.081
100.712
76.075
23.136
22.211
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

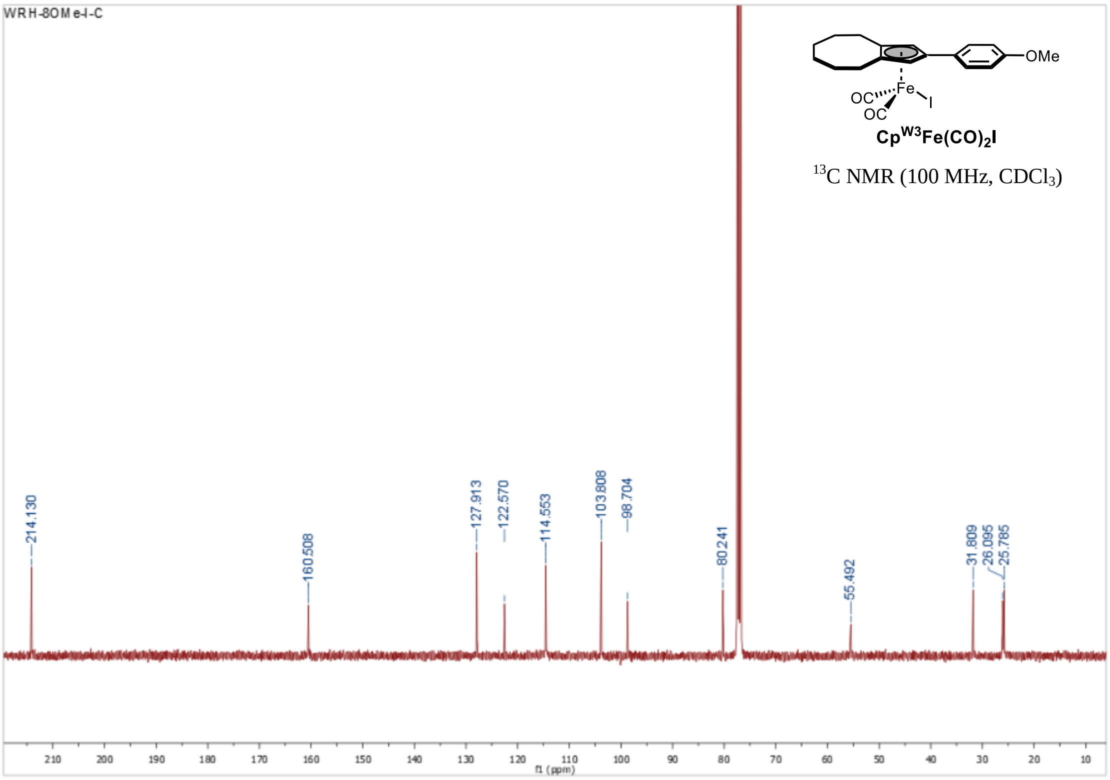

WRH-8Ph
OC
OC
Fe
I
$Cp^{W2}Fe(CO)_2I$
^1H NMR (400 MHz, $CDCl_3$)
7.490
7.391
7.373
7.260
5.156
2.549
1.928
1.514
2.11
3.09
2.00
4.29
2.12
6.64
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


WRH-8Ph-C
WRH-8Ph
OC
OC
Fe
I
$Cp^{W2}Fe(CO)_2I$
^{13}C NMR (100 MHz, $CDCl_3$)
214.001
130.783
129.265
129.106
126.478
104.103
96.848
81.512
31.831
26.060
25.781
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



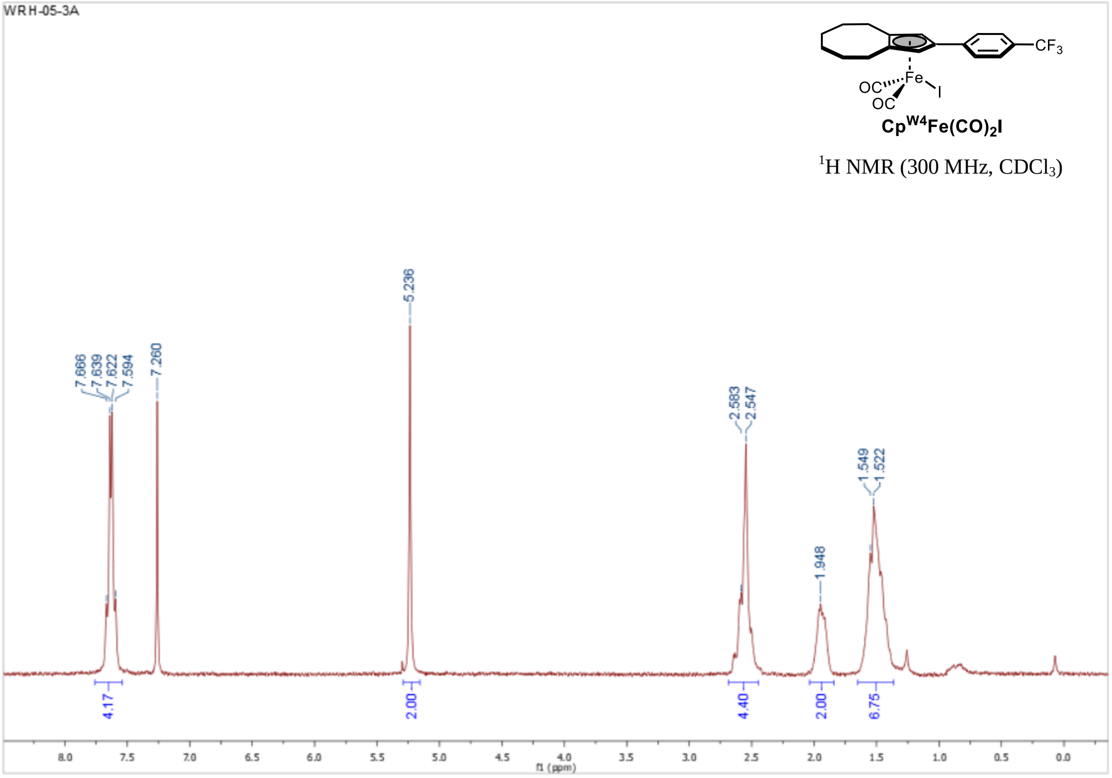
Cp^{W3}Fe(CO)$_2$I

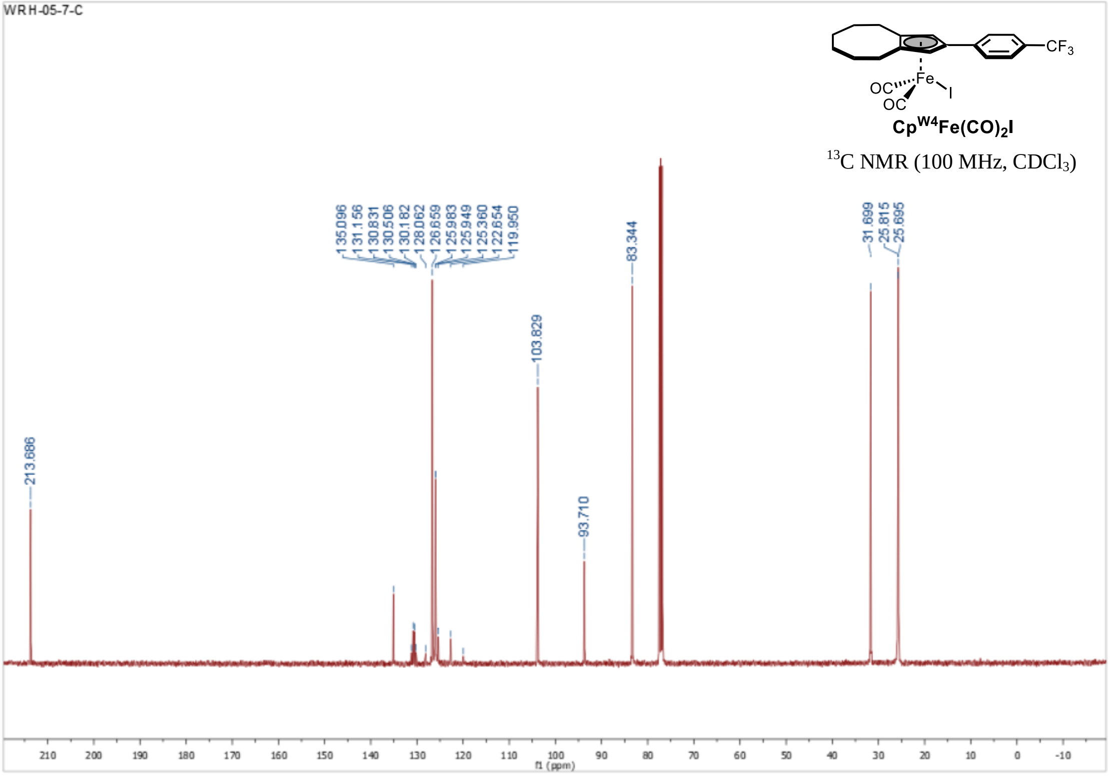
^{1}H NMR (500 MHz, CDCl$_3$)

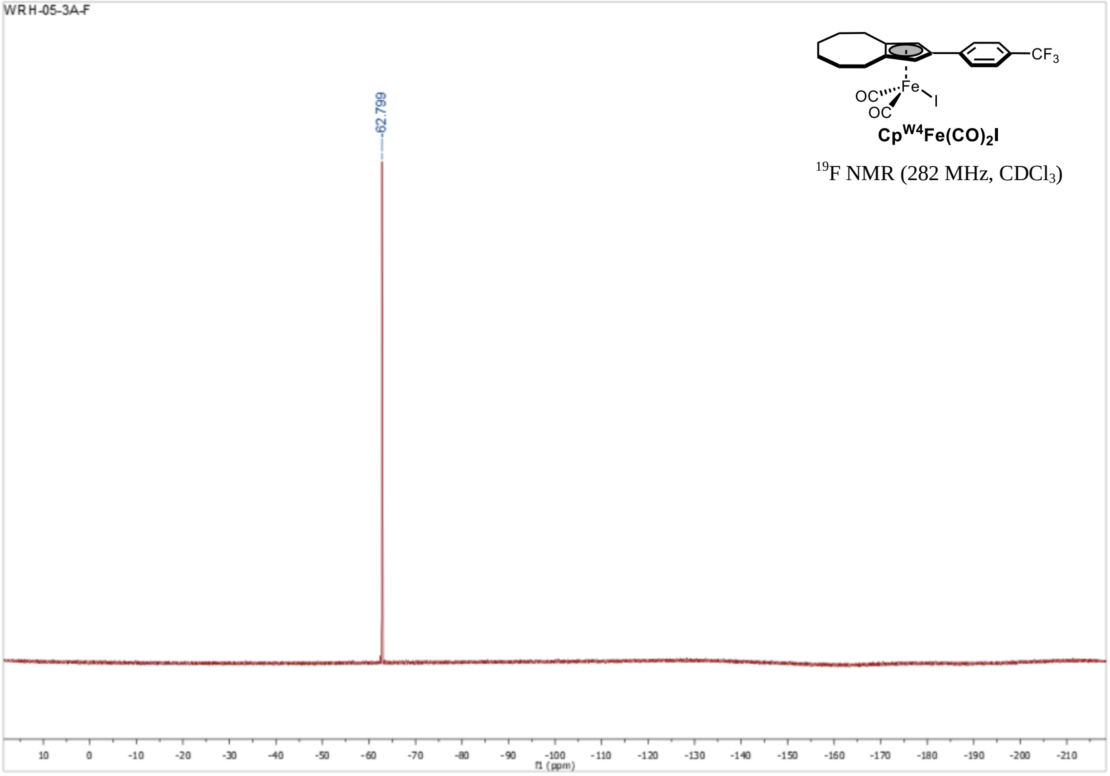


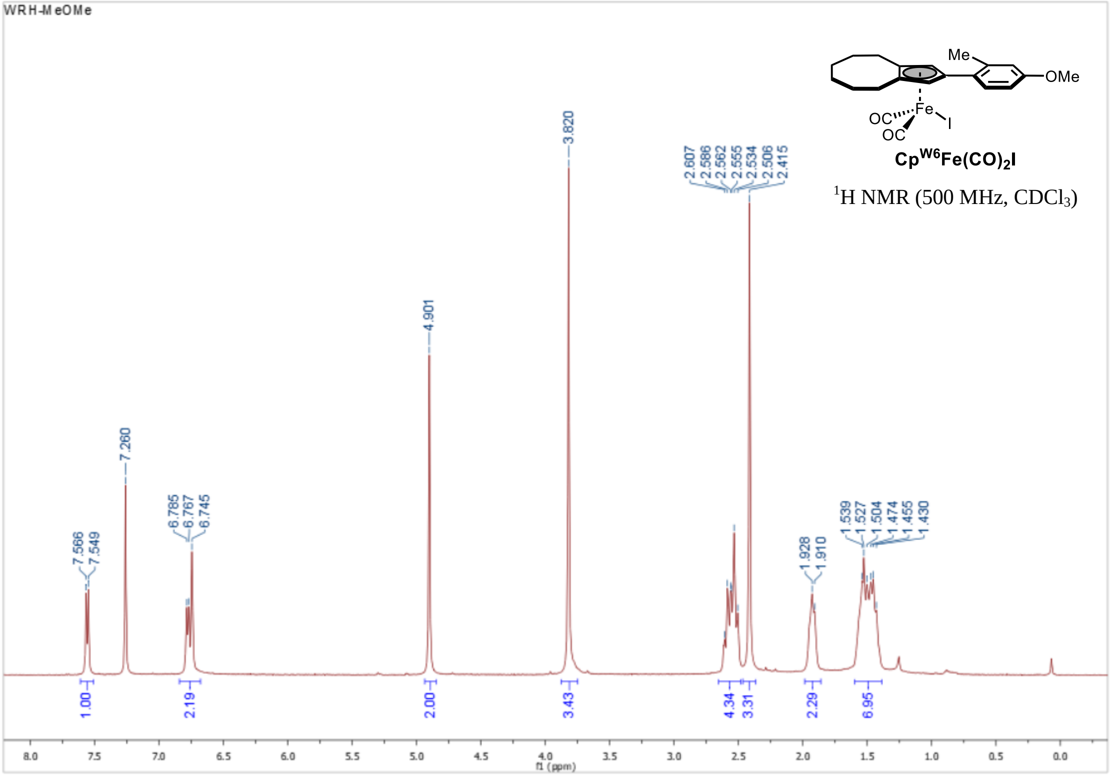
Cp^{W3}Fe(CO)$_2$I

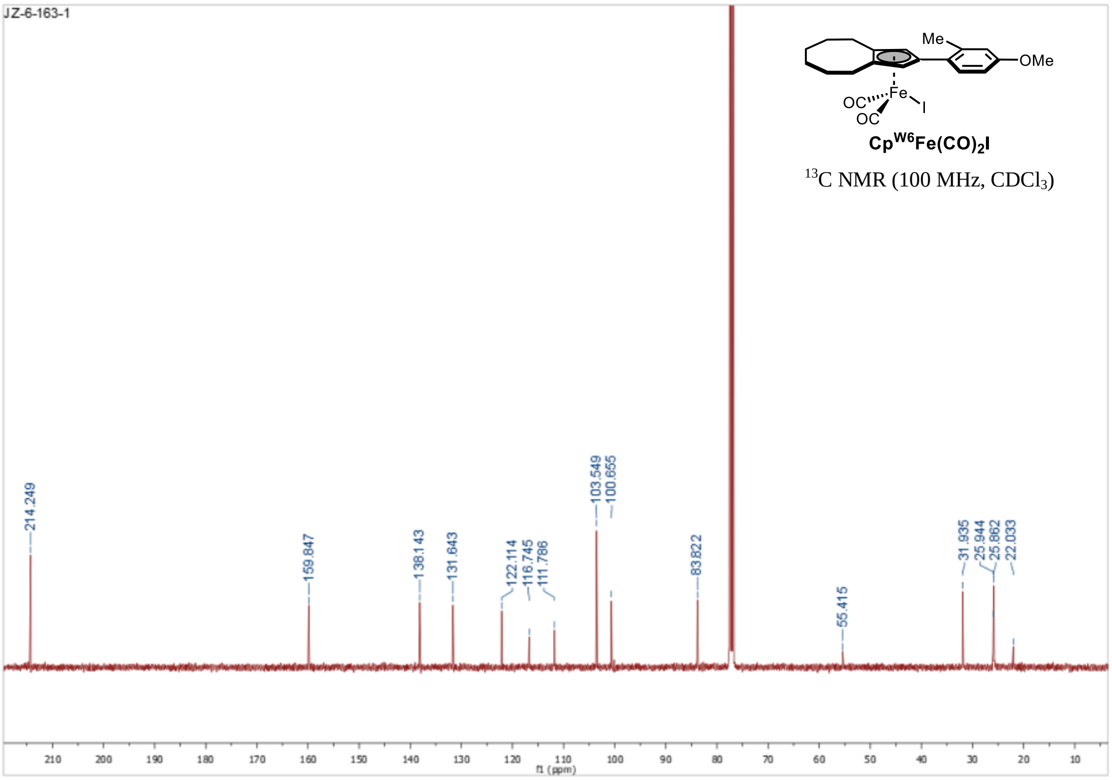
^{13}C NMR (100 MHz, CDCl$_3$)

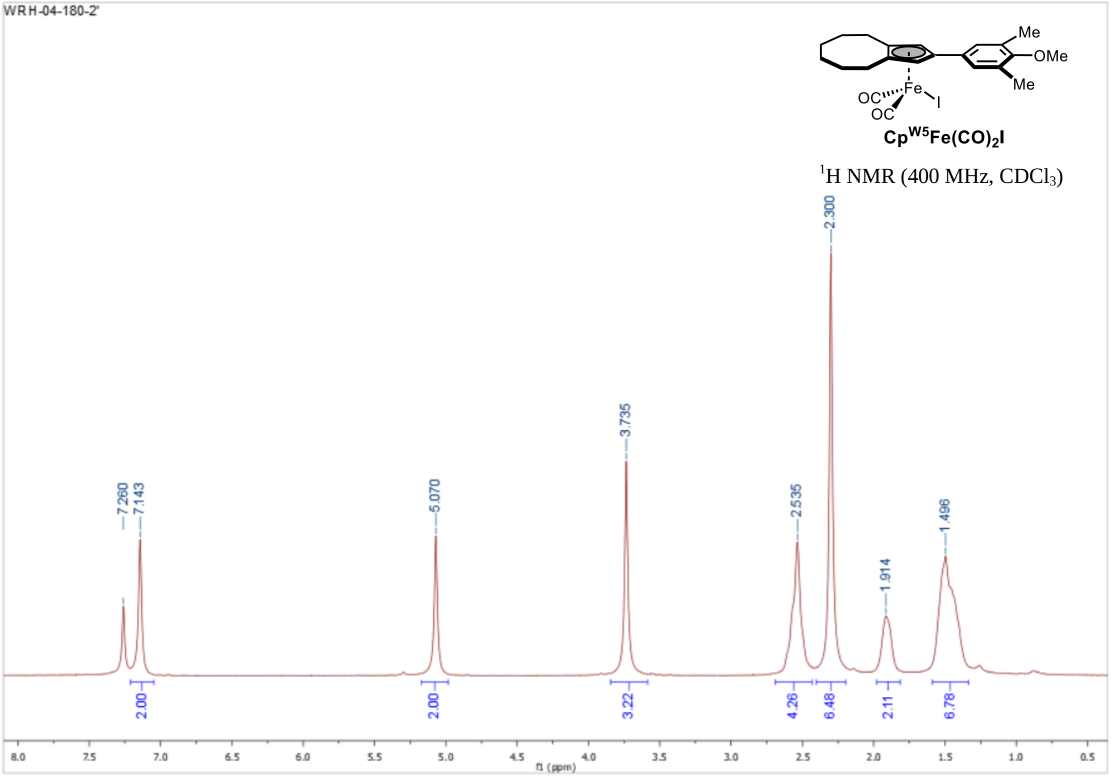

WRH-05-3A
CF3
Fe
OC
OC
I
CpW4Fe(CO)2I
1H NMR (300 MHz, CDCl3)
7.666
7.639
7.622
7.594
7.260
5.236
2.583
2.547
1.948
1.549
1.522
4.17
2.00
4.40
2.00
6.75
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

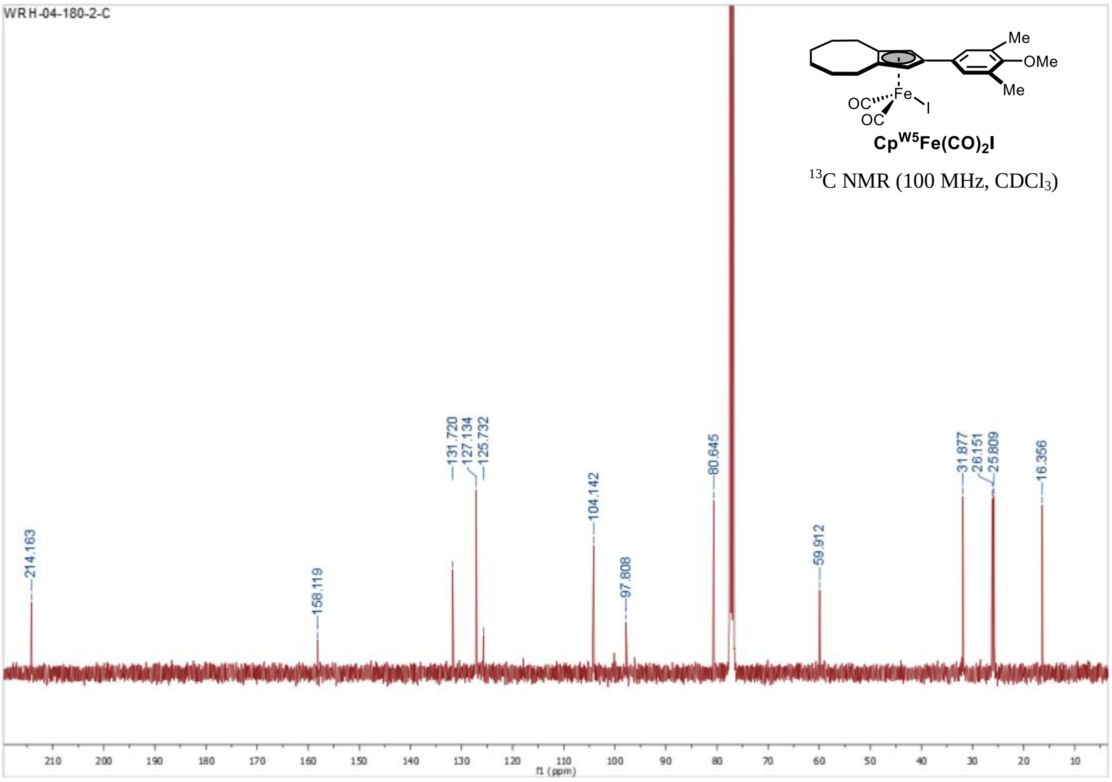

WRH-05-7-C
CF3
Fe
OC
OC
I
CpW4Fe(CO)2I
13C NMR (100 MHz, CDCl3)
213.686
135.096
131.156
130.831
130.506
130.182
128.062
126.659
125.983
125.949
125.360
122.654
119.950
103.829
93.710
83.344
31.699
25.815
25.695
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

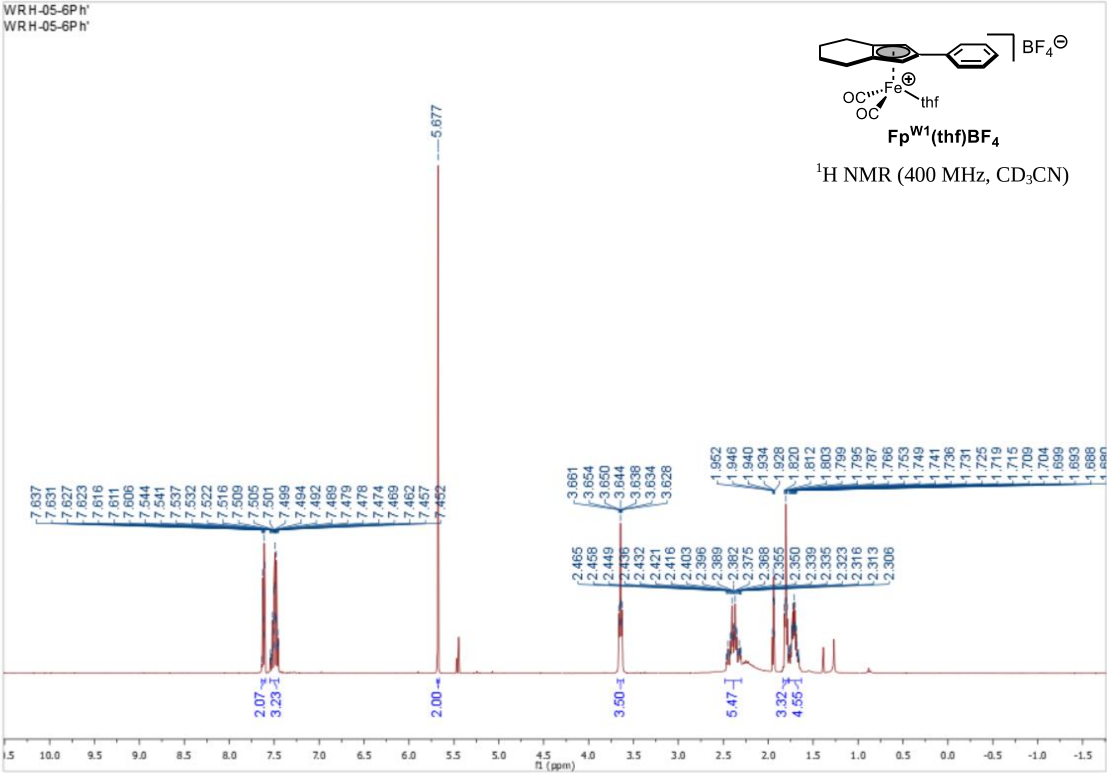

WRH-05-3A-F
-62.799
CF3
OC
OC
Fe
I
Cp^W4Fe(CO)2I
19F NMR (282 MHz, CDCl3)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


WRH-MeOMe
Me
OMe
OC
OC
Fe
I
Cp^W6Fe(CO)2I
1H NMR (500 MHz, CDCl3)
7.566
7.549
7.260
6.785
6.767
6.745
4.901
3.820
2.607
2.586
2.562
2.555
2.534
2.506
2.415
1.928
1.910
1.539
1.527
1.504
1.474
1.455
1.430
1.00
2.19
2.00
3.43
4.34
3.31
2.29
6.95
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


JZ-6-163-1
Me
OMe
OC
OC
Fe
I
Cp^W6Fe(CO)2I
13C NMR (100 MHz, CDCl3)
214.249
159.847
138.143
131.643
122.114
116.745
111.786
103.549
100.655
83.822
55.415
31.935
25.944
25.862
22.033
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

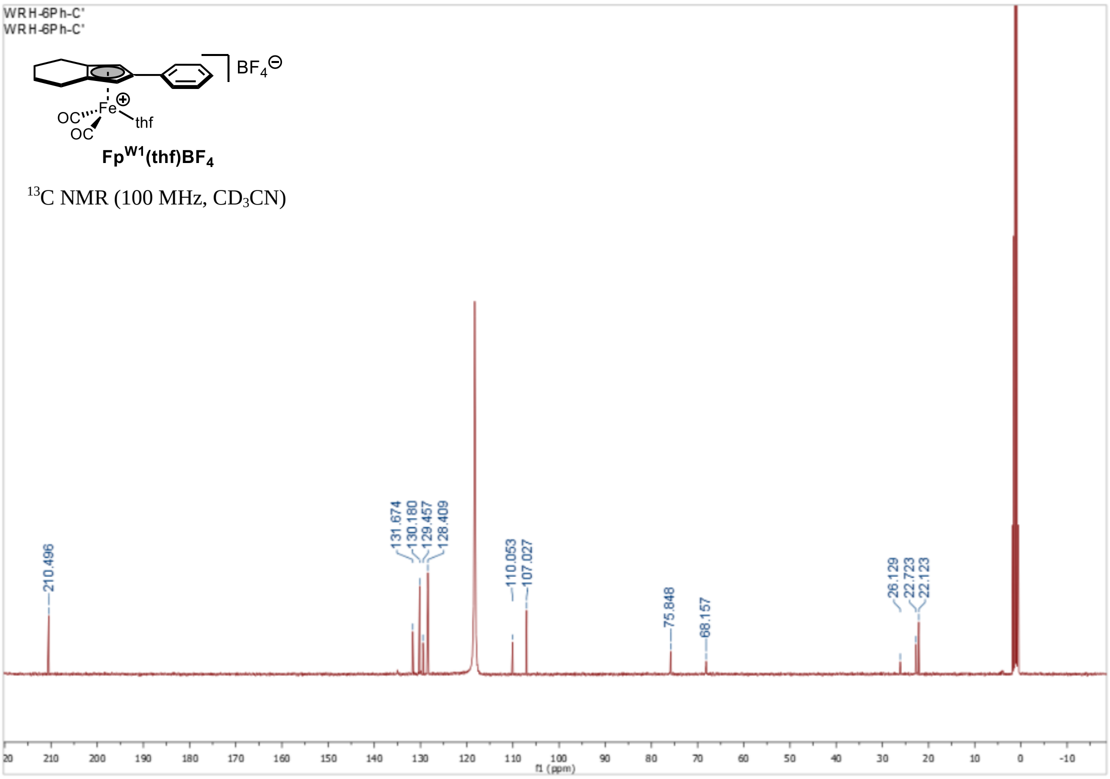

WRH-04-180-2'
Me
OMe
Me
OC
OC
Fe
I
Cp^W5Fe(CO)2I
1H NMR (400 MHz, CDCl3)
7.260
7.143
5.070
3.735
2.535
2.300
1.914
1.496
2.00
2.00
3.22
4.26
6.48
2.11
6.78
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


WRH-04-180-2-C
Me
OMe
Me
OC
OC
Fe
I
Cp^W5Fe(CO)2I
13C NMR (100 MHz, CDCl3)
214.163
158.119
131.720
127.134
125.732
104.142
97.808
80.645
59.912
31.877
26.151
25.809
16.356
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



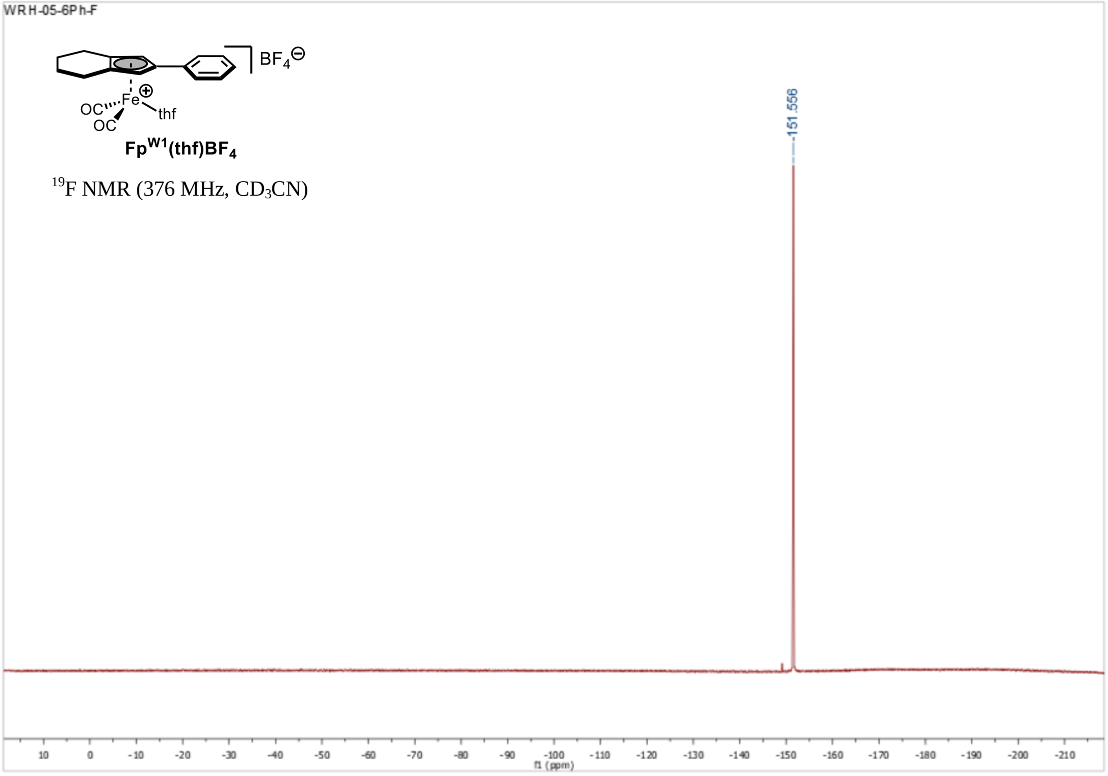
Fp^{W1}(thf)BF$_4$

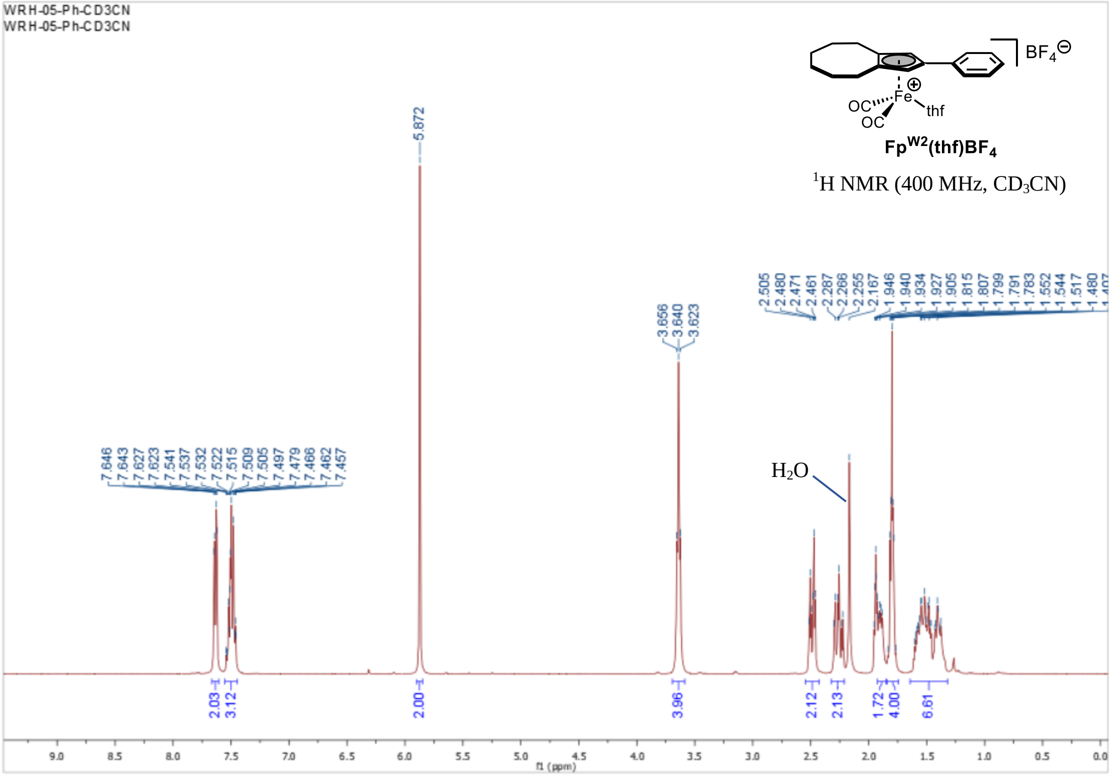
^{1}H NMR (400 MHz, CD$_3$CN)

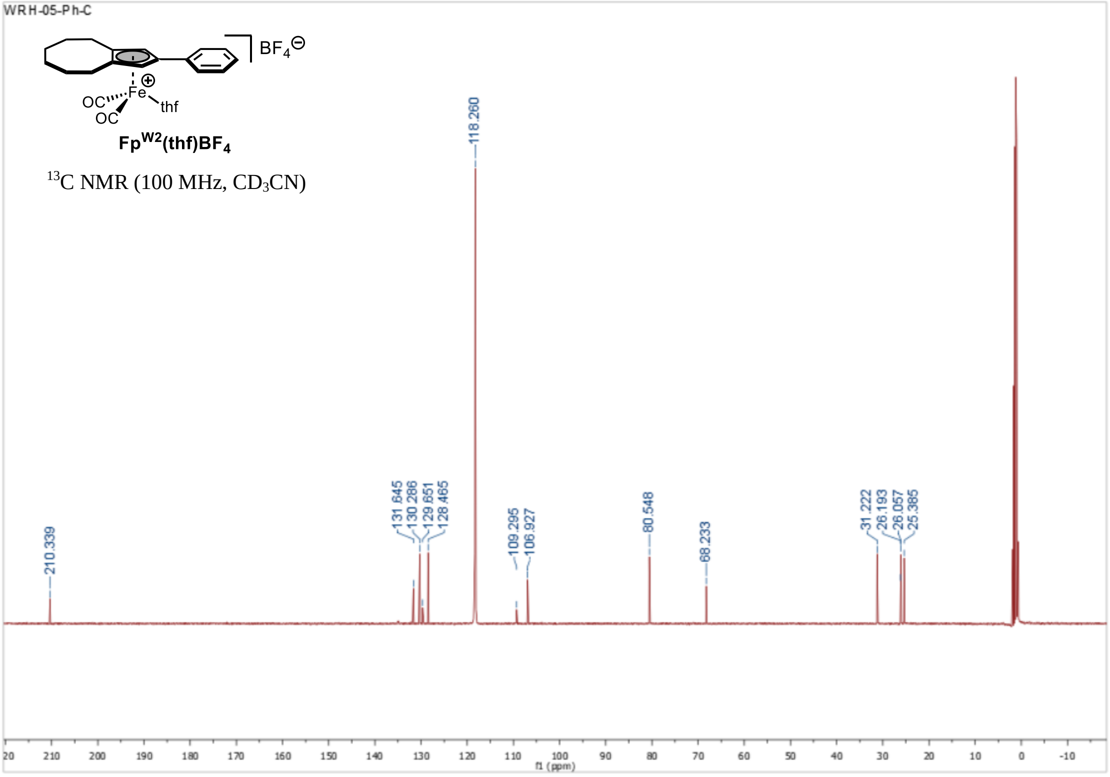


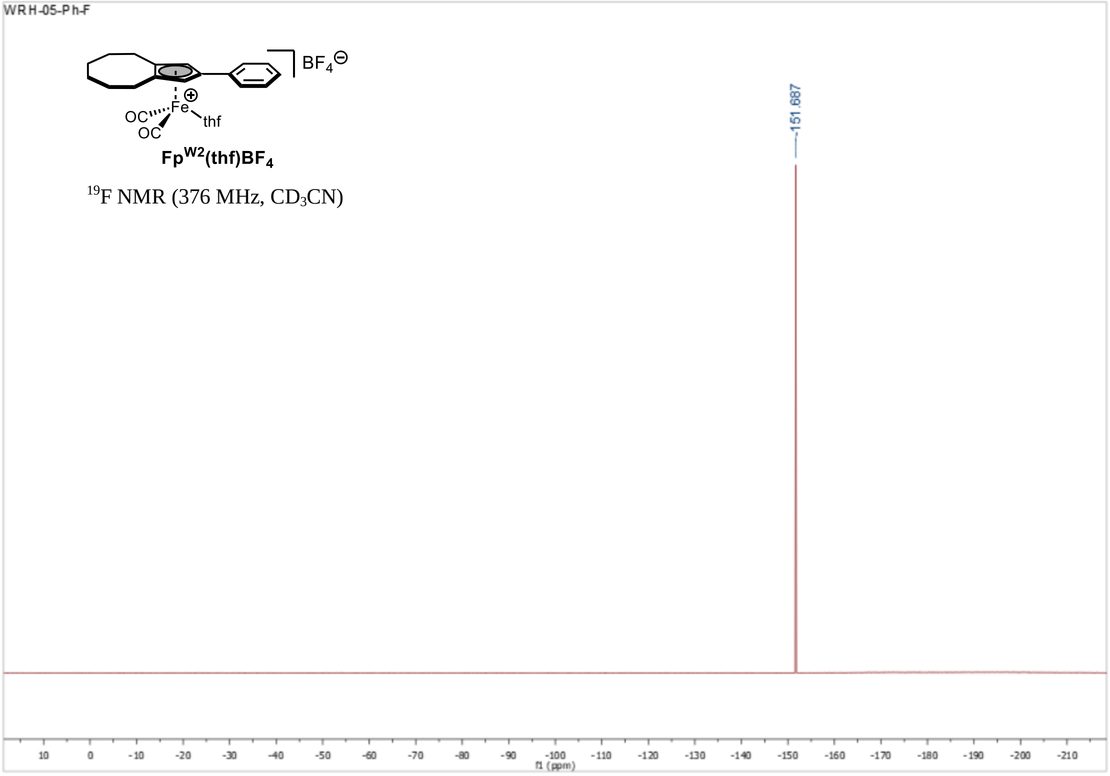
Fp^{W1}(thf)BF$_4$

^{13}C NMR (100 MHz, CD$_3$CN)


WRH-05-6Ph-F
BF4⊖
OC
OC
Fe⊕
thf
FpW1(thf)BF4
19F NMR (376 MHz, CD3CN)
-151.556
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

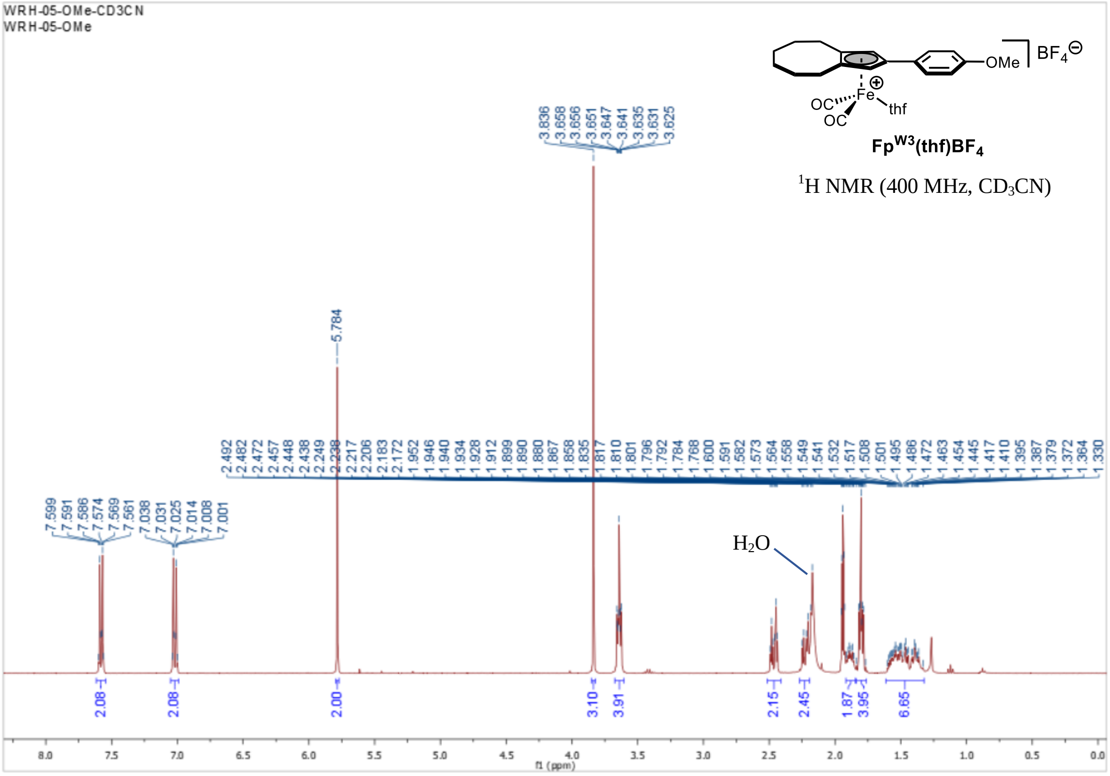

WRH-05-Ph-CD3CN
WRH-05-Ph-CD3CN
BF$_4^⊖$
⊕
Fe
OC
OC
thf
Fp^{W2}(thf)BF$_4$
^{1}H NMR (400 MHz, CD$_3$CN)
7.646
7.643
7.627
7.623
7.541
7.537
7.532
7.522
7.515
7.509
7.505
7.497
7.479
7.466
7.462
7.457
5.872
3.656
3.640
3.623
2.505
2.480
2.471
2.461
2.287
2.266
2.255
2.167
1.946
1.940
1.934
1.927
1.905
1.815
1.807
1.799
1.791
1.783
1.552
1.544
1.517
1.480
H$_2$O
2.03
3.12
2.00
3.96
2.12
2.13
1.72
4.00
6.61
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


WRH-05-Ph-C
BF$_4^⊖$
⊕
Fe
OC
OC
thf
Fp^{W2}(thf)BF$_4$
^{13}C NMR (100 MHz, CD$_3$CN)
210.339
131.645
130.286
129.651
128.465
118.260
109.295
106.927
80.548
68.233
31.222
26.193
26.057
25.385
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



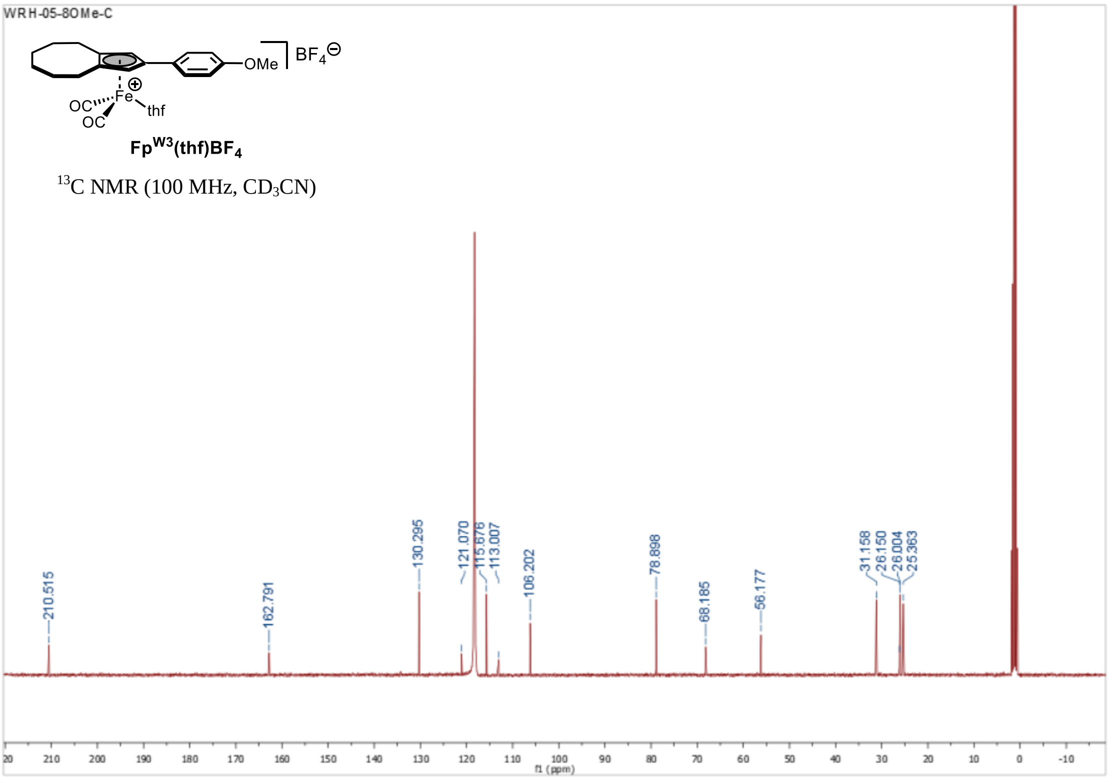
$Fp^{W2}(thf)BF_4$

^{19}F NMR (376 MHz, CD_3CN)



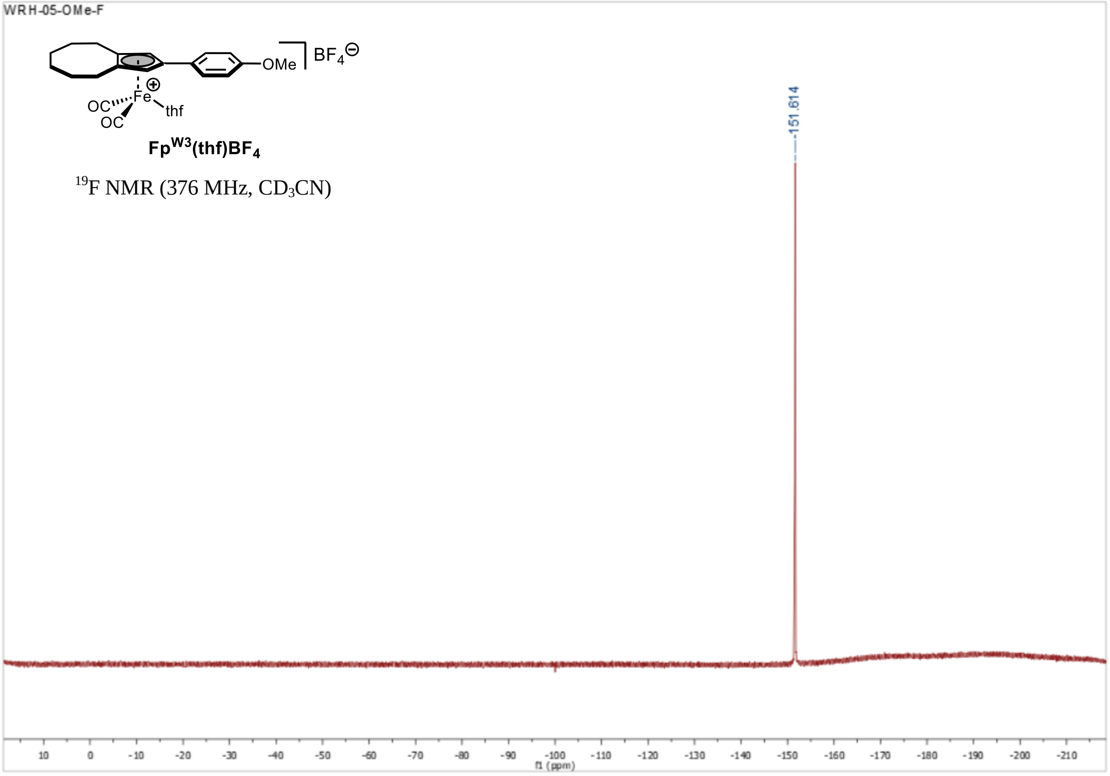
Fp^{W3}(thf)BF$_4$

^{1}H NMR (400 MHz, CD$_3$CN)



