Supporting Information（SI）

Chemodivergent and Stereoselective Construction of *gem*-Difluoroallylic Amines from Masked Difluorodiazo Reagents

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1. General information

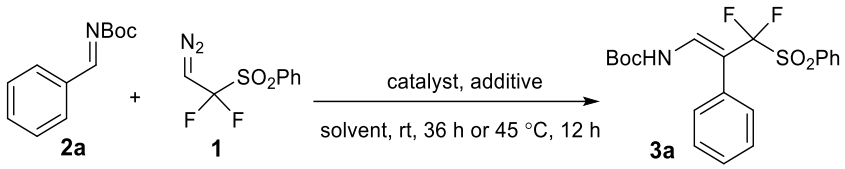
^{1}H, ^{13}C and ^{19}F were recorded on Bruker AV 400 MHz instrument at 400 MHz (^{1}H NMR), 100MHz (^{13}C NMR), as well as 376 MHz (^{19}F NMR), or Bruker AV 600 MHz instrument at 600MHz (^{1}H NMR), 150 MHz (^{13}C NMR), as well as 565 MHz (^{19}F NMR). Chemical shifts were reported in ppm down field from internal Me_4Si and external CCl_3F, respectively. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br (broad). Coupling constants were reported in Hertz (Hz). MS were recorded on a VG ZABHS spectrometer with the ESI resource. High resolution mass spectrometry (HRMS) spectra were obtained on a Bruker microTOF-QII instrument. Optical rotations were determined using an Autopol IV-T. HPLC analyses were carried out on a HewlettPackard Model HP 1200 instrument. X-ray structural analysis was conducted on the XtaLAB mini instrument.

Materials: Tetrahydrofuran (THF), diethyl ether, and toluene were distilled from sodium/benzophenone prior to use; CH_2Cl_2 was distilled from CaH_2; All purchased reagents were used without further purification. Analytical thin layer chromatography was performed on 0.20 mm Qingdao Haiyang silica gel plates. Silica gel (200-300 mesh) (from Qingdao Haiyang Chem. Company, Ltd.) was used for flash chromatography. The $PhSO_2CF_2CHN_2$ **1** and *N*-Boc imines **2** were prepared according to the reported procedures.[1, 2]

2. Experimental Section

2.1 General procedure for the one-pot olefination reaction of difluorodiazo compound 1 with *N*-Boc imines 2

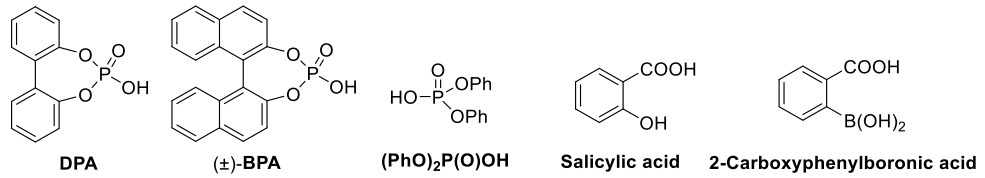
Table S1. Optimization of One-Pot Olefination Reaction Conditions [a]

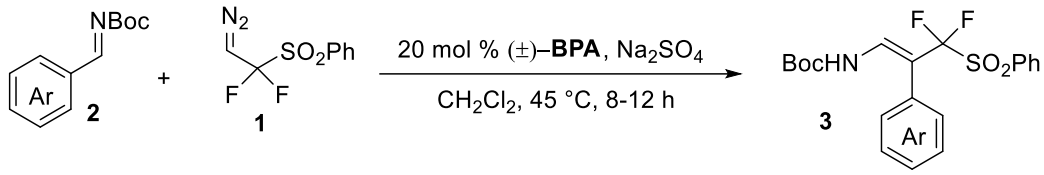


entry	catalyst	equiv	solvent	additive	yield (%)[b]
1	H_3PO_4	0.2	CH_2Cl_2	Na_2SO_4	45
2	H_3PO_4	0.5	CH_2Cl_2	Na_2SO_4	46[c]
3	H_3PO_4	1.0	CH_2Cl_2	Na_2SO_4	54[c]
4	H_3PO_4	2.0	CH_2Cl_2	Na_2SO_4	20[c]
5	CH_3COOH	0.2	CH_2Cl_2	Na_2SO_4	25
6	CF_3COOH	0.2	CH_2Cl_2	Na_2SO_4	58
7	CF_3COOH	0.5	CH_2Cl_2	Na_2SO_4	60[c]
8	CF_3COOH	1.0	CH_2Cl_2	Na_2SO_4	64[c]
9	CF_3COOH	2.0	CH_2Cl_2	Na_2SO_4	52[c]
10	CF_3SO_3H	0.2	CH_2Cl_2	Na_2SO_4	38
11	*p*-$CH_3C_6H_4SO_3H$	0.2	CH_2Cl_2	Na_2SO_4	45
12	*o*-$NO_2C_6H_4SO_3H$	0.2	CH_2Cl_2	Na_2SO_4	33[c]
13	$(CF_3SO_2)_2NH$	0.2	CH_2Cl_2	Na_2SO_4	20
14	$(PhO)_2P(O)OH$	0.2	CH_2Cl_2	Na_2SO_4	45[c]
15	Salicylic acid	0.2	CH_2Cl_2	Na_2SO_4	0
16	2-Carboxyphenylboronic acid	0.2	CH_2Cl_2	Na_2SO_4	47[c]
17	$BF_3 \cdot Et_2O$	1.0	CH_2Cl_2	Na_2SO_4	31
18	DPA	0.2	CH_2Cl_2	Na_2SO_4	15
19	(±)-**BPA**	0.2	CH_2Cl_2	Na_2SO_4	76 (89[c])
20	(±)-**BPA**	0.2	CH_2Cl_2	Na_2SO_4	83[c]
21	(±)-**BPA**	0.2	DCE	Na_2SO_4	58[c]
22	(±)-**BPA**	0.2	$CHCl_3$	Na_2SO_4	63[c]
23	(±)-**BPA**	0.2	THF	Na_2SO_4	51[c]

24	(±)-**BPA**	0.2	Et_2O	Na_2SO_4	22[c]
25	(±)-**BPA**	0.2	CH_2Cl_2	4 Å MS	55[c]
26	(±)-**BPA**	0.2	CH_2Cl_2	5 Å MS	57[c]
27	(±)-**BPA**	0.2	CH_2Cl_2	-	43[c]
28	(±)-**BPA**	0.1	CH_2Cl_2	Na_2SO_4	72[c]

[a] Reaction conditions: **1** (0.1 mmol), **2a** (0.2 mmol), catalyst (x equiv), additive (100 mg), solvent (2 mL), 45 °C for 12 hours (entries 1–19), or rt for 36 hours (entries 20–28), unless otherwise noted. [b] Yield of isolated product. [c] F-NMR yield, $PhCF_3$ as internal standard.

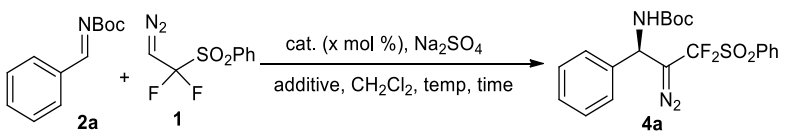




To a 25 mL Schlenk flask equipped with a stirring bar was added *N*-Boc imines **2** (0.6 mmol, 2.0 equiv.), racemic phosphoric acid (±)-**BPA** (21 mg, 0.06 mmol, 20 mol %), anhydrous sodium sulfate (300 mg), and CH_2Cl_2 (5.0 mL). Then the difluorodiazo compound **1** (69.6 mg, 0.3 mmol, 1.0 equiv.) was added to the reaction mixture. The resulting mixture was warmed up to 45 °C and stirred about 12 hours until completion indicated by thin layer chromatography (TLC). Then, the reaction mixture was concentrated under vacuum to yield the crude expected product **3**, which was subjected to column chromatography on silica gel (eluent: petrol ether / ethyl acetate = 9:1) to give the pure product.

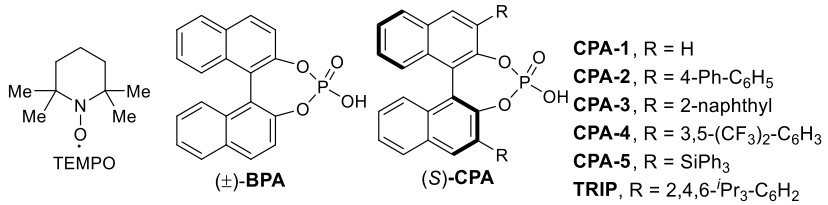
2.2 General procedure for the catalytic enantioselective Mannich-type reaction of difluorodiazo compound 1 with *N*-Boc imines 2

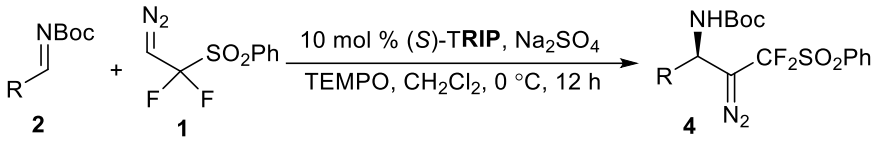
Table S2. Optimization of Mannich-type Reaction Conditions [a]



entry	cat. (*x* mol %)	additive (equiv)	temp (°C)/ time (h)	yield (%)[b]/ *ee* (%)[c]
1	(±)-**BPA** (20)	TEMPO (3)	rt / 12	86 / -
2	(±)-**BPA** (20)	K_3PO_4 (1)	rt / 12	85 / -
3	**CPA-1** (10)	TEMPO (3)	rt / 12	95 / 5
4	**CPA-2** (10)	TEMPO (3)	rt / 12	33 / 22
5	**CPA-3** (10)	TEMPO (3)	rt / 12	56 / 30
6	**CPA-4** (10)	TEMPO (3)	rt / 12	10 / nd
7	**CPA-5** (10)	TEMPO (3)	rt / 12	15 / nd
8	(*S*)-**TRIP** (10)	TEMPO (3)	rt / 12	90 / 86
9	(*S*)-**TRIP** (10)	TEMPO (3)	0 / 12	98 / 94
10	(*S*)-**TRIP** (10)	TEMPO (3)	-20 / 24	98 / 94
11	(*S*)-**TRIP** (5)	TEMPO (3)	0 / 12	91 / 83
12	(*S*)-**TRIP** (10)	TEMPO (1)	0 / 12	91 / 88
13[d]	(*S*)-**TRIP** (10)	TEMPO (3)	0 / 20	95 / 94
14	(*S*)-**TRIP** (10)	-	0 / 12	63 / 82
15	(*S*)-**TRIP** (10)	Na_2CO_3 (0.2)	0 / 20	84 / 55
16	(*S*)-**TRIP** (10)	$NaHCO_3$ (0.2)	0 / 20	83 / 83
17	(*S*)-**TRIP** (10)	K_3PO_4 (0.2)	0 / 30	83 / 94
18	(*S*)-**TRIP** (10)	K_3PO_4 (0.5)	0 / 30	89 / 95
19	(*S*)-**TRIP** (10)	K_3PO_4 (1.0)	0 / 30	85 / 95
20	(*S*)-**TRIP** (10)	K_2HPO_4 (0.75)	0 / 30	53 / 95
21	(*S*)-**TRIP** (10)	KH_2PO_4 (1.5)	0 / 30	81 / 93

[a] Reaction conditions: $PhSO_2CF_2CHN_2$ **1** (0.1 mmol), imine **2a** (0.2 mmol), catalyst (*x* mol %), Na_2SO_4 (100 mg), additive, CH_2Cl_2 (2 mL), react at indicated temperature for 12 hours unless otherwise noted. [b] Yield of isolated product. [c] The *ee* was determined by HPLC analysis. [d] 3 mmol scale of $PhSO_2CF_2CHN_2$ experiment.

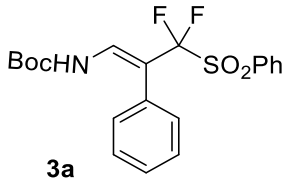




To a 10 mL Schlenk flask equipped with a stirring bar was added *N*-Boc imines **2** (0.4 mmol, 2.0 equiv.), chiral phosphoric acid (*S*)-**TRIP** (14.5 mg, 0.02 mmol, 10 mol %), TEMPO (94 mg, 0.6 mmol, 3.0 equiv.), anhydrous sodium sulfate (400 mg), and CH_2Cl_2 (2.0 mL). Difluorodiazo compound **1** (46 mg, 0.2 mmol, 1.0 equiv.) was added to the mixture, which was stirred at 0 ºC until the completion of the reaction (monitored by TLC). Then, the reaction mixture was concentrated under vacuum to yield the crude expected product **4**, which was subjected to column chromatography on silica gel (eluent: petrol ether / ethyl acetate = 9:1) to give the pure product.

2.3 Characterization data for the enamines 3 and diazo-Mannich adducts 4

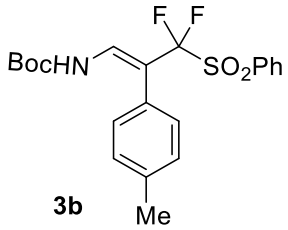
***tert*-Butyl (*E*)-(3,3-difluoro-2-phenyl-3-(phenylsulfonyl)prop-1-en-1-yl)carbamate**



3a

White solid, 94 mg, 76% yield, mp 154–155 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.7 Hz, 2H), 7.70 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.8 Hz, 2H), 7.43 (m, 6H), 6.50 (d, J = 8.1 Hz, 1H), 1.46 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -96.17(s). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.4, 134.9, 133.6, 133.1 (t, J = 8.9 Hz), 130.9, 130.7, 129.2, 129.2, 129.0, 121.9 (t, J = 287.3 Hz), 105.8 (t, J = 22.6 Hz), 82.4, 28.1. **HRMS** (ESI^+): Calculated for $C_{20}H_{21}F_2NNaO_4S^+$ $[M+Na]^+$: 432.1052; Found: 432.1050.

***tert*-Butyl (*E*)-(3,3-difluoro-3-(phenylsulfonyl)-2-(*p*-tolyl)prop-1-en-1-yl) carbamate**

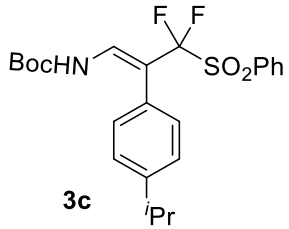


3b

White solid, 104 mg, 82% yield, mp 129–130 ºC. 402 mg, 95% yield (To a 50 mL

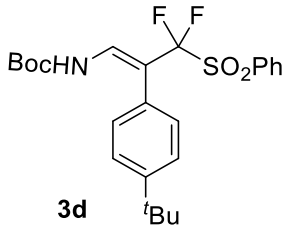
Schlenk flask equipped with a stirring bar was added *N*-Boc imines **2b** (438 mg, 2 mmol, 2.0 equiv.), racemic phosphoric acid (±)-**BPA** (70 mg, 0.2 mmol, 20 mol %), anhydrous sodium sulfate (1000 mg), and CH_2Cl_2 (16 mL). Then the difluorodiazo compound **1** (232 mg, 1 mmol, 1.0 equiv.) was added to the reaction mixture. The resulting mixture was warmed up to 45 ºC and stirred about 12 hours until completion indicated by thin layer chromatography (TLC). Then, 20 mL of water was added and extracted with CH_2Cl_2 (15 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum to yield the crude expected product. The residue was subjected to column chromatography on silica gel (eluent: petrol ether / ethyl acetate = 20:1) to give the pure product **3b**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.8 Hz, 2H), 7.72 (t, J = 7.4 Hz, 1H), 7.57 (m, 3H), 7.40 – 7.21 (m, 4H), 6.52 (d, J = 8.0 Hz, 1H), 2.41 (s, 3H), 1.48 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -96.32(s). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.5, 138.9, 134.8, 133.7, 133.0 (t, J = 9.3 Hz), 130.7, 130.7, 129.9, 129.1, 127.2, 122.0 (t, J = 287.1 Hz), 105.8 (t, J = 22.1 Hz), 82.3, 28.1, 21.3. **HRMS** (ESI^+): Calculated for $C_{21}H_{23}F_2NNaO_4S^+$ $[M+Na]^+$: 446.1208; Found: 446.1196.

***tert*-Butyl (*E*)-(3,3-difluoro-2-(4-isopropylphenyl)-3-(phenylsulfonyl)prop-1-en-1-yl)carbamate**



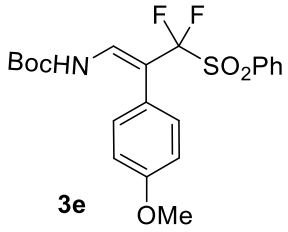
Yellow solid, 125 mg, 93% yield, mp 103–104 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.6 Hz, 2H), 7.70 (t, J = 7.5 Hz, 1H), 7.55 (t, J = 7.8 Hz, 3H), 7.31 (s, 4H), 6.53 (d, J = 9.2 Hz, 1H), 2.94 (dt, J = 13.8, 6.9 Hz, 1H), 1.46 (s, 9H), 1.29 (d, J = 6.9 Hz, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -96.05. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.5, 149.5, 136.6, 134.8, 133.7, 133.0, 130.7, 129.1, 127.3, 126.4, 122.0 (t, J = 287.8 Hz), 105.8 (t, J = 22.7 Hz), 82.3, 33.9, 28.1, 27.9, 23.8. **HRMS** (ESI^+): Calculated for $C_{23}H_{27}F_2NNaO_4S^+$ $[M+Na]^+$: 474.1521; Found: 474.1512.

***tert*-Butyl (*E*)-(2-(4-(*tert*-butyl)phenyl)-3,3-difluoro-3-(phenylsulfonyl)prop-1-en-1-yl)carbamate**



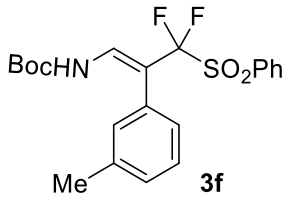
Yellow solid, 136 mg, 98% yield, mp 117–118 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.8 Hz, 2H), 7.70 (t, J = 7.4 Hz, 1H), 7.61 – 7.40 (m, 5H), 7.31 (d, J = 7.5 Hz, 2H), 6.53 (s, 1H), 1.47 (s, 9H), 1.35 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -96.00. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.8, 151.5, 134.8, 133.7, 133.0, 130.7, 130.4, 129.1, 127.2, 126.2, 122.0 (t, J = 287.0 Hz), 105.8 (t, J = 20.7 Hz), 82.3, 34.7, 31.3, 28.1. **HRMS** (ESI^+): Calculated for $C_{24}H_{29}F_2NNaO_4S^+$ $[M+Na]^+$: 488.1678； Found: 488.1667.

***tert*-Butyl (*E*)-(3,3-difluoro-2-(4-methoxyphenyl)-3-(phenylsulfonyl)prop-1-en-1-yl)carbamate**



White solid, 117 mg, 89% yield, mp 153–154 ºC. **^{1}H NMR** (400 MHz, CD_3CN) δ 7.97 (d, J = 7.5 Hz, 2H), 7.88 – 7.81 (m, 1H), 7.73 – 7.65 (m, 2H), 7.29 (m, 4H), 7.04 – 6.98 (m, 2H), 3.85 (s, 3H), 1.45 (s, 9H). **^{19}F NMR** (376 MHz, CD_3CN) δ -96.63. **^{13}C NMR** (100 MHz, CD_3CN) δ 160.6, 152.6, 136.1, 134.0 (t, J = 9.4 Hz), 133.8, 132.9, 131.0, 130.1, 122.8 (t, J = 285.7 Hz), 122.7, 115.0, 105.7 (t, J = 22.7 Hz), 82.2, 55.6, 27.8. **HRMS** (ESI^+): Calculated for $C_{21}H_{23}F_2NNaO_5S^+$ $[M+Na]^+$: 462.1157; Found: 462.1154.

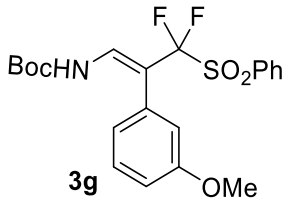
***tert*-Butyl (*E*)-(3,3-difluoro-3-(phenylsulfonyl)-2-(*m*-tolyl)prop-1-en-1-yl) carbamate**



3f

White solid, 104 mg, 87% yield, mp 72–73 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.7 Hz, 2H), 7.70 (t, J = 7.5 Hz, 1H), 7.55 (m, 3H), 7.35 (t, J = 7.8 Hz, 1H), 7.24 – 7.09 (m, 3H), 6.48 (d, J = 8.9 Hz, 1H), 2.39 (s, 3H), 1.46 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -96.12. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.5, 138.94, 134.9, 133.7, 133.0 (t, J = 8.9 Hz), 131.4, 130.7, 130.1, 129.8, 129.1, 129.1, 127.9, 121.9 (t, J = 286.9 Hz), 106.0 (t, J = 22.6 Hz), 82.3, 28.1, 21.5. **HRMS** (ESI^+): Calculated for $C_{21}H_{23}F_2NNaO_4S^+$ $[M+Na]^+$: 446.1208; Found: 446.1195.

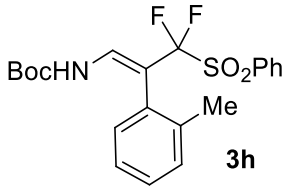
***tert*-Butyl (*E*)-(3,3-difluoro-2-(3-methoxyphenyl)-3-(phenylsulfonyl)prop-1-en-1-yl)carbamate**



3g

White solid, 112 mg, 86% yield, mp 120–121 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.7 Hz, 2H), 7.71 (t, J = 7.5 Hz, 1H), 7.56 (m, 3H), 7.37 (t, J = 7.6 Hz, 1H), 6.96 (t, J = 9.8 Hz, 3H), 6.54 (d, J = 9.0 Hz, 1H), 3.83 (s, 3H), 1.46 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -96.07. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.0, 151.4, 134.9, 133.6, 133.2 (t, J = 9.2 Hz), 131.5, 130.7, 130.2, 129.1, 123.0, 121.9 (t, J = 287.3 Hz), 116.2, 114.7, 105.7 (t, J = 22.5 Hz), 82.4, 55.3, 28.1. **HRMS** (ESI^+): Calculated for $C_{21}H_{23}F_2NNaO_5S^+$ $[M+Na]^+$: 462.1157; Found: 462.1147.

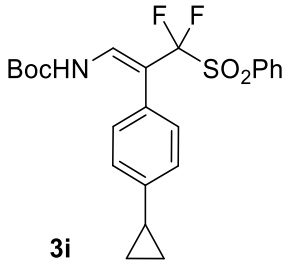
***tert*-butyl (*E*)-(3,3-difluoro-3-(phenylsulfonyl)-2-(*o*-tolyl)prop-1-en-1-yl)carbamate**



3h

This compound was prepared from diazo-Mannich adduct (±)-**4f** under identical reaction conditions (0.15 mmol of substrate, (±)-**BPA** (20 mol %), Na_2SO_4 (150 mg), CH_2Cl_2 (3 mL), 45 °C for 12 hours); white solid, 72 mg, 84% yield, mp 156–157 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.8 Hz, 2H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.65 – 7.50 (m, 3H), 7.39 (d, *J* = 6.9 Hz, 1H), 7.36 – 7.24 (m, 3H), 6.18 (d, *J* = 8.7 Hz, 1H), 2.31 (s, 3H), 1.46 (s, 9H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -92.11 (d, *J* = 223.9 Hz), -99.24 (d, *J* = 223.6 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.5, 138.9, 135.0, 133.8, 133.4 (t, *J* = 9.0 Hz), 132.0, 130.8, 130.8, 129.5, 129.2, 126.6, 122.1 (dd, *J* = 289.2, 284.3 Hz), 105.0 (dd, *J* = 25.8, 20.8 Hz), 82.5, 28.2, 19.8. **HRMS** (ESI^+): Calculated for $C_{21}H_{23}F_2NNaO_4S^+$ $[M+Na]^+$: 446.1208; Found: 446.1211.

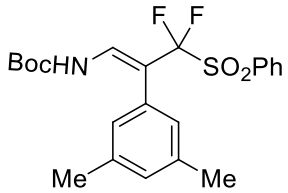
***tert*-Butyl (*E*)-(2-(4-cyclopropylphenyl)-3,3-difluoro-3-(phenylsulfonyl)prop-1-en-1-yl)carbamate**



3i

White solid, 130 mg, 97% yield, mp 143–144 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.94 (d, *J* = 7.6 Hz, 2H), 7.69 (t, *J* = 7.3 Hz, 1H), 7.55 (m, 3H), 7.28 (d, *J* = 7.3 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 2H), 6.51 (d, *J* = 8.3 Hz, 1H), 1.97 – 1.87 (m, 1H), 1.45 (s, 9H), 1.01 (d, *J* = 6.9 Hz, 2H), 0.75 (d, *J* = 4.4 Hz, 2H). **^{19}F NMR** (565 MHz, $CDCl_3$) *δ* -96.23. **^{13}C NMR** (150 MHz, $CDCl_3$) *δ* 151.5, 145.0, 134.9, 133.0 (t, *J* = 8.6 Hz), 132.93, 130.7, 130.6, 129.1, 126.3, 122.0 (t, *J* = 287.0 Hz), 105.8 (t, *J* = 22.6 Hz), 82.3, 28.1, 15.3, 9.6. **HRMS** (ESI^+): Calculated for $C_{23}H_{25}F_2NNaO_4S^+$ $[M+Na]^+$: 472.1365; Found: 472.1355.

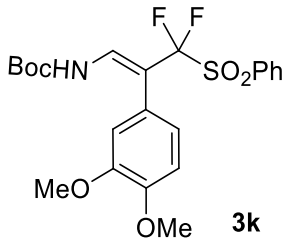
***tert*-Butyl (*E*)-(2-(3,5-dimethylphenyl)-3,3-difluoro-3-(phenylsulfonyl)prop-1-en-1-yl)carbamate**



3j

White solid, 131 mg, 94% yield, mp 108–109 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.7 Hz, 2H), 7.70 (t, J = 7.5 Hz, 1H), 7.62 – 7.42 (m, 3H), 7.01 (d, J = 18.4 Hz, 3H), 6.47 (s, 1H), 2.35 (s, 6H), 1.47 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -96.03. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.5, 138.7, 134.8, 133.7, 132.9, 130.7, 130.0, 129.1, 128.4, 122.0 (t, J = 286.9 Hz), 106.1 (t, J = 22.7 Hz), 82.2, 28.1, 21.3. **HRMS** (ESI^+): Calculated for $C_{22}H_{25}F_2NNaO_4S^+$ $[M+Na]^+$: 460.1365; Found: 460.1350.

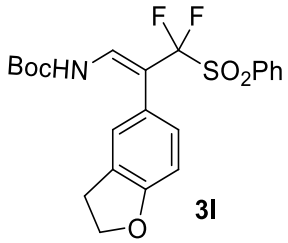
***tert*-Butyl (*E*)-(2-(3,4-dimethoxyphenyl)-3,3-difluoro-3-(phenylsulfonyl)prop-1-en-1-yl)carbamate**



3k

White solid, 140 mg, 89% yield, mp 155–156 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.8 Hz, 2H), 7.74 (t, J = 7.4 Hz, 1H), 7.66 – 7.46 (m, 3H), 6.97 (s, 3H), 6.54 (d, J = 8.8 Hz, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 1.50 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -96.19. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.4, 149.5, 149.3, 134.9, 133.7, 133.3 (t, J = 8.9 Hz), 130.7, 129.1, 123.5, 122.0 (t, J = 287.0 Hz), 122.3,113.8, 111.6, 105.7 (t, J = 24.6 Hz), 82.3, 56.0, 55.9, 28.1. **HRMS** (ESI^+): Calculated for $C_{22}H_{25}F_2NNaO_6S^+$ $[M+Na]^+$: 492.1263; Found: 492.1264.

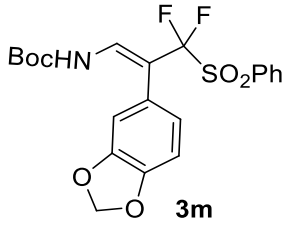
***tert*-Butyl (*E*)-(2-(2,3-dihydrobenzofuran-5-yl)-3,3-difluoro-3-(phenylsulfonyl) prop-1-en-1-yl)carbamate**



3l

White solid, 133 mg, 98% yield, mp 121–122 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.7 Hz, 2H), 7.73 (t, J = 6.9 Hz, 1H), 7.59 (t, J = 7.8 Hz, 2H), 7.51 (d, J = 9.7 Hz, 1H), 7.23 (s, 1H), 7.13 (d, J = 8.0 Hz, 1H), 6.86 (d, J = 8.2 Hz, 1H), 6.49 (d, J = 10.0 Hz, 1H), 4.63 (t, J = 8.7 Hz, 2H), 3.27 (t, J = 8.7 Hz, 2H), 1.48 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -96.33. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.7, 151.5, 134.8, 133.8, 133.1 (t, J = 8.9 Hz), 130.9, 130.6, 129.1, 128.2, 127.5, 122.0 (t, J = 287.7 Hz), 121.7, 109.9, 105.9 (t, J = 22.5 Hz), 82.2, 71.5, 29.6, 28.1. **HRMS** (ESI^+): Calculated for $C_{22}H_{23}F_2NNaO_5S^+$ $[M+Na]^+$: 474.1157; Found: 474.1152.

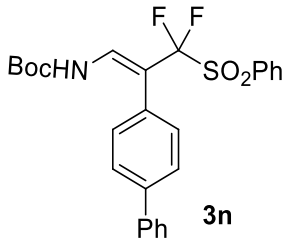
***tert*-Butyl (*E*)-(2-(benzo[*d*][1,3]dioxol-5-yl)-3,3-difluoro-3-(phenylsulfonyl)prop-1-en-1-yl)carbamate**



3m

White solid, 122 mg, 90% yield, mp 162–163 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.7 Hz, 2H), 7.71 (t, J = 7.4 Hz, 1H), 7.63 – 7.40 (m, 3H), 6.87 (s, 3H), 6.52 (d, J = 8.4 Hz, 1H), 6.00 (s, 2H), 1.46 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -96.41. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.4, 148.3, 148.2, 134.9, 133.6, 133.4 (t, J = 8.1 Hz), 130.7, 129.2 124.7, 123.3, 121.9 (t, J = 287.3 Hz), 111.1, 109.0, 105.4 (t, J = 22.2 Hz), 101.4, 82.4, 28.1. **HRMS** (ESI^+): Calculated for $C_{21}H_{21}F_2NNaO_6S^+$ $[M+Na]^+$: 476.0950; Found: 476.0945.

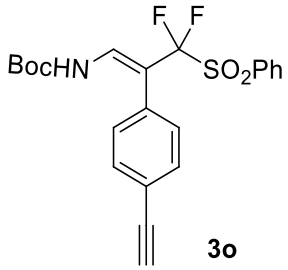
***tert*-Butyl (*E*)-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoro-3-(phenylsulfonyl)prop-1-en-1-yl)carbamate**



3n

White solid, 82 mg, 73% yield, mp 173–174 ºC. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.97 (d, J = 7.8 Hz, 2H), 7.73 – 7.65 (m, 3H), 7.63 (d, J = 7.4 Hz, 2H), 7.57 (t, J = 7.8 Hz, 3H), 7.47 (m, 4H), 7.38 (t, J = 7.4 Hz, 1H), 6.57 (d, J = 9.8 Hz, 1H), 1.46 (s, 9H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -96.20. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.5, 141.7, 140.3, 134.9, 133.6, 133.3, 131.3, 130.7, 129.2, 128.9, 127.9, 127.7, 127.1, 122.0 (t, J = 287.4 Hz), 105.5 (t, J = 21.5 Hz), 82.4, 28.1. **HRMS** (ESI^+): Calculated for $C_{26}H_{25}F_2NNaO_4S^+$ $[M+Na]^+$: 508.1365; Found: 508.1353.

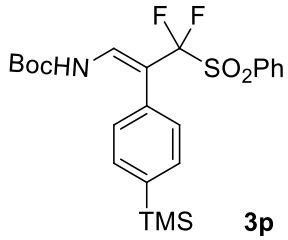
***tert*-Butyl (*E*)-(2-(4-ethynylphenyl)-3,3-difluoro-3-(phenylsulfonyl)prop-1-en-1-yl)carbamate**



3o

White solid, 87 mg, 67% yield, mp 142–143 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.7 Hz, 2H), 7.72 (t, J = 7.5 Hz, 1H), 7.57 (dt, J = 16.7, 7.0 Hz, 5H), 7.38 (d, J = 7.9 Hz, 2H), 6.44 (d, J = 9.4 Hz, 1H), 3.15 (s, 1H), 1.46 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -96.32. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.3, 135.0, 133.5, 133.4, 133.3, 132.9, 130.9, 130.7, 129.2, 122.9, 121.8 (t, J = 287.6 Hz), 105.0 (t, J = 22.1 Hz), 83.0, 82.6, 78.5, 28.1. **HRMS** (ESI^+): Calculated for $C_{20}H_{20}F_3NNaO_4S^+$ $[M+Na]^+$: 456.1052; Found: 456.1039.

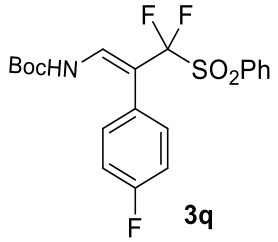
***tert*-Butyl (*E*)-(3,3-difluoro-3-(phenylsulfonyl)-2-(4-(trimethylsilyl)phenyl)prop-1-en-1-yl)carbamate**



3p

Yellow solid, 132 mg, 91% yield, mp 102–103 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.7 Hz, 2H), 7.70 (dd, J = 10.7, 4.3 Hz, 1H), 7.52 ~ 7.61 (m, 5H), 7.38 (d, J = 7.3 Hz, 2H), 6.54 (d, J = 7.8 Hz, 1H), 1.47 (s, 9H), 0.30 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -96.04. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.6, 142.6, 136.0, 135.3, 134.8, 134.3, 131.8, 131.1, 130.3, 123.1 (t, J = 287.6 Hz), 106.9 (t, J = 22.4 Hz), 83.6, 29.2, 0.00. **HRMS** (ESI^+): Calculated for $C_{23}H_{29}F_2NNaO_4SiS^+$ $[M+Na]^+$: 504.1447; Found: 504.1439.

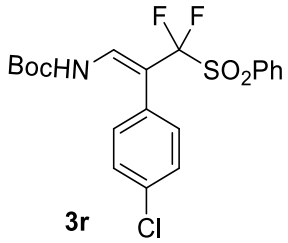
***tert*-Butyl (*E*)-(3,3-difluoro-2-(4-fluorophenyl)-3-(phenylsulfonyl)prop-1-en-1-yl)carbamate**



3q

White solid, 103 mg, 81% yield, mp 157–158 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.7 Hz, 2H), 7.75 (t, J = 7.3 Hz, 1H), 7.60 (m, 3H), 7.42 (m, 2H), 7.18 (t, J = 8.3 Hz, 2H), 6.43 (m, 1H), 1.50 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -96.46 (s), -112.01 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 (d, J = 249.2 Hz), 151.3, 135.0, 133.6, 133.5 (t, J = 8.6 Hz), 132.9 (d, J = 8.3 Hz), 130.7, 129.2, 126.1, 121.8 (t, J = 287.4 Hz), 116.4 (d, J = 21.6 Hz), 104.8 (t, J = 23.0 Hz), 82.6, 28.1. **HRMS** (ESI^+): Calculated for $C_{20}H_{20}F_3NNaO_4S^+$ $[M+Na]^+$: 450.0957; Found: 450.0947.

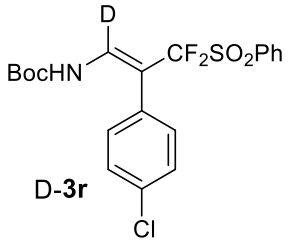
***tert*-Butyl (*E*)-(2-(4-chlorophenyl)-3,3-difluoro-3-(phenylsulfonyl)prop-1-en-1-yl)carbamate**



3r

White solid, 112 mg, 84% yield, mp 160–161 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.7 Hz, 2H), 7.76 – 7.69 (m, 1H), 7.57 (m, 3H), 7.44 (d, J = 8.5 Hz, 2H), 7.36 (d, J = 8.3 Hz, 2H), 6.42 (d, J = 9.4 Hz, 1H), 1.47 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -96.49. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.3, 135.2, 135.0, 133.6 (t, J = 9.4 Hz), 133.4, 132.3, 130.7, 129.6, 129.2, 128.7, 121.7 (t, J = 287.4 Hz), 104.5 (t, J = 22.8 Hz), 82.7, 28.1. **HRMS** (ESI^+): Calculated for $C_{20}H_{20}ClF_2NNaO_4S^+$ $[M+Na]^+$: 466.0662; Found: 466.0658.

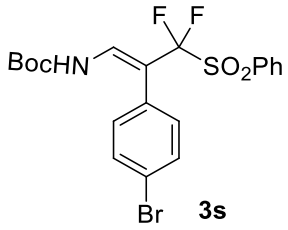
***tert*-Butyl (*E*)-(2-(4-chlorophenyl)-3,3-difluoro-3-(phenylsulfonyl)prop-1-en-1-yl-1-*d*)carbamate**



D-3r

White solid, 57 mg, 86% yield, mp 172–173 °C, D/H > 99:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.8 Hz, 2H), 7.72 (t, J = 7.4 Hz, 1H), 7.58 (t, J = 7.8 Hz, 2H), 7.40 (dd, J = 32.8, 8.2 Hz, 4H), 6.40 (s, 1H), 1.47 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -96.45. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.2, 135.2, 135.0, 133.4, 132.3, 130.7, 129.5, 129.2, 128.7 (t, J = 17.8 Hz), 128.6, 121.7 (t, J = 287.3 Hz), 104.5 (t, J = 23.9 Hz), 82.7, 28.0. **HRMS** (ESI^+): Calculated for $C_{20}H_{19}DClF_2NNaO_4S^+$ $[M+Na]^+$: 467.0725; Found: 467.0723.

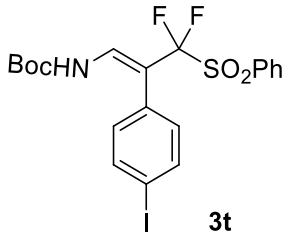
***tert*-Butyl (*E*)-(2-(4-bromophenyl)-3,3-difluoro-3-(phenylsulfonyl)prop-1-en-1-yl)carbamate**



3s

White solid, 120 mg, 82% yield, mp 161–162 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.7 Hz, 2H), 7.72 (t, J = 7.4 Hz, 1H), 7.66 – 7.48 (m, 5H), 7.30 (d, J = 8.0 Hz, 2H), 6.40 (s, 1H), 1.47 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -96.49. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.3, 135.0, 133.5 (t, J = 9.1 Hz), 133.4, 132.6, 132.5, 130.7, 129.2, 123.5, 121.7 (t, J = 287.0 Hz), 104.5 (t, J = 22.4 Hz), 82.7, 28.1. **HRMS** (ESI^+): Calculated for $C_{20}H_{20}BrF_2NNaO_4S^+$ $[M+Na]^+$: 510.0157; Found: 510.0160.

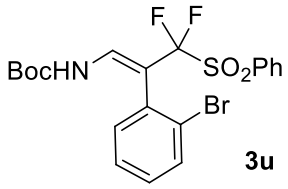
***tert*-Butyl (*E*)-(3,3-difluoro-2-(4-iodophenyl)-3-(phenylsulfonyl)prop-1-en-1-yl)carbamate**



3t

White solid, 126 mg, 78% yield, mp 168–169 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.8 Hz, 2H), 7.80 (d, J = 8.1 Hz, 2H), 7.72 (t, J = 7.4 Hz, 1H), 7.56 (m, 3H), 7.16 (d, J = 7.9 Hz, 2H), 6.44 (d, J = 8.7 Hz, 1H), 1.47 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -96.47. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.3, 138.5, 137.4, 135.0, 133.5 (t, J = 9.3 Hz), 133.4, 132.7, 130.7, 129.8, 129.2, 121.7 (t, J = 287.4 Hz), 104.6 (t, J = 23.5 Hz), 95.4, 82.7, 28.1. **HRMS** (ESI^+): Calculated for $C_{20}H_{20}IF_2NNaO_4S^+$ $[M+Na]^+$: 558.0018; Found: 558.0020.

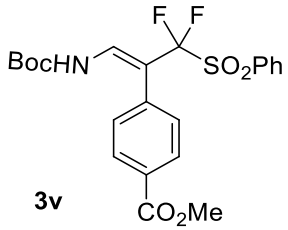
***tert*-butyl (*E*)-(2-(2-bromophenyl)-3,3-difluoro-3-(phenylsulfonyl)prop-1-en-1-yl)carbamate**



3u

This compound was prepared from diazo-Mannich adduct (±)-**4r** under identical reaction conditions (0.15 mmol of substrate, (±)-**BPA** (20 mol %), Na_2SO_4 (150 mg), CH_2Cl_2 (3 mL), 45 ºC for 12 hours); White solid, 60 mg, 61% yield, mp 75–76 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.8 Hz, 2H), 7.71 (t, *J* = 8.2 Hz, 2H), 7.63 – 7.56 (m, 4H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.32 – 7.28 (m, 1H), 6.18 (d, *J* = 9.4 Hz, 1H), 1.47 (s, 9H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -90.86 (d, *J* = 225.6 Hz), -100.86 (d, *J* = 226.3 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.3, 135.1, 134.5 (t, *J* = 8.5 Hz), 133.9, 133.9, 133.7, 133.5, 131.1, 130.9, 129.3, 128.2, 126.4, 121.6 (dd, *J* = 292.1, 284.3 Hz), 104.8 (dd, *J* = 27.5, 21.3 Hz), 82.8, 28.2. **HRMS** (ESI^+): Calculated for $C_{20}H_{20}BrF_2NNaO_4S^+$ $[M+Na]^+$: 510.0157; Found: 510.0160.

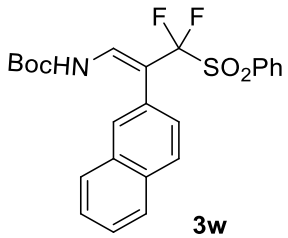
Methyl (*E*)-4-(1-((*tert*-butoxycarbonyl)amino)-3,3-difluoro-3-(phenylsulfonyl) prop-1-en-2-yl)benzoate



3v

White solid, 95 mg, 68% yield, mp 122–123 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.11 (d, *J* = 8.0 Hz, 2H), 7.94 (d, *J* = 7.7 Hz, 2H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.65 – 7.40 (m, 5H), 6.48 (d, *J* = 7.4 Hz, 1H), 3.93 (s, 3H), 1.45 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) *δ* -96.26. **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 166.5, 151.2, 135.1, 135.0, 133.6 (t, *J* = 9.3 Hz), 133.4, 131.0, 130.7, 130.6, 130.4, 129.2, 121.7 (t, *J* = 287.7 Hz), 104.8 (t, *J* = 22.9 Hz), 82.7, 52.3, 28.0. **HRMS** (ESI^+): Calculated for $C_{22}H_{23}F_3NNaO_6S^+$ $[M+Na]^+$: 490.1106; Found: 490.1122.

***tert*-Butyl (*E*)-(3,3-difluoro-2-(naphthalen-2-yl)-3-(phenylsulfonyl)prop-1-en-1-yl) carbamate**

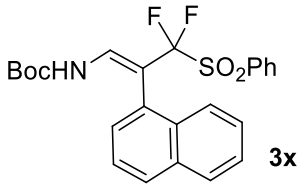


3w

White solid, 92 mg, 68% yield, mp 125–126 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.96 ~ 7.87(m, 6H), 7.68(t, *J* =7.49Hz, 1H), 7.63(br, 1H), 7.56~7.49(m, 5H), 6.51(br, 1H),

1.43(s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -96.03. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.5, 134.9, 133.6, 133.5, 133.4, 133.2, 130.7, 130.6, 129.2, 129.0, 128.3, 128.0, 127.8, 127.0, 126.6, 122.0 (t, J = 287.3 Hz), 105.8 (t, J = 22.89 Hz), 82.4, 28.1. **HRMS** (ESI^+): Calculated for $C_{24}H_{23}F_2NNaO_4S^+$ $[M+Na]^+$: 482.1208; Found: 482.1204.

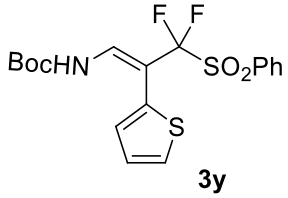
***tert*-butyl (*E*)-(3,3-difluoro-2-(naphthalen-1-yl)-3-(phenylsulfonyl)prop-1-en-1-yl)carbamate**



3x

This compound was prepared from diazo-Mannich adduct (±)-**4u** under identical reaction conditions (0.15 mmol of substrate, (±)-**BPA** (20 mol %), Na_2SO_4 (150 mg), CH_2Cl_2 (3 mL), 45 ºC for 12 hours); White solid, 70 mg, 76% yield, mp 92–93 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 – 7.77 (m, 6H), 7.68 (t, J = 6.9 Hz, 2H), 7.62 – 7.49 (m, 5H), 6.18 (d, J = 8.8 Hz, 1H), 1.41 (s, 9H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -91.79 (d, J = 223.8 Hz), -98.43 (d, J = 223.9 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.5, 135.0, 134.7 – 134.5 (m), 134.1, 133.8, 132.3, 130.8, 130.3, 130.0, 129.2, 128.7, 127.4, 127.1, 126.5, 125.9, 125.5, 122.2 (dd, J = 289.4, 285.1 Hz), 103.6 (dd, J = 25.7, 21.1 Hz), 82.6, 28.1. **HRMS** (ESI^+): Calculated for $C_{24}H_{23}F_2NNaO_4S^+$ $[M+Na]^+$: 482.1208; Found: 482.1213.

***tert*-Butyl (*E*)-(3,3-difluoro-3-(phenylsulfonyl)-2-(thiophen-2-yl)prop-1-en-1-yl) carbamate**

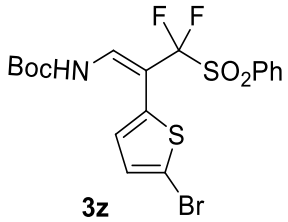


3y

White solid, 114 mg, 92% yield, mp 161–162 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.7 Hz, 2H), 7.71 (t, J = 7.3 Hz, 1H), 7.57 (t, J = 7.5 Hz, 3H), 7.45 (d, J = 4.9 Hz, 1H), 7.20 – 7.07 (m, 2H), 6.90 (d, J = 3.4 Hz, 1H), 1.48 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -97.13. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.2, 135.2 (t, J = 8.5 Hz), 135.0, 133.5, 130.7, 130.2, 129.2, 128.2, 127.7, 121.4 (t, J = 287.9 Hz), 98.4 (t, J = 23.7 Hz), 82.8, 28.1. **HRMS** (ESI^+): Calculated for $C_{18}H_{19}F_2NNaO_4S_2^+$ $[M+Na]^+$: 438.0616;

Found: 438.0609.

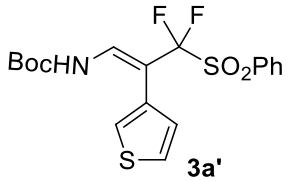
***tert*-Butyl (*E*)-(2-(5-bromothiophen-2-yl)-3,3-difluoro-3-(phenylsulfonyl)prop-1-en-1-yl)carbamate**



3z

White solid, 136 mg, 92% yield, mp 137–138 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.7 Hz, 2H), 7.73 (t, J = 7.3 Hz, 1H), 7.59 (t, J = 7.6 Hz, 3H), 7.08 (d, J = 3.4 Hz, 1H), 6.99 – 6.74 (m, 2H), 1.49 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -97.31. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.1, 136.0 (t, J = 8.3 Hz), 135.1, 133.2, 131.8, 130.9, 130.7, 130.6, 129.3, 121.0 (t, J = 287.9 Hz), 114.9, 97.6 (t, J = 23.3 Hz), 83.1, 28.0. **HRMS** (ESI^+): Calculated for $C_{18}H_{18}BrF_2NNaO_4S_2^+$ $[M+Na]^+$: 515.9721; Found: 515.9722.

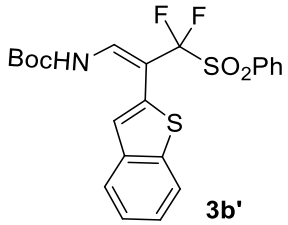
***tert*-Butyl (*E*)-(3,3-difluoro-3-(phenylsulfonyl)-2-(thiophen-3-yl)prop-1-en-1-yl)carbamate**



3a'

White solid, 117 mg, 94% yield, mp 164–165 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.7 Hz, 2H), 7.71 (t, J = 7.4 Hz, 1H), 7.57 (t, J = 7.7 Hz, 2H), 7.46 (dd, J = 24.4, 6.5 Hz, 3H), 7.15 (s, 1H), 6.69 (d, J = 7.5 Hz, 1H), 1.48 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -97.03. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.4, 134.9, 133.5, 133.5 (d, J = 9.8 Hz), 130.6, 129.9, 129.2, 128.9, 126.8, 126.5, 121.8 (t, J = 287.4 Hz), 100.9 (t, J = 22.9 Hz), 82.5, 28.1. **HRMS** (ESI^+): Calculated for $C_{18}H_{19}F_2NNaO_4S_2^+$ $[M+Na]^+$: 438.0616; Found: 438.0621.

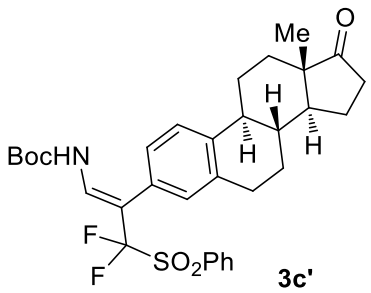
***tert*-Butyl (*E*)-(2-(benzo[*b*]thiophen-2-yl)-3,3-difluoro-3-(phenylsulfonyl)prop-1-en-1-yl)carbamate**



3b'

White solid, 132 mg, 95% yield, mp 154–155 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.7 Hz, 2H), 7.84 (t, J = 8.6 Hz, 2H), 7.75 – 7.53 (m, 4H), 7.46 – 7.34 (m, 3H), 7.05 (d, J = 9.1 Hz, 1H), 1.48 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -96.92. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.2, 140.9, 139.6, 135.8 (t, J = 8.9 Hz), 135.1, 133.3, 130.7, 129.2, 127.3, 125.1, 124.7, 124.2, 122.3, 121.4 (t, J = 288.2 Hz), 98.4 (t, J = 24.4 Hz), 82.9, 28.1. **HRMS** (ESI^+): Calculated for $C_{22}H_{21}F_2NNaO_4S_2^+$ $[M+Na]^+$: 488.0772; Found: 488.0763.

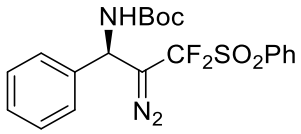
***tert*-Butyl ((*E*)-3,3-difluoro-2-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14, 15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)-3-(phenylsulfonyl)prop-1-en-1-yl)carbamate**



3c'

White solid, 78 mg, 89%, m.p.= 127-128 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.7 Hz, 2H), 7.71 (t, J = 7.4 Hz, 1H), 7.57 (t, J = 7.7 Hz, 2H), 7.51 (d, J = 10.1 Hz, 1H), 7.36 (d, J = 7.8 Hz, 1H), 7.21 – 7.05 (m, 2H), 6.53 (d, J = 10.2 Hz, 1H), 2.95 (d, J = 4.7 Hz, 2H), 2.59 – 2.39 (m, 2H), 2.34 (t, J = 7.9 Hz, 1H), 2.23 – 1.97 (m, 4H), 1.71 – 1.42 (m, 15H), 0.94 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -96.21 (s). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.5, 140.6, 137.5, 134.9, 133.7, 133.0, 131.2, 130.69, 129.1, 128.1, 126.2, 122.0 (t, J = 285 Hz), 105.7 (t, J = 22.3 Hz), 82.3, 50.5, 48.0, 44.5, 37.9, 35.9, 31.6, 29.3, 28.1, 26.4, 25.6, 21.6, 13.9. **HRMS** (ESI^+): Calculated for $C_{32}H_{37}F_2NNaO_5S^+$ $[M+Na]^+$: 608.2253; Found: 608.2261.

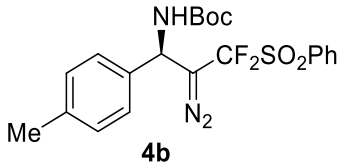
***tert*-Butyl (*R*)-(2-diazo-3,3-difluoro-1-phenyl-3-(phenylsulfonyl)propyl)carbama--te**



4a

Yellow oil, 86 mg, 98% yield, 94% ee. 1.25 g, 95% yield, 94% ee (To a 50 mL Schlenk flask equipped with a stirring bar was added *N*-Boc imines **2a** (1.23 g, 6 mmol, 2.0 equiv.), chiral phosphoric acid (*S*)-**TRIP** (225 mg, 0.3 mmol, 10 mol %), TEMPO (1.4 g, 9 mmol, 3.0 equiv.), anhydrous sodium sulfate (4.0 g), and CH_2Cl_2 (20 mL). The difluorodiazo compound **1** (696 mg, 3 mmol, 1.0 equiv.) was added at 0 °C. The reaction was stirred at 0 °C until the completion of the reaction (monitored by TLC). Then, the reaction mixture was concentrated under vacuum to yield the crude expected product **4a**, which was subjected to column chromatography on silica gel (eluent: petrol ether / ethyl acetate = 9:1) to give the pure product. HPLC (DAICEL Chiralpak IC, hexane/IPA= 85:15, 0.6 mL/min, 254 nm): t_R(major) = 11.66 min, t_R(minor) = 16.22 min, $[\alpha]_D^{20}$ +74 (c 1.0 CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.7 Hz, 2H), 7.76 (t, J = 7.4 Hz, 1H), 7.62 (t, J = 7.7 Hz, 2H), 7.47 – 7.36 (m, 4H), 7.31 (t, J = 6.8 Hz, 1H), 5.76 (s, 1H), 5.45 (d, J = 6.7 Hz, 1H), 1.45 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.33 (d, J = 231.4 Hz), -99.27 (d, J = 231.8 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.7, 137.4, 135.5, 132.7, 130.7, 129.5, 129.0, 128.3, 126.3, 122.0 (t, J = 292.1 Hz), 80.4, 53.7 (t, J = 34.1 Hz), 50.8, 28.3. **HRMS** (ESI^+): Calculated for $C_{20}H_{21}F_2N_3NaO_4S^+$ $[M+Na]^+$: 460.1113; Found: 460.1120.

***tert*-Butyl (*R*)-(2-diazo-3,3-difluoro-3-(phenylsulfonyl)-1-(*p*-tolyl)propyl)carbam-ate**

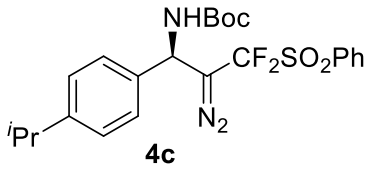


4b

Yellow oil, 85 mg, 94% yield, 94% ee. HPLC (DAICEL Chiralpak OJ-H, hexane/IPA= 85:15, 0.8 mL/min, 254 nm): t_R(major) = 12.14 min, t_R(minor) = 19.38 min, $[\alpha]_D^{20}$ +72 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.8 Hz, 2H), 7.67 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 7.8 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H),

5.64 (d, *J* = 5.6 Hz, 1H), 5.37 (d, *J* = 7.5 Hz, 1H), 2.25 (s, 3H), 1.36 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.36 (d, *J* = 231.4 Hz), -99.19 (d, *J* = 233.7 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.7, 138.0, 135.5, 134.4, 132.8, 130.6, 129.7, 129.5, 126.2, 122.0 (t, *J* = 291.8 Hz), 80.3, 53.7 (t, *J* = 34.5 Hz), 50.6, 28.3, 21.1. **HRMS** (ESI^+): Calculated for $C_{21}H_{23}F_2N_3NaO_4S^+$ $[M+Na]^+$: 474.1270; Found: 474.1258.

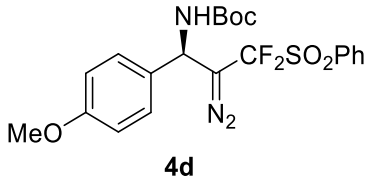
***tert*-Butyl (*R*)-(2-diazo-3,3-difluoro-1-(4-isopropylphenyl)-3-(phenylsulfonyl) propyl)carbamate**



4c

Yellow oil, 88 mg, 92% yield, 88% ee. HPLC (DAICEL Chiralpak IA, hexane/IPA= 85:15, 0.6 mL/min, 254 nm): t_R(major) = 16.75 min, t_R(minor) = 19.39 min, $[\alpha]_D^{20}$ +64 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 2H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 5.73 (d, *J* = 4.8 Hz, 1H), 5.45 (d, *J* = 6.8 Hz, 1H), 2.90 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.44 (s, 9H), 1.23 (d, *J* = 6.9 Hz, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.33 (d, *J* = 231.3 Hz), -99.26 (d, *J* = 232.5 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.7, 148.9, 135.5, 134.7, 132.8, 130.6, 129.5, 127.1, 126.3, 122.0 (t, *J* = 291.8 Hz), 80.3, 53.7 (t, *J* = 33.9 Hz), 50.7, 33.8, 28.3, 23.9. **HRMS** (ESI^+): Calculated for $C_{23}H_{27}F_2N_3NaO_4S^+$ $[M+Na]^+$: 502.1583; Found: 502.1602.

***tert*-Butyl (*R*)-(2-diazo-3,3-difluoro-1-(4-methoxyphenyl)-3-(phenylsulfonyl) propyl)carbamate**

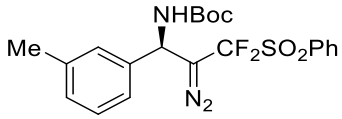


4d

Yellow oil, 86 mg, 92% yield, 90% ee. HPLC (DAICEL Chiralpak AD-H, hexane/IPA= 85:15, 0.6 mL/min, 254 nm): t_R(major) = 32.02 min, t_R(minor) = 37.60 min, $[\alpha]_D^{20}$ +61 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 2H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 6.91 (d,

J = 8.7 Hz, 2H), 5.71 (d, *J* = 6.3 Hz, 1H), 5.41 (d, *J* = 7.3 Hz, 1H), 3.79 (s, 3H), 1.44 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.42 (d, *J* = 231.5 Hz), -99.19 (d, *J* = 234.6 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.4, 154.7, 135.5, 132.8, 130.6, 129.5, 129.4, 127.6, 122.0 (t, *J* = 291.9 Hz), 114.4, 80.4, 55.3, 53.7 (t, *J* = 34.2 Hz), 50.3, 28.3. **HRMS** (ESI^+): Calculated for $C_{21}H_{23}F_2N_3NaO_5S^+$ $[M+Na]^+$: 490.1219; Found: 490.1216.

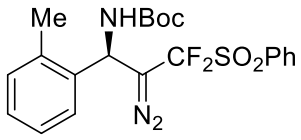
***tert*-Butyl (*R*)-(2-diazo-3,3-difluoro-3-(phenylsulfonyl)-1-(m-tolyl)propyl) carbamate**



4e

Yellow oil, 89 mg, 98% yield, 94% ee. HPLC (DAICEL Chiralpak AD-H, hexane/IPA= 85:15, 0.6 mL/min, 254 nm): t_R(major) = 21.48 min, t_R(minor) = 19.63 min, $[\alpha]_D^{20}$ +66 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 2H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 2H), 7.29 – 7.24 (m, 1H), 7.22 (s, 2H), 7.12 (d, *J* = 7.3 Hz, 1H), 5.72 (d, *J* = 5.3 Hz, 1H), 5.43 (d, *J* = 7.4 Hz, 1H), 2.36 (s, 3H), 1.45 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.39 (d, *J* = 231.5 Hz), -99.11 (d, *J* = 232.5 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.7, 138.7, 137.2, 135.5, 132.8, 130.6, 129.5, 129.1, 128.9, 127.0, 123.4, 122.0 (t, *J* = 291.8 Hz), 80.4, 53.6 (t, *J* = 34.6 Hz), 50.8, 28.3, 21.5. **HRMS** (ESI^+): Calculated for $C_{21}H_{23}F_2N_3NaO_4S^+$ $[M+Na]^+$: 474.1270; Found: 474.1267.

***tert*-Butyl (*R*)-(2-diazo-3,3-difluoro-3-(phenylsulfonyl)-1-(*o*-tolyl)propyl) carbamate**

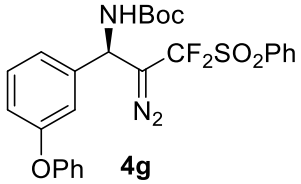


4f

Yellow oil, 70 mg, 76% yield, 87% ee. HPLC (DAICEL Chiralpak AD-H, hexane/IPA= 80:20, 0.6 mL/min, 254 nm): t_R(major) = 14.76 min, t_R(minor) = 17.37 min, $[\alpha]_D^{20}$ +80 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.8 Hz, 2H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.62 (t, *J* = 7.8 Hz, 2H), 7.42 – 7.34 (m, 1H), 7.24 –7.21 (m, 3H), 5.91 (d, *J* = 5.2 Hz, 1H), 5.49 (s, 1H), 2.43 (s, 3H), 1.44 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -

97.55 (d, J = 233.1 Hz), -99.23 (d, J = 233.0 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.6, 135.5, 135.3, 132.7, 131.1, 130.7, 129.5, 128.4, 126.5, 125.7, 122.0 (t, J = 291.5 Hz), 80.3, 52.6 (t, J = 34.6 Hz), 47.7, 28.3, 18.9. **HRMS** (ESI^+): Calculated for $C_{21}H_{23}F_2N_3NaO_4S^+$ $[M+Na]^+$: 474.1270; Found: 474.1266.

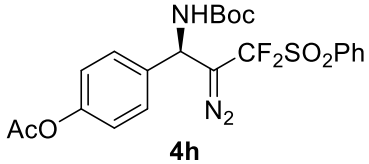
tert-Butyl (_R_)-(2-diazo-3,3-difluoro-1-(3-phenoxyphenyl)-3-(phenylsulfonyl) propyl)carbamate



4g

Yellow oil, 105 mg, 96% yield, 98% ee. HPLC (DAICEL Chiralpak IA, hexane/IPA= 90:10, 0.6 mL/min, 254 nm): t_R(major) = 26.15 min, t_R(minor) = 18.98 min, $[\alpha]_D^{20}$ +72 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.8 Hz, 2H), 7.76 (t, J = 7.5 Hz, 1H), 7.61 (t, J = 7.8 Hz, 2H), 7.36 (dt, J = 13.8, 7.0 Hz, 3H), 7.20 (d, J = 7.7 Hz, 1H), 7.16 – 7.07 (m, 2H), 7.01 (d, J = 7.8 Hz, 2H), 6.95 (d, J = 8.0 Hz, 1H), 5.74 (s, 1H), 5.48 (s, 1H), 1.45 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.45 (d, J = 231.6 Hz), -99.40 (d, J = 232.5 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8, 156.9, 154.7, 139.6, 135.5, 132.7, 130.6, 130.5, 129.9, 129.5, 123.5, 121.9 (t, J = 292.1 Hz), 121.2, 119.0, 118.5, 116.8, 80.5, 53.6 (t, J = 37.6 Hz), 50.7, 28.3. **HRMS** (ESI^+): Calculated for $C_{26}H_{25}F_2N_3NaO_5S^+$ $[M+Na]^+$: 552.1375; Found: 552.1376.

(_R_)-4-(1-((_tert_-Butoxycarbonyl)amino)-2-diazo-3,3-difluoro-3-(phenylsulfonyl) propyl)phenyl acetate

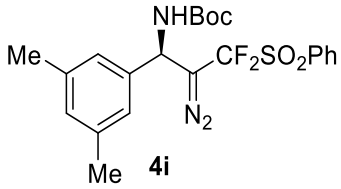


4h

Yellow oil, 94 mg, 95% yield, 96% ee. HPLC (DAICEL Chiralpak IA, hexane/IPA= 85:15, 0.6 mL/min, 254 nm): t_R(major) = 24.49 min, t_R(minor) = 27.18 min, $[\alpha]_D^{20}$ +60 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.8 Hz, 2H), 7.76 (t, J = 7.5 Hz, 1H), 7.61 (t, J = 7.8 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H), 7.13 (d, J = 8.5 Hz, 2H), 5.74 (d, J = 6.5 Hz, 1H), 5.46 (d, J = 7.3 Hz, 1H), 2.29 (s, 3H), 1.44 (s, 9H). **^{19}F NMR**

(376 MHz, $CDCl_3$) δ -98.36 (d, J = 231.7 Hz), -99.42 (d, J = 231.8 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.2, 154.6, 150.5, 135.5, 135.0, 132.7, 130.6, 129.5, 127.5, 122.1, 121.9 (t, J = 291.9 Hz), 80.6, 53.6 (t, J = 34.1 Hz), 50.5, 28.3, 21.1. **HRMS** (ESI^+): Calculated for $C_{22}H_{23}F_2N_3NaO_6S^+$ $[M+Na]^+$: 518.1168; Found: 518.1149.

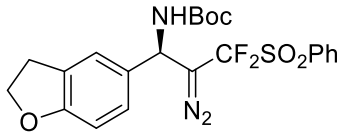
***tert*-Butyl (*R*)-(2-diazo-1-(3,5-dimethylphenyl)-3,3-difluoro-3-(phenylsulfonyl) propyl)carbamate**



4i

Yellow oil, 93 mg, 90% yield, 81% ee. HPLC (DAICEL Chiralpak AD-H, hexane/IPA= 90:10, 0.6 mL/min, 254 nm): t_R(major) = 23.88 min, t_R(minor) = 20.99 min, $[\alpha]_D^{20}$ +88 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.8 Hz, 2H), 7.77 (d, J = 7.5 Hz, 1H), 7.64 (t, J = 7.8 Hz, 2H), 7.03 (s, 2H), 6.96 (s, 1H), 5.71 (d, J = 6.3 Hz, 1H), 5.42 (d, J = 7.1 Hz, 1H), 2.34 (s, 6H), 1.48 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.64 (s). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.7, 138.6, 137.3, 135.4, 132.9, 130.6, 130.0, 129.5, 124.1, 122.0 (t, J = 291.8 Hz), 80.3, 53.6 (t, J = 34.3 Hz), 50.7, 28.3, 21.4. **HRMS** (ESI^+): Calculated for $C_{22}H_{25}F_2N_3NaO_4S^+$ $[M+Na]^+$:488.1426; Found: 488.1424.

***tert*-Butyl (*R*)-(2-diazo-1-(2,3-dihydrobenzofuran-5-yl)-3,3-difluoro-3-(phenylsulfonyl)propyl)carbamate**

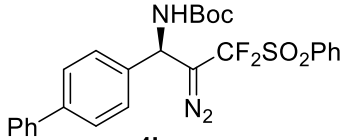


4j

Yellow oil, 87 mg, 91% yield, 93% ee. HPLC (DAICEL Chiralpak IA, hexane/IPA= 92:8, 0.8 mL/min, 254 nm): t_R(major) = 39.22 min, t_R(minor) = 43.57 min, $[\alpha]_D^{20}$ +88 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.7 Hz, 2H), 7.76 (t, J = 7.5 Hz, 1H), 7.61 (t, J = 7.8 Hz, 2H), 7.25 (s, 1H), 7.14 (dd, J = 8.3, 1.2 Hz, 1H), 6.77 (d, J = 8.3 Hz, 1H), 5.69 (d, J = 7.1 Hz, 1H), 5.39 (d, J = 7.0 Hz, 1H), 4.57 (t, J = 8.7 Hz, 2H), 3.20 (t, J = 8.7 Hz, 2H), 1.44 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.42 (d, J = 231.6 Hz), -99.12 (d, J = 233.9 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.1, 154.6, 135.5, 132.8, 130.6, 129.5, 129.4, 127.9, 126.2, 123.2, 122.0 (t, J = 291.9 Hz), 109.5,

80.3, 77.4, 77.1, 76.7, 71.5, 53.8 (t, J = 34.0 Hz), 50.5. **HRMS** (ESI^+): Calculated for $C_{22}H_{23}F_2N_3NaO_5S^+$ $[M+Na]^+$: 502.1219; Found: 502.1208.

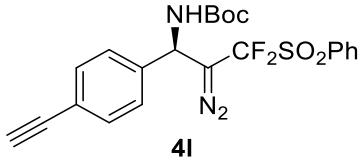
***tert*-Butyl (*R*)-(1-([1,1'-biphenyl]-4-yl)-2-diazo-3,3-difluoro-3-(phenylsulfonyl) propyl)carbamate**



4k

Yellow oil, 100 mg, 98% yield, 96% ee. HPLC (DAICEL Chiralpak IA, hexane/IPA= 80:20, 0.6 mL/min, 254 nm): t_R(major) = 23.15 min, t_R(minor) = 30.91 min, $[\alpha]_D^{20}$ +32 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.7 Hz, 2H), 7.77 (t, J = 7.5 Hz, 1H), 7.68 – 7.57 (m, 6H), 7.51 (d, J = 8.2 Hz, 2H), 7.45 (t, J = 7.5 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 5.82 (d, J = 6.3 Hz, 1H), 5.48 (d, J = 7.3 Hz, 1H), 1.48 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.34 (d, J = 231.3 Hz), -99.24 (d, J = 234.3 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.8, 141.2, 140.4, 136.4, 135.5, 132.7, 130.7, 129.5, 128.8, 127.8, 127.5, 127.1, 126.8, 122.0 (t, J = 292.0 Hz), 80.5, 53.6 (t, J = 33.8 Hz), 50.7, 28.3. **HRMS** (ESI^+): Calculated for $C_{26}H_{25}F_2N_3NaO_4S^+$ $[M+Na]^+$: 536.1426; Found: 536.1432.

***tert*-Butyl (*R*)-(2-diazo-1-(4-ethynylphenyl)-3,3-difluoro-3-(phenylsulfonyl)propyl) carbamate**

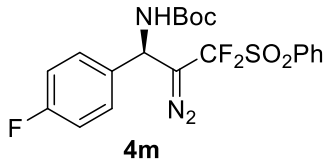


4l

Yellow oil, 92 mg, 98% yield, 97% ee. HPLC (DAICEL Chiralpak IC, hexane/IPA= 85:15, 0.6 mL/min, 254 nm): t_R(major) = 11.78 min, t_R(minor) = 14.52 min, $[\alpha]_D^{20}$ +70 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.7 Hz, 2H), 7.76 (t, J = 7.5 Hz, 1H), 7.61 (t, J = 7.8 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 5.74 (s, 1H), 5.56 (s, 1H), 3.10 (s, 1H), 1.43 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.42 (d, J = 231.3 Hz), -99.46 (d, J = 231.9 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.7, 138.2, 135.6, 132.8, 132.6, 130.6, 129.5, 126.4, 124.8, 122.1, 121.8 (t, J = 292.1 Hz),

83.1, 80.6, 77.9, 54.5 (t, *J* = 35.5 Hz), 50.8, 28.3. **HRMS** (ESI^+): Calculated for $C_{22}H_{21}F_2N_3NaO_4S^+$ $[M+Na]^+$: 484.1113; Found: 484.1115.

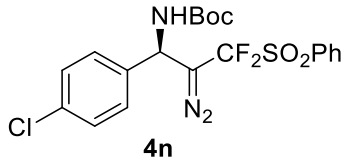
***tert*-Butyl (*R*)-(2-diazo-3,3-difluoro-1-(4-fluorophenyl)-3-(phenylsulfonyl) propyl)carbamate**



4m

Yellow oil, 78 mg, 86% yield, 97% ee. HPLC (DAICEL Chiralpak IC, hexane/IPA= 85:15, 0.6 mL/min, 254 nm): t_R(major) = 10.16 min, t_R(minor) = 13.23 min, $[\alpha]_D^{20}$ +96 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 2H), 7.77 (t, *J* = 7.5 Hz, 1H), 7.62 (t, *J* = 7.8 Hz, 2H), 7.42 (dd, *J* = 8.2, 5.3 Hz, 2H), 7.08 (t, *J* = 8.5 Hz, 2H), 5.73 (d, *J* = 5.1 Hz, 1H), 5.47 (d, *J* = 6.5 Hz, 1H), 1.44 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.48 (d, *J* = 231.5 Hz), -99.40 (d, *J* = 231.8 Hz), -113.82 (s). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.5 (d, *J* = 247.1 Hz), 154.7, 135.6, 133.2, 132.6, 130.7, 129.5, 128.2 (d, *J* = 8.3 Hz), 121.9 (t, *J* = 292.0 Hz), 116.0 (d, *J* = 21.8 Hz), 80.6, 53.6 (t, *J* = 34.5 Hz), 50.4, 28.3. **HRMS** (ESI^+): Calculated for $C_{20}H_{20}F_3N_3NaO_4S^+$ $[M+Na]^+$: 478.1019; Found: 478.1004.

***tert*-Butyl (*R*)-(1-(4-chlorophenyl)-2-diazo-3,3-difluoro-3-(phenylsulfonyl) propyl)carbamate**

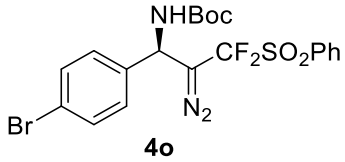


4n

Yellow oil, 94 mg, 98% yield, 98% ee. HPLC (DAICEL Chiralpak IC, hexane/IPA= 85:15, 0.6 mL/min, 254 nm): t_R(major) = 10.34 min, t_R(minor) = 12.96 min, $[\alpha]_D^{20}$ +36 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.80 (t, *J* = 7.5 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 2H), 7.44 – 7.35 (m, 4H), 5.74 (d, *J* = 6.3 Hz, 1H), 5.52 (d, *J* = 5.2 Hz, 1H), 1.47 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.42 (d, *J* = 231.4 Hz), -99.41 (d, *J* = 230.9 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.7, 136.0, 135.6, 134.1, 132.6, 130.6, 129.5, 129.2, 127.8, 121.9 (t, *J* = 292.0 Hz), 80.7, 51.5 (t, *J* = 36.0

Hz), 50.5, 28.3. **HRMS** (ESI^+): Calculated for $C_{20}H_{20}ClF_2N_3NaO_4S^+$ $[M+Na]^+$: 494.0723; Found: 494.0741.

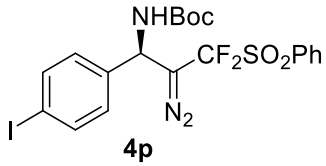
***tert*-Butyl (*R*)-(1-(4-bromophenyl)-2-diazo-3,3-difluoro-3-(phenylsulfonyl) propyl)carbamate**



4o

Yellow oil, 101 mg, 98% yield, 98% ee. HPLC (DAICEL Chiralpak IC, hexane/IPA= 85:15, 0.6 mL/min, 254 nm): t_R(major) = 10.70 min, t_R(minor) = 13.33 min, $[\alpha]_D^{20}$ +70 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.7 Hz, 2H), 7.68 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.8 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 5.61 (s, 1H), 5.48 (s, 1H), 1.36 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.46 (d, J = 231.5 Hz), -99.50 (d, J = 232.1 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.7, 136.6, 135.6, 132.5, 132.2, 130.6, 129.6, 128.1, 122.3, 121.8 (t, J = 292.0 Hz), 80.7, 53.4 (t, J = 33.0 Hz), 50.5, 28.3. **HRMS** (ESI^+): Calculated for $C_{20}H_{20}BrF_2N_3NaO_4S^+$ $[M+Na]^+$: 538.0218; Found: 538.0223.

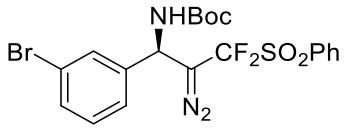
***tert*-Butyl (*R*)-(2-diazo-3,3-difluoro-1-(4-iodophenyl)-3-(phenylsulfonyl)propyl) carbamate**



4p

Yellow oil, 109 mg, 97% yield, 97% ee. HPLC (DAICEL Chiralpak OD-H, hexane/IPA= 85:15, 0.6 mL/min, 254 nm): t_R(major) = 13.77 min, t_R(minor) = 11.57 min, $[\alpha]_D^{20}$ +64 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.8 Hz, 2H), 7.77 (t, J = 7.5 Hz, 1H), 7.72 (d, J = 8.3 Hz, 2H), 7.62 (t, J = 7.8 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), 5.67 (s, 1H), 5.52 (s, 1H), 1.44 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.43 (d, J = 232.7 Hz), -99.46 (d, J = 236.5 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.7, 138.1, 137.3, 135.6, 132.6, 130.6, 129.5, 128.3, 121.8 (t, J = 292.2 Hz), 94.0, 80.7, 53.4 (t, J = 33.7 Hz), 50.7, 28.3. **HRMS** (ESI^+): Calculated for $C_{20}H_{20}IF_2N_3NaO_4S^+$ $[M+Na]^+$: 586.0079; Found: 586.0073.

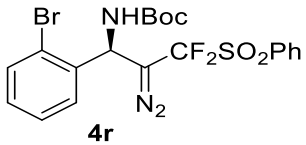
***tert*-Butyl (*R*)-(1-(3-bromophenyl)-2-diazo-3,3-difluoro-3-(phenylsulfonyl) propyl)carbamate**



4q

Yellow oil, 102 mg, 98% yield, 97% ee. HPLC (DAICEL Chiralpak IC, hexane/IPA= 85:15, 0.6 mL/min, 254 nm): t_R(major) = 10.47 min, t_R(minor) = 13.15 min, $[\alpha]_D^{20}$ +60 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 2H), 7.77 (t, *J* = 7.5 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 2H), 7.57 (s, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 1H), 5.71 (s, 1H), 5.56 (s, 1H), 1.45 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.45 (d, *J* = 231.7 Hz), -99.47 (d, *J* = 232.3 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.7, 139.8, 135.6, 132.5, 131.5, 130.6, 130.6, 129.6, 129.4, 125.2, 123.1, 121.8 (t, *J* = 292.1 Hz), 80.7, 53.5 (t, *J* = 34.8 Hz), 50.5, 28.3. **HRMS** (ESI^+): Calculated for $C_{20}H_{20}BrF_2N_3NaO_4S^+$ $[M+Na]^+$: 538.0218; Found: 538.0234.

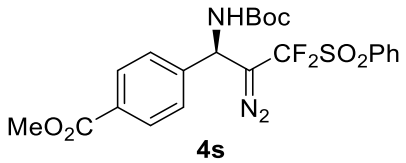
***tert*-Butyl (*R*)-(1-(2-bromophenyl)-2-diazo-3,3-difluoro-3-(phenylsulfonyl)propyl) carbamate**



4r

Yellow oil, 86 mg, 89% yield, 89% ee. HPLC (DAICEL Chiralpak IA, hexane/IPA= 85:15, 0.6 mL/min, 254 nm): t_R(major) = 20.96 min, t_R(minor) = 26.16 min, $[\alpha]_D^{20}$ +28 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.7 Hz, 2H), 7.76 (dd, *J* = 10.7, 4.3 Hz, 1H), 7.65 – 7.54 (m, 3H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.35 (td, *J* = 7.7, 1.0 Hz, 1H), 7.18 (td, *J* = 7.8, 1.5 Hz, 1H), 5.97 (d, *J* = 5.9 Hz, 1H), 5.80 (s, 1H), 1.45 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -97.46 (d, *J* = 233.7 Hz), 100.61 (d, *J* = 233.6 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.6, 136.7, 135.6, 133.5, 132.4, 130.7, 129.9, 129.5, 128.0, 127.9, 122.7, 122.0 (t, *J* = 291.0 Hz), 80.5, 52.5 (t, *J* = 33.6 Hz), 51.1, 28.3. **HRMS** (ESI^+): Calculated for $C_{20}H_{20}BrF_2N_3NaO_4S^+$ $[M+Na]^+$: 538.0218; Found: 538.0227.

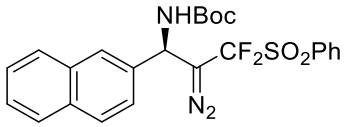
Methyl (*R*)-4-(1-((*tert*-butoxycarbonyl)amino)-2-diazo-3,3-difluoro-3-(phenylsulfonyl)propyl)benzoate



4s

Yellow oil, 89 mg, 90% yield, 98% ee. HPLC (DAICEL Chiralpak AD-H, hexane/IPA= 80:20, 0.6 mL/min, 254 nm): t_R(major) = 26.17 min, t_R(minor) = 23.47 min, $[\alpha]_D^{20}$ +50 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.99 (d, *J* = 7.6 Hz, 2H), 7.77 (t, *J* = 7.3 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 2H), 7.52 (d, *J* = 7.9 Hz, 2H), 5.77 (s, 1H), 5.53 (d, *J* = 6.7 Hz, 1H), 3.91 (s, 3H), 1.44 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.42 (d, *J* = 230.4 Hz), -99.48 (d, *J* = 231.2 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 154.7, 142.5, 135.6, 132.6, 130.7, 130.3, 130.1, 129.5, 126.4, 121.8 (t, *J* = 292.0 Hz), 80.7, 53.5 (t, *J* = 34.0 Hz), 52.2, 50.9, 28.3. **HRMS** (ESI^+): Calculated for $C_{22}H_{23}F_2N_3NaO_6S^+$ $[M+Na]^+$: 518.1168; Found: 518.1149.

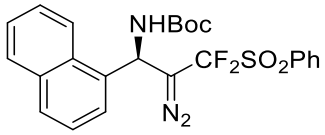
***tert*-Butyl (*R*)-(2-diazo-3,3-difluoro-1-(naphthalen-2-yl)-3-(phenylsulfonyl) propyl)carbamate**



4t

Yellow oil, 96 mg, 98% yield, 95% ee. HPLC (DAICEL Chiralpak IA, hexane/IPA= 85:15, 0.6 mL/min, 254 nm): t_R(major) = 23.02 min, t_R(minor) = 27.87 min, $[\alpha]_D^{20}$ +68 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.7 Hz, 2H), 7.94 – 7.80 (m, 4H), 7.74 (t, *J* = 7.5 Hz, 1H), 7.59 (dd, *J* = 14.5, 7.2 Hz, 3H), 7.54 – 7.48 (m, 2H), 5.97 (s, 1H), 5.69 (s, 1H), 1.48 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.23 (d, *J* = 231.5 Hz), -99.16 (d, *J* = 232.2 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.8, 135.5, 134.9, 133.3, 133.13, 132.7, 130.7, 129.5, 129.1, 128.2, 127.7, 126.5, 126.5, 125.3, 124.3, 122.0 (t, *J* = 292.0 Hz), 80.5, 53.8 (t, *J* = 35.0 Hz), 51.1, 28.3. **HRMS** (ESI^+): Calculated for $C_{24}H_{23}F_2N_3NaO_4S^+$ $[M+Na]^+$: 510.1270; Found: 510.1275.

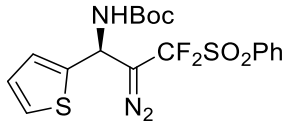
***tert*-Butyl (*R*)-(2-diazo-3,3-difluoro-1-(naphthalen-1-yl)-3-(phenylsulfonyl) propyl)carbamate**



4u

Yellow oil, 87 mg, 90% yield, 91% ee. HPLC (DAICEL Chiralpak AS-H, hexane/IPA= 85:15, 0.6 mL/min, 254 nm): t_R(major) = 35.89 min, t_R(minor) = 16.82 min, $[\alpha]_D^{20}$ +43(c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.77 (t, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 7.1 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 3H), 7.53 (dt, *J* = 20.2, 7.6 Hz, 2H), 6.55 (s, 1H), 5.66 (s, 1H), 1.50 (s, 9H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -97.45 (d, *J* = 233.3 Hz), -99.02 (d, *J* = 233.6 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.7, 135.5, 134.0, 132.7, 130.7, 130.0, 129.5, 129.4, 129.0, 127.1, 126.2, 125.2, 124.2, 122.5, 122.1 (t, *J* = 291.4 Hz), 80.5, 53.4 (t, *J* = 34.1 Hz), 47.7, 28.3. **HRMS** (ESI^+): Calculated for $C_{24}H_{23}F_2N_3NaO_4S^+$ $[M+Na]^+$: 510.1270; Found: 510.1268.

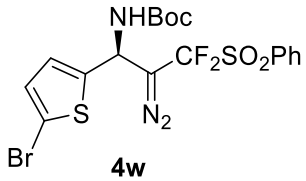
***tert*-Butyl (*S*)-(2-diazo-3,3-difluoro-3-(phenylsulfonyl)-1-(thiophen-2-yl)propyl) carbamate**



4v

Yellow oil, 88 mg, 98% yield, 98% ee. HPLC (DAICEL Chiralpak OD-H, hexane/IPA= 85:15, 0.6 mL/min, 254 nm): t_R(major) = 28.18 min, t_R(minor) = 24.21 min, $[\alpha]_D^{20}$ +54 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 2H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 4.0 Hz, 1H), 7.14 (d, *J* = 3.2 Hz, 1H), 7.06 – 6.98 (m, 1H), 5.93 (d, *J* = 7.4 Hz, 1H), 5.55 (d, *J* = 7.8 Hz, 1H), 1.49 (s, 9H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -98.50 (d, *J* = 232.1 Hz), -99.44 (d, *J* = 232.3 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.5, 141.6, 135.5, 132.7, 130.7, 129.5, 127.4, 125.6, 125.4, 121.7 (t, *J* = 280.6 Hz), 80.8, 55.0 (t, *J* = 31.8 Hz), 47.9, 28.3. **HRMS** (ESI^+): Calculated for $C_{18}H_{19}F_2N_3NaO_4S_2^+$ $[M+Na]^+$: 466.0677; Found: 466.664.

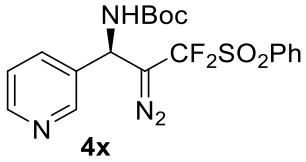
***tert*-Butyl (*S*)-(1-(5-bromothiophen-2-yl)-2-diazo-3,3-difluoro-3-(phenylsulfonyl) propyl)carbamate**



4w

Yellow oil, 98 mg, 94% yield, 98% ee. HPLC (DAICEL Chiralpak IA, hexane/IPA= 85:15, 0.6 mL/min, 254 nm): t_R(major) = 20.90 min, t_R(minor) = 17.49 min, $[\alpha]_D^{20}$ +32 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.7 Hz, 2H), 7.77 (t, *J* = 7.5 Hz, 1H), 7.62 (t, *J* = 7.8 Hz, 2H), 6.95 (d, *J* = 3.8 Hz, 1H), 6.91 – 6.80 (m, 1H), 5.76 (d, *J* = 7.6 Hz, 1H), 5.54 (s, 1H), 1.46 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.65 (d, *J* = 231.8 Hz), -99.66 (d, *J* = 231.8 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.5, 143.1, 143.0, 135.6, 132.5, 130.7, 130.2, 129.6, 125.7, 121.6 (t, *J* = 292.2 Hz), 112.3, 81.0, 53.6 (t, *J* = 35.0 Hz), 48.0, 28.3. **HRMS** (ESI^+): Calculated for $C_{18}H_{18}BrF_2N_3NaO_4S_2^+$ $[M+Na]^+$: 543.9782; Found: 543.9809.

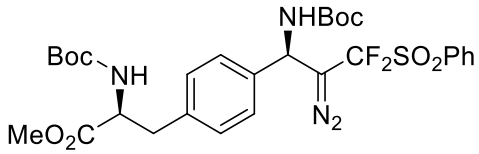
***tert*-Butyl (*R*)-(2-diazo-3,3-difluoro-3-(phenylsulfonyl)-1-(pyridin-3-yl)propyl) carbamate**



4x

Yellow oil, 55 mg, 63% yield, 99% ee. HPLC (DAICEL Chiralpak AD-H, hexane/IPA= 85:15, 0.6 mL/min, 254 nm): t_R(major) = 30.39 min, t_R(minor) = 27.69 min, $[\alpha]_D^{20}$ +64 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 1.8 Hz, 1H), 8.56 (d, *J* = 3.8 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 2H), 7.77 (dd, *J* = 15.6, 7.9 Hz, 2H), 7.61 (t, *J* = 7.8 Hz, 2H), 7.33 (dd, *J* = 7.9, 4.8 Hz, 1H), 5.83 (d, *J* = 7.2 Hz, 1H), 5.76 (s, 1H), 1.43 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.44 (d, *J* = 231.5 Hz), -99.68 (d, *J* = 231.8 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.8, 149.6, 148.1, 135.6, 134.4, 133.3, 132.4, 130.7, 129.6, 123.7, 121.7 (t, *J* = 292.1 Hz), 80.8, 60.4, 53.4 (t, *J* = 34.6 Hz), 49.3, 28.2. **HRMS** (ESI^+): Calculated for $C_{19}H_{20}F_2N_4NaO_4S^+$ $[M+Na]^+$:461.1066; Found: 461.1060.

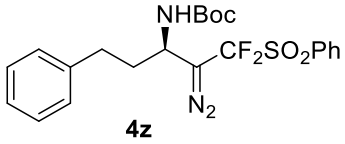
Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(4-((*R*)-1-((*tert*-butoxycarbonyl) amino)-2-diazo-3,3-difluoro-3-(phenylsulfonyl)propyl)phenyl)propanoate



4y

Yellow solid, 0.4 mmol scale, 232 mg, 91% yield, dr: 97:3, mp 56–57 °C. HPLC (DAICEL Chiralpak AD-H, hexane/IPA= 70:30, 1.0 mL/min, 254 nm): t_R(major) = 30.91 min, t_R(minor) = 20.52 min, $[\alpha]_D^{20}$ +66 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.7 Hz, 2H), 7.78 (t, *J* = 7.5 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 5.75 (d, *J* = 6.9 Hz, 1H), 5.43 (d, *J* = 7.1 Hz, 1H), 5.02 (d, *J* = 7.8 Hz, 1H), 4.60 (d, *J* = 6.7 Hz, 1H), 3.70 (s, 3H), 3.10 (tt, *J* = 19.9, 9.9 Hz, 2H), 1.46 (s, 9H), 1.43 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.32 (d, *J* = 231.5 Hz), -99.27 (d, *J* = 233.5 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 155.0, 154.6, 136.3, 136.2, 135.5, 132.8, 130.6, 129.9, 129.5, 126.6, 122.0 (t, *J* = 291.9 Hz), 80.4, 80.0, 54.3, 53.6 (t, *J* = 34.8 Hz), 52.2, 50.7, 38.0, 28.3. **HRMS** (ESI^+): Calculated for $C_{29}H_{36}F_2N_4NaO_8S^+$ $[M+Na]^+$: 661.2114; Found: 661.2102.

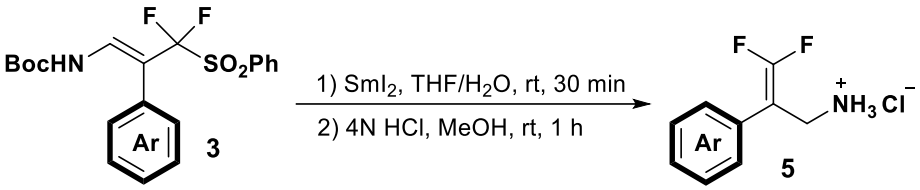
***tert*-Butyl (*R*)-(2-diazo-1,1-difluoro-5-phenyl-1-(phenylsulfonyl)pentan-3-yl) carbamate**



4z

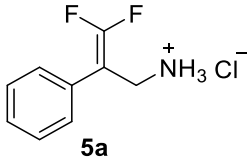
Yellow oil, 54 mg, 58% yield, 95% ee. HPLC (DAICEL Chiralpak OD-H, hexane/IPA= 92:8, 0.6 mL/min, 254 nm): t_R(major) = 13.48 min, t_R(minor) = 15.85 min, $[\alpha]_D^{20}$ +72 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.98 (d, *J* = 7.7 Hz, 2H), 7.74 (dd, *J* = 10.7, 4.3 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 2H), 7.33 – 7.26 (m, 2H), 7.23 – 7.17 (m, 3H), 5.11 (d, *J* = 8.1 Hz, 1H), 4.38 (d, *J* = 5.6 Hz, 1H), 2.85 – 2.66 (m, 2H), 2.10 (dt, *J* = 20.7, 7.1 Hz, 2H), 1.46 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) *δ* -98.11 (d, *J* = 231.7 Hz), -98.77 (d, *J* = 232.4 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 155.2, 140.5, 135.5, 132.9, 130.6, 129.5, 128.6, 128.5, 126.3, 122.5 (t, *J* = 291.1 Hz), 80.0, 52.0 (t, *J* = 34.4 Hz), 47.9, 35.1, 32.6, 28.3. **HRMS** (ESI^+): Calculated for $C_{22}H_{25}F_2N_3NaO_4S^+$ $[M+Na]^+$: 488.1426; Found: 488.1436.

2.4 General procedure for synthesis of *gem*-difluoroallylic amines 5 from enamines 3



A solution of phenylsulfonyl difluoroalkyl enamine compound **3** (0.2 mmol) in THF/H_2O (10/1, 11 mL) was degassed for 30 min at room temperature. Then the solution of SmI_2 in THF (ca. 0.1 M, 10 equiv.) was added to the reaction mixture and the resulting deep purple-dark solution was stirred at room temperature for 30 min. The reaction was quenched with saturated $NaHCO_3$ solution and extracted with EtOAc (20 mL, 3 times). The combined organic phase was washed with brine and dried over Na_2SO_4. The crude product was purified by flash column chromatography on silical gel (eluent: petrol ether / ethyl acetate = 10:1) to give the desired *N*-Boc difluoroalkenylamine. The obtained compound was dissolved in MeOH (3 mL) and treated with a solution of 4 M HCl in dioxane (2 mL). The mixture was stirred for 1 h at room temperature. Concentration of the reaction mixture under vacuum would give the expected product **5**, which is pure enough for characterization.

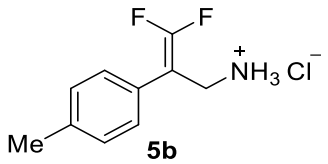
3,3-Difluoro-2-phenylprop-2-en-1-aminium chloride



5a

White solid, 26 mg, 64%, mp 151–152 °C. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.48 – 7.34 (m, 5H), 4.02 (s, 2H). **^{19}F NMR** (376 MHz, CD_3OD) δ -87.04 (dt, J = 29.2, 2.2 Hz, 1F), -88.14 (d, J = 29.2 Hz, 1F). **^{13}C NMR** (100 MHz, CD_3OD) δ 155.2 (t, J = 292.9 Hz), 129.5 (t, J = 3.1 Hz), 128.8 (s), 128.5 (s), 128.4 (t, J = 3.0 Hz), 88.1 (t, J = 19.4 Hz), 36.9 (d, J = 4.0 Hz). **HRMS** (ESI^+): Calculated for $C_9H_{10}F_2N^+$ $[M\text{-}Cl^-]^+$: 170.0776; Found: 170.0782.

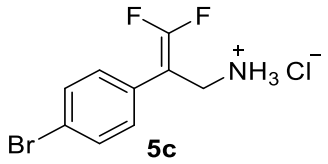
3,3-Difluoro-2-(*p*-tolyl)prop-2-en-1-aminium chloride



5b

White solid, 31 mg, 70%, mp 144–145 ºC. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.31 (d, J = 7.9 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 3.99 (s, 2H), 2.33 (s, 3H). **^{19}F NMR** (376 MHz, CD_3OD) δ -87.48 (d, J = 30.4 Hz, 1F), -88.51 (d, J = 30.4 Hz, 1F). **^{13}C NMR** (100 MHz, CD_3OD) δ 155.1 (t, J = 292.7 Hz), 138.7 (s), 129.4 (s), 128.2 (t, J = 3.0 Hz), 126.4 (t, J = 3.0 Hz), 87.9 (t, J = 19.4 Hz), 36.9 (d, J = 4.4 Hz), 19.9 (s). **HRMS** (ESI^+): Calculated for $C_{10}H_{12}F_2N^+$ $[M\text{-}Cl^-]^+$: 184.0932; Found: 184.0933.

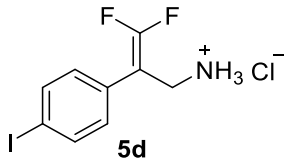
2-(4-Bromophenyl)-3,3-difluoroprop-2-en-1-aminium chloride



5c

White solid, 43 mg, 76%, mp 165–166 ºC. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.63 – 7.58 (m, 2H), 7.40 – 7.33 (m, 2H), 4.01 (t, J = 2.1 Hz, 2H). **^{19}F NMR** (376 MHz, CD_3OD) δ -86.01 (dt, J = 27.0, 2.2 Hz, 1F), -87.11 (d, J = 27.0 Hz, 1F). **^{13}C NMR** (100 MHz, CD_3OD) δ 155.2 (t, J = 293.6 Hz), 132.0, 130.3 (t, J = 3.1 Hz), 128.7 (t, J = 3.3 Hz), 122.5, 87.4 (t, J = 19.7 Hz), 36.6 (d, J = 3.1 Hz). **HRMS** (ESI^+): Calculated for $C_9H_9BrF_2N^+$ $[M\text{-}Cl^-]^+$: 247.9881; Found: 247.9878.

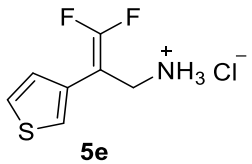
3,3-Difluoro-2-(4-iodophenyl)prop-2-en-1-aminium chloride



5d

White solid, 53 mg, 80%, mp 189–190 ºC. **^{1}H NMR** (600 MHz, CD_3OD) δ 7.83 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 7.6 Hz, 2H), 4.03 (t, J = 2.0 Hz, 2H). **^{19}F NMR** (376 MHz, CD_3OD) δ -85.81 (dt, J = 26.8, 2.2 Hz), -86.96 (d, J = 26.9 Hz). **^{13}C NMR** (150 MHz, CD_3OD) δ 156.6 (t, J = 293.7 Hz), 139.5 (d, J = 8.5 Hz), 131.7 (d, J = 2.7 Hz), 130.6 (t, J = 3.2 Hz), 95.4, 89.0 (t, J = 19.6 Hz), 38.0 (d, J = 3.2 Hz). **HRMS** (ESI^+): Calculated for $C_9H_9F_2IN^+$ $[M\text{-}Cl^-]^+$: 295.9742; Found: 295.9749.

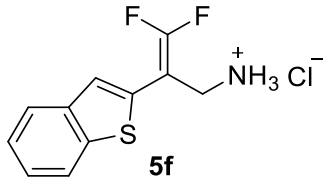
3,3-Difluoro-2-(thiophen-3-yl)prop-2-en-1-aminium chloride



5e

White solid, 33 mg, 78%, mp 198–199 ºC.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (dd, J = 2.9, 1.3 Hz, 1H), 7.54 (dd, J = 5.1, 2.9 Hz, 1H), 7.25 (ddd, J = 5.1, 2.5, 1.4 Hz, 1H), 4.03 (s, 2H).**^{19}F NMR** (376 MHz, CD_3OD) δ -80.82 (dd, J = 27.8, 1.8 Hz, 1F), -83.82 (dt, J = 27.7, 2.3 Hz, 1F). **^{13}C NMR** (100 MHz, CD_3OD) δ 159.3 (dd, J = 295.8, 291.9 Hz), 133.5 (dd, J = 4.5, 2.7 Hz), 130.7 (s), 130.3 (dd, J = 5.9, 2.1 Hz), 127.7 (dd, J = 5.3, 4.1 Hz), 91.7 – 86.8 (m), 40.3 (d, J = 5.1 Hz). **HRMS** (ESI^+): Calculated for $C_7H_8F_2NS^+$ $[M\text{-}Cl^-]^+$: 176.0340; Found: 176.0339.

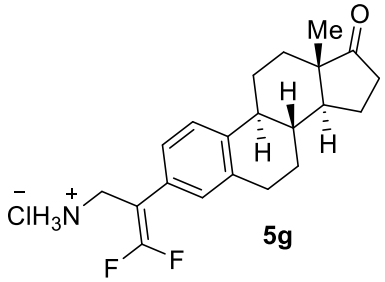
2-(Benzo[*b*]thiophen-2-yl)-3,3-difluoroprop-2-en-1-aminium chloride



5f

White solid, 41 mg, 78%, mp 135-136 ºC. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.93 – 7.76 (m, 2H), 7.60 (s, 1H), 7.45 – 7.31 (m, 2H), 4.16 (s, 2H). **^{19}F NMR** (376 MHz, CD_3OD) δ -80.51 (d, J = 18.1 Hz, 1F), -83.56 – -85.07 (m, 1F). **^{13}C NMR** (101 MHz, CD_3OD) δ 155.6 (d, J = 294.9, 294.8 Hz), 139.8 (dd, J = 5.7, 1.2 Hz), 139.3, 131.3 (dd, J = 7.1, 2.4 Hz), 125.0, 124.6, 123.7 (dd, J = 6.8, 2.7 Hz), 123.6, 121.6, 84.9 (dd, J = 23.9, 18.2 Hz), 36.2 (dd, J = 1.8, 1.6 Hz). **HRMS** (ESI^+): Calculated for $C_{11}H_{10}F_2NS^+$ $[M\text{-}Cl^-]^+$: 226.0497; Found: 226.0516.

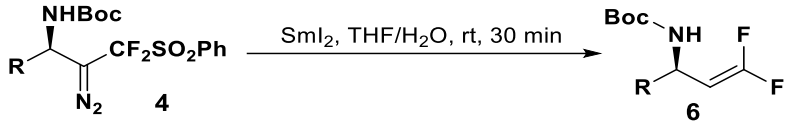
3,3-Difluoro-2-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)prop-2-en-1-aminium chloride



5g

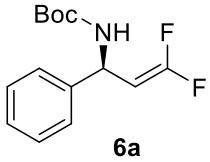
White solid, 42 mg, 75%, mp > 250 °C. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.41 (d, J = 8.1 Hz, 1H), 7.25 – 7.14 (m, 2H), 4.02 (s, 2H), 3.68 (dd, J = 11.4, 5.7 Hz, 1H), 2.99 – 2.85 (m, 2H), 2.45 – 2.33 (m, 1H), 2.27 (dd, J = 14.6, 7.0 Hz, 1H), 2.10 – 1.90 (m, 3H), 1.73 (dd, J = 7.1, 2.6 Hz, 1H), 1.60 – 1.15 (m, 8H), 0.79 (s, 3H). **^{19}F NMR** (376 MHz, CD_3OD) δ -88.01 (dd, J = 282.1, 30.6 Hz). **^{13}C NMR** (100 MHz, CD_3OD) δ 155.1 (t, J = 292.6 Hz), 141.1, 137.4, 128.6 (t, J = 2.7 Hz), 126.3 (t, J = 2.9 Hz), 125.8, 125.5 (t, J = 2.8 Hz), 87.9 (t, J = 19.3 Hz), 81.0, 49.9, 44.3, 42.9, 36.8 (d, J = 3.6 Hz), 36.8, 36.6, 29.3, 29.1, 26.8, 25.9, 22.6, 10.3. **HRMS** (ESI^+): Calculated for $C_{21}H_{26}F_2NO^+$ $[M+H_2-Cl^-]^+$: 348.2133; Found: 348.2138.

2.5 General procedure for synthesis of enantioenriched *gem*-difluoroallylic amines 6



A solution of compound **4** (0.2 mmol) in THF/H_2O (10/1, 11 mL) was degassed for 30 min at room temperature. Then a solution of SmI_2 in THF (ca. 0.1 M, 20 mL) was added to the reaction mixture and the resulting deep purple-dark solution was stirred at room temperature for 30 min. Then the reaction mixture was quenched with saturated $NaHCO_3$ solution and extracted with EtOAc (10 mL, 3 times). The combined organic phase was washed with brine and dried over Na_2SO_4. The mixture was concentrated under vacuum to yield the crude expected product **6**, which was subjected to column chromatography on silica gel (eluent: petrol ether / ethyl acetate = 15:1) to give the pure product.

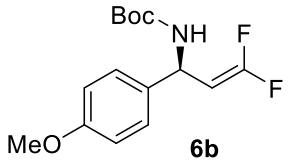
tert-Butyl (*S*)-(3,3-difluoro-1-phenylallyl)carbamate



White solid, 36 mg, 83%, 93% ee, mp 113–114 °C, HPLC (DAICEL Chiralpak AS-H, hexane/IPA= 95:5, 1.0 mL/min, 210 nm): t_R(major) =8.80 min, t_R(minor) = 5.71 min, $[\alpha]_D^{20}$ -5.8 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 5H), 5.61 –

5.27 (m, 1H), 4.94 (s, 1H), 4.49 (dd, *J* = 25.7, 9.5 Hz, 1H), 1.44 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -86.58 (dd, *J* = 210.9, 175.5 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.7 (t, *J* = 290.4 Hz), 154.8, 140.7, 128.9, 127.8, 126.2, 81.0 (t, *J* = 20.2 Hz), 80.1, 49.0, 28.3. **HRMS** (ESI^+): Calculated for $C_{14}H_{18}F_2NO_2^+$ $[M+H]^+$: 270.1300; Found: 270.1305.

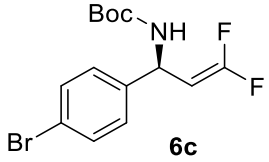
***tert*-Butyl (*S*)-(3,3-difluoro-1-(4-methoxyphenyl)allyl)carbamate**



6b

White solid, 54 mg, 90%, 89% ee, mp 89–90 °C, HPLC (DAICEL Chiralpak AS-H, hexane/IPA= 95:5, 0.8 mL/min, 210 nm): t_R(major) =23.15 min, t_R(minor) = 10.96 min, $[\alpha]_D^{20}$ -8.0 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.38 (s, 1H), 4.93 (s, 1H), 4.48 (dd, *J* = 26.0, 9.5 Hz, 1H), 3.79 (s, 3H), 1.44 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -86.95 (dd, *J* = 210.2, 176.0 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.2, 156.6 (t, *J* = 289.9 Hz), 154.8, 132.9, 127.4, 114.2, 81.1 (t, *J* = 19.9 Hz), 80.0, 55.3, 48.6, 28.3. **HRMS** (ESI^+): Calculated for $C_{15}H_{19}F_2NNaO_3^+$ $[M+Na]^+$: 322.1225; Found: 322.1224.

