Supporting Information for:

Stereoselective [3+2] Cycloaddition of *N*-*tert*-Butanesulfinyl Imines to Arynes Facilitated by Removable $PhSO_2CF_2$ Group: Synthesis and Transformation of Cyclic Sulfoximines

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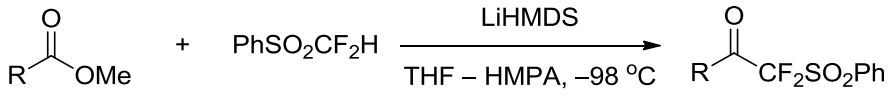
General

Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. The solvent THF was distilled from sodium, and the solvents MeCN, CH_2Cl_2, HMPA (hexamethylphosphoramide) and DMF were distilled from CaH_2 before being used. ^1H, ^{19}F and ^{13}C NMR spectra were recorded on a 400 MHz or 300 MHz NMR spectrometer. ^1H NMR chemical shifts were determined relative to internal $(CH_3)_4Si$ (TMS) at δ 0.0 or to the signal of the residual protonated solvent: $CDCl_3$ δ 7.26. ^{13}C NMR chemical shifts were determined relative to internal TMS at δ 0.0. For the isolated compounds, ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ at δ 0.0. Mass spactra were obtained on a mass spectrometer. High-resolution mass data were recorded on a high-resolution mass spectrometer in the EI mode.

1. Preparation of N-*tert*-Butanesulfinyl Imines

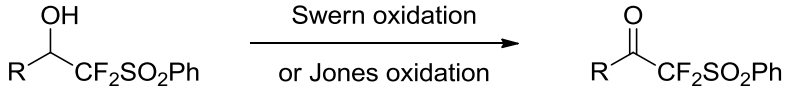
1.1 Preparation of Difluoro(phenylsulfonyl)methyl Ketones:

Method 1: Ketones **S1a**, **S1d-e**, **S1g-i**, and **S1j** were prepared by difluoro(phenylsulfonyl)methylation of the corresponding methyl esters according to the reported procedures.[1]

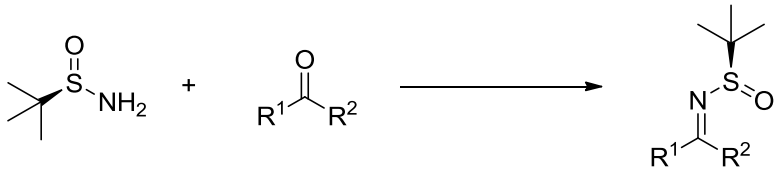


Method 2: Ketones **S1b-c** and **S1k** were prepared by oxidation of the corresponding known α-difluoro(phenylsulfonyl)methyl alcohols with DMSO/$(COCl)_2$/Et_3N (Swern Oxidation). Ketone **S1f** was prepared by oxidation with Jones' reagent.

[1] Ni, C.; Zhang, L.; Hu, J. *J. Org. Chem.* **2009**, *74*, 3767.



1.2 Condensation of *N-tert*-Butylsulfinamide and the Corresponding Ketones.



Non-fluorinated imines **1a-c**,[2] difluoromethyl imine **1d**, trifluoromethyl imine **1e**,[3] and monofluoromethyl imine **1f** were prepared by condensation of (*R*)-*N*-*tert*-butylsulfinamide and the corresponding carbonyl compounds. The *Z*-configuration of the imino bond in difluoromethyl imine **1d** was established by single-crystal X-ray analysis of its analogue **S2** (see SI Section 3.1), and the assumption was made that monofluoromethyl imine **1f** possessed a similar geometry.

Difluoro(phenylsulfonyl)methyl imines **2a-k** (Table S1) were prepared according to the following typical procedures:

Typical procedures:

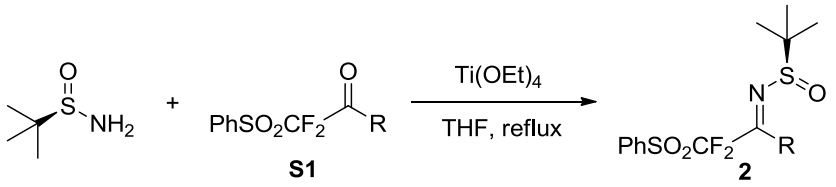
Under N_2 atmosphere, a mixture of (*R*)-*N*-*tert*-butylsulfinamide (> 99% ee, 9.6 mmol, 1.162 g), (phenylsulfonyl)difluoromethyl phenyl ketone (**S1a**; 8.0 mmol, 2.368 g), $Ti(OEt)_4$ (48.0 mmol, 10.944 g) in THF (50.0 mL) was heated to reflux for 36 h, then the reaction mixture was cooled to room temperature and poured into an equal volume of brine while rapidly stirring. The resulting suspension was filtered through a plug of celite, and the filter cake was washed with EtOAc. The filtrate was transferred to a separatory funnel where the organic layer was washed with brine. The brine layer was extracted with EtOAc for three times, and the combined organic phase was dried over anhydrous $MgSO_4$. The volatile solvents were removed under vacuum, and the crude product was purified by

[2] (a) Liu, G.; Cogan, D. A.; Owens, T. D.; Tang, T. P.; Ellman, J. A. *J. Org Chem.* **1999**, *64*, 1278. (b) Plobeck, N.; Powell, D. *Tetrahedron: Asym.* **2002**, *13*, 303. (c) Morton, D.; Pearson, D.; Fielda, R. A.; Stockman, R. A. *Chem. Commun.* **2006**, 1833.

[3] Wang, H.; Zhao, X.; Li, Y.; Lu, L. *Org. Lett.* **2006**, *8*, 1379.

column chromatography (silica gel; ethyl acetate/petroleum ether = 1:10 – 1:5 v/v) to afford **2a** (2.171 g, 68% yield).

Table S1. Preparation of $PhSO_2CF_2$-Sulfinimines

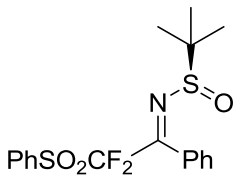


entry	ketone	R	$Ti(OEt)_4$ (equiv)	time (h)	sulfinimine	yield (%)[a]
1	**S1a**	Ph	6.0	36	**2a**	68
2	**S1b**	3-MeC_6H_4	5.0	24	**2b**	43[b]
3	**S1c**	4-MeC_6H_4	5.0	24	**2c**	41[b]
4	**S1d**	4-ClC_6H_4	5.0	24	**2d**	48
5	**S1e**	4-BrC_6H_4	4.0	24	**2e**	55
6	**S1f**	3-$MeOC_6H_4$	6.0	36	**2f**	52[b]
7	**S1g**	4-$MeOC_6H_4$	6.0	24	**2g**	46[b]
8	**S1h**	4-$CF_3C_6H_4$	4.0	36	**2h**	71
9	**S1i**	6-Br-2-Naph	5.0	48	**2i**	60
10	**S1j**	(*E*)-PhCH=CH	5.0	24	**2j**	75
11	**S1k**	*i*Pr	6.0	48	**2k**	53

[a] Isolated yield. [b] The isolated product **2** is contaminated by trace amount (1 – 2%) of difluoro(phenylsulfonyl)methyl alcohol due to the reduction of ketone **S1** during the condensation reaction using $Ti(OEt)_4$ (for details, see the ^{19}F NMR spectrum).

Characterization Data:

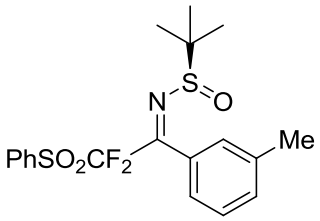
(*R*,*E*)-*N*-[2,2-Difluoro-1-phenyl-2-(phenylsulfonyl)ethylidene]-2-methylpropane-2-sulfin amide **(2a)**



Mp: 57–59 °C. $[\alpha]_D^{22}$ –171.3 (*c* 1.00, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 8.00 (d, J = 7.6 Hz, 2H), 7.76 (t, J = 7.5 Hz, 1H), 7.61 (t, J = 7.6 Hz, 2H), 7.52–7.38 (m, 5H), 1.33 (s,

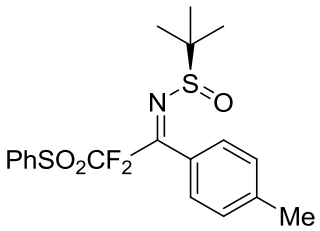
9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –97.8 (d, J = 231.4 Hz, 1F), –99.3 (d, J = 231.4 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8 (t, J = 25.3 Hz), 135.6, 133.1, 130.9, 130.8, 130.6, 129.4, 128.3, 127.8, 116.5 (t, J = 295.5 Hz), 60.2, 22.8. IR (film): 2979, 1605, 1580, 1447, 1150, 1111, 1086 cm^{-1}. MS (ESI, *m/z*): 422.0 (M + Na^+). Anal. Calcd for $C_{18}H_{19}F_2NO_3S_2$: C, 54.12; H, 4.79; N, 3.51; Found: C, 54.35; H, 4.95; N, 3.13.

(*R*,*E*)-*N*-[2,2-Difluoro-2-(phenylsulfonyl)-1-*m*-tolylethylidene]-2-methylpropane-2-sulfin amide **(2b)**



$[\alpha]_D^{22}$ –175.0 (*c* 1.00, $CHCl_3$). ^{1}H NMR (300 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), 7.31–7.24 (m, 4H), 2.38 (s, 3H), 1.33 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –98.1 (d, J = 233.9 Hz, 1F), –99.6 (d, J = 233.9 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3 (t, J = 20.1 Hz), 137.6, 135.6, 133.1, 131.7, 130.9, 130.6, 129.4, 128.5, 127.7, 125.5, 116.5 (t, J = 295.6 Hz), 59.9, 22.7, 21.5. IR (film): 2963, 1618, 1584, 1449, 1351, 1171, 1145, 1107 cm^{-1}. MS (ESI, *m/z*): 436.0 (M + Na^+). HRMS (ESI): calcd. for $C_{19}H_{21}F_2NO_3S_2$: (M + Na^+): 436.0823; Found: 436.0834.

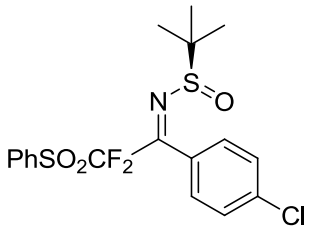
(*R*,*E*)-*N*-[2,2-Difluoro-2-(phenylsulfonyl)-1-*p*-tolylethylidene]-2-methylpropane-2-sulfin amide **(2c)**



$[\alpha]_D^{22}$ –198.1 (*c* 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 7.6 Hz, 2H),

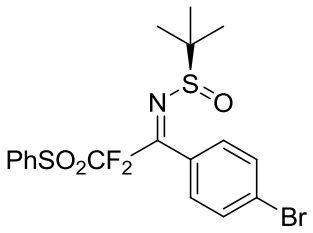
7.76 (t, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 2.38 (s, 3H), 1.32 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$): δ –99.0 (d, *J* = 232.0 Hz, 1F), –101.1 (d, *J* = 232.0 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9 (t, *J* = 24.2 Hz), 141.3, 135.6, 133.1, 130.9, 129.4, 128.5, 128.4, 127.7, 116.6 (t, *J* = 295.5 Hz), 60.0, 22.7, 21.6. IR (film): 2964, 1608, 1585, 1509, 1447, 1449, 1351, 1151 cm^{-1}. MS (ESI, *m/z*): 436.0 (M + Na^+). HRMS (ESI): calcd. for $C_{19}H_{21}F_2NO_3S_2$: (M + Na^+): 436.0823; Found: 436.0831.

(*R*,*E*)-*N*-[1-(4-Chlorophenyl)-2,2-difluoro-2-(phenylsulfonyl)ethylidene]-2-methylpropane-2-sulfinamide **(2d)**



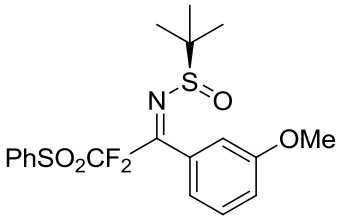
Mp: 61–63 °C. $[\alpha]_D^{22}$ –179.8 (*c* 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.78 (t, *J* = 7.2 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 8.9 Hz, 2H), 7.39 (d, *J* = 8.9 Hz, 2H), 1.34 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –98.7 (d, *J* = 231.5 Hz, 1F), –99.9 (d, *J* = 231.5 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1 (t, *J* = 24.7 Hz), 137.2, 135.8, 132.8, 130.9, 129.8, 129.5, 128.8, 128.1, 116.4 (t, *J* = 294.7 Hz), 60.7, 22.9. IR (film): 1627, 1590, 1488, 1449, 1351, 1151, 1109, 1091cm^{-1}. MS (ESI, *m/z*): 456.0 (M + Na^+). HRMS (ESI): calcd. for $C_{18}H_{18}ClF_2NO_3S_2$: (M + Na^+): 456.0277; Found: 456.0294.

(*R*,*E*)-*N*-[1-(4-Bromophenyl)-2,2-difluoro-2-(phenylsulfonyl)ethylidene]-2-methylpropane-2-sulfinamide **(2e)**



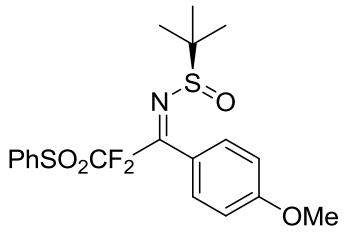
Mp: 95–97 °C. $[\alpha]_D^{22}$ –193.5 (*c* 1.00, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 7.99 (d, *J* = 7.9 Hz, 2H), 7.78 (t, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.3 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 1.34 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –98.7 (d, *J* = 231.5 Hz, 1F), –99.9 (d, *J* = 231.5 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2 (t, *J* = 25.5 Hz), 135.8, 132.8, 131.0, 130.9, 129.9, 129.5, 129.3, 125.7, 116.3 (t, *J* = 296.0 Hz), 60.7, 22.9. IR (film): 2961, 1628, 1583, 1485, 1449, 1350, 1149, 1108 cm^{-1}. MS (ESI, *m/z*): 500.0 (M + Na^+). HRMS (ESI): calcd. for $C_{18}H_{18}BrF_2NO_3S_2$: (M + Na^+): 499.9772; Found: 499.9790.

(*R*,*E*)-*N*-[2,2-Difluoro-1-(3-methoxyphenyl)-2-(phenylsulfonyl)ethylidene]-2-methylpropane-2-sulfinamide **(2f)**



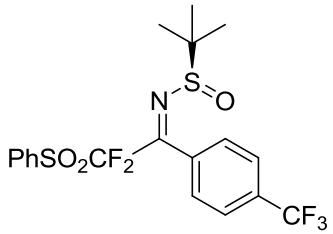
$[\alpha]_D^{22}$ –163.3 (*c* 1.00, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.7 Hz, 2H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.08–6.97 (m, 3H), 3.82 (s, 3H), 1.33 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –98.9 (d, *J* = 231.5 Hz, 1F), –100.3 (d, *J* = 231.6 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9 (t, *J* = 24.7 Hz), 158.9, 135.7, 133.1, 131.9, 131.0, 129.5, 129.1, 120.7, 116.0, 116.56 (t, *J* = 295.8 Hz), 113.8, 60.1, 55.4, 22.8. IR (film): 2964, 1600, 1581, 1487, 1450, 1351, 1293, 1147 cm^{-1}. MS (ESI, *m/z*): 452.1 (M + Na^+). HRMS (ESI): calcd. for $C_{19}H_{21}F_2NO_4S_2$: (M + Na^+): 452.0772; Found: 452.0782.

(*R*,*E*)-*N*-[2,2-Difluoro-1-(4-methoxyphenyl)-2-(phenylsulfonyl)ethylidene]-2-methylpropane-2-sulfinamide **(2g)**



Mp: 58–60 °C. $[\alpha]_D^{22}$ –229.2 (*c* 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.5 Hz, 2H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 3.83 (s, 3H), 1.32 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –97.9 (d, *J* = 233.4 Hz, 1F), –99.9 (d, *J* = 233.4 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4 (t, *J* = 24.5 Hz), 161.7, 135.5, 133.2, 130.6, 129.5, 122.5, 116.8 (t, *J* = 294.1 Hz), 113.9, 113.2, 60.0, 55.3, 22.7. IR (film): 2970, 1607, 1593, 1513, 1348, 1147, 1085 cm^{-1}. MS (ESI, *m/z*): 452.0 ($M + Na^+$). Anal. Calcd for $C_{19}H_{21}F_2NO_4S_2$: C, 53.13; H, 4.93; N, 3.26; Found: C, 53.13; H, 4.98; N, 2.93.

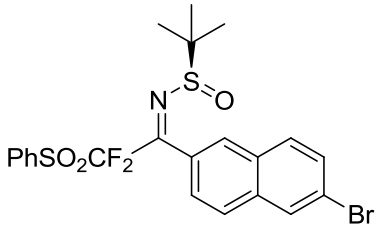
(*R*,*E*)-*N*-{2,2-difluoro-2-(phenylsulfonyl)-1-[4-(trifluoromethyl)phenyl]ethylidene}-2-methylpropane-2-sulfinamide (**2h**)



Yellow solid. Mp: 84–86 °C. $[\alpha]_D^{28}$ = –179.9 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.5Hz, 2H), 7.81–7.76 (m, 1H), 7.70–7.61 (m, 6H), 1.36 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –64.2 (s, 3F), –100.6 (d, *J* = 231 Hz, 1F), –101.6 (d, *J* = 231 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.7 (t, *J* = 25.5 Hz), 135.9, 134.2, 132.8, 132.4 (q, *J* = 32.9 Hz), 130.9, 129.5 128.8, 124.7 (q, *J* = 3.6 Hz), 123.6 (q, *J* = 271.2 Hz),

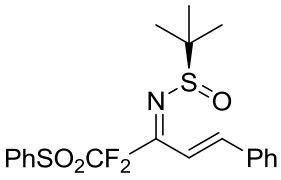
116.3 (t, *J* = 293.9 Hz), 60.9, 22.9. IR (KBr): 3078, 2980, 1614, 1450, 1324, 1512, 1109, 1067, 1012, 839, 685, 620, 587, 536 cm^{-1}. MS (ESI, *m/z*): 468($[M + H]^+$). HRMS (ESI, *m/z*): Calcd. for $C_{19}H_{18}F_5NO_3S_2Na^+$ ($[M + Na]^+$): 490.0546; Found: 490.0554.

(*R*,*E*)-*N*-[1-(6-Bromonaphthalen-2-yl)-2,2-difluoro-2-(phenylsulfonyl)ethylidene]-2-methylpropane-2-sulfinamide **(2i)**



Mp: 42–45 °C. $[\alpha]_D^{20}$ –217.0 (*c* 1.00, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 8.01(s, 2H), 7.99 (s, 1H), 7.95 (s, 1H), 7.81–7.71 (m, 3H), 7.64–7.54 (m, 4H), 1.35 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –98.4 (d, *J* = 231.6 Hz, 1F), –99.8 (d, *J* = 231.6 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0 (t, *J* = 24.8 Hz), 135.7, 134.8, 132.8, 130.8, 130.5, 130.3, 130.2, 129.9, 129.4, 128.6, 128.4, 126.4, 125.9, 122.0, 116.5 (t, *J* = 291.5 Hz), 60.4, 22.7. IR (film): 2963, 1625, 1583, 1448, 1350, 1148, 1129, 1102 cm^{-1}. MS (ESI, *m/z*): 528.0 ($M + H^+$). HRMS (ESI): calcd. for $C_{22}H_{20}BrF_2NO_3S_2$: ($M + Na^+$): 549.9928; Found: 549.9936.

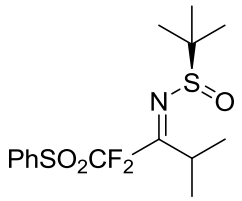
(*R*,*E*)-*N*-[(*E*)-1,1-Difluoro-4-phenyl-1-(phenylsulfonyl)but-3-en-2-ylidene]-2-methylpropane-2-sulfinamide **(2j)**



Mp: 76–78 °C. $[\alpha]_D^{22}$ –616.9 (*c* 1.00, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 8.12–8.00 (m, 3H), 7.77 (t, *J* = 7.5 Hz, 1H), 7.64 (t, *J* = 7.9 Hz, 2H), 7.60–7.53 (m, 2H), 7.47 (d, *J* = 17.2 Hz, 1H), 7.41–7.35 (m, 3H), 1.34 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –95.9 (d, *J*

= 237.8 Hz, 1F), –98.7 (d, J = 237.8 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7 (t, J = 22.6 Hz), 145.2 (t, J = 4.6 Hz), 135.6, 135.1, 133.0, 130.9, 130.8, 129.4, 128.9, 128.5, 117.8 (t, J = 295.3 Hz), 116.7, 61.2, 23.0. IR (film): 2975, 1614, 1576, 1559, 1449, 1353, 1172, 1117 cm^{-1}. MS (ESI, *m/z*): 448.0 (M + Na$^+$). Anal. Calcd for $C_{20}H_{21}F_2NO_3S_2$: C, 56.45; H, 4.97; N, 3.29; Found: C, 56.62; H, 5.07; N, 2.89.

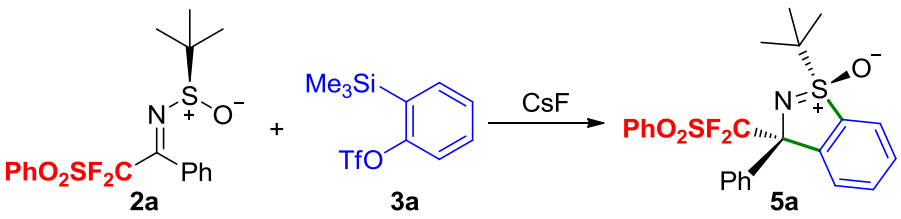
(*R*,*E*)-*N*-[1,1-Difluoro-3-methyl-1-(phenylsulfonyl)butan-2-ylidene]-2-methylpropane-2-sulfinamide **(2k)**



$[\alpha]_D^{22}$ –35.9 (*c* 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (d, J = 7.7 Hz, 2H), 7.77 (t, J = 7.5 Hz, 1H), 7.63 (t, J = 7.8 Hz, 2H), 3.94–3.78 (m, 1H), 1.38–1.28 (m, 15H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –96.6 (d, J = 237.6 Hz, 1F), –100.7 (d, J = 237.7 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.9 (t, J = 22.2 Hz), 135.5, 133.3, 130.8, 129.4, 117.6 (t, J = 297.9 Hz), 60.0, 32.6, 22.8, 20.1, 19.3. IR (film): 2970, 1630, 1585, 1450, 1351, 1165, 1091 cm^{-1}. MS (ESI, *m/z*): 388.0 (M + Na$^+$). HRMS (ESI): calcd. for $C_{15}H_{21}F_2NO_3S_2$: (M + Na$^+$): 388.0823; Found: 388.0831.

2. Screening of Reaction Conditions

Table S2. Reaction between 2a and 3a under Various Conditions

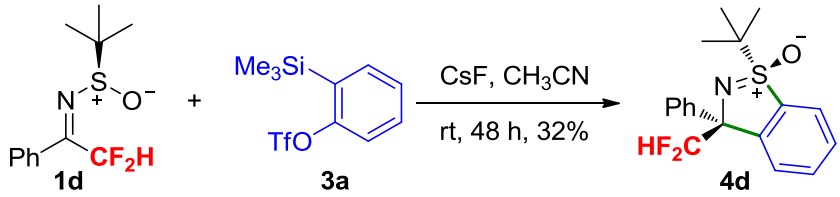


entry	**2a**:**3a**:CsF	solvent	temp. (°C)	time (h)	yield (%)[a]	dr[b]	er[c]
1	1.0:2.0:3.0	CH_3CN	rt	48	74	>99:1	>99:1
2	1.0:2.0:3.0	$PhCH_3$	rt	24	0	—	—
3	1.0:2.0:3.0	THF	rt	24	trace	—	—
4	1.0:1.5:2.0	CH_3CN	rt	48	59	>99:1	>99:1
5	1.0:1.5:2.0	CH_3CN	60	24	55	>99:1	>99:1
6	1.0:2.0:3.0	CH_3CN	60	18	70	>99:1	>99:1
7	1.0:2.5:4.0	CH_3CN	60	12	76	>99:1	>99:1
8	1.0:2.5:4.0	CH_3CN	rt	12	84	>99:1	>99:1
9	1.0:3.0:5.0	CH_3CN	80	12	78	>99:1	>99:1
10	1.0:3.0:5.0	CH_3CN	rt	12	87	>99:1	>99:1
11	1.0:3.0:5.0	CH_3CN	rt	4	80	>99:1	>99:1

[a] Isolated yield. [b] Determined by ^{19}F NMR spectroscopy of the crude product. [c] Determined by chiral HPLC.

3. [3 + 2] Cycloaddition of $PhSO_2CF_2$-Sulfinimines with Arynes and Further Transformation

3.1 [3 + 2] Cycloaddition.



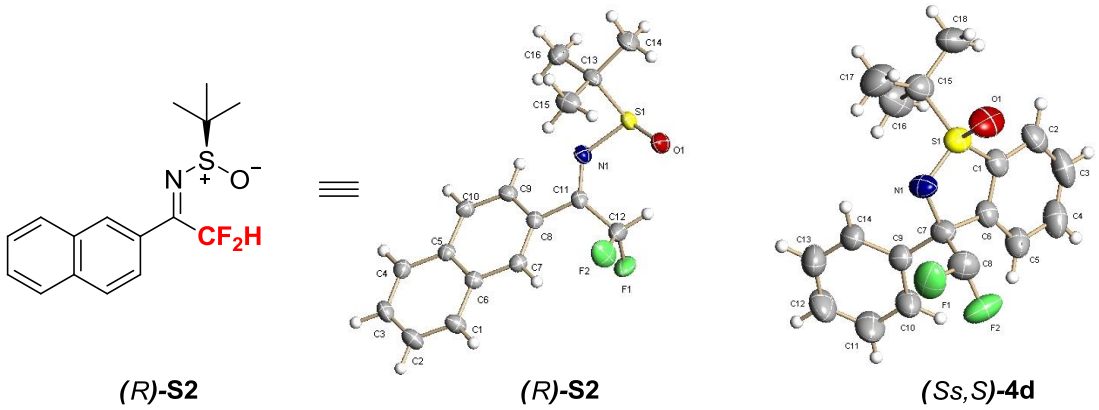


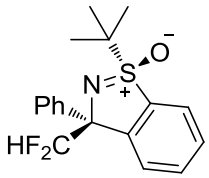
Figure S1 Structures of Difluomethyl Imine (*R*)-**S2** and Cyclic Sulfinamide (*Ss*,*S*)-**4d** in the Crystals

Experimental Procedures:

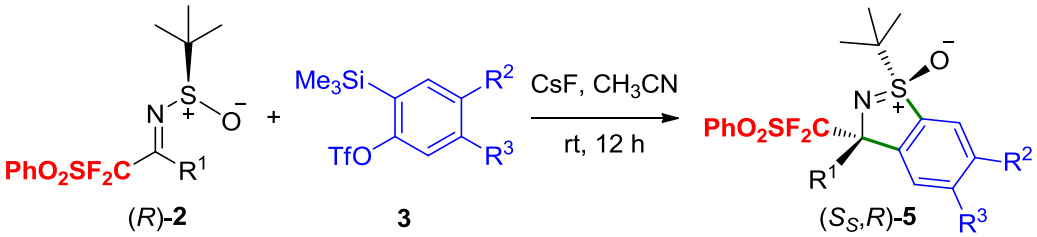
To a Schlenk tube containing sulfinimine (*R*)-**1d** (0.104 g, 0.4 mmol), aryne precursor **3a** (0.238 g, 0.8 mmol), and CH_3CN (8.0 mL) was added CsF (0.182 g, 1.2 mmol). The tube was sealed with a rubber septum, and then the reaction mixture was stirred at room temperature for 48 h. After quenched with brine, the reaction mixture was extracted with Et_2O (30 mL × 3), and the combined organic phase was dried over anhydrous $MgSO_4$. The volatile solvents were removed under vacuum, and the crude product was purified by column chromatography (silica gel; ethyl acetate/petroleum ether = 1:3 v/v) to give enantiopure product (*Ss*,*S*)-**4d** as a white solid (0.043 g, 32% yield).

The diastereoselectivity was determined by HPLC-MS (ESI) analysis of the crude product, and the enantioselectivity was determined by chiral HPLC analysis of the isolated product. The absolute configuration of *N*-TBS imine **1d** was determined by the X-ray crystal structure of its analogue **S2**, and that of product **4d** was determined by its X-ray crystal structure (Figure S1).

(*1S*,*3S*)-1-(*tert*-butyl)-3-(difluoromethyl)-3-phenylbenzo[*d*]isothiazole 1-oxide (**4d**)



Mp: 145–148 °C. $[\alpha]_D^{20}$ –183.8 (*c* 0.60, $CHCl_3$), >99:1 er. The enantiomeric ratio was determined by Lux 5u Cellulose–2 (250 × 4.6 mm), hexane / IPA= 80 / 20 (v/v%), 0.7 mL/min, λ = 214 nm, t_R (major) = 9.03 min, t_R (minor) = 9.68 min. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.40–7.28 (m, 3H), 6.09 (t, *J* = 56.5 Hz, 1H), 1.33 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –123.4 (dd, *J* = 267.4, 56.5 Hz, 1F), –124.9 (dd, *J* = 267.3, 56.4 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3 (d, *J* = 1.2 Hz), 138.5 (d, *J* = 2.4 Hz), 136.6, 132.7, 130.2, 128.3, 128.1, 127.9, 127.8 (dd, *J* = 3.3, 1.6 Hz), 124.7, 117.1 (t, *J* = 249.8 Hz), 79.2 (t, *J* = 21.1 Hz), 62.6, 24.2. IR (film) 1448, 1365, 1226, 1105, 1064, 965, 753, 705 cm^{-1}. MS (ESI, *m/z*): 336.2 (M + H^+). Anal. Calcd for $C_{18}H_{19}F_2NOS$: C, 64.46; H, 5.71; N, 4.18; Found: C, 64.43; H, 5.77; N, 4.01.



Typical Procedures:

Method A (at rt for compounds **5a-l**, **5p**, and **5u**):

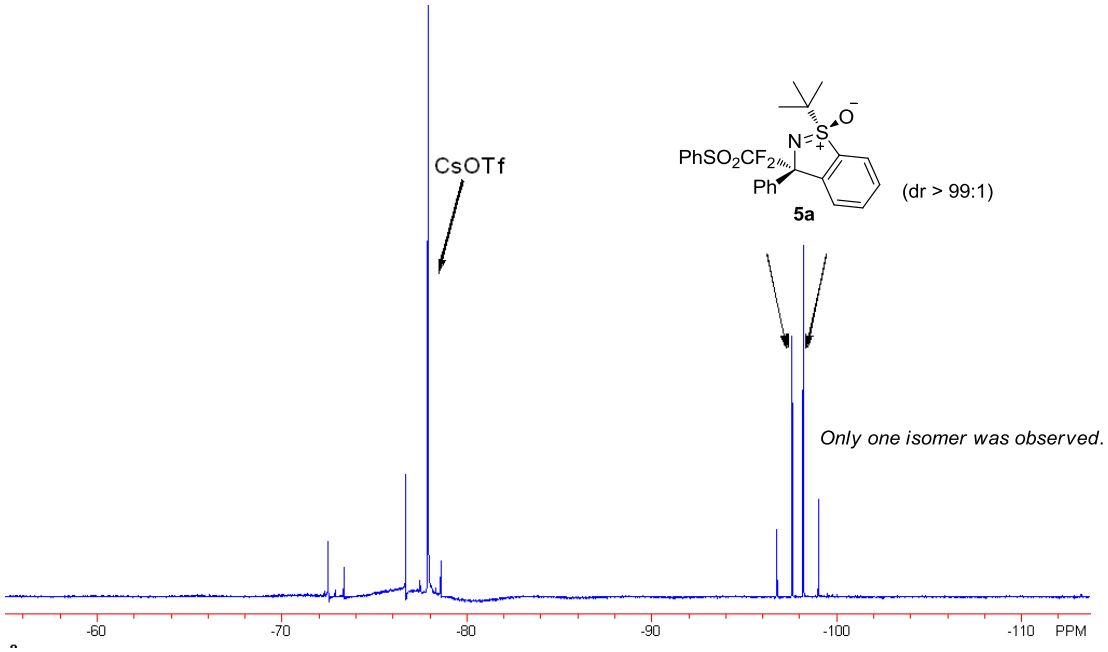
To a Schlenk tube containing sulfinimine (*R*)-**2a** (R^1 = Ph) (0.120 g, 0.3 mmol), aryne precursor **3a** (R^2, R^3 = H) (0.268 g, 0.9 mmol), and CH_3CN (5.0 mL) was added CsF (0.228 g, 1.5 mmol). The tube was sealed, and then the reaction mixture was stirred at room temperature for 12 h. After quenched with brine, the reaction mixture was extracted with Et_2O (30 mL × 3), and the combined organic phase was dried over anhydrous $MgSO_4$. The volatile solvents were removed under vacuum, and the crude product was

purified by column chromatography (silica gel; ethyl acetate/petroleum ether = 1:3 v/v) to give product (*Ss*,*R*)-**5a** (R^1 = Ph; R^2, R^3 = H) as a white solid (0.124 g, 87% yield).

Method B (at 80 °C for compounds **5m-o** and **5q-t**):

To a Schlenk tube containing sulfinimine (*R*)-**2a** (R^1 = Ph) (0.239 g, 0.6 mmol), aryne precursor **3d** (R^2, R^3 = OMe) (0.644 g, 1.8 mmol), and CH_3CN (5.0 mL) was added CsF (0.456 g, 3.0 mmol). The tube was sealed, and then the reaction mixture was stirred at 80 °C for 12 h. After cooled to rt and quenched with brine, the reaction mixture was extracted with Et_2O (40 mL × 3), and the combined organic phase was dried over anhydrous $MgSO_4$. The volatile solvents were removed under vacuum, and the crude product was purified by column chromatography (silica gel; ethyl acetate/petroleum ether = 1:1.5 v/v) to give product (*Ss*,*R*)-**5s** (R^1 = Ph; R^2, R^3 = OMe) as a white solid (0.200 g, 62% yield).

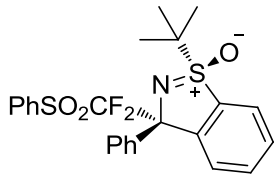
Example of Diastereoselectivity Determination by ^{19}F NMR



Characterization Data:

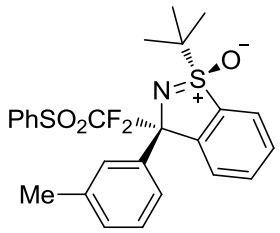
(1*S*,3*R*)-1-(*tert*-Butyl)-3-[difluoro(phenylsulfonyl)methyl]-3-phenylbenzo[*d*]isothiazole

1-oxide (**5a**)



Mp: 138–140 °C. $[\alpha]_D^{22}$ –45.1 (*c* 0.80, $CHCl_3$), >99:1 er. The enantiomeric ratio was determined by CHIRALPAK OD (250 × 4.6 mm), hexane / IPA= 60 / 40 (v/v), 0.7 mL/min, λ = 214 nm, t_R (major) = 8.69 min, t_R (minor) = 10.24 min. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03–7.87 (m, 5H), 7.69–7.55 (m, 3H), 7.47 (t, *J* = 7.4 Hz, 3H), 7.26 (d, *J* = 7.4 Hz, 3H), 1.47 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –97.7 (d, *J* = 233.9 Hz, 1F), –100.0 (d, *J* = 233.8 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 138.9, 136.1, 134.9, 134.6, 133.0, 131.1, 129.9, 128.7, 128.2, 128.0, 127.5 (d, *J* = 5.2 Hz), 126.0 (d, *J* = 1.9 Hz), 123.6, 122.7 (t, *J* = 298.7 Hz), 80.9 (t, *J* = 23.5 Hz), 63.6, 24.7 (d, *J* = 1.4 Hz). IR (film): 3061, 1585, 1451, 1360, 1222, 1153, 1113 cm^{-1}. MS (ESI, *m/z*): 498.1 ($M + Na^+$). Anal. Calcd for $C_{24}H_{23}F_2NO_3S_2$: C, 60.61; H, 4.87; N, 2.95; Found: C, 60.93; H, 4.78; N, 2.73.

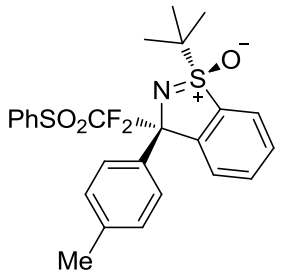
(1*S*,3*R*)-1-(*tert*-Butyl)-3-[difluoro(phenylsulfonyl)methyl]-3-(*m*-tolyl)benzo[*d*]isothiazole 1-oxide (**5b**)



Mp: 147–149 °C. $[\alpha]_D^{22}$ –42.6 (*c* 0.75, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (d, *J* = 7.8 Hz, 1H), 7.90 (d, *J* = 7.4 Hz, 2H), 7.77–7.55 (m, 5H), 7.47 (q, *J* = 7.0 Hz, 3H), 7.15 (t, *J* = 7.7 Hz, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 2.30 (s, 3H), 1.51 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –97.1 (d, *J* = 234.3 Hz, 1F), –99.8 (d, *J* = 234.3 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9 (d, *J* = 1.8 Hz), 138.8 (t, *J* = 2.8 Hz), 137.5, 136.1, 135.0, 134.6,

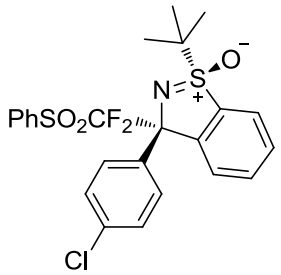
133.0, 131.1, 129.9, 129.0, 128.7, 128.3 (d, J = 3.7 Hz), 127.9, 126.1 (d, J = 2.8 Hz), 124.5 (d, J = 6.4 Hz), 123.6, 122.8 (t, J = 296.9 Hz), 80.9 (t, J = 21.8 Hz), 63.7, 24.8 (d, J = 2.4 Hz), 21.8. IR (film): 1736, 1449, 1349, 1224, 1113, 964, 755, 607 cm^{-1}. MS (ESI, *m/z*): 512.1 (M + Na^+). HRMS (ESI): calcd. for $C_{25}H_{25}F_2NO_3S_2$: (M + Na^+): 512.1136; Found: 512.1143.

(1*S*,3*R*)-1-(*tert*-Butyl)-3-[difluoro(phenylsulfonyl)methyl]-3-(*p*-tolyl)benzo[*d*]isothiazole 1-oxide (**5c**)



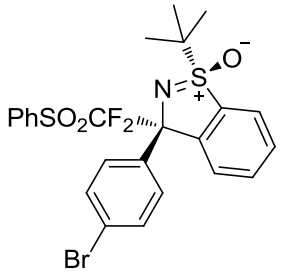
Mp: 148–150 °C. $[\alpha]_D^{23}$ –35.9 (*c* 0.90, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (d, J = 7.9 Hz, 1H), 7.92 (d, J = 7.9 Hz, 2H), 7.83 (d, J = 7.6 Hz, 2H), 7.69–7.55 (m, 3H), 7.48 (t, J = 7.9 Hz, 3H), 7.08 (d, J = 7.6 Hz, 2H), 2.28 (s, 3H), 1.46 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –98.0 (d, J = 233.1 Hz, 1F), –99.9 (d, J = 233.1 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2 (d, J = 2.6 Hz), 138.1, 136.3, 136.2 (t, J = 2.6 Hz), 135.0, 134.7, 133.2, 131.3, 129.9, 129.0, 128.9, 127.6 (d, J = 4.8 Hz), 126.2 (d, J = 3.1 Hz), 123.8, 122.9 (t, J = 295.3 Hz), 80.9 (t, J = 21.4 Hz), 63.7, 24.9 (d, J = 2.5 Hz), 21.2. IR (film): 1450, 1337, 1330, 1213, 1171, 1114 cm^{-1}. MS (ESI, *m/z*): 512.1 (M + Na^+). HRMS (ESI): calcd. for $C_{25}H_{25}F_2NO_3S_2$: (M + H^+): 490.1317; Found: 490.1328.

(1*S*,3*R*)-1-(*tert*-Butyl)-3-(4-chlorophenyl)-3-[difluoro(phenylsulfonyl)methyl]benzo[*d*]iso thiazole 1-oxide (**5d**)



Mp: 139–141 °C. $[\alpha]_D^{23}$ –36.7 (*c* 1.00, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 4H), 7.71–7.57 (m, 3H), 7.55–7.46 (m, 3H), 7.23 (d, *J* = 8.5 Hz, 2H), 1.46 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –97.9 (d, *J* = 239.4 Hz, 1F), –100.5 (d, *J* = 239.4 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6 (d, *J* = 1.7 Hz), 137.8 (t, *J* = 2.6 Hz), 136.1, 135.1, 134.9, 134.5, 133.4, 131.2, 130.3, 129.2 (d, *J* = 5.1 Hz), 129.0, 128.3, 126.0 (d, *J* = 2.9 Hz), 123.9, 122.6 (t, *J* = 296.8 Hz), 80.6 (t, *J* = 21.8 Hz), 63.9, 24.9 (d, *J* = 2.3 Hz). IR (film): 1492, 1445, 1344, 1221, 1168, 1114, 963 cm^{-1}. MS (ESI, *m/z*): 532.1 ($M + Na^+$). Anal. Calcd for $C_{24}H_{22}ClF_2NO_3S_2$: C, 56.52; H, 4.35; N, 2.75; Found: C, 56.16; H, 4.45; N, 2.55.

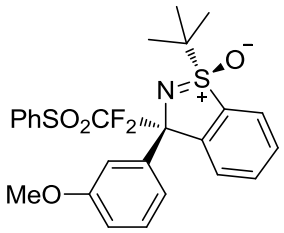
(1*S*,3*R*)-3-(4-Bromophenyl)-1-(*tert*-butyl)-3-[difluoro(phenylsulfonyl)methyl]benzo[*d*]iso thiazole 1-oxide (**5e**)



Mp: 148–150 °C. $[\alpha]_D^{23}$ –35.5 (*c* 0.90, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.71–7.57 (m, 3H), 7.55–7.45 (m, 3H), 7.38 (d, *J* = 8.0 Hz, 2H), 1.46 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –97.9 (d, *J* = 238.6 Hz, 1F), –100.5 (d, *J* = 236.3 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5 (d, *J* = 2.3 Hz), 138.4 (t, *J* = 2.9 Hz), 136.0, 135.1, 134.9, 133.4, 131.3, 131.2, 130.3, 129.6 (dd, *J* = 5.2, 1.7 Hz), 129.0, 126.0 (d, *J* = 2.9 Hz), 123.9, 122.9, 122.6 (t, *J* =

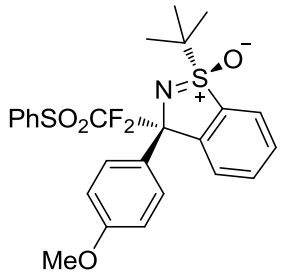
298.3 Hz), 80.7 (t, *J* = 21.8 Hz), 63.9, 24.9 (d, *J* = 2.3 Hz). IR (film): 1580, 1487, 1446, 1335, 1223, 1154, 1012, 961 cm^{-1}. MS (ESI, *m/z*): 576.0 ($M + Na^+$). HRMS (ESI): calcd. for $C_{24}H_{22}BrF_2NO_3S_2$: ($M + H^+$): 554.0265; Found: 554.0277.

(1*S*,3*R*)-1-(*tert*-Butyl)-3-[difluoro(phenylsulfonyl)methyl]-3-(3-methoxyphenyl)benzo[*d*]isothiazole 1-oxide (**5f**)



Mp: 126–128 °C. $[\alpha]_D^{23}$ –42.7 (*c* 0.80, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.6 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 2H), 7.69–7.43 (m, 8H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.76 (dd, *J* = 8.0, 2.7 Hz, 1H), 3.76 (s, 3H), 1.49 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –97.2 (d, *J* = 231.0 Hz, 1F), –99.8 (d, *J* = 231.0 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 147.7, 140.6, 136.0, 134.9, 134.6, 133.0, 131.1, 129.9, 128.8, 128.7, 126.0 (d, *J* = 2.2 Hz), 123.6, 122.7 (t, *J* = 300.0 Hz), 119.7 (d, *J* = 8.0 Hz), 113.7, 113.6, 80.9 (t, *J* = 22.1 Hz), 63.6, 55.2, 24.7 (d, *J* = 1.6 Hz). IR (film): 1736, 1604, 1584, 1450, 1347, 1223, 1113, 755 cm^{-1}. MS (ESI, *m/z*): 528.1 ($M + Na^+$). HRMS (ESI): calcd. for $C_{25}H_{25}F_2NO_4S_2$: ($M + H^+$): 506.1266; Found: 506.1288.

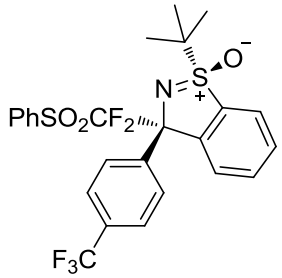
(1*S*,3*R*)-1-(*tert*-Butyl)-3-[difluoro(phenylsulfonyl)methyl]-3-(4-methoxyphenyl)benzo[*d*]isothiazole 1-oxide (**5g**)



Mp: 149–151 °C. $[\alpha]_D^{23}$ –28.4 (*c* 0.80, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 7.98 (d, *J*

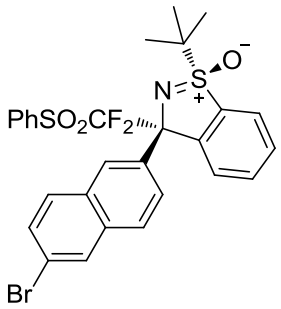
= 8.0 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.69–7.55 (m, 3H), 7.48 (t, *J* = 7.5 Hz, 3H), 6.78 (d, *J* = 8.0 Hz, 2H), 3.74 (s, 3H), 1.47 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –97.9 (d, *J* = 233.0 Hz, 1F), –100.2 (d, *J* = 233.1 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 148.1, 136.1, 134.7, 134.5, 132.9, 130.9, 130.8 (t, *J* = 2.9 Hz), 129.7, 128.8 (d, *J* = 5.1 Hz), 128.6, 125.8 (d, *J* = 3.3 Hz), 123.5, 122.6 (t, *J* = 297.8 Hz), 113.2, 80.5 (t, *J* = 21.8 Hz), 63.4, 55.1, 24.6 (d, *J* = 2.4 Hz). IR (film): 1608, 1510, 1450, 1344, 1253, 1218, 1181, 1114 cm^{-1}. MS (ESI, *m/z*): 528.1 (M + Na$^+$). HRMS (ESI): calcd. for $C_{25}H_{25}F_2NO_4S_2$: (M + Na$^+$): 528.1085; Found: 528.1102.

(*1S,3R*)-1-(*tert*-Butyl)-3-[difluoro(phenylsulfonyl)methyl]-3-[4-(trifluoromethyl)phenyl]benzo[*d*]isothiazole 1-oxide (**5h**)



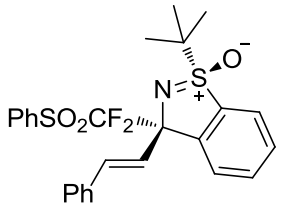
White solid. M.p.: 154–156 ^{o}C. $[\alpha]_D^{29}$ = –35.5 (*c* = 0.95, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08 (d, *J* = 7.8 Hz, 2H), 7.98 (d, *J* = 7.5 Hz, 1H), 7.95 (d, *J* = 7.5 Hz, 2H), 7.71–7.59 (m, 4H), 7.56–7.46 (m, 4H), 1.49 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –61.7 (s, 3F), –96.2 (d, *J* = 234.9 Hz, 1F), –99.3 (d, *J* = 235.8 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 143.1, 135.8, 135.1, 134.8, 133.3, 131.0, 130.7, 130.3 (q, *J* = 32.1 Hz), 128.8, 128.0 (d, *J* = 5.1 Hz), 125.9 (d, *J* = 2.9 Hz), 124.9 (d, *J* = 3.6 Hz), 124.1 (q, *J* = 270.6 Hz), 123.8, 122.4 (t, *J* = 296 Hz), 80.6 (t, *J* = 21.9 Hz), 63.8, 24.6. IR (KBr): 3073, 2981, 1616, 1450, 1316, 1224, 1124, 1045, 963, 828, 8005, 605, 555 cm^{-1}. MS (ESI, *m/z*): 566 ([M+Na]$^+$). HRMS (ESI, *m/z*): Calcd. for $C_{25}H_{22}F_5NNaO_3S_2$ ([M + Na]$^+$): 566.0859; Found: 566.0863.

(1*S*,3*R*)-3-(6-Bromonaphthalen-2-yl)-1-(*tert*-butyl)-3-[difluoro(phenylsulfonyl)methyl)benzo[*d*]isothiazole 1-oxide (**5i**)



Mp: 100–103 °C. $[\alpha]_D^{20}$ –36.0 (*c* 0.80, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.40 (s, 1H), 8.06 (t, *J* = 7.9 Hz, 2H), 7.90 (s, 1H), 7.87 (d, *J* = 7.4 Hz, 2H), 7.69 (t, *J* = 8.3 Hz, 2H), 7.65–7.44 (m, 5H), 7.40 (t, *J* = 7.9 Hz, 2H), 1.52 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –96.6 (d, *J* = 234.3 Hz, 1F), –99.6 (d, *J* = 234.2 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3 (d, *J* = 2.1 Hz), 136.8 (t, *J* = 2.1 Hz), 135.6, 134.8, 134.6, 133.8, 133.1, 131.2, 130.9, 130.5, 129.9, 129.2, 129.1, 128.6, 127.3 (d, *J* = 2.2 Hz), 126.5, 125.9 (d, *J* = 2.8 Hz), 125.8, 123.7, 122.5 (t, *J* = 299.9 Hz), 120.3, 80.8 (t, *J* = 21.6 Hz), 63.6, 24.6 (d, *J* = 2.3 Hz). IR (film): 1734, 1585, 1449, 1348, 1223, 1154, 1113, 1062 cm^{-1}. MS (ESI, *m/z*): 626.1 (M + Na^+). HRMS (ESI): calcd. for $C_{28}H_{24}BrF_2NO_3S_2$: (M + Na^+): 626.0241; Found: 626.0272.

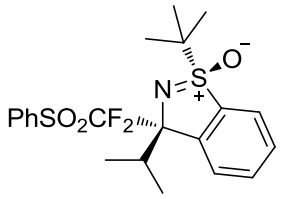
(1*S*,3*R*)-1-(*tert*-Butyl)-3-[difluoro(phenylsulfonyl)methyl]-3-[(*E*)-styryl]benzo[*d*]isothiazole 1-oxide (**5j**)



Mp: 145–147 °C. $[\alpha]_D^{23}$ –34.6 (*c* 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.7 Hz, 2H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.65–7.46 (m, 5H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.28–7.14 (m, 3H), 6.91 (d, *J* = 15.3 Hz, 1H), 6.72 (dd, *J* = 15.2, 3.3 Hz, 1H), 1.48 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –100.9 (d, *J* = 235.2 Hz, 1F), –105.4 (d, *J* = 233.0 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.8 (d, *J* = 3.0 Hz), 136.3, 135.6, 134.8, 134.2, 133.1, 131.6, 131.2, 130.0, 128.7, 128.2, 127.7, 127.1, 126.0 (dd, *J* = 3.7, 2.4 Hz), 125.4

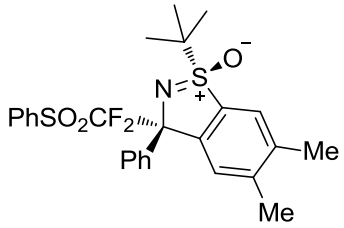
(d, *J* = 4.3 Hz), 124.1, 122.3 (t, *J* = 298.1 Hz), 80.4 (t, *J* = 21.7, Hz), 63.4, 24.6 (d, *J* = 2.3 Hz). IR (film): 1581, 1449, 1341, 1222, 1156, 1113, 1017, 600 cm^{-1}. MS (ESI, *m/z*): 524.1 (M + Na^+). Anal. Calcd for $C_{26}H_{25}F_2NO_3S_2$: C, 62.26; H, 5.02; N, 2.79; Found: C, 61.96; H, 5.12; N, 2.62.

(1*S*,3*R*)-1-(*tert*-Butyl)-3-[difluoro(phenylsulfonyl)methyl]-3-isopropylbenzo[*d*]isothiazole 1-oxide (**5k**)



Mp: 58–60 °C. $[\alpha]_D^{23}$ –25.8 (*c* 0.60, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.62–7.50 (m, 4H), 3.17–3.05 (m, 1H), 1.39 (s, 9H), 1.02 (dd, *J* = 6.6, 3.6 Hz, 3H), 0.91 (d, *J* = 7.0 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –92.8 (d, *J* = 240.4 Hz, 1F), –94.2 (d, *J* = 240.4 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2 (d, *J* = 3.5 Hz), 136.9, 135.6, 134.7, 132.3, 130.8, 129.9, 128.9, 126.3 (d, *J* = 3.0 Hz), 123.7, 123.6 (t, *J* = 295.7 Hz), 84.8 (dd, *J* = 20.1, 16.5 Hz), 63.7, 34.9, 24.7, 19.1 (d, *J* = 2.9 Hz), 18.6 (d, *J* = 7.5 Hz). IR (film): 2973, 1449, 1349, 1222, 1157, 1104, 754, 589 cm^{-1}. MS (ESI, *m/z*): 464.1 (M + Na^+). HRMS (ESI): calcd. for $C_{21}H_{25}F_2NO_3S_2$: (M + Na^+): 464.1136; Found: 464.1152.

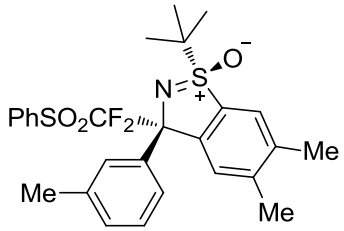
(1*S*,3*R*)-1-(*tert*-Butyl)-3-[difluoro(phenylsulfonyl)methyl]-5,6-dimethyl-3-phenylbenzo[*d*]isothiazole 1-oxide (**5l**)



Mp: 95–97 °C. $[\alpha]_D^{23}$ –11.5 (*c* 0.90, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 7.90–7.78

(m, 4H), 7.63 (s, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.31 (s, 1H), 7.22–7.10 (m, 3H), 2.26 (s, 3H), 2.19 (s, 3H), 1.37 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –97.4 (d, *J* = 238.9 Hz, 1F), –99.9 (d, *J* = 238.8 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 143.1, 139.4, 136.2, 134.5, 132.6, 131.2, 128.4, 128.04, 128.02, 127.5, 127.4 (d, *J* = 1.3 Hz), 126.6 (d, *J* = 2.9 Hz), 123.9, 122.9 (t, *J* = 295.4 Hz), 80.5 (t, *J* = 22.4 Hz), 63.4, 24.8 (d, *J* = 2.4 Hz), 20.9, 20.1. IR (film): 1449, 1347, 1224, 1164, 1113, 1052, 962, 686 cm^{-1}. MS (ESI, *m/z*): 526.1 (M + Na$^+$). HRMS (ESI): calcd. for $C_{26}H_{27}F_2NO_3S_2$: (M + H$^+$): 504.1473; Found: 504.1485.

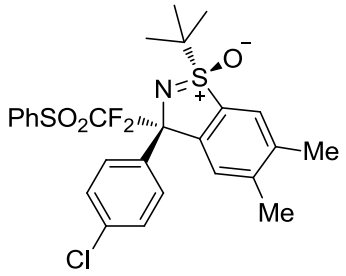
(1*S*,3*R*)-1-(*tert*-Butyl)-3-[difluoro(phenylsulfonyl)methyl]-5,6-dimethyl-3-(m-tolyl)benzo[*d*]isothiazole 1-oxide (**5m**)



White solid. Mp: 143–144 ^{o}C. $[\alpha]_D^{28}$ = –11.2 (*c* 0.20, $CHCl_3$). IR (KBr): 2964, 2926, 1604, 1448, 1341, 1367, 1182, 1112, 958, 724, 687, 634, 597, 561 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 (d, *J* = 7.5 Hz, 2H), 7.73–7.67 (m, 3H), 7.62–7.56 (m, 1H), 7.47–7.39 (m, 3H), 7.17–7.15 (m, 1H), 7.01 (d, *J* = 7.2 Hz, 1H), 2.34 (s, 3H), 2.29 (s, 3H), 2.28 (s, 3H), 1.49 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –95.9 (d, *J* = 232.7 Hz, 1F), –99.0 (d, *J* = 231.8 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 142.9, 139.3 (d, *J* = 1.7 Hz), 139.2, 137.4, 136.2, 134.4, 132.6, 131.1, 128.8, 128.5, 128.1 (d, *J* = 4.3 Hz), 127.7, 126.6 (d, *J* = 2.6 Hz), 124.3 (d, *J* = 6.9 Hz), 123.8, 122.9 (t, *J* = 294.7 Hz), 80.5 (t, *J* = 21.6 Hz), 63.3, 24.8 (d, *J* = 2.6 Hz), 21.7, 20.8, 20.0. MS (ESI, *m/z*): 518 ([M + H]$^+$). HRMS (ESI, *m/z*): Calcd. for $C_{27}H_{30}F_2NO_3S_2$ ([M + H]$^+$): 518.1635; found: 518.1614.

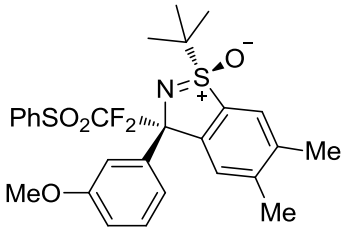
(1*S*,3*R*)-1-(*tert*-Butyl)-3-(4-chlorophenyl)-3-[difluoro(phenylsulfonyl)methyl]-5,6-dimeth

ylbenzo[*d*]isothiazole 1-oxide (**5n**)



Mp: 159–161 °C. $[\alpha]_D^{22}$ –1.0 (*c* 0.75, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86–7.78 (m, 4H), 7.56 (t, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.32 (s, 1H), 7.14 (d, *J* = 8.2 Hz, 2H), 2.27 (s, 3H), 2.21 (s, 3H), 1.36 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –97.6 (d, *J* = 231.8 Hz, 1F), –100.4 (d, *J* = 231.9 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 143.3, 139.6, 138.2, 136.1, 134.6, 134.1, 132.5, 131.0, 129.0 (d, *J* = 5.5 Hz), 128.8, 128.0, 126.3 (d, *J* = 2.9 Hz), 123.9, 122.6 (t, *J* = 298.1 Hz), 80.1 (t, *J* = 21.9 Hz), 63.4, 24.7 (d, *J* = 1.8 Hz), 20.8, 20.0. IR (film): 1492, 1449, 1348, 1224, 1165, 964, 686 cm^{-1}. MS (ESI, *m/z*): 560.1 (M + Na^+). HRMS (ESI): calcd. for $C_{26}H_{26}ClF_2NO_3S_2$: (M + Na^+): 560.0903; Found: 560.0898.

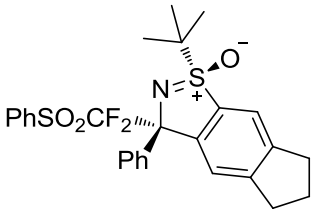
(1*S*,3*R*)-1-(*tert*-Butyl)-3-(difluoro(phenylsulfonyl)methyl)-3-(3-methoxyphenyl)-5,6-dim ethylbenzo[*d*]isothiazole 1-oxide (**5o**)



Mp: 149–151 °C. $[\alpha]_D^{21}$ –6.8 (*c* 0.75, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.7 Hz, 2H), 7.66 (s, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 3H), 7.40 (s, 1H), 7.18 (t, *J* = 8.1 Hz, 1H), 6.75 (dd, *J* = 8.2, 2.5 Hz, 1H), 3.76 (s, 3H), 2.33 (s, 3H), 2.28 (s, 3H), 1.48 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –96.7 (d, *J* = 229.8 Hz, 1F), –99.5 (d, *J* = 229.8 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 145.7, 142.9, 140.9, 139.3, 136.1, 134.4, 132.4, 131.1, 128.8, 128.5, 126.5, 123.7, 122.8 (t, *J* =

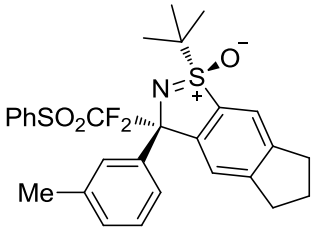
298.8 Hz), 119.5 (d, J = 7.5 Hz), 113.5, 113.4 (d, J = 4.5 Hz), 80.4 (t, J = 21.4 Hz), 63.3, 55.1, 24.7 (d, J = 2.2 Hz), 20.7, 19.9. IR (film): 1600, 1450, 1351, 1223, 1162, 1123, 1055, 968 cm^{-1}. MS (ESI, *m/z*): 556.1 (M + Na^+). HRMS (ESI): calcd. for $C_{27}H_{29}F_2NO_4S_2$: (M + Na^+): 556.1398; Found: 556.1407.

(1*S*,3*R*)-1-(*tert*-Butyl)-3-[difluoro(phenylsulfonyl)methyl]-3-phenyl-3,5,6,7-tetrahydroindeno[5,6-*d*]isothiazole 1-oxide (**5p**)



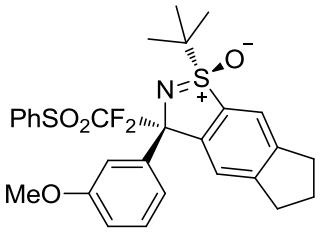
Mp: 85–88 °C. $[\alpha]_D^{22}$ –10.5 (*c* 0.95, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, J = 7.4 Hz, 2H), 7.82 (d, J = 7.8 Hz, 2H), 7.67 (s, 1H), 7.52 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.8 Hz, 3H), 7.23–7.10 (m, 3H), 2.92–2.70 (m, 4H), 2.14–1.92 (m, 2H), 1.38 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –97.4 (d, J = 232.4 Hz, 1F), –99.8 (d, J = 233.8 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.3, 147.4, 146.8, 139.6, 136.3, 134.6, 133.2, 131.0, 128.7, 127.9, 127.5, 127.4, 122.9 (t, J = 297.6 Hz), 121.5 (d, J = 2.9 Hz), 118.9, 80.1 (t, J = 21.3 Hz), 63.3, 32.9, 32.3, 25.9, 24.7 (d, J = 1.4 Hz). IR (film): 2968, 1448, 1347, 1223, 1168, 1112, 1048, 964 cm^{-1}. MS (ESI, *m/z*): 538.2 (M + Na^+). HRMS (ESI): calcd. for $C_{27}H_{27}F_2NO_3S_2$: (M + H^+): 516.1473; Found: 516.1487.

(1*S*,3*R*)-1-(*tert*-Butyl)-3-[difluoro(phenylsulfonyl)methyl]-3-(*m*-tolyl)-3,5,6,7-tetrahydroindeno[5,6-*d*]isothiazole 1-oxide (**5q**)



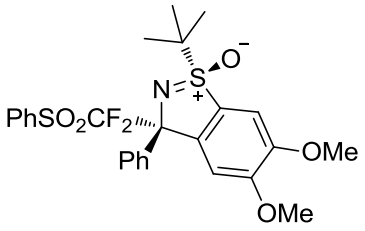
Mp: 92–95 °C. $[\alpha]_D^{22}$ –8.5 (*c* 0.80, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 (d, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.9 Hz, 3H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 3H), 7.07 (t, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 7.4 Hz, 1H), 2.92–2.70 (m, 4H), 2.21 (s, 3H), 2.13–1.93 (m, 2H), 1.41 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –96.5 (d, *J* = 232.7 Hz, 1F), –99.6 (d, *J* = 234.7 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2, 147.2, 146.9, 139.3, 137.4, 136.2, 134.4, 133.2, 131.0, 128.8, 128.5, 128.1 (d, *J* = 4.6 Hz), 127.8, 124.3 (d, *J* = 6.8 Hz), 123.0 (t, *J* = 298.4 Hz), 121.5 (d, *J* = 3.0 Hz), 118.8, 80.1 (t, *J* = 21.4 Hz), 63.4, 32.9, 32.3, 25.9, 24.8 (d, *J* = 2.3 Hz), 21.8. IR (film): 2968, 1449, 1348, 1223, 1167, 1116, 964, 597 cm^{-1}. MS (ESI, *m/z*): 552.2 (M + Na^+). HRMS (ESI): calcd. for $C_{28}H_{29}F_2NO_3S_2$: (M + Na^+): 552.1449; Found: 552.1454.

(1*S*,3*R*)-1-(*tert*-Butyl)-3-[difluoro(phenylsulfonyl)methyl]-3-(3-methoxyphenyl)-3,5,6,7-tetrahydroindeno[5,6-*d*]isothiazole 1-oxide (**5r**)



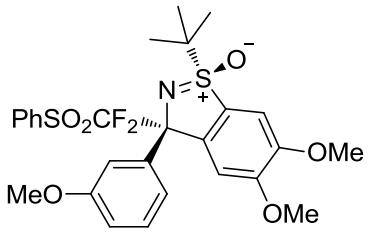
Mp: 83–86 °C. $[\alpha]_D^{21}$ –4.7 (*c* 0.70, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.7 Hz, 2H), 7.70 (s, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 4H), 7.17 (t, *J* = 8.2 Hz, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 3.76 (s, 3H), 3.01–2.78 (m, 4H), 2.22–2.00 (m, 2H), 1.48 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –96.6 (d, *J* = 234.5 Hz, 1F), –99.5 (d, *J* = 234.6 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 151.3, 147.3, 146.8, 141.1, 136.2, 134.4, 133.2, 131.1, 128.8, 128.6, 123.0 (t, *J* = 300.4 Hz), 121.5 (d, *J* =3.3 Hz), 119.5 (d, *J* = 7.7 Hz), 118.8, 113.5, 113.4, 80.1 (t, *J* = 21.7 Hz), 63.4, 55.2, 32.9, 32.3, 25.9, 24.8 (d, *J* = 2.2 Hz). IR (film): 2960, 1601, 1450, 1347, 1222, 1167, 1116, 1049 cm^{-1}. MS (ESI, *m/z*): 568.2 (M + Na^+). HRMS (ESI): calcd. for $C_{28}H_{29}F_2NO_4S_2$: (M + Na^+): 568.1398; Found: 568.1393.

(1*S*,3*R*)-1-(*tert*-Butyl)-3-[difluoro(phenylsulfonyl)methyl]-5,6-dimethoxy-3-phenylbenzo[*d*]isothiazole 1-oxide (**5s**)



Mp: 135–137 °C. $[\alpha]_D^{22}$ –29.9 (*c* 0.85, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92 (t, *J* = 7.3 Hz, 4H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.9 Hz, 2H), 7.35–7.20 (m, 4H), 6.98 (s, 1H), 3.96 (s, 3H), 3.83 (s, 3H), 1.45 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –97.2 (d, *J* = 233.4 Hz, 1F), –99.4 (d, *J* = 233.3 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4, 150.7, 141.9, 139.3, 136.1, 134.6, 131.1, 128.7, 128.1, 127.2, 127.1, 126.0, 122.9 (t, *J* = 297.8 Hz), 107.1, 104.4, 80.4 (t, *J* = 21.4 Hz), 63.4, 56.4, 56.3, 27.8 (d, *J* = 2.3 Hz). IR (film): 1585, 1501, 1449, 1348, 1279, 1218, 1168 cm^{-1}. MS (ESI, *m/z*): 558.1 ($M + Na^+$). HRMS (ESI): calcd. for $C_{26}H_{27}F_2NO_5S_2$: ($M + Na^+$): 558.1191; Found: 558.1193.

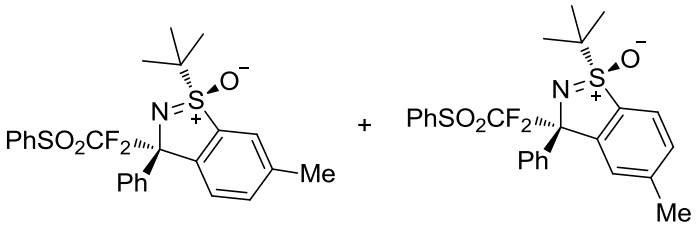
(1*S*,3*R*)-1-(*tert*-Butyl)-3-[difluoro(phenylsulfonyl)methyl]-5,6-dimethoxy-3-(3-methoxyphenyl)benzo[*d*]isothiazole 1-oxide (**5t**)



Mp: 81–83 °C. $[\alpha]_D^{21}$ –21.2 (*c* 0.80, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.53–7.42 (m, 4H), 7.28 (s, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.98 (s, 1H), 6.76 (dd, *J* = 8.0, 2.5 Hz, 1H), 3.94 (s, 3H), 3.85 (s, 3H), 3.76 (s, 3H), 1.46 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –96.5 (d, *J* = 234.8 Hz, 1F), –99.1 (d, *J* =

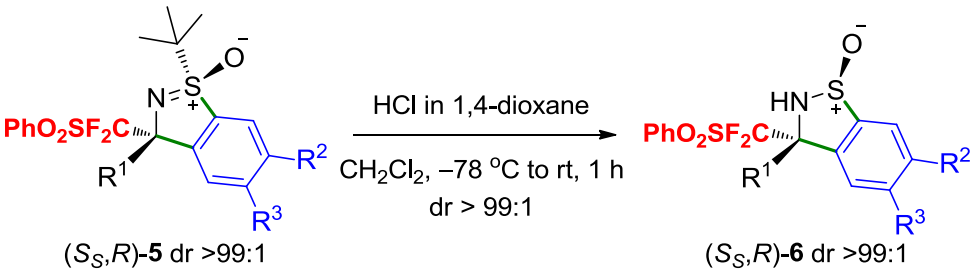
234.9 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 153.4, 150.8, 141.8, 141.0 (t, J = 3.0 Hz), 136.1, 134.5, 131.1, 128.9, 128.6, 126.0, 122.9 (t, J = 297.5 Hz), 119.2 (d, J = 7.2 Hz), 113.5, 113.4, 107.2, 104.5, 80.4 (t, J = 21.1 Hz), 63.5, 56.4, 56.3, 55.2, 24.8 (d, J = 1.5 Hz). IR (film): 1601, 1500, 1348, 1279, 1217, 1170, 1056 cm^{-1}. MS (ESI, *m/z*): 588.1 (M + Na^+). HRMS (ESI): calcd. for $C_{27}H_{29}F_2NO_6S_2$: (M + Na^+): 588.1297; Found: 588.1294.

(1*S*,3*R*)-1-(*tert*-Butyl)-3-[difluoro(phenylsulfonyl)methyl]-6-methyl-3-phenylbenzo[*d*]isothiazole 1-oxide and (1*S*,3*R*)-1-(*tert*-butyl)-3-[difluoro(phenylsulfonyl)methyl]-5-methyl-3-phenylbenzo[*d*]isothiazole 1-oxide (**5u**)



A mixture of two inseperable regio-isomers. $[\alpha]_D^{28}$ –24.4 (*c* 0.95, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00–7.83 (m, 4.54H), 7.75 (s, 0.46H), 7.61 (t, J = 7.5 Hz, 1H), 7.56–7.17 (m, 7H), 2.44 (s, 1.38H), 2.38 (s, 1.62H), 1.47 (s, 4.86H), 1.44 (s, 4.14H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –97.4 (d, J = 233.9 Hz, 0.46F), –97.7 (d, J = 234.2 Hz, 0.54F), –99.9 (d, J = 234.2 Hz, 0.46F), –100.0 (d, J = 234.1 Hz, 0.54F). MS (ESI, *m/z*): 512.4 (M + Na^+). HRMS (ESI): calcd. for $C_{25}H_{25}F_2NO_3S_2$: (M + Na^+): 512.1136; Found: 512.1139.

3.2 Synthesis of Cyclic Sulfinamides

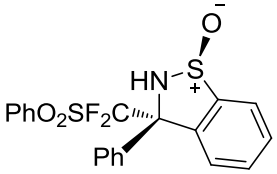


Typical Procedures:

To a solution of (*Ss*,*R*)-**5a** (R^1 = Ph; R^2, R^3 = H) (3.92 g, 8.25 mmol) in CH_2Cl_2 (40 mL) was added HCl (2.5 M in 1,4-dioxane, 66 mL, 165 mmol) at –78 °C. Then the reaction mixture was allowed to warm up to room temperature in 1 h. The reaction mixture was diluted with water (20 mL) and treated with saturated $NaHCO_3$ solution (200 mL). The aqueous phase was extracted with ethyl acetate (40 mL × 3), and the combined organic phases were washed with brine (40 mL) and dried over Na_2SO_4. The volatile solvents were removed under vacuum, and the residue was purified by flash column chromatography (silica gel; ethyl acetate/petroleum ether = 1:3 v/v) to give cyclic sulfinamide (*Ss*,*R*)-**6a** (R^1 = Ph; R^2, R^3 = H) as a white solid (3.310 g, 96% yield).

Characterization Data:

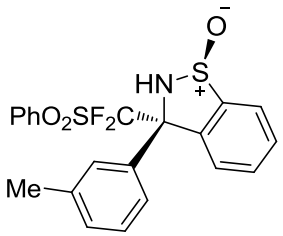
(1*S*,3*R*)-3-[Difluoro(phenylsulfonyl)methyl]-3-phenyl-2,3-dihydrobenzo[*d*]isothiazole 1-oxide **(6a)**



Mp: 165–167 °C. $[\alpha]_D^{26}$ –90.4 (*c* 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, J = 6.0 Hz, 2H), 7.87–7.76 (m, 3H), 7.70 (t, J = 7.1 Hz, 2H), 7.62–7.47 (m, 4H), 7.34 (d, J = 5.5 Hz, 3H), 6.48 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –99.3 (d, J = 237.5 Hz, 1F), –100.9 (d, J = 237.4 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 137.9, 135.8, 135.4, 133.6, 131.9, 130.6, 130.4, 129.2, 129.0, 128.7, 126.8 (dd, J = 3.9, 2.0 Hz), 125.6 (dd, J =

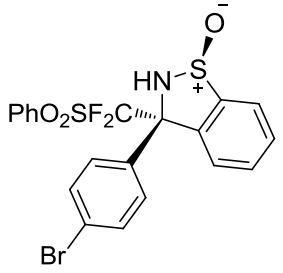
3.1, 1.6 Hz), 125.4, 120.9 (dd, J = 301.7, 299.2 Hz), 79.8 (t, J = 20.8 Hz). IR (film): 3385, 1633, 1583, 1449, 1339, 1149, 1085, 1060 cm^{-1}. MS (ESI, *m/z*): 420.3 ($M + H^+$). HRMS (ESI): calcd. for $C_{20}H_{15}F_2NO_3S_2$: ($M + H^+$): 420.0534; Found: 420.0531.

(1*S*,3*R*)-3-[Difluoro(phenylsulfonyl)methyl]-3-(*m*-tolyl)-2,3-dihydrobenzo[*d*]isothiazole 1-oxide (**6b**)



White solid. Mp: 135–136 °C. $[\alpha]_D^{26}$ = –85.6 (*c* = 0.85, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 7.83–7.80 (m, 1H), 7.76 (d, J = 7.8 Hz, 2H), 7.70–7.64 (m, 4H), 7.55–7.47 (m, 4H), 7.26–7.19 (m, 1H), 7.11 (d, J = 8.1 Hz, 1H), 6.42 (s, 1H), 2.30 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –97.2 (d, J = 236.6 Hz, 1F), –98.1 (d, J = 236.9 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 138.5, 138.0, 135.9, 135.4, 133.9, 132.0, 130.6, 130.4, 129.9, 129.2, 128.6, 127.5, 125.8, 125.4, 124.0, 121.2 (t, J = 293.1 Hz), 79.9 (t, J = 20.4 Hz), 28.8, 21.7. IR (KBr): 3381, 3064, 1606, 1582, 1448, 1332, 1147, 1080, 1061 cm^{-1}. MS (ESI, *m/z*): 434 ($[M + H]^+$). HRMS (ESI, *m/z*): Calcd. for $C_{21}H_{18}F_2NO_3S_2$ ($[M + H]^+$): 434.0696; Found: 434.0688.

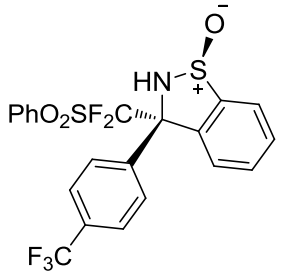
(1*S*,3*R*)-3-(4-Bromophenyl)-3-[difluoro(phenylsulfonyl)methyl]-2,3-dihydrobenzo[*d*]isot hiazole 1-oxide (**6c**)



White solid. Mp: 96–98 °C. $[\alpha]_D^{29}$ = –103.4 (*c* = 1.00, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ7.84–7.71 (m, 6H), 7.65–7.52 (m, 5H), 7.48–7.43 (m, 2H), 6.46 (s, 1H). ^{19}F

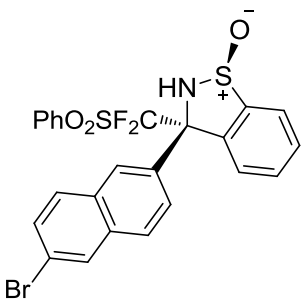
NMR (282 MHz, $CDCl_3$): δ –99.5 (d, J = 236.9 Hz, 1F), –100.5 (d, J = 236.6 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 137.6, 135.6, 135.1, 133.5, 132.1, 131.9, 130.9, 130.5, 129.4, 128.7, 128.6, 125.6, 123.3, 120.8 (t, J = 297.5 Hz), 79.5 (t, J = 21.9 Hz). IR (KBr): 3375, 3068, 1491, 1336, 1150, 1070 cm^{-1}. MS (ESI, *m/z*): 498 ([M + H] $^{+}$). HRMS (ESI, *m/z*): Calcd. for $C_{20}H_{15}BrF_2NO_3S_2^{+}$ ([M + H]$^{+}$): 497.9645; Found: 497.9651.

