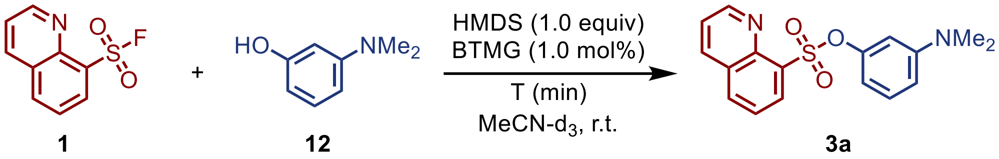
Table of Contents

General Information

The petroleum ether used refers to the fraction with 40–60 °C boiling point. Commercial solvents and reagents were used as supplied. Unless otherwise stated, all reactions were monitored by TLC on Polygram® SIL/G_{25} plates and visualized using UV light and stained using basic $KMnO_4$ or acidic vanillin. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on either a Bruker Ascend™ 400 (400 MHz) or an Ultrashield™ 500 PLUS (500 MHz) instrument as dilute solutions in the stipulated solvent. All chemical shifts (δ) are reported in parts per million (ppm) with ^1H and ^{13}C NMR referenced to solvent signals [^1H NMR: $CDCl_3$ (7.26), DMSO-d_6 (2.50), MeCN-d_3 (1.94); ^{13}C NMR: $CDCl_3$ (77.16), DMSO-d_6 (39.52), MeCN-d_3 (1.32)]. Coupling constants (J) are reported in Hertz (Hz) and recorded after averaging. The multiplicity of the ^1H NMR signals are designated by one of the following abbreviations: s=singlet, d=doublet, t=triplet, q=quartet, p=pentet, hept=heptet, m=multiplet, br=broad signal. Infra-red spectra were recorded using either a Shimadzu IRAffinity-1S FT-IR or Perkin Elmer Spectrum Two FT-IR spectrophotometer, with the peaks recorded as v_{max} (cm^{-1}). HRMS were obtained using an Agilent 6530 accurate-mass Q-TOF LC/MS in electrospray ionization (ESI) or atmospheric solids analysis probe (ASAP) mode, or a Thermo Fisher Scientific Q Exactive HF utilizing a heated electrospray ionization (HESI-II) probe. Flash column chromatography was performed using a Biotage® Isolera™ on Biotage® KP-Sil SNAP cartridges using ethyl acetate and hexanes as elution solvents. Melting points data were collected using a Gallenkamp melting point apparatus or a Mettler Toledo MP50 Melting Point System. Reactions requiring microwave irradiation were conducted in a Biotage® Initiator+ system.

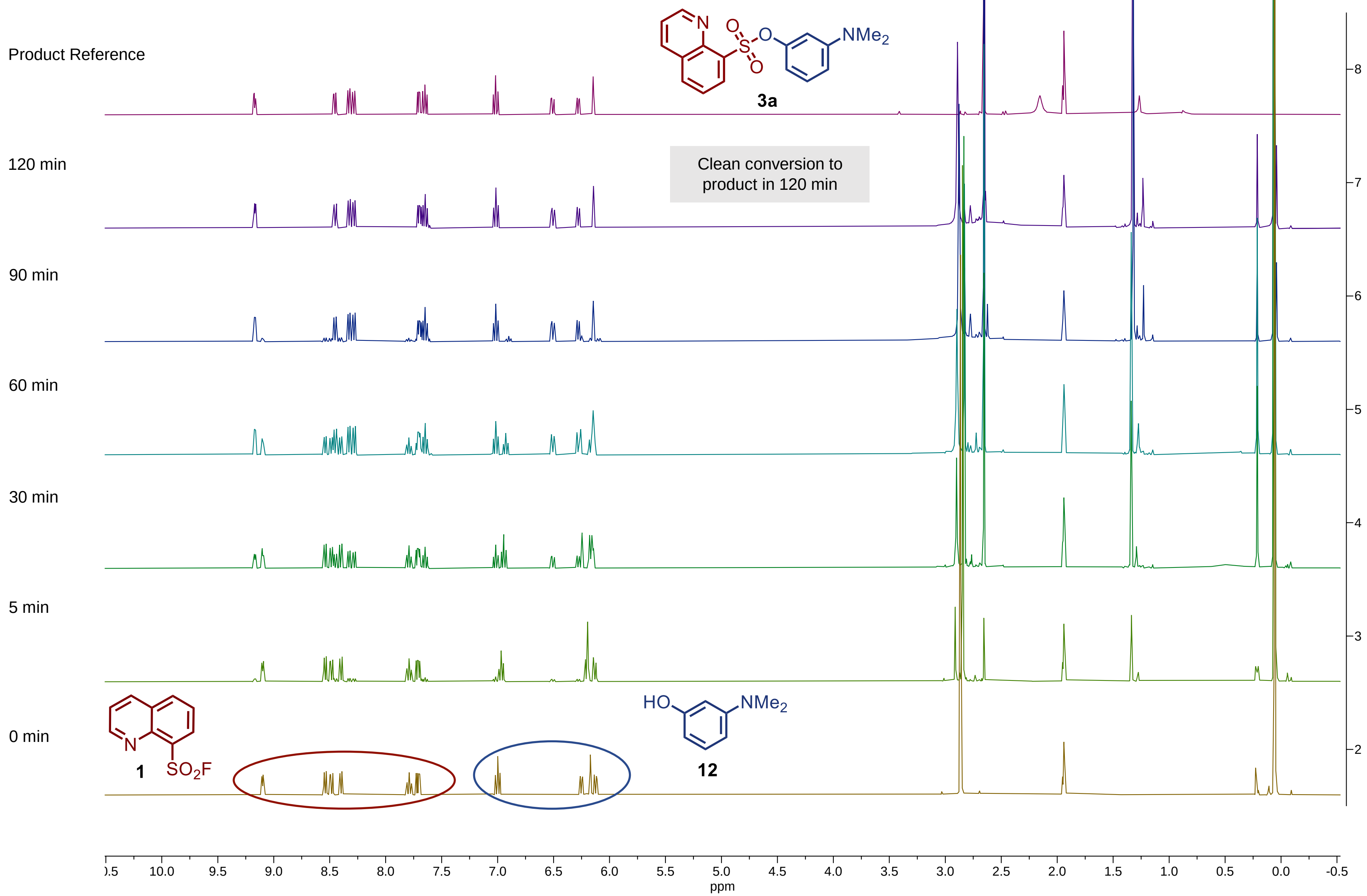
NMR Experiments

HMDS-BTMG mediated SuFEx reaction between sulfonyl fluoride 1 and phenol 12 monitored by ^{1}H NMR (400 MHz, MeCN-d_3)



In an effort to monitor the BTMG-HMDS mediated accelerated SuFEx reaction by ^{1}H NMR, the relatively slow reaction between 8-quinolinesulfonyl fluoride (**1**) and 3-(dimethylamino)phenol (**12**) was chosen. Phenol **12** (0.1 mmol) was added to MeCN-d_3 (0.5 mL) in an NMR tube and vortexed for 5 minutes. HMDS (0.1 mmol) was added and vortexed for a further 5 minutes. Sulfonyl fluoride **1** (0.1 mmol) was then added and vortexed for 5 minutes. BTMG (1.0 mol%) was then added and vortexed for a further 5 minutes. ^{1}H NMR spectra were taken after regular intervals of vortexing until the reaction reached completion – this was noted at 120 min.

Fig S1. ^{1}H NMR spectra for the BTMG-HMDS mediated SuFEx reaction between **1** and **12** (400 MHz, MeCN-d_3)



Titration of BTMG to sulfonyl fluoride 1 monitored by ^{1}H NMR (MeCN-d_3)

8-Quinolinesulfonyl fluoride (**1**, 0.05 mmol) was added to MeCN-d_3 (0.5 mL) in an NMR tube and vortexed. An initial ^{1}H NMR was taken. A solution of BTMG (0.05 mmol) in MeCN-d_3 (0.4 mL) was prepared. Aliquots of this solution (0.1 mL) were added to the NMR tube followed by immediate NMR analysis.

Fig S2. ^{1}H NMR spectrum for the titration of BTMG to sulfonyl fluoride **1** (400 MHz, MeCN-d_3)

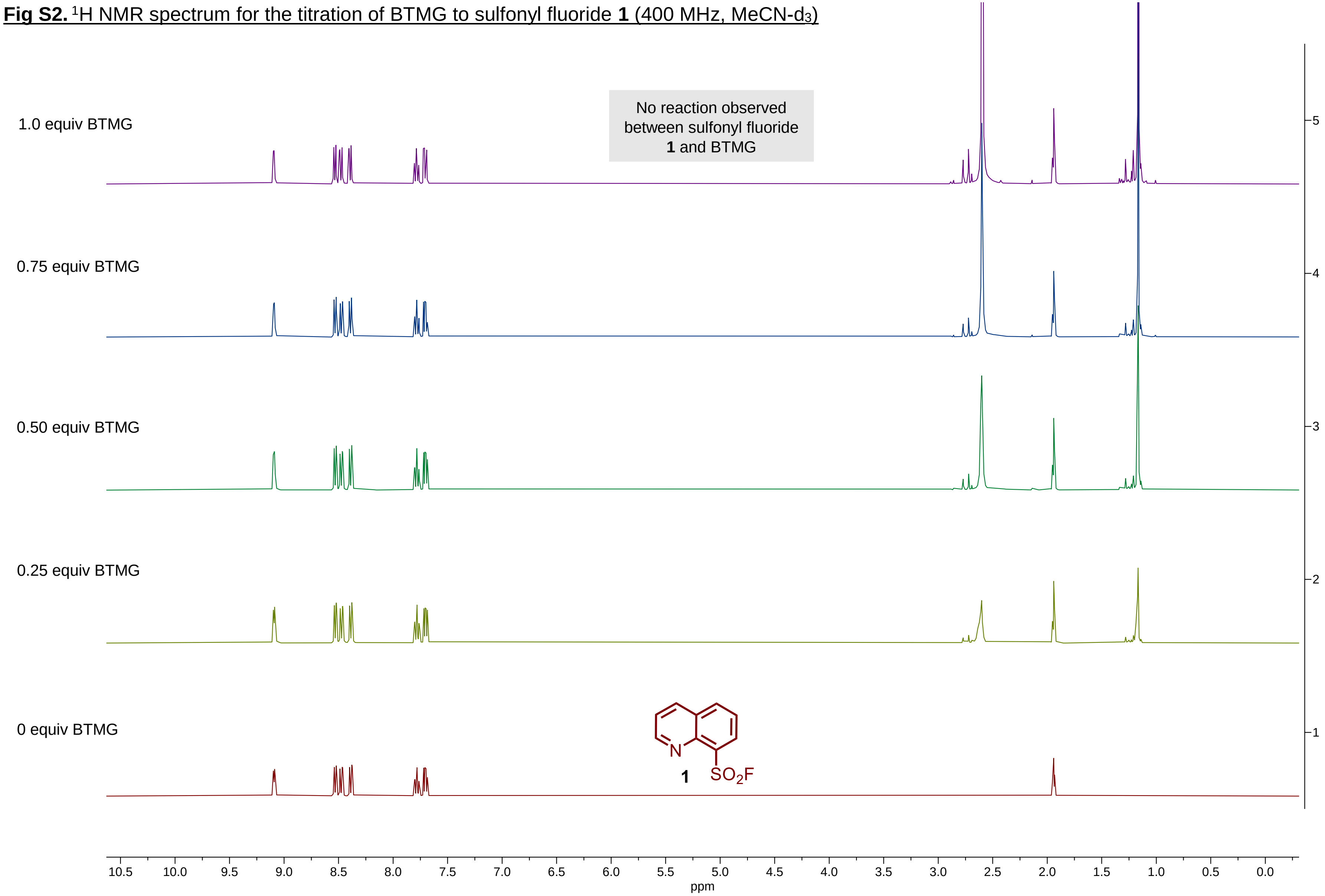


Fig S3. ^{1}H NMR spectrum (7.3–9.8 ppm) for the titration of BTMG to sulfonyl fluoride **1** (400 MHz, MeCN-d_3)

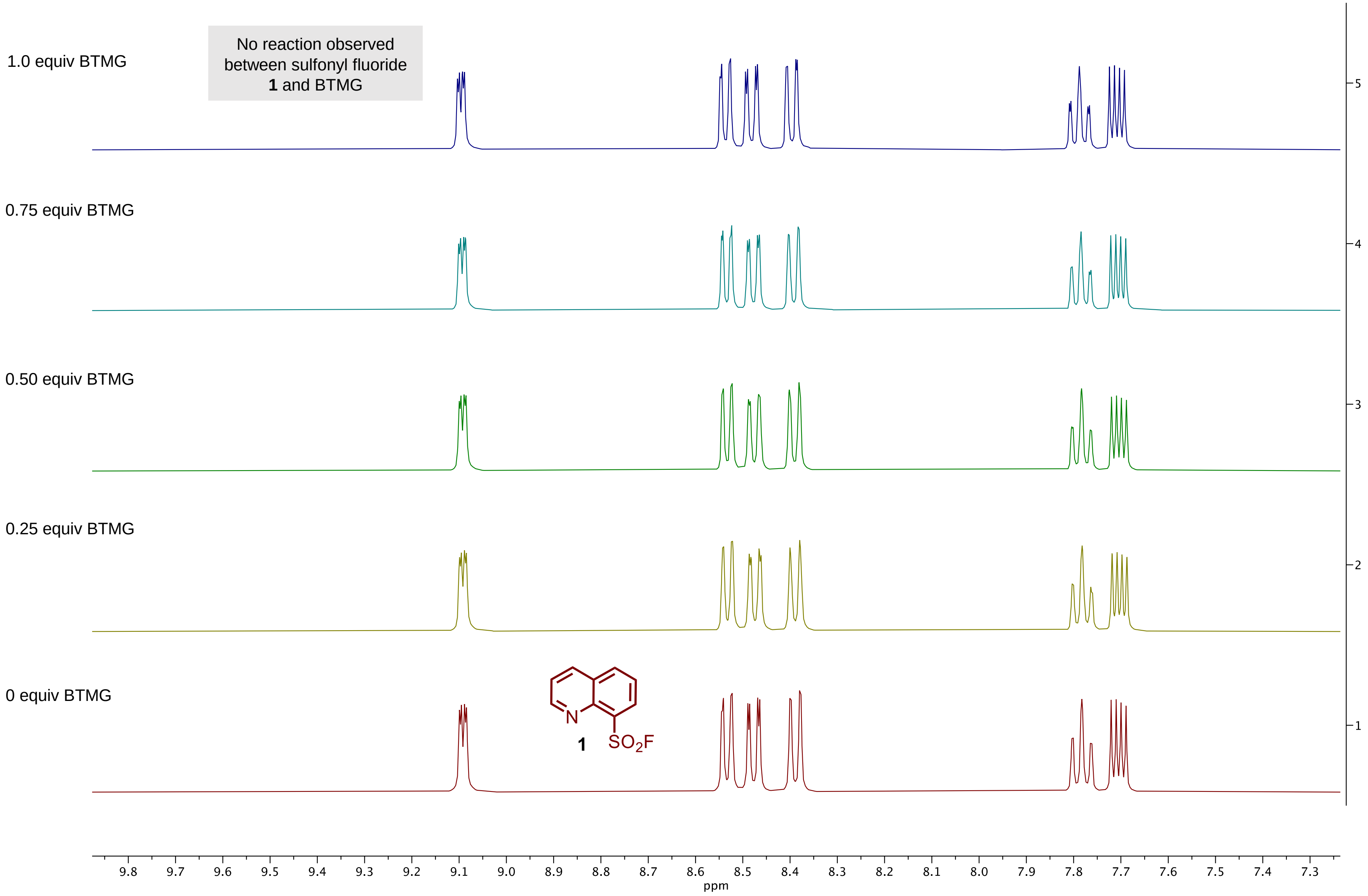
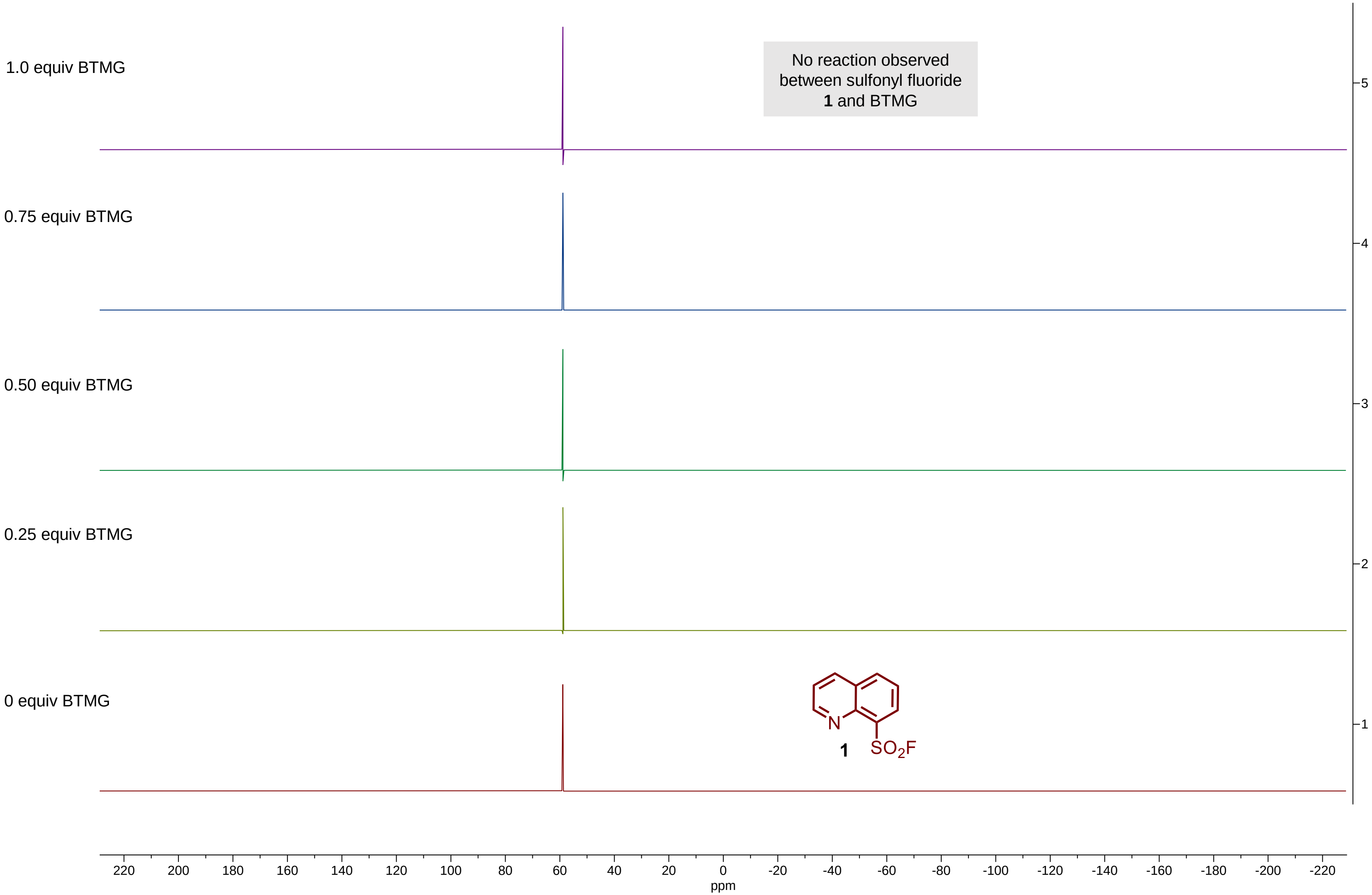
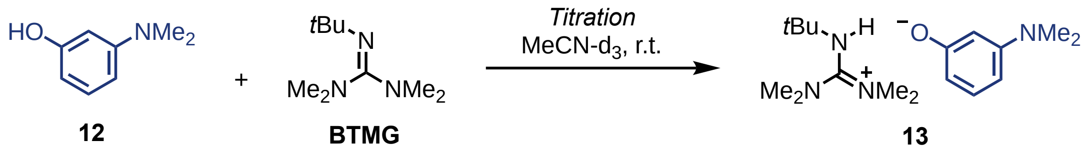


Fig S4. ^{19}F NMR spectrum for the titration of BTMG to sulfonyl fluoride **1** (376 MHz, MeCN-d_3)

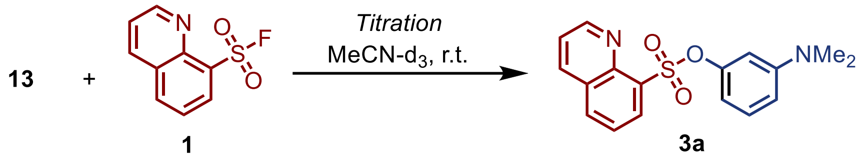


No reaction observed between sulfonyl fluoride **1** and BTMG

Titration of BTMG to phenol 12 and subsequent SuFEx with sulfonyl fluoride 1 monitored by ^{1}H NMR (MeCN-d_3)

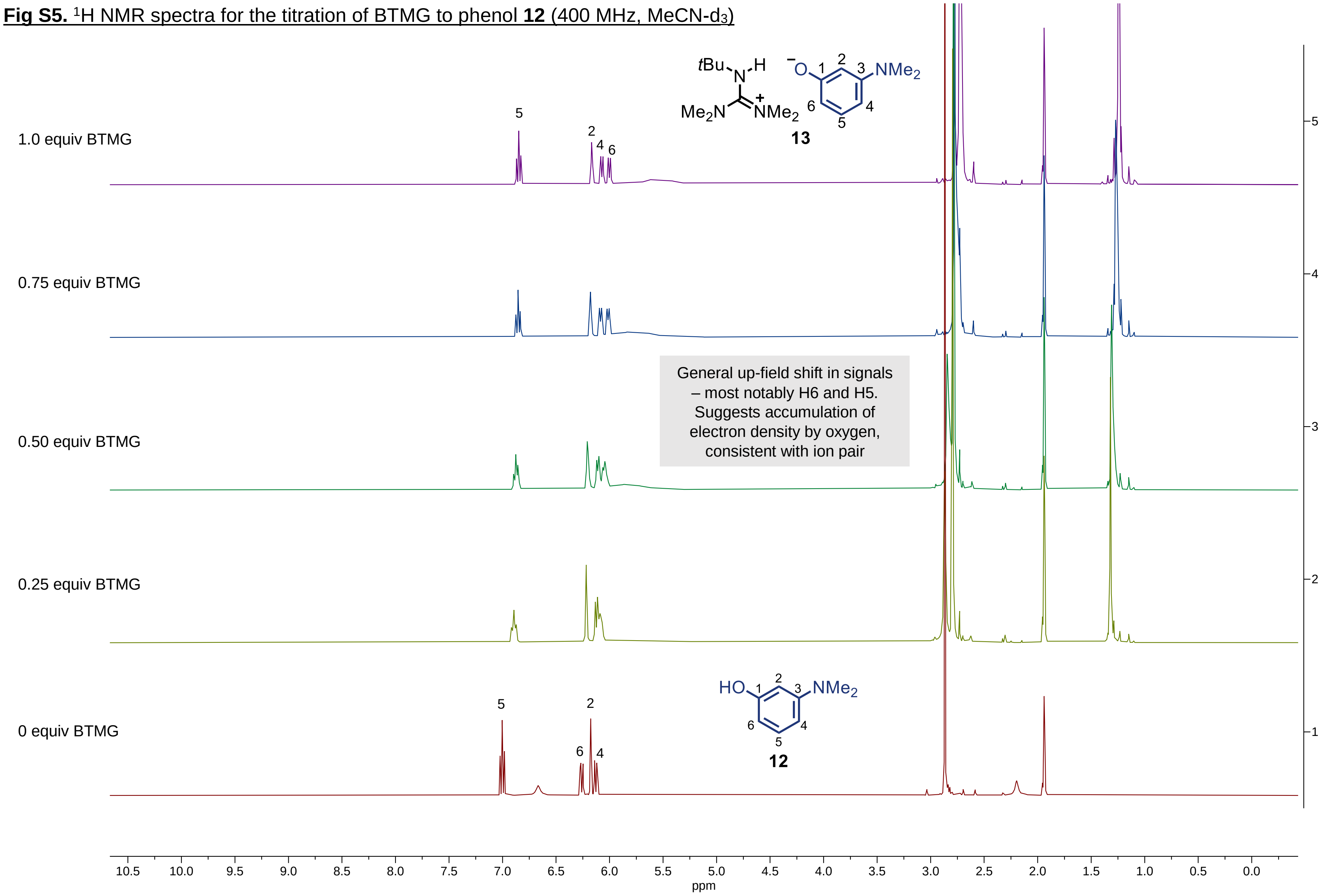


To elucidate the reactive intermediates involved in the SuFEx catalytic cycle, a collection of titration experiments was performed. Phenol **12** (0.05 mmol) was added to MeCN-d_3 (0.5 mL) in an NMR tube and vortexed before an initial ^{1}H NMR was taken. A solution of BTMG (0.05 mmol) in MeCN-d_3 (0.4 mL) was prepared. Aliquots of this solution (0.1 mL) were added to the NMR tube followed by immediate NMR analysis. Characterization of intermediate **13** was carried out after evaporation of the deuterated solvent under a stream of nitrogen and resuspension in MeCN-d_3.



Once characterized, a SuFEx reaction with sulfonyl fluoride **1** was carried out. Sulfonyl fluoride **1** (0.05 mmol) was taken up in MeCN-d_3 (0.4 mL). Aliquots of 0.1 mL were added to the NMR tube containing intermediate **13** followed by vortexing and immediate NMR analysis.

Fig S5. ^{1}H NMR spectra for the titration of BTMG to phenol **12** (400 MHz, MeCN-d$_3$)



General up-field shift in signals – most notably H6 and H5. Suggests accumulation of electron density by oxygen, consistent with ion pair

Fig S6. ^{1}H NMR spectra (4.4–9.0 ppm) for the titration of BTMG to phenol **12** (400 MHz, MeCN-d_3)

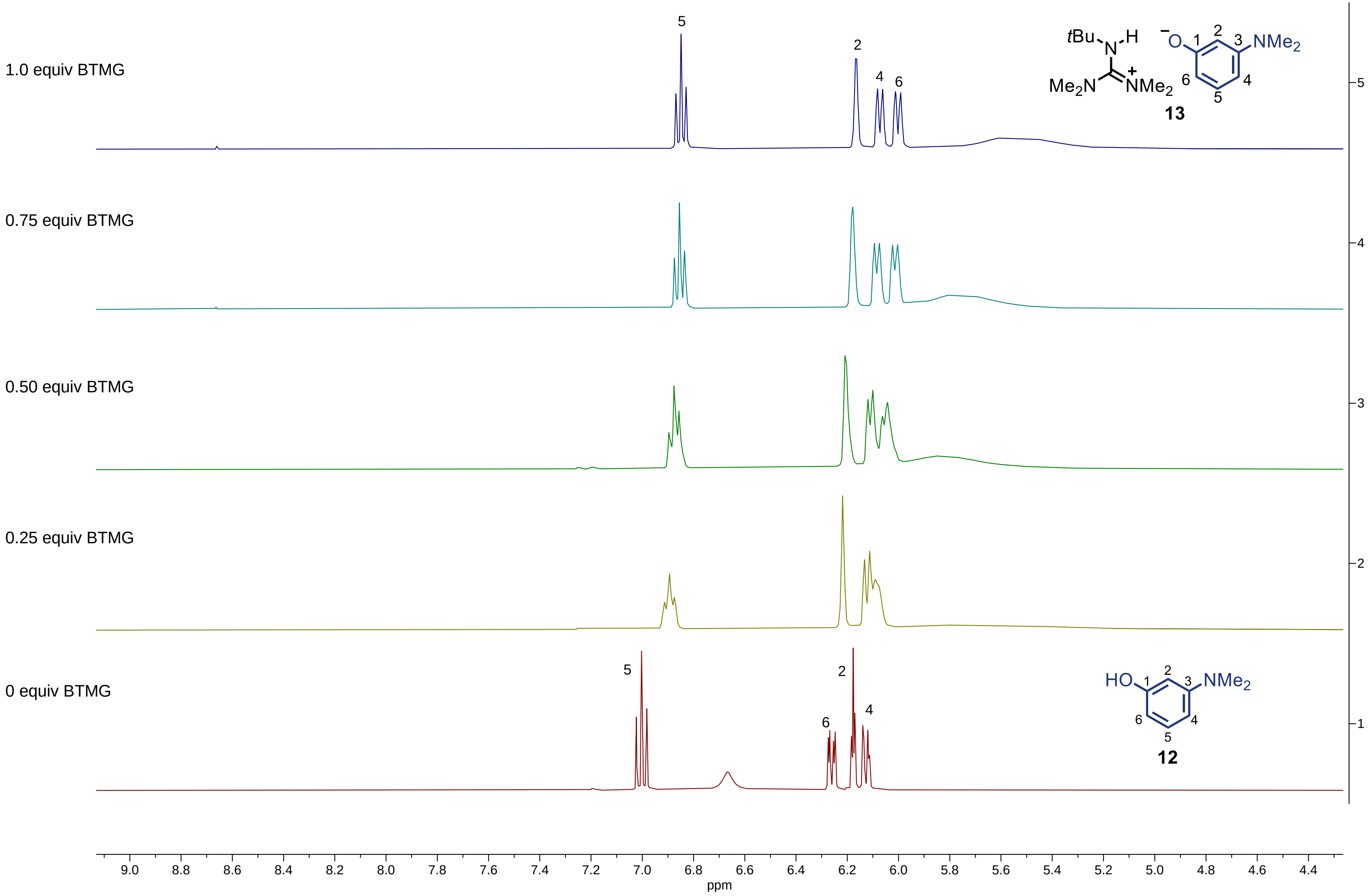


Fig S7. ^{1}H NMR spectra (0.4–4.2 ppm) for the titration of BTMG to phenol **12** (400 MHz, MeCN-d_3)

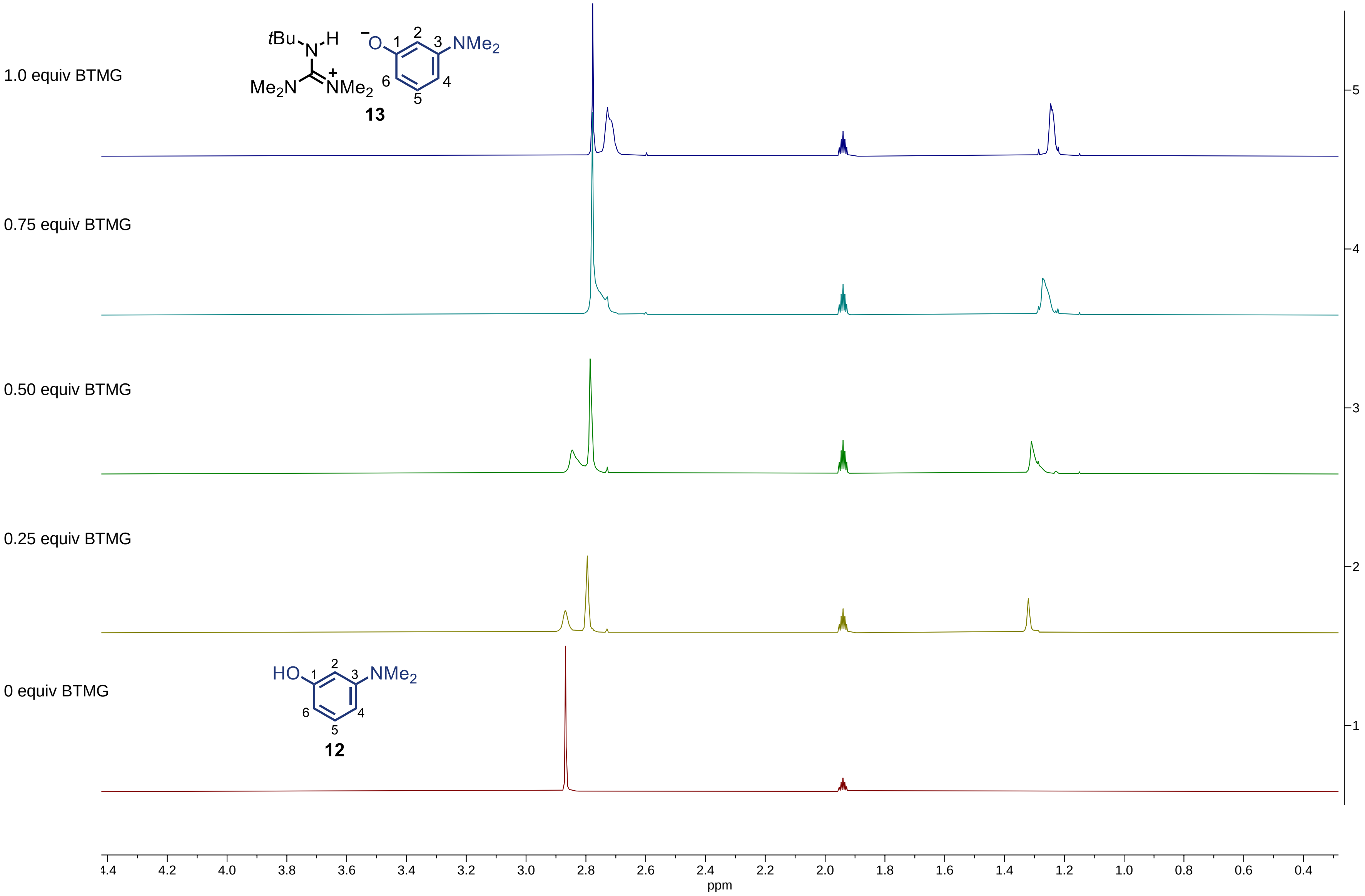


Fig S8. ^{1}H NMR spectra for the titration of sulfonyl fluoride **1** to BTMG-phenoxide **13** (400 MHz, MeCN-d_3)

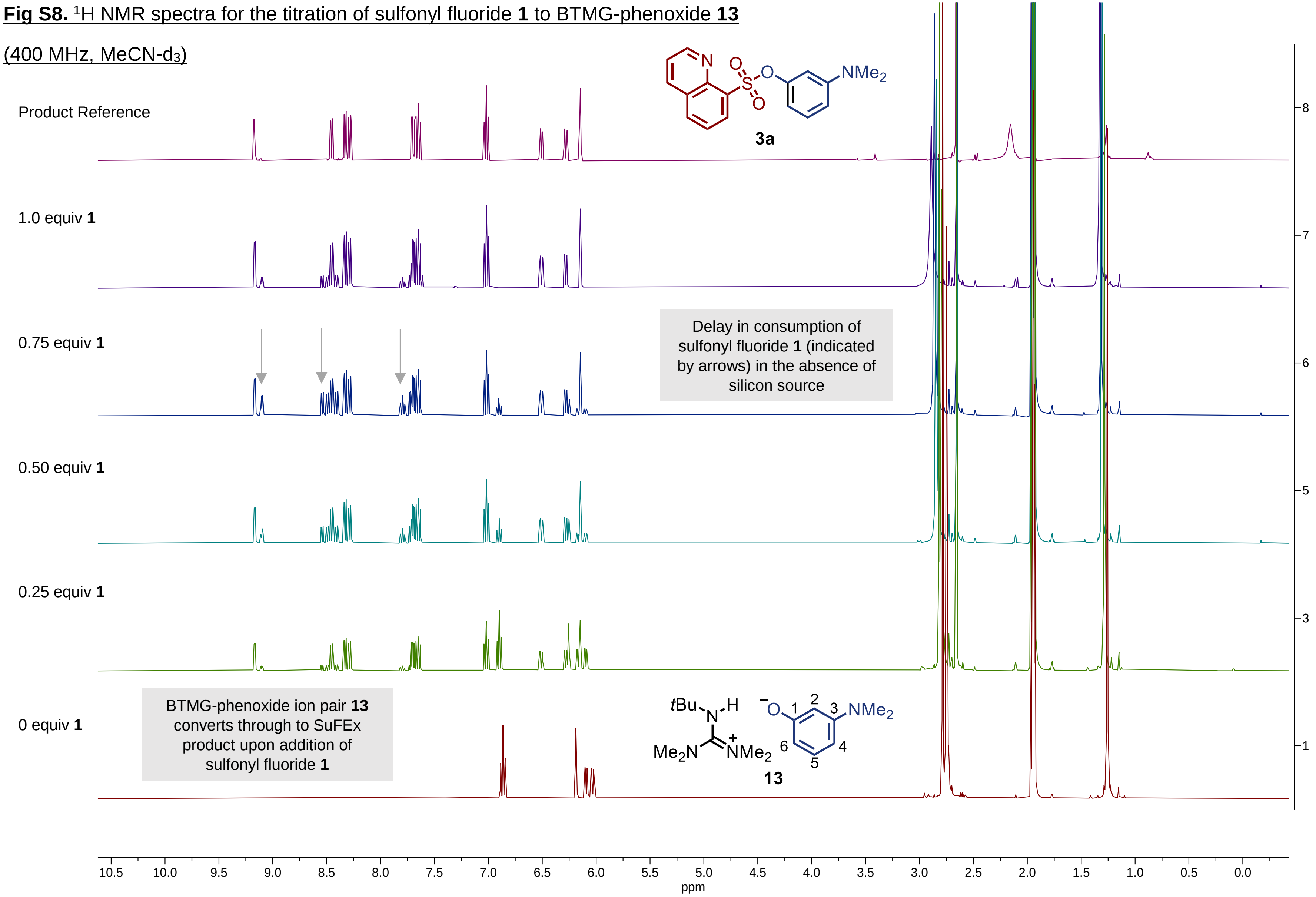
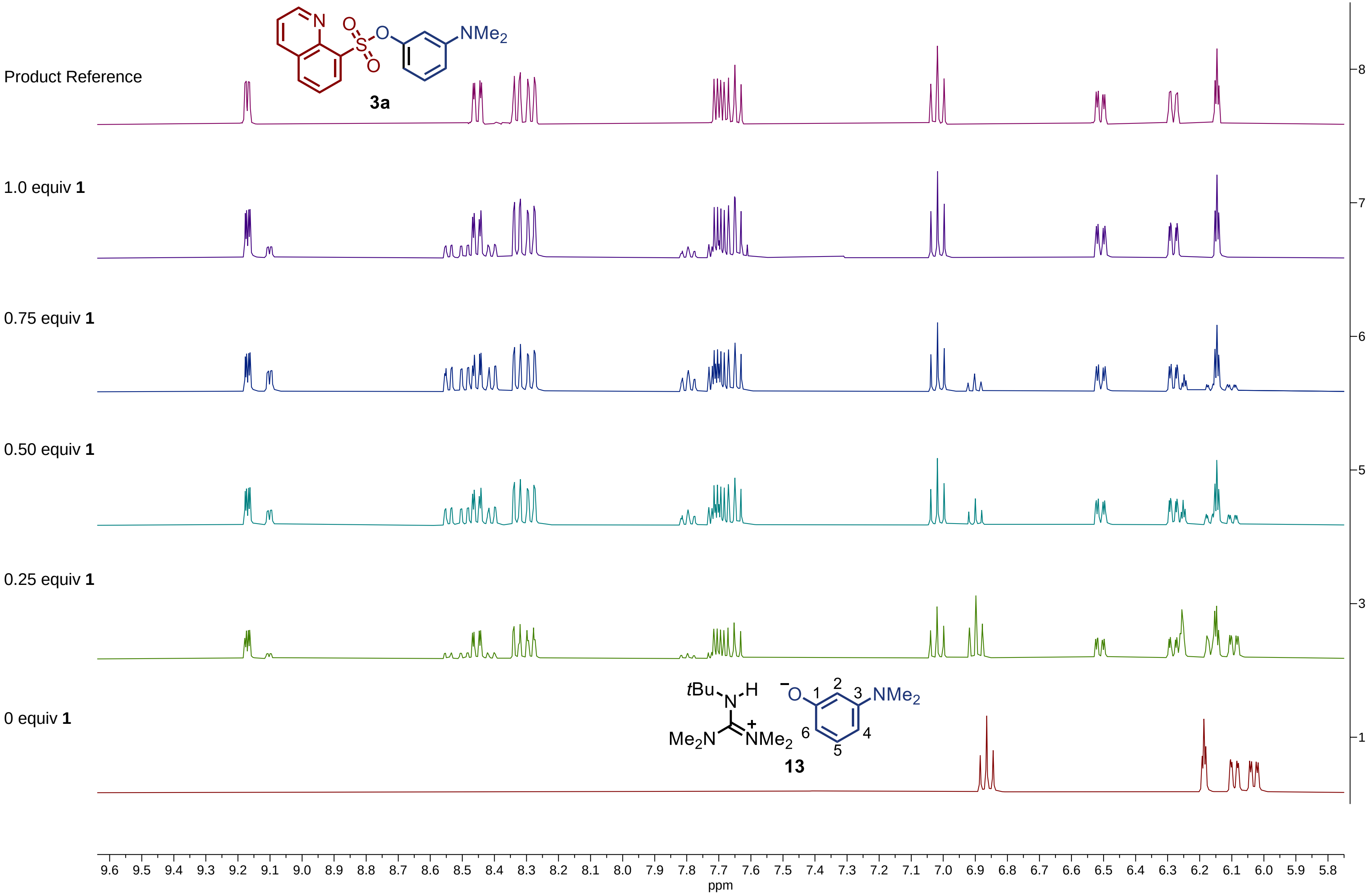
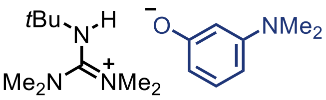


Fig S9. ^{1}H NMR spectra (5.8–9.6 ppm) for the titration of sulfonyl fluoride **1** to BTMG-phenoxide **13** (400 MHz, MeCN-d_3)

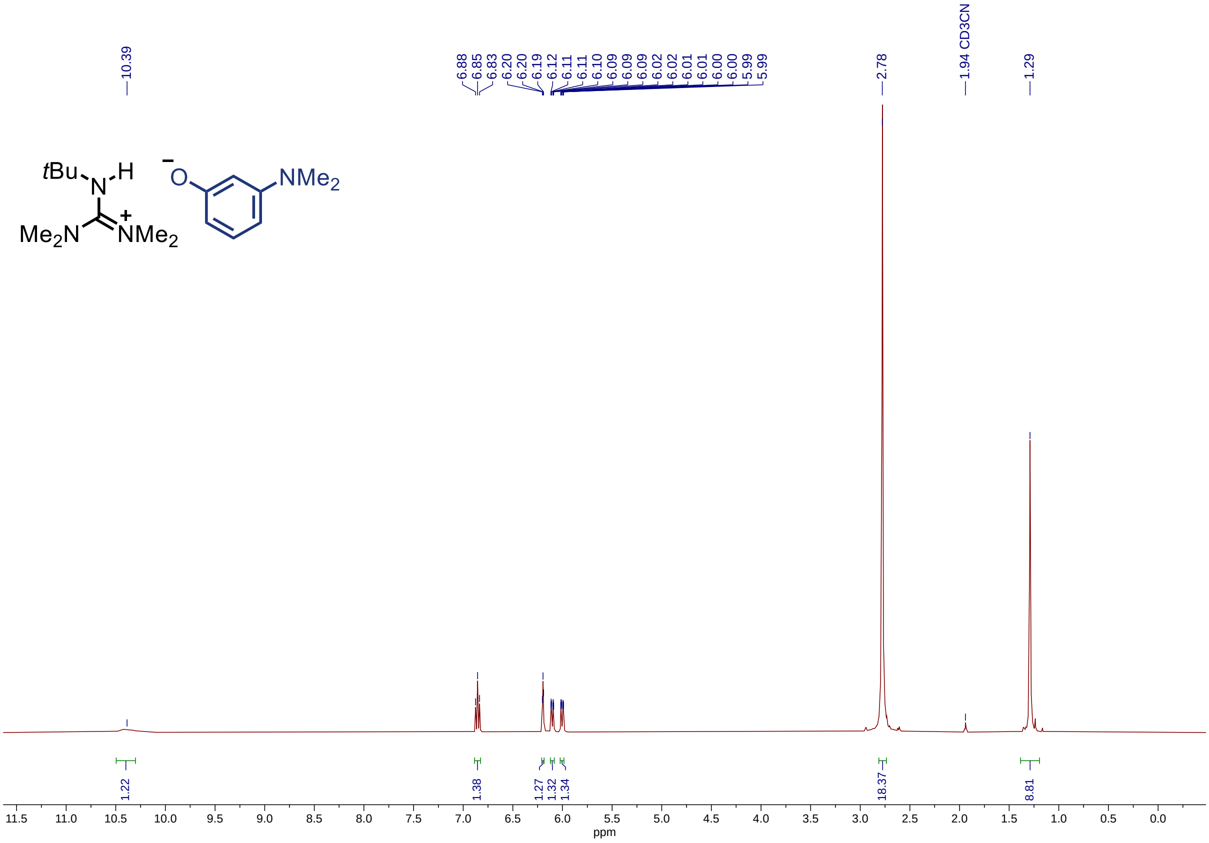


BTMG-3-dimethylaminophenol ion pair (13)

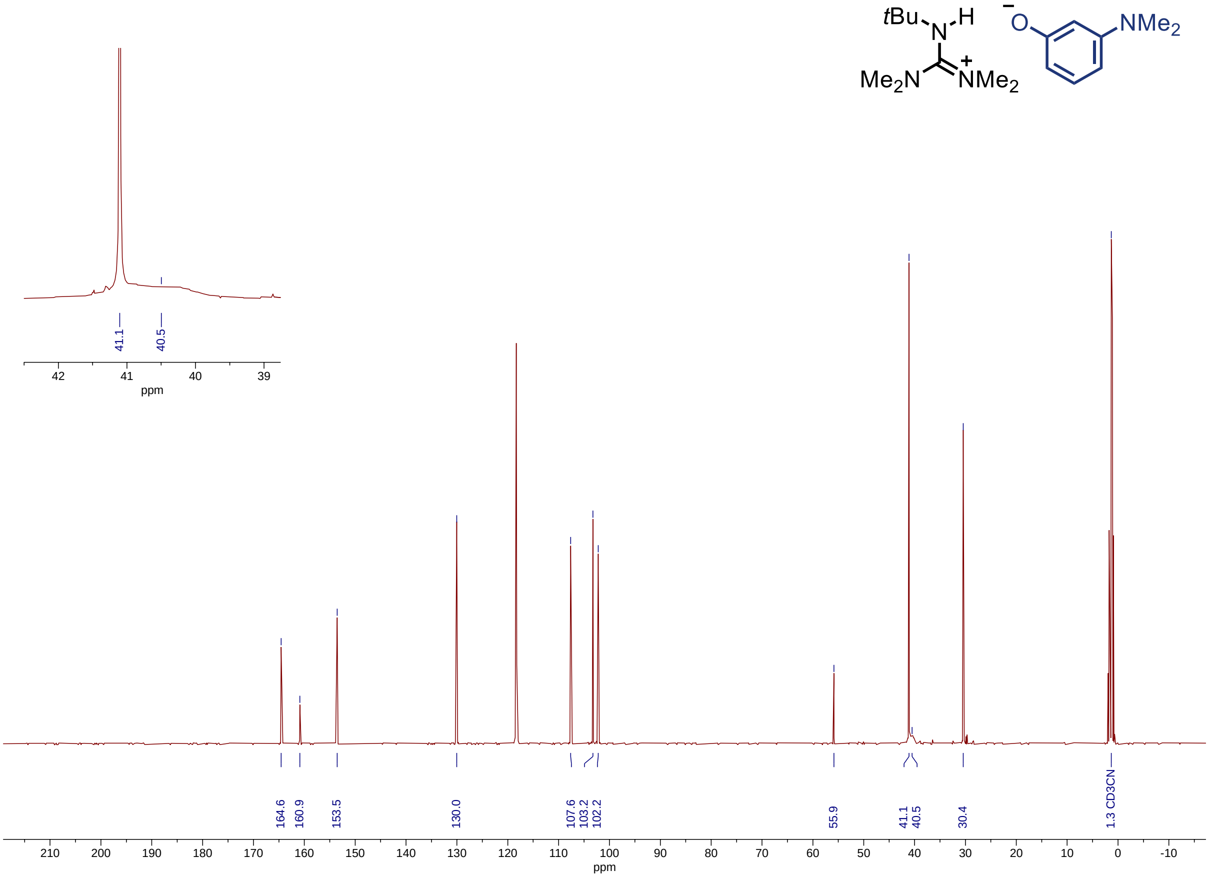


Following the general titration procedure and subsequent evaporation of volatile components, the title compound was isolated as a dark brown oil. **^{1}H NMR** (400 MHz, MeCN-d$_3$) δ 10.39 (br s, 1H), 6.85 (t, J = 8.0 Hz, 1H), 6.20 (t, J = 2.3 Hz, 1H), 6.13–6.07 (m, 1H), 6.03–5.97 (m, 1H), 2.78 (s, 18 H), 1.29 (s, 9H); **^{13}C NMR** (101 MHz, MeCN-d$_3$) δ 164.6, 160.9, 153.5, 130.0, 107.6, 103.2, 102.2, 55.9, 41.1, 40.5 (m), 30.4; **IR** ν_{max} (ATR)/cm^{-1}: 2946, 1609, 1566, 1443, 1400, 1370, 1244, 1224, 1146, 1128, 997, 978, 834, 754, 689.

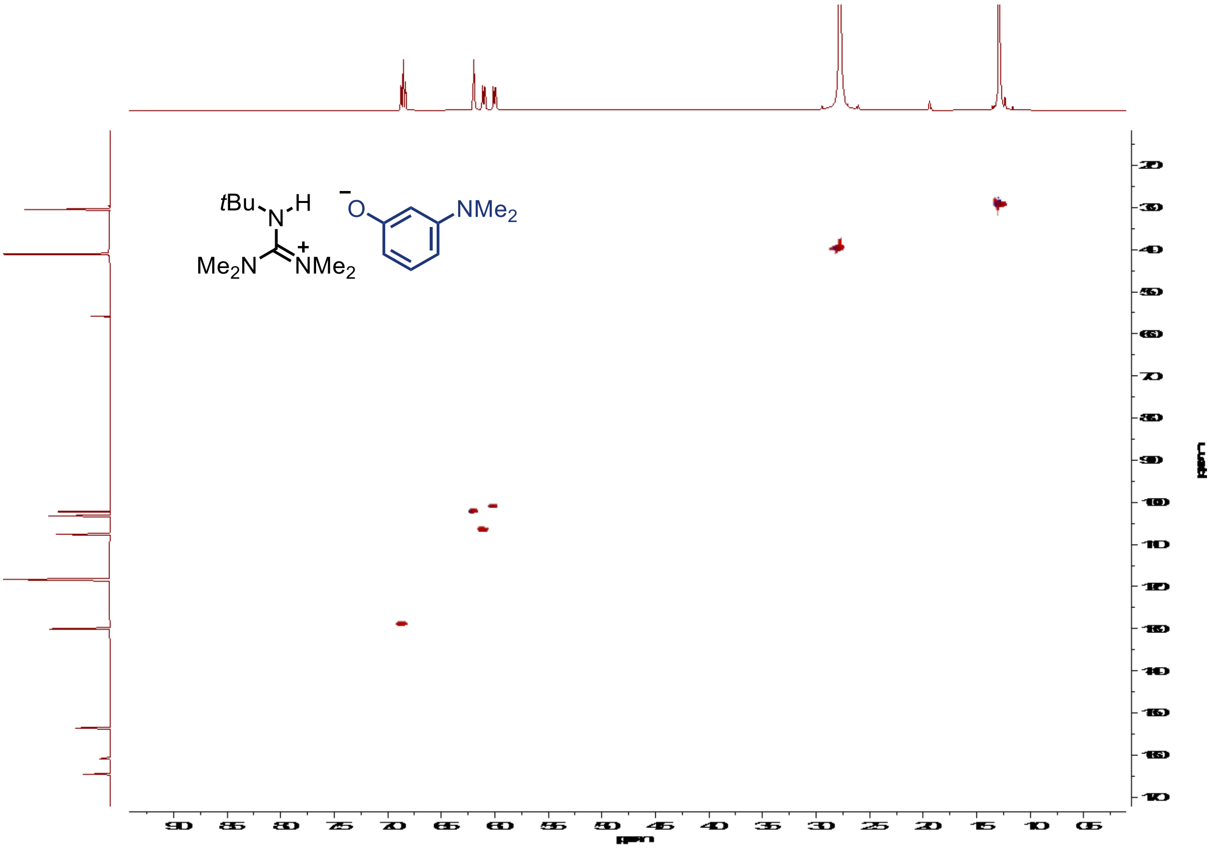
<u>^{1}H NMR spectrum for BTMG-phenoxide ion pair **13** (400 MHz, MeCN-d$_3$)</u>



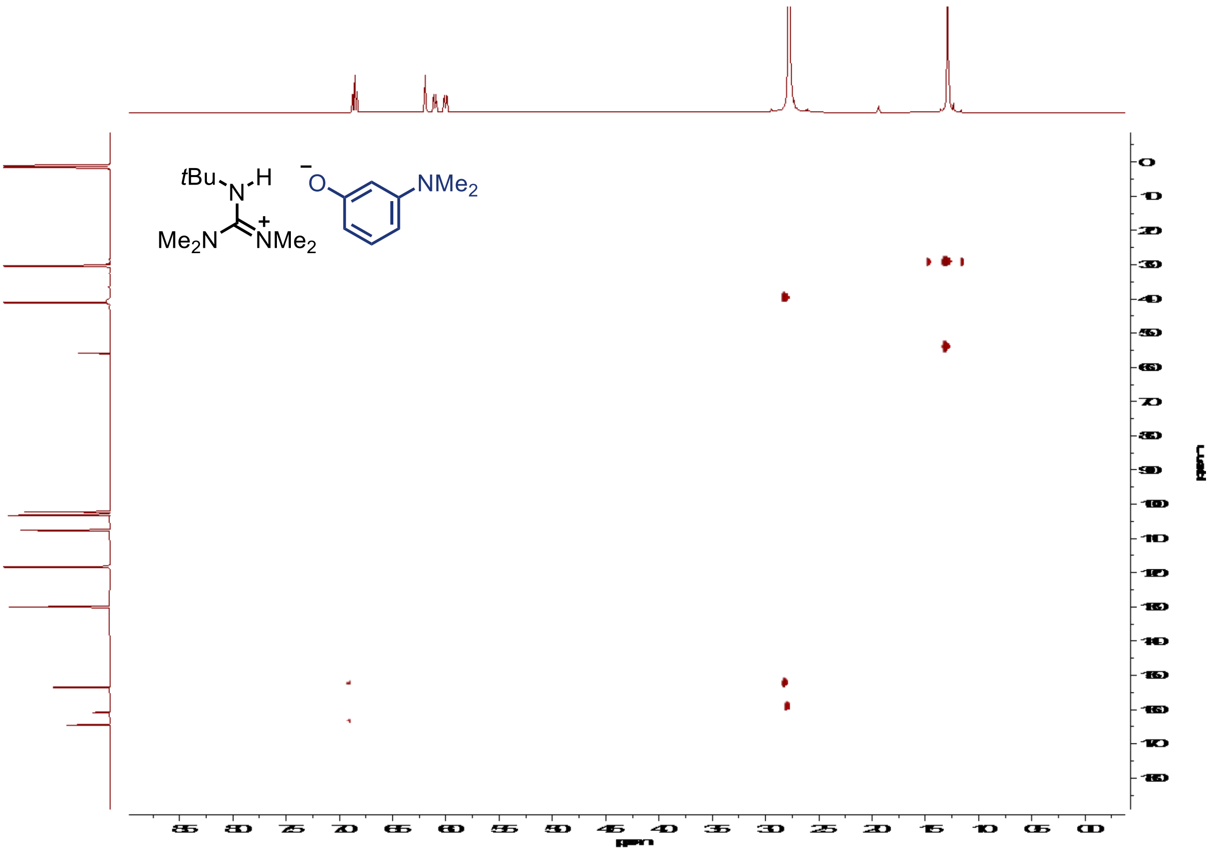
^{13}C NMR spectrum for BTMG-phenoxide ion pair **13** (101 MHz, MeCN-d$_3$)



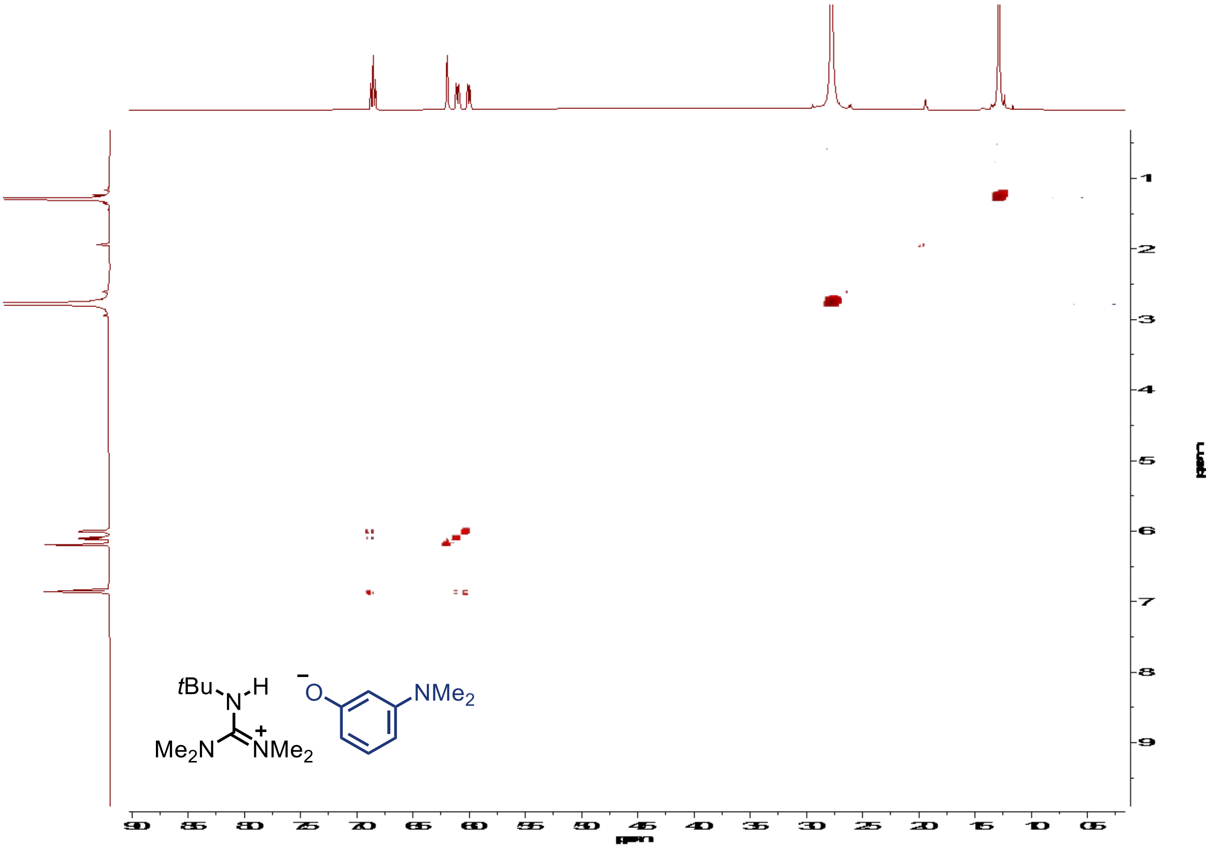
^{1}H-^{13}C HSQC spectrum for BTMG-phenoxide ion pair **13** (MeCN-d$_3$)



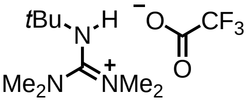
^{1}H-^{13}C HMBC spectrum for BTMG-phenoxide ion pair **13** (MeCN-d_3)



^{1}H-^{1}H COSY Spectrum for BTMG-phenoxide ion pair **13** (MeCN-d_3)

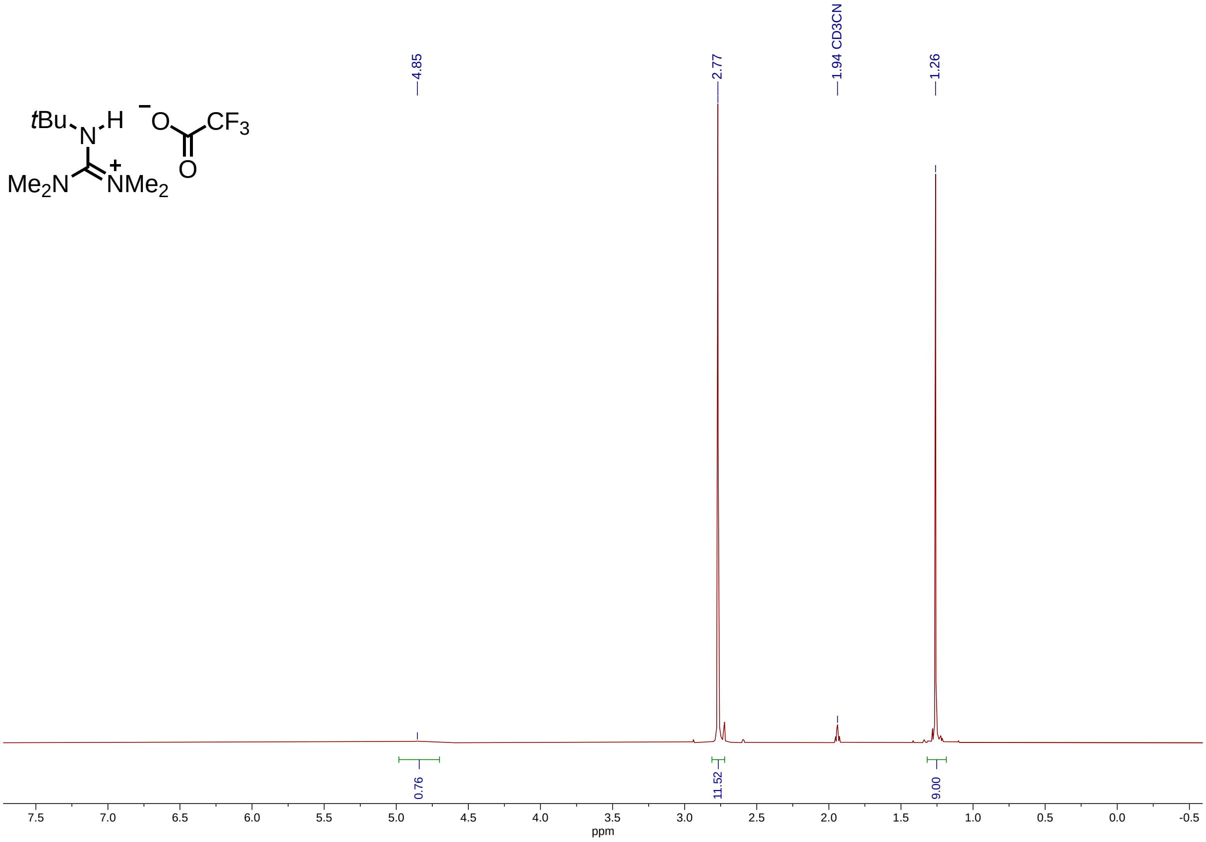


BTMG-trifluoroacetate ion pair (16)



To corroborate the formation of the BTMG-phenoxide ion pair **13** in the SuFEx catalytic cycle, synthesis of the trifluoroacetate ion pair of BTMG was carried out. To a stirred solution of BTMG (80.6 μL, 0.40 mmol) in MeCN (0.5 mL) was added trifluoroacetic acid (30.6 μL, 0.40 mmol). The resulting reaction was stirred for 2 h before being concentrated *in vacuo* to afford the title compound as a colorless oil. **^{1}H NMR** (400 MHz, MeCN-d_3) δ 4.85 (br s, 1H), 2.77 (s, 12H), 1.26 (s, 9H); **^{13}C NMR** (101 MHz, MeCN-d_3) δ 162.1, 160.1 (q, *J* = 31.3 Hz), 118.7 (q, *J* = 298.4 Hz), 57.0, 41.0 (m), 29.9; **IR** ν_{max} (ATR)/cm^{-1}: 3251, 2975, 1688, 1612, 1566, 1473, 1432, 1403, 1372, 1320, 1197, 1161, 1117, 1065, 1052, 886, 823, 799, 717, 519, 476.