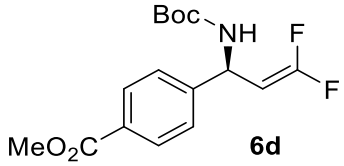
***tert*-Butyl (*S*)-(1-(4-bromophenyl)-3,3-difluoroallyl)carbamate**



6c

White solid, 65 mg, 93%, 99% ee, mp 95–96 °C, HPLC (DAICEL Chiralpak AS-H, hexane/IPA= 95:5, 0.8 mL/min, 210 nm): t_R(major) =17.20 min, t_R(minor) = 8.27 min, $[\alpha]_D^{20}$ +6.8 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 5.31 (s, 1H), 4.97 (s, 1H), 4.38 (dd, *J* = 25.3, 9.5 Hz, 1H), 1.35 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -84.73 – -87.39 (m). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.7 (t, *J* = 290.9 Hz), 154.8, 140.0, 131.9, 127.9, 121.6, 80.5 (t, *J* = 20.8 Hz), 80.3, 48.6, 28.3. **HRMS** (ESI^-): Calculated for $C_{14}H_{15}BrF_2NO_2^-$ $[M-H]^-$: 346.0260; Found: 346.0244.

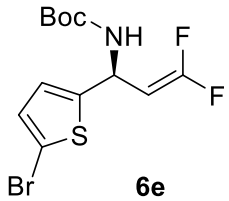
Methyl (*S*)-4-(1-((*tert*-butoxycarbonyl)amino)-3,3-difluoroallyl)benzoate



6d

White solid, 48 mg, 73%, 98% ee, mp 96–97 ºC, HPLC (DAICEL Chiralpak AS-H, hexane/IPA= 90:10, 0.8 mL/min, 254 nm): t_R(major) =19.37 min, t_R(minor) = 8.92 min, $[\alpha]_D^{20}$ +14 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.3 Hz, 2H), 5.48 (s, 1H), 5.01 (d, J = 7.3 Hz, 1H), 4.49 (dd, J = 25.4, 9.6 Hz, 1H), 3.91 (s, 3H), 1.43 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -68.19 – -99.65 (m). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.6, 156.9 (t, J = 290.9 Hz), 154.7, 145.9, 130.1, 129.7, 126.1, 80.5 (t, J = 20.8 Hz), 80.4, 52.1, 49.0, 28.3. **HRMS** (ESI^+): Calculated for $C_{16}H_{20}F_2NO_4^+$ $[M+H]^+$: 328.1355; Found: 328.1351.

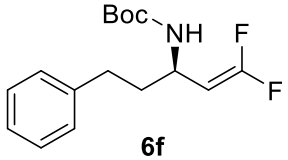
***tert*-Butyl (*S*)-(1-(5-bromothiophen-2-yl)-3,3-difluoroallyl)carbamate**



6e

White solid, 60 mg, 85%, 99% ee, mp 71–72 ºC, HPLC (DAICEL Chiralpak AS-H, hexane/IPA= 95:5, 0.8 mL/min, 254 nm): t_R(major) =15.46 min, t_R(minor) = 8.11 min, $[\alpha]_D^{20}$ +8.2 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.88 (d, J = 3.8 Hz, 1H), 6.73 – 6.67 (m, 1H), 5.57 (s, 1H), 5.03 (d, J = 6.7 Hz, 1H), 4.53 (ddd, J = 23.5, 9.5, 1.4 Hz, 1H), 1.45 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -83.73 – -86.49 (m). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.0 (dd, J = 292.7, 290.9 Hz), 154.5, 146.4, 129.7, 124.7, 111.74, 80.6, 80.1 (dd, J = 23.2, 18.1 Hz), 45.5, 28.3. **HRMS** (ESI^-): Calculated for $C_{12}H_{13}BrF_2NO_2S^+$ $[M-H]^-$: 351.9824; Found: 351.9819.

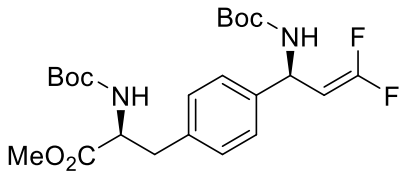
***tert*-Butyl (*R*)-(1,1-difluoro-5-phenylpent-1-en-3-yl)carbamate**



6f

White solid, 42.5 mg, 72%, 97% ee, mp 72–73 °C, HPLC (DAICEL Chiralpak AD-H, hexane/IPA= 99:1, 0.8 ml/min, 210 nm): t_R(major) =16.97 min, t_R(minor) = 14.93 min, $[\alpha]_D^{20}$ -8.4 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 2H), 7.11 (dd, *J* = 13.6, 7.2 Hz, 3H), 4.49 (s, 1H), 4.16 (d, *J* = 22.1 Hz, 2H), 2.57 (t, *J* = 8.0 Hz, 2H), 1.84 (s, 1H), 1.71 (dt, *J* = 21.2, 7.6 Hz, 1H), 1.37 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -85.64 – -87.70 (m). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.8 (t, *J* = 289.9 Hz), 155.0, 141.0, 128.5, 128.3, 126.1, 80.8, 79.7, 45.5, 37.4, 32.1, 28.4. **HRMS** (ESI^+): Calculated for $C_{16}H_{21}F_2NNaO_2^+$ $[M+Na]^+$: 320.1433; Found: 320.1429.

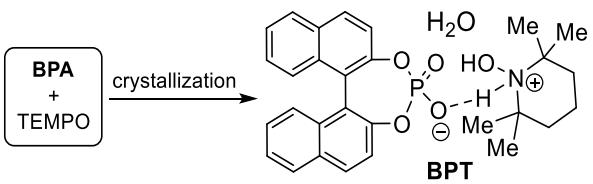
Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(4-((*S*)-1-((*tert*-butoxycarbonyl) amino)-3,3-difluoroallyl)phenyl)propanoate



6g

White solid, 70.5 mg, 75%, dr: 97:3, mp 125–126 °C, HPLC (DAICEL Chiralpak AS-H, hexane/IPA= 70:30, 0.8 ml/min, 210 nm): t_R(major) =12.86 min, t_R(minor) = 28.22 min, $[\alpha]_D^{20}$ +264 (c 1.0, CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.41 (s, 1H), 4.96 (d, *J* = 7.6 Hz, 1H), 4.86 (s, 1H), 4.57 (d, *J* = 7.0 Hz, 1H), 4.47 (dd, *J* = 25.8, 9.5 Hz, 1H), 3.71 (s, 3H), 3.07 (ddd, *J* = 37.8, 13.8, 5.8 Hz, 2H), 1.44 (s, 9H), 1.41 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -86.04 – -87.01 (m). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.2, 156.7 (t, *J* = 290.3 Hz), 155.0, 154.8, 139.4, 135.7, 129.8, 126.4, 80.9 (t, *J* = 20.5 Hz), 80.0, 54.3, 52.3, 48.7, 37.9, 28.3, 28.3. **HRMS** (ESI^+): Calculated for $C_{23}H_{33}F_2N_2O_6^+$ $[M+H]^+$: 471.2301; Found: 471.2304.

2.6 Crystallization of BPA with TEMPO to give BPT

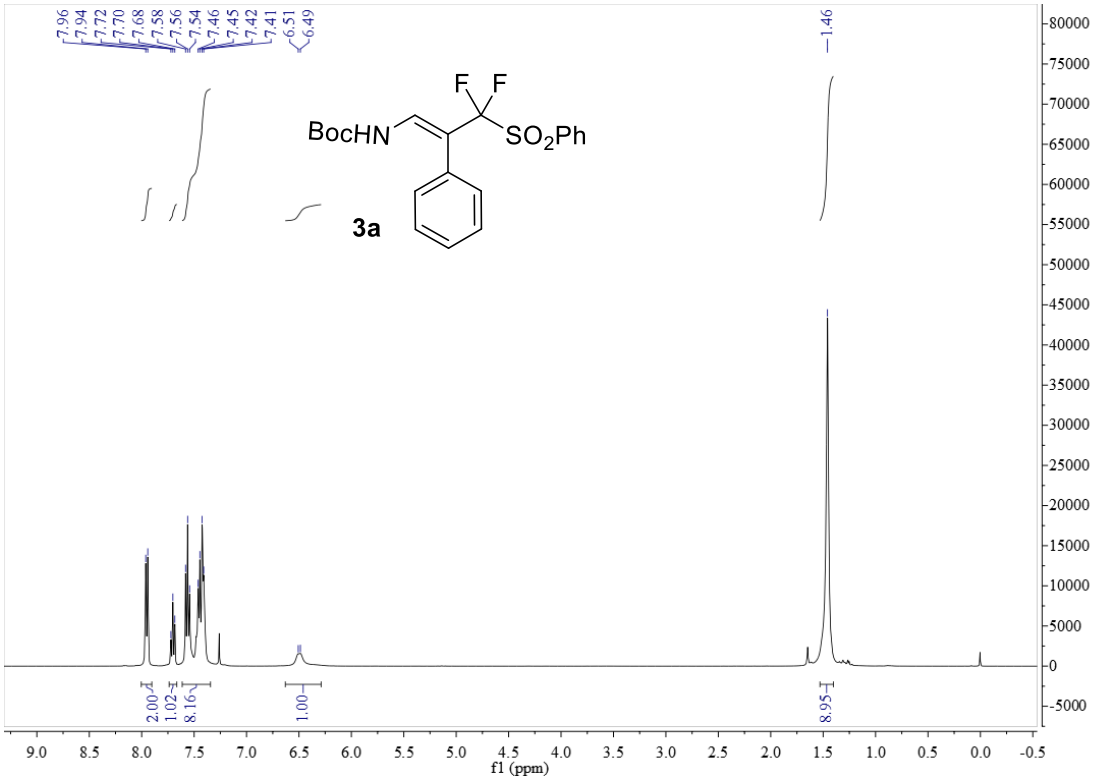


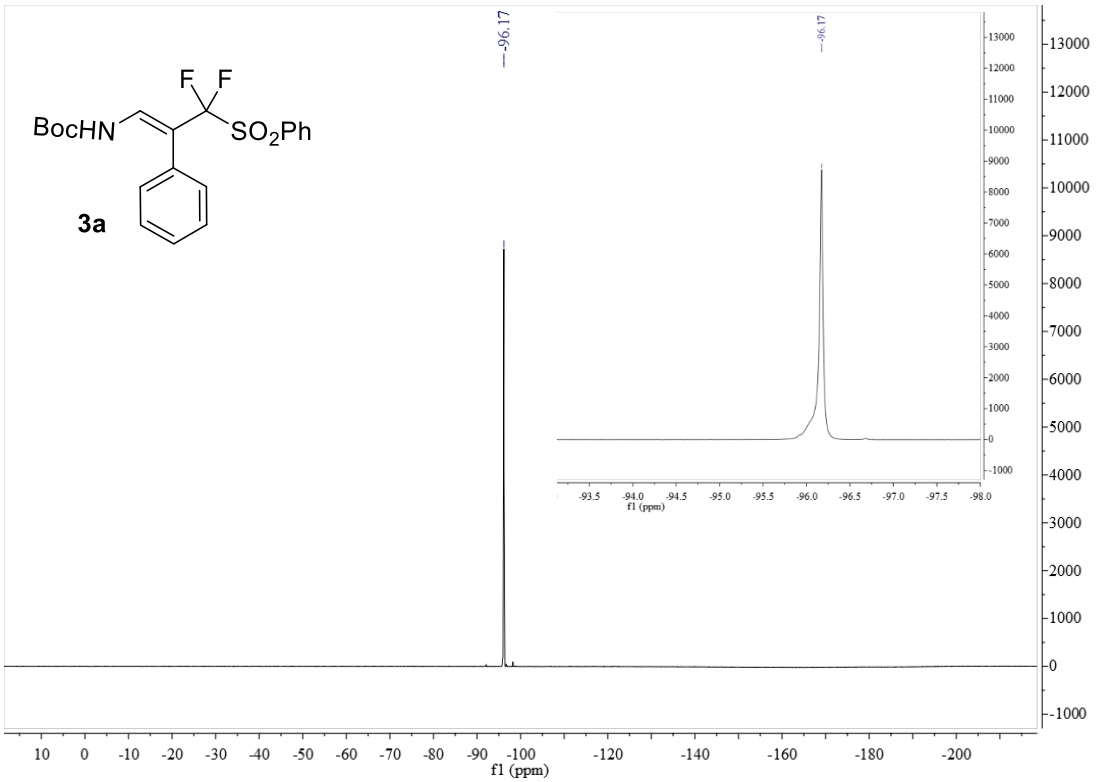
BPT

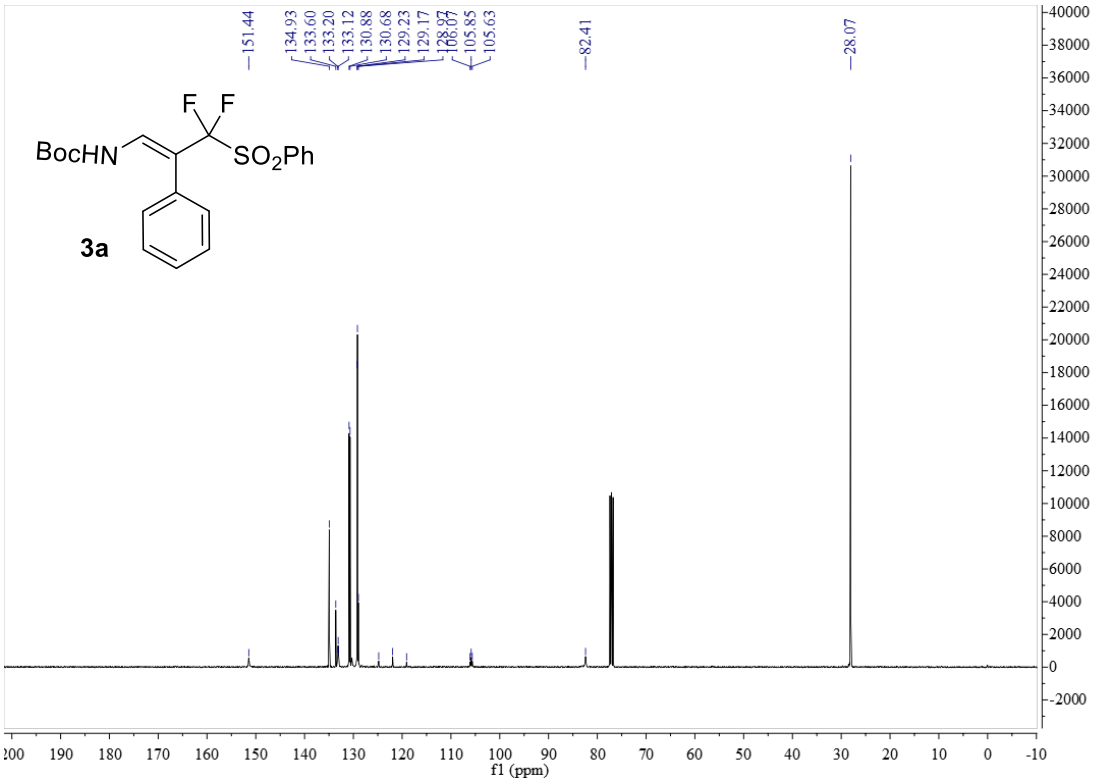
(±)-**BPA** (35 mg, 0.1 mmol) and TEMPO (16 mg, 0.1 mmol) was put in a vial with 4 mL of CH_3CN at rt. The crystal **BPT** was obtained a few days later after solvent

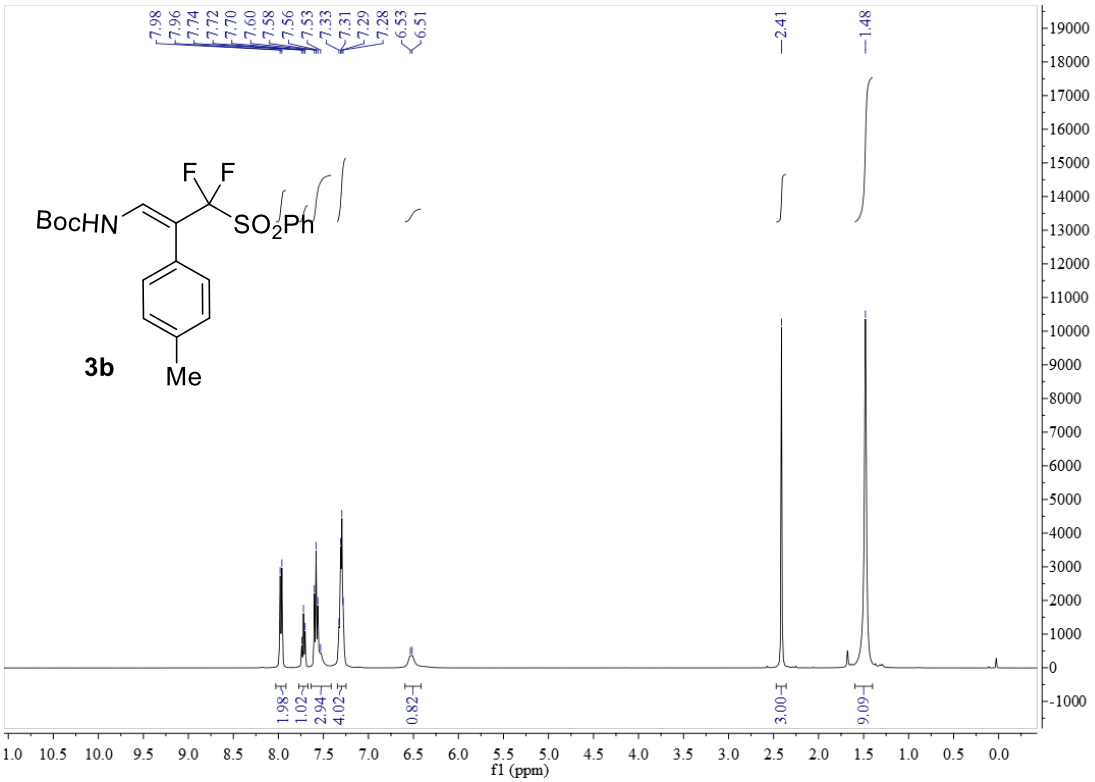
volatilizing. **^{1}H NMR** (600 MHz, d^{6}-DMSO) δ 11.52 (s, 1H), 11.20 (s, 1H), 8.07 (d, *J* = 8.8 Hz, 2H), 8.03 (d, *J* = 8.1 Hz, 2H), 7.47 – 7.40 (m, 4H), 7.31 (t, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 1.73 (s, 5H), 1.31 (dd, *J* = 41.9, 12.3 Hz, 13H); **^{31}P NMR** (162 MHz, d^{6}-DMSO) δ 5.09; **^{13}C NMR** (150 MHz, d^{6}-DMSO) δ 149.7, 149.6, 131.9, 130.4, 129.9, 128.4, 126.1, 126.0, 124.5, 122.4, 121.6, 67.0, 35.7, 27.5, 19.1.

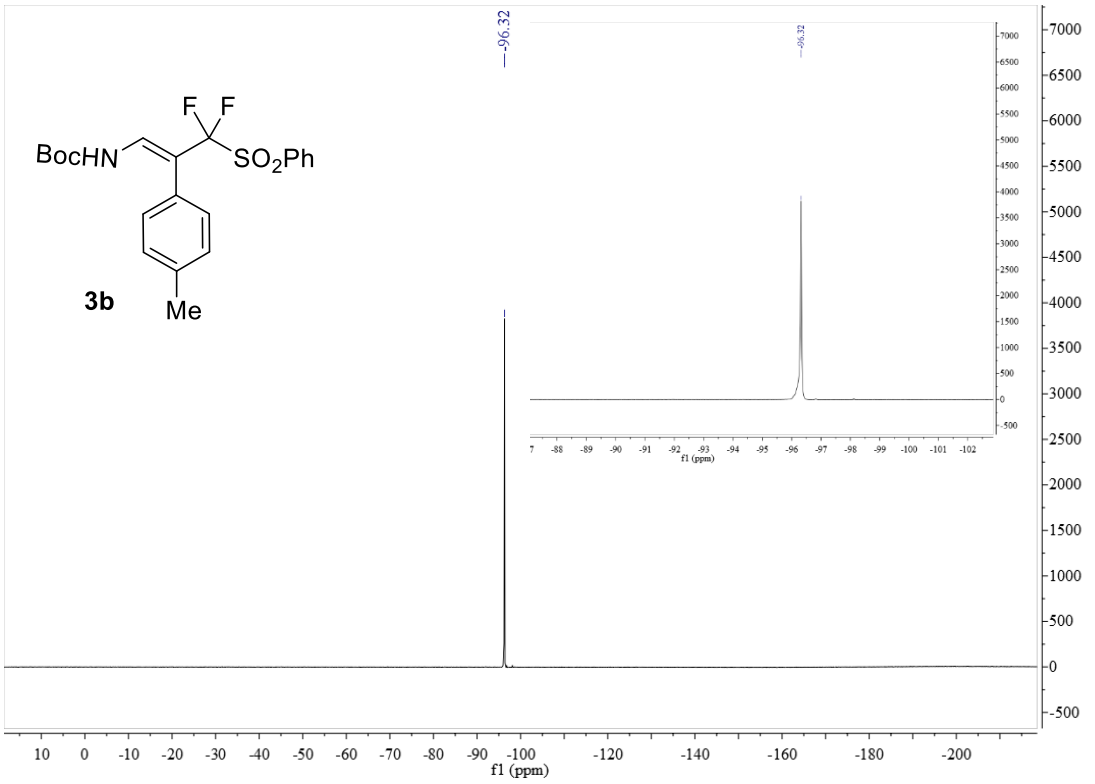
3. NMR spectra of all the new compounds

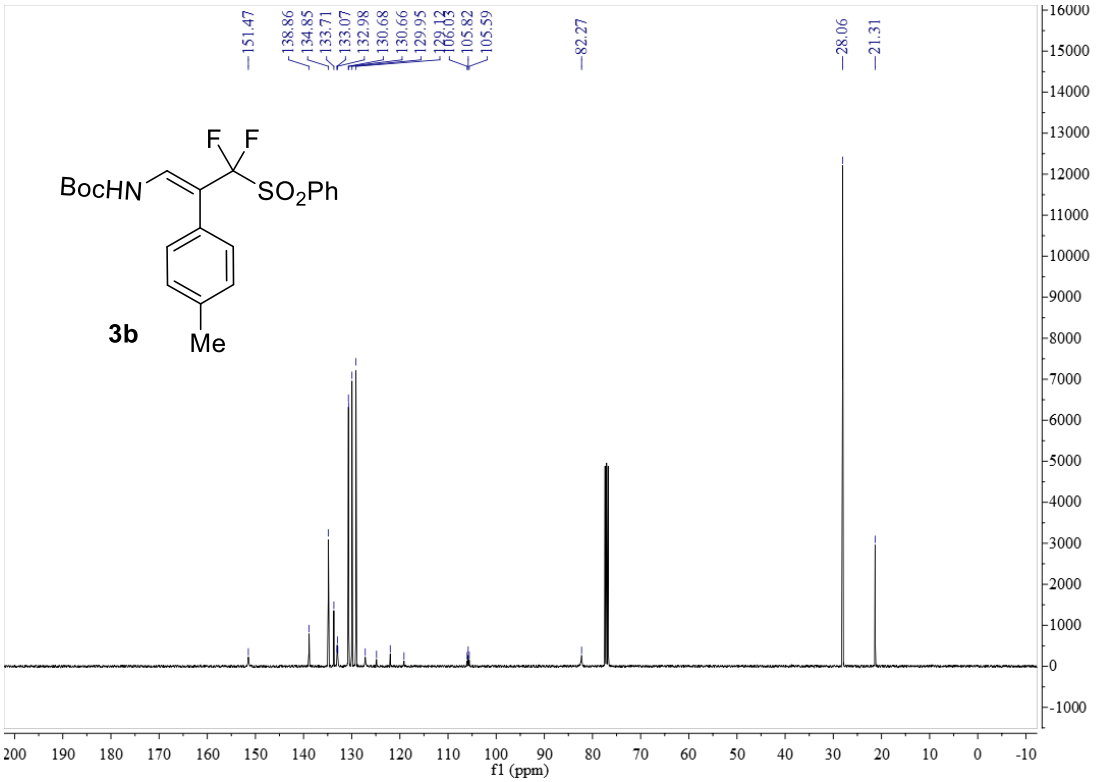



F F
BocHN
SO2Ph
3a
-96.17
f1 (ppm)


F F
BocHN
SO2Ph
3a
151.44
134.93
133.60
133.20
133.12
130.88
130.68
129.23
129.17
128.97
128.07
105.85
105.63
82.41
28.07
f1 (ppm)


7.98
7.96
7.74
7.72
7.70
7.60
7.58
7.56
7.53
7.33
7.31
7.29
7.28
6.53
6.51
2.41
1.48
F F
BocHN
SO2Ph
3b
Me
1.98
1.02
2.94
4.02
0.82
3.00
9.09
f1 (ppm)


-96.32
F F
BocHN
SO2Ph
3b
Me
f1 (ppm)


151.47
138.86
134.85
133.71
133.07
132.98
130.68
130.66
129.95
105.82
105.59
82.27
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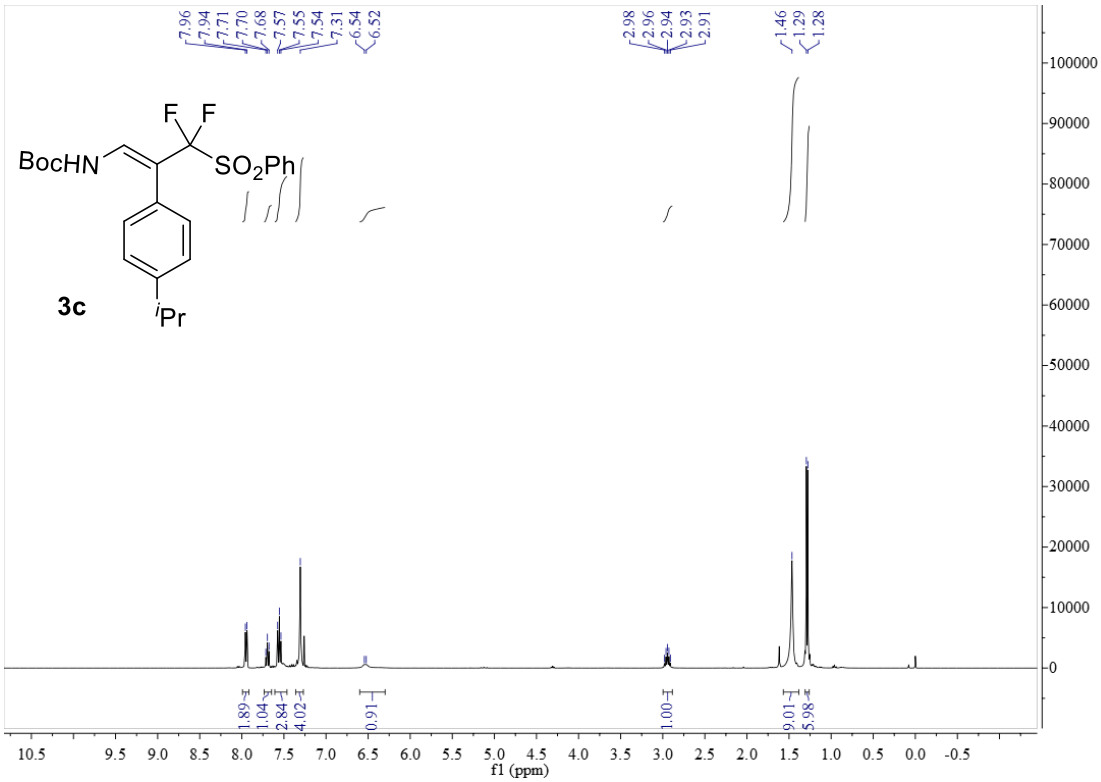
21.31
F F
BocHN
SO2Ph
3b
Me
f1 (ppm)


7.96
7.94
7.71
7.70
7.68
7.57
7.55
7.54
7.31
6.54
6.52
2.98
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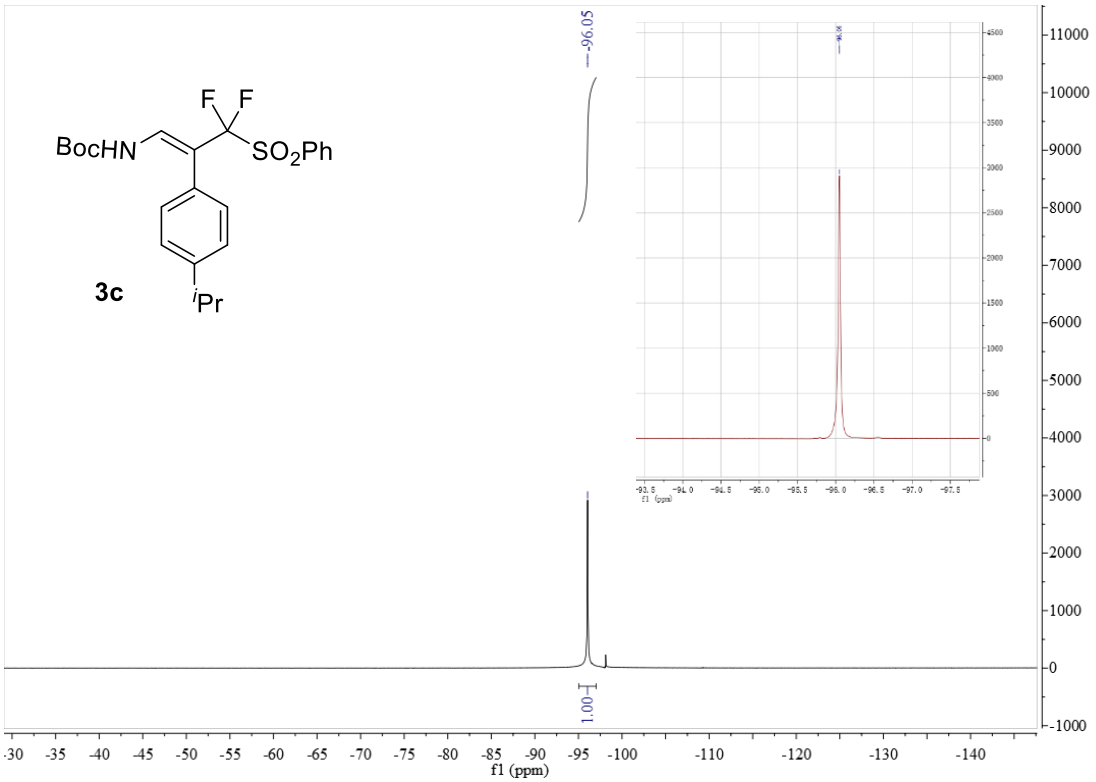
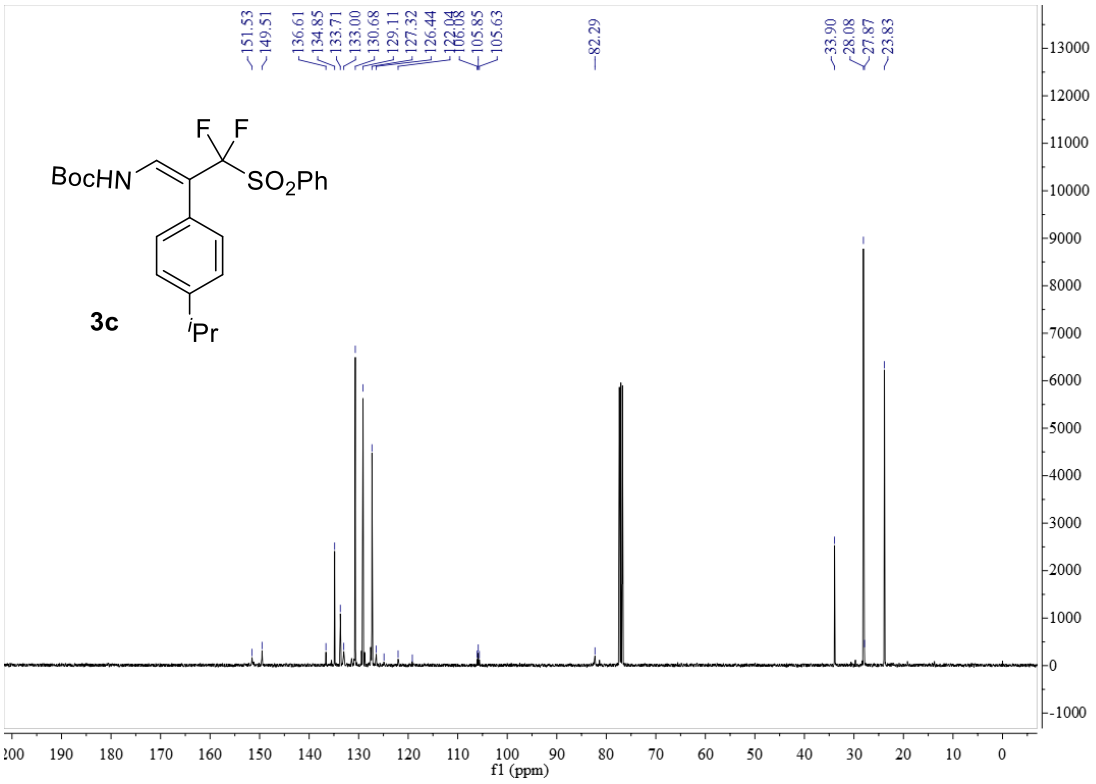
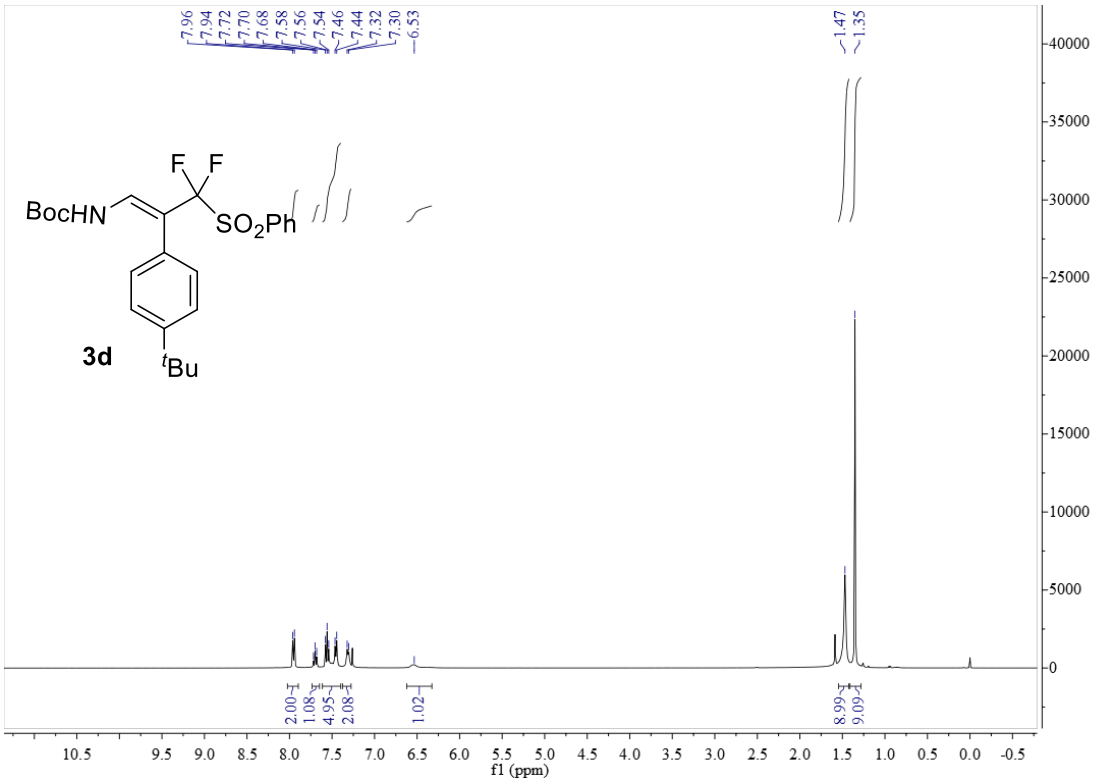
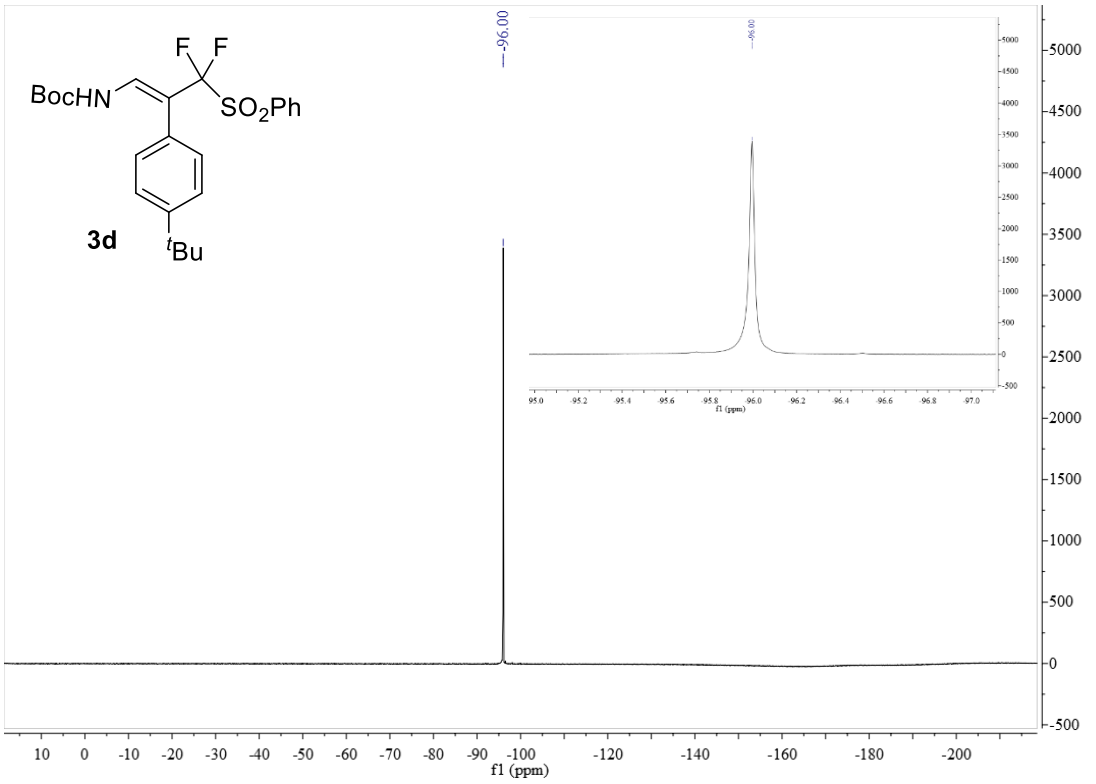
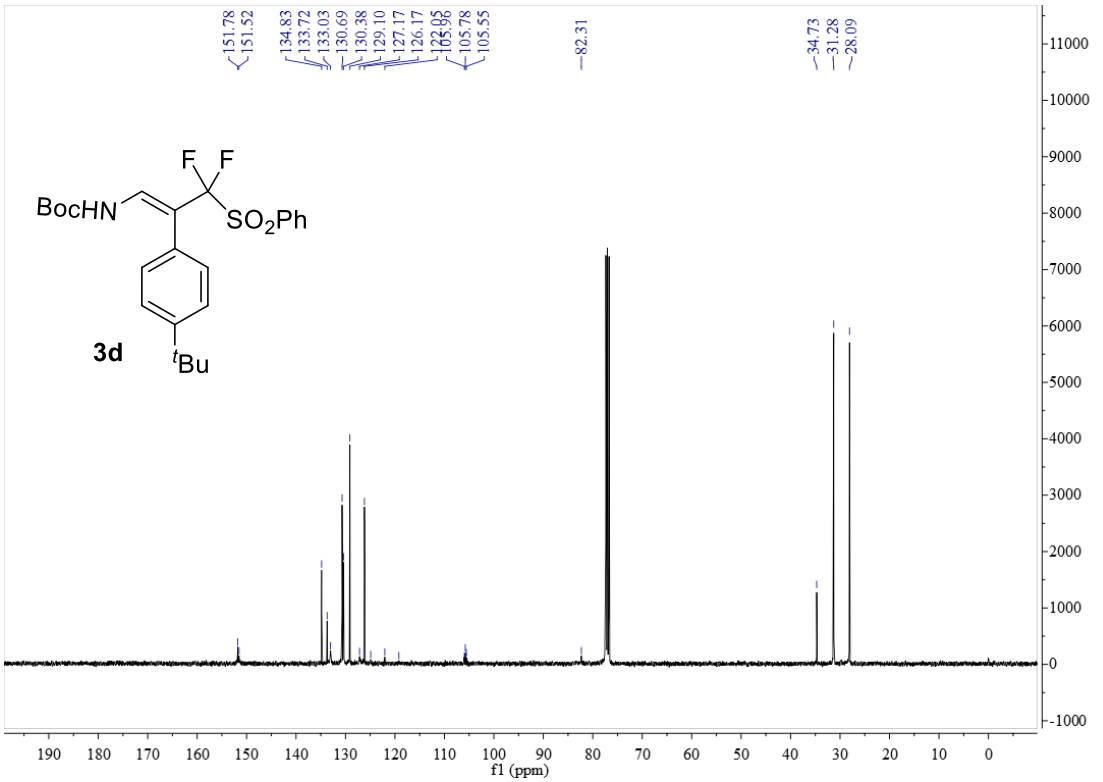
2.94
2.93
2.91
1.46
1.29
1.28
F F
BocHN
SO2Ph
3c
iPr
1.89
1.04
2.84
4.02
0.91
1.00
9.01
5.98
f1 (ppm)


F F
BocHN
SO2Ph
3c
iPr
-96.05
1.00
f1 (ppm)


151.53
149.51
136.61
134.85
133.71
133.00
130.68
129.11
127.32
126.44
122.04
105.85
105.63
82.29
33.90
28.08
27.87
23.83
F F
BocHN
SO2Ph
3c
iPr
f1 (ppm)


7.96
7.94
7.72
7.70
7.68
7.58
7.56
7.54
7.46
7.44
7.32
7.30
6.53
1.47
1.35
F F
BocHN
SO2Ph
3d
tBu
2.00
1.08
4.95
2.08
1.02
8.99
9.09
f1 (ppm)