(1*S*,3*R*)-3-[Difluoro(phenylsulfonyl)methyl]-3-[4-(trifluoromethyl)phenyl]-2,3-dihydrobenzo[*d*]isothiazole 1-oxide (**6d**)



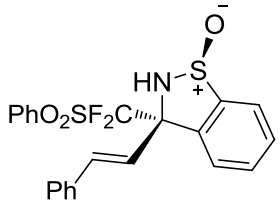
White solid. Mp: 88–90 ^{o}C. $[\alpha]_D^{28}$ = –89.6 (*c* = 0.90, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 (d, J = 8.4 Hz, 2H), 7.85–7.79 (m, 3H), 7.75–7.51 (m, 8H), 6.56 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.4 (s, 3F), –99.8 (d, J = 237.7 Hz, 1F), –100.5 (d, J = 237.7 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.8, 140.0, 137.5, 135.8, 133.3, 132.2, 131.2 (q, J = 32.8 Hz), 131.0, 130.5, 129.4, 127.5, 125.68 (q, J = 3.5 Hz), 125.64, 125.57, 123.8 (q, J = 270.5 Hz), 120.8 (t, J = 296.7 Hz), 79.6 (t, J = 21.1 Hz). IR (KBr): 3207, 1619, 1449, 1329, 1124, 1072 cm^{-1}. MS (ESI, *m/z*): 488 ([M + H]$^{+}$). HRMS (ESI, *m/z*): Calcd. for $C_{21}H_{15}F_5NO_3S_2^{+}$ ([M + H]$^{+}$): 488.0414; Found: 488.0413.

(1*S*,3*R*)-3-(6-Bromonaphthalen-2-yl)-3-[difluoro(phenylsulfonyl)methyl]-2,3-dihydrobenzo[*d*]isothiazole 1-oxide **(6e)**



Mp: 113–115 °C. $[\alpha]_D^{26}$ –105.8 (*c* 0.90, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.38 (s, 1H), 7.98 (d, *J* = 8.6 Hz, 1H), 7.93 (s, 1H), 7.84 (d, *J* = 7.4 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.75–7.49 (m, 7H), 7.44 (t, *J* = 7.4 Hz, 2H), 6.61 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –99.2 (d, *J* = 238.5 Hz, 1F), –100.7 (d, *J* = 238.4 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6, 137.6 (d, *J* = 1.5 Hz), 135.5, 134.1, 133.7 (t, *J* = 1.5 Hz), 133.4, 132.0, 131.2, 130.8, 130.5, 130.4, 129.9, 129.3, 129.2, 127.5, 126.7 (dd, *J* = 3.7, 2.2 Hz), 125.7 (d, *J* = 2.2 Hz), 125.5, 125.1 (dd, *J* = 4.5, 2.3 Hz), 121.1, 120.9 (t, *J* = 299.5 Hz), 79.9 (t, *J* = 22.3 Hz). IR (film): 3370, 1585, 1449, 1336, 1149, 1062 cm^{-1}. MS (ESI, *m/z*): 548.4 ($M + H^+$). HRMS (ESI): calcd. for $C_{24}H_{16}BrF_2NO_3S_2$: ($M + H^+$): 547.9796; Found: 547.9795.

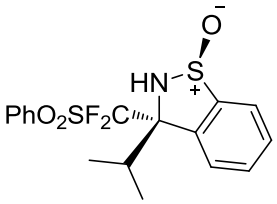
(1*S*,3*R*)-3-[Difluoro(phenylsulfonyl)methyl]-3-[(*E*)-styryl]-2,3-dihydrobenzo[*d*]isothiazol e 1-oxide **(6f)**



Mp: 82–84 °C. $[\alpha]_D^{27}$ –71.4 (*c* 0.70, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 5.8 Hz, 1H), 7.72 (t, *J* = 7.0 Hz, 1H), 7.63–7.51 (m, 5H), 7.41 (d, *J* = 6.4 Hz, 2H), 7.35–7.17 (m, 4H), 6.75 (d, *J* = 15.6 Hz, 1H), 6.27 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –105.9 (d, *J* = 233.6 Hz, 1F), –107.1 (d, *J* = 233.6 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 137.2, 135.6, 135.5, 134.7 (d, *J* = 1.2 Hz), 133.1, 132.0, 130.8, 130.7, 129.3, 128.48, 128.47, 127.3, 125.5, 125.1 (d, *J* = 4.4 Hz), 122.7 (d, *J* = 2.8 Hz),

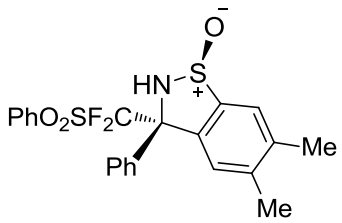
120.2 (t, J = 299.6 Hz), 78.7 (t, J = 20.9 Hz). IR (film): 1449, 1336, 1189, 1151, 1092, 1062 cm^{-1}. MS (ESI, *m/z*): 446.3 ($M + H^+$). HRMS (ESI): calcd. for $C_{22}H_{17}F_2NO_3S_2$: ($M + H^+$): 446.0691; Found: 446.0696.

(1*S*,3*R*)-3-[Difluoro(phenylsulfonyl)methyl]-3-isopropyl-2,3-dihydrobenzo[*d*]isothiazole 1-oxide **(6g)**



Mp: 106–108 °C. $[\alpha]_D^{27}$ –33.8 (*c* 0.60, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 7.84 (d, J = 8.2 Hz, 3H), 7.72 (t, J = 7.7 Hz, 1H), 7.67–7.50 (m, 5H), 5.55 (s, 1H), 2.80–2.65 (m, 1H), 1.11 (d, J = 6.7 Hz, 3H), 0.95 (d, J = 6.7 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –98.6 (d, J = 241.8 Hz, 1F), –101.3 (d, J = 241.8 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.8 (d, J = 1.5 Hz), 135.5 (d, J = 4.5 Hz), 135.3, 133.6, 131.5, 130.9, 130.4, 129.2, 125.5, 125.47 (t, J = 1.9 Hz), 121.7 (t, J = 300.4 Hz), 81.1 (t, J = 25.3 Hz), 33.6, 18.4 (dd, J = 4.9, 1.0 Hz), 17.7 (d, J = 1.8 Hz). IR (film): 2977, 1584, 1450, 1348, 1158, 1047 cm^{-1}. MS (ESI, *m/z*): 386.2 ($M + H^+$). HRMS (ESI): calcd. for $C_{17}H_{17}F_2NO_3S_2$: ($M + H^+$): 386.0691; Found: 386.0687.

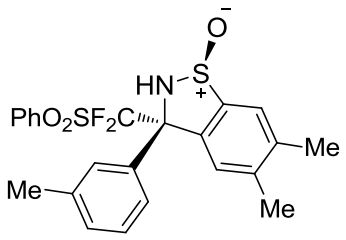
(1*S*,3*R*)-3-[Difluoro(phenylsulfonyl)methyl]-5,6-dimethyl-3-phenyl-2,3-dihydrobenzo[*d*]isothiazole 1-oxide **(6h)**



Mp: 161–163 °C. $[\alpha]_D^{27}$ –88.5 (*c* 0.80, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 7.88 (d, J =

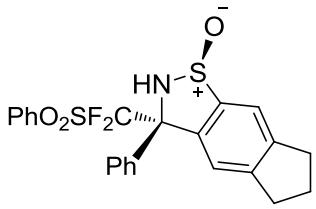
7.5 Hz, 2H), 7.77 (d, J = 7.4 Hz, 2H), 7.67 (t, J = 8.0 Hz, 1H), 7.57–7.45 (m, 3H), 7.38 (s, 1H), 7.37–7.28 (m, 3H), 6.35 (s, 1H), 2.28 (s, 3H), 2.27 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –99.5 (d, J = 239.3 Hz, 1F), –100.8 (d, J = 239.3 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 141.5, 140.0, 136.1, 135.5 (d, J = 0.8 Hz), 135.3, 133.7, 130.3, 129.1, 128.8, 128.6, 126.8 (dd, J = 3.9, 2.4 Hz), 126.2 (dd, J = 2.8, 0.7 Hz), 125.8, 121.0 (t, J = 302.7 Hz), 79.5 (t, J = 21.0 Hz), 20.4, 19.8. IR (film): 1583, 1449, 1338, 1184, 1149, 1066, 686, 587 cm^{-1}. MS (ESI, *m/z*): 448.3 (M + H$^+$). HRMS (ESI): calcd. for $C_{22}H_{19}F_2NO_3S_2$: (M + H$^+$): 448.0847; Found: 448.0842.

(1*S*,3*R*)-3-[Difluoro(phenylsulfonyl)methyl]-5,6-dimethyl-3-(*m*-tolyl)-2,3-dihydrobenzo[*d*]isothiazole 1-oxide (**6i**)



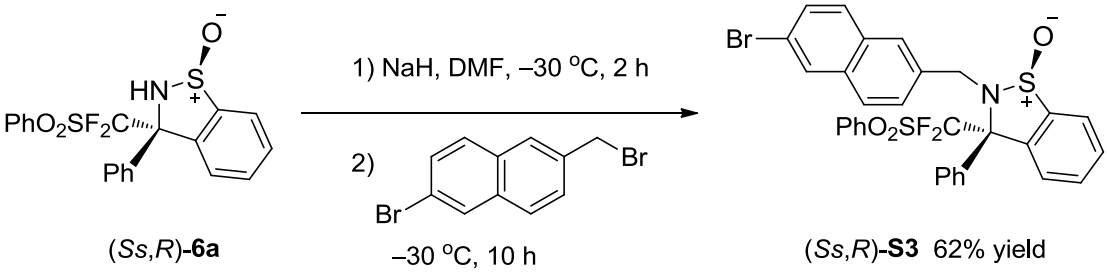
White solid. M.p.: 183–184 ^{o}C. $[\alpha]_D^{26}$ = –63.8 (c = 0.95, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 (d, J = 7.8 Hz, 2H), 7.65 (t, J = 6.3 Hz, 3H), 7.55 (s, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.36 (s, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.10 (d, J = 7.5 Hz, 1H), 6.29 (s, 1H), 2.29 (s, 6H), 2.28 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –98.5 (d, J = 235.8 Hz, 1F), –99.7 (d, J = 236.9 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 141.5, 140.0, 138.4, 136.2, 135.6, 135.3, 134.0, 130.4, 129.7, 129.2, 128.5, 127.5, 126.3, 125.8, 124.0, 121.3 (t, J = 298 Hz), 79.6 (t, J = 20.4 Hz), 21.7, 20.5, 19.9. IR (KBr): 3243, 2921, 1733, 1605, 1448, 1350, 1172, 1148, 1058 cm^{-1}. MS (ESI, *m/z*): 462 ([M + H] $^+$). HRMS (ESI, *m/z*): Calcd. for $C_{23}H_{22}F_2NO_3S_2$ ([M + H]$^+$): 462.1009; Found: 462.1009.

(1*S*,3*R*)-3-[Difluoro(phenylsulfonyl)methyl]-3-phenyl-3,5,6,7-tetrahydro-2*H*-indeno[5,6-*d*]isothiazole 1-oxide **(6j)**



Mp: 191–193 °C. $[\alpha]_D^{27}$ –94.6 (*c* 0.90, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, *J* = 6.7 Hz, 2H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.68 (t, *J* = 7.3 Hz, 1H), 7.59 (s, 1H), 7.50 (t, *J* = 7.3 Hz, 2H), 7.44 (s, 1H), 7.32 (d, *J* = 5.5 Hz, 3H), 6.36 (s, 1H), 3.00–2.80 (m, 4H), 2.20–2.00 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –99.3 (d, *J* = 238.4 Hz, 1F), –100.8 (d, *J* = 238.4 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 147.8, 143.8, 136.2 (d, *J* = 4.5 Hz), 135.3, 133.7, 130.4, 129.1, 128.8, 128.6, 126.8 (d, *J* = 2.1 Hz), 126.7, 121.2 (d, *J* = 2.4 Hz), 120.8, 121.1 (dd, *J* = 301.2, 298.4 Hz), 79.3 (t, *J* = 20.7 Hz), 32.8, 32.4, 25.7. IR (film): 3167, 1583, 1447, 1347, 1145, 1108, 1066, 1042 cm^{-1}. MS (ESI, *m/z*): 460.3 (M + H^+). HRMS (ESI): calcd. for $C_{23}H_{19}F_2NO_3S_2$: (M + H^+): 460.0847; Found: 460.0846.

3.3 *N*-(6-Bromonaphthalen-2-yl)methylation of Cyclic Sulfinamide 6a



(*Ss*,*R*)-**6a** (*Ss*,*R*)-**S3** 62% yield

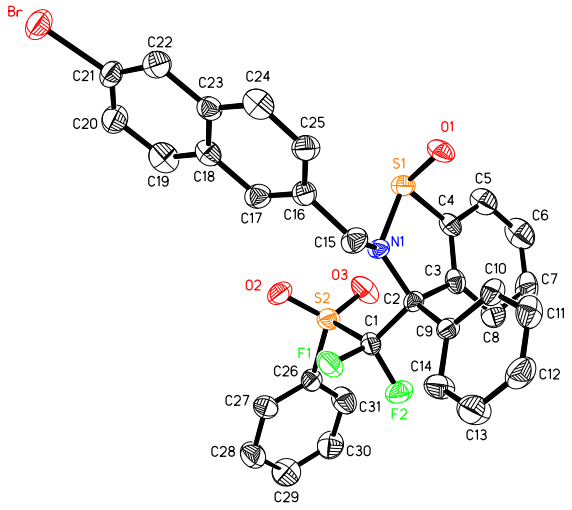


Figure S2 Structure of Cyclic Sulfinamide (*Ss*,*R*)-**S3** in the Crystal

Experimental Procedures:

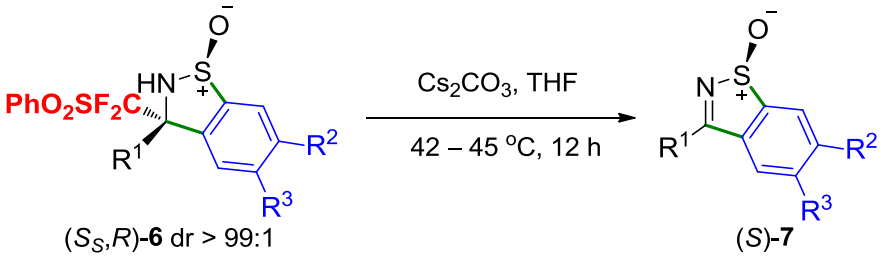
Under N_2 atmosphere, to a solution of cyclic sulfinamide **6a** (0.126 g, 0.3 mmol) in DMF (6.0 mL) was added NaH (0.0144 g, 0.6 mmol) at –30 °C. After stirring at this temperature for 2 h, 2-bromo-6-(bromomethyl)naphthalene (0.180 g, 0.6 mmol) was added, and then the reaction mixture was stirred at the same temperature for 10 h. After quenched with saturated NH_4Cl solution, the reaction mixture was extracted with diethyl ether (3 × 30 mL), and the combined organic phases were dried over anhydrous $MgSO_4$. The volatile solvents were removed under vacuum, and the crude product was purified by flash column chromatography (silica gel; ethyl acetate/petroleum ether = 1:5, v/v) to give **S3** as a white solid (0.118 g; 62% yield).

(1*S*,3*R*)-2-[(6-Bromonaphthalen-2-yl)methyl]-3-[difluoro(phenylsulfonyl)methyl]-3-phenyl-2,3-dihydrobenzo[*d*]isothiazole 1-oxide **(S3)**

Mp: 225 – 228 °C. $[\alpha]_D^{28}$ –52.0 (*c* 0.75, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 8.07 (s, 1H), 8.01 (s, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.81 – 7.66 (m, 5H),

7.65 – 7.44 (m, 7H), 7.41 – 7.22 (m, 4H), 4.47 (d, J = 13.3 Hz, 1H), 4.20 (d, J = 13.3 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –87.6 (d, J = 242.7 Hz, 1F), –95.7 (d, J = 242.7 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7 (d, J = 1.3 Hz), 140.1 (dd, J = 6.4, 1.8 Hz), 135.1, 134.9, 134.4, 134.2, 133.1, 131.9, 131.6, 130.7, 130.3, 129.8, 129.7, 129.6, 129.3, 129.2, 129.1, 128.9, 128.7 (t, J = 2.5 Hz), 128.6, 127.1, 126.7 (d, J = 6.4 Hz), 125.4 (t, J = 305.1 Hz), 124.6, 120.1, 82.8 (t, J = 21.9 Hz), 49.0 (d, J = 6.6 Hz). IR (film): 3053, 1585, 1498, 1448, 1354, 1181, 1147, 1091 cm^{-1}. MS (ESI, *m/z*): 638.4 (M + H$^+$). HRMS (ESI): calcd. for $C_{31}H_{22}BrF_2NO_3S_2$: (M + H$^+$): 638.0265; Found: 638.0274.

3.4 Synthesis of Cyclic Sulfinimines



(*S*$_S$,*R*)-**6** dr > 99:1 (*S*)-**7**

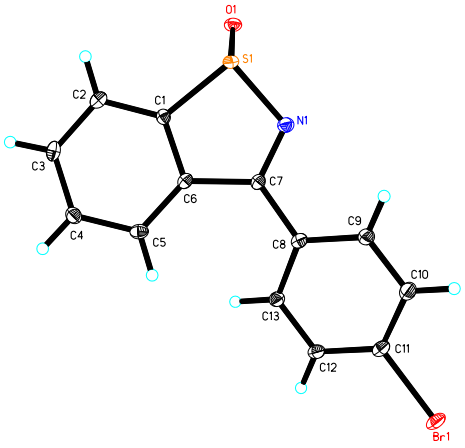


Figure S3 Structure of Cyclic Sulfinimine (*S*)-**7c** in the Crystal

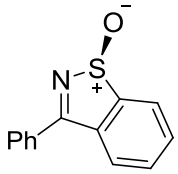
Typical Procedures:

Under N_2 atmosphere, Cs_2CO_3 (260 mg, 0.8 mmol) was added to a solution of cyclic

sulfinamide (*Ss*,*R*)-**6a** (R^1 = Ph; R^2, R^3 = H) (89 mg, 0.2 mmol) in dry THF, and then reaction mixture was heated at 42–45 °C for 12 h. After diluted with water (10 mL), the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were washed with brine (40 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by flash chromatography (silica gel; *n*-hexane/ethyl acetate = 3: 1 v/v) to afford cyclic sulfinimine (*S*)-**7a** (R^1 = Ph; R^2, R^3 = H) as a white solid (31.7 mg; 70% yield; 98:2 er).

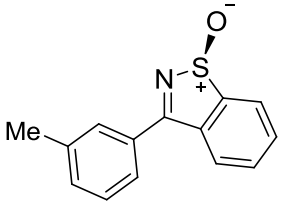
The er of **7a** could be improved to > 99:1 after a single recrystallization from ethyl acetate/petroleum ether (1:1, v/v; 0.073 mol/L) at 0 °C.

(*S*)-3-Phenylbenzo[*d*]isothiazole 1-oxide (**7a**)



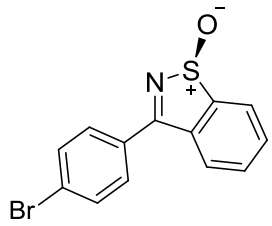
Pale yellow solid. Mp: 74–75 °C. $[\alpha]_D^{29}$ –292.6 (*c* 1.00, $CHCl_3$), 98:2 er. The enantiomeric ratio was determined by Lux 5u Cellulose–2 (250×4.6 mm), MeOH / IPA= 50 / 50 (v/v), 0.7 mL/min, λ= 214 nm, t_R (major) = 22.39 min, t_R (minor) = 33.02 min on Dionex Utimate 3000. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14–8.10 (m, 1H), 7.98–7.93 (m, 3H), 7.74–7.69 (m, 2H), 7.67–7.56 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.1, 155.0, 135.1, 132.4, 132.2, 131.5, 129.2, 129.1, 127.0, 125.8. IR (KBr): 1598, 1512, 1443, 1335, 1095 cm^{-1}. MS (ESI, *m/z*): 227. HRMS (ESI, *m/z*): Calcd. for $C_{13}H_9NOS$ ($[M]^+$): 227.0405; Found: 227.0404.

(*S*)-3-(*m*-Tolyl)benzo[*d*]isothiazole 1-oxide (**7b**)



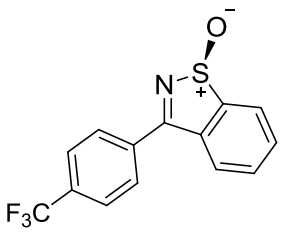
White solid. Mp: 79–80 °C. $[\alpha]_D^{28}$ –301.9 (*c* 1.00, $CHCl_3$), 96:4 er. The enantiomeric ratio was determined by Lux 5u Cellulose–1 (250×4.6 mm), MeOH / IPA= 60 / 40 (v/v), 0.7 mL/min, λ= 214 nm, t_R (major) = 9.46 min, t_R (minor) = 10.44 min on Dionex Utimate 3000. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.13–8.10 (m, 1H), 7.98–7.94 (m, 1H), 7.77 (s, 1H), 7.75–7.69 (m, 3H), 7.48–7.45 (m, 2H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.3, 154.9, 139.1, 135.2, 133.2, 132.3, 132.1, 131.5, 129.6, 128.9, 127.1, 126.3, 125.7, 21.5. IR (KBr): 2965, 1511, 1301, 1078 cm^{-1}. MS (ESI, *m/z*): 241($[M]^+$). HRMS (ESI, *m/z*): Calcd. for $C_{14}H_{11}NOS$ ($[M]^+$): 241.0561; Found: 241.0558.

(*S*)-3-(4-Bromophenyl)benzo[*d*]isothiazole 1-oxide (**7c**)



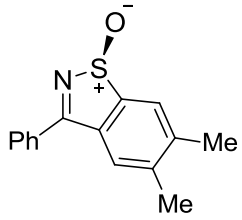
White solid. Mp: 150–152 °C. $[\alpha]_D^{29}$ –356.2 (*c* 0.55, $CHCl_3$), 97:3 er. The enantiomeric ratio was determined by Lux 5u Cellulose–1 (250×4.6 mm), MeOH / IPA= 70 / 30 (v/v), 0.7 mL/min, λ= 214 nm, t_R (major) = 14.13 min, t_R (minor) = 15.39 min on Dionex Utimate 3000. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.15–8.12 (m, 1H), 7.93–7.91 (m, 1H), 7.85–7.82 (m, 2H), 7.76–7.71 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.0, 155.0, 134.8, 132.5, 132.4, 131.7, 131.1, 130.6, 127.3, 126.7, 125.9. IR (KBr): 3078, 1586, 1504, 1485, 1309, 1075, 1008 cm^{-1}. MS (ESI, *m/z*): 305 ($[M]^+$). HRMS (ESI, *m/z*): Calcd. for $C_{13}H_8BrNOS^+$ ($[M]^+$): 304.9510; Found: 304.9513.

(*S*)-3-[4-(Trifluoromethyl)phenyl]benzo[*d*]isothiazole 1-oxide (**7d**)



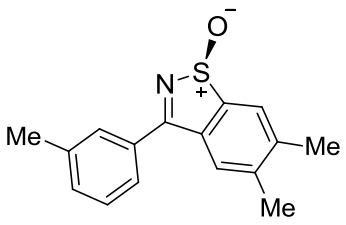
White solid. Mp: 176–177 °C. $[\alpha]_D^{28}$ –217.3 (*c* 1.10, $CHCl_3$), 95:5 er. The enantiomeric ratio was determined by Lux 5u Cellulose–1 (250×4.6 mm), MeOH / IPA= 80 / 20 (v/v), 0.7 mL/min, λ= 214 nm, t_R (major) = 17.41 min, t_R (minor) = 18.85 min on Dionex Utimate 3000. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17–8.14 (m, 1H), 8.07 (d, *J* = 8.4 Hz, 2H), 7.92–7.85 (m, 3H), 7.79–7.73 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –63.0 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.9, 155.1, 135.5, 134.7, 133.8 (q, *J* = 32.8 Hz), 132.6, 131.9, 129.5, 126.6, 126.1 (q, *J* = 3.7 Hz), 126.0, 123.6 (q, *J* = 270.5 Hz). IR (KBr): 3105, 1590, 1505, 1411, 1328, 1122, 1081, 1070 cm^{-1}. MS (ESI, *m/z*): 295 ($[M]^+$). HRMS (ESI, *m/z*): Calcd. for $C_{14}H_8F_3NOS^+$ ($[M + Na]^+$): 295.0279; Found: 295.0275.

(*S*)-5,6-Dimethyl-3-phenylbenzo[*d*]isothiazole 1-oxide (**7e**)



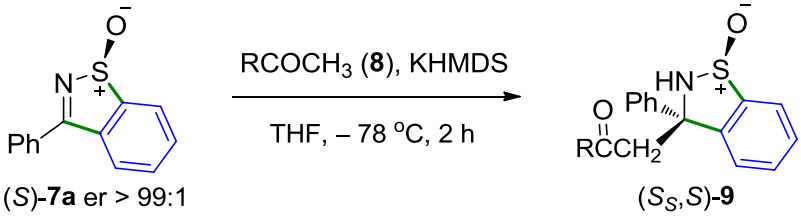
White solid. Mp: 90–91 °C. $[\alpha]_D^{29}$ –241.8 (*c* 0.80, $CHCl_3$), 93:7 er. The enantiomeric ratio was determined by Lux 5u Cellulose–2 (250×4.6 mm), MeOH / IPA= 60 / 40 (v/v), 1.0 mL/min, λ= 214 nm, t_R (major) = 43.63 min, t_R (minor) = 57.64 min on Dionex Utimate 3000. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.5 Hz, 2H), 7.89 (s, 1H), 7.68 (s, 1H), 7.64–7.55 (m, 3H), 2.43 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.0, 152.7, 141.8, 141.6, 133.4, 132.5, 132.1, 129.1, 129.0, 127.6, 126.6, 20.5, 20.3. IR (KBr): 3445, 3055, 2917, 1595, 1540, 1441, 1335, 1080 cm^{-1}. MS (ESI, *m/z*): 255. HRMS (ESI, *m/z*): Calcd. for $C_{15}H_{13}NOS$ ($[M]^+$): 255.0718; Found: 255.0720.

(*S*)-5,6-Dimethyl-3-(*m*-tolyl)benzo[*d*]isothiazole 1-oxide (**7f**)



White solid, Mp: 113–114 °C. $[\alpha]_D^{28}$ –248.8 (*c* 0.75, $CHCl_3$), 95:5 er. The enantiomeric ratio was determined by Lux 5u Cellulose–1 (250×4.6mm), MeOH / IPA= 60 / 40 (v/v), 0.7 mL/min, λ= 214 nm, t_R (major) = 8.67 min, t_R (minor) = 9.45 min on Dionex Utimate 3000. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (s, 1H), 7.75 (s, 1H), 7.71 (d, *J* = 6.6 Hz, 1H), 7.67 (s, 1H), 7.49–7.44 (m, 2H), 2.47 (s, 3H), 2.43 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.3, 152.6, 141.8, 141.5, 139.0, 133.5, 132.9, 132.5, 129.6, 128.8, 127.6, 126.5, 126.2, 21.5, 20.5, 20.3. IR (KBr): 2919, 1592, 1508, 1336, 1083 cm^{-1}. MS (ESI, *m/z*): 269 ($[M]^+$). HRMS (ESI, *m/z*): Calcd. for $C_{16}H_{15}NOS$ ($[M]^+$): 269.0874; Found: 269.0876.

3.5 Addition to Cyclic Sulfinimines



(*S*)-**7a** er > 99:1 (*S*$_S$,*S*)-**9**

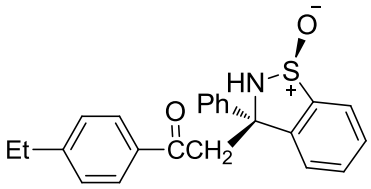
Typical Procedures:

Under N_2 atmosphere, to a solution of **8a** (R = 4-EtC_6H_4) (119 mg, 0.8 mmol) in dry THF (1 mL) was added KHMDS (1.0 M in THF, 0.8 mL, 0.8 mmol) at –78 °C. After 10 min, chiral sulfinimine (*S*)-**7a** (91 mg, 0.4 mmol) in THF (0.4 mL) was added to the enolate solution of **8a** at –78 °C. The whole mixture was stirred for 2 h at –78 °C. The reaction mixture was diluted with water (10 mL) and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were washed with brine (40 mL) and dried over anhydrous Na_2SO_4. After the solution was filtered and the solvent was evaporated under vacuum, the residue was subjected to fast column chromatography

(silica gel; *n*-hexane/ethyl acetate 3: 1, v/v) to give product **9a** as a white solid (140 mg; 93% yield).

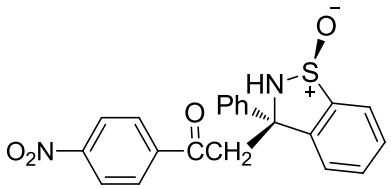
Characterization Data:

1-(4-Ethylphenyl)-2-{(*1S,3S*)-1-oxido-3-phenyl-2,3-dihydrobenzo[*d*]isothiazol-3-yl}etha none (**9a**)



White solid. Mp: 152–154 °C. $[\alpha]_D^{28}$ +288.5 (*c* 1.05, $CHCl_3$), 95:5 dr, 99:1 er. The dr and er were determined by CHIRALPAK AS–RH (250 × 4.6 mm), MeOH / IPA= 85 / 15 (v/v), 0.3 mL/min, λ= 230 nm, t_R (major) = 10.37 min, t_R (minor) = 20.14 min on Dionex Utimate 3000. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.1 Hz, 3H), 7.46–7.45 (m, 2H), 7.33–7.25 (m, 7H), 7.13 (s, 1H), 6.43 (s, 1H), 4.69 (d, *J* = 18.6 Hz, 1H), 3.90 (d, *J* = 18 Hz, 1H), 2.71 (q, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.4, 150.9, 146.3, 145.5, 141.9, 134.4, 131.8, 129.1, 128.8, 128.4, 128.3, 127.6, 125.4, 124.8, 124.2, 74.5, 50.1, 29.0, 15.2. IR (KBr): 3323, 3060, 2963, 2932, 1674, 1605, 1448, 1414, 1364, 1224, 1181, 1073 cm^{-1}. MS (ESI, *m/z*): 376 ($[M + H]^+$). HRMS (ESI, *m/z*): Calcd. for $C_{23}H_{22}NO_2S^+$ ($[M + H]^+$): 376.1371; Found: 376.1369.

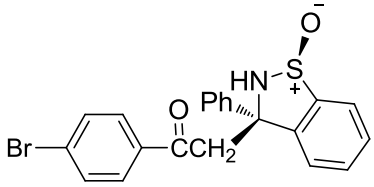
1-(4-Nitrophenyl)-2-{(*1S,3S*)-1-oxido-3-phenyl-2,3-dihydrobenzo[*d*]isothiazol-3-yl}etha none (**9b**)



White solid. Mp: 96–98 °C. $[\alpha]_D^{29}$ +218.9 (*c* 0.70, $CHCl_3$). 88:12 dr, 99:1 er. The dr and er were determined by Lux 5u Cellulose–1 (250 × 4.6 mm), MeOH / IPA= 90 / 10 (v/v),

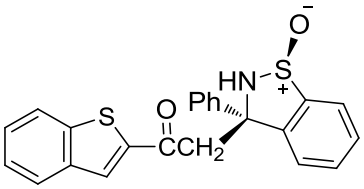
0.5 mL/min, λ= 230 nm, t_R (major) = 12.87 min, t_R (minor) = 23.69 min on Dionex Utimate 3000. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.31 (d, *J* = 8.7 Hz, 2H), 8.10 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 5.1 Hz, 1H), 7.49 (t, *J* = 3.6 Hz, 2H), 7.32–7.14 (m, 5H), 7.17 (s, 1H), 6.25 (s, 1H), 4.70 (d, *J* = 18.6 Hz, 1H), 4.03 (d, *J* = 18.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.4, 150.6, 145.8, 145.3, 141.3, 140.9, 132.0, 129.3, 129.2, 129.0, 127.9, 125.3, 124.9, 124.2, 124.0, 74.2, 50.9. IR (KBr): 3356, 3064, 2906, 1690, 1602, 1525, 1345, 1214, 1073, 1053 cm^{-1}. MS (ESI, *m/z*): 393($[M + H]^+$). HRMS (ESI, *m/z*): Calcd. for $C_{21}H_{17}N_2O_4S^+$ ($[M + H]^+$): 393.0909; Found: 393.0893.

1-(4-Bromophenyl)-2-{(*1S,3S*)-1-oxido-3-phenyl-2,3-dihydrobenzo[*d*]isothiazol-3-yl}ethanone (**9c**)



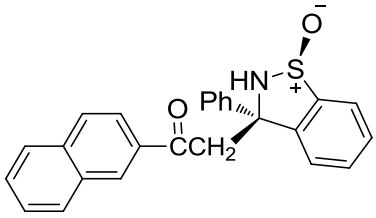
White solid. Mp: 68–70 °C. $[\alpha]_D^{28}$ +239.8 (*c* 1.00, $CHCl_3$). 92:8 dr, 99:1 er. The dr and er were determined by Lux 5u Cellulose–3 (250 × 4.6 mm), MeOH / IPA= 90 / 10 (v/v), 0.5 mL/min, λ= 230 nm, t_R (major) = 9.38 min, t_R (minor) = 8.92 min on Dionex Utimate 3000. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87–7.78 (m, 3H), 7.63–7.59 (m, 2H), 7.50–7.45 (m, 2H), 7.32–7.25 (m, 5H), 7.16–7.11 (m, 1H), 6.34 (s, 1H), 4.64 (d, *J* =18.3 Hz, 1H), 3.91 (d, *J* =18.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.8, 146.1, 145.4, 141.6, 135.3, 132.1, 131.9, 129.7, 129.2, 129.1, 128.9, 127.7, 125.3, 124.8, 124.2, 74.3, 50.2. IR (KBr): 3447, 3060, 2923, 1682, 1584, 1449, 1355, 1216, 1071, 1053 cm^{-1}. MS (ESI, *m/z*): 426 ($[M + H]^+$). HRMS (ESI, *m/z*): Calcd. for $C_{21}H_{17}BrNO_2S^+$ ($[M + H]^+$): 426.0163; Found: 426.0150.

1-(Benzo[*b*]thiophen-2-yl)-2-{(*1S,3S*)-1-oxido-3-phenyl-2,3-dihydrobenzo[*d*]isothiazol-3-yl}ethanone (**9d**)



White solid. Mp: 90–92 °C. $[\alpha]_D^{28}$ +278.3 (*c* 1.05, $CHCl_3$). 94:6 dr, 99:1 er. The dr and er were determined by Lux 5u Cellulose–1 (250 × 4.6 mm), MeOH / IPA= 90 / 10 (v/v), 0.5 mL/min, λ= 230 nm, t_R (major) = 10.81 min, t_R (minor) = 14.50 min on Dionex Utimate 3000. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.90–7.85 (m, 3H), 7.48–7.37 (m, 6H), 7.32–7.24 (m, 3H), 7.17 (s, 1H), 6.38 (s, 1H), 4.74 (d, *J* = 18.3 Hz, 1H), 4.01 (d, *J* = 18.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.1, 146.0, 145.5, 143.1, 142.8, 141.5, 139.0, 131.9, 130.0, 129.2, 128.9, 127.9, 127.8, 126.2, 125.4, 125.3, 124.8, 124.2, 123.0, 74.5, 50.6. IR (KBr): 3337, 3058, 2923, 1730, 1660, 1514, 1449, 1355, 1224, 1169, 1073, 1052 cm^{-1}. MS (ESI, *m/z*): 404 ($[M + H]^+$). HRMS (ESI, *m/z*): Calcd. for $C_{23}H_{18}NO_2S_2^+$ ($[M + H]^+$): 404.0779; Found: 404.0773.

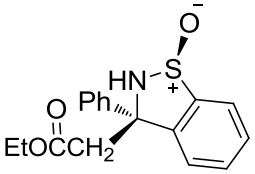
1-(Naphthalen-2-yl)-2-{(*1S,3S*)-1-oxido-3-phenyl-2,3-dihydrobenzo[*d*]isothiazol-3-yl}ethanone (**9e**)



White solid. Mp: 88–90 °C. $[\alpha]_D^{29}$ +284.0 (*c* 1.00, $CHCl_3$). 95:5 d, 99:1 er. The dr and er were determined by CHIRALPAK AD–H (250 × 4.6 mm), MeOH / IPA= 90 / 10 (v/v), 0.5 mL/min, λ= 230 nm, t_R (major) = 10.76 min, t_R (minor) = 22.89 min on Dionex Utimate 3000. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.49 (s, 1H), 8.00–7.87 (m, 5H), 7.64–7.53 (m, 2H), 7.50–7.47 (m, 2H), 7.38–7.25 (m, 5H), 7.20–7.19 (m, 1H), 6.46 (s, 1H), 4.86 (d, *J* = 18.3 Hz, 1H), 4.08 (d, *J* = 18.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 146.3, 145.5, 141.9, 135.9, 134.0, 132.5, 131.9, 130.2, 129.7, 129.2, 128.9, 128.8, 128.7, 127.9,

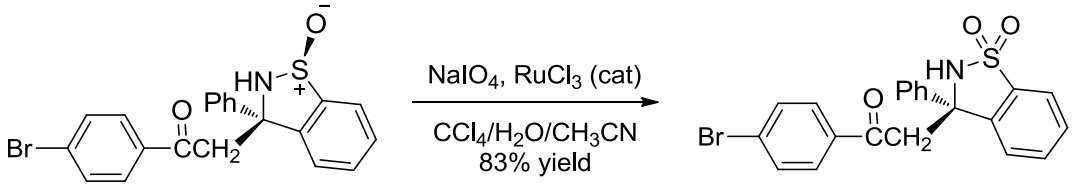
127.7, 127.1, 125.4, 124.8, 124.3, 123.6, 74.6, 50.3. IR (KBr): 3339, 3057, 2922, 1675, 1626, 1449, 1359, 1172, 1124, 1053 cm^{-1}. MS (ESI, *m/z*): 398 ($[M + H]^+$). HRMS (ESI, *m/z*): Calcd. for $C_{25}H_{20}NO_2S^+$ ($[M + H]^+$): 398.1215; Found: 398.1191.

Ethyl 2-{(*1S,3S*)-1-oxido-3-phenyl-2,3-dihydrobenzo[*d*]isothiazol-3-yl}acetate (**9f**)



White solid. Mp: 66–68 °C. $[\alpha]_D^{28}$ +189.2 (*c* 1.10, $CHCl_3$). 95:5 dr, 99:1 er. The dr and er were determined by Lux 5u Cellulose–3 (250 × 4.6 mm), MeOH / IPA= 85 / 15, 0.3 mL/min, λ= 230 nm, t_R (major) = 12.61 min, t_R (minor) = 12.13 min on Dionex Utimate 3000. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 (d, *J* = 3.9 Hz, 1H), 7.42–7.39 (m, 4H), 7.35–7.26 (m, 3H), 7.10 (s, 1H), 6.29 (s, 1H), 4.11 (q, *J* = 6.6 Hz, 2H), 3.77 (d, *J* = 17.1 Hz, 1H), 3.43 (d, *J* = 16.8 Hz, 1H), 1.71 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.0, 145.5, 145.2, 141.6, 131.9, 129.2, 128.9, 127.9, 125.4, 124.7, 124.1, 74.0, 61.1, 46.9, 14.1. IR (KBr): 3334, 2980, 2927, 1725, 1496, 1449, 1372, 1348, 1201, 1075, 1019 cm^{-1}. MS (ESI, *m/z*): 316 ($[M + H]^+$). HRMS (ESI, *m/z*): Calcd. for $C_{17}H_{18}NO_3S^+$ ($[M + H]^+$): 316.1007; Found: 316.1007.

3.6 Oxidation of Cyclic Sulfinamide 9c



(*Ss,S*)-**9c**
dr = 92:8

(*S*)-**S4**
er = 90.5:9.5

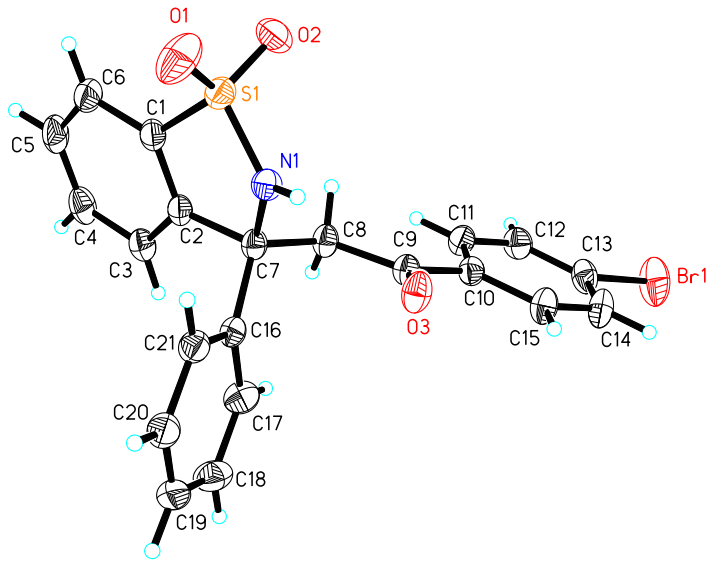
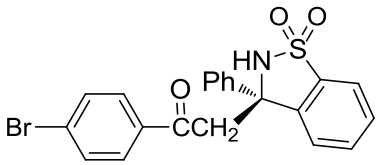


Figure S4 Structure of Cyclic Sulfonamide (*S*)-**S4** in the Crystal

Experimental Procedures:

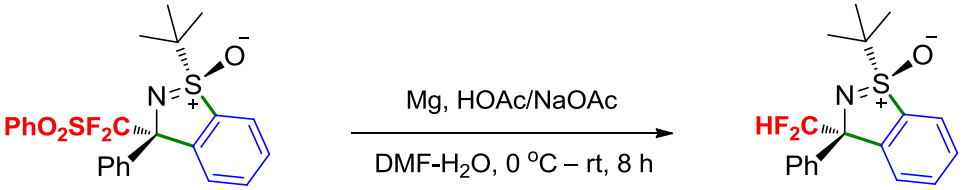
To a solution of **8d** (85 mg, 0.2 mmol) in a mixture solvent of H_2O (1 mL), CCl_4 (0.5 mL), and CH_3CN (0.5 mL) was added $NaIO_4$ (128 mg, 0.6 mmol) and $RuCl_3$ (0.25 mg, 0.01 mmol). The whole mixture was stirred at rt for 2 h. The reaction mixture was diluted with water (5 mL) and the aqueous phase was extracted with Et_2O (3 × 10 mL). The combined organic phases were washed with brine (10 mL) and dried over anhydrous Na_2SO_4. After the solution was filtered and the solvent was evaporated under vacuum, the residue was subjected to fast column chromatography (silica gel; *n*-hexane/EtOAc = 2: 1, v/v) to give product **S4** as a white solid (74 mg; 83% yield). The single crystal of the major enatiomer of **S4** that is suitable for X-ray crystallographic analysis (Figure S4) was obtained by recrystallization from ethyl acetate / petroleum ether (5:2, v/v; 0.024 mol/L) at room temperature.

(*S*)-1-(4-Bromophenyl)-2-(1,1-dioxido-3-phenyl-2,3-dihydrobenzo[*d*]isothiazol-3-yl)etha none (**S4**)



White solid. Mp: 183–185 °C. $[\alpha]_D^{29}$ +239.0 (*c* 0.95, $CHCl_3$); 90.5:9.5 er. The enantiomeric excess was determined by Lux 5u Cellulose–1 (250 × 4.6 mm), MeOH / IPA= 60 / 40 (v/v), 0.7 mL/min, λ= 230 nm, t_R (major) = 21.92 min, t_R (minor) = 31.35 min on Dionex Utimate 3000. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 6.6 Hz, 2H), 7.63 (d, *J* = 6.6 Hz, 2H), 7.58–7.51 (m, 2H), 7.48 (d, *J* = 5.7 Hz, 2H), 7.33–7.23 (m, 4H), 6.62 (s, 1H), 4.46 (d, *J* = 13.5 Hz, 1H), 3.62 (d, *J* = 13.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.5, 142.6, 141.1, 135.0, 134.0, 133.5, 132.3, 129.7, 129.6, 129.1, 128.2, 125.5, 124.4, 121.7, 65.8, 46.7, 29.7. IR (KBr): 3353, 3284, 2921, 2851, 1678, 1584, 1484, 1359, 1286, 1198, 1162, 1130, 1068 cm^{-1}. MS (ESI, *m/z*): 464 ($[M + Na]^+$). HRMS (ESI, *m/z*): Calcd. for $C_{21}H_{16}BrNNaO_3S^+$ ($[M + Na]^+$): 463.9932; Found: 463.9943.

3.7 Reductive Desulfonylation



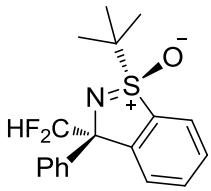
(*S*$_S$,*R*)-**5a** dr > 99:1 (*S*$_S$,*R*)-**10** dr > 99:1

Experimental Procedures:

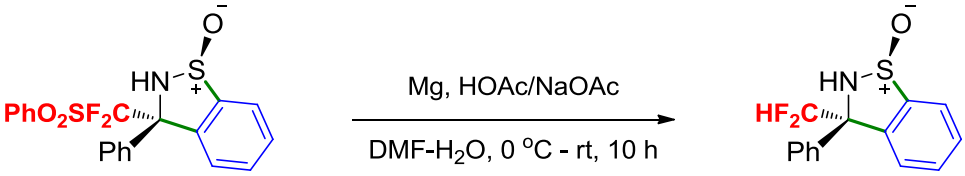
To a solution of (*Ss,R*)-**5a** (0.095 g, 0.2 mmol) in DMF (6.0 mL), HOAc/NaOAc (1:1) buffer solution ($M_{(OAc)}$ = 8 mol/L; 4.0 ml) and magnesium turnings (0.192 g, 8.0 mmol) were added slowly at 0 °C. Then the reaction temperature was allowed to raise to rt slowly with vigorous stirring. After 8 h, the reaction mixture was diluted with water (10 mL) and the aqueous phase was extracted with diethyl ether (3 × 20 mL). The combined organic phases were washed with brine (20 mL) and dried over anhydrous Na_2SO_4. After the solution was filtered and the solvent was evaporated under vacuum, the residue was

subjected to fast column chromatography (silica gel; ethyl acetate/petroleum ether = 1:3, v/v) to give (*Ss*,*R*)-**10** (0.063 g; 94% yield).

(1*S*,3*R*)-1-(*tert*-Butyl)-3-(difluoromethyl)-3-phenylbenzo[*d*]isothiazole 1-oxide (**10**)



$[\alpha]_D^{21}$ +20.2 (*c* 1.10, $CHCl_3$). ^{1}H NMR: δ 7.83 (d, *J* = 7.8 Hz, 1H), 7.80–7.70 (q, *J* = 7.4 Hz, 3H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.35–7.21 (m, 3H), 6.15 (t, *J* = 55.9 Hz, 1H), 1.61 (s, 9H). ^{19}F NMR: δ –122.3 (dd, *J* = 271.7, 56.9 Hz, 1F), –123.4 (dd, *J* = 271.7, 56.9 Hz, 1F). ^{13}C NMR: δ 147.7, 141.0, 136.9, 133.6, 130.6, 129.3, 128.7, 127.9 (t, *J* = 1.9 Hz), 127.6 (t, *J* = 1.9 Hz), 124.6, 118.2 (t, *J* = 250.7 Hz), 80.1 (t, *J* = 21.8 Hz), 63.9, 25.7. IR (film): 2974, 1452, 1366, 1218, 1080, 962, 757 cm^{-1}. MS (ESI, *m/z*): 336.1 ($M + H^+$). HRMS (ESI): calcd. for $C_{18}H_{19}F_2NOS$: ($M + H^+$): 336.1228; Found: 336.1225.



(*S*$_S$,*R*)-**6a** dr > 99:1

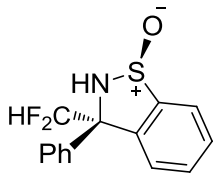
(*S*$_S$,*R*)-**11** dr > 99:1

Experimental Procedures:

To a solution of (*Ss*,*R*)-**6a** (0.419 g, 1.0 mmol) in DMF (16 mL), HOAc/NaOAc (1:1) buffer solution ($M_{(OAc)}$ = 8 mol/L; 10 ml) and magnesium turnings (0.480 g, 20 mmol) were added slowly at 0 °C. Then the reaction temperature was allowed to raise to rt slowly with vigorous stirring. After 10 h, the reaction mixture was diluted with water (20 mL) and the aqueous phase was extracted with diethyl ether (3 × 30 mL). The combined organic phases were washed with brine (40 mL) and dried over anhydrous Na_2SO_4. After the solution was filtered and the solvent was evaporated under vacuum, the residue was

subjected to fast column chromatography (silica gel; ethyl acetate/petroleum ether = 1:3, v/v) to give (*Ss*,*R*)-**11** as a white solid (0.203 g; 73% yield).

(*1S*,*3R*)-3-(Difluoromethyl)-3-phenyl-2,3-dihydrobenzo[*d*]isothiazole 1-oxide (**11**)



White solid. Mp: 152–154 ^{o}C. $[\alpha]_D^{25}$ –140.9 (*c* 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85–7.83 (m, 1H), 7.70 (d, *J* = 6.9 Hz, 2H), 7.57–7.54 (m, 2H), 7.44 (d, *J* = 4.8 Hz, 1H), 7.39–7.31 (m, 3H), 6.13 (t, *J* = 55.2 Hz, 1H), 5.47 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ –122.7 (dd, *J* = 274.7 Hz, 54.4 Hz, 1F), –125.9 (dd, *J* = 274.9 Hz, 55.5 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): 145.9, 138.7, 137.4, 132.2, 130.4, 128.9, 128.6, 127.1 (t, *J* = 1.5 Hz), 125.3, 125.1 (d, *J* = 1.5 Hz), 115.9 (t, *J* = 249.0 Hz), 78.0 (t, *J* = 21.3 Hz). IR (KBr): 3154, 2788, 1497, 1450, 1406, 1361, 1347, 1133, 1077, 1042, 1025, 861 cm^{-1}. MS (EI, *m/z*): 279 (M^+, 4.96), 228 (100). HRMS (EI, *m/z*): Calcd. for $C_{14}H_{11}F_2NOS^+$ ($[M + H]^+$): 279.0529; Found: 279.0534.

4. Determination of the Enantioselectivity

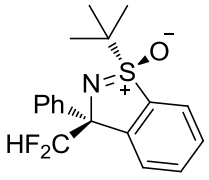
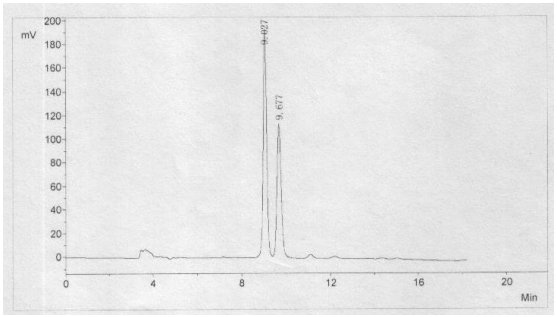
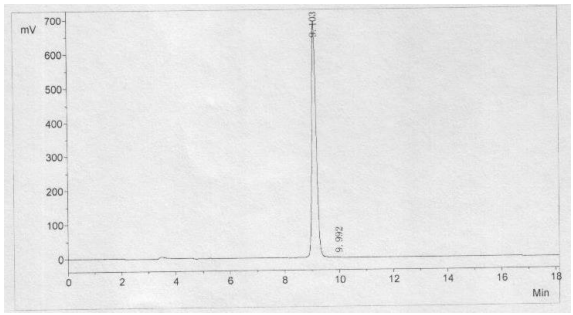


Table 1, entry 4

For racemic product 4d and enantioenriched product 4d (er > 99:1):





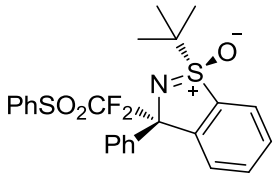
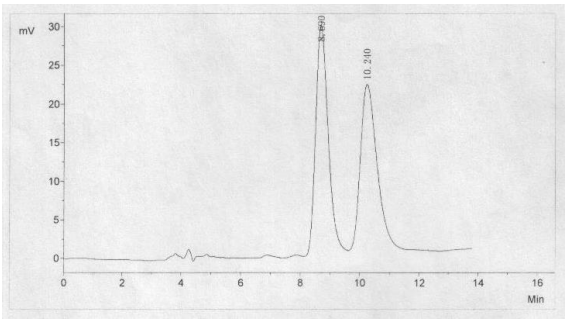
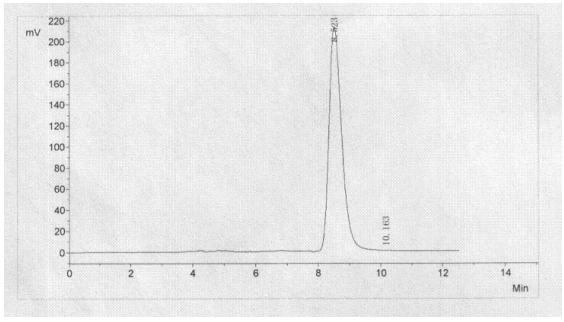


Table S2, entry 7

For racemic product 5a and enantioenriched product 5a (er > 99:1):





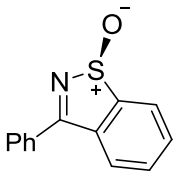
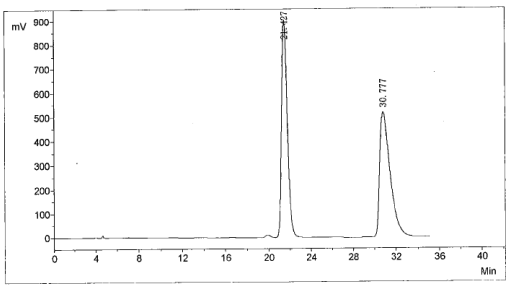
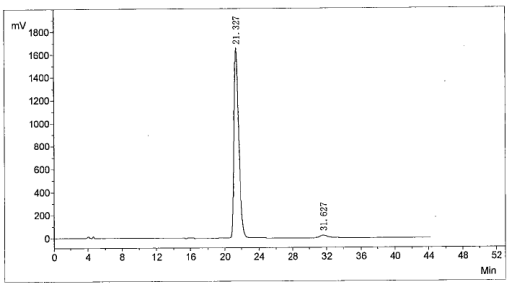


Table 4, entry 1

For racemic product 7a and enantioenriched product 7a (er 98:2):

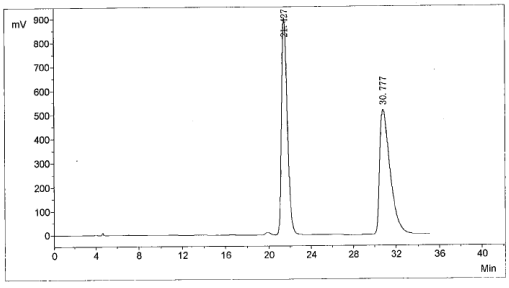


No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1		21.427	901927.1	34493775.5	49.7685
2	2		30.777	519230.3	34814664.8	50.2315
Total				1421157.4	69308440.3	100.0000

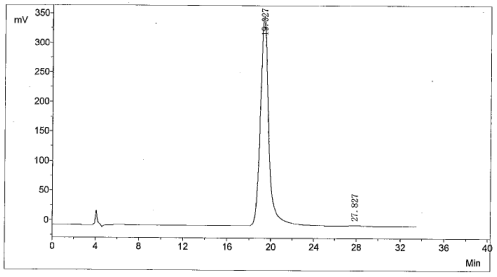


No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1		21.327	1650354.1	64670127.4	98.0238
2	2		31.627	20031.7	1303748.4	1.9762
Total				1670385.8	65973875.8	100.0000

racemic product 7a and enantioenriched product 7a (after a single recrystallization; er > 99:1):



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1		21.427	901927.1	34493775.5	49.7685
2	2		30.777	519230.3	34814664.8	50.2315
Total				1421157.4	69308440.3	100.0000



No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1		19.327	353089.0	19199844.0	99.6395
2	2		27.827	956.9	69462.0	0.3605
Total				354045.9	19269306.0	100.0000

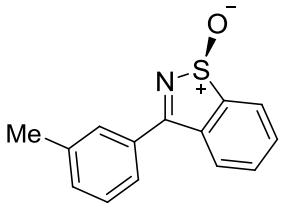
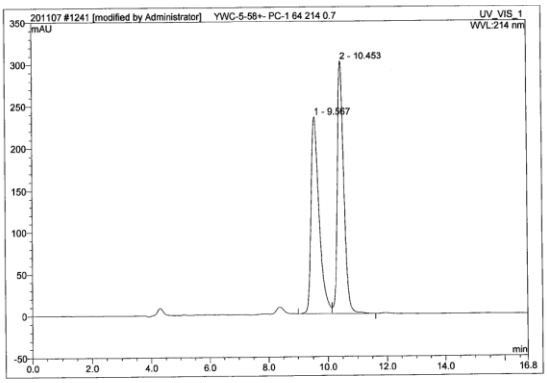
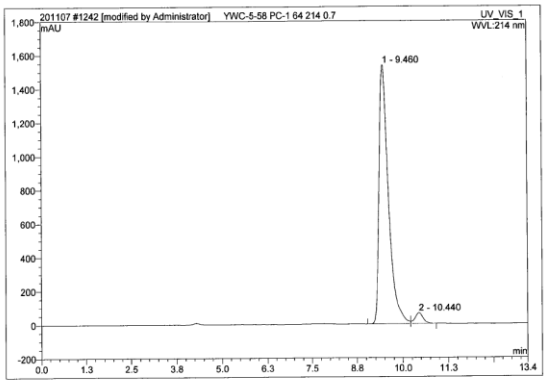


Table 4, entry 2

For racemic product 7b and enantioenriched product 7b (er 96:4):



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.57	n.a.	234.597	74.592	49.77	n.a.	BM *
2	10.45	n.a.	301.546	75.279	50.23	n.a.	MB*
Total:			536.143	149.871	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.46	n.a.	1536.727	451.294	96.51	n.a.	BM *
2	10.44	n.a.	63.894	16.316	3.49	n.a.	MB*
Total:			1600.620	467.610	100.00	0.000	

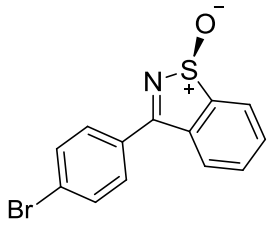
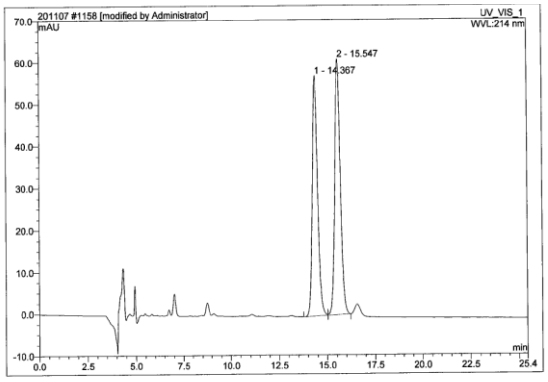
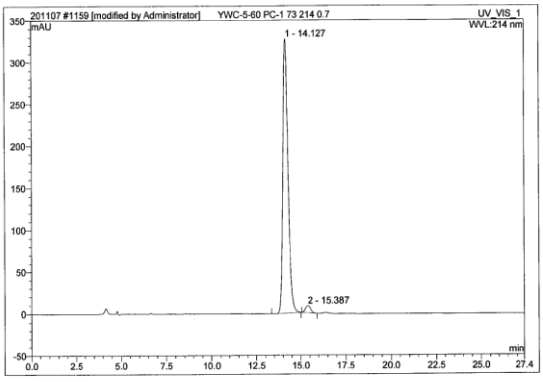


Table 4, entry 3

For racemic product 7c and enantioenriched product 7c (er 97:3):



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.37	n.a.	57.366	18.795	47.08	n.a.	BM *
2	15.55	n.a.	60.995	21.125	52.92	n.a.	MB*
Total:			118.361	39.920	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.13	n.a.	327.520	109.799	97.56	n.a.	BMB*
2	15.39	n.a.	8.352	2.748	2.44	n.a.	BMB*
Total:			335.872	112.547	100.00	0.000	

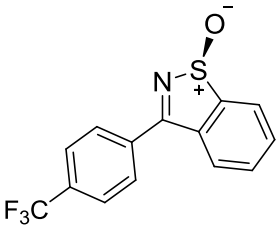
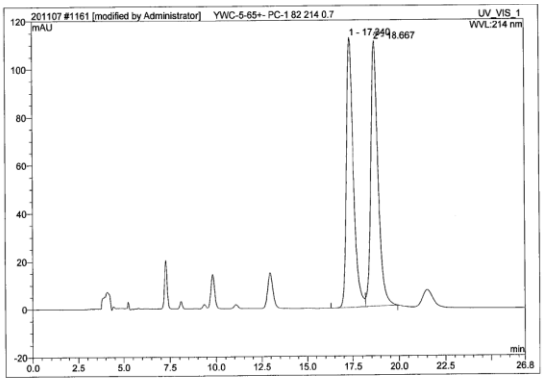
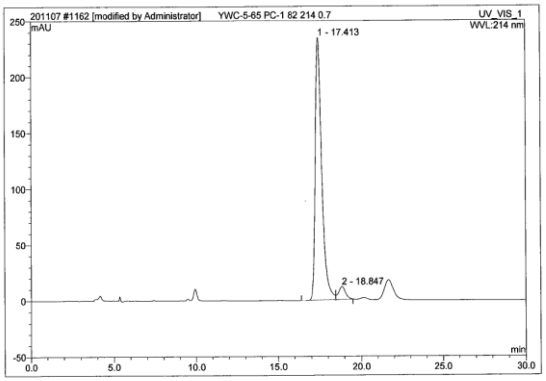


Table 4, entry 4

For racemic product 7d and enantioenriched product 7d (er 95:5):



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.34	n.a.	112.333	49.829	49.11	n.a.	BM *
2	18.67	n.a.	110.479	51.643	50.89	n.a.	MB*
Total:			222.813	101.472	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.41	n.a.	234.611	106.517	95.10	n.a.	BM *
2	18.85	n.a.	11.445	5.483	4.90	n.a.	MB*
Total:			246.056	112.000	100.00	0.000	

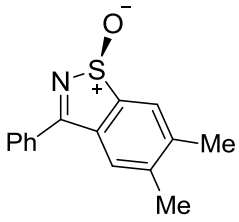
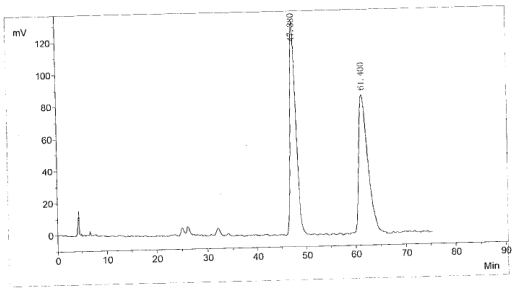
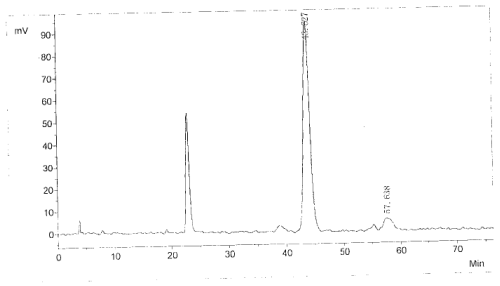


Table 4, entry 5

For racemic product 7e and enantioenriched product 7e (er 93:7):



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		47.380	131707.0	10911694.6	50.7361
2	2		61.400	86185.4	10595058.3	49.2639
Total				217892.4	21506752.9	100.0000



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		43.627	95541.6	7293687.7	92.9286
2	2		57.638	5131.7	555013.8	7.0714
Total				100673.4	7848701.5	100.0000

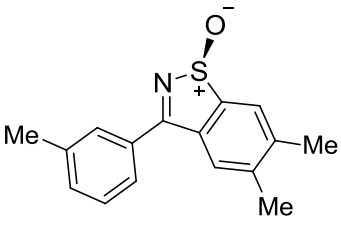
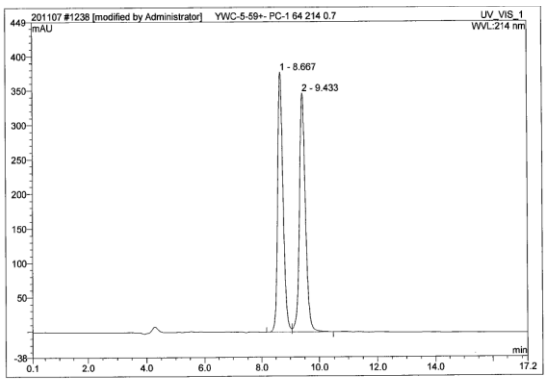
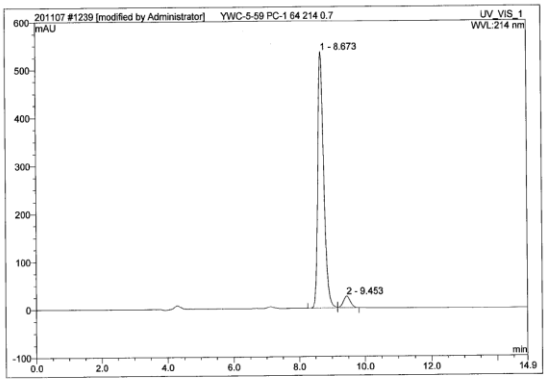


Table 4, entry 6

For racemic product 7f and enantioenriched product 7f (er 95:5):



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.67	n.a.	377.523	81.709	49.66	n.a.	BM *
2	9.43	n.a.	346.562	82.840	50.34	n.a.	MB*
Total:			724.085	164.548	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.67	n.a.	534.743	114.023	95.07	n.a.	BM *
2	9.45	n.a.	24.157	5.909	4.93	n.a.	MB*
Total:			558.900	119.932	100.00	0.000	

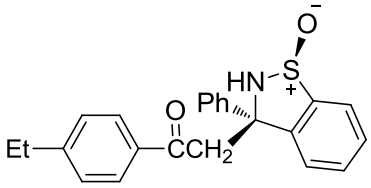
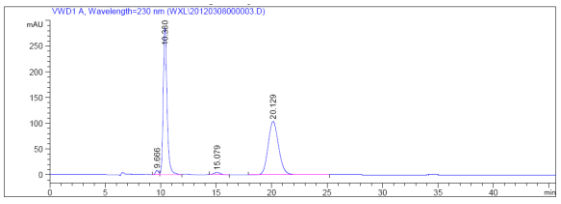
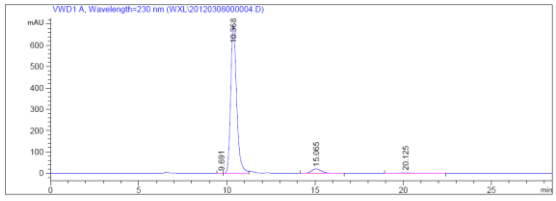


Table 5, entry 1

For racemic product 9a and enantioenriched product 9a (dr 95:5; er 99:1):



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.666	BV	0.3056	163.58873	8.31279	1.1700
2	10.380	VV	0.3646	6851.72998	285.87903	49.0045
3	15.079	BB	0.5551	163.35159	4.28141	1.1683
4	20.129	BB	1.0138	6803.17529	103.77577	48.6572
Totals :				1.39818e4	402.24900	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.691	BB	0.2010	3.64134	2.91068e-1	0.0213
2	10.368	BV	0.3581	1.62053e4	692.18268	94.7172
3	15.065	BB	0.5868	772.05377	20.25074	4.5125
4	20.125	BB	0.8225	128.14476	1.95050	0.7490
Totals :				1.71091e4	714.67499	

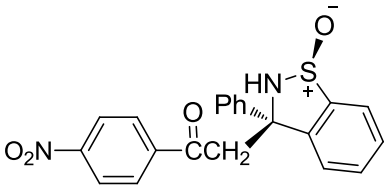
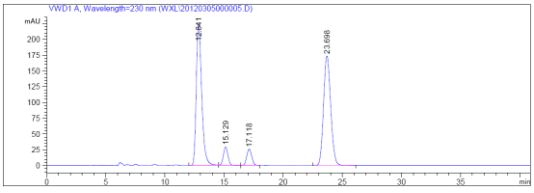
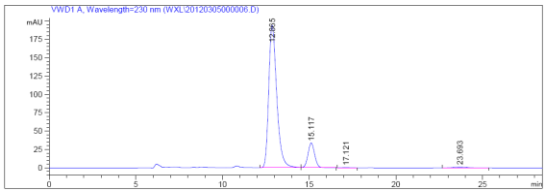


Table 5, entry 2

For racemic product 9b and enantioenriched product 9b (dr 88:12; er 99:1):



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.841	BV	0.4895	7188.75049	223.97156	44.8805
2	15.129	VB	0.4157	780.22742	29.19925	4.8711
3	17.118	BB	0.4593	750.94043	25.51740	4.6882
4	23.698	MM	0.7007	7297.63574	173.58002	45.5602
Totals :				1.60176e4	452.26822	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.865	BV	0.4916	6256.29395	193.79486	86.7624
2	15.117	VB	0.4149	892.22308	33.48107	12.3734
3	17.121	MM	0.6122	11.81188	3.21550e-1	0.1638
4	23.693	BB	0.6093	50.50572	1.17315	0.7004
Totals :				7210.83463	228.77063	

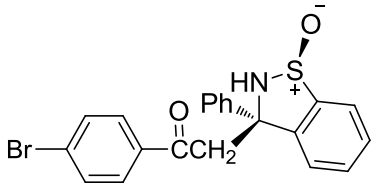
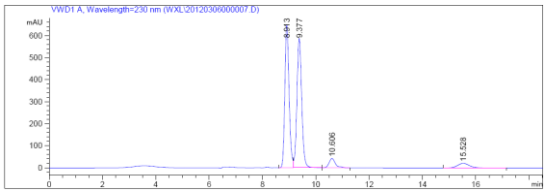
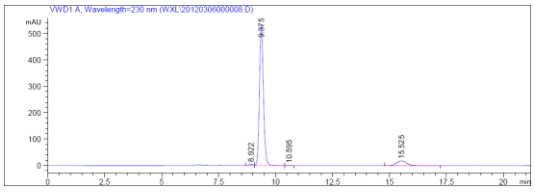


Table 5, entry 3

For racemic product 9c and enantioenriched product 9c (dr 92:8; er 99:1):



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.913	BV	0.1712	7159.23975	646.52527	45.3411
2	9.377	VB	0.1915	7326.48633	587.47137	46.4003
3	10.606	BB	0.2494	680.10400	41.67731	4.3073
4	15.528	BB	0.4693	623.91388	20.54512	3.9514
Totals :				1.57897e4	1296.21908	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.922	BV	0.1668	50.57066	4.61703	0.7123
2	9.375	VV	0.1887	6518.44873	532.82629	91.8194
3	10.595	VB	0.2058	3.05975	2.16552e-1	0.0431
4	15.525	VB	0.4718	527.12561	17.28636	7.4251
Totals :				7099.20475	554.94623	

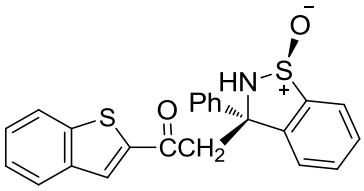
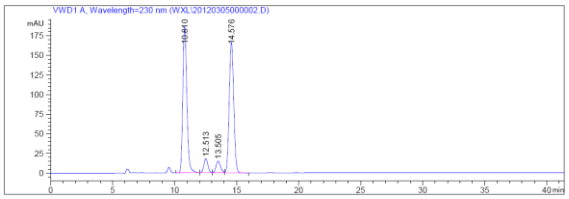
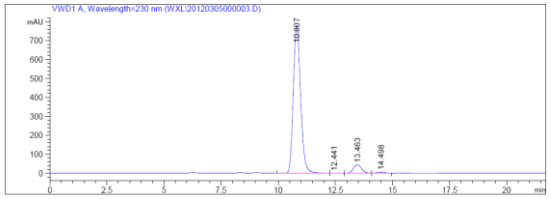


Table 5, entry 4

For racemic product 9d and enantioenriched product 9d (dr 94:6; er 99:1):



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.810	BB	0.3510	4237.83154	186.59039	46.0434
2	12.513	BV	0.3451	396.82645	17.93722	4.3115
3	13.505	VV	0.3916	379.79050	14.98961	4.1264
4	14.576	VB	0.3949	4189.54785	166.28526	45.5188
Totals :				9203.99634	385.80248	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.807	BV	0.3435	1.73742e4	781.18713	93.2256
2	12.441	VB	0.3286	17.60062	7.50541e-1	0.0944
3	13.463	BV	0.3870	1094.60071	44.19531	5.8734
4	14.498	VV	0.3934	150.32062	5.93607	0.8066
Totals :				1.86367e4	832.06905	

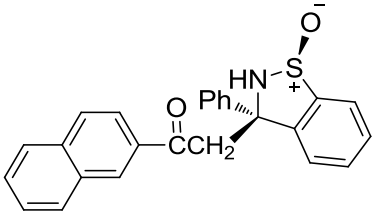
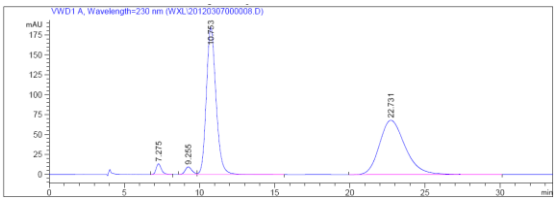
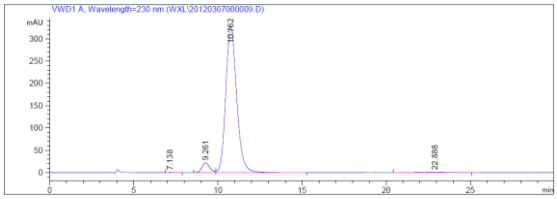


Table 5, entry 5

For racemic product 9e and enantioenriched product 9e (dr 95:5; er 99:1):



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.275	BB	0.3706	314.50177	13.16936	1.8523
2	9.255	VV	0.4741	291.67807	9.37292	1.7179
3	10.753	VB	0.6878	8226.77734	184.30013	48.4531
4	22.731	BB	1.7812	8145.87842	68.26195	47.9767
Totals :				1.69788e4	275.10436	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.138	MM	0.3023	12.48527	6.88352e-1	0.0803
2	9.261	VV	0.4848	693.42529	21.87630	4.4623
3	10.762	VB	0.6865	1.47145e4	329.16595	94.6903
4	22.888	MM	1.9746	119.19521	1.00606	0.7670
Totals :				1.55397e4	352.73667	

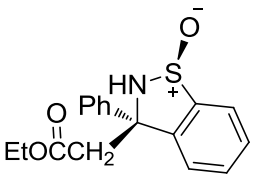
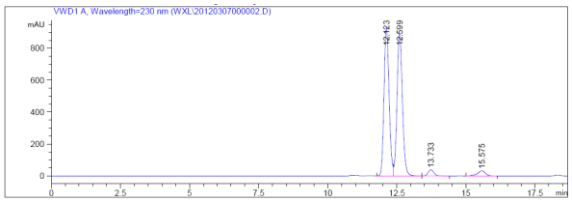
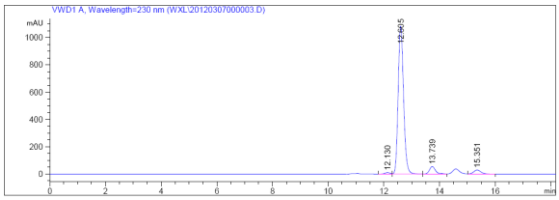


Table 5, entry 6

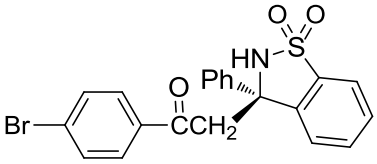
For racemic product 9f and enantioenriched product 9f (dr 95:5; er 99:1):



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.123	BV	0.1980	1.18647e4	929.21362	47.2776
2	12.599	VB	0.2084	1.20484e4	892.97437	48.0098
3	13.733	BB	0.2190	538.30145	38.06496	2.1450
4	15.575	VV	0.2968	644.37830	32.42722	2.5677
Totals :				2.50958e4	1892.68016	

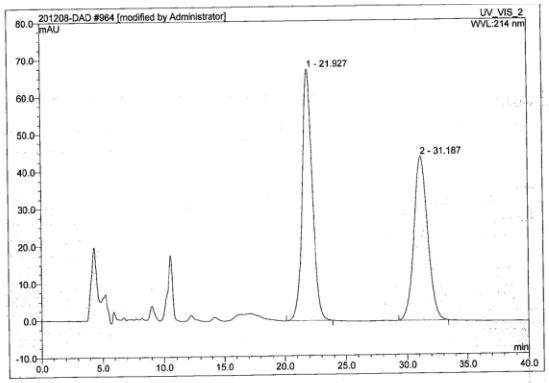


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.130	BV	0.1901	128.13869	10.44580	0.8009
2	12.605	VB	0.2088	1.45606e4	1083.50818	91.0041
3	13.739	BB	0.2241	791.95721	54.31679	4.9497
4	15.351	VB	0.2781	519.24432	28.69657	3.2453
Totals :				1.60000e4	1176.96734	

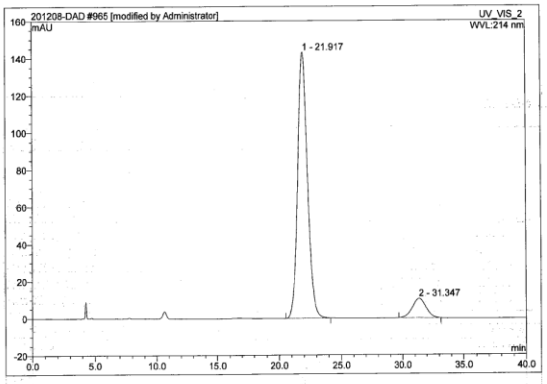


SI Section 3.6

For racemic product S4 and enantioenriched product S4 (er 90.5:9.5):