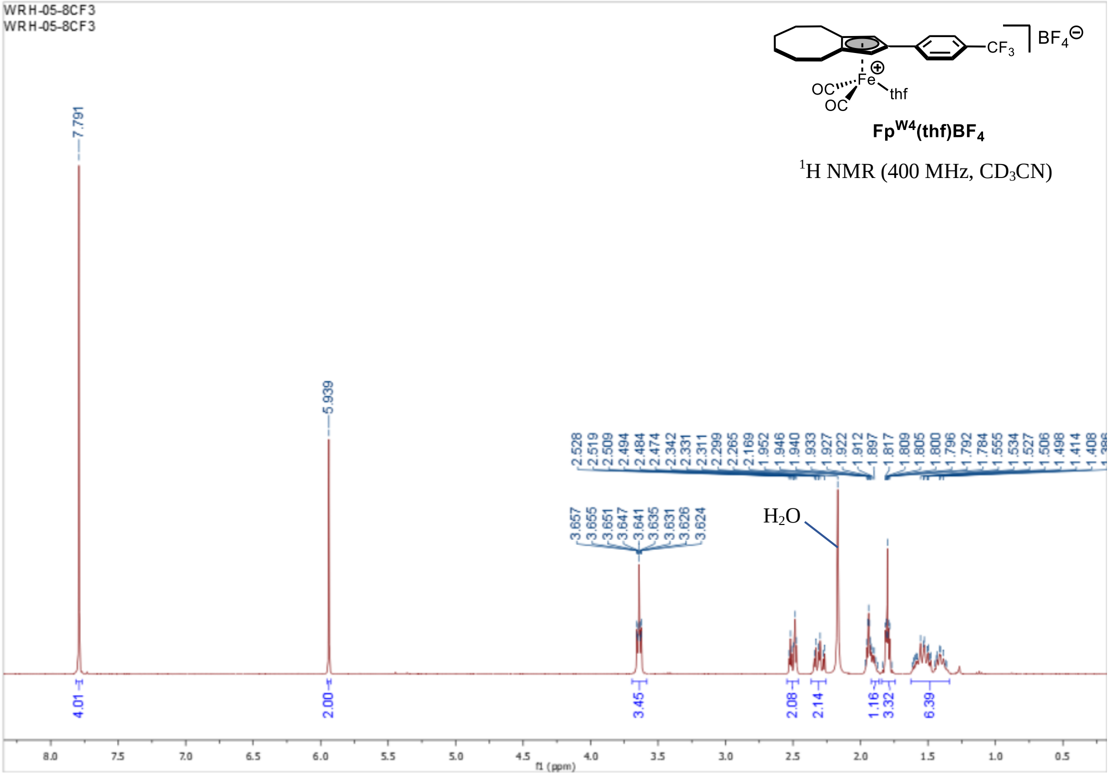
Fp^{W3}(thf)BF$_4$

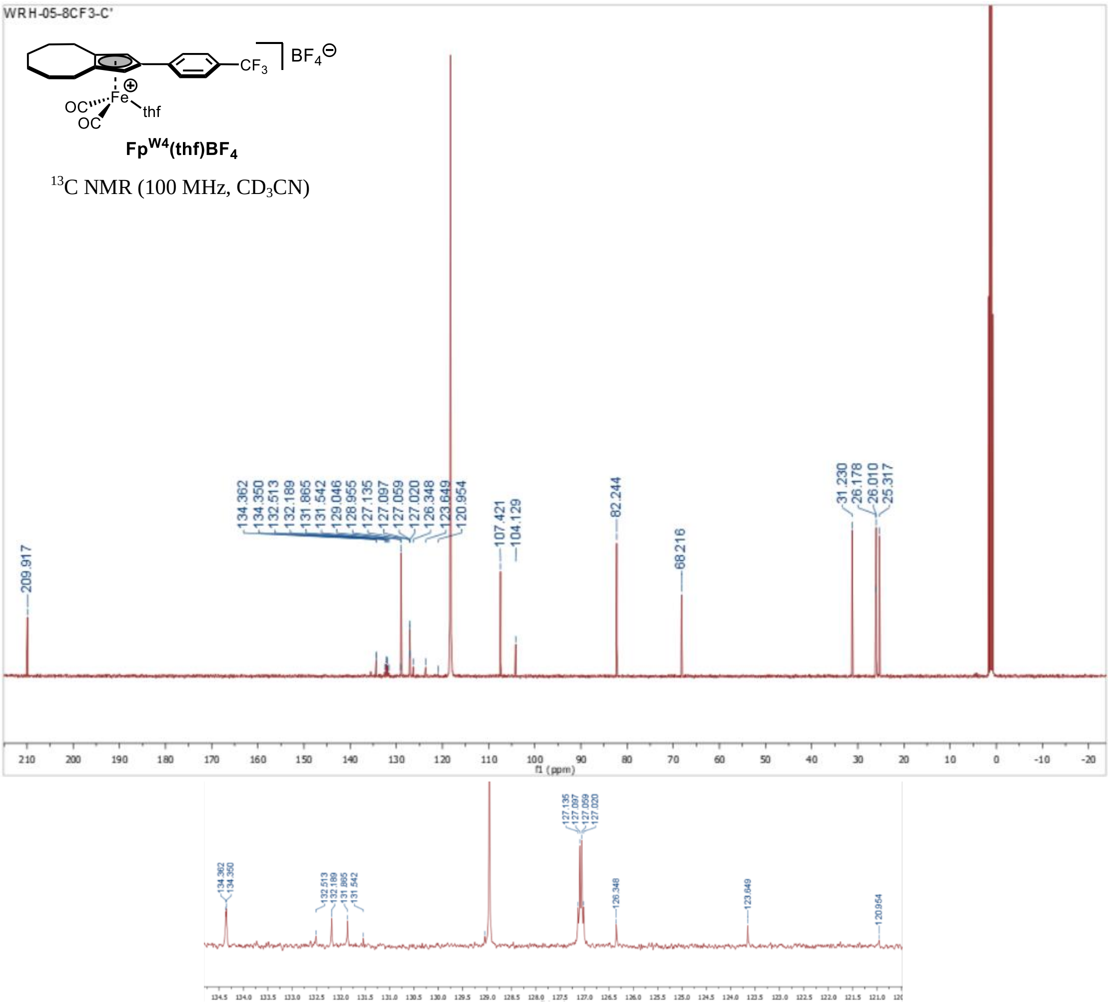
^{13}C NMR (100 MHz, CD$_3$CN)

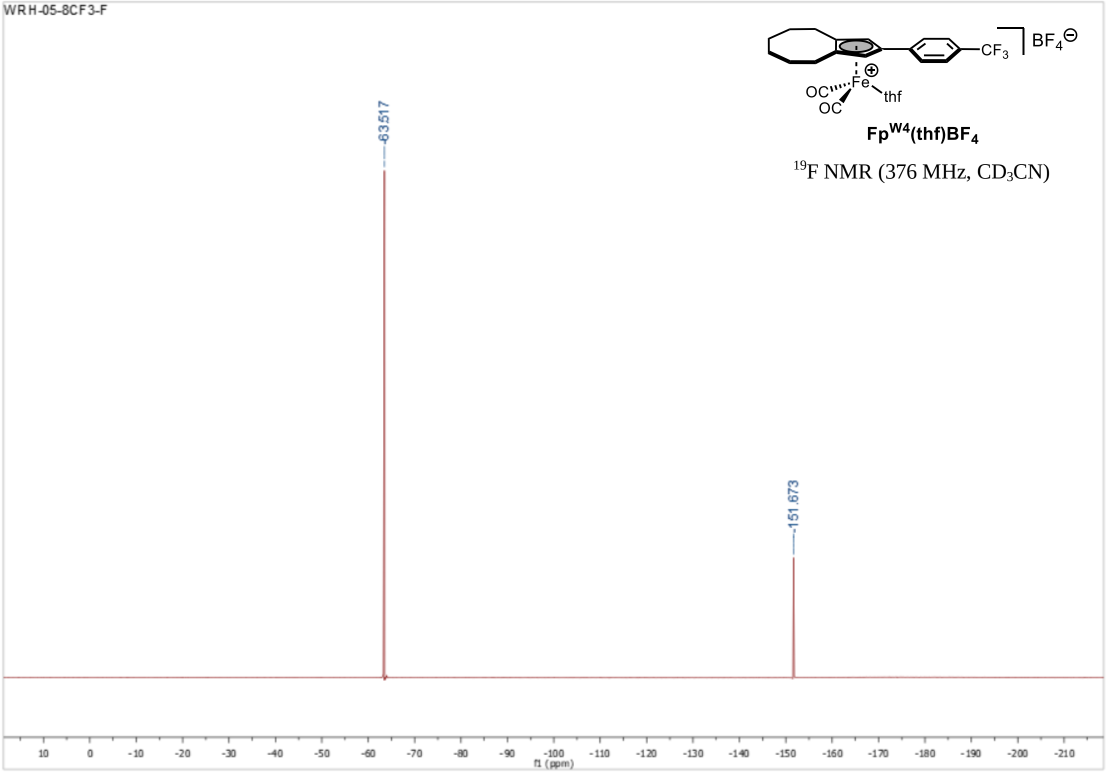


Fp^{W3}(thf)BF$_4$

^{19}F NMR (376 MHz, CD$_3$CN)

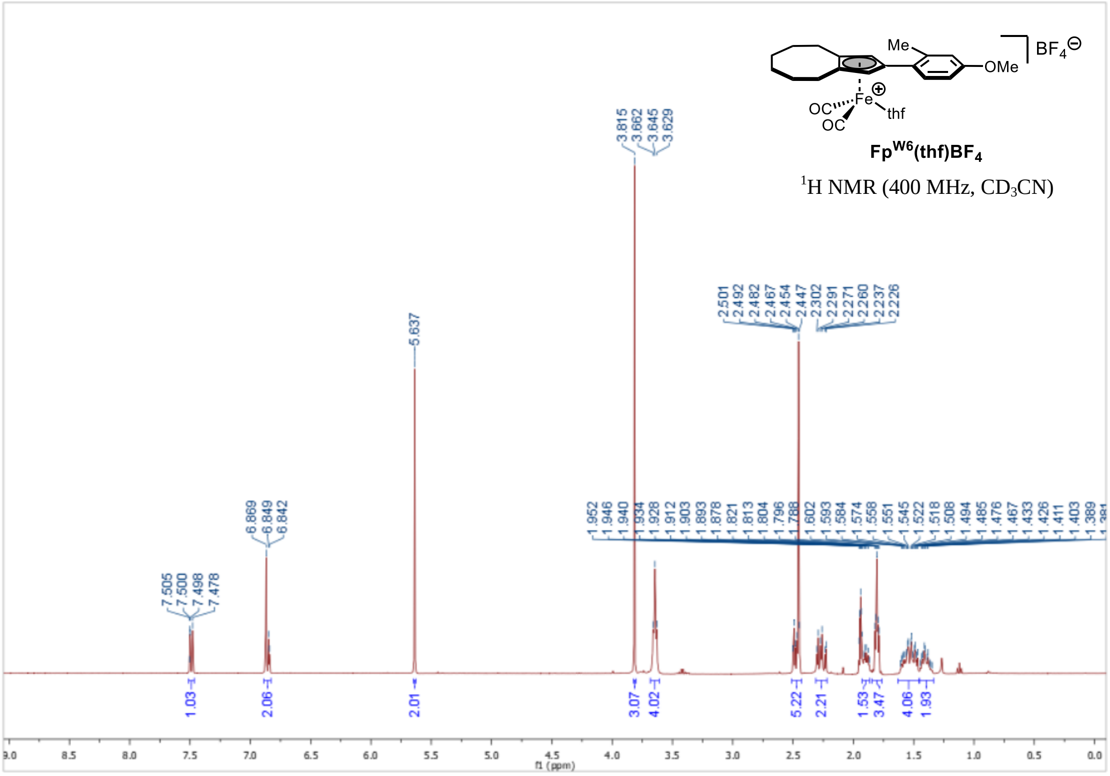

WRH-05-8CF3
WRH-05-8CF3
CF3
BF4⊖
⊕
Fe
OC
OC
thf
FpW4(thf)BF4
1H NMR (400 MHz, CD3CN)
7.791
5.939
3.657 3.655 3.651 3.647 3.641 3.635 3.631 3.626 3.624
2.528 2.519 2.509 2.494 2.484 2.474 2.342 2.331 2.311 2.299 2.265 2.169 1.952 1.946 1.940 1.933 1.927 1.922 1.912 1.897 1.817 1.809 1.805 1.800 1.796 1.792 1.784 1.555 1.534 1.527 1.506 1.498 1.414 1.408
H2O
4.01
2.00
3.45
2.08
2.14
1.16
3.32
6.39
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


WRH-05-8CF3-C'
CF3
BF4⊖
⊕
Fe
OC
OC
thf
FpW4(thf)BF4
13C NMR (100 MHz, CD3CN)
209.917
134.362 134.350 132.513 132.189 131.865 131.542 129.046 128.955 127.135 127.097 127.059 127.020 126.348 123.649 120.954
107.421
104.129
82.244
68.216
31.230 26.178 26.010 25.317
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)
134.362 134.350
132.513 132.189 131.865 131.542
127.135 127.097 127.059 127.020
126.348
123.649
120.954



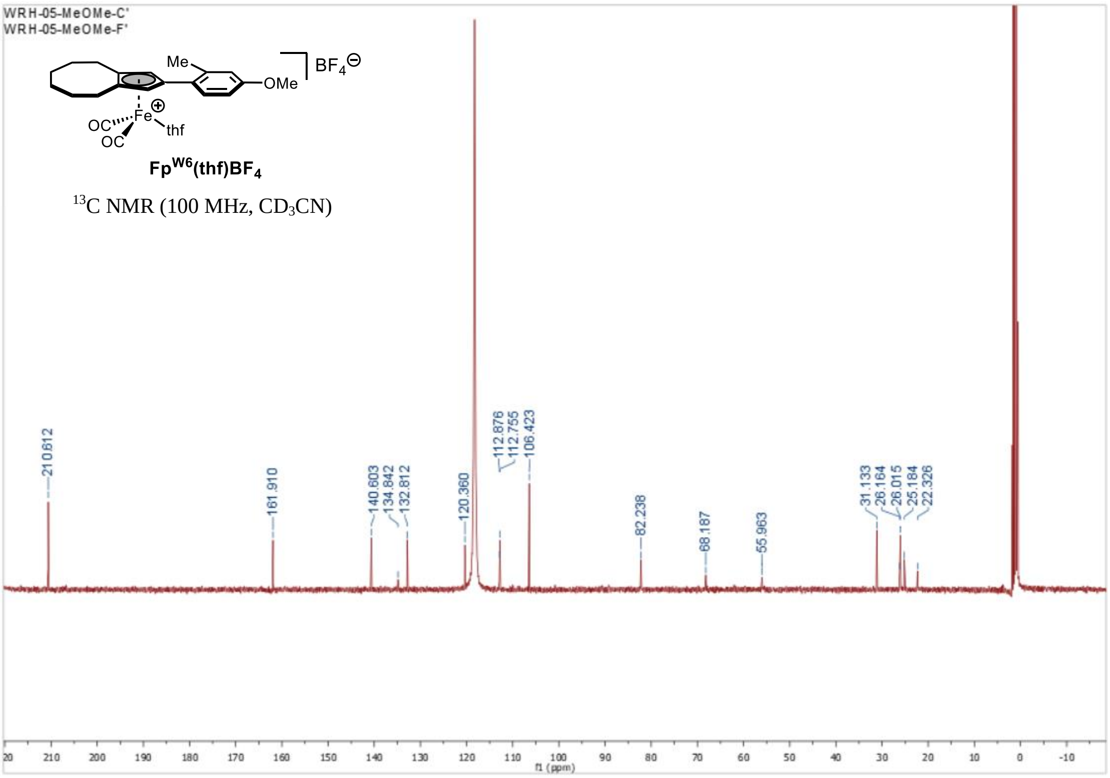
Fp^{W4}(thf)BF$_4$

^{19}F NMR (376 MHz, CD$_3$CN)



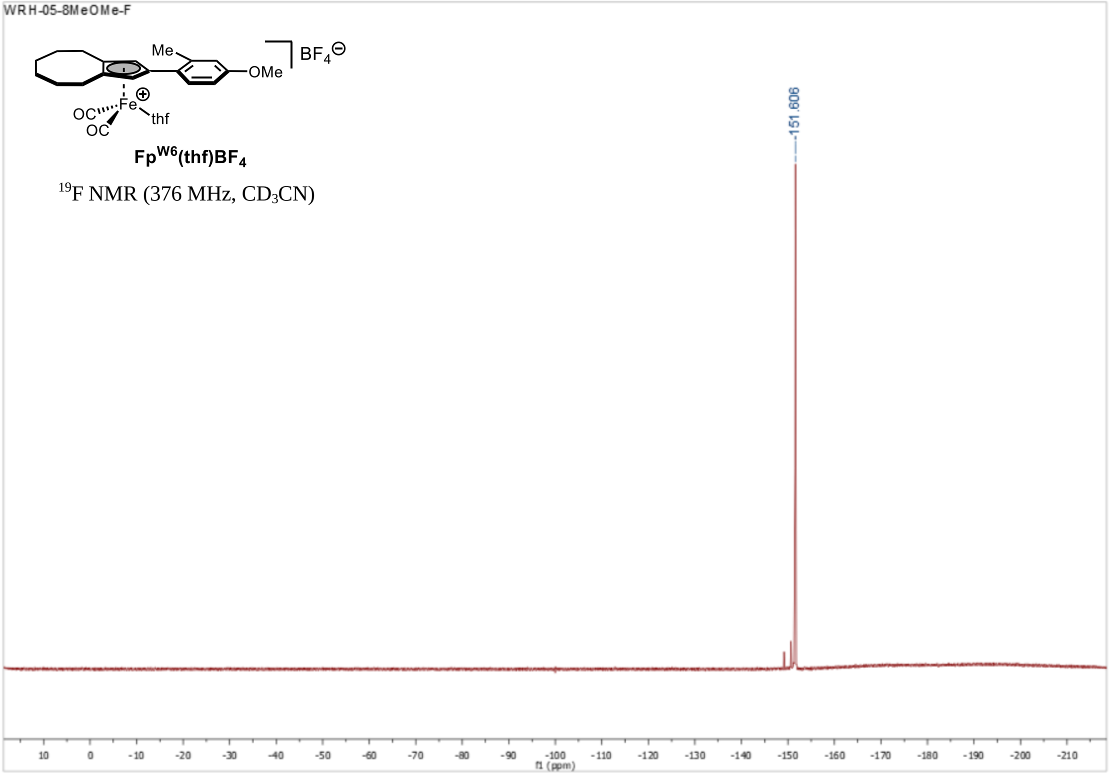
Fp^{W6}(thf)BF$_4$

^{1}H NMR (400 MHz, CD$_3$CN)



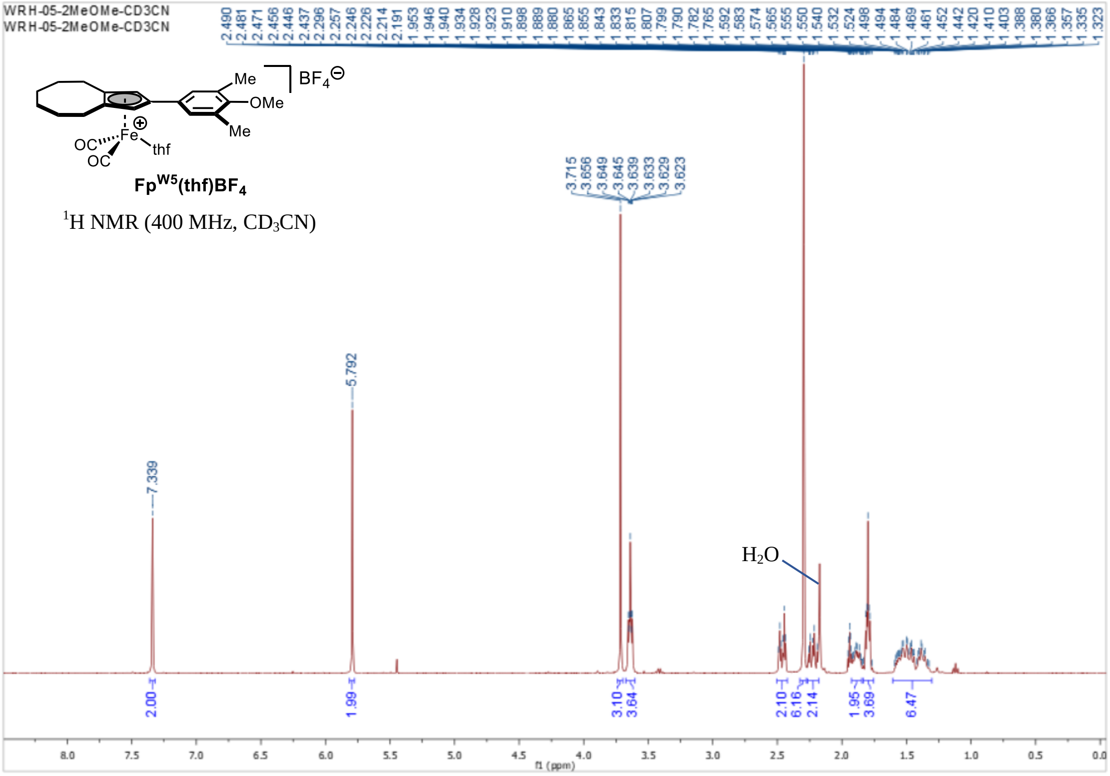
Fp^{W6}(thf)BF$_4$

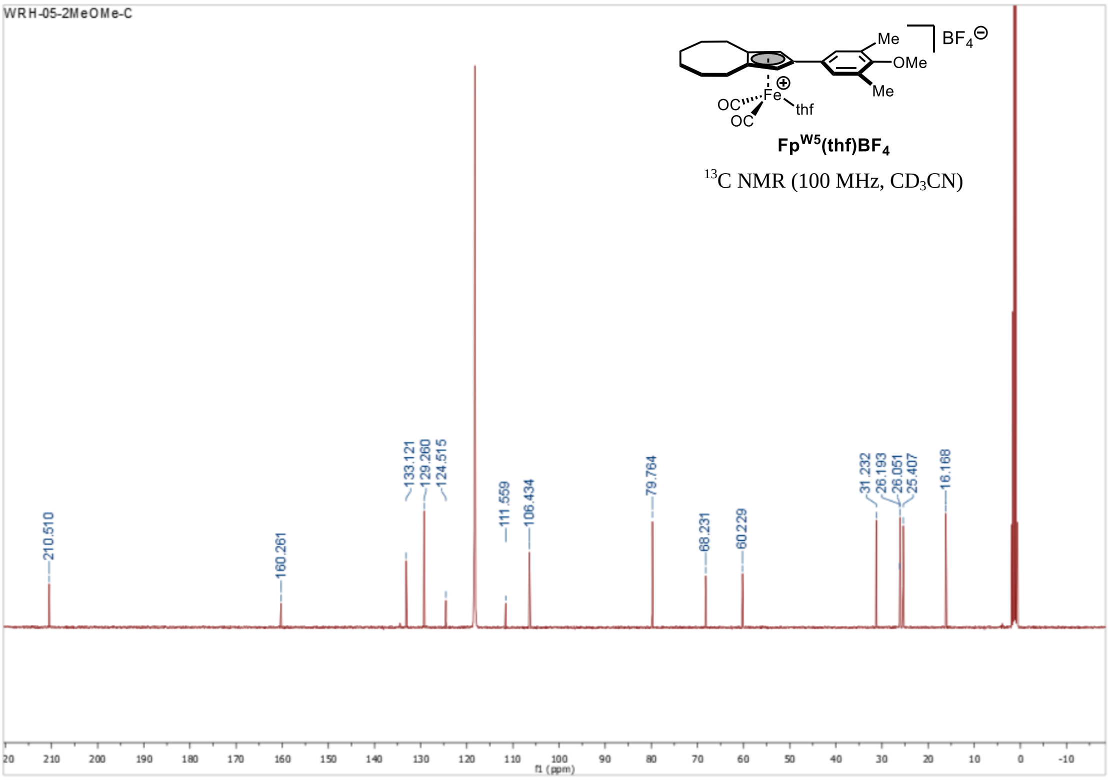
^{13}C NMR (100 MHz, CD$_3$CN)

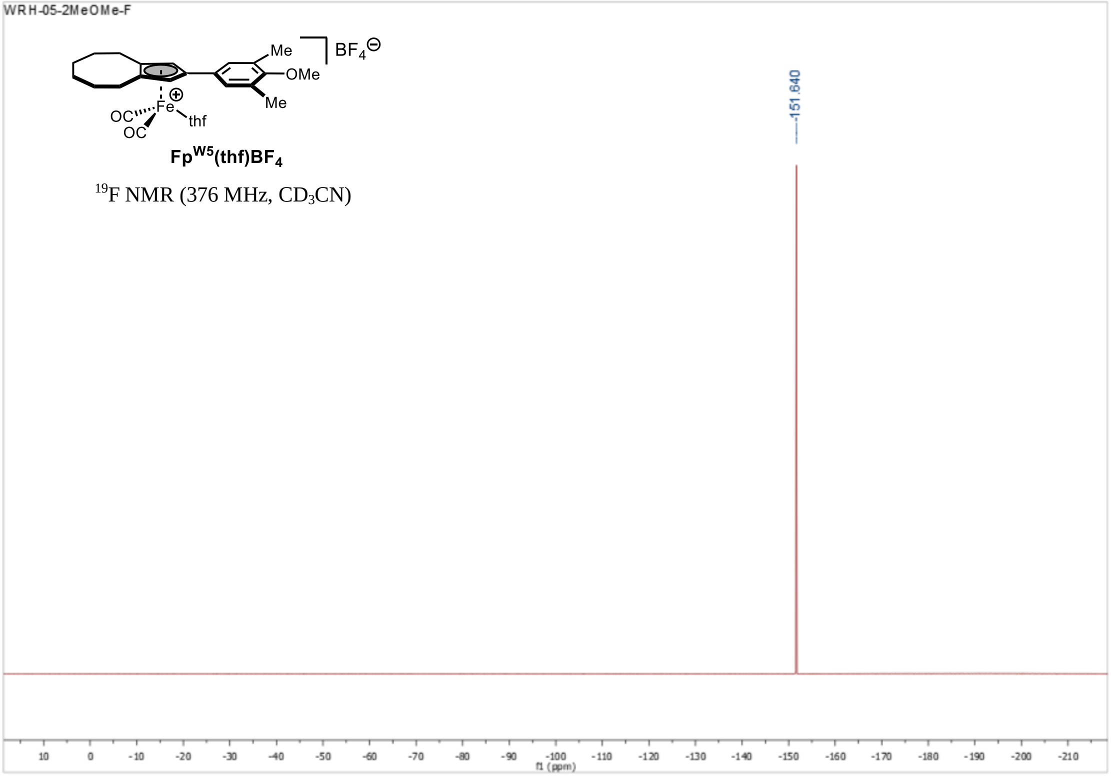


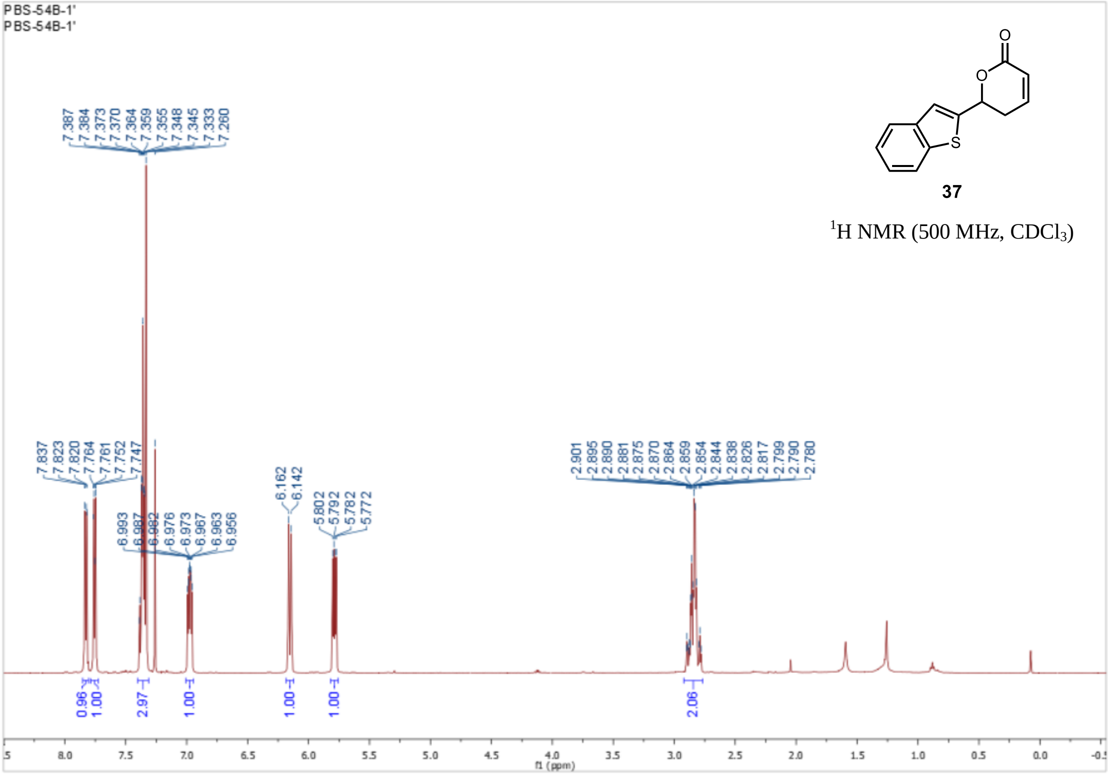
Fp^{W6}(thf)BF$_4$

^{19}F NMR (376 MHz, CD$_3$CN)


WRH-05-2MeOMe-CD3CN
WRH-05-2MeOMe-CD3CN
Me
BF4⊖
OMe
Me
⊕
Fe
OC
OC
thf
FpW5(thf)BF4
1H NMR (400 MHz, CD3CN)
2.490 2.481 2.471 2.456 2.446 2.437 2.296 2.257 2.246 2.226 2.214 2.191 1.953 1.946 1.940 1.934 1.928 1.923 1.910 1.898 1.889 1.880 1.865 1.855 1.843 1.833 1.815 1.807 1.799 1.790 1.782 1.765 1.592 1.583 1.574 1.565 1.555 1.550 1.540 1.532 1.524 1.498 1.494 1.484 1.469 1.461 1.452 1.442 1.420 1.410 1.403 1.388 1.380 1.366 1.357 1.335 1.323
3.715 3.656 3.649 3.645 3.639 3.633 3.629 3.623
5.792
7.339
H2O
2.00
1.99
3.10
3.64
2.10
6.16
2.14
1.95
3.69
6.47
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

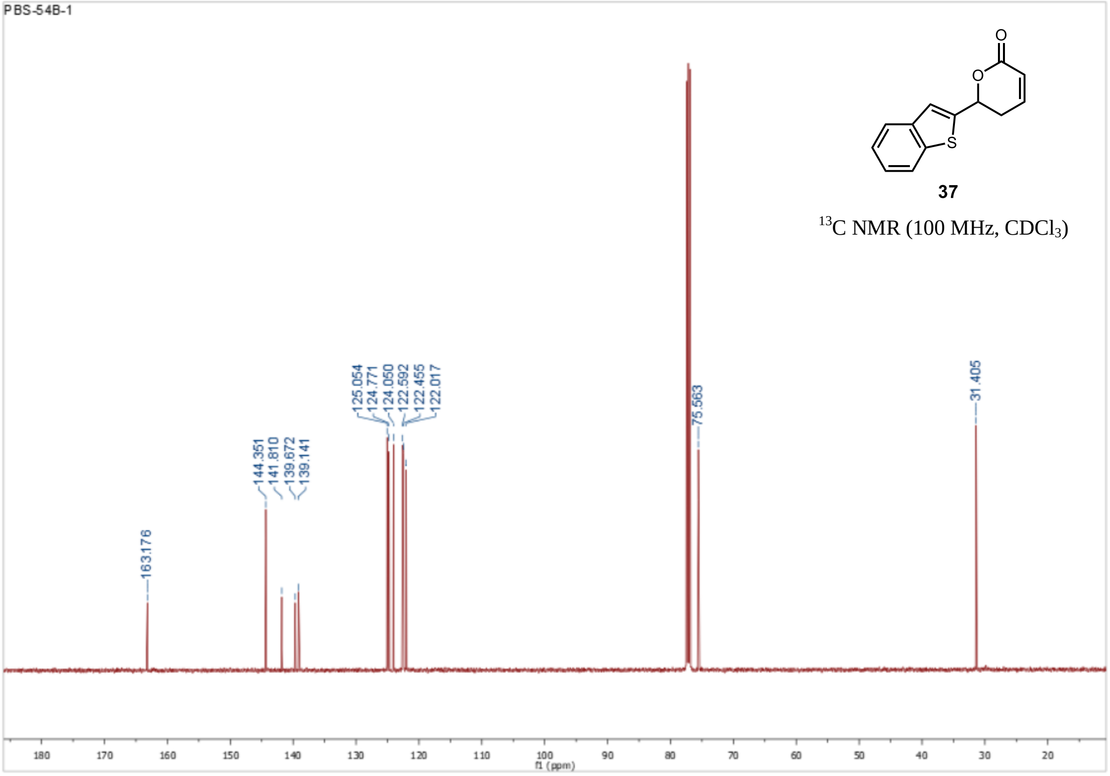

WRH-05-2MeOMe-C
Me
BF4⊖
OMe
Me
⊕
Fe
OC
OC
thf
FpW5(thf)BF4
13C NMR (100 MHz, CD3CN)
210.510
160.261
133.121
129.260
124.515
111.559
106.434
79.764
68.231
60.229
31.232
26.193
26.051
25.407
16.168
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


WRH-05-2MeOMe-F
Me
OMe
Me
BF4
Fe
OC
OC
thf
Fp^{W5}(thf)BF$_4$
^{19}F NMR (376 MHz, CD$_3$CN)
-151.640
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)



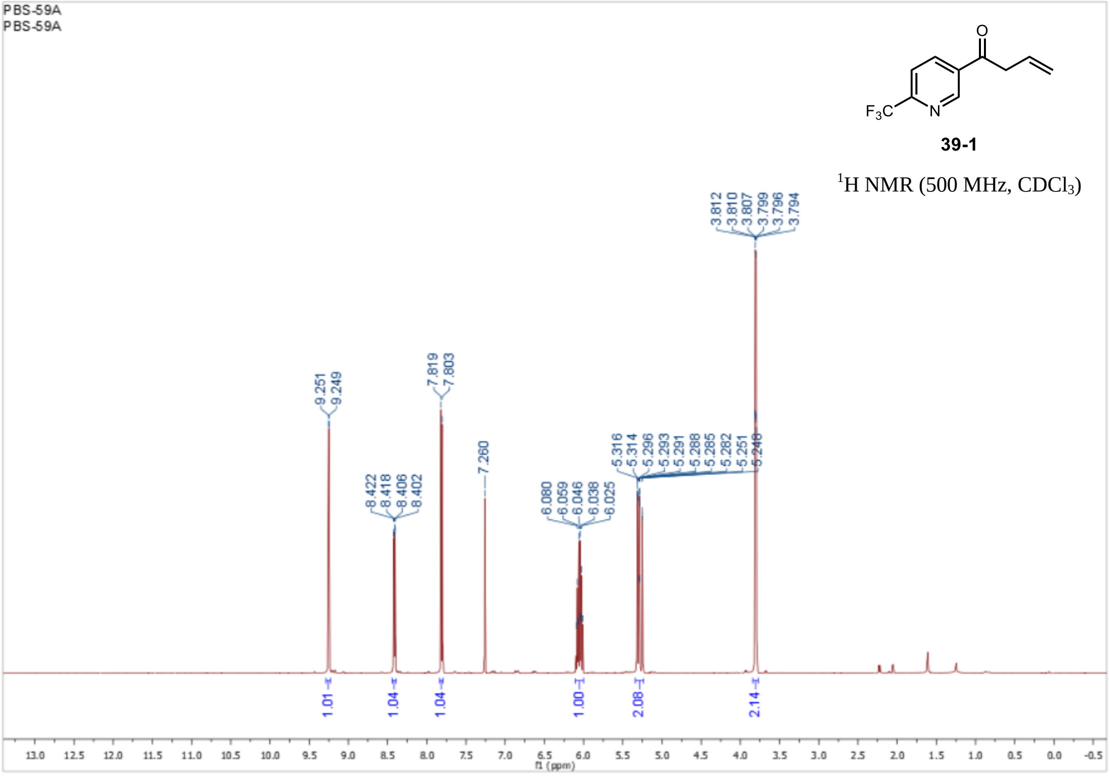
37

^{1}H NMR (500 MHz, $CDCl_3$)



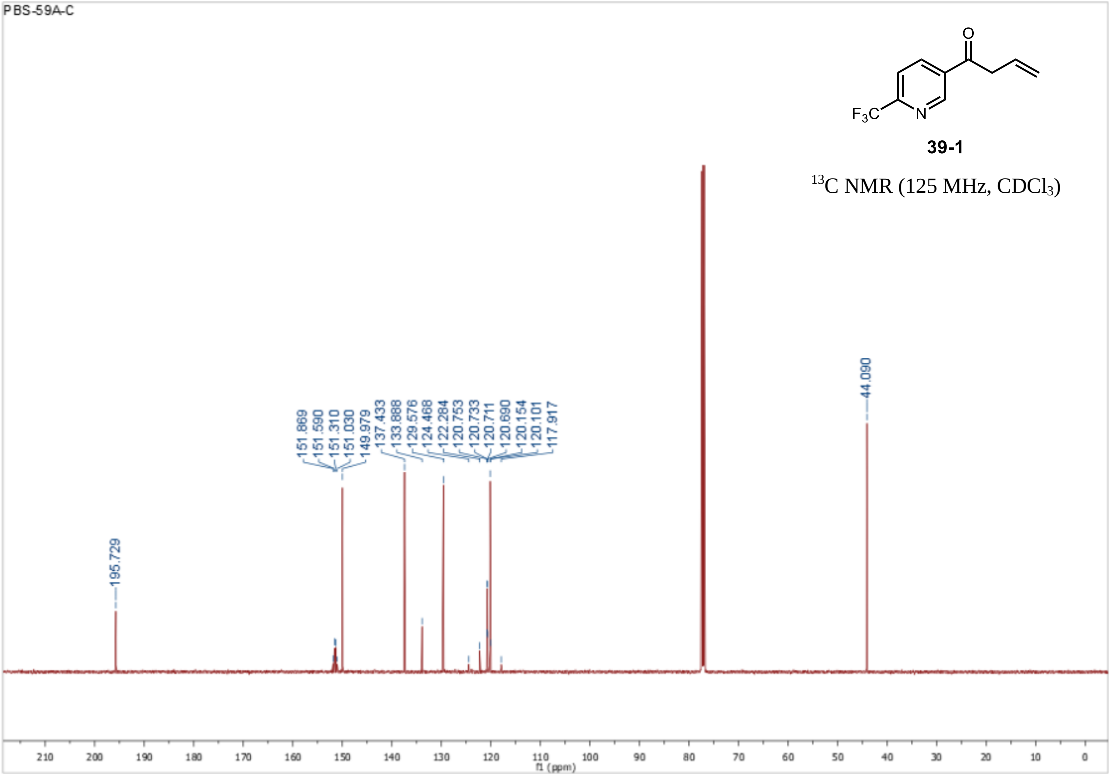
37

^{13}C NMR (100 MHz, $CDCl_3$)



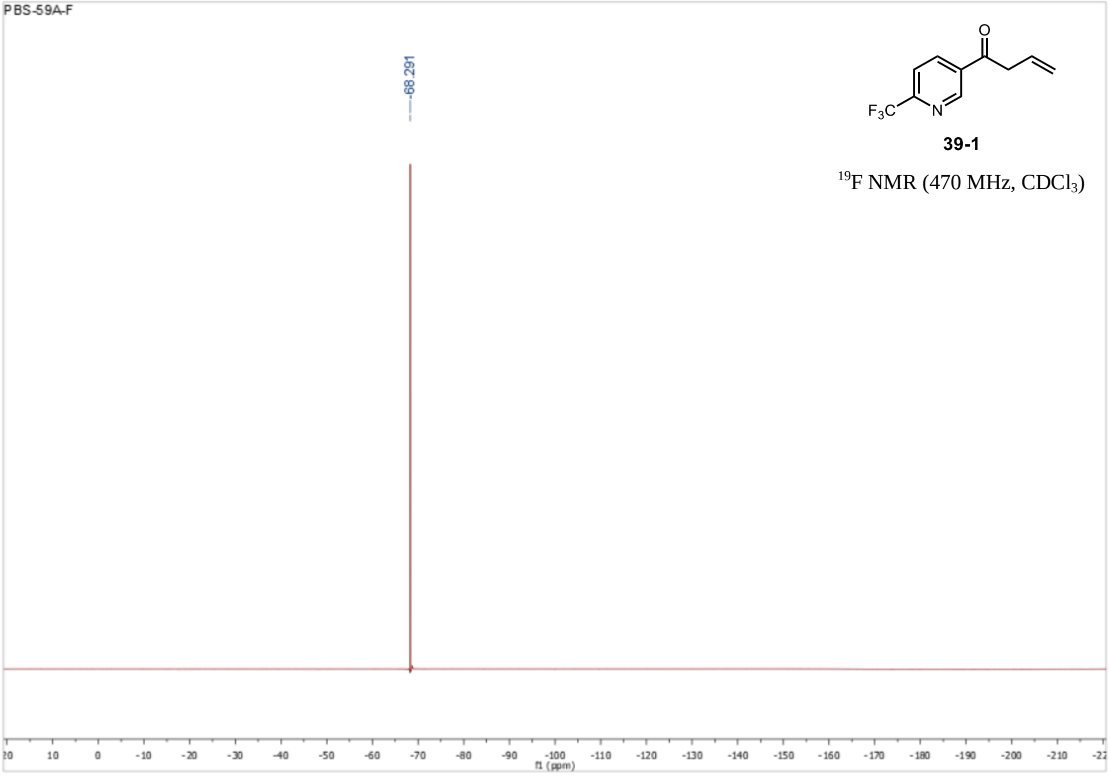
39-1

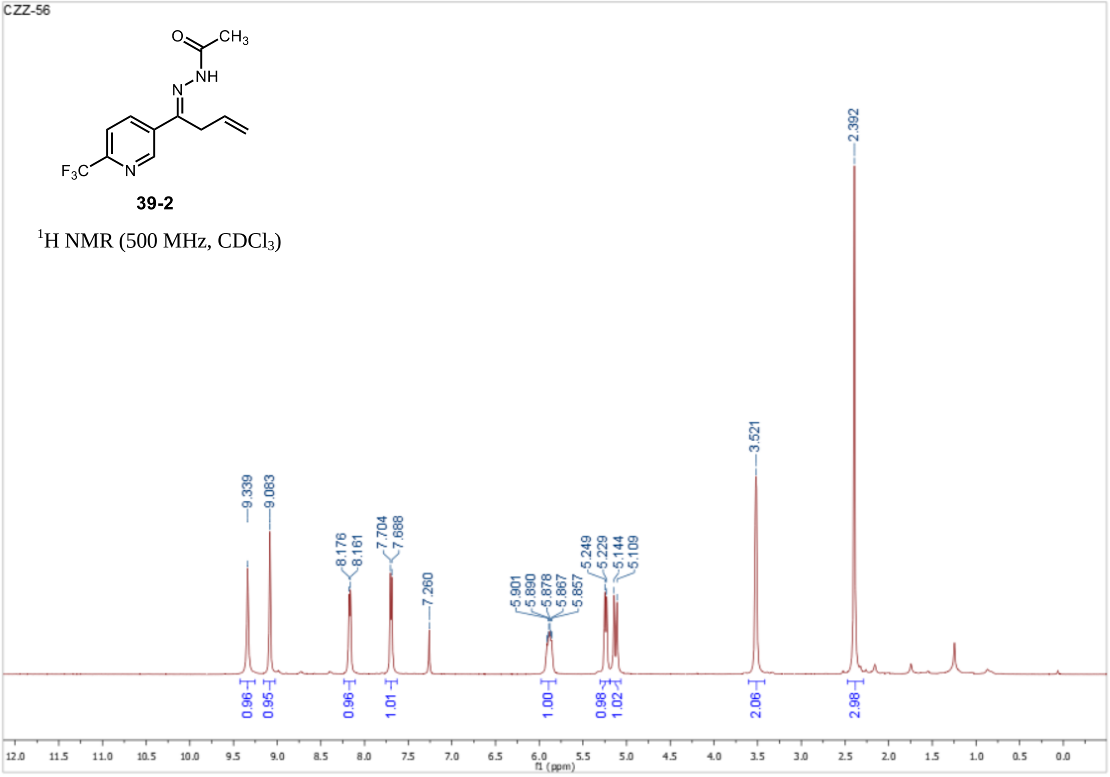
^{1}H NMR (500 MHz, CDCl$_3$)



39-1

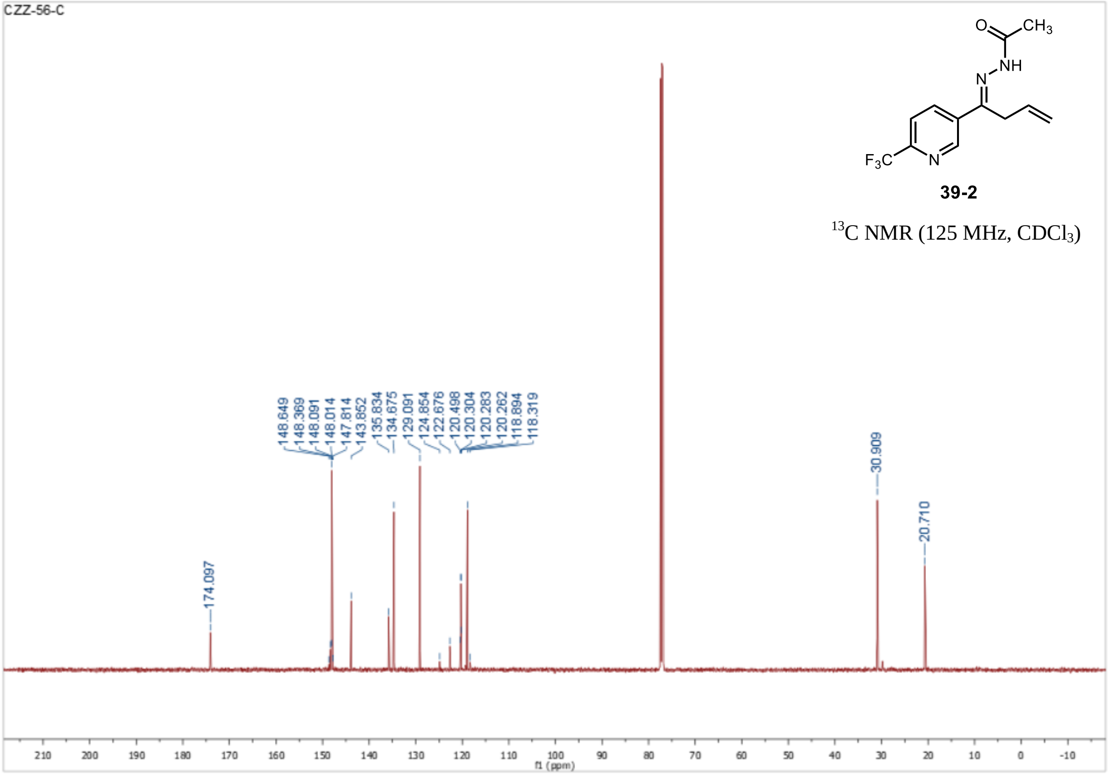
^{13}C NMR (125 MHz, CDCl$_3$)


PBS-59A-F
-68.291
O
F$_3$C
N
39-1
^{19}F NMR (470 MHz, CDCl$_3$)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)



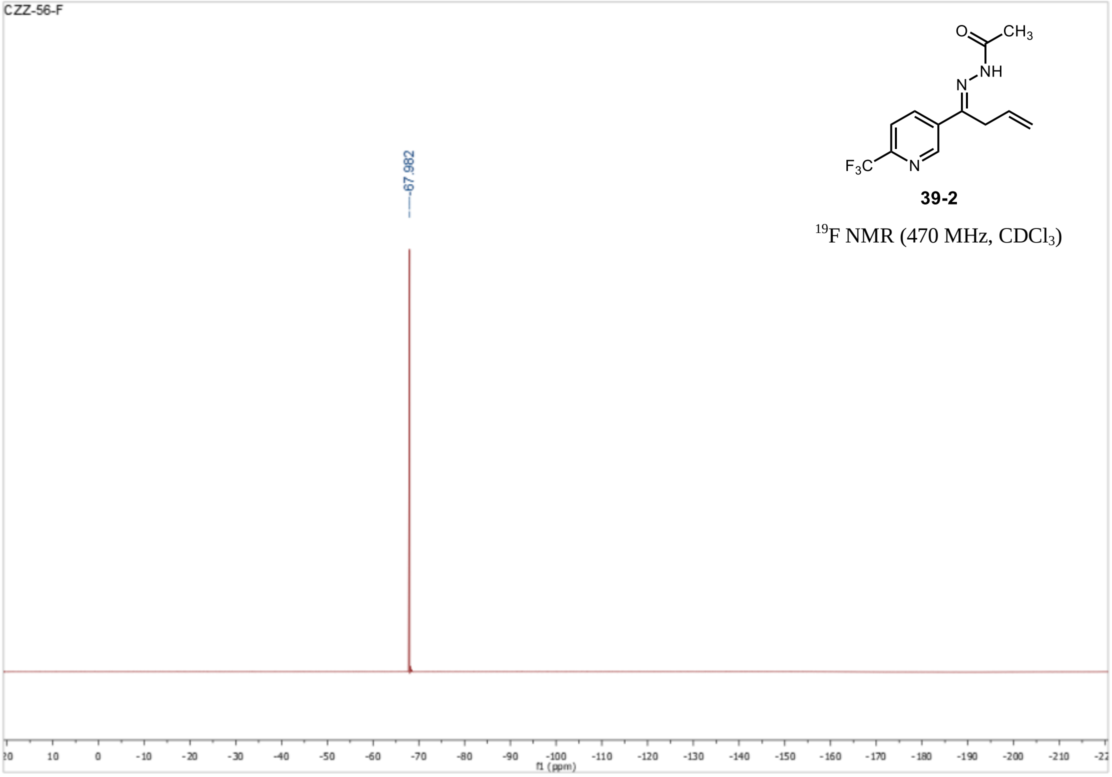
39-2

^{1}H NMR (500 MHz, $CDCl_3$)



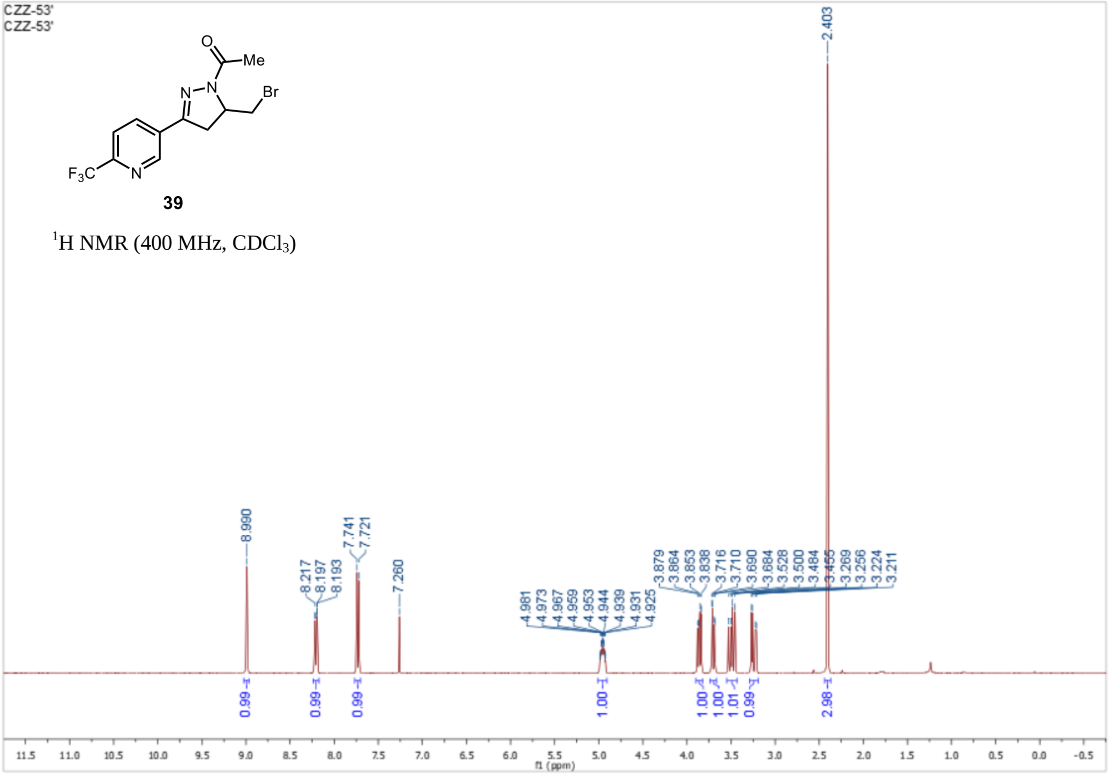
39-2

^{13}C NMR (125 MHz, $CDCl_3$)