F F
BocHN
SO2Ph
3d
tBu
-96.00
f1 (ppm)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126.17
122.05
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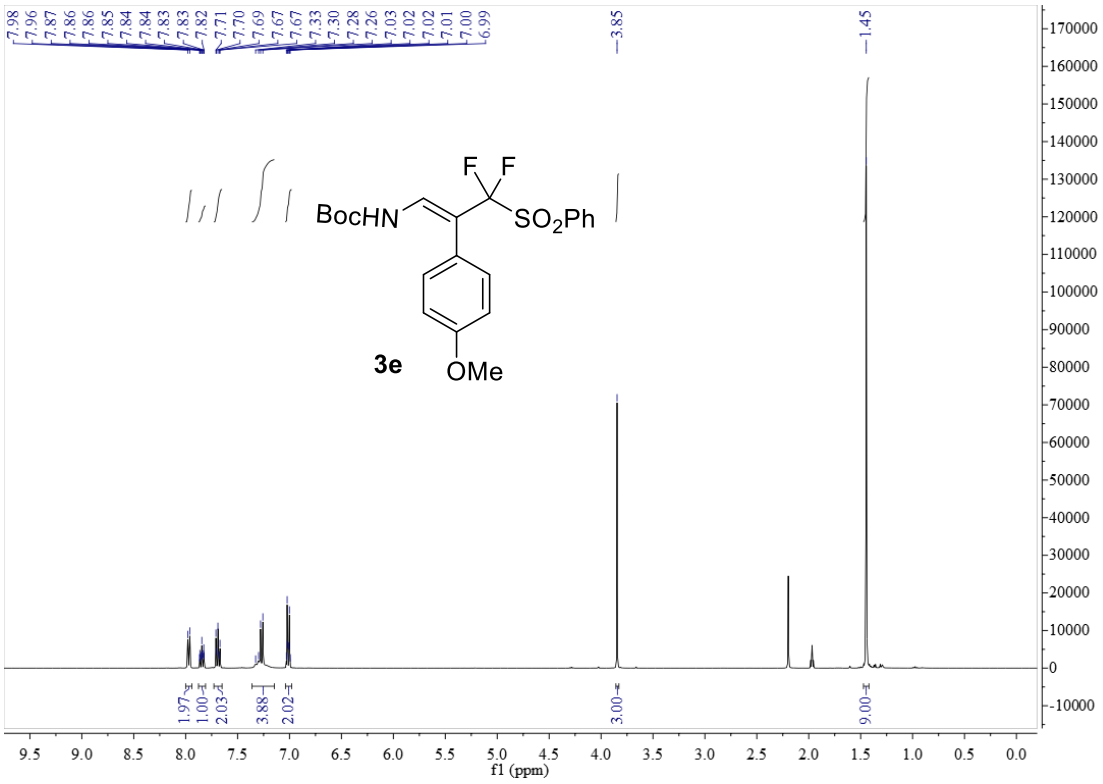
34.73
31.28
28.09
F F
BocHN
SO2Ph
3d
tBu
f1 (ppm)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7.84
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7.83
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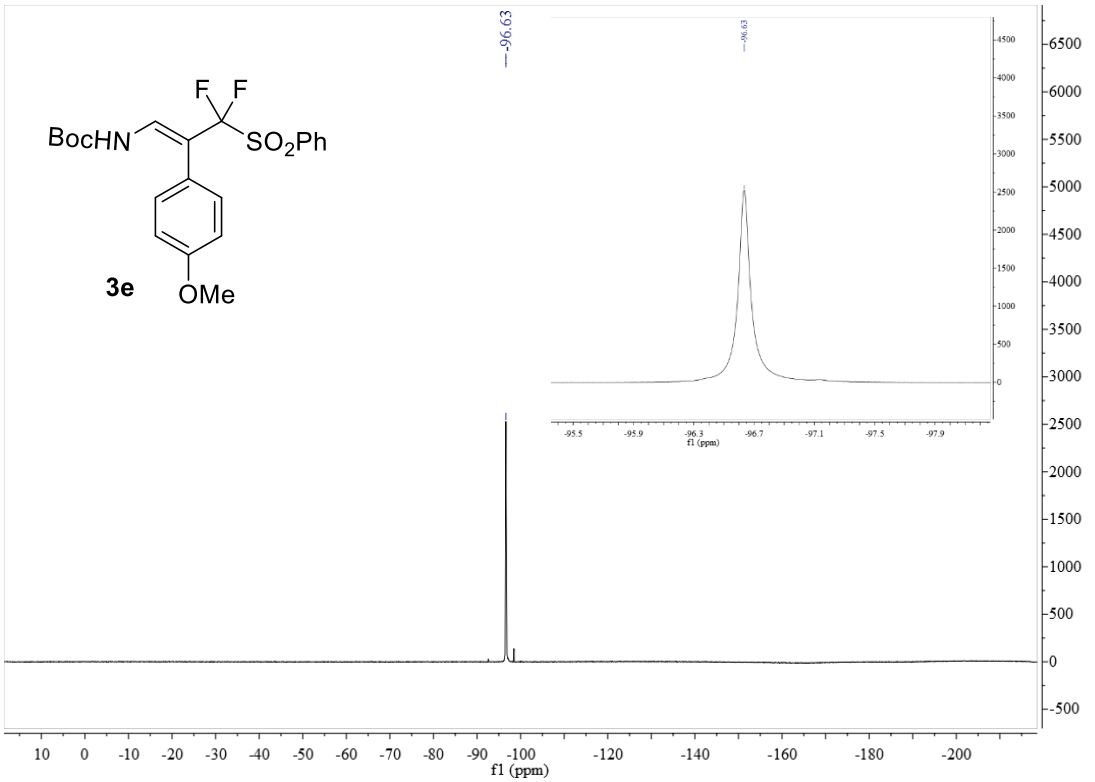
7.69
7.67
7.67
7.33
7.30
7.28
7.26
7.03
7.02
7.02
7.01
7.00
6.99
3.85
1.45
F F
BocHN
SO2Ph
3e
OMe
1.97
1.00
2.03
3.88
2.02
3.00
9.00
f1 (ppm)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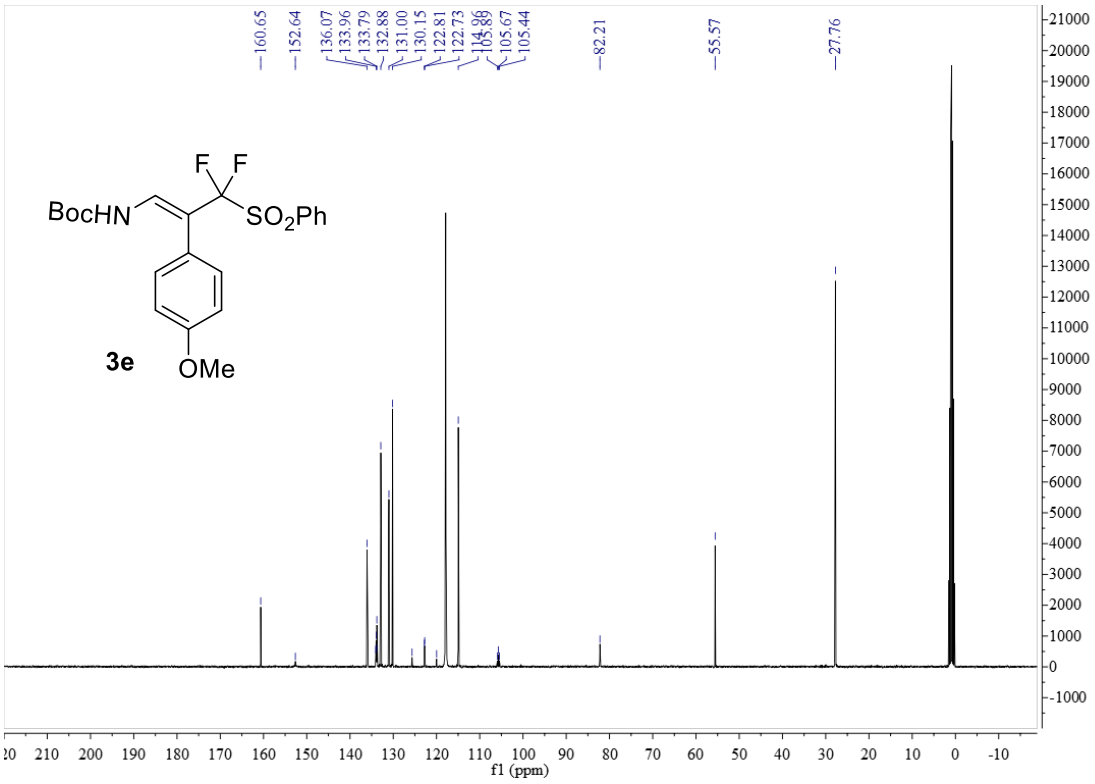
SO2Ph
3e
OMe
-96.63
f1 (ppm)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82.21
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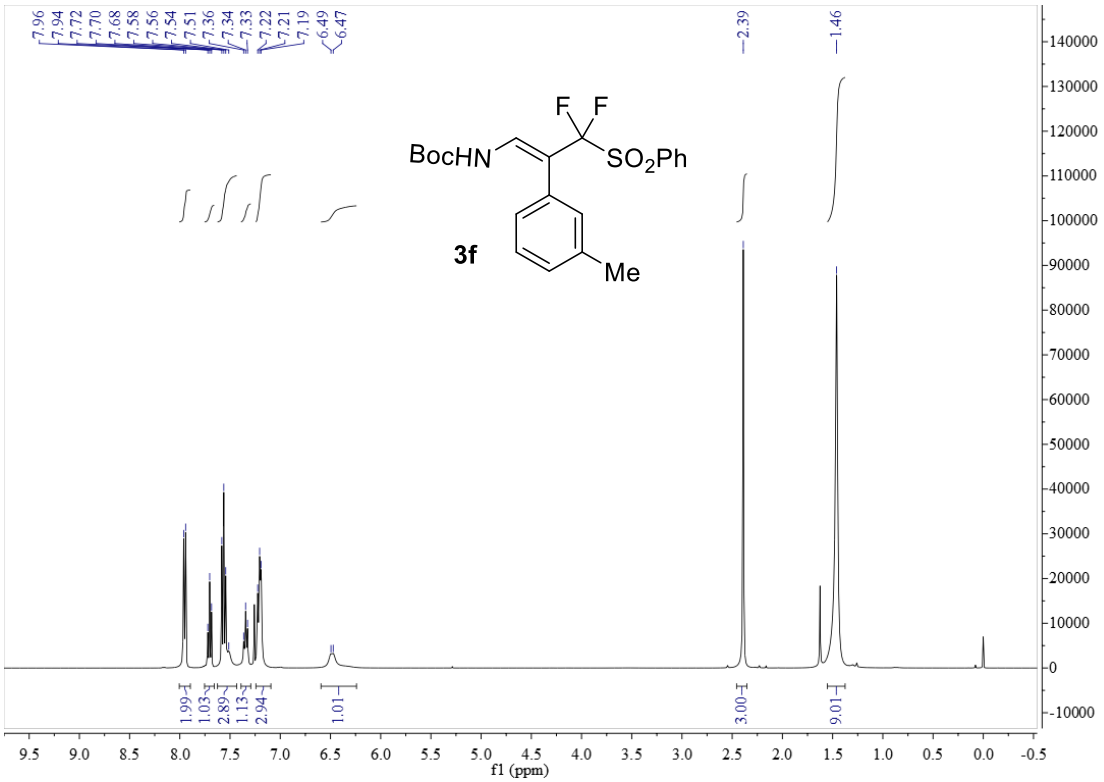
27.76
F F
BocHN
SO2Ph
3e
OMe
f1 (ppm)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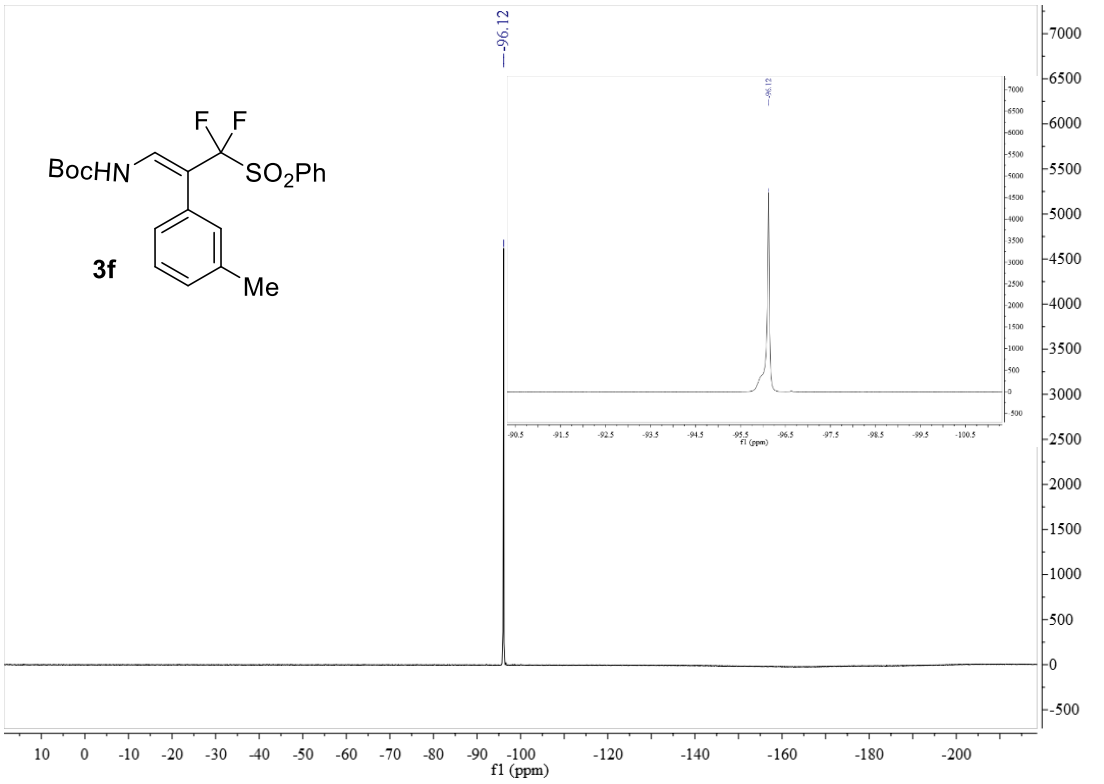
7.56
7.54
7.51
7.36
7.34
7.33
7.22
7.21
7.19
6.49
6.47
2.39
1.46
F F
BocHN
SO2Ph
3f
Me
1.99
1.03
2.89
1.13
2.94
1.01
3.00
9.01
f1 (ppm)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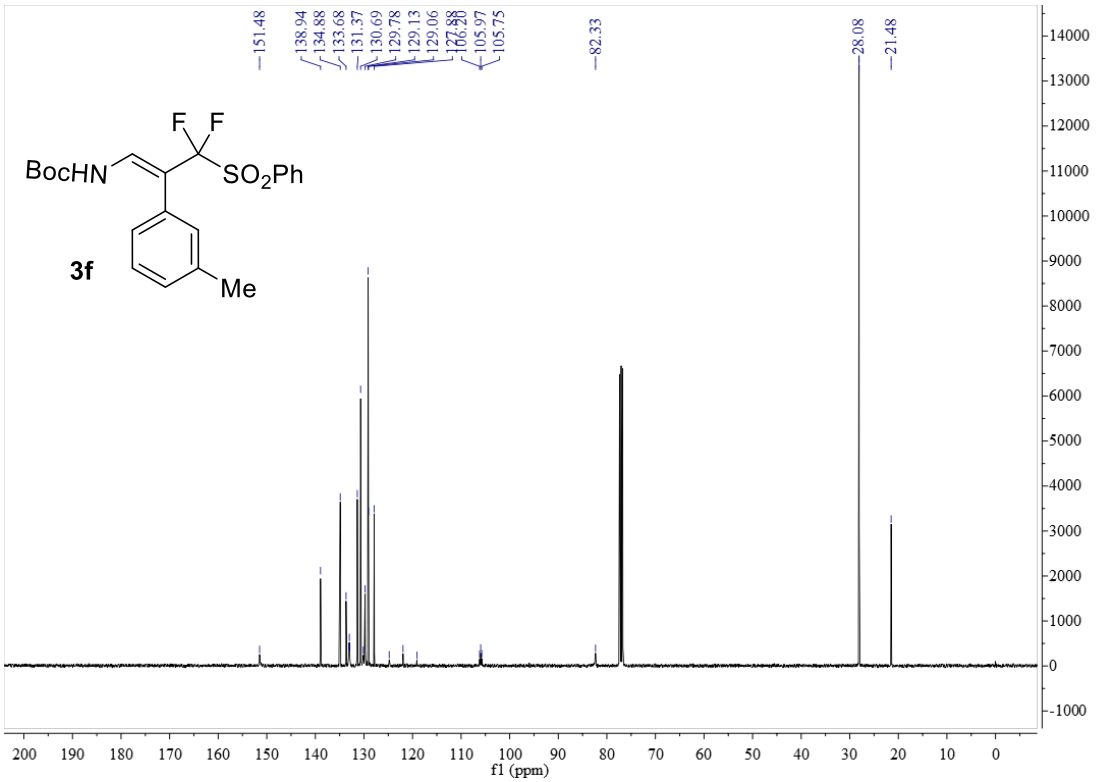
f1 (ppm)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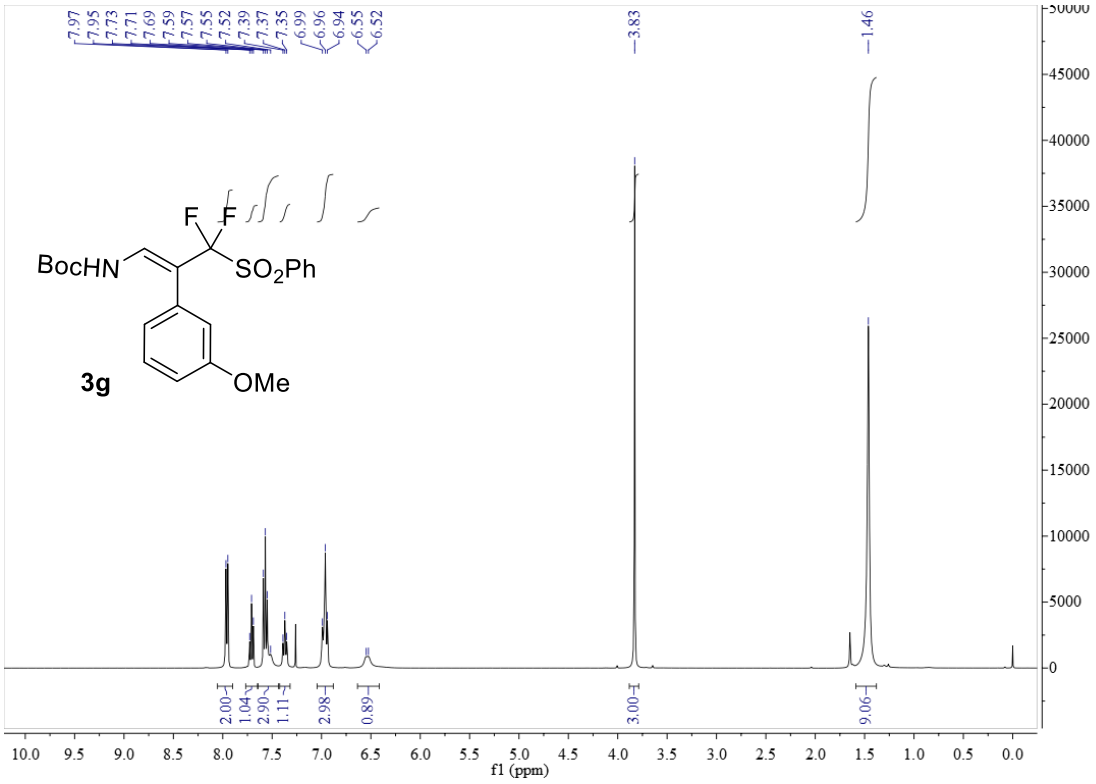
21.48
F F
BocHN
SO2Ph
3f
Me
f1 (ppm)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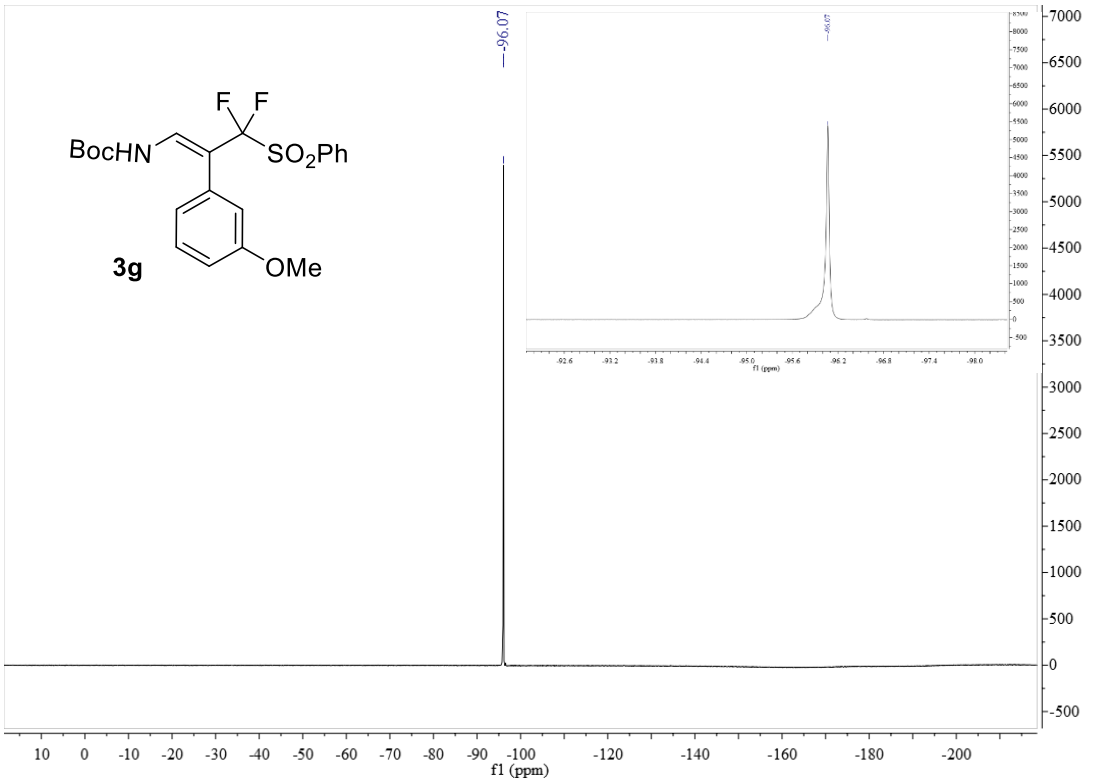
7.39
7.37
7.35
6.99
6.96
6.94
6.55
6.52
3.83
1.46
F F
BocHN
SO2Ph
3g
OMe
2.00
1.04
2.90
1.11
2.98
0.89
3.00
9.06
f1 (ppm)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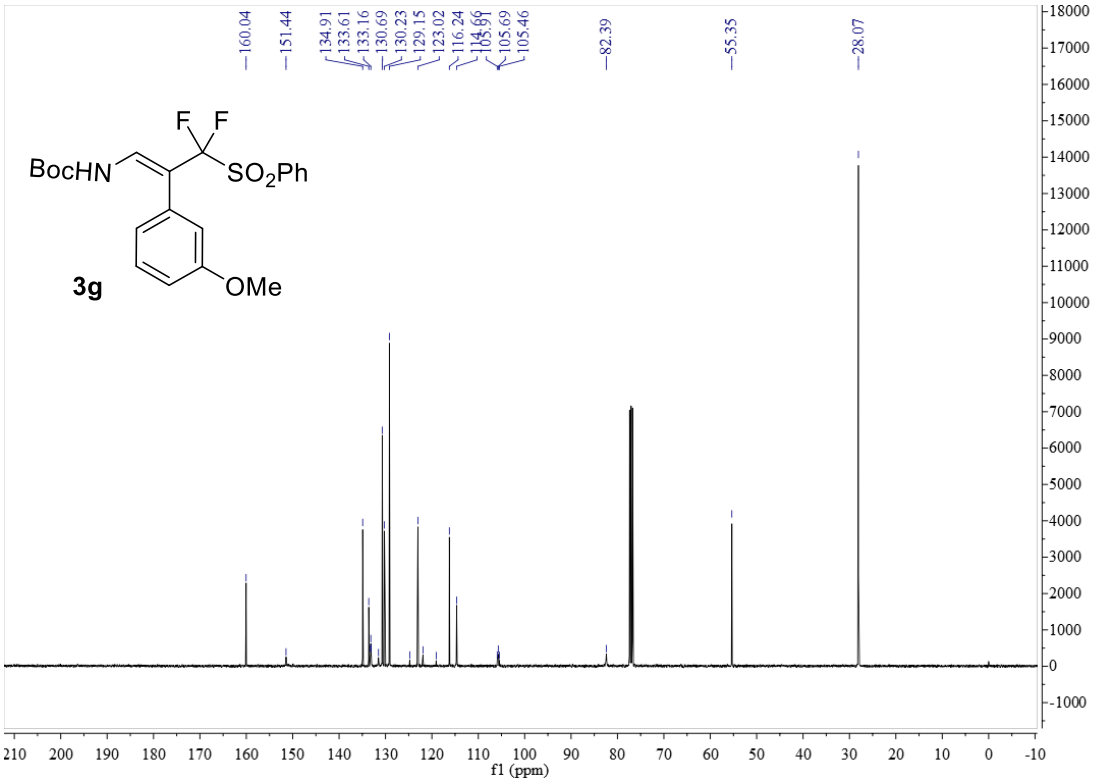
BocHN
SO2Ph
3g
OMe
-96.07
f1 (ppm)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130.23
129.15
123.02
116.24
114.66
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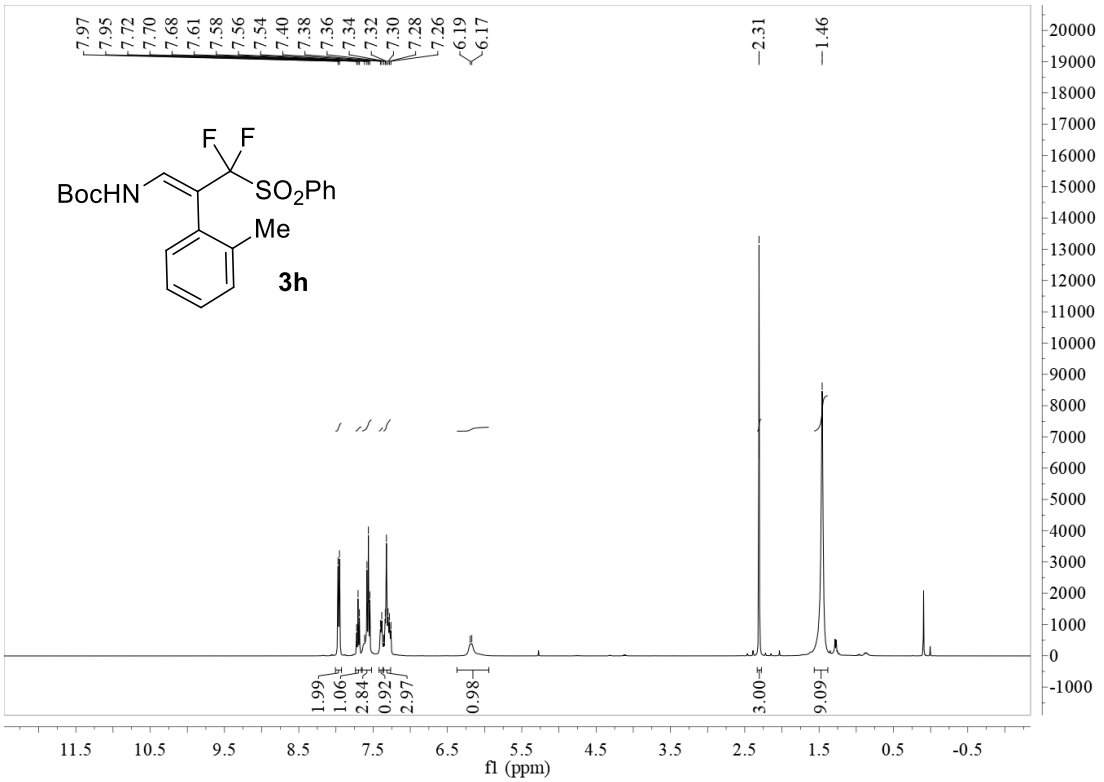
105.46
82.39
55.35
28.07
F F
BocHN
SO2Ph
3g
OMe
f1 (ppm)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7.56
7.54
7.40
7.38
7.36
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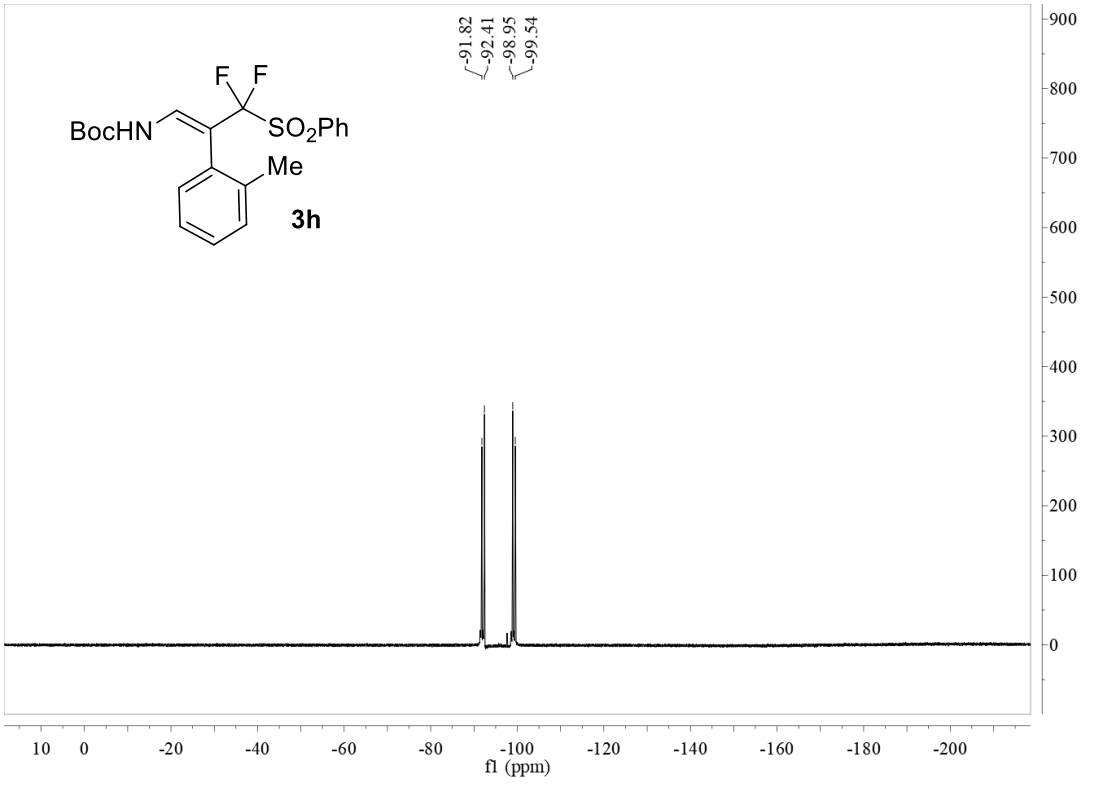
7.32
7.30
7.28
7.26
6.19
6.17
2.31
1.46
F F
BocHN
SO2Ph
Me
3h
1.99
1.06
2.84
0.92
2.97
0.98
3.00
9.09
fl (ppm)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-92.41
-98.95
-99.54
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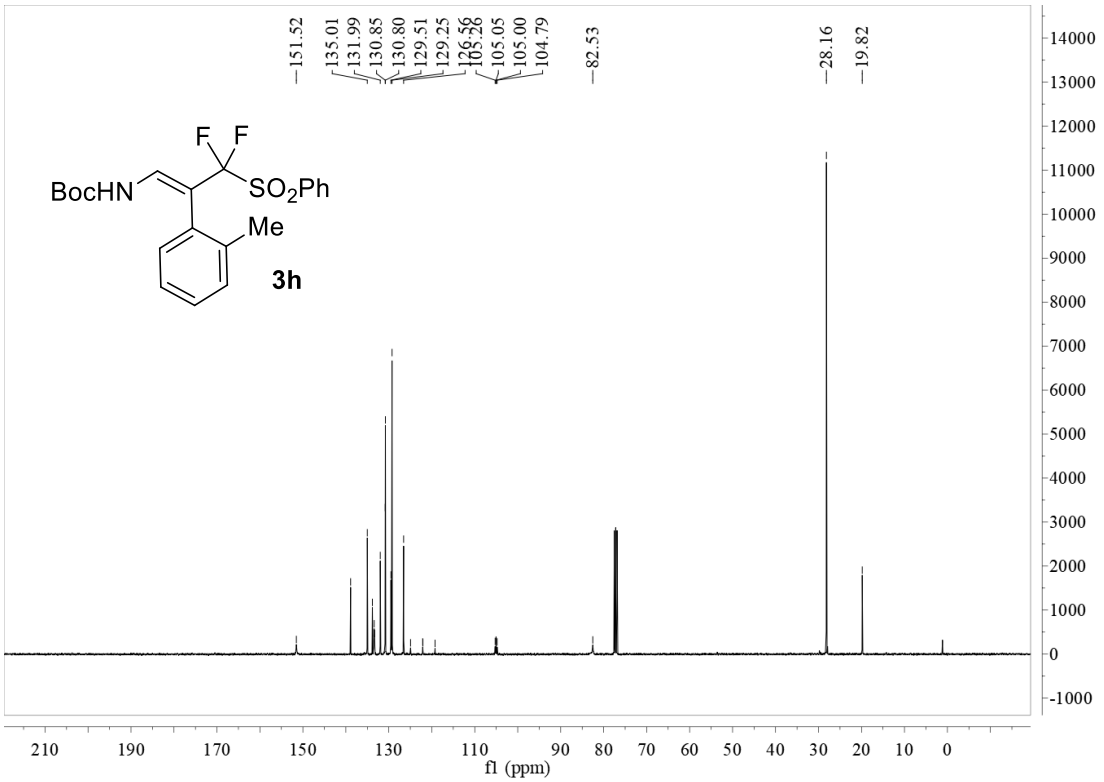
SO2Ph
Me
3h
fl (ppm)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129.51
129.25
105.05
105.00
104.79
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28.16
19.82
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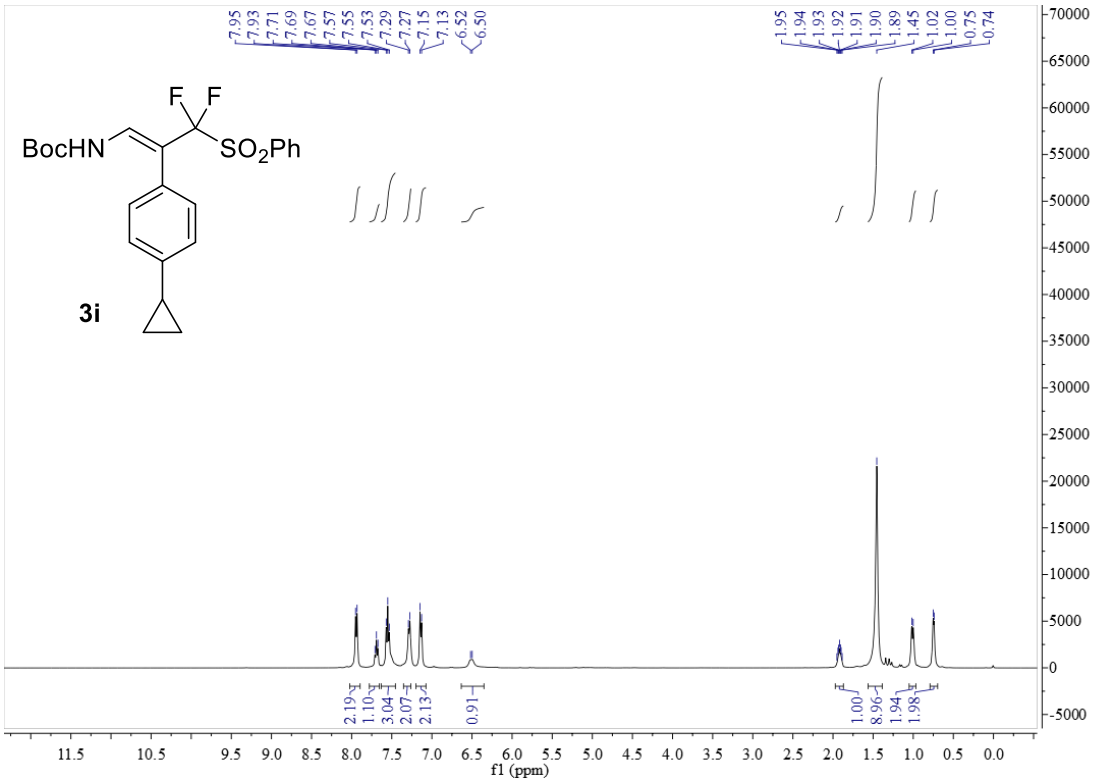
BocHN
SO2Ph
Me
3h
fl (ppm)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7.93
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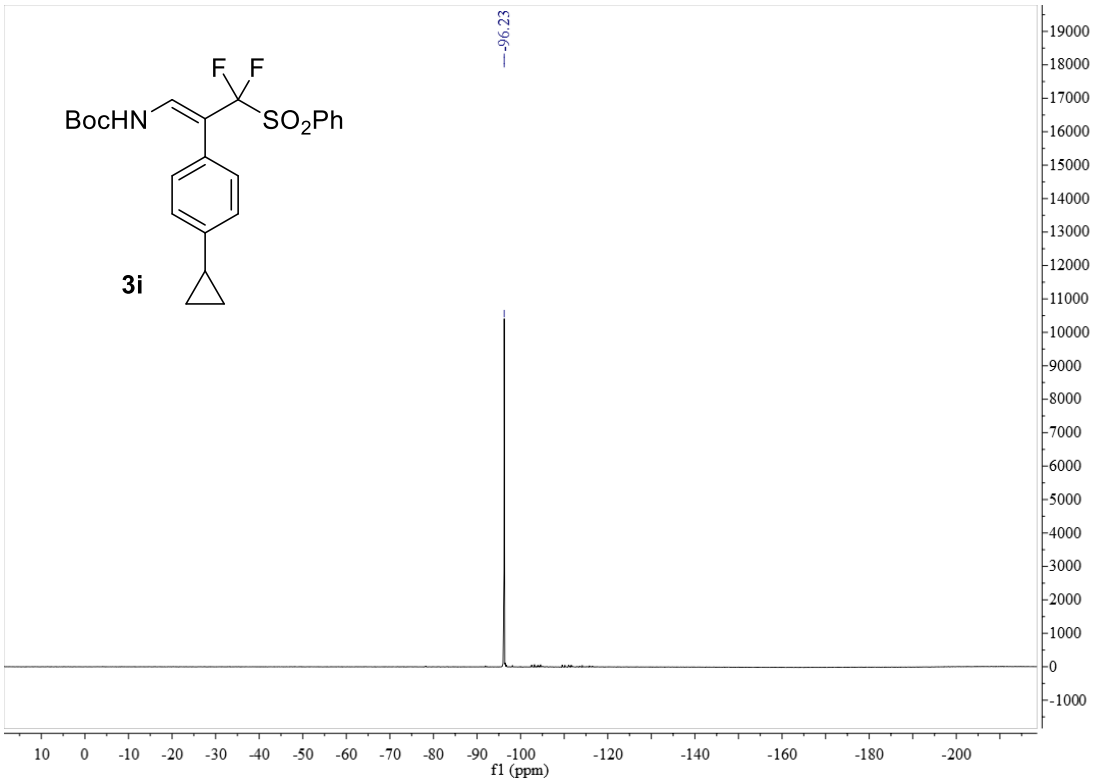
7.27
7.15
7.13
6.52
6.50
1.95
1.94
1.93
1.92
1.91
1.90
1.89
1.45
1.02
1.00
0.75
0.74
F F
BocHN
SO2Ph
3i
2.19
1.10
3.04
2.07
2.13
0.91
1.00
8.96
1.94
1.98
fl (ppm)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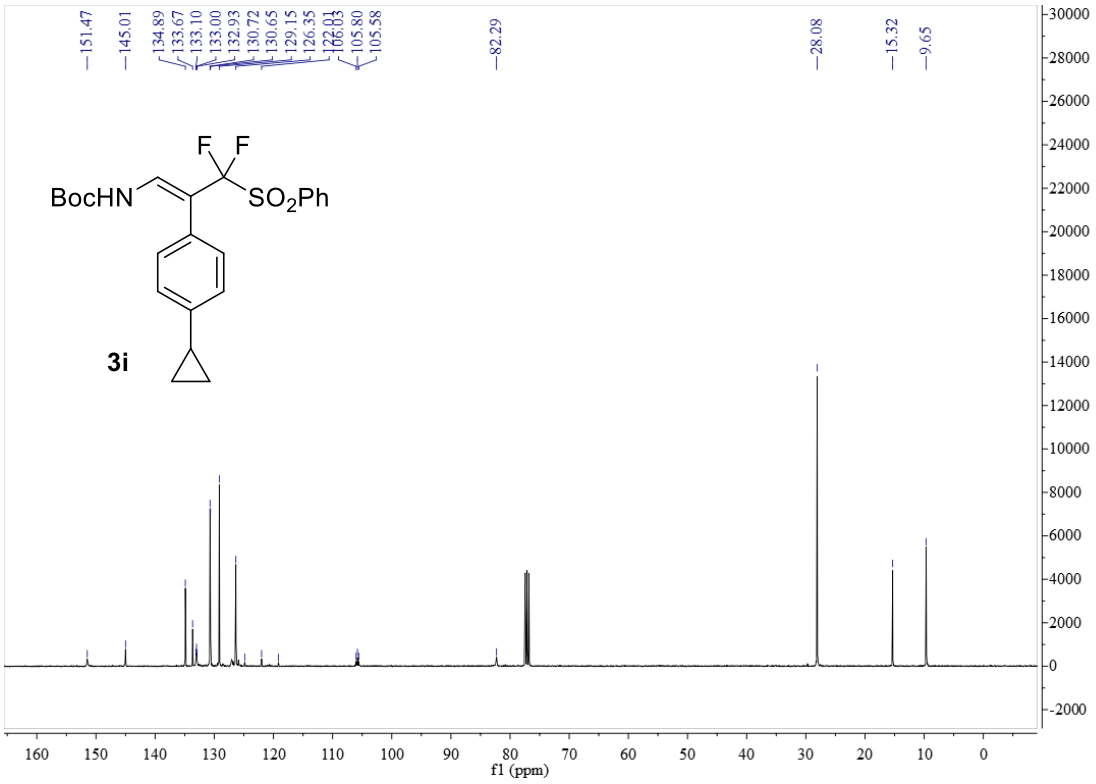
SO2Ph
3i
-96.23
f1 (ppm)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133.00
132.93
130.72
130.65
129.15
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105.58
82.29
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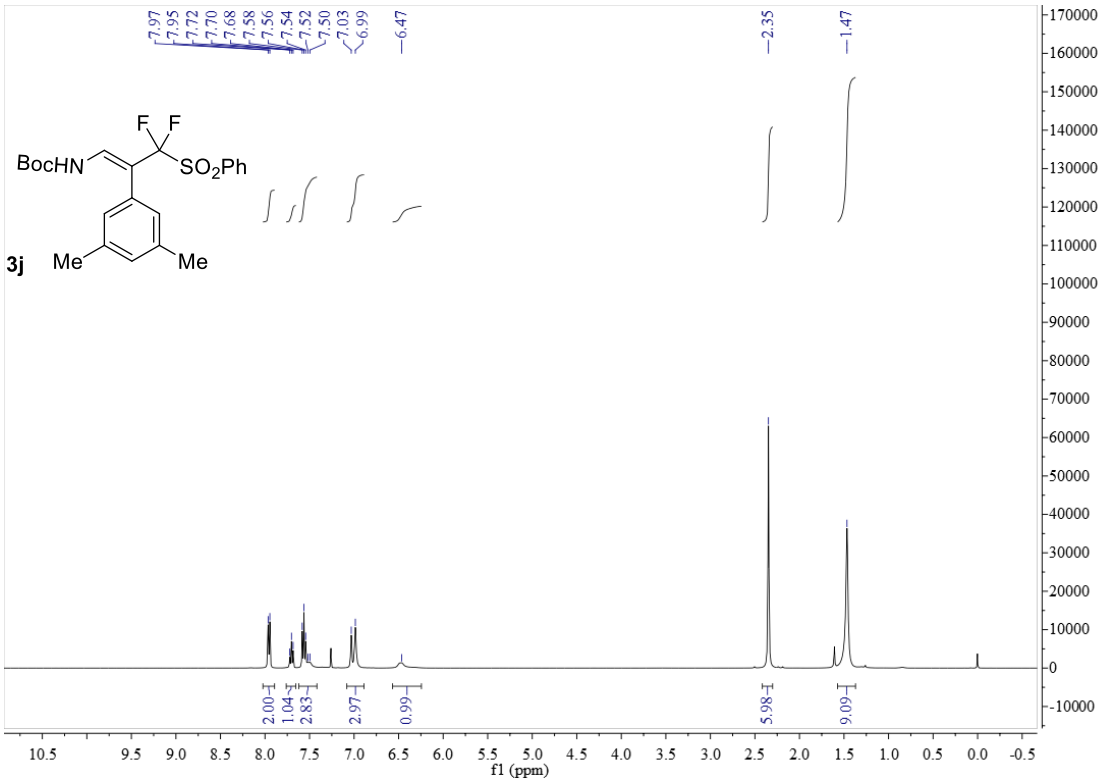
15.32
9.65
F F
BocHN
SO2Ph
3i
f1 (ppm)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7.50
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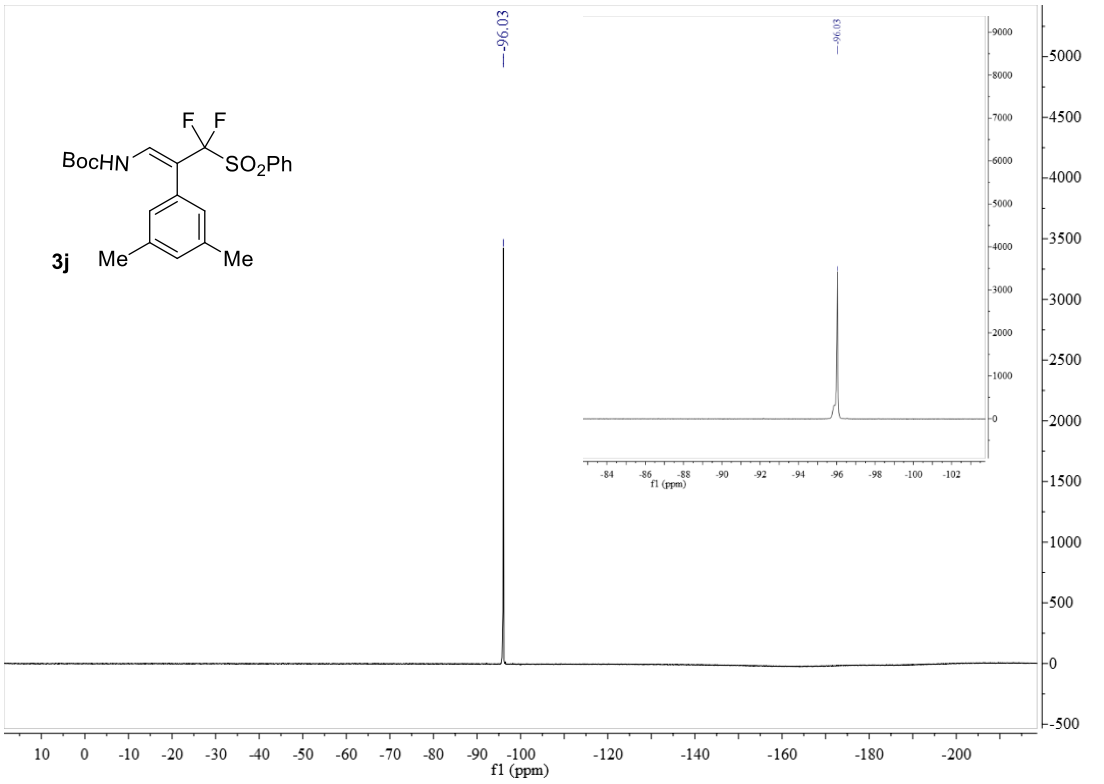
6.47
2.35
1.47
F F
BocHN
SO2Ph
3j
Me
Me
2.00
1.04
2.83
2.97
0.99
5.98
9.09
f1 (ppm)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SO2Ph
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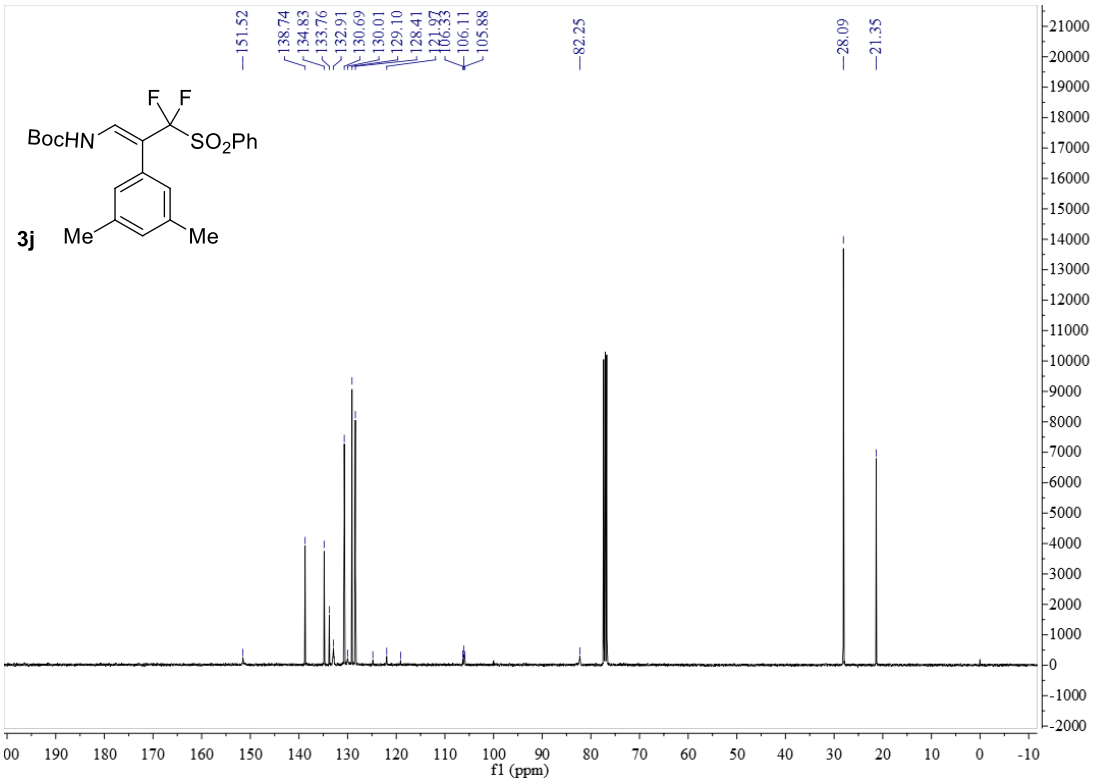
Me
Me
f1 (ppm)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129.10
128.41
121.97
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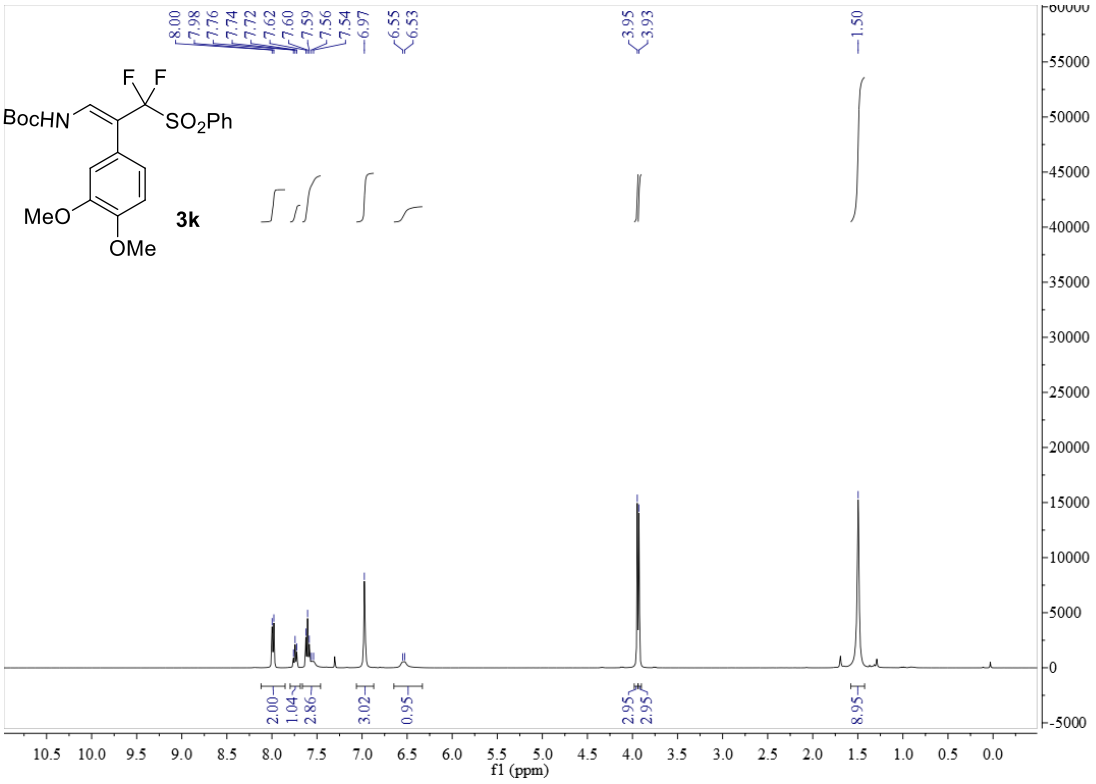
82.25
28.09
21.35
F F
BocHN
SO2Ph
3j
Me
Me
f1 (ppm)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7.60
7.59
7.56
7.54
6.97
6.55
6.53
3.95
3.93
1.50
F F
BocHN
SO2Ph
MeO
OMe
3k
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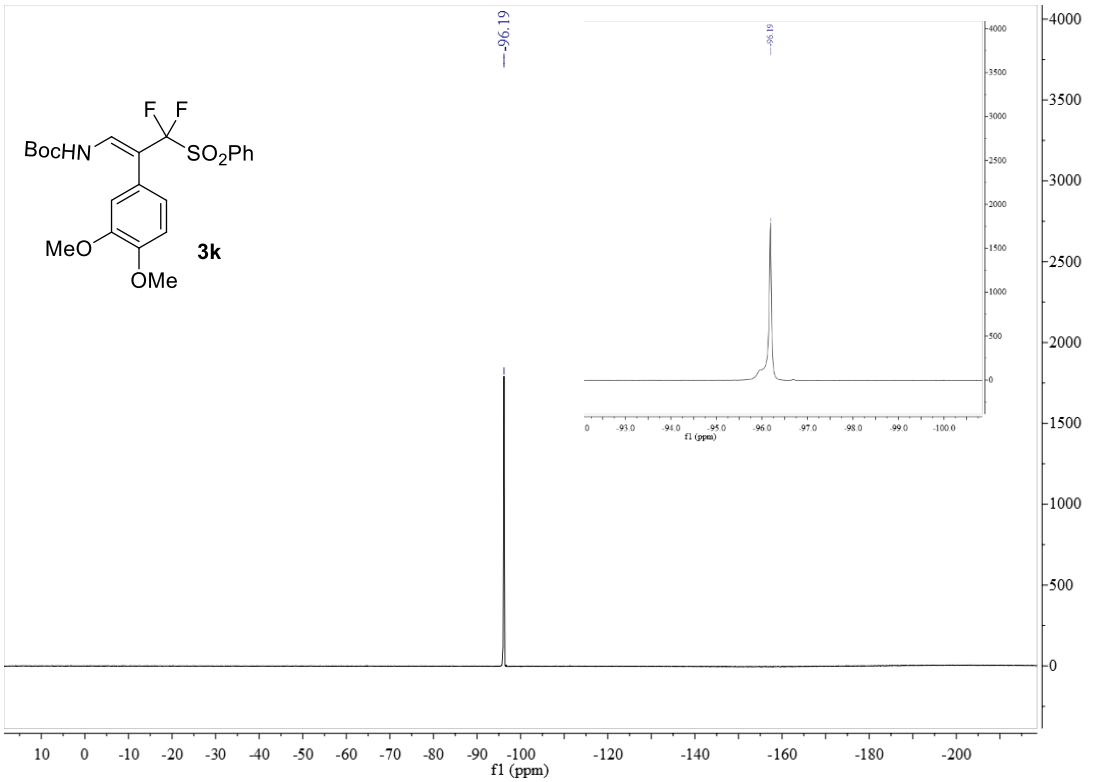
1.04
2.86
3.02
0.95
2.95
2.95
8.95
f1 (ppm)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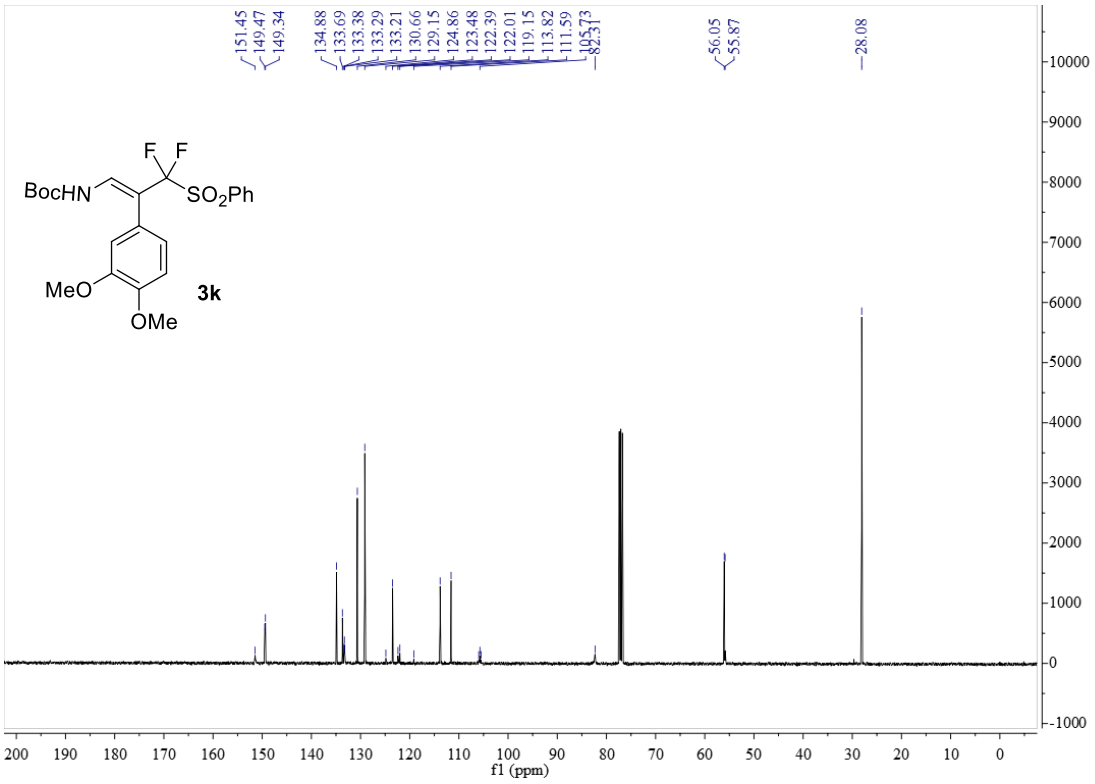
SO2Ph
MeO
OMe
3k
-96.19
f1 (ppm)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122.39
122.01
119.15
113.82
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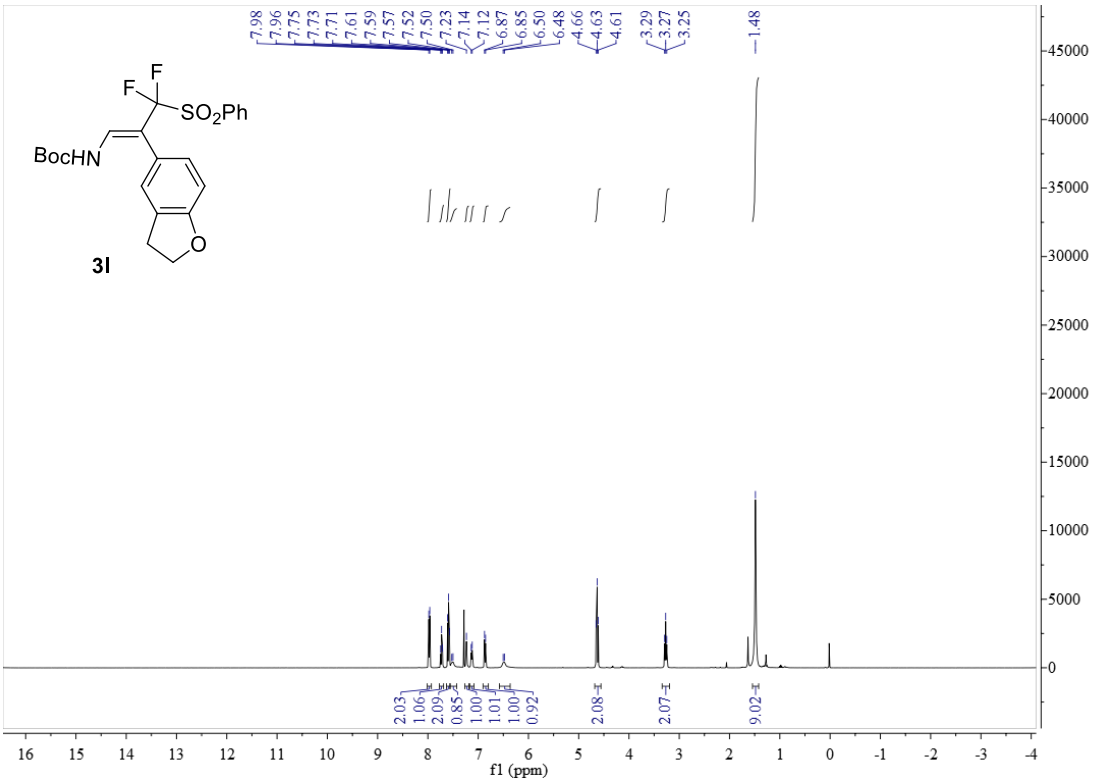
56.05
55.87
28.08
F F
BocHN
SO2Ph
MeO
OMe
3k
f1 (ppm)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7.12
6.87
6.85
6.50
6.48
4.66
4.63
4.61
3.29
3.27
3.25
1.48
F
F
SO2Ph
BocHN
O
3l
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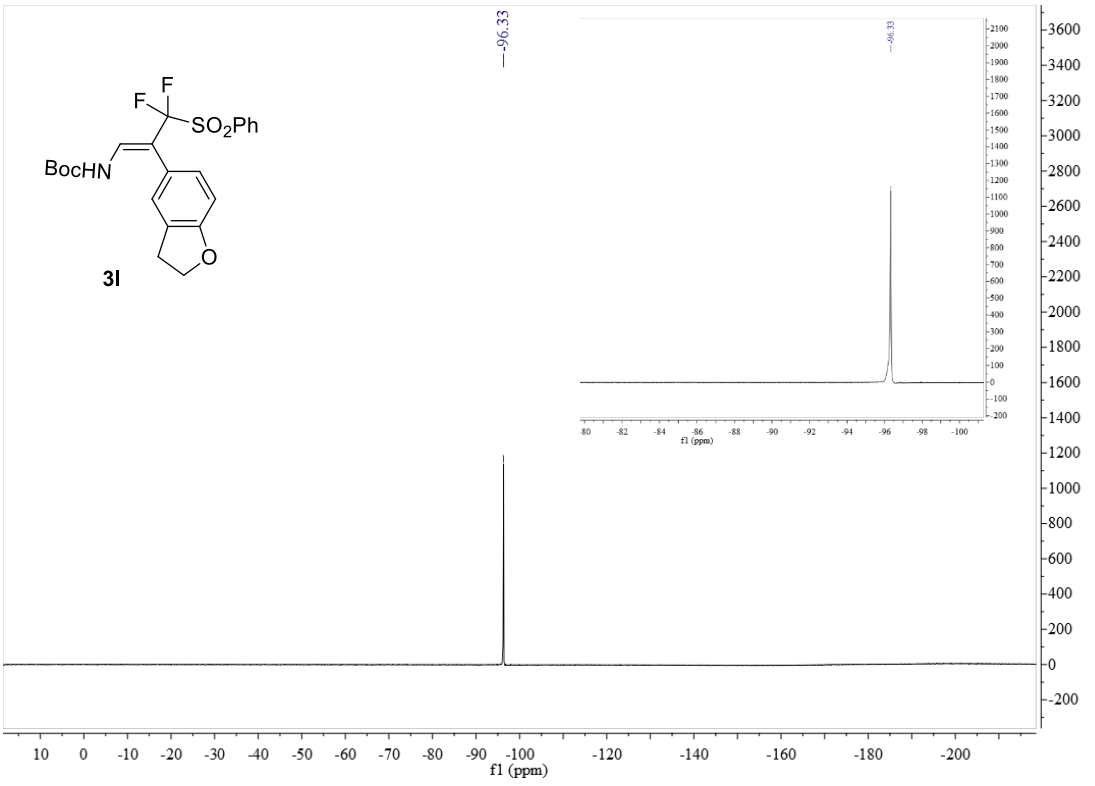
0.85
1.00
1.01
1.00
0.92
2.08
2.07
9.02
f1 (ppm)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F
SO2Ph
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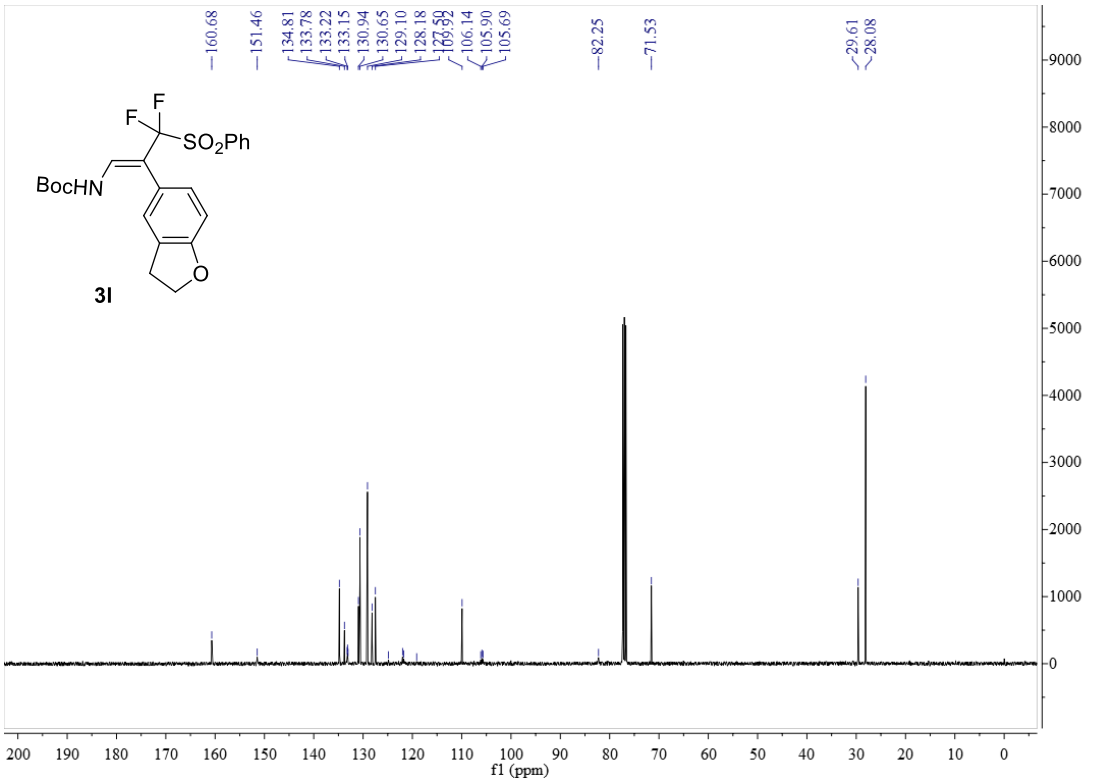
O
3l
f1 (ppm)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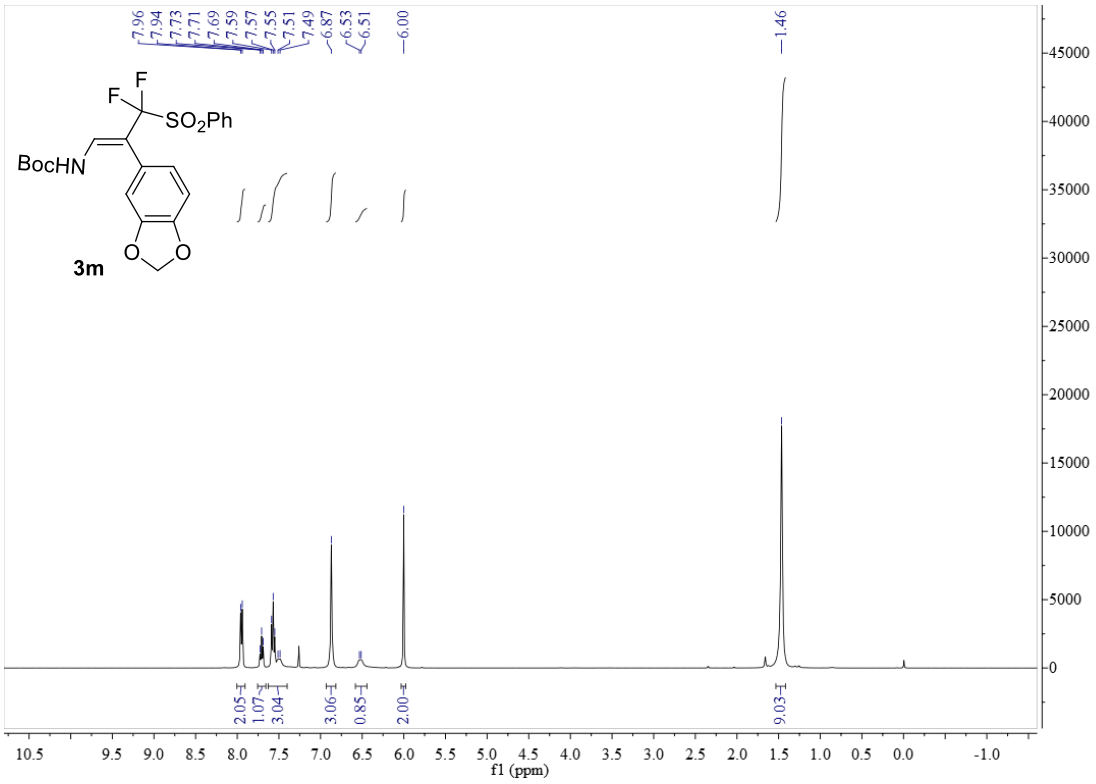
29.61
28.08
F
F
SO2Ph
BocHN
O
3l
f1 (ppm)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7.49
6.87
6.53
6.51
6.00
1.46
F
F
SO2Ph
BocHN
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O
3m
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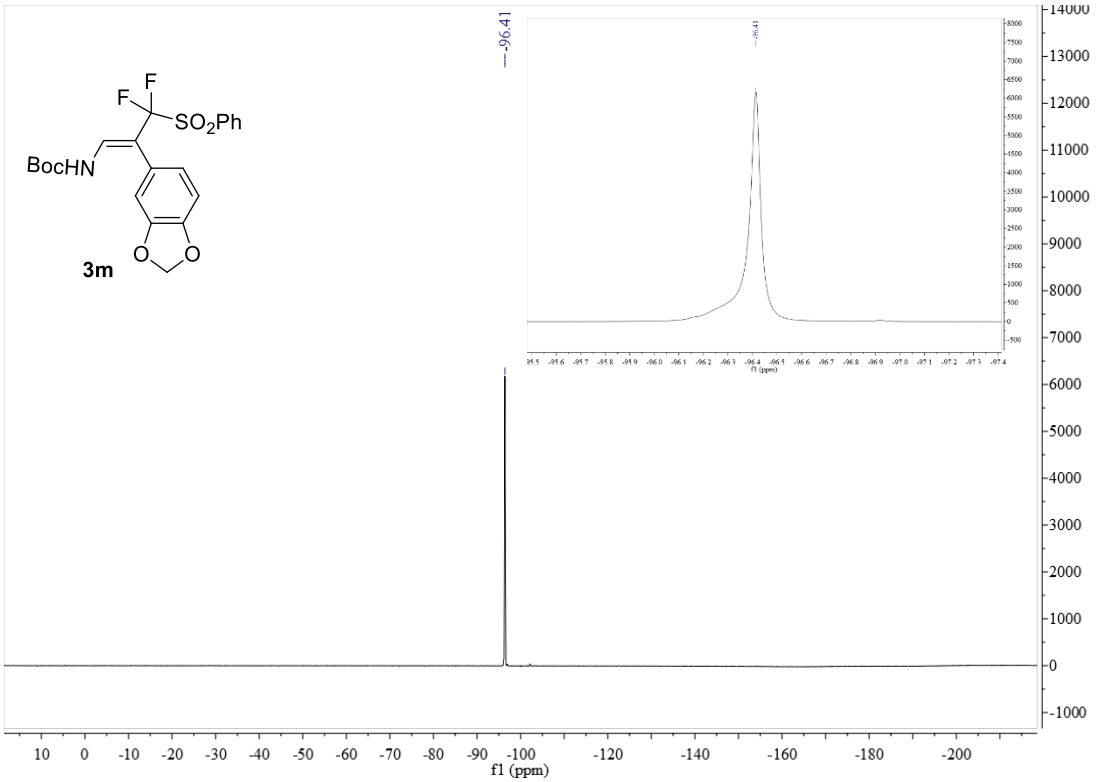
1.07
3.04
3.06
0.85
2.00
9.03
f1 (ppm)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BocHN
O
O
3m
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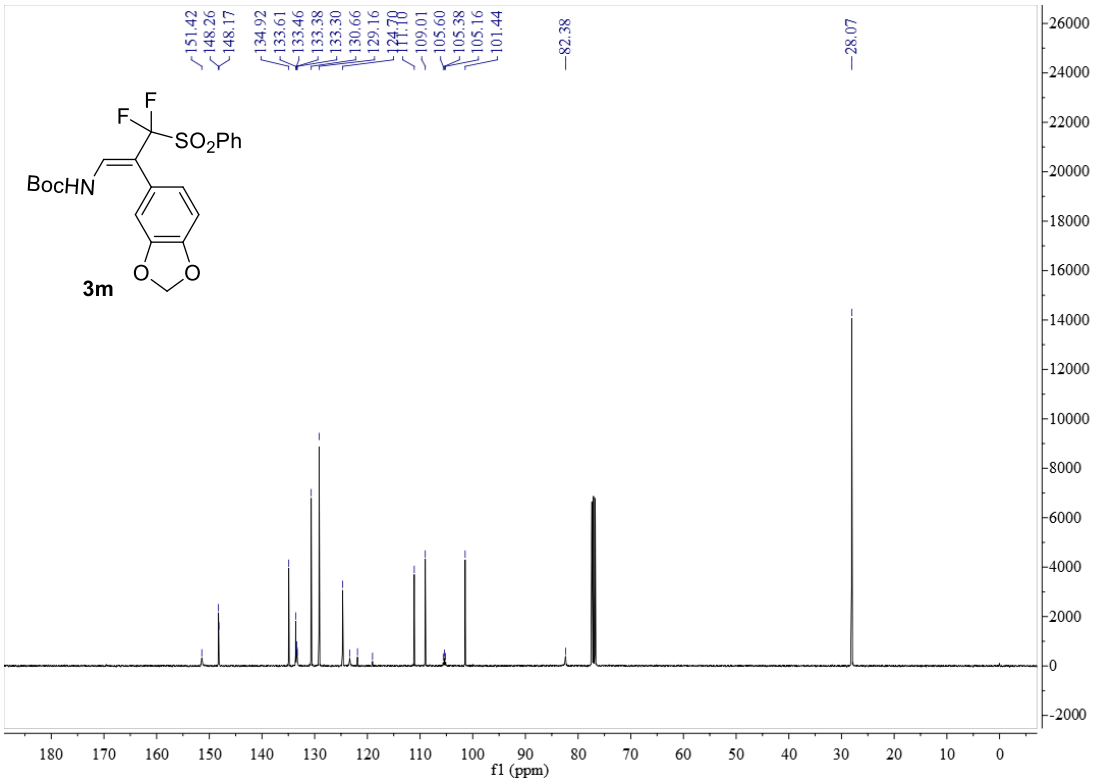
f1 (ppm)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109.01
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101.44
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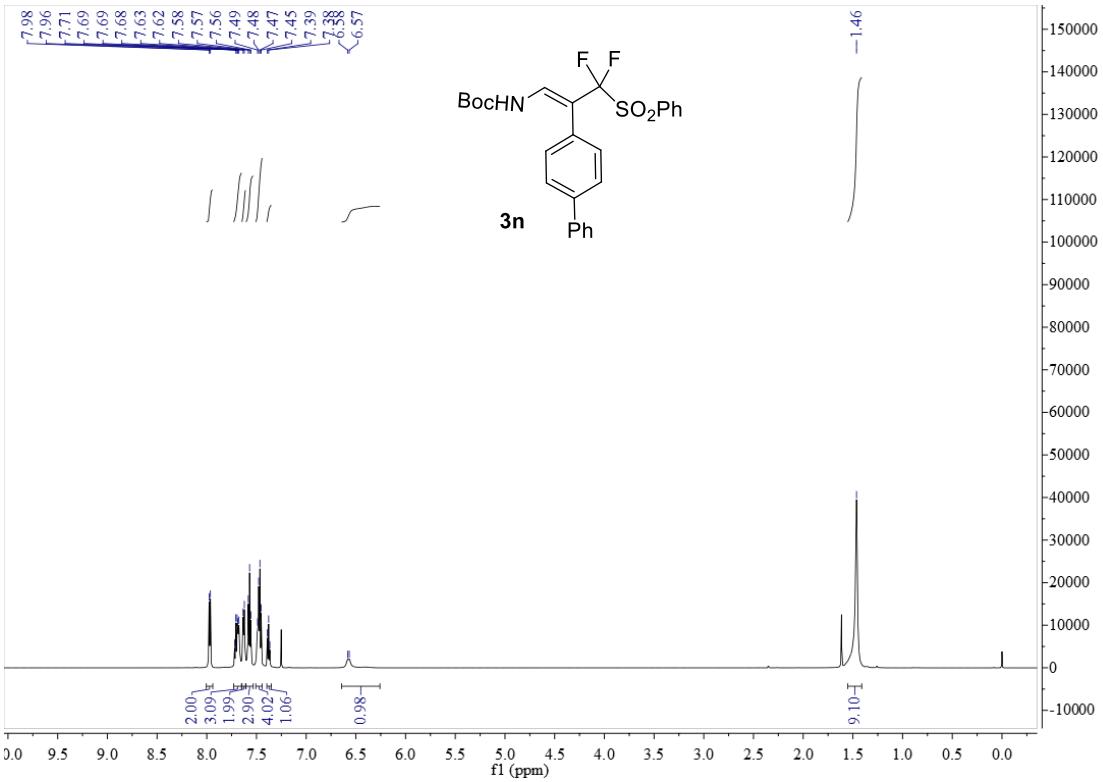
F
F
SO2Ph
BocHN
O
O
3m
f1 (ppm)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7.48
7.47
7.45
7.39
7.38
6.58
6.57
1.46
F F
BocHN
SO2Ph
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Ph
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2.90
4.02
1.06
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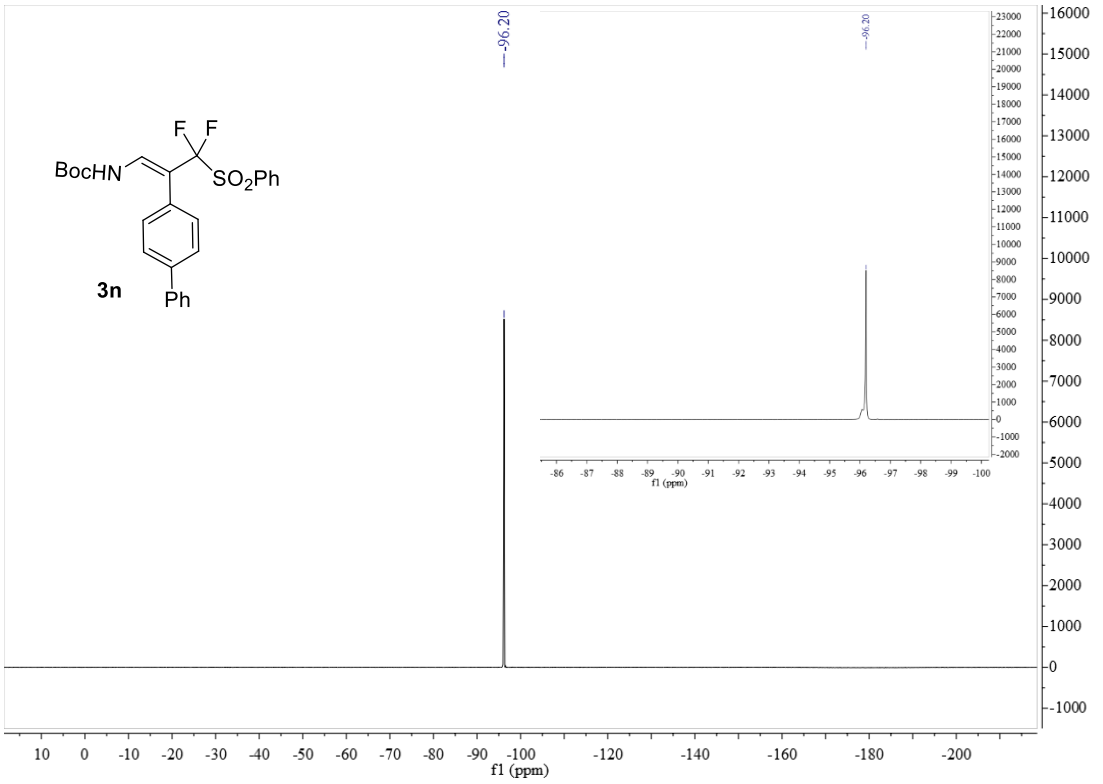
9.10
f1 (ppm)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SO2Ph
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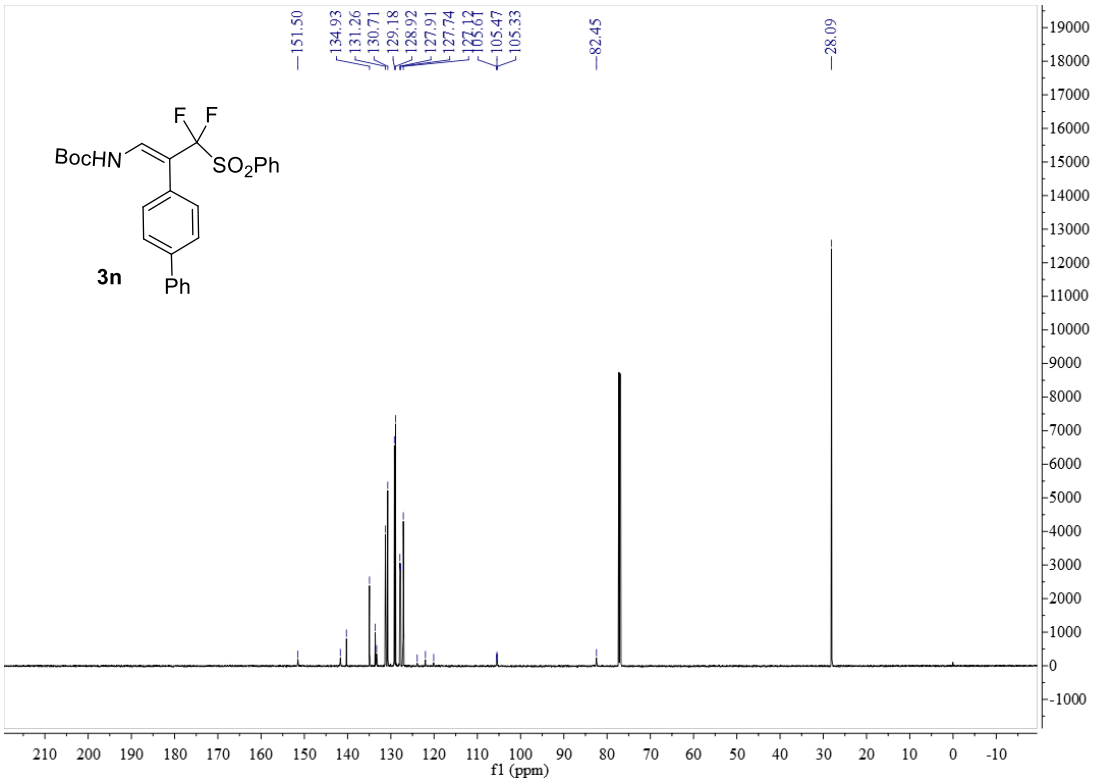
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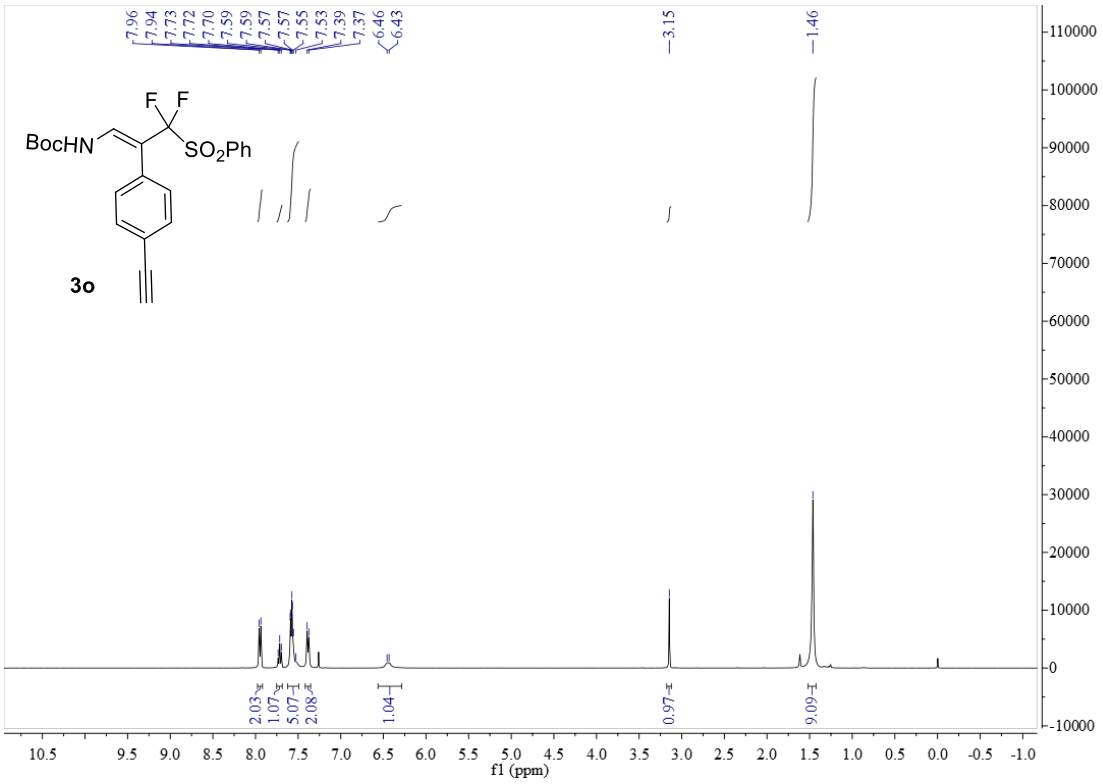
105.47
105.33
82.45
28.09
F F
BocHN
SO2Ph
Ph
3n
f1 (ppm)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7.39
7.37
6.46
6.43
3.15
1.46
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BocHN
SO2Ph
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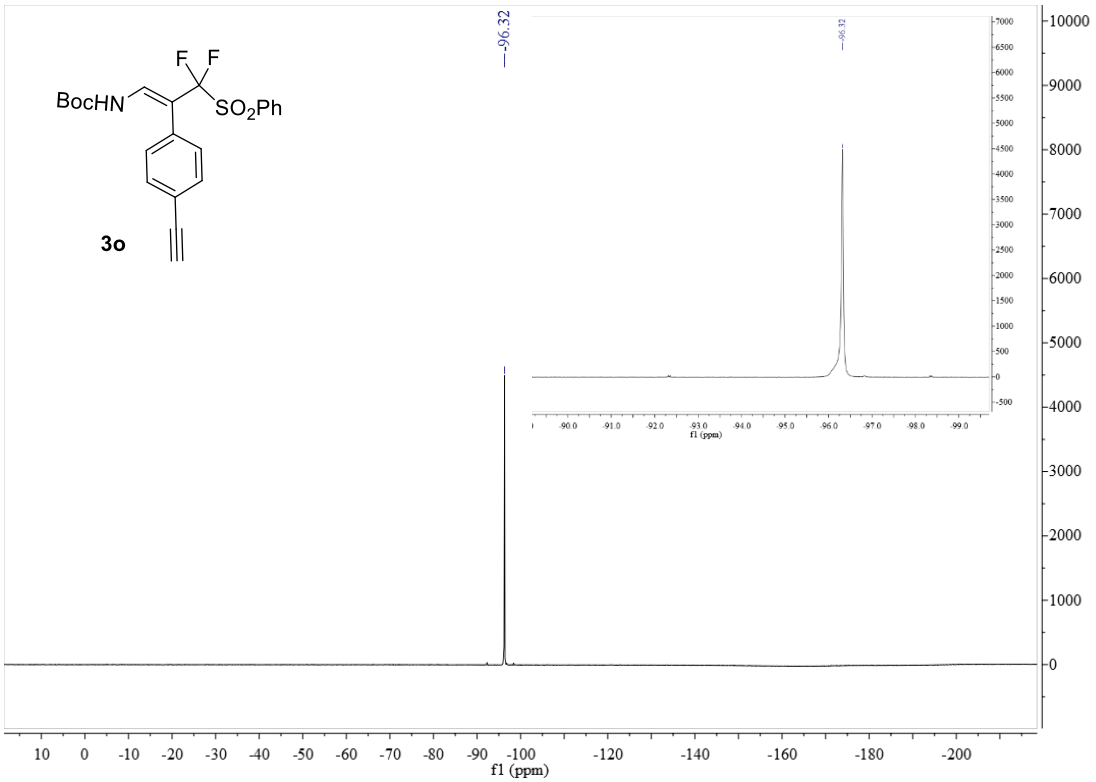
1.07
5.07
2.08
1.04
0.97
9.09
f1 (ppm)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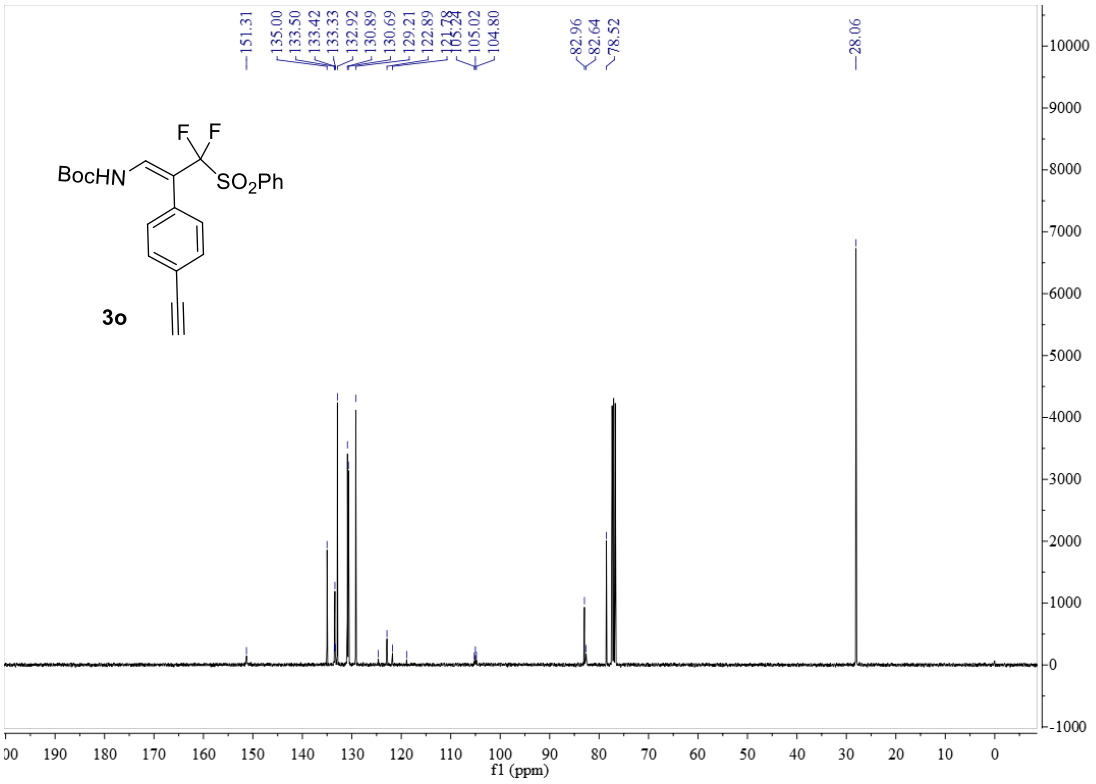
SO2Ph
3o
-96.32
f1 (ppm)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121.78
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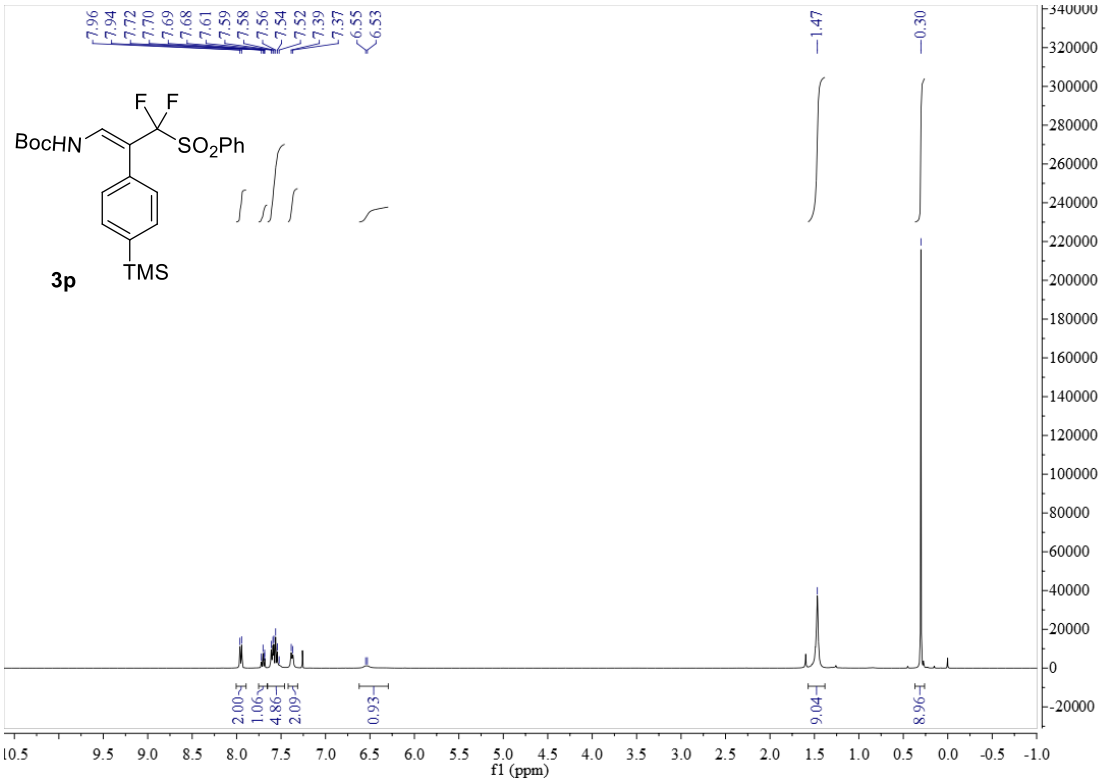
F F
BocHN
SO2Ph
3o
f1 (ppm)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7.58
7.56
7.54
7.52
7.39
7.37
6.55
6.53
1.47
0.30
F F
BocHN
SO2Ph
TMS
3p
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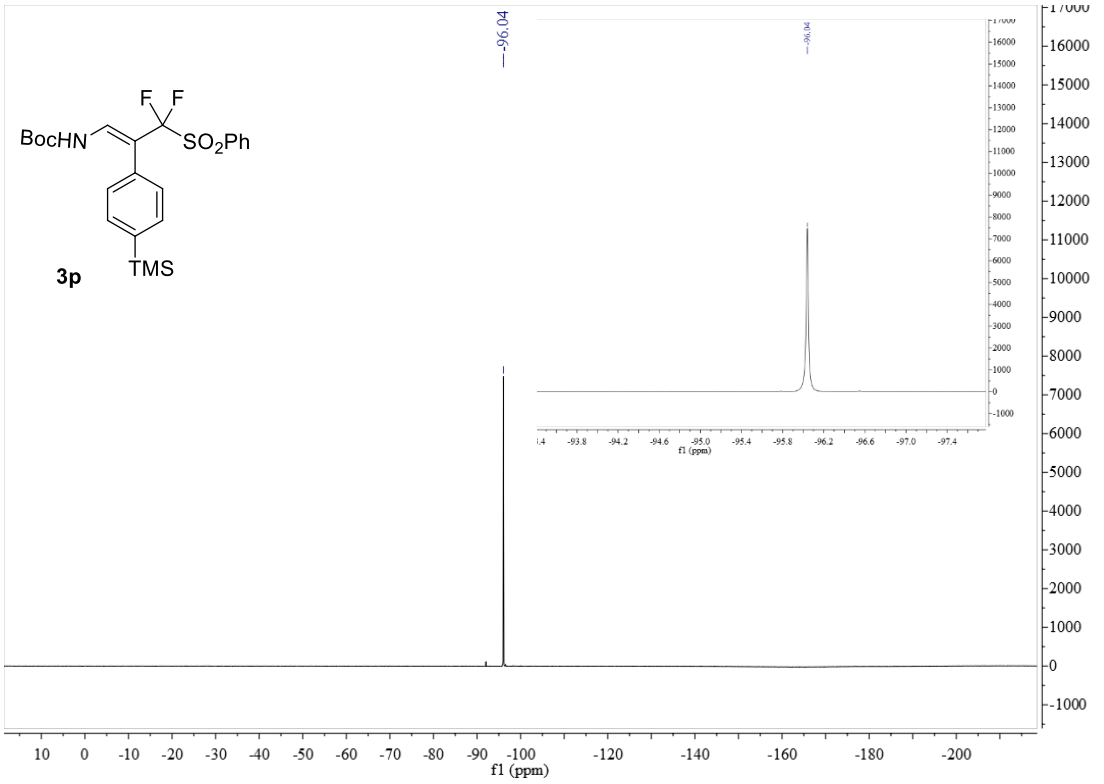
1.06
4.86
2.09
0.93
9.04
8.96
f1 (ppm)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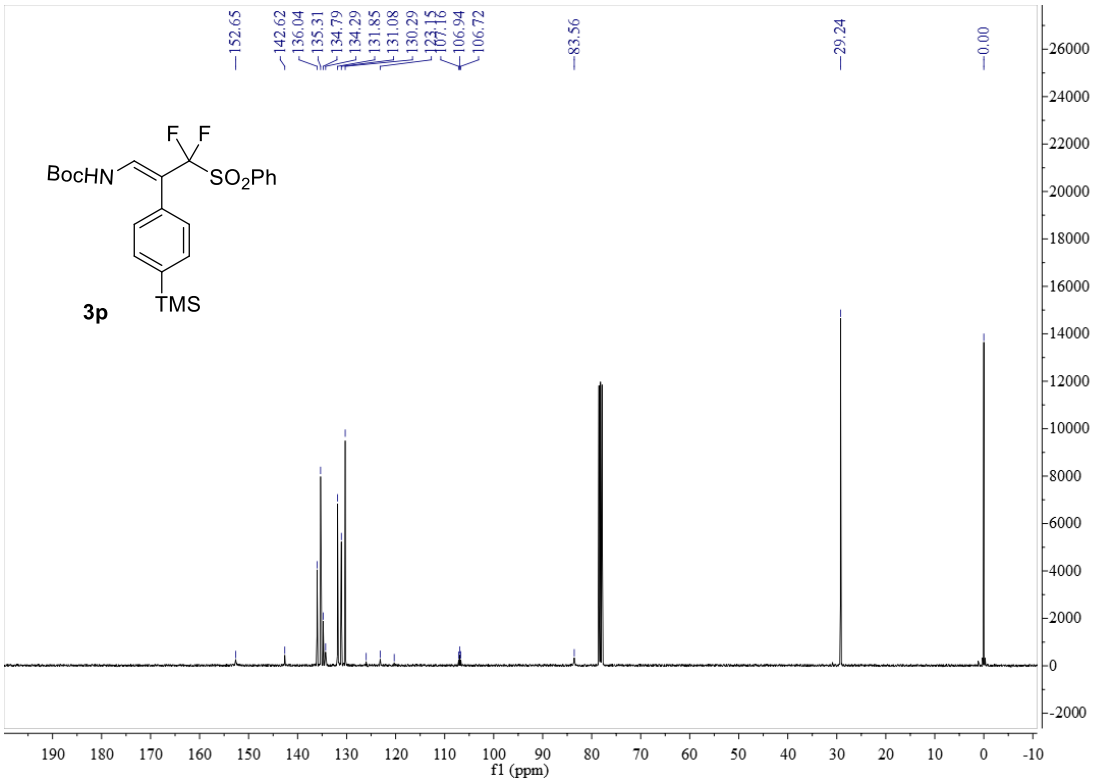
SO2Ph
TMS
3p
f1 (ppm)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134.29
131.85
131.08
130.29
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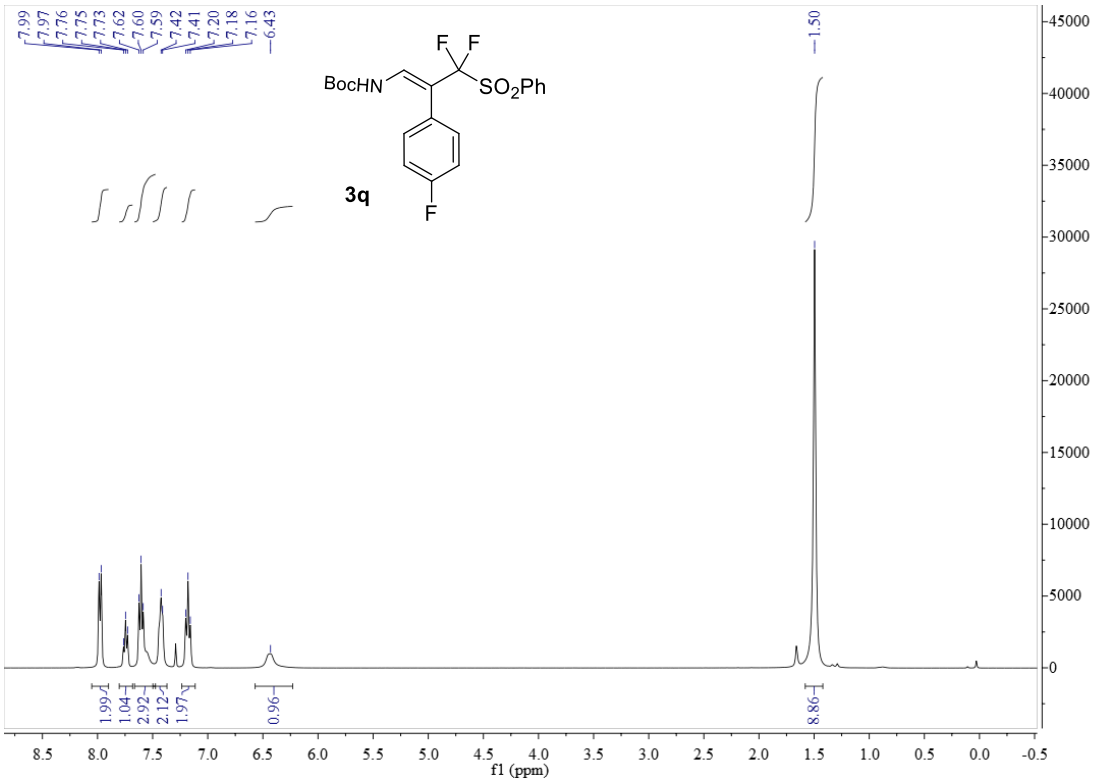
106.72
83.56
29.24
0.00
F F
BocHN
SO2Ph
TMS
3p
f1 (ppm)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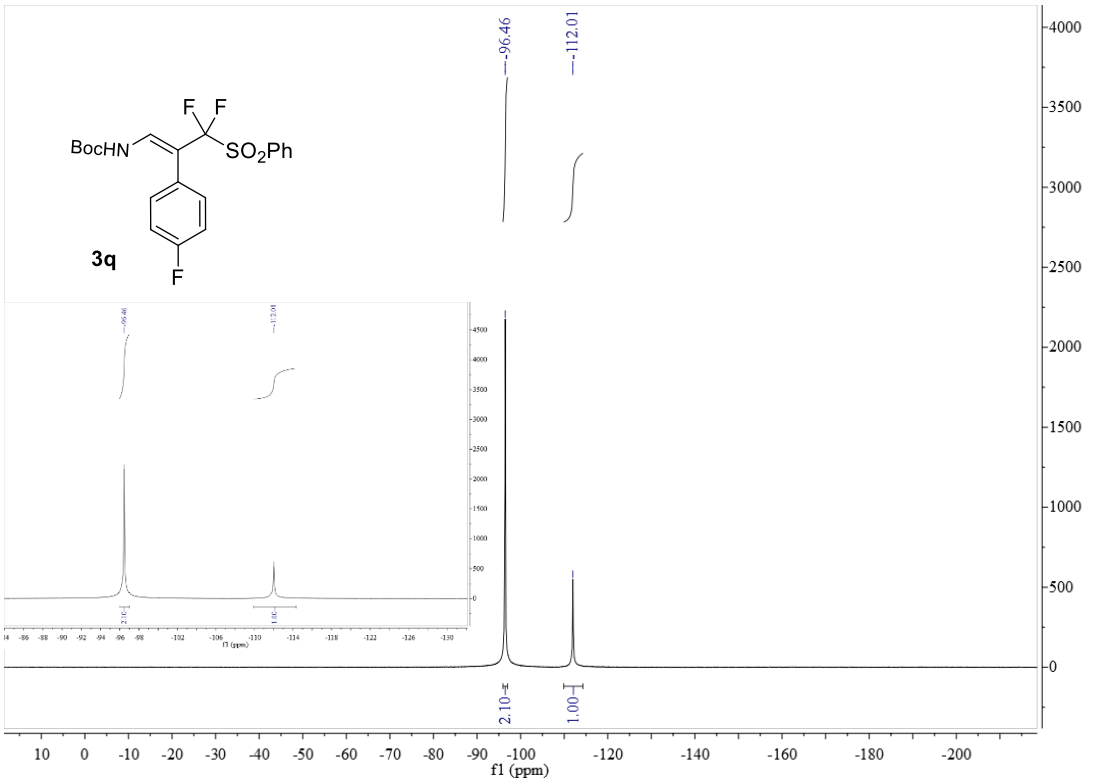
7.62
7.60
7.59
7.42
7.41
7.20
7.18
7.16
6.43
1.50
F F
BocHN
SO2Ph
F
3q
1.99
1.04
2.92
2.12
1.97
0.96
8.86
f1 (ppm)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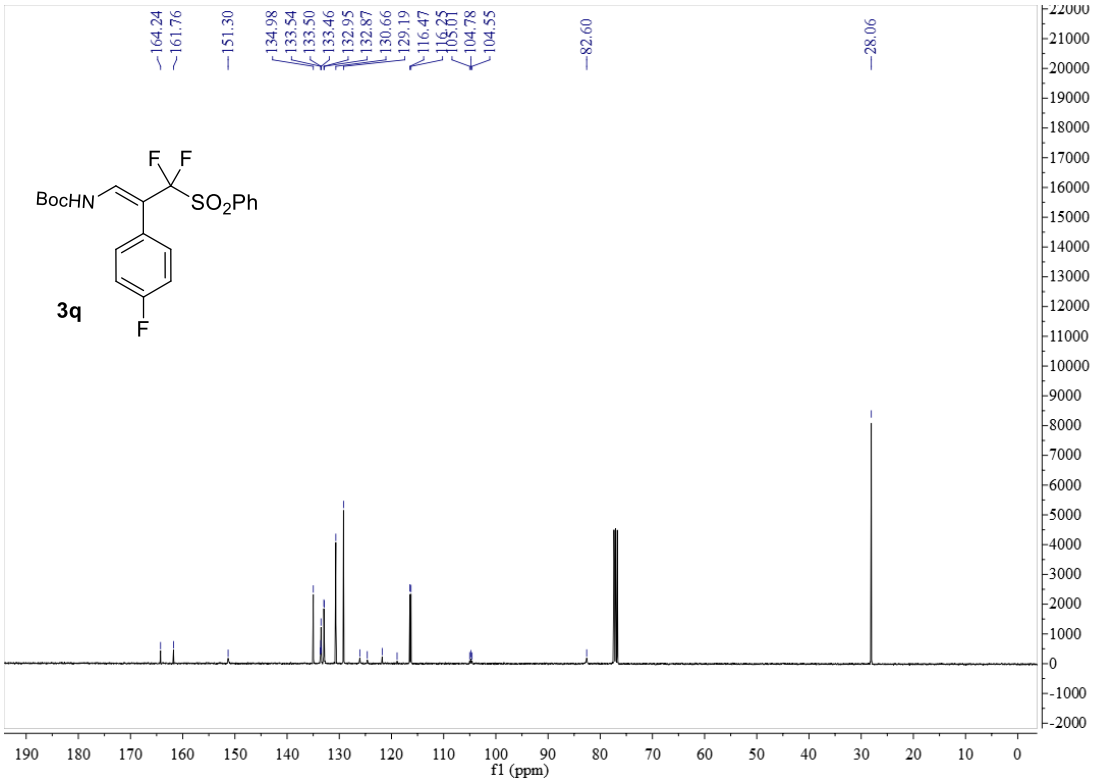
BocHN
SO2Ph
F
3q
-96.46
-112.01
2.10
1.00
f1 (ppm)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129.19
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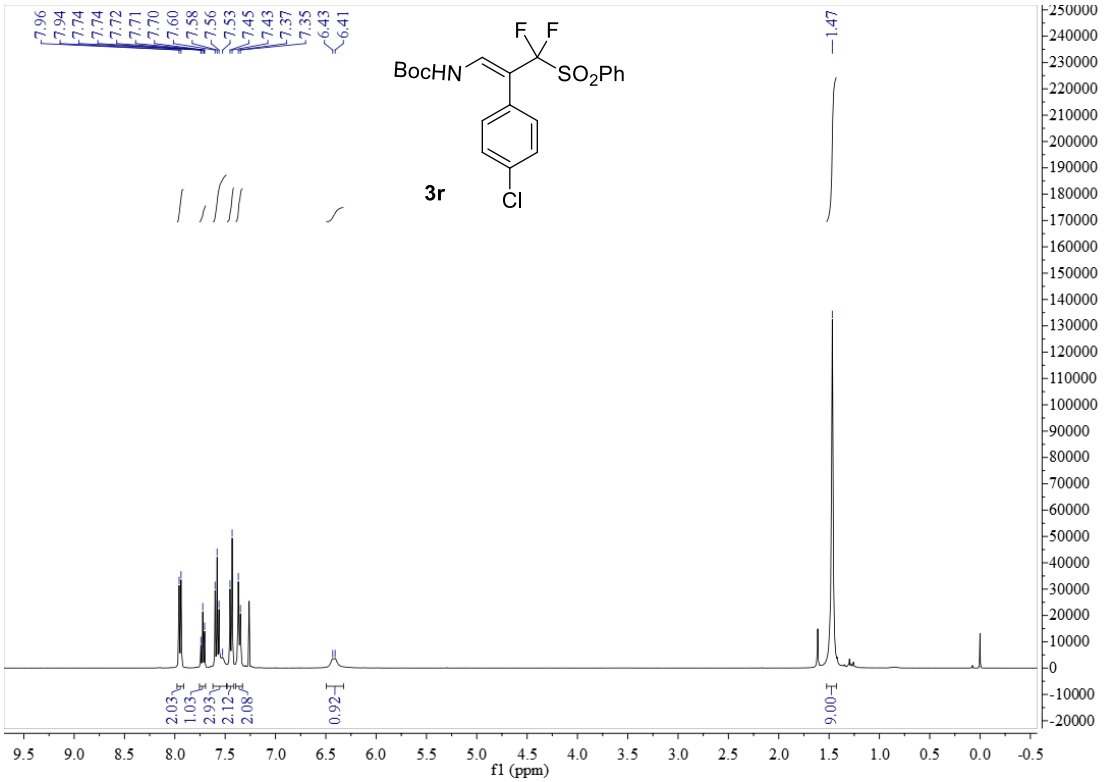
104.55
82.60
28.06
F F
BocHN
SO2Ph
F
3q
f1 (ppm)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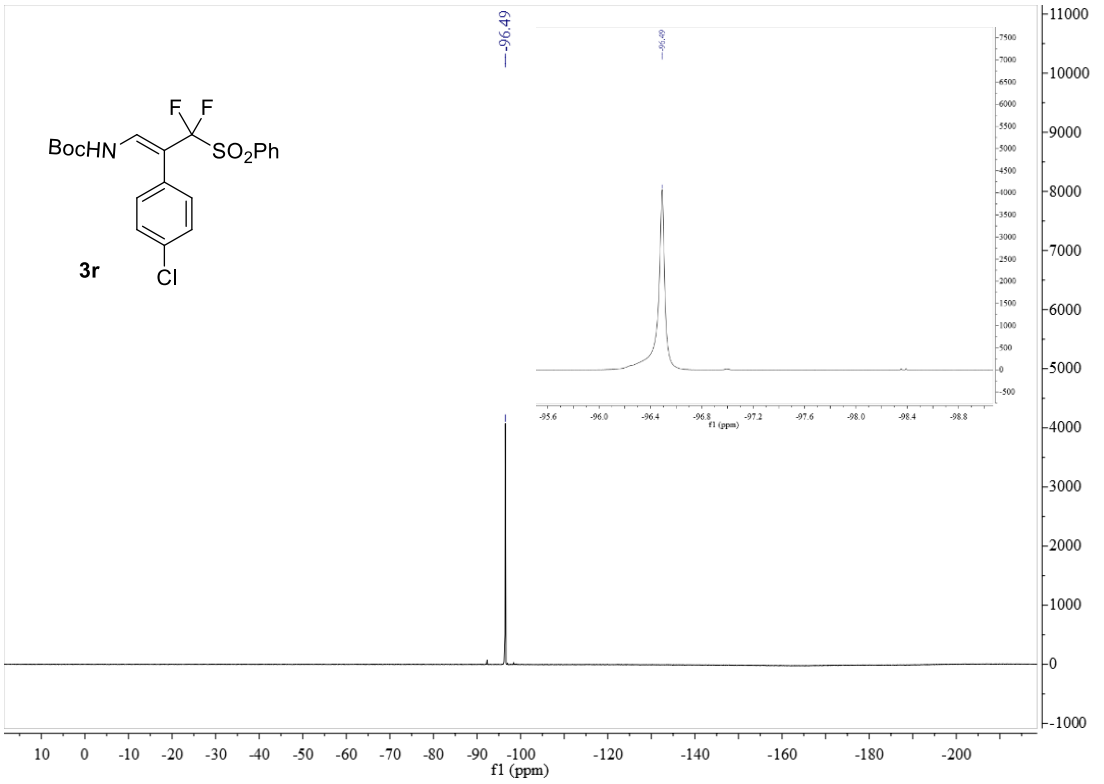
7.71
7.70
7.60
7.58
7.56
7.53
7.45
7.43
7.37
7.35
6.43
6.41
1.47
F F
BocHN
SO2Ph
3r
Cl
2.03
1.03
2.93
2.12
2.08
0.92
9.00
f1 (ppm)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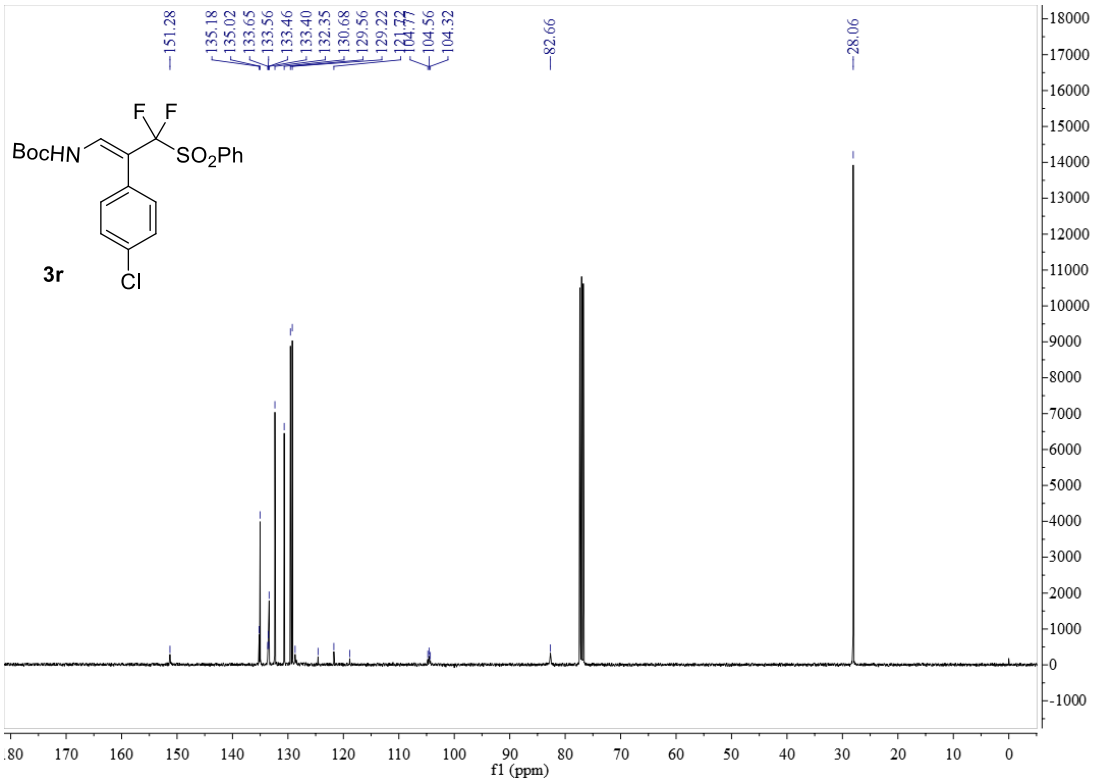
F F
BocHN
SO2Ph
3r
Cl
f1 (ppm)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104.32
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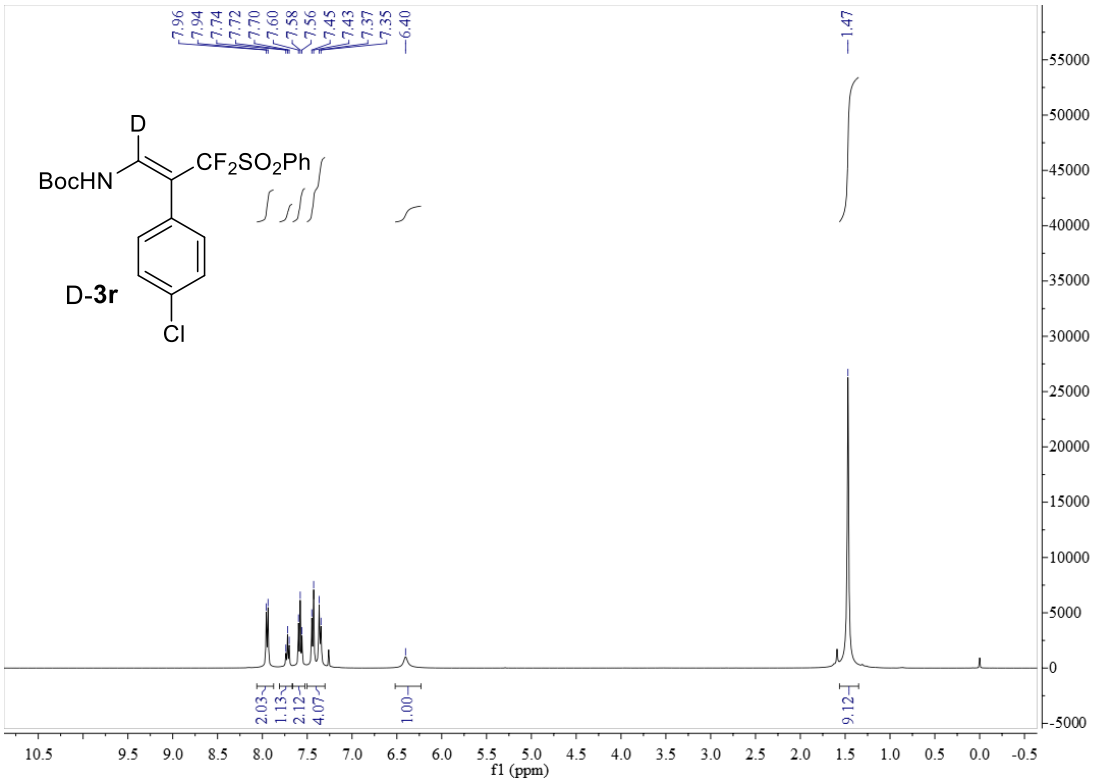
F
F
BocHN
SO2Ph
Cl
3r
f1 (ppm)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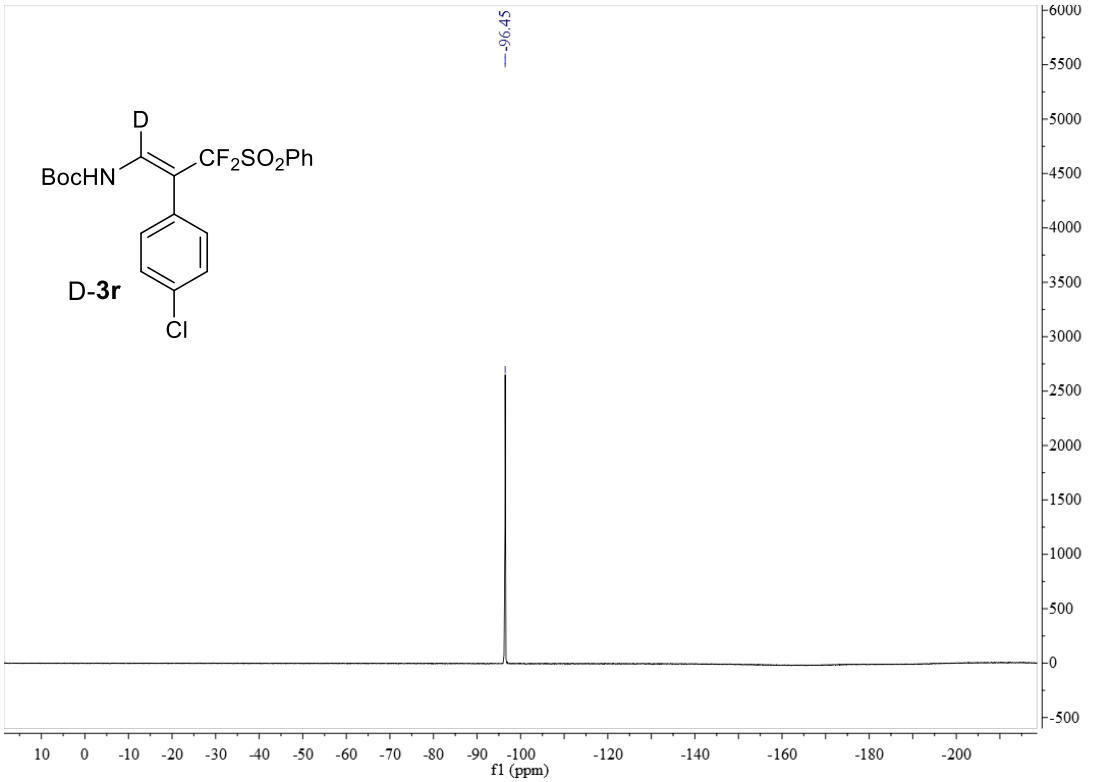
7.72
7.70
7.60
7.58
7.56
7.45
7.43
7.37
7.35
6.40
1.47
D
BocHN
CF2SO2Ph
Cl
D-3r
2.03
1.13
2.12
4.07
1.00
9.12
f1 (ppm)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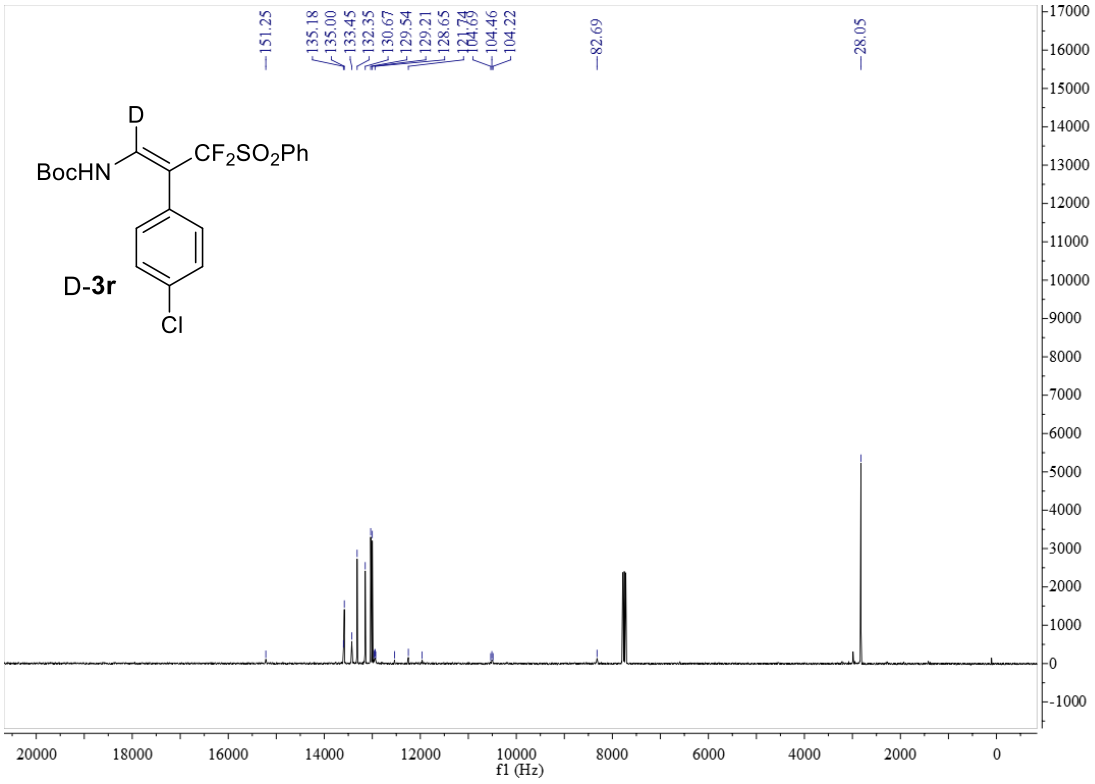
CF2SO2Ph
D-3r
Cl
f1 (ppm)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130.67
129.54
129.21
128.65
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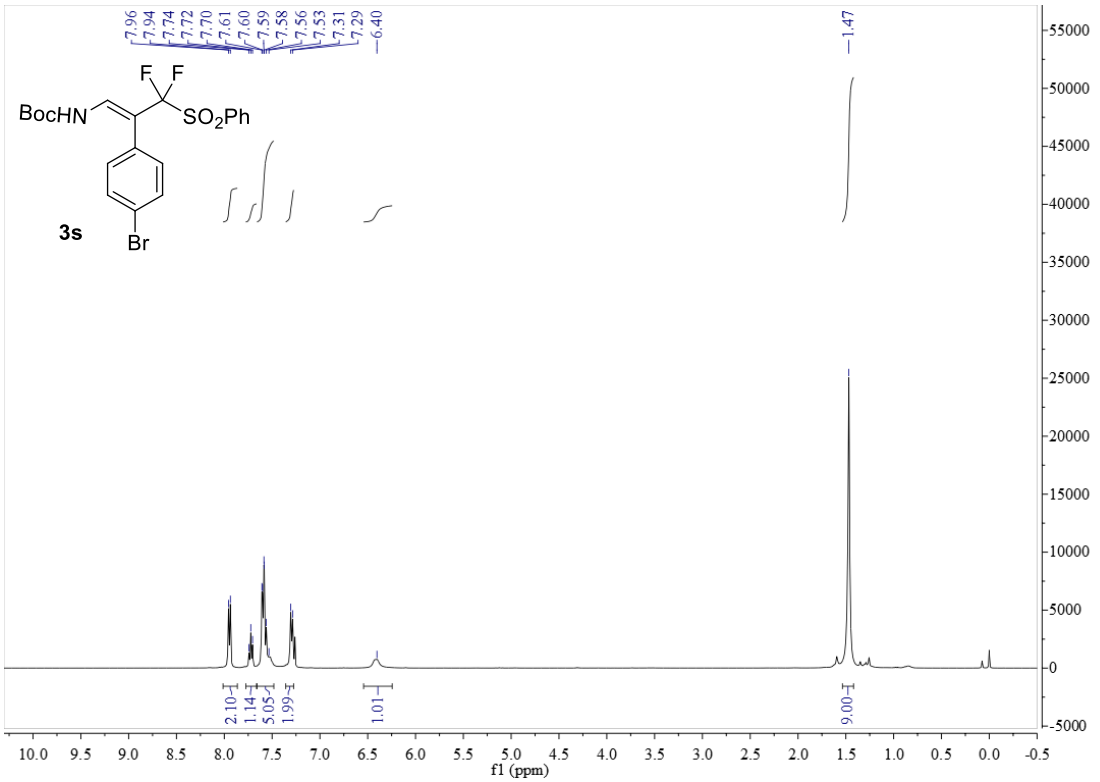
104.22
82.69
28.05
D
BocHN
CF2SO2Ph
D-3r
Cl
f1 (Hz)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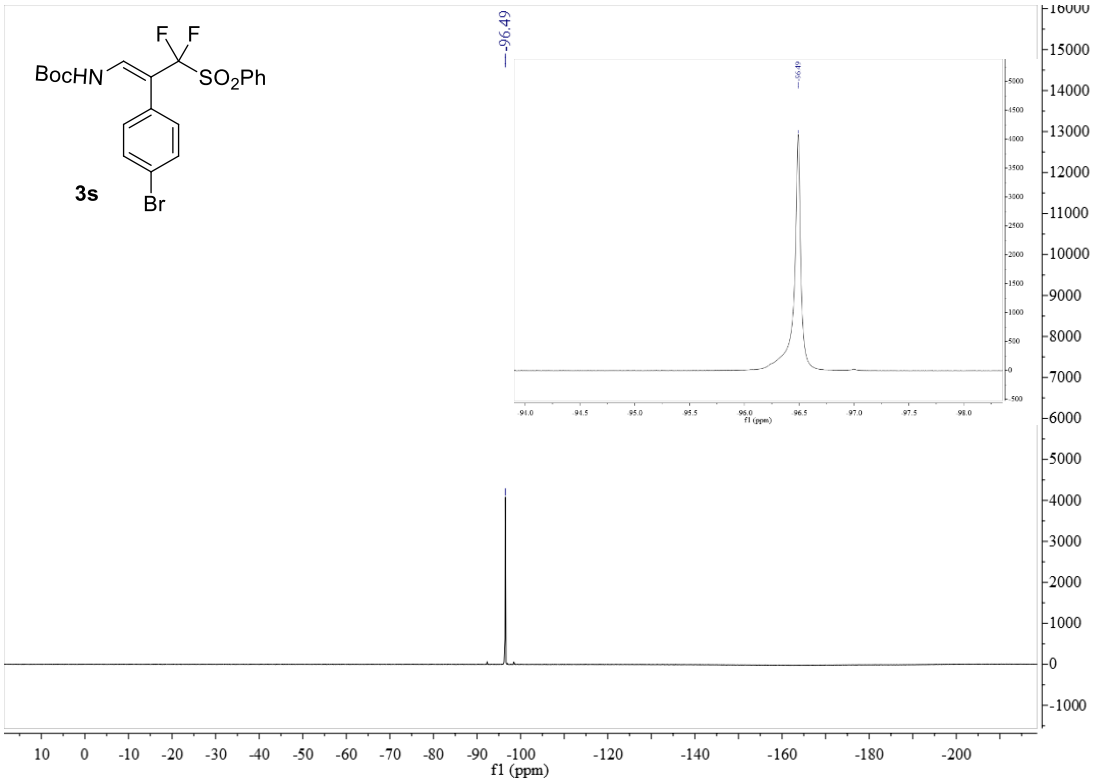
7.74
7.72
7.70
7.61
7.60
7.59
7.58
7.56
7.53
7.31
7.29
6.40
1.47
F F
BocHN
SO2Ph
3s
Br
2.10
1.14
5.05
1.99
1.01
9.00
f1 (ppm)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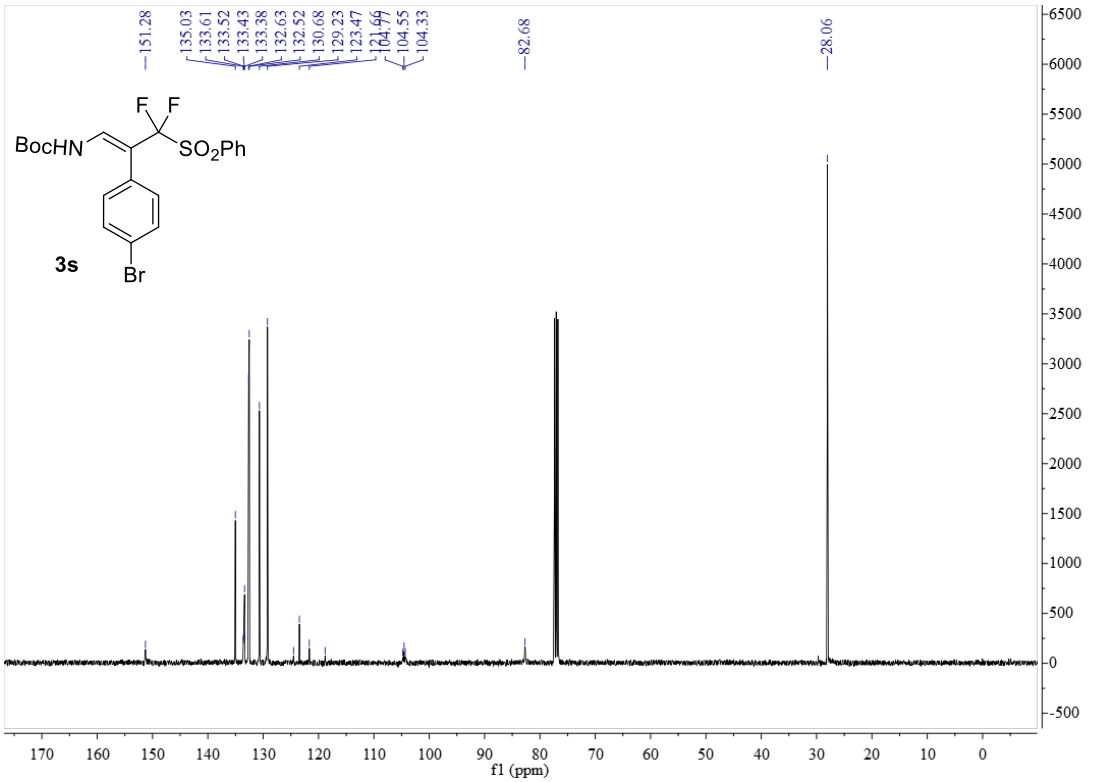
F F
BocHN
SO2Ph
3s
Br
f1 (ppm)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133.38
132.63
132.52
130.68
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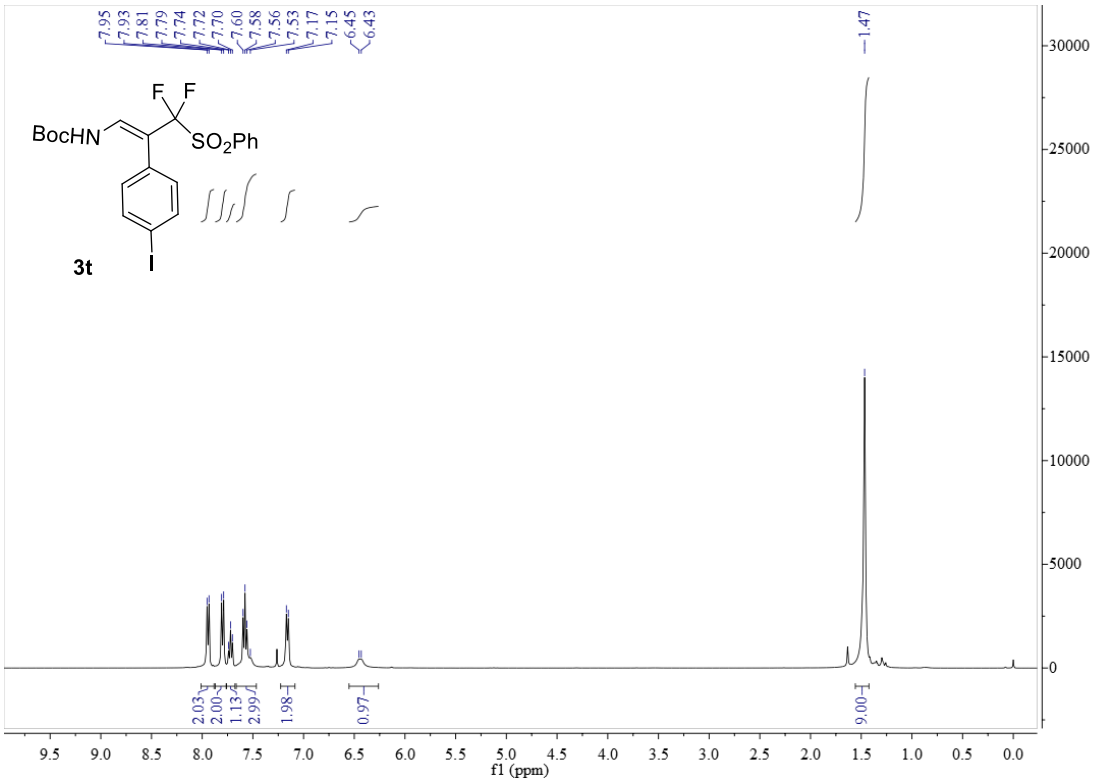
104.55
104.33
82.68
28.06
BocHN
F F
SO2Ph
Br
3s
f1 (ppm)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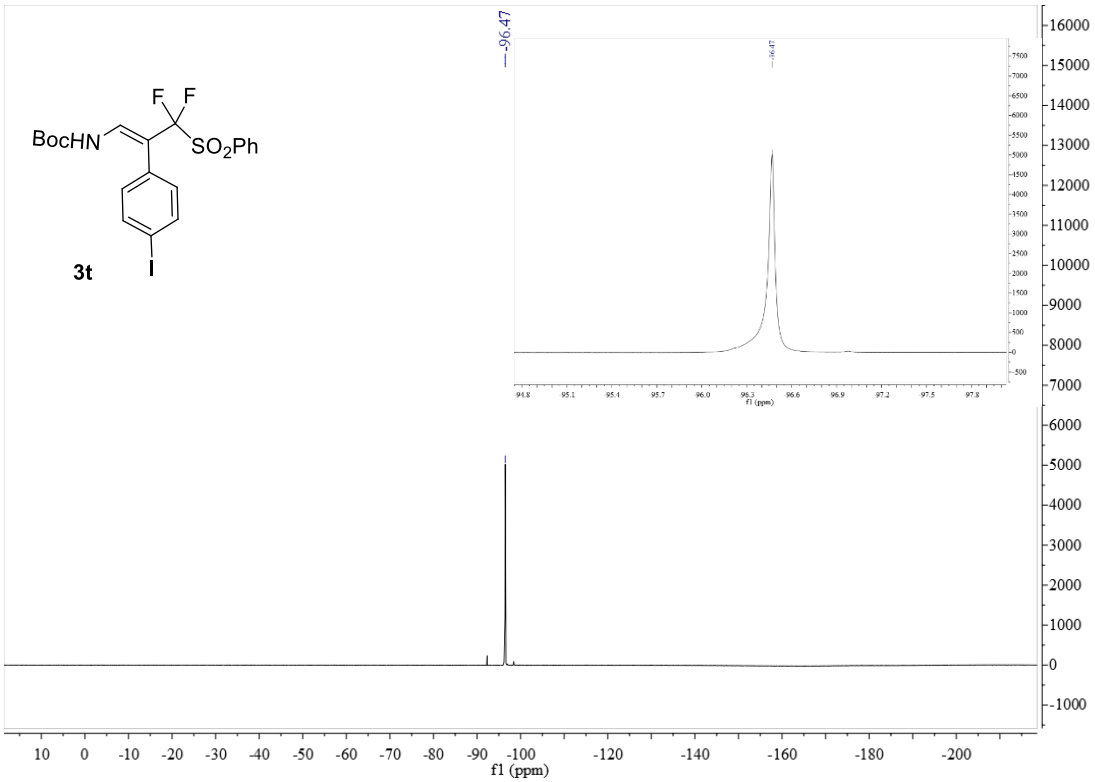
7.72
7.70
7.60
7.58
7.56
7.53
7.17
7.15
6.45
6.43
1.47
BocHN
F F
SO2Ph
I
3t
2.03
2.00
1.13
2.99
1.98
0.97
9.00
f1 (ppm)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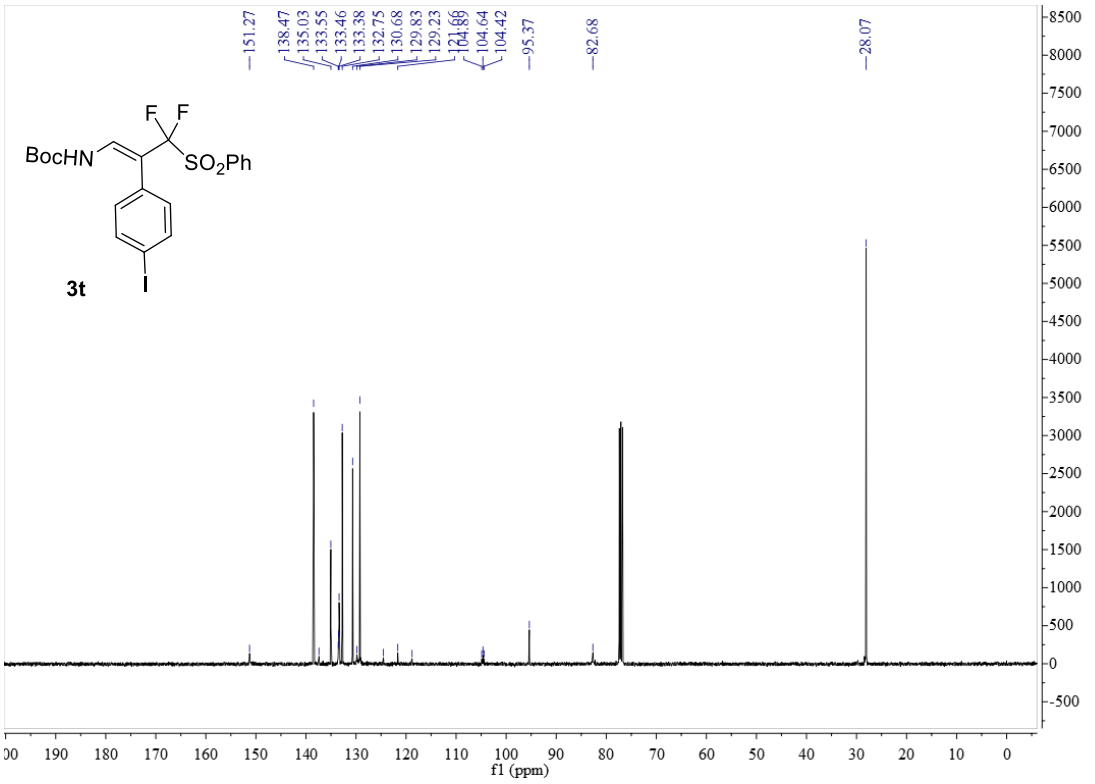
SO2Ph
I
3t
-96.47
f1 (ppm)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133.38
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130.68
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104.42
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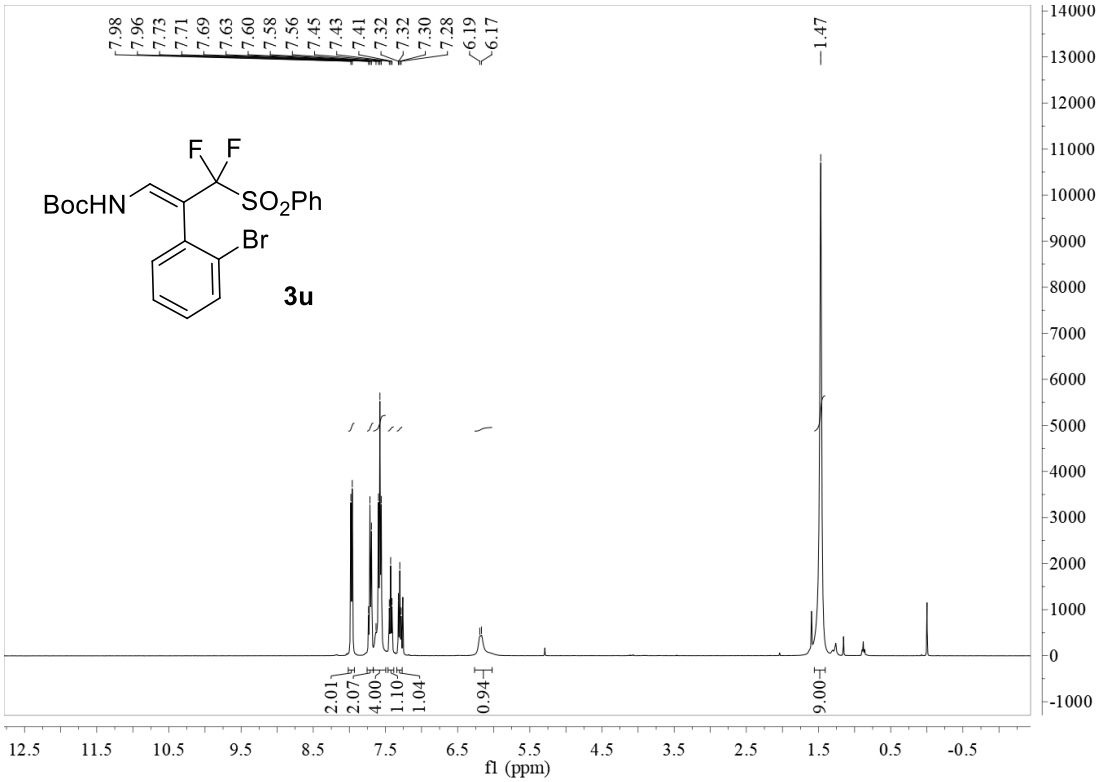
82.68
28.07
F F
BocHN
SO2Ph
I
3t
f1 (ppm)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7.60
7.58
7.56
7.45
7.43
7.41
7.32
7.32
7.30
7.28
6.19
6.17
1.47
F F
BocHN
SO2Ph
Br
3u
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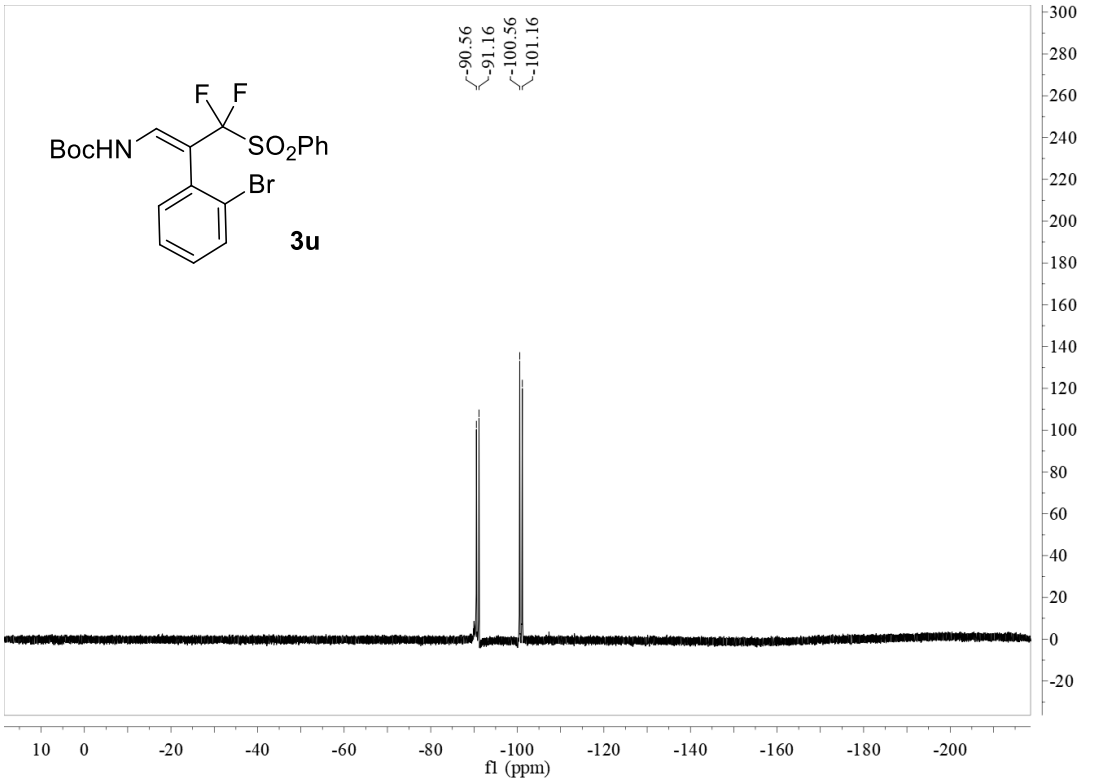
2.07
4.00
1.10
1.04
0.94
9.00
fl (ppm)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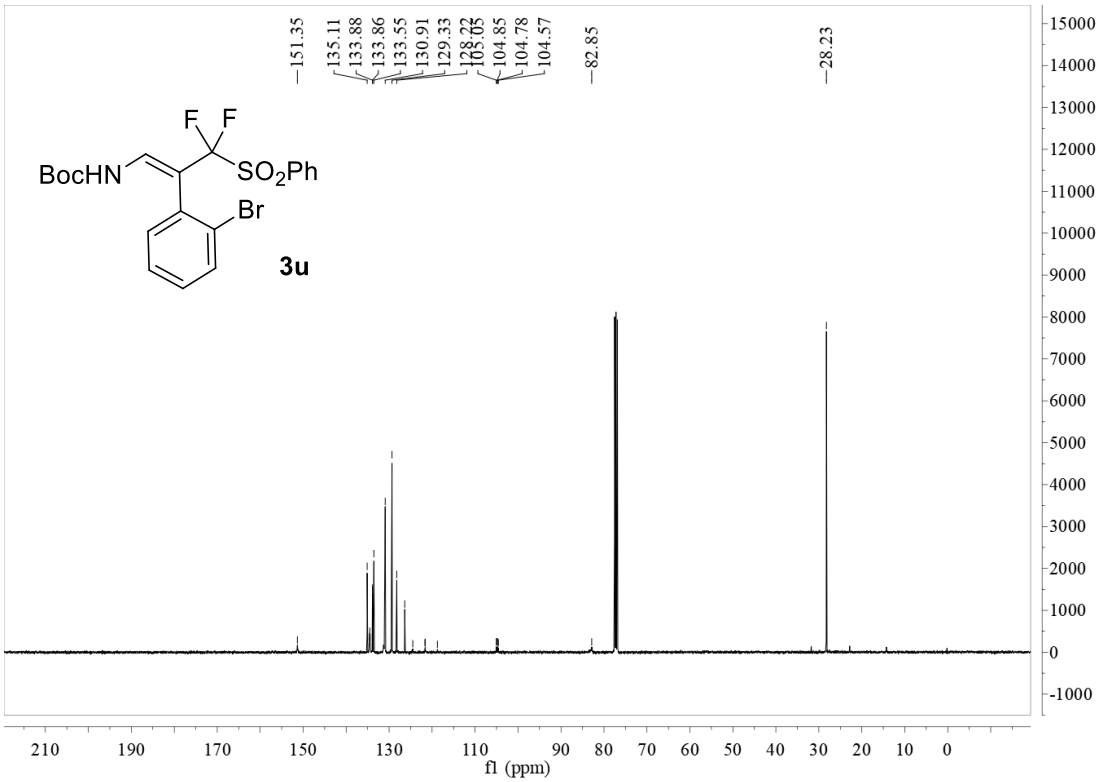
-101.16
F F
BocHN
SO2Ph
Br
3u
fl (ppm)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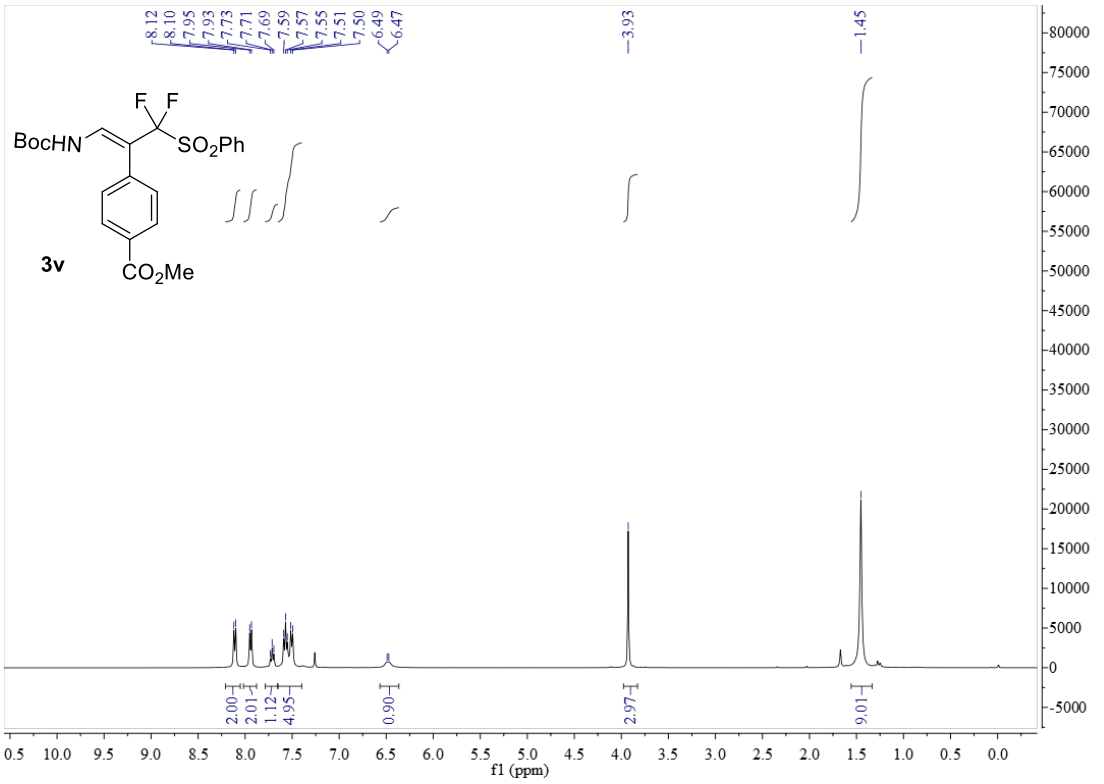
F F
BocHN
SO2Ph
Br
3u
f1 (ppm)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8.10
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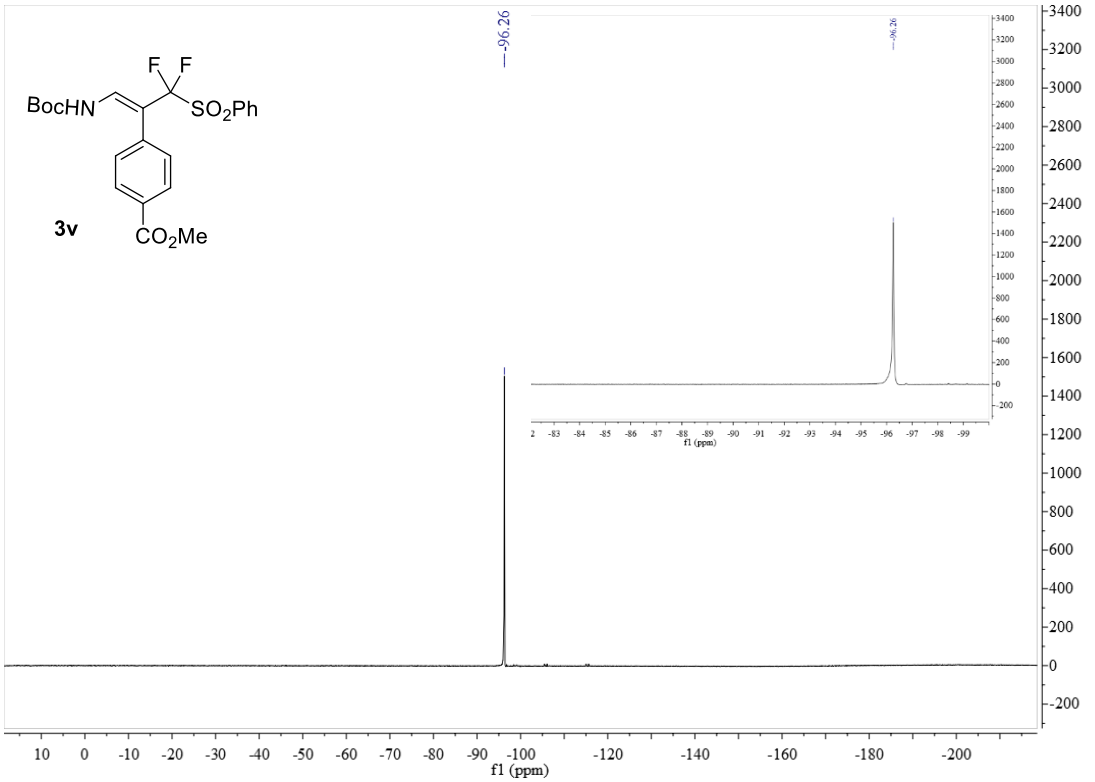
7.71
7.69
7.59
7.57
7.55
7.51
7.50
6.49
6.47
3.93
1.45
F F
BocHN
SO2Ph
3v
CO2Me
2.00
2.01
1.12
4.95
0.90
2.97
9.01
f1 (ppm)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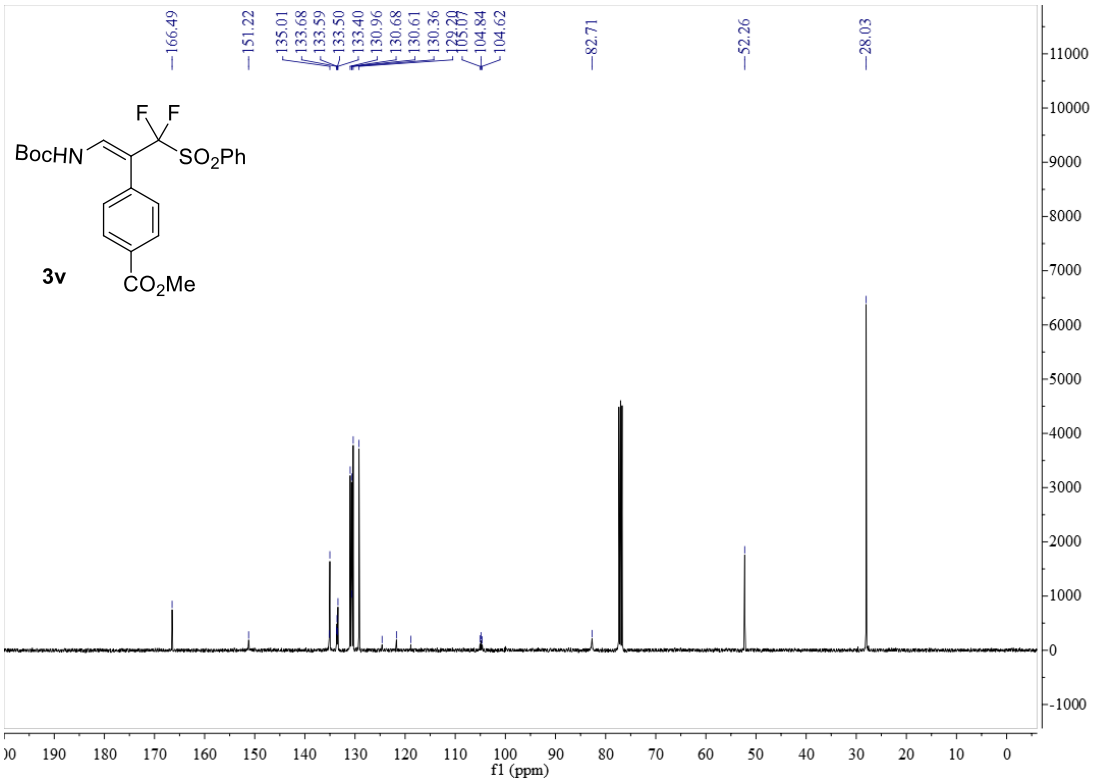
SO2Ph
3v
CO2Me
-96.26
f1 (ppm)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82.71
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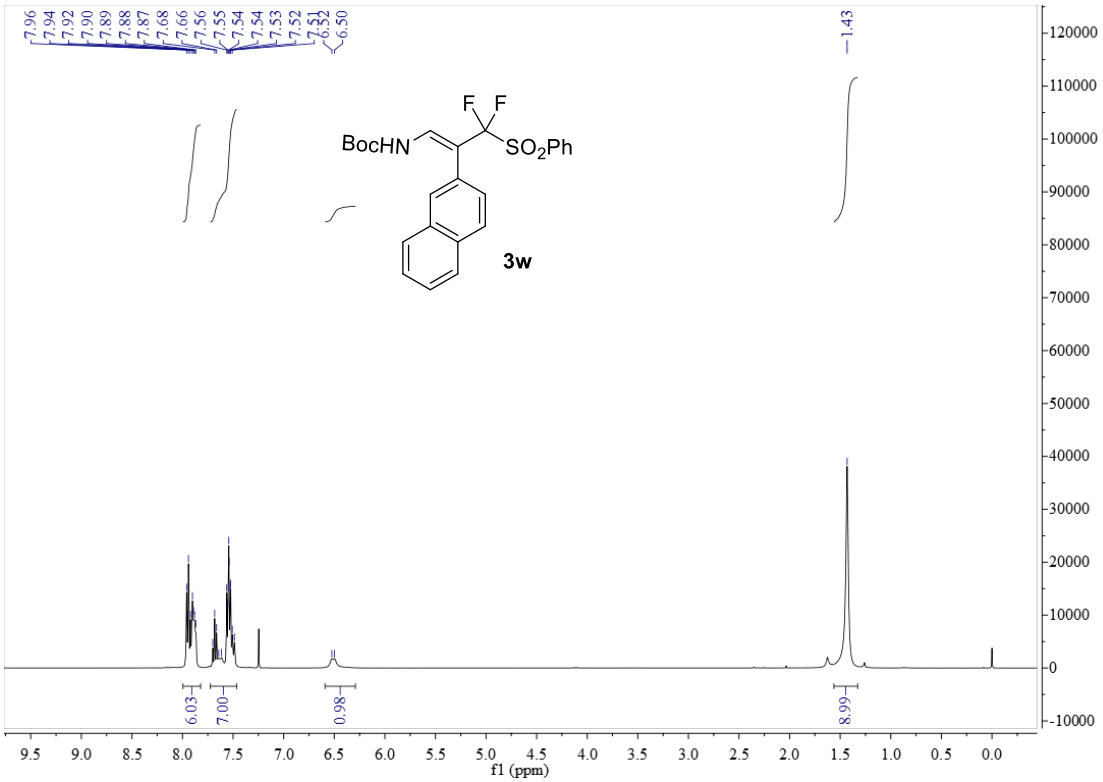
F F
BocHN
SO2Ph
3v
CO2Me
f1 (ppm)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7.55
7.54
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7.53
7.52
7.51
6.52
6.50
1.43
F F
BocHN
SO2Ph
3w
6.03
7.00
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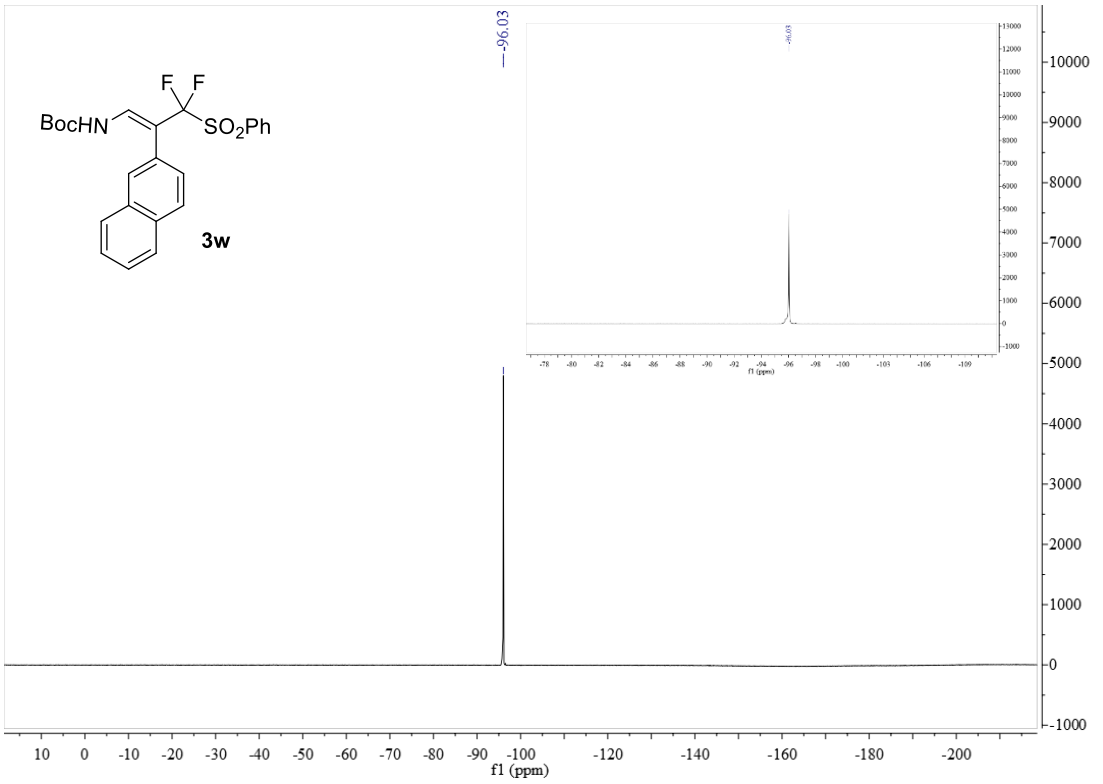
8.99
f1 (ppm)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SO2Ph
3w
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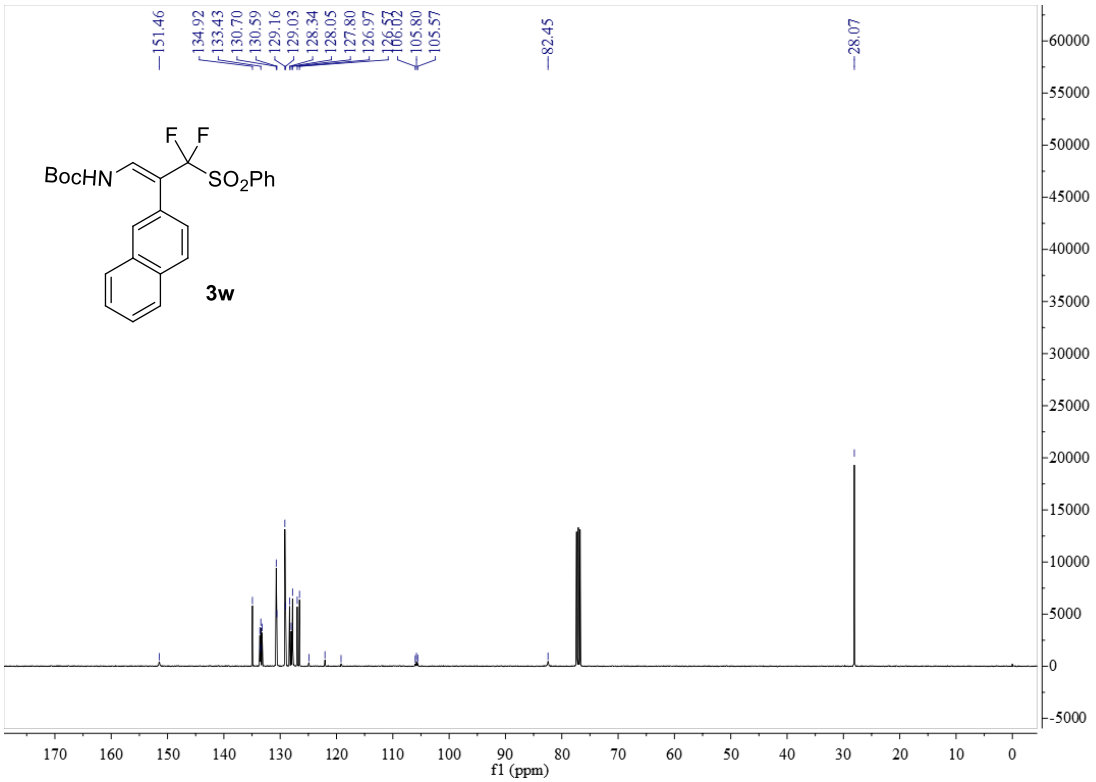
f1 (ppm)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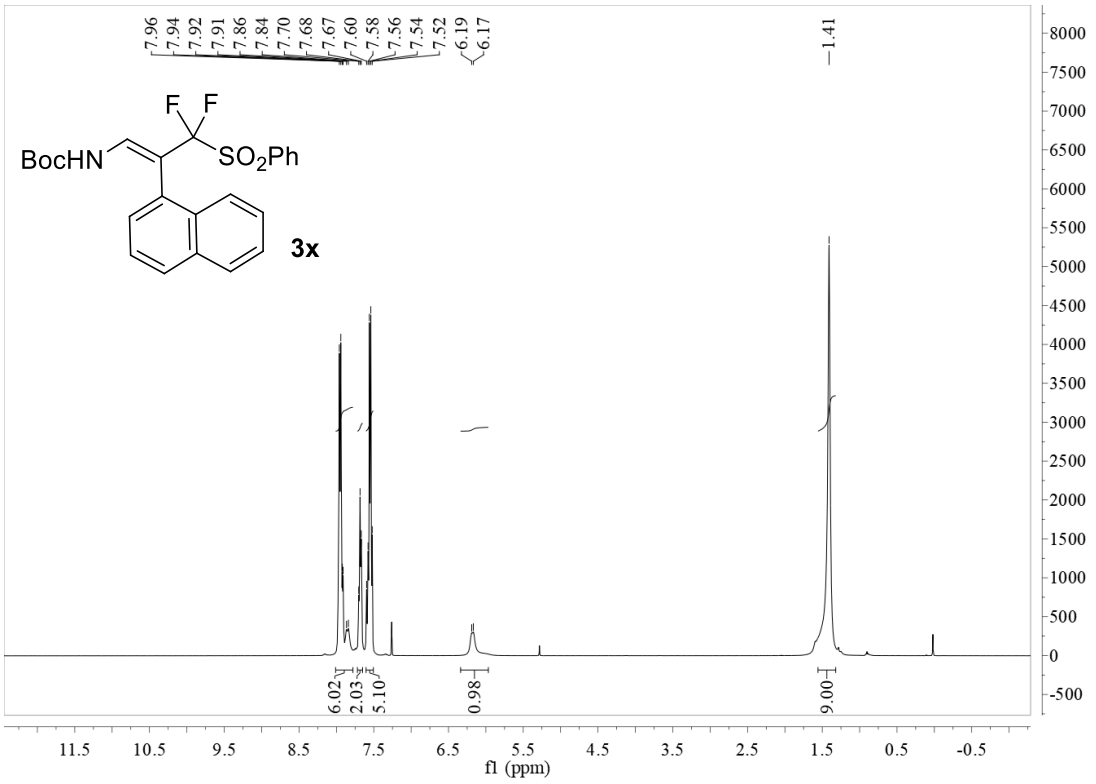
105.80
105.57
82.45
28.07
F F
BocHN
SO2Ph
3w
f1 (ppm)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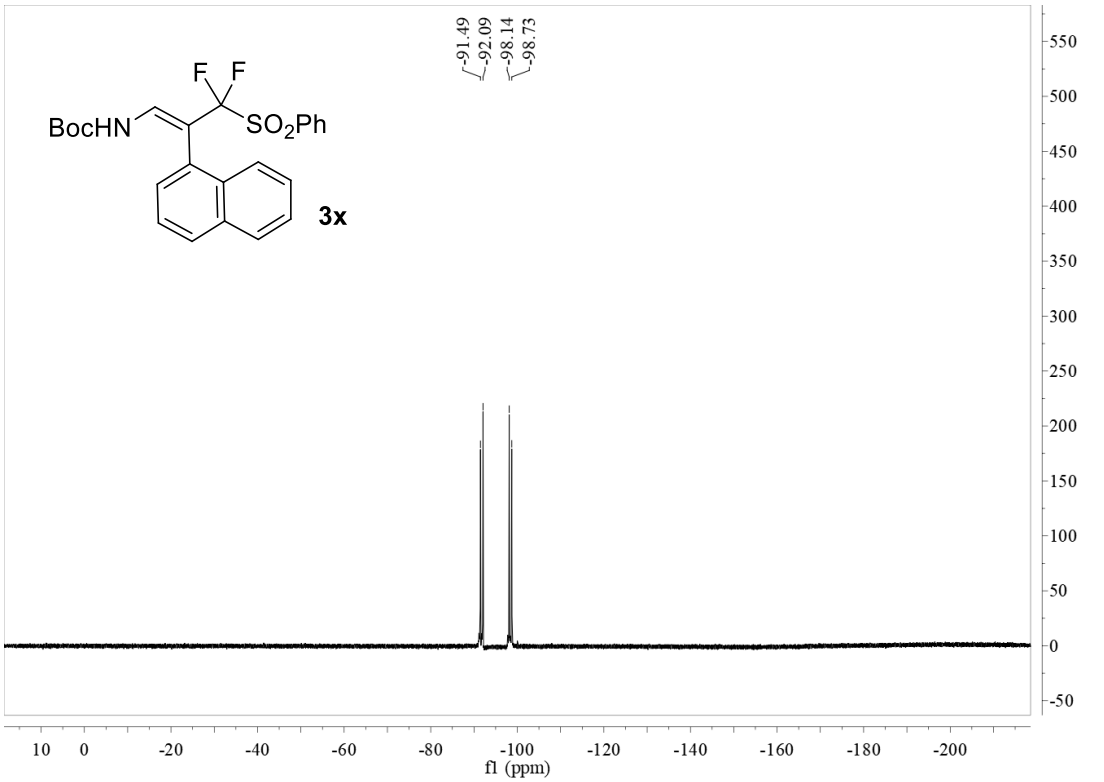
7.54
7.52
6.19
6.17
1.41
F F
BocHN
SO2Ph
3x
6.02
2.03
5.10
0.98
9.00
f1 (ppm)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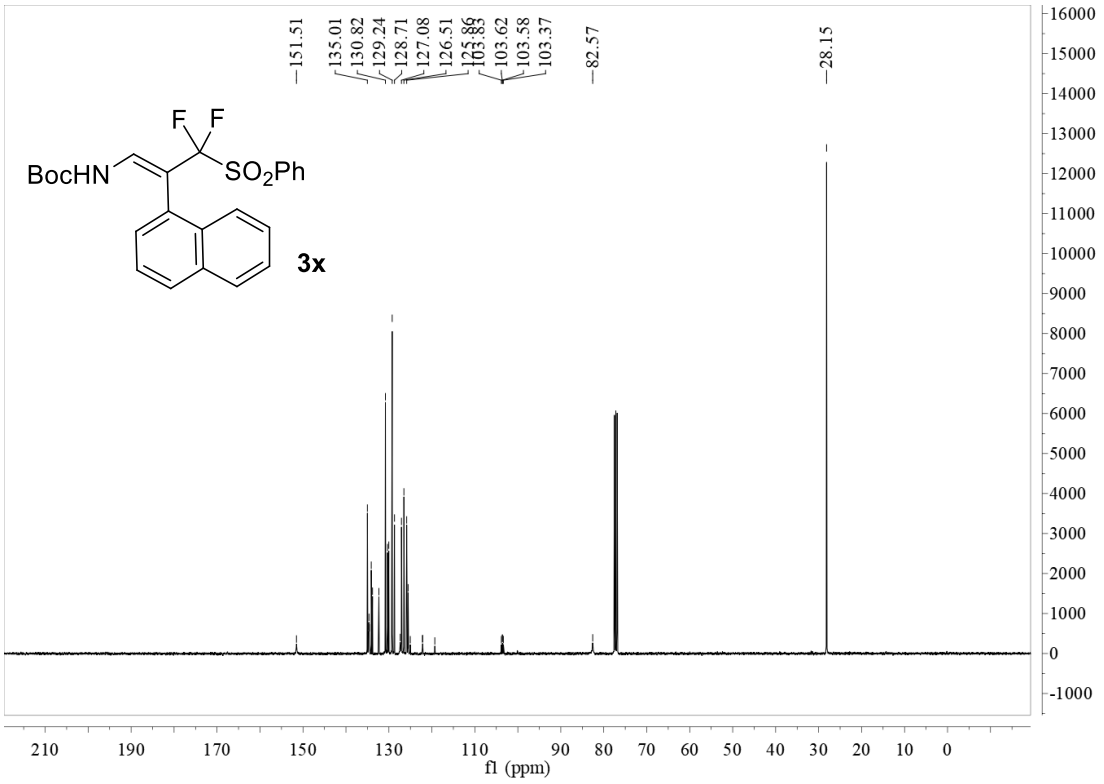
3x
fl (ppm)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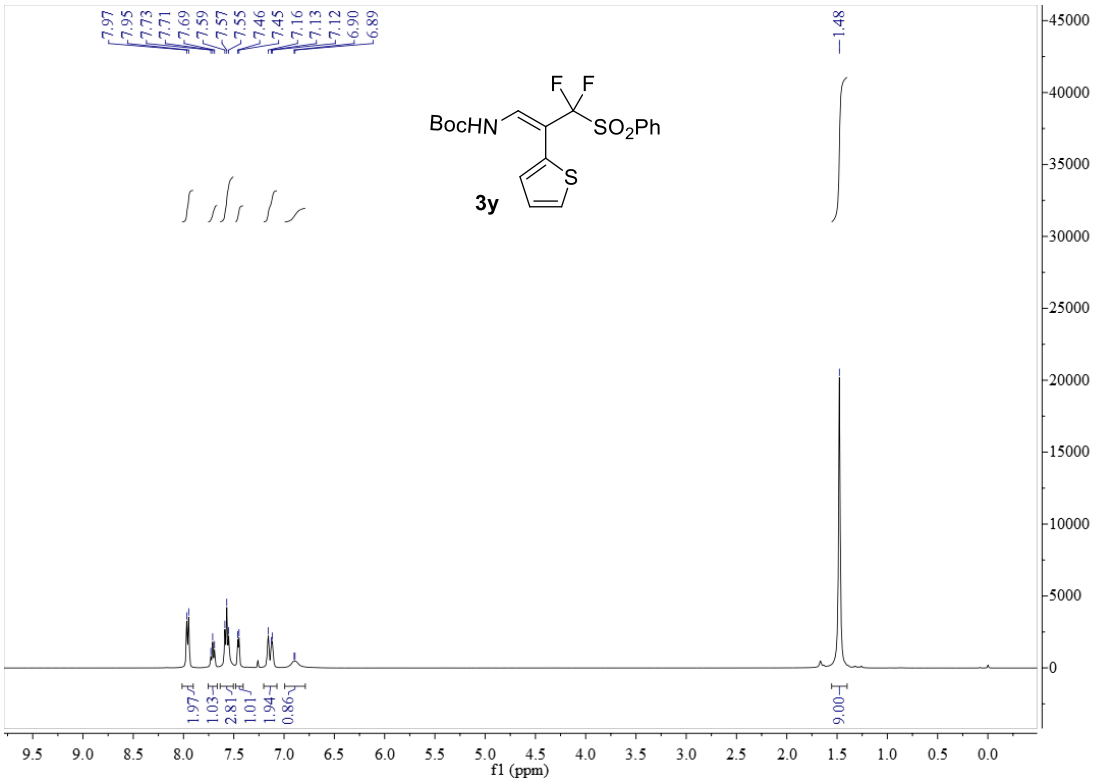
SO2Ph
3x
fl (ppm)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7.16
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7.12
6.90
6.89
1.48
F F
BocHN
SO2Ph
S
3y
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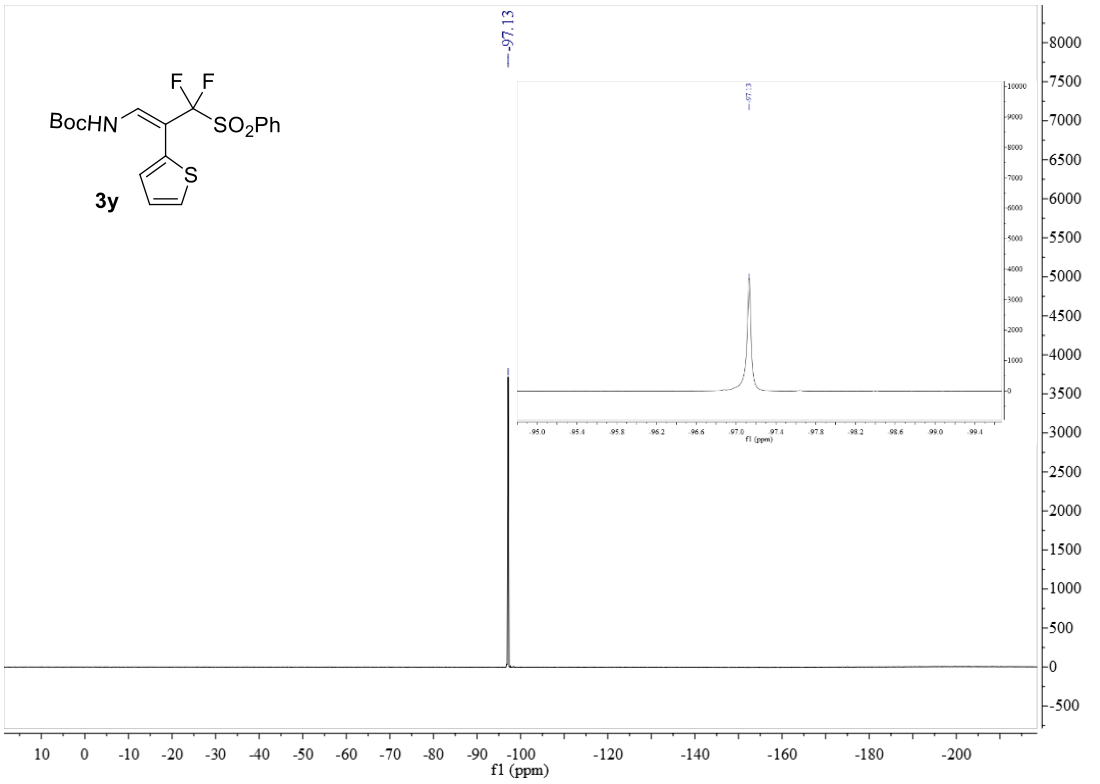
2.81
1.01
1.94
0.86
9.00
f1 (ppm)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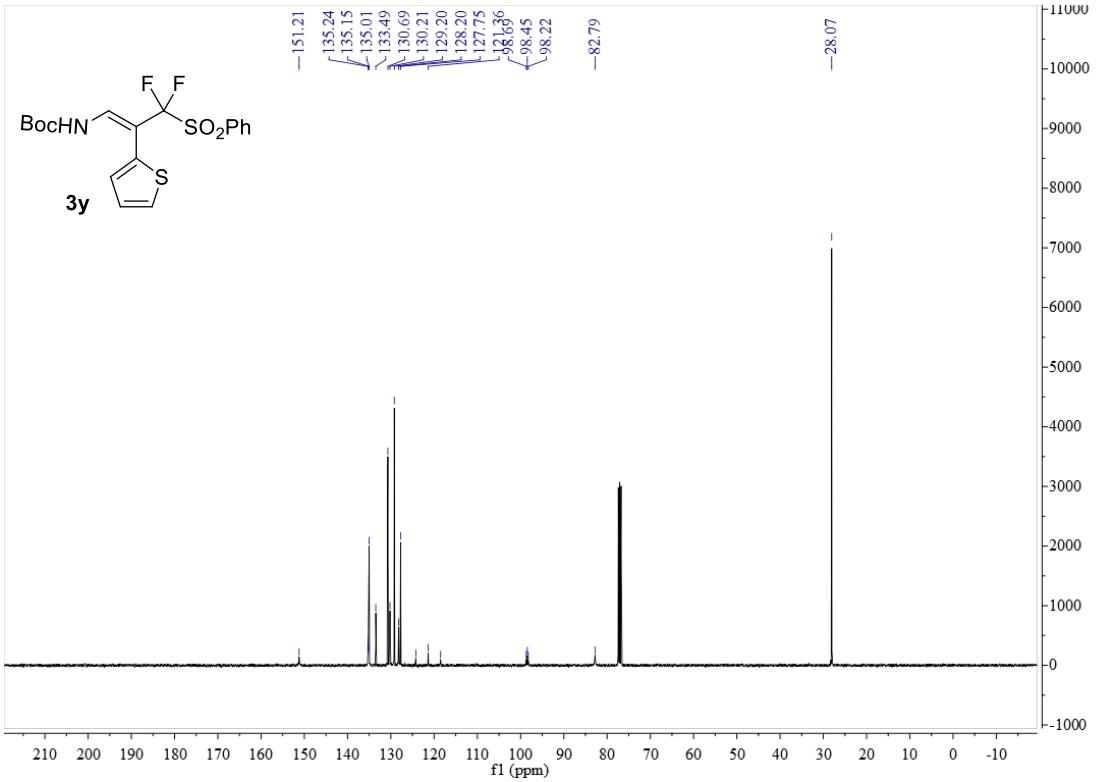
SO2Ph
S
3y
f1 (ppm)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129.20
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98.22
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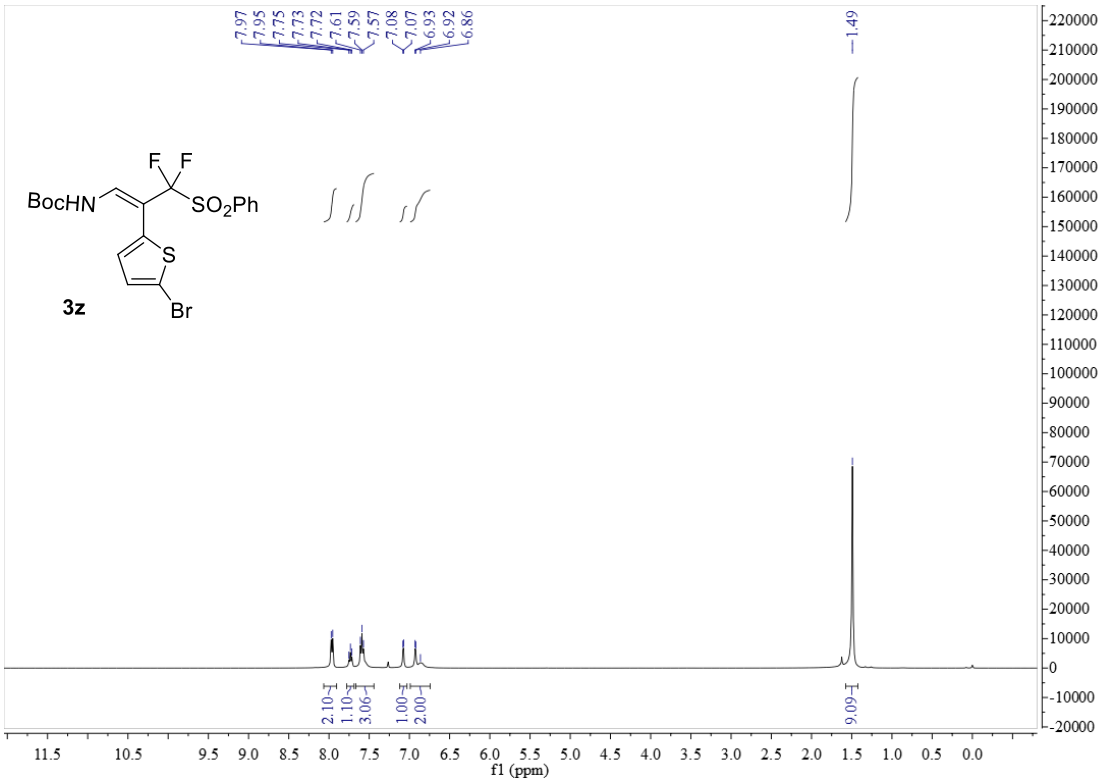
28.07
F F
BocHN
SO2Ph
S
3y
f1 (ppm)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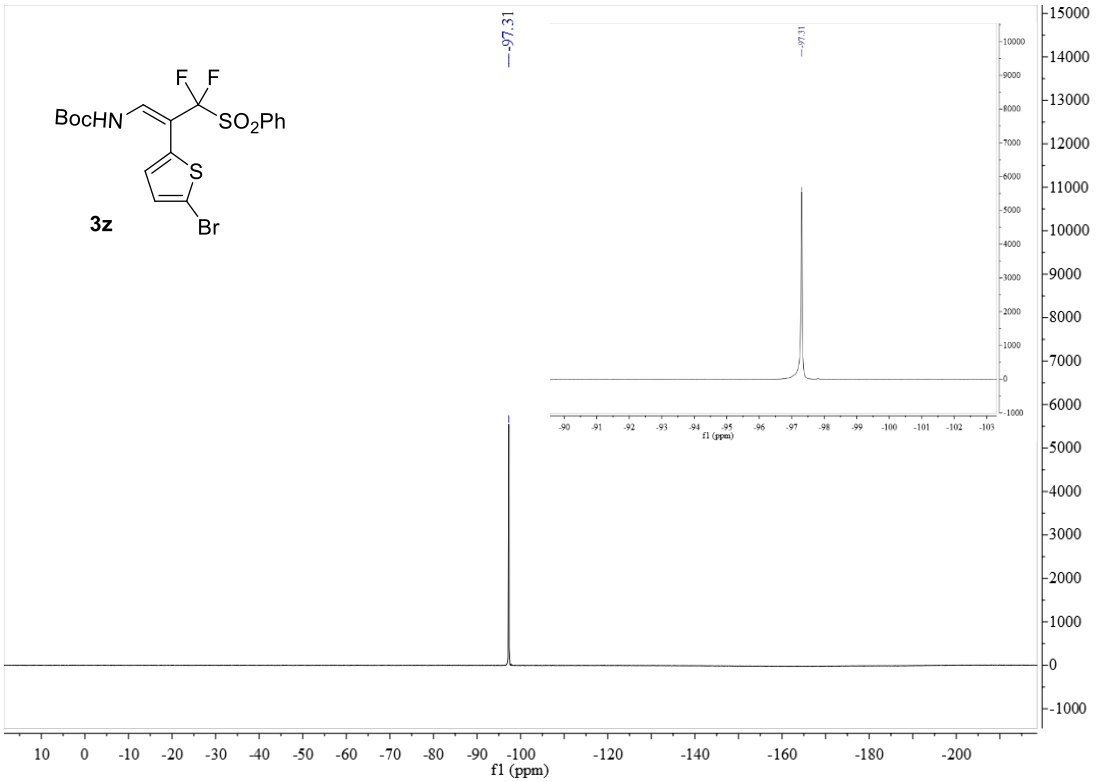
7.75
7.73
7.72
7.61
7.59
7.57
7.08
7.07
6.93
6.92
6.86
1.49
F F
BocHN
SO2Ph
S
Br
3z
2.10
1.10
3.06
1.00
2.00
9.09
f1 (ppm)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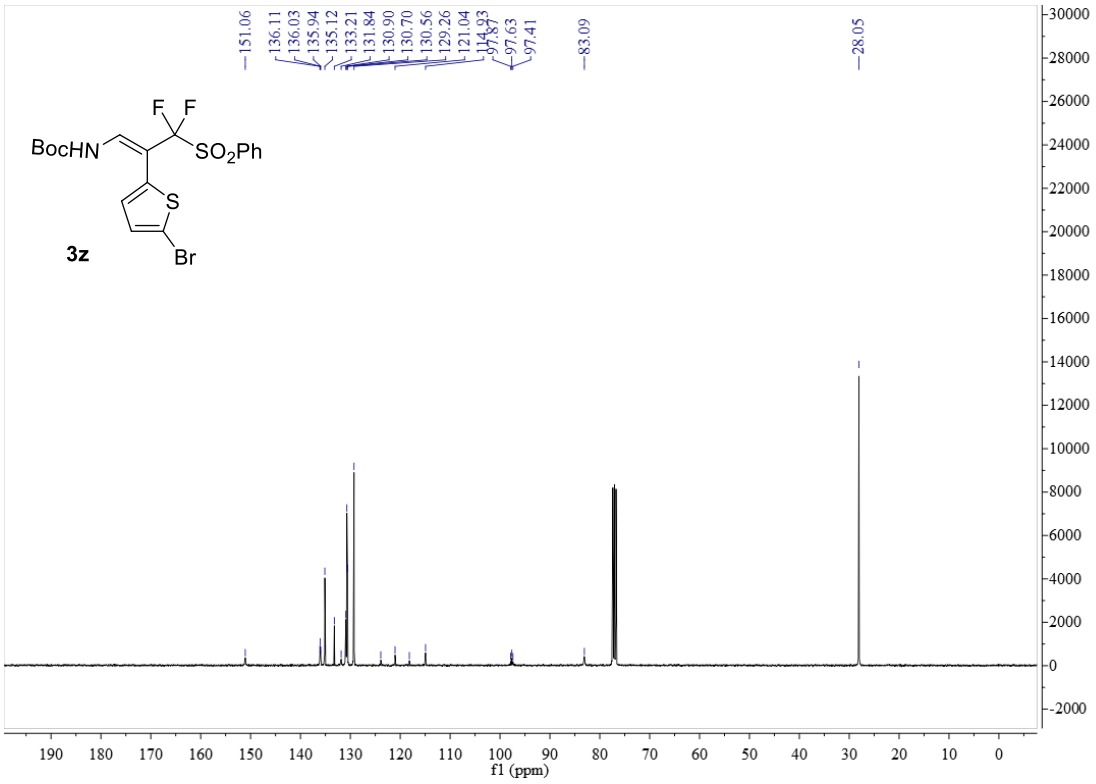
SO2Ph
S
Br
3z
-97.31
f1 (ppm)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130.56
129.26
121.04
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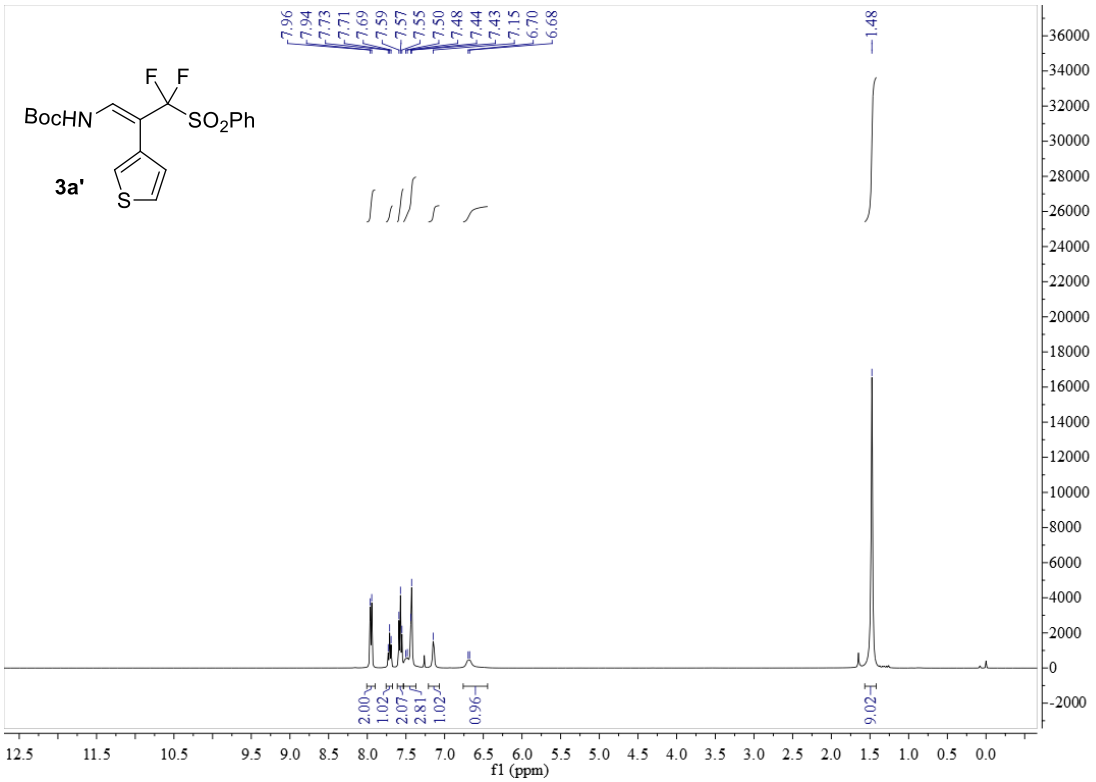
97.41
83.09
28.05
F F
BocHN
SO2Ph
S
Br
3z
f1 (ppm)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7.48
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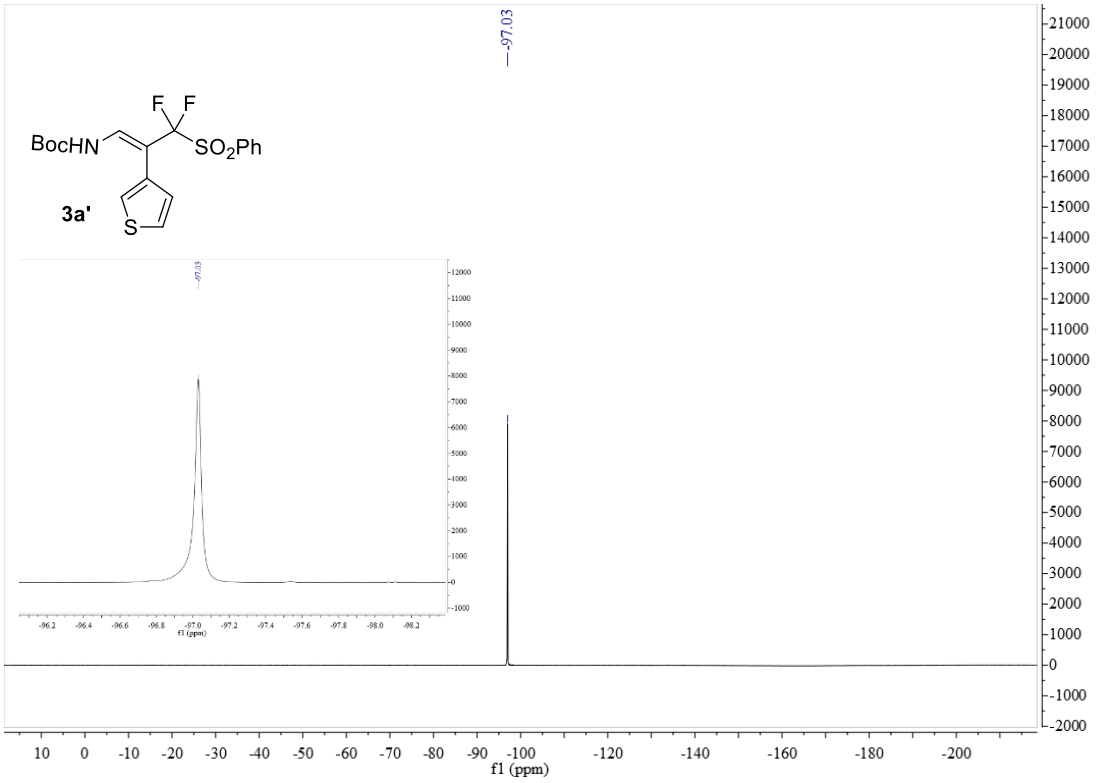
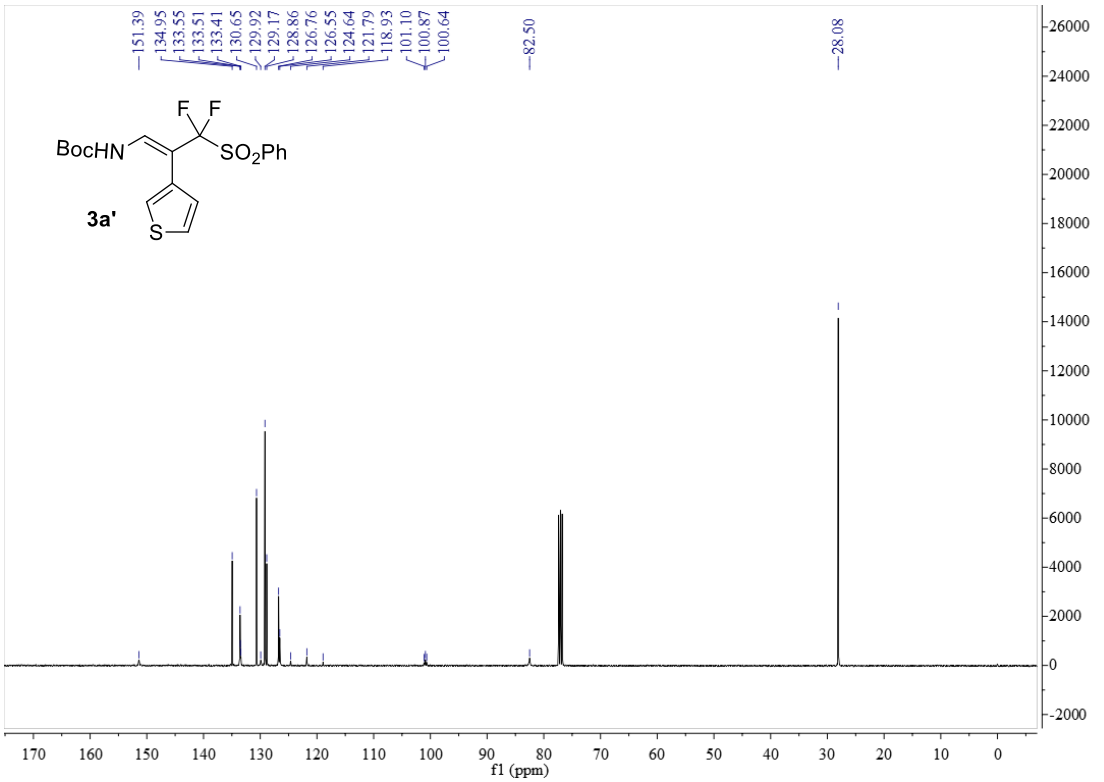
7.43
7.15
6.70
6.68
1.48
F F
BocHN
SO2Ph
3a'
S
2.00
1.02
2.07
2.81
1.02
0.96
9.02
f1 (ppm)