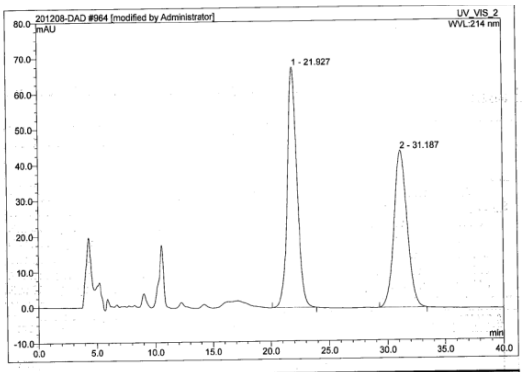


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.93	n.a.	67.579	64.171	52.23	n.a.	BMB
2	31.19	n.a.	44.061	58.687	47.77	n.a.	BMB
Total:			111.641	122.857	100.00	0.000	

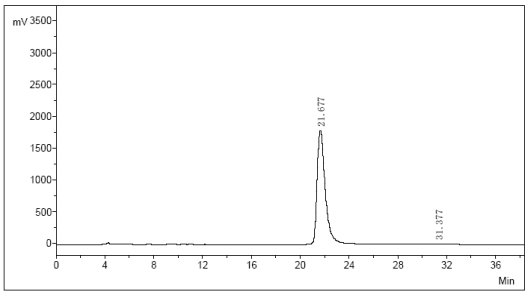


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.92	n.a.	143.206	130.271	90.56	n.a.	BMB
2	31.35	n.a.	10.418	13.582	9.44	n.a.	BMB
Total:			153.624	143.853	100.00	0.000	

For racemic product S4 and enantioenriched product S4 (after a single recrystallization; er > 99:1):

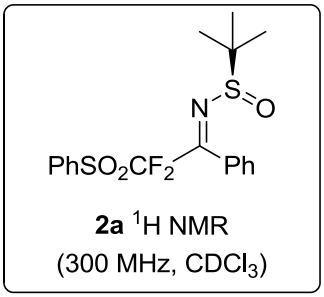


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.93	n.a.	67.579	64.171	52.23	n.a.	BMB
2	31.19	n.a.	44.061	58.687	47.77	n.a.	BMB
Total:			111.641	122.857	100.00	0.000	

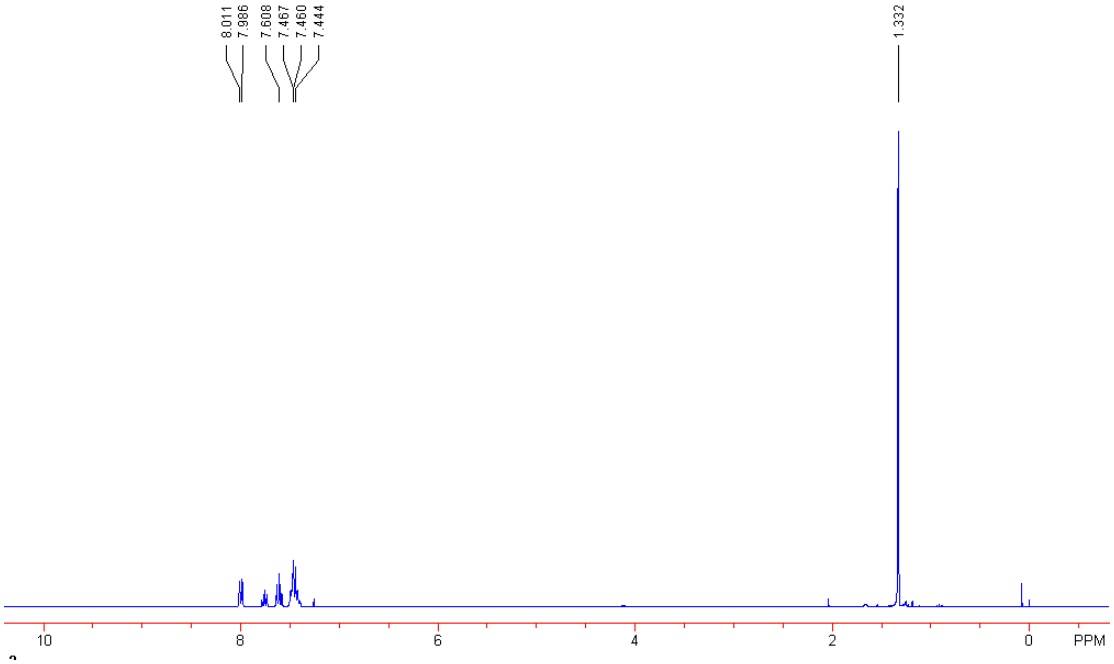


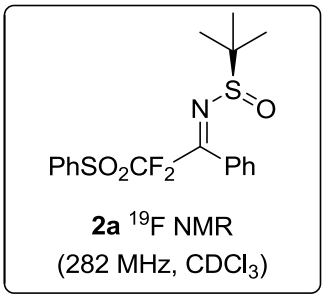
No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1		21.677	1780675.6	83914698.6	99.5743
2	2		31.377	5652.5	358744.7	0.4257
Total				1786328.1	84273443.3	100.0000

5. ^{1}H, ^{19}F, and ^{13}C NMR Spectrum of New Compounds

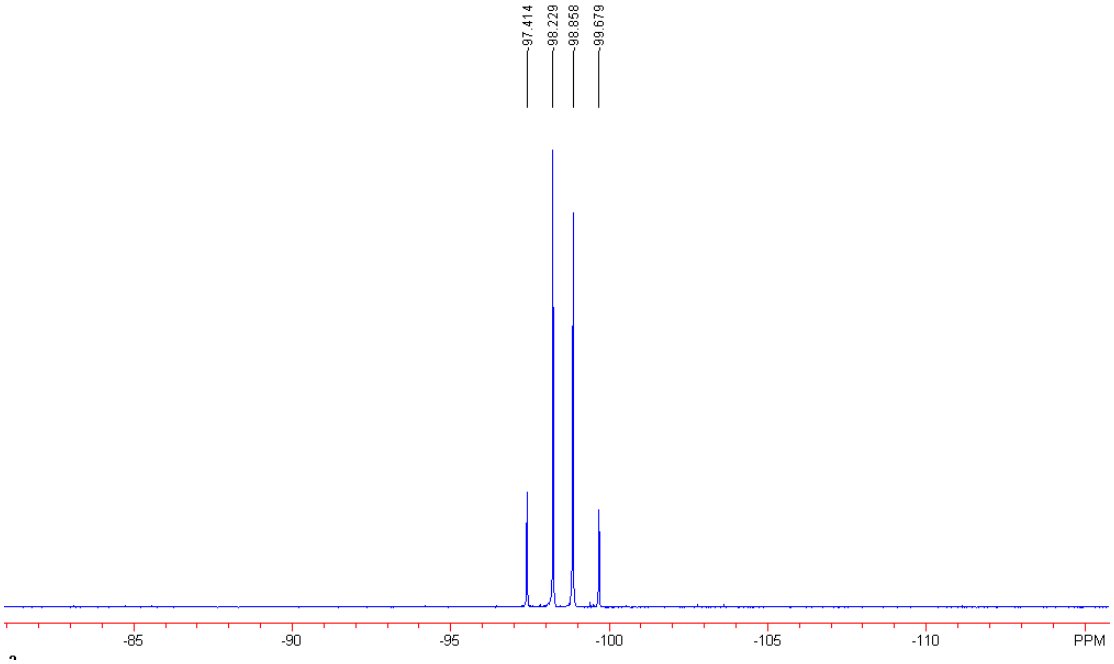


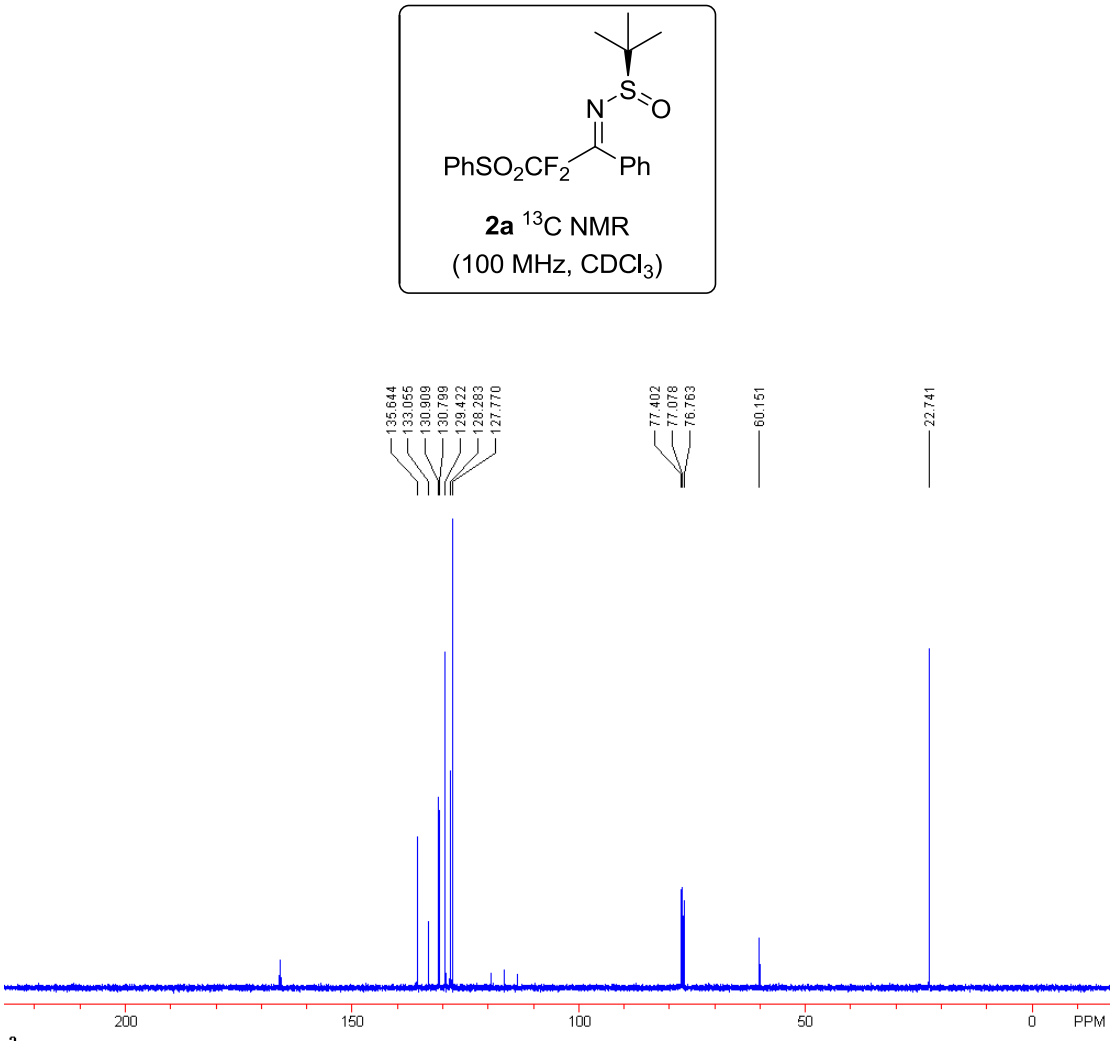
2a ^{1}H NMR
(300 MHz, $CDCl_3$)

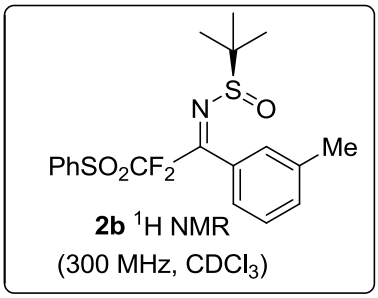


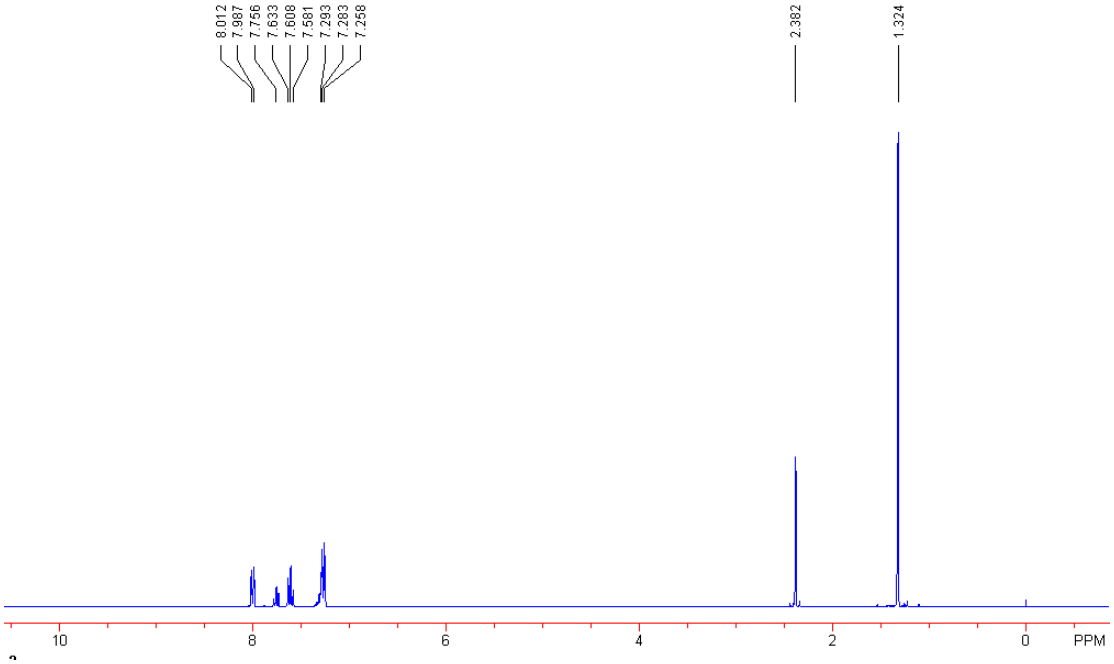


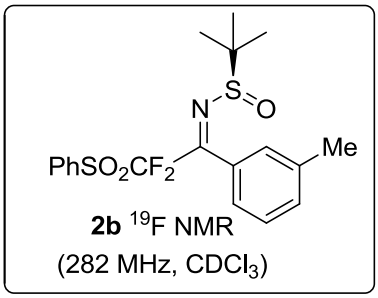
2a ^{19}F NMR
(282 MHz, $CDCl_3$)




PhSO2CF2
Ph
2a 13C NMR
(100 MHz, CDCl3)
135.644
133.055
130.909
130.799
129.422
128.283
127.770
77.402
77.078
76.763
60.151
22.741
200
150
100
50
0
PPM

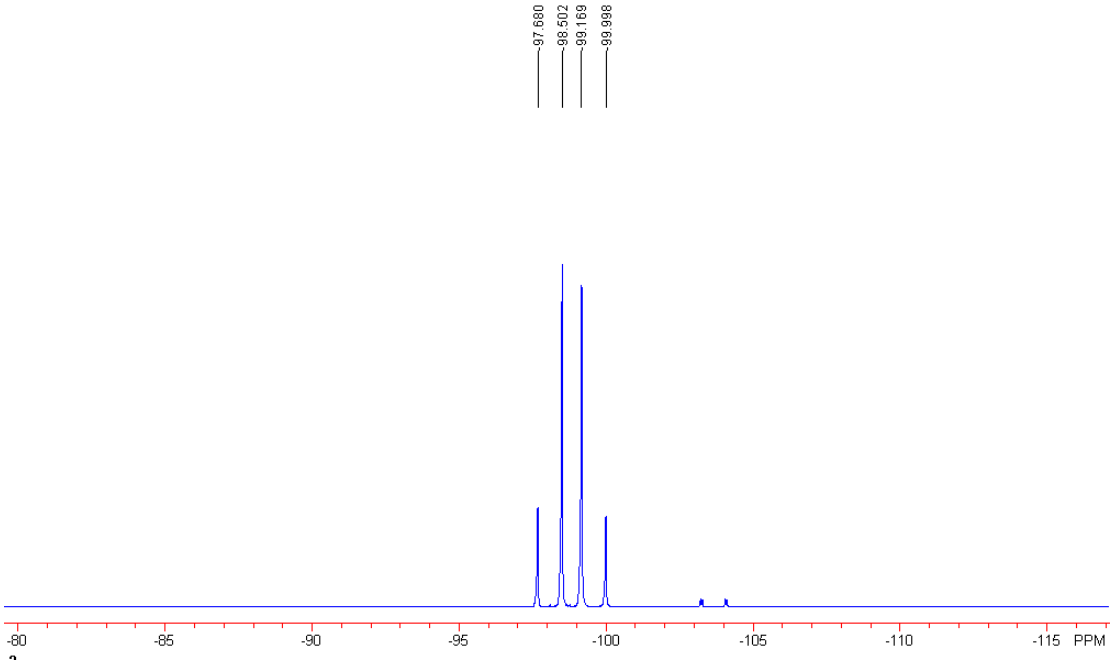

N
S
O
Me
PhSO2CF2
2b 1H NMR
(300 MHz, CDCl3)

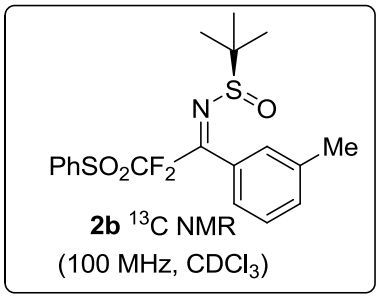

8.012
7.987
7.756
7.633
7.608
7.581
7.293
7.283
7.258
2.382
1.324
10
8
6
4
2
0
PPM

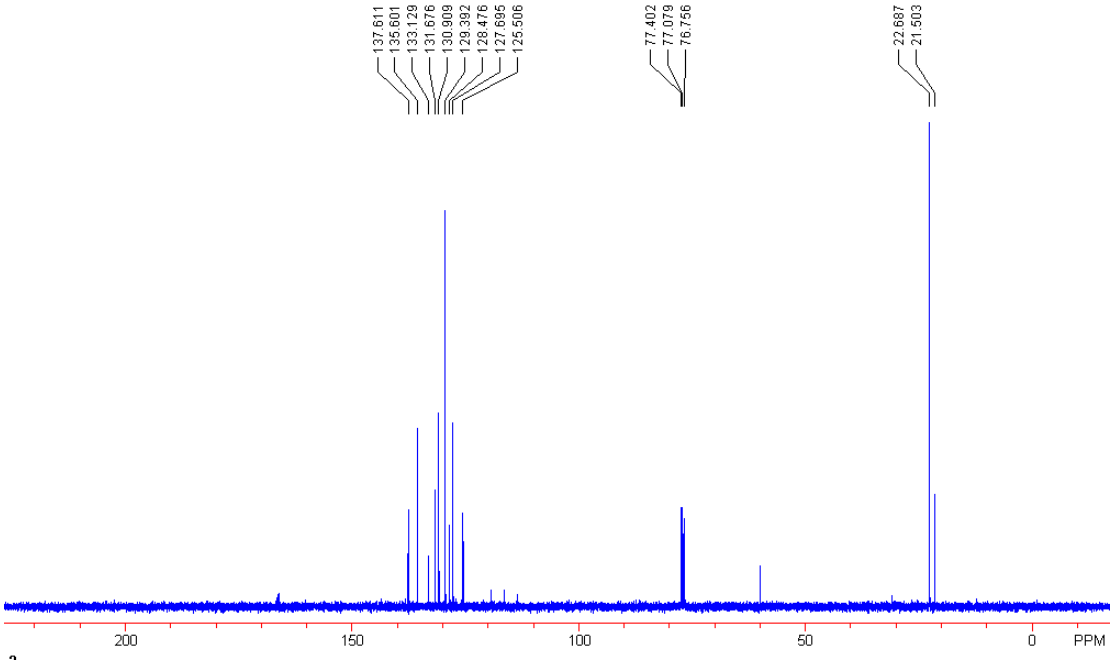


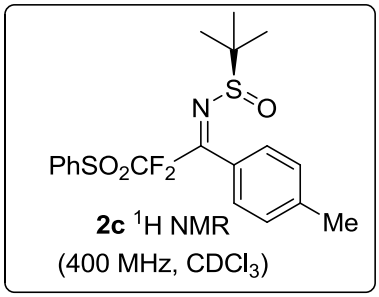
2b ^{19}F NMR

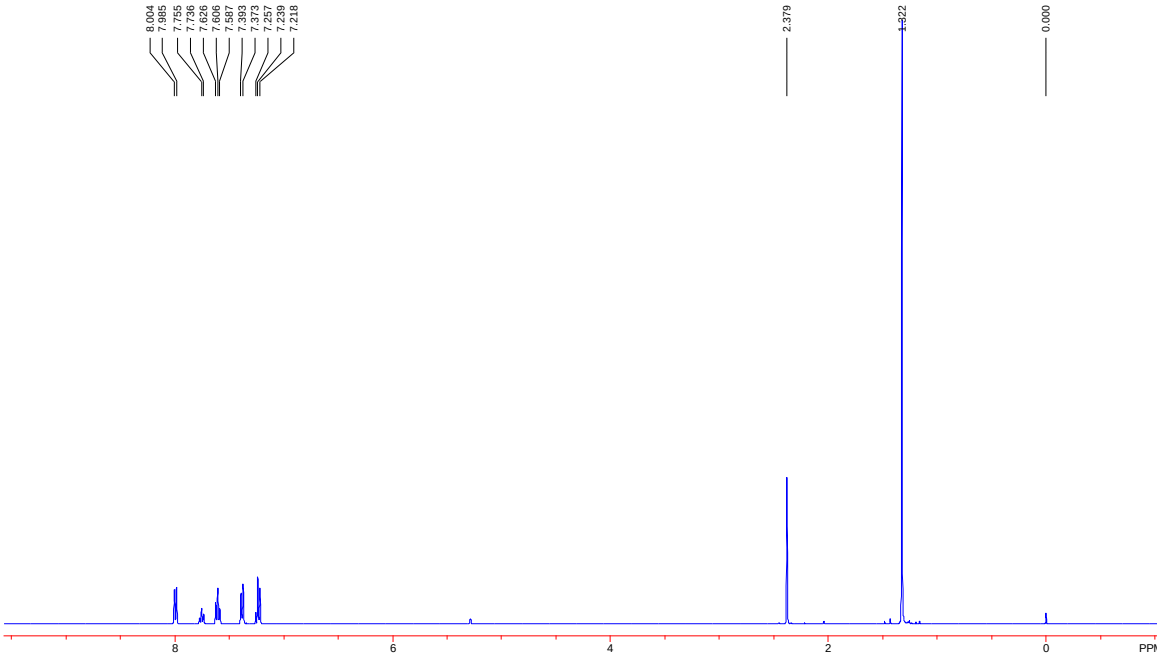
(282 MHz, $CDCl_3$)

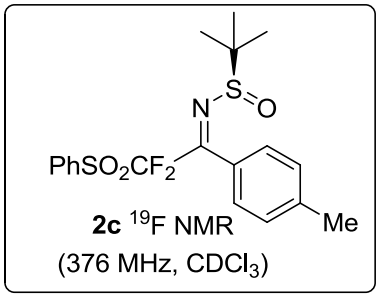


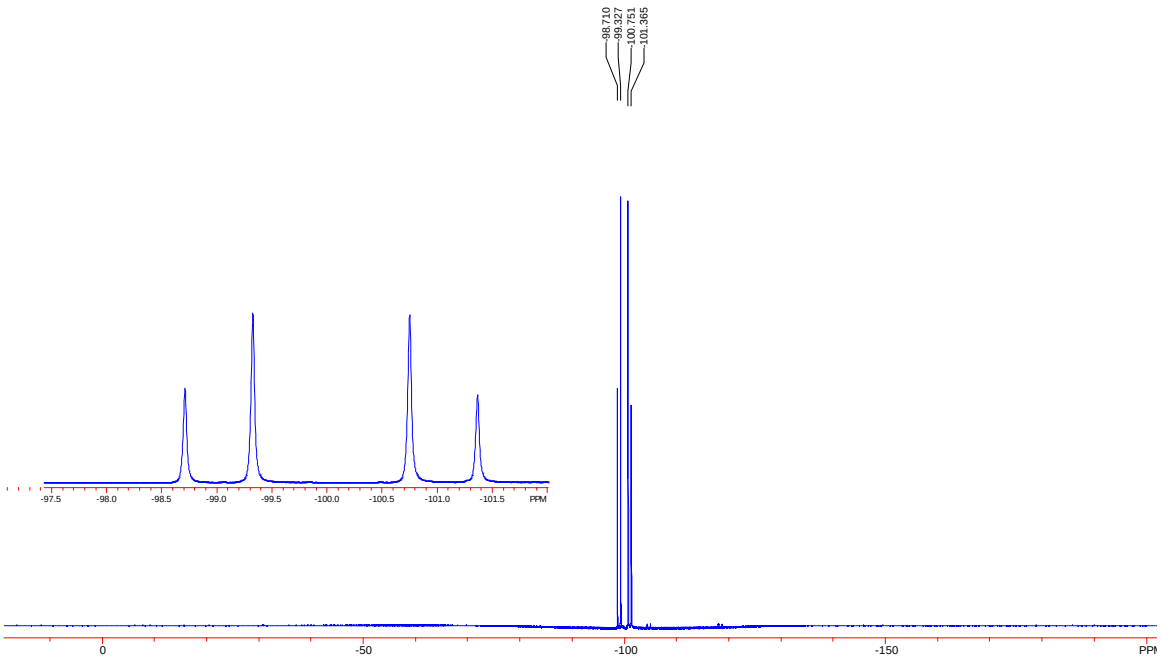

N
S
O
Me
PhSO2CF2
2b 13C NMR
(100 MHz, CDCl3)

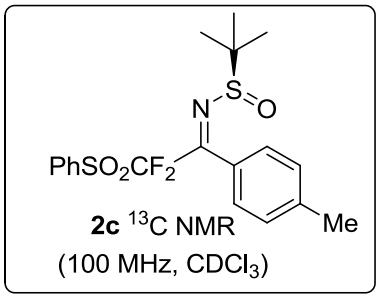

137.611
135.601
133.129
131.676
130.909
129.392
128.476
127.695
125.506
77.402
77.079
76.756
22.687
21.503
200
150
100
50
0
PPM

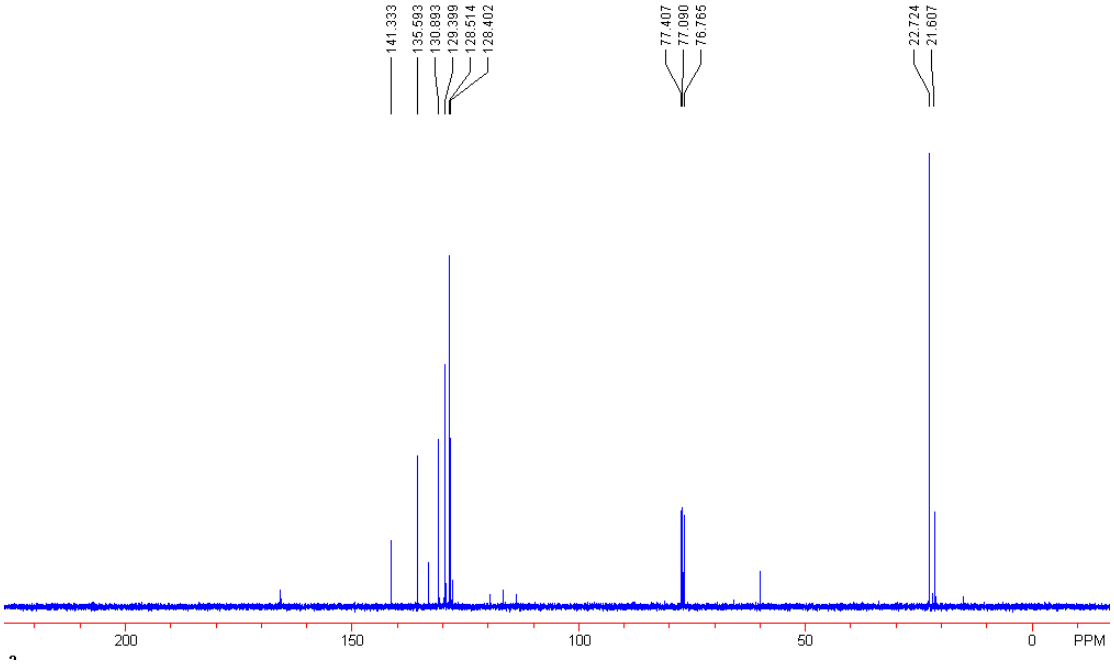

N
S
O
PhSO2CF2
Me
2c 1H NMR
(400 MHz, CDCl3)

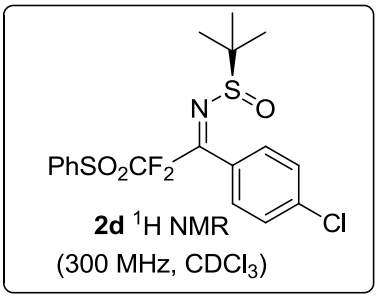

8.004
7.985
7.755
7.736
7.626
7.606
7.587
7.393
7.373
7.257
7.239
7.218
2.379
1.322
0.000
8
6
4
2
0
PPM

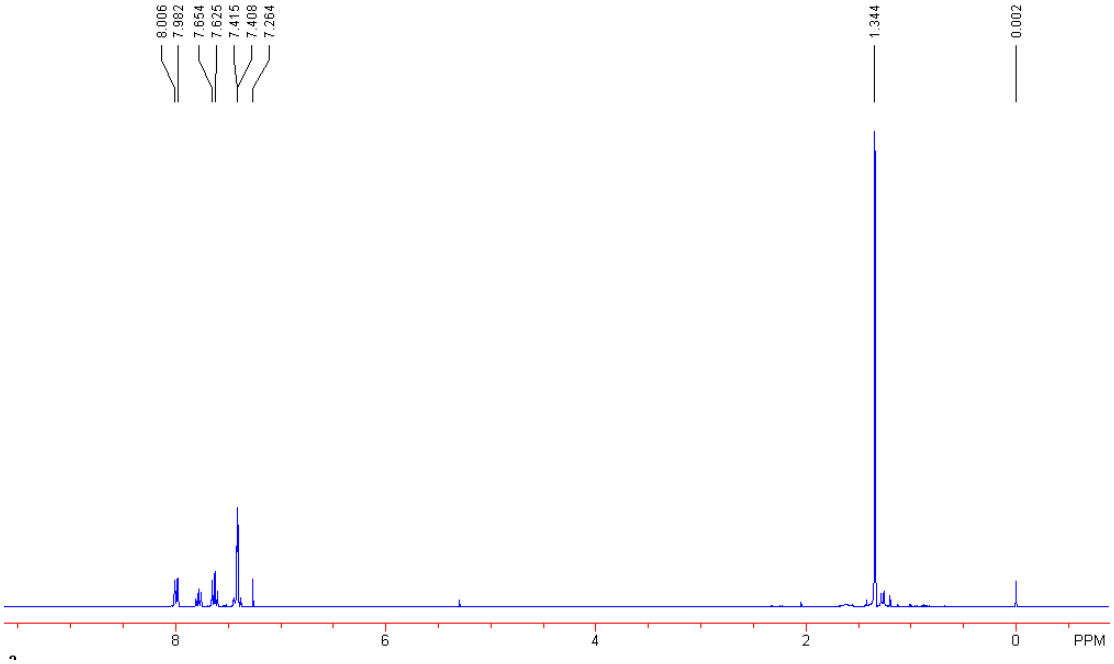

PhSO2CF2
N
S
O
Me
2c 19F NMR
(376 MHz, CDCl3)

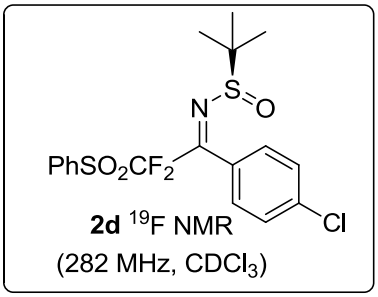

-98.710
-99.377
-100.751
-101.365
-97.5
-98.0
-98.5
-99.0
-99.5
-100.0
-100.5
-101.0
-101.5
PPM
0
-50
-100
-150
PPM

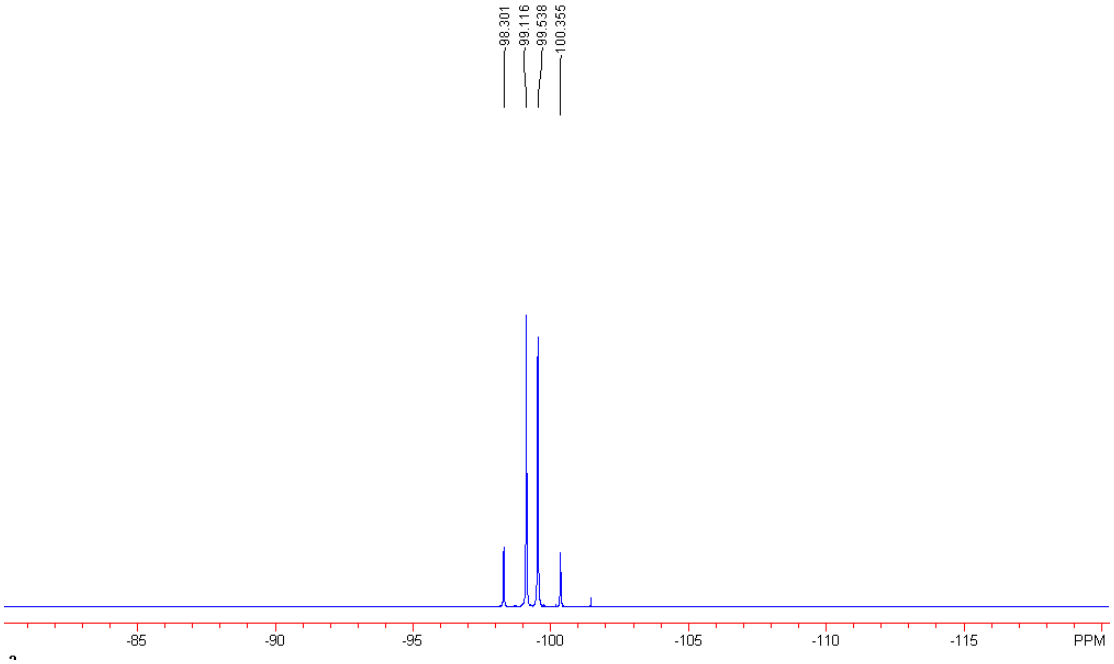

N
S
O
PhSO2CF2
Me
2c 13C NMR
(100 MHz, CDCl3)

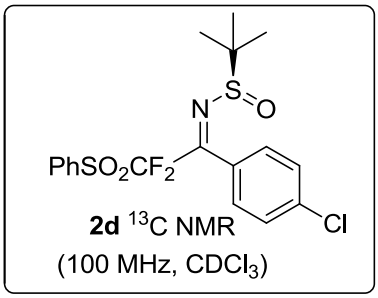

141.333
135.593
130.893
129.399
128.514
128.402
77.407
77.090
76.765
22.724
21.607
200
150
100
50
0
PPM

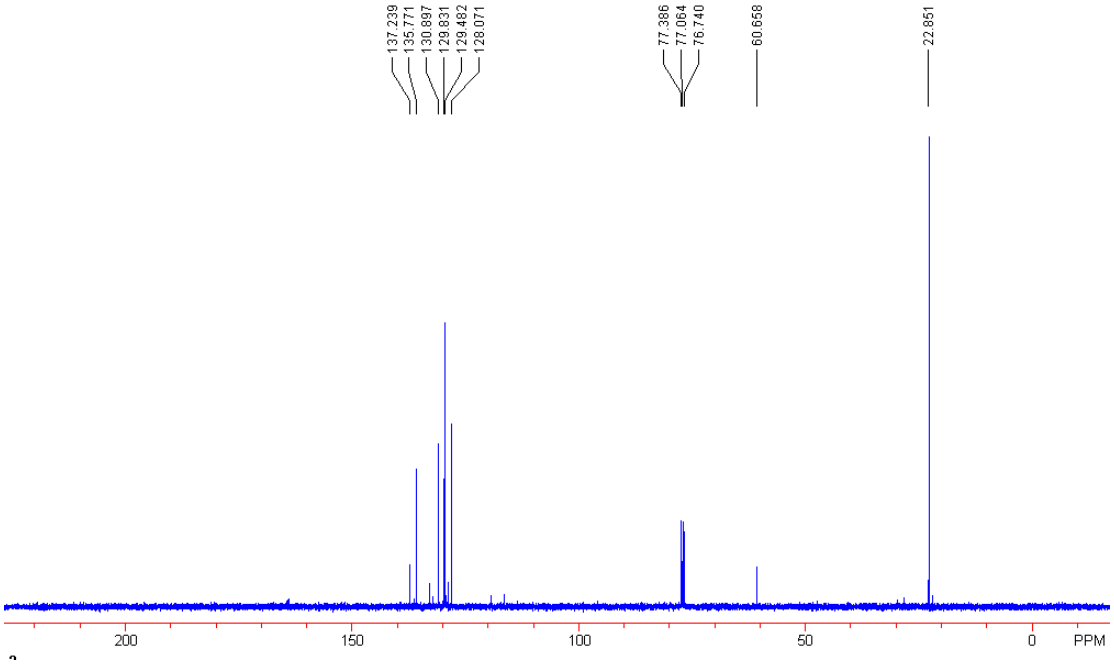

PhSO2CF2
N
S
O
Cl
2d 1H NMR
(300 MHz, CDCl3)

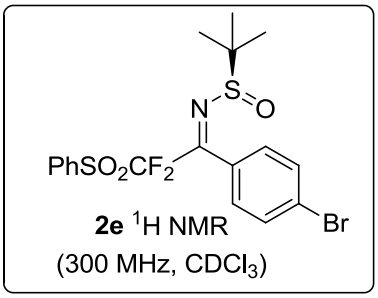

8.006
7.982
7.654
7.625
7.415
7.408
7.264
1.344
0.002
8
6
4
2
0
PPM

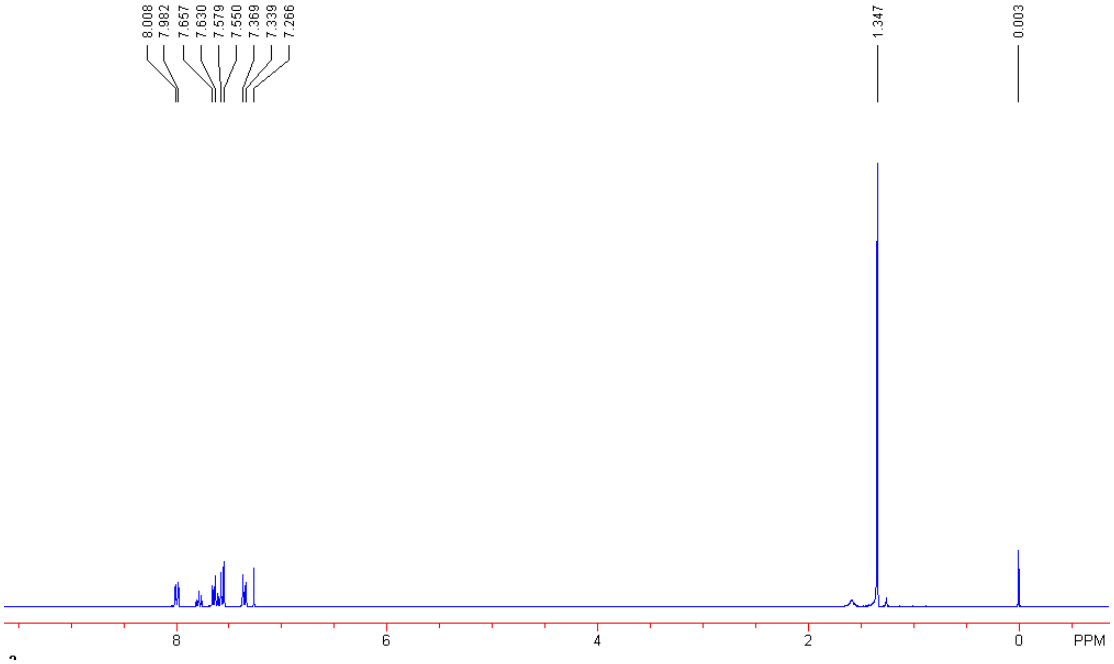

PhSO2CF2
N
S
O
Cl
2d 19F NMR
(282 MHz, CDCl3)

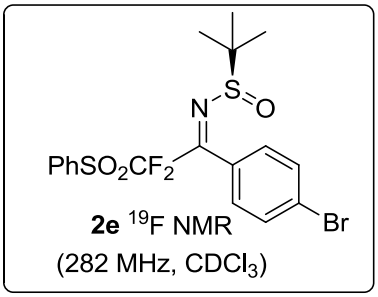

-98.301
-99.116
-99.538
-100.355
-85
-90
-95
-100
-105
-110
-115
PPM

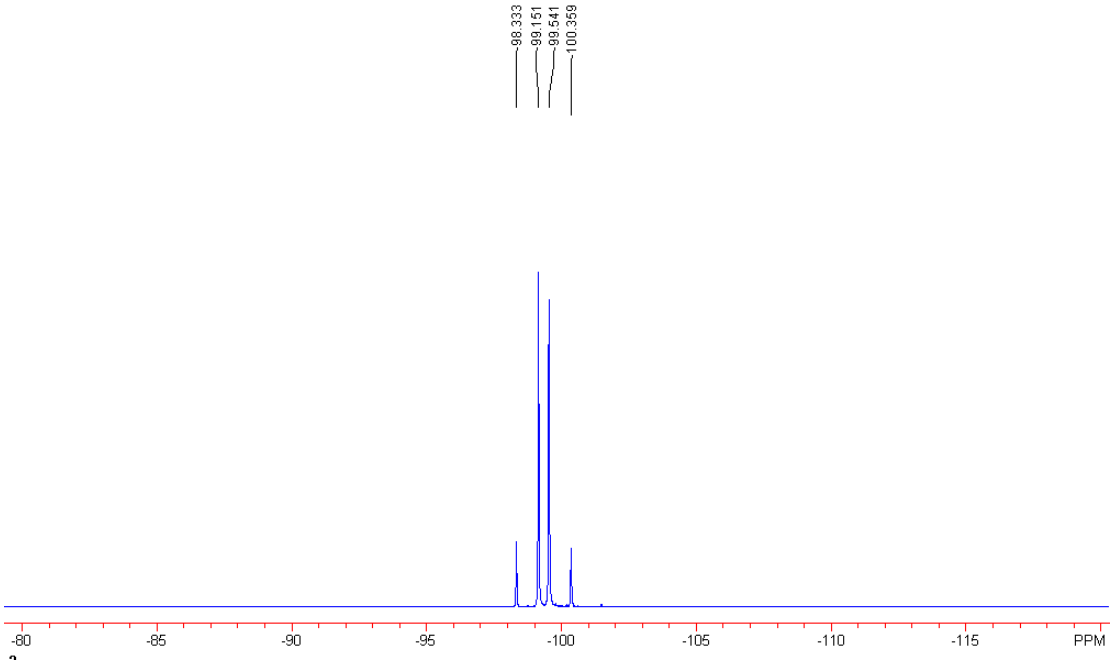

PhSO2CF2
N
S
O
Cl
2d 13C NMR
(100 MHz, CDCl3)

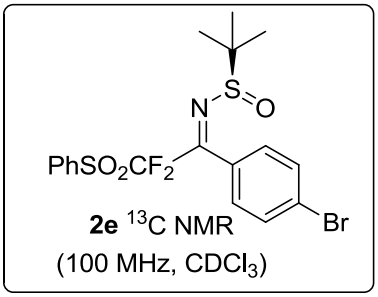

137.239
135.771
130.897
129.831
129.482
128.071
77.386
77.064
76.740
60.658
22.851
200
150
100
50
0
PPM

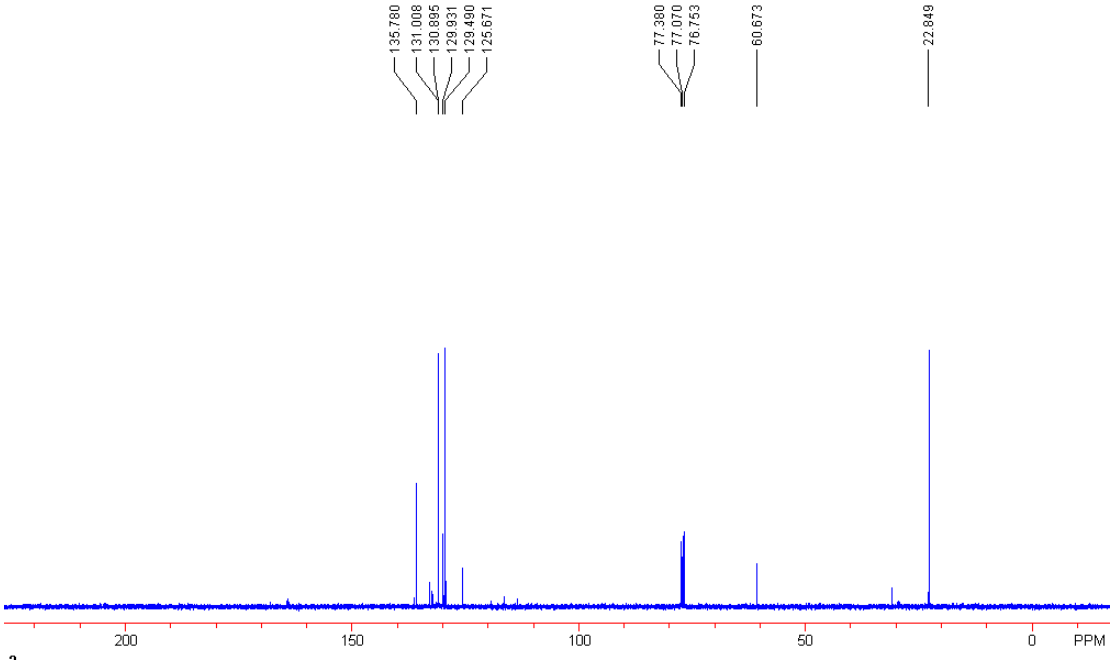

PhSO2CF2
N
S
O
Br
2e 1H NMR
(300 MHz, CDCl3)

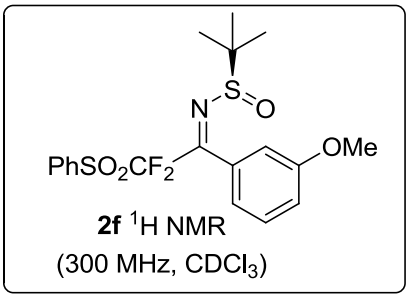

8.008
7.982
7.657
7.630
7.579
7.550
7.369
7.339
7.266
1.347
0.003
8
6
4
2
0
PPM

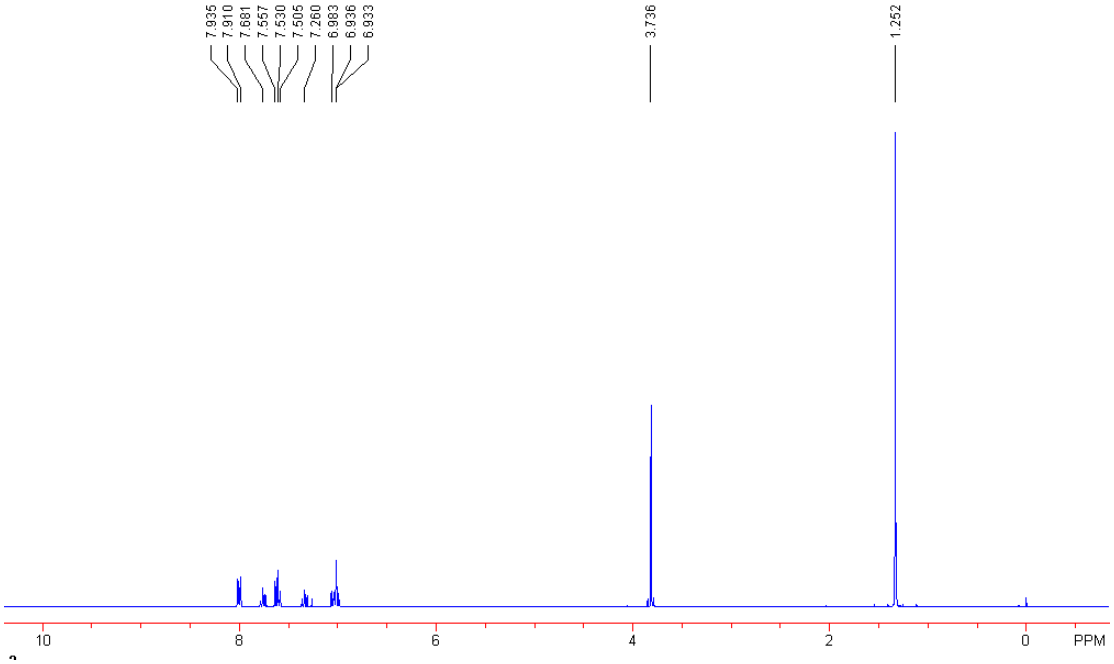

PhSO2CF2
N
S
O
Br
2e 19F NMR
(282 MHz, CDCl3)

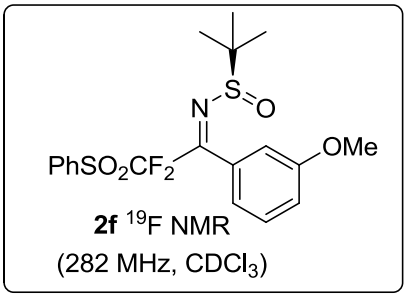

-98.333
-99.151
-99.541
-100.359
-80
-85
-90
-95
-100
-105
-110
-115
PPM

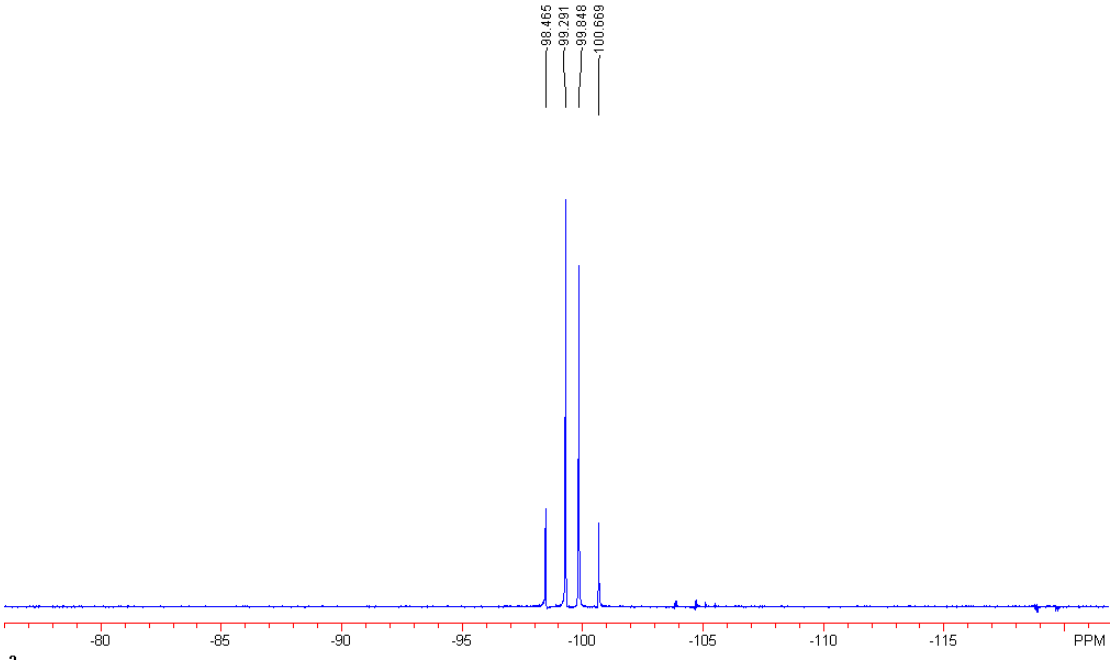

N
S
O
PhSO2CF2
Br
2e 13C NMR
(100 MHz, CDCl3)

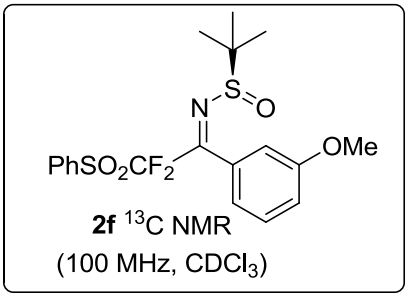

135.780
131.008
130.895
129.931
129.490
125.671
77.380
77.070
76.753
60.673
22.849
200
150
100
50
0
PPM

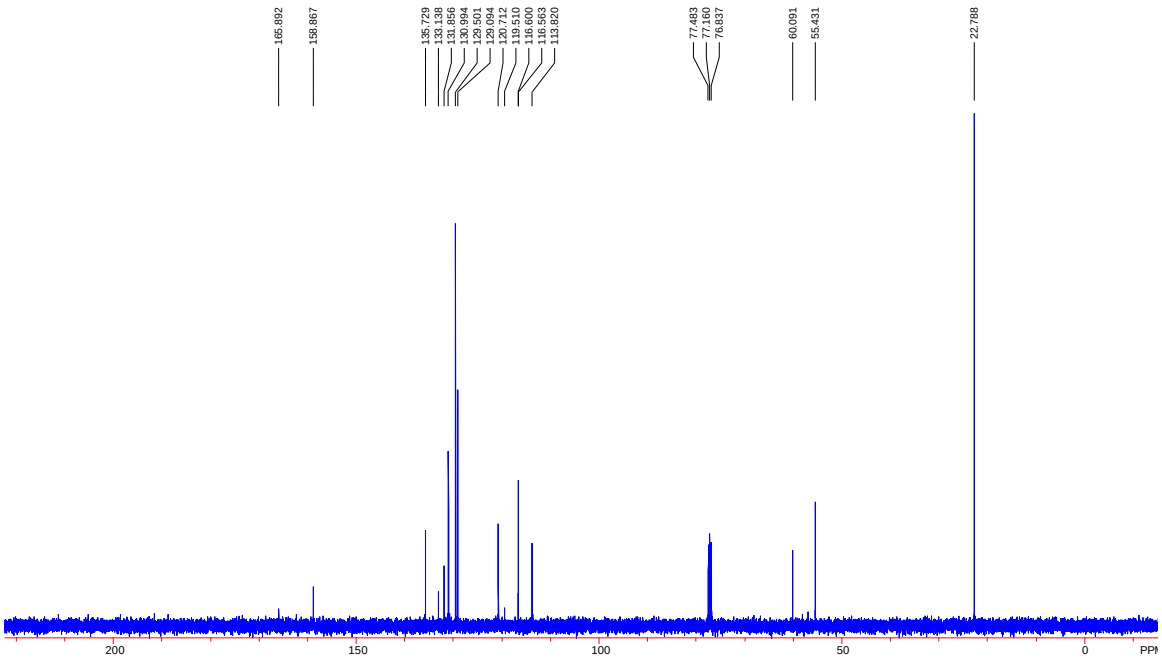

N
S
O
PhSO2CF2
OMe
2f 1H NMR
(300 MHz, CDCl3)

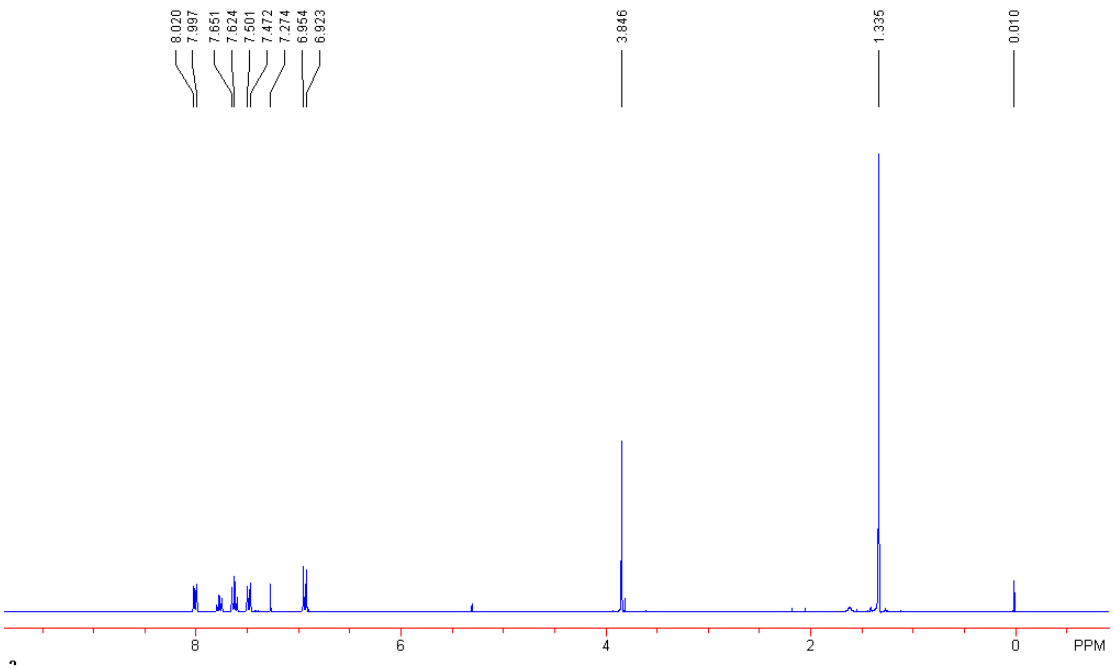

7.935
7.910
7.681
7.557
7.530
7.505
7.260
6.983
6.936
6.933
3.736
1.252
10
8
6
4
2
0
PPM

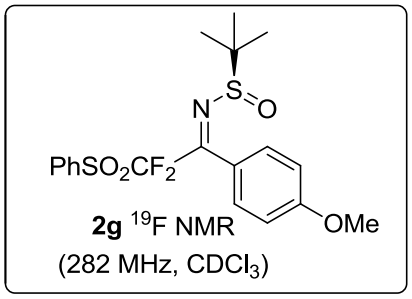

N
S
O
OMe
PhSO2CF2
2f 19F NMR
(282 MHz, CDCl3)

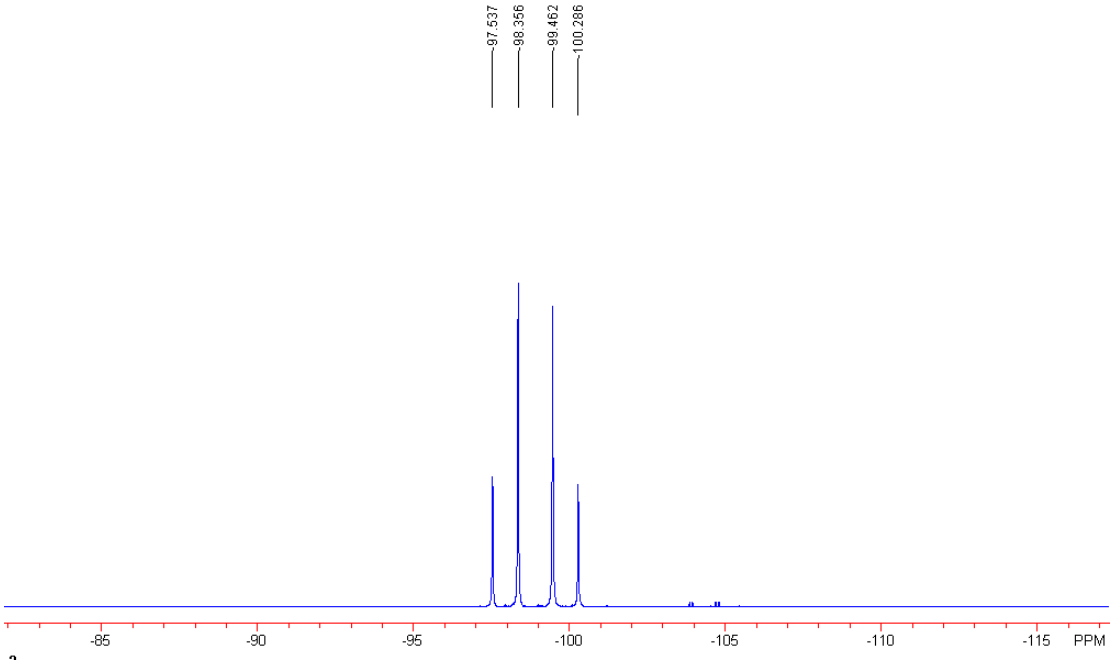

-98.465
-99.291
-99.848
-100.669
-80
-85
-90
-95
-100
-105
-110
-115
PPM

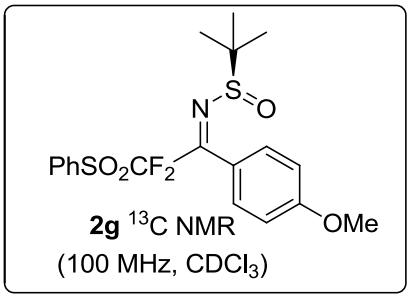

S
N
O
OMe
PhSO2CF2
2f 13C NMR
(100 MHz, CDCl3)

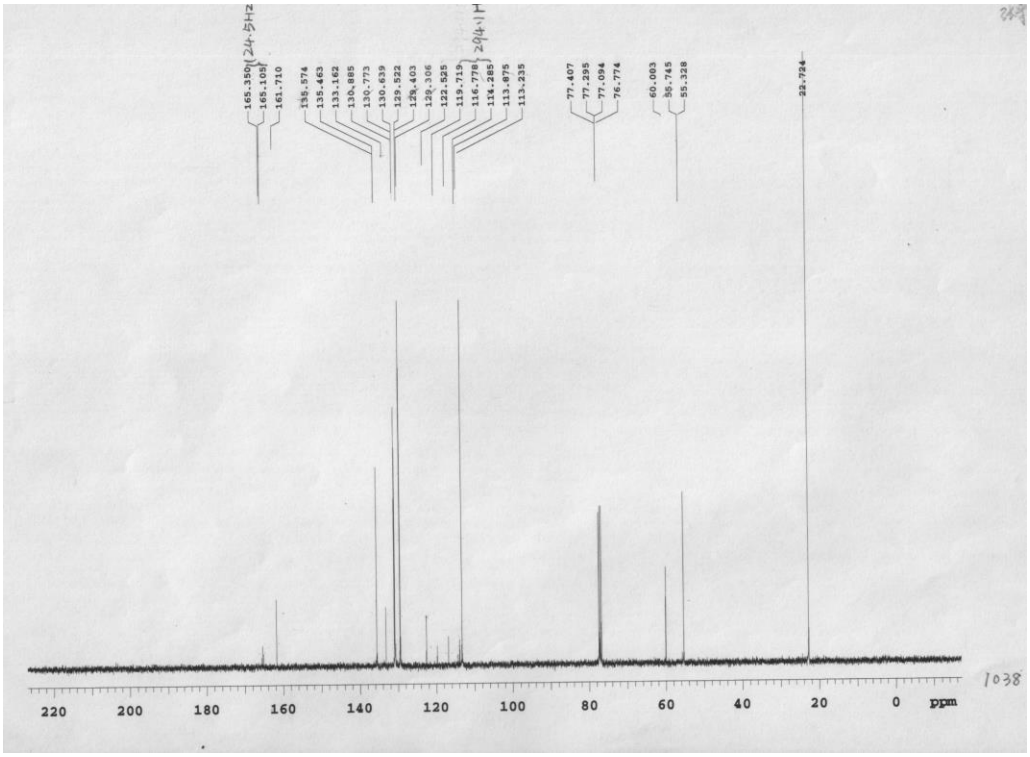

165.892
158.867
135.729
133.138
131.956
130.994
129.501
129.094
120.712
119.510
116.600
116.563
113.820
77.483
77.160
76.837
60.091
55.431
22.788
200
150
100
50
0
PPM


PhSO2CF2
N
S
O
OMe
2g 1H NMR
(300 MHz, CDCl3)
8.020
7.997
7.651
7.624
7.501
7.472
7.274
6.954
6.923
3.846
1.335
0.010
8
6
4
2
0
PPM


PhSO2CF2
N
S
O
OMe
2g 19F NMR
(282 MHz, CDCl3)


97.537
98.356
99.462
100.286
-85
-90
-95
-100
-105
-110
-115
PPM


PhSO2CF2
OMe
2g 13C NMR
(100 MHz, CDCl3)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130.773
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122.525
119.713
116.778
114.285
113.875
113.235
77.407
77.295
77.094
76.774
60.003
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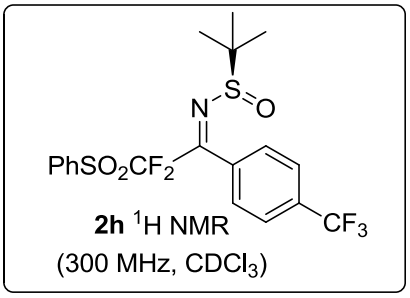
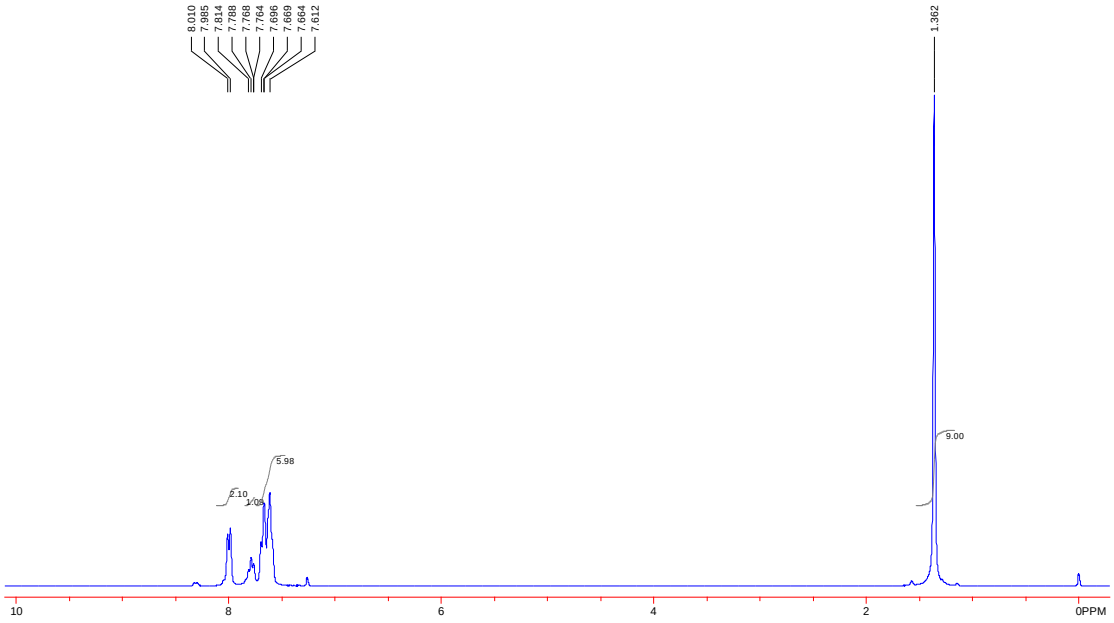
55.328
22.724
220
200
180
160
140
120
100
80
60
40
20
0
ppm


PhSO2CF2
N
S
O
CF3
2h 1H NMR
(300 MHz, CDCl3)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7.985
7.814
7.788
7.768
7.764
7.696
7.669
7.664
7.612
1.362
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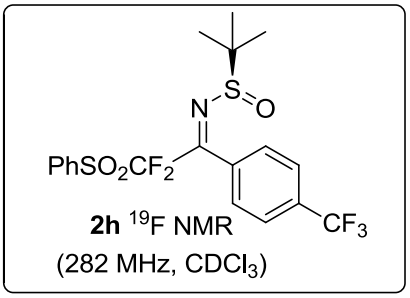
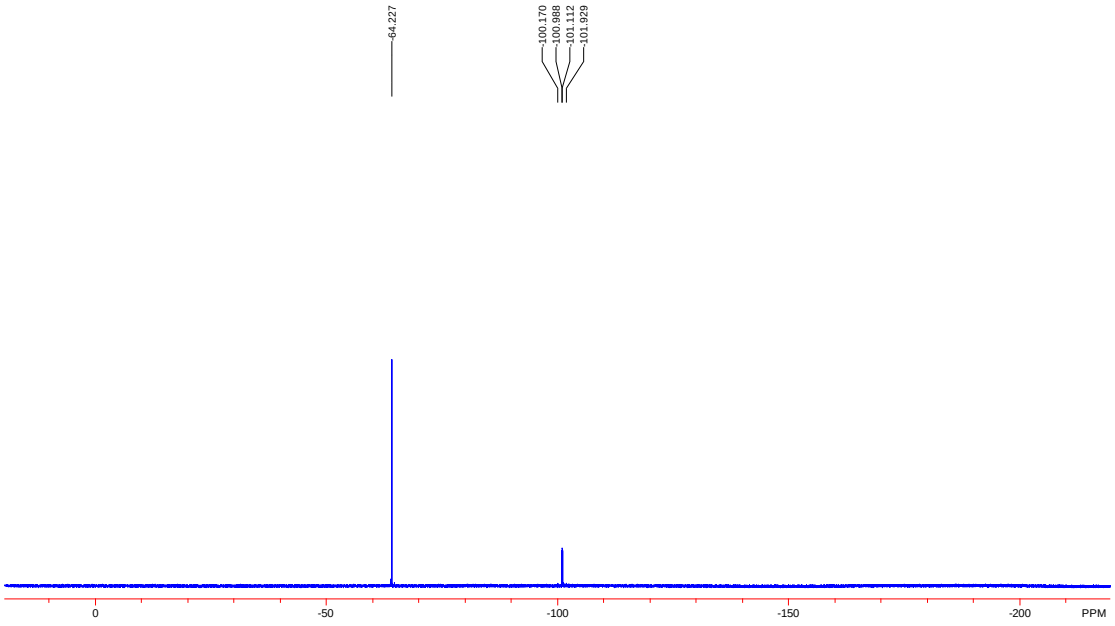
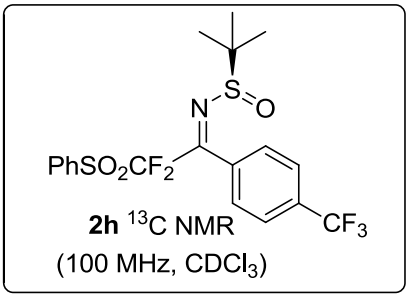
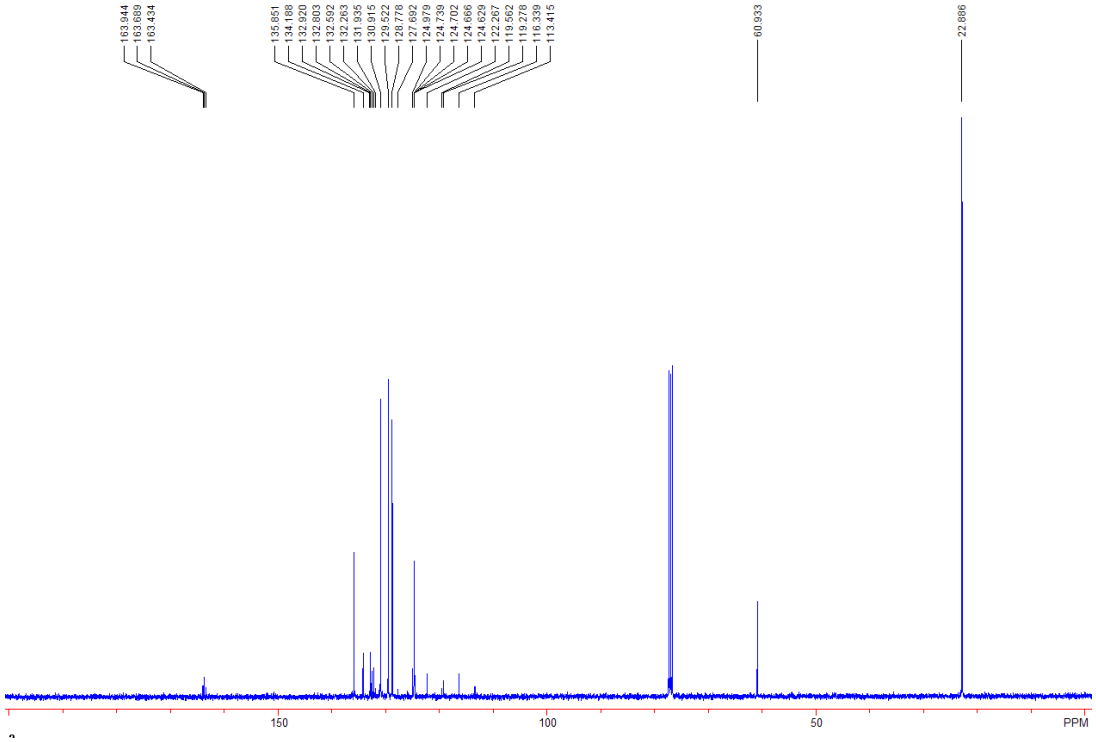
2.10
1.06
10
8
6
4
2
0PPM


PhSO2CF2
CF3
2h 19F NMR
(282 MHz, CDCl3)


-64.227
-100.170
-100.988
-101.112
-101.929
0
-50
-100
-150
-200
PPM


PhSO2CF2
N
S
O
CF3
2h 13C NMR
(100 MHz, CDCl3)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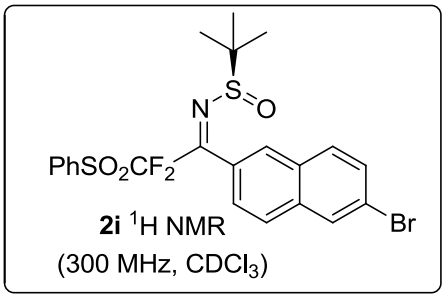
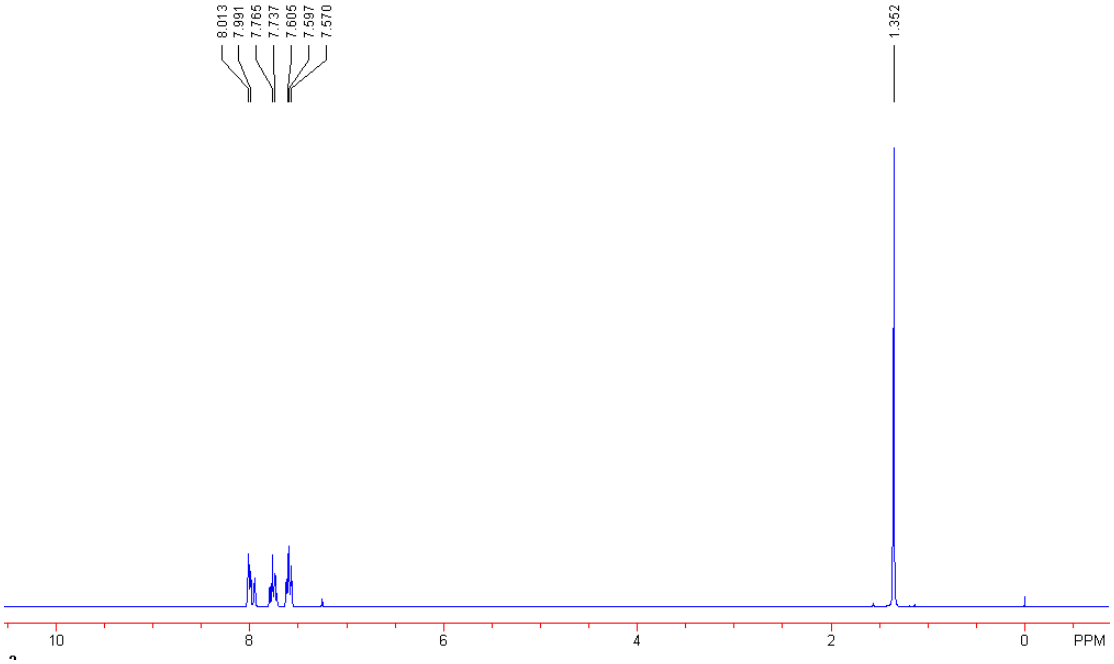
163.689
163.434
135.851
134.188
132.920
132.803
132.592
132.263
131.935
130.915
129.522
128.778
127.692
124.979
124.739
124.702
124.666
124.629
122.267
119.562
119.278
116.339
113.415
60.933
22.886
150
100
50
PPM


