Supporting Information

Catalytic Diastereo- and Enantioselective Fluoroamination of Alkenes

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General experimental procedures. All reactions for the preparation of substrates were performed in standard, dry glassware fitted with rubber septa under an inert atmosphere of nitrogen unless otherwise described. All difluorination reactions were performed in low density polyethylene tubes sealed with a low density polyethylene cap under an atmosphere of air. Reported concentrations refer to solution volumes at room temperature. Concentration of organic solutions under reduced pressure was performed using house vacuum (ca. 40 mm Hg) at 30 °C. Column chromatography was performed with ZEOprep® 60 (40–63 micron) silica gel from American Scientific. Thin layer chromatography (TLC) was used for reaction monitoring and product detection was performed using pre-coated glass plates covered with 0.20 mm silica gel with fluorescent indicator; plates were visualized by exposure to UV light (λ_{ex} = 254 nm) or by staining with potassium permanganate or ninhydrin.

CAUTION: Pyridine•9HF is a corrosive and toxic substance that will etch glassware. Safe handling can be conducted with plastic syringes and metal needles, with $NaHCO_3$ (aq.) or NaOH (aq.) employed to quench excess HF. Though reactions should not be conducted in glassware when employing pyridine•9HF, glassware may be used to quench reactions provided sufficient quantities of base are present. Always handle pyridine•9HF while wearing gloves and in a fumehood. As a precautionary measure, have calcium gluconate gel nearby and apply immediately and liberally on skin exposed to HF.

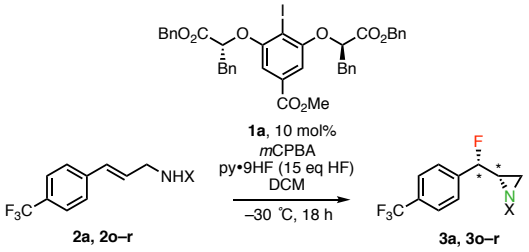
Materials. Reagents were purchased in reagent grade from commercial suppliers and used as received, unless otherwise described. Anhydrous solvents (benzene, dichloromethane, diethyl ether, *N*,*N*-dimethylformamide, tetrahydrofuran, and toluene) were prepared by passing the solvent through an activated alumina column. Triethylamine and diisopropylethylamine were distilled over calcium hydride at atmospheric pressure.

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Varian Mercury-400 or an Inova-500 spectrometer, are reported in parts per million downfield from tetramethylsilane, and are referenced to the residual protium resonances of the NMR solvent ($CDCl_3$: 7.26 [$CHCl_3$]). Proton-decoupled carbon-13 nuclear magnetic resonance (^{13}C {^{1}H} NMR) spectra were recorded on an Inova-500 spectrometer, are reported in parts per million downfield from tetramethylsilane, and are referenced to the carbon resonances of the NMR solvent ($CDCl_3$: 77.23). Chemical shifts for fluorine-19 nuclear magnetic resonance (^{19}F NMR) were recorded on an Inova-500 spectrometer and are reported in parts per million downfield from chlorotrifluoromethane, and are referenced to the fluorine resonance of chlorotrifluoromethane ($\delta = 0$). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, sept = septet, m = multiplet), coupling constants in Hertz (Hz), integration. Infrared spectra were recorded using a Bruker Tensor 27 FT-IR spectrometer. Data are represented as follows: frequency of absorption (cm^{-1}), intensity of absorption (s = strong, m = medium, w = weak, br = broad). High-resolution mass spectrometric data were obtained on an Agilent 6210 time-of-flight HPLC/MS spectrometer (ESI-TOF). Low-resolution mass spectrometric data were obtained on a Waters Quattro Micro GCMS (EI^{+}). GC analysis was performed using an Agilent 7890A GC system using commercially available columns. Chiral HPLC analysis was performed using an Agilent 1200 series quaternary HPLC system using commercially available CHIRALCEL analytical columns (4.6 x 250 mm).

Optimization Experiments.

General procedure for *N*-protecting group optimization

Catalyst **1a** (8.0 mg, 5.20 μmol, 10.0 mol%), p-trifluoromethyl-cinnamyl sulfonamide (52.0 μmol, 1.00 equiv) and dichloromethane (0.30 mL) were combined in a polyethylene tube. The reaction mixture was cooled to –78 ˚C. Pyridinium poly(hydrogen fluoride) (pyr•9HF, 70% hydrogen fluoride by weight, 100 μL, 15 equiv hydrogen fluoride) was added via micropipette followed by *m*-chloroperbenzoic acid (*m*CPBA, 77% by weight, 12.8 mg, 57.2 μmol, 1.10 equiv). The reaction was warmed to –30 ˚C and stirred for 18 hours at that temperature. The reaction was cooled to –78 ˚C and basic alumina (approximately 400 mg) was added slowly. The reaction was allowed to warm to room temperature with stirring and was filtered. The crude mixture was analyzed by ^{1}H NMR using mesitylene as an internal standard to determine the yield of product and by chiral HPLC to determine the enantioselectivity.



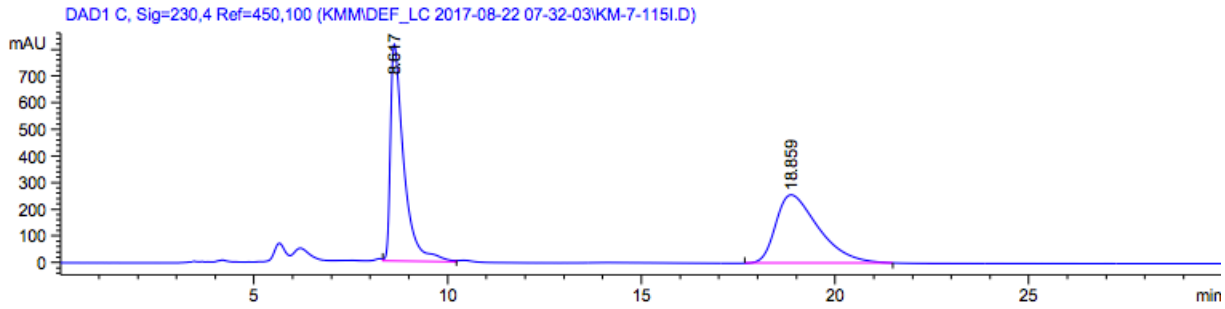
X	Yield	ee
Ts	100%	94%
Ns	76%	94%
$SO_2C_6H_5$	90%	94%
$SO_2C_6H_4$(*p*-OMe)	95%	94%
Ms	99%	94%

Table S1. *N*-Protecting group optimization

X = Ts (3a)

94% ee, Chiral HPLC (OJ-H, 50% isopropanol in hexanes, 1.0 mL/min, λ = 230 nm); t_R(minor) = 8.4 min, t_R(major) = 17.7 min.

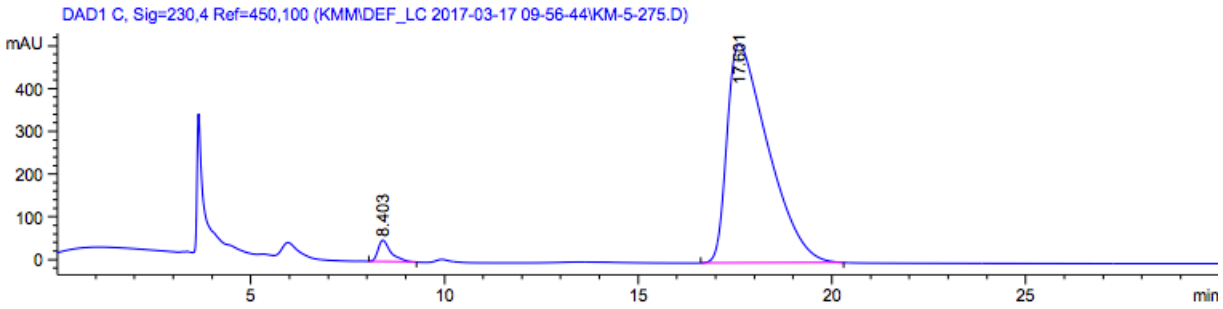
Racemic sample:



Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.617	VB	0.3503	1.95753e4	814.81110	49.8014
2	18.859	BB	1.1274	1.97315e4	256.50644	50.1986
Totals :				3.93067e4	1071.31754	

Enriched sample:



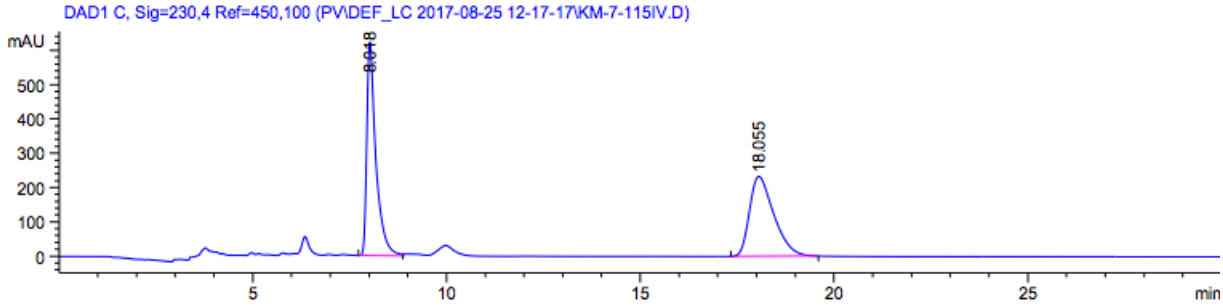
Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.403	BB	0.3418	1155.48096	49.95803	2.9786
2	17.601	BB	1.0699	3.76372e4	511.83502	97.0214
Totals :				3.87927e4	561.79305	

X = Ns (3o)

94% ee, Chiral HPLC (OJ-H, 50% isopropanol in hexanes, 1.0 mL/min, λ = 230 nm); t_R(major) = 7.1 min, t_R(minor) = 18.3 min.

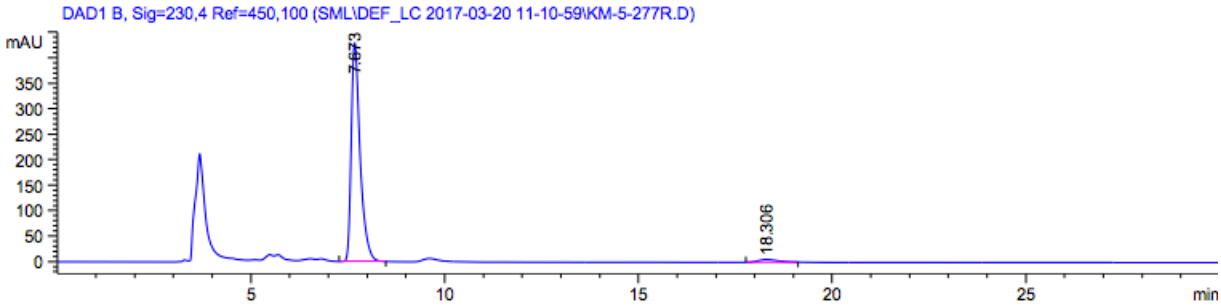
Racemic sample:



Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.018	VV	0.2370	1.01980e4	622.86884	50.0240
2	18.055	BB	0.6560	1.01882e4	233.07854	49.9760
Totals :				2.03862e4	855.94737	

Enriched sample:



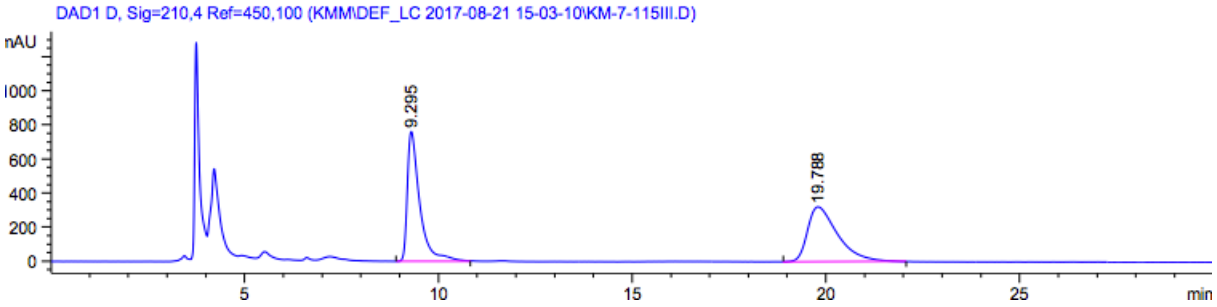
Signal 2: DAD1 B, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.673	VB	0.2378	6832.35889	429.04306	97.2353
2	18.306	BB	0.5252	194.26431	5.38117	2.7647
Totals :				7026.62320	434.42423	

X = $SO_2C_6H_5$ (3p)

94% ee, Chiral HPLC (OJ-H, 50% isopropanol in hexanes, 1.0 mL/min, λ = 210 nm); t_R(minor) = 8.9 min, t_R(major) = 19.1 min.

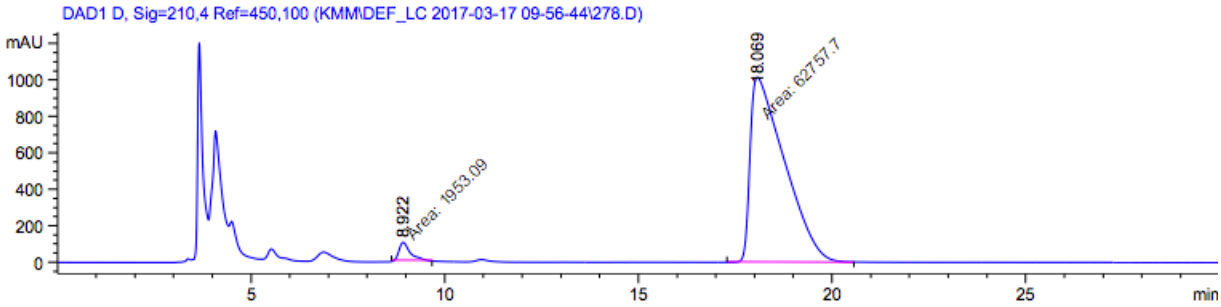
Racemic sample:



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.295	BV	0.3346	1.73198e4	763.76923	49.8517
2	19.788	BB	0.7452	1.74228e4	322.03442	50.1483
Totals :				3.47426e4	1085.80365	

Enriched sample:



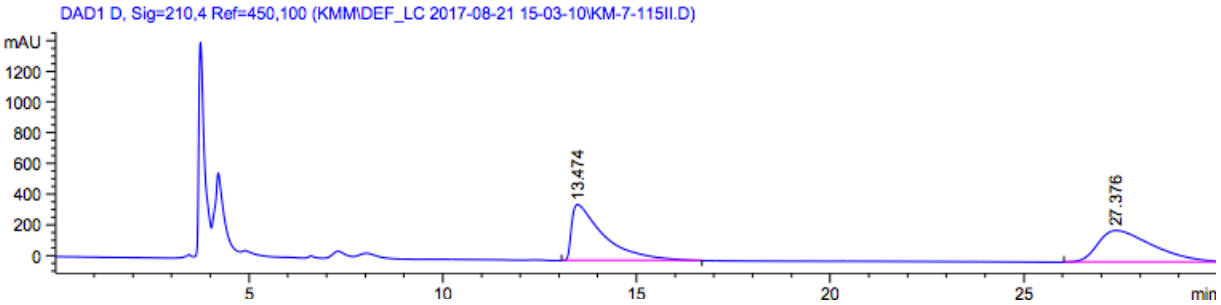
Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.922	MM	0.3280	1953.08704	99.22910	3.0182
2	18.069	MM	1.0308	6.27577e4	1014.73376	96.9818
Totals :				6.47108e4	1113.96287	

X = $SO_2C_6H_4$(*p*-OMe) (3q)

94% ee, Chiral HPLC (OJ-H, 50% isopropanol in hexanes, 1.0 mL/min, λ = 210 nm); t_R(minor) = 14.2 min, t_R(major) = 25.6 min.

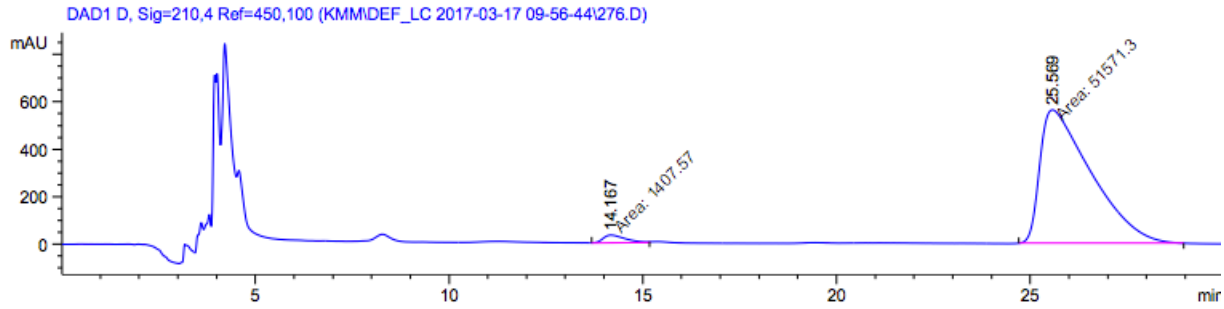
Racemic sample:



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.474	BB	0.7661	2.11041e4	364.19147	51.1759
2	27.376	VBA	1.1700	2.01342e4	204.97517	48.8241
Totals :				4.12383e4	569.16664	

Enriched sample:



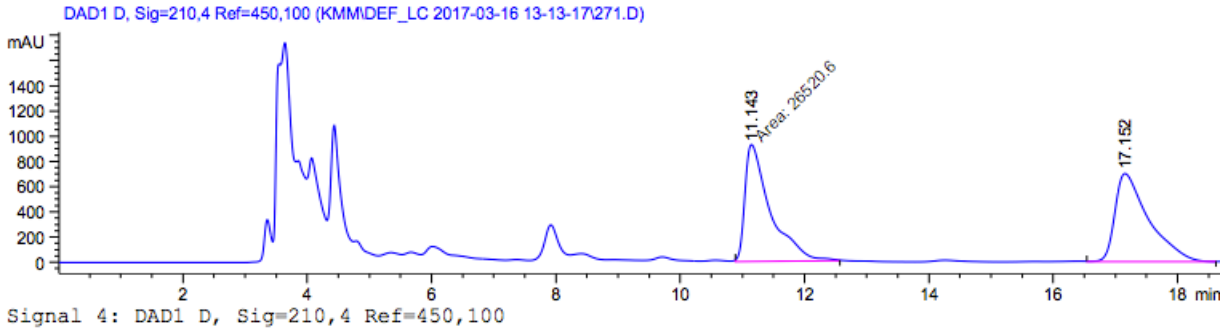
Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.167	MM	0.6997	1407.57104	33.52897	2.6569
2	25.569	MM	1.5284	5.15713e4	562.36053	97.3431
Totals :				5.29789e4	595.88951	

X = Ms (3r)

94% ee, Chiral HPLC (OJ-H, 50% isopropanol in hexanes, 1.0 mL/min, λ = 210 nm); t_R(minor) = 11.4 min, t_R(major) = 17.1 min.

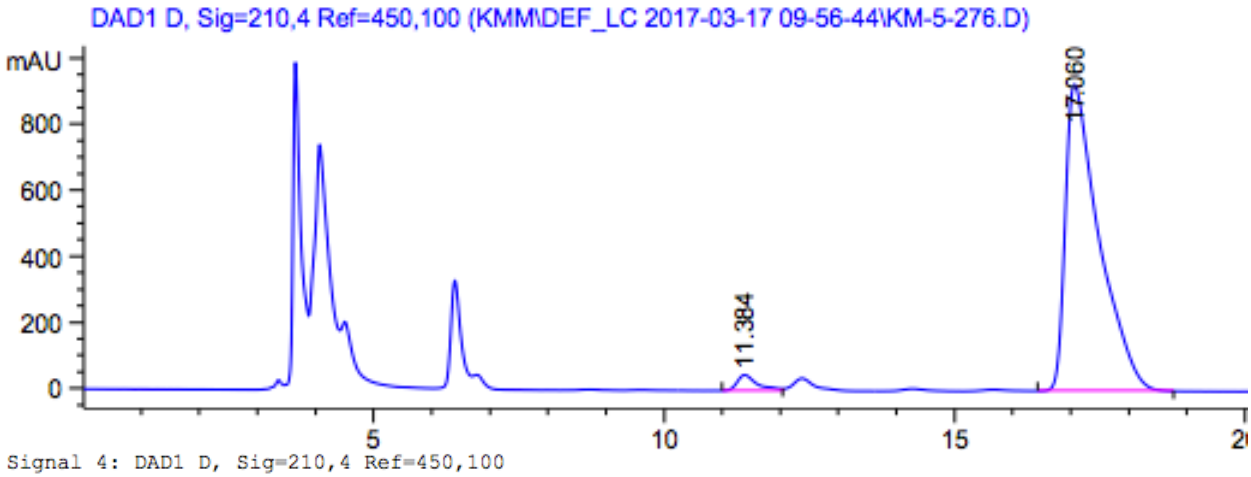
Racemic sample:



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.143	MM	0.4756	2.65206e4	929.37671	50.0303
2	17.152	VV	0.5513	2.64885e4	700.32471	49.9697
Totals :				5.30091e4	1629.70142	

Enriched sample:

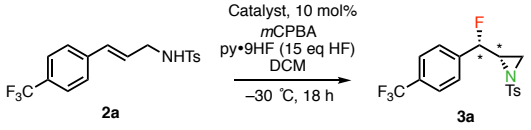


Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.384	BV	0.3592	1177.55298	47.84172	3.0421
2	17.060	VB	0.5720	3.75315e4	927.64667	96.9579
Totals :				3.87090e4	975.48839	

General procedure for catalyst optimization

Catalyst (**1a–i**, 5.2 μmol, 10.0 mol%), p-trifluoromethyl-cinnamyl tosylamide (**2a**, 17.8 mg, 52.0 μmol, 1.00 equiv) and dichloromethane (0.30 mL) were combined in a polyethylene tube. The reaction mixture was cooled to –78 ˚C. Pyridinium poly(hydrogen fluoride) (pyr•9HF, 70% hydrogen fluoride by weight, 210 μL, 15 equiv hydrogen fluoride) was added via micropipette followed by *m*-chloroperbenzoic acid (*m*CPBA, 77% by weight, 12.8 mg, 57.2 μmol, 1.10 equiv). The reaction was warmed to –30 ˚C and stirred for 18 hours at that temperature. The reaction was cooled to –78 ˚C and basic alumina (approximately 750 mg) was added slowly. The reaction was allowed to warm to room temperature with stirring and was filtered. The crude mixture was analyzed by ^{1}H NMR using mesitylene as an internal standard to determine the yield of product and by chiral HPLC GC to determine the enantioselectivity.



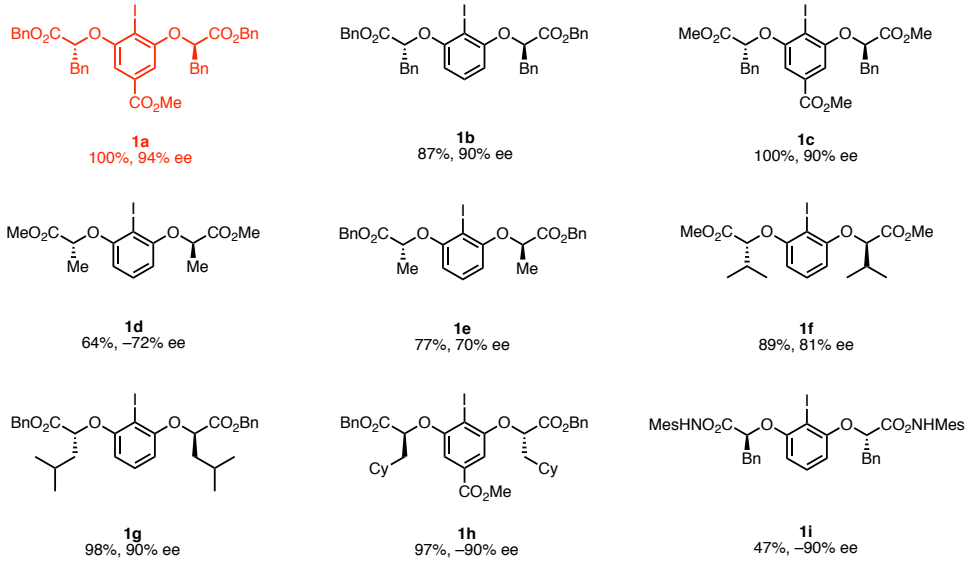
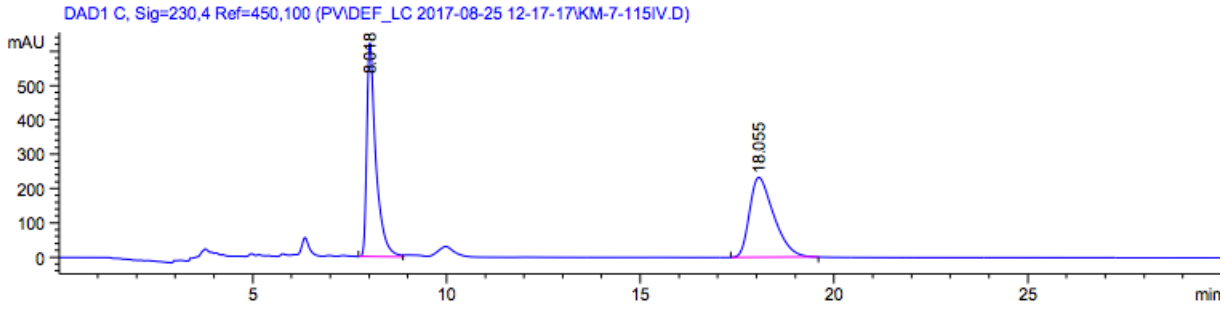


Table S2. Catalyst optimization

Racemic sample:

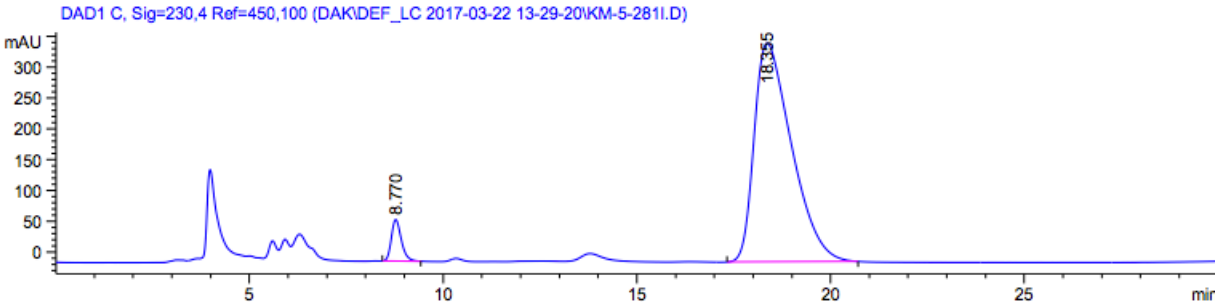


Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.018	VV	0.2370	1.01980e4	622.86884	50.0240
2	18.055	BB	0.6560	1.01882e4	233.07854	49.9760
Totals :				2.03862e4	855.94737	

Catalyst **1b**
90% ee, Chiral HPLC (OJ-H, 50% isopropanol in hexanes, 1.0 mL/min, λ = 230 nm); t_R(minor) = 8.8 min, t_R(major) = 18.4 min.

Enriched sample:

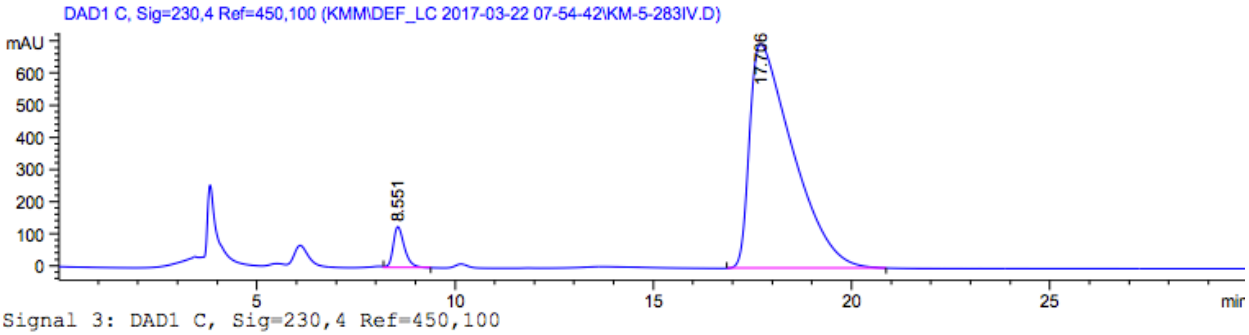


Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.770	BB	0.2757	1213.22131	67.48472	4.8392
2	18.355	BB	1.0173	2.38577e4	355.32098	95.1608
Totals :				2.50710e4	422.80570	

Catalyst **1c**
90% ee, Chiral HPLC (OJ-H, 50% isopropanol in hexanes, 1.0 mL/min, λ = 230 nm); t_R(minor) = 8.6 min, t_R(major) = 17.8 min.

Enriched sample:

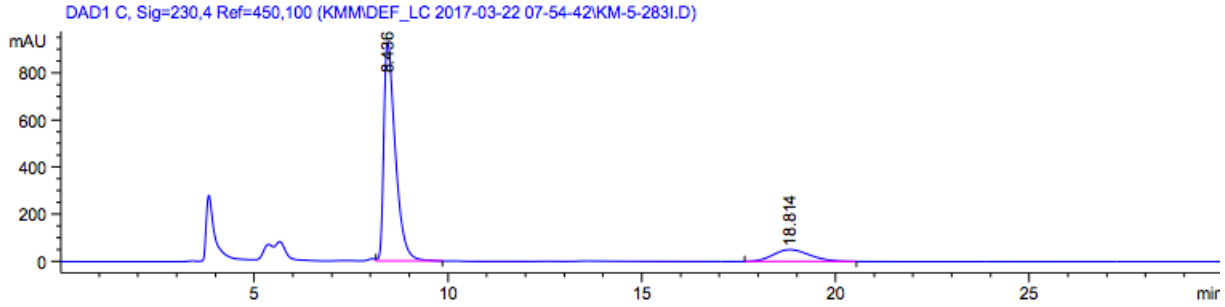


Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.551	VB	0.3020	2536.97534	127.57331	4.5663
2	17.706	BB	1.0779	5.30214e4	698.23096	95.4337
Totals :				5.55584e4	825.80427	

Catalyst **1d**
–72% ee, Chiral HPLC (OJ-H, 50% isopropanol in hexanes, 1.0 mL/min, λ = 230 nm); t_R(major) = 8.5 min, t_R(minor) = 18.8 min.

Enriched sample:

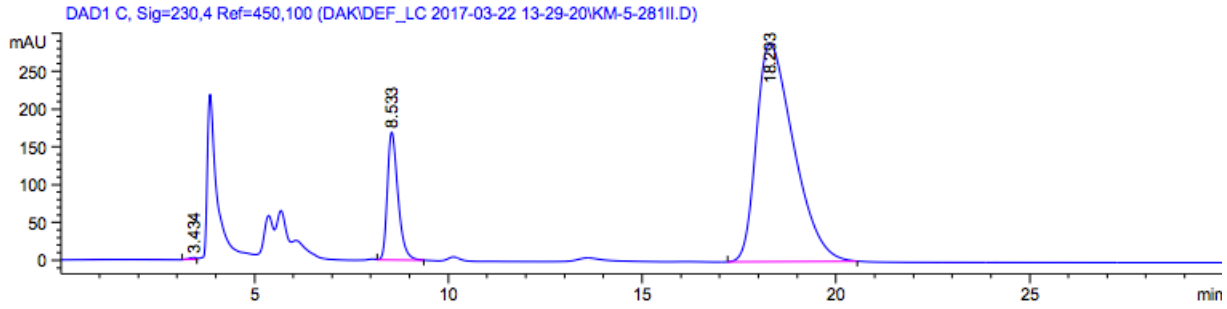


Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.436	VB	0.3109	1.91469e4	927.42902	85.2549
2	18.814	BB	0.9450	3311.52393	50.23888	14.7451
Totals :				2.24585e4	977.66790	

Catalyst **1e**
70% ee, Chiral HPLC (OJ-H, 50% isopropanol in hexanes, 1.0 mL/min, λ = 230 nm); t_R(minor) = 8.5 min, t_R(major) = 18.3 min.

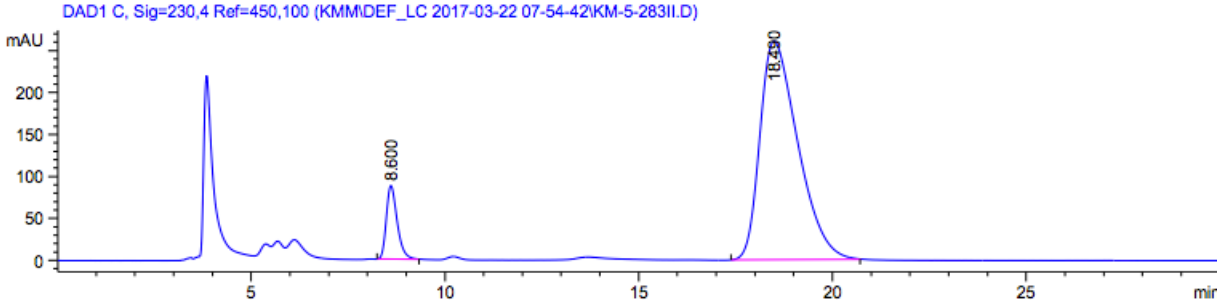
Enriched sample:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.434	BV	0.1567	37.35361	3.14161	0.1649
2	8.533	VB	0.2937	3248.10229	169.38814	14.3349
3	18.293	BB	1.0055	1.93732e4	289.22510	85.5002
Totals :				2.26587e4	461.75485	

Catalyst **1f**
81% ee, Chiral HPLC (OJ-H, 50% isopropanol in hexanes, 1.0 mL/min, λ = 230 nm); t_R(minor) = 8.6 min, t_R(major) = 18.5 min.

Enriched sample:

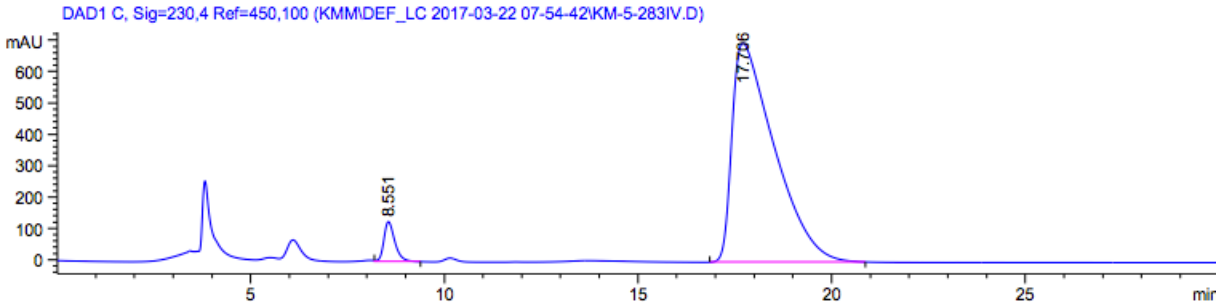


Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.600	BB	0.2998	1710.93127	87.63212	8.8052
2	18.490	BB	1.0313	1.77199e4	260.59326	91.1948
Totals :				1.94309e4	348.22538	

Catalyst **1g**
90% ee, Chiral HPLC (OJ-H, 50% isopropanol in hexanes, 1.0 mL/min, λ = 230 nm); t_R(minor) = 8.6 min, t_R(major) = 17.8 min.

Enriched sample:

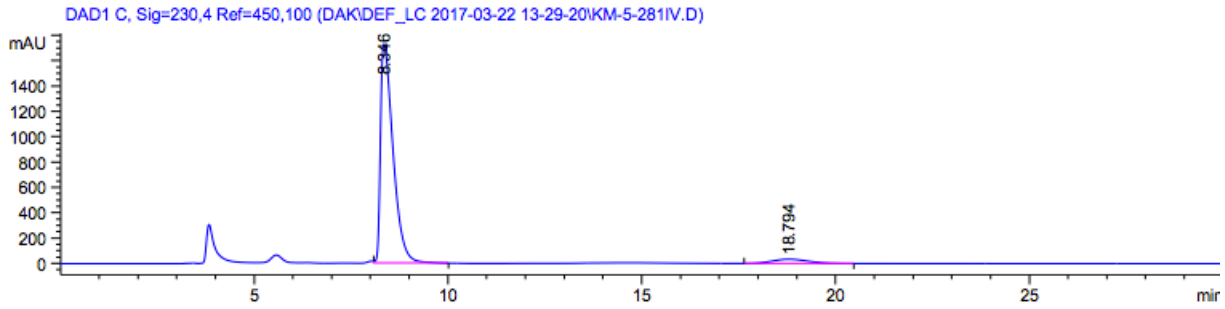


Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.551	VB	0.3020	2536.97534	127.57331	4.5663
2	17.706	BB	1.0779	5.30214e4	698.23096	95.4337
Totals :				5.55584e4	825.80427	

Catalyst **1h**
–90% ee, Chiral HPLC (OJ-H, 50% isopropanol in hexanes, 1.0 mL/min, λ = 230 nm); t_R(major) = 8.3 min, t_R(minor) = 18.8 min.

Enriched sample:

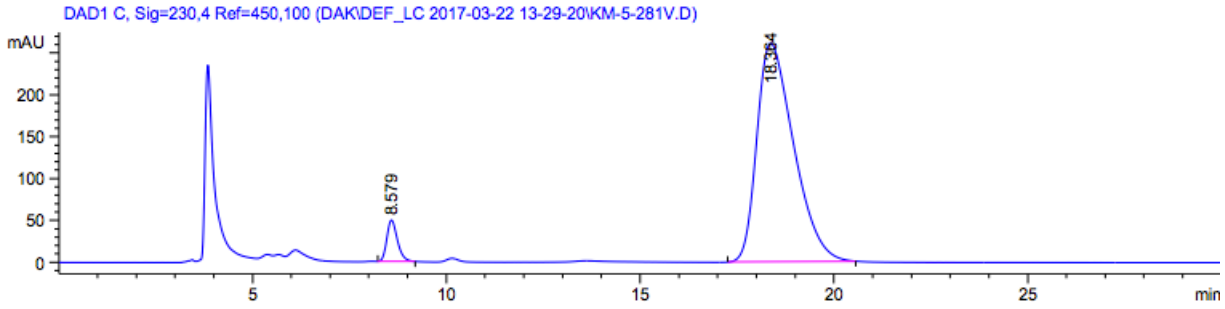


Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.346	VB	0.3451	3.89807e4	1728.34973	94.7775
2	18.794	BB	0.9057	2147.95630	33.33636	5.2225
Totals :				4.11286e4	1761.68610	

Catalyst **1i**
–90% ee, Chiral HPLC (OJ-H, 50% isopropanol in hexanes, 1.0 mL/min, λ = 230 nm); t_R(major) = 8.3 min, t_R(minor) = 18.8 min.

Enriched sample:

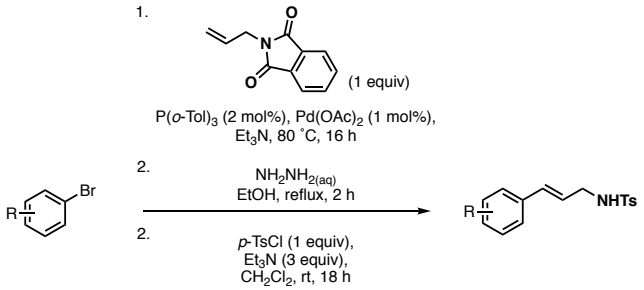


Signal 3: DAD1 C, Sig=230,4 Ref=450,100

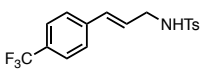
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.579	BB	0.2904	941.48804	49.37883	5.1649
2	18.364	BB	0.9916	1.72872e4	261.39069	94.8351
Totals :				1.82287e4	310.76952	

Synthesis of Substrates.

General Procedure A:

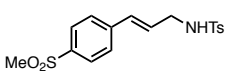


To a suspension of aryl bromide (5.50 mmol, 1 equiv), 2-allylisoindoline-1,3-dione (1.03 g, 5.50 mmol, 1.0 equiv) and tri(*o*-tolyl)phosphine (33.5 mg, 0.11 mmol, 2 mol%) in anhydrous triethylamine (4.0 mL) was added palladium(II) acetate (12.7 mg, 0.057 mmol, 1 mol%). The reaction mixture was stirred at 80 °C for 16 hours. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (100 mL), washed with water (20 mL), dried over $NaSO_4$, filtered and concentrated under reduced pressure. The crude residue was added to a solution of ethanol (40 mL) and hydrazine hydrate (~80% in water, 2 mL) and heated under reflux for 2 hours. After cooling, the suspension was filtered, washing with cold ethanol. The filtrate was concentrated under reduced pressure, re-dissolved in ethyl acetate (50 mL), washed with 1 M $NaOH_{(aq)}$ (2 x 20 mL) and brine (10 mL), dried over $NaSO_4$, filtered and concentrated under reduced pressure. The crude residue was dissolved in dichloromethane (22 mL). Triethylamine (2.3 mL, 16.5 mmol, 3 equiv) followed by p-toluenesulfonyl chloride (1.05 g, 5.50 mmol, 1 equiv). The resulting solution was stirred at room temperature. After 18 hours, the reaction mixture was washed with brine (10 mL), dried over $NaSO_4$, filtered and concentrated under reduced pressure.



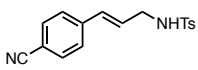
2a

Prepared according to general procedure A using 1-bromo-4-(trifluoromethyl)benzene (0.77 mL, 5.50 mmol). The crude residue was purified by silica gel column chromatography (10 to 100% ethyl acetate in hexanes) to give **2a** (1.45 g, 74% overall yield) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.41–7.27 (m, 4H), 6.48 (dd, *J* = 15.9, 1.6 Hz, 1H), 6.12 (dt, *J* = 15.9, 6.1 Hz, 1H), 5.20 (t, *J* = 6.3 Hz, 1H), 3.78 (td, *J* = 6.2, 1.6 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 143.8, 139.8, 137.1, 131.4, 129.9, 129.7 (q, *J* = 32.3 Hz), 127.3, 127.2, 126.7, 125.6 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 271.8 Hz), 83.39–74.57 (m), 45.3, 21.5; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -62.6 (s); FTIR (thin film) ν 3259 (w), 1715 (w), 1370 (s), 1159 (s), 906 (s), 728 (s), 552 (s) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{17}H_{16}F_3NO_2S$ $[M+H]^+$: 356.0927; found 356.0920.



2b

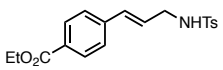
Prepared according to general procedure A using 4-bromophenyl methyl sulfone (1.29 g, 5.50 mmol). The crude residue was purified by silica gel column chromatography (10 to 100% ethyl acetate in hexanes) to give **2b** (1.38 g, 68% overall yield) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88–7.69 (m, 4H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.47 (dd, *J* = 15.9, 1.9 Hz, 1H), 6.17 (ddd, *J* = 16.0, 6.8, 5.1 Hz, 1H), 5.28 (t, *J* = 6.3 Hz, 1H), 3.75 (td, *J* = 6.2, 1.6 Hz, 2H), 3.03 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 143.7, 141.8, 139.2, 137.1, 130.7, 129.9, 129.0, 127.7, 127.3, 127.1, 45.1, 44.6, 21.6; FTIR (thin film) ν 3270 (br. s), 1596 (m), 1294 (s), 1146 (s), 959 (m), 550 (s) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{17}H_{19}NO_4S_2$ $[M+H]^+$: 366.0828; found 366.0826.



2d

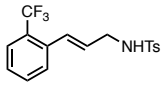
Prepared according to general procedure A using 4-bromobenzonitrile (1.00 g, 5.50 mmol). The crude residue was purified by silica gel column chromatography (10

to 100% ethyl acetate in hexanes) to give **2d** (1.43 g, 81% overall yield) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.3 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.22 (dd, *J* = 8.1, 4.9 Hz, 3H), 6.41 (d, *J* = 15.9 Hz, 1H), 6.11 (dt, *J* = 15.9, 6.0 Hz, 1H), 5.54 (t, *J* = 6.3 Hz, 1H), 3.84–3.59 (m, 1H), 2.32 (s, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 143.5, 140.8, 136.9, 132.2, 130.6, 129.7, 128.6, 127.1, 126.8, 118.8, 110.6, 44.9, 21.4; FTIR (thin film) ν 3272 (br. s), 2225 (m), 1604 (m), 1322 (s), 1153 (s), 661 (s), 549 (s) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{17}H_{16}N_2O_2S$ $[M+H]^+$: 313.1005; found 313.1004.



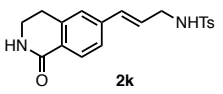
2f

Prepared according to general procedure A using ethyl 4-bromobenzoate (0.9 mL, 5.50 mmol). The crude residue was purified by silica gel column chromatography (10 to 100% ethyl acetate in hexanes) to give **2f** (1.52 g, 77% overall yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.87–7.70 (m, 2H), 7.46–7.18 (m, 4H), 6.65–6.35 (m, 1H), 6.13 (ddd, *J* = 16.0, 6.8, 5.5 Hz, 1H), 4.90 (t, *J* = 6.3 Hz, 1H), 4.56–4.16 (m, 2H), 4.01–3.59 (m, 2H), 2.42 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 166.4, 143.7, 140.6, 137.2, 132.0, 130.0, 129.9, 129.8, 127.3, 127.1, 126.4, 61.1, 45.4, 21.6, 14.5; FTIR (thin film) ν 3241 (m), 1697 (s), 1293 (s), 1154 (s), 981 (m), 581 (s) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{19}H_{21}NO_4S$ $[M+H]^+$: 360.1264; found 360.1261.



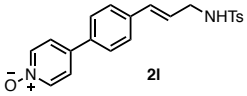
2j

Prepared according to general procedure A using 1-bromo-2-(trifluoromethyl)benzene (0.75 mL, 5.50 mmol). The crude residue was purified by silica gel column chromatography (10 to 100% ethyl acetate in hexanes) to give **2j** (1.59 g, 81% overall yield) as a colorless, viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ .81 (d, *J* = 8.1 Hz, 2H), 7.64–7.55 (m, 1H), 7.49–7.40 (m, 2H), 7.37–7.25 (m, 3H), 6.81 (dd, *J* = 15.7, 2.1 Hz, 1H), 6.04 (dt, *J* = 15.6, 6.3 Hz, 1H), 5.17 (t, *J* = 6.3 Hz, 1H), 3.78 (td, *J* = 6.3, 1.4 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 143.7, 137.0, 135.3, 131.9, 129.9, 129.0, 128.8, 128.8, 127.6, 127.6, 127.3, 125.7 (q, *J* = 5.7 Hz), 124.3 (q, *J* = 274.0 Hz), 45.5, 21.5; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -59.5 (s); FTIR (thin film) ν 3274 (br. m), 1598 (w), 1312 (s), 1153 (s), 965 (m), 658 (s) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{17}H_{16}F_3NO_2S$ $[M+H]^+$: 356.0927; found 356.0919.



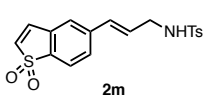
2k

Prepared according to general procedure A using 6-bromo-3,4-dihydroisoquinolin-1(2H)-one (1.24 g, 5.50 mmol). The crude residue was purified by recrystallization from methanol to give **2k** (1.18 g, 60% overall yield) as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.93–7.82 (m, 2H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.27–7.22 (m, 1H), 7.19 (s, 1H), 6.65–6.36 (m, 1H), 6.16 (dt, *J* = 15.9, 5.9 Hz, 1H), 3.59 (s, 2H), 3.35 (dt, *J* = 6.7, 3.2 Hz, 2H), 2.85 (t, *J* = 6.5 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 64.3, 142.6, 139.6, 139.4, 137.9, 130.3, 129.6, 128.4, 127.8, 127.4, 126.6, 125.0, 124.4, 45.5, 44.5, 27.7, 20.9; FTIR (thin film) ν 1653 (s), 1156 (s), 845 (m), 550 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{19}H_{20}N_2O_3S$ $[M+H]^+$: 357.1267; found 357.1273.



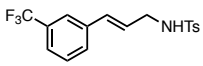
2l

Prepared according to general procedure A using 4-(4-bromophenyl)pyridine (1.29 g, 5.50 mmol). The crude residue was dissolved in dichloromethane (22 mL). *m*CPBA (77% by weight, 1.35 g, 5.50 mmol, 1.0 equiv) was added and the reaction mixture was stirred at room temperature. After 16 hours, the reaction mixture was washed with sat. $NaHCO_{3(aq)}$ (3 x 10 mL) and brine (10 mL), dried over $NaSO_4$, filtered, concentrate under reduced pressure and purified by silica gel column chromatography (0 to 10% methanol in dichloromethane) to give **2l** (1.15 g, 55%) as white solid. ^{1}H NMR (500 MHz, CD_3OD): δ 8.35 (d, *J* = 7.3 Hz, 2H), 7.86 (d, *J* = 7.3 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.39–7.34 (m, 2H), 6.50 (d, *J* = 16.0 Hz, 1H), 6.16 (dt, *J* = 15.8, 6.1 Hz, 1H), 3.70 (dd, *J* = 6.1, 1.6 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (125.7 MHz, 5% CD_3CO_2D/$CDCl_3$): δ 143.5, 141.9, 139.7, 137.9, 137.2, 134.5, 131.4, 129.8, 127.4, 127.2, 126.8, 126.7, 123.5, 45.2, 21.6; FTIR (thin film) ν 3051 (br. s), 1711 (br. s), 1479 (m), 1155 (s), 844 (m), 569 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{21}H_{20}N_2O_3S$ $[M+H]^+$: 381.1267; found 381.1261.



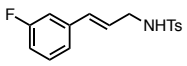
2m

Prepared according to general procedure A using 5-bromobenzo[*b*]thiophene (1.17 g, 5.50 mmol). The crude residue was dissolved in dichloromethane (22 mL). *m*CPBA (77% by weight, 2.70 g, 11.0 mmol, 1.0 equiv) was added and the reaction mixture was stirred at room temperature. After 16 hours, the reaction mixture was washed with sat. $NaHCO_{3(aq)}$ (3 x 10 mL) and brine (10 mL), dried over $NaSO_4$, filtered, concentrate under reduced pressure and purified by silica gel column chromatography (10 to 100% ethyl acetate in hexanes) to give **2m** (1.49, 72%) as white solid. ^{1}H NMR (500 MHz, 10% $CD_3OD/CDCl_3$): δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.24–7.08 (m, 5H), 6.64 (d, *J* = 6.9 Hz, 1H), 6.34 (d, *J* = 15.9 Hz, 1H), 6.05 (dt, *J* = 15.9, 5.9 Hz, 1H), 3.70 (s, 1H), 3.59 (dd, *J* = 5.9, 1.6 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (125.7 MHz, 10% $CD_3OD/CDCl_3$): δ 143.5, 142.3, 136.9, 134.8, 132.5, 131.8, 130.8, 129.9, 129.6, 129.1, 128.5, 126.9, 122.9, 121.3, 44.6, 21.2; FTIR (thin film) ν 3279 (br. m), 1599 (w), 1291 (s), 1138 (s), 730 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{18}H_{17}NO_4S_2$ $[M+H]^+$: 376.0672; found 376.0666.



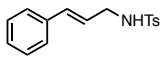
2s

Prepared according to general procedure A using 1-bromo-3-(trifluoromethyl)benzene (0.77 mL, 5.50 mmol). The crude residue was purified by silica gel column chromatography (10 to 100% ethyl acetate in hexanes) to give **2s** (1.41 g, 72% overall yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (dd, *J* = 8.1, 1.3 Hz, 2H), 7.48–7.44 (m, 1H), 7.42–7.36 (m, 3H), 7.27 (d, *J* = 7.6 Hz, 2H), 6.45 (dd, *J* = 15.9, 1.5 Hz, 1H), 6.06 (dtd, *J* = 15.9, 6.2, 1.2 Hz, 1H), 5.35 (t, *J* = 6.2 Hz, 1H), 3.96–3.62 (m, 2H), 2.37 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 43.7, 137.2, 137.1, 131.3, 130.9 (q, *J* = 32.1 Hz), 129.8, 129.7, 127.3, 124.3 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 272.3 Hz), 123.0 (q, *J* = 3.9 Hz), 45.2, 21.4; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -62.87 (s); FTIR (thin film) ν 3277 (br. s), 1598 (w), 1328 (s), 1154 (s), 965 (m), 661 (s) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{17}H_{16}F_3NO_2S$ $[M+H]^+$: 356.0927; found 356.0923.



2t

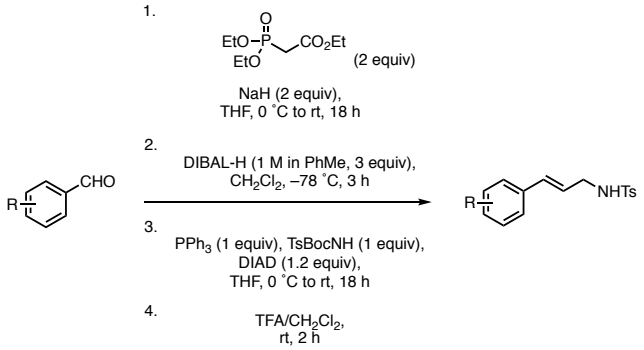
Prepared according to general procedure A using 1-bromo-3-fluoro-benzene (0.77 mL, 5.50 mmol). The crude residue was purified by silica gel column chromatography (10 to 100% ethyl acetate in hexanes) to give **2t** (1.68 g, 78% overall yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.37–7.15 (m, 3H), 7.09–6.79 (m, 3H), 6.38 (d, *J* = 15.8 Hz, 1H), 5.98 (dt, *J* = 15.9, 6.2 Hz, 1H), 5.25 (t, *J* = 6.2 Hz, 1H), 3.74 (td, *J* = 6.2, 1.6 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 163.0 (d, *J* = 245.2 Hz), 143.6, 138.6 (d, *J* = 8.0 Hz), 137.1, 131.6 (d, *J* = 2.8 Hz), 130.0 (d, *J* = 8.4 Hz), 129.8, 127.3, 125.8, 122.4 (d, *J* = 3.0 Hz), 114.6 (d, *J* = 21.4 Hz), 112.8 (d, *J* = 22.0 Hz), 45.2, 21.5; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -113.36 (td, *J* = 9.1, 5.9 Hz); FTIR (thin film) ν 3275 (br. s), 1583 (m), 1092 (s), 964 (m), 661 (s) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{16}H_{16}FNO_2S$ $[M+H]^+$: 306.0959; found 306.0953.



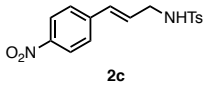
2w

Prepared according to general procedure A using bromobenzene (0.77 mL, 5.50 mmol). The crude residue was purified by silica gel column chromatography (10 to 100% ethyl acetate in hexanes) to give **2w** (1.19 g, 75% overall yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.32–7.17 (m, 7H), 6.43 (dd, *J* = 15.8, 1.6 Hz, 1H), 6.00 (dtd, *J* = 15.9, 6.4, 1.7 Hz, 1H), 5.04 (t, *J* = 6.4 Hz, 1H), 3.74 (td, *J* = 6.3, 1.6 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 143.6, 137.2, 136.2, 133.0, 129.8, 128.6, 127.9, 127.3, 126.5, 124.2, 45.5, 21.6; FTIR (thin film) ν 3278 (br. s), 1598 (w), 1324 (m), 1157 (s), 967 (m), 493 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{16}H_{17}NO_2S$ $[M+H]^+$: 288.1053; found 288.1047.

General Procedure B:

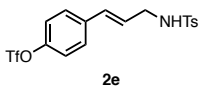


To a solution of triethyl phosphonoacetate (2.78 mL, 14.0 mmol, 2.0 equiv) in anhydrous tetrahydrofuran (28 mL) at 0 °C was added sodium hydride (60% by weight, 560 mg, 14.0 mmol, 2.0 equiv). The reaction mixture was stirred at that temperature for 30 minutes before the addition of benzaldehyde (7.00 mmol, 1.0 equiv) as a solution in tetrahydrofuran (5 mL). The resulting solution was allowed to warm to room temperature. After 18 hours, the reaction mixture was quenched with 1 M $HCl_{(aq)}$ (10 mL). The organic and aqueous layers were separated and the aqueous layer was extracted with ethyl acetate (2 x 20 mL). The combined organic layers were washed with brine (10 mL), dried over $NaSO_4$, filtered and concentrate under reduced pressure. The crude residue was dissolved in anhydrous dichloromethane (28 mL) and cooled to –78 °C. Diisobutylammonium hydride (1.0 M in toluene, 21.0 mmol, 3.0 equiv) was added dropwise, and reaction mixture was stirred at –78 °C for 3 hours. The reaction was quenched with a 1:1 mixture of 4 M $NaOH_{(aq)}$ and sat. Rochelle salt solution (20 mL), and the reaction mixture was allowed to warm to room temperature. The organic and aqueous layers were separated and the aqueous layer was extracted with ethyl acetate (2 x 40 mL). The combined organic layers were washed with brine (20 mL), dried over $NaSO_4$, filtered and concentrated under reduced pressure. The crude residue was dissolved in anhydrous tetrahydrofuran (28 mL) at 0 °C. Triphenylphosphine (1.84 g, 7.00 mmol, 1.0 equiv) and *N*-(*tert*-butoxycarbonyl)-*p*-toluenesulfonamide (1.90 g, 7.00 mmol, 1.0 equiv) were added followed by diisopropyl azodicarboxylate (1.65 mL, 8.40 mmol, 1.2 equiv). The reaction mixture was allowed to warm to room temperature. After 18 hours, the reaction mixture was concentrated under reduced pressure and purified by silica gel column chromatography (10 to 100% diethyl ether in hexanes). To a solution of the retrieved compound in dichloromethane (8 mL) was added trifluoroacetic acid (2 mL). The reaction mixture was stirred at room temperature for 2 hours. 1 M $NaOH_{(aq)}$ was added until the pH registered as neutral. The organic and aqueous layers were separated and the aqueous layer was extracted with ethyl acetate (2 x 20 mL). The combined organic layers were washed with brine (10 mL), dried over $NaSO_4$, filtered and concentrated under reduced pressure.



2c

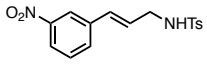
Prepared according to general procedure B using 4-nitrobenzaldehyde (1.06 mg, 7.00 mmol) to give **2c** (1.83 g, 79% overall yield) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.9 Hz, 1H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.35 (d, *J* = 8.8 Hz, 1H), 7.32– 7.24 (m, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.22 (dt, *J* = 15.9, 6.0 Hz, 1H), 5.21 (t, *J* = 6.3 Hz, 1H), 3.80 (td, *J* = 6.1, 1.6 Hz, 2H), 2.40 (s, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 147.1, 143.8, 142.8, 137.0, 130.5, 129.9, 129.6, 127.3, 127.0, 124.0, 45.1, 21.6; FTIR (thin film) ν 3279 (br. m), 1597 (m), 1515 (s), 1341 (s), 1158 (s), 551 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{16}H_{16}N_2O_4S$ $[M+H]^+$: 333.0904; found 333.0915.



2e

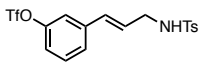
Prepared according to general procedure B using 4-formylphenyl trifluoromethanesulfonate[1] (1.78 g, 7.00 mmol) to give **2e** (2.04 g, 67% overall yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 4H), 7.17 (d, *J* = 8.7 Hz, 2H), 6.44 (d, *J* = 15.9 Hz, 1H), 6.04 (ddd, *J* = 15.9, 6.5, 5.7 Hz, 1H), 5.22 (t, *J* = 6.2 Hz,

1H), 3.76 (td, *J* = 6.2, 1.4 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 148.9, 143.8, 137.1, 136.8, 129.9, 128.1, 127.2, 126.7, 121.5, 118.8 (q, *J* = 321.0 Hz), 45.2, 21.5; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -72.8 (s); FTIR (thin film) ν 3274 (br. m), 1598 (w), 1500 (m), 1422 (s), 1093 (s), 885 (s), 551 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{17}H_{16}F_3NO_5S_2$ [M+H]$^+$: 436.0495; found 436.0490.



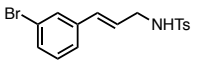
2g

Prepared according to general procedure B using 3-nitrobenzaldehyde (1.06 mg, 7.00 mmol) to give **2g** (1.74 g, 75% overall yield) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.3 Hz, 1H), 7.99 (s, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.46–7.39 (m, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 6.49 (d, *J* = 15.9 Hz, 1H), 6.25–6.08 (m, 1H), 5.30 (s, 1H), 4.14–3.28 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 148.5, 143.8, 138.1, 137.1, 132.3, 130.3, 129.9, 129.5, 127.9, 127.3, 122.4, 121.0, 45.0, 21.5; FTIR (thin film) ν 3279 (br. s), 1598 (w), 1526 (s), 1350 (s), 1157 (s), 815 (m), 550 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{16}H_{16}N_2O_4S$ [M+H]$^+$: 333.0904; found 333.0900.



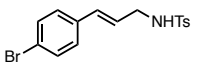
2h

Prepared according to general procedure B using 3-formylphenyl trifluoromethanesulfonate[2] (1.78 g, 7.00 mmol) to give **2h** (2.16 g, 67% overall yield) as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.26–7.20 (m, 1H), 7.16–7.07 (m, 2H), 6.43 (dd, *J* = 15.9, 1.7 Hz, 1H), 6.06 (dt, *J* = 15.8, 6.1 Hz, 1H), 5.26 (t, *J* = 6.3 Hz, 1H), 3.77 (td, *J* = 6.2, 1.6 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 149.9, 143.8, 139.1, 137.1, 130.7, 130.4, 129.9, 127.3, 127.3, 126.4, 120.3, 119.0, 118.8 (q, *J* = 321.1 Hz), 45.1, 21.5; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -72.9 (s); FTIR (thin film) ν 3277 (br. m), 1599 (w), 1419 (s), 1208 (s), 844 (s), 571 (s) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{17}H_{16}F_3NO_5S_2$ [M+H]$^+$: 436.0495; found 436.0487.



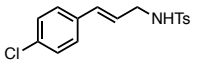
2i

Prepared according to general procedure B using 3-bromobenzaldehyde (1.30 g, 7.00 mmol) to give **2i** (1.95 g, 76% overall yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.38–7.25 (m, 4H), 7.17–7.08 (m, 2H), 6.34 (dd, *J* = 15.9, 1.6 Hz, 1H), 5.97 (dt, *J* = 15.9, 6.2 Hz, 1H), 5.21 (t, *J* = 6.3 Hz, 1H), 3.75 (td, *J* = 6.2, 1.6 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 143.7, 138.5, 137.2, 131.3, 130.7, 130.1, 129.8, 129.3, 127.3, 126.0, 125.2, 122.7, 45.2, 21.6; FTIR (thin film) ν 3274 (br. s), 1592 (w), 1323 (m), 1154 (s), 814 (m), 572 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{16}H_{16}BrNO_2S$ [M+H]$^+$: 366.0158; found 366.0149.



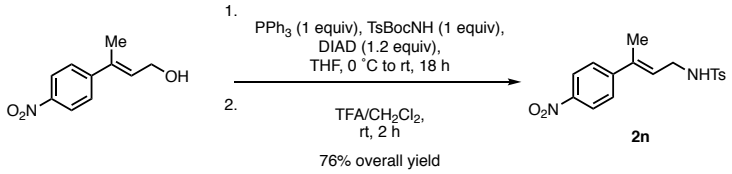
2u

Prepared according to general procedure B using 4-bromobenzaldehyde (1.30 g, 7.00 mmol) to give **2u** (2.07 g, 81% overall yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 2H), 6.36 (dd, *J* = 15.9, 1.8 Hz, 1H), 5.99 (dtd, *J* = 15.8, 6.2, 1.5 Hz, 1H), 5.08 (s, 1H), 3.74–3.70 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 143.6, 137.1, 135.2, 131.7, 129.8, 127.3, 125.2, 121.7, 45.4, 21.6; FTIR (thin film) ν 3260 (br. s), 1598 (w), 1487 (m), 1320 (m), 1156 (s), 811 (m), 575 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{16}H_{16}BrNO_2S$ [M+H]$^+$: 365.0080; found 365.0078.

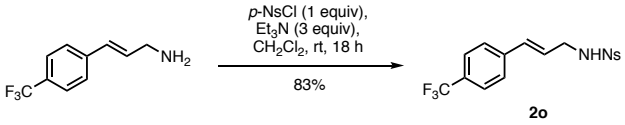


2v

Prepared according to general procedure B using 4-chlorobenzaldehyde (1.30 g, 7.00 mmol) to give **2v** (1.87 g, 83% overall yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81–7.76 (m, 2H), 7.30–7.26 (m, 2H), 7.25–7.21 (m, 2H), 7.18–7.11 (m, 2H), 6.38 (dd, *J* = 15.8, 1.7 Hz, 1H), 6.11–5.82 (m, 1H), 5.10 (s, 1H), 3.71–3.75 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 43.6, 137.1, 134.8, 133.5, 131.7, 129.8, 128.7, 127.7, 127.3, 125.0, 45.4, 21.6; FTIR (thin film) ν 3275 (br. s), 1597 (w), 1491 (s), 1154 (s), 967 (m), 550 (s) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{16}H_{16}ClNO_2S$ [M+H]$^+$: 321.0585; found 321.0585.

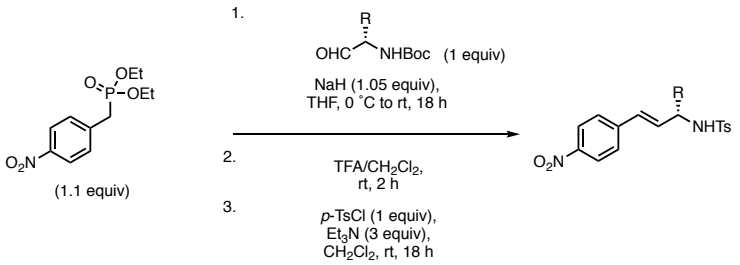


(E)-3-(4-Nitrophenyl)but-2-en-1-ol[3] (965 g, 5.00 mmol, 1.0 equiv) was dissolved in anhydrous tetrahydrofuran (50 mL) at 0 °C. Triphenylphosphine (1.32 g, 5.00 mmol, 1.0 equiv) and *N*-(*tert*-butoxycarbonyl)-*p*-toluenesulfonamide (1.36 g, 5.00 mmol, 1.0 equiv) were added followed by diisopropyl azodicarboxylate (1.18 mL, 6.0 mmol, 1.2 equiv). The reaction mixture was allowed to warm to room temperature. After 18 hours, the reaction mixture was concentrated under reduced pressure and purified by silica gel column chromatography (10 to 100% diethyl ether in hexanes). To a solution of the retrieved compound in dichloromethane (8 mL) was added trifluoroacetic acid (2 mL). The reaction mixture was stirred at room temperature for 2 hours. 1 M $NaOH_{(aq)}$ was added until the pH registered as neutral. The organic and aqueous layers were separated and the aqueous layer was extracted with ethyl acetate (2 x 20 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered, concentrated under reduced pressure and purified by silica gel column chromatography (10 to 100% diethyl ether in hexanes) to give **2n** (1.32 g, 76%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.7 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.37–7.25 (m, 4H), 5.77–5.71 (m, 1H), 5.37 – 5.31 (m, 1H), 3.89–3.74 (m, 2H), 2.40 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 148.9, 146.9, 143.7, 137.1, 137.0, 129.8, 127.3, 126.5, 126.4, 123.5, 41.7, 21.6, 15.9; FTIR (thin film) ν 3277 (br. m), 1595 (m), 1512 (s), 1341 (s), 1155(s), 666 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{17}H_{18}N_2O_4S$ $[M+H]^+$: 347.1060; found 347.1054.

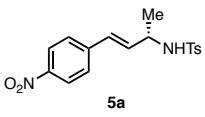


To a solution of (*E*)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-amine[4] (302 mg, 1.50 mmol, 1 equiv) in dichloromethane (7.5 mL) was added triethylamine (0.63 mL, 4.50 mmol, 3 equiv) followed by 4-nitrobenzenesulfonyl chloride (332 mg, 1.50 mmol, 1 equiv). The reaction mixture was allowed to stir at room temperature overnight before being quenched by 1 M $HCl_{(aq)}$ (3 mL). The organic and aqueous layers were separated and the aqueous layer was extracted with dichloromethane (2 x 5 mL). The combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, filtered, concentrated under reduced pressure and purified by silica gel column chromatography (20 to 70% ethyl acetate in hexanes) to give **2o** (481 mg, 83%) as a yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.37 (d, *J* = 7.8 Hz, 2H), 8.16-8.10 (m, 2H), 8.10-8.04 (m, 2H), 7.56 (d, *J* = 7.8 Hz, 2H), 6.59 (d, *J* = 16.4 Hz, 1H), 6.38-6.29 (m, 1H), 4.83-4.72 (m, 1H), 3.78-3.67 (m, 2H); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ ^{13}C NMR (DMSO-d_6) 156.2, 149.5, 146.4, 142.8, 130.6, 129.5, 128.2, 127.1, 124.6, 123.8, 123.7 (q, *J* = 272.4Hz), 44.6; ^{19}F NMR ($CDCl_3$) -62.8 (s); HRMS (ESI-TOF) Calc'd for $C_{16}H_{13}F_3N_2O_4S$ $[M+H]^+$: 387.0632; found 387.0630.

General Procedure C:



To a solution of diethyl (4-nitrobenzyl)phosphonate[5] (901 mg, 3.30 mmol, 1.1 equiv) in anhydrous tetrahydrofuran (12 mL) at 0 °C was added sodium hydride (60% by weight, 119 mg, 2.99 mmol, 1.0 equiv). The reaction mixture was allowed to stir at 0 °C for 30 minutes before the addition of a solution of aldehyde (3.00 mmol, 1 equiv). The reaction mixture was allowed to warm to room temperature. After 18 hours, the reaction was quenched with 1 M $HCl_{(aq)}$ (10 mL). The organic and aquoeus layers were separated and the aqueous layer was extracted with ethyl acetate (2 x 20 mL). The combined organic layers were washed with brine (10 mL), dried over $NaSO_4$, filtered and concentrated under reduced pressure. The crude residue was dissolved in dichloromethane (6 mL) was added trifluoroacetic acid (1.5 mL). The reaction mixture was stirred at room temperature for 2 hours. 1 M $NaOH_{(aq)}$ was added until the pH registered as neutral. The organic and aqueous layers were separated and the aqueous layer was extracted with ethyl acetate (2 x 20 mL). The combined organic layers were washed with brine (10 mL), dried over $NaSO_4$, filtered and concentrated under reduced pressure. The crude residue was dissolved in dichloromethane (15 mL). Triethylamine (1.26 mL, 9.00 mmol, 3 equiv) followed by p-toluenesulfonyl chloride (573 mg, 3.00 mmol, 1 equiv). The resulting solution was stirred at room temperature. After 18 hours, the reaction mixture was washed with brine (10 mL), dried over $NaSO_4$, filtered and concentrated under reduced pressure.

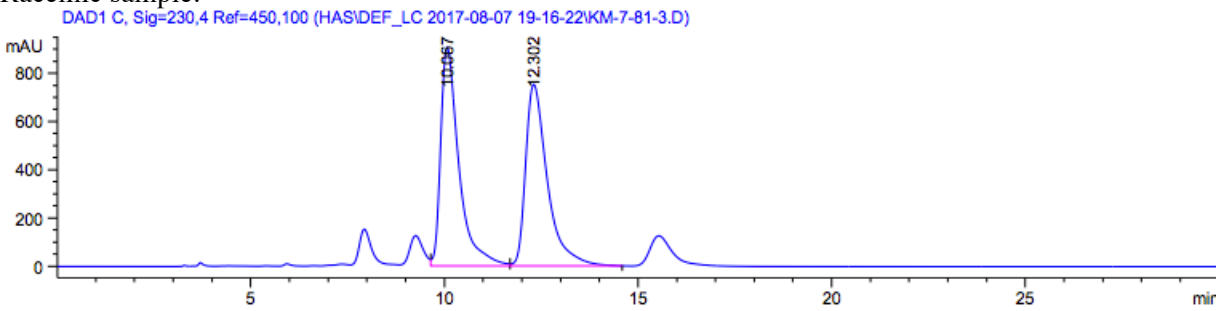


5a

Prepared according to general procedure C using Boc-L-alaninal (520 mg, 3.00 mmol) followed by purification by silica gel column chromatography (10 to 100% diethyl ether in hexanes) to give **5a** as a yellow solid (823 mg, 72% overall yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14–8.03 (m, 2H), 7.78 (d, J = 8.3 Hz, 2H), 7.36–7.15 (m, 4H), 6.40 (d, J = 15.9 Hz, 1H), 6.16–6.01 (m, 1H), 5.38 (d, J = 7.7 Hz, 1H), 4.24–3.99 (m, 1H), 2.33 (s, 3H), 1.27 (d, J = 6.8 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 147.0, 143.6, 143.0, 138.0, 135.4, 129.7, 128.4, 127.3, 127.0, 123.9, 51.6, 21.6 (d, J = 17.2 Hz); FTIR (thin film) ν 3271 (br. m), 1595 (m), 1512 (s), 1339 (s), 1147 (s), 814 (s), 663 (s) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{17}H_{18}N_2O_4S$ $[M+H]^+$: 347.1060; found 347.1054; $[\alpha]_D^{24} = -169°$ (c 1.0, $CHCl_3$).

98% ee, Chiral HPLC (OD-H, 30% isopropanol in hexanes, 1.0 mL/min, λ = 230 nm); t_R(major) = 10.0 min, t_R(minor) = 12.4 min.

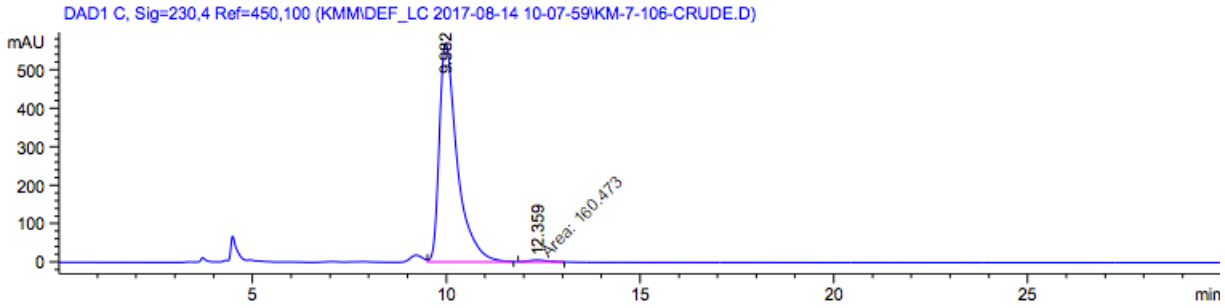
Racemic sample:



Signal 3: DAD1 C, Sig=230,4 Ref=450,100

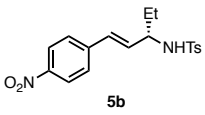
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.067	VV	0.4907	2.97686e4	907.42834	50.2442
2	12.302	VB	0.5870	2.94793e4	752.63397	49.7558
Totals :				5.92479e4	1660.06232	

Enriched sample:



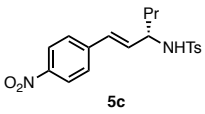
Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.982	VB	0.4816	1.84537e4	570.11945	99.1379
2	12.359	MM	0.5673	160.47330	4.71452	0.8621
Totals :				1.86141e4	574.83396	



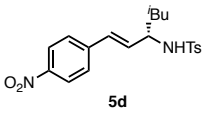
5b

Prepared according to general procedure C using (S)-tert-butyl 1-oxobutan-2-ylcarbamate[6] (562 mg, 3.00 mmol) followed by purification by silica gel column chromatography (10 to 100% diethyl ether in hexanes) to give **5b** as a yellow solid (756 mg, 70% overall yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.30 (d, *J* = 15.9 Hz, 1H), 5.97 (dd, *J* = 15.9, 7.4 Hz, 1H), 5.47 (d, *J* = 8.0 Hz, 1H), 4.05–3.61 (m, 1H), 2.27 (s, 3H), 1.81–1.36 (m, *J* = 6.9 Hz, 2H), 0.85 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 146.9, 143.4, 143.0, 138.1, 134.1, 129.6, 129.3, 127.3, 126.9, 123.8, 57.6, 28.6, 21.4, 10.0; FTIR (thin film) ν 3274 (br. m), 1595 (m), 1339 (s), 663 (s) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{18}H_{20}N_2O_4S$ $[M+H]^+$: 361.1217; found 361.1216; $[\alpha]_D^{24}$ = –142.7° (c 1.0, CH_3CN).



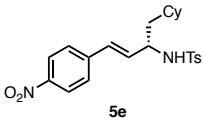
5c

Prepared according to general procedure C using carbamic acid, [(1S)-1-formylbutyl], 1,1-dimethylethyl ester[7] (604 mg, 3.00 mmol) followed by purification by silica gel column chromatography (10 to 100% diethyl ether in hexanes) to give **5c** as a yellow solid (764 mg, 68% overall yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 7.7 Hz, 2H), 6.29 (dd, *J* = 16.0, 0.9 Hz, 1H), 5.97 (dd, *J* = 15.9, 7.5 Hz, 1H), 5.39 (d, *J* = 8.3 Hz, 1H), 4.00–3.87 (m, 1H), 2.27 (s, 3H), 1.63–1.45 (m, 2H), 1.42–1.18 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 146.9, 143.4, 143.0, 138.1, 134.4, 129.6, 129.1, 127.3, 126.9, 123.8, 56.0, 37.7, 21.5, 18.7, 13.7; FTIR (thin film) ν 3275 (br. m), 1596 (m), 1340 (s), 1158 (s), 667 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{19}H_{22}N_2O_4S$ $[M+H]^+$: 375.1373; found 375.1375; $[\alpha]_D^{24}$ = –122° (c 1.0, CH_3CN).



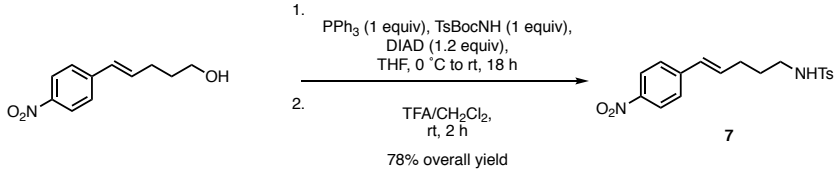
5d

Prepared according to general procedure C using commercially available tert-butyl [(1S)-1-formyl-3-methylbutyl]carbamate (646 mg, 3.00 mmol) followed by purification by silica gel column chromatography (10 to 100% diethyl ether in hexanes) to give **5d** as a yellow solid (862 mg, 74% overall yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.7 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.8 Hz, 2H), 7.18–7.14 (m, 2H), 6.29 (d, *J* = 15.9 Hz, 1H), 5.93 (dd, *J* = 15.9, 7.6 Hz, 1H), 5.30 (d, *J* = 8.0 Hz, 1H), 4.07–3.93 (m, 1H), 2.26 (s, 3H), 1.72–1.59 (m, 1H), 1.51–1.42 (m, 1H), 1.42–1.31 (m, 1H), 0.83 (dd, *J* = 17.8, 6.6 Hz, 6H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 146.9, 143.4, 143.0, 138.2, 134.5, 129.6, 129.0, 127.4, 126.9, 123.8, 54.6, 44.8, 24.4, 22.5, 22.2, 21.5; FTIR (thin film) ν 2956 (br. m), 1596 (m), 1367(s), 663 (s) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{20}H_{24}N_2O_4S$ [M+H]$^+$: 389.1530; found 389.1531; $[\alpha]_D^{27}$ = –60.3° (c 1.0, CH_3CN).



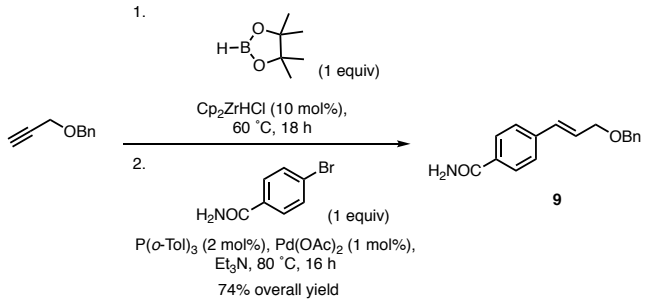
5e

Prepared according to general procedure C using commercially available tert-butyl N-(1-cyclohexyl-3-oxopropan-2-yl)carbamate (766 mg, 3.00 mmol) followed by purification by silica gel column chromatography (10 to 100% diethyl ether in hexanes) to give **5e** as a yellow solid (913 mg, 71% overall yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13–8.03 (m, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 6.33 (d, *J* = 15.8 Hz, 1H), 5.97 (ddd, *J* = 15.9, 7.3, 0.8 Hz, 1H), 5.21 (d, *J* = 7.8 Hz, 1H), 4.10–3.92 (m, 1H), 2.28 (s, 3H), 1.74–0.67 (m, 13H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 146.9, 143.4, 143.1, 138.1, 134.9, 129.6, 128.8, 127.4, 126.9, 123.8, 53.7, 43.4, 33.7, 33.3, 32.8, 26.4, 26.2, 26.0, 21.5; FTIR (thin film) ν 2921 (br. m), 1596 (m), 1339 (s), 1157 (s), 667 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{23}H_{28}N_2O_4S$ [M+H]$^+$: 429.1843; found 429.1838; $[\alpha]_D^{24}$ = –83.3° (c 1.0, CH_3CN).

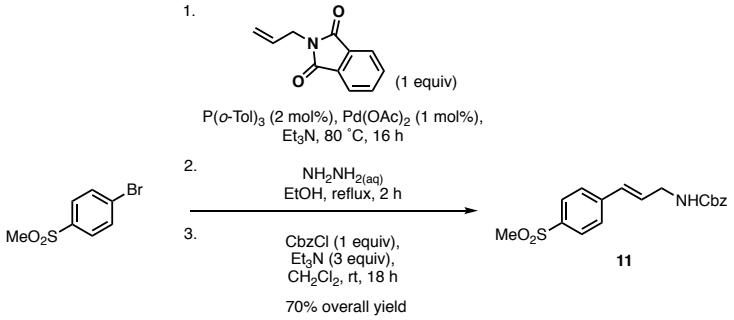


7

(E)-5-(3-Nitrophenyl)pent-4-en-1-ol[8] (1.04 g, 5.00 mmol, 1.0 equiv) was dissolved in anhydrous tetrahydrofuran (25 mL) at 0 °C. Triphenylphosphine (1.32 g, 5.00 mmol, 1.0 equiv) and *N*-(*tert*-butoxycarbonyl)-*p*-toluenesulfonamide (1.36 g, 5.00 mmol, 1.0 equiv) were added followed by diisopropyl azodicarboxylate (1.18 mL, 6.0 mmol, 1.2 equiv). The reaction mixture was allowed to warm to room temperature. After 18 hours, the reaction mixture was concentrated under reduced pressure and purified by silica gel column chromatography (10 to 100% diethyl ether in hexanes). To a solution of the retrieved compound in dichloromethane (8 mL) was added trifluoroacetic acid (2 mL). The reaction mixture was stirred at room temperature for 2 hours. 1 M $NaOH_{(aq)}$ was added until the pH registered as neutral. The organic and aqueous layers were separated and the aqueous layer was extracted with ethyl acetate (2 x 20 mL). The combined organic layers were washed with brine (10 mL), dried over $NaSO_4$, filtered, concentrated under reduced pressure and purified by silica gel column chromatography (10 to 100% diethyl ether in hexanes) to give **7** (1.41 g, 78%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (s, 1H), 8.05–7.99 (m, 2H), 7.82–7.72 (m, 4H), 7.62–7.55 (m, 2H), 7.49–7.40 (m, 2H), 7.30 (m, 5H), 6.38 (dd, *J* = 15.9, 1.5 Hz, 2H), 6.31–6.18 (m, 2H), 5.16–5.09 (m, 3H), 3.06–2.94 (m, 5H), 2.41 (s, 6H), 2.32–2.23 (m, 5H), 1.76–1.63 (m, 6H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 148.6, 143.5, 139.3, 137.0, 132.6, 132.0, 129.8, 129.4, 128.86, 127.2, 121.7, 120.5, 42.5, 29.8, 28.9, 21.6; FTIR (thin film) ν 3281 (br. m), 1654 (w), 1524 (s), 1153 (s), 965 (m), 550 (s) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{18}H_{20}N_2O_4S$ [M+H]$^+$: 361.1217; found 361.1210.

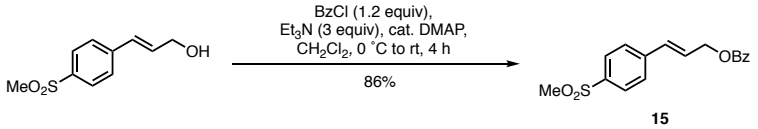


A mixture of benzyl propargyl ether (0.80 mL, 5.50 mmol, 1 equiv), pinacol borane (0.80 mL, 5.50 mmol, 1 equiv) and bis(cyclopentadienyl)zirconium(IV) chloride hydride (142 mg, 0.55 mmol, 10 mol%) was stirred at 60 °C for 18 hours and then flushed through a plug of silica with diethyl ether. To this crude residue was added 4-bromophenyl methyl sulfone (1.29 g, 5.50 mmol), tri(*o*-tolyl)phosphine (33.5 mg, 0.11 mmol, 2 mol%) and anhydrous triethylamine (4.0 mL) followed by palladium(II) acetate (12.7 mg, 0.057 mmol, 1 mol%). The reaction mixture was stirred at 80 °C for 16 hours. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (100 mL), washed with water (20 mL), dried over $NaSO_4$, filtered, concentrated under reduced pressure and purified by silica gel column chromatography (20 to 100% ethyl acetate in hexanes) to give **9** (1.09 g, 74%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.42–7.34 (m, 4H), 7.34–7.28 (m, 1H), 6.72–6.63 (m, 1H), 6.43 (ddd, *J* = 16.0, 6.0, 5.4 Hz, 1H), 4.59 (s, 2H), 4.22 (dd, *J* = 5.8, 1.5 Hz, 2H); ^{13}C NMR (125.7 MHz, 10% CD_3OD/$CDCl_3$): δ 69.9, 140.6, 138.1, 132.2, 131.3, 128.6, 128.0, 127.9, 127.9, 126.7, 72.6, 70.6; FTIR (thin film) ν 2531 (br. m), 2350 (br. m), 1623 (s), 1114 (m), 697 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{17}H_{17}NO_2$ $[M+H]^+$: 268.1332; found 268.1339.



To a suspension of 4-bromophenyl methyl sulfone (1.29 g, 5.50 mmol), 2-allylisoindoline-1,3-dione (1.03 g, 5.50 mmol, 1.0 equiv) and tri(*o*-tolyl)phosphine (33.5 mg, 0.11 mmol, 2 mol%) in anhydrous triethylamine (4.0 mL) was added palladium(II) acetate (12.7 mg, 0.057 mmol, 1 mol%). The reaction mixture was stirred at 80 °C for 16 hours. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (100 mL), washed with water (20 mL), dried over $NaSO_4$, filtered and concentrated under reduced pressure. The crude residue was added to a solution of ethanol (40 mL) and hydrazine hydrate (~80% in water, 2 mL) and heated under reflux for 2 hours. After cooling, the suspension was filtered, washing with cold ethanol. The filtrate was concentrated under reduced pressure, re-dissolved in ethyl acetate (50 mL), washed with 1 M $NaOH_{(aq)}$ (2 x 20 mL) and brine (10 mL), dried over $NaSO_4$, filtered and concentrated under reduced pressure. The crude residue was dissolved in dichloromethane (22 mL). Triethylamine (2.3 mL, 16.5 mmol, 3 equiv) followed by benzyl chloroformate (0.79 mL, 5.50 mmol, 1 equiv). The resulting solution was stirred at room temperature. After 18 hours, the reaction mixture was washed with brine (10 mL), dried over $NaSO_4$, filtered, concentrated under reduced pressure and purified by silica gel column chromatography (0 to 10% methanol in dichloromethane) to give **11** (1.33 g, 70%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.40–7.29 (m, 5H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.42 – 6.28 (m, 1H),

5.25–5.20 (m, 1H), 5.17–5.09 (m, 2H), 4.00 (dd, J = 8.3, 3.7 Hz, 2H), 3.01 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 156.5, 142.2, 139.0, 136.5, 130.7, 129.4, 128.6, 128.3, 128.2, 127.7, 127.1, 66.9, 44.6, 42.9; FTIR (thin film) ν 3358 (br. s), 1703 (m), 1144 (s), 764 (m), 535 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{18}H_{19}NO_4S$ [M+H]$^+$: 346.1108; found 346.1113.

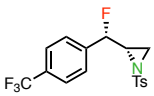


15

To a solution of (E)-3-(4-(methylsulfonyl)phenyl)prop-2-en-1-ol[9] (1.06 g, 5.00 mmol, 1 equiv) in dichloromethane at 0 °C was added triethylamine (2.09 mL, 15.0 mmol, 3.0 equiv), a catalytic amount of 4-dimethylaminopyridine and benzoyl chloride (0.70 mL, 6.00 mmol, 1.2 equiv). The reaction mixture was stirred at room temperature for 4 hours and then washed with water (10 mL), dried over $NaSO_4$, filtered, concentrated under reduced pressure and purified by silica gel column chromatography (10 to 100% diethyl ether in hexanes) to give **15** (1.36 g, 86%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12–8.06 (m, 2H), 7.90 (d, J = 8.4 Hz, 2H), 7.63–7.57 (m, 3H), 7.47 (t, J = 7.8 Hz, 2H), 6.85–6.75 (m, 1H), 6.62–6.52 (m, 1H), 5.03 (dd, J = 5.9, 1.5 Hz, 2H), 3.05 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 167.6, 142.1, 138.8, 134.2, 131.6, 130.5, 129.6, 128.6, 127.6, 127.2, 127.0, 44.6, 41.8; FTIR (thin film) ν 2925 (w), 1638 (m), 1293 (s), 1143 (s), 957 (m), 540 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{17}H_{16}O_4S$ [M+H]$^+$: 317.0842; found 317.0836.

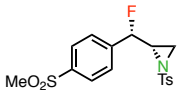
Synthesis of Products.

To a solution of substrate (0.52 mmol, 1 equiv) and catalyst **1a**[10] (40.0 mg, 0.052 mmol, 10 mol%) in dichloromethane (3 mL) in a low-density polyethylene tube at –78 °C was added HF•pyridine (py•9HF, 70% hydrogen fluoride by weight, 210 μL, 15 equiv hydrogen fluoride) followed by *m*CPBA (77% by weight, 128 mg, 0.57 mmol, 1.1 equiv). The reaction mixture was warmed to –30 °C and stirred at that temperature for 16 hours. The heterogeneous mixture was transferred carefully into a vigorously stirred suspension of basic alumina (4.0 g) in dichloromethane at –78 °C. The resulting suspension was allowed to warm to room temperature and filtered, washing with 200 mL dichloromethane. The combined filtrate was concentrated under reduced pressure.



3a

Prepared according to the general procedure using **2a** (185 mg, 0.52 mmol). After work-up, the crude residue was purified by silica gel column chromatography (10 to 30% diethyl ether in hexanes) to give **3a** (138 mg, 71%) as a white solid in 94% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.40 (dd, *J* = 45.8, 4.5 Hz, 1H), 3.12 (ddt, *J* = 15.8, 7.1, 4.3 Hz, 1H), 2.81 (dd, *J* = 7.2, 1.9 Hz, 1H), 2.47 (d, *J* = 4.3 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 145.1, 140.1 (d, *J* = 21.6 Hz), 134.4, 131.0 (q, *J* = 32.1 Hz), 129.7, 128.0, 126.0 (d, *J* = 7.0 Hz), 125.5 (d, *J* = 3.8 Hz), 123.9 (q, *J* = 272.3 Hz), 89.7 (d, *J* = 181.2 Hz), 42.8 (d, *J* = 25.9 Hz), 29.4 (d, *J* = 7.1 Hz), 21.6; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -62.7, -188.7 (dd, *J* = 45.7, 15.8 Hz); FTIR (thin film) ν 2934 (w), 1596 (w), 1319 (s), 1064 (s), 683 (s), 520 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{17}H_{15}F_4NO_2S$ $[M+H]^+$: 374.0832; found 374.0830; $[\alpha]_D^{25}$ = +13.9° (c 1.0, CH_3CN)

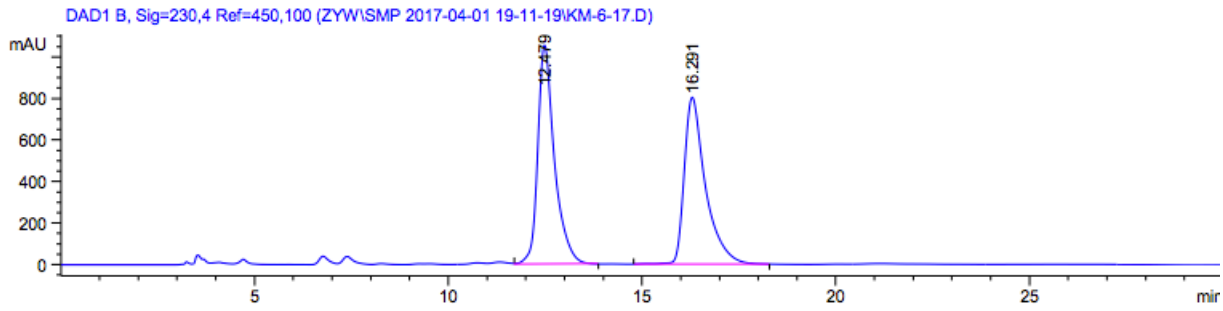


3b

Prepared according to the general procedure using **2b** (190 mg, 0.52 mmol). After work-up, the crude residue was purified by silica gel column chromatography (dichloromethane) to give **3b** (173 mg, 87%) as a white solid in 94% ee. Crystals of **3b** were grown by allowing a hot solution of the compound in ethyl acetate cool to room temperature. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 5.44 (dd, *J* = 45.9, 4.5 Hz, 1H), 3.14 (ddt, *J* = 15.7, 7.0, 4.4 Hz, 1H), 3.02 (s, 3H), 2.80 (d, *J* = 7.1, 1H), 2.48–2.45 (m, 4H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 145.4, 142.1 (d, *J* = 21.6 Hz), 141.1, 134.2, 129.9, 128.0, 127.7, 126.7 (d, *J* = 7.2 Hz), 89.6 (d, *J* = 181.9 Hz), 44.6, 42.4 (d, *J* = 26.3 Hz), 29.6 (d, *J* = 6.9 Hz), 21.8; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -188.9 (dd, *J* = 45.9, 15.5 Hz); FTIR (thin film) ν 2926 (w), 1597 (w), 1307 (s), 1161 (s), 941 (m), 564 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{17}H_{18}FNO_4S_2$ $[M+H]^+$: 384.0734; found 384.0730; $[\alpha]_D^{27}$ = +18.8° (c 1.0, CH_3CN).

94% ee, Chiral HPLC (AD-H, 40% isopropanol in hexanes, 1.0 mL/min, λ = 230 nm); t_R(major) = 12.4 min, t_R(minor) = 16.3 min.

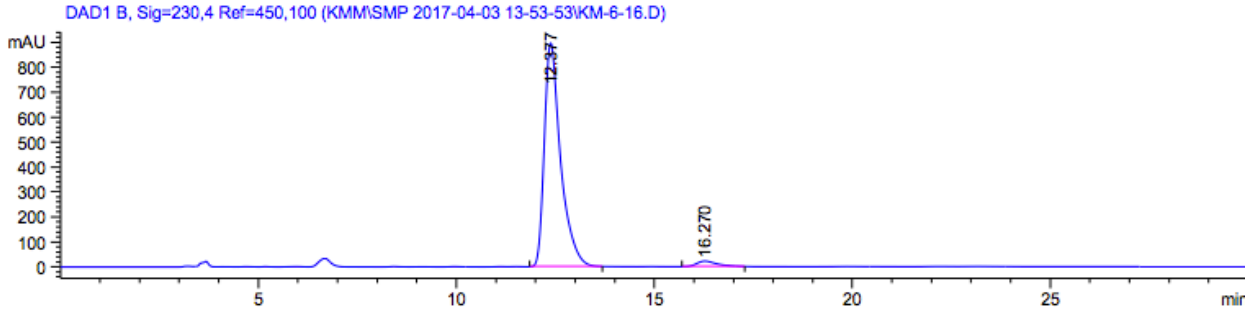
Racemic sample:



Signal 2: DAD1 B, Sig=230,4 Ref=450,100

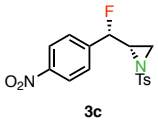
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.479	VB	0.4436	3.15563e4	1053.15369	50.7936
2	16.291	BB	0.5603	3.05703e4	802.69446	49.2064
Totals :				6.21266e4	1855.84814	

Enriched sample:



Signal 2: DAD1 B, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.377	BB	0.4251	2.55935e4	896.32416	96.9632
2	16.270	BB	0.5404	801.55267	22.03313	3.0368
Totals :				2.63950e4	918.35729	

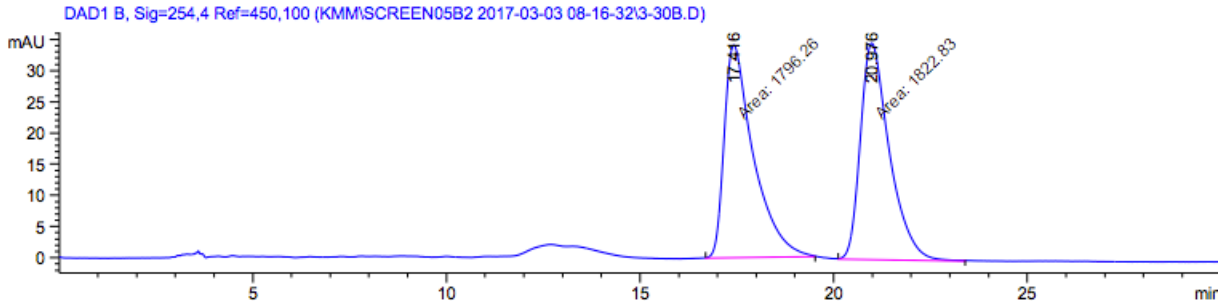


3c

Prepared according to the general procedure using **2c** (173 mg, 0.52 mmol). After work-up, the crude residue was purified by silica gel column chromatography (dichloromethane to give **3c** (135 mg, 74%) as a white solid in 97% ee. **3c** in 99% ee was obtained following precipitation of the compound from dichloromethane/hexanes. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.6 Hz, 2H), 7.64–7.57 (m, 2H), 7.38–7.32 (m, 2H), 7.21–7.16 (m, 2H), 5.52 (dd, *J* = 45.8, 3.7 Hz, 1H), 3.10 (dddt, *J* = 15.4, 7.0, 4.2, 2.1 Hz, 1H), 2.82 (d, *J* = 7.1 Hz, 1H), 8.02 (d, *J* = 8.6 Hz, 1H), 7.64–7.57 (m, 1H), 7.38–7.32 (m, 2H), 7.21–7.16 (m, 2H), 5.52 (dd, *J* = 45.8, 3.7 Hz, 1H), 3.10 (dddt, *J* = 15.4, 7.0, 4.2, 2.1 Hz, 1H), 2.82 (d, *J* = 7.1 Hz, 1H), 2.53 (d, *J* = 4.3 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 148.0, 145.3, 143.1 (d, *J* = 21.7 Hz), 134.2, 129.7, 128.1, 126.5 (d, *J* = 7.3 Hz), 123.7, 88.8 (d, *J* = 182.8 Hz), 42.6 (d, *J* = 25.2 Hz), 29.5 (d, *J* = 7.3 Hz), 21.6; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -191.6 (dd, *J* = 45.5, 17.1 Hz); FTIR (thin film) ν 2923 (w), 1595 (w), 1519 (s), 1319 (s), 1158 (s), 727 (s), 563 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{16}H_{15}FN_2O_4S$ $[M+H]^+$: 351.0809; found 351.0808; $[\alpha]_D^{24}$ = +6.0° (c 1.0, CH_3CN).