-97.03
F F
BocHN
SO2Ph
3a'
S
f1 (ppm)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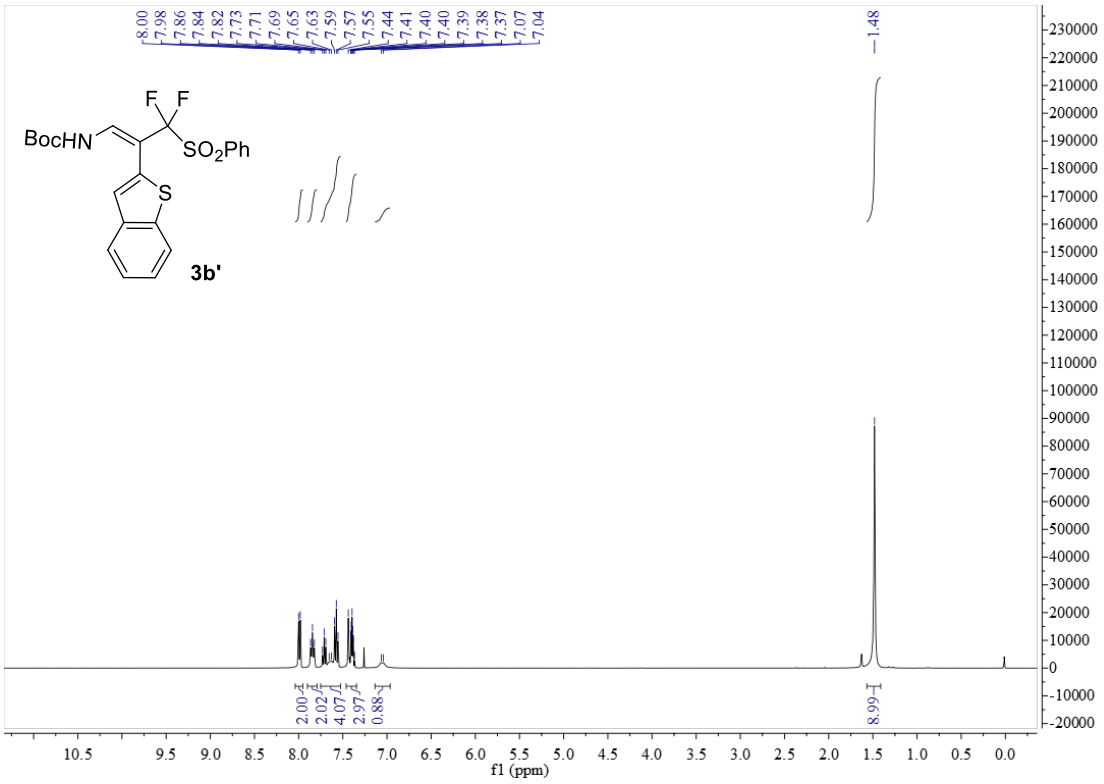
133.55
133.51
133.41
130.65
129.92
129.17
128.86
126.76
126.55
124.64
121.79
118.93
101.10
100.87
100.64
82.50
28.08
F F
BocHN
SO2Ph
S
3a'
f1 (ppm)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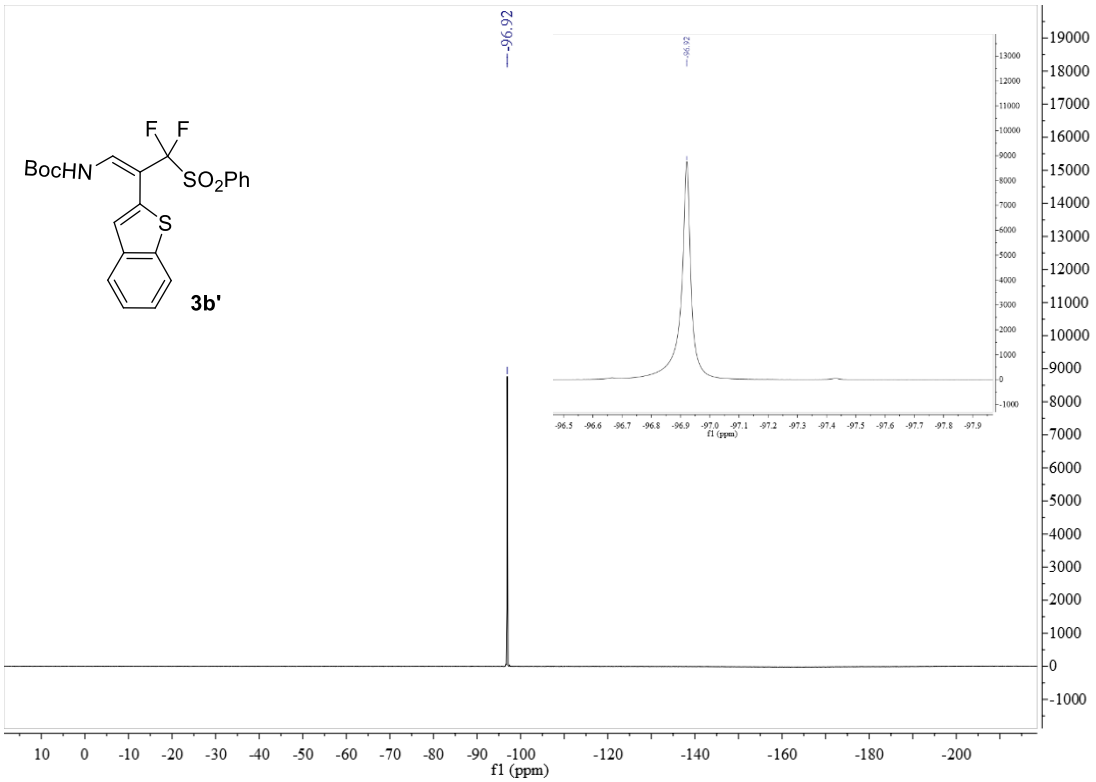
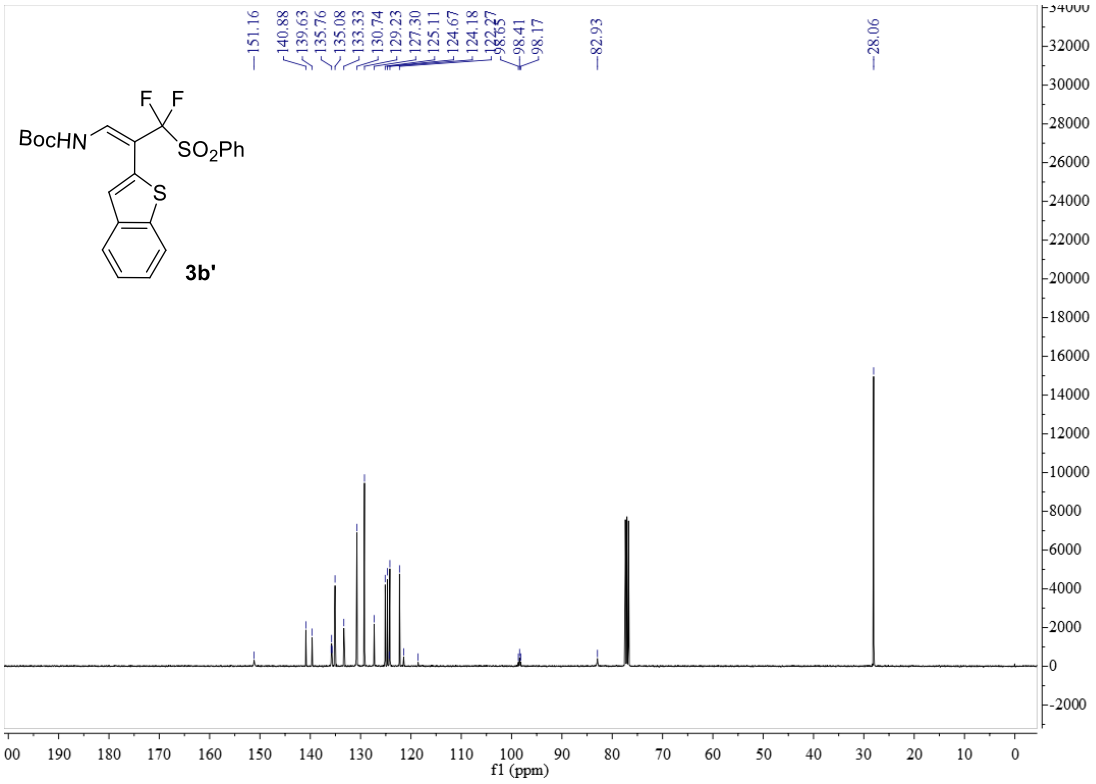
7.86
7.84
7.82
7.73
7.71
7.69
7.65
7.63
7.59
7.57
7.55
7.44
7.41
7.40
7.40
7.39
7.38
7.37
7.07
7.04
1.48
F F
BocHN
SO2Ph
S
3b'
2.00
2.02
4.07
2.97
0.88
8.99
f1 (ppm)


F F
BocHN
SO2Ph
S
3b'
-96.92
f1 (ppm)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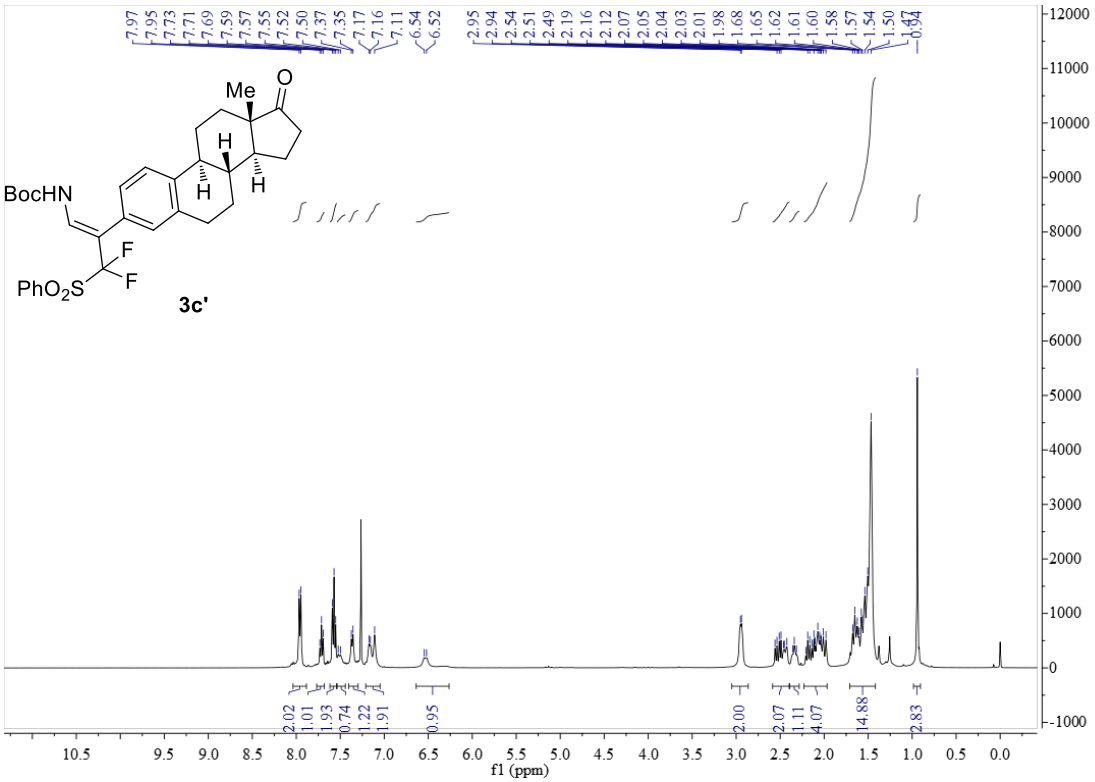
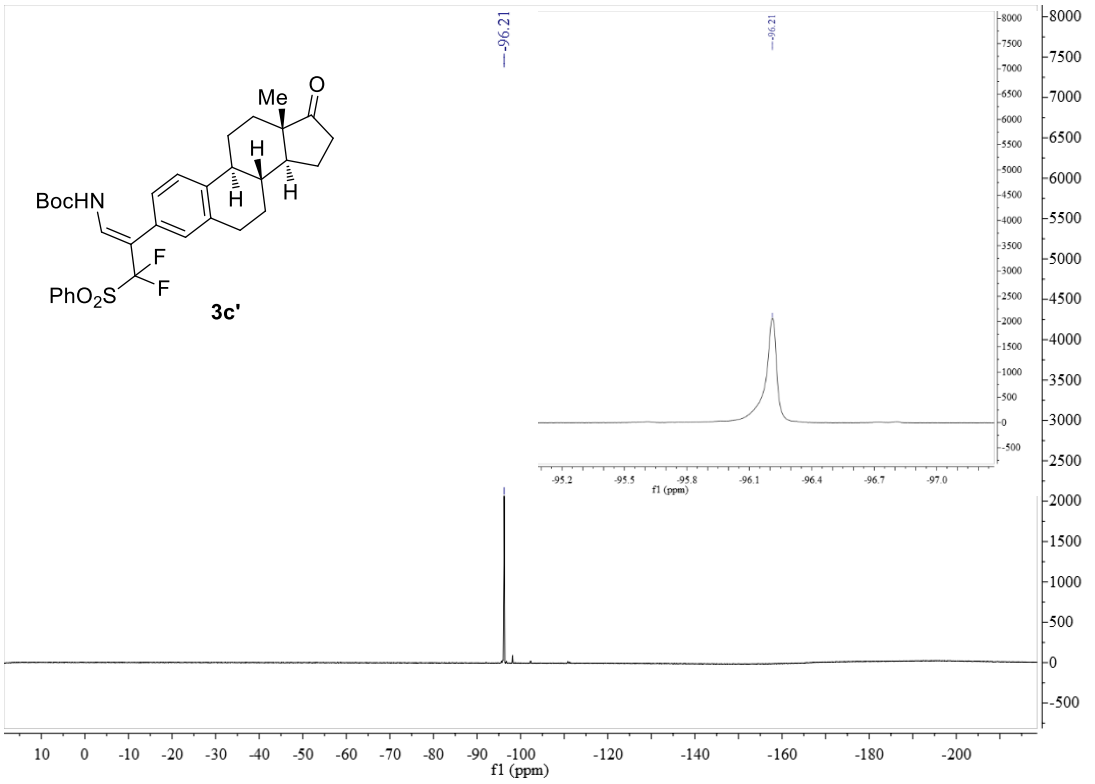
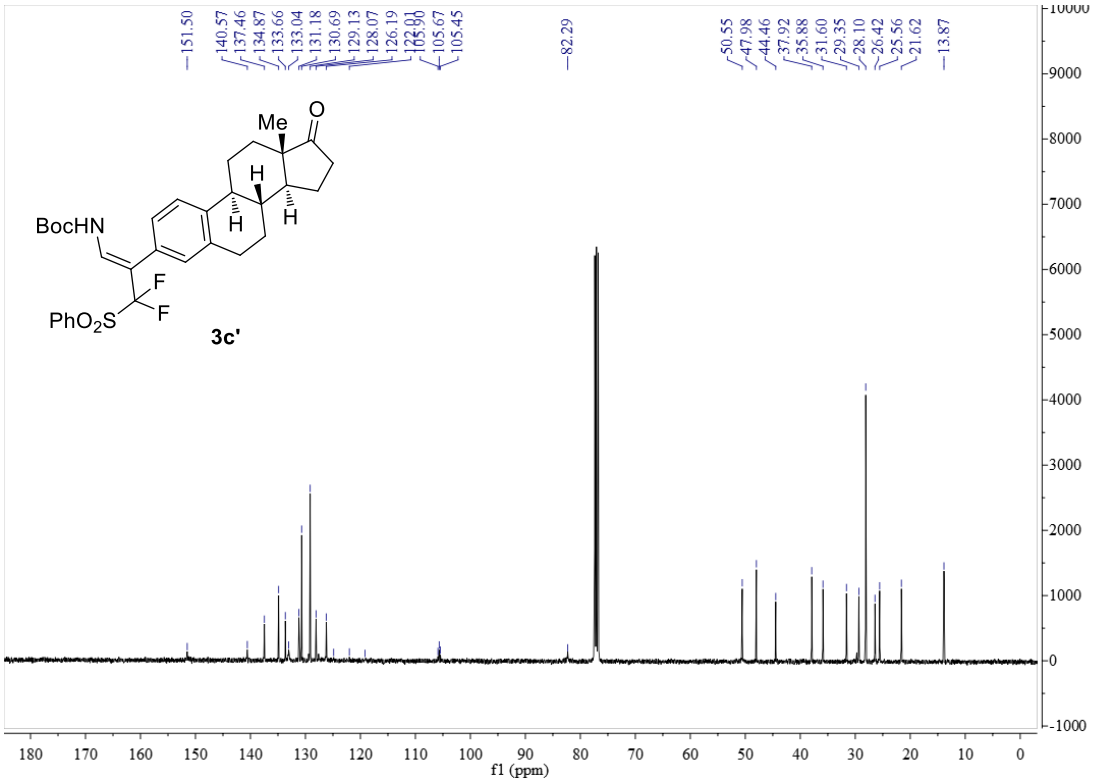
140.88
139.63
135.76
135.08
133.33
130.74
129.23
127.30
125.11
124.67
124.18
122.27
98.65
98.41
98.17
82.93
28.06
F F
BocHN
SO2Ph
S
3b'
f1 (ppm)


Me
O
H
H
H
BocHN
F
F
PhO2S
3c'
f1 (ppm)


Me
O
H
H
H
BocHN
F
F
PhO2S
3c'
-96.21
f1 (ppm)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131.18
130.69
129.13
128.07
126.19
105.67
105.45
82.29
50.55
47.98
44.46
37.92
35.88
31.60
29.35
28.10
26.42
25.56
21.62
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Me
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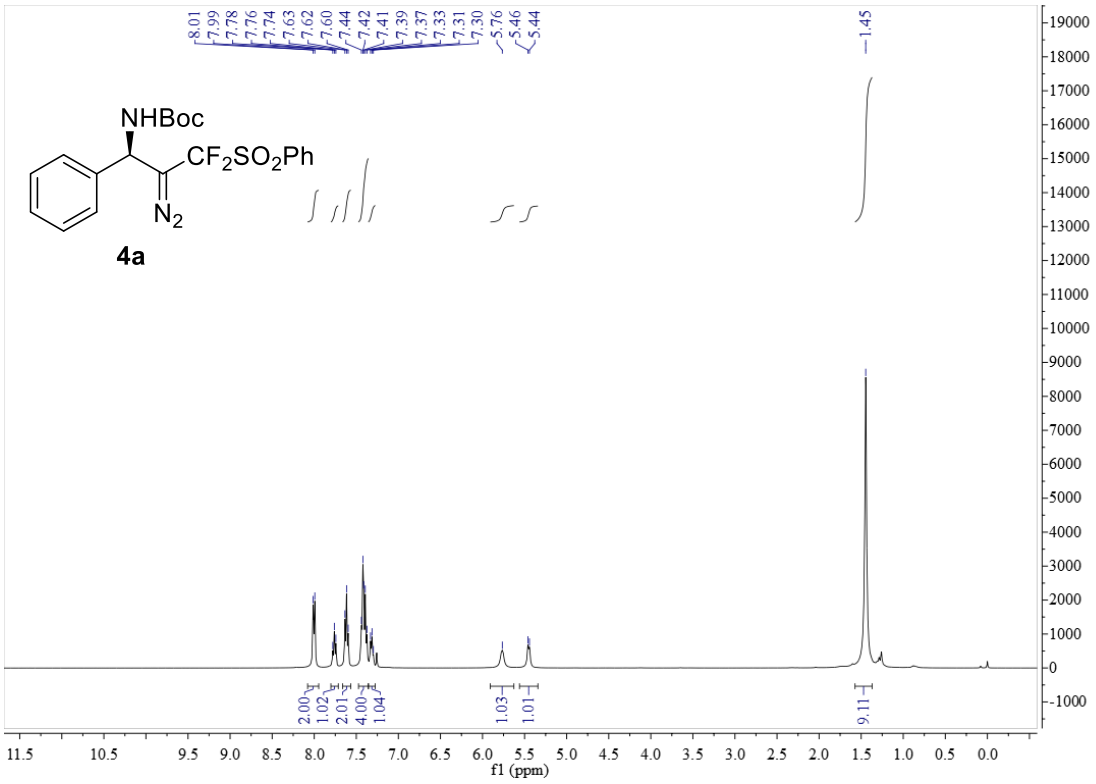
H
H
BocHN
F
F
PhO2S
3c'
f1 (ppm)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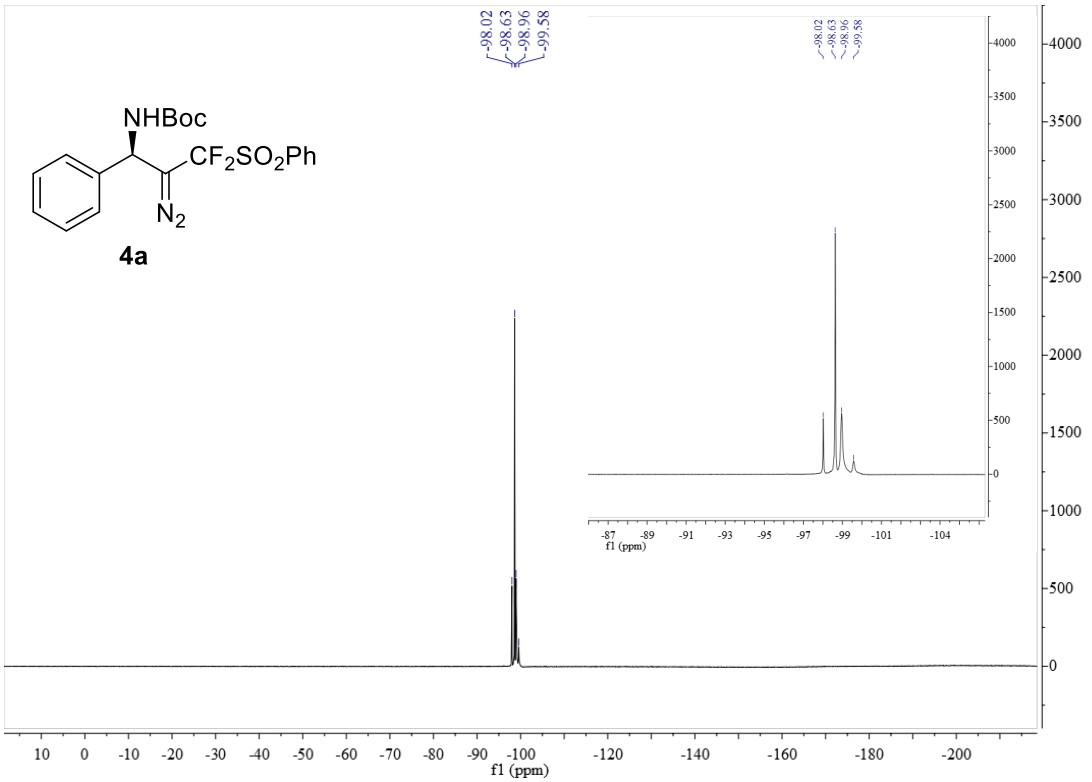
7.76
7.74
7.63
7.62
7.60
7.44
7.42
7.41
7.39
7.37
7.33
7.31
7.30
5.76
5.46
5.44
1.45
NHBoc
CF2SO2Ph
N2
4a
2.00
1.02
2.01
4.00
1.04
1.03
1.01
9.11
f1 (ppm)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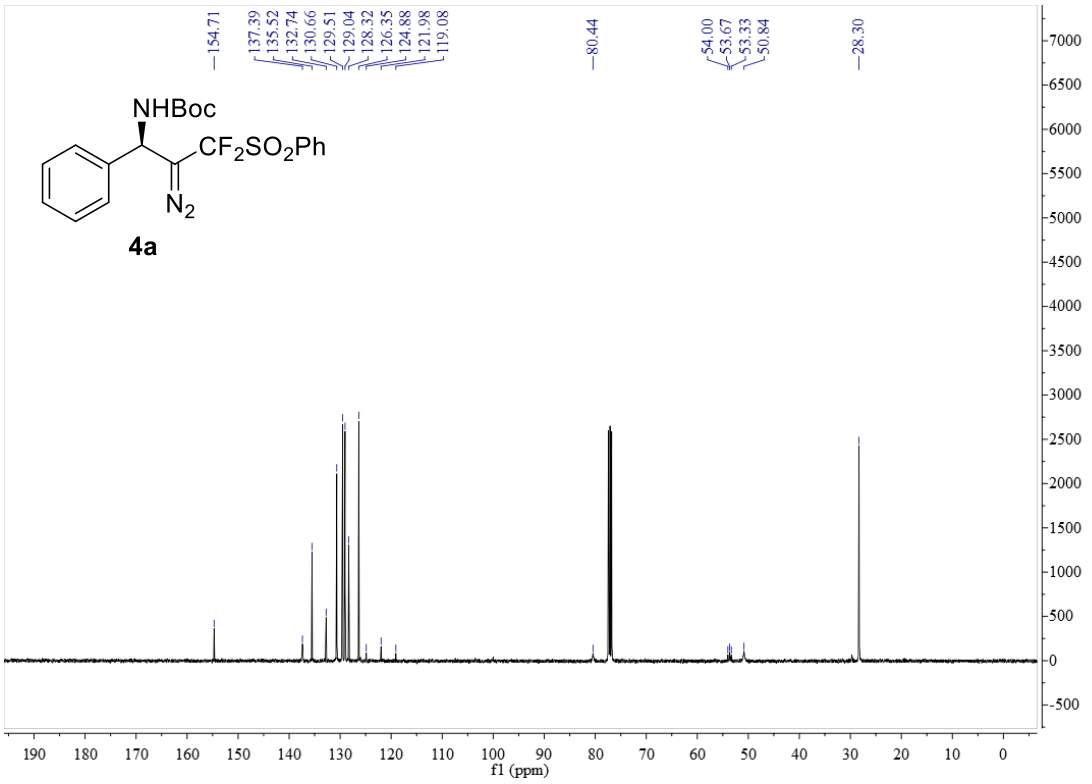
-98.96
-99.58
NHBoc
CF2SO2Ph
N2
4a
f1 (ppm)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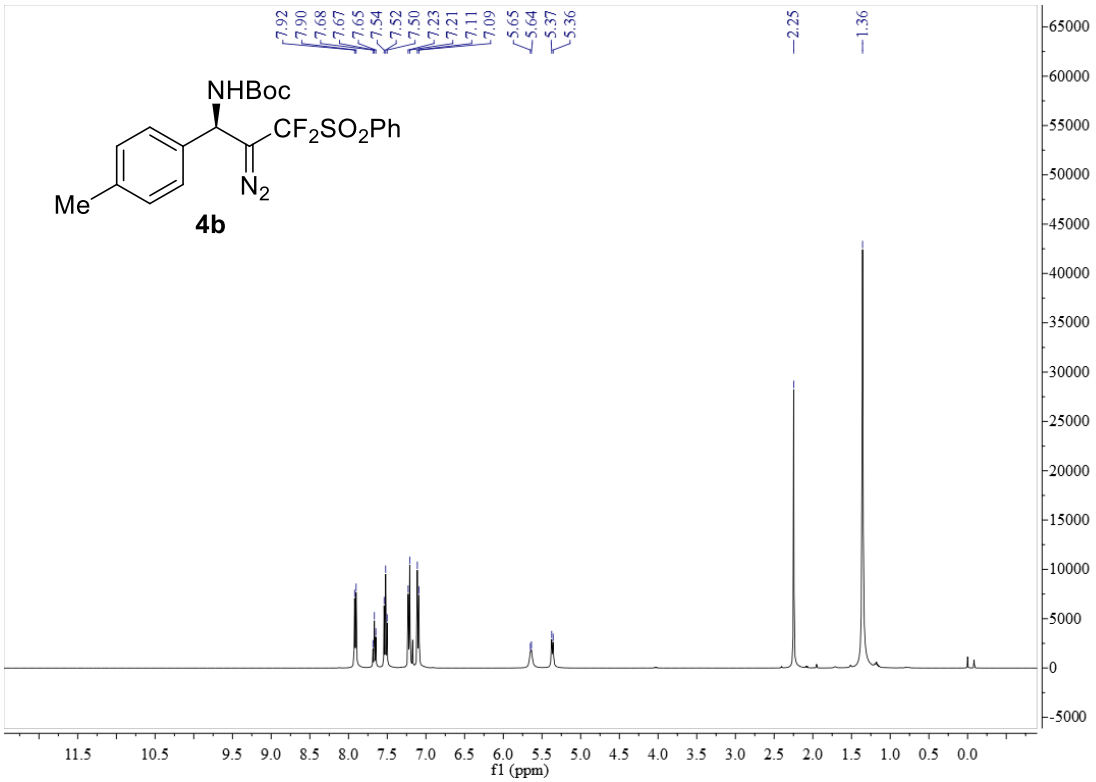
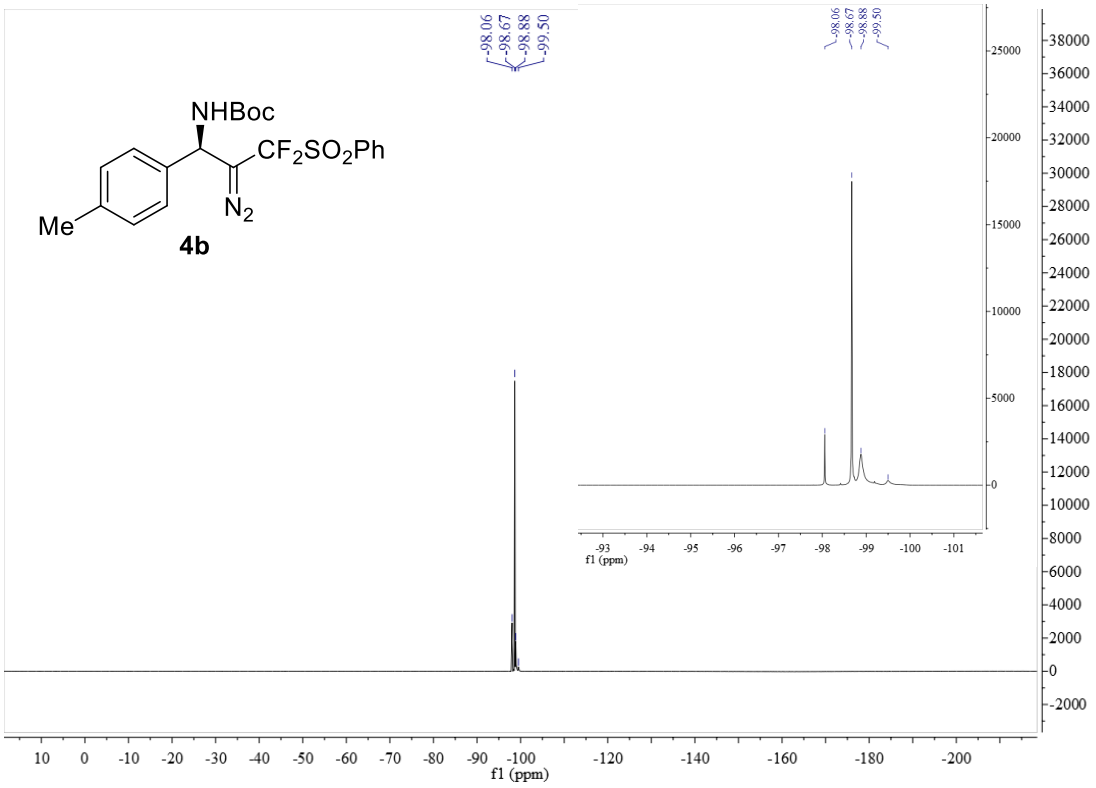
137.39
135.52
132.74
130.66
129.51
129.04
128.32
126.35
124.88
121.98
119.08
80.44
54.00
53.67
53.33
50.84
28.30
NHBoc
CF2SO2Ph
N2
4a
f1 (ppm)


7.92
7.90
7.68
7.67
7.65
7.54
7.52
7.50
7.23
7.21
7.11
7.09
5.65
5.64
5.37
5.36
2.25
1.36
NHBoc
CF2SO2Ph
N2
Me
4b
f1 (ppm)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-99.50
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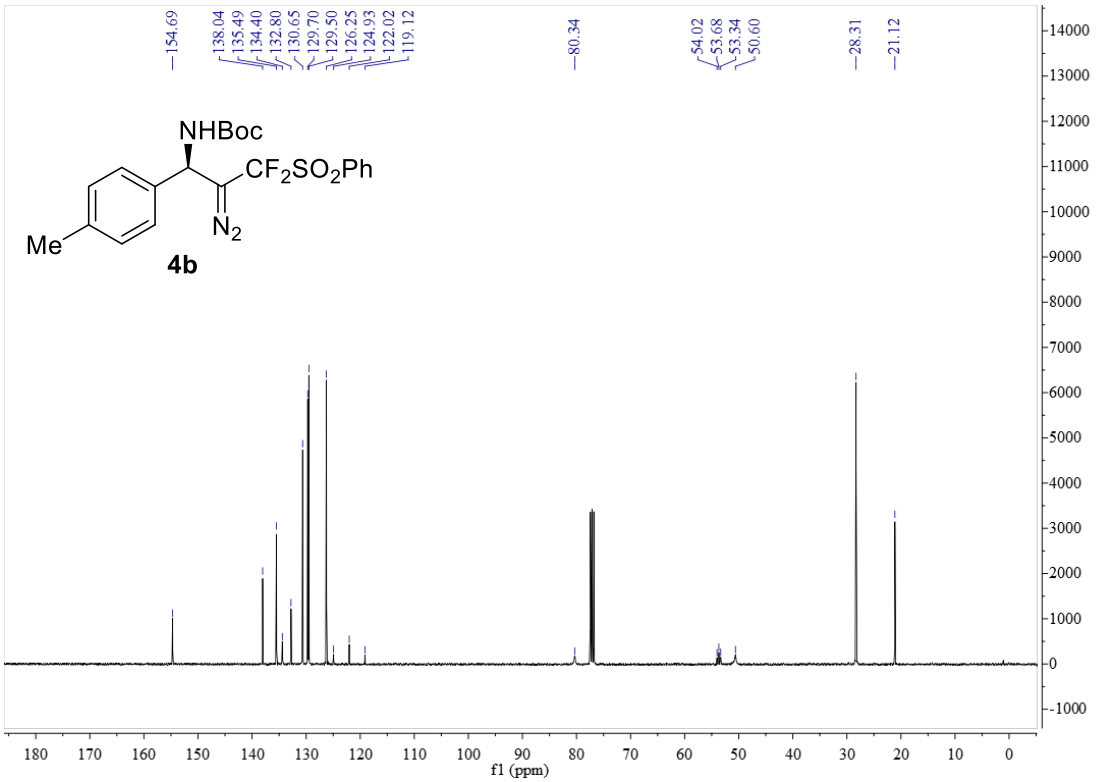
CF2SO2Ph
N2
Me
4b
f1 (ppm)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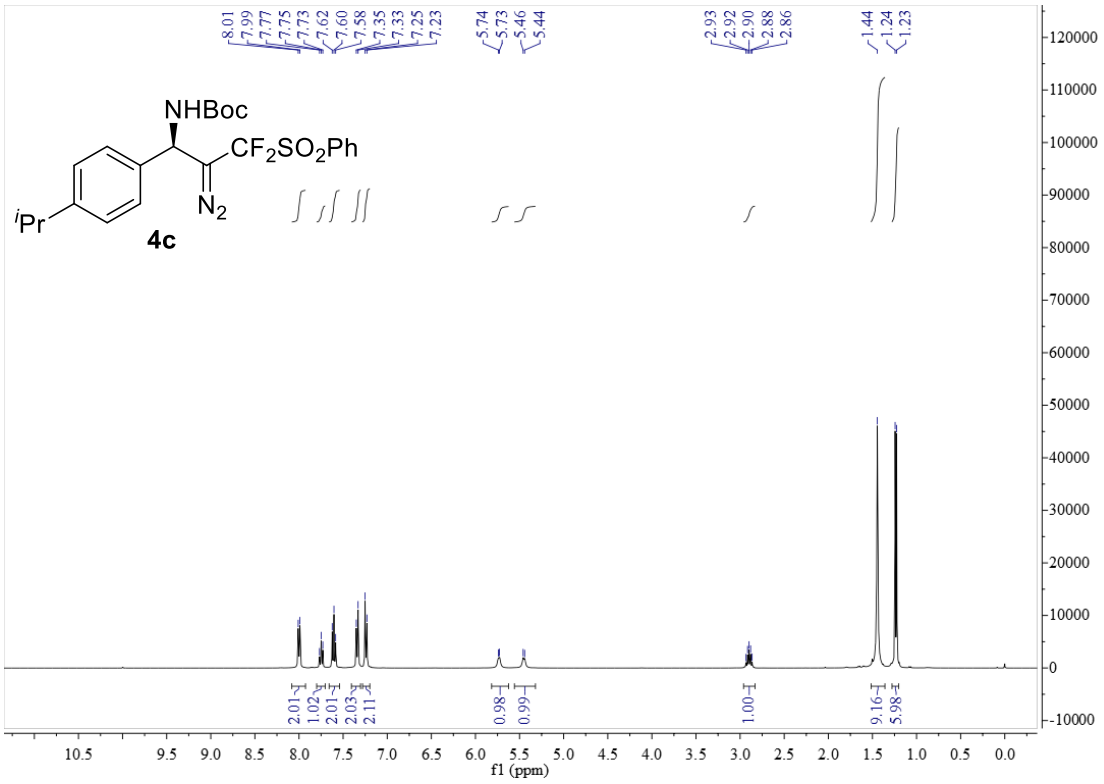
135.49
134.40
132.80
130.65
129.70
129.50
126.25
124.93
122.02
119.12
80.34
54.02
53.68
53.34
50.60
28.31
21.12
NHBoc
CF2SO2Ph
N2
Me
4b
f1 (ppm)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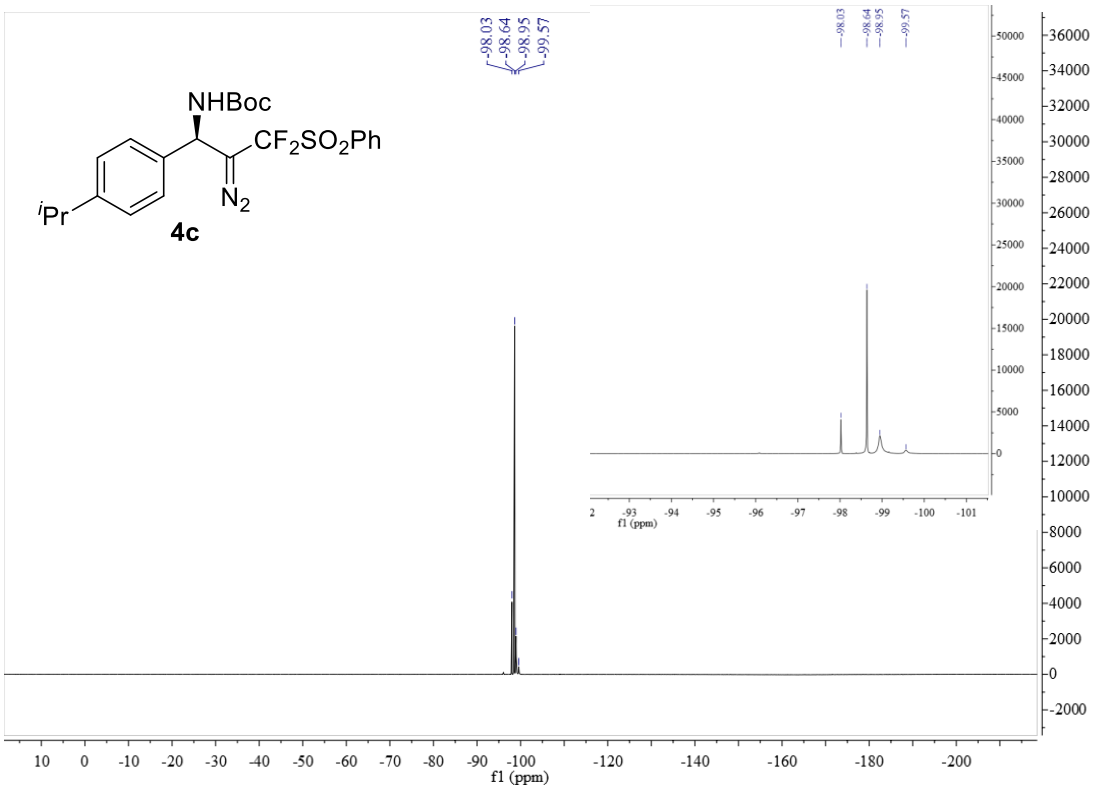
7.99
7.77
7.75
7.73
7.62
7.60
7.58
7.35
7.33
7.25
7.23
5.74
5.73
5.46
5.44
2.93
2.92
2.90
2.88
2.86
1.44
1.24
1.23
NHBoc
CF2SO2Ph
N2
iPr
4c
2.01
1.02
2.01
2.03
2.11
0.98
0.99
1.00
9.16
5.98
f1 (ppm)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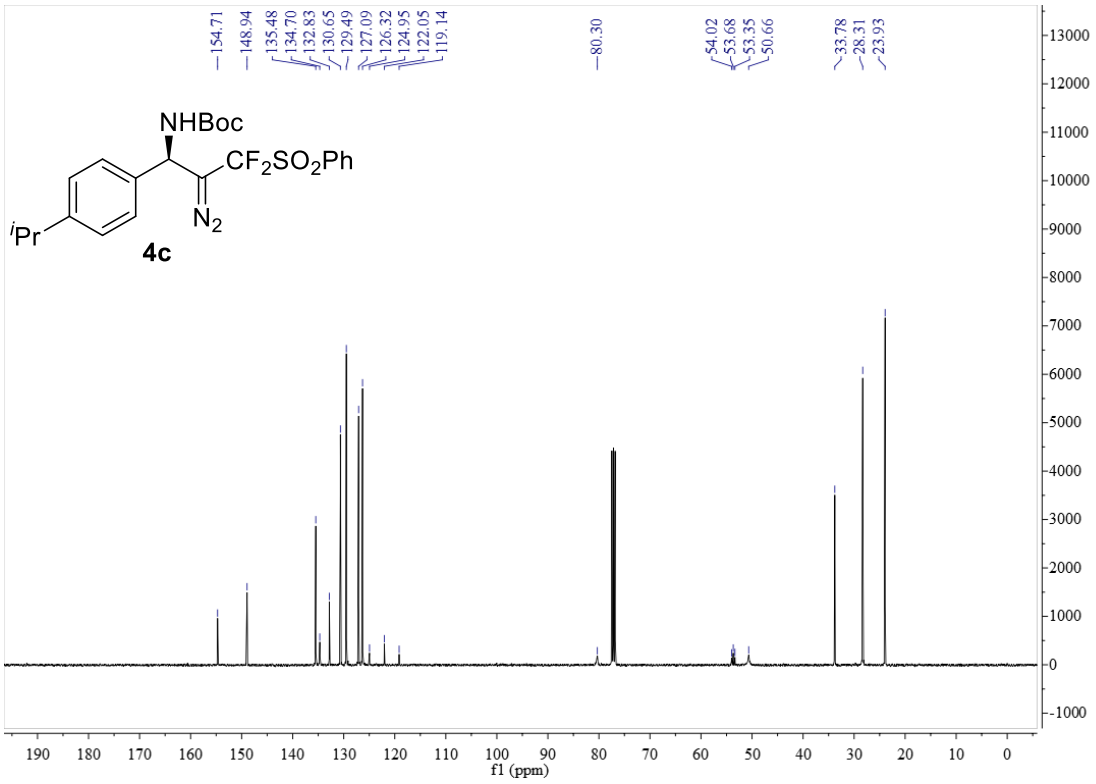
-98.95
-99.57
NHBoc
CF2SO2Ph
N2
iPr
4c
f1 (ppm)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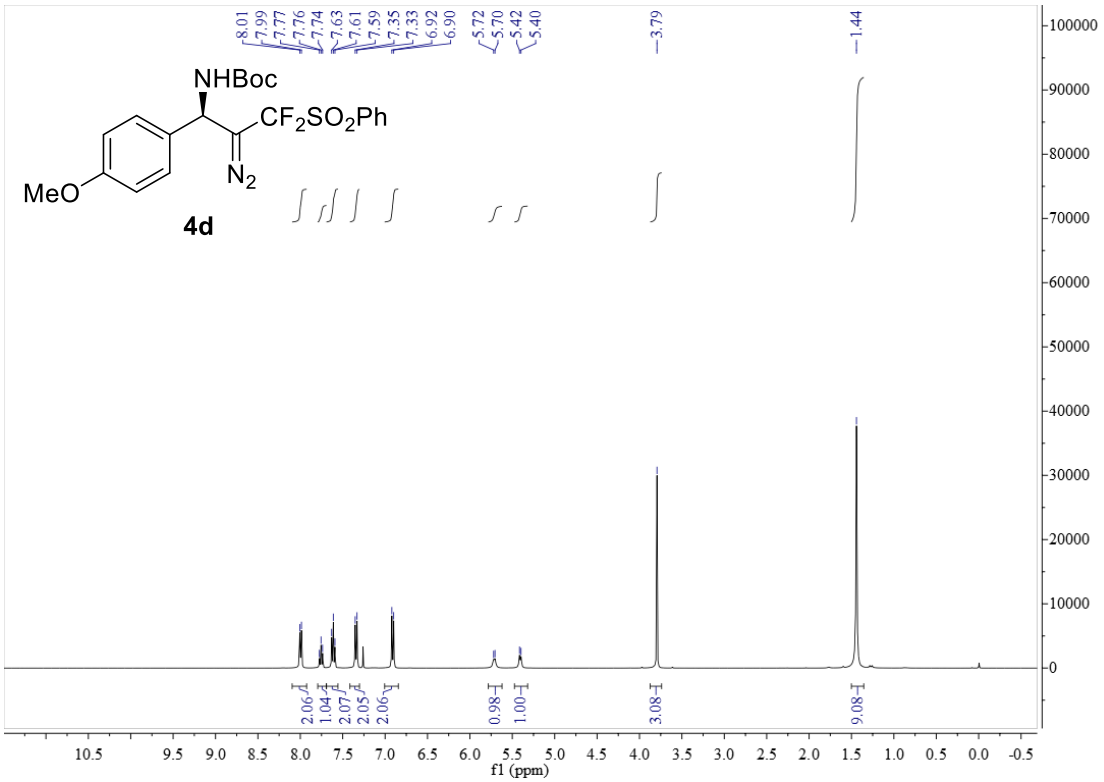
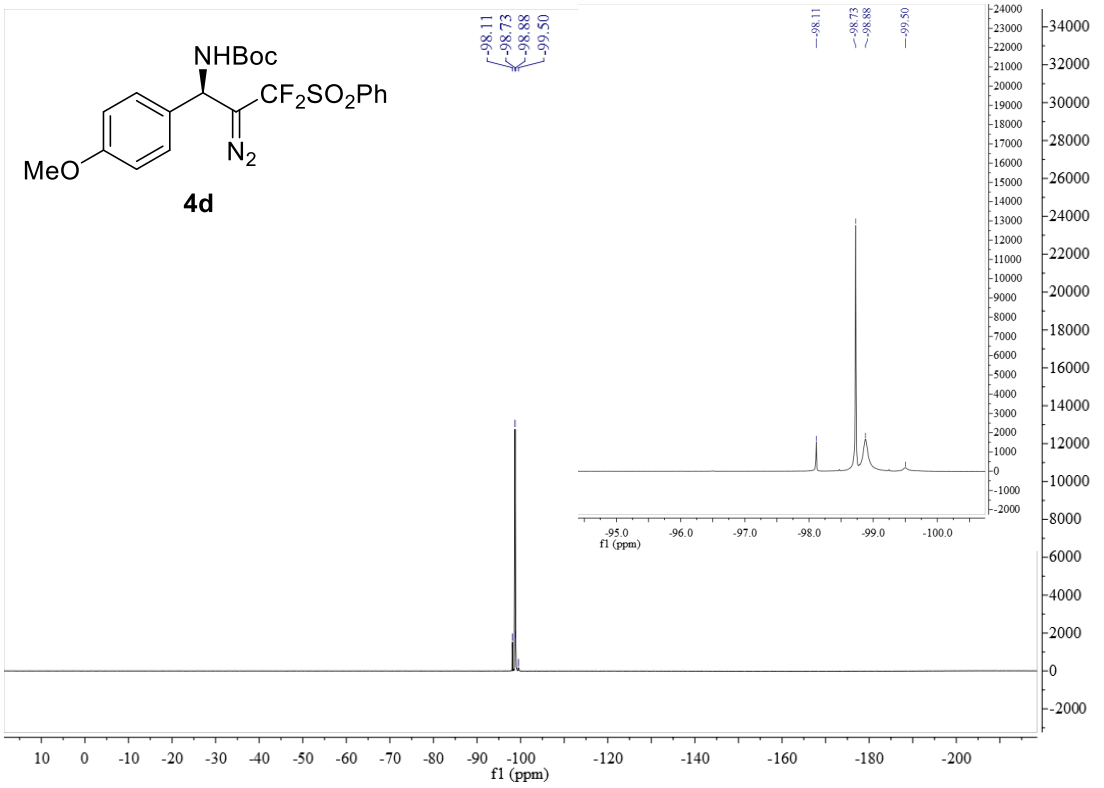
132.83
130.65
129.49
127.09
126.32
124.95
122.05
119.14
80.30
54.02
53.68
53.35
50.66
33.78
28.31
23.93
NHBoc
CF2SO2Ph
N2
iPr
4c
f1 (ppm)


NHBoc
CF2SO2Ph
N2
MeO
4d
8.01
7.99
7.77
7.76
7.74
7.63
7.61
7.59
7.35
7.33
6.92
6.90
5.72
5.70
5.42
5.40
3.79
1.44
2.06
1.04
2.07
2.05
2.06
0.98
1.00
3.08
9.08
f1 (ppm)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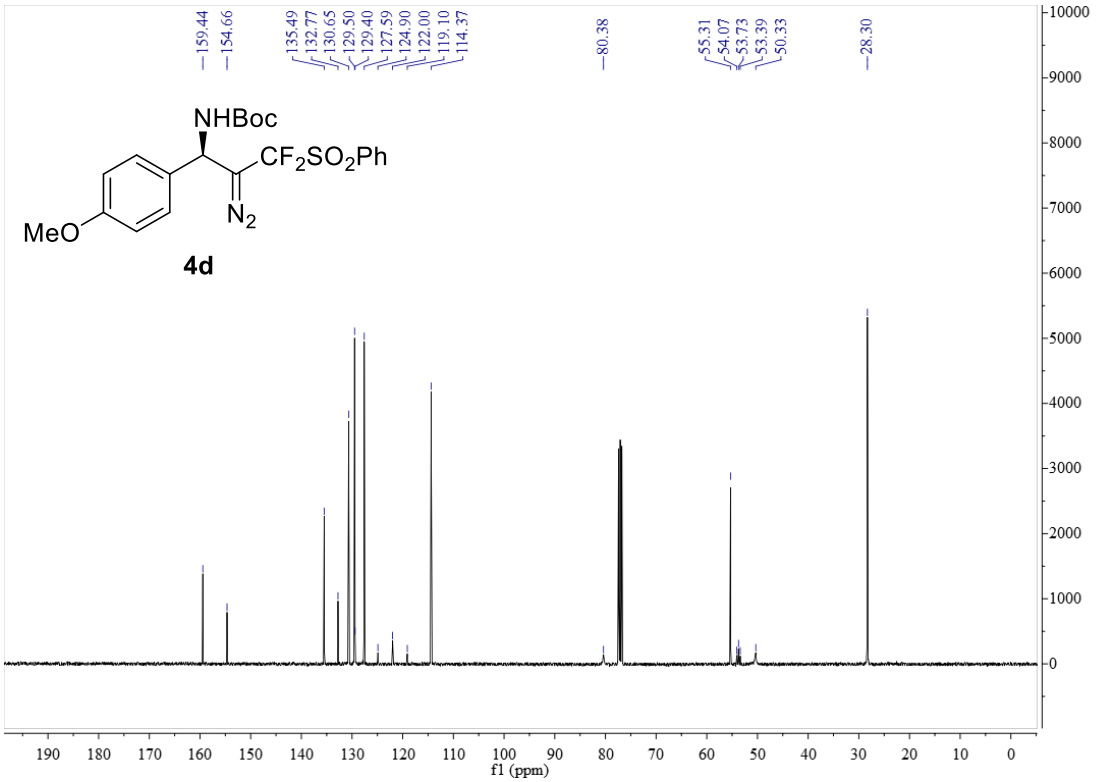
CF2SO2Ph
N2
MeO
4d
-98.11
-98.73
-98.88
-99.50
f1 (ppm)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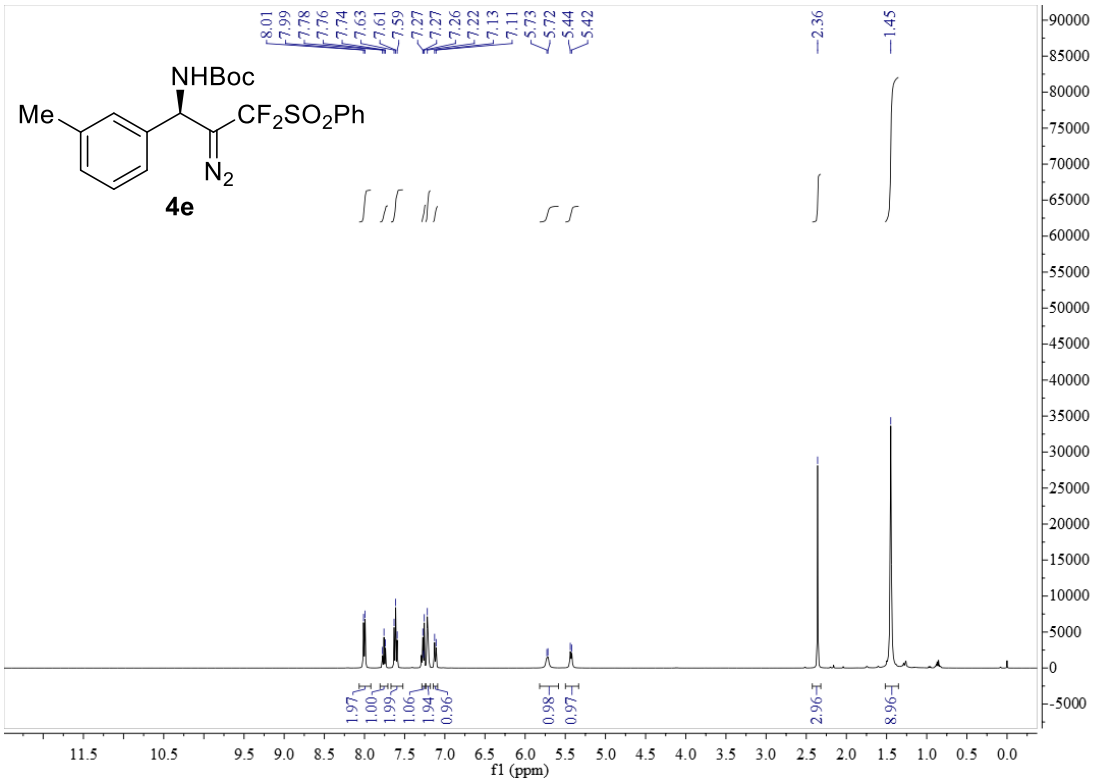
135.49
132.77
130.65
129.50
129.40
127.59
124.90
122.00
119.10
114.37
80.38
55.31
54.07
53.73
53.39
50.33
28.30
NHBoc
CF2SO2Ph
N2
MeO
4d
f1 (ppm)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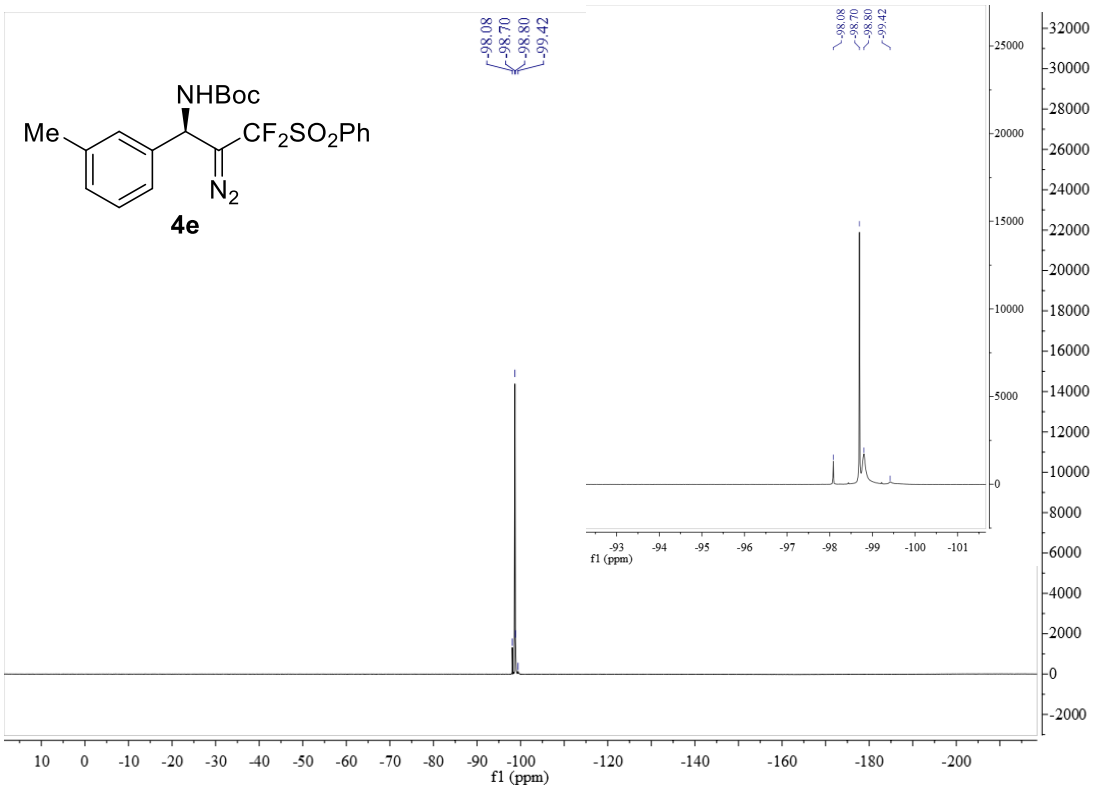
7.99
7.78
7.76
7.74
7.63
7.61
7.59
7.27
7.27
7.26
7.22
7.13
7.11
5.73
5.72
5.44
5.42
2.36
1.45
NHBoc
Me
CF2SO2Ph
N2
4e
1.97
1.00
1.99
1.06
1.94
0.96
0.98
0.97
2.96
8.96
f1 (ppm)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Me
CF2SO2Ph
N2
4e
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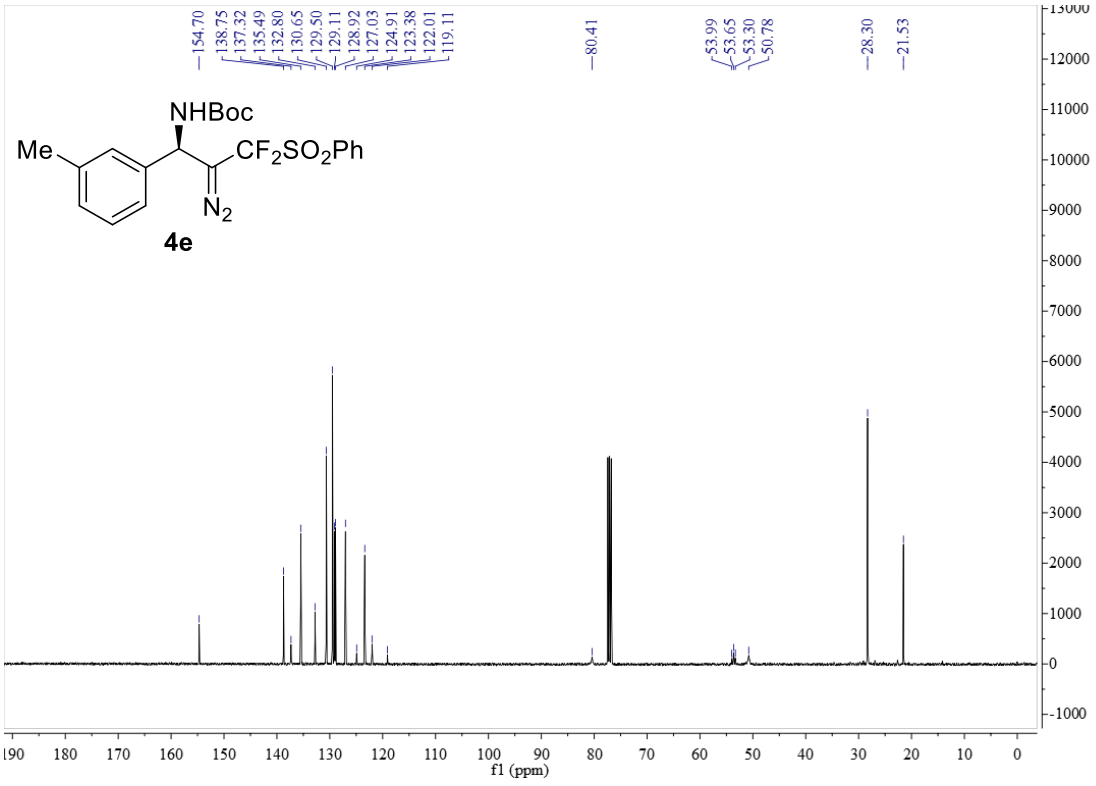
-98.70
-98.80
-99.42
f1 (ppm)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Me
CF2SO2Ph
N2
4e
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137.32
135.49
132.80
130.65
129.50
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128.92
127.03
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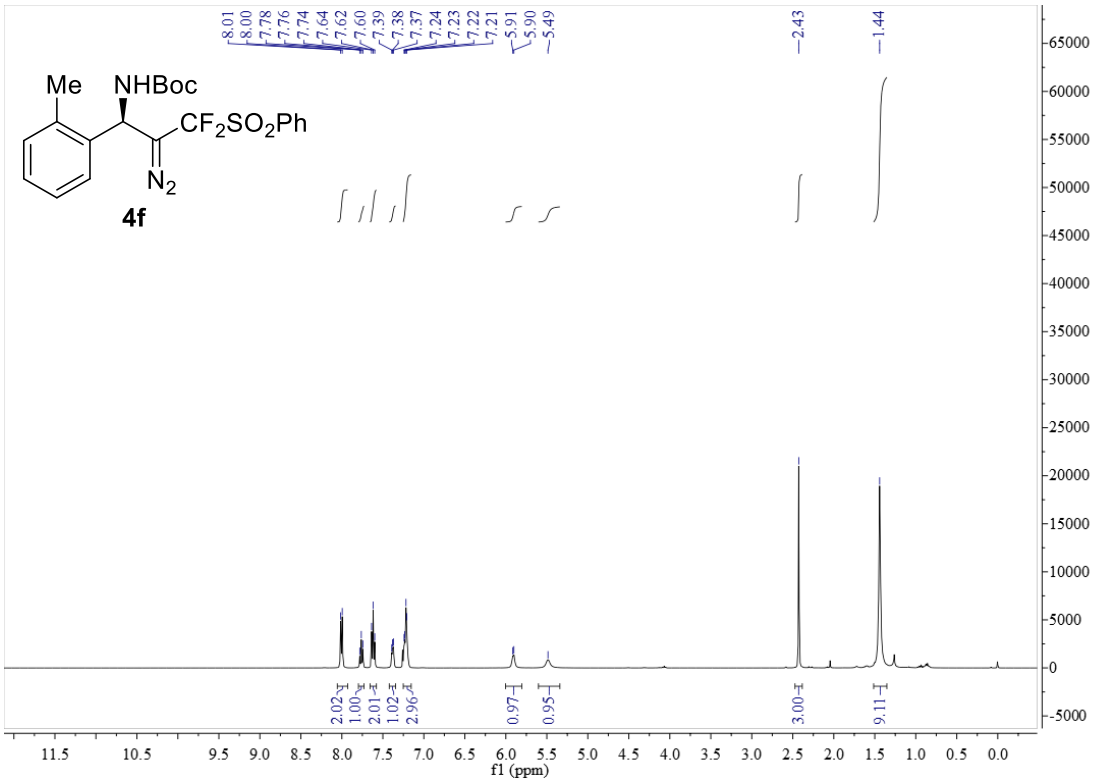
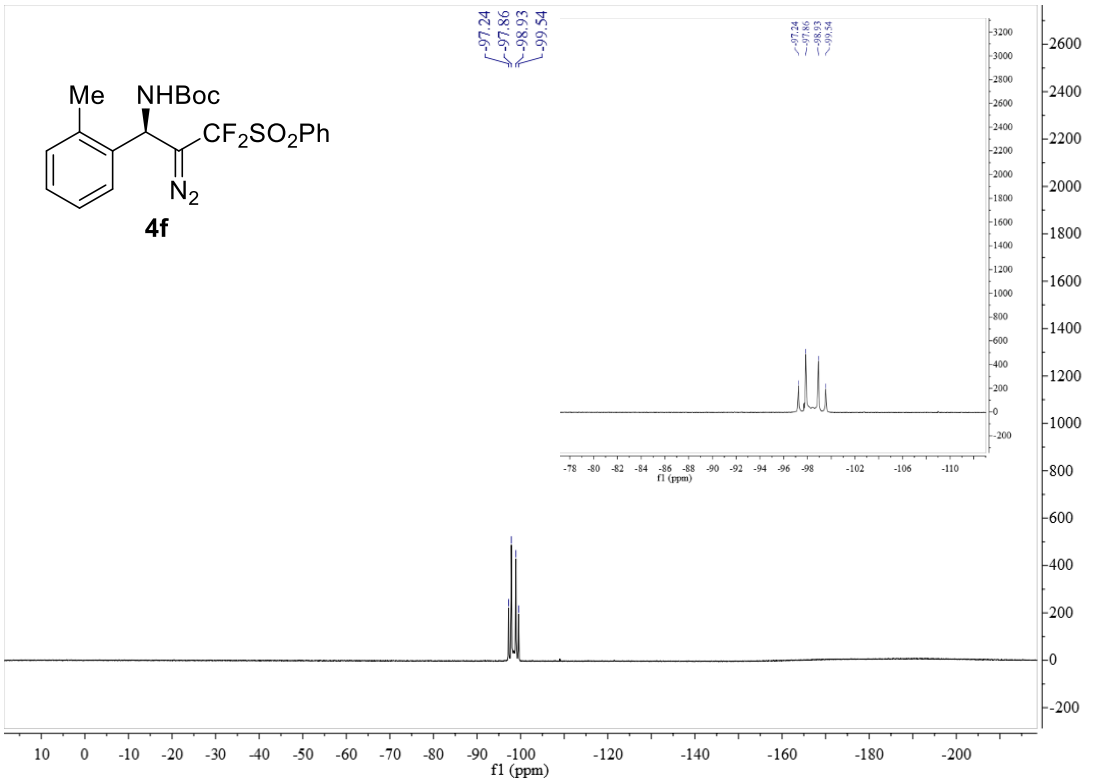
80.41
53.99
53.65
53.30
50.78
28.30
21.53
f1 (ppm)