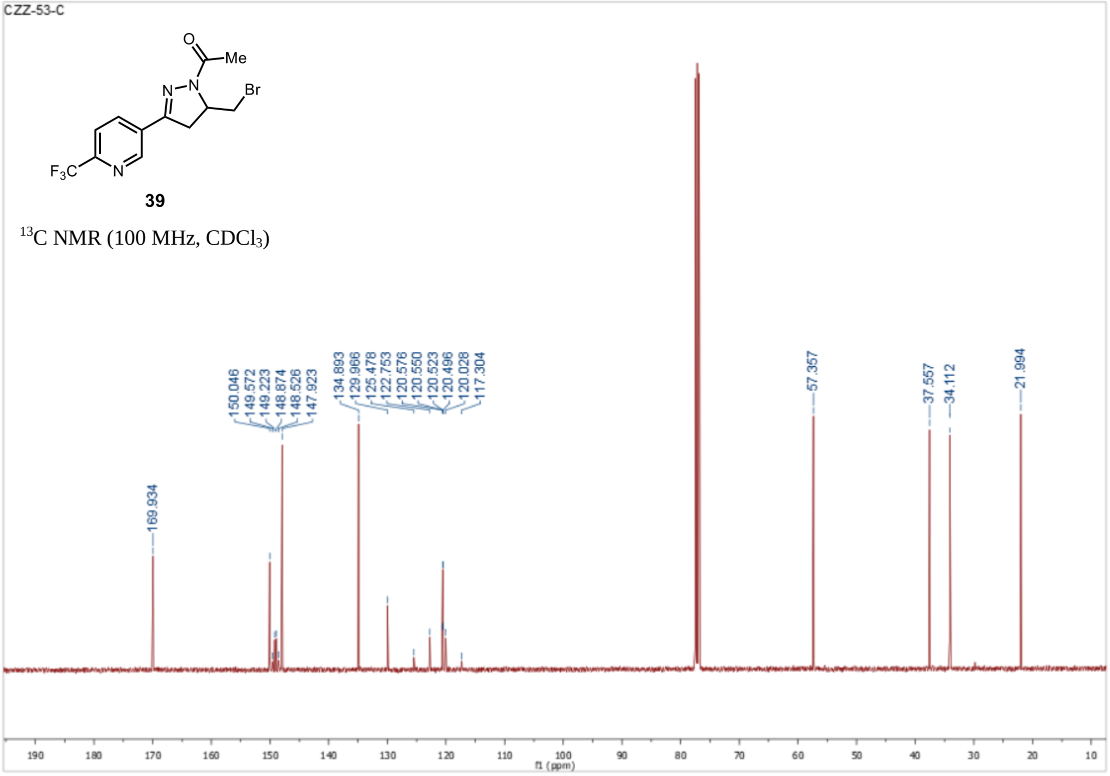
39-2

^{19}F NMR (470 MHz, $CDCl_3$)



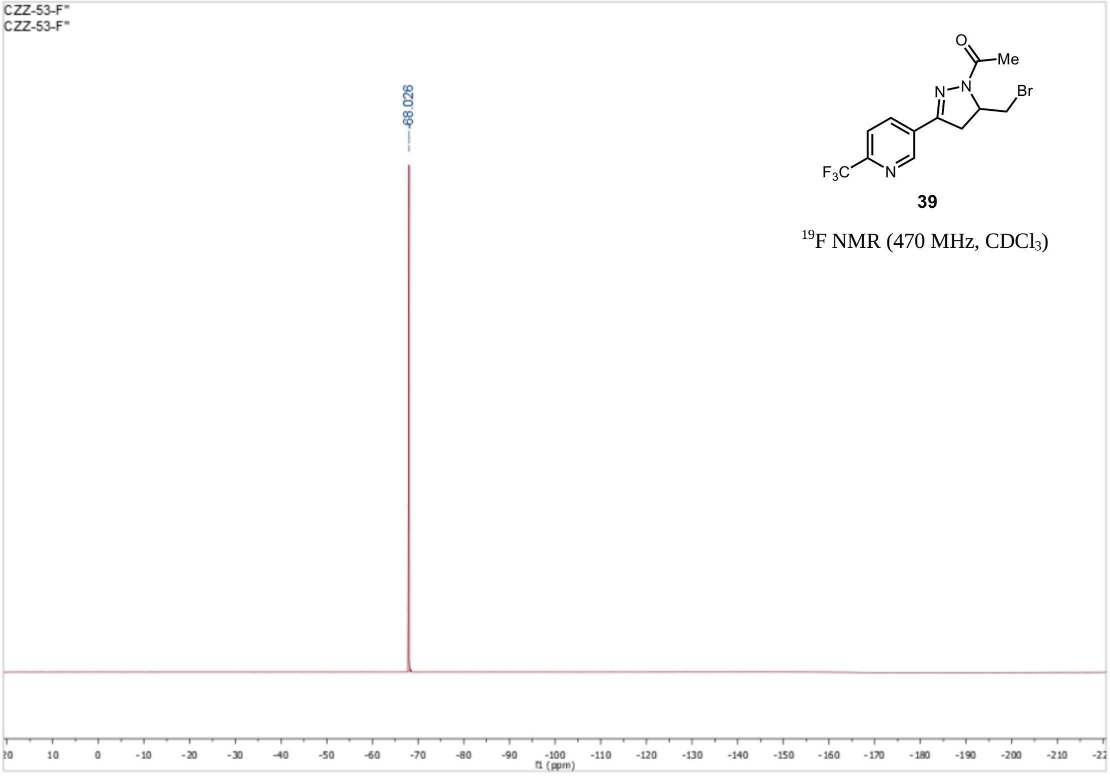
39

^{1}H NMR (400 MHz, $CDCl_3$)



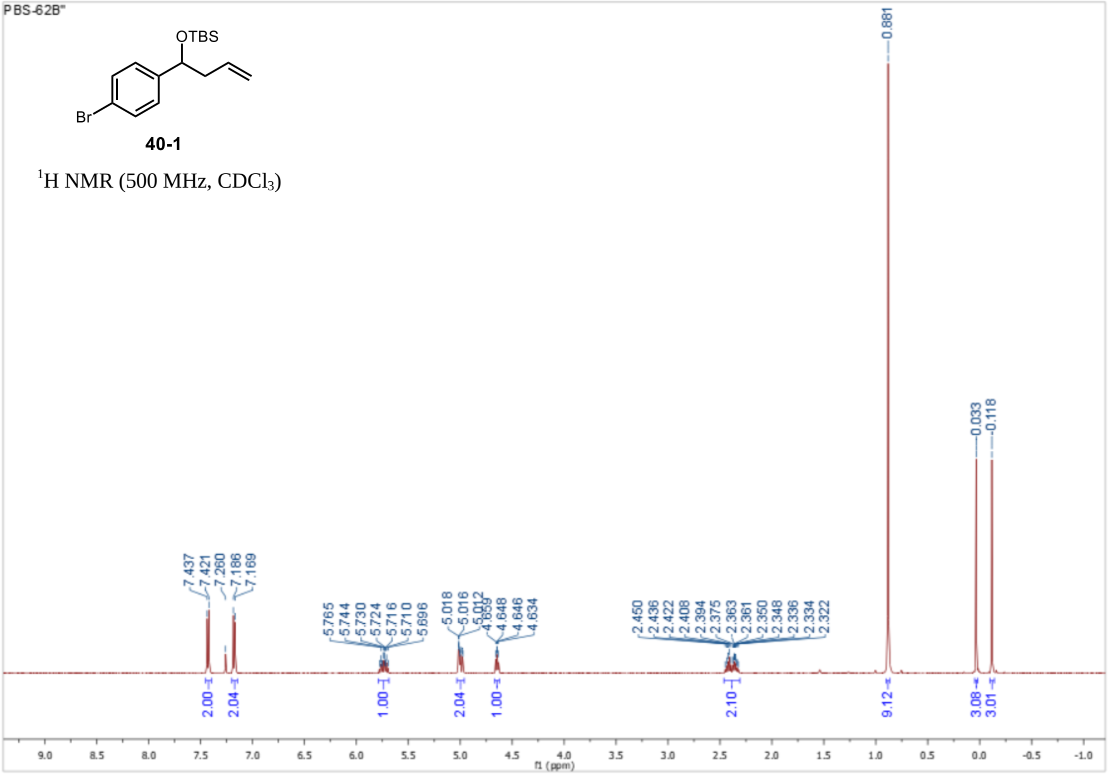
39

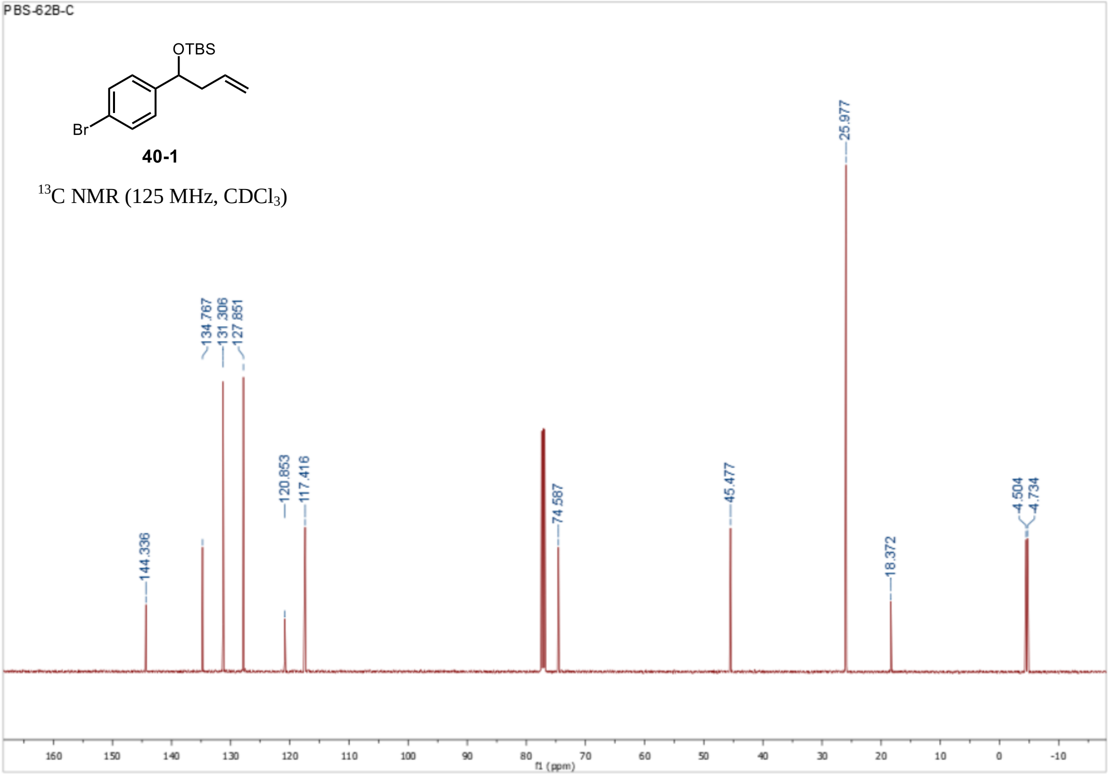
^{13}C NMR (100 MHz, $CDCl_3$)

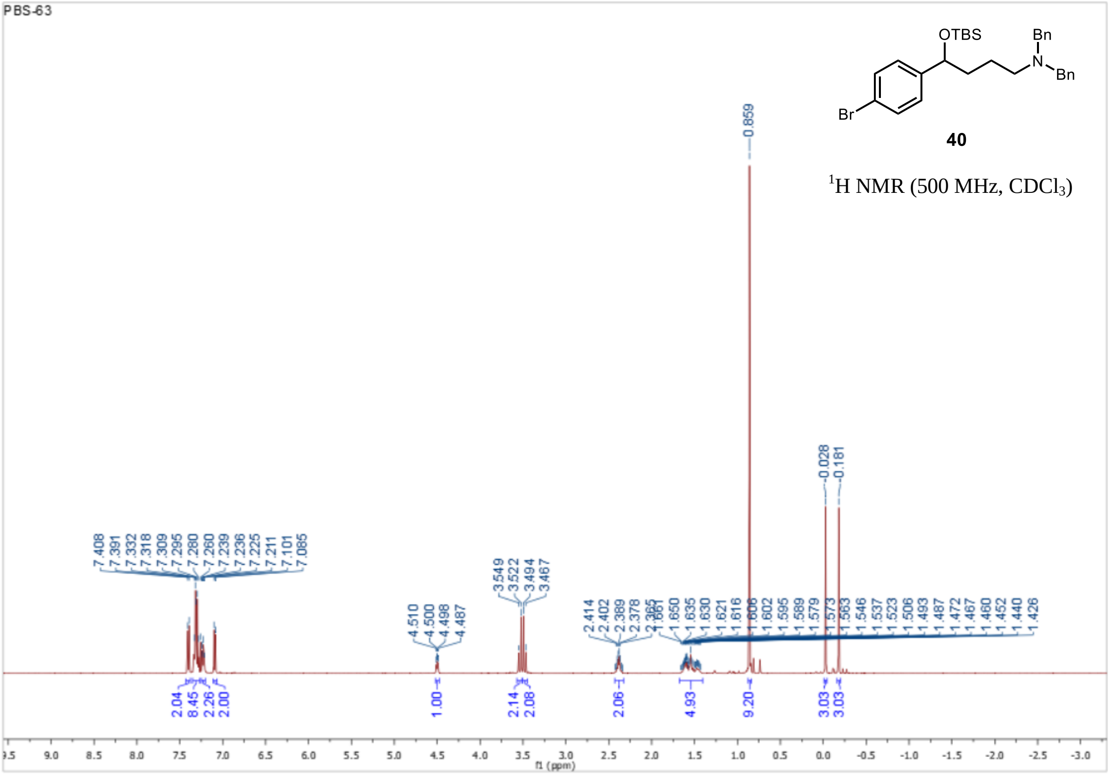


39

^{19}F NMR (470 MHz, CDCl$_3$)

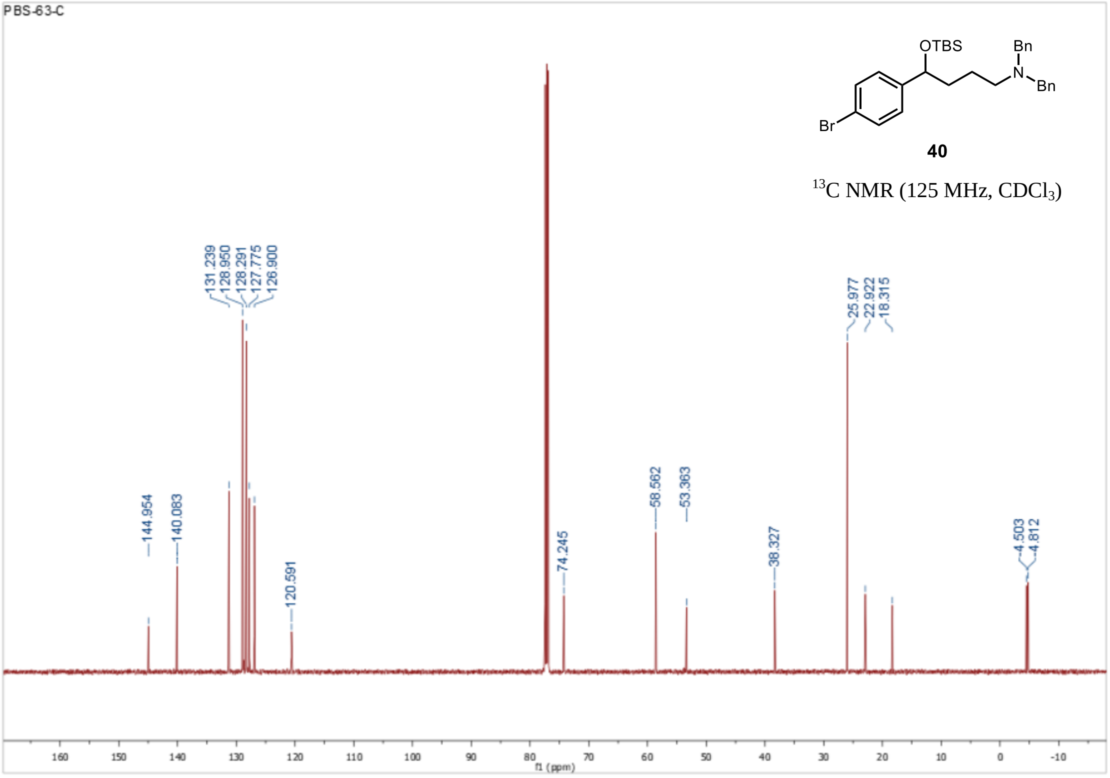

PBS-62B''
OTBS
Br
40-1
^{1}H NMR (500 MHz, CDCl$_3$)
7.437
7.421
7.260
7.186
7.169
5.765
5.744
5.730
5.724
5.716
5.710
5.696
5.018
5.016
5.012
4.659
4.648
4.646
4.634
2.450
2.436
2.422
2.408
2.394
2.375
2.363
2.361
2.350
2.348
2.336
2.334
2.322
0.881
0.033
-0.118
2.00
2.04
1.00
2.04
1.00
2.10
9.12
3.08
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


PBS-62B-C
OTBS
Br
40-1
^{13}C NMR (125 MHz, CDCl$_3$)
144.336
134.767
131.306
127.851
120.853
117.416
74.587
45.477
25.977
18.372
-4.504
-4.734
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



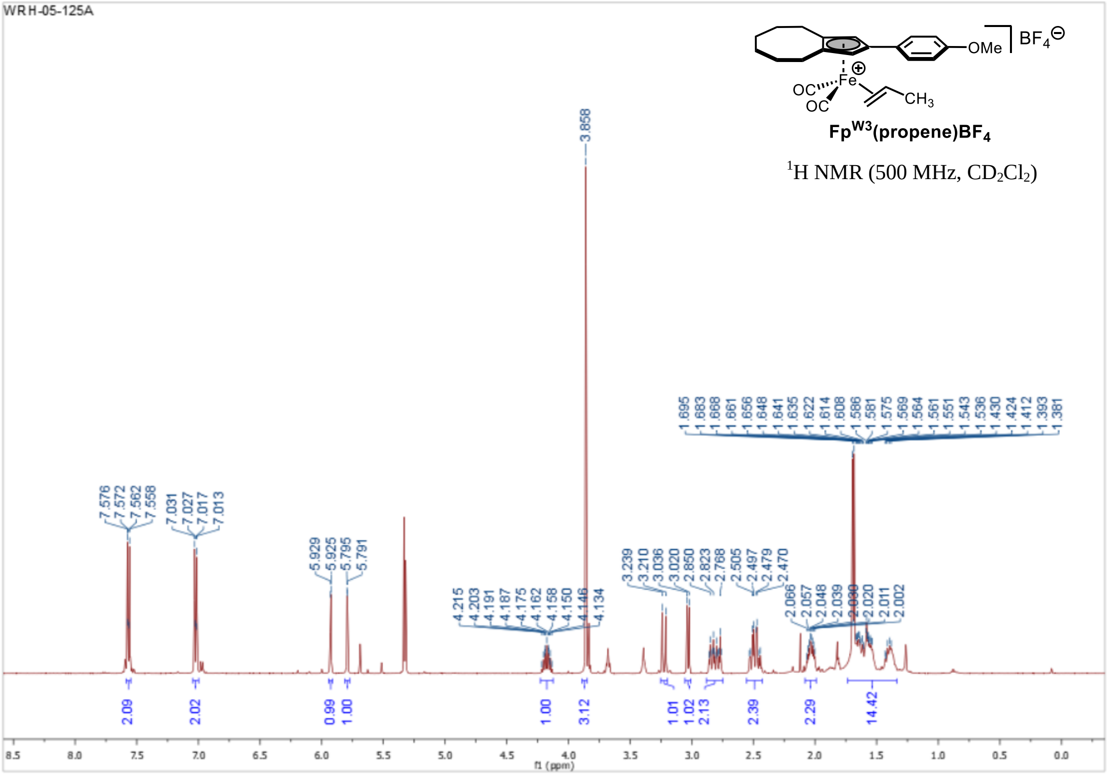
40

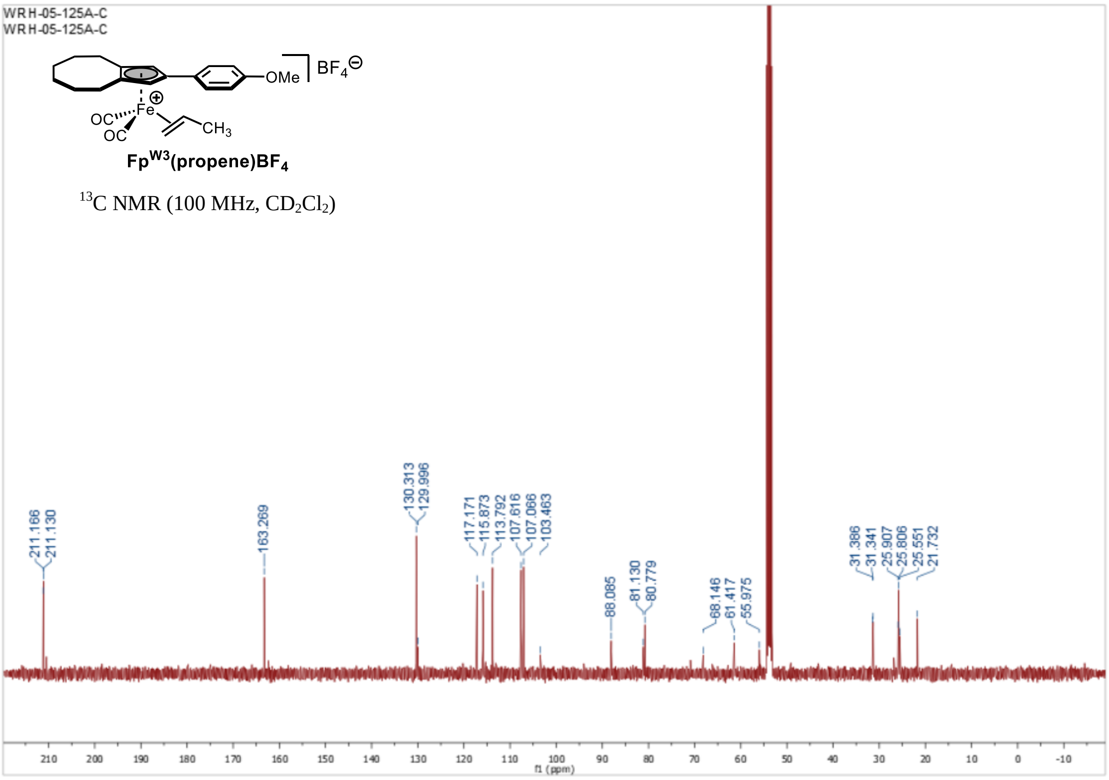
^{1}H NMR (500 MHz, CDCl$_3$)

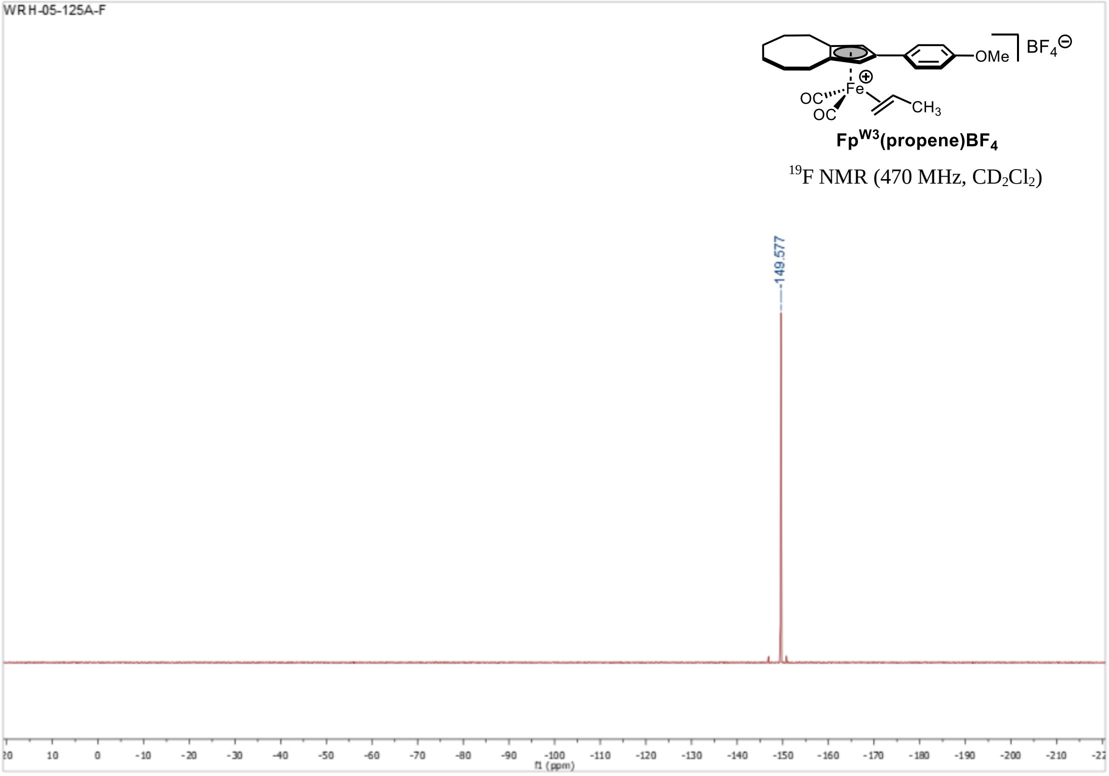


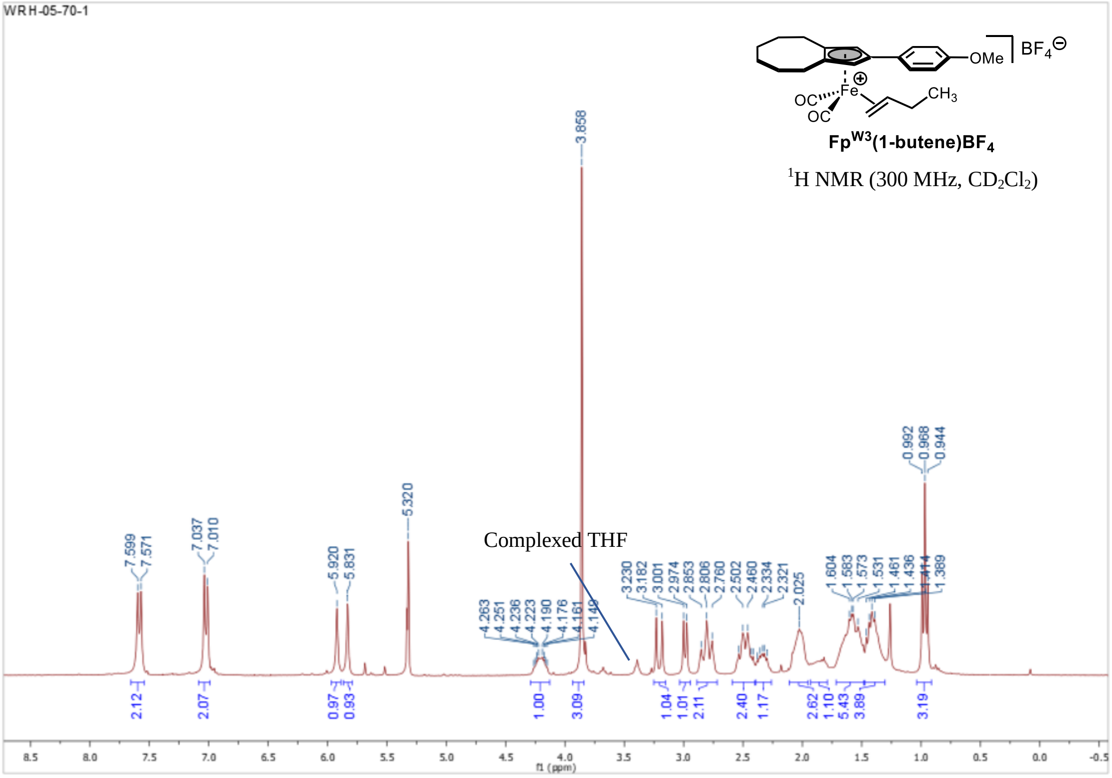
40

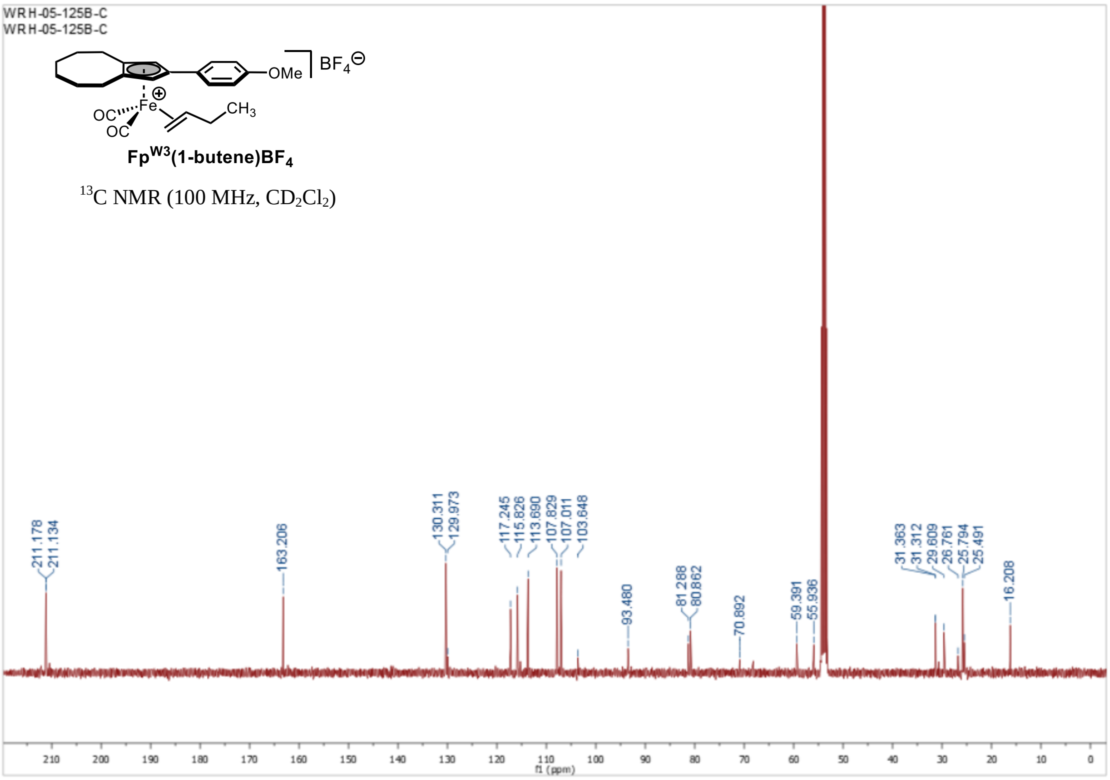
^{13}C NMR (125 MHz, CDCl$_3$)

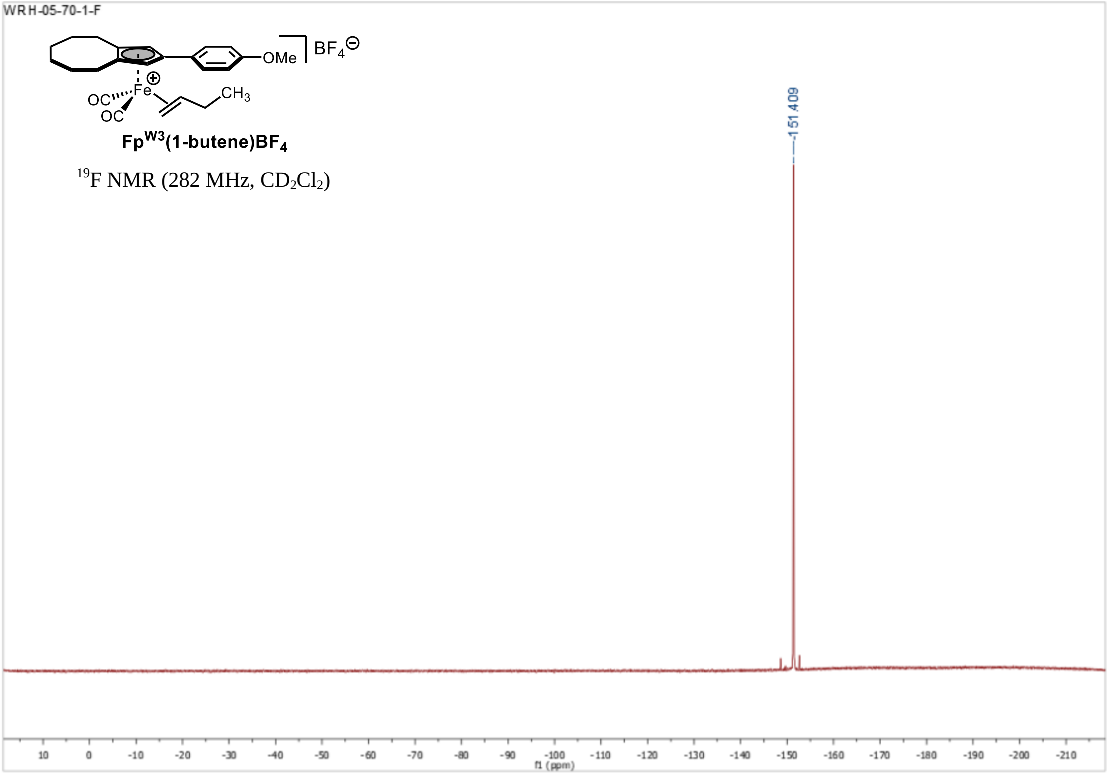

WRH-05-125A
OMe
BF4⊖
⊕
Fe
OC
OC
CH3
FpW3(propene)BF4
1H NMR (500 MHz, CD2Cl2)
7.576
7.572
7.562
7.558
7.031
7.027
7.017
7.013
5.929
5.925
5.795
5.791
4.215
4.203
4.191
4.187
4.175
4.162
4.158
4.150
4.146
4.134
3.858
3.239
3.210
3.036
3.020
2.850
2.823
2.768
2.505
2.497
2.479
2.470
2.066
2.057
2.048
2.039
2.030
2.020
2.011
2.002
1.695
1.683
1.668
1.661
1.656
1.648
1.641
1.635
1.622
1.614
1.608
1.586
1.581
1.575
1.569
1.564
1.561
1.551
1.543
1.536
1.430
1.424
1.412
1.393
1.381
2.09
2.02
0.99
1.00
1.00
3.12
1.01
1.02
2.13
2.39
2.29
14.42
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

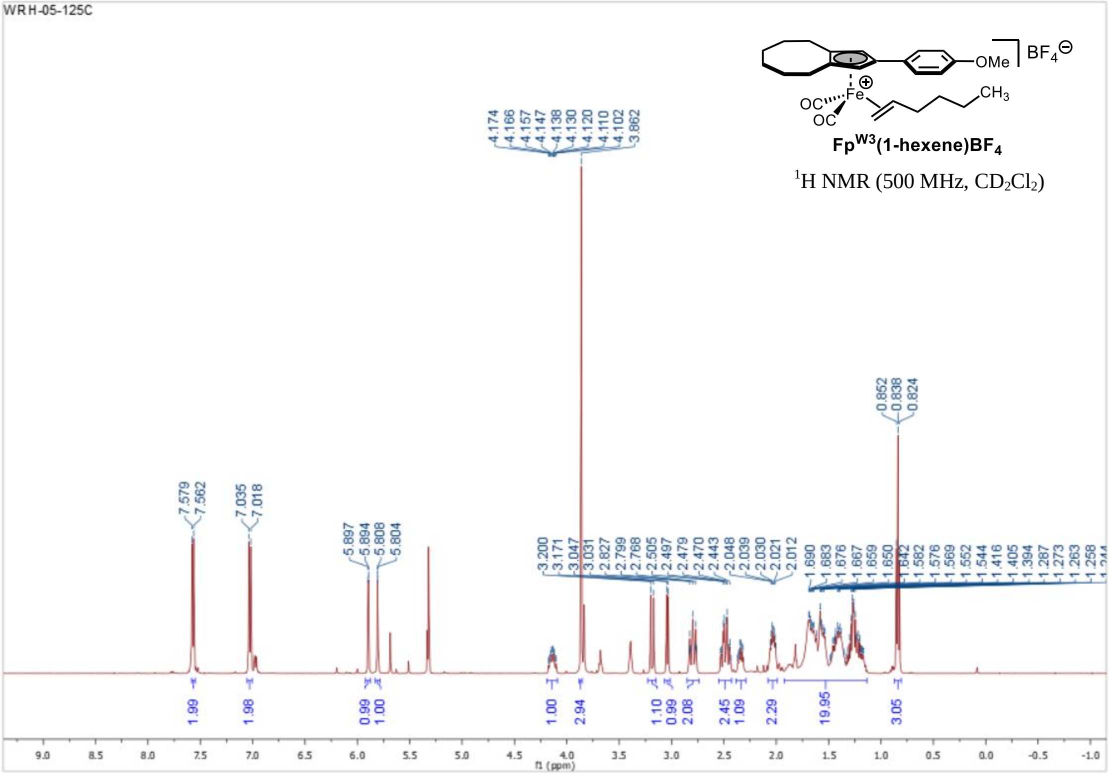

WRH-05-125A-C
WRH-05-125A-C
OMe
BF4⊖
⊕
Fe
OC
OC
CH3
FpW3(propene)BF4
13C NMR (100 MHz, CD2Cl2)
211.166
211.130
163.269
130.313
129.996
117.171
115.873
113.792
107.616
107.066
103.463
88.085
81.130
80.779
68.146
61.417
55.975
31.386
31.341
25.907
25.806
25.551
21.732
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


WRH-05-125A-F
OMe
BF4
Fe
OC
OC
CH3
Fp^W3(propene)BF4
19F NMR (470 MHz, CD2Cl2)
-149.577
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


WRH-05-70-1
OMe
$BF_4^{\ominus}$
⊕
Fe
OC
OC
CH_3
Fp^{W3}(1-butene)BF_4
^{1}H NMR (300 MHz, CD_2Cl_2)
Complexed THF
7.599
7.571
7.037
7.010
5.920
5.831
5.320
4.263
4.251
4.236
4.223
4.190
4.176
4.161
4.149
3.858
3.230
3.182
3.001
2.974
2.853
2.806
2.760
2.502
2.460
2.334
2.321
2.025
1.804
1.583
1.573
1.531
1.461
1.436
1.414
1.389
0.992
0.968
0.944
2.12
2.07
0.97
0.93
1.00
3.09
1.04
1.01
2.11
2.40
1.17
2.62
1.10
5.43
3.89
3.19
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

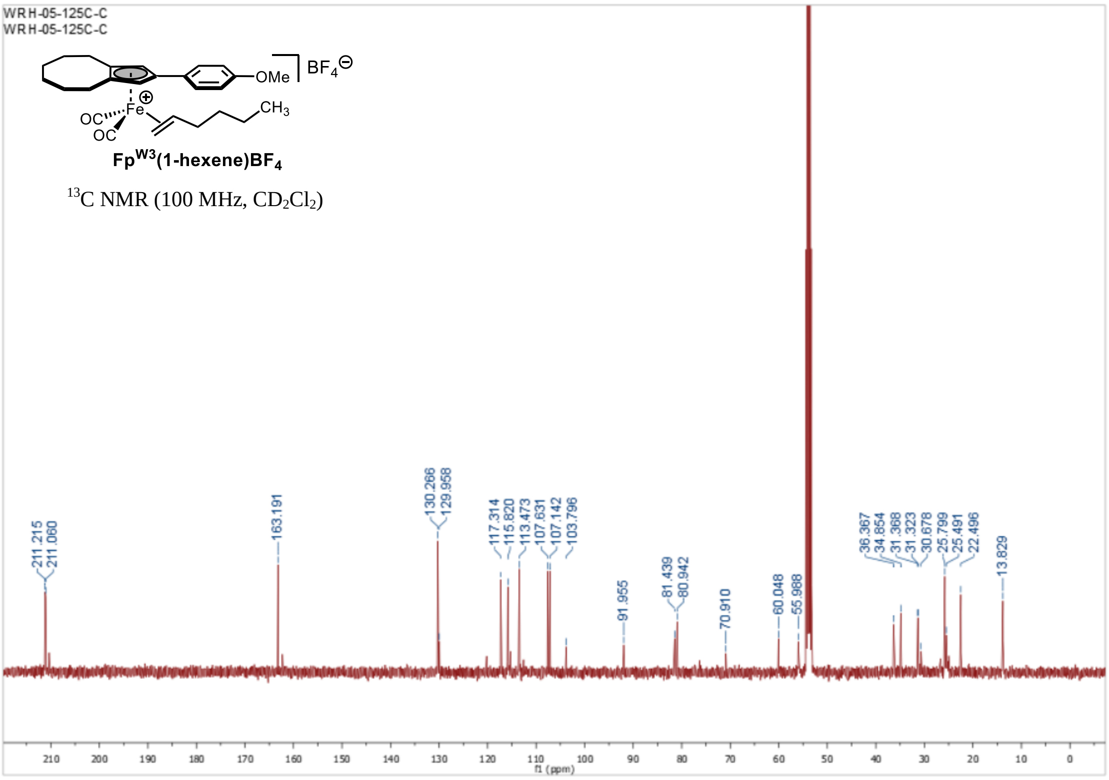

WRH-05-125B-C
WRH-05-125B-C
OMe
$BF_4^{\ominus}$
⊕
Fe
OC
OC
CH_3
Fp^{W3}(1-butene)BF_4
^{13}C NMR (100 MHz, CD_2Cl_2)
211.178
211.134
163.206
130.311
129.973
117.245
115.826
113.690
107.829
107.011
103.648
93.480
81.288
80.862
70.892
59.391
55.936
31.363
31.312
29.609
28.761
25.794
25.491
16.208
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


WRH-05-70-1-F
OMe
BF$_4^{\ominus}$
⊕
Fe
OC
OC
CH$_3$
Fp^{W3}(1-butene)BF$_4$
^{19}F NMR (282 MHz, CD$_2$Cl$_2$)
-151.409
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)



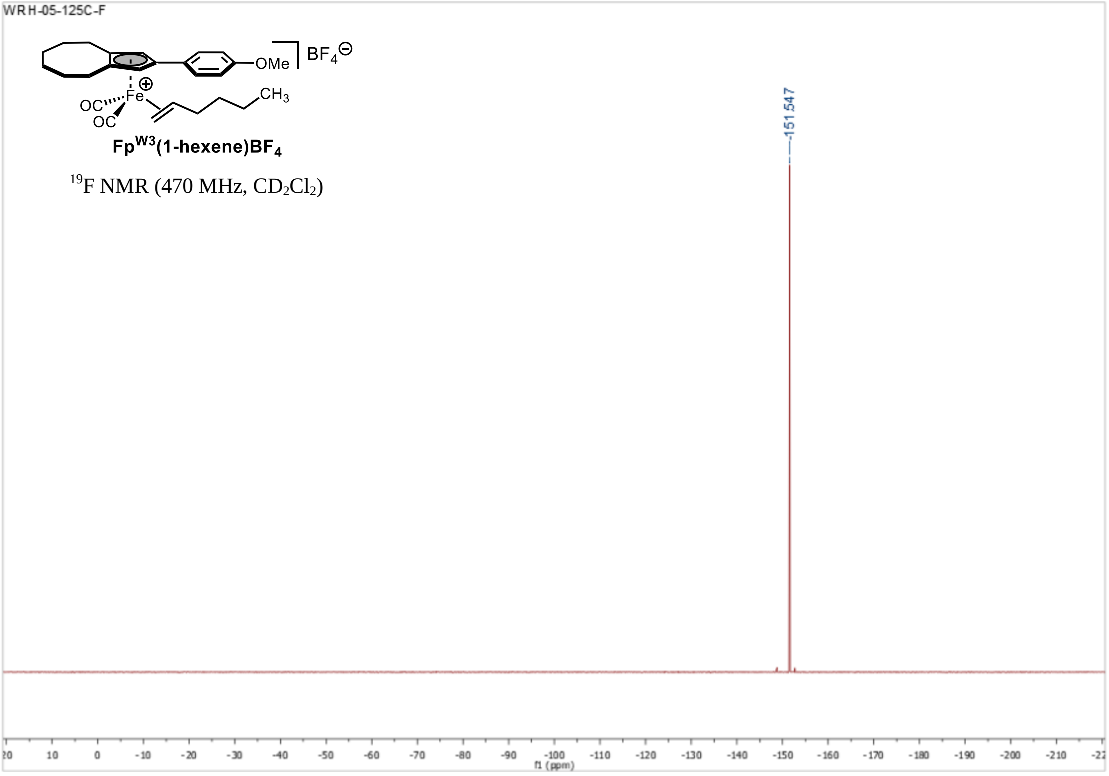
Fp^{W3}(1-hexene)BF$_4$

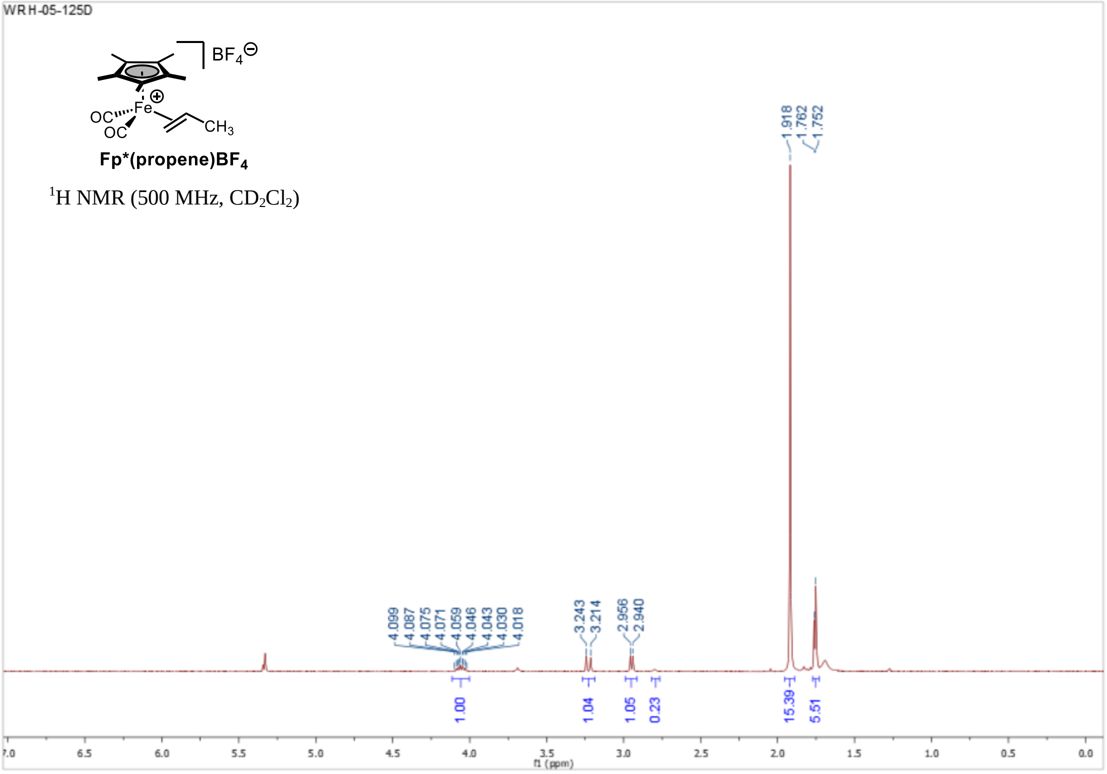
^{1}H NMR (500 MHz, CD$_2$Cl$_2$)