97% ee, Chiral HPLC (OD-H, 30% isopropanol in hexanes, 1.0 mL/min, λ = 254 nm); t_R(major) = 17.8 min, t_R(minor) = 22.4 min.

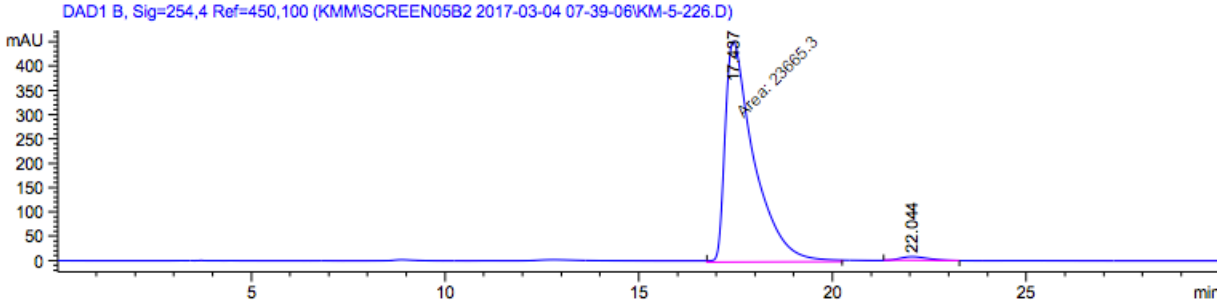
Racemic sample:



Signal 2: DAD1 B, Sig=254,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.416	MM	0.8773	1796.26318	34.12587	49.6330
2	20.976	MM	0.8735	1822.82703	34.77885	50.3670
Totals :				3619.09021	68.90472	

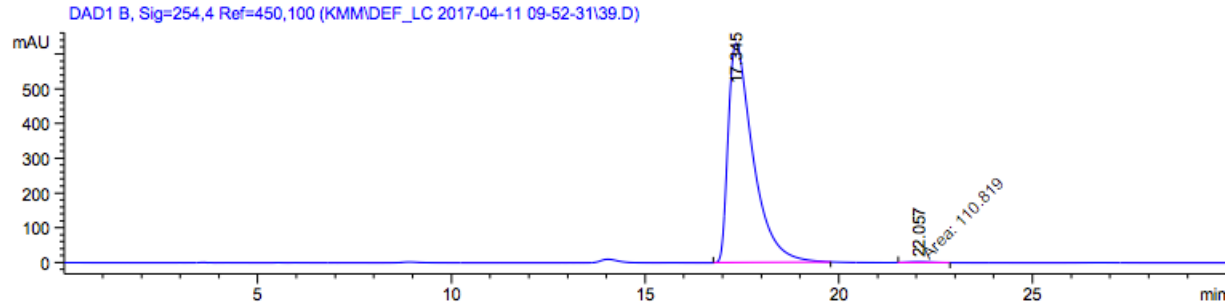
Enriched sample:



Signal 2: DAD1 B, Sig=254,4 Ref=450,100

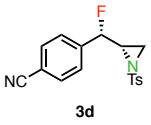
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.437	MM	0.8680	2.36653e4	454.40854	98.3205
2	22.044	BB	0.6873	404.23941	7.89612	1.6795
Totals :				2.40695e4	462.30466	

Upgraded (99% ee) sample:



Signal 2: DAD1 B, Sig=254,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.345	BB	0.6671	2.81967e4	631.22870	99.6085
2	22.057	MM	0.7423	110.81932	2.48825	0.3915
Totals :				2.83075e4	633.71694	

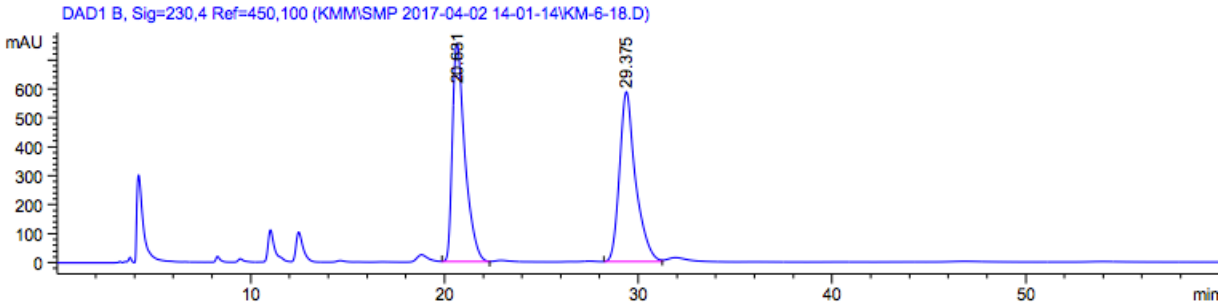


3d

Prepared according to the general procedure using **2d** (162 mg, 0.52 mmol). After work-up, the crude residue was purified by silica gel column chromatography (10 to 40% diethyl ether in hexanes) to give **3d** (131 mg, 76%) as a white solid in 96% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.51–7.47 (m, 2H), 7.33–7.28 (m, 2H), 7.25–7.20 (m, 2H), 5.43 (dd, *J* = 45.8, 4.3 Hz, 1H), 3.09 (ddt, *J* = 16.4, 7.1, 4.3 Hz, 1H), 2.79 (dd, *J* = 7.1, 1.9 Hz, 1H), 2.50–2.44 (m, 4H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 145.2, 141.2 (d, *J* = 21.7 Hz), 134.2, 132.3, 129.7, 128.0, 126.3 (d, *J* = 7.3 Hz), 118.3, 112.7, 89.2 (d, *J* = 182.1 Hz), 42.5 (d, *J* = 25.5 Hz), 29.5 (d, *J* = 7.2 Hz), 21.7; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -190.6 (dd, *J* = 45.8, 16.5 Hz); FTIR (thin film) ν 3060 (w), 2227 (m), 1595 (m), 1415 (s), 977 (s), 562 (s) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{17}H_{15}FN_2O_2S$ $[M+H]^+$: 331.0911; found. 331.0905; $[\alpha]_D^{25}$ = +29.2° (c 1.0, CH_3CN)

96% ee, Chiral HPLC (AD-H, 20% isopropanol in hexanes, 1.0 mL/min, λ = 230 nm); t_R(major) = 20.6 min, t_R(minor) = 29.1 min.

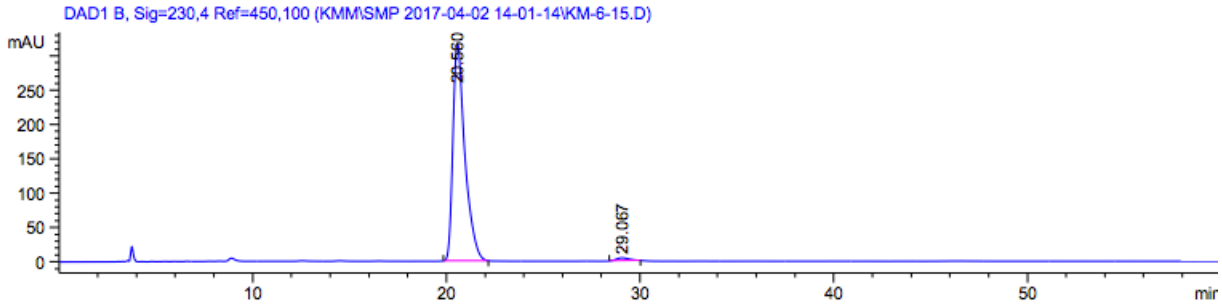
Racemic sample:



Signal 2: DAD1 B, Sig=230,4 Ref=450,100

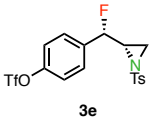
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.631	BB	0.6713	3.38637e4	754.92334	50.0459
2	29.375	BB	0.8364	3.38015e4	586.50360	49.9541
Totals :				6.76652e4	1341.42694	

Enriched sample:



Signal 2: DAD1 B, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.560	BB	0.6383	1.36080e4	317.32004	98.4951
2	29.067	BB	0.6358	207.91110	4.31747	1.5049
Totals :				1.38159e4	321.63751	

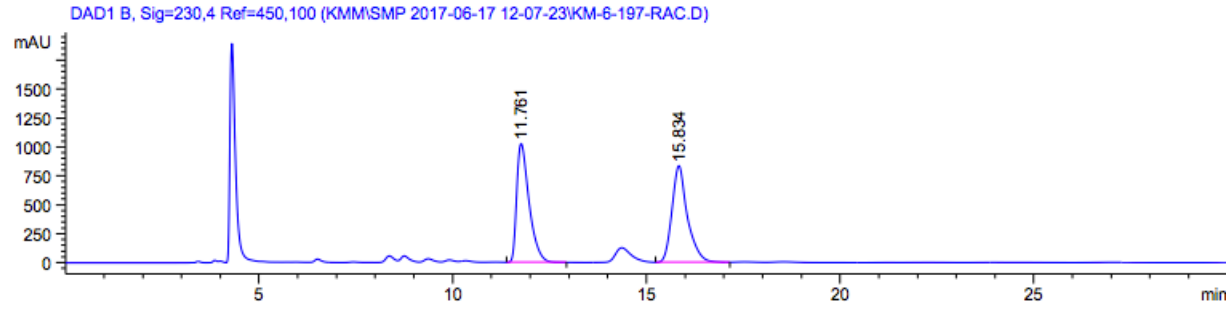


3e

Prepared according to the general procedure using **2e** (226 mg, 0.52 mmol). After work-up, the crude residue was purified by silica gel column chromatography (10 to 50% diethyl ether in hexanes) to give **3e** (174 mg, 74%) as a white solid in 88% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.22–7.16 (m, 2H), 5.33 (dd, *J* = 45.8, 4.7 Hz, 1H), 3.15 (ddt, *J* = 14.4, 7.1, 4.7 Hz, 1H), 2.79 (dd, *J* = 7.2, 2.1 Hz, 1H), 2.45 (s, 3H), 2.41 (d, *J* = 4.5 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 149.4, 145.0, 139.1 (d, *J* = 22.0 Hz), 134.2, 130.6, 129.8, 128.0, 125.6 (d, *J* = 6.8 Hz), 121.7, 118.8 (d, *J* = 7.8 Hz), 118.7 (q, *J* = 320.6 Hz), 89.5 (d, *J* = 181.5 Hz), 42.3 (d, *J* = 26.5 Hz), 29.5 (d, *J* = 7.1 Hz), 21.6; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -73.0, -185.1 (dd, *J* = 45.9, 14.5 Hz); FTIR (thin film) ν 1598 (w), 1503 (m), 1419 (s), 1135 (s), 883 (s), 529 (s) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{17}H_{15}F_4NO_5S_2$ $[M+H]^+$: 454.0401; found 454.0391. $[\alpha]_D^{23}$ = +16.3° (c 1.0, $CHCl_3$).

88% ee, Chiral HPLC (AD-H, 20% isopropanol in hexanes, 1.0 mL/min, λ = 230 nm); t_R(major) = 11.8 min, t_R(minor) = 15.9 min.

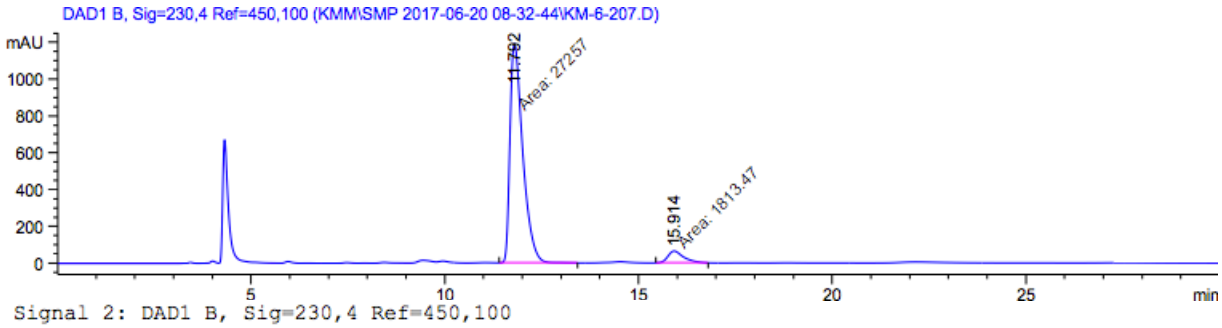
Racemic sample:



Signal 2: DAD1 B, Sig=230,4 Ref=450,100

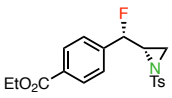
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.792	MM	0.3815	2.72570e4	1190.68335	93.7618
2	15.914	MM	0.4711	1813.46936	64.15755	6.2382
Totals :				2.90705e4	1254.84090	

Enriched sample:



Signal 2: DAD1 B, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.792	MM	0.3815	2.72570e4	1190.68335	93.7618
2	15.914	MM	0.4711	1813.46936	64.15755	6.2382
Totals :				2.90705e4	1254.84090	

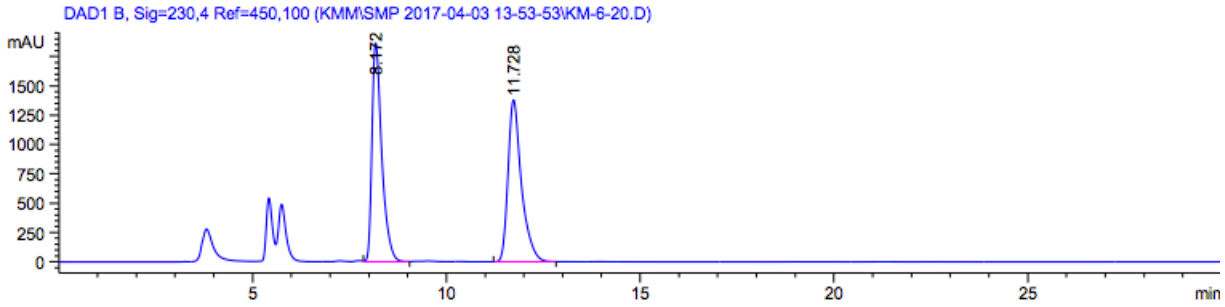


3f

Prepared according to the general procedure using **2f** (187 mg, 0.52 mmol). After work-up, the crude residue was purified by silica gel column chromatography (10 to 40% diethyl ether in hexanes) to give **3f** (183 mg, 93%) as a white solid in 90% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93–7.88 (m, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.24–7.18 (m, 2H), 5.38 (dd, *J* = 46.0, 4.7 Hz, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 3.13 (ddt, *J* = 15.0, 7.3, 4.5 Hz, 1H), 2.81 (dd, *J* = 7.2, 2.0 Hz, 1H), 2.47 (d, *J* = 4.4 Hz, 1H), 2.40 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 165.9, 144.9, 140.8 (d, *J* = 21.4 Hz), 134.3, 130.9, 129.7, 129.6, 128.0, 125.5 (d, *J* = 6.9 Hz), 90.1 (d, *J* = 180.8 Hz), 61.2, 42.7 (d, *J* = 26.2 Hz), 29.4 (d, *J* = 7.2 Hz), 21.6, 14.4; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -188.09 (dd, *J* = 45.9, 15.2 Hz); FTIR (thin film) ν 2982 (br. w), 1714 (s), 1273 (s), 1090 (s), 724 (s), 564 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{19}H_{20}FNO_4S$ $[M+H]^+$: 378.1170; found 378.1168; $[\alpha]_D^{25}$ = +13.1° (c 1.0, CH_3CN).

90% ee, Chiral HPLC (AD-H, 40% isopropanol in hexanes, 1.0 mL/min, λ = 230 nm); t_R(major) = 8.2 min, t_R(minor) = 11.8 min.

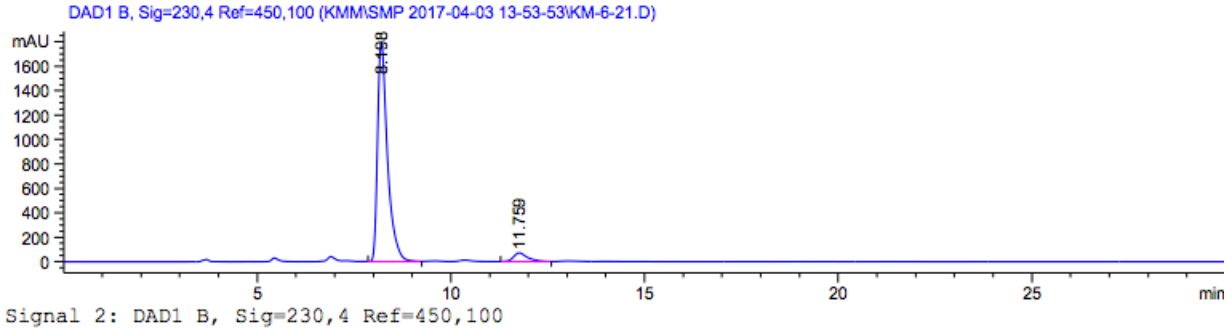
Racemic sample:



Signal 2: DAD1 B, Sig=230,4 Ref=450,100

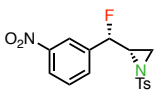
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.172	VB	0.2651	3.27591e4	1863.62451	49.6587
2	11.728	BB	0.3569	3.32093e4	1379.49377	50.3413
Totals :				6.59684e4	3243.11829	

Enriched sample:



Signal 2: DAD1 B, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.198	VB	0.2679	3.20187e4	1796.49976	94.7411
2	11.759	BB	0.3681	1777.29785	70.98157	5.2589
Totals :				3.37960e4	1867.48132	

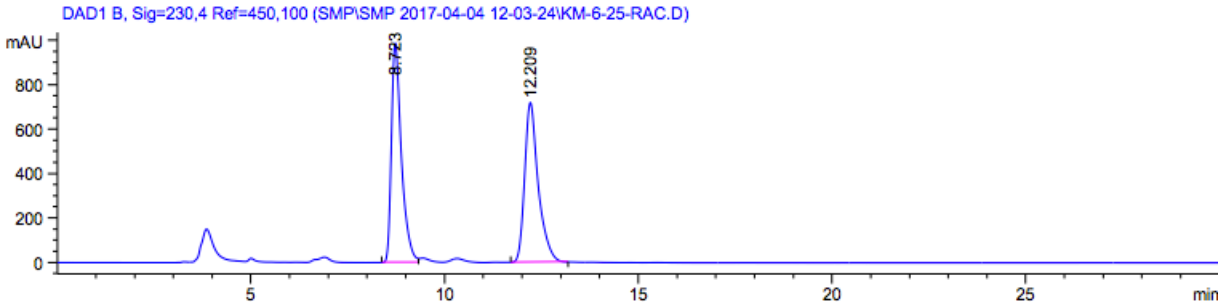


3g

Prepared according to the general procedure using **2g** (173 mg, 0.52 mmol). After work-up, the crude residue was purified by silica gel column chromatography (dichloromethane) to give **3g** (144 mg, 79%) as a white solid in 91% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (ddd, *J* = 8.2, 2.3, 1.1 Hz, 1H), 8.04 (t, *J* = 0.7 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.57 (ddd, *J* = 7.8, 1.8, 1.0 Hz, 1H), 7.51–7.43 (m, 1H), 7.18 (dd, *J* = 8.7, 0.7 Hz, 2H), 5.51 (dd, *J* = 45.5, 4.2 Hz, 1H), 3.13 (ddt, *J* = 16.5, 7.1, 4.2 Hz, 1H), 2.84 (dd, *J* = 7.1, 1.8 Hz, 1H), 2.51 (d, *J* = 4.3 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 148.1, 145.0, 138.3 (d, *J* = 22.3 Hz), 134.1, 131.6 (d, *J* = 6.8 Hz), 129.7, 129.6, 127.9, 123.6, 120.9 (d, *J* = 7.7 Hz), 88.7 (d, *J* = 182.2 Hz), 42.5 (d, *J* = 25.4 Hz), 29.5 (d, *J* = 7.2 Hz), 21.6; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -189.8 (dd, *J* = 45.5, 16.7 Hz); FTIR (thin film) ν 3093 (w), 1569 (w), 1530 (s), 1159 (s), 915 (s), 725 (s), 537 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{16}H_{15}FN_2O_4S$ $[M+H]^+$: 351.0809; found 351.0808; $[\alpha]_D^{25}$ = –20.1° (c 1.0, CH_3CN).

91% ee, Chiral HPLC (AD-H, 40% isopropanol in hexanes, 1.0 mL/min, λ = 230 nm); t_R(major) = 8.7 min, t_R(minor) = 12.2 min.

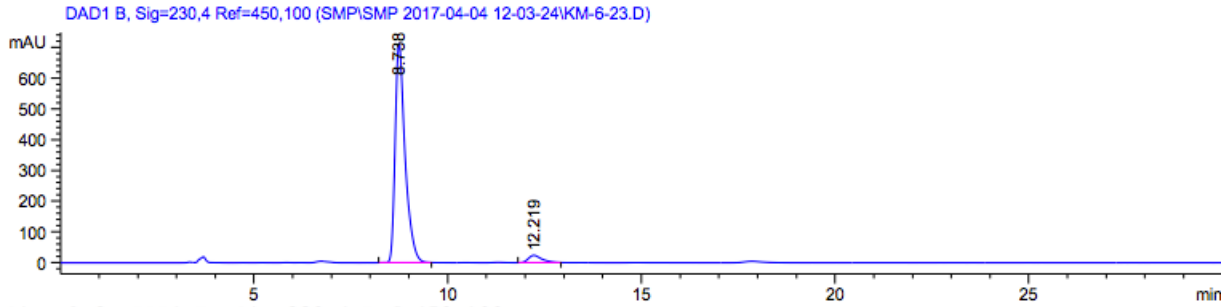
Racemic sample:



Signal 2: DAD1 B, Sig=230,4 Ref=450,100

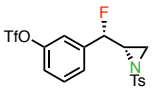
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.723	BV	0.2672	1.76847e4	986.33575	50.2257
2	12.209	BB	0.3606	1.75258e4	718.56067	49.7743
Totals :				3.52105e4	1704.89642	

Enriched sample:



Signal 2: DAD1 B, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.738	BB	0.2663	1.27388e4	713.42920	95.5959
2	12.219	BB	0.3618	586.87427	23.95986	4.4041
Totals :				1.33257e4	737.38906	



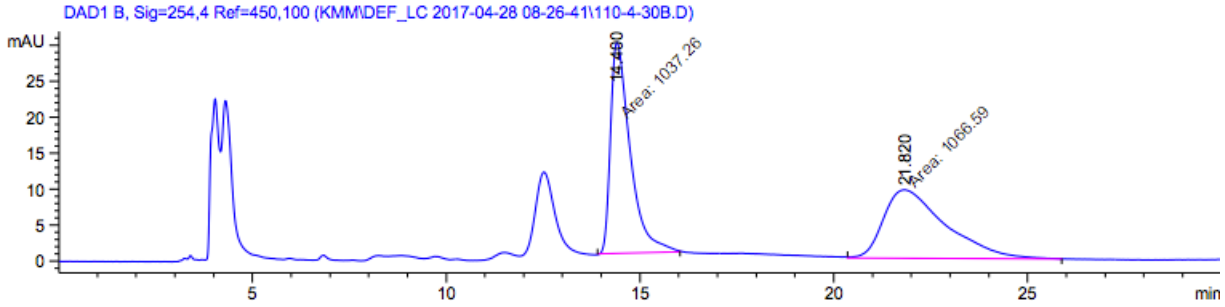
3h

Prepared according to the general procedure using **2h** (226 mg, 0.52 mmol). After work-up, the crude residue was purified by silica gel column chromatography (10 to 50% diethyl ether in hexanes) to give **3h** (189 mg, 80%) as a white solid in 94% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73–7.67 (m, 2H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 1H), 7.16 (s, 1H), 5.38 (dd, *J* = 45.6, 4.7 Hz, 1H), 3.13 (ddt, *J* = 15.0, 7.3, 4.5 Hz, 1H), 2.79 (dd, *J* = 7.1, 1.9 Hz, 1H), 2.48 – 2.36 (m, 4H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 149.5, 145.0, 139.1 (d, *J* = 21.9 Hz), 134.2, 130.6, 129.8, 128.0, 125.64 (d, *J* = 6.7 Hz), 121.7, 118.8 (d, *J* = 7.9 Hz), 118.7 (q, *J* = 320.5 Hz), 89.5 (d, *J* = 181.6 Hz), 42.3 (d, *J* = 26.5 Hz), 29.5 (d, *J* = 6.8 Hz), 21.6; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -73.0, -187.3 (dd, *J* = 45.7, 14.8 Hz); FTIR (thin film) ν 1616 (w), 1421 (s), 1209 (s),

713 (s), 474 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{17}H_{15}F_4NO_5S_2$ $[M+H]^+$: 454.0401; found 454.0394. $[\alpha]_D^{24} = -3.1^\circ$ (c 1.0, $CHCl_3$).

94% ee, Chiral HPLC (OJ-H, 30% isopropanol in hexanes, 1.0 mL/min, λ = 254 nm); t_R(major) = 12.3 min, t_R(minor) = 21.8 min.

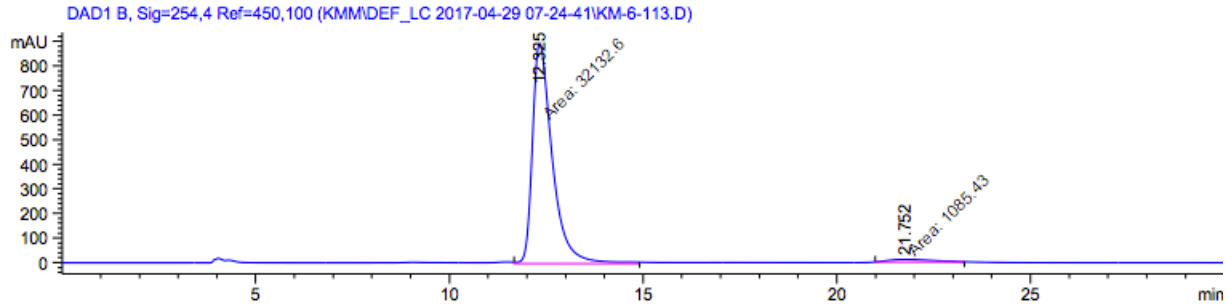
Racemic sample:



Signal 2: DAD1 B, Sig=254,4 Ref=450,100

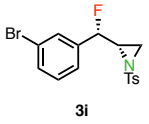
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.400	MM	0.5888	1037.25598	29.35960	49.3028
2	21.820	MM	1.8643	1066.59009	9.53506	50.6972
Totals :				2103.84607	38.89466	

Enriched sample:



Signal 2: DAD1 B, Sig=254,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.325	MM	0.5972	3.21326e4	896.72174	96.7324
2	21.752	MM	1.4931	1085.42749	12.11568	3.2676
Totals :				3.32180e4	908.83742	



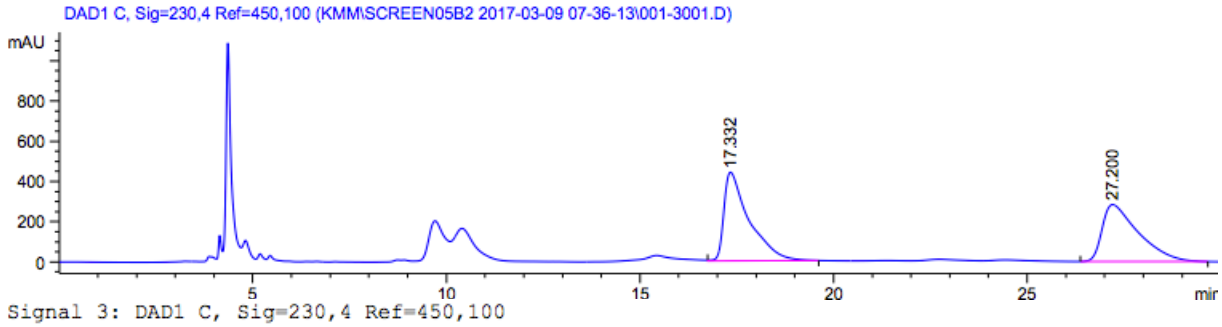
3i

Prepared according to the general procedure using **2i** (190 mg, 0.52 mmol). After work-up, the crude residue was purified by silica gel column chromatography (0 to 25% diethyl ether in hexanes) to give **3i** (112 mg, 56%) as a colorless oil in 90% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76–7.67 (m, 2H), 7.45–7.39 (m, 1H), 7.37 (s, 1H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.21–7.12 (m, 2H), 5.25 (dd, *J* = 45.8, 5.0 Hz, 1H), 3.12 (ddt, *J* = 14.2, 6.9, 4.6 Hz, 1H),

2.81 (dd, J = 7.2, 2.1 Hz, 1H), 2.53–2.37 (m, 4H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 144.9, 138.3 (d, J = 21.6 Hz), 134.3, 132.0, 130.2, 129.8, 128.9 (d, J = 7.3 Hz), 128.0, 124.3 (d, J = 6.7 Hz), 122.8, 90.1 (d, J = 181.2 Hz), 42.7 (d, J = 26.8 Hz), 29.6 (d, J = 7.2 Hz), 21.8; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -185.6 (dd, J = 45.8, 14.4 Hz); FTIR (thin film) ν 2924 (w), 1597 (w), 1324 (m), 1159 (s), 724 (m), 600 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{16}H_{15}BrFNO_2S$ $[M+H]^+$: 384.0064; found 384.0060; $[\alpha]_D^{25}$ = +0.9° (c 1.0, CH_3CN).

90% ee, Chiral HPLC (OJ-H, 30% isopropanol in hexanes, 1.0 mL/min, λ = 230 nm); t_R(minor) = 17.6 min, t_R(major) = 26.8 min.

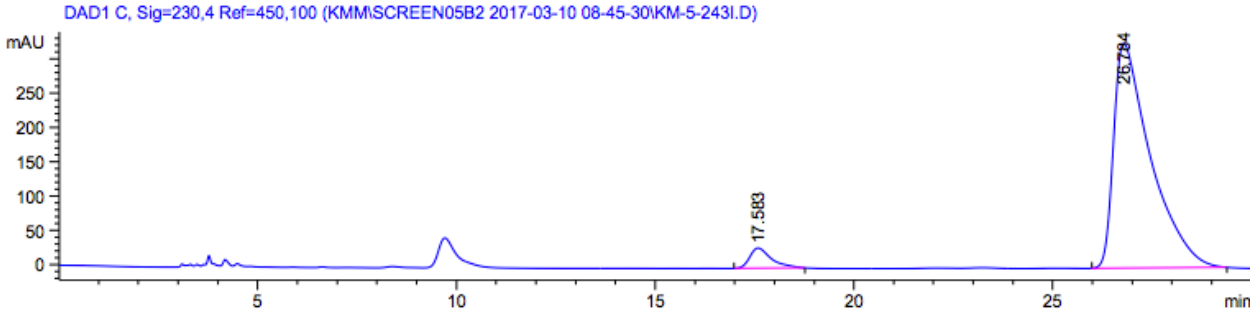
Racemic sample:



Signal 3: DAD1 C, Sig=230,4 Ref=450,100

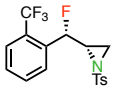
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.332	VB	0.6411	2.00325e4	441.74008	52.0870
2	27.200	BB	0.9356	1.84272e4	283.03888	47.9130
Totals :				3.84597e4	724.77896	

Enriched sample:



Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.583	BB	0.5589	1132.05652	29.55073	5.0693
2	26.784	BB	0.9175	2.11996e4	328.25854	94.9307
Totals :				2.23316e4	357.80927	

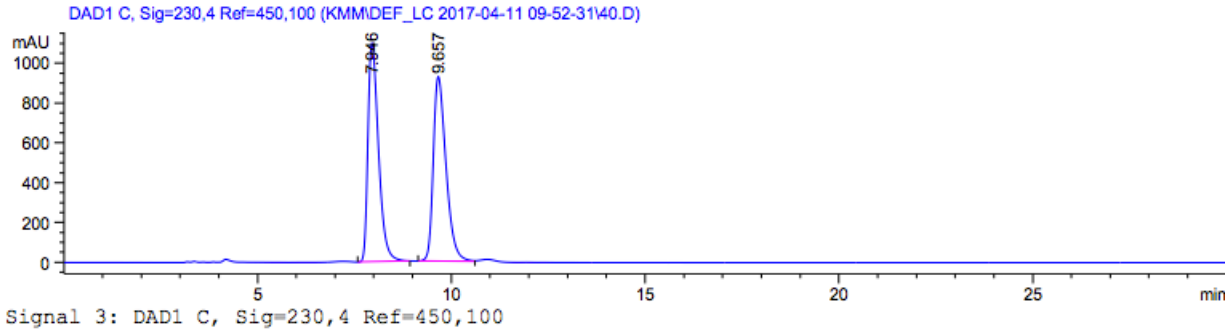


3j

Prepared according to the general procedure using **2j** (185 mg, 0.52 mmol). After work-up, the crude residue was purified by silica gel column chromatography (0 to 15% diethyl ether in hexanes) to give **3j** (161 mg, 83%) as a colorless oil in 80% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.55 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.51 (dd, *J* = 7.2, 1.9 Hz, 1H), 7.39–7.30 (m, 2H), 7.20–7.14 (m, 2H), 5.86–5.67 (m, 1H), 3.14 (ddt, *J* = 17.3, 7.3, 4.2 Hz, 1H), 2.79 (dd, *J* = 7.2, 1.9 Hz, 1H), 2.54 (d, *J* = 4.4 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 144.7, 134.8 (d, *J* = 22.5 Hz), 134.3, 132.3, 129.7, 128.8 (d, *J* = 1.9 Hz), 128.5 (d, *J* = 8.7 Hz), 128.0, 125.4 (q, *J* = 5.7 Hz), 124.0 (q, *J* = 273.6 Hz), 85.7 (dd, *J* = 178.4, 2.6 Hz), 42.7 (d, *J* = 25.4 Hz), 29.8 (d, *J* = 7.2 Hz), 21.6; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -57.93 (s, 3F), -185.14 (dd, *J* = 44.9, 17.3 Hz, 1F); FTIR (thin film) ν 1597 (w), 1312 (s), 1159 (s), 941 (m), 716 (s), 563 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{17}H_{15}F_4NO_5S_2$ $[M+H]^+$: 374.0832; found 374.0826. $[\alpha]_D^{23}$ = +6.8° (c 1.0, $CHCl_3$).

80% ee, Chiral HPLC (OJ-H, 30% isopropanol in hexanes, 1.0 mL/min, λ = 230 nm); t_R(minor) = 8.0 min, t_R(major) = 9.6 min.

Racemic sample:

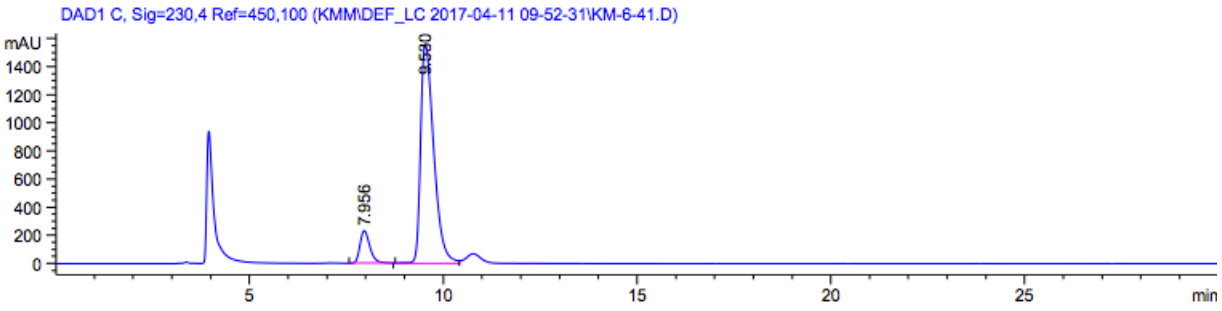



```
Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.946 VB    0.2909 2.08105e4  1099.03418  49.4876
   2   9.657 BV    0.3490 2.12415e4   928.29474  50.5124

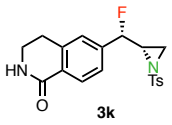
Totals :                 4.20520e4  2027.32892
```

Enriched sample:



Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.956	VB	0.2766	4179.44287	231.53537	10.2289
2	9.530	BV	0.3606	3.66799e4	1558.64014	89.7711
Totals :				4.08593e4	1790.17551	

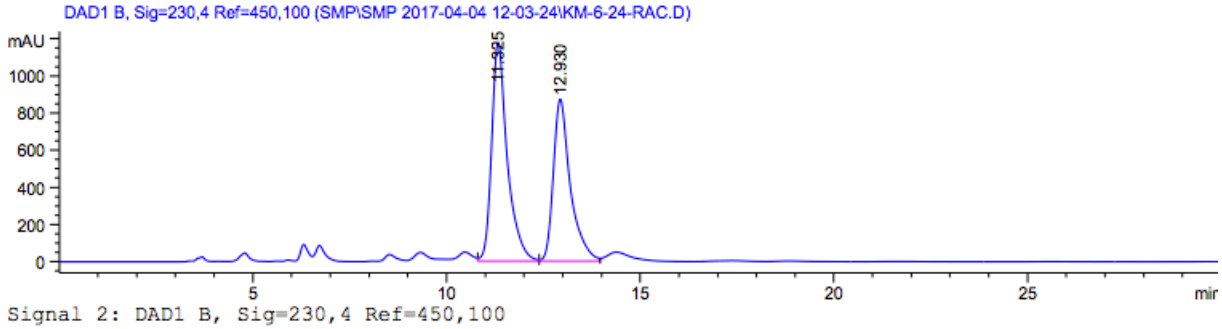


3k

Prepared according to the general procedure using **2k** (185 mg, 0.52 mmol). After work-up, the crude residue was purified by silica gel column chromatography (20 to 100% ethyl acetate in hexanes) to give **3k** (150 mg, 77%) as a white solid in 94% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.67 (dd, *J* = 8.3, 1.6 Hz, 2H), 7.45 (s, 1H), 7.21 (d, *J* = 7.7 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 1H), 7.10 (s, 1H), 5.29 (dd, *J* = 46.1, 5.0 Hz, 1H), 3.52 (dt, *J* = 7.3, 3.6 Hz, 2H), 3.19–3.08 (m, 1H), 2.87 (t, *J* = 6.9 Hz, 2H), 2.77 (dd, *J* = 7.2, 2.3 Hz, 1H), 2.46 – 2.32 (m, 4H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 166.0, 144.9, 140.0 (d, *J* = 21.0 Hz), 139.3, 134.2, 129.6, 129.5, 128.1, 127.9, 124.3 (dd, *J* = 38.4, 6.9 Hz), 90.5 (d, *J* = 180.6 Hz), 42.7 (d, *J* = 26.7 Hz), 39.9, 29.5 (d, *J* = 7.4 Hz), 28.1, 21.6; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -186.0 (dd, *J* = 46.3, 14.2 Hz); FTIR (thin film) ν 3207 (br. s), 1665 (s), 1323 (s), 1159 (s), 908 (s), 710 (s) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{19}H_{19}FN_2O_3S$ $[M+H]^+$: 375.1173; found 375.1177; $[\alpha]_D^{25}$ = +1.3° (c 1.0, CH_3CN).

94% ee, Chiral HPLC (AD-H, 40% isopropanol in hexanes, 1.0 mL/min, λ = 230 nm); t_R(major) = 11.3 min, t_R(minor) = 13.0 min.

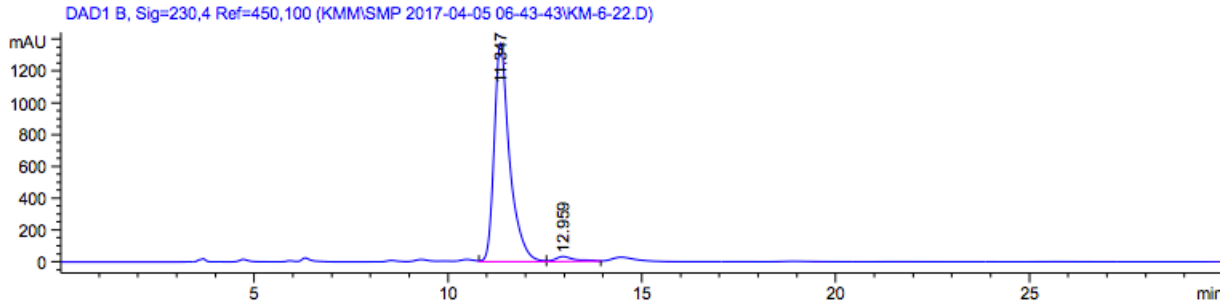
Racemic sample:



Signal 2: DAD1 B, Sig=230,4 Ref=450,100

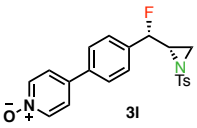
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.325	VV	0.4126	3.32390e4	1180.19873	55.3532
2	12.930	VV	0.4499	2.68099e4	873.84082	44.6468
Totals :				6.00490e4	2054.03955	

Enriched sample:



Signal 2: DAD1 B, Sig=230,4 Ref=450,100

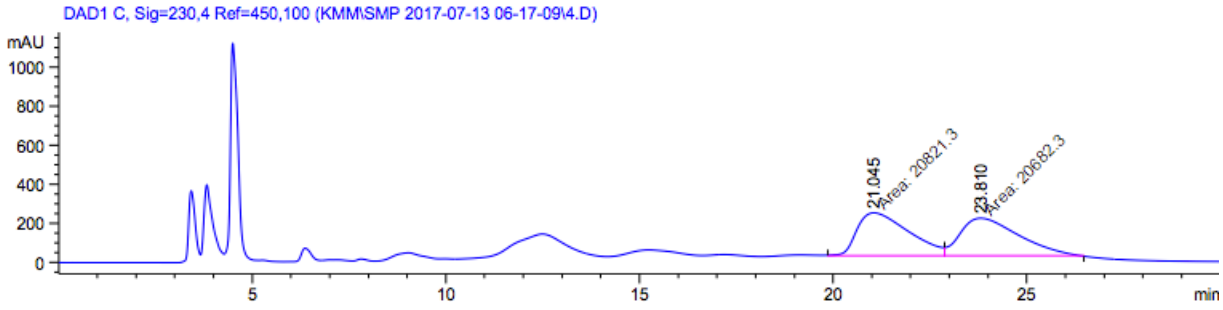
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.347	VV	0.4088	3.80237e4	1374.08093	96.8467
2	12.959	VV	0.5457	1238.01978	32.25899	3.1533
Totals :				3.92617e4	1406.33992	



Prepared according to the general procedure using **2l** (98.9 mg, 0.26 mmol). After work-up, the crude residue was purified by silica gel column chromatography (0 to 10% methanol in dichloromethane) to give **3l** (74.6 mg, 72%) as a yellow solid in 90% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.28 (d, *J* = 7.2 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.57–7.47 (m, 4H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.32–7.24 (m, 2H), 5.32 (dd, *J* = 46.0, 5.4 Hz, 1H), 3.21 (dddd, *J* = 12.9, 7.1, 5.5, 4.4 Hz, 1H), 2.77 (dd, *J* = 7.1, 2.2 Hz, 1H), 2.41 (d, *J* = 4.3 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 144.9, 139.5, 137.8, 137.0 (d, *J* = 21.3 Hz), 136.9, 134.5, 129.7, 128.1, 127.0 (d, *J* = 6.5 Hz), 126.6, 123.7, 90.9 (d, *J* = 179.8 Hz), 42.5 (d, *J* = 27.6 Hz), 29.8 (d, *J* = 6.9 Hz), 21.7; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -183.29 (dd, *J* = 46.0, 13.2 Hz); FTIR (thin film) ν 3379 (br. s), 1597 (w), 1478 (m), 1243 (m), 1160 (s), 728 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{21}H_{19}FN_2O_3S$ $[M+H]^+$: 399.1173; found 399.1166. $[\alpha]_D^{23}$ = +51.9° (c 1.0, $CHCl_3$).

90% ee, Chiral HPLC (OJ-H, 50% isopropanol in hexanes, 1.0 mL/min, λ = 230 nm); t_R(minor) = 21.9 min, t_R(major) = 23.9 min.

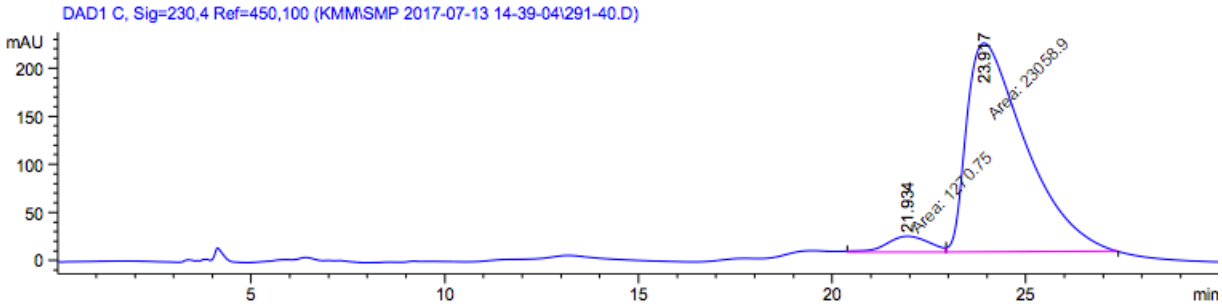
Racemic sample:



Signal 3: DAD1 C, Sig=230,4 Ref=450,100

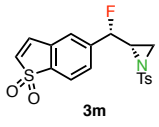
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.045	MM	1.5611	2.08213e4	222.28683	50.1675
2	23.810	MM	1.7709	2.06823e4	194.65215	49.8325
Totals :				4.15036e4	416.93898	

Enriched sample:



Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.934	MM	1.2837	1270.75439	16.49884	5.2231
2	23.917	MM	1.7708	2.30589e4	217.02835	94.7769
Totals :				2.43297e4	233.52719	

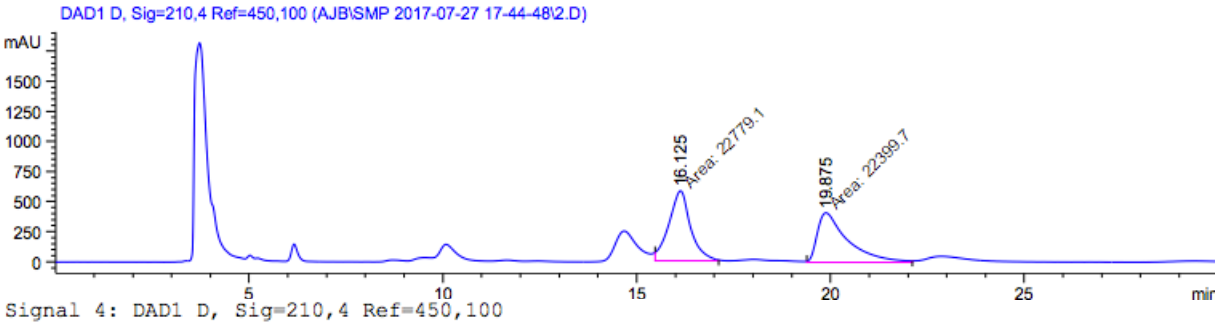


3m

Prepared according to the general procedure using **2m** (195 mg, 0.52 mmol). After work-up, the crude residue was purified by silica gel column chromatography (10 to 100% diethyl ether in hexanes) to give **3m** (158 mg, 77%) as a white solid in 97% ee. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.76 (d, J = 7.8 Hz, 1H), 7.61 (d, J = 8.3 Hz, 2H), 7.56–7.48 (m, 2H), 7.45–7.37 (m, 2H), 7.32–7.24 (m, 2H), 5.67 (dd, J = 45.8, 4.7 Hz, 1H), 3.33–3.26 (m, 1H), 2.77 (dd, J = 7.3, 2.1 Hz, 1H), 2.64 (d, J = 4.3 Hz, 1H), 2.36 (d, J = 1.9 Hz, 3H); ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 144.8, 142.5 (d, J = 21.2 Hz), 136.3, 133.7, 132.5, 131.5 (d, J = 3.8 Hz), 129.7, 128.2 (d, J = 7.4 Hz), 127.6, 123.0 (d, J = 7.2 Hz), 121.0, 89.1 (d, J = 178.2 Hz), 42.5 (d, J = 23.9 Hz), 29.2 (d, J = 7.9 Hz), 21.1; ^{19}F NMR (470.4 MHz, DMSO-d_6): δ -188.86 (dd, J = 45.7, 16.7 Hz); FTIR (thin film) ν 1298 (s), 1158 (s), 914 (m), 726 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{18}H_{16}FNO_4S_2$ [M+H]$^+$: 394.0578; found 394.0573. $[\alpha]_D^{24}$ = –0.97° (c 1.0, CH_2Cl_2).

97% ee, Chiral HPLC (AD-H, 40% isopropanol in hexanes, 1.0 mL/min, λ = 210 nm); t_R(major) = 16.5 min, t_R(minor) = 21.0 min.

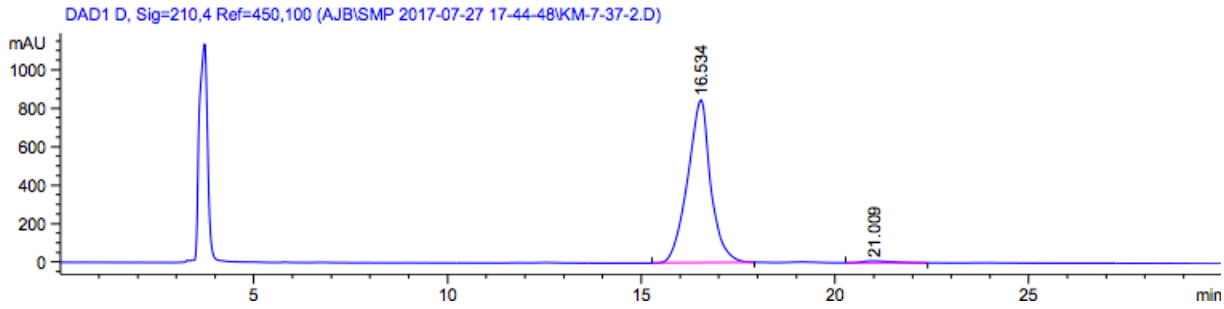
Racemic sample:



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

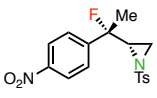
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.125	MM	0.6514	2.27791e4	582.78949	50.4199
2	19.875	MM	0.9080	2.23997e4	411.14539	49.5801
Totals :				4.51788e4	993.93488	

Enriched sample:



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.534	VB	0.5802	3.50054e4	846.99823	98.4646
2	21.009	BV	0.6358	545.83673	10.17539	1.5354
Totals :				3.55513e4	857.17362	

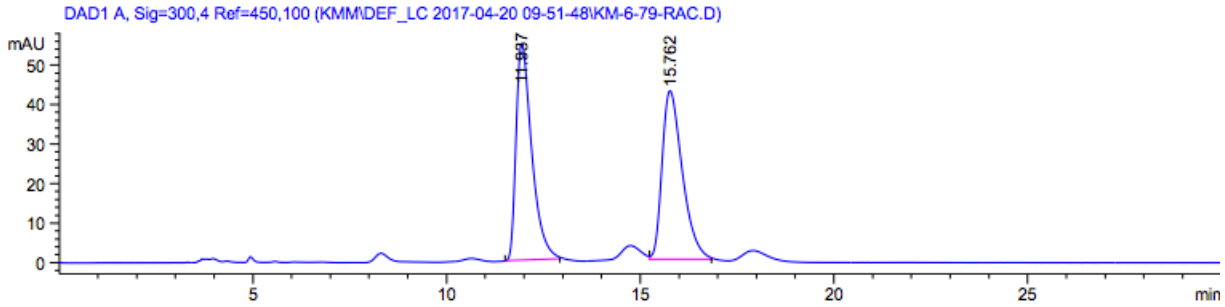


3n

Prepared according to the general procedure using **2n** (180 mg, 0.52 mmol). After work-up, the crude residue was purified by silica gel column chromatography (dichloromethane) to give **3n** (83.4 mg, 44%) as a white solid in 61% ee. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.9 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 3.05 (ddd, *J* = 16.2, 7.0, 4.2 Hz, 1H), 2.80 (dd, *J* = 7.0, 1.1 Hz, 1H), 2.43 (d, *J* = 4.2 Hz, 1H), 2.36 (s, 3H), 1.71 (d, *J* = 22.4 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 147.9, 147.6 (d, *J* = 29.9 Hz), 145.2, 134.3, 129.6, 128.0, 125.5 (d, *J* = 9.6 Hz), 123.4 (d, *J* = 1.8 Hz), 92.7 (d, *J* = 181.2 Hz), 46.0 (d, *J* = 26.9 Hz), 29.6 (d, *J* = 6.5 Hz), 24.5 (d, *J* = 24.1 Hz), 21.6; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -159.6 (dd, *J* = 22.4, 16.2 Hz); FTIR (thin film) ν 3084 (w), 1598 (w), 1522 (m), 1409 (m), 1161 (s), 733 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{17}H_{17}FN_2O_4S$ $[M+H]^+$: 365.0966; found 365.0960. $[\alpha]_D^{24}$ = –2.3° (c 1.0, $CHCl_3$).

61% ee, Chiral HPLC (OD-H, 30% isopropanol in hexanes, 1.0 mL/min, λ = 300 nm); t_R(major) = 11.9 min, t_R(minor) = 15.7 min.

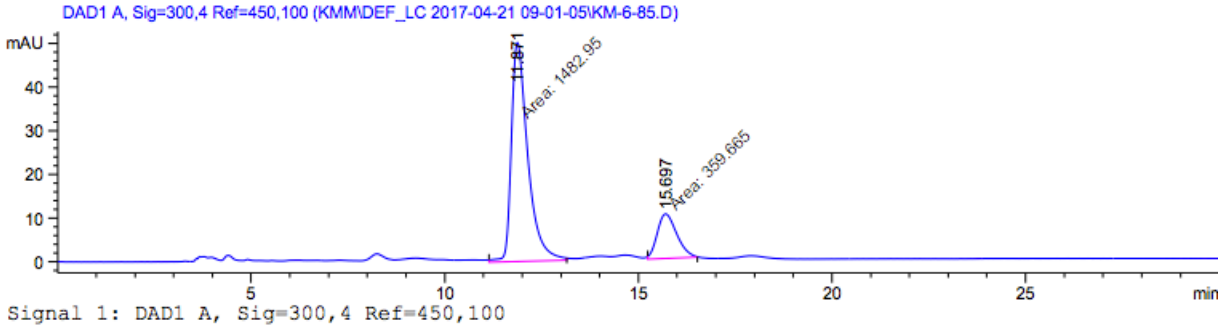
Racemic sample:



Signal 1: DAD1 A, Sig=300,4 Ref=450,100

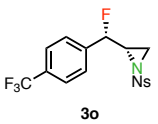
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.937	BB	0.4267	1545.68359	54.86849	49.9175
2	15.762	VB	0.5542	1550.79480	42.65345	50.0825
Totals :				3096.47839	97.52195	

Enriched sample:



Signal 1: DAD1 A, Sig=300,4 Ref=450,100

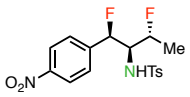
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.871	MM	0.4928	1482.94702	50.15132	80.4807
2	15.697	MM	0.5861	359.66513	10.22727	19.5193
Totals :				1842.61215	60.37860	



3o

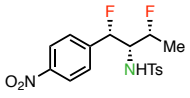
Prepared according to the general procedure using **2o** (402 mg, 1.04 mmol). After work-up, the crude residue was purified by silica gel column chromatography (dichloromethane) to give **3o** (235 mg, 56%) as a white solid in 94% ee. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.31 (d, *J* = 8.9 Hz, 2H), 8.03 (d, *J* = 8.8 Hz, 2H), 7.61–7.50 (m, 2H), 7.44–7.35 (m, 2H), 5.38 (dd, *J* = 45.9, 5.1 Hz, 1H), 3.27 (dddd, *J* = 14.3, 7.2, 5.1, 4.4 Hz, 1H), 2.94 (ddd, *J* = 7.2, 2.2, 0.6 Hz, 1H), 2.57 (d, *J* = 4.5 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 150.90, 143.28, 139.74 (d, *J* = 21.5 Hz), 131.0 (q, *J* = 32.1 Hz), 129.4, 126.0 (d, *J* = 7.1 Hz), 125.8 (q, *J* = 3.8 Hz), 124.3, 124.0 (q, *J* = 273.6 Hz), 90.1 (d, *J* = 181.7 Hz), 43.6 (d, *J* = 26.4 Hz), 30.3 (d, *J* = 7.6 Hz); ^{19}F NMR (470.4 MHz,

$CDCl_3$): δ -62.86, -187.28 (dd, *J* = 45.8, 14.4 Hz); HRMS (ESI-TOF) Calc'd for $C_{16}H_{12}F_4N_2O_4S$ $[M+H]^+$: 405.0527; found 405.0532; $[\alpha]_D^{24}$ = +10.1° (c 1.0, CH_3CN).



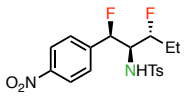
6a(*anti*)

Prepared according to the general procedure using **5a** (180 mg, 0.52 mmol) with the following modification: 25 equiv hydrogen fluoride and 20 mol% of catalyst *ent*-**1a**[10] (enantiomer of catalyst **1a**, 80 mg) were used instead. The diastereomeric ratio (d.r.) of the crude residue was determined to be >20:1 by ^{19}F NMR. The crude residue was purified by silica gel column chromatography (10 to 40% diethyl ether in hexanes) to give **6a***(anti)* (156 mg, 78%) as a white solid in >20:1 d.r. Crystals of **6a***(anti)* were grown by vapor diffusion of pentane into a solution of the compound in ethyl acetate. ^1H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.7 Hz, 2H), 7.18 (t, *J* = 8.6 Hz, 4H), 6.91 (d, *J* = 8.0 Hz, 2H), 5.87 (d, *J* = 45.4 Hz, 1H), 4.77 (ddq, *J* = 47.0, 8.7, 6.3 Hz, 1H), 3.91–3.53 (m, 1H), 2.24 (s, 3H), 1.47 (dd, *J* = 25.1, 6.3 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 147.4, 143.9 (d, *J* = 21.2 Hz), 143.3, 138.5, 129.3, 126.1, 125.9 (d, *J* = 9.1 Hz), 123.3 (d, *J* = 1.9 Hz), 90.1 (dd, *J* = 157.3, 3.9 Hz), 88.7 (dd, *J* = 151.6, 3.8 Hz), 62.3 (dd, *J* = 25.8, 19.2 Hz), 50.5–48.1 (m), 21.1, 18.1 (d, *J* = 21.7 Hz); ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -177.7–-178.1 (m), -203.4 (ddd, *J* = 45.5, 29.3, 5.0 Hz); FTIR (thin film) ν 3246 (br. w), 1605 (w), 1514 (s), 1161 (s), 478 (s) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{17}H_{18}F_2N_2O_4S$ $[M+H]^+$: 385.1028; found 385.1022. $[\alpha]_D^{24}$ = –21.5° (c 1.0, $CHCl_3$).



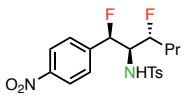
6a(*syn*)

Prepared according to the general procedure using **5a** (180 mg, 0.52 mmol) with the following modification: 50 equiv hydrogen fluoride and 20 mol% of catalyst **1a** were used instead. The diastereomeric ratio (d.r.) of the crude residue was determined to be 13:1 by ^{19}F NMR. The crude residue was purified by silica gel column chromatography (10 to 40% diethyl ether in hexanes) to give **6a***(syn)* (138 mg, 69%) as a white solid in >20:1 d.r. Crystals of **6a***(syn)* were grown by vapor diffusion of pentane into a solution of the compound in ethyl acetate. ^1H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 5.70 (dd, *J* = 45.8, 3.9 Hz, 1H), 4.77 (ddd, *J* = 46.2, 6.4, 3.4 Hz, 1H), 3.73 (dddd, *J* = 22.1, 18.2, 6.0, 2.6 Hz, 1H), 2.32 (s, 3H), 1.36 (dd, *J* = 24.6, 6.4 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 147.8, 143.6, 143.5 (d, *J* = 21.1 Hz), 129.5, 126.6, 126.4 (d, *J* = 8.3 Hz), 123.5, 91.1 (dd, *J* = 181.1, 2.6 Hz), 89.2 (d, *J* = 173.0 Hz), 61.5–59.7 (m), 21.3, 17.0 (d, *J* = 22.2 Hz); ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -182.4–-183.0 (m), -192.7 (ddd, *J* = 45.6, 21.7, 3.9 Hz); FTIR (thin film) ν 3250 (br. w), 1608 (w), 1345 (s), 1160 (s), 815 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{17}H_{18}F_2N_2O_4S$ $[M+H]^+$: 385.1028; found 385.1022; $[\alpha]_D^{25}$ = +40.4° (c 1.0, CH_3OH).



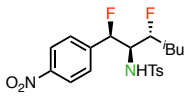
6b(*anti*)

Prepared according to the general procedure using **5b** (187 mg, 0.52 mmol) with the following modification: 25 equiv hydrogen fluoride and 20 mol% of catalyst *ent*-**1a** (enantiomer of catalyst **1a**, 80 mg) were used instead. The diastereomeric ratio (d.r.) of the crude residue was determined to be >20:1 by ^{19}F NMR. The crude residue was purified by silica gel column chromatography (10 to 40% diethyl ether in hexanes) to give **6b***(anti)* (176 mg, 85%) as a white solid in >20:1 d.r. ^1H NMR (500 MHz, 10% $CD_3OD/CDCl_3$): δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.7 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.88 (d, *J* = 7.9 Hz, 2H), 5.84 (d, *J* = 45.3 Hz, 1H), 4.48 (dtd, *J* = 47.6, 8.9, 2.7 Hz, 1H), 3.72 (dt, *J* = 29.4, 8.0 Hz, 1H), 2.21 (s, 3H), 2.02–1.80 (m, 1H), 1.75–1.58 (m, 1H), 0.99 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125.7 MHz, 10% $CD_3OD/CDCl_3$): δ 147.3, 144.0 (d, *J* = 21.1 Hz), 143.2, 138.5, 129.2, 126.0, 125.8 (d, *J* = 9.1 Hz), 123.2 (d, *J* = 1.7 Hz), 93.2 (dd, *J* = 176.7, 3.2 Hz), 90.1 (dd, *J* = 179.3, 4.7 Hz), 60.9 (dd, *J* = 25.7, 19.4 Hz), 24.8 (d, *J* = 20.6 Hz), 21.0, 9.2 (d, *J* = 4.3 Hz); ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -188.84 (dddt, *J* = 45.4, 37.0, 17.2, 7.5 Hz), -204.14 (ddd, *J* = 45.4, 28.6, 6.9 Hz); FTIR (thin film) ν 2961 (br. w), 1521 (s), 1158 (s), 543 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{18}H_{20}F_2N_2O_4S$ $[M+H]^+$: 399.1185; found 399.1196; $[\alpha]_D^{24}$ = –22.6° (c 1.0, CH_3CN).



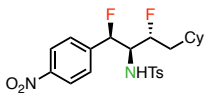
6c(*anti*)

Prepared according to the general procedure using **5c** (195 mg, 0.52 mmol) with the following modification: 25 equiv hydrogen fluoride and 20 mol% of catalyst *ent*-**1a** (enantiomer of catalyst **1a**, 80 mg) were used instead. The diastereomeric ratio (d.r.) of the crude residue was determined to be >20:1 by ^{19}F NMR. The crude residue was purified by silica gel column chromatography (10 to 40% diethyl ether in hexanes) to give **6c***(anti)* (165 mg, 77%) as a white solid in >20:1 d.r. ^{1}H NMR (500 MHz, 10% $CD_3OD/CDCl_3$): δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 5.90 (d, *J* = 45.5 Hz, 1H), 4.60 (dtd, *J* = 47.7, 9.1, 2.5 Hz, 1H), 3.86–3.63 (m, 1H), 2.27 (s, 3H), 1.93–1.32 (m, 4H), 0.90 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125.7 MHz, 10% $CD_3OD/CDCl_3$): δ 147.1, 144.1 (d, *J* = 21.0 Hz), 142.9, 138.7, 129.0, 125.9, 125.8, 123.0 (d, *J* = 1.7 Hz), 91.6 (d, *J* = 176.0 Hz), 90.0 (dd, *J* = 179.6, 4.6 Hz), 61.1 (dd, *J* = 25.7, 19.3 Hz), 33.5 (d, *J* = 20.2 Hz), 20.7, 18.1 (d, *J* = 3.4 Hz), 13.3; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -187.11–-187.49 (m), -203.61–-203.89 (m); FTIR (thin film) ν 1517(s), 1332 (s), 852 (s), 533 (s) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{19}H_{22}F_2N_2O_4S$ $[M+H]^+$: 413.1341; found 413.1349; $[\alpha]_D^{24}$ = –10.9° (c 1.0, CH_3CN).



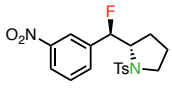
6d(*anti*)

Prepared according to the general procedure using **5d** (202 mg, 0.52 mmol) with the following modification: 25 equiv hydrogen fluoride and 20 mol% of catalyst *ent*-**1a** (enantiomer of catalyst **1a**, 80 mg) were used instead. The diastereomeric ratio (d.r.) of the crude residue was determined to be >20:1 by ^{19}F NMR. The crude residue was purified by silica gel column chromatography (10 to 40% diethyl ether in hexanes) to give **6d***(anti)* (184 mg, 83%) as a white solid in >20:1 d.r. ^{1}H NMR (500 MHz, 10% $CD_3OD/CDCl_3$): δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 5.90 (d, *J* = 45.4 Hz, 1H), 4.67 (dddd, *J* = 48.2, 10.6, 8.4, 2.5 Hz, 1H), 3.72 (dt, *J* = 30.0, 8.2 Hz, 1H), 2.27 (s, 3H), 1.92–1.77 (m, 1H), 1.67–1.47 (m, 2H), 0.90 (dd, *J* = 6.7, 2.1 Hz, 6H); ^{13}C NMR (125.7 MHz, 10% $CD_3OD/CDCl_3$): δ 147.2, 144.0 (d, *J* = 21.2 Hz), 143.0, 138.6, 129.1, 125.9, 125.9, 123.1, 91.96–90.37 (m), 90.37–88.54 (m), 61.50 (dd, *J* = 25.6, 19.1 Hz), 40.41 (d, *J* = 20.0 Hz), 24.40 (d, *J* = 2.2 Hz), 23.13, 21.07, 20.84; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -186.44 (dddt, *J* = 50.1, 42.4, 16.0, 8.2 Hz), -203.15 (ddd, *J* = 45.3, 28.9, 7.2 Hz); FTIR (thin film) ν 3371 (w), 1597 (w), 1518 (s), 1155 (s), 533 (s) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{20}H_{24}F_2N_2O_4S$ $[M+H]^+$: 427.1498; found 427.1496; $[\alpha]_D^{24}$ = –6.05° (c 1.0, CH_3CN).



6e(*anti*)

Prepared according to the general procedure using **5e** (223 mg, 0.52 mmol) with the following modification: 25 equiv hydrogen fluoride and 20 mol% of catalyst *ent*-**1a** (enantiomer of catalyst **1a**, 80 mg) were used instead. The diastereomeric ratio (d.r.) of the crude residue was determined to be >20:1 by ^{19}F NMR. The crude residue was purified by silica gel column chromatography (10 to 40% diethyl ether in hexanes) to give **6e***(anti)* (189 mg, 78%) as a white solid in >20:1 d.r. ^{1}H NMR (500 MHz, 10% $CD_3OD/CDCl_3$): δ 7.85 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 4.4 Hz, 2H), 7.19 (d, *J* = 3.9 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 5.87 (d, *J* = 45.4 Hz, 1H), 4.81–4.54 (m, 1H), 3.67 (dtd, *J* = 29.1, 8.3, 1.6 Hz, 1H), 2.25 (s, 3H), 1.85–0.71 (m, 13H); ^{13}C NMR (125.7 MHz, 10% $CD_3OD/CDCl_3$): δ 147.4, 144.0 (d, *J* = 21.1 Hz), 143.3, 138.5, 129.3, 126.1, 125.9 (d, *J* = 9.1 Hz), 123.3 (d, *J* = 1.7 Hz), 93.4–88.0 (m), 61.6 (dd, *J* = 25.4, 19.1 Hz), 39.3 (d, *J* = 20.0 Hz), 34.0, 33.9, 32.1, 26.4, 26.1 (d, *J* = 31.3 Hz), 21.1; ^{19}F NMR (470.4 MHz, 10% $CD_3OD/CDCl_3$): δ -185.61–-185.99 (m), -203.12 (ddd, *J* = 45.4, 28.8, 7.5 Hz); FTIR (thin film) ν 1523 (s), 1447 (m), 1161 (s), 542 (s) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{23}H_{28}F_2N_2O_4S$ $[M+H]^+$: 467.1811; found 467.1817; $[\alpha]_D^{24}$ = –6.5° (c 1.0, CH_3CN).



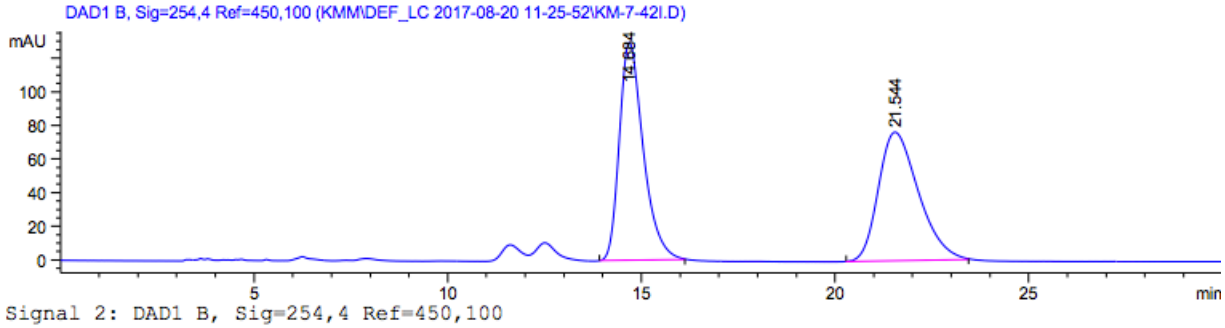
8

Prepared according to the general procedure using **7** (187 mg, 0.52 mmol) with the following modification: 10 equiv hydrogen fluoride was used instead. After work-up, the crude residue was purified by silica gel column chromatography (0 to 30% diethyl ether in hexanes) to give **8** (161 mg, 82%) as a white solid in 86% ee. Crystals of **8** were grown by vapor diffusion of pentane into a solution of the compound in ethyl acetate. These crystals were

filtered and dried *in vacuo* to give **8** in >99% ee (128 mg, 65%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26–8.10 (m, 1H), 7.79–7.65 (m, 2H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 6.07 (dd, *J* = 47.6, 2.1 Hz, 1H), 3.90 (ddt, *J* = 27.9, 5.4, 2.8 Hz, 1H), 3.55–3.39 (m, 1H), 3.23 (dt, *J* = 10.2, 6.9 Hz, 1H), 2.41 (s, 2H), 2.02–1.83 (m, 1H), 1.64–1.48 (m, 1H), 1.49–1.32 (m, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 148.5, 144.0, 139.9 (d, *J* = 21.2 Hz), 134.4, 131.2 (d, *J* = 8.2 Hz), 130.0, 129.8, 127.5, 123.2, 120.0 (d, *J* = 9.9 Hz), 94.5 (d, *J* = 183.7 Hz), 64.4 (d, *J* = 22.2 Hz), 49.5, 24.8 (d, *J* = 2.1 Hz), 21.6; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -202.5 (dd, *J* = 47.6, 28.0 Hz); FTIR (thin film) ν 3091 (w), 1598 (w), 1531 (s), 1400 (s), 1156 (s), 588(s) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{18}H_{19}FN_2O_4S$ $[M+H]^+$: 379.1122; found 379.1115; $[\alpha]_D^{24}$ = –120° (c 1.0, $CHCl_3$).

86% ee, Chiral HPLC (AS-H, 50% isopropanol in hexanes, 1.0 mL/min, λ = 254 nm); t_R(minor) = 14.9 min, t_R(major) = 21.4 min.

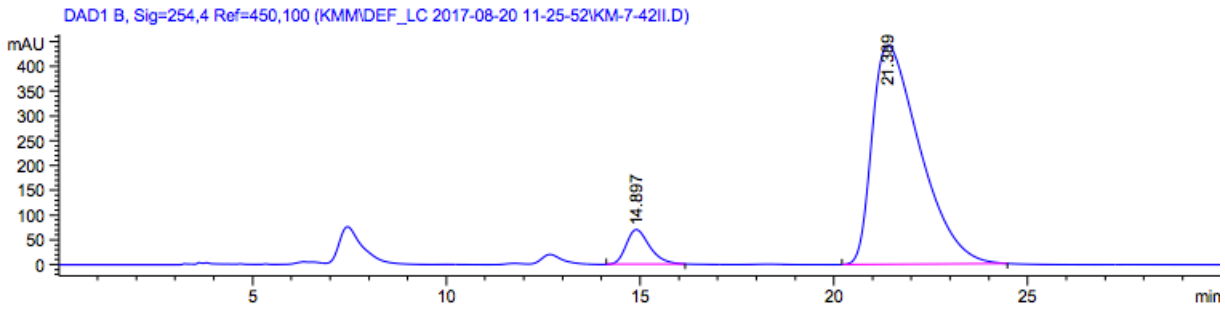
Racemic sample:



Signal 2: DAD1 B, Sig=254,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.684	BB	0.6498	5586.34180	129.87555	50.3545
2	21.544	BB	1.0773	5507.68604	76.56126	49.6455
Totals :				1.10940e4	206.43681	

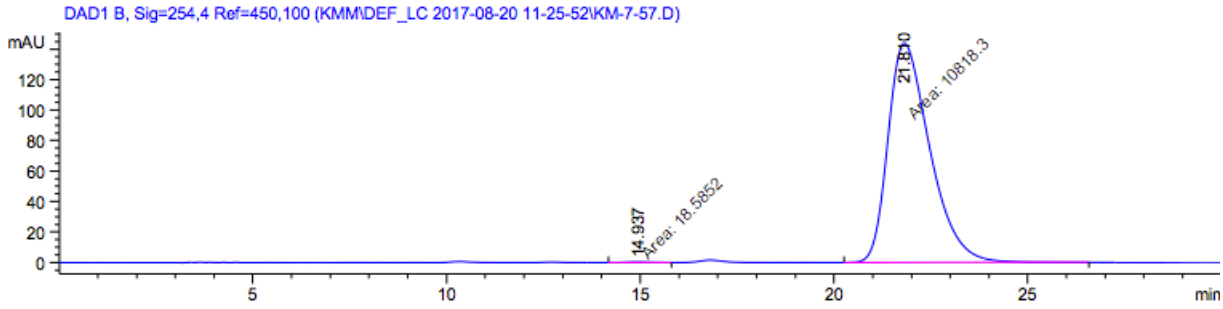
Enriched sample:



Signal 2: DAD1 B, Sig=254,4 Ref=450,100

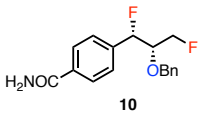
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.897	BB	0.6486	2964.25171	69.91708	7.2321
2	21.389	BB	1.2659	3.80234e4	441.88013	92.7679
Totals :				4.09877e4	511.79721	

Upgraded (>99% ee) sample:



Signal 2: DAD1 B, Sig=254,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.937	MM	0.7423	18.58518	4.17295e-1	0.1715
2	21.810	MM	1.2532	1.08183e4	143.87566	99.8285
Totals :				1.08369e4	144.29295	

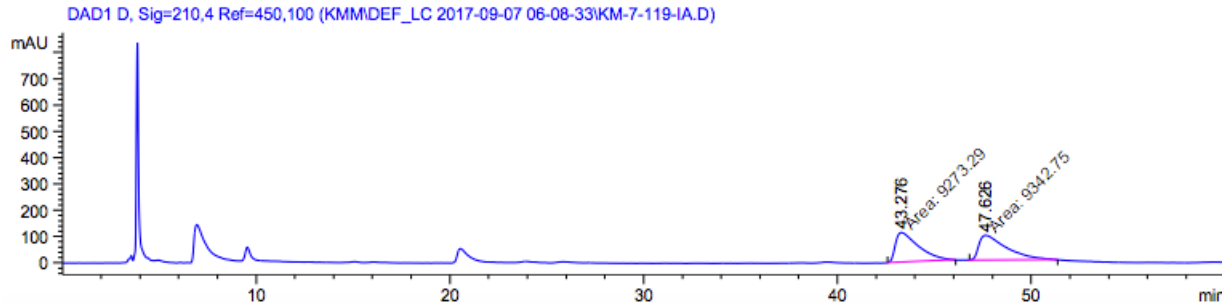


10

Prepared according to the general procedure using **9** (187 mg, 0.52 mmol) with the following modification: 100 equiv hydrogen fluoride and 20 mol% of catalyst **1a** were used instead. After work-up, the crude residue was purified by silica gel column chromatography (10 to 100% diethyl ether in hexanes) to give **10** (159 mg, 64%) as a white solid in 92% ee. Absolute configuration was assigned by analogy to an X-ray crystal structure of **4a**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.8 Hz, 2H), 7.51–7.41 (m, 2H), 7.32–7.27 (m, 3H), 7.23–7.18 (m, 2H), 6.10 (br. s, 1H), 5.80 (br. s, 1H), 5.67 (dd, *J* = 45.9, 4.6 Hz, 1H), 4.68–4.47 (m, 3H), 4.32 (ddd, *J* = 46.9, 9.9, 5.3 Hz, 1H), 3.91 (dddt, *J* = 19.6, 17.6, 5.4, 4.6 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 169.3, 140.5 (d, *J* = 20.6 Hz), 137.4, 133.9, 128.6, 128.1, 127.7, 126.4 (d, *J* = 7.7 Hz), 92.4 (dd, *J* = 178.9, 6.5 Hz), 82.1 (dd, *J* = 172.3, 6.3 Hz), 79.4 (dd, *J* = 22.1, 19.5 Hz), 73.9; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -194.57 (dd, *J* = 46.0, 19.5 Hz), -230.43 (td, *J* = 46.9, 17.5 Hz); FTIR (thin film) ν 3369 (br. s), 3176 (br. s), 1651 (s), 1394 (m), 1119 (m), 695 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{17}H_{17}F_2NO_4S$ $[M+H]^+$: 274.0544; found 274.0555; $[\alpha]_D^{24}$ = +13.3° (c 1.0, CH_3CN).

92% ee, Chiral HPLC (IA, 5% isopropanol in hexanes, 1.0 mL/min, λ = 210 nm); t_R(minor) = 43.9 min, t_R(major) = 46.6 min.

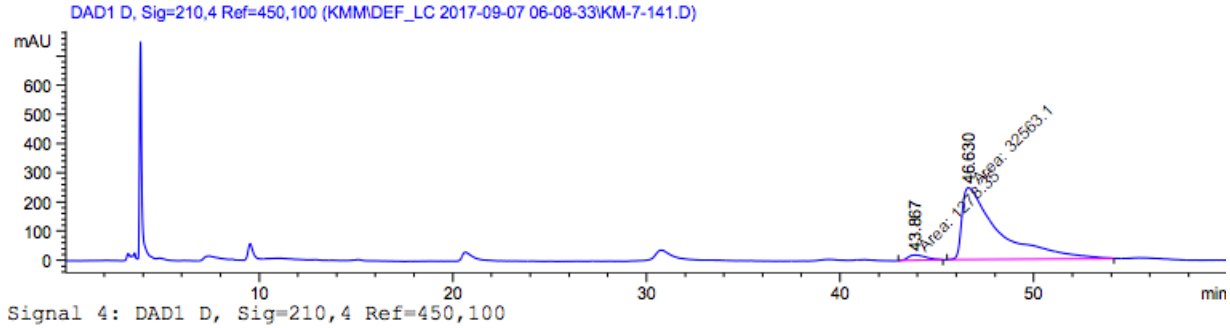
Racemic sample:



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

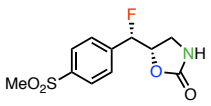
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.276	MM	1.3718	9273.28711	112.66366	49.8134
2	47.626	MM	1.6608	9342.74512	93.75551	50.1866
Totals :				1.86160e4	206.41917	

Enriched sample:



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.867	MM	1.1051	1278.34875	19.27968	3.7775
2	46.630	MM	2.2030	3.25631e4	246.35051	96.2225
Totals :				3.38414e4	265.63019	

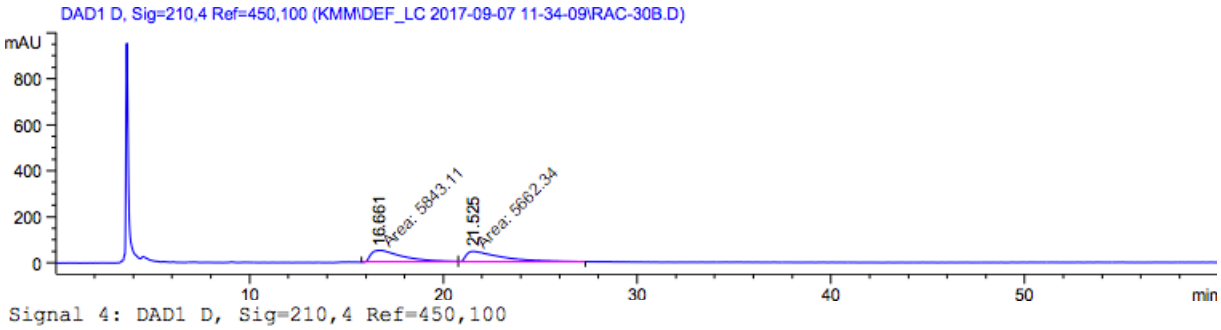


12

Prepared according to the general procedure using **11** (180 mg, 0.52 mmol) with the following modification: 100 equiv hydrogen fluoride and 20 mol% of catalyst **1a** were used instead. After work-up, the crude residue was purified by silica gel column chromatography (0 to 2% methanol in dichloromethane) to give **12** (109 mg, 77%) as a white solid in 93% ee. Crystals of **12** were grown by slow cooling of a solution of the compound in ethyl acetate. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.72–7.56 (m, 2H), 5.65 (dd, *J* = 45.0, 3.5 Hz, 1H), 5.17 (s, 1H), 4.96 (dddd, *J* = 18.9, 9.5, 6.3, 3.5 Hz, 1H), 3.89–3.46 (m, 2H), 3.08 (s, 3H); ^{13}C NMR (125.7 MHz, 10% $CD_3OD/CDCl_3$): δ 159.3, 140.9 (d, *J* = 13.0 Hz), 140.8 (d, *J* = 13.0 Hz), 127.6, 127.2 (d, *J* = 7.5 Hz), 91.5 (d, *J* = 182.4 Hz), 76.6 (d, *J* = 23.2 Hz), 44.1, 41.4 (d, *J* = 4.7 Hz); ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -193.99 (dd, *J* = 45.2, 20.6 Hz); FTIR (thin film) ν 1749 (s), 1410 (m), 1090 (s), 766 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{11}H_{12}FNO_4S$ $[M+H]^+$: 274.0544; found 274.0555; $[\alpha]_D^{24}$ = +38.2° (c 1.0, CH_3OH).

93% ee, Chiral HPLC (IA, 30% isopropanol in hexanes, 1.0 mL/min, λ = 210 nm); t_R(major) = 16.3 min, t_R(minor) = 23.8 min.

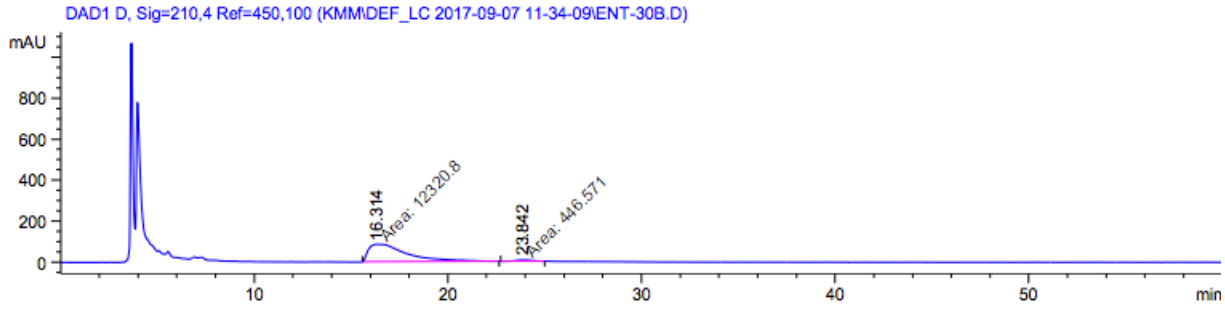
Racemic sample:



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

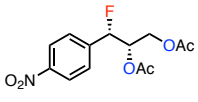
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.661	MM	1.9167	5843.11377	50.80884	50.7856
2	21.525	MM	2.0973	5662.34033	44.99783	49.2144
Totals :				1.15055e4	95.80667	

Enriched sample:



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.314	MM	2.3692	1.23208e4	86.67197	96.5022
2	23.842	MM	1.0891	446.57083	6.83378	3.4978
Totals :				1.27674e4	93.50574	



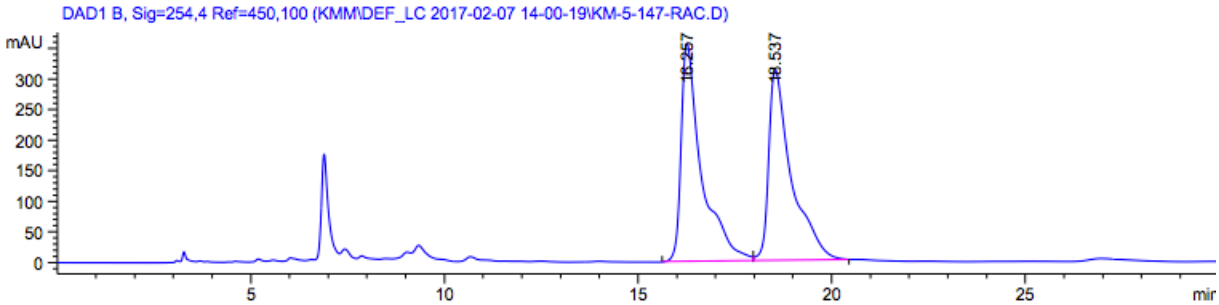
14

Prepared according to the general procedure using **13** (187 mg, 0.52 mmol) with the following modification: 100 equiv hydrogen fluoride and 20 mol% of catalyst **1a** were used instead. After work-up, the crude residue was purified by silica gel column chromatography (10 to 100% diethyl ether in hexanes) to give **14** (120 mg, 77%) as a white solid in 94% ee. The absolute configuration was assigned by analogy to an X-ray crystal structure of **16**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.32–8.12 (m, 2H), 7.61–7.41 (m, 2H), 5.74 (dd, *J* = 45.9, 4.0 Hz, 1H), 5.51–5.34 (m, 1H), 4.39 (ddd, *J* = 11.9, 4.7, 1.0 Hz, 1H), 4.03 (dd, *J* = 11.9, 6.5 Hz, 1H), 2.03 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 170.4, 169.7, 148.3, 142.5 (d, *J* = 20.8

Hz), 126.9 (d, J = 7.9 Hz), 123.8, 90.8 (d, J = 182.1 Hz), 71.8 (d, J = 21.2 Hz), 61.8 (d, J = 6.2 Hz), 20.7, 20.5; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -195.72 (dd, J = 46.0, 22.9 Hz); FTIR (thin film) ν 1742 (s), 1523 (s), 1212 (s), 1043 (s), 721 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{13}H_{14}FNO_6$ $[M+H]^+$: 300.0878; found 300.0893; $[\alpha]_D^{26}$ = +1.4° (c 1.0, CH_3CN).

94% ee, Chiral HPLC (whelk, 10% isopropanol in hexanes, 1.0 mL/min, λ = 254 nm); t_R(minor) = 17.1 min, t_R(major) = 18.9 min.

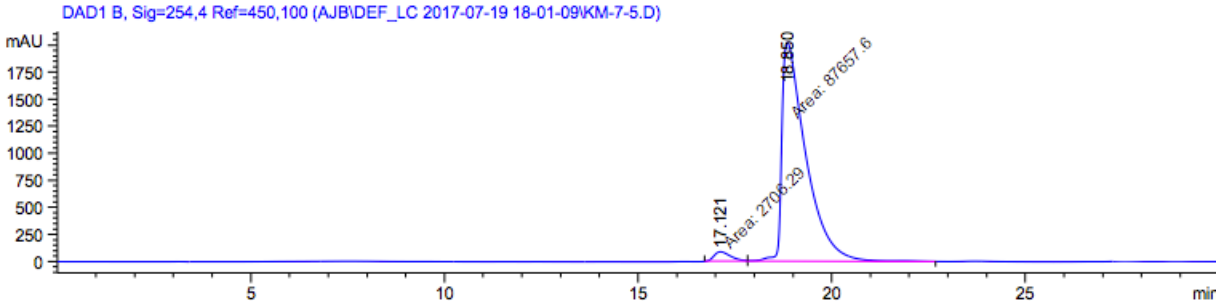
Racemic sample:



Signal 2: DAD1 B, Sig=254,4 Ref=450,100

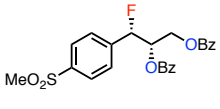
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.257	BV	0.5212	1.31420e4	357.23099	50.6881
2	18.537	VB	0.5814	1.27852e4	312.45844	49.3119
Totals :				2.59273e4	669.68942	

Enriched sample:



Signal 2: DAD1 B, Sig=254,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.121	MM	0.5083	2706.29297	88.74250	2.9949
2	18.850	MM	0.7215	8.76576e4	2024.92297	97.0051
Totals :				9.03639e4	2113.66547	



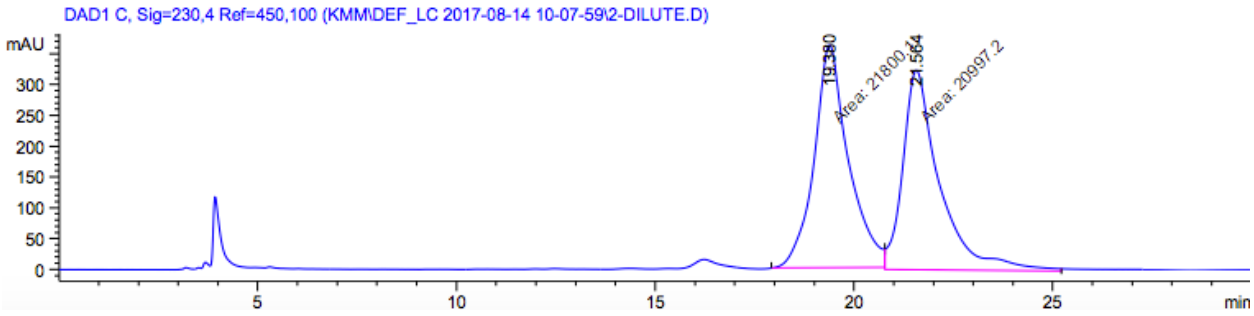
16

Prepared according to the general procedure using **15** (187 mg, 0.52 mmol) with the following modification: 100 equiv hydrogen fluoride and 20 mol% of catalyst **1a** were used instead. After work-up, the crude residue was purified by silica gel column chromatography (10 to 100% diethyl ether in hexanes) to give **16** (173 mg, 73%) as a

white solid in 94% ee. Crystals of **16** were grown by vapor diffusion of pentane into a solution of the compound in ethyl acetate.^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03–7.86 (m, 6H), 7.69–7.61 (m, 2H), 7.58–7.51 (m, 2H), 7.45–7.37 (m, 4H), 6.07–5.82 (m, 2H), 4.74 (ddd, *J* = 11.9, 4.7, 0.9 Hz, 1H), 4.49 (dd, *J* = 11.9, 6.4 Hz, 1H), 2.97 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 165.9, 165.2, 141.5 (d, *J* = 20.6 Hz), 141.1, 133.6, 133.4, 129.8, 129.7, 129.2, 128.9, 128.6, 128.5, 127.8, 127.0 (d, *J* = 7.8 Hz), 91.1 (d, *J* = 182.1 Hz), 72.4 (d, *J* = 22.0 Hz), 62.3 (d, *J* = 5.8 Hz), 44.3; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -194.0 (dd, *J* = 45.6, 21.2 Hz); FTIR (thin film) ν 3064 (w), 1720 (s), 1451 (w), 1150 (s), 909 (m), 708 (s) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{24}H_{21}FO_6S$ $[M+H]^+$: 457.1116; found 457.1107. $[\alpha]_D^{24}$ = +20.8° (c 1.0, CH_3OH).

94% ee, Chiral HPLC (AD-H, 30% isopropanol in hexanes, 1.0 mL/min, λ = 230 nm); t_R(minor) = 19.9 min, t_R(major) = 21.8 min.