Me
NHBoc
CF2SO2Ph
N2
4f
8.01
8.00
7.78
7.76
7.74
7.64
7.62
7.60
7.39
7.38
7.37
7.24
7.23
7.22
7.21
5.91
5.90
5.49
2.43
1.44
2.02
1.00
2.01
1.02
2.96
0.97
0.95
3.00
9.11
f1 (ppm)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N2
4f
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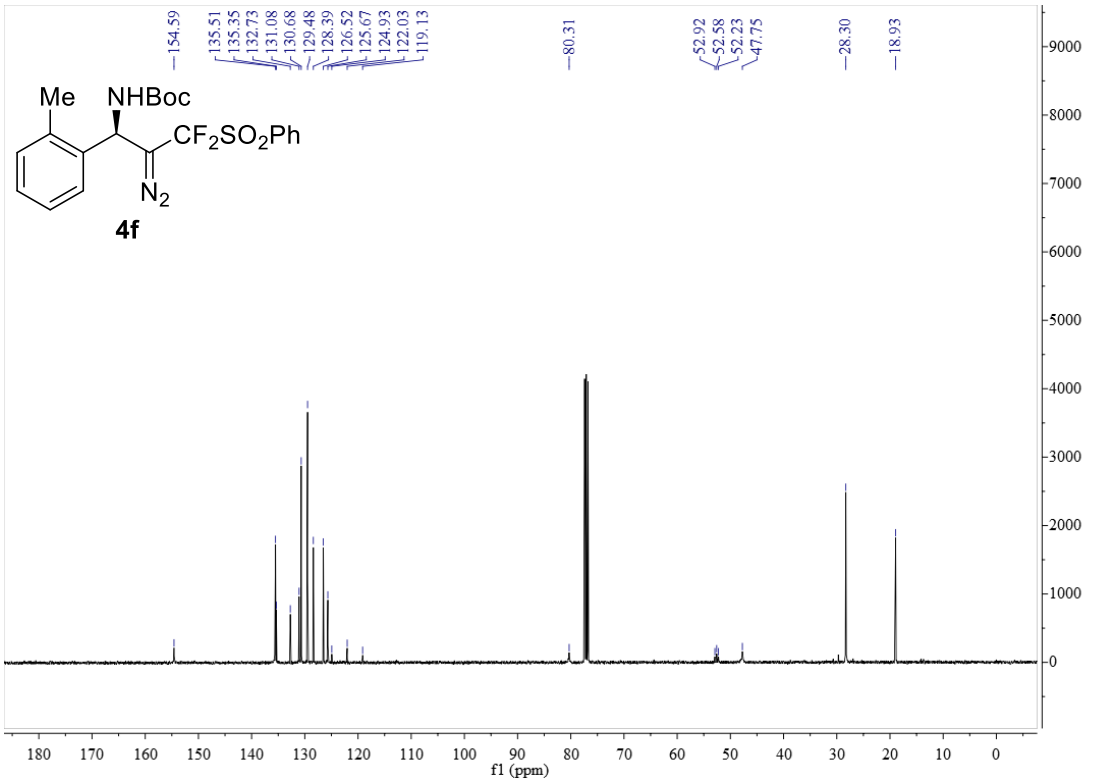
-97.86
-98.93
-99.54
f1 (ppm)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131.08
130.68
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126.52
125.67
124.93
122.03
119.13
80.31
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47.75
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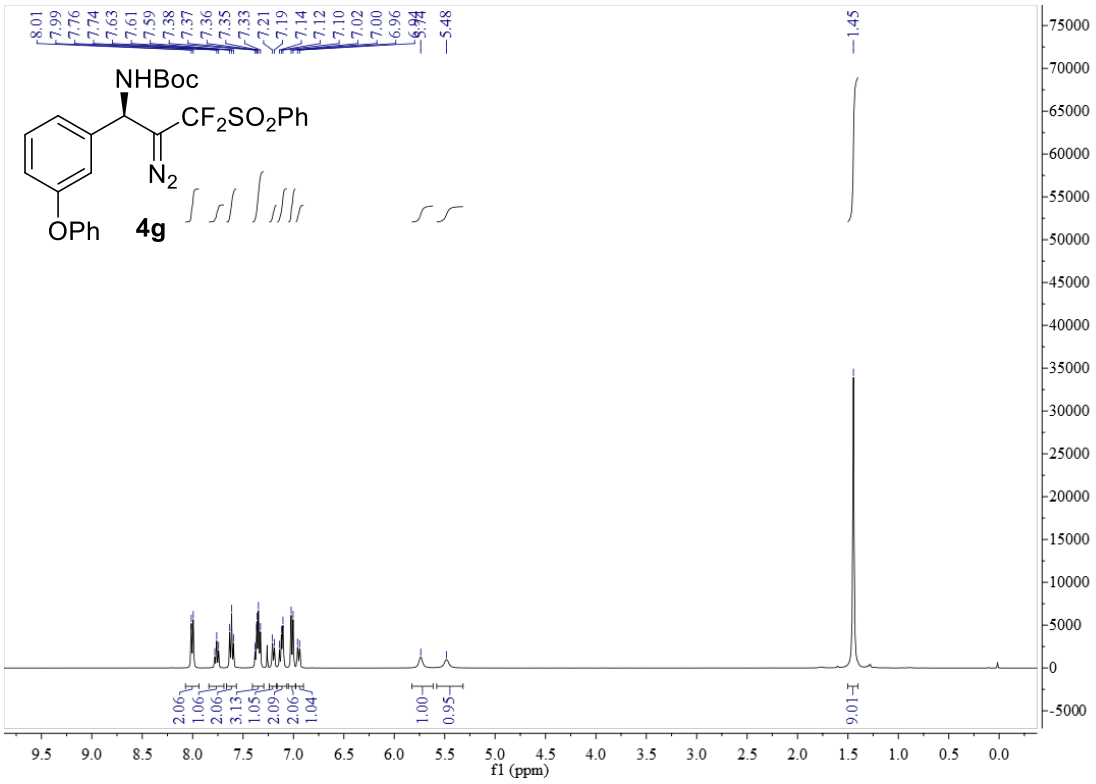
18.93
Me
NHBoc
CF2SO2Ph
N2
4f
f1 (ppm)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7.76
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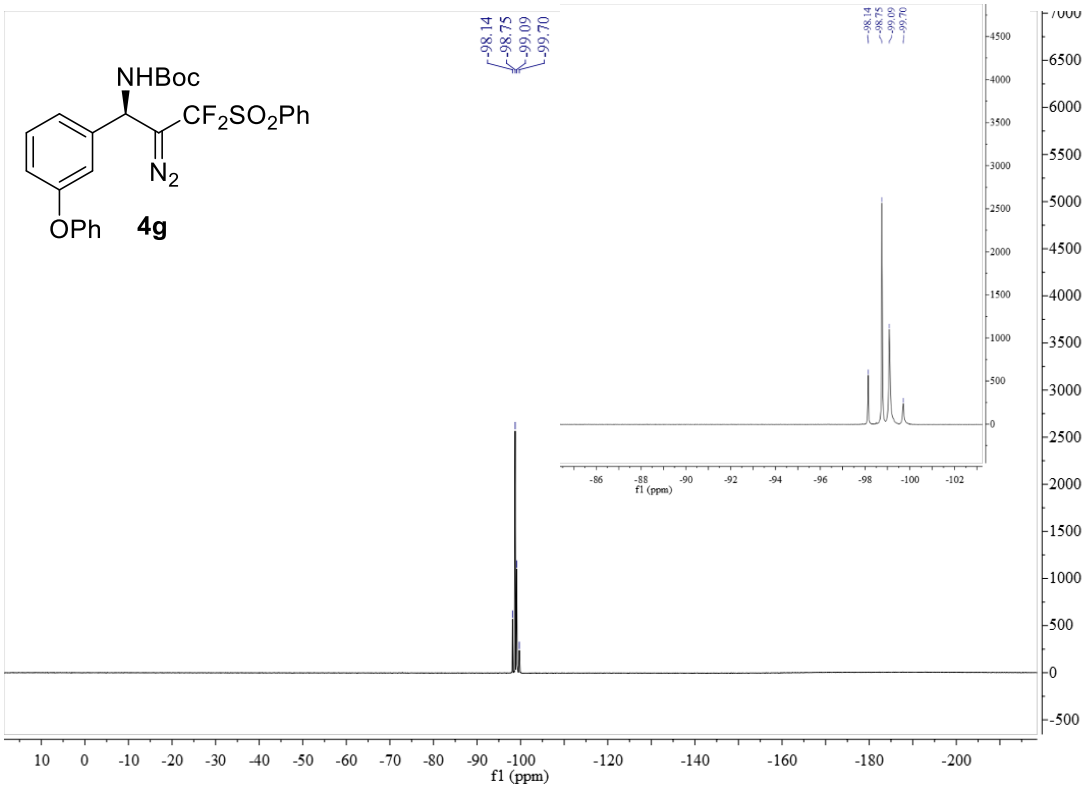
7.63
7.61
7.59
7.38
7.37
7.36
7.35
7.33
7.21
7.19
7.14
7.12
7.10
7.02
7.00
6.96
5.48
1.45
NHBoc
CF2SO2Ph
N2
OPh
4g
2.06
1.06
2.06
3.13
1.05
2.09
2.06
1.04
1.00
0.95
9.01
f1 (ppm)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N2
OPh
4g
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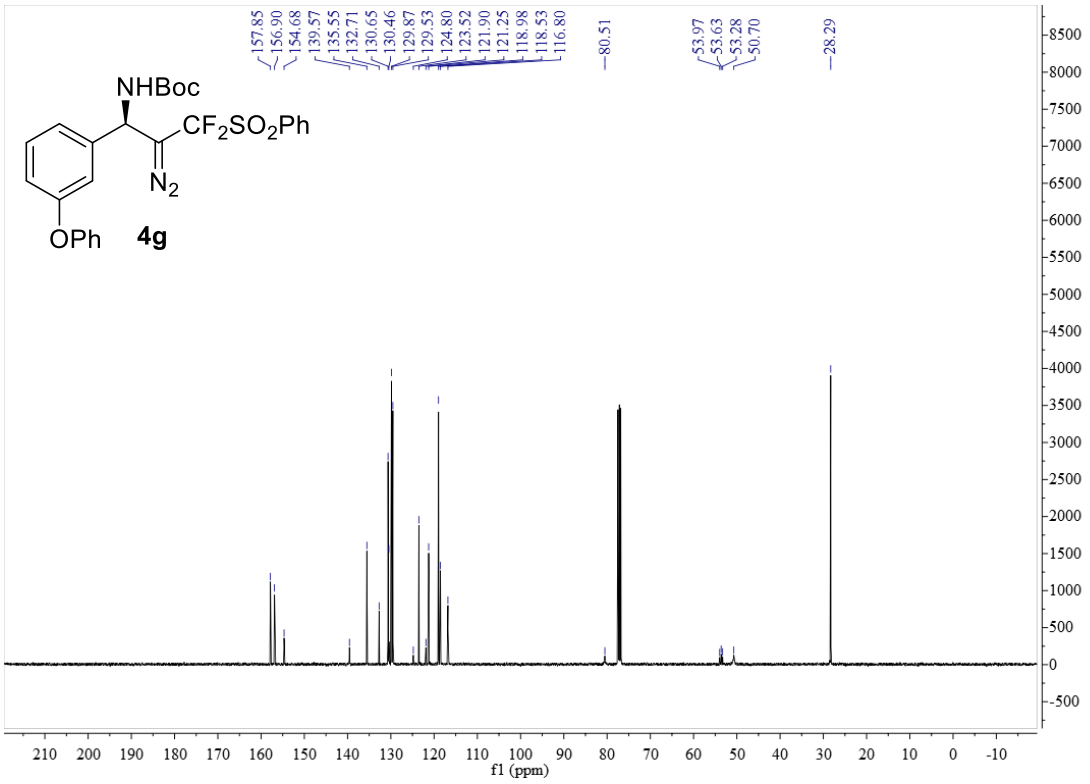
-98.75
-99.09
-99.70
f1 (ppm)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CF2SO2Ph
N2
OPh
4g
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130.46
129.87
129.53
124.80
123.52
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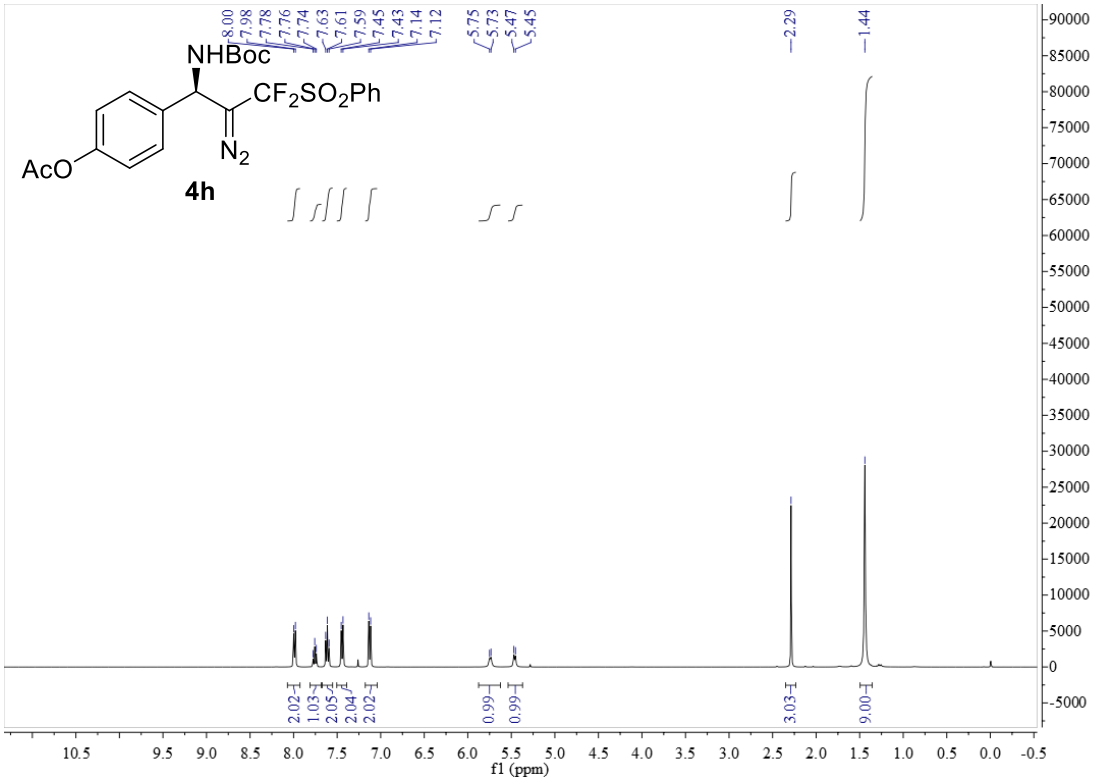
118.53
116.80
80.51
53.97
53.63
53.28
50.70
28.29
f1 (ppm)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CF2SO2Ph
N2
AcO
4h
8.00
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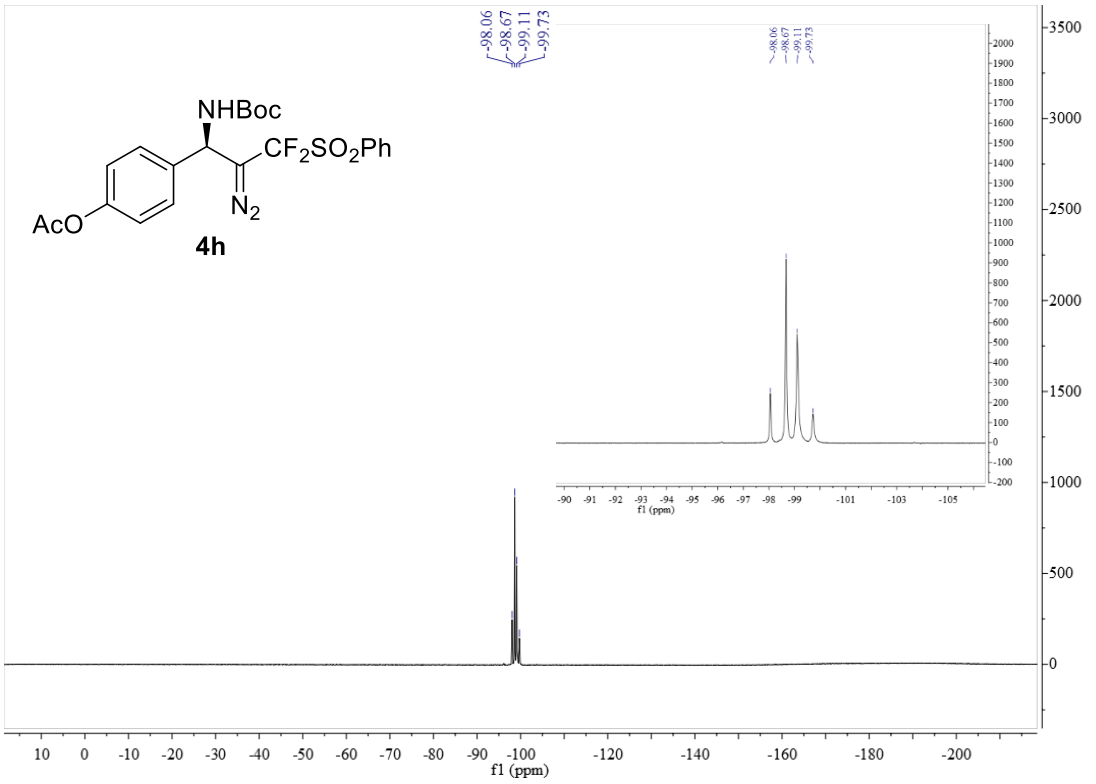
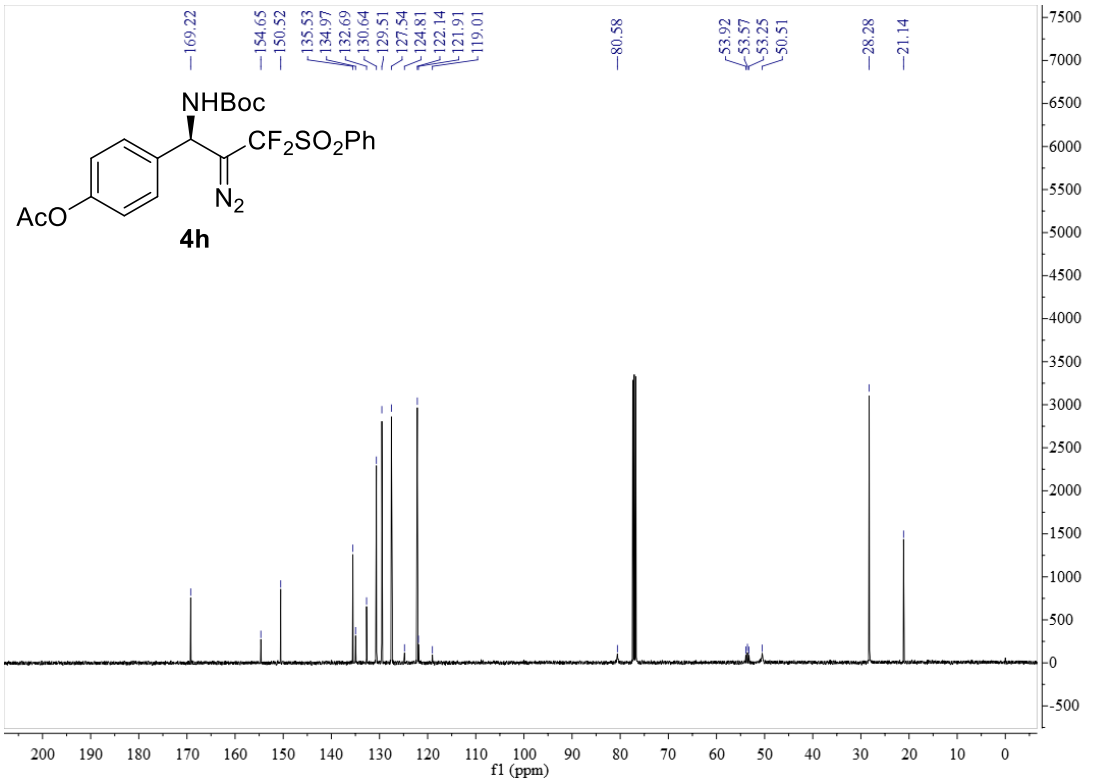
7.74
7.63
7.61
7.59
7.45
7.43
7.14
7.12
5.75
5.73
5.47
5.45
2.29
1.44
2.02
1.03
2.05
2.04
2.02
0.99
0.99
3.03
9.00
f1 (ppm)


NHBoc
CF2SO2Ph
N2
AcO
4h
-98.06
-98.67
-99.11
-99.73
f1 (ppm)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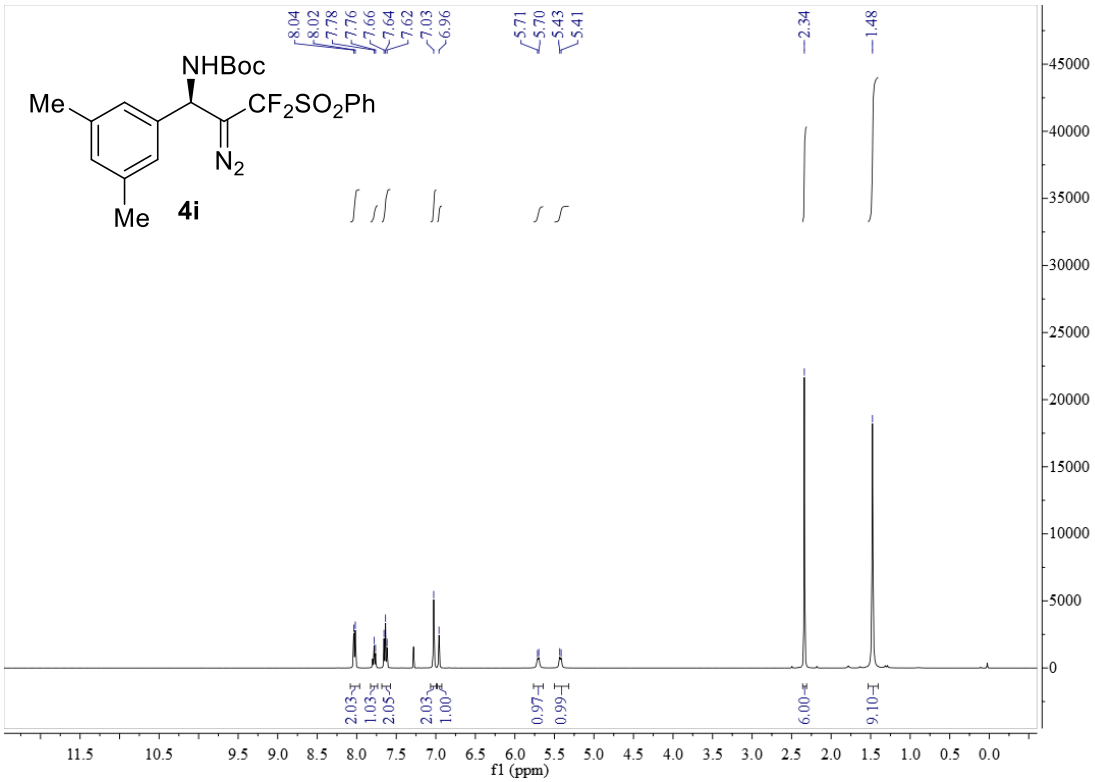
129.51
127.54
124.81
122.14
121.91
119.01
80.58
53.92
53.57
53.25
50.51
28.28
21.14
NHBoc
CF2SO2Ph
N2
AcO
4h
f1 (ppm)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7.76
7.66
7.64
7.62
7.03
6.96
5.71
5.70
5.43
5.41
2.34
1.48
NHBoc
CF2SO2Ph
N2
Me
Me
4i
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1.03
2.05
2.03
1.00
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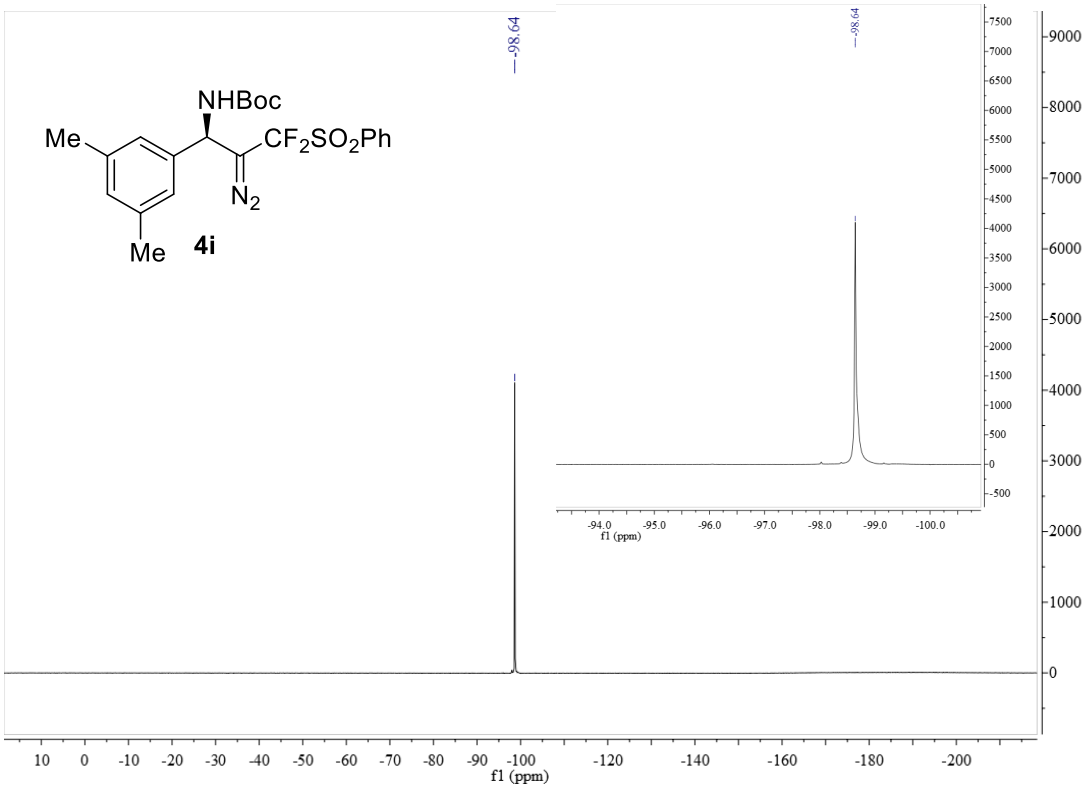
0.99
6.00
9.10
f1 (ppm)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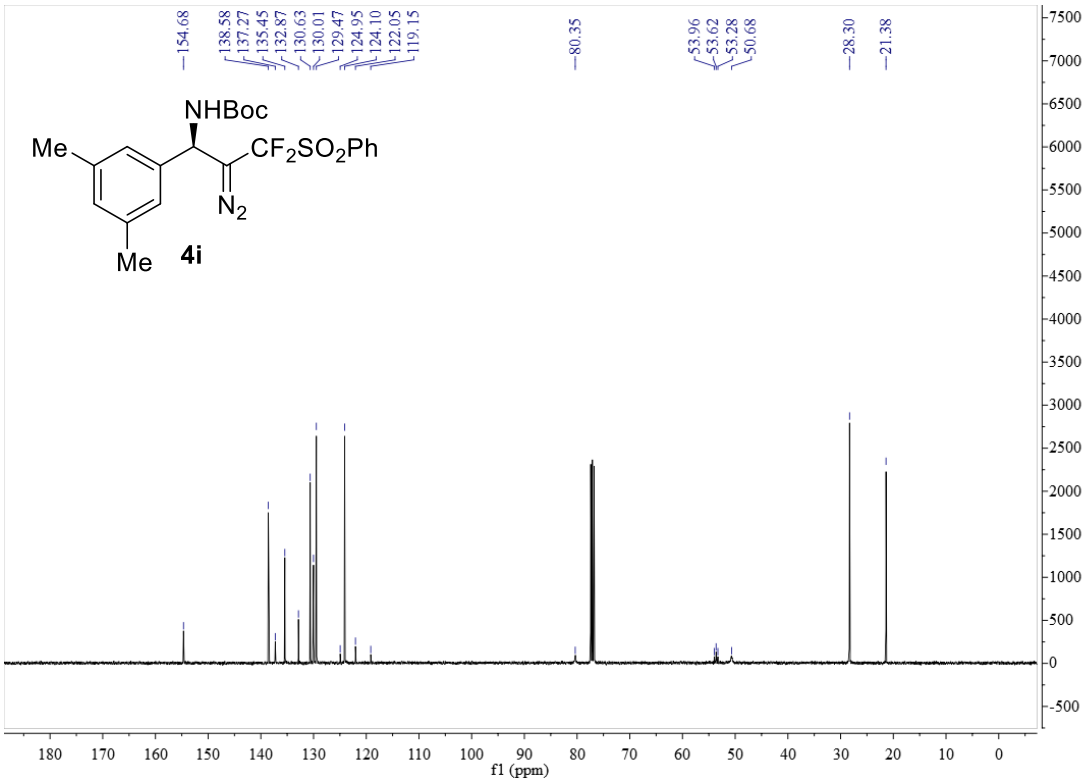
Me
CF2SO2Ph
N2
Me
4i
-98.64
f1 (ppm)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130.63
130.01
129.47
124.95
124.10
122.05
119.15
80.35
53.96
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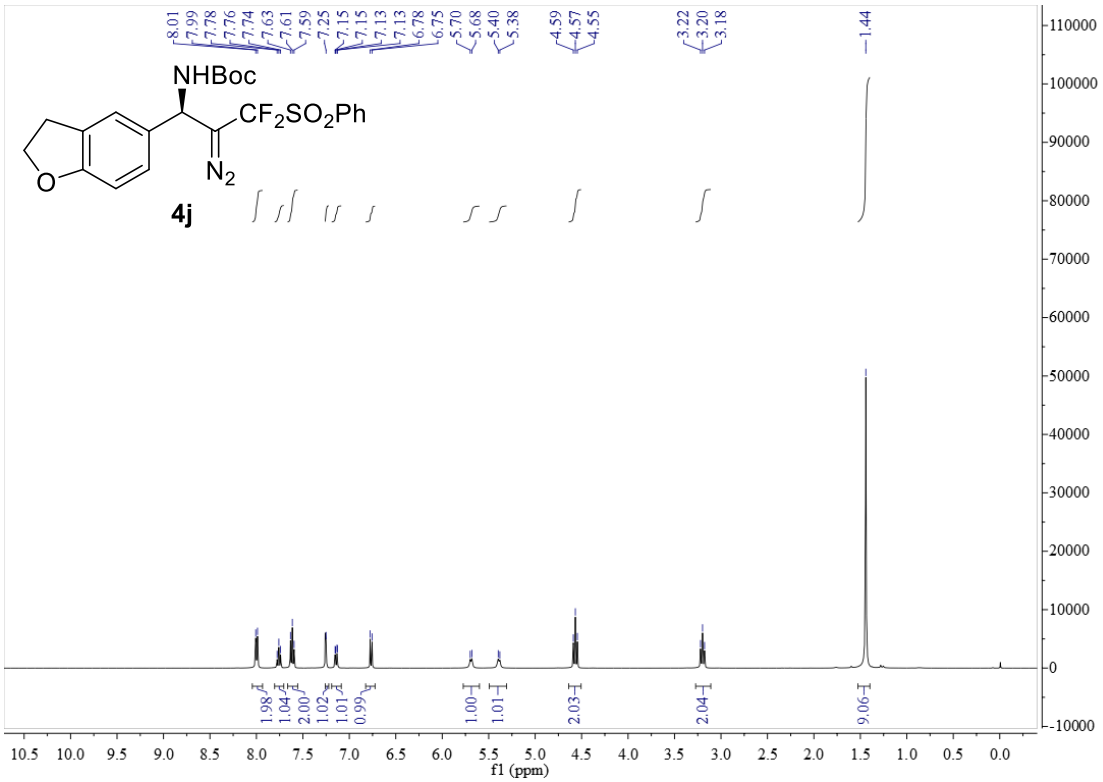
50.68
28.30
21.38
NHBoc
Me
CF2SO2Ph
N2
Me
4i
f1 (ppm)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N2
O
4j
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7.74
7.63
7.61
7.59
7.25
7.15
7.15
7.13
7.13
6.78
6.75
5.70
5.68
5.40
5.38
4.59
4.57
4.55
3.22
3.20
3.18
1.44
1.98
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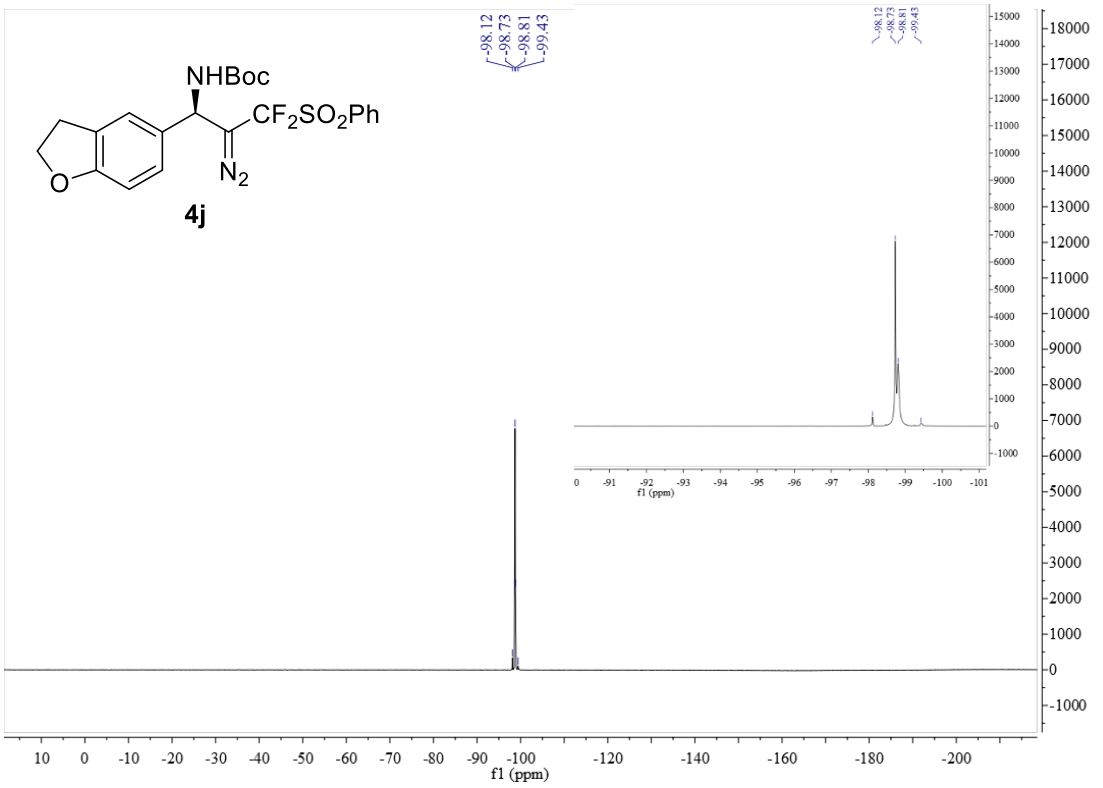
1.02
1.01
0.99
1.00
1.01
2.03
2.04
9.06
f1 (ppm)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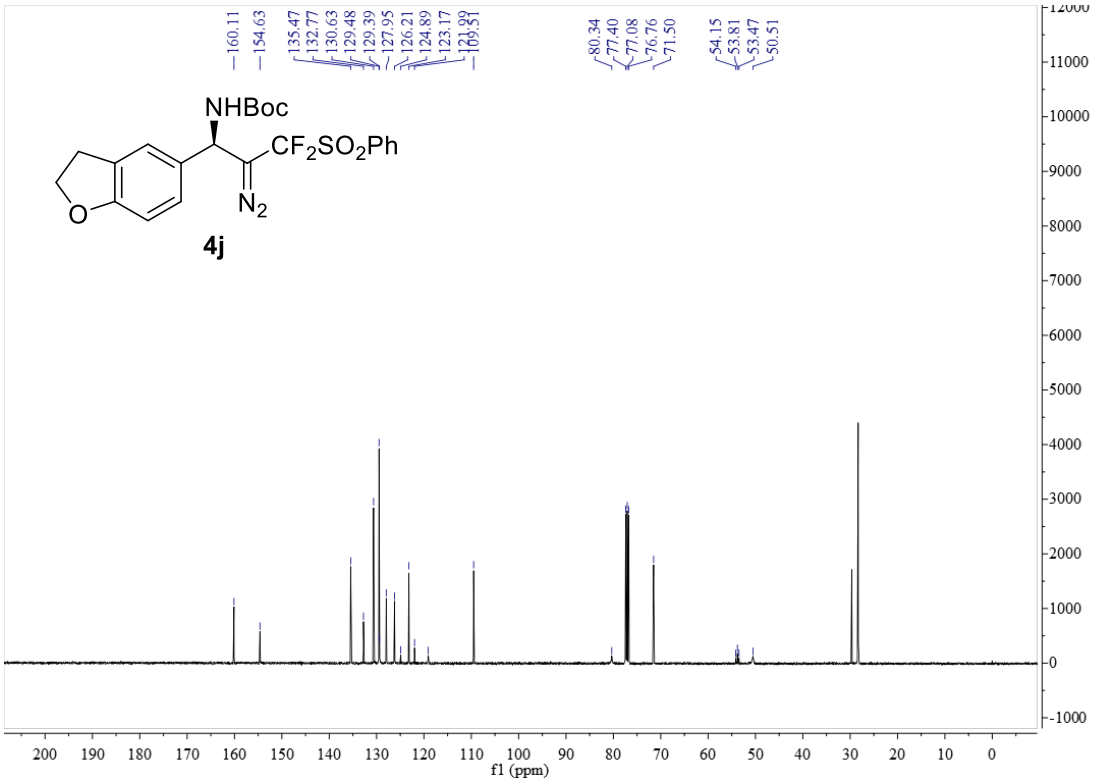
N2
O
4j
-98.12
-98.73
-98.81
-99.43
f1 (ppm)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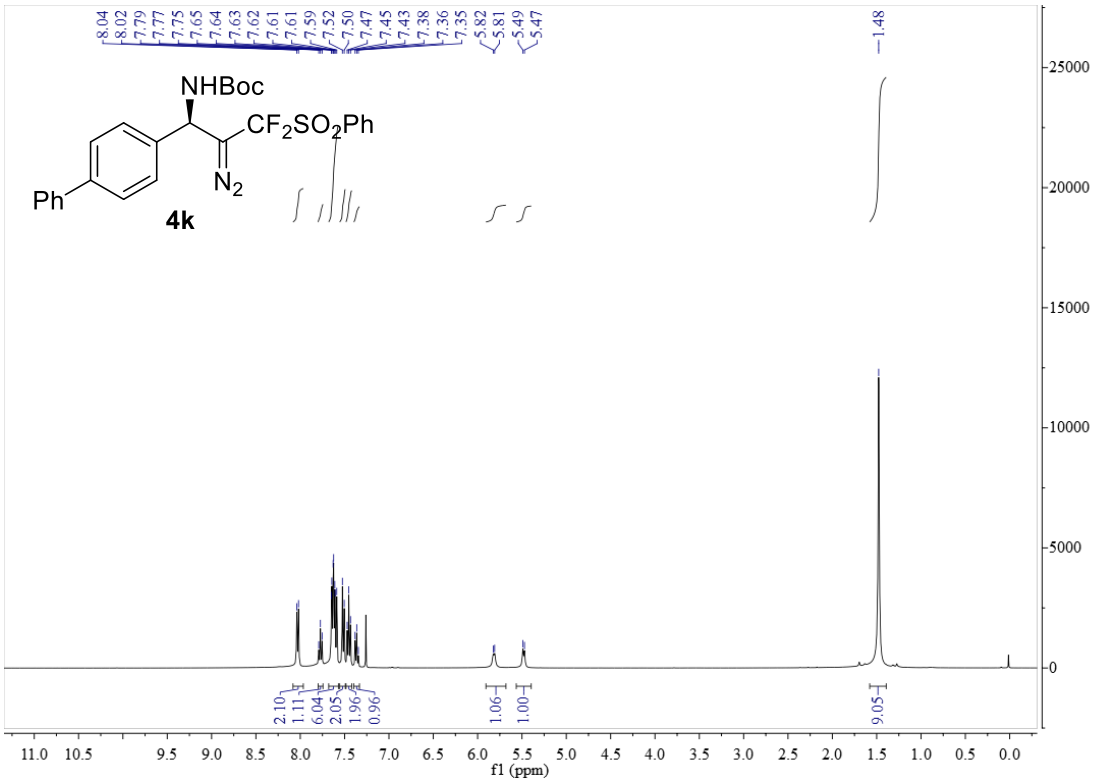
126.21
124.89
123.17
121.99
109.51
80.34
77.40
77.08
76.76
71.50
54.15
53.81
53.47
50.51
NHBoc
CF2SO2Ph
N2
O
4j
f1 (ppm)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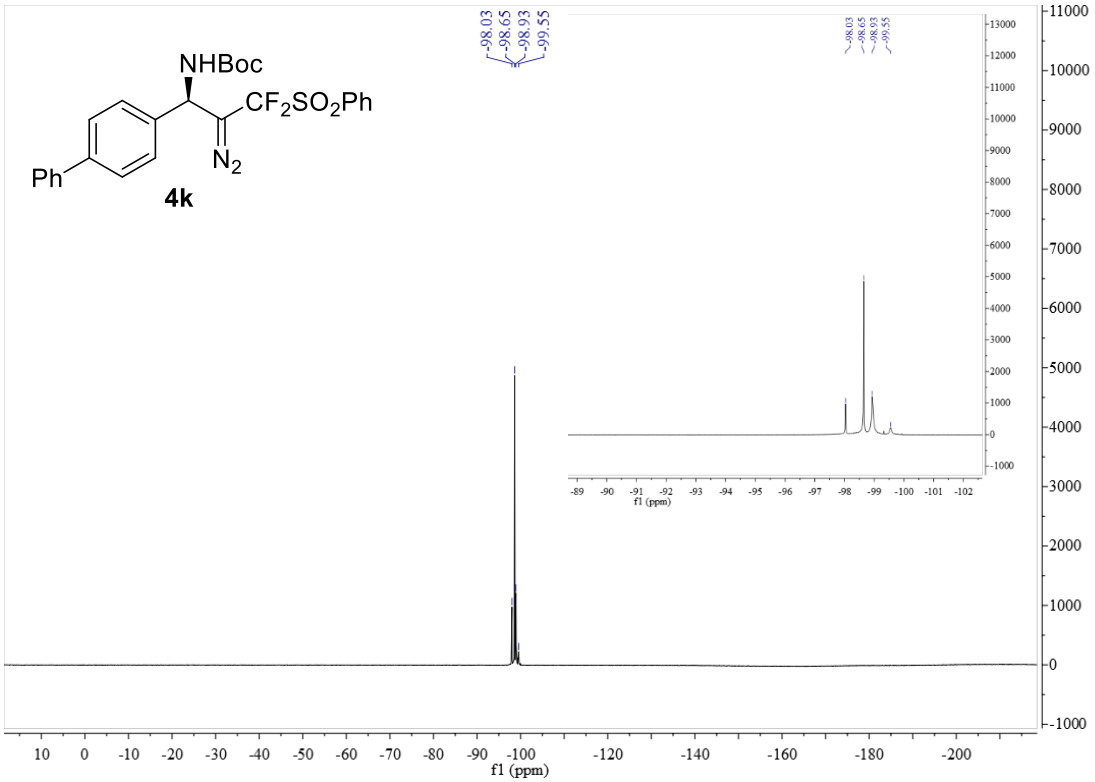
7.63
7.62
7.61
7.61
7.59
7.52
7.50
7.47
7.45
7.43
7.38
7.36
7.35
5.82
5.81
5.49
5.47
1.48
NHBoc
CF2SO2Ph
N2
Ph
4k
2.10
1.11
6.04
2.05
1.96
0.96
1.06
1.00
9.05
f1 (ppm)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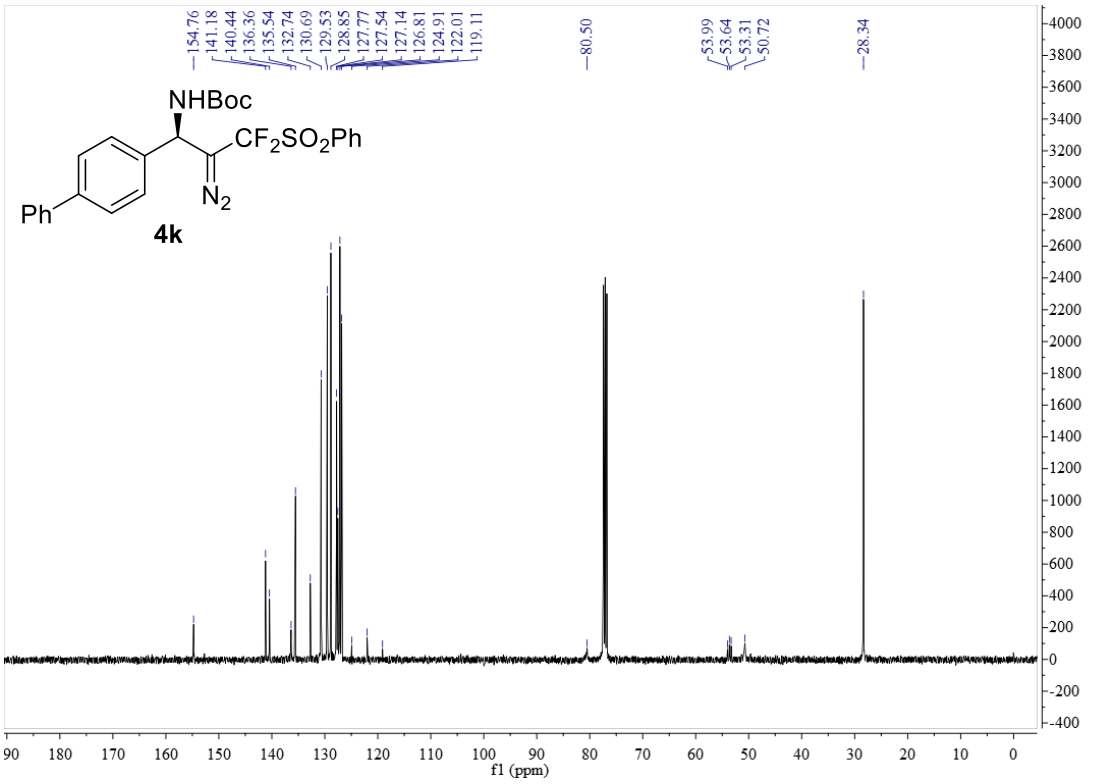
CF2SO2Ph
N2
Ph
4k
-98.03
-98.65
-98.93
-99.55
f1 (ppm)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129.53
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127.77
127.54
127.14
126.81
124.91
122.01
119.11
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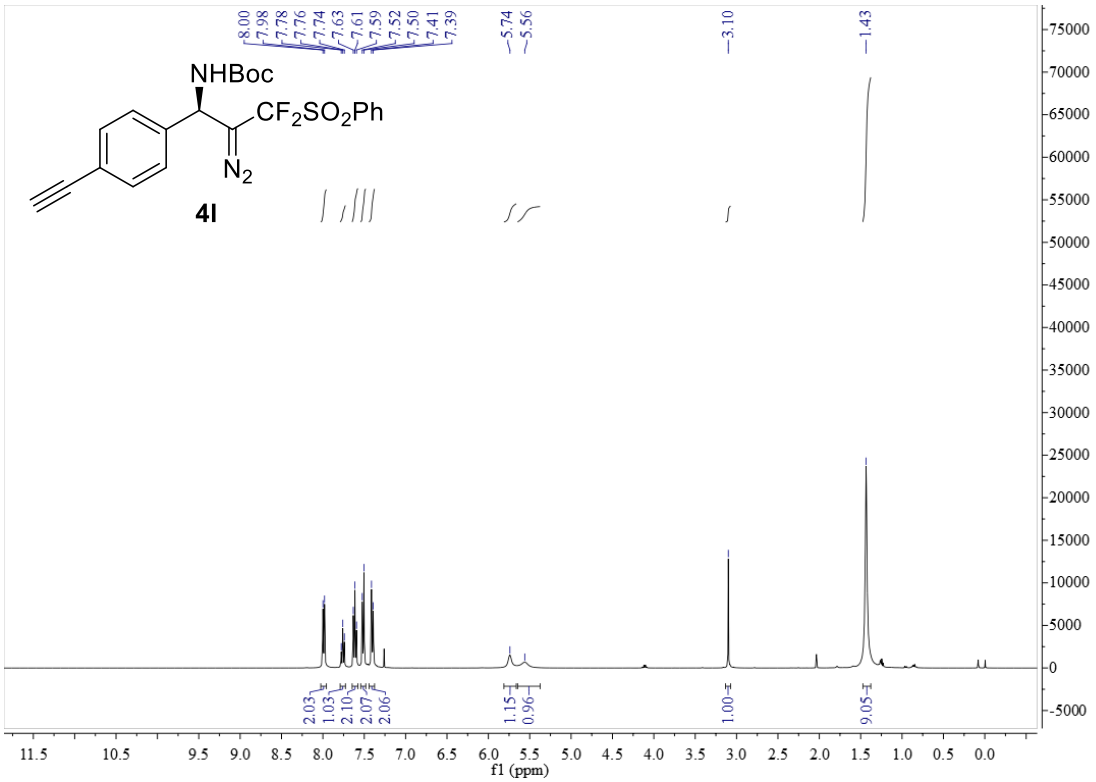
53.99
53.64
53.31
50.72
28.34
NHBoc
CF2SO2Ph
N2
Ph
4k
f1 (ppm)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CF2SO2Ph
N2
4l
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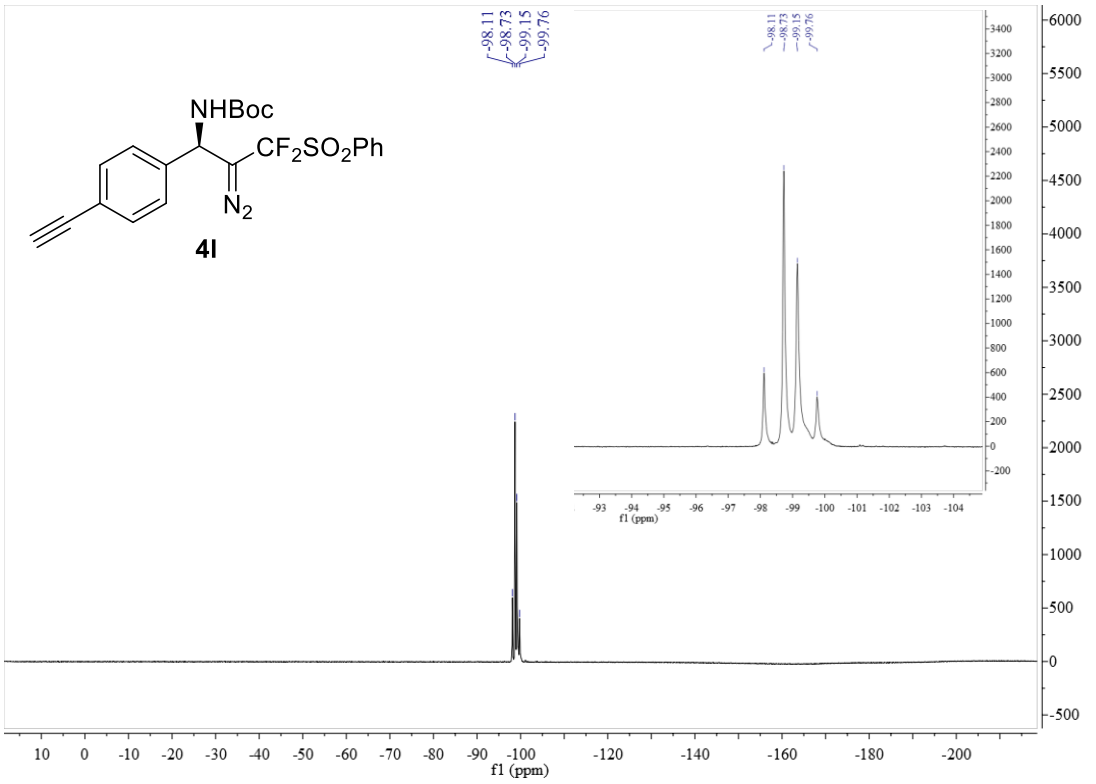
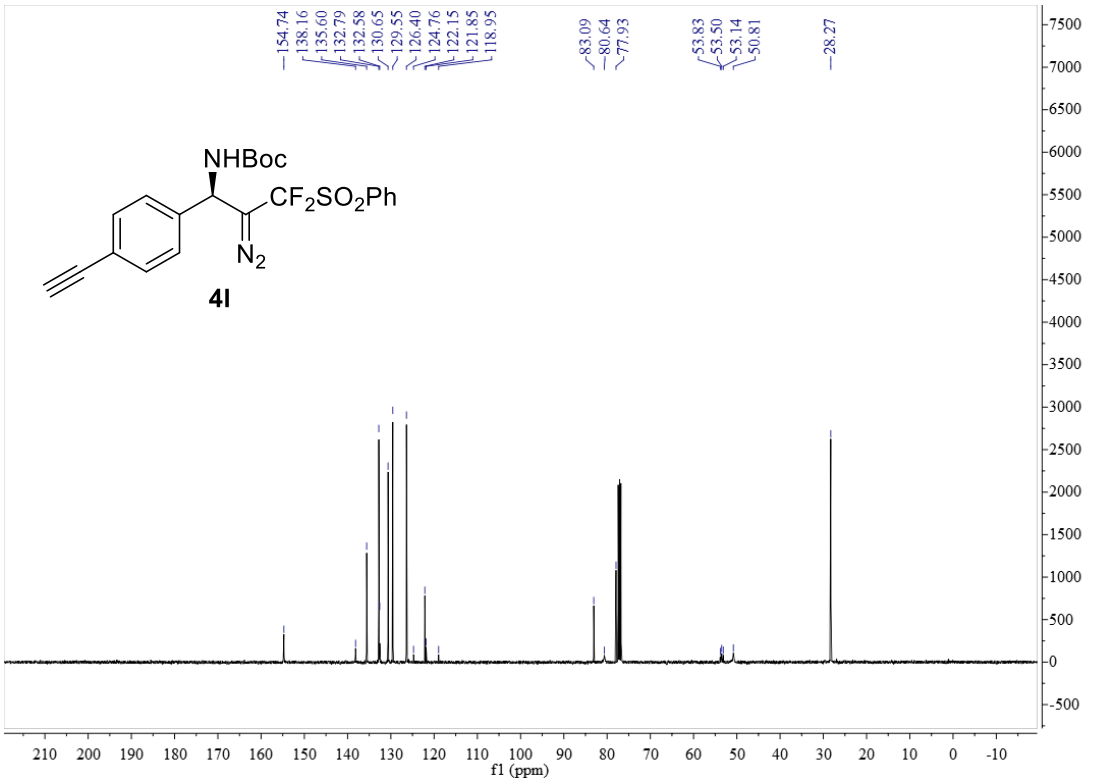
7.78
7.76
7.74
7.63
7.61
7.59
7.52
7.50
7.41
7.39
5.74
5.56
3.10
1.43
2.03
1.03
2.10
2.07
2.06
1.15
0.96
1.00
9.05
f1 (ppm)


NHBoc
CF2SO2Ph
N2
4l
-98.11
-98.73
-99.15
-99.76
f1 (ppm)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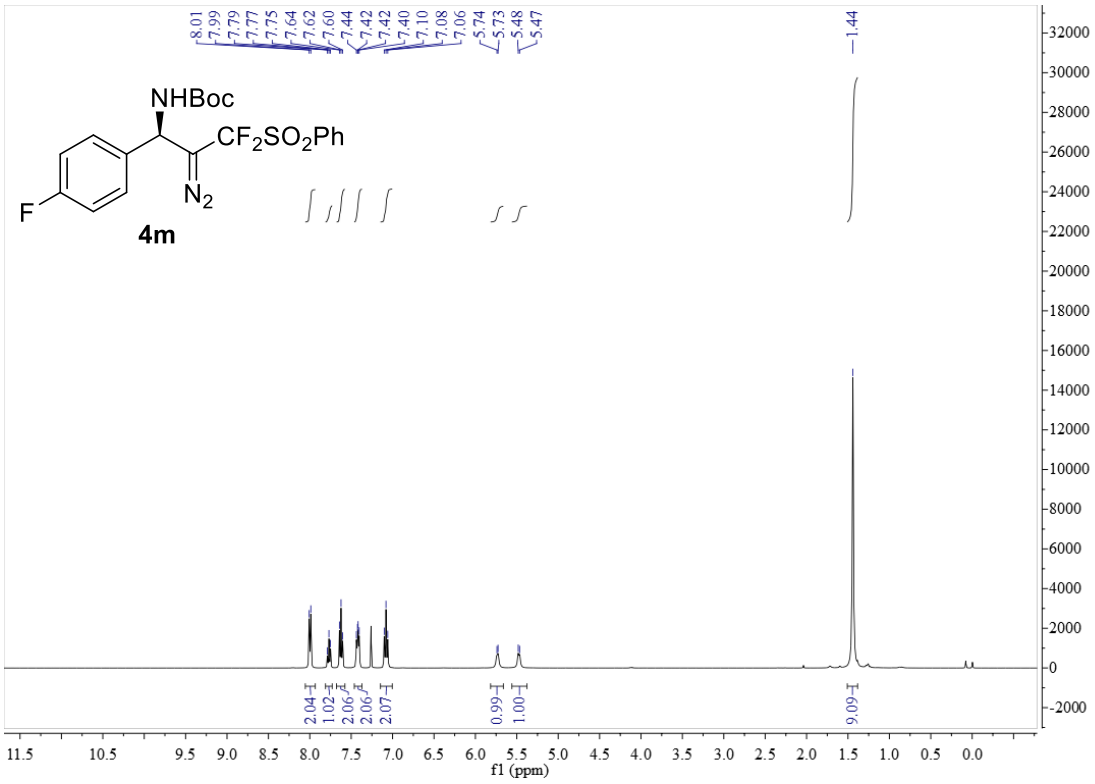
129.55
126.40
124.76
122.15
121.85
118.95
83.09
80.64
77.93
53.83
53.50
53.14
50.81
28.27
NHBoc
CF2SO2Ph
N2
4l
f1 (ppm)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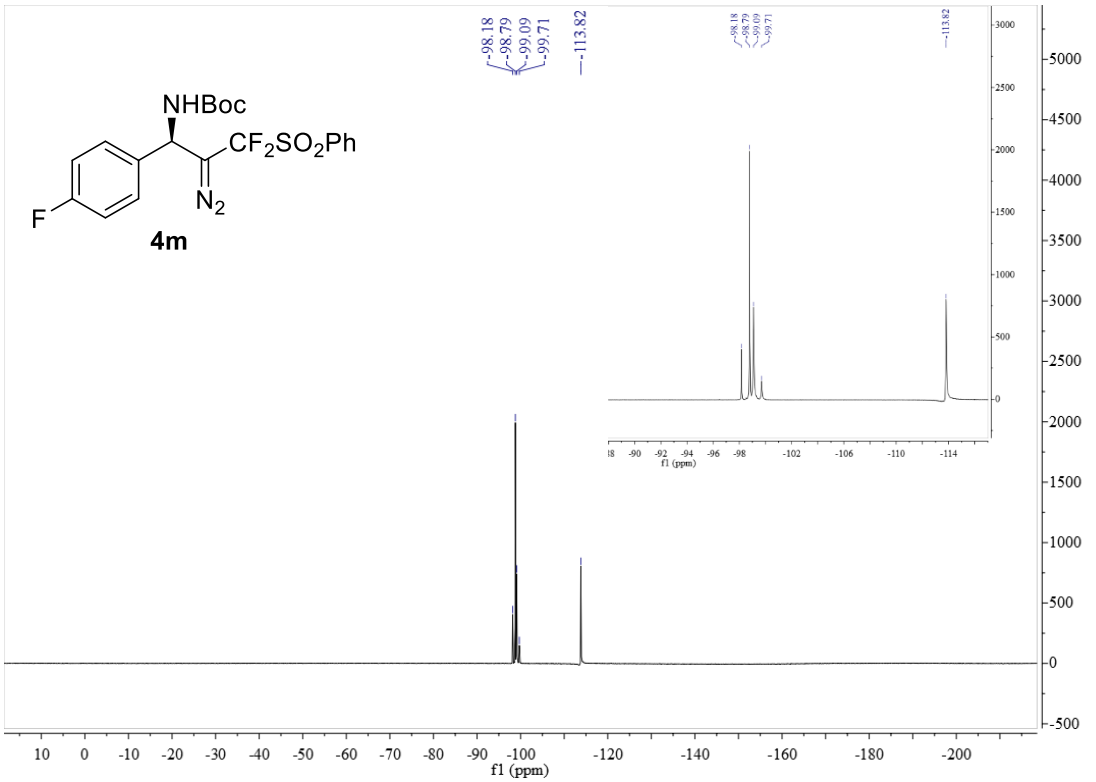
7.99
7.79
7.77
7.75
7.64
7.62
7.60
7.44
7.42
7.42
7.40
7.10
7.08
7.06
5.74
5.73
5.48
5.47
1.44
NHBoc
CF2SO2Ph
N2
F
4m
2.04
1.02
2.06
2.06
2.07
0.99
1.00
9.09
f1 (ppm)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N2
F
4m
-98.18
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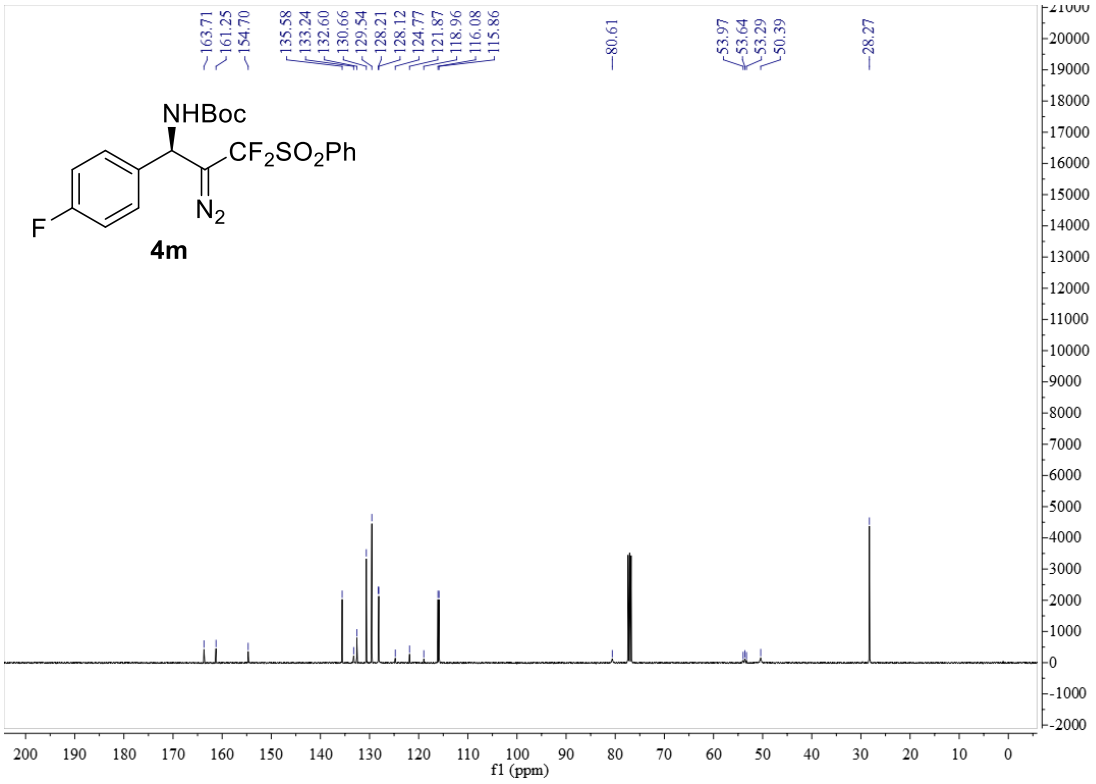
-99.09
-99.71
-113.82
f1 (ppm)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CF2SO2Ph
N2
F
4m
163.71
161.25
154.70
135.58
133.24
132.60
130.66
129.54
128.21
128.12
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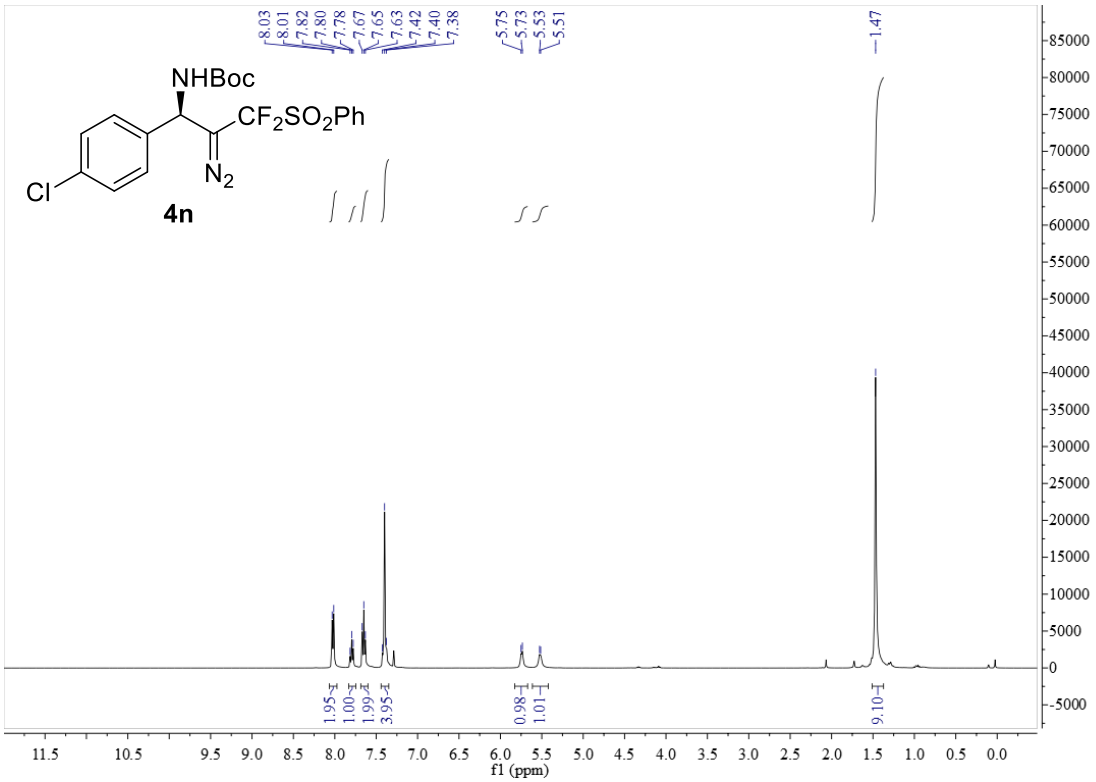
121.87
118.96
116.08
115.86
80.61
53.97
53.64
53.29
50.39
28.27
f1 (ppm)


NHBoc
CF2SO2Ph
N2
Cl
4n
8.03
8.01
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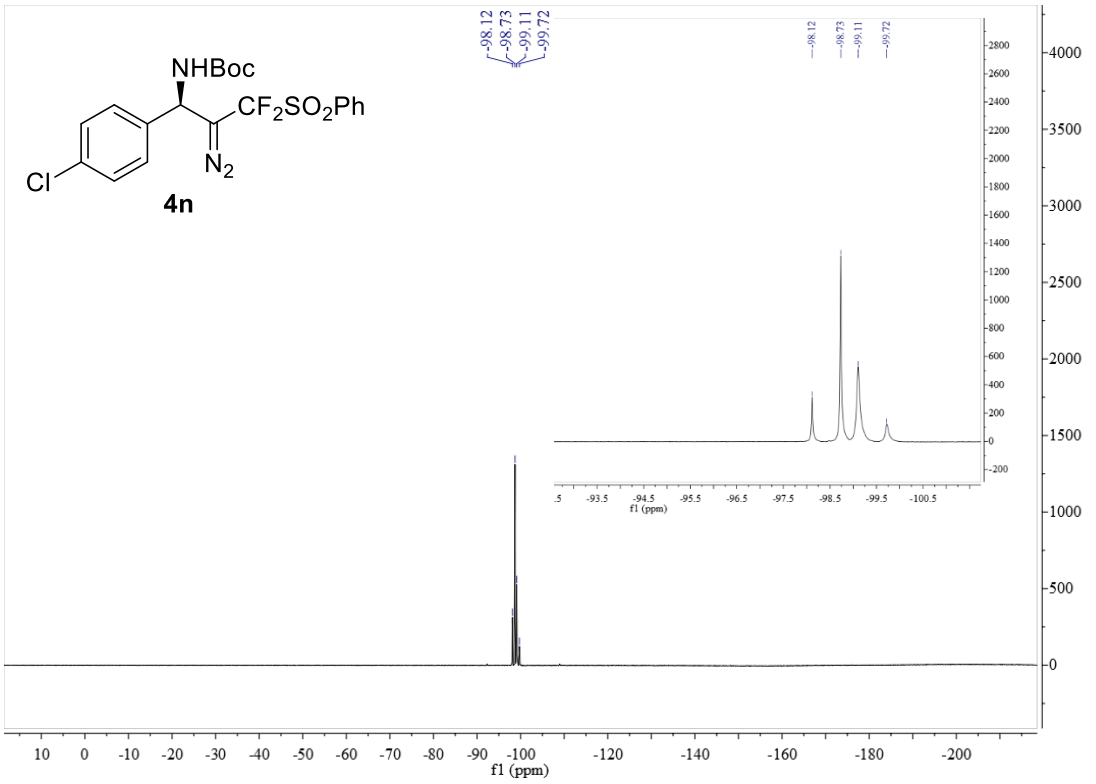
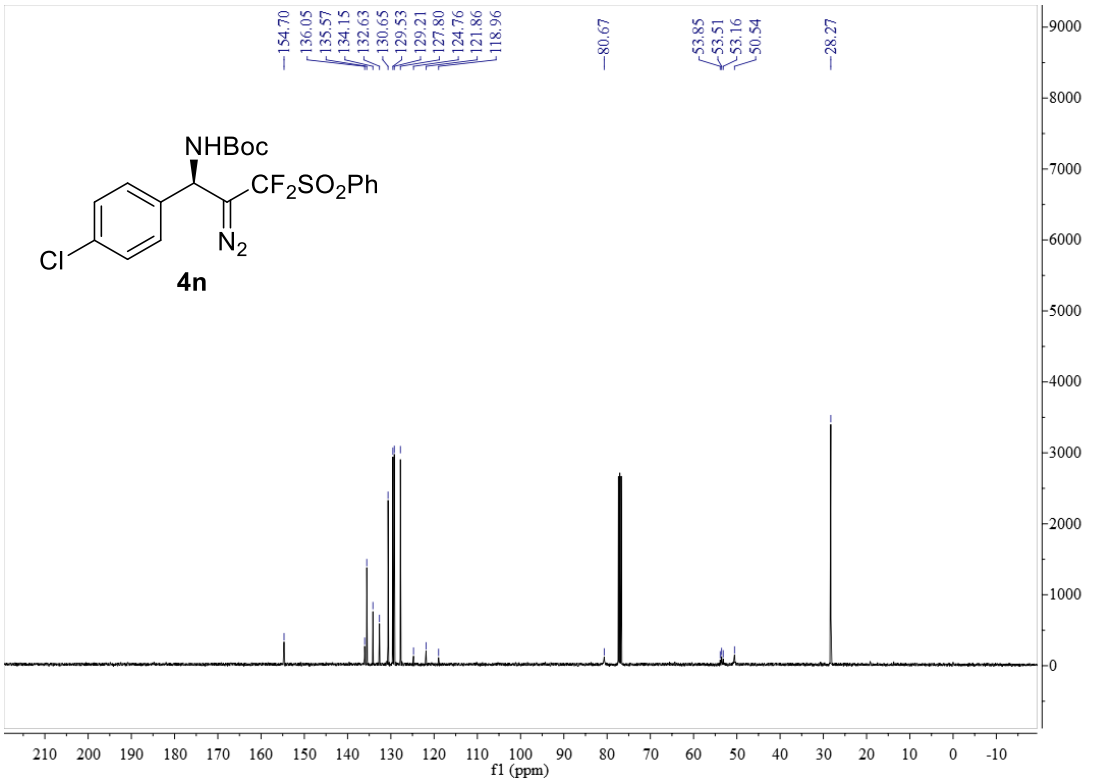
7.80
7.78
7.67
7.65
7.63
7.42
7.40
7.38
5.75
5.73
5.53
5.51
1.47
1.95
1.00
1.99
3.95
0.98
1.01
9.10
f1 (ppm)


NHBoc
CF2SO2Ph
N2
Cl
4n
-98.12
-98.73
-99.11
-99.72
f1 (ppm)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134.15
132.63
130.65
129.53
129.21
127.80
124.76
121.86
118.96
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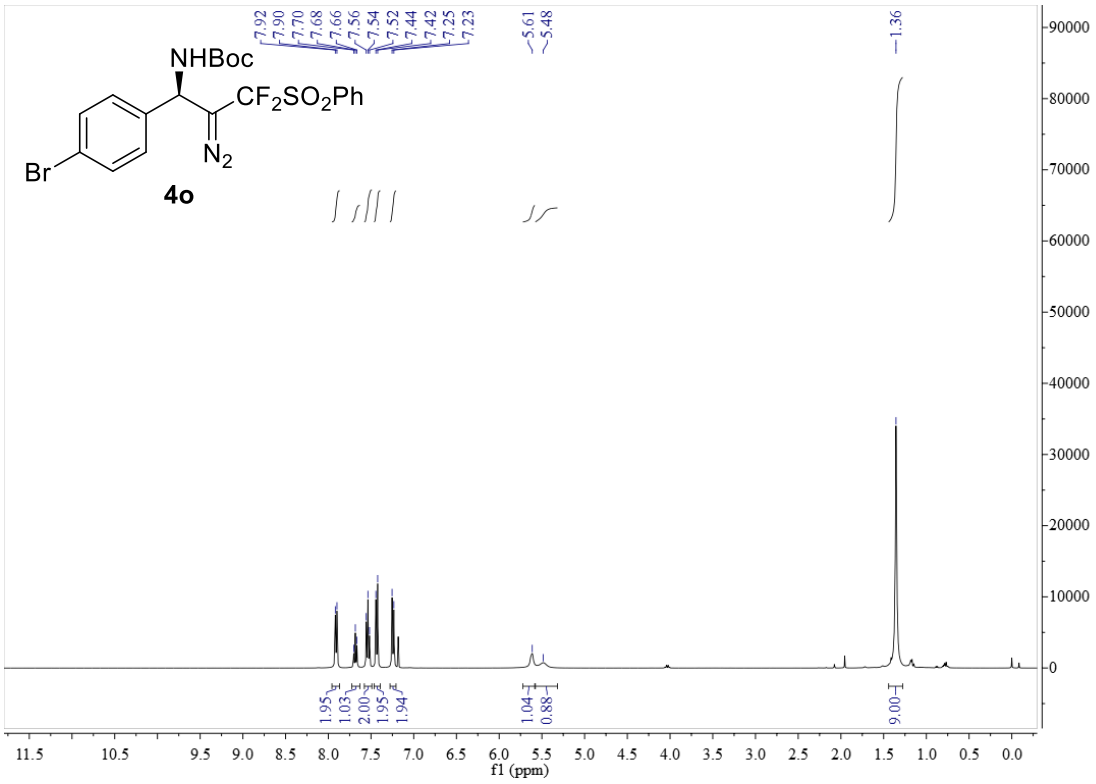
53.51
53.16
50.54
28.27
NHBoc
CF2SO2Ph
N2
Cl
4n
f1 (ppm)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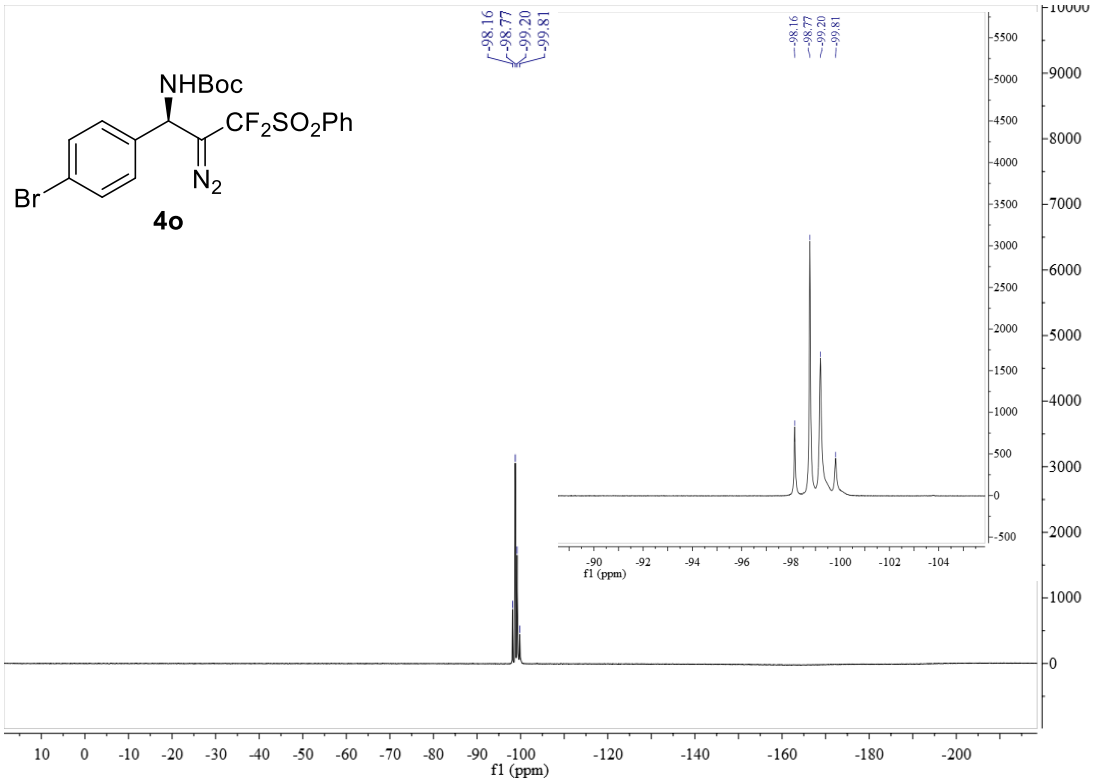
7.56
7.54
7.52
7.44
7.42
7.25
7.23
5.61
5.48
1.36
NHBoc
CF2SO2Ph
N2
Br
4o
1.95
1.03
2.00
1.95
1.94
1.04
0.88
9.00
f1 (ppm)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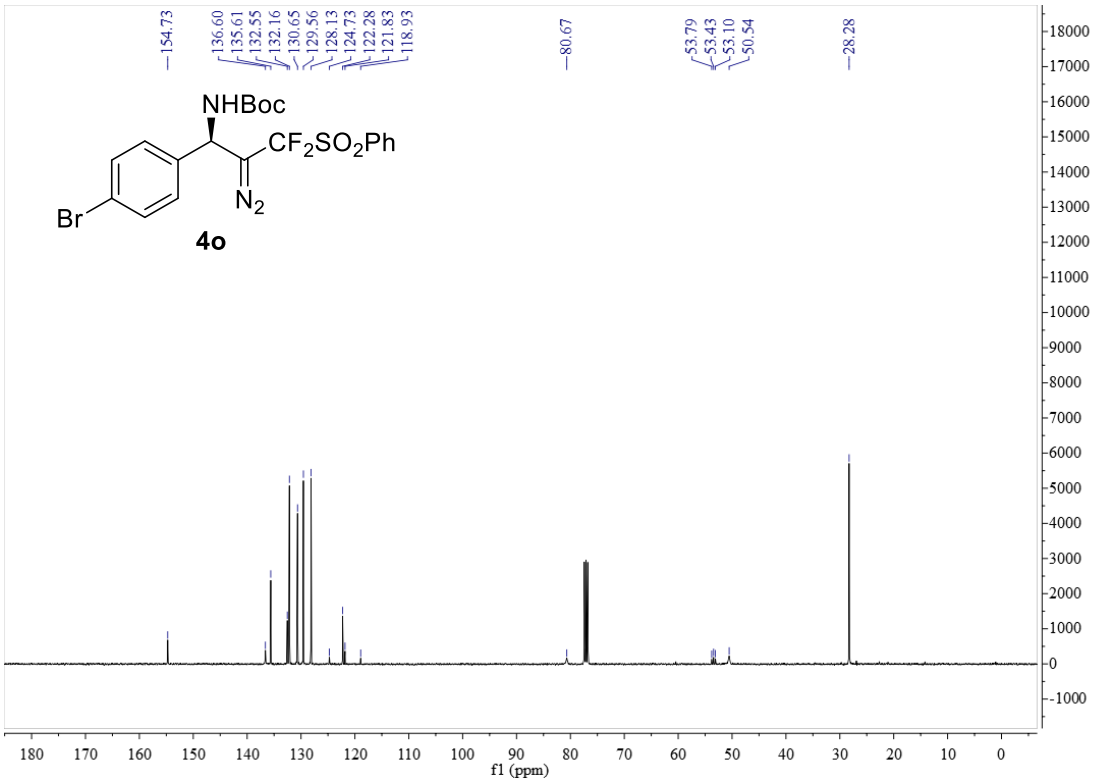
CF2SO2Ph
N2
Br
4o
-98.16
-98.77
-99.20
-99.81
f1 (ppm)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130.65
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128.13
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122.28
121.83
118.93
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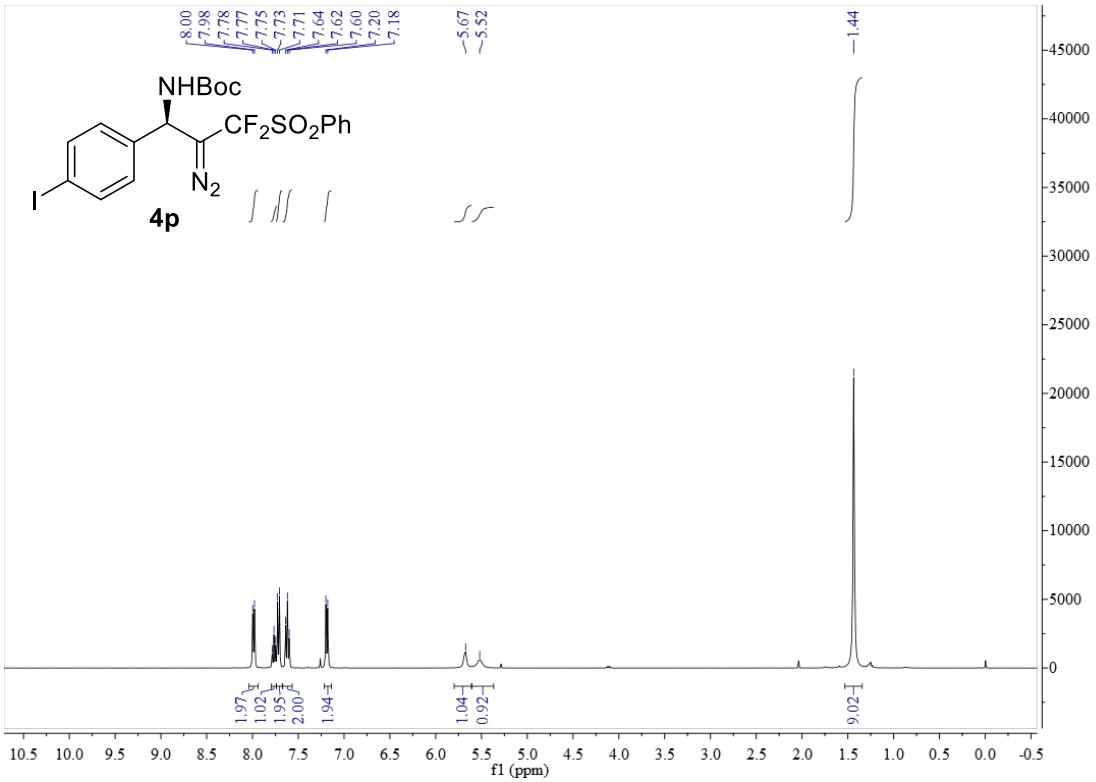
53.10
50.54
28.28
NHBoc
CF2SO2Ph
N2
Br
4o
f1 (ppm)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7.98
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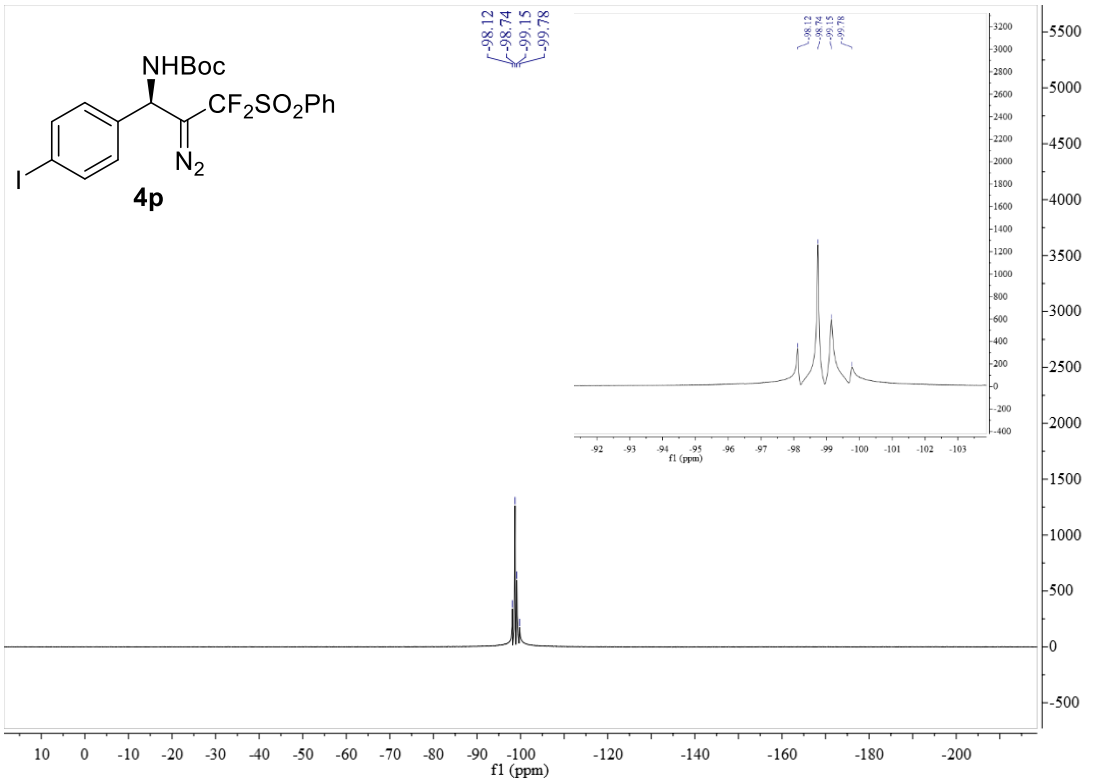
7.75
7.73
7.71
7.64
7.62
7.60
7.20
7.18
5.67
5.52
1.44
NHBoc
CF2SO2Ph
N2
I
4p
1.97
1.02
1.95
2.00
1.94
1.04
0.92
9.02
f1 (ppm)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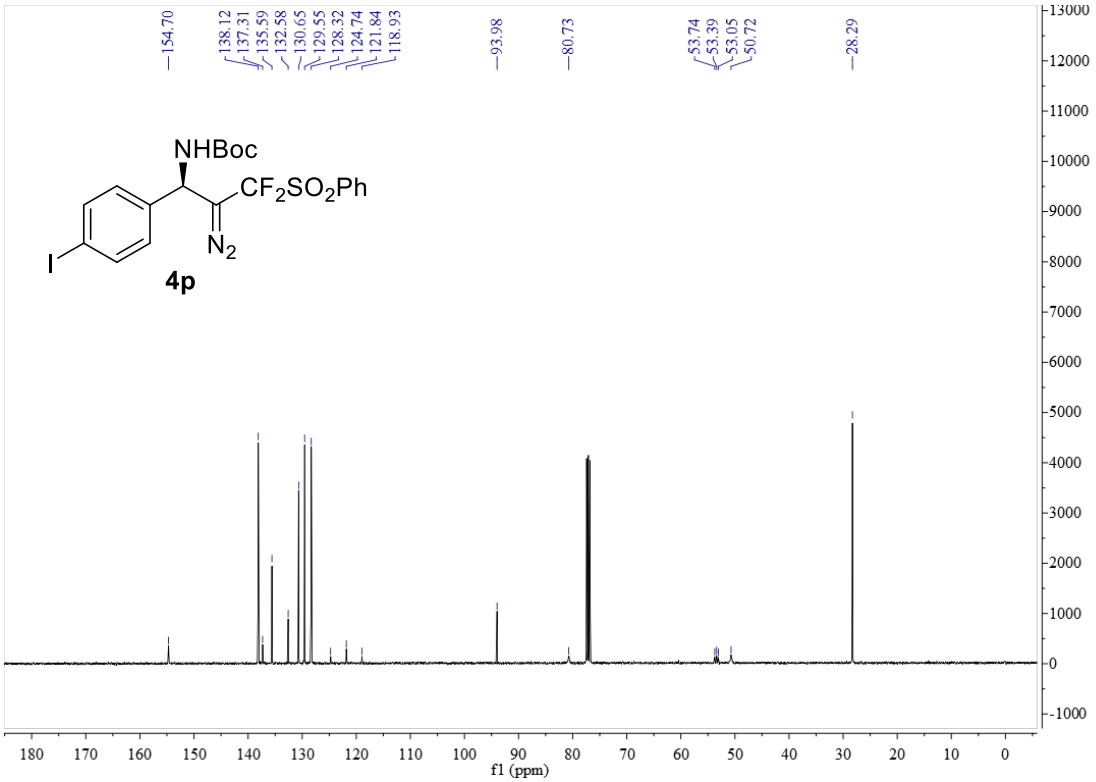
-99.78
NHBoc
CF2SO2Ph
N2
I
4p
f1 (ppm)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128.32
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121.84
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93.98
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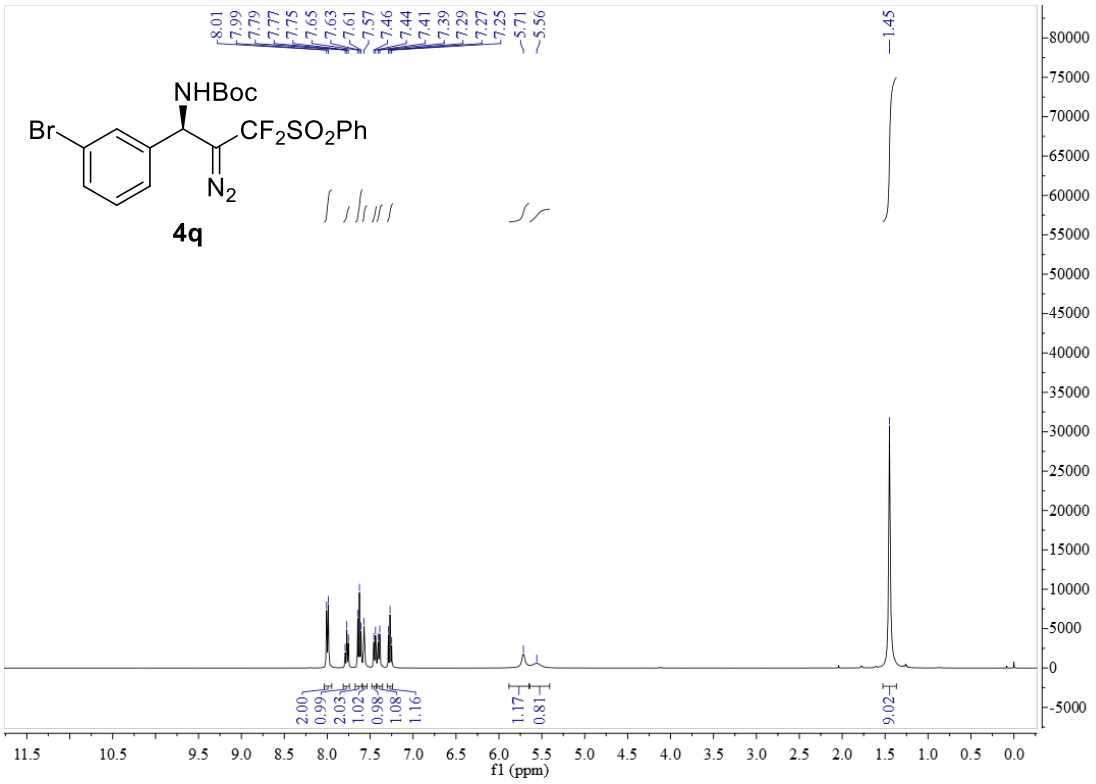
53.39
53.05
50.72
28.29
NHBoc
CF2SO2Ph
N2
I
4p
f1 (ppm)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7.61
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7.41
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7.29
7.27
7.25
5.71
5.56
1.45
NHBoc
Br
CF2SO2Ph
N2
4q
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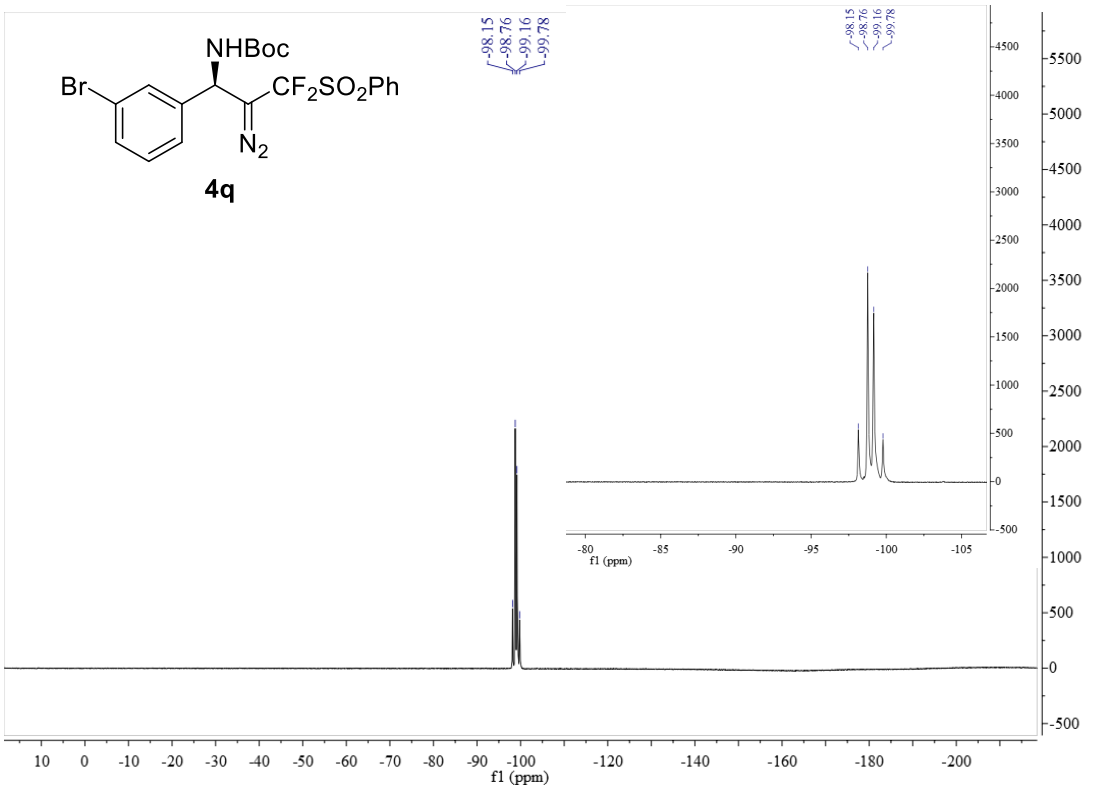
2.03
1.02
0.98
1.08
1.16
1.17
0.81
9.02
f1 (ppm)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N2
4q
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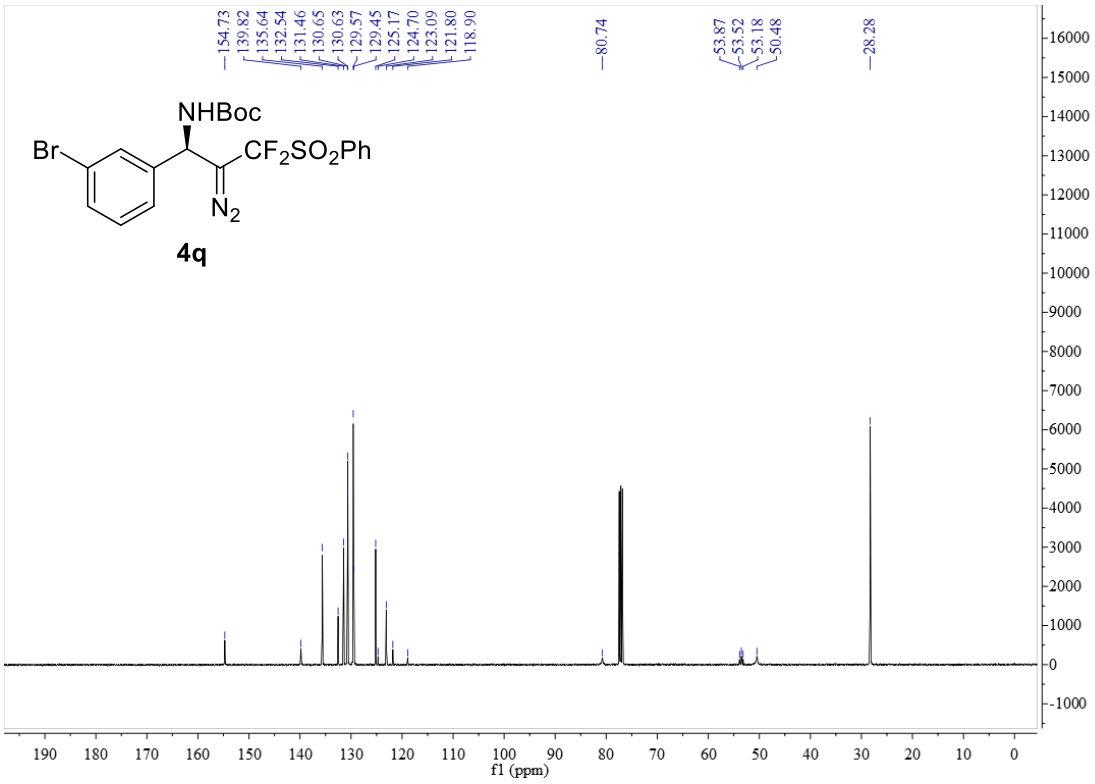
-99.78
f1 (ppm)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129.57
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124.70
123.09
121.80
118.90
80.74
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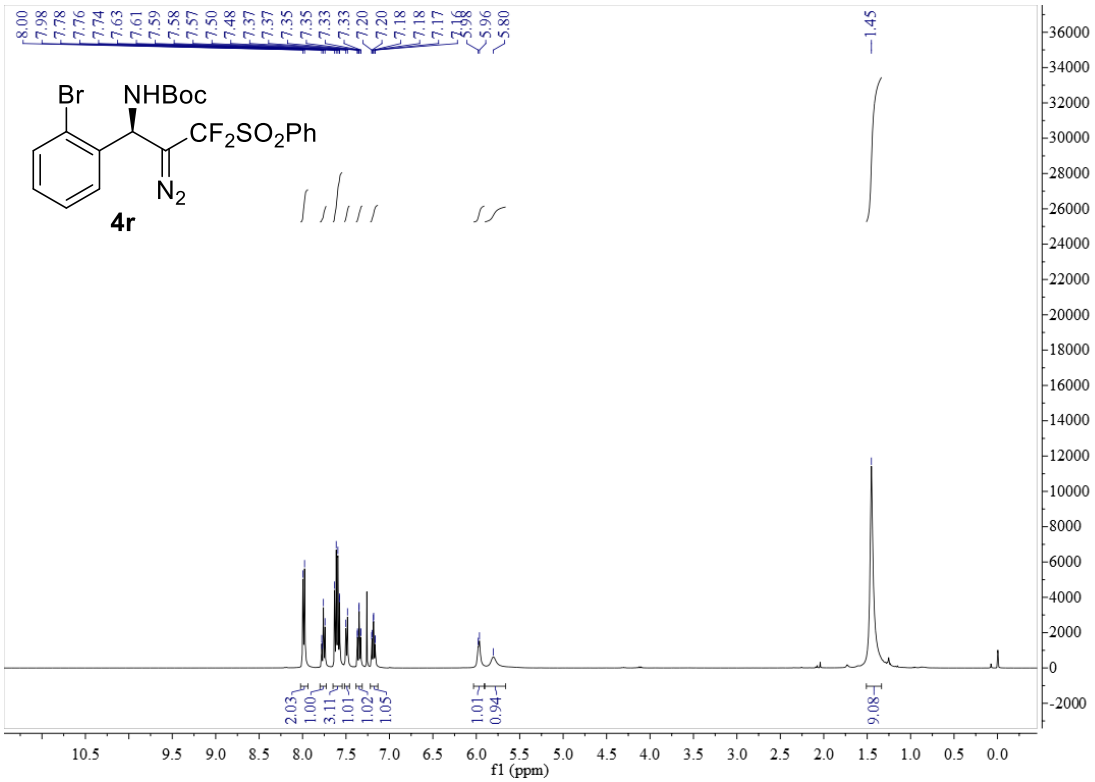
53.52
53.18
50.48
28.28
NHBoc
Br
CF2SO2Ph
N2
4q
f1 (ppm)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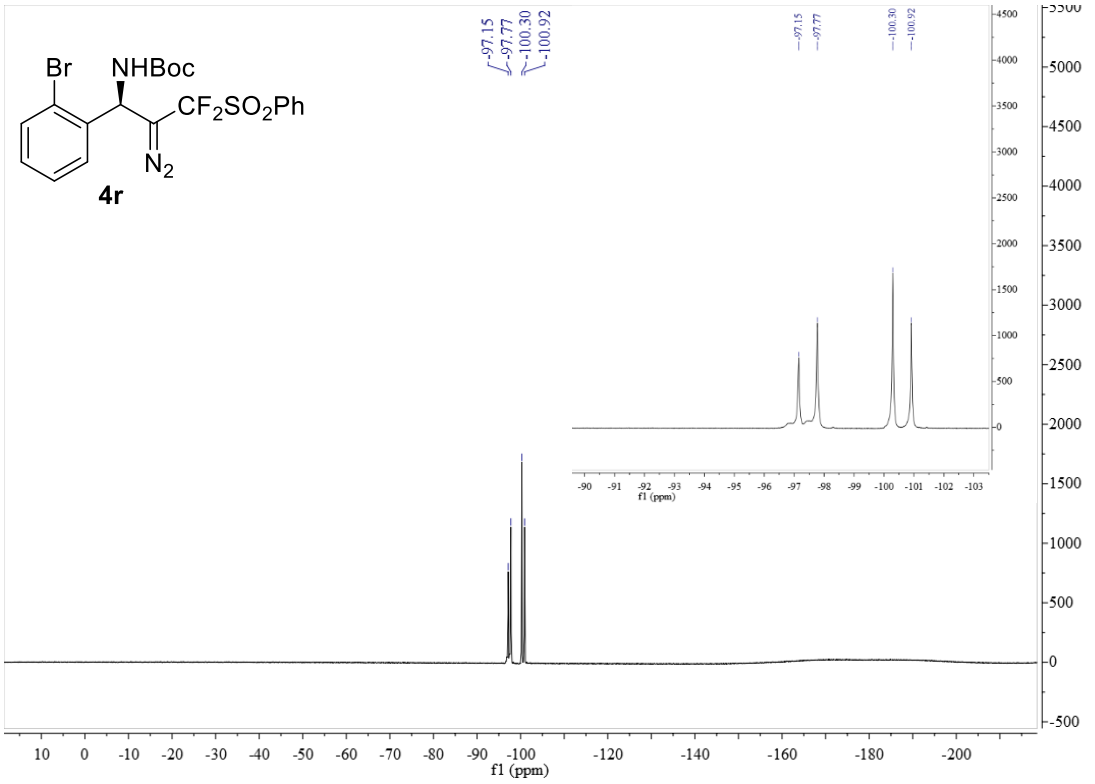
N2
4r
f1 (ppm)