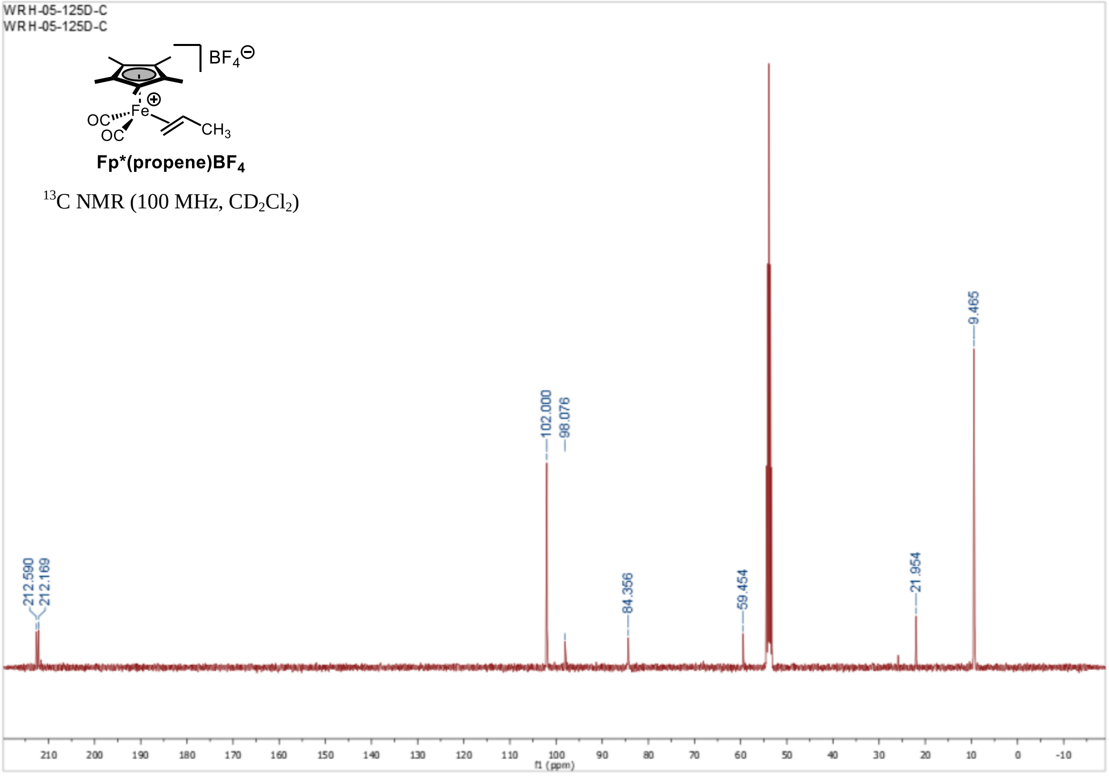


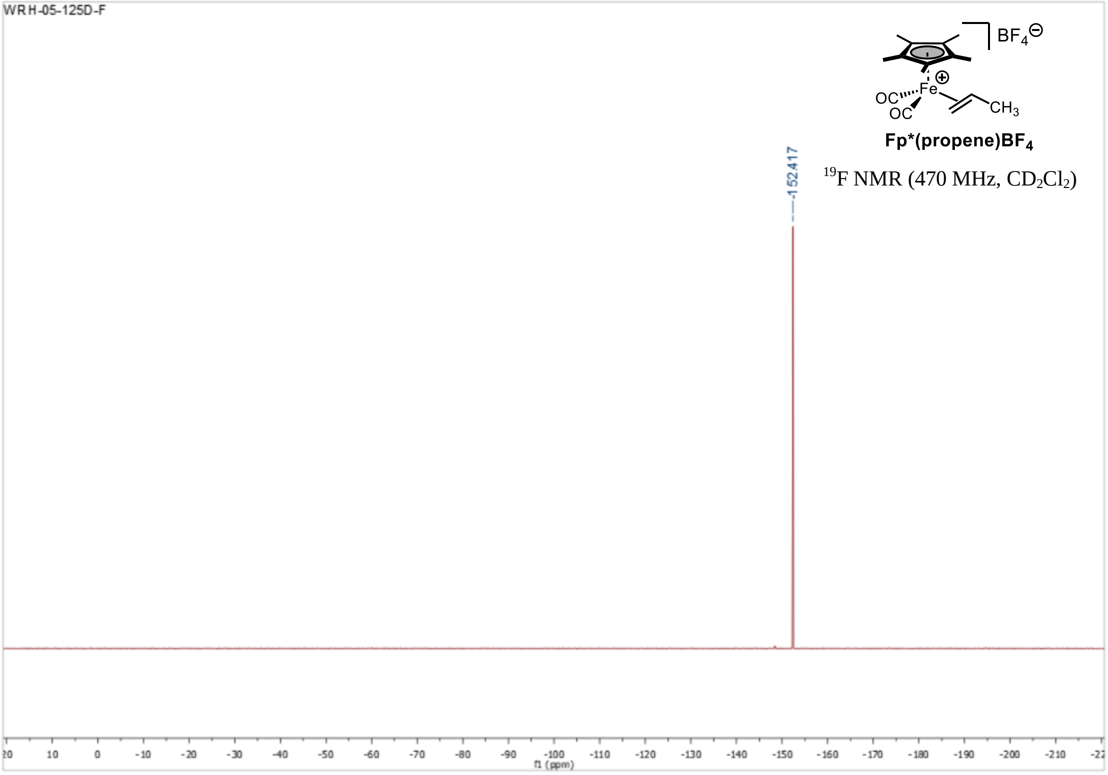
Fp^{W3}(1-hexene)BF$_4$

^{13}C NMR (100 MHz, CD$_2$Cl$_2$)


WRH-05-125C-F
OMe
BF4⊖
Fe⊕
OC
OC
CH3
Fp^W3(1-hexene)BF4
19F NMR (470 MHz, CD2Cl2)
-151.547
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-22
f1 (ppm)

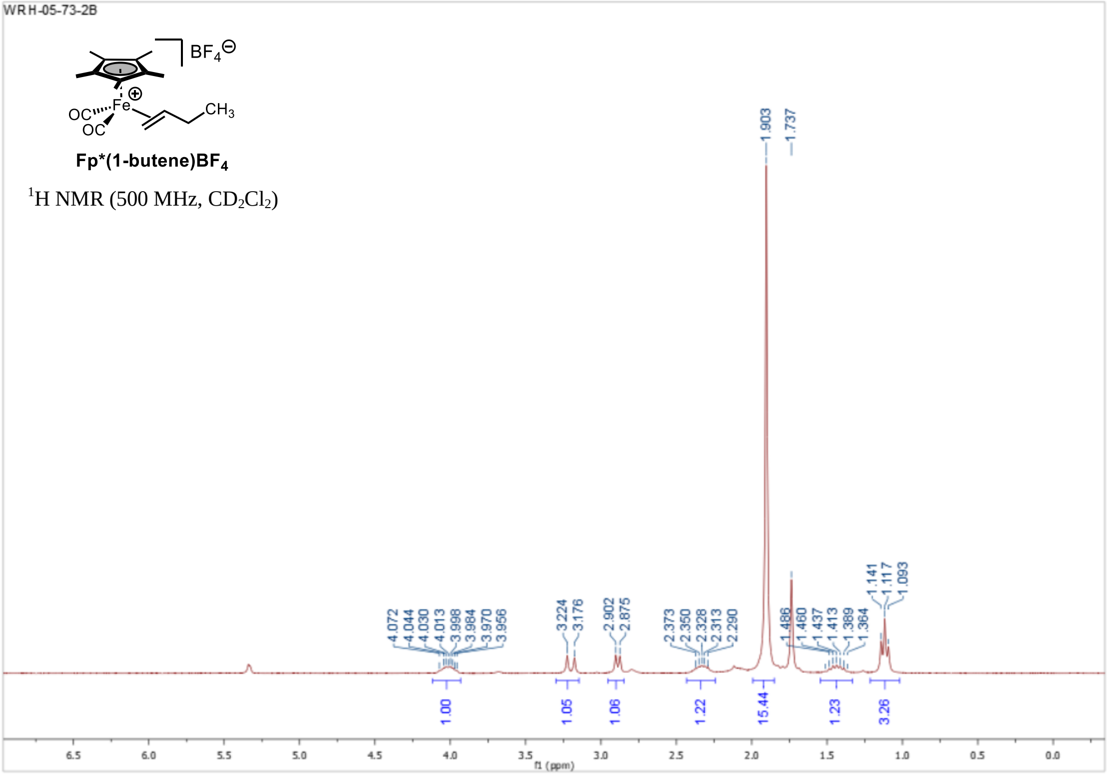

WRH-05-125D
BF4⊖
⊕
Fe
OC
OC
CH3
Fp*(propene)BF4
1H NMR (500 MHz, CD2Cl2)
1.918
1.762
1.752
4.099
4.087
4.075
4.071
4.059
4.046
4.043
4.030
4.018
3.243
3.214
2.956
2.940
1.00
1.04
1.05
0.23
15.39
5.51
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

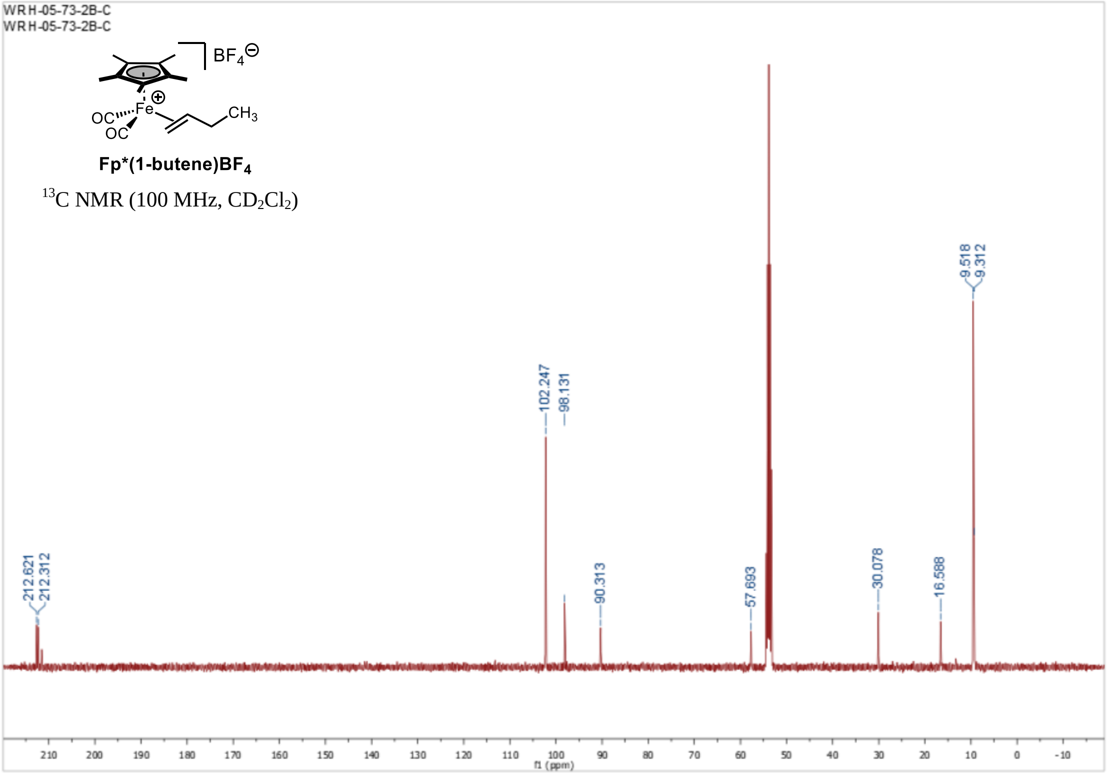

WRH-05-125D-C
WRH-05-125D-C
BF4⊖
⊕
Fe
OC
OC
CH3
Fp*(propene)BF4
13C NMR (100 MHz, CD2Cl2)
212.590
212.169
102.000
98.076
84.356
59.454
21.954
9.465
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

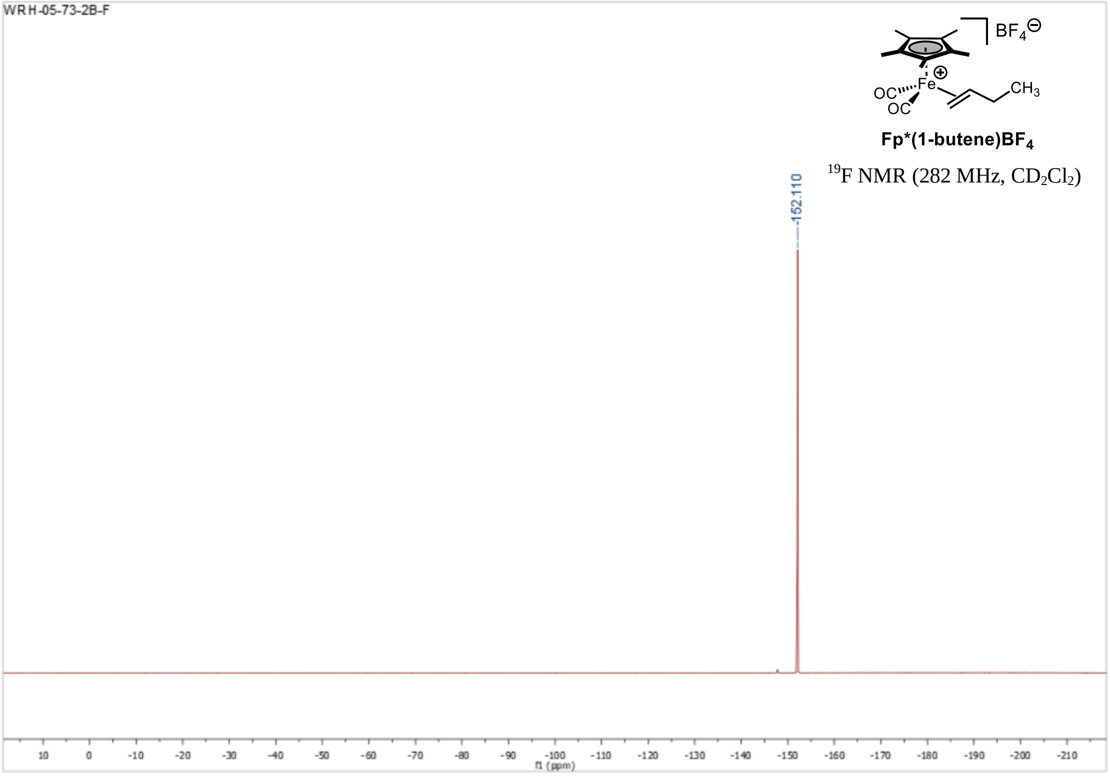


Fp*(propene)BF$_4$

^{19}F NMR (470 MHz, CD$_2$Cl$_2$)

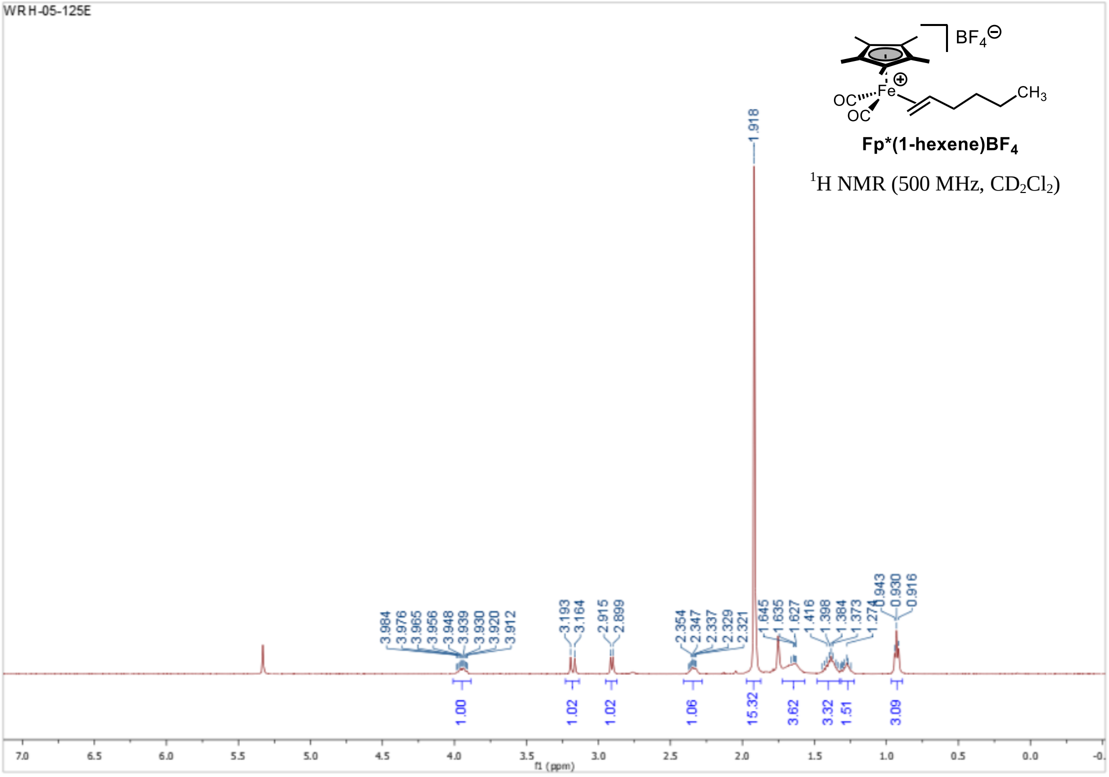

WRH-05-73-2B
BF$_4^⊖$
⊕
Fe
OC
OC
CH$_3$
Fp*(1-butene)BF$_4$
^{1}H NMR (500 MHz, CD$_2$Cl$_2$)
1.903
1.737
4.072
4.044
4.030
4.013
3.998
3.984
3.970
3.956
3.224
3.176
2.902
2.875
2.373
2.350
2.328
2.313
2.290
1.486
1.460
1.437
1.413
1.389
1.364
1.141
1.117
1.093
1.00
1.05
1.06
1.22
15.44
1.23
3.26
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

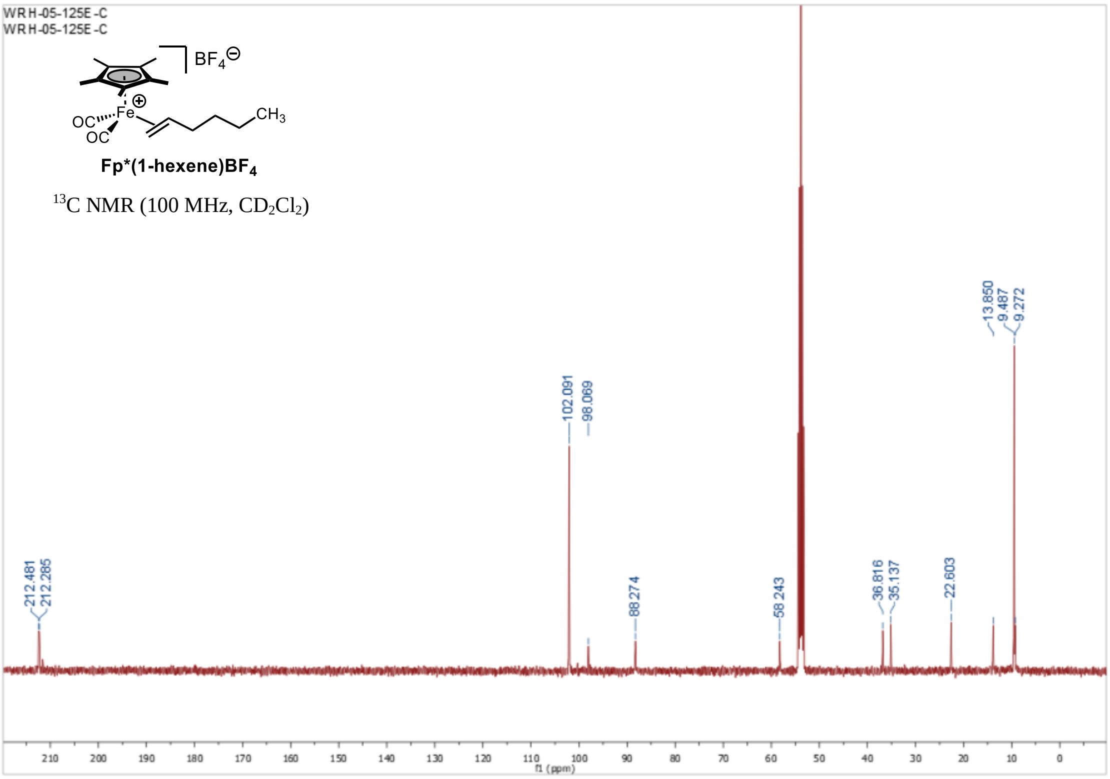

WRH-05-73-2B-C
WRH-05-73-2B-C
BF$_4^⊖$
⊕
Fe
OC
OC
CH$_3$
Fp*(1-butene)BF$_4$
^{13}C NMR (100 MHz, CD$_2$Cl$_2$)
212.621
212.312
102.247
98.131
90.313
57.693
30.078
16.588
9.518
9.312
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

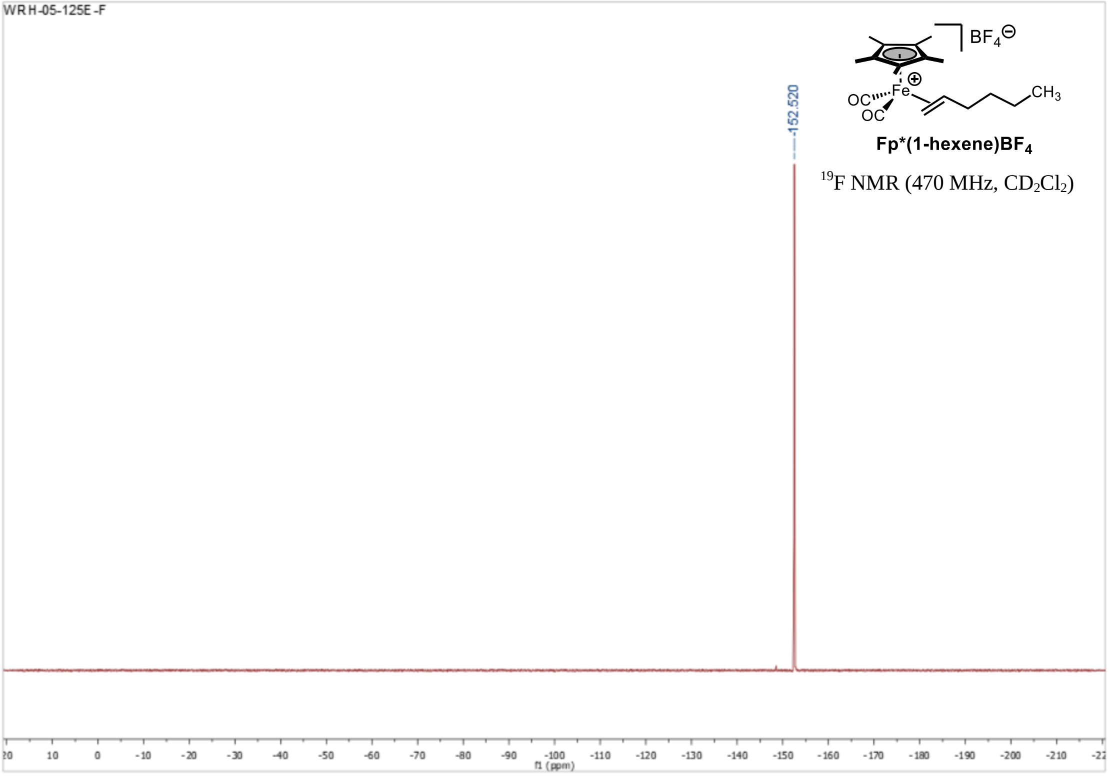


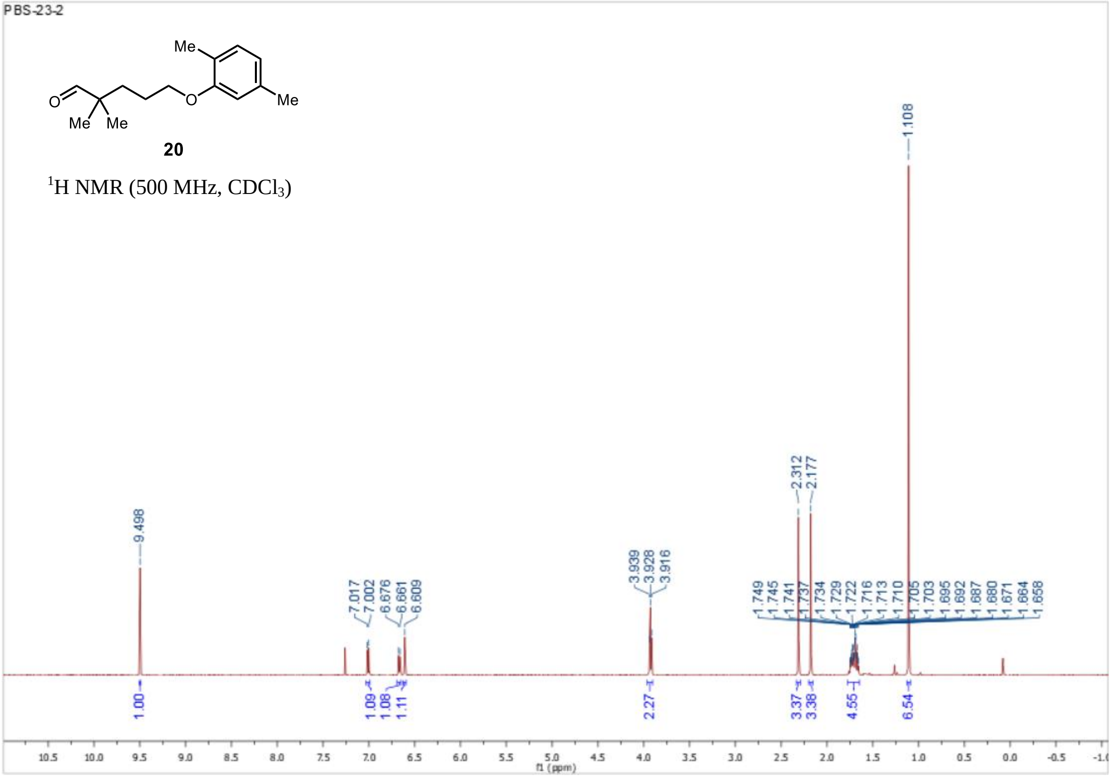
Fp*(1-butene)BF$_4$

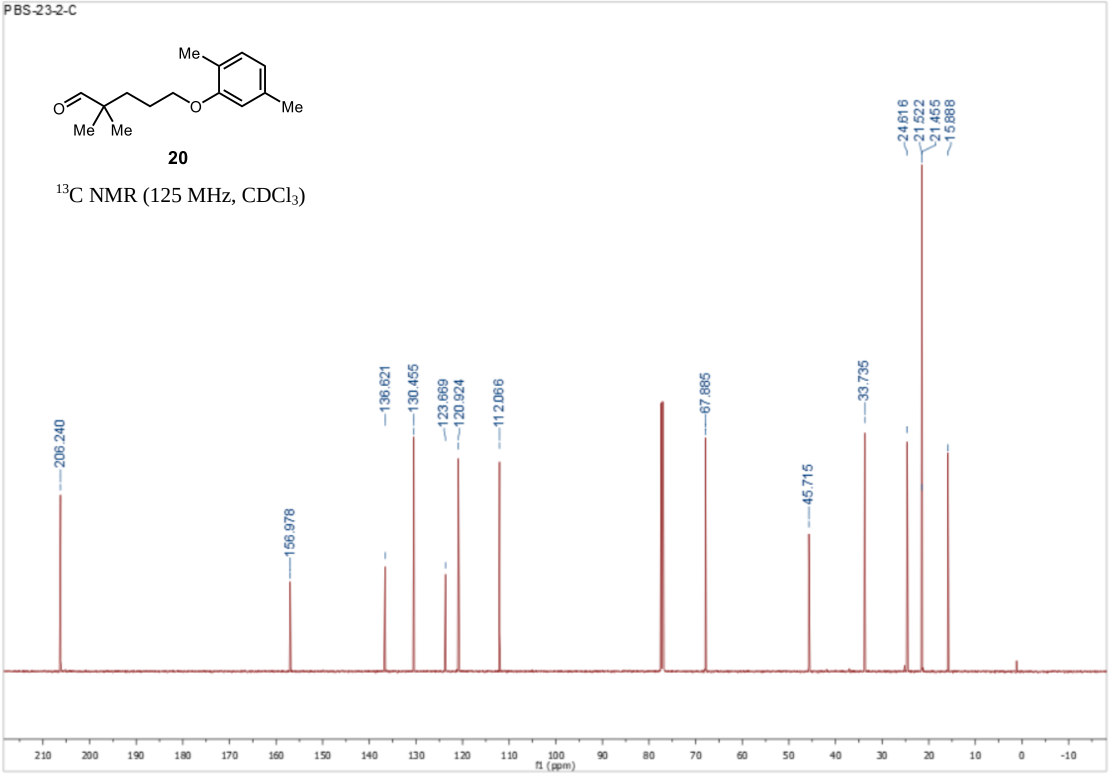
^{19}F NMR (282 MHz, CD$_2$Cl$_2$)

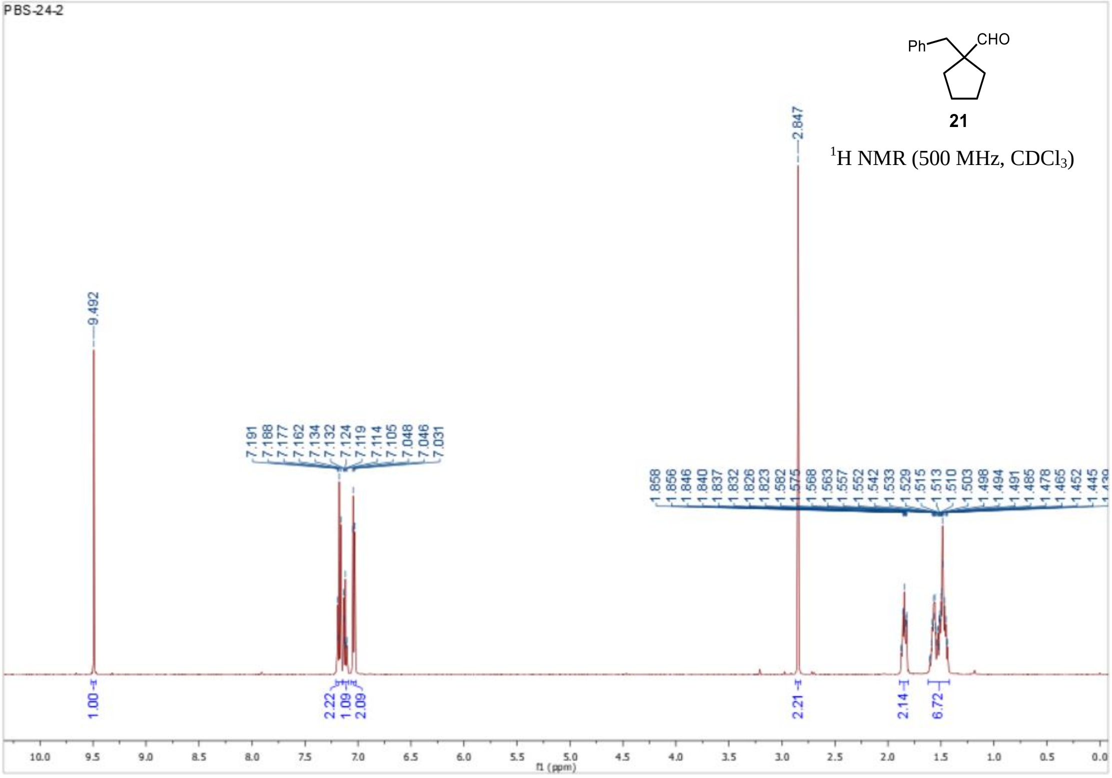

WRH-05-125E
BF4⊖
⊕
Fe
OC
OC
CH3
Fp*(1-hexene)BF4
1H NMR (500 MHz, CD2Cl2)
1.918
3.984
3.976
3.965
3.956
3.948
3.939
3.930
3.920
3.912
3.193
3.164
2.915
2.899
2.354
2.347
2.337
2.329
2.321
1.645
1.635
1.627
1.416
1.398
1.384
1.373
1.274
0.943
0.930
0.916
1.00
1.02
1.02
1.06
15.32
3.62
3.32
1.51
3.09
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

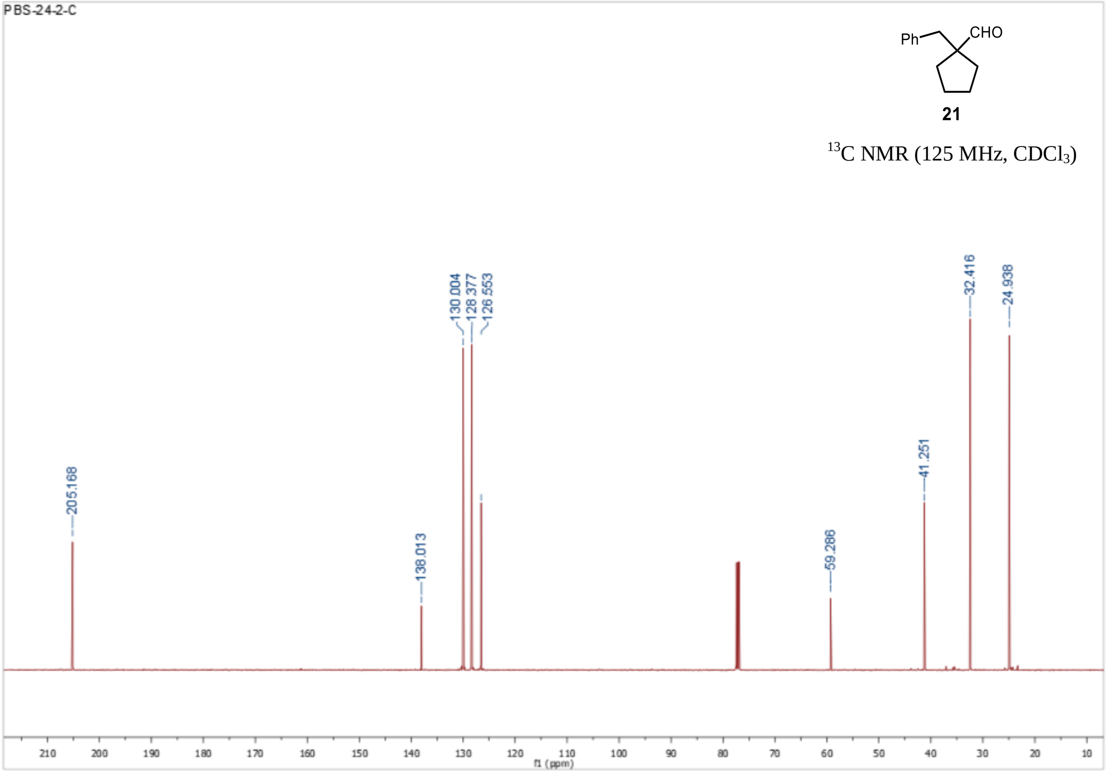

WRH-05-125E-C
WRH-05-125E-C
BF4⊖
⊕
Fe
OC
OC
CH3
Fp*(1-hexene)BF4
13C NMR (100 MHz, CD2Cl2)
212.481
212.285
102.091
98.069
88.274
58.243
36.816
35.137
22.603
13.850
9.487
9.272
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

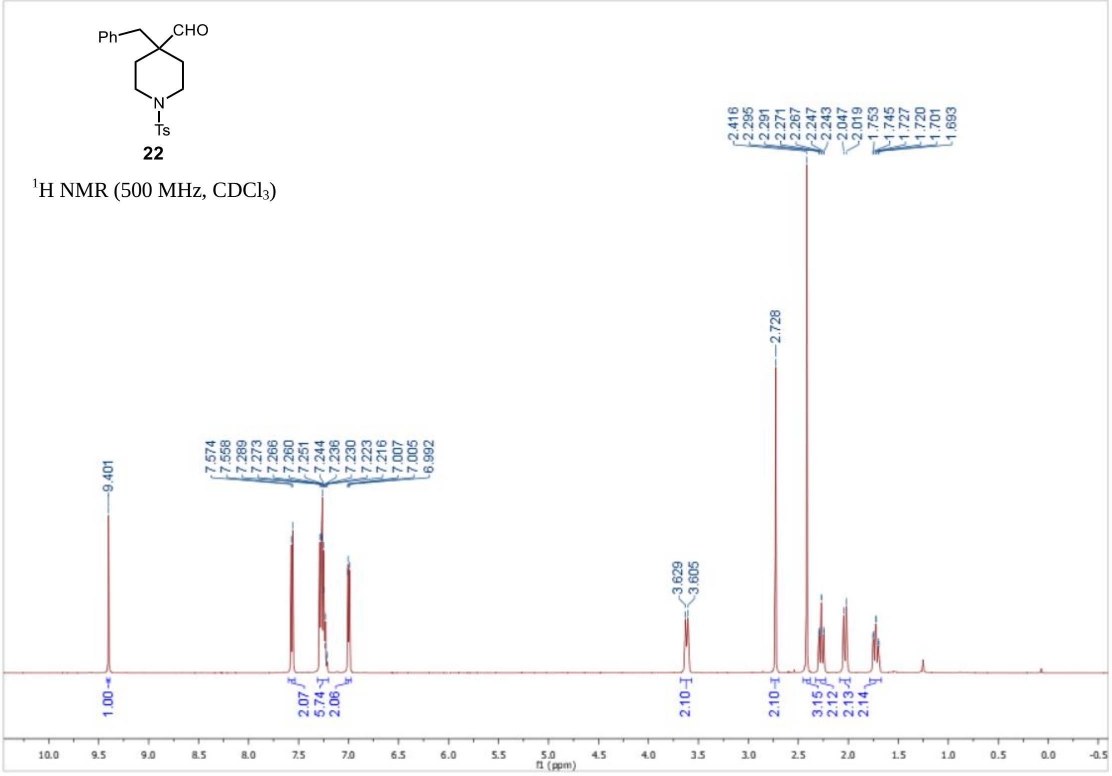

WRH-05-125E-F
BF4⊖
⊕
Fe
OC
OC
CH3
Fp*(1-hexene)BF4
19F NMR (470 MHz, CD2Cl2)
-152.520
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-22
f1 (ppm)


PBS-23-2
Me
Me
O
O
Me Me
20
1H NMR (500 MHz, CDCl3)
9.498
7.017
7.002
6.676
6.661
6.609
3.939
3.928
3.916
2.312
2.177
1.749
1.745
1.741
1.737
1.734
1.729
1.722
1.716
1.713
1.710
1.705
1.703
1.695
1.692
1.687
1.680
1.671
1.664
1.658
1.108
1.00
1.09
1.08
1.11
2.27
3.37
3.38
4.55
6.54
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


PBS-23-2-C
Me
Me
O
O
Me Me
20
13C NMR (125 MHz, CDCl3)
206.240
156.978
136.621
130.455
123.669
120.924
112.066
67.885
45.715
33.735
24.616
21.522
21.455
15.888
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

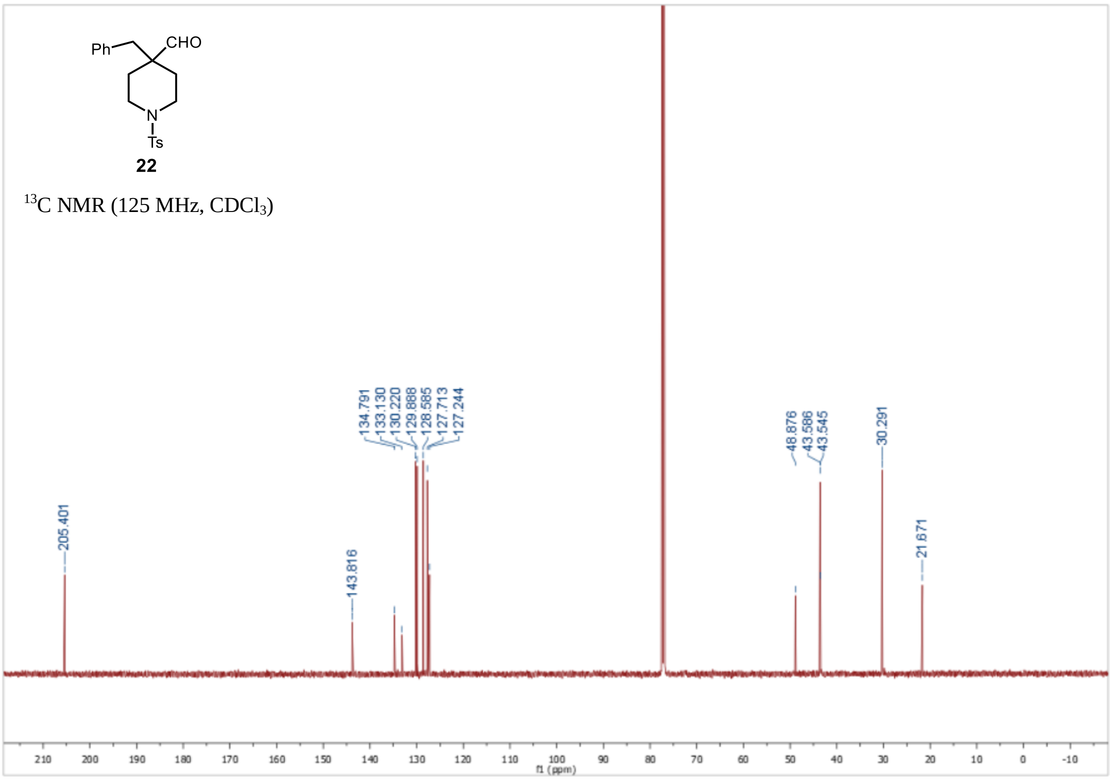

PBS-24-2
Ph
CHO
21
^{1}H NMR (500 MHz, CDCl$_3$)
9.492
7.191
7.188
7.177
7.162
7.134
7.132
7.124
7.119
7.114
7.105
7.048
7.046
7.031
2.847
1.858
1.856
1.846
1.840
1.837
1.832
1.826
1.823
1.582
1.575
1.568
1.563
1.557
1.552
1.542
1.533
1.529
1.515
1.513
1.510
1.503
1.498
1.494
1.491
1.485
1.478
1.465
1.452
1.445
1.00
2.22
1.09
2.09
2.21
2.14
6.72
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


PBS-24-2-C
Ph
CHO
21
^{13}C NMR (125 MHz, CDCl$_3$)
205.168
138.013
130.004
128.377
126.553
59.286
41.251
32.416
24.938
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



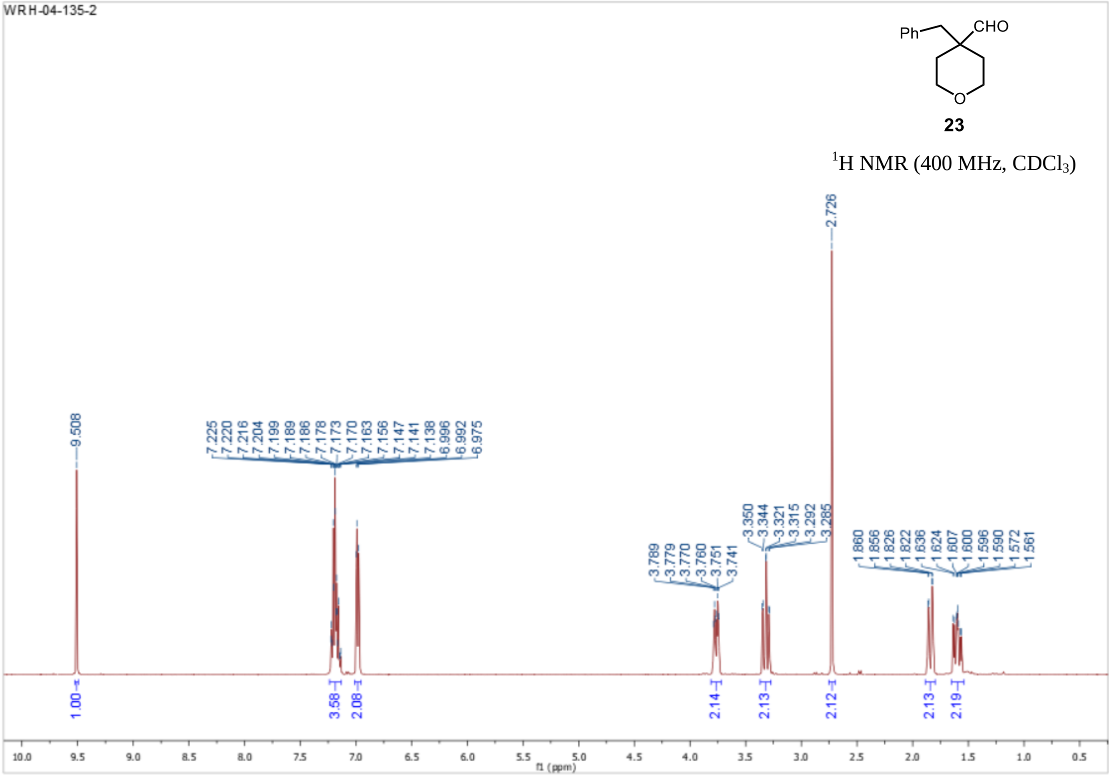
22

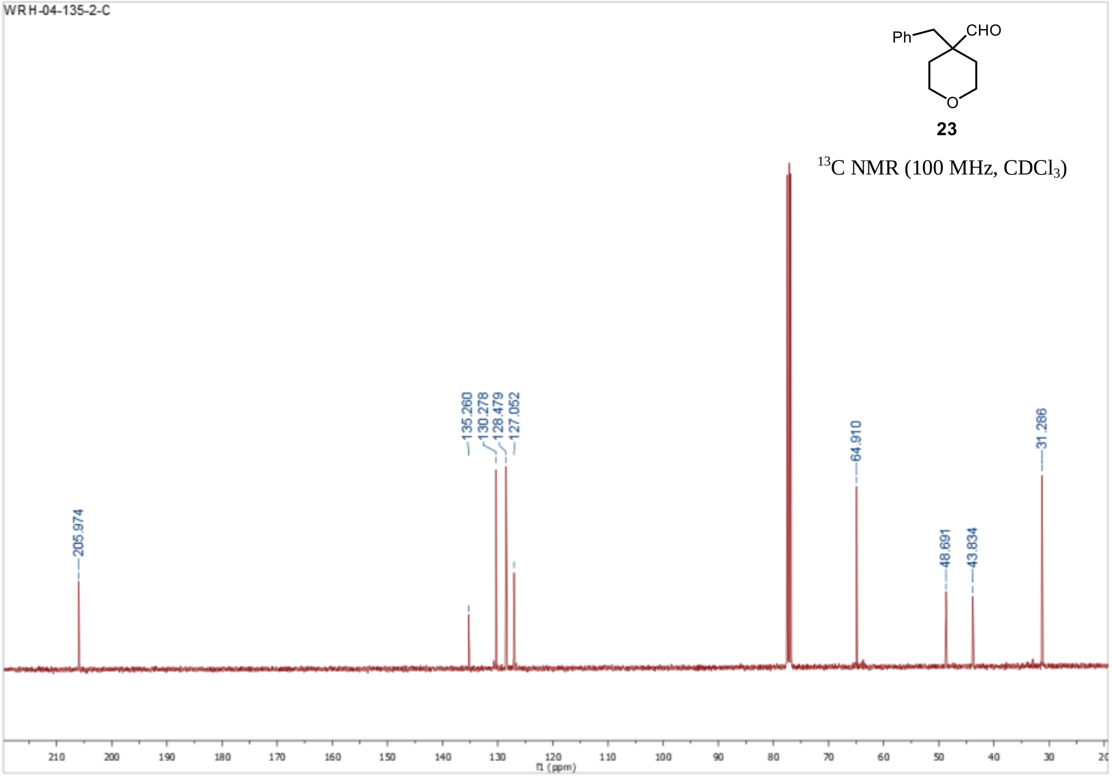
^{1}H NMR (500 MHz, CDCl$_3$)

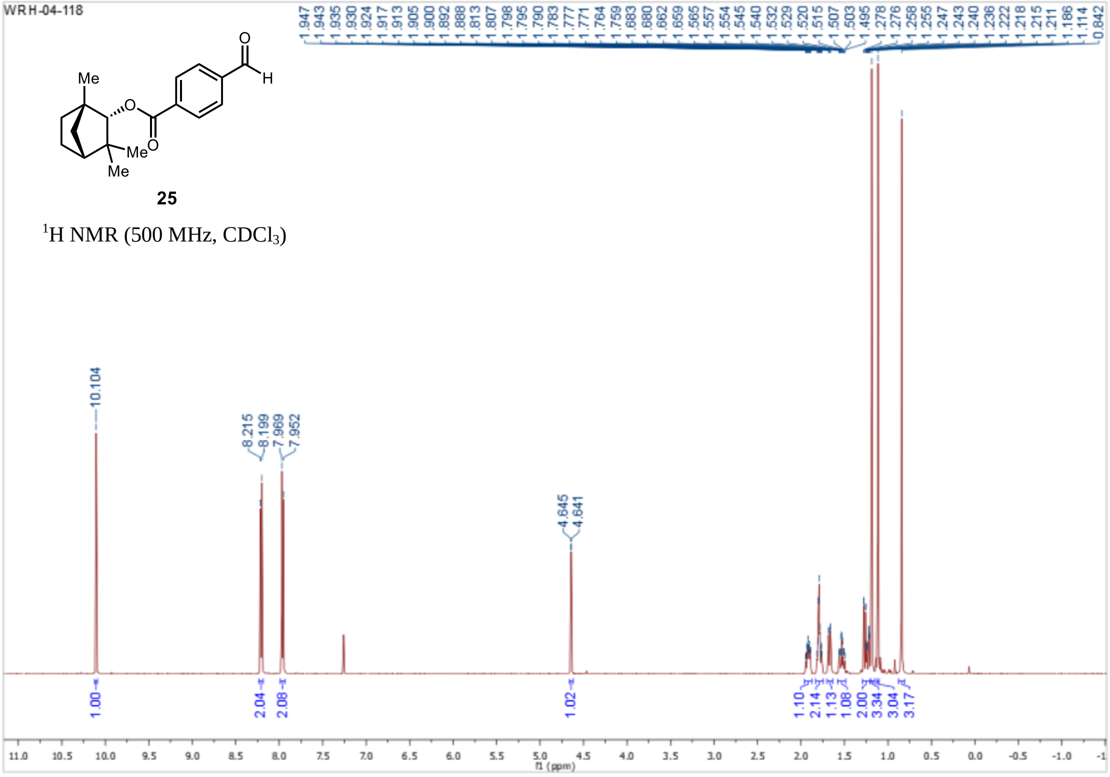


22

^{13}C NMR (125 MHz, CDCl$_3$)

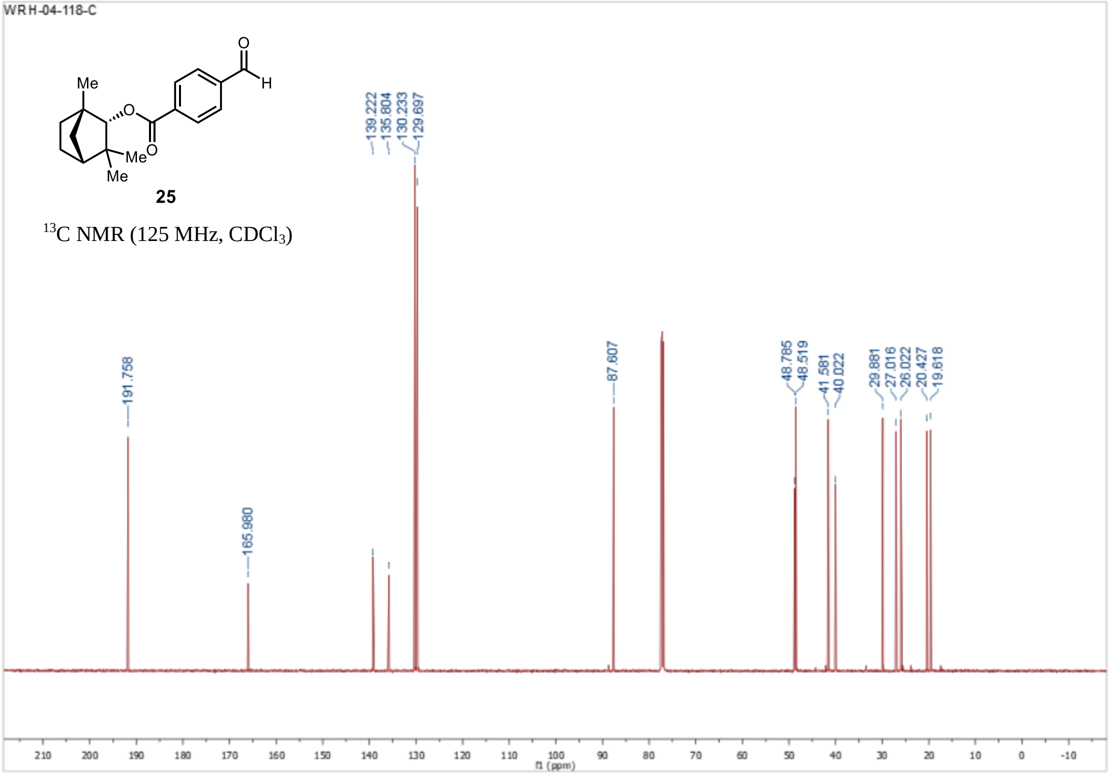

WRH-04-135-2
Ph
CHO
O
23
^{1}H NMR (400 MHz, CDCl$_3$)
9.508
7.225
7.220
7.216
7.204
7.199
7.189
7.186
7.178
7.173
7.170
7.163
7.156
7.147
7.141
7.138
6.996
6.992
6.975
3.789
3.779
3.770
3.760
3.751
3.741
3.350
3.344
3.321
3.315
3.292
3.285
2.726
1.860
1.856
1.826
1.822
1.636
1.624
1.607
1.600
1.596
1.590
1.572
1.561
1.00
3.58
2.08
2.14
2.13
2.12
2.13
2.19
f1 (ppm)