Racemic sample:




```
Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  19.380 MM    1.0044 2.18001e4   361.76038  50.9380
   2  21.564 MM    1.0784 2.09972e4   324.51047  49.0620

Totals :                 4.27972e4   686.27084
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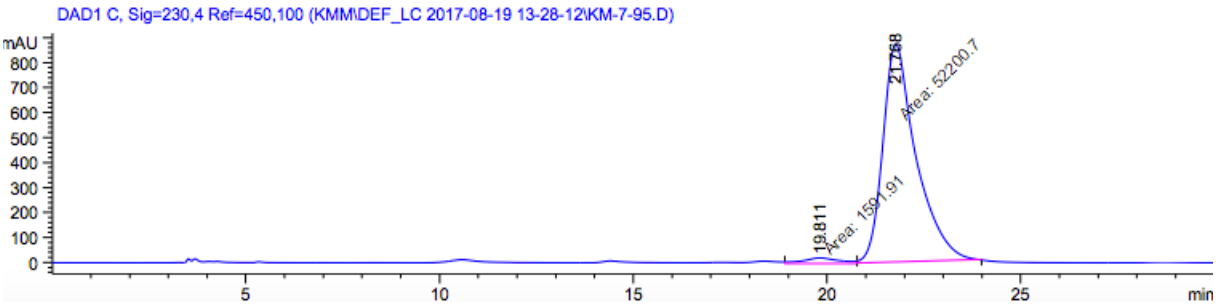
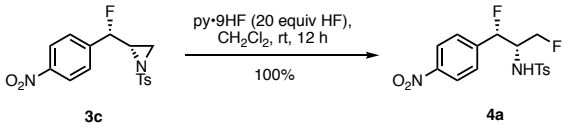
Enriched sample:



Signal 3: DAD1 C, Sig=230,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.811	MM	1.1281	1591.90503	23.51830	2.9593
2	21.768	MM	0.9961	5.22007e4	873.43707	97.0407
Totals :				5.37926e4	896.95537	

Synthetic Elaboration Studies.

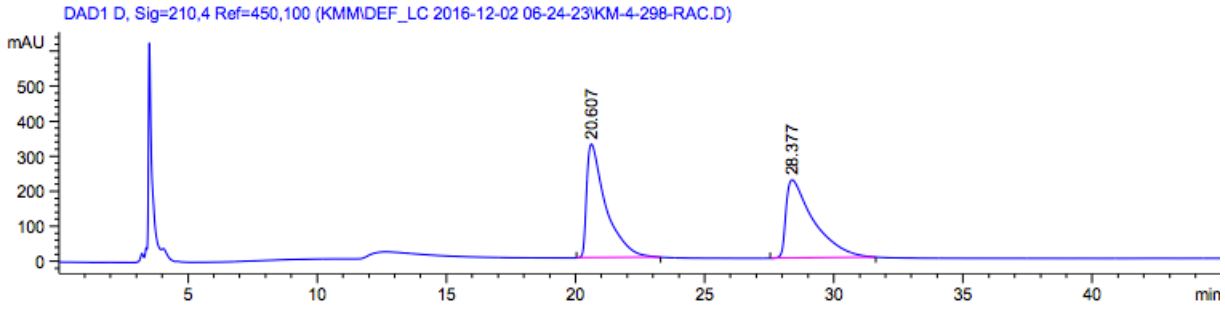


3c **4a**

To a solution of **3c** (65.0 mg, 0.186 mmol, 1 equiv) in dichloromethane (1 mL) in a low-density polyethylene tube was added HF•pyridine (py•9HF, 70% hydrogen fluoride by weight, 100 µL, 20 equiv hydrogen fluoride). The reaction mixture was stirred at room temperature for 12 hours. The heterogeneous mixture was transferred carefully into a vigorously stirred suspension of basic alumina (0.5 g) in dichloromethane at –78 °C. The resulting suspension was allowed to warm to room temperature and filtered, washing with 10 mL dichloromethane. The combined filtrate was concentrated under reduced pressure to give **4a** as a white solid (68.6 mg, 100%). Crystals of **4a** were grown by vapor diffusion of pentane into a solution of the compound in ethyl acetate. ^{1}H NMR (500 MHz, 10% $CD_3OD/CDCl_3$): δ 7.99 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 7.06 (d, *J* = 8.7 Hz, 2H), 5.83 (d, *J* = 45.6 Hz, 1H), 4.96 (d, *J* = 9.5 Hz, 1H), 4.72–4.45 (m, 2H), 3.90-3.72 (m, 1H), 2.35 (s, 3H); ^{13}C NMR (125.7 MHz, 10% $CD_3OD/CDCl_3$): δ 147.5, 143.5, 143.3 (d, *J* = 21.1 Hz), 137.2, 129.3, 126.4, 126.0 (d, *J* = 8.6 Hz), 123.3, 89.8 (dd, *J* = 180.1, 2.4 Hz), 80.8 (dd, *J* =176.3, 4.3 Hz), 56.9 (dd, *J* = 22.0, 20.6 Hz), 21.1; ^{19}F NMR (470.4 MHz, 10% $CD_3OD/CDCl_3$): -203.2 (dd, *J* =45.3, 25.6 Hz, 1F), -223.2 (td, *J* =46.7, 10.7 Hz, 1F); FTIR (thin film) ν 3281 (br. m), 1790 (w), 1522 (s), 1346 (s), 1160 (s), 548 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{16}H_{16}F_2N_2O_4S$ $[M+H]^+$: 371.0872; found 371.0866; $[\alpha]_D^{26}$ = +33.45° (c 1.0, CH_3CN).

99% ee, Chiral HPLC (whelk, 10% isopropanol in hexanes, 1.0 mL/min, λ = 210 nm); t_R(minor) = 21.0 min, t_R(major) = 26.8 min.

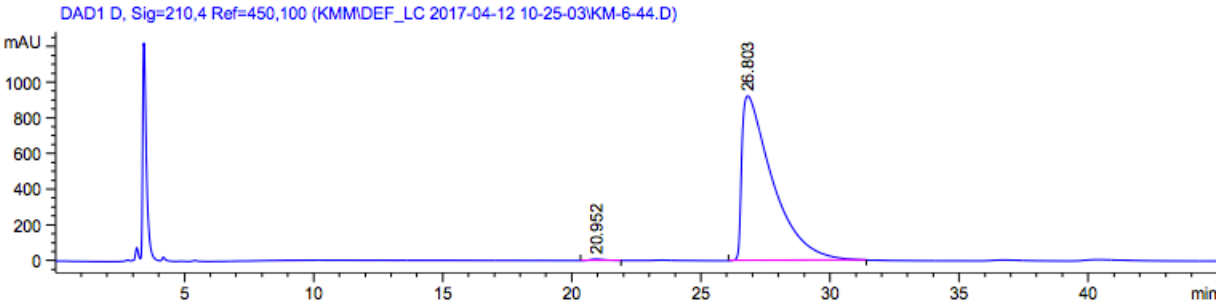
Racemic sample:



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

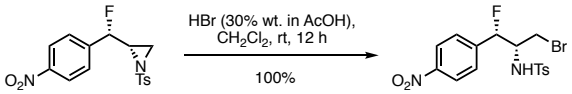
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.607	BB	0.7391	1.67828e4	324.67023	50.2482
2	28.377	BB	1.0231	1.66170e4	223.05663	49.7518
Totals :				3.33998e4	547.72685	

Enriched sample:



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.952	BB	0.4807	307.36530	7.61842	0.3997
2	26.803	BB	1.0921	7.65846e4	922.89575	99.6003
Totals :				7.68920e4	930.51417	

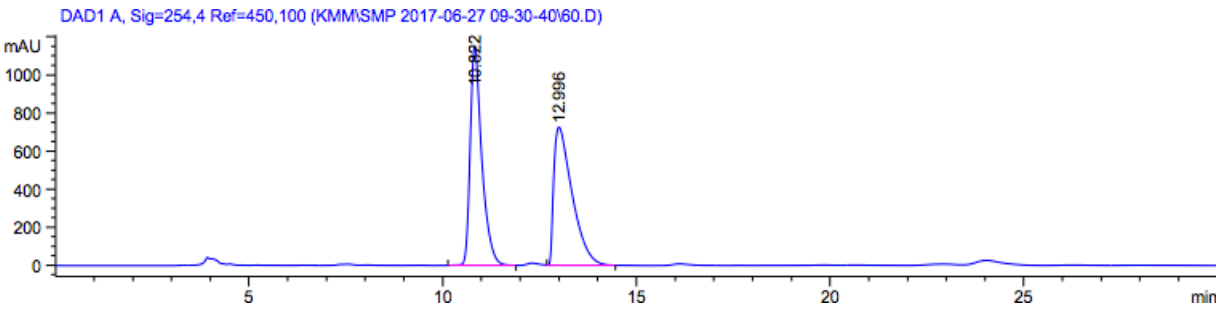


4b

To a solution of **3c** (65.0 mg, 0.186 mmol, 1 equiv) in dichloromethane (1 mL) was added hydrobromic acid (33 wt. % in acetic acid, 1 mL). The reaction mixture was stirred at room temperature for 12 hours. The solution was transferred carefully into a vigorously stirred suspension of basic alumina (0.5 g) in dichloromethane at –78 °C. The resulting suspension was allowed to warm to room temperature and filtered, washing with 10 mL 1:1 diethyl ether:dichloromethane. The combined filtrate was concentrated under reduced pressure to give **4b** as an orange solid (80.0 mg, 100%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.6 Hz, 2H), 7.39–7.33 (m, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.07 (d, *J* = 44.6 Hz, 1H), 4.90 (d, *J* = 9.3 Hz, 1H), 3.77–3.66 (m, 1H), 3.66–3.56 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 147.67, 144.12, 142.96 (d, *J* = 19.8 Hz), 136.4, 129.7, 127.1, 126.1 (d, *J* = 6.6 Hz), 123.6, 90.3 (d, *J* = 180.7 Hz), 59.1 (d, *J* = 19.6 Hz), 31.6, 21.4; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -202.6 (dd, *J* = 45.6, 23.1 Hz); FTIR (thin film) ν 3274 (br. m), 1608 (w), 1522 (s), 1157 (s), 946 (m), 548 (s) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{16}H_{16}BrFN_2O_4S$ $[M+H]^+$: 431.0071; found 431.0066; $[\alpha]_D^{25}$ = +14.2° (c 1.0, CH_3OH).

99% ee, Chiral HPLC (AD-H, 20% isopropanol in hexanes, 1.0 mL/min, λ = 254 nm); t_R(minor) = 10.9 min, t_R(major) = 13.4 min.

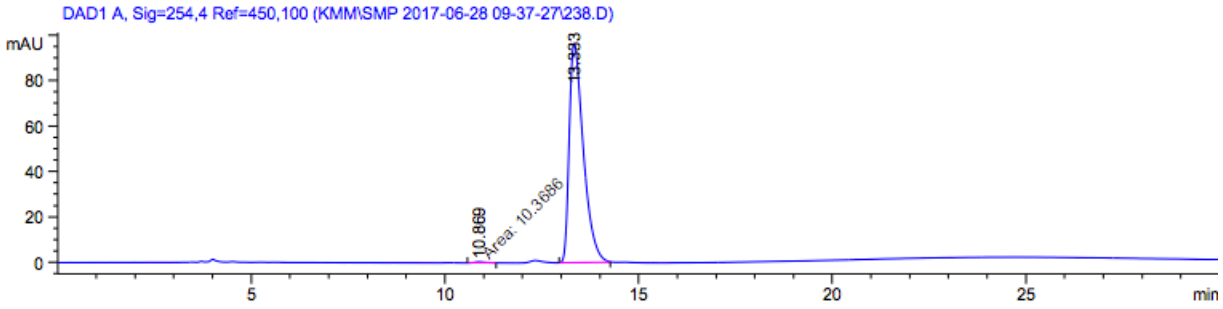
Racemic sample:



Signal 1: DAD1 A, Sig=254,4 Ref=450,100

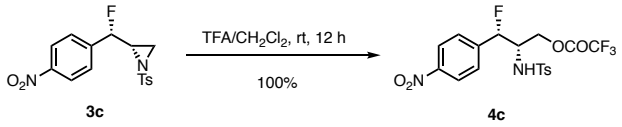
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.822	BB	0.3083	2.39347e4	1152.55505	50.0350
2	12.996	VB	0.4959	2.39012e4	726.38916	49.9650
Totals :				4.78360e4	1878.94421	

Enriched sample:



Signal 1: DAD1 A, Sig=254,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.869	MM	0.3400	10.36864	5.08316e-1	0.4226
2	13.333	BB	0.3839	2442.94775	96.32810	99.5774
Totals :				2453.31639	96.83642	

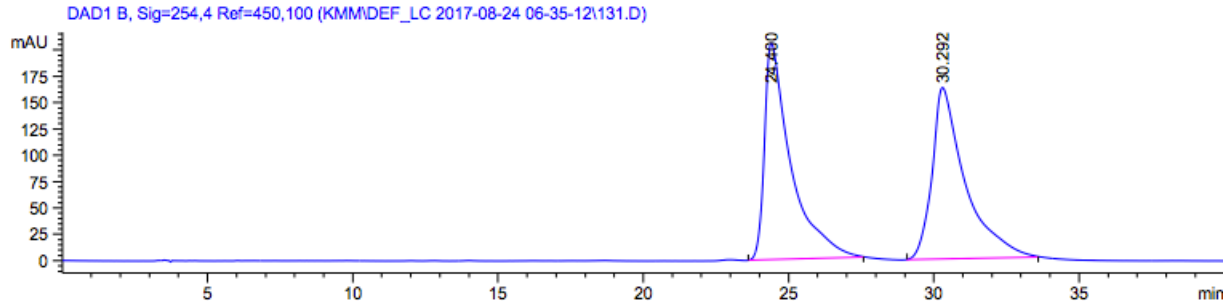


3c **4c**

To a solution of **3c** (65.0 mg, 0.186 mmol, 1 equiv) in dichloromethane (1 mL) was added trifluoroacetic acid (0.5 mL). The reaction mixture was stirred at room temperature for 12 hours, concentrated under reduced pressure to give **4c** as a white solid (86.2 mg, 100%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 1H), 5.76 (dd, *J* = 45.5, 2.1 Hz, 1H), 5.55 (d, *J* = 9.3 Hz, 1H), 4.78–4.35 (m, 2H), 4.18–3.90 (m, 1H), 2.34 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 157.0 (q, *J* = 43.3 Hz), 147.9, 144.3, 142.2 (d, *J* = 20.8 Hz), 136.5, 129.7, 126.7, 125.9 (d, *J* = 9.0 Hz), 123.6 (d, *J* = 1.5 Hz), 121.1–109.0 (m), 90.4 (d, *J* = 181.5 Hz), 66.0 (d, *J* = 3.9 Hz), 56.1 (d, *J* = 20.7 Hz), 21.4; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -74.7 (s, 3F), -201.6 (dd, *J* = 45.5, 25.9 Hz, 1F); FTIR (thin film) ν 3277 (br. w), 1788 (m), 1523 (m), 1151 (s), 733 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{18}H_{16}F_4N_2O_6S$ $[M+H]^+$: 465.0738; found 465.0749; $[\alpha]_D^{25}$ = +20.8° (c 1.0, CH_3OH).

99% ee, Chiral HPLC (OJ-H, 40% isopropanol in hexanes, 1.0 mL/min, λ = 254 nm); t_R(minor) = 22.8 min, t_R(major) = 30.4 min.

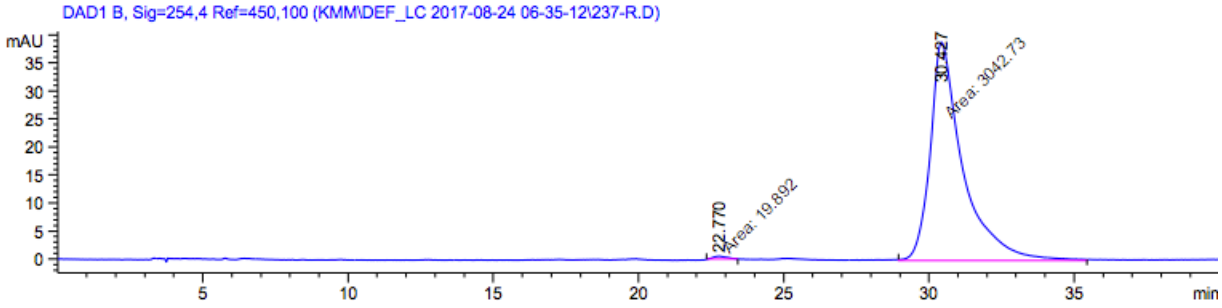
Racemic sample:



Signal 2: DAD1 B, Sig=254,4 Ref=450,100

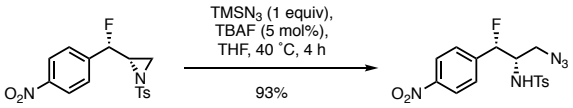
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.400	BB	0.8763	1.30050e4	205.51227	50.2024
2	30.292	BB	1.0910	1.29001e4	162.69958	49.7976
Totals :				2.59051e4	368.21185	

Enriched sample:



Signal 2: DAD1 B, Sig=254,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.770	MM	0.5845	19.89203	5.67209e-1	0.6495
2	30.427	MM	1.3026	3042.73462	38.93262	99.3505
Totals :				3062.62665	39.49983	



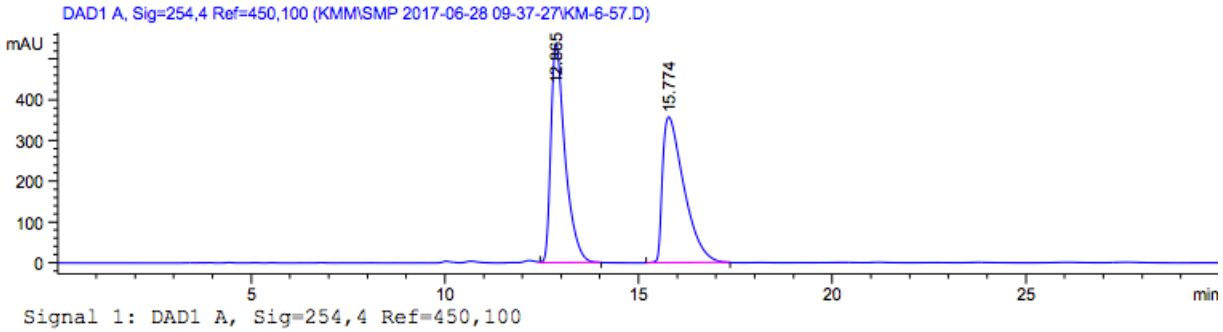
3c **4d**

To a solution of **3c** (65.0 mg, 0.186 mmol, 1 equiv) in anhydrous tetrahydrofuran (2.1 mL) under nitrogen atmosphere was added azidotrimethylsilane (25.0 µL, 0.188 mmol, 1.0 equiv) followed by tetrabutylammonium fluoride (1.0 M in THF, 8.9 µL, 5 mol%). The reaction mixture was warmed to 40 °C and stirred for 4 hours. After cooling to room temperature, the solution was filtered through a plug of silica, washing with diethyl ether. The filtrate was concentrated under reduced pressure to give **4d** as a white solid (66.6 mg, 93%). ^{1}H NMR (500 MHz, CD_3CN): δ 7.95 (d, J = 8.6 Hz, 2H), 7.53–7.23 (m, 4H),

7.09 (d, J = 7.9 Hz, 2H), 6.11 (s, 1H), 5.78 (d, J = 45.5 Hz, 1H), 3.88–3.73 (m, 1H), 3.54 (ddd, J = 64.3, 12.7, 6.8 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (125.7 MHz, CD_3CN): δ 148.6, 144.57 (d, J = 20.8 Hz), 144.2, 138.9, 130.3, 127.3, 127.3, 124.1, 58.38 (d, J = 20.7 Hz), 53.16 (d, J = 3.9 Hz), 21.3; ^{19}F NMR (470.4 MHz, CD_3CN): δ -200.8–-201.2 (m); FTIR (thin film) ν 3259 (m), 2108 (s), 1521 (s), 1346 (s), 1159 (s), 562 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{16}H_{16}FN_5O_4S$ $[M+H]^+$: 394.0980; found 394.0971; $[\alpha]_D^{25}$ = +47.2° (c 1.0, CH_3OH).

99% ee, Chiral HPLC (AD-H, 20% isopropanol in hexanes, 1.0 mL/min, λ = 254 nm); t_R(minor) = 12.2 min, t_R(major) = 16.1 min.

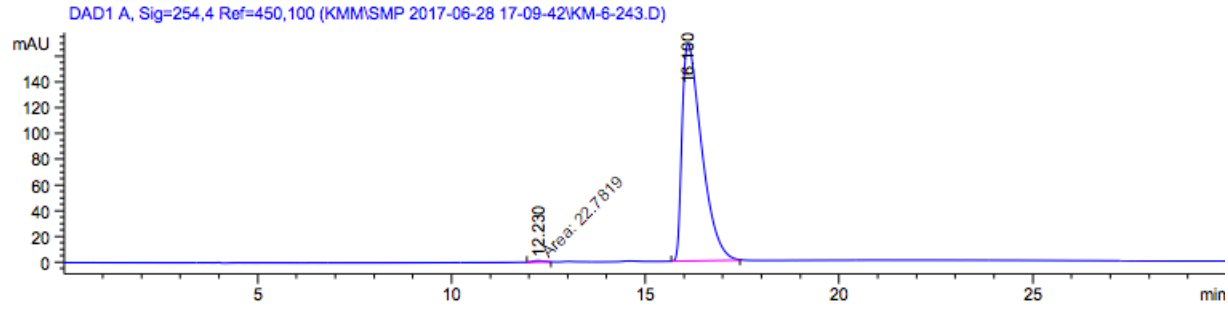
Racemic sample:



Signal 1: DAD1 A, Sig=254,4 Ref=450,100

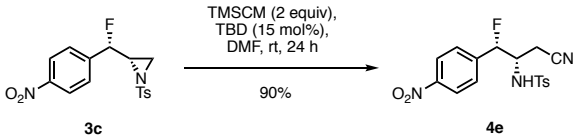
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.865	VB	0.3801	1.37566e4	538.43182	49.8704
2	15.774	BB	0.5865	1.38281e4	358.09665	50.1296
Totals :				2.75847e4	896.52847	

Enriched sample:



Signal 1: DAD1 A, Sig=254,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.230	MM	0.3299	22.78185	1.15102	0.3807
2	16.100	BB	0.5378	5961.09375	168.88438	99.6193
Totals :				5983.87560	170.03540	

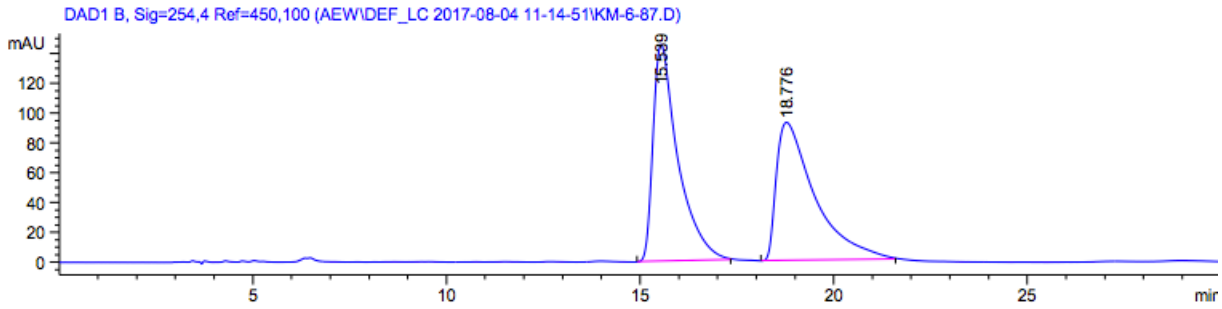


3c **4e**

To a solution of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (3.8 mg, 0.027 mmol, 15 mol%) in anhydrous dimethylformamide (0.6 mL) was added **3c** (65.0 mg, 0.186 mmol, 1 equiv) followed by trimethylsilyl cyanide (47.0 µL, 0.376 mmol, 2.0 equiv). The reaction mixture was stirred at room temperature. After 24 hours, the solution was diluted with diethyl ether (10 mL) and washed with 1 M $HCl_{(aq)}$ (5 mL), water (3 x 5 mL) and brine (5 mL), dried over $NaSO_4$, filtered and concentrated under reduced pressure to **4e** as a white solid (63.2 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.44–7.32 (m, 4H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 1H), 5.83 (dd, *J* = 45.6, 2.2 Hz, 1H), 5.63 (d, *J* = 9.3 Hz, 1H), 3.90 (dddd, *J* = 25.2, 10.4, 8.0, 3.4 Hz, 1H), 3.16–2.81 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 147.9, 144.5, 142.0 (d, *J* = 20.9 Hz), 136.2, 129.7, 126.7, 125.9 (d, *J* = 8.8 Hz), 123.6, 116.4, 91.8 (d, *J* = 182.4 Hz), 54.8 (d, *J* = 20.9 Hz), 22.4 (d, *J* = 3.7 Hz), 21.4; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -201.0 (dd, *J* = 45.6, 25.9 Hz); FTIR (thin film) ν 3270 (br. m), 1609 (w), 1523 (s), 1346 (s), 1158 (s), 732 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{17}H_{16}FN_3O_4S$ $[M+H]^+$: 378.0918; found 378.0914; $[\alpha]_D^{25}$ = +21.4° (c 1.0, CH_3OH).

99% ee, Chiral HPLC (AD-H, 20% isopropanol in hexanes, 1.0 mL/min, λ = 254 nm); t_R(minor) = 15.3 min, t_R(major) = 17.7 min.

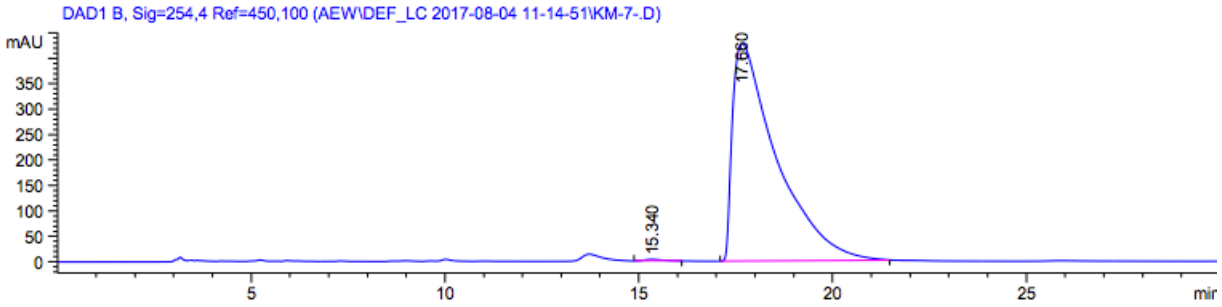
Racemic sample:



Signal 2: DAD1 B, Sig=254,4 Ref=450,100

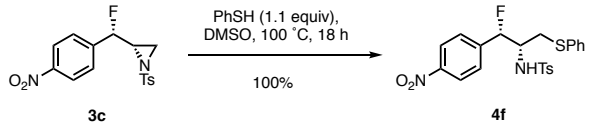
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.539	BB	0.6484	6524.58691	145.71365	50.4887
2	18.776	BB	0.9749	6398.27490	92.74018	49.5113
Totals :				1.29229e4	238.45383	

Enriched sample:



Signal 2: DAD1 B, Sig=254,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.340	BB	0.4146	104.34280	3.11625	0.3078
2	17.660	BB	1.1266	3.37971e4	428.31116	99.6922
Totals :				3.39015e4	431.42741	

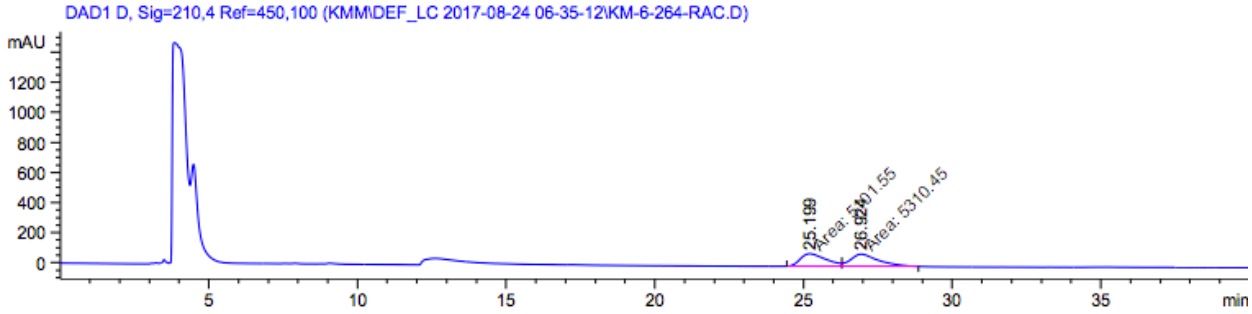


3c **4f**

To a solution of **3c** (65.0 mg, 0.186 mmol, 1 equiv) in dimethyl sulfoxide (0.36 mL) was added thiophenol (21.6 µL, 0.210 mmol, 1.1 equiv). The reaction mixture was heated to 100 °C for 18 hours. After cooling to room temperature, the crude mixture was purified by silica gel column chromatography (10 to 100% diethyl ether in hexanes) to give **4f** as a white solid (85.7 mg, 100%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.8 Hz, 2H), 7.47–7.42 (m, 2H), 7.41–7.35 (m, 2H), 7.34–7.28 (m, 1H), 7.16 (dd, *J* = 8.3, 1.8 Hz, 2H), 7.07 (dd, *J* = 8.8, 1.9 Hz, 2H), 6.93 (dd, *J* = 8.2, 1.9 Hz, 2H), 6.13 (d, *J* = 45.2 Hz, 1H), 5.28 (dd, *J* = 9.4, 2.1 Hz, 1H), 3.63–3.32 (m, 2H), 3.34–3.08 (m, 1H), 2.31 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 147.5, 143.9, 143.7 (d, *J* = 21.0 Hz), 136.2, 133.6, 123.0, 129.5, 129.4, 127.2, 126.8, 125.6 (d, *J* = 9.0 Hz), 123.3 (d, *J* = 1.7 Hz), 90.0 (d, *J* = 180.7 Hz), 57.0 (d, *J* = 20.8 Hz), 35.0, 21.4; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -204.2 (dd, *J* = 45.1, 26.6 Hz); FTIR (thin film) ν 3272 (br. m), 1607 (w), 1523 (s), 1344 (s), 1158 (s), 742 (m) cm^{-1}; HRMS (ESI-TOF) Calc'd for $C_{22}H_{21}FN_2O_4S_2$ $[M+H]^+$: 461.1000; found 461.0993; $[\alpha]_D^{25}$ = +53.2° (c 1.0, CH_3OH).

99% ee, Chiral HPLC (AD-H, 10% isopropanol in hexanes, 1.0 mL/min, λ = 210 nm); t_R(major) = 25.2 min, t_R(minor) = 28.3 min.

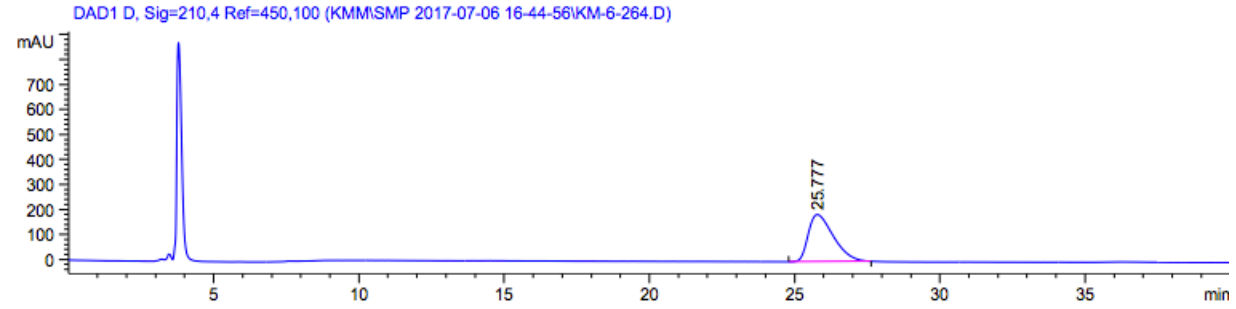
Racemic sample:



Signal 4: DAD1 D, Sig=210,4 Ref=450,100

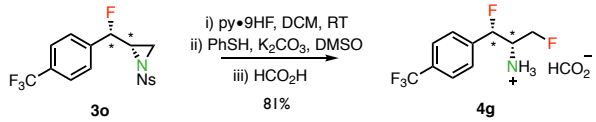
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.199	MM	1.0066	5101.55322	84.47024	48.9969
2	26.924	MM	1.0829	5310.44678	81.72871	51.0031
Totals :				1.04120e4	166.19895	

Enriched sample:



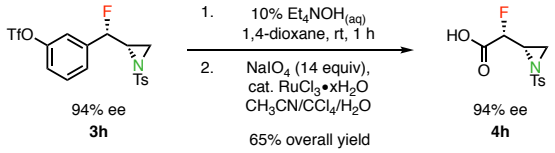
Signal 4: DAD1 D, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.777	BB	0.8456	1.13442e4	188.10159	100.0000
Totals :				1.13442e4	188.10159	



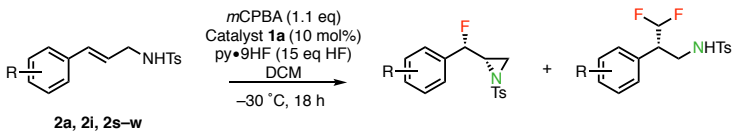
To a solution of **3o** (75.2 mg, 0.186 mmol, 1 equiv) in dichloromethane (1 mL) in a low-density polyethylene tube was added HF•pyridine (py•9HF, 70% hydrogen fluoride by weight, 100 µL, 20 equiv hydrogen fluoride). The reaction mixture was stirred at room temperature for 12 hours. The heterogeneous mixture was transferred carefully into a vigorously stirred suspension of basic alumina (0.5 g) in dichloromethane at –78 °C. The resulting suspension was allowed to warm to room temperature and filtered, washing with 10 mL dichloromethane. The combined filtrate was concentrated under reduced pressure. The crude residue was dissolved in DMSO (0.37 mL) to which thiophenol (95.5 µL, 0.93 mmol,