Br
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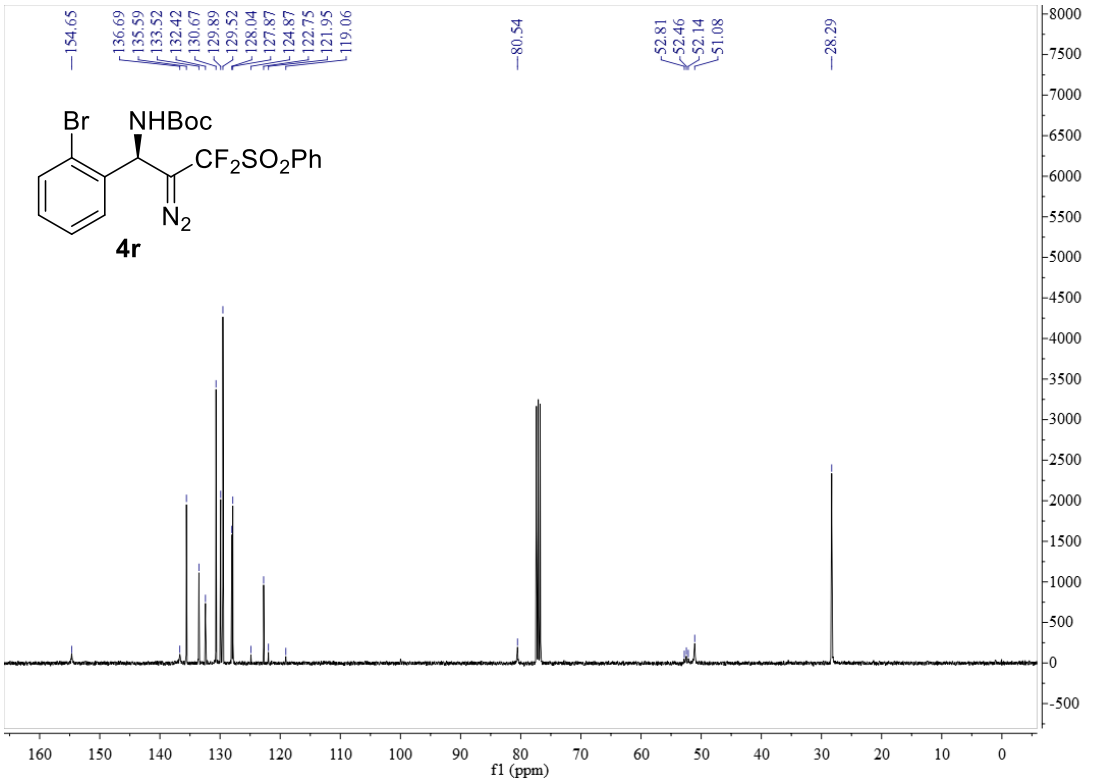
N2
4r
f1 (ppm)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122.75
121.95
119.06
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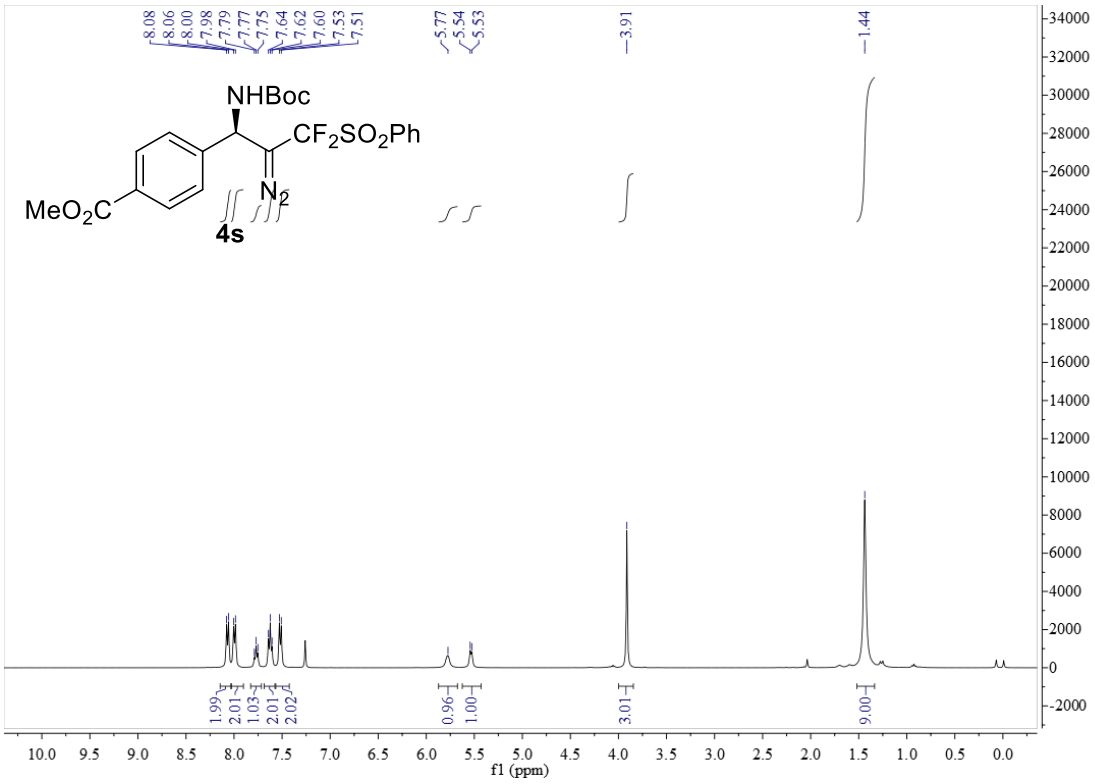
52.46
52.14
51.08
28.29
Br
NHBoc
CF2SO2Ph
N2
4r
f1 (ppm)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7.64
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7.53
7.51
5.77
5.54
5.53
3.91
1.44
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N2
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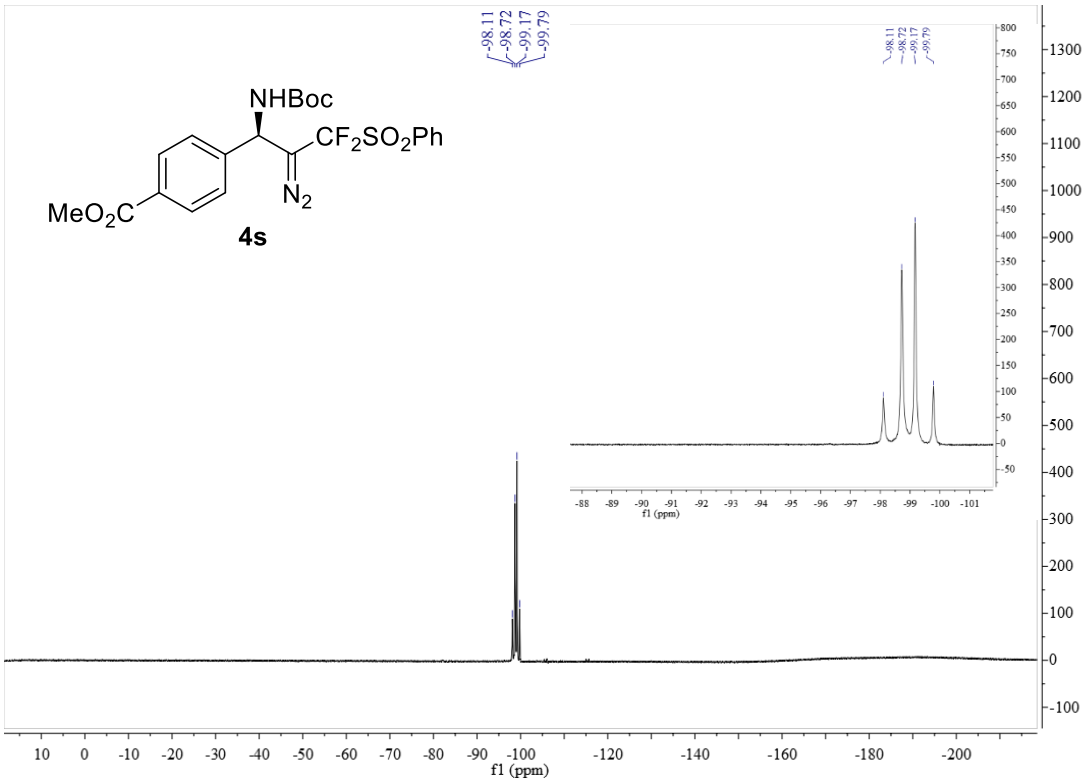
1.03
2.01
2.02
0.96
1.00
3.01
9.00
f1 (ppm)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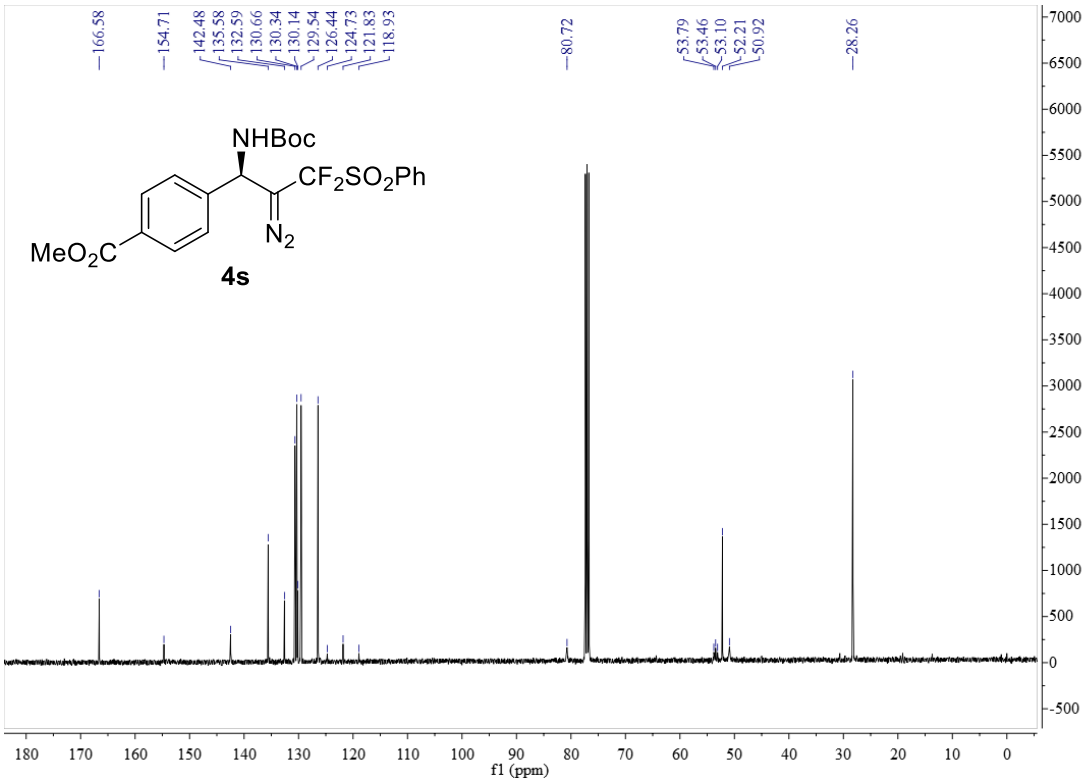
NHBoc
CF2SO2Ph
N2
MeO2C
4s
f1 (ppm)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121.83
118.93
80.72
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52.21
50.92
28.26
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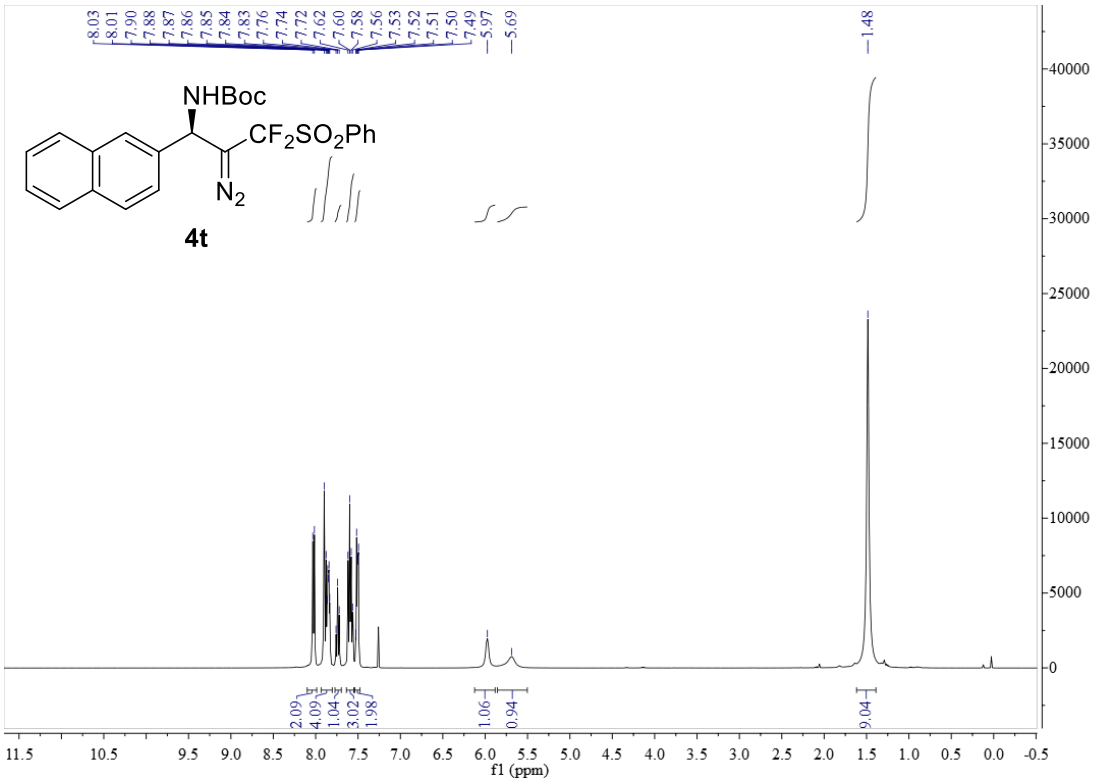
CF2SO2Ph
N2
MeO2C
4s
f1 (ppm)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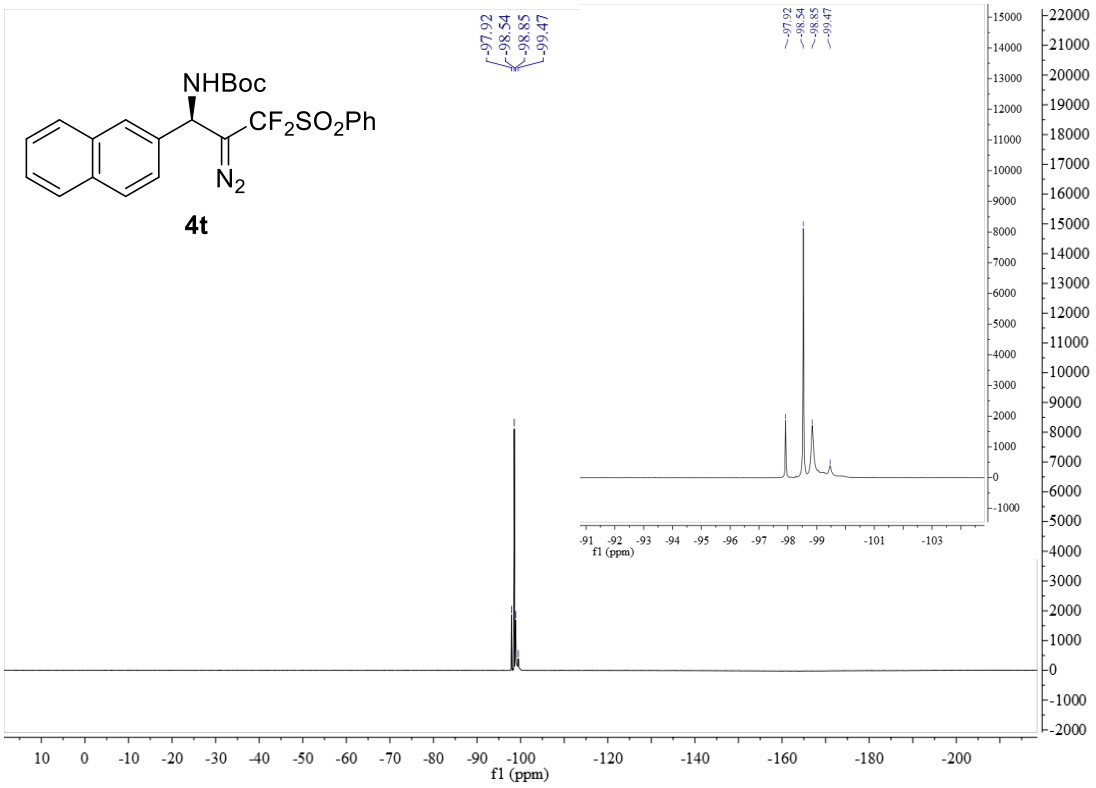
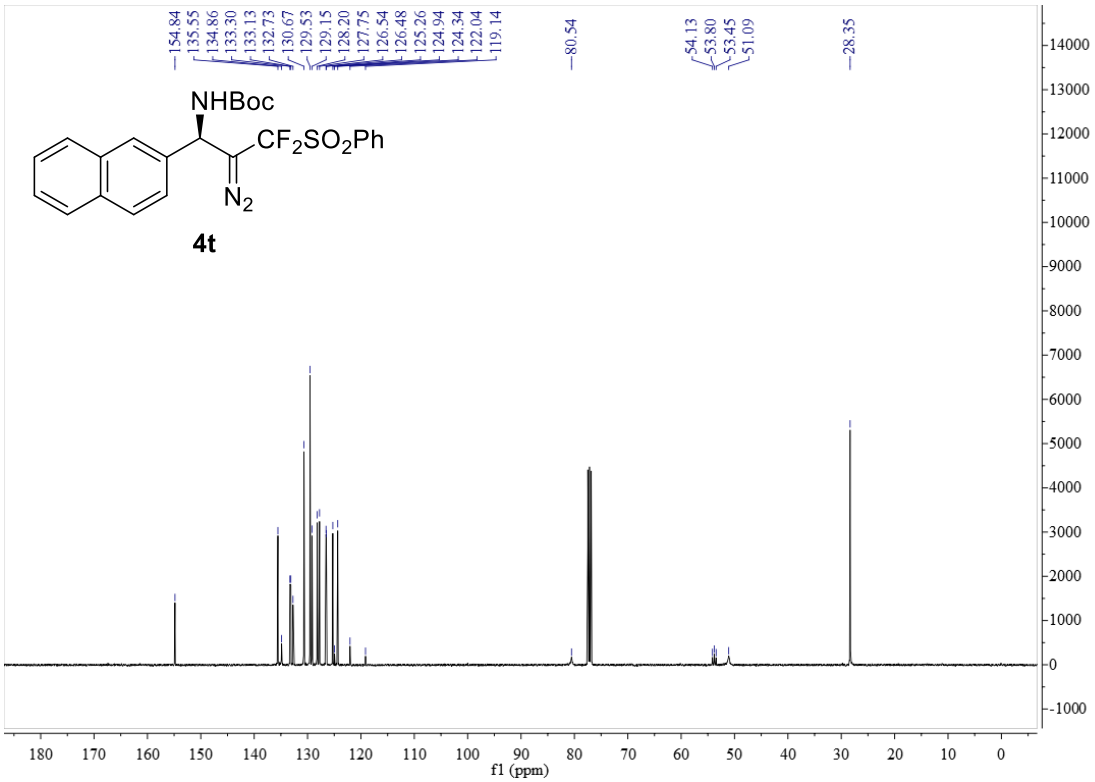
N2
4t
f1 (ppm)


NHBoc
CF2SO2Ph
N2
4t
f1 (ppm)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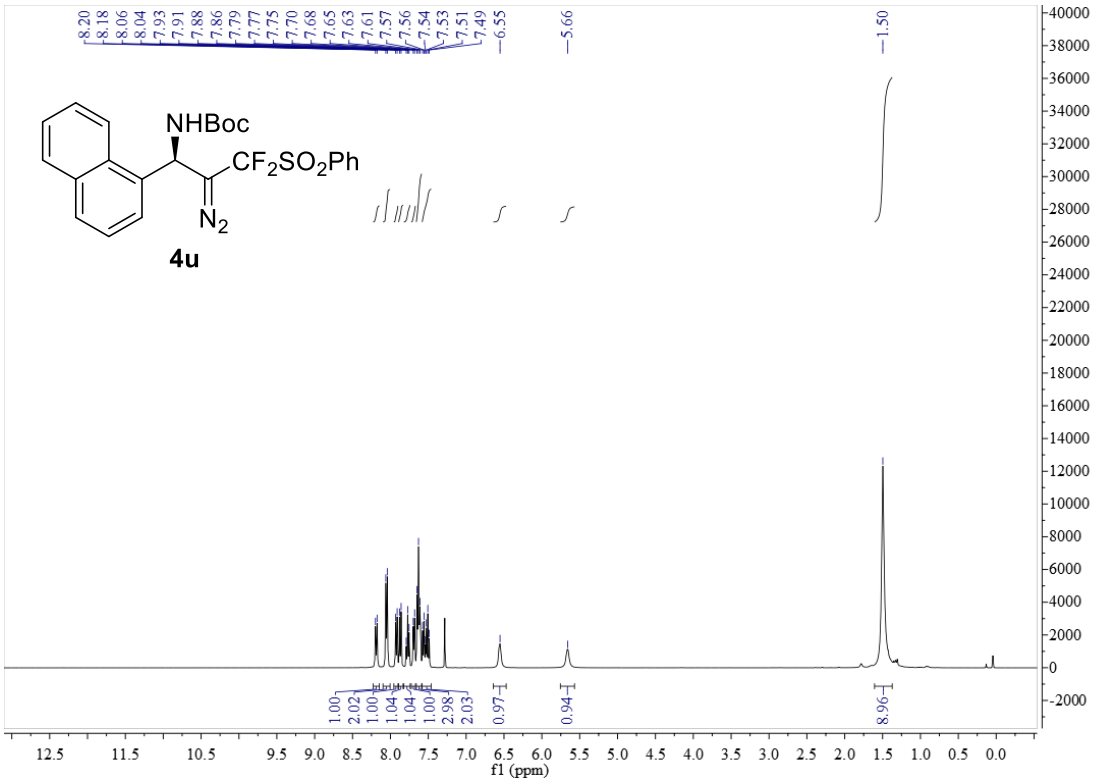
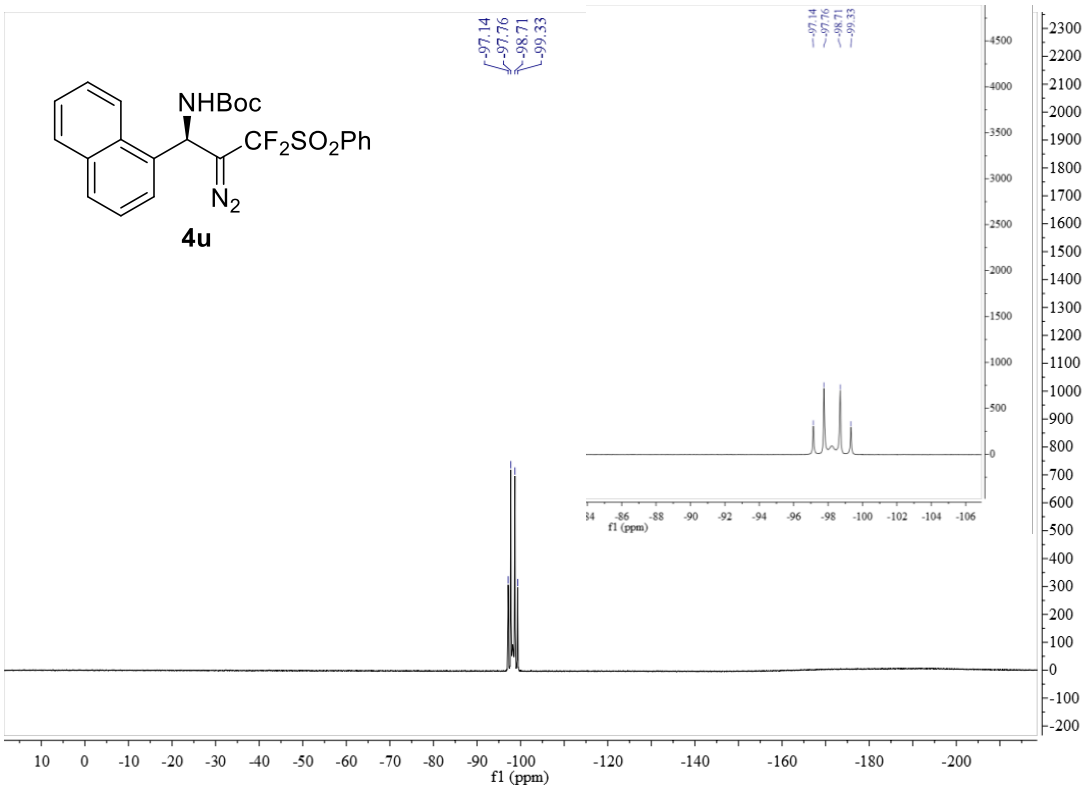
126.54
126.48
125.26
124.94
124.34
122.04
119.14
80.54
54.13
53.80
53.45
51.09
28.35
NHBoc
CF2SO2Ph
N2
4t
f1 (ppm)


8.20
8.18
8.06
8.04
7.93
7.91
7.88
7.86
7.79
7.77
7.75
7.70
7.68
7.65
7.63
7.61
7.57
7.56
7.54
7.53
7.51
7.49
6.55
5.66
1.50
NHBoc
CF2SO2Ph
N2
4u
1.00
2.02
1.00
1.04
1.04
1.00
2.98
2.03
0.97
0.94
8.96
f1 (ppm)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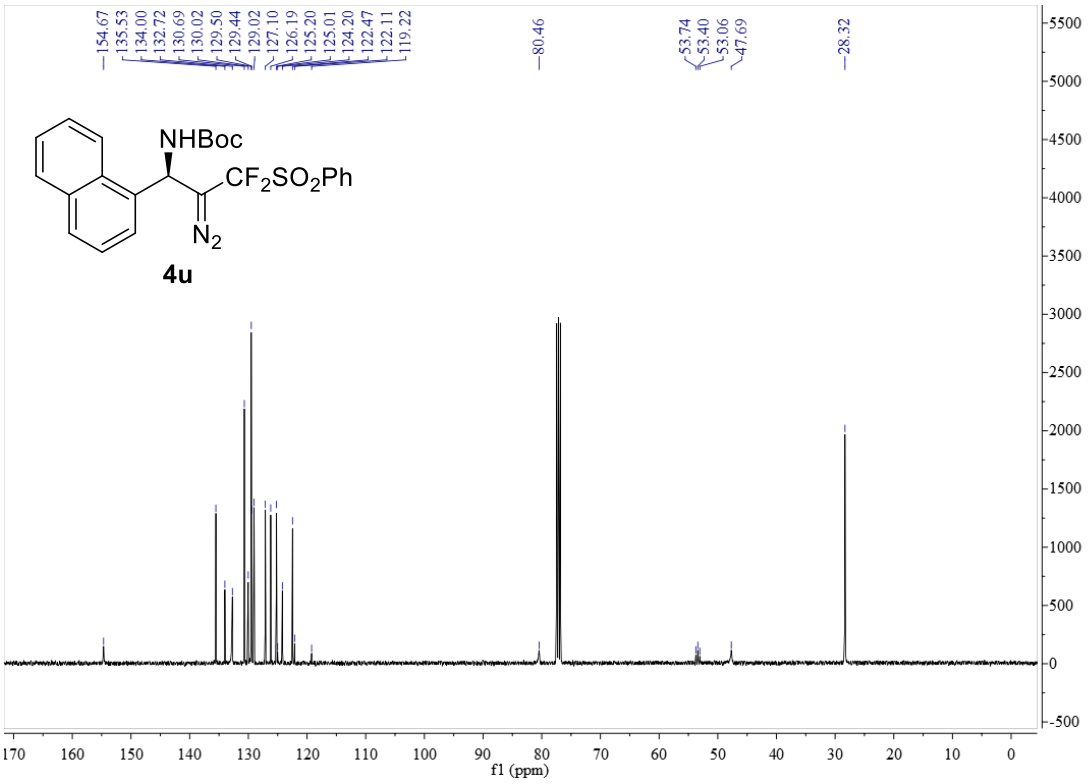
-97.76
-98.71
-99.33
NHBoc
CF2SO2Ph
N2
4u
f1 (ppm)


154.67
135.53
134.00
132.72
130.69
130.02
129.50
129.44
129.02
127.10
126.19
125.20
125.01
124.20
122.47
122.11
119.22
80.46
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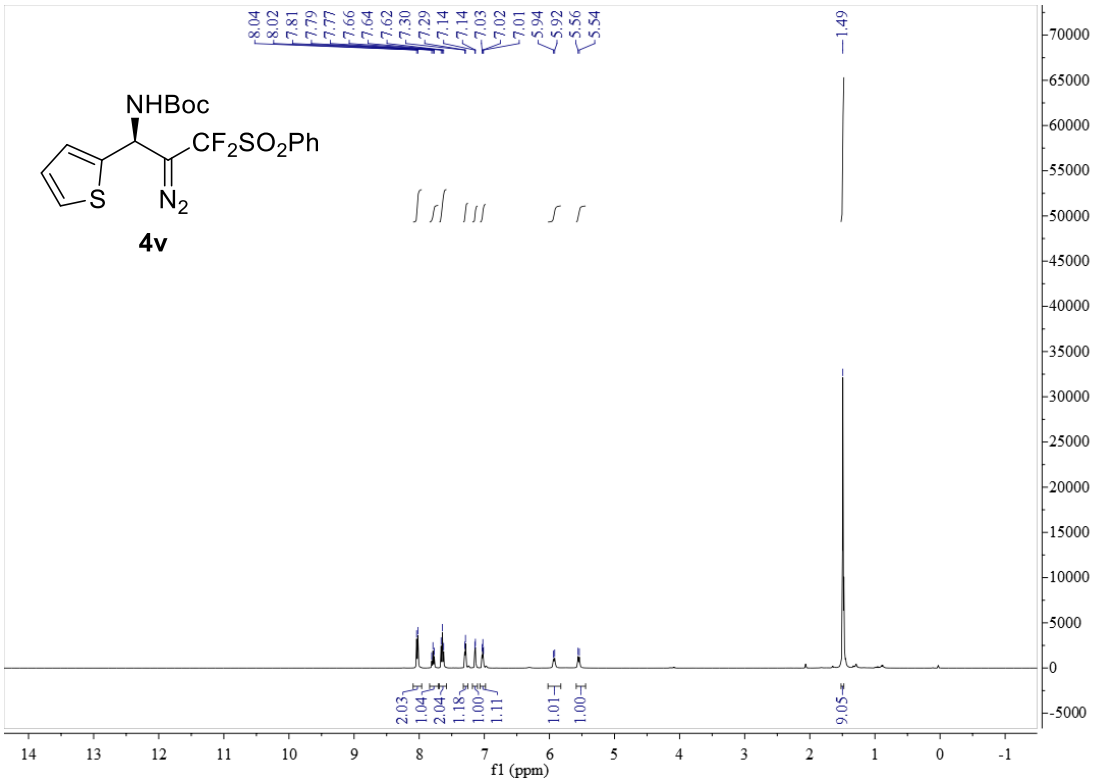
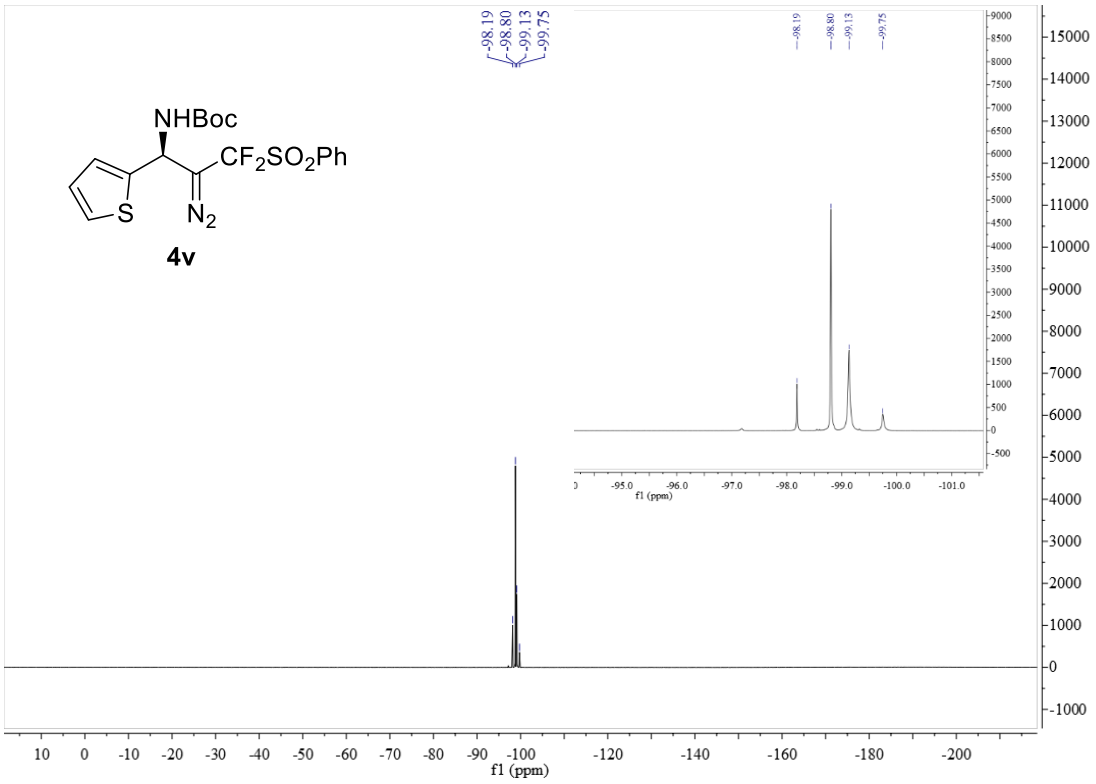
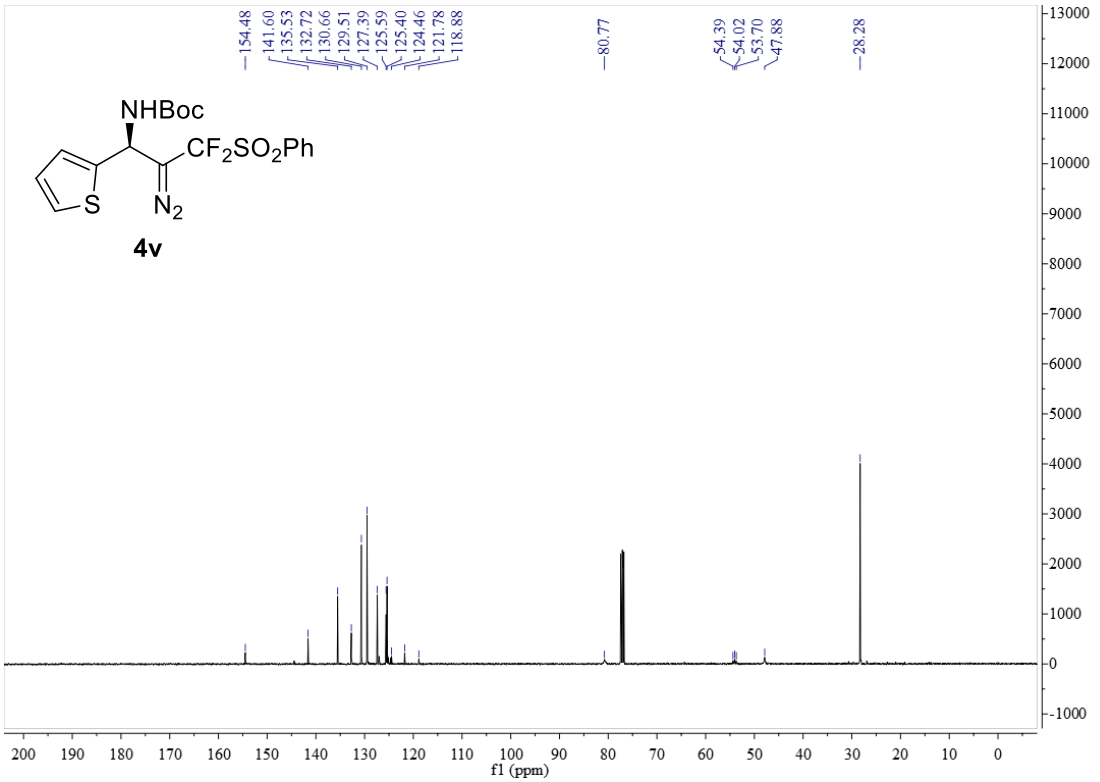
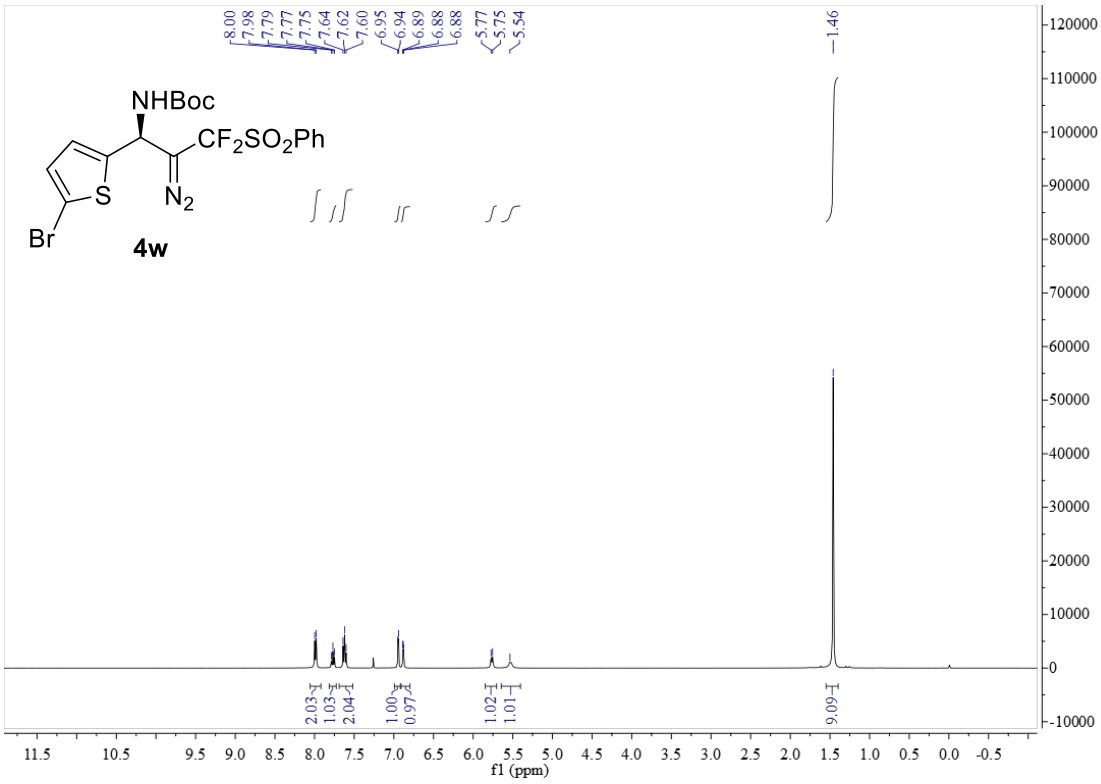
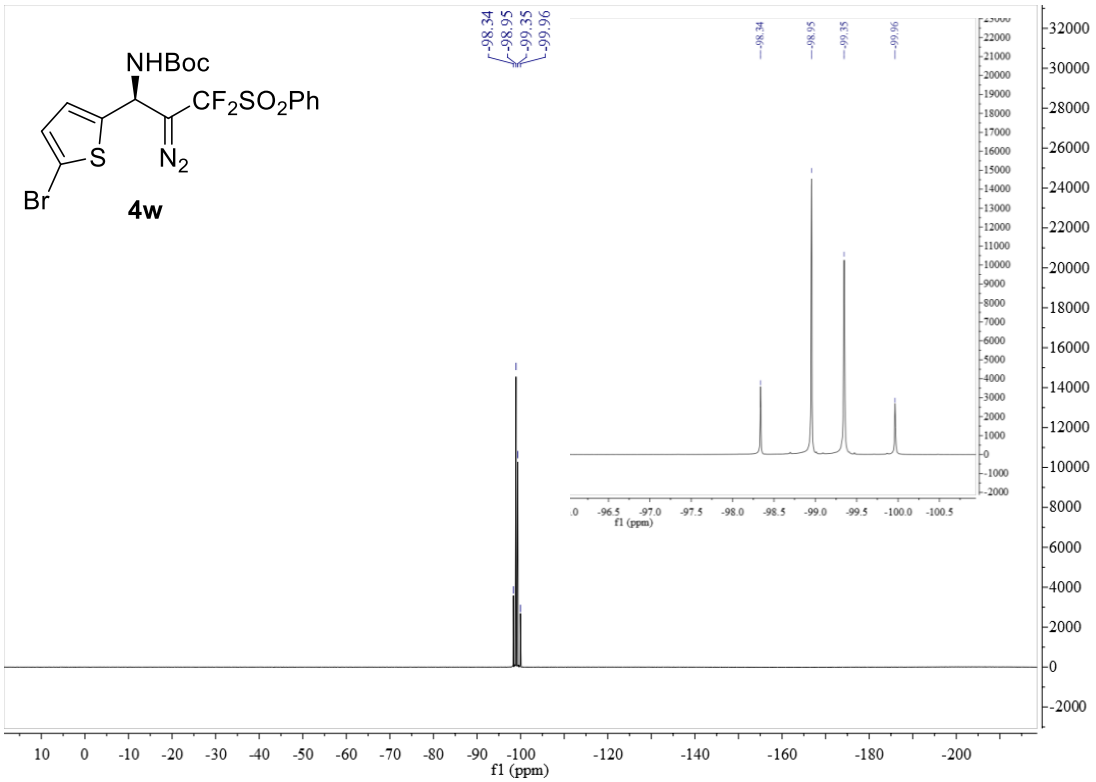
53.40
53.06
47.69
28.32
NHBoc
CF2SO2Ph
N2
4u
f1 (ppm)

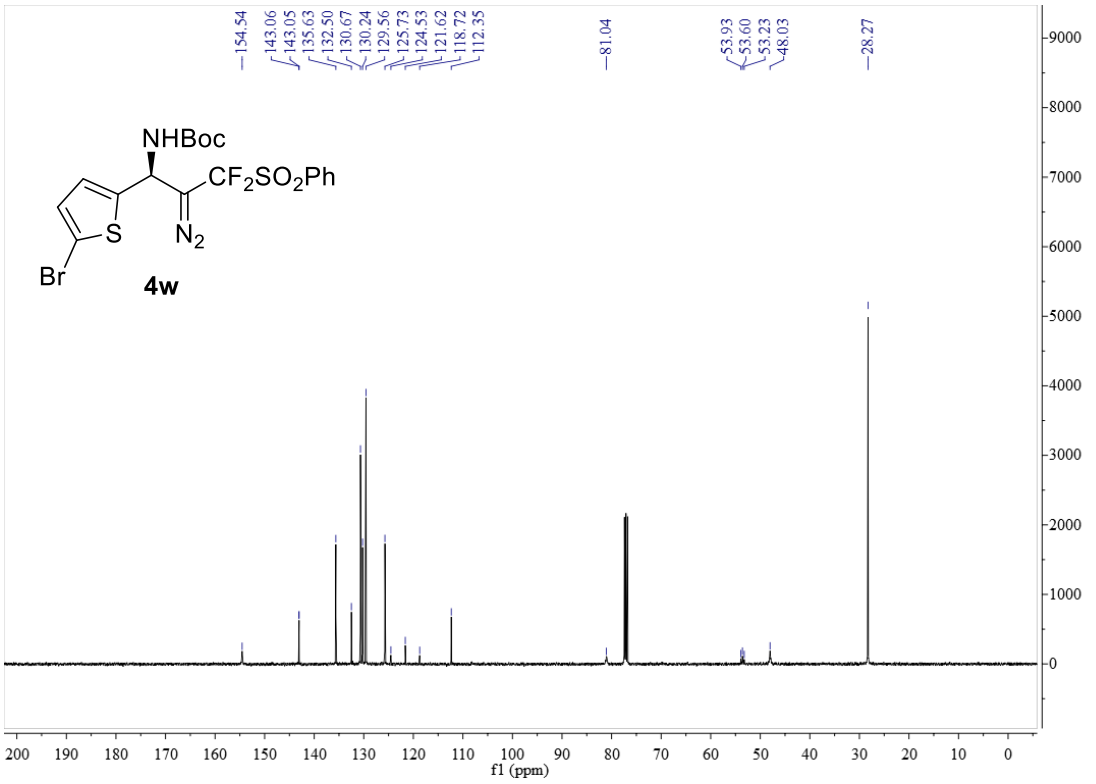

NHBoc
CF2SO2Ph
S
N2
4v
8.04
8.02
7.81
7.79
7.77
7.66
7.64
7.62
7.30
7.29
7.14
7.14
7.03
7.02
7.01
5.94
5.92
5.56
5.54
1.49
2.03
1.04
2.04
1.18
1.00
1.11
1.01
1.00
9.05
f1 (ppm)

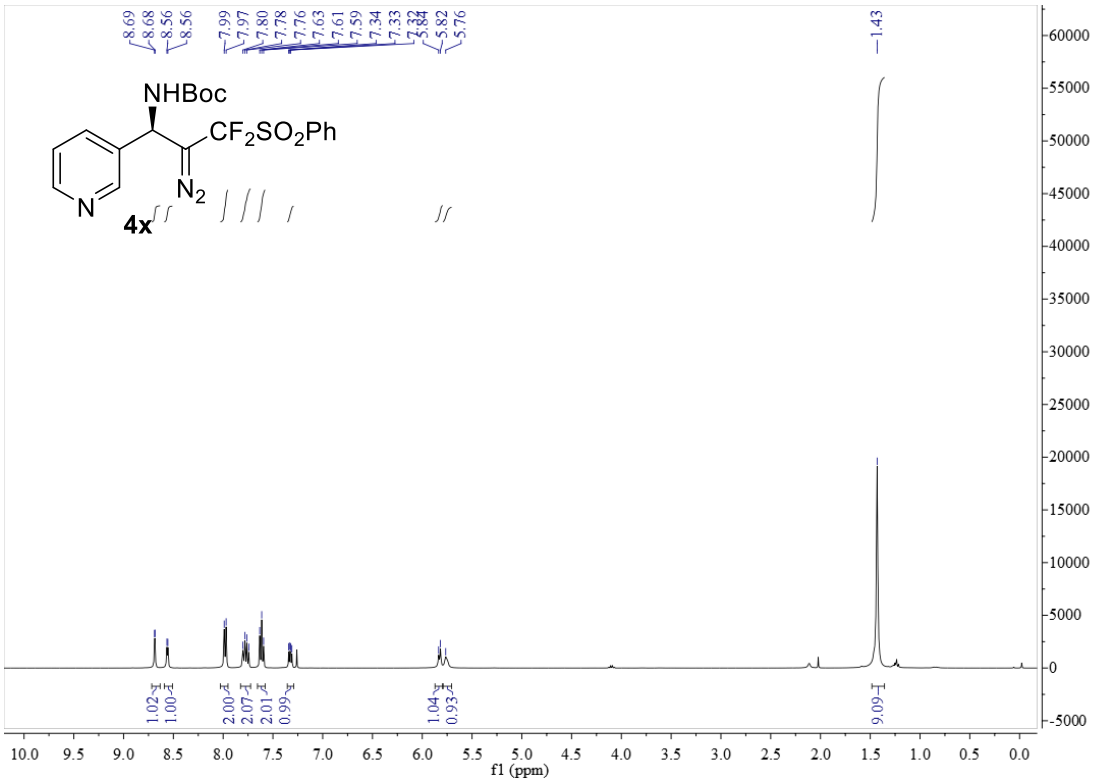

NHBoc
CF2SO2Ph
S
N2
4v
-98.19
-98.80
-99.13
-99.75
f1 (ppm)

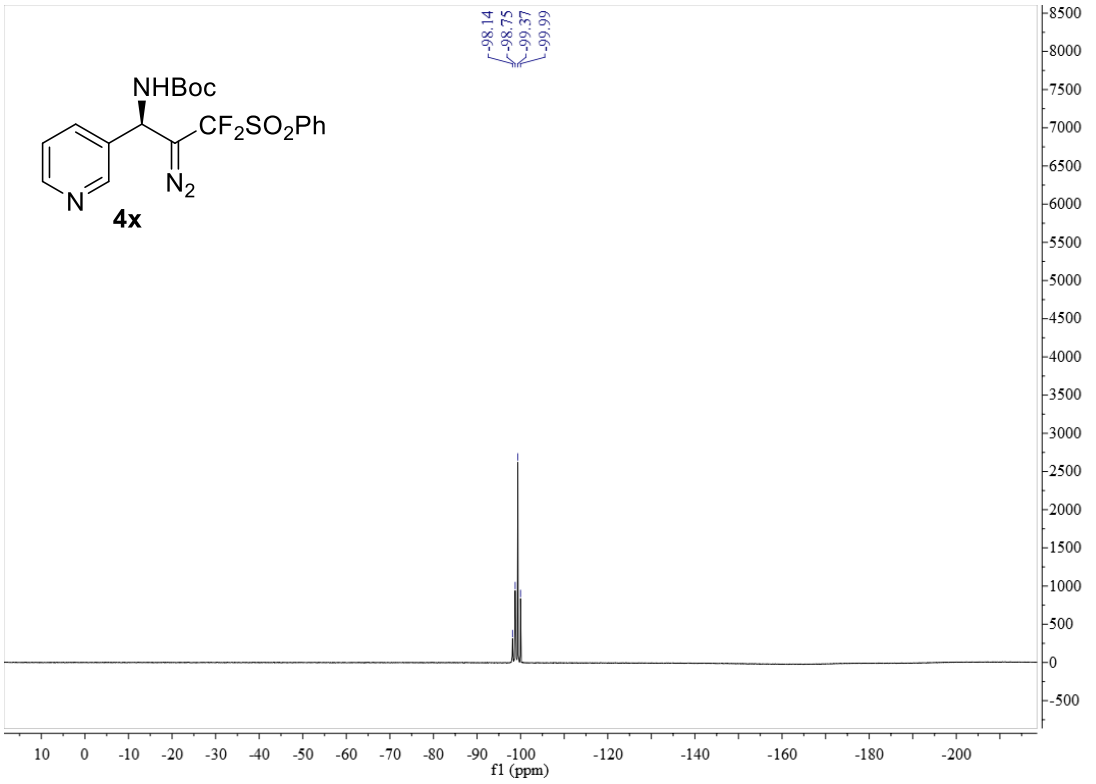

154.48
141.60
135.53
132.72
130.66
129.51
127.39
125.59
125.40
124.46
121.78
118.88
80.77
54.39
54.02
53.70
47.88
28.28
NHBoc
CF2SO2Ph
S
N2
4v
f1 (ppm)

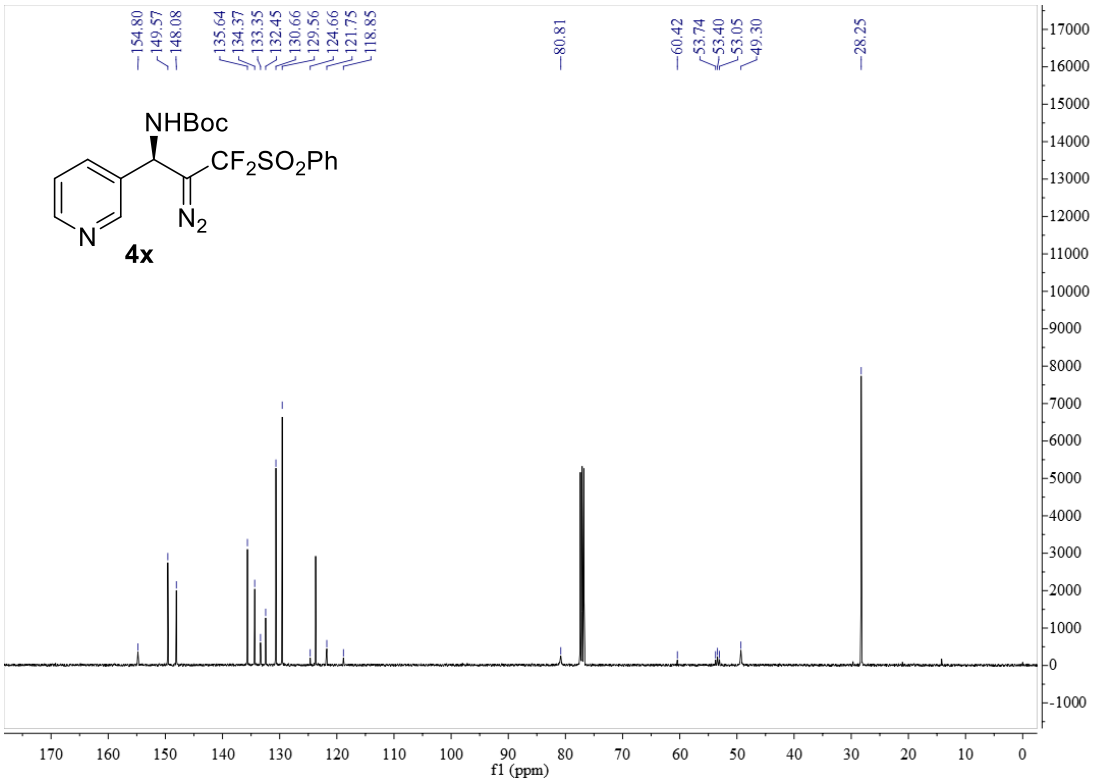

8.00
7.98
7.79
7.77
7.75
7.64
7.62
7.60
6.95
6.94
6.89
6.88
6.88
5.77
5.75
5.54
1.46
NHBoc
CF2SO2Ph
S
N2
Br
4w
2.03
1.03
2.04
1.00
0.97
1.02
1.01
9.09
f1 (ppm)

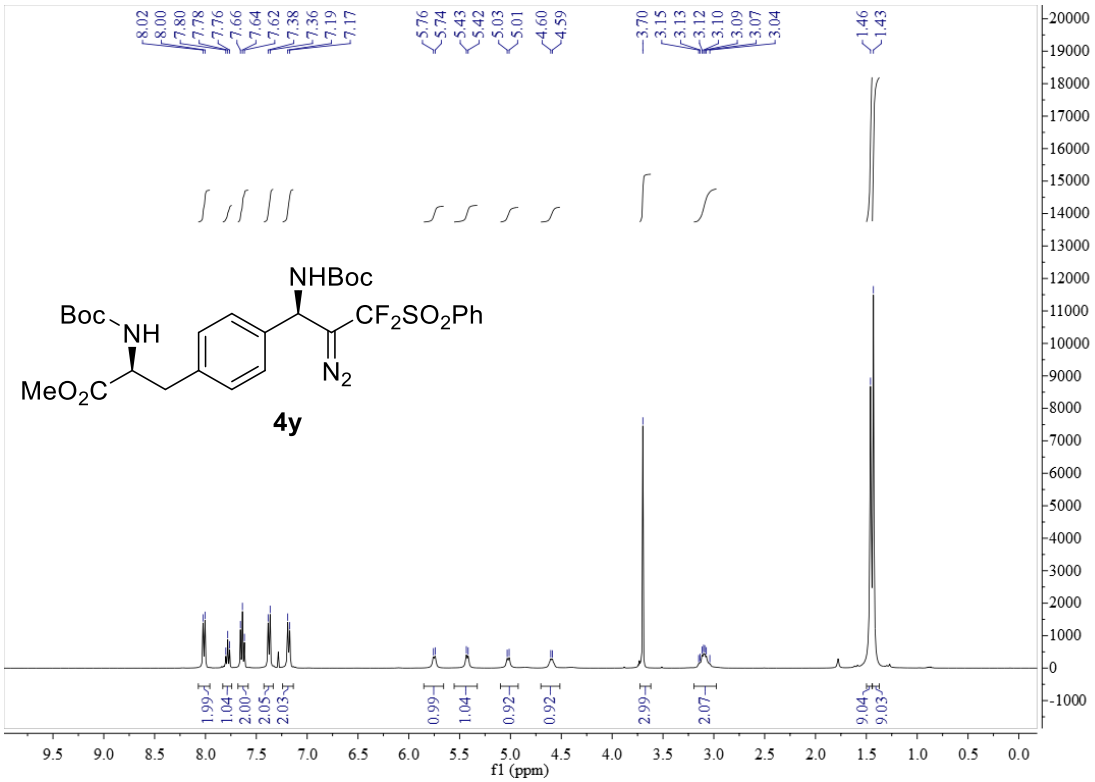

NHBoc
CF2SO2Ph
S
N2
Br
4w
-98.34
-98.95
-99.35
-99.96
f1 (ppm)

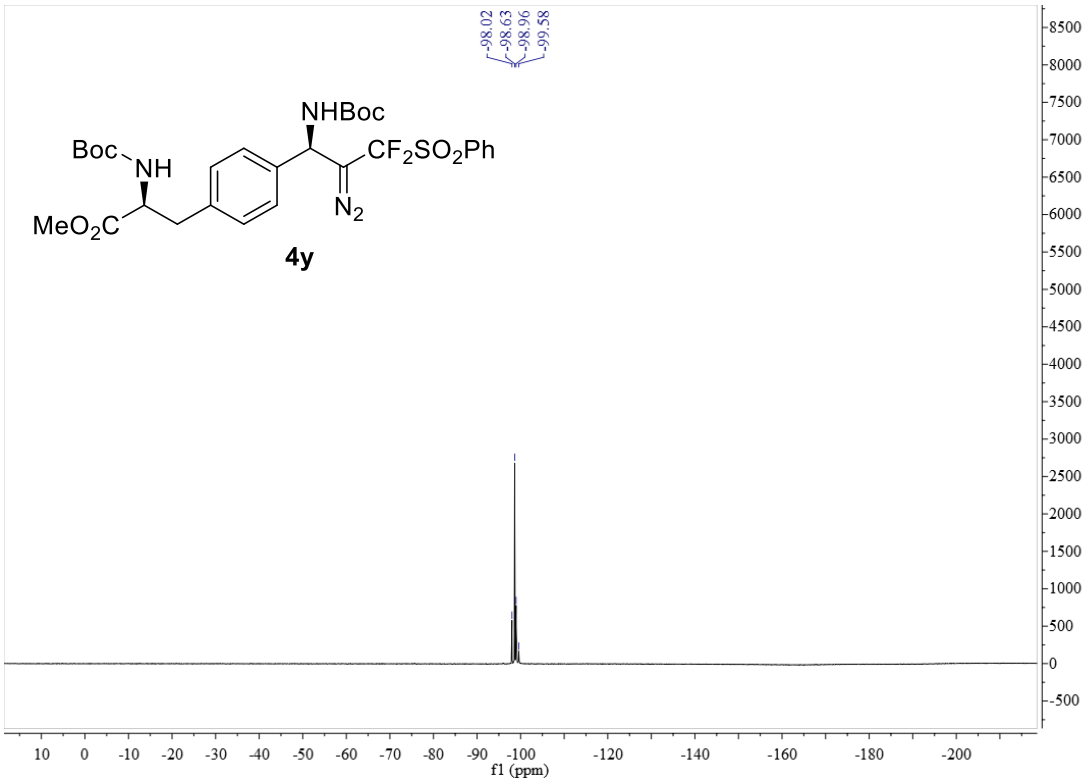

NHBoc
CF2SO2Ph
S
N2
Br
4w
154.54
143.06
143.05
135.63
132.50
130.67
130.24
129.56
125.73
124.53
121.62
118.72
112.35
81.04
53.93
53.60
53.23
48.03
28.27
f1 (ppm)


8.69
8.68
8.56
8.56
7.99
7.97
7.80
7.78
7.76
7.63
7.61
7.59
7.34
7.33
5.84
5.82
5.76
1.43
NHBoc
CF2SO2Ph
N2
N
4x
1.02
1.00
2.00
2.07
2.01
0.99
1.04
0.93
9.09
f1 (ppm)


-98.14
-98.75
-99.37
-99.99
NHBoc
CF2SO2Ph
N2
N
4x
f1 (ppm)


154.80
149.57
148.08
135.64
134.37
133.35
132.45
130.66
129.56
124.66
121.75
118.85
80.81
60.42
53.74
53.40
53.05
49.30
28.25
NHBoc
CF2SO2Ph
N2
N
4x
f1 (ppm)


8.02
8.00
7.80
7.78
7.76
7.66
7.64
7.62
7.38
7.36
7.19
7.17
5.76
5.74
5.43
5.42
5.03
5.01
4.60
4.59
3.70
3.15
3.13
3.12
3.10
3.09
3.07
3.04
1.46
1.43
NHBoc
Boc
NH
CF2SO2Ph
N2
MeO2C
4y
1.99
1.04
2.00
2.05
2.03
0.99
1.04
0.92
0.92
2.99
2.07
9.04
9.03
f1 (ppm)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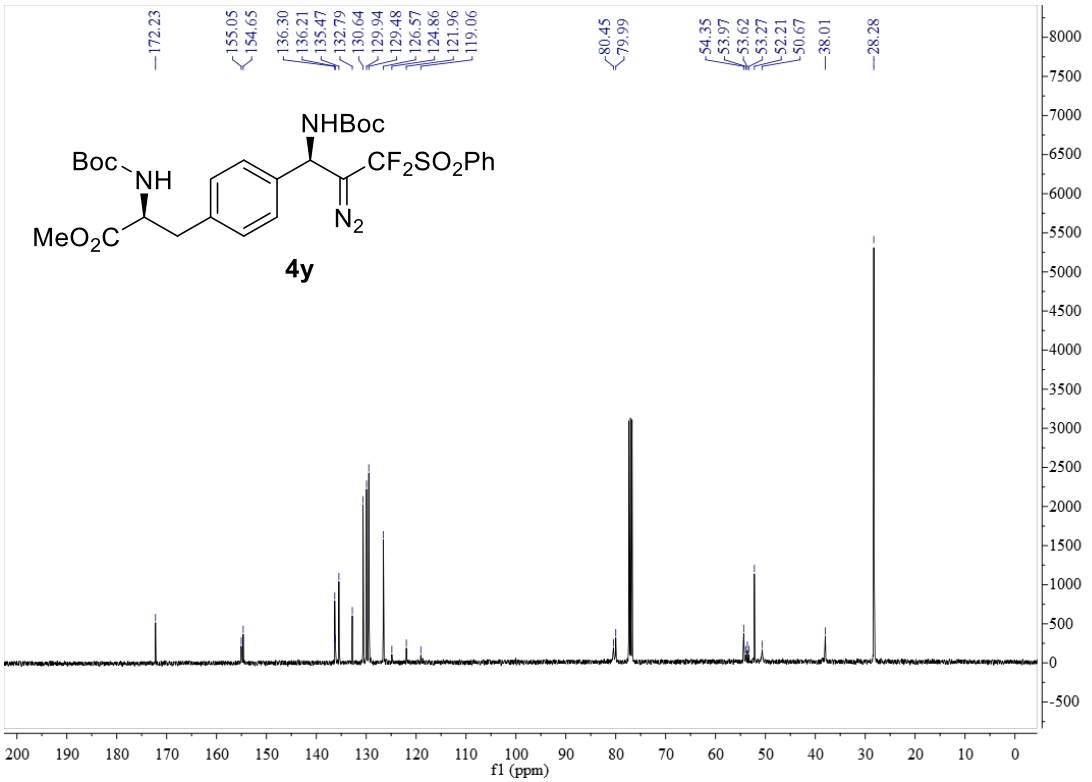
NHBoc
Boc
NH
CF2SO2Ph
N2
MeO2C
4y
f1 (ppm)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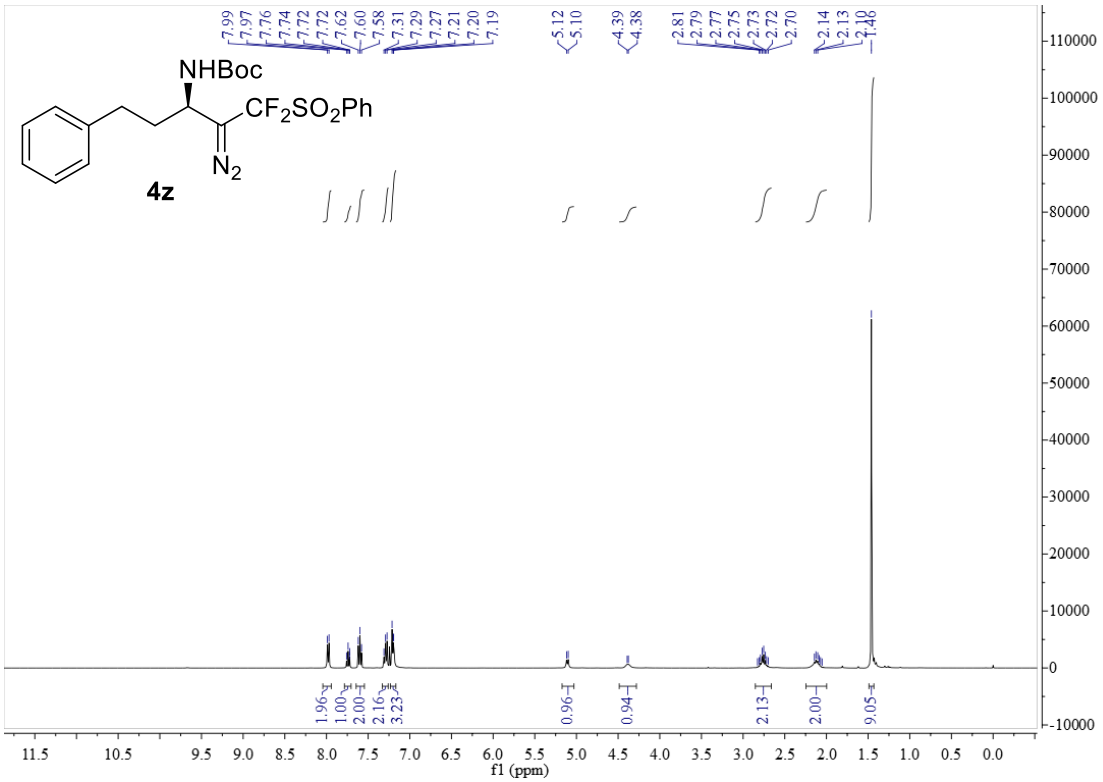
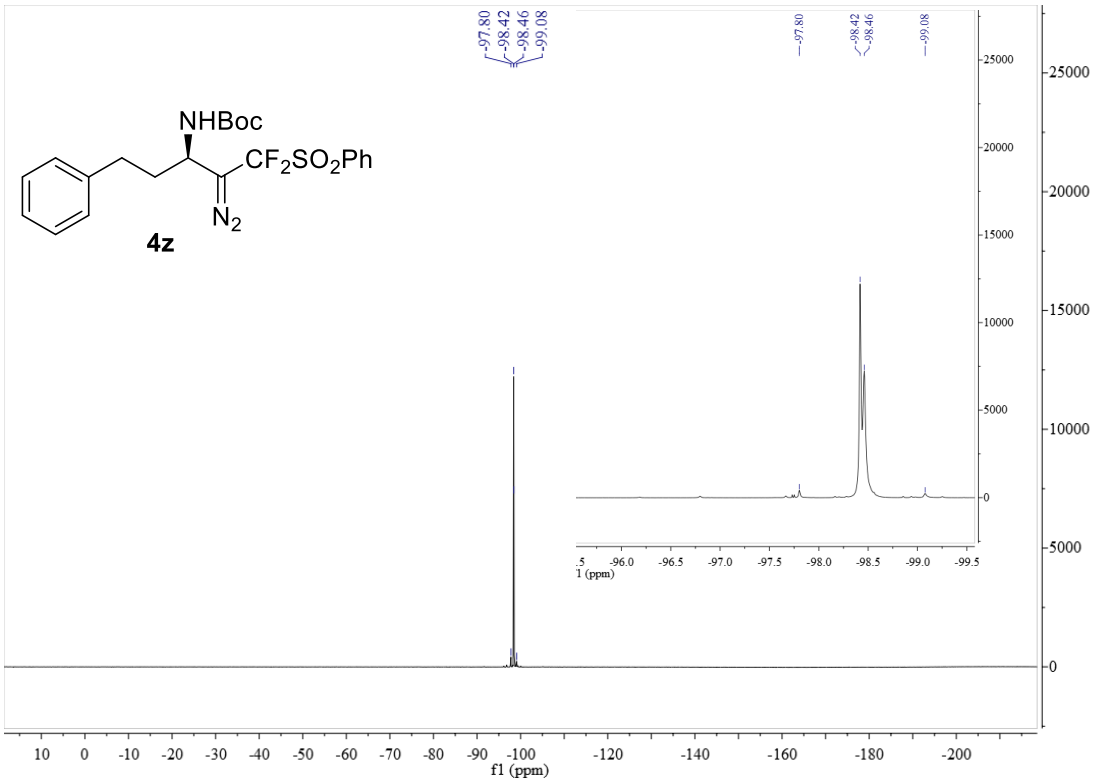
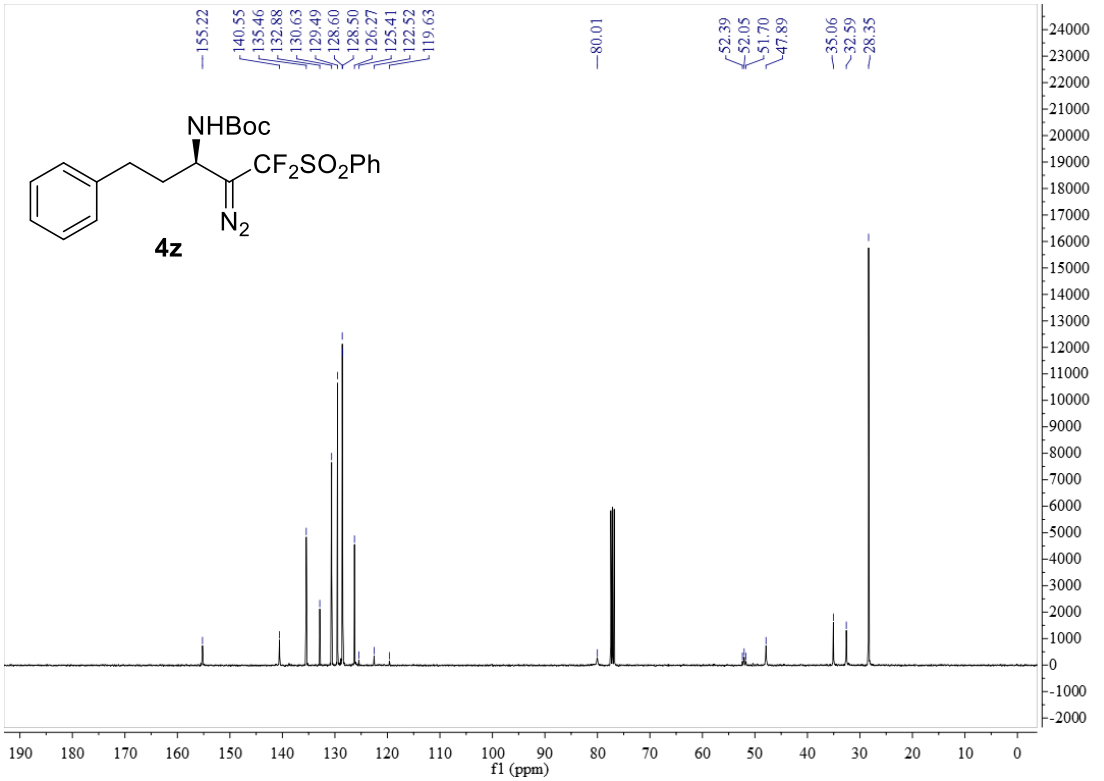
154.65
136.30
136.21
135.47
132.79
130.64
129.94
129.48
126.57
124.86
121.96
119.06
80.45
79.99
54.35
53.97
53.62
53.27
52.21
50.67
38.01
28.28
NHBoc
Boc
NH
CF2SO2Ph
N2
MeO2C
4y
f1 (ppm)


NHBoc
CF2SO2Ph
N2
4z
f1 (ppm)


NHBoc
CF2SO2Ph
N2
4z
f1 (ppm)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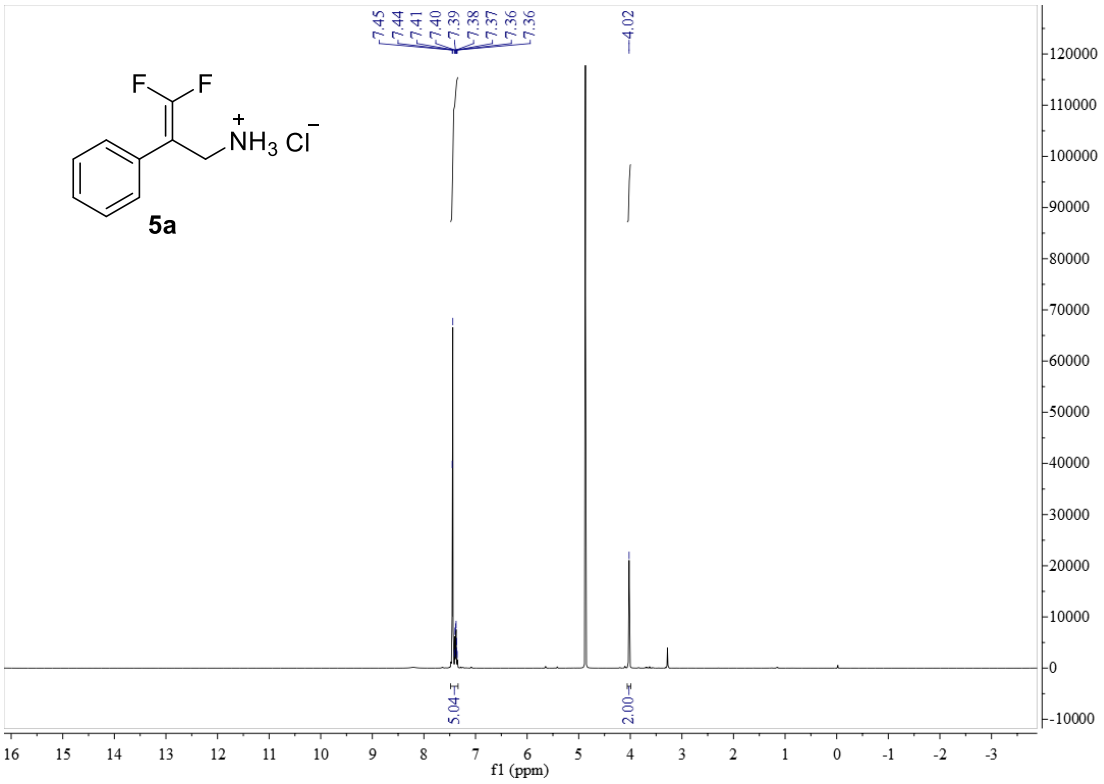
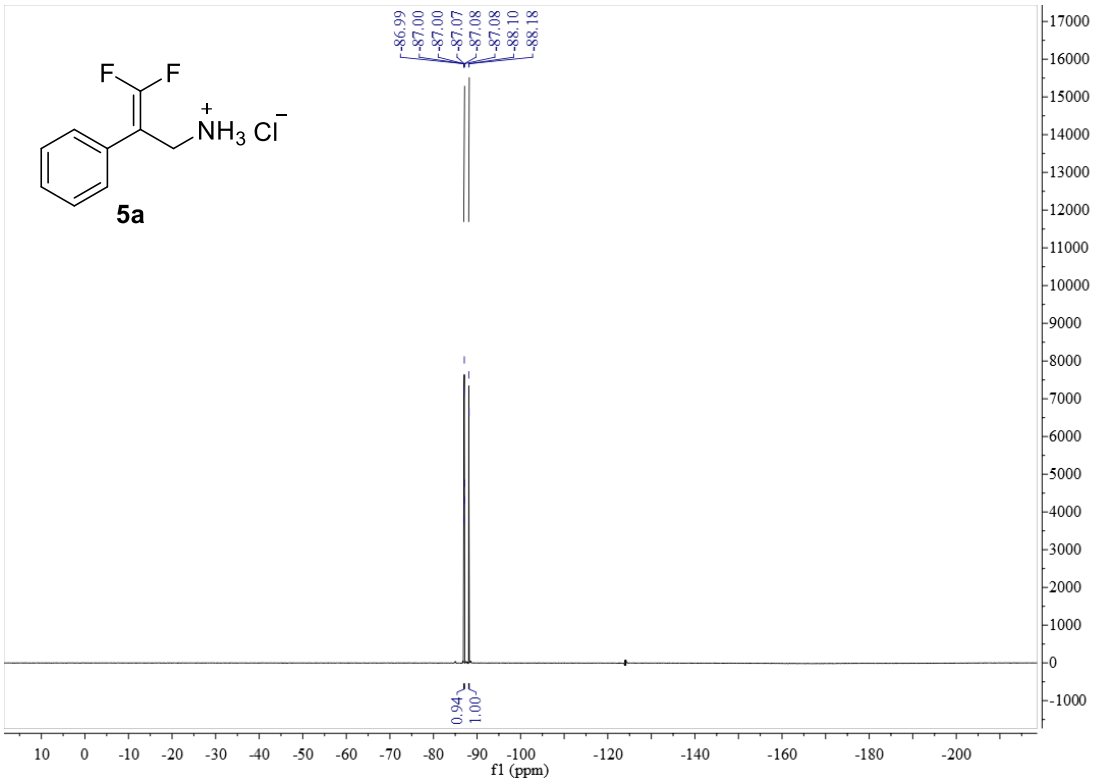
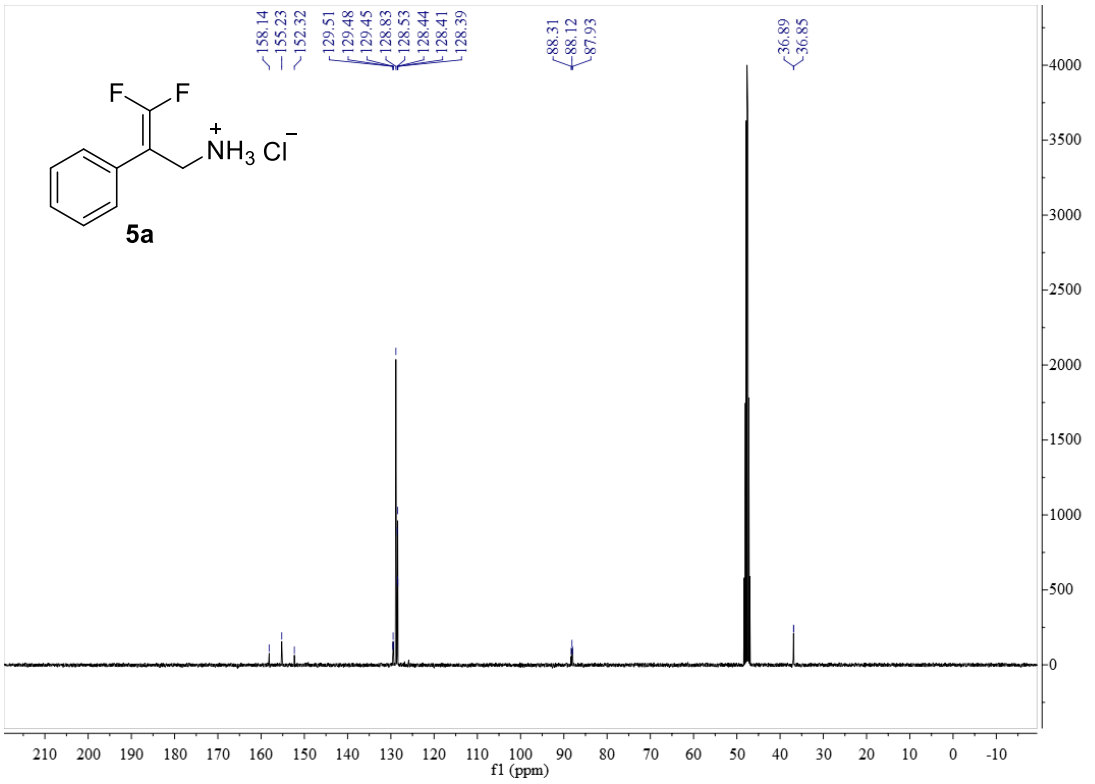
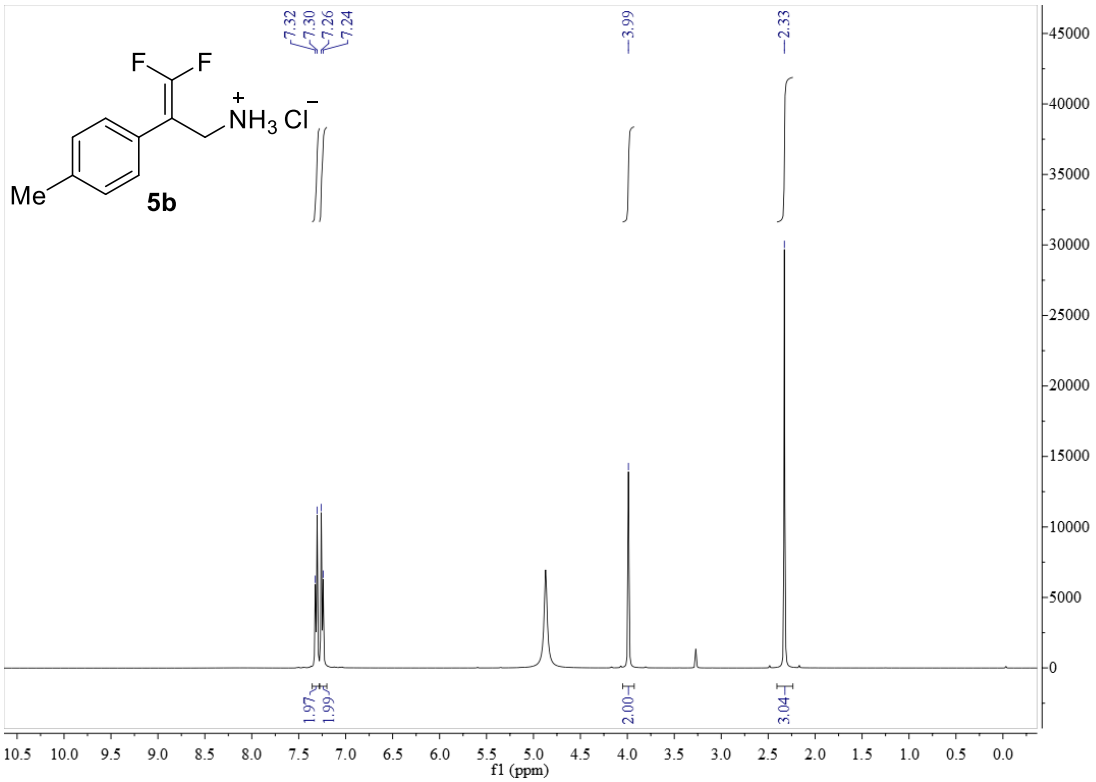
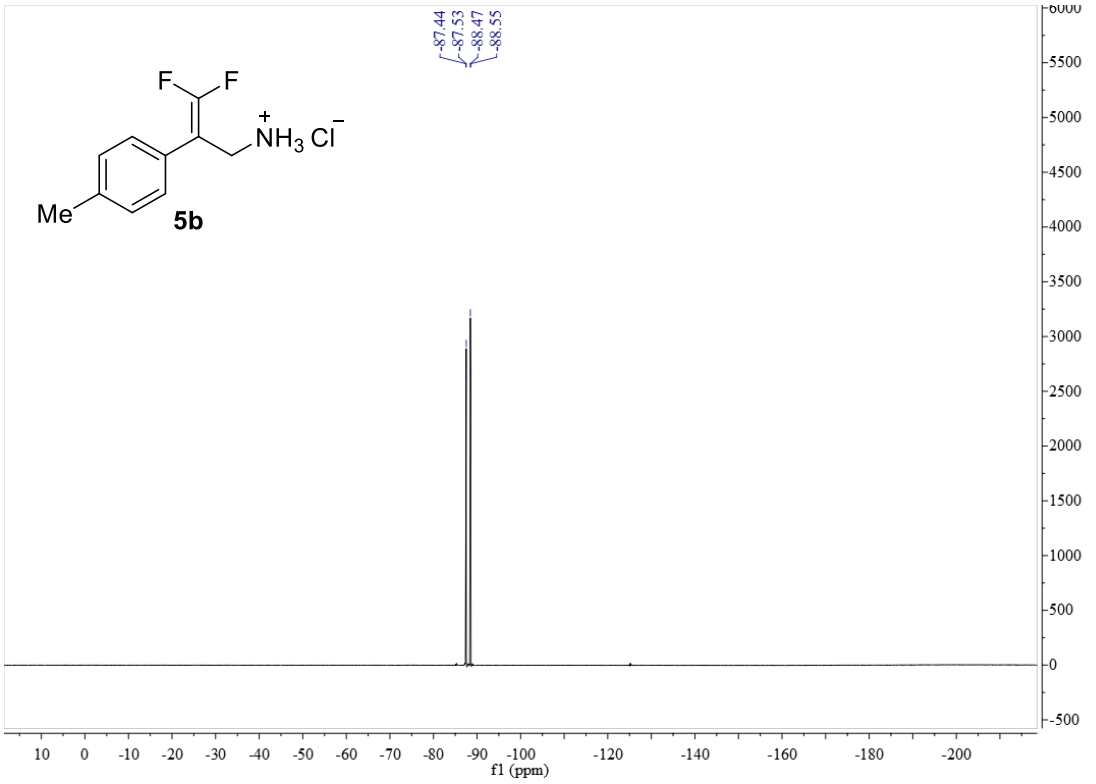
140.55
135.46
132.88
130.63
129.49
128.60
128.50
126.27
125.41
122.52
119.63
80.01
52.39
52.05
51.70
47.89
35.06
32.59
28.35
NHBoc
CF2SO2Ph
N2
4z
f1 (ppm)


7.45
7.44
7.41
7.40
7.39
7.38
7.37
7.36
7.36
4.02
F
F
NH3 Cl
5a
5.04
2.00
f1 (ppm)


F
F
NH3 Cl
5a
-86.99
-87.00
-87.00
-87.07
-87.08
-87.08
-88.10
-88.18
0.94
1.00
f1 (ppm)


F
F
NH3 Cl
5a
158.14
155.23
152.32
129.51
129.48
129.45
128.83
128.53
128.44
128.41
128.39
88.31
88.12
87.93
36.89
36.85
f1 (ppm)


7.32
7.30
7.26
7.24
3.99
2.33
F
F
NH3 Cl
Me
5b
1.97
1.99
2.00
3.04
f1 (ppm)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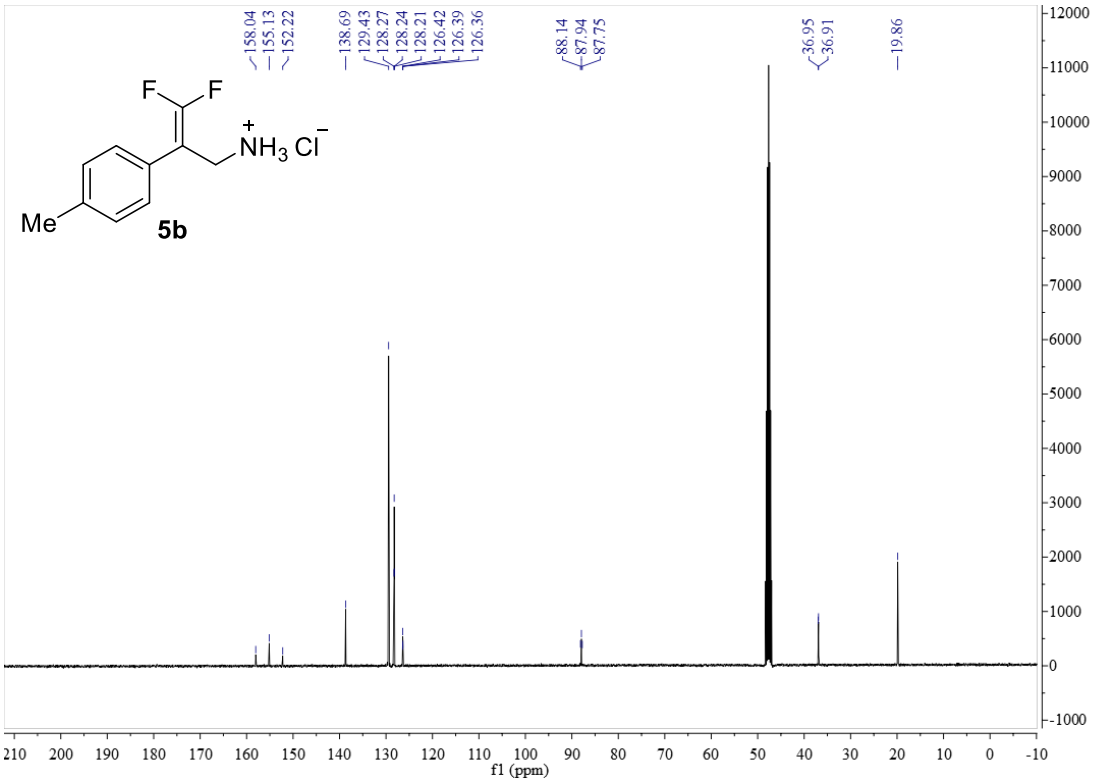
-87.53
-88.47
-88.55
F
F
NH3 Cl
Me
5b
f1 (ppm)


158.04
155.13
152.22
138.69
129.43
128.27
128.24
128.21
126.42
126.39
126.36
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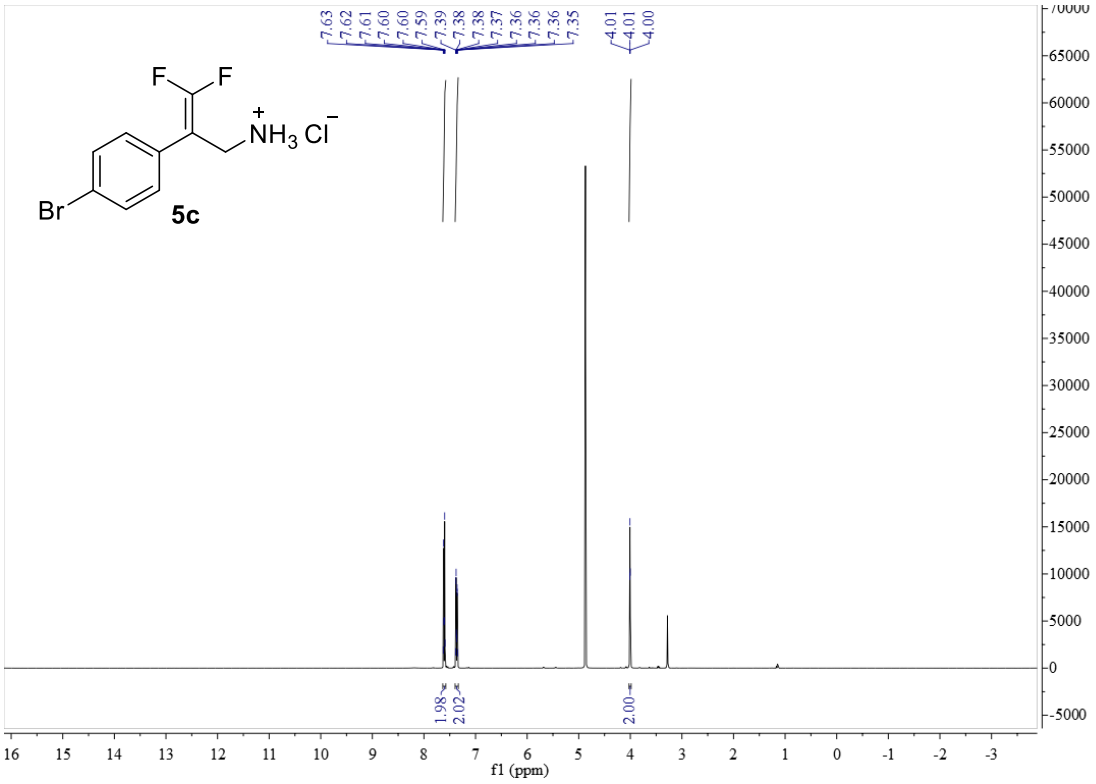
87.75
36.95
36.91
19.86
F
F
NH3 Cl
Me
5b
f1 (ppm)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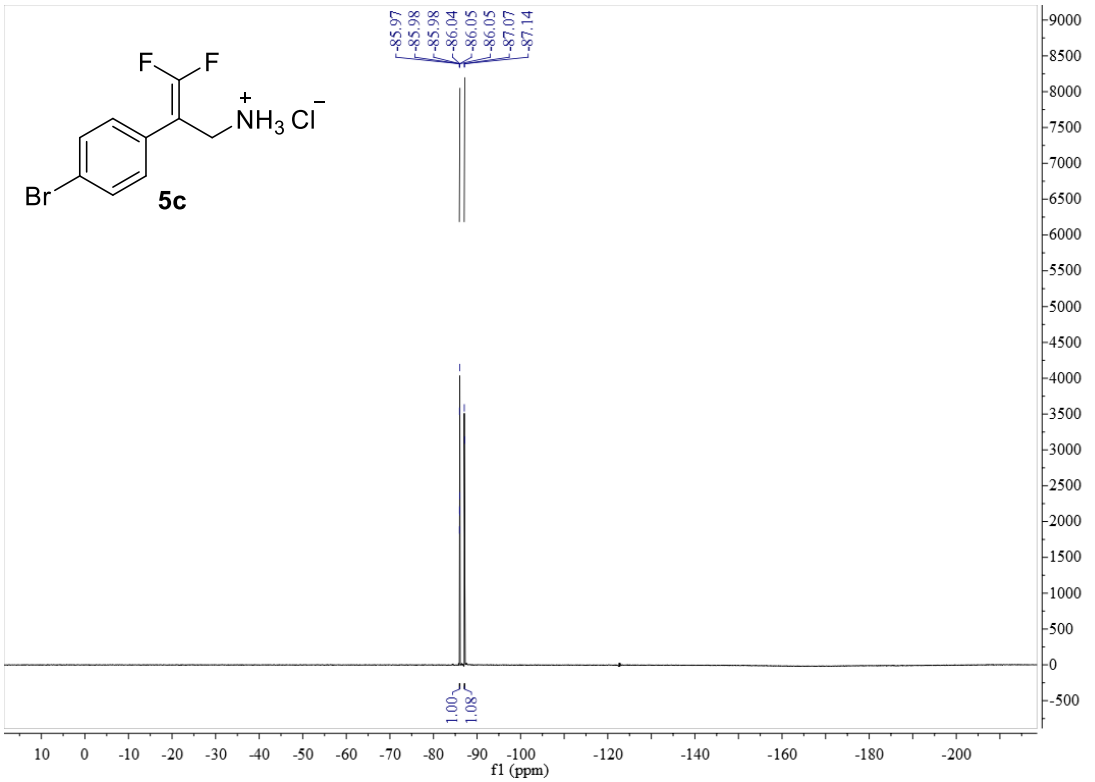
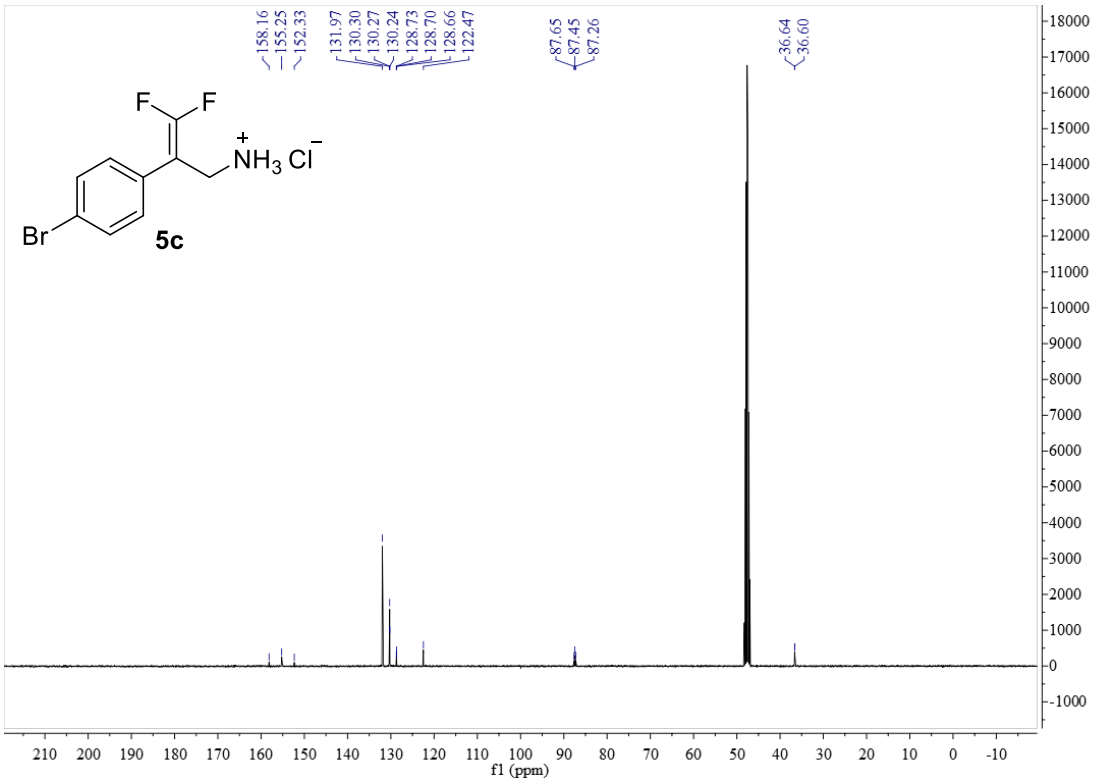
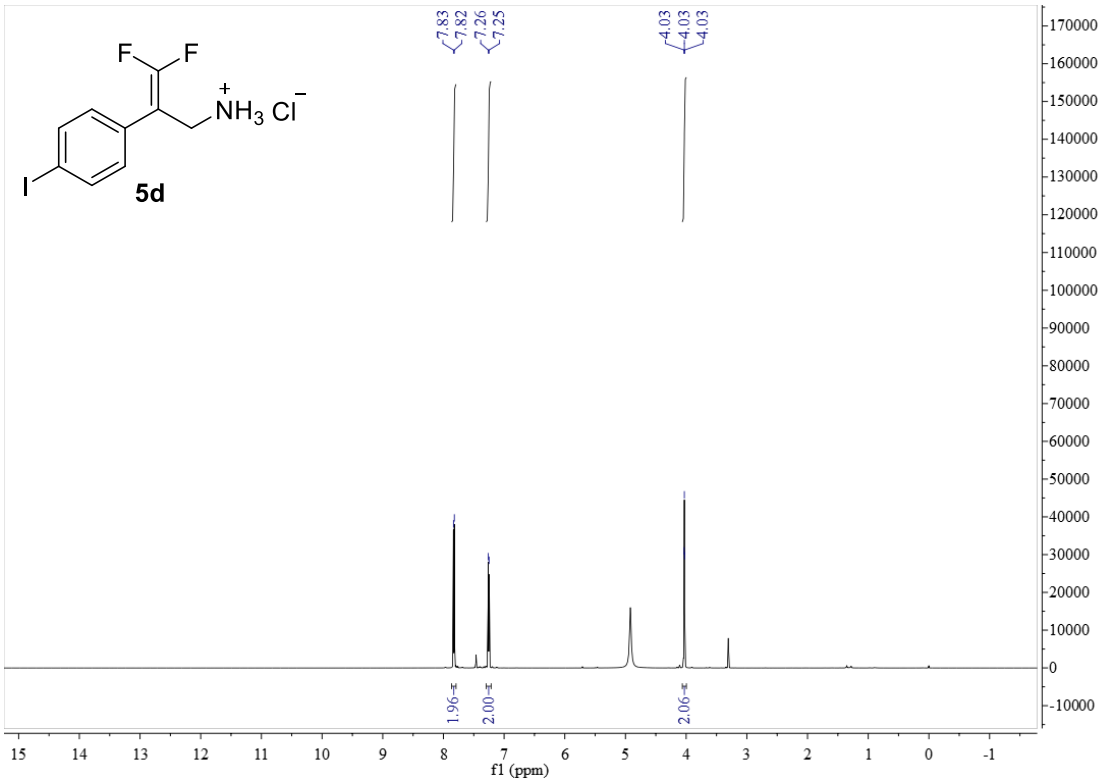
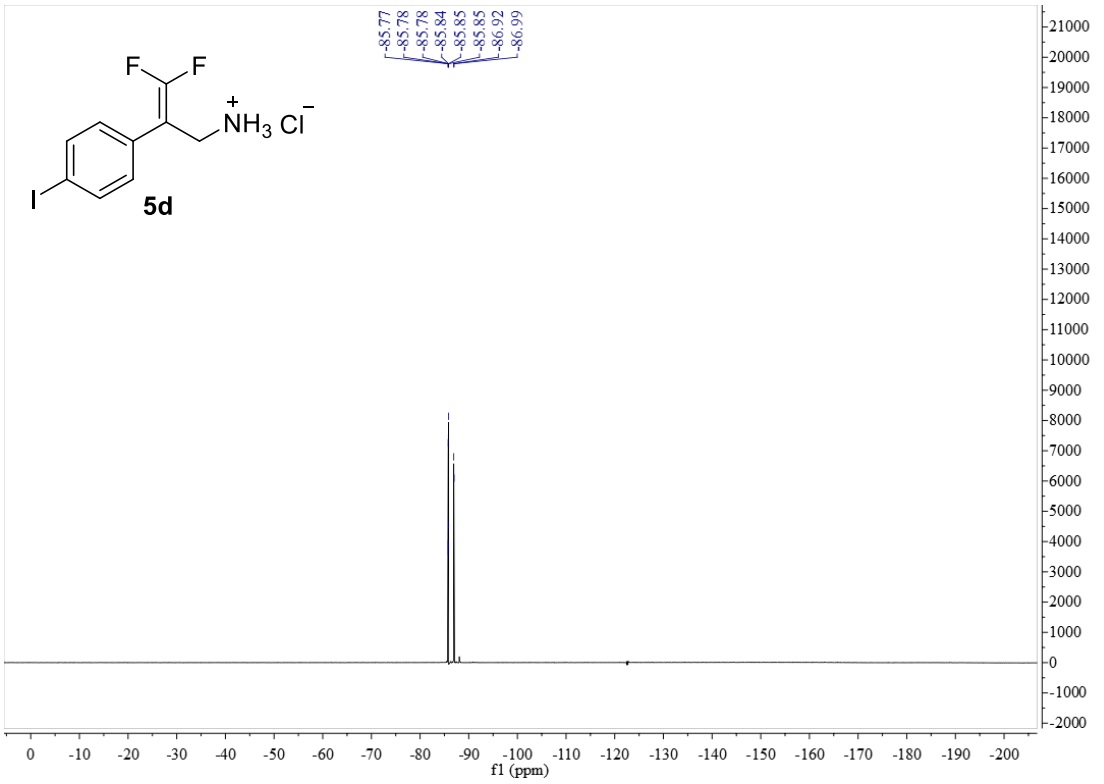
7.62
7.61
7.60
7.60
7.59
7.39
7.38
7.38
7.37
7.36
7.36
7.36
7.35
4.01
4.01
4.00
F
F
NH3 Cl
Br
5c
1.98
2.02
2.00
f1 (ppm)


F
F
NH3 Cl
Br
5c
-85.97
-85.98
-85.98
-86.04
-86.05
-86.05
-87.07
-87.14
1.00
1.08
f1 (ppm)


F
F
NH3 Cl
Br
5c
158.16
155.25
152.33
131.97
130.30
130.27
130.24
128.73
128.70
128.66
122.47
87.65
87.45
87.26
36.64
36.60
f1 (ppm)


F
F
NH3 Cl
I
5d
7.83
7.82
7.26
7.25
4.03
4.03
4.03
1.96
2.00
2.06
f1 (ppm)