PhSO2CF2
N
S
O
Br
2i 1H NMR
(300 MHz, CDCl3)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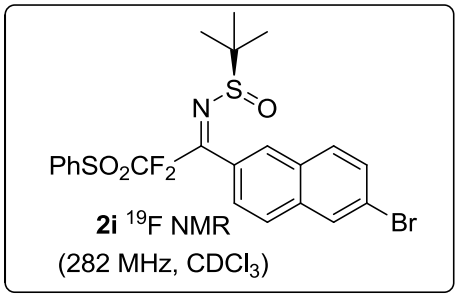
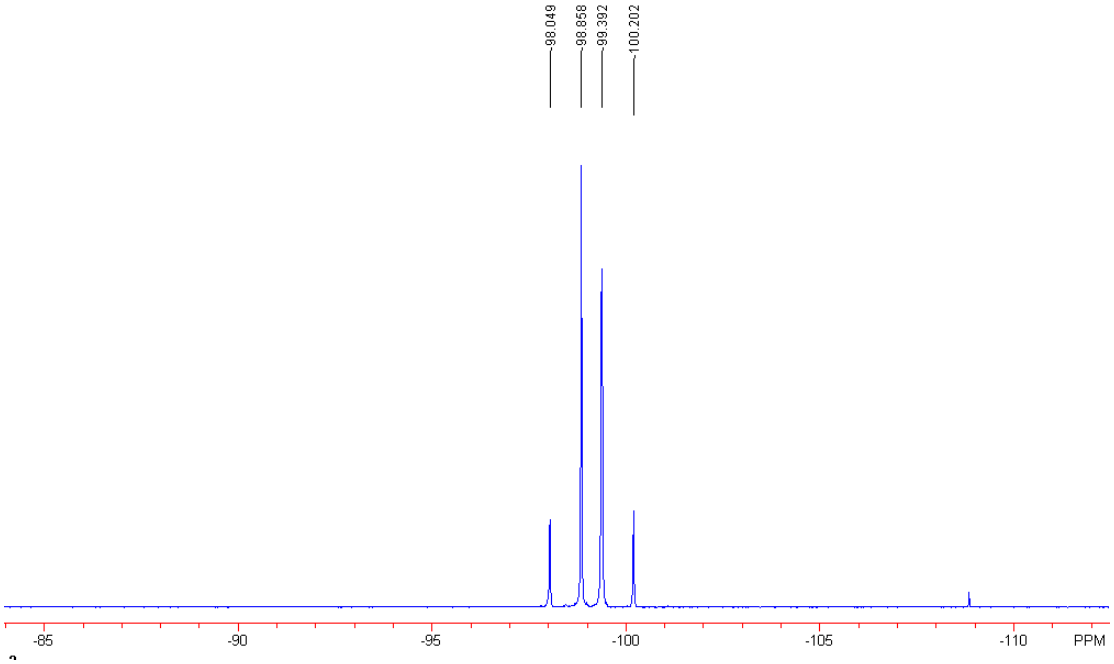
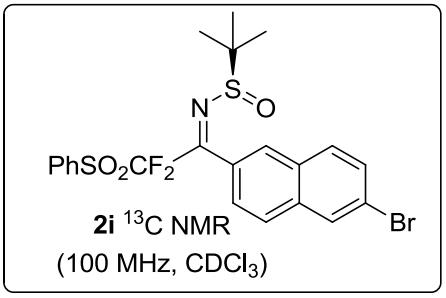
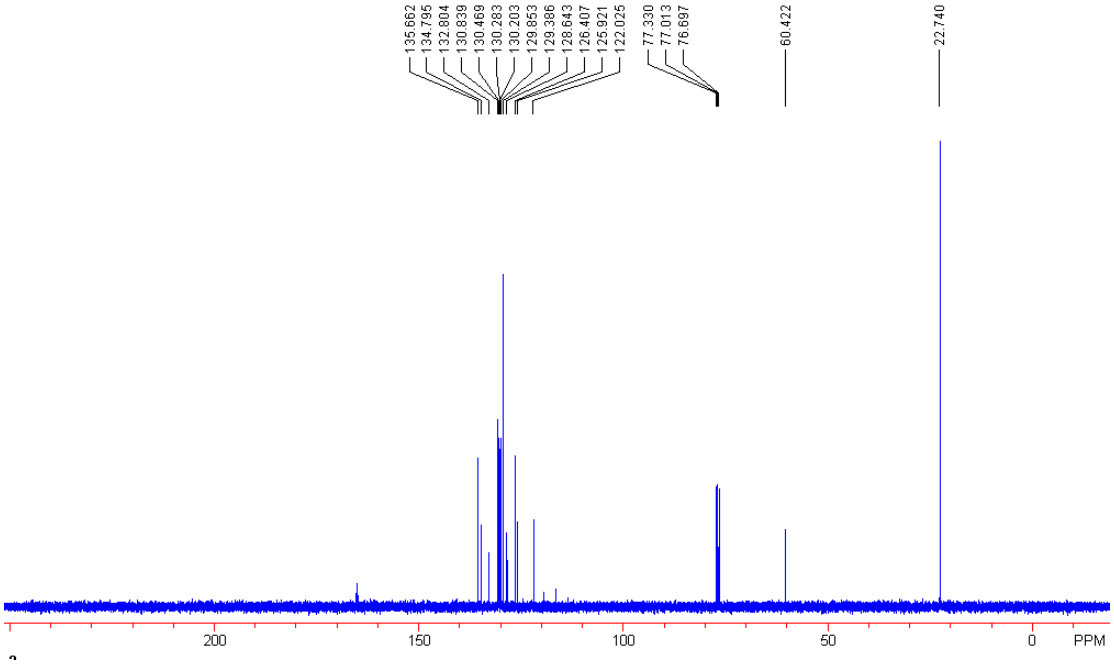
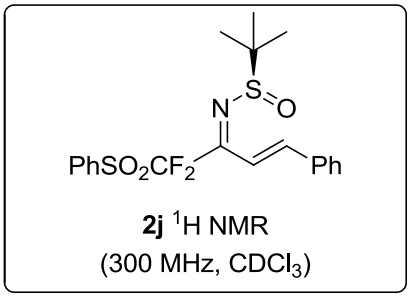
7.991
7.765
7.737
7.605
7.597
7.570
1.352
10
8
6
4
2
0
PPM


N
S
O
PhSO2CF2
Br
2i 19F NMR
(282 MHz, CDCl3)

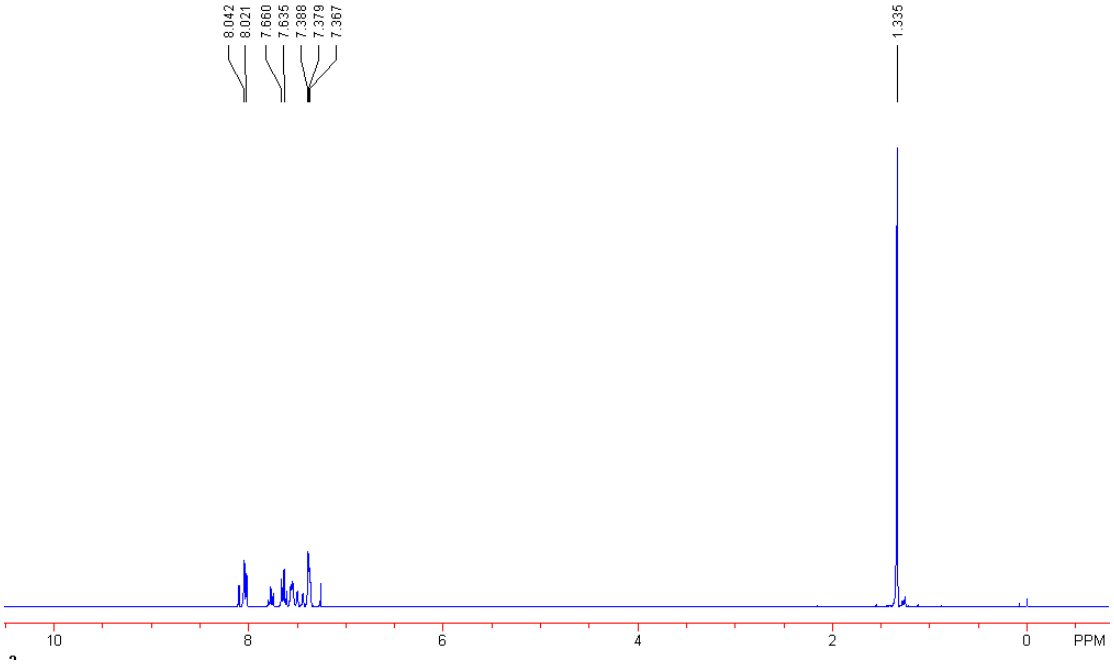

-98.049
-98.858
-99.392
-100.202
-85
-90
-95
-100
-105
-110
PPM

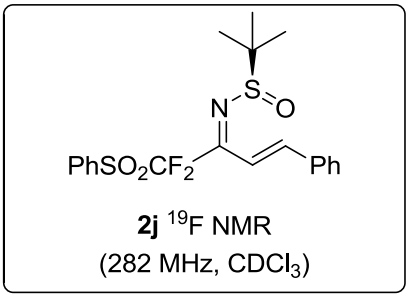

PhSO2CF2
N
S
O
Br
2i 13C NMR
(100 MHz, CDCl3)


135.662
134.795
132.804
130.839
130.469
130.283
130.203
129.853
129.386
128.643
126.407
125.921
122.025
77.330
77.013
76.697
60.422
22.740
200
150
100
50
0
PPM

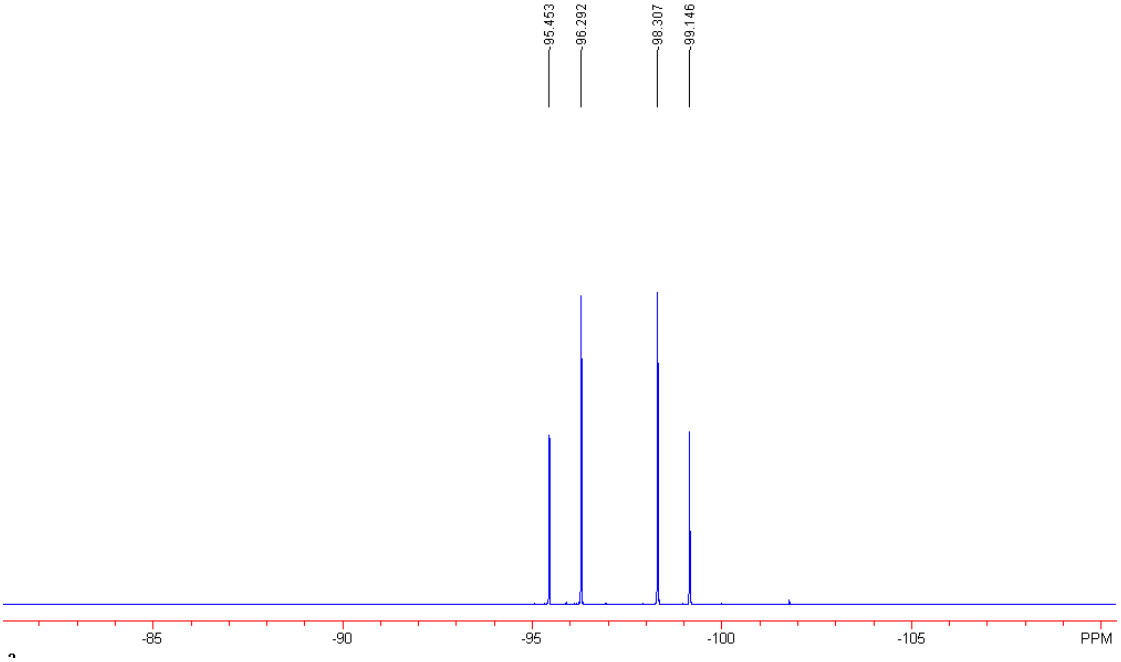


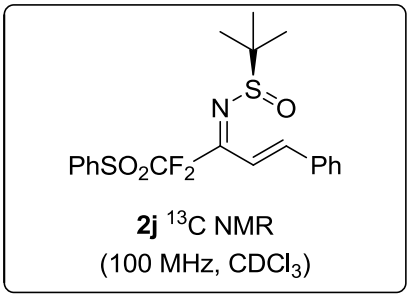
2j ^{1}H NMR
(300 MHz, $CDCl_3$)



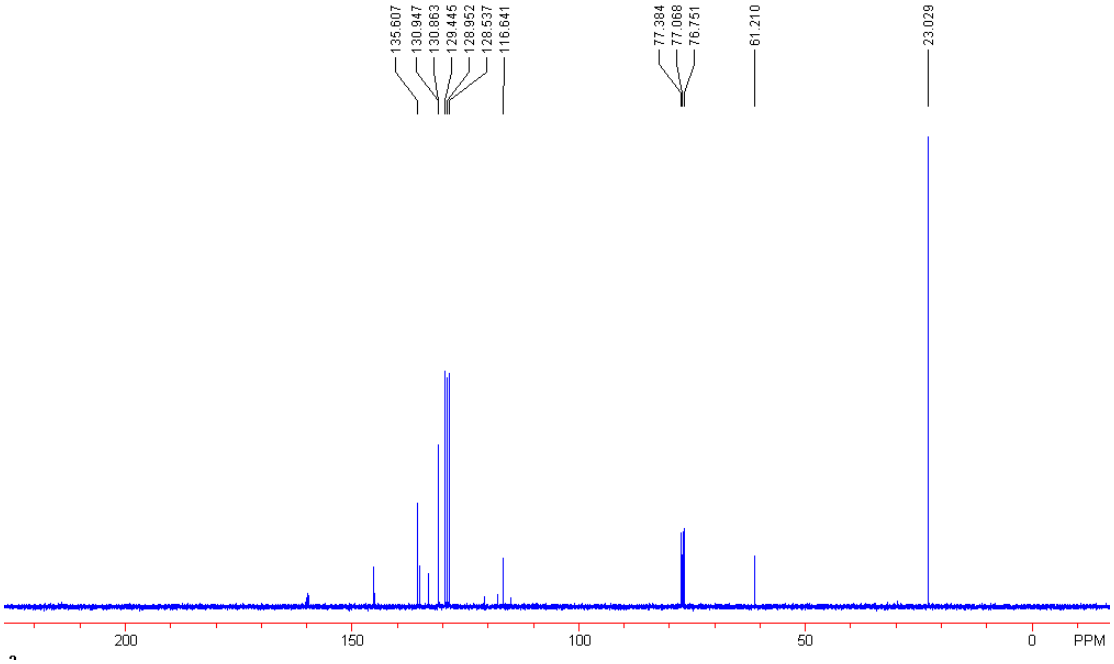


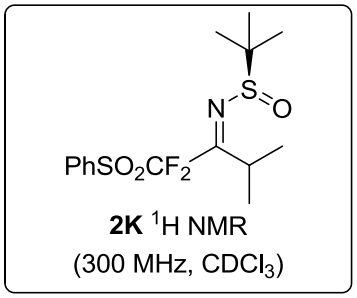
2j ^{19}F NMR
(282 MHz, $CDCl_3$)



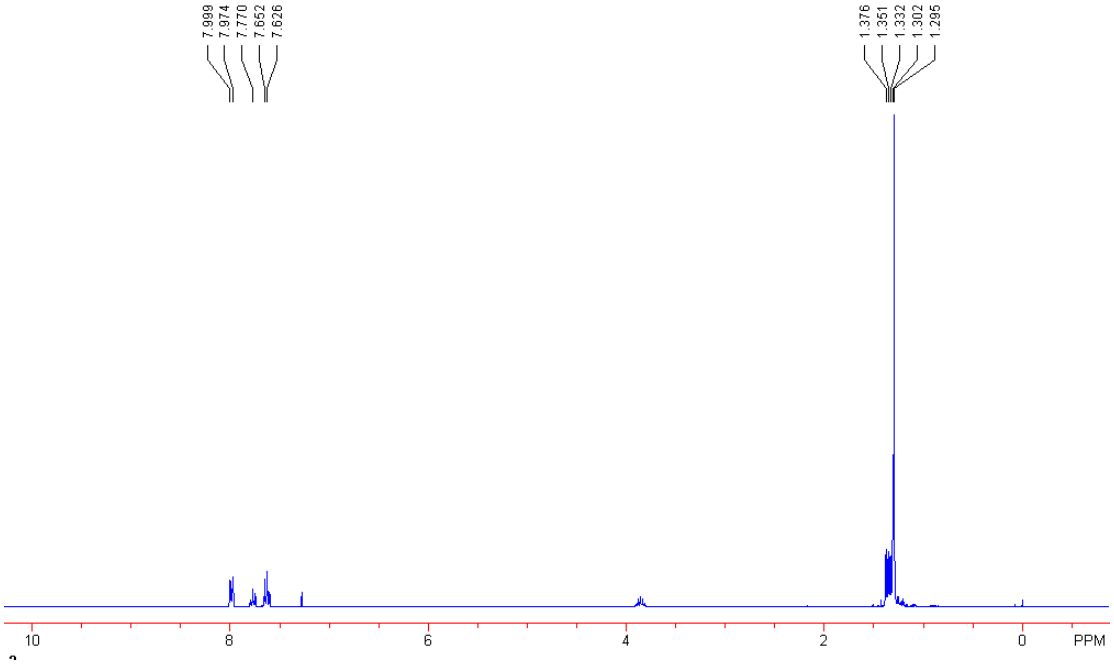


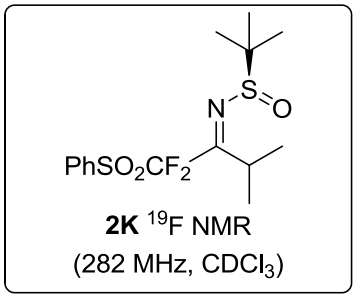
2j ^{13}C NMR
(100 MHz, $CDCl_3$)



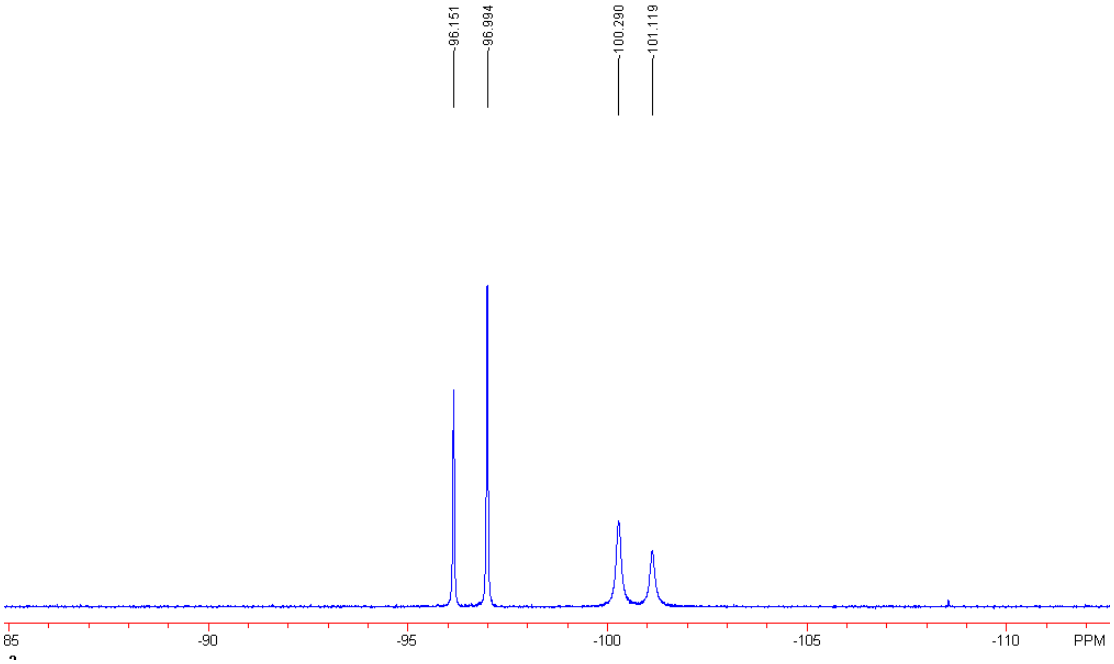


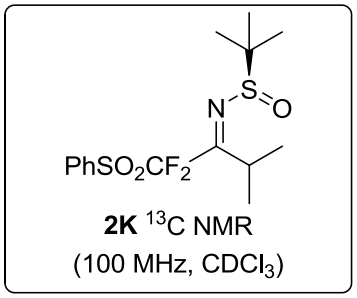
2K ^{1}H NMR
(300 MHz, $CDCl_3$)



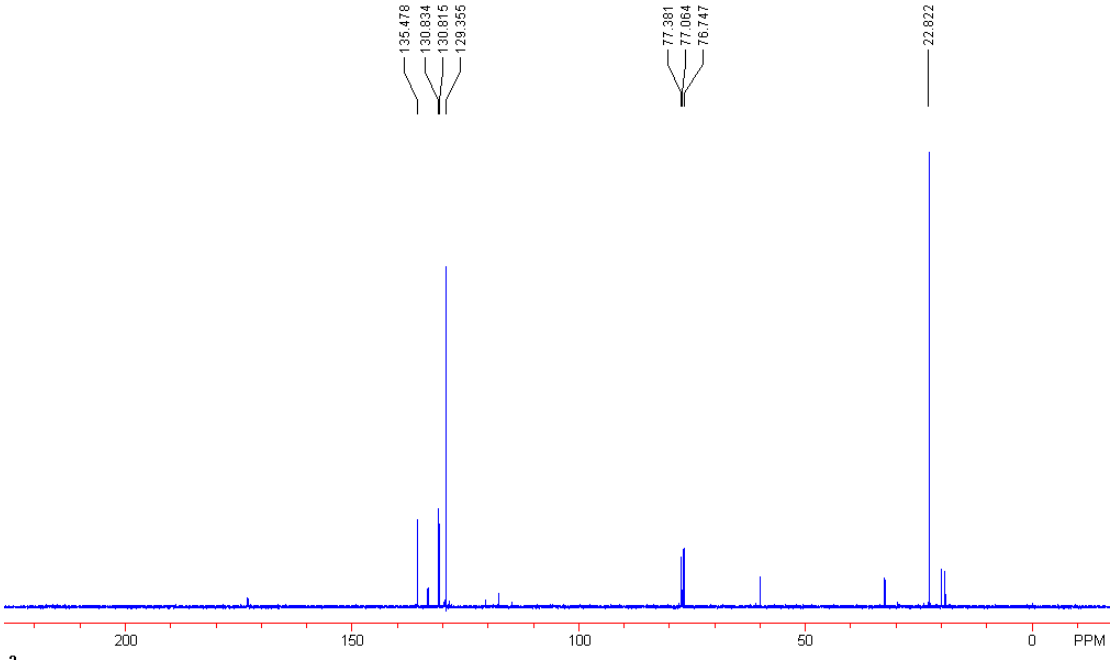


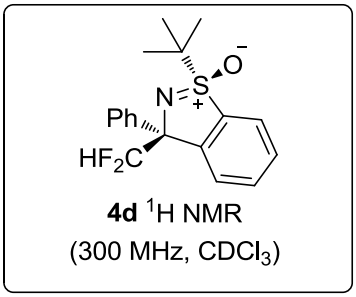
2K ^{19}F NMR
(282 MHz, $CDCl_3$)



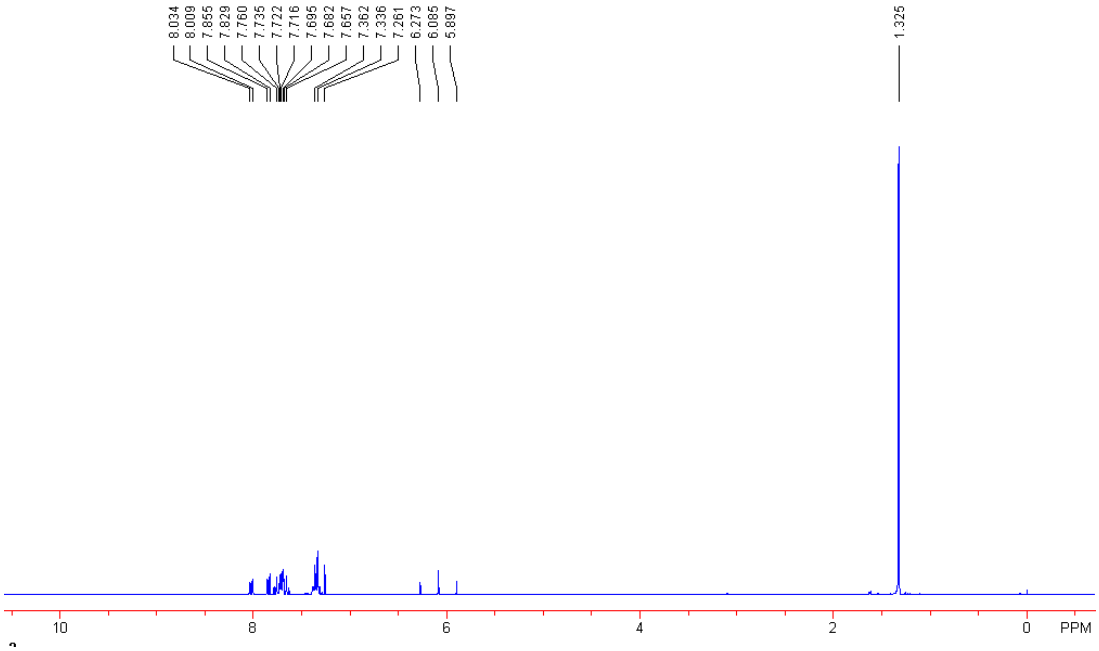


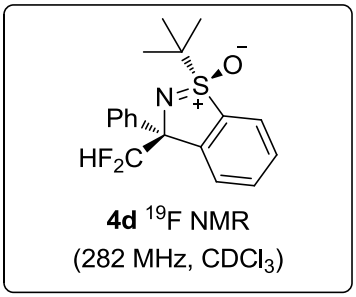
2K ^{13}C NMR
(100 MHz, $CDCl_3$)



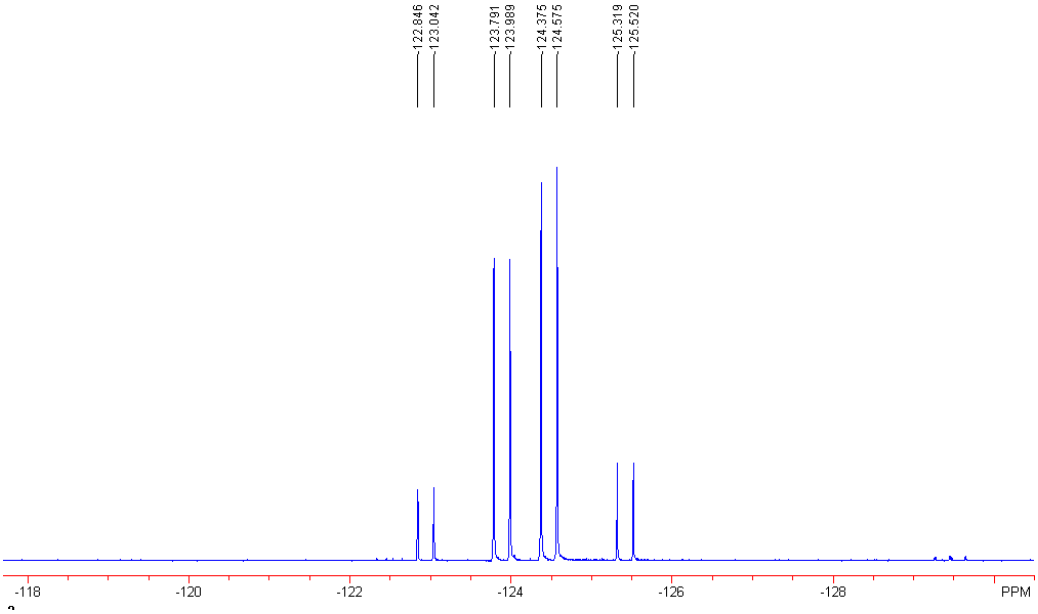


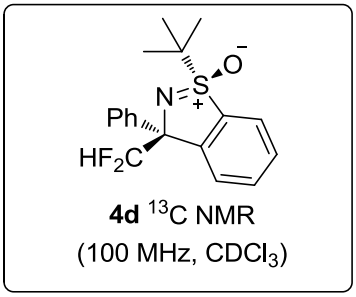
4d ^{1}H NMR
(300 MHz, $CDCl_3$)



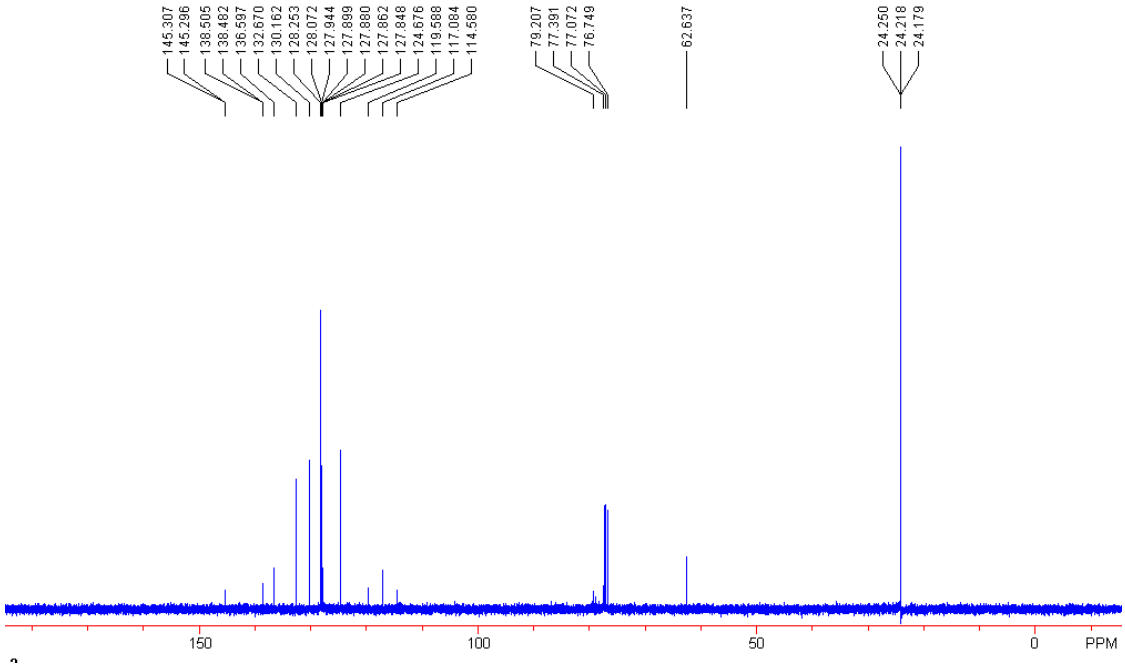


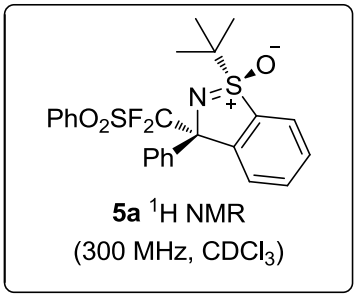
4d ^{19}F NMR
(282 MHz, $CDCl_3$)



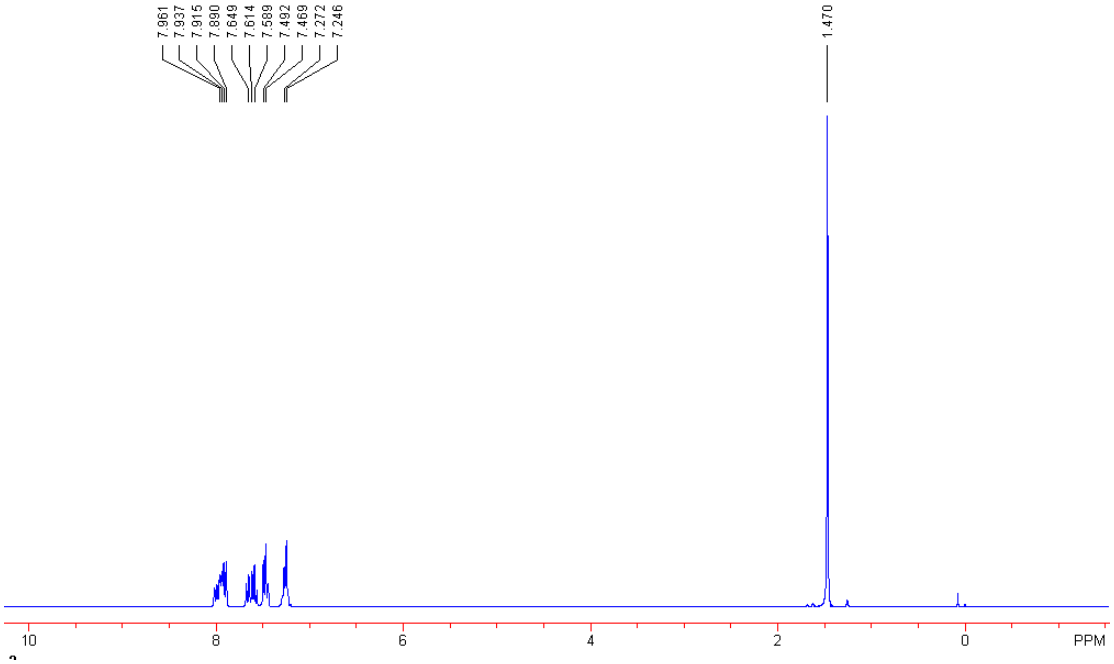


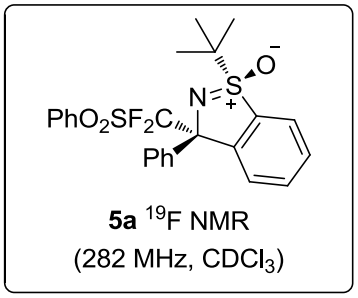
4d ^{13}C NMR
(100 MHz, $CDCl_3$)



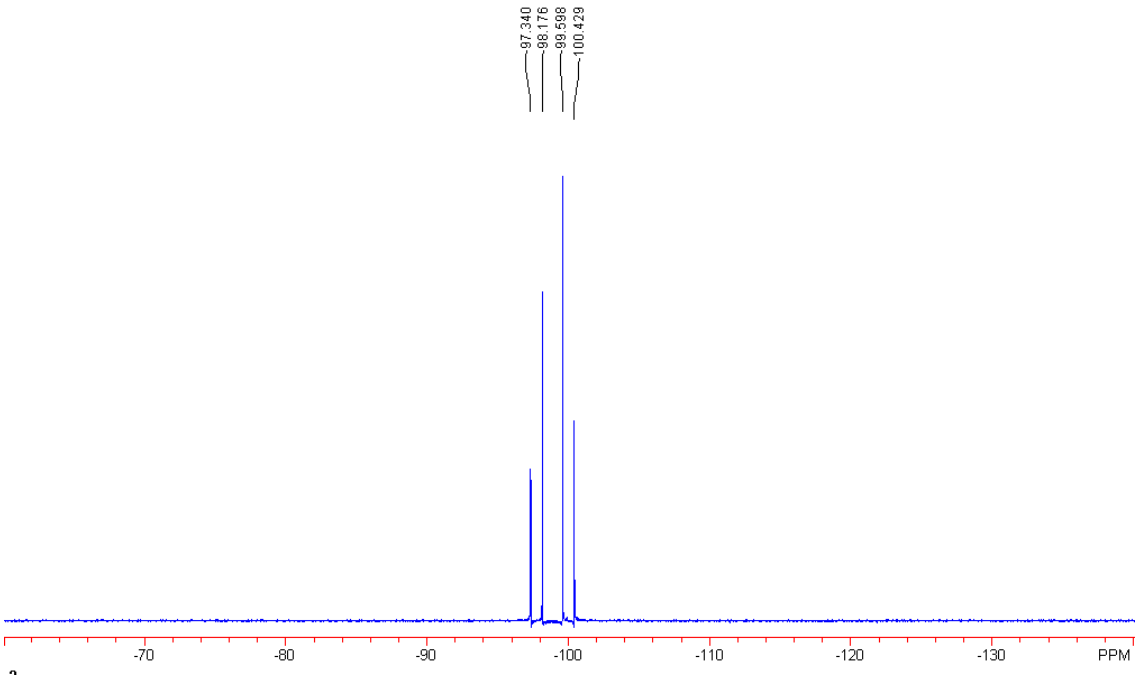


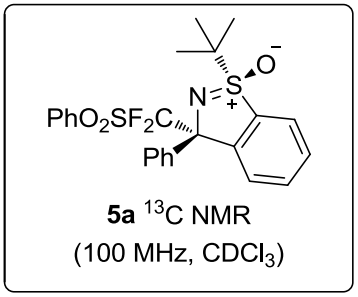
5a ^{1}H NMR
(300 MHz, $CDCl_3$)



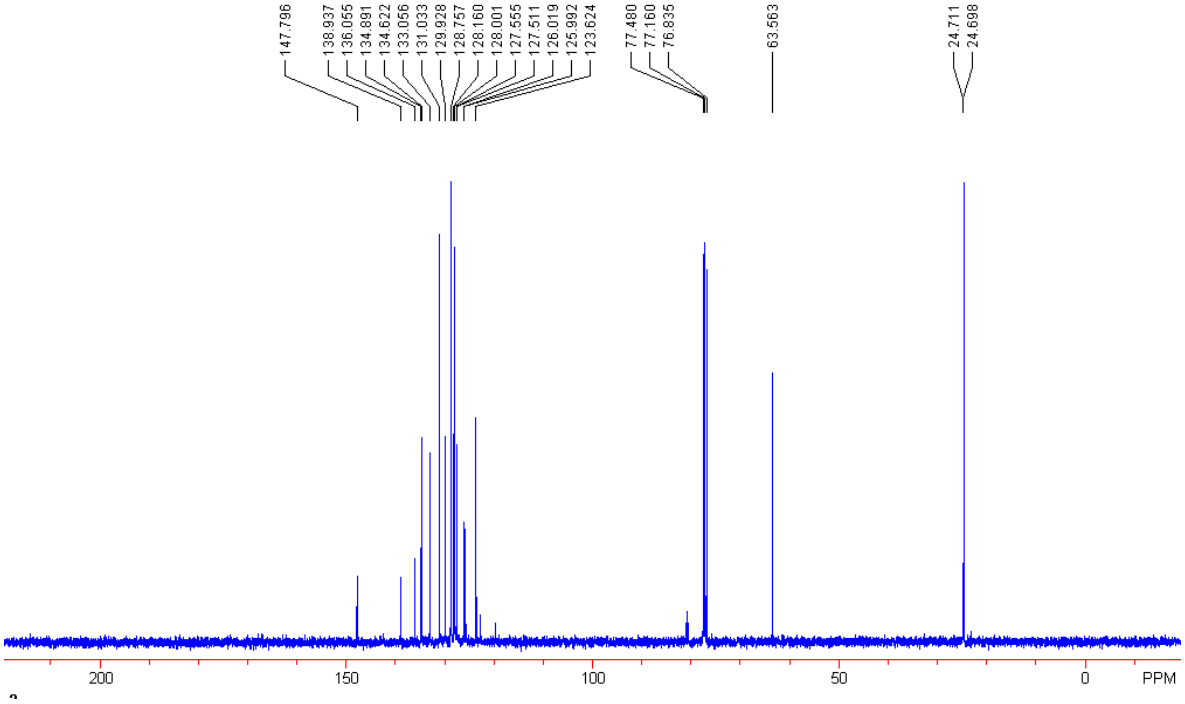


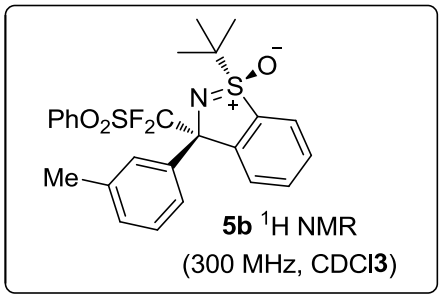
5a ^{19}F NMR
(282 MHz, $CDCl_3$)

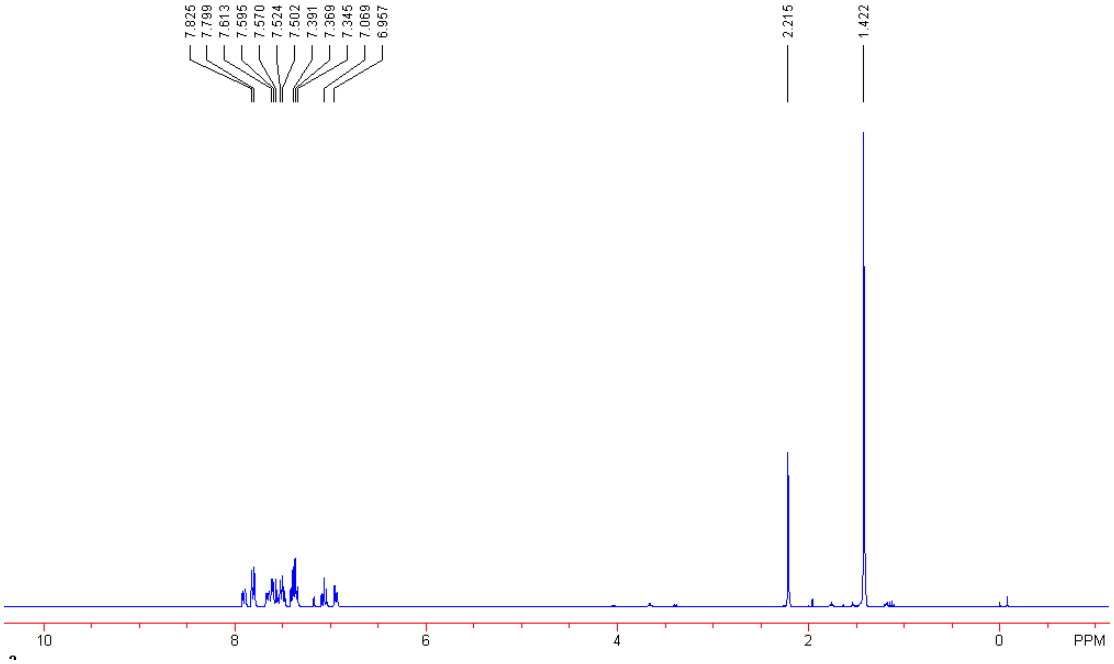




5a ^{13}C NMR
(100 MHz, $CDCl_3$)




PhO2SF2C
Me
5b 1H NMR
(300 MHz, CDCl3)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7.799
7.613
7.595
7.570
7.524
7.502
7.391
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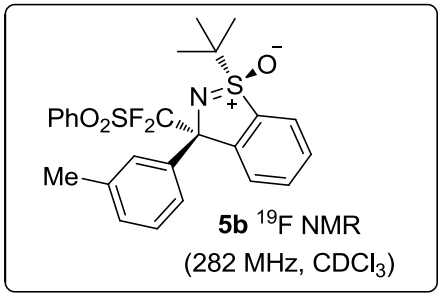
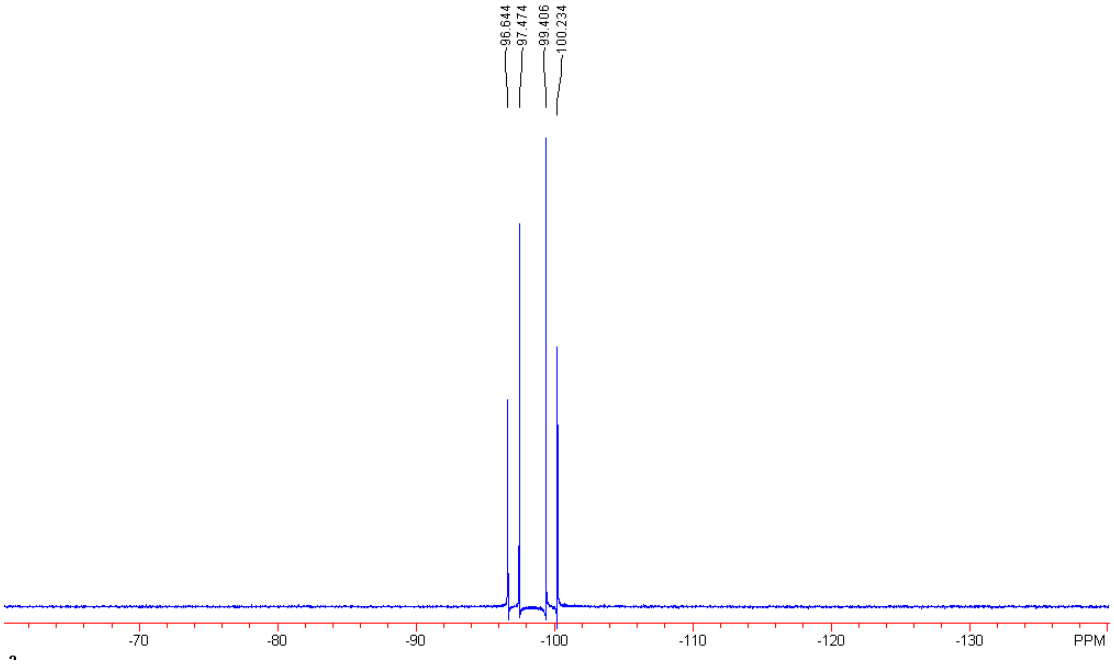
7.345
7.069
6.957
2.215
1.422
10
8
6
4
2
0
PPM


O
N
S
PhO2SF2C
Me
5b 19F NMR
(282 MHz, CDCl3)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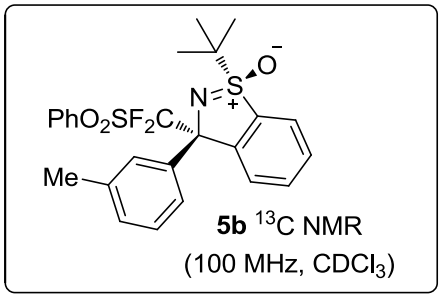
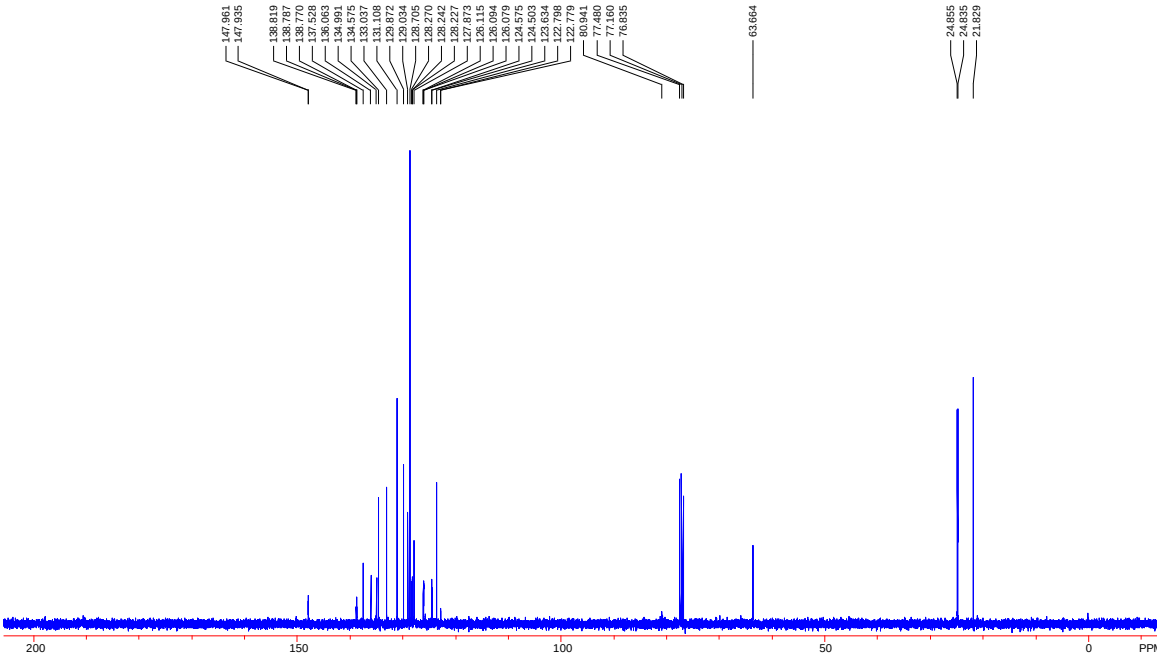
-100.234
-70
-80
-90
-100
-110
-120
-130
PPM


PhO2SF2C
Me
5b 13C NMR
(100 MHz, CDCl3)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147.935
138.819
138.787
138.770
137.528
136.063
135.091
134.575
133.037
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129.872
129.034
128.705
128.270
128.242
128.227
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126.115
126.094
125.779
124.575
124.503
123.634
122.798
122.779
80.941
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76.835
63.664
24.855
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21.829
200
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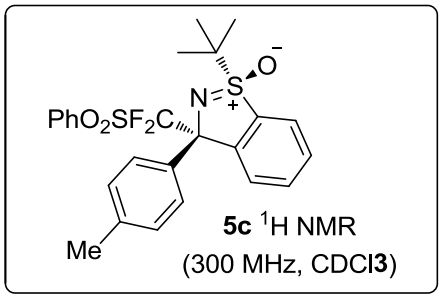
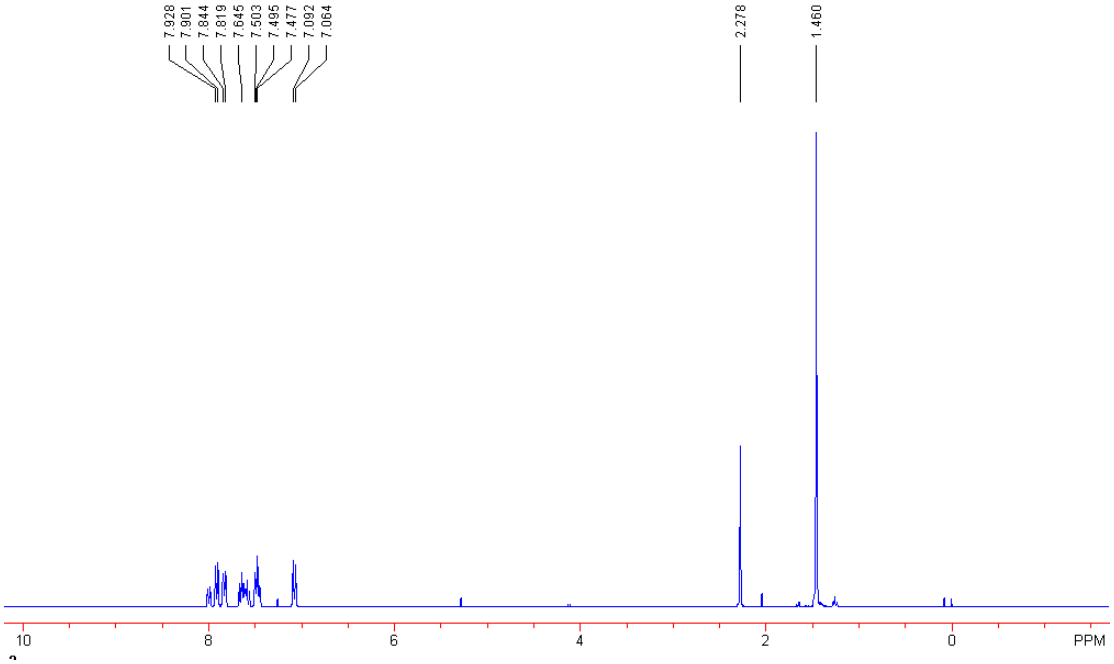
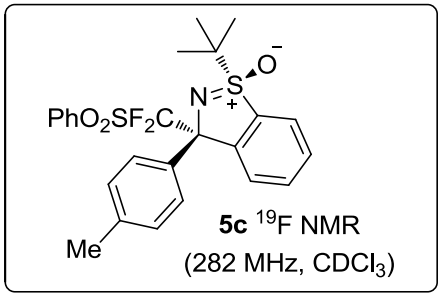
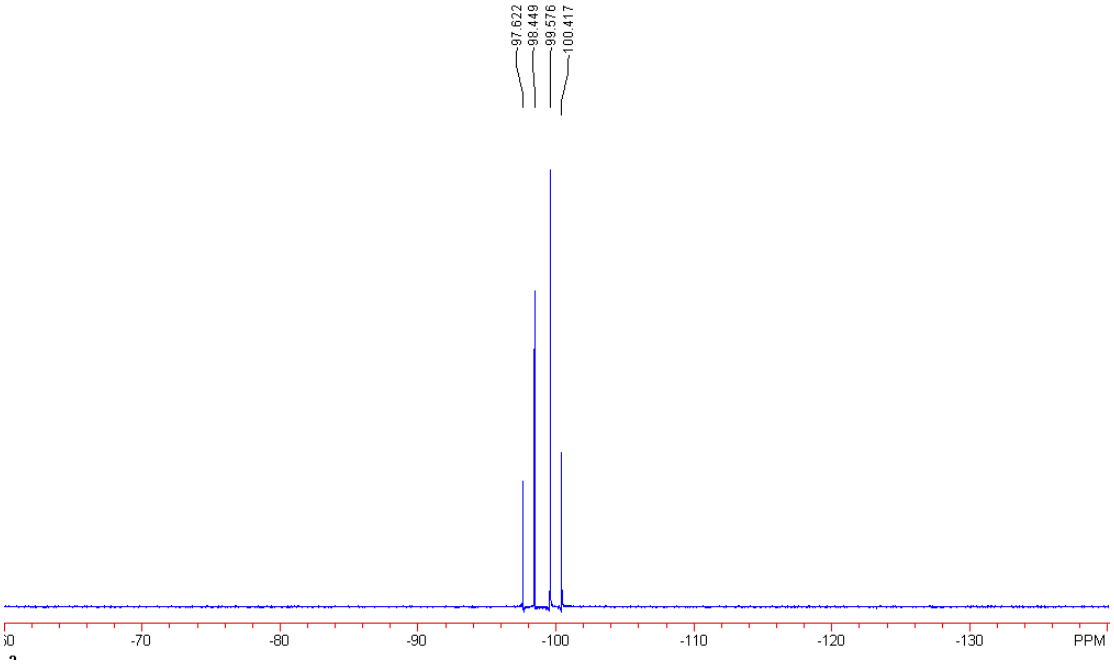
PPM


PhO2SF2C
N
S
O
Me
5c 1H NMR
(300 MHz, CDCl3)


7.928
7.901
7.844
7.819
7.645
7.503
7.495
7.477
7.092
7.064
2.278
1.460
10
8
6
4
2
0
PPM


PhO2SF2C
N
S
O
Me
5c 19F NMR
(282 MHz, CDCl3)


97.622
98.449
99.576
100.417
-70
-80
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-100
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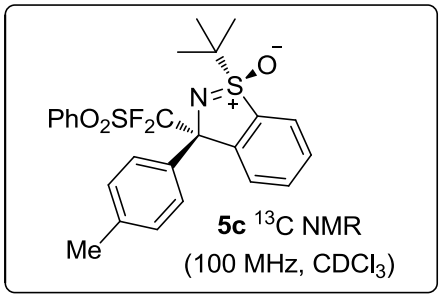
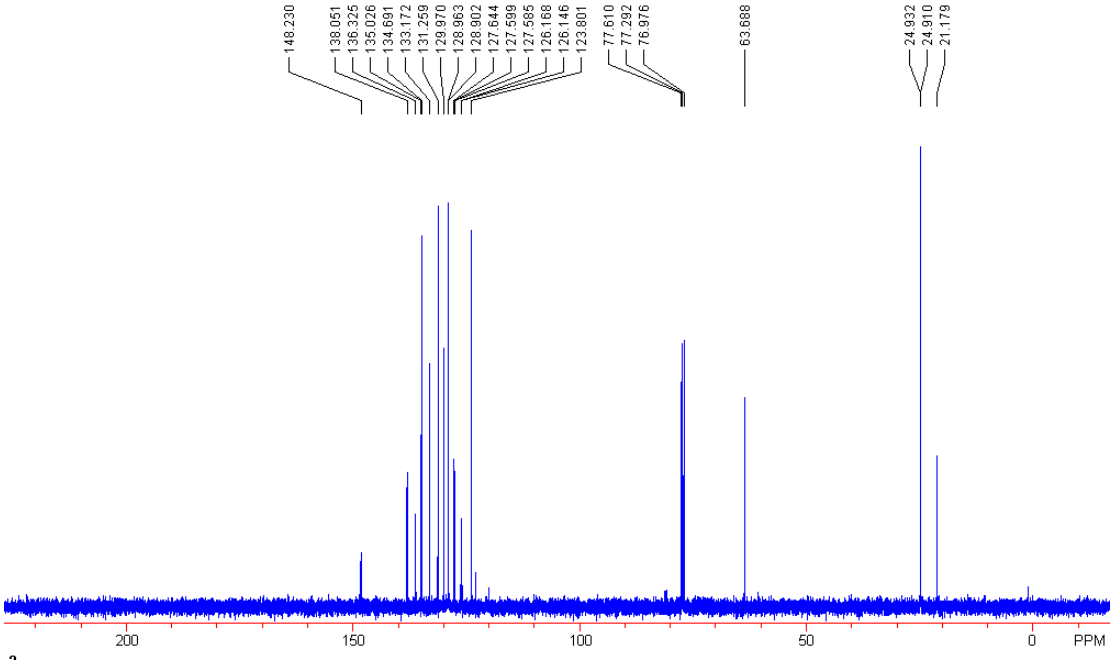
-120
-130
PPM


O
N
S
PhO2SF2C
Me
5c 13C NMR
(100 MHz, CDCl3)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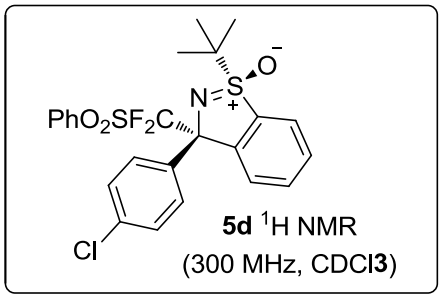
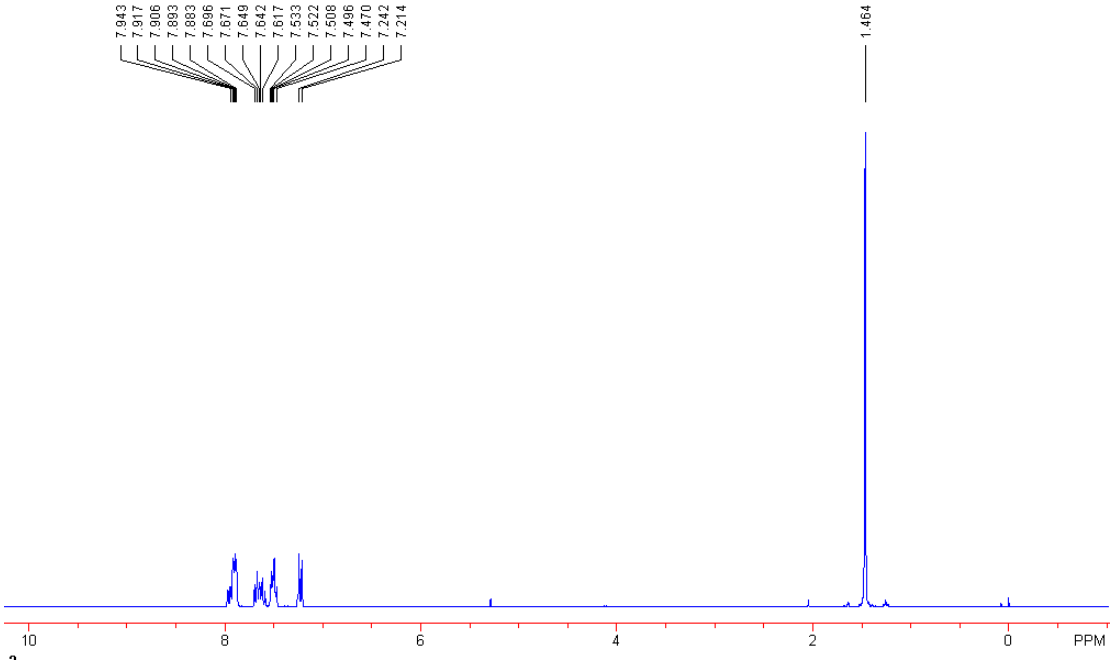
138.051
136.325
135.026
134.691
133.172
131.259
129.970
128.963
128.902
127.644
127.599
127.585
126.168
126.146
123.801
77.610
77.292
76.976
63.688
24.932
24.910
21.179
200
150
100
50
0
PPM


PhO2SF2C
N
S
O
Cl
5d 1H NMR
(300 MHz, CDCl3)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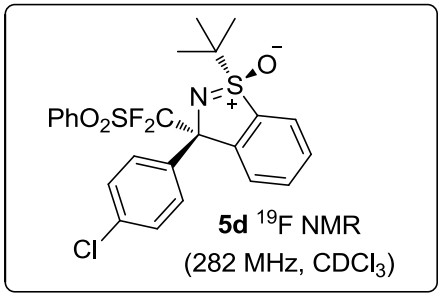
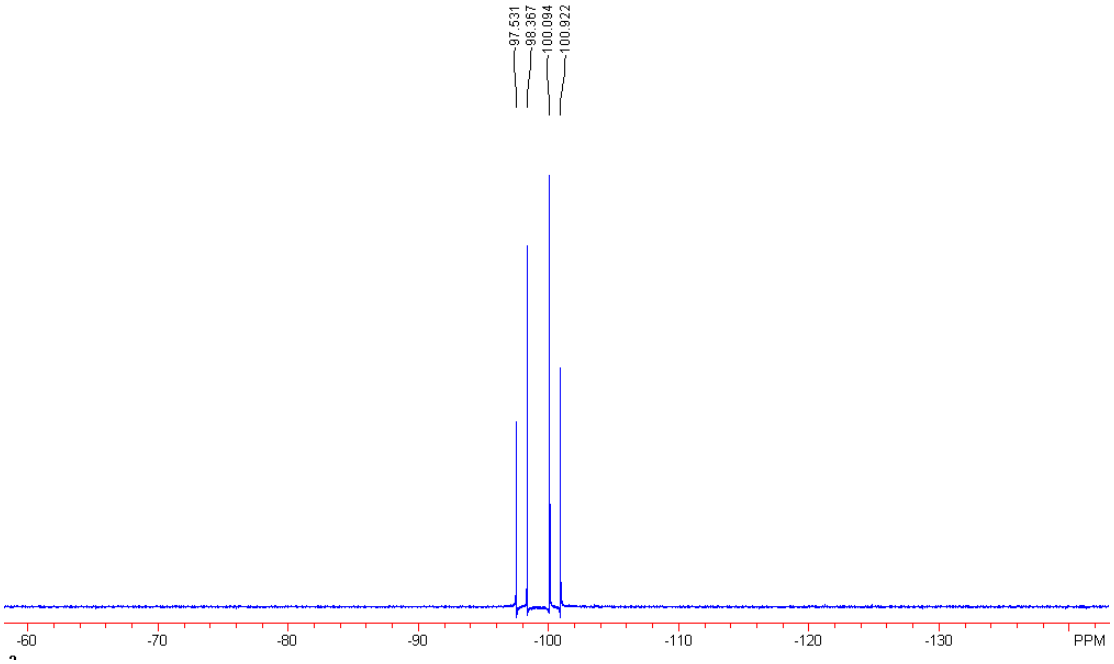
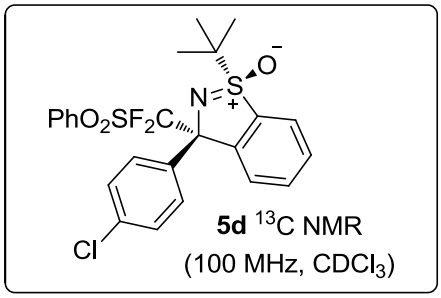
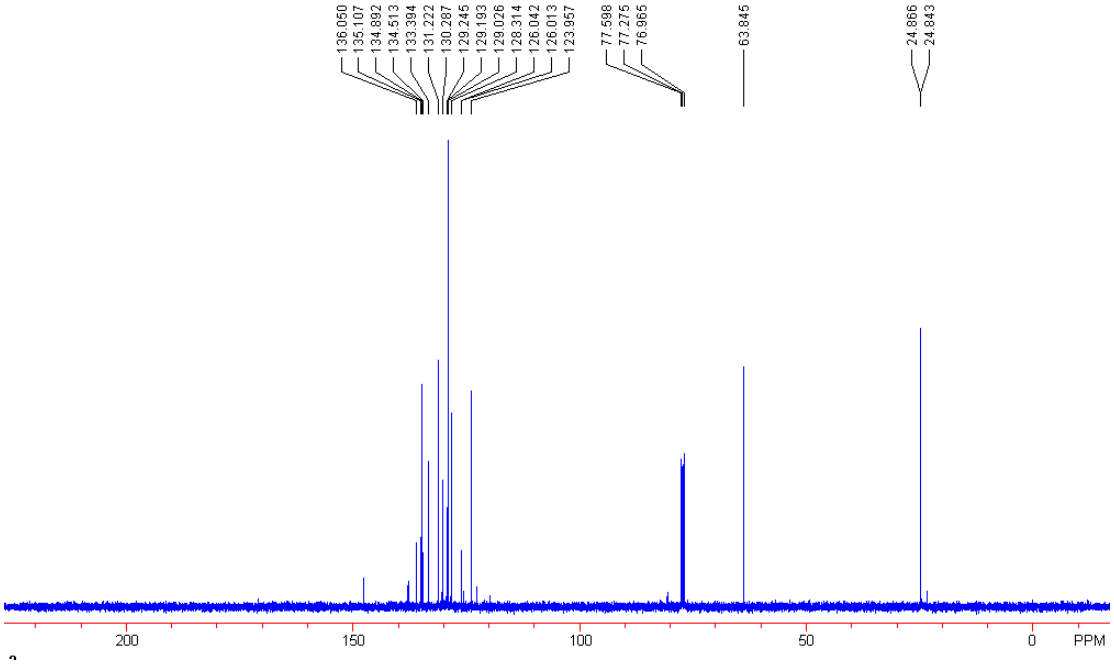
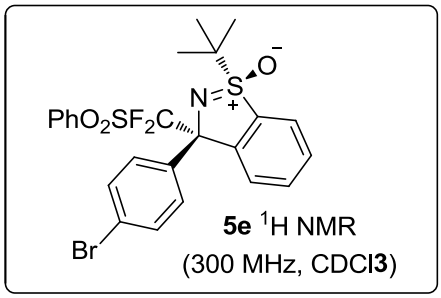
7.917
7.906
7.893
7.883
7.696
7.671
7.649
7.642
7.617
7.533
7.522
7.508
7.496
7.470
7.242
7.214
1.464
10
8
6
4
2
0
PPM

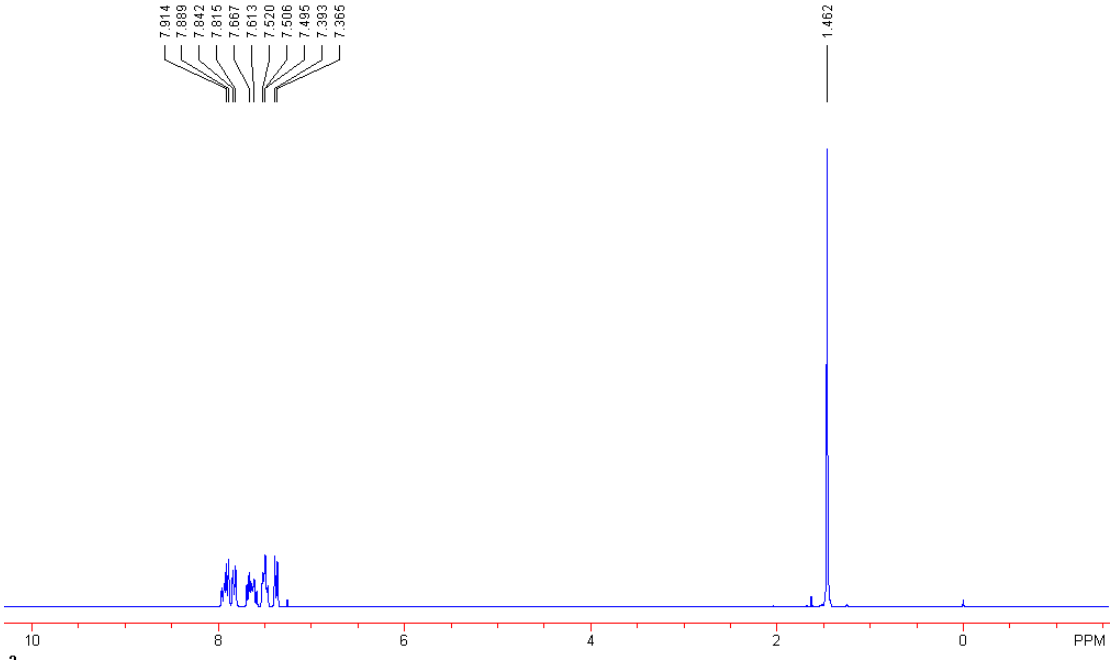

O
N
S
PhO2SF2C
Cl
5d 19F NMR
(282 MHz, CDCl3)

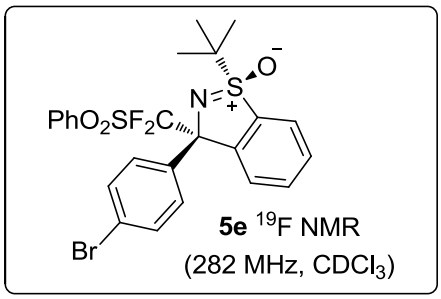

97.531
98.367
100.094
100.922
-60
-70
-80
-90
-100
-110
-120
-130
PPM

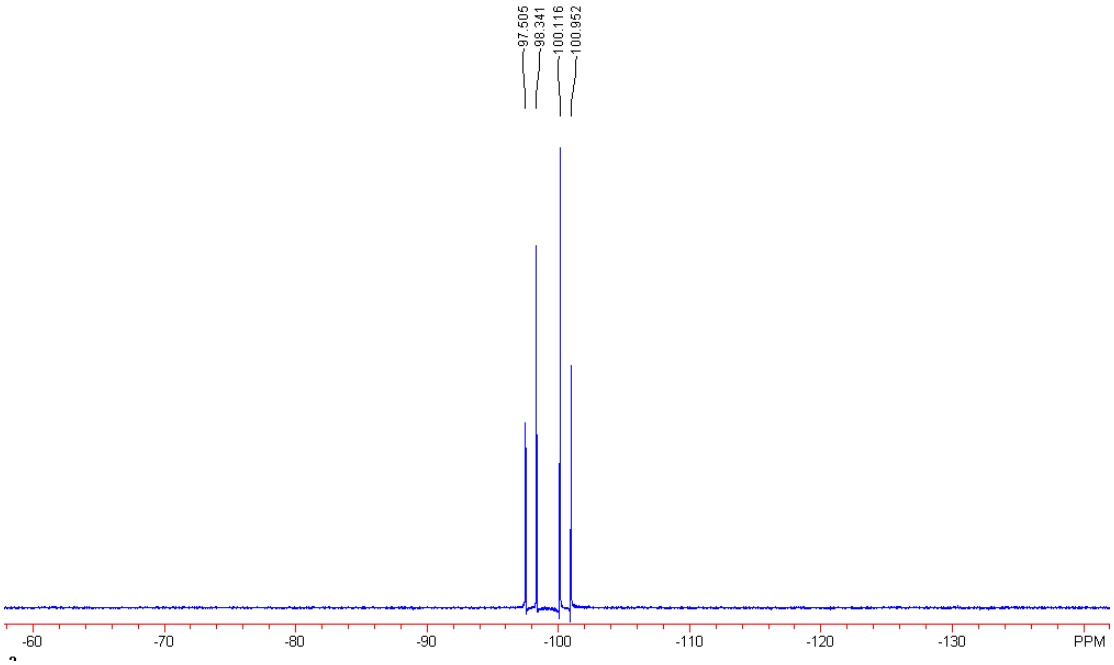

PhO2SF2C
N
S
O
Cl
5d 13C NMR
(100 MHz, CDCl3)

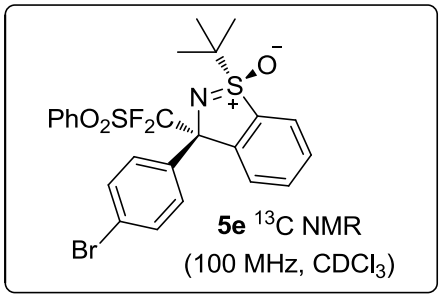

136.050
135.107
134.892
134.513
133.394
131.222
130.287
129.245
129.193
129.026
128.314
126.042
126.013
123.957
77.598
77.275
76.965
63.845
24.866
24.843
200
150
100
50
0
PPM

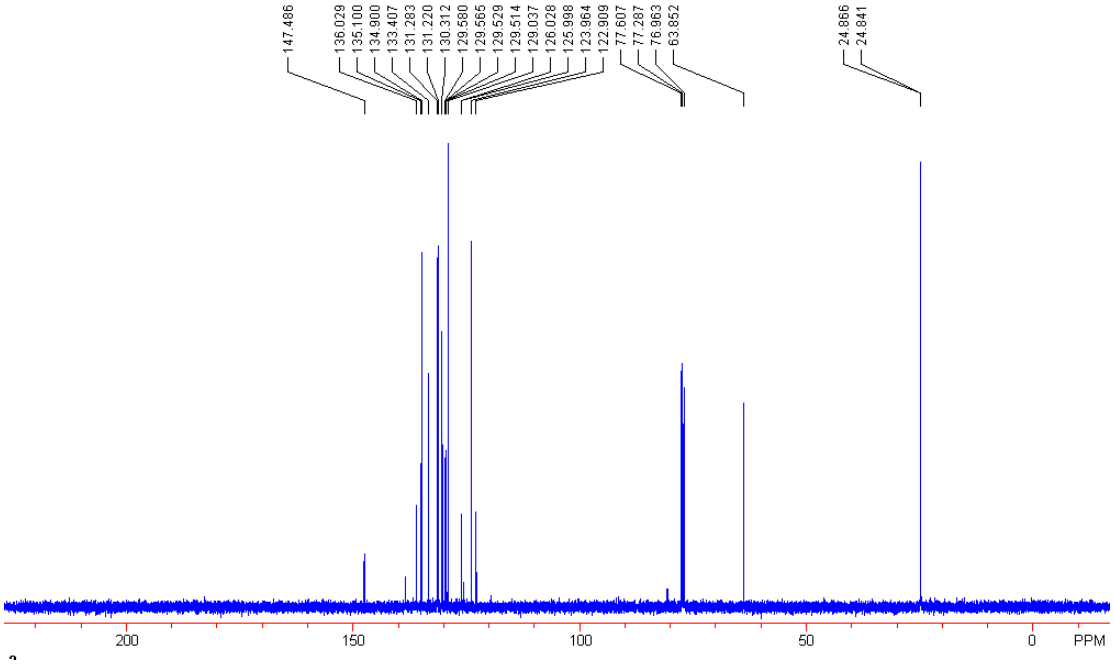

PhO2SF2C
N
S
O
Br
5e 1H NMR
(300 MHz, CDCl3)

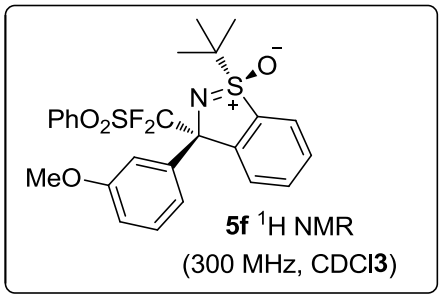

7.914
7.889
7.842
7.815
7.667
7.613
7.520
7.506
7.495
7.393
7.365
1.462
10
8
6
4
2
0
PPM

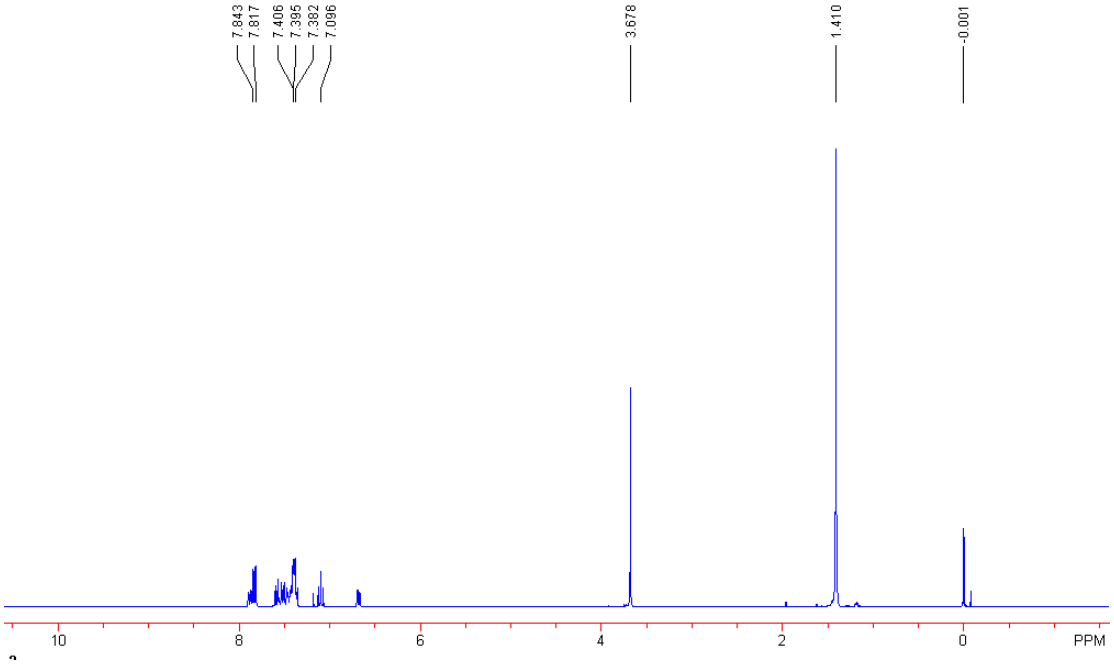

PhO2SF2C
N
S
O
Br
5e 19F NMR
(282 MHz, CDCl3)

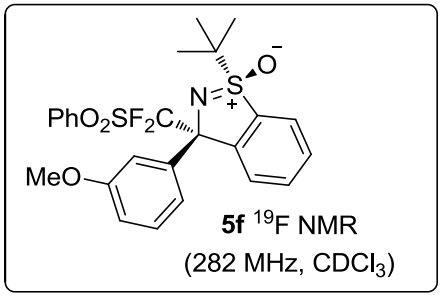

97.505
98.341
100.116
100.952
-60
-70
-80
-90
-100
-110
-120
-130
PPM

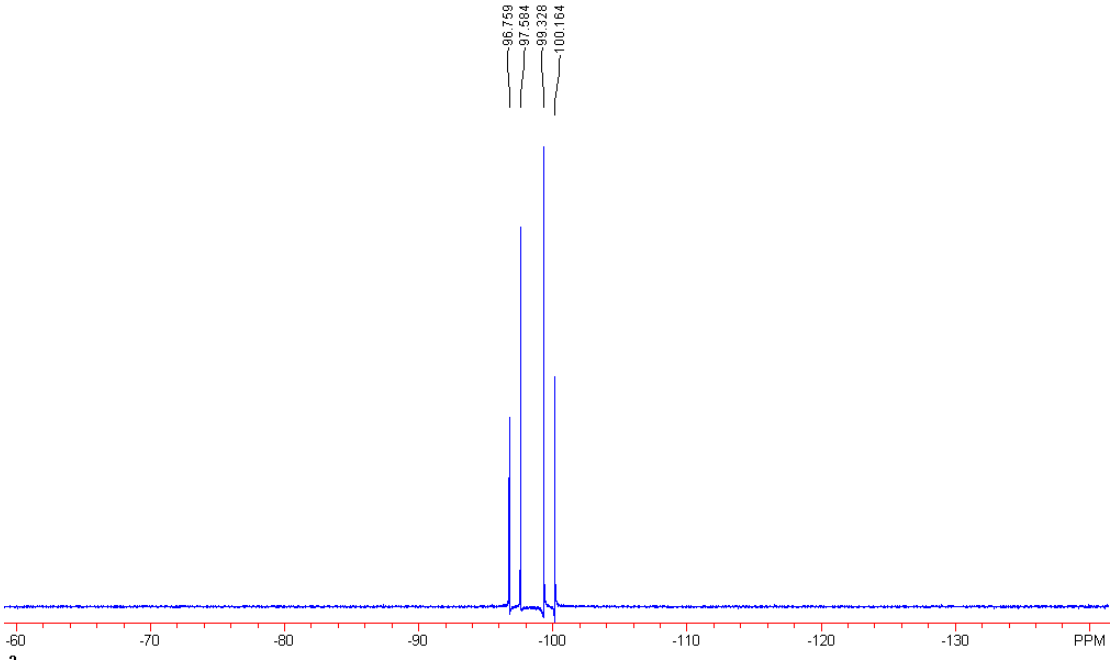

PhO2SF2C
N
S
O
Br
5e 13C NMR
(100 MHz, CDCl3)