5 equiv) and potassium carbonate (129 mg, 0.93 mmol, 5 equiv) were added. The reaction mixture was stirred at room temperature. After 24 h, the crude mixture was purified by silica gel column chromatography (0% to 5% CH_3OH/CH_2Cl_2) followed by prep HPLC (0% to 50% (0.1% $HCO_2H_{(aq)}$)/CH_3CN) to give **4g** (43.0 mg, 81%) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 7.9 Hz, 2H), 5.60 (dd, *J* = 46.9, 5.2 Hz, 1H), 4.49 (dddd, *J* = 46.9, 9.5, 5.4, 1.8 Hz, 1H), 4.34 (ddd, *J* = 46.8, 9.5, 4.8 Hz, 1H), 3.38 (br. s, 1H), 3.38–3.23 (m, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 163.8, 141.0 (d, *J* = 20.6 Hz), 131.2 (q, *J* = 32.6 Hz), 126.3 (d, *J* = 7.7 Hz). 125.8 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 272.3 Hz), 93.1 (dd, *J* = 175.0, 2.8 Hz), 83.5 (dd, *J* = 171.2, 6.2 Hz), 56.4 (dd, *J* = 22.5, 19.2 Hz); ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -62.8 (s, 3H), -196.5 (dd, *J* = 47.1, 19.7 Hz, 1H), -230.4 (td, *J* = 47.1, 19.1 Hz, 1H); HRMS (ESI-TOF) Calc'd for $C_{11}H_{12}F_2NO_2$ $[M–HCO_2^-]^+$: 240.0806; found 240.0807; $[\alpha]_D^{25}$ = +13.8° (c 1.0, CH_3CN).



To a solution of **3h** (84.3 mg, 0.186 mmol, 1 equiv) in 1,4-dioxane (1.10 mL) was added 10% $Et_4NOH_{(aq)}$ (0.55 mL). The reaction mixture was stirred at room temperature. After 1 h, the reaction was quenched with 1 M $HCl_{(aq)}$ (0.5 mL). Diethyl ether (5 mL) was added, and the aqueous and organic layers were separated. The aqueous layer was extracted with diethyl ether (3 x 5 mL), washed with brine (2 mL), dried over Na_2SO_4, filtered and concentrated to give a colorless oil. The crude residue was dissolved in acetonitrile (0.5 mL) and carbon tetrachloride (0.5 mL). Water (1.0 mL), sodium periodate (557 mg, 2.60 mmol, 14 equiv) and a catalytic amount of ruthenium(III) chloride hydrate were added. The reaction mixture was allowed to stir at room temperature under air. After 18 h, diethyl ether (5 mL) was added, and the aqueous and organic layers were separated. The aqueous layer was extracted with diethyl ether (3 x 5 mL), washed with brine (2 mL), dried over Na_2SO_4, filtered, concentrated and purified by prep HPLC (H_2O/CH_3CN) to give **4h** as a colorless oil (33.0 mg, 65%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.20–7.90 (br. s, 1H), 7.83 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 4.85 (dd, *J* = 47.4, 5.0 Hz, 1H), 3.36–3.17 (m, 1H), 2.81 (d, *J* = 7.3 Hz, 1H), 2.51 (d, *J* = 4.1 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 170.48 (d, *J* = 25.0 Hz), 145.42, 133.98, 129.94, 128.37, 85.51 (d, *J* = 192.4 Hz), 38.93 (d, *J* = 23.5 Hz), 29.75 (d, *J* = 7.8 Hz), 21.83; ^{19}F NMR (470.4 MHz, $CDCl_3$): δ -198.7 (d, *J* = 43.5 Hz); HRMS (ESI-TOF) Calc'd for $C_{11}H_{12}F_5NO_2$ $[M–H]^-$: 272.0398; found 272.0410.

Competition between Aziridinium versus Phenonium Ion Formation.



2a, 2i, 2s–w

To a solution of substrate (0.104 mmol, 1 equiv) and catalyst **1a** (8.0 mg, 0.0104 mmol, 10 mol%) in dichloromethane (0.6 mL) in a low-density polyethylene tube at –78 °C was added HF•pyridine (py•9HF, 70% hydrogen fluoride by weight, 42 µL, 15 equiv hydrogen fluoride) followed by *m*CPBA (77% by weight, 25.6 mg, 0.114 mmol, 1.1 equiv). The reaction mixture was warmed to –30 °C and stirred at that temperature for 16 hours. The heterogeneous mixture was transferred carefully into a vigorously stirred suspension of basic alumina (400 mg) in dichloromethane at –78 °C. The resulting suspension was allowed to warm to room temperature and filtered, washing with 20 mL dichloromethane. The combined filtrate was concentrated under reduced pressure. The ratio of aziridine product (NHTs) to the total of aziridine and 1,1-difluoromethylated product (NHTs + Ar) was determined by ^{19}F NMR analysis of the crude mixture.

R	Sigma +	NHTs/(Ar + NHTs)		NHTs/Ar	log(NHTs/Ar)
H	0	0.052	0.052	0.05485232	-1.260805
p-Cl	0.114	0.146	0.146	0.17096019	-0.767105
p-Br	0.15	0.2	0.2	0.25	-0.60206
m-F	0.352	0.671	0.671	2.03951368	0.30952662
m-Br	0.405	0.778	0.778	3.5045045	0.54462662
m-CF3	0.52	1	0.99	99	1.99563519
p-CF3	0.612	1	0.99	99	1.99563519

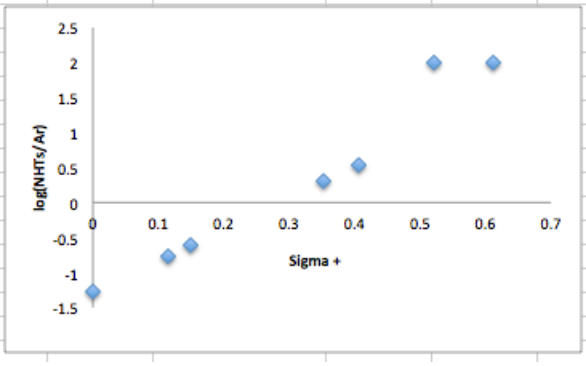
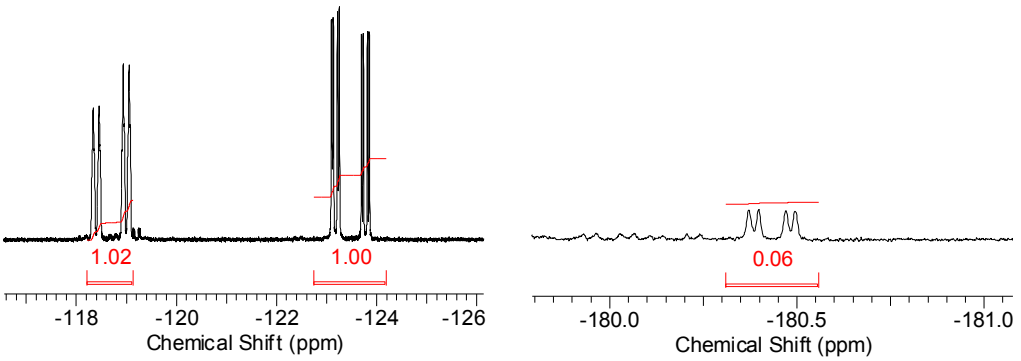


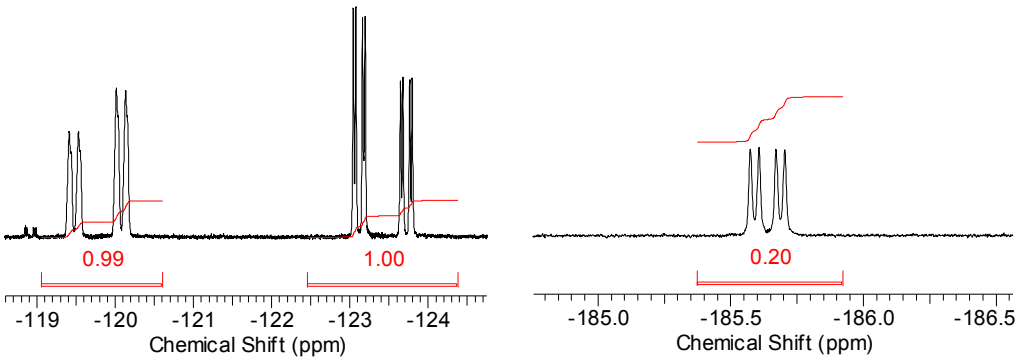
Figure S1. Hammett plot of the product selectivity for fluoroaziridine versus 1,1-product as a function of substituent. For the *m*-CF_3 and *p*-CF_3 derivatives, the reactions were completely selective (>99:1) for the fluoroaziridine. The points on the plot depict the lower boundaries for the value of log ([fluoroaziridine]/[1,1-product]).

^{19}F NMR
145.7 Hz
$CDCl_3$

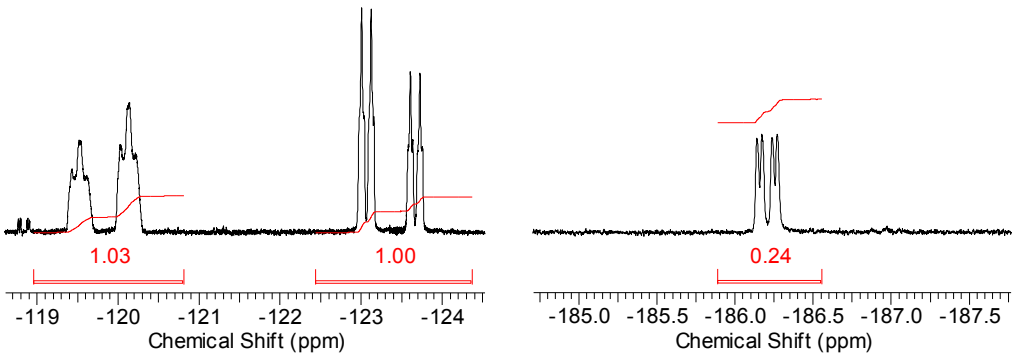
R = H:



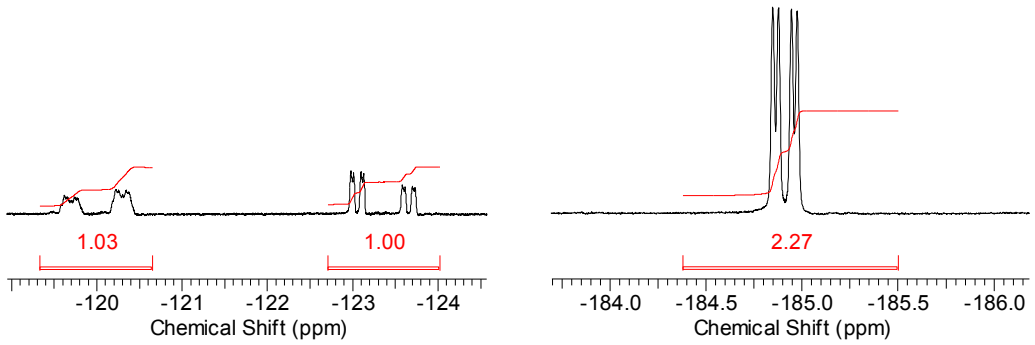
R = *p*-Cl:



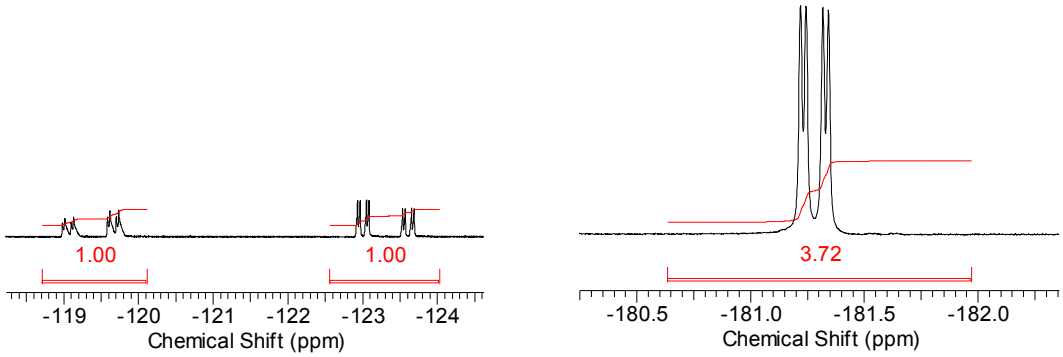
R = *p*-Br



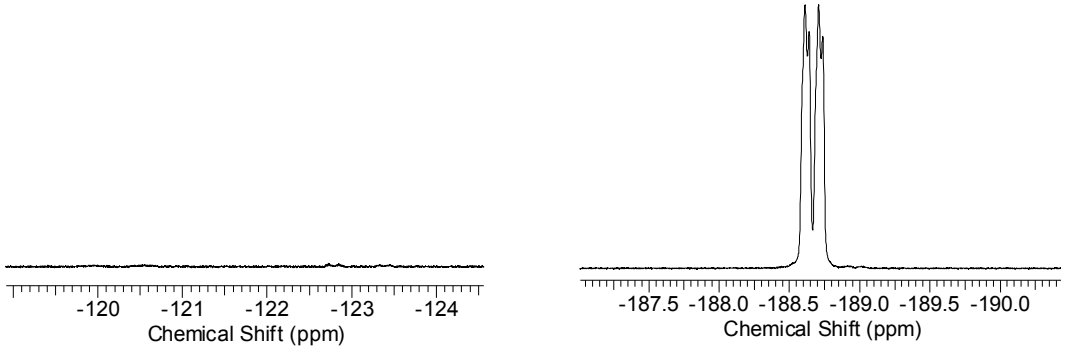
R = *m*-F



R = *m*-Br

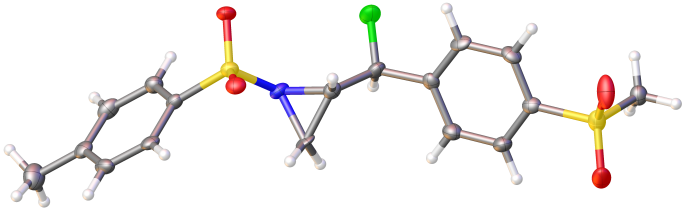


R = *m*-CF_3



X-ray Crystallography Information.

X-Ray Crystallographic Information Data for 3b



X-Ray Crystallography: A crystal mounted on a diffractometer was collected data at 100 K. The intensities of the reflections were collected by means of a Bruker APEX II CCD diffractometer ($Mo_{K\alpha}$ radiation, λ=0.71073 Å), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 0.5° scans in ω at 28° in 2θ. Data integration down to 0.84 Å resolution was carried out using SAINT V8.37A with reflection spot size optimization.[11] Absorption corrections were made with the program TWINABS. The structure was solved by the Intrinsic Phasing methods and refined by least-squares methods again F^2 using SHELXT-2014[12] and SHELXL-2014[13] with OLEX 2 interface.[14] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table S3, and geometric parameters are shown in Table S4. The Ortep plots produced with SHELXL-2014 program, and the other drawings were produced with Accelrys DS Visualizer 2.0.[15]

Table S3. Experimental details

Crystal data	
Chemical formula	$C_{17}H_{18}FNO_4S_2$
M_r	383.44
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	100
a, b, c (Å)	5.5270 (4), 8.6617 (6), 36.032 (3)
V (Å^3)	1725.0 (2)
Z	4
Radiation type	Mo Ka
m (mm^{-1})	0.34
Crystal size (mm)	0.10 × 0.02 × 0.01
Data collection	
Diffractometer	Bruker D8 goniometer with CCD area detector
Absorption correction	Multi-scan *SADABS*

T_{min}, T_{max}	0.833, 0.862
No. of measured, independent and observed [$I > 2s(I)$] reflections	29926, 3065, 2507
R_{int}	0.130
$(\sin q/l)_{max}$ (Å^{-1})	0.596
Refinement	
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, S	0.068, 0.129, 1.17
No. of reflections	3065
No. of parameters	228
H-atom treatment	H-atom parameters constrained
$D\rho_{max}$, $D\rho_{min}$ (e Å^{-3})	0.36, -0.45
Absolute structure	Flack x determined using 795 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	0.11 (8)

Computer programs: *APEX3* v2016.9-0 (Bruker-AXS, 2016), *SAINT* 8.37A (Bruker-AXS, 2015), *SHELXT2014* (Sheldrick, 2015), *SHELXL2014* (Sheldrick, 2015), Bruker *SHELXTL* (Sheldrick, 2015).

Table S4. Geometric parameters (Å, º)

S1—O2	1.428 (5)	C6—H6	0.9500
S1—O1	1.434 (5)	C7—C8	1.379 (9)
S1—N1	1.659 (6)	C8—C9	1.389 (9)
S1—C10	1.743 (7)	C8—H8	0.9500
S2—O3	1.428 (6)	C9—H9	0.9500
S2—O4	1.438 (6)	C10—C15	1.387 (9)
S2—C17	1.737 (7)	C10—C11	1.391 (10)
S2—C7	1.779 (7)	C11—C12	1.382 (10)
F1—C3	1.410 (7)	C11—H11	0.9500
N1—C1	1.481 (8)	C12—C13	1.375 (10)
N1—C2	1.482 (8)	C12—H12	0.9500
C1—C2	1.480 (9)	C13—C14	1.395 (10)
C1—H1A	0.9900	C13—C16	1.506 (10)
C1—H1B	0.9900	C14—C15	1.384 (9)
C2—C3	1.504 (9)	C14—H14	0.9500
C2—H2	1.0000	C15—H15	0.9500

C3—C4	1.505 (10)	C16—H16A	0.9800
C3—H3	1.0000	C16—H16B	0.9800
C4—C5	1.381 (10)	C16—H16C	0.9800
C4—C9	1.383 (9)	C17—H17A	0.9800
C5—C6	1.384 (10)	C17—H17B	0.9800
C5—H5	0.9500	C17—H17C	0.9800
C6—C7	1.378 (9)		
O2—S1—O1	117.8 (3)	C5—C6—H6	120.7
O2—S1—N1	111.7 (3)	C6—C7—C8	121.5 (6)
O1—S1—N1	104.8 (3)	C6—C7—S2	118.7 (5)
O2—S1—C10	109.0 (3)	C8—C7—S2	119.7 (5)
O1—S1—C10	109.6 (3)	C7—C8—C9	118.9 (6)
N1—S1—C10	102.8 (3)	C7—C8—H8	120.6
O3—S2—O4	119.7 (4)	C9—C8—H8	120.6
O3—S2—C17	107.9 (4)	C4—C9—C8	120.7 (6)
O4—S2—C17	109.1 (4)	C4—C9—H9	119.6
O3—S2—C7	107.8 (3)	C8—C9—H9	119.6
O4—S2—C7	107.0 (3)	C15—C10—C11	120.3 (7)
C17—S2—C7	104.2 (3)	C15—C10—S1	120.0 (5)
C1—N1—C2	59.9 (4)	C11—C10—S1	119.6 (5)
C1—N1—S1	117.3 (5)	C12—C11—C10	118.7 (7)
C2—N1—S1	114.1 (4)	C12—C11—H11	120.6
C2—C1—N1	60.1 (4)	C10—C11—H11	120.6
C2—C1—H1A	117.8	C13—C12—C11	122.3 (7)
N1—C1—H1A	117.8	C13—C12—H12	118.8
C2—C1—H1B	117.8	C11—C12—H12	118.8
N1—C1—H1B	117.8	C12—C13—C14	118.1 (7)
H1A—C1—H1B	114.9	C12—C13—C16	122.7 (7)
C1—C2—N1	60.0 (4)	C14—C13—C16	119.2 (7)
C1—C2—C3	121.2 (6)	C15—C14—C13	121.0 (7)
N1—C2—C3	113.4 (6)	C15—C14—H14	119.5
C1—C2—H2	116.5	C13—C14—H14	119.5
N1—C2—H2	116.5	C14—C15—C10	119.6 (7)
C3—C2—H2	116.5	C14—C15—H15	120.2

F1—C3—C2	106.8 (5)	C10—C15—H15	120.2
F1—C3—C4	108.3 (6)	C13—C16—H16A	109.5
C2—C3—C4	113.2 (6)	C13—C16—H16B	109.5
F1—C3—H3	109.4	H16A—C16—H16B	109.5
C2—C3—H3	109.4	C13—C16—H16C	109.5
C4—C3—H3	109.4	H16A—C16—H16C	109.5
C5—C4—C9	119.0 (6)	H16B—C16—H16C	109.5
C5—C4—C3	118.7 (6)	S2—C17—H17A	109.5
C9—C4—C3	122.3 (6)	S2—C17—H17B	109.5
C4—C5—C6	121.4 (7)	H17A—C17—H17B	109.5
C4—C5—H5	119.3	S2—C17—H17C	109.5
C6—C5—H5	119.3	H17A—C17—H17C	109.5
C7—C6—C5	118.5 (7)	H17B—C17—H17C	109.5
C7—C6—H6	120.7		
O2—S1—N1—C1	30.2 (6)	C17—S2—C7—C6	99.6 (6)
O1—S1—N1—C1	158.9 (5)	O3—S2—C7—C8	34.4 (6)
C10—S1—N1—C1	-86.5 (5)	O4—S2—C7—C8	164.4 (5)
O2—S1—N1—C2	-37.0 (5)	C17—S2—C7—C8	-80.1 (6)
O1—S1—N1—C2	91.6 (5)	C6—C7—C8—C9	-1.0 (10)
C10—S1—N1—C2	-153.8 (5)	S2—C7—C8—C9	178.7 (6)
S1—N1—C1—C2	-103.4 (5)	C5—C4—C9—C8	0.1 (10)
N1—C1—C2—C3	-100.8 (7)	C3—C4—C9—C8	-179.1 (6)
S1—N1—C2—C1	108.8 (5)	C7—C8—C9—C4	0.4 (10)
C1—N1—C2—C3	113.7 (6)	O2—S1—C10—C15	-10.4 (6)
S1—N1—C2—C3	-137.5 (5)	O1—S1—C10—C15	-140.6 (5)
C1—C2—C3—F1	142.5 (6)	N1—S1—C10—C15	108.3 (6)
N1—C2—C3—F1	74.5 (7)	O2—S1—C10—C11	167.2 (5)
C1—C2—C3—C4	-98.4 (7)	O1—S1—C10—C11	36.9 (7)
N1—C2—C3—C4	-166.4 (6)	N1—S1—C10—C11	-74.1 (6)
F1—C3—C4—C5	-162.0 (6)	C15—C10—C11—C12	0.7 (10)
C2—C3—C4—C5	79.7 (8)	S1—C10—C11—C12	-176.9 (5)
F1—C3—C4—C9	17.3 (9)	C10—C11—C12—C13	-0.2 (11)

C2—C3—C4—C9	-101.1 (7)	C11—C12—C13—C14	-0.3 (10)
C9—C4—C5—C6	0.0 (10)	C11—C12—C13—C16	-179.8 (7)
C3—C4—C5—C6	179.2 (7)	C12—C13—C14—C15	0.4 (10)
C4—C5—C6—C7	-0.6 (11)	C16—C13—C14—C15	179.9 (6)
C5—C6—C7—C8	1.1 (10)	C13—C14—C15—C10	0.1 (10)
C5—C6—C7—S2	-178.6 (5)	C11—C10—C15—C14	-0.6 (10)
O3—S2—C7—C6	-145.9 (6)	S1—C10—C15—C14	176.9 (5)
O4—S2—C7—C6	-15.8 (7)		

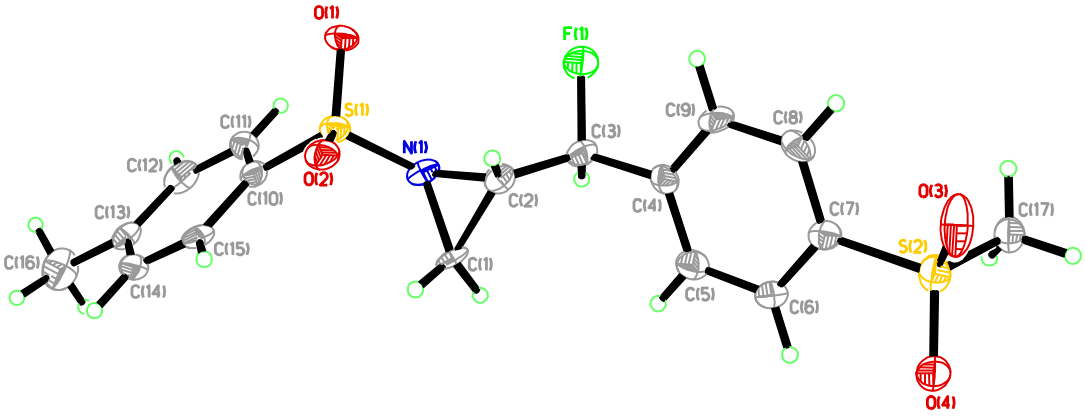


Figure S2. Perspective views showing 50% probability displacement

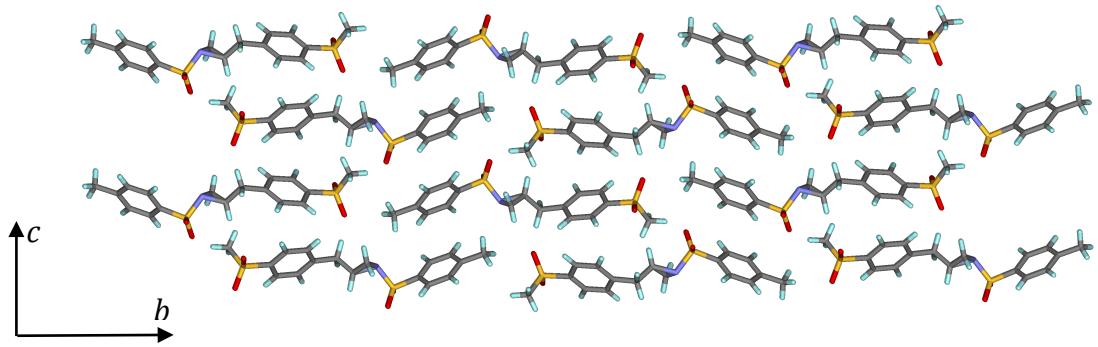
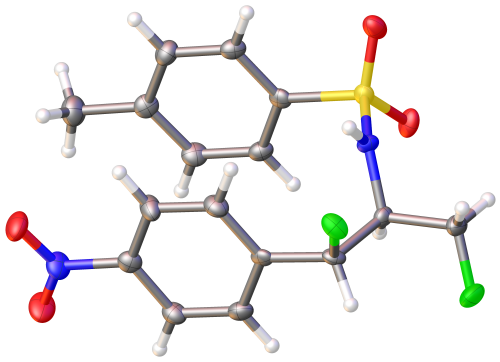


Figure S3. Three-dimensional supramolecular architecture viewed along the *a*-axis direction.

X-Ray Crystallographic Information Data for 4a



X-ray Crystallography: A crystal mounted on a diffractometer was collected data at 100 K. The intensities of the reflections were collected by means of a Bruker APEX II DUO CCD diffractometer ($Cu_{K\alpha}$ radiation, λ=1.54178 Å), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 1.0° scans in *ω* at -30°, -55°, -80°, 30°, 55°, 80° and 115° in *2θ*. Data integration down to 0.84 Å resolution was carried out using SAINT V8.37 A with reflection spot size optimization.[11] Absorption corrections were made with the program SADABS. The structure was solved by the Intrinsic Phasing methods and refined by least-squares methods again F^2 using SHELXT-2014[9] and SHELXL-2014[13] with OLEX 2 interface.[14] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table S5, geometric parameters are shown in Table S6 and hydrogen-bond parameters are listed in Table S7. The Ortep plots produced with SHELXL-2014 program, and the other drawings were produced with Accelrys DS Visualizer 2.0.[15]

Table S5. Experimental details

Crystal data	
Chemical formula	$C_{16}H_{16}F_2N_2O_4S$
M_r	370.37
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	100
a, *b*, *c* (Å)	13.7281 (5), 7.7633 (3), 15.1716 (5)
b (°)	96.176 (2)
V (Å^3)	1607.53 (10)
Z	4
Radiation type	Cu *K*a
m (mm^{-1})	2.23
Crystal size (mm)	0.24 × 0.10 × 0.01

Data collection	
Diffractometer	Bruker D8 goniometer with CCD area detector
Absorption correction	Multi-scan *SADABS*
T_{min}, T_{max}	0.815, 0.864
No. of measured, independent and observed [$I > 2s(I)$] reflections	27659, 5129, 4476
R_{int}	0.085
$(\sin q/l)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, S	0.064, 0.174, 1.14
No. of reflections	5129
No. of parameters	455
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$D\rho_{max}$, $D\rho_{min}$ (e Å^{-3})	0.46, -0.64
Absolute structure	Flack x determined using 1569 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	0.01 (3)

Computer programs: *APEX3* v2016.1-0 (Bruker-AXS, 2016), *SAINT* 8.37A (Bruker-AXS, 2015), *SHELXT2014* (Sheldrick, 2015), *SHELXL2014* (Sheldrick, 2015), Bruker *SHELXTL* (Sheldrick, 2015).

Table S6. Geometric parameters (Å, º)

S1—O3	1.425 (5)	S2—O7	1.431 (5)
S1—O4	1.432 (4)	S2—O8	1.438 (4)
S1—N2	1.606 (6)	S2—N4	1.618 (6)
S1—C10	1.762 (7)	S2—C30	1.778 (7)
F1—C7	1.418 (6)	F3—C27	1.414 (6)
F2—C9	1.410 (8)	F4—C29	1.395 (9)
O1—N1	1.245 (7)	O5—N3	1.233 (7)
O2—N1	1.223 (7)	O6—N3	1.228 (7)
N1—C3	1.463 (9)	N3—C23	1.468 (9)
N2—C8	1.463 (8)	N4—C28	1.456 (9)

N2—H2	0.8698	N4—H4A	0.8575
C1—C2	1.372 (10)	C21—C22	1.381 (10)
C1—C6	1.393 (9)	C21—C26	1.395 (9)
C1—H1	0.9500	C21—H21	0.9500
C2—C3	1.379 (9)	C22—C23	1.382 (9)
C2—H2A	0.9500	C22—H22	0.9500
C3—C4	1.392 (9)	C23—C24	1.387 (9)
C4—C5	1.379 (10)	C24—C25	1.370 (9)
C4—H4	0.9500	C24—H24	0.9500
C5—C6	1.410 (9)	C25—C26	1.401 (9)
C5—H5	0.9500	C25—H25	0.9500
C6—C7	1.499 (9)	C26—C27	1.500 (10)
C7—C8	1.507 (10)	C27—C28	1.525 (9)
C7—H7	1.0000	C27—H27	1.0000
C8—C9	1.524 (9)	C28—C29	1.522 (9)
C8—H8	1.0000	C28—H28	1.0000