^{1}H NMR spectrum for the BTMG-trifluoroacetate ion pair (**16**) (400 MHz, MeCN-d_3)



^{13}C NMR spectrum for the BTMG-trifluoroacetate ion pair (**16**) (101 MHz, CDCl$_3$)

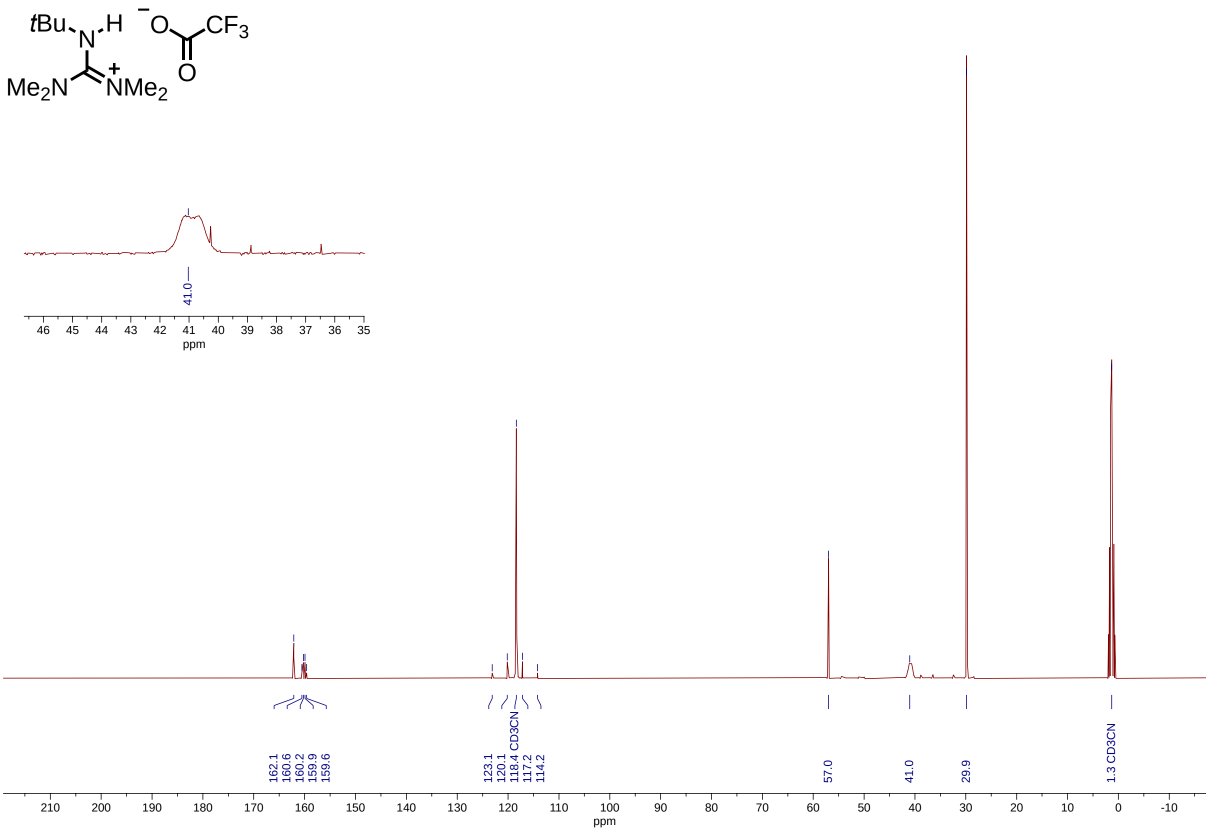
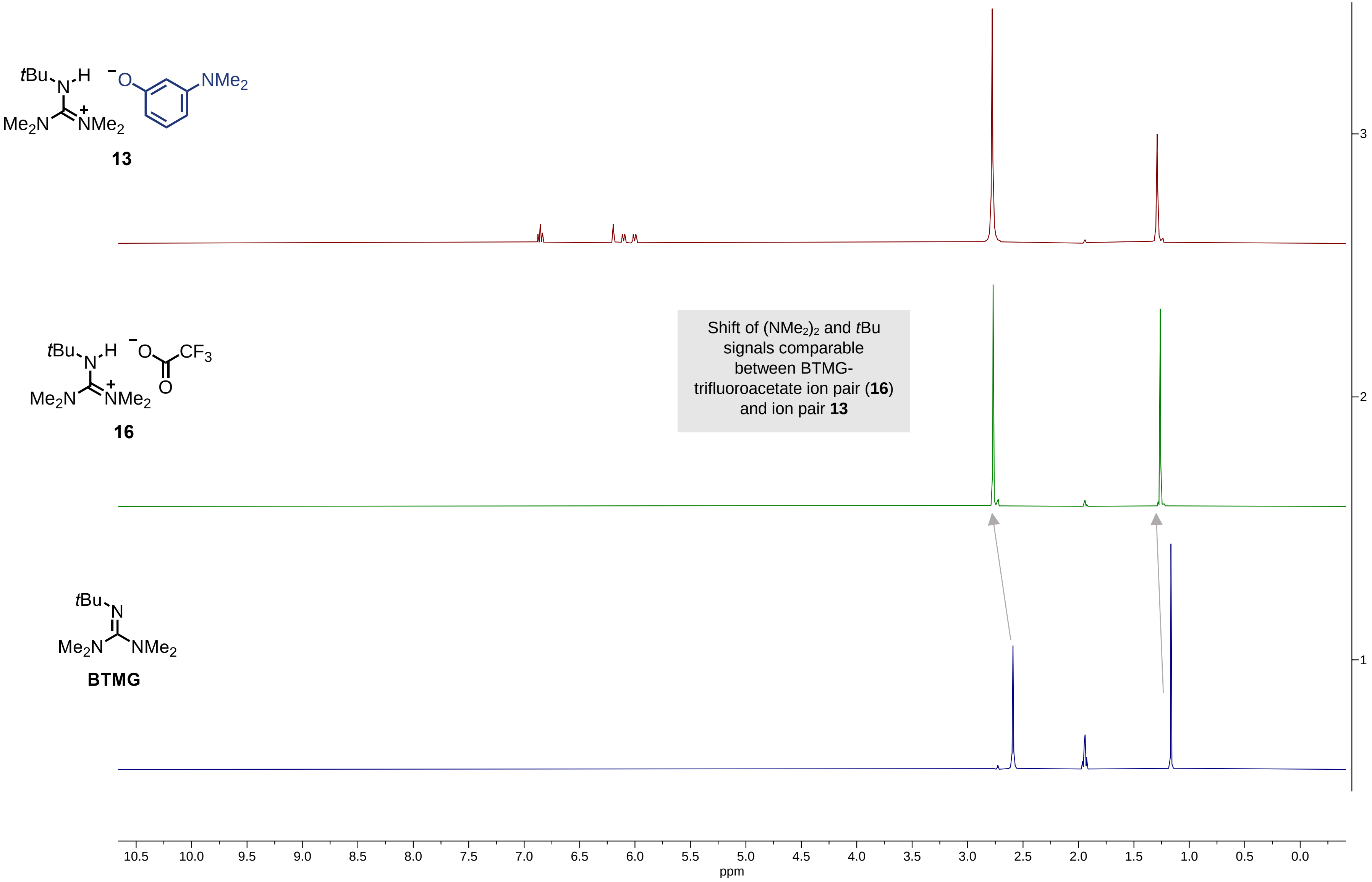
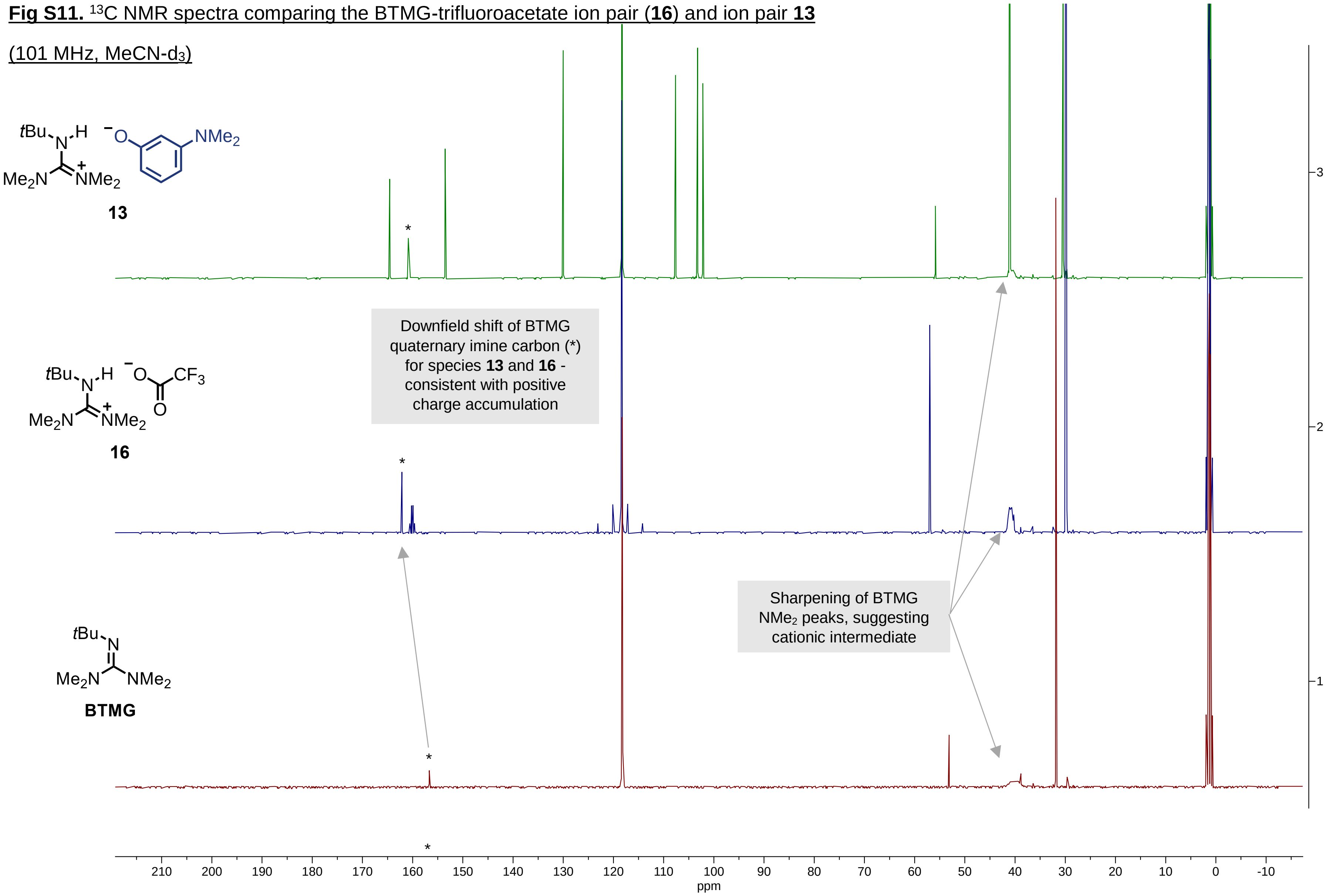


Fig S10. ^{1}H NMR spectra comparing the BTMG-trifluoroacetate ion pair (**16**) and ion pair **13** (400 MHz, MeCN-d_3)



Shift of $(NMe_2)_2$ and *t*Bu signals comparable between BTMG-trifluoroacetate ion pair (**16**) and ion pair **13**

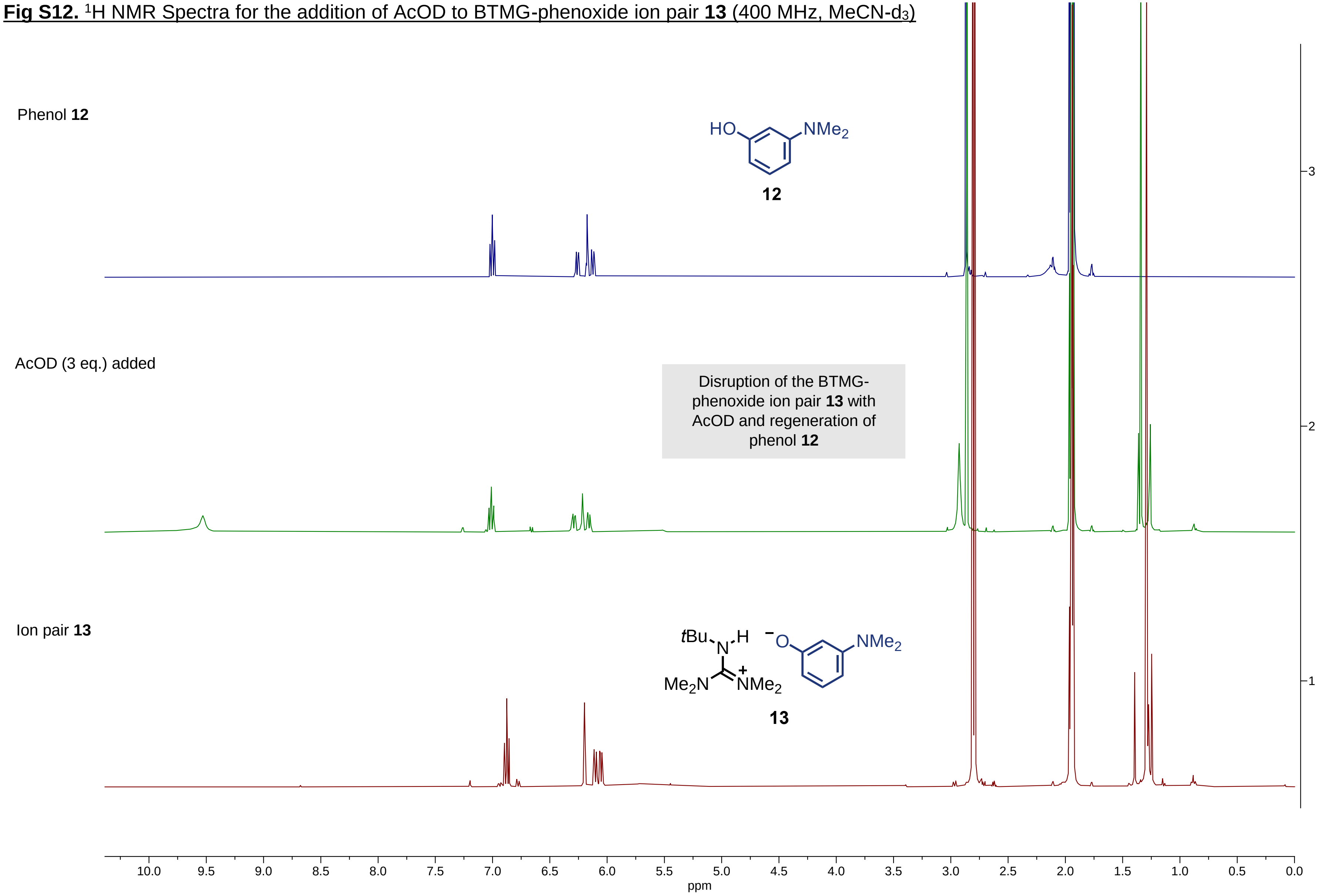
Fig S11. ^{13}C NMR spectra comparing the BTMG-trifluoroacetate ion pair (**16**) and ion pair **13** (101 MHz, MeCN-d$_3$)



Downfield shift of BTMG quaternary imine carbon (*) for species **13** and **16** - consistent with positive charge accumulation

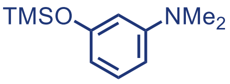
Sharpening of BTMG NMe$_2$ peaks, suggesting cationic intermediate

Fig S12. ^{1}H NMR Spectra for the addition of AcOD to BTMG-phenoxide ion pair **13** (400 MHz, MeCN-d_3)



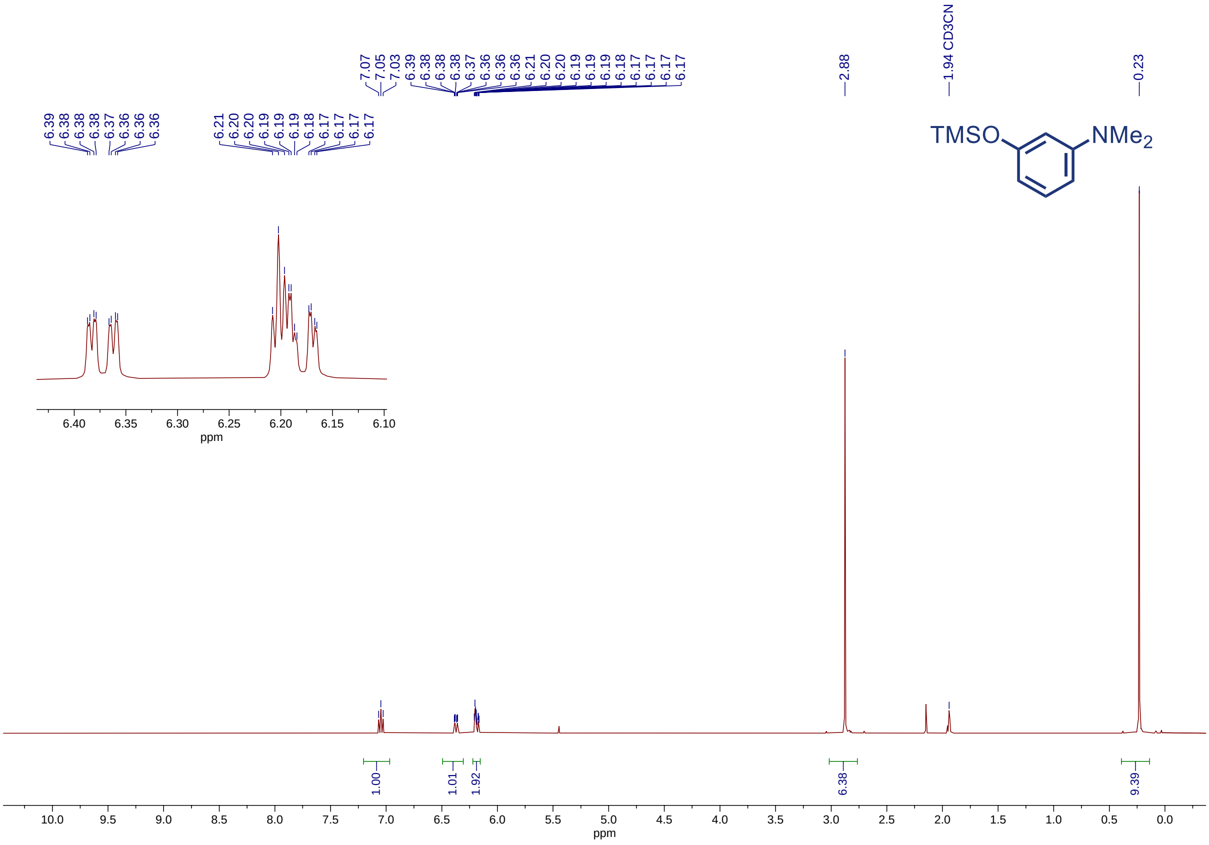
Disruption of the BTMG-phenoxide ion pair **13** with AcOD and regeneration of phenol **12**

3-Dimethylamino-*O*-trimethylsilylphenol (14)

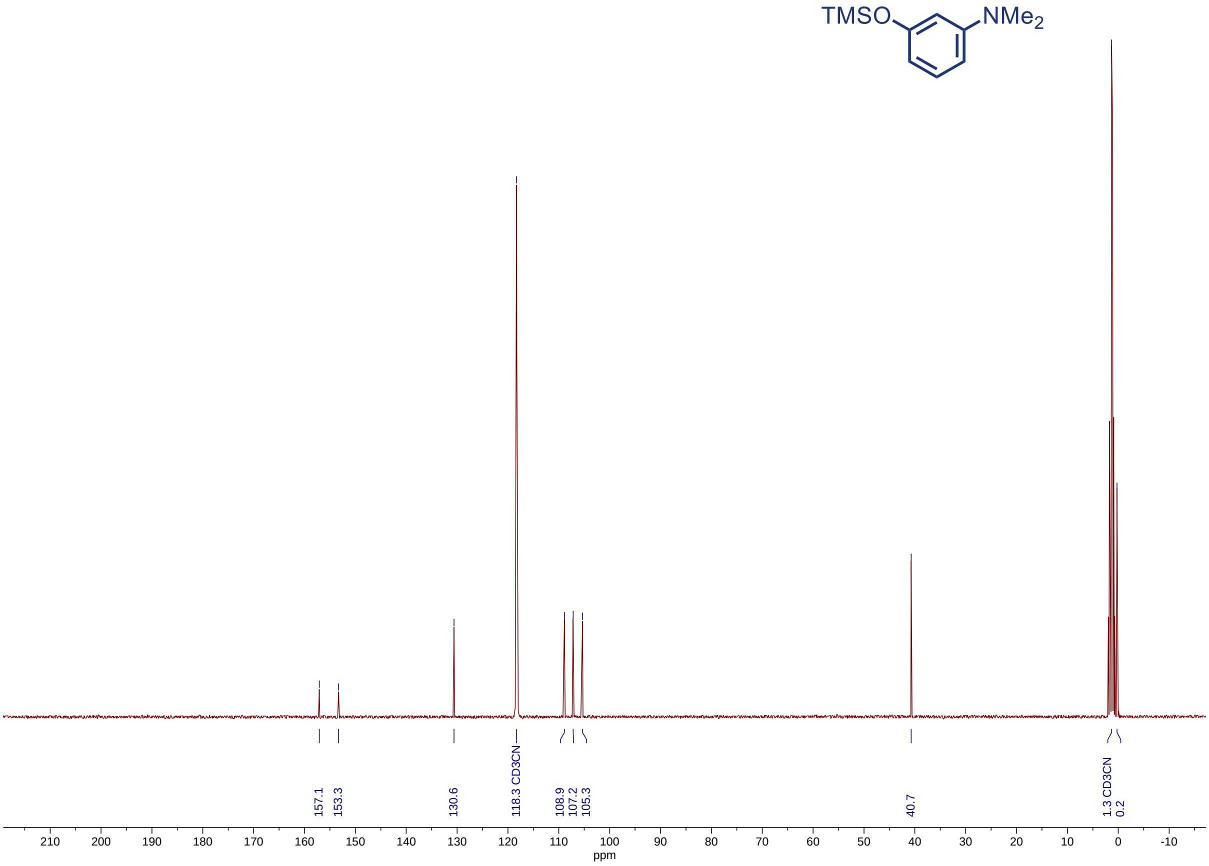


As a suspected catalytic intermediate, the TMS ether of phenol **12** was synthesized and subjected to BTMG mediated SuFEx conditions. 3-Dimethylaminophenol (500 mg, 3.65 mmol) and 4-dimethylaminopyridine (89 mg, 0.73 mmol, 20 mol%) were taken up in dichloromethane (35 mL) and cooled to 0 °C. Triethylamine (0.76 mL, 5.47 mmol) was slowly added and the reaction mixture was stirred for 10 min. Trimethylsilyl chloride (0.55 mL, 4.37 mmol) in dichloromethane (15 mL) was added dropwise. The resulting reaction was then warmed to room temperature and allowed to stir for 1 h. After this time, the reaction was cooled back to 0 °C and an additional portion of trimethylsilyl chloride (0.55 mL, 4.37 mmol) in dichloromethane (15 mL) was added. After a further 3 h stirring at room temperature, the reaction was concentrated *in vacuo* and the resulting crude was purified by flash column chromatography to afford the title compound as a dark brown oil (492 mg, 64%). ^{1}**H NMR** (400 MHz, MeCN-d$_3$) δ 7.05 (t, *J* = 8.1 Hz, 1H), 6.37 (ddd, *J* = 8.3, 2.5, 0.9 Hz, 1H), 6.21–6.17 (m, 2H), 2.88 (s, 6H), 0.23 (s, 9H); ^{13}**C NMR** (101 MHz, MeCN-d$_3$) δ 157.1, 153.3, 130.6, 108.9, 107.2, 105.3, 40.7, 0.2; **HRMS** (ESI): *m/z* calcd for $C_{11}H_{19}NOS+H^+$: 210.1309 [M+H]$^+$; found: 210.1303; **IR** ν_{max} (ATR)/cm^{-1}: 2959, 2807, 1602, 1574, 1498, 1448, 1353, 1242, 1151, 1061, 1003, 986, 925, 838, 756, 686.

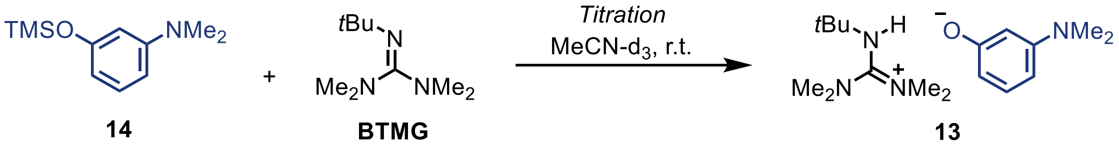
^{1}H NMR spectrum for compound **14** (400 MHz, MeCN-d$_3$)



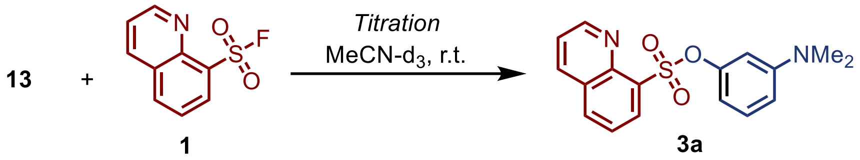
^{13}C NMR spectrum for compound **14** (101 MHz, MeCN-d_3)



Titration of BTMG to TMS ether 14 monitored by ^{1}H NMR (MeCN-d$_3$)

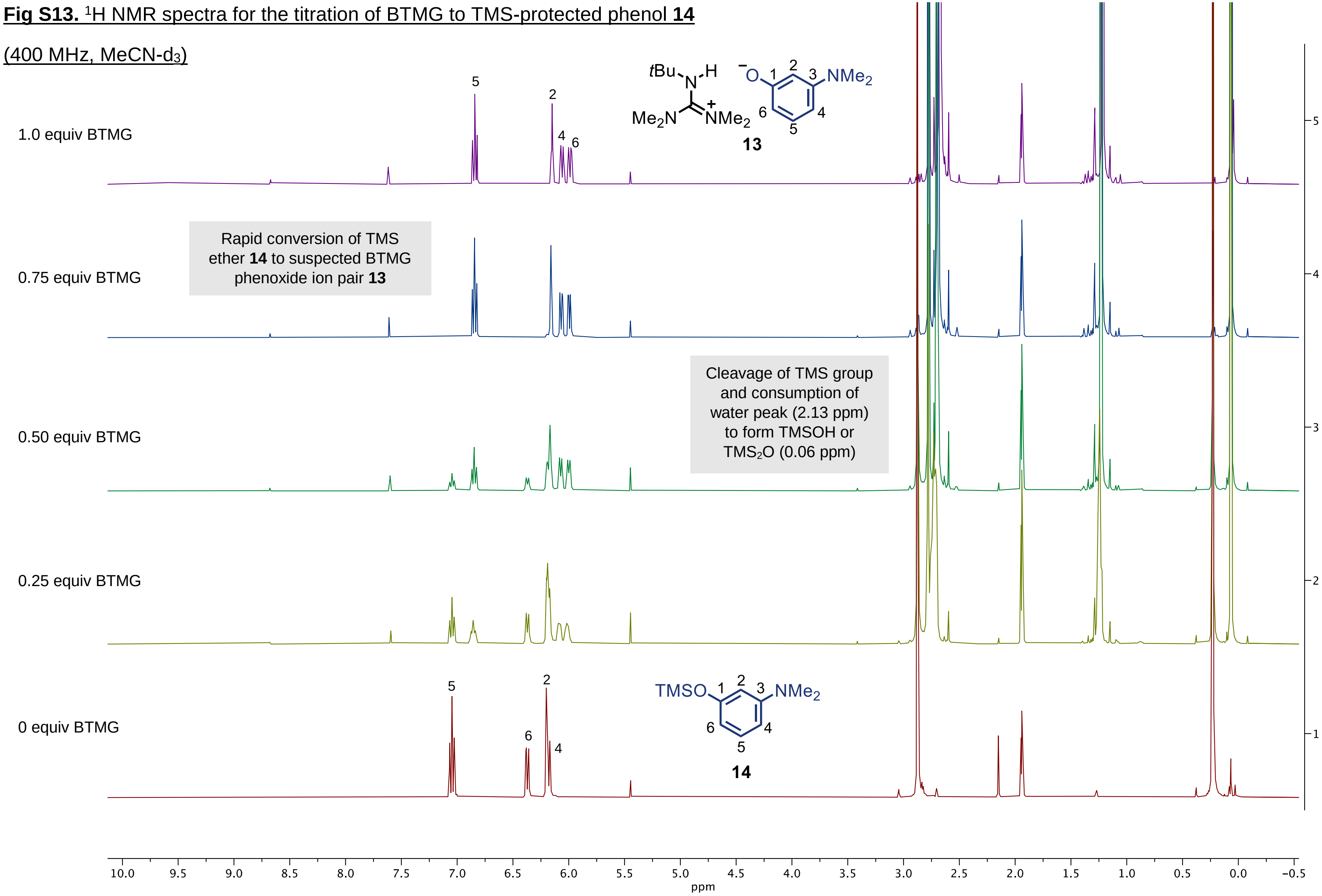


TMS ether **14** (0.05 mmol) was added to MeCN-d$_3$ (0.5 mL) in an NMR tube and vortexed before an initial ^{1}H NMR was taken. A solution of BTMG (0.05 mmol) in MeCN-d$_3$ (0.4 mL) was prepared. Aliquots of this solution (0.1 mL) were added to the NMR tube followed by immediate NMR analysis. Characterization of intermediate **13** was carried out after evaporation of the deuterated solvent under a stream of nitrogen and resuspension in MeCN-d$_3$.



Once characterized, a SuFEx reaction with sulfonyl fluoride **1** was carried out as previously described.

Fig S13. ^{1}H NMR spectra for the titration of BTMG to TMS-protected phenol **14** (400 MHz, MeCN-d_3)



Rapid conversion of TMS ether **14** to suspected BTMG phenoxide ion pair **13**

Cleavage of TMS group and consumption of water peak (2.13 ppm) to form TMSOH or TMS_2O (0.06 ppm)

Fig S14. ^{1}H NMR spectra (-1.0–5.0 ppm) for the titration of BTMG to TMS-protected phenol **14** (400 MHz, MeCN-d$_3$)

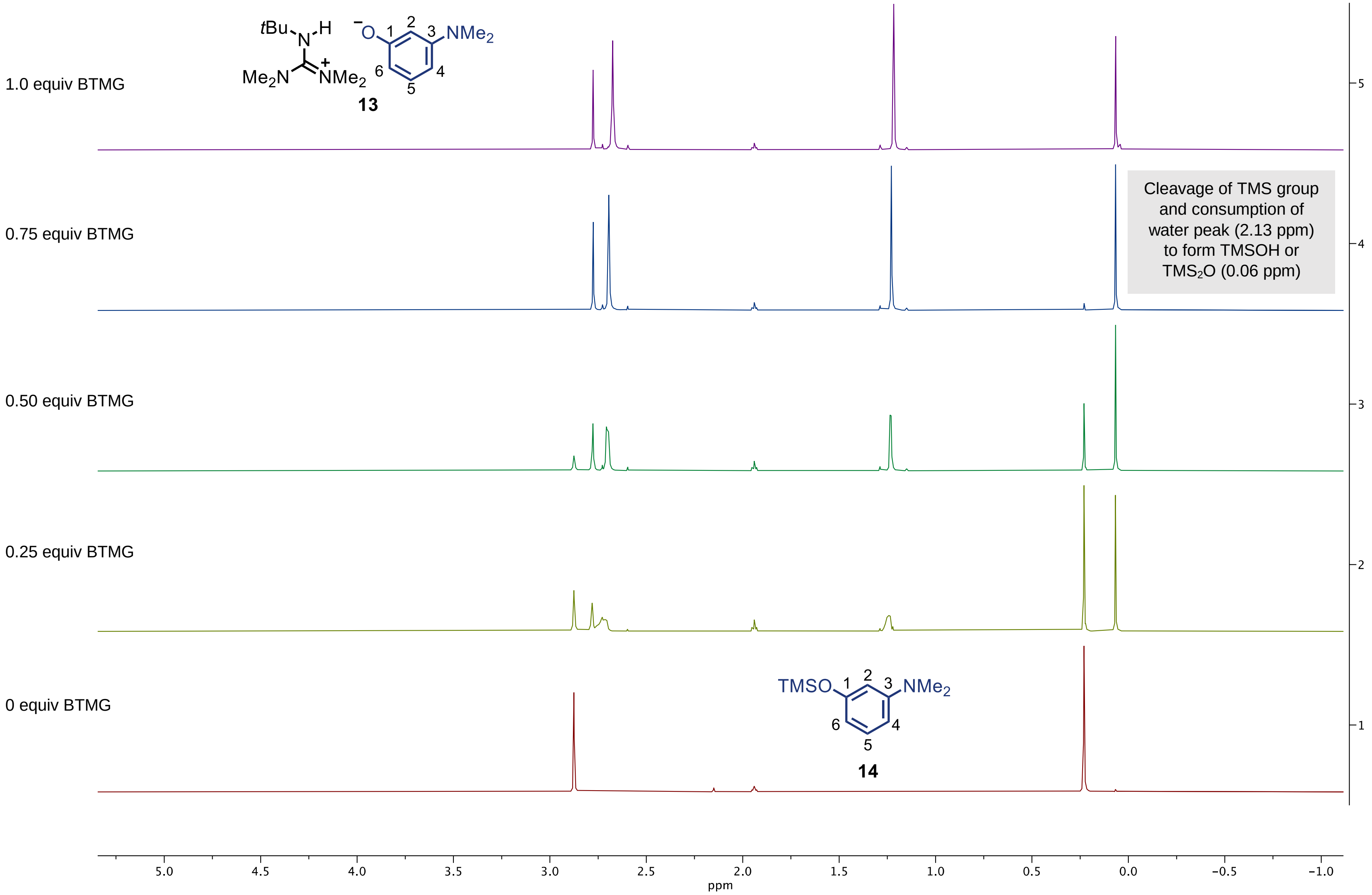
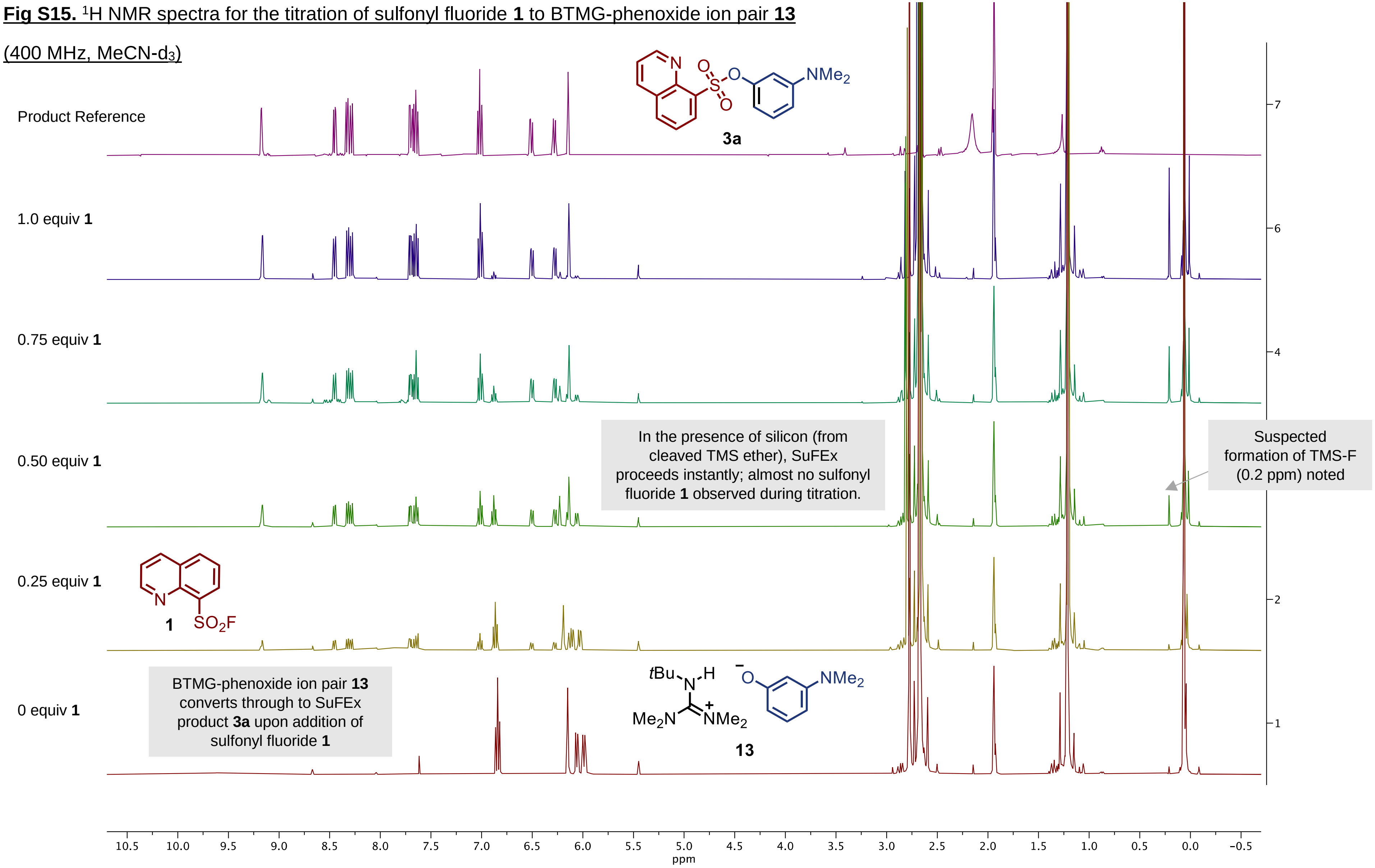


Fig S15. ^1H NMR spectra for the titration of sulfonyl fluoride **1** to BTMG-phenoxide ion pair **13** (400 MHz, MeCN-d_3)

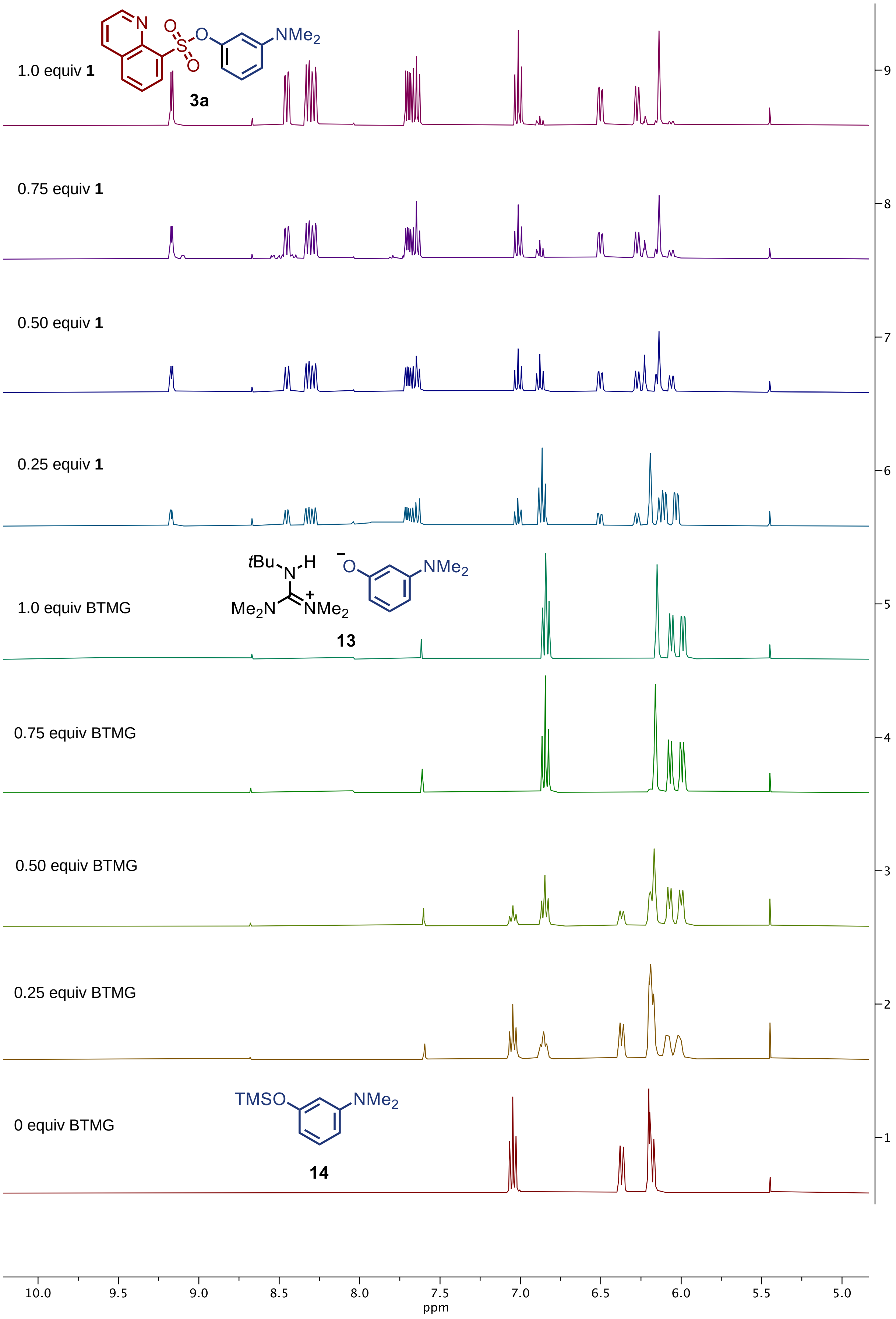


In the presence of silicon (from cleaved TMS ether), SuFEx proceeds instantly; almost no sulfonyl fluoride **1** observed during titration.

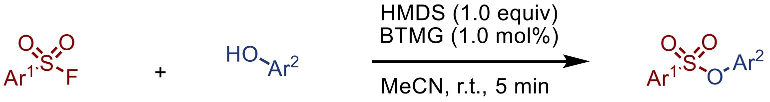
Suspected formation of TMS-F (0.2 ppm) noted

BTMG-phenoxide ion pair **13** converts through to SuFEx product **3a** upon addition of sulfonyl fluoride **1**

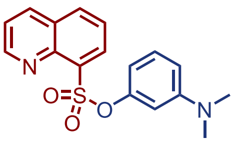
Fig S16. ^{1}H NMR spectra (5.8–9.6 ppm) for the titration of BTMG to TMS-protected phenol **14** and subsequent titration of sulfonyl fluoride **1** (400 MHz, MeCN-d



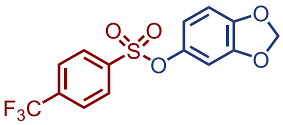
Synthesis and Experimental Data for Sulfonates 3a–3x



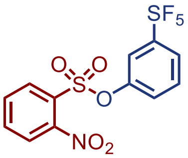
3



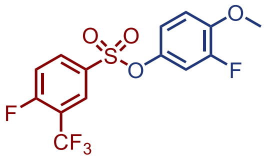
3a[a]
97%



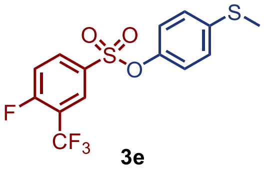
3b
>99%



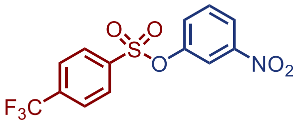
3c
>99%



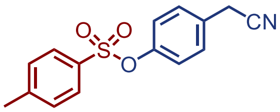
3d[a]
92%



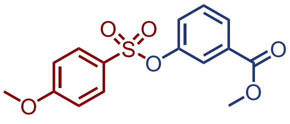
3e
95%



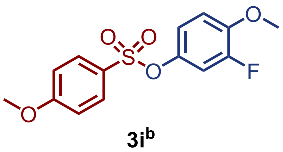
3f
99%



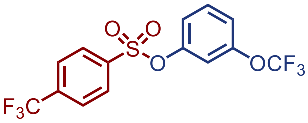
3g
>99%



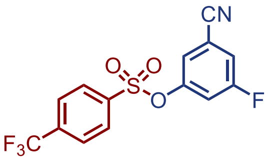
3h[b]
>99%



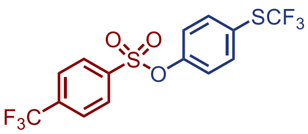
3i[b]
94%



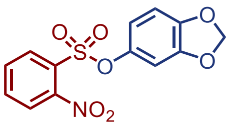
3j
95%



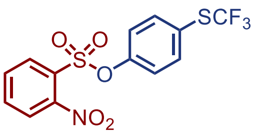
3k[c]
86%



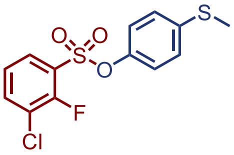
3l
>99%



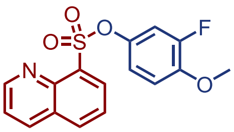
3m
>99%



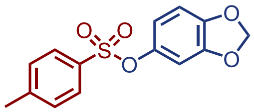
3n
>99%



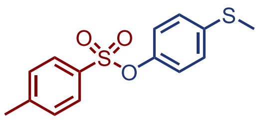
3o
73%



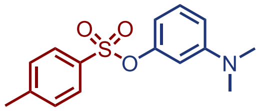
3p[a]
>99%



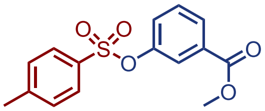
3q[c]
>99%



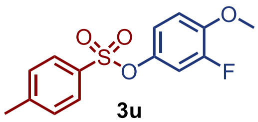
3r[a]
97%



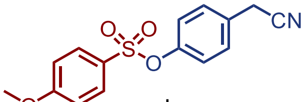
3s
97%



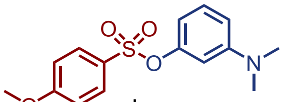
3t
84%



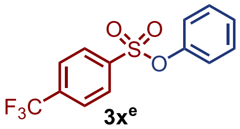
3u
97%



3v[d]
>99%



3w[d]
94%



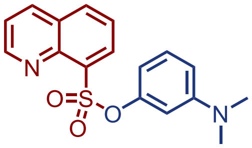
3x[e]
89%

[a] Reaction stirred for 30 min using 5 mol% BTMG; [b] Reaction stirred for 60 min using 10 mol% BTMG; [c] Reaction stirred for 10 min; [d] Reaction stirred for 30 min using 10 mol% BTMG; [e] Reaction conducted on a 2.2 mmol scale, stirred for 5 h.

General Procedure A:

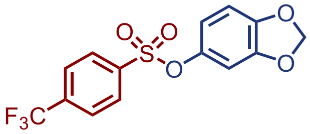
To a solution of the required sulfonyl fluoride (0.1 mmol) and the required phenol (0.1 mmol) in MeCN (0.5 mL) was added HMDS (0.1 mmol) and BTMG (1 mol%). The resulting reaction was stirred at room temperature for 5 min. Upon completion the solvent was removed and, if needed, crude was filtered through a short silica plug to obtain the analytically pure product.

3-(Dimethylamino)phenyl quinoline-8-sulfonate (3a)



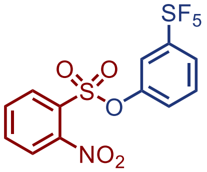
Following general procedure A (5 mol% BTMG, 30 min reaction time), the title compound was isolated as a yellow oil (32 mg, 97%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.25 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.38 (dd, *J* = 7.3, 1.1 Hz, 1H), 8.27 (dt, *J* = 12.9, 6.5 Hz, 1H), 8.10 (appt. d, *J* = 8.2 Hz, 1H), 7.60–7.54 (m, 2H), 6.97 (appt. t, *J* = 8.2 Hz, 1H), 6.45 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.33–6.26 (m, 1H), 6.27 (dd, *J* = 8.1, 1.2 Hz, 1H), 2.74 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.3, 151.5, 151.1, 144.3, 136.7, 135.2, 134.2, 133.1, 129.6, 129.0, 125.3, 122.6, 110.8, 109.2, 106.1, 40.2; **HRMS** (ESI): *m/z* calcd for $C_{17}H_{17}N_2O_3S^+$: 329.0954 [*M*+H]$^+$; found: 329.0957; **IR** ν_{max} (ATR)/cm^{-1}: 3019, 1611, 1570, 1566, 1508, 1501, 1215, 1177, 1126, 997.

Benzo[*d*][1,3]dioxol-5-yl 4-(trifluoromethyl)benzenesulfonate (3b)



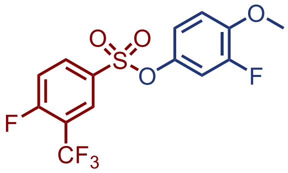
Following general procedure A, the title compound was isolated as a colourless solid (35 mg, >99%). **m.p.** 88.7–89.7 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (appt. d, *J* = 8.2 Hz, 2H), 7.81 (appt. d, *J* = 8.3 Hz, 2H), 6.66 (d, *J* = 8.5 Hz, 1H), 6.56 (d, *J* = 2.4 Hz, 1H), 6.37 (dd, *J* = 8.5, 2.4 Hz, 1H), 5.99 (s, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.4, 146.9, 143.5, 139.0, 136.0 (q, *J* = 33.3 Hz), 129.3, 126.5 (q, *J* = 3.7 Hz), 123.1 (q, *J* = 273.2 Hz), 115.1, 108.1, 104.3, 102.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.3; **HRMS** (ESI): *m/z* calcd for $C_{14}H_9F_3O_5S+Na^+$: 369.0015 [*M*+Na]$^+$; found: 369.0023; **IR** ν_{max} (ATR)/cm^{-1}: 3105, 2907, 1609, 1504, 1485, 1408, 1383, 1090, 1248, 1038, 1018, 943, 856.

3-(Pentafluoro-λ^6-sulfaneyl)phenyl 2-nitrobenzenesulfonate (3c)



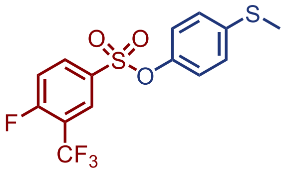
Following general procedure A, the title compound was isolated as a colourless oil (41 mg, >99%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 1H), 7.88–7.87 (m, 2H), 7.74–7.70 (m, 2H), 7.53–7.45 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.4 (p, *J* = 19.1 Hz), 148.9, 148.5, 136.1, 132.3, 132.3, 130.3, 127.9, 126.1, 125.4 (p, *J* = 4.8 Hz), 123.1 120.8 (p, *J* = 4.8 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ 83.1–81.5 (m), 62.8 (d, *J* = 150.6 Hz); **HRMS** (ESI): *m/z* calcd for $C_{12}H_8F_5NO_5S_2$+Na$^+$: 427.9656 [*M*+Na]$^+$; found: 427.9658; **IR** ν_{max} (ATR)/cm^{-1}: 3105, 2924, 1593, 1549, 1479, 1435, 1385, 1267, 1206, 1180, 1167, 1128, 1105, 1059, 924.

3-Fluoro-4-methoxyphenyl 4-fluoro-3-(trifluoromethyl)benzenesulfonate (3d)



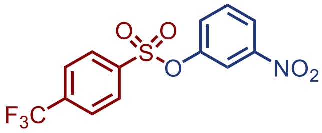
Following general procedure A (5 mol% BTMG, 30 min reaction time), the title compound was isolated as a colourless oil (34 mg, 92%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 6.3, 2.1 Hz, 1H), 8.04 (ddd, *J* = 8.6, 4.3, 2.5 Hz, 1H), 7.40 (appt. t, *J* = 9.1 Hz, 1H), 6.89 (appt. t, *J* = 9.0 Hz, 1H), 6.83 (dd, *J* = 10.9, 2.8 Hz, 1H), 6.74 (ddd, *J* = 9.0, 2.8, 1.7 Hz, 1H), 3.87 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.2 (dq, *J* = 267.7, 1.8 Hz), 152.0 (d, *J* = 250.7 Hz), 147.5 (d, *J* = 10.5 Hz), 141.8 (d, *J* = 9.3 Hz), 134.9 (d, *J* = 10.2 Hz), 132.0 (d, *J* = 3.9 Hz), 128.8–128.6 (m), 121.5 (qd, *J* = 273.2, 1.8 Hz), 120.2 (qd, *J* = 34.6, 13.6 Hz), 118.61 (d, *J* = 22.2 Hz), 118.03 (d, *J* = 4.0 Hz), 113.45 (d, *J* = 2.7 Hz), 111.36 (d, *J* = 21.6 Hz), 56.64; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -61.8 (d, *J* = 13.3 Hz), -102.9– -103.0 (m), -130.1 – -130.2 (m); **HRMS** (ESI): *m/z* calcd for $C_{14}H_9F_5O_4S$+Na$^+$: 391.0034 [*M*+Na]$^+$; found: 391.0038; **IR** ν_{max} (ATR)/cm^{-1}: 3080, 2940, 2847, 1620, 1591, 1514, 1393, 1250, 1221, 1192, 1109, 1057, 1026, 959.

4-(Methylthio)phenyl 4-fluoro-3-(trifluoromethyl)benzenesulfonate (3e)



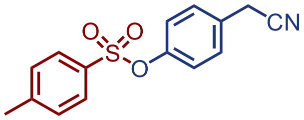
Following general procedure A, the title compound was isolated as a yellow oil (35 mg, 95%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 6.3, 2.3 Hz, 1H), 8.02 (ddd, *J* = 8.7, 4.4, 2.4 Hz, 1H), 7.38 (appt. t, *J* = 9.1 Hz, 1H), 7.18 (appt. d, *J* = 8.9 Hz, 2H), 6.92 (appt. d, *J* = 8.8 Hz, 2H), 2.46 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.1 (qd, *J* = 267.4, 1.8 Hz), 146.7, 138.8, 134.9 (d, *J* = 10.3 Hz), 132.2 (d, *J* = 3.9 Hz), 128.7 – 128.6 (m), 127.7, 122.7, 121.5 (qd, *J* = 273.4, 0.8 Hz), 120.1 (qd, *J* = 34.5, 13.8 Hz), 118.5 (d, *J* = 22.1 Hz), 16.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -61.8 (d, *J* = 13.3 Hz), -103.2 – -103.3 (m); **HRMS** (ESI): *m/z* calcd for $C_{14}H_{10}F_4O_3S_2+Na^+$: 388.9900 [*M*+Na]$^+$; found: 388.9904; **IR** ν_{max} (ATR)/cm^{-1}: 3021, 1618, 1591, 1487, 1387, 1321, 1215, 1198, 1180, 1153, 1099, 1058, 878.

3-Nitrophenyl 4-(trifluoromethyl)benzenesulfonate (3f)



Following general procedure A, the title compound was isolated as an orange solid (35 mg, 99%). **m.p.** 109.7–110.6 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20 (ddd, *J* = 8.3, 2.1, 1.0 Hz, 1H), 8.05 (appt. d, *J* = 8.2 Hz, 2H), 7.91 (appt. t, *J* = 2.2 Hz, 1H), 7.88 (appt. d, *J* = 8.3 Hz, 2H), 7.58 (appt. t, *J* = 8.2 Hz, 1H), 7.44 (ddd, *J* = 8.2, 2.3, 1.0 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.4, 149.0, 138.5, 136.6 (q, *J* = 33.5 Hz), 130.8, 129.2, 128.6, 126.9 (q, *J* = 3.7 Hz), 123.0 (q, *J* = 273.4 Hz), 122.6, 118.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.4; **HRMS** (ESI): *m/z* calcd for $C_{13}H_8F_3NO_5S+Na^+$: 369.9967 [*M*+Na]$^+$; found: 369.9977; **IR** ν_{max} (ATR)/cm^{-1}: 2953, 2926, 2855, 1537, 1408, 1389, 1354, 1323, 1265, 1179, 1140, 1063, 934.

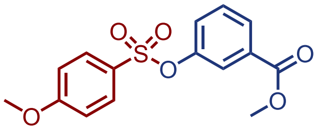
4-(Cyanomethyl)phenyl 4-methylbenzenesulfonate (3g)[1]



Following general procedure A, the title compound was isolated as a colourless solid (29 mg, >99%). **m.p.** 80.4–82.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (appt. d, *J* = 8.3 Hz, 2H), 7.32 (appt. d, *J* = 8.3 Hz, 2H), 7.26 (appt. d, *J* = 8.4 Hz, 2H), 7.00 (appt. d, *J* = 8.6 Hz, 2H), 3.72 (s, 2H), 2.46 (s, 3H); **^{13}C NMR** (101 MHz,

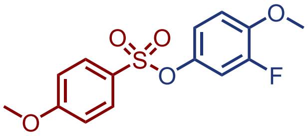
$CDCl_3$) δ 149.5, 145.8, 132.3, 130.0, 129.4, 129.0, 128.6, 123.3, 117.4, 23.2, 21.9; **HRMS** (ESI): *m/z* calcd for $C_{15}H_{13}NO_3S+Na^+$: 310.0508 [*M*+Na]$^+$; found: 310.0510; **IR** ν_{max} (ATR)/cm^{-1}: 3021, 1597, 1504, 1375, 1215, 1179, 1155, 1094, 866.

Methyl 3-(((4-methoxyphenyl)sulfonyl)oxy)benzoate (3h)



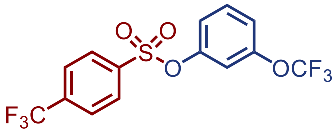
Following general procedure A (10 mol% BTMG, 60 min reaction time), the title compound was isolated as a low melting colourless solid (32 mg, >99%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93–7.91 (m, 1H), 7.75 (appt. d, *J* = 9.1 Hz, 2H), 7.66 (dd, *J* = 2.1, 1.6 Hz, 1H), 7.37 (appt. t, *J* = 8.0 Hz, 1H), 7.20 (ddd, *J* = 8.2, 2.5, 1.1 Hz, 1H), 6.97 (appt. d, *J* = 9.0 Hz, 2H), 3.89 (s, 3H), 3.88 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8, 164.4, 149.7, 132.1, 130.9, 129.8, 128.3, 127.0, 126.5, 123.7, 114.6, 55.9, 52.5; **HRMS** (ESI): *m/z* calcd for $C_{15}H_{14}O_6S+Na^+$: 345.0403 [*M*+Na]$^+$; found: 345.0408; **IR** ν_{max} (ATR)/cm^{-1}: 2951, 2924, 1726, 1595, 1499, 1443, 1375, 1296, 1267, 1198, 1169, 1094, 1024, 897, 816.

3-Fluoro-4-methoxyphenyl 4-methoxybenzenesulfonate (3i)



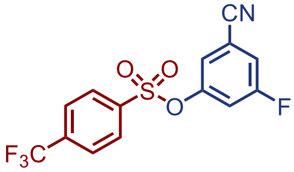
Following general procedure A (10 mol% BTMG, 60 min reaction time), the title compound was isolated as a colourless oil (29 mg, 94%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (appt. d, *J* = 9.1 Hz, 2H), 6.97 (appt. d, *J* = 9.0 Hz, 2H), 6.85–6.81 (m, 1H), 6.76–6.72 (m, 2H), 3.88 (s, 3H), 3.84 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.4, 151.8 (d, *J* = 249.3 Hz), 146.9 (d, *J* = 10.5 Hz), 142.5 (d, *J* = 9.4 Hz), 130.9, 126.4, 118.4 (d, *J* = 3.9 Hz), 114.5, 113.2 (d, *J* = 2.6 Hz), 111.5 (d, *J* = 21.3 Hz), 56.6, 55.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -131.2 (appt. t, *J* = 9.8 Hz); **HRMS** (ESI): *m/z* calcd for $C_{14}H_{13}FO_5S+Na^+$: 335.0360 [*M*+Na]$^+$; found: 335.0363; **IR** ν_{max} (ATR)/cm^{-1}: 2941, 2843, 1597, 1578, 1510, 1373, 1194, 1171, 1094, 1026, 959, 818.

3-(Trifluoromethoxy)phenyl 4-(trifluoromethyl)benzenesulfonate (3j)



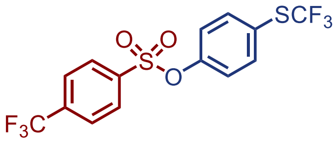
Following general procedure A, the title compound was isolated as a colourless oil (37 mg, 95%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (appt. d, *J* = 8.2 Hz, 2H), 7.82 (appt. d, *J* = 8.3 Hz, 2H), 7.38 (appt. t, *J* = 8.3 Hz, 1H), 7.18 – 7.15 (m, 1H), 7.04 (ddd, *J* = 8.3, 2.2, 0.8 Hz, 1H), 6.83 – 6.81 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.8, 149.7 (q, *J* = 1.8 Hz), 138.6, 136.4 (q, *J* = 33.4 Hz), 130.9, 129.2, 126.7 (q, *J* = 3.7 Hz), 123.0 (q, *J* = 273.3 Hz), 121.0, 120.3 (q, *J* = 258.7 Hz), 120.2, 115.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.2, -63.5; **HRMS** (ESI): *m/z* calcd for $C_{14}H_8F_6O_4S+Na^+$: 408.9940 [*M*+Na]$^+$; found: 408.9904; **IR** ν$_{max}$ (ATR)/cm^{-1}: 1599, 1485, 1408, 1387, 1323, 1265, 1194, 1179, 1142. 976.

3-Cyano-5-fluorophenyl 4-(trifluoromethyl)benzenesulfonate (3k)



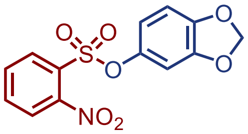
Following general procedure A (10 min reaction time), the title compound was isolated as a colourless solid (30 mg, 86%). **m.p.** 82.7–85.3 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (appt. d, *J* = 8.2 Hz, 2H), 7.89 (appt. d, *J* = 8.3 Hz, 2H), 7.34 (ddd, *J* = 7.5, 2.4, 1.3 Hz, 1H), 7.20 – 7.18 (m, 1H), 7.13 (dt, *J* = 8.5, 2.3 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.6 (d, *J* = 254.6 Hz), 150.3 (d, *J* = 11.1 Hz), 138.3, 136.8 (q, *J* = 33.6 Hz), 129.2, 127.0 (q, *J* = 3.7 Hz), 122.9 (q, *J* = 273.4 Hz), 122.1 (d, *J* = 4.0 Hz), 118.7 (d, *J* = 24.5 Hz), 116.2 (d, *J* = 3.5 Hz), 115.7 (d, *J* = 24.5 Hz), 115.0 (d, *J* = 10.9 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.4, -105.0 (t, *J* = 8.7 Hz); **HRMS** (ESI): *m/z* calcd for $C_{14}H_7F_4NO_3S+Na^+$: 367.9975 [*M*+Na]$^+$; found: 367.9982; **IR** ν$_{max}$ (ATR)/cm^{-1}: 1593, 1408, 1391, 1321, 1265, 1196, 1063, 991.

4-((Trifluoromethyl)thio)phenyl 4-(trifluoromethyl)benzenesulfonate (3l)



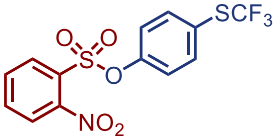
Following general procedure A, the title compound was isolated as a colourless solid (40 mg, >99%). **m.p.** 50.3–51.6 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (appt. d, *J* = 8.2 Hz, 1H), 7.83 (appt. d, *J* = 8.3 Hz, 2H), 7.63 (appt. d, *J* = 8.7 Hz, 1H), 7.09 (appt. d, *J* = 8.8 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.3, 138.9, 138.1, 136.4 (q, *J* = 33.4 Hz), 129.4 (q, *J* = 308.4 Hz), 129.2, 126.7 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 2.2 Hz), 123.4; 123.0 (q, *J* = 273.3 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -42.6, -63.4; **HRMS** (ESI): *m/z* calcd for $C_{14}H_8F_6O_3S_2$+Na^+: 424.9711 [*M*+Na]$^+$; found: 424.9718; **IR** v_{max} (ATR)/cm^{-1}: 3105, 2924, 2853, 1584, 1487, 1408. 1389, 1323, 1206, 1180, 1157, 1134, 1119, 1018.

Benzo[*d*][1,3]dioxol-5-yl 2-nitrobenzenesulfonate (3m)[2]



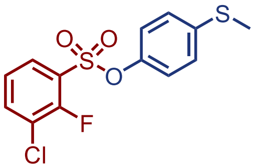
Following general procedure A, the title compound was isolated as a colourless solid (32 mg, >99%). **m.p.** 126.0–127.8 °C (lit. 126-127 °C);[2] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97–7.95 (m, 1H), 7.85–7.81 (m, 2H), 7.69 (ddd, *J* = 8.0, 5.6, 3.3 Hz, 1H), 6.73 (d, *J* = 2.3 Hz, 1H), 6.69 (d, *J* = 8.5 Hz, 1H), 6.64 (dd, *J* = 8.5, 2.4 Hz, 1H), 5.99 (s, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.4, 147.0, 143.2, 135.6, 132.4, 132.1, 128.4, 125.0, 115.3, 108.2, 104.4, 102.3; **HRMS** (ESI): *m/z* calcd for $C_{13}H_9F_5NO_7S$+Na^+: 345.9992 [*M*+Na]$^+$; found: 345.9993; **IR** v_{max} (ATR)/cm^{-1}: 3100, 2918, 1547, 1504, 1483, 1385, 1248, 1194, 1165, 1111, 1092, 1037.

4-((Trifluoromethyl)thio)phenyl 2-nitrobenzenesulfonate (3n)



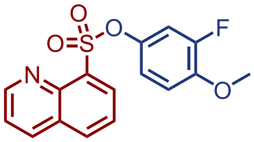
Following general procedure A, the title compound was isolated as a colourless solid (38 mg, >99%). **m.p.** 80.3–82.6 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.9 Hz, 1H), 7.87 (d, *J* = 4.2 Hz, 2H), 7.75–7.70 (m, 1H), 7.66 (appt. d, *J* = 8.4 Hz, 2H), 7.29 (appt. d, *J* = 8.5 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.1, 148.9, 138.1, 135.9, 132.3, 132.2, 129.4 (q, *J* = 308.3 Hz), 128.3, 125.2, 124.2 (q, *J* = 2.2 Hz), 123.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -42.6 (s); **HRMS** (ASAP): *m/z* calcd for $C_{13}H_8F_3NO_5S_2$+Na^+: 401.9688 [*M*+Na]$^+$; found: 401.9685; **IR** v_{max} (ATR)/cm^{-1}: 3030, 2922, 1597, 1487, 1373, 1198, 1177, 1157, 1092, 862.

4-(Methylthio)phenyl 3-chloro-2-fluorobenzenesulfonate (3o)



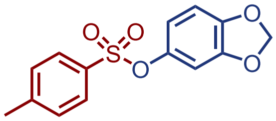
Following general procedure A, the title compound was isolated as a colourless oil (24 mg, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74–7.67 (m, 2H), 7.23 (appt. td, *J* = 8.0, 1.2 Hz, 1H), 7.18 (appt. d, *J* = 8.9 Hz, 2H), 7.05 (appt. d, *J* = 8.8 Hz, 2H), 2.45 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.3 (d, *J* = 262.0 Hz), 146.7, 138.6, 137.2, 129.8, 127.7, 125.4 (d, *J* = 13.9 Hz), 124.9 (d, *J* = 5.1 Hz), 123.6 (d, *J* = 17.5 Hz), 122.5, 16.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -108.0 (appt. t, *J* = 6.0 Hz); **HRMS** (ESI): *m/z* calcd for $C_{13}H_{10}ClFO_3S_2$+Na^+: 354.9636 [*M*+Na]$^+$; found: 354.9633; **IR** ν_{max} (ATR)/cm^{-1}: 3080, 1593, 1504, 1462, 1450, 1427, 1416, 1323, 1281, 1217, 1150, 1134, 1067, 920.

3-Fluoro-4-methoxyphenyl quinoline-8-sulfonate (3p)



Following general procedure A (5 mol% BTMG, 30 min reaction time), the title compound was isolated as a grey solid (32 mg, >99%). **m.p.** 131.4–133.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.24 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.37 (d, *J* = 7.4 Hz, 1H), 8.30 (dd, *J* = 8.3, 1.5 Hz, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 7.64–7.58 (m, 2H), 6.84–6.74 (m, 3H), 3.79 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.5, 151.8 (d, *J* = 249.0 Hz), 146.8 (d, *J* = 10.5 Hz), 144.1, 142.6 (d, *J* = 9.6 Hz), 136.8, 135.6, 134.3, 132.5, 129.1, 125.4, 122.8, 118.2 (d, *J* = 3.9 Hz), 113.2 (d, *J* = 2.6 Hz), 111.3 (d, *J* = 21.5 Hz), 56.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -131.4 (appt. t, *J* = 9.7 Hz); **HRMS** (ESI): *m/z* calcd for $C_{16}H_{13}FNO_4S^+$: 334.0544 [*M*+H]$^+$; found: 334.0547; **IR** ν_{max} (ATR)/cm^{-1}: 3015, 1597, 1560, 1508, 1460, 1443, 1279, 1258, 1219, 1179, 1134, 1105, 1026, 959, 845, 818.

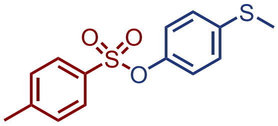
Benzo[*d*][1,3]dioxol-5-yl 4-methylbenzenesulfonate (3q)[2]



Following general procedure A (10 min reaction time), the title compound was isolated as a colourless solid (28 mg, >99%). **m.p.** 84.7–86.1 °C (lit. 84–85 °C);[2] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (appt. d, *J* = 8.3 Hz, 2H), 7.32 (appt. d, *J* = 8.0 Hz, 2H), 6.64 (d, *J* = 8.5 Hz, 1H), 6.53 (d, *J* = 2.4 Hz, 1H), 6.38 (dd, *J* = 8.5, 2.4

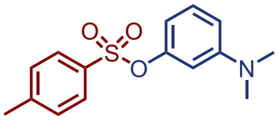
Hz, 1H), 5.96 (s, 2H), 2.45 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.1, 146.5, 145.5, 143.9, 132.4, 129.9, 128.7, 115.4, 108.0, 104.6, 102.1, 21.9; **HRMS** (ESI): *m/z* calcd for $C_{14}H_{13}O_5S^+$: 293.0478 [*M*+H]$^+$; found: 293.0484; **IR** ν_{max} (ATR)/cm^{-1}: 2920, 1597, 1503, 1483, 1371, 1246, 1194, 1180, 1165, 1088, 943, 854, 831.

4-(Methylthio)phenyl 4-methylbenzenesulfonate (3r)[3]



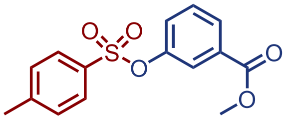
Following general procedure A (5 mol% BTMG, 30 min reaction time), the title compound was isolated as a colourless oil (28 mg, 97%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (appt. d, *J* = 8.3 Hz, 2H), 7.31 (appt. d, *J* = 8.1 Hz, 2H), 7.13 (appt. d, *J* = 8.8 Hz, 2H), 6.89 (appt. d, *J* = 8.8 Hz, 2H), 2.44 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.2, 145.5, 137.8, 132.4, 129.9, 128.7, 127.5, 123.0, 21.8, 16.1; **HRMS** (ESI): *m/z* calcd for $C_{14}H_{14}O_3S_2+Na^+$: 317.0277 [*M*+Na]$^+$; found: 317.0276; **IR** ν_{max} (ATR)/cm^{-1}: 3030, 2922, 1597, 1487, 1373, 1198, 1177, 1157, 1092, 862.