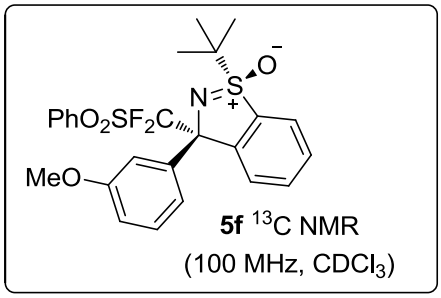

147.486
136.029
135.100
134.900
133.407
131.283
131.220
130.312
129.580
129.565
129.529
129.514
129.037
126.028
125.998
123.964
122.909
77.607
77.287
76.963
63.852
24.866
24.841
200
150
100
50
0
PPM

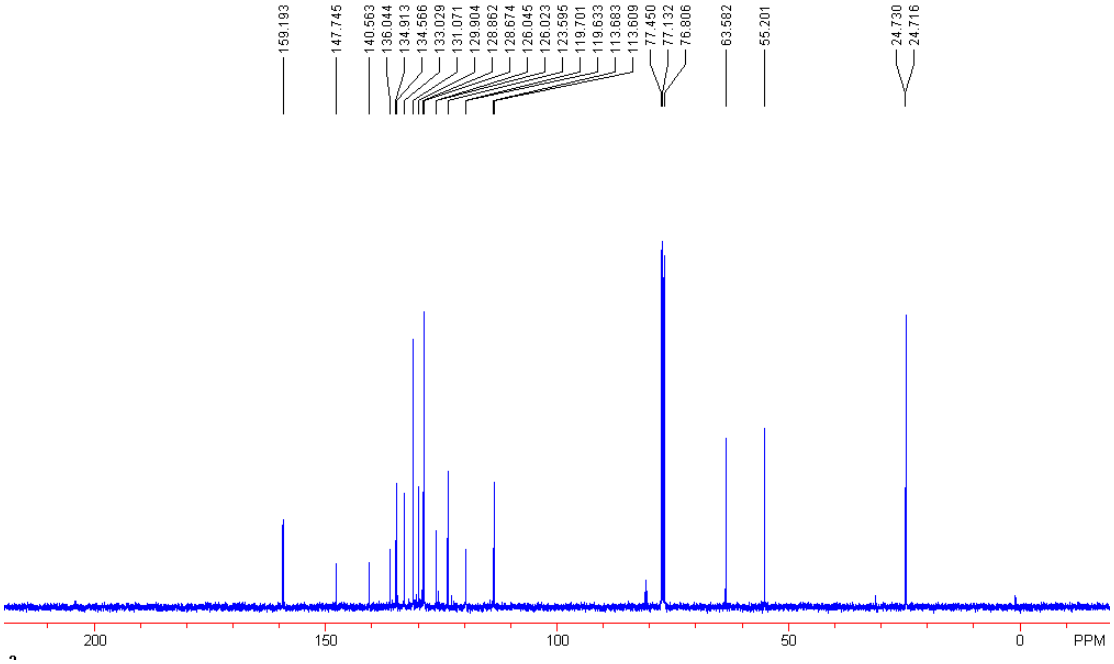

PhO2SF2C
MeO
5f 1H NMR
(300 MHz, CDCl3)

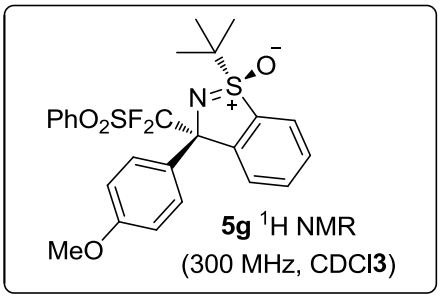

7.843
7.817
7.406
7.395
7.382
7.096
3.678
1.410
-0.001
10
8
6
4
2
0
PPM

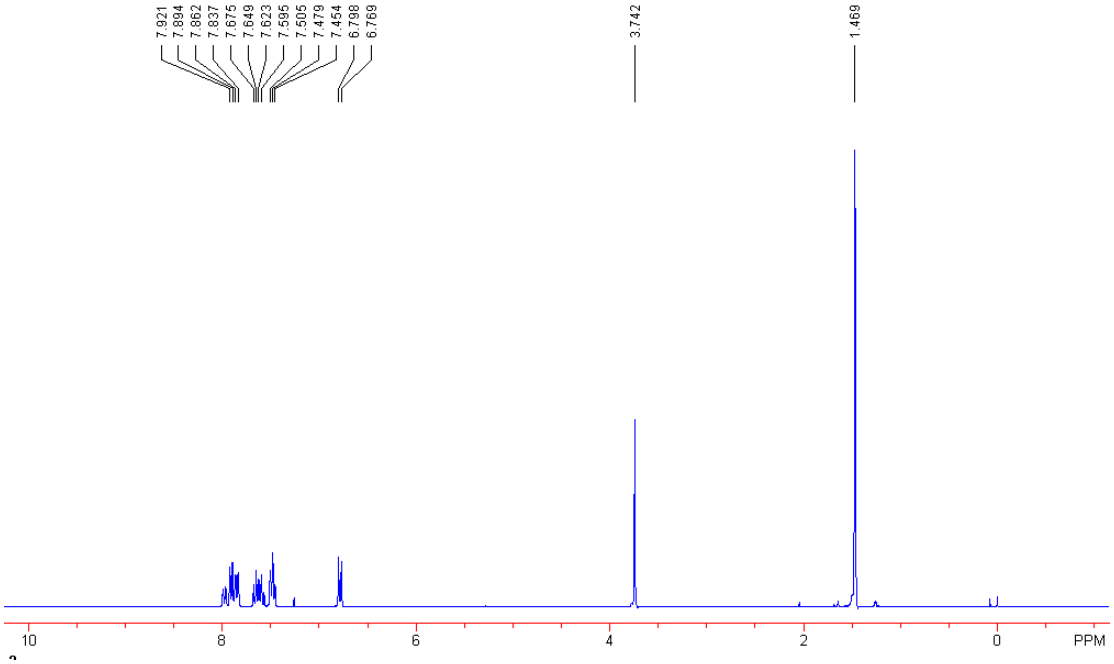

PhO2SF2C
MeO
5f 19F NMR
(282 MHz, CDCl3)

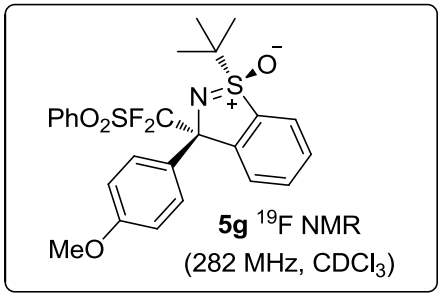

-96.759
-97.584
-99.328
-100.164
-60
-70
-80
-90
-100
-110
-120
-130
PPM

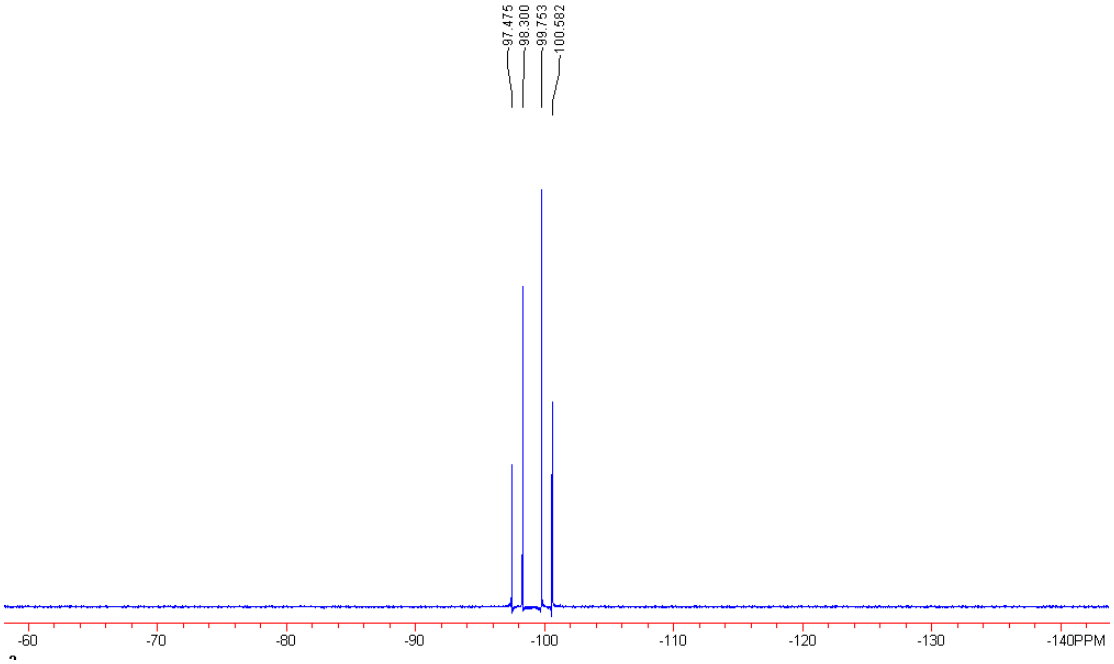

O
N
S
PhO2SF2C
MeO
5f 13C NMR
(100 MHz, CDCl3)

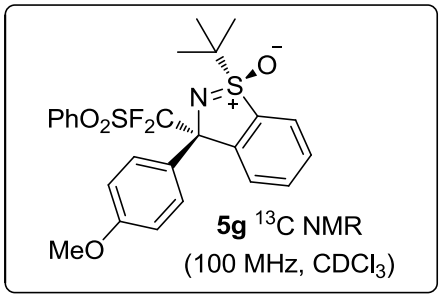

159.193
147.745
140.563
136.044
134.913
134.566
133.029
131.071
129.904
128.862
128.674
126.045
126.023
123.595
119.701
119.633
113.683
113.609
77.450
77.132
76.806
63.582
55.201
24.730
24.716
200
150
100
50
0
PPM

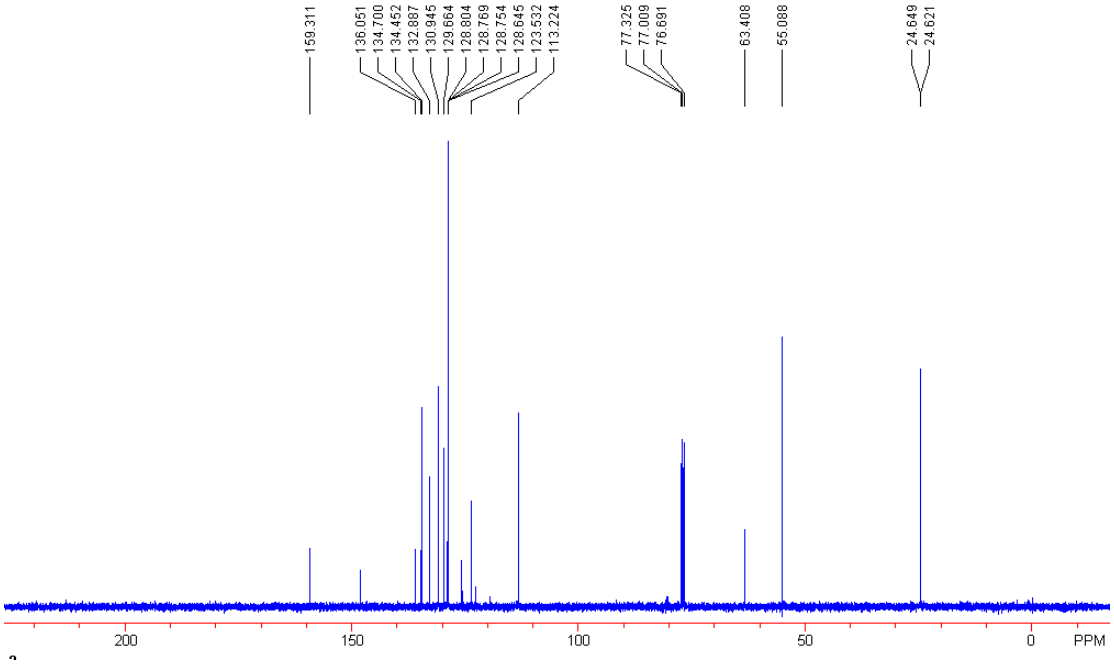

PhO2SF2C
N
S
O
MeO
5g 1H NMR
(300 MHz, CDCl3)

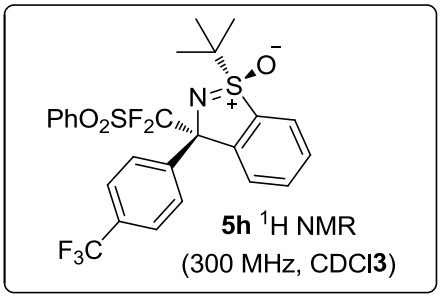

7.921
7.894
7.862
7.837
7.675
7.649
7.623
7.595
7.505
7.479
7.454
6.798
6.769
3.742
1.469
10
8
6
4
2
0
PPM

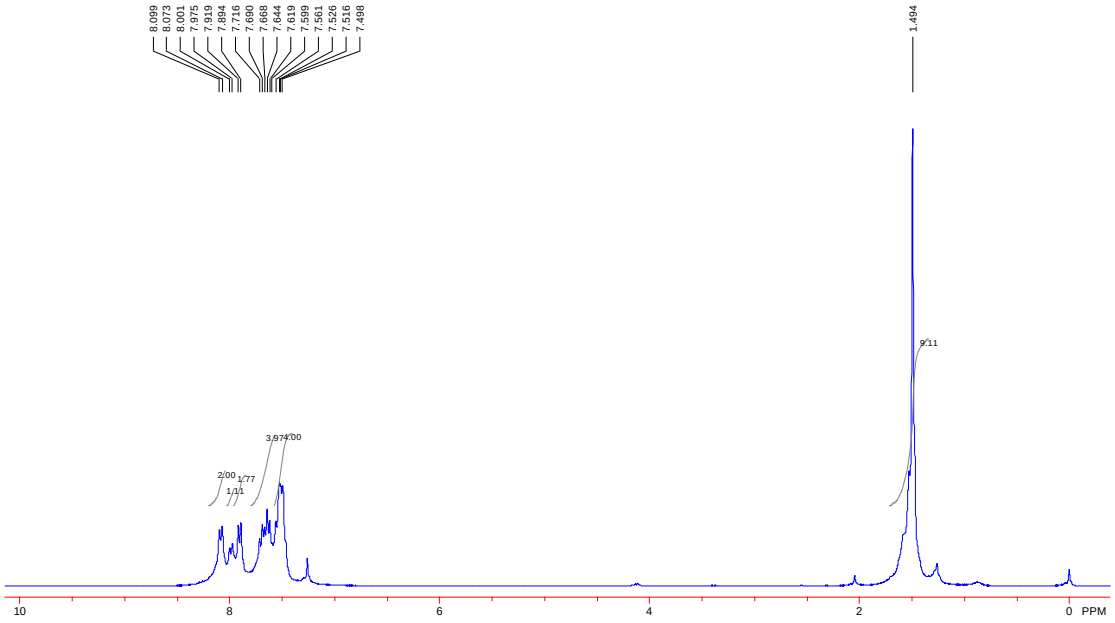

PhO2SF2C
N
S
O
MeO
5g 19F NMR
(282 MHz, CDCl3)

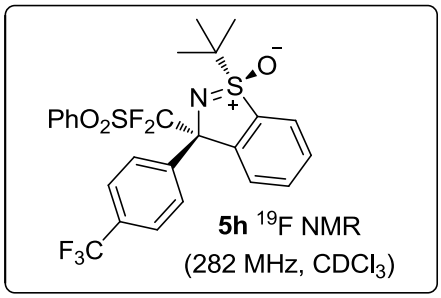

97.475
98.300
99.753
100.582
-60
-70
-80
-90
-100
-110
-120
-130
-140PPM

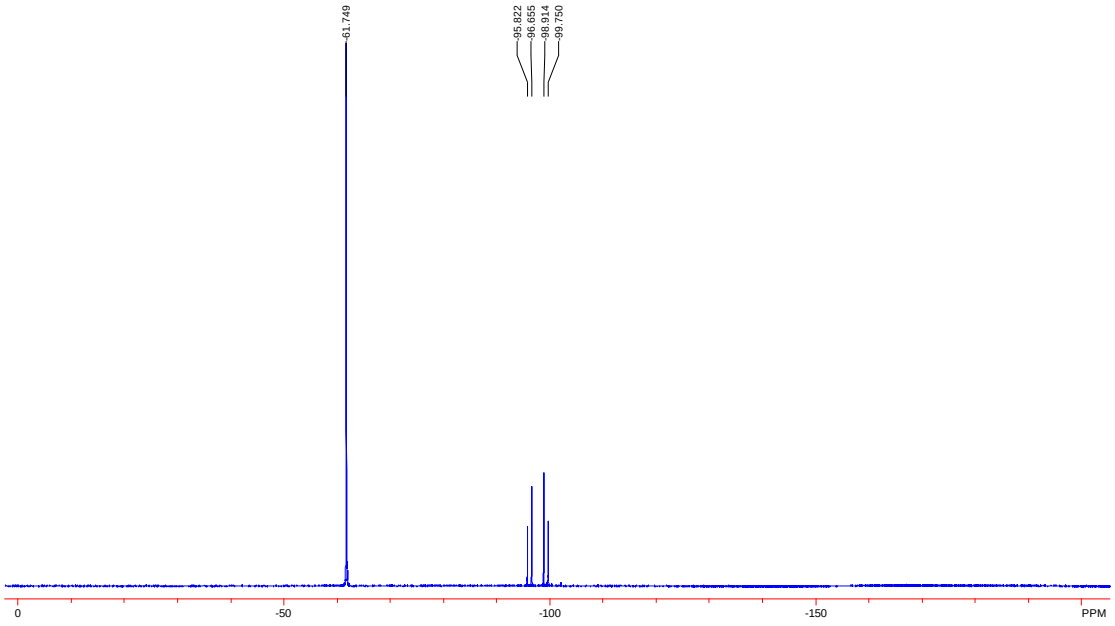

O
N
S
PhO2SF2C
MeO
5g 13C NMR
(100 MHz, CDCl3)


159.311
136.051
134.700
134.452
132.887
130.945
129.664
128.804
128.769
128.754
128.645
123.532
113.224
77.325
77.009
76.691
63.408
55.088
24.649
24.621
200
150
100
50
0
PPM


PhO2SF2C
N
S
O
F3C
5h 1H NMR
(300 MHz, CDCl3)


8.099
8.073
8.001
7.975
7.919
7.894
7.716
7.690
7.668
7.644
7.619
7.599
7.561
7.526
7.516
7.498
1.494
9.11
3.97
4.00
2.00
1.77
1.11
10
8
6
4
2
0
PPM


PhO2SF2C
N
S
O
F3C
5h 19F NMR
(282 MHz, CDCl3)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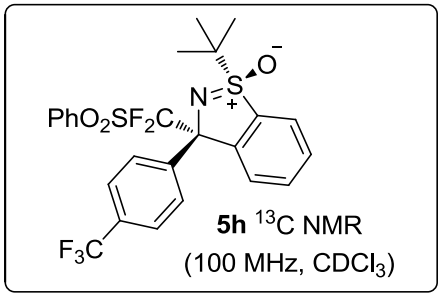
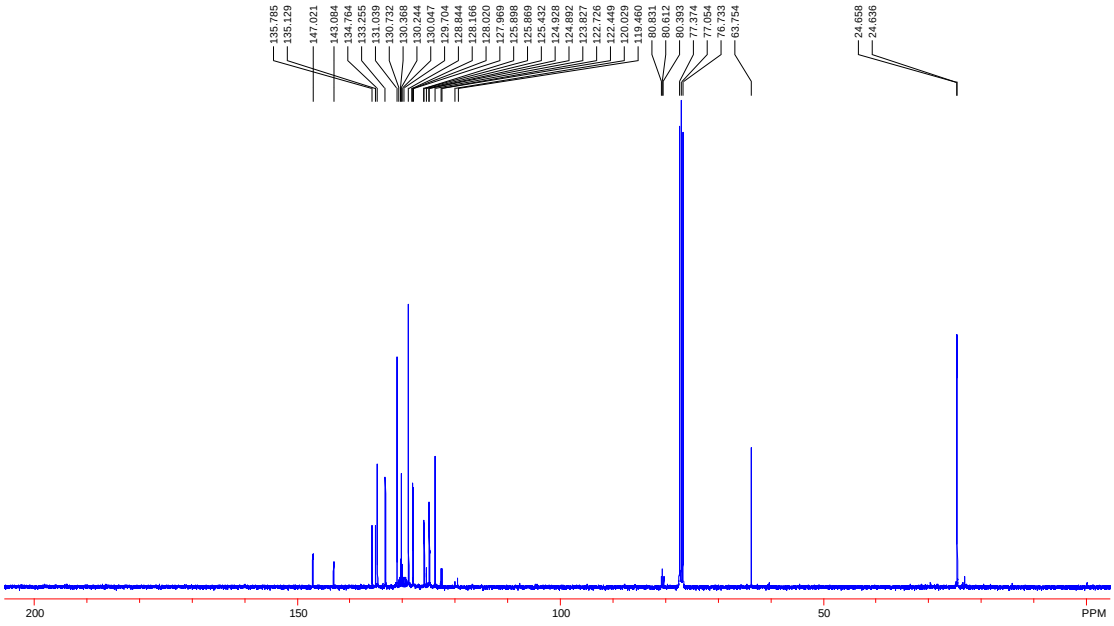
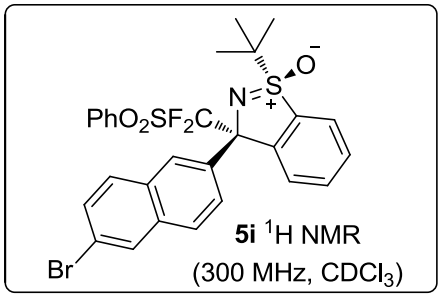
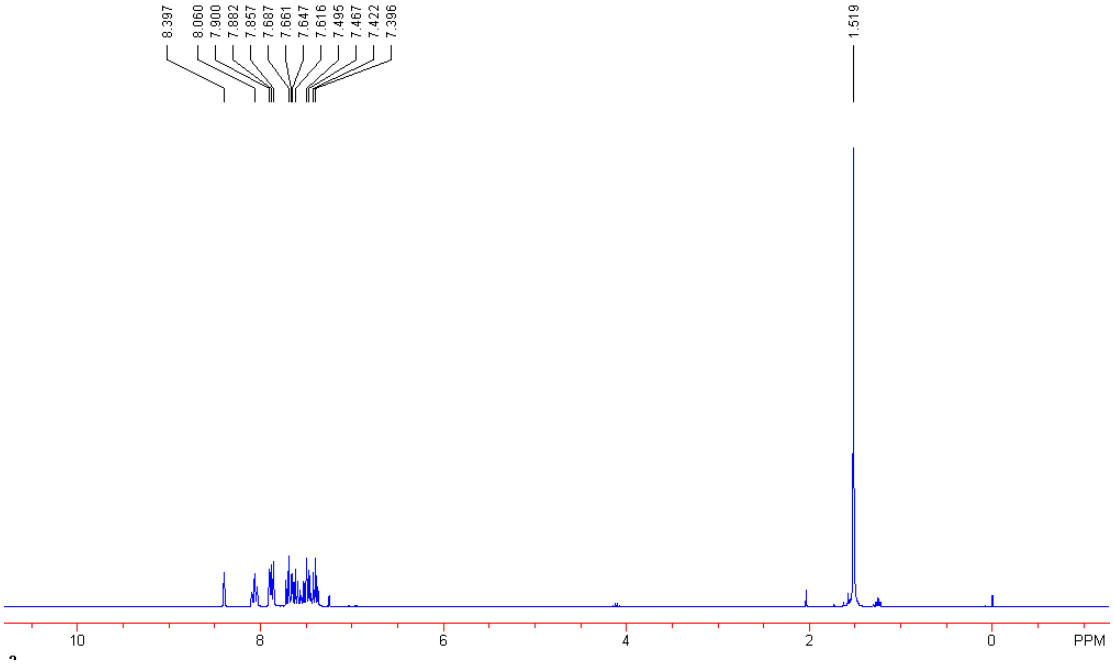
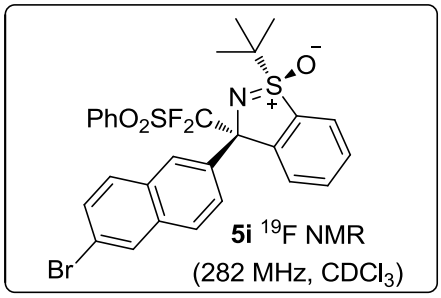
-95.822
-96.655
-98.914
-99.750
0
-50
-100
-150
PPM

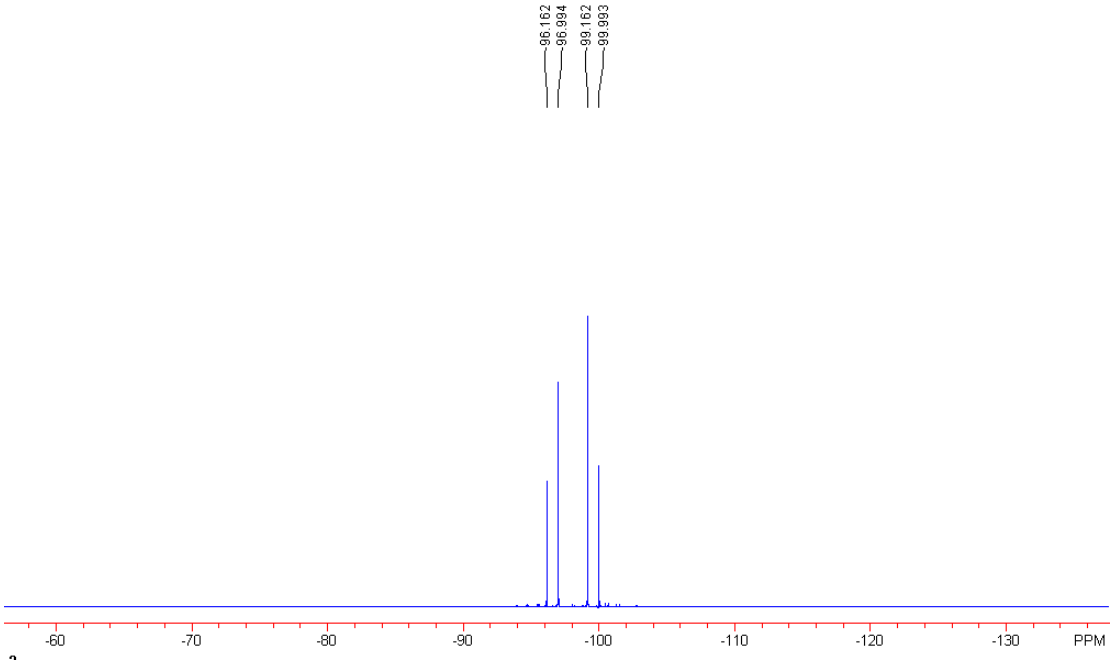

PhO2SF2C
N
S
O
F3C
5h 13C NMR
(100 MHz, CDCl3)

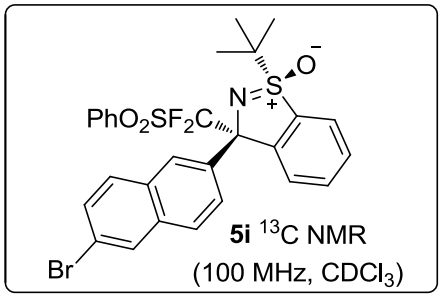

135.785
135.129
147.021
143.084
134.764
133.255
131.039
130.732
130.368
130.244
130.047
129.704
128.844
128.166
128.020
127.969
125.898
125.869
125.432
124.928
124.892
123.827
122.726
122.449
120.029
119.460
80.831
80.612
80.393
77.374
77.054
76.733
63.754
24.658
24.636
200
150
100
50
PPM

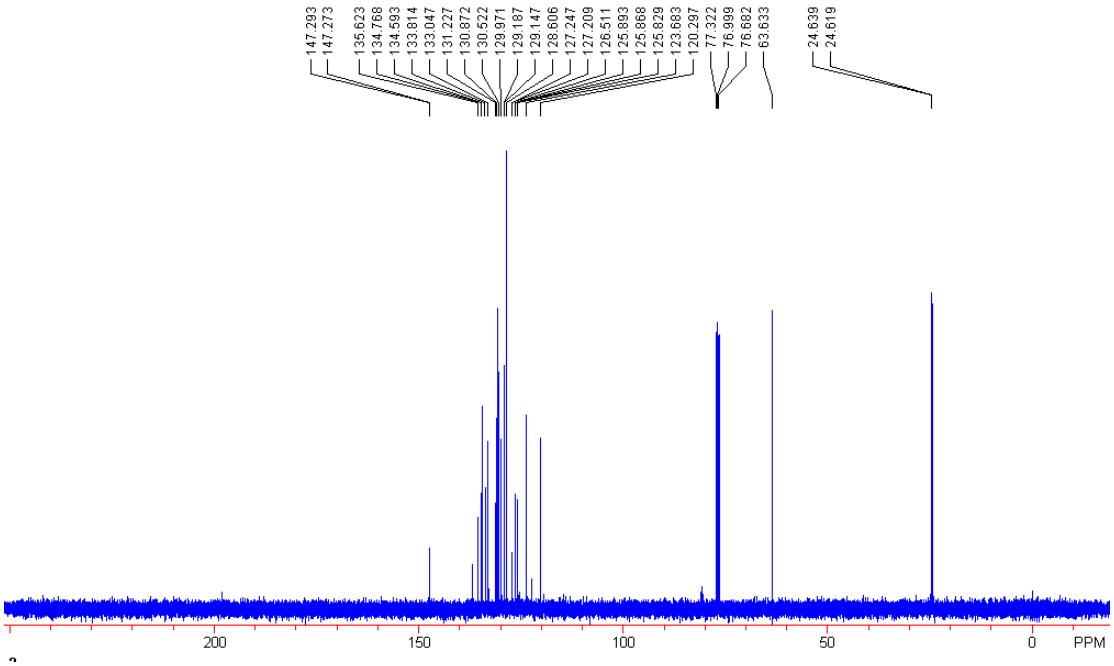

PhO2SF2C
N
S
O
Br
5i 1H NMR
(300 MHz, CDCl3)


8.397
8.060
7.900
7.882
7.857
7.687
7.661
7.647
7.616
7.495
7.467
7.422
7.396
1.519
10
8
6
4
2
0
PPM


O
N
S
+
PhO2SF2C
Br
5i 19F NMR
(282 MHz, CDCl3)


96.162
96.994
99.162
99.993
-60
-70
-80
-90
-100
-110
-120
-130
PPM


PhO2SF2C
N
S
O
Br
5i 13C NMR
(100 MHz, CDCl3)


147.293
147.273
135.623
134.768
134.593
133.814
133.047
131.227
130.872
130.522
129.971
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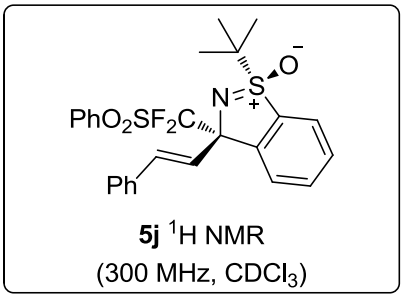
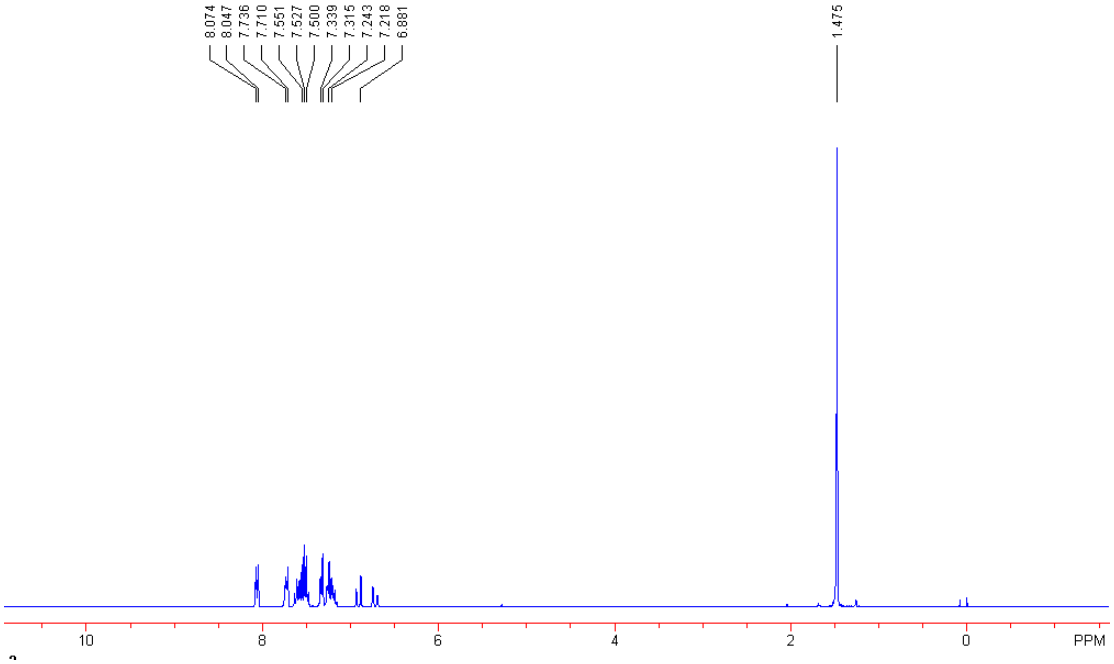
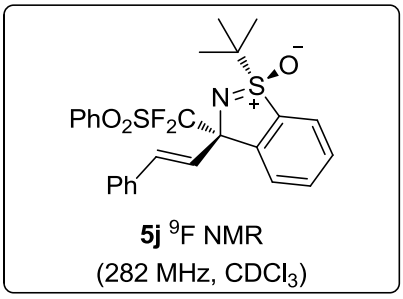
129.147
128.606
127.247
127.209
126.511
125.893
125.868
125.829
123.683
120.297
77.322
76.999
76.682
63.633
24.639
24.619
200
150
100
50
0
PPM

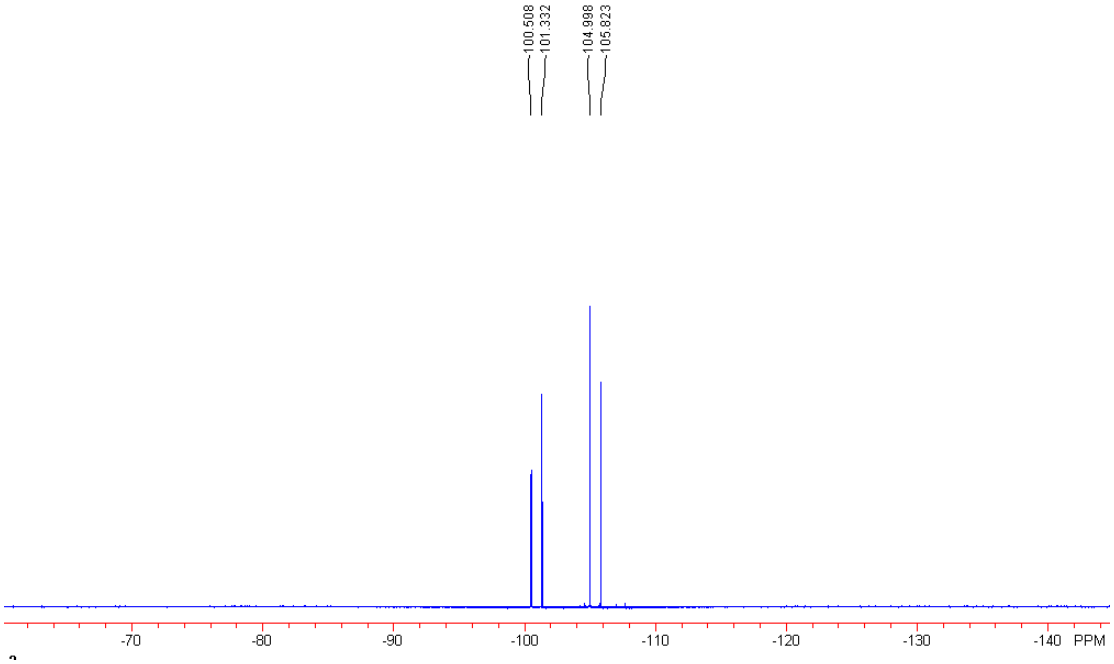


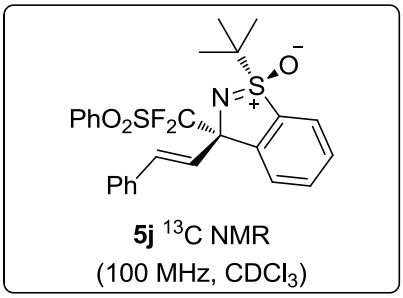
5j ^{1}H NMR
(300 MHz, $CDCl_3$)



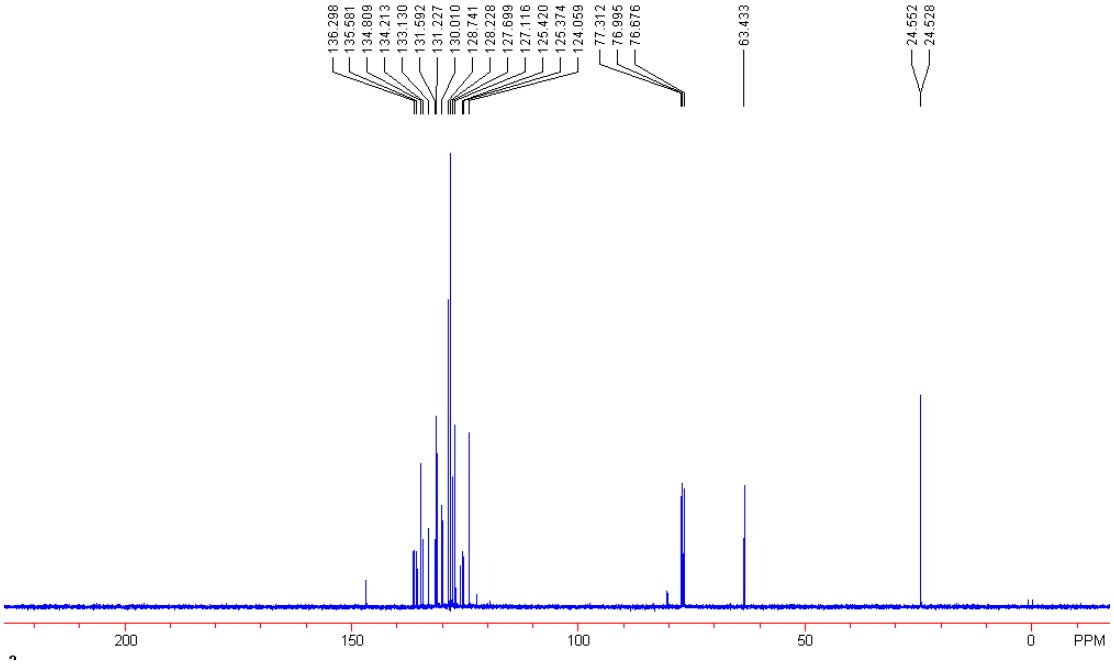


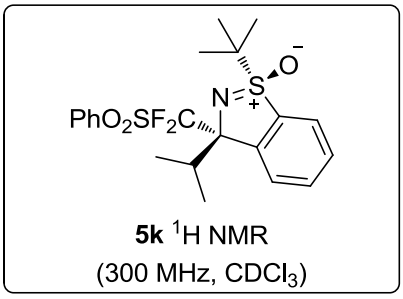
5j ^{9}F NMR
(282 MHz, $CDCl_3$)



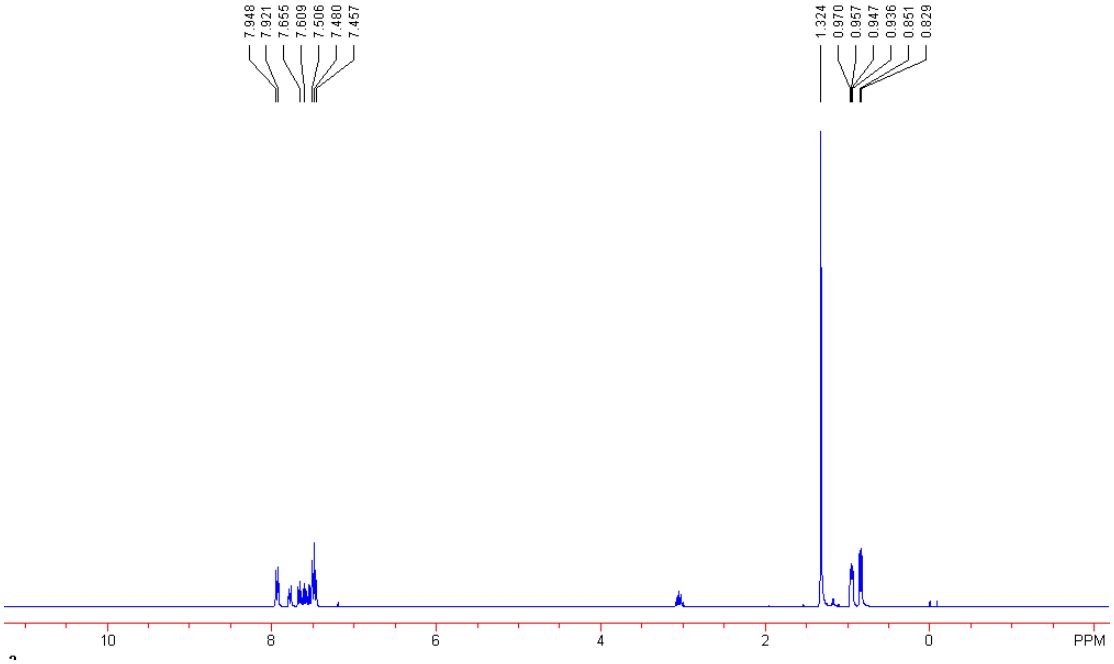


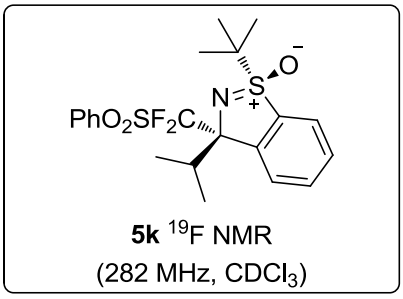
5j ^{13}C NMR
(100 MHz, $CDCl_3$)

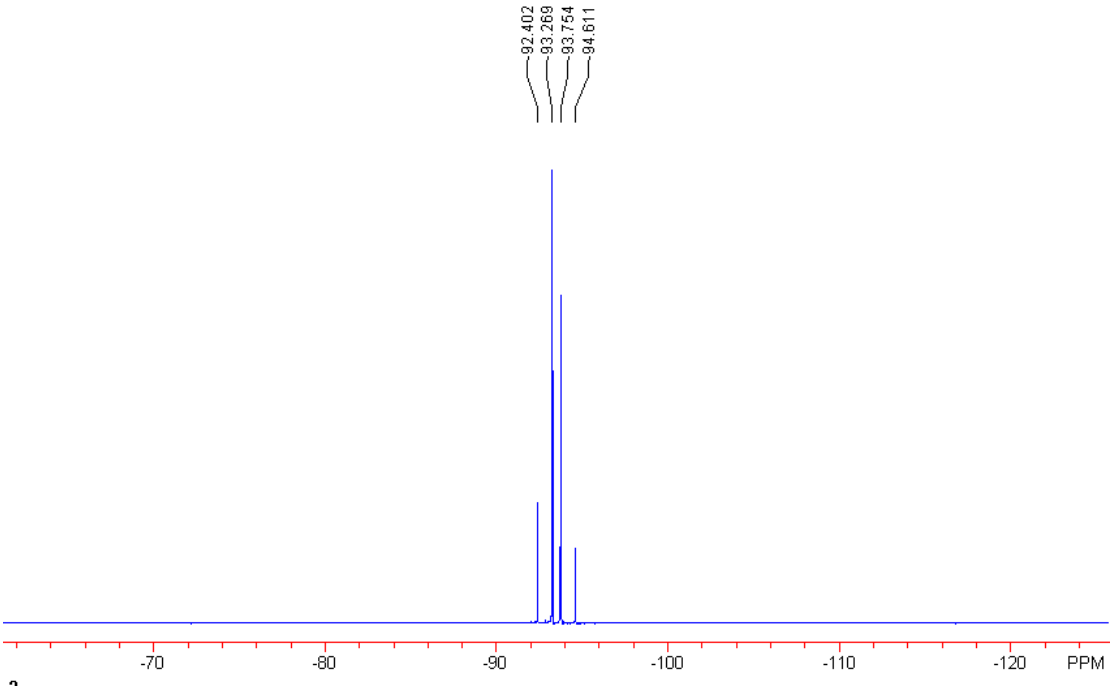


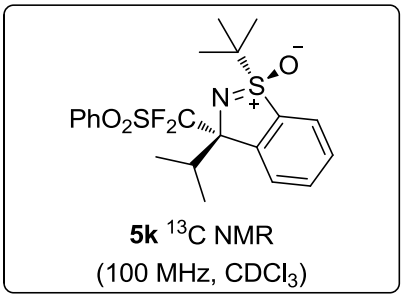


5k ^{1}H NMR
(300 MHz, $CDCl_3$)

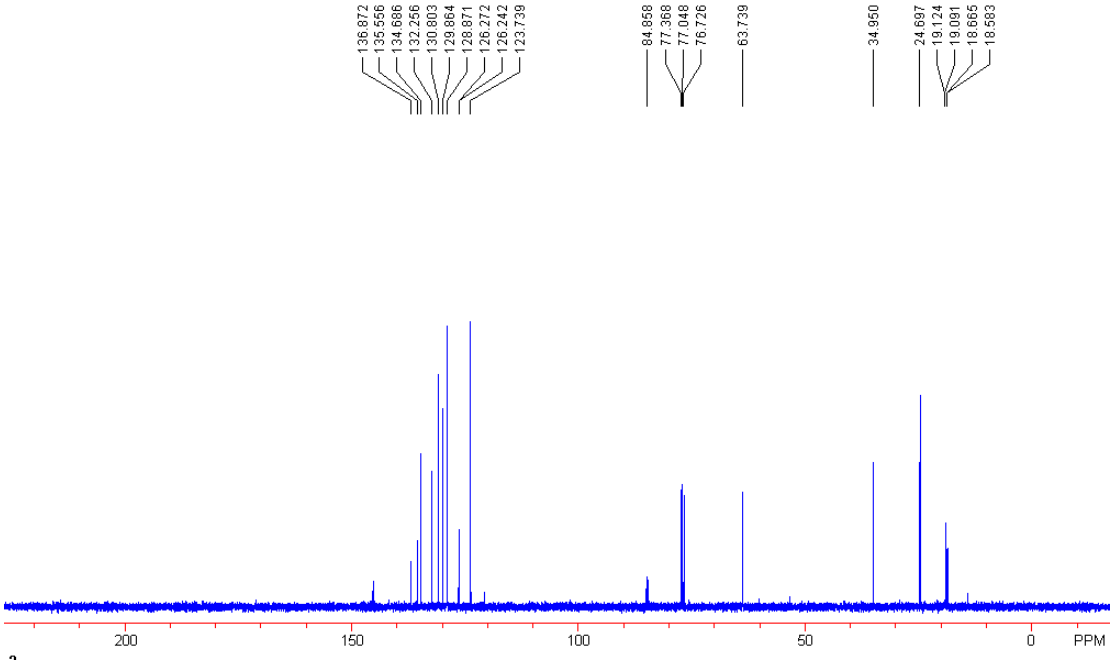


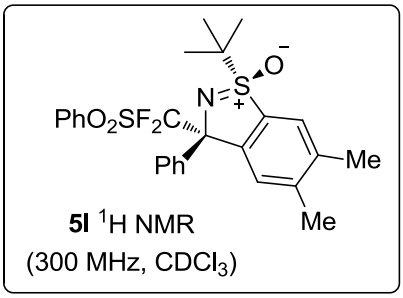

PhO2SF2C
N
S
O
5k 19F NMR
(282 MHz, CDCl3)

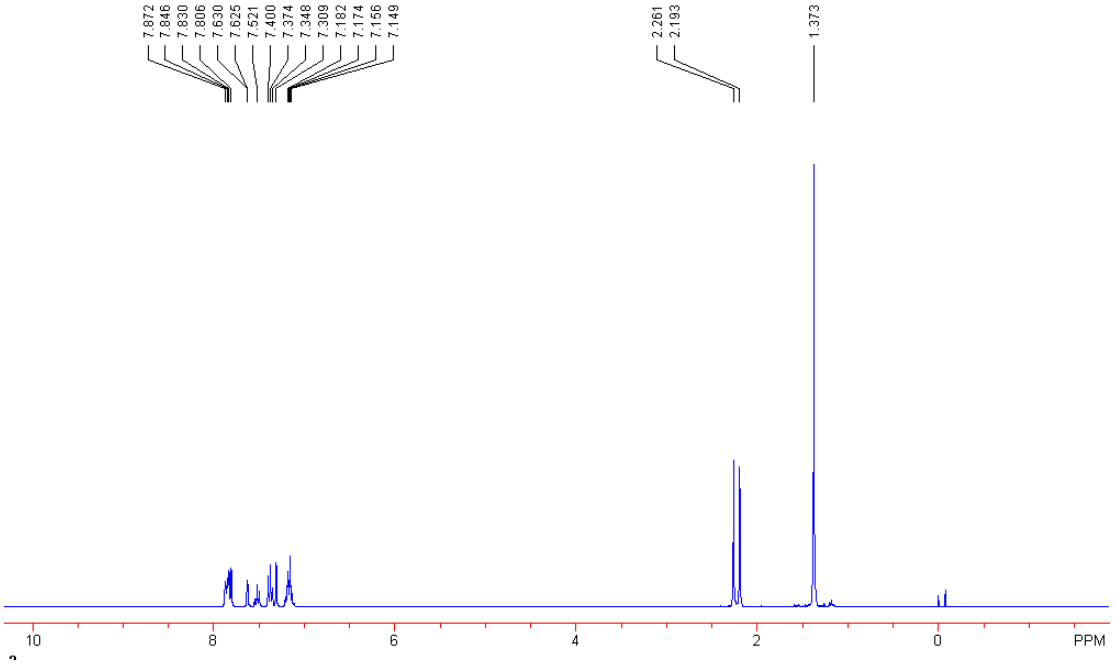

92.402
93.269
93.754
94.611
-70
-80
-90
-100
-110
-120
PPM

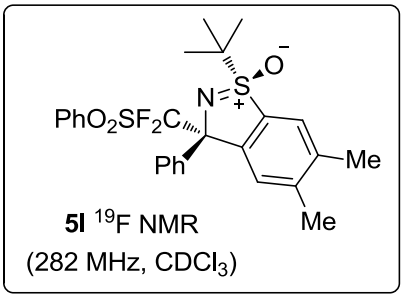


5k ^{13}C NMR
(100 MHz, $CDCl_3$)

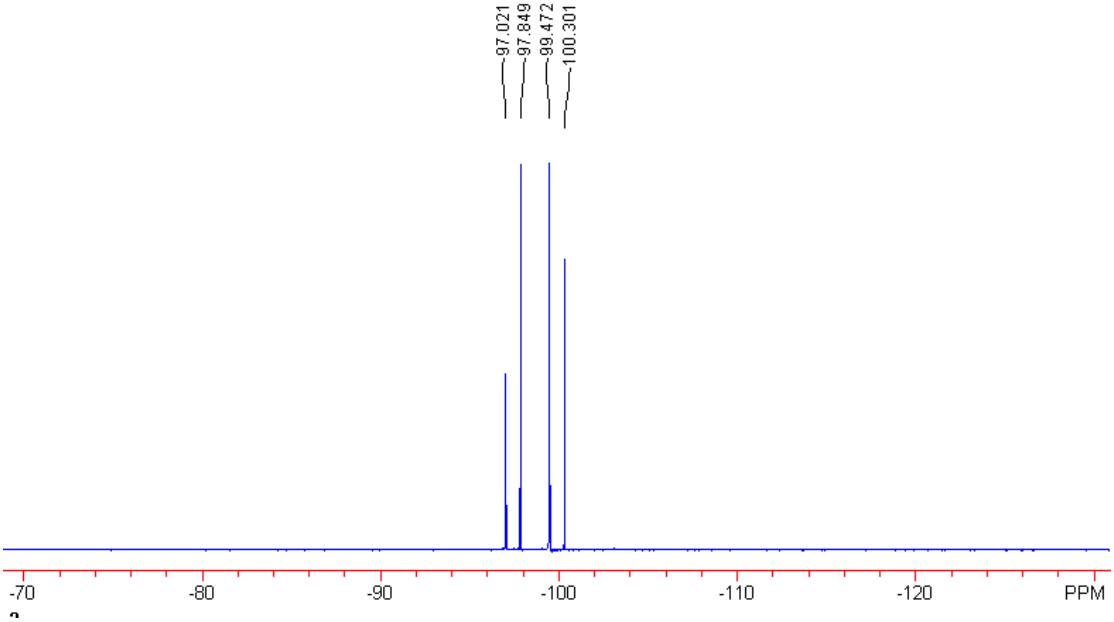


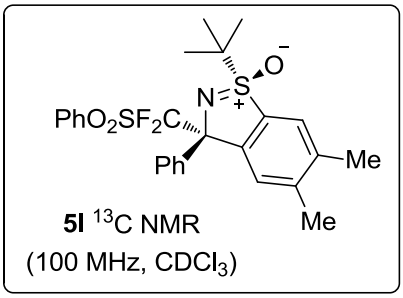

PhO2SF2C
Ph
Me
Me
5l 1H NMR
(300 MHz, CDCl3)

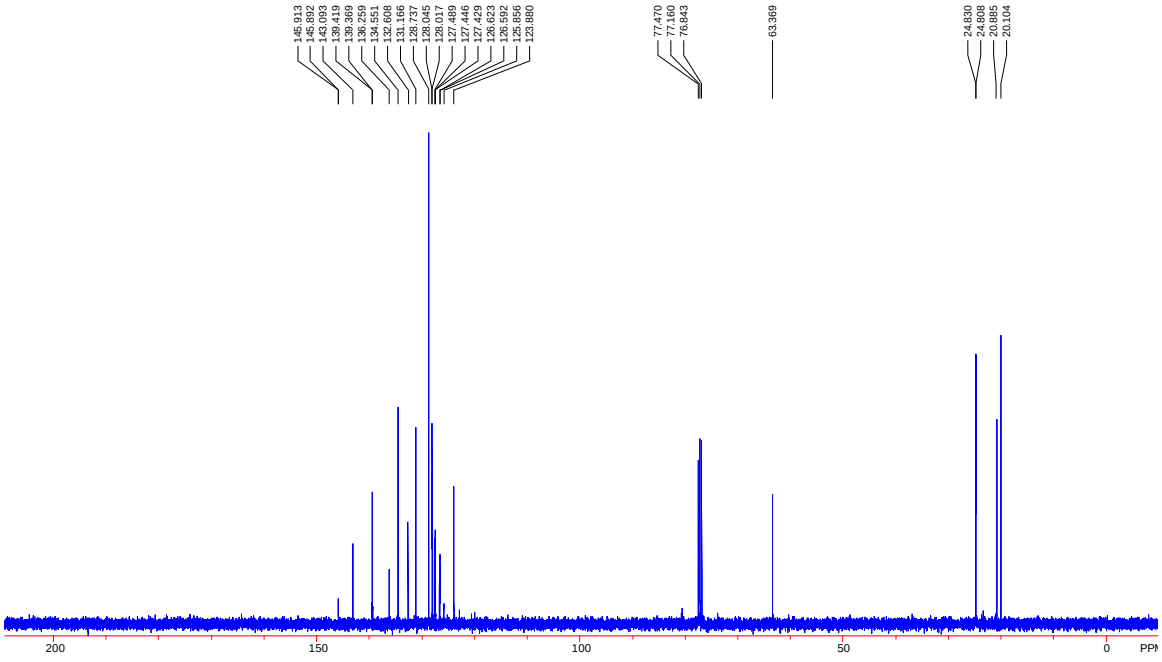

7.872
7.846
7.830
7.806
7.630
7.625
7.521
7.400
7.374
7.348
7.309
7.182
7.174
7.156
7.149
2.261
2.193
1.373
10
8
6
4
2
0
PPM

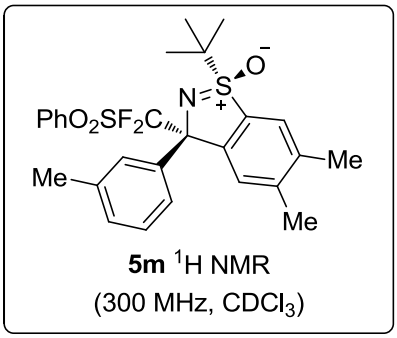


5l ^{19}F NMR
(282 MHz, $CDCl_3$)

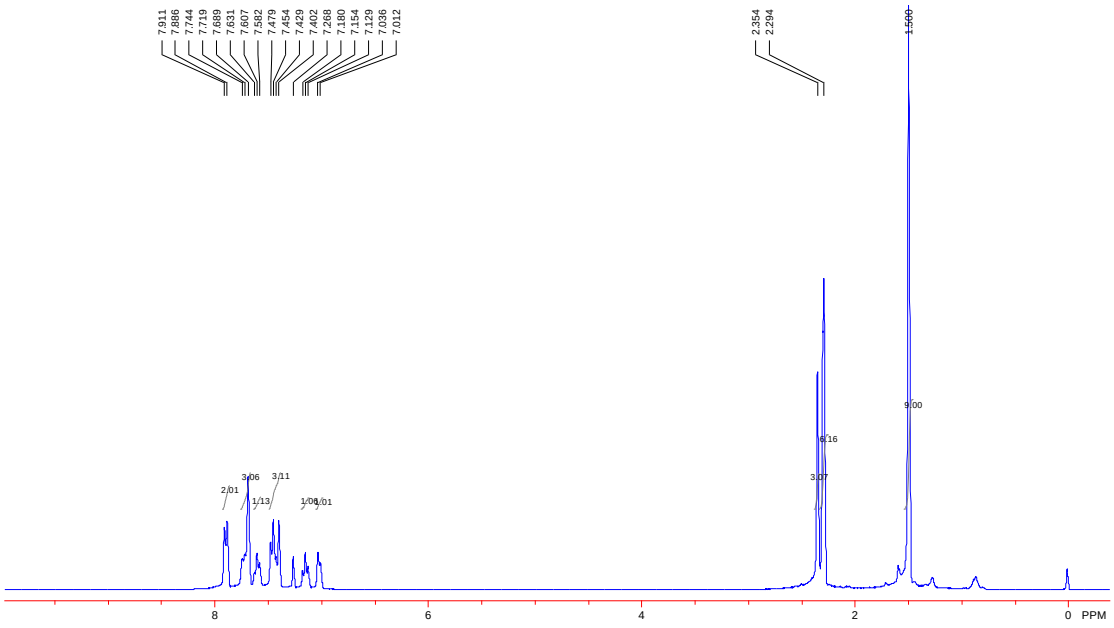


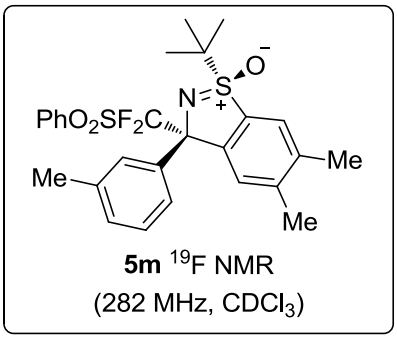

O
N
S
PhO2SF2C
Ph
Me
Me
5l 13C NMR
(100 MHz, CDCl3)


145.913
145.892
143.093
139.419
139.369
136.259
134.551
132.608
131.166
128.737
128.045
128.017
127.489
127.446
127.429
126.623
126.592
125.856
123.880
77.470
77.160
76.843
63.369
24.830
24.808
20.885
20.104
200
150
100
50
0
PPM

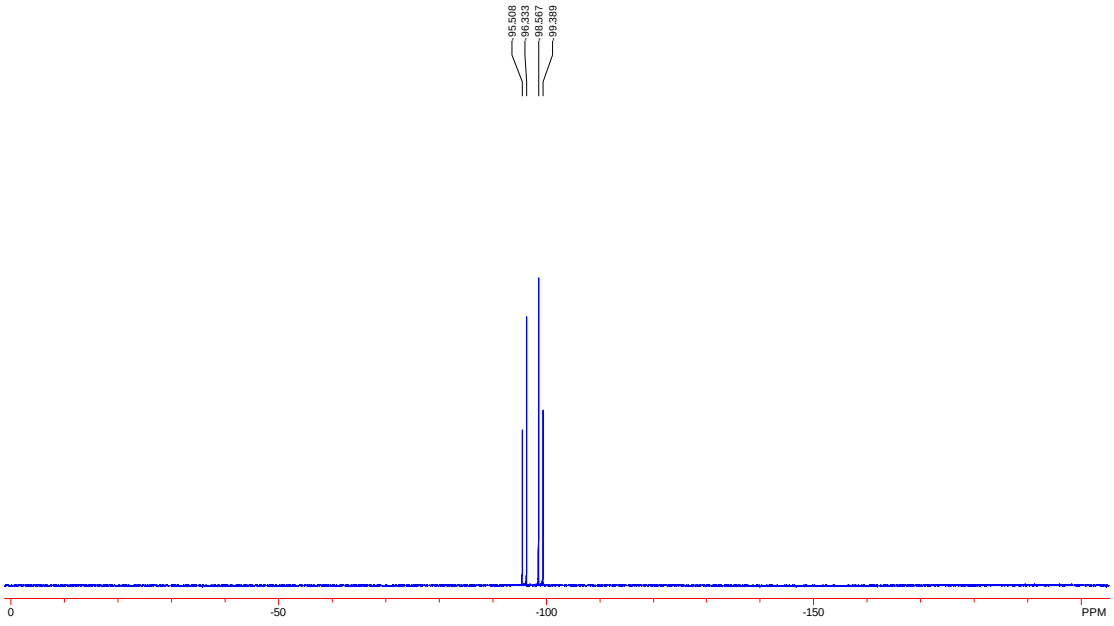


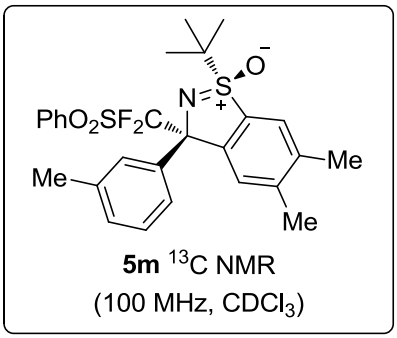
5m ^{1}H NMR
(300 MHz, $CDCl_3$)



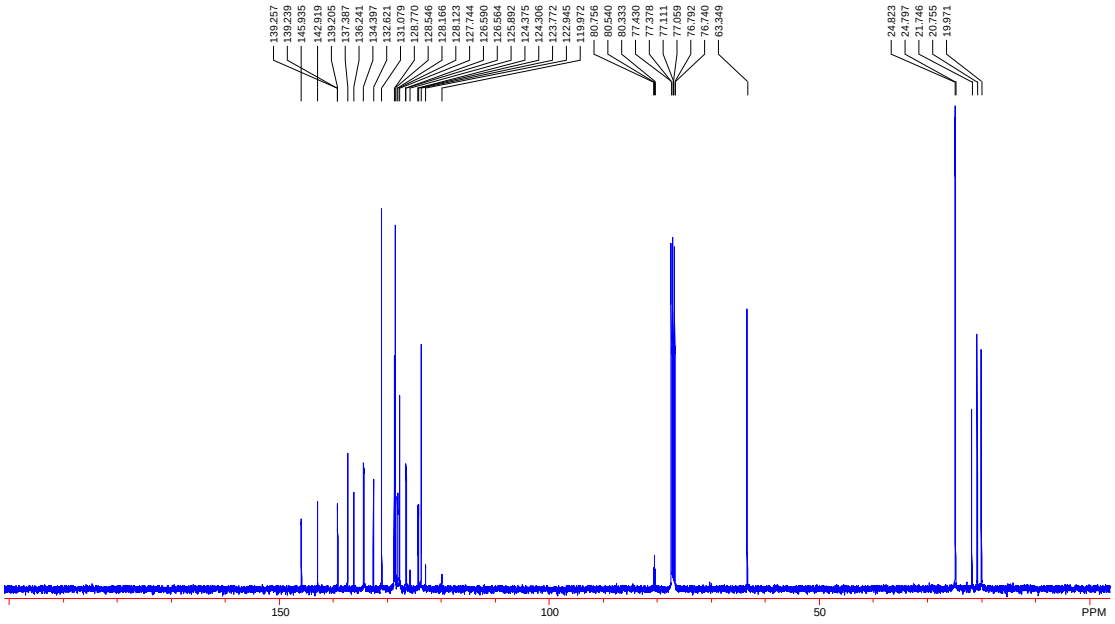


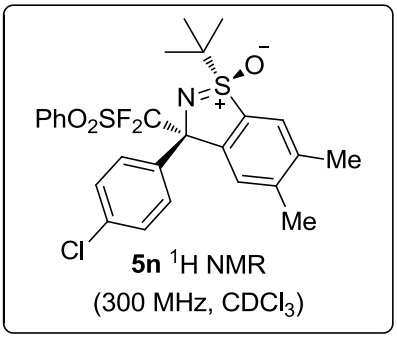
5m ^{19}F NMR
(282 MHz, $CDCl_3$)



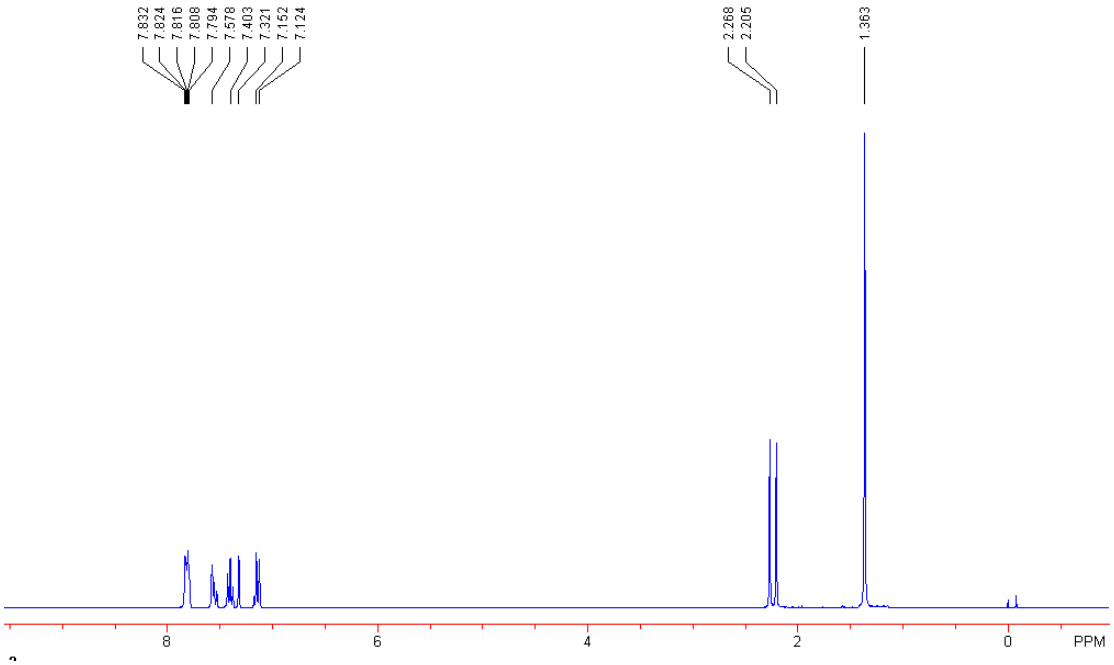


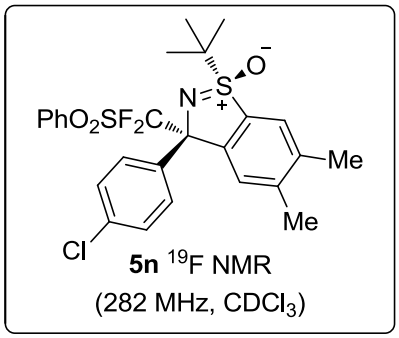
5m ^{13}C NMR
(100 MHz, $CDCl_3$)



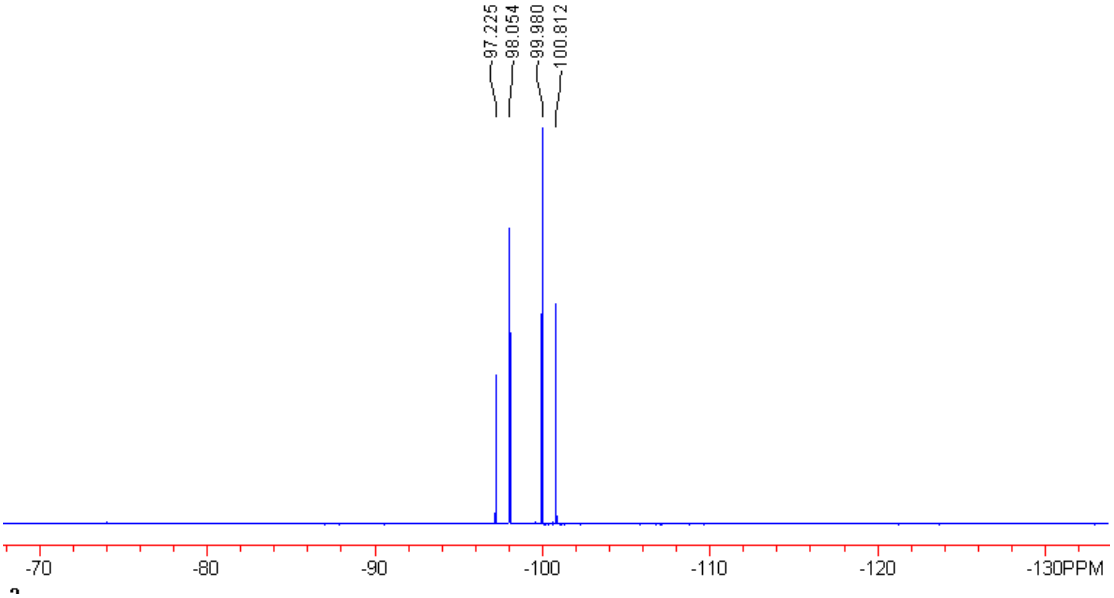


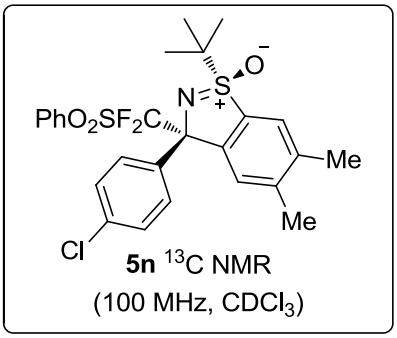
5n ^{1}H NMR
(300 MHz, $CDCl_3$)

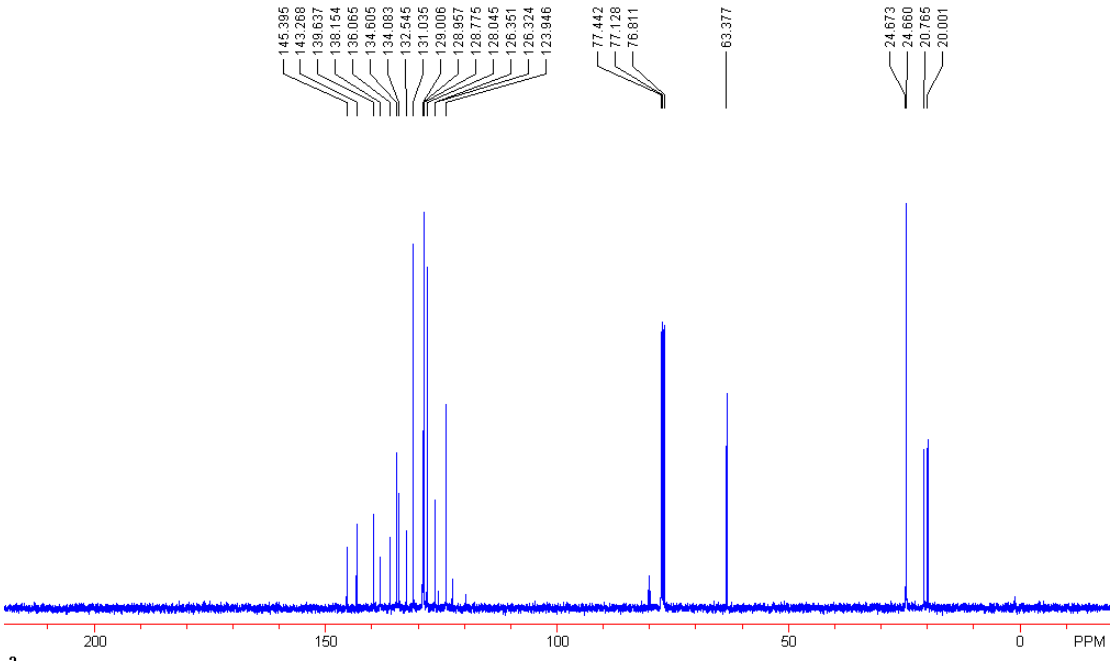


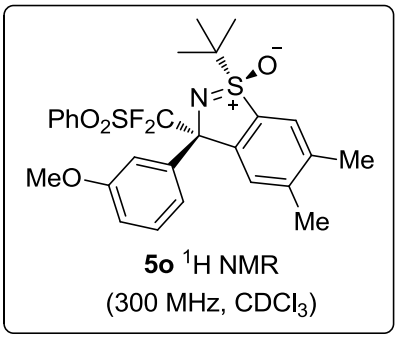


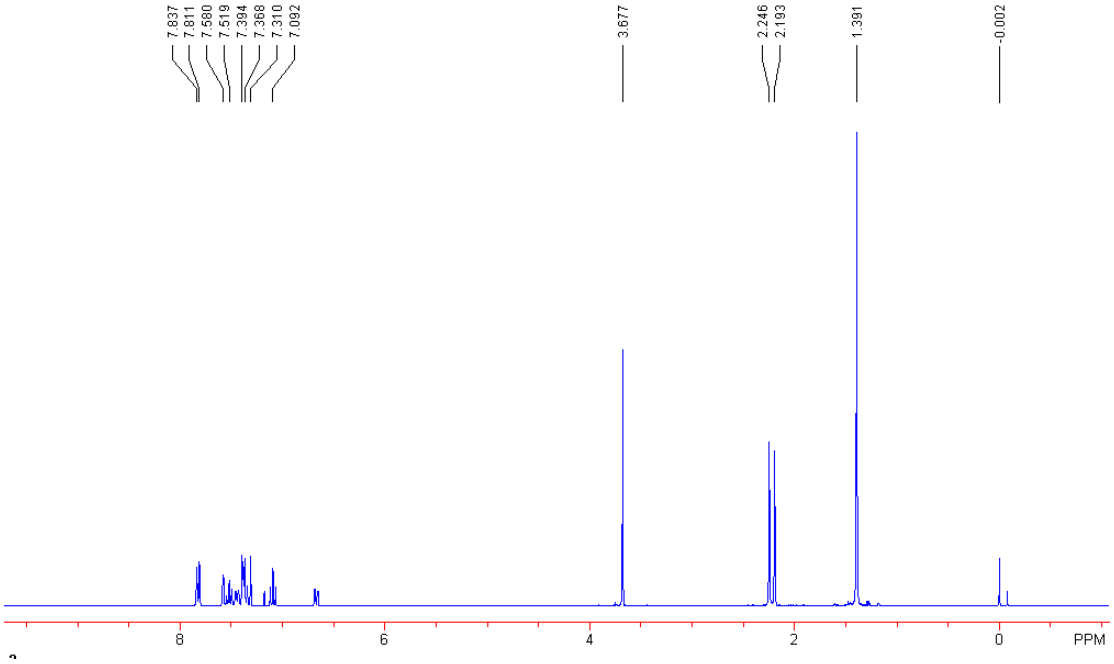
5n ^{19}F NMR
(282 MHz, $CDCl_3$)

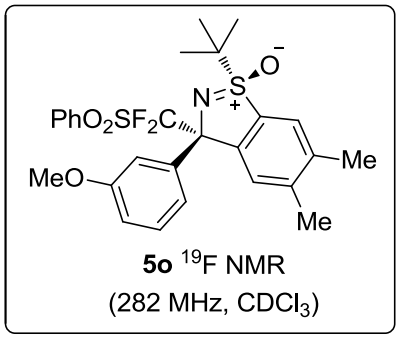



PhO2SF2C
N
S
O
Me
Me
Cl
5n 13C NMR
(100 MHz, CDCl3)