C9—H9A	0.9900	C29—H29A	0.9900
C9—H9B	0.9900	C29—H29B	0.9900
C10—C15	1.395 (9)	C30—C31	1.387 (9)
C10—C11	1.397 (9)	C30—C35	1.392 (9)
C11—C12	1.378 (10)	C31—C32	1.383 (10)
C11—H11	0.9500	C31—H31	0.9500
C12—C13	1.401 (9)	C32—C33	1.392 (10)
C12—H12	0.9500	C32—H32	0.9500
C13—C14	1.397 (9)	C33—C34	1.400 (10)
C13—C16	1.511 (10)	C33—C36	1.507 (10)
C14—C15	1.371 (10)	C34—C35	1.367 (10)
C14—H14	0.9500	C34—H34	0.9500
C15—H15	0.9500	C35—H35	0.9500
C16—H16A	0.9800	C36—H36A	0.9800
C16—H16B	0.9800	C36—H36B	0.9800
C16—H16C	0.9800	C36—H36C	0.9800
O3—S1—O4	120.2 (3)	O7—S2—O8	119.8 (3)
O3—S1—N2	106.4 (3)	O7—S2—N4	107.1 (3)

O4—S1—N2	106.4 (3)	O8—S2—N4	106.0 (3)
O3—S1—C10	107.5 (3)	O7—S2—C30	107.4 (3)
O4—S1—C10	108.0 (3)	O8—S2—C30	107.7 (3)
N2—S1—C10	107.8 (3)	N4—S2—C30	108.5 (3)
O2—N1—O1	123.3 (6)	O6—N3—O5	123.2 (6)
O2—N1—C3	118.5 (5)	O6—N3—C23	119.4 (6)
O1—N1—C3	118.3 (5)	O5—N3—C23	117.4 (5)
C8—N2—S1	124.7 (4)	C28—N4—S2	124.3 (4)
C8—N2—H2	117.9	C28—N4—H4A	130.9
S1—N2—H2	115.4	S2—N4—H4A	104.3
C2—C1—C6	120.7 (6)	C22—C21—C26	120.0 (6)
C2—C1—H1	119.7	C22—C21—H21	120.0
C6—C1—H1	119.7	C26—C21—H21	120.0
C1—C2—C3	119.0 (6)	C21—C22—C23	118.4 (6)
C1—C2—H2A	120.5	C21—C22—H22	120.8
C3—C2—H2A	120.5	C23—C22—H22	120.8
C2—C3—C4	122.2 (6)	C22—C23—C24	122.9 (7)
C2—C3—N1	118.5 (6)	C22—C23—N3	118.7 (6)
C4—C3—N1	119.2 (6)	C24—C23—N3	118.3 (6)
C5—C4—C3	118.4 (6)	C25—C24—C23	118.3 (6)
C5—C4—H4	120.8	C25—C24—H24	120.8
C3—C4—H4	120.8	C23—C24—H24	120.8
C4—C5—C6	120.3 (6)	C24—C25—C26	120.3 (6)
C4—C5—H5	119.9	C24—C25—H25	119.8
C6—C5—H5	119.9	C26—C25—H25	119.8
C1—C6—C5	119.3 (6)	C21—C26—C25	120.1 (7)
C1—C6—C7	121.5 (5)	C21—C26—C27	121.0 (6)
C5—C6—C7	119.2 (6)	C25—C26—C27	118.8 (6)
F1—C7—C6	108.4 (5)	F3—C27—C26	109.2 (5)
F1—C7—C8	106.1 (5)	F3—C27—C28	106.1 (5)
C6—C7—C8	115.0 (6)	C26—C27—C28	113.9 (6)
F1—C7—H7	109.1	F3—C27—H27	109.2
C6—C7—H7	109.1	C26—C27—H27	109.2
C8—C7—H7	109.1	C28—C27—H27	109.2
N2—C8—C7	111.2 (5)	N4—C28—C29	108.1 (6)

N2—C8—C9	107.3 (5)	N4—C28—C27	110.1 (5)
C7—C8—C9	112.1 (6)	C29—C28—C27	112.2 (6)
N2—C8—H8	108.7	N4—C28—H28	108.8
C7—C8—H8	108.7	C29—C28—H28	108.8
C9—C8—H8	108.7	C27—C28—H28	108.8
F2—C9—C8	107.7 (5)	F4—C29—C28	108.5 (6)
F2—C9—H9A	110.2	F4—C29—H29A	110.0
C8—C9—H9A	110.2	C28—C29—H29A	110.0
F2—C9—H9B	110.2	F4—C29—H29B	110.0
C8—C9—H9B	110.2	C28—C29—H29B	110.0
H9A—C9—H9B	108.5	H29A—C29—H29B	108.4
C15—C10—C11	120.2 (6)	C31—C30—C35	121.3 (6)
C15—C10—S1	120.5 (5)	C31—C30—S2	118.6 (5)
C11—C10—S1	119.2 (5)	C35—C30—S2	120.0 (5)
C12—C11—C10	120.0 (6)	C32—C31—C30	118.5 (6)
C12—C11—H11	120.0	C32—C31—H31	120.7
C10—C11—H11	120.0	C30—C31—H31	120.7
C11—C12—C13	120.3 (6)	C31—C32—C33	121.7 (6)
C11—C12—H12	119.8	C31—C32—H32	119.2
C13—C12—H12	119.8	C33—C32—H32	119.2
C14—C13—C12	118.7 (6)	C32—C33—C34	117.8 (7)
C14—C13—C16	120.8 (6)	C32—C33—C36	121.1 (7)
C12—C13—C16	120.5 (6)	C34—C33—C36	121.1 (7)
C15—C14—C13	121.6 (6)	C35—C34—C33	121.8 (6)
C15—C14—H14	119.2	C35—C34—H34	119.1
C13—C14—H14	119.2	C33—C34—H34	119.1
C14—C15—C10	119.2 (6)	C34—C35—C30	118.8 (6)
C14—C15—H15	120.4	C34—C35—H35	120.6
C10—C15—H15	120.4	C30—C35—H35	120.6
C13—C16—H16A	109.5	C33—C36—H36A	109.5
C13—C16—H16B	109.5	C33—C36—H36B	109.5
H16A—C16—H16B	109.5	H36A—C36—H36B	109.5
C13—C16—H16C	109.5	C33—C36—H36C	109.5
H16A—C16—H16C	109.5	H36A—C36—H36C	109.5
H16B—C16—H16C	109.5	H36B—C36—H36C	109.5

O3—S1—N2—C8	-157.7 (5)	O7—S2—N4—C28	-149.4 (5)
O4—S1—N2—C8	-28.4 (6)	O8—S2—N4—C28	-20.4 (6)
C10—S1—N2—C8	87.3 (6)	C30—S2—N4—C28	95.0 (6)
C6—C1—C2—C3	0.7 (11)	C26—C21—C22—C23	1.0 (11)
C1—C2—C3—C4	-2.8 (11)	C21—C22—C23—C24	-1.0 (12)
C1—C2—C3—N1	175.8 (6)	C21—C22—C23—N3	-178.0 (6)
O2—N1—C3—C2	169.3 (7)	O6—N3—C23—C22	163.0 (8)
O1—N1—C3—C2	-10.8 (10)	O5—N3—C23—C22	-18.4 (11)
O2—N1—C3—C4	-12.1 (10)	O6—N3—C23—C24	-14.1 (11)
O1—N1—C3—C4	167.8 (7)	O5—N3—C23—C24	164.4 (7)
C2—C3—C4—C5	2.5 (11)	C22—C23—C24—C25	0.3 (12)
N1—C3—C4—C5	-176.0 (6)	N3—C23—C24—C25	177.3 (7)
C3—C4—C5—C6	-0.3 (11)	C23—C24—C25—C26	0.3 (11)
C2—C1—C6—C5	1.5 (10)	C22—C21—C26—C25	-0.4 (11)
C2—C1—C6—C7	-179.4 (6)	C22—C21—C26—C27	179.0 (7)
C4—C5—C6—C1	-1.7 (10)	C24—C25—C26—C21	-0.3 (11)
C4—C5—C6—C7	179.2 (6)	C24—C25—C26—C27	-179.7 (7)
C1—C6—C7—F1	32.5 (9)	C21—C26—C27—F3	24.0 (9)
C5—C6—C7—F1	-148.4 (6)	C25—C26—C27—F3	-156.6 (6)
C1—C6—C7—C8	-86.0 (7)	C21—C26—C27—C28	-94.4 (7)
C5—C6—C7—C8	93.1 (7)	C25—C26—C27—C28	85.0 (8)
S1—N2—C8—C7	-133.3 (5)	S2—N4—C28—C29	104.5 (6)
S1—N2—C8—C9	103.8 (6)	S2—N4—C28—C27	-132.7 (5)
F1—C7—C8—N2	-52.4 (7)	F3—C27—C28—N4	-54.6 (7)
C6—C7—C8—N2	67.3 (6)	C26—C27—C28—N4	65.6 (7)
F1—C7—C8—C9	67.7 (6)	F3—C27—C28—C29	65.8 (7)
C6—C7—C8—C9	-172.5 (5)	C26—C27—C28—	-174.0 (5)

		C29	
N2—C8—C9—F2	-179.7 (5)	N4—C28—C29—F4	-177.2 (5)
C7—C8—C9—F2	57.9 (6)	C27—C28—C29—F4	61.2 (7)
O3—S1—C10—C15	162.7 (6)	O7—S2—C30—C31	-21.2 (6)
O4—S1—C10—C15	31.6 (7)	O8—S2—C30—C31	-151.5 (5)
N2—S1—C10—C15	-83.0 (6)	N4—S2—C30—C31	94.2 (6)
O3—S1—C10—C11	-18.9 (6)	O7—S2—C30—C35	158.6 (5)
O4—S1—C10—C11	-150.0 (5)	O8—S2—C30—C35	28.3 (7)
N2—S1—C10—C11	95.4 (6)	N4—S2—C30—C35	-86.0 (6)
C15—C10—C11—C12	1.0 (10)	C35—C30—C31—C32	-1.1 (10)
S1—C10—C11—C12	-177.3 (5)	S2—C30—C31—C32	178.7 (5)
C10—C11—C12—C13	-0.2 (10)	C30—C31—C32—C33	0.1 (11)
C11—C12—C13—C14	-0.4 (11)	C31—C32—C33—C34	0.5 (11)
C11—C12—C13—C16	179.4 (7)	C31—C32—C33—C36	-178.1 (7)
C12—C13—C14—C15	0.1 (11)	C32—C33—C34—C35	-0.1 (11)
C16—C13—C14—C15	-179.7 (7)	C36—C33—C34—C35	178.4 (7)
C13—C14—C15—C10	0.7 (11)	C33—C34—C35—C30	-0.8 (11)
C11—C10—C15—C14	-1.3 (10)	C31—C30—C35—C34	1.4 (11)
S1—C10—C15—C14	177.0 (5)	S2—C30—C35—C34	-178.4 (6)

Table S7. Hydrogen-bond parameters

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
N2—H2···O8	0.87	2.13	2.968 (6)	161.7
N4—H4A···O1^{i}	0.86	2.24	3.086 (7)	171.4

Symmetry code(s): (i) -*x*+1, *y*+1/2, -*z*.

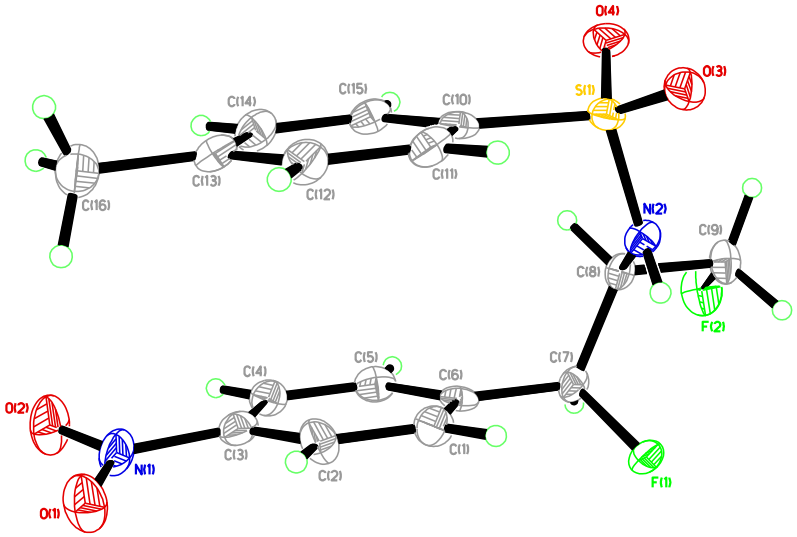


Figure S4. Perspective views showing 50% probability displacement

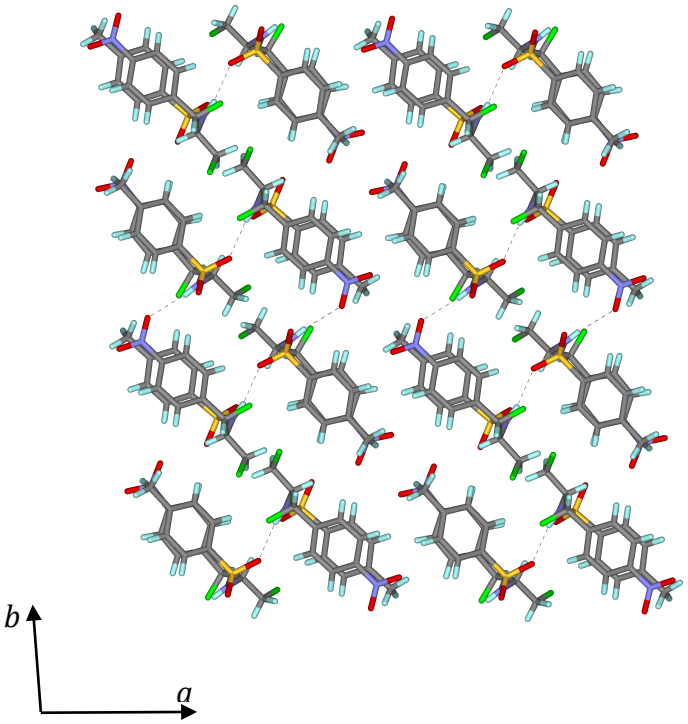
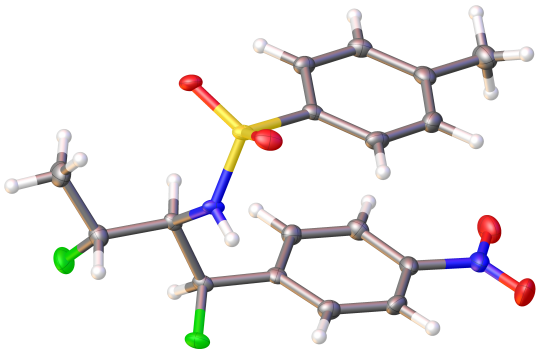


Figure S5. Three-dimensional supramolecular architecture viewed along the *c*-axis direction.

X-Ray Crystallographic Information Data for 6a*(anti)*



X-ray Crystallography: A crystal mounted on a diffractometer was collected data at 100 K. The intensities of the reflections were collected by means of a Bruker APEX II CCD diffractometer ($Mo_{K\alpha}$ radiation, λ=0.71073 Å), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 0.5° scans in ω at 28° in 2θ. Data integration down to 0.78 Å resolution was carried out using SAINT V8.37A with reflection spot size optimization.[11] Absorption corrections were made with the program SADABS. The structure was solved by the Intrinsic Phasing methods and refined by least-squares methods again F^2 using SHELXT-2014[9] and SHELXL-2014[13] with OLEX 2 interface.[14] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table S8, geometric parameters are shown in Table S9 and hydrogen-bond parameters are listed in Table S10. The Ortep plots produced with SHELXL-2014 program, and the other drawings were produced with Accelrys DS Visualizer 2.0.[15]

Table S8. Experimental details

Crystal data	
Chemical formula	$C_{17}H_{18}F_2N_2O_4S$
M_r	384.39
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	100
a, b, c (Å)	7.5617 (3), 9.7752 (5), 23.9131 (10)
V (Å^3)	1767.59 (14)
Z	4
Radiation type	Mo Ka
m (mm^{-1})	0.23
Crystal size (mm)	0.18 × 0.14 × 0.10
Data collection	
Diffractometer	Bruker D8 goniometer with CCD area detector

Absorption correction	Multi-scan *SADABS*
T_{min}, T_{max}	0.809, 0.862
No. of measured, independent and observed [$I > 2s(I)$] reflections	22510, 3906, 3600
R_{int}	0.032
$(\sin q/l)_{max}$ (Å^{-1})	0.642
Refinement	
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, S	0.032, 0.075, 1.06
No. of reflections	3906
No. of parameters	241
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$D\rho_{max}$, $D\rho_{min}$ (e Å^{-3})	0.33, -0.33
Absolute structure	Flack x determined using 1437 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	-0.01 (2)

Computer programs: *APEX3* v2016.9-0 (Bruker-AXS, 2016), *SAINT* 8.37A (Bruker-AXS, 2015), *SHELXT2014* (Sheldrick, 2015), *SHELXL2014* (Sheldrick, 2015), Bruker *SHELXTL* (Sheldrick, 2015).

Table S9. Geometric parameters (Å, º)

S1—O3	1.4320 (17)	C7—H7	1.0000
S1—O4	1.4388 (16)	C8—C9	1.534 (3)
S1—N2	1.6108 (18)	C8—H8	1.0000
S1—C11	1.765 (2)	C9—C10	1.505 (3)
F1—C7	1.415 (2)	C9—H9	1.0000
F2—C9	1.405 (3)	C10—H10A	0.9800
O1—N1	1.229 (3)	C10—H10B	0.9800
O2—N1	1.228 (3)	C10—H10C	0.9800
N1—C3	1.469 (3)	C11—C12	1.392 (3)
N2—C8	1.453 (3)	C11—C16	1.393 (3)
N2—H2	0.83 (3)	C12—C13	1.383 (4)
C1—C2	1.374 (3)	C12—H12	0.9500
C1—C6	1.397 (3)	C13—C14	1.395 (4)

C1—H1	0.9500	C13—H13	0.9500
C2—C3	1.385 (3)	C14—C15	1.395 (3)
C2—H2A	0.9500	C14—C17	1.509 (4)
C3—C4	1.378 (4)	C15—C16	1.387 (3)
C4—C5	1.389 (3)	C15—H15	0.9500
C4—H4	0.9500	C16—H16	0.9500
C5—C6	1.389 (3)	C17—H17A	0.9800
C5—H5	0.9500	C17—H17B	0.9800
C6—C7	1.504 (3)	C17—H17C	0.9800
C7—C8	1.528 (3)		
O3—S1—O4	119.99 (10)	N2—C8—H8	108.8
O3—S1—N2	104.82 (10)	C7—C8—H8	108.8
O4—S1—N2	107.62 (10)	C9—C8—H8	108.8
O3—S1—C11	108.22 (11)	F2—C9—C10	108.1 (2)
O4—S1—C11	106.10 (10)	F2—C9—C8	107.10 (18)
N2—S1—C11	109.91 (10)	C10—C9—C8	115.0 (2)
O2—N1—O1	123.5 (2)	F2—C9—H9	108.8
O2—N1—C3	118.2 (2)	C10—C9—H9	108.8
O1—N1—C3	118.3 (2)	C8—C9—H9	108.8
C8—N2—S1	124.67 (15)	C9—C10—H10A	109.5
C8—N2—H2	119.2 (19)	C9—C10—H10B	109.5
S1—N2—H2	114.0 (18)	H10A—C10—H10B	109.5
C2—C1—C6	120.3 (2)	C9—C10—H10C	109.5
C2—C1—H1	119.9	H10A—C10—H10C	109.5
C6—C1—H1	119.9	H10B—C10—H10C	109.5
C1—C2—C3	118.5 (2)	C12—C11—C16	120.8 (2)
C1—C2—H2A	120.8	C12—C11—S1	119.42 (17)
C3—C2—H2A	120.8	C16—C11—S1	119.73 (18)
C4—C3—C2	122.7 (2)	C13—C12—C11	119.1 (2)
C4—C3—N1	119.0 (2)	C13—C12—H12	120.5
C2—C3—N1	118.2 (2)	C11—C12—H12	120.5
C3—C4—C5	118.2 (2)	C12—C13—C14	121.4 (2)
C3—C4—H4	120.9	C12—C13—H13	119.3
C5—C4—H4	120.9	C14—C13—H13	119.3

C4—C5—C6	120.2 (2)	C15—C14—C13	118.6 (2)
C4—C5—H5	119.9	C15—C14—C17	120.5 (2)
C6—C5—H5	119.9	C13—C14—C17	120.9 (2)
C5—C6—C1	120.0 (2)	C16—C15—C14	121.0 (2)
C5—C6—C7	121.7 (2)	C16—C15—H15	119.5
C1—C6—C7	118.2 (2)	C14—C15—H15	119.5
F1—C7—C6	108.65 (18)	C15—C16—C11	119.2 (2)
F1—C7—C8	106.70 (17)	C15—C16—H16	120.4
C6—C7—C8	114.91 (18)	C11—C16—H16	120.4
F1—C7—H7	108.8	C14—C17—H17A	109.5
C6—C7—H7	108.8	C14—C17—H17B	109.5
C8—C7—H7	108.8	H17A—C17—H17B	109.5
N2—C8—C7	110.47 (18)	C14—C17—H17C	109.5
N2—C8—C9	108.84 (18)	H17A—C17—H17C	109.5
C7—C8—C9	110.97 (18)	H17B—C17—H17C	109.5
O3—S1—N2—C8	170.18 (18)	C6—C7—C8—N2	-57.0 (2)
O4—S1—N2—C8	41.4 (2)	F1—C7—C8—C9	-57.3 (2)
C11—S1—N2—C8	-73.7 (2)	C6—C7—C8—C9	-177.83 (19)
C6—C1—C2—C3	-0.3 (4)	N2—C8—C9—F2	-170.71 (18)
C1—C2—C3—C4	-1.6 (4)	C7—C8—C9—F2	-48.9 (2)
C1—C2—C3—N1	178.0 (2)	N2—C8—C9—C10	69.1 (2)
O2—N1—C3—C4	-2.6 (3)	C7—C8—C9—C10	-169.1 (2)
O1—N1—C3—C4	177.1 (2)	O3—S1—C11—C12	35.1 (2)
O2—N1—C3—C2	177.8 (2)	O4—S1—C11—C12	165.13 (18)
O1—N1—C3—C2	-2.5 (3)	N2—S1—C11—C12	-78.8 (2)
C2—C3—C4—C5	1.8 (4)	O3—S1—C11—C16	-142.08 (18)
N1—C3—C4—C5	-177.8 (2)	O4—S1—C11—C16	-12.1 (2)
C3—C4—C5—C6	-0.1 (4)	N2—S1—C11—C16	103.99 (19)
C4—C5—C6—C1	-1.8 (4)	C16—C11—C12—C13	-0.2 (3)
C4—C5—C6—C7	175.9 (2)	S1—C11—C12—C13	-177.43 (19)
C2—C1—C6—C5	2.0 (4)	C11—C12—C13—C14	-0.2 (4)
C2—C1—C6—C7	-175.8 (2)	C12—C13—C14—C15	0.3 (4)

C5—C6—C7—F1	-14.4 (3)	C12—C13—C14—C17	-178.7 (2)
C1—C6—C7—F1	163.30 (19)	C13—C14—C15—C16	0.0 (4)
C5—C6—C7—C8	105.0 (2)	C17—C14—C15—C16	179.0 (2)
C1—C6—C7—C8	-77.3 (3)	C14—C15—C16—C11	-0.4 (3)
S1—N2—C8—C7	129.16 (18)	C12—C11—C16—C15	0.6 (3)
S1—N2—C8—C9	-108.77 (19)	S1—C11—C16—C15	177.74 (18)
F1—C7—C8—N2	63.5 (2)		

Table S10. Hydrogen-bond parameters

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
N2—H2···O4^{i}	0.83 (3)	2.08 (3)	2.903 (2)	169 (3)

Symmetry code(s): (i) -*x*+1, *y*+1/2, -*z*+1/2.

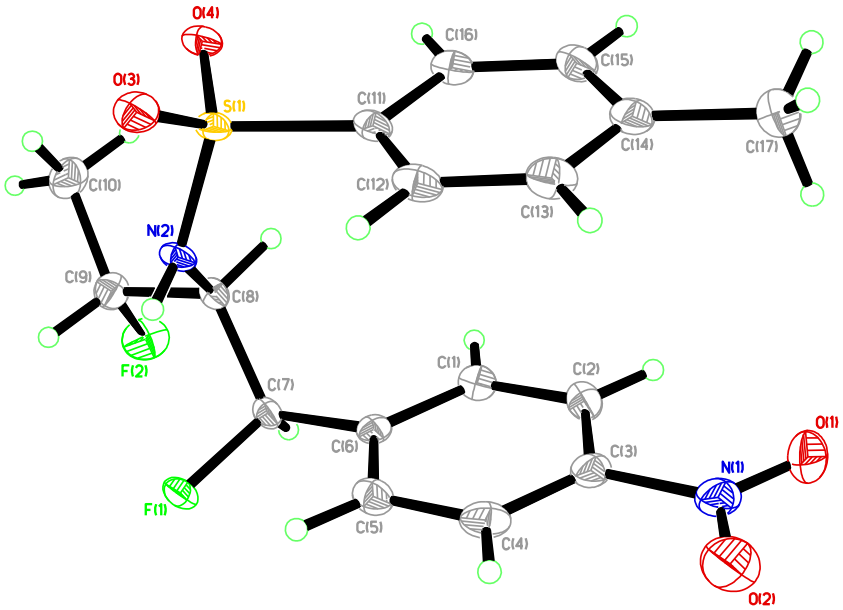


Figure S6. Perspective views showing 50% probability displacement

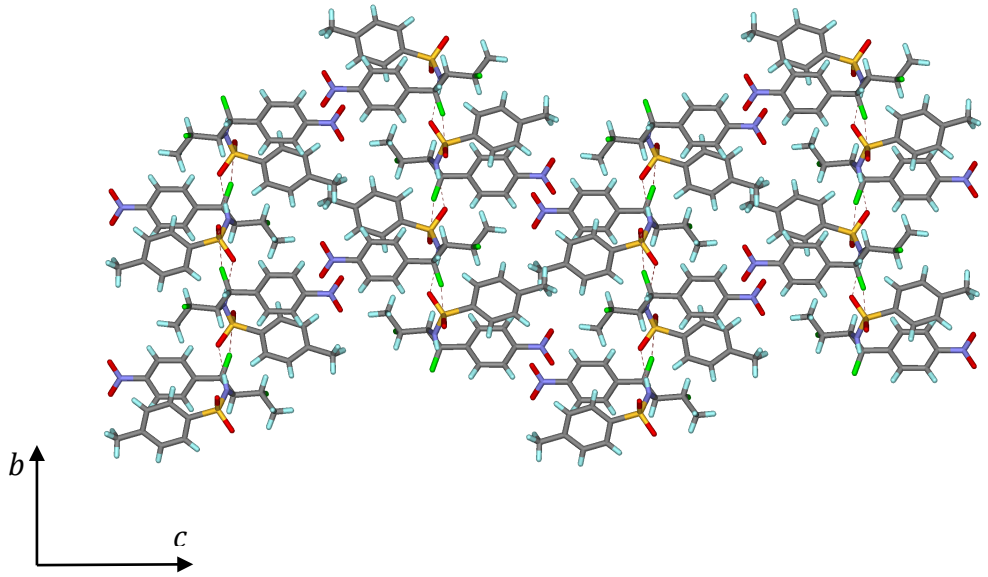
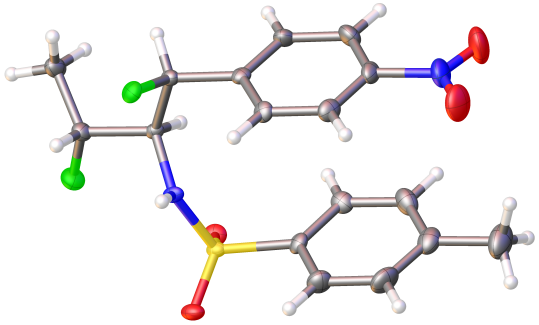


Figure S7. Three-dimensional supramolecular architecture viewed along the *a*-axis direction.

X-Ray Crystallographic Information Data for 6a*(syn)*



X-ray Crystallography: A crystal mounted on a diffractometer was collected data at 100 K. The intensities of the reflections were collected by means of a Bruker APEX II CCD diffractometer ($Mo_{K\alpha}$ radiation, λ=0.71073 Å), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 0.5° scans in ω at 28° in 2θ. Data integration down to 0.78 Å resolution was carried out using SAINT V8.37A with reflection spot size optimization.[11] Absorption corrections were made with the program SADABS. The structure was solved by the Intrinsic Phasing methods and refined by least-squares methods again F^2 using SHELXT-2014[12] and SHELXL-2014[13] with OLEX 2 interface.[14] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table S11, geometric parameters are shown in Table S12, and hydrogen bond parameters are listed in Table S13. The Ortep plots produced with SHELXL-2014 program, and the other drawings were produced with Accelrys DS Visualizer 2.0.[15]

Table S11. Experimental details

Crystal data	
Chemical formula	$C_{17}H_{18}F_2N_2O_4S$
M_r	384.39
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	100
a, b, c (Å)	7.8163 (5), 9.2956 (6), 12.4965 (8)
b (°)	98.9206 (10)
V (Å^3)	896.98 (10)
Z	2
Radiation type	Mo Ka
m (mm^{-1})	0.23
Crystal size (mm)	0.24 × 0.18 × 0.15
Data collection	
Diffractometer	Bruker D8 goniometer with CCD area detector

Absorption correction	Multi-scan *SADABS*
T_{min}, T_{max}	0.760, 0.801
No. of measured, independent and observed [$I > 2s(I)$] reflections	18368, 3934, 3786
R_{int}	0.039
$(\sin q/l)_{max}$ (Å^{-1})	0.641
Refinement	
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, S	0.030, 0.078, 1.04
No. of reflections	3934
No. of parameters	241