WRH-04-135-2-C
Ph
CHO
O
23
^{13}C NMR (100 MHz, CDCl$_3$)
205.974
135.260
130.278
128.479
127.052
64.910
48.691
43.834
31.286
f1 (ppm)



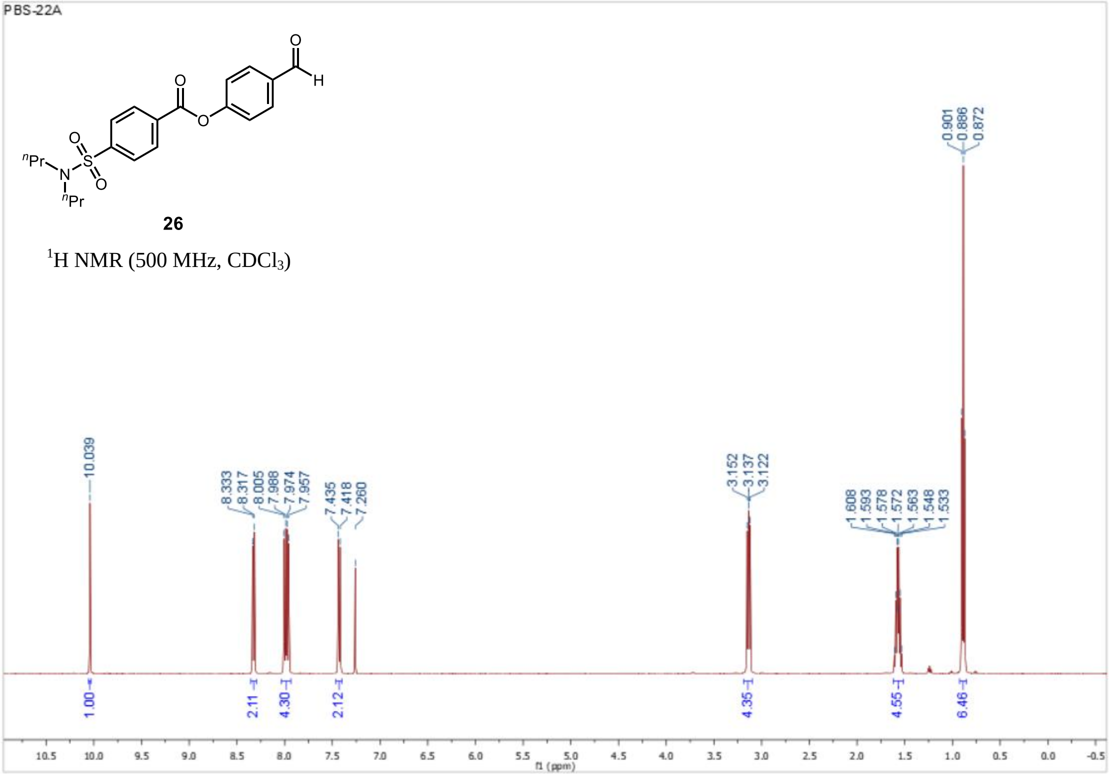
25

^{1}H NMR (500 MHz, CDCl$_3$)



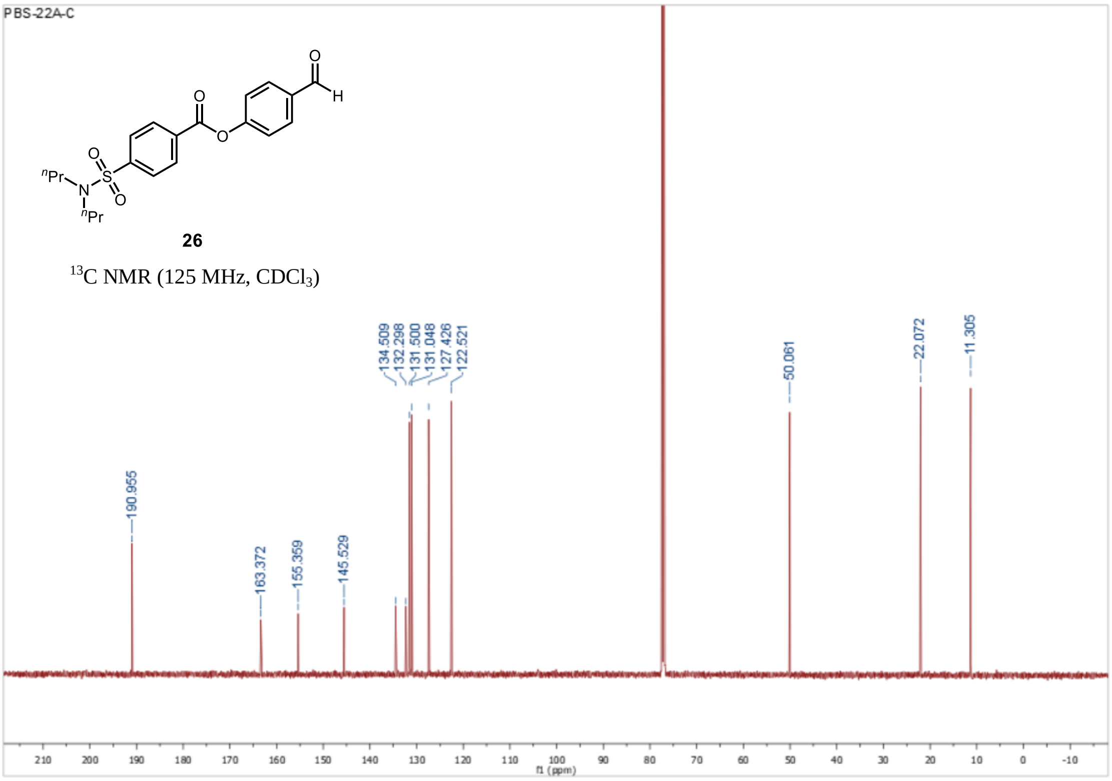
25

^{13}C NMR (125 MHz, CDCl$_3$)



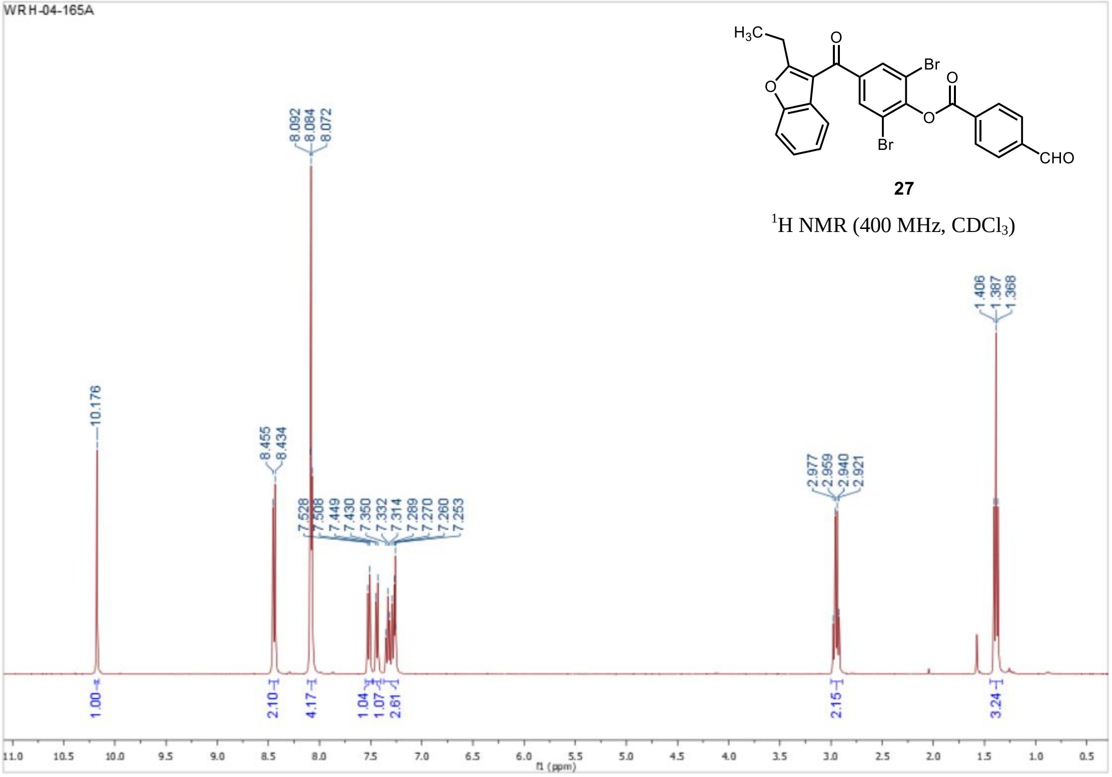
26

^{1}H NMR (500 MHz, CDCl$_3$)



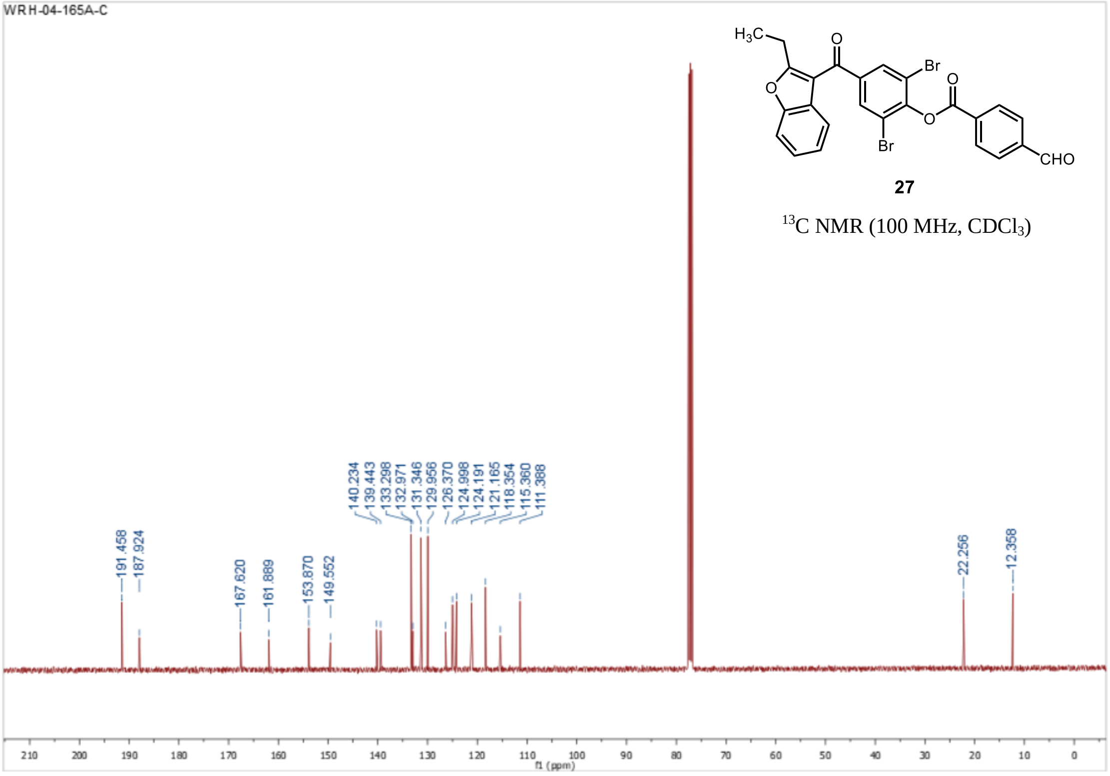
26

^{13}C NMR (125 MHz, CDCl$_3$)



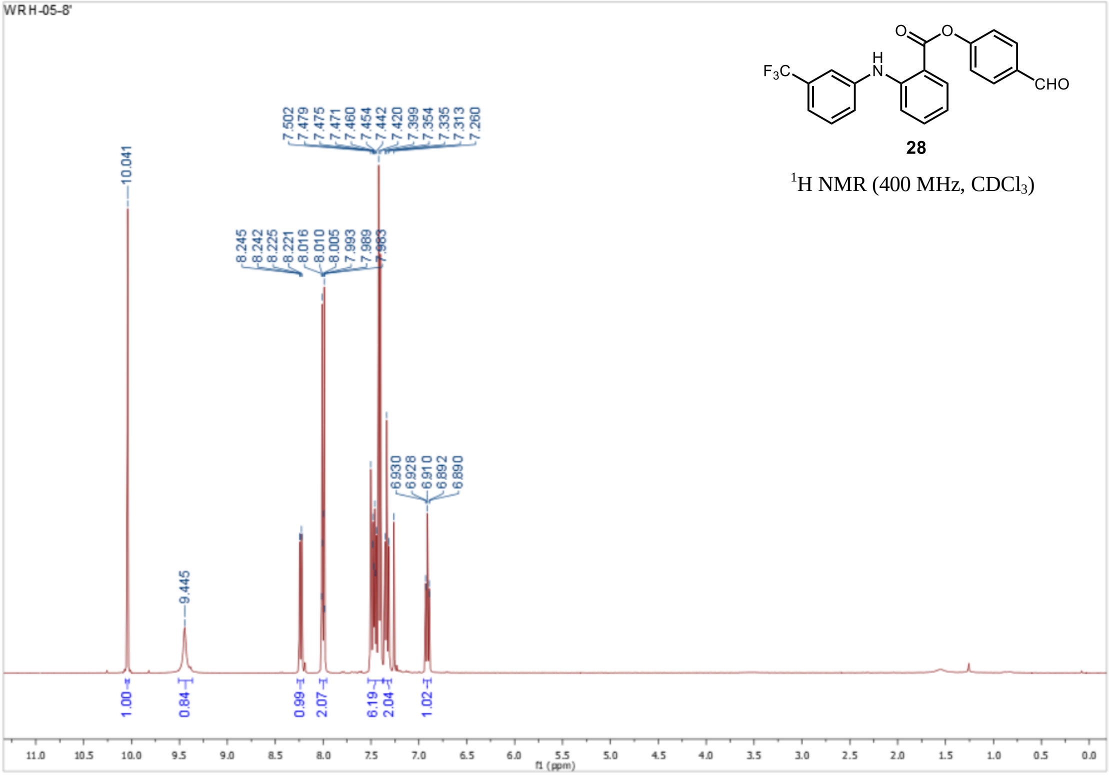
27

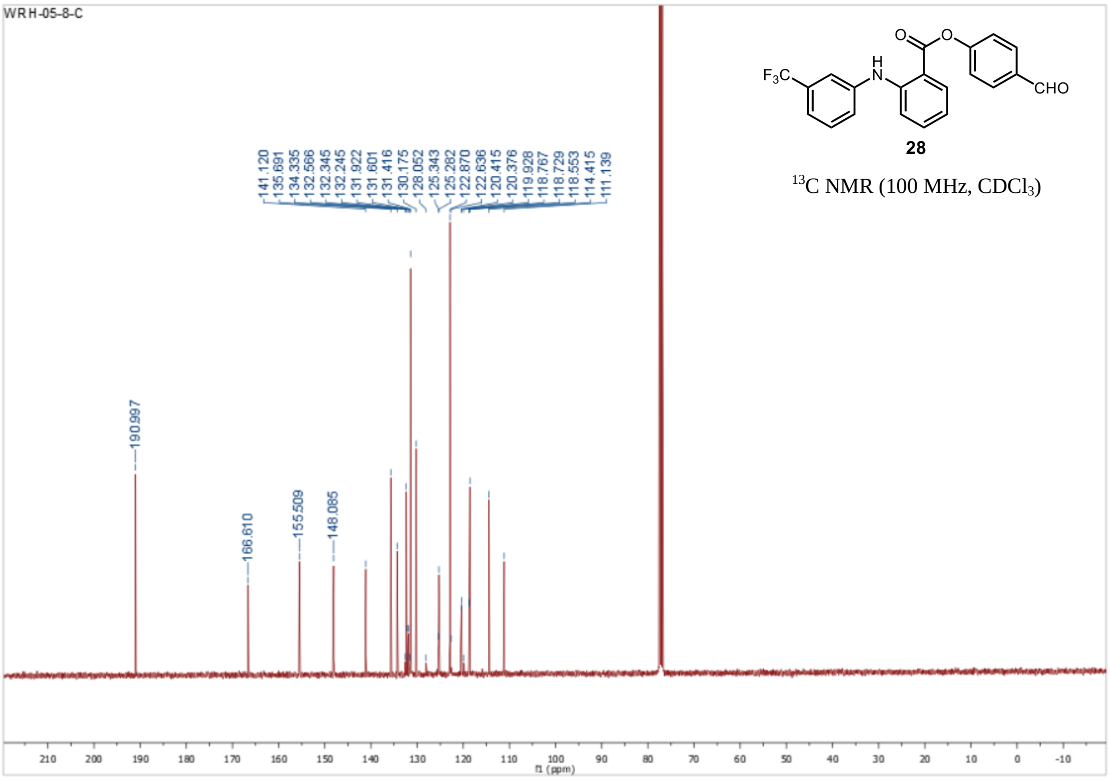
^{1}H NMR (400 MHz, CDCl$_3$)

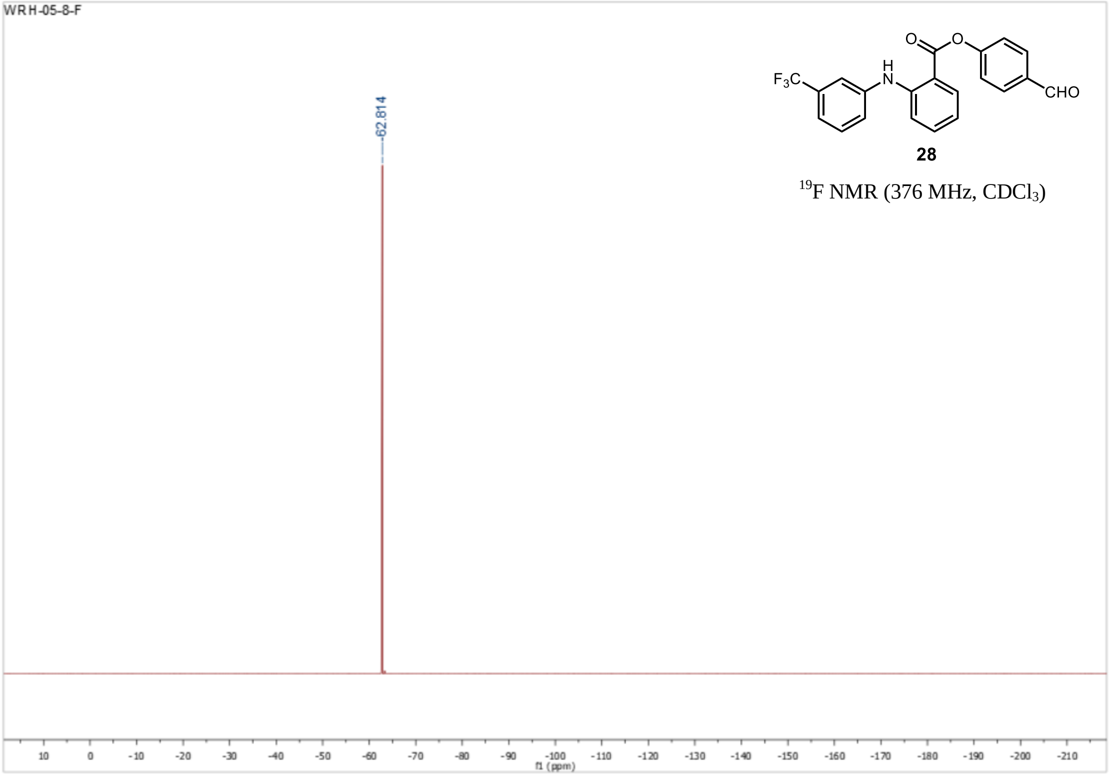


27

^{13}C NMR (100 MHz, CDCl$_3$)

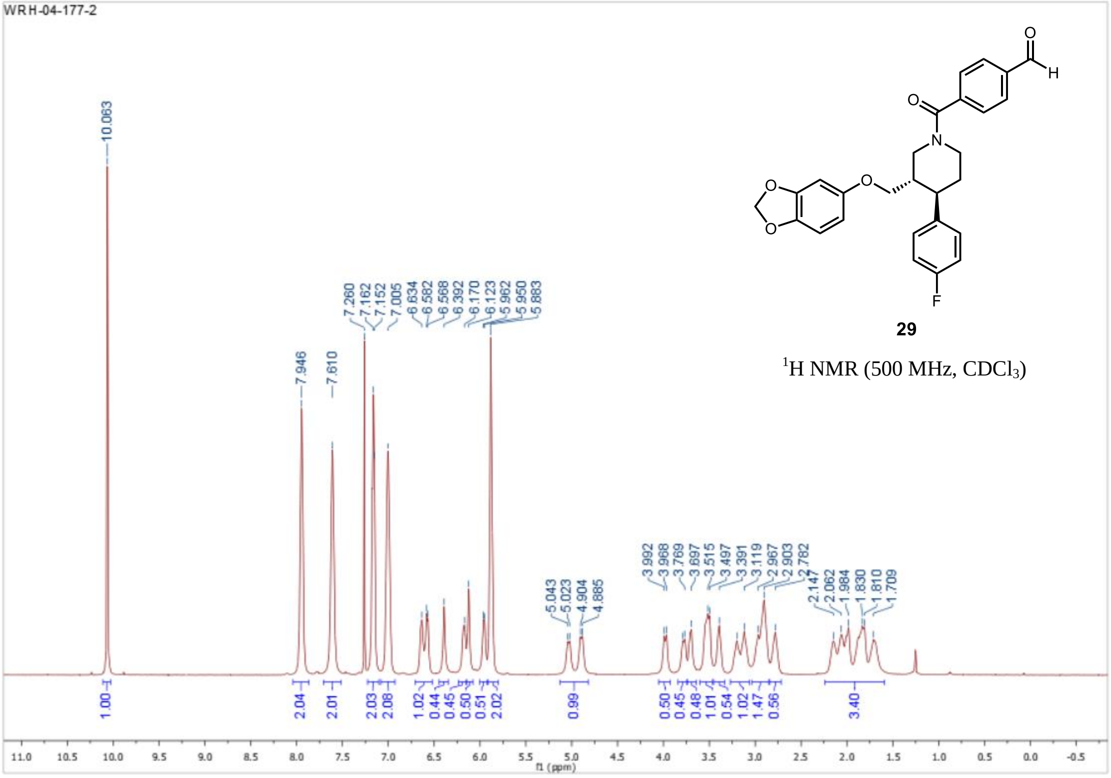

WRH-05-8'
F3C
H
N
O
O
CHO
28
1H NMR (400 MHz, CDCl3)
10.041
9.445
8.245
8.242
8.225
8.221
8.016
8.010
8.005
7.993
7.989
7.983
7.502
7.479
7.475
7.471
7.460
7.454
7.442
7.420
7.399
7.354
7.335
7.313
7.260
6.930
6.928
6.910
6.892
6.890
1.00
0.84
0.99
2.07
6.19
2.04
1.02
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


WRH-05-8-C
F3C
H
N
O
O
CHO
28
13C NMR (100 MHz, CDCl3)
190.997
166.610
155.509
148.085
141.120
135.691
134.335
132.566
132.345
132.245
131.922
131.601
131.416
130.175
128.052
125.343
125.282
122.870
122.636
120.415
120.376
119.928
118.767
118.729
118.553
114.415
111.139
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



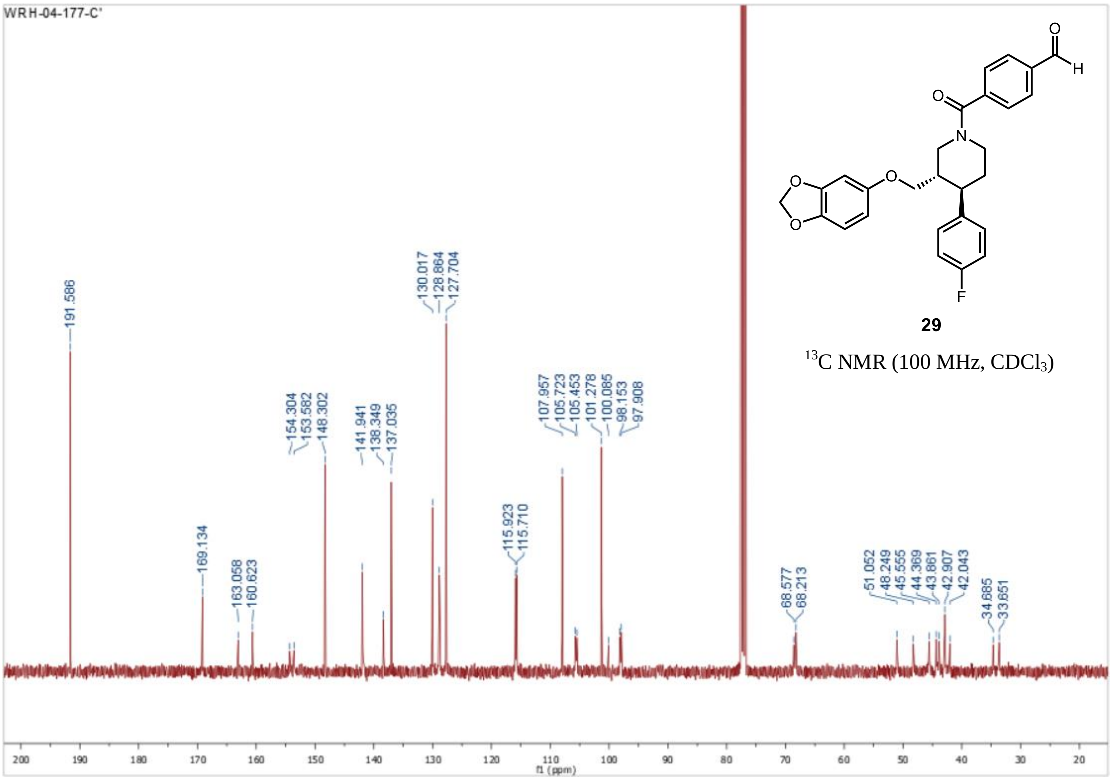
28

^{19}F NMR (376 MHz, $CDCl_3$)



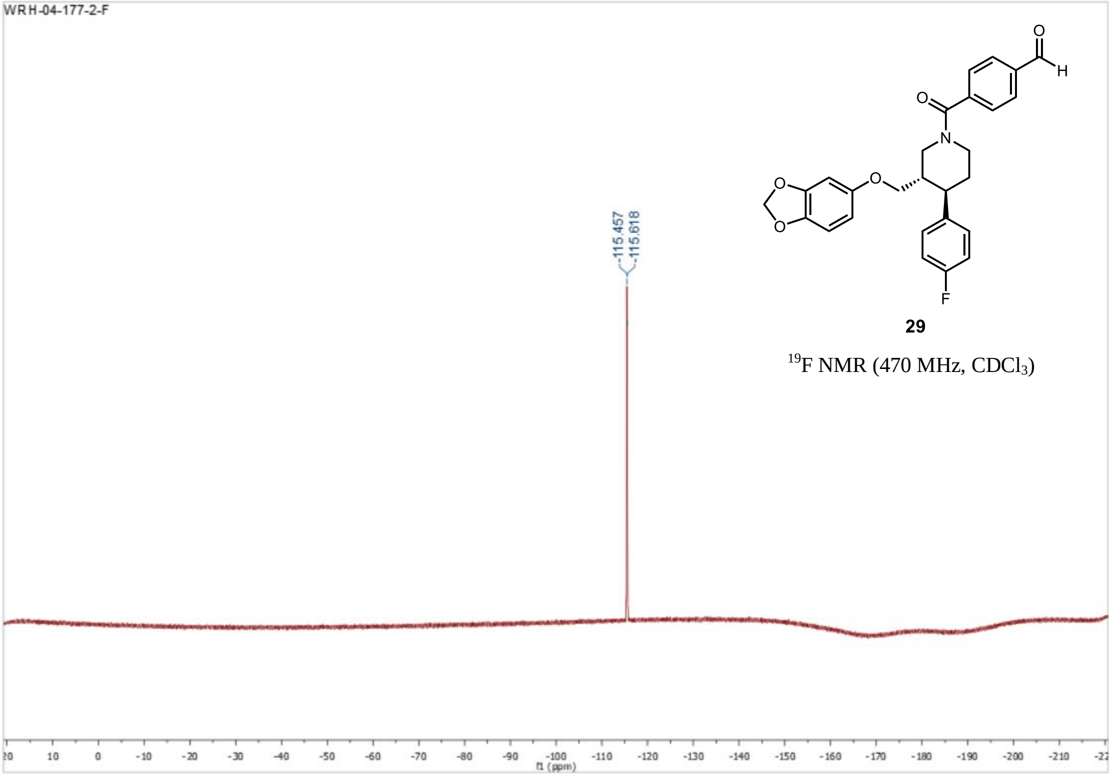
29

^{1}H NMR (500 MHz, CDCl$_3$)



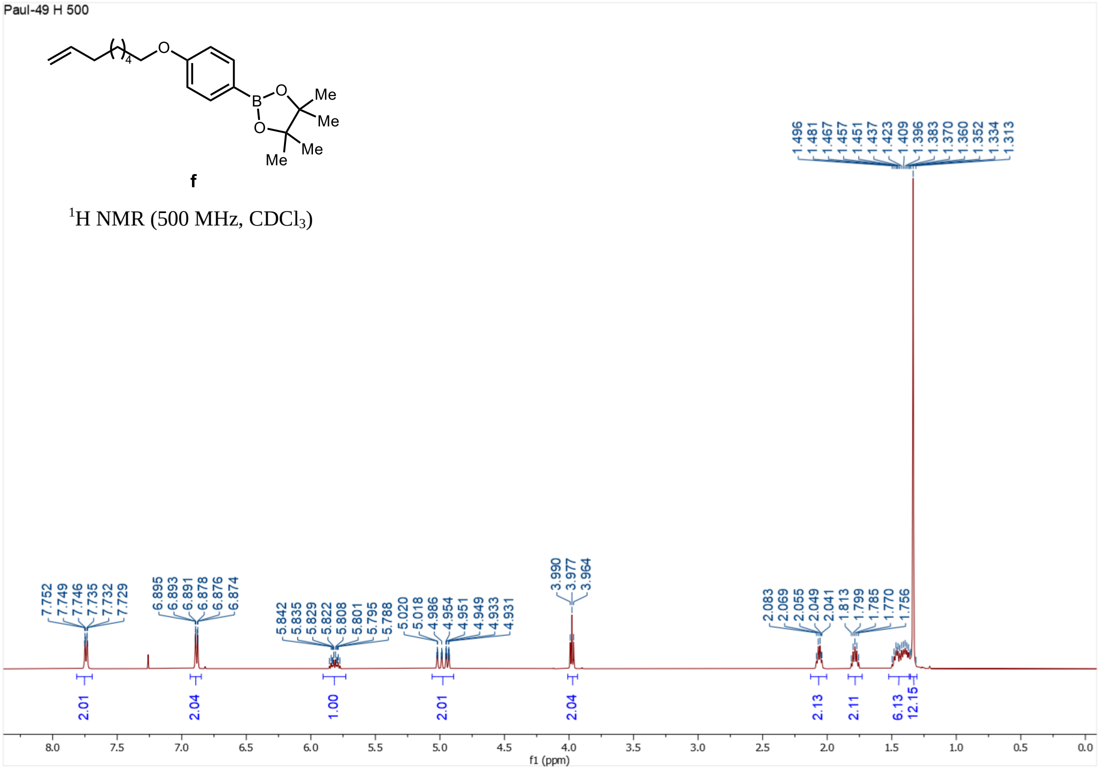
29

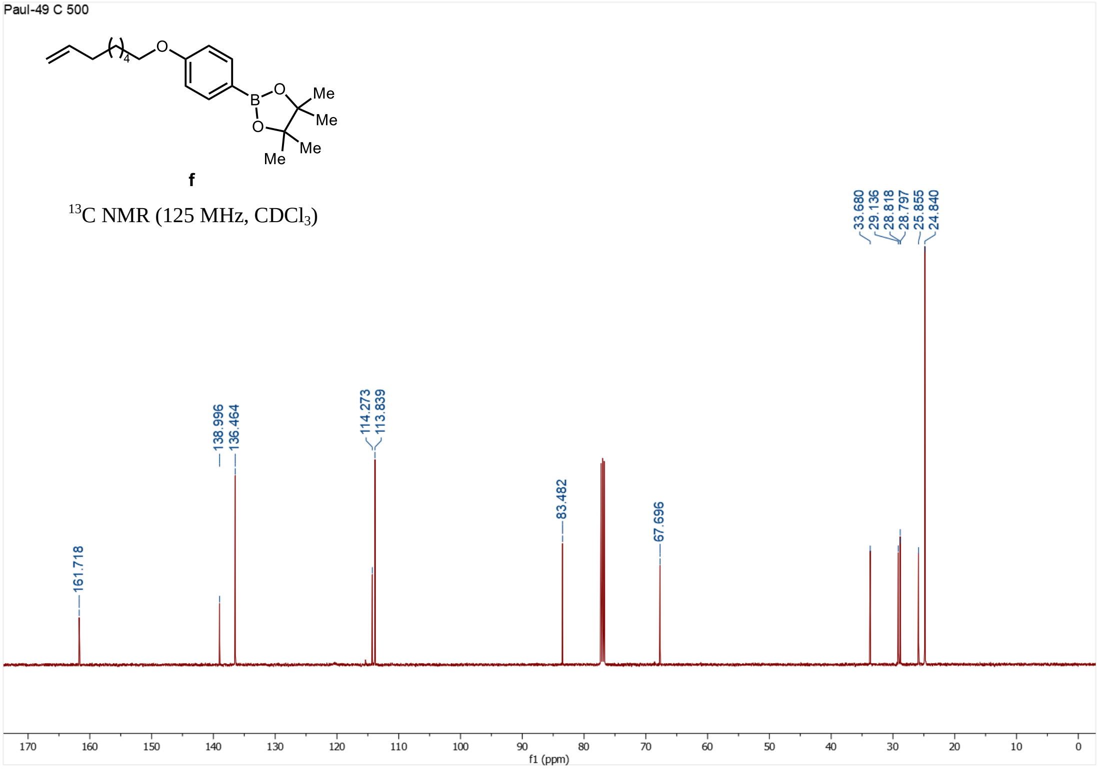
^{13}C NMR (100 MHz, CDCl$_3$)

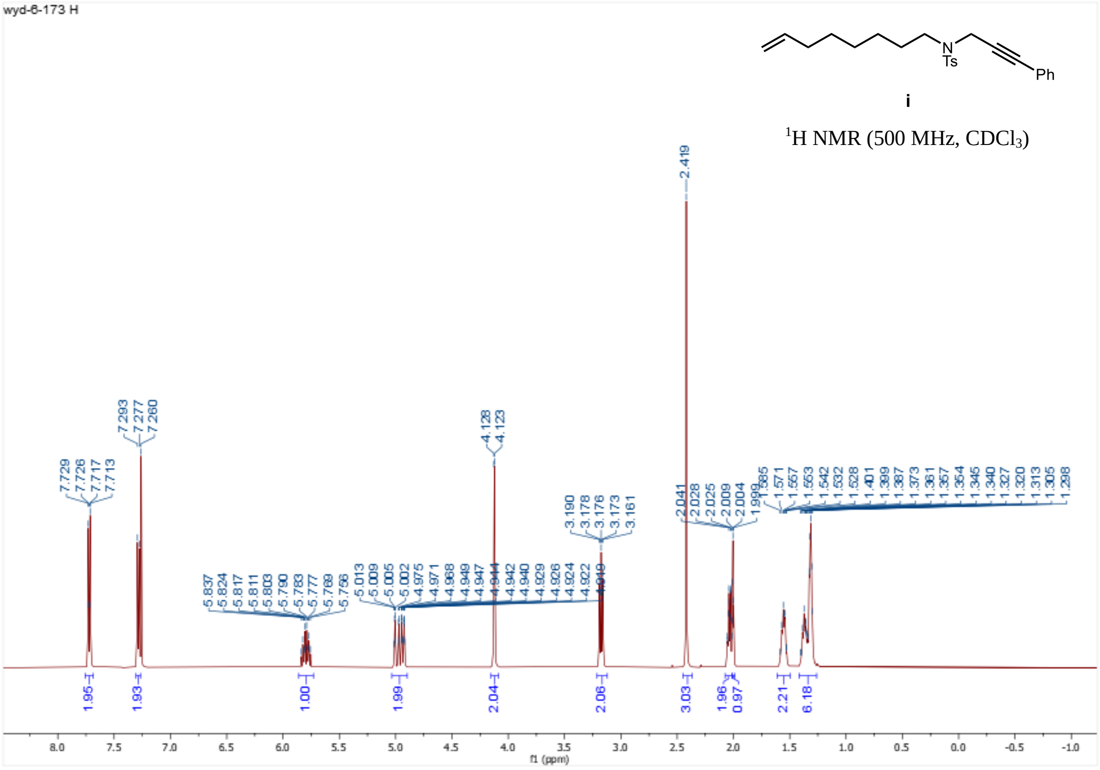


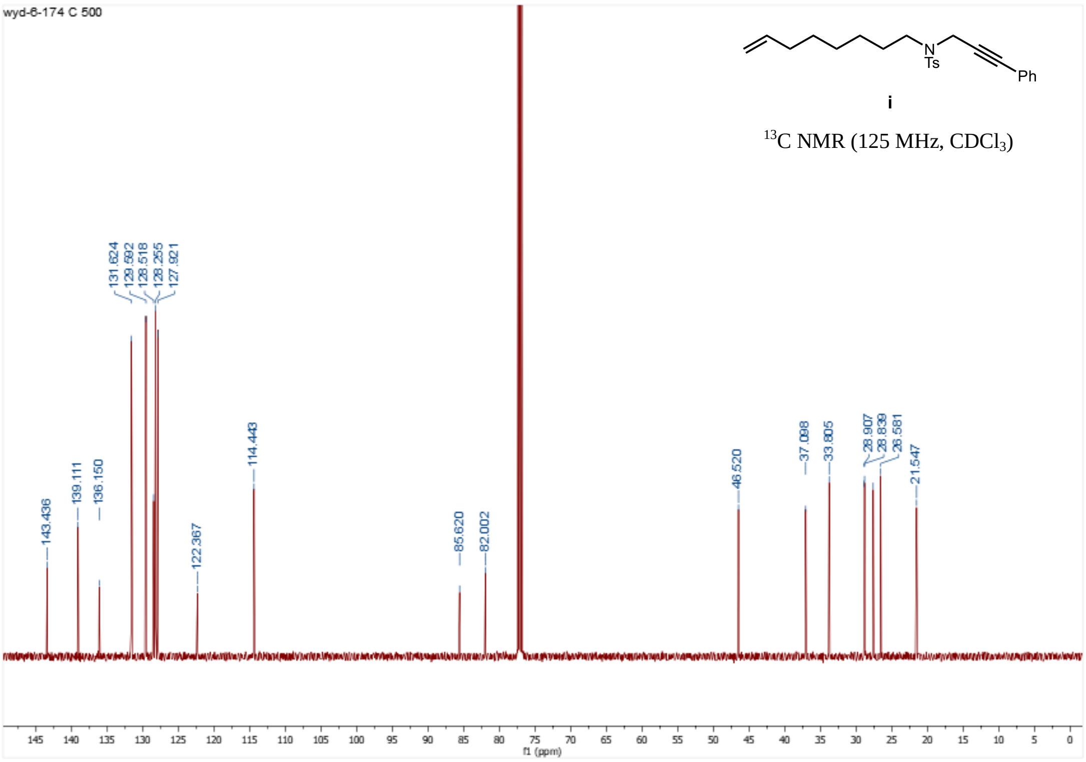
29

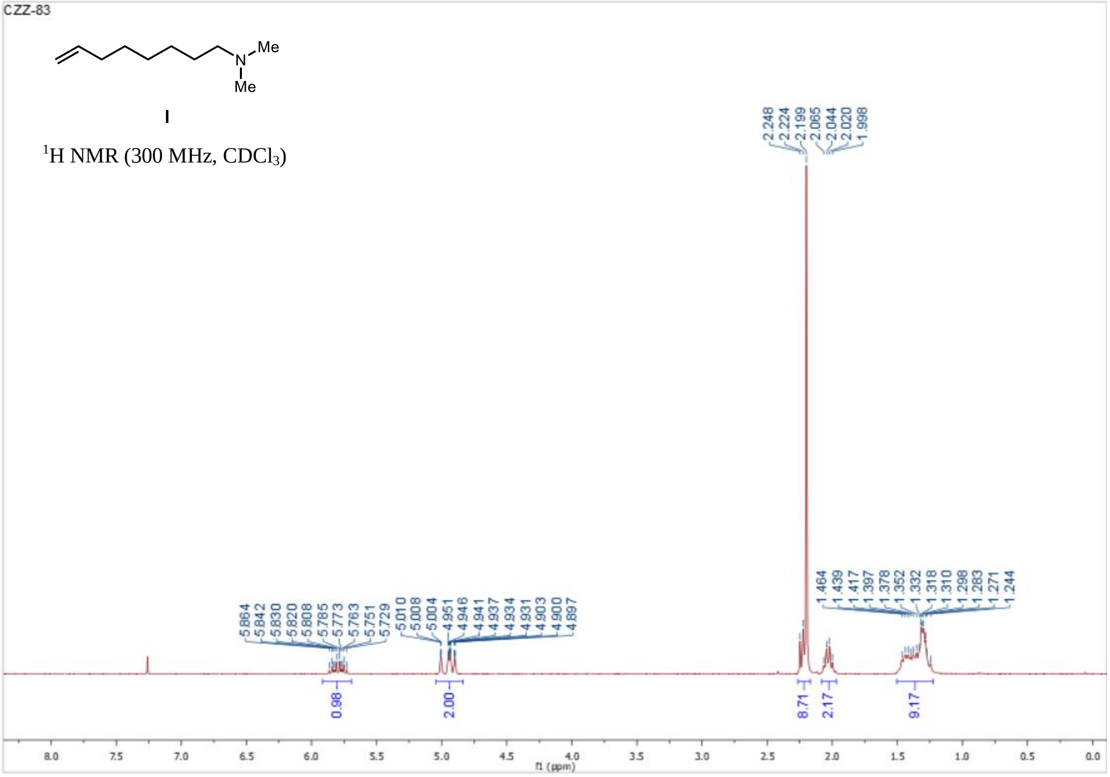
^{19}F NMR (470 MHz, CDCl$_3$)


Paul-49 H 500
O
B
O
O
Me
Me
Me
Me
4
f
^{1}H NMR (500 MHz, CDCl$_3$)
7.752
7.749
7.746
7.735
7.732
7.729
6.895
6.893
6.891
6.878
6.876
6.874
5.842
5.835
5.829
5.822
5.808
5.801
5.795
5.788
5.020
5.018
4.986
4.954
4.951
4.949
4.933
4.931
3.990
3.977
3.964
2.083
2.069
2.055
2.049
2.041
1.813
1.799
1.785
1.770
1.756
1.496
1.481
1.467
1.457
1.451
1.437
1.423
1.409
1.396
1.383
1.370
1.360
1.352
1.334
1.313
2.01
2.04
1.00
2.01
2.04
2.13
2.11
6.13
12.15
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Paul-49 C 500
O
B
O
O
Me
Me
Me
Me
4
f
^{13}C NMR (125 MHz, CDCl$_3$)
161.718
138.996
136.464
114.273
113.839
83.482
67.696
33.680
29.136
28.818
28.797
25.855
24.840
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

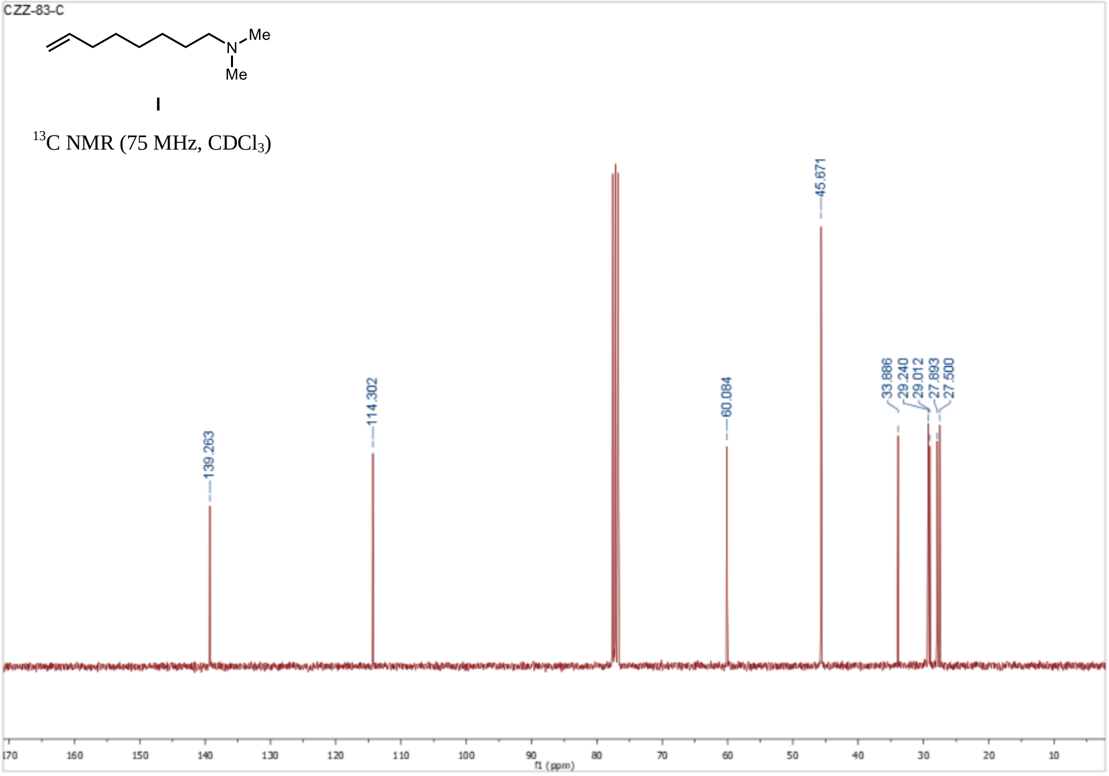

wyd-6-173 H
N
Ts
Ph
i
^{1}H NMR (500 MHz, CDCl$_3$)
7.729 7.726 7.717 7.713
7.293 7.277 7.260
5.837 5.824 5.817 5.811 5.803 5.790 5.783 5.777 5.769 5.756
5.013 5.009 5.005 5.002 4.975 4.971 4.968 4.949 4.947 4.944 4.942 4.940 4.929 4.926 4.924 4.922 4.919
4.128 4.123
3.190 3.178 3.176 3.173 3.161
2.419
2.041 2.028 2.025 2.009 2.004 1.999
1.585 1.571 1.567 1.563 1.542 1.532 1.528 1.401 1.399 1.387 1.373 1.361 1.357 1.354 1.345 1.340 1.327 1.320 1.313 1.305 1.298
1.95 1.93 1.00 1.99 2.04 2.06 3.03 1.96 0.97 2.21 6.18
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


wyd-6-174 C 500
N
Ts
Ph
i
^{13}C NMR (125 MHz, CDCl$_3$)
143.436
139.111
136.150
131.624 129.592 128.518 128.255 127.921
122.367
114.443
85.620
82.002
46.520
37.098
33.805
28.907 28.839 26.581
21.547
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)



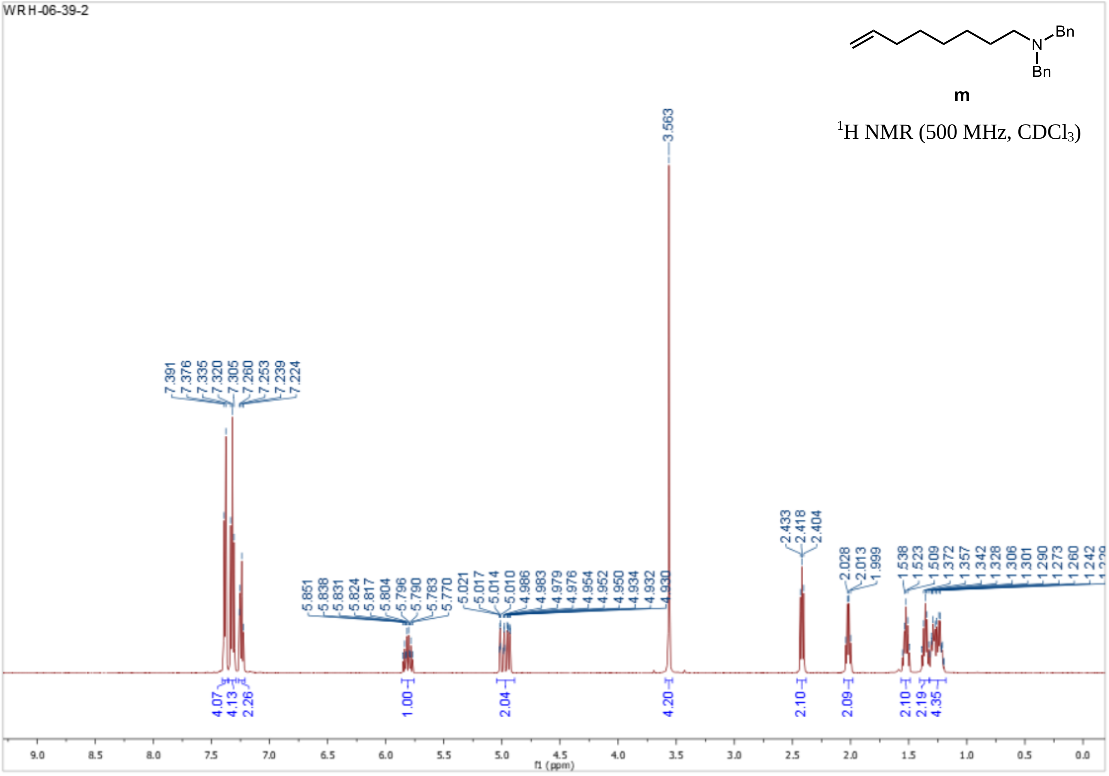
I

^{1}H NMR (300 MHz, CDCl$_3$)



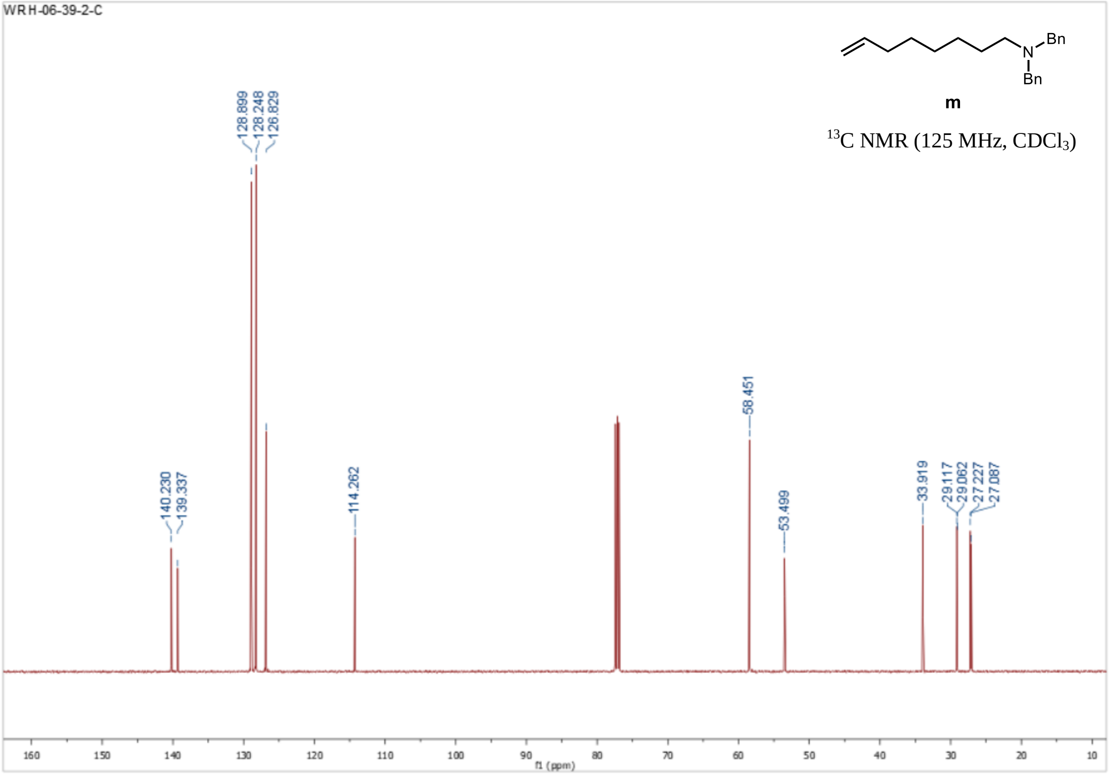
I

^{13}C NMR (75 MHz, CDCl$_3$)