3-(Dimethylamino)phenyl 4-methylbenzenesulfonate (3s)



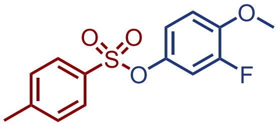
Following general procedure A, the title compound was isolated as a pink oil (28 mg, 97%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (appt. d, *J* = 8.1 Hz, 2H), 7.30 (appt. d, *J* = 8.0 Hz, 2H), 7.07 (appt. t, *J* = 8.2 Hz, 1H), 6.55 (dd, *J* = 8.5, 1.4 Hz, 1H), 6.30–6.29 (m, 1H), 6.25 (appt. d, *J* = 8.1 Hz, 1H), 2.86 (s, 6H), 2.44 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.6, 151.0, 145.1, 133.0, 129.8, 129.7, 128.7, 110.8, 109.6, 106.3, 40.4, 21.8; **HRMS** (ESI): *m/z* calcd for $C_{15}H_{18}NO_3S^+$: 292.1002 [*M*+H]$^+$; found: 292.1008; **IR** ν_{max} (ATR)/cm^{-1}: 3019, 1611, 1570, 1508, 1369, 1215, 1177, 1132, 1094, 997, 895.

Methyl 3-(tosyloxy)benzoate (3t)[4]



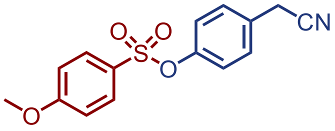
Following general procedure A, the title compound was isolated as a colourless oil (26 mg, 84%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (appt. d, *J* = 7.8 Hz, 1H), 7.71 (appt. d, *J* = 8.2 Hz, 2H), 7.66–7.65 (m, 1H), 7.39–7.31 (m, 3H), 7.20 (dd, *J* = 8.2, 1.3 Hz, 1H), 3.89 (s, 3H), 2.45 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.8, 149.7, 145.8, 132.3, 132.1, 130.0, 129.8, 128.6, 128.3, 127.0, 123.7, 52.5, 21.9; **HRMS** (ESI): *m/z* calcd for $C_{15}H_{14}O_5S+Na^+$: 329.0454 [*M*+Na]$^+$; found: 329.0459; **IR** ν_{max} (ATR)/cm^{-1}: 3026, 2953, 1726, 1597, 1585, 1445, 1377, 1298, 1287, 1269, 1215, 1169, 1092, 989, 897, 822.

3-Fluoro-4-methoxyphenyl 4-methylbenzenesulfonate (3u)[5]



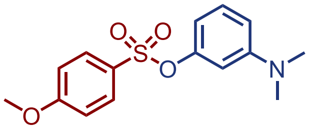
Following general procedure A, the title compound was isolated as a colourless oil (29 mg, 97%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (appt. d, *J* = 8.3 Hz, 2H), 7.32 (appt. d, *J* = 8.0 Hz, 2H), 6.86–6.81 (m, 1H), 6.76–6.71 (m, 2H), 3.85 (s, 3H), 2.45 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.9 (d, *J* = 249.4 Hz), 147.0 (d, *J* = 10.5 Hz), 145.7, 142.5 (d, *J* = 9.4 Hz), 132.2, 130.0, 128.7, 118.3 (d, *J* = 3.9 Hz), 113.3 (d, *J* = 2.6 Hz), 111.4 (d, *J* = 21.3 Hz), 56.6, 21.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -131.2 (appt. t, *J* = 9.8 Hz); **HRMS** (ESI): *m/z* calcd for $C_{14}H_{13}FO_4S+Na^+$: 319.0411 [*M*+Na]$^+$; found: 319.0415; **IR** ν_{max} (ATR)/cm^{-1}: 3019, 1510, 1375, 1215, 1192, 1179, 1092, 961.

4-(Cyanomethyl)phenyl 4-methoxybenzenesulfonate (3v)



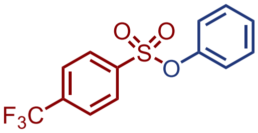
Following general procedure A (10 mol% BTMG, 30 min reaction time), the title compound was isolated as a colourless oil (30 mg, >99%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (appt. d, *J* = 8.9 Hz, 2H), 7.26 (appt. d, *J* = 8.6 Hz, 2H), 7.00 (appt. d, *J* = 8.6 Hz, 2H), 6.97 (appt. d, *J* = 9.0 Hz, 2H), 3.88 (s, 3H), 3.72 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.4, 149.5, 130.9 (d, *J* = 10.6 Hz), 129.4, 128.7, 126.5, 123.3, 117.5, 114.5, 55.9, 23.2; **HRMS** (ESI): *m/z* calcd for $C_{15}H_{13}NO_4S+Na^+$: 326.0457 [*M*+Na]$^+$; found: 326.0453; **IR** ν_{max} (ATR)/cm^{-1}: 3021, 1597, 1499, 1375, 1265, 1215, 1171, 1155, 1096.

3-(Dimethylamino)phenyl 4-methoxybenzenesulfonate (3w)



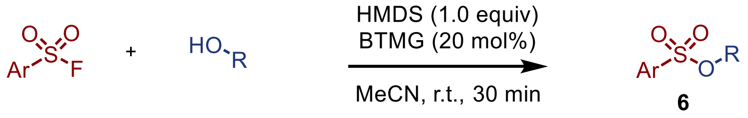
Following general procedure A (10 mol% BTMG, 30 min reaction time), the title compound was isolated as a pink oil (29 mg, 94%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (appt. d, *J* = 9.0 Hz, 2H), 7.07 (appt. t, *J* = 8.2 Hz, 1H), 6.96 (appt. d, *J* = 9.0 Hz, 2H), 6.55 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.31 (appt. t, *J* = 2.3 Hz, 1H), 6.25 (dd, *J* = 8.0, 1.6 Hz, 1H), 3.87 (s, 3H), 2.86 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.1, 151.6, 151.0, 130.9, 129.7, 127.3, 114.3, 110.9, 109.6, 106.4, 55.8, 40.4; **HRMS** (ESI): *m/z* calcd for $C_{15}H_{18}NO_4S^+$: 308.0951 [*M*+H]$^+$; found: 308.0957; **IR** ν_{max} (ATR)/cm^{-1}: 2926, 1609, 1597, 1499, 1368, 1263, 1169, 1132, 1096, 997, 895, 835, 808.

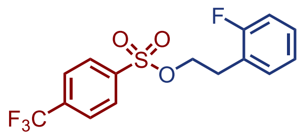
Phenyl 4-(trifluoromethyl)benzenesulfonate (3x)



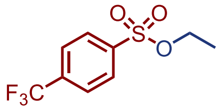
Following general procedure A, the title compound was isolated as an off-white solid (590 mg, 89%). **m.p.** 70.2–71.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (appt. d, *J* = 8.2 Hz, 2 H), 7.80 (appt. d, *J* = 8.2, Hz, 2H), 7.35–7.26 (m, 3H), 7.01–6.98 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.4, 139.1 (br), 135.9 (q, *J* = 33.3 Hz), 130.0, 129.2, 127.7, 126.4 (q, *J* = 3.7 Hz), 123.1 (q, *J* = 273.7), 122.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.3; **HRMS** (ESI): *m/z* calcd for $C_{13}H_{10}F_3O_3S^+$: 303.0297 [*M*+H]$^+$; found: 303.0291; **IR** ν_{max} (ATR)/cm^{-1}: 2932, 1736, 1378, 1321, 1199, 1174, 1147, 1108, 1091, 1063, 863, 739, 727, 600, 547.

Synthesis and Experimental Data for Sulfonates 6a–6r

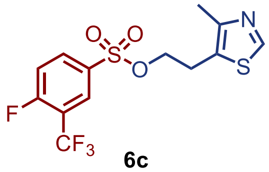




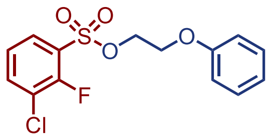
6a
92%



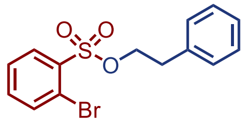
6b
84%



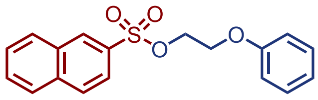
6c
78%



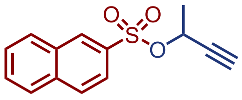
6d
96%



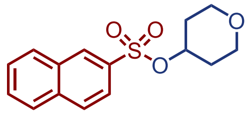
6e
92%



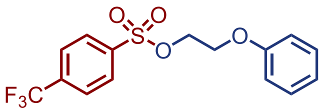
6f
97%



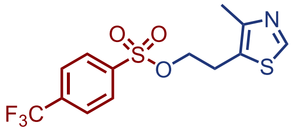
6g[a]
61%



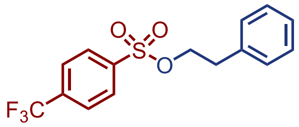
6h[a]
92%



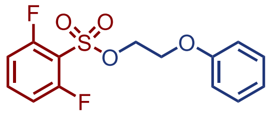
6i
80%



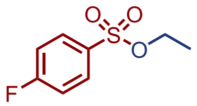
6j
66%



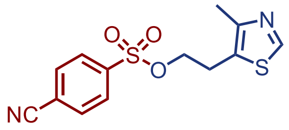
6k
82%



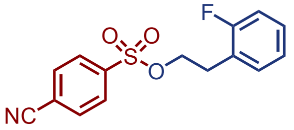
6l
71%



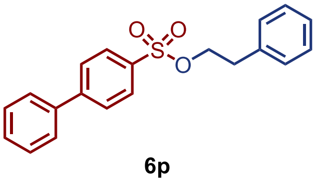
6m
>99%



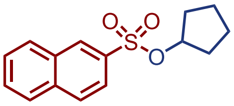
6n
54%



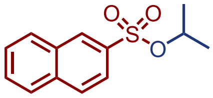
6o
98%



6p
60%



6q[a]
79%



6r[a]
50%

[a] Reaction stirred under microwave irradiation for 30 min at 60 °C, 0.2 mmol of aromatic sulfonyl fluoride was used.

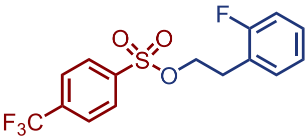
General Procedure B

To a solution of the required sulfonyl fluoride (0.1 mmol) and the required alkyl alcohol (0.1 mmol) in MeCN (0.5 mL) was added HMDS (0.1 mmol) and BTMG (20 mol%). The resulting reaction was stirred at room temperature or for 30 minutes. Upon completion the solvent was removed and, if needed, crude was filtered through a short silica plug to obtain the analytically pure product.

General Procedure C

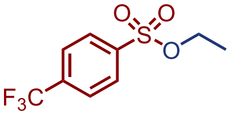
To a solution of the required sulfonyl fluoride (0.2 mmol) and the required alkyl alcohol (0.1 mmol) in MeCN (0.5 mL) in a microwave vial was added HMDS (0.1 mmol) and BTMG (20 mol%). The resulting reaction was stirred in a microwave reactor for 30 minutes at 60 °C. Upon completion the solvent was removed and flash column chromatography was used to obtain the analytically pure product.

2-Fluorophenethyl 4-(trifluoromethyl)benzenesulfonate (6a)



Following general procedure B, the title compound was isolated as a colourless solid (38 mg, 92%). **m.p.** 58–59 °C; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.88 (appt. d, *J* = 8.3 Hz, 2H), 7.71 (appt. d, *J* = 8.3 Hz, 2H), 7.21–7.19 (m, 1H), 7.12 (dt, *J* = 7.6, 3.7 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.95–6.88 (m, 1H), 4.33 (t, *J* = 6.6 Hz, 2H), 3.01 (t, *J* = 6.6 Hz, 2H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 161.2 (d, *J* = 245.8 Hz), 139.6, 135.4 (q, *J* = 33.2 Hz), 131.6 (d, *J* = 4.5 Hz), 129.2 (d, *J* = 8.2 Hz), 128.4, 126.4 (q, *J* = 3.7 Hz), 124.4 (d, *J* = 3.6 Hz), 123.2 (q, *J* = 273.1 Hz), 123.0 (d, *J* = 15.4 Hz), 115.5 (d, *J* = 21.7 Hz), 70.2 (d, *J* = 1.7 Hz), 29.3 (d, *J* = 2.4 Hz); **^{19}F NMR** (376 MHz, CDCl$_3$) δ -63.3, -118.3– -118.5 (m); **HRMS** (ESI): *m/z* calcd for $C_{15}H_{12}F_4O_3S+Na^+$: 371.0335 [*M*+Na]$^+$; found: 371.0338; **IR** ν_{max} (ATR)/cm^{-1}: 3018, 1492, 1323, 1190, 1182, 711.

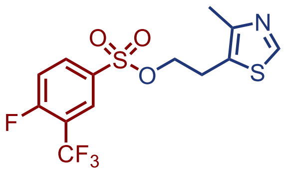
Ethyl 4-(trifluoromethyl)benzenesulfonate (6b)[6]



Following general procedure B, the title compound was isolated as colourless oil (21 mg, 84%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.06 (appt. d, *J* = 8.2 Hz, 2H), 7.83 (appt, d, *J* = 8.3 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 140.1, 135.5 (q, *J* = 33.2 Hz), 128.5, 126.6 (q, *J* =

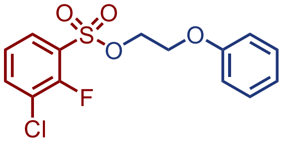
3.7 Hz), 123.2 (q, *J* = 273.1 Hz), 67.8, 14.9; ^{19}**F NMR** (376 MHz, CDCl$_3$) δ -63.2; **HRMS** (ESI): *m/z* calcd for $C_9H_9F_3O_3S+Na^+$: 277.0117 [*M*+Na]$^+$; found: 277.0129; **IR** ν$_{max}$ (ATR)/cm^{-1}: 2989, 2927, 2854, 1406, 1373, 1298, 1217, 1109, 844.

2-(4-Methylthiazol-5-yl)ethyl 4-fluoro-3-(trifluoromethyl)benzenesulfonate (6c)



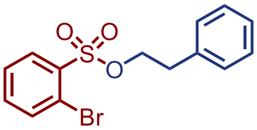
Following general procedure B, the title compound was isolated as a colourless oil (29 mg, 78%). ^{1}**H NMR** (400 MHz, CDCl$_3$) δ 8.58 (s, 1H), 8.11 (dd, *J* = 6.3, 2.1 Hz, 1H), 8.01 (ddd, *J* = 8.5, 4.3, 2.3 Hz, 1H), 7.36 (t, *J* = 9.1 Hz, 1H), 4.27 (t, *J* = 6.4 Hz, 2H), 3.17 (t, *J* = 6.4 Hz, 2H), 2.35 (s, 3H); ^{13}**C NMR** (101 MHz, CDCl$_3$) δ 162.9 (d, *J* = 266.9 Hz), 150.7, 150.5, 134.1 (d, *J* = 10.1 Hz), 132.7 (d, *J* = 3.9 Hz), 128.0–127.9 (m), 125.1, 121.5 (q, *J* = 273.5 Hz), 118.6 (d, *J* = 22.1 Hz), 70.3, 26.2, 14.9; ^{19}**F NMR** (376 MHz, CDCl$_3$) δ -61.8 (d, *J* = 12.6 Hz), -103.8 – -103.9 (m); **HRMS** (ESI): *m/z* calcd for $C_{13}H_{12}F_4NO_3S_2^+$: 370.0189 [*M*+H]$^+$; found: 370.0185; **IR** ν$_{max}$ (ATR)/cm^{-1}: 2953, 2929, 2852, 1490, 1319, 1284, 1124.

2-Phenoxyethyl 3-chloro-2-fluorobenzenesulfonate (6d)



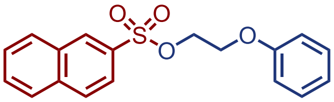
Following general procedure B, the title compound was isolated as a colourless oil (32 mg, 96%). ^{1}**H NMR** (400 MHz, CDCl$_3$) δ 7.84 (ddd, *J* = 7.9, 6.0, 1.7 Hz, 1H), 7.68 (ddd, *J* = 8.3, 6.7, 1.7 Hz, 1H), 7.30–7.22 (m, 3H), 6.98–6.94 (m, 1H), 6.80–6.77 (m, 2H), 4.59–4.56 (m, 2H), 4.22–4.20 (m, 2H); ^{13}**C NMR** (101 MHz, CDCl$_3$) δ 157.9, 155.2 (d, *J* = 261.1 Hz), 136.6, 129.7, 129.1, 126.3 (d, *J* = 14.2 Hz), 124.8 (d, *J* = 5.1 Hz), 123.6 (d, *J* = 17.6 Hz), 121.7, 114.7 (d, *J* = 4.9 Hz), 69.8, 65.4; ^{19}**F NMR** (376 MHz, CDCl$_3$) δ -108.5– -108.6 (m); **HRMS** (ESI): *m/z* calcd for $C_{14}H_{13}ClFO_4S^+$: 331.0202 [*M*+H]$^+$; found: 331.0201; **IR** ν$_{max}$ (ATR)/cm^{-1}:3082, 2962, 2873, 1598, 1377, 1247, 1220, 933.

Phenethyl 2-bromobenzenesulfonate (6e)



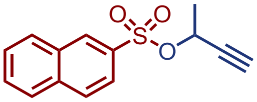
Following general procedure B, the title compound was isolated as a colourless solid (31 mg, 92%). **m.p.** 48–49 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08–8.05 (m, 1H), 7.76–7.73 (m, 1H), 7.46–7.44 (m, 2H), 7.29–7.22 (m, 3H), 7.16 (appt. d, *J* = 7.6 Hz, 2H), 4.32 (t, *J* = 7.2 Hz, 2H), 3.04 (t, *J* = 7.1 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.1, 136.1, 135.8, 134.7, 132.1, 129.1, 128.8, 127.7, 127.1, 121.0, 71.6, 35.5; **HRMS** (ESI): *m/z* calcd for $C_{14}H_{13}BrO_3S+Na^+$: 362.9661 [*M*+Na]$^+$; found: 362.9658; **IR** ν_{max} (ATR)/cm^{-1}: 3018, 2962, 1614, 1473, 1215, 1008, 790.

2-Phenoxyethyl naphthalene-2-sulfonate (6f)



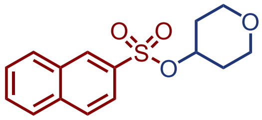
Following general procedure B, the title compound was isolated as a colourless solid (32 mg, 97%). **m.p.** 48–49 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.01–7.88 (m, 4H), 7.68 (dt, *J* = 15.0, 6.9 Hz, 2H), 7.26 (s, 1H), 7.20 (t, *J* = 8.0 Hz, 2H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 2H), 4.44–4.42 (m, 2H), 4.17–4.15 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.1, 135.5, 132.9, 132.1, 130.0 129.8, 129.6, 129.6, 129.5, 128.2, 128.0, 122.8, 121.5, 114.7, 68.6, 65.5; **HRMS** (ESI): *m/z* calcd for $C_{18}H_{17}O_4S^+$: 329.0842 [*M*+H]$^+$; found: 329.0854; **IR** ν_{max} (ATR)/cm^{-1}: 3059, 3028, 2926, 1357, 1201, 1078, 929.

1-Methyl-2-propyn-1-yl naphthalene-2-sulfonate (6g)



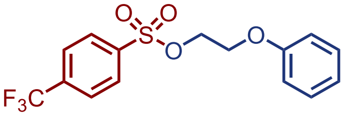
Following general procedure C, the title compound was isolated as a colourless oil (16 mg, 61%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 1.8 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 2H), 7.95–7.88 (m, 2H), 7.71–7.62 (m, 2H), 5.24 (qd, *J* = 6.7, 2.1 Hz, 1H), 2.33 (d, *J* = 2.2 Hz, 1H), 1.60 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.5, 133.8, 132.0, 130.0, 129.6, 129.5, 129.5, 128.1, 127.9, 122.9, 79.9, 75.9, 67.9, 22.7; **HRMS** (ESI): *m/z* calcd for $C_{14}H_{13}O_3S^+$: 261.0580 [*M*+H]$^+$; found: 261.0581; **IR** ν_{max} (ATR)/cm^{-1}: 3292, 2924, 1351, 1175, 903, 658.

4-Hydroxytetrahydropyranyl naphthalene-2-sulfonate (6h)



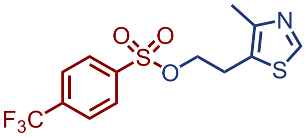
Following general procedure C, the title compound was isolated as a colourless solid (27 mg, 92%). **m.p.** 123–125 °C **;** ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 1.9 Hz, 1H), 8.01–7.98 (m, 2H), 7.95–7.91 (m, 1H), 7.87 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.71–7.62 (m, 2H), 4.76 (tt, *J* = 8.2, 4.2 Hz, 1H), 3.86 (ddd, *J* = 11.9, 5.8, 4.1 Hz, 2H), 3.46 (ddd, *J* = 11.7, 8.3, 3.3 Hz, 2H), 1.89–1.73 (m, 4H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 135.3, 134.2, 132.0, 129.8, 129.5, 129.4, 129.4, 128.1, 128.0, 122.4, 77.8, 64.8, 32.5; **HRMS** (ESI): *m/z* calcd for $C_{15}H_{17}O_4S^+$: 293.0842 $[M+H]^+$; found: 293.0841; **IR** ν_{max} (ATR)/cm^{-1}: 1350, 1327, 1174, 1114, 1067, 934, 909, 878, 818, 752, 672.

2-Phenoxyethyl 4-(trifluoromethyl)benzenesulfonate (6i)



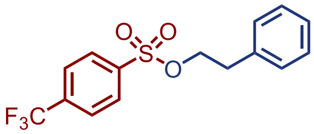
Following general procedure B, the title compound was isolated as a colourless solid (28 mg, 80%). **m.p.** 82–83 °C; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.07 (appt. d, *J* = 8.2 Hz, 2H), 7.80 (appt. d, *J* = 8.3 Hz, 2H), 7.27–7.23 (m, 2H), 6.96 (appt. t, *J* = 7.4 Hz, 1H), 6.74–6.71 (m, 2H), 4.49–4.46 (m, 2H), 4.418–4.16 (m, 2H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 157.9, 139.8, 135.6 (q, *J* = 33.3 Hz), 129.7, 128.7, 126.5 (q, *J* = 3.7 Hz), 123.2 (q, *J* = 273.1 Hz), 121.8, 114.6, 69.3, 65.3; ^{19}**F NMR** (376 MHz, $CDCl_3$) δ -63.3; **HRMS** (ESI): *m/z* calcd for $C_{15}H_{13}F_3O_4S+Na^+$: 369.0379 $[M+Na]^+$; found: 369.0383; **IR** ν_{max} (ATR)/cm^{-1}: 3018, 1743, 1521, 1215, 1018, 756.

2-(4-Methylthiazol-5-yl)ethyl 4-(trifluoromethyl)benzenesulfonate (6j)



Following general procedure B, the title compound was isolated as a colourless solid (23 mg, 66%). **m.p.** 203–204 °C; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.94 (appt. d, *J* = 8.2 Hz, 2H), 7.78 (appt. d, *J* = 8.3 Hz, 2H), 4.25 (t, *J* = 6.5 Hz, 2H), 3.16 (t, *J* = 6.4 Hz, 2H), 2.34 (s, 3H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 150.8, 150.4, 139.5, 135.7 (q, *J* = 33.3 Hz), 128.5, 126.6 (q, *J* = 3.7 Hz), 125.0, 123.1 (q, *J* = 273.2 Hz), 70.2, 26.3, 15.0; ^{19}**F NMR** (376 MHz, CDCl$_3$) δ -63.3; **HRMS** (ESI): *m/z* calcd for $C_{13}H_{13}F_3NO_3S_2^+$: 352.0283 [*M*+H]$^+$; found: 352.0294; **IR** ν$_{max}$ (ATR)/cm^{-1}: 3018, 2926, 1745, 1215, 756.

Phenethyl 4-(trifluoromethyl)benzenesulfonate (6k)

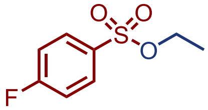


Following general procedure B, the title compound was isolated as a colourless solid (27 mg, 82%). **m.p.** 49-50 °C; ^{1}**H NMR** (400 MHz, CDCl$_3$) δ 7.86 (appt. d, *J* = 8.1 Hz, 2H), 7.71 (appt. d, *J* = 8.3 Hz, 2H), 7.25–7.20 (m, 3H), 7.09–7.07 (m, 2H), 4.30 (t, *J* = 6.8 Hz, 2H), 2.98 (t, *J* = 6.8 Hz, 2H); ^{13}**C NMR** (101 MHz, CDCl$_3$) δ 139.7, 136.1, 135.4 (d, *J* = 33.1 Hz), 129.0, 128.8, 128.4, 127.2, 126.4 (q, *J* = 3.7 Hz), 123.2 (q, *J* = 273.6 Hz), 71.7, 35.5; ^{19}**F NMR** (376 MHz, CDCl$_3$) δ -63.3; **HRMS** (ESI): *m/z* calcd for $C_{15}H_{13}F_3O_3S+Na^+$: 353.0429 [*M*+Na]$^+$; found: 353.0420; **IR** ν$_{max}$ (ATR)/cm^{-1}: 3028, 1323, 1180, 1062, 960.

2-Phenoxyethyl 2,6-difluorobenzenesulfonate (6l)

Following general procedure B, the title compound was isolated as a colourless oil (22 mg, 71%). ^{1}**H NMR** (400 MHz, CDCl$_3$) δ 7.57 (tt, *J* = 8.4, 5.9 Hz, 1H), 7.27–7.23 (m, 2H), 7.07–7.02 (m, 2H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.77 (dd, *J* = 8.7, 0.9 Hz, 2H), 4.63 (dd, *J* = 5.4, 3.8 Hz, 2H), 4.23–4.21 (m, 2H); ^{13}**C NMR** (101 MHz, CDCl$_3$) δ 161.3 (d, *J* = 3.4 Hz), 158.7 (d, *J* = 3.4 Hz), 158.0, 135.9 (t, *J* = 10.9 Hz), 129.6, 121.6, 114.7 (d, *J* = 16.8 Hz), 113.3 (dd, *J* = 23.1, 3.5 Hz), 69.9, 65.4; ^{19}**F NMR** (376 MHz, CDCl$_3$) δ -105.0 – -105.1 (m); **HRMS** (ESI): *m/z* calcd for $C_{14}H_{12}F_2O_4S+K^+$: 353.0056 [*M*+K]$^+$; found: 353.0059; **IR** ν$_{max}$ (ATR)/cm^{-1}: 3018, 2926, 1473, 1215, 1008, 931.

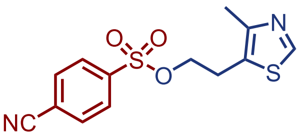
Ethyl 4-fluorobenzenesulfonate (6m)



Following general procedure B, the title compound was isolated as a colourless oil (20 mg, >99%). ^{1}**H NMR** (400 MHz, CDCl$_3$) δ 7.97 (appt. dd, *J* = 8.7, 5.0 Hz, 2H), 7.27 (appt. dd, *J* = 14.0, 5.4 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}**C NMR** (101 MHz, CDCl$_3$) δ 165.9 (d, *J* = 256.3 Hz), 132.6 (d, *J* =

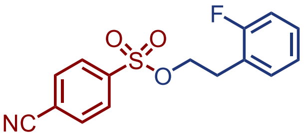
3.3 Hz), 130.8 (d, *J* = 9.5 Hz), 116.7 (d, *J* = 22.7 Hz), 67.3, 14.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.3– -103.4 (m); **HRMS** (ESI): *m/z* calcd for $C_8H_9FO_3S+Na^+$: 227.0149 [*M*+Na]$^+$; found: 227.0158; **IR** ν_{max} (ATR)/cm^{-1}: 3020, 2927, 2399, 1595, 1496, 1215, 1184, 921.

2-(4-Methylthiazol-5-yl)ethyl 4-cyanobenzenesulfonate (6n)



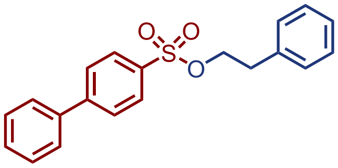
Following general procedure B, the title compound was isolated as a colourless oil (17 mg, 54%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.94–7.91 (m, 2H), 7.83–7.81 (m, 2H), 4.26 (t, *J* = 6.4 Hz, 2H), 3.17 (t, *J* = 6.4 Hz, 2H), 2.35 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.9, 150.4, 140.1, 133.2, 128.5, 125.0, 117.8, 117.0, 70.5, 26.3, 15.1; **HRMS** (ESI): *m/z* calcd for $C_{13}H_{13}N_2O_3S_2^+$: 309.0362 [*M*+H]$^+$; found: 309.0367; **IR** ν_{max} (ATR)/cm^{-1}: 2924, 2852, 1716, 1541, 1361, 1188, 1010.

2-Fluorophenethyl 4-cyanobenzenesulfonate (6o)



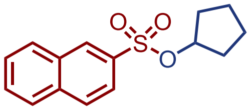
Following general procedure B, the title compound was isolated as a colourless solid (30 mg, 98%). **m.p.** 58–59 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87–7.85 (m, 2H), 7.76–7.74 (m, 2H), 7.24–7.20 (m, 1H), 7.13 (td, *J* = 7.4, 1.7 Hz, 1H), 7.04 (td, *J* = 7.4, 0.9 Hz, 1H), 6.97–6.92 (m, 1H), 4.33 (t, *J* = 6.6 Hz, 2H), 3.02 (t, *J* = 6.6 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.2 (d, *J* = 245.9 Hz), 140.3, 133.0, 131.6 (d, *J* = 4.4 Hz), 129.3 (d, *J* = 8.2 Hz), 128.5, 124.4 (d, *J* = 3.6 Hz), 123.0 (d, *J* = 15.4 Hz), 117.3 (d, *J* = 41.9 Hz), 115.6 (d, *J* = 21.7 Hz), 70.4 (d, *J* = 1.8 Hz), 29.3 (d, *J* = 2.3 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.3– -118.4 (m); **HRMS** (ESI): *m/z* calcd for $C_{15}H_{12}FNO_3S+Na^+$: 328.0414 [*M*+Na]$^+$; found: 328.0420; **IR** ν_{max} (ATR)/cm^{-1}: 3095, 2966, 2850, 1490, 1367, 1188, 1111, 906.

Phenethyl [1,1'-biphenyl]-4-sulfonate (6p)



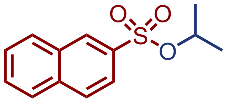
Following general procedure B, the title compound was isolated as a colourless solid (20 mg, 60%). **m.p.** 51–52 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (appt. d, *J* = 8.3 Hz, 2H), 7.52 (appt. d, *J* = 8.3 Hz, 2H), 7.44 (appt. d, *J* = 7.1 Hz, 2H), 7.34 (appt. t, *J* = 7.2 Hz, 2H), 7.30–7.26 (m, 1H), 7.11–7.06 (m, 3H), 6.97 (appt. d, *J* = 7.6 Hz, 2H), 4.12 (t, *J* = 7.0 Hz, 2H), 2.83 (t, *J* = 7.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.7, 139.2, 136.3, 134.6, 129.3, 129.1, 128.8, 128.8, 128.4, 127.9, 127.5, 127.0, 71.0, 35.5; **HRMS** (ESI): *m/z* calcd for $C_{20}H_{18}O_3S+K^+$: 377.0608 [*M*+K]$^+$; found: 377.0626; **IR** ν_{max} (ATR)/cm^{-1}: 3064, 3018, 2960, 1361, 1101, 964.

Cyclopentyl naphthalene-2-sulfonate (6q)



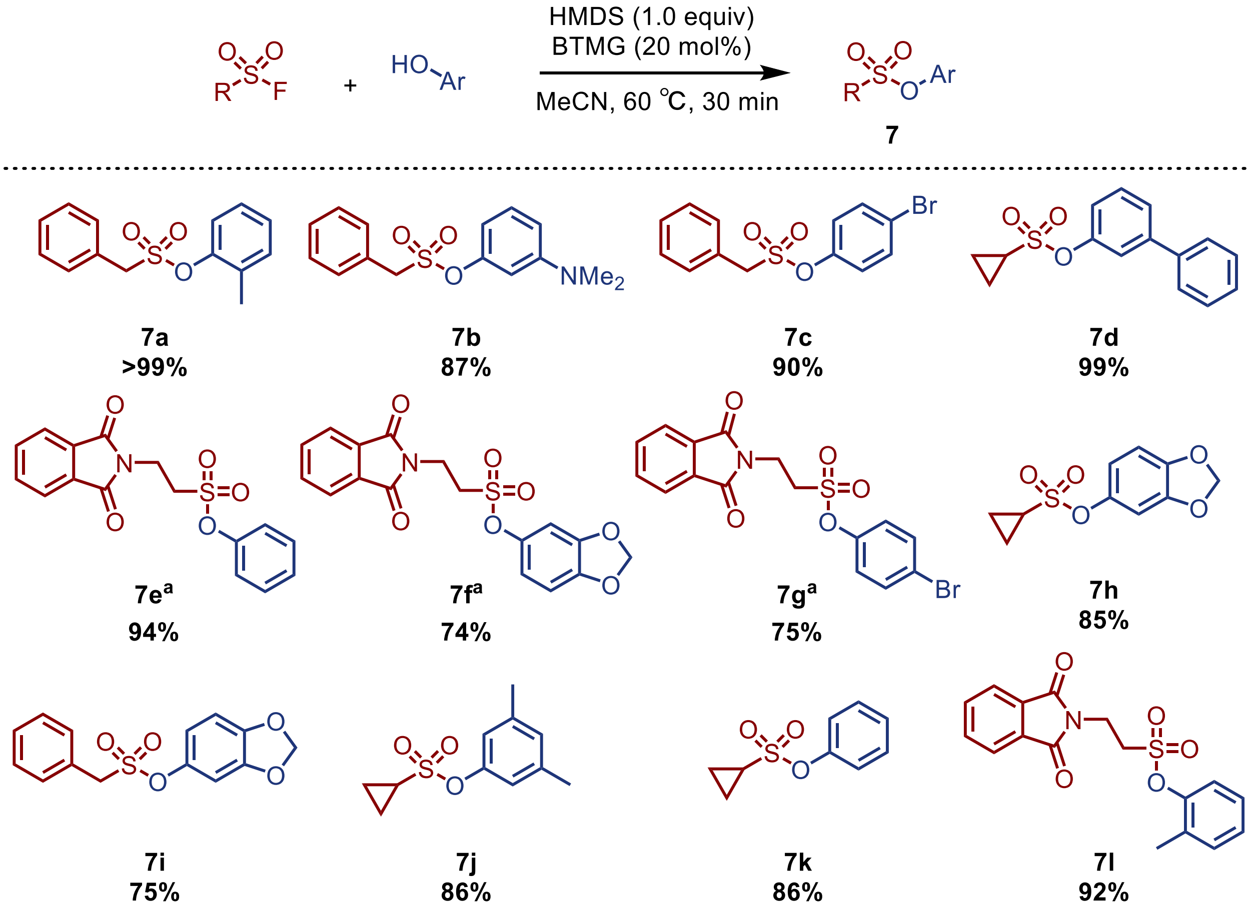
Following general procedure C, the title compound was isolated as a colourless solid (22 mg, 79%). **m.p.** 48–49 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 0.9 Hz, 1H), 8.00–7.97 (m, 2H), 7.94–7.92 (m, 1H), 7.86 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.69–7.63 (m, 2H), 5.03 (tt, *J* = 5.5, 3.0 Hz, 1H), 1.88–1.70 (m, 6H), 1.57–1.48 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.2, 134.4, 132.1, 129.7, 129.44, 129.42, 129.3, 128.1, 127.8, 122.6, 86.1, 33.3, 23.2; **HRMS** (ESI): *m/z* calcd for $C_{15}H_{17}O_3S^+$: 277.0894 [*M*+H]$^+$; found: 277.0893; **IR** ν_{max} (ATR)/cm^{-1}: 2957, 2917, 2850, 1349, 1180, 1077, 884, 748, 552.

1-Methylethyl naphthalene-2-sulfonate (6r)[7]



Following general procedure C, the title compound was isolated as an off-white solid (13 mg, 50%). **m.p.** 52–56 °C, (lit. 55–56 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 1.9 Hz, 1H), 8.01–7.98 (m, 2H), 7.95–7.92 (m, 1H), 7.87 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.70–7.62 (m, 2H), 4.81 (p, *J* = 6.3 Hz, 1H), 1.29 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.3, 134.5, 132.1, 129.7, 129.5, 129.4, 129.3, 128.1, 127.9, 122.7, 77.7, 23.0; **HRMS** (ESI): *m/z* calcd for $C_{13}H_{15}O_3S^+$: 251.0736 [M+H]$^+$; found: 251.0736; **IR** ν_{max} (ATR)/cm^{-1}: 3400, 2918, 2850, 1614, 1344, 1176, 909, 886, 553.

Synthesis and Experimental Data for Sulfonates 7a–7l

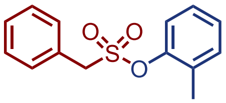


[a]Reaction conducted on a 0.2 mmol scale using 1.0 equivalent of alkyl sulfonyl fluoride.

General Procedure D

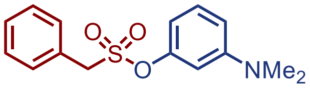
To a solution of the required sulfonyl fluoride (0.2 mmol) and the required alkyl alcohol (0.1 mmol) in MeCN (0.5 mL) in a microwave vial was added HMDS (0.1 mmol) and BTMG (20 mol%). The resulting reaction was stirred in a microwave reactor for 30 minutes at 60 °C. Upon completion the solvent was removed and flash column chromatography was used to obtain the analytically pure product.

2-Methylphenyl benzenemethanesulfonate (7a)



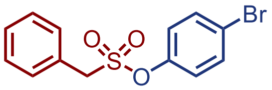
Following general procedure D, the title compound was isolated as a white solid (26 mg, >99%). **m.p.** 81.1–82.1 °C; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.50–7.48 (m, 2H), 7.45–7.41 (m, 3H), 7.23–7.14 (m, 3H), 7.04–7.02 (m, 1H), 4.57 (s, 2H), 2.19 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 147.8, 131.9, 131.6, 131.1, 129.4, 129.1, 127.6, 127.3, 127.2, 122.1, 57.4, 16.6; **HRMS** (ESI): *m/z* calcd for $C_{14}H_{15}O_3S^+$: 263.0736 [*M*+H]$^+$; found: 263.0738; **IR** ν$_{max}$ (ATR)/cm^{-1}: 3075, 2925, 1489, 1457, 1363, 1185, 1149, 869, 780, 766.

3-Dimethylaminophenyl benzenemethanesulfonate (7b)



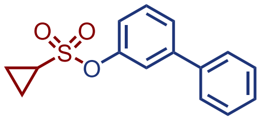
Following general procedure D, the title compound was isolated as a colourless oil (25 mg, 87%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.48–7.38 (m, 5H), 7.18 (t, *J* = 8.2 Hz, 1H), 6.60 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.48 (dd, *J* = 8.0, 2.2 Hz, 1H), 6.40 (t, *J* = 2.4 Hz, 1H), 4.50 (s, 2H), 2.92 (s, 6H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 151.8, 150.6, 131.1, 130.1, 129.3, 129.1, 127.6, 111.0, 109.0, 105.7, 56.6, 40.5; **HRMS** (ESI$^+$): calculated for $C_{15}H_{18}O_3NS^+$: 292.1002 [*M*+H]$^+$; found: 292.1003, **IR** ν$_{max}$ (ATR)/cm^{-1}: 2927, 2811, 1608, 1568, 1504, 1354, 1170, 1124, 996, 794, 546.

4-Bromophenyl benzenemethanesulfonate (7c)[8]



Following general procedure D, the title compound was isolated as a colourless solid (29 mg, 90%). **m.p.** 84.2–85.3 °C (lit. 84–85 °C); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.48–7.42 (m, 7H), 6.98–6.94 (m, 2H), 4.52 (s, 2H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 148.2, 133.1, 131.0, 129.6, 129.2, 127.1, 123.9, 120.7, 57.1; **HRMS** (ESI): *m/z* calcd for $C_{13}H_{10}O_3BrS^-$: 324.9540 [*M*-H]$^-$; found 324.9541; **IR** ν$_{max}$ (ATR)/cm^{-1}: 3066, 1481, 1271, 1150, 1011, 866, 695, 539, 519.

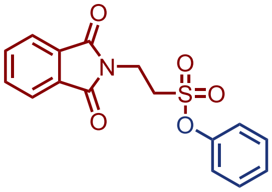
3-Phenylphenyl cyclopropylsulfonate (7d)



Following general procedure D, the title compound was isolated as a colourless oil (27 mg, 99%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.62–7.53 (m, 4H), 7.49–7.44 (m, 3H), 7.40–7.39 (m, 1H), 7.30 (ddd, *J* = 8.1, 2.3, 1.3 Hz, 1H), 2.64 (tt, *J* = 8.0, 4.8 Hz, 1H), 1.33–1.29 (m, 2H), 1.17–1.11 (m, 2H); **^{13}C NMR** (100 MHz, CDCl$_3$)

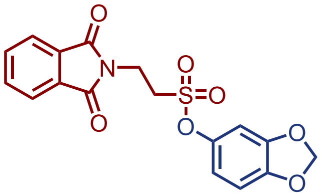
δ 150.2, 143.5, 139.7, 130.2, 129.1, 128.1, 127.3, 126.0, 121.1, 121.0, 27.9, 6.4; **HRMS** (ESI): *m/z* calcd for $C_{15}H_{15}O_3S^+$: 275.0736 [*M*+H]$^+$; found: 275.0738; **IR** ν_{max} (ATR)/cm^{-1}: 3061, 1476, 1366, 1140, 883, 758, 694.

Phenyl 1,3-dihydro-1,3-dioxo-2*H*-isoindole-2-ethanesulfonate (7e)



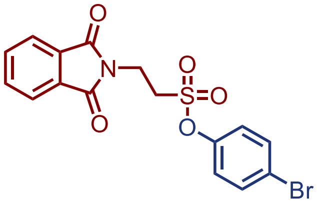
Following general procedure D, the title compound was isolated as a colourless solid (62 mg, 94%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 1H), 7.75 (dd, *J* = 5.5, 3.0 Hz, 1H), 7.45–7.40 (m, 1H), 7.37–7.30 (m, 2H), 4.34–4.31 (m, 1H), 3.66 (dd, *J* = 7.6, 6.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 148.9, 134.7, 134.5, 131.9, 130.2, 127.6, 123.9, 123.8, 122.3, 47.6, 32.6. **HRMS** (ESI): *m/z* calcd for $C_{16}H_{14}NO_5S^+$: 332.0587 [*M*+H]$^+$; found: 332.0589; **IR** ν_{max} (ATR)/cm^{-1}: 1770, 1702, 1365, 1144, 870, 714, 504.

Benzo-1,3-dioxol-5-yl 2-(1,3-dioxoisoindolin-2-yl)ethane-1-sulfonate (7f)



Following general procedure D, the title compound was isolated as a white solid (55 mg, 74%). **m.p.** 138.4–139.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.77–7.74 (m, 2H), 6.88–6.77 (m, 3H), 6.01 (s, 2H), 4.30 (dd, *J* = 7.6, 6.3 Hz, 2H), 3.64 (dd, *J* = 7.6, 6.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 148.5, 146.9, 142.8, 134.5, 131.9, 123.8, 115.2, 108.3, 104.5, 102.2, 47.3, 32.5; **HRMS** (ESI): *m/z* calcd for $C_{17}H_{14}NO_7S^+$: 376.0485 [*M*+H]$^+$; found: 376.0484; **IR** ν_{max} (ATR)/cm^{-1} 1705, 1485, 1367, 1244, 1156, 1117, 1083, 1034, 943, 929, 867, 839, 718, 711, 503.

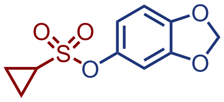
4-Bromophenyl 1,3-dihydro-1,3-dioxo-2*H*-isoindole-2-ethanesulfonate (7g)



Following general procedure D, the title compound was isolated as a colourless solid (61 mg, 75%). **m.p.** 140.3–141.7 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.5, 3.0 Hz, 1H), 7.78–7.73 (m, 1H), 7.56–7.52

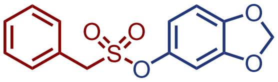
(m, 1H), 7.26–7.23 (m, 1H), 4.32 (dd, *J* = 7.5, 6.4 Hz, 1H), 3.67 (dd, *J* = 7.5, 6.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 147.7, 134.6, 133.3, 131.8, 124.2, 123.9, 121.2, 47.7, 32.5; **HRMS** (ESI): *m/z* calcd for $C_{16}H_{13}NO_5BrS^+$: 409.9692 [*M*+H]$^+$; found: 409.9687; **IR** ν_{max} (ATR)/cm^{-1} 3095, 3010, 1777, 1710, 1480, 1438, 1402, 1327, 1338, 1264, 1222, 1192, 1167, 1144, 1012, 989, 943, 859, 832, 767, 713, 700, 530, 490.

1,3-Benzodioxol-5-yl cyclopropylsulfonate (7h)



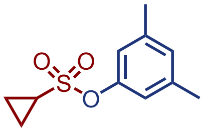
Following general procedure D, the title compound was isolated as a colourless oil (21 mg, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.82–6.81 (m, 1H), 6.77 (d, *J* = 1.7 Hz, 2H), 6.01 (s, 2H), 2.57 (tt, *J* = 8.0, 4.8 Hz, 1H), 1.30–1.25 (m, 2H), 1.15–1.10 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.3, 146.7, 143.8, 115.3, 108.2, 104.5, 102.2 27.6, 6.4.; **HRMS** (ESI): *m/z* calcd for $C_{10}H_{11}O_5S^+$: 243.0322 [*M*+H]$^+$; found: 243.0321; **IR** ν_{max} (ATR)/cm^{-1}: 2905, 1503, 1479, 1362, 1111, 942, 804, 557.

1,3-Benzodioxol-5-yl benzenemethanesulfonate (7i)



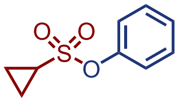
Following general procedure D, the title compound was isolated as a colourless oil (22 mg, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47–7.40 (m, 5H), 6.75–6.72 (m, 1H), 6.61–6.58 (m, 2H), 5.99 (s, 2H), 4.50 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.4, 146.7, 143.3, 131.0, 129.4, 129.1, 127.3, 115.0, 108.2, 104.3, 102.2, 56.7; **HRMS** (ESI): *m/z* calcd for $C_{14}H_{13}O_5S^+$: 292.0478 [*M*+H]$^+$; found: 293.0468; **IR** ν_{max} (ATR)/cm^{-1}: 3315, 2926, 1539, 1320, 1290, 1171, 1124, 913, 779, 697, 546.

3,5-Dimethylphenyl cyclopropylsulfonate (7j)



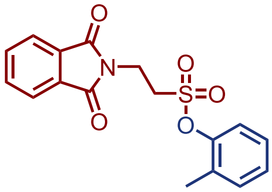
Following general procedure D, the title compound was isolated as a brown oil (20 mg, 86%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.94–6.92 (m, 3H), 2.59 (tt, *J* = 8.0, 4.8 Hz, 1H), 2.33 (s, 6H), 1.29–1.26 (m, 2H), 1.14–1.08 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.6, 139.9, 128.9, 119.8, 27.9, 21.3, 6.3; **HRMS** (ESI): *m/z* calcd for $C_{11}H_{15}O_3S^+$: 227.0736 [*M*+H]$^+$; found: 227.0737; **IR** ν_{max} (ATR)/cm^{-1}: 2923, 1617, 1592, 1468, 1363, 1173, 1122, 1019, 943, 853, 790, 579.

Phenyl cyclopropylsulfonate (7k)



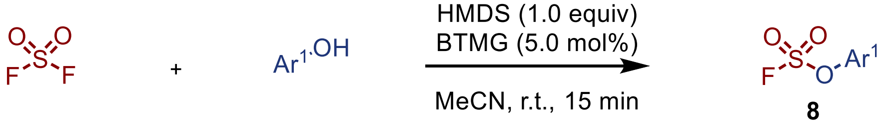
Following general procedure D, the title compound was isolated as a colourless oil (17 mg, 86%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.43–7.38 (m, 2H), 7.34–7.29 (m, 3H), 2.59 (tt, *J* = 8.0, 4.8 Hz, 1H), 1.30–1.25 (m, 2H), 1.16–1.09 (m, 2H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 149.8, 130.0, 127.3, 122.5, 27.8, 6.4; **HRMS** (ESI): *m/z* calcd for $C_9H_{11}O_3S^+$: 199.0423 [*M*+H]$^+$; found: 199.0425; **IR** ν_{max} (ATR)/cm^{-1}: 3062, 1588, 1488, 1365, 1167, 1142, 857, 777.

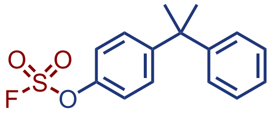
2-Methylphenyl 1,3-dihydro-1,3-dioxo-2*H*-isoindole-2-ethanesulfonate (7l)



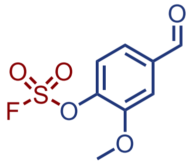
Following general procedure D, the title compound was isolated as a colourless solid (32 mg, 92%). **m.p.** 92.1–93.1 °C; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.89 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.77–7.74 (m, 2H), 7.34–7.32 (m, 1H), 7.27–7.18 (s, 3H), 4.35 (appt. t, *J* = 6. Hz, 2H), 3.73 (appt. t, *J* = 6.5 Hz, 2H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 167.7, 147.7, 134.5, 132.1, 131.9, 131.7, 127.5, 127.5, 123.8, 122.2, 48.5, 32.6, 16.9; **HRMS** (ESI): *m/z* calcd for $C_{17}H_{16}NO_5S^+$: 346.0744 [*M*+H]$^+$; found: 346.0742; **IR** ν_{max} (ATR)/cm^{-1} 2923, 1617, 1592, 1363, 1173, 1122, 943, 853, 790, 579.

Synthesis and Experimental Data for Fluorosulfates 8a–8p

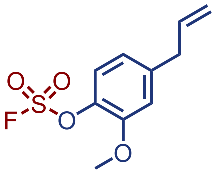




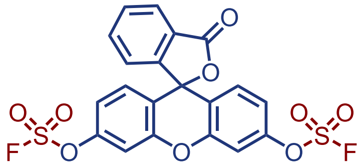
8a
98%



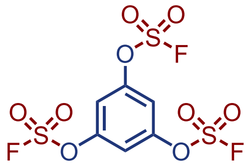
8b
95%



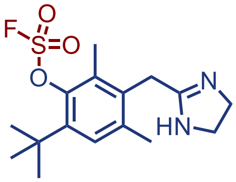
8c[a]
>99%
12.3 g



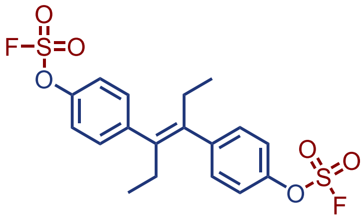
8d
>99%



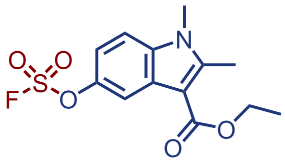
8e
65%



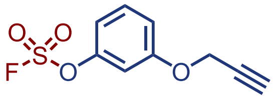
8f
87%



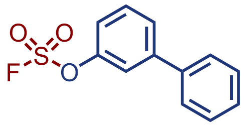
8g
93%



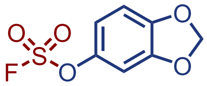
8h
80%



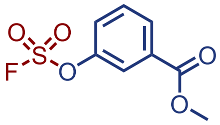
8i[d]
67%



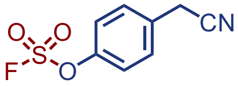
8j
92%



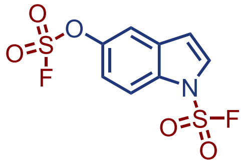
8k
>99%



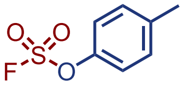
8l
70%



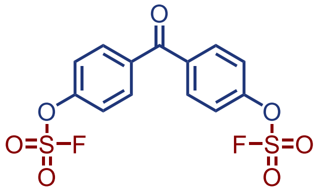
8m
95%



8n[b]
69%



8o[c]
67%



8p[e]
98%

[a]Conducted on a 50 mmol scale; [b]Reaction conducted on a 3.8 mmol scale, stirred for 1 h; [c]Reaction conducted on a 1.6 mmol scale, stirred for 16 h; [d]Reaction conducted on a 3.9 mmol scale, stirred for 4 h; [e]Reaction conducted on a 10.0 mmol scale, stirred for 19 h.

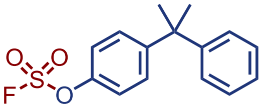
General Procedure E

To a solution of the required phenol (0.1 mmol) in MeCN (0.5 mL) under an atmosphere of sulfuryl fluoride (1 balloon) was added HMDS (0.1 mmol) and BTMG (5.0 mol%). The resulting reaction was stirred at room temperature for 15 minutes. Upon completion the solvent was removed and the crude was filtered through a short silica plug to obtain the analytically pure product.

General Procedure F

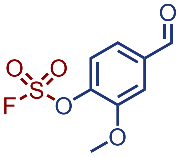
To a solution of the required phenol (50 mmol) in MeCN (250 mL) under an atmosphere of sulfuryl fluoride (4 balloons) was added HMDS (50 mmol) and BTMG (5.0 mol%). The resulting reaction was stirred at room temperature for 5 minutes. Upon completion the solvent was removed and the crude was filtered through a short silica plug to obtain the analytically pure product.

4-(2-Phenylpropan-2-yl)phenyl sulfurofluoridate (8a)[9]



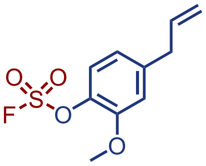
Following general procedure E, the title compound was isolated as a colourless oil (29 mg, 98%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34–7.29 (m, 4H), 7.24–7.21 (m, 5H), 1.70 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.8, 149.6, 148.1, 128.9, 128.4, 126.8, 126.2, 120.4 (d, *J* = 0.6 Hz), 43.1, 30.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 37.3; **IR** ν_{max} (ATR)/cm^{-1}: 3059, 3024, 2972, 2935, 1500, 1188, 1072, 945.

4-Formyl-2-methoxyphenyl sulfurofluoridate (8b)[9]



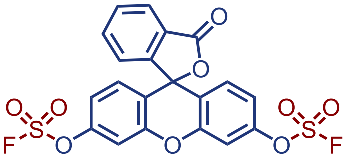
Following general procedure E, the title compound was isolated as a colourless solid (22 mg, 95%). **m.p.** 50–51 °C (lit. 51–52 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.58 (s, 1H), 7.55–7.50 (m, 2H), 4.00 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.5, 152.2, 143.0, 137.2, 124.1, 123.3, 112.2, 56.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 41.0; **IR** ν_{max} (ATR)/cm^{-1}: 2978, 2943, 2852, 2736, 1705, 1166, 1143, 906.

4-Allyl-2-methoxyphenyl sulfurofluoridate (8c)[10]



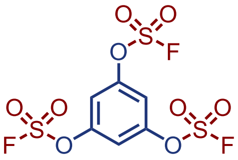
Following general procedure F, the title compound was isolated as a colourless oil (12.3 g, >99%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.86 (d, *J* = 1.8 Hz, 1H), 6.81 (dd, *J* = 8.3, 2.0 Hz, 1H), 5.94 (ddt, *J* = 17.5, 10.9, 6.7 Hz, 1H), 5.15–5.14 (m, 1H), 5.12–5.10 (m, 1H), 3.90 (s, 3H), 3.40 (d, *J* = 6.7 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.1, 142.3, 137.5, 136.4, 122.2, 120.9, 117.0, 113.8, 56.3, 40.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 39.4; **IR** ν_{max} (ATR)/cm^{-1}: 3080, 3010, 2980, 2943, 1639, 1537, 1145, 995.

3-Oxo-3*H*-spiro[isobenzofuran-1,9'-xanthene]-3',6'-diyl bis(sulfurofluoridate) (8d)[11],[12]



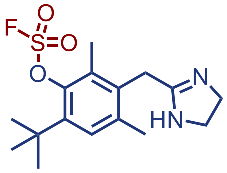
Following general procedure E, the title compound was isolated as a colourless solid (49 mg, 99%). **m.p.** 154–155 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.4 Hz, 1H), 7.76–7.68 (m, 2H), 7.38 (s, 2H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 9.0 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.6, 152.4, 151.5, 150.7, 136.0, 130.9, 130.3, 125.9, 125.7, 123.9, 119.8, 117.4, 110.5, 80.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 38.8; **HRMS** (ESI): *m/z* calcd for $C_{20}H_{10}F_2O_9S_2$+Na^+: 518.9626 [*M*+Na]$^+$; found: 518.9626; **IR** ν_{max} (ATR)/cm^{-1}: 3093, 3026, 2926, 2852, 1774, 1286, 1132, 1078, 948.

Benzene-1,3,5-triyl tris(sulfurofluoridate) (8e)[9]



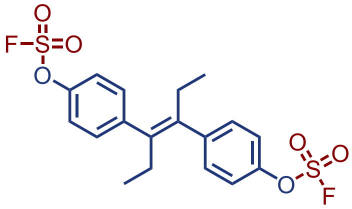
Following general procedure E, the title compound was isolated as a colourless solid (24 mg, 65%). **m.p.** 80–81 °C (lit.[9] 96–97 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.4, 115.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 40.0; **IR** ν_{max} (ATR)/cm^{-1}: 3111, 1610, 1450, 1273, 1109, 877.

6-(*tert*-Butyl)-3-((4,5-dihydro-1*H*-imidazol-2-yl)methyl)-2,4-dimethylphenyl sulfurofluoridate (8f)



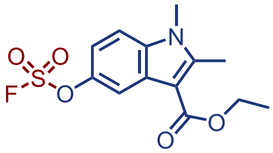
Following general procedure E, the title compound was isolated as a colourless oil (30 mg, 87%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 6.98 (s, 1H), 4.70 (s, 1H), 4.04–4.00 (m, 2H), 3.91–3.84 (m, 4H), 2.21 (s, 3H), 2.11 (s, 3H), 1.40 (s, 9H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 154.9 (d, *J* = 2.3 Hz), 150.9, 134.7, 130.2, 127.9, 126.5, 122.8, 53.4, 49.7, 34.4, 30.4, 30.0, 20.0, 12.4; **^{19}F NMR** (376 MHz, CDCl$_3$) δ 48.3; **HRMS** (ESI): *m/z* calcd for $C_{16}H_{24}FN_2O_3S^+$: 343.1486 [*M*+H]$^+$; found: 343.1503; **IR** ν_{max} (ATR)/cm^{-1}: 2954, 2908, 2870, 1662, 1436, 1361, 1222, 1114, 1006.

(*E*)-4-(4-(4-((Fluorosulfonyl)oxy)phenyl)hex-3-en-3-yl)phenyl sulfurofluoridate (8g)[10]



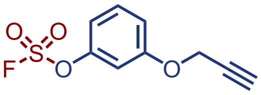
Following general procedure E, the title compound was isolated as a colourless solid (40 mg, 93%). **m.p.** 122–123 °C (lit.[10] 122–123 °C); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.37–7.35 (m, 4H), 7.31–7.29 (m, 4H), 2.11 (q, *J* = 7.4 Hz, 4H), 0.77 (t, *J* = 7.5 Hz, 6H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 148.9, 142.8, 138.9, 130.7, 120.8, 28.6, 13.2; **^{19}F NMR** (376 MHz, CDCl$_3$) δ 37.6; **IR** ν_{max} (ATR)/cm^{-1}: 3018, 2974, 2933, 2873, 1498, 1176, 1101, 1016, 848.

Ethyl 5-((fluorosulfonyl)oxy)-1,2-dimethyl-1*H*-indole-3-carboxylate (8h)[13]



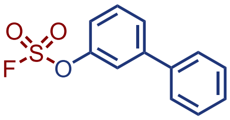
Following general procedure E (conducted on a 3.8 mmol scale, stirred for 1 h), the title compound was isolated as a colourless solid (25 mg, 80%). **m.p.** 134–135 °C; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.08 (s, 1H), 7.30 (appt. d, *J* = 8.9 Hz, 1H), 7.18 (appt. dd, *J* = 8.9, 1.3 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 3.71 (s, 3H), 2.77 (s, 3H), 1.45 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 165.4, 147.7, 145.9, 135.6, 127.3, 114.7, 113.9, 110.3, 105.1, 59.9, 30.1, 14.7, 12.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 36.6; **HRMS** (ESI): *m/z* calcd for $C_{13}H_{14}FNO_5S+Na^+$: 316.0649 [*M*+Na]$^+$; found: 316.0665; **IR** ν_{max} (ATR)/cm^{-1}: 3018, 1689, 1446, 1230, 1215, 1170, 939.

3-(Prop-2-yn-1-yloxy)phenyl sulfurofluoridate (8i)



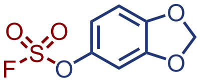
Following general procedure E (conducted on a 3.9 mmol scale, stirred for 4 h), the title compound was isolated as a colourless oil (600 mg, 67%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (t, *J* = 8.3 Hz, 1H), 7.05–6.97 (m, 3H), 4.73 (d, *J* = 2.5 Hz, 2H), 2.58 (t, *J* = 2.4 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.8, 150.7, 130.9, 115.3, 113.8, 108.3, 108.3, 77.5, 76.6, 56.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 37.8; **HRMS** (ESI): *m/z* calcd for $C_9H_8FO_4S^+$: 231.0122 [*M*+H]$^+$; found: 231.0125; **IR** ν_{max} (ATR)/cm^{-1}: 3302, 1610, 1587, 1486, 1443, 1288, 1224, 1109, 1030, 948, 924, 862, 802, 772, 678, 574, 545.

[1,1'-Biphenyl]-3-yl sulfurofluoridate (8j)[14]



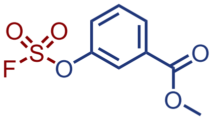
Following general procedure E, the title compound was isolated as a colourless oil (25 mg, 92%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68–7.63 (m, 1H), 7.59–7.53 (m, 4H), 7.50–7.47 (m, 2H), 7.44–7.40 (m, 1H), 7.34–7.31 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.7, 144.3, 139.1, 130.8, 129.2, 128.5, 127.4, 127.3, 121.3, 119.6(d, *J* = 17.9 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ 37.8; **IR** ν_{max} (ATR)/cm^{-1}: 3064, 3035, 2926, 2852, 1477, 1421, 1134, 931.

Benzo[*d*][1,3]dioxol-5-yl sulfurofluoridate (8k)[15]



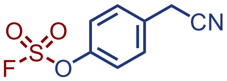
Following general procedure E, the title compound was isolated as a colourless oil (22 mg, >99%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.83–6.82 (m, 3H), 6.06 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.8, 147.8, 144.2, 114.2 (d, *J* = 0.9 Hz), 108.4, 103.1 (d, *J* = 1.1 Hz), 102.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 36.6; **IR** ν_{max} (ATR)/cm^{-1}: 3018, 2912, 1483, 1450, 1232, 1215, 947.

Methyl 3-((fluorosulfonyl)oxy)benzoate (8l)[16]



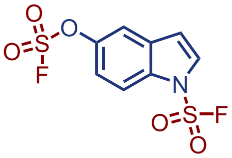
Following general procedure E, the title compound was isolated as a colourless oil (16 mg, 70%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (appt. dt, *J* = 7.4, 1.5 Hz, 1H), 8.01 (m, 1H), 7.60–7.53 (m, 2H), 3.96 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 150.0, 133.0, 130.7, 129.9, 125.4, 122.3, 52.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 38.2; **IR** ν_{max} (ATR)/cm^{-1}: 3018, 2954, 1728, 1452, 1232, 1215, 931

4-(Cyanomethyl)phenyl sulfurofluoridate (8m)[16]



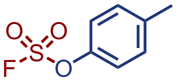
Following general procedure E, the title compound was isolated as a colourless solid (21 mg, 95%). **m.p.** 35–36 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (appt. d, *J* = 9.0 Hz, 2H), 7.38 (appt. d, *J* = 8.4 Hz, 2H), 3.81 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.8, 131.0, 130.2, 121.9 (d, *J* = 0.8 Hz), 117.0, 23.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 37.9; **IR** ν_{max} (ATR)/cm^{-1}: 3022, 2926, 1303, 1263, 1182, 1107, 823.

1-(Fluorosulfonyl)-1*H*-indol-5-yl sulfurofluoridate (8n)[15]



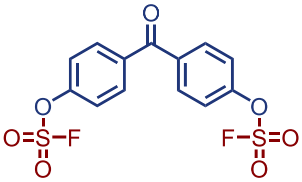
Following general procedure E (conducted on a 3.8 mmol scale, stirred for 1 h), the title compound was isolated as a colorless oil (770 mg, 69%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 9.1 Hz, 1H), 7.66 (d, *J* = 2.5 Hz, 1H), 7.58 (d, *J* = 3.8 Hz, 1H), 7.44 – 7.41 (m, 1H), 6.88 (dd, *J* = 3.9, 0.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.2, 133.9 (d, *J* = 1.0 Hz), 131.6, 128.7 (d, *J* = 2.0 Hz), 118.7, 115.3, 114.6 (d, *J* = 1.0 Hz), 110.8 (d, *J* = 1.5 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ 55.8, 37.3; **HRMS** (ESI): *m/z* calcd for $C_8H_6O_5NF_2S_2$+Na^+: 297.950 [*M*+Na]$^+$; found: 297.9649; **IR** ν_{max} (ATR)/cm^{-1}: 3156, 1440, 1236, 1220, 1138, 1105, 952, 901, 797, 716, 629, 607, 558, 514.

***p*-Tolyl sulfurofluoridate (8o)**[17]



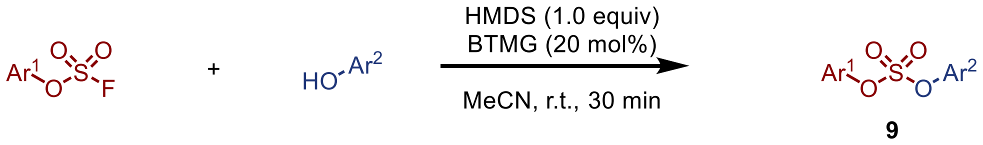
Following general procedure E (conducted on a 1.6 mmol scale, stirred for 16 h), the title compound was isolated as a colorless oil (210 mg, 67%). **^{1}H NMR** δ (400 MHz, CDCl$_3$) 7.32–7.24 (m, 4H), 2.50 (s, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 147.5, 140.2, 127.7, 121.4, 15.9; **^{19}F NMR** (376 MHz, CDCl$_3$) δ 37.3; **IR** ν_{max} (ATR)/cm^{-1}: 1485, 1446, 1401, 1232, 1181, 1140, 1096, 1014, 937, 906, 806, 771, 583, 541, 496.

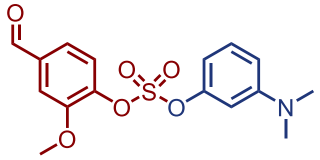
Carbonylbis(4,1-phenylene) bis(sulfurofluoridate) (8p)[18]

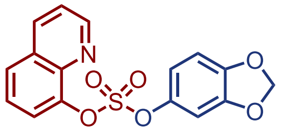


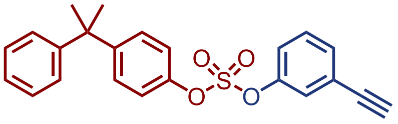
Following general procedure E (conducted on a 10.0 mmol scale, stirred for 19 h), the title compound was isolated as a white solid (3.7 g, 98%). **m.p.** 90–91 °C (lit.[ref] 91–94 °C); **^{1}H NMR** δ (400 MHz, CDCl$_3$) 7.94–7.91 (m, 4H), 7.52–7.48 (m, 4H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 192.8, 152.7, 137.0, 132.3, 121.3; **^{19}F NMR** (376 MHz, CDCl$_3$) δ 38.9; **IR** ν_{max} (ATR)/cm^{-1}: 3277, 1603, 1450, 1352, 1313, 1234, 1218, 1176, 1141, 1015, 910, 862, 812, 761, 572, 539.