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$D\rho_{max}$, $D\rho_{min}$ (e Å^{-3})	0.35, -0.20
Absolute structure	Flack x determined using 1695 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	0.04 (3)

Computer programs: *APEX3* v2016.9-0 (Bruker-AXS, 2016), *SAINT* 8.37A (Bruker-AXS, 2015), *SHELXT2014* (Sheldrick, 2015), *SHELXL2014* (Sheldrick, 2015), Bruker *SHELXTL* (Sheldrick, 2015).

Table S12. Geometric parameters (Å, º)

S1—O4	1.4376 (19)	C7—H7	1.0000
S1—O3	1.4402 (19)	C8—C9	1.533 (3)
S1—N2	1.603 (2)	C8—H8	1.0000
S1—C13	1.771 (3)	C9—C10	1.495 (4)
F1—C7	1.414 (3)	C9—H9	1.0000
F2—C9	1.408 (3)	C10—H10A	0.9800
O1—N1	1.226 (4)	C10—H10B	0.9800
O2—N1	1.238 (4)	C10—H10C	0.9800
N1—C3	1.476 (3)	C11—C12	1.381 (4)
N2—C8	1.458 (3)	C11—C16	1.390 (5)
N2—H2	0.79 (3)	C11—H11	0.9500
C1—C2	1.384 (4)	C12—C13	1.397 (4)

C1—C6	1.390 (4)	C12—H12	0.9500
C1—H1	0.9500	C13—C14	1.394 (4)
C2—C3	1.384 (4)	C14—C15	1.382 (4)
C2—H2A	0.9500	C14—H14	0.9500
C3—C4	1.380 (4)	C15—C16	1.393 (4)
C4—C5	1.385 (4)	C15—H15	0.9500
C4—H4	0.9500	C16—C17	1.513 (4)
C5—C6	1.398 (4)	C17—H17A	0.9800
C5—H5	0.9500	C17—H17B	0.9800
C6—C7	1.507 (3)	C17—H17C	0.9800
C7—C8	1.528 (3)		
O4—S1—O3	119.41 (11)	N2—C8—H8	109.1
O4—S1—N2	106.72 (11)	C7—C8—H8	109.1
O3—S1—N2	107.25 (11)	C9—C8—H8	109.1
O4—S1—C13	106.51 (12)	F2—C9—C10	109.0 (2)
O3—S1—C13	107.36 (11)	F2—C9—C8	106.71 (19)
N2—S1—C13	109.33 (11)	C10—C9—C8	114.7 (2)
O1—N1—O2	124.0 (3)	F2—C9—H9	108.8
O1—N1—C3	118.1 (3)	C10—C9—H9	108.8
O2—N1—C3	117.8 (3)	C8—C9—H9	108.8
C8—N2—S1	126.63 (17)	C9—C10—H10A	109.5
C8—N2—H2	118 (2)	C9—C10—H10B	109.5
S1—N2—H2	115 (2)	H10A—C10—H10B	109.5
C2—C1—C6	120.3 (3)	C9—C10—H10C	109.5
C2—C1—H1	119.9	H10A—C10—H10C	109.5
C6—C1—H1	119.9	H10B—C10—H10C	109.5
C3—C2—C1	117.9 (3)	C12—C11—C16	121.2 (3)
C3—C2—H2A	121.0	C12—C11—H11	119.4
C1—C2—H2A	121.0	C16—C11—H11	119.4
C4—C3—C2	123.2 (2)	C11—C12—C13	119.4 (3)
C4—C3—N1	117.8 (2)	C11—C12—H12	120.3
C2—C3—N1	119.0 (3)	C13—C12—H12	120.3
C3—C4—C5	118.5 (2)	C14—C13—C12	120.3 (2)
C3—C4—H4	120.7	C14—C13—S1	120.73 (19)

C5—C4—H4	120.7	C12—C13—S1	118.9 (2)
C4—C5—C6	119.5 (2)	C15—C14—C13	119.0 (3)
C4—C5—H5	120.3	C15—C14—H14	120.5
C6—C5—H5	120.3	C13—C14—H14	120.5
C1—C6—C5	120.6 (2)	C14—C15—C16	121.6 (3)
C1—C6—C7	119.0 (2)	C14—C15—H15	119.2
C5—C6—C7	120.4 (2)	C16—C15—H15	119.2
F1—C7—C6	108.9 (2)	C11—C16—C15	118.4 (3)
F1—C7—C8	106.48 (18)	C11—C16—C17	121.0 (3)
C6—C7—C8	113.34 (19)	C15—C16—C17	120.6 (3)
F1—C7—H7	109.3	C16—C17—H17A	109.5
C6—C7—H7	109.3	C16—C17—H17B	109.5
C8—C7—H7	109.3	H17A—C17—H17B	109.5
N2—C8—C7	109.34 (19)	C16—C17—H17C	109.5
N2—C8—C9	109.40 (19)	H17A—C17—H17C	109.5
C7—C8—C9	110.80 (19)	H17B—C17—H17C	109.5
O4—S1—N2—C8	-147.6 (2)	C6—C7—C8—N2	58.2 (3)
O3—S1—N2—C8	-18.5 (2)	F1—C7—C8—C9	59.1 (2)
C13—S1—N2—C8	97.6 (2)	C6—C7—C8—C9	178.8 (2)
C6—C1—C2—C3	-0.6 (4)	N2—C8—C9—F2	-62.9 (3)
C1—C2—C3—C4	0.1 (4)	C7—C8—C9—F2	176.5 (2)
C1—C2—C3—N1	178.8 (3)	N2—C8—C9—C10	176.4 (2)
O1—N1—C3—C4	172.5 (3)	C7—C8—C9—C10	55.7 (3)
O2—N1—C3—C4	-5.6 (4)	C16—C11—C12—C13	-0.1 (5)
O1—N1—C3—C2	-6.3 (4)	C11—C12—C13—C14	-1.9 (4)
O2—N1—C3—C2	175.7 (3)	C11—C12—C13—S1	176.3 (2)
C2—C3—C4—C5	0.5 (4)	O4—S1—C13—C14	156.4 (2)
N1—C3—C4—C5	-178.2 (2)	O3—S1—C13—C14	27.4 (2)
C3—C4—C5—C6	-0.5 (4)	N2—S1—C13—C14	-88.6 (2)
C2—C1—C6—C5	0.7 (4)	O4—S1—C13—C12	-21.7 (2)
C2—C1—C6—C7	-178.5 (2)	O3—S1—C13—C12	-150.7 (2)
C4—C5—C6—C1	-0.1 (4)	N2—S1—C13—C12	93.2 (2)

C4—C5—C6—C7	179.0 (2)	C12—C13—C14—C15	2.2 (4)
C1—C6—C7—F1	-153.5 (2)	S1—C13—C14—C15	-175.9 (2)
C5—C6—C7—F1	27.4 (3)	C13—C14—C15—C16	-0.7 (4)
C1—C6—C7—C8	88.2 (3)	C12—C11—C16—C15	1.5 (4)
C5—C6—C7—C8	-90.9 (3)	C12—C11—C16—C17	-178.1 (3)
S1—N2—C8—C7	-130.93 (19)	C14—C15—C16—C11	-1.2 (4)
S1—N2—C8—C9	107.6 (2)	C14—C15—C16—C17	178.5 (3)
F1—C7—C8—N2	-61.6 (2)		

Table S13. Hydrogen-bond parameters

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
N2—H2···O3^{i}	0.79 (3)	2.05 (3)	2.827 (3)	167 (3)

Symmetry code(s): (i) -*x*+1, *y*+1/2, -*z*+1.

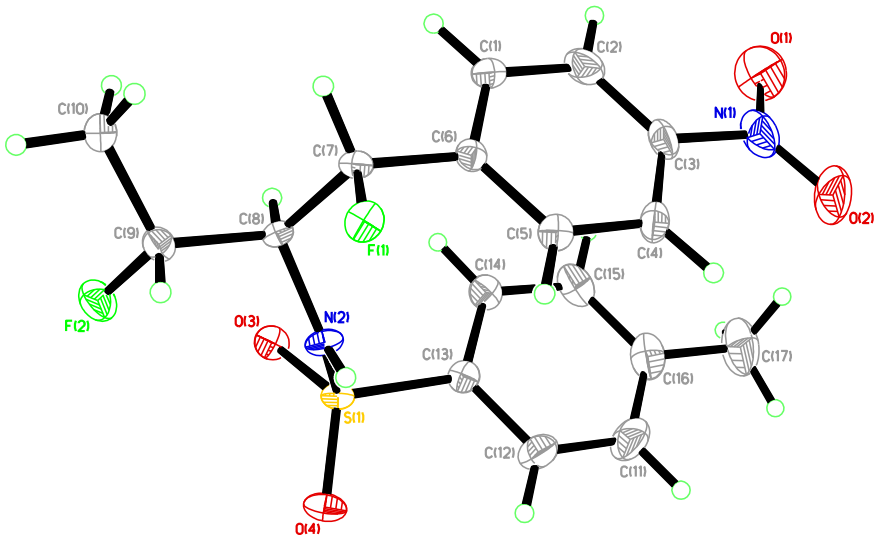


Figure S8. Perspective views showing 50% probability displacement

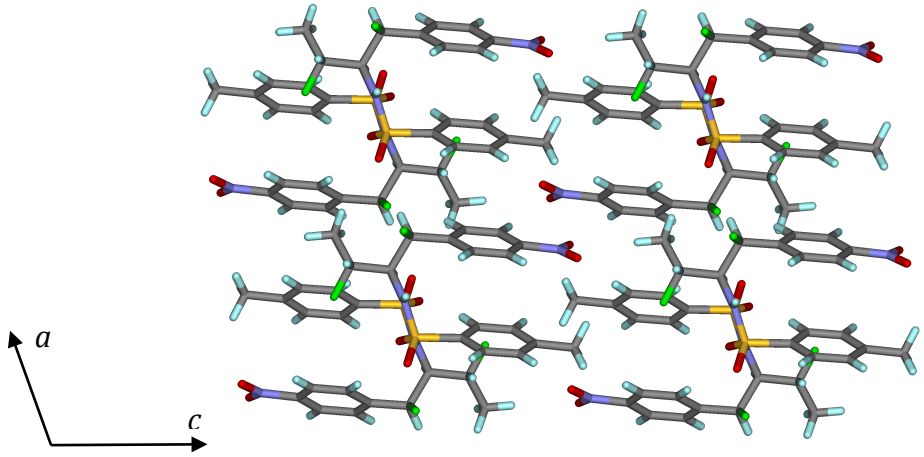
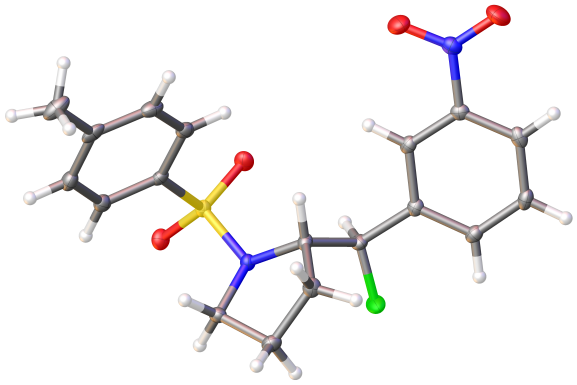


Figure S9. Three-dimensional supramolecular architecture viewed along the *b*-axis direction.

X-Ray Crystallographic Information Data for 8



X-ray Crystallography: A crystal mounted on a diffractometer was collected data at 100 K. The intensities of the reflections were collected by means of a Bruker APEX II CCD diffractometer ($Mo_{K\alpha}$ radiation, λ=0.71073 Å), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 0.5° scans in ω at 28° in 2θ. Data integration down to 0.78 Å resolution was carried out using SAINT V8.37A with reflection spot size optimization.[11] Absorption corrections were made with the program SADABS. The structure was solved by the Intrinsic Phasing methods and refined by least-squares methods again F^2 using SHELXT-2014[12] and SHELXL-2014[13] with OLEX 2 interface.[14] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table S14, and geometric parameters are shown in Table S15. The Ortep plots produced with SHELXL-2014 program, and the other drawings were produced with Accelrys DS Visualizer 2.0.[15]

Table S14. Experimental details

Crystal data	
Chemical formula	$C_{18}H_{19}FN_2O_4S$
M_r	378.41
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	100
a, b, c (Å)	7.4092 (7), 10.2119 (9), 22.525 (2)
V (Å^3)	1704.3 (3)
Z	4
Radiation type	Mo Ka
m (mm^{-1})	0.23
Crystal size (mm)	0.24 × 0.18 × 0.12
Data collection	
Diffractometer	Bruker D8 goniometer with CCD area detector

Absorption correction	Multi-scan *SADABS*
T_{min}, T_{max}	0.746, 0.801
No. of measured, independent and observed [$I > 2s(I)$] reflections	19152, 3766, 3651
R_{int}	0.025
(sin q/l)$_{max}$ (Å^{-1})	0.641
Refinement	
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, S	0.031, 0.077, 1.10
No. of reflections	3766
No. of parameters	236
H-atom treatment	H-atom parameters constrained
Dρ$_{max}$, Dρ$_{min}$ (e Å^{-3})	0.38, -0.28
Absolute structure	Flack x determined using 1497 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	-0.024 (19)

Computer programs: *APEX3* v2016.9-0 (Bruker-AXS, 2016), *SAINT* 8.37A (Bruker-AXS, 2015), *SHELXT2014* (Sheldrick, 2015), *SHELXL2014* (Sheldrick, 2015), Bruker *SHELXTL* (Sheldrick, 2015).

Table S15. Geometric parameters (Å, º)

S1—O4	1.4306 (17)	C8—H8	1.0000
S1—O3	1.4370 (17)	C9—C10	1.530 (3)
S1—N2	1.632 (2)	C9—H9A	0.9900
S1—C12	1.765 (2)	C9—H9B	0.9900
F1—C7	1.406 (3)	C10—C11	1.521 (3)
O1—N1	1.225 (3)	C10—H10A	0.9900
O2—N1	1.225 (3)	C10—H10B	0.9900
N1—C2	1.474 (3)	C11—H11A	0.9900
N2—C8	1.482 (3)	C11—H11B	0.9900
N2—C11	1.482 (3)	C12—C13	1.387 (3)
C1—C2	1.376 (3)	C12—C17	1.395 (3)
C1—C6	1.397 (3)	C13—C14	1.382 (3)
C1—H1	0.9500	C13—H13	0.9500
C2—C3	1.387 (3)	C14—C15	1.391 (3)

C3—C4	1.388 (3)	C14—H14	0.9500
C3—H3	0.9500	C15—C16	1.396 (4)
C4—C5	1.394 (3)	C15—C18	1.503 (3)
C4—H4	0.9500	C16—C17	1.384 (4)
C5—C6	1.391 (3)	C16—H16	0.9500
C5—H5	0.9500	C17—H17	0.9500
C6—C7	1.505 (3)	C18—H18A	0.9800
C7—C8	1.528 (3)	C18—H18B	0.9800
C7—H7	1.0000	C18—H18C	0.9800
C8—C9	1.535 (3)		
O4—S1—O3	120.35 (10)	C10—C9—C8	104.71 (18)
O4—S1—N2	106.78 (10)	C10—C9—H9A	110.8
O3—S1—N2	106.19 (10)	C8—C9—H9A	110.8
O4—S1—C12	107.70 (10)	C10—C9—H9B	110.8
O3—S1—C12	108.86 (11)	C8—C9—H9B	110.8
N2—S1—C12	106.11 (11)	H9A—C9—H9B	108.9
O2—N1—O1	124.0 (2)	C11—C10—C9	103.97 (18)
O2—N1—C2	117.97 (19)	C11—C10—H10A	111.0
O1—N1—C2	118.0 (2)	C9—C10—H10A	111.0
C8—N2—C11	111.28 (18)	C11—C10—H10B	111.0
C8—N2—S1	117.76 (15)	C9—C10—H10B	111.0
C11—N2—S1	118.14 (14)	H10A—C10—H10B	109.0
C2—C1—C6	118.7 (2)	N2—C11—C10	102.67 (17)
C2—C1—H1	120.6	N2—C11—H11A	111.2
C6—C1—H1	120.6	C10—C11—H11A	111.2
C1—C2—C3	123.4 (2)	N2—C11—H11B	111.2
C1—C2—N1	118.0 (2)	C10—C11—H11B	111.2
C3—C2—N1	118.6 (2)	H11A—C11—H11B	109.1
C2—C3—C4	117.4 (2)	C13—C12—C17	120.7 (2)
C2—C3—H3	121.3	C13—C12—S1	119.24 (17)
C4—C3—H3	121.3	C17—C12—S1	119.94 (17)
C3—C4—C5	120.6 (2)	C14—C13—C12	119.4 (2)
C3—C4—H4	119.7	C14—C13—H13	120.3
C5—C4—H4	119.7	C12—C13—H13	120.3

C6—C5—C4	120.7 (2)	C13—C14—C15	121.1 (2)
C6—C5—H5	119.6	C13—C14—H14	119.4
C4—C5—H5	119.6	C15—C14—H14	119.4
C5—C6—C1	119.1 (2)	C14—C15—C16	118.6 (2)
C5—C6—C7	122.4 (2)	C14—C15—C18	120.7 (2)
C1—C6—C7	118.4 (2)	C16—C15—C18	120.7 (2)
F1—C7—C6	109.59 (18)	C17—C16—C15	121.2 (2)
F1—C7—C8	108.64 (18)	C17—C16—H16	119.4
C6—C7—C8	113.42 (19)	C15—C16—H16	119.4
F1—C7—H7	108.4	C16—C17—C12	118.9 (2)
C6—C7—H7	108.4	C16—C17—H17	120.5
C8—C7—H7	108.4	C12—C17—H17	120.5
N2—C8—C7	109.29 (18)	C15—C18—H18A	109.5
N2—C8—C9	104.38 (17)	C15—C18—H18B	109.5
C7—C8—C9	115.24 (19)	H18A—C18—H18B	109.5
N2—C8—H8	109.2	C15—C18—H18C	109.5
C7—C8—H8	109.2	H18A—C18—H18C	109.5
C9—C8—H8	109.2	H18B—C18—H18C	109.5
O4—S1—N2—C8	165.87 (16)	S1—N2—C8—C9	143.46 (16)
O3—S1—N2—C8	36.29 (18)	F1—C7—C8—N2	-72.7 (2)
C12—S1—N2—C8	-79.45 (17)	C6—C7—C8—N2	165.16 (19)
O4—S1—N2—C11	-55.83 (18)	F1—C7—C8—C9	44.4 (3)
O3—S1—N2—C11	174.59 (17)	C6—C7—C8—C9	-77.7 (2)
C12—S1—N2—C11	58.86 (18)	N2—C8—C9—C10	19.6 (2)
C6—C1—C2—C3	1.1 (4)	C7—C8—C9—C10	-100.2 (2)
C6—C1—C2—N1	179.1 (2)	C8—C9—C10—C11	-34.1 (2)
O2—N1—C2—C1	5.7 (3)	C8—N2—C11—C10	-23.5 (2)
O1—N1—C2—C1	-174.1 (2)	S1—N2—C11—C10	-164.34 (15)
O2—N1—C2—C3	-176.1 (2)	C9—C10—C11—N2	34.9 (2)
O1—N1—C2—C3	4.1 (3)	O4—S1—C12—C13	22.4 (2)
C1—C2—C3—C4	-0.2 (3)	O3—S1—C12—C13	154.44 (19)
N1—C2—C3—C4	-178.2 (2)	N2—S1—C12—C13	-91.6 (2)
C2—C3—C4—C5	-0.9 (3)	O4—S1—C12—C17	-160.69 (19)
C3—C4—C5—C6	1.1 (4)	O3—S1—C12—C17	-28.7 (2)

C4—C5—C6—C1	-0.2 (3)	N2—S1—C12—C17	85.3 (2)
C4—C5—C6—C7	177.0 (2)	C17—C12—C13—C14	0.4 (4)
C2—C1—C6—C5	-0.9 (3)	S1—C12—C13—C14	177.31 (19)
C2—C1—C6—C7	-178.1 (2)	C12—C13—C14—C15	-0.2 (4)
C5—C6—C7—F1	4.3 (3)	C13—C14—C15—C16	-0.6 (4)
C1—C6—C7—F1	-178.59 (19)	C13—C14—C15—C18	178.1 (2)
C5—C6—C7—C8	125.9 (2)	C14—C15—C16—C17	1.3 (4)
C1—C6—C7—C8	-57.0 (3)	C18—C15—C16—C17	-177.4 (2)
C11—N2—C8—C7	126.3 (2)	C15—C16—C17—C12	-1.1 (4)
S1—N2—C8—C7	-92.7 (2)	C13—C12—C17—C16	0.2 (4)
C11—N2—C8—C9	2.5 (2)	S1—C12—C17—C16	-176.62 (18)

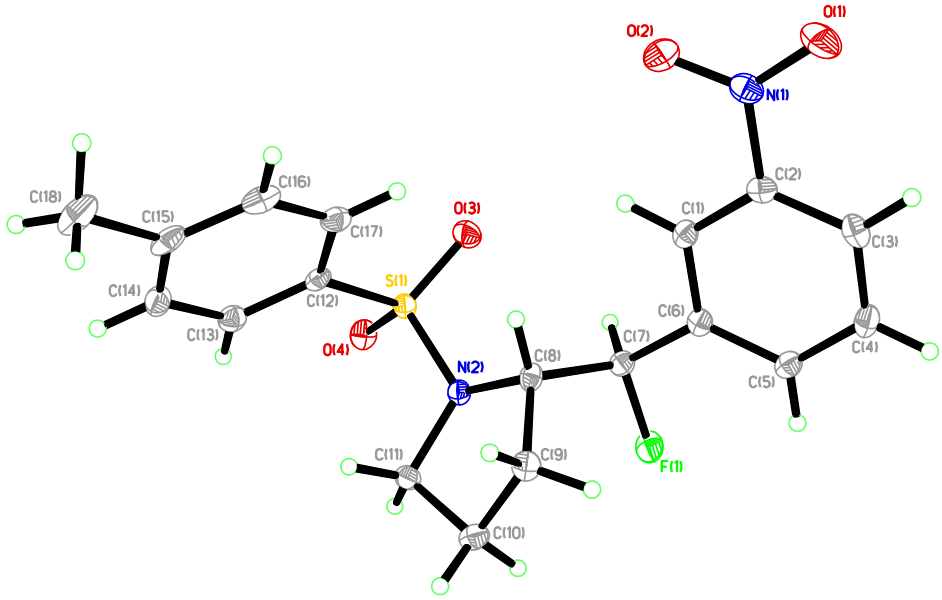


Figure S10. Perspective views showing 50% probability displacement

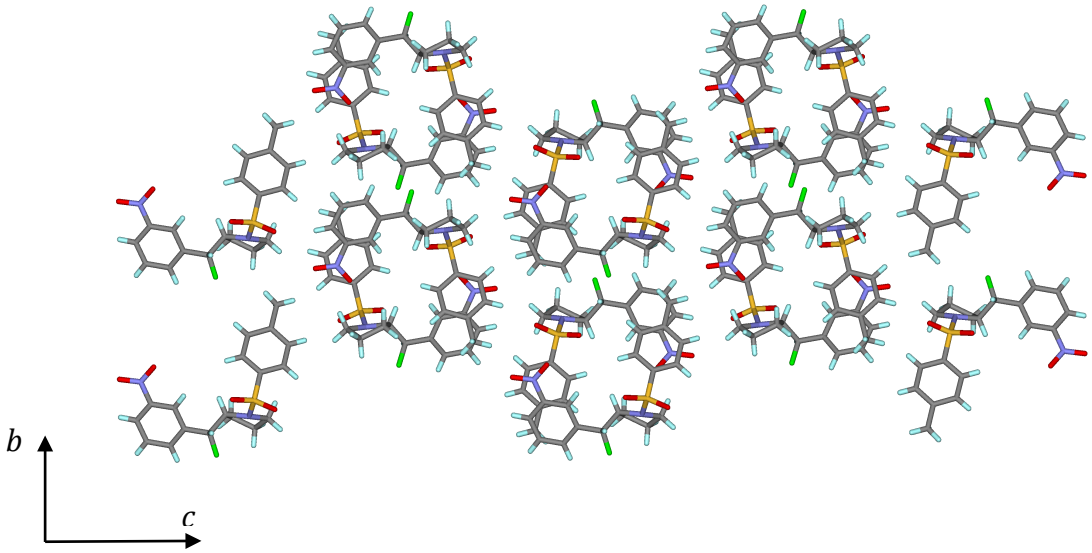
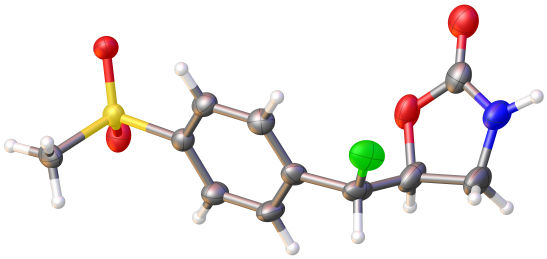


Figure S11. Three-dimensional supramolecular architecture viewed along the *a*-axis direction.

X-Ray Crystallographic Information Data for 12



X-ray Crystallography: A crystal mounted on a diffractometer was collected data at 100 K. The intensities of the reflections were collected by means of a Bruker APEX DUO CCD diffractometer ($Cu_{K\alpha}$ radiation, λ=1.54178 Å), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 1.0° scans in ω at -30°, -55°, -80°, 30°, 55°, 80° and 115° in 2θ. Data integration down to 0.84 Å resolution was carried out using SAINT V8.37 A with reflection spot size optimization.[11] Absorption corrections were made with the program SADABS (Bruker diffractometer, 2015). The structure was solved by the Intrinsic Phasing methods and refined by least-squares methods again F^2 using SHELXT-2014[12] and SHELXL-2014[13] with OLEX 2 interface.[14] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table S16, geometric parameters are shown in Table S17 and hydrogen-bond parameters are listed in Table S18. The Ortep plots produced with SHELXL-2014 program, and the other drawings were produced with Accelrys DS Visualizer 2.0.[15]

Table S16. Experimental details

Crystal data	
Chemical formula	$C_{11}H_{12.50}FNO_{4.25}S$
M_r	277.78
Crystal system, space group	Hexagonal, $P6_2$
Temperature (K)	100
a, c (Å)	17.8047 (4), 6.9972 (2)
V (Å^3)	1920.99 (10)
Z	6
Radiation type	Cu *K*a
m (mm^{-1})	2.48
Crystal size (mm)	0.24 × 0.18 × 0.12
Data collection	
Diffractometer	Bruker D8 goniometer with CCD area detector
Absorption correction	Multi-scan *SADABS*
T_{min}, T_{max}	0.660, 0.806

No. of measured, independent and observed [$I > 2s(I)$] reflections	14238, 2181, 2133
R_{int}	0.046
$(\sin q/l)_{max}$ ($Å^{-1}$)	0.595
Refinement	
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, S	0.033, 0.090, 1.07
No. of reflections	2181
No. of parameters	177
No. of restraints	7
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$D\rho_{max}$, $D\rho_{min}$ (e $Å^{-3}$)	0.30, -0.20
Absolute structure	Flack x determined using 924 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	-0.021 (19)

Computer programs: *APEX3* v2016.9-0 (Bruker-AXS, 2016), *SAINT* 8.37A (Bruker-AXS, 2015), *SHELXT2014* (Sheldrick, 2015), *SHELXL2014* (Sheldrick, 2015), Bruker *SHELXTL* (Sheldrick, 2015).

Table S17. Geometric parameters (Å, º)

S1—O4	1.441 (2)	C5—C6	1.378 (5)
S1—O3	1.445 (2)	C5—C10	1.398 (5)
S1—C11	1.760 (3)	C6—C7	1.386 (5)
S1—C8	1.771 (3)	C6—H6	0.9500
F1—C4	1.405 (4)	C7—C8	1.378 (5)
O1—C1	1.363 (5)	C7—H7	0.9500
O1—C3	1.447 (5)	C8—C9	1.386 (5)
O2—C1	1.214 (5)	C9—C10	1.383 (5)
N1—C1	1.335 (5)	C9—H9	0.9500
N1—C2	1.452 (6)	C10—H10	0.9500
N1—H1	0.95 (7)	C11—H11A	0.9800
C2—C3	1.534 (5)	C11—H11B	0.9800
C2—H2A	0.9900	C11—H11C	0.9800
C2—H2B	0.9900	O1W—O2W	1.0 (2)
C3—C4	1.502 (6)	O1W—H1WA	0.8124

C3—H3	1.0000	O1W—H1WB	0.8201
C4—C5	1.505 (4)	O2W—H2WA	0.7833
C4—H4	1.0000	O2W—H2WB	0.8183
O4—S1—O3	118.24 (14)	C6—C5—C10	120.3 (3)
O4—S1—C11	108.27 (15)	C6—C5—C4	120.8 (3)
O3—S1—C11	108.42 (14)	C10—C5—C4	118.9 (3)
O4—S1—C8	107.82 (14)	C5—C6—C7	120.2 (3)
O3—S1—C8	107.47 (15)	C5—C6—H6	119.9
C11—S1—C8	105.97 (15)	C7—C6—H6	119.9
C1—O1—C3	110.6 (3)	C8—C7—C6	119.1 (3)
C1—N1—C2	112.7 (3)	C8—C7—H7	120.5
C1—N1—H1	115 (3)	C6—C7—H7	120.5
C2—N1—H1	131 (3)	C7—C8—C9	121.7 (3)
O2—C1—N1	129.8 (4)	C7—C8—S1	119.1 (2)
O2—C1—O1	120.7 (3)	C9—C8—S1	119.2 (3)
N1—C1—O1	109.5 (3)	C10—C9—C8	119.0 (3)
N1—C2—C3	101.9 (3)	C10—C9—H9	120.5
N1—C2—H2A	111.4	C8—C9—H9	120.5
C3—C2—H2A	111.4	C9—C10—C5	119.7 (3)
N1—C2—H2B	111.4	C9—C10—H10	120.1