F
F
NH3 Cl
I
5d
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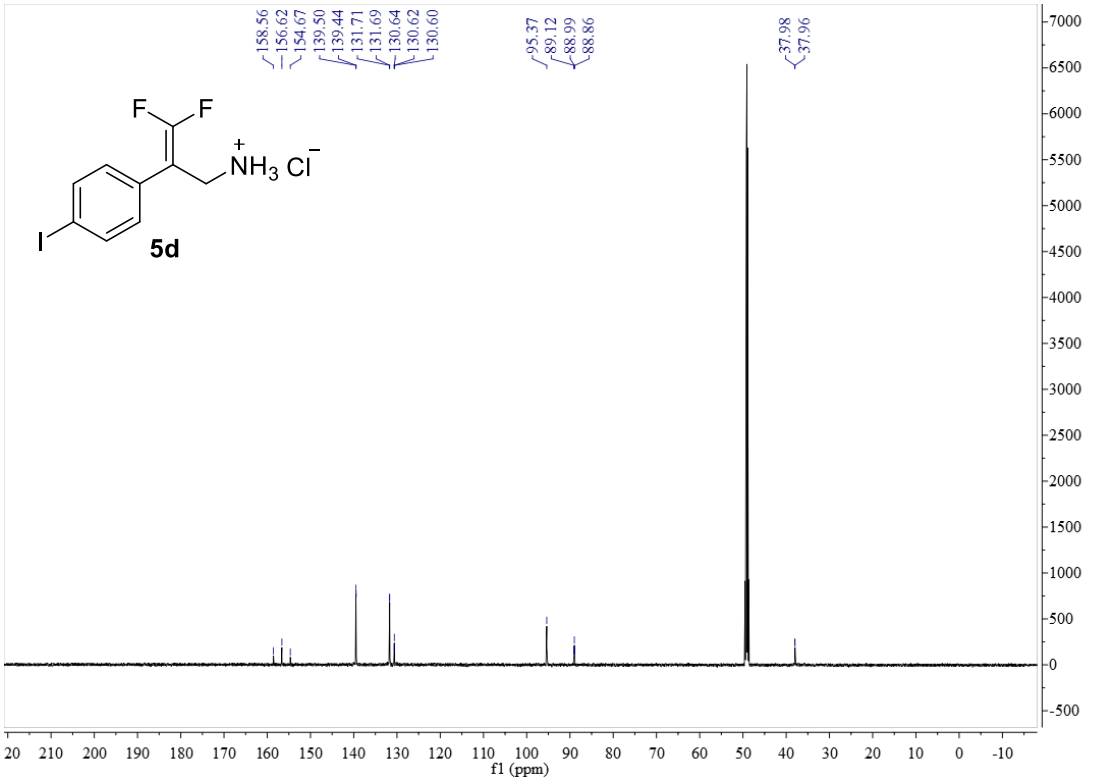
-85.78
-85.78
-85.84
-85.85
-85.85
-86.92
-86.99
f1 (ppm)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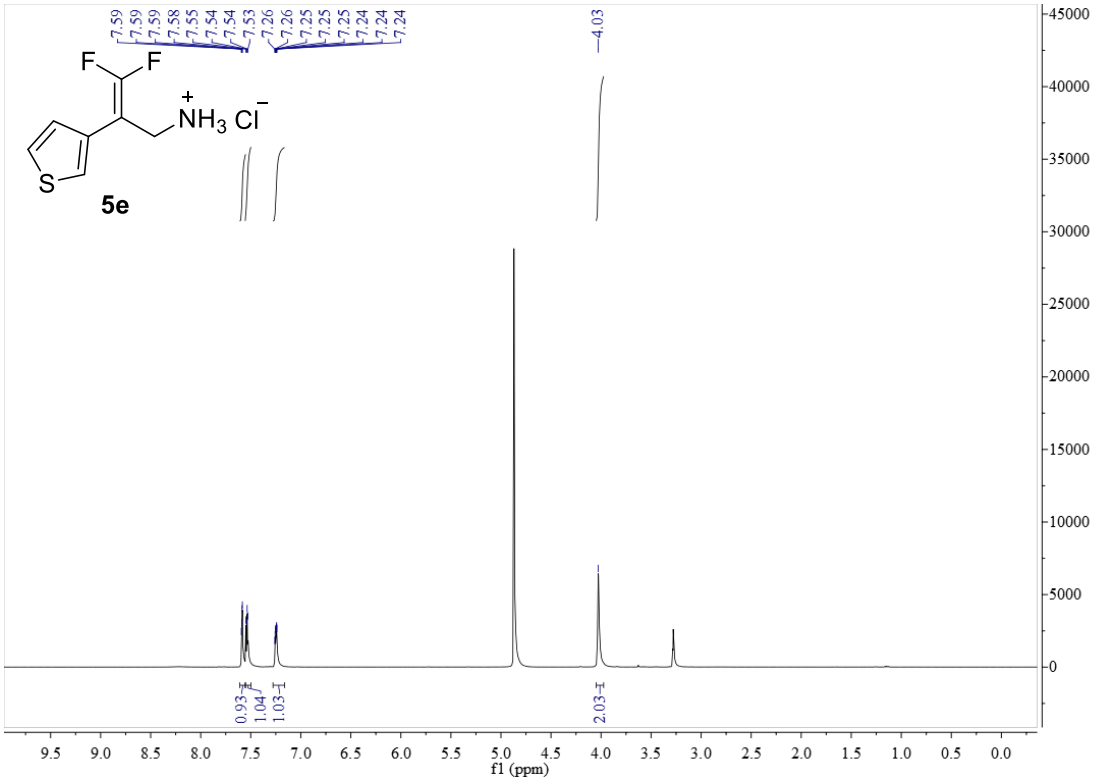
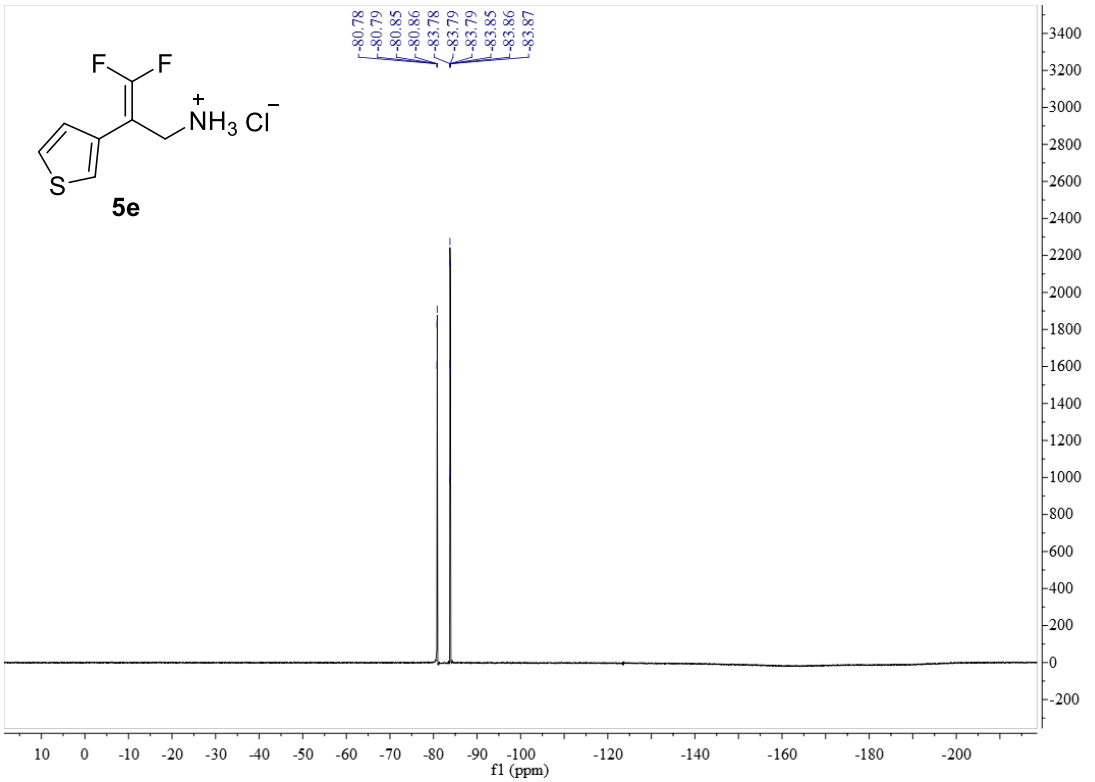
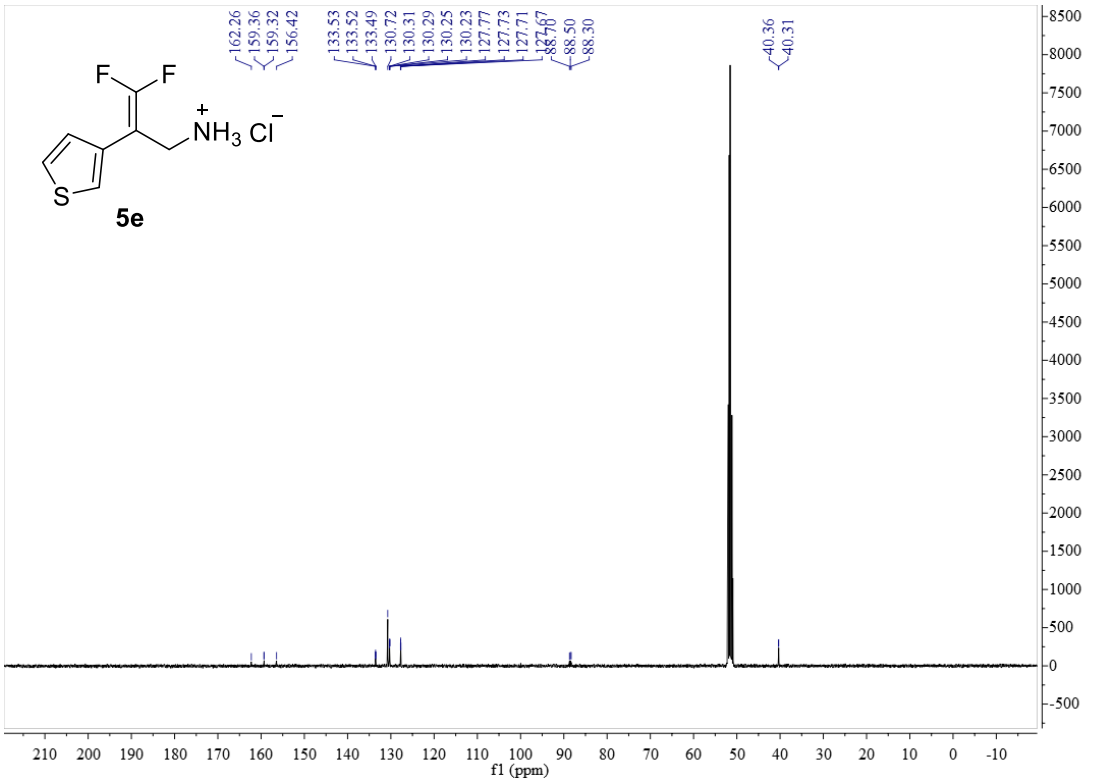
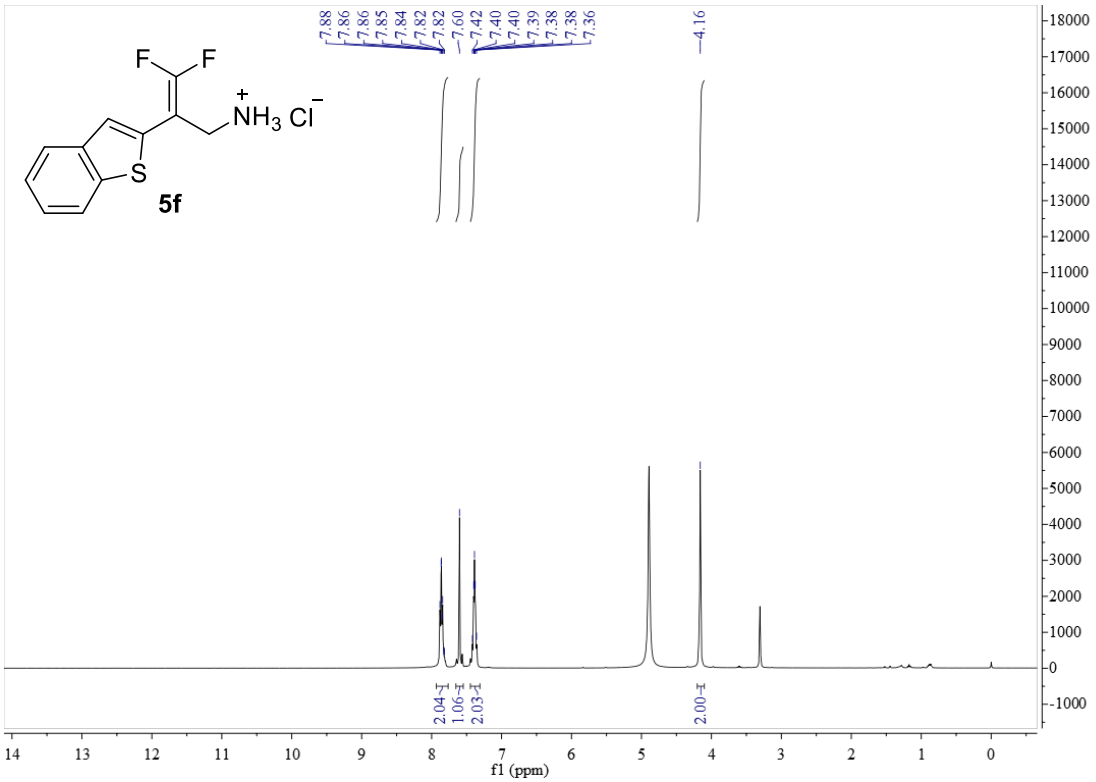
156.62
154.67
139.50
139.44
131.71
131.69
130.64
130.62
130.60
95.37
89.12
88.99
88.86
37.98
37.96
F
F
NH3 Cl
I
5d
f1 (ppm)


7.59
7.59
7.59
7.58
7.55
7.54
7.54
7.53
7.26
7.26
7.25
7.25
7.25
7.24
7.24
7.24
4.03
F
F
NH3 Cl
S
5e
0.93
1.04
1.03
2.03
f1 (ppm)


-80.78
-80.79
-80.85
-80.86
-83.78
-83.79
-83.79
-83.85
-83.86
-83.87
F
F
NH3 Cl
S
5e
f1 (ppm)


162.26
159.36
159.32
156.42
133.53
133.52
133.49
130.72
130.31
130.29
130.25
130.23
127.77
127.73
127.71
88.70
88.50
88.30
40.36
40.31
F
F
NH3 Cl
S
5e
f1 (ppm)


F
F
NH3 Cl
S
5f
7.88
7.86
7.86
7.85
7.84
7.82
7.82
7.60
7.42
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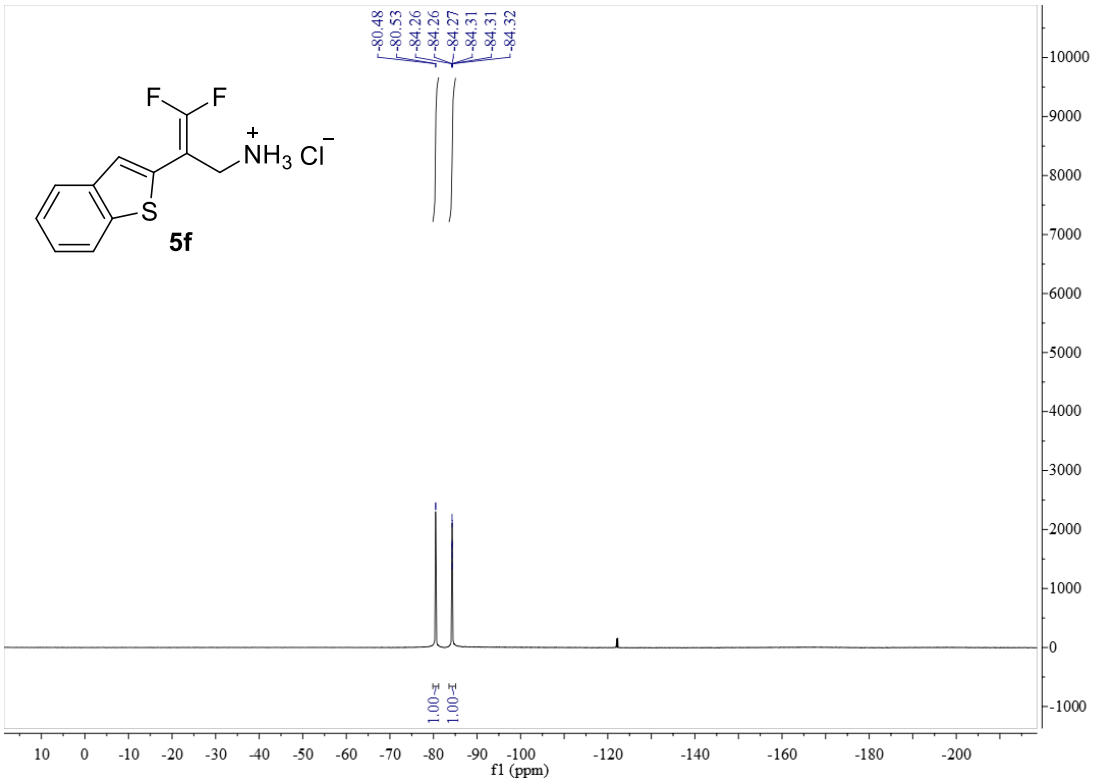
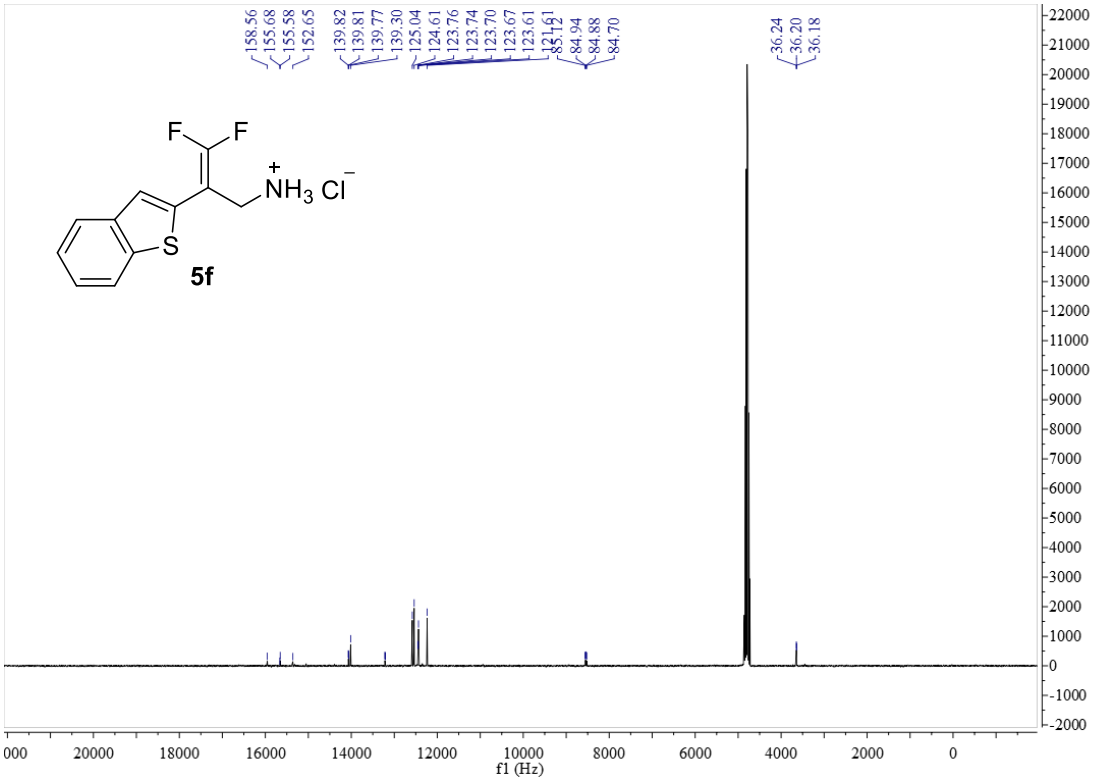
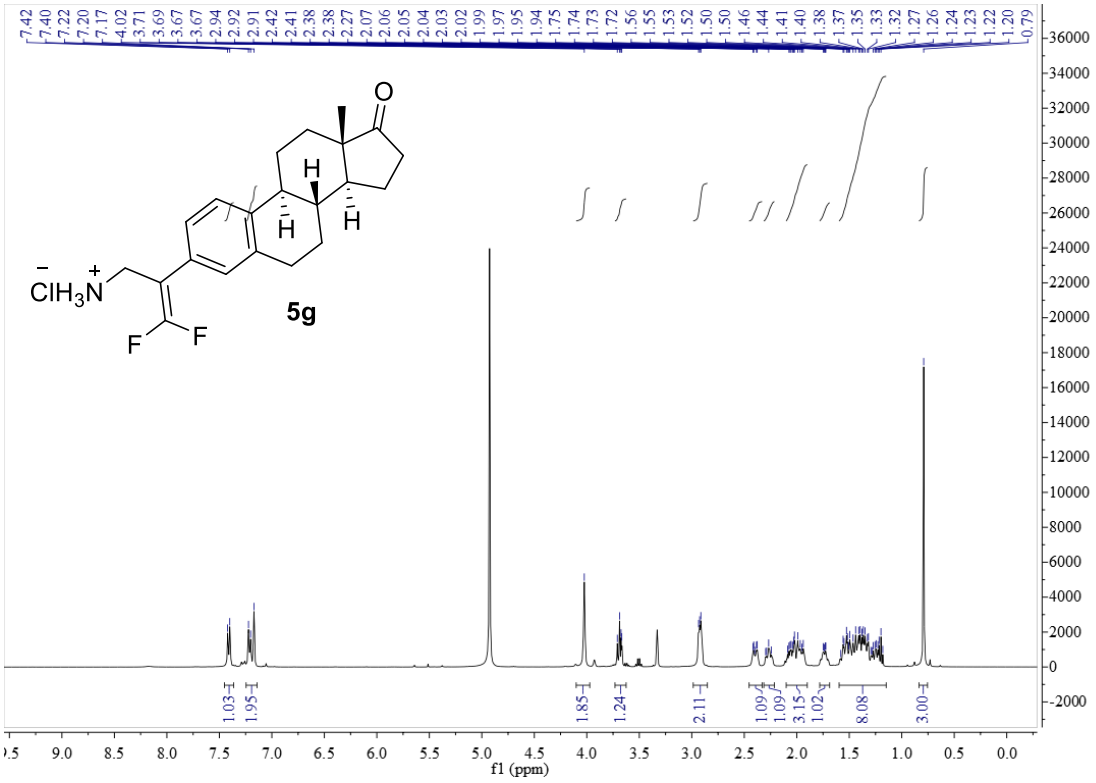
2.04
1.06
2.03
2.00
f1 (ppm)


F
F
NH3 Cl
S
5f
80.48
80.53
84.26
84.26
84.27
84.31
84.31
84.32
1.00
1.00
f1 (ppm)


158.56
155.68
155.58
152.65
139.82
139.81
139.77
139.30
125.04
124.61
123.76
123.74
123.70
123.67
123.61
121.61
84.94
84.88
84.70
36.24
36.20
36.18
F
F
NH3 Cl
S
5f
f1 (Hz)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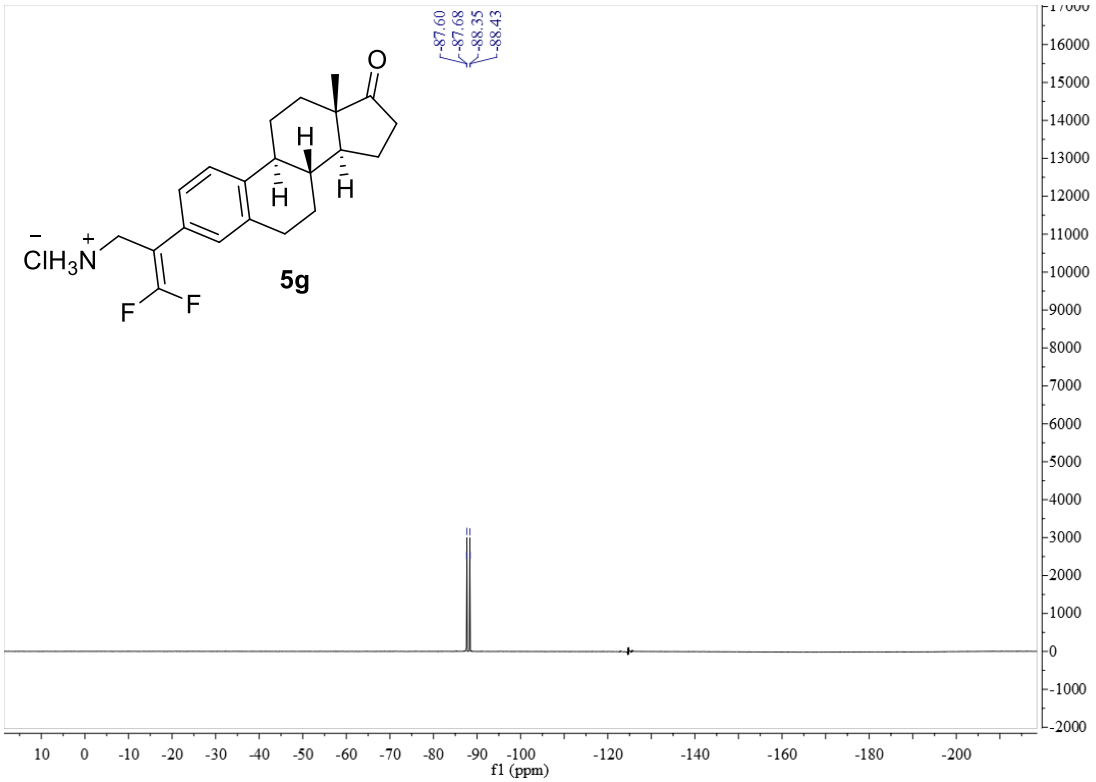
7.40
7.22
7.20
7.17
4.02
3.71
3.69
3.67
3.67
2.94
2.92
2.91
2.42
2.41
2.38
2.38
2.27
2.07
2.06
2.05
2.04
2.03
2.02
1.99
1.97
1.95
1.94
1.75
1.74
1.73
1.72
1.56
1.55
1.53
1.52
1.50
1.50
1.46
1.44
1.41
1.40
1.38
1.37
1.35
1.33
1.32
1.27
1.26
1.24
1.23
1.22
1.20
0.79
O
H
H
H
ClH3N
F
F
5g
1.03
1.95
1.85
1.24
2.11
1.09
1.09
3.15
1.02
8.08
3.00
f1 (ppm)


-87.60
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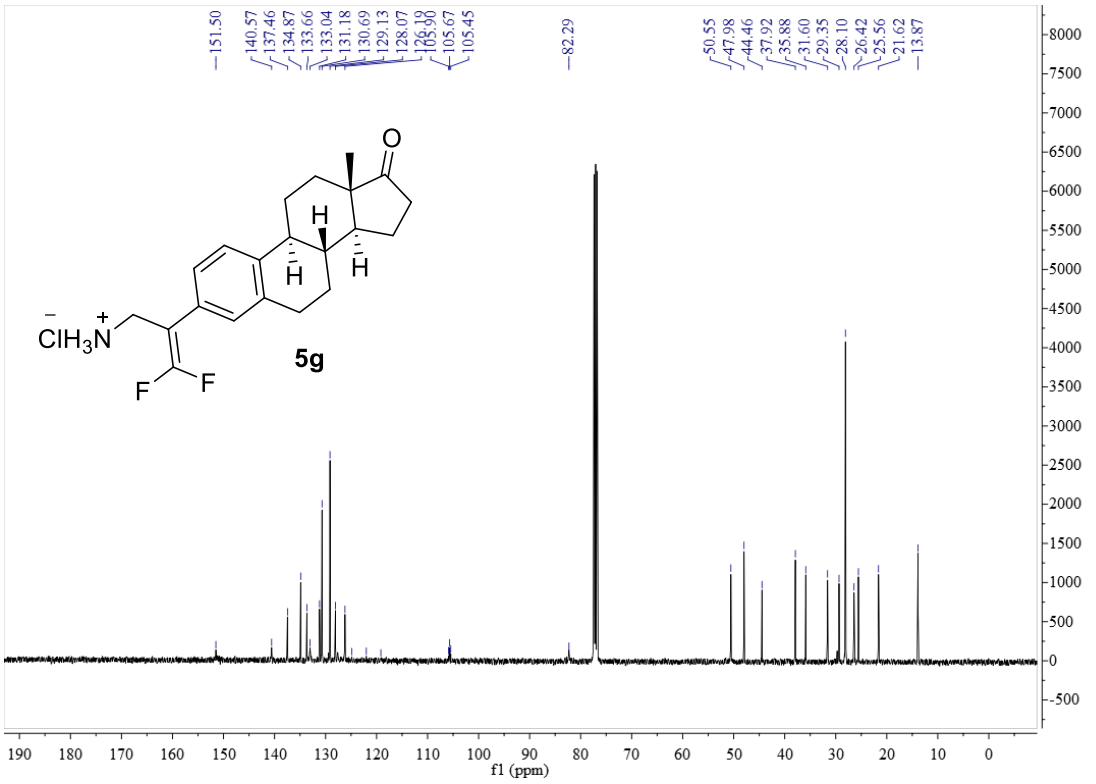
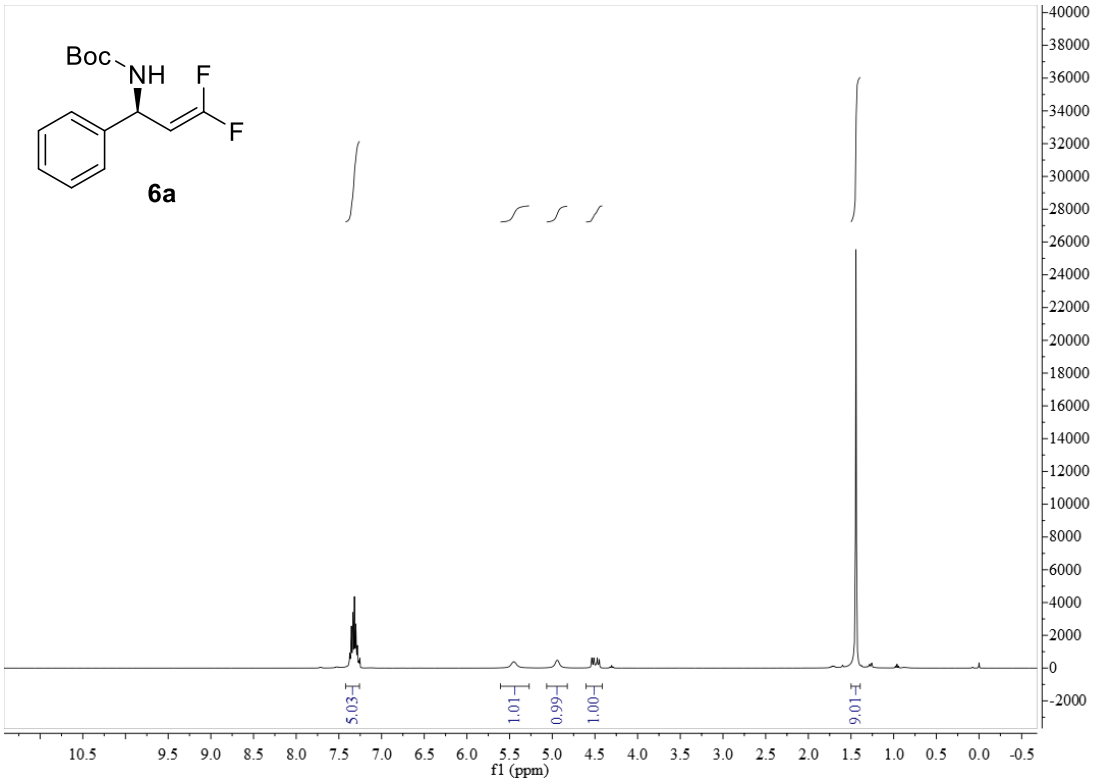
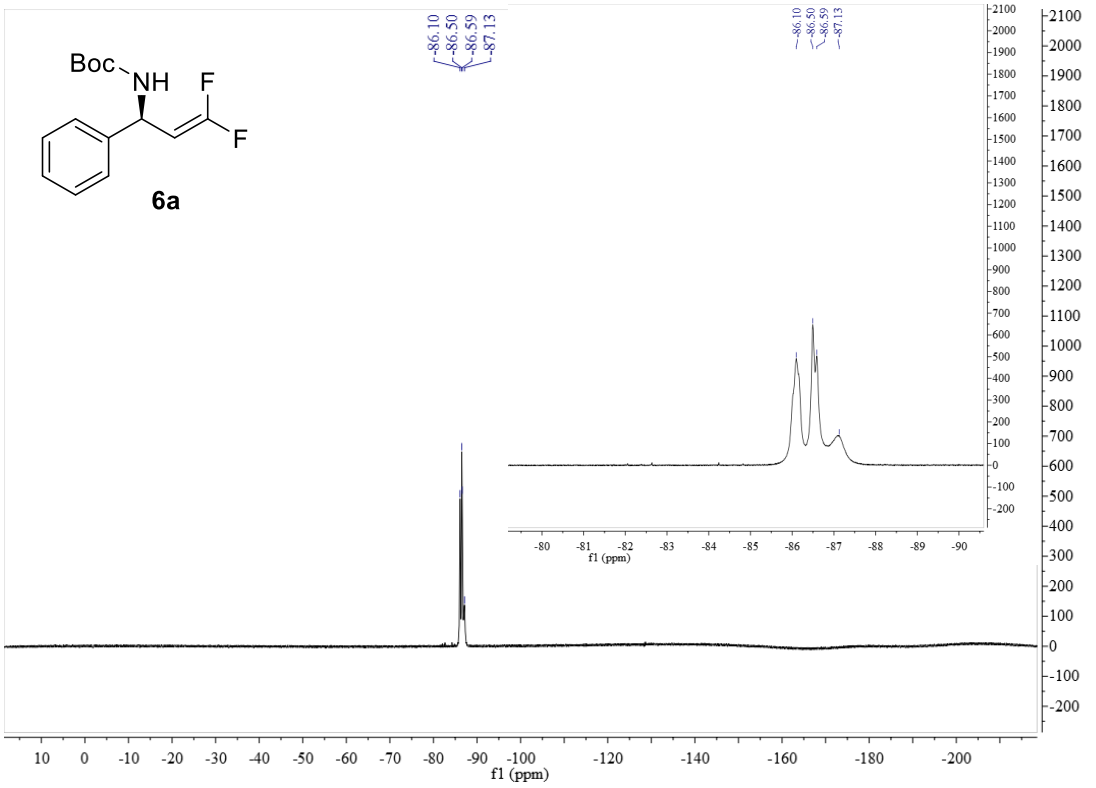
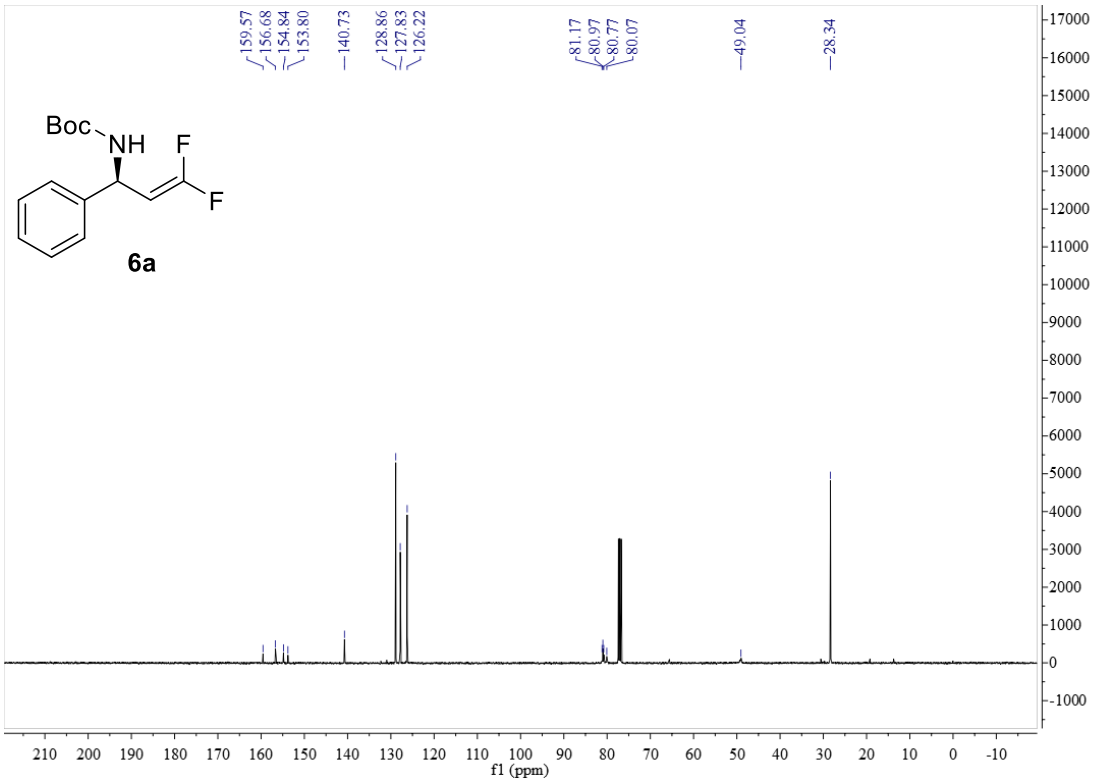
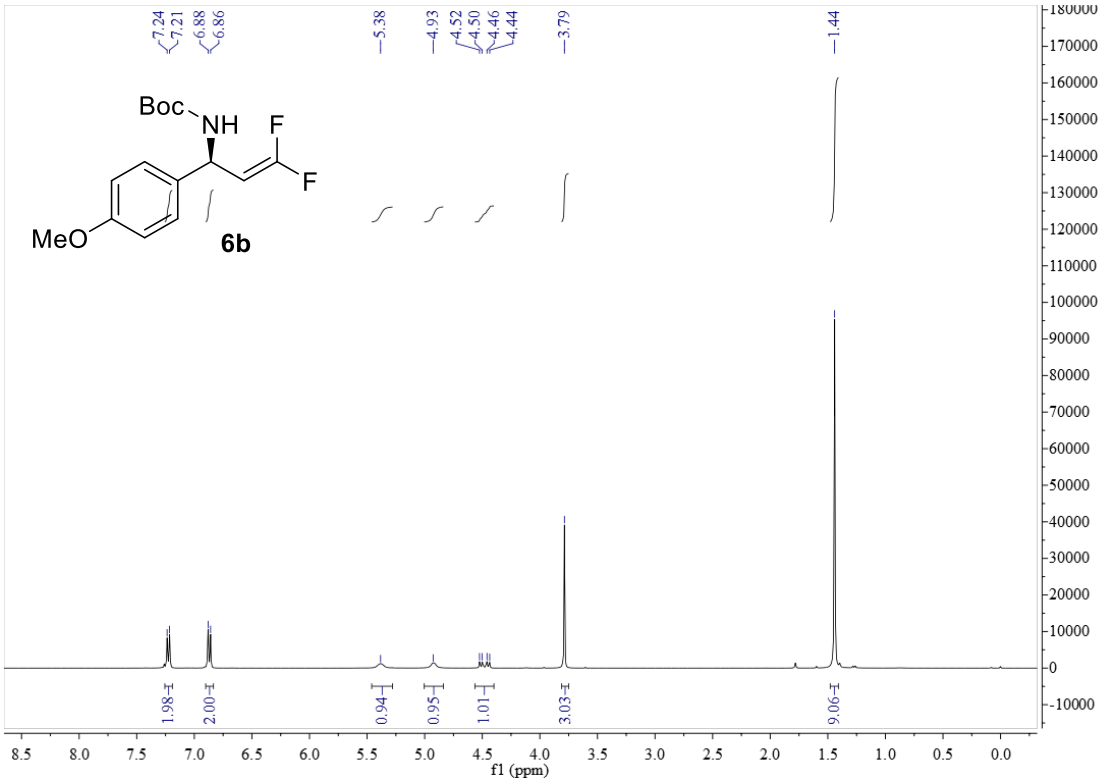
-88.43
O
H
H
H
ClH3N
F
F
5g
f1 (ppm)

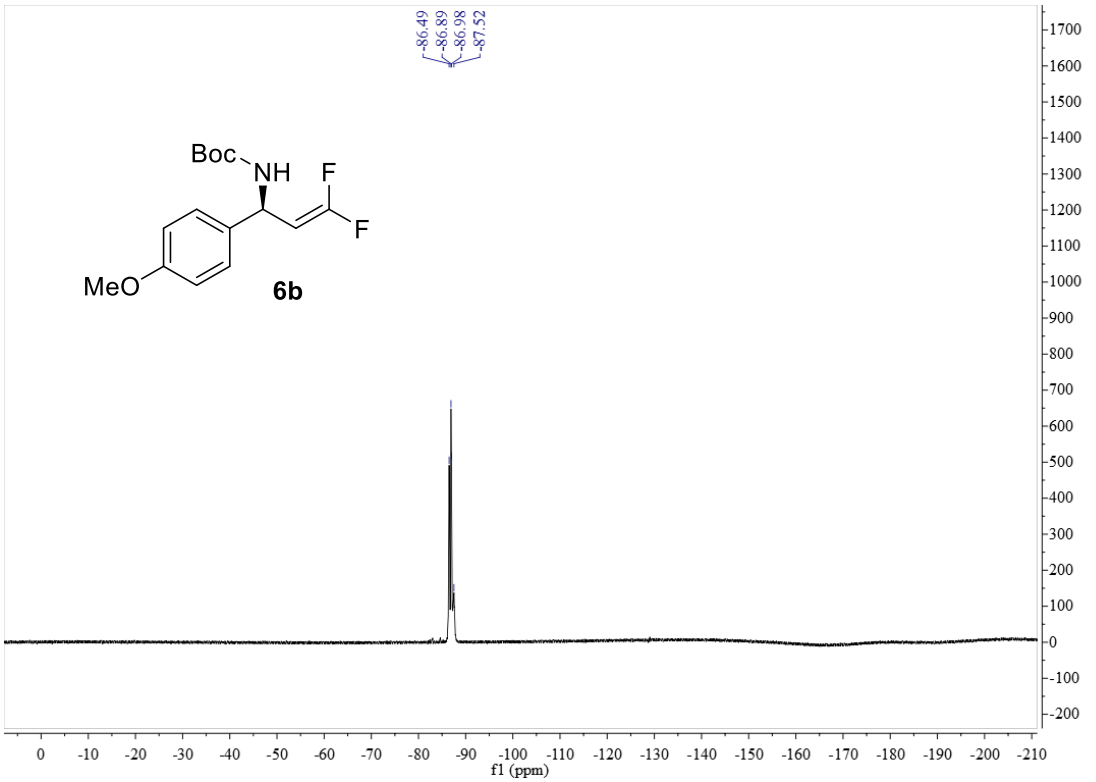

151.50
140.57
137.46
134.87
133.66
133.04
131.18
130.69
129.13
128.07
126.19
125.90
105.67
105.45
82.29
50.55
47.98
44.46
37.92
35.88
31.60
29.35
28.10
26.42
25.56
21.62
13.87
O
H
H
H
ClH3N
F
F
5g
f1 (ppm)

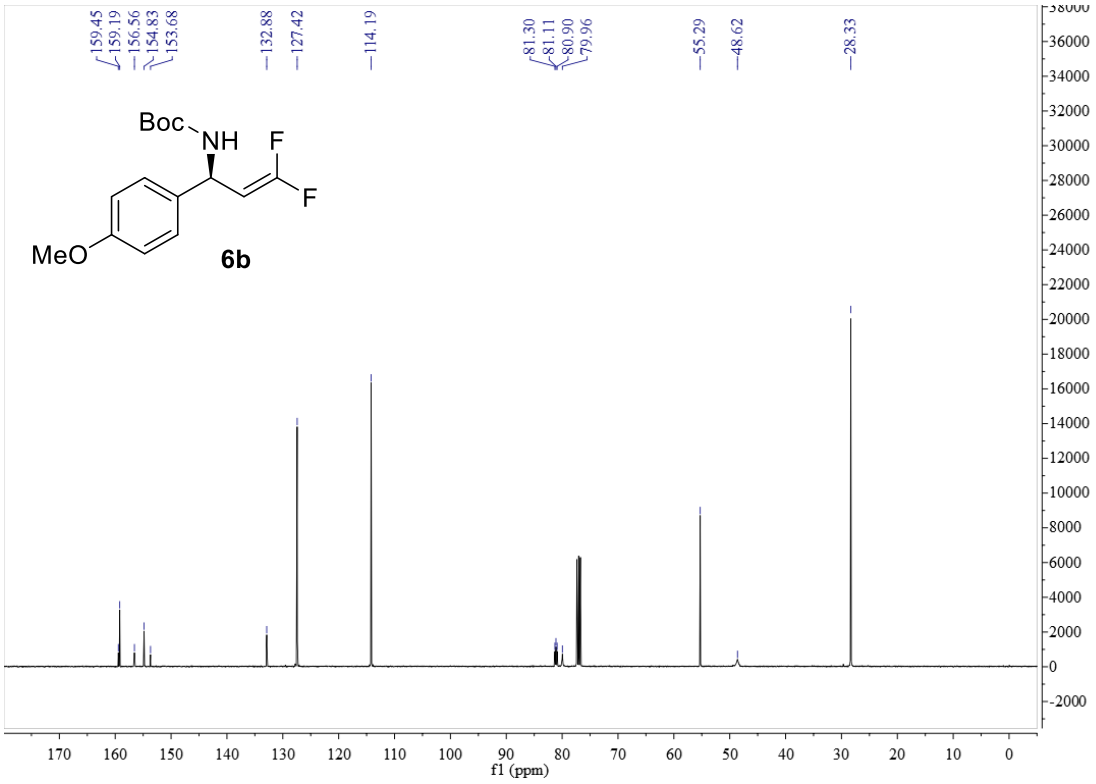

Boc
NH
F
F
6a
5.03
1.01
0.99
1.00
9.01
f1 (ppm)

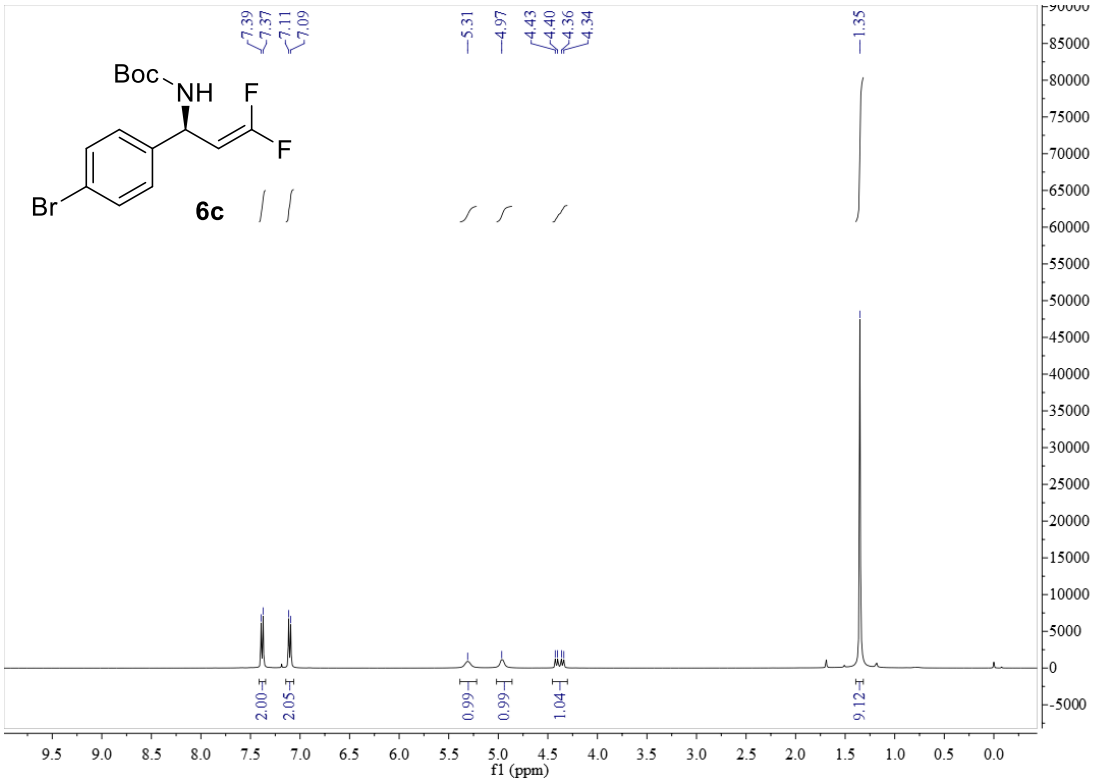

Boc
NH
F
F
6a
-86.10
-86.50
-86.59
-87.13
f1 (ppm)

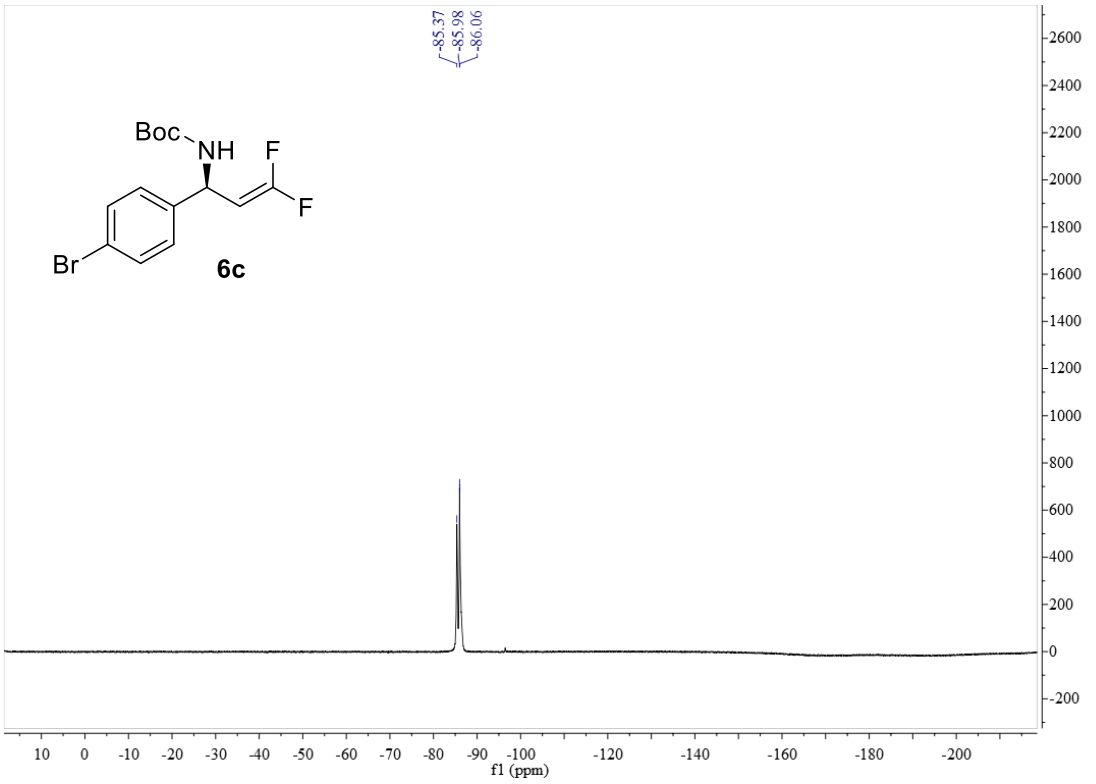

159.57
156.68
154.84
153.80
140.73
128.86
127.83
126.22
81.17
80.97
80.77
80.07
49.04
28.34
Boc
NH
F
F
6a
f1 (ppm)

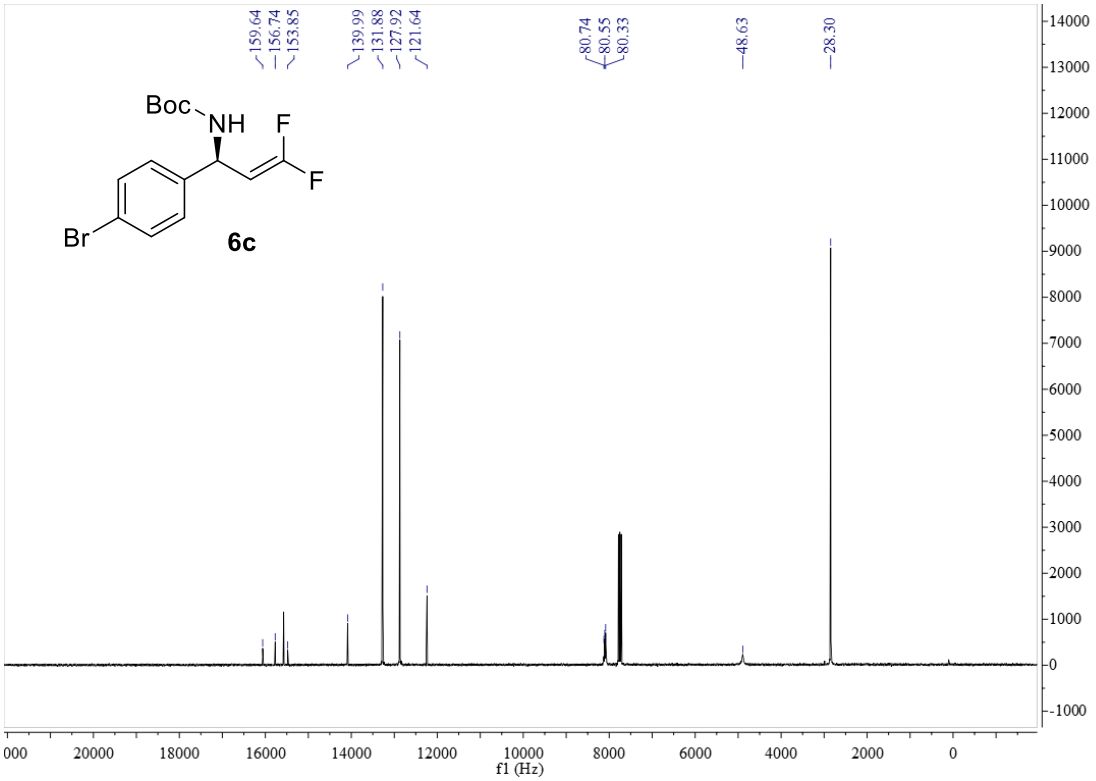

7.24
7.21
6.88
6.86
5.38
4.93
4.52
4.50
4.46
4.44
3.79
1.44
Boc
NH
F
F
MeO
6b
1.98
2.00
0.94
0.95
1.01
3.03
9.06
f1 (ppm)

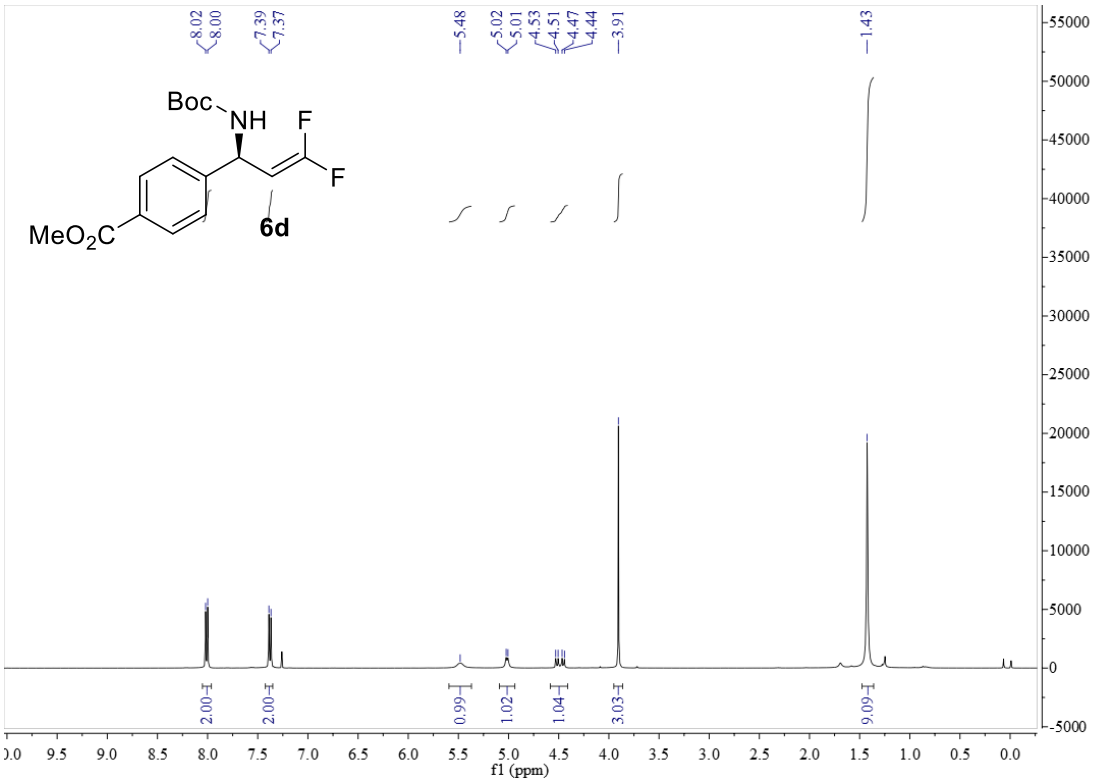

-86.49
-86.89
-86.98
-87.52
Boc
NH
F
F
MeO
6b
f1 (ppm)

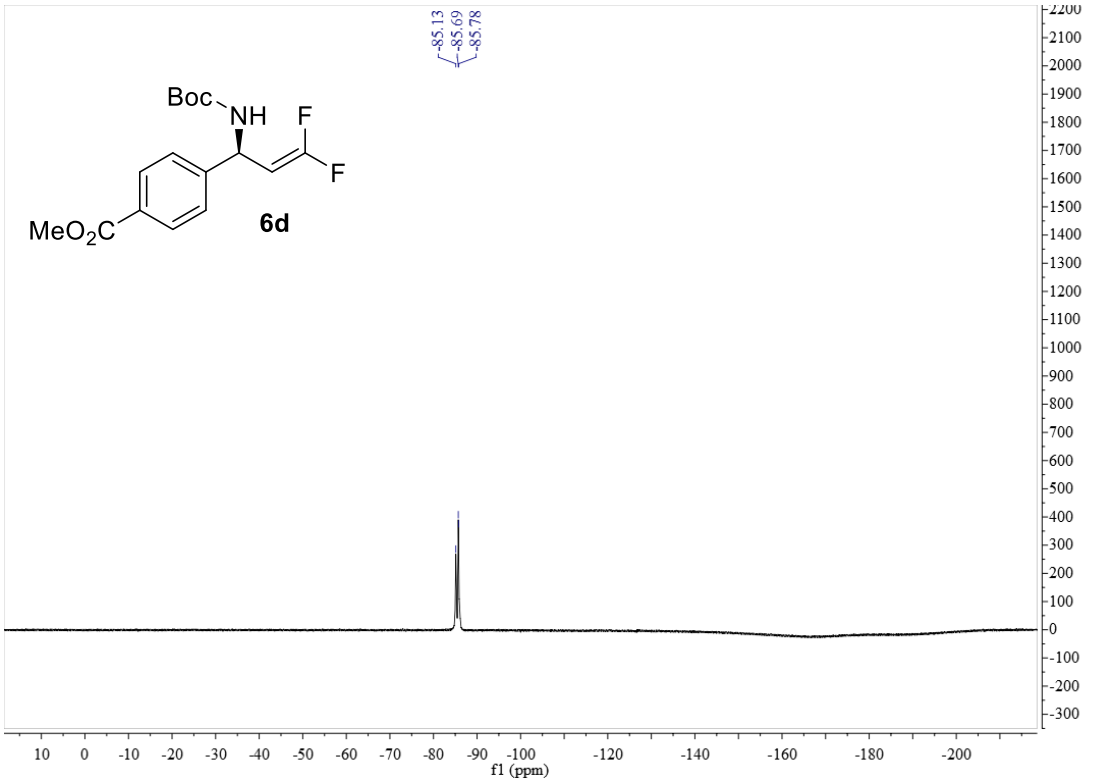

159.45
159.19
156.56
154.83
153.68
132.88
127.42
114.19
81.30
81.11
80.90
79.96
55.29
48.62
28.33
Boc
NH
F
F
MeO
6b
f1 (ppm)


7.39
7.37
7.11
7.09
5.31
4.97
4.43
4.40
4.36
4.34
1.35
Boc
NH
F
F
Br
6c
2.00
2.05
0.99
0.99
1.04
9.12
f1 (ppm)


-85.37
-85.98
-86.06
Boc
NH
F
F
Br
6c
f1 (ppm)


159.64
156.74
153.85
139.99
131.88
127.92
121.64
80.74
80.55
80.33
48.63
28.30
Boc
NH
F
F
Br
6c
f1 (Hz)


8.02
8.00
7.39
7.37
5.48
5.02
5.01
4.53
4.51
4.47
4.44
3.91
1.43
Boc
NH
F
F
MeO2C
6d
2.00
2.00
0.99
1.02
1.04
3.03
9.09
f1 (ppm)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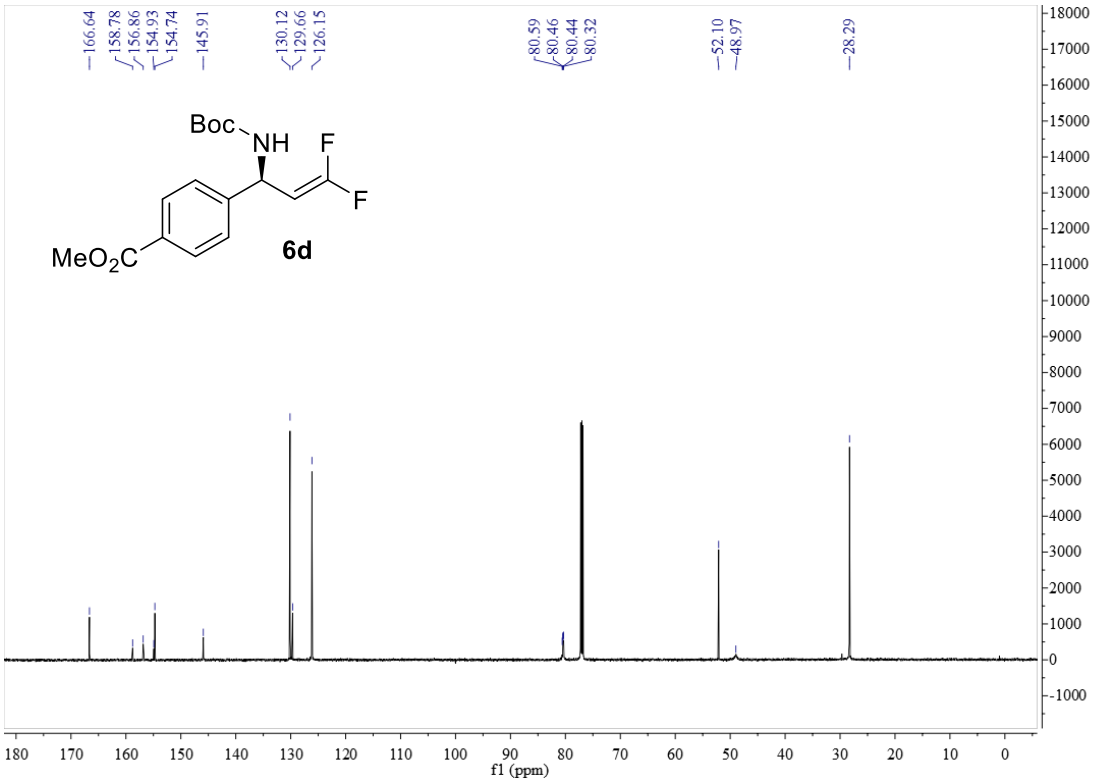
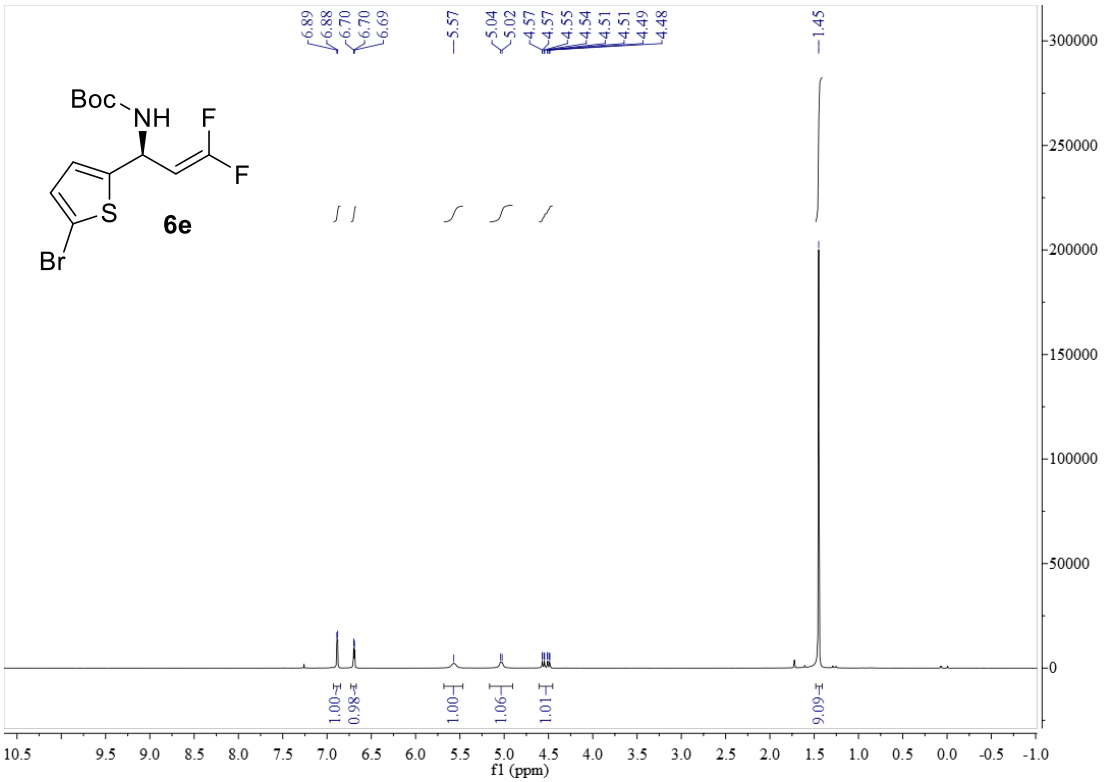
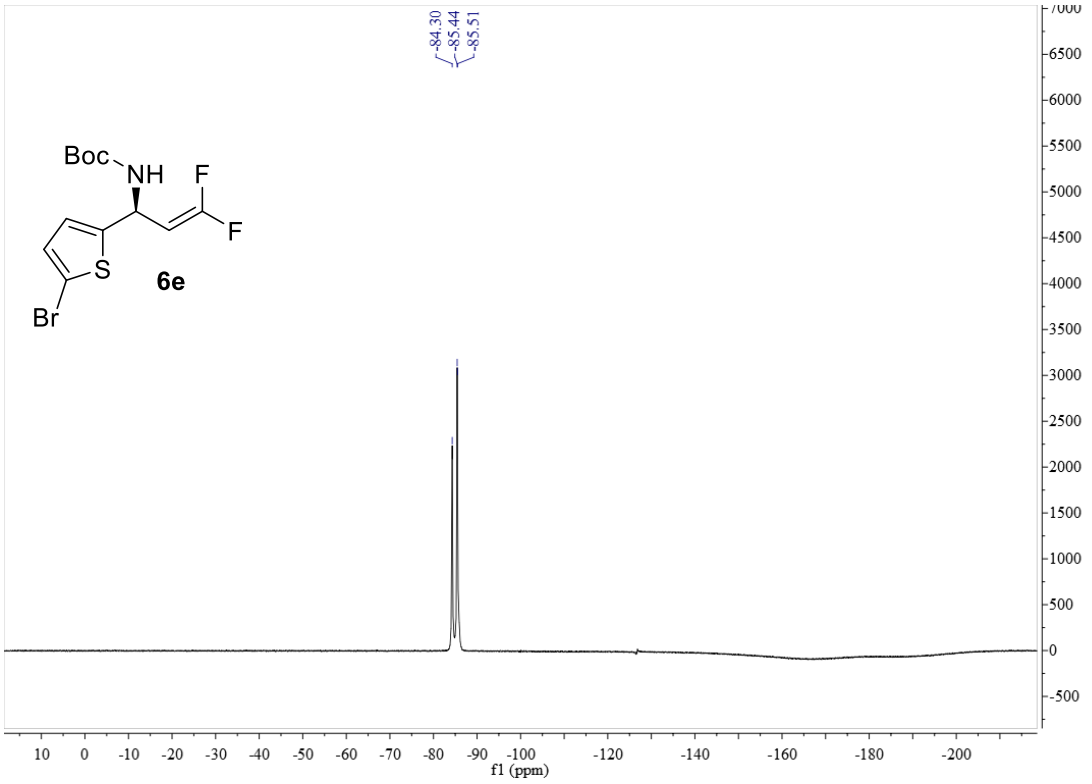
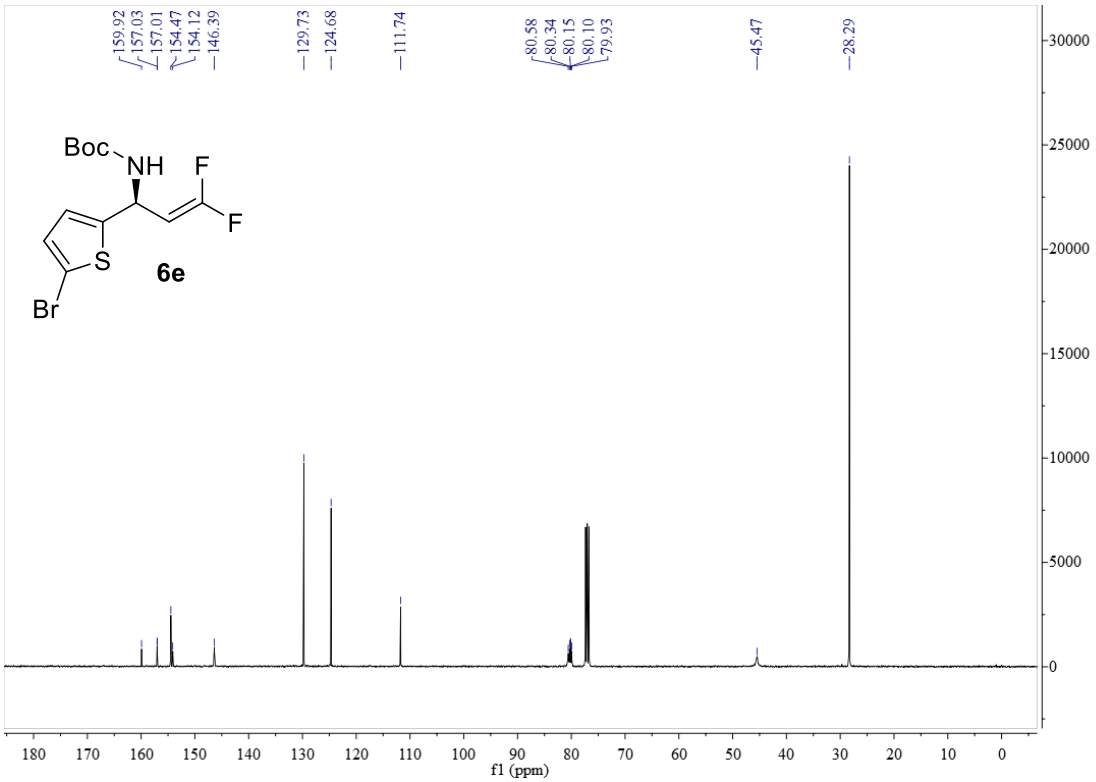
-85.69
-85.78
Boc
NH
F
F
MeO2C
6d
f1 (ppm)


166.64
158.78
156.86
154.93
154.74
145.91
130.12
129.66
126.15
80.59
80.46
80.44
80.32
52.10
48.97
28.29
Boc
NH
F
F
MeO2C
6d
f1 (ppm)


Boc
NH
F
F
S
Br
6e
6.89
6.88
6.70
6.70
6.69
5.57
5.04
5.02
4.57
4.57
4.55
4.54
4.51
4.51
4.49
4.48
1.45
1.00
0.98
1.00
1.06
1.01
9.09
f1 (ppm)


Boc
NH
F
F
S
Br
6e
-84.30
-85.44
-85.51
f1 (ppm)


159.92
157.03
157.01
154.47
154.12
146.39
129.73
124.68
111.74
80.58
80.34
80.15
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79.93
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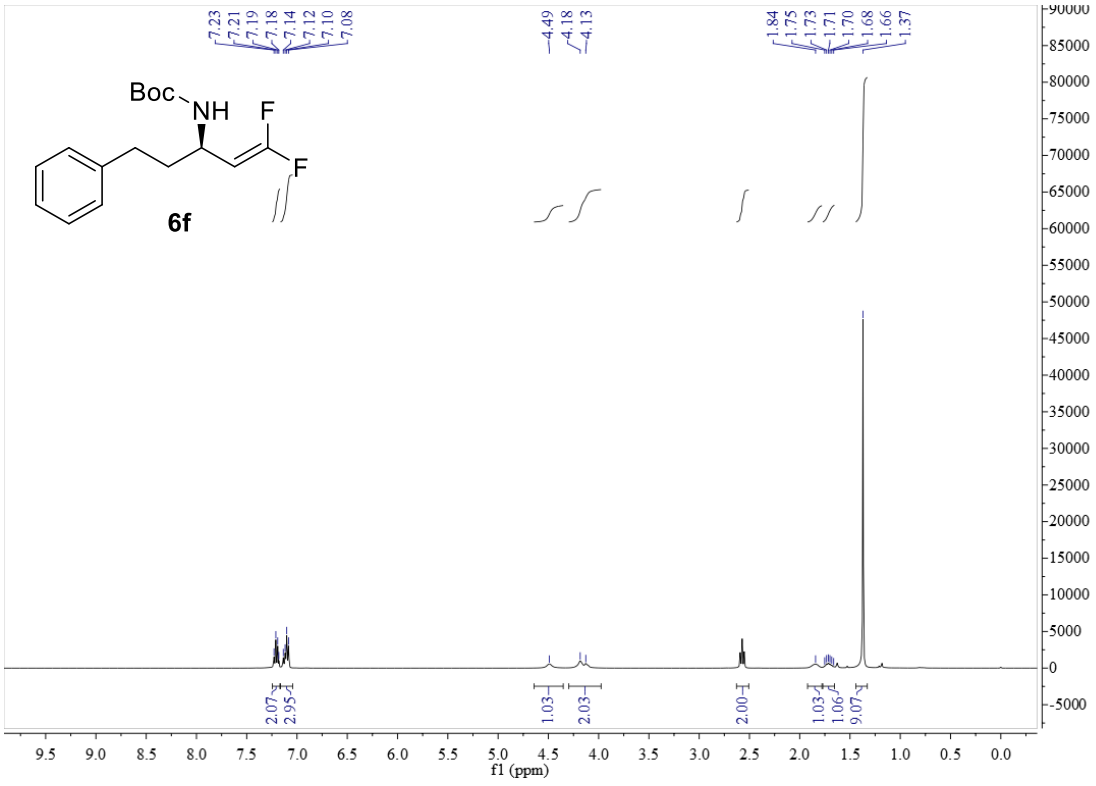
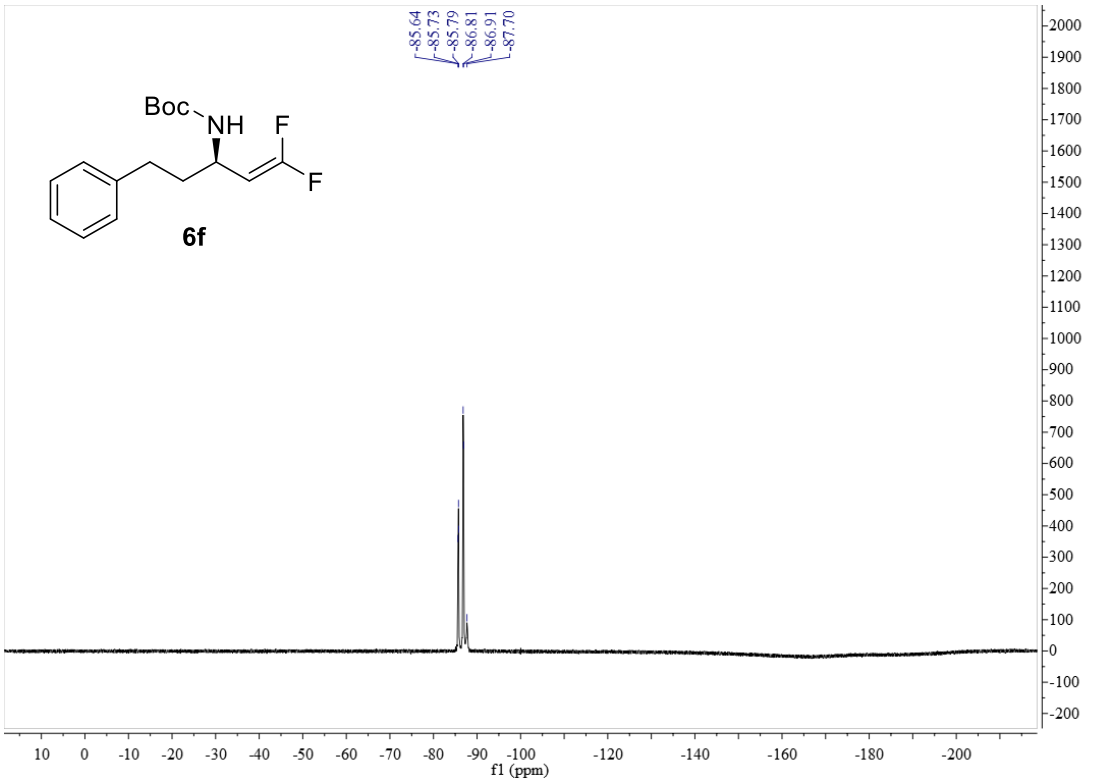
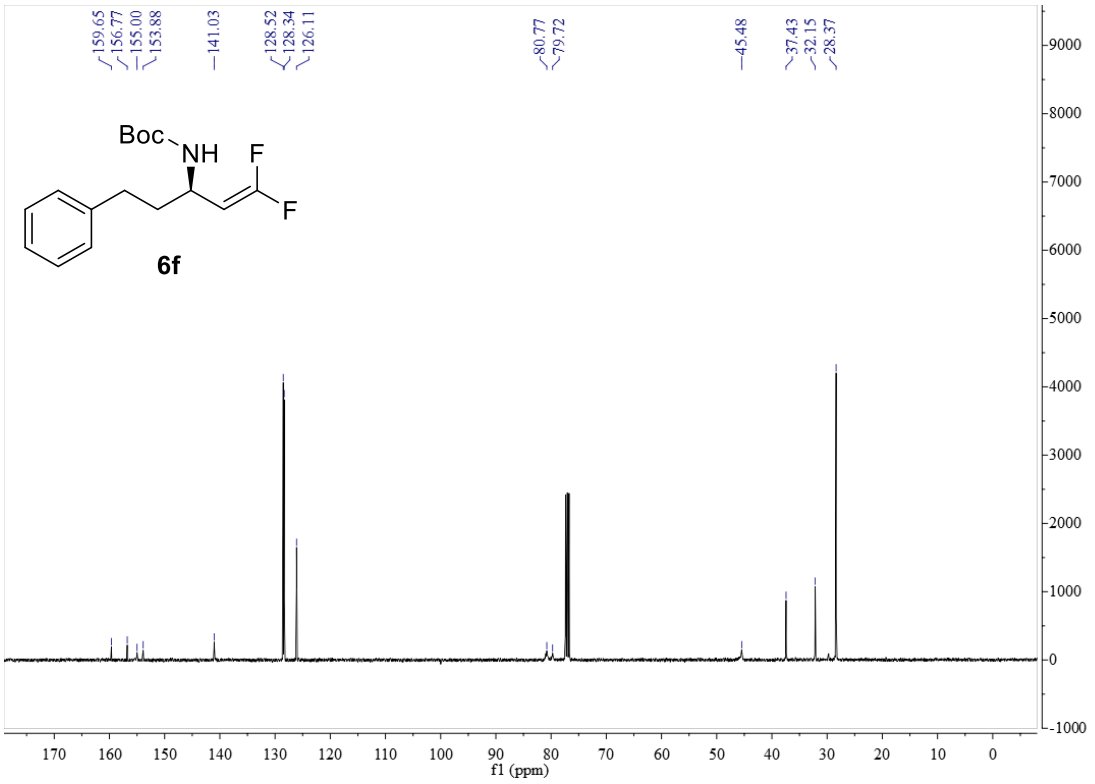
28.29
Boc
NH
F
F
S
Br
6e
f1 (ppm)


7.23
7.21
7.19
7.18
7.14
7.12
7.10
7.08
4.49
4.18
4.13
1.84
1.75
1.73
1.71
1.70
1.68
1.66
1.37
Boc
NH
F
F
6f
2.07
2.95
1.03
2.03
2.00
1.03
1.06
9.07
f1 (ppm)


-85.64
-85.73
-85.79
-86.81
-86.91
-87.70
Boc
NH
F
F
6f
f1 (ppm)


159.65
156.77
155.00
153.88
141.03
128.52
128.34
126.11
80.77
79.72
45.48
37.43
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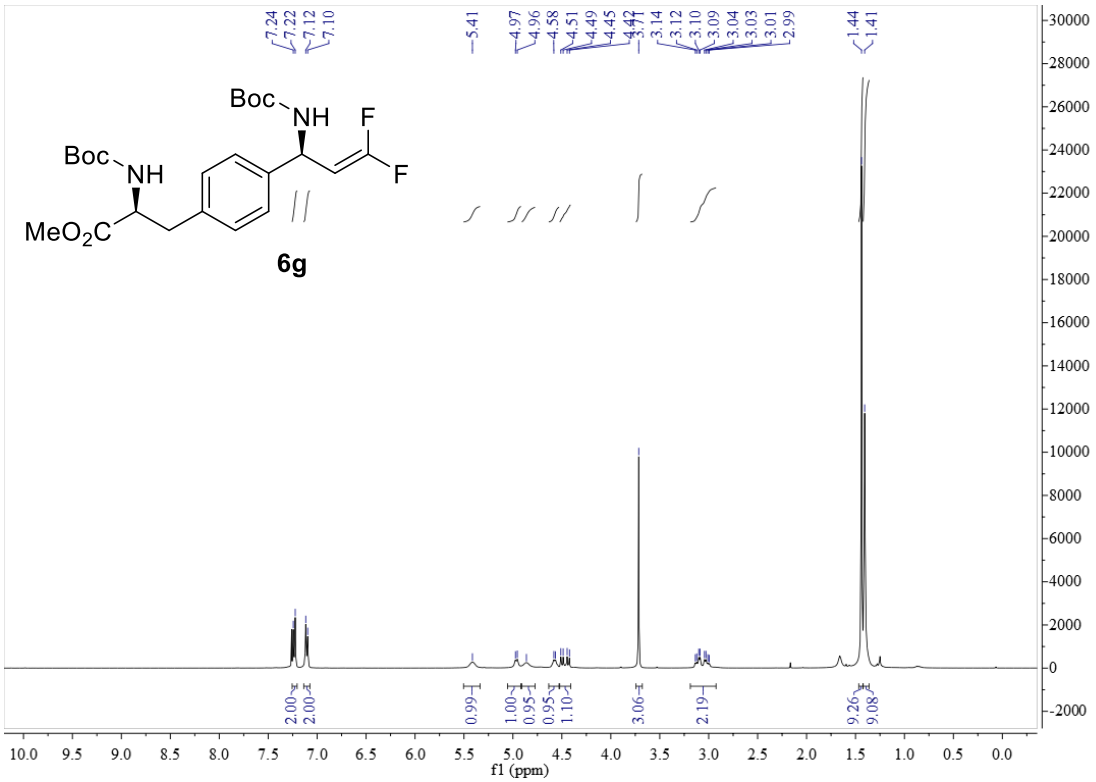
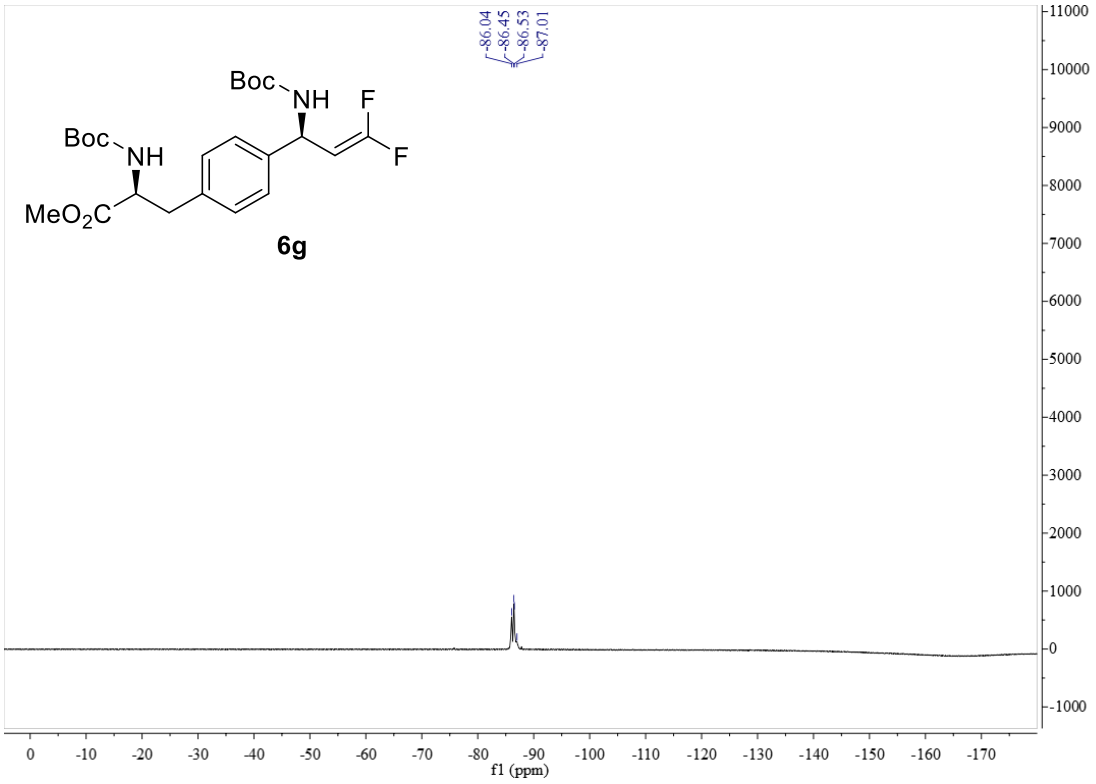
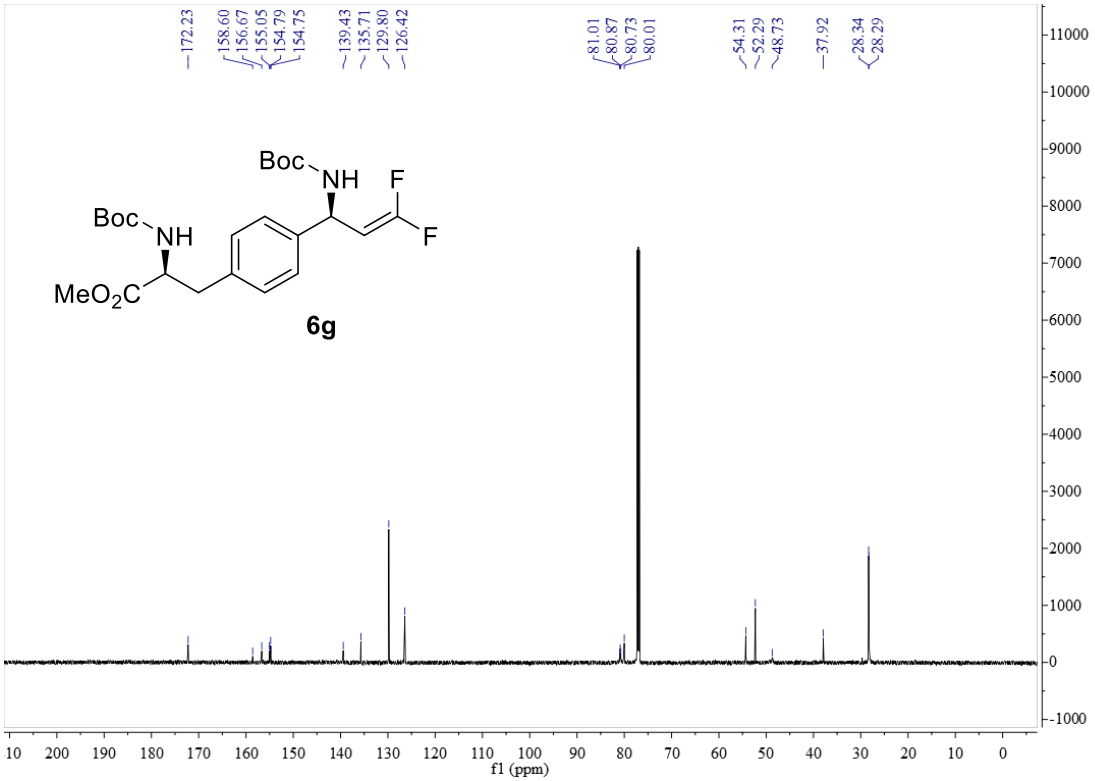
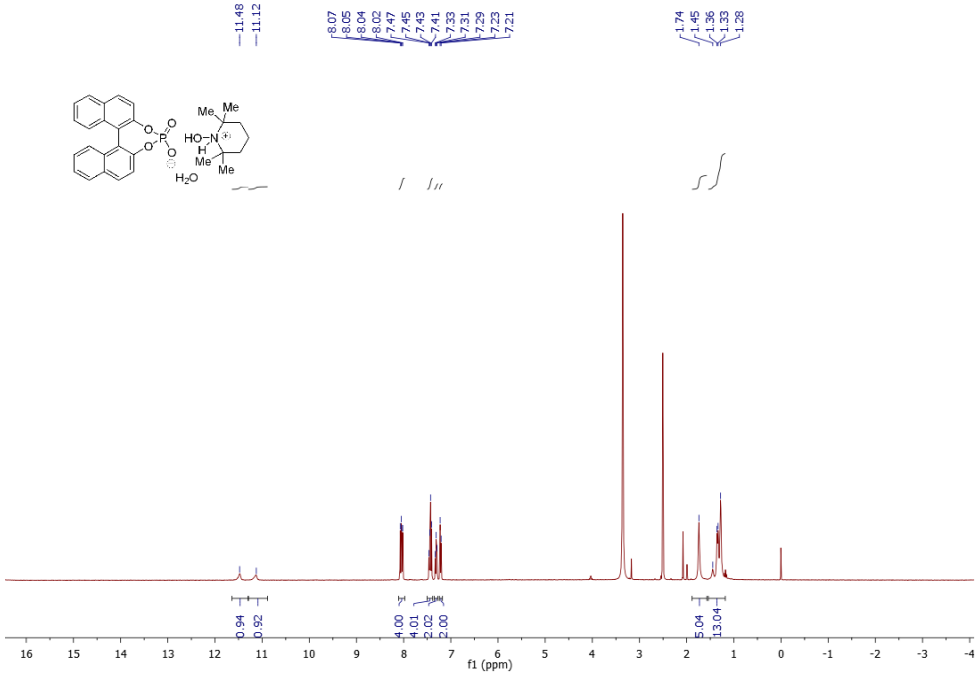
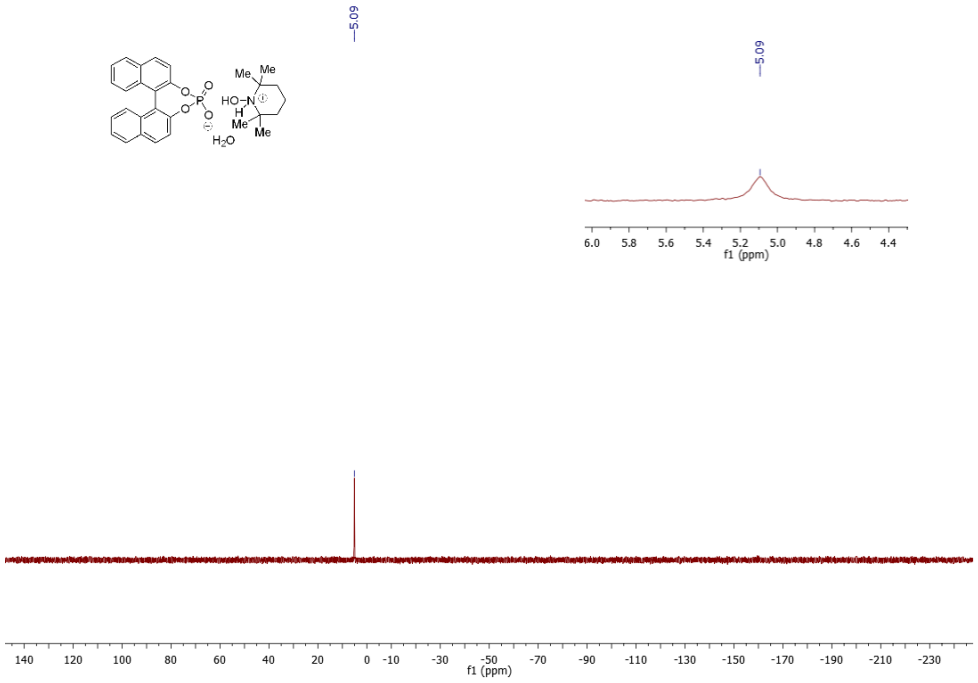
28.37
Boc
NH
F
F
6f
f1 (ppm)

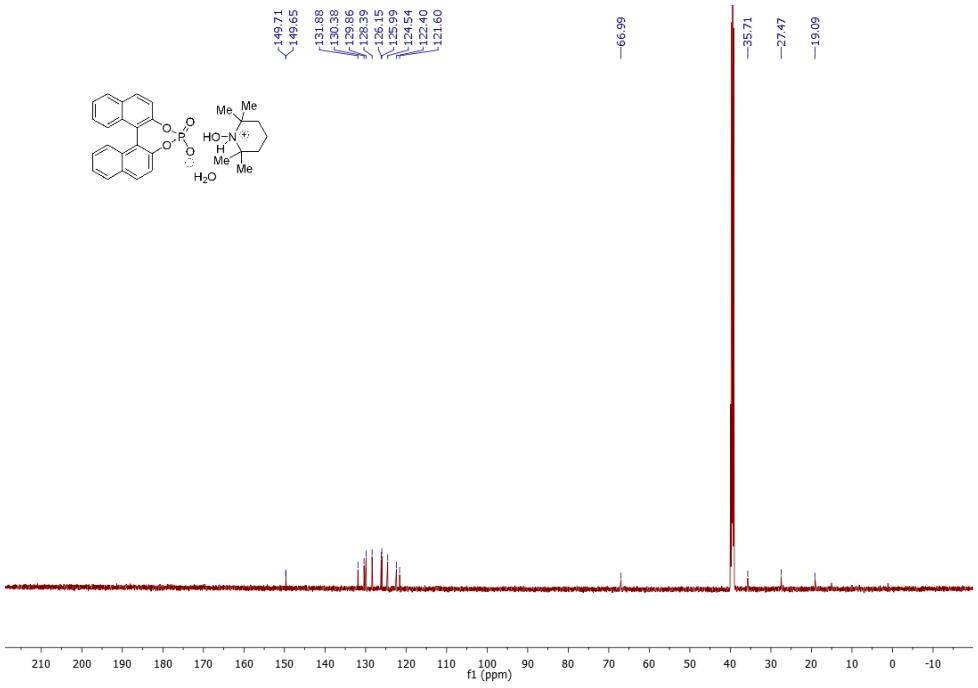

7.24
7.22
7.12
7.10
5.41
4.97
4.96
4.58
4.51
4.49
4.45
3.14
3.12
3.10
3.09
3.04
3.03
3.01
2.99
1.44
1.41
Boc
NH
F
F
Boc
NH
MeO2C
6g
2.00
2.00
0.99
1.00
0.95
0.95
1.10
3.06
2.19
9.26
9.08
f1 (ppm)


-86.04
-86.45
-86.53
-87.01
Boc
NH
F
F
Boc
NH
MeO2C
6g
f1 (ppm)

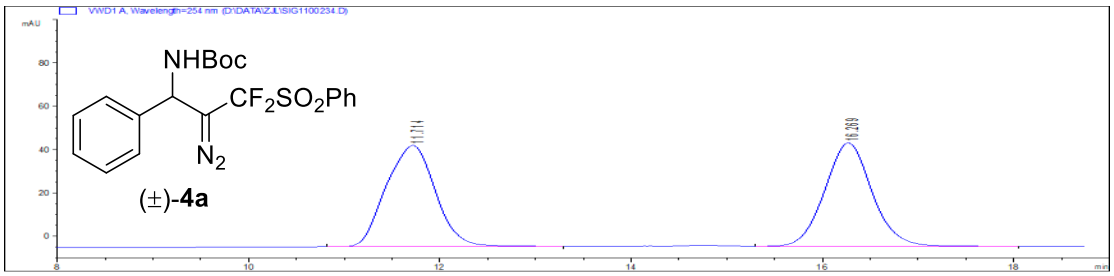

172.23
158.60
156.67
155.05
154.79
154.75
139.43
135.71
129.80
126.42
81.01
80.87
80.73
80.01
54.31
52.29
48.73
37.92
28.34
28.29
Boc
NH
F
F
Boc
NH
MeO2C
6g
f1 (ppm)


11.48
11.12
8.07
8.05
8.04
8.02
7.47
7.45
7.43
7.41
7.33
7.31
7.29
7.23
7.21
1.74
1.45
1.36
1.33
1.28
Me
Me
HO–N
H
Me
Me
H2O
0.94
0.92
4.00
4.01
2.02
2.00
5.04
13.04
f1 (ppm)

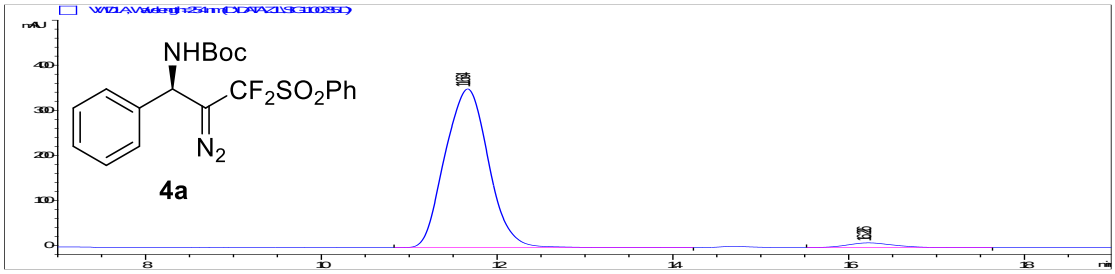

5.09
5.09
Me
Me
HO–N
H
Me
Me
H_2O
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4
f1 (ppm)
140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)


149.71
149.65
131.88
130.38
129.86
128.39
126.15
125.99
124.54
122.40
121.60
66.99
35.71
27.47
19.09
Me
Me
HO–N
H
Me
Me
H_2O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

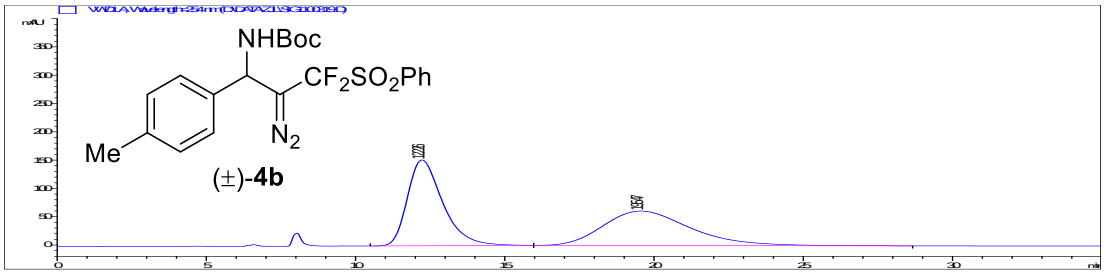
4. HPLC Charts of the related compounds



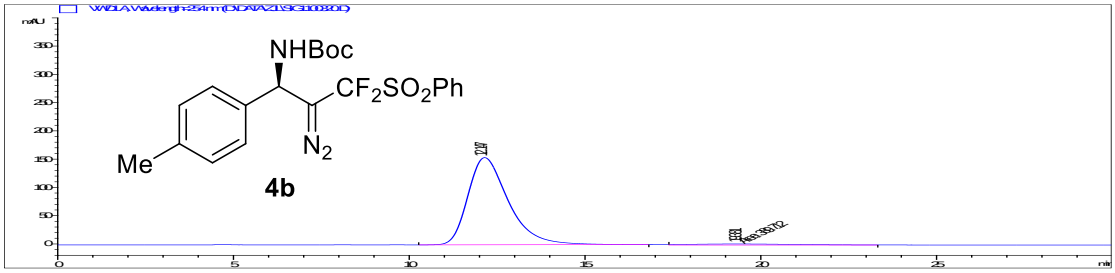
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	11.714	1665.5	46.6	0.5973	1.101	50.512
2	16.269	1631.7	47.6	0.5195	0.957	49.488



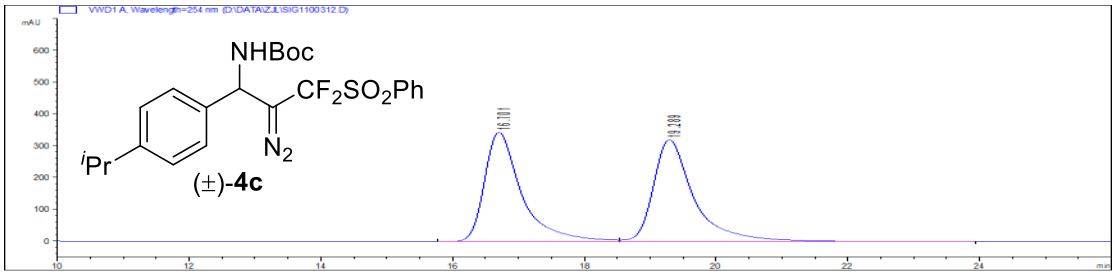
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	11.664	12053.7	351.9	0.5511	1.026	96.941
2	16.226	380.3	10.4	0.5449	0.8	3.059



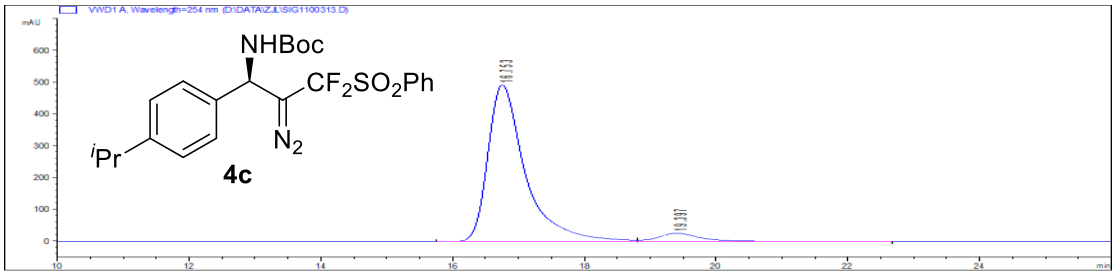
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	12.226	12466.8	151.7	1.2326	0.659	50.215
2	19.547	12360.3	60.9	2.4808	0.709	49.785



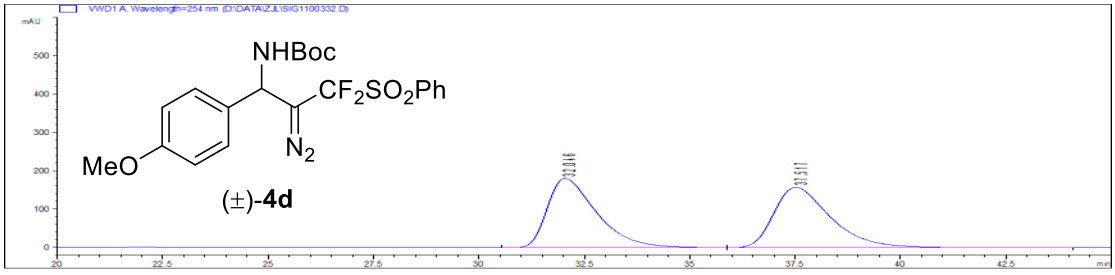
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	12.147	12374.2	154.2	1.198	0.66	96.947
2	19.381	389.7	1.9	3.4741	0.803	3.053



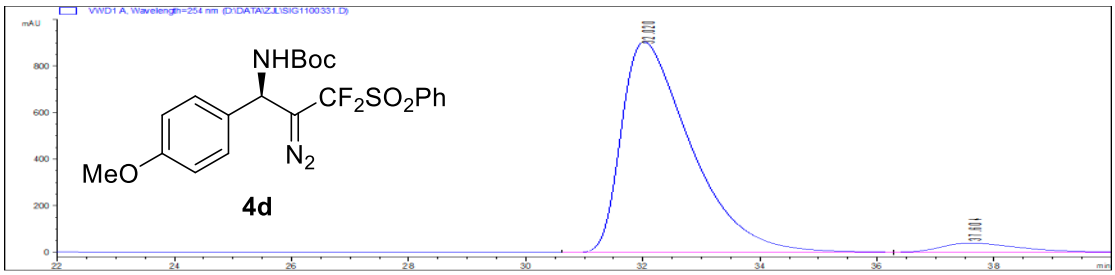
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	16.701	13466.8	343.6	0.5767	0.581	49.549
2	19.289	13711.9	320.4	0.6333	0.593	50.451



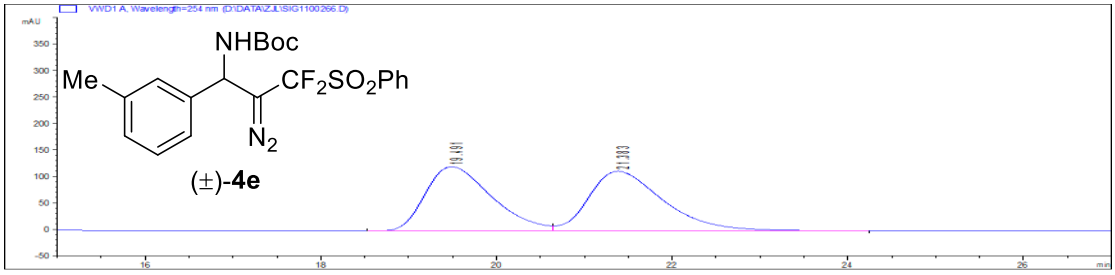
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	16.753	19526.5	493.5	0.581	0.577	94.085
2	19.397	1227.6	26.4	0.6762	0.672	5.915



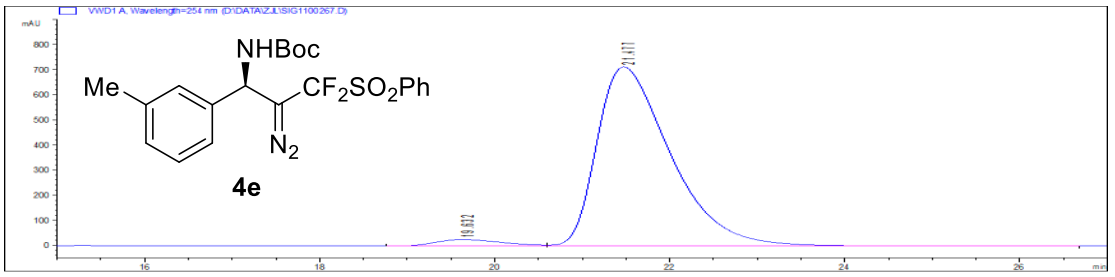
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	32.046	14712.1	180.4	1.2193	0.529	49.853
2	37.517	14798.7	157.7	1.4096	0.591	50.147



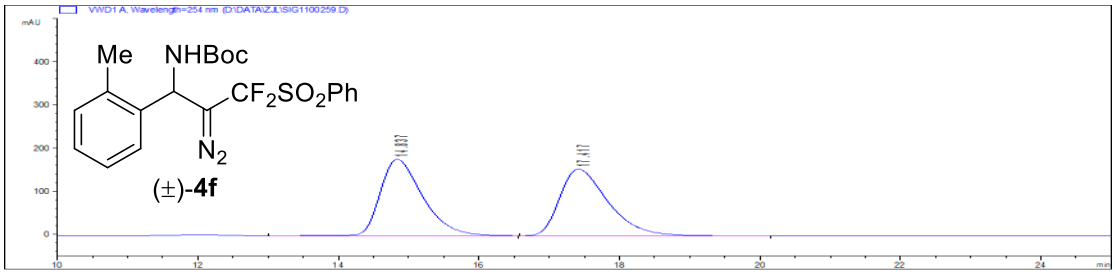
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	32.02	74734.5	905.2	1.1991	0.452	95.095
2	37.604	3854.9	40.5	1.3794	0.577	4.905



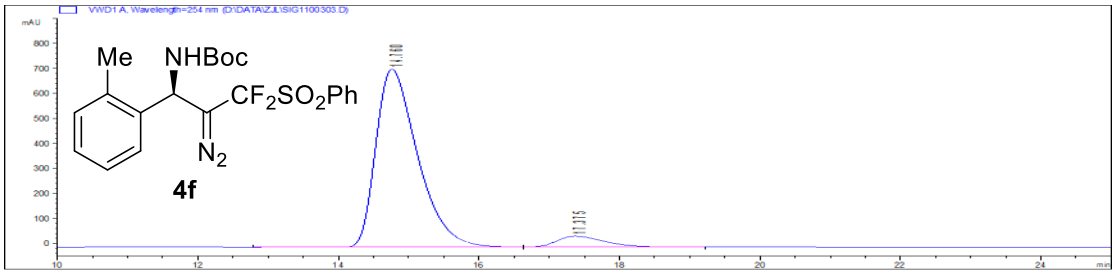
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	19.491	6348.4	121	0.7838	0.623	48.997
2	21.383	6608.2	112.4	0.8691	0.604	51.003