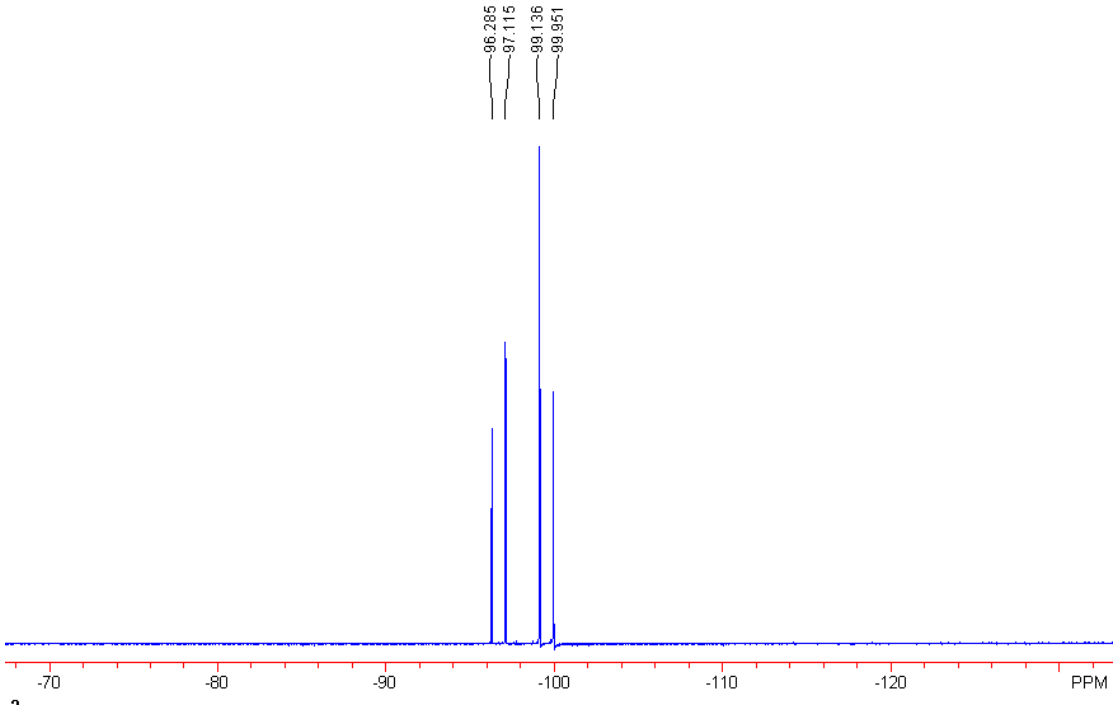

145.395
143.268
139.637
138.154
136.065
134.605
134.083
132.545
131.035
129.006
128.957
128.775
128.045
126.351
126.324
123.946
77.442
77.128
76.811
63.377
24.673
24.660
20.765
20.001
200
150
100
50
0
PPM

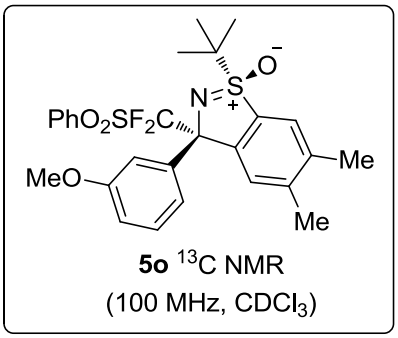

PhO2SF2C
MeO
Me
Me
O
N
S
+
5o 1H NMR
(300 MHz, CDCl3)


7.837
7.811
7.580
7.519
7.394
7.368
7.310
7.092
3.677
2.246
2.193
1.391
-0.002
8
6
4
2
0
PPM

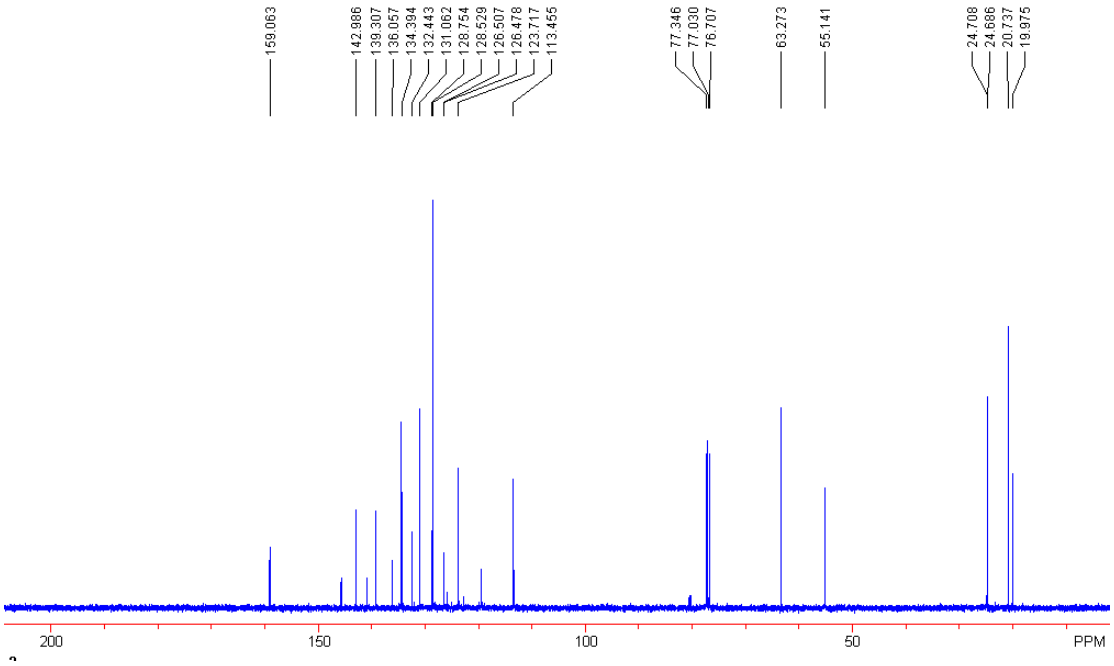


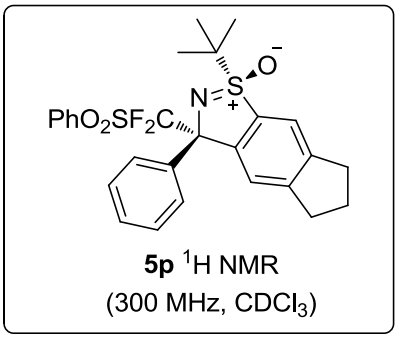
5o ^{19}F NMR
(282 MHz, $CDCl_3$)



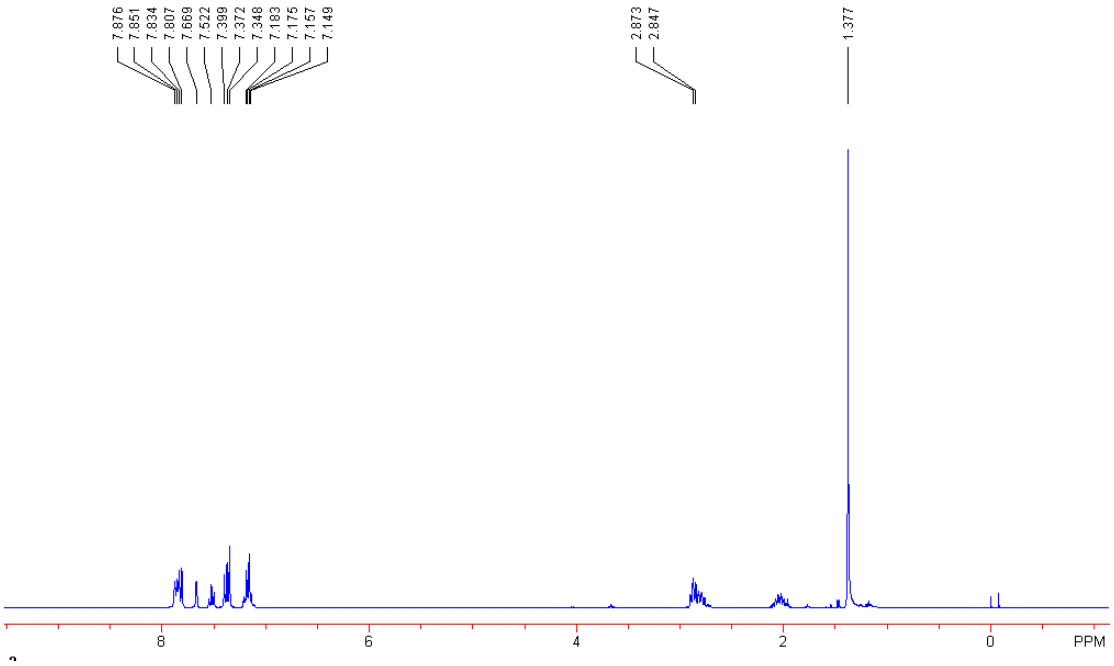


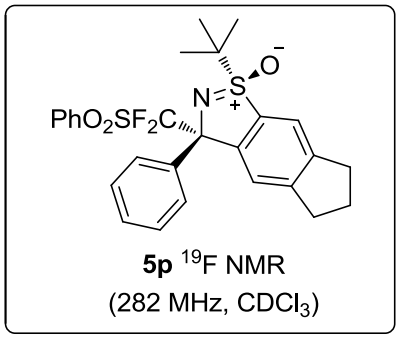
5o ^{13}C NMR
(100 MHz, $CDCl_3$)



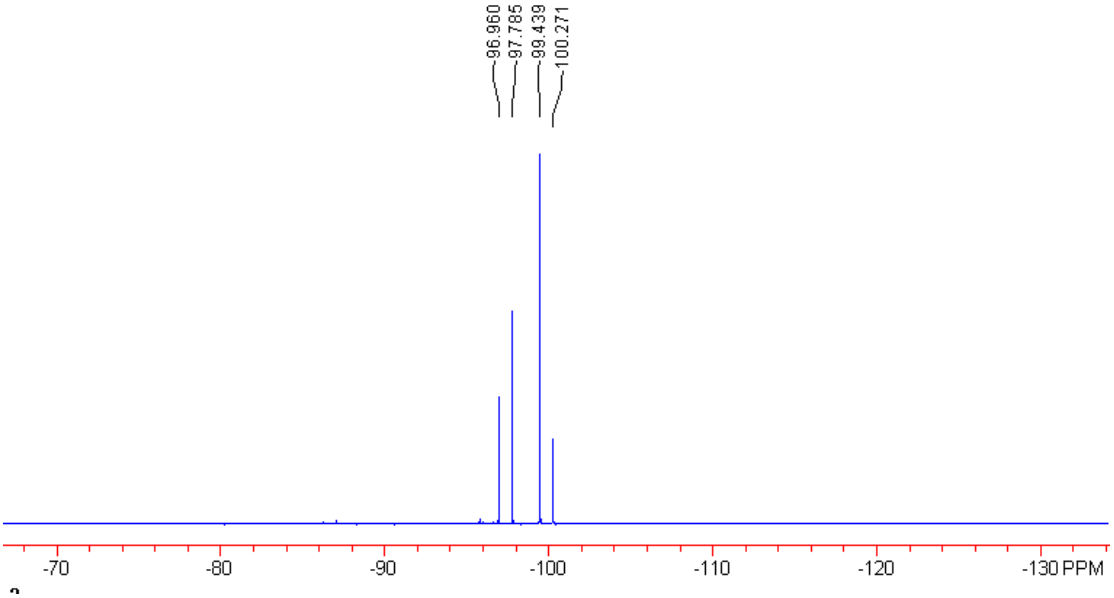


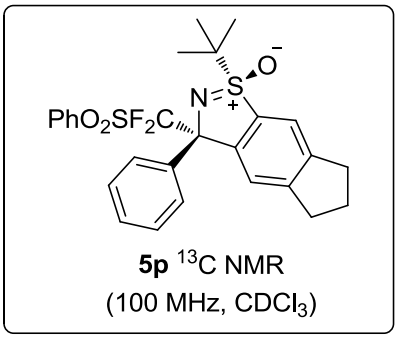
5p ^{1}H NMR
(300 MHz, $CDCl_3$)



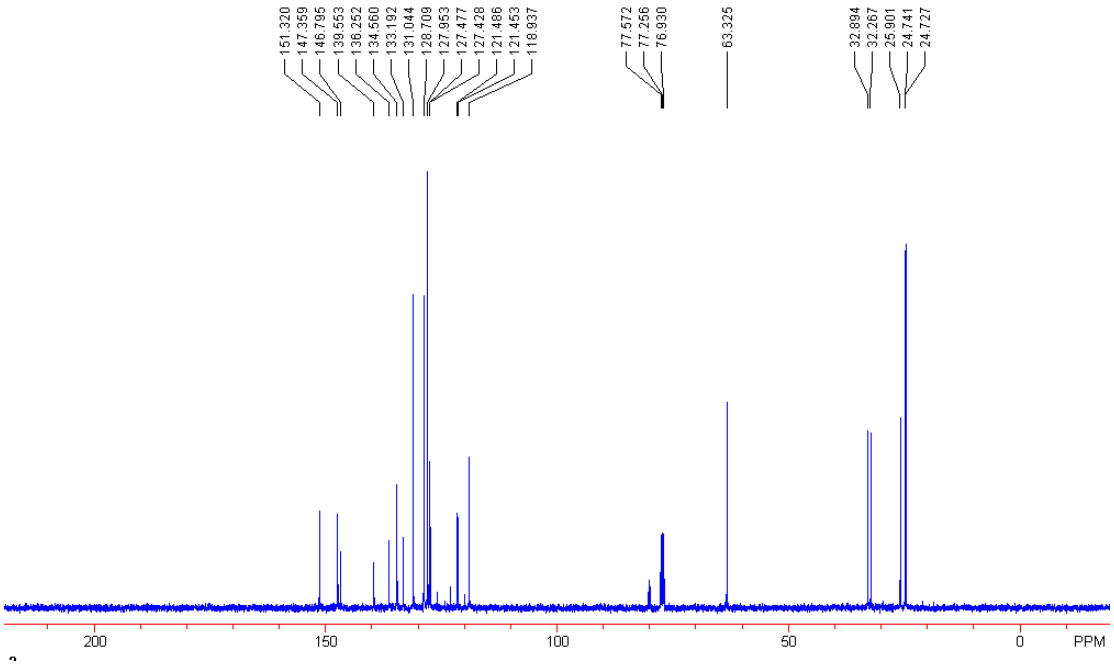


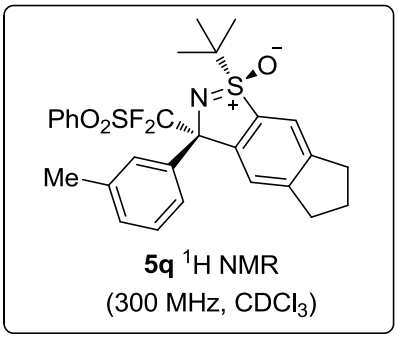
5p ^{19}F NMR
(282 MHz, $CDCl_3$)



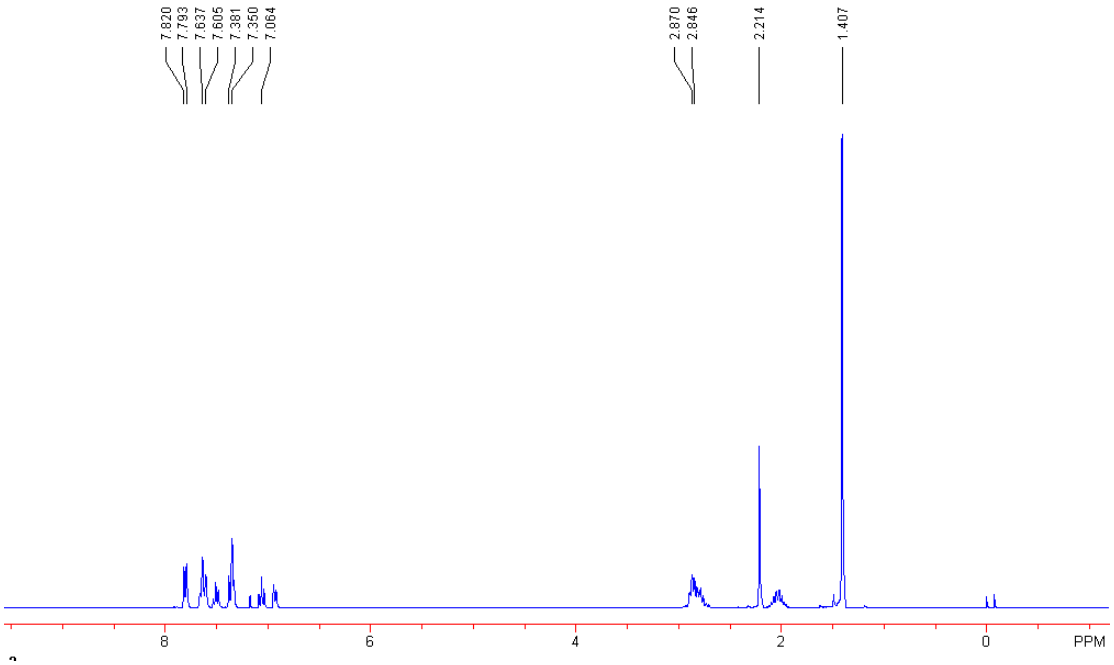


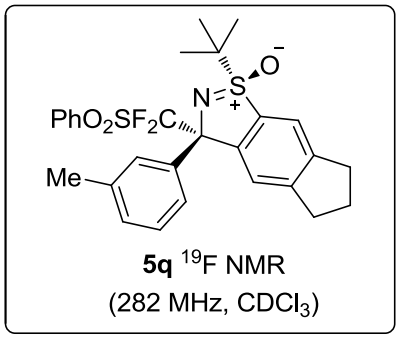
5p ^{13}C NMR
(100 MHz, $CDCl_3$)

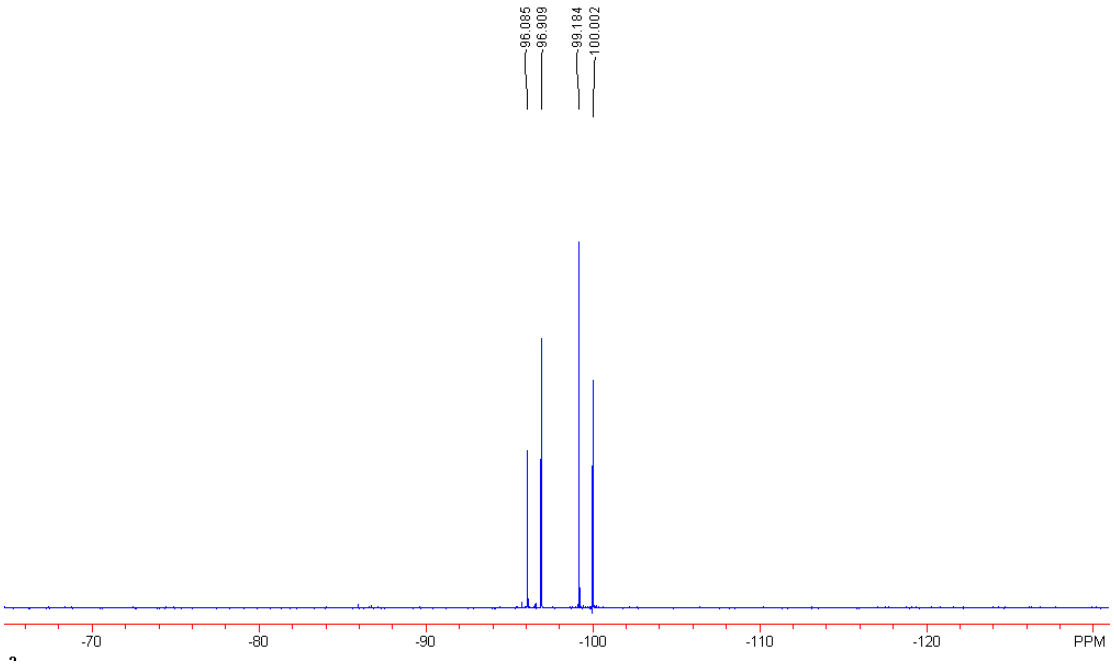


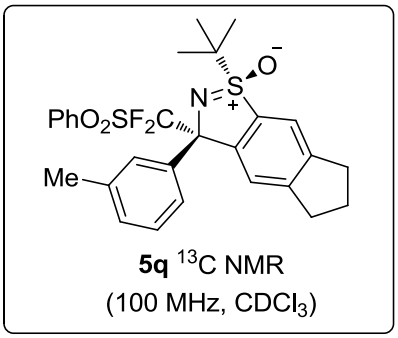


5q ^{1}H NMR
(300 MHz, $CDCl_3$)

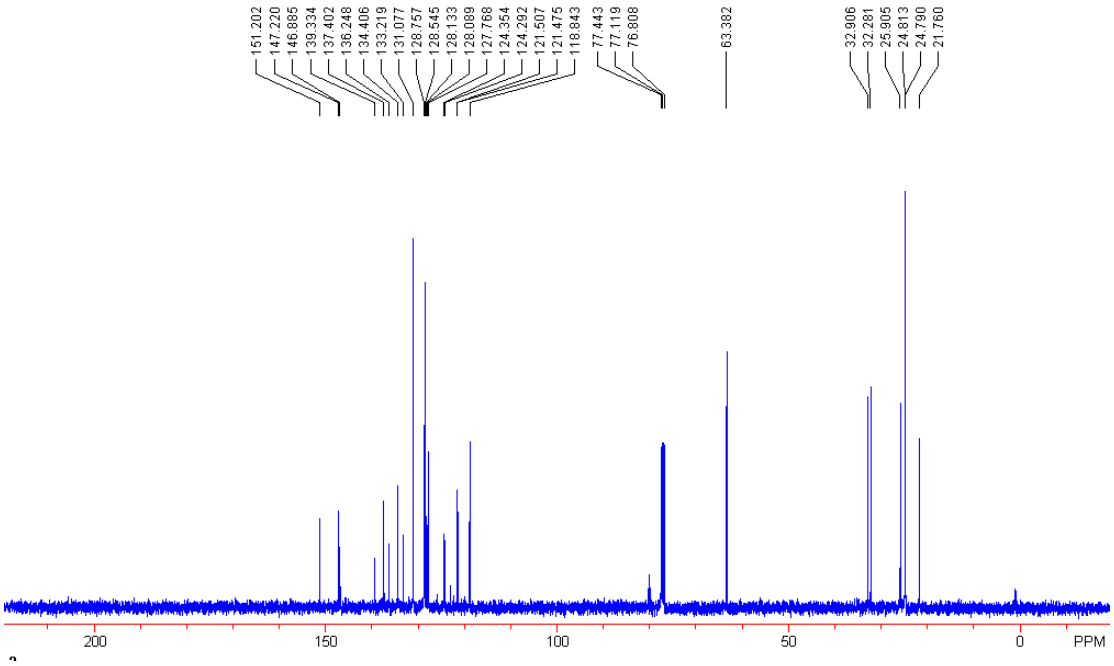


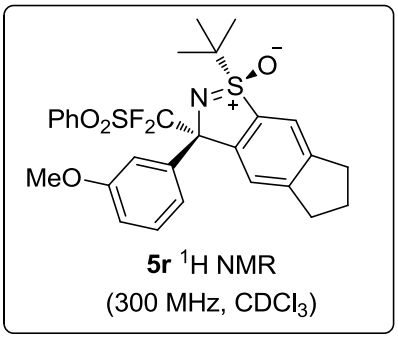

PhO2SF2C
Me
N
S
O
5q 19F NMR
(282 MHz, CDCl3)


96.085
96.909
99.184
100.002
-70
-80
-90
-100
-110
-120
PPM

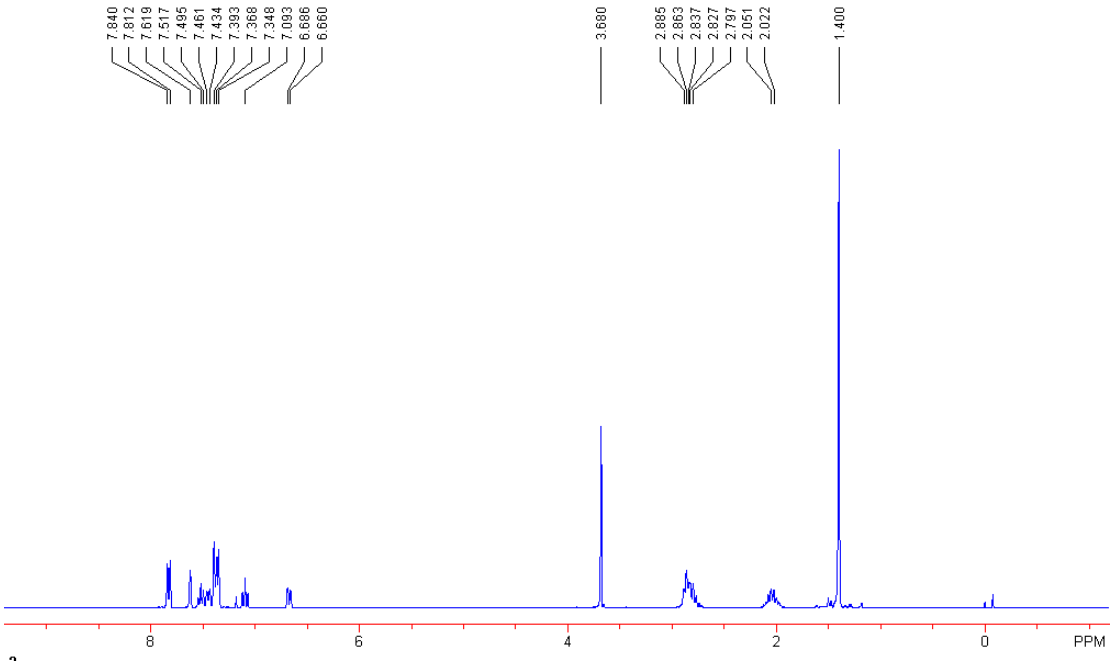


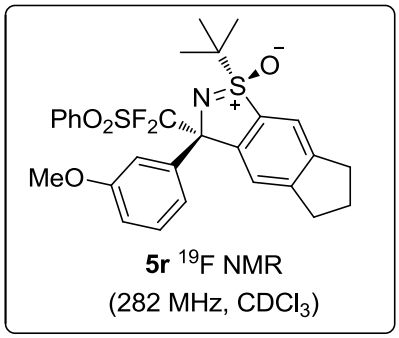
5q ^{13}C NMR
(100 MHz, $CDCl_3$)



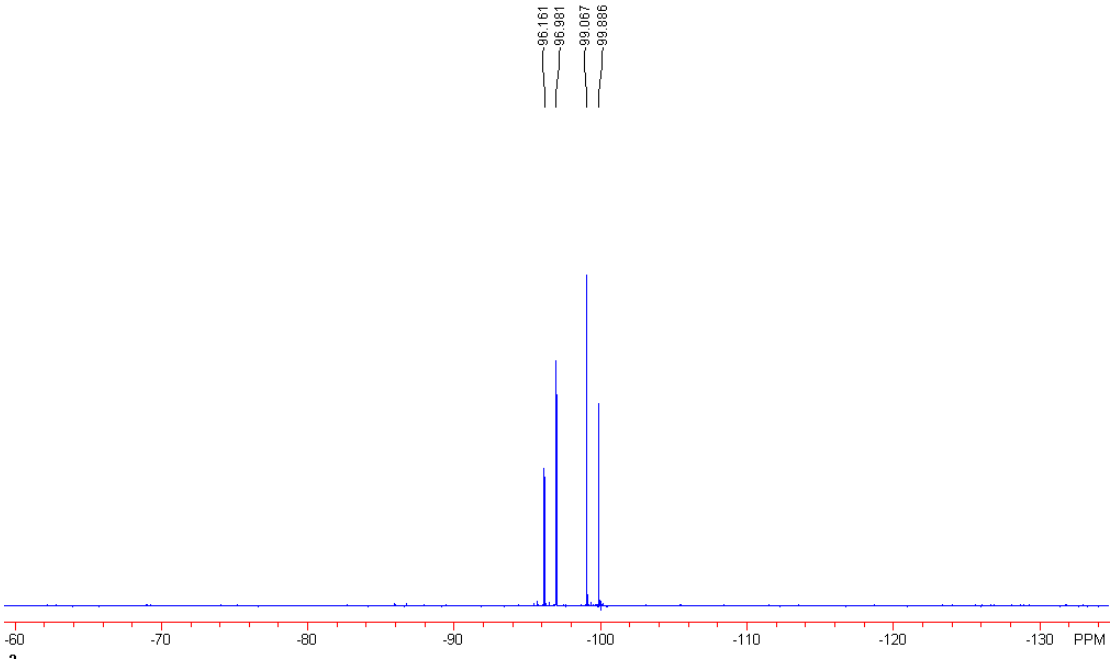


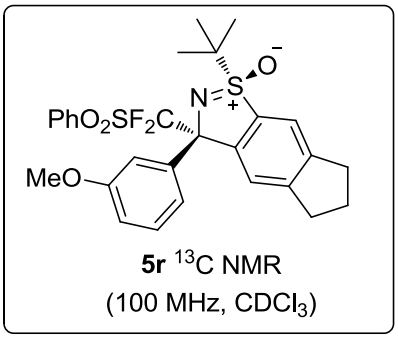
5r ^{1}H NMR
(300 MHz, $CDCl_3$)



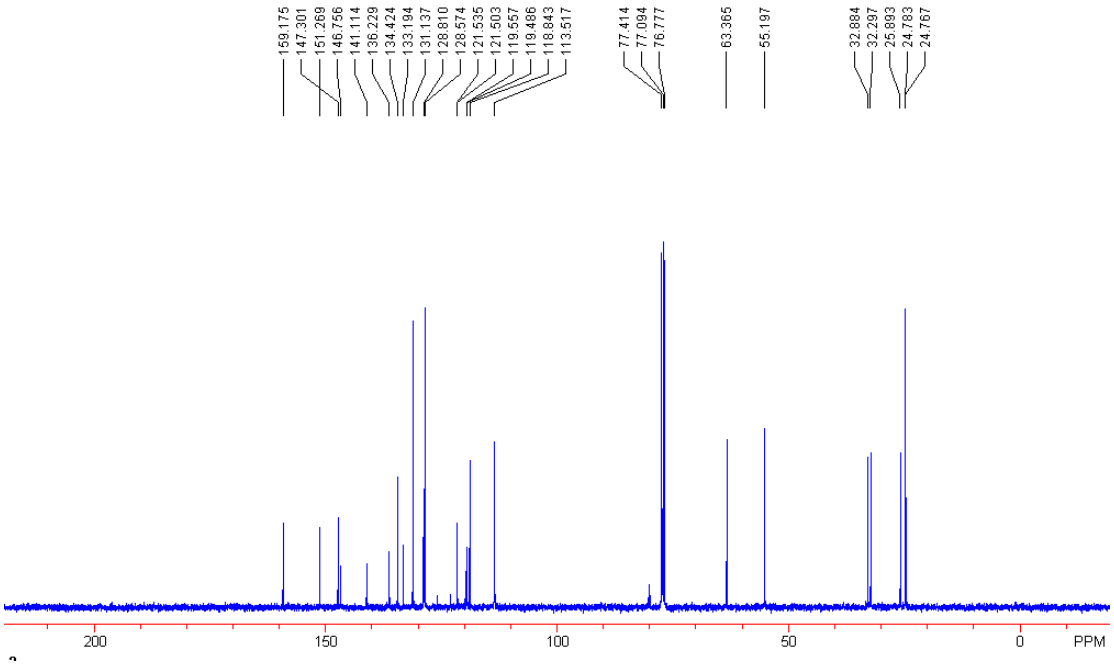


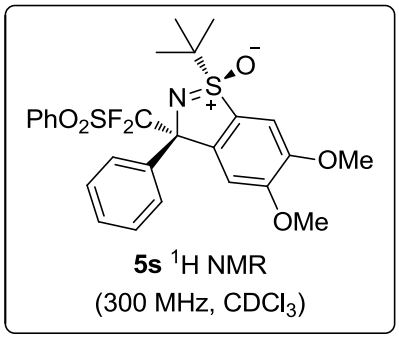
5r ^{19}F NMR
(282 MHz, $CDCl_3$)



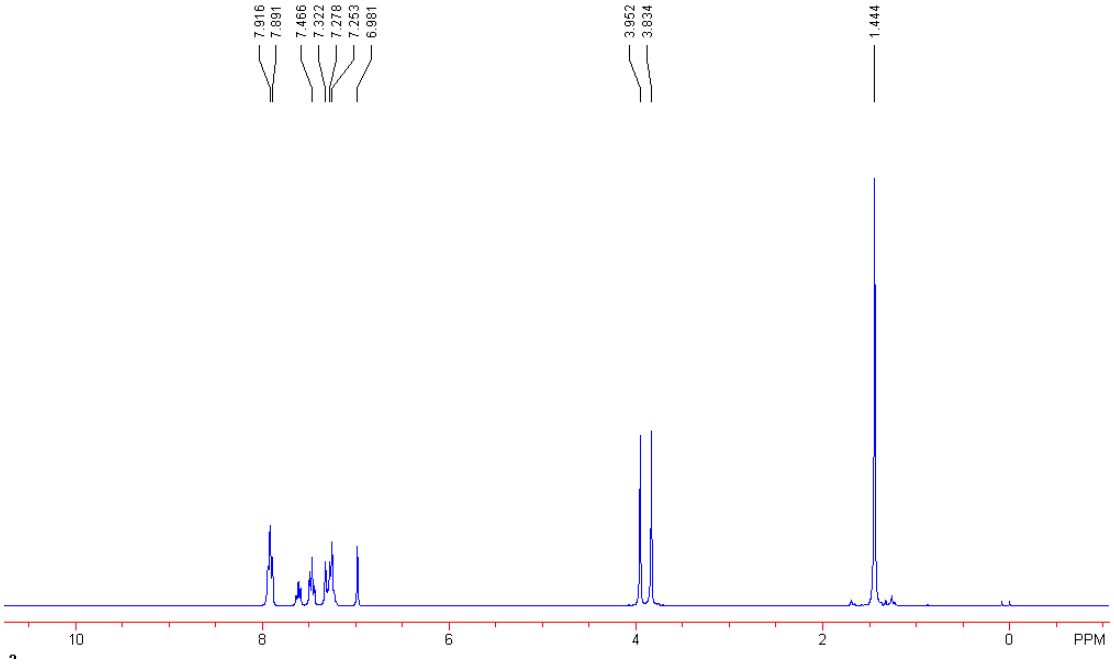


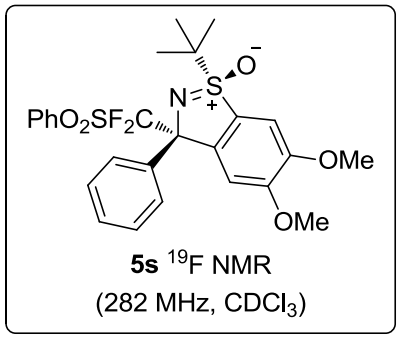
5r ^{13}C NMR
(100 MHz, $CDCl_3$)



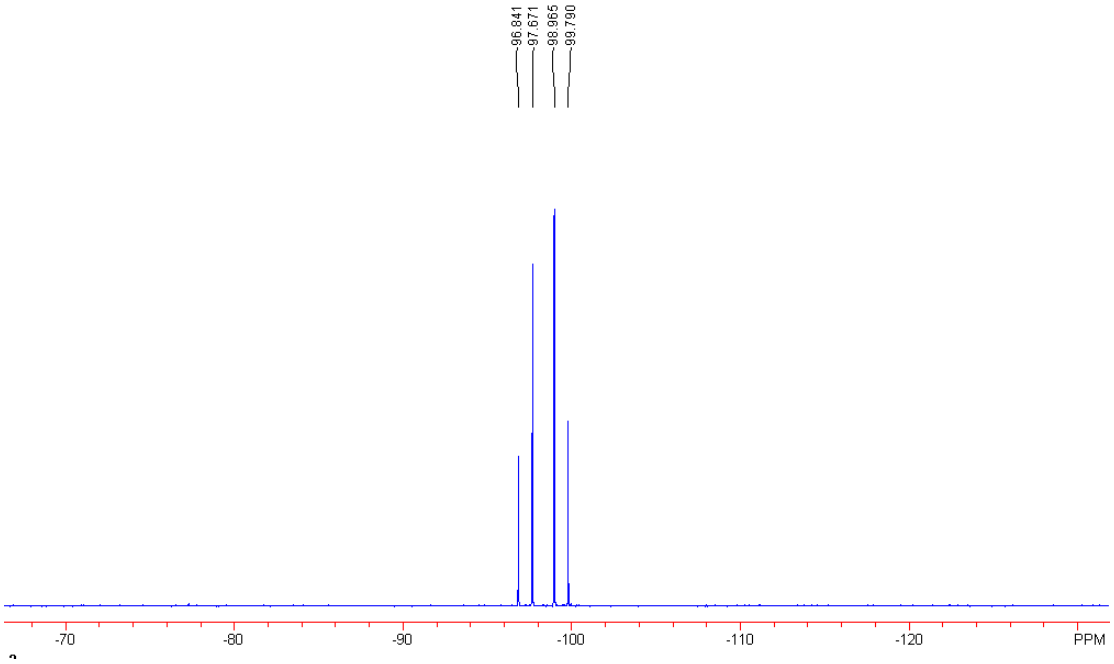


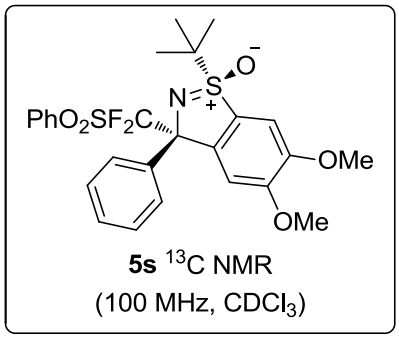
5s ^{1}H NMR
(300 MHz, $CDCl_3$)



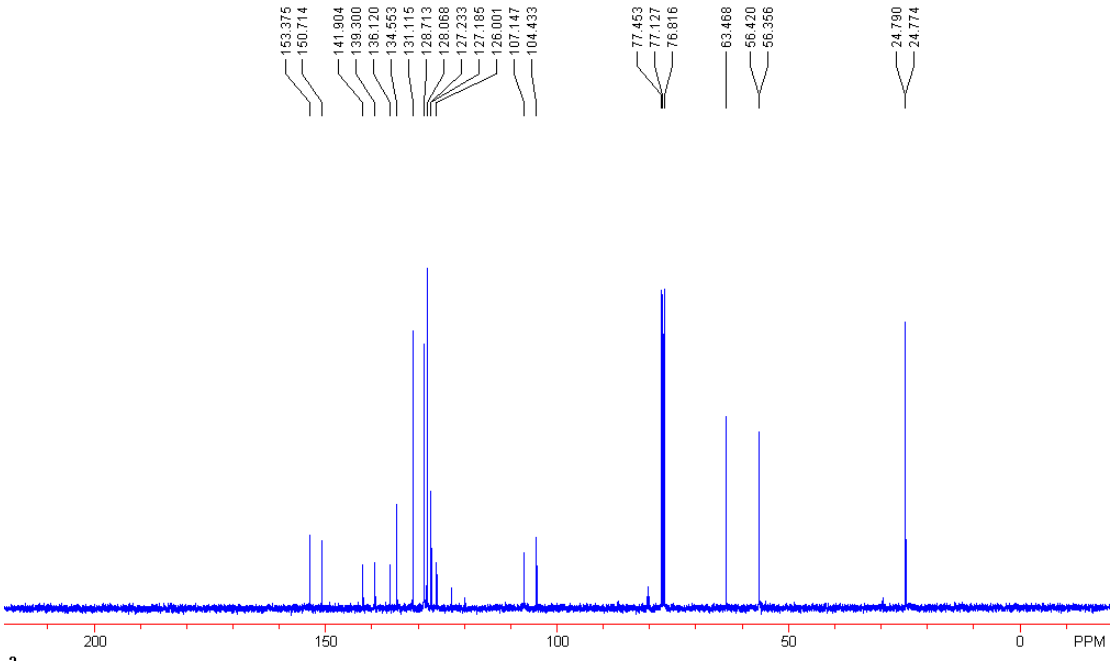


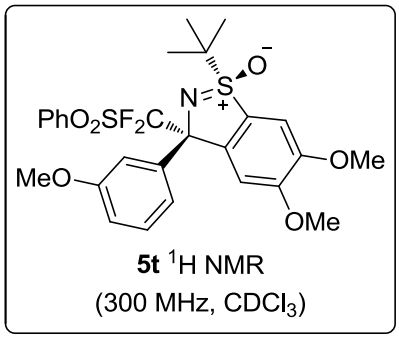
5s ^{19}F NMR
(282 MHz, $CDCl_3$)



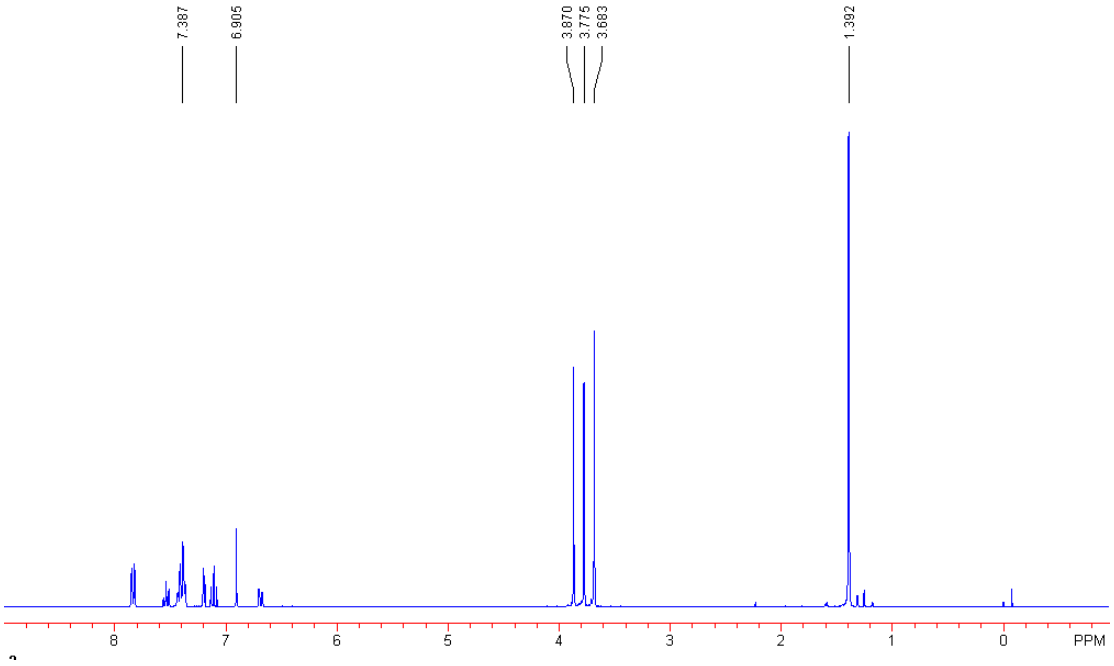


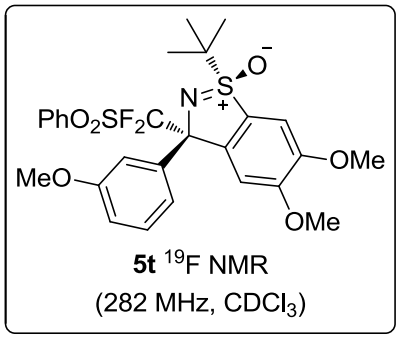
5s ^{13}C NMR
(100 MHz, $CDCl_3$)

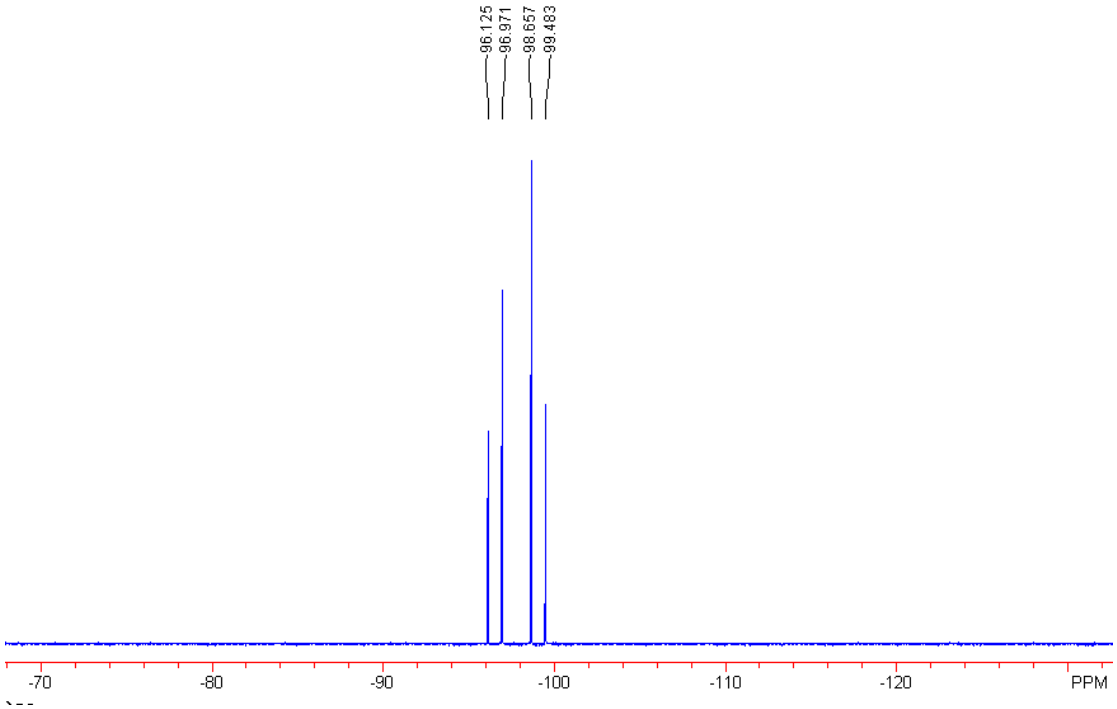


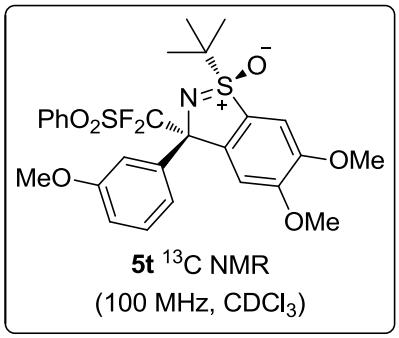


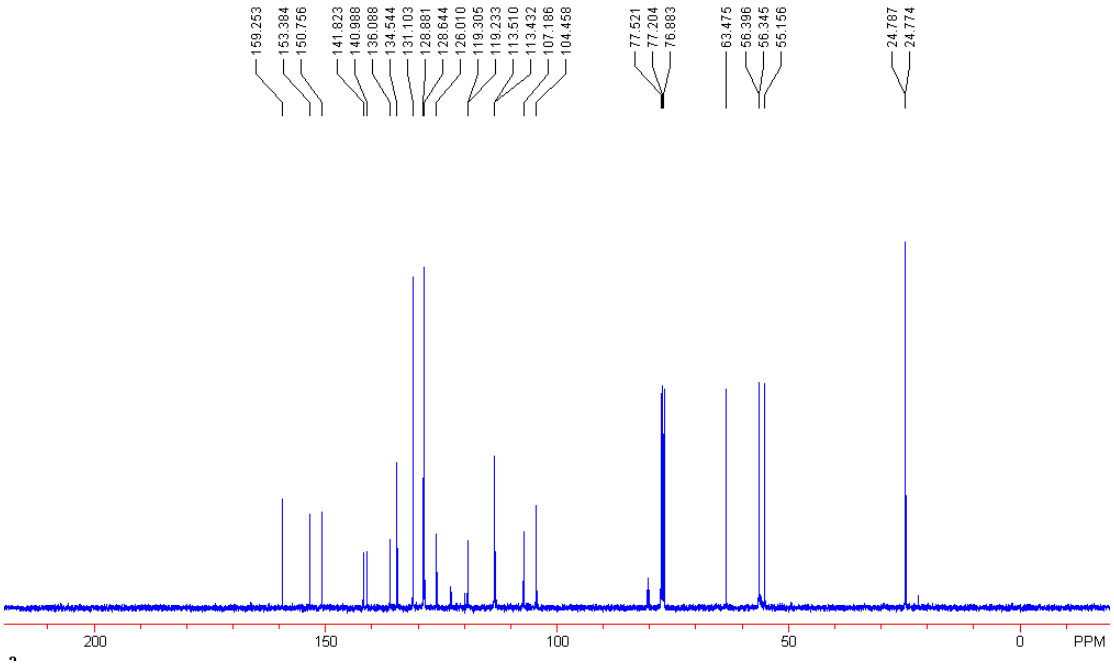
5t ^{1}H NMR
(300 MHz, $CDCl_3$)

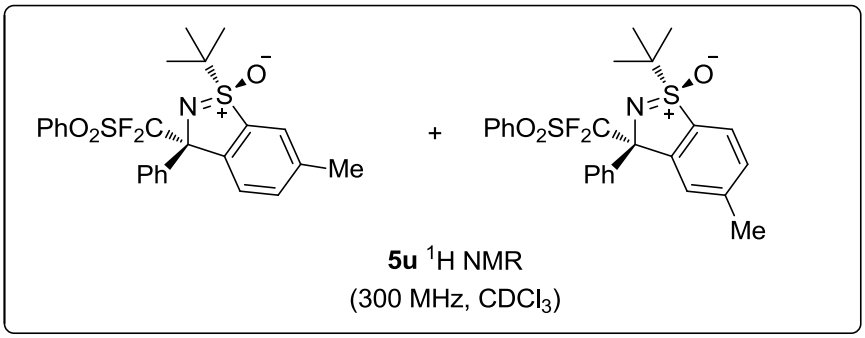


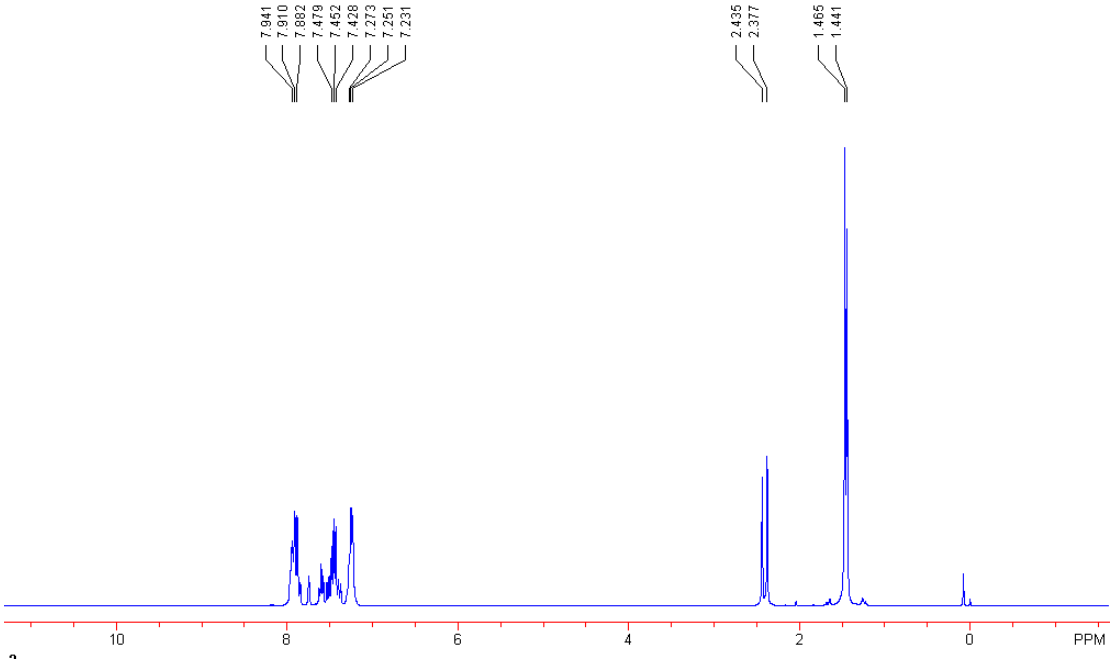

PhO2SF2C
MeO
OMe
OMe
5t 19F NMR
(282 MHz, CDCl3)

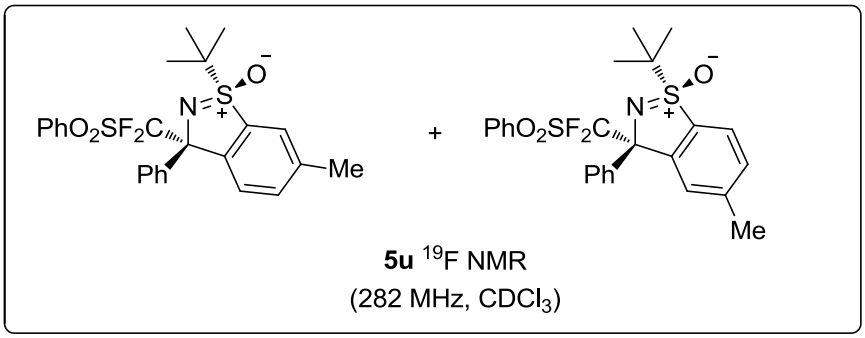

96.125
96.971
98.657
99.483
-70
-80
-90
-100
-110
-120
PPM


PhO2SF2C
MeO
OMe
OMe
5t 13C NMR
(100 MHz, CDCl3)

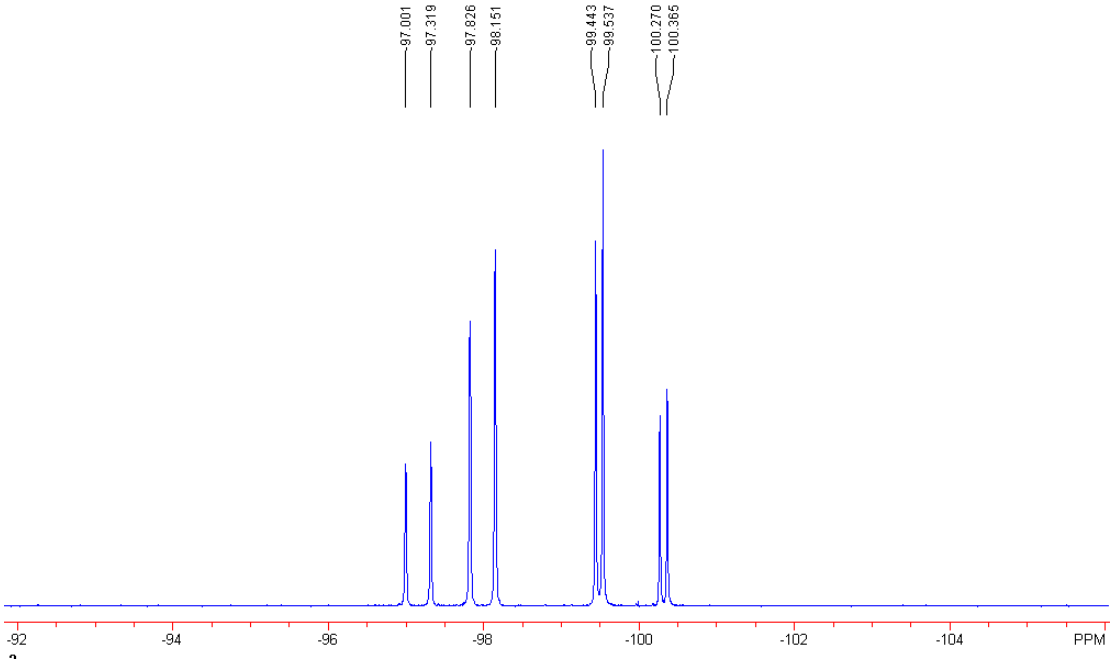

159.253
153.384
150.756
141.823
140.988
136.088
134.544
131.103
128.881
128.644
126.010
119.305
119.233
113.510
113.432
107.186
104.458
77.521
77.204
76.883
63.475
56.396
56.345
55.156
24.787
24.774
200
150
100
50
0
PPM

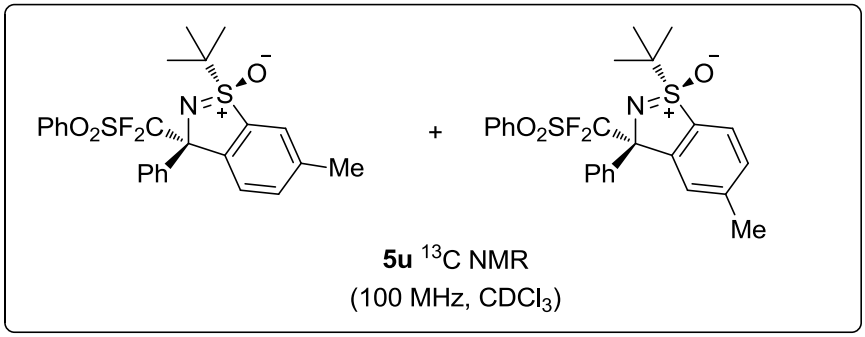

PhO2SF2C
Ph
Me
+
PhO2SF2C
Ph
Me
5u 1H NMR
(300 MHz, CDCl3)

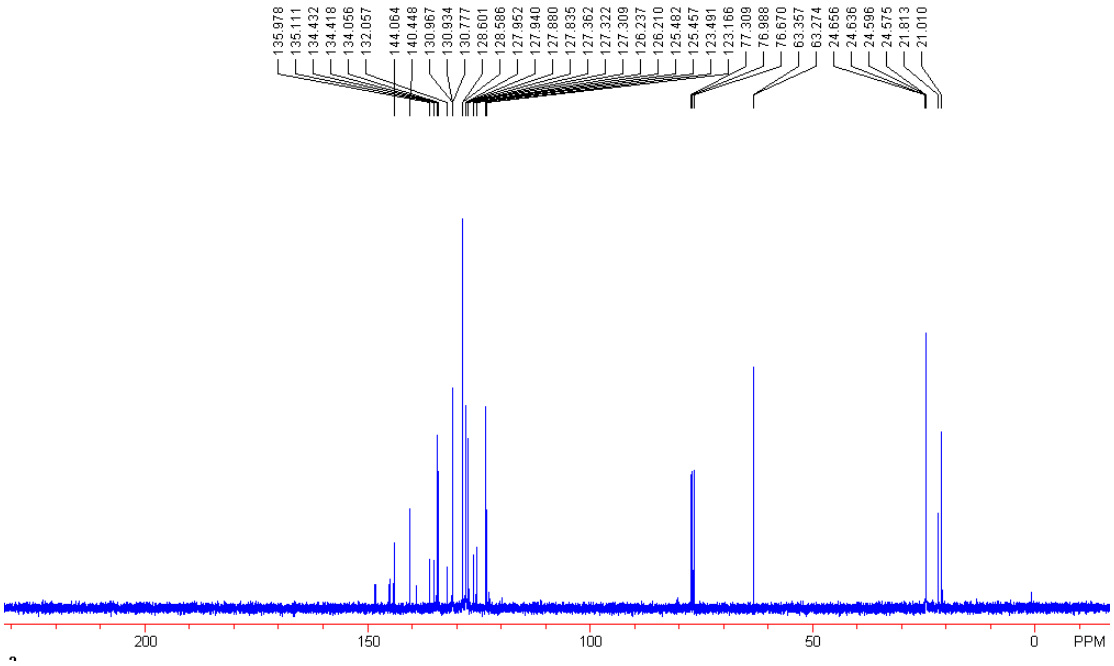

7.941
7.910
7.882
7.479
7.452
7.428
7.273
7.251
7.231
2.435
2.377
1.465
1.441
10
8
6
4
2
0
PPM

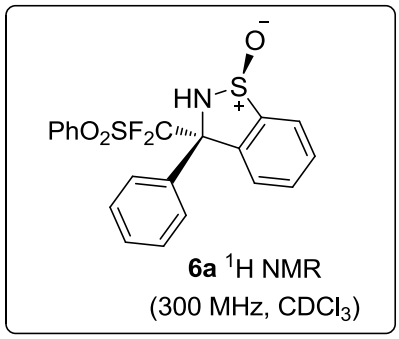


5u ^{19}F NMR
(282 MHz, $CDCl_3$)

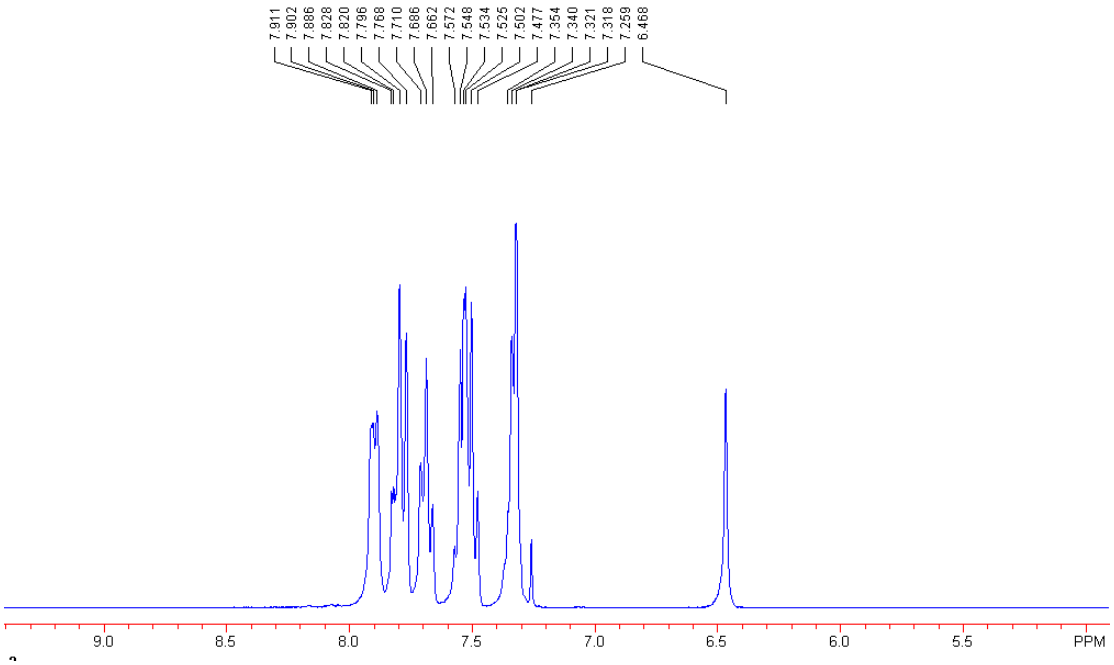


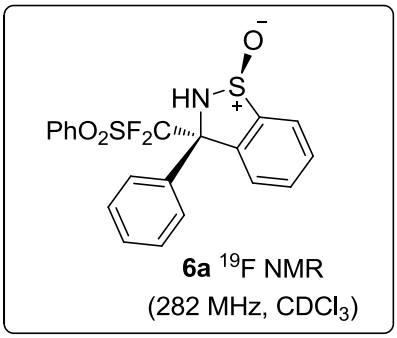

PhO2SF2C
Ph
Me
+
PhO2SF2C
Ph
Me
5u 13C NMR
(100 MHz, CDCl3)


135.978
135.111
134.432
134.418
134.056
132.057
144.064
140.448
130.967
130.934
130.777
128.601
128.586
127.952
127.940
127.880
127.835
127.362
127.322
127.309
126.237
126.210
125.482
125.457
123.491
123.166
77.309
76.988
76.670
63.357
63.274
24.656
24.636
24.596
24.575
21.813
21.010
200
150
100
50
0
PPM

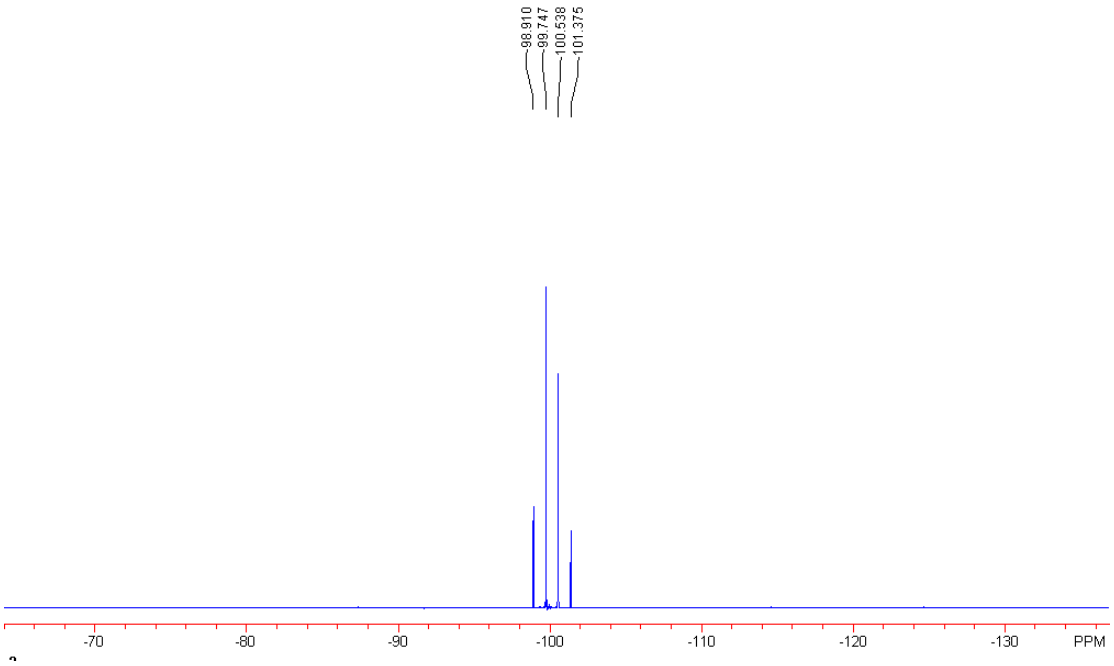


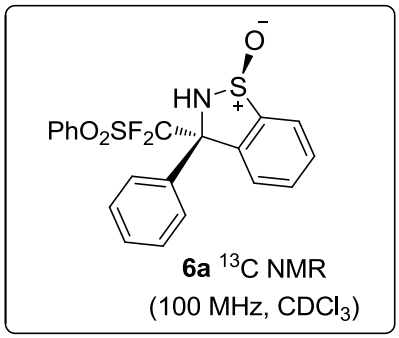
6a ^{1}H NMR
(300 MHz, $CDCl_3$)



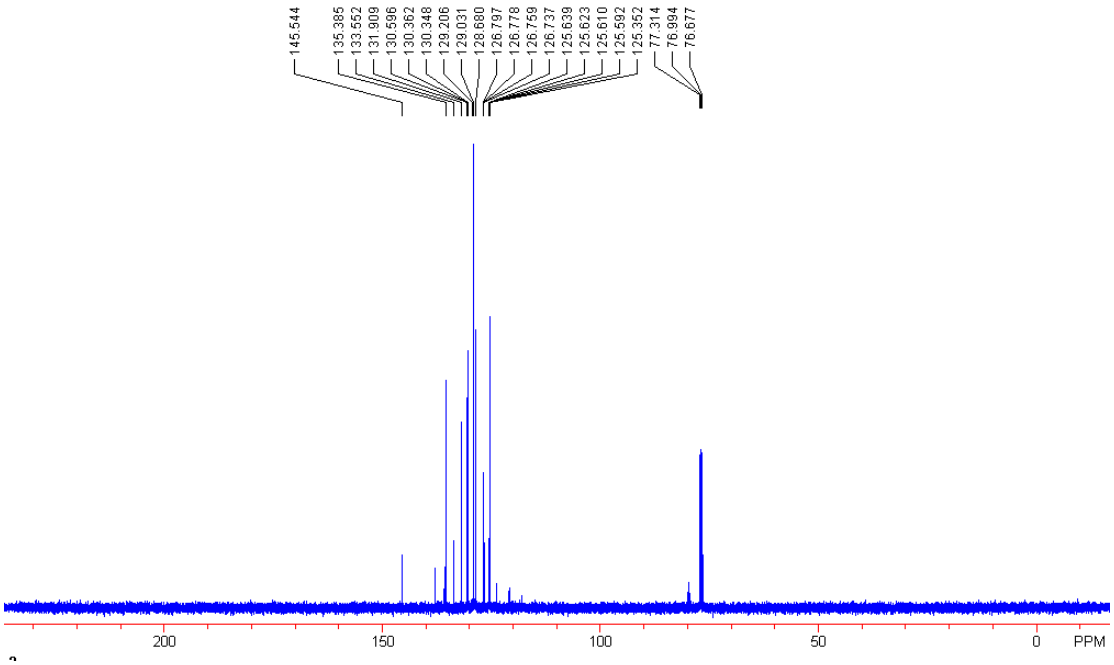


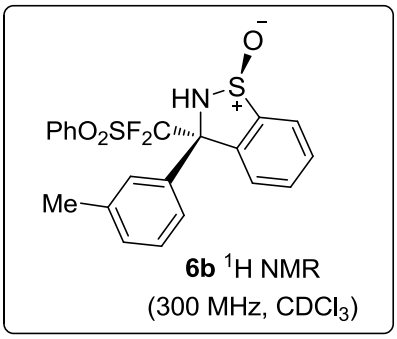
6a ^{19}F NMR
(282 MHz, $CDCl_3$)

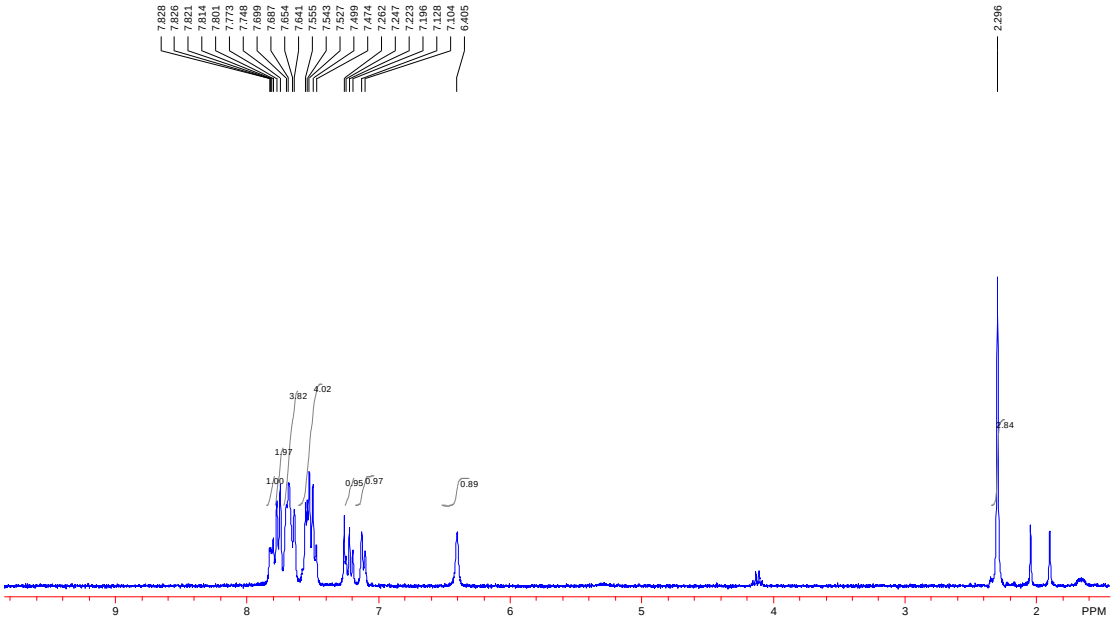


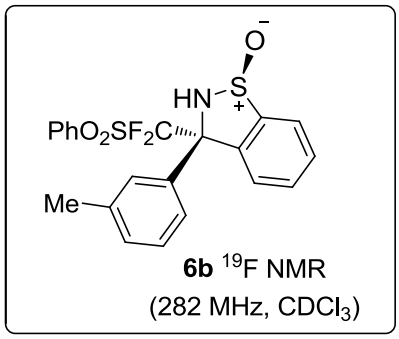


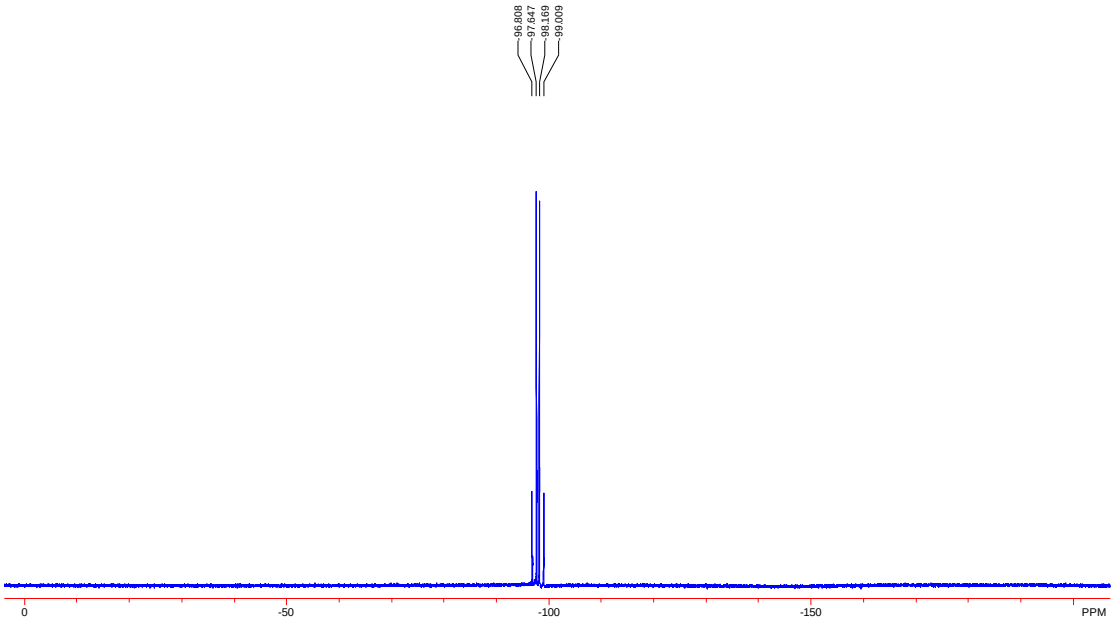
6a ^{13}C NMR
(100 MHz, $CDCl_3$)

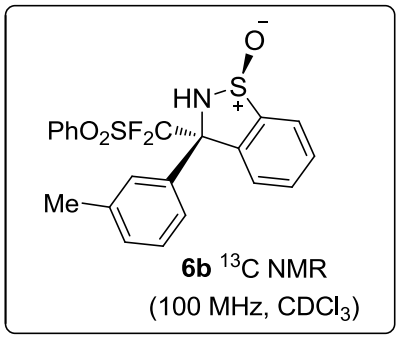


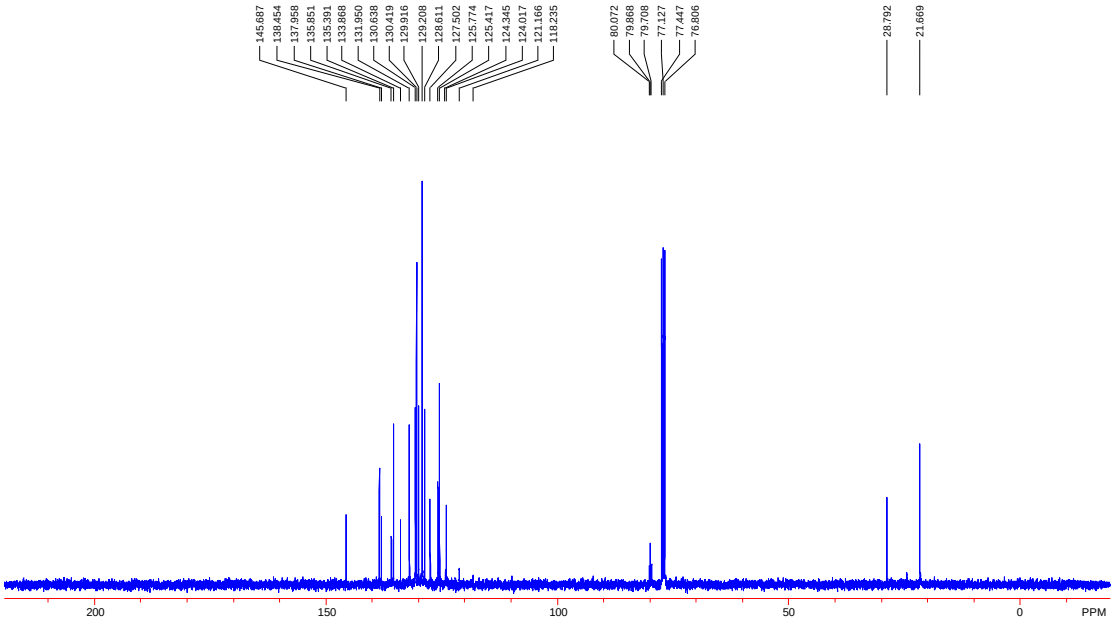

O
HN
S
PhO2SF2C
Me
6b 1H NMR
(300 MHz, CDCl3)

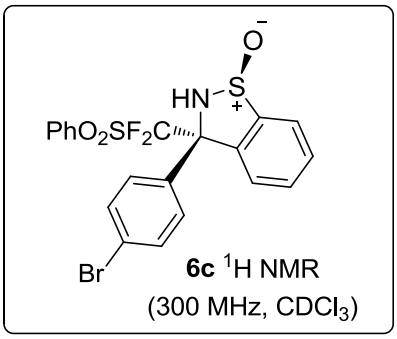

7.828
7.826
7.821
7.814
7.801
7.773
7.748
7.699
7.687
7.654
7.641
7.555
7.543
7.527
7.499
7.474
7.262
7.247
7.223
7.196
7.128
7.104
6.405
2.296
3.82
4.02
1.97
1.00
0.95
0.97
0.89
7.84
9
8
7
6
5
4
3
2
PPM

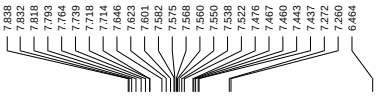

O
HN
S
PhO2SF2C
Me
6b 19F NMR
(282 MHz, CDCl3)