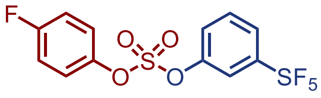
Synthesis and Experimental Data for Sulfates 9a–9s

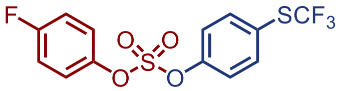


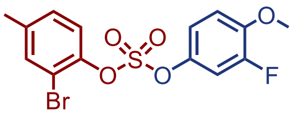

9a
97%

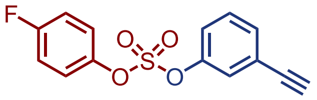

9b
83%

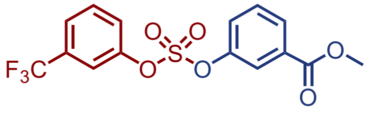

9c
>99%

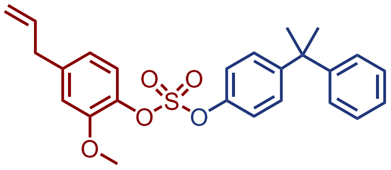

9d[a]
90%

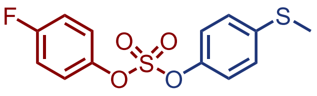

9e
>99%

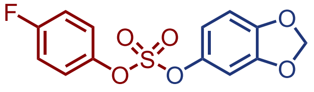

9f
95%

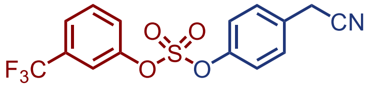

9g
97%

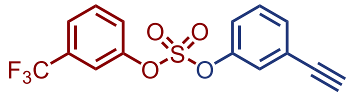

9h
97%

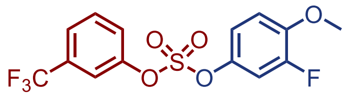

9i[b]
91%

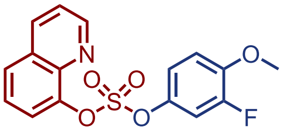

9j[a]
97%


9k
97%

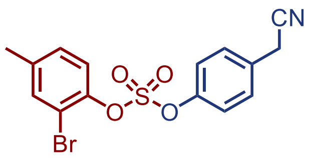

9l
94%

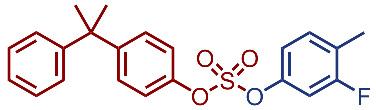

9m
>99%

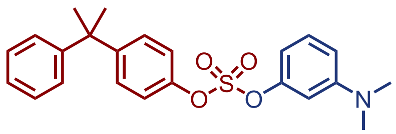

9n
95%


9o
86%


9p[c]
80%


9q
97%


9r
>99%


9s
95%

[a]Reaction run for 20 min; [b]Reaction conducted on a 40.6 mmol scale, stirred for 180 min with 5 mol% BTMG; [c]Reaction run for 60 min.

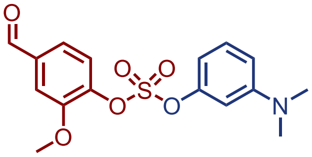
Procedure G

To a solution of the required fluorosulfate (0.1 mmol) and the required phenol (0.1 mmol) in MeCN (0.5 mL) was added HMDS (0.1 mmol) and BTMG (20 mol%). The resulting solution was stirred at room temperature for 30 min. Upon completion the solvent was removed or filtered through a short silica plug to obtain the analytically pure product.

General Procedure H

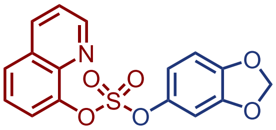
To a solution of the required fluorosulfate (25 mmol) and the required phenol (25 mmol) in MeCN (125 mL) was added HMDS (25 mmol) and BTMG (20 mol%). The resulting solution was stirred at room temperature for 3 hours. Upon completion the solvent was removed or filtered through a short silica plug to obtain the analytically pure product.

3-(Dimethylamino)phenyl (4-formyl-2-methoxyphenyl) sulfate (9a)



Following general procedure G, the title compound was isolated as a purple oil (34 mg, 97%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 9.96 (s, 1H), 7.53 (s, 1H), 7.47 (d, *J* = 1.0 Hz, 2H), 7.26–7.22 (m, 1H), 6.72 (ddd, *J* = 8.2, 2.1, 0.9 Hz, 1H), 6.66–6.64 (m, 2H), 3.93 (s, 3H), 2.96 (s, 6H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 190.8, 152.4, 151.9, 151.9, 144.0, 136.1, 130.2, 124.3, 123.2, 111.8, 111.4, 108.1, 104.7, 56.4, 40.4; **HRMS** (ESI): *m/z* calcd for $C_{16}H_{18}NO_6S^+$: 352.0849 [*M*+H]$^+$; found: 352.0852; **IR** ν_{max} (ATR)/cm^{-1}: 3053, 2986, 1705, 1612, 1501, 1420, 1265, 1115, 895, 874.

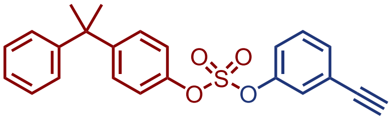
Benzo[*d*][1,3]dioxol-5-yl quinolin-8-yl sulfate (9b)



Following general procedure G, the title compound was isolated after purification by flash column chromatography (0–20% EtOAc in petroleum ether) as a grey solid (29 mg, 83%). **m.p.** 83.9–85.8 °C; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 9.05 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.22 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.83 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.74 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.56 (appt. t, *J* = 8.0 Hz, 1H), 7.52 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.17

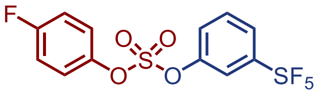
(d, *J* = 2.5 Hz, 1H), 7.01 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.80 (d, *J* = 8.5 Hz, 1H), 6.02 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.5, 148.4, 146.9, 146.6, 145.0, 141.0, 136.1, 130.0, 127.6, 126.2, 122.5, 121.4, 114.8, 108.2, 104.1, 102.3; **HRMS** (ESI): *m/z* calcd for $C_{16}H_{12}NO_6S^+$: 346.0380 [*M*+H]$^+$; found: 346.0374; **IR** ν_{max} (ATR)/cm^{-1}: 3059, 2913, 1497, 1406, 1227, 1211, 1161, 1043, 1026, 866.

3-Ethynylphenyl (4-(2-phenylpropan-2-yl)phenyl) sulfate (9c)



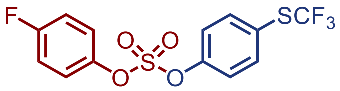
Following general procedure G, the title compound was isolated as a yellow oil (39 mg, >99%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (appt. d, *J* = 7.5 Hz, 1H), 7.43–7.42 (m, 1H), 7.38 (appt. t, *J* = 7.9 Hz, 1H), 7.34–7.26 (m, 5H), 7.24–7.18 (m, 6H), 3.15 (s, 1H), 1.69 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.8, 150.2, 149.9, 148.3, 131.4, 130.1, 128.7, 128.3, 126.8, 126.1, 124.8, 124.4, 121.8, 120.6, 81.9, 79.2, 43.0, 30.9; **HRMS** (ESI): *m/z* calcd for $C_{23}H_{20}O_4S+Na^+$: 415.0975 [*M*+Na]$^+$; found: 415.0974; **IR** ν_{max} (ATR)/cm^{-1}: 3291, 2970, 1501, 1420, 1404, 1204, 1152, 1121, 887.

4-Fluorophenyl (3-(pentafluoro-λ^6-sulfaneyl)phenyl) sulfate (9d)



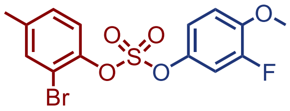
Following general procedure G (20 min reaction time), the title compound was isolated as a colourless oil (35 mg, 90%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (ddd, *J* = 8.1, 1.8, 1.2 Hz, 1H), 7.67 (appt. t, *J* = 2.1 Hz, 1H), 7.58 (appt. t, *J* = 8.2 Hz, 1H), 7.53 (appt. d, *J* = 8.4 Hz, 1H), 7.33–7.28 (m, 2H), 7.16–7.12 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.6 (d, *J* = 248.4 Hz), 154.7 (p, *J* = 19.3 Hz), 149.7, 146.1 (d, *J* = 3.0 Hz), 130.5, 125.4 (p, *J* = 4.7 Hz), 124.7, 123.0 (d, *J* = 8.8 Hz), 119.8 (p, *J* = 4.7 Hz), 117.2 (d, *J* = 24.0 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ 82.9–81.3 (m), 62.8 (d, *J* = 150.6 Hz), -112.9 (m); **HRMS** (ESI): *m/z* calcd for $C_{12}H_8F_6O_4S_2+Na^+$: 416.9660 [*M*+Na]$^+$; found: 416.9652; **IR** ν_{max} (ATR)/cm^{-1}: 1501, 1427, 1410, 1275, 1267, 1219, 1182, 1169, 1153, 841.

4-Fluorophenyl (4-((trifluoromethyl)thio)phenyl) sulfate (9e)



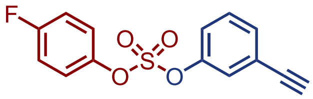
Following general procedure G, the title compound was isolated as a colourless oil (37 mg, >99%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.74 (appt. d, *J* = 8.7 Hz, 2H), 7.39 (appt. d, *J* = 8.9 Hz, 2H), 7.31–7.26 (m, 2H), 7.15–7.09 (m, 2H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 161.6 (d, *J* = 248.1 Hz), 152.3, 146.2 (d, *J* = 3.0 Hz), 138.4, 129.4 (q, *J* = 308.4 Hz), 124.3 (q, *J* = 2.1 Hz), 123.1 (d, *J* = 8.8 Hz), 122.2, 117.1 (d, *J* = 24.0 Hz); **^{19}F NMR** (376 MHz, CDCl$_3$) δ -42.5, -113.0 – -113.1 (m); **HRMS** (ESI): *m/z* calcd for $C_{13}H_8F_4O_4S_2+Na^+$: 390.9692 [*M*+Na]$^+$; found: 390.9702; **IR** ν_{max} (ATR)/cm^{-1}: 3053, 1501, 1487, 1423, 1404, 1265, 1153, 1119, 885.

2-Bromo-4-methylphenyl (3-fluoro-4-methoxyphenyl) sulfate (9f)



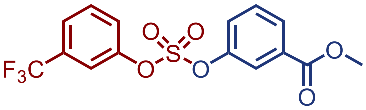
Following general procedure G, the title compound was isolated as a colourless oil (37 mg, 95%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.47 (d, *J* = 1.9 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.18–7.12 (m, 3H), 6.97 (appt. t, *J* = 9.2 Hz, 1H), 3.90 (d, *J* = 5.6 Hz, 3H), 2.36 (s, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 152.0 (d, *J* = 250.5 Hz), 147.5 (d, *J* = 10.4 Hz), 145.5, 143.0 (d, *J* = 9.5 Hz), 139.4, 134.7, 129.6, 122.0, 117.4 (d, *J* = 4.0 Hz), 115.3, 113.5 (d, *J* = 2.6 Hz), 110.8 (d, *J* = 22.2 Hz), 56.7, 20.8; **^{19}F NMR** (376 MHz, CDCl$_3$) δ -130.2 (appt. t, *J* = 9.5 Hz); **HRMS** (ESI): *m/z* calcd for $C_{14}H_{12}BrFNO_5S+Na^+$: 412.9465 [*M*+Na]$^+$; found: 412.9458; **IR** ν_{max} (ATR)/cm^{-1}: 2928, 2845, 1601, 1514, 1483, 1422, 1279, 1209, 1182, 1136, 1026, 895, 962, 876.

3-Ethynylphenyl (4-fluorophenyl) sulfate (9g)



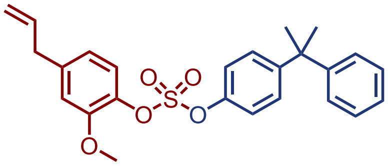
Following general procedure G, the title compound was isolated as a yellow oil (28 mg, 97%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.48 (appt. d, *J* = 7.6 Hz, 1H), 7.44 (appt. s, *J* = 4.6 Hz, 1H), 7.39 (appt. t, *J* = 7.9 Hz, 1H), 7.33–7.28 (m, 3H), 7.14–7.10 (m, 2H), 3.16 (s, 1H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 161.5 (d, *J* = 247.8 Hz), 150.1, 146.2 (d, *J* = 3.1 Hz), 131.6, 130.2, 124.7, 124.5, 123.1 (d, *J* = 8.8 Hz), 121.7, 117.0 (d, *J* = 24.0 Hz), 81.8, 79.3; **^{19}F NMR** (376 MHz, CDCl$_3$) δ -113.3 – -113.4 (m); **HRMS** (ESI): *m/z* calcd for $C_{14}H_9FO_4S+Na^+$: 315.0098 [*M*+Na]$^+$; found: 315.0096; **IR** ν_{max} (ATR)/cm^{-1}: 3298, 3082, 2928, 1607, 1574, 1454, 1423, 1327, 1281, 1227, 1092, 945.

Methyl 3-(((3-(trifluoromethyl)phenoxy)sulfonyl)oxy)benzoate (9h)



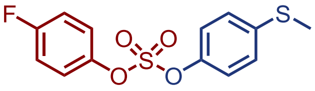
Following general procedure G, the title compound was isolated as a colourless oil (36 mg, 97%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07–8.05 (m, 1H), 7.97–7.96 (m, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.61–7.53 (m, 5H), 3.94 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.5, 150.3, 150.2, 132.9 (q, *J* = 33.6 Hz), 132.7, 131.1, 130.5, 129.2, 125.6, 124.9–124.8 (m), 123.2 (q, *J* = 272.7 Hz), 122.3, 118.7 (q, *J* = 3.9 Hz), 52.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.8; **HRMS** (ESI): *m/z* calcd for $C_{15}H_{11}F_3O_6S+Na^+$: 399.0121 [*M*+Na]$^+$; found: 399.0126; **IR** ν_{max} (ATR)/cm^{-1}: 3082, 2957, 1732, 1585, 1487, 1447, 1427, 1327, 1300, 1134, 1096, 988, 910.

4-Allyl-2-methoxyphenyl (4-(2-phenylpropan-2-yl)phenyl) sulfate (9i)



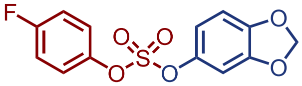
Following general procedure H, the title compound was isolated as a colourless oil (10.0 g, 91%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29–7.24 (m, 6H)[19], 7.21–7.11 (m, 4H), 6.79 (s, 1H), 6.73 (d, *J* = 8.1 Hz, 1H), 5.97–5.87 (m, 1H), 5.11–5.07 (m, 2H), 3.79 (s, 3H), 3.36 (d, *J* = 6.8 Hz, 2H), 1.67 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.4, 150.3, 150.0, 148.7, 141.0, 138.0, 136.7, 128.4, 128.3, 126.9, 126.1, 122.5, 120.8, 120.8, 116.7, 113.5, 56.1, 42.9, 40.2, 30.9; **HRMS** (ESI): *m/z* calcd for $C_{25}H_{27}O_5S^+$: 439.1574 [*M*+H]$^+$; found: 439.1575; **IR** ν_{max} (ATR)/cm^{-1}: 3082, 3059, 2970, 2937, 1637, 1365, 1307, 1072, 995, 729.

4-Fluorophenyl (4-(methylthio)phenyl) sulfate (9j)



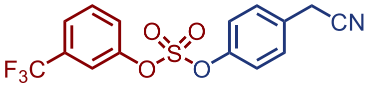
Following general procedure G (20 min reaction time), the title compound was isolated as a colourless oil (30 mg, 97%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31–7.20 (m, 6H), 7.13–7.07 (m, 2H), 2.48 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.4 (d, *J* = 247.6 Hz), 147.9, 146.2 (d, *J* = 3.0 Hz), 138.8, 127.9, 123.1 (d, *J* = 8.8 Hz), 121.6, 117.0 (d, *J* = 23.9 Hz), 16.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.5 – -113.6 (m); **HRMS** (ESI): *m/z* calcd for $C_{13}H_{11}FO_4S_2+Na^+$: 336.9975 [*M*+Na]$^+$; found: 336.9981; **IR** ν_{max} (ATR)/cm^{-1}: 2924, 1501, 1487, 1422, 1402, 1182, 1153, 1092, 1015, 883, 822.

Benzo[*d*][1,3]dioxol-5-yl (4-fluorophenyl) sulfate (9k)



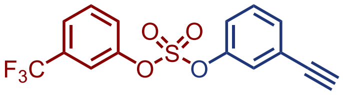
Following general procedure G, the title compound was isolated as a yellow oil (30 mg, 97%). ^{1}**H NMR** (400 MHz, CDCl$_3$) δ 7.31 (ddd, *J* = 10.6, 5.3, 3.1 Hz, 2H), 7.15–7.09 (m, 2H), 6.82–6.78 (m, 2H), 6.03 (s, 2H); ^{13}**C NMR** (101 MHz, CDCl$_3$) δ 161.4 (d, *J* = 247.6 Hz), 148.6, 147.1, 146.3 (d, *J* = 3.0 Hz), 144.5, 123.1 (d, *J* = 8.8 Hz), 117.0 (d, *J* = 23.9 Hz), 114.3, 108.3, 103.4, 102.4; ^{19}**F NMR** (376 MHz, CDCl$_3$) δ -113.6 (m); **HRMS** (ESI): *m/z* calcd for $C_{13}H_{10}FO_6S^+$: 313.0177 [*M*+H]$^+$; found: 313.0177; **IR** ν$_{max}$ (ATR)/cm^{-1}: 3121, 3084, 2907, 1634, 1614, 1504, 1485, 1402, 1250, 1211, 1157, 1113, 1092, 1038, 945, 889, 866.

4-(Cyanomethyl)phenyl (3-(trifluoromethyl)phenyl) sulfate (9l)



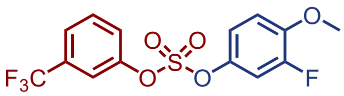
Following general procedure G, the title compound was isolated as a yellow oil (34 mg, 94%). ^{1}**H NMR** (500 MHz, CDCl$_3$) δ 7.64 (appt. d, *J* = 7.7 Hz, 1H), 7.61–7.58 (m, 1H), 7.55–7.53 (m, 2H), 7.43 (appt. d, *J* = 8.9 Hz, 2H), 7.35 (appt. d, *J* = 8.8 Hz, 2H), 3.79 (s, 2H); ^{13}**C NMR** (126 MHz, CDCl$_3$) δ 150.3, 150.0, 132.9 (q, *J* = 33.5 Hz), 131.1, 130.1, 130.0, 124.8–124.7 (m), 123.1 (q, *J* = 272.7 Hz), 118.6 (q, *J* = 3.8 Hz), 117.2, 23.3; ^{19}**F NMR** (376 MHz, CDCl$_3$) δ -62.8; **HRMS** (ESI): *m/z* calcd for $C_{15}H_{10}F_3NO_4S$+Na$^+$: 380.0175 [*M*+Na]$^+$; found: 380.0174; **IR** ν$_{max}$ (ATR)/cm^{-1}: 3053, 2986, 2305, 1504, 1422, 1325, 1265, 1175, 1148, 895.

3-Ethynylphenyl (3-(trifluoromethyl)phenyl) sulfate (9m)



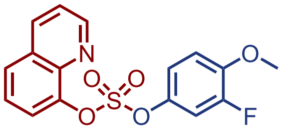
Following general procedure G, the title compound was isolated as a yellow oil (34 mg, >99%). ^{1}**H NMR** (400 MHz, CDCl$_3$) δ 7.65–7.53 (m, 4H), 7.49 (appt. d, *J* = 7.6 Hz, 1H), 7.45–7.39 (m, 2H), 7.33 (dd, *J* = 8.3, 1.4 Hz, 1H), 3.16 (s, 1H); ^{13}**C NMR** (101 MHz, CDCl$_3$) δ 150.3, 150.0, 133.0 (q, *J* = 33.6 Hz), 131.8, 131.0, 130.3, 124.8–124.6 (m), 123.2 (q, *J* = 272.6 Hz), 121.7, 118.7 (q, *J* = 3.9 Hz), 81.7, 79.4; ^{19}**F NMR** (376 MHz, CDCl$_3$) δ -62.8; **HRMS** (ESI): *m/z* calcd for $C_{15}H_9F_3O_4S$+Na$^+$: 365.0066 [*M*+Na]$^+$; found: 365.0068; **IR** ν$_{max}$ (ATR)/cm^{-1}: 3298, 2082, 2928, 1607, 1574, 1481, 1543, 1450, 1433, 1327, 1281, 1227, 1175, 993, 945.

3-Fluoro-4-methoxyphenyl (3-(trifluoromethyl)phenyl) sulfate (9n)



Following general procedure G, the title compound was isolated as a colourless oil (35 mg, 95%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 (appt. d, *J* = 7.8 Hz, 1H), 7.60 (appt. t, *J* = 7.8 Hz, 1H), 7.55–7.53 (m, 2H), 7.12 (dd, *J* = 10.7, 2.7 Hz, 1H), 7.08 (ddd, *J* = 9.0, 2.9, 1.6 Hz, 1H), 6.99 (t, *J* = 9.0 Hz, 1H), 3.91 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.1 (d, *J* = 251.0 Hz), 150.3, 147.7 (d, *J* = 10.4 Hz), 142.8 (d, *J* = 9.5 Hz), 132.9 (q, *J* = 33.5 Hz), 131.0, 124.8 – 124.7 (m), 123.2 (q, *J* = 272.7 Hz), 118.6 (q, *J* = 3.9 Hz), 117.1 (d, *J* = 4.1 Hz), 113.6 (d, *J* = 2.7 Hz), 110.5 (d, *J* = 22.2 Hz), 56.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.8, -129.6 – -129.8 (m); **HRMS** (ESI): *m/z* calcd for $C_{14}H_{10}F_4O_5S+Na^+$: 389.0077 [M+Na]$^+$; found: 389.0076; **IR** ν$_{max}$ (ATR)/cm^{-1}: 1599, 1514, 1449, 1423, 1327, 1207, 1175, 1136, 916.

3-Fluoro-4-methoxyphenyl quinolin-8-yl sulfate (9o)

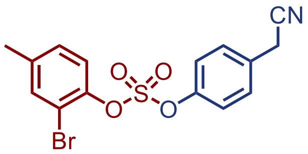


Following general procedure G, the title compound was isolated as a colourless solid (30 mg, 86%). **m.p.** 81.2–83.9 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.03 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.22 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.82 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.74 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.58–7.49 (m, 3H), 7.30 (ddd, *J* = 9.0, 2.9, 1.8 Hz, 1H), 6.97 (appt. t, *J* = 9.1 Hz, 1H), 3.90 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.0 (d, *J* = 249.7 Hz), 151.4, 147.3 (d, *J* = 10.4 Hz), 146.5, 143.5 (d, *J* = 9.7 Hz), 140.8, 136.1, 130.0, 127.7, 126.2, 122.5, 121.4, 117.6 (d, *J* = 4.0 Hz), 113.4 (d, *J* = 2.6 Hz), 111.1 (d, *J* = 22.4 Hz), 56.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -130.6 (appt. t, *J* = 10.1 Hz); **HRMS** (ESI): *m/z* calcd for $C_{16}H_{13}FNO_5S^+$: 350.0493 [M+H]$^+$; found: 350.0497; **IR** ν$_{max}$ (ATR)/cm^{-1}: 3071, 3013, 1936, 1845, 1597, 1514, 1416, 1315, 1279, 1198, 1136, 1076, 1047, 1026, 901, 847.

Quinolin-8-yl (4-((trifluoromethyl)thio)phenyl) sulfate (9p)

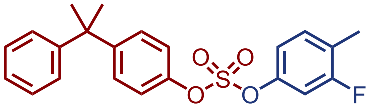
Following general procedure G the title compound was isolated after purification by flash column chromatography (ethyl acetate–petroleum ether) as a colourless oil (32 mg, 80%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.97 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.22 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.83 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.75–7.70 (m, 3H), 7.66 (appt. d, *J* = 8.9 Hz, 2H), 7.56 (appt. t, *J* = 8.0 Hz, 1H), 7.51 (dd, *J* = 8.4, 4.2 Hz, 1H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 152.8, 151.5, 146.4, 140.9, 138.1, 136.1, 130.0, 129.5 (q, *J* = 308.6 Hz), 127.9, 126.1, 123.7 (q, *J* = 2.2 Hz), 122.8, 122.6, 121.5; **^{19}F NMR** (376 MHz, CDCl$_3$) δ -42.6; **HRMS** (ESI): *m/z* calcd for $C_{16}H_{11}F_3NO_4S_2^+$: 402.0076 [*M*+H]$^+$; found: 402.0073; **IR** ν$_{max}$ (ATR)/cm^{-1}: 3061, 2926, 1584, 1487, 1422, 1206, 1159, 1117, 1082, 833.

2-Bromo-4-methylphenyl (4-(cyanomethyl)phenyl) sulfate (9q)



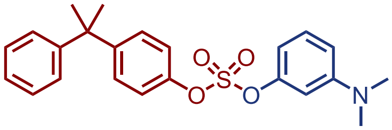
Following general procedure G, the title compound was isolated as a colourless oil (37 mg, 97%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.47 (dd, *J* = 1.4, 0.5 Hz, 1H), 7.42–7.40 (m, 4H), 7.53–7.33 (m, 1H), 7.16 (ddd, *J* = 8.4, 1.4, 0.6 Hz, 1H), 3.78 (s, 2H), 2.36 (s, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 150.2, 145.5, 139.5, 134.7, 129.9, 129.8, 129.6, 122.3, 122.1, 117.3, 115.3, 23.3, 20.8; **HRMS** (ESI): *m/z* calcd for $C_{15}H_{12}BrNO_4S$+Na$^+$: 403.9563 [*M*+Na]$^+$; found: 403.9565; **IR** ν$_{max}$ (ATR)/cm^{-1}: 2924, 1504, 1483, 1416, 1404, 1217, 1182, 1150, 1043, 855.

3-Fluoro-4-methylphenyl (4-(2-phenylpropan-2-yl)phenyl) sulfate (9r)



Following general procedure G, the title compound was isolated as a colourless oil (40 mg, >99%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.32–7.27 (m, 4H), 7.25–7.19 (m, 6H), 7.04 (dd, *J* = 8.3, 2.5 Hz, 1H), 7.00 (dd, *J* = 9.5, 2.4 Hz, 1H), 2.29 (d, *J* = 1.8 Hz, 3H), 1.70 (s, 6H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 161.0 (d, *J* = 248.5 Hz), 150.7, 149.9, 148.8 (d, *J* = 10.8 Hz), 148.3, 132.1 (d, *J* = 6.2 Hz), 128.6, 128.3, 126.8, 126.1, 124.8 (d, *J* = 17.1 Hz), 120.6, 116.7 (d, *J* = 3.9 Hz), 109.0 (d, *J* = 26.5 Hz), 43.0, 30.9, 14.3 (d, *J* = 3.2 Hz); **^{19}F NMR** (376 MHz, CDCl$_3$) δ -112.4 (appt. t, *J* = 8.6 Hz); **HRMS** (ESI): *m/z* calcd for $C_{22}H_{21}FO_4S$+Na$^+$: 423.1037 [*M*+Na]$^+$; found: 423.1028; **IR** ν$_{max}$ (ATR)/cm^{-1}: 2970, 1601, 1499, 1418, 1404, 1211, 1186, 1152, 1101, 955, 887, 843.

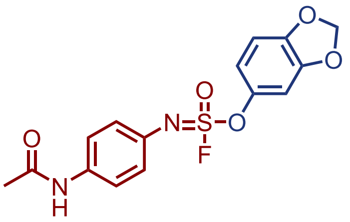
3-(Dimethylamino)phenyl (4-(2-phenylpropan-2-yl)phenyl) sulfate (9s)



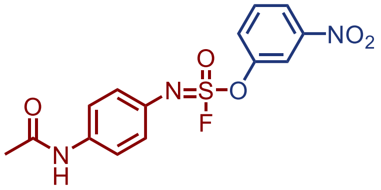
Following general procedure G, the title compound was isolated as a pink oil (39 mg, 95%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31–7.20 (m, 10H), 6.66–6.63 (m, 2H), 6.58 (appt. t, *J* = 2.4 Hz, 1H), 2.95 (s, 6H), 1.69 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.9, 151.9, 150.4, 150.0, 148.5, 130.2, 128.5, 128.3, 126.8, 126.1, 120.7, 111.2, 108.0, 104.6, 43.0, 40.4, 30.9; **HRMS** (ESI): *m/z* calcd for $C_{23}H_{26}NO_4S^+$: 412.1577 [*M*+H]$^+$; found: 412.1578; **IR** ν_{max} (ATR)/cm^{-1}: 3059, 2970, 2812, 1620, 1573, 1514, 1495, 1402, 1231, 1215, 1186, 1153, 1126, 997, 980, 891.

Synthesis and Experimental Data for Sulfurofluoridoimidates 10a–10h

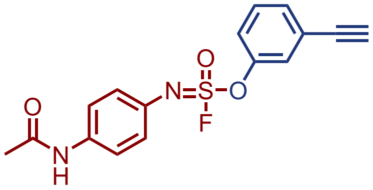
10



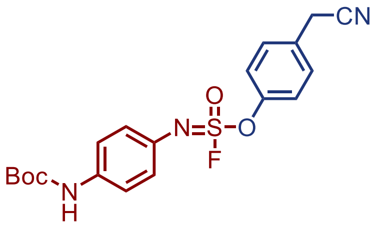
10a
>99%



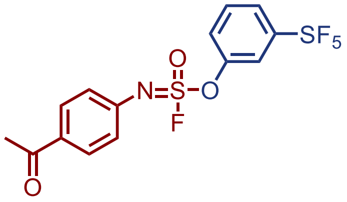
10b
>99%



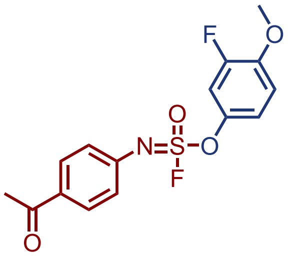
10c
>99%



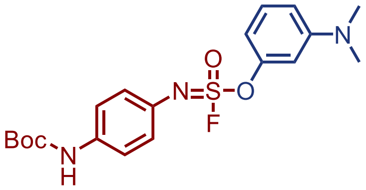
10d
83%



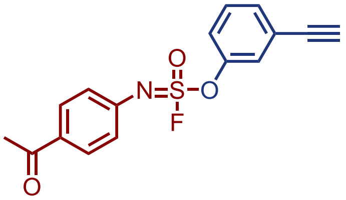
10e
69%



10f
94%



10g
>99%

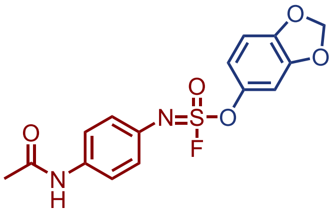


10h
91%

General Procedure I

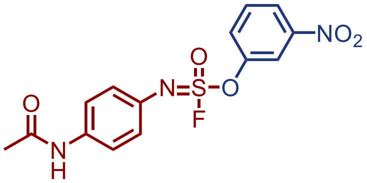
To a solution of the required iminosulfur oxydifluoride (0.1 mmol) and the required phenol (0.1 mmol) in MeCN (0.5 mL) was added HMDS (0.1 mmol) and BTMG (5.0 mol%). The resulting reaction was stirred at room temperature for 5 min. Upon completion the solvent was removed or filtered through a short silica plug to obtain the analytically pure product.

Benzo[*d*][1,3]dioxol-5-yl (4-acetamidophenyl)sulfurofluoridoimidate (10a)



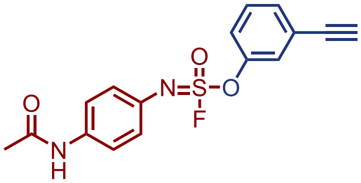
Following general procedure I, the title compound was isolated as a yellow oil (35 mg, >99%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.45 (appt.d, *J* = 8.6 Hz, 2H), 7.36 (br. s, 1H), 7.09 (appt. d, *J* = 8.6 Hz, 2H), 6.80 (s, 1H), 6.77 (s, 2H), 6.02 (s, 2H), 2.16 (s, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 168.4, 148.6, 147.4 144.3, 135.0, 134.9 (d, *J* = 3.7 Hz), 124.2 (d, *J* = 3.3 Hz), 121.1, 114.6, 108.3, 103.6, 102.5, 24.6; **^{19}F NMR** (376 MHz, CDCl$_3$) δ 48.8; **HRMS** (ESI): *m/z* calcd for $C_{15}H_{13}FN_2O_5S$+Na$^+$: 375.0421 [*M*+Na]$^+$; found: 375.0417; **IR** ν$_{max}$ (ATR)/cm^{-1}: 3053, 1668, 1603, 1510, 1481, 1404, 1265, 1103, 1088, 941, 864.

3-Nitrophenyl (4-acetamidophenyl)sulfurofluoridoimidate (10b)



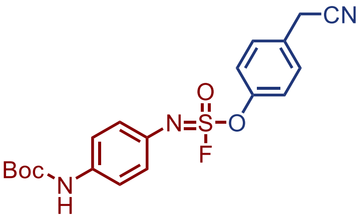
Following general procedure I, the title compound was isolated as a yellow oil (35 mg, >99%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.26 (appt. d, *J* = 7.2 Hz, 1H), 8.19 (appt. s, 1H), 7.70–7.66 (m, 2H), 7.48 (appt. d, *J* = 8.6 Hz, 2H), 7.41 (br. s, 1H), 7.09 (appt. d, *J* = 8.6 Hz, 2H), 2.17 (s, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 168.6, 150.1, 149.1, 135.5, 134.0 (d, *J* = 3.6 Hz), 131.2, 127.8, 124.2 (d, *J* = 3.3 Hz), 123.2, 121.3, 117.4, 24.6; **^{19}F NMR** (376 MHz, CDCl$_3$) δ 51.5; **HRMS** (ESI): *m/z* calcd for $C_{14}H_{12}FN_3O_5S$+Na$^+$: 376.0374 [*M*+Na]$^+$; found: 376.0377; **IR** ν$_{max}$ (ATR)/cm^{-1}: 3053, 1694, 1674, 1537, 1510, 1406, 1354, 1265, 1179, 1107, 930, 835.

3-Ethynylphenyl (4-acetamidophenyl)sulfurofluoridoimidate (10c)



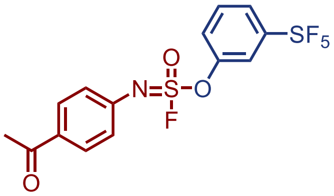
Following general procedure I, the title compound was isolated as a colourless solid (33 mg, >99%). **m.p.** 117.3–118.6 °C; **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.49–7.43 (m, 4H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.34 (br. s, 1H), 7.30 (dd, J = 8.3, 2.1 Hz, 1H), 7.10 (appt. d, J = 8.8 Hz, 2H), 3.16 (s, 1H), 2.17 (s, 3H); **^{13}C NMR** (126 MHz, CDCl$_3$) δ 168.4, 150.0, 135.1, 134.6 (d, J = 3.4 Hz), 132.0, 130.3, 125.0, 124.6, 124.2 (d, J = 3.2 Hz), 122.0, 121.1, 81.7, 79.5, 24.6; **^{19}F NMR** (376 MHz, CDCl$_3$) δ 50.3; **HRMS** (ESI): *m/z* calcd for $C_{16}H_{13}FN_2O_3S+Na^+$: 355.0523 [*M*+Na]$^+$; found: 355.0527; **IR** ν_{max} (ATR)/cm^{-1}: 3292, 1665, 1605, 1510, 1406, 1315, 1213, 1105, 926.

4-(Cyanomethyl)phenyl (4-((tert-butoxycarbonyl)amino)phenyl)sulfurofluoridoimidate (10d)



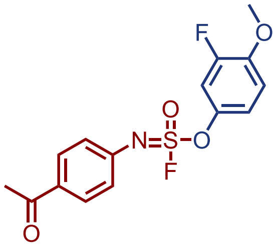
Following general procedure I, the title compound was isolated as a yellow oil (34 mg, 83%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.40 (appt. d, J = 8.5 Hz, 2H), 7.34–7.31 (m, 4H), 7.06 (appt. d, J = 8.7 Hz, 2H), 6.51 (br. s, 1H), 3.77 (s, 2H), 1.51 (s, 9H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 152.9, 150.0, 135.6, 133.5 (d, J = 3.7 Hz), 130.2, 129.9, 124.2 (d, J = 3.4 Hz), 122.3, 119.8, 117.2, 80.8, 28.4, 23.2; **^{19}F NMR** (376 MHz, CDCl$_3$) δ 50.2; **HRMS** (ESI): *m/z* calcd for $C_{19}H_{20}FN_3O_4S+Na^+$: 428.1051 [*M*+Na]$^+$; found: 428.1054; **IR** ν_{max} (ATR)/cm^{-1}: 3426, 3348, 2982, 1722, 1520, 1504, 1404, 1265, 1159, 1107, 874, 839.

3-(Pentafluoro-λ^6-sulfaneyl)phenyl (4-acetylphenyl)sulfurofluoridoimidate (10e)



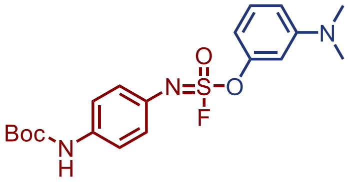
Following general procedure I, the title compound was isolated as a yellow oil (29 mg, 69%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.95 (appt. d, J = 8.6 Hz, 2H), 7.82 (ddd, J = 8.1, 1.9, 1.1 Hz, 1H), 7.73 (appt. t, J = 2.0 Hz, 1H), 7.60 (t, J = 8.2 Hz, 1H), 7.55 (appt. d, J = 8.7 Hz, 1H), 7.20 (appt. d, J = 8.8 Hz, 2H), 2.59 (s, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 196.9, 154.9–154.6 (m), 149.4, 142.6 (d, J = 3.6 Hz), 134.2, 130.7, 130.1, 126.1 (p, J = 4.7 Hz), 124.9, 123.7 (d, J = 3.4 Hz), 120.2 (p, J = 5.2 Hz), 26.6; **^{19}F NMR** (376 MHz, CDCl$_3$) δ 82.7–81.0 (m), 62.9 (d, J = 150.7 Hz), 52.1; **HRMS** (ESI): *m/z* calcd for $C_{14}H_{11}F_6NO_3S_2+Na^+$: 441.9977 [*M*+Na]$^+$; 441.9984; **IR** ν_{max} (ATR)/cm^{-1}: 1682, 1601, 1506, 1418, 1265, 1179, 1165, 1107, 858.

3-Fluoro-4-methoxyphenyl (4-acetylphenyl)sulfurofluoridoimidate (10f)



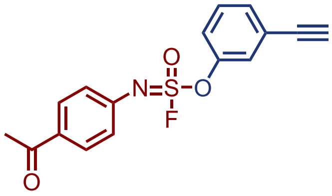
Following general procedure I, the title compound was isolated as a colourless solid (32 mg, 94%). **m.p.** 54.6–55.6 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (appt. d, *J* = 8.6 Hz, 2H), 7.20 (appt. d, *J* = 8.8 Hz, 2H), 7.14–7.07 (m, 2H), 6.98 (appt. t, *J* = 8.9 Hz, 1H), 3.91 (s, 3H), 2.58 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.0, 152.0 (d, *J* = 251.6 Hz), 148.1 (d, *J* = 10.3 Hz), 143.2 (d, *J* = 3.6 Hz), 142.5 (d, *J* = 9.4 Hz), 134.0, 130.0, 123.7 (d, *J* = 3.5 Hz), 117.4 (d, *J* = 3.9 Hz), 113.6 (d, *J* = 2.6 Hz), 110.7 (d, *J* = 22.4 Hz), 56.7, 26.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 50.1, -129.4 (appt. t, *J* = 9.4 Hz); **HRMS** (ESI): *m/z* calcd for $C_{15}H_{13}F_2NO_4S+Na^+$: 364.0426 [*M*+Na]$^+$; found: 364.0425; **IR** ν_{max} (ATR)/cm^{-1}: 3057, 2970, 1682, 1601, 1510, 1408, 1267, 1219, 1103, 953, 847.

3-(Dimethylamino)phenyl (4-((*tert*-butoxycarbonyl)amino)phenyl)sulfurofluoridoimidate (10g)



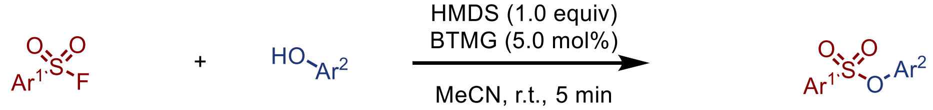
Following general procedure I, the title compound was isolated as a pink solid (41 mg, >99%). **m.p.** 82.8–83.8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (appt. d, *J* = 8.7 Hz, 2H), 7.22 (appt. t, *J* = 8.3 Hz, 1H), 7.09 (appt. d, *J* = 8.8 Hz, 2H), 6.65 – 6.60 (m, 2H), 6.54 (appt. t, *J* = 2.2 Hz, 1H), 6.48 (br. s, 1H), 2.94 (s, 6H), 1.52 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.9, 151.9, 151.6, 135.3, 134.2 (d, *J* = 3.7 Hz), 130.3, 124.3 (d, *J* = 3.4 Hz), 119.7, 111.6, 108.1, 104.7, 80.7, 40.4, 28.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 49.5; **HRMS** (ESI): *m/z* calcd for $C_{19}H_{24}FN_3O_4S+Na^+$: 432.1364 [*M*+Na]$^+$; found: 432.1369; **IR** ν_{max} (ATR)/cm^{-1}: 3406, 3331, 2978, 2930, 1726, 1614, 1568, 1504, 1393, 1314, 1231, 1105, 995, 897.

3-Ethynylphenyl (4-acetylphenyl)sulfurofluoridoimidate (10h)

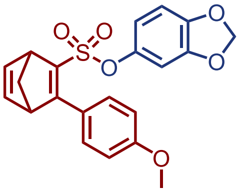


Following general procedure I, the title compound was isolated as a yellow oil (29 mg, 91%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.94 (appt. d, *J* = 8.6 Hz, 2H), 7.50 (appts. dt, *J* = 7.6, 1.2 Hz, 1H), 7.44 (appt. s, *J* = 5.7 Hz, 1H), 7.41 (appt. t, *J* = 8.0 Hz, 1H), 7.34–7.31 (m, 1H), 7.21 (appt. d, *J* = 8.6 Hz, 2H), 3.17 (s, 1H), 2.58 (s, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 197.0, 149.9, 143.1 (d, *J* = 3.5 Hz), 134.0, 132.2, 130.4, 130.1, 125.0, 124.8, 123.7 (d, *J* = 3.4 Hz), 122.0, 81.6, 79.7, 26.6; **^{19}F NMR** (376 MHz, CDCl$_3$) δ 51.3; **HRMS** (ESI): *m/z* calcd for $C_{16}H_{12}FNO_3S+Na^+$: 340.0414 [*M*+Na]$^+$; found: 340.0410; **IR** ν_{max} (ATR)/cm^{-1}: 3298, 2926, 1682, 1601, 1508, 1410, 1267, 1213, 1107, 934, 843.

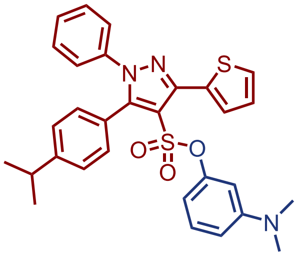
Synthesis and Experimental Data for Sulfonates 11a–11i



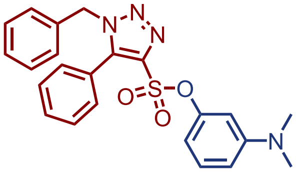
11



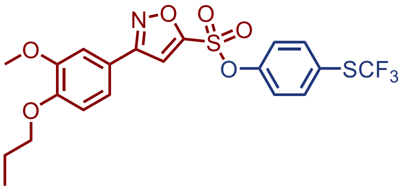
11a
88%



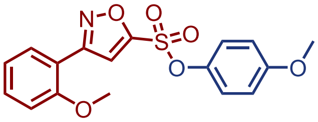
11b
76%



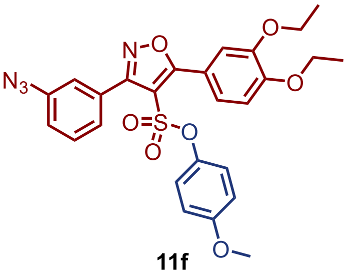
11c
80%



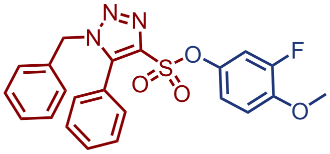
11d
>99%



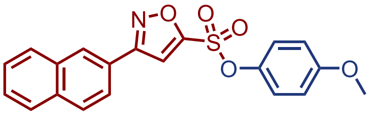
11e
81%



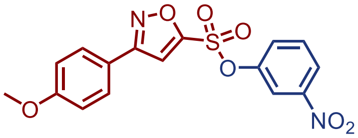
11f
83%



11g
73%



11h
66%

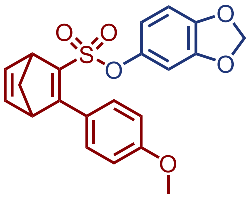


11i
63%

General Procedure J

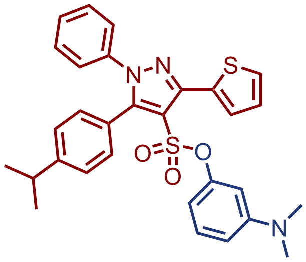
To a solution of the required sulfonyl fluoride (0.1 mmol) and the required phenol (0.1 mmol) in MeCN (0.5 mL) was added HMDS (0.1 mmol) and BTMG (5.0 mol%). The resulting reaction was stirred at room temperature for 5 min. Upon completion the solvent was removed or filtered through a short silica plug to obtain the analytically pure product.

Benzo[d][1,3]dioxol-5-yl 3-(4-methoxyphenyl)bicyclo[2.2.1]hepta-2,5-diene-2-sulfonate (11a)[16]



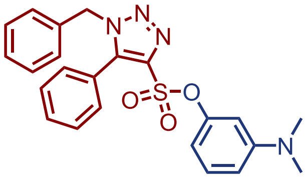
Following general procedure H, the title compound was isolated as a colourless oil (56 mg, 88%). **^{1}H NMR** (400 MHz, CDCl$_3$) ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.45 (appt. d, *J* = 9.0 Hz, 2H), 6.90 (appt. d, *J* = 9.0 Hz, 4H), 6.66 (d, *J* = 8.4 Hz, 1H), 6.59 (d, *J* = 2.3 Hz, 1H), 6.52 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.96 (s, 2H), 4.05–4.03 (m, 1H), 3.98–3.96 (m, 1H), 3.83 (s, 3H), 2.31–2.29 (m, 1H), 2.09–2.06 (m, 1H).; **^{13}C NMR** (101 MHz, CDCl$_3$) δ 168.4, 161.2, 148.0, 146.4, 143.7, 143.3, 140.0, 138.0, 130.0, 125.5, 115.5, 113.7, 107.8, 104.7, 102.0, 70.3, 59.4, 55.5, 55.1; **APCI-MS** (m/z): 399.1 [M+H]$^+$; **IR** ν_{max} (ATR)/cm^{-1}: 3018, 2937, 2900, 1604, 1517, 1504, 1481, 1247, 1159, 1037, 756.

3-(Dimethylamino)phenyl-5-(4-isopropylphenyl)-1-phenyl-3-(thiophen-2-yl)-1*H*-pyrazole-4-sulfonate (11b)



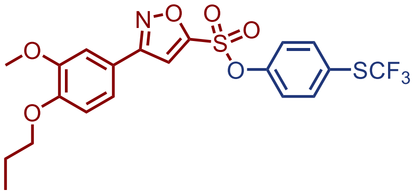
Following general procedure J, the title compound was isolated after purification by flash column chromatography (0–20% EtOAc in petroleum ether) as a colourless solid (41 mg, 76%). **m.p.** 164.0–165.7 °C; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.24 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.59 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.43–7.39 (m, 3H), 7.35–7.28 (m, 4H), 7.22 (appt. d, *J* = 8.0 Hz, 2H), 6.91 (appt. d, *J* = 8.3 Hz, 2H), 6.77 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.53 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.48 (appt. t, *J* = 2.3 Hz, 1H), 3.05–3.01 (m, 7H), 1.38 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 151.7, 150.8, 150.5, 148.6, 146.1, 138.6, 132.3, 130.5, 129.9, 129.8, 128.9, 128.5, 128.1, 127.2, 126.1, 125.6, 124.6, 112.9, 111.1, 109.9, 106.7, 40.5, 34.0, 23.8; **HRMS** (ESI): *m/z* calcd for $C_{30}H_{30}N_3O_3S_2^+$: 544.1723 [*M*+H]$^+$; found: 544.1717; **IR** ν_{max} (ATR)/cm^{-1}: 3019, 1611, 1508, 1499, 1379.

3-(Dimethylamino)phenyl 1-benzyl-5-phenyl-1*H*-1,2,3-triazole-4-sulfonate (11c)



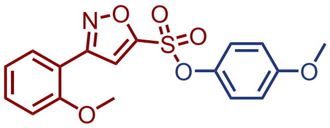
Following general procedure J, the title compound was isolated as a colourless solid (35 mg, 80%). **m.p.** 105–106.6 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47–7.43 (m, 1H), 7.35–7.24 (m, 5H), 7.06 (appt. t, *J* = 8.2 Hz, 1H), 6.93 (appt. d, *J* = 6.6 Hz, 2H), 6.82 (appt. d, *J* = 7.1 Hz, 2H), 6.57–6.54 (m, 1H), 6.33–6.28 (m, 2H), 5.36 (s, 2H), 2.82 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.6, 150.6, 141.3, 140.0, 134.1, 130.7, 129.8, 129.8, 129.0, 128.8, 128.6, 127.6, 123.8, 111.1, 109.6, 106.3, 52.8, 40.4; **HRMS** (ESI): *m/z* calcd for $C_{23}H_{23}N_4O_3S^+$: m/z = 435.1485 [*M*+H]$^+$; found: 435.1481; **IR** ν_{max} (ATR)/cm^{-1}: 3019, 1611, 1508, 1499, 1389, 1179, 1126.

4-((Trifluoromethyl)thio)phenyl 3-(3-methoxy-4-propoxyphenyl)isoxazole-5-sulfonate (11d)



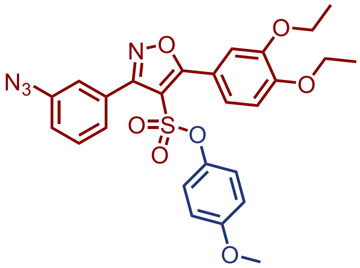
Following general procedure J, the title compound was isolated as a colourless solid (49 mg, >99%). **m.p.** 131.2–132.8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (appt. d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 1.6 Hz, 1H), 7.26 (dd, *J* = 14.7, 5.4 Hz, 3H), 7.18 (s, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 4.04 (t, *J* = 6.8 Hz, 2H), 3.94 (s, 3H), 1.95–1.87 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.7, 161.1, 151.6, 151.1, 150.1, 138.2, 129.3 (q, *J* = 308.4 Hz), 124.8 (q, *J* = 4.4, 2.2 Hz), 123.3, 120.6, 119.0, 112.7, 109.7, 109.5, 70.7, 56.3, 22.5, 10.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -42.4; **HRMS** (ESI): *m/z* calcd for $C_{20}H_{18}F_3NO_6S_2$+Na$^+$: 512.0420 [*M*+Na]$^+$; found: 512.0420; **IR** ν_{max} (ATR)/cm^{-1}: 2963, 2928, 1607, 1524, 1479, 1435, 1402, 1265, 1180, 1155, 1119, 978, 876.

4-Methoxyphenyl 3-(2-methoxyphenyl)isoxazole-5-sulfonate (11e)[20]



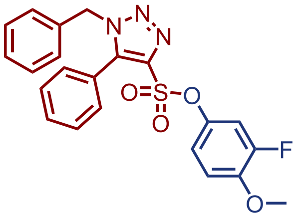
Following general procedure J, the title compound was isolated after purification by flash column chromatography (0-15% EtOAc in petroleum ether) as a brown oil (29 mg, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.50–7.46 (m, 1H), 7.40 (s, 1H), 7.10–7.05 (m, 3H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.85 (appt. d, *J* = 9.2 Hz, 2H), 3.88 (s, 3H), 3.78 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.5, 160.5, 159.0, 157.4, 142.8, 132.7, 129.4, 123.2, 121.3, 115.8, 115.0, 113.0, 111.7, 55.8, 55.7; **HRMS** (ESI): *m/z* calcd for $C_{17}H_{15}NO_6S+Na^+$: 384.0512 [*M*+Na]$^+$; found: 385.0514; **IR** ν_{max} (ATR)/cm^{-1}: 3017, 2965, 2841, 1605, 1504, 1470, 1402, 1254, 1146, 1026, 878, 837, 802.

4-Methoxyphenyl 3-(3-azidophenyl)-5-(3,4-diethoxyphenyl)isoxazole-4-sulfonate (11f)[21]



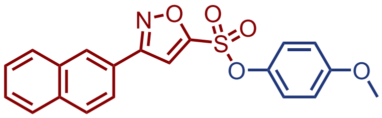
Following general procedure J, the title compound was isolated as a brown solid (45 mg, 83%). **m.p.** 86.8–88.3 °C (lit 87-88 °C);[21] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.48 (d, *J* = 1.8 Hz, 1H), 7.40 (appt. t, *J* = 7.9 Hz, 1H), 7.24 (appt. d, *J* = 7.8 Hz, 1H), 7.15–7.13 (m, 1H), 7.07–7.05 (m, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 6.89 (appt. d, *J* = 9.1 Hz, 2H), 6.79 (appt. d, *J* = 9.1 Hz, 2H), 4.20–4.11 (m, 4H), 3.78 (s, 3H), 1.52–1.46 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.8, 161.8, 158.8, 152.6, 148.5, 142.5, 140.3, 129.7, 128.7, 126.1, 123.5, 123.3, 121.0, 120.2, 117.1, 114.9, 113.9, 112.4, 110.1, 64.9, 64.7, 55.8, 14.8; **HRMS** (ESI): *m/z* calcd for $C_{26}H_{25}N_4O_7S^+$: 537.1438 [*M*+H]$^+$; found: 537.1440; **IR** ν_{max} (ATR)/cm^{-1}: 3017, 2984, 2932, 2106, 1603, 1503, 1393, 1265, 1256, 1217, 1169, 1038, 868.

3-Fluoro-4-methoxyphenyl 1-benzyl-5-phenyl-1*H*-1,2,3-triazole-4-sulfonate (11g)



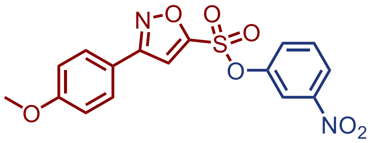
Following general procedure J, the title compound was isolated as a colourless oil (32 mg, 73%). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.50 (appt. t, *J* = 7.6 Hz, 1H), 7.38 (appt. t, *J* = 7.7 Hz, 2H), 7.30–7.25 (m, 3H), 6.95–6.91 (m, 4H), 6.81–6.78 (m, 3H), 5.40 (s, 2H), 3.85 (s, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 151.8 (d, *J* = 250.0 Hz), 147.2 (d, *J* = 10.5 Hz), 142.1 (d, *J* = 9.4 Hz), 141.3, 139.8, 134.0, 131.1, 129.7, 129.1, 128.9, 128.8, 127.6, 123.5, 118.4 (d, *J* = 4.0 Hz), 113.3 (d, *J* = 2.6 Hz), 111.5 (d, *J* = 21.6 Hz), 56.7, 53.0; **^{19}F NMR** (376 MHz, CDCl$_3$) δ -130.7 – -130.8 (m); **HRMS** (ESI): *m/z* calcd for $C_{22}H_{19}FN_4O_4S^+$: m/z = 440.1075 [*M*+H]$^+$; found: 440.1069; **IR** ν_{max} (ATR)/cm^{-1}: 3019, 1508, 1395, 1179, 1134, 1107, 1028, 961.

4-Methoxyphenyl 3-(naphthalen-2-yl)isoxazole-5-sulfonate (11h)[20]



Following general procedure J, the title compound was isolated as a colourless solid (25 mg, 66%). **m.p.** 94.9–96.0 °C (lit. 80–81 °C);[20] **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.22 (s, 1H), 7.97–7.88 (m, 4H), 7.59–7.56 (m, 2H), 7.30 (s, 1H), 7.11 (appt. d, *J* = 9.1 Hz, 2H), 6.86 (appt. d, *J* = 9.1 Hz, 2H), 3.78 (s, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 162.9, 162.0, 159.1, 142.7, 134.6, 133.1, 129.4, 128.7, 128.1, 127.9, 127.5, 127.3, 124.3, 123.5, 123.1, 115.1, 109.6, 55.8; **HRMS** (ESI): *m/z* calcd for $C_{20}H_{15}NO_5S+Na^+$: 404.0563 [*M*+Na]$^+$; found: 404.0568; **IR** ν_{max} (ATR)/cm^{-1}: 3019, 1501, 1400, 1202, 1169.

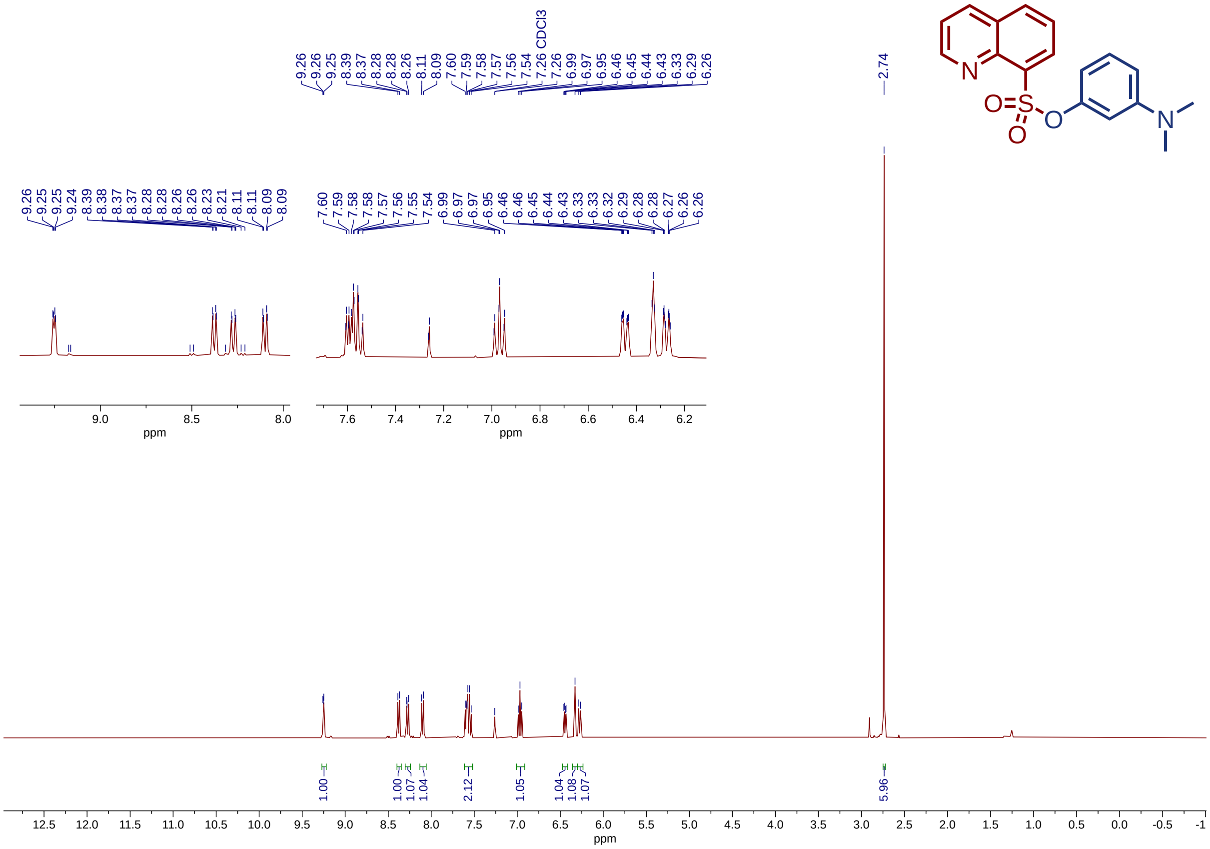
3-Nitrophenyl 3-(4-methoxyphenyl)isoxazole-5-sulfonate (11i)



Following general procedure J, the title compound was isolated after purification by flash column chromatography (0–30% Et$_2$O in petroleum ether) as a colourless solid (24 mg, 63%). **m.p.** 106.0–108.0 °C; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.23 (ddd, *J* = 8.1, 2.1, 1.2 Hz, 1H), 8.11 (appt. t, *J* = 2.2 Hz, 1H), 7.73 (appt. d, *J* = 8.9 Hz, 2H), 7.62 (appt. t, *J* = 8.1 Hz, 1H), 7.57 (ddd, *J* = 8.2, 2.3, 1.2 Hz, 1H), 7.21 (s, 1H), 7.00

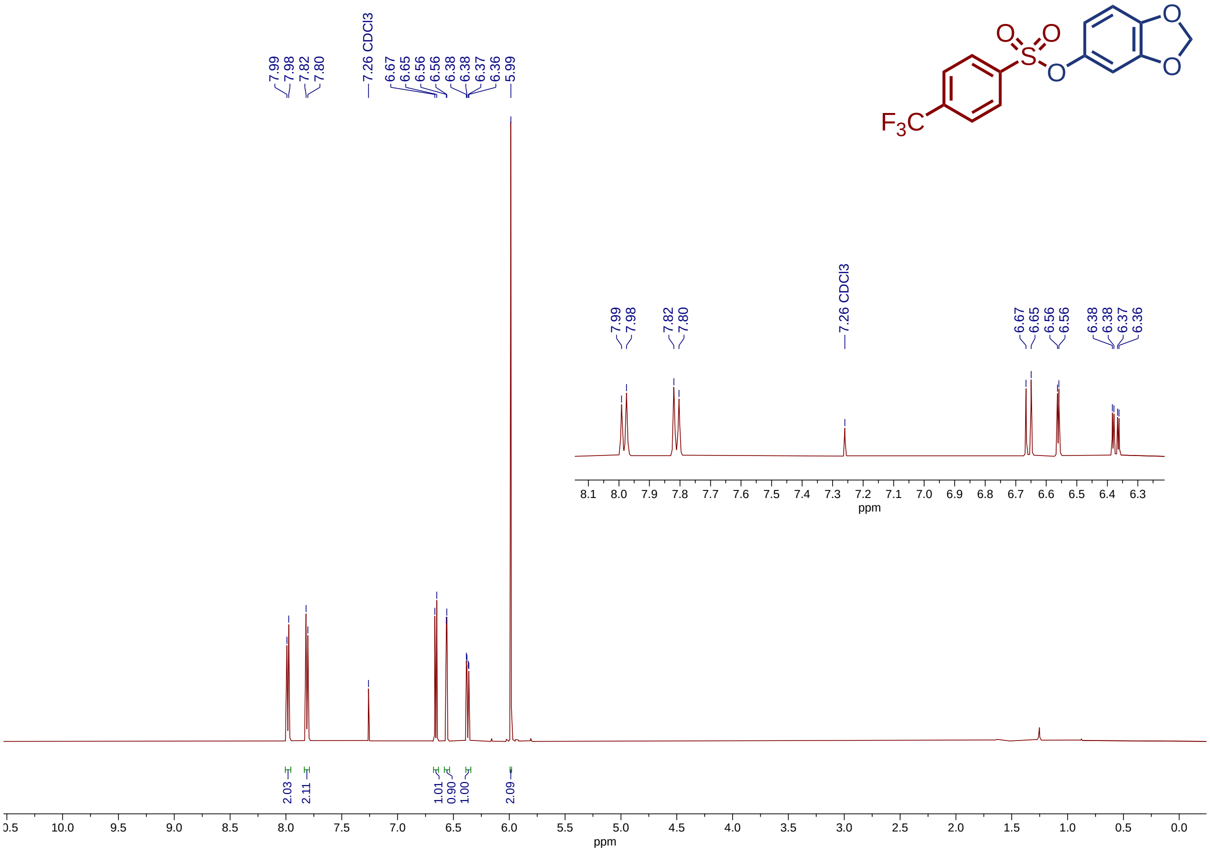
(appt. d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.7, 162.3, 160.9, 149.3, 149.2, 131.1, 128.7, 128.3, 123.1, 119.0, 118.0, 114.9, 109.6, 55.6; **HRMS** (ESI): *m/z* calcd for $C_{16}H_{12}N_2O_7S+Na^+$: 399.0257 $[M+Na]^+$; found: 399.0260; **IR** ν_{max} (ATR)/cm^{-1}: 3107, 2924, 1611, 1533, 1429, 1408, 1356, 1252, 1204, 1177, 1028, 935, 837.