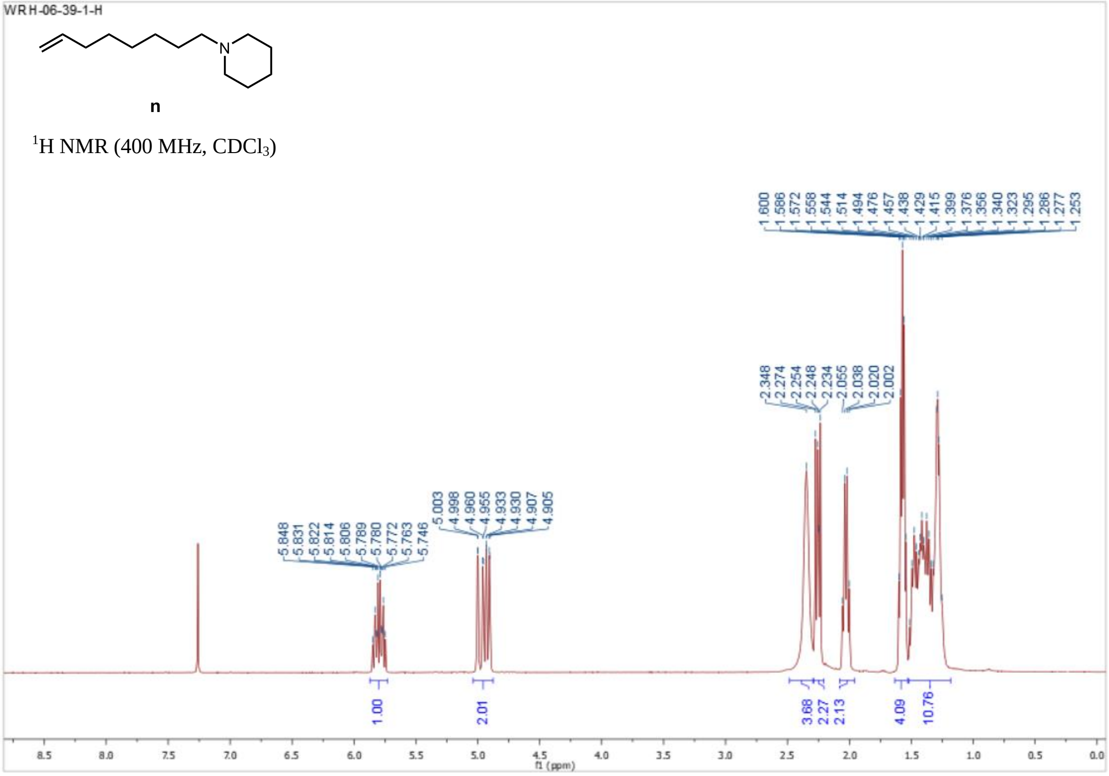
m

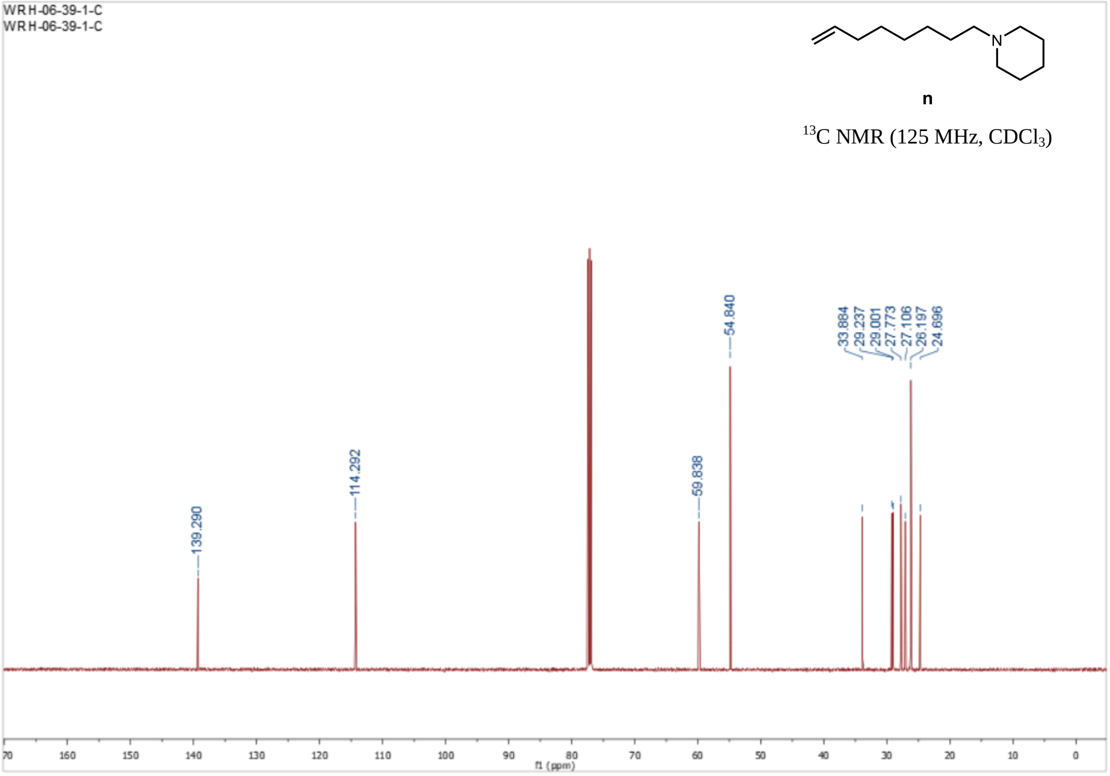
^{1}H NMR (500 MHz, $CDCl_3$)

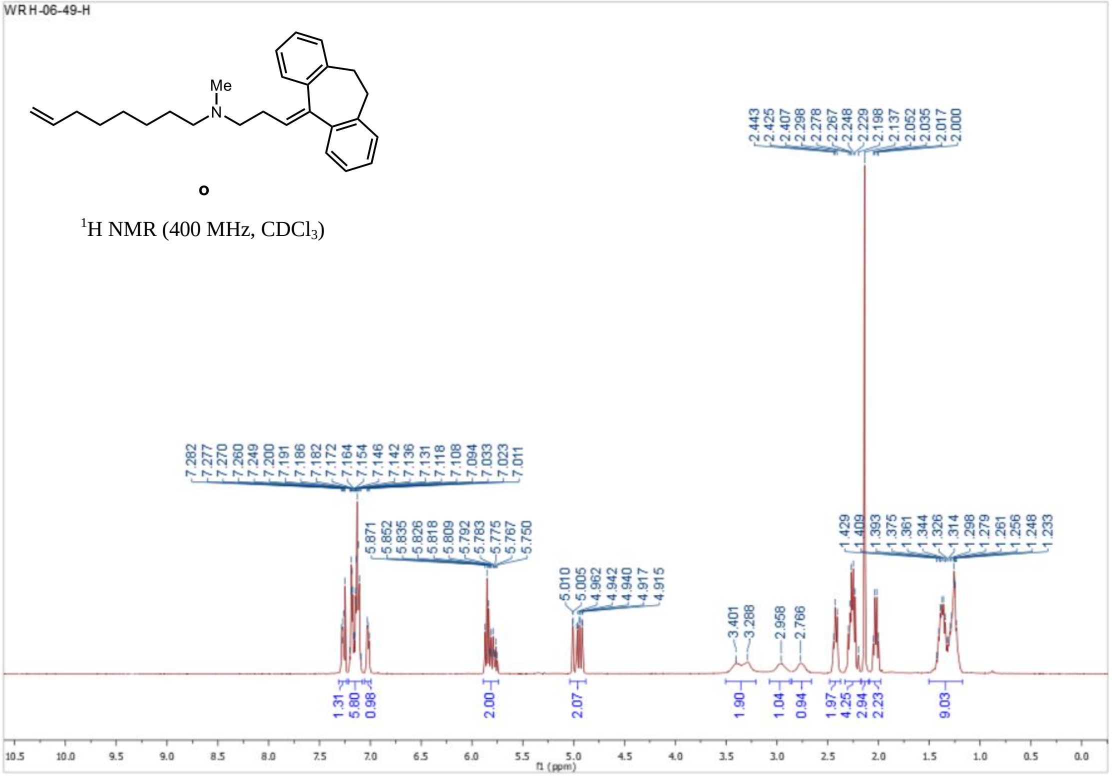


m

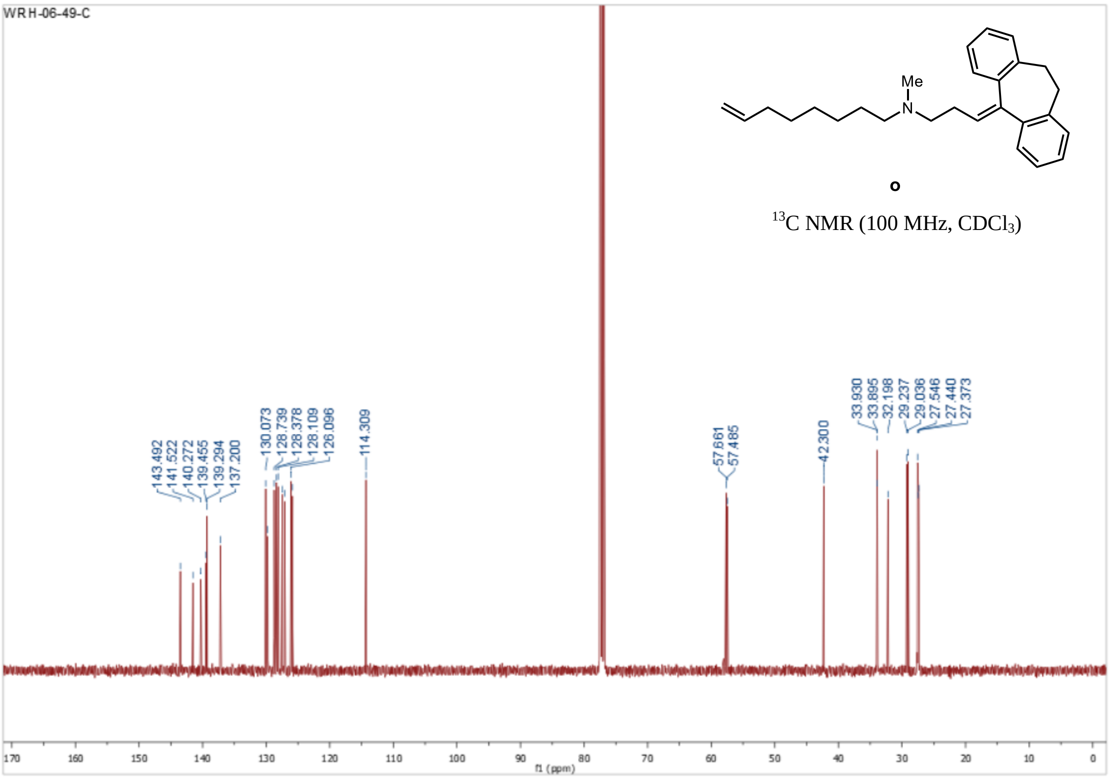
^{13}C NMR (125 MHz, $CDCl_3$)


WRH-06-39-1-H
N
n
^{1}H NMR (400 MHz, CDCl$_3$)
5.848 5.831 5.822 5.814 5.806 5.789 5.780 5.772 5.763 5.746
5.003 4.998 4.960 4.955 4.933 4.930 4.907 4.905
2.348 2.274 2.254 2.248 2.234 2.055 2.038 2.020 2.002
1.600 1.586 1.572 1.558 1.544 1.514 1.494 1.476 1.457 1.438 1.429 1.415 1.399 1.376 1.356 1.340 1.323 1.295 1.286 1.277 1.253
1.00
2.01
3.68
2.27
2.13
4.09
10.76
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

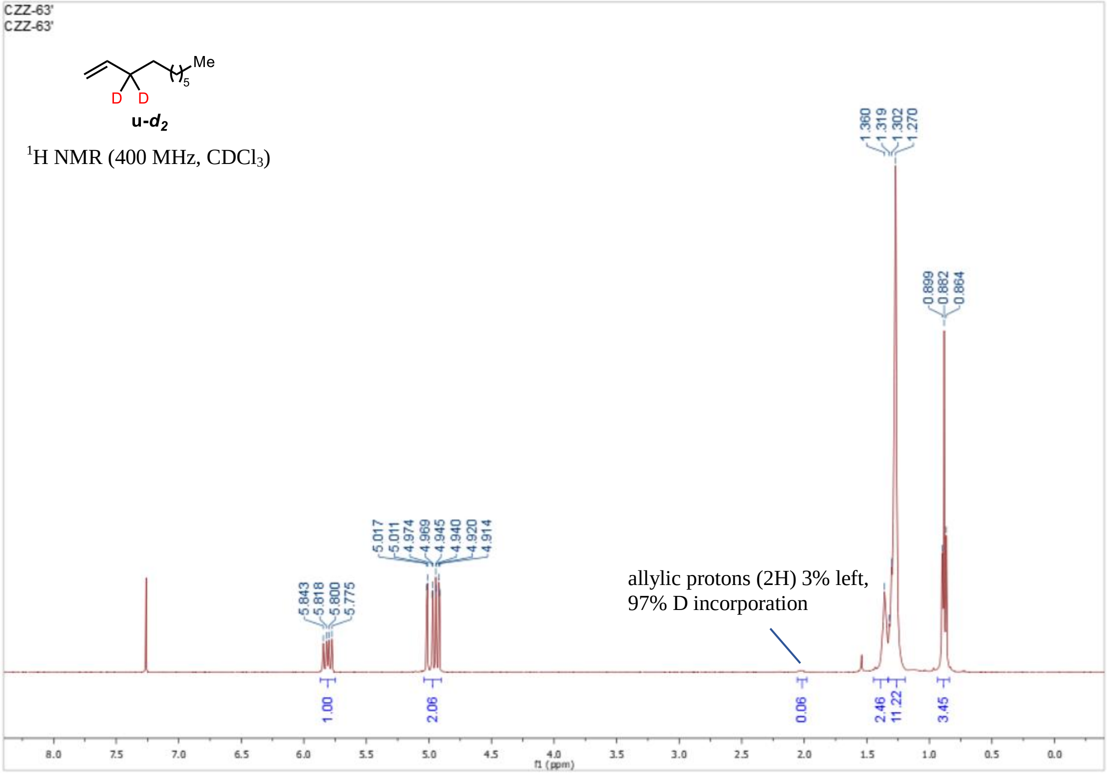

WRH-06-39-1-C
WRH-06-39-1-C
N
n
^{13}C NMR (125 MHz, CDCl$_3$)
139.290
114.292
59.838
54.840
33.884 29.237 29.001 27.773 27.106 26.197 24.696
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



^{1}H NMR (400 MHz, CDCl$_3$)



^{13}C NMR (100 MHz, CDCl$_3$)



u-d_2

^{1}H NMR (400 MHz, $CDCl_3$)

allylic protons (2H) 3% left,
97% D incorporation

Cartesian Coordinates (Å) and Energies of the Optimized Structures

41

B3LYP-D3 SCF energy (au): -1281.55639934
B3LYP-D3 enthalpy (au): -1281.04544034
B3LYP-D3 free energy (au): -1281.13276234
M06 SCF energy in toluene (au): -1280.95844434
M06 enthalpy in toluene (au): -1280.44748534
M06 free energy in toluene (au): -1280.53480734
M06 free energy in toluene (quasi-harmonic) (au): -1280.53027000
M06 SCF energy in dichloromethane (au): -1280.979640
M06 enthalpy in dichloromethane (au): -1279.936526
M06 free energy in dichloromethane (au): -1280.023848
M06 free energy in dichloromethane (quasi-harmonic) (au): -1280.019311

Cartesian coordinates

ATOM	X	Y	Z
C	1.808771	-0.410711	-0.686447
C	1.772026	-0.918588	0.649273
C	3.363861	-2.795341	-1.462429
C	2.958015	-1.298980	1.487669
C	4.262587	-2.820549	-0.202390
C	3.536848	-2.690446	1.148145
H	3.746704	-0.545175	1.377961
H	3.668218	-3.602094	-2.137766
H	5.040595	-2.047530	-0.274967
H	2.328667	-3.029668	-1.179058
H	2.662107	-1.287880	2.542674
H	4.801672	-3.773586	-0.178390
H	4.244328	-2.941070	1.946989
H	2.733627	-3.437487	1.202910
C	3.051212	-0.209072	-1.494750
H	3.881407	0.051191	-0.830597
H	2.928204	0.623503	-2.195359
C	3.393344	-1.495384	-2.281951
H	2.692955	-1.592475	-3.120654
H	4.388738	-1.358156	-2.720515
C	0.386849	-1.131534	0.984140
C	0.463055	-0.257033	-1.129076
C	-0.430877	-0.769673	-0.119833
C	-1.885188	-0.847249	-0.204522
C	-2.541071	-0.732064	-1.448598
C	-2.675073	-1.044784	0.940424
C	-3.918792	-0.806155	-1.540014
H	-1.961451	-0.609858	-2.358388
C	-4.060909	-1.118141	0.864860
H	-2.204373	-1.136593	1.914954
C	-4.696953	-0.997903	-0.382901
H	-4.425876	-0.730557	-2.495591
H	-4.636124	-1.269185	1.769722

H	0.176041	0.117800	-2.101056
H	0.039178	-1.545079	1.921403
O	-6.026452	-1.054441	-0.574682
C	-6.879079	-1.271068	0.550005
H	-6.784530	-0.456901	1.277880
H	-7.892595	-1.288447	0.150534
H	-6.656864	-2.229707	1.032442
Fe	0.772362	0.936769	0.607356
C	1.963901	2.187454	0.141507
C	1.026300	1.183984	2.359399
O	1.198132	1.281406	3.488739
O	2.788396	2.931605	-0.141821
C	-1.014155	2.177758	1.102539
H	-0.717446	2.997852	1.752304
H	-1.683971	1.439152	1.531122
C	-0.916236	2.311310	-0.263561
H	-1.461846	1.592898	-0.869012
C	-0.473461	3.549501	-0.995903
H	-1.383790	4.155967	-1.121027
H	0.202695	4.151218	-0.378631
C	0.121791	3.283318	-2.382775
H	1.057037	2.717864	-2.324165
H	-0.579133	2.713389	-3.003774
H	0.333199	4.224161	-2.897962

41-triplet
B3LYP-D3 SCF energy (au): -1281.52185327
B3LYP-D3 enthalpy (au): -1281.01363927
B3LYP-D3 free energy (au): -1281.10934127
M06 SCF energy in toluene (au): -1280.93051236
M06 enthalpy in toluene (au): -1280.42229836
M06 free energy in toluene (au): -1280.51800036
M06 free energy in toluene (quasi-harmonic) (au): -1280.51133809

Cartesian coordinates

ATOM	X	Y	Z
C	1.634955	-0.655574	-0.593443
C	1.454069	-1.328004	0.697642
C	3.061813	-3.120644	-1.440276
C	2.556086	-1.840738	1.576995
C	3.883041	-3.310692	-0.142167
C	3.087014	-3.235356	1.171053
H	3.394255	-1.133082	1.581763
H	3.333506	-3.902407	-2.157721
H	4.712185	-2.589835	-0.108334
H	1.995688	-3.278803	-1.228054
H	2.184943	-1.893031	2.606734
H	4.357124	-4.297716	-0.168064
H	3.731931	-3.577488	1.988887
H	2.243896	-3.937213	1.126409

C	2.950281	-0.523451	-1.292711
H	3.745913	-0.385543	-0.552774
H	2.955493	0.363967	-1.933198
C	3.249347	-1.773360	-2.153871
H	2.602301	-1.750708	-3.039350
H	4.281036	-1.688054	-2.515964
C	0.086076	-1.415627	0.930752
C	0.352242	-0.413147	-1.141430
C	-0.637332	-0.824710	-0.192870
C	-2.080816	-0.716583	-0.334526
C	-2.655461	-0.072760	-1.454869
C	-2.951273	-1.230835	0.643477
C	-4.023662	0.054400	-1.583967
H	-2.018520	0.326257	-2.237743
C	-4.330100	-1.113407	0.526583
H	-2.550141	-1.740930	1.513054
C	-4.880875	-0.464665	-0.592345
H	-4.467969	0.543581	-2.443811
H	-4.966947	-1.527899	1.297941
H	0.162673	0.016170	-2.114651
H	-0.367557	-1.823971	1.823892
O	-6.194752	-0.292187	-0.809433
C	-7.128397	-0.803698	0.143426
H	-6.987116	-0.332412	1.122693
H	-8.113466	-0.550239	-0.246873
H	-7.036967	-1.891711	0.236039
Fe	0.615196	0.824006	0.637916
C	2.097333	1.580415	1.505546
C	-0.594011	1.310578	2.038246
O	-1.327085	1.568688	2.873138
O	2.994331	2.037300	2.047048
C	-0.378485	2.969765	-0.483188
H	-0.491423	3.638143	0.367537
H	-1.246356	2.374442	-0.758249
C	0.718995	3.023809	-1.263399
H	0.758473	2.395998	-2.154371
C	1.886586	3.946395	-1.062738
H	1.739521	4.806398	-1.732997
H	1.873051	4.351248	-0.043421
C	3.244753	3.308471	-1.383972
H	3.467007	2.467180	-0.720136
H	3.270018	2.938803	-2.415534
H	4.049324	4.040811	-1.273234

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B3LYP-D3 SCF energy (au): -1690.78415982
B3LYP-D3 enthalpy (au): -1689.98660082
B3LYP-D3 free energy (au): -1690.10222582
M06 SCF energy in toluene (au): -1689.93116709
M06 enthalpy in toluene (au): -1689.13360809

M06 free energy in toluene (au): -1689.24923309
M06 free energy in toluene (quasi-harmonic) (au): -1689.24094027

Cartesian coordinates

ATOM	X	Y	Z
C	-3.405507	-0.225694	-0.756480
C	-3.761962	0.477969	0.433112
C	-5.750834	0.983936	-2.079437
C	-5.086576	0.416863	1.137667
C	-6.713169	0.826387	-0.877340
C	-6.175536	1.297138	0.485393
H	-5.438981	-0.620665	1.176385
H	-6.297383	1.418552	-2.923315
H	-7.051767	-0.216134	-0.795881
H	-4.970828	1.716380	-1.830694
H	-4.949279	0.737962	2.176225
H	-7.617778	1.410815	-1.076743
H	-7.012627	1.338869	1.191919
H	-5.799693	2.324937	0.392588
C	-4.319279	-1.122139	-1.530975
H	-5.020693	-1.608109	-0.845306
H	-3.754177	-1.918076	-2.027147
C	-5.098785	-0.310436	-2.591019
H	-4.417945	-0.059194	-3.413755
H	-5.867495	-0.969176	-3.012124
C	-2.665604	1.357346	0.754115
C	-2.088474	0.184534	-1.125195
C	-1.651388	1.226242	-0.232289
C	-0.381933	1.942757	-0.302963
C	0.374947	1.935744	-1.493440
C	0.137242	2.632362	0.804391
C	1.604757	2.562839	-1.561377
H	-0.012498	1.442576	-2.379207
C	1.376677	3.260636	0.752914
H	-0.423435	2.665394	1.734029
C	2.130726	3.211478	-0.430425
H	2.190808	2.556610	-2.473213
H	1.754545	3.765768	1.632795
H	-1.544884	-0.185461	-1.982675
H	-2.654030	2.046598	1.587873
O	3.363742	3.735191	-0.579177
C	3.964050	4.405801	0.528863
H	4.093037	3.722369	1.375941
H	4.939084	4.740779	0.176047
H	3.366758	5.271964	0.835242
Fe	-2.043563	-0.688294	0.814945
C	-2.358685	-2.421258	0.506619
C	-2.457666	-0.791456	2.549121
O	-2.757713	-0.810877	3.655943
O	-2.635340	-3.515246	0.304247

C	-0.000199	-0.813657	1.701637
H	0.016783	-1.578806	2.474290
H	0.152740	0.207720	2.034213
C	0.251117	-1.156801	0.392274
H	0.478646	-0.346493	-0.293110
C	0.621580	-2.515168	-0.111567
H	0.264005	-3.306132	0.557293
C	0.228985	-2.779553	-1.568378
H	-0.856493	-2.812796	-1.708117
H	0.631152	-1.997403	-2.223153
H	0.636782	-3.735777	-1.908014
H	1.725205	-2.500355	-0.046279
N	3.906471	-1.682707	0.011156
C	4.464760	-1.404745	-1.341837
C	4.340556	-0.838173	1.158894
C	5.990579	-1.160791	-1.292164
C	4.177700	-2.653851	-2.187257
C	3.740177	-0.214572	-1.993576
C	5.871129	-0.625653	1.161438
C	3.919422	-1.598518	2.424229
C	3.612274	0.517088	1.156293
C	6.397326	-0.164718	-0.201772
H	6.342265	-0.825271	-2.275616
H	6.487951	-2.120514	-1.091558
H	3.100241	-2.830862	-2.273490
H	4.587835	-2.537772	-3.195540
H	4.637748	-3.545524	-1.743453
H	3.980128	-0.173846	-3.061704
H	2.656665	-0.328438	-1.886096
H	4.019919	0.747500	-1.561148
H	6.355211	-1.577533	1.422699
H	6.143628	0.090646	1.946920
H	4.223666	-1.052308	3.322921
H	2.831664	-1.731796	2.451770
H	4.386792	-2.590129	2.464729
H	2.544885	0.379394	0.969615
H	3.730535	0.999524	2.133561
H	3.998355	1.206559	0.404655
H	6.018347	0.837493	-0.439528
H	7.488981	-0.076269	-0.168690
H	4.196994	-2.633140	0.242255

42'
B3LYP-D3 SCF energy (au): -1690.78423090
B3LYP-D3 enthalpy (au): -1689.98662290
B3LYP-D3 free energy (au): -1690.10252390
M06 SCF energy in toluene (au): -1689.93010513
M06 enthalpy in toluene (au): -1689.13249713
M06 free energy in toluene (au): -1689.24839813
M06 free energy in toluene (quasi-harmonic) (au): -1689.23992823

Cartesian coordinates

ATOM	X	Y	Z
C	3.618202	0.029107	0.773927
C	3.766992	0.324025	-0.612827
C	6.064687	1.616134	1.259262
C	4.971738	0.029011	-1.458335
C	6.849984	1.082819	0.036743
C	6.094249	1.079643	-1.303413
H	5.372278	-0.960665	-1.210365
H	6.702566	2.305024	1.823446
H	7.232576	0.073184	0.242329
H	5.216789	2.223147	0.913627
H	4.666223	-0.009436	-2.509714
H	7.738634	1.706979	-0.106178
H	6.814804	0.890115	-2.107410
H	5.679781	2.079312	-1.490293
C	4.683490	-0.558827	1.644954
H	5.298892	-1.241364	1.049872
H	4.243418	-1.152663	2.452630
C	5.567511	0.554259	2.252847
H	5.004699	1.056680	3.049435
H	6.425185	0.070572	2.735318
C	2.588093	1.018128	-1.033883
C	2.359360	0.580741	1.198876
C	1.745785	1.256899	0.102803
C	0.474535	1.972602	0.122161
C	-0.274992	2.085392	1.313341
C	-0.056083	2.551623	-1.042111
C	-1.506483	2.710569	1.327806
H	0.110325	1.674329	2.240689
C	-1.295511	3.182677	-1.043659
H	0.502955	2.513659	-1.971827
C	-2.042073	3.246250	0.142437
H	-2.088013	2.788896	2.239128
H	-1.675694	3.606453	-1.964483
H	1.983784	0.535594	2.211650
H	2.414263	1.368841	-2.041735
O	-3.274677	3.780625	0.248975
C	-3.878263	4.354559	-0.911036
H	-4.012698	3.600864	-1.695138
H	-4.850709	4.721841	-0.584285
H	-3.279271	5.188751	-1.293118
Fe	2.050887	-0.909611	-0.293198
C	2.051941	-2.234287	0.903331
C	2.571869	-1.929261	-1.665172
O	2.941815	-2.557847	-2.549766
O	2.121137	-3.037613	1.719406
C	0.092073	-0.973349	-1.372598
H	0.069591	-1.763168	-2.116583

H	0.081272	0.037850	-1.758495
C	-0.312455	-1.229957	-0.081562
H	-0.502621	-0.375189	0.561922
C	-0.870524	-2.530737	0.413744
H	-1.958059	-2.324723	0.448737
N	-4.055316	-1.528264	0.157155
C	-4.661340	-1.018344	1.419099
C	-4.373483	-0.845437	-1.127078
C	-6.164159	-0.702931	1.242735
C	-4.490643	-2.140087	2.453488
C	-3.898469	0.216021	1.930155
C	-5.884777	-0.548363	-1.252126
C	-3.939856	-1.811490	-2.238634
C	-3.556574	0.448751	-1.280642
C	-6.448922	0.139891	-0.004616
H	-6.544747	-0.205026	2.143092
H	-6.709994	-1.653201	1.154704
H	-3.430149	-2.359619	2.621061
H	-4.937270	-1.852294	3.410518
H	-4.983787	-3.062297	2.121665
H	-4.182249	0.422256	2.968012
H	-2.819831	0.032164	1.897167
H	-4.104121	1.119533	1.353714
H	-6.416049	-1.499411	-1.400097
H	-6.069955	0.056877	-2.148648
H	-4.165609	-1.392818	-3.224702
H	-2.862315	-2.005703	-2.184491
H	-4.465231	-2.771039	-2.157430
H	-2.507644	0.272780	-1.030155
H	-3.608305	0.795636	-2.319231
H	-3.921524	1.257724	-0.647288
H	-6.017844	1.143136	0.106771
H	-7.529334	0.284364	-0.116319
H	-4.391448	-2.486057	0.053341
H	-0.570027	-2.702670	1.454082
C	-0.605808	-3.766094	-0.445064
H	-1.053527	-4.648054	0.021419
H	-1.047025	-3.664267	-1.442318
H	0.464394	-3.970112	-0.569581

43
B3LYP-D3 SCF energy (au): -1281.13576085
B3LYP-D3 enthalpy (au): -1280.63860485
B3LYP-D3 free energy (au): -1280.72735585
M06 SCF energy in toluene (au): -1280.51401683
M06 enthalpy in toluene (au): -1280.01686083
M06 free energy in toluene (au): -1280.10561183
M06 free energy in toluene (quasi-harmonic) (au): -1280.10006198
M06 SCF energy in dichloromethane (au): -1280.517295
M06 enthalpy in dichloromethane (au): -1280.020139

M06 free energy in dichloromethane (au): -1280.10889
M06 free energy in dichloromethane (quasi-harmonic) (au): -1280.10334

Cartesian coordinates

ATOM	X	Y	Z
C	1.533154	1.357246	0.395801
C	1.720602	0.280767	-0.546941
C	3.169892	3.063212	-1.391297
C	3.035393	-0.242041	-1.050804
C	4.227859	1.985741	-1.734051
C	3.678227	0.612517	-2.161035
H	3.746216	-0.331939	-0.219356
H	3.436724	4.002093	-1.891274
H	4.915765	1.851111	-0.886850
H	2.200637	2.768298	-1.812827
H	2.872672	-1.257177	-1.426100
H	4.848482	2.354949	-2.559334
H	4.506610	0.029447	-2.584087
H	2.951841	0.752154	-2.973702
C	2.641847	2.168166	0.992312
H	3.525579	1.533219	1.119610
H	2.363817	2.518512	1.992681
C	2.996580	3.379076	0.103295
H	2.207017	4.134931	0.206581
H	3.917725	3.833960	0.491215
C	0.431417	-0.133130	-0.972164
C	0.141770	1.565700	0.537804
C	-0.568908	0.636239	-0.310008
C	-2.024896	0.514855	-0.468518
C	-2.592991	-0.571729	-1.160485
C	-2.896480	1.468786	0.068958
C	-3.965787	-0.698552	-1.299323
H	-1.949811	-1.333818	-1.587920
C	-4.280899	1.354345	-0.060844
H	-2.495477	2.326888	0.599479
C	-4.824635	0.263686	-0.747654
H	-4.401900	-1.539084	-1.829137
H	-4.917545	2.116674	0.371885
H	-0.309244	2.288363	1.204823
H	0.255103	-0.959168	-1.644675
O	-6.157230	0.050003	-0.936517
C	-7.064582	0.985984	-0.379855
H	-6.920670	1.988091	-0.805222
H	-8.062434	0.625372	-0.634706
H	-6.965180	1.041293	0.712195
Fe	0.608657	-0.421695	1.137713
C	-0.584560	-0.442966	2.430718
C	1.983121	-0.928555	2.100618
O	2.921414	-1.250956	2.695872
O	-1.394754	-0.443287	3.253594

C	0.146092	-2.416957	0.816444
H	0.059815	-2.907514	1.791987
H	-0.840942	-2.424758	0.341929
C	1.165784	-3.098141	-0.013130
H	2.139243	-3.255804	0.458265
C	1.014940	-3.516702	-1.279633
H	0.045068	-3.381964	-1.764652
C	2.082339	-4.182739	-2.100627
H	2.311397	-3.612158	-3.012456
H	3.011985	-4.287778	-1.529827
H	1.775291	-5.185010	-2.430130

43'

B3LYP-D3 SCF energy (au): -1281.13186078
B3LYP-D3 enthalpy (au): -1280.63466378
B3LYP-D3 free energy (au): -1280.72460678
M06 SCF energy in toluene (au): -1280.51241684
M06 enthalpy in toluene (au): -1280.01521984
M06 free energy in toluene (au): -1280.10516284
M06 free energy in toluene (quasi-harmonic) (au): -1280.09908006

Cartesian coordinates

ATOM	X	Y	Z
C	-1.609534	-1.189141	0.700629
C	-1.630127	-0.786570	-0.684805
C	-3.140191	-3.600905	-0.102281
C	-2.850211	-0.621576	-1.545753
C	-4.093304	-2.877141	-1.084923
C	-3.423251	-1.939257	-2.105348
H	-3.638414	-0.104769	-0.984090
H	-3.405188	-4.664197	-0.060666
H	-4.855650	-2.315965	-0.525699
H	-2.116506	-3.565988	-0.495860
H	-2.592664	0.036621	-2.384119
H	-4.646122	-3.631795	-1.657031
H	-4.167498	-1.675075	-2.867818
H	-2.625442	-2.485677	-2.627207
C	-2.820870	-1.573357	1.493202
H	-3.676171	-0.976128	1.158054
H	-2.673638	-1.336364	2.552837
C	-3.144922	-3.074730	1.342129
H	-2.414008	-3.653121	1.922164
H	-4.125994	-3.263574	1.797896
C	-0.280566	-0.644298	-1.099663
C	-0.256498	-1.266929	1.104370
C	0.595377	-0.921956	-0.008478
C	2.064446	-0.877291	-0.022822
C	2.808599	-0.920431	1.171423
C	2.773832	-0.779777	-1.225524
C	4.192680	-0.864330	1.160359

H	2.294784	-0.979404	2.125662
C	4.167716	-0.718105	-1.253277
H	2.235748	-0.760841	-2.167965
C	4.886930	-0.760202	-0.054504
H	4.763581	-0.890932	2.082638
H	4.674837	-0.643638	-2.207750
H	0.078163	-1.534809	2.097772
H	0.025254	-0.299500	-2.077586
O	6.245412	-0.709832	0.039277
C	6.988863	-0.581090	-1.160728
H	8.037872	-0.547279	-0.862226
H	6.828189	-1.438525	-1.827690
H	6.732227	0.343082	-1.695115
Fe	-0.682125	0.730775	0.485262
C	0.333348	1.480281	1.712075
C	-2.142641	1.643264	0.835913
O	-3.141396	2.184537	1.047574
O	1.027702	1.924780	2.521496
C	-0.093177	2.185285	-0.858008
H	0.940023	1.907579	-1.094151
H	-0.713257	2.024548	-1.743864
C	-0.164679	3.585300	-0.376803
H	0.649513	3.894315	0.280879
C	-1.123167	4.493792	-0.625747
H	-1.024947	5.477811	-0.167496
C	-2.348541	4.296987	-1.472969
H	-2.401542	5.045455	-2.275734
H	-2.379996	3.306480	-1.936221
H	-3.262301	4.408722	-0.874008

43-triplet

B3LYP-D3 SCF energy (au): -1281.09654062
B3LYP-D3 enthalpy (au): -1280.60232862
B3LYP-D3 free energy (au): -1280.69698362
M06 SCF energy in toluene (au): -1280.48033538
M06 enthalpy in toluene (au): -1279.98612338
M06 free energy in toluene (au): -1280.08077838
M06 free energy in toluene (quasi-harmonic) (au): -1280.07412376

Cartesian coordinates

ATOM	X	Y	Z
C	-1.495526	-1.402156	0.459348
C	-1.695608	-0.439858	-0.559989
C	-3.185273	-3.295233	-1.086846
C	-3.014373	0.030637	-1.100367
C	-4.237738	-2.246579	-1.522449
C	-3.683585	-0.932077	-2.102105
H	-3.714387	0.211969	-0.272294
H	-3.478814	-4.280096	-1.470311
H	-4.909141	-2.016056	-0.682574

H	-2.224439	-3.063617	-1.562883
H	-2.858224	0.999280	-1.586434
H	-4.876953	-2.692611	-2.294071
H	-4.514448	-0.390059	-2.572968
H	-2.971256	-1.165250	-2.905499
C	-2.588075	-2.141390	1.164683
H	-3.470039	-1.493538	1.243266
H	-2.289236	-2.382533	2.191890
C	-2.973983	-3.442995	0.428460
H	-2.185657	-4.188963	0.594633
H	-3.886655	-3.844640	0.889294
C	-0.399920	-0.012001	-1.006519
C	-0.090630	-1.543633	0.650804
C	0.606842	-0.738568	-0.308380
C	2.058832	-0.594687	-0.451249
C	2.619662	0.492410	-1.151417
C	2.942651	-1.529010	0.104946
C	3.991483	0.636124	-1.283578
H	1.967654	1.242424	-1.588129
C	4.326166	-1.394774	-0.014735
H	2.547731	-2.390379	0.635182
C	4.859890	-0.306398	-0.713144
H	4.419810	1.476856	-1.819679
H	4.970676	-2.142938	0.431259
H	0.369945	-2.187759	1.389354
H	-0.238983	0.718972	-1.785839
O	6.191971	-0.075941	-0.895005
C	7.106733	-0.992862	-0.320626
H	6.978886	-2.002223	-0.734107
H	8.102031	-0.623004	-0.572654
H	7.000498	-1.036572	0.771483
Fe	-0.534096	0.628575	1.079454
C	0.523687	0.742356	2.547390
C	-2.214542	1.158720	2.132716
O	-2.919449	1.961709	2.554057
O	1.249823	0.786037	3.442258
C	-0.249224	2.609048	0.620052
H	-0.248835	3.187215	1.549115
H	0.761552	2.616498	0.194307
C	-1.267577	3.101106	-0.331134
H	-2.264111	3.274627	0.081700
C	-1.089656	3.338225	-1.641566
H	-0.096875	3.188820	-2.071885
C	-2.159232	3.812004	-2.582843
H	-2.323203	3.098937	-3.403762
H	-3.113774	3.947540	-2.061917
H	-1.892032	4.769236	-3.051485

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B3LYP-D3 SCF energy (au): -1951.33466569

B3LYP-D3 enthalpy (au): -1950.69619369
B3LYP-D3 free energy (au): -1950.80632469
M06 SCF energy in toluene (au): -1950.54539642
M06 enthalpy in toluene (au): -1949.90692442
M06 free energy in toluene (au): -1950.01705542
M06 free energy in toluene (quasi-harmonic) (au): -1950.00935973

Cartesian coordinates

ATOM	X	Y	Z
Fe	-1.480878	0.462125	-0.309952
C	-1.732299	1.926743	0.692326
O	-2.011844	2.808146	1.367558
C	-1.712627	1.347763	-1.844094
O	-1.928075	1.842736	-2.855195
C	0.590120	0.690249	-1.043439
H	0.709525	1.642926	-1.540901
H	0.707211	-0.217693	-1.625250
C	0.735967	0.635111	0.329386
H	0.890202	-0.346826	0.762386
C	1.162596	1.768748	1.213071
H	0.550713	2.655383	1.077682
C	1.123785	1.369196	2.688045
H	1.686623	0.448085	2.876219
H	1.544546	2.161324	3.315851
H	0.089241	1.204076	3.016918
C	2.579611	2.271971	0.694159
O	2.439947	2.894448	-0.534005
B	1.513984	4.040619	-0.658763
F	1.411309	4.721331	0.562071
F	1.935607	4.841550	-1.694721
F	0.183280	3.531270	-0.973153
H	2.921876	2.976202	1.468902
C	3.557215	1.113904	0.583564
C	4.132011	0.536605	1.723334
C	3.849056	0.556534	-0.666976
C	4.938439	-0.597893	1.623060
H	3.957360	0.985267	2.697398
C	4.661932	-0.573001	-0.770753
H	3.443651	1.041662	-1.546821
C	5.200764	-1.163451	0.373829
H	5.374373	-1.031675	2.519298
H	4.888225	-0.981498	-1.753292
H	5.831810	-2.044016	0.296519
C	-3.049679	-0.501081	0.762459
C	-3.217673	-0.689564	-0.639172
C	-6.197900	-1.217422	1.077339
C	-4.456457	-0.348160	-1.407105
C	-5.704116	-2.173181	-0.035928
C	-5.451491	-1.528906	-1.408558
H	-4.924645	0.534156	-0.957941

H	-6.618205	-0.304407	0.632248
H	-6.446397	-2.965805	-0.184822
H	-7.031434	-1.696084	1.604045
H	-4.210172	-0.078918	-2.439694
H	-4.792344	-2.684252	0.300089
H	-6.400655	-1.171987	-1.827770
H	-5.080332	-2.303228	-2.092185
C	-4.040134	0.131878	1.697657
H	-4.492701	1.012719	1.227748
H	-3.507136	0.493307	2.583905
C	-5.160197	-0.830025	2.146186
H	-4.707898	-1.742084	2.558993
H	-5.686490	-0.343734	2.976604
C	-2.079165	-1.426681	-1.116530
C	-1.795522	-1.084029	1.128777
C	-1.219848	-1.722004	-0.020669
C	0.051152	-2.446352	-0.060968
C	0.719994	-2.796059	1.130167
C	0.683058	-2.746797	-1.276174
C	1.972365	-3.382357	1.105218
H	0.255847	-2.593429	2.089923
C	1.943076	-3.335613	-1.317675
H	0.198787	-2.495560	-2.214781
C	2.604691	-3.644384	-0.121248
H	2.496333	-3.632845	2.020735
H	2.405386	-3.531342	-2.276926
H	-1.379489	-1.075001	2.126183
H	-1.933747	-1.738365	-2.141809
O	3.834772	-4.200574	-0.044058
C	4.556468	-4.407821	-1.251690
H	5.522883	-4.815705	-0.953743
H	4.043569	-5.125122	-1.904470
H	4.705072	-3.462817	-1.786419

44'

B3LYP-D3 SCF energy (au): -1951.31966855
B3LYP-D3 enthalpy (au): -1950.68147955
B3LYP-D3 free energy (au): -1950.79265355
M06 SCF energy in toluene (au): -1950.53972438
M06 enthalpy in toluene (au): -1949.90153538
M06 free energy in toluene (au): -1950.01270938
M06 free energy in toluene (quasi-harmonic) (au): -1950.00469583

Cartesian coordinates

ATOM	X	Y	Z
Fe	-1.680322	-0.458516	0.818712
C	-1.665714	-2.180598	0.301582
O	-1.762124	-3.263903	-0.053485
C	-2.174940	-0.818271	2.485451
O	-2.531739	-1.002221	3.562431

C	0.301192	-0.450561	1.809193
H	0.391170	-1.347942	2.417944
H	0.299934	0.495610	2.343013
C	0.739363	-0.492774	0.495540
H	0.894957	0.457803	-0.002972
C	1.283497	-1.675868	-0.184044
H	0.871529	-2.595476	0.229904
C	1.118769	-1.661973	-1.700665
H	1.648111	-2.521785	-2.111571
H	0.061769	-1.748451	-1.982913
H	1.521617	-0.740940	-2.140101
C	2.849914	-1.815090	0.233709
O	3.350859	-2.955821	-0.323457
B	2.724899	-4.253903	0.092368
F	3.689807	-5.234303	0.025820
F	2.200405	-4.109170	1.401055
F	1.648178	-4.528739	-0.782836
H	2.829281	-1.863512	1.332856
C	3.641874	-0.597184	-0.200756
C	3.691837	0.549763	0.601043
C	4.331673	-0.599283	-1.418043
C	4.406691	1.677628	0.195342
H	3.187608	0.551793	1.564624
C	5.042970	0.527565	-1.830811
H	4.320691	-1.507846	-2.009382
C	5.083861	1.669243	-1.026359
H	4.447478	2.550750	0.840949
H	5.583210	0.508701	-2.773834
H	5.666250	2.533484	-1.337265
C	-2.934452	-0.030048	-0.846323
C	-3.517148	0.466441	0.357010
C	-5.320571	0.917309	-2.302995
C	-4.872823	0.112655	0.898323
C	-6.349579	0.470388	-1.236095
C	-6.033681	0.867636	0.217153
H	-5.040691	-0.966643	0.800592
H	-5.853175	1.352678	-3.156177
H	-6.502094	-0.616854	-1.290369
H	-4.703837	1.730085	-1.897071
H	-4.891186	0.331581	1.972129
H	-7.321338	0.913921	-1.481160
H	-6.930396	0.693273	0.824358
H	-5.835881	1.947369	0.262194
C	-3.602055	-0.971124	-1.800049
H	-4.267677	-1.640742	-1.245505
H	-2.862093	-1.603819	-2.300722
C	-4.409063	-0.188592	-2.858980
H	-3.709125	0.262562	-3.573511
H	-5.009872	-0.911356	-3.424676
C	-2.619640	1.461791	0.886757

C	-1.677176	0.621919	-1.025317
C	-1.504187	1.596483	0.017269
C	-0.365083	2.501028	0.165369
C	0.453429	2.792816	-0.936087
C	-0.027890	3.067821	1.409612
C	1.576021	3.603636	-0.814679
H	0.214399	2.377881	-1.910005
C	1.089823	3.872969	1.546381
H	-0.636967	2.855816	2.283515
C	1.907951	4.141942	0.435590
H	2.194419	3.786907	-1.683465
H	1.363627	4.299816	2.505196
H	-0.991113	0.433202	-1.838145
H	-2.797871	2.041766	1.782519
O	2.989004	4.920000	0.673632
C	3.819417	5.274024	-0.429413
H	3.257535	5.852390	-1.173144
H	4.616485	5.890295	-0.012657
H	4.247917	4.383949	-0.901095

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B3LYP-D3 SCF energy (au): -1236.67478628
B3LYP-D3 enthalpy (au): -1236.12961728
B3LYP-D3 free energy (au): -1236.21535028
M06 SCF energy in toluene (au): -1236.14293134
M06 enthalpy in toluene (au): -1235.59776234
M06 free energy in toluene (au): -1235.68349534
M06 free energy in toluene (quasi-harmonic) (au): -1235.69152706

Cartesian coordinates

ATOM	X	Y	Z
C	-5.372586	-1.136464	0.648108
H	-5.787842	-0.307594	1.219634
H	-6.085180	-1.844069	0.232505
C	-4.059587	-1.273371	0.465083
H	-3.665890	-2.099450	-0.123797
C	-3.019418	-0.330951	1.018871
H	-3.538702	0.552769	1.411960
C	-2.274014	-1.023755	2.173000
H	-2.963223	-1.207462	3.003558
H	-1.881565	-1.987858	1.840152
H	-1.431821	-0.432920	2.548818
C	-2.079765	0.149379	-0.121675
O	-0.983993	-0.748174	-0.309962
B	-0.963241	-1.484224	-1.599869
F	-0.960625	-0.571481	-2.665190
F	0.277273	-2.213978	-1.609494
F	-2.025242	-2.366702	-1.697614
C	-1.531580	1.561225	0.043041
C	-1.328752	2.184667	1.280052

C	-1.191224	2.266406	-1.122235
C	-0.799725	3.477109	1.352194
H	-1.601307	1.674911	2.197767
C	-0.672180	3.558074	-1.054519
H	-1.336898	1.778334	-2.081176
C	-0.472829	4.169507	0.186250
H	-0.653539	3.944648	2.322319
H	-0.425544	4.089380	-1.969854
H	-0.070334	5.177051	0.242843
H	-2.676063	0.160048	-1.039920
H	0.679202	-0.323748	0.007091
N	1.687576	-0.616655	-0.071079
C	2.525329	0.471902	-0.726586
C	2.112427	-1.260484	1.240445
C	3.989820	0.004189	-0.732379
C	1.993786	0.593517	-2.160381
C	2.342947	1.803309	0.009264
C	3.602774	-1.623440	1.140197
C	1.259958	-2.529084	1.379834
C	1.816029	-0.312086	2.408557
C	4.481584	-0.475036	0.636477
H	4.606675	0.829799	-1.104297
H	4.093997	-0.816945	-1.455017
H	0.943669	0.888498	-2.176450
H	2.582053	1.344698	-2.696513
H	2.072303	-0.357584	-2.695948
H	2.725215	2.608004	-0.625615
H	1.289142	2.009448	0.202109
H	2.884992	1.845980	0.955347
H	3.707637	-2.476423	0.455802
H	3.934290	-1.969785	2.125537
H	1.547768	-3.055571	2.295034
H	0.198597	-2.281185	1.427566
H	1.403913	-3.200672	0.528795
H	0.807450	0.103698	2.325976
H	1.872306	-0.877064	3.343877
H	2.522371	0.516181	2.478406
H	4.486081	0.351956	1.356003
H	5.519284	-0.816611	0.555545
H	1.555474	-1.375596	-0.762365

45'
B3LYP-D3 SCF energy (au): -1236.67466083
B3LYP-D3 enthalpy (au): -1236.12987983 .544781
B3LYP-D3 free energy (au): -1236.21571383 .458948
M06 SCF energy in toluene (au): -1236.14174296
M06 enthalpy in toluene (au): -1235.59696196 .544781
M06 free energy in toluene (au): -1235.68279596 .458948
M06 free energy in toluene (quasi-harmonic) (au): -1235.69050613