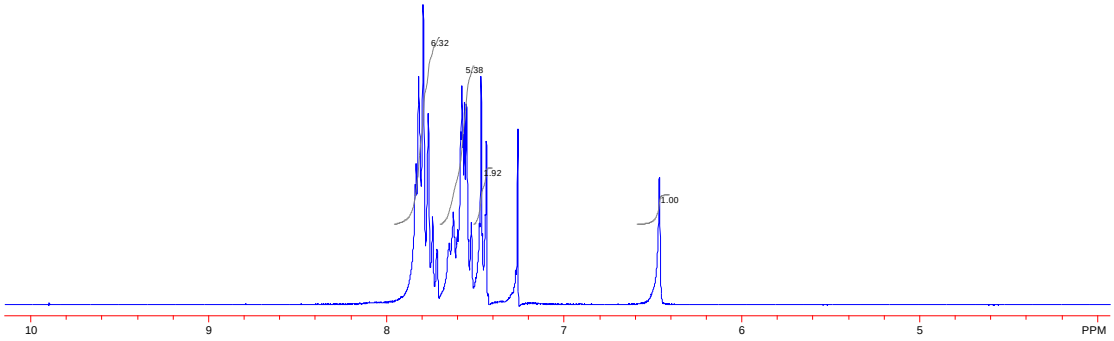

-96.808
-97.647
-98.169
-99.009
0
-50
-100
-150
PPM

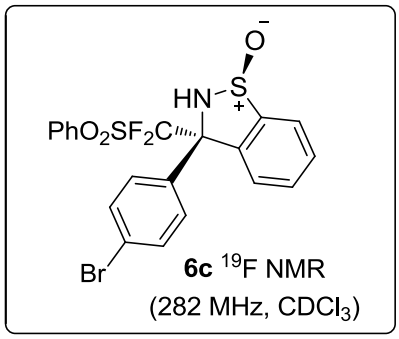

O
HN
S
+
PhO2SF2C
Me
6b 13C NMR
(100 MHz, CDCl3)

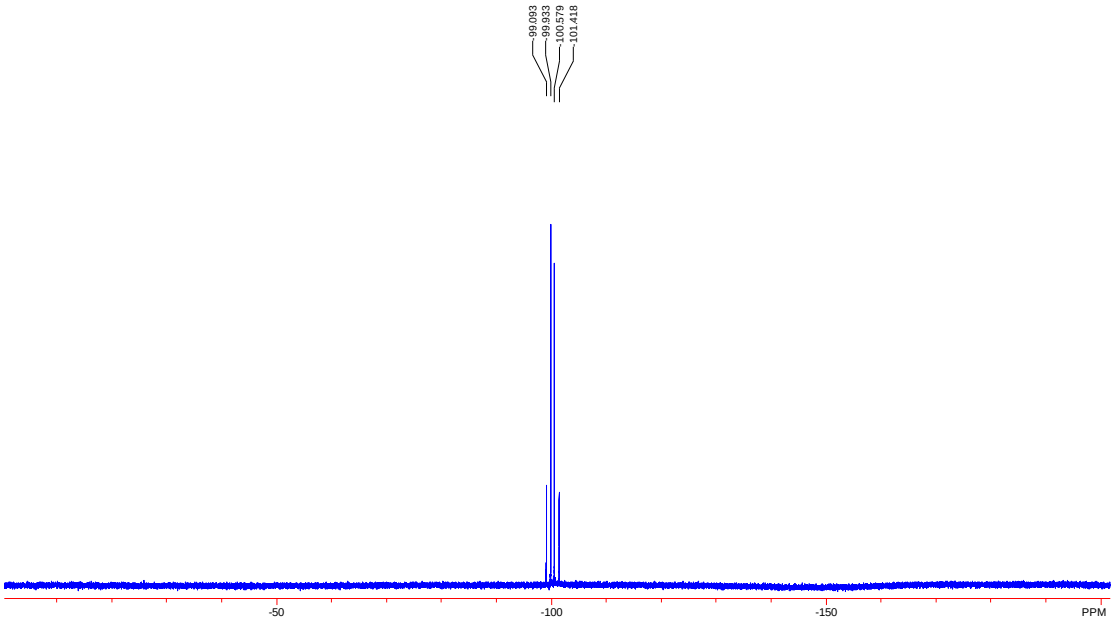

145.687
138.454
137.958
135.851
135.391
133.868
131.950
130.638
130.419
129.916
129.208
128.611
127.502
125.774
125.417
124.345
124.017
121.166
118.235
80.072
79.868
79.708
77.127
77.447
76.806
28.792
21.669
200
150
100
50
0
PPM

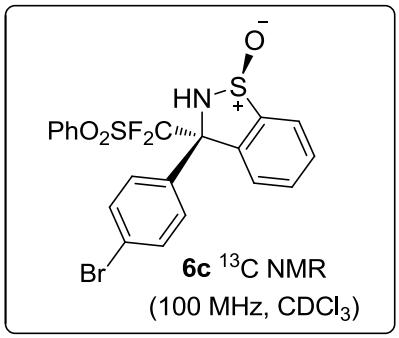

O
HN
S
PhO2SF2C
Br
6c 1H NMR
(300 MHz, CDCl3)

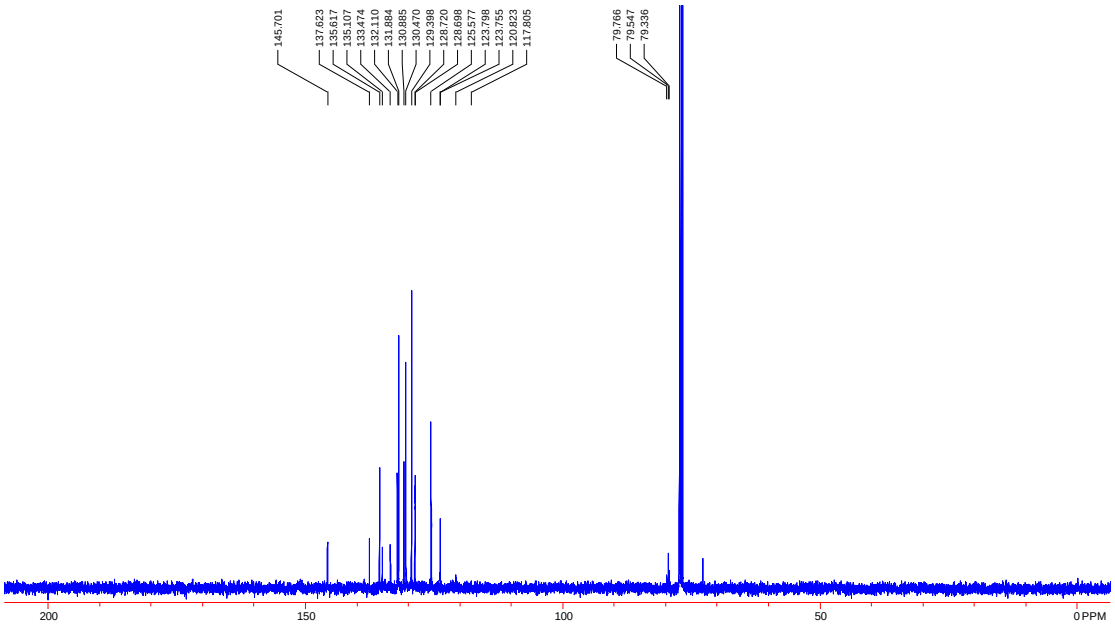

7.838
7.832
7.818
7.793
7.764
7.739
7.718
7.714
7.646
7.623
7.601
7.582
7.575
7.568
7.560
7.550
7.538
7.522
7.476
7.467
7.460
7.443
7.437
7.272
7.260
6.464

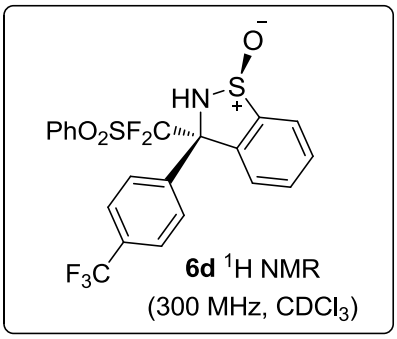

6.32
5.38
1.92
1.00
10
9
8
7
6
5
PPM

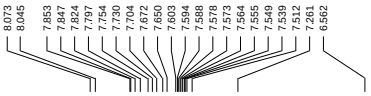

O
HN
S
PhO2SF2C
Br
6c 19F NMR
(282 MHz, CDCl3)

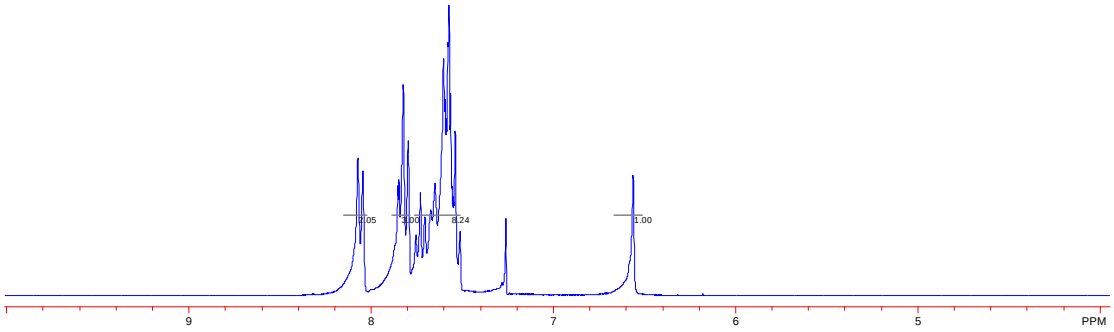

-99.093
-99.933
-100.579
-101.418
-50
-100
-150
PPM

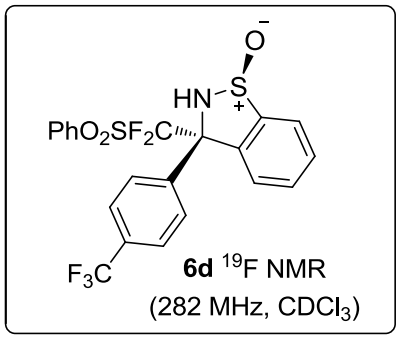

O
HN
S
PhO2SF2C
Br
6c 13C NMR
(100 MHz, CDCl3)

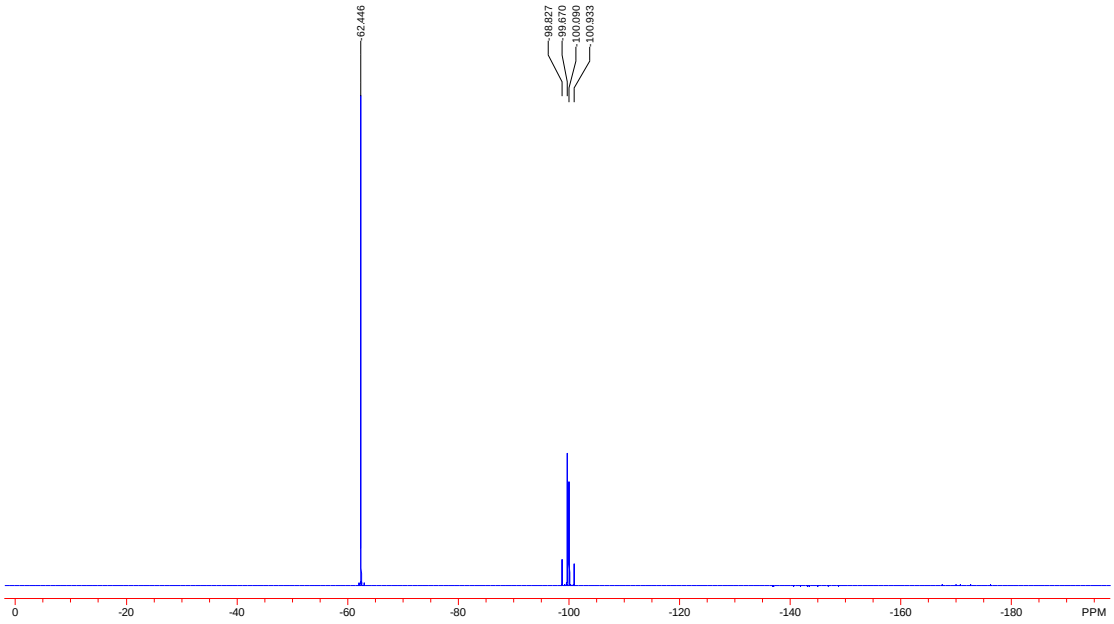

145.701
137.623
135.617
135.107
133.474
132.110
131.884
130.885
130.470
129.398
128.720
128.698
125.577
123.798
123.755
120.823
117.805
79.766
79.547
79.336
200
150
100
50
0 PPM

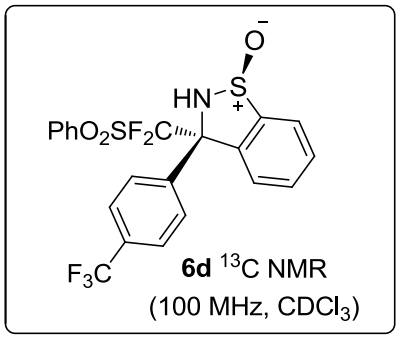

O
HN
S
PhO2SF2C
F3C
6d 1H NMR
(300 MHz, CDCl3)

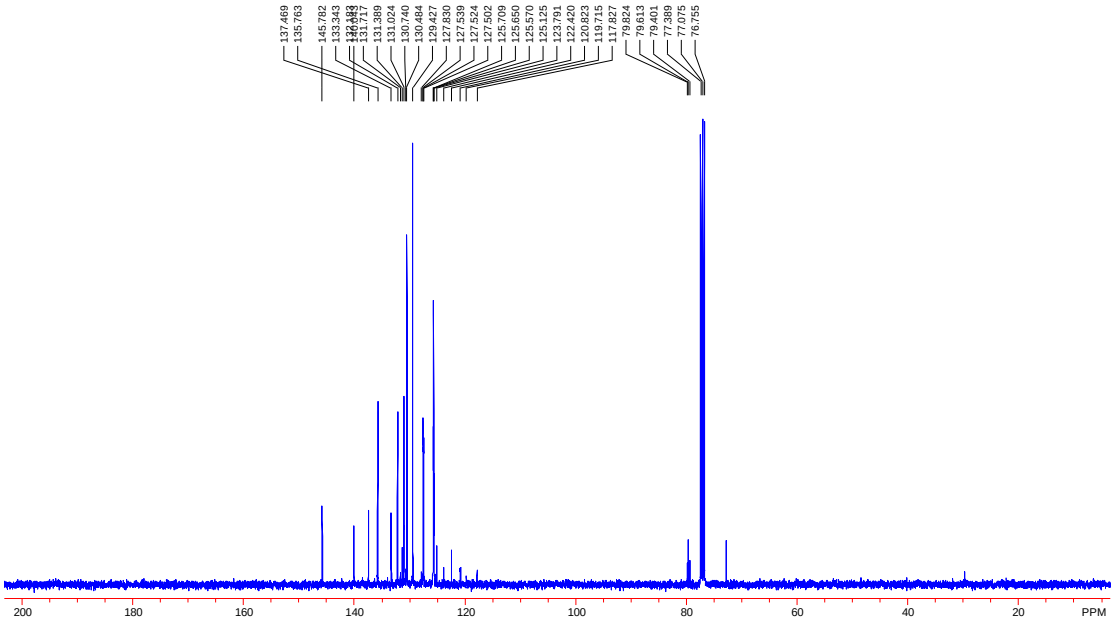

8.073
8.045
7.853
7.847
7.824
7.797
7.754
7.730
7.704
7.672
7.650
7.603
7.594
7.588
7.578
7.573
7.564
7.555
7.549
7.539
7.512
7.261
6.562

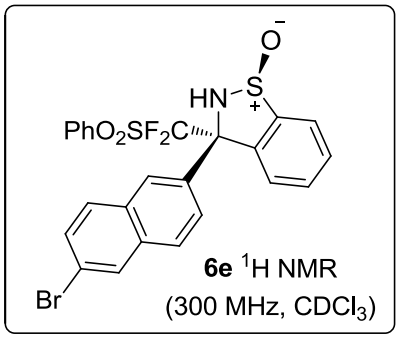

2.05
3.00
8.24
1.00
9
8
7
6
5
PPM

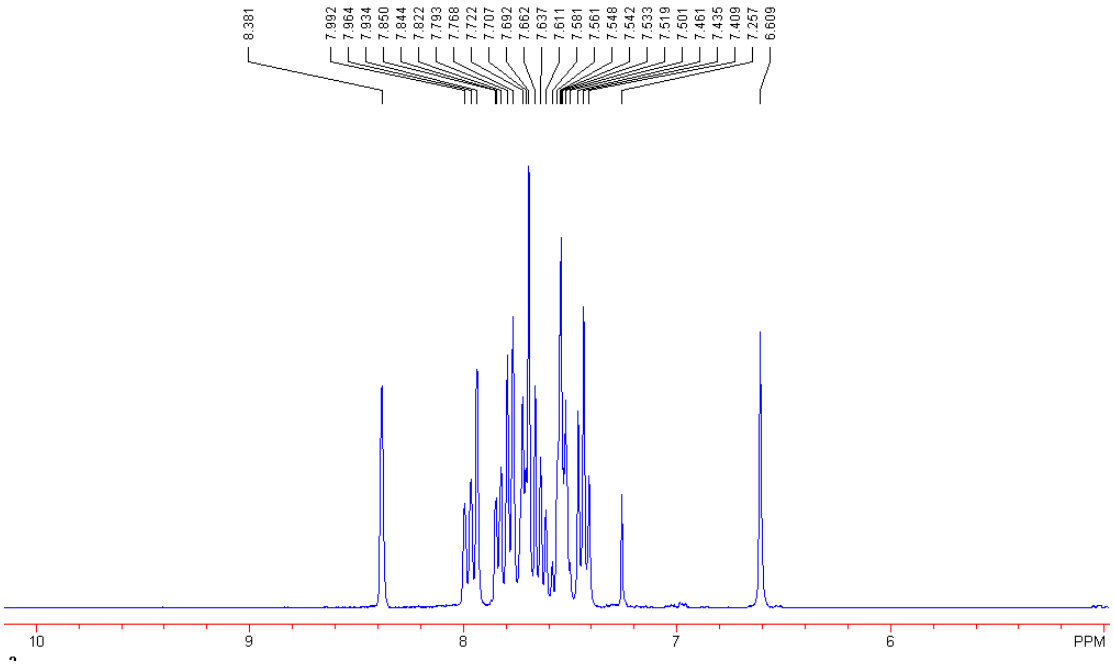

O
HN
S
PhO2SF2C
F3C
6d 19F NMR
(282 MHz, CDCl3)

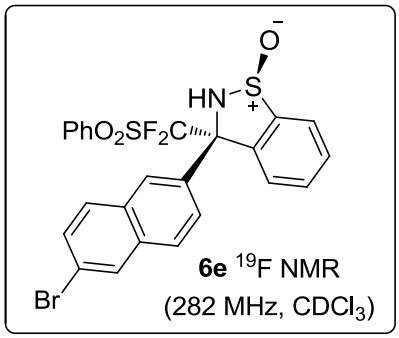

-62.446
-98.827
-99.670
-100.090
-100.933
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
PPM

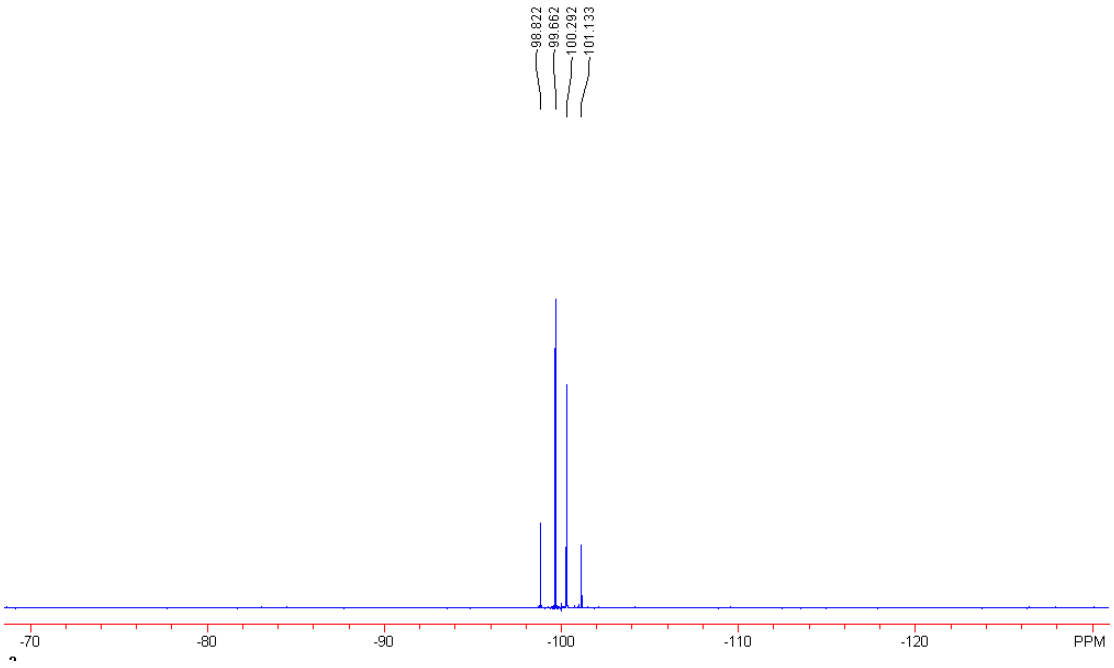

O
HN
S
PhO2SF2C
F3C
6d 13C NMR
(100 MHz, CDCl3)


137.469
135.763
145.782
133.343
131.717
131.389
131.024
130.740
130.484
129.427
127.830
127.539
127.524
127.502
125.709
125.650
125.570
125.125
123.791
122.420
120.823
119.715
117.827
79.824
79.613
79.401
77.389
77.075
76.755
200
180
160
140
120
100
80
60
40
20
PPM


O
HN
S
PhO2SF2C
Br
6e 1H NMR
(300 MHz, CDCl3)


8.381
7.992
7.964
7.934
7.850
7.844
7.822
7.793
7.768
7.722
7.707
7.692
7.662
7.637
7.611
7.581
7.561
7.548
7.542
7.533
7.519
7.501
7.461
7.435
7.409
7.257
6.609
10
9
8
7
6
PPM


O
HN
S
PhO2SF2C
Br
6e 19F NMR
(282 MHz, CDCl3)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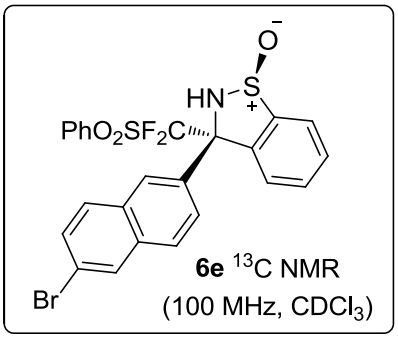
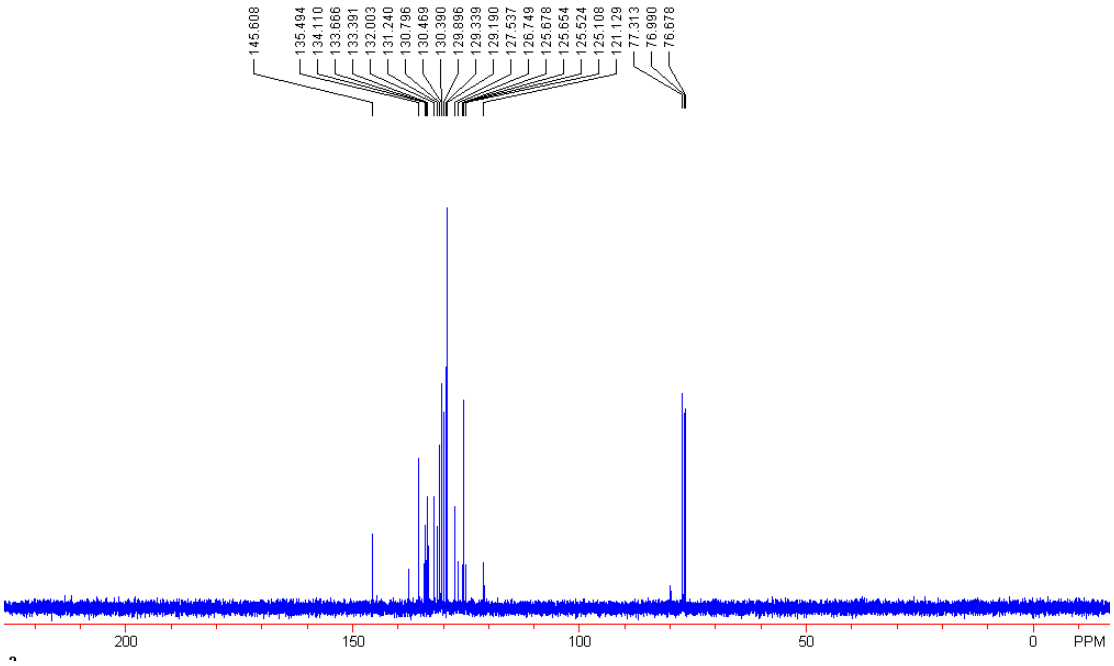
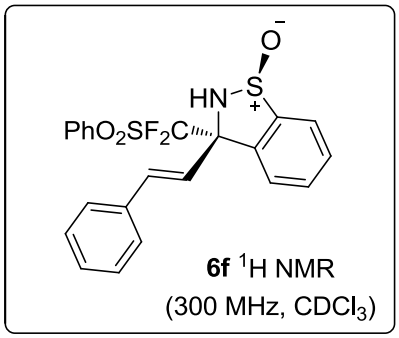
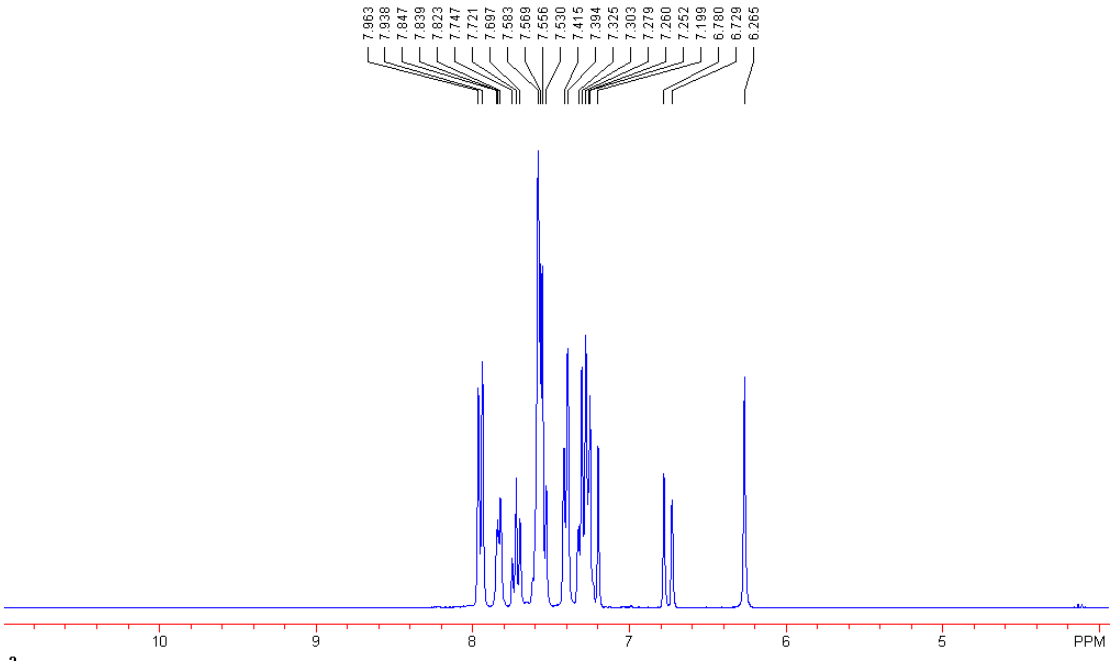
-99.662
-100.292
-101.133
-70
-80
-90
-100
-110
-120
PPM


O
HN
S
PhO2SF2C
Br
6e 13C NMR
(100 MHz, CDCl3)


145.608
135.494
134.110
133.666
133.391
132.003
131.240
130.796
130.469
130.390
129.896
129.339
129.190
127.537
126.749
125.678
125.654
125.524
125.108
121.129
77.313
76.990
76.678
200
150
100
50
0
PPM


O
HN
S
PhO2SF2C
6f 1H NMR
(300 MHz, CDCl3)


7.963
7.938
7.847
7.839
7.823
7.747
7.721
7.697
7.583
7.569
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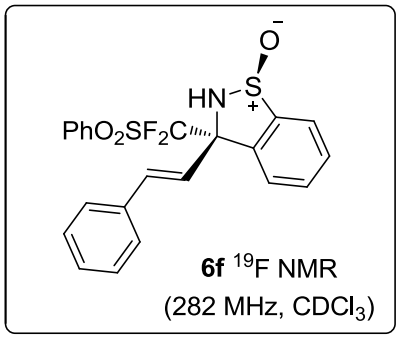
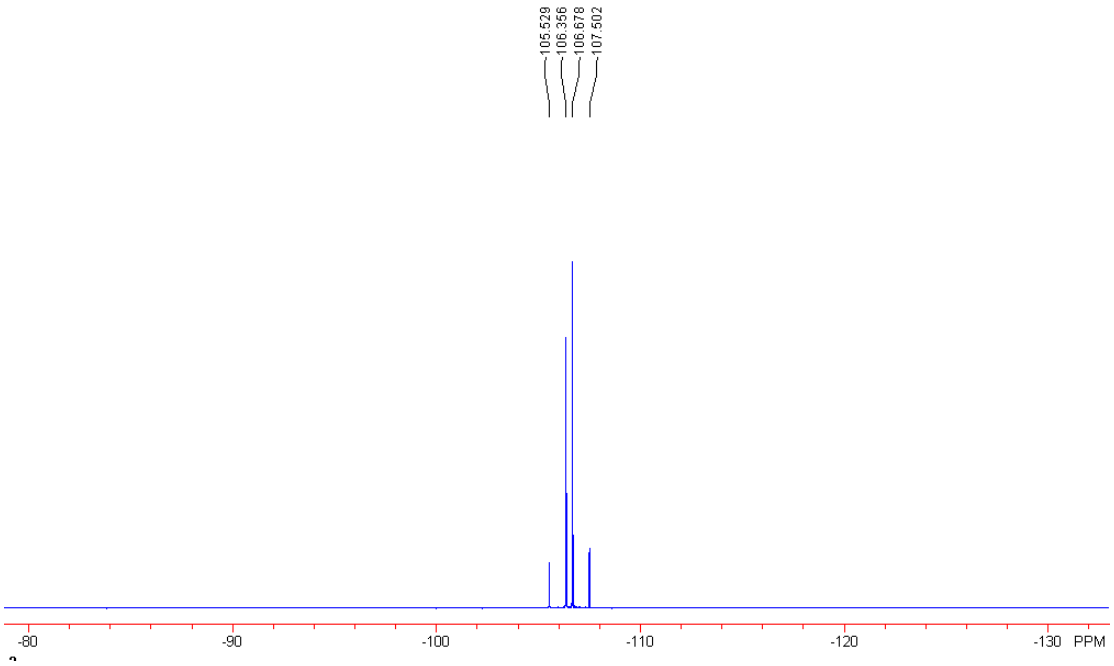
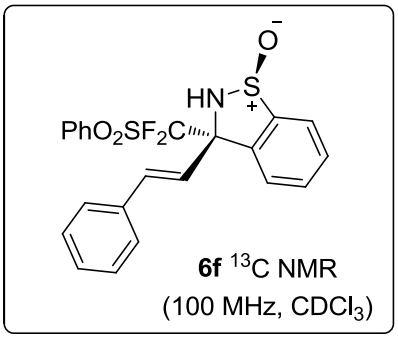
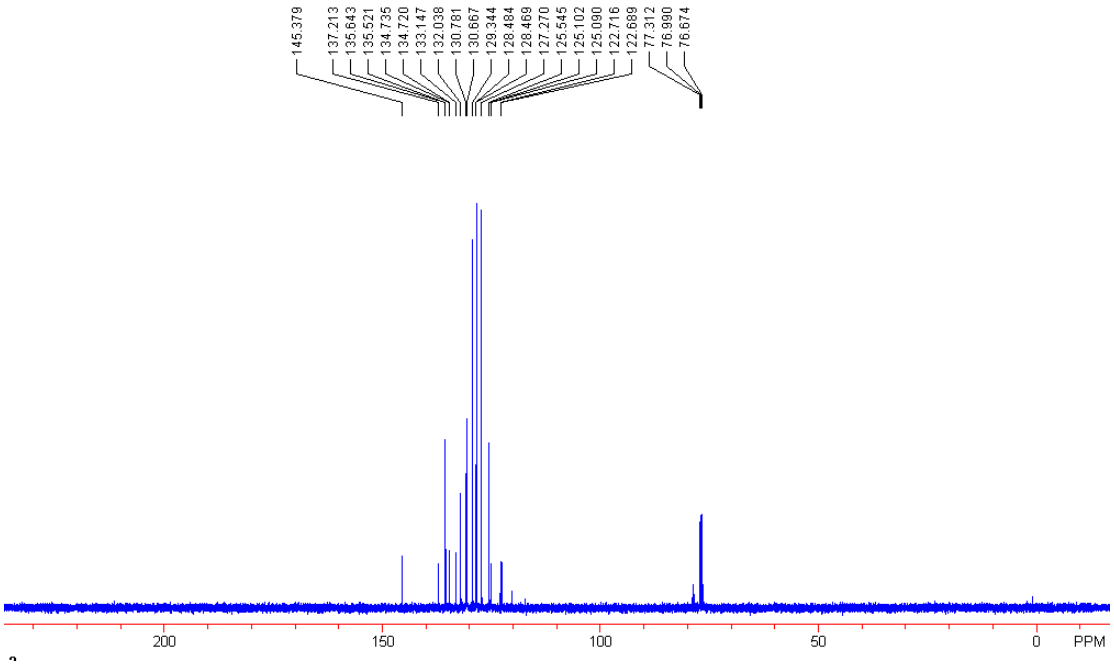
7.530
7.415
7.394
7.325
7.303
7.279
7.260
7.252
7.199
6.780
6.729
6.265
10
9
8
7
6
5
PPM

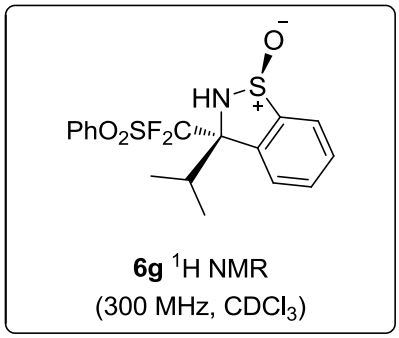


6f ^{19}F NMR
(282 MHz, $CDCl_3$)

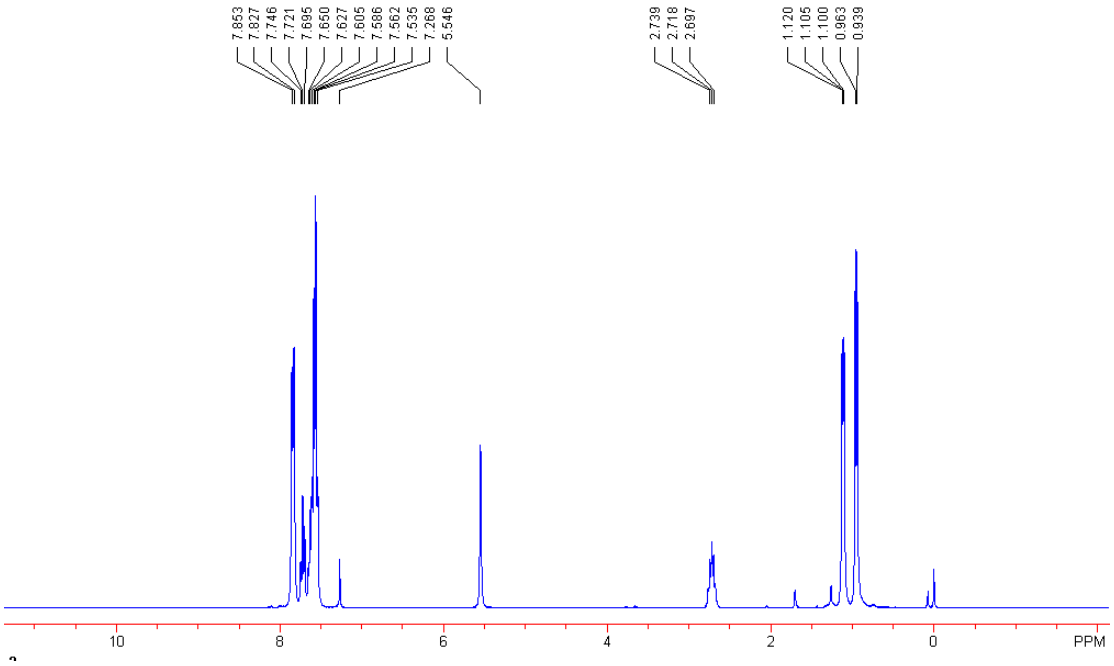


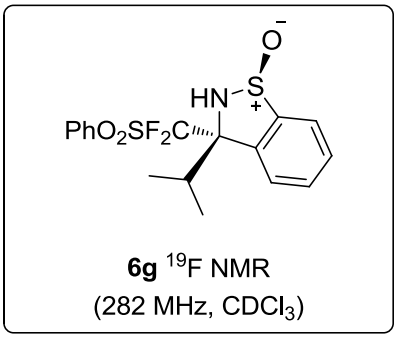

O
HN
S
PhO2SF2C
6f 13C NMR
(100 MHz, CDCl3)


145.379
137.213
135.643
135.521
134.735
134.720
133.147
132.038
130.781
130.667
129.344
128.484
128.469
127.270
125.545
125.102
125.090
122.716
122.689
77.312
76.990
76.674
200
150
100
50
0
PPM

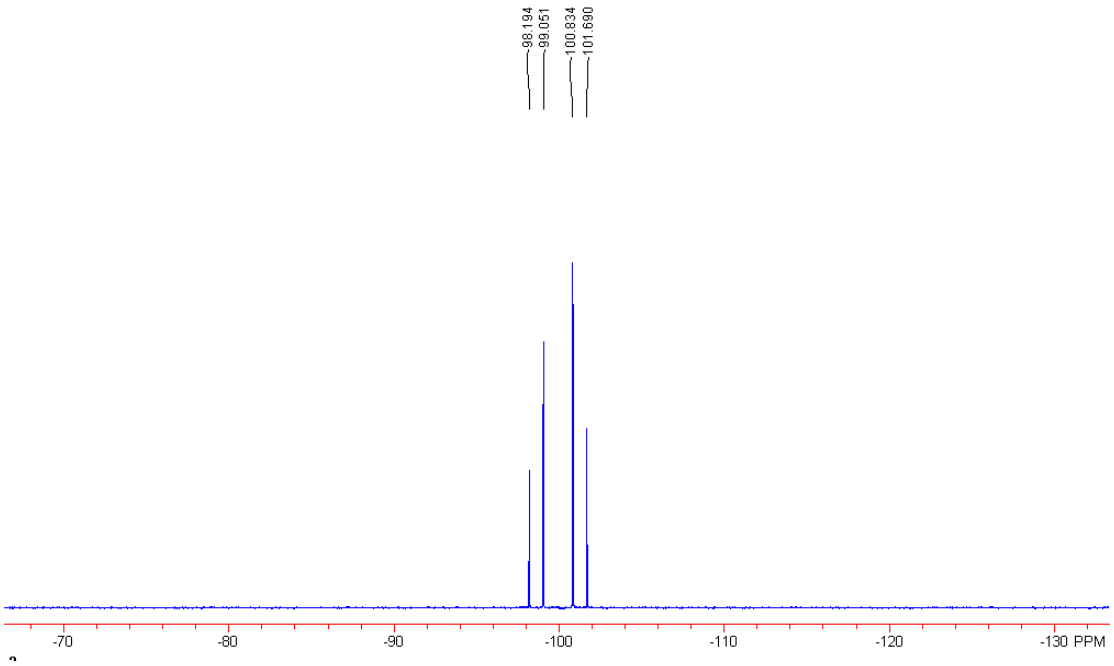


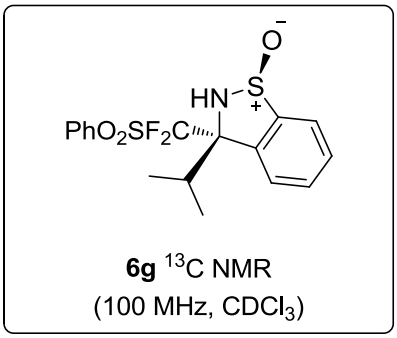
6g ^{1}H NMR
(300 MHz, $CDCl_3$)



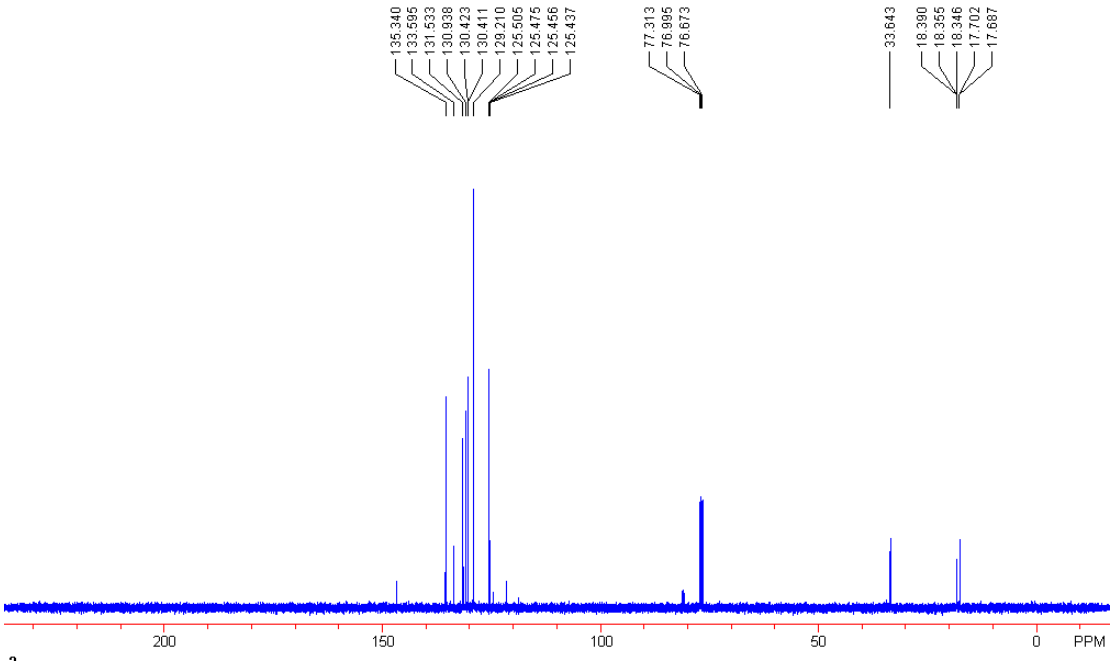


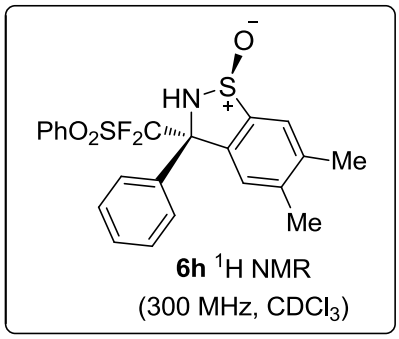
6g ^{19}F NMR
(282 MHz, $CDCl_3$)



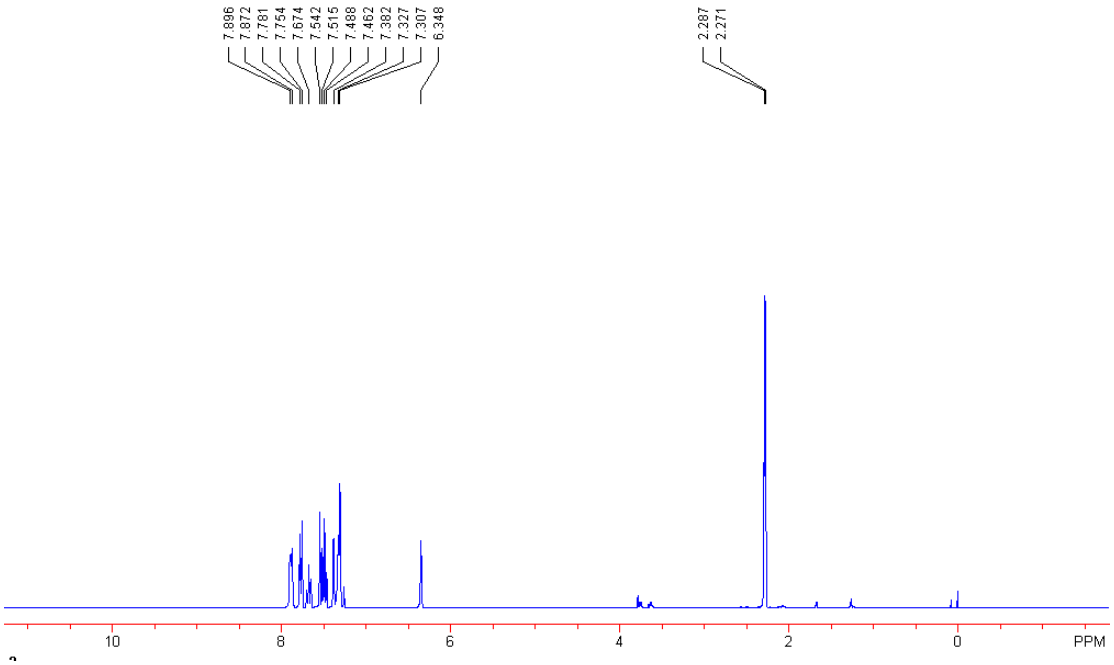


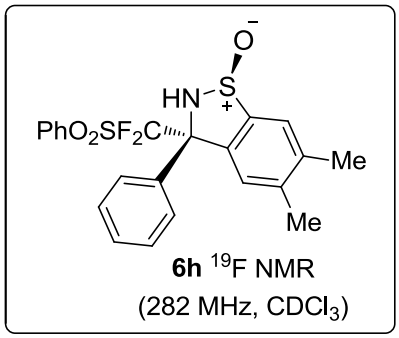
6g ^{13}C NMR
(100 MHz, $CDCl_3$)



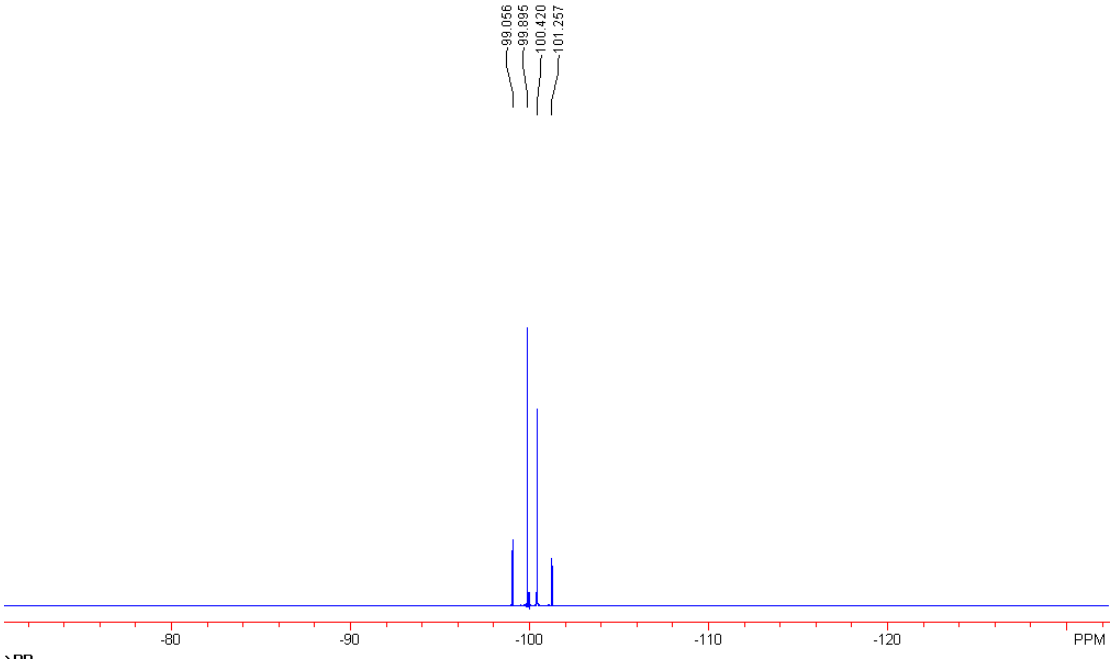


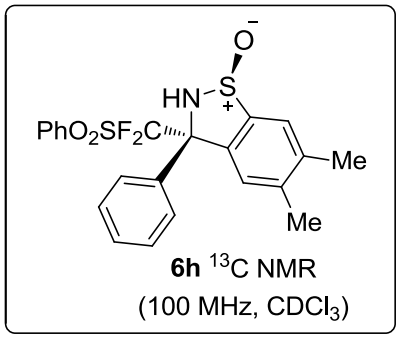
6h ^{1}H NMR
(300 MHz, $CDCl_3$)



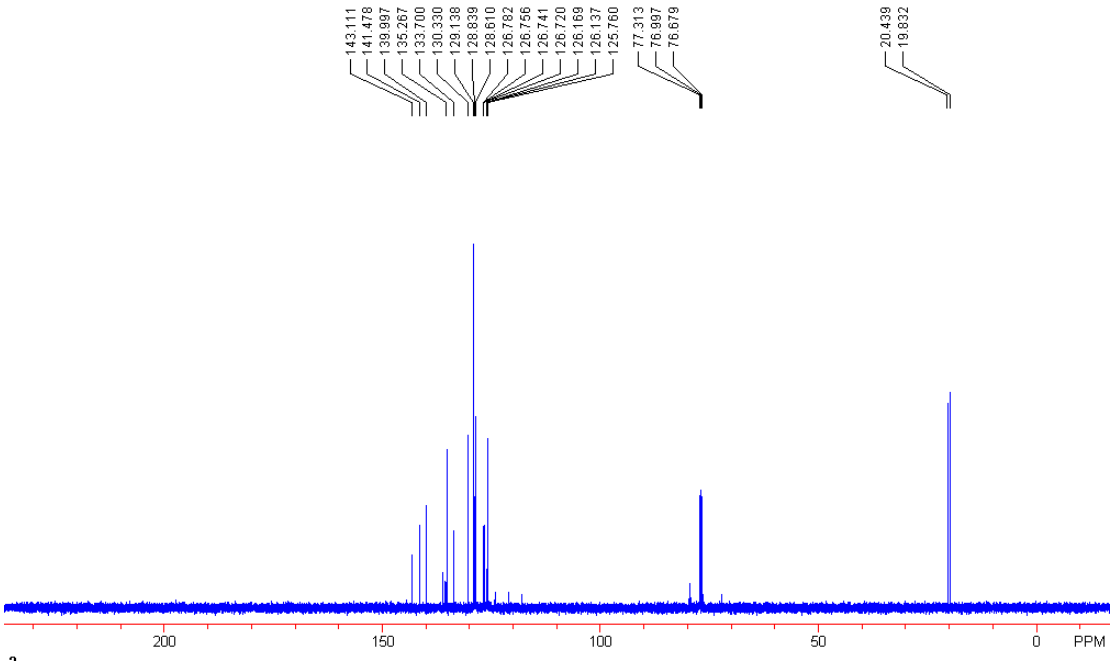


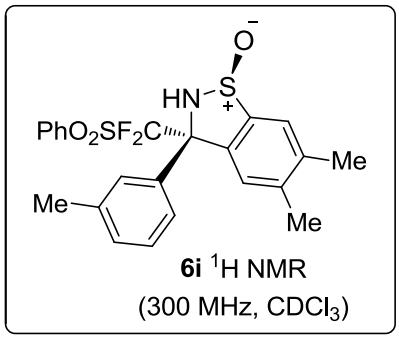
6h ^{19}F NMR
(282 MHz, $CDCl_3$)



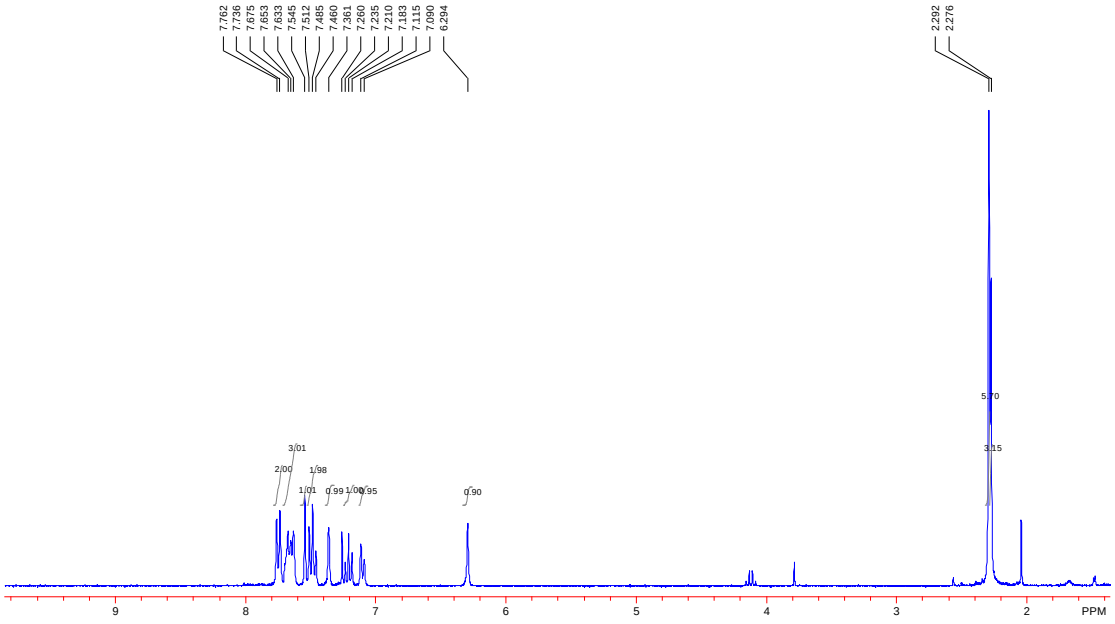


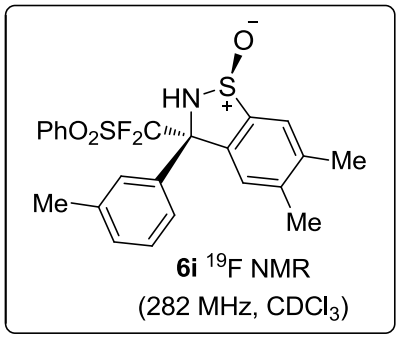
6h ^{13}C NMR
(100 MHz, $CDCl_3$)



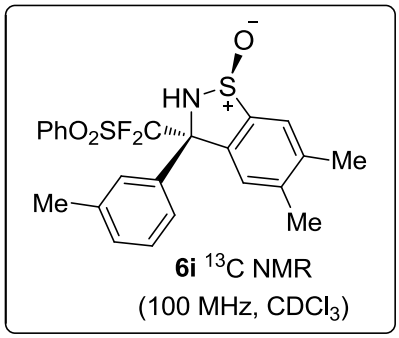


6i ^{1}H NMR
(300 MHz, $CDCl_3$)

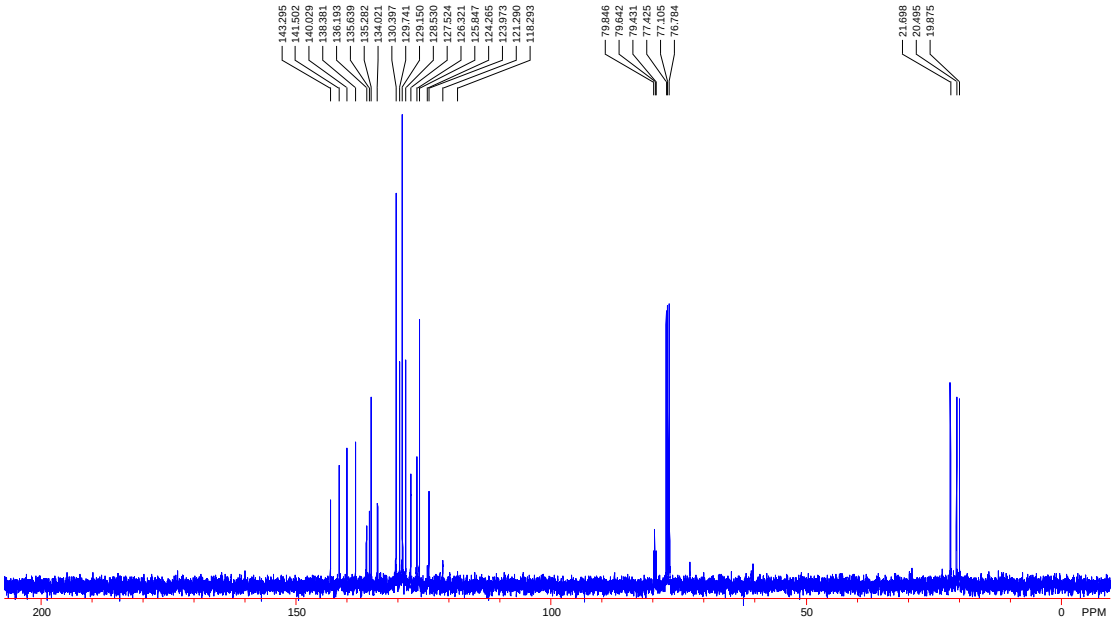


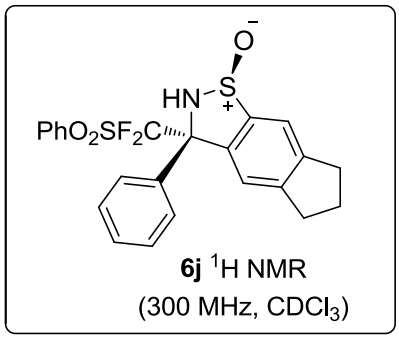


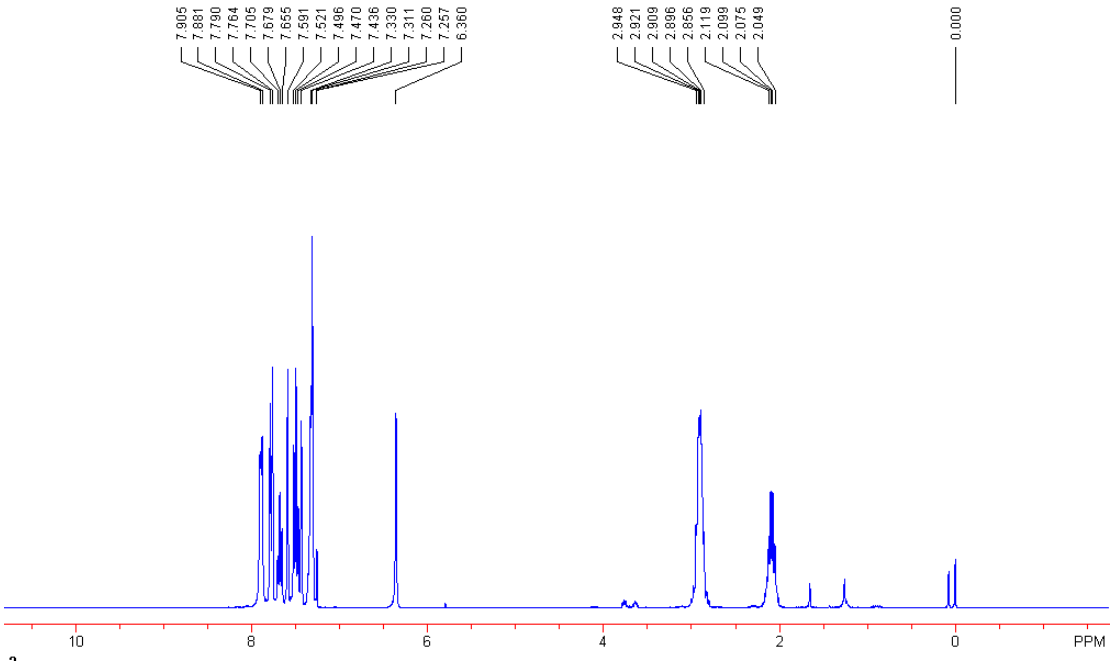
6i ^{19}F NMR
(282 MHz, $CDCl_3$)



6i ^{13}C NMR
(100 MHz, $CDCl_3$)




O
HN
S
+
PhO2SF2C
6j 1H NMR
(300 MHz, CDCl3)


7.905
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7.790
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7.679
7.655
7.591
7.521
7.496
7.470
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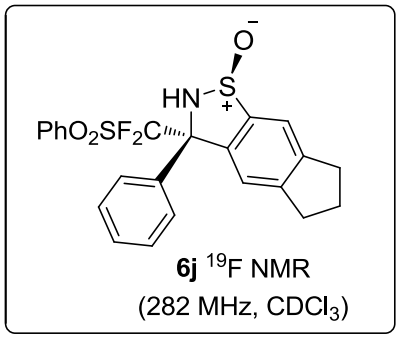
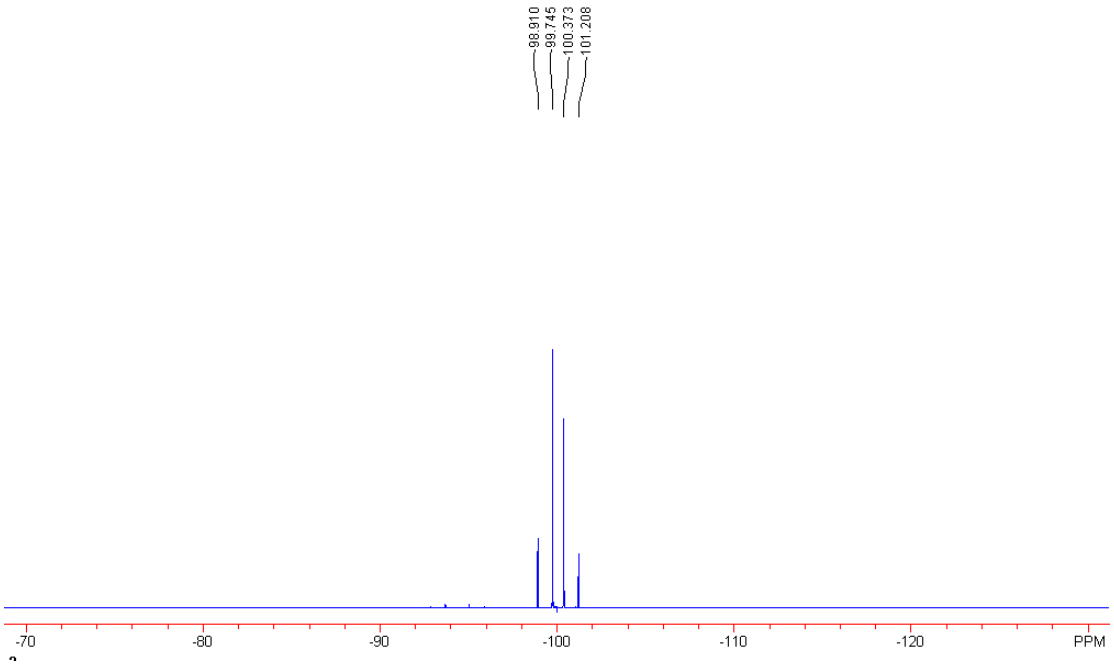
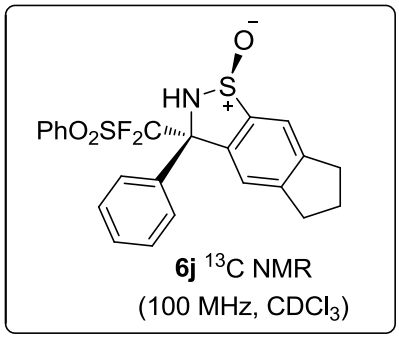
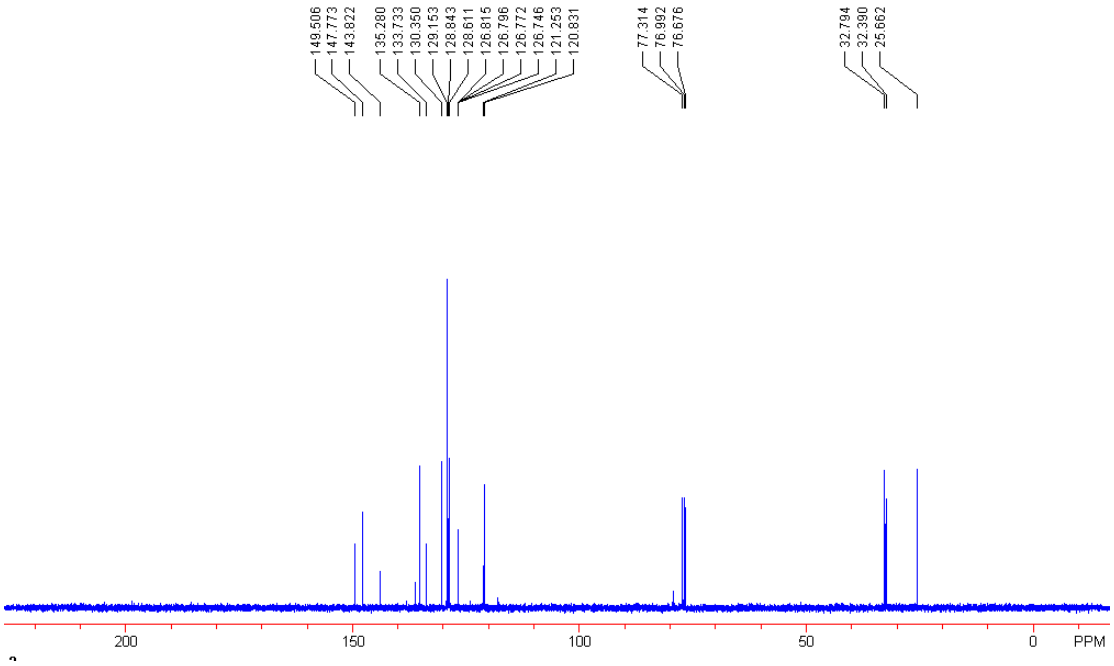
7.330
7.311
7.260
7.257
6.360
2.948
2.921
2.909
2.896
2.856
2.119
2.099
2.075
2.049
0.000
10
8
6
4
2
0
PPM

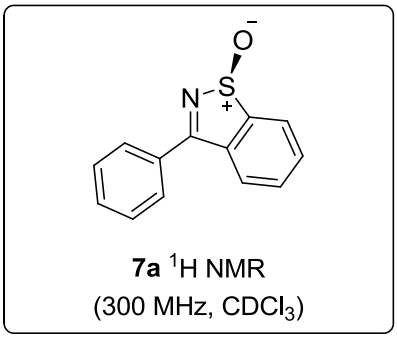


6j ^{19}F NMR
(282 MHz, $CDCl_3$)

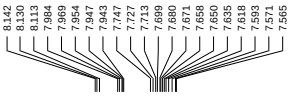


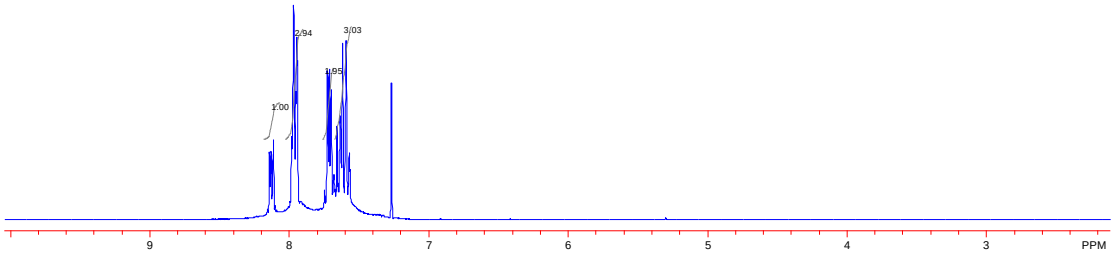

O
HN
S
PhO2SF2C
6j 13C NMR
(100 MHz, CDCl3)

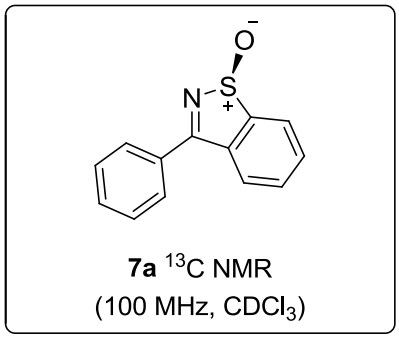

149.506
147.773
143.822
135.280
133.733
130.350
129.153
128.843
128.611
126.815
126.796
126.772
126.746
121.253
120.831
77.314
76.992
76.676
32.794
32.390
25.662
200
150
100
50
0
PPM



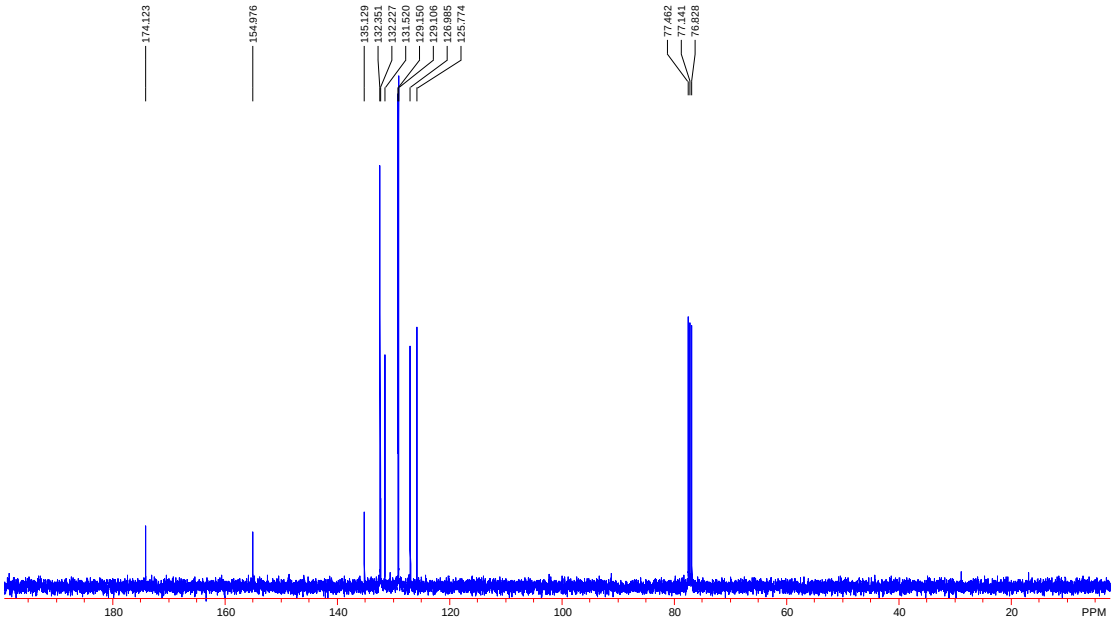
7a ^{1}H NMR
(300 MHz, $CDCl_3$)

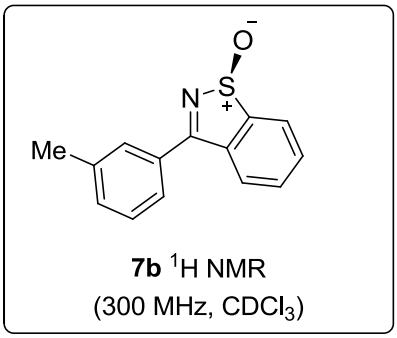




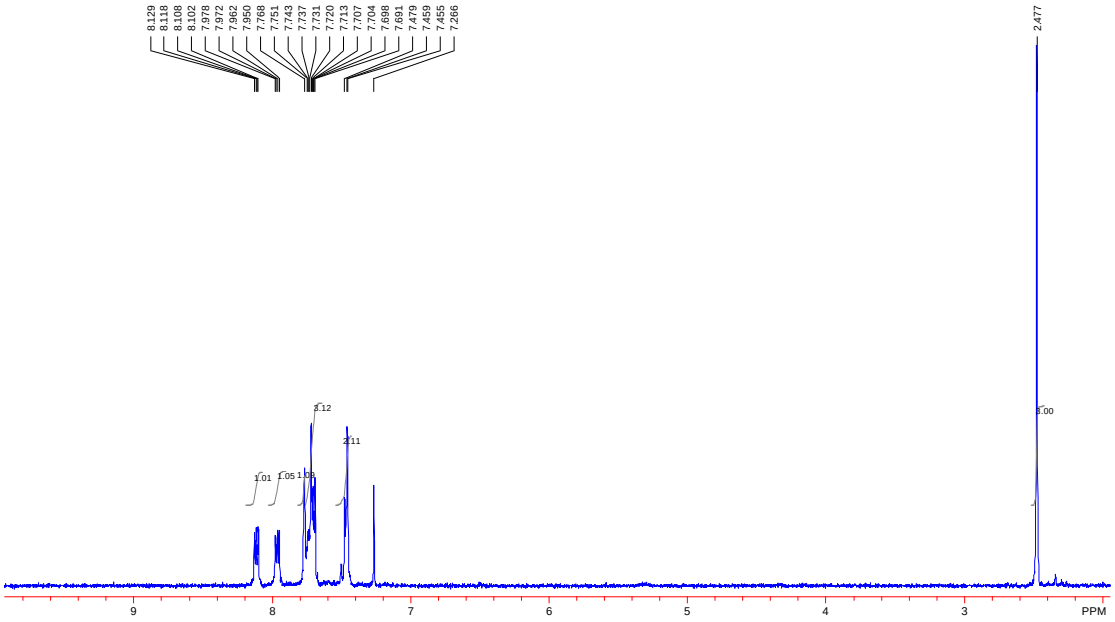


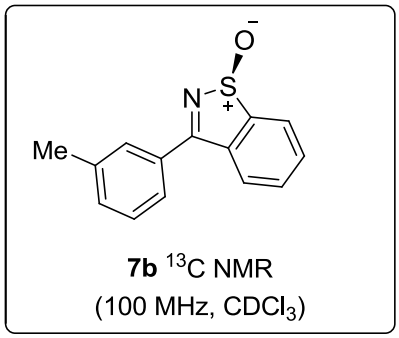
7a ^{13}C NMR
(100 MHz, $CDCl_3$)



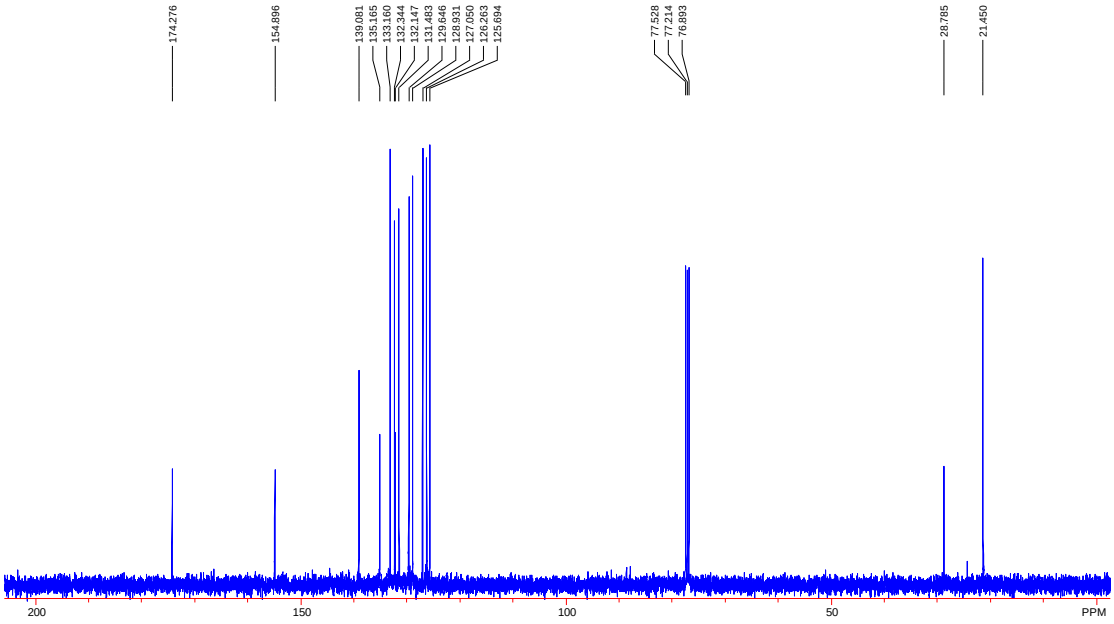


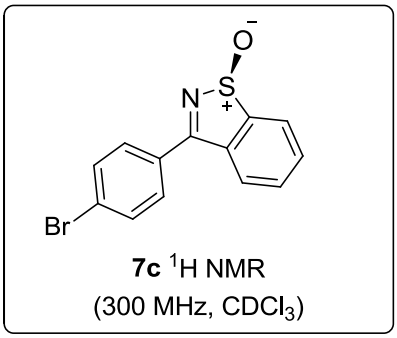
7b ^{1}H NMR
(300 MHz, $CDCl_3$)



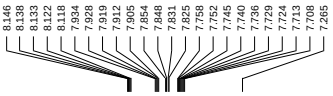


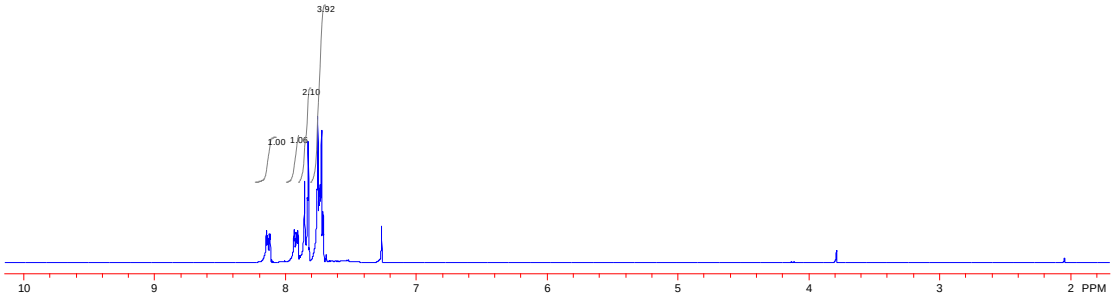
7b ^{13}C NMR
(100 MHz, $CDCl_3$)