^{1}H NMR Spectrum for Compound 3a (400 MHz, $CDCl_3$)

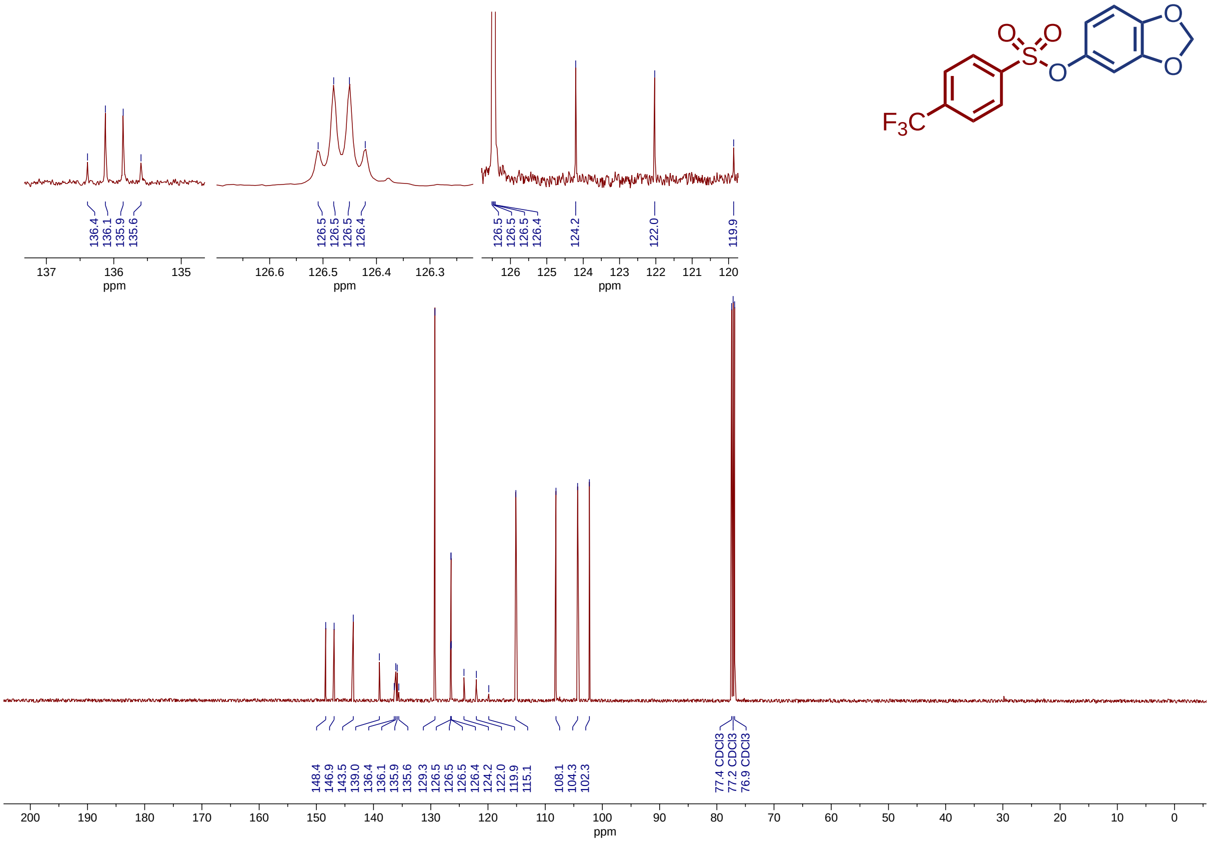


^{13}C NMR Spectrum for Compound **3a** (101 MHz, $CDCl_3$)

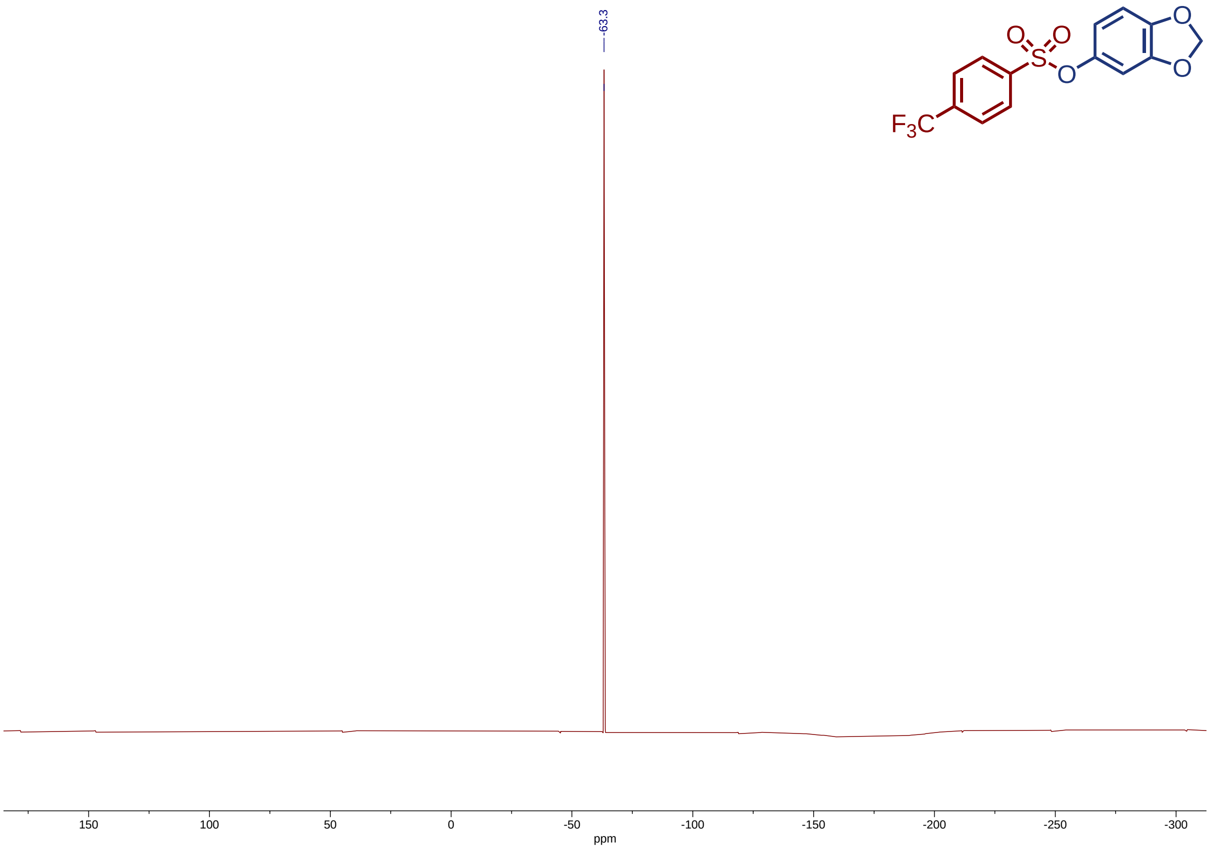
^{1}H NMR Spectrum for Compound **3b** (500 MHz, CDCl$_3$)



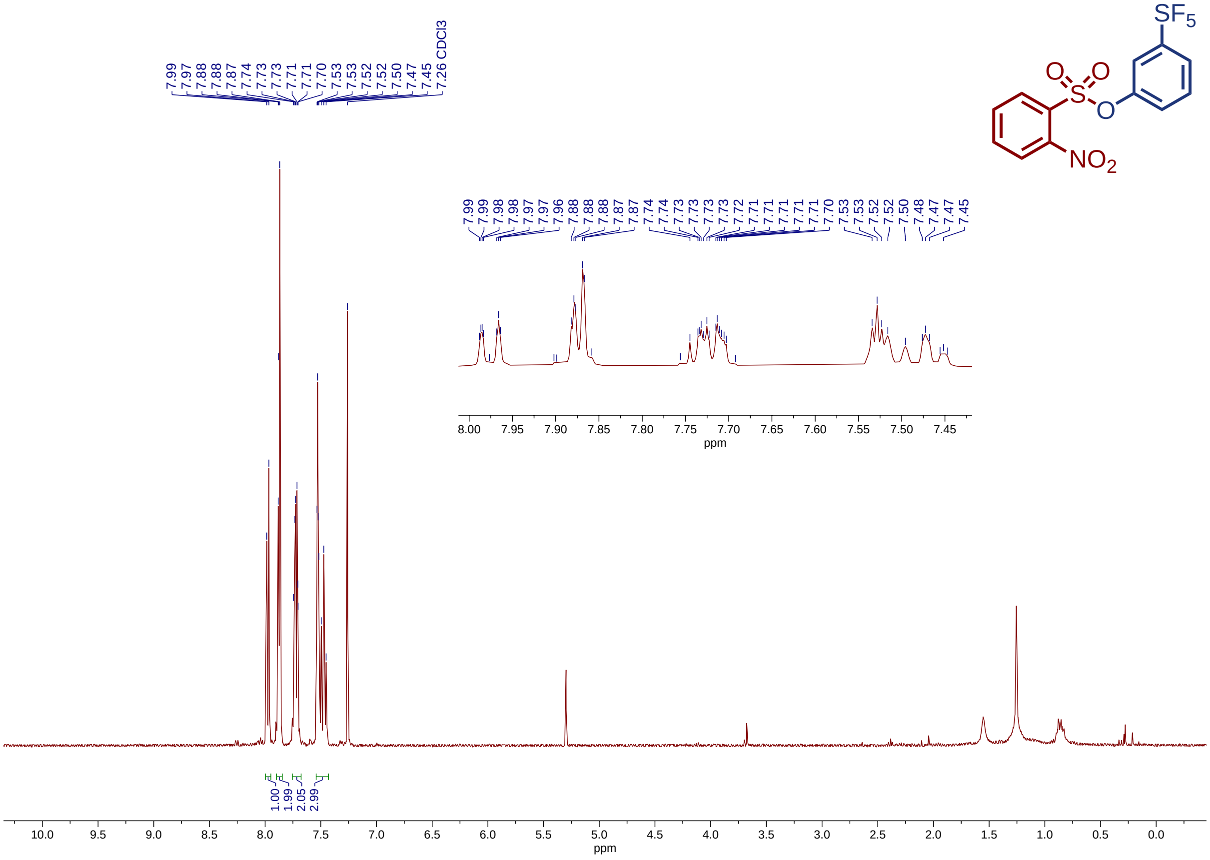
^{13}C NMR Spectrum for Compound **3b** (126 MHz, CDCl$_3$)



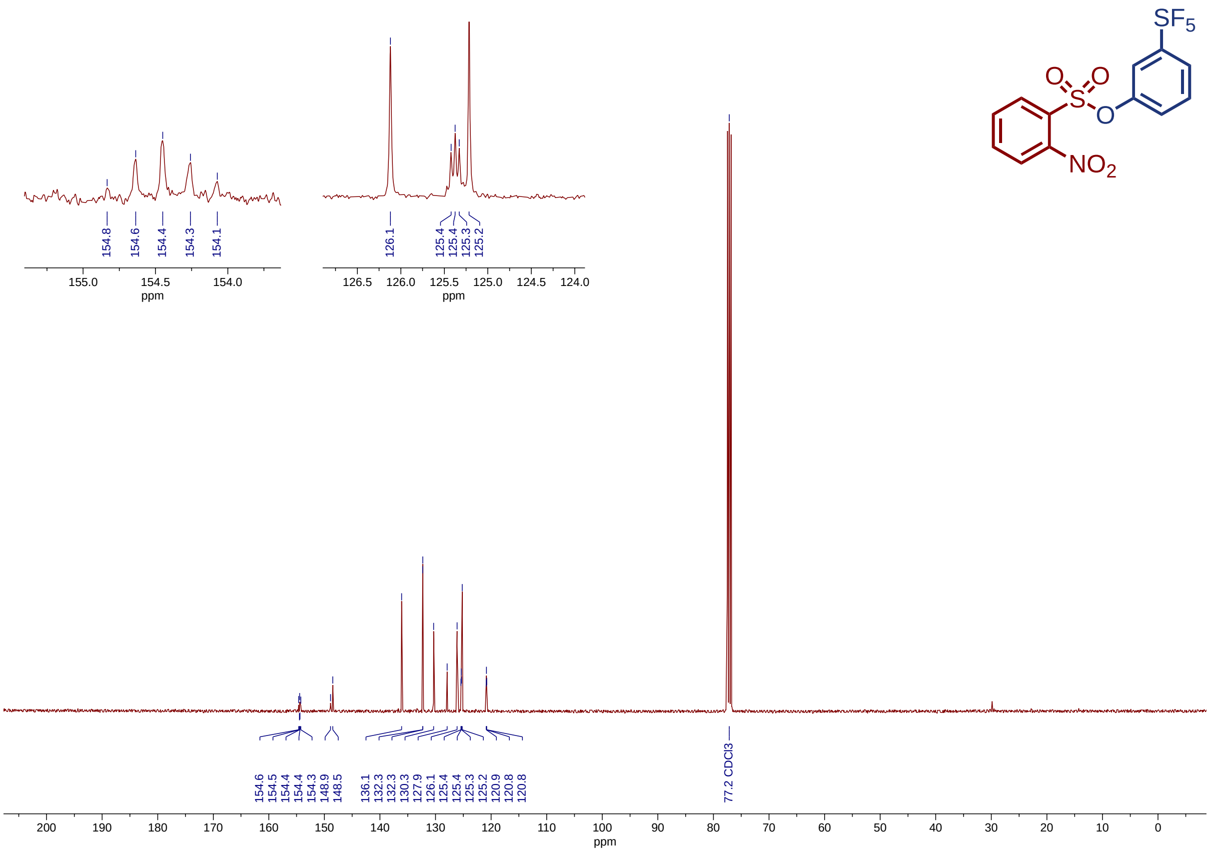
^{19}F NMR Spectrum for Compound **3b** (376 MHz, $CDCl_3$)



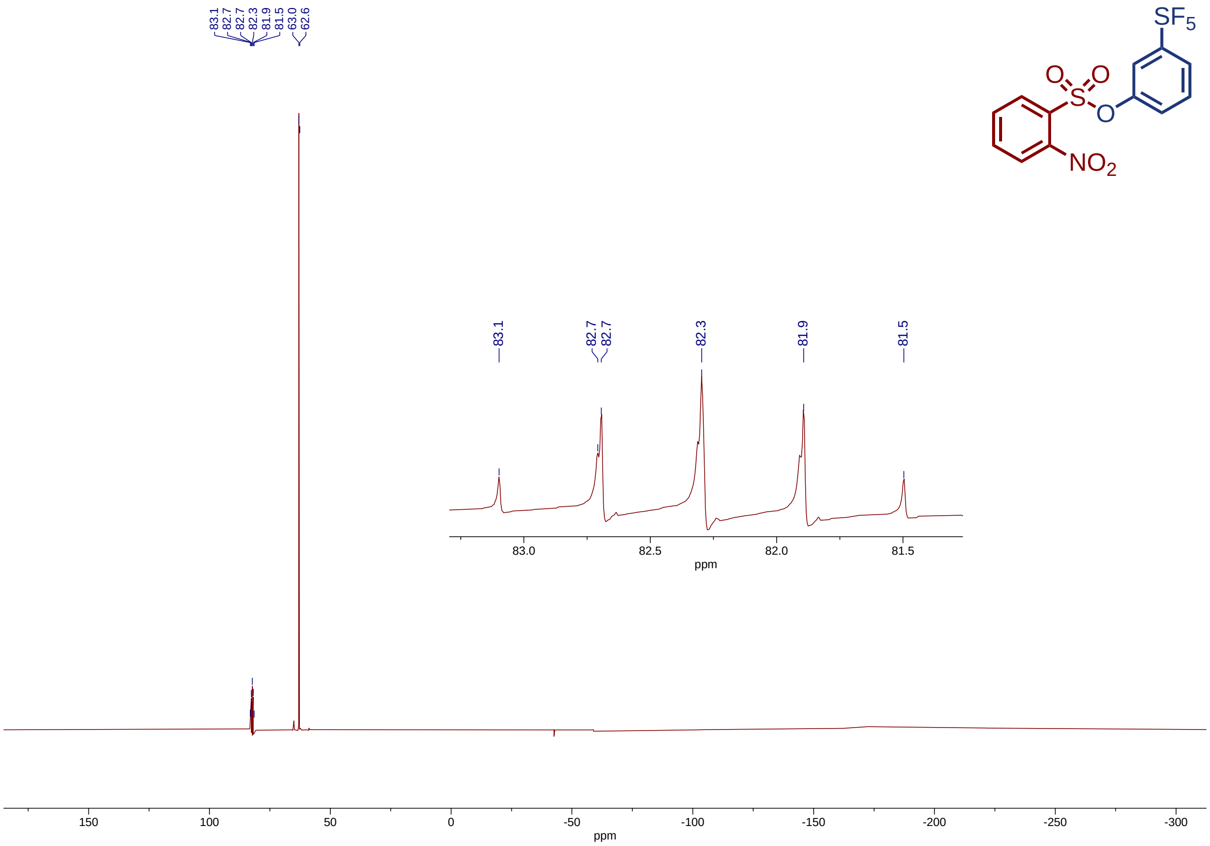
^{1}H NMR Spectrum for Compound **3c** (400 MHz, $CDCl_3$)



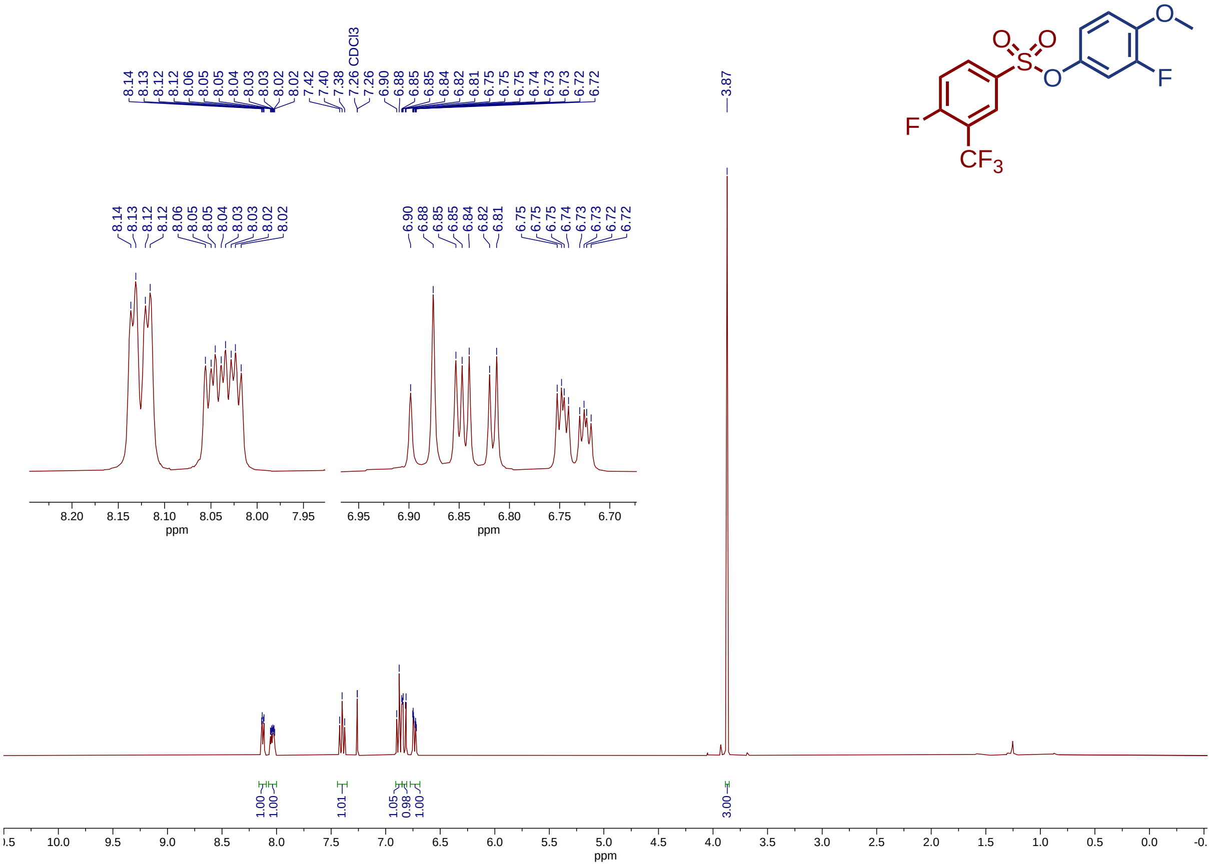
^{13}C NMR Spectrum for Compound **3c** (101 MHz, $CDCl_3$)



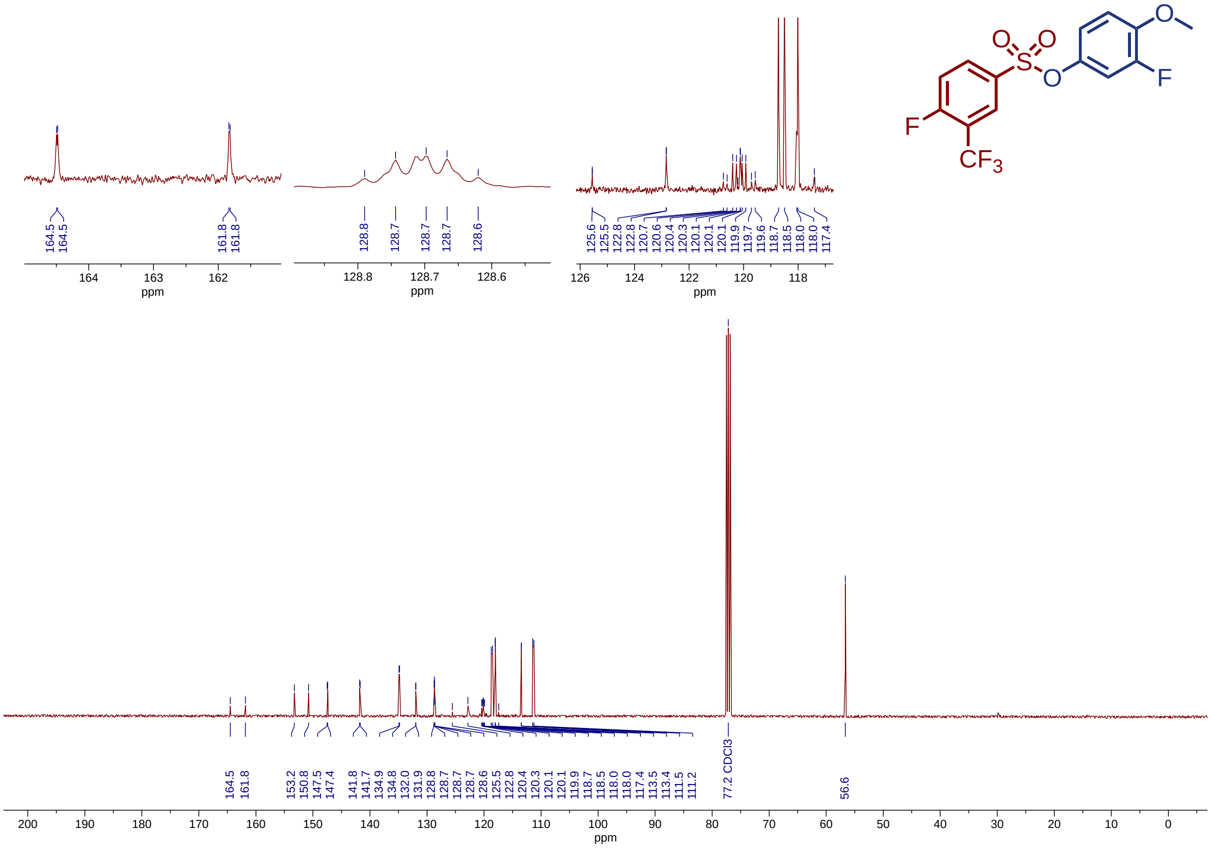
^{19}F NMR Spectrum for Compound **3c** (376 MHz, $CDCl_3$)



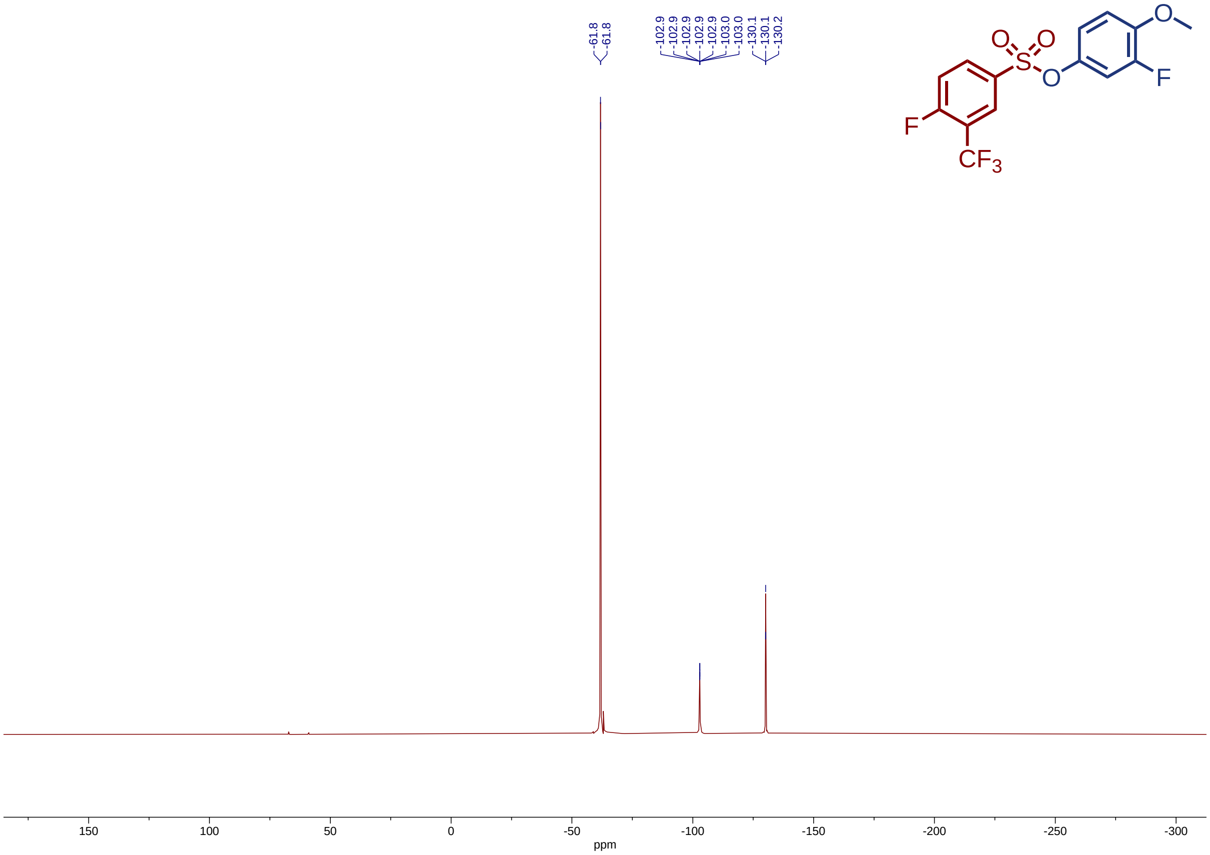
^{1}H NMR Spectrum for Compound **3d** (400 MHz, $CDCl_3$)



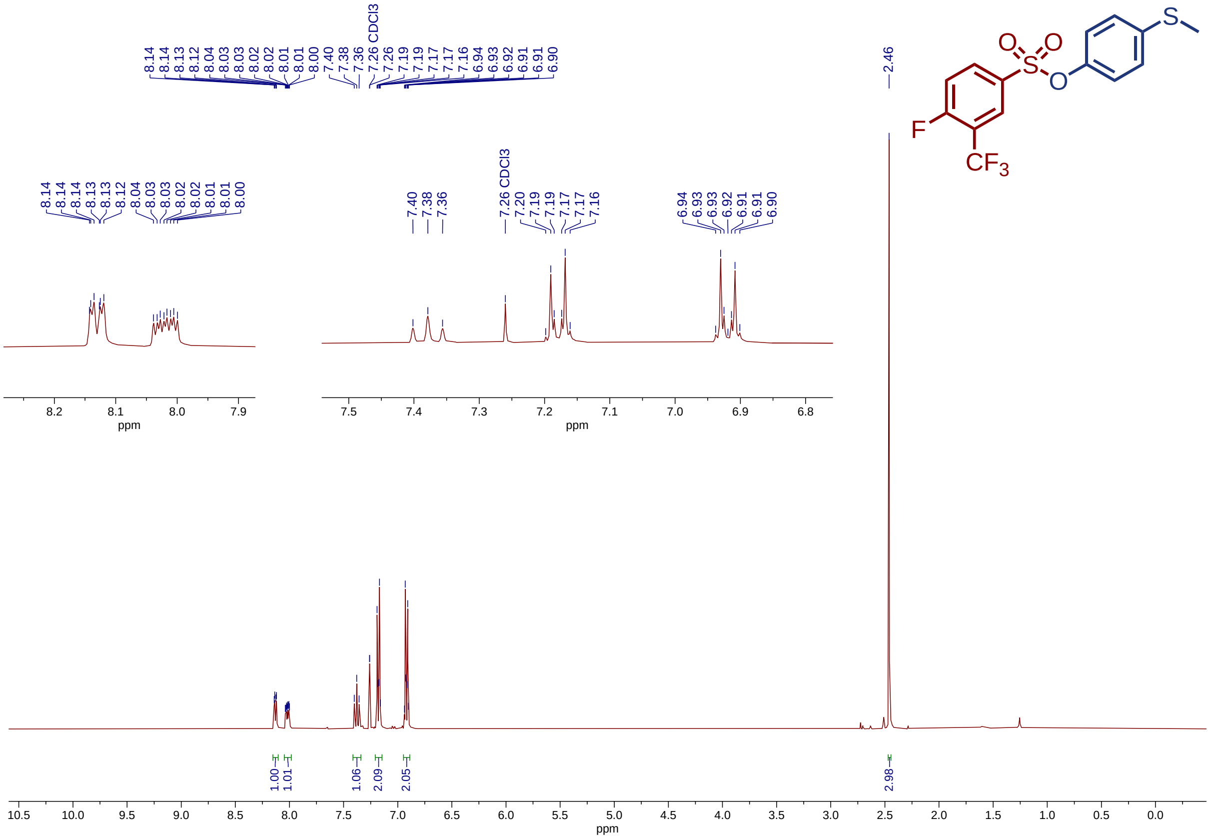
^{13}C NMR Spectrum for Compound **3d** (101 MHz, $CDCl_3$)



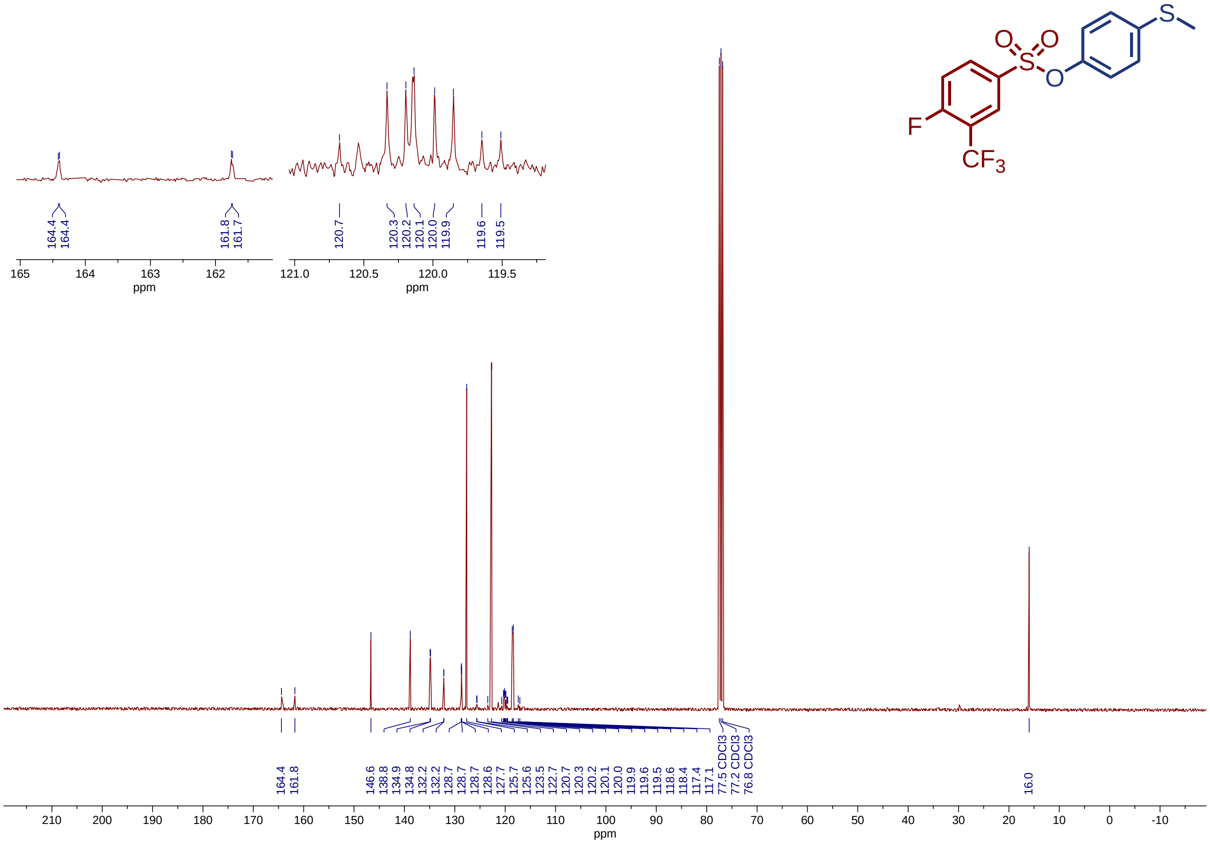
^{19}F NMR Spectrum for Compound **3d** (376 MHz, $CDCl_3$)



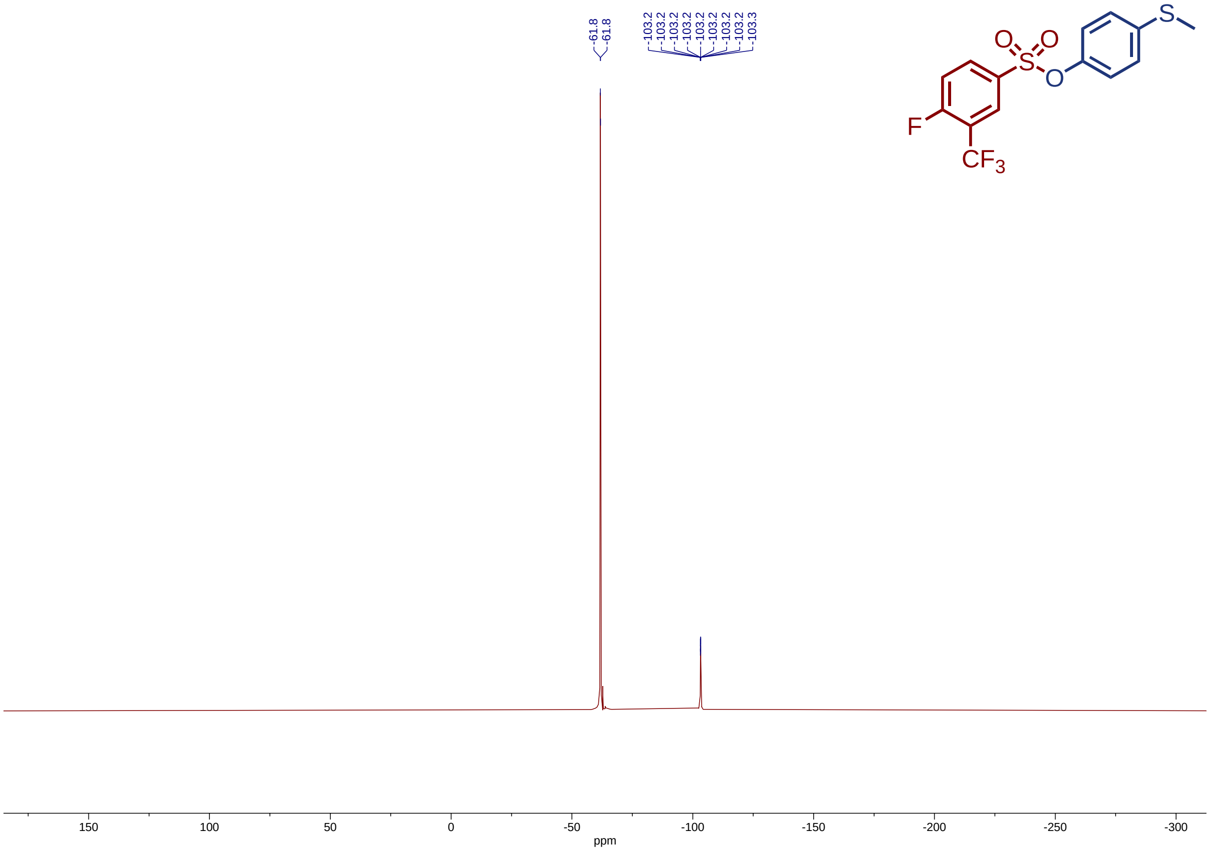
^{1}H NMR Spectrum for Compound **3e** (400 MHz, $CDCl_3$)



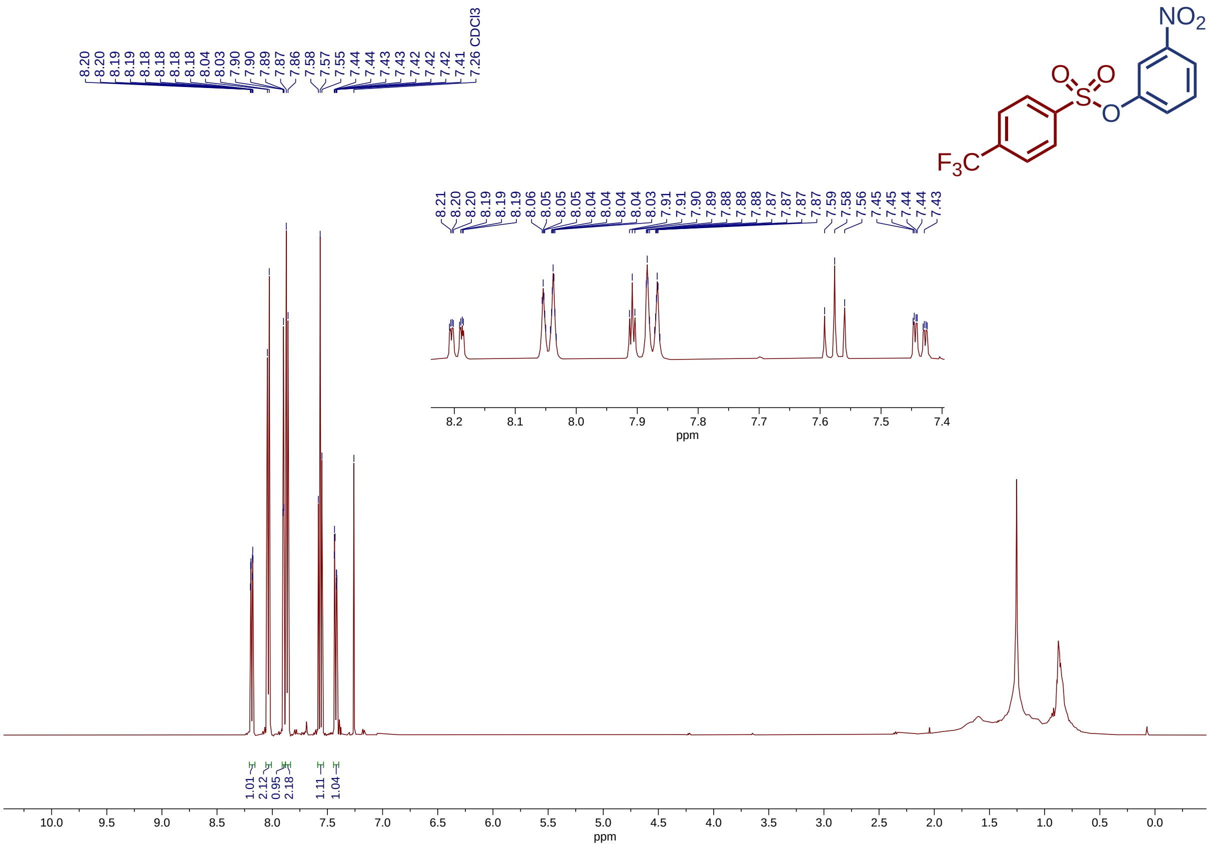
^{13}C NMR Spectrum for Compound **3e** (101 MHz, $CDCl_3$)



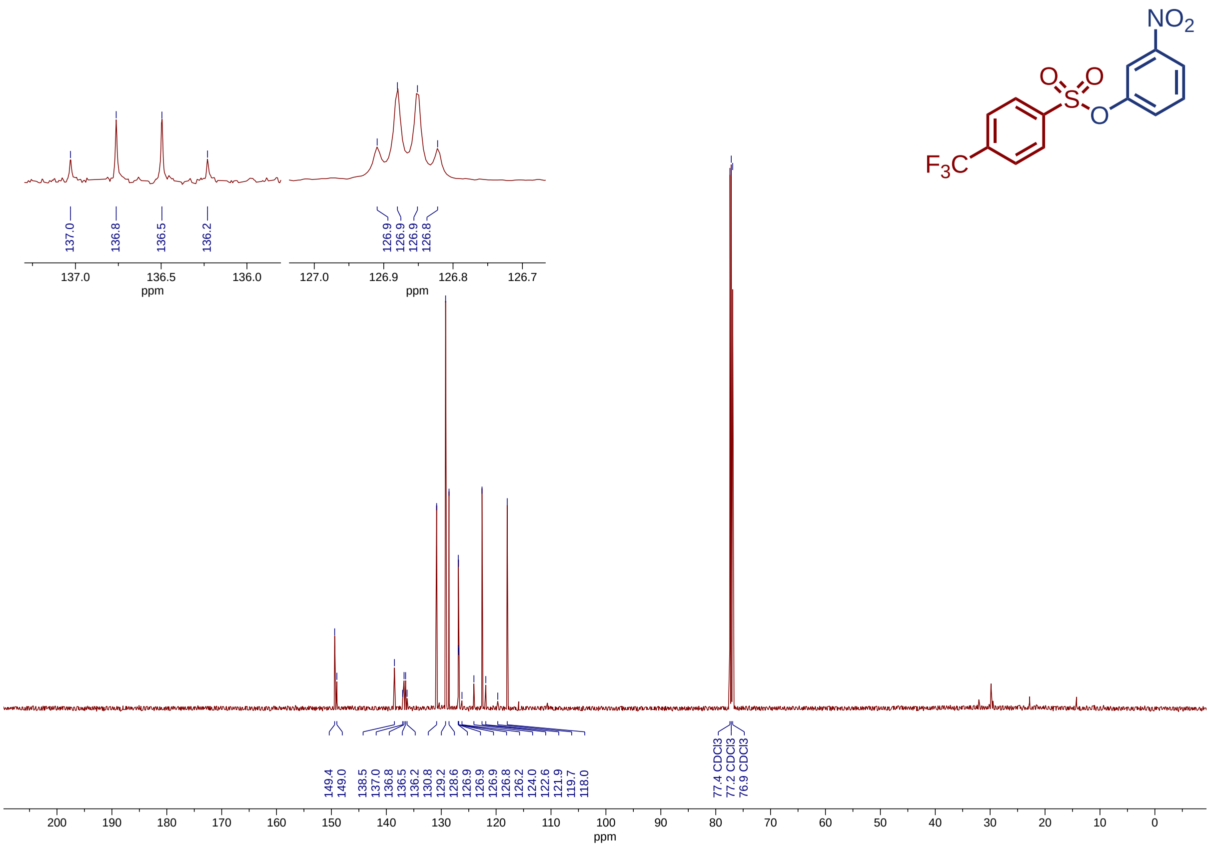
^{19}F NMR Spectrum for Compound **3e** (376 MHz, $CDCl_3$)



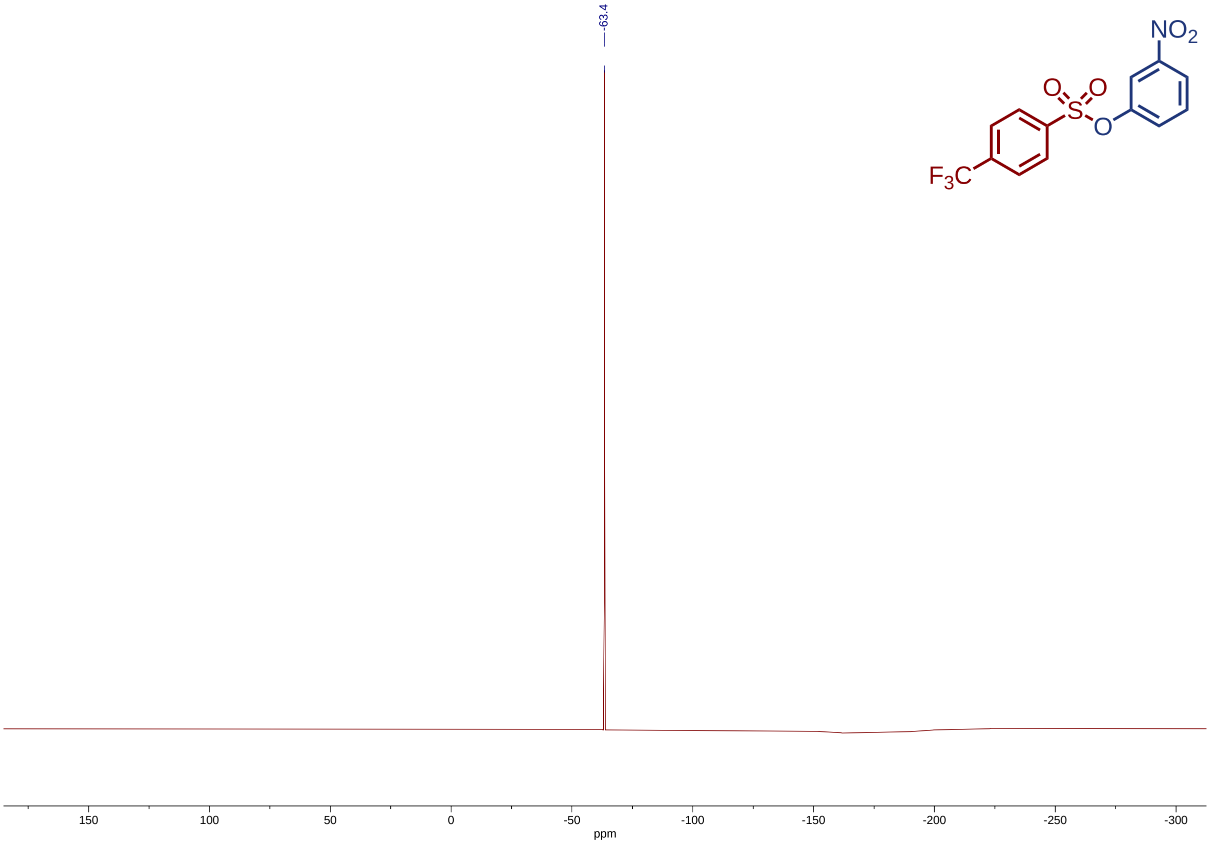
^{1}H NMR Spectrum for Compound **3f** (500 MHz, $CDCl_3$)



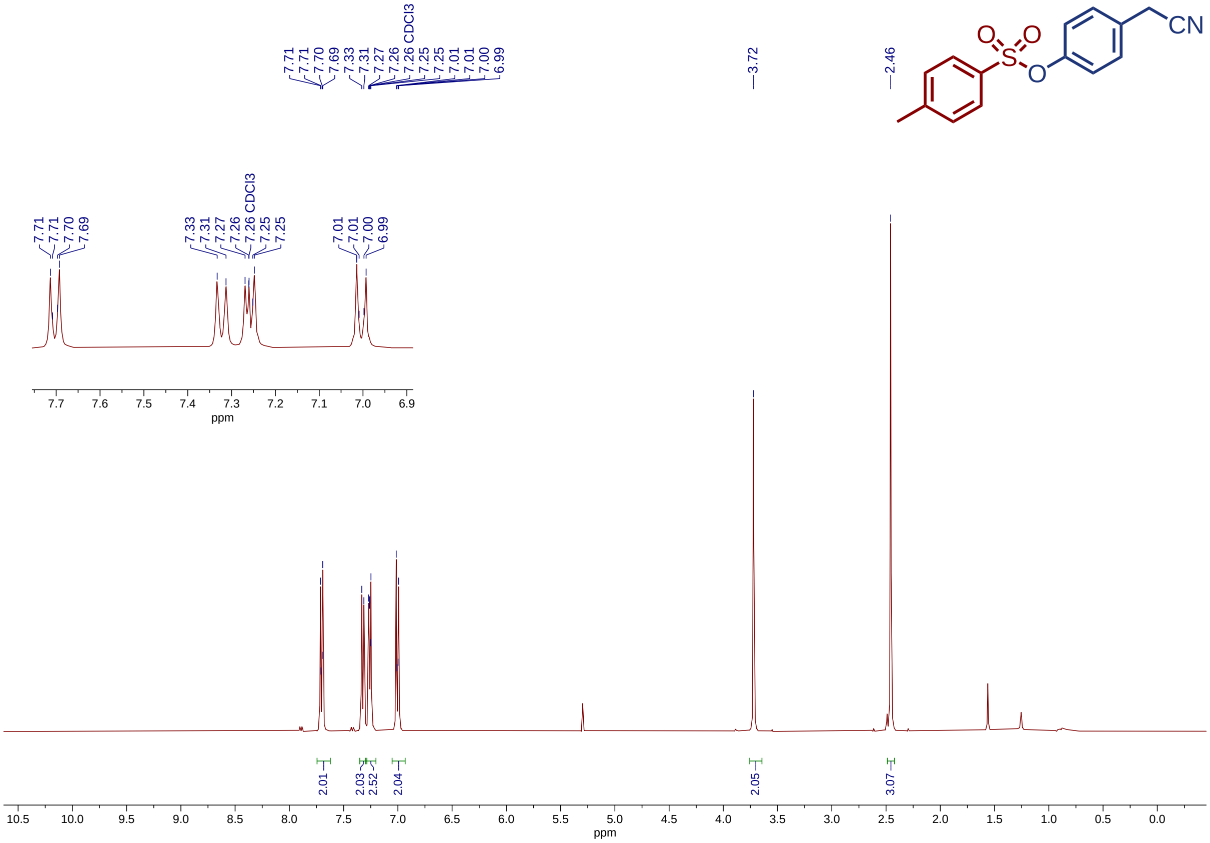
^{13}C NMR Spectrum for Compound **3f** (126 MHz, $CDCl_3$)



^{19}F NMR Spectrum for Compound **3f** (376 MHz, CDCl$_3$)

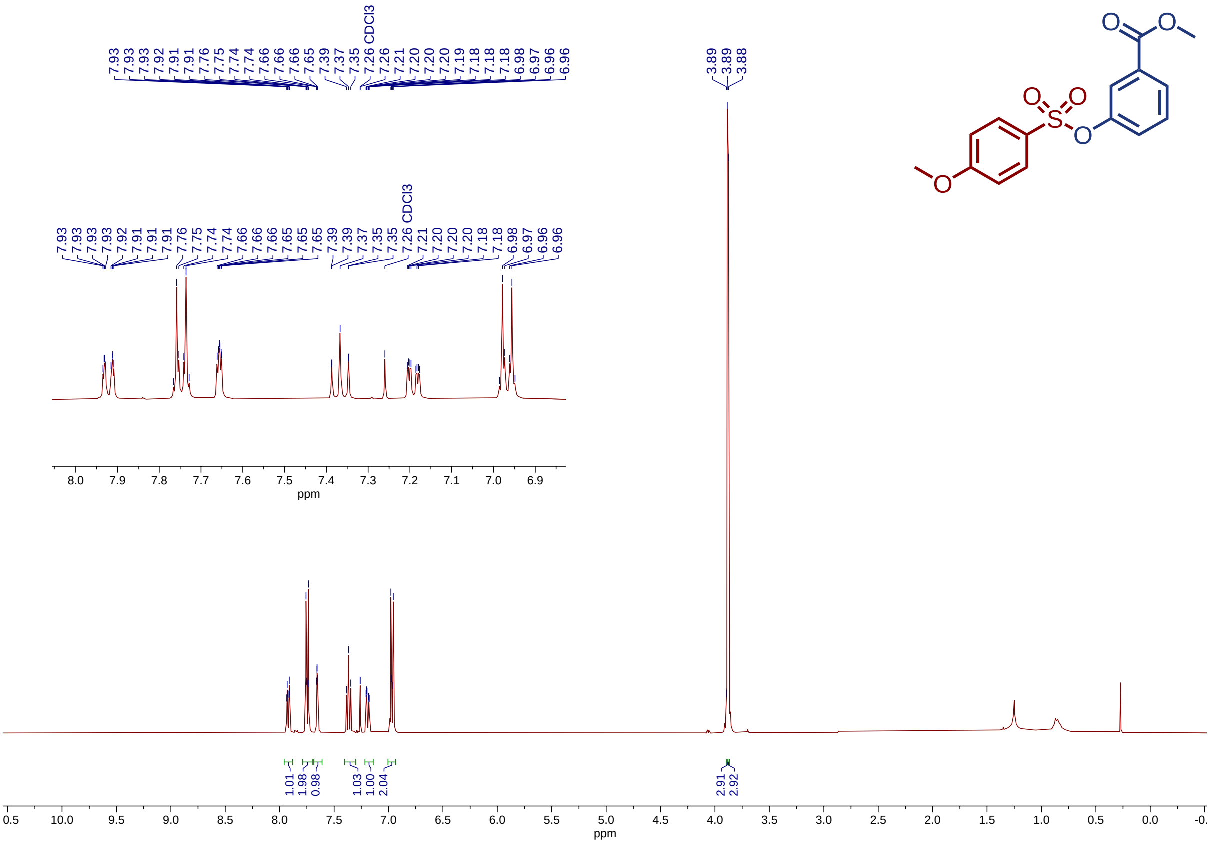


^{1}H NMR Spectrum for Compound **3g** (400 MHz, CDCl$_3$)

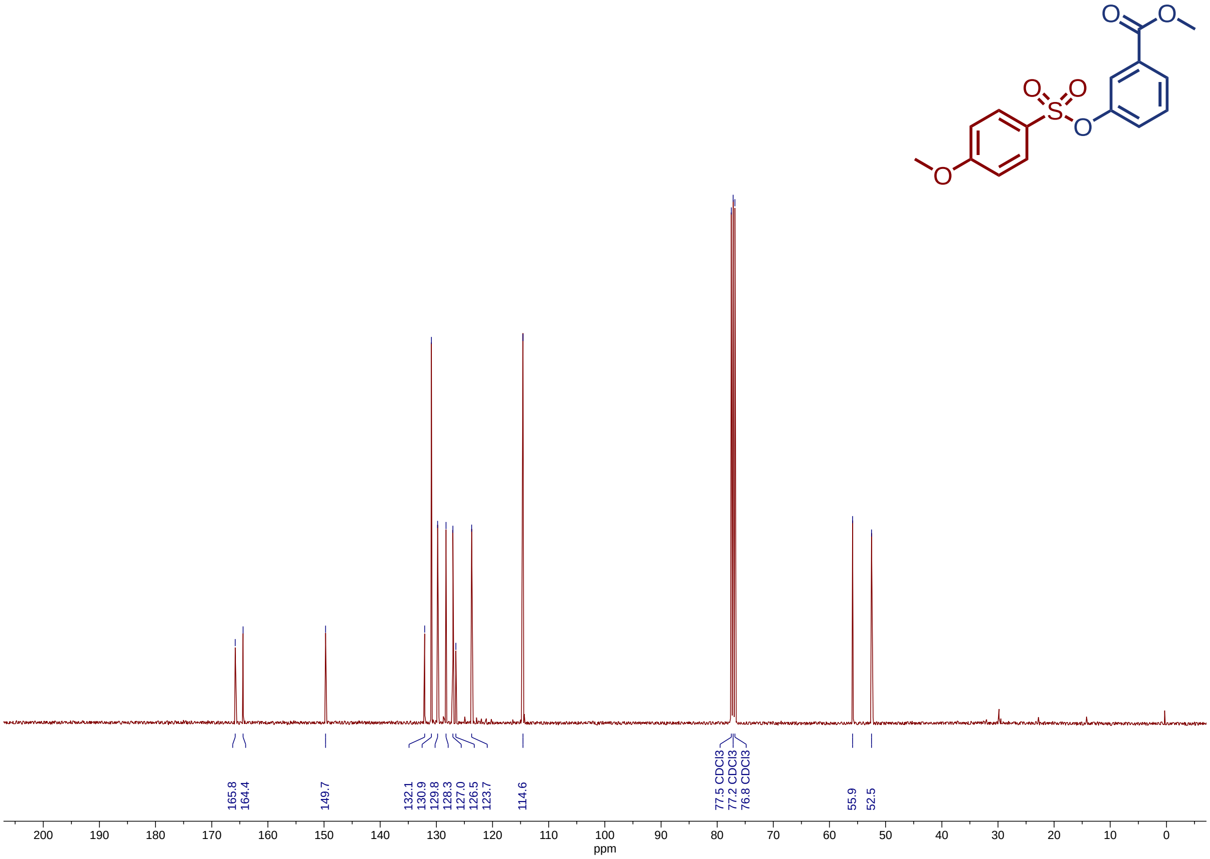


^{13}C NMR Spectrum for Compound **3g** (101 MHz, $CDCl_3$)

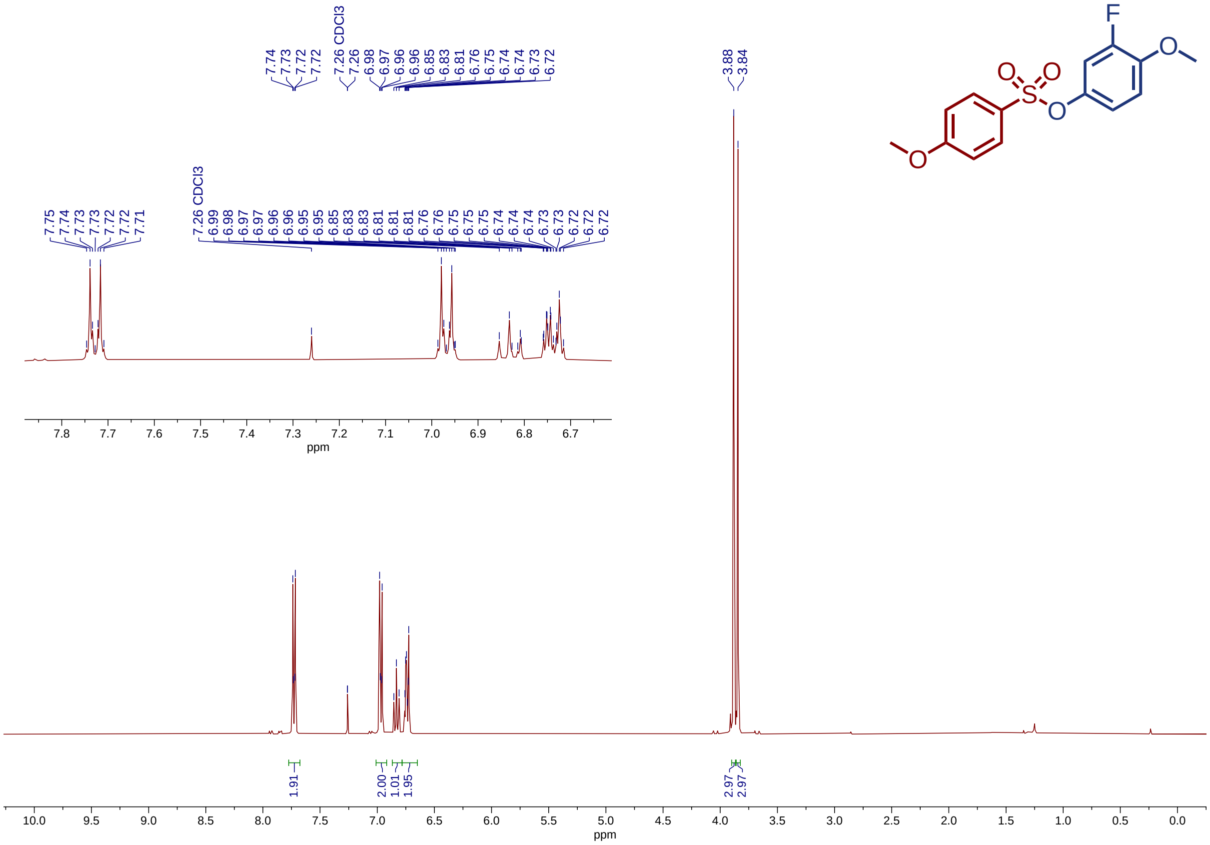
^{1}H NMR Spectrum for Compound **3h** (400 MHz, $CDCl_3$)



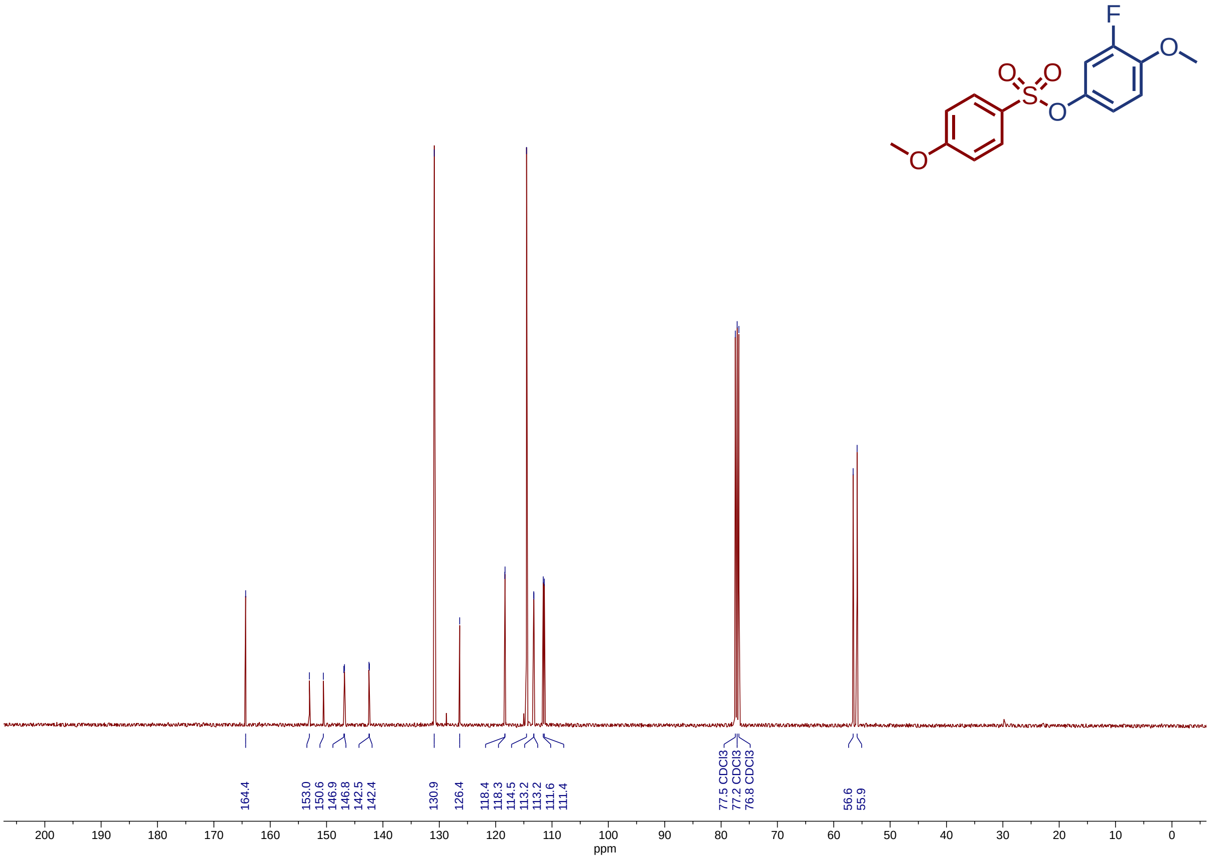
^{13}C NMR Spectrum for Compound **3h** (101 MHz, CDCl$_3$)



^{1}H NMR Spectrum for Compound **3i** (400 MHz, CDCl$_3$)

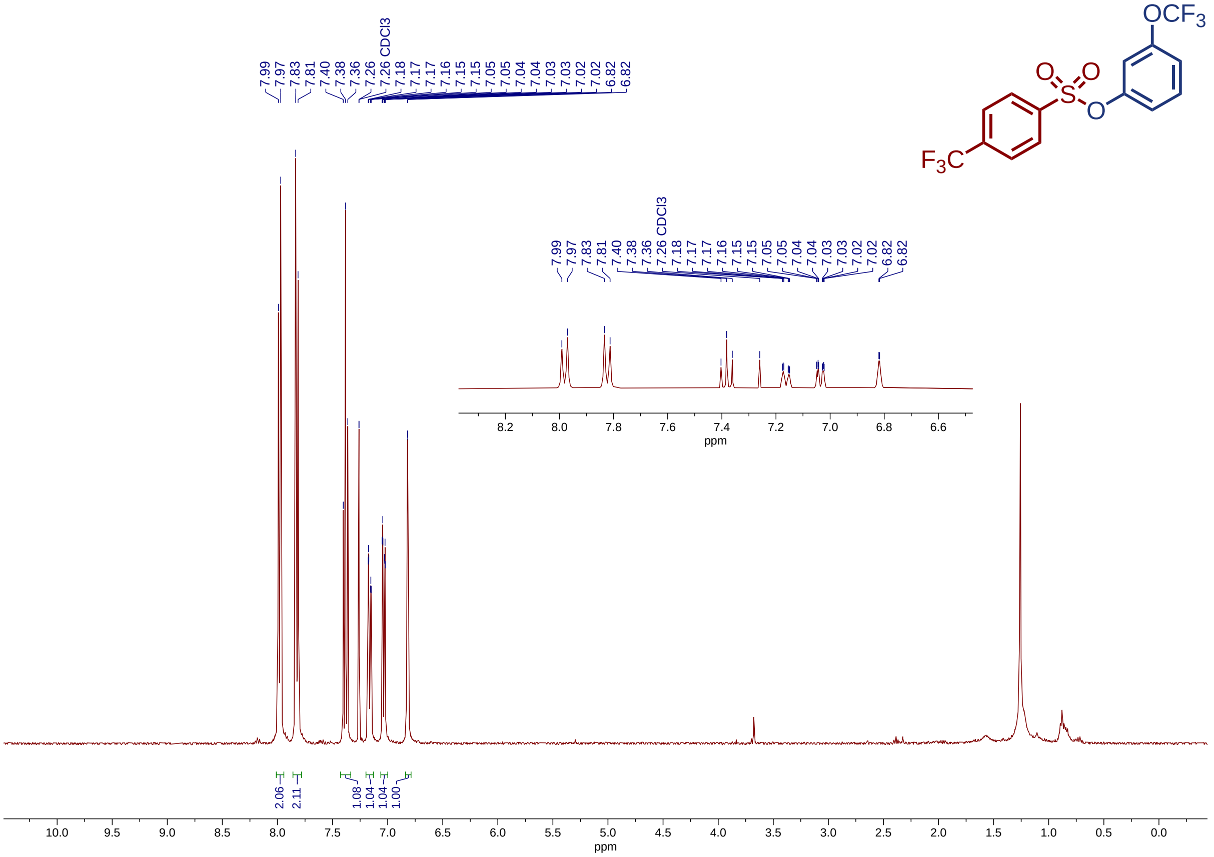


^{13}C NMR Spectrum for Compound **3i** (101 MHz, CDCl$_3$)

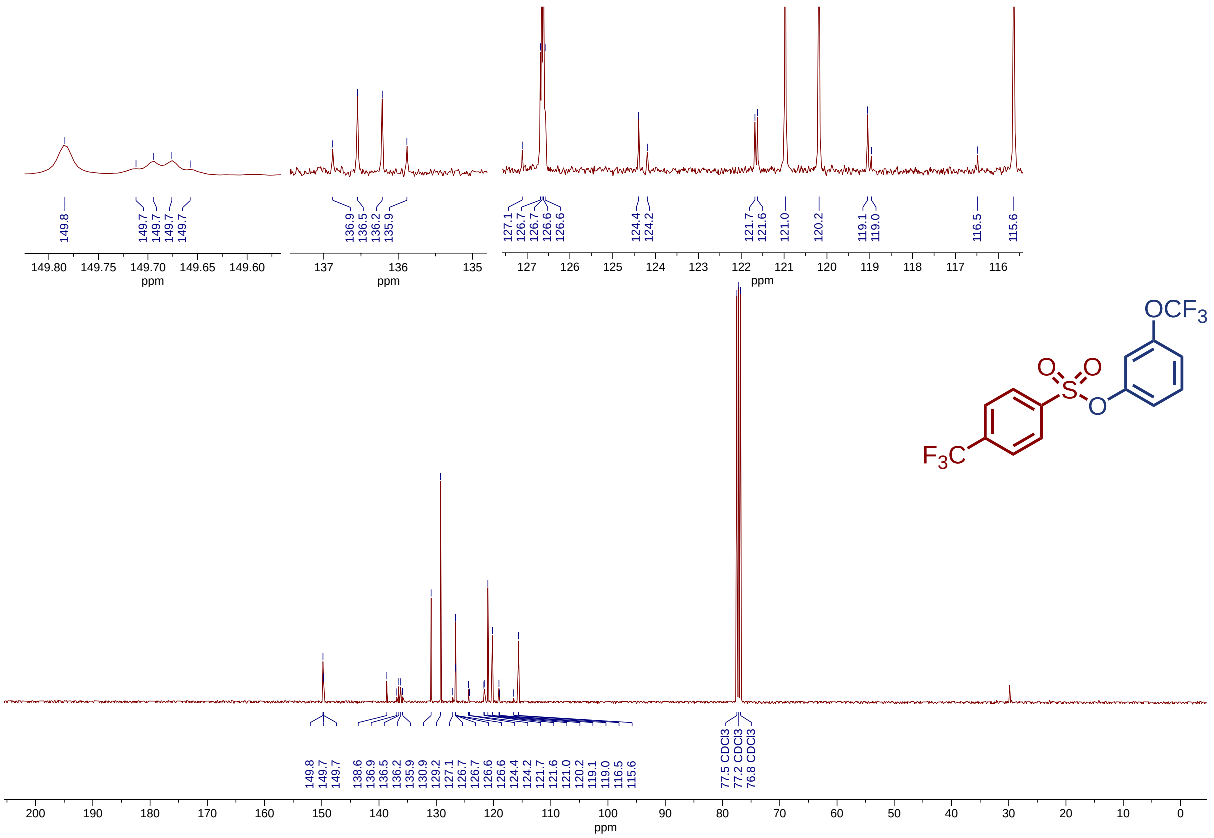


^{19}F NMR Spectrum for Compound **3i** (376 MHz, CDCl$_3$)