Cartesian coordinates

ATOM	X	Y	Z
C	-1.548753	-3.726971	-0.087751
H	-1.570390	-3.278054	0.898376
H	-1.373640	-4.799426	-0.137728
C	-1.709806	-3.024598	-1.210217
H	-1.665143	-3.552442	-2.165789
C	-2.029069	-1.554401	-1.365588
H	-1.286527	-1.143451	-2.068800
C	-3.417177	-1.422681	-2.025237
H	-3.472932	-2.032404	-2.933753
H	-4.193921	-1.778391	-1.338671
H	-3.644330	-0.387166	-2.292714
C	-1.959001	-0.726005	-0.070503
O	-0.662807	-0.842549	0.511118
B	-0.584835	-0.881862	1.996020
F	-1.388060	-1.891912	2.509371
F	0.796688	-1.147274	2.295551
F	-0.932740	0.354161	2.545382
H	-2.690092	-1.140343	0.633927
C	-2.279835	0.750702	-0.277380
C	-1.832585	1.460268	-1.399837
C	-2.977635	1.449770	0.713553
C	-2.075762	2.828946	-1.530738
H	-1.300124	0.941757	-2.192566
C	-3.221259	2.817521	0.590036
H	-3.305190	0.918760	1.600923
C	-2.770784	3.513621	-0.532938
H	-1.726671	3.357395	-2.414215
H	-3.761901	3.340567	1.374029
H	-2.962872	4.578414	-0.631938
H	0.770531	-0.080533	-0.007539
N	1.807863	0.021458	0.152425
C	2.538490	-0.948810	-0.765887
C	2.211158	1.485294	0.258154
C	4.049806	-0.749092	-0.568526
C	2.116217	-2.356677	-0.320479
C	2.102301	-0.730431	-2.219251
C	3.738691	1.540122	0.419987
C	1.508266	2.020588	1.512686
C	1.727654	2.273737	-0.962694
C	4.489507	0.716916	-0.631306
H	4.573385	-1.349302	-1.321063
H	4.329028	-1.160733	0.411030
H	1.045308	-2.518634	-0.464673
H	2.671902	-3.094526	-0.908156
H	2.333503	-2.519633	0.738978
H	2.456236	-1.573045	-2.820916
H	1.010537	-0.704364	-2.294684
H	2.503898	0.182897	-2.660299

H	3.999335	1.164037	1.418959
H	4.046841	2.591064	0.389994
H	1.788263	3.068725	1.657547
H	0.421308	1.951129	1.429813
H	1.800095	1.456683	2.403848
H	0.658629	2.117656	-1.128352
H	1.877094	3.339844	-0.765430
H	2.268337	2.030284	-1.878429
H	4.321849	1.128017	-1.633873
H	5.567718	0.783446	-0.449146
H	1.835989	-0.380413	1.106043

BF3
B3LYP-D3 SCF energy (au): -324.551160925
B3LYP-D3 enthalpy (au): -324.534169925
B3LYP-D3 free energy (au): -324.563078925
M06 SCF energy in toluene (au): -324.551174561
M06 enthalpy in toluene (au): -324.534183561
M06 free energy in toluene (au): -324.563092561
M06 free energy in toluene (quasi-harmonic) (au): -324.563398636

Cartesian coordinates

ATOM	X	Y	Z
B	0.000000	0.000000	0.000000
F	-0.000000	1.317971	0.000000
F	1.141396	-0.658985	0.000000
F	-1.141396	-0.658985	0.000000

butene
B3LYP-D3 SCF energy (au): -157.230749590
B3LYP-D3 enthalpy (au): -157.115444590
B3LYP-D3 free energy (au): -157.149124590
M06 SCF energy in toluene (au): -157.128466782
M06 enthalpy in toluene (au): -157.013161782
M06 free energy in toluene (au): -157.046841782
M06 free energy in toluene (quasi-harmonic) (au): -157.049303192

Cartesian coordinates

ATOM	X	Y	Z
C	1.854724	0.012154	-0.283279
H	1.945869	0.911096	-0.890068
H	2.734093	-0.623221	-0.220904
C	0.721232	-0.287646	0.351446
H	0.670988	-1.201961	0.945971
C	-0.540912	0.528272	0.303847
H	-0.807566	0.847621	1.322234
H	-0.365807	1.442826	-0.276406
C	-1.720934	-0.254098	-0.295036
H	-1.507049	-0.548853	-1.328154
H	-1.919041	-1.167978	0.277795

H	-2.636150	0.348379	-0.292345

cis-TS2

B3LYP-D3 SCF energy (au): -1951.33433919
B3LYP-D3 enthalpy (au): -1950.69790019
B3LYP-D3 free energy (au): -1950.80824319
M06 SCF energy in toluene (au): -1950.52552795
M06 enthalpy in toluene (au): -1949.88908895
M06 free energy in toluene (au): -1949.99943195
M06 free energy in toluene (quasi-harmonic) (au): -1949.99181276

Cartesian coordinates

ATOM	X	Y	Z
Fe	1.766106	-1.041628	-0.504838
C	1.931736	-2.279472	0.750605
O	2.100866	-3.056055	1.584921
C	2.054964	-2.117802	-1.871080
O	2.253249	-2.789932	-2.786883
C	-0.312037	-1.454062	-0.874968
H	-0.491549	-2.480662	-1.189690
H	-0.527327	-0.720508	-1.648078
C	-0.690969	-1.107366	0.445690
H	-0.669162	-0.057604	0.696471
C	-1.214165	-1.916325	1.459337
H	-1.066047	-1.545178	2.470147
C	-1.400600	-3.401647	1.312312
H	-2.099325	-3.782011	2.066298
H	-1.795075	-3.666315	0.325742
H	-0.454626	-3.940753	1.453130
C	-3.083090	-0.935117	1.414426
O	-2.873815	0.344012	1.575752
B	-2.306184	0.908089	2.868810
F	-0.891143	0.818041	2.782642
F	-2.703818	2.230992	2.900726
F	-2.765426	0.146935	3.927955
H	-3.370874	-1.506648	2.300109
C	-3.684198	-1.348073	0.131522
C	-4.357126	-2.572080	0.020023
C	-3.576493	-0.516880	-0.994080
C	-4.908802	-2.962675	-1.199792
H	-4.455700	-3.211537	0.892935
C	-4.131956	-0.906304	-2.208719
H	-3.058954	0.428797	-0.898048
C	-4.796954	-2.131612	-2.316627
H	-5.432926	-3.911026	-1.276387
H	-4.046921	-0.250425	-3.070671
H	-5.230648	-2.435126	-3.265308
C	3.138433	0.197089	0.542915
C	3.477778	0.152253	-0.839109
C	5.518390	1.893532	0.977527

C	4.788501	-0.296177	-1.419598
C	6.457906	1.100498	0.036332
C	5.898378	0.773685	-1.360233
H	5.134455	-1.199332	-0.902104
H	6.081932	2.710356	1.443336
H	6.781859	0.169598	0.523496
H	4.733132	2.379230	0.384095
H	4.629986	-0.582663	-2.465933
H	7.373285	1.684068	-0.116742
H	6.725839	0.418886	-1.987745
H	5.531342	1.698151	-1.826850
C	4.065225	-0.151563	1.665946
H	4.748781	-0.943734	1.341359
H	3.505084	-0.546945	2.519685
C	4.871707	1.086066	2.114682
H	4.208086	1.752399	2.679782
H	5.647776	0.750175	2.814356
C	2.371524	0.715425	-1.566524
C	1.828446	0.762341	0.658872
C	1.373604	1.148117	-0.645740
C	0.100038	1.794249	-0.958852
C	-0.703190	2.310320	0.068256
C	-0.387972	1.870113	-2.279580
C	-1.965526	2.836113	-0.183685
H	-0.378388	2.259943	1.099235
C	-1.637735	2.402872	-2.547952
H	0.205074	1.480624	-3.101862
C	-2.449657	2.865308	-1.495549
H	-2.566358	3.143386	0.661511
H	-2.028444	2.441410	-3.559490
H	1.284632	0.898748	1.584227
H	2.340295	0.837068	-2.640894
O	-3.691091	3.287460	-1.842614
C	-4.604195	3.570167	-0.784705
H	-4.709477	2.707362	-0.116578
H	-4.281401	4.441306	-0.202067
H	-5.558162	3.787283	-1.266975

cis-TS2'
B3LYP-D3 SCF energy (au): -1951.31200115
B3LYP-D3 enthalpy (au): -1950.67568315
B3LYP-D3 free energy (au): -1950.78796215
M06 SCF energy in toluene (au): -1950.52279472
M06 enthalpy in toluene (au): -1949.88647672
M06 free energy in toluene (au): -1949.99875572
M06 free energy in toluene (quasi-harmonic) (au): -1949.99017157

Cartesian coordinates

ATOM	X	Y	Z
Fe	-1.752242	-0.570184	0.800007

C	-1.514571	-2.309820	0.499825
O	-1.455077	-3.432288	0.259895
C	-2.010371	-0.717688	2.540491
O	-2.202440	-0.777050	3.674434
C	0.271648	-0.113559	1.364454
H	0.569607	-0.572770	2.303705
H	0.211480	0.968976	1.411611
C	0.808200	-0.685398	0.191261
H	0.677167	-0.122687	-0.728794
C	1.635287	-1.828639	0.092881
H	1.572587	-2.351515	-0.860268
C	1.847573	-2.742349	1.276752
H	2.201075	-2.193301	2.156383
H	0.922024	-3.263249	1.550548
H	2.589935	-3.493461	1.004567
C	3.298443	-1.044128	-0.324193
O	4.120700	-2.066273	-0.464248
B	3.952958	-2.985858	-1.679302
F	3.250518	-2.272277	-2.663679
F	5.213316	-3.348379	-2.082434
F	3.188202	-4.074767	-1.248603
H	3.017271	-0.542840	-1.254386
C	3.648991	-0.108535	0.787069
C	3.173025	1.208158	0.770708
C	4.441476	-0.536190	1.857665
C	3.465243	2.079266	1.818263
H	2.572849	1.551375	-0.066586
C	4.734881	0.336304	2.906148
H	4.831035	-1.547888	1.841473
C	4.244388	1.643925	2.893302
H	3.081023	3.095959	1.796648
H	5.352218	-0.003581	3.733134
H	4.473826	2.321254	3.711396
C	-3.339569	-0.521808	-0.619944
C	-3.659272	0.300299	0.494690
C	-6.518474	-0.595039	-1.274779
C	-4.901096	0.178344	1.321666
C	-6.269348	0.852583	-0.785704
C	-6.050073	1.020984	0.726493
H	-5.198463	-0.874704	1.369616
H	-6.841350	-1.226888	-0.435041
H	-7.128856	1.476614	-1.056633
H	-7.361886	-0.586354	-1.974762
H	-4.713131	0.497703	2.352585
H	-5.414801	1.278388	-1.327455
H	-6.972473	0.763829	1.262606
H	-5.854722	2.081187	0.932729
C	-4.141946	-1.687003	-1.125682
H	-4.502433	-2.287802	-0.282073
H	-3.485336	-2.339728	-1.711411

C	-5.344257	-1.276024	-2.000832
H	-4.992729	-0.623020	-2.811254
H	-5.719301	-2.188036	-2.481249
C	-2.672492	1.342223	0.564889
C	-2.151370	0.013322	-1.223334
C	-1.771663	1.206553	-0.534402
C	-0.645262	2.082092	-0.864941
C	0.053892	1.933186	-2.080100
C	-0.205347	3.076120	0.021160
C	1.150922	2.722152	-2.381263
H	-0.264593	1.187021	-2.800747
C	0.894599	3.879650	-0.267496
H	-0.716328	3.221124	0.967871
C	1.590930	3.698208	-1.471266
H	1.696100	2.596389	-3.310245
H	1.207800	4.628193	0.449686
H	-1.659482	-0.408081	-2.089175
H	-2.666978	2.136324	1.298849
O	2.683784	4.402242	-1.843860
C	3.264954	5.297954	-0.903809
H	4.148578	5.708285	-1.393238
H	2.577103	6.114034	-0.649521
H	3.564614	4.768230	0.008579

TS2'-a (1-butene + p-BrPhCHO)
B3LYP-D3 SCF energy (au): -4522.12472773
B3LYP-D3 enthalpy (au): -4521.49727373
B3LYP-D3 free energy (au): -4521.61425573
M06 SCF energy in toluene (au): -4523.94396709
M06 enthalpy in toluene (au): -4523.31651309
M06 free energy in toluene (au): -4523.43349509
M06 free energy in toluene (quasi-harmonic) (au): -4523.42400736
ωB97X-D SCF energy in toluene (au): -5664.806176
ωB97X-D enthalpy in toluene (au): -5664.178722
ωB97X-D free energy in toluene (au): -5664.295704
ωB97X-D free energy in toluene (quasi-harmonic) (au): -5664.286216
DLPNO-CCSD(T) SCF energy in toluene (au): -5659.228999
DLPNO-CCSD(T) enthalpy in toluene (au): -5658.601545
DLPNO-CCSD(T) free energy in toluene (au): -5658.718527
DLPNO-CCSD(T) free energy in toluene (quasi-harmonic) (au): -5658.709039

Cartesian coordinates

ATOM	X	Y	Z
Fe	2.509868	0.230729	0.801364
C	2.902699	1.887822	0.280770
O	3.203860	2.930435	-0.094296
C	3.093331	0.427949	2.456985
O	3.477944	0.509331	3.539362
C	0.614441	0.818954	1.618077
H	0.751996	1.701083	2.243430

H	0.281025	-0.064184	2.159830
C	0.037811	1.043559	0.344518
H	-0.368409	0.173174	-0.164515
C	-0.169275	2.287802	-0.273776
H	0.345917	3.135585	0.171807
C	-0.290233	2.357540	-1.777322
H	-0.737408	3.311364	-2.063724
H	-0.897579	1.534405	-2.172583
C	-1.914542	2.795480	0.434402
O	-2.152678	3.954659	-0.124981
B	-1.297591	5.175765	0.289624
F	-2.150873	6.245362	0.352938
F	-0.703457	4.873344	1.521967
F	-0.322325	5.308700	-0.697315
H	-1.614817	2.817007	1.484755
C	-2.858846	1.703929	0.064553
C	-3.045282	0.609054	0.917659
C	-3.551542	1.746420	-1.150781
C	-3.880612	-0.443826	0.555707
H	-2.527020	0.576689	1.872401
C	-4.381379	0.693339	-1.532694
H	-3.433589	2.615537	-1.787882
C	-4.527247	-0.397820	-0.678629
H	-4.027222	-1.292730	1.210659
H	-4.909191	0.718700	-2.479375
C	3.468759	-0.528672	-0.946749
C	3.982601	-1.174923	0.214590
C	5.395089	-2.086288	-2.561231
C	5.419525	-1.211277	0.650909
C	6.583110	-1.941081	-1.579125
C	6.280145	-2.247671	-0.101196
H	5.868765	-0.218025	0.529955
H	5.724276	-2.646615	-3.443949
H	7.017882	-0.934540	-1.658837
H	4.612359	-2.701000	-2.098067
H	5.454171	-1.435045	1.723576
H	7.378704	-2.628221	-1.889470
H	7.233660	-2.327421	0.435683
H	5.801249	-3.233784	-0.027990
C	4.296843	0.194887	-1.963017
H	5.159316	0.654137	-1.468402
H	3.724507	1.010088	-2.418173
C	4.779541	-0.771294	-3.066324
H	3.931838	-1.012626	-3.720195
H	5.510269	-0.237516	-3.686891
C	2.886509	-1.873653	0.829989
C	2.068960	-0.806162	-1.024243
C	1.708962	-1.680249	0.055585
C	0.384465	-2.248058	0.321161
C	-0.570471	-2.362386	-0.708152

C	0.026653	-2.690880	1.601408
C	-1.826621	-2.892350	-0.466063
H	-0.319595	-2.037756	-1.713354
C	-1.232148	-3.227769	1.861067
H	0.734562	-2.599176	2.419969
C	-2.167712	-3.330228	0.823415
H	-2.572791	-2.965865	-1.249302
H	-1.475037	-3.551128	2.865878
H	1.407442	-0.440332	-1.796706
H	2.962960	-2.483338	1.720475
O	-3.426303	-3.814181	0.967319
C	-3.845007	-4.245052	2.254803
H	-3.803940	-3.424989	2.983072
H	-4.878303	-4.571715	2.135278
H	-3.233324	-5.081889	2.614453
Br	-5.623398	-1.870660	-1.211660
H	0.703797	2.304273	-2.242608

TS2-a (1-butene + p-BrPhCHO)
B3LYP-D3 SCF energy (au): -4522.13233396
B3LYP-D3 enthalpy (au): -4521.50508196
B3LYP-D3 free energy (au): -4521.62197196
M06 SCF energy in toluene (au): -4523.94434550
M06 enthalpy in toluene (au): -4523.31709350
M06 free energy in toluene (au): -4523.43398350
M06 free energy in toluene (quasi-harmonic) (au): -4523.42452454
ωB97X-D SCF energy in toluene (au): -5664.806502
ωB97X-D enthalpy in toluene (au): -5664.17925
ωB97X-D free energy in toluene (au): -5664.29614
ωB97X-D free energy in toluene (quasi-harmonic) (au): -5664.286681
DLPNO-CCSD(T) SCF energy in toluene (au): -5659.229981
DLPNO-CCSD(T) enthalpy in toluene (au): -5658.602729
DLPNO-CCSD(T) free energy in toluene (au): -5658.719619
DLPNO-CCSD(T) free energy in toluene (quasi-harmonic) (au): -5658.71016

Cartesian coordinates

ATOM	X	Y	Z
Fe	2.419798	0.353674	0.465071
C	2.889229	1.811495	-0.437453
O	3.242363	2.709314	-1.061751
C	2.841242	1.009278	2.053854
O	3.123741	1.383857	3.104165
C	0.468061	1.097423	0.922210
H	0.560935	2.080007	1.373046
H	0.054861	0.325102	1.566679
C	0.026680	1.085983	-0.422274
H	-0.380578	0.149379	-0.798892
C	-0.088373	2.200702	-1.268629
H	0.466836	3.090780	-0.989794
C	-0.273381	1.993782	-2.751899

H	-0.907084	1.124013	-2.961681
H	0.693726	1.833537	-3.248853
C	-1.790058	2.950117	-0.474226
O	-1.494757	3.392299	0.717415
B	-0.573907	4.621311	0.864318
F	-0.622325	5.333639	-0.329965
F	-1.028031	5.321650	1.947768
F	0.729814	4.117997	1.067164
H	-1.825561	3.690201	-1.277618
C	-2.802515	1.867048	-0.546939
C	-3.448914	1.582458	-1.756356
C	-3.110414	1.101871	0.586499
C	-4.365457	0.537100	-1.848729
H	-3.240242	2.188024	-2.633393
C	-4.025922	0.056387	0.507894
H	-2.627445	1.344658	1.526079
C	-4.641722	-0.221396	-0.712860
H	-4.868184	0.320508	-2.784389
H	-4.267773	-0.534325	1.382857
C	3.525864	-0.868931	-0.895778
C	3.881697	-1.172777	0.449535
C	6.342888	-2.216959	-1.780679
C	5.276398	-1.160509	0.993155
C	5.843746	-3.116034	-0.623193
C	5.973025	-2.523123	0.789231
H	5.848697	-0.372165	0.492177
H	7.019225	-1.442285	-1.392176
H	6.406279	-4.056940	-0.630637
H	6.953726	-2.825649	-2.457483
H	5.271450	-0.910218	2.059913
H	4.798205	-3.396538	-0.804943
H	7.034455	-2.406318	1.043211
H	5.558530	-3.243789	1.506055
C	4.460913	-0.406501	-1.977212
H	5.168410	0.328196	-1.575102
H	3.878964	0.114189	-2.746177
C	5.252141	-1.552856	-2.640373
H	4.548562	-2.321443	-2.988573
H	5.727033	-1.139394	-3.538823
C	2.700597	-1.666716	1.103234
C	2.129703	-1.135970	-1.049803
C	1.620295	-1.677490	0.178062
C	0.248733	-2.121572	0.442053
C	-0.637051	-2.411799	-0.613732
C	-0.230312	-2.254250	1.752502
C	-1.941144	-2.809464	-0.369326
H	-0.294388	-2.331697	-1.640953
C	-1.536573	-2.657671	2.015574
H	0.419378	-2.017587	2.589615
C	-2.401980	-2.938095	0.950356

H	-2.631409	-3.020151	-1.178627
H	-1.870221	-2.741542	3.042652
H	1.569280	-0.986099	-1.961720
H	2.658962	-2.008305	2.128675
O	-3.690288	-3.332671	1.089327
C	-4.241028	-3.412477	2.394915
H	-5.286596	-3.689077	2.257606
H	-3.732184	-4.174811	2.998319
H	-4.186399	-2.445722	2.911702
Br	-5.905028	-1.648393	-0.835236
H	-0.730490	2.870852	-3.224551

43-a (Fp* instead of Fp^{W3})

B3LYP-D3 SCF energy (au): -897.431825206
B3LYP-D3 enthalpy (au): -897.066289206
B3LYP-D3 free energy (au): -897.143255206
M06 SCF energy in toluene (au): -897.012148836
M06 enthalpy in toluene (au): -896.646612836
M06 free energy in toluene (au): -896.723578836
M06 free energy in toluene (quasi-harmonic) (au): -896.720310630
M06 SCF energy in dichloromethane (au): -897.014288
M06 enthalpy in dichloromethane (au): -896.648752
M06 free energy in dichloromethane (au): -896.725718
M06 free energy in dichloromethane (quasi-harmonic) (au): -896.7224498

Cartesian coordinates

ATOM	X	Y	Z
C	-1.859934	-0.930432	-0.673316
C	-2.139284	0.456685	-0.550967
C	-1.801249	0.863491	0.794265
C	-1.354952	-0.293274	1.499575
C	-1.346580	-1.396432	0.595172
Fe	-0.062009	0.113311	-0.187748
C	0.435601	1.626446	-0.923487
O	0.700160	2.647981	-1.399331
C	0.958619	-0.954316	-1.141309
O	1.585744	-1.705046	-1.756718
C	-0.979882	-2.810709	0.933920
H	-0.637543	-3.358449	0.051216
H	-0.175564	-2.845553	1.674860
H	-1.837487	-3.356073	1.349985
C	-2.109232	-1.783952	-1.881772
H	-2.050599	-1.199111	-2.803909
H	-1.381667	-2.596800	-1.959272
H	-3.107843	-2.238167	-1.837596
C	-2.737926	1.339160	-1.606289
H	-3.831969	1.364268	-1.517483
H	-2.377879	2.368611	-1.524185
H	-2.494062	0.983083	-2.611036
C	-1.996009	2.231226	1.378116

H	-2.983919	2.326782	1.848214
H	-1.244437	2.447267	2.143390
H	-1.918860	3.008620	0.612533
C	-1.010017	-0.351949	2.954743
H	-0.267130	-1.125471	3.165472
H	-0.612077	0.599503	3.317012
H	-1.905987	-0.582689	3.545469
C	3.841518	-0.245227	0.469270
H	3.713776	-1.275662	0.808276
C	2.819277	0.609541	0.616675
H	2.958519	1.635100	0.265061
C	1.485353	0.282279	1.173281
H	1.146756	1.066227	1.859284
H	1.513162	-0.672986	1.707989
C	5.168792	0.094399	-0.144237
H	5.208467	1.146902	-0.446989
H	5.998044	-0.087621	0.553891
H	5.368715	-0.518978	-1.034176

41-a (Fp* instead of Fp^{W3})

B3LYP-D3 SCF energy (au): -897.847690040
B3LYP-D3 enthalpy (au): -897.468288040
B3LYP-D3 free energy (au): -897.544061040
M06 SCF energy in toluene (au): -897.457326206
M06 enthalpy in toluene (au): -897.077924206
M06 free energy in toluene (au): -897.153697206
M06 free energy in toluene (quasi-harmonic) (au): -897.151066166
M06 SCF energy in dichloromethane (au): -897.479032
M06 enthalpy in dichloromethane (au): -897.09963
M06 free energy in dichloromethane (au): -897.175403
M06 free energy in dichloromethane (quasi-harmonic) (au): -897.172772

Cartesian coordinates

ATOM	X	Y	Z
C	0.738646	1.013610	1.357365
C	1.654460	1.144861	0.243067
C	2.125053	-0.160070	-0.095247
C	1.487891	-1.107241	0.781341
C	0.671777	-0.369051	1.698700
Fe	0.003761	-0.048984	-0.351255
C	0.239968	-0.854624	-1.930611
O	0.443687	-1.375231	-2.930918
C	-0.747016	1.424809	-1.028799
O	-1.148925	2.417132	-1.438333
C	-0.061942	-0.955414	2.864133
H	-0.592983	-1.877407	2.609357
H	0.658445	-1.211578	3.650632
H	-0.776987	-0.252340	3.296219
C	0.093195	2.146217	2.097021
H	0.741440	2.481425	2.915816

H	-0.084761	3.006062	1.446532
H	-0.864836	1.853106	2.534200
C	2.140427	2.430438	-0.354694
H	2.386785	2.317607	-1.413531
H	1.405145	3.232645	-0.261009
H	3.050563	2.755405	0.164297
C	3.179003	-0.473690	-1.112905
H	4.167913	-0.390301	-0.645479
H	3.085010	-1.489495	-1.503459
H	3.154032	0.221650	-1.955554
C	1.767812	-2.577738	0.836205
H	0.933887	-3.135692	1.270344
H	1.972342	-2.991220	-0.154858
H	2.647160	-2.771942	1.462837
C	-1.537133	-1.617868	-0.165765
H	-1.838344	-2.022432	-1.128645
H	-1.038708	-2.318209	0.492713
C	-2.152222	-0.478216	0.309231
H	-2.063329	-0.243076	1.366328
C	-3.298739	0.194090	-0.405244
H	-3.301694	1.271073	-0.208360
H	-3.203342	0.057127	-1.488936
C	-4.631565	-0.408008	0.079469
H	-4.755141	-0.281720	1.160600
H	-5.469183	0.092365	-0.415225
H	-4.686994	-1.477304	-0.147784

TS2'-b (1-octene + p-BrPhCHO)
B3LYP-D3 SCF energy (au): -4679.40210017
B3LYP-D3 enthalpy (au): -4678.65434517
B3LYP-D3 free energy (au): -4678.78343517
M06 SCF energy in toluene (au): -4681.11224938
M06 enthalpy in toluene (au): -4680.36449438
M06 free energy in toluene (au): -4680.49358438
M06 free energy in toluene (quasi-harmonic) (au): -4680.48227921
ωB97X-D SCF energy in toluene (au): -5822.081381
ωB97X-D enthalpy in toluene (au): -5821.333626
ωB97X-D free energy in toluene (au): -5821.462716
ωB97X-D free energy in toluene (quasi-harmonic) (au): -5821.451411
DLPNO-CCSD(T) SCF energy in toluene (au): -5816.17264
DLPNO-CCSD(T) enthalpy in toluene (au): -5815.424885
DLPNO-CCSD(T) free energy in toluene (au): -5815.553975
DLPNO-CCSD(T) free energy in toluene (quasi-harmonic) (au): -5815.54267

Cartesian coordinates

ATOM	X	Y	Z
Fe	-2.251594	-0.606096	-1.291065
C	-2.863089	1.065056	-1.364478
O	-3.310521	2.121975	-1.397344
C	-2.648806	-0.988922	-2.968329

O	-2.907655	-1.285129	-4.050869
C	-0.342830	-0.035406	-2.082499
H	-0.497480	0.629359	-2.932567
H	0.119542	-0.986624	-2.340725
C	0.103069	0.577770	-0.885973
H	0.540487	-0.081546	-0.140876
C	0.154425	1.953732	-0.611391
H	-0.411807	2.594261	-1.283671
C	0.174824	2.424139	0.827001
H	0.780514	3.332627	0.890936
H	0.646260	1.661147	1.463459
C	1.870578	2.461968	-1.373748
O	1.953456	3.744777	-1.122762
B	0.962214	4.713389	-1.805443
F	1.668535	5.845134	-2.112215
F	0.446082	4.062402	-2.933386
F	-0.054394	4.941159	-0.873542
H	1.628827	2.182727	-2.402093
C	2.899801	1.617054	-0.705137
C	3.230248	0.357807	-1.221897
C	3.524667	2.057147	0.467012
C	4.140501	-0.466236	-0.566769
H	2.764890	0.014891	-2.142136
C	4.430560	1.238575	1.139632
H	3.294410	3.047980	0.841083
C	4.720659	-0.021522	0.620812
H	4.396541	-1.440503	-0.962255
H	4.907213	1.573945	2.053804
C	-3.318728	-0.926802	0.530315
C	-3.650715	-1.937476	-0.418564
C	-5.249323	-2.153652	2.402416
C	-5.026979	-2.267014	-0.921588
C	-6.338008	-2.447301	1.341214
C	-5.858731	-3.132497	0.048239
H	-5.575363	-1.341879	-1.136620
H	-5.615129	-2.463514	3.388182
H	-6.873576	-1.522259	1.084367
H	-4.369613	-2.780001	2.204931
H	-4.933623	-2.797451	-1.876531
H	-7.091486	-3.106290	1.787950
H	-6.741530	-3.479376	-0.503337
H	-5.284488	-4.032284	0.308674
C	-4.313600	-0.039999	1.213515
H	-5.159743	0.138692	0.541587
H	-3.875903	0.937877	1.435384
C	-4.813495	-0.684423	2.523357
H	-4.017885	-0.616355	3.276360
H	-5.650211	-0.081791	2.898584
C	-2.440934	-2.656239	-0.712998
C	-1.916401	-1.010626	0.791413

C	-1.371162	-2.112651	0.050539
C	0.019379	-2.576002	0.060015
C	0.872141	-2.278228	1.141141
C	0.544686	-3.318861	-1.005386
C	2.190611	-2.701450	1.152763
H	0.491969	-1.711510	1.985665
C	1.867588	-3.755227	-1.007202
H	-0.082121	-3.547614	-1.862357
C	2.699126	-3.446933	0.077212
H	2.857531	-2.459737	1.972816
H	2.239502	-4.321203	-1.852572
H	-1.372266	-0.366665	1.466697
H	-2.371129	-3.502442	-1.383590
O	4.003069	-3.804681	0.172957
C	4.593368	-4.518460	-0.903633
H	4.547892	-3.942726	-1.837066
H	5.635847	-4.668300	-0.621835
H	4.107802	-5.491043	-1.052767
C	-1.233291	2.750881	1.340525
H	-1.888225	1.878842	1.207954
H	-1.643451	3.552186	0.715069
C	-1.256868	3.172679	2.810978
H	-0.787619	2.390162	3.427560
H	-0.639775	4.072697	2.938362
C	-2.671134	3.444880	3.333687
H	-3.143250	4.214971	2.708802
H	-3.282001	2.537060	3.212852
C	-2.696666	3.882817	4.800080
H	-3.719408	4.066767	5.148152
H	-2.254306	3.116496	5.448822
H	-2.123635	4.806667	4.942625
Br	5.930701	-1.166912	1.557085

TS2-b (1-octene + p-BrPhCHO)
B3LYP-D3 SCF energy (au): -4679.40823381
B3LYP-D3 enthalpy (au): -4678.66067781
B3LYP-D3 free energy (au): -4678.78953781
M06 SCF energy in toluene (au): -4681.11260254
M06 enthalpy in toluene (au): -4680.36504654
M06 free energy in toluene (au): -4680.49390654
M06 free energy in toluene (quasi-harmonic) (au): -4680.48275373
ωB97X-D SCF energy in toluene (au): -5822.081808
ωB97X-D enthalpy in toluene (au): -5821.334252
ωB97X-D free energy in toluene (au): -5821.463112
ωB97X-D free energy in toluene (quasi-harmonic) (au): -5821.451959
DLPNO-CCSD(T) SCF energy in toluene (au): -5816.17351
DLPNO-CCSD(T) enthalpy in toluene (au): -5815.425954
DLPNO-CCSD(T) free energy in toluene (au): -5815.554814
DLPNO-CCSD(T) free energy in toluene (quasi-harmonic) (au): -5815.543661

Cartesian coordinates

ATOM	X	Y	Z
Fe	-2.146591	-0.292257	-1.150947
C	-2.802718	1.346814	-0.943748
O	-3.287149	2.376143	-0.781434
C	-2.381106	-0.315761	-2.903903
O	-2.536340	-0.385925	-4.041657
C	-0.187839	0.403981	-1.654892
H	-0.267639	1.146267	-2.442418
H	0.332409	-0.511496	-1.926572
C	0.091171	0.917359	-0.366439
H	0.489162	0.217103	0.366458
C	0.066842	2.269822	0.013956
H	-0.490448	2.950066	-0.623645
C	0.073446	2.626064	1.482700
H	0.479560	3.637656	1.620899
H	0.739634	1.942835	2.028095
C	1.816666	2.810896	-0.832252
O	1.645859	2.772523	-2.125773
B	0.698948	3.788258	-2.795979
F	0.570841	4.879181	-1.941056
F	1.250609	4.095869	-4.009206
F	-0.547970	3.139104	-2.930182
H	1.735384	3.790808	-0.355452
C	2.849263	1.901927	-0.273871
C	3.354539	2.111831	1.015321
C	3.308790	0.805126	-1.015867
C	4.274443	1.227801	1.575242
H	3.027971	2.975493	1.587026
C	4.229345	-0.084239	-0.468956
H	2.935005	0.664543	-2.023595
C	4.697279	0.130471	0.827666
H	4.664948	1.390855	2.573266
H	4.583705	-0.935258	-1.037235
C	-3.324444	-1.007351	0.488847
C	-3.558798	-1.791754	-0.678495
C	-6.162198	-2.105232	1.618262
C	-4.904675	-2.056006	-1.278029
C	-5.543341	-3.328600	0.898610
C	-5.575703	-3.290527	-0.638029
H	-5.538392	-1.173751	-1.136368
H	-6.828875	-1.562108	0.933350
H	-6.075556	-4.235243	1.209399
H	-6.806100	-2.465496	2.429019
H	-4.820980	-2.207227	-2.360099
H	-4.507969	-3.464517	1.236912
H	-6.616329	-3.332837	-0.984675
H	-5.084326	-4.196392	-1.016239
C	-4.359148	-0.240921	1.263365
H	-5.054302	0.254013	0.574986

H	-3.860941	0.556815	1.824768
C	-5.165413	-1.114140	2.246172
H	-4.469054	-1.663301	2.894705
H	-5.723397	-0.432294	2.900019
C	-2.313956	-2.418900	-1.028166
C	-1.940671	-1.122592	0.821050
C	-1.312143	-2.030506	-0.096382
C	0.094453	-2.443467	-0.097192
C	0.906145	-2.264626	1.039619
C	0.682784	-3.004873	-1.238626
C	2.244185	-2.623620	1.031895
H	0.479640	-1.844125	1.945350
C	2.024623	-3.375272	-1.261825
H	0.091836	-3.135088	-2.140149
C	2.815172	-3.183759	-0.121392
H	2.878019	-2.471900	1.898478
H	2.443343	-3.797982	-2.166924
H	-1.462631	-0.631213	1.655441
H	-2.176530	-3.098521	-1.858474
O	4.131285	-3.496655	-0.036751
C	4.785702	-3.999908	-1.191509
H	5.829444	-4.131985	-0.905198
H	4.363636	-4.963589	-1.503515
H	4.724475	-3.290223	-2.026663
Br	5.949301	-1.090055	1.596749
C	-1.331216	2.569044	2.105287
H	-1.749640	1.567347	1.939561
H	-1.992724	3.262731	1.570477
C	-1.355698	2.881180	3.602924
H	-0.666295	2.204386	4.129734
H	-0.973208	3.897839	3.772010
C	-2.755017	2.754732	4.214905
H	-3.130993	1.734628	4.044699
H	-3.443211	3.425595	3.682337
C	-2.787542	3.066988	5.712961
H	-3.798605	2.965728	6.122938
H	-2.129951	2.389639	6.271484
H	-2.448873	4.091574	5.907790

PhCHO-BF3 (46)
B3LYP-D3 SCF energy (au): -670.167169539
B3LYP-D3 enthalpy (au): -670.030215539
B3LYP-D3 free energy (au): -670.079772539
M06 SCF energy in toluene (au): -669.997014046
M06 enthalpy in toluene (au): -669.860060046
M06 free energy in toluene (au): -669.909617046
M06 free energy in toluene (quasi-harmonic) (au): -669.911057507

Cartesian coordinates
ATOMX Y Z

C	3.917640	0.274599	-0.000008
C	3.025830	1.355258	0.000019
C	1.657278	1.123876	0.000032
C	1.176910	-0.199292	0.000021
C	2.075549	-1.279644	-0.000011
C	3.446160	-1.040966	-0.000023
H	4.987566	0.461667	-0.000020
H	3.405694	2.372003	0.000030
H	0.944305	1.941383	0.000050
H	1.692375	-2.296604	-0.000024
H	4.144929	-1.871299	-0.000046
C	-0.244936	-0.476283	0.000034
H	-0.579503	-1.520101	0.000101
O	-1.102888	0.420756	-0.000010
B	-2.768294	0.030691	-0.000011
F	-3.186322	0.606154	1.152148
F	-3.186132	0.605783	-1.152427
F	-2.767255	-1.339920	0.000241

PhCHO
B3LYP-D3 SCF energy (au): -345.590832665
B3LYP-D3 enthalpy (au): -345.473262665
B3LYP-D3 free energy (au): -345.510999665
M06 SCF energy in toluene (au): -345.422011338
M06 enthalpy in toluene (au): -345.304441338
M06 free energy in toluene (au): -345.342178338
M06 free energy in toluene (quasi-harmonic) (au): -345.344749673

Cartesian coordinates

ATOM	X	Y	Z
C	2.214948	-0.251977	-0.000001
C	1.323746	-1.331755	-0.000001
C	-0.047122	-1.100459	0.000002
C	-0.533240	0.215416	0.000003
C	0.361355	1.292489	-0.000000
C	1.735649	1.059823	-0.000001
H	3.285754	-0.435585	-0.000000
H	1.704679	-2.348888	-0.000003
H	-0.762973	-1.916276	0.000002
H	-0.025013	2.309325	-0.000005
H	2.430770	1.894177	0.000001
C	-1.989924	0.469552	0.000004
H	-2.271086	1.546507	-0.000004
O	-2.844326	-0.395974	-0.000003

45'-a (Alkoxytrifluoroborate after dissociation from 45')
B3LYP-D3 SCF energy (au): -826.889875291
B3LYP-D3 enthalpy (au): -826.647646291
B3LYP-D3 free energy (au): -826.707409291
M06 SCF energy in toluene (au): -826.675389221

M06 enthalpy in toluene (au): -826.433160221
M06 free energy in toluene (au): -826.492923221
M06 free energy in toluene (quasi-harmonic) (au): -826.495792930

Cartesian coordinates

ATOM	X	Y	Z
C	-3.064991	1.704184	0.173482
H	-2.980105	0.699431	0.575880
H	-4.042100	2.184238	0.223695
C	-2.042010	2.338001	-0.401444
H	-2.211377	3.337731	-0.814721
C	-0.608642	1.868496	-0.531406
H	-0.383854	1.769026	-1.605841
C	0.315216	2.960774	0.039489
H	0.073739	3.938144	-0.398295
H	0.187032	3.046626	1.126084
H	1.368737	2.746790	-0.159988
C	-0.360631	0.463028	0.079489
O	-1.106139	-0.457919	-0.651949
B	-1.535824	-1.660772	0.080436
F	-2.409328	-1.278726	1.142890
F	-2.208246	-2.487394	-0.820018
F	-0.428571	-2.323630	0.645522
H	-0.684882	0.497159	1.133381
C	1.126425	0.116676	0.061370
C	1.683877	-0.466356	-1.081561
C	1.965539	0.397818	1.143437
C	3.048980	-0.738649	-1.149933
H	1.012866	-0.728084	-1.892957
C	3.333640	0.124273	1.083583
H	1.537724	0.828527	2.046309
C	3.883303	-0.440357	-0.068487
H	3.465127	-1.196499	-2.045273
H	3.968520	0.344031	1.939815
H	4.947863	-0.659480	-0.118347

45'-b (product alcohol from 45'-a)
B3LYP-D3 SCF energy (au): -502.830082498
B3LYP-D3 enthalpy (au): -502.593318498
B3LYP-D3 free energy (au): -502.643731498
M06 SCF energy in toluene (au): -502.563043803
M06 enthalpy in toluene (au): -502.326279803
M06 free energy in toluene (au): -502.376692803
M06 free energy in toluene (quasi-harmonic) (au): -502.380765305

Cartesian coordinates

ATOM	X	Y	Z
C	3.725890	-0.131589	-0.592360
H	3.244761	-0.272794	-1.557272
H	4.809154	-0.211401	-0.582152

C	3.041297	0.138959	0.522955
H	3.599672	0.282111	1.448962
C	1.544142	0.328322	0.655011
H	1.228001	-0.154798	1.590622
C	1.232142	1.831442	0.766986
H	1.835004	2.293791	1.556080
H	1.468049	2.342780	-0.173505
H	0.176637	1.998771	0.997459
C	0.748290	-0.362435	-0.478943
O	1.041230	-1.755462	-0.519604
H	1.024728	0.116984	-1.433191
C	-0.744422	-0.208308	-0.288445
C	-1.426802	-1.036063	0.610452
C	-1.455116	0.782813	-0.971532
C	-2.793223	-0.866309	0.828583
H	-0.879167	-1.823863	1.116912
C	-2.822170	0.958417	-0.751316
H	-0.934287	1.420536	-1.681772
C	-3.494754	0.134122	0.151491
H	-3.313464	-1.518242	1.525173
H	-3.361409	1.732535	-1.290340
H	-4.559907	0.264834	0.321154
H	2.000746	-1.843773	-0.398590

45-a (Alkoxytrifluoroborate after dissociation from 45)
B3LYP-D3 SCF energy (au): -826.895073933
B3LYP-D3 enthalpy (au): -826.652736933
B3LYP-D3 free energy (au): -826.713799933
M06 SCF energy in toluene (au): -826.677119434
M06 enthalpy in toluene (au): -826.434782434
M06 free energy in toluene (au): -826.495845434
M06 free energy in toluene (quasi-harmonic) (au): -826.498228501

Cartesian coordinates

ATOM	X	Y	Z
C	-2.395570	3.144446	-0.541768
H	-1.707885	3.964229	-0.752213
H	-3.444294	3.323172	-0.770845
C	-1.972851	1.983461	-0.036709
H	-2.671316	1.168089	0.144103
C	-0.538381	1.673990	0.297435
H	0.105935	2.420867	-0.188656
C	-0.304925	1.738665	1.815624
H	-0.569804	2.727446	2.208187
H	-0.916250	0.980075	2.311086
H	0.745896	1.534698	2.053964
C	-0.163684	0.255472	-0.246120
O	-0.812364	-0.722900	0.494750
B	-1.830358	-1.578264	-0.145894
F	-1.480029	-1.840363	-1.485884

F	-1.900420	-2.761064	0.594456
F	-3.095037	-0.930016	-0.127364
C	1.350151	0.056377	-0.197536
C	2.216054	0.857806	-0.953080
C	1.900713	-0.938796	0.615669
C	3.598197	0.678540	-0.891735
H	1.801669	1.624620	-1.604691
C	3.283275	-1.119982	0.682473
H	1.209945	-1.563039	1.171694
C	4.139727	-0.311436	-0.067692
H	4.253528	1.308249	-1.490453
H	3.694594	-1.900270	1.319915
H	5.217077	-0.454644	-0.017975
H	-0.465244	0.212748	-1.302889

45-b (product alcohol from 45-a)

B3LYP-D3 SCF energy (au): -502.829726107
B3LYP-D3 enthalpy (au): -502.593147107
B3LYP-D3 free energy (au): -502.644642107
M06 SCF energy in toluene (au): -502.563000124
M06 enthalpy in toluene (au): -502.326421124
M06 free energy in toluene (au): -502.377916124
M06 free energy in toluene (quasi-harmonic) (au): -502.381442017

Cartesian coordinates

ATOM	X	Y	Z
C	-3.862957	1.055655	-0.298188
H	-3.521909	2.084910	-0.392165
H	-4.901140	0.863303	-0.555099
C	-3.048091	0.086671	0.121307
H	-3.440245	-0.927837	0.220101
C	-1.593815	0.266974	0.478797
H	-1.400971	1.339776	0.610096
C	-1.252418	-0.474003	1.777877
H	-1.924324	-0.166761	2.585901
H	-1.355165	-1.555092	1.635561
H	-0.222755	-0.271964	2.085910
C	-0.695351	-0.199021	-0.709831
O	-0.929427	-1.566841	-1.029087
C	0.775239	-0.016248	-0.409373
C	1.317024	1.274349	-0.384639
C	1.602265	-1.105174	-0.118873
C	2.659210	1.476776	-0.067391
H	0.684140	2.127078	-0.621125
C	2.947394	-0.903979	0.195791
H	1.184712	-2.104696	-0.149521
C	3.479873	0.385327	0.225584
H	3.065703	2.484377	-0.055098
H	3.580821	-1.758811	0.417095
H	4.527130	0.539718	0.469995

H	-0.957382	0.433809	-1.572347
H	-1.853447	-1.637053	-1.312981

BF$_3$•TMPH
B3LYP-D3 SCF energy (au): -733.798851669
B3LYP-D3 enthalpy (au): -733.493713669
B3LYP-D3 free energy (au): -733.549751669
M06 SCF energy in toluene (au): -733.548047902
M06 enthalpy in toluene (au): -733.242909902
M06 free energy in toluene (au): -733.298947902
M06 free energy in toluene (quasi-harmonic) (au): -733.304744233

Cartesian coordinates

ATOM	X	Y	Z
B	-1.859768	-0.000005	-0.029628
F	-2.195811	1.134219	0.674705
F	-2.335836	0.000156	-1.325409
F	-2.195910	-1.134355	0.674448
N	-0.143974	-0.000040	-0.320437
C	0.586303	1.317490	-0.007967
C	0.586307	-1.317465	-0.007976
C	2.036654	1.240342	-0.526564
C	-0.123672	2.431974	-0.797658
C	0.562274	1.642088	1.491427
C	2.036676	-1.240324	-0.526563
C	-0.123630	-2.432024	-0.797624
C	0.562283	-1.642064	1.491418
C	2.796339	0.000011	-0.068701
H	2.549831	2.156403	-0.212318
H	2.018741	1.255629	-1.626244
H	-1.115509	2.641268	-0.403543
H	0.482080	3.342197	-0.739398
H	-0.218384	2.164535	-1.857194
H	0.888666	2.679213	1.622937
H	-0.444709	1.547587	1.894054
H	1.239874	1.012830	2.070284
H	2.018764	-1.255609	-1.626244
H	2.549853	-2.156381	-0.212315
H	0.482119	-3.342243	-0.739283
H	-1.115478	-2.641282	-0.403518
H	-0.218304	-2.164648	-1.857180
H	-0.444741	-1.547766	1.894000
H	0.888872	-2.679124	1.622939
H	1.239720	-1.012668	2.070315
H	2.922428	0.000010	1.019927
H	3.805432	0.000026	-0.496426
H	-0.191801	-0.000017	-1.342034

TMPH$_2^+$
B3LYP-D3 SCF energy (au): -409.601310687

B3LYP-D3 enthalpy (au): -409.302015687
B3LYP-D3 free energy (au): -409.348895687
M06 SCF energy in toluene (au): -409.393484027
M06 enthalpy in toluene (au): -409.094189027
M06 free energy in toluene (au): -409.141069027
M06 free energy in toluene (quasi-harmonic) (au): -409.147804340
M06 SCF energy in dichloromethane (au): -409.422639
M06 enthalpy in dichloromethane (au): -409.123344
M06 free energy in dichloromethane (au): -409.170224
M06 free energy in dichloromethane (quasi-harmonic) (au): -409.1769593

Cartesian coordinates

ATOM	X	Y	Z
C	1.260288	1.256288	-0.437650
C	0.000011	1.959041	0.077812
C	-1.260353	1.256326	-0.437534
C	-1.354883	-0.221718	-0.030257
C	1.354872	-0.221713	-0.030259
H	-2.163516	1.755911	-0.072909
H	0.000053	2.006577	1.172170
H	0.000002	2.995724	-0.271265
H	1.288607	1.325554	-1.533758
H	2.163521	1.755928	-0.073275
H	-1.288861	1.325733	-1.533621
C	-2.400120	-0.967066	-0.866805
H	-2.465049	-2.025727	-0.590283
H	-3.382874	-0.520535	-0.693088
H	-2.192333	-0.892095	-1.940886
C	-1.641347	-0.419634	1.459662
H	-2.682532	-0.142579	1.645906
H	-1.525461	-1.467491	1.758955
H	-1.018451	0.198228	2.105355
C	2.400159	-0.967067	-0.866755
H	3.382890	-0.520480	-0.693034
H	2.465112	-2.025708	-0.590175
H	2.192399	-0.892175	-1.940845
C	1.641366	-0.419546	1.459661
H	1.525614	-1.467409	1.758981
H	2.682517	-0.142352	1.645899
H	1.018418	0.198248	2.105363
N	0.000001	-0.881881	-0.396997
H	-0.000024	-1.840223	-0.029515
H	0.000005	-0.981431	-1.418251

TMPH
B3LYP-D3 SCF energy (au): -409.204234712
B3LYP-D3 enthalpy (au): -408.920257712
B3LYP-D3 free energy (au): -408.966777712
M06 SCF energy in toluene (au): -408.958146722
M06 enthalpy in toluene (au): -408.674169722

M06 free energy in toluene (au): -408.720689722
M06 free energy in toluene (quasi-harmonic) (au): -408.727085010
M06 SCF energy in dichloromethane (au): -408.960582
M06 enthalpy in dichloromethane (au): -408.676605
M06 free energy in dichloromethane (au): -408.723125
M06 free energy in dichloromethane (quasi-harmonic) (au): -408.7295203

Cartesian coordinates

ATOM	X	Y	Z
C	1.253787	1.237395	-0.430464
C	0.000010	1.948203	0.087157
C	-1.253921	1.237411	-0.430177
C	-1.286611	-0.256635	-0.053688
C	1.286720	-0.256556	-0.053585
H	-2.162614	1.723457	-0.054256
H	0.000152	1.974858	1.184158
H	-0.000040	2.993861	-0.243964
H	1.272811	1.315091	-1.525406
H	2.162614	1.723680	-0.055190
H	-1.273544	1.315664	-1.525073
C	-2.362082	-0.967170	-0.891525
H	-2.420339	-2.031653	-0.629248
H	-3.350618	-0.527074	-0.716905
H	-2.120991	-0.892133	-1.955933
C	-1.651002	-0.435493	1.439227
H	-2.692412	-0.141639	1.617921
H	-1.545351	-1.486456	1.734269
H	-1.022570	0.161904	2.103013
C	2.362319	-0.967044	-0.891247
H	3.350814	-0.526937	-0.716410
H	2.420550	-2.031549	-0.629030
H	2.121510	-0.891996	-1.955722
C	1.650794	-0.435404	1.439311
H	1.545621	-1.486527	1.734069
H	2.692008	-0.141139	1.618469
H	1.021785	0.161407	2.103021
N	0.000066	-0.856251	-0.451603
H	0.000061	-1.847312	-0.216614

TS1
B3LYP-D3 SCF energy (au): -1690.76704946
B3LYP-D3 enthalpy (au): -1689.97436046
B3LYP-D3 free energy (au): -1690.08772846
M06 SCF energy in toluene (au): -1689.90825477
M06 enthalpy in toluene (au): -1689.11556577
M06 free energy in toluene (au): -1689.22893377
M06 free energy in toluene (quasi-harmonic) (au): -1689.22133431
M06 SCF energy in dichloromethane (au): -1689.927515
M06 enthalpy in dichloromethane (au): -1689.134826
M06 free energy in dichloromethane (au): -1689.248194