C3—C2—H2B	111.4	C5—C10—H10	120.1
H2A—C2—H2B	109.2	S1—C11—H11A	109.5
O1—C3—C4	108.8 (3)	S1—C11—H11B	109.5
O1—C3—C2	104.4 (3)	H11A—C11—H11B	109.5
C4—C3—C2	114.5 (4)	S1—C11—H11C	109.5
O1—C3—H3	109.7	H11A—C11—H11C	109.5
C4—C3—H3	109.7	H11B—C11—H11C	109.5
C2—C3—H3	109.7	O2W—O1W—H1WA	150.7
F1—C4—C3	108.0 (3)	O2W—O1W—H1WB	96.4
F1—C4—C5	109.2 (3)	H1WA—O1W—H1WB	112.3
C3—C4—C5	113.3 (3)	O1W—O2W—H2WA	173.4
F1—C4—H4	108.7	O1W—O2W—H2WB	77.8
C3—C4—H4	108.7	H2WA—O2W—	105.9

		H2WB	
C5—C4—H4	108.7		
C2—N1—C1—O2	-174.4 (4)	C10—C5—C6—C7	-0.9 (5)
C2—N1—C1—O1	6.4 (5)	C4—C5—C6—C7	175.8 (3)
C3—O1—C1—O2	-179.7 (4)	C5—C6—C7—C8	-1.4 (5)
C3—O1—C1—N1	-0.4 (4)	C6—C7—C8—C9	2.3 (5)
C1—N1—C2—C3	-9.2 (5)	C6—C7—C8—S1	-175.8 (2)
C1—O1—C3—C4	117.4 (3)	O4—S1—C8—C7	151.1 (2)
C1—O1—C3—C2	-5.2 (4)	O3—S1—C8—C7	22.6 (3)
N1—C2—C3—O1	8.2 (5)	C11—S1—C8—C7	-93.2 (3)
N1—C2—C3—C4	-110.6 (4)	O4—S1—C8—C9	-27.1 (3)
O1—C3—C4—F1	-68.6 (3)	O3—S1—C8—C9	-155.6 (3)
C2—C3—C4—F1	47.7 (4)	C11—S1—C8—C9	88.7 (3)
O1—C3—C4—C5	52.6 (4)	C7—C8—C9—C10	-0.7 (5)
C2—C3—C4—C5	168.9 (3)	S1—C8—C9—C10	177.4 (3)
F1—C4—C5—C6	13.7 (4)	C8—C9—C10—C5	-1.6 (5)
C3—C4—C5—C6	-106.8 (4)	C6—C5—C10—C9	2.5 (5)
F1—C4—C5—C10	-169.6 (3)	C4—C5—C10—C9	-174.3 (3)
C3—C4—C5—C10	70.0 (4)		

Table S18. Hydrogen-bond parameters

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
N1—H1···O1^{i}	0.95 (7)	2.68 (5)	3.077 (4)	106 (4)
N1—H1···O2^{i}	0.95 (7)	2.08 (7)	2.978 (5)	158 (5)
C2—H2B···O1^{i}	0.99	2.54	3.096 (5)	115.4

Symmetry code(s): (i) x-y+1, x, z+1/3.

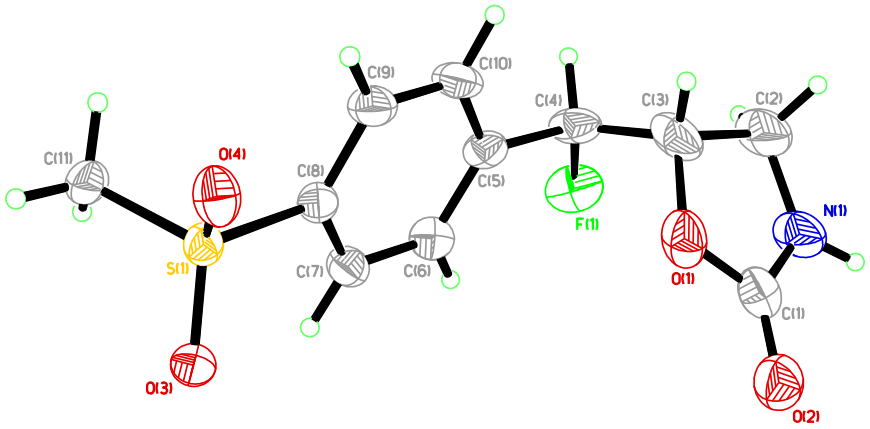


Figure S12. Perspective views showing 50% probability displacement

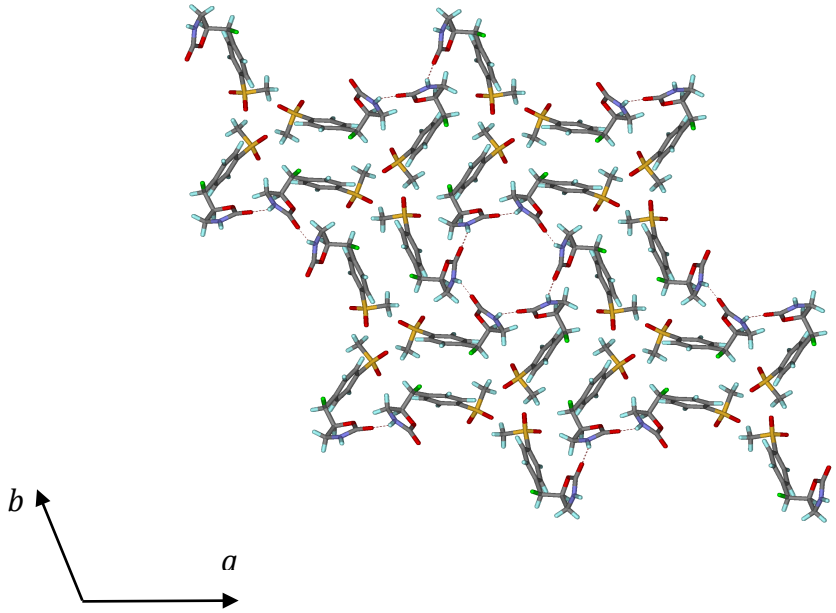
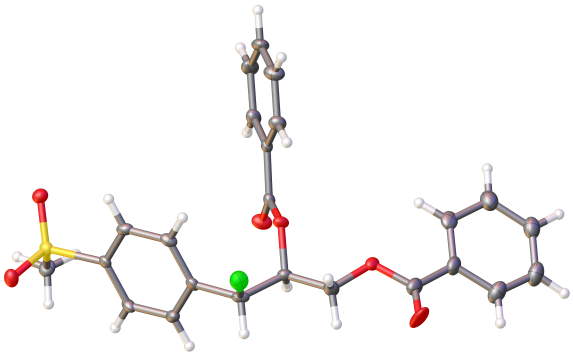


Figure S13. Three-dimensional supramolecular architecture viewed along the *c*-axis direction.

X-Ray Crystallographic Information Data for 16



X-ray Crystallography: A crystal mounted on a diffractometer was collected data at 100 K. The intensities of the reflections were collected by means of a Bruker APEX II CCD diffractometer ($Mo_{K\alpha}$ radiation, λ=0.71073 Å), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 0.5° scans in ω at 28° in 2θ. Data integration down to 0.78 Å resolution was carried out using SAINT V8.37A with reflection spot size optimization.[11] Absorption corrections were made with the program SADABS. The structure was solved by the Intrinsic Phasing methods and refined by least-squares methods again F^2 using SHELXT-2014[12] and SHELXL-2014[13] with OLEX 2 interface.[14] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table S19, and geometric parameters are shown in Table S20. The Ortep plots produced with SHELXL-2014 program, and the other drawings were produced with Accelrys DS Visualizer 2.0.[15]

Table S19. Experimental details

Crystal data	
Chemical formula	$C_{24}H_{21}FO_6S$
M_r	456.47
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	100
a, b, c (Å)	5.2733 (3), 10.7709 (6), 37.817 (2)
V (Å^3)	2147.9 (2)
Z	4
Radiation type	Mo Ka
m (mm^{-1})	0.20
Crystal size (mm)	0.18 × 0.04 × 0.02
Data collection	

Diffractometer	Bruker D8 goniometer with CCD area detector
Absorption correction	Multi-scan *SADABS*
T_{min}, T_{max}	0.719, 0.862
No. of measured, independent and observed [$I > 2s(I)$] reflections	15038, 4709, 3791
R_{int}	0.051
(sin q/l)$_{max}$ (Å^{-1})	0.642
Refinement	
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, S	0.052, 0.093, 1.08
No. of reflections	4709
No. of parameters	318
No. of restraints	72
H-atom treatment	H-atom parameters constrained
Dρ$_{max}$, Dρ$_{min}$ (e Å^{-3})	0.30, -0.35
Absolute structure	Flack x determined using 1250 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	-0.01 (5)

Computer programs: *APEX3* v2016.9-0 (Bruker-AXS, 2016), *SAINT* 8.37A (Bruker-AXS, 2015), *SHELXT2014* (Sheldrick, 2015), *SHELXL2014* (Sheldrick, 2015), Bruker *SHELXTL* (Sheldrick, 2015).

Table S20. Selected geometric parameters (Å, º)

S1—O2	1.440 (2)	C13—H13	0.9500
S1—O1	1.449 (2)	C14—C15	1.375 (6)
S1—C10	1.753 (4)	C14—H14	0.9500
S1—C3	1.778 (3)	C15—C16	1.384 (5)
F1—C7	1.407 (4)	C15—H15	0.9500
O3—C11	1.358 (4)	C16—C17	1.380 (5)
O3—C8	1.439 (4)	C16—H16	0.9500
O4—C11	1.207 (4)	C17—H17	0.9500
C1—C2	1.387 (4)	O5—C18	1.313 (16)
C1—C6	1.389 (5)	C18—O6	1.195 (16)
C1—H1	0.9500	C18—C19	1.483 (17)
C2—C3	1.389 (5)	C19—C20	1.380 (18)

C2—H2	0.9500	C19—C24	1.396 (16)
C3—C4	1.382 (4)	C20—C21	1.394 (16)
C4—C5	1.384 (4)	C20—H20	0.9500
C4—H4	0.9500	C21—C22	1.386 (16)
C5—C6	1.391 (5)	C21—H21	0.9500
C5—H5	0.9500	C22—C23	1.369 (15)
C6—C7	1.514 (4)	C22—H22	0.9500
C7—C8	1.519 (5)	C23—C24	1.387 (16)
C7—H7	1.0000	C23—H23	0.9500
C8—C9	1.510 (4)	C24—H24	0.9500
C8—H8	1.0000	O5A—C18A	1.324 (11)
C9—O5	1.42 (4)	C18A—O6A	1.207 (12)
C9—O5A	1.47 (2)	C18A—C19A	1.486 (13)
C9—H9AA	0.9900	C19A—C20A	1.381 (16)
C9—H9AB	0.9900	C19A—C24A	1.394 (12)
C9—H9BC	0.9900	C20A—C21A	1.390 (12)
C9—H9BD	0.9900	C20A—H20A	0.9500
C10—H10A	0.9800	C21A—C22A	1.378 (12)
C10—H10B	0.9800	C21A—H21A	0.9500
C10—H10C	0.9800	C22A—C23A	1.374 (12)
C11—C12	1.481 (5)	C22A—H22A	0.9500
C12—C17	1.381 (5)	C23A—C24A	1.394 (12)
C12—C13	1.399 (5)	C23A—H23A	0.9500
C13—C14	1.375 (5)	C24A—H24A	0.9500
O2—S1—O1	117.74 (15)	C13—C12—C11	118.4 (3)
O2—S1—C10	108.75 (16)	C14—C13—C12	120.2 (4)
O1—S1—C10	108.67 (16)	C14—C13—H13	119.9
O2—S1—C3	107.73 (14)	C12—C13—H13	119.9
O1—S1—C3	106.87 (14)	C13—C14—C15	120.2 (3)
C10—S1—C3	106.54 (17)	C13—C14—H14	119.9
C11—O3—C8	117.4 (3)	C15—C14—H14	119.9
C2—C1—C6	120.6 (3)	C14—C15—C16	120.2 (4)
C2—C1—H1	119.7	C14—C15—H15	119.9
C6—C1—H1	119.7	C16—C15—H15	119.9

C1—C2—C3	118.9 (3)	C17—C16—C15	119.9 (4)
C1—C2—H2	120.5	C17—C16—H16	120.1
C3—C2—H2	120.5	C15—C16—H16	120.1
C4—C3—C2	121.0 (3)	C16—C17—C12	120.5 (3)
C4—C3—S1	117.8 (3)	C16—C17—H17	119.8
C2—C3—S1	121.1 (2)	C12—C17—H17	119.8
C3—C4—C5	119.7 (3)	C18—O5—C9	116 (3)
C3—C4—H4	120.1	O6—C18—O5	118 (2)
C5—C4—H4	120.1	O6—C18—C19	126 (2)
C4—C5—C6	120.1 (3)	O5—C18—C19	114.6 (19)
C4—C5—H5	120.0	C20—C19—C24	120.1 (16)
C6—C5—H5	120.0	C20—C19—C18	122.1 (18)
C1—C6—C5	119.7 (3)	C24—C19—C18	117.8 (18)
C1—C6—C7	119.1 (3)	C19—C20—C21	119.4 (19)
C5—C6—C7	121.3 (3)	C19—C20—H20	120.3
F1—C7—C6	108.8 (3)	C21—C20—H20	120.3
F1—C7—C8	108.4 (3)	C22—C21—C20	119.4 (17)
C6—C7—C8	113.4 (3)	C22—C21—H21	120.3
F1—C7—H7	108.7	C20—C21—H21	120.3
C6—C7—H7	108.7	C23—C22—C21	121.8 (17)
C8—C7—H7	108.7	C23—C22—H22	119.1
O3—C8—C9	107.6 (3)	C21—C22—H22	119.1
O3—C8—C7	109.4 (3)	C22—C23—C24	118.5 (18)
C9—C8—C7	110.9 (3)	C22—C23—H23	120.7
O3—C8—H8	109.6	C24—C23—H23	120.7
C9—C8—H8	109.6	C23—C24—C19	120.5 (16)
C7—C8—H8	109.6	C23—C24—H24	119.7
O5—C9—C8	110.4 (13)	C19—C24—H24	119.7
O5A—C9—C8	103.8 (8)	C18A—O5A—C9	118.2 (19)
O5—C9—H9AA	109.6	O6A—C18A—O5A	123.3 (17)
C8—C9—H9AA	109.6	O6A—C18A—C19A	123.3 (15)
O5—C9—H9AB	109.6	O5A—C18A—C19A	113.3 (13)
C8—C9—H9AB	109.6	C20A—C19A—C24A	119.4 (12)
H9AA—C9—H9AB	108.1	C20A—C19A—C18A	122.2 (13)
O5A—C9—H9BC	111.0	C24A—C19A—C18A	118.4 (15)

C8—C9—H9BC	111.0	C19A—C20A—C21A	120.1 (13)
O5A—C9—H9BD	111.0	C19A—C20A—H20A	120.0
C8—C9—H9BD	111.0	C21A—C20A—H20A	120.0
H9BC—C9—H9BD	109.0	C22A—C21A—C20A	120.2 (12)
S1—C10—H10A	109.5	C22A—C21A—H21A	119.9
S1—C10—H10B	109.5	C20A—C21A—H21A	119.9
H10A—C10—H10B	109.5	C23A—C22A—C21A	120.2 (12)
S1—C10—H10C	109.5	C23A—C22A—H22A	119.9
H10A—C10—H10C	109.5	C21A—C22A—H22A	119.9
H10B—C10—H10C	109.5	C22A—C23A—C24A	119.8 (12)
O4—C11—O3	123.7 (3)	C22A—C23A—H23A	120.1
O4—C11—C12	125.4 (3)	C24A—C23A—H23A	120.1
O3—C11—C12	110.9 (3)	C19A—C24A—C23A	120.1 (13)
C17—C12—C13	119.1 (3)	C19A—C24A—H24A	120.0
C17—C12—C11	122.5 (3)	C23A—C24A—H24A	120.0
C6—C1—C2—C3	0.0 (5)	C11—C12—C13—C14	178.7 (3)
C1—C2—C3—C4	1.1 (5)	C12—C13—C14—C15	1.2 (5)
C1—C2—C3—S1	-174.7 (3)	C13—C14—C15—C16	-0.3 (6)
O2—S1—C3—C4	27.0 (3)	C14—C15—C16—C17	-0.3 (6)
O1—S1—C3—C4	-100.4 (3)	C15—C16—C17—C12	-0.1 (6)
C10—S1—C3—C4	143.5 (3)	C13—C12—C17—C16	1.0 (5)
O2—S1—C3—C2	-157.1 (3)	C11—C12—C17—C16	-179.3 (3)
O1—S1—C3—C2	75.5 (3)	C8—C9—O5—C18	-150.0 (17)
C10—S1—C3—C2	-40.6 (3)	C9—O5—C18—O6	-21 (3)
C2—C3—C4—C5	-1.2 (5)	C9—O5—C18—C19	167 (4)
S1—C3—C4—C5	174.7 (3)	O6—C18—C19—C20	-158 (6)
C3—C4—C5—C6	0.2 (5)	O5—C18—C19—C20	13 (9)
C2—C1—C6—C5	-0.9 (5)	O6—C18—C19—C24	19 (8)
C2—C1—C6—C7	179.6 (3)	O5—C18—C19—C24	-170 (5)
C4—C5—C6—C1	0.8 (5)	C24—C19—C20—C21	-3 (10)
C4—C5—C6—C7	-179.7 (3)	C18—C19—C20—C21	174 (4)
C1—C6—C7—F1	-143.7 (3)	C19—C20—C21—C22	4 (7)
C5—C6—C7—F1	36.8 (4)	C20—C21—C22—C23	0 (4)
C1—C6—C7—C8	95.6 (4)	C21—C22—C23—C24	-5 (5)

C5—C6—C7—C8	-84.0 (4)	C22—C23—C24—C19	5 (6)
C11—O3—C8—C9	133.9 (3)	C20—C19—C24—C23	-1 (9)
C11—O3—C8—C7	-105.5 (3)	C18—C19—C24—C23	-179 (5)
F1—C7—C8—O3	-60.9 (3)	C8—C9—O5A—C18A	-152.6 (12)
C6—C7—C8—O3	60.0 (4)	C9—O5A—C18A—O6A	17 (2)
F1—C7—C8—C9	57.7 (4)	C9—O5A—C18A—C19A	-166 (3)
C6—C7—C8—C9	178.6 (3)	O6A—C18A—C19A—C20A	-166 (4)
O3—C8—C9—O5	-55.3 (12)	O5A—C18A—C19A—C20A	17 (6)
C7—C8—C9—O5	-175.0 (12)	O6A—C18A—C19A—C24A	14 (6)
O3—C8—C9—O5A	-67.4 (9)	O5A—C18A—C19A—C24A	-164 (3)
C7—C8—C9—O5A	173.0 (8)	C24A—C19A—C20A—C21A	3 (7)
C8—O3—C11—O4	0.8 (4)	C18A—C19A—C20A—C21A	-178 (3)
C8—O3—C11—C12	-179.4 (3)	C19A—C20A—C21A—C22A	-3 (5)
O4—C11—C12—C17	-177.7 (3)	C20A—C21A—C22A—C23A	1 (3)
O3—C11—C12—C17	2.5 (4)	C21A—C22A—C23A—C24A	2 (3)
O4—C11—C12—C13	2.0 (5)	C20A—C19A—C24A—C23A	1 (6)
O3—C11—C12—C13	-177.8 (3)	C18A—C19A—C24A—C23A	-179 (3)
C17—C12—C13—C14	-1.5 (5)	C22A—C23A—C24A—C19A	-3 (4)

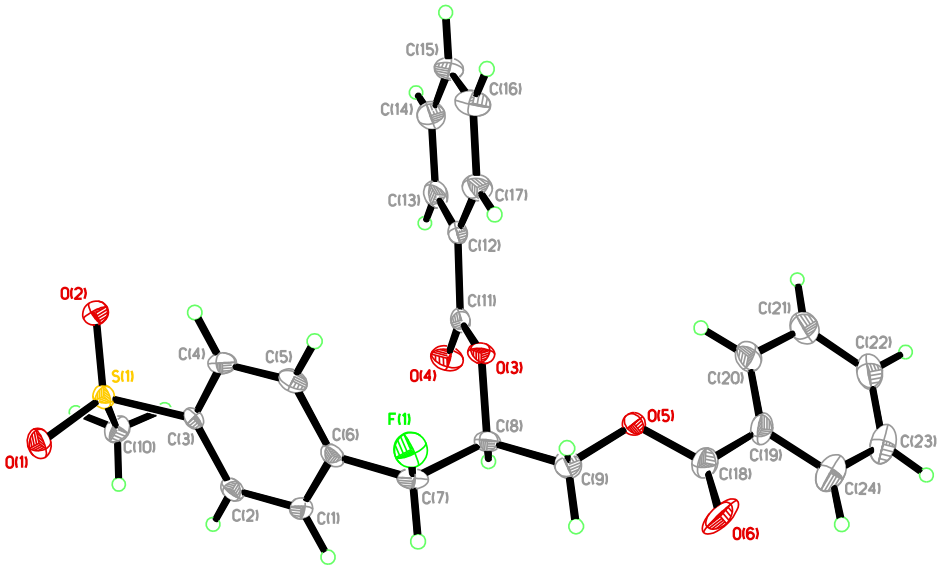


Figure S14. Perspective views showing 50% probability displacement

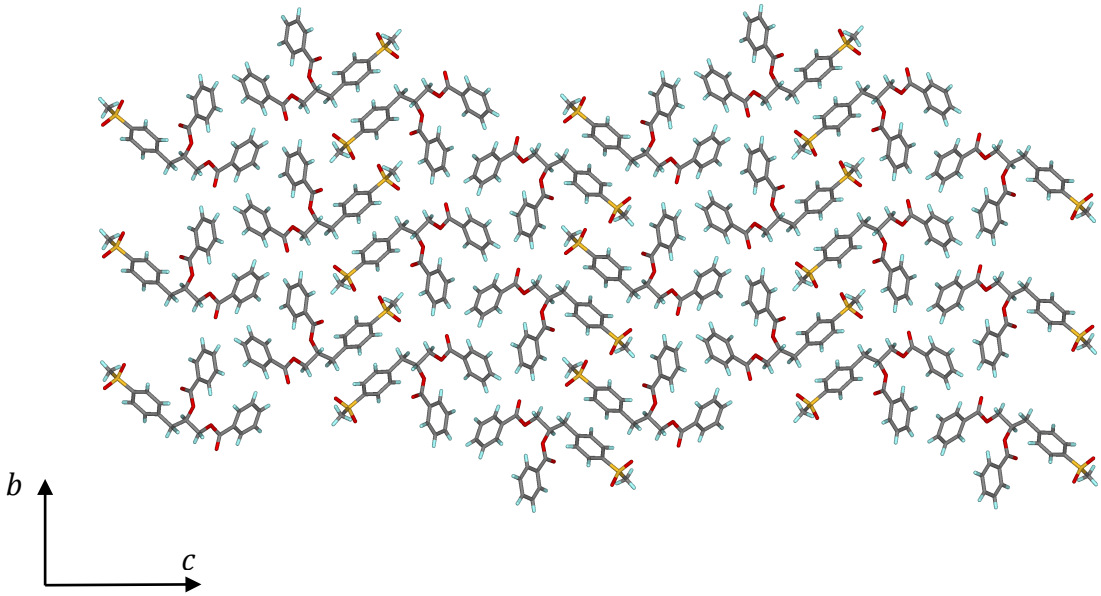


Figure S15. Three-dimensional supramolecular architecture viewed along the *a*-axis direction.

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^{1}H NMR
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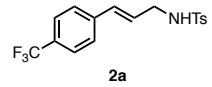
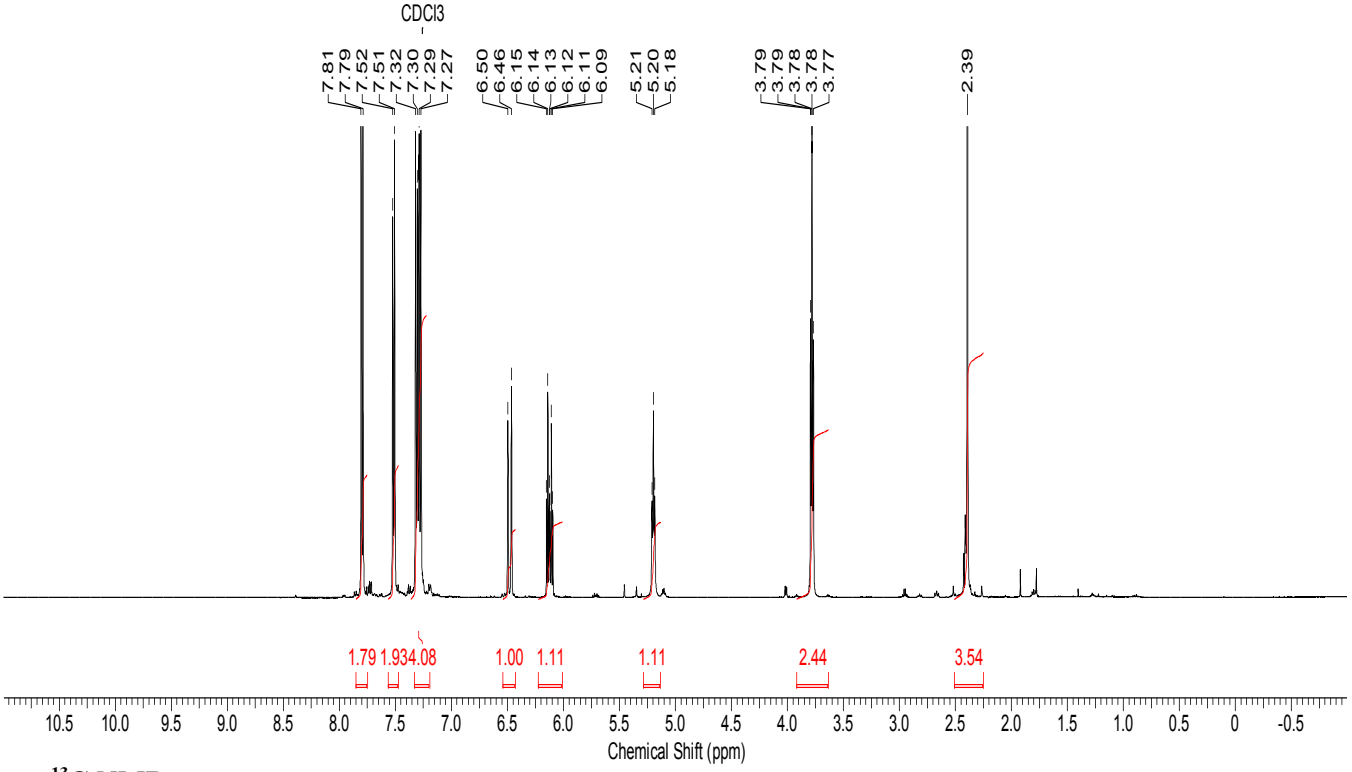


2a



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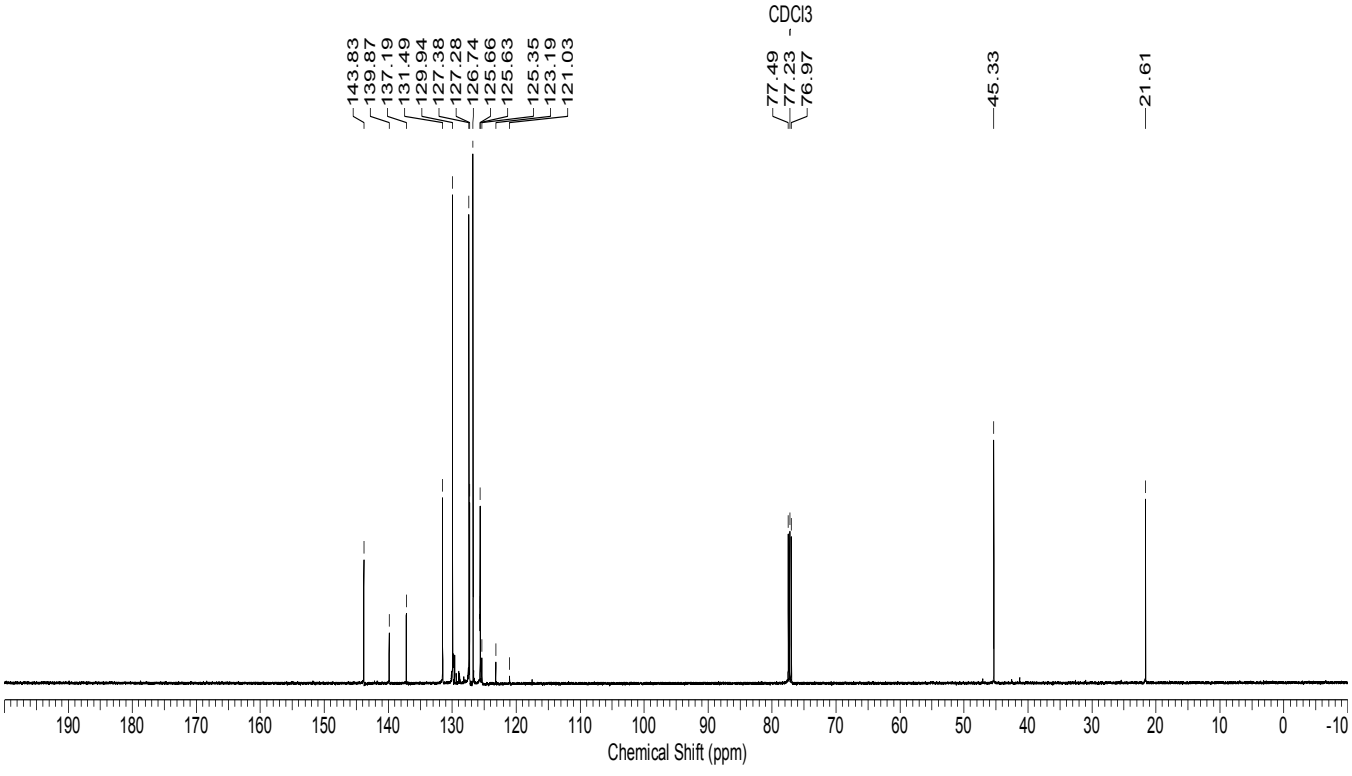

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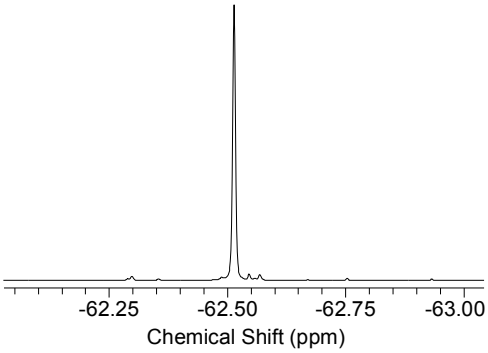

^{1}H NMR
500 MHz
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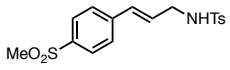
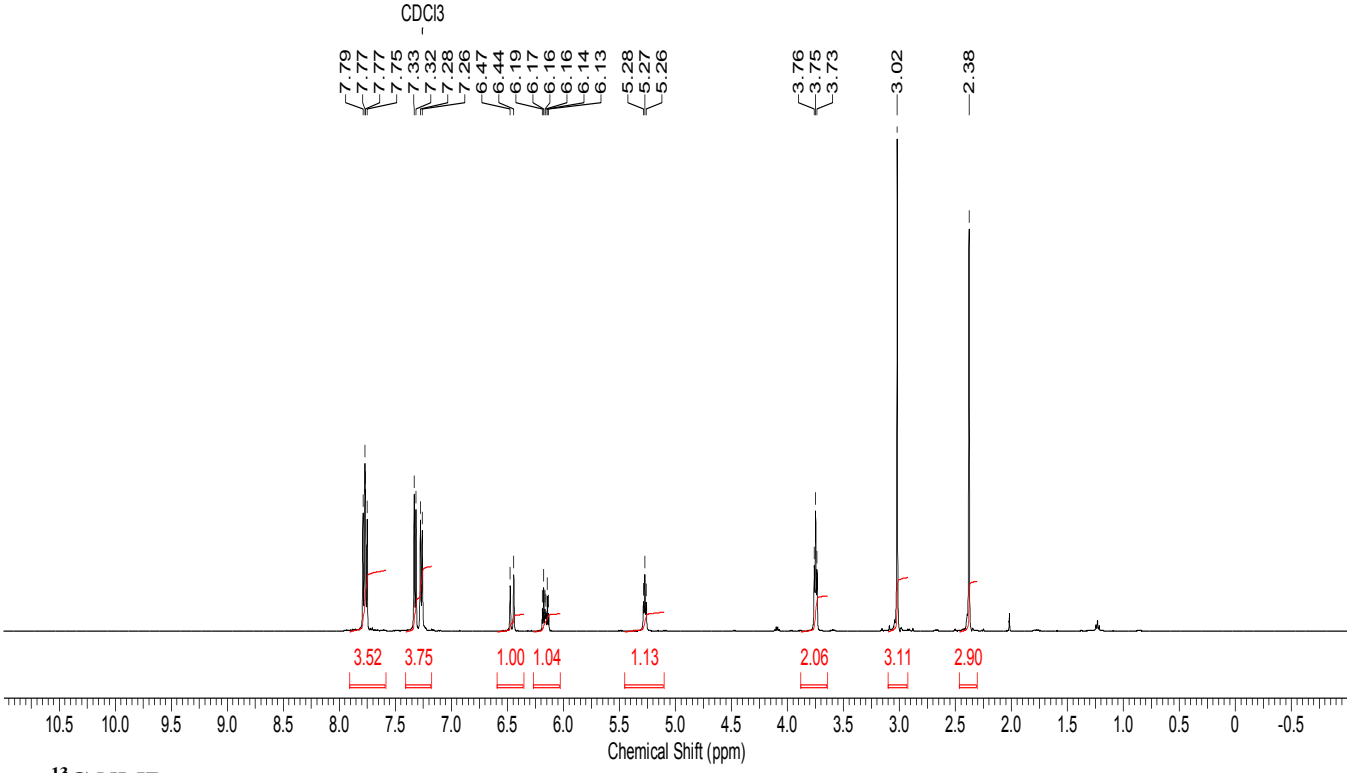


2b



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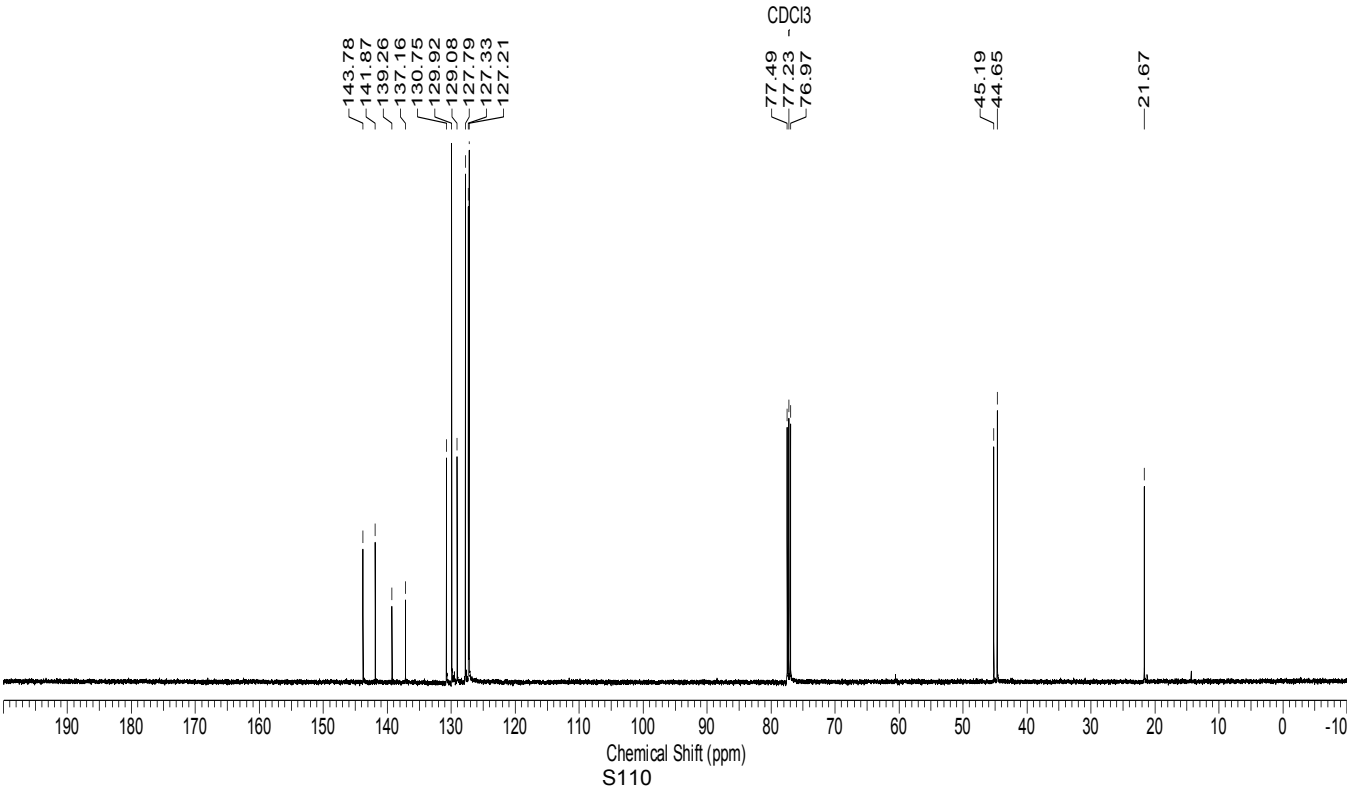

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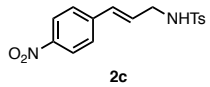
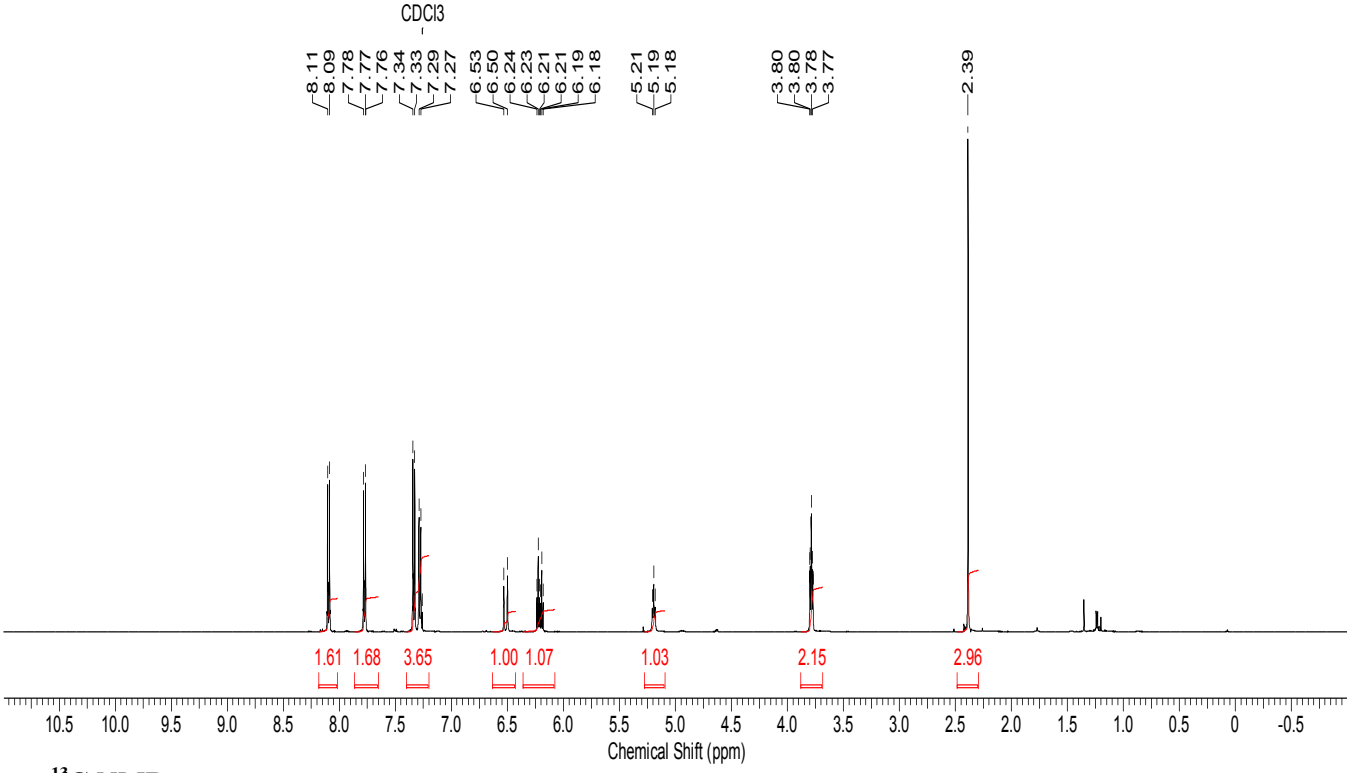
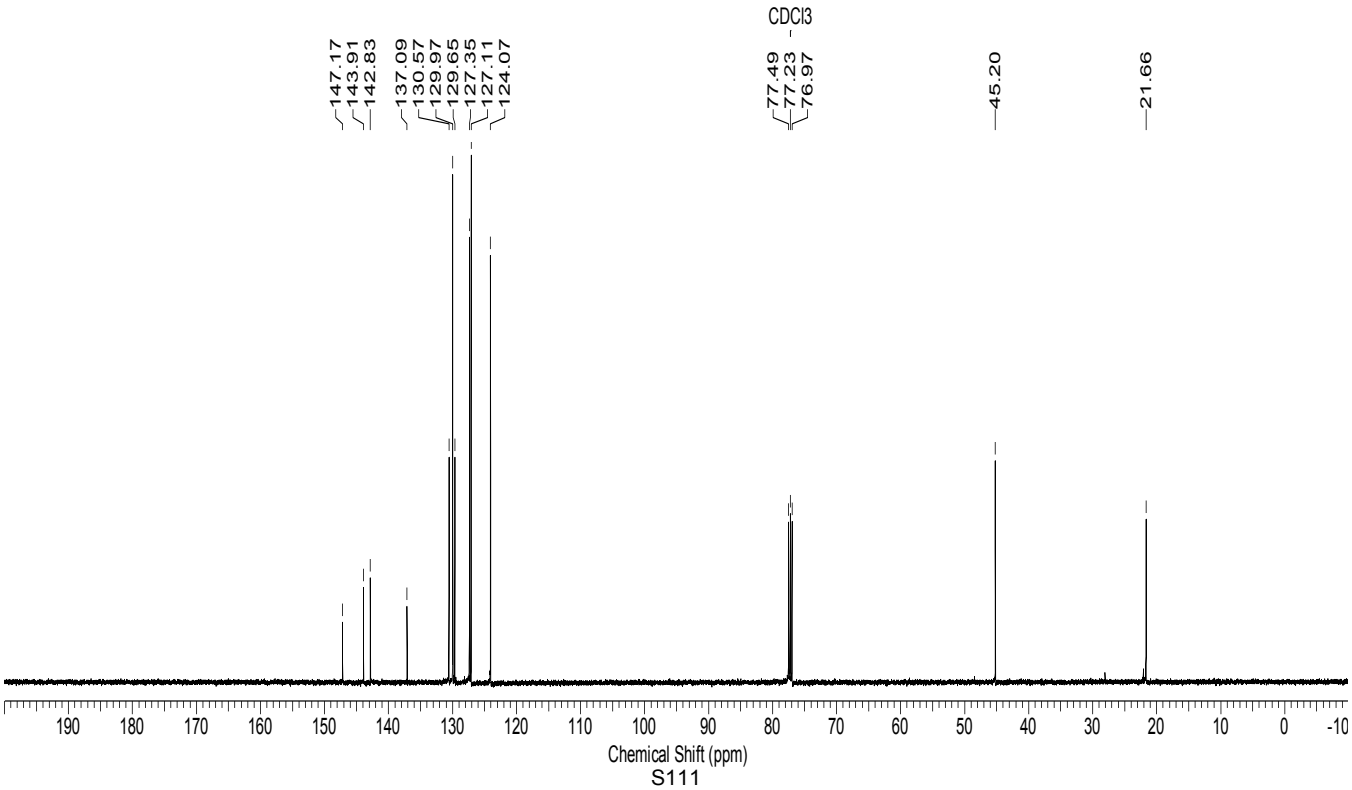


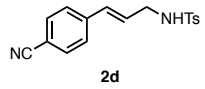
2c



^{13}C NMR
125.7 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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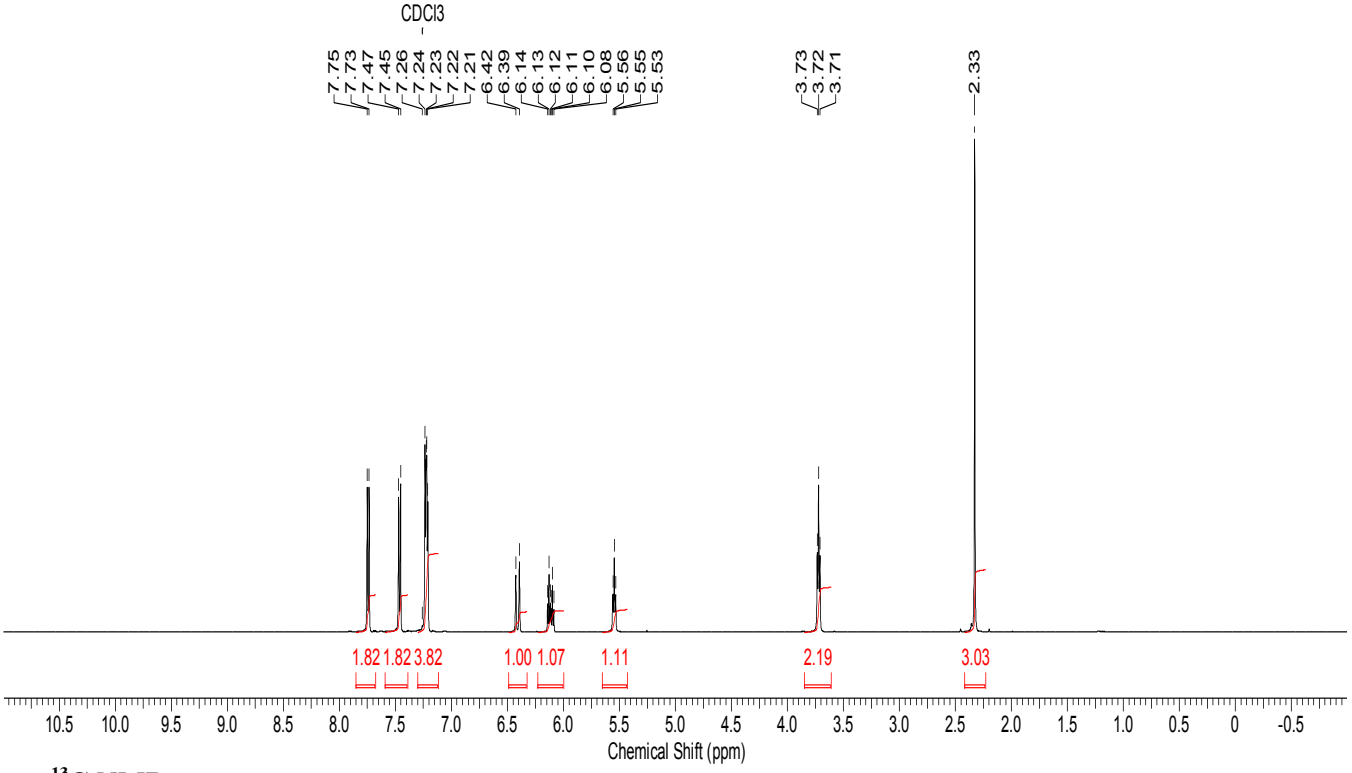
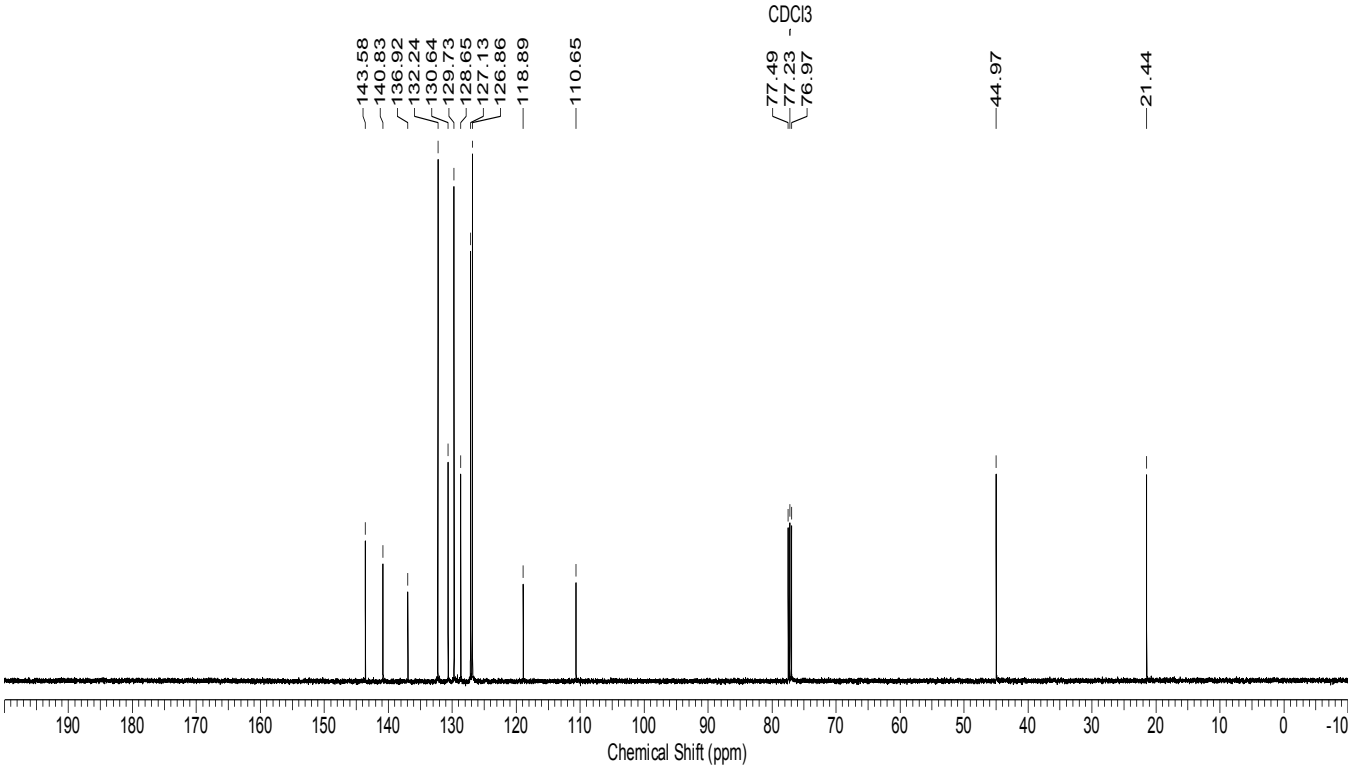
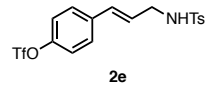


^{13}C NMR
125.7 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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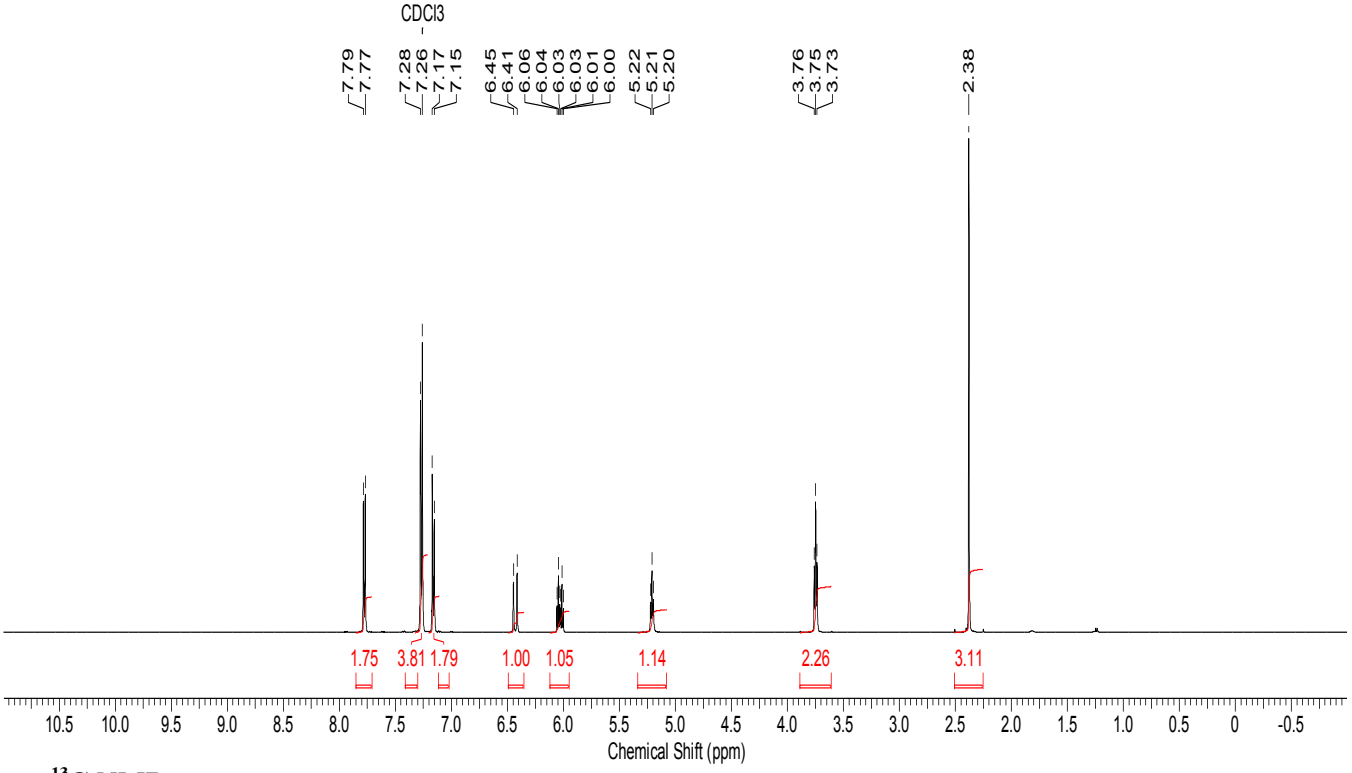
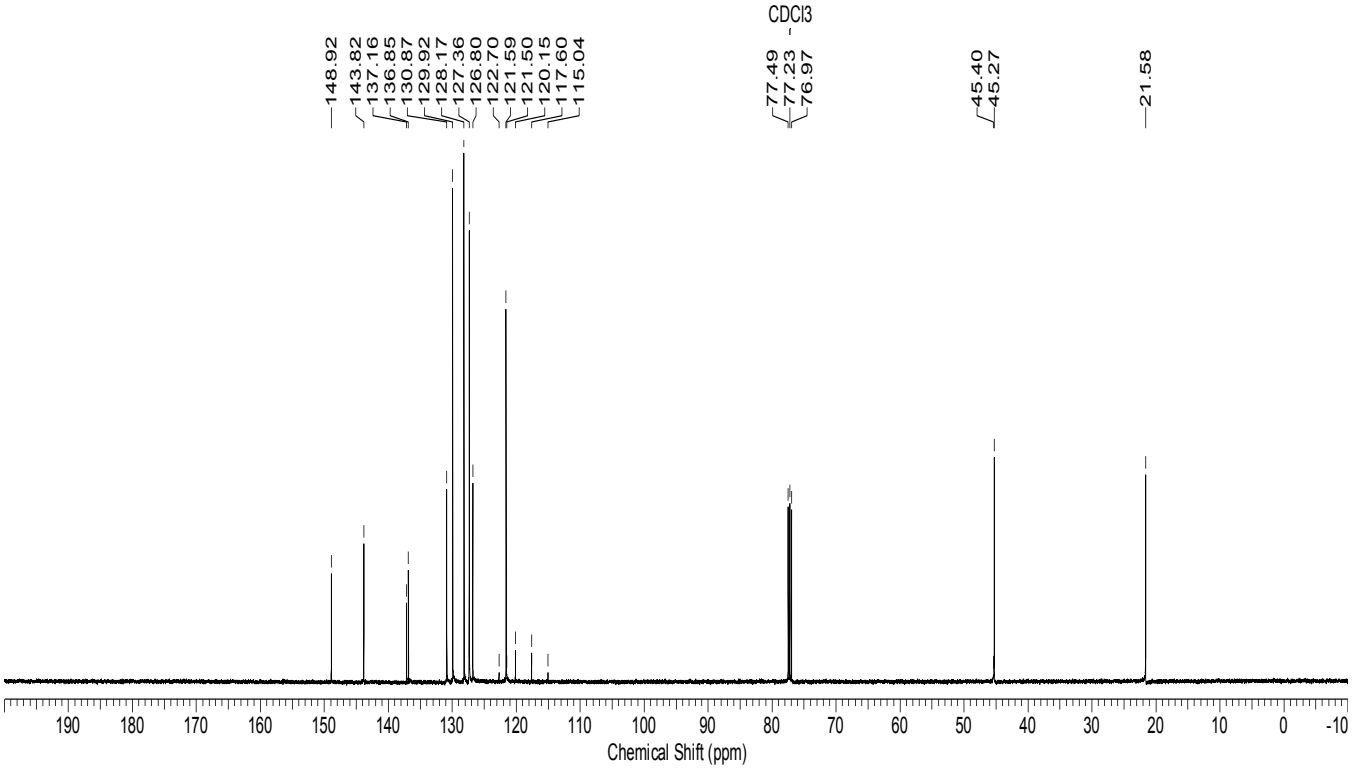
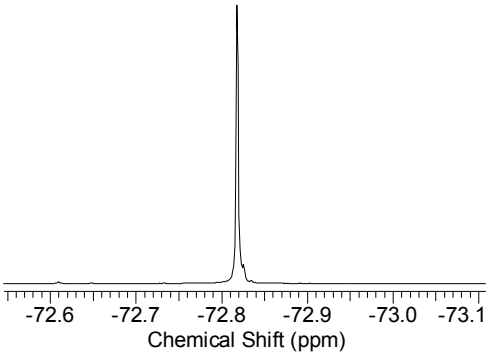


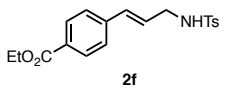
^{13}C NMR
125.7 MHz
$CDCl_3$



^{19}F NMR
470.4 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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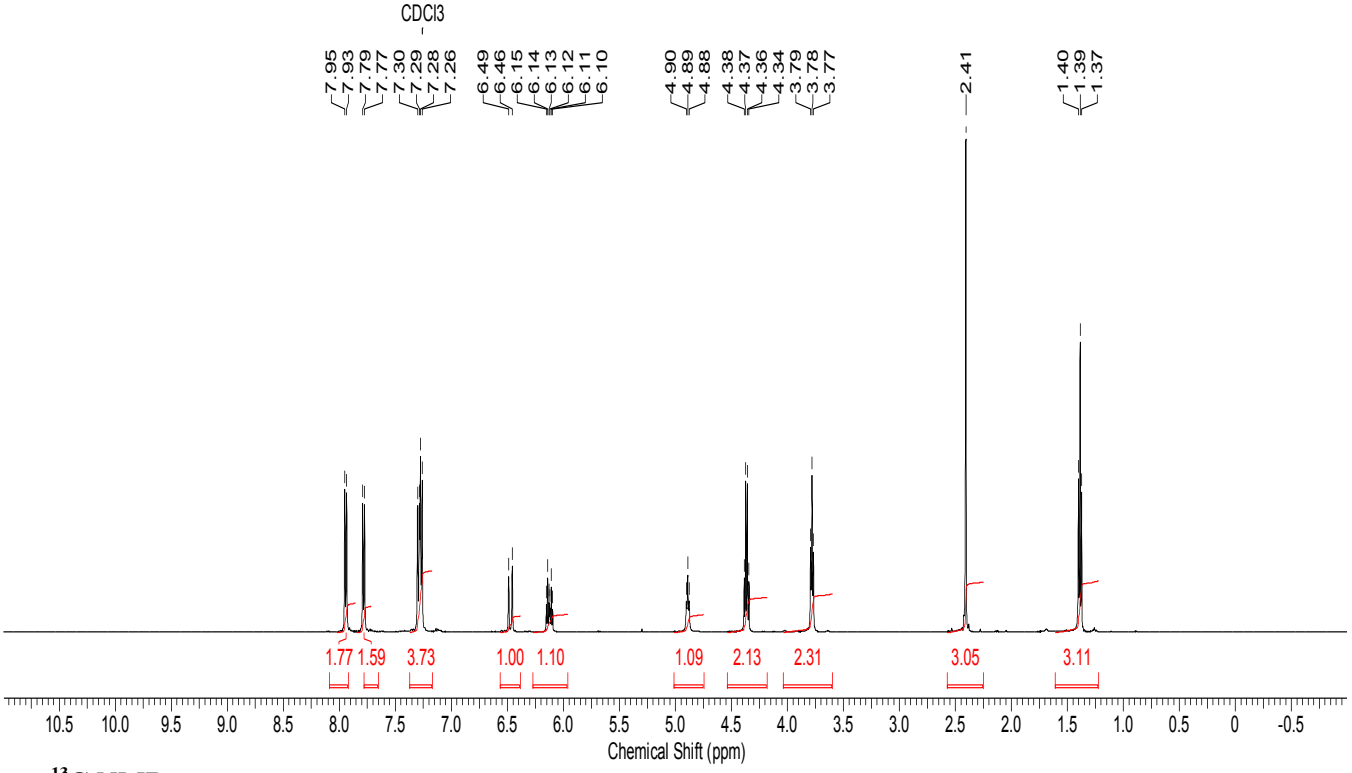
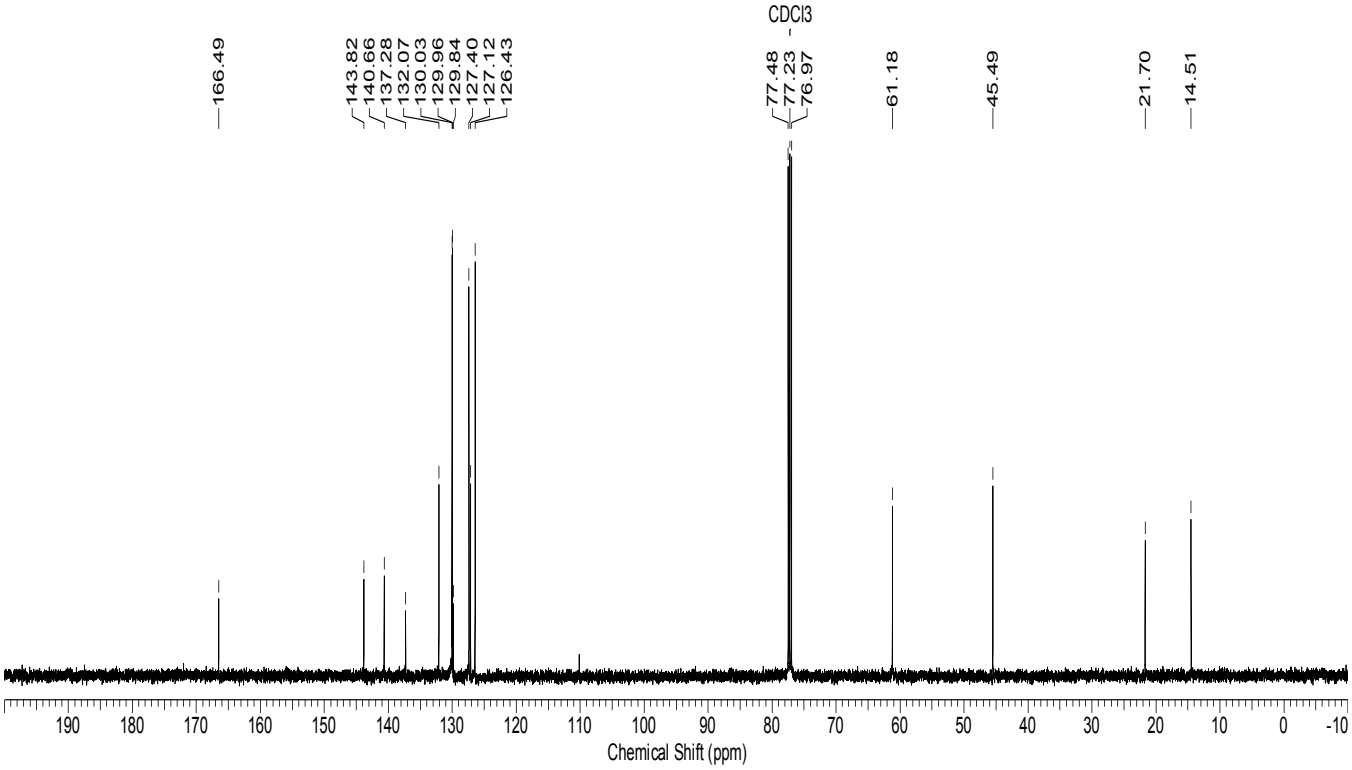
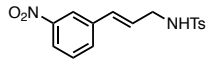


^{13}C NMR
125.7 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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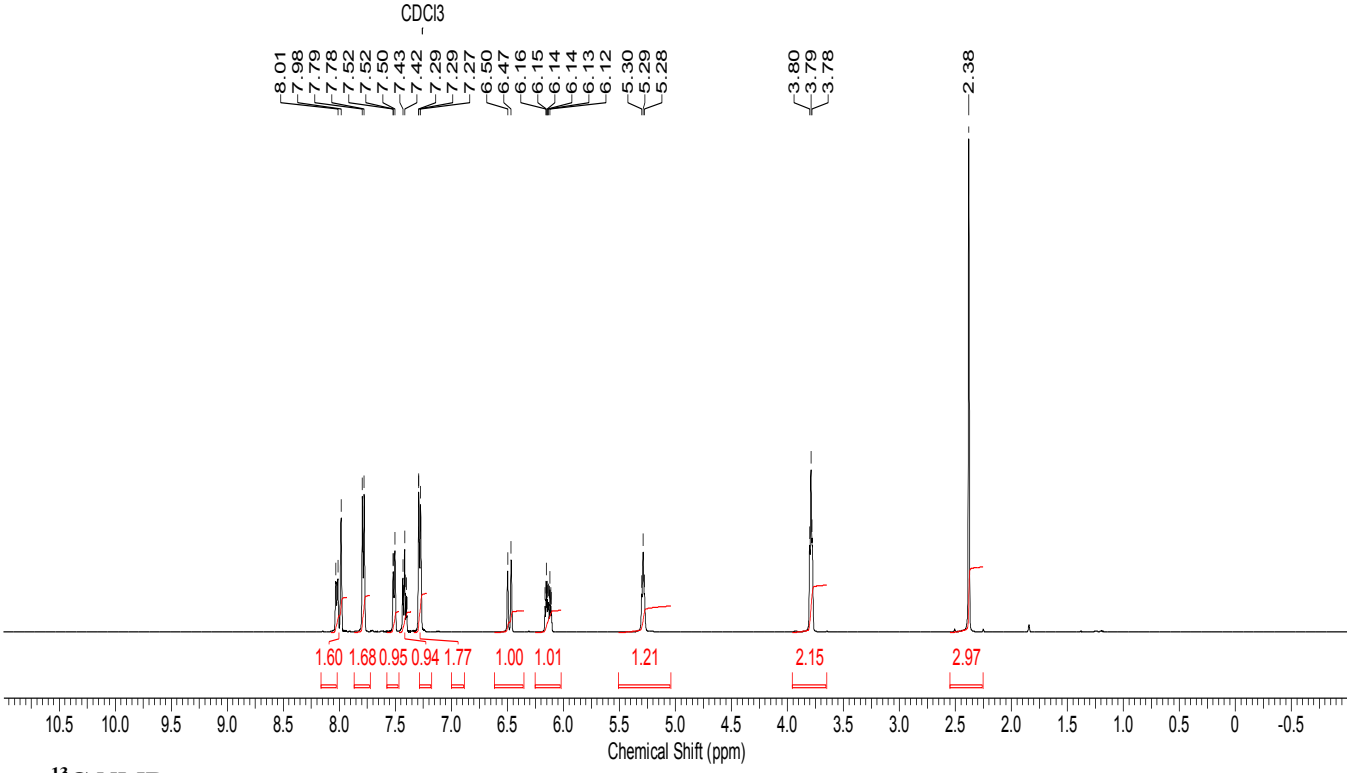
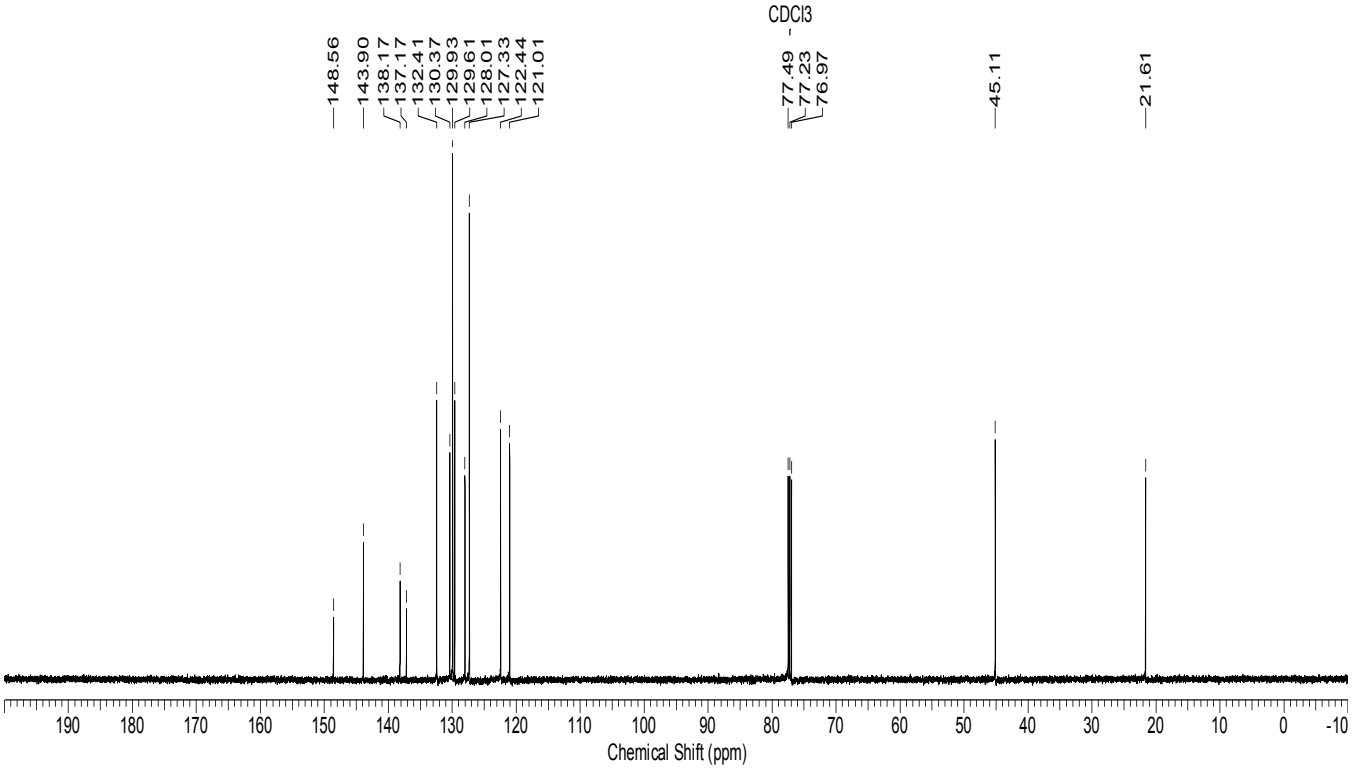
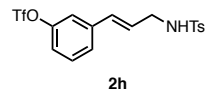


^{13}C NMR
125.7 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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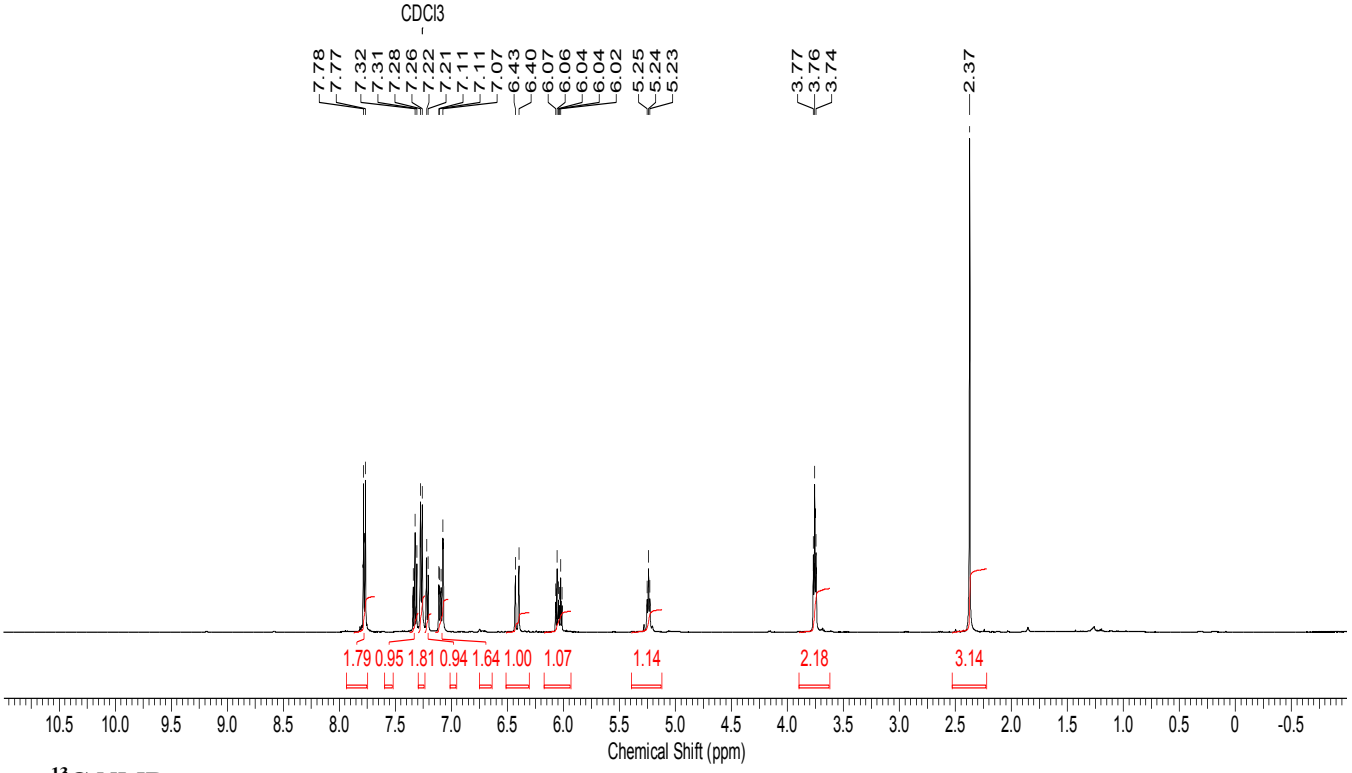
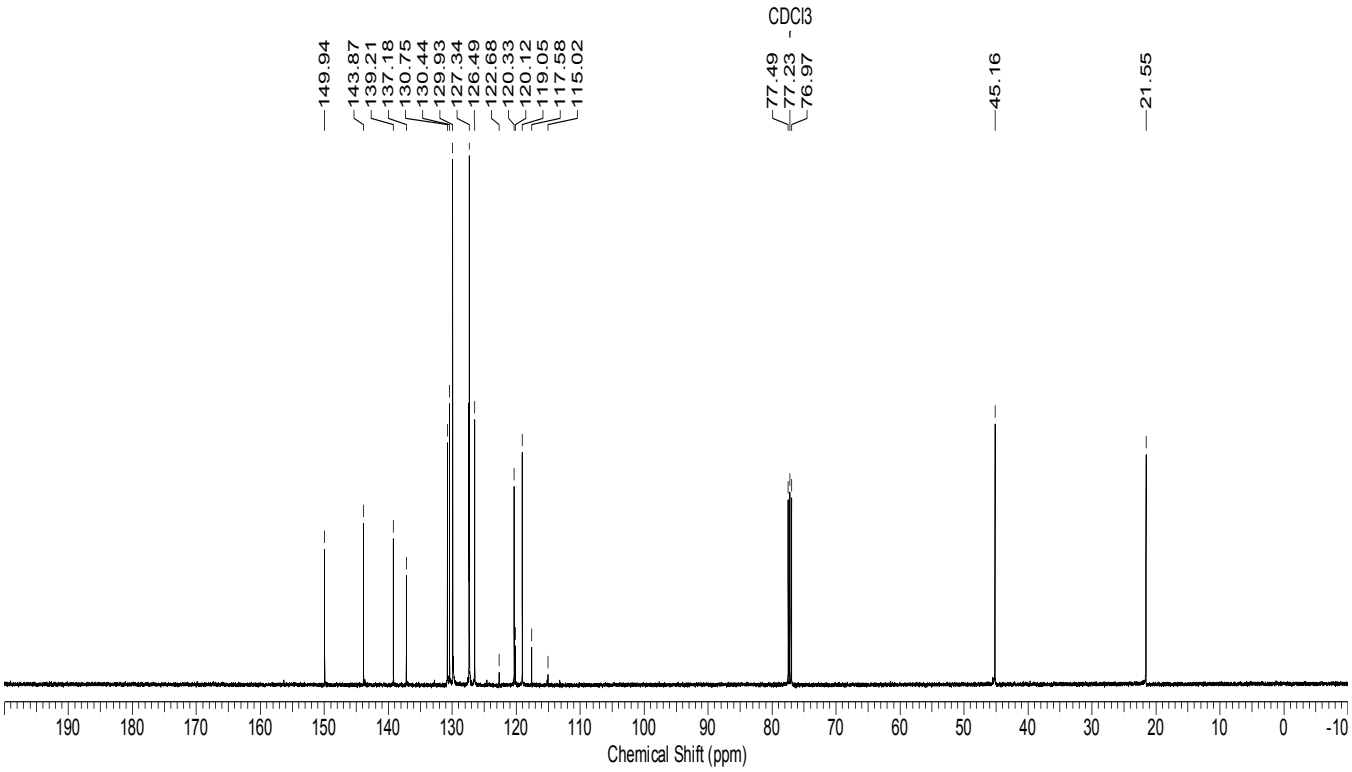
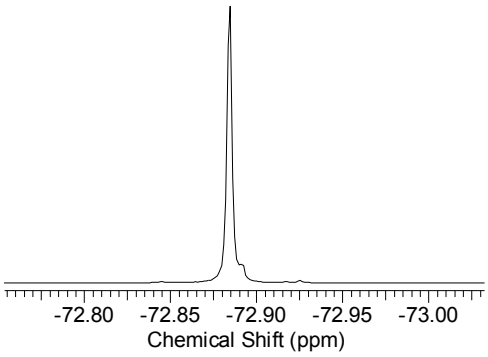


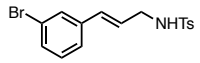
^{13}C NMR
125.7 MHz
$CDCl_3$



^{19}F NMR
470.4 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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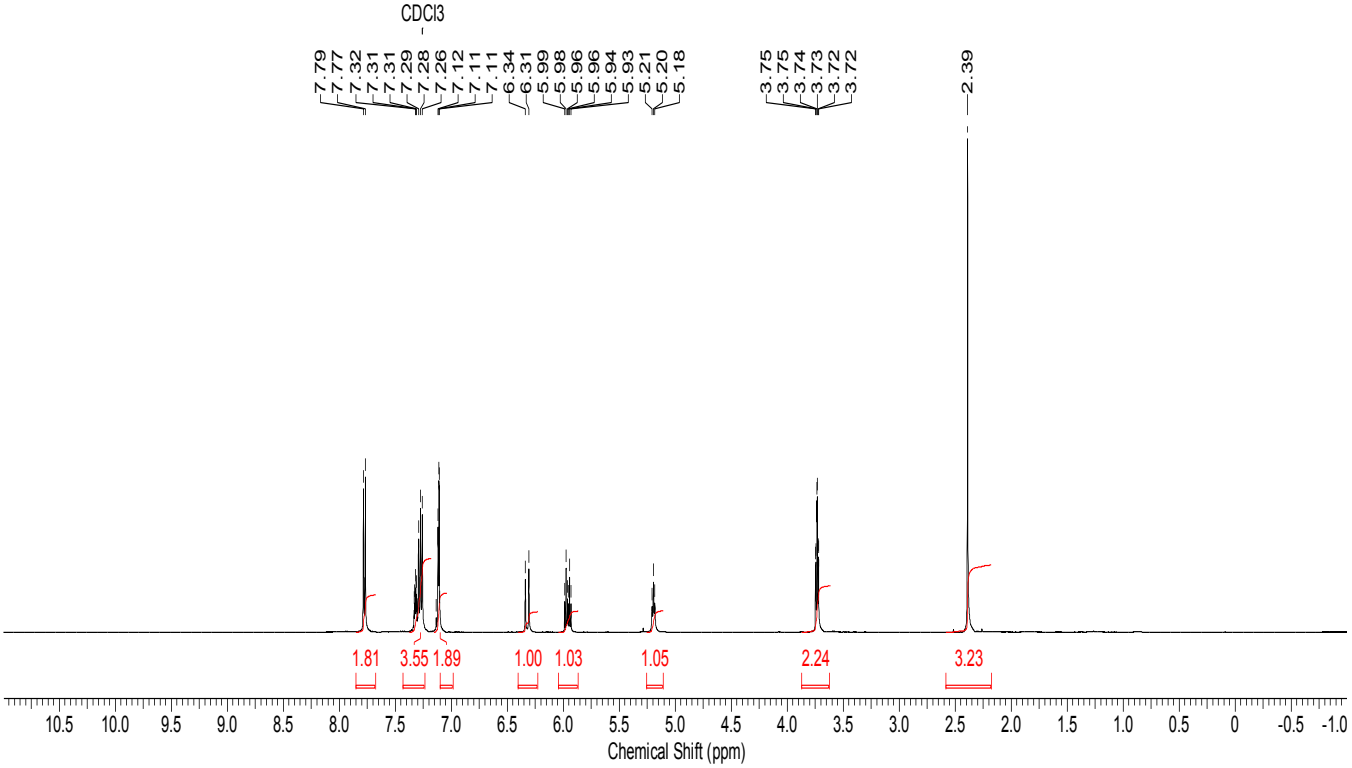
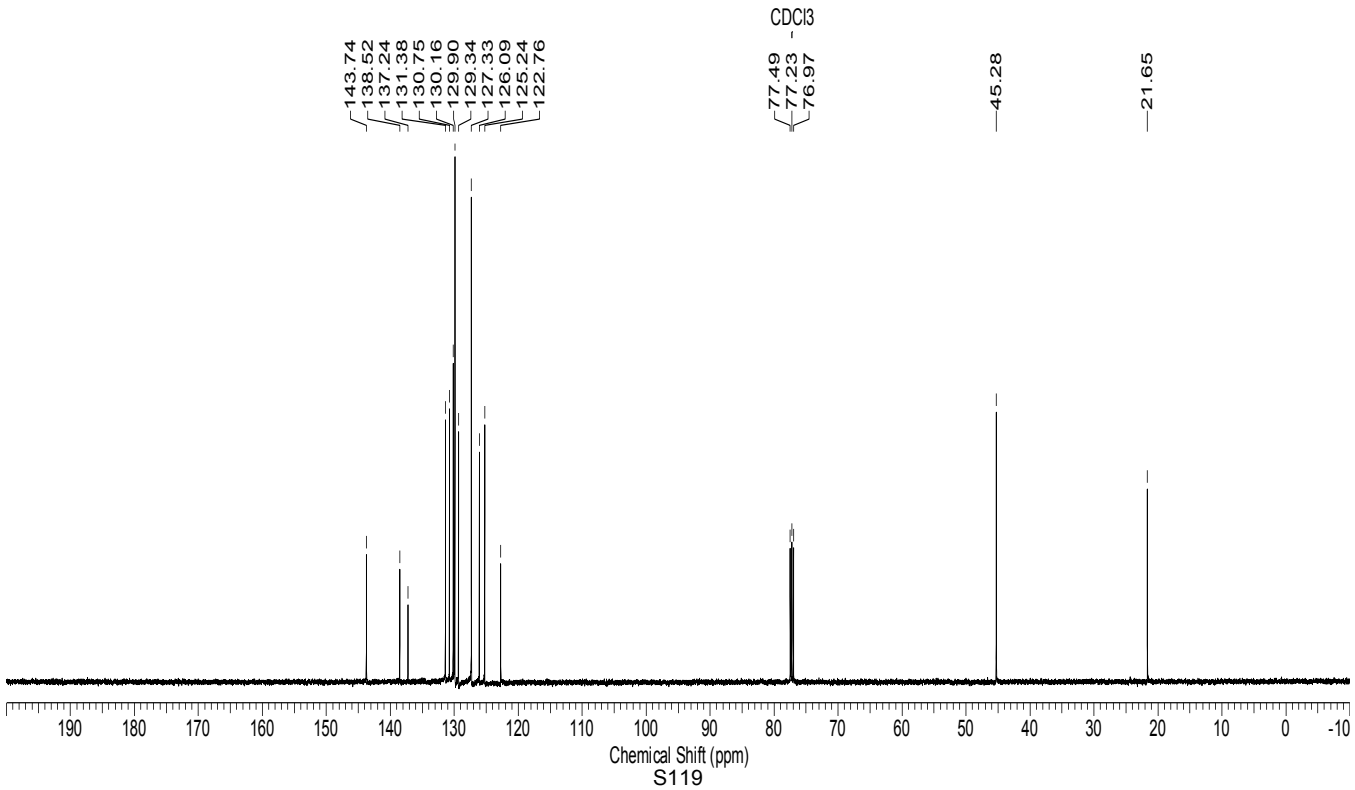
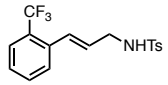


^{13}C NMR
125.7 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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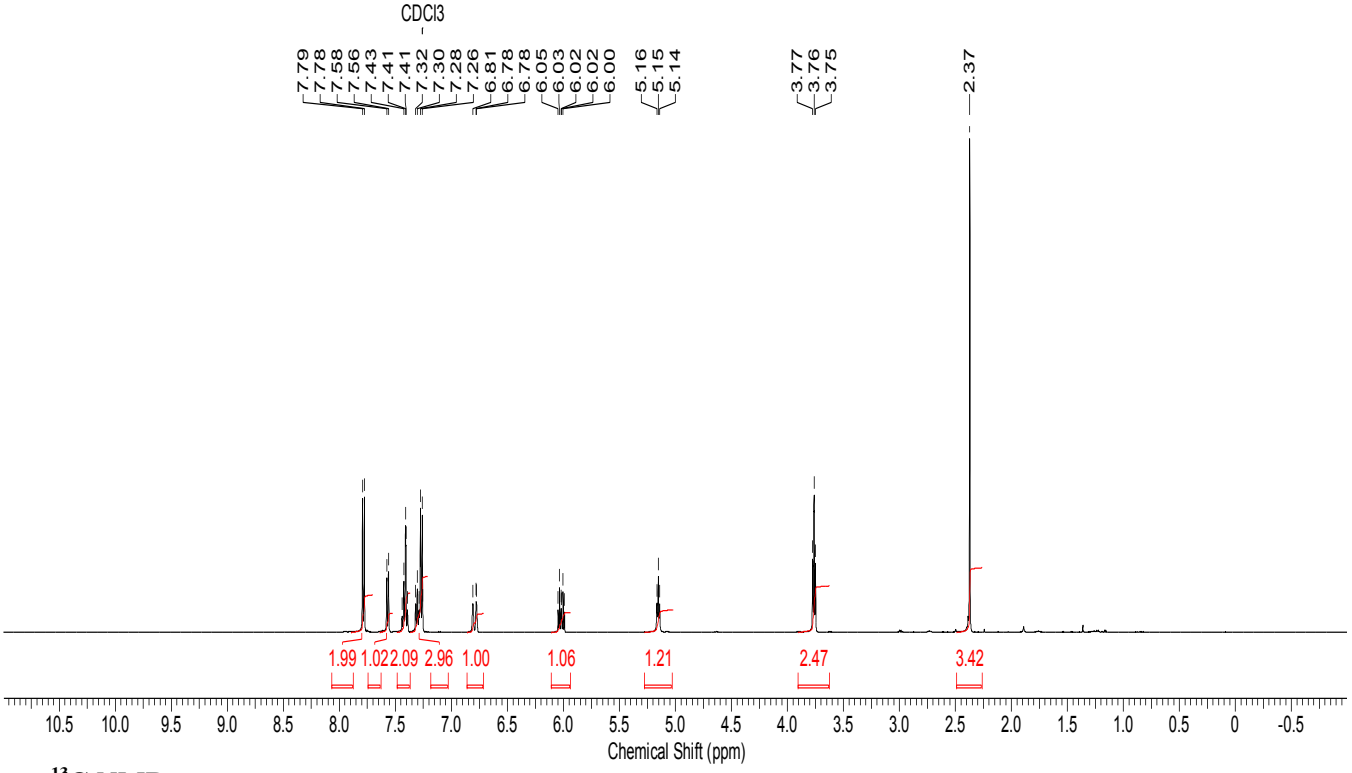
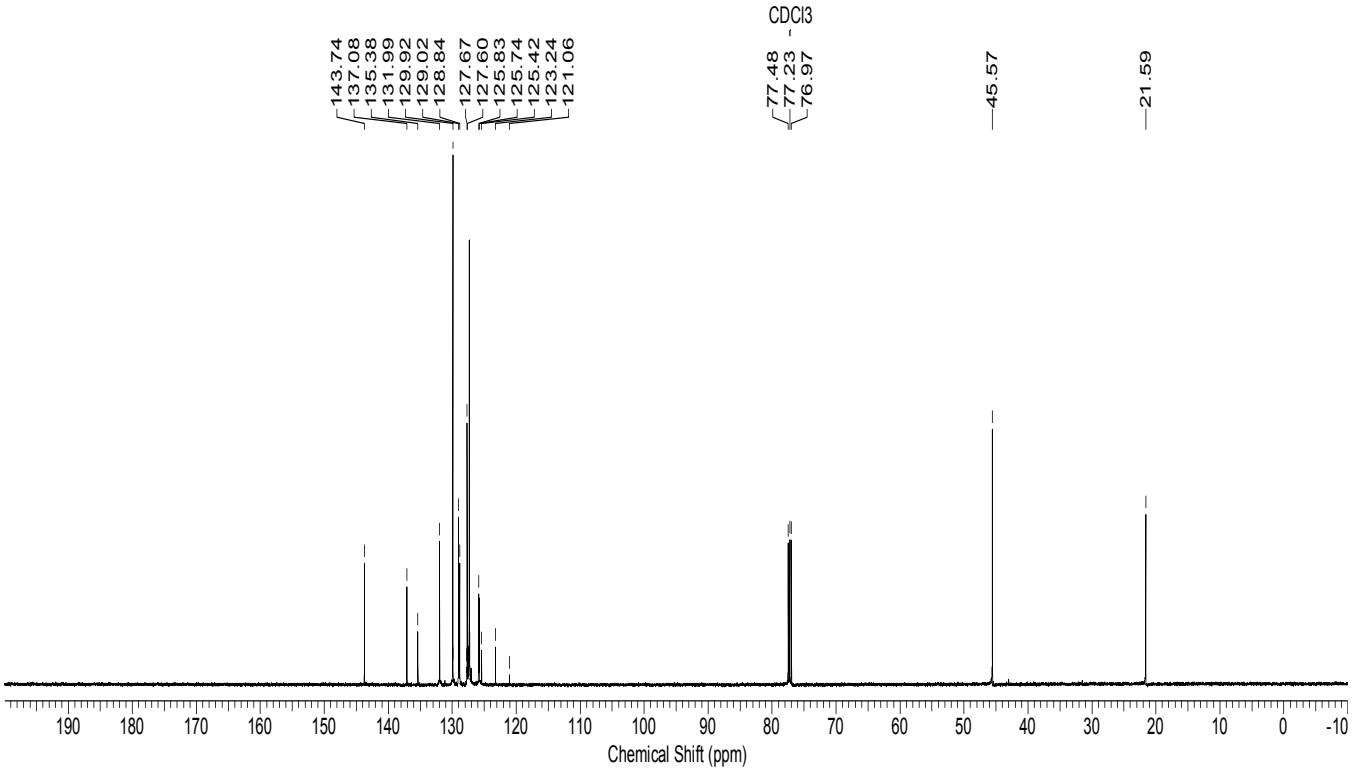
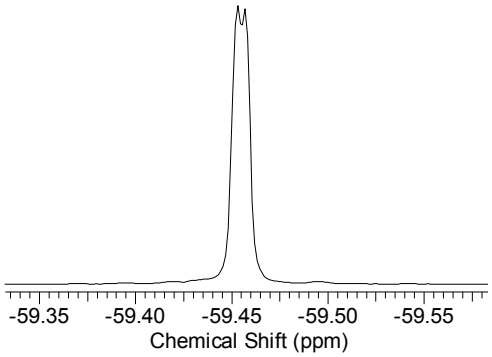


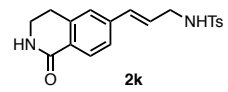
^{13}C NMR
125.7 MHz
$CDCl_3$



^{19}F NMR
470.4 MHz
$CDCl_3$



^{1}H NMR
500 MHz
DMSO-*d*$_6$



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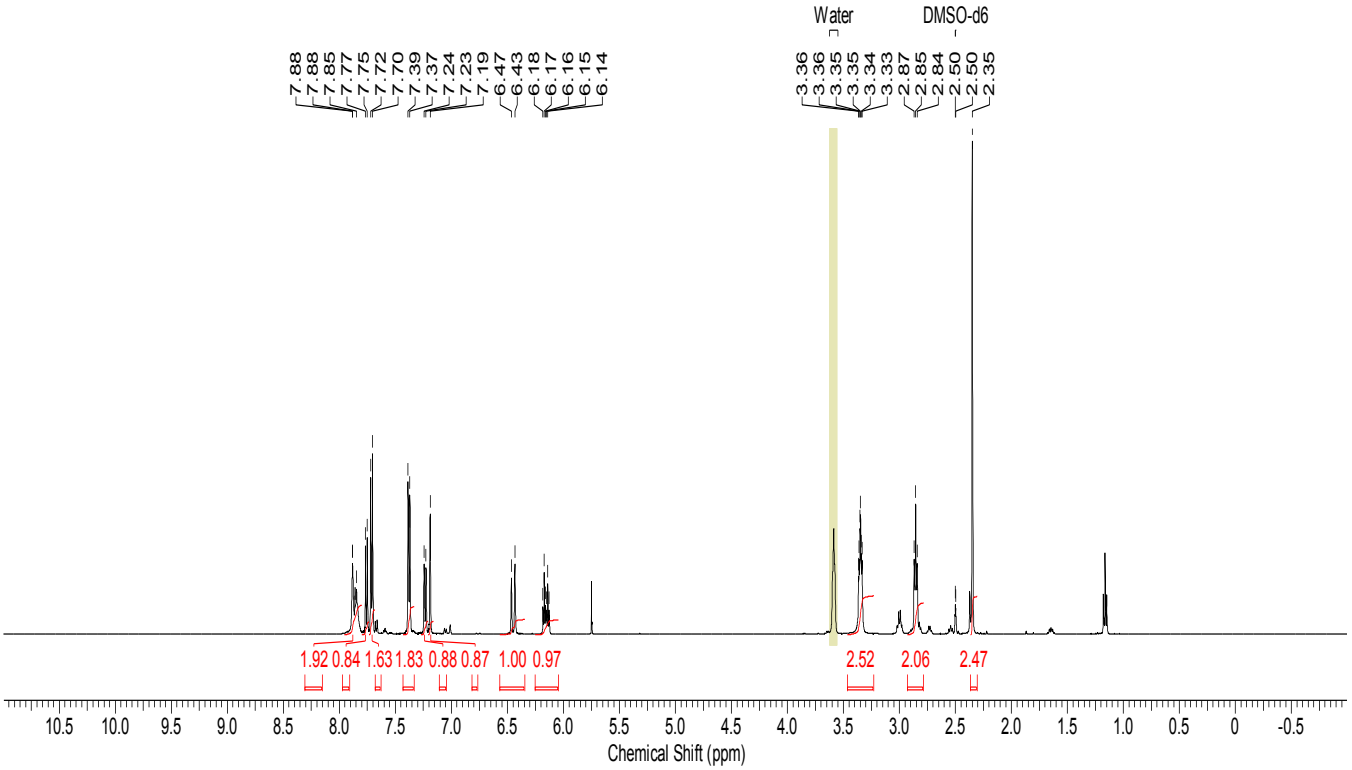
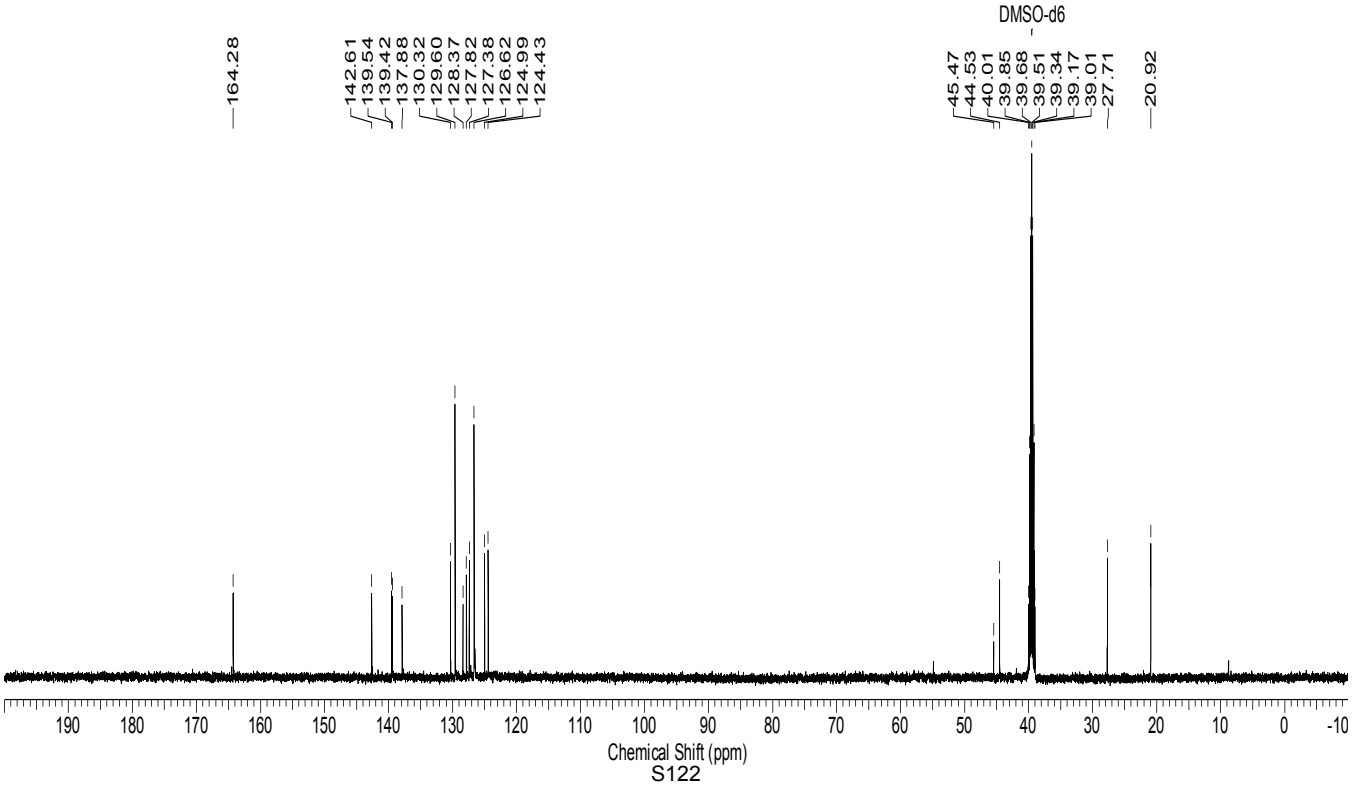
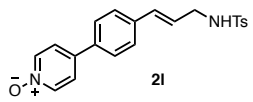
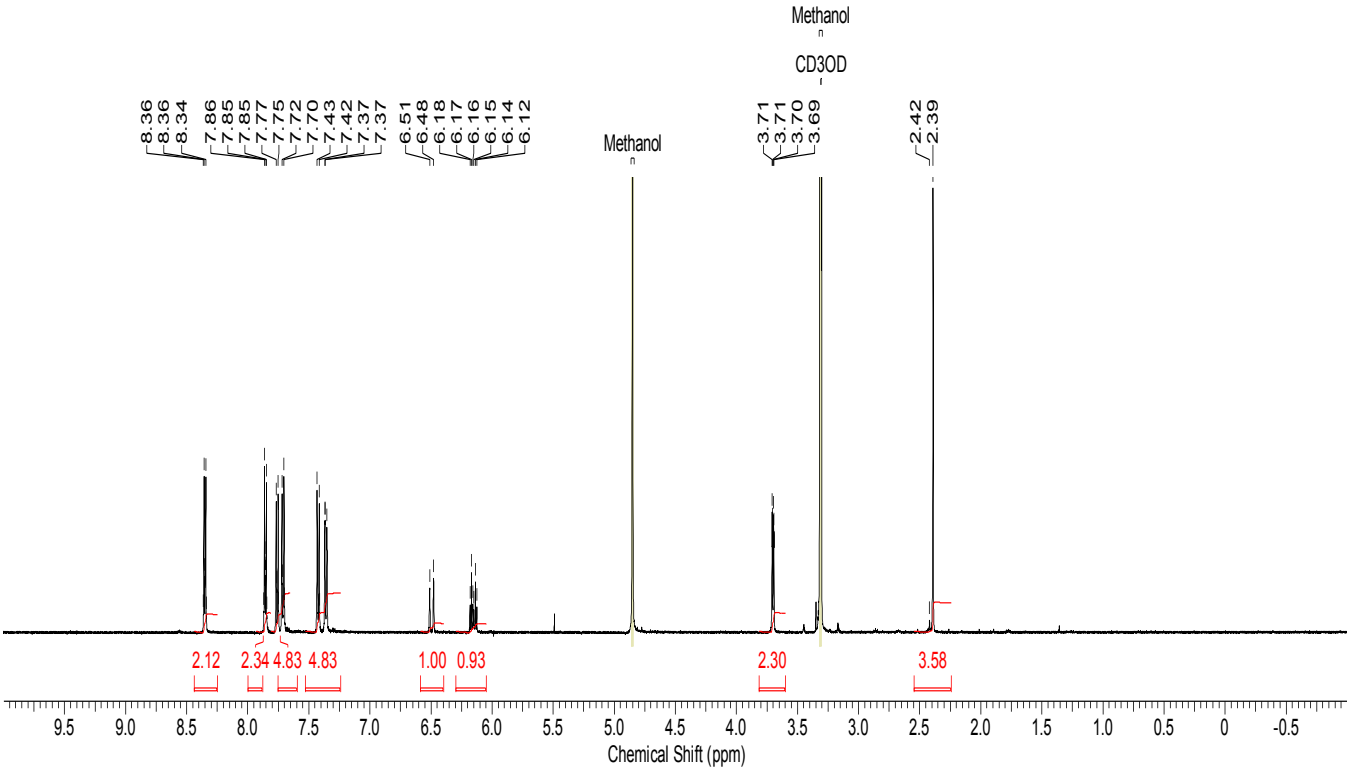


^{13}C NMR
125.7 MHz
DMSO-*d*$_6$

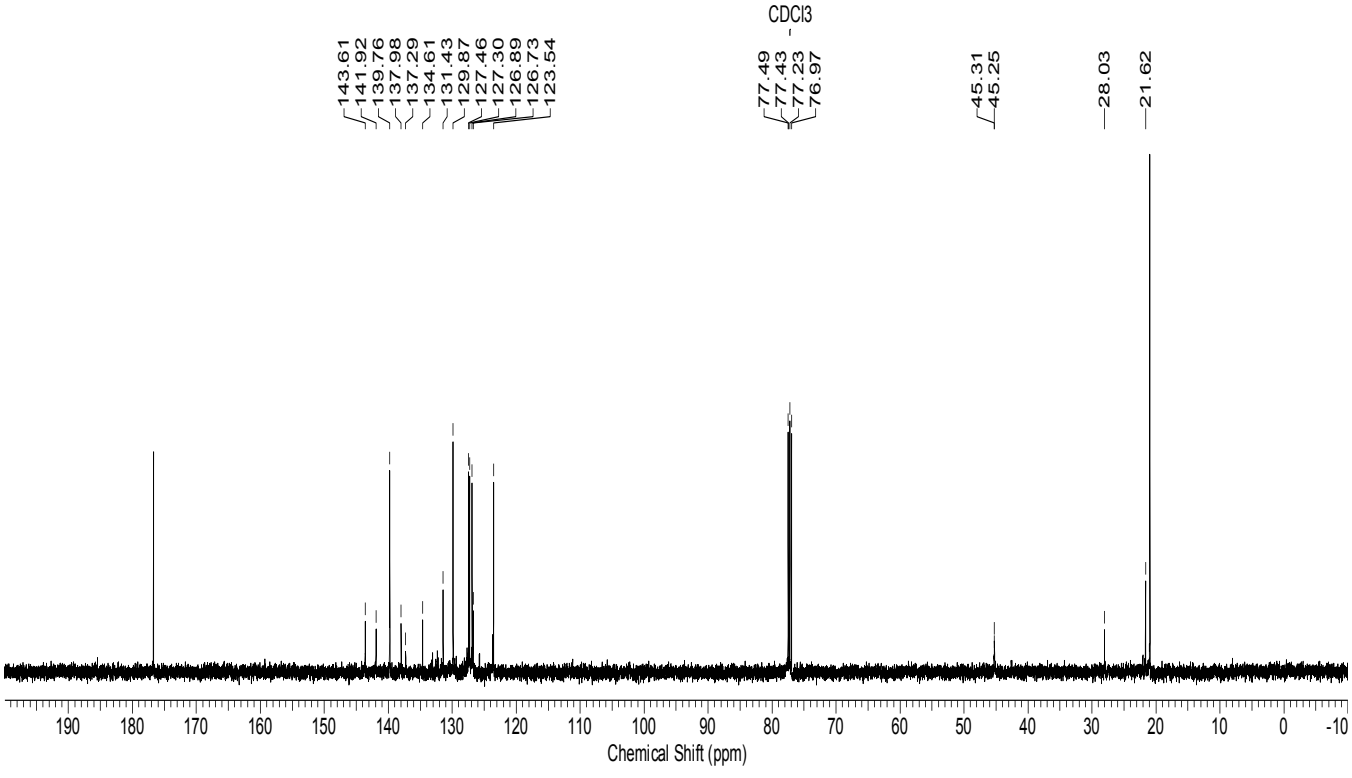


^{1}H NMR
500 MHz
CD_3OD

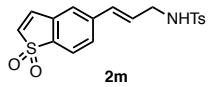


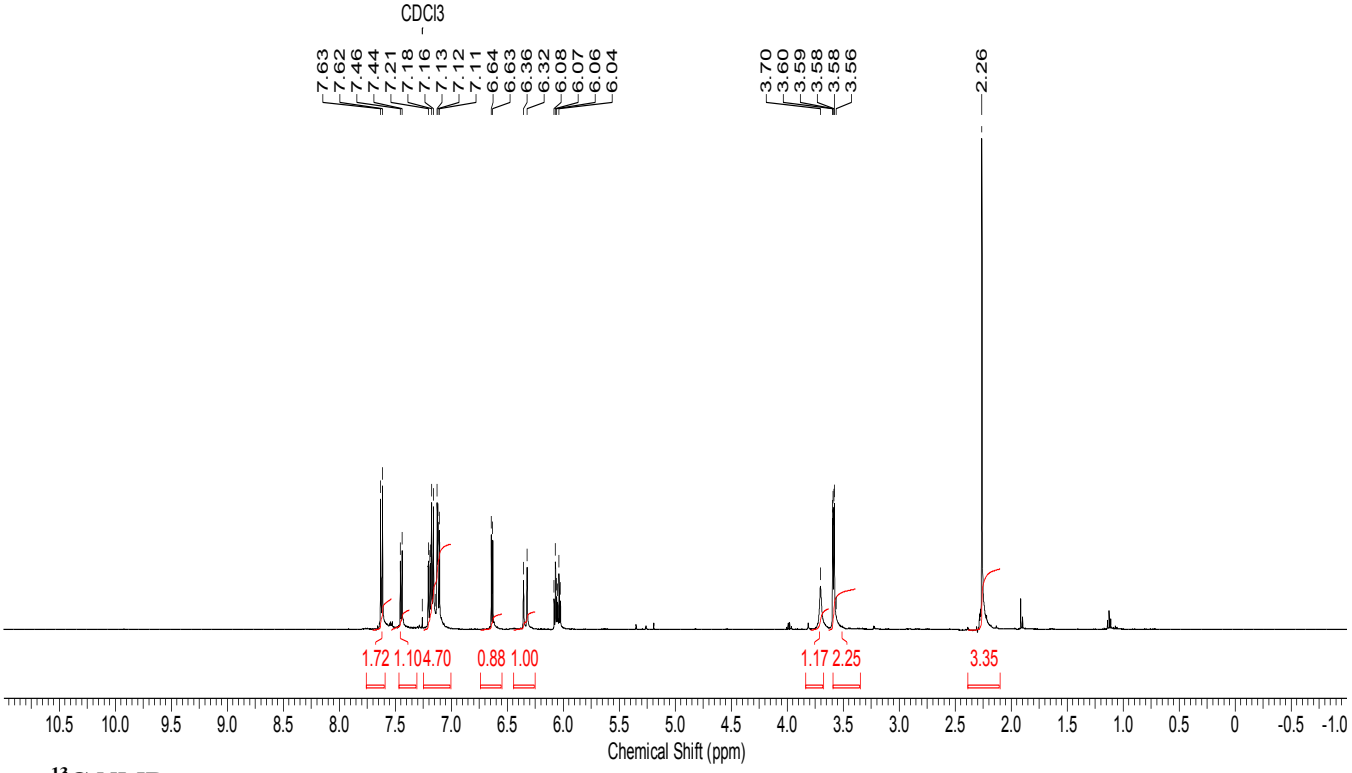


^{13}C NMR
125.7 MHz
5% $CH_3CO_2D/CDCl_3$

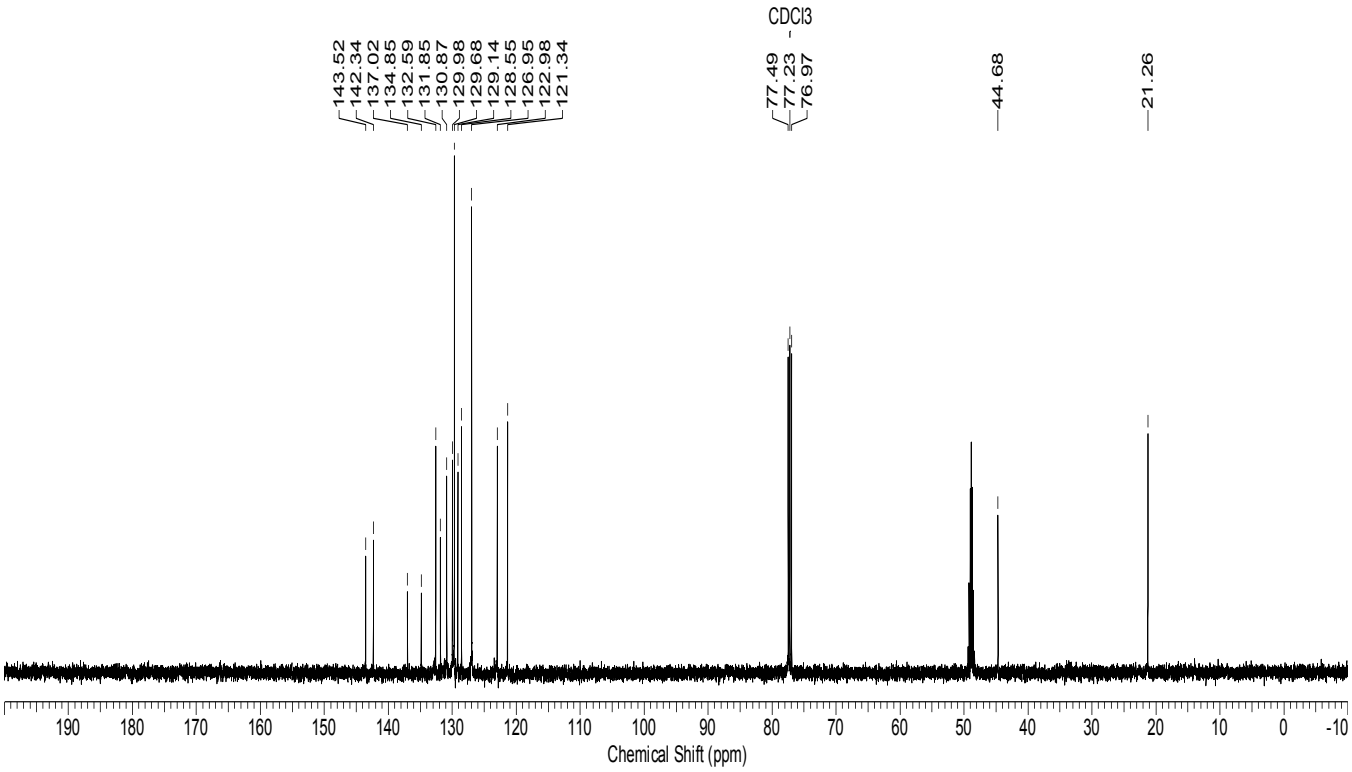


^{1}H NMR
500 MHz
10% $CD_3OD/CDCl_3$

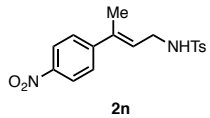




^{13}C NMR
125.7 MHz
10% $CD_3OD/CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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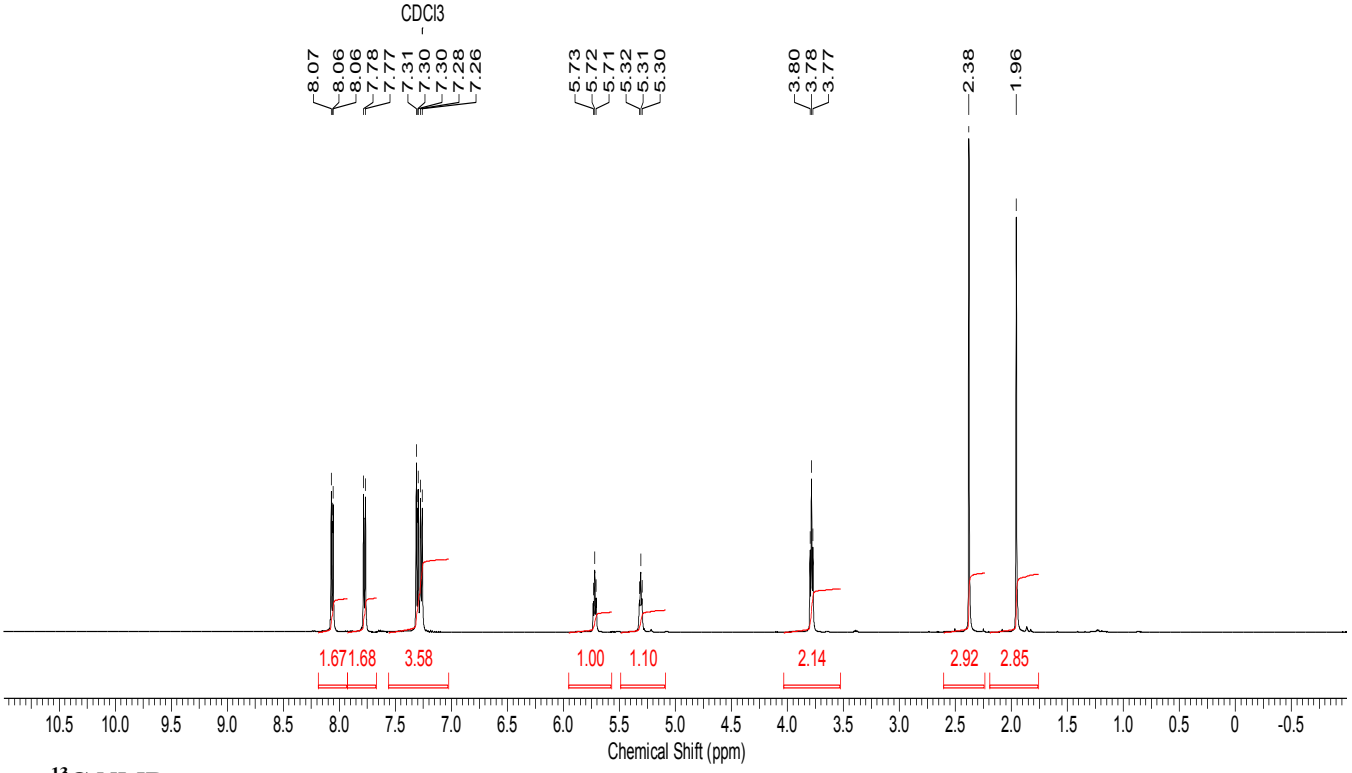
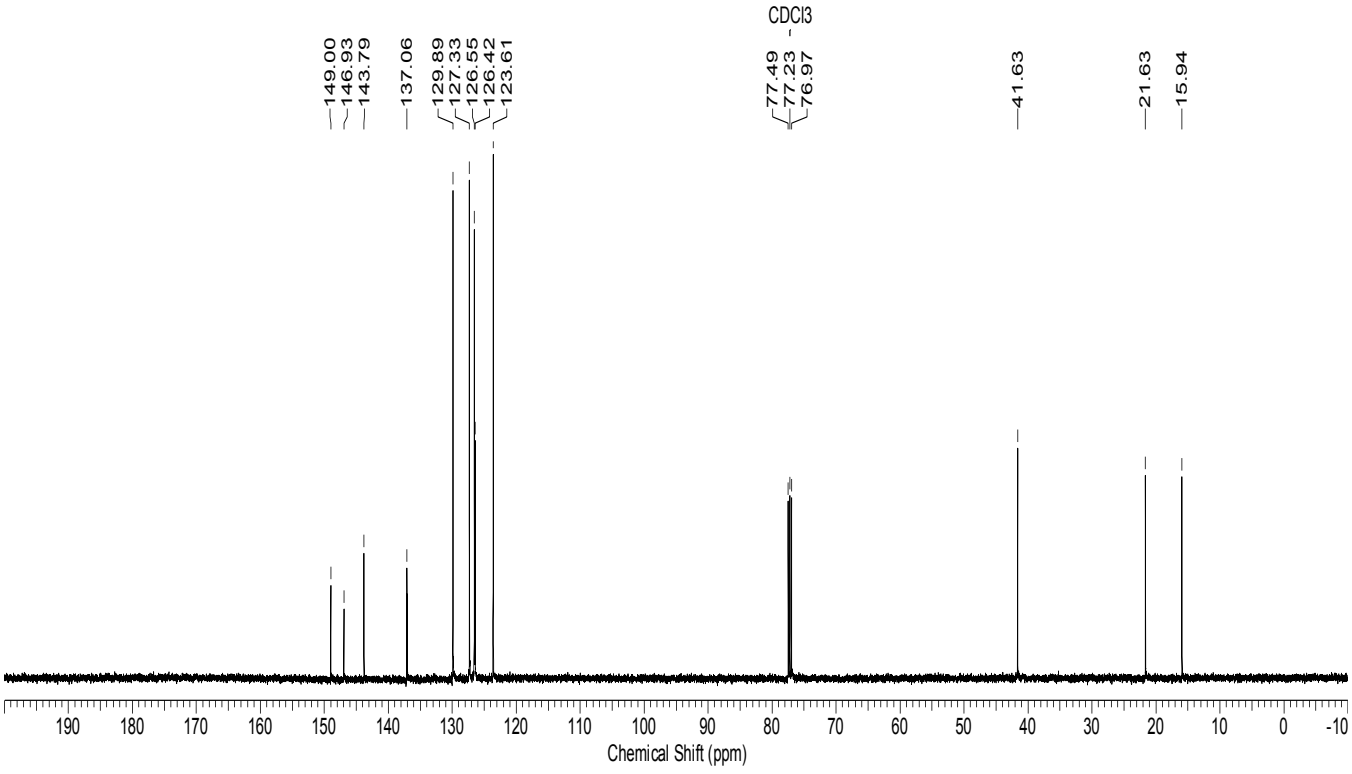
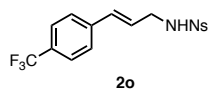


^{13}C NMR
125.7 MHz
$CDCl_3$



^{1}H NMR
500 MHz
DMSO-d_6



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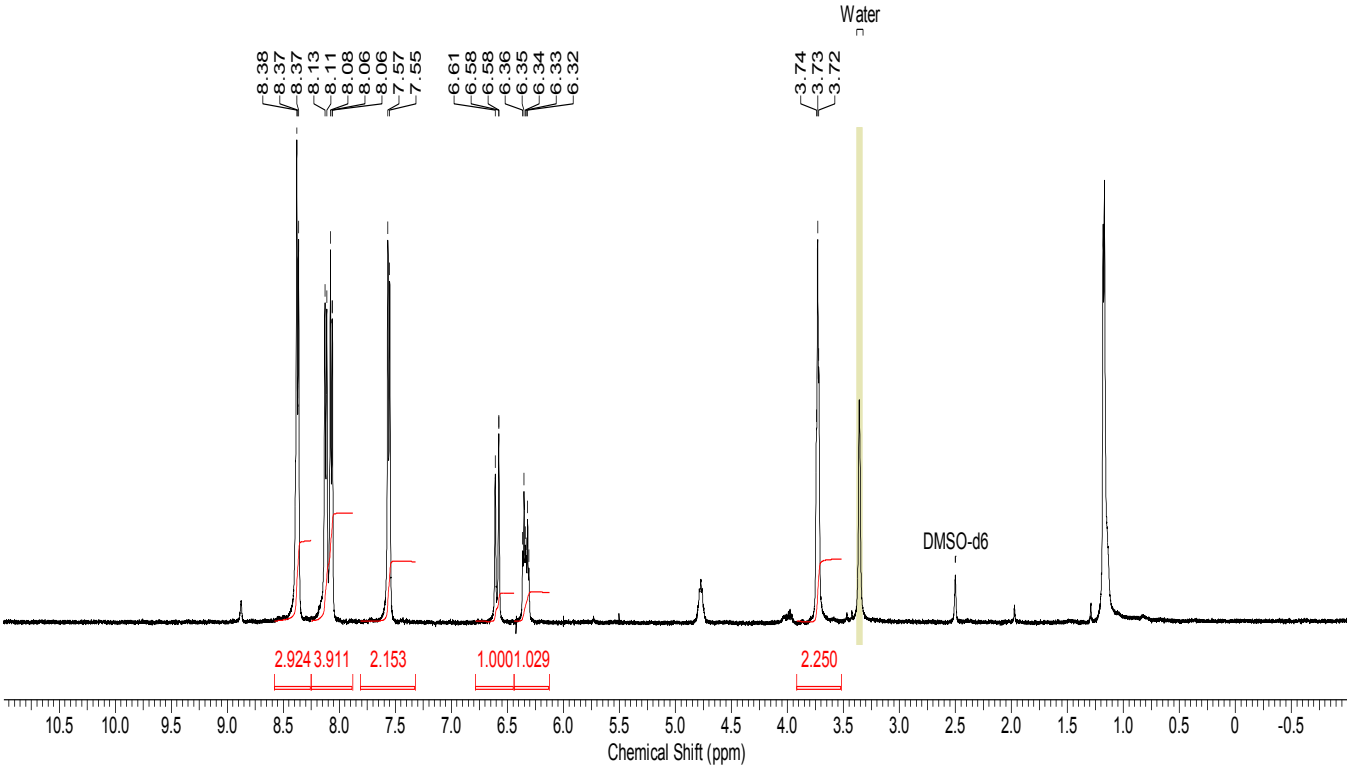
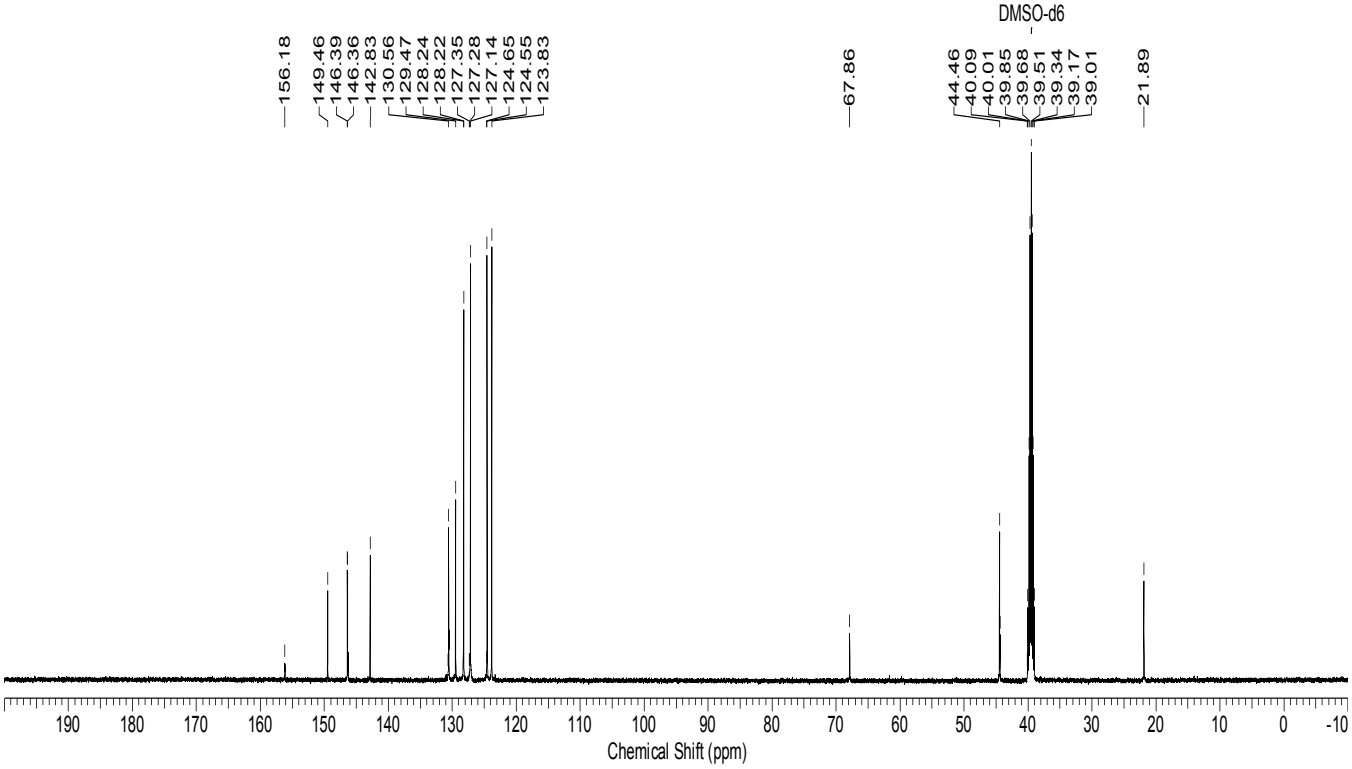
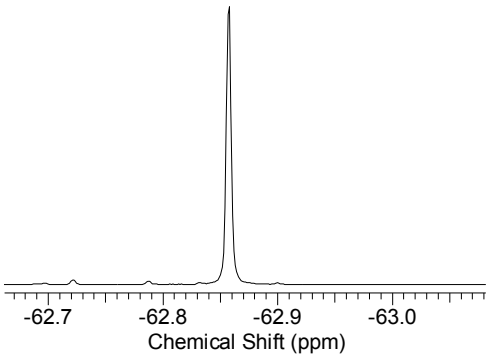


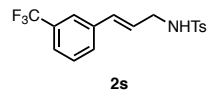
^{13}C NMR
125.7 MHz
DMSO-d_6



^{19}F NMR