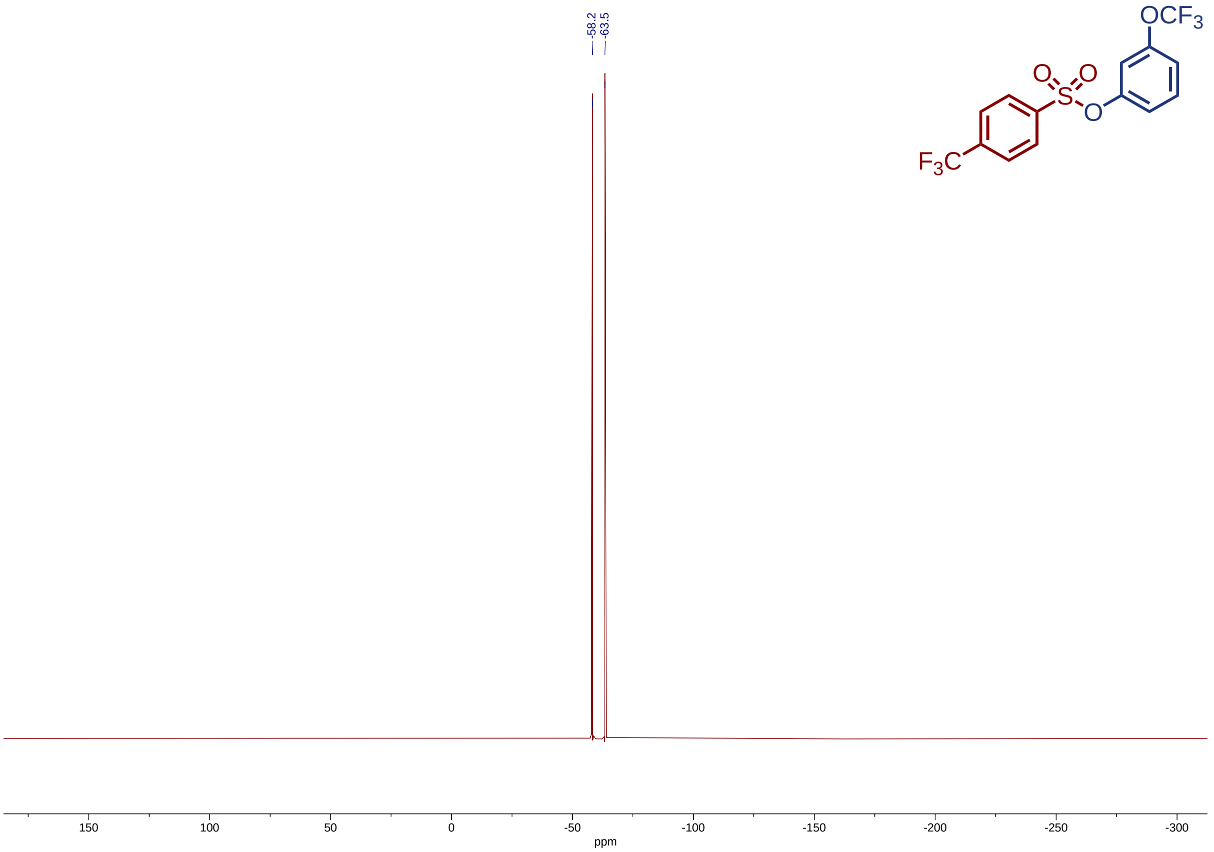
^{1}H NMR Spectrum for Compound **3j** (400 MHz, $CDCl_3$)



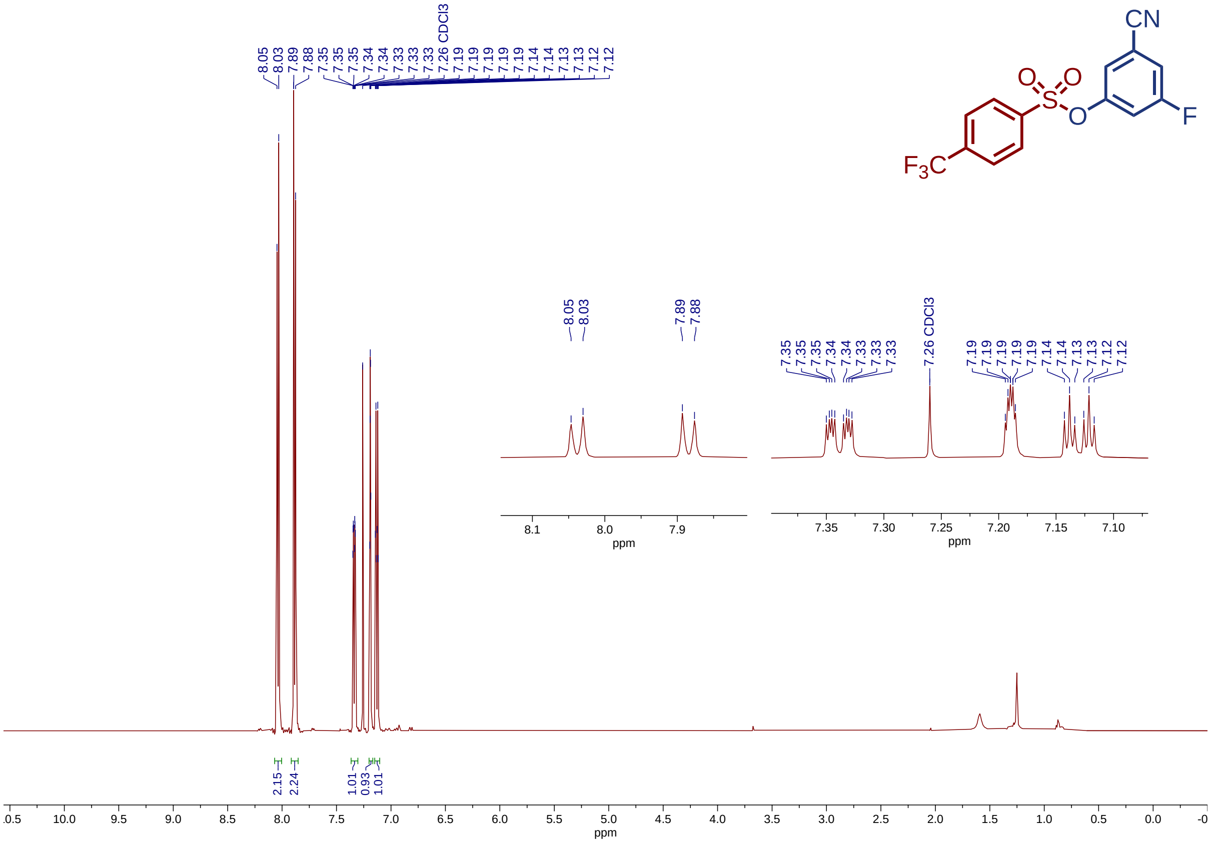
^{13}C NMR Spectrum for Compound **3j** (101 MHz, $CDCl_3$)



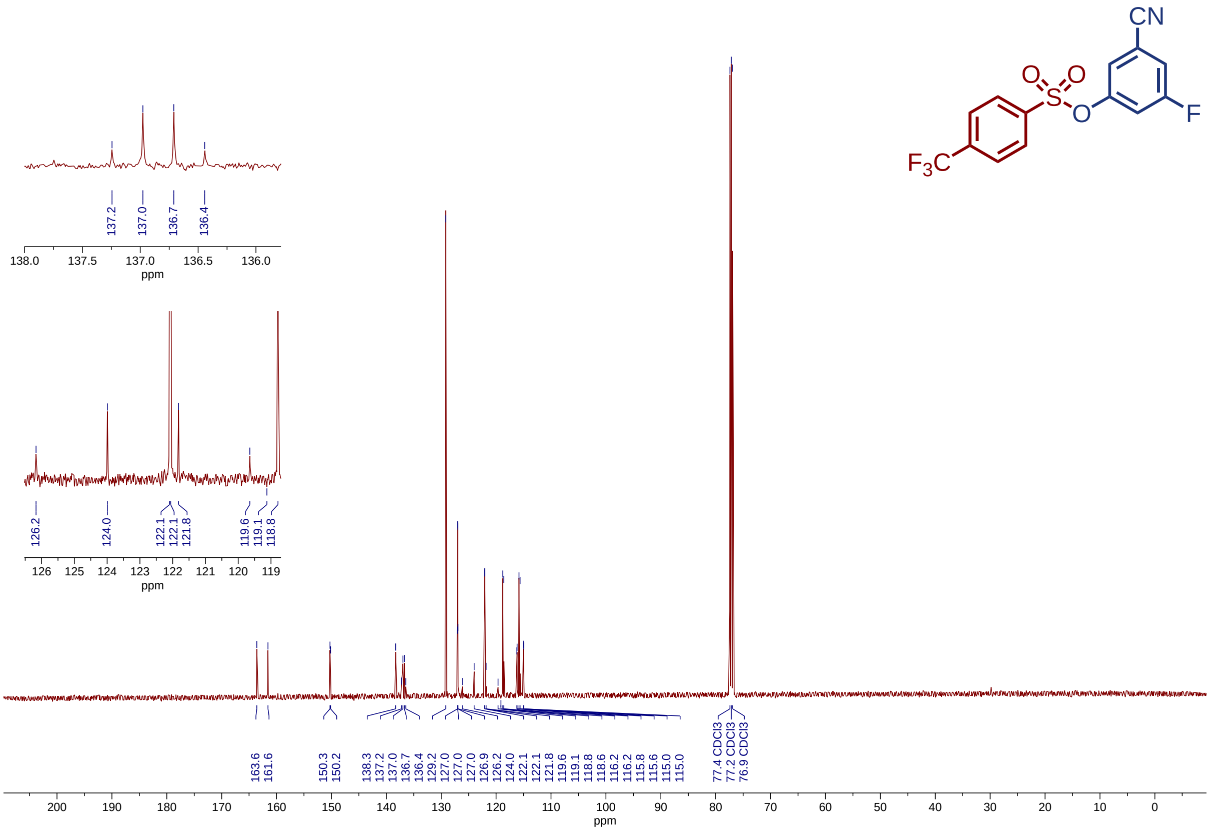
^{19}F NMR Spectrum for Compound **3j** (376 MHz, CDCl$_3$)



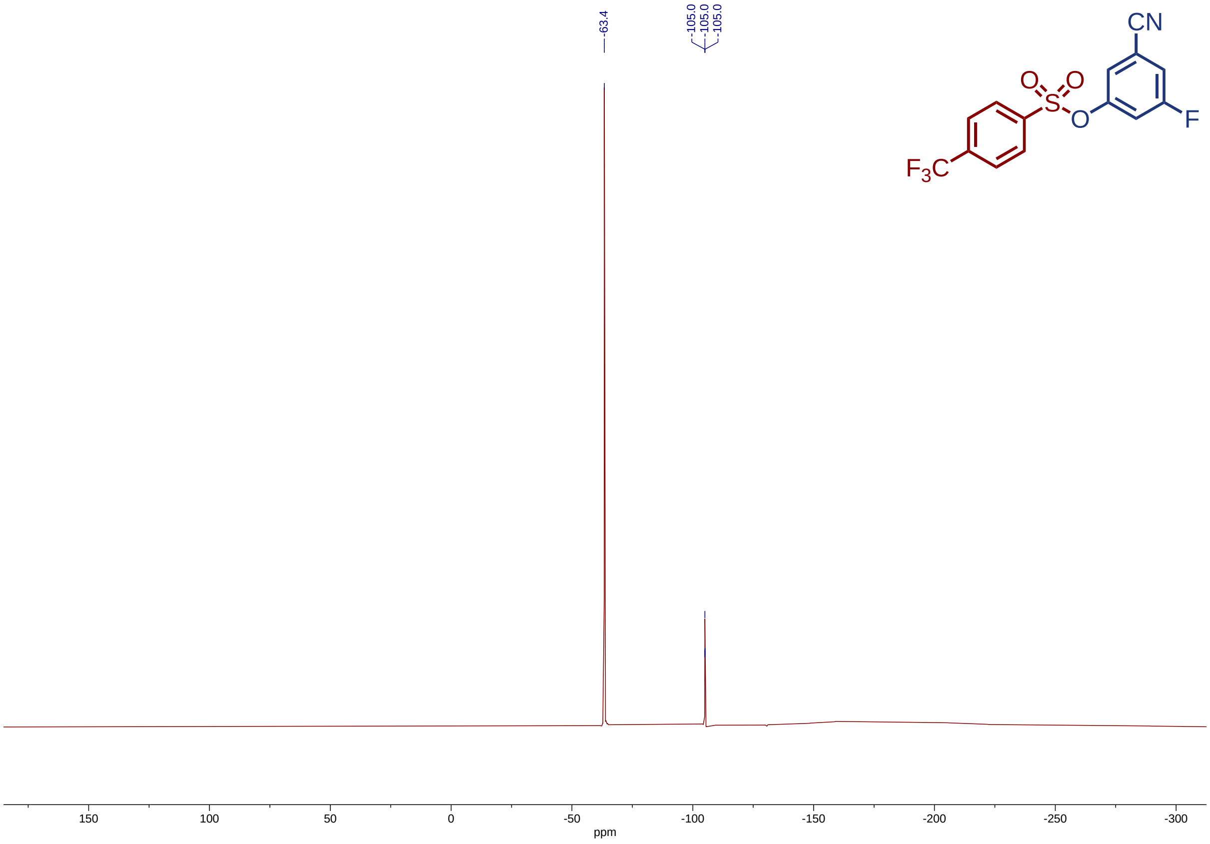
^{1}H NMR Spectrum for Compound **3k** (500 MHz, CDCl$_3$)



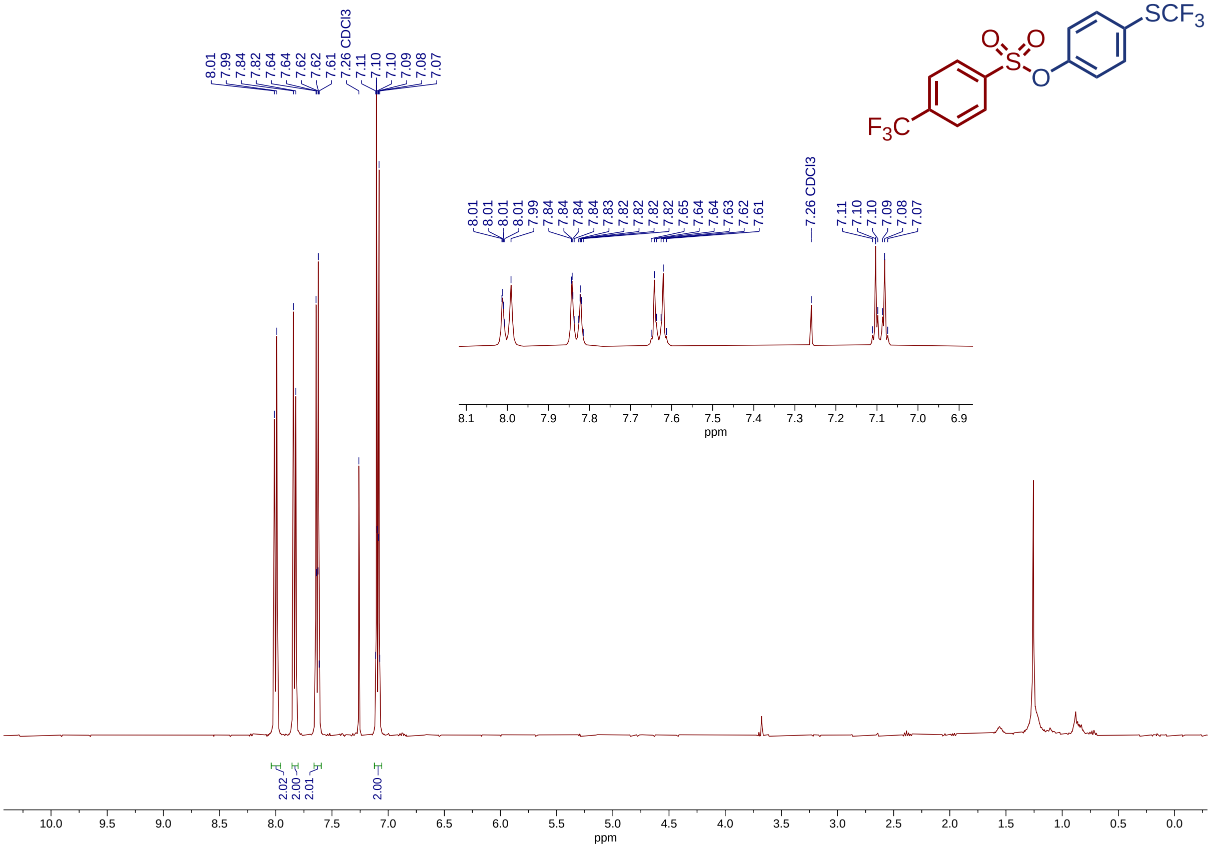
^{13}C NMR Spectrum for Compound **3k** (126 MHz, CDCl$_3$)



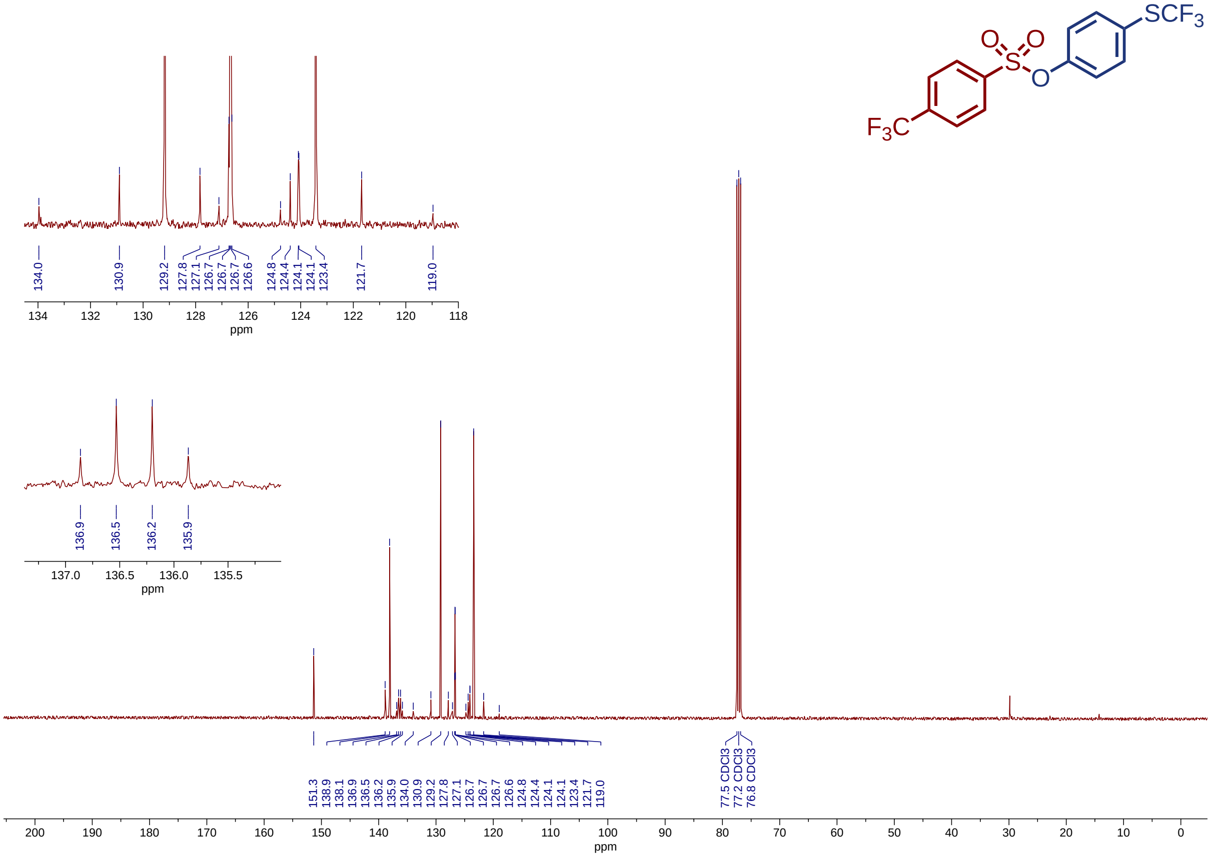
^{19}F NMR Spectrum for Compound **3k** (376 MHz, CDCl$_3$)



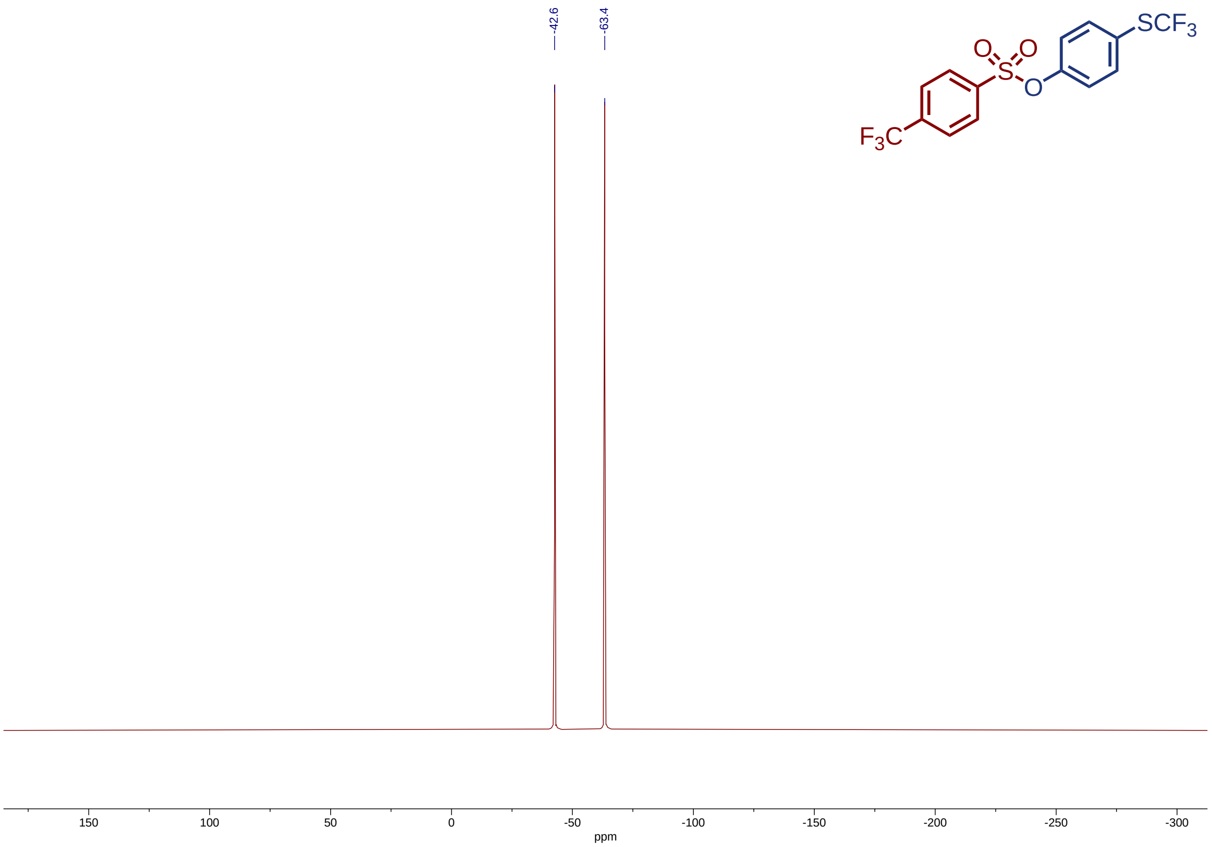
^{1}H NMR Spectrum for Compound **3l** (400 MHz, $CDCl_3$)



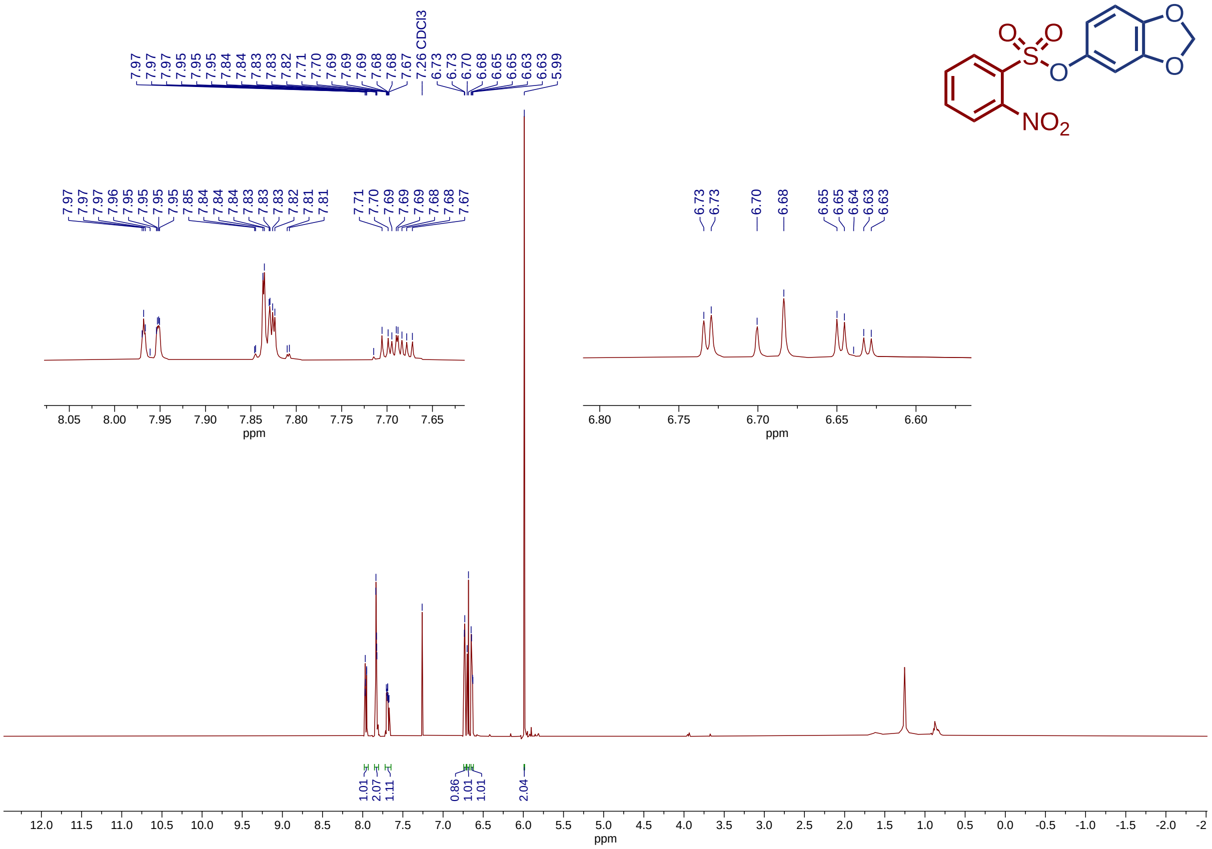
^{13}C NMR Spectrum for Compound **3l** (101 MHz, $CDCl_3$)



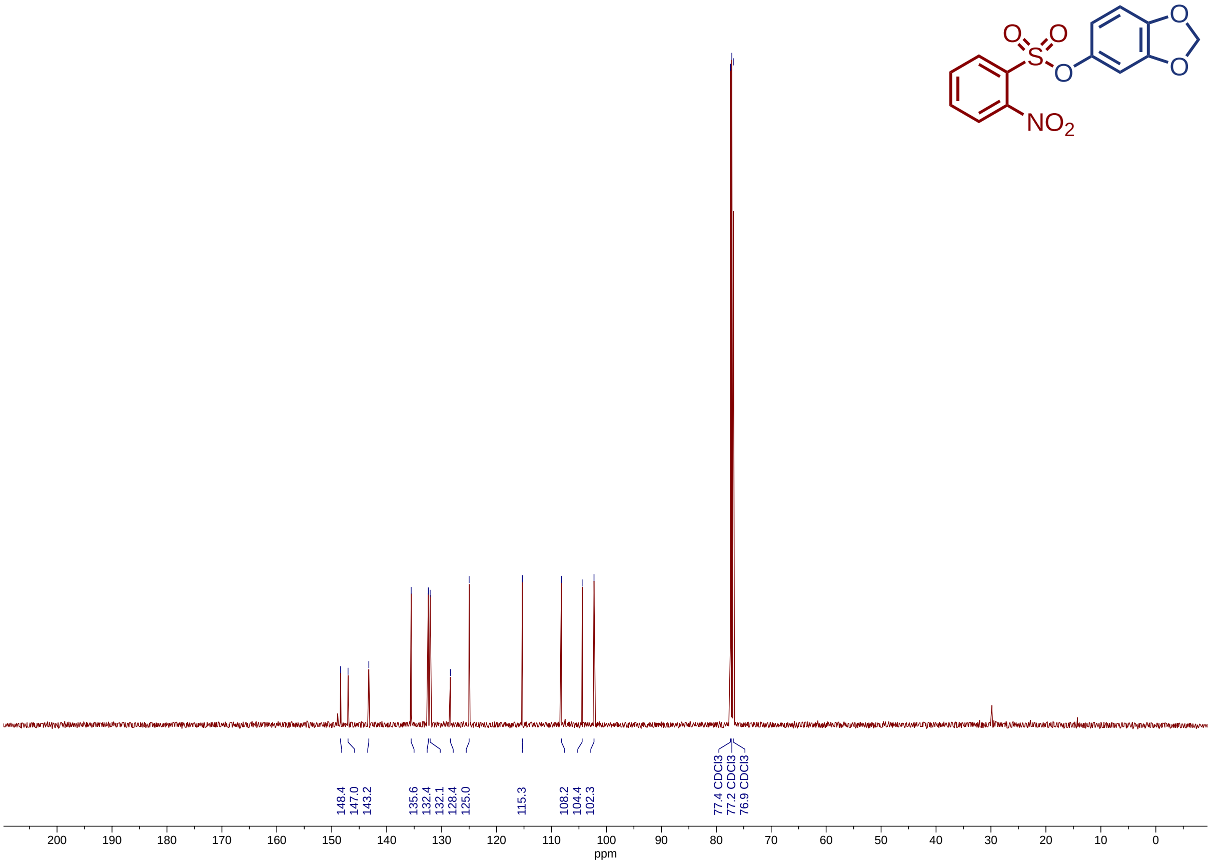
^{19}F NMR Spectrum for Compound **3l** (376 MHz, $CDCl_3$)



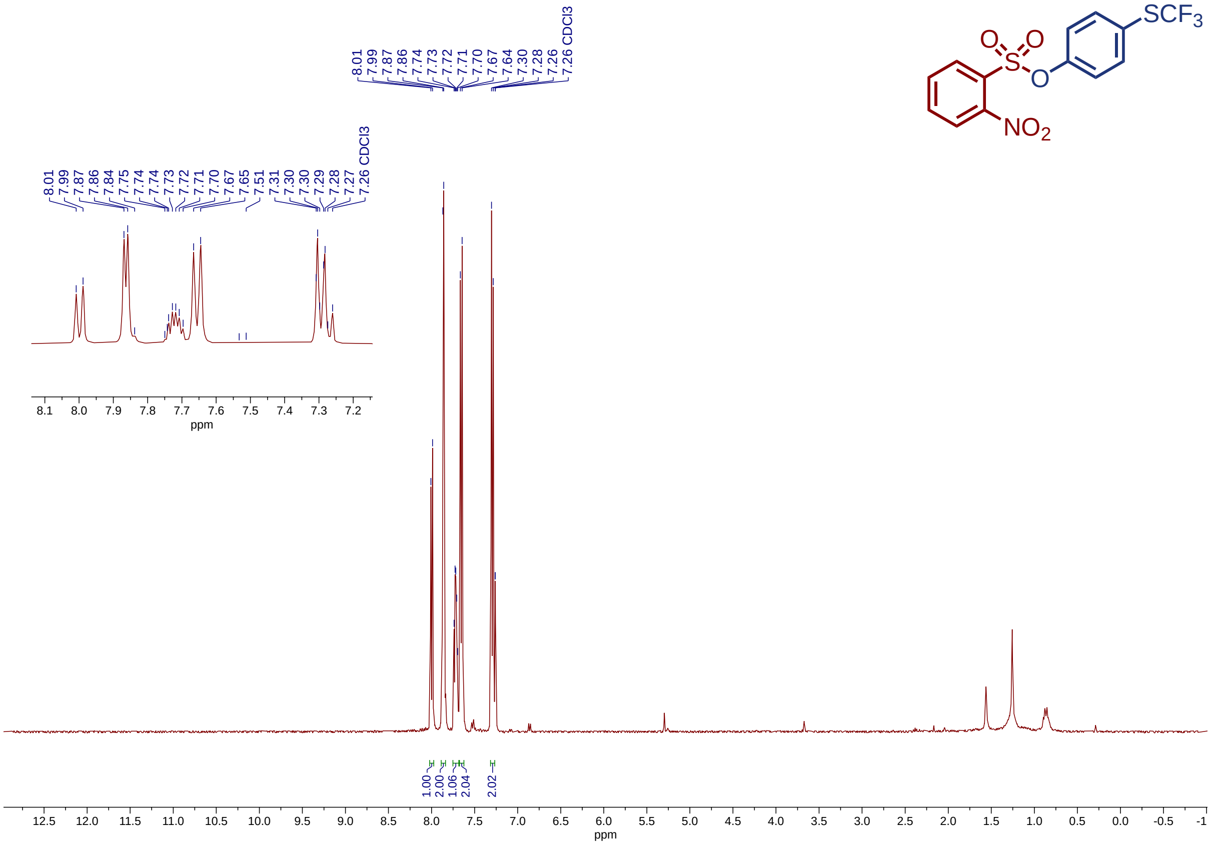
^{1}H NMR Spectrum for Compound **3m** (500 MHz, $CDCl_3$)



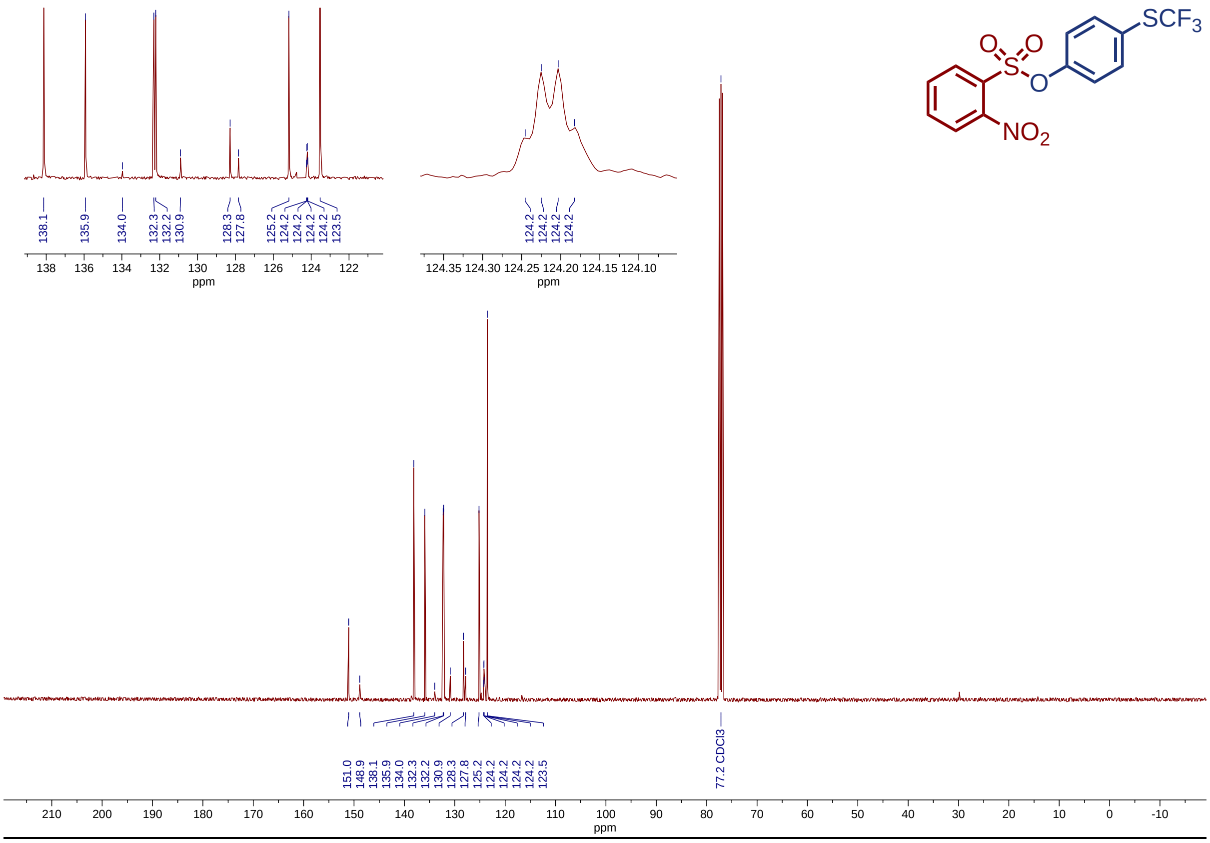
^{13}C NMR Spectrum for Compound **3m** (126 MHz, CDCl$_3$)



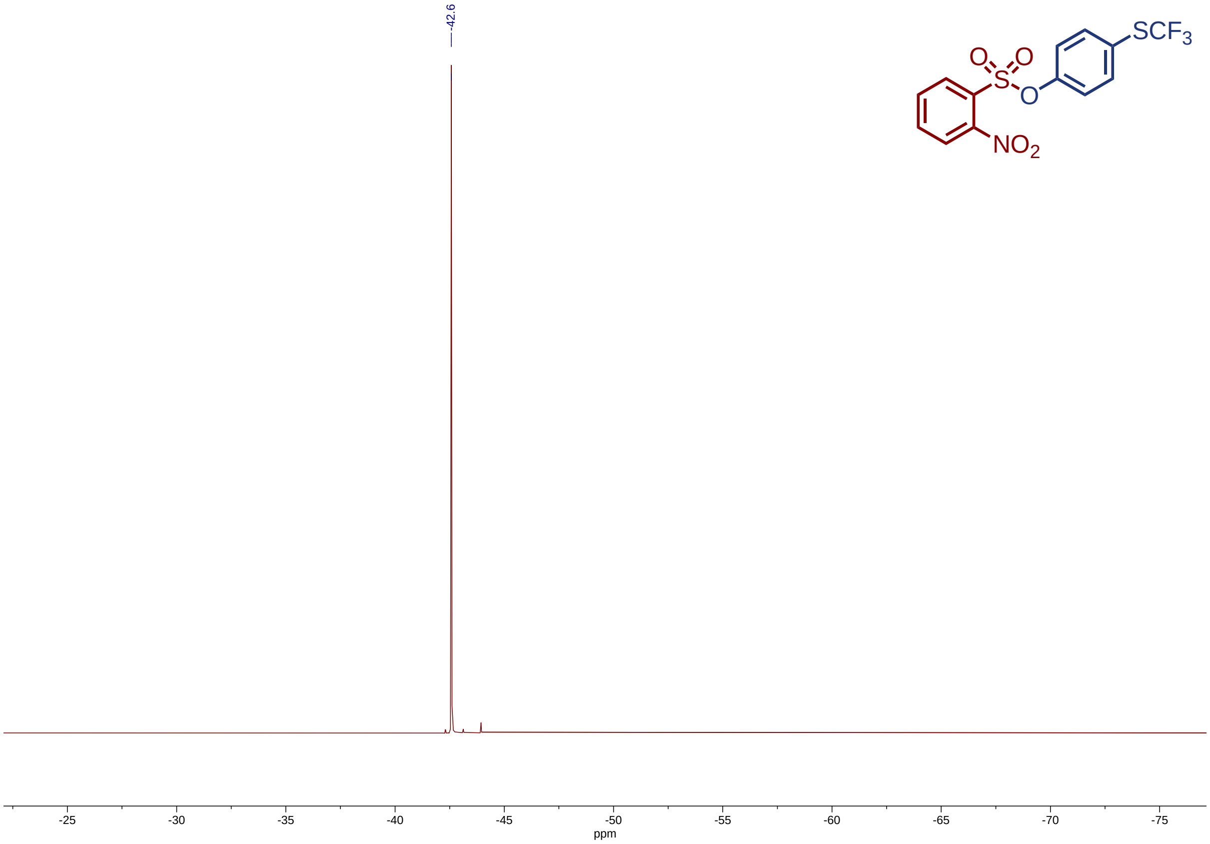
^{1}H NMR Spectrum for Compound **3n** (400 MHz, CDCl$_3$)



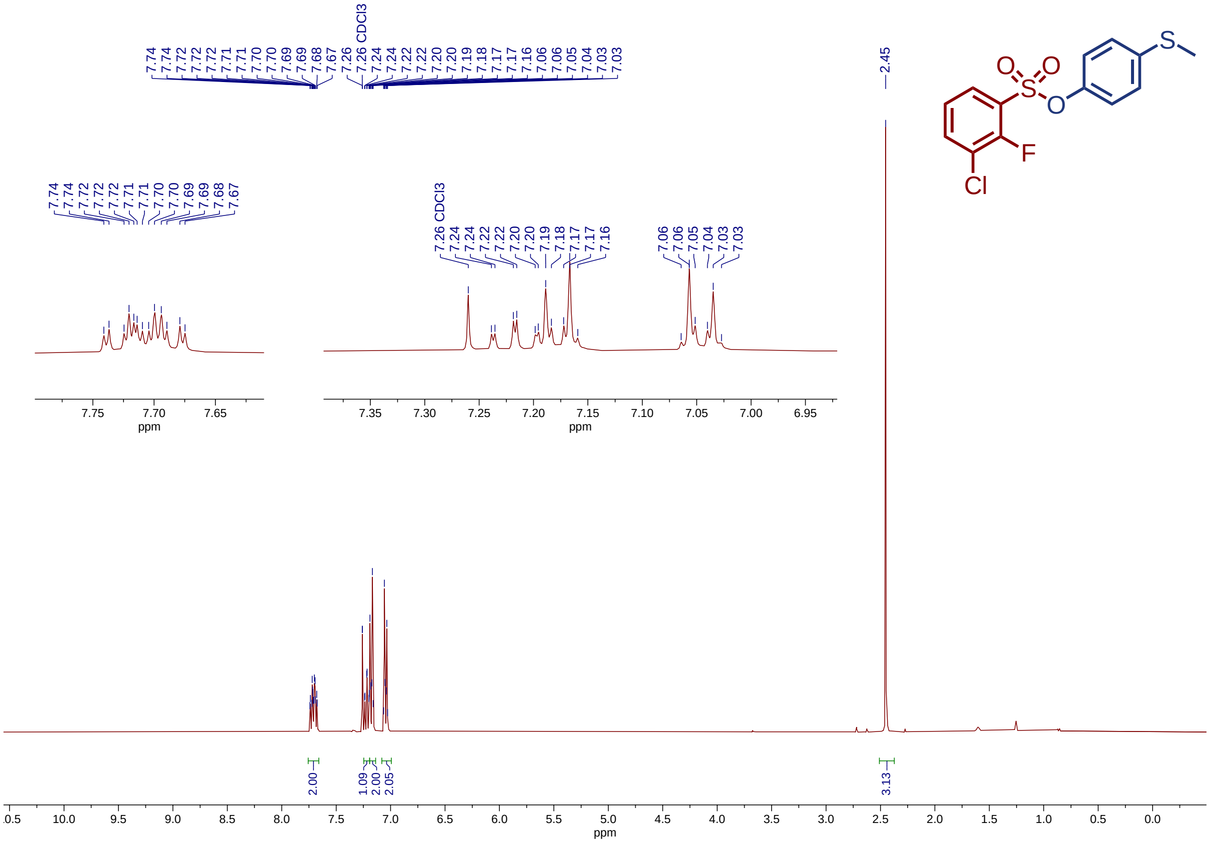
^{13}C NMR Spectrum for Compound **3n** (101 MHz, $CDCl_3$)



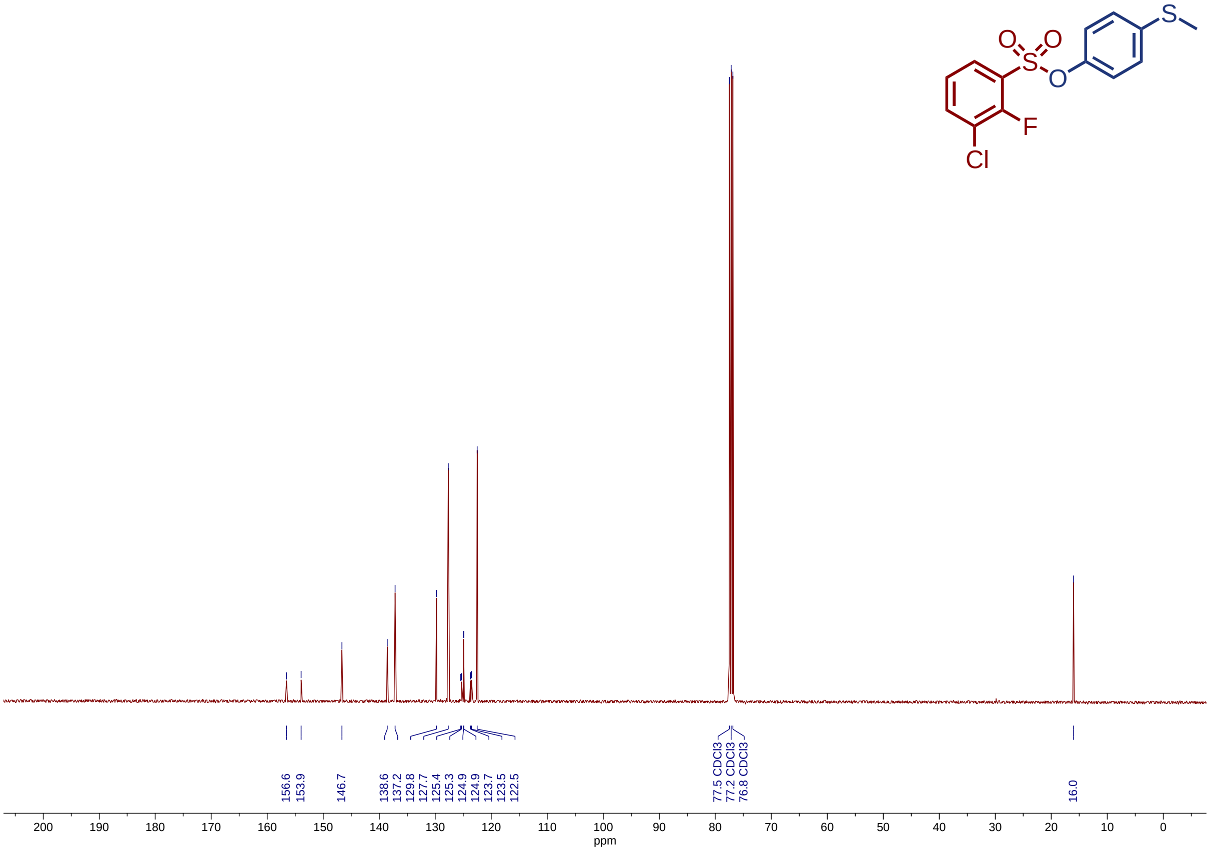
^{19}F NMR Spectrum for Compound **3n** (376 MHz, $CDCl_3$)



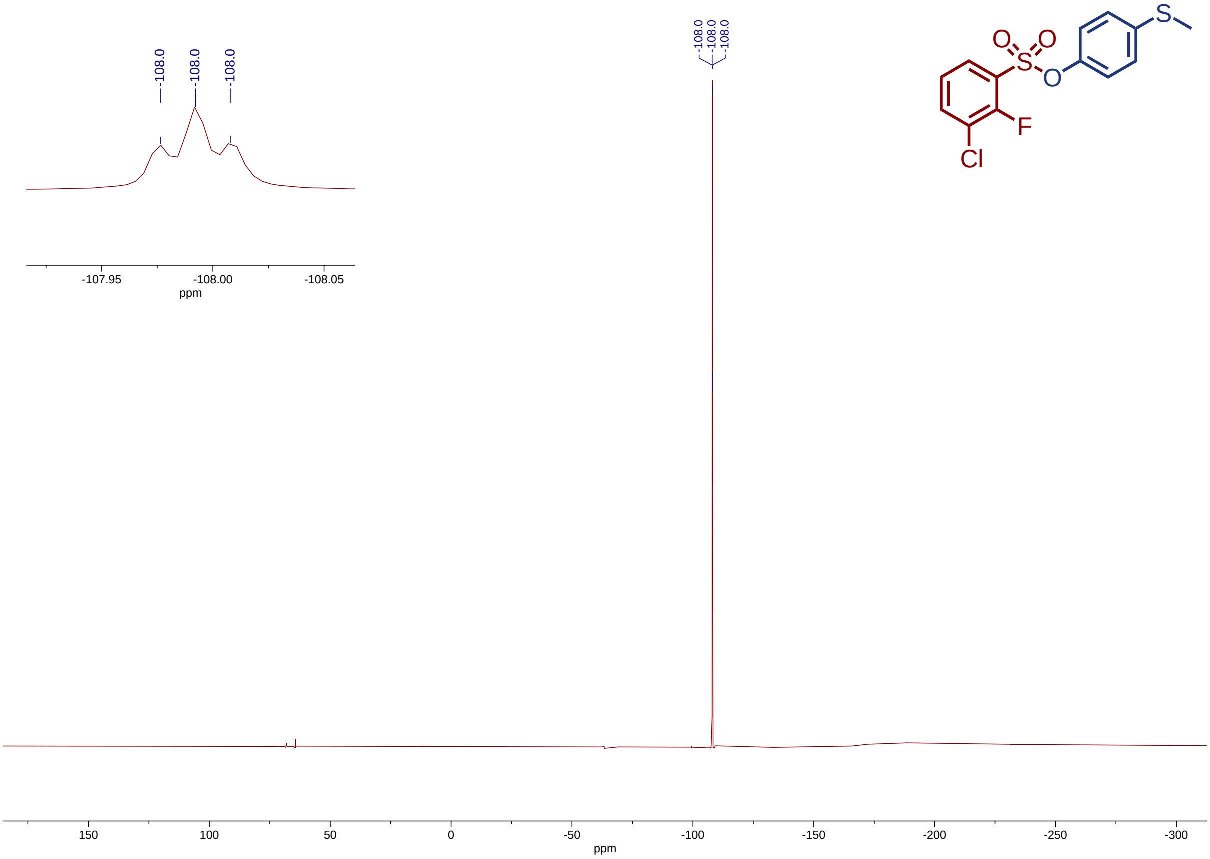
^{1}H NMR Spectrum for Compound **3o** (400 MHz, CDCl$_3$)



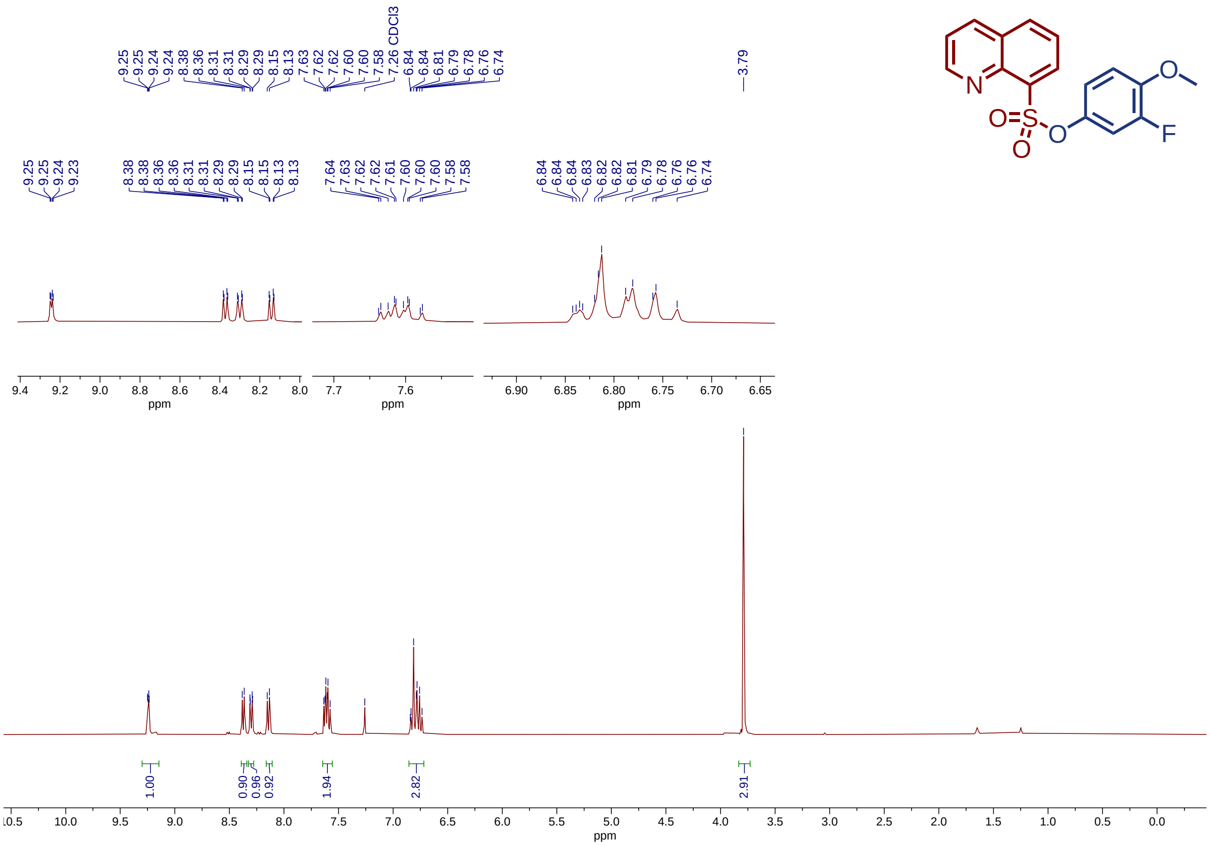
^{13}C NMR Spectrum for Compound **3o** (101 MHz, CDCl$_3$)



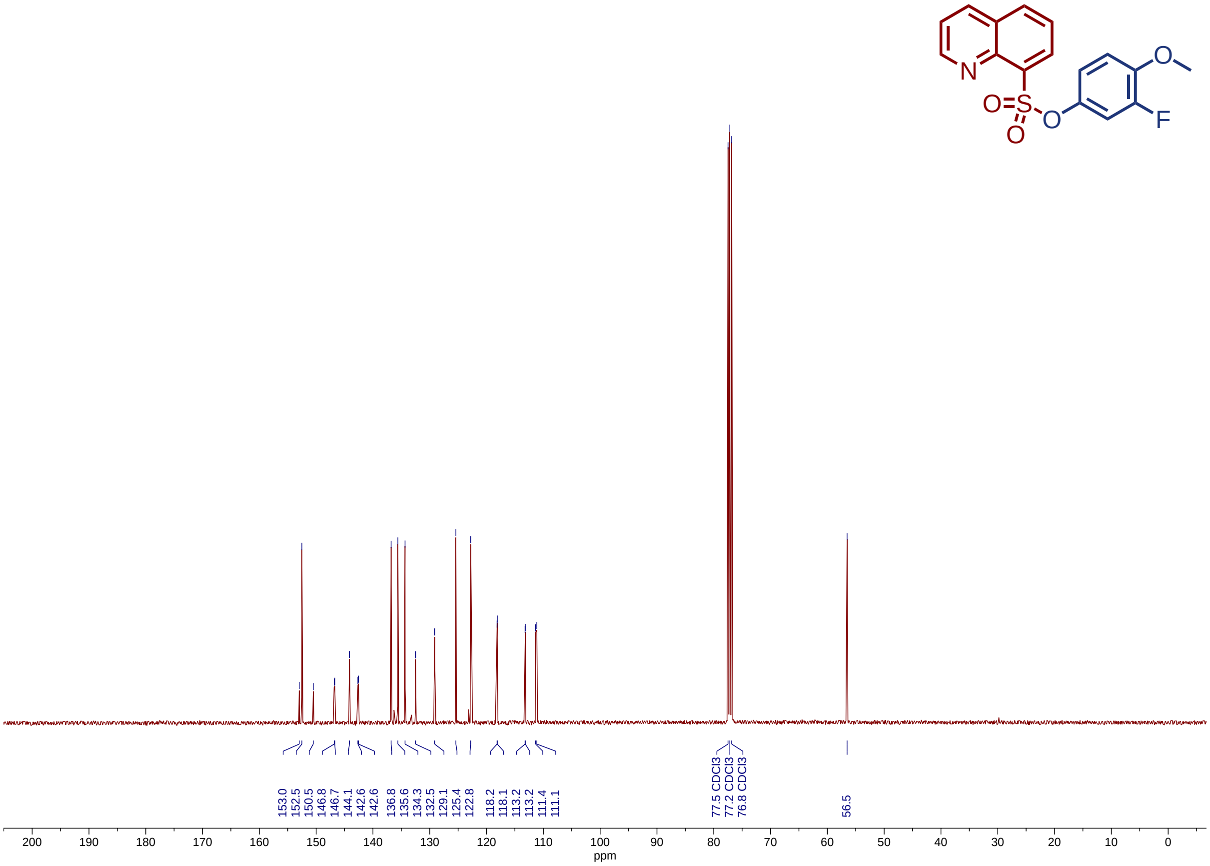
^{19}F NMR Spectrum for Compound **3o** (376 MHz, $CDCl_3$)



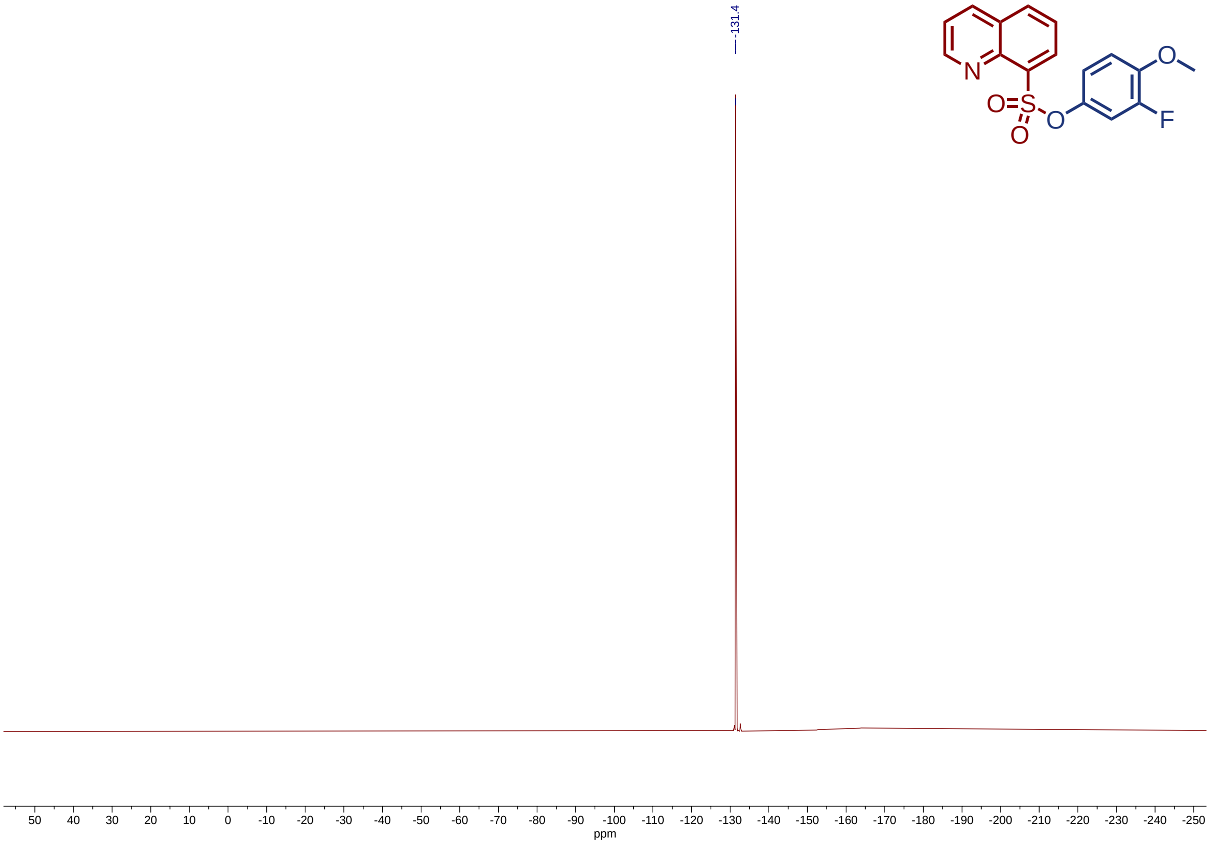
^{1}H NMR Spectrum for Compound **3p** (400 MHz, $CDCl_3$)



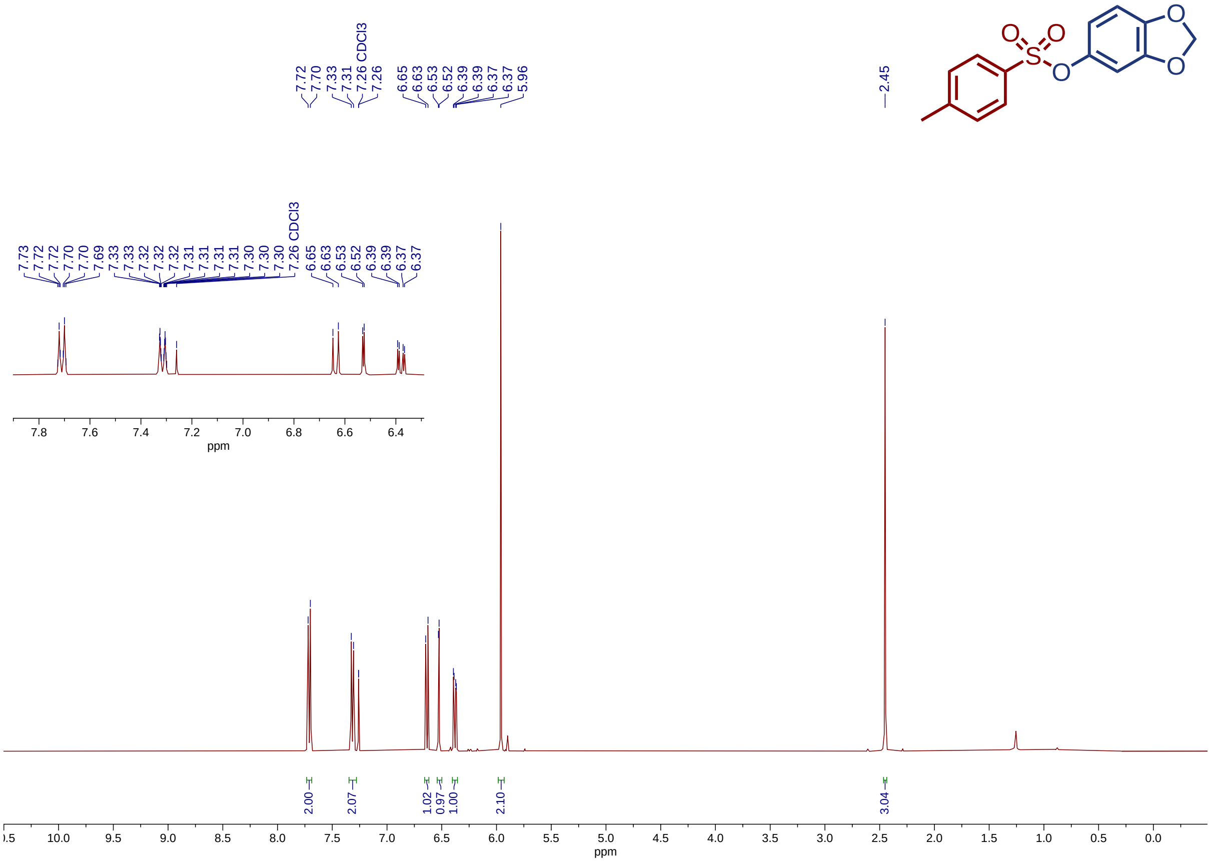
^{13}C NMR Spectrum for Compound **3p** (101 MHz, CDCl$_3$)



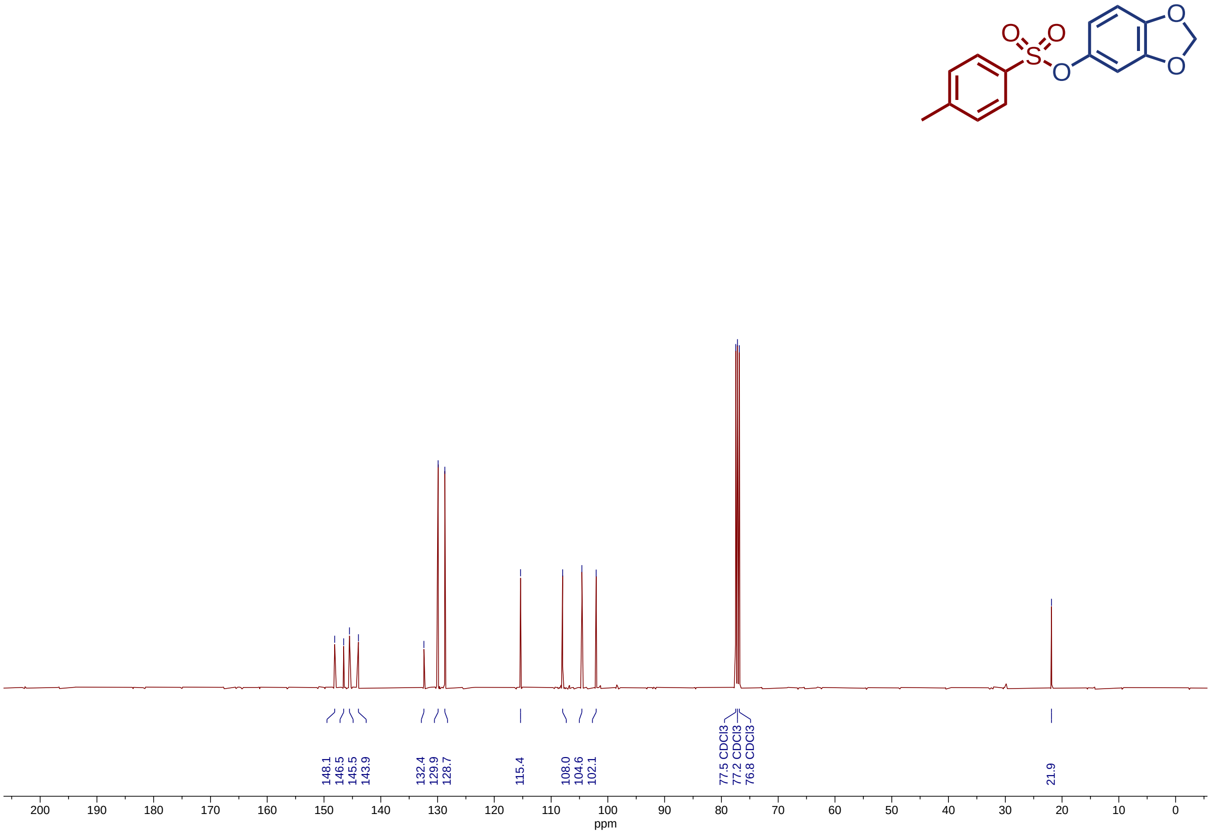
^{19}F NMR Spectrum for Compound **3p** (376 MHz, CDCl$_3$)