M06 free energy in dichloromethane (quasi-harmonic) (au): -1689.240595

Cartesian coordinates

ATOM	X	Y	Z
C	-3.554469	-0.275982	-0.684018
C	-3.826493	0.116324	0.655447
C	-6.182182	0.844069	-1.451866
C	-5.028405	-0.271759	1.468354
C	-6.949132	0.313408	-0.216297
C	-6.287158	0.563925	1.150316
H	-5.254857	-1.333520	1.314479
H	-6.883372	1.363657	-2.114278
H	-7.154230	-0.760508	-0.330108
H	-5.460506	1.608086	-1.133326
H	-4.787651	-0.156490	2.531217
H	-7.932367	0.795491	-0.183153
H	-7.021600	0.344998	1.934544
H	-6.044013	1.630882	1.245200
C	-4.461759	-1.106917	-1.536637
H	-5.003364	-1.816113	-0.902128
H	-3.884693	-1.702009	-2.252634
C	-5.465216	-0.216472	-2.302660
H	-4.936524	0.290696	-3.119740
H	-6.206541	-0.874343	-2.772448
C	-2.786694	1.025255	1.059056
C	-2.350913	0.389036	-1.096603
C	-1.906698	1.246016	-0.040333
C	-0.737541	2.127751	-0.075288
C	-0.130286	2.464745	-1.301666
C	-0.162060	2.632755	1.099404
C	1.022506	3.230813	-1.345205
H	-0.573967	2.129140	-2.233691
C	0.996091	3.406148	1.071800
H	-0.610366	2.405081	2.061656
C	1.610983	3.688976	-0.155198
H	1.490558	3.490900	-2.288379
H	1.416758	3.765348	2.002853
H	-1.896647	0.292326	-2.072972
H	-2.735800	1.513442	2.022884
O	2.773370	4.371454	-0.296786
C	3.352770	4.973317	0.858727
H	2.656669	5.679009	1.326171
H	3.655818	4.216345	1.592678
H	4.233242	5.508850	0.503622
Fe	-1.945974	-0.878388	0.571347
C	-1.805570	-2.421396	-0.297072
C	-2.185372	-1.588303	2.179077
O	-2.355762	-2.017091	3.232035
O	-1.743719	-3.406379	-0.888225
C	0.129219	-0.816961	1.122657

H	0.396358	-1.674671	1.740213
H	0.171029	0.131143	1.652101
C	0.615894	-0.833775	-0.206107
H	0.527850	0.096775	-0.762985
C	1.295353	-1.879381	-0.857873
H	1.267812	-2.842478	-0.338680
C	1.239010	-1.983919	-2.376765
H	1.293019	-0.992657	-2.843017
H	2.070751	-2.582157	-2.766418
H	0.312151	-2.462425	-2.714589
H	2.599245	-1.480220	-0.647380
N	3.973005	-1.262037	-0.652268
C	4.303166	0.201091	-0.469309
C	4.654666	-2.305412	0.200194
C	5.833006	0.376809	-0.407071
C	3.741748	0.919253	-1.704078
C	3.628969	0.778576	0.783916
C	6.169422	-2.022888	0.257403
C	4.406914	-3.650813	-0.497290
C	4.031966	-2.348649	1.603647
C	6.501922	-0.567167	0.596017
H	6.054806	1.423630	-0.169082
H	6.250082	0.187349	-1.406191
H	2.653944	0.823282	-1.763501
H	3.975834	1.986383	-1.649228
H	4.179637	0.524688	-2.629127
H	2.565287	0.536431	0.821388
H	4.090211	0.438431	1.711389
H	3.719502	1.867543	0.749093
H	6.607065	-2.266486	-0.720872
H	6.625090	-2.706911	0.982367
H	3.343319	-3.906328	-0.519426
H	4.783659	-3.640862	-1.527493
H	4.933671	-4.446703	0.037170
H	2.939430	-2.370410	1.551495
H	4.363693	-3.259123	2.111680
H	4.326714	-1.503393	2.226294
H	6.188252	-0.327966	1.618879
H	7.587090	-0.423591	0.569492
H	4.219190	-1.482874	-1.619436

TS1'
B3LYP-D3 SCF energy (au): -1690.76646273
B3LYP-D3 enthalpy (au): -1689.97365473
B3LYP-D3 free energy (au): -1690.08684573
M06 SCF energy in toluene (au): -1689.90788365
M06 enthalpy in toluene (au): -1689.11507565
M06 free energy in toluene (au): -1689.22826665
M06 free energy in toluene (quasi-harmonic) (au): -1689.22083692

Cartesian coordinates

ATOM	X	Y	Z
C	3.614887	-0.079081	0.767004
C	3.824279	0.307646	-0.585667
C	6.111070	1.352696	1.460394
C	5.049410	0.028435	-1.408148
C	6.915018	0.875590	0.226628
C	6.209625	1.010083	-1.134571
H	5.397209	-0.995260	-1.226247
H	6.758867	1.966709	2.095821
H	7.241419	-0.164660	0.366305
H	5.303633	2.021692	1.133879
H	4.782805	0.083443	-2.469579
H	7.837042	1.463843	0.162637
H	6.952599	0.852130	-1.925334
H	5.845786	2.039469	-1.254590
C	4.622384	-0.775250	1.627885
H	5.230902	-1.437932	1.003612
H	4.126630	-1.410946	2.369364
C	5.530133	0.243643	2.351978
H	4.959375	0.712081	3.163882
H	6.347373	-0.312787	2.826971
C	2.683761	1.072325	-1.000420
C	2.355506	0.475830	1.183750
C	1.801950	1.239960	0.114131
C	0.545484	1.992695	0.144142
C	-0.174968	2.147645	1.346470
C	-0.002468	2.552584	-1.018829
C	-1.403681	2.784345	1.371816
H	0.233160	1.764039	2.275917
C	-1.234506	3.203210	-1.008390
H	0.531340	2.474720	-1.960628
C	-1.957392	3.298478	0.187815
H	-1.959683	2.898311	2.296009
H	-1.626275	3.612240	-1.931394
H	1.934430	0.363436	2.173282
H	2.563516	1.509460	-1.982117
O	-3.193416	3.841585	0.303858
C	-3.770643	4.465606	-0.840593
H	-3.936133	3.740043	-1.646366
H	-4.728217	4.866383	-0.507955
H	-3.137794	5.282494	-1.205665
Fe	2.059422	-0.889151	-0.432885
C	1.924503	-2.313741	0.621734
C	2.511218	-1.779347	-1.898252
O	2.816207	-2.332346	-2.858796
O	1.898736	-3.198858	1.356510
C	0.065900	-0.950870	-1.249307
H	-0.061408	-1.766515	-1.957952
H	0.039704	0.031380	-1.711841

C	-0.578781	-1.087600	0.002221
H	-0.600809	-0.197082	0.625433
C	-1.297667	-2.193792	0.500820
H	-2.589209	-1.740719	0.276760
N	-3.956534	-1.534748	0.118743
C	-4.568098	-1.076558	1.422033
C	-4.258992	-0.784934	-1.157674
C	-6.070569	-0.792872	1.221014
C	-4.395032	-2.241827	2.407201
C	-3.826017	0.152769	1.968040
C	-5.777509	-0.547542	-1.262253
C	-3.781657	-1.689105	-2.301880
C	-3.486253	0.539673	-1.224819
C	-6.366119	0.085025	0.002201
H	-6.464655	-0.336548	2.136281
H	-6.593111	-1.752073	1.099597
H	-3.340633	-2.443917	2.616903
H	-4.886794	-2.000450	3.354090
H	-4.854462	-3.160619	2.022648
H	-4.124216	0.311079	3.009080
H	-2.742807	0.003238	1.948701
H	-4.049048	1.070510	1.423349
H	-6.274645	-1.510688	-1.445300
H	-5.974081	0.077746	-2.140975
H	-4.051929	-1.243206	-3.263623
H	-2.694795	-1.815458	-2.281084
H	-4.249391	-2.680017	-2.254244
H	-2.430592	0.405271	-0.985833
H	-3.544913	0.924294	-2.248270
H	-3.888970	1.306876	-0.564738
H	-5.965810	1.095089	0.149590
H	-7.448989	0.199773	-0.112509
H	-4.295812	-2.487353	-0.031876
H	-1.342343	-2.234210	1.593607
C	-1.240883	-3.556628	-0.167591
H	-2.024532	-4.212232	0.227918
H	-1.385254	-3.487980	-1.251141
H	-0.283286	-4.061543	0.005569

TS2-1

B3LYP-D3 SCF energy (au): -1951.32290113
B3LYP-D3 enthalpy (au): -1950.68696713
B3LYP-D3 free energy (au): -1950.79839313
M06 SCF energy in toluene (au): -1950.52298571
M06 enthalpy in toluene (au): -1949.88705171
M06 free energy in toluene (au): -1949.99847771
M06 free energy in toluene (quasi-harmonic) (au): -1949.99034758

Cartesian coordinates
ATOMX Y Z

Fe	-1.656571	0.633204	-0.417380
C	-1.718190	2.078727	0.619156
O	-1.823494	2.973165	1.332122
C	-1.889997	1.511153	-1.936726
O	-2.066213	2.035704	-2.945101
C	0.416260	0.879595	-0.847585
H	0.570329	1.887924	-1.217097
H	0.611644	0.085516	-1.564806
C	0.877341	0.640499	0.468251
H	1.047984	-0.397095	0.747009
C	1.296330	1.606884	1.398570
H	0.937148	2.621117	1.260678
C	1.514488	1.196722	2.835777
H	1.952187	0.193900	2.904977
H	2.181298	1.896697	3.352200
H	0.566681	1.190962	3.391721
C	3.043113	2.049140	0.554685
O	2.783540	2.722008	-0.537180
B	2.121216	4.105058	-0.447336
F	2.331487	4.600841	0.837557
F	2.672699	4.875818	-1.434109
F	0.737969	3.894008	-0.654398
H	3.317688	2.635707	1.435828
C	3.789004	0.775440	0.368150
C	4.447755	0.170994	1.446071
C	3.824349	0.159052	-0.890994
C	5.119011	-1.039985	1.273912
H	4.445169	0.658533	2.417094
C	4.488699	-1.052518	-1.059408
H	3.335602	0.652307	-1.723030
C	5.139048	-1.655258	0.020913
H	5.639923	-1.492483	2.113606
H	4.509877	-1.528104	-2.035496
H	5.673156	-2.589298	-0.122694
C	-3.154100	-0.321479	0.760395
C	-3.428950	-0.500358	-0.623866
C	-6.289566	-0.970062	1.302467
C	-4.715239	-0.135762	-1.297447
C	-5.899987	-1.935721	0.156672
C	-5.732292	-1.295076	-1.230629
H	-5.133268	0.753593	-0.813534
H	-6.717137	-0.045983	0.888057
H	-6.669181	-2.711253	0.062851
H	-7.095689	-1.428688	1.886948
H	-4.539468	0.133744	-2.344729
H	-4.977573	-2.466435	0.425667
H	-6.702094	-0.919423	-1.581537
H	-5.426098	-2.076463	-1.938165
C	-4.061308	0.326339	1.767901
H	-4.525379	1.220654	1.335280

H	-3.457506	0.671800	2.614680
C	-5.168898	-0.609588	2.294601
H	-4.709543	-1.533763	2.671511
H	-5.624201	-0.115397	3.161958
C	-2.334701	-1.242443	-1.190416
C	-1.883981	-0.927018	1.033074
C	-1.399654	-1.549474	-0.162639
C	-0.164708	-2.326450	-0.299481
C	0.450932	-2.888511	0.826982
C	0.454759	-2.515184	-1.549555
C	1.646499	-3.596108	0.730232
H	-0.012012	-2.777284	1.802723
C	1.643590	-3.216532	-1.661431
H	0.009326	-2.086112	-2.441789
C	2.255244	-3.758660	-0.520235
H	2.092063	-4.009346	1.626316
H	2.129045	-3.351054	-2.621993
H	-1.395924	-0.938181	1.997742
H	-2.268516	-1.559849	-2.222362
O	3.419864	-4.423374	-0.729038
C	4.064429	-5.004777	0.395715
H	4.969042	-5.476720	0.009760
H	4.335704	-4.240851	1.133779
H	3.429831	-5.764783	0.868848

TS2'-1
B3LYP-D3 SCF energy (au): -1951.31502160
B3LYP-D3 enthalpy (au): -1950.67854160
B3LYP-D3 free energy (au): -1950.79069360
M06 SCF energy in toluene (au): -1950.52112318
M06 enthalpy in toluene (au): -1949.88464318
M06 free energy in toluene (au): -1949.99679518
M06 free energy in toluene (quasi-harmonic) (au): -1949.98824758

Cartesian coordinates

ATOM	X	Y	Z
Fe	1.776001	-0.747424	-0.449303
C	1.515311	-2.164934	0.596468
O	1.407840	-3.054491	1.315442
C	2.098809	-1.671427	-1.923007
O	2.337410	-2.234553	-2.897366
C	-0.226557	-0.716867	-1.193075
H	-0.498745	-1.653329	-1.678460
H	-0.193943	0.138523	-1.863227
C	-0.816154	-0.515379	0.077473
H	-0.818875	0.494187	0.480801
C	-1.545255	-1.494482	0.783379
H	-1.351506	-2.521020	0.483543
C	-1.779165	-1.338269	2.268379
H	-2.625921	-1.956815	2.580960

H	-0.899561	-1.676368	2.831725
H	-1.990695	-0.299208	2.543838
C	-3.217602	-1.393930	-0.120702
O	-3.727035	-2.604030	0.011738
B	-3.092030	-3.741147	-0.795037
F	-4.106717	-4.569855	-1.194878
F	-2.397335	-3.172439	-1.882359
F	-2.176167	-4.373439	0.055001
H	-2.873126	-1.151183	-1.127177
C	-3.980980	-0.295147	0.540865
C	-3.698650	1.042334	0.232492
C	-4.979159	-0.586950	1.475869
C	-4.395696	2.075424	0.855335
H	-2.928105	1.274820	-0.499233
C	-5.676591	0.446426	2.102137
H	-5.203541	-1.626968	1.685048
C	-5.385294	1.777128	1.797348
H	-4.171657	3.107693	0.604017
H	-6.452158	0.211623	2.826018
H	-5.930344	2.580424	2.285703
C	3.281729	-0.012446	0.856074
C	3.678754	0.194456	-0.493295
C	5.878592	1.126721	1.700182
C	4.929784	-0.327256	-1.141208
C	6.725001	0.417491	0.614983
C	6.189533	0.505694	-0.825655
H	5.101832	-1.366295	-0.835458
H	6.541378	1.713282	2.346979
H	6.873453	-0.638409	0.882457
H	5.211861	1.856479	1.222773
H	4.782002	-0.346235	-2.227033
H	7.727400	0.861015	0.608769
H	6.979796	0.167148	-1.507242
H	5.996555	1.558063	-1.075297
C	4.084930	-0.747407	1.884068
H	4.648935	-1.549071	1.395402
H	3.428608	-1.229162	2.616667
C	5.054952	0.205754	2.614790
H	4.480108	0.830996	3.310039
H	5.730924	-0.402822	3.228800
C	2.708167	1.064845	-1.100365
C	2.072268	0.728872	1.073631
C	1.746121	1.445481	-0.119697
C	0.613269	2.358209	-0.296392
C	-0.031239	2.920182	0.823381
C	0.109537	2.670812	-1.565941
C	-1.145008	3.729475	0.680379
H	0.346245	2.715780	1.820131
C	-1.014195	3.479838	-1.726441
H	0.583231	2.257946	-2.451223

C	-1.655730	4.005727	-0.597719
H	-1.649156	4.150352	1.543150
H	-1.384500	3.681499	-2.723970
H	1.524448	0.763045	2.005158
H	2.749762	1.421596	-2.120722
O	-2.771059	4.778891	-0.633247
C	-3.401500	4.994063	-1.890907
H	-3.699625	4.043658	-2.349749
H	-4.288772	5.591321	-1.679396
H	-2.745349	5.544600	-2.576093

TS2-2

B3LYP-D3 SCF energy (au): -1951.32846263
B3LYP-D3 enthalpy (au): -1950.69249963
B3LYP-D3 free energy (au): -1950.80295863
M06 SCF energy in toluene (au): -1950.52275758
M06 enthalpy in toluene (au): -1949.88679458
M06 free energy in toluene (au): -1949.99725358
M06 free energy in toluene (quasi-harmonic) (au): -1949.98960795

Cartesian coordinates

ATOM	X	Y	Z
Fe	-1.704770	-0.899151	0.755918
C	-1.236508	-2.480735	0.113768
O	-0.978978	-3.514135	-0.326321
C	-1.947889	-1.444697	2.415332
O	-2.134179	-1.768036	3.506240
C	0.281558	-0.417170	1.396239
H	0.640649	-1.161830	2.108722
H	0.156478	0.573575	1.826120
C	0.873557	-0.469185	0.107462
H	0.734458	0.390071	-0.538777
C	1.707167	-1.491861	-0.381706
H	1.760616	-2.387827	0.237094
C	1.818205	-1.724132	-1.870300
H	1.894484	-0.770149	-2.396951
H	2.702231	-2.325111	-2.106984
H	0.940039	-2.269171	-2.241913
C	3.509436	-0.644081	0.098470
O	3.838091	0.199136	-0.849757
B	3.192435	1.565061	-0.905940
F	4.156062	2.491896	-1.253457
F	2.180319	1.497219	-1.884165
F	2.639486	1.845807	0.349606
H	3.215228	-0.215361	1.056386
C	4.324509	-1.880580	0.175616
C	4.276629	-2.681755	1.325662
C	5.149177	-2.257746	-0.892502
C	5.032860	-3.847529	1.404093
H	3.644677	-2.382697	2.158943

C	5.906054	-3.425847	-0.811836
H	5.197469	-1.614553	-1.763888
C	5.847694	-4.224418	0.332069
H	4.993586	-4.459827	2.300519
H	6.546892	-3.710997	-1.641413
H	6.439414	-5.133415	0.392948
C	-3.127255	-0.658610	-0.809663
C	-3.719516	-0.360731	0.449662
C	-6.134127	-1.099025	-1.945617
C	-4.966221	-0.994198	0.983794
C	-6.269303	0.103935	-0.980254
C	-6.225864	-0.231653	0.519368
H	-5.014652	-2.034106	0.642604
H	-6.370393	-2.034503	-1.418468
H	-7.222805	0.610841	-1.169196
H	-6.895030	-1.004974	-2.729174
H	-4.944434	-1.026431	2.078902
H	-5.491981	0.844057	-1.209471
H	-7.106420	-0.829515	0.788056
H	-6.300765	0.705732	1.085488
C	-3.591407	-1.704405	-1.783453
H	-3.875128	-2.618912	-1.248859
H	-2.753346	-1.973917	-2.436175
C	-4.777213	-1.246891	-2.657759
H	-4.518985	-0.296684	-3.144633
H	-4.889647	-1.984928	-3.461796
C	-3.018791	0.771354	0.995840
C	-2.048320	0.260925	-1.011492
C	-2.019240	1.198030	0.075795
C	-1.099645	2.319730	0.233624
C	-0.326733	2.767856	-0.846396
C	-0.916229	2.948518	1.482470
C	0.627258	3.764151	-0.694991
H	-0.438546	2.309970	-1.822705
C	0.034728	3.938976	1.648153
H	-1.498066	2.627637	2.341792
C	0.845355	4.327844	0.566390
H	1.249297	4.026386	-1.539490
H	0.208231	4.398478	2.615424
H	-1.400483	0.272771	-1.876607
H	-3.259414	1.250779	1.934972
O	1.806623	5.235982	0.840363
C	2.815015	5.458058	-0.148931
H	3.544047	6.118415	0.323043
H	3.292938	4.518296	-0.442336
H	2.396310	5.957896	-1.031839

TS2'-2

B3LYP-D3 SCF energy (au): -1951.32438266
B3LYP-D3 enthalpy (au): -1950.68792066

B3LYP-D3 free energy (au): -1950.79919666
M06 SCF energy in toluene (au): -1950.52103008
M06 enthalpy in toluene (au): -1949.88456808
M06 free energy in toluene (au): -1949.99584408
M06 free energy in toluene (quasi-harmonic) (au): -1949.98776942

Cartesian coordinates

ATOM	X	Y	Z
Fe	-1.424683	-0.759542	-0.951054
C	-0.636813	-0.205116	-2.449005
O	-0.188289	0.192212	-3.431865
C	-1.776281	-2.402133	-1.492037
O	-2.034091	-3.480767	-1.805417
C	0.290308	-1.679236	-0.038686
H	0.662091	-2.558288	-0.563618
H	-0.089926	-1.880922	0.958865
C	1.015077	-0.485614	-0.207777
H	0.775565	0.331773	0.455212
C	2.193118	-0.311143	-0.969598
H	2.419170	-1.113266	-1.671885
C	2.590449	1.075210	-1.433224
H	3.638954	1.088649	-1.753513
H	1.983118	1.403263	-2.285162
H	2.468258	1.797149	-0.622841
C	3.388556	-0.715825	0.565105
O	2.790391	-0.834124	1.744273
B	2.315694	0.354629	2.528935
F	0.898168	0.233759	2.647765
F	2.904577	0.345295	3.766439
F	2.605047	1.531322	1.810515
H	3.973259	0.196009	0.425251
C	4.026256	-1.967244	0.081674
C	5.012503	-1.922191	-0.914161
C	3.624968	-3.207619	0.594624
C	5.581368	-3.097586	-1.397190
H	5.332244	-0.959947	-1.307115
C	4.192750	-4.384012	0.106574
H	2.884985	-3.225835	1.386463
C	5.168743	-4.333697	-0.890858
H	6.349863	-3.051911	-2.163769
H	3.879271	-5.342369	0.511521
H	5.613074	-5.251123	-1.266518
C	-3.477562	-0.374061	-0.540187
C	-2.789528	-0.735056	0.674703
C	-6.222110	-1.195894	0.988391
C	-3.196484	-1.843316	1.594136
C	-5.374543	-0.518519	2.093429
C	-4.209207	-1.352445	2.650252
H	-3.637086	-2.657586	1.007842
H	-6.066692	-2.284058	1.006768

H	-6.023753	-0.265075	2.939487
H	-7.283051	-1.048152	1.221369
H	-2.317605	-2.259159	2.098917
H	-4.989691	0.440001	1.721721
H	-4.604062	-2.228491	3.180705
H	-3.675545	-0.749116	3.395154
C	-4.674330	-1.069265	-1.122007
H	-4.552442	-2.156627	-1.054128
H	-4.732561	-0.829120	-2.190034
C	-6.005384	-0.677846	-0.445327
H	-6.105979	0.415991	-0.454218
H	-6.813238	-1.067578	-1.077316
C	-1.794189	0.252018	0.909520
C	-2.859679	0.798239	-1.043796
C	-1.814652	1.219868	-0.139664
C	-0.951057	2.399322	-0.267584
C	-0.982505	3.206447	-1.420932
C	-0.029525	2.721341	0.737504
C	-0.119512	4.279897	-1.565358
H	-1.678877	2.984736	-2.224152
C	0.851945	3.789957	0.598816
H	0.053787	2.112668	1.629510
C	0.813299	4.576544	-0.557019
H	-0.135534	4.899594	-2.455758
H	1.582367	3.955812	1.379425
H	-3.146951	1.298615	-1.958855
H	-1.075865	0.223463	1.719637
O	1.633819	5.631633	-0.800284
C	2.631908	5.929939	0.167003
H	2.185164	6.198098	1.132565
H	3.314691	5.083214	0.309314
H	3.184199	6.783745	-0.228161

TS2-3
B3LYP-D3 SCF energy (au): -1951.30627981
B3LYP-D3 enthalpy (au): -1950.67031181
B3LYP-D3 free energy (au): -1950.78312181
M06 SCF energy in toluene (au): -1950.51798792
M06 enthalpy in toluene (au): -1949.88201992
M06 free energy in toluene (au): -1949.99482992
M06 free energy in toluene (quasi-harmonic) (au): -1949.98585411

Cartesian coordinates

ATOM	X	Y	Z
Fe	-1.772523	-0.473027	0.877654
C	-1.531370	-2.232660	0.937751
O	-1.427198	-3.377513	0.963691
C	-1.993956	-0.273832	2.618351
O	-2.163329	-0.104218	3.744801
C	0.276849	-0.022972	1.306612

H	0.615279	-0.474279	2.238174
H	0.255932	1.061937	1.334611
C	0.754322	-0.631721	0.124699
H	0.618760	-0.083407	-0.803495
C	1.531851	-1.806992	0.028335
H	1.631872	-2.365882	0.961461
C	1.370664	-2.681162	-1.202472
H	1.451926	-2.092127	-2.122382
H	2.144211	-3.448902	-1.233446
H	0.389521	-3.173594	-1.186622
C	3.286004	-1.097570	-0.083028
O	4.067932	-2.154474	-0.045703
B	4.639916	-2.763371	-1.345510
F	6.008571	-2.666041	-1.244658
F	4.200751	-4.081837	-1.392080
F	4.135730	-2.022901	-2.421507
H	3.224063	-0.599585	-1.054079
C	3.432037	-0.154354	1.068935
C	3.136230	1.202570	0.896803
C	3.844421	-0.613389	2.323637
C	3.235869	2.088807	1.968550
H	2.820592	1.563406	-0.079239
C	3.938563	0.271881	3.397315
H	4.103435	-1.661163	2.434374
C	3.632202	1.624613	3.224570
H	3.001563	3.140439	1.823309
H	4.260507	-0.091272	4.369456
H	3.711213	2.312911	4.061567
C	-3.287894	-0.685126	-0.608989
C	-3.712446	0.222164	0.401184
C	-6.417974	-1.055934	-1.378284
C	-4.984372	0.103482	1.181561
C	-6.289099	0.449808	-1.041693
C	-6.156016	0.794307	0.450590
H	-5.214156	-0.956803	1.332554
H	-6.737279	-1.615957	-0.487746
H	-7.173310	0.978765	-1.415729
H	-7.225964	-1.182446	-2.108011
H	-4.868515	0.542714	2.178622
H	-5.438681	0.874542	-1.590745
H	-7.084895	0.531715	0.972784
H	-6.041327	1.881720	0.546438
C	-3.984517	-1.952981	-1.014533
H	-4.345392	-2.483929	-0.125543
H	-3.256941	-2.615194	-1.497085
C	-5.167935	-1.725076	-1.977751
H	-4.822223	-1.138986	-2.840119
H	-5.457886	-2.707728	-2.369553
C	-2.801732	1.336092	0.392189
C	-2.107430	-0.141810	-1.212372

C	-1.835141	1.141972	-0.635039
C	-0.734070	2.040443	-0.990459
C	-0.039463	1.883024	-2.206287
C	-0.298782	3.045470	-0.115077
C	1.055288	2.672469	-2.516417
H	-0.361716	1.129549	-2.918178
C	0.799823	3.847598	-0.411715
H	-0.805189	3.190420	0.834410
C	1.495625	3.655237	-1.614099
H	1.597836	2.542741	-3.446438
H	1.114009	4.601286	0.299583
H	-1.544595	-0.617821	-2.003220
H	-2.881820	2.205025	1.031347
O	2.589867	4.355808	-1.991860
C	3.154772	5.278140	-1.068475
H	2.457221	6.093405	-0.839110
H	3.450950	4.774629	-0.139786
H	4.039428	5.684628	-1.559199

TS2'-3

B3LYP-D3 SCF energy (au): -1951.32559768
B3LYP-D3 enthalpy (au): -1950.68946168
B3LYP-D3 free energy (au): -1950.80000068
M06 SCF energy in toluene (au): -1950.51843008
M06 enthalpy in toluene (au): -1949.88229408
M06 free energy in toluene (au): -1949.99283308
M06 free energy in toluene (quasi-harmonic) (au): -1949.98505740

Cartesian coordinates

ATOM	X	Y	Z
Fe	1.659058	-0.454294	-1.062527
C	1.930162	-2.205657	-1.010424
O	2.169607	-3.331843	-0.973459
C	1.770009	-0.319119	-2.817403
O	1.853804	-0.185540	-3.959262
C	-0.465520	-0.568502	-1.417286
H	-0.744073	-1.069388	-2.343999
H	-0.713426	0.488106	-1.396942
C	-0.638210	-1.310472	-0.228326
H	-0.505751	-0.798475	0.713562
C	-1.167098	-2.610655	-0.113736
H	-1.440126	-3.089012	-1.056988
C	-0.722531	-3.564754	0.973907
H	-0.471131	-3.030954	1.890164
H	-1.505988	-4.292754	1.210571
H	0.158071	-4.126854	0.637007
C	-2.957728	-1.846562	0.551339
O	-2.784393	-0.912025	1.458764
B	-2.303785	-1.185031	2.862713
F	-2.825582	-0.178648	3.649939

F	-2.685113	-2.459573	3.241343
F	-0.873880	-1.090138	2.852690
H	-3.247096	-2.834654	0.920120
C	-3.601929	-1.393567	-0.704756
C	-4.108300	-2.323551	-1.622642
C	-3.676149	-0.024886	-1.000778
C	-4.675669	-1.895016	-2.820534
H	-4.057233	-3.385260	-1.392529
C	-4.243986	0.401004	-2.200095
H	-3.298001	0.686525	-0.276406
C	-4.742227	-0.529799	-3.114141
H	-5.070611	-2.623255	-3.523279
H	-4.297765	1.464037	-2.420767
H	-5.185347	-0.195746	-4.048177
C	3.101144	-0.165602	0.489105
C	3.387783	0.666959	-0.632056
C	6.195923	0.222199	1.374306
C	4.696085	0.710892	-1.357973
C	5.785857	1.610376	0.824578
C	5.667656	1.717338	-0.704452
H	5.141014	-0.290217	-1.354986
H	6.665577	-0.374888	0.579442
H	6.523797	2.355779	1.143344
H	6.974834	0.363486	2.132596
H	4.545310	0.981262	-2.409268
H	4.838519	1.918899	1.284935
H	6.657285	1.583247	-1.160176
H	5.343955	2.735676	-0.955901
C	4.014836	-1.198151	1.085653
H	4.522535	-1.758407	0.291356
H	3.409050	-1.922369	1.641495
C	5.075819	-0.602257	2.034196
H	4.573899	0.011003	2.794534
H	5.536210	-1.441518	2.570054
C	2.278665	1.569450	-0.785487
C	1.812241	0.197537	0.986917
C	1.316573	1.316267	0.234592
C	0.039059	2.004495	0.428806
C	-0.792839	1.690744	1.520579
C	-0.424665	2.949145	-0.500648
C	-2.041274	2.273277	1.665900
H	-0.494315	0.950210	2.250590
C	-1.672841	3.549043	-0.364529
H	0.183607	3.211531	-1.361076
C	-2.493573	3.205754	0.722263
H	-2.687094	1.969333	2.481318
H	-1.999203	4.268075	-1.106105
H	1.311390	-0.276585	1.820569
H	2.215945	2.340973	-1.540792
O	-3.736389	3.711007	0.931524

C	-4.274573	4.597201	-0.035481
H	-5.276657	4.848715	0.314397
H	-3.677380	5.514610	-0.119183
H	-4.342455	4.119332	-1.021987

TS2-4

B3LYP-D3 SCF energy (au): -1951.32403383
B3LYP-D3 enthalpy (au): -1950.68742283
B3LYP-D3 free energy (au): -1950.79902883
M06 SCF energy in toluene (au): -1950.51613599
M06 enthalpy in toluene (au): -1949.87952499
M06 free energy in toluene (au): -1949.99113099
M06 free energy in toluene (quasi-harmonic) (au): -1949.98280816

Cartesian coordinates

ATOM	X	Y	Z
Fe	-1.396454	-0.788113	1.146874
C	-0.749789	-2.415116	1.402269
O	-0.373410	-3.493818	1.554124
C	-1.674015	-0.453207	2.853111
O	-1.874729	-0.206135	3.961351
C	0.493011	0.176949	1.502602
H	0.914578	-0.110967	2.466973
H	0.226464	1.229729	1.436573
C	1.096471	-0.405516	0.355861
H	0.835140	0.011979	-0.604635
C	2.059602	-1.420485	0.309648
H	2.397502	-1.817640	1.267912
C	2.102726	-2.388744	-0.846183
H	1.851131	-1.883683	-1.781000
H	3.096121	-2.839151	-0.946291
H	1.386055	-3.204188	-0.679871
C	3.565299	-0.061030	-0.283609
O	3.500547	0.006141	-1.585446
B	2.603029	1.007184	-2.296909
F	3.222247	1.351480	-3.463812
F	1.357858	0.358813	-2.547211
F	2.385124	2.089318	-1.440333
H	3.239754	0.817643	0.272542
C	4.701082	-0.809735	0.295566
C	5.508434	-1.617951	-0.516522
C	4.979813	-0.709886	1.667018
C	6.573101	-2.323823	0.041933
H	5.300112	-1.660952	-1.579625
C	6.042831	-1.416081	2.220990
H	4.356804	-0.075613	2.293438
C	6.840664	-2.228720	1.408979
H	7.199475	-2.944520	-0.592464
H	6.255133	-1.330992	3.282893
H	7.671993	-2.778548	1.840934

C	-2.378308	-1.432705	-0.662657
C	-3.328006	-1.137833	0.371948
C	-4.692342	-3.208049	-2.079208
C	-4.389196	-2.076723	0.854725
C	-5.450154	-1.979982	-1.517681
C	-5.672820	-1.967552	0.003417
H	-4.004806	-3.102056	0.814956
H	-4.722021	-4.033954	-1.353976
H	-6.438451	-1.920932	-1.988493
H	-5.227940	-3.575112	-2.962448
H	-4.630380	-1.876513	1.904935
H	-4.927357	-1.062067	-1.815588
H	-6.342295	-2.791289	0.283709
H	-6.193926	-1.038283	0.268336
C	-2.214760	-2.746103	-1.373188
H	-2.297794	-3.576206	-0.661539
H	-1.201876	-2.790484	-1.788716
C	-3.234785	-2.963348	-2.509744
H	-3.197478	-2.106043	-3.195079
H	-2.895003	-3.833276	-3.085328
C	-3.192471	0.253788	0.676569
C	-1.654753	-0.245438	-0.943445
C	-2.157899	0.823875	-0.124685
C	-1.686447	2.211213	-0.105335
C	-0.546051	2.593832	-0.837643
C	-2.326634	3.184834	0.673775
C	-0.056270	3.887596	-0.773634
H	-0.014001	1.882609	-1.455309
C	-1.854171	4.493799	0.734115
H	-3.213474	2.928713	1.245868
C	-0.707722	4.850985	0.009604
H	0.845112	4.153269	-1.313053
H	-2.379718	5.219269	1.343258
H	-0.870944	-0.162627	-1.683549
H	-3.777629	0.778128	1.420447
O	-0.156849	6.093981	0.006803
C	-0.771435	7.101386	0.792543
H	-1.801443	7.294614	0.464980
H	-0.776153	6.833709	1.857400
H	-0.171597	8.001234	0.648363

TS2'-4
B3LYP-D3 SCF energy (au): -1951.31990610
B3LYP-D3 enthalpy (au): -1950.68432110
B3LYP-D3 free energy (au): -1950.79540810
M06 SCF energy in toluene (au): -1950.51644880
M06 enthalpy in toluene (au): -1949.88086380
M06 free energy in toluene (au): -1949.99195080
M06 free energy in toluene (quasi-harmonic) (au): -1949.98411470

Cartesian coordinates

ATOM	X	Y	Z
Fe	-1.623488	-0.922761	0.445406
C	-1.187758	-2.379669	-0.464716
O	-0.966518	-3.326489	-1.083466
C	-1.647685	-1.694614	2.032161
O	-1.693465	-2.173605	3.079082
C	0.395698	-0.415837	1.008127
H	0.831630	-1.174298	1.656759
H	0.259795	0.541507	1.494706
C	0.883683	-0.398889	-0.314715
H	0.675430	0.483893	-0.911309
C	1.761687	-1.361410	-0.855268
H	1.812949	-2.299117	-0.302058
C	1.865115	-1.502793	-2.357210
H	1.909711	-0.519609	-2.841181
H	2.756839	-2.068448	-2.642827
H	0.998820	-2.040249	-2.765236
C	3.533418	-0.582308	-0.225714
O	3.424200	0.036547	0.929113
B	3.126488	1.524654	0.951245
F	2.580995	1.868564	-0.301774
F	2.219412	1.751018	1.982816
F	4.304659	2.225958	1.156440
H	3.663628	0.047913	-1.106572
C	4.338458	-1.829396	-0.199962
C	5.027535	-2.256659	-1.342590
C	4.426356	-2.587933	0.977098
C	5.775362	-3.434318	-1.317814
H	4.997338	-1.651019	-2.244006
C	5.170297	-3.763410	0.999422
H	3.917401	-2.229865	1.865679
C	5.842563	-4.193856	-0.149448
H	6.311914	-3.752141	-2.207318
H	5.234681	-4.344318	1.915315
H	6.424692	-5.110831	-0.128505
C	-3.397878	-0.657783	-0.680741
C	-3.621482	-0.277205	0.670784
C	-6.615371	-0.980210	-0.958767
C	-4.704795	-0.825307	1.546859
C	-6.436761	0.266292	-0.057994
C	-6.007424	-0.010959	1.391857
H	-4.887284	-1.872521	1.282180
H	-6.740066	-1.879304	-0.338389
H	-7.384048	0.816223	-0.013189
H	-7.553923	-0.877062	-1.515774
H	-4.395328	-0.817004	2.597572
H	-5.719265	0.953425	-0.524492
H	-6.808606	-0.547571	1.916183
H	-5.886423	0.950480	1.907035

C	-4.148583	-1.712013	-1.443982
H	-4.313089	-2.589819	-0.807313
H	-3.527180	-2.050524	-2.280999
C	-5.505761	-1.229817	-1.996288
H	-5.349570	-0.315233	-2.584579
H	-5.859273	-1.993203	-2.700784
C	-2.743100	0.820821	0.967168
C	-2.380832	0.210903	-1.206694
C	-2.026847	1.178608	-0.215572
C	-1.071342	2.267748	-0.379923
C	-0.687348	2.695147	-1.667330
C	-0.460519	2.880106	0.725006
C	0.302184	3.646518	-1.836379
H	-1.168964	2.270368	-2.543132
C	0.543764	3.823428	0.568782
H	-0.727332	2.573234	1.731101
C	0.963931	4.181373	-0.718348
H	0.621160	3.960268	-2.824563
H	1.056113	4.196447	1.444869
H	-1.986094	0.163800	-2.212272
H	-2.699210	1.340921	1.914311
O	1.987579	5.021260	-0.981027
C	2.920954	5.291095	0.068650
H	3.347514	4.362087	0.459065
H	3.704554	5.895704	-0.390610
H	2.454647	5.866899	0.877844

TS2

B3LYP-D3 SCF energy (au): -1951.32264171
B3LYP-D3 enthalpy (au): -1950.68680871
B3LYP-D3 free energy (au): -1950.79862871
M06 SCF energy in toluene (au): -1950.52309207
M06 enthalpy in toluene (au): -1949.88725907
M06 free energy in toluene (au): -1949.99907907
M06 free energy in toluene (quasi-harmonic) (au): -1949.99074936
ωB97X-D SCF energy in toluene (au): -3091.190516
ωB97X-D enthalpy in toluene (au): -3090.554683
ωB97X-D free energy in toluene (au): -3090.666503
ωB97X-D free energy in toluene (quasi-harmonic) (au): -3090.658173
DLPNO-CCSD(T) SCF energy in toluene (au): -3087.118356
DLPNO-CCSD(T) enthalpy in toluene (au): -3086.482523
DLPNO-CCSD(T) free energy in toluene (au): -3086.594343
DLPNO-CCSD(T) free energy in toluene (quasi-harmonic) (au): -3086.586013

Cartesian coordinates

ATOM	X	Y	Z
Fe	1.618082	-0.588654	-0.531589
C	1.755361	-2.177682	0.257108
O	1.910997	-3.173703	0.807705
C	1.762787	-1.216582	-2.179047

O	1.876950	-1.576388	-3.265847
C	-0.477865	-0.800790	-0.876292
H	-0.660880	-1.754252	-1.361475
H	-0.724707	0.079487	-1.465984
C	-0.823604	-0.740825	0.494007
H	-0.965853	0.249636	0.920648
C	-1.169108	-1.825199	1.318686
H	-0.854232	-2.812479	0.997951
C	-1.218807	-1.625683	2.814614
H	-1.604583	-0.633387	3.076110
H	-1.854497	-2.377350	3.296548
H	-0.217368	-1.725554	3.256328
C	-3.013813	-2.103660	0.610828
O	-2.892094	-2.624021	-0.583277
B	-2.276013	-4.020130	-0.753055
F	-2.387908	-4.691382	0.462348
F	-2.942791	-4.626756	-1.782820
F	-0.910257	-3.814389	-1.058581
H	-3.220721	-2.799019	1.429158
C	-3.709381	-0.790721	0.678563
C	-4.174759	-0.290080	1.901180
C	-3.866490	-0.020246	-0.481846
C	-4.749102	0.978963	1.972105
H	-4.085296	-0.897303	2.797617
C	-4.445094	1.243706	-0.408124
H	-3.531590	-0.432867	-1.426422
C	-4.878060	1.754319	0.818367
H	-5.102620	1.359282	2.926568
H	-4.562416	1.833079	-1.313098
H	-5.307941	2.749476	0.872356
C	3.108459	0.211581	0.771254
C	3.403793	0.540392	-0.582122
C	6.239976	0.763400	1.425892
C	4.696824	0.242937	-1.275524
C	5.875386	1.854702	0.389847
C	5.723994	1.375662	-1.063083
H	5.099800	-0.700612	-0.891730
H	6.666865	-0.112541	0.917002
H	6.651850	2.628629	0.394764
H	7.040559	1.146378	2.069444
H	4.533374	0.096720	-2.349070
H	4.953076	2.360662	0.703276
H	6.695809	1.031286	-1.439654
H	5.436664	2.235285	-1.682379
C	3.995338	-0.555270	1.711011
H	4.459571	-1.398736	1.186499
H	3.375793	-0.988775	2.504244
C	5.101730	0.304825	2.355496
H	4.644114	1.185098	2.827500
H	5.539805	-0.288265	3.167934

C	2.325399	1.356416	-1.070769
C	1.841199	0.791635	1.095120
C	1.373715	1.547388	-0.031005
C	0.143091	2.340567	-0.104510
C	-0.518046	2.757302	1.067129
C	-0.421587	2.699763	-1.335511
C	-1.692388	3.488833	1.008508
H	-0.099815	2.508907	2.037742
C	-1.598017	3.441392	-1.410720
H	0.050804	2.378198	-2.258720
C	-2.243898	3.837799	-0.233253
H	-2.208198	3.799762	1.910061
H	-2.007191	3.688142	-2.382644
H	1.344960	0.699766	2.050994
H	2.275807	1.788477	-2.061179
O	-3.396527	4.555105	-0.189818
C	-3.984308	4.956193	-1.419029
H	-4.878807	5.520175	-1.152008
H	-3.305661	5.597464	-1.995391
H	-4.268918	4.089448	-2.028299

TS2'
B3LYP-D3 SCF energy (au): -1951.31521489
B3LYP-D3 enthalpy (au): -1950.67902589
B3LYP-D3 free energy (au): -1950.79133989
M06 SCF energy in toluene (au): -1950.52275628
M06 enthalpy in toluene (au): -1949.88656728
M06 free energy in toluene (au): -1949.99888128
M06 free energy in toluene (quasi-harmonic) (au): -1949.99035439
ωB97X-D SCF energy in toluene (au): -3091.190119
ωB97X-D enthalpy in toluene (au): -3090.55393
ωB97X-D free energy in toluene (au): -3090.666244
ωB97X-D free energy in toluene (quasi-harmonic) (au): -3090.657717
DLPNO-CCSD(T) SCF energy in toluene (au): -3087.116959
DLPNO-CCSD(T) enthalpy in toluene (au): -3086.48077
DLPNO-CCSD(T) free energy in toluene (au): -3086.593084
DLPNO-CCSD(T) free energy in toluene (quasi-harmonic) (au): -3086.584557

Cartesian coordinates

ATOM	X	Y	Z
Fe	-1.781406	-0.649218	0.751341
C	-1.609234	-2.292289	0.085634
O	-1.555106	-3.338973	-0.383148
C	-2.161955	-1.164677	2.398549
O	-2.432900	-1.458261	3.478345
C	0.241237	-0.604099	1.445864
H	0.443098	-1.512041	2.014449
H	0.283572	0.307831	2.038359
C	0.821397	-0.551168	0.154306
H	0.898548	0.427810	-0.311552

C	1.424211	-1.626538	-0.519369
H	1.183492	-2.614631	-0.136463
C	1.594379	-1.575505	-2.019213
H	2.321235	-2.331104	-2.325270
H	0.645264	-1.805891	-2.521804
H	1.932788	-0.588363	-2.355423
C	3.186386	-1.620611	0.237645
O	3.755920	-2.681273	-0.286770
B	3.241232	-4.077639	0.113050
F	4.341131	-4.886104	0.231764
F	2.530886	-3.940451	1.316389
F	2.377543	-4.473805	-0.908804
H	2.880304	-1.712429	1.282558
C	3.837068	-0.322202	-0.112027
C	3.647363	0.807319	0.694782
C	4.662359	-0.228475	-1.238590
C	4.275110	2.012084	0.385049
H	3.015109	0.737436	1.576333
C	5.284192	0.978951	-1.555125
H	4.823728	-1.117457	-1.837582
C	5.095997	2.099493	-0.743446
H	4.132104	2.876927	1.025223
H	5.930361	1.040504	-2.426486
H	5.605683	3.030925	-0.976231
C	-3.130344	-0.155621	-0.819368
C	-3.664683	0.269507	0.429346
C	-5.610513	0.809340	-2.108339
C	-4.983544	-0.142550	1.018800
C	-6.575292	0.285868	-1.016391
C	-6.194441	0.616840	0.438034
H	-5.133980	-1.219439	0.875351
H	-6.194232	1.275637	-2.910519
H	-6.706516	-0.800825	-1.118380
H	-4.989566	1.612728	-1.691111
H	-4.950450	0.021489	2.102138
H	-7.567582	0.717582	-1.191047
H	-7.055992	0.390889	1.078697
H	-6.017892	1.697511	0.527990
C	-3.829287	-1.059155	-1.787595
H	-4.451613	-1.770751	-1.234628
H	-3.105092	-1.651782	-2.356457
C	-4.705736	-0.246174	-2.764513
H	-4.053304	0.257596	-3.489170
H	-5.320129	-0.952870	-3.336548
C	-2.755023	1.242266	0.974390
C	-1.894173	0.536582	-1.028048
C	-1.684779	1.446195	0.059290
C	-0.572805	2.388453	0.203608
C	0.139375	2.823031	-0.922609
C	-0.177700	2.876802	1.463312

C	1.213585	3.701626	-0.812547
H	-0.151925	2.475170	-1.908877
C	0.890325	3.749779	1.588605
H	-0.703007	2.551622	2.356353
C	1.598692	4.167227	0.450397
H	1.744777	4.004952	-1.705604
H	1.205407	4.119124	2.558712
H	-1.250020	0.413111	-1.887440
H	-2.898443	1.771246	1.907166
O	2.637893	5.009980	0.676831
C	3.372606	5.482048	-0.446947
H	2.731718	6.062981	-1.121861
H	4.153360	6.126418	-0.041262
H	3.828454	4.651318	-0.996839

TS3

B3LYP-D3 SCF energy (au): -1307.05476723
B3LYP-D3 enthalpy (au): -1306.39391123
B3LYP-D3 free energy (au): -1306.49724023
M06 SCF energy in toluene (au): -1306.40360341
M06 enthalpy in toluene (au): -1305.74274741
M06 free energy in toluene (au): -1305.84607641
M06 free energy in toluene (quasi-harmonic) (au): -1305.84002618
M06 SCF energy in dichloromethane (au): -1306.422865
M06 enthalpy in dichloromethane (au): -1305.762009
M06 free energy in dichloromethane (au): -1305.865338
M06 free energy in dichloromethane (quasi-harmonic) (au): -1305.859288

Cartesian coordinates

ATOM	X	Y	Z
C	-2.557948	-1.647413	-0.532540
C	-2.884664	-0.621437	-1.469590
C	-3.961134	0.160693	-0.902127
C	-4.260480	-0.368947	0.385380
C	-3.362580	-1.473080	0.634069
Fe	-2.250434	0.323386	0.347496
C	-2.424776	0.919076	2.007640
O	-2.560491	1.272142	3.093713
C	-1.823848	1.884149	-0.386378
O	-1.597485	2.890063	-0.898114
C	-3.370351	-2.375494	1.830955
H	-4.028740	-3.237293	1.663360
H	-2.370251	-2.764192	2.045149
H	-3.726340	-1.858781	2.726066
C	-1.598280	-2.778456	-0.743447
H	-0.893582	-2.892636	0.086728
H	-2.155086	-3.720159	-0.819252
H	-1.027942	-2.664757	-1.668023
C	-2.338911	-0.465489	-2.857847
H	-1.315525	-0.840734	-2.937679

H	-2.952742	-1.020215	-3.578509
H	-2.330936	0.581818	-3.171194
C	-4.702354	1.264592	-1.595129
H	-5.546116	0.852153	-2.162153
H	-5.104920	1.989249	-0.882777
H	-4.065599	1.804517	-2.300556
C	-5.371527	0.081090	1.285485
H	-6.294882	-0.454903	1.033333
H	-5.152553	-0.119254	2.337224
H	-5.570339	1.150683	1.179459
C	-0.255972	-0.178687	0.966291
H	0.102331	0.530065	1.712463
H	-0.395738	-1.181612	1.363492
C	0.313427	-0.054365	-0.322724
H	0.152454	-0.883823	-1.009719
C	1.146683	0.979621	-0.793829
H	2.407399	0.484255	-0.534553
N	3.759443	0.201758	-0.460682
C	4.440783	1.134961	0.512331
C	3.986072	-1.288175	-0.368214
C	5.928873	0.751076	0.639892
C	4.319654	2.540851	-0.093221
C	3.729613	1.114271	1.873247
C	5.494194	-1.569801	-0.224650
C	3.462858	-1.872159	-1.688463
C	3.192244	-1.900933	0.795983
C	6.150319	-0.743937	0.885830
H	6.376108	1.349317	1.441791
H	6.443599	1.036855	-0.288149
H	3.276910	2.865322	-0.161642
H	4.855438	3.259926	0.533133
H	4.763499	2.583079	-1.095489
H	4.083844	1.959017	2.471462
H	2.646701	1.216023	1.755377
H	3.927208	0.206496	2.443925
H	5.987911	-1.339381	-1.179265
H	5.635168	-2.642645	-0.049851
H	3.654620	-2.948611	-1.720625
H	2.384368	-1.716825	-1.796347
H	3.964670	-1.421028	-2.553004
H	2.157477	-1.550600	0.805623
H	3.181496	-2.989063	0.678955
H	3.631882	-1.685197	1.769958
H	5.756744	-1.035637	1.866507
H	7.224165	-0.955207	0.914695
C	1.217446	1.267074	-2.288664
H	2.121933	1.832287	-2.541071
H	1.233619	0.337152	-2.870162
H	0.361799	1.859986	-2.631326
H	1.156450	1.875273	-0.164670

H	4.086448	0.476627	-1.389271