470.4 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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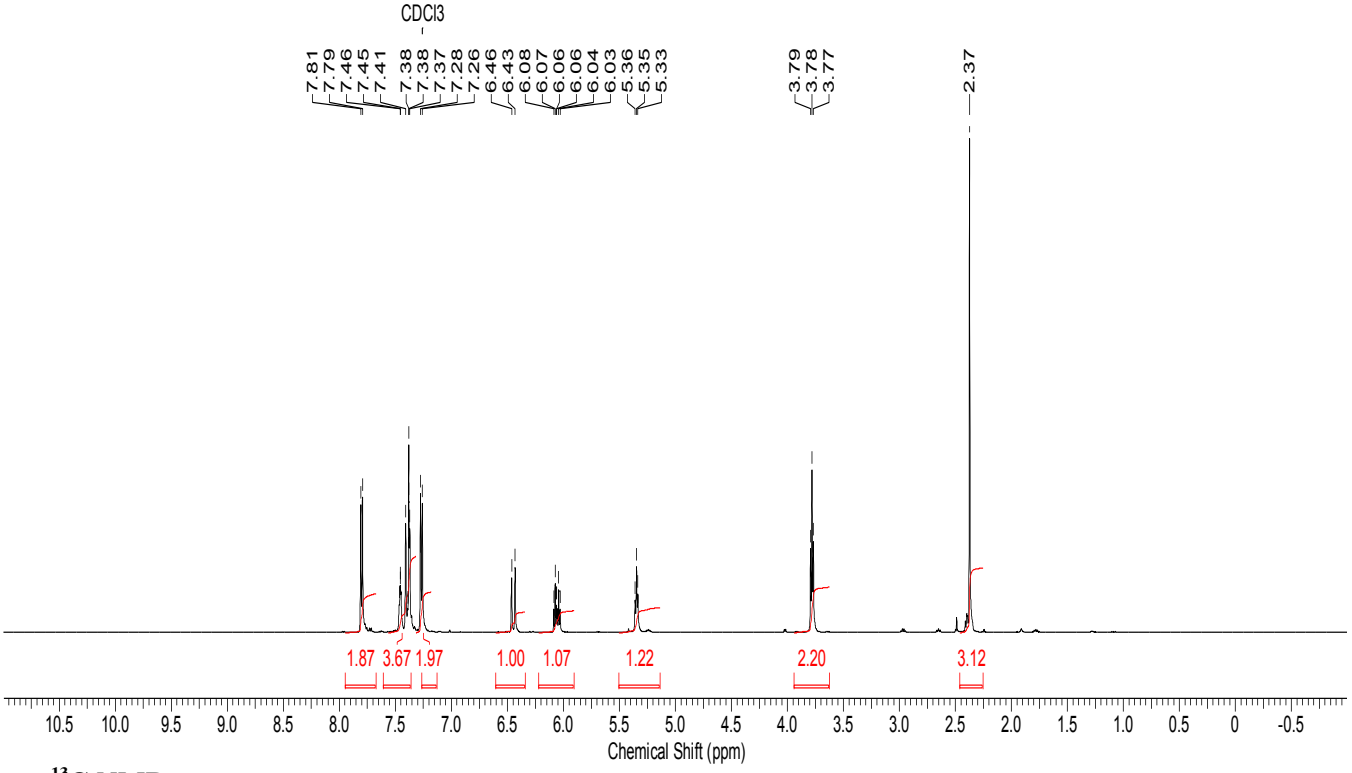
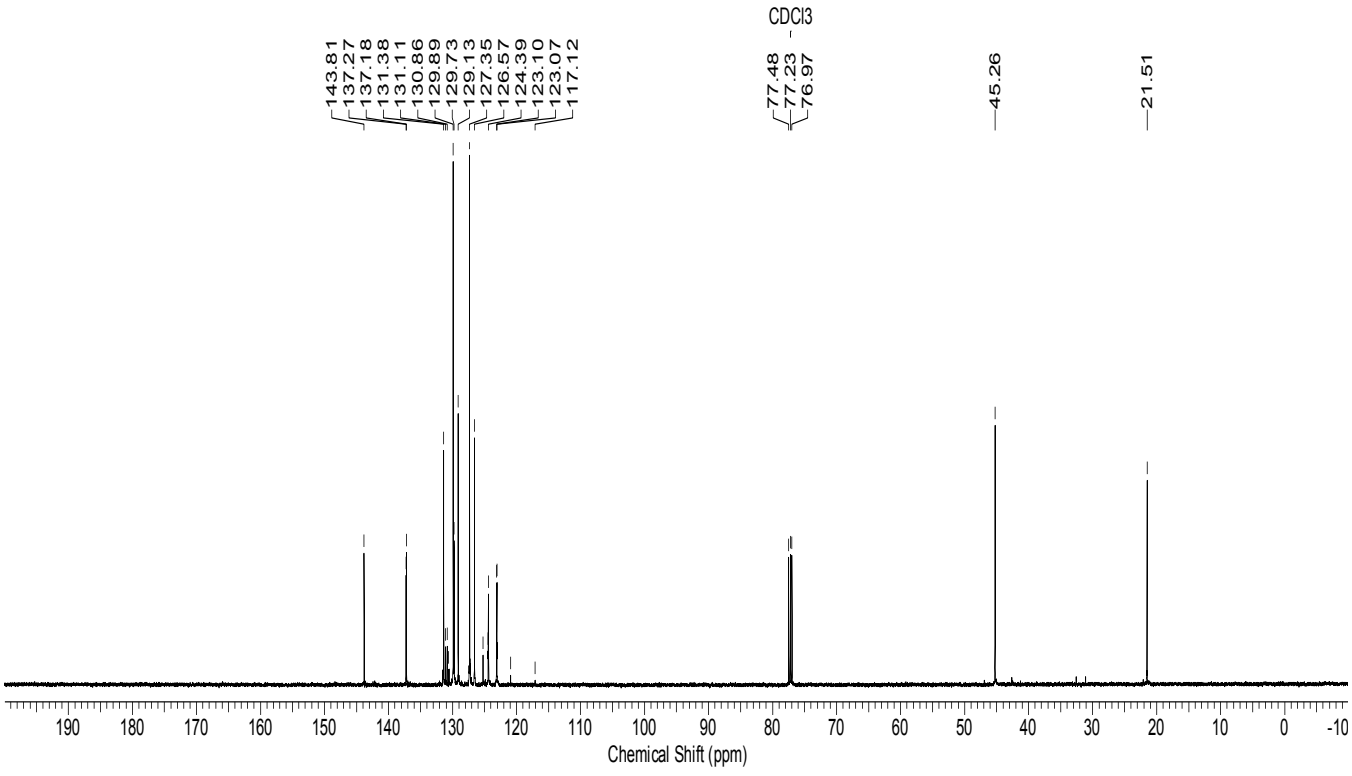
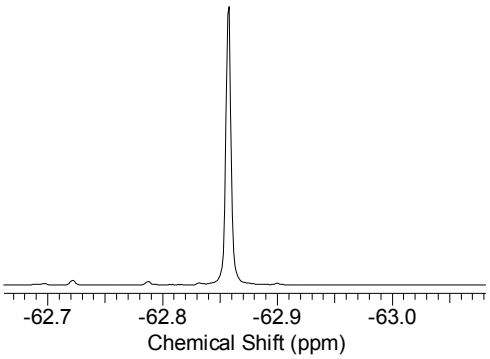


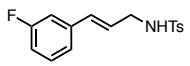
^{13}C NMR
125.7 MHz
$CDCl_3$



^{19}F NMR
470.4 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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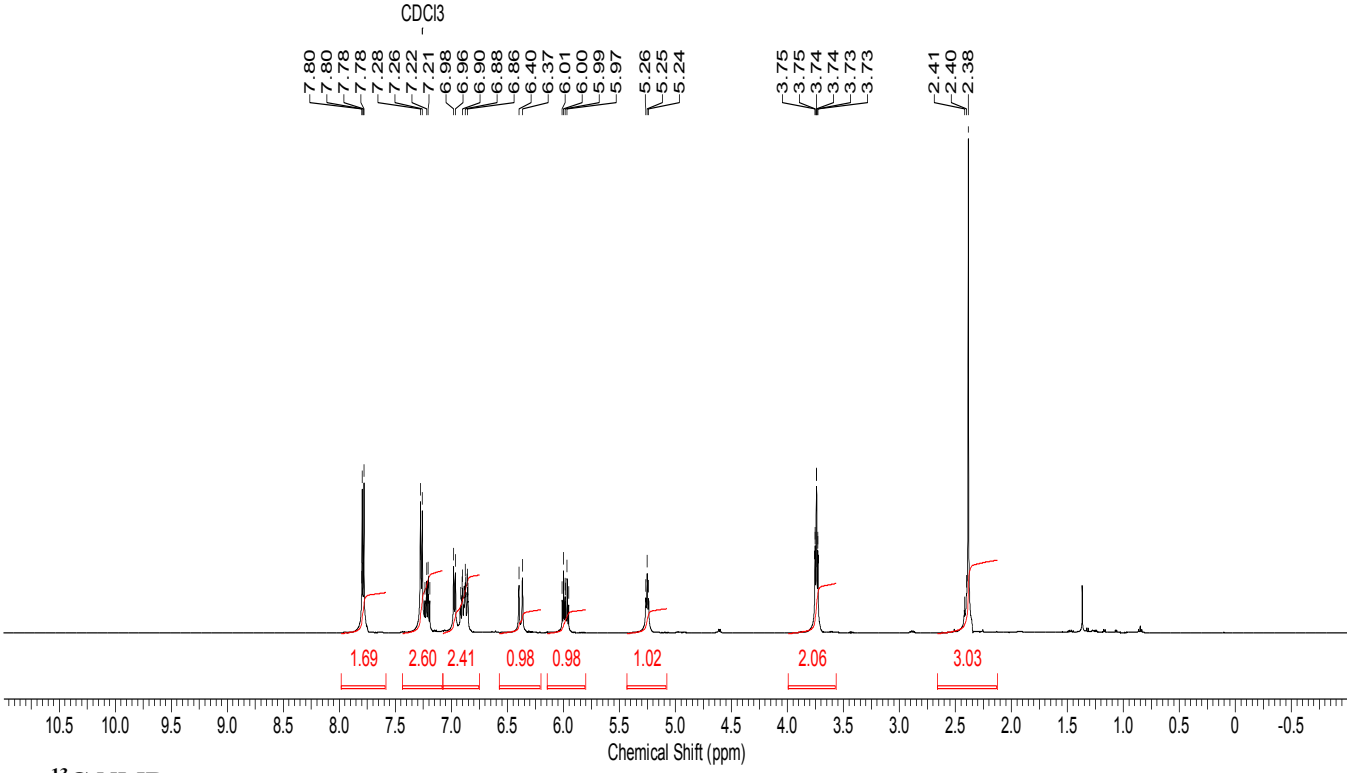
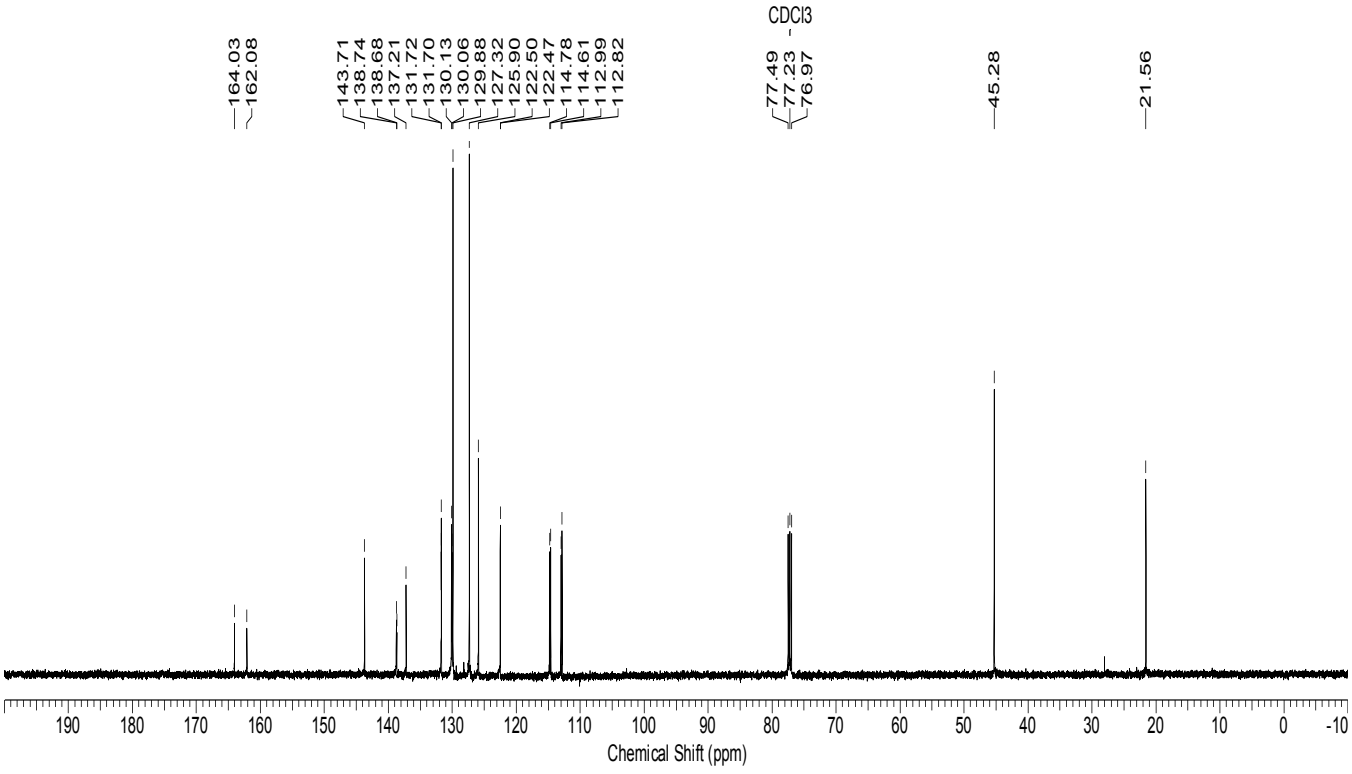
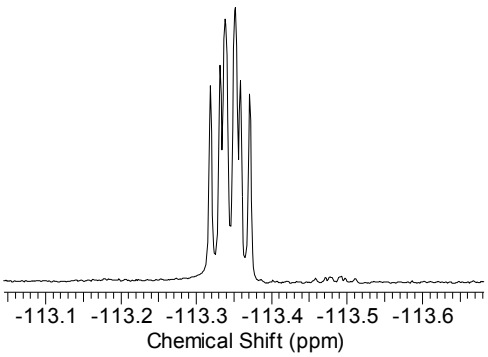


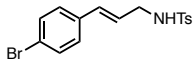
^{13}C NMR
125.7 MHz
$CDCl_3$



^{19}F NMR
470.4 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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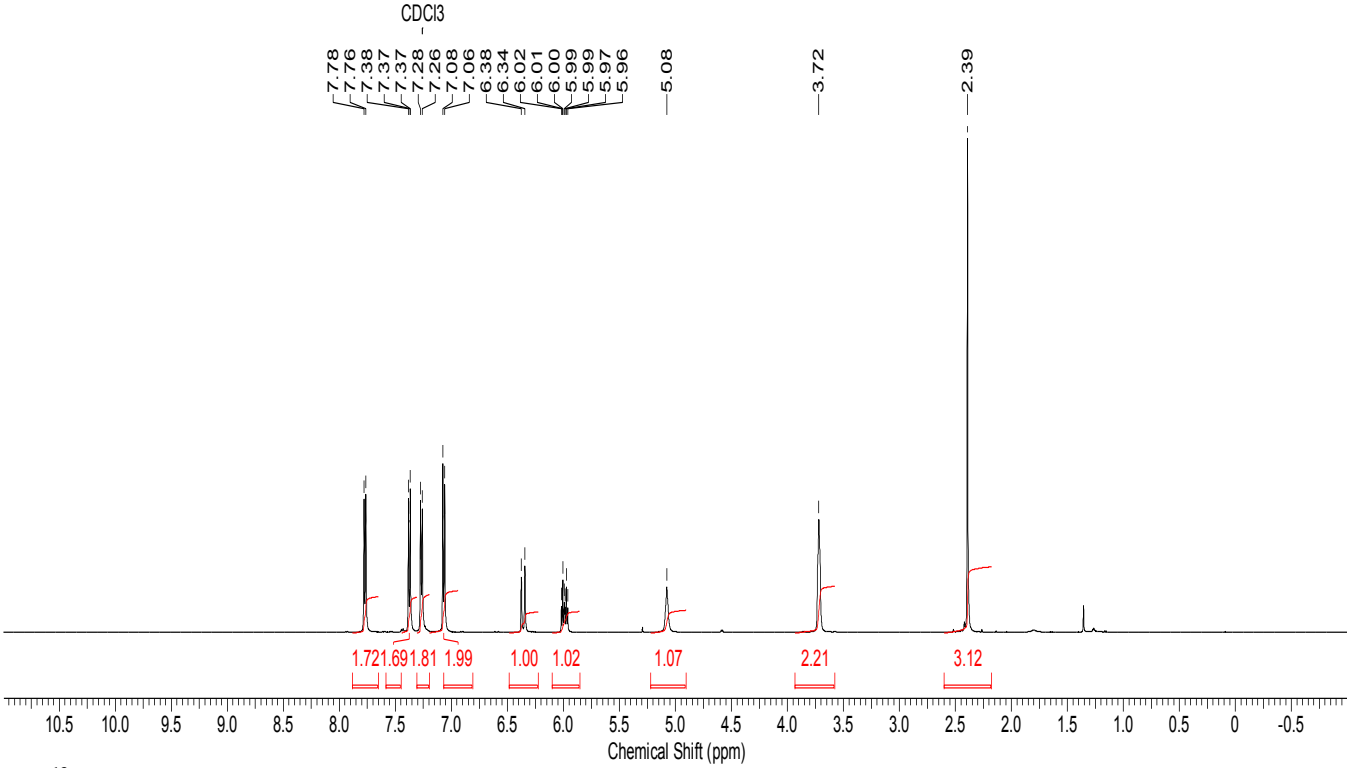
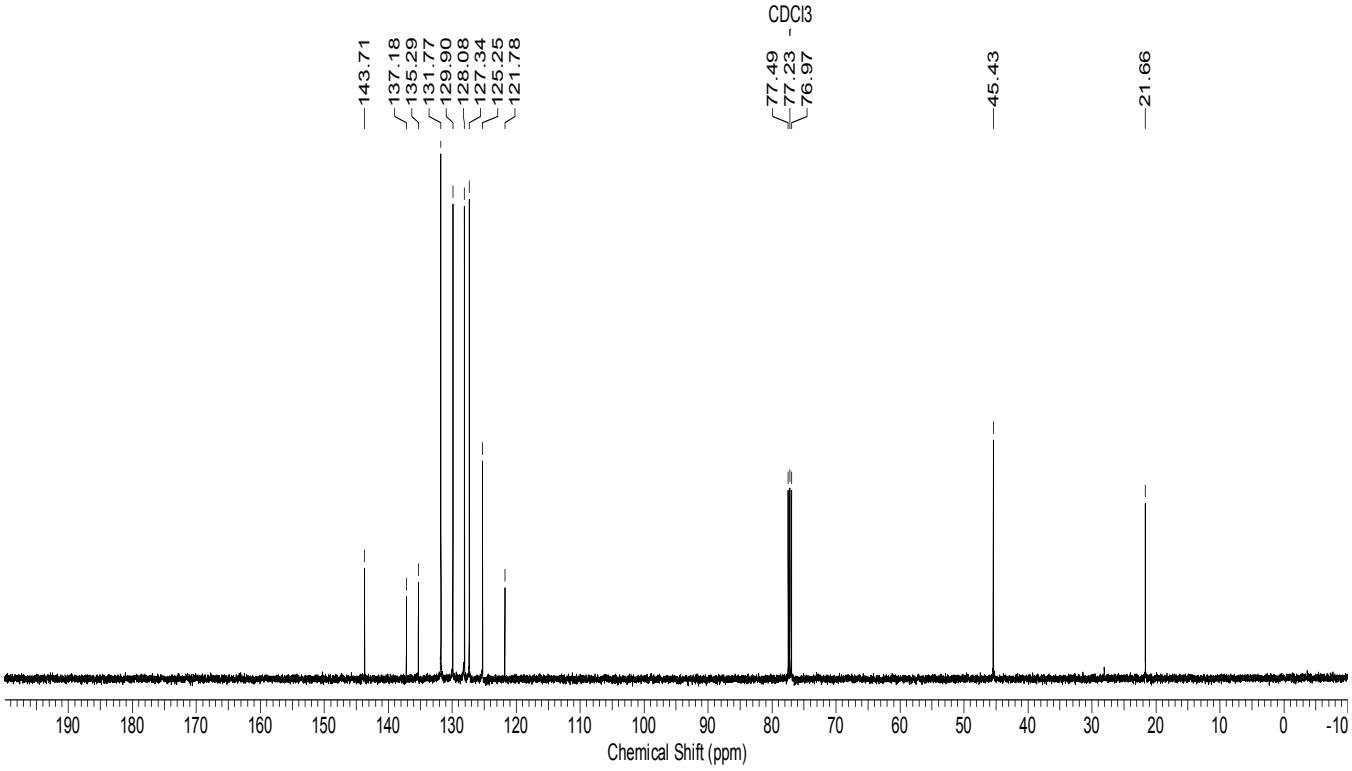
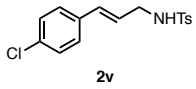


^{13}C NMR
125.7 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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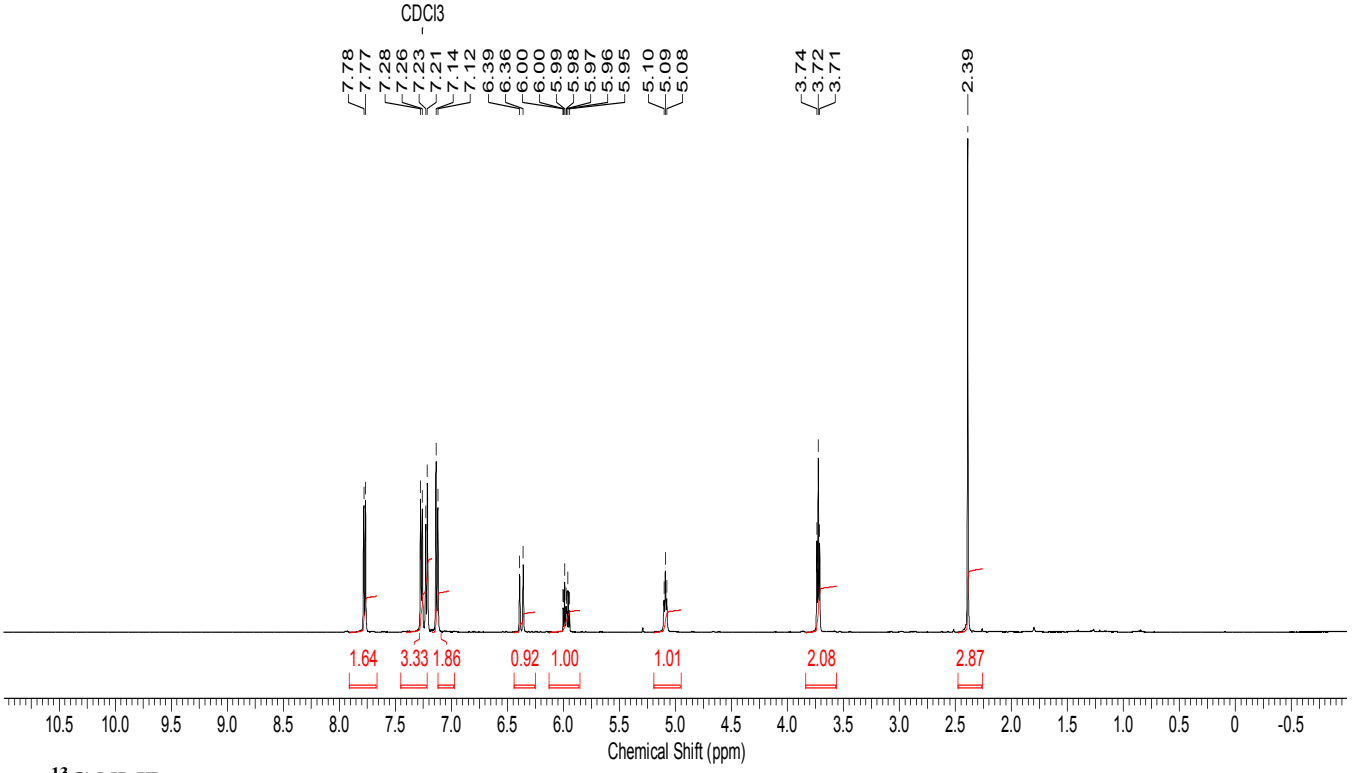
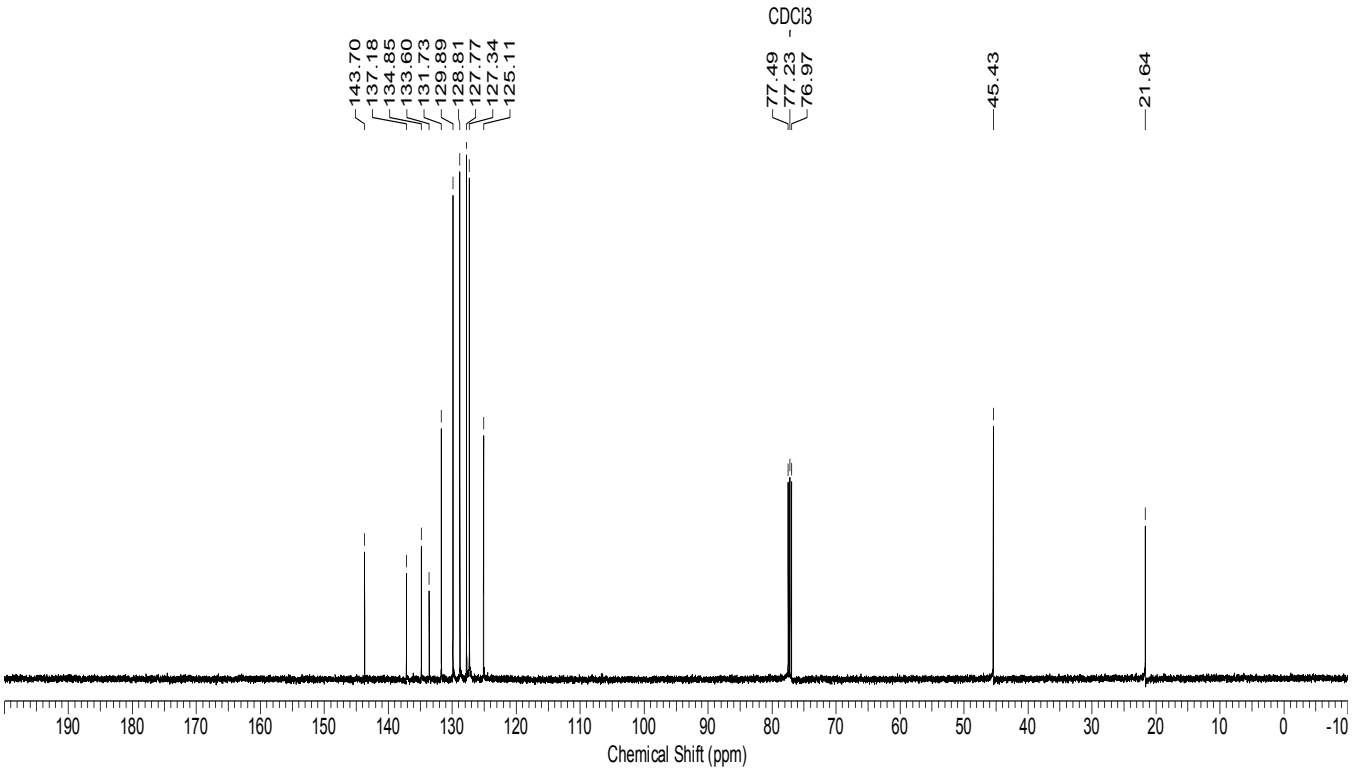
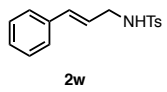


^{13}C NMR
125.7 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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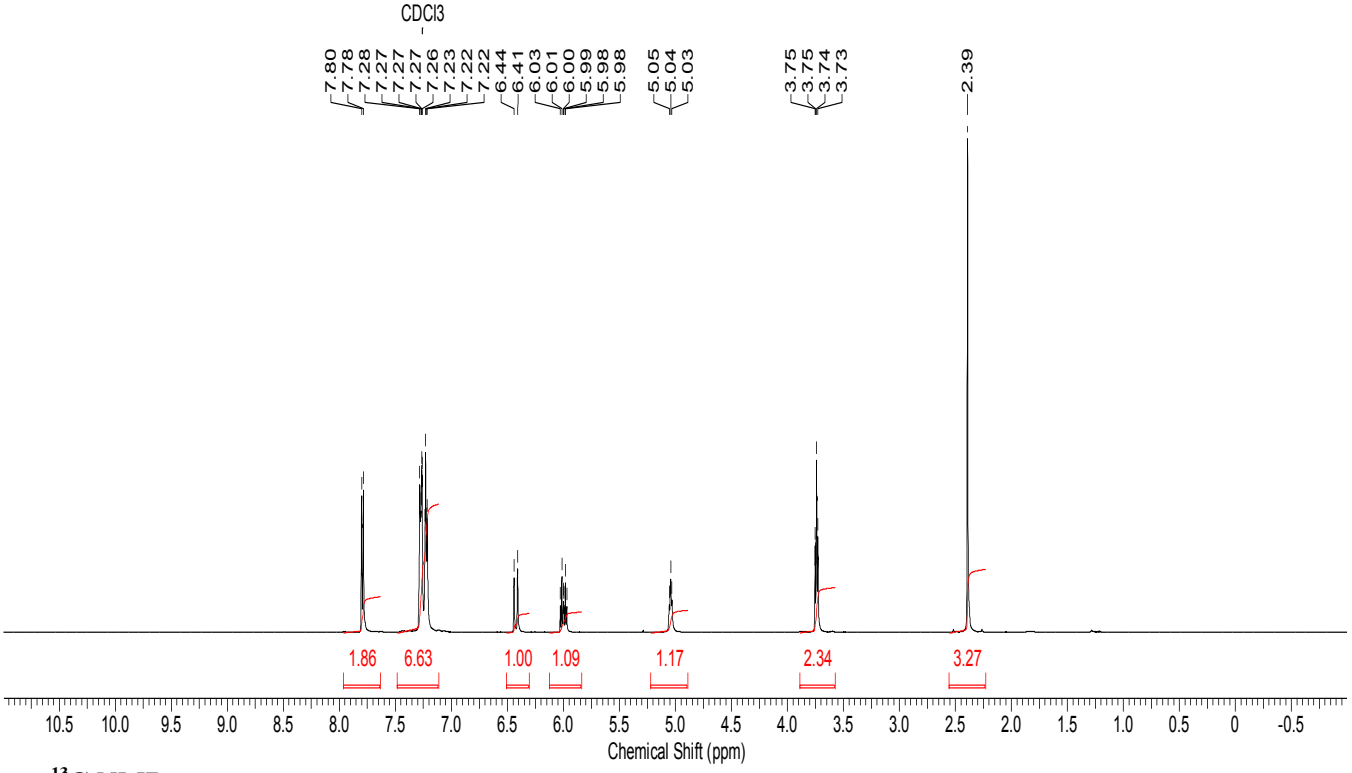
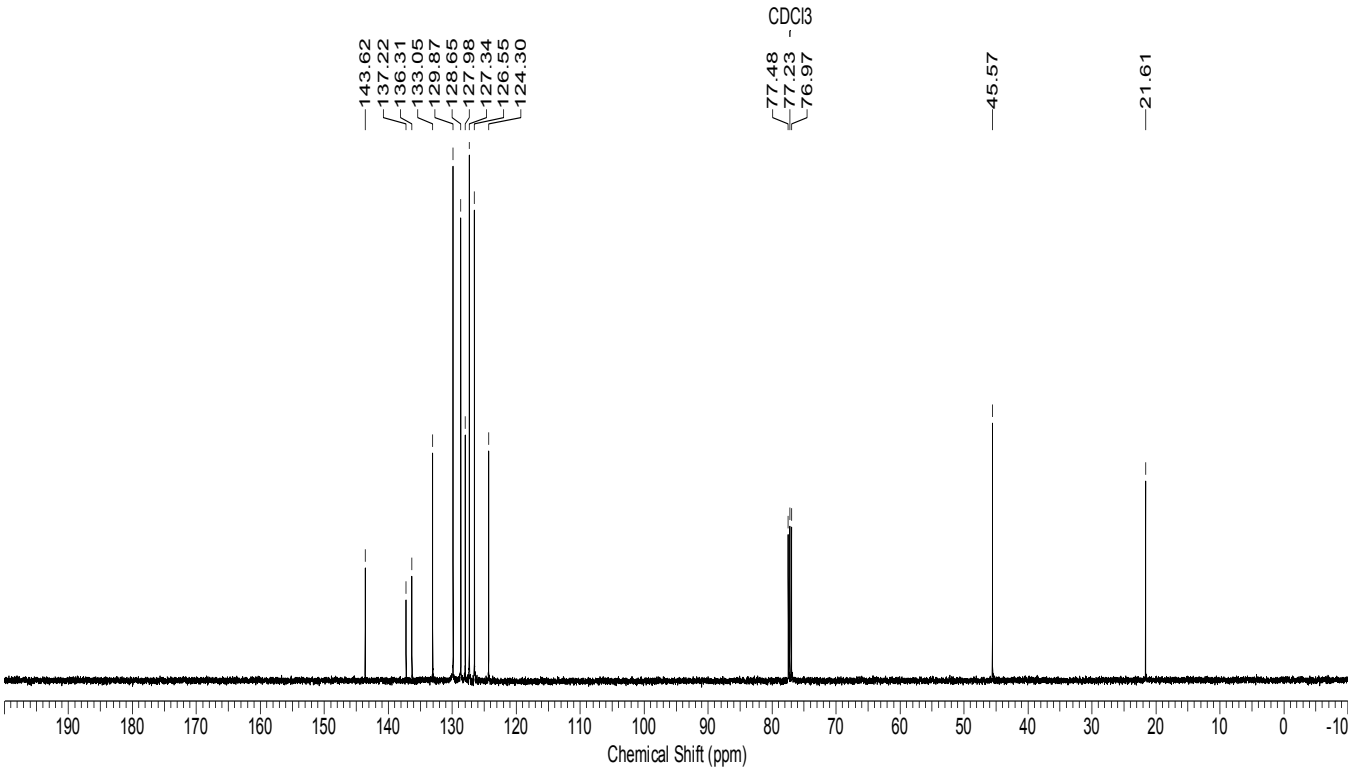
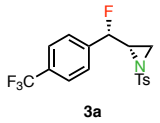


^{13}C NMR
125.7 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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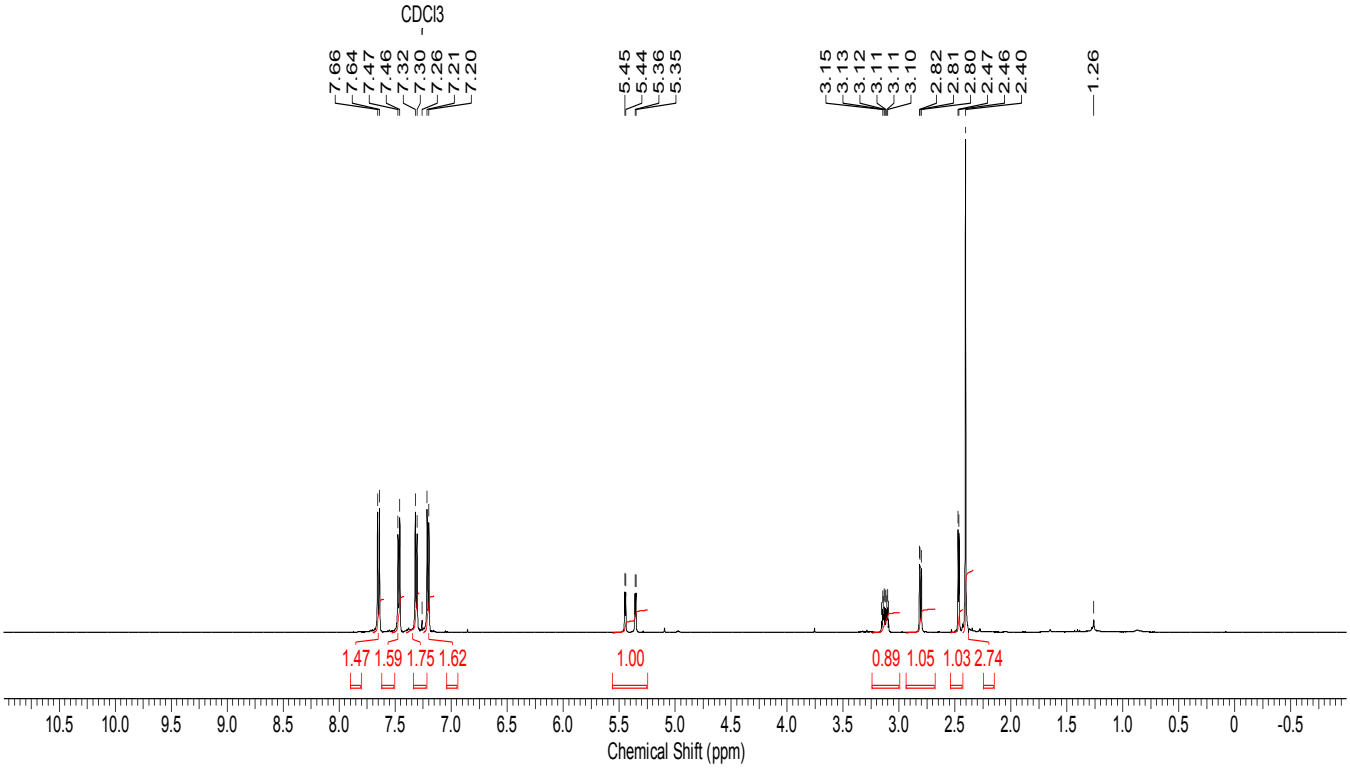
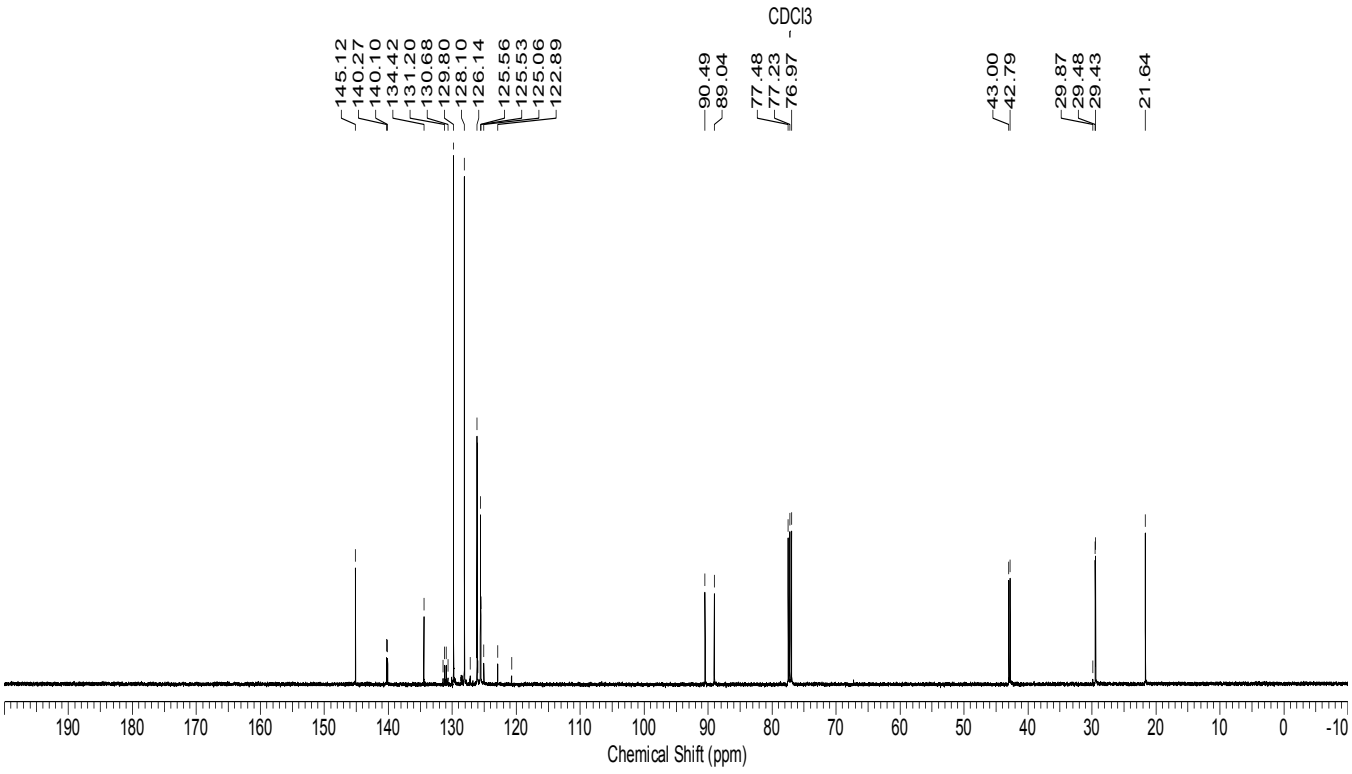
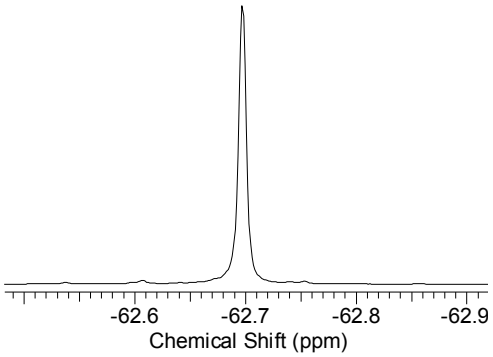
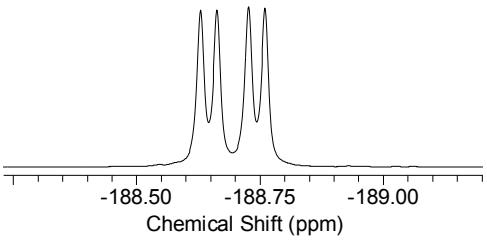


^{13}C NMR
125.7 MHz
$CDCl_3$

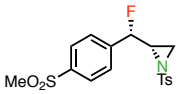


^{19}F NMR
470.4 MHz
$CDCl_3$





^{1}H NMR
500 MHz
$CDCl_3$



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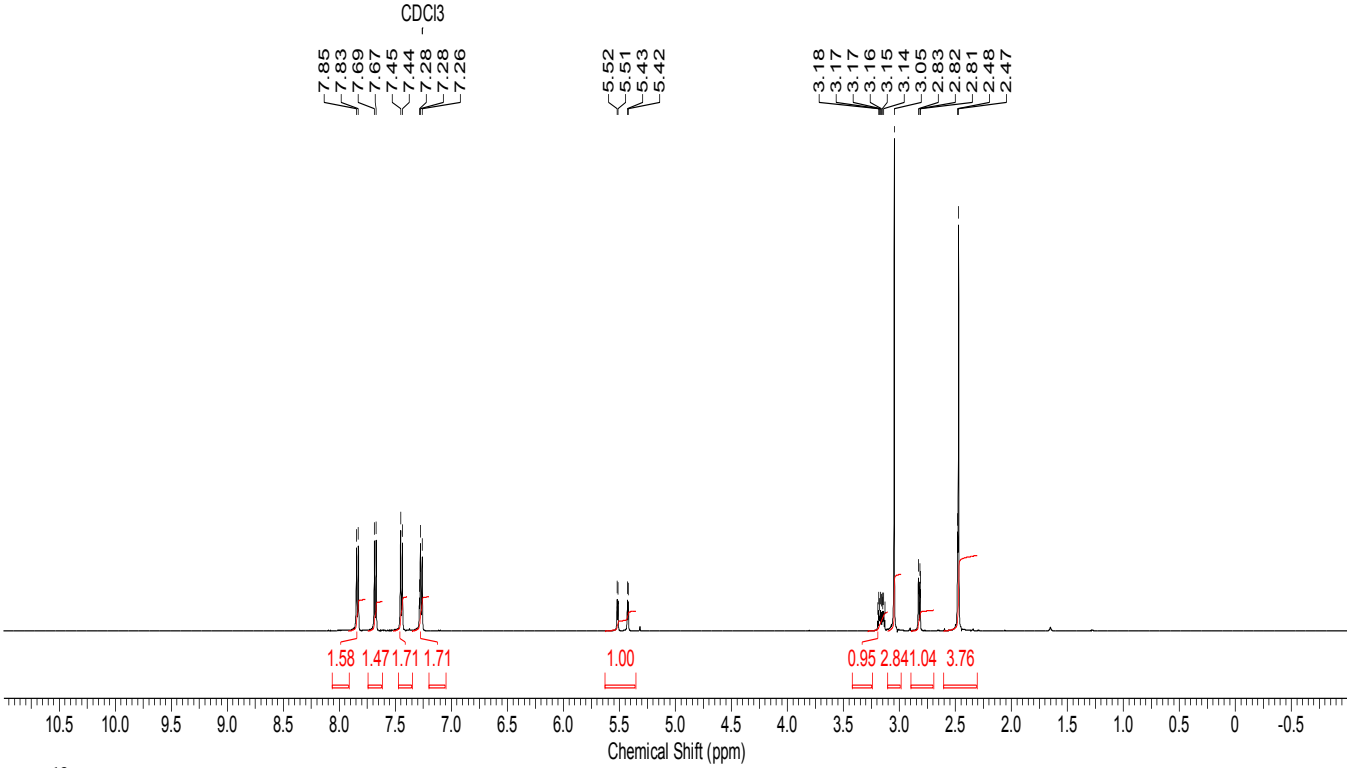
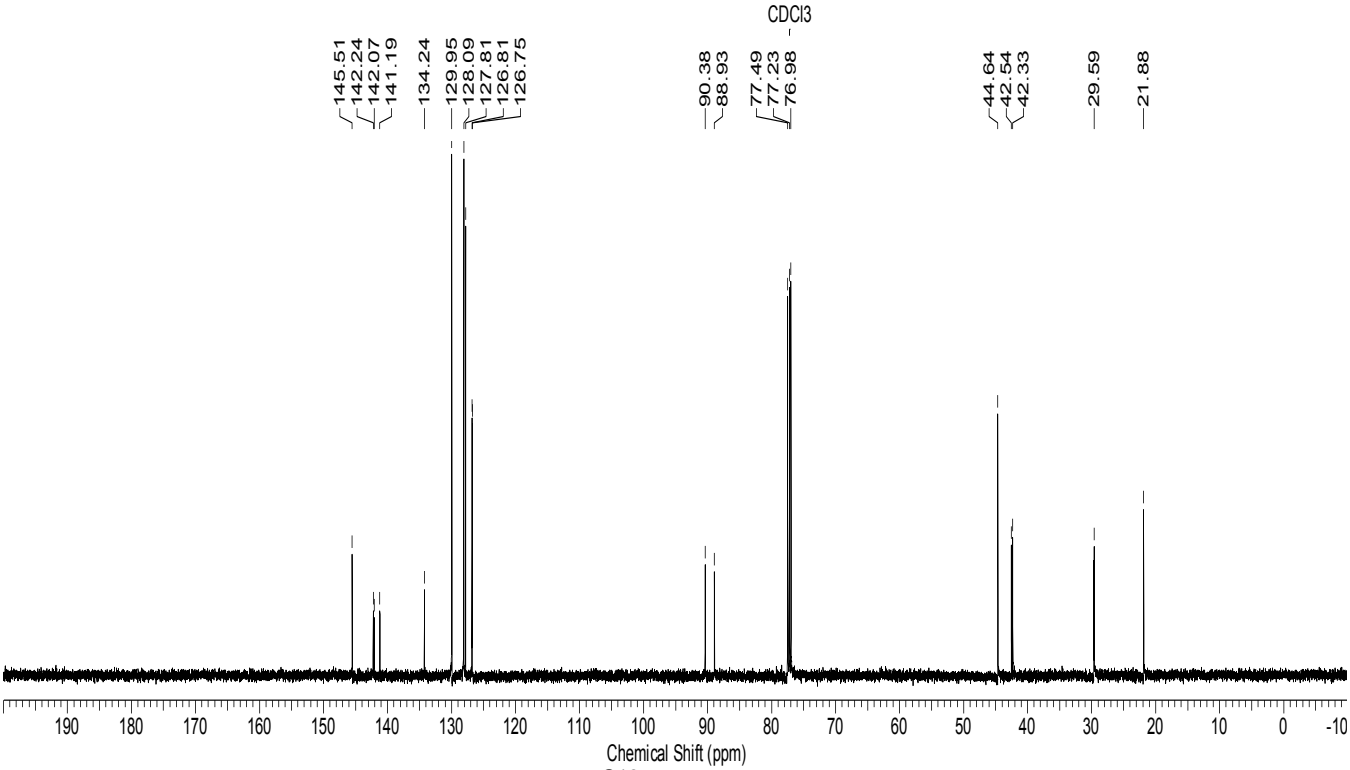
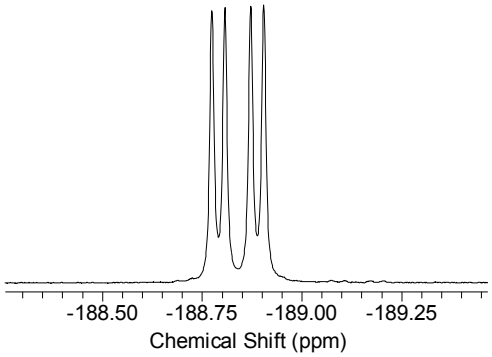


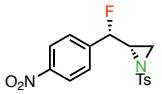
^{13}C NMR
125.7 MHz
$CDCl_3$



^{19}F NMR
470.4 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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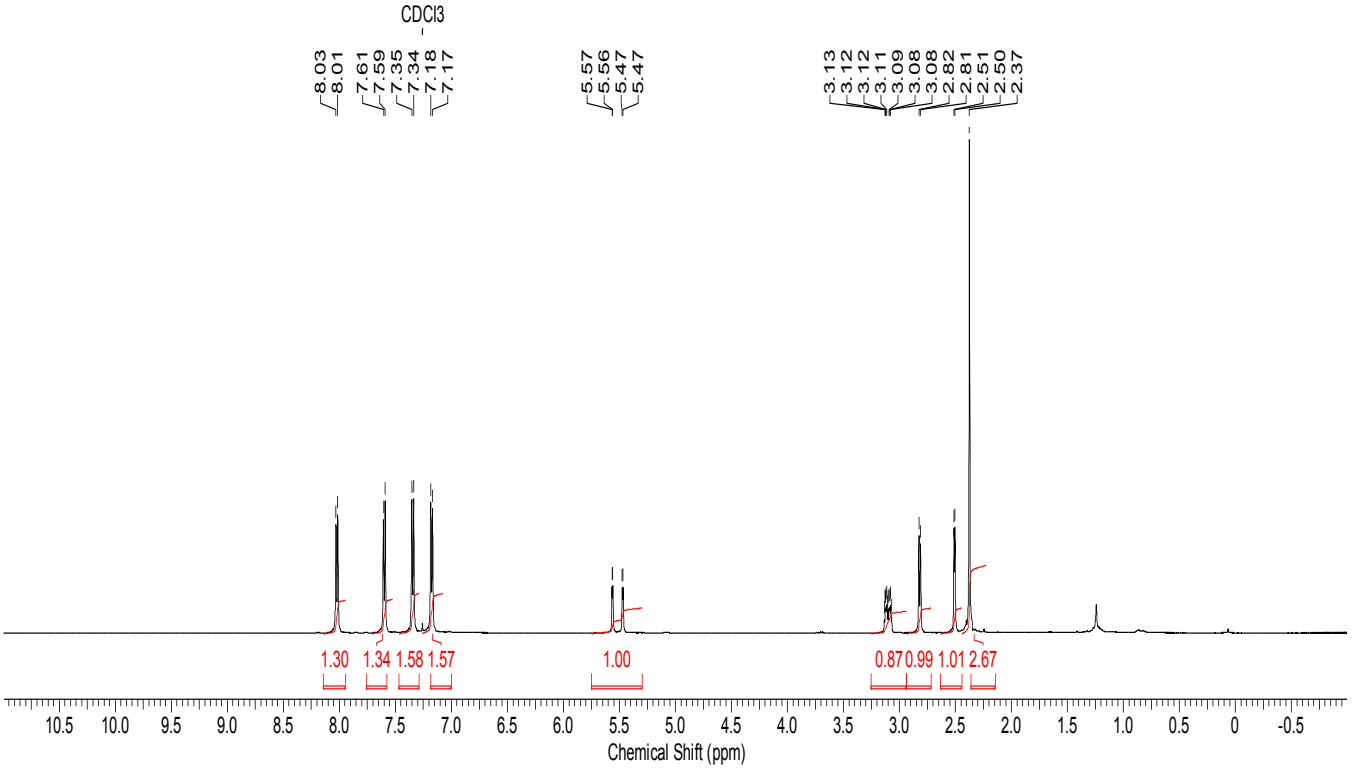
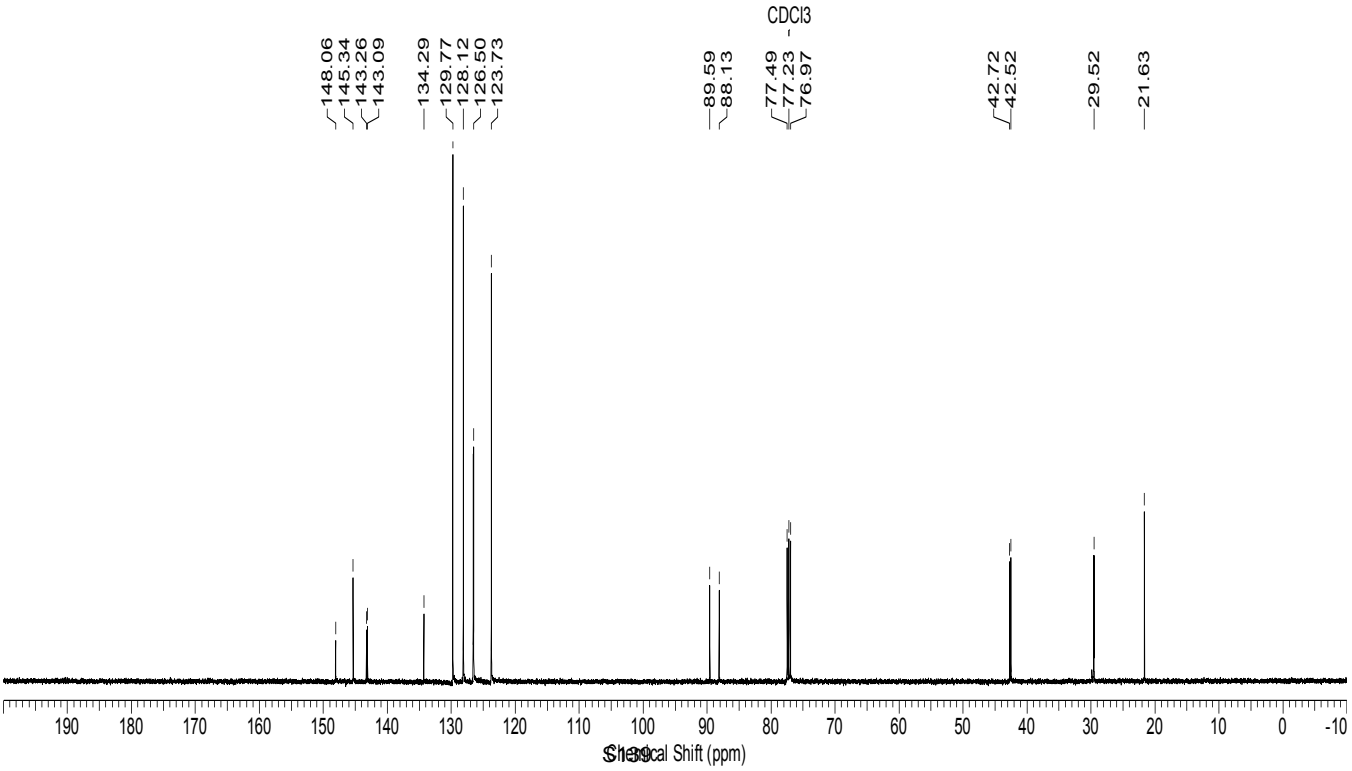
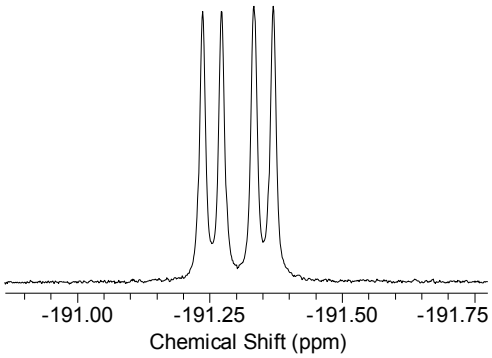


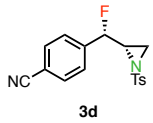
^{13}C NMR
125.7 MHz
$CDCl_3$



^{19}F NMR
470.4 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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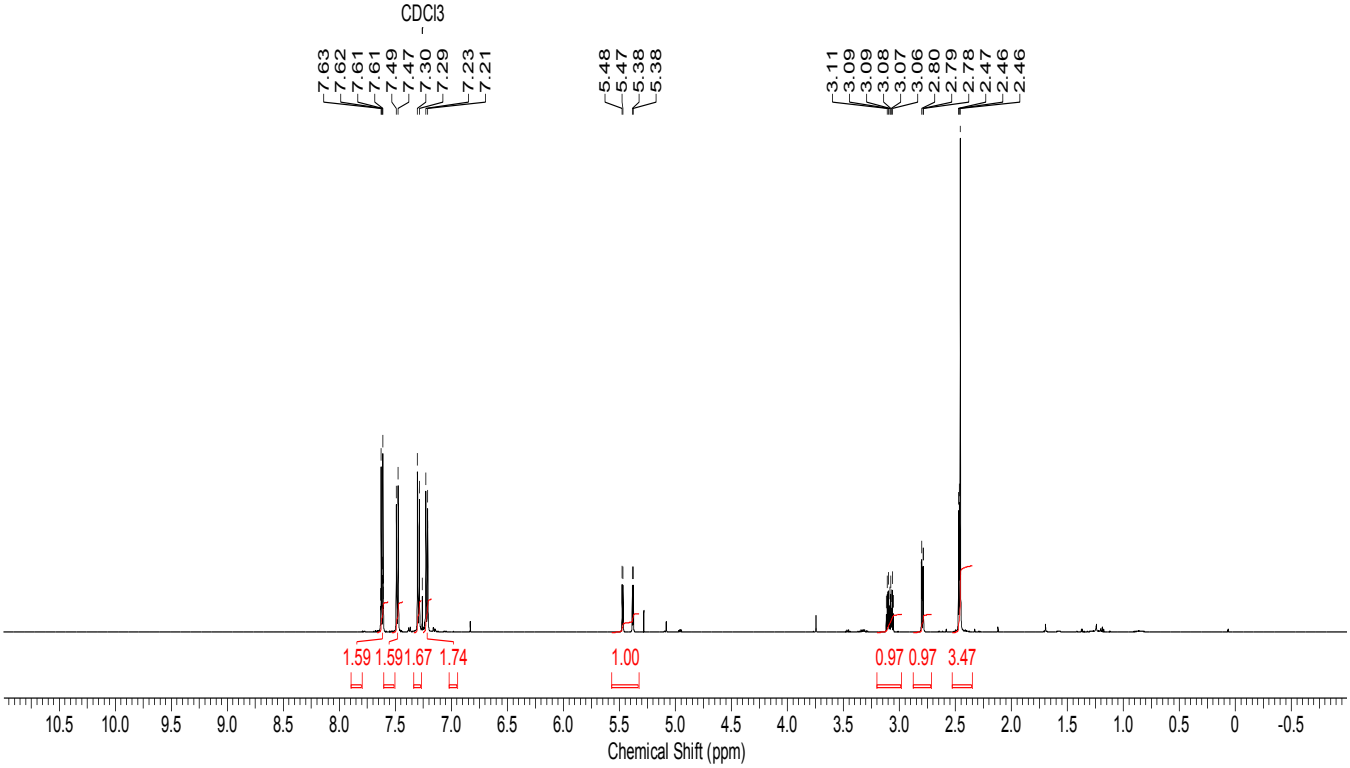
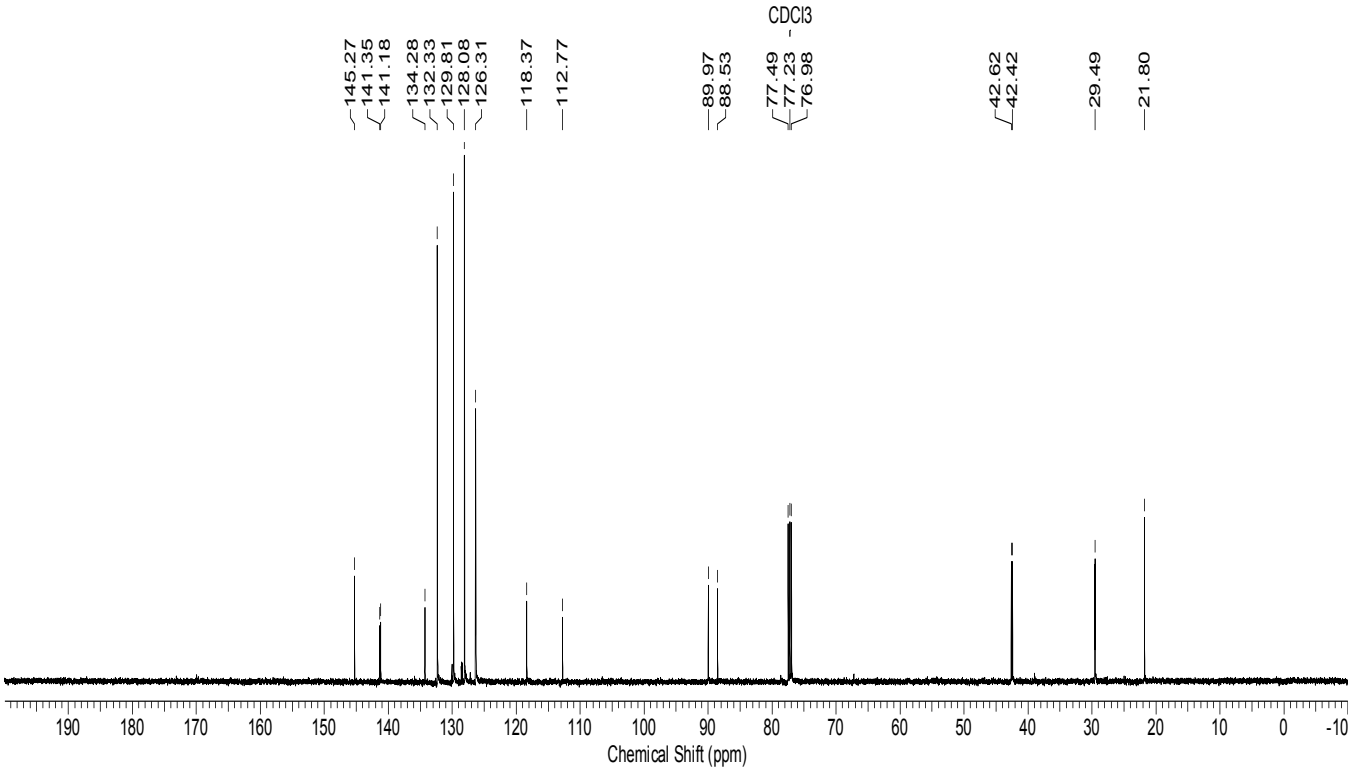
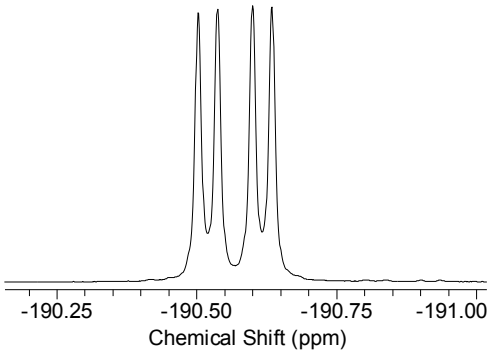


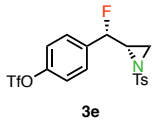
^{13}C NMR
125.7 MHz
$CDCl_3$



^{19}F NMR
470.4 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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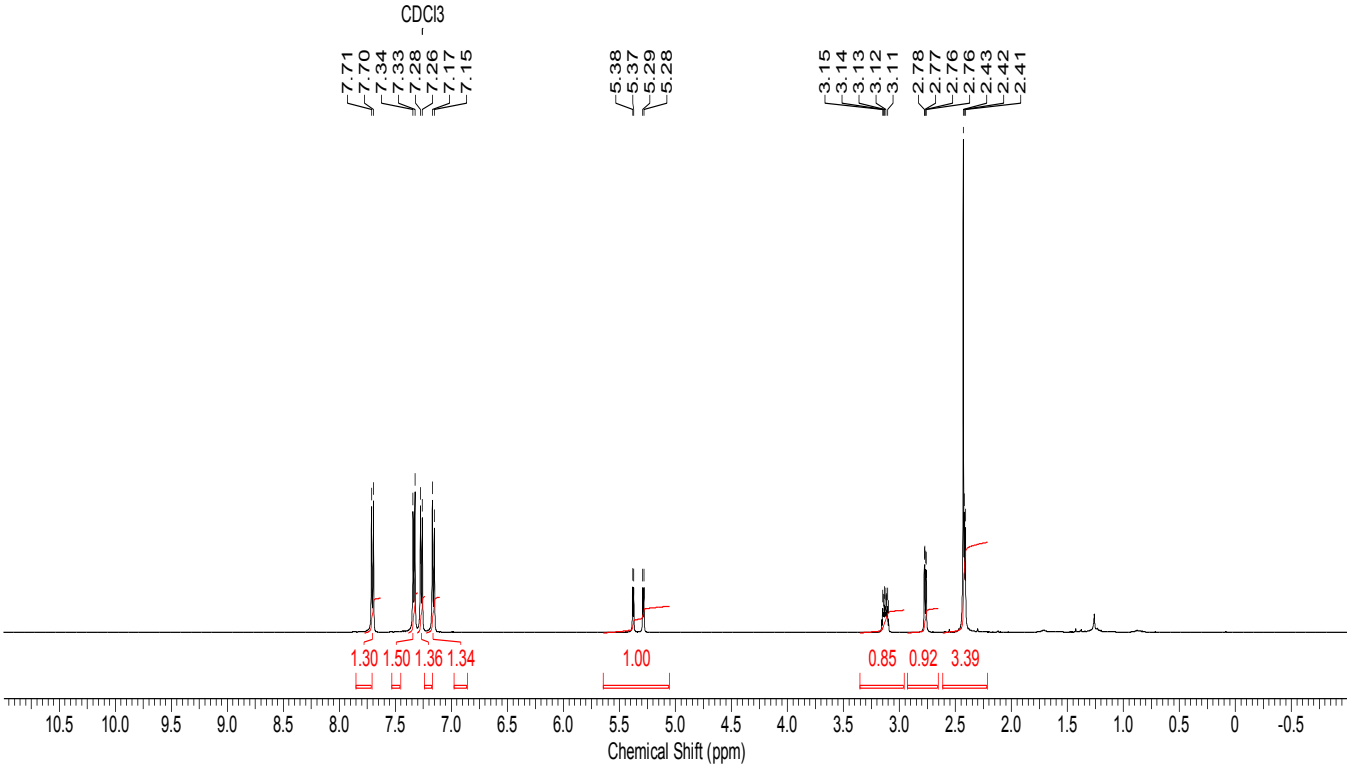
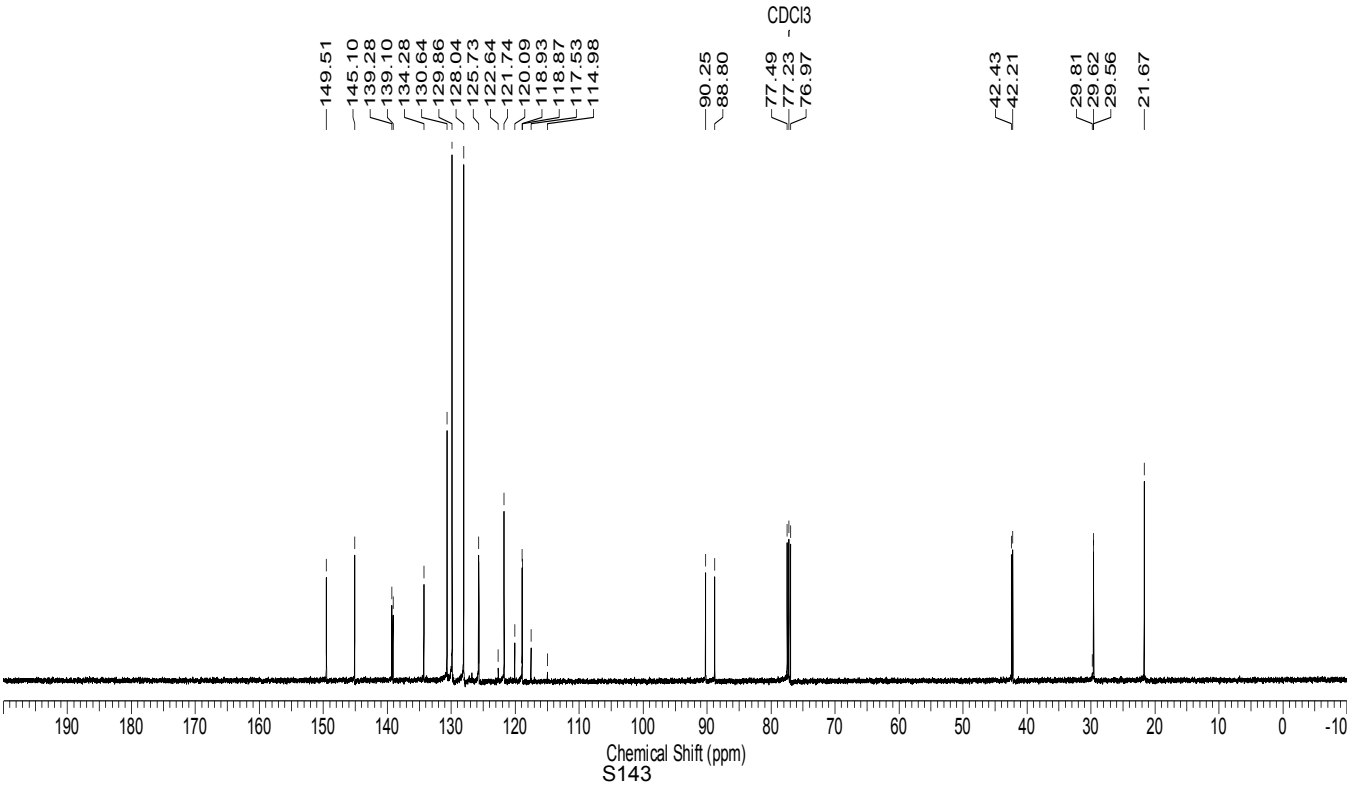
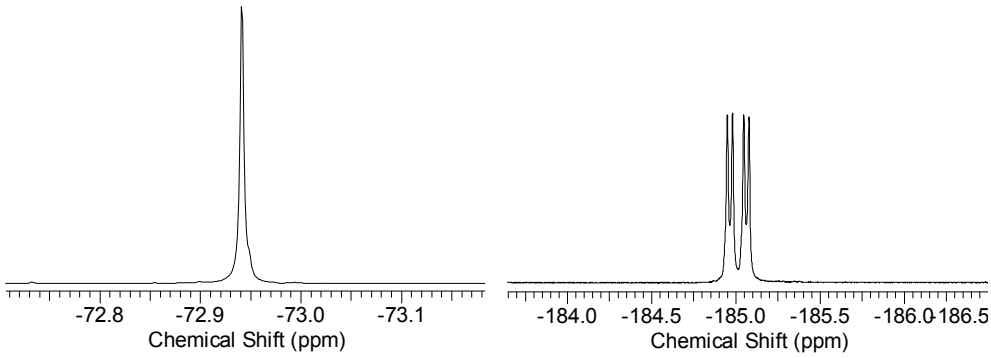


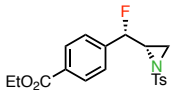
^{13}C NMR
125.7 MHz
$CDCl_3$



^{19}F NMR
470.4 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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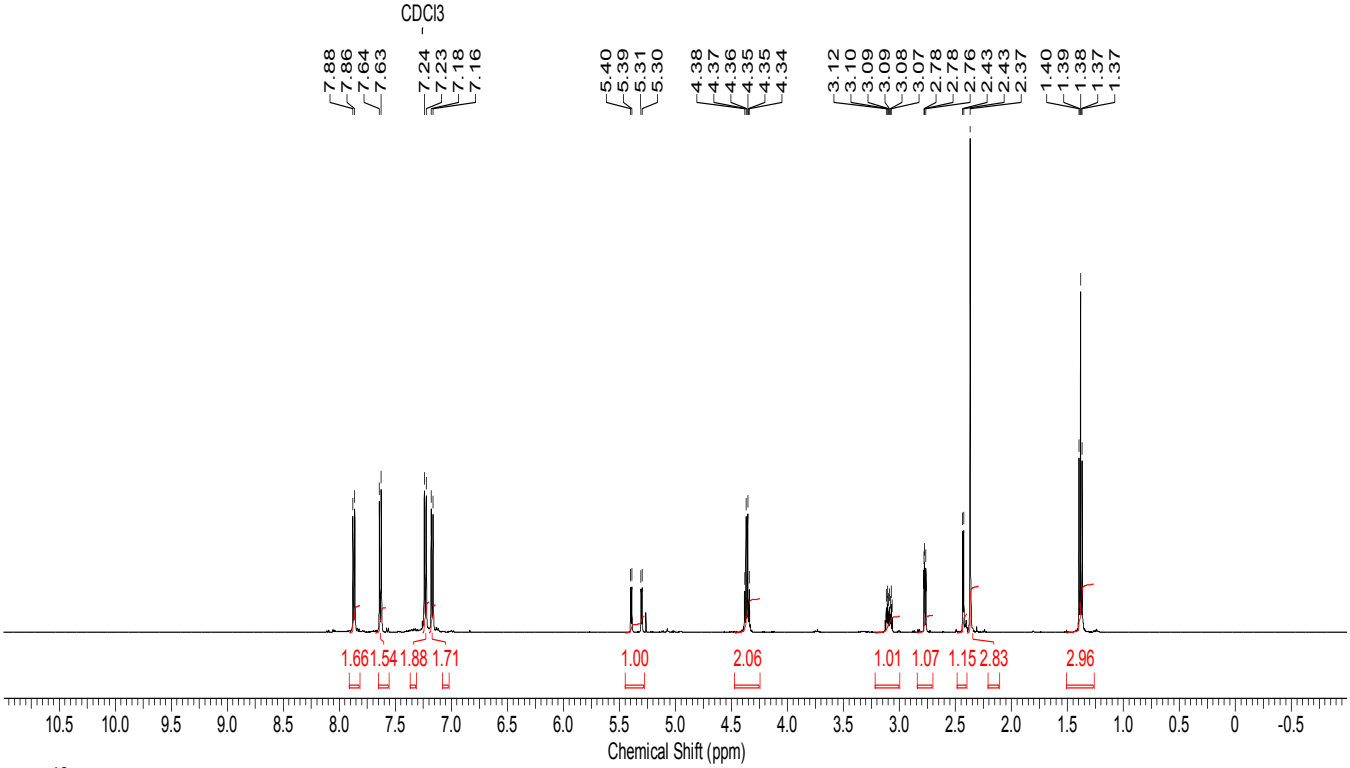
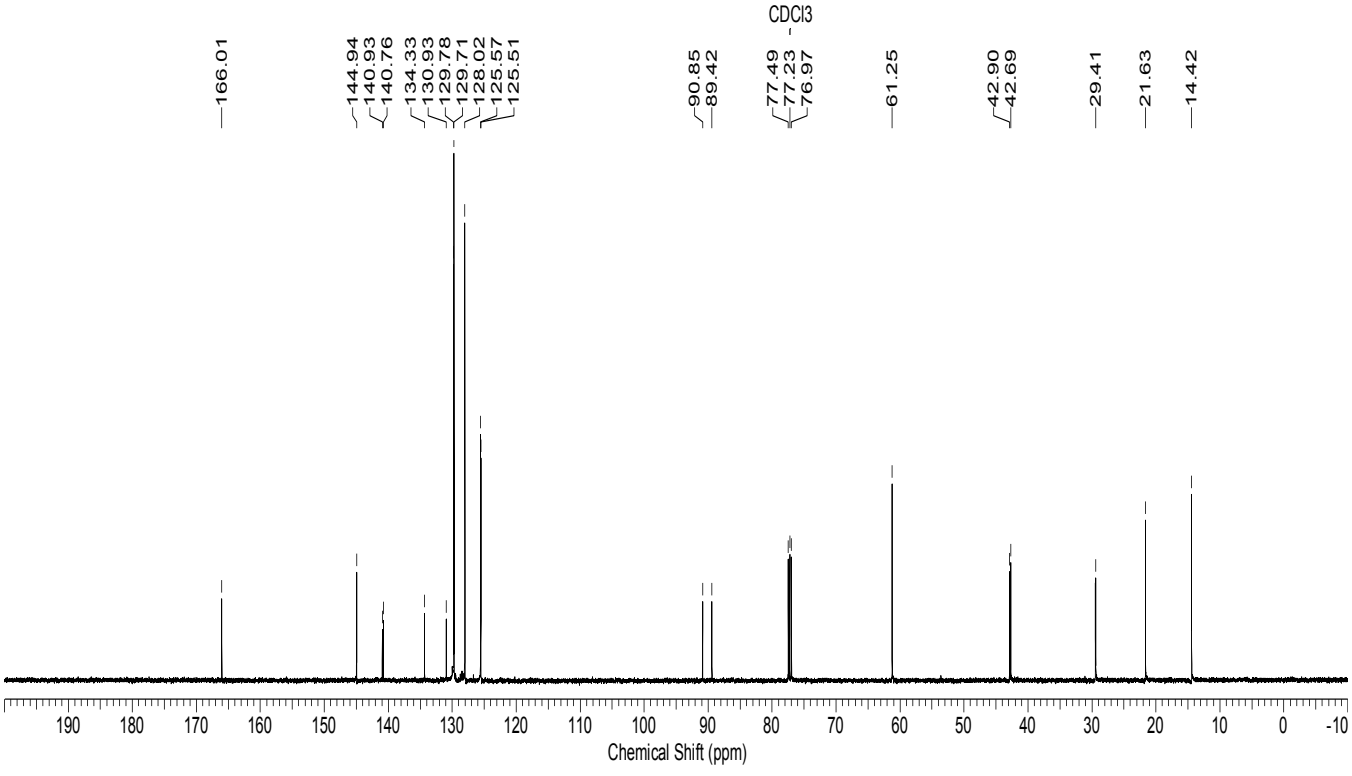
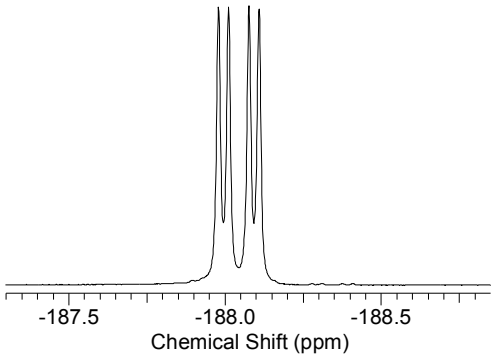


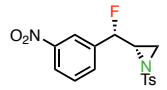
^{13}C NMR
125.7 MHz
$CDCl_3$



^{19}F NMR
470.4 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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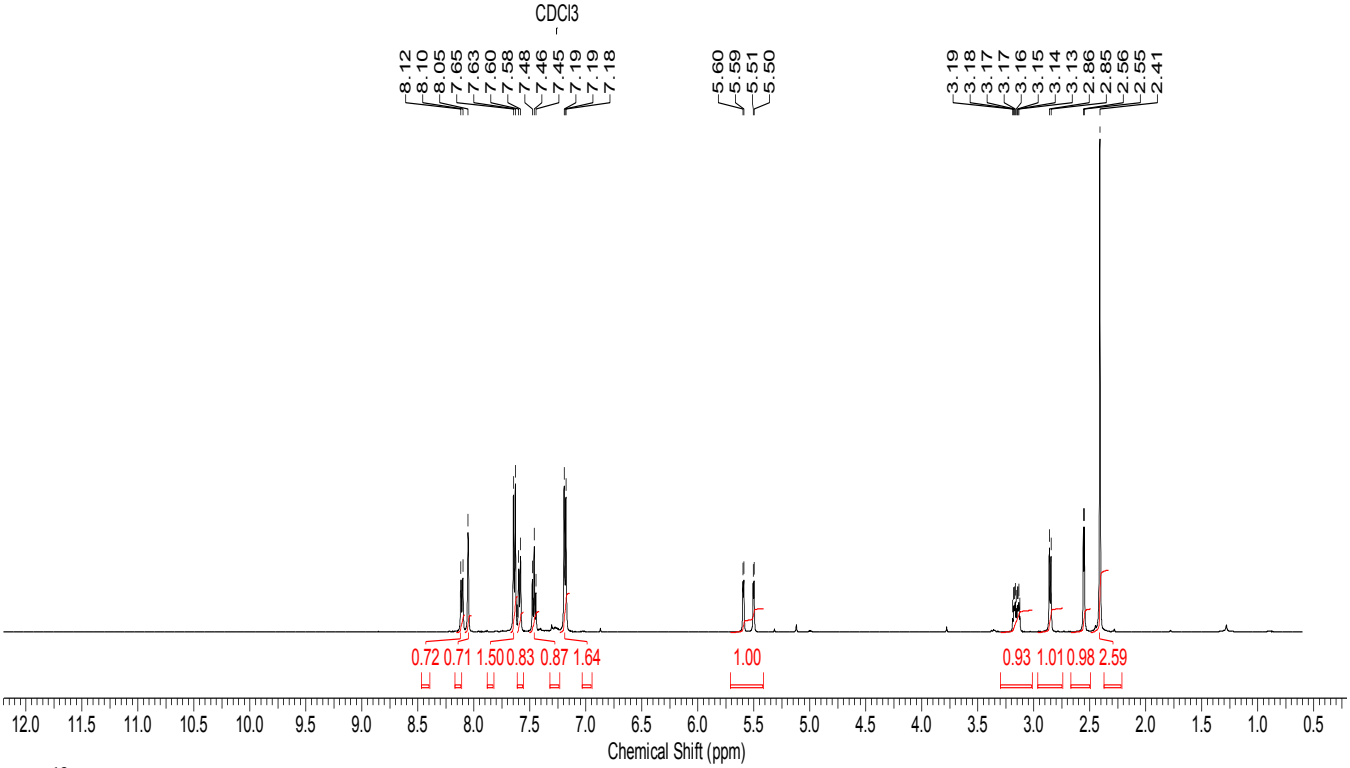
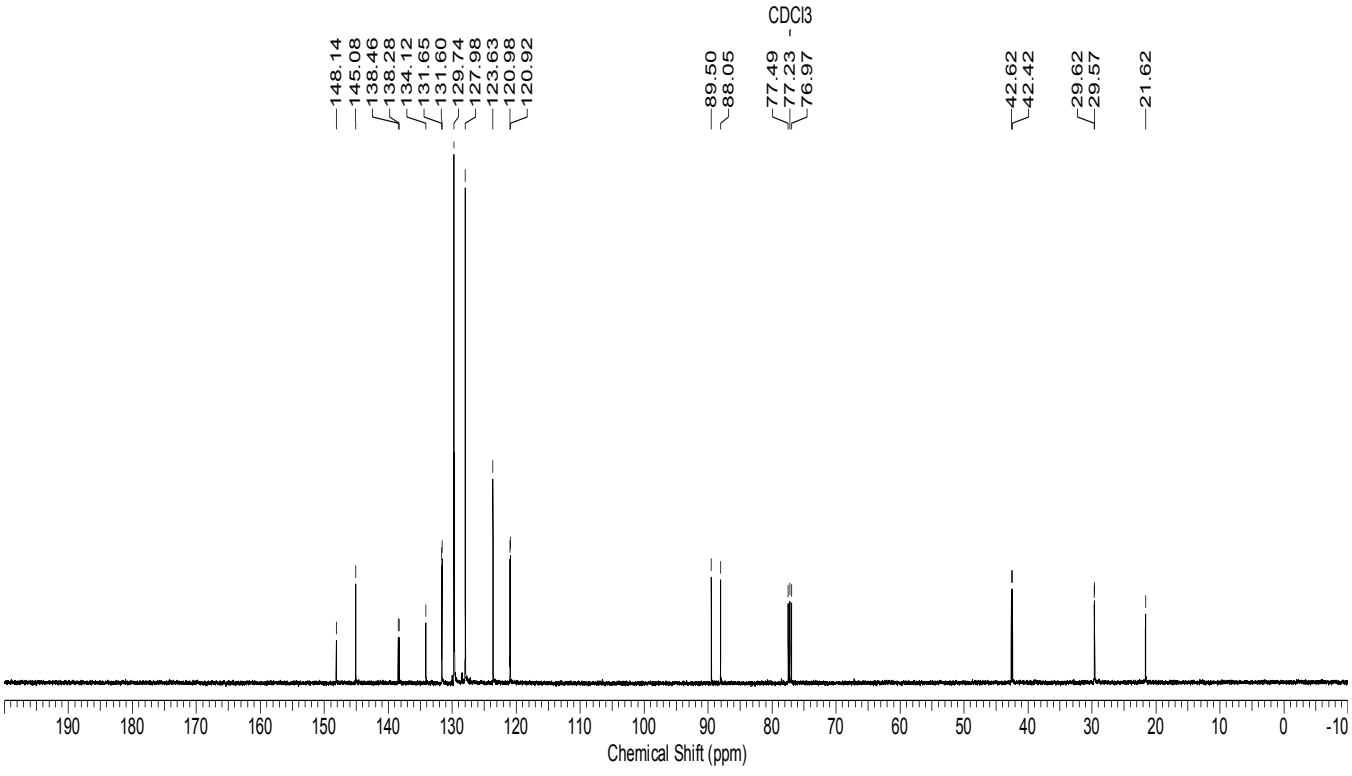
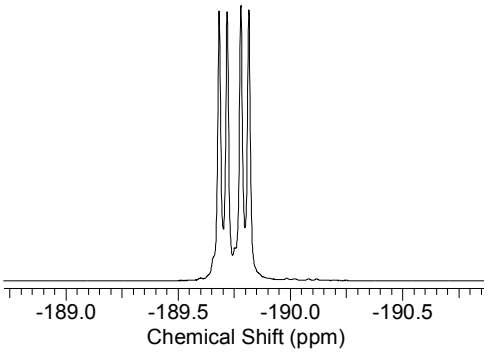


^{13}C NMR
125.7 MHz
$CDCl_3$



^{19}F NMR
470.4 MHz
$CDCl_3$



^{1}H NMR
500 MHz
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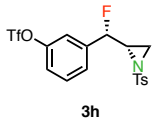

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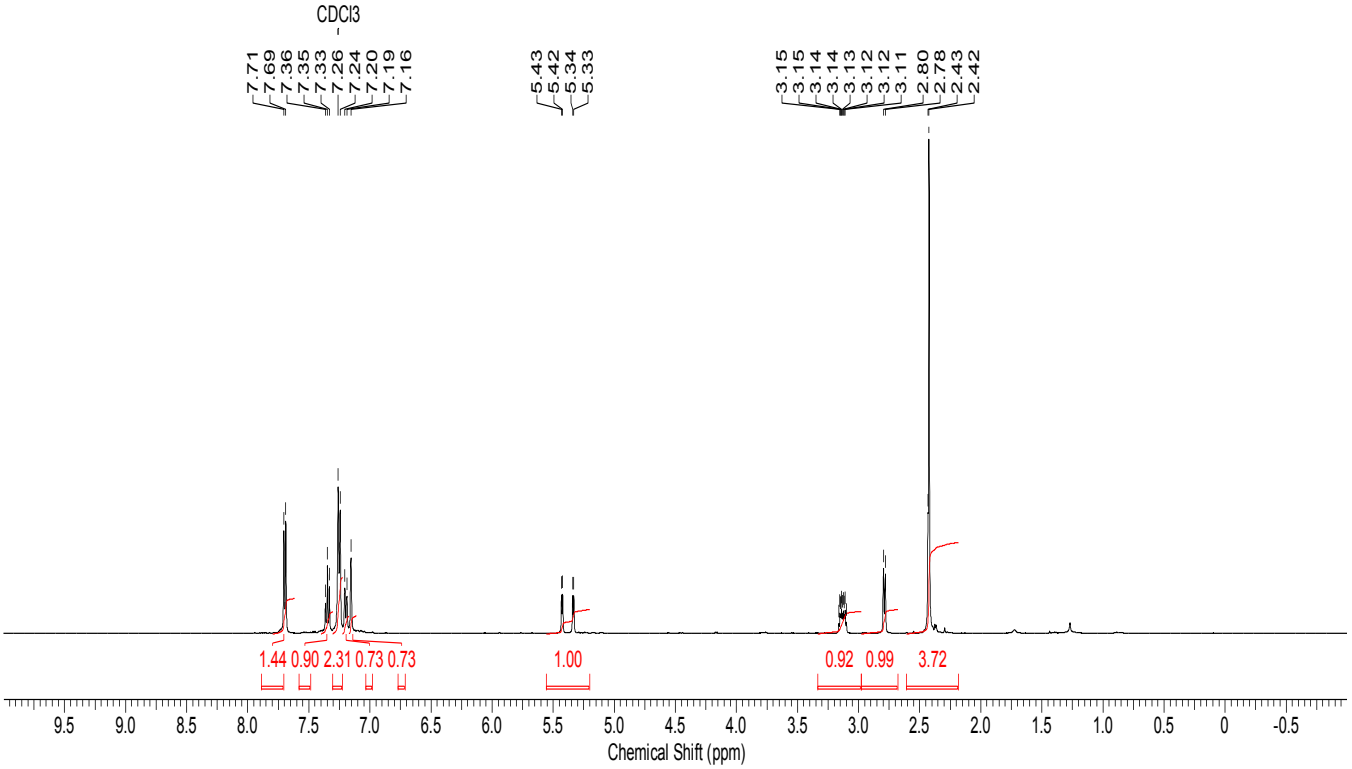
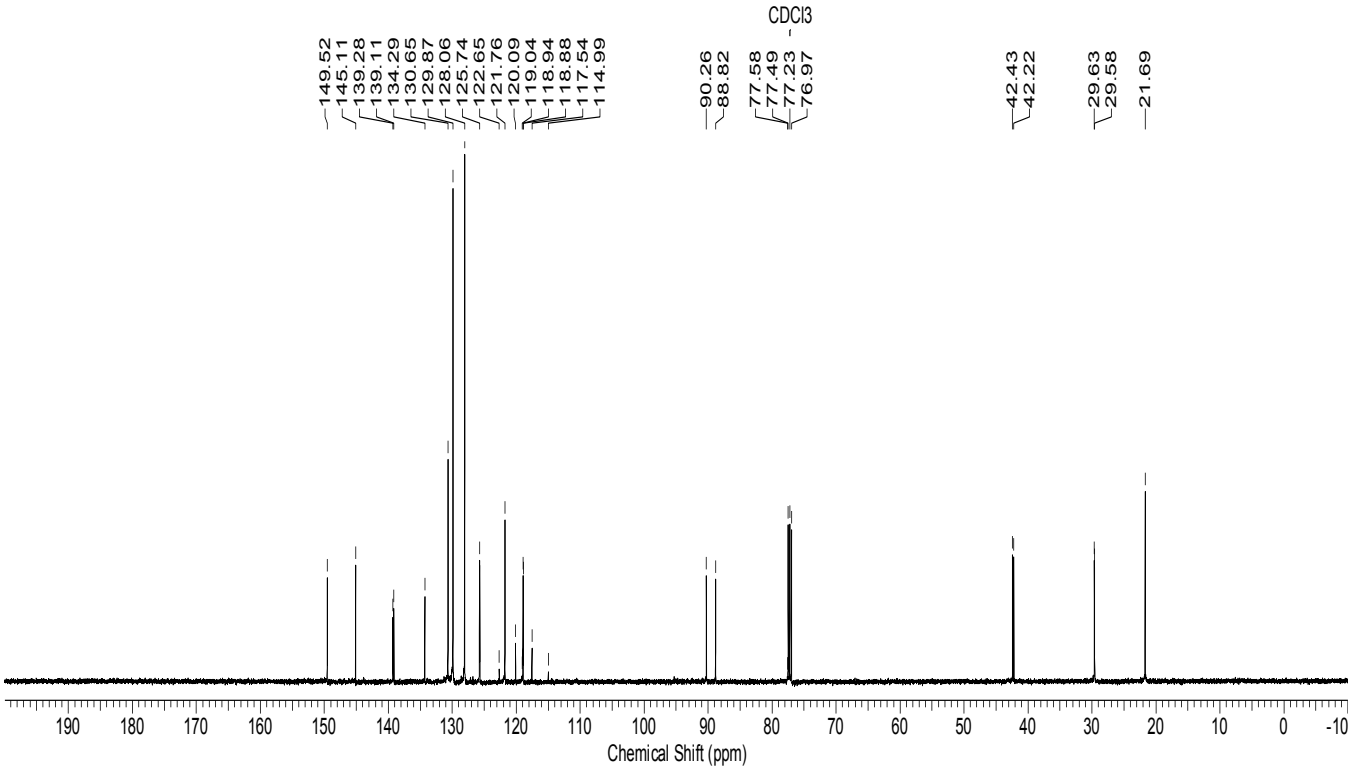
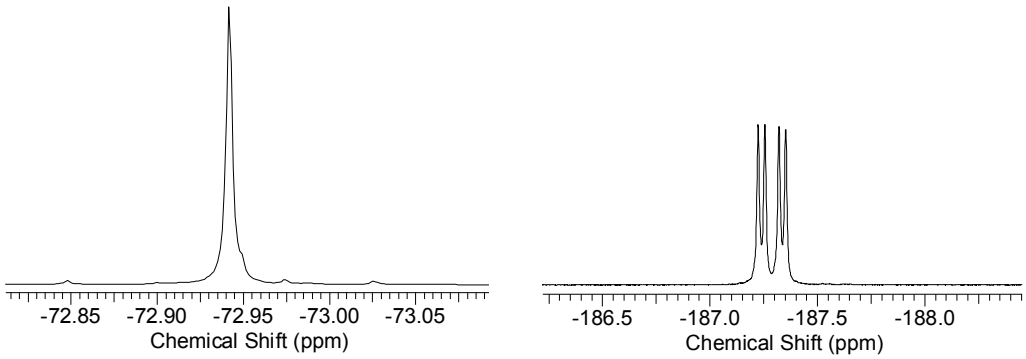


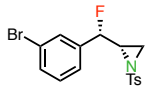
^{13}C NMR
125.7 MHz
$CDCl_3$



^{19}F NMR
470.4 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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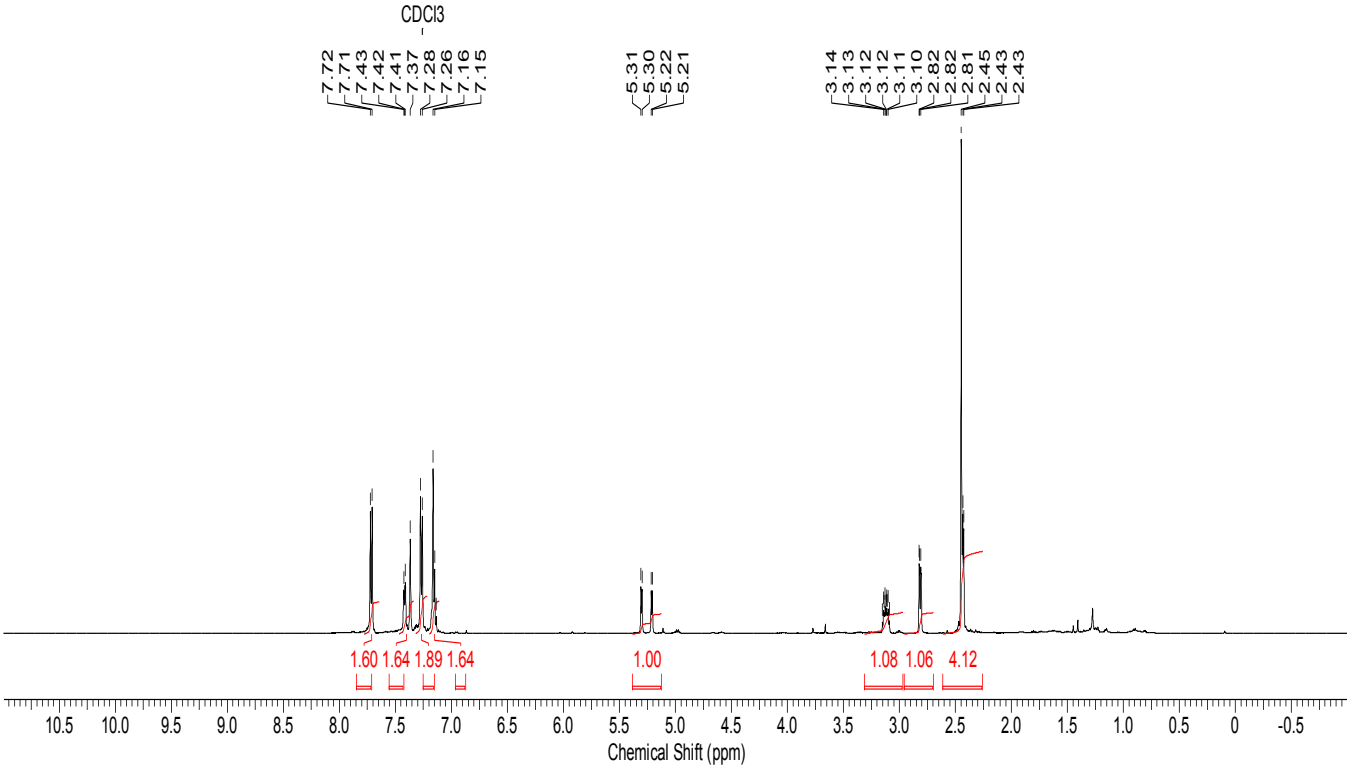
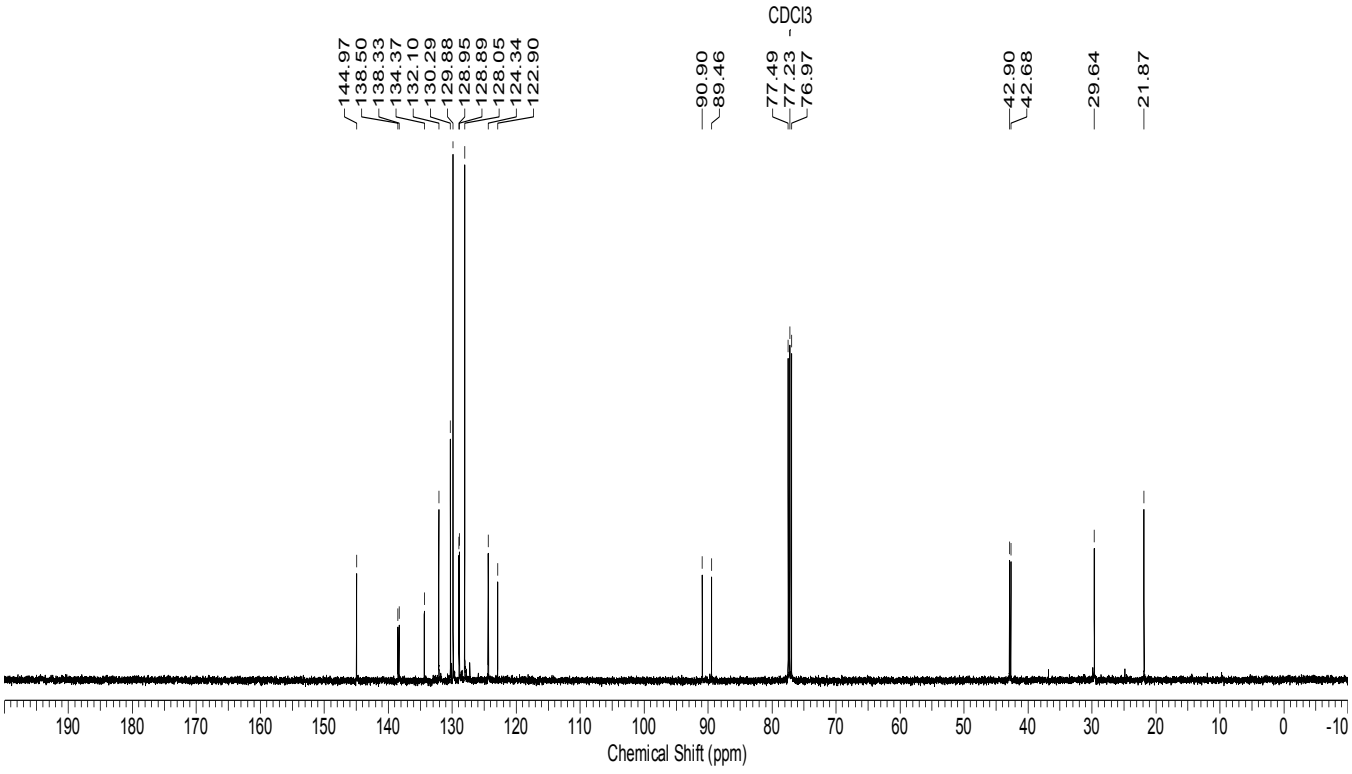
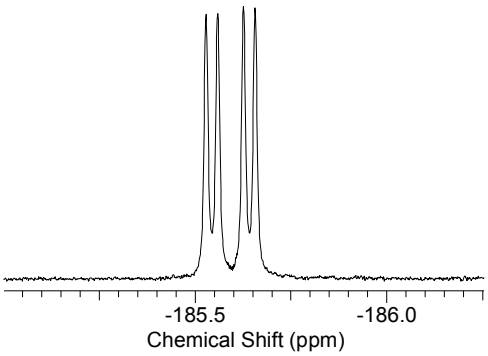


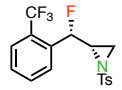
^{13}C NMR
125.7 MHz
$CDCl_3$



^{19}F NMR
470.4 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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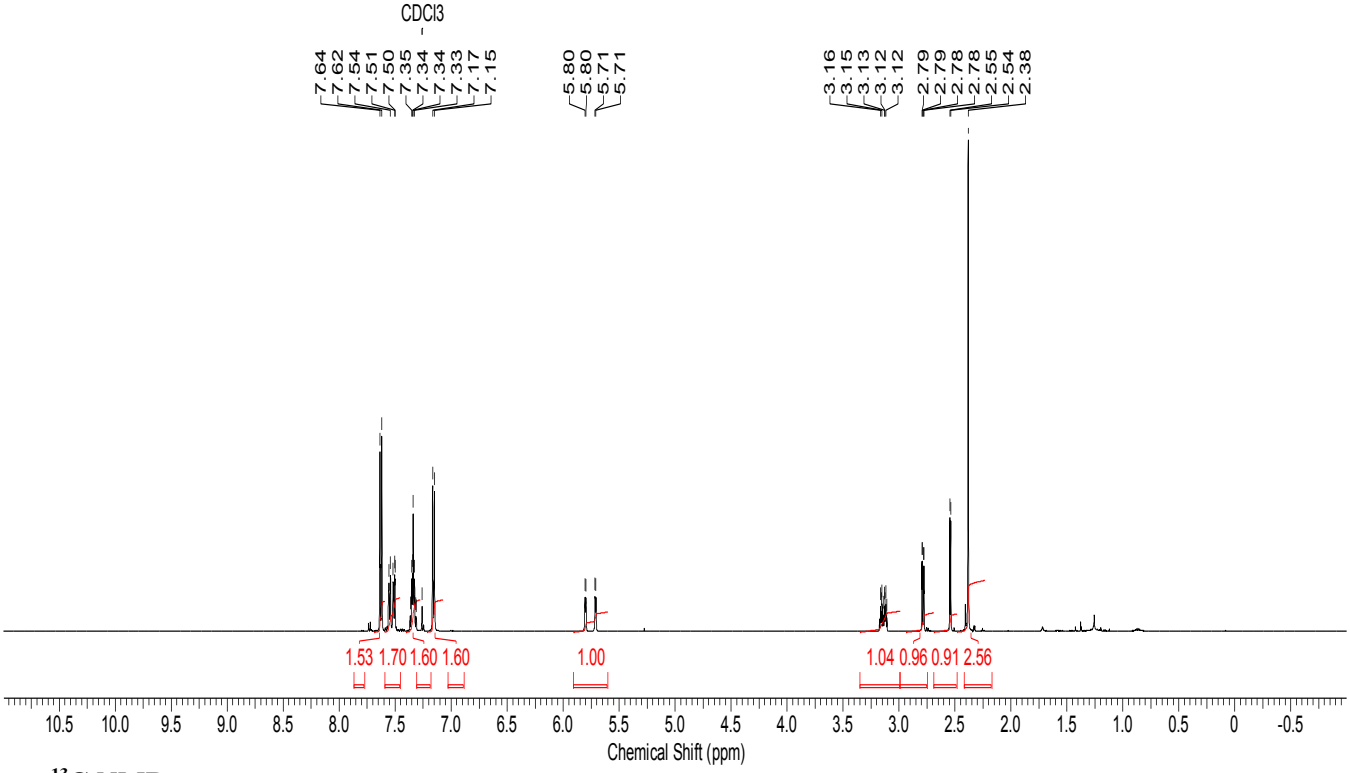
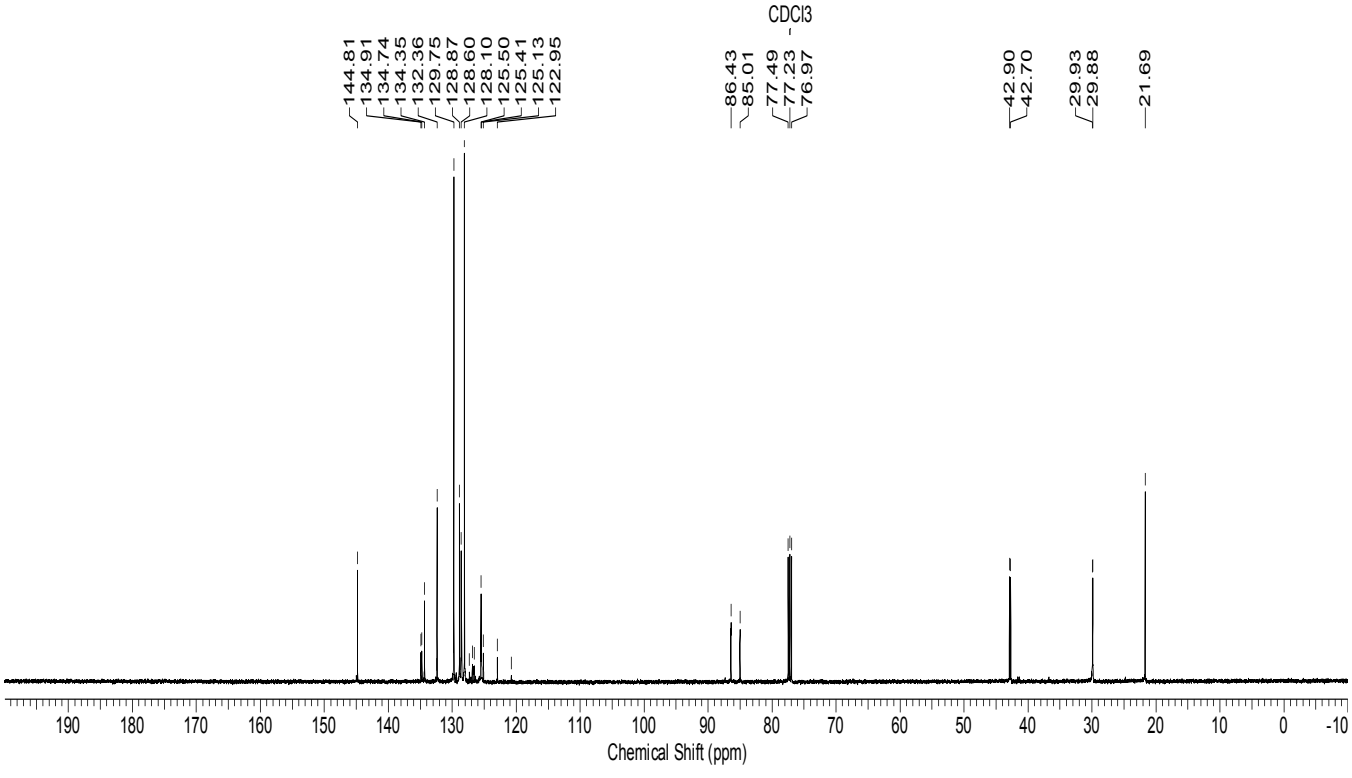
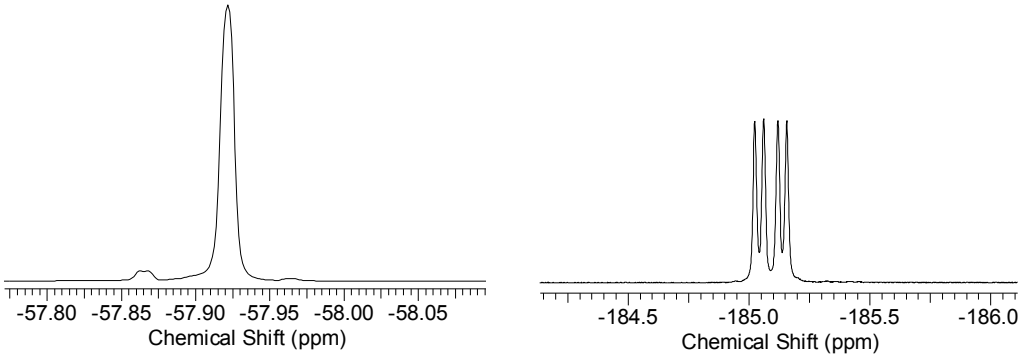


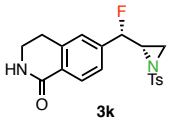
^{13}C NMR
125.7 MHz
$CDCl_3$



^{19}F NMR
470.4 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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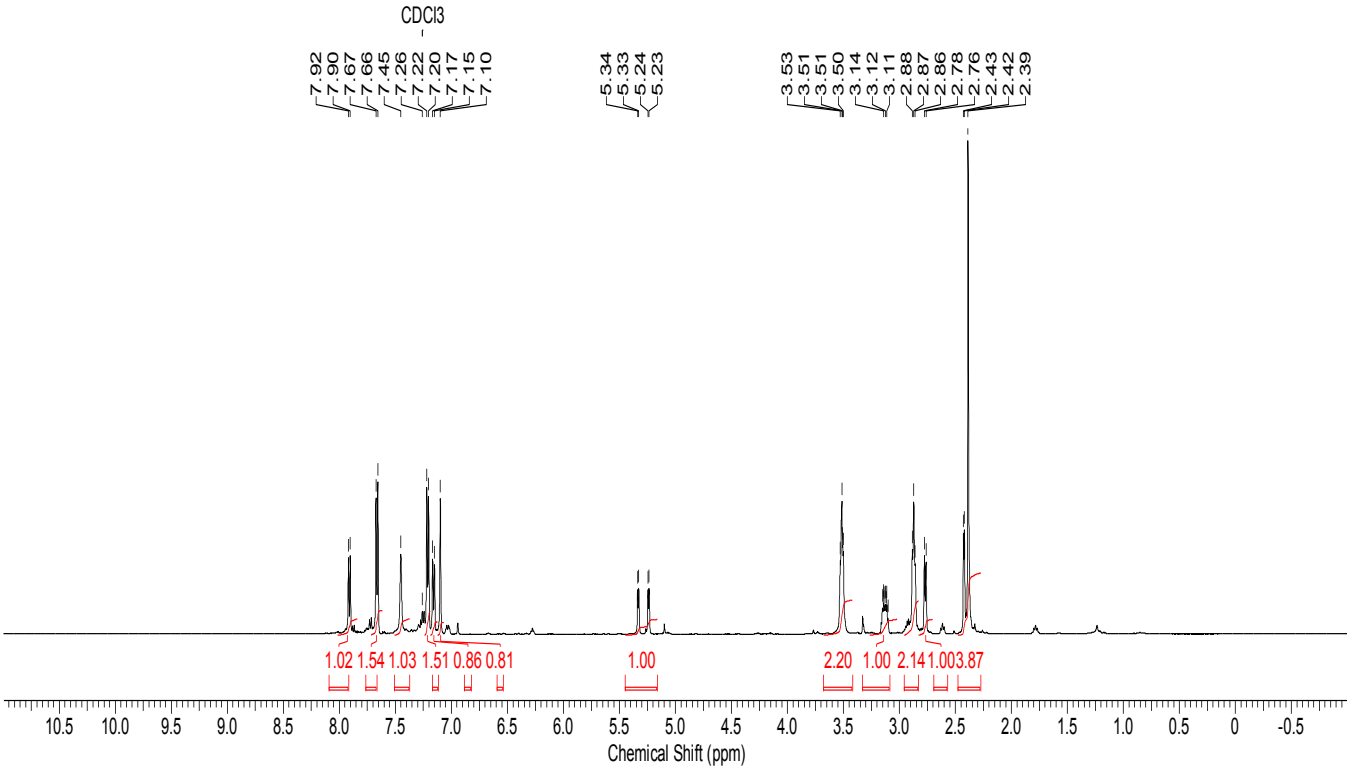
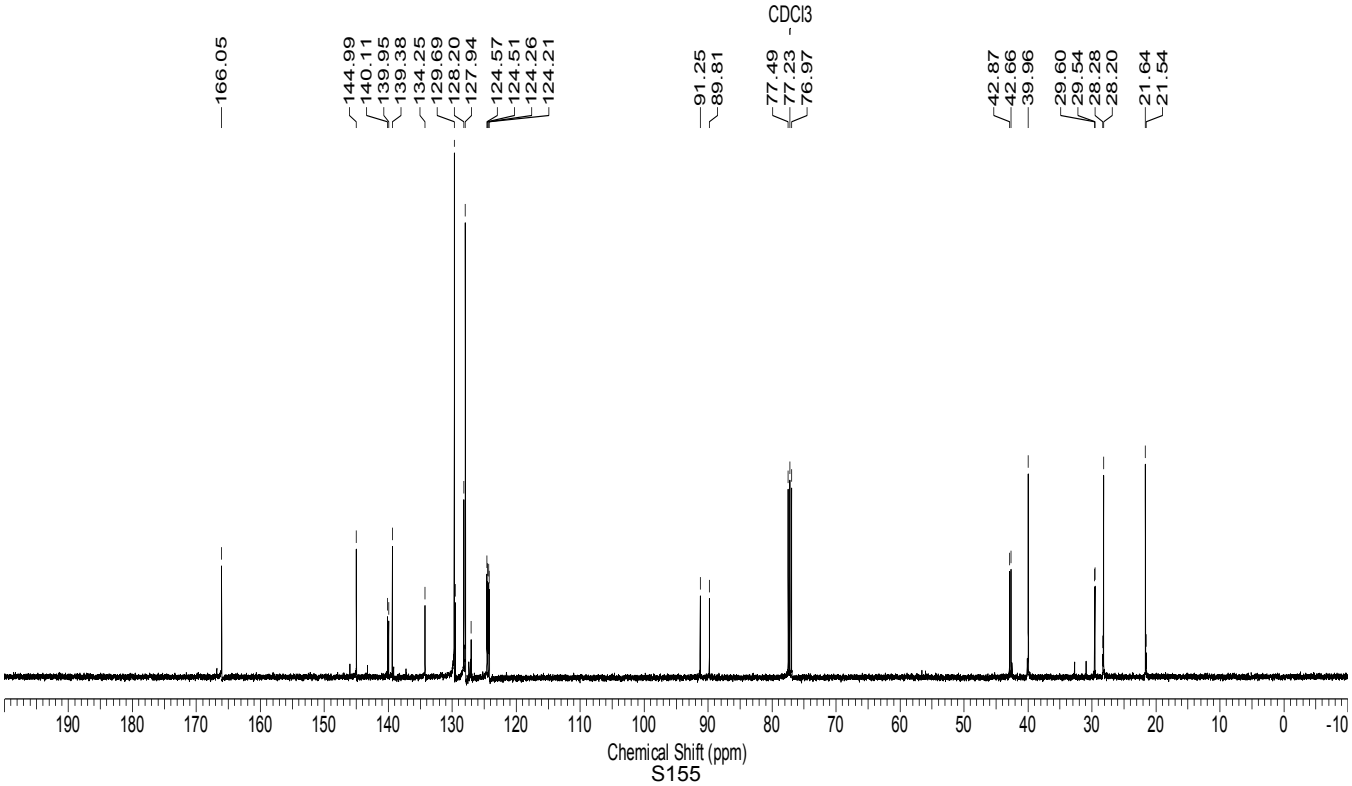
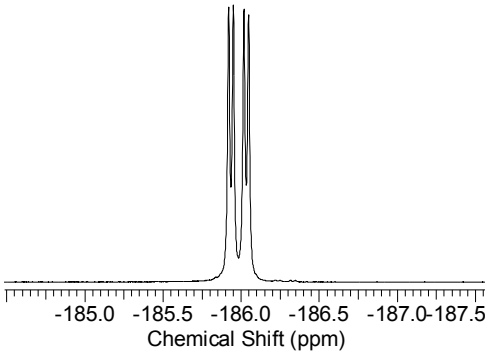


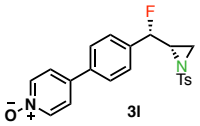
^{13}C NMR
125.7 MHz
$CDCl_3$

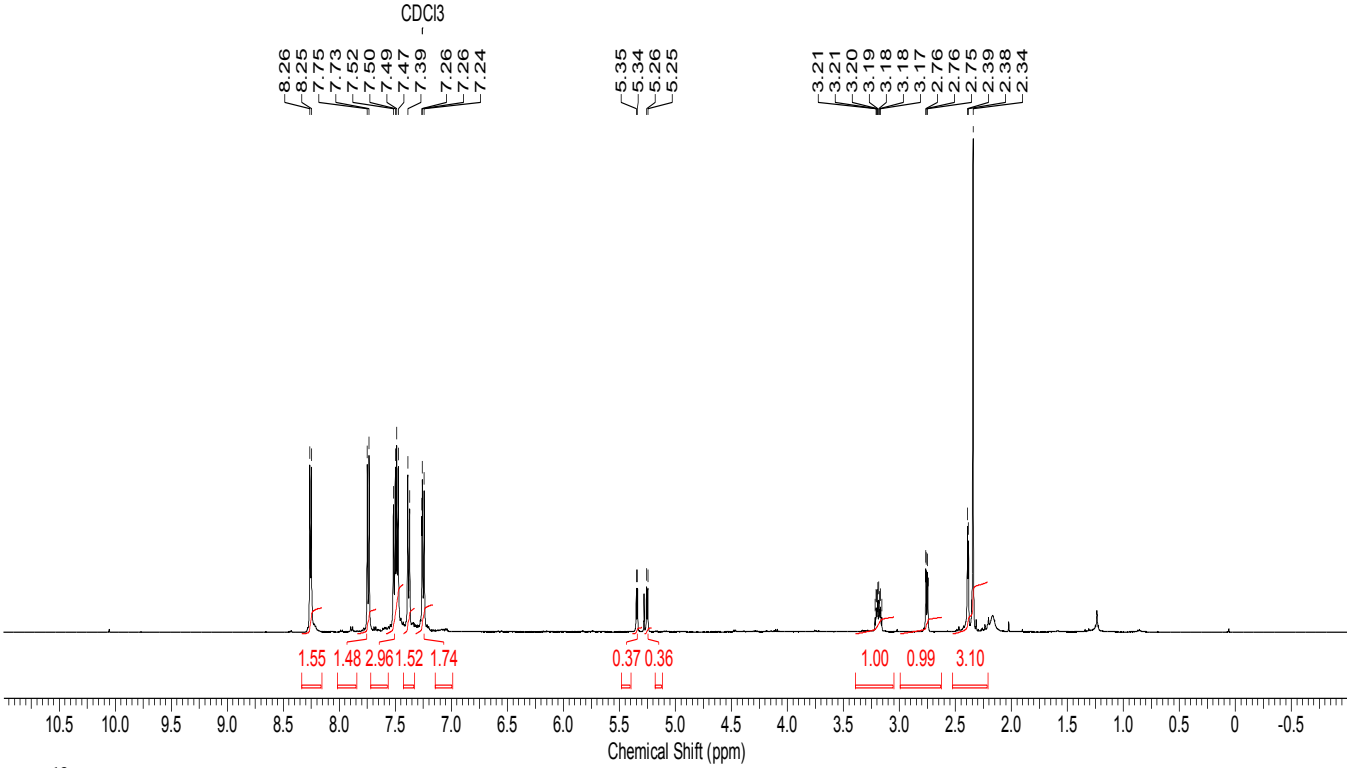


^{19}F NMR
470.4 MHz
$CDCl_3$

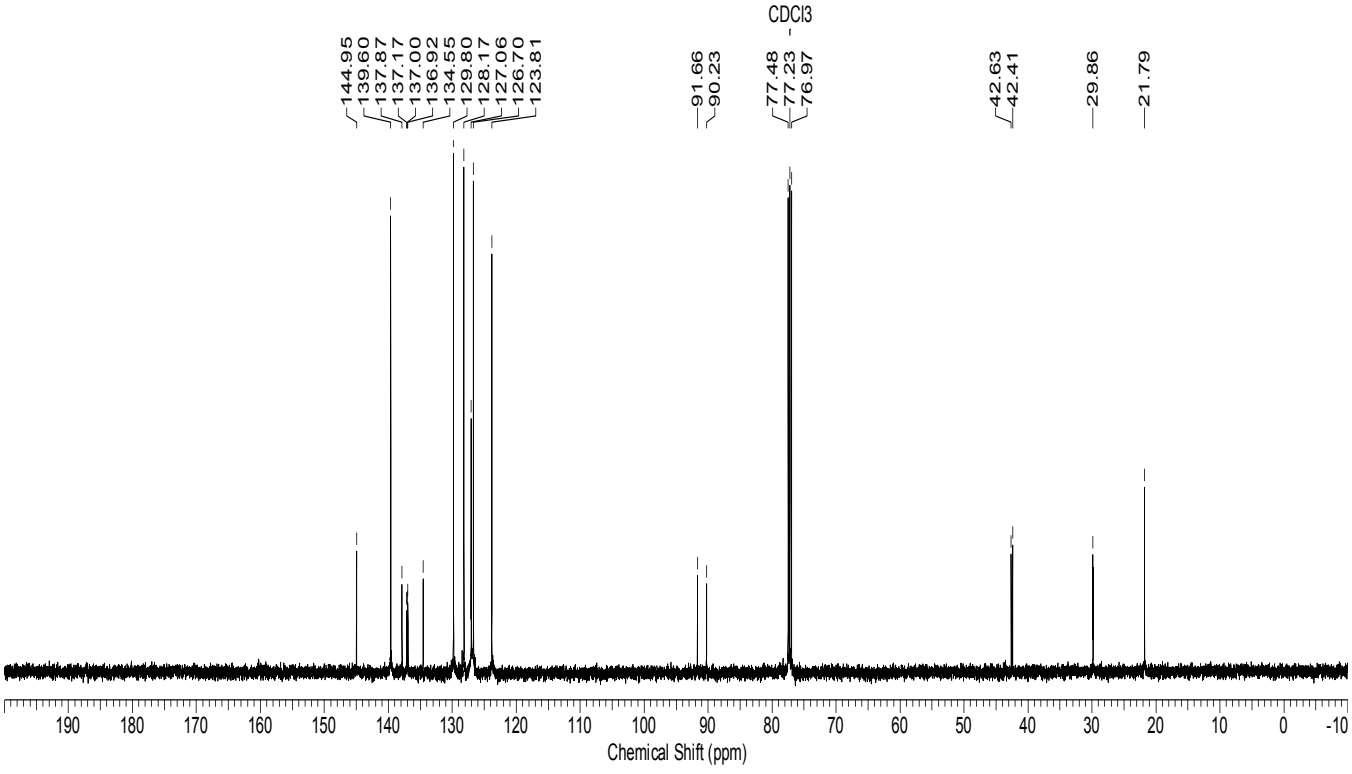


^{1}H NMR
500 MHz
$CDCl_3$

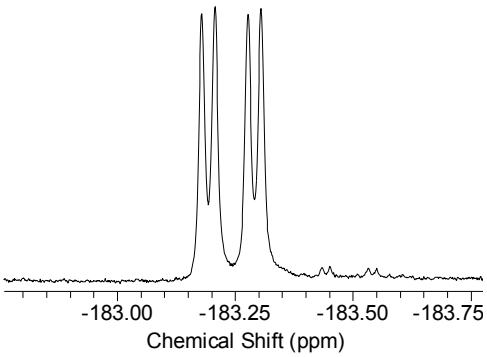




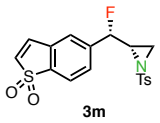
^{13}C NMR
125.7 MHz
$CDCl_3$



^{19}F NMR
470.4 MHz
$CDCl_3$



^{1}H NMR
500 MHz
DMSO-d_6



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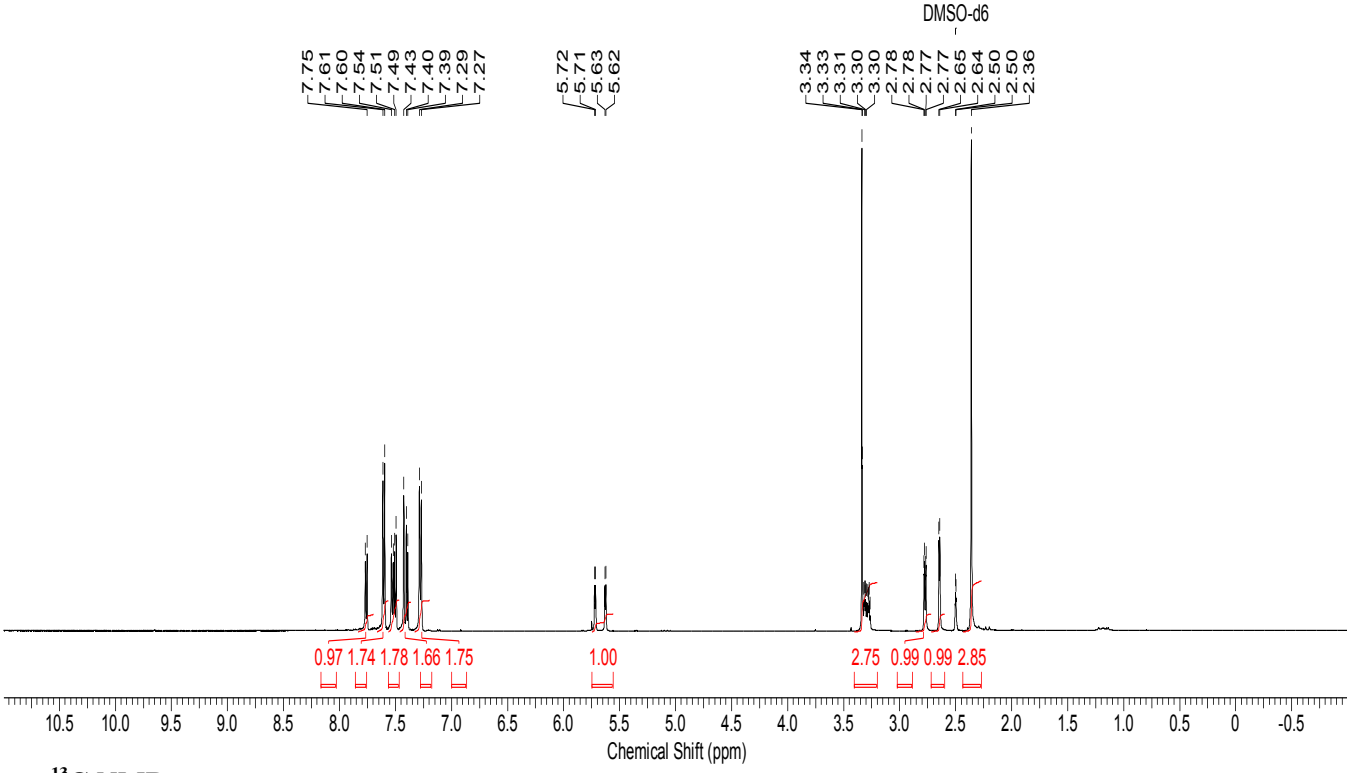
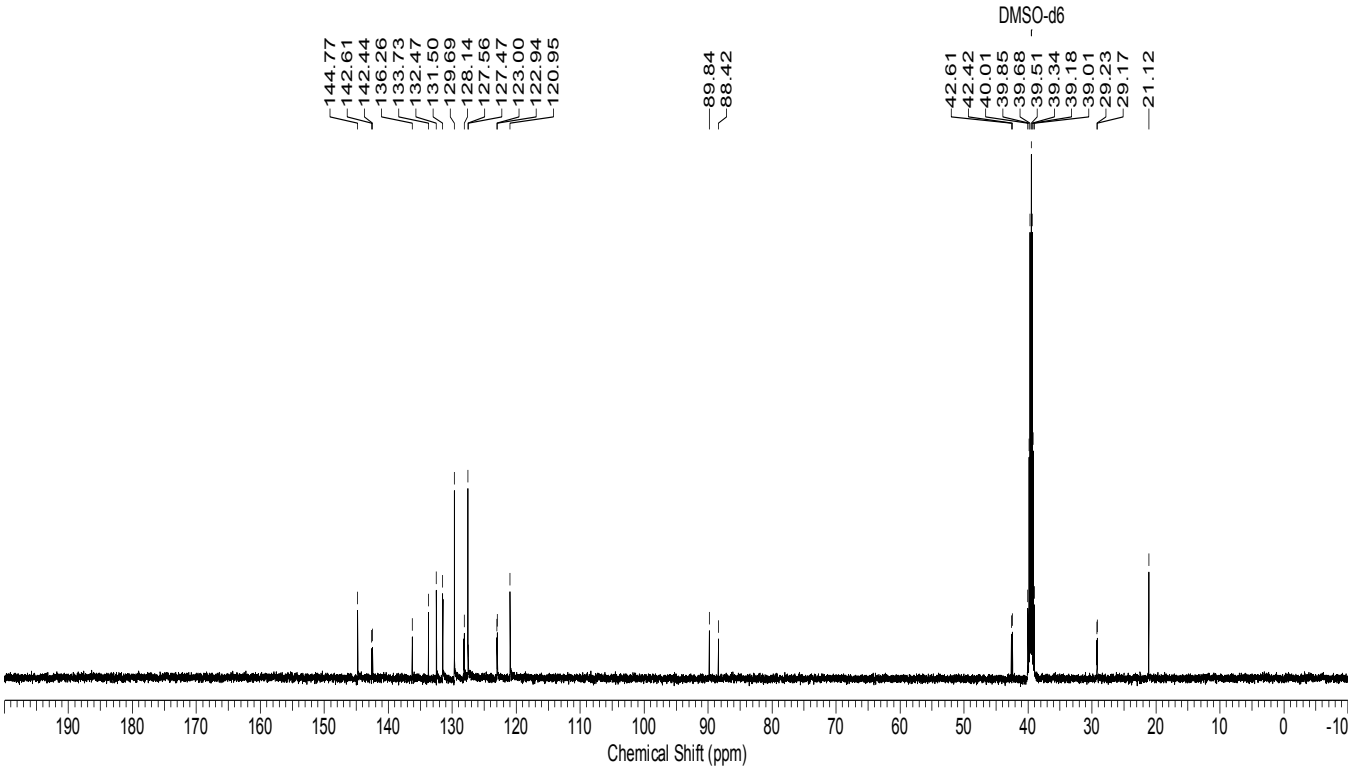
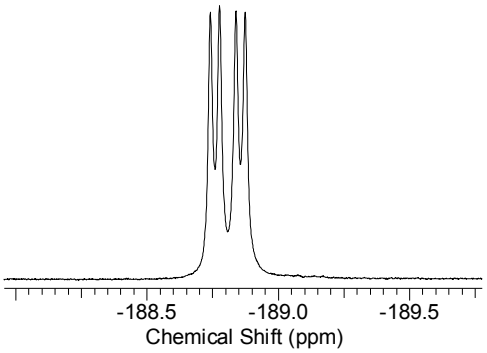


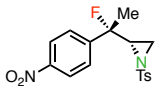
^{13}C NMR
125.7 MHz
$CDCl_3$



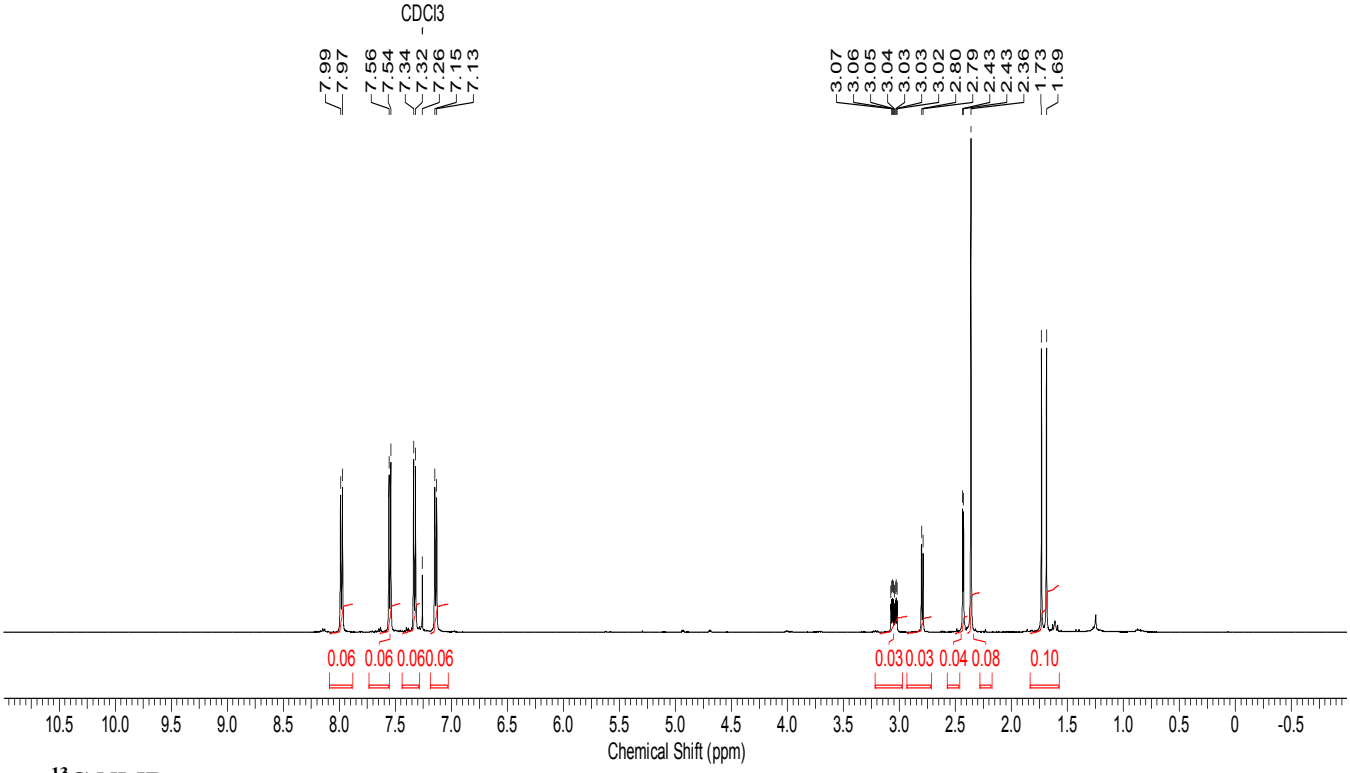
^{19}F NMR
470.4 MHz
DMSO-d_6



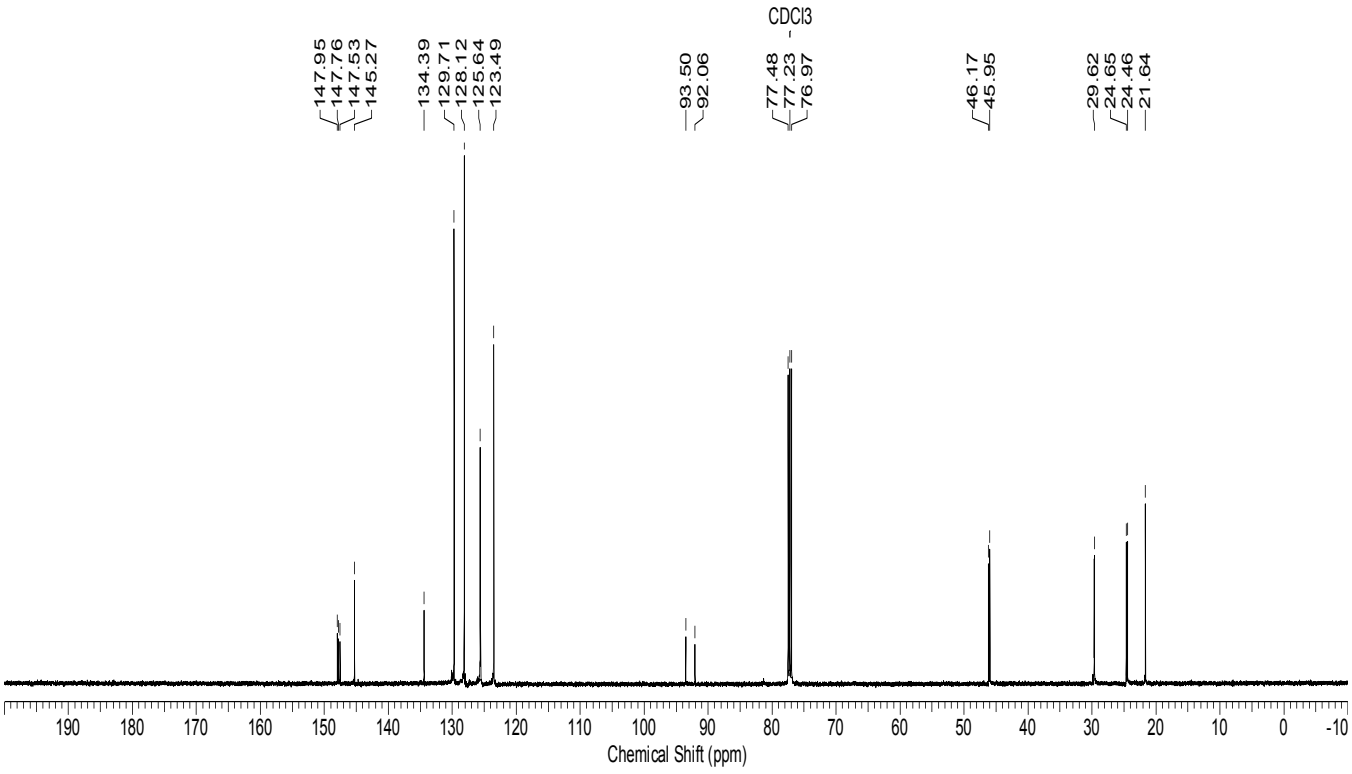
^{1}H NMR
500 MHz
$CDCl_3$



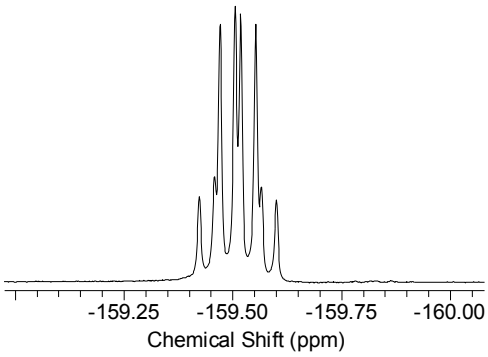
3n



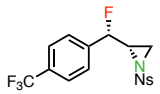
^{13}C NMR
125.7 MHz
$CDCl_3$



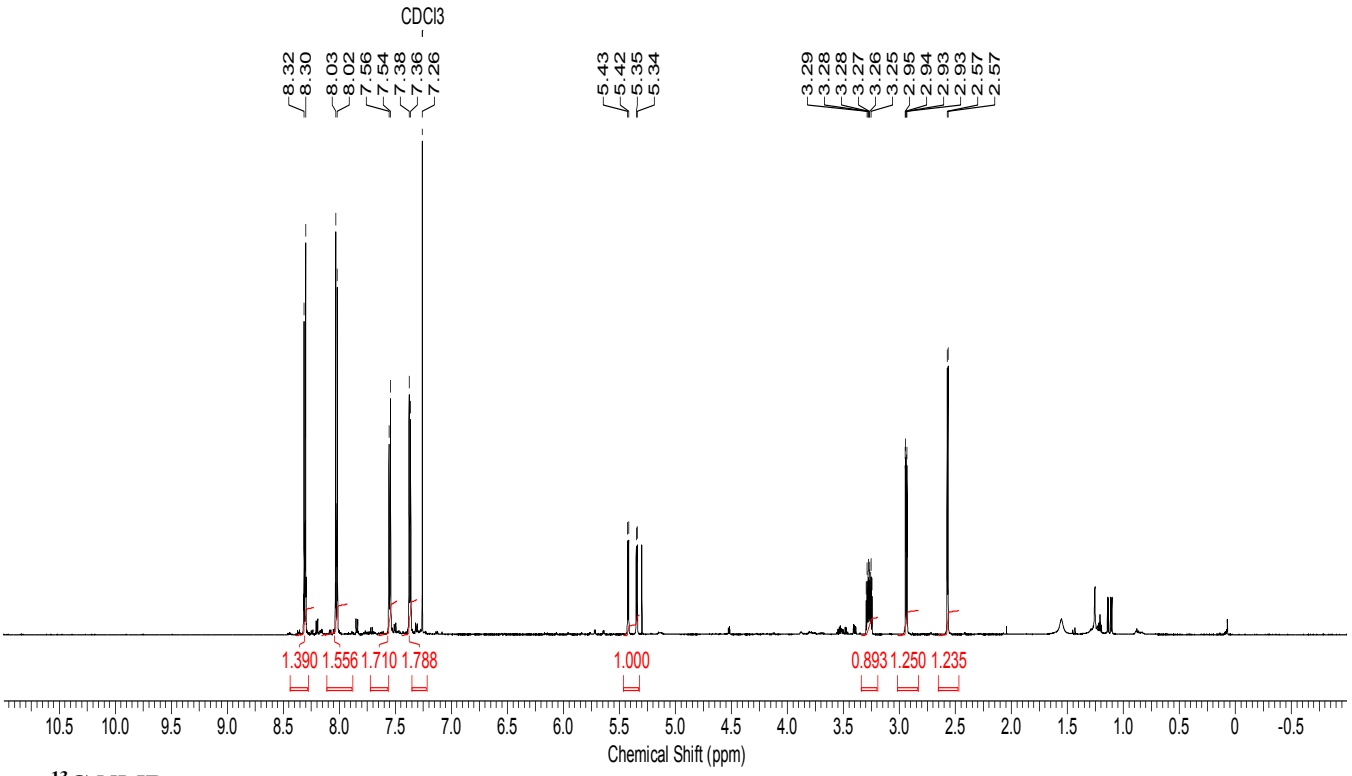
^{19}F NMR
470.4 MHz
$CDCl_3$



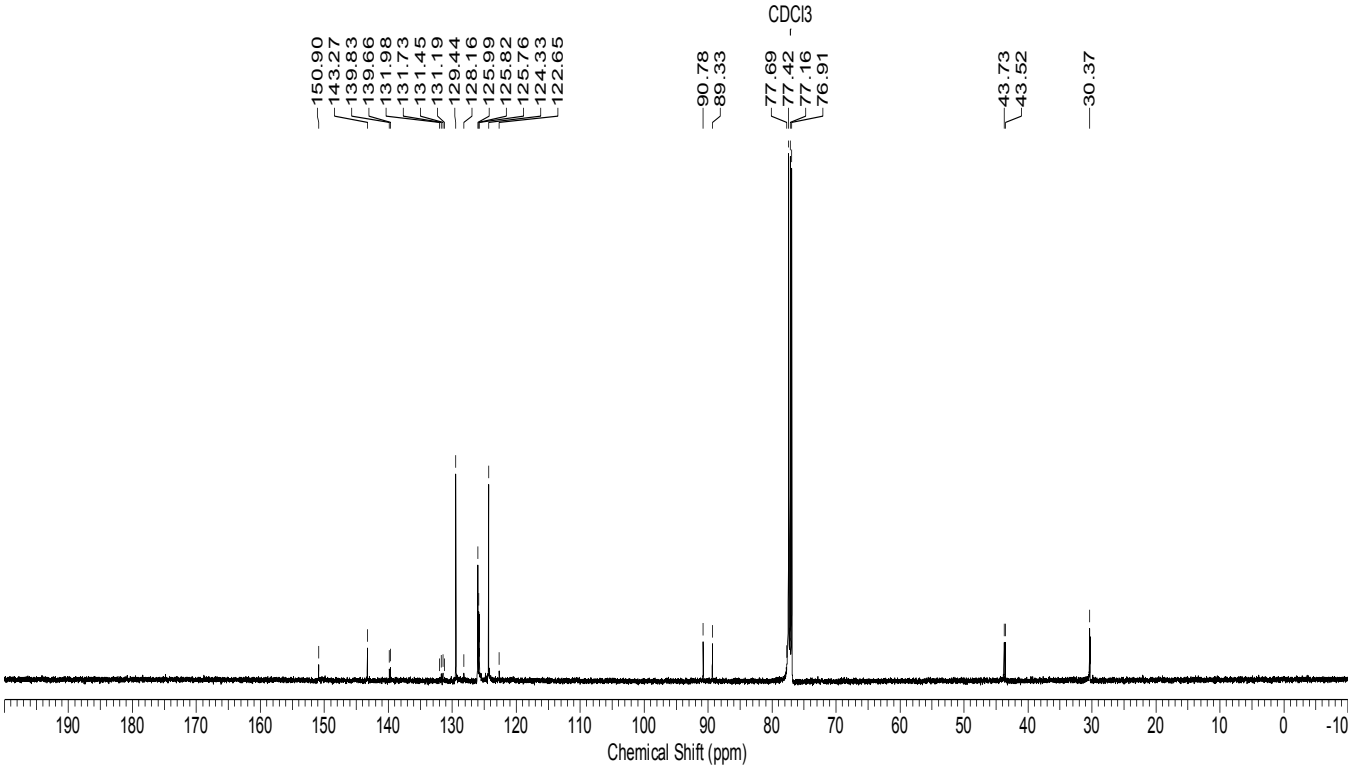
^{1}H NMR
600 MHz
$CDCl_3$



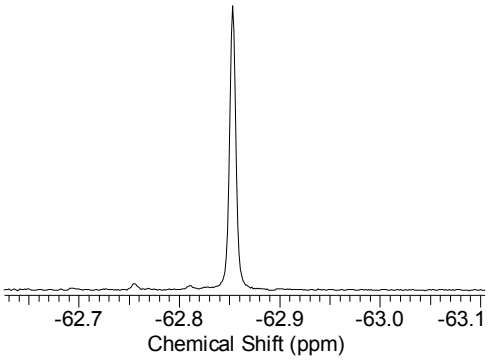
3o

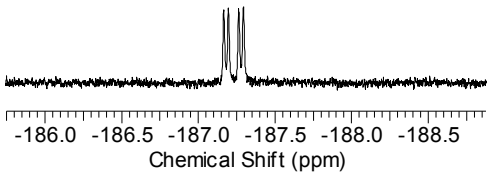


^{13}C NMR
125.7 MHz
$CDCl_3$

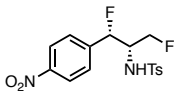


^{19}F NMR
470.4 MHz
$CDCl_3$

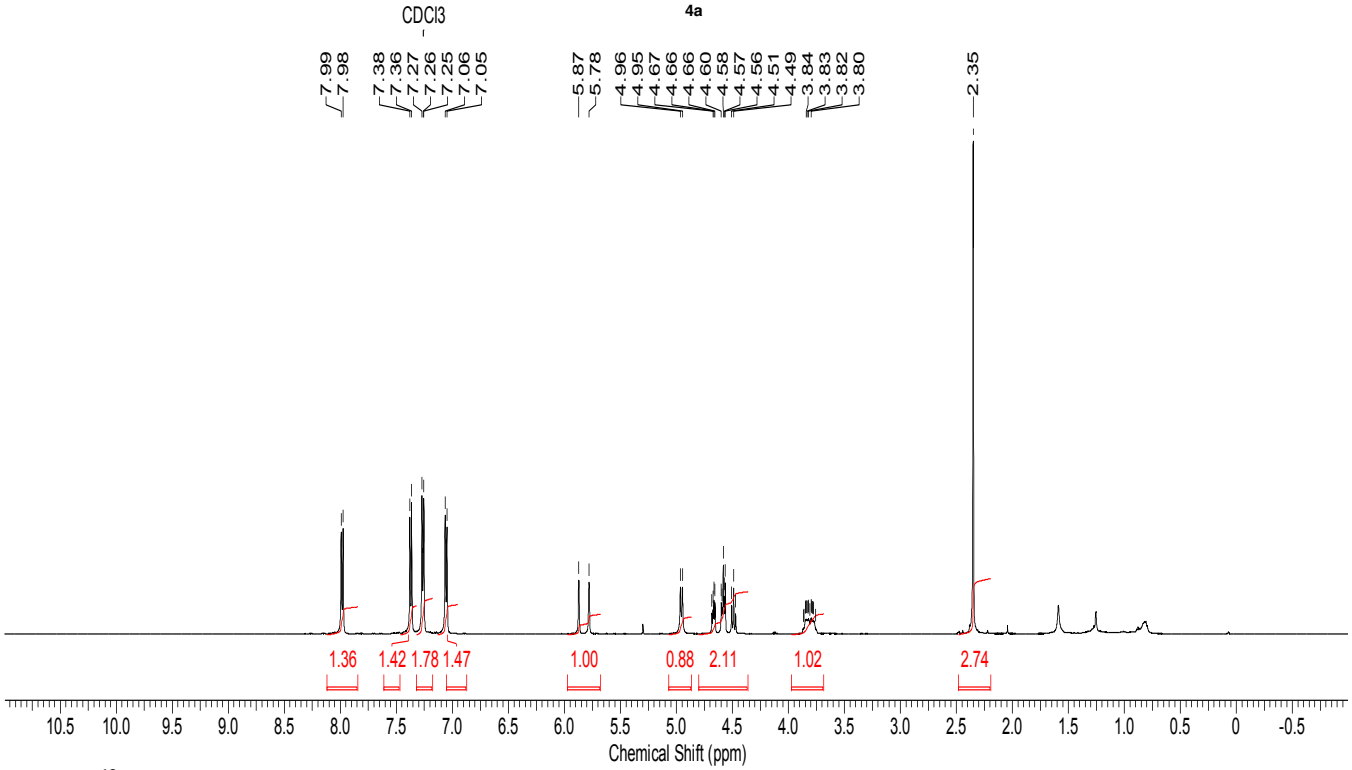




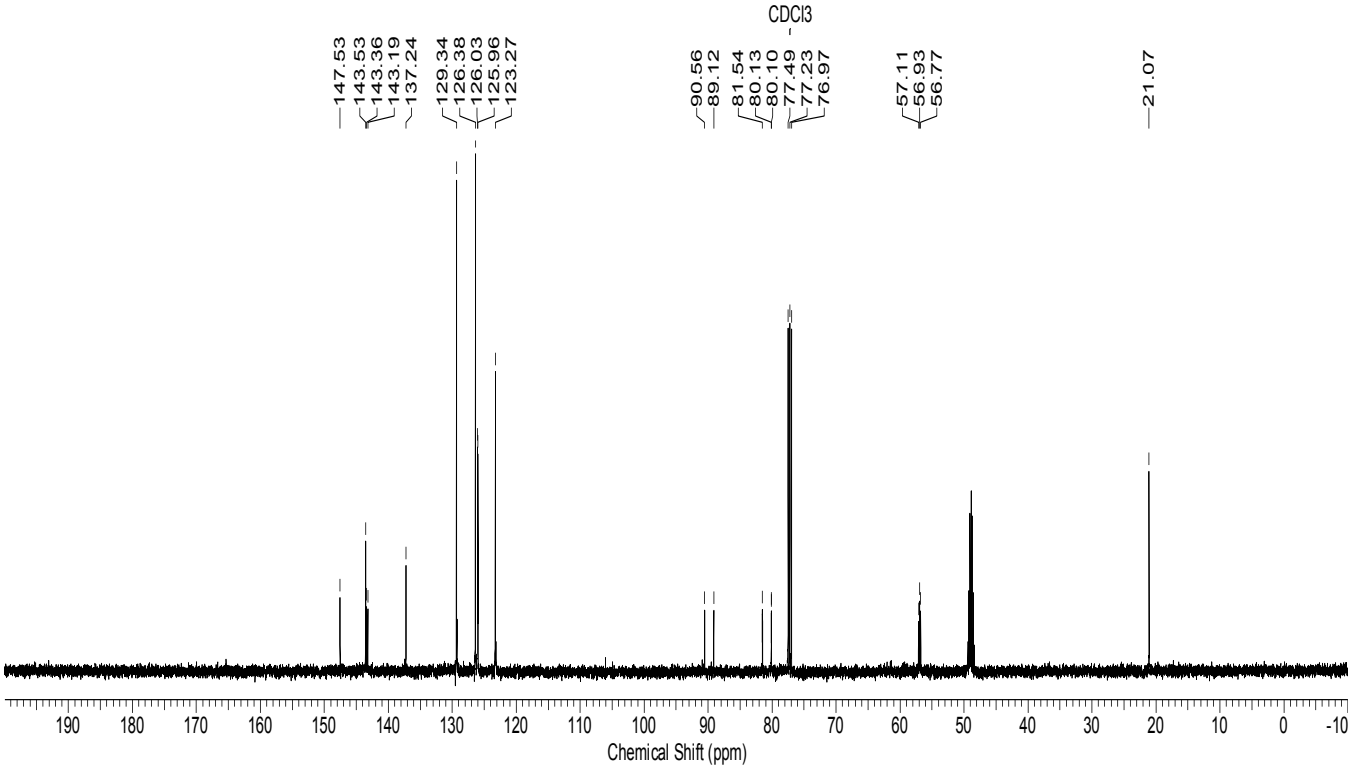
^{1}H NMR
500 MHz
$CDCl_3$



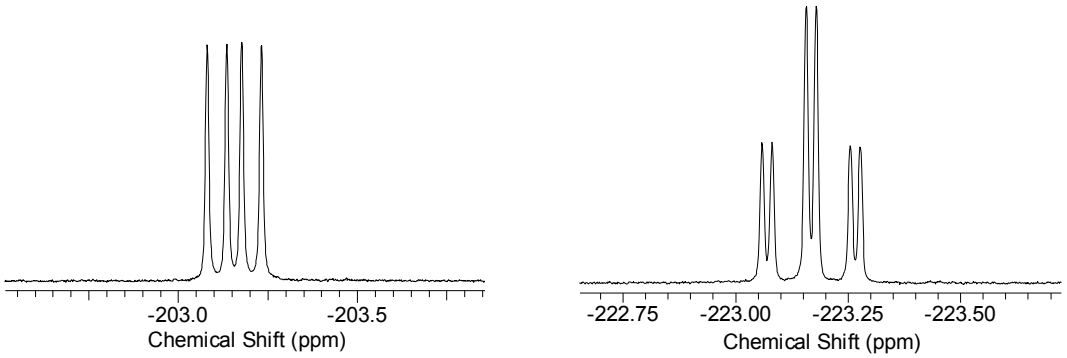
4a



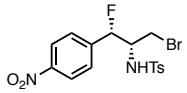
^{13}C NMR
125.7 MHz
10% $CD_3OD/CDCl_3$



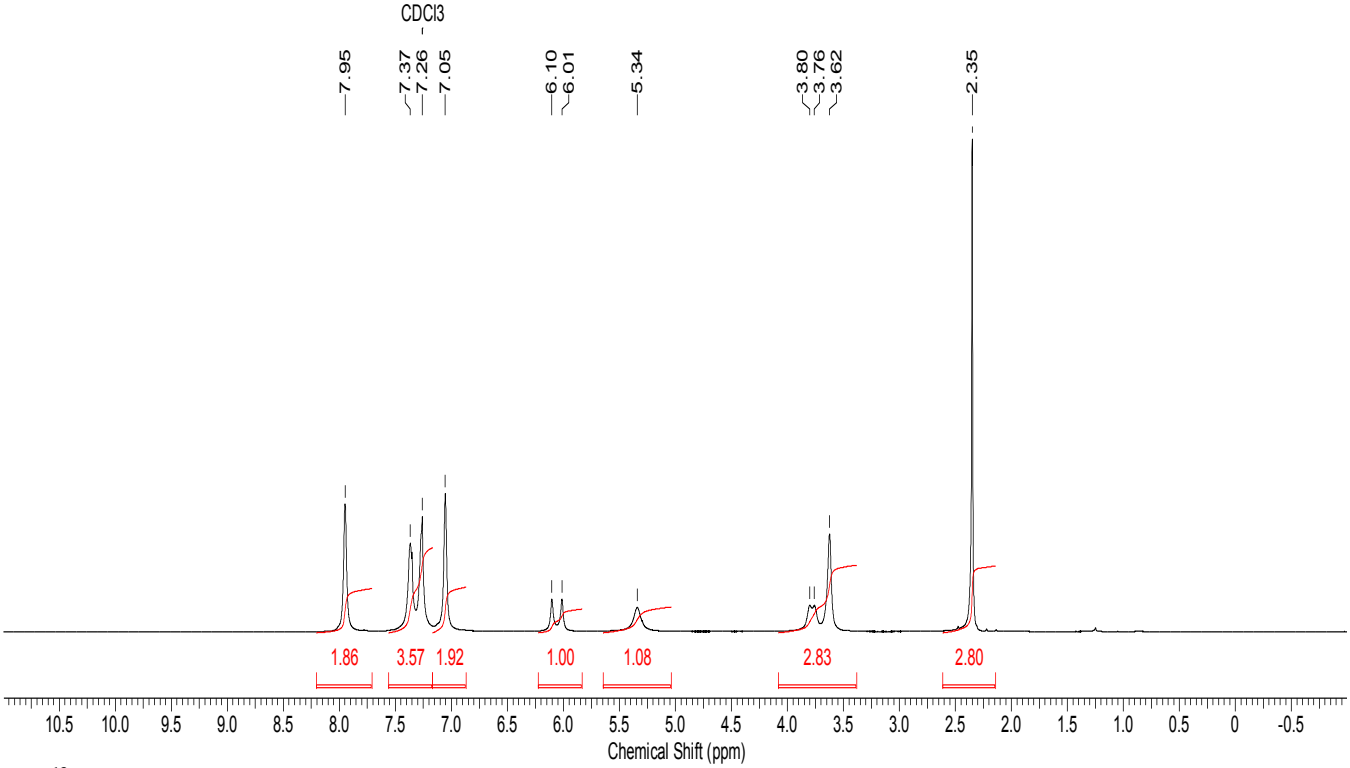
^{19}F NMR
470.4 MHz
$CDCl_3$



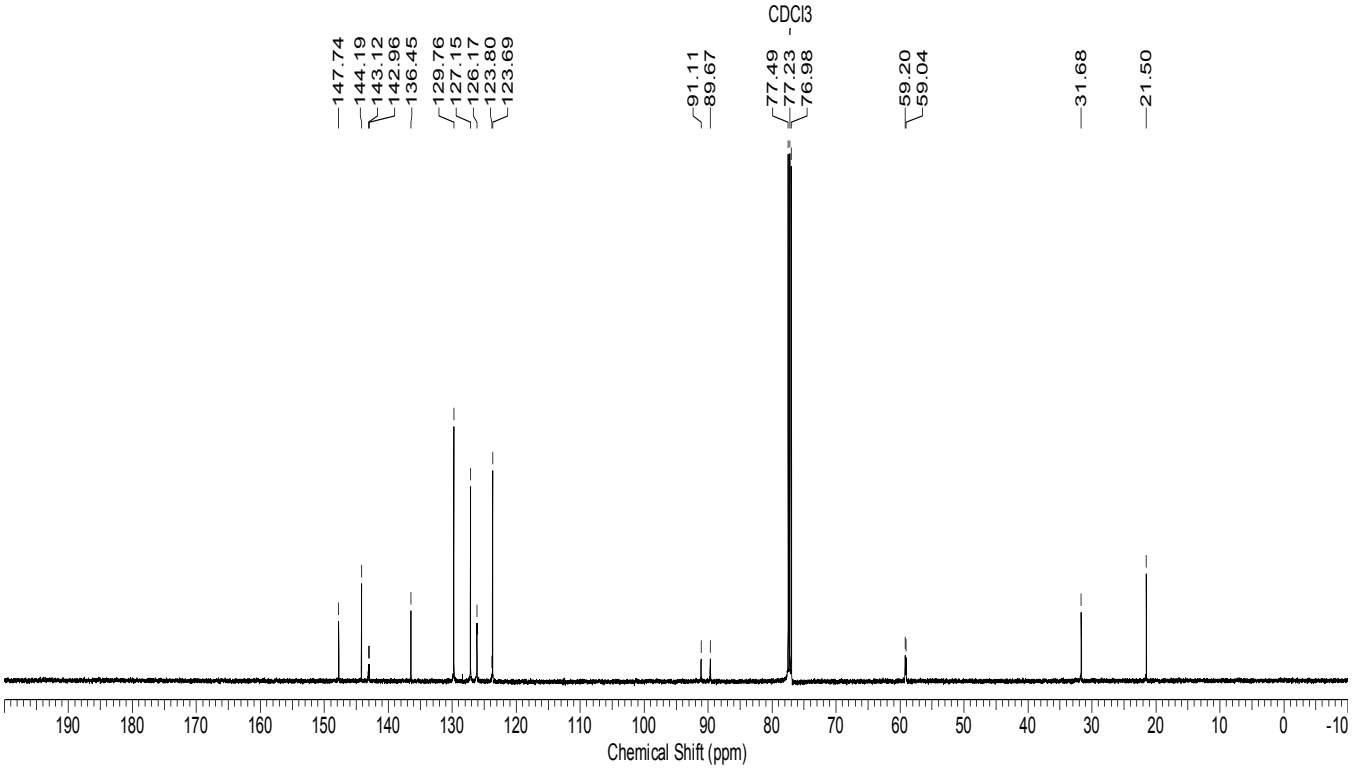
^{1}H NMR
500 MHz
$CDCl_3$



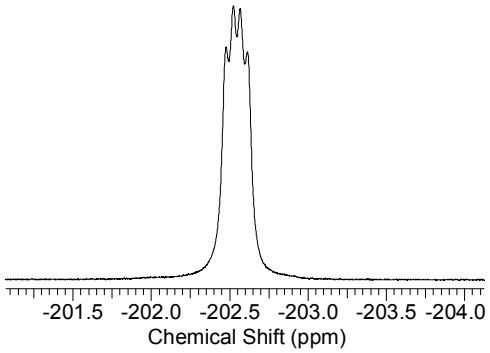
4b



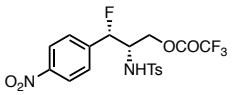
^{13}C NMR
125.7 MHz
$CDCl_3$



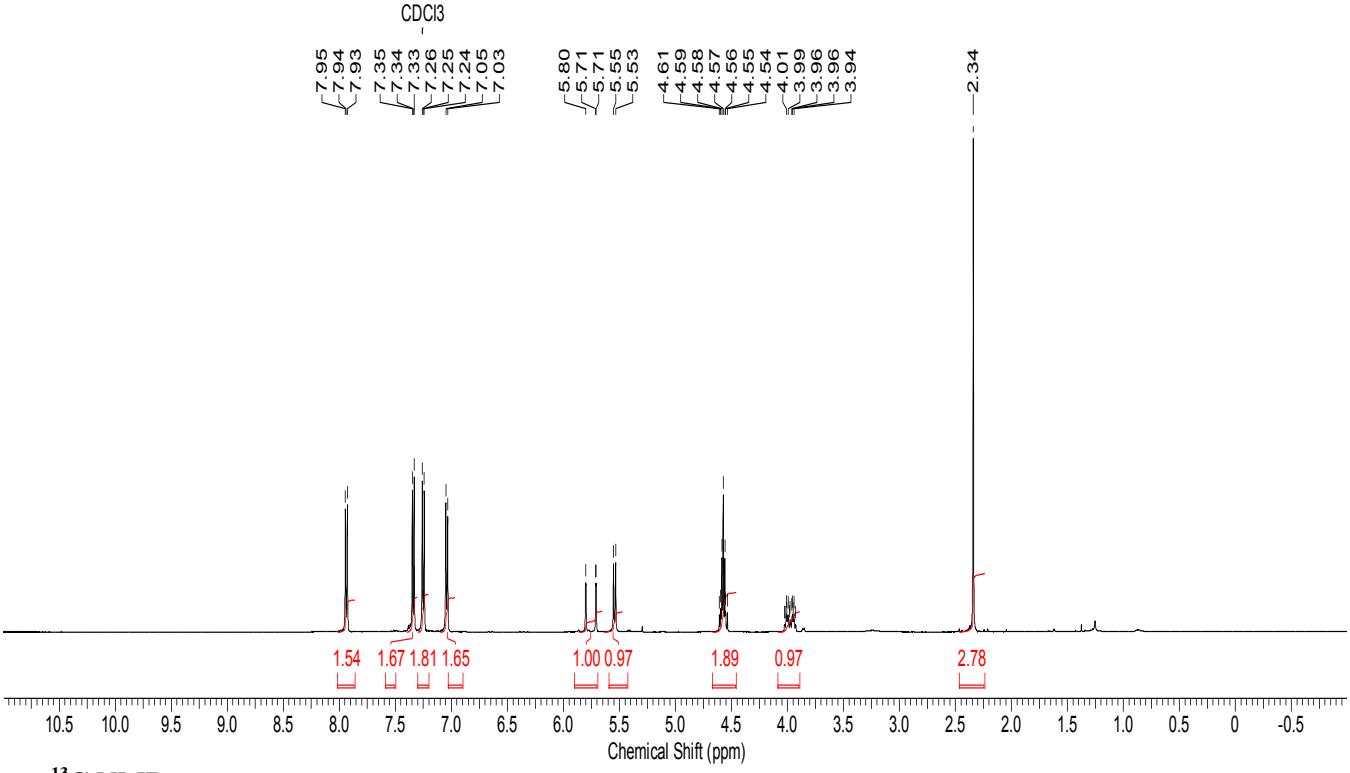
^{19}F NMR
470.4 MHz
$CDCl_3$



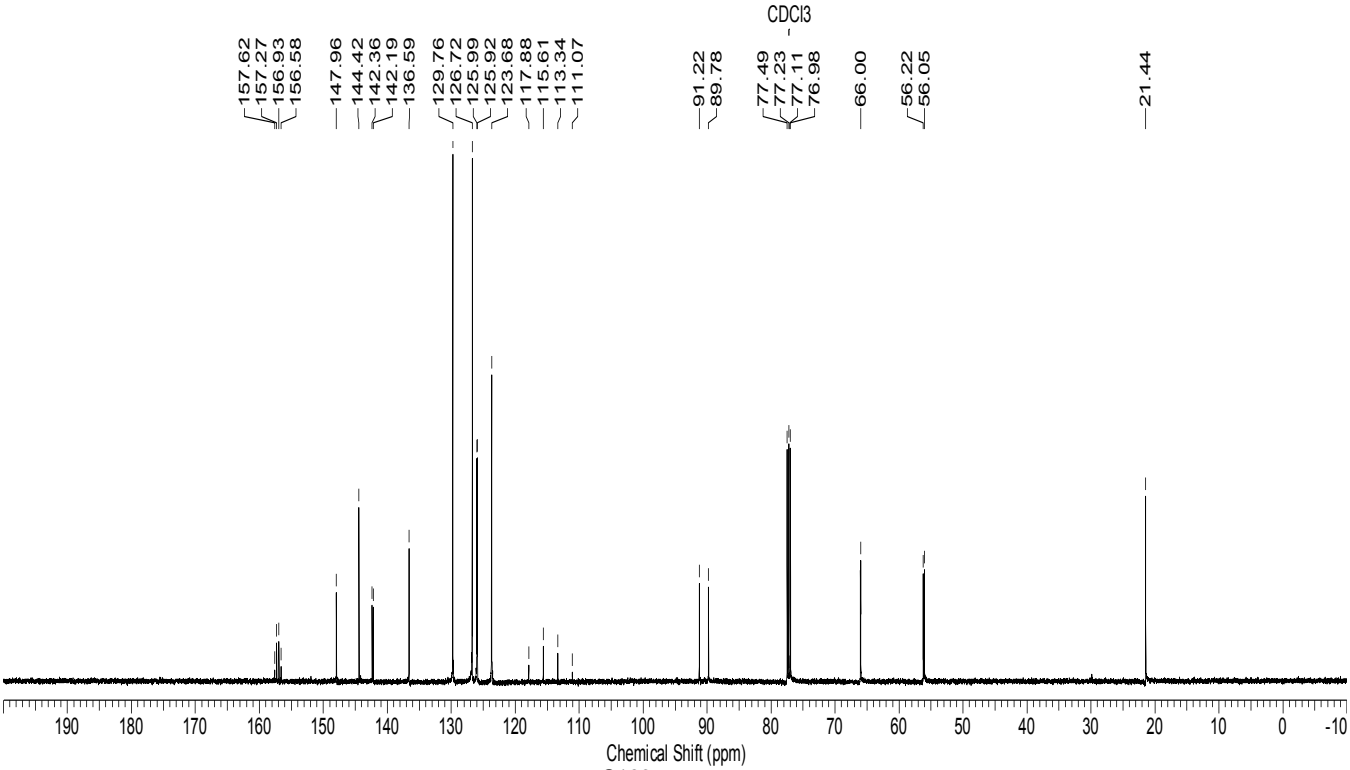
^{1}H NMR
500 MHz
$CDCl_3$



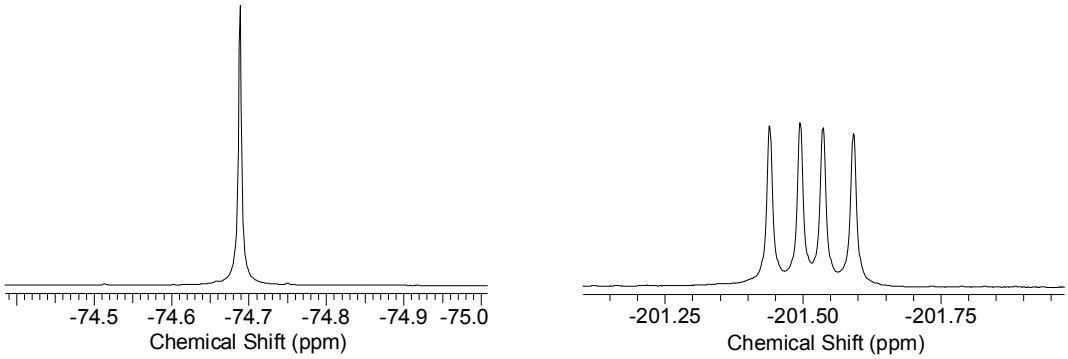
4c



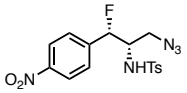
^{13}C NMR
125.7 MHz
$CDCl_3$



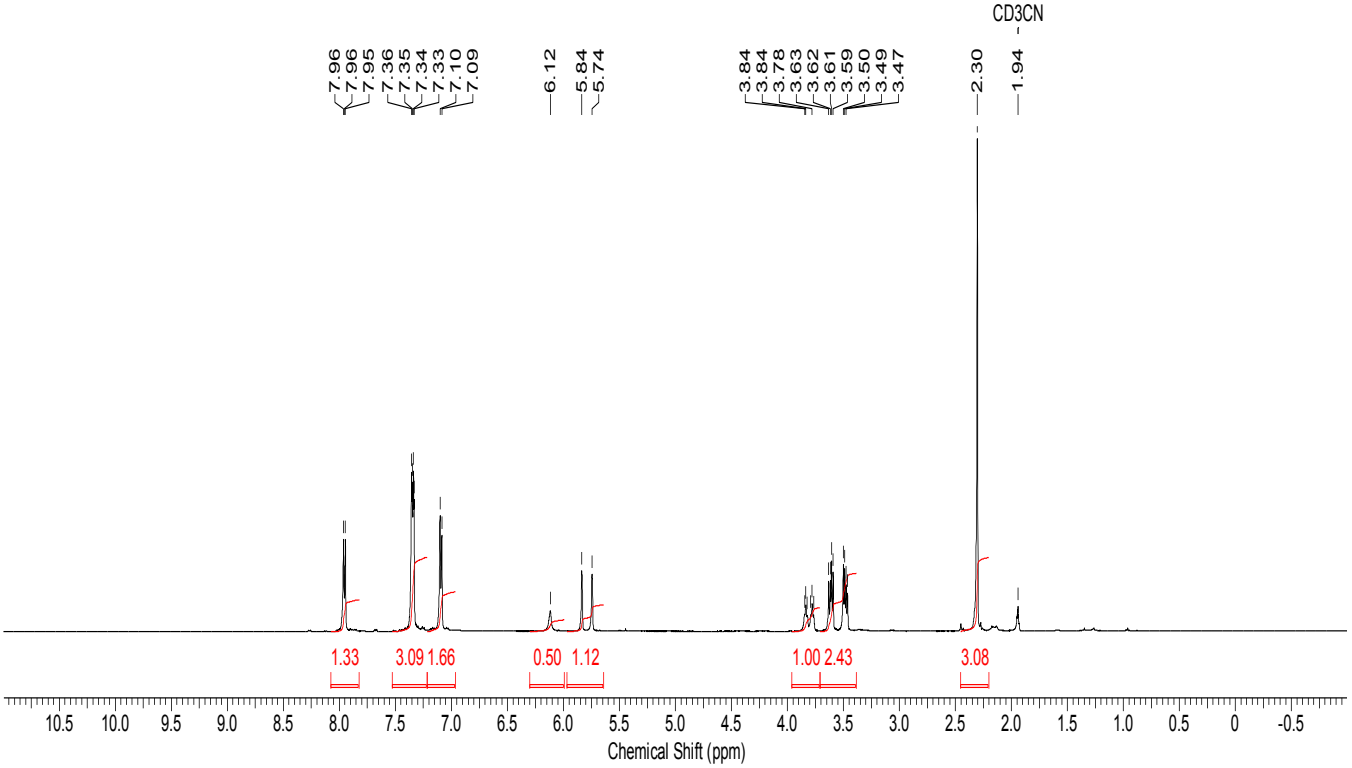
^{19}F NMR
470.4 MHz
$CDCl_3$



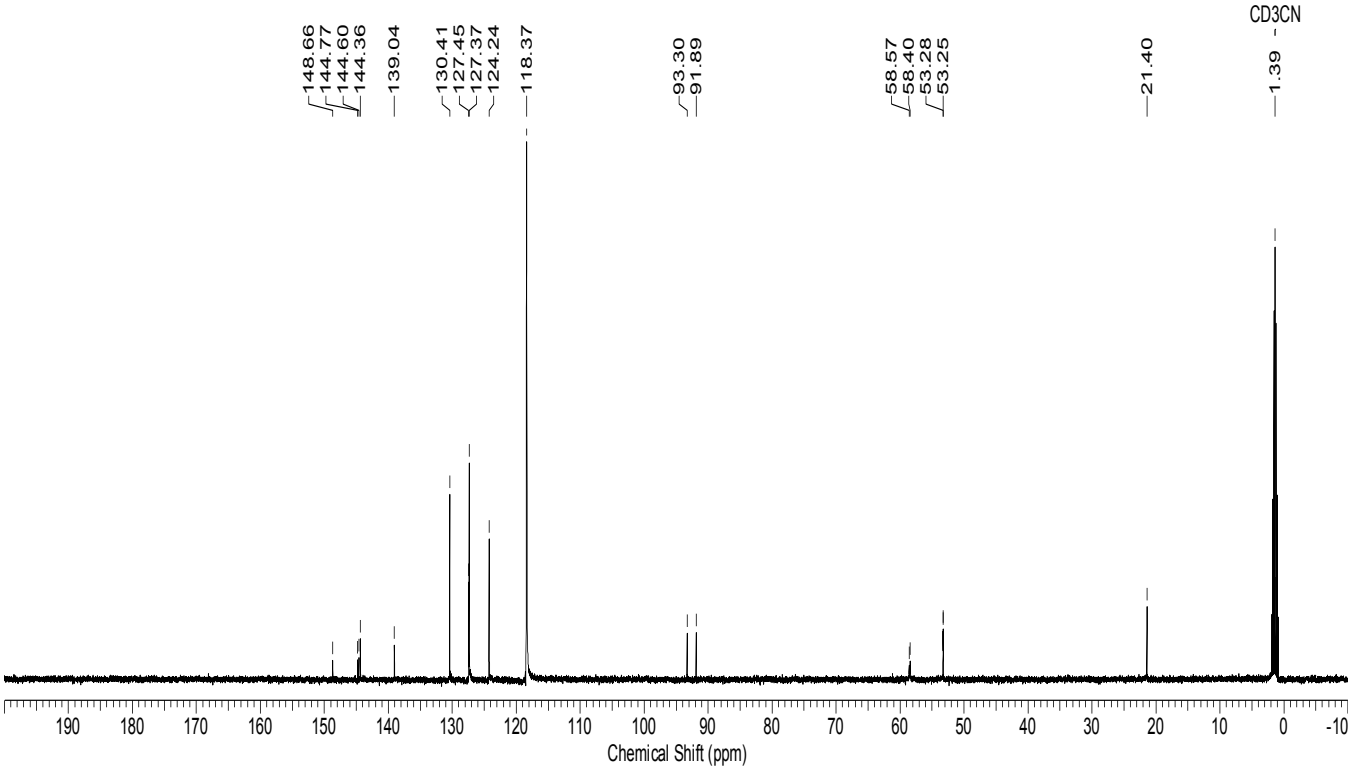
^{1}H NMR
500 MHz
CD_3CN



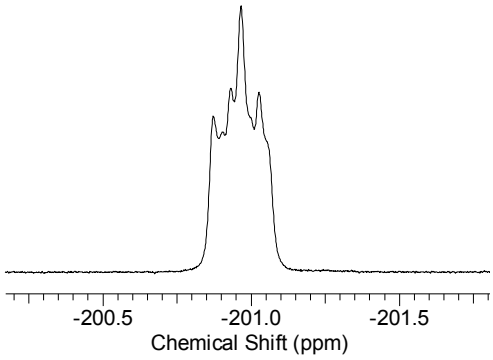
4d



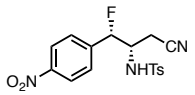
^{13}C NMR
125.7 MHz
CD_3CN



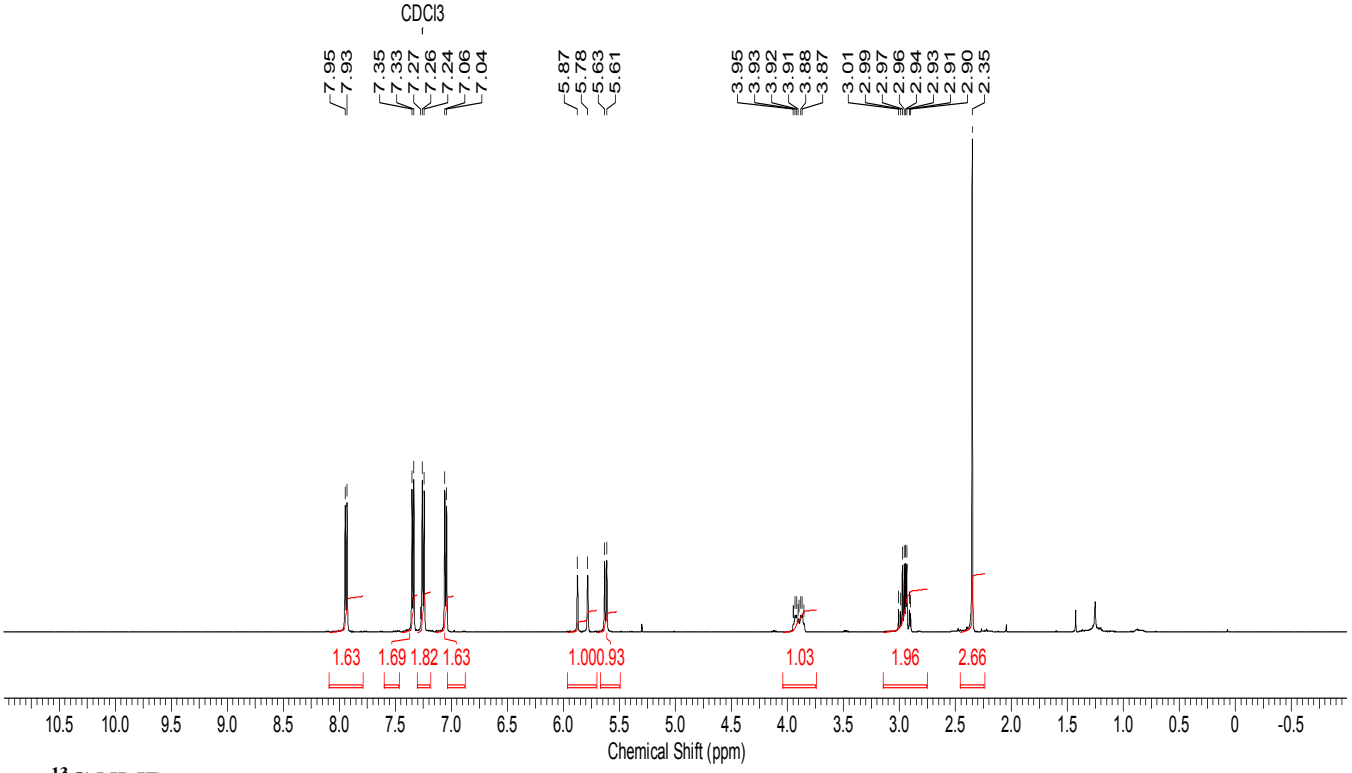
^{19}F NMR
470.4 MHz
CD_3CN



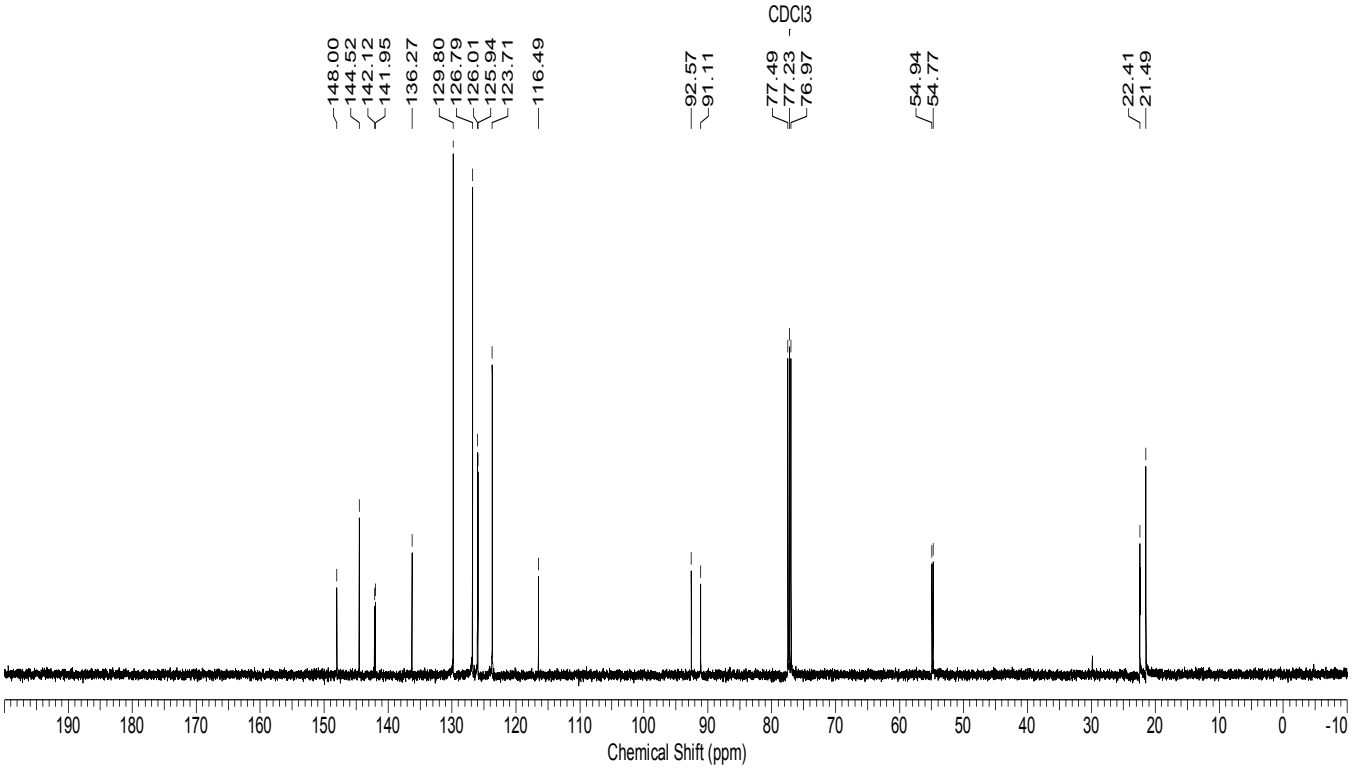
^{1}H NMR
500 MHz
$CDCl_3$



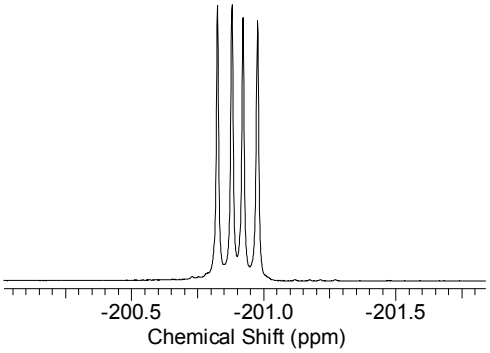
4e



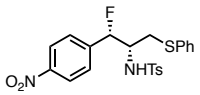
^{13}C NMR
125.7 MHz
$CDCl_3$



^{19}F NMR
470.4 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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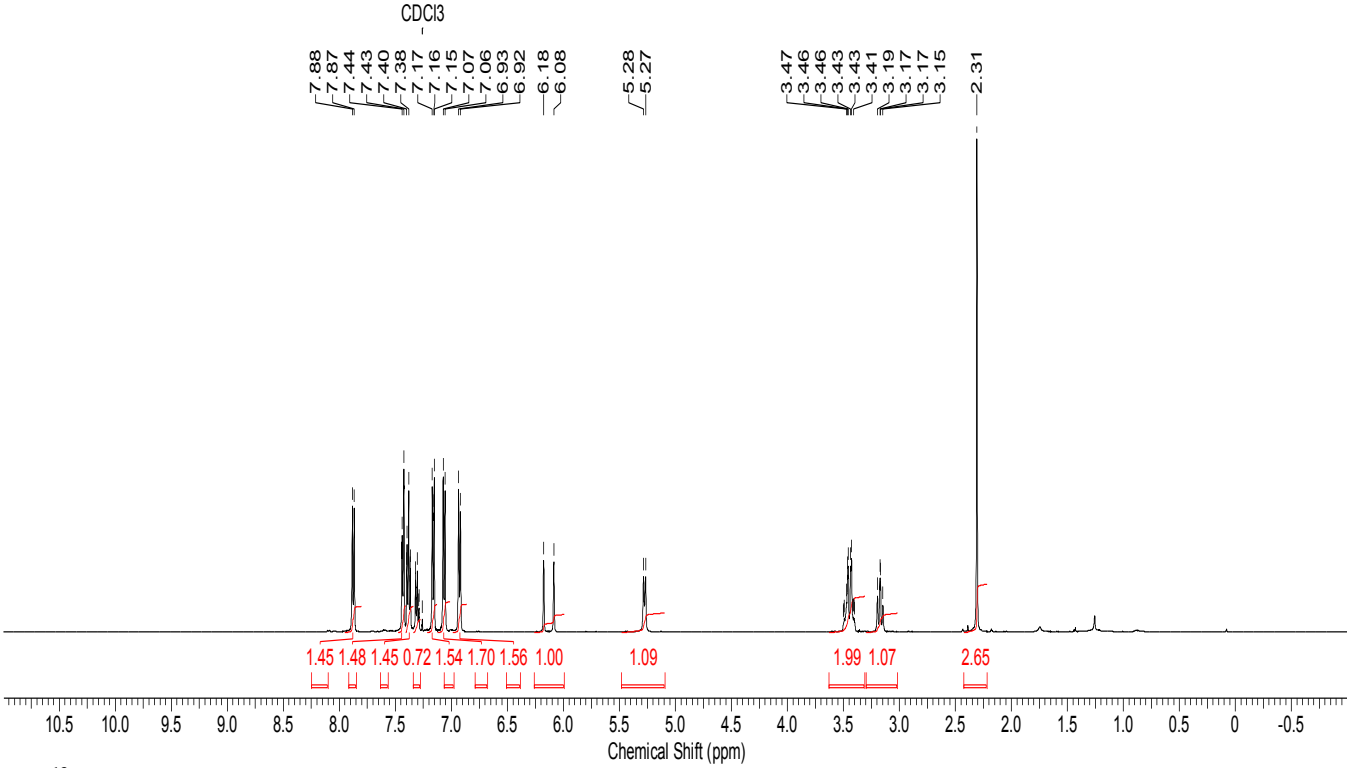
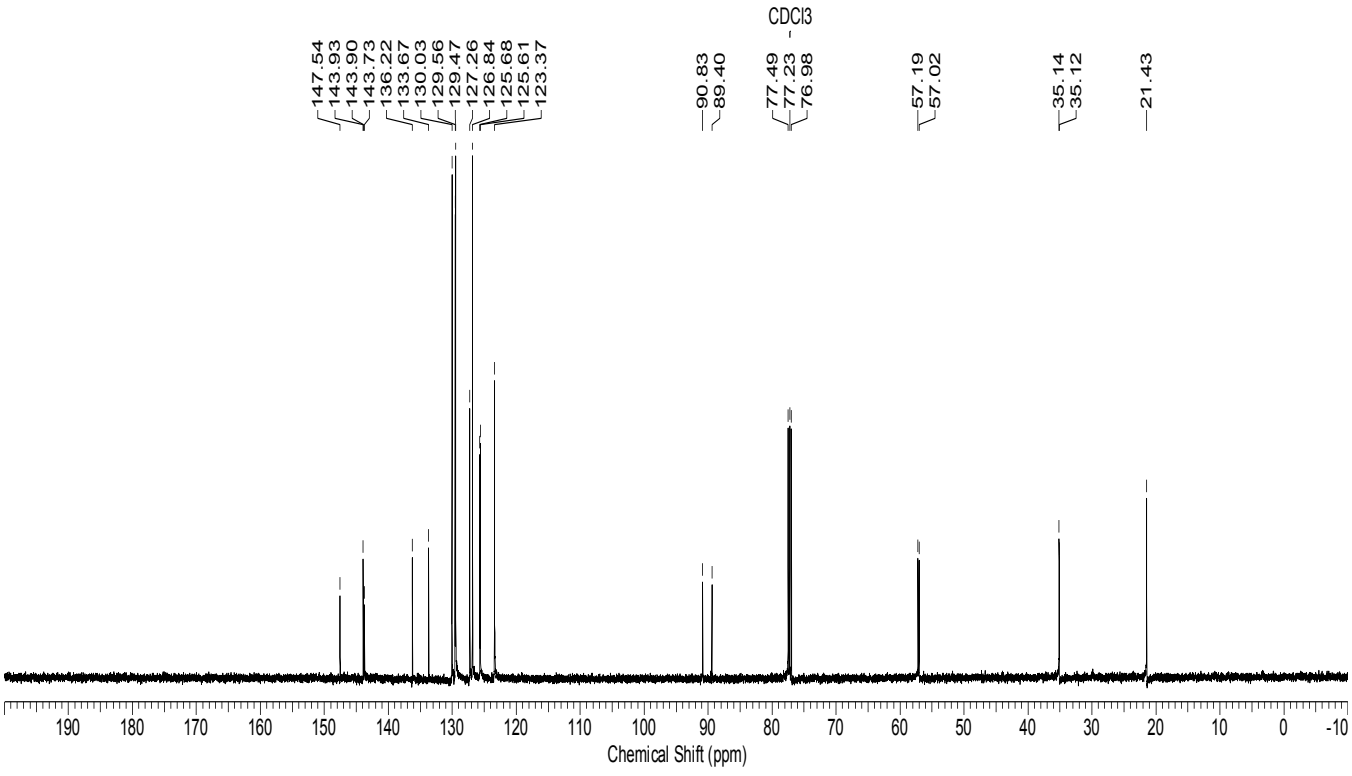
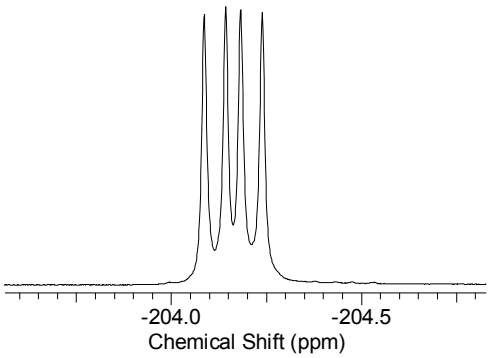


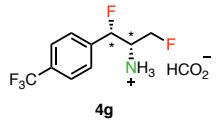
^{13}C NMR
125.7 MHz
$CDCl_3$

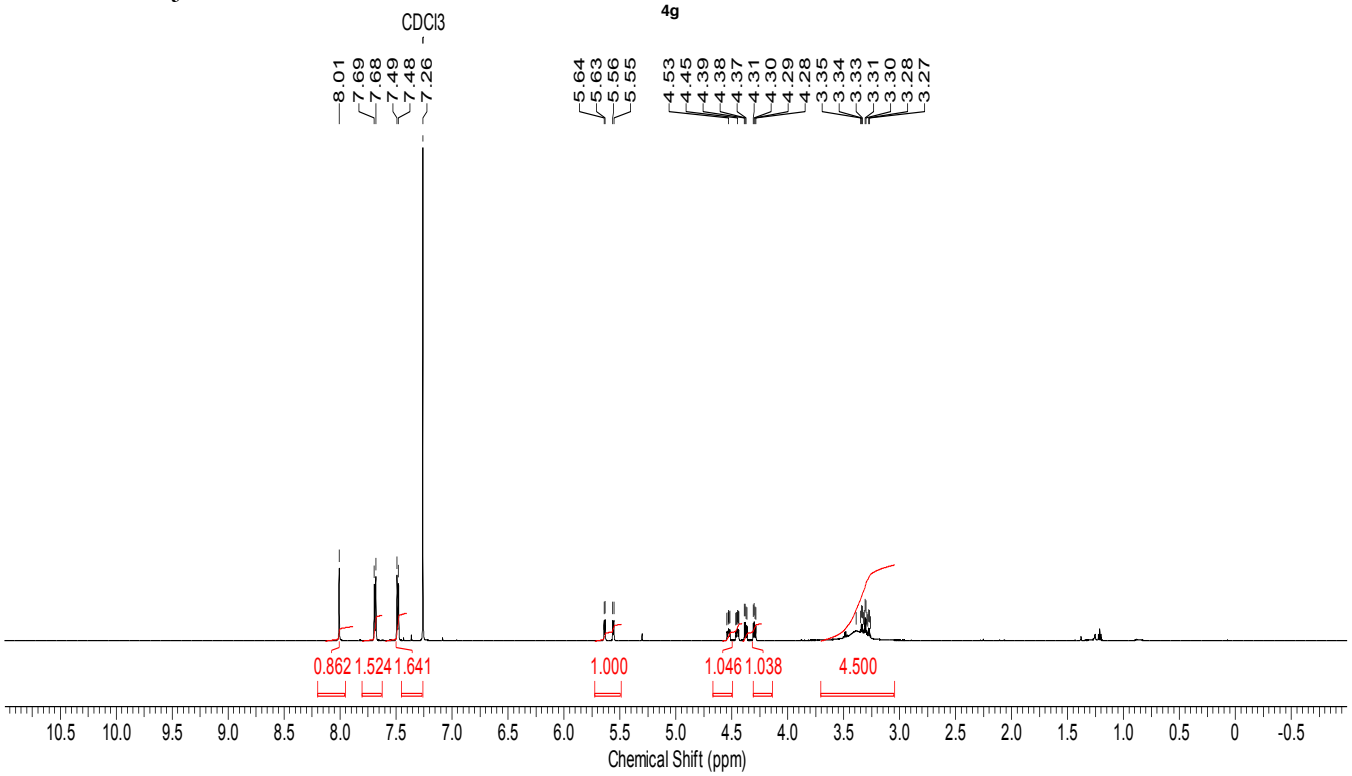


^{19}F NMR
470.4 MHz
$CDCl_3$

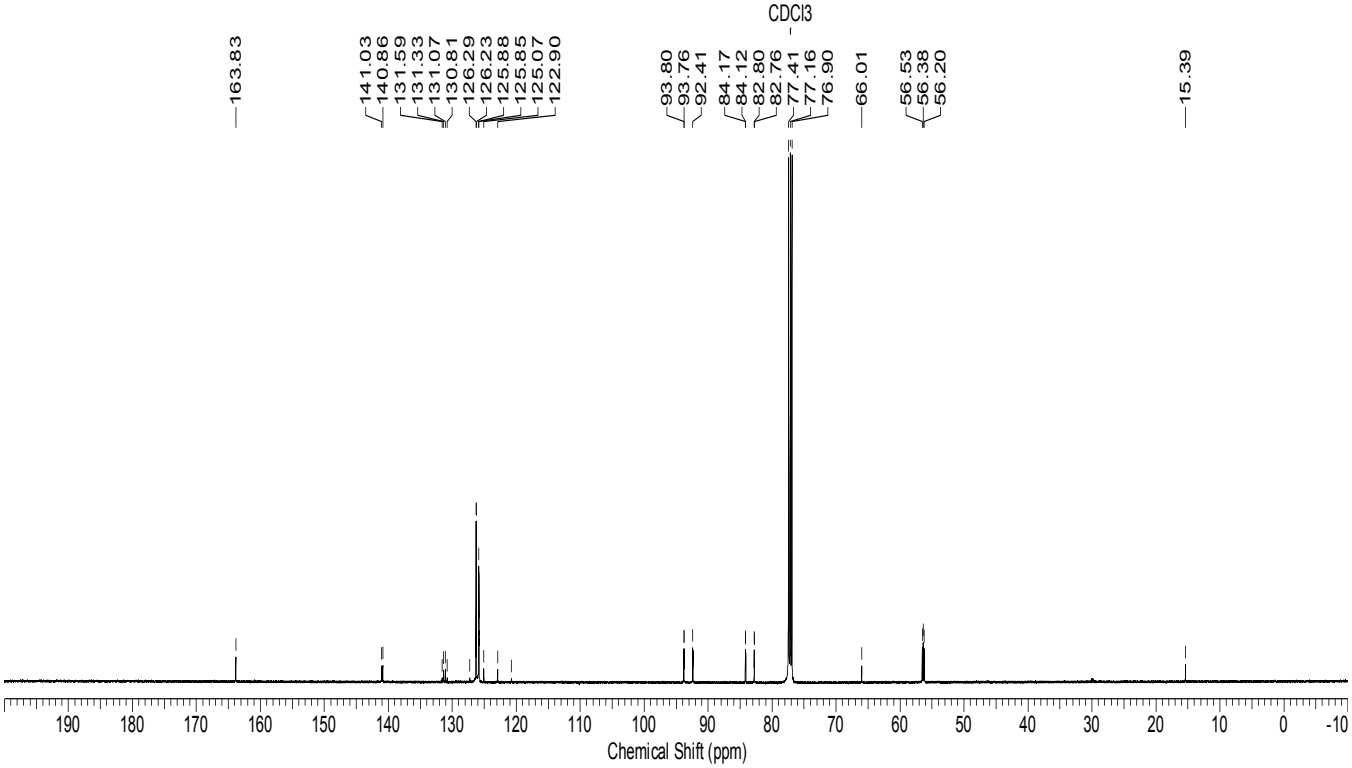


^{1}H NMR
500 MHz
$CDCl_3$

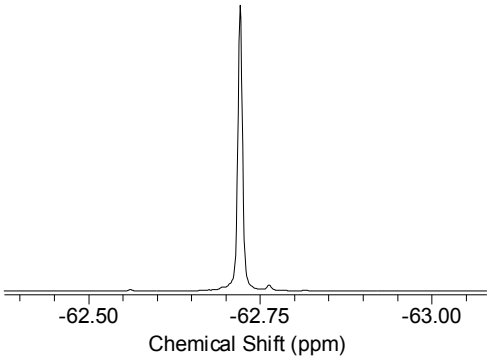


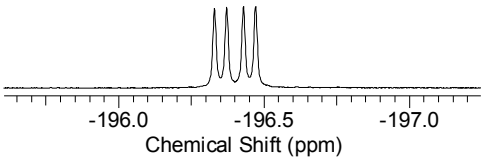


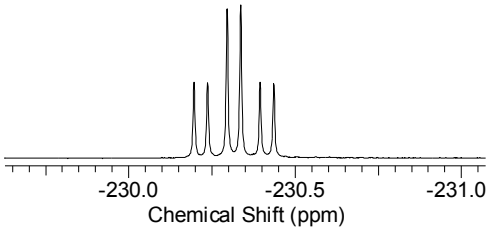
^{13}C NMR
125.7 MHz
$CDCl_3$



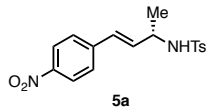
^{19}F NMR
470.4 MHz
$CDCl_3$



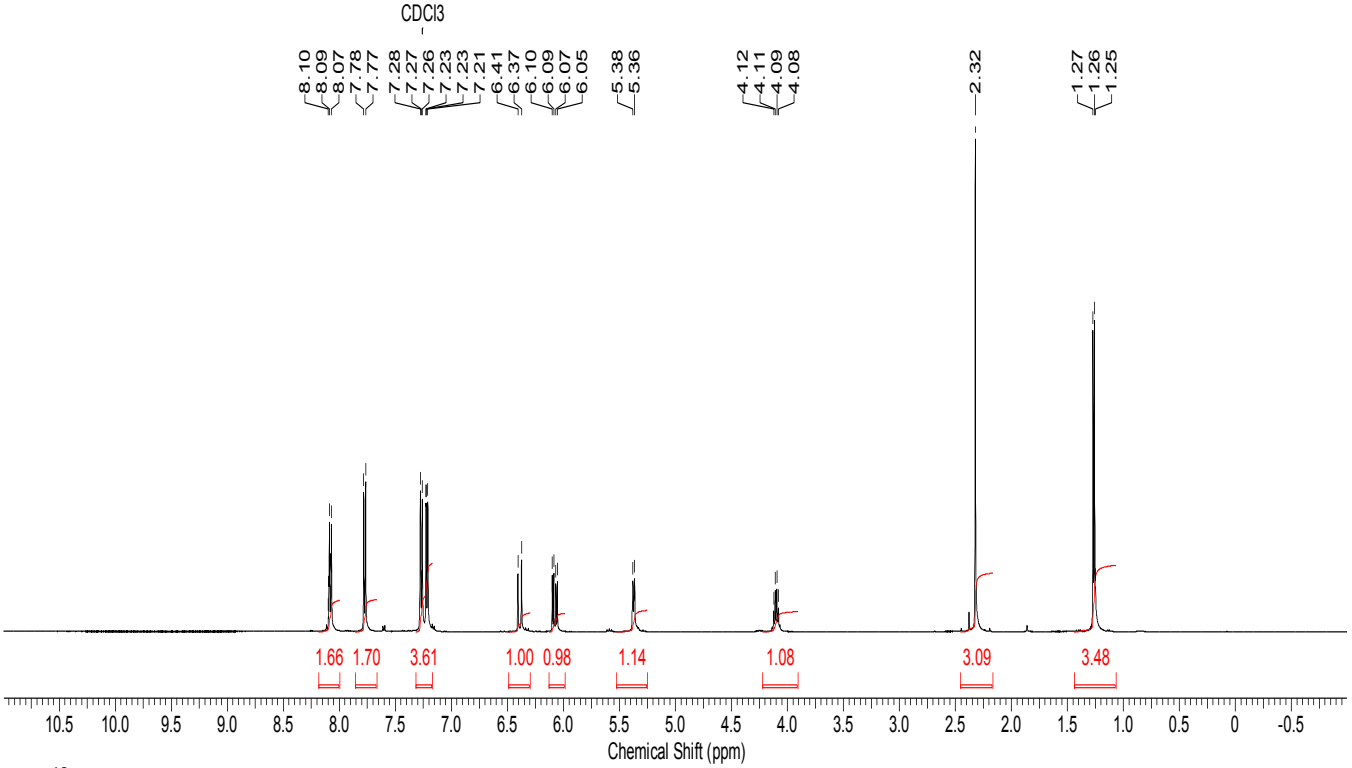




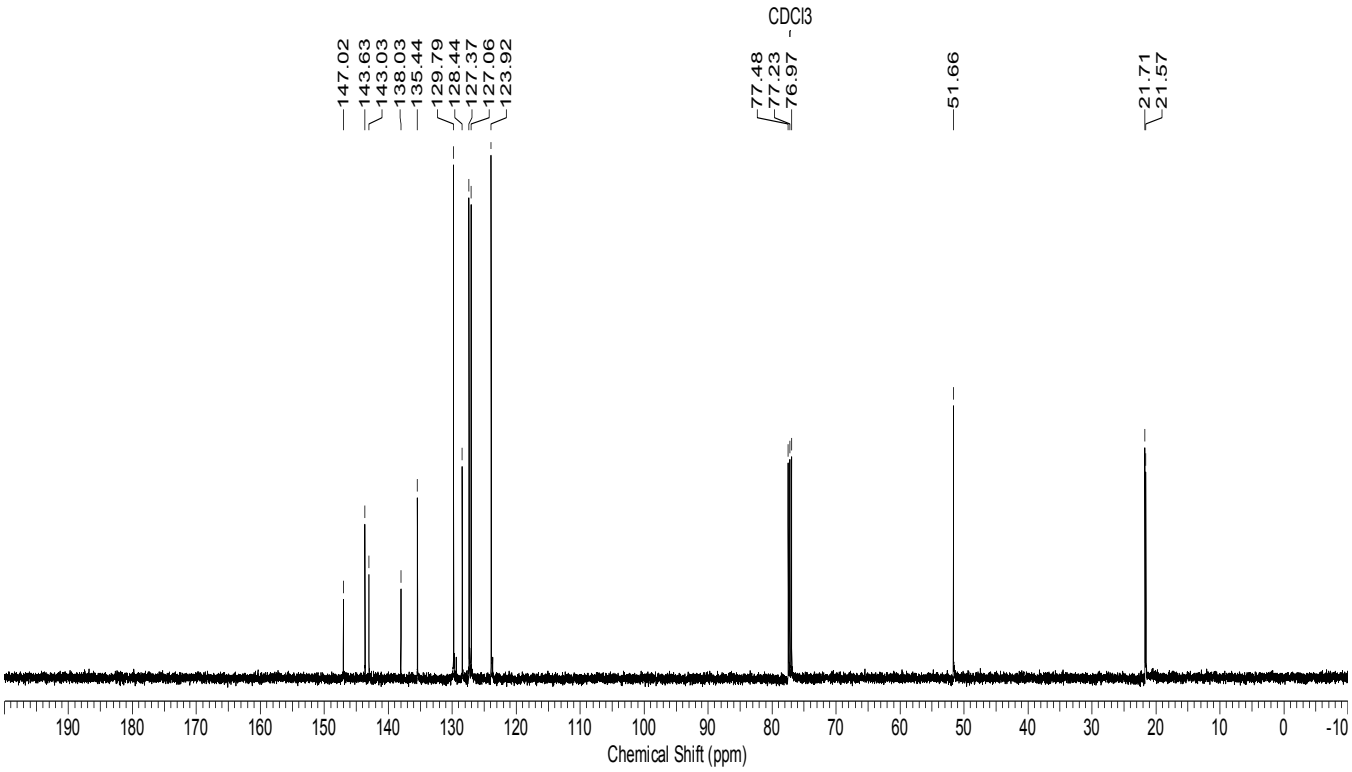
^{1}H NMR
500 MHz
$CDCl_3$



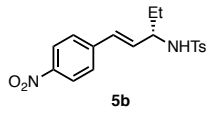
5a



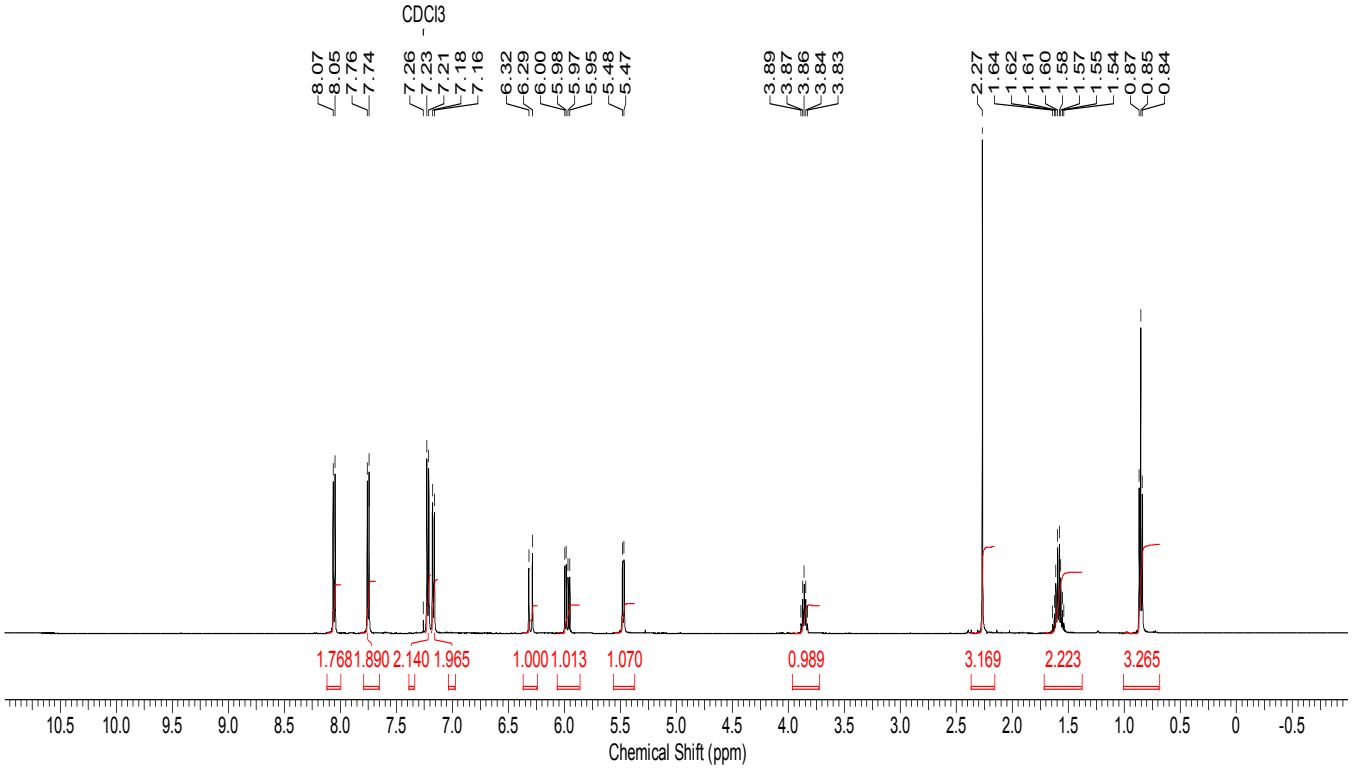
^{13}C NMR
125.7 MHz
$CDCl_3$



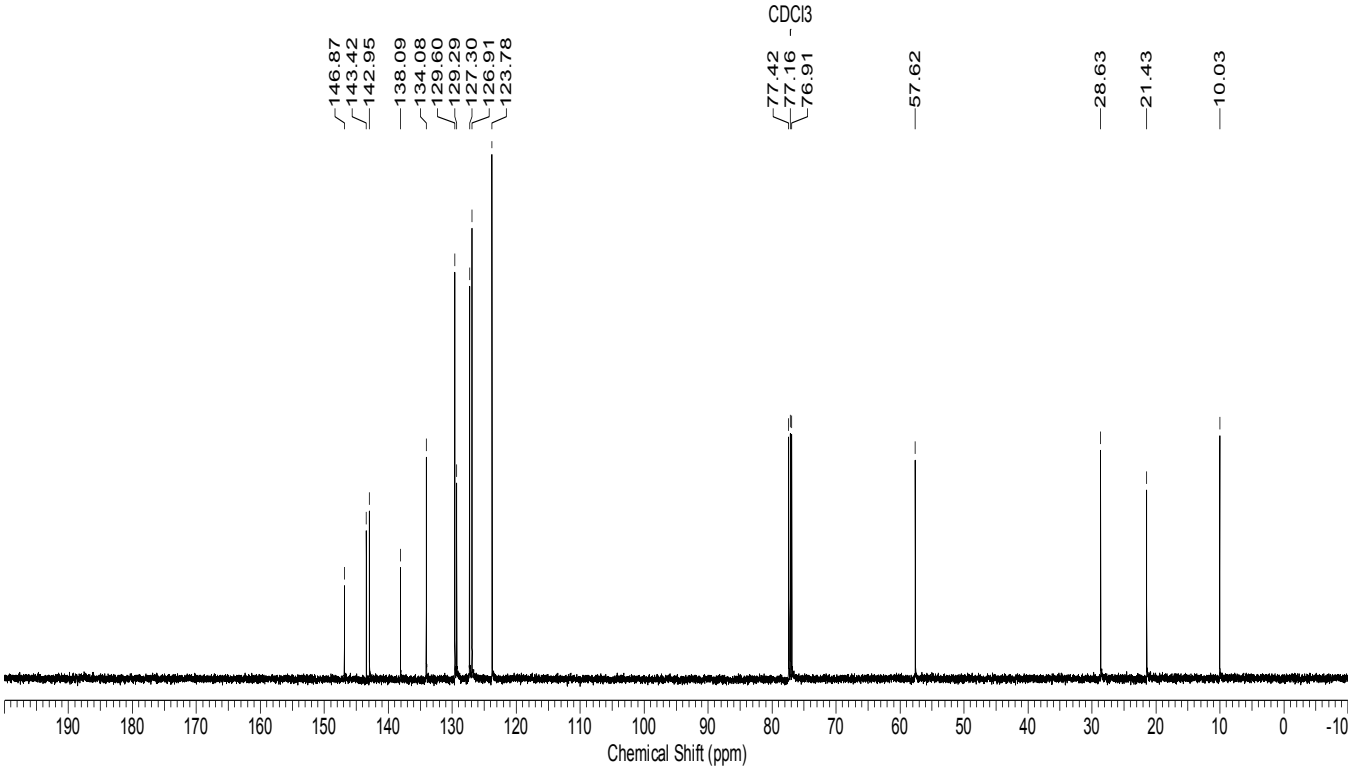
^{1}H NMR
500 MHz
$CDCl_3$



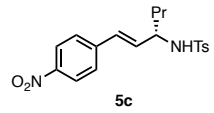
5b



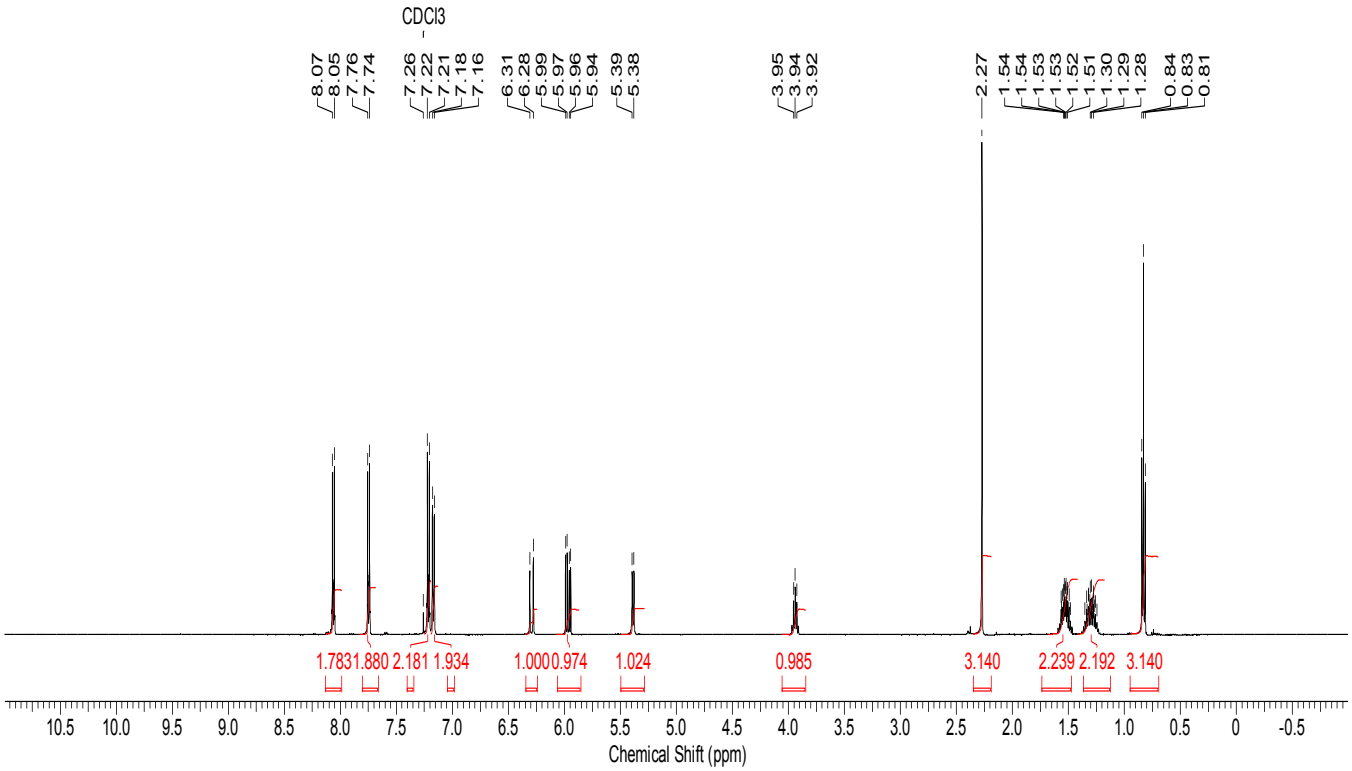
^{13}C NMR
125.7 MHz
$CDCl_3$



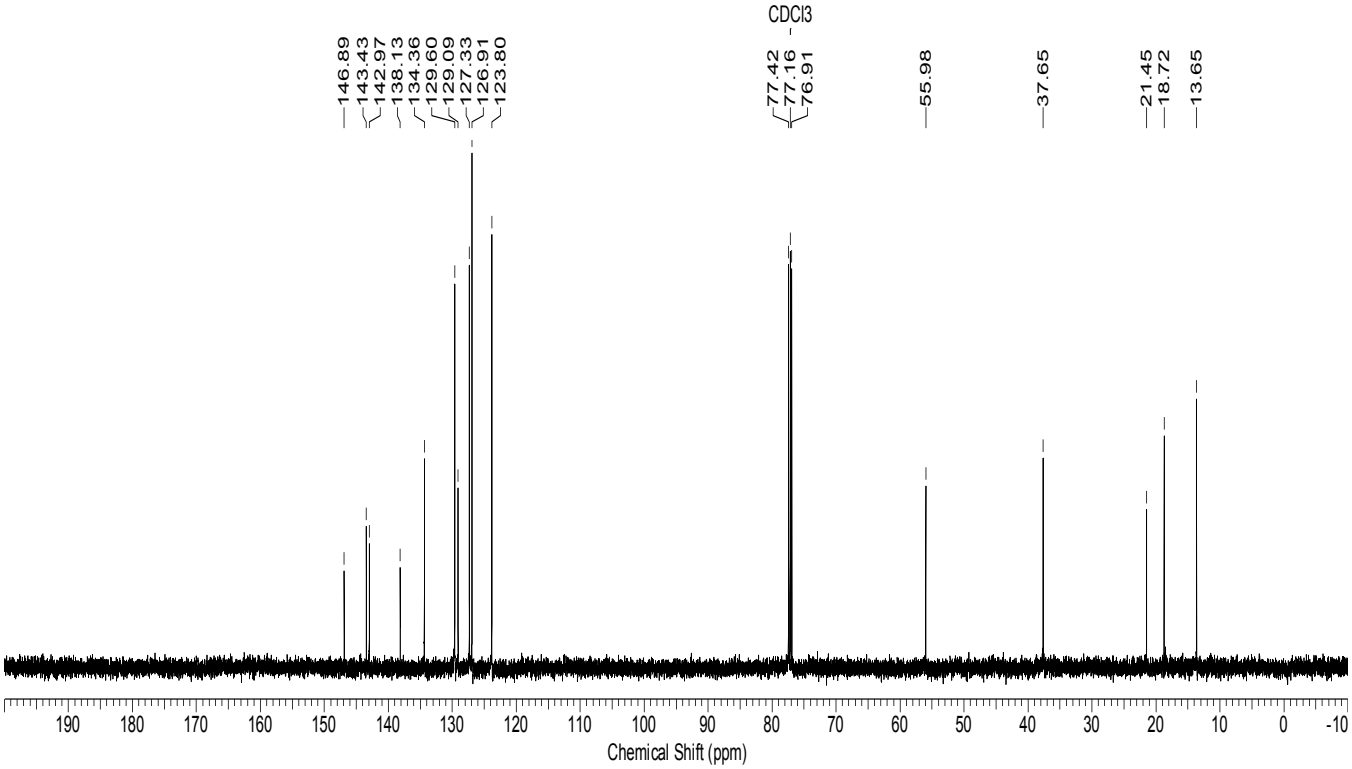
^{1}H NMR
500 MHz
$CDCl_3$



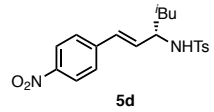
5c



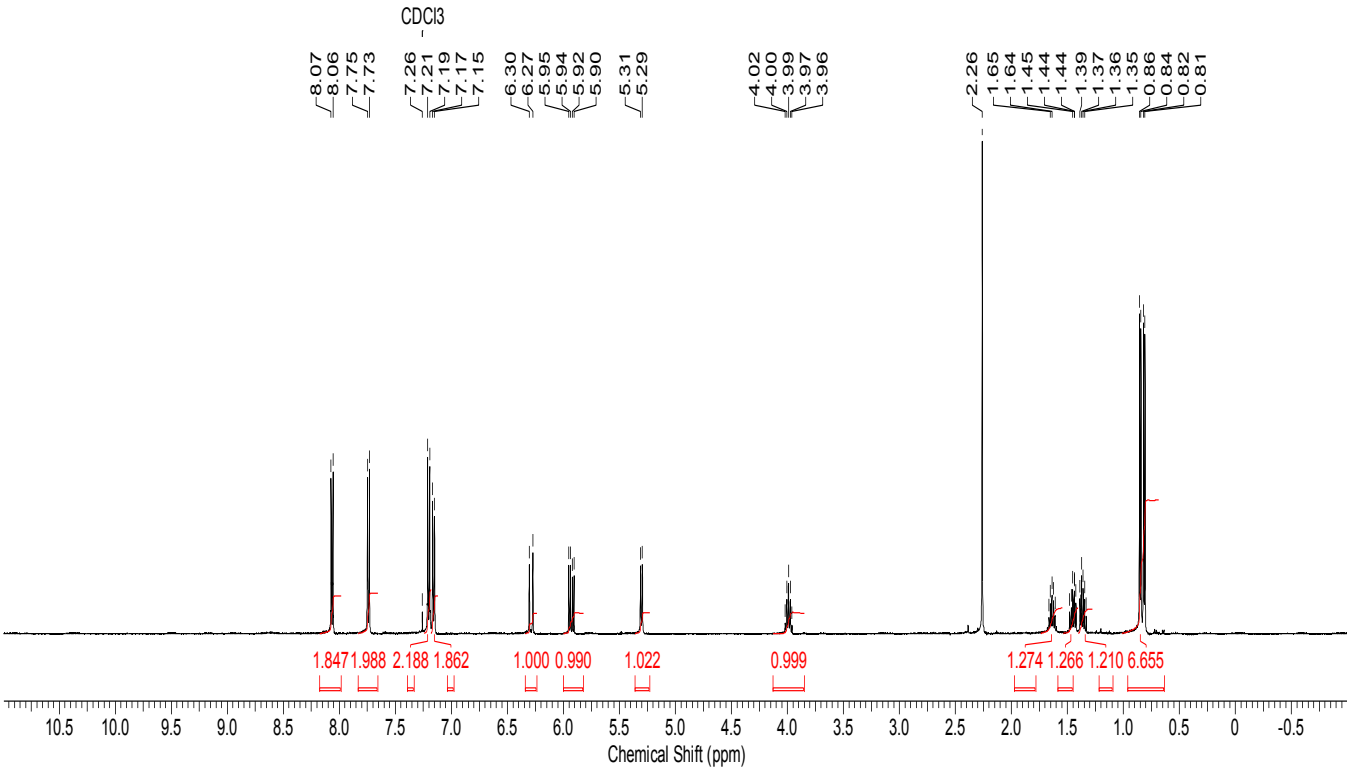
^{13}C NMR
125.7 MHz
$CDCl_3$



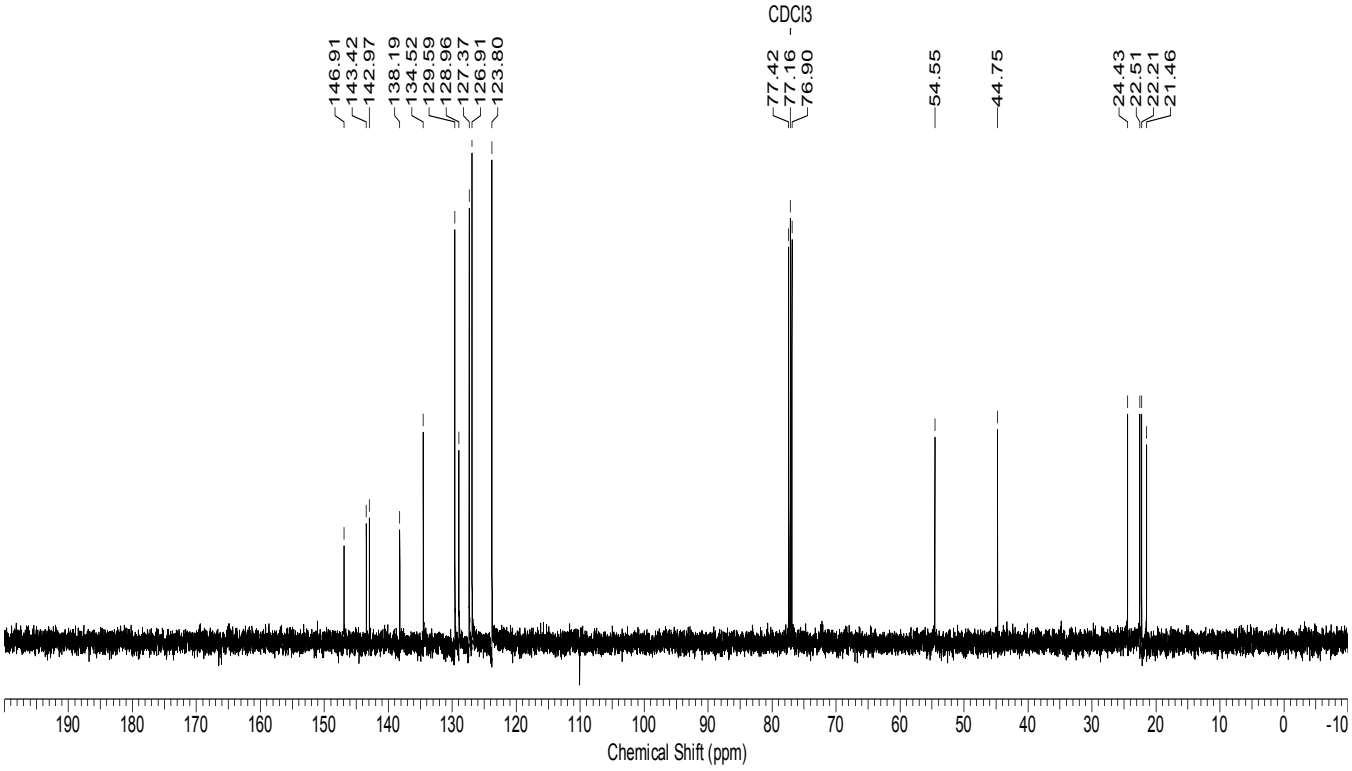
^{1}H NMR
500 MHz
$CDCl_3$



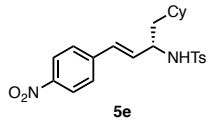
5d



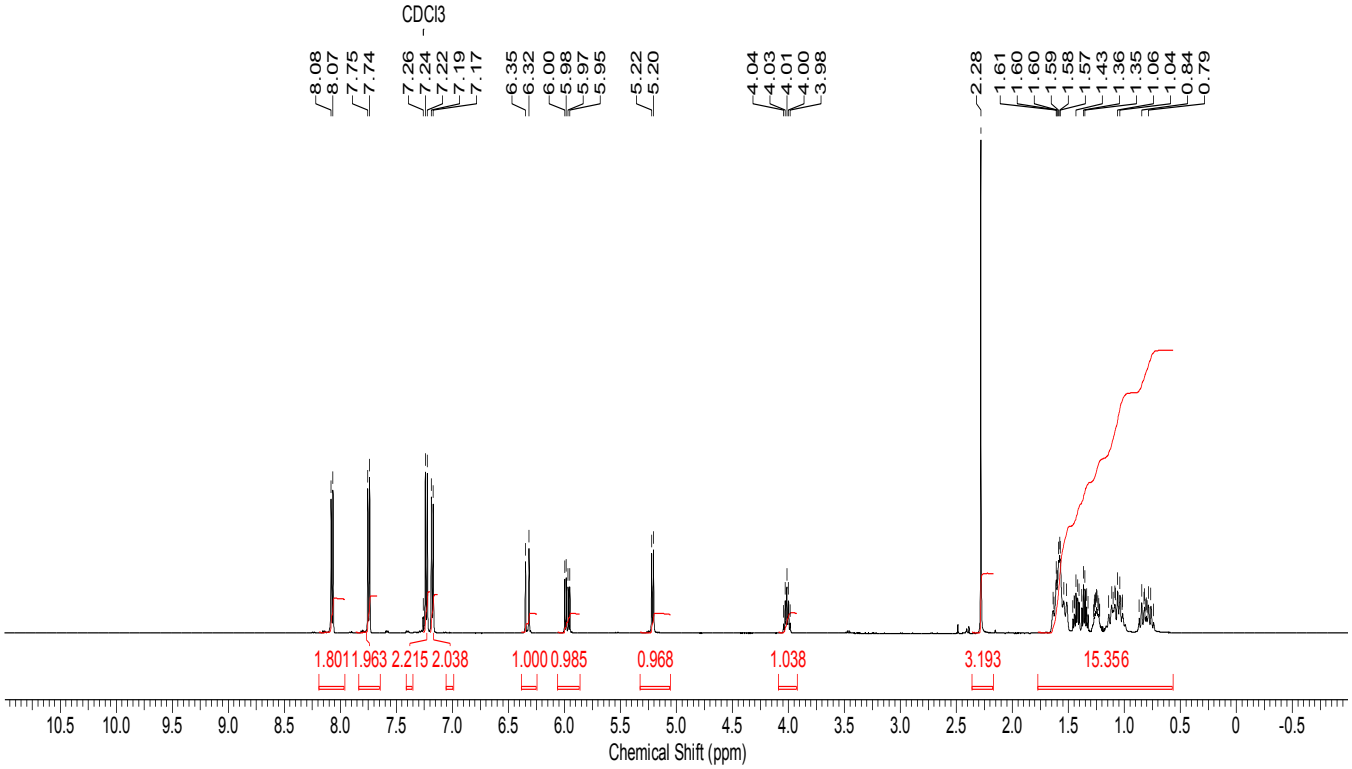
^{13}C NMR
125.7 MHz
$CDCl_3$



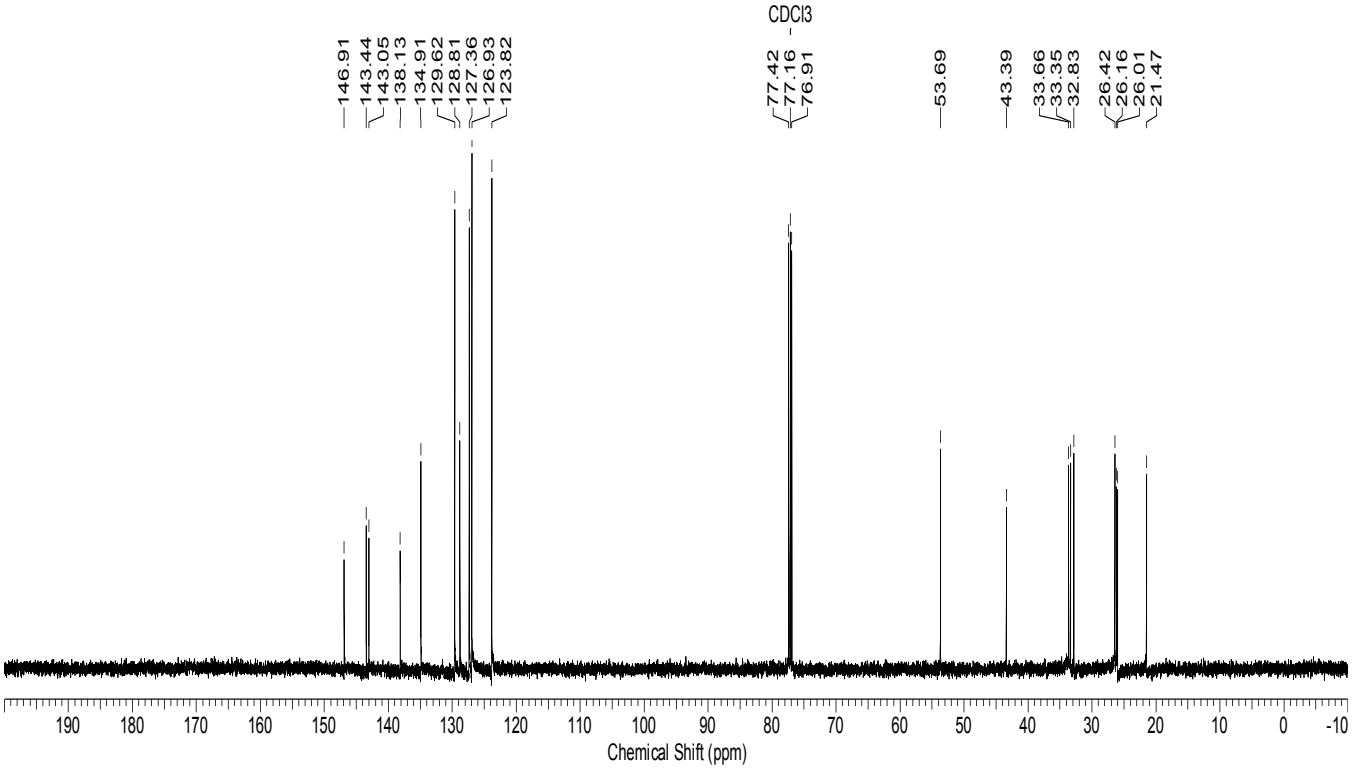
^{1}H NMR
500 MHz
$CDCl_3$



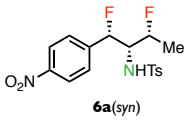
5e



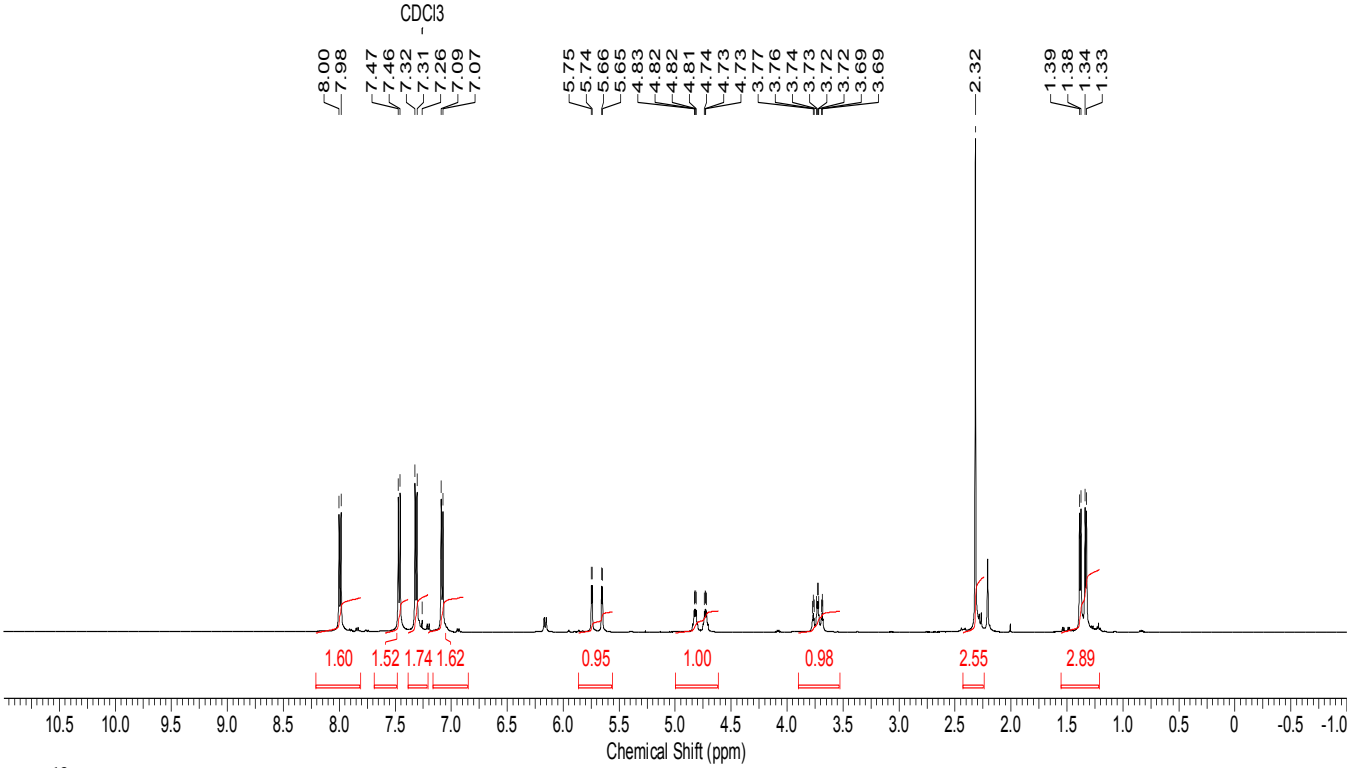
^{13}C NMR
125.7 MHz
$CDCl_3$



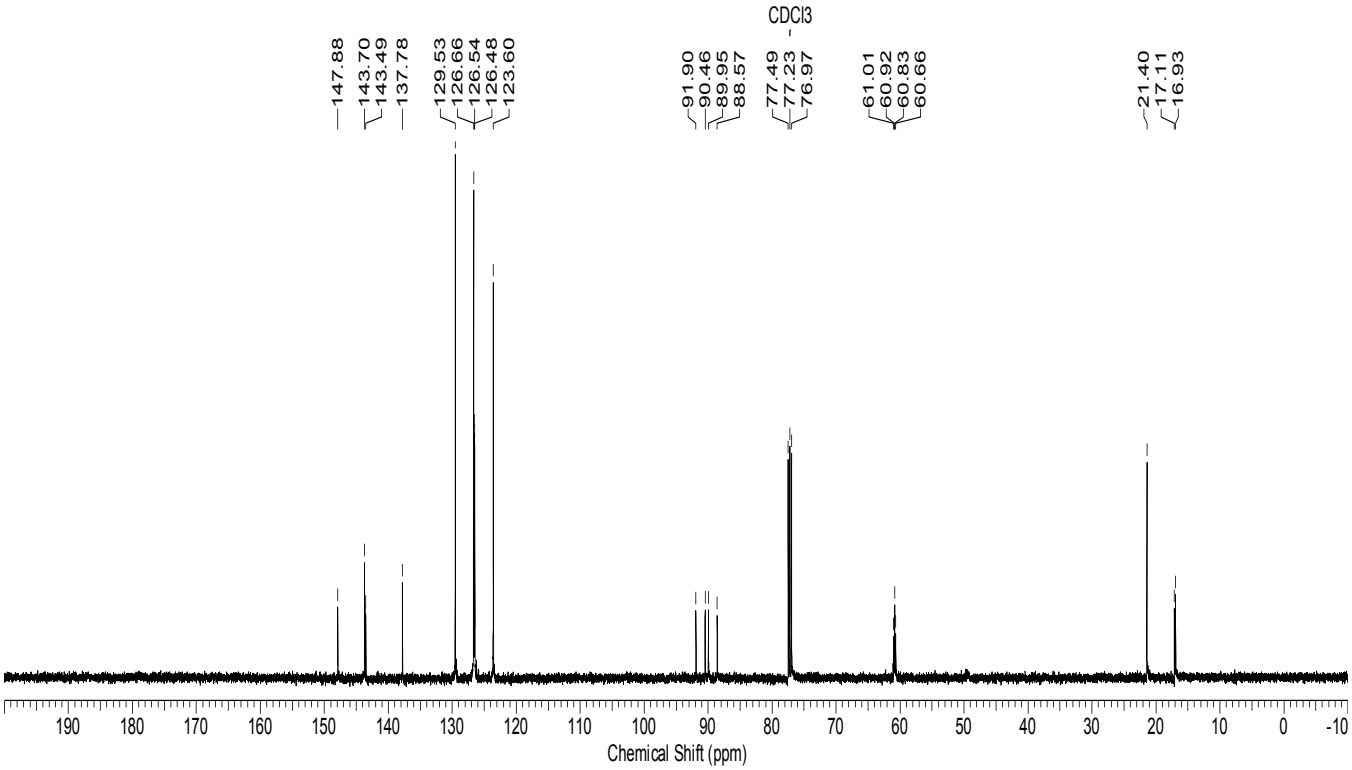
^{1}H NMR
500 MHz
$CDCl_3$



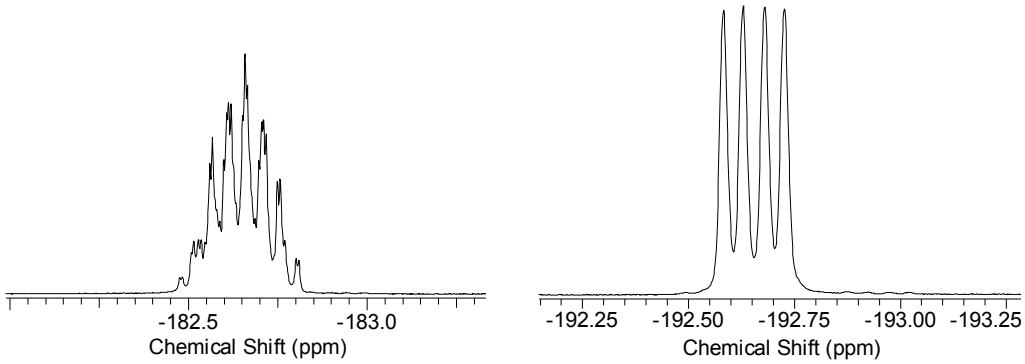
6a(*syn*)



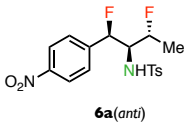
^{13}C NMR
125.7 MHz
$CDCl_3$



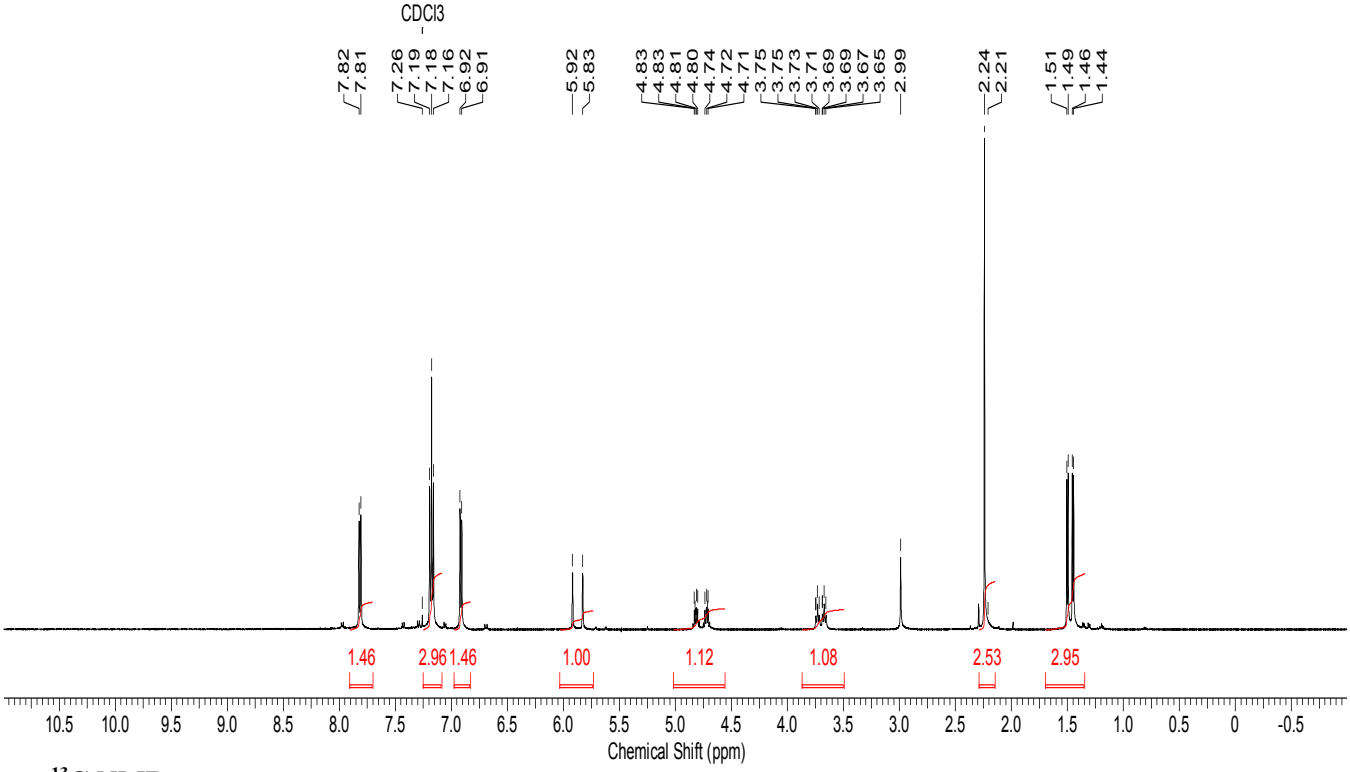
^{19}F NMR
470.4 MHz
$CDCl_3$



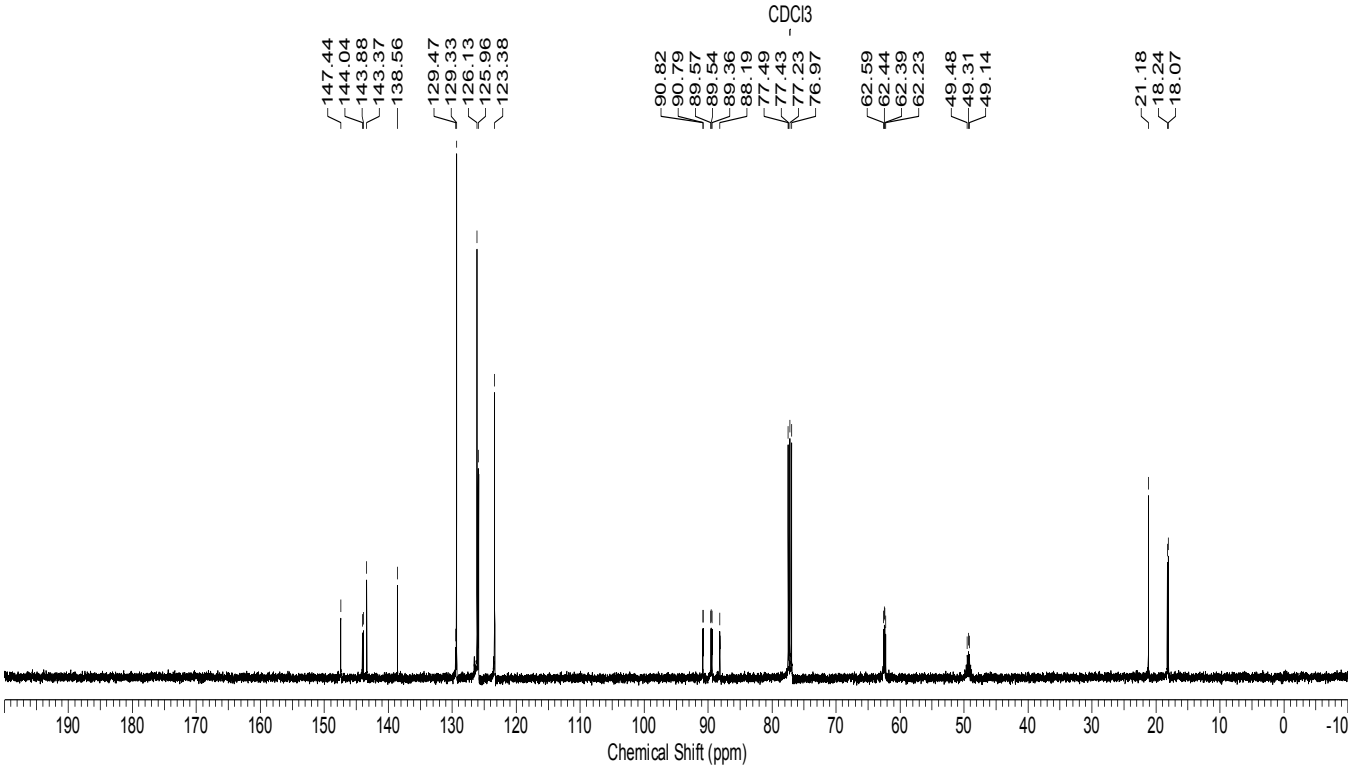
^{1}H NMR
500 MHz
$CDCl_3$



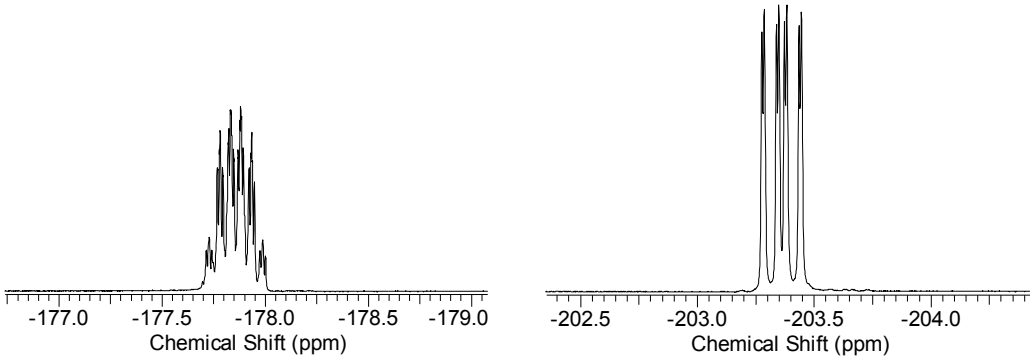
6a(*anti*)



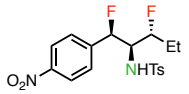
^{13}C NMR
125.7 MHz
$CDCl_3$



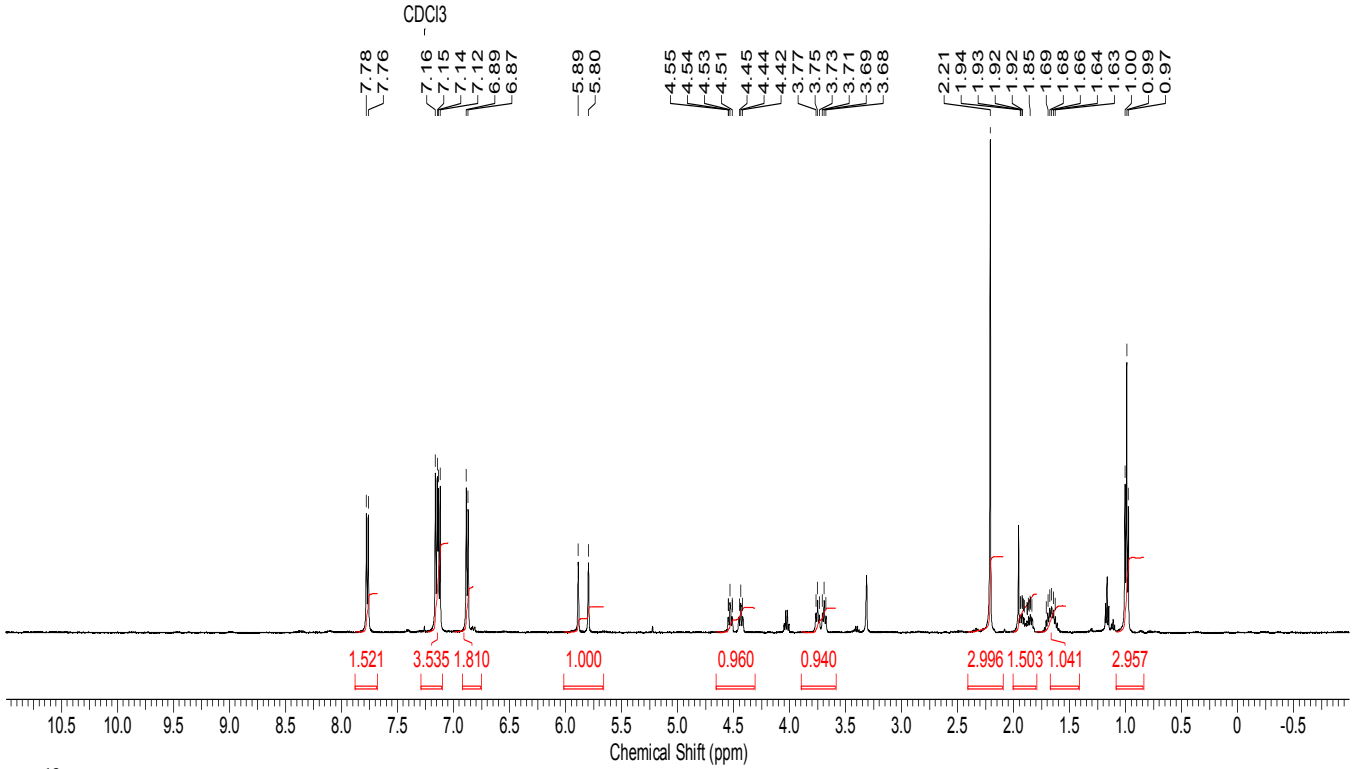
^{19}F NMR
470.4 MHz
$CDCl_3$



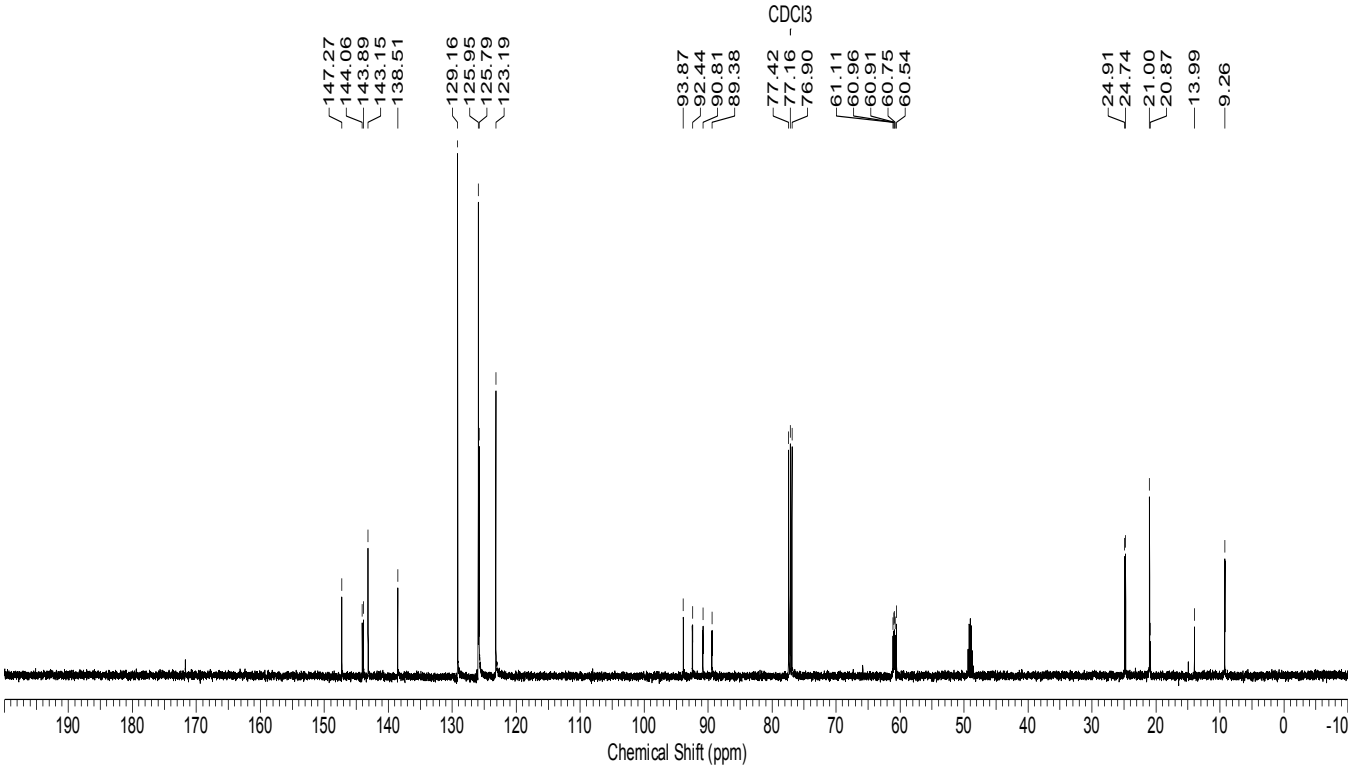
^{1}H NMR
500 MHz
10% $CD_3OD/CDCl_3$



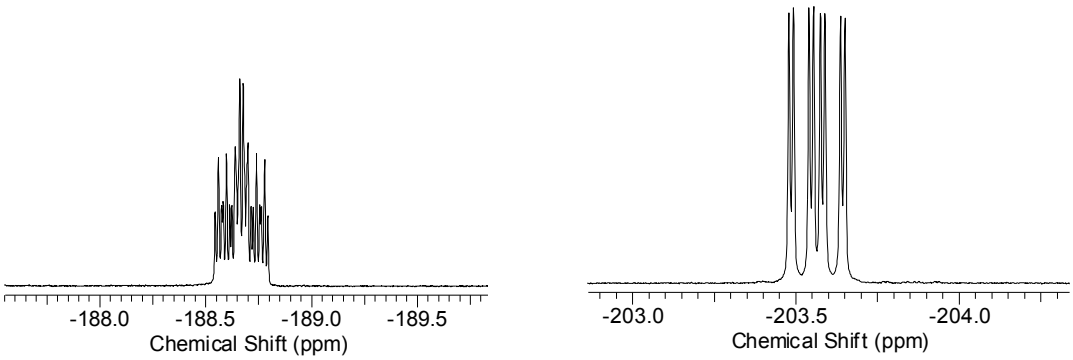
6b(*anti*)



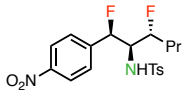
^{13}C NMR
125.7 MHz
10% $CD_3OD/CDCl_3$



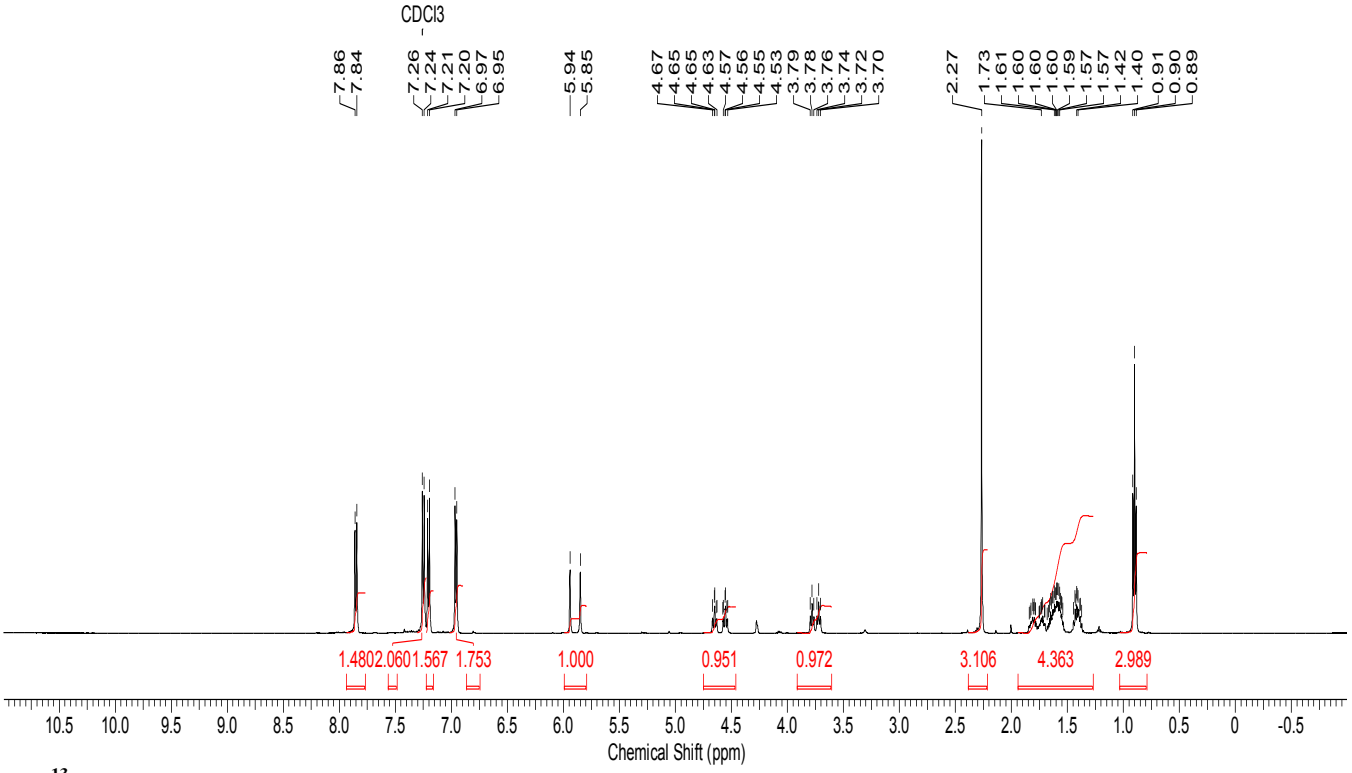
^{19}F NMR
470.4 MHz
$CDCl_3$



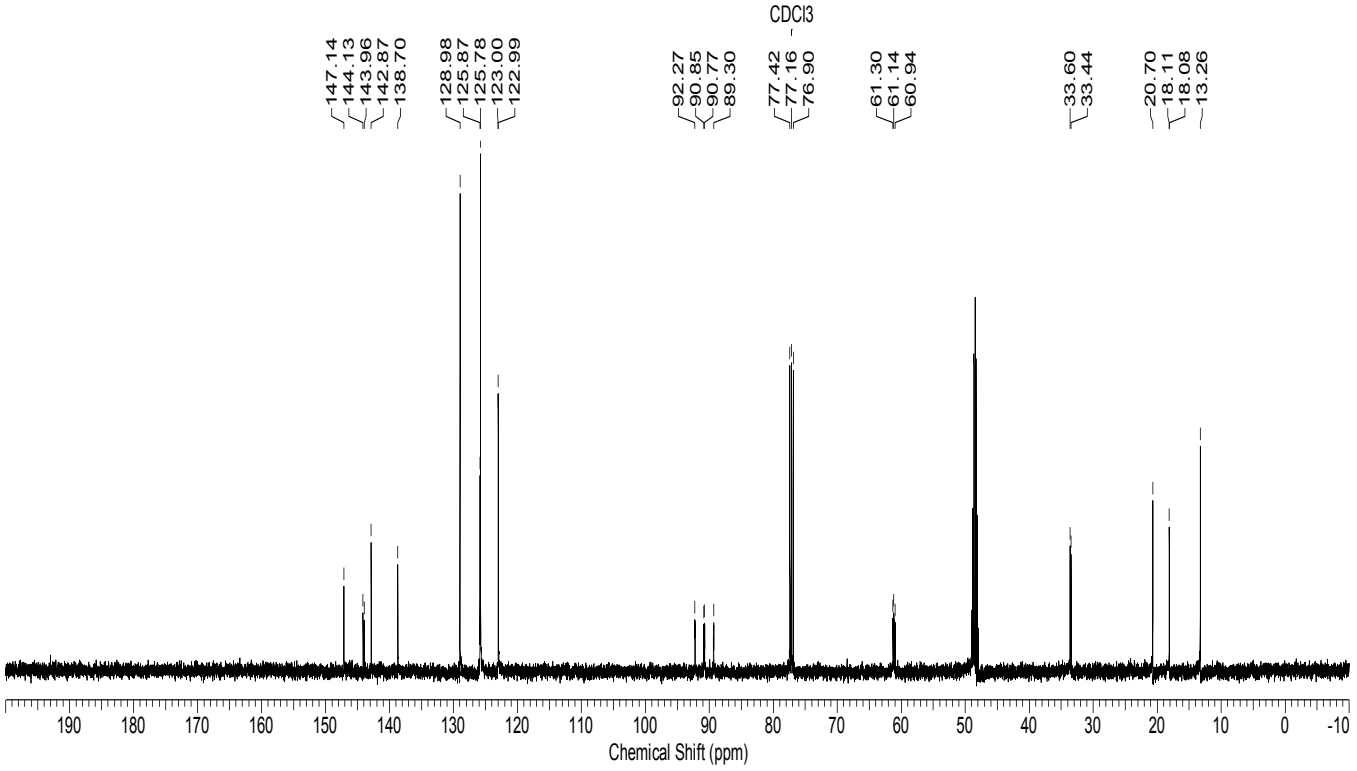
^{1}H NMR
500 MHz
10% $CD_3OD/CDCl_3$



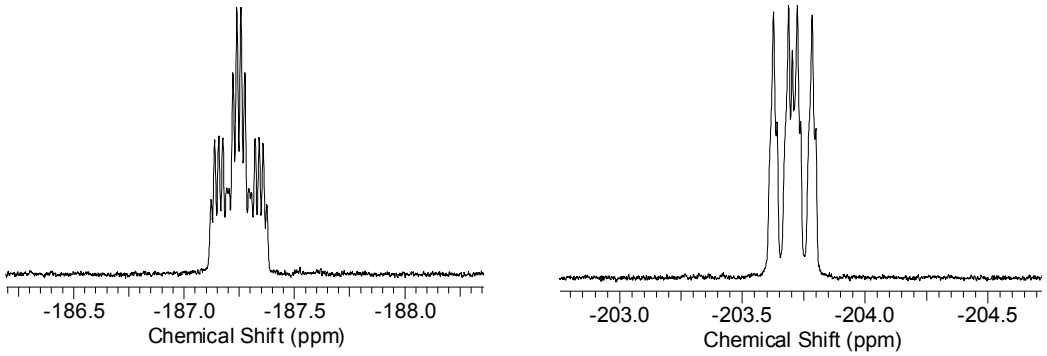
6c(*anti*)



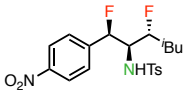
^{13}C NMR
125.7 MHz
10% $CD_3OD/CDCl_3$



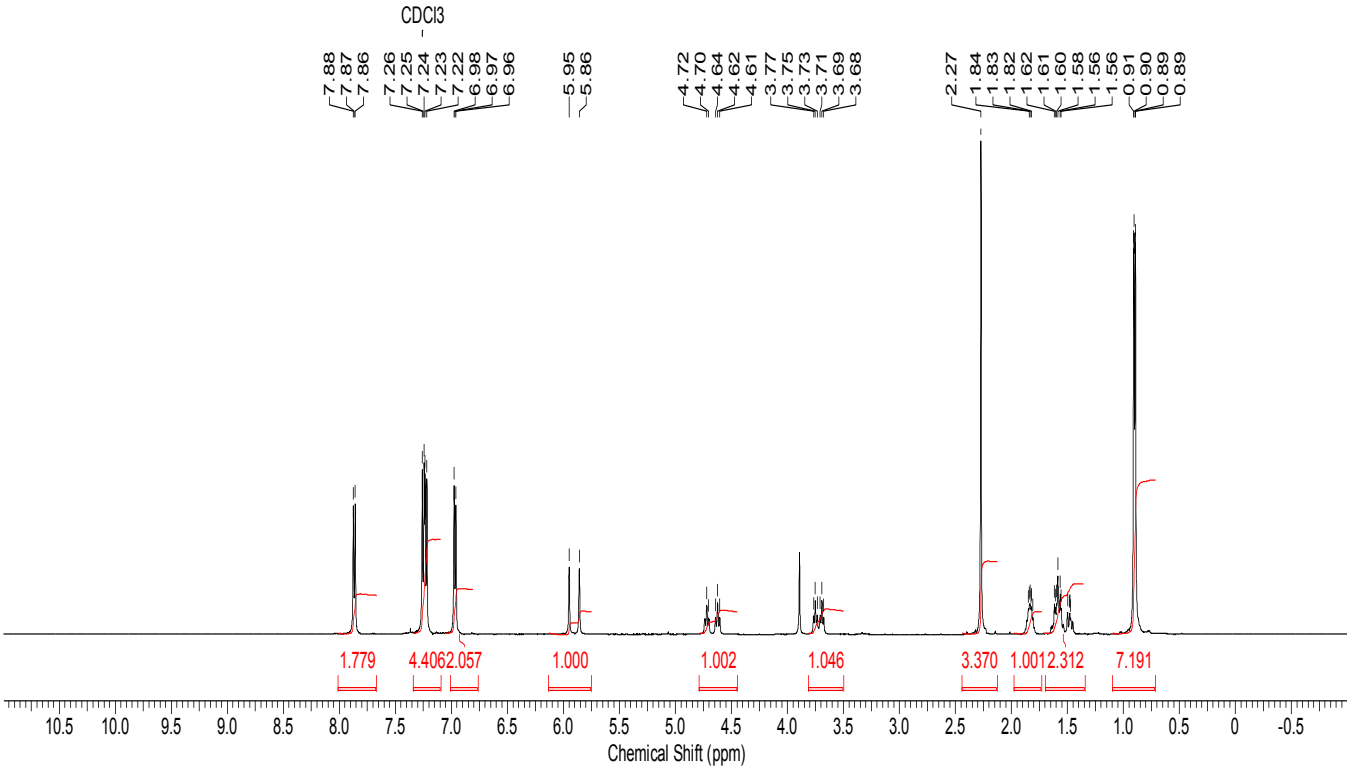
^{19}F NMR
470.4 MHz
$CDCl_3$



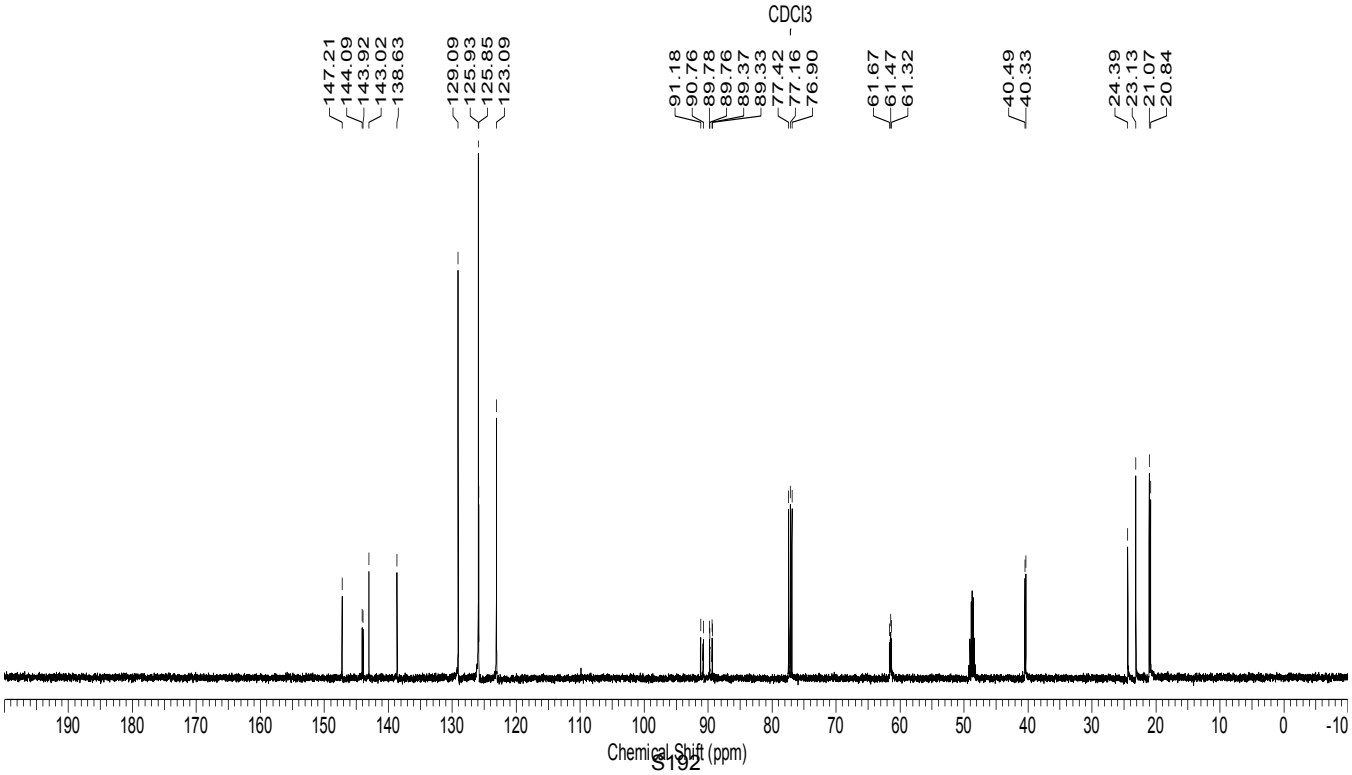
^{1}H NMR
500 MHz
10% $CD_3OD/CDCl_3$



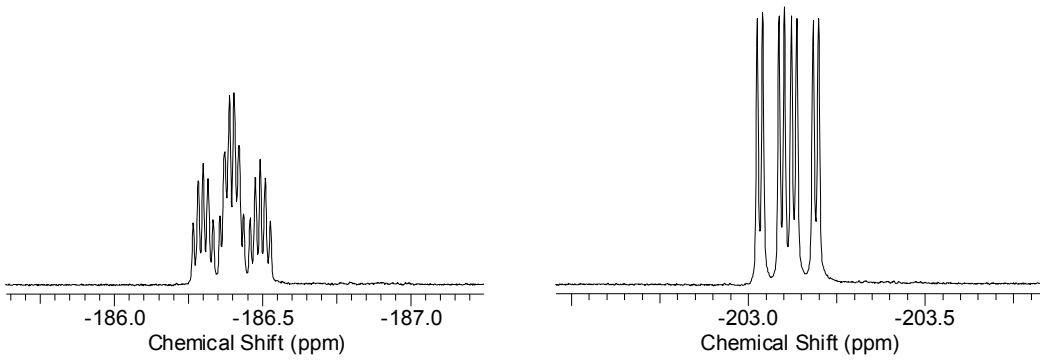
6d(*anti*)



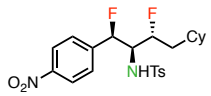
^{13}C NMR
125.7 MHz
10% $CD_3OD/CDCl_3$



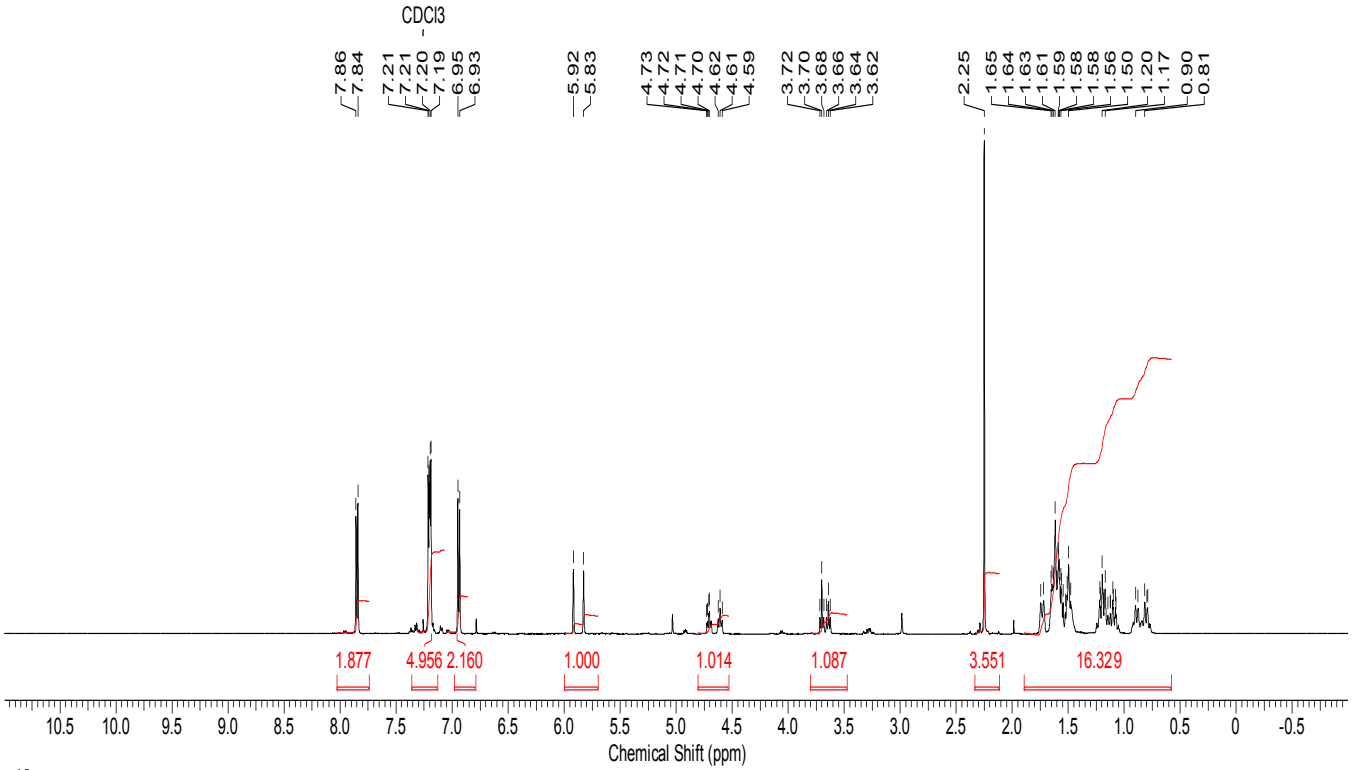
^{19}F NMR
470.4 MHz
$CDCl_3$



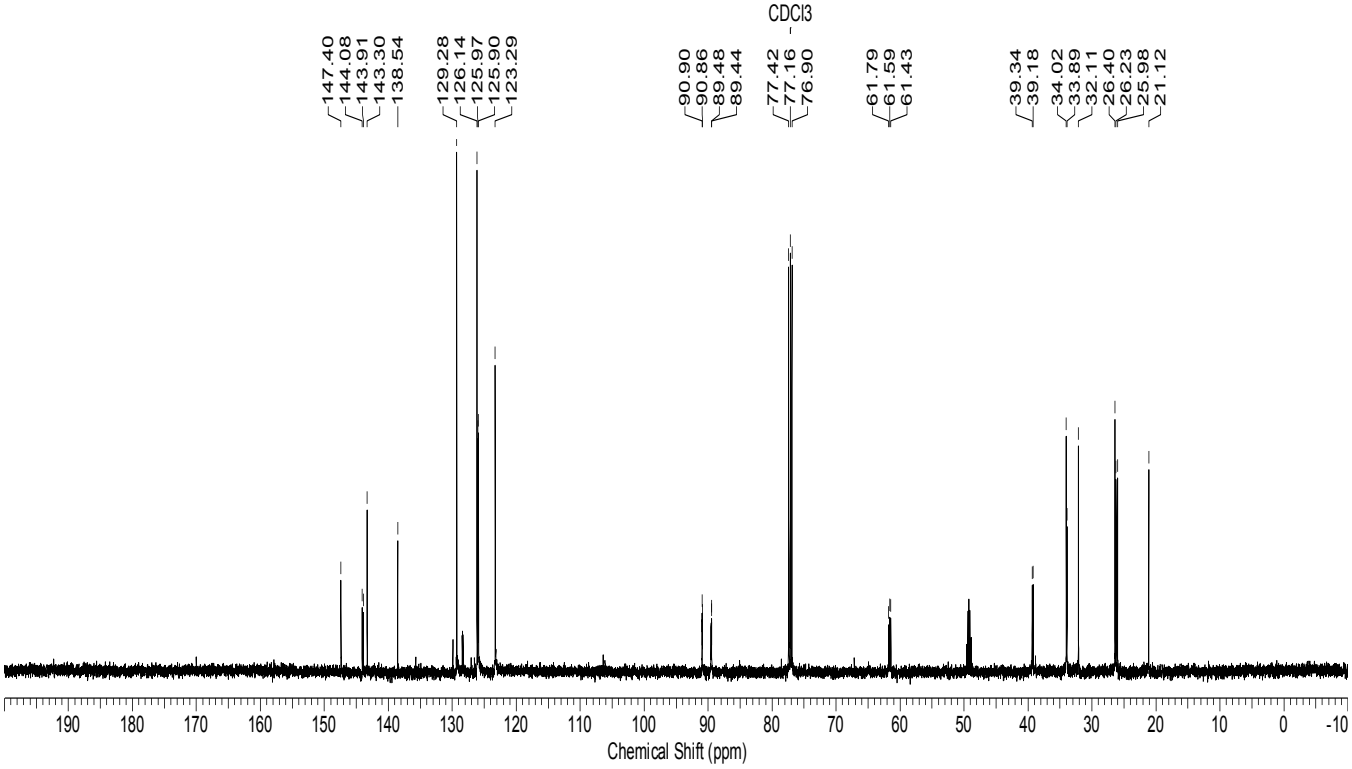
^{1}H NMR
500 MHz
10% $CD_3OD/CDCl_3$



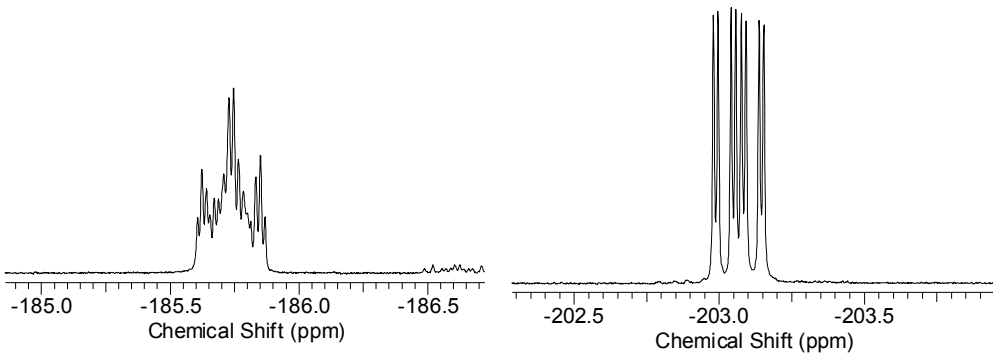
6e(*anti*)



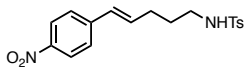
^{13}C NMR
125.7 MHz
10% $CD_3OD/CDCl_3$



^{19}F NMR
470.4 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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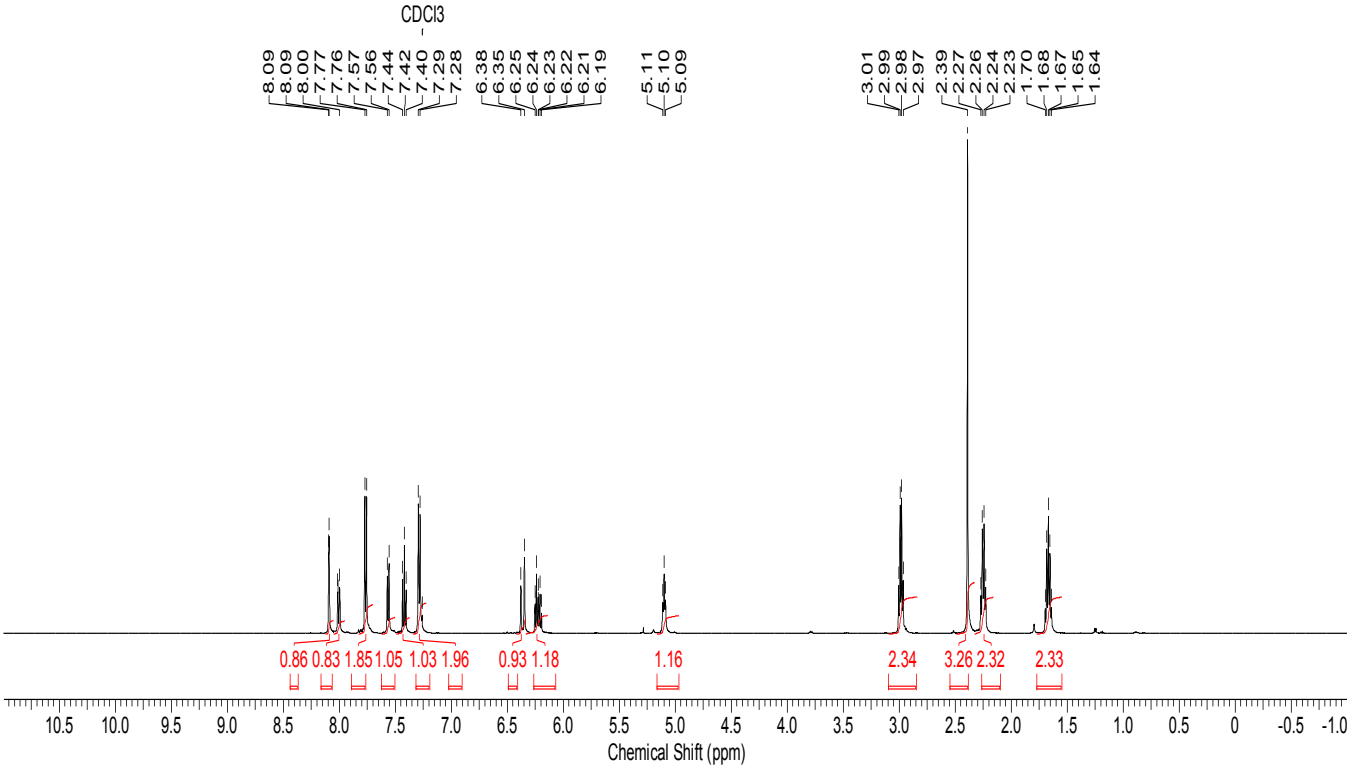
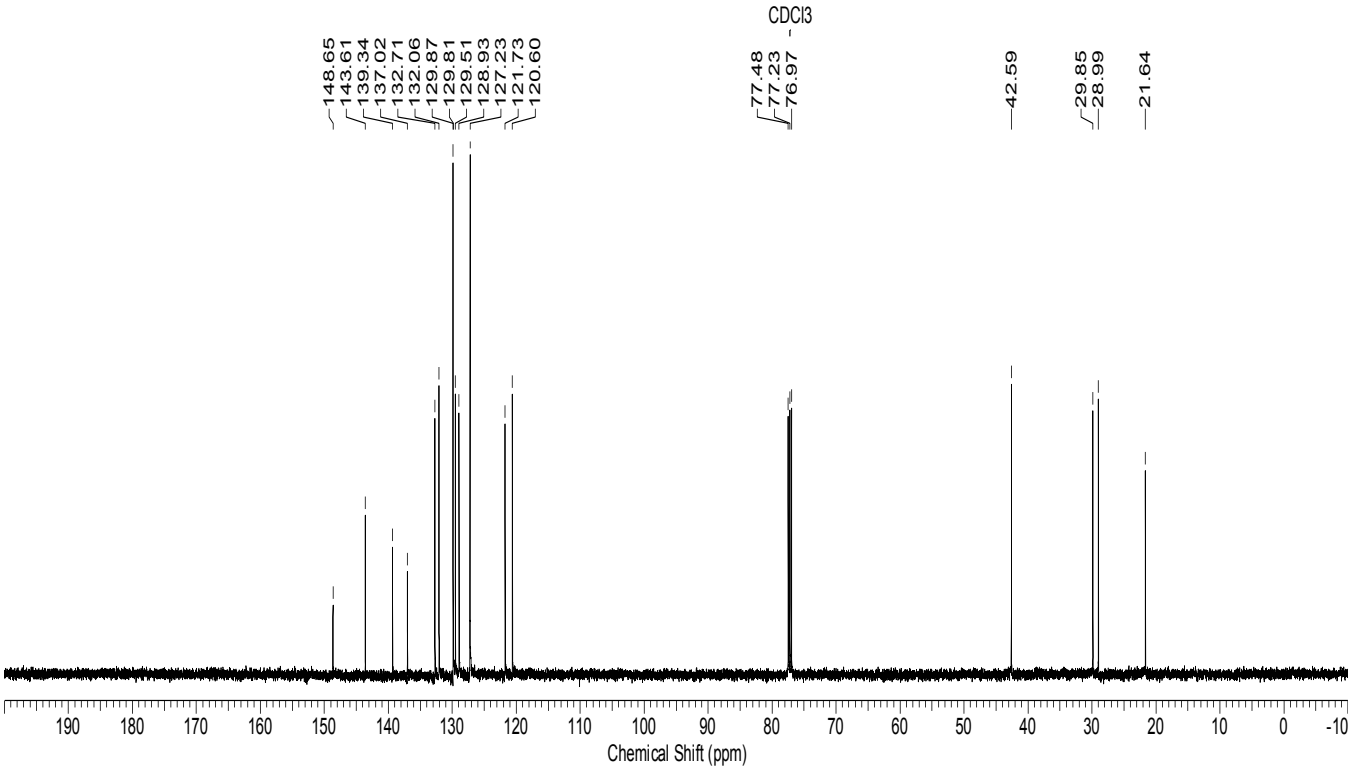
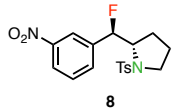


^{13}C NMR
125.7 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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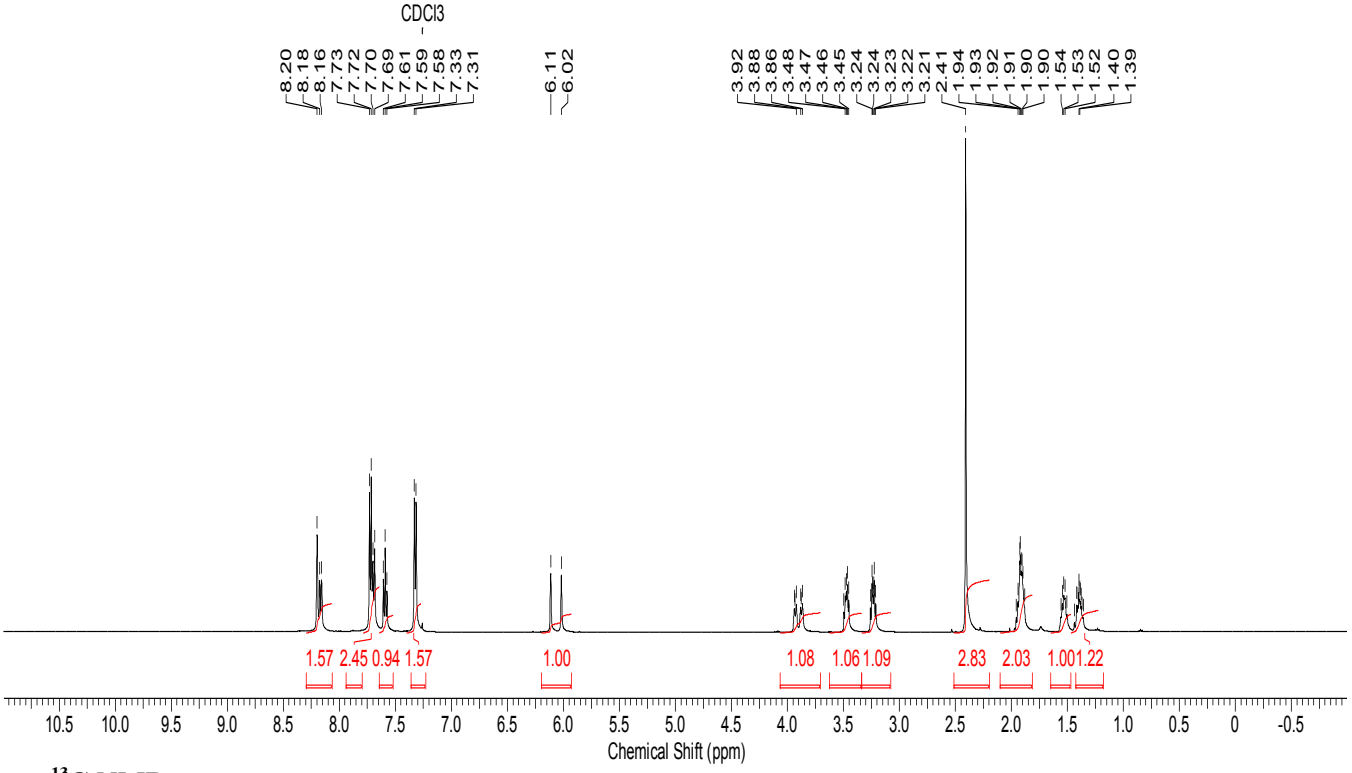
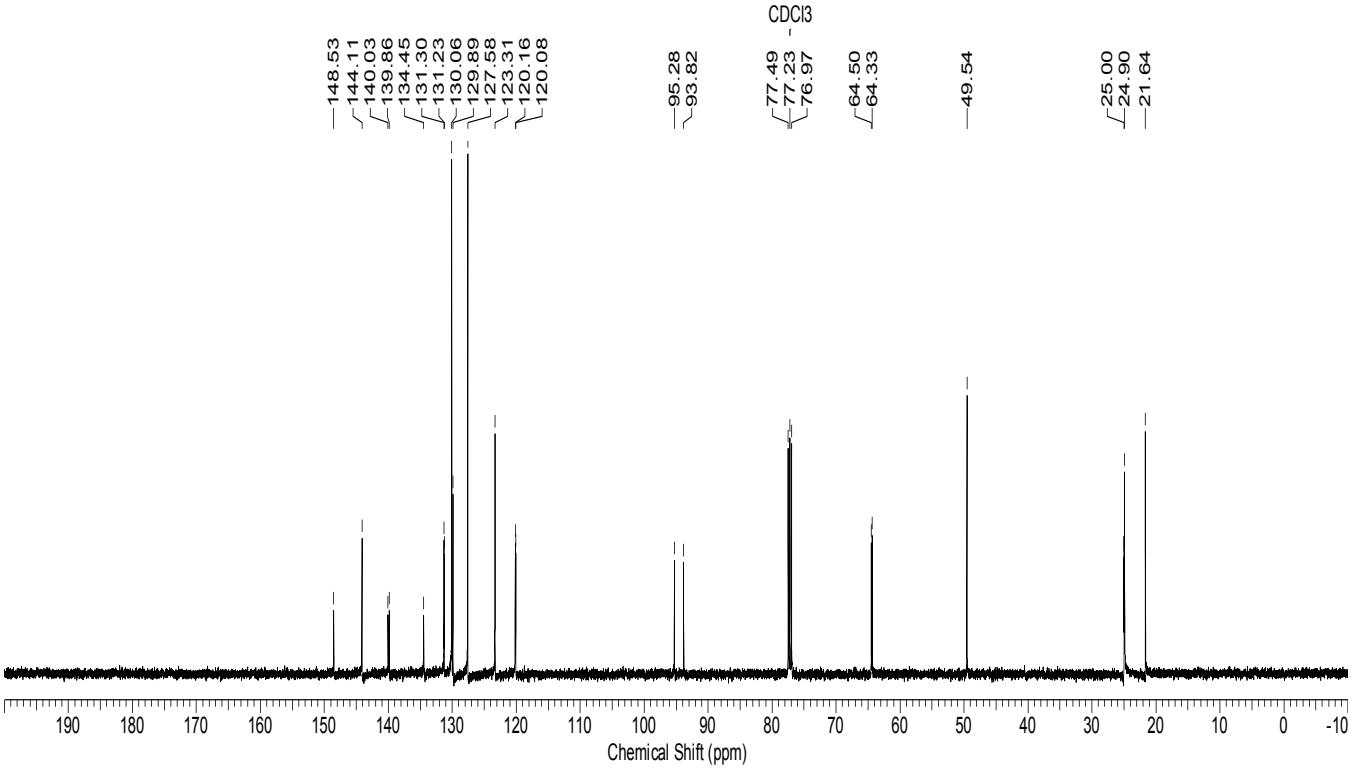
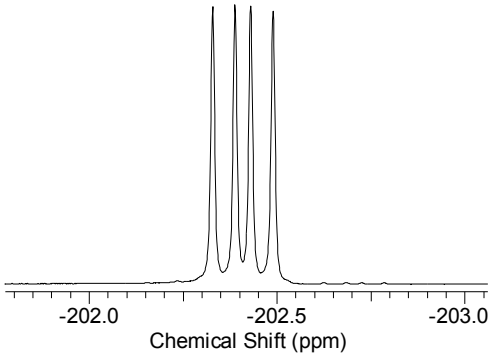


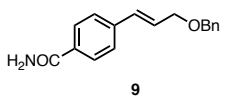
^{13}C NMR
125.7 MHz
$CDCl_3$



^{19}F NMR
470.4 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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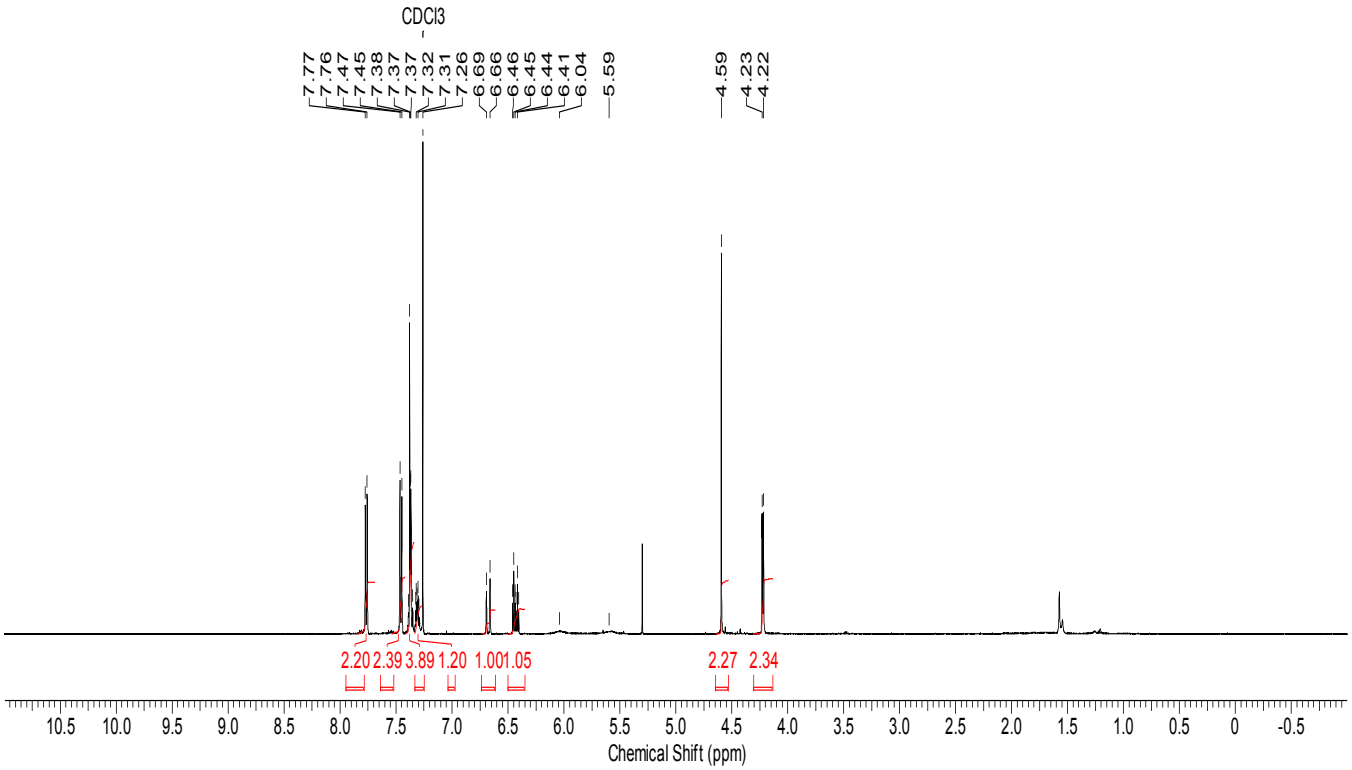
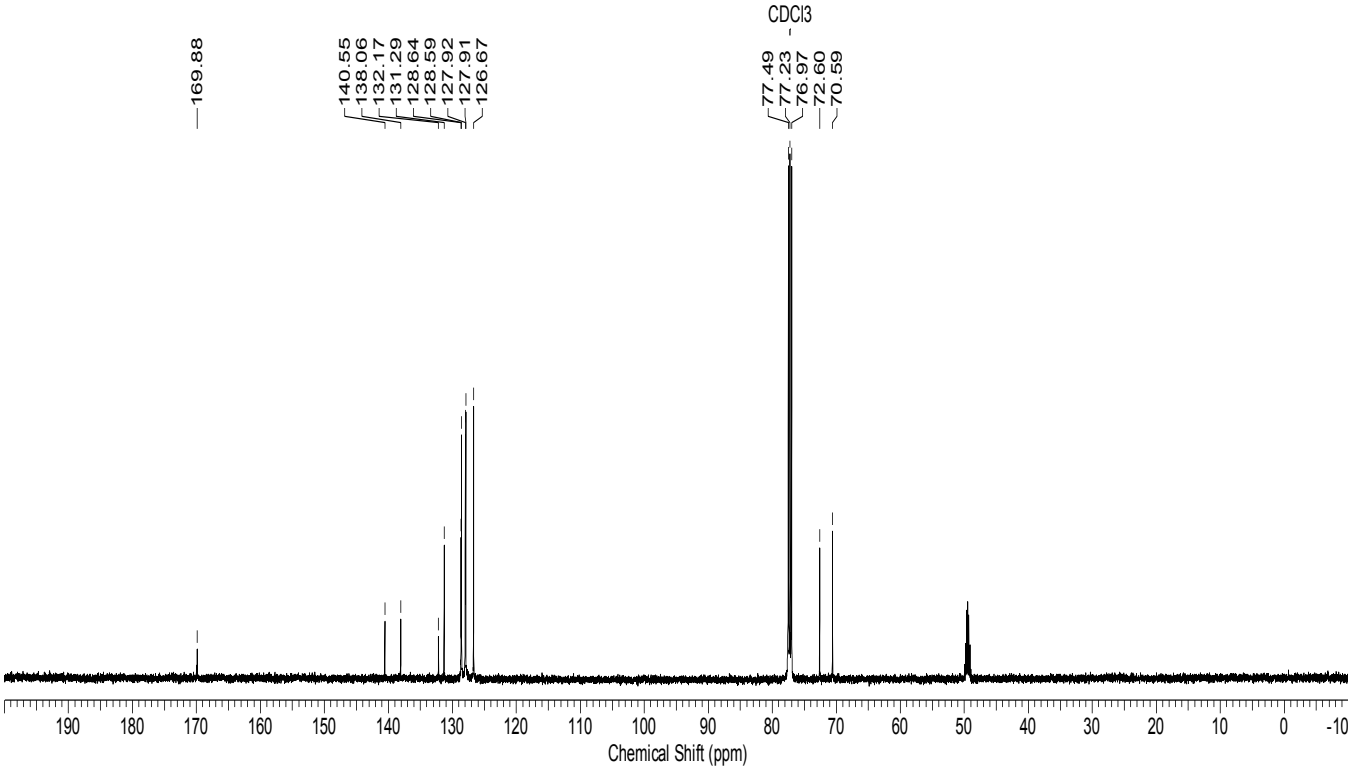
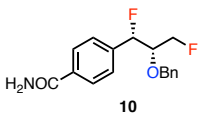


^{13}C NMR
125.7 MHz
10% $CD_3OD/CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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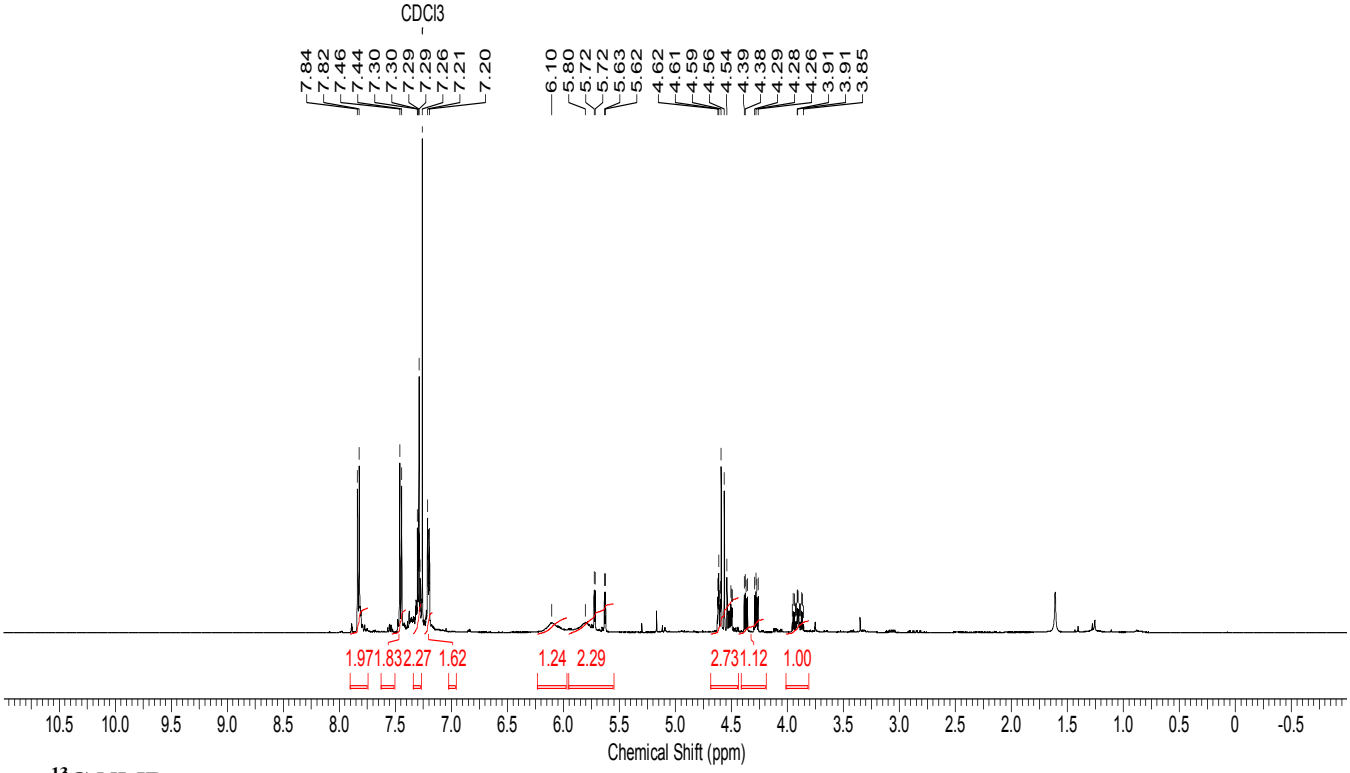
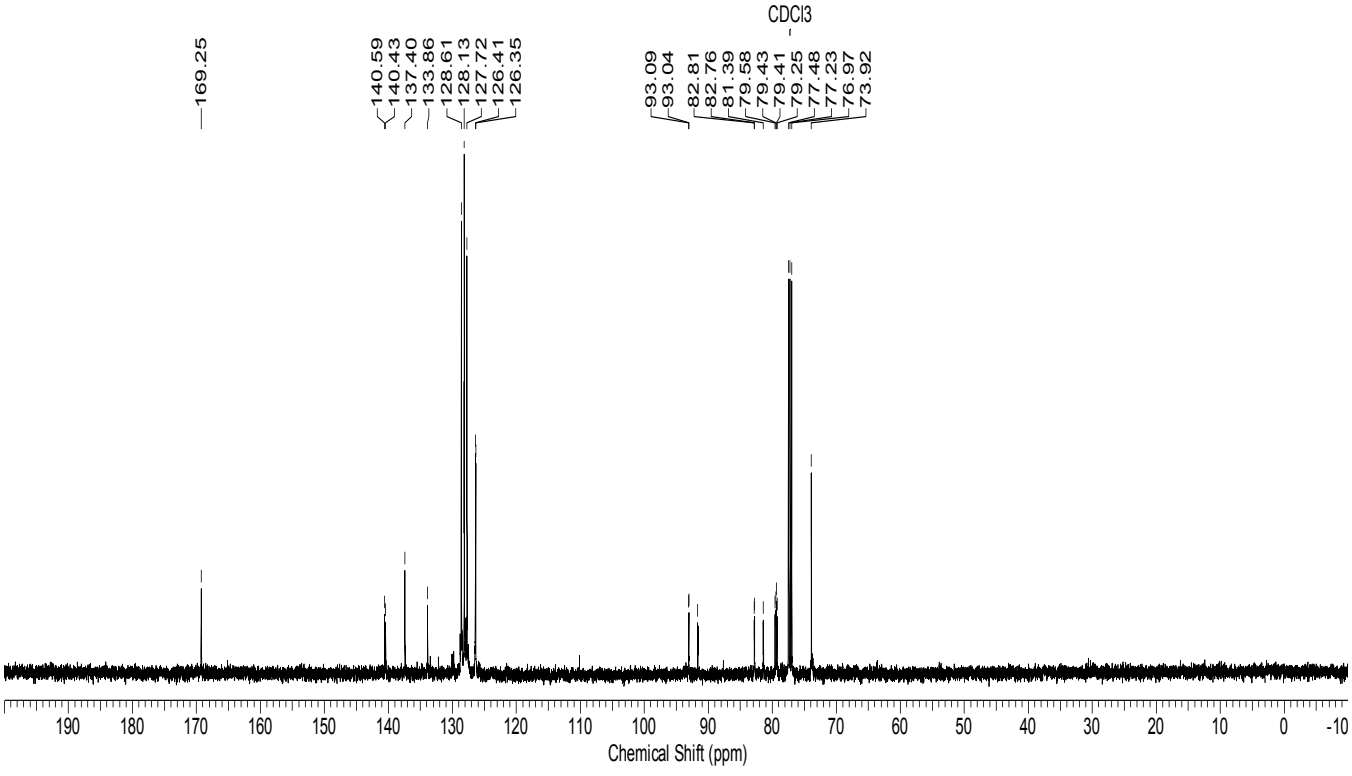
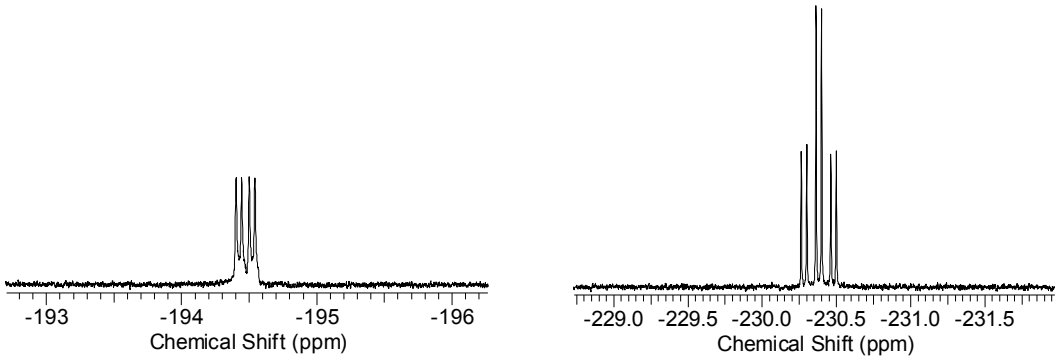


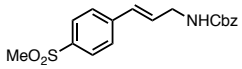
^{13}C NMR
125.7 MHz
$CDCl_3$



^{19}F NMR
470.4 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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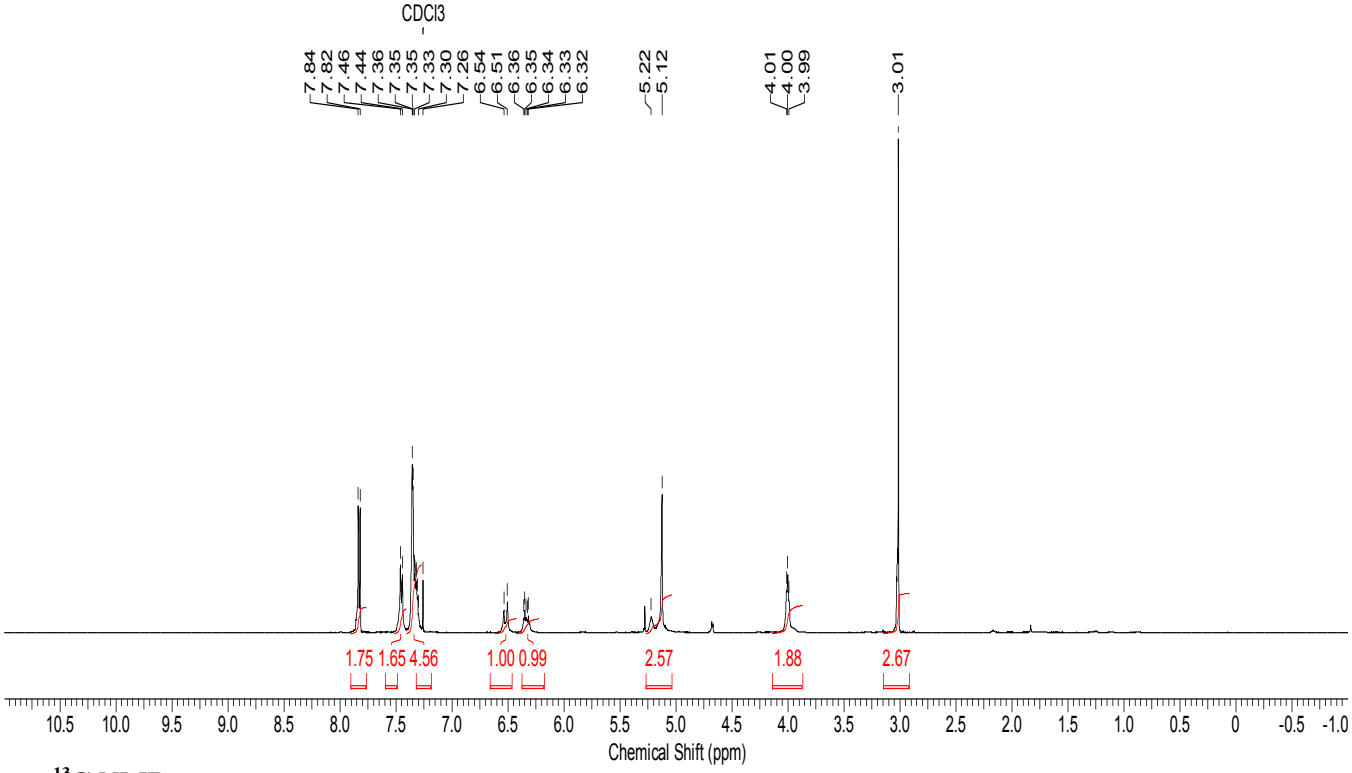
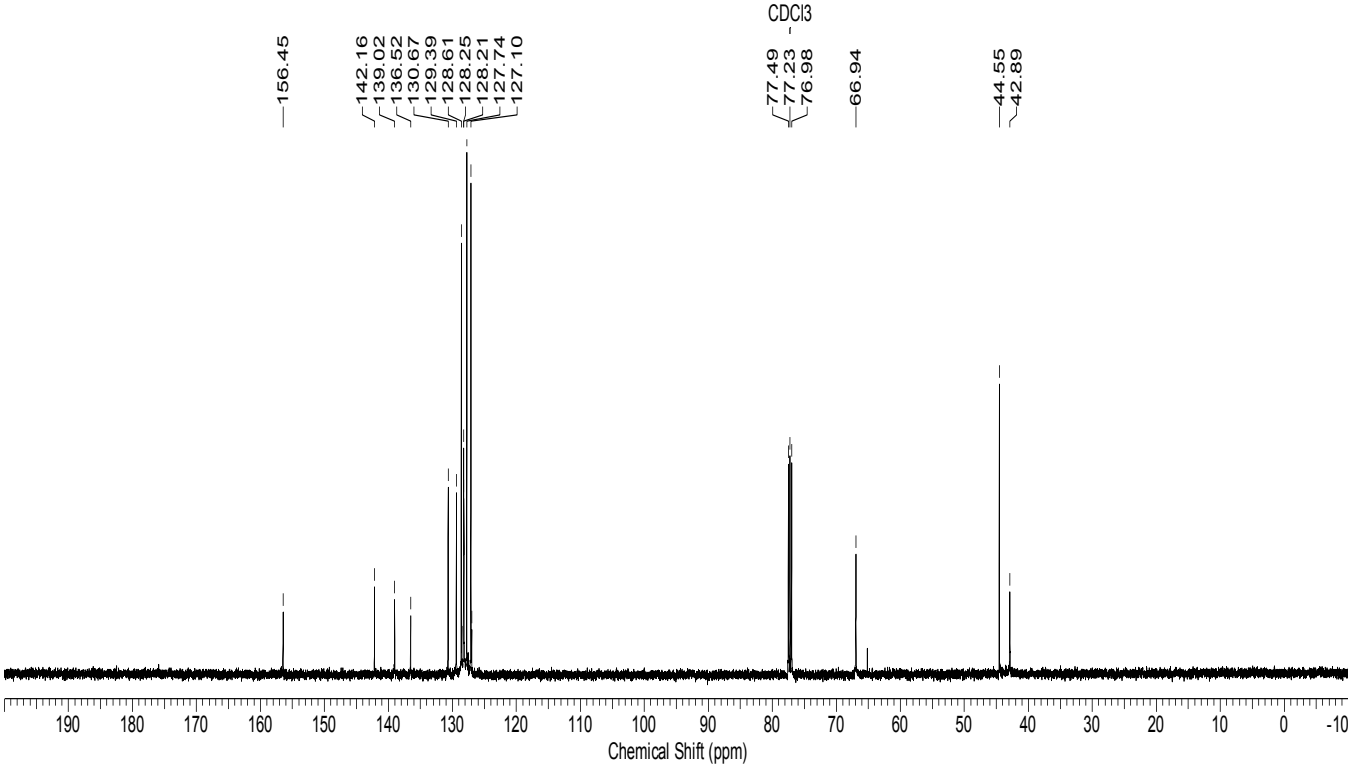
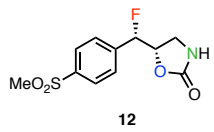


^{13}C NMR
125.7 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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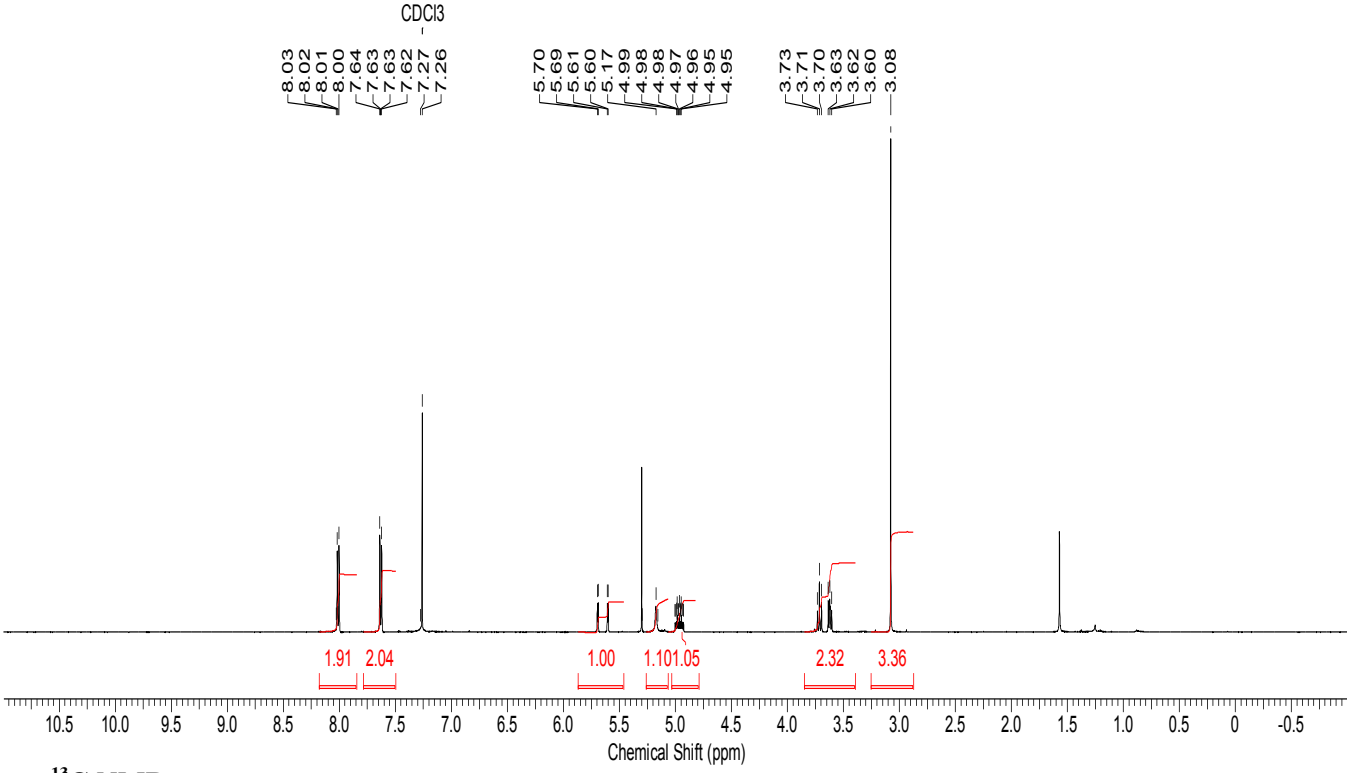
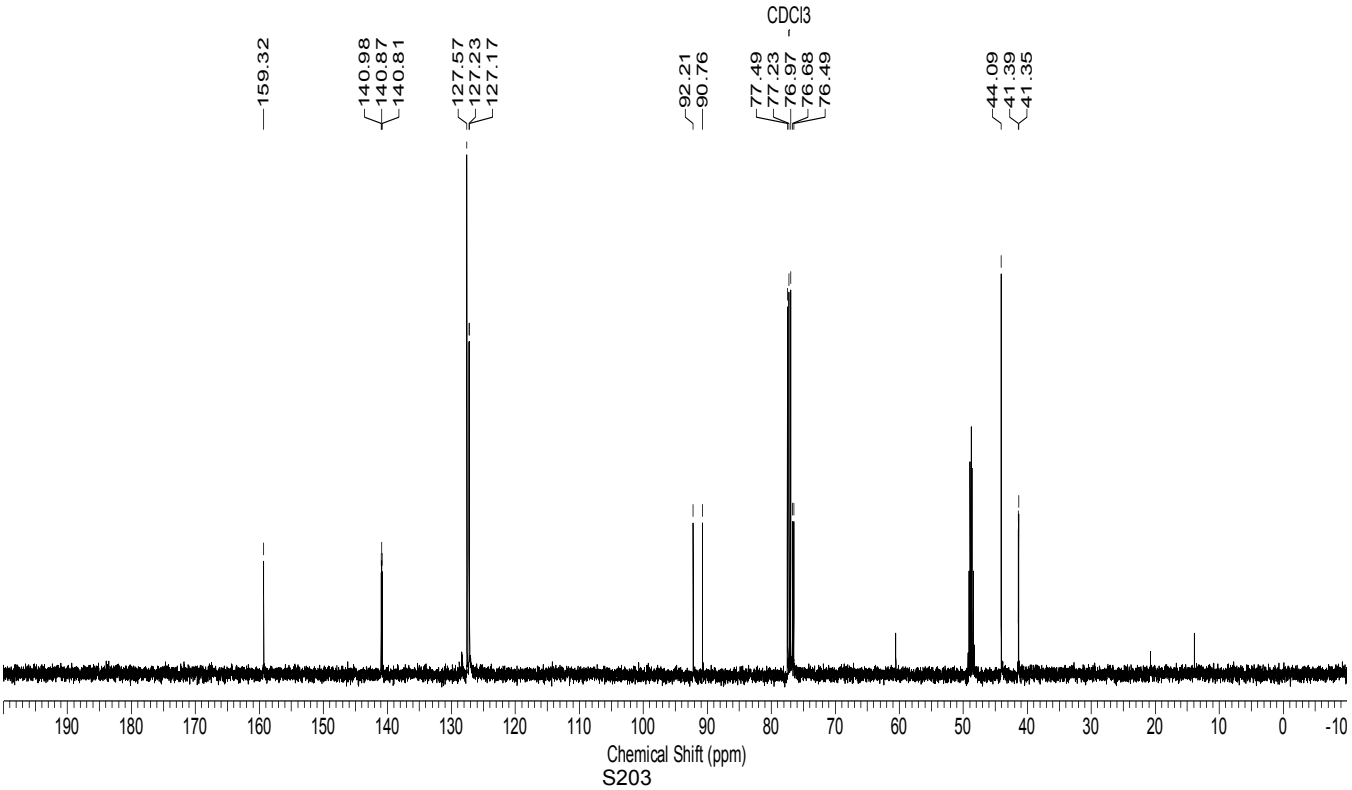
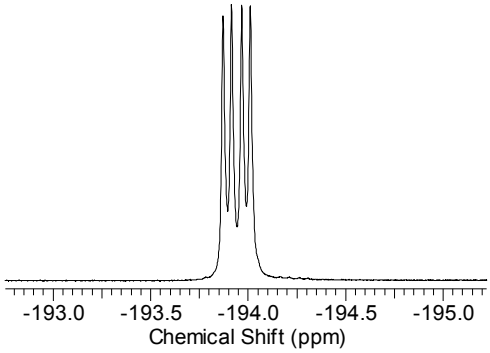


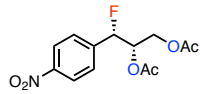
^{13}C NMR
500 MHz
10% $CD_3OD/CDCl_3$



^{19}F NMR
470.4 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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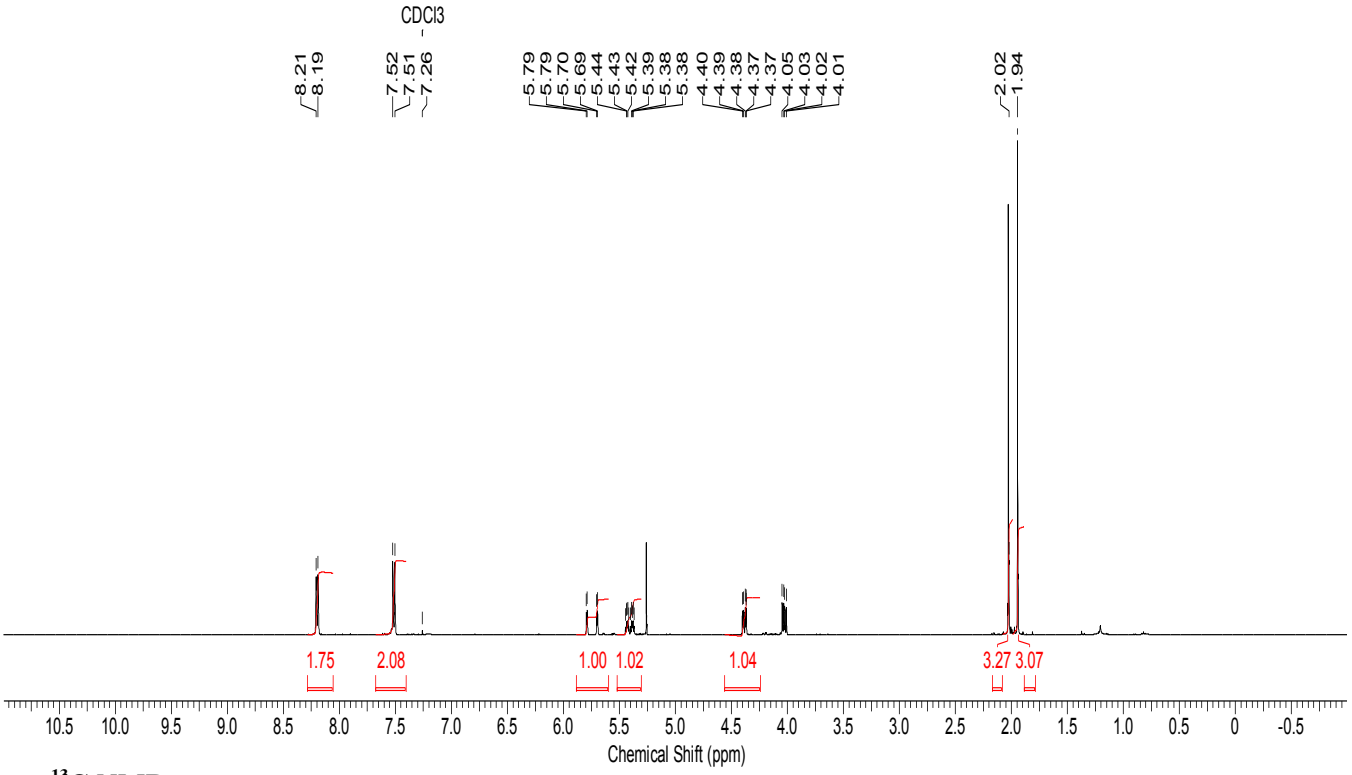
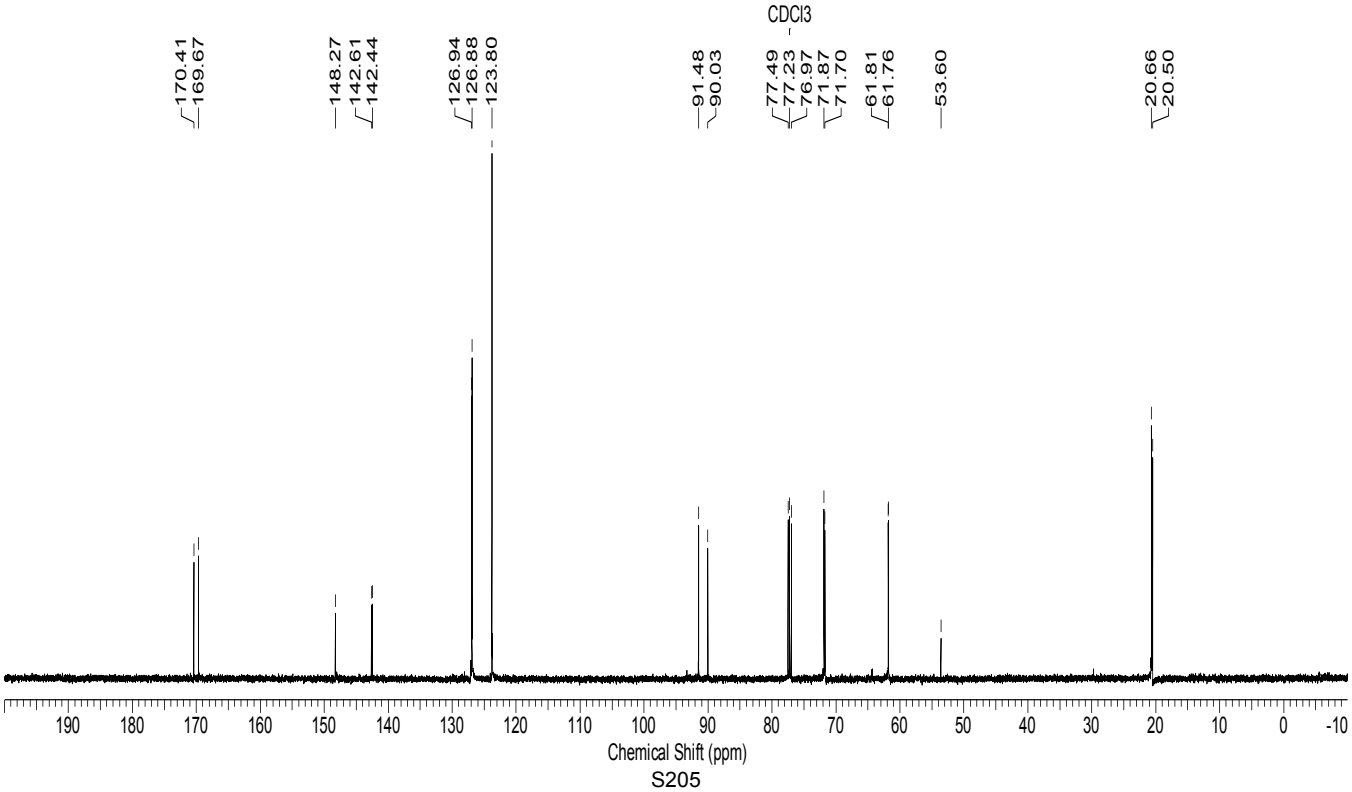
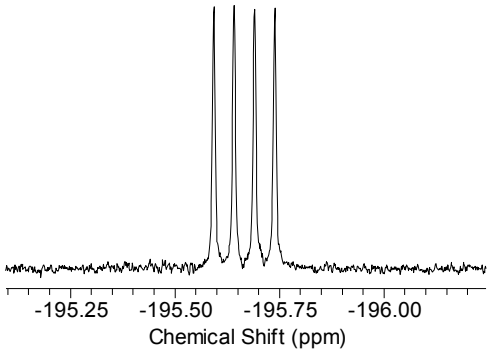


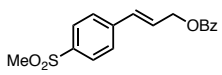
^{13}C NMR
125.7 MHz
$CDCl_3$



^{19}F NMR
470.4 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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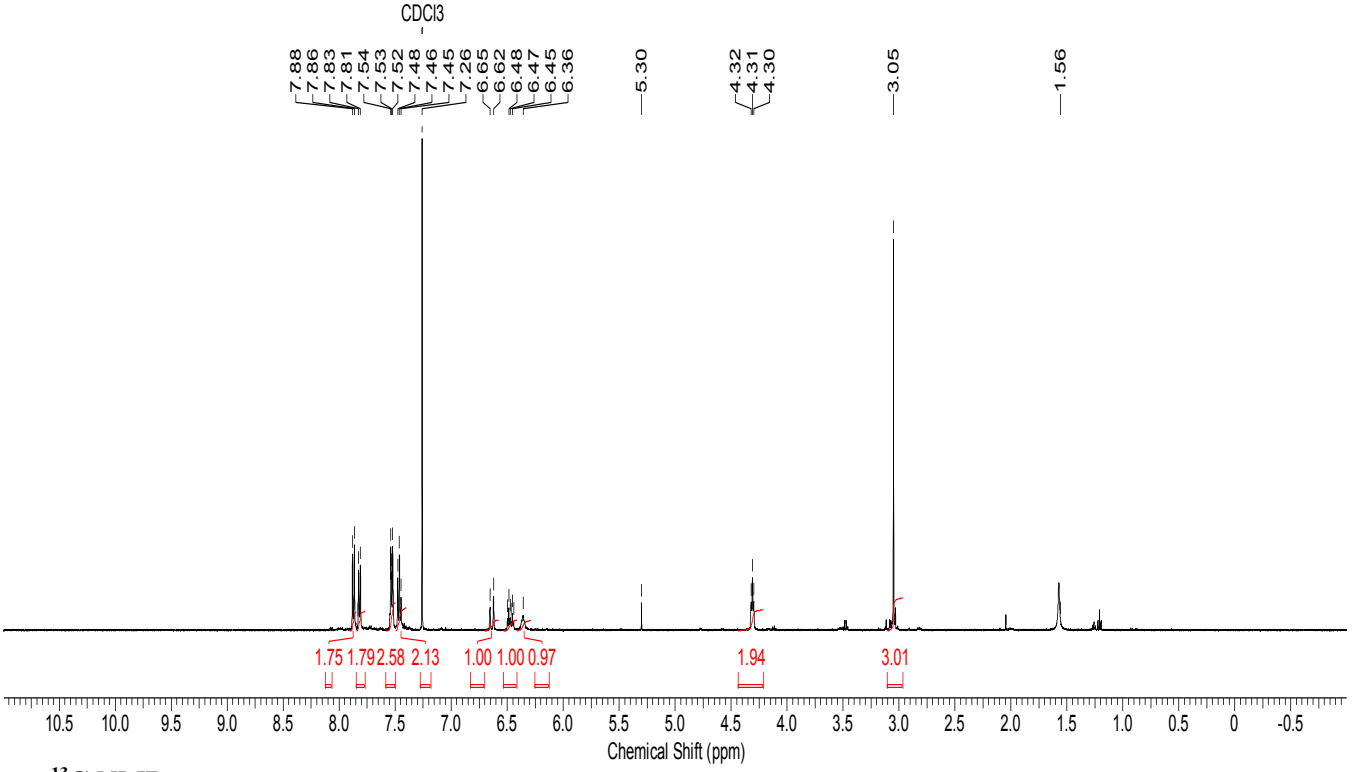
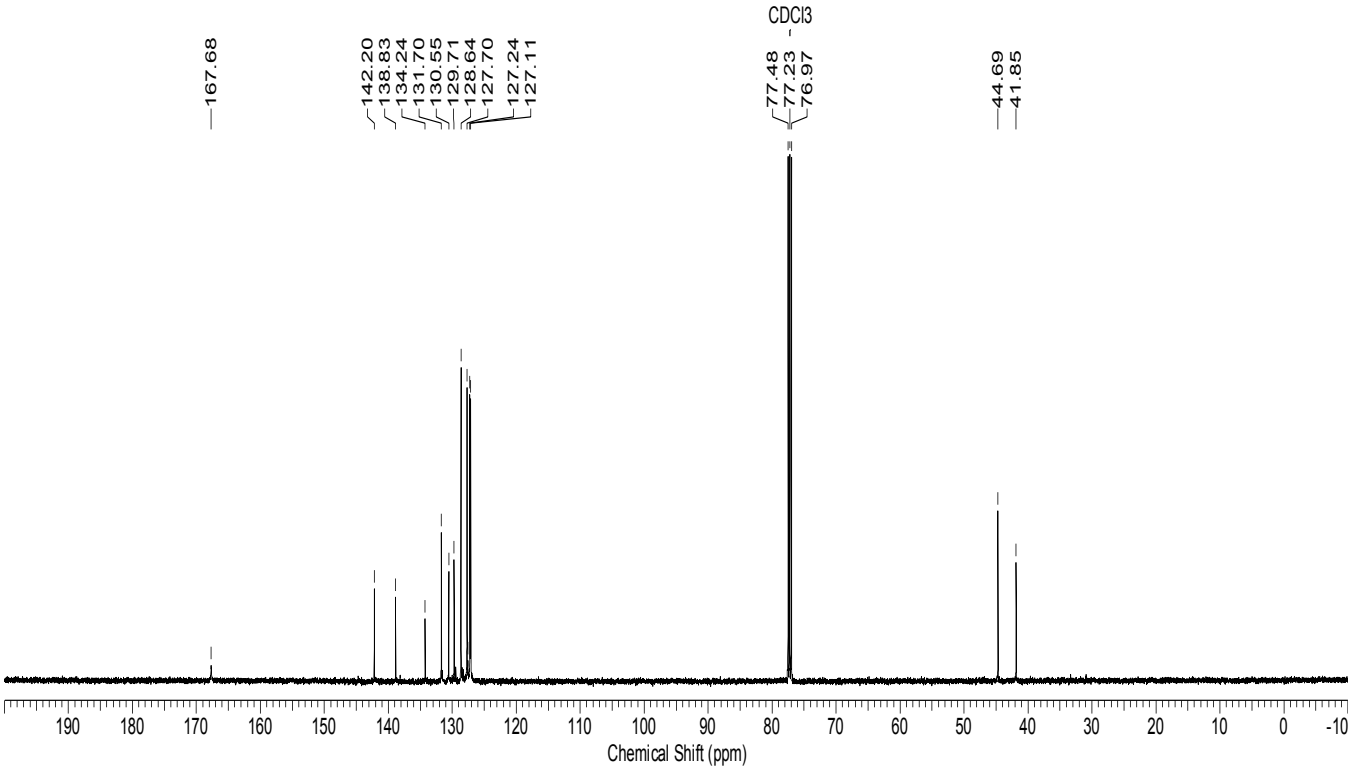
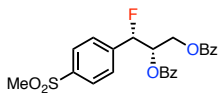


^{13}C NMR
125.7 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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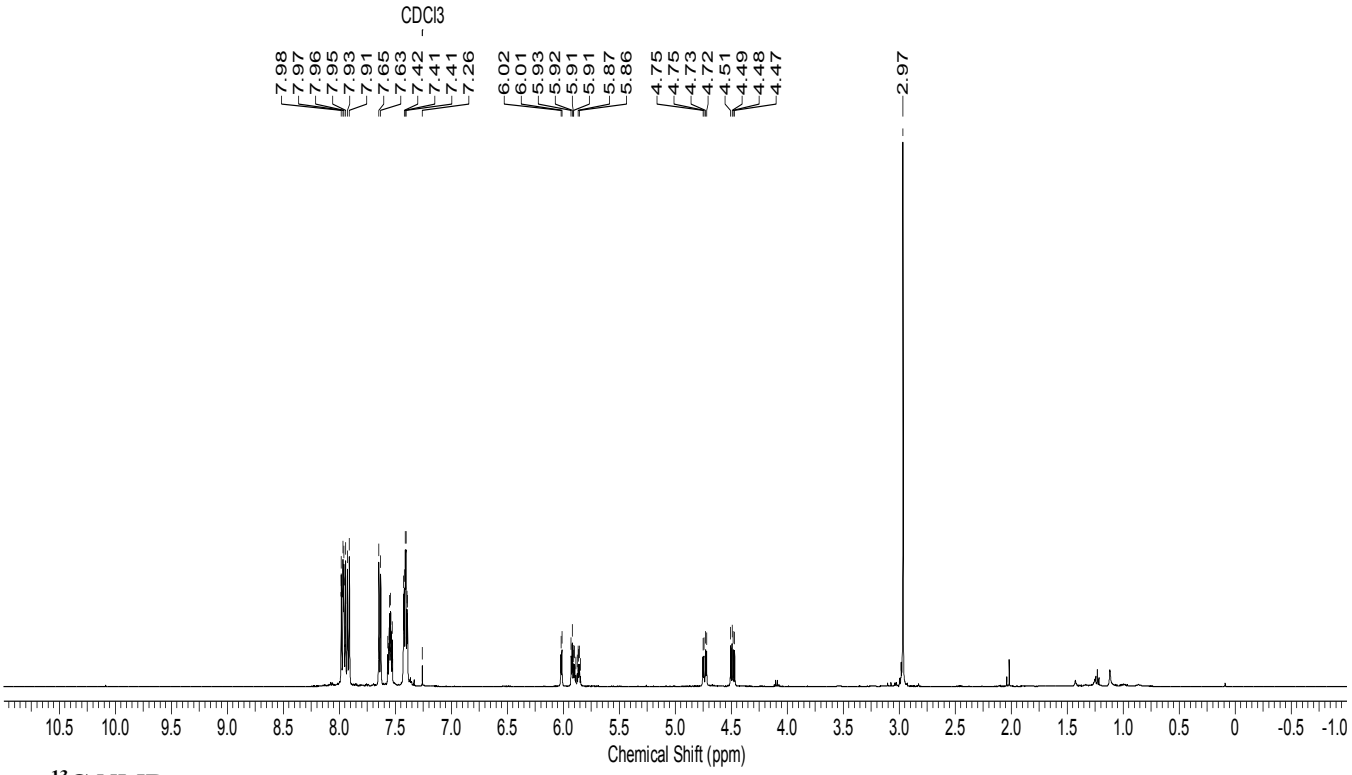
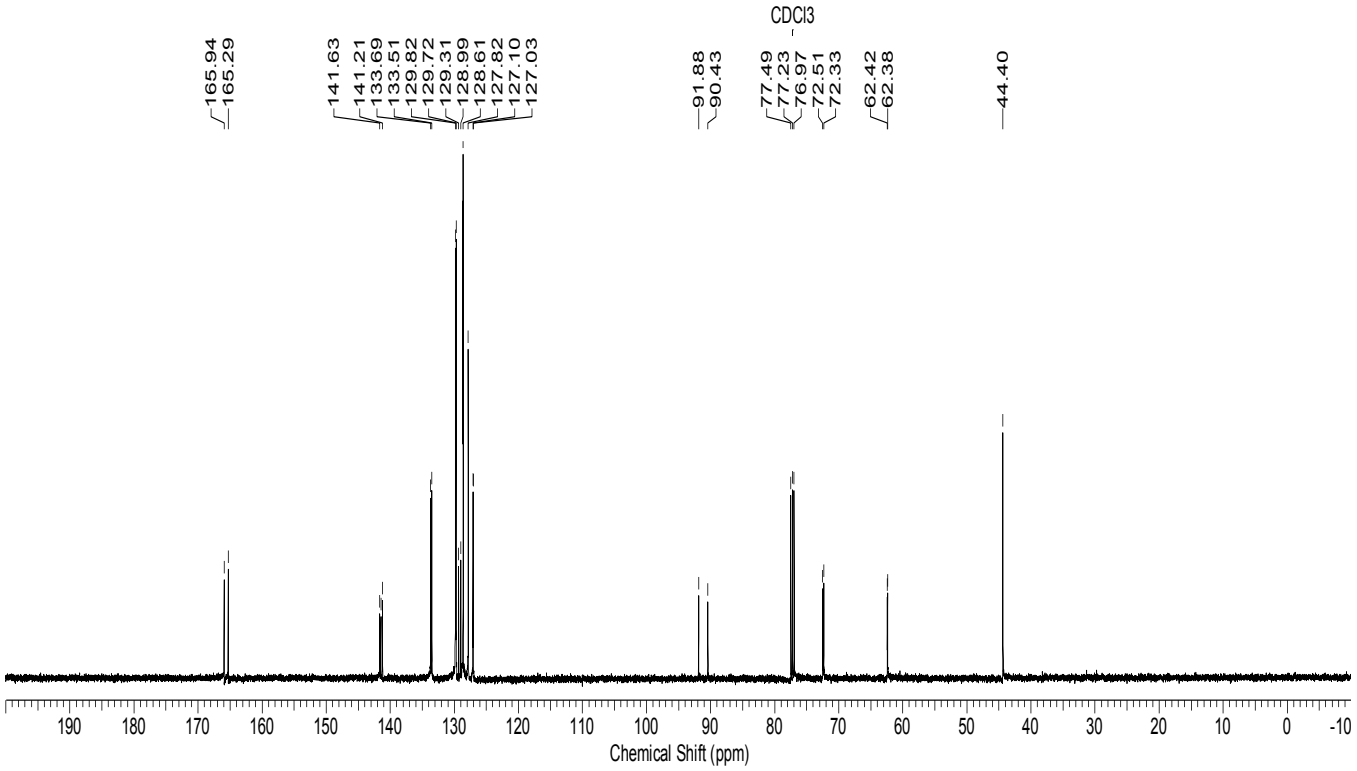
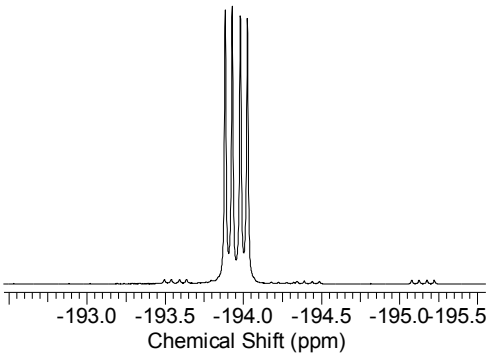


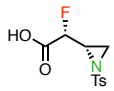
^{13}C NMR
125.7 MHz
$CDCl_3$



^{19}F NMR
470.4 MHz
$CDCl_3$



^{1}H NMR
500 MHz
$CDCl_3$



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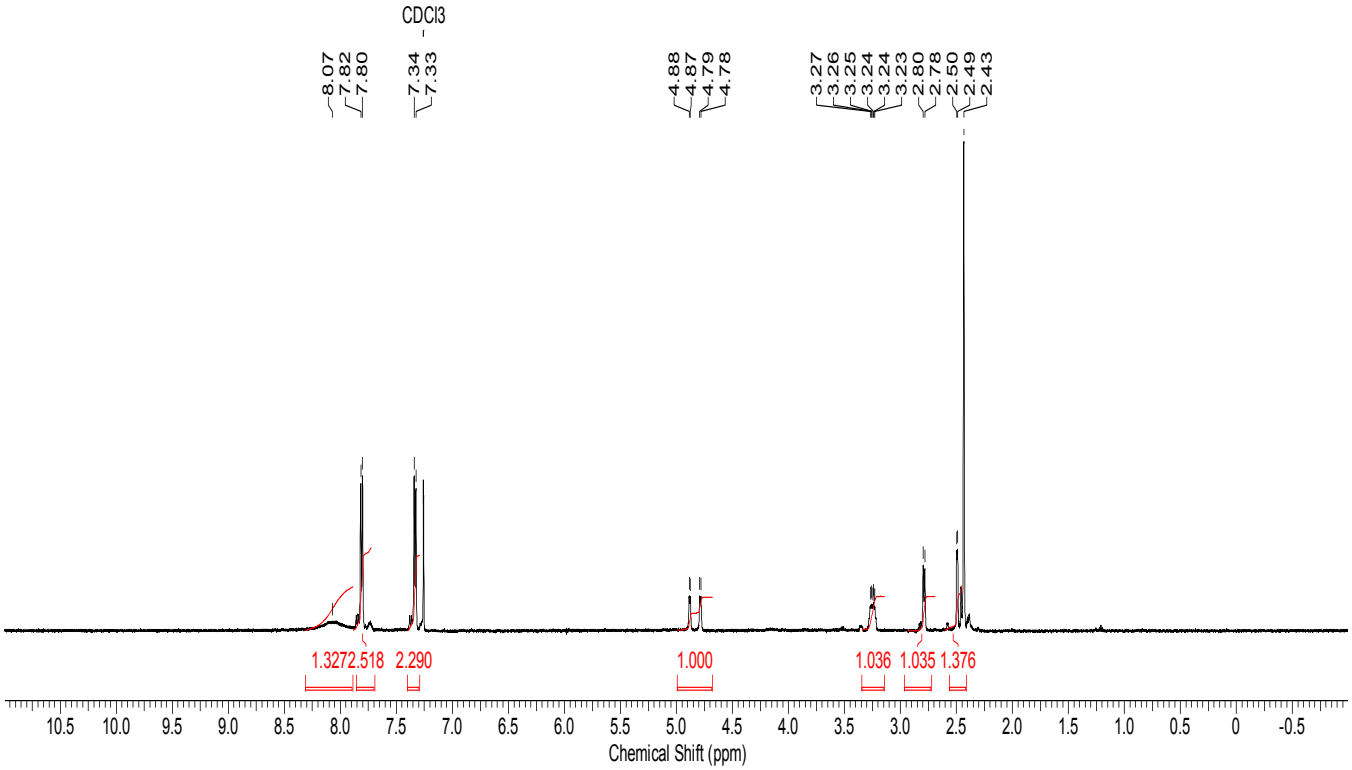
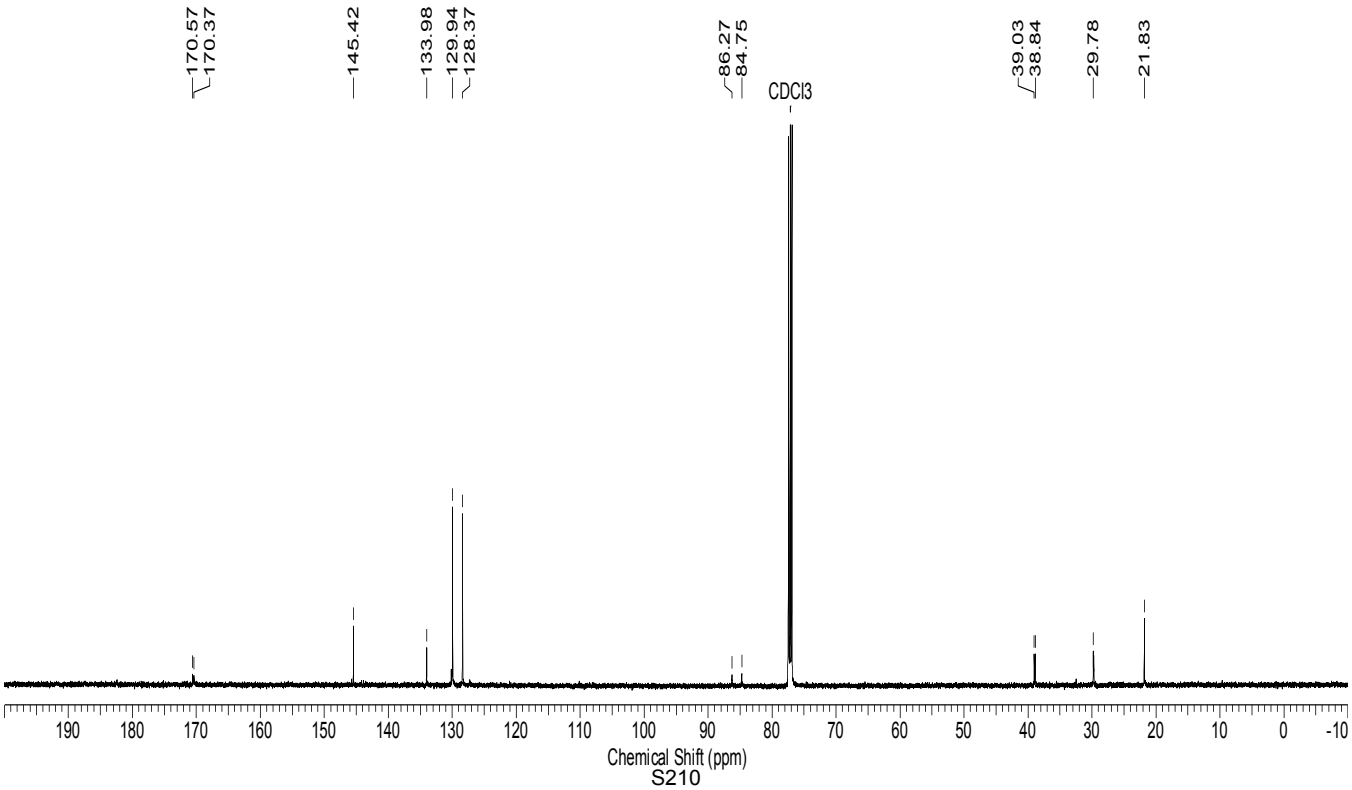


^{13}C NMR
125.7 MHz
$CDCl_3$



^{19}F NMR
470.4 MHz
$CDCl_3$