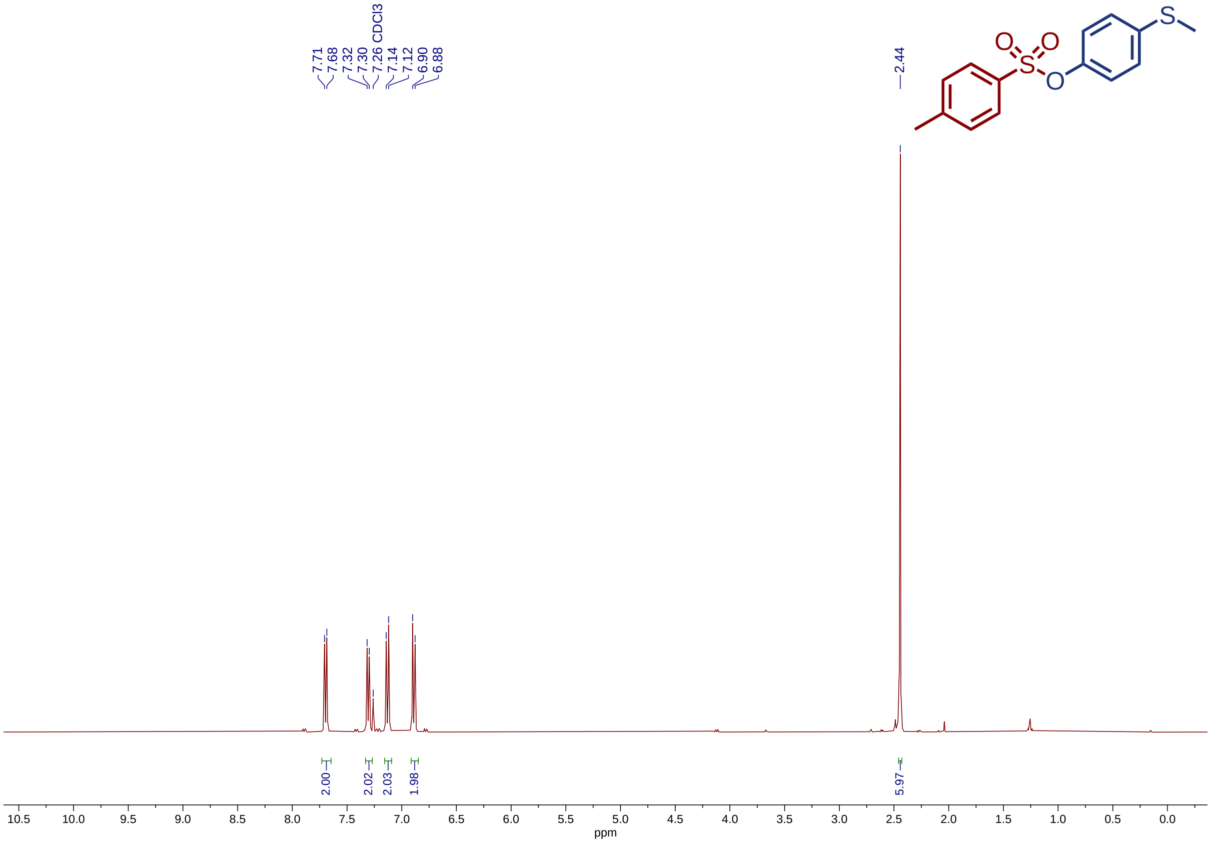
^1H NMR Spectrum for Compound **3q** (400 MHz, $CDCl_3$)



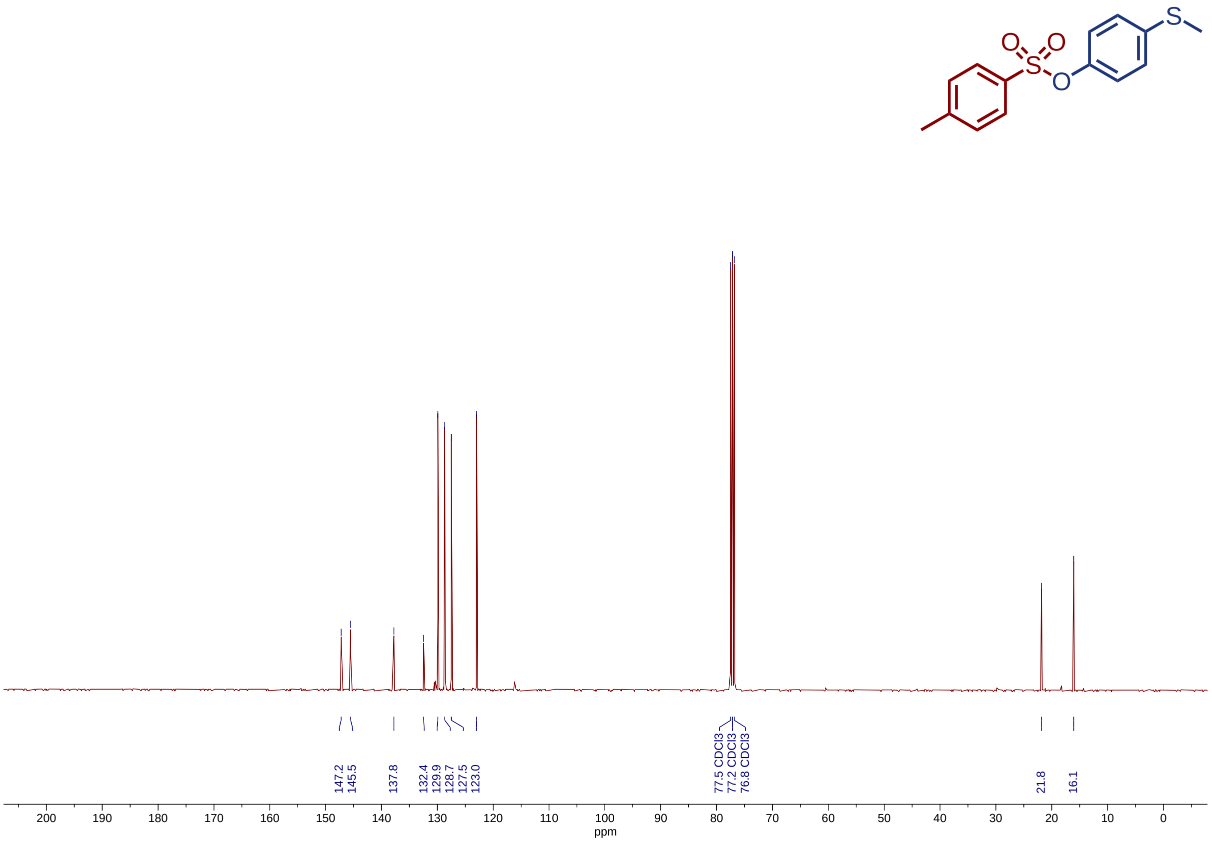
^{13}C NMR Spectrum for Compound **3q** (101 MHz, $CDCl_3$)



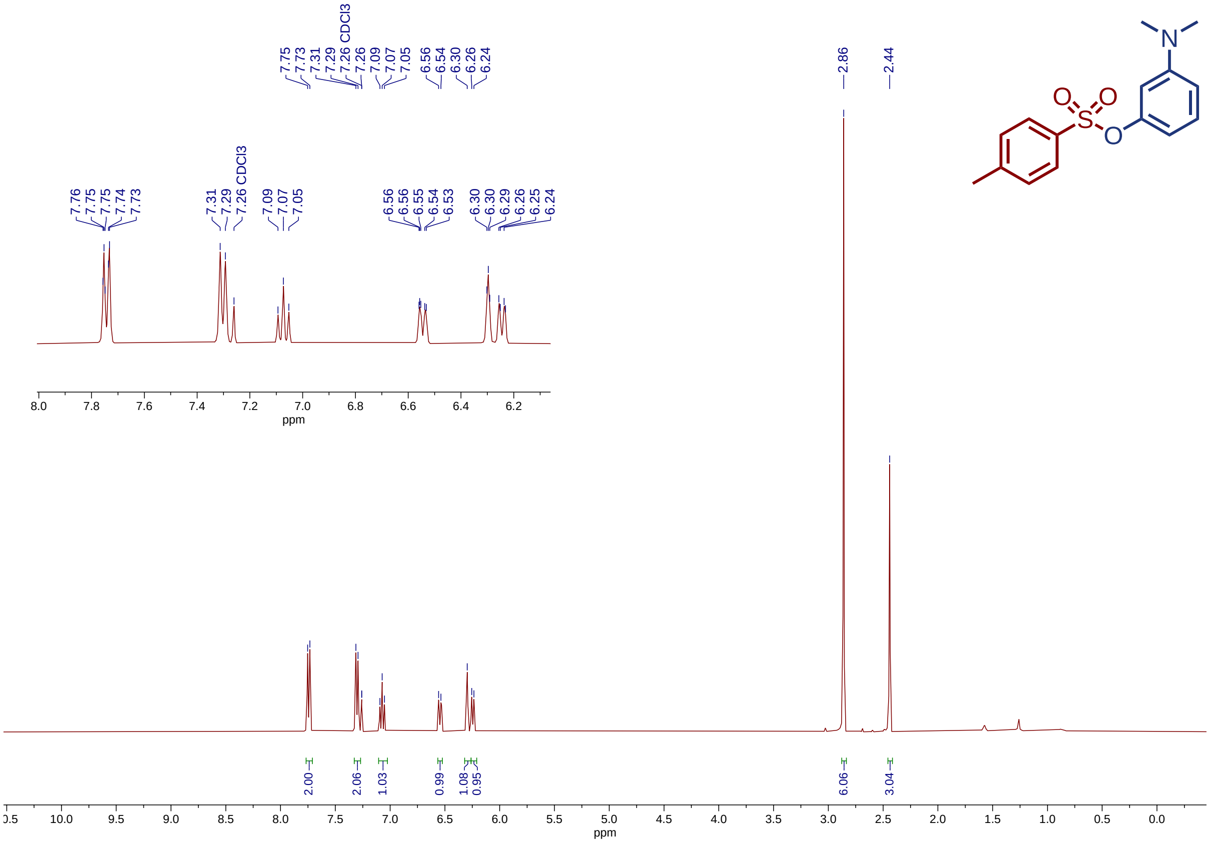
^{1}H NMR Spectrum for Compound **3r** (400 MHz, $CDCl_3$)



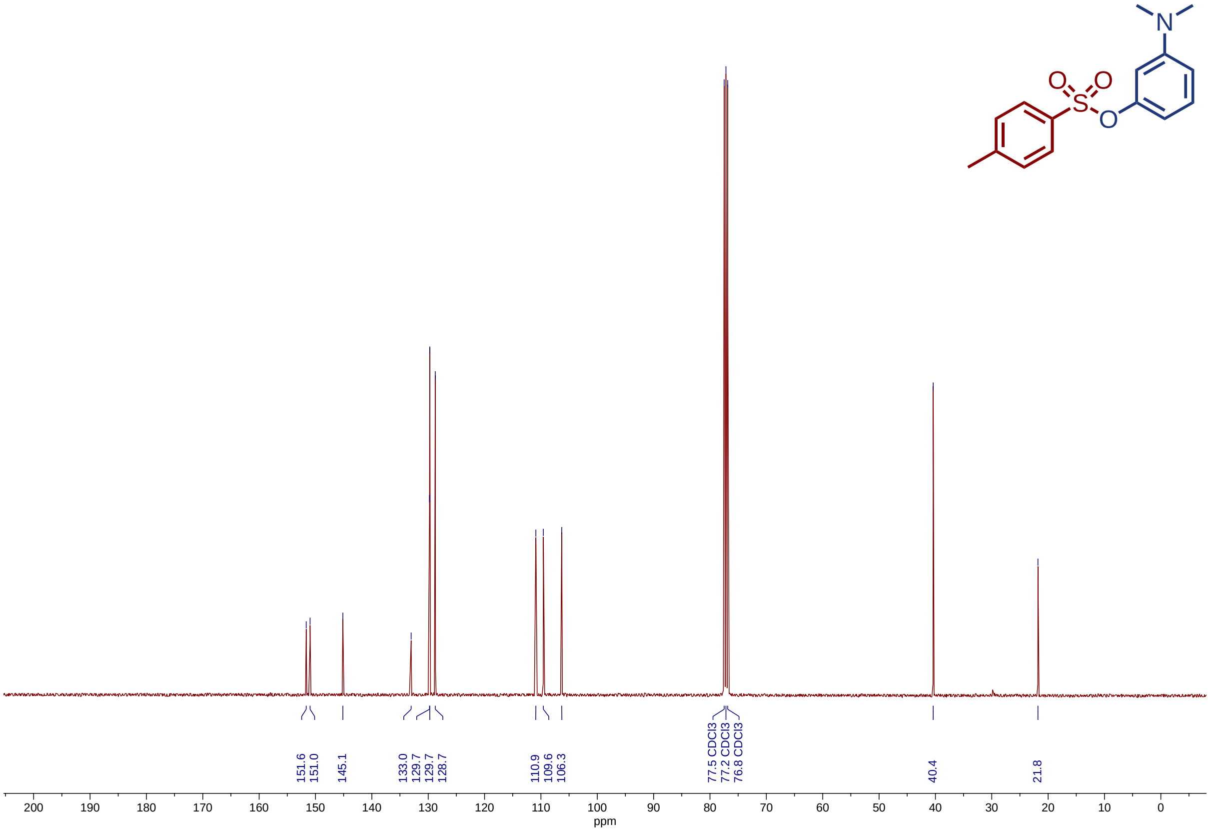
^{13}C NMR Spectrum for Compound **3r** (101 MHz, $CDCl_3$)



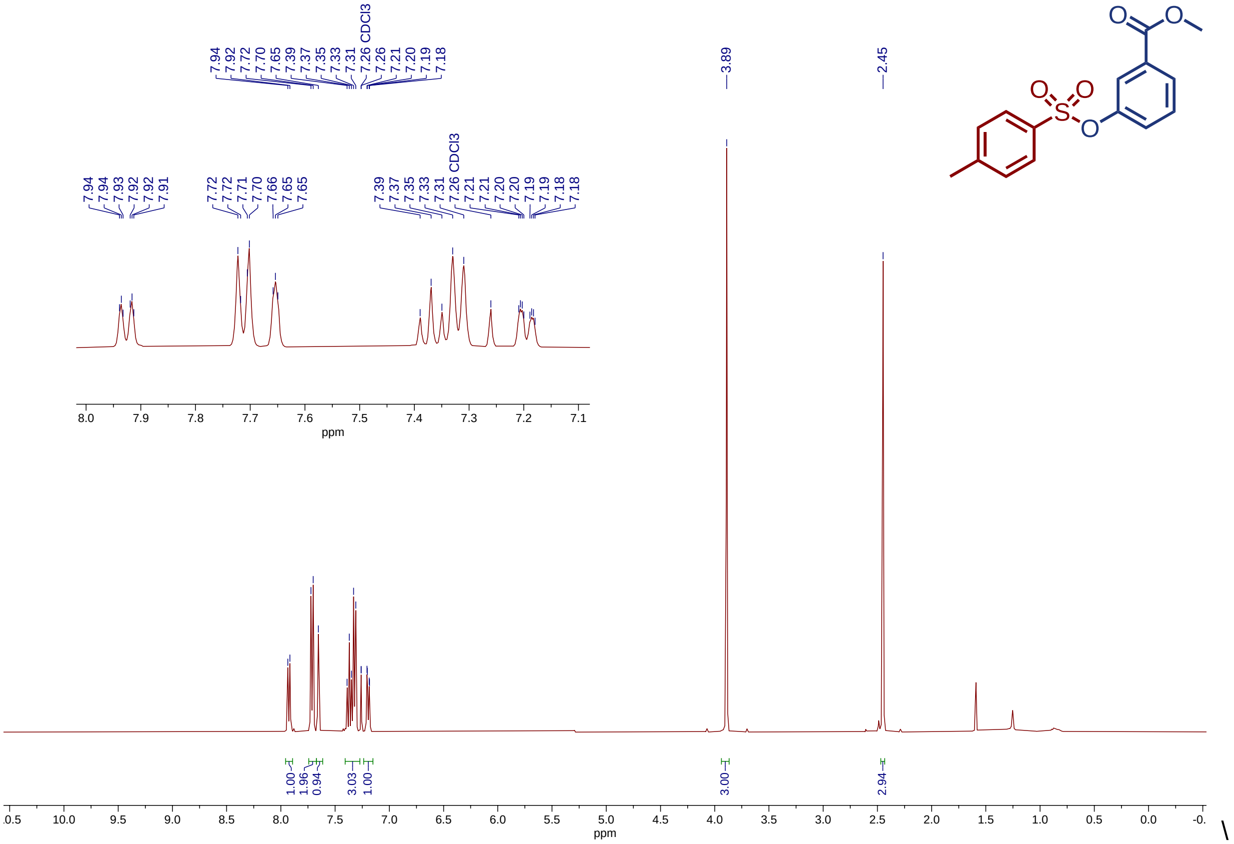
^{1}H NMR Spectrum for Compound **3s** (400 MHz, $CDCl_3$)



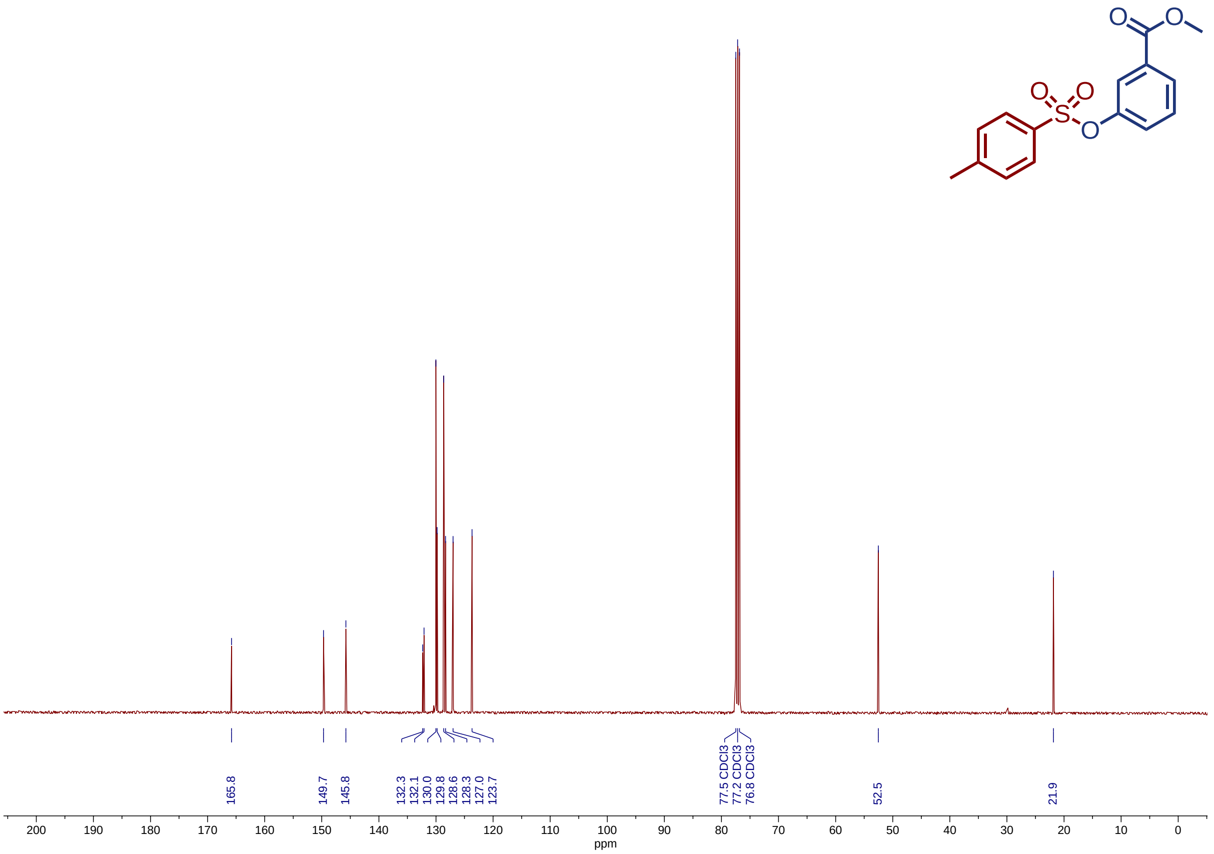
^{13}C NMR Spectrum for Compound **3s** (101 MHz, $CDCl_3$)



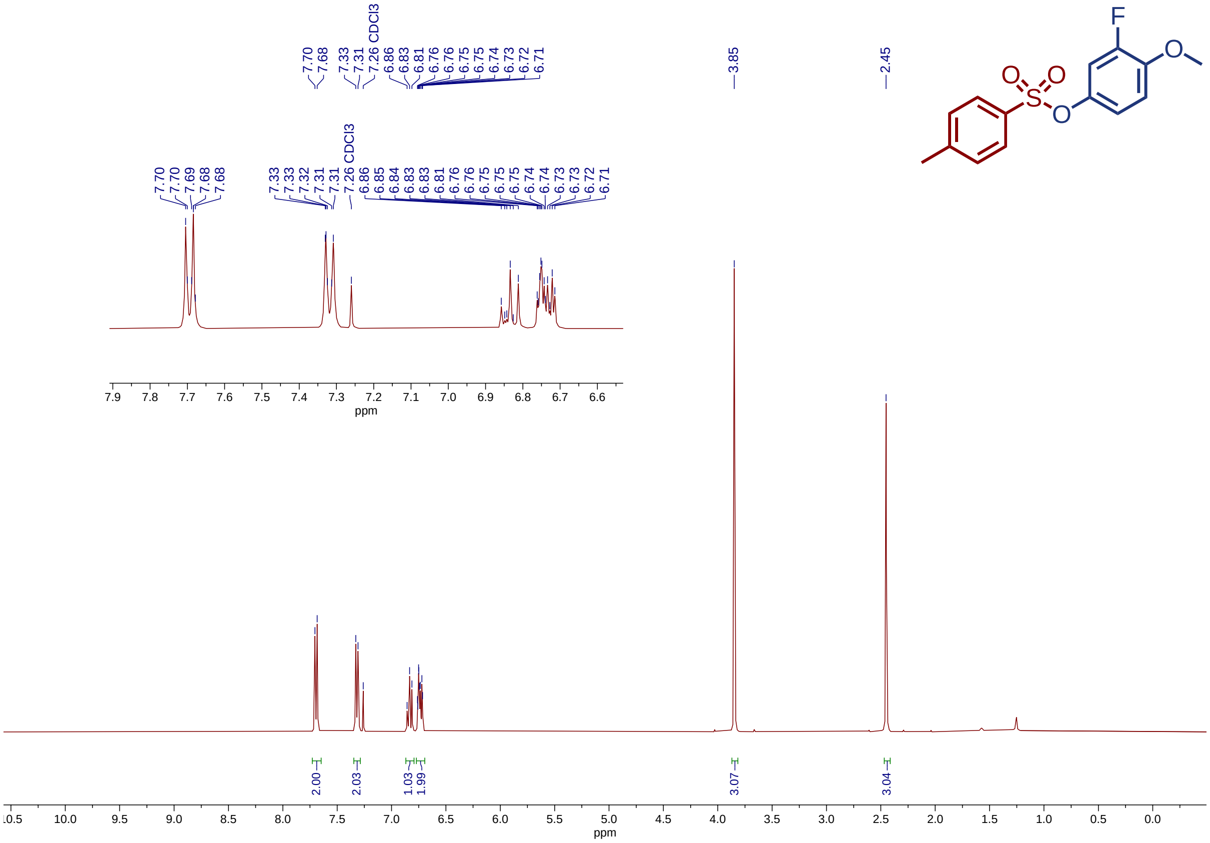
^{1}H NMR Spectrum for Compound **3t** (400 MHz, $CDCl_3$)



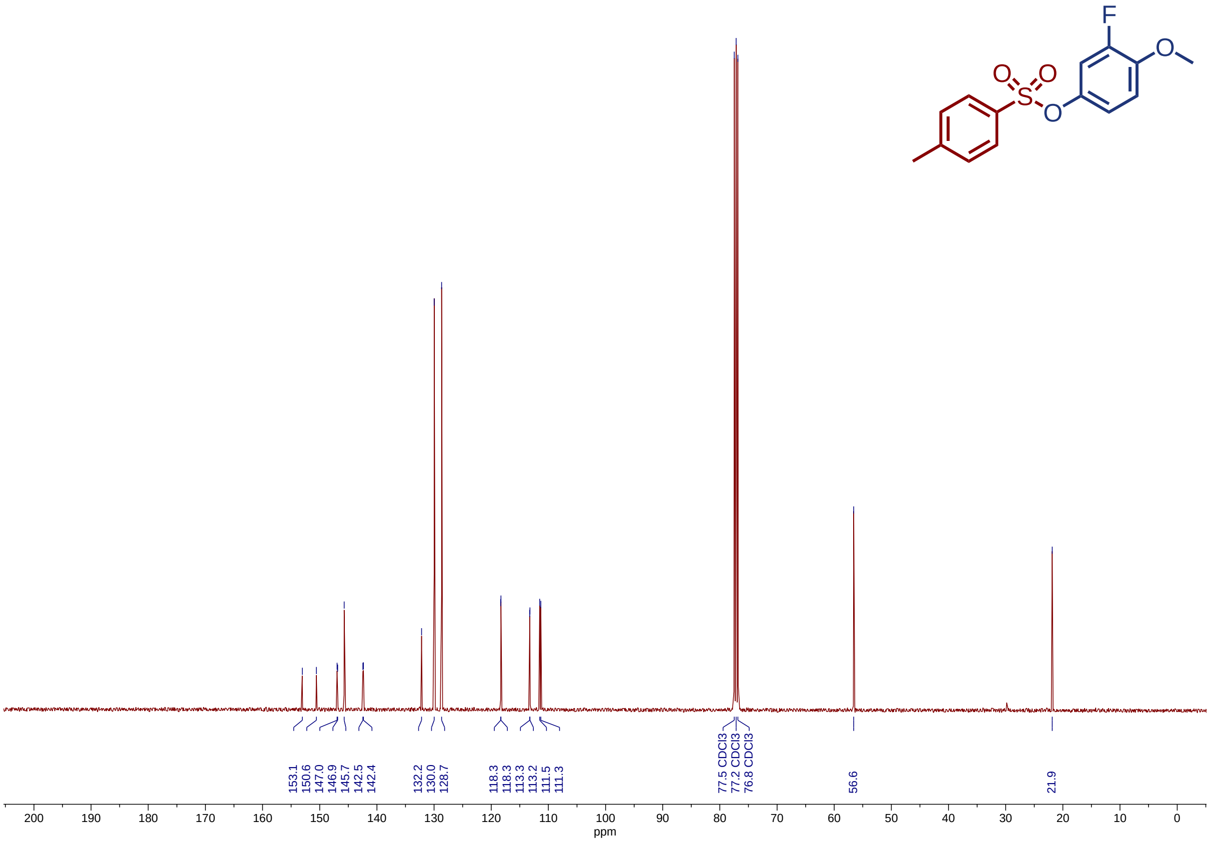
^{13}C NMR Spectrum for Compound **3t** (101 MHz, $CDCl_3$)



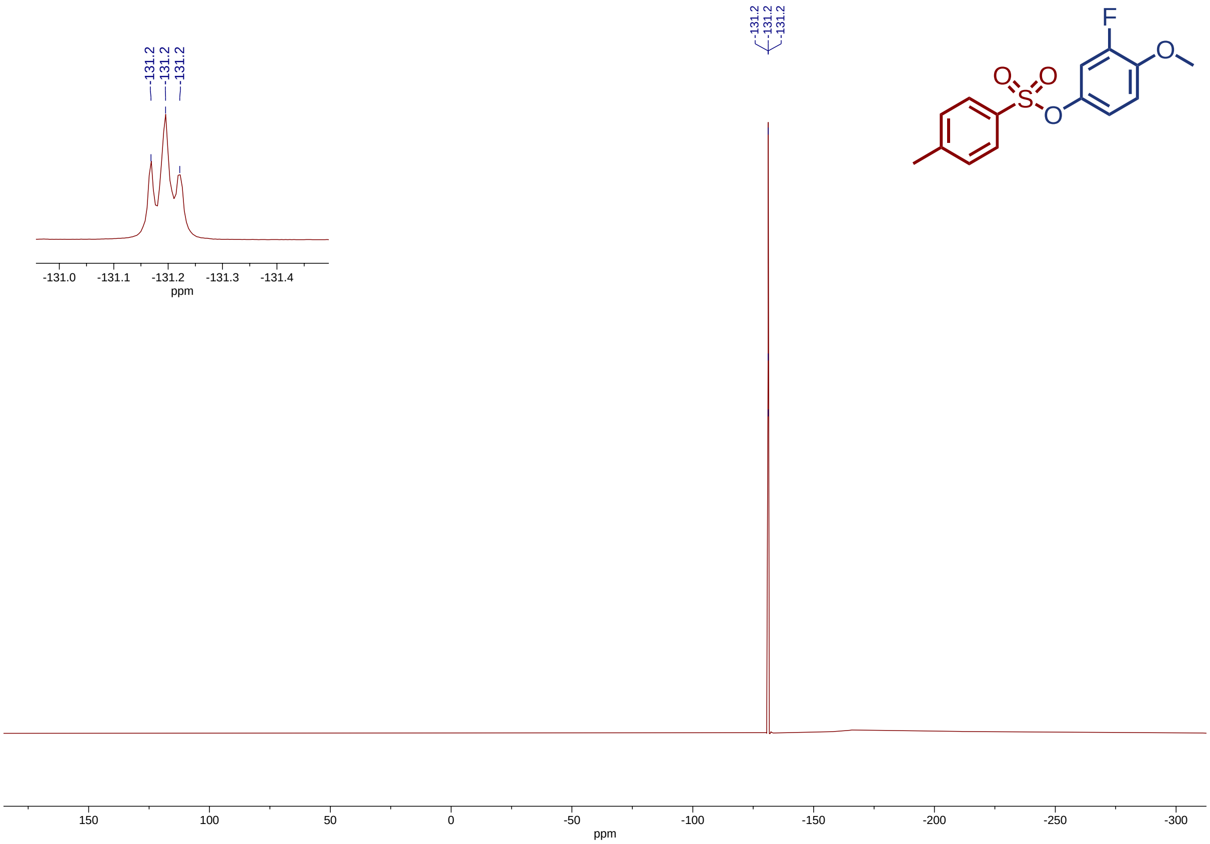
^{1}H NMR Spectrum for Compound **3u** (400 MHz, $CDCl_3$)



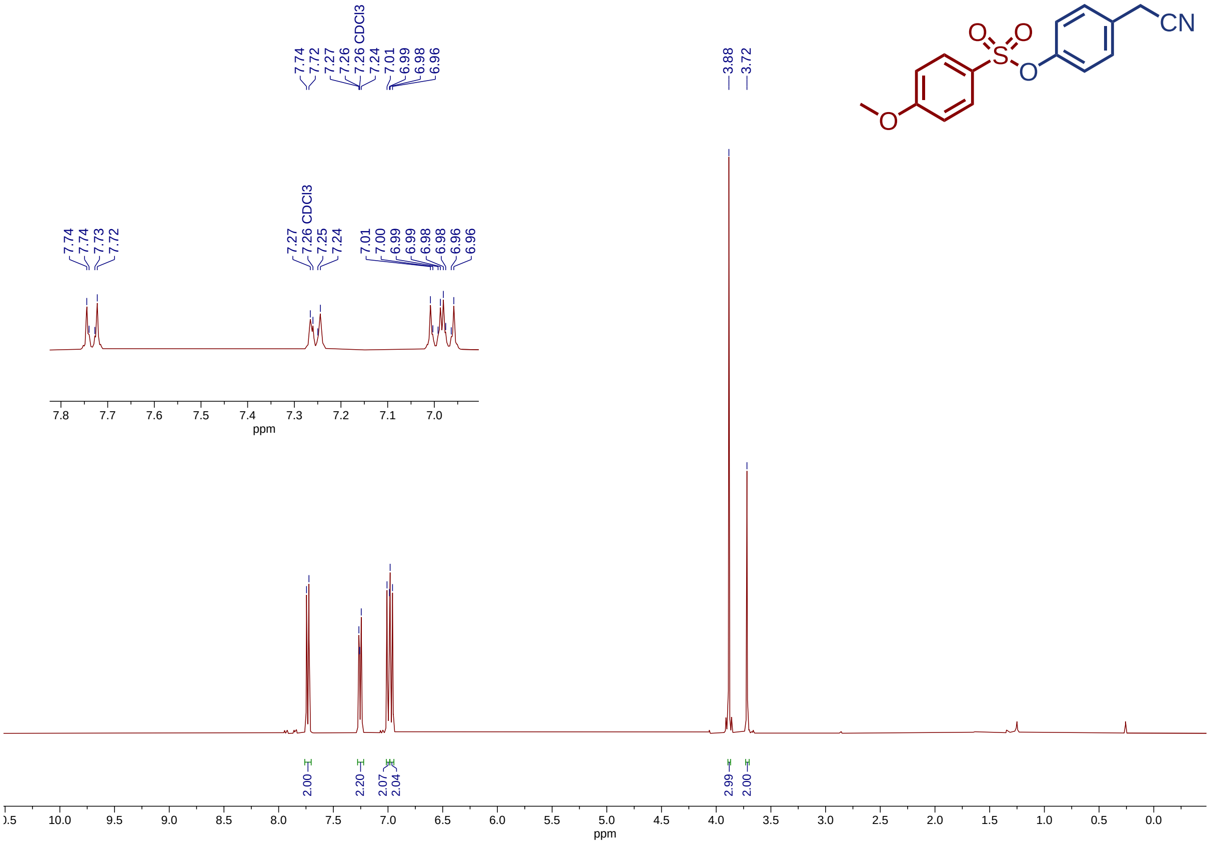
^{13}C NMR Spectrum for Compound **3u** (101 MHz, $CDCl_3$)



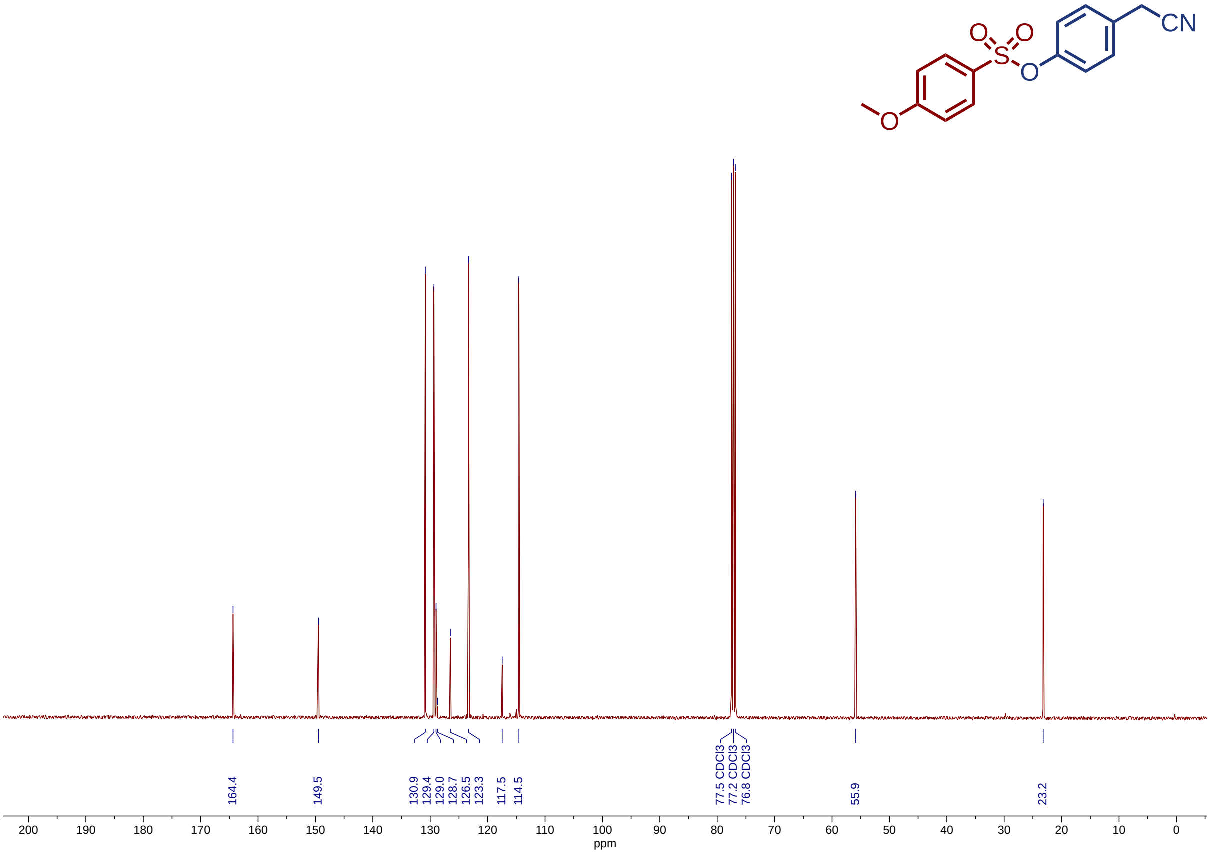
^{19}F NMR Spectrum for Compound **3u** (376 MHz, $CDCl_3$)



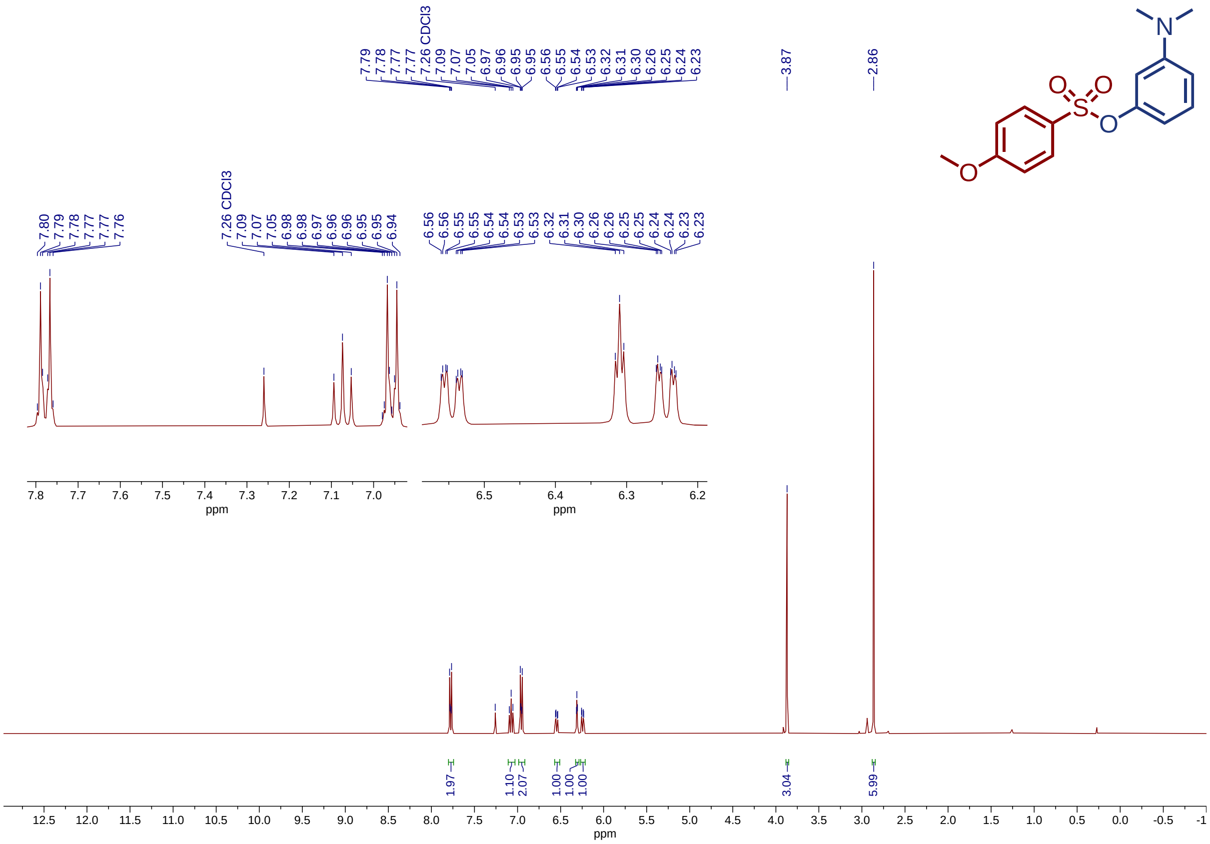
^1H NMR Spectrum for Compound **3v** (400 MHz, $CDCl_3$)



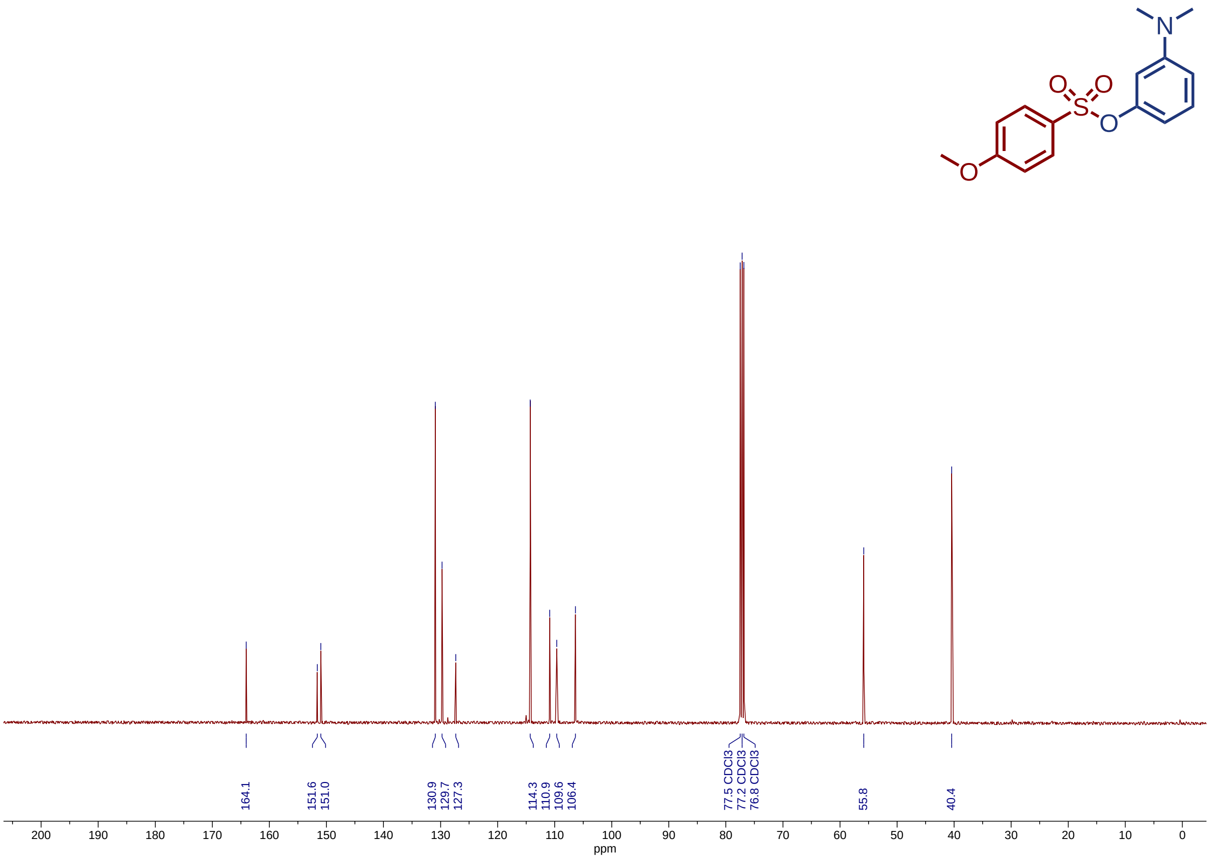
^{13}C NMR Spectrum for Compound **3v** (101 MHz, CDCl$_3$)



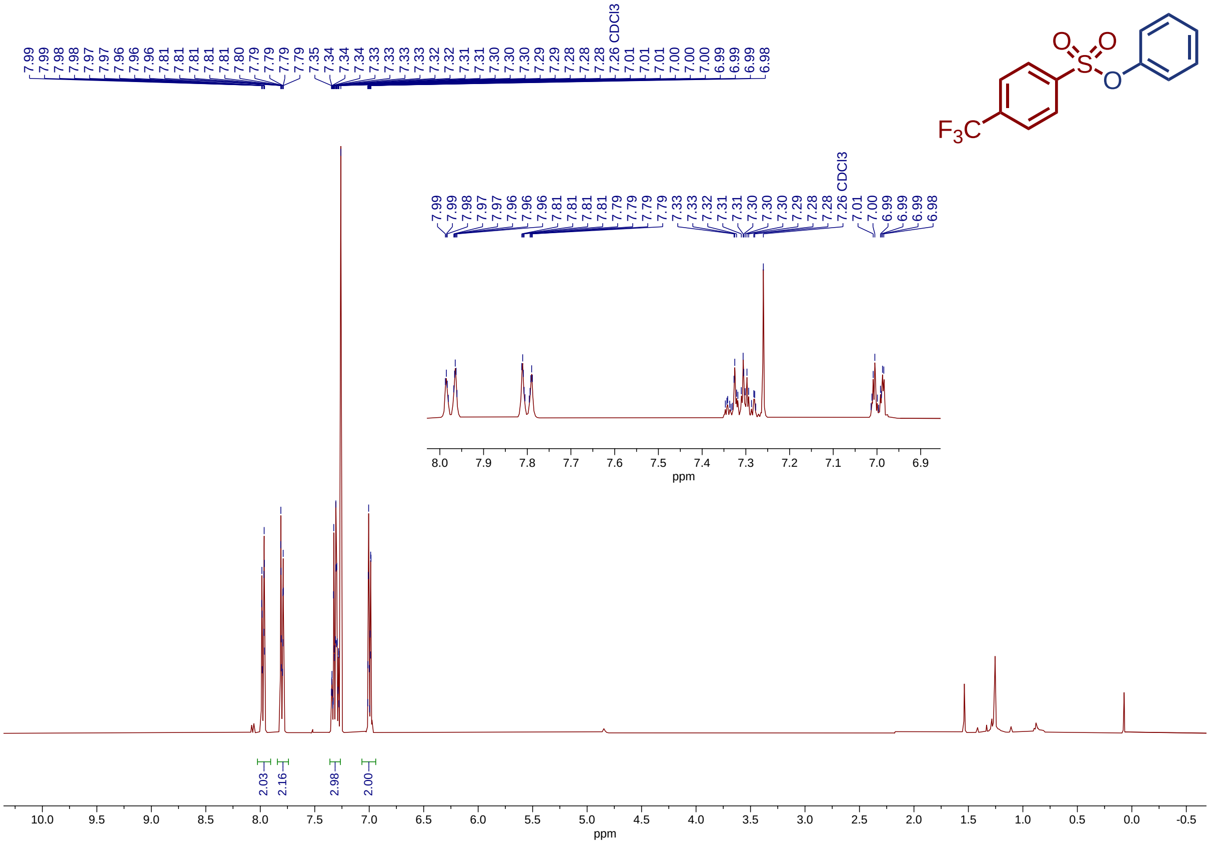
^{1}H NMR Spectrum for Compound **3w** (400 MHz, CDCl$_3$)



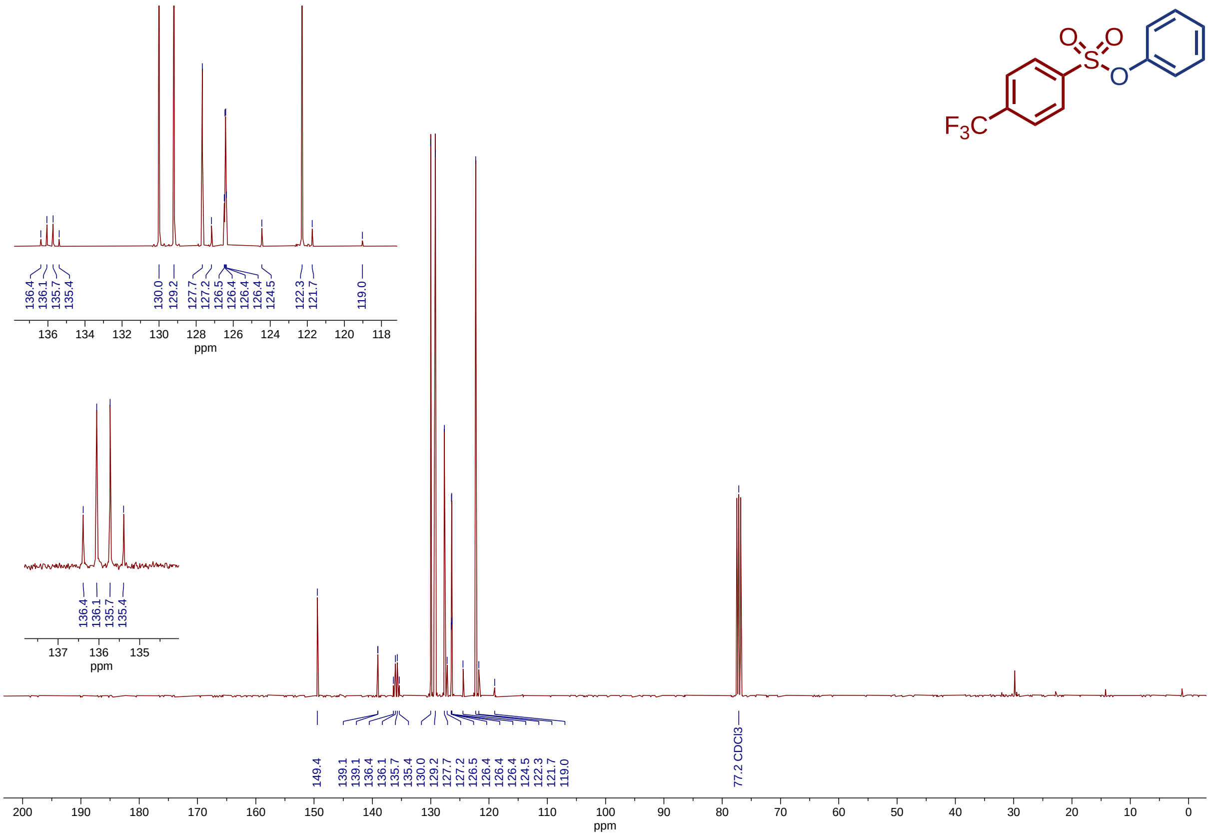
^{13}C NMR Spectrum for Compound **3w** (101 MHz, $CDCl_3$)



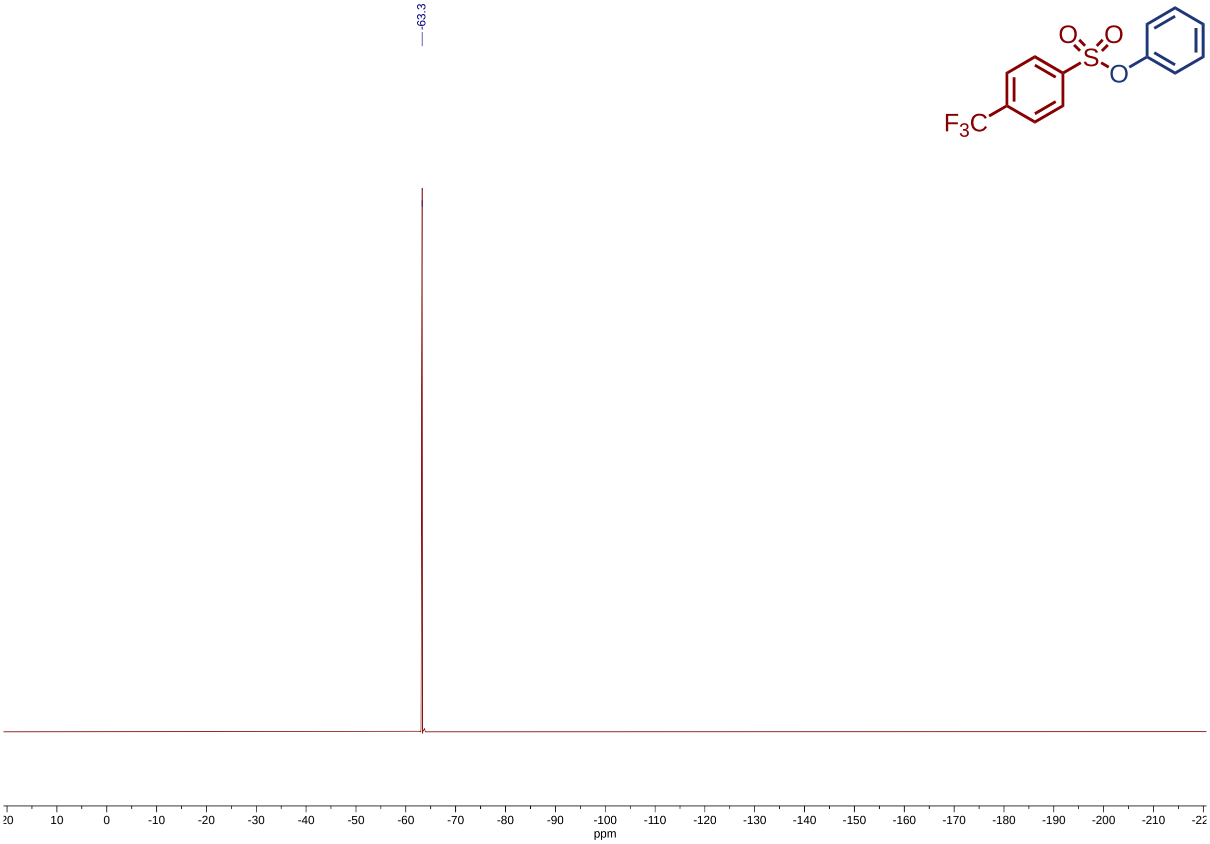
^{1}H NMR Spectrum for Compound **3x** (400 MHz, $CDCl_3$)



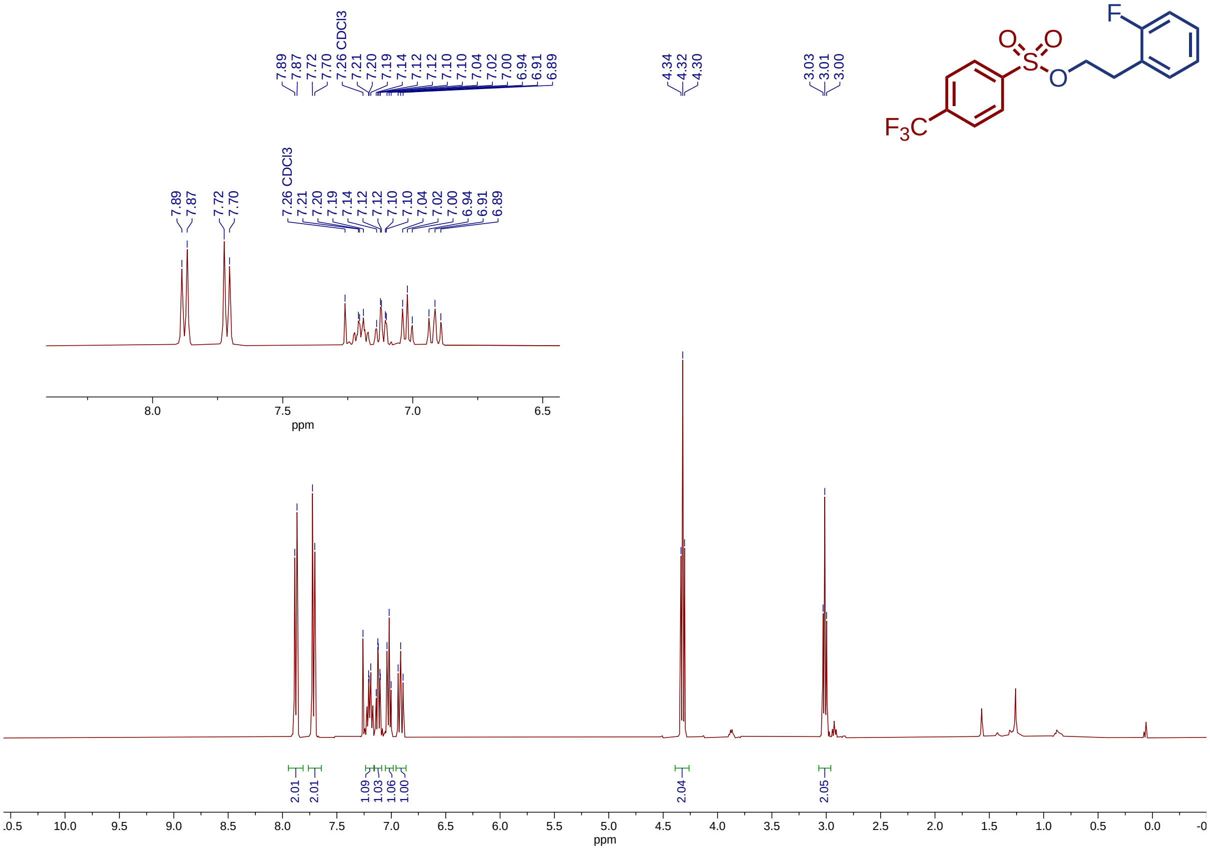
^{13}C NMR Spectrum for Compound **3x** (101 MHz, $CDCl_3$)



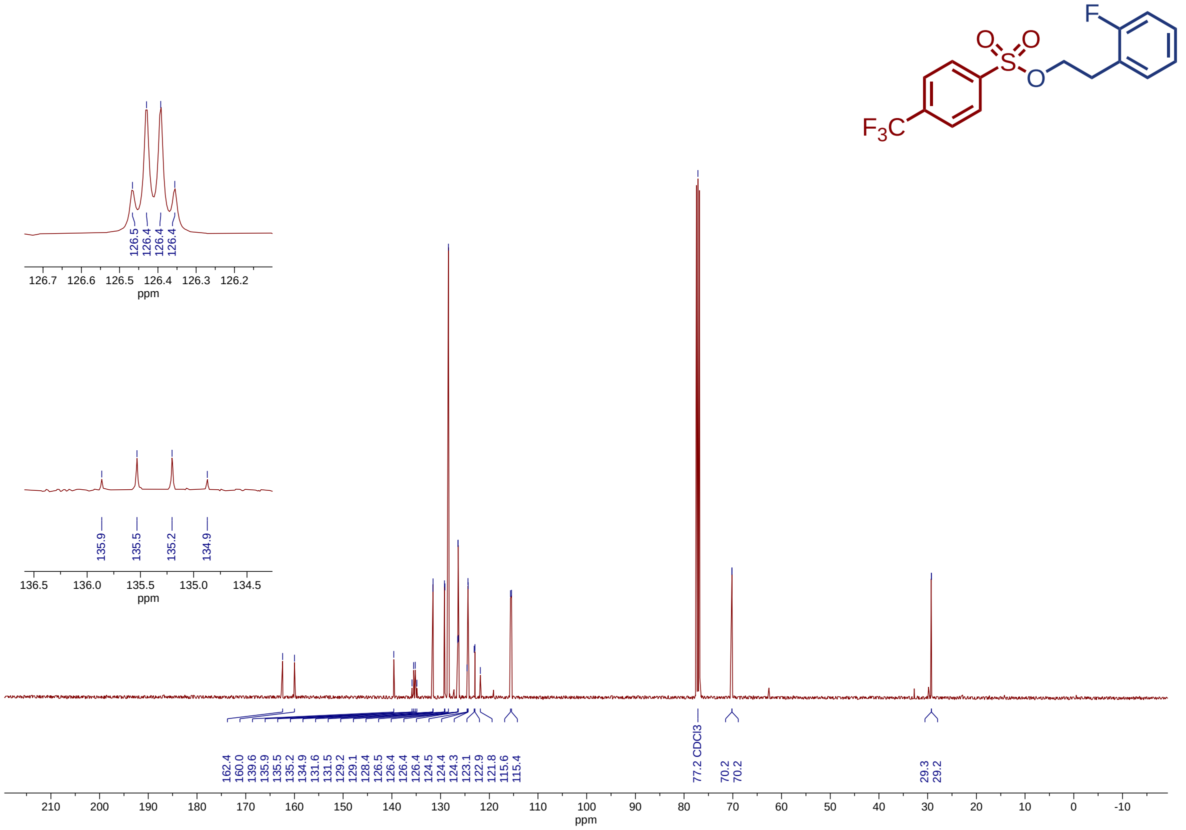
^{19}F NMR Spectrum for Compound **3x** (376 MHz, $CDCl_3$)



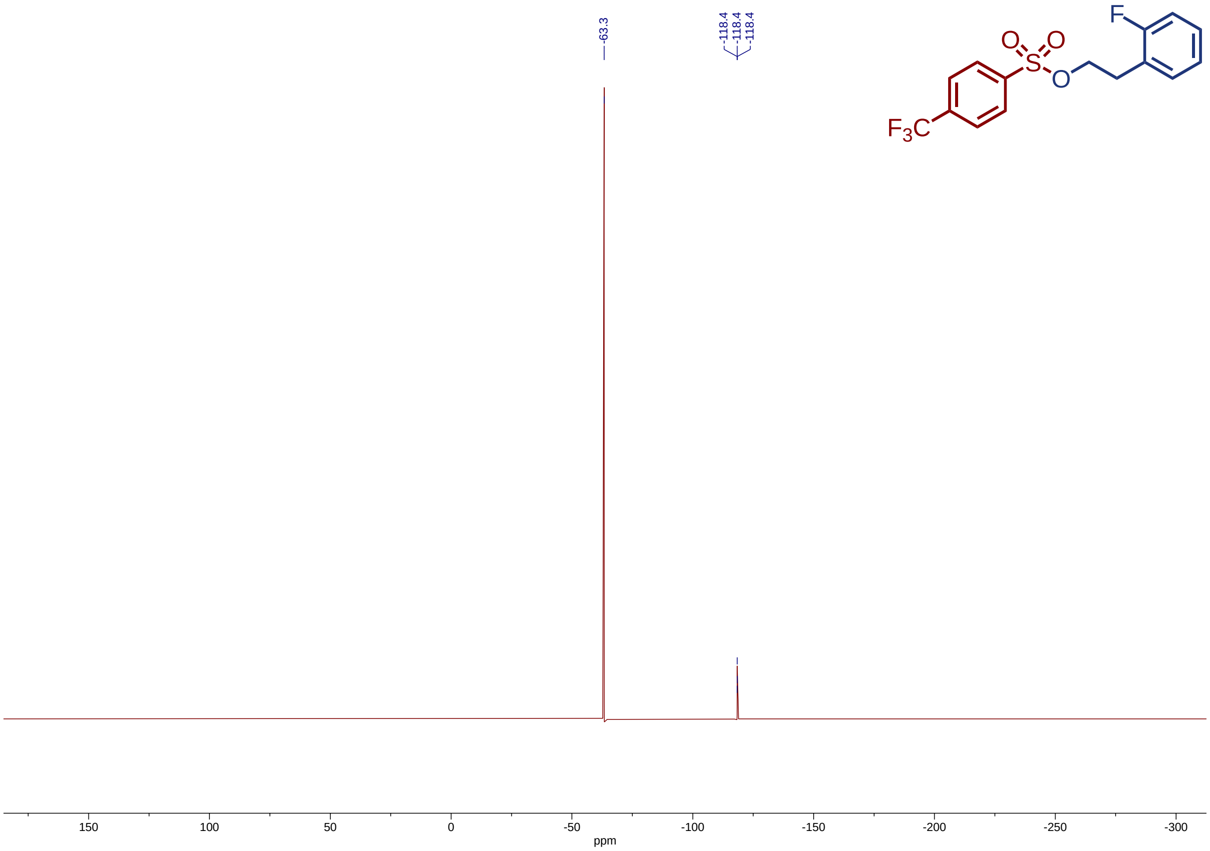
^{1}H NMR Spectrum for Compound **6a** (400 MHz, $CDCl_3$)



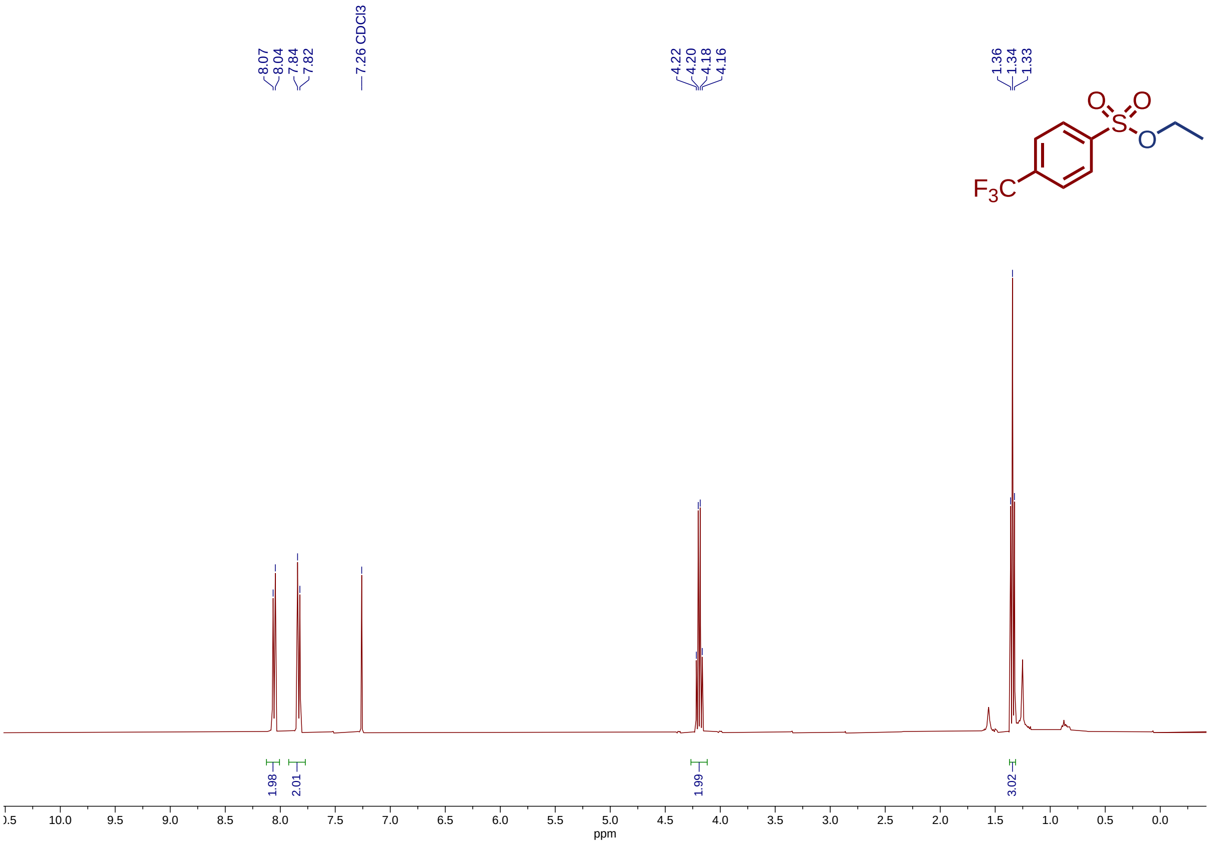
^{13}C NMR Spectrum for Compound **6a** (101 MHz, $CDCl_3$)