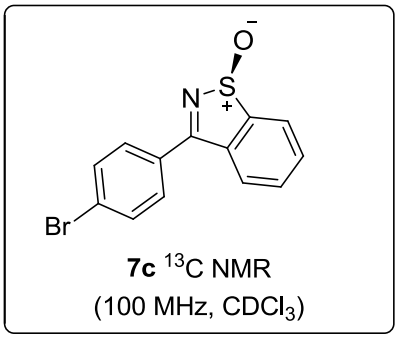




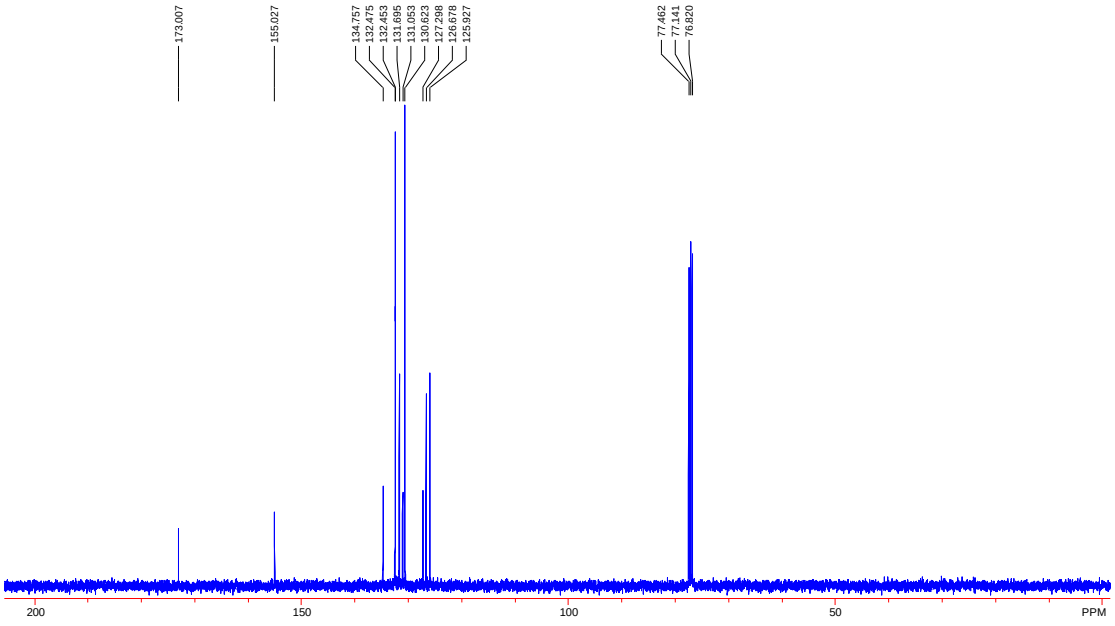
7c ^{1}H NMR
(300 MHz, $CDCl_3$)

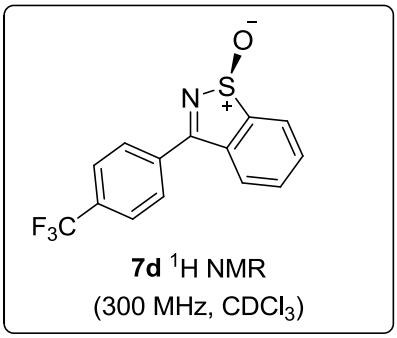


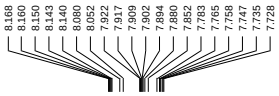




7c ^{13}C NMR
(100 MHz, $CDCl_3$)




O
N
S
+
F3C
7d 1H NMR
(300 MHz, CDCl3)


8.168
8.160
8.150
8.143
8.140
8.080
8.052
7.922
7.917
7.909
7.902
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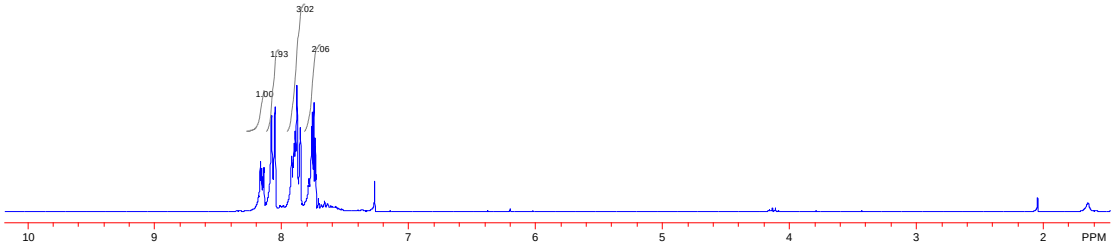
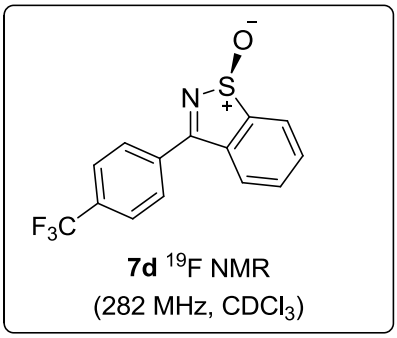
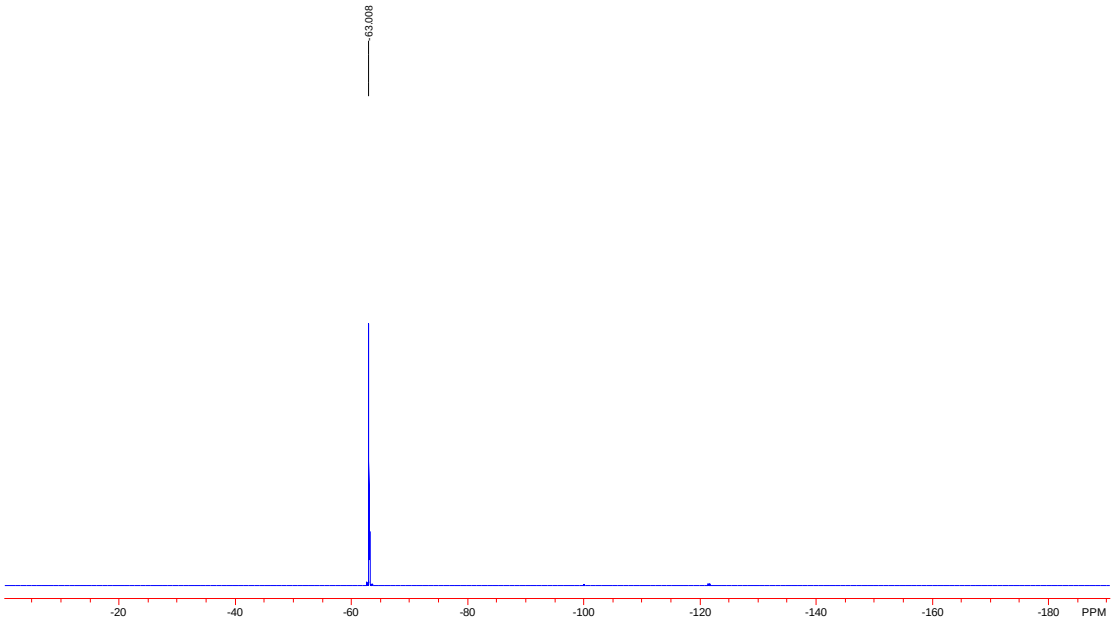
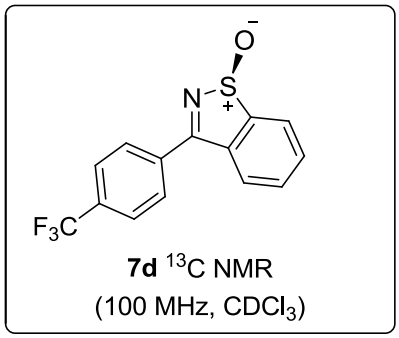
7.765
7.758
7.747
7.735
7.728


3.02
1.93
2.06
1.00
10
9
8
7
6
5
4
3
2
PPM

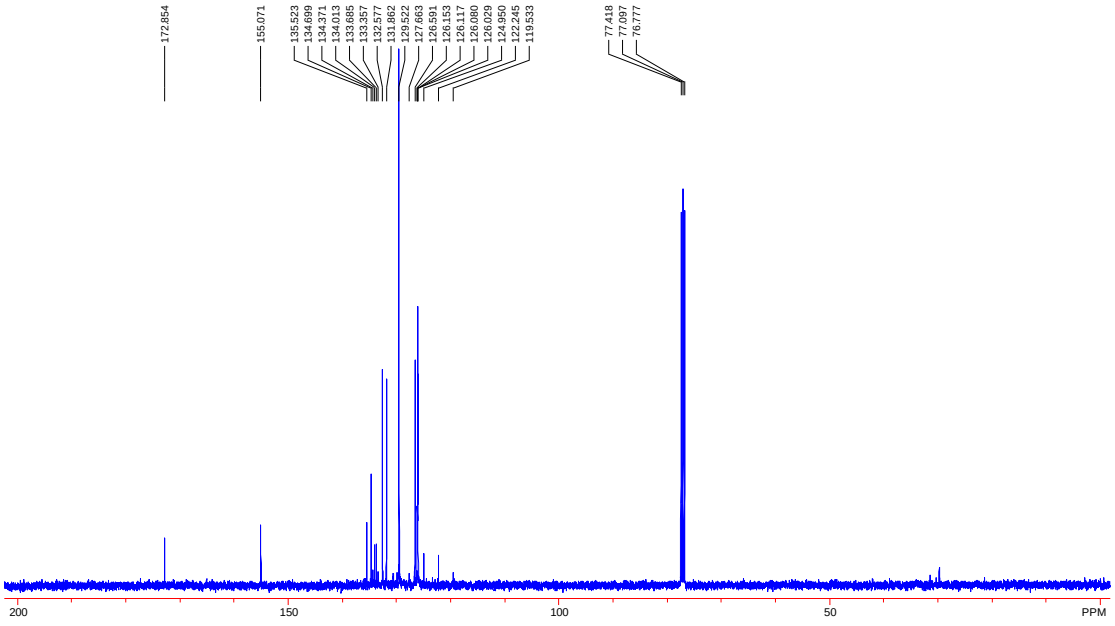


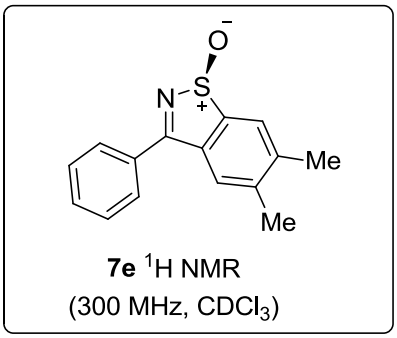
7d ^{19}F NMR
(282 MHz, $CDCl_3$)



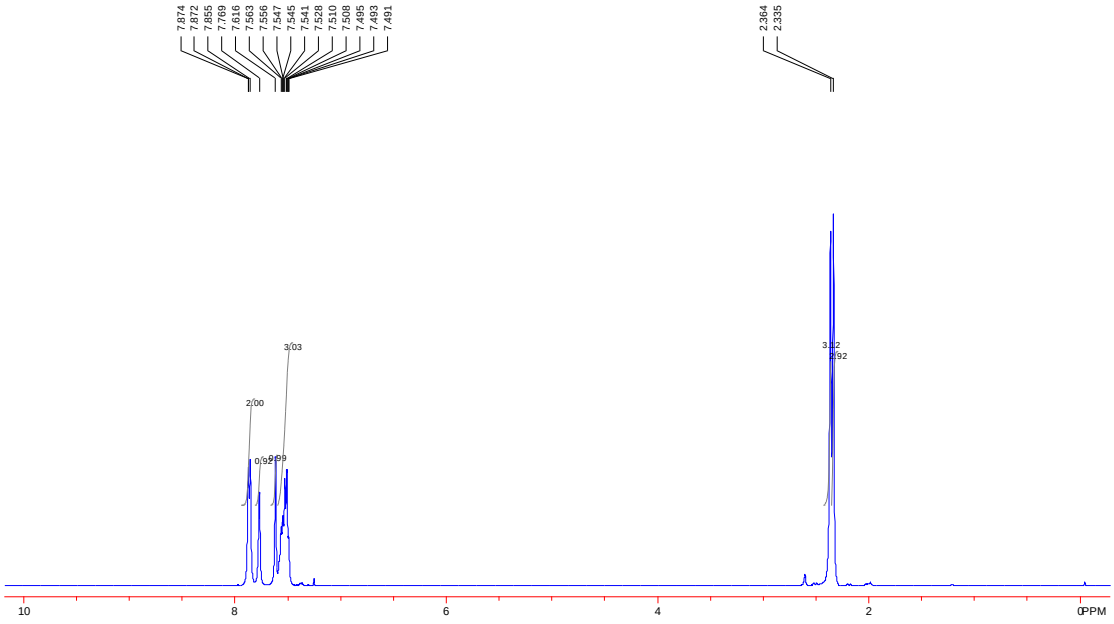


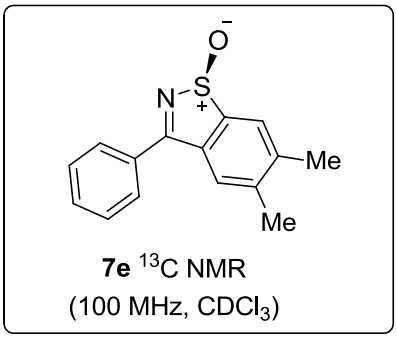
7d ^{13}C NMR
(100 MHz, $CDCl_3$)



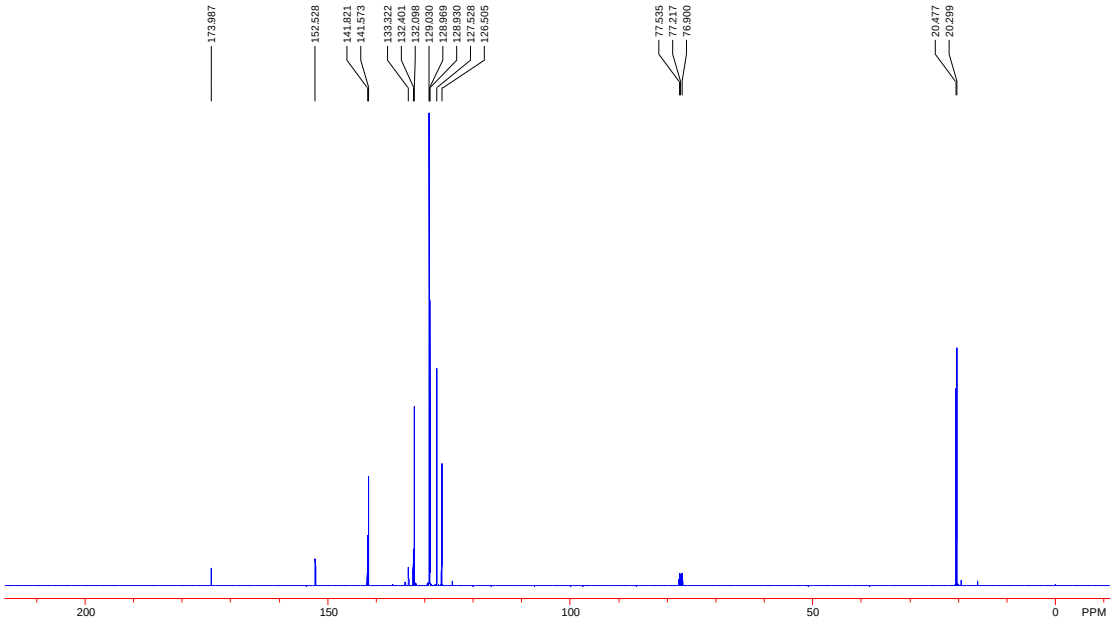


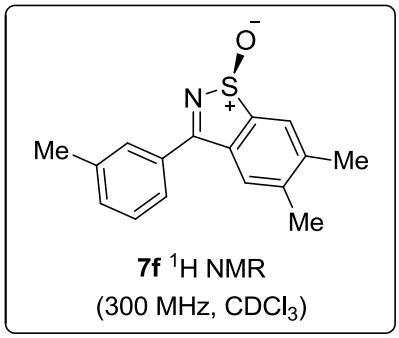
7e ^{1}H NMR
(300 MHz, $CDCl_3$)



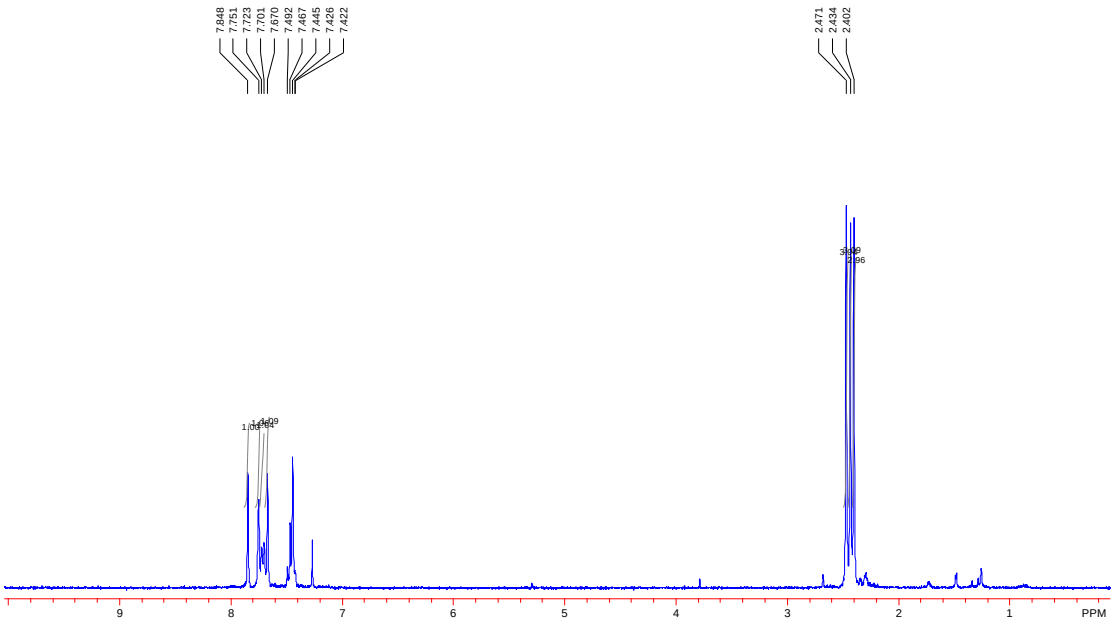


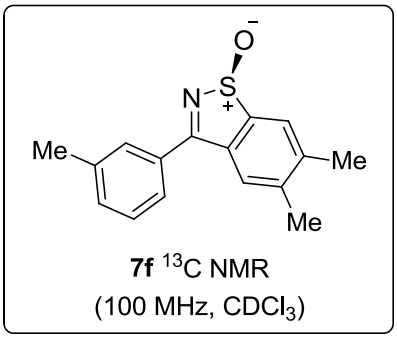
7e ^{13}C NMR
(100 MHz, $CDCl_3$)



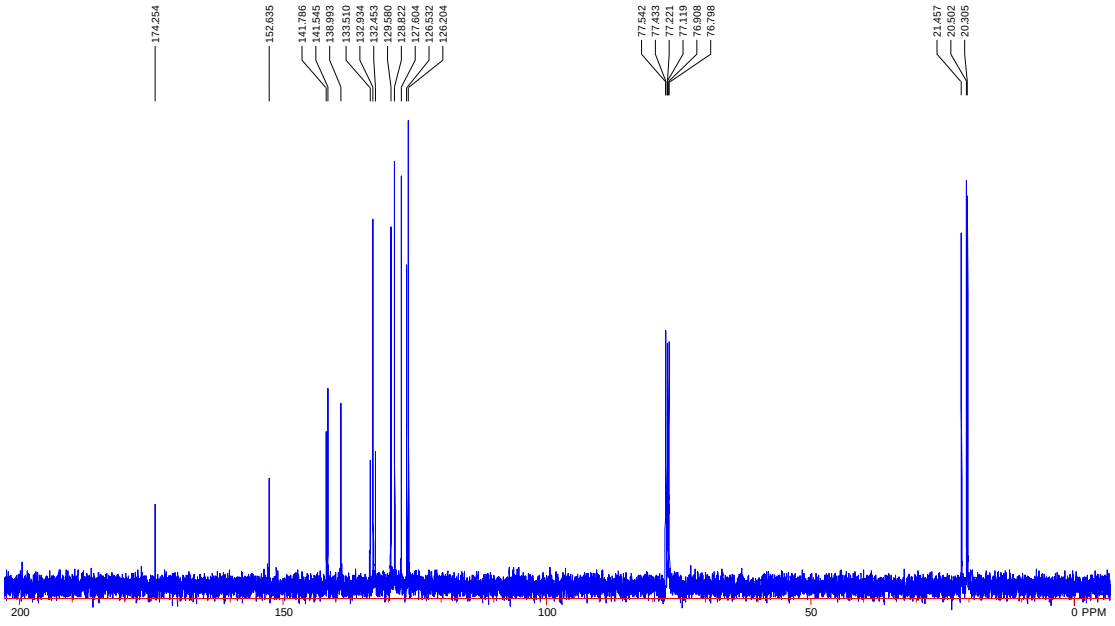


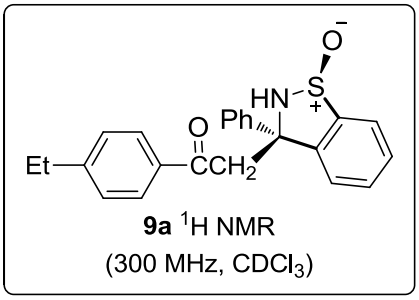
7f ^{1}H NMR
(300 MHz, $CDCl_3$)





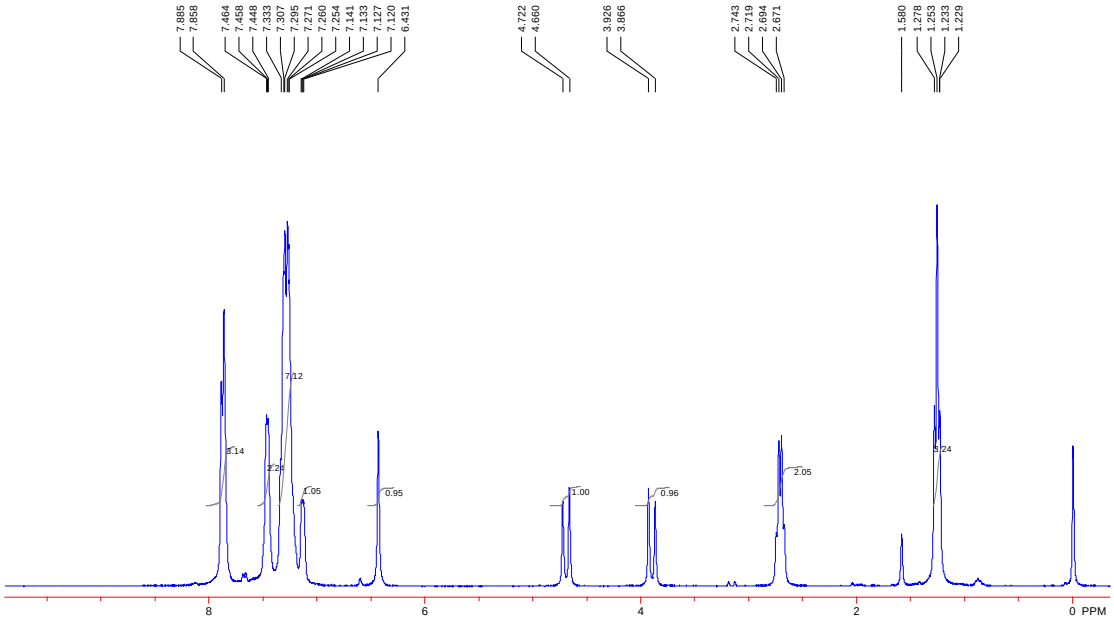
7f ^{13}C NMR
(100 MHz, $CDCl_3$)

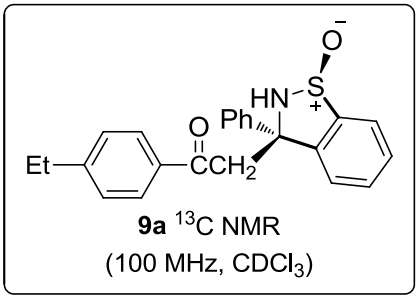


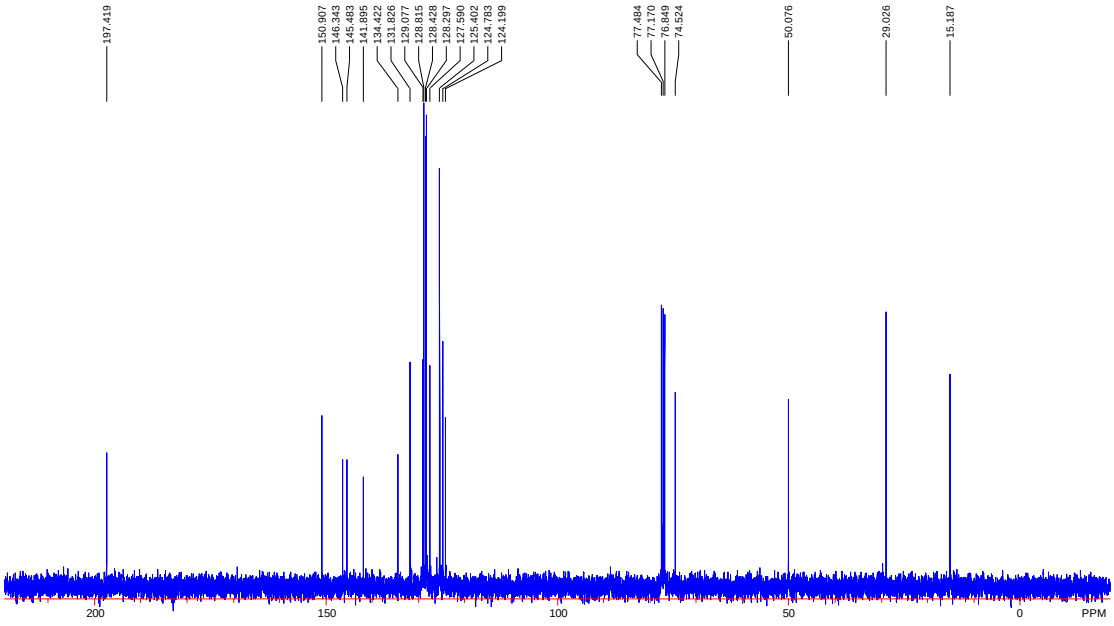


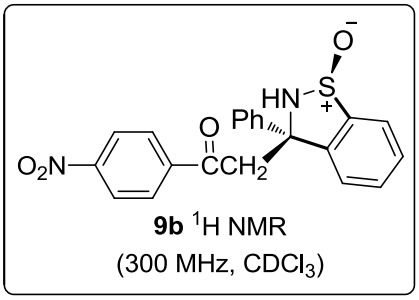
9a ^{1}H NMR

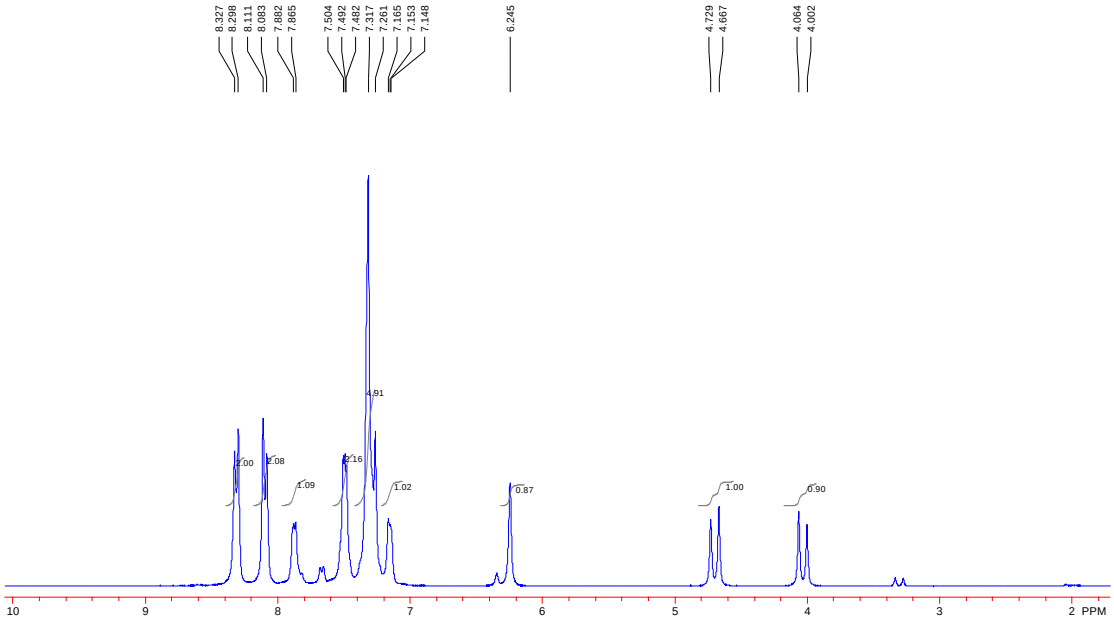
(300 MHz, $CDCl_3$)

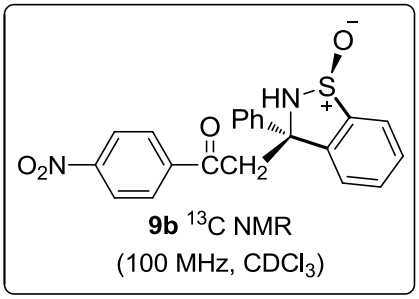



O
HN
S
+
Ph
O
Et
CCH2
9a 13C NMR
(100 MHz, CDCl3)

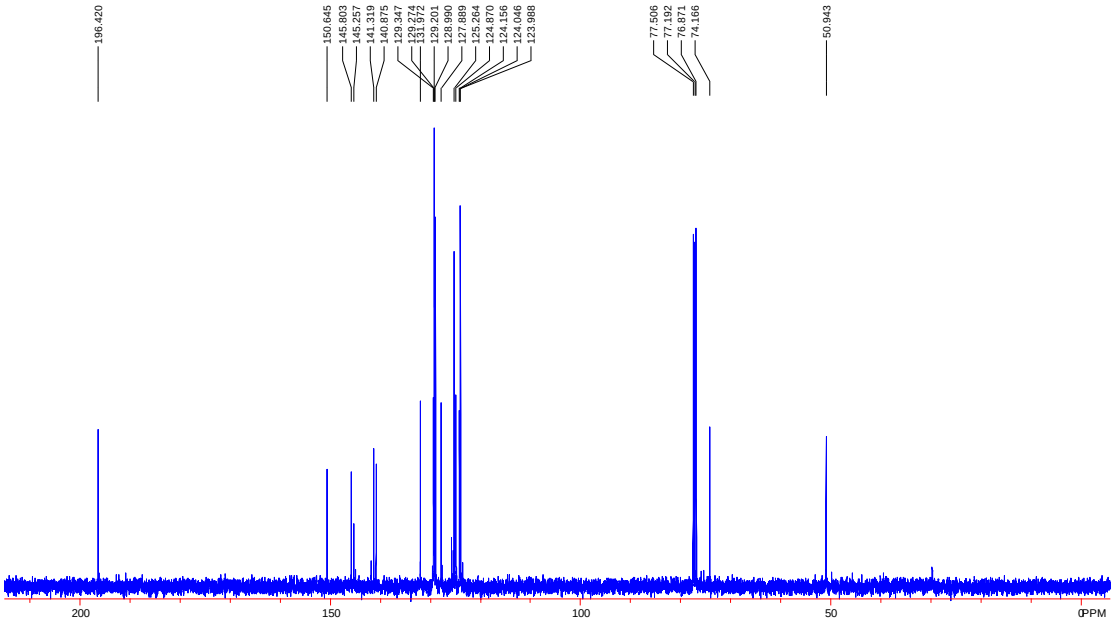

197.419
150.907
146.343
145.483
141.895
134.422
131.826
129.077
128.815
128.428
128.297
127.590
125.402
124.783
124.199
77.484
77.170
76.849
74.524
50.076
29.026
15.187
200
150
100
50
0
PPM

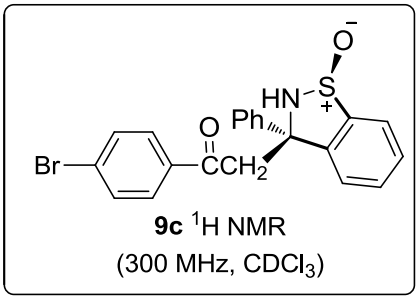

O
HN
S
+
Ph
O
O2N
CCH2
9b 1H NMR
(300 MHz, CDCl3)


8.327
8.298
8.111
8.083
7.882
7.865
7.504
7.492
7.482
7.317
7.261
7.165
7.153
7.148
6.245
4.729
4.667
4.064
4.002
2.00
2.08
1.09
3.16
4.91
1.02
0.87
1.00
0.90
10
9
8
7
6
5
4
3
2 PPM



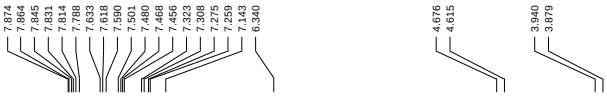
9b ^{13}C NMR
(100 MHz, $CDCl_3$)

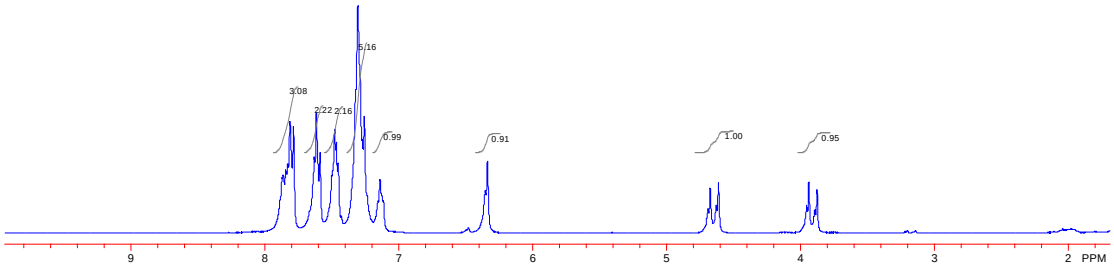


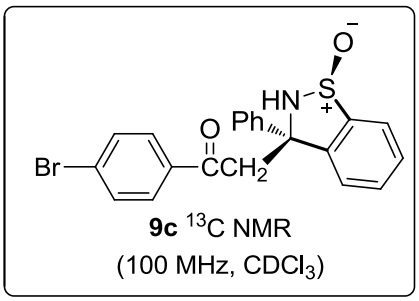


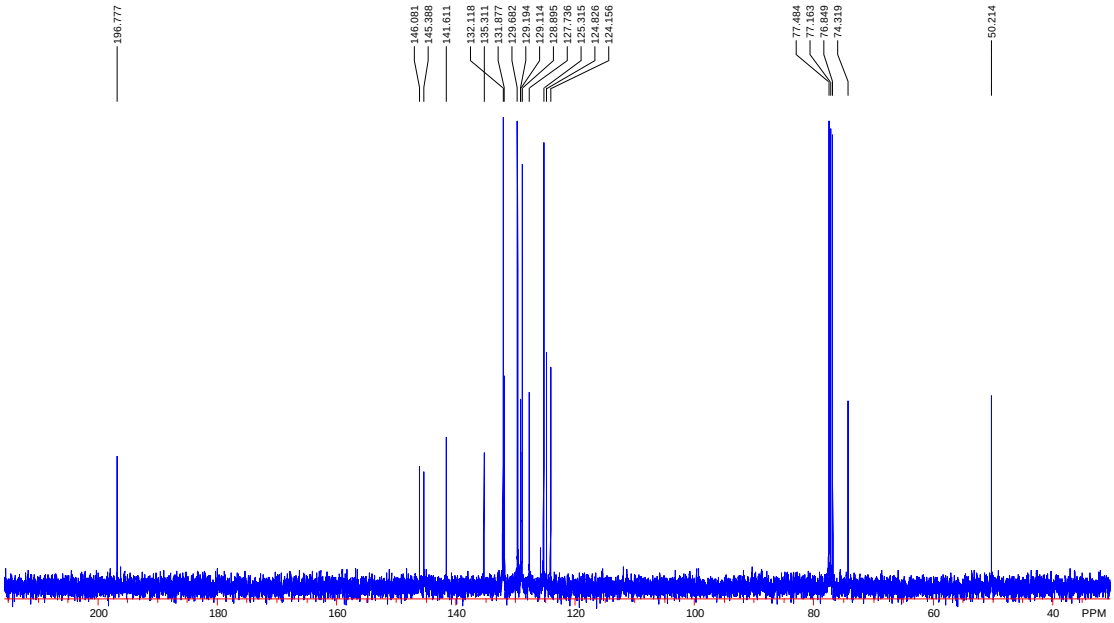
9c ^{1}H NMR

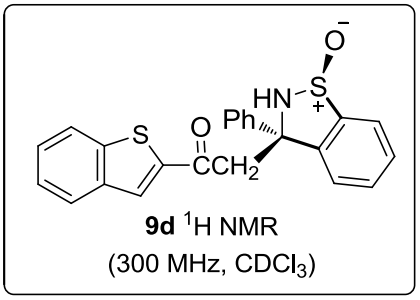
(300 MHz, $CDCl_3$)





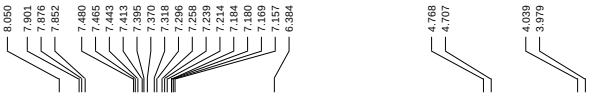

O
HN
S
+
Ph
O
Br
CCH2
9c 13C NMR
(100 MHz, CDCl3)

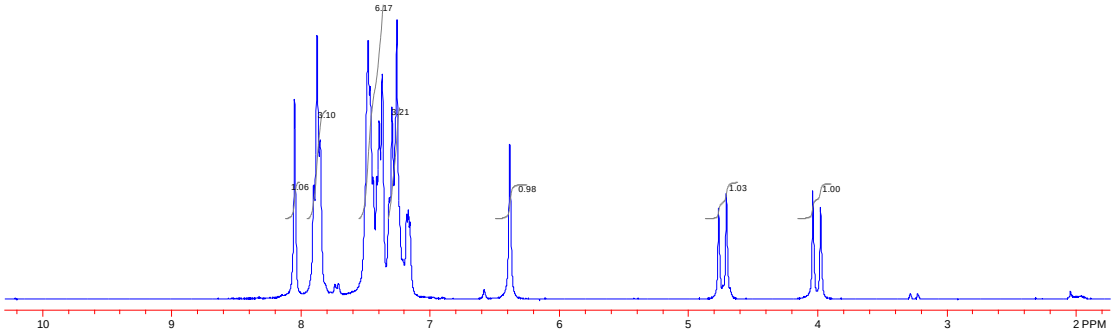

196.777
146.081
145.388
141.611
132.118
135.311
131.877
129.682
129.194
129.114
128.895
127.736
123.315
124.826
124.456
77.484
77.163
76.849
74.319
50.214
200
180
160
140
120
100
80
60
40
PPM

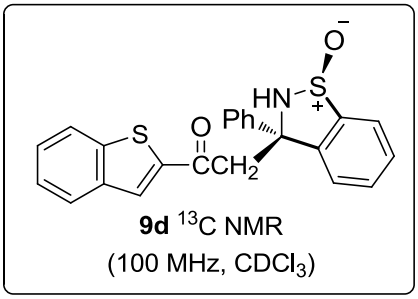


9d ^{1}H NMR

(300 MHz, $CDCl_3$)

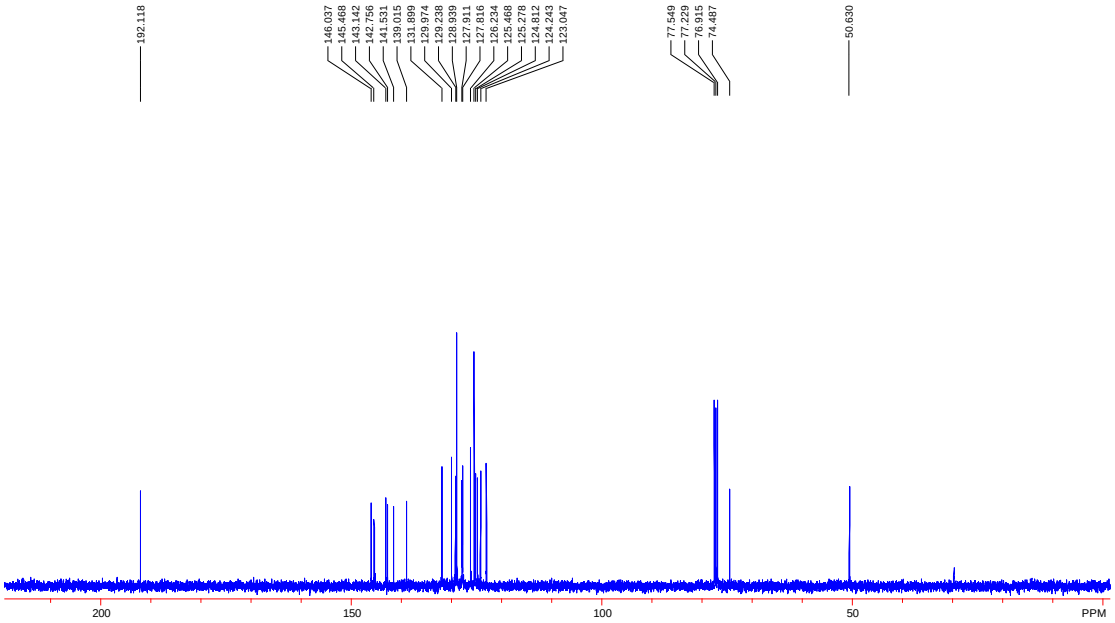


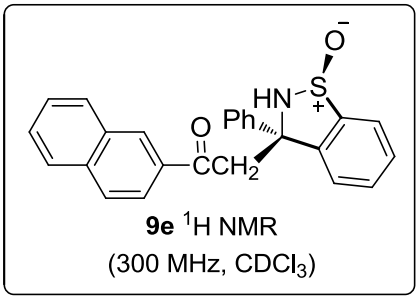




9d ^{13}C NMR

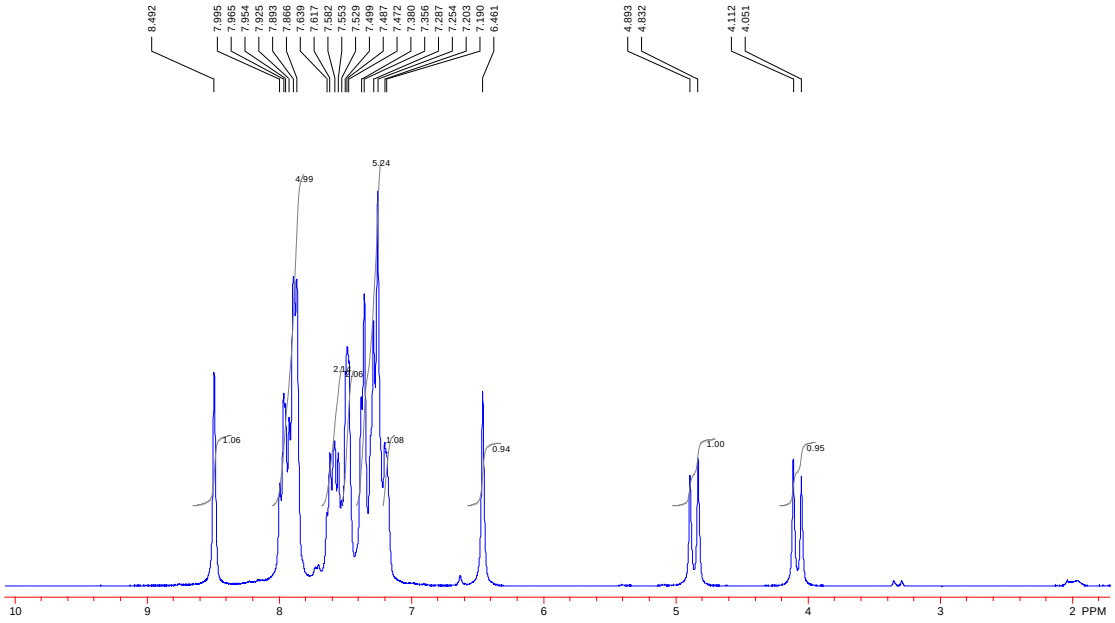
(100 MHz, $CDCl_3$)

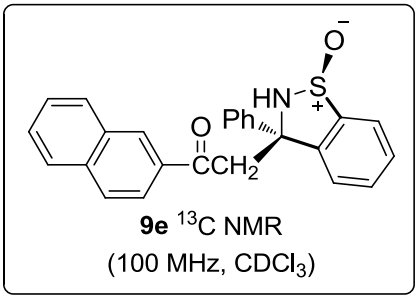




9e ^{1}H NMR

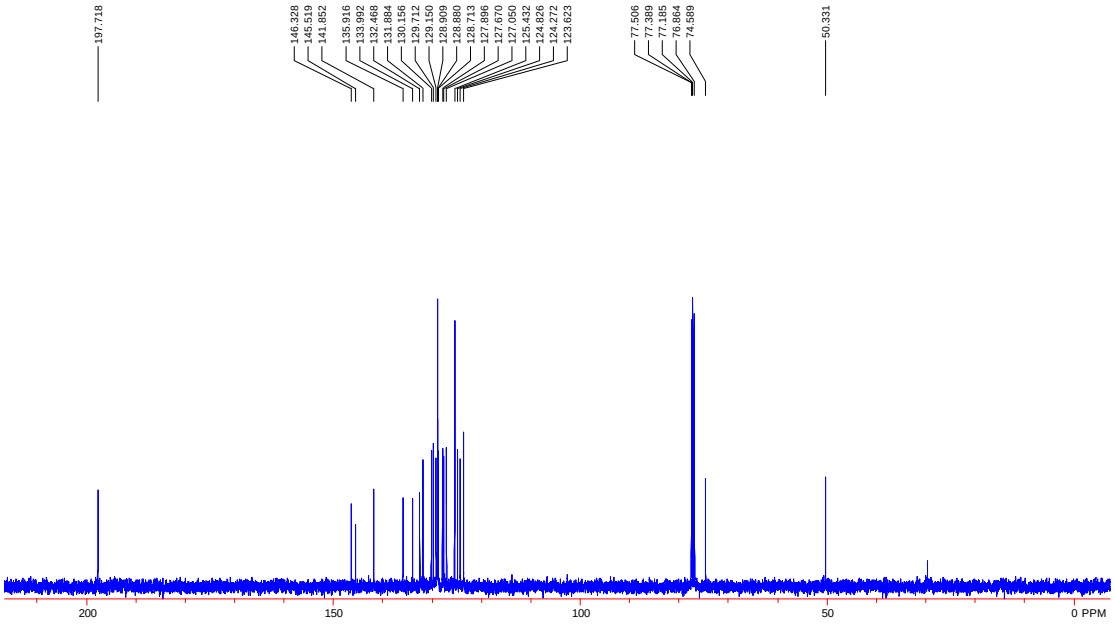
(300 MHz, $CDCl_3$)

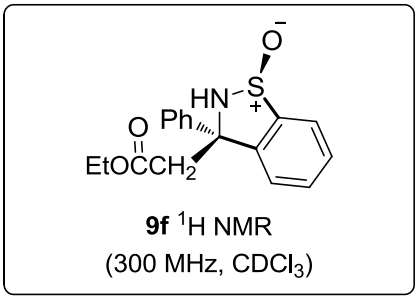




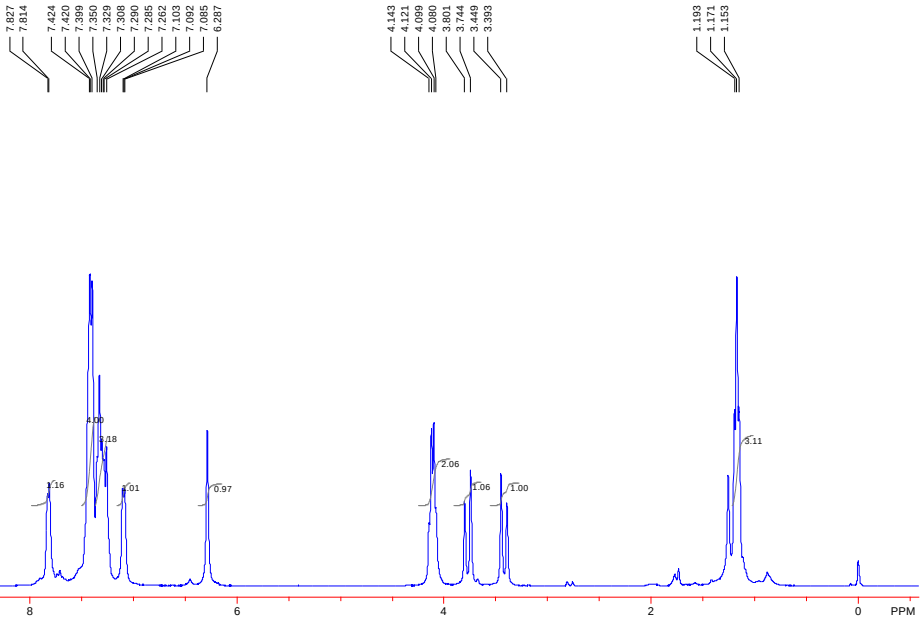
9e ^{13}C NMR

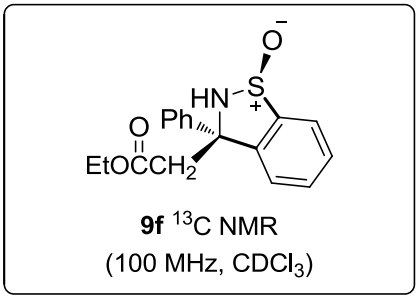
(100 MHz, $CDCl_3$)



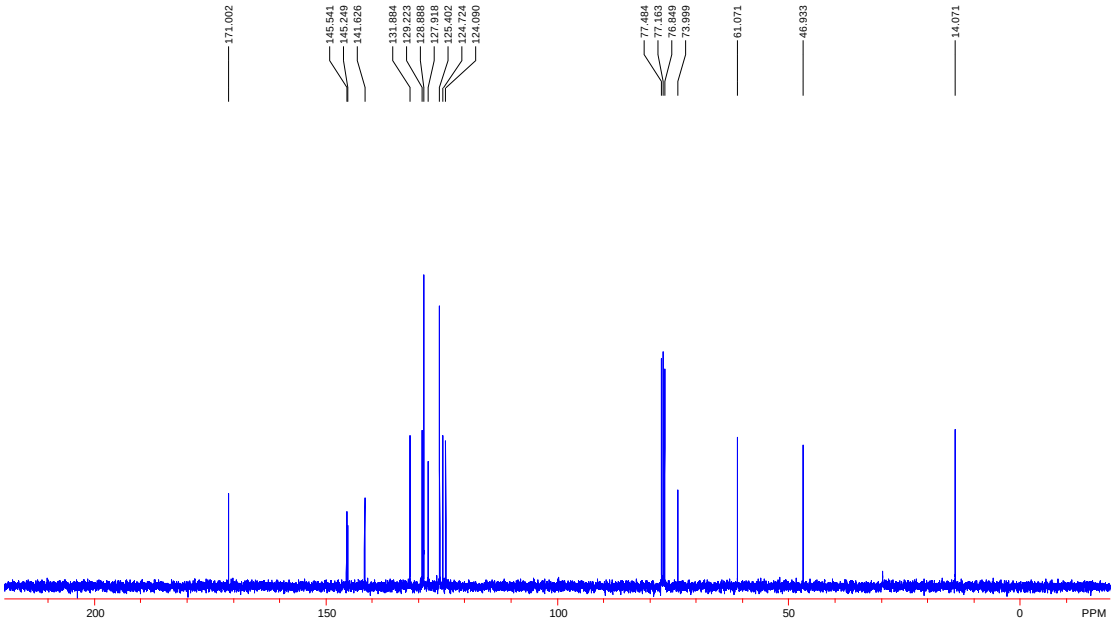


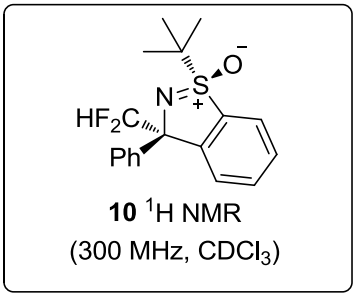
9f ^{1}H NMR
(300 MHz, $CDCl_3$)



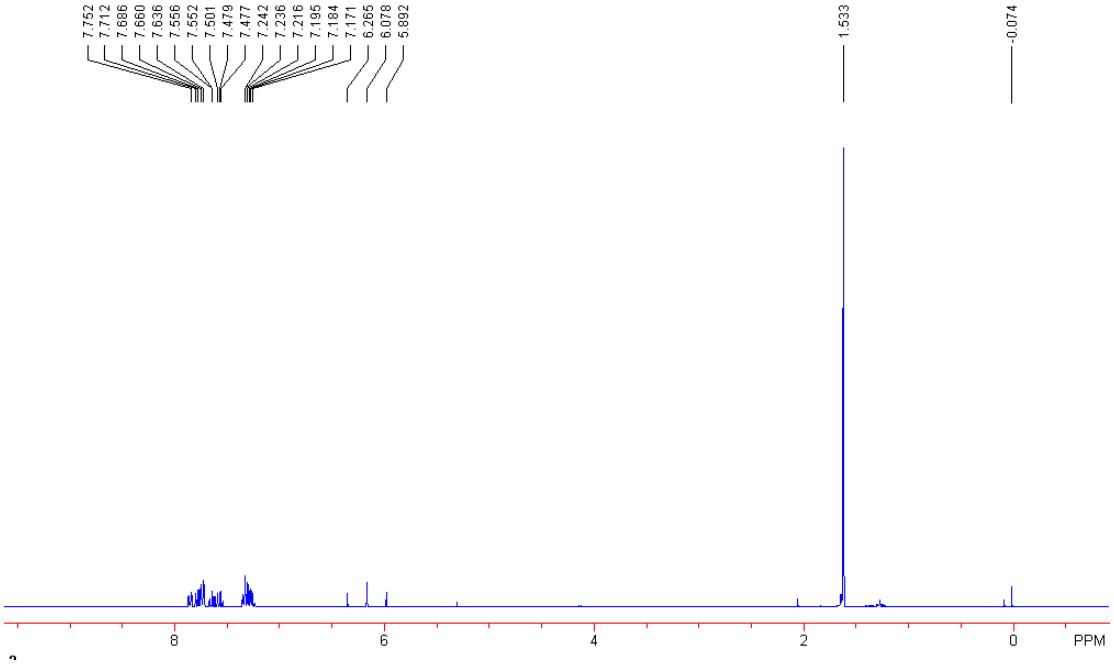


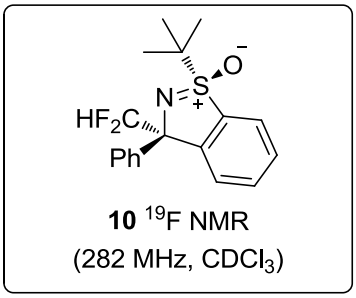
9f ^{13}C NMR
(100 MHz, $CDCl_3$)



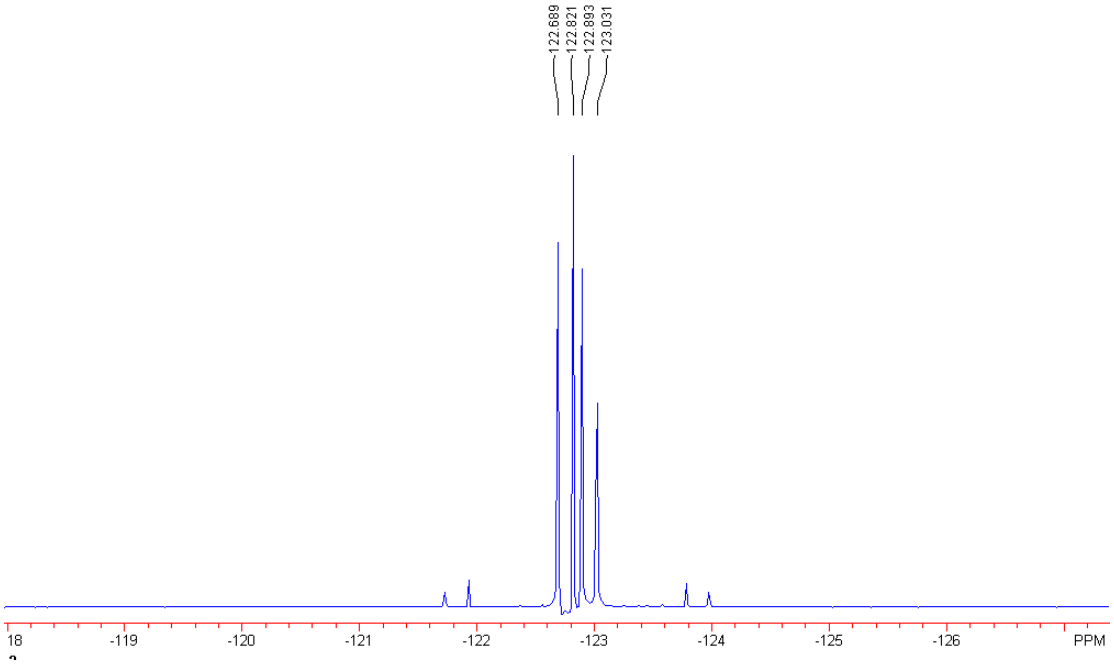


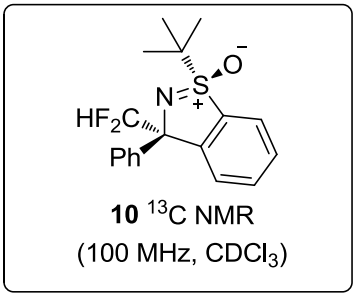
10 ^{1}H NMR
(300 MHz, $CDCl_3$)

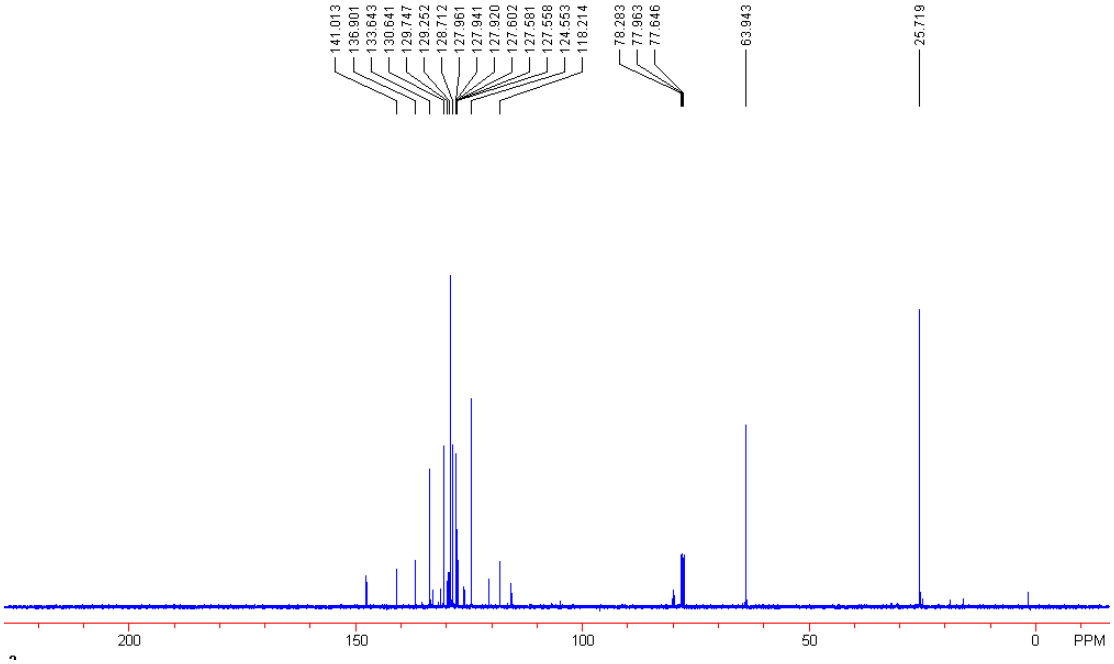


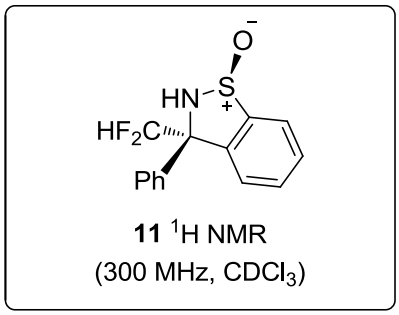


10 ^{19}F NMR
(282 MHz, $CDCl_3$)

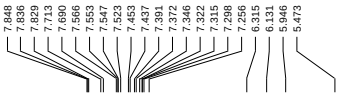


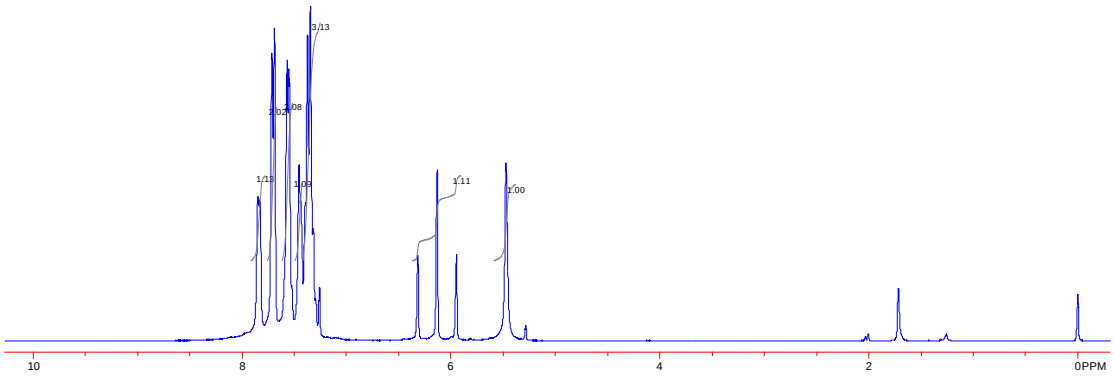

O
N
S
+
HF2C
Ph
10 13C NMR
(100 MHz, CDCl3)

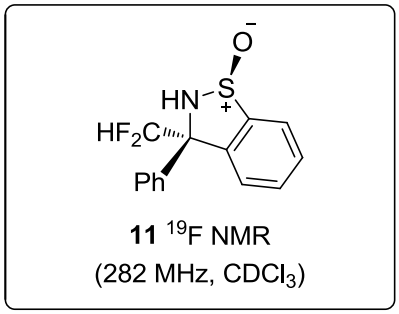

141.013
136.901
133.643
130.641
129.747
129.252
128.712
127.961
127.941
127.920
127.602
127.581
127.558
124.553
118.214
78.283
77.963
77.646
63.943
25.719
200
150
100
50
0
PPM



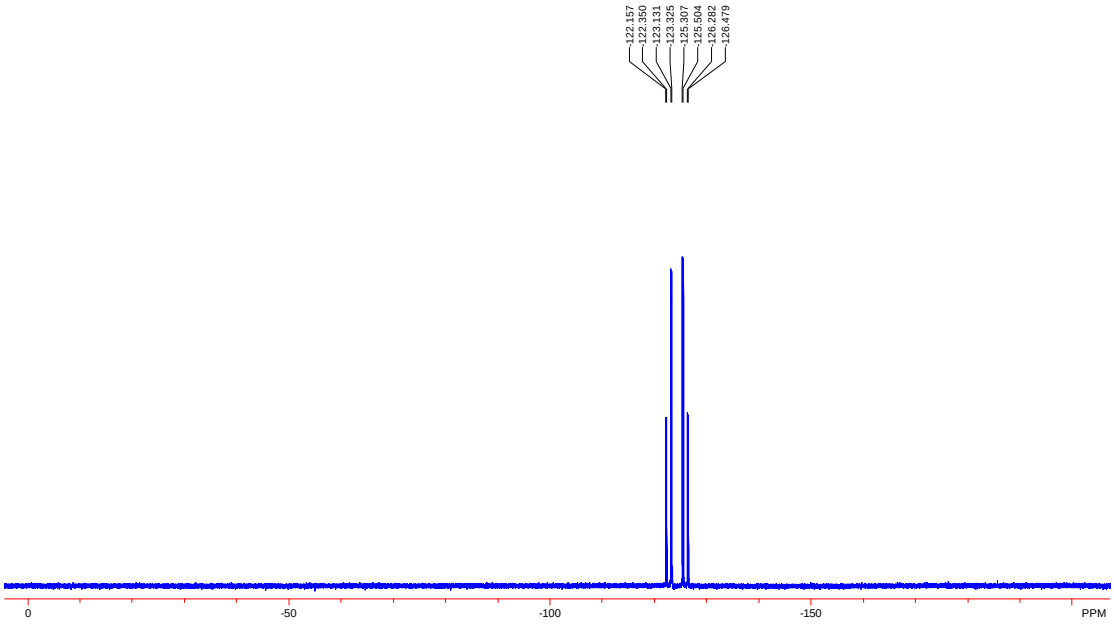
11 ^{1}H NMR
(300 MHz, $CDCl_3$)

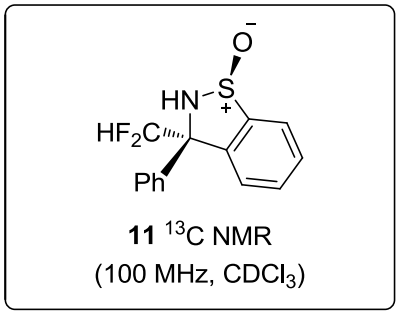




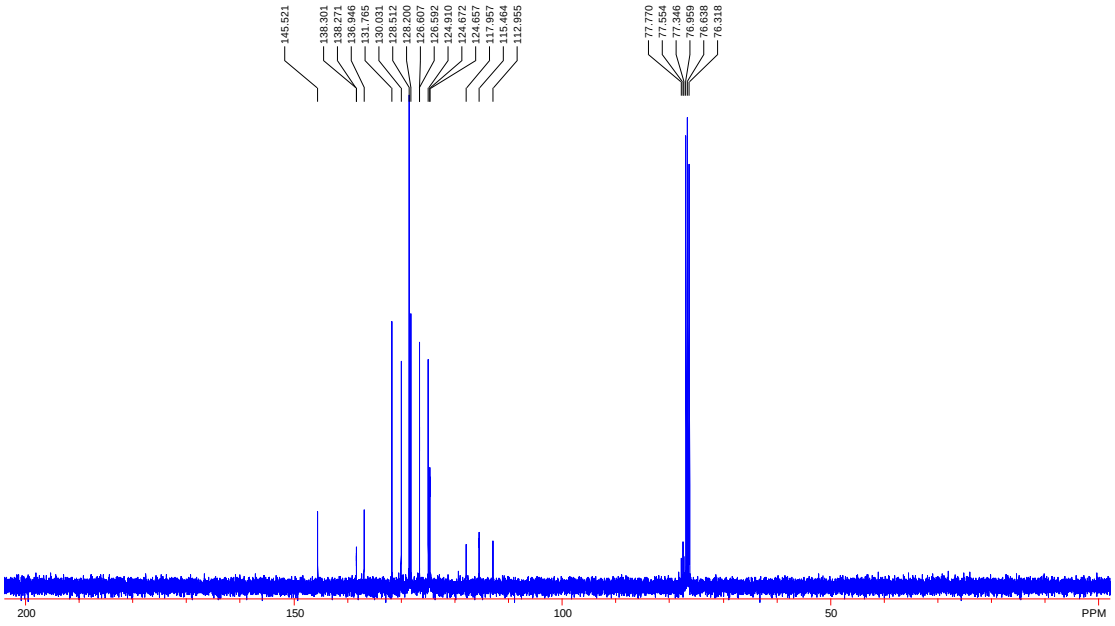


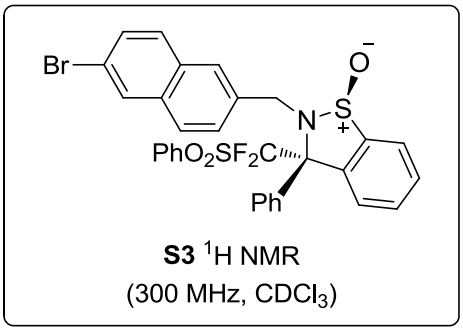
11 ^{19}F NMR
(282 MHz, $CDCl_3$)



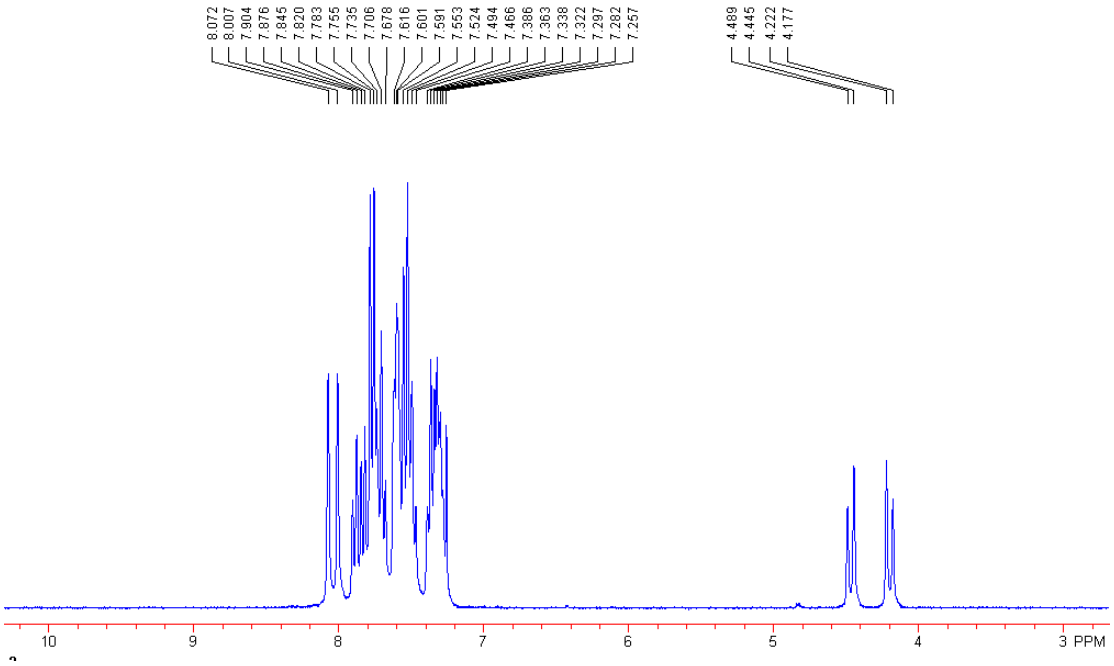


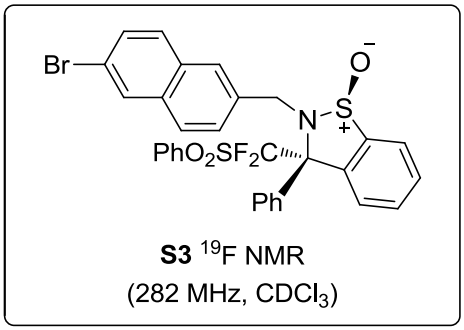
11 ^{13}C NMR
(100 MHz, $CDCl_3$)



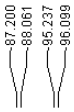


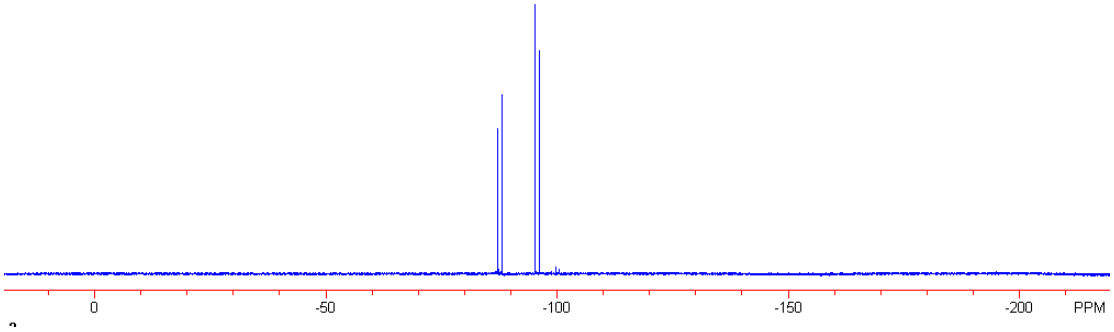
S3 ^{1}H NMR
(300 MHz, $CDCl_3$)

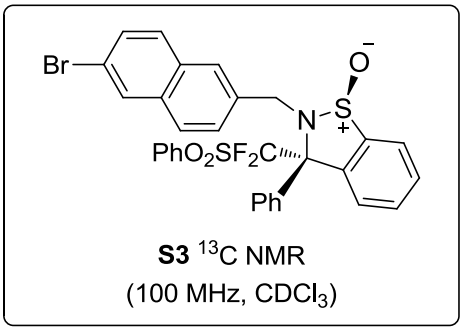




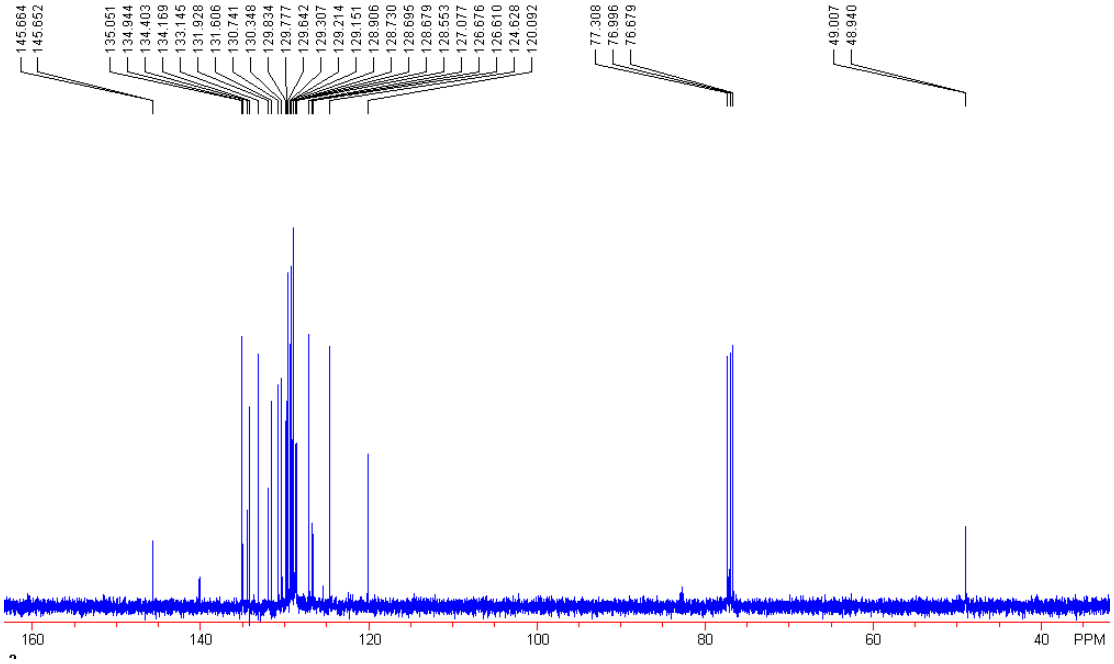
S3 ^{19}F NMR
(282 MHz, $CDCl_3$)

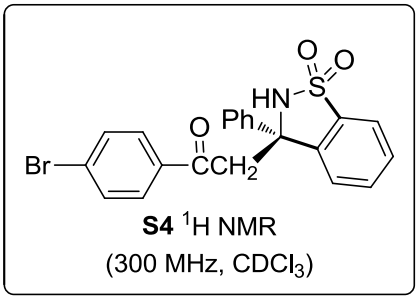






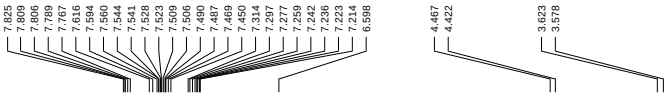
S3 ^{13}C NMR
(100 MHz, $CDCl_3$)

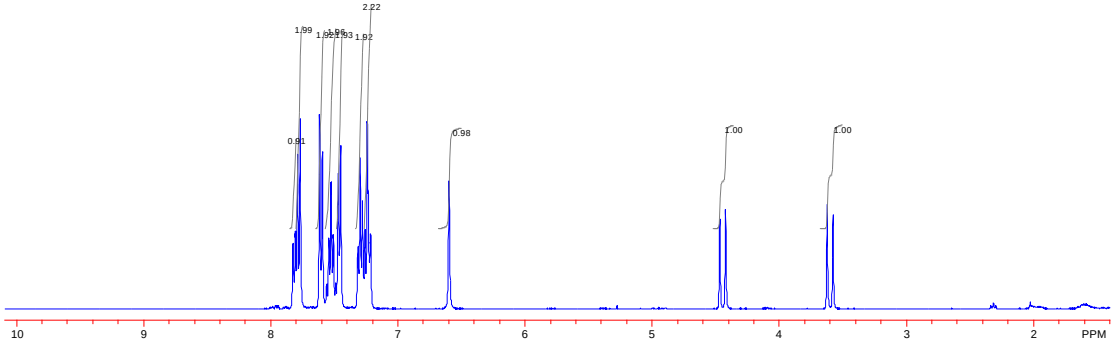


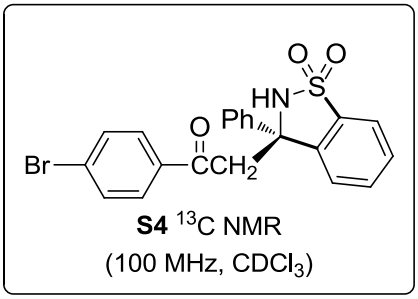


S4 ^{1}H NMR

(300 MHz, $CDCl_3$)







S4 ^{13}C NMR

(100 MHz, $CDCl_3$)