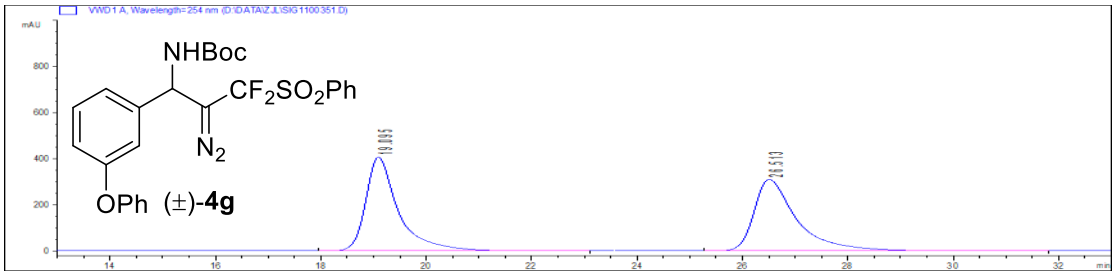
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	19.632	1326.2	25.6	0.7955	0.644	3.081
2	21.477	41720.7	713.6	0.8947	0.537	96.919



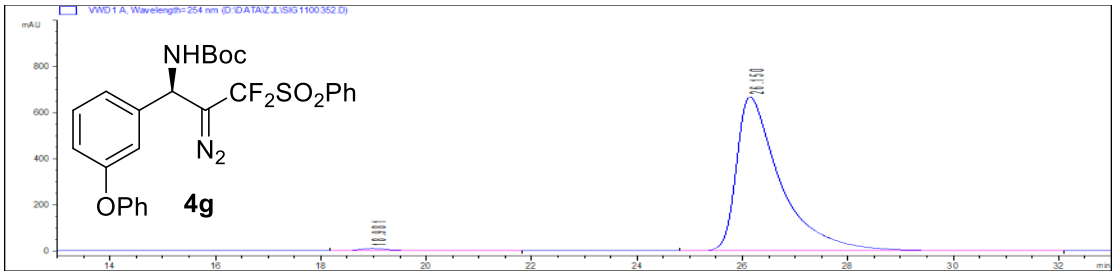
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	14.837	7446.5	177	0.6276	0.644	50.339
2	17.417	7346.2	154.3	0.7214	0.604	49.661



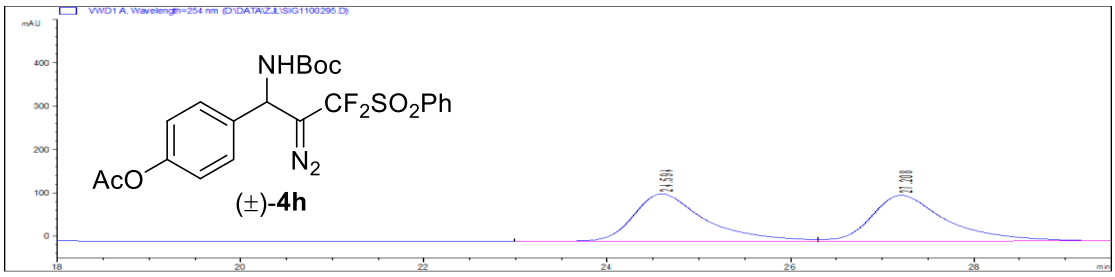
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	14.76	29381.3	711.4	0.6158	0.593	93.495
2	17.375	2044.3	43.4	0.6977	0.628	6.505



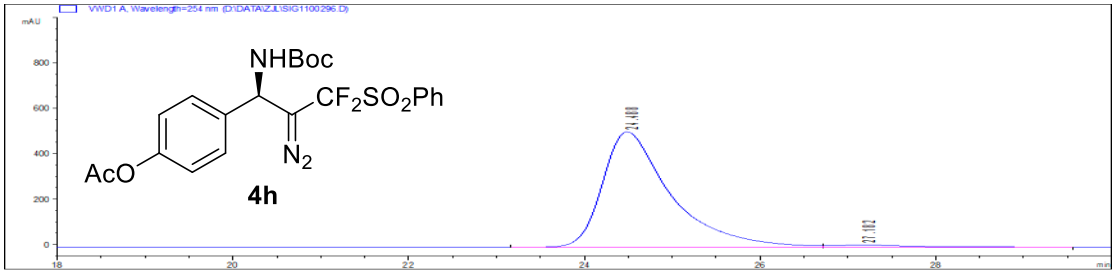
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	19.095	17444.9	405.3	0.6303	0.587	50.053
2	26.513	17407.8	309.3	0.8285	0.514	49.947



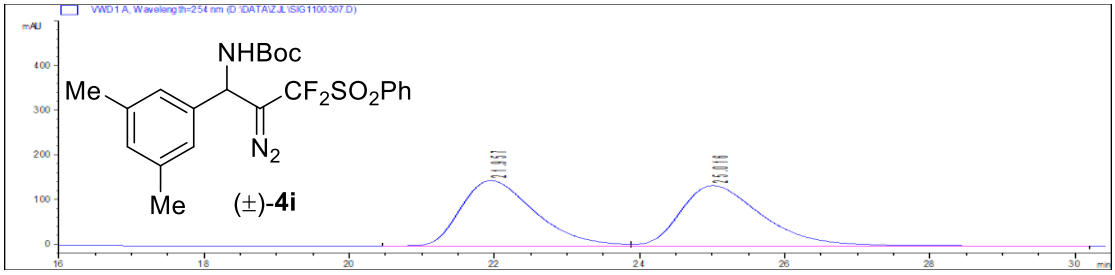
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	18.981	391.7	9.3	0.6206	0.641	1.009
2	26.15	38439.7	666.3	0.8448	0.418	98.991



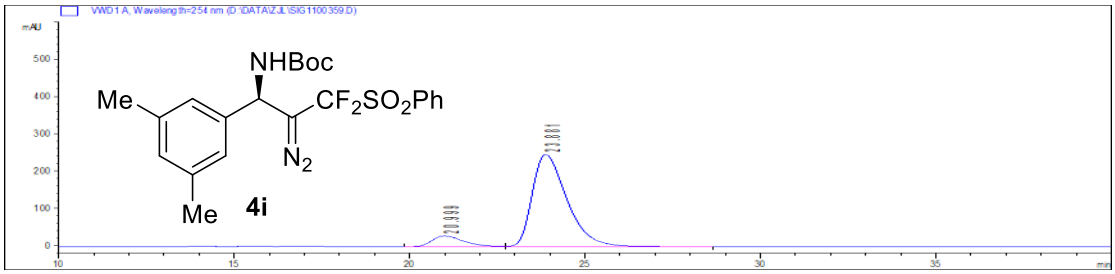
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	24.594	5870.1	108.9	0.795	0.609	49.570
2	27.208	5971.9	105.3	0.8274	0.609	50.430



Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	24.488	27435.8	507.6	0.7821	0.525	97.949
2	27.182	574.6	9.6	0.8408	0.608	2.051

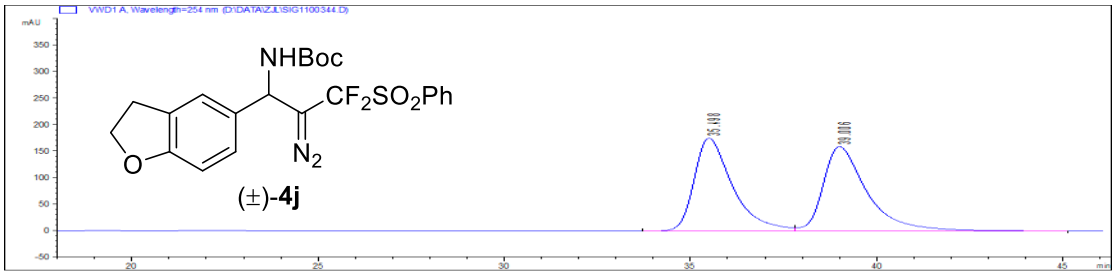


Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	21.957	10291.7	146.2	1.0894	0.645	49.722
2	25.016	10407	134.5	1.182	0.625	50.278

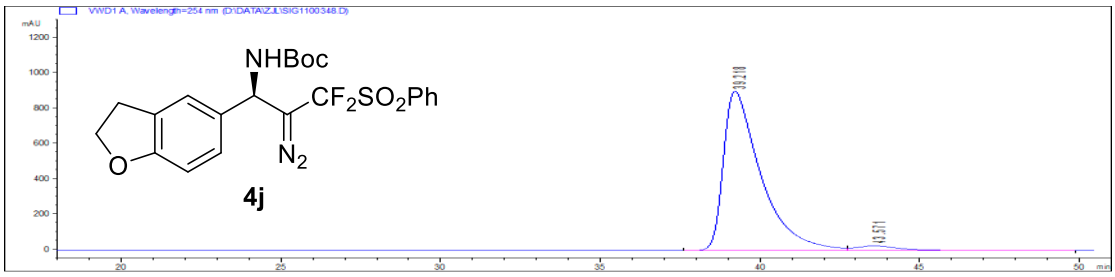


Peak	RetTime	Area	Height	Width	Symmetry	Area

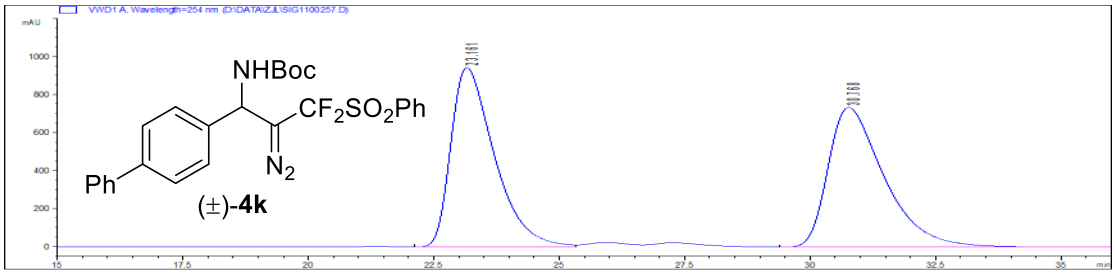
#	(min)	mAU *s	(mAU)	(min)	Factor	(%)
1	20.999	1730.8	28.1	0.9517	0.634	9.293
2	23.881	16894.5	246.8	1.0548	0.601	90.707



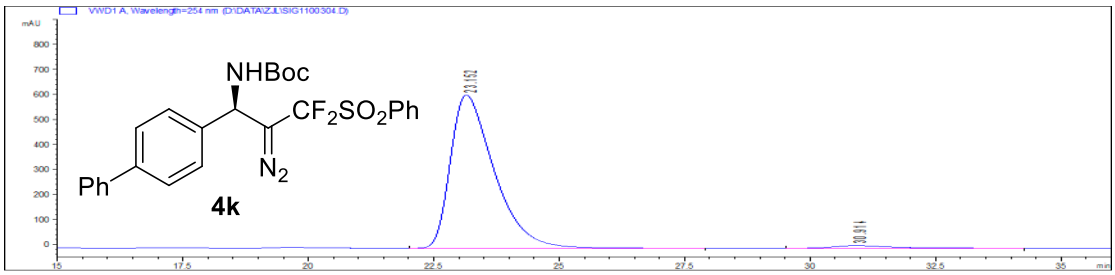
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	35.498	12590.6	175.3	1.0738	0.586	49.195
2	39.006	13002.5	159.1	1.2212	0.557	50.805



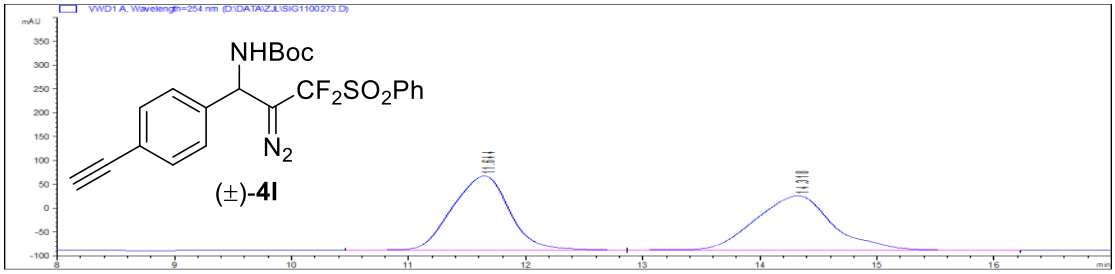
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	39.218	73664.3	902.7	1.2054	0.414	96.611
2	43.571	2583.7	26.9	1.3984	0.608	3.389



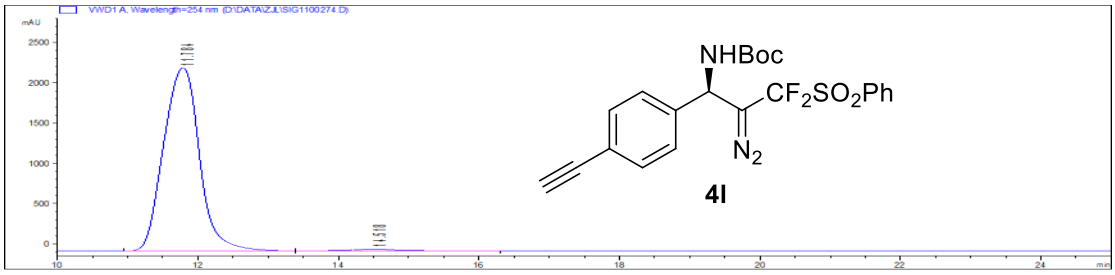
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	23.161	56838.9	943.4	0.9155	0.543	49.914
2	30.768	57034.3	734.5	1.168	0.542	50.086



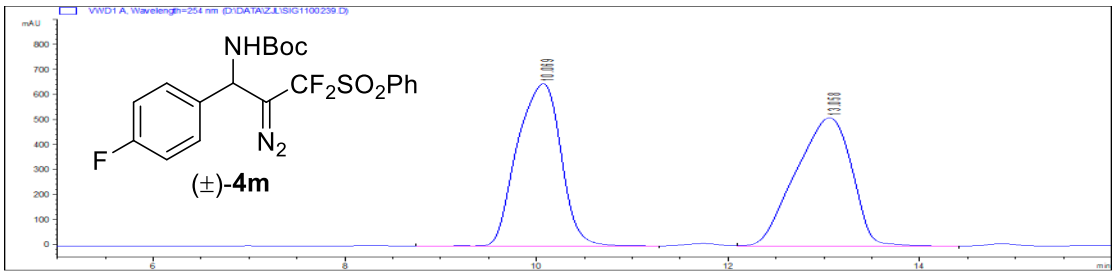
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	23.152	37055	613.1	0.874	0.542	97.872
2	30.914	805.5	10.4	1.0401	0.586	2.128



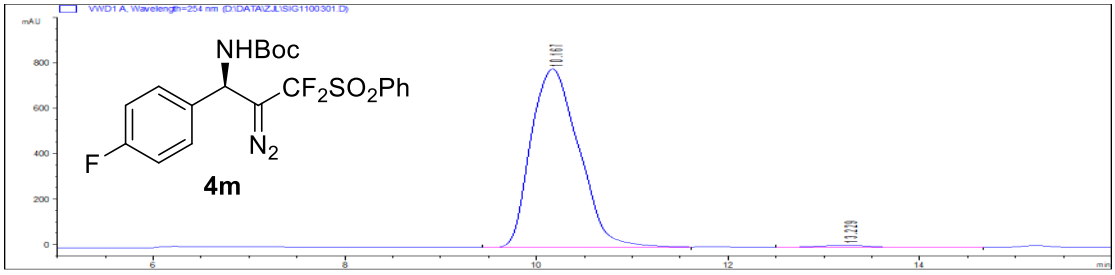
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	11.644	5356.8	156.1	0.5636	1.173	50.205
2	14.318	5313	114.4	0.7107	1.114	49.795



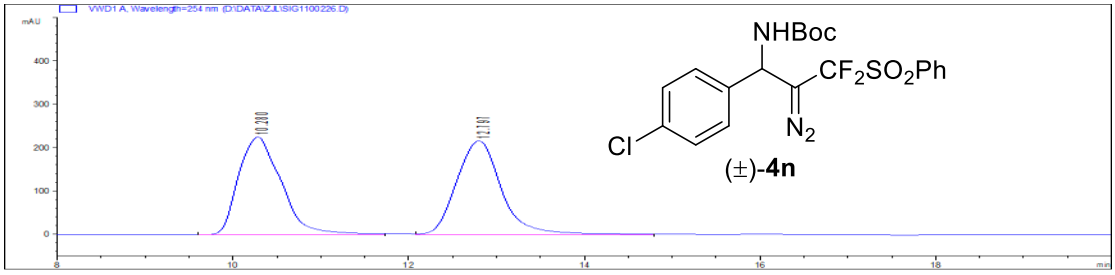
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	11.784	80471.1	2271.3	0.5648	1.083	98.603
2	14.518	1139.9	24.2	0.6838	1.129	1.397



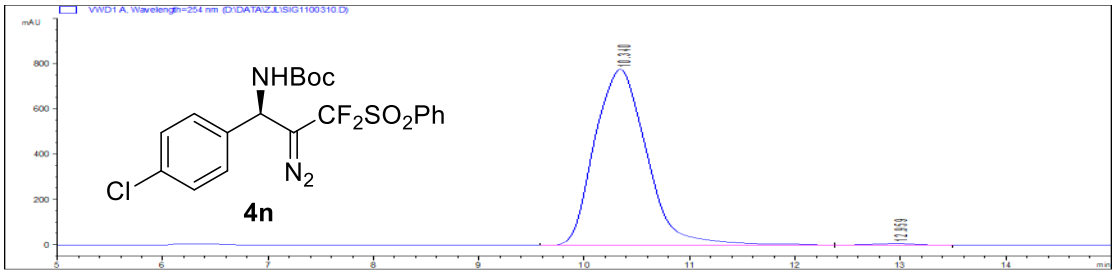
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	10.069	20559.3	648.9	0.5327	1.361	49.731
2	13.058	20781.5	512.9	0.6242	1.461	50.269



Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	10.167	27420.9	786.5	0.5378	0.77	98.671
2	13.229	369.5	9.5	0.5899	1.165	1.329

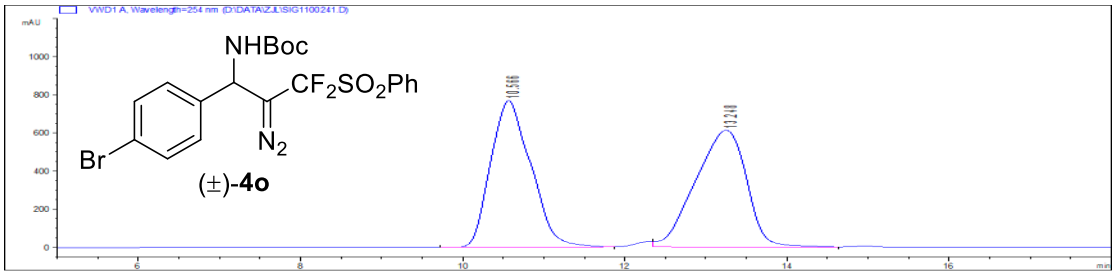


Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	10.28	7574.1	225.1	0.509	0.756	49.479
2	12.797	7733.5	216.6	0.5505	0.896	50.521

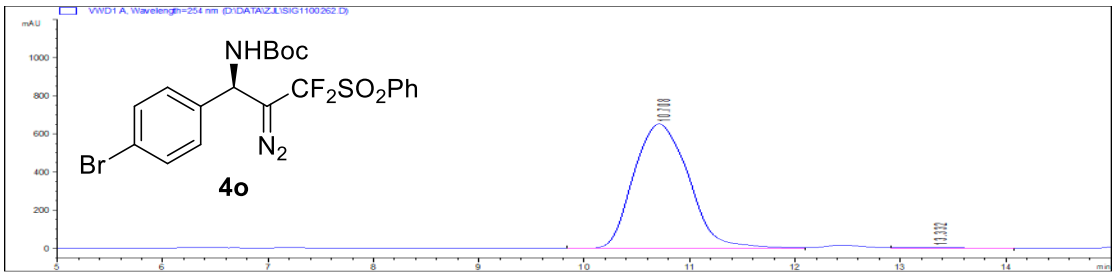


Peak	RetTime	Area	Height	Width	Symmetry	Area

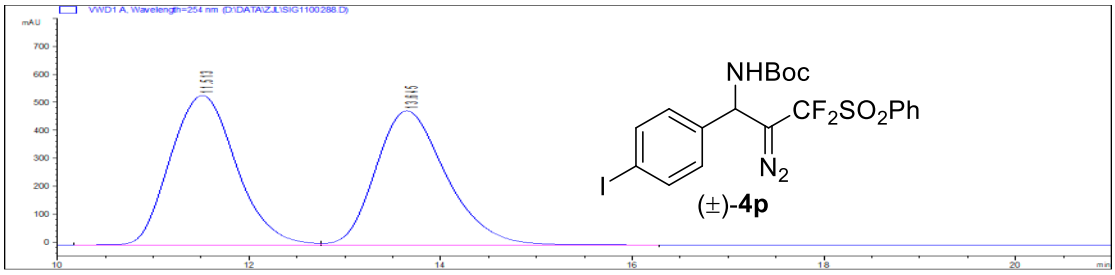
#	(min)	mAU *s	(mAU)	(min)	Factor	(%)
1	10.34	26753.4	778.1	0.5351	0.896	99.056
2	12.959	255.1	7.6	0.4988	1.294	0.944



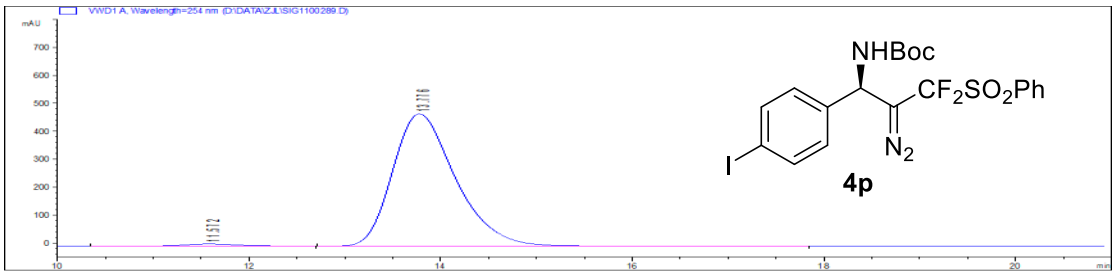
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	10.566	26457.9	768.6	0.521	0.775	49.668
2	13.248	26811.5	612.7	0.6765	1.43	50.332



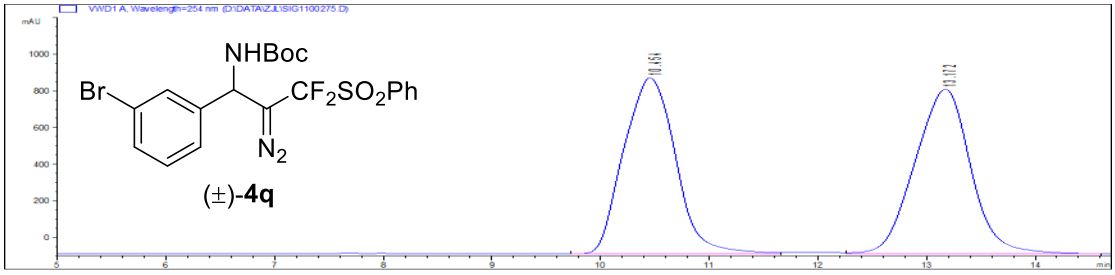
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	10.708	23639	653	0.6058	0.812	99.161
2	13.332	200.1	5.1	0.552	1.154	0.839



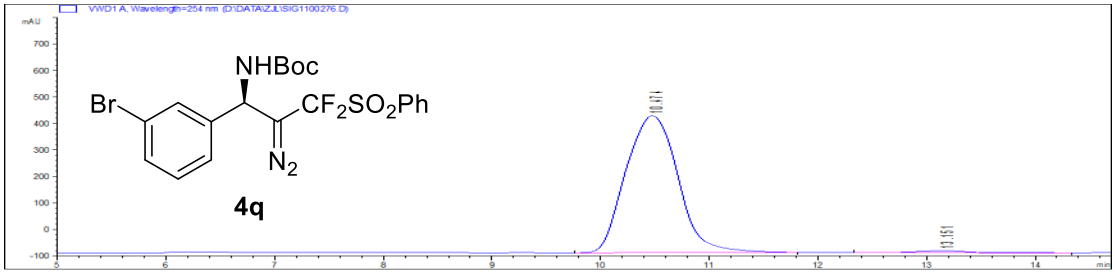
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	11.513	25448.1	534.4	0.7274	0.898	51.011
2	13.645	24438.9	479.5	0.7636	0.749	48.989



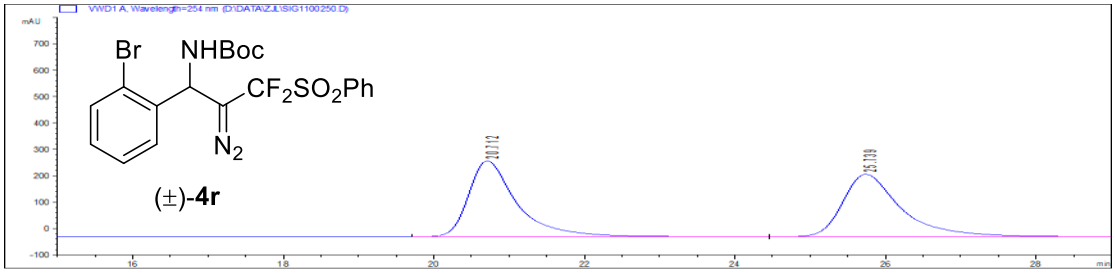
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	11.572	292.9	7.2	0.5774	0.855	1.342
2	13.776	21537.9	472.8	0.6974	0.702	98.658



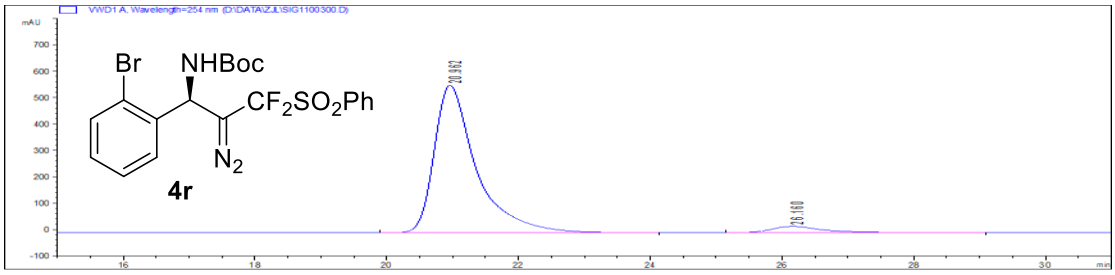
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	10.454	31726	958.9	0.5607	0.973	49.887
2	13.172	31870.3	896	0.5344	1.143	50.113



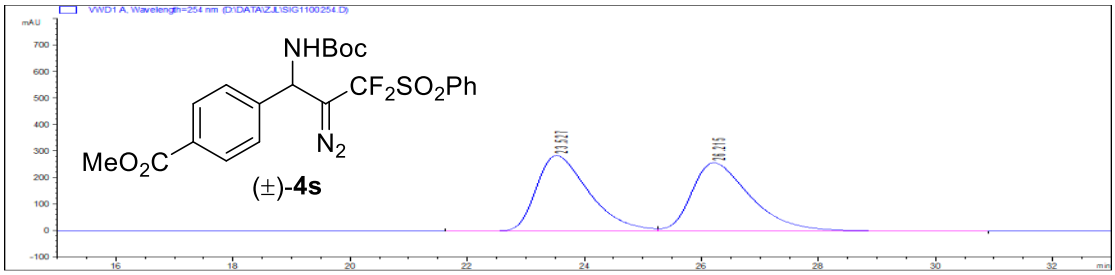
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	10.474	17174.2	516.8	0.5566	0.98	98.634
2	13.151	237.9	7.3	0.5115	1.195	1.366



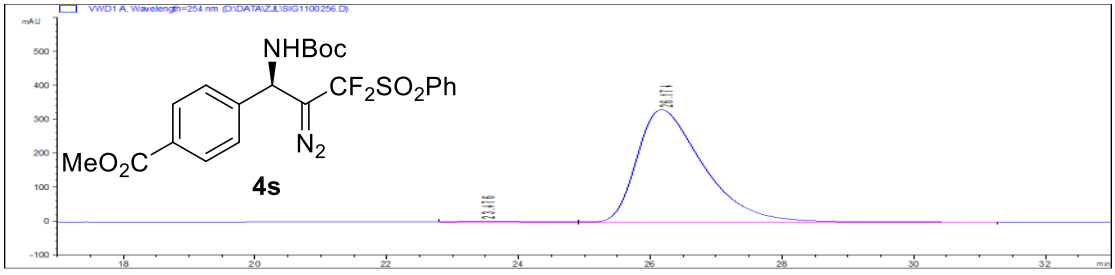
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	20.712	12774.4	287.1	0.653	0.579	50.015
2	25.739	12766.8	236.3	0.7962	0.605	49.985



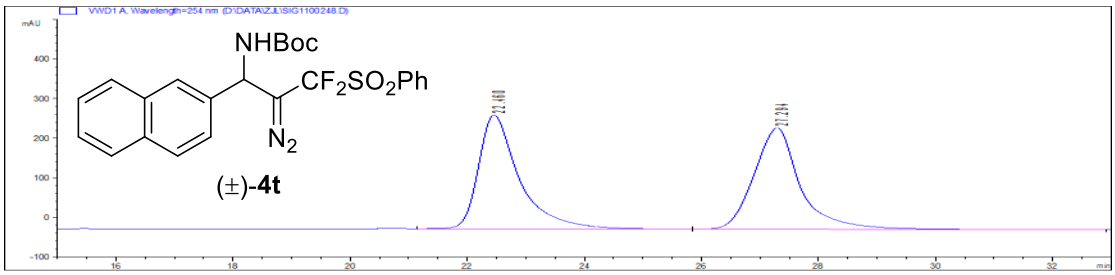
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	20.962	24634.9	557.8	0.6492	0.556	95.152
2	26.16	1255.3	23.4	0.7912	0.625	4.848



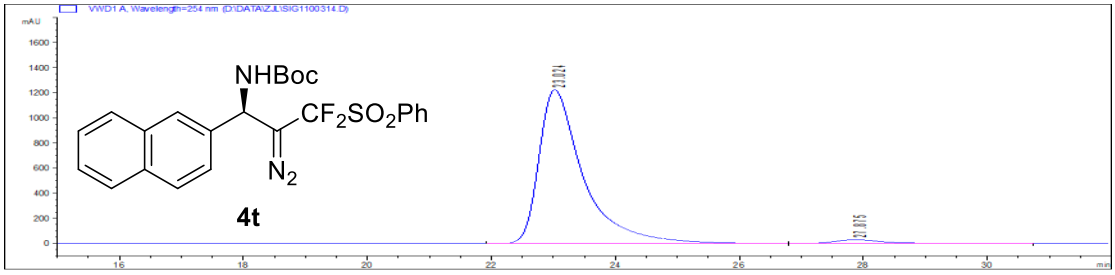
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	23.527	17838.8	285.7	0.9498	0.589	49.672
2	26.215	18074.2	258.2	1.0526	0.573	50.328



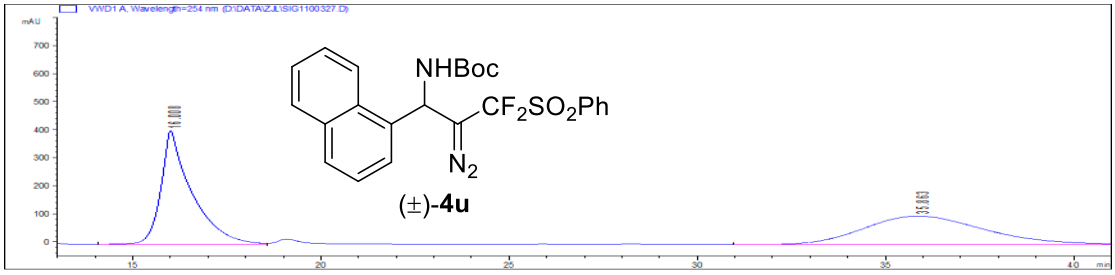
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	23.476	217.6	3.2	0.9136	0.655	0.933
2	26.174	23113.5	331.5	1.0494	0.554	99.067



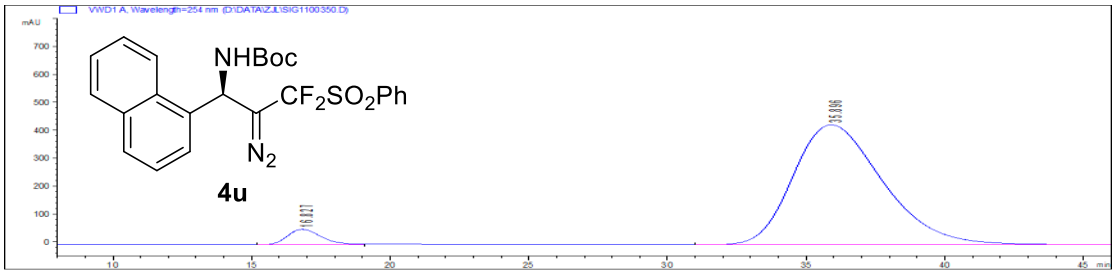
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	22.46	14061.2	288	0.7153	0.578	50.174
2	27.294	13963.8	255.3	0.7924	0.916	49.826



Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	23.024	60887.1	1225.3	0.7282	0.506	97.432
2	27.875	1604.5	29.4	0.7907	0.656	2.568

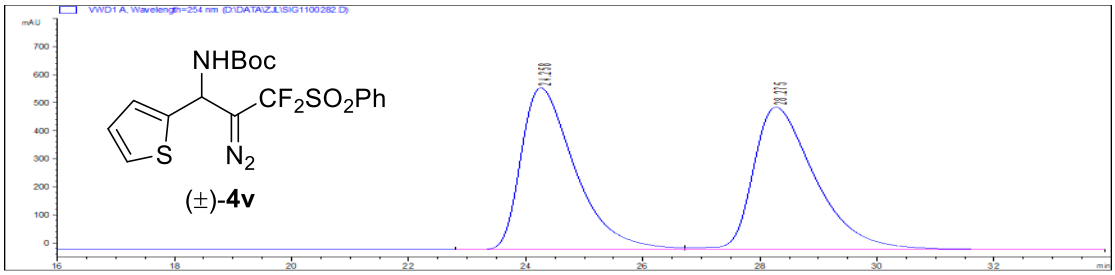


Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	16.008	23061	405.1	0.7311	0.447	50.523
2	35.863	22583.8	101.2	3.2521	0.792	49.477

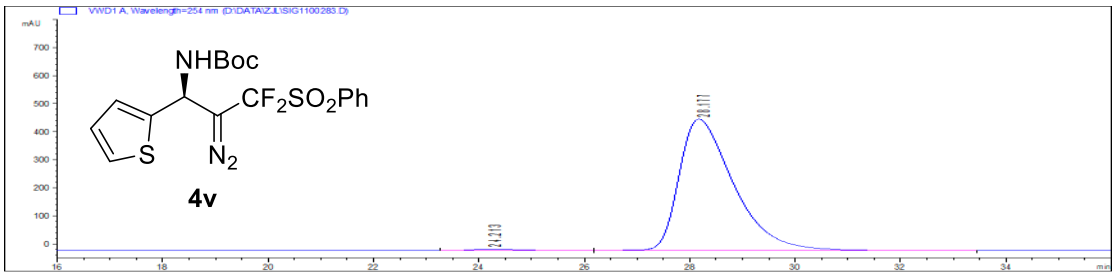


Peak	RetTime	Area	Height	Width	Symmetry	Area

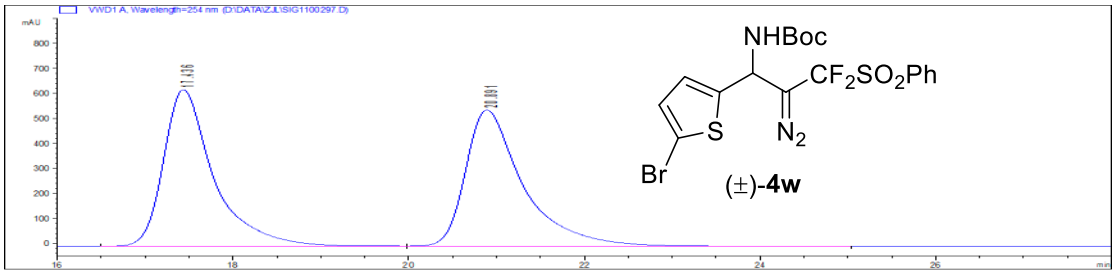
#	(min)	mAU *s	(mAU)	(min)	Factor	(%)
1	16.827	4628.6	54.8	1.3056	0.73	4.576
2	35.896	96524.6	428.7	3.3837	0.704	95.424



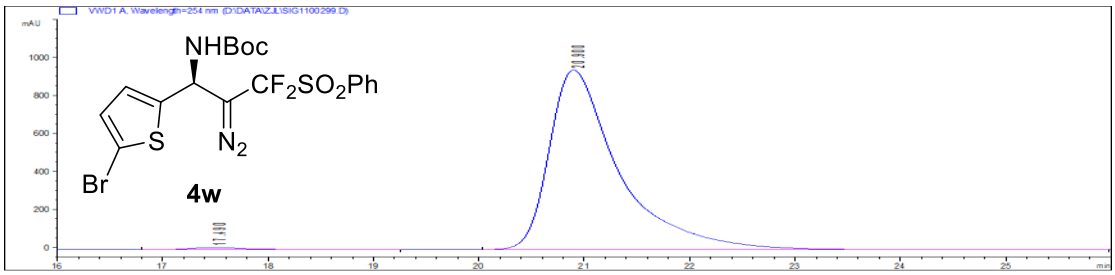
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	24.258	36843.7	576.3	0.9759	0.541	49.741
2	28.275	37227.5	507.5	1.1063	0.547	50.259



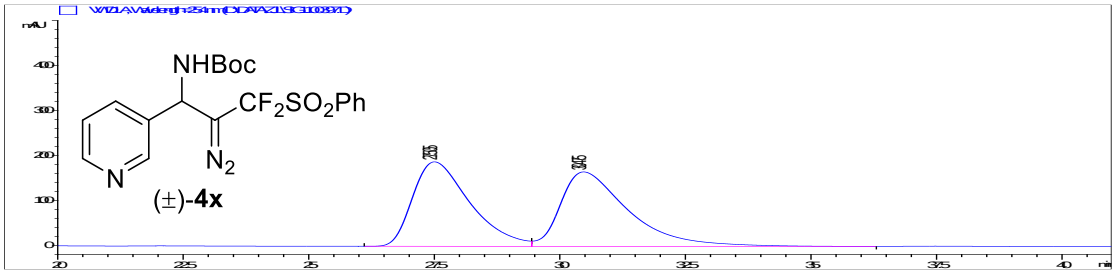
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	24.213	308.7	5	0.8293	0.595	0.908
2	28.177	33706.1	468.3	1.0406	0.543	99.092



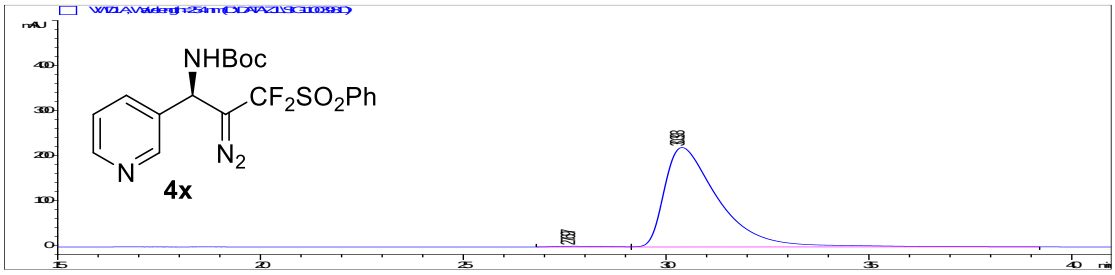
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	17.436	24728.5	625.6	0.5805	0.613	50.033
2	20.891	24696.4	543.9	0.6637	0.541	49.967



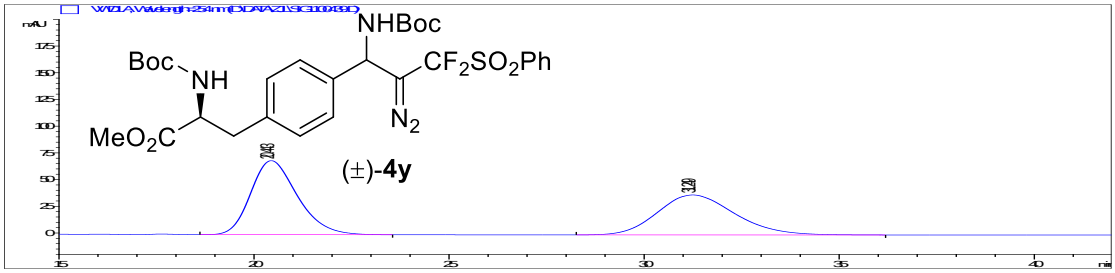
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	17.49	427.9	10.7	0.5819	0.605	0.974
2	20.90	43484	945.2	0.6678	0.497	99.026



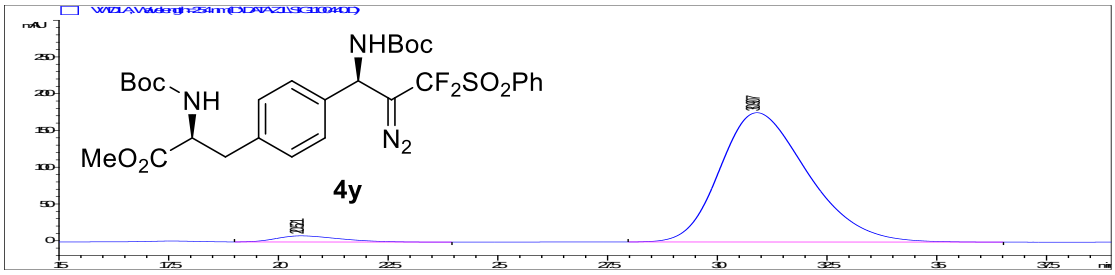
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	27.505	14862.1	187.7	1.1744	0.581	48.934
2	30.475	15509.5	165.4	1.3443	0.486	51.066



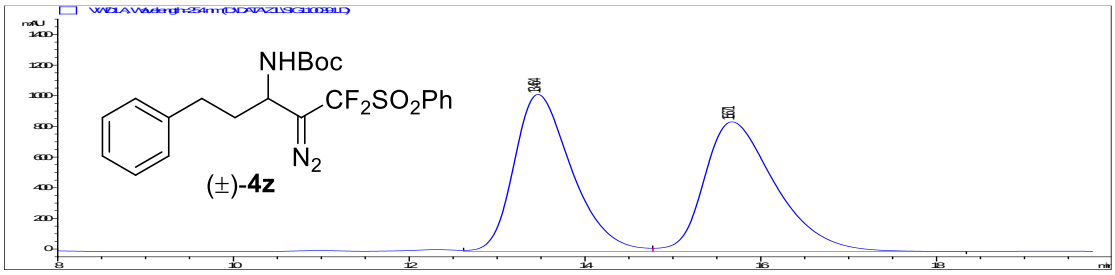
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	27.697	122.6	1.6	0.9006	0.52	0.596
2	30.393	20459.6	220.8	1.3342	0.435	99.404



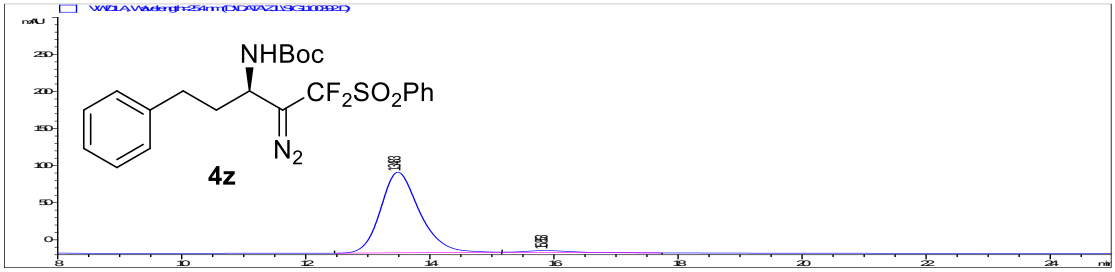
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	20.443	5769.5	69.3	1.2801	0.744	52.756
2	31.249	5166.7	37.4	1.9096	0.813	47.244



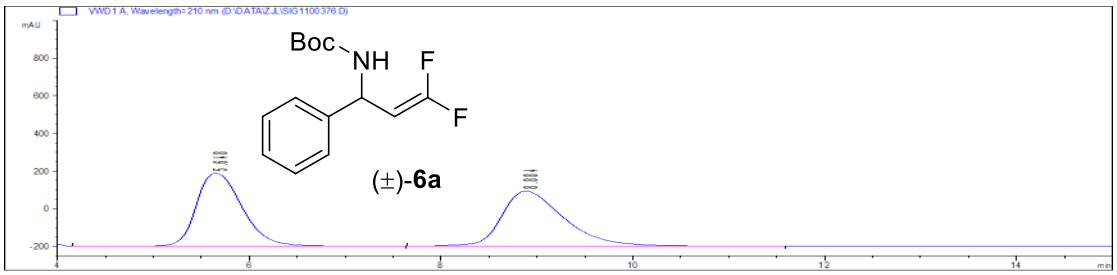
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	20.521	827.7	8.3	1.3171	0.605	3.265
2	30.907	24520.7	176	2.1091	0.701	96.735



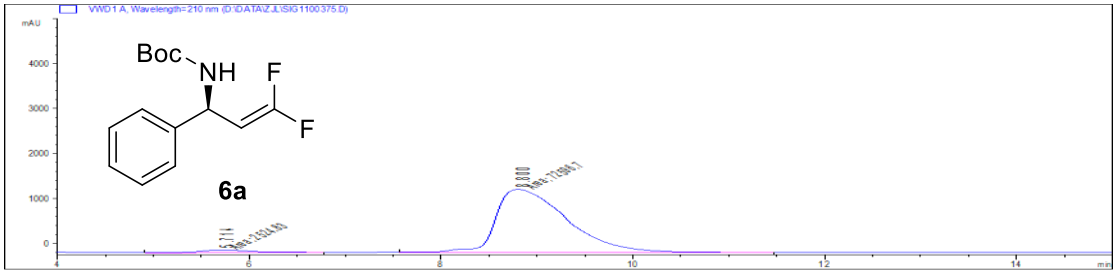
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	13.464	46565.5	1023.4	0.6881	0.673	49.591
2	15.671	47333.7	844.8	0.8488	0.609	50.409



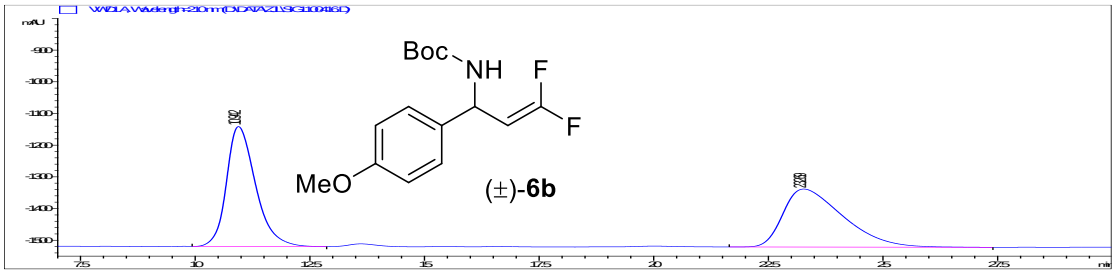
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	13.483	4719.8	108.6	0.6587	0.761	97.612
2	15.853	115.4	2.5	0.6689	0.696	2.388



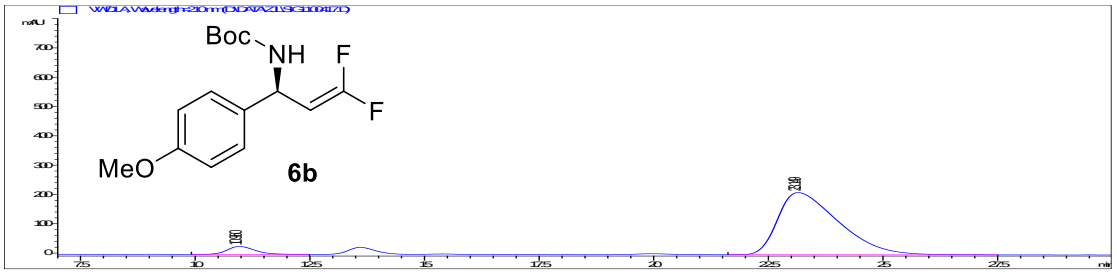
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	5.648	12732.4	386.5	0.5125	0.699	49.223
2	8.884	13134.2	291.9	0.6881	0.604	50.777



Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	5.714	2524.8	58.1	0.7248	0.768	3.361
2	8.8	72596.7	1402.1	0.863	0.453	96.639

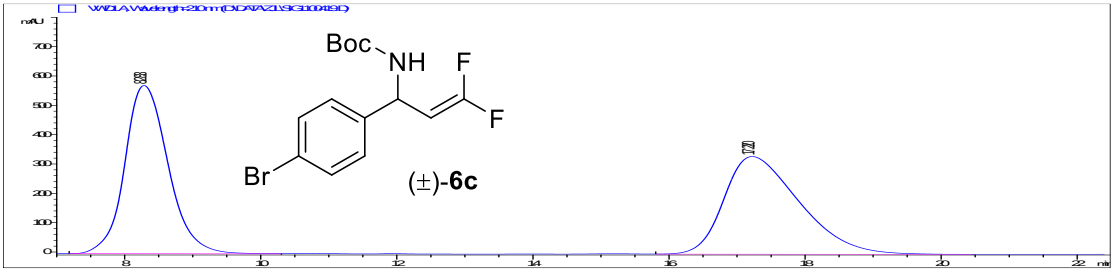


Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	10.942	16745.5	378.6	0.6732	0.672	50.170
2	23.269	16632.1	183	1.3776	0.512	49.830

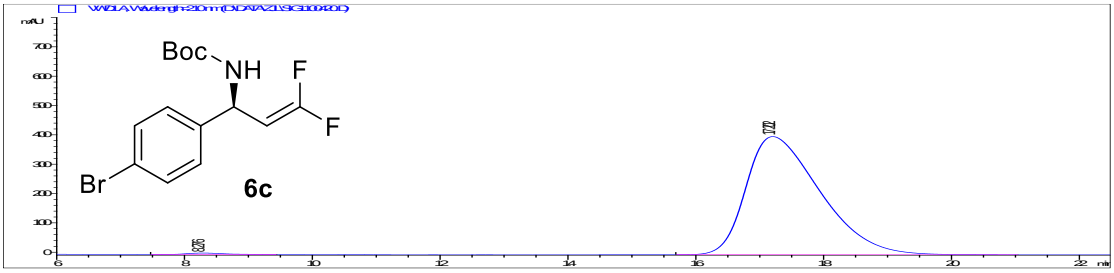


Peak	RetTime	Area	Height	Width	Symmetry	Area

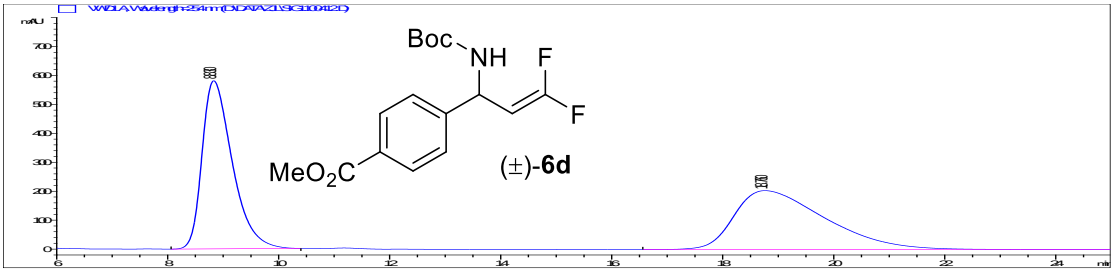
#	(min)	mAU *s	(mAU)	(min)	Factor	(%)
1	10.96	1175.9	27.3	0.6652	0.743	5.690
2	23.149	19491.5	212.3	1.3594	0.484	94.310



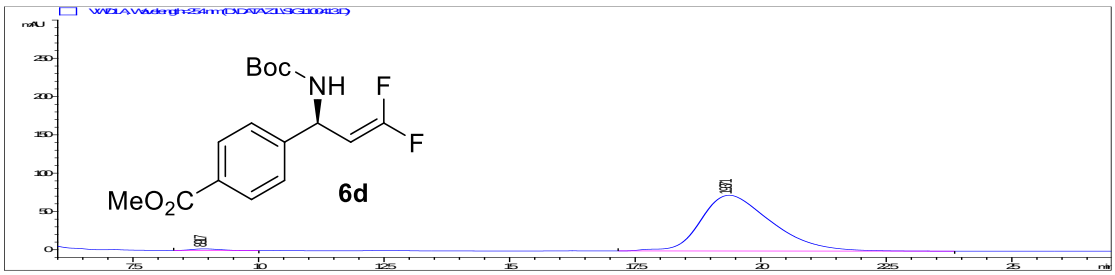
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	8.283	25413.8	573.2	0.6862	0.773	49.774
2	17.22	25644.2	332.9	1.1812	0.572	50.226



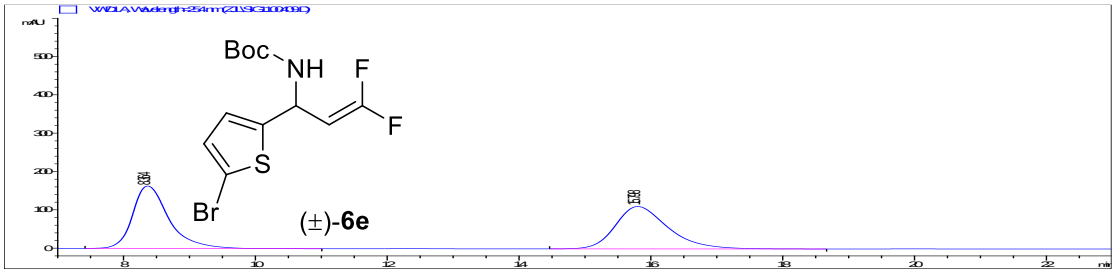
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	8.276	240.7	5.3	0.6447	0.658	0.736
2	17.202	32465.4	402.9	1.2255	0.539	99.264



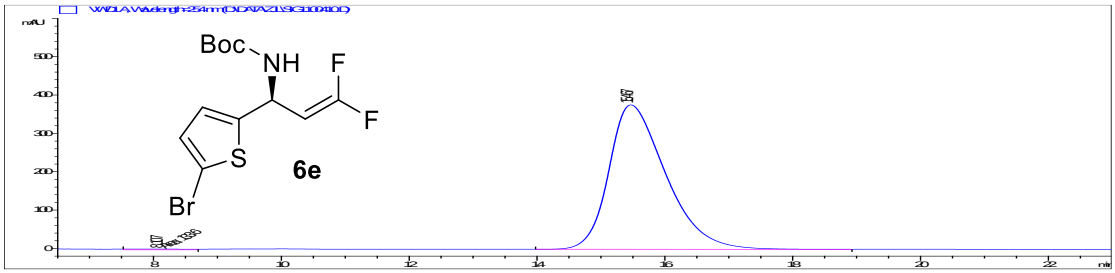
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	8.83	21912.8	580.5	0.5831	0.594	48.606
2	18.76	23169.3	203.4	1.6814	0.486	51.394



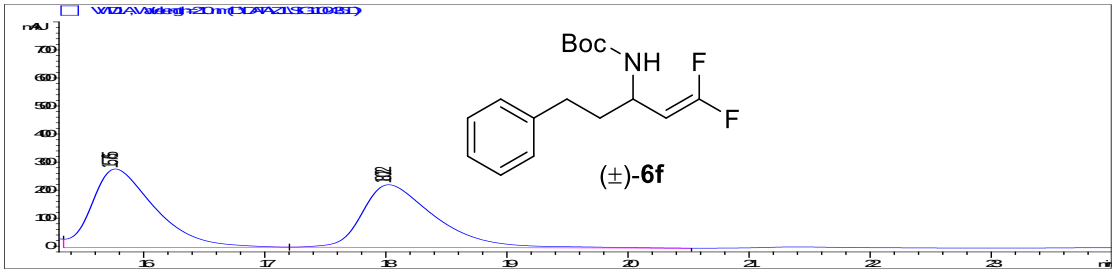
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	8.917	85.4	2.2	0.5684	0.699	1.187
2	19.371	7112.3	72.8	1.454	0.643	98.813



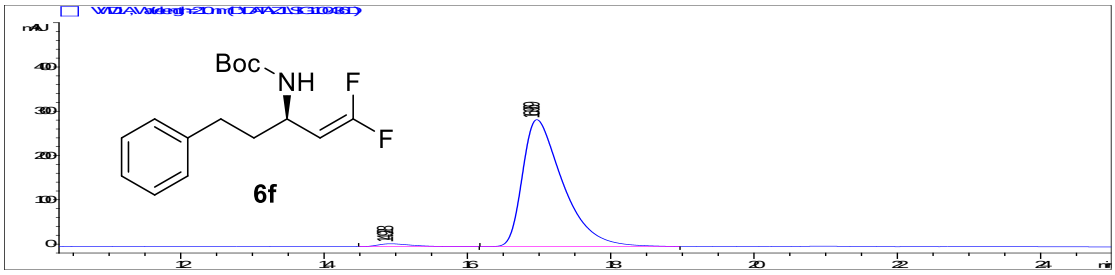
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	8.364	6272.9	163.1	0.5857	0.662	50.475
2	15.798	6154.9	110.6	0.8416	0.703	49.525



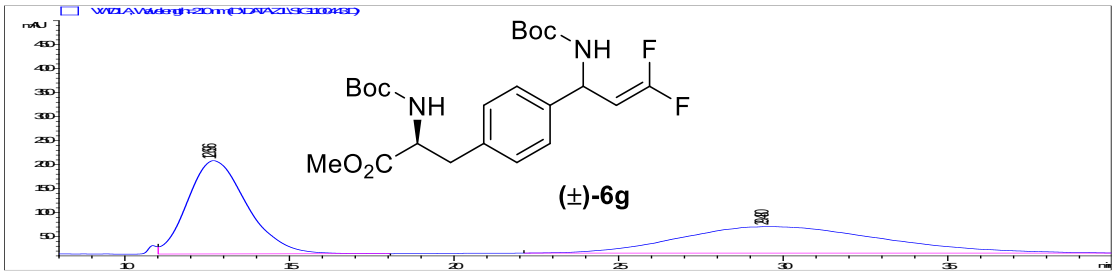
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	8.107	133.6	2	1.1274	1.024	0.571
2	15.467	23273.5	376.6	0.9306	0.604	99.429



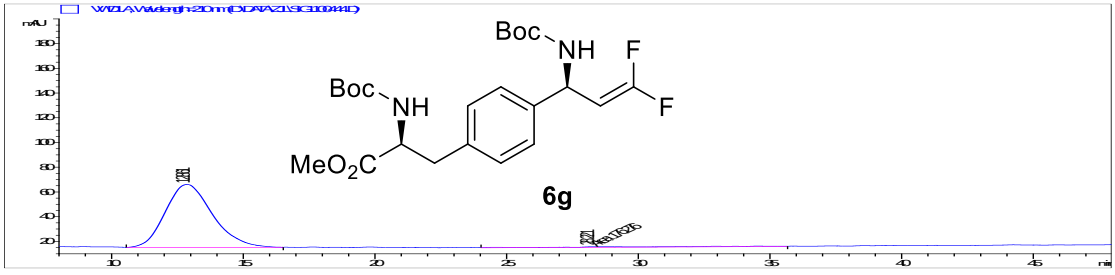
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	15.765	10126.1	280.4	0.5436	0.568	51.975
2	18.022	9356.5	223.4	0.6254	0.534	48.025



Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	14.928	197.1	6.3	0.4688	0.577	1.732
2	16.969	11185.9	286.4	0.5838	0.515	98.268



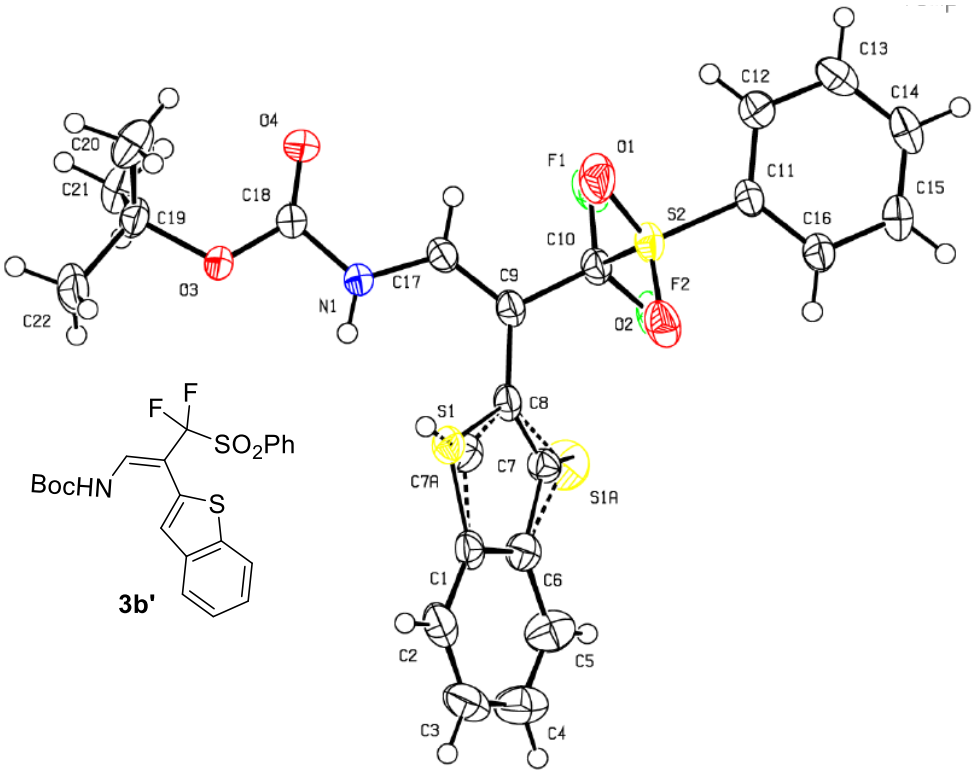
Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	12.696	24382.3	194.5	1.8904	0.737	50.709
2	29.48	23700.7	55.3	5.0193	0.731	49.291



Peak #	RetTime (min)	Area mAU *s	Height (mAU)	Width (min)	Symmetry Factor	Area (%)
1	12.861	6293.9	50.9	1.6824	0.809	97.276
2	28.221	176.3	5.1E-1	5.7269	0.38	2.724

5. X-Ray crystallographic data

The X-ray crystallographic structures for compound **3b'**. ORTEP representation with 50% probability thermal ellipsoids. Solvent is omitted for clarity. Crystal data have been deposited to CCDC, number 1852012.

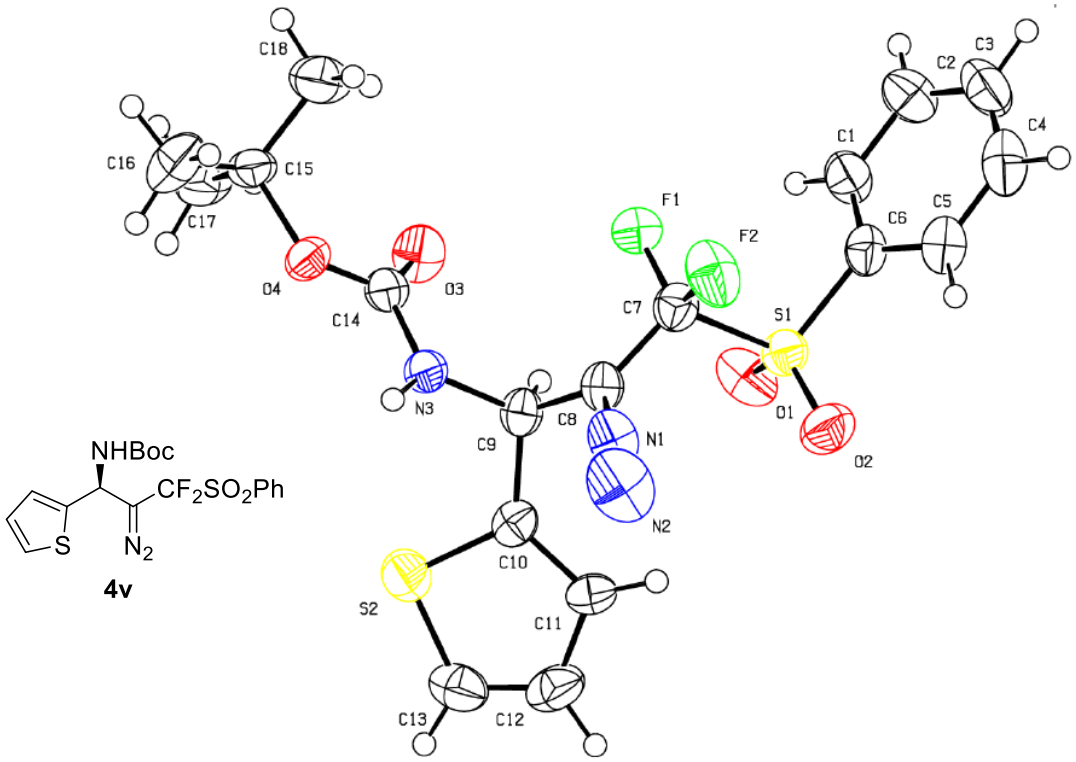


Crystal data and structure refinement for **3b'**.

Empirical formula	C_{22} H_{22} F_2 N O_4 S_2
Identification code	3b'
Formula weight	466.52
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 10.377(2) Å a= 64.87(3)°. b = 10.882(2) Å b= 86.68(3)°. c = 12.216(2) Å g = 65.47(3)°.
Volume	1124.4(5) $Å^3$
Z, Calculated density	2, 1.378 g/cm^3
Absorption coefficient	0.282 mm^{-1}

F(000)	486
Crystal size	0.210 x 0.170 x 0.020 mm^3
Theta range for data collection	1.861 to 27.477°
Limiting indices	-13<=h<=13, -14<=k<=13, -15<=l<=15
Reflections collected / unique	12915/5117 [R(int) = 0.0372]
Completeness to theta = 26.00	99.6%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5117 / 45 / 302
Goodness-of-fit on F^2	1.070
Final R indices [I>2sigma(I)]	R1 = 0.0497, wR2 = 0.1147
R indices (all data)	R1 = 0.0564, wR2 = 0.1196
Largest diff. peak and hole	0.507 and -0.563 e.$Å^{-3}$

The X-ray crystallographic structures for compound **4v**. ORTEP representation with 50% probability thermal ellipsoids. Solvent is omitted for clarity. Crystal data have been deposited to CCDC, number 1852013.

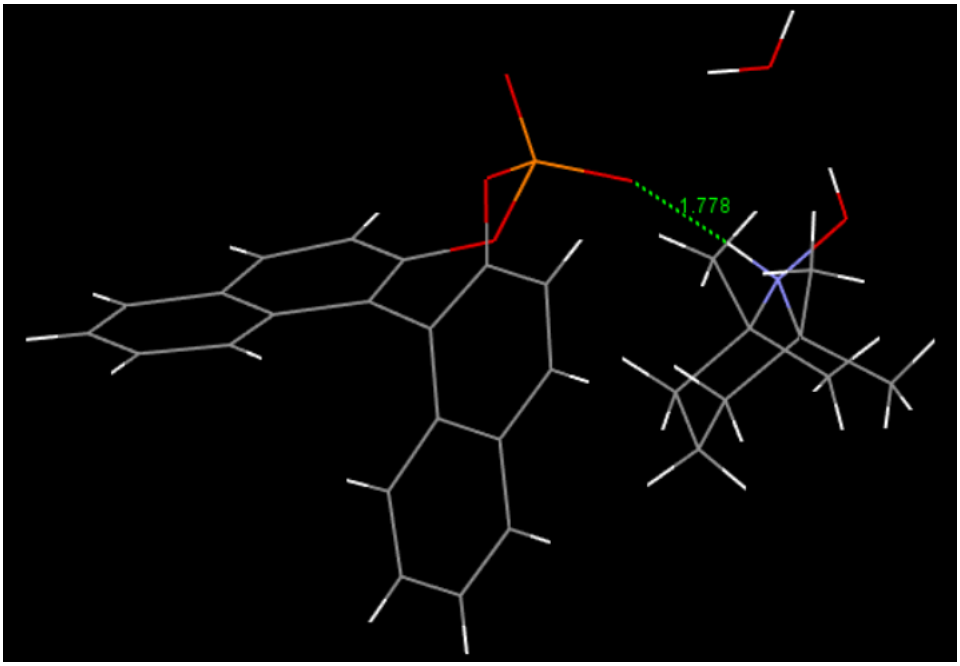


Crystal data and structure refinement for **4v**.

Empirical formula	C_{18} H_{19} F_2 N_3 O_4 S_2
Identification code	4v
Formula weight	443.48

Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Unit cell dimensions	a = 7.1566(9) Å a= 90° b = 15.0524(19) Å b= 90° c = 19.437(3) Å g = 90°
Volume	2093.8(5) $Å^3$
Z, Calculated density	4, 1.407 g/cm^3
Absorption coefficient	0.301 mm^{-1}
F(000)	920
Crystal size	0.500 x 0.100 x 0.100 mm^3
Theta range for data collection	2.902 to 30.874°
Limiting indices	-9<=h<=6, -21<=k<=21, -26<=l<=24
Reflections collected / unique	10959/5547 [R(int) = 0.0688]
Completeness to theta = 26.00	99.8%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5547 / 1 / 266
Goodness-of-fit on F^2	1.040
Final R indices [I>2sigma(I)]	R1 = 0.0721, wR2 = 0.1337
R indices (all data)	R1 = 0.1426, wR2 = 0.1787
Largest diff. peak and hole	0.446 and -0.511 $e.Å^{-3}$

The X-ray crystallographic structures for complex **BPT**. ORTEP representation with 50% probability thermal ellipsoids. Crystal data have been deposited to CCDC, number 1877090.

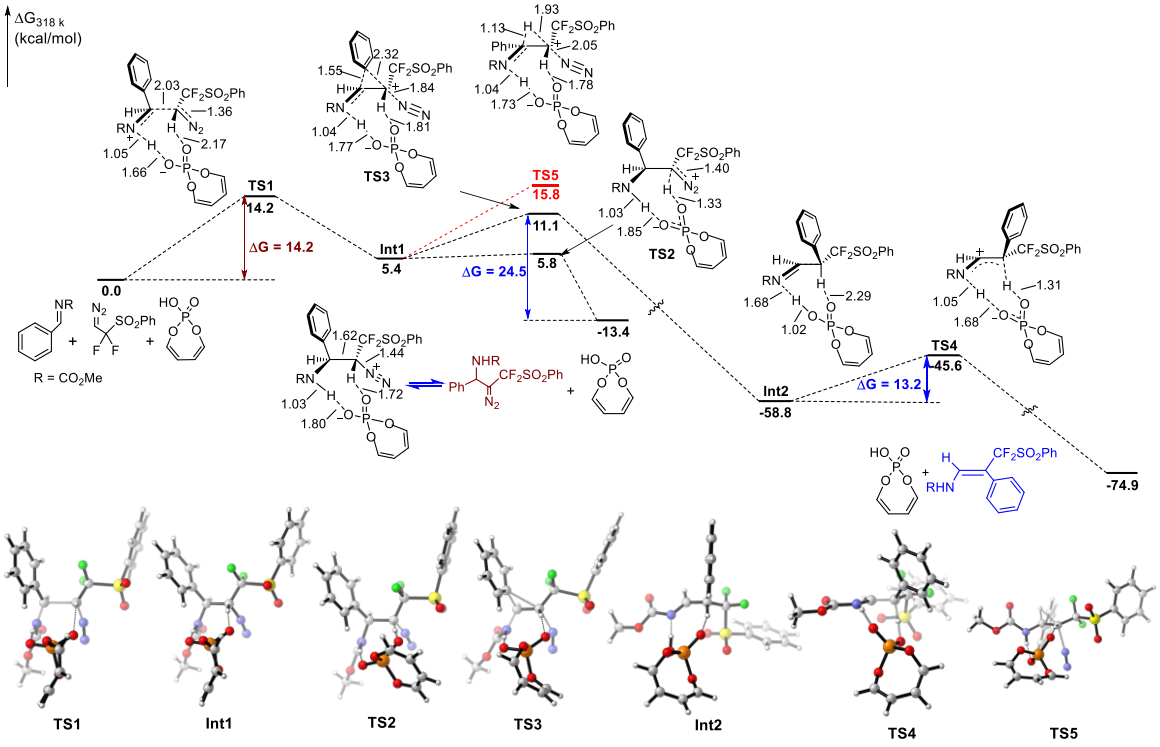


Crystal data and structure refinement for BPT

Empirical formula	$C_{29}H_{34}NO_6P+H_2O$
Identification code	BPT
Formula weight	523.54
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Unit cell dimensions	a = 10.460(10) Å a = 90° b=21.236(2) Å b = 90° c = 25.247(2) Å g = 90°
Volume	5608.4(9) Å
Z, Calculated density	4, 1.2389 g/cm^3
Absorption coefficient	0.140 mm^{-1}
F(000)	2220
Limiting indices	-13<=h=<13, -27<=k<=16, -32=<l<=29
Reflections collected / unique	127310/9093[R(int) = 0.0361]

6. Calculation Details

Quantum chemical calculations were carried out with the GAUSSIAN 16 packages.[3] The B3LYP[2] functional in conjunction with the 6-31G(d,p) basis set was used for geometry optimizations and frequencies. The SMD[4] solvation model was used to account for the effects of dichloromethane environment. Optimized geometries were verified by frequency computations as minima (zero imaginary frequencies) or transition structures (a single imaginary frequency) at the same level of theory. More accurate electronic energies were obtained by single point energy calculations with the M06-2X[5] functional and the 6-311+G(d,p) basis set. All energetics reported throughout the text are in kcal/mol and the bond lengths are in angstroms (Å). Structures were generated using CYLview.[6]



Calculated free energy profile (kcal/mol) for model reaction of (±)-**BPA**-catalyzed olefination reaction in dichloromethane at 318 K The selected bond lengths are in Å. Calculated at SMD-MO6-2X/6-311+G(d,p)//B3LYP/6-31G(d,p) level of theory.

Imine

C	-3.35910000	0.16147700	-0.45411300
C	-3.17287700	-1.15137000	-0.01582000
C	-1.92571800	-1.55605800	0.47074000
C	-0.86061500	-0.66021100	0.50799500
C	-1.03379800	0.66210100	0.05759200
C	-2.29895000	1.06381800	-0.40780800
H	-2.44065400	2.08782100	-0.74293300

C	0.03307000	1.67868900	0.04675200
N	1.30230900	1.55861600	0.15031800
C	2.01517500	0.37358200	0.30148300
O	2.42326800	-0.05358800	1.36692000
O	2.31775100	-0.15294200	-0.89990100
C	3.19167500	-1.30041800	-0.87208700
H	-0.32980600	2.70182300	-0.08484800
H	0.08802500	-0.98324900	0.92041300
H	-1.78579700	-2.57142200	0.82903900
H	-3.99885200	-1.85609900	-0.04330400
H	-4.32788500	0.48208900	-0.82495200
H	4.13952600	-1.05187500	-0.38889000
H	2.72079300	-2.13355000	-0.34434900
H	3.35717100	-1.56327700	-1.91695300

Zero-point correction= 0.165686 (Hartree/Particle)
Thermal correction to Energy= 0.177803
Thermal correction to Enthalpy= 0.178811
Thermal correction to Gibbs Free Energy= 0.123918
SCF Done: E(RM062X) = -553.507032599

$PhSO_2CF_2CHN_2$

C	3.12857000	1.59563100	-0.03457900
C	1.83205300	1.30025200	0.38451800
C	1.40138700	-0.02896000	0.33941700
C	2.22518400	-1.06134100	-0.11878600
C	3.51846000	-0.74755600	-0.53435800
C	3.96666500	0.57560900	-0.49323300
H	4.97547300	0.81257400	-0.81764100
H	4.17549800	-1.53628200	-0.88699700
H	1.86594800	-2.08417000	-0.13587900
S	-0.26594500	-0.41729900	0.85720100
C	-1.31527100	-0.26197900	-0.71697100
F	-1.11107700	1.00326700	-1.16917300
F	-0.77853000	-1.14467000	-1.59876300
C	-2.74100000	-0.54557200	-0.48242300
N	-3.54203700	0.44317700	-0.21281500
N	-4.25921400	1.30154200	-0.00203200
H	-3.12302700	-1.55286600	-0.39010900
O	-0.33840200	-1.83463800	1.25567000
O	-0.75860300	0.63978500	1.75909100
H	1.17243500	2.07880500	0.75114200
H	3.48377400	2.62064800	0.00003800

Zero-point correction= 0.136290 (Hartree/Particle)

Thermal correction to Energy= 0.151788

Thermal correction to Enthalpy= 0.152795

Thermal correction to Gibbs Free Energy= 0.089678

SCF Done: E(RM062X) = -1166.08487885

Model catalyst

P	-1.03991100	-0.06399900	-0.08985000
O	-2.00986700	-0.56988400	-1.08135200
O	-1.65952000	0.58113800	1.24086800
O	-0.06132400	1.04382400	-0.74530200
O	-0.04609500	-1.12190900	0.61547900
C	1.09441400	1.52794800	-0.13651300
C	2.16014900	0.75903100	0.11650900
C	1.18133100	-1.52047800	0.09238500
C	2.21144100	-0.68390400	-0.08177200
H	-2.58244100	0.85930900	1.10576600
H	1.23499700	-2.59203600	-0.06234100
H	3.15790300	-1.13006800	-0.37469800
H	3.05351200	1.26154700	0.47720700
H	1.06512800	2.60029600	0.02061100

Zero-point correction= 0.095094 (Hartree/Particle)

Thermal correction to Energy= 0.104557

Thermal correction to Enthalpy= 0.105564

Thermal correction to Gibbs Free Energy= 0.058509

SCF Done: E(RM062X) = -797.693924628

Mannich product

C	5.07796600	-0.68899500	-1.29354100
C	5.83762000	-1.20108700	-0.23927800
C	5.29775800	-1.24162100	1.04814800
C	4.00368100	-0.77201400	1.27784300
C	3.23760100	-0.25753800	0.22457300
C	3.78295200	-0.22111000	-1.06378700
H	3.20126000	0.18517700	-1.88572600
C	1.81502600	0.22294400	0.50060200
N	1.39572300	1.33850300	-0.33807900
C	1.23589500	2.58437300	0.19852900
O	1.57750000	2.92046800	1.32291800
O	0.66119700	3.41020300	-0.70595800
C	0.47305600	4.76595100	-0.26498300
H	1.43024300	5.23236500	-0.01802000
H	0.01043500	5.28342900	-1.10585800
H	-0.18458100	4.80518600	0.60718000
H	0.90864900	1.14518600	-1.20545200

C	0.80579000	-0.92466400	0.39035900
N	1.18333800	-2.11479600	0.01677900
N	1.54247800	-3.15245900	-0.28824000
C	-0.63886900	-0.76009000	0.68186800
F	-1.16064800	-1.80291700	1.38827000
F	-0.86328400	0.38659300	1.36550300
S	-1.69936900	-0.67788200	-0.89443500
O	-1.25236000	0.52036700	-1.63325100
O	-1.56814800	-2.01422700	-1.50374000
C	-3.37387200	-0.42661300	-0.32664000
C	-3.85022400	0.87990100	-0.18313800
C	-5.15553400	1.06534700	0.27008400
C	-5.95567800	-0.03911000	0.57514200
C	-5.46097700	-1.33804900	0.42854400
C	-4.15834900	-1.54356700	-0.02325700
H	-3.76338200	-2.54525600	-0.15102300
H	-6.08876100	-2.19183800	0.66283300
H	-6.97164600	0.11304700	0.92677400
H	-5.54712800	2.07142700	0.38146300
H	-3.21951200	1.72549400	-0.43361400
H	1.77958200	0.59585800	1.52857200
H	3.58675200	-0.79909900	2.28151900
H	5.88467800	-1.63168900	1.87467700
H	6.84616600	-1.56205200	-0.41913500
H	5.49317800	-0.65178600	-2.29658000

Zero-point correction= 0.306236 (Hartree/Particle)
Thermal correction to Energy= 0.334868
Thermal correction to Enthalpy= 0.335875
Thermal correction to Gibbs Free Energy= 0.239151
SCF Done: E(RM062X) = -1719.63880010

Enamine product

C	1.64050300	3.89352700	-1.04366400
C	1.17442400	2.59431500	-1.24414100
C	1.30153500	1.62622400	-0.23311100
C	1.90820200	1.99482200	0.98038500
C	2.38004300	3.29374200	1.17535700
C	2.24598800	4.24726000	0.16450300
H	1.53490500	4.62921300	-1.83589000
H	0.71535700	2.32603900	-2.18956900
H	1.99495300	1.26279700	1.77821700
H	2.84303100	3.56083100	2.12093900
H	2.60940500	5.25942000	0.31688500
C	1.65066700	-0.85802900	-0.37678600

H	1.26877000	-1.86252700	-0.51304300
N	3.00569200	-0.81249600	-0.16258600
C	3.78683600	-1.95488100	-0.14616100
H	3.47108300	0.07801900	-0.03128800
C	-0.60799400	-0.04078200	-0.67552300
C	0.83766100	0.22343100	-0.44554700
O	3.36801300	-3.08639200	-0.29989000
O	5.06865100	-1.61274100	0.06706600
C	6.00265200	-2.71099400	0.11156400
H	6.00225900	-3.25447000	-0.83604400
H	6.97666100	-2.25407000	0.28463400
H	5.75386600	-3.39352100	0.92734400
F	-1.22202200	0.93008300	-1.40964600
F	-0.84254600	-1.23273600	-1.29529000
S	-1.61803100	-0.14816900	0.93385400
O	-1.10475000	-1.32576200	1.65845900
O	-1.57617800	1.18653600	1.55938300
C	-3.28972600	-0.48318300	0.38086600
C	-4.14050200	0.59264200	0.11247100
C	-3.69809300	-1.80969400	0.21684700
C	-5.43766800	0.32562400	-0.32414400
H	-3.79815700	1.61145100	0.25580200
C	-4.99853500	-2.05894400	-0.22024100
H	-3.01812100	-2.62423900	0.43973800
C	-5.86337500	-0.99496800	-0.49083000
H	-6.11489600	1.14825300	-0.53115800
H	-5.33591400	-3.08291400	-0.34651700
H	-6.87502800	-1.19603200	-0.83040000

Zero-point correction= 0.297066 (Hartree/Particle)
Thermal correction to Energy= 0.323282
Thermal correction to Enthalpy= 0.324290
Thermal correction to Gibbs Free Energy= 0.234809
SCF Done: E(RM062X) = -1610.20189297

Nitrogen

N	0.00000000	0.00000000	0.55252600
N	0.00000000	0.00000000	-0.55252600

Zero-point correction= 0.005607 (Hartree/Particle)
Thermal correction to Energy= 0.008126
Thermal correction to Enthalpy= 0.009134
Thermal correction to Gibbs Free Energy= -0.014308
SCF Done: E(RM062X) = -109.516347525

TS1

P	3.34785400	-0.86942300	-0.10647000
O	1.96824000	-1.40879100	0.13334600
O	3.56288300	0.62594800	-0.21680900
O	4.31170100	-1.51076900	1.07394800
O	4.03106600	-1.49434500	-1.47646000
C	5.67528300	-1.66954300	0.97820000
C	6.26739300	-2.51102600	0.11583500
C	4.50031700	-2.78312500	-1.59676300
C	5.56499300	-3.24966600	-0.92534300
C	1.26934600	1.81645100	-3.76120700
C	1.31974300	1.64182300	-2.38044600
C	0.21204800	2.00043600	-1.59221600
C	-0.93597400	2.53075300	-2.20773100
C	-0.97520900	2.70746000	-3.58821700
C	0.12666400	2.34725400	-4.36757400
H	2.12812500	1.54168200	-4.36596200
H	2.21735700	1.24395500	-1.91731600
H	-1.79197200	2.80514100	-1.59859100
H	-1.86158100	3.12723400	-4.05361000
H	0.09735800	2.48340500	-5.44462100
C	0.20654100	1.90736800	-0.11458400
H	-0.60704000	2.43720400	0.37404300
N	1.36819200	1.99077400	0.59655900
C	1.35675000	2.58445900	1.86289600
H	2.26280200	1.54426900	0.26115800
C	-6.70880700	-0.37665300	1.18326600
C	-7.31604500	-0.75737100	-0.01685400
C	-6.57623000	-1.38620500	-1.02203200
C	-5.21770300	-1.63770400	-0.83730800
C	-4.62899700	-1.25064000	0.37075000
C	-5.35186600	-0.61899000	1.38796700
H	-7.29083600	0.10613400	1.96159700
H	-8.37388900	-0.56527200	-0.16836600
H	-7.05579700	-1.68396600	-1.94886000
H	-4.63199000	-2.13309300	-1.60347100
H	-4.86743100	-0.33841600	2.31638500
S	-2.89109500	-1.56138800	0.61379200
O	-2.43917800	-2.63993000	-0.27651200
O	-2.57382800	-1.58244500	2.05335800
C	-2.05339900	0.01946300	-0.01557900
F	-2.29953500	0.09326500	-1.33843900
F	-2.67556300	1.05372300	0.60715700
C	-0.55842400	0.05429100	0.20896400
O	0.36348100	3.03522000	2.40283500

O	2.59474400	2.59380300	2.36188700
C	2.73356600	3.18563900	3.67209400
N	-0.17443300	-0.20257000	1.49334200
N	0.33433400	-0.23887400	2.48819500
H	0.04461400	-0.58919600	-0.43919900
H	3.98671800	-3.36021400	-2.36113600
H	5.92891000	-4.23738800	-1.19749500
H	7.33966000	-2.65595400	0.22233000
H	6.22675500	-1.12193700	1.73787600
H	2.42338300	4.23260600	3.65304700
H	3.79356700	3.10735100	3.91043600
H	2.13742300	2.63544000	4.40354500

Zero-point correction= 0.401414 (Hartree/Particle)
Thermal correction to Energy= 0.440404
Thermal correction to Enthalpy= 0.441411
Thermal correction to Gibbs Free Energy= 0.321968
SCF Done: E(RM062X) = -2517.31310846

Int1

P	2.97274600	-1.19355200	-0.27255900
O	1.55456500	-1.52709800	0.12707700
O	3.33655000	0.23269300	-0.59583000
O	3.91972800	-1.80538300	0.93334300
O	3.45599200	-2.08432500	-1.57467700
C	5.24723900	-2.14441600	0.78699600
C	5.67173900	-3.15738700	0.01568300
C	3.76282600	-3.42689500	-1.53912200
C	4.81252000	-3.93064400	-0.87153000
C	0.74175500	1.96185700	-3.72049300
C	0.89165400	1.65036200	-2.36897200
C	0.01691200	2.20470900	-1.42367900
C	-1.00175400	3.06900400	-1.84733800
C	-1.14567200	3.37906700	-3.19972300
C	-0.27550600	2.82299000	-4.13943000
H	1.42571400	1.53281500	-4.44679200
H	1.70127600	0.99956500	-2.05124500
H	-1.68052900	3.50067400	-1.11694500
H	-1.93368200	4.05593500	-3.51624400
H	-0.38623200	3.06306100	-5.19292000
C	0.16286300	1.92336300	0.06332100
H	-0.45260300	2.62339800	0.63020700
N	1.50465000	2.03139800	0.56088800
C	1.78662200	2.87645800	1.60217100
H	2.26620500	1.48159200	0.12652900

C	-6.43920100	-0.77371600	1.32887100
C	-7.01602100	-1.15002600	0.11245100
C	-6.22449300	-1.62949700	-0.93483600
C	-4.84406200	-1.73619700	-0.77592200
C	-4.28669900	-1.35476300	0.44913100
C	-5.06078300	-0.86983900	1.50829200
H	-7.06128900	-0.40775300	2.13917300
H	-8.09083600	-1.07165600	-0.01937400
H	-6.68039900	-1.92439200	-1.87433200
H	-4.21743100	-2.11655000	-1.57476300
H	-4.59832600	-0.58986900	2.44804600
S	-2.52419700	-1.49218800	0.65926500
O	-1.97859800	-2.49304800	-0.26399900
O	-2.18032800	-1.50579200	2.09376400
C	-1.87569100	0.18747500	0.06262600
F	-2.01989800	0.20872500	-1.27161200
F	-2.66359000	1.14088200	0.61537900
C	-0.39720300	0.44603900	0.41107600
O	0.95715100	3.51466800	2.23668400
O	3.11265800	2.89787000	1.83578400
C	3.53475400	3.73359200	2.92980300
N	-0.21392000	0.30536400	1.83028300
N	0.10851200	0.33758900	2.88897500
H	0.29428600	-0.35621700	0.00937400
H	3.13027900	-4.02921000	-2.18531600
H	5.03703600	-4.98339000	-1.02412800
H	6.72453600	-3.42113000	0.07927400
H	5.91064200	-1.57504900	1.43222300
H	3.27011200	4.77755800	2.74523900
H	4.61821900	3.62325500	2.97538500
H	3.08313000	3.40284400	3.86840700

Zero-point correction= 0.402324 (Hartree/Particle)

Thermal correction to Energy= 0.441666

Thermal correction to Enthalpy= 0.442673

Thermal correction to Gibbs Free Energy= 0.322173

SCF Done: E(RM062X) = -2517.32731534

TS3

C	0.65529400	1.89856100	-3.62760600
C	0.83072800	1.61695700	-2.27389300
C	-0.08276700	2.12525200	-1.33477000
C	-1.18211100	2.88795300	-1.76329600
C	-1.34485800	3.16719600	-3.11725200
C	-0.42995900	2.66945200	-4.05079100

H	1.36830800	1.51582700	-4.35116200
H	1.68903600	1.03881000	-1.94328700
H	-1.89134700	3.27385500	-1.03862400
H	-2.18189900	3.77639600	-3.44409400
H	-0.56274800	2.88584300	-5.10667200
C	0.12521400	1.87117100	0.17524100
H	-0.50875900	2.55056700	0.74582700
N	1.47020300	2.01150500	0.64989600
C	1.77153300	3.05577400	1.48265300
H	2.23130100	1.42383900	0.26290400
C	-1.89142400	0.20923200	0.08084900
C	-0.39600000	0.45503200	0.24393600
O	0.96209000	3.84588000	1.94842300
O	3.09635900	3.08283600	1.72941100
C	3.53789400	4.12542300	2.61766300
N	-0.05952400	-0.02059200	1.99369800
N	0.59495300	-0.03118100	2.88318800
H	0.25998700	-0.36258300	-0.12969400
H	3.31428400	5.11114100	2.20206800
H	4.61614500	3.99159900	2.70645800
H	3.06540400	4.02782200	3.59827400
F	-2.12886200	-0.10016000	-1.21349200
F	-2.62458200	1.29493700	0.41607600
S	-2.60688100	-1.24008500	1.09483300
O	-1.84109500	-2.42487500	0.68975800
O	-2.61304700	-0.77811900	2.49235800
C	-4.27413500	-1.32717500	0.47426100
C	-4.53853100	-2.15134700	-0.62468600
C	-5.26865500	-0.57340400	1.10648200
C	-5.84801900	-2.22182900	-1.09576000
H	-3.74617000	-2.72856800	-1.08761700
C	-6.57095300	-0.65886300	0.61835300
H	-5.03204600	0.04884900	1.96201600
C	-6.85698800	-1.47780900	-0.47767500
H	-6.07912900	-2.85902800	-1.94308300
H	-7.36113000	-0.08934400	1.09657900
H	-7.87467100	-1.53910700	-0.85086800
P	2.98824000	-1.22235300	-0.29909800
O	1.55844300	-1.62320000	-0.04817600
O	3.33607900	0.23712200	-0.45717700
O	3.98956100	-1.79844900	0.88262400
O	3.48424200	-2.09157600	-1.61544200
C	4.32116200	-3.12601500	1.04000300
C	5.07253400	-3.80790500	0.16133700

C	4.78547200	-2.44614200	-1.88849000
C	5.50756900	-3.28288300	-1.12627300
H	3.99838100	-3.54325900	1.99012200
H	5.38630200	-4.80874100	0.44759300
H	6.47381900	-3.59542700	-1.51460000
H	5.14393700	-2.06170500	-2.83967700

Zero-point correction= 0.400566 (Hartree/Particle)
Thermal correction to Energy= 0.440169
Thermal correction to Enthalpy= 0.441177
Thermal correction to Gibbs Free Energy= 0.319273
SCF Done: E(RM062X) = -2517.31525112

TS2

P	-2.73955800	1.62927700	-0.22454800
O	-1.22898700	1.57434000	0.03975700
O	-3.52215200	0.36285000	-0.35547200
O	-3.43174900	2.51541800	0.97116500
O	-2.99060200	2.52197500	-1.57521500
C	-3.10865600	3.81941600	1.27732900
C	-2.56048000	4.75732000	0.48706200
C	-2.32789200	3.71554800	-1.80446700
C	-2.14782200	4.69829400	-0.91104200
C	-1.19548000	-1.38765000	-3.84226400
C	-1.36771500	-1.28774900	-2.46143600
C	-0.52098700	-1.99338500	-1.59510200
C	0.49170500	-2.79977900	-2.13246600
C	0.66167700	-2.89650200	-3.51377100
C	-0.18037800	-2.18756000	-4.37224400
H	-1.86047900	-0.84122900	-4.50456000
H	-2.17440200	-0.67902200	-2.06631900
H	1.14555600	-3.35700700	-1.46833600
H	1.44580400	-3.53101000	-3.91622800
H	-0.05144300	-2.26301200	-5.44804200
C	-0.69078900	-1.94852600	-0.08279900
H	-0.19542900	-2.81809300	0.35266900
N	-2.05528100	-1.97658600	0.36853800
C	-2.48938500	-2.95802800	1.21894900
H	-2.71093500	-1.24154100	0.07481700
C	6.30276900	-0.36782600	0.72468600
C	6.70281200	0.44225200	-0.34189000
C	5.81123500	1.34844500	-0.92262300
C	4.50706000	1.45228300	-0.44218900
C	4.12625300	0.63281800	0.62563200
C	5.00241900	-0.28171900	1.21847400

H	7.00244600	-1.06501000	1.17410300
H	7.71763800	0.36918900	-0.72075700
H	6.13021200	1.97758400	-1.74719300
H	3.80766500	2.15826300	-0.87575800
H	4.67752900	-0.89609000	2.05056900
S	2.46283100	0.76169100	1.25212000
O	1.90988200	2.08899900	0.95677800
O	2.38685300	0.19488900	2.61117100
C	1.50594000	-0.47122300	0.17766600
F	1.57646900	-0.02077500	-1.09051600
F	2.18974500	-1.64406200	0.25590600
C	0.03181000	-0.65052500	0.55098300
O	-1.78840800	-3.83489700	1.70449500
O	-3.80993500	-2.81564000	1.45011300
C	-4.38480600	-3.76905600	2.36230000
N	-0.13463600	-0.75337500	1.93292300
N	-0.48249500	-0.85240800	2.98640000
H	-0.60981000	0.41963500	0.26134900
H	-1.98714200	3.79423300	-2.83124900
H	-1.62977700	5.57454800	-1.29006200
H	-2.40460500	5.71257200	0.98017700
H	-3.38515300	4.04387600	2.30195200
H	-4.25061600	-4.78925700	1.99533100
H	-5.44598600	-3.52333500	2.40619000
H	-3.93700800	-3.67593700	3.35503500

Zero-point correction= 0.399047 (Hartree/Particle)
Thermal correction to Energy= 0.437758
Thermal correction to Enthalpy= 0.438766
Thermal correction to Gibbs Free Energy= 0.319982
SCF Done: E(RM062X) = -2517.32446501

Int2

C	-0.40996400	3.38773300	3.32519500
C	-0.34006700	2.32136300	2.42772100
C	0.59811100	2.33963000	1.38694500
C	1.45255200	3.44327300	1.24495500
C	1.37636600	4.50664900	2.14552100
C	0.44688700	4.48171200	3.18714000
H	-1.13652200	3.36181800	4.13218900
H	-1.01021800	1.47305600	2.52622400
H	2.18314800	3.47337700	0.44433400
H	2.04492500	5.35470400	2.03027000
H	0.38944100	5.31145900	3.88568600
C	0.26149400	1.66299000	-0.95999100

H	0.95207200	2.34694500	-1.45869200
N	-0.86222800	1.37262800	-1.50398300
C	-1.11360200	2.00503900	-2.76574100
H	-1.96536700	0.18238500	-1.07519900
C	1.99368900	0.46183800	0.41883100
C	0.63039800	1.15575000	0.40806800
O	-0.42659200	2.85677100	-3.28908600
O	-2.23941600	1.50055800	-3.26484200
C	-2.64260300	2.02051400	-4.55149900
H	-0.10472000	0.41445100	0.73656900
H	-2.82312700	3.09576000	-4.48535400
H	-3.56250600	1.49325400	-4.80043700
H	-1.87203100	1.82017500	-5.29911000
F	2.33265800	0.09374600	1.67679800
F	2.99173300	1.24878300	-0.06955300
S	2.02086100	-1.10177900	-0.63210500
O	1.02468600	-2.01544400	-0.04779600
O	1.88895800	-0.63391200	-2.02483300
C	3.66304900	-1.75634500	-0.37099400
C	3.87340300	-2.64910200	0.68418300
C	4.69505800	-1.35281900	-1.22327500
C	5.15783000	-3.15349100	0.88183700
H	3.05081900	-2.94957000	1.32344200
C	5.97273100	-1.86826900	-1.01017800
H	4.49865200	-0.66520700	-2.03814200
C	6.20185000	-2.76303500	0.03867400
H	5.34124900	-3.85238600	1.69161300
H	6.78679600	-1.57300400	-1.66439900
H	7.19958800	-3.16072400	0.19793400
P	-2.95228700	-0.95762300	0.54779700
O	-2.05812300	-0.41687800	1.60076300
O	-2.62317000	-0.58163700	-0.94369200
O	-3.03981700	-2.57003600	0.41796700
O	-4.48321600	-0.50515700	0.84865900
C	-3.80676900	-3.37224500	1.25469100
C	-5.14517500	-3.33364600	1.27478100
C	-5.61227600	-1.10129600	0.30307000
C	-5.95894900	-2.37308700	0.54039200
H	-3.21157800	-4.08963100	1.80888700
H	-5.64971800	-4.09118500	1.86851600
H	-6.92772000	-2.69574800	0.16848200
H	-6.22712700	-0.40130900	-0.25249000

Zero-point correction= 0.393406 (Hartree/Particle)

Thermal correction to Energy= 0.430441

Thermal correction to Enthalpy= 0.431449

Thermal correction to Gibbs Free Energy= 0.315471

SCF Done: E(RM062X) = -2407.89228221

TS4

C	1.11281700	-1.19895400	-3.80804600
C	0.66935100	-1.02199200	-2.49719500
C	0.19267900	0.22576400	-2.07311700
C	0.15121000	1.28787600	-2.98962300
C	0.60350100	1.10998000	-4.29731200
C	1.08545400	-0.13371100	-4.71010900
H	1.48294900	-2.17055500	-4.12172200
H	0.69814500	-1.85171000	-1.79985500
H	-0.23838500	2.25434700	-2.68365600
H	0.56953800	1.94225700	-4.99438200
H	1.43505600	-0.27210700	-5.72902400
C	-0.08893900	1.65694400	-0.00312800
H	-0.85200100	2.17836800	0.57017100
N	1.10682000	2.20397700	0.03045400
C	1.32278300	3.42646800	0.72991000
H	1.94941500	1.65927500	-0.29192200
C	-1.81967600	0.00462700	-0.58024800
C	-0.35855700	0.41029200	-0.65956000
O	0.43862400	4.06973500	1.24510500
O	2.61624400	3.70960700	0.69052000
C	3.01307000	4.93416500	1.35789100
H	0.40156700	-0.39976600	0.05919700
H	2.50142000	5.78800300	0.90958900
H	4.08835400	5.00559800	1.20356200
H	2.78024900	4.87199700	2.42261900
F	-2.05139200	-1.13765300	-1.27180600
F	-2.65295700	0.96517300	-1.08766900
S	-2.46213500	-0.34480100	1.16474200
O	-2.24132900	0.89411200	1.93876800
O	-1.85406700	-1.61223700	1.59664100
C	-4.21883400	-0.58039800	0.92049800
C	-4.69611500	-1.87031600	0.67179400
C	-5.06773400	0.52817300	0.98537000
C	-6.06684400	-2.04855100	0.48840600
H	-4.01372700	-2.71222500	0.63720900
C	-6.43512300	0.33082400	0.79989400
H	-4.66820300	1.51537800	1.18860600
C	-6.93086100	-0.95212000	0.55101900
H	-6.45844600	-3.04320100	0.30058100

H	-7.11208300	1.17759200	0.85238600
H	-7.99726200	-1.09865200	0.40815000
P	2.77972000	-0.82433600	0.43793500
O	3.12385800	0.45615600	-0.26864900
O	1.29378000	-1.13725100	0.67260800
O	3.50095700	-2.03679200	-0.38289800
O	3.43283300	-0.94211300	1.93089500
C	3.76239900	-3.29118900	0.14455000
C	4.63216500	-3.50070800	1.14231700
C	4.75622100	-1.25759600	2.18767800
C	5.30228600	-2.44510600	1.89084200
H	5.27540200	-0.48143100	2.74084900
H	6.30942200	-2.62889100	2.25578500
H	4.85918500	-4.53446600	1.38950500
H	3.26443500	-4.09006600	-0.39532500

Zero-point correction= 0.388894 (Hartree/Particle)
Thermal correction to Energy= 0.425131
Thermal correction to Enthalpy= 0.426139
Thermal correction to Gibbs Free Energy= 0.313900
SCF Done: E(RM062X) = -2407.86962615

TS5

C	0.10883200	1.81057800	-0.36795800
N	1.53958300	1.95742600	-0.31044500
C	2.11183200	2.71942700	-1.29104000
H	2.12379000	1.30813500	0.25570000
C	-1.79581900	0.03208300	-0.34117900
C	-0.31317600	0.40842000	-0.29083400
O	1.48021800	3.28583800	-2.17613900
O	3.44669100	2.76661200	-1.14739200
C	4.15088000	3.52441700	-2.15045500
N	-0.01473600	-0.10066000	1.66752600
N	0.28579200	-0.30959100	2.70733500
H	0.42285800	-0.36513200	-0.62487500
H	3.98258200	3.10201700	-3.14409800
H	5.20458700	3.44703300	-1.88283400
H	3.83451200	4.57009000	-2.13838900
F	-2.26384900	0.52235200	-1.51603300
F	-2.50020100	0.55709200	0.67897800
S	-2.11507000	-1.83606800	-0.36248700
O	-1.56843200	-2.30209200	-1.64184900
O	-1.60585300	-2.32900600	0.92551300

C	-3.89429500	-1.91814600	-0.38802600
C	-4.54908700	-1.92333900	-1.62423300
C	-4.58501300	-1.97515800	0.82703200
C	-5.94095800	-1.99204600	-1.63466100
H	-3.98415400	-1.88947800	-2.54886100
C	-5.97636500	-2.04387600	0.79395400
H	-4.04738800	-1.98027100	1.76837600
C	-6.64928700	-2.04995000	-0.43115900
H	-6.47041600	-2.00386100	-2.58173400
H	-6.53314900	-2.09545500	1.72389100
H	-7.73351800	-2.10421000	-0.44818900
P	2.93115900	-1.25261800	0.24303900
O	1.74242700	-1.55757200	-0.63245800
O	2.91795500	0.01028700	1.07142300
O	3.23216300	-2.47309000	1.31195800
O	4.25248900	-1.32683700	-0.74352700
C	3.79429500	-3.68711300	0.98461300
C	5.05578600	-3.82817900	0.54825100
C	5.53974200	-1.55625600	-0.30913200
C	5.94405400	-2.71936700	0.22470700
H	3.14930000	-4.53254100	1.20773600
H	5.43475900	-4.84248300	0.45065700
H	7.00934600	-2.83709700	0.40735000
H	6.22069400	-0.73877700	-0.52953800
H	-0.16797500	1.93812000	-1.45280600
C	-0.67670600	2.87070300	0.40839800
C	-0.21286400	3.27323100	1.66625800
C	-1.83180600	3.44930700	-0.12709000
C	-0.91804100	4.23380300	2.39196000
H	0.69845000	2.84526400	2.07201000
C	-2.53004500	4.41421200	0.60006100
H	-2.18544100	3.15287400	-1.11019200
C	-2.07663100	4.80555400	1.86111500
H	-0.55622900	4.53927100	3.36919100
H	-3.42191100	4.86493800	0.17533600
H	-2.61822900	5.55975500	2.42432700

Zero-point correction= 0.398754 (Hartree/Particle)

Thermal correction to Energy= 0.438429

Thermal correction to Enthalpy= 0.439436

Thermal correction to Gibbs Free Energy= 0.317816

SCF Done: E(RM062X) = -2517.30638372

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