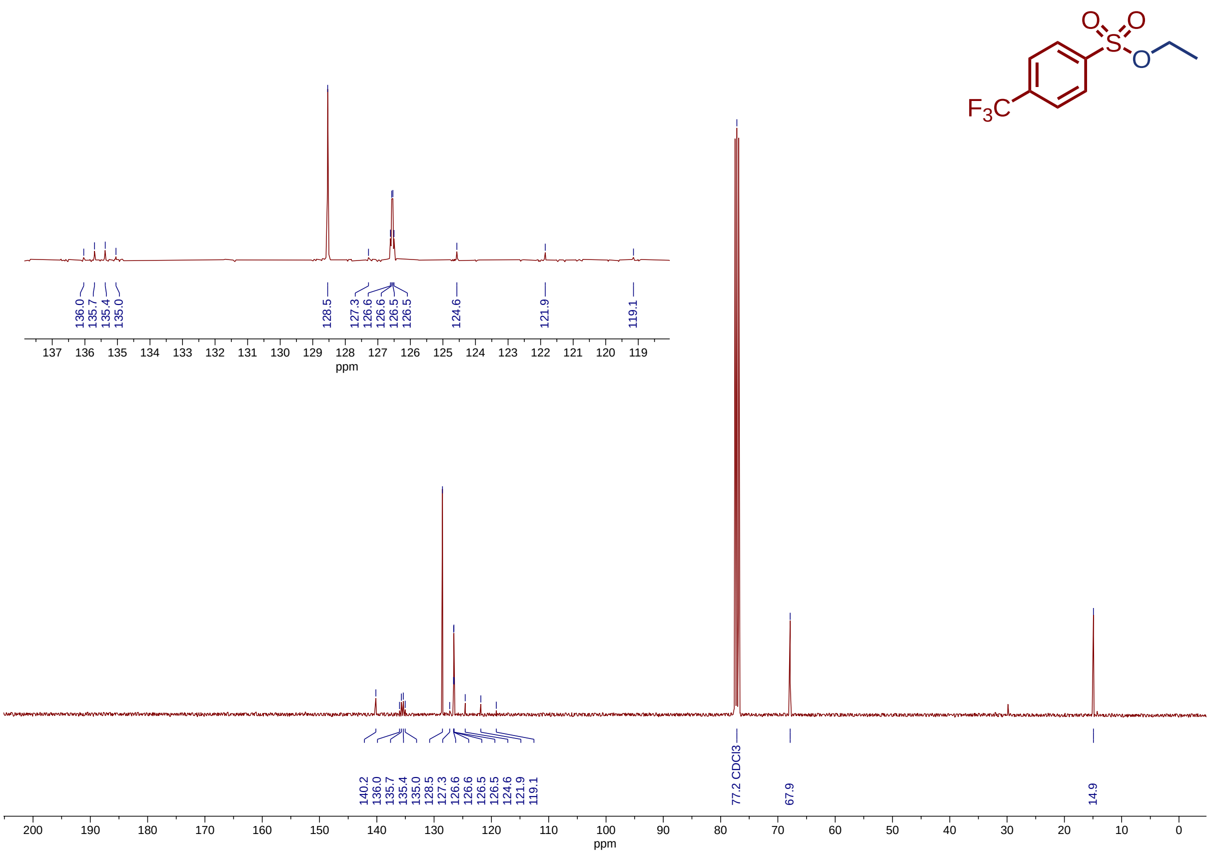
^{19}F NMR Spectrum for Compound **6a** (376 MHz, CDCl$_3$)



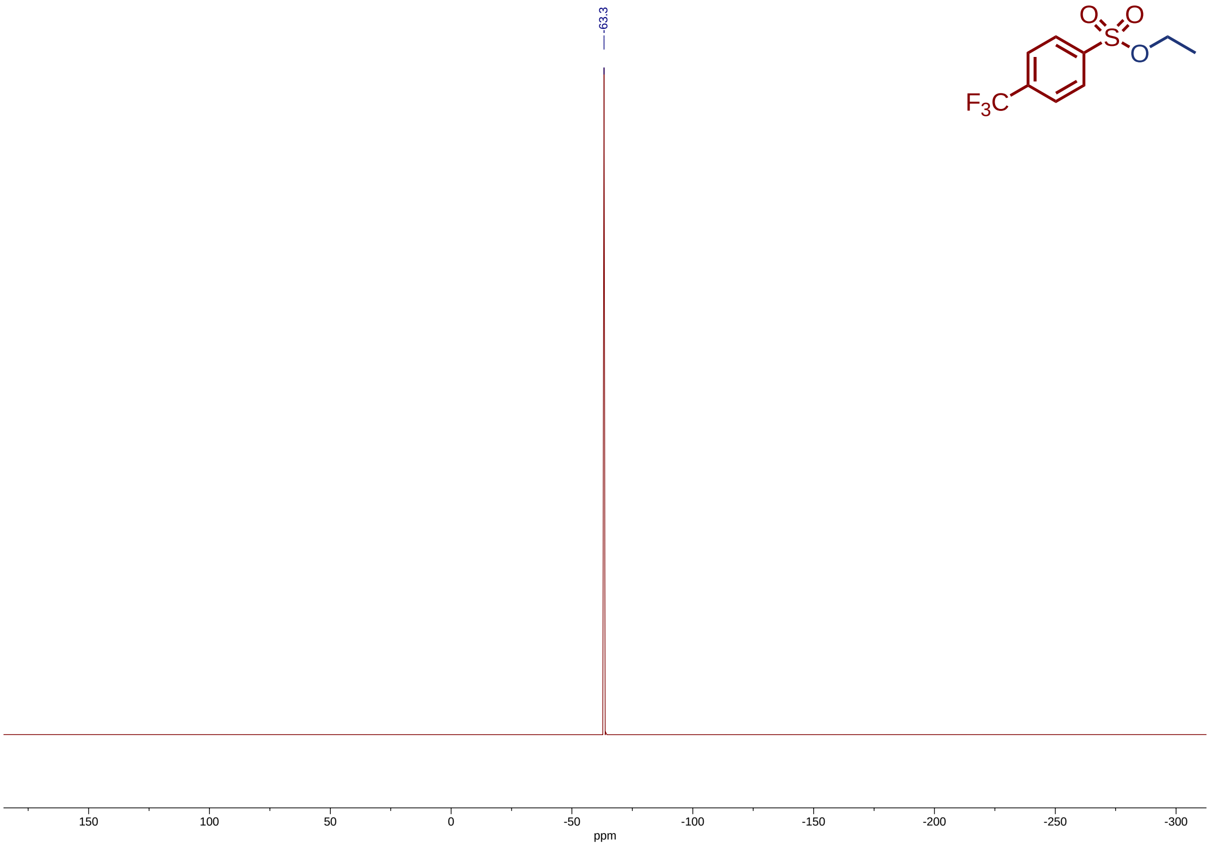
^{1}H NMR Spectrum for Compound **6b** (400 MHz, CDCl$_3$)



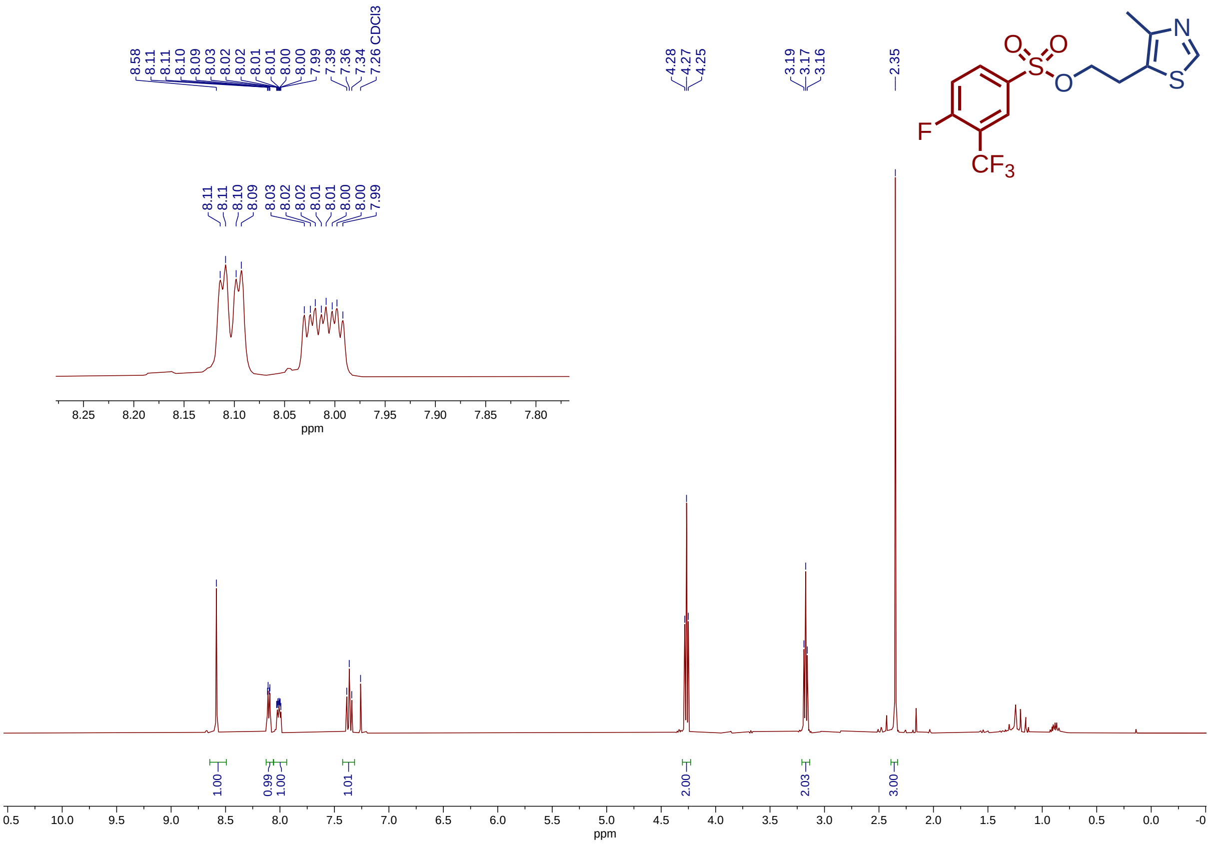
^{13}C NMR Spectrum for Compound **6b** (101 MHz, $CDCl_3$)



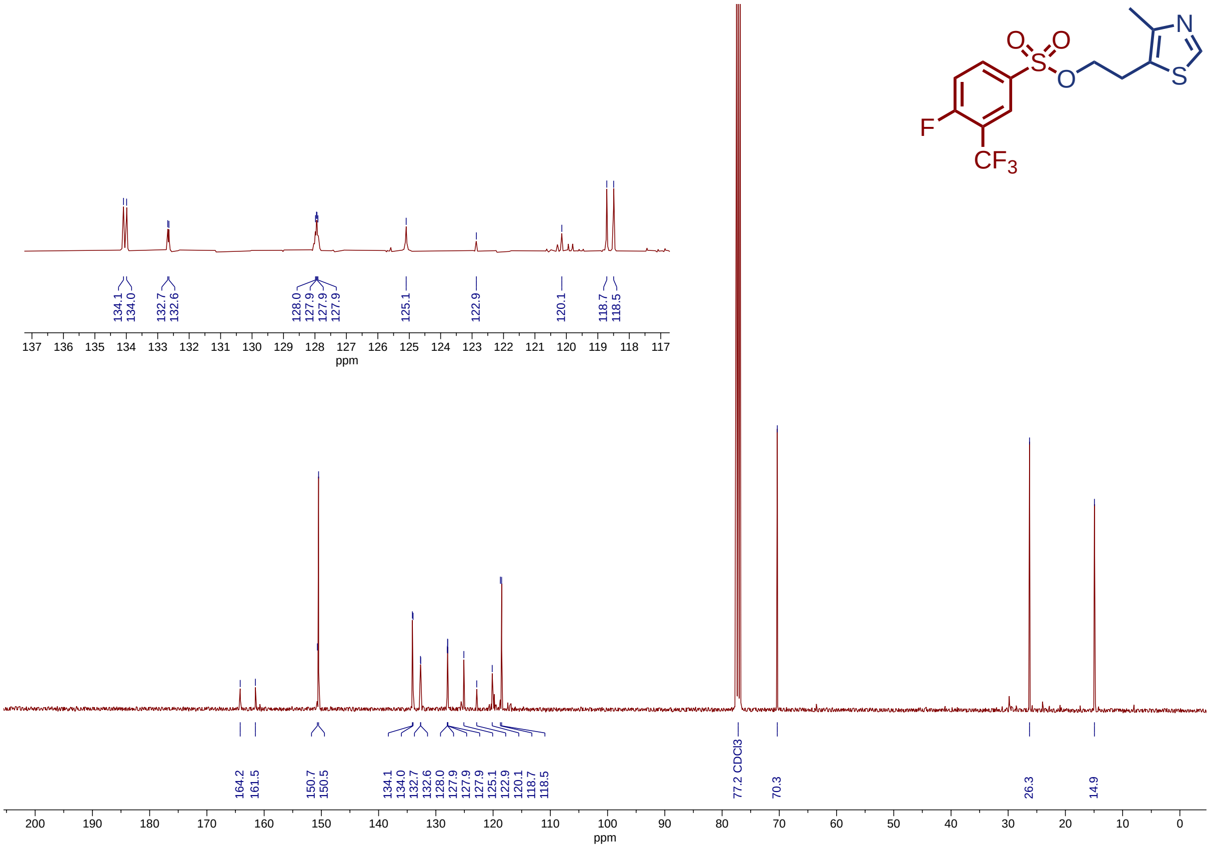
^{19}F NMR Spectrum for Compound **6b** (376 MHz, $CDCl_3$)



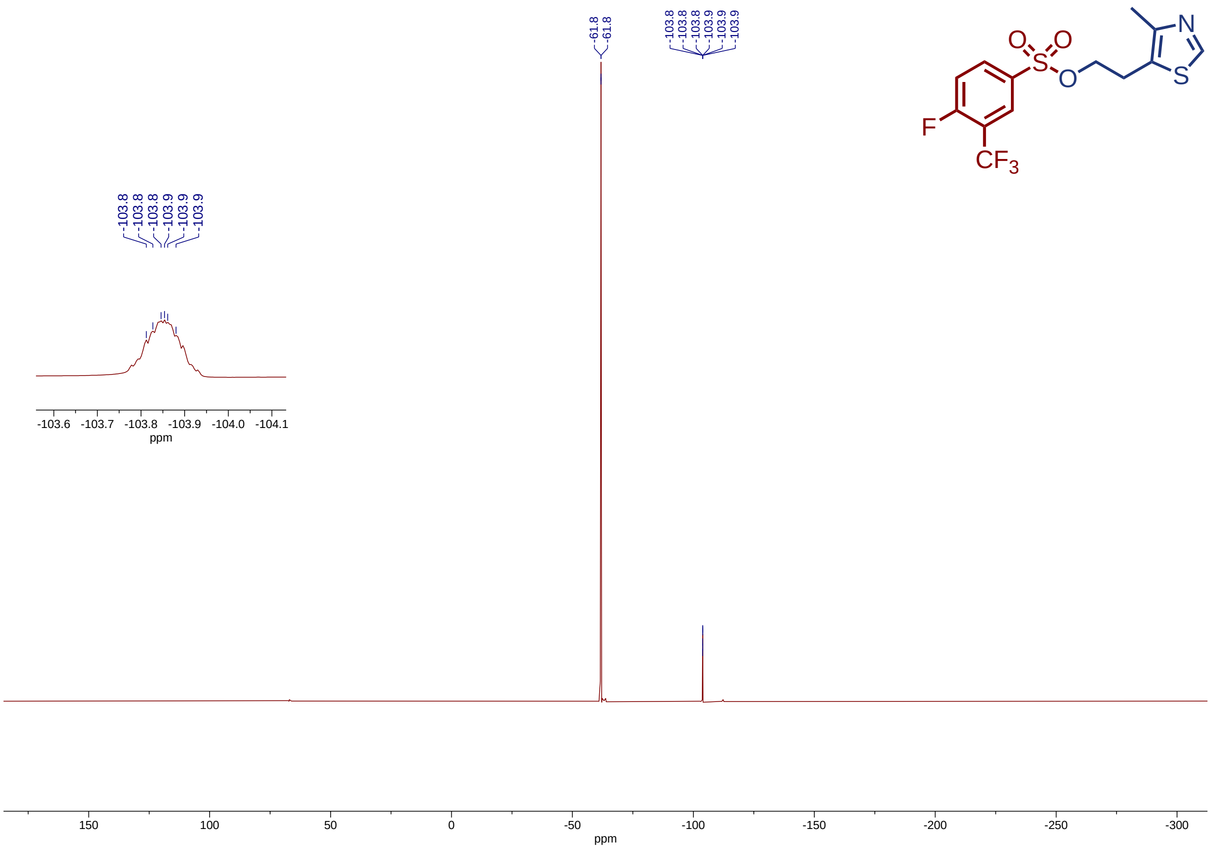
^{1}H NMR Spectrum for Compound **6c** (400 MHz, $CDCl_3$)



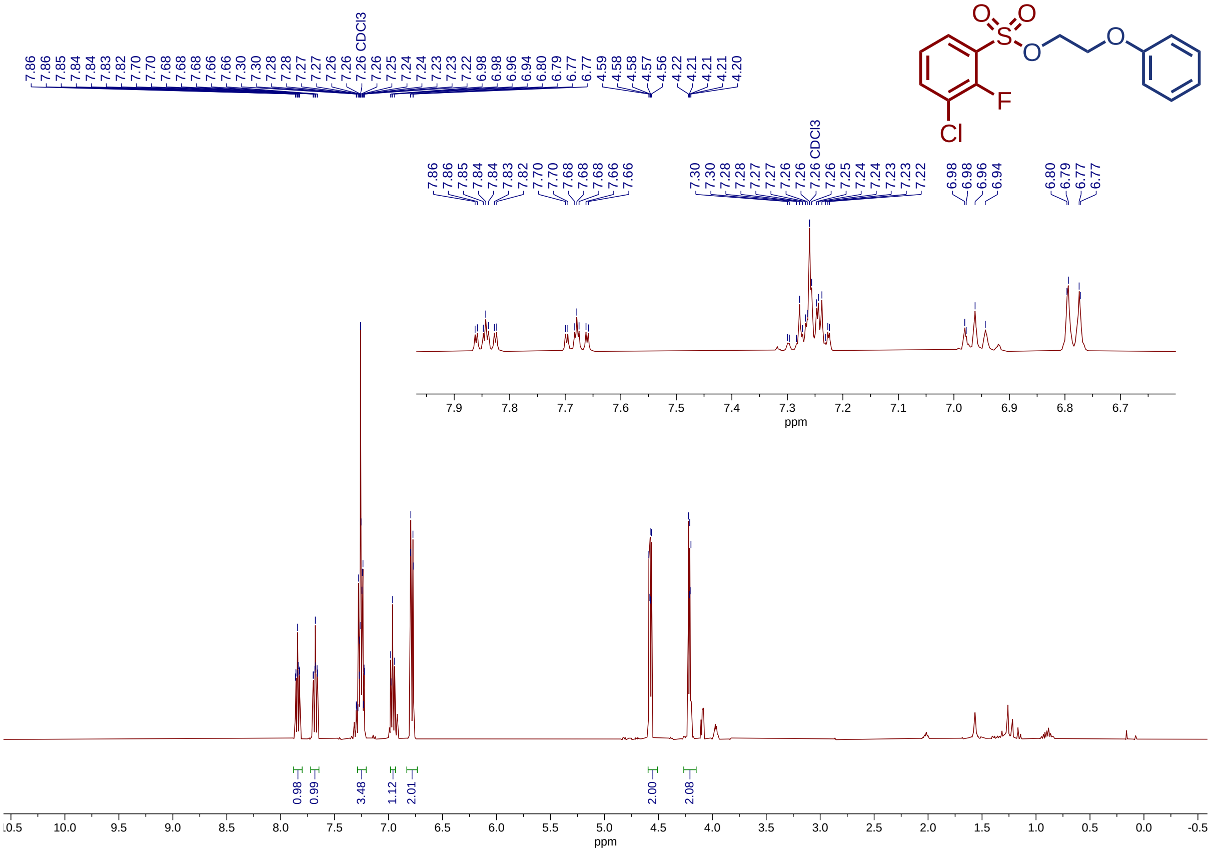
^{13}C NMR Spectrum for Compound **6c** (101 MHz, $CDCl_3$)



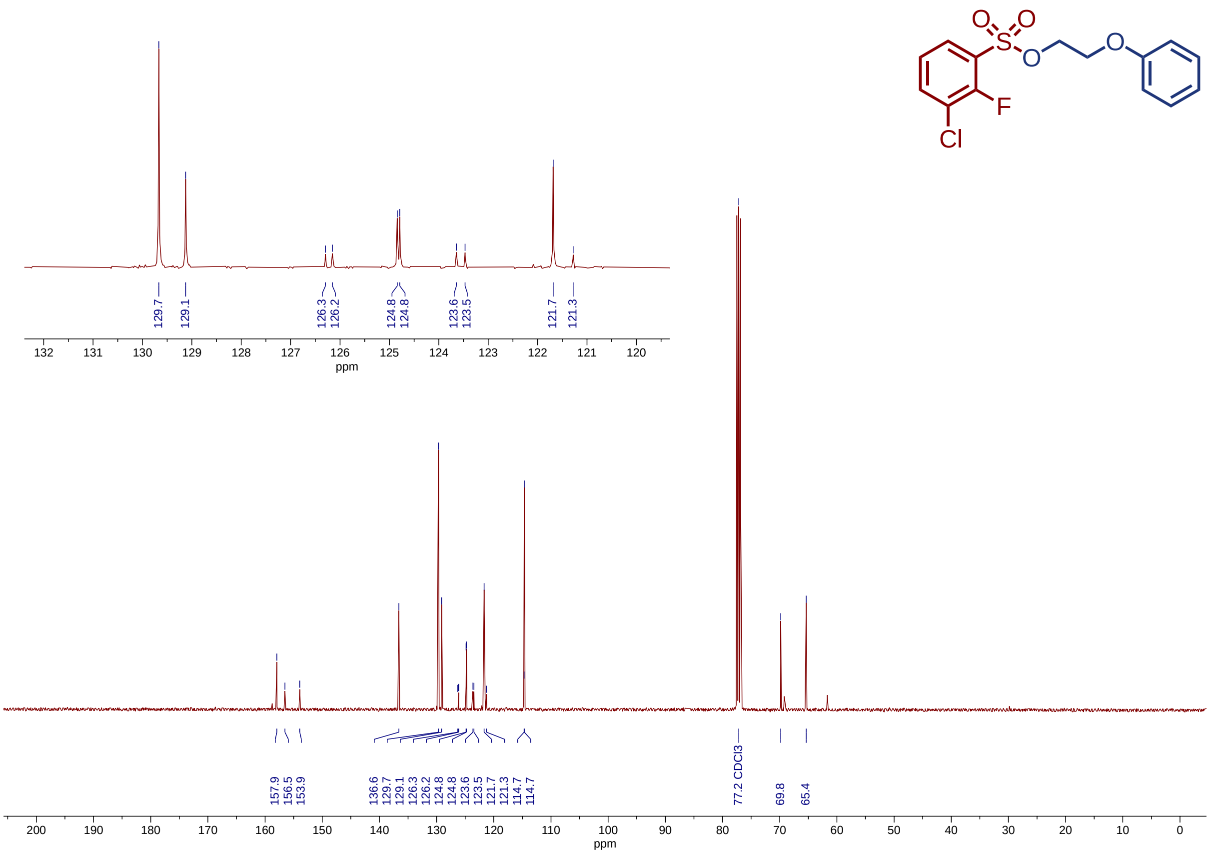
^{19}F NMR Spectrum for Compound **6c** (376 MHz, CDCl$_3$)



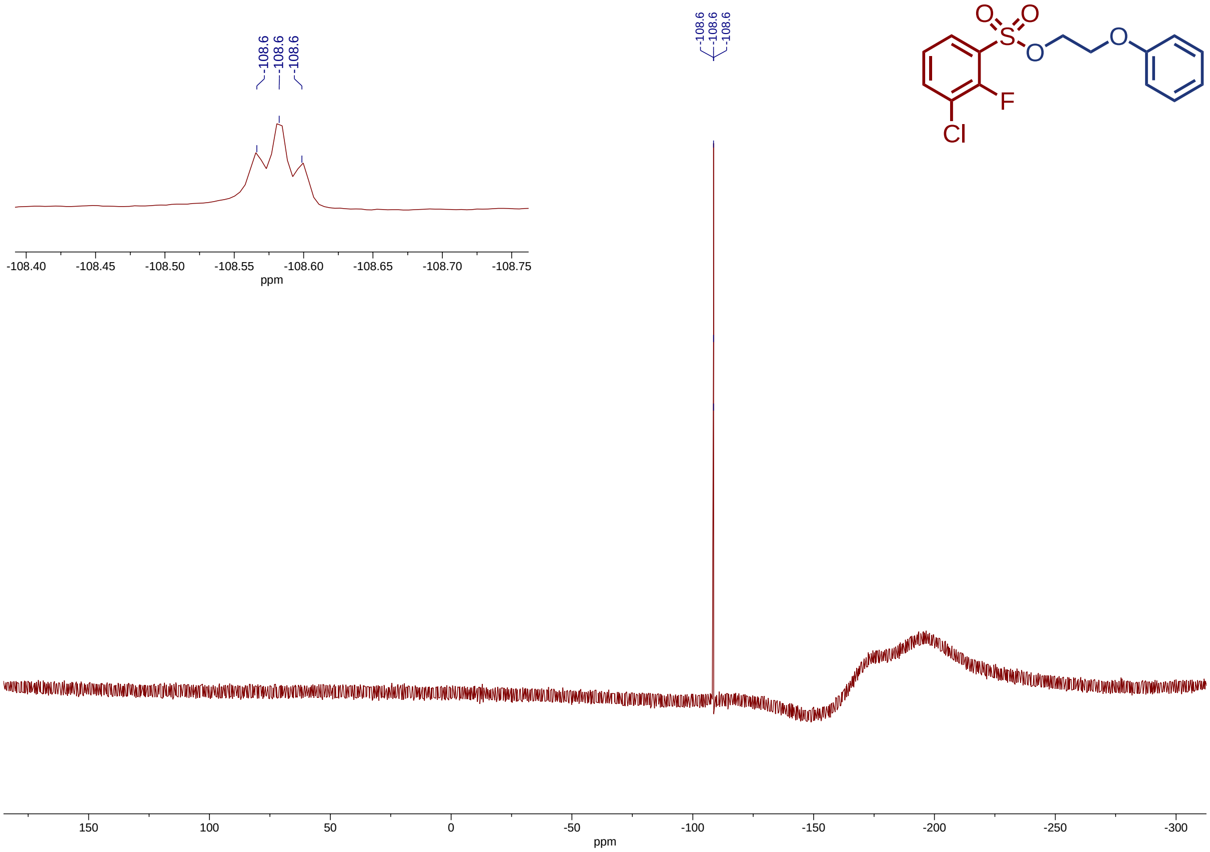
^{1}H NMR Spectrum for Compound **6d** (400 MHz, CDCl$_3$)



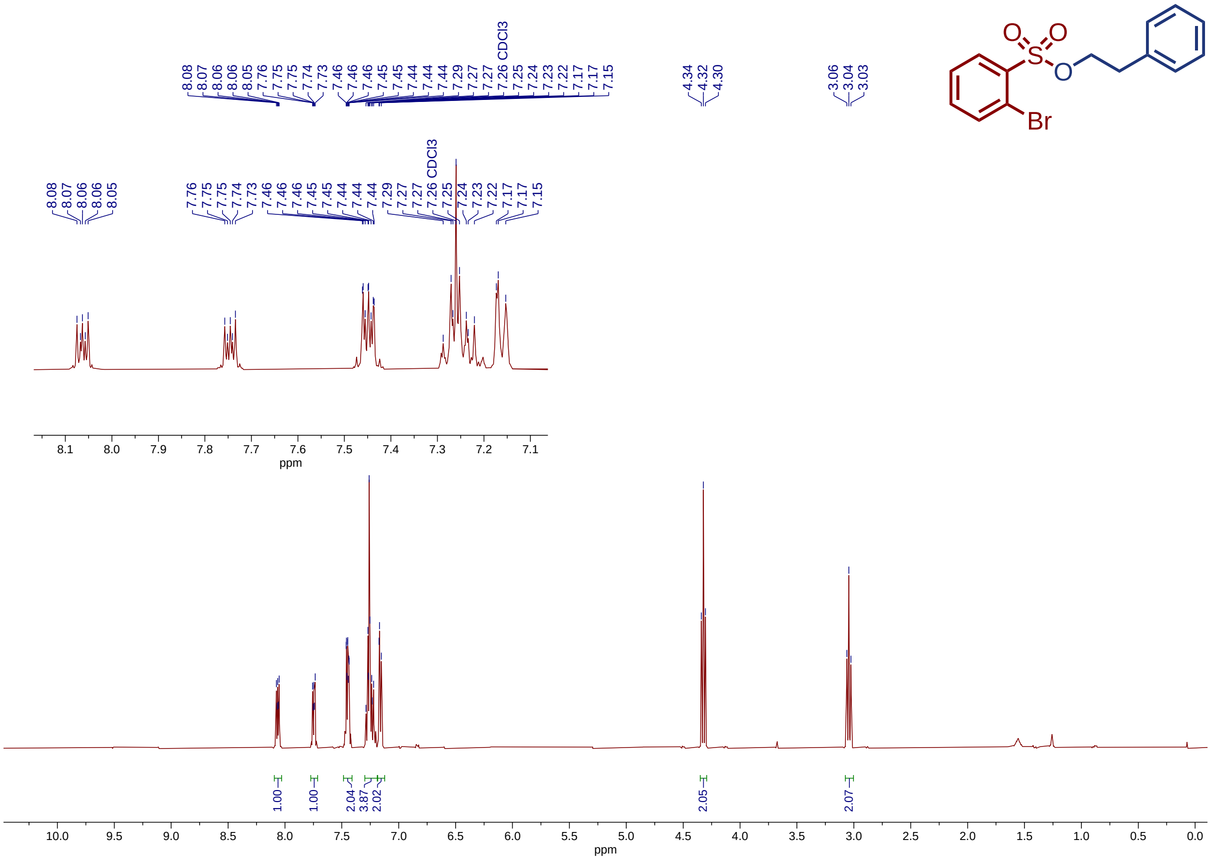
^{13}C NMR Spectrum for Compound **6d** (101 MHz, $CDCl_3$)



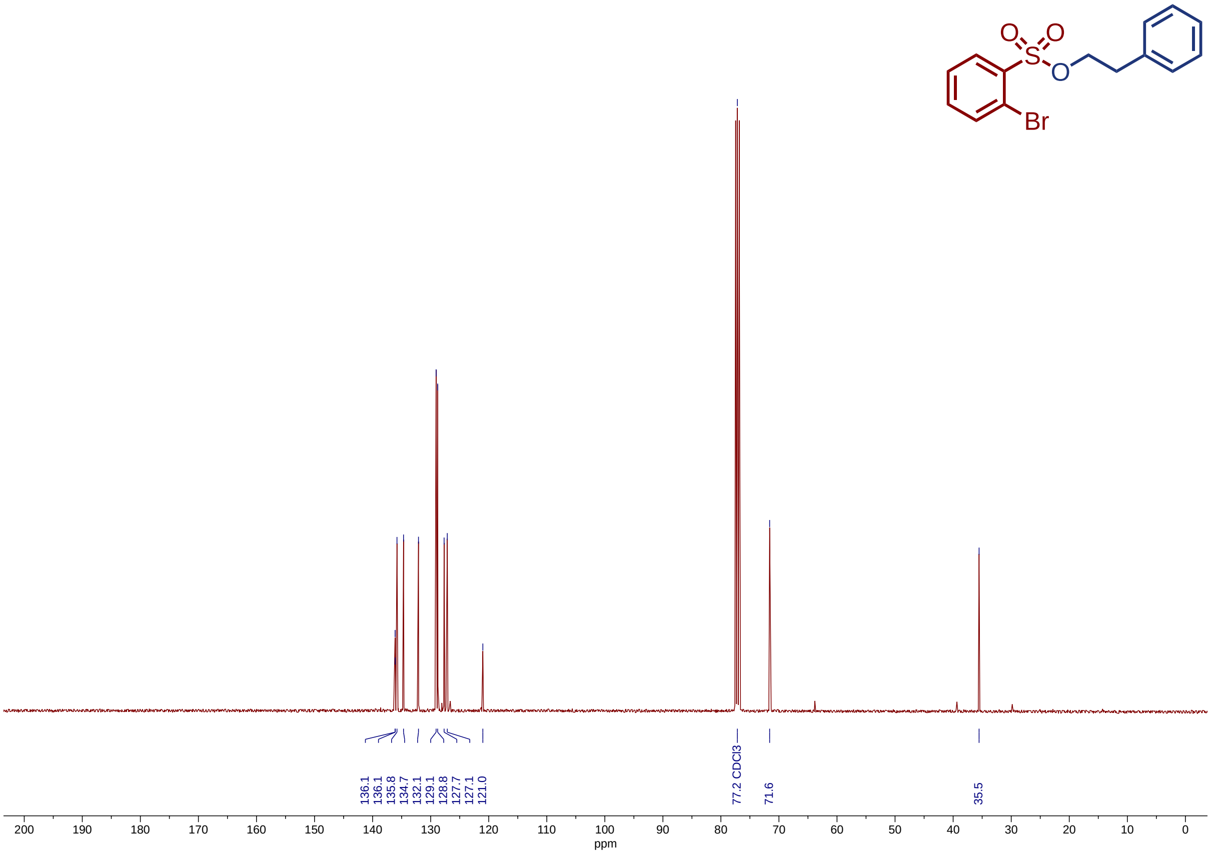
^{19}F NMR Spectrum for Compound **6d** (376 MHz, $CDCl_3$)



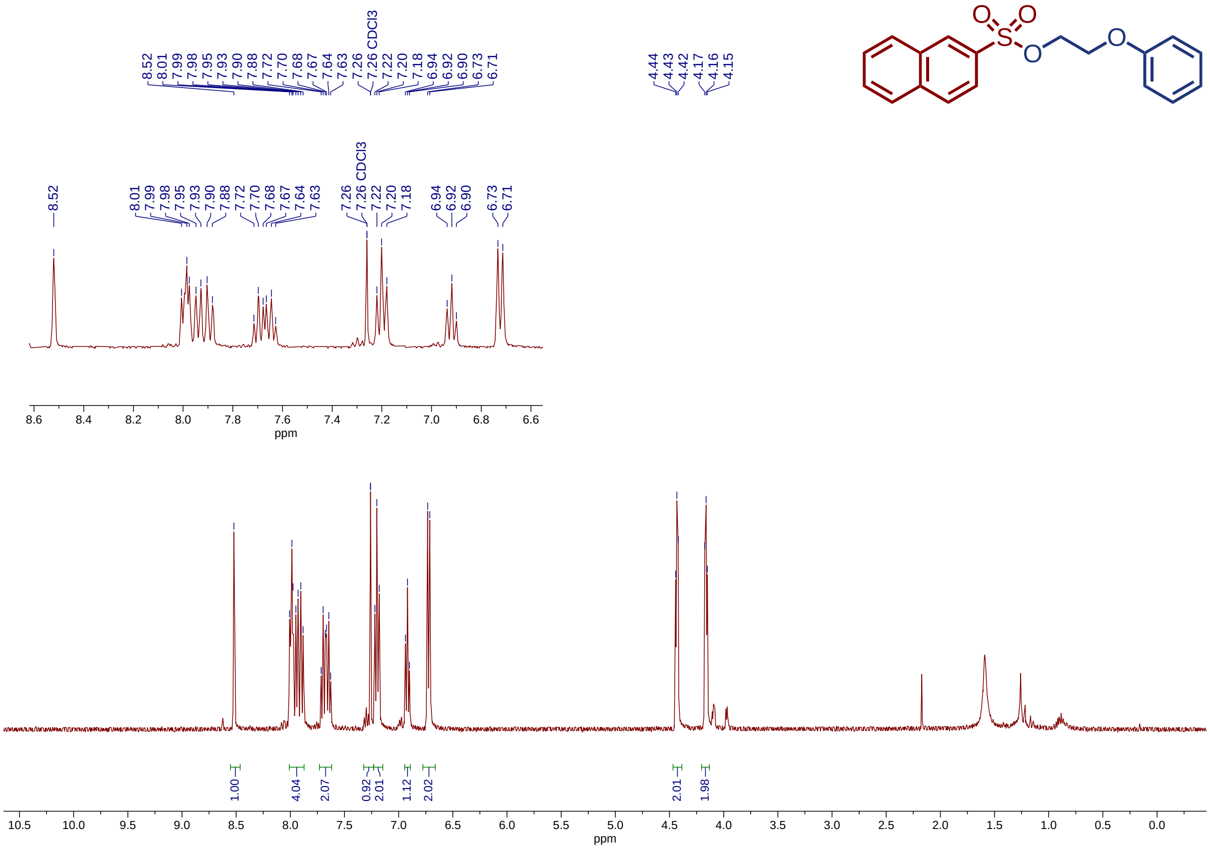
^{1}H NMR Spectrum for Compound **6e** (400 MHz, CDCl$_3$)



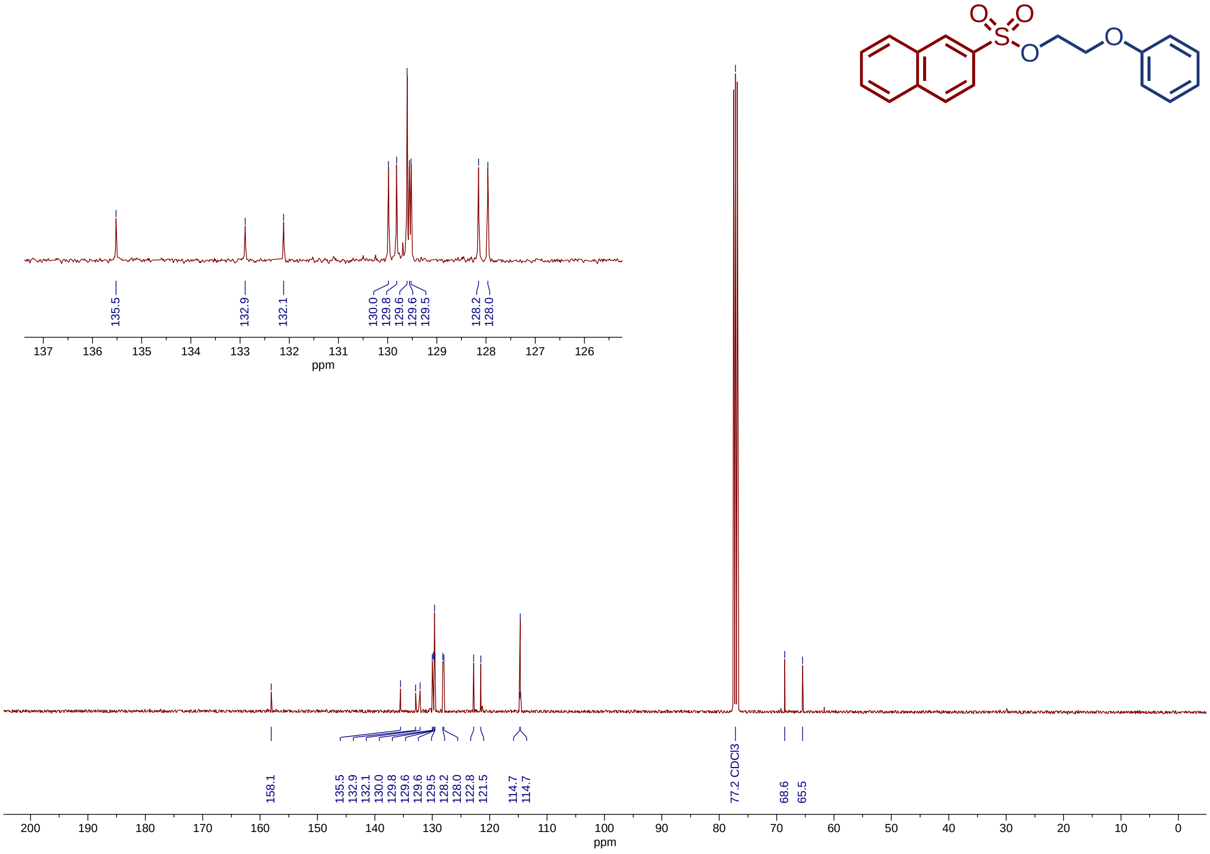
^{13}C NMR Spectrum for Compound **6e** (101 MHz, CDCl$_3$)



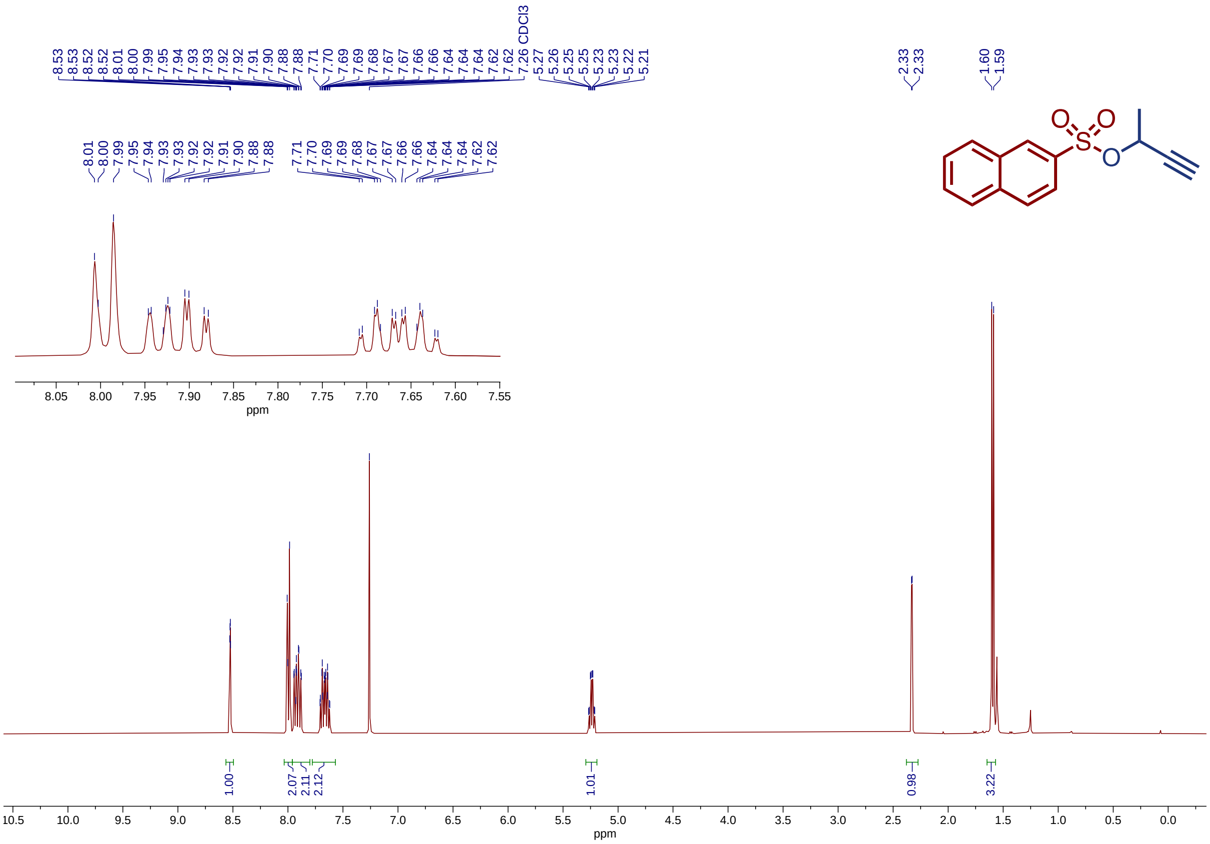
^{1}H NMR Spectrum for Compound **6f** (400 MHz, $CDCl_3$)



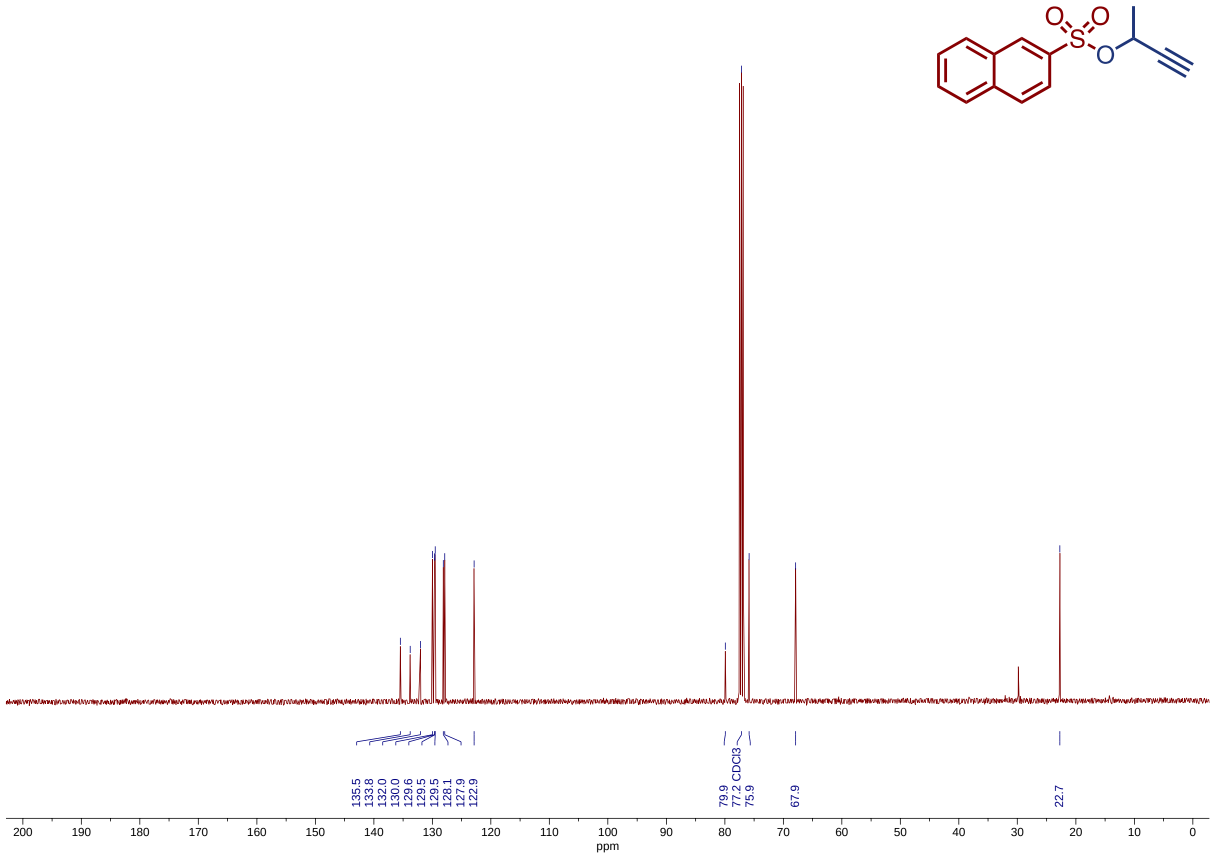
^{13}C NMR Spectrum for Compound **6f** (101 MHz, $CDCl_3$)



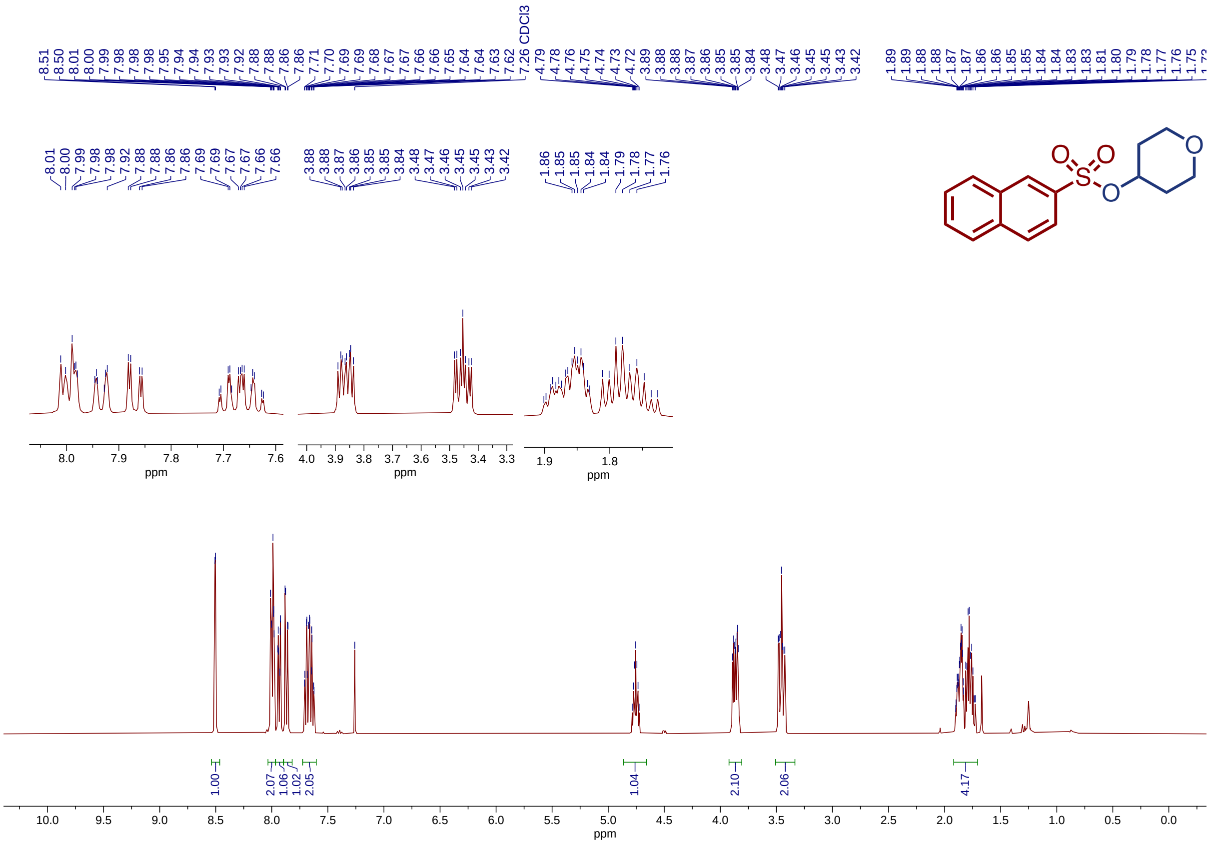
^{1}H NMR Spectrum for Compound **6g** (400 MHz, $CDCl_3$)



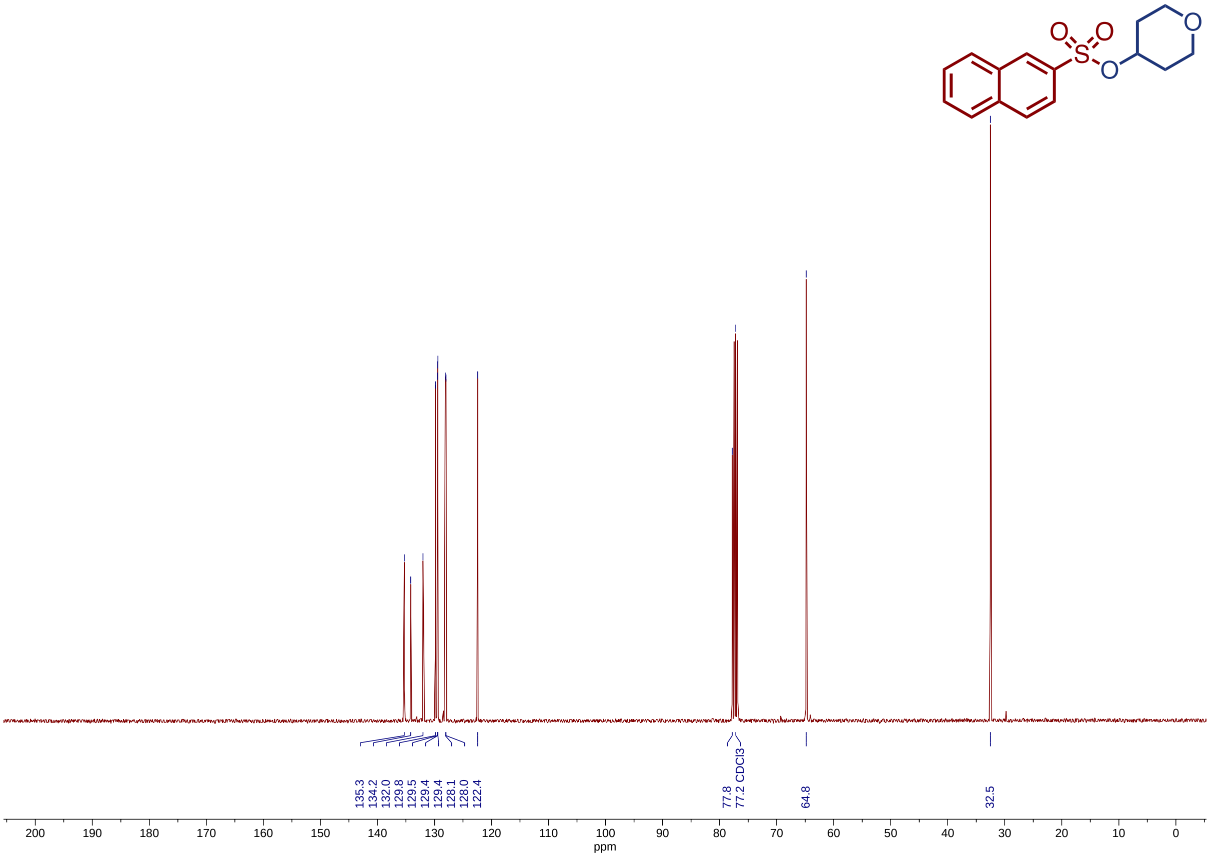
^{13}C NMR Spectrum for Compound **6g** (101 MHz, $CDCl_3$)



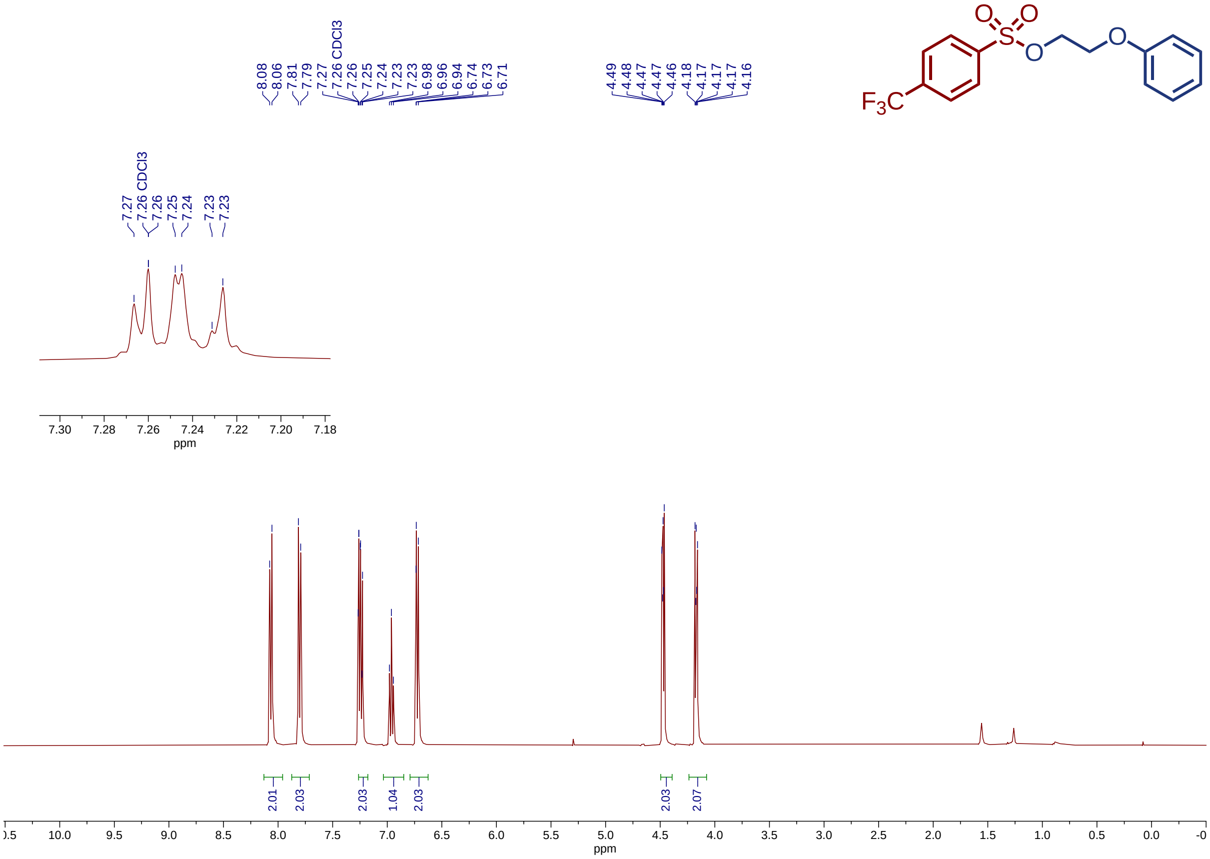
^{1}H NMR Spectrum for Compound **6h** (400 MHz, $CDCl_3$)



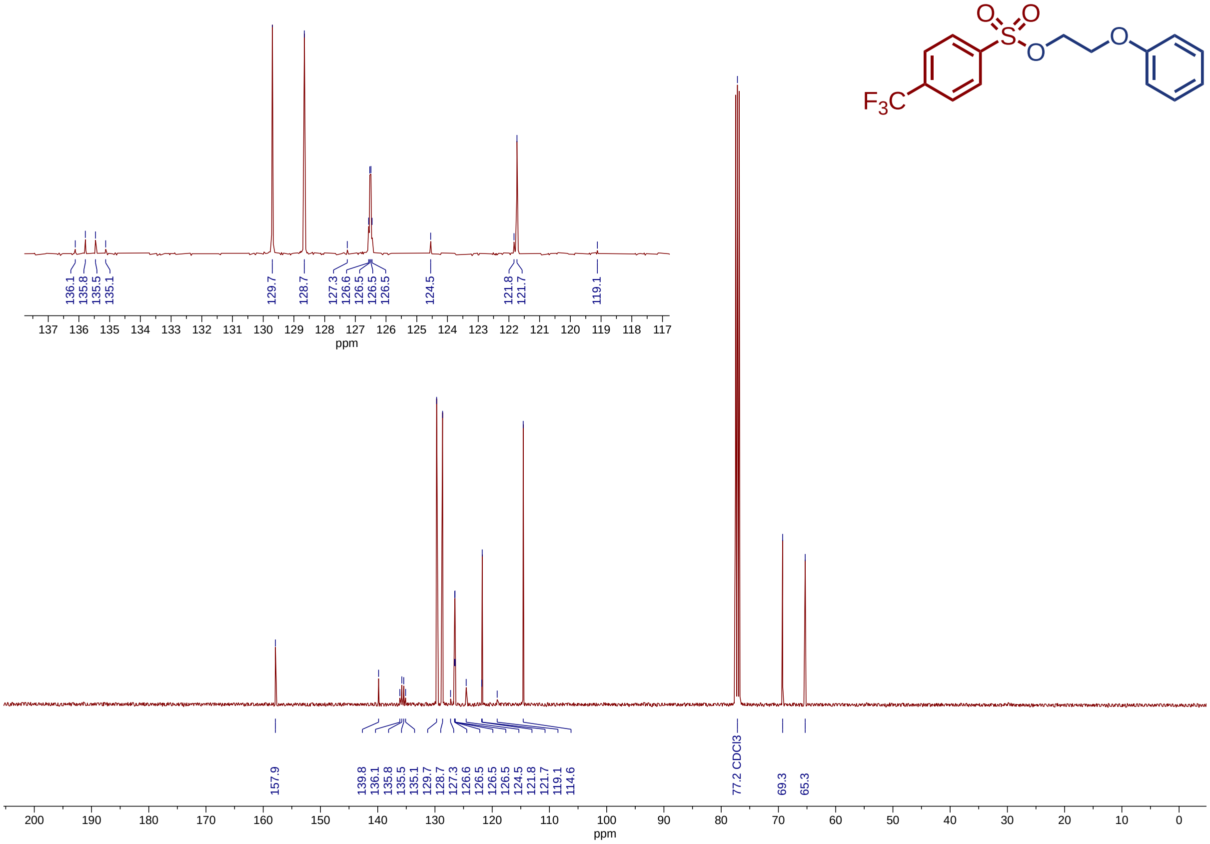
^{13}C NMR Spectrum for Compound **6h** (101 MHz, $CDCl_3$)



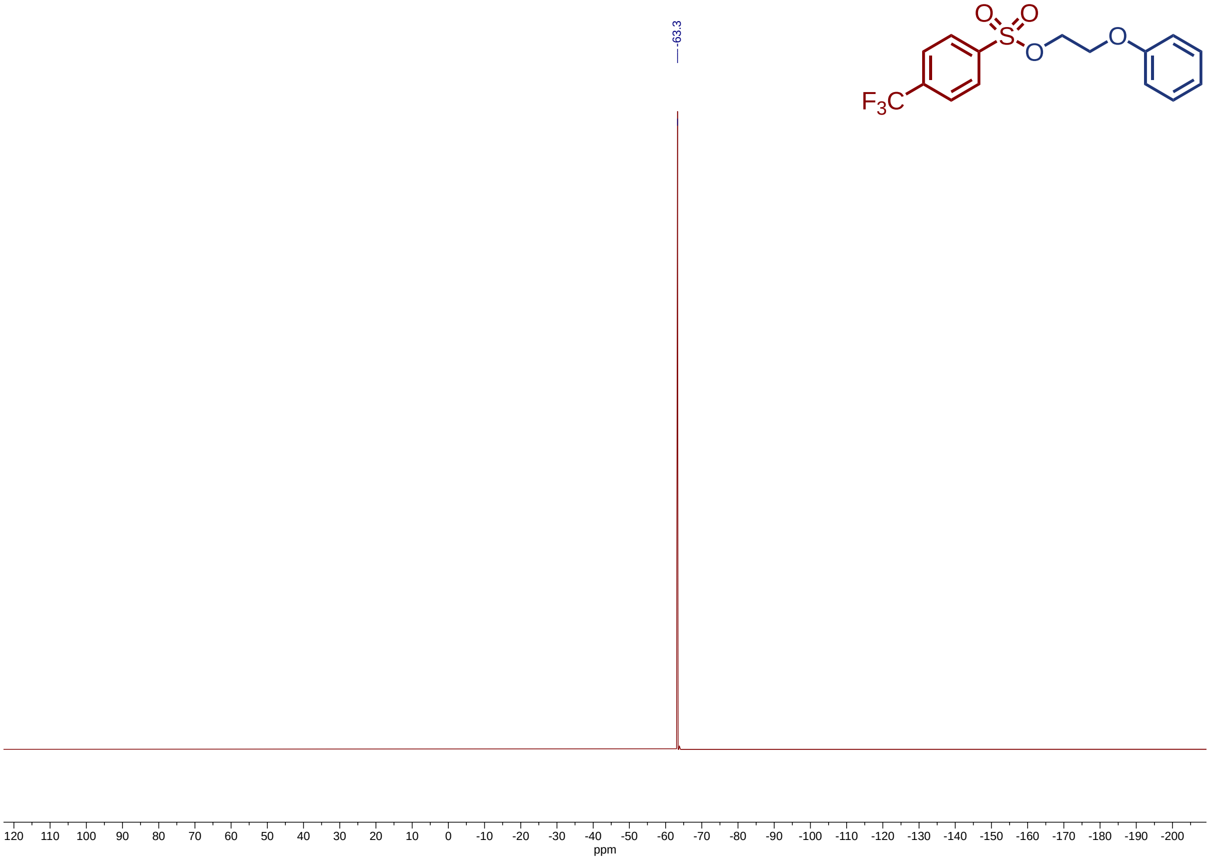
^{1}H NMR Spectrum for Compound **6i** (400 MHz, $CDCl_3$



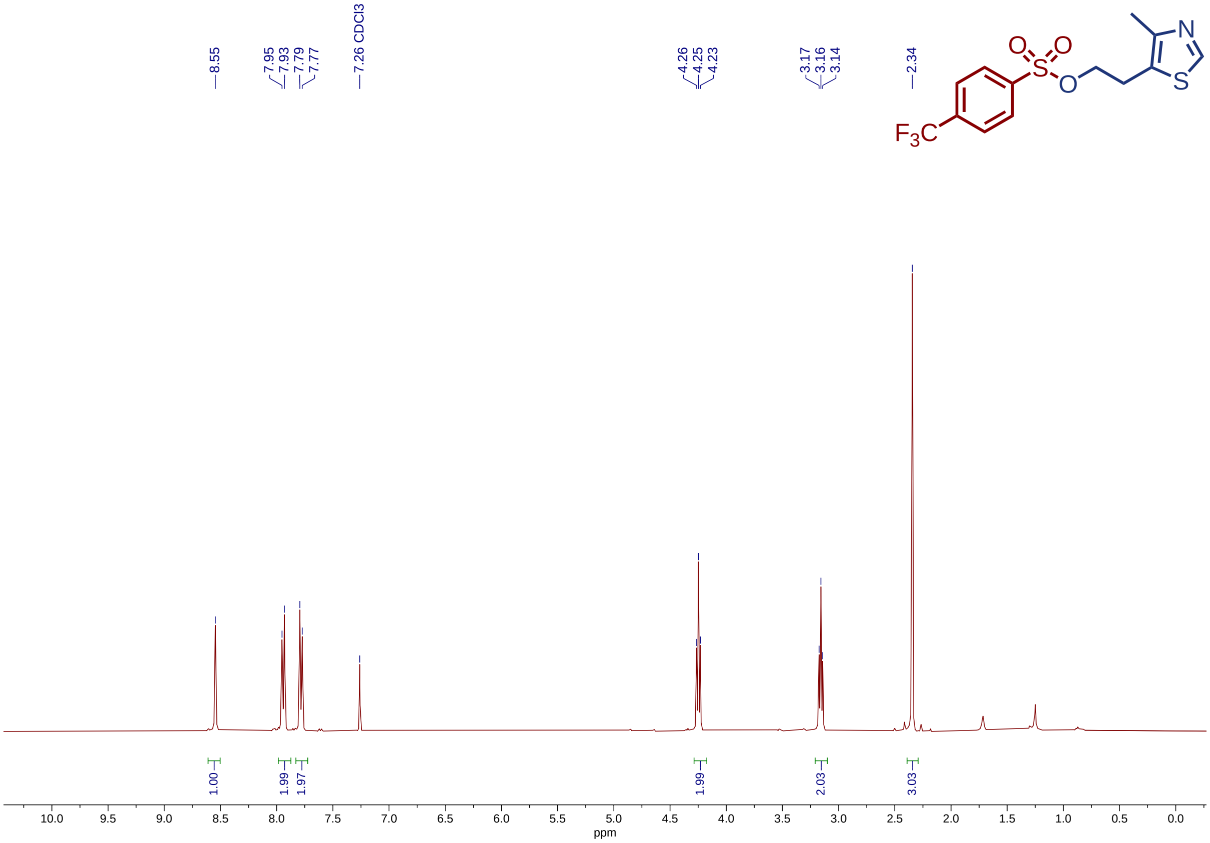
^{13}C NMR Spectrum for Compound **6i** (101 MHz, $CDCl_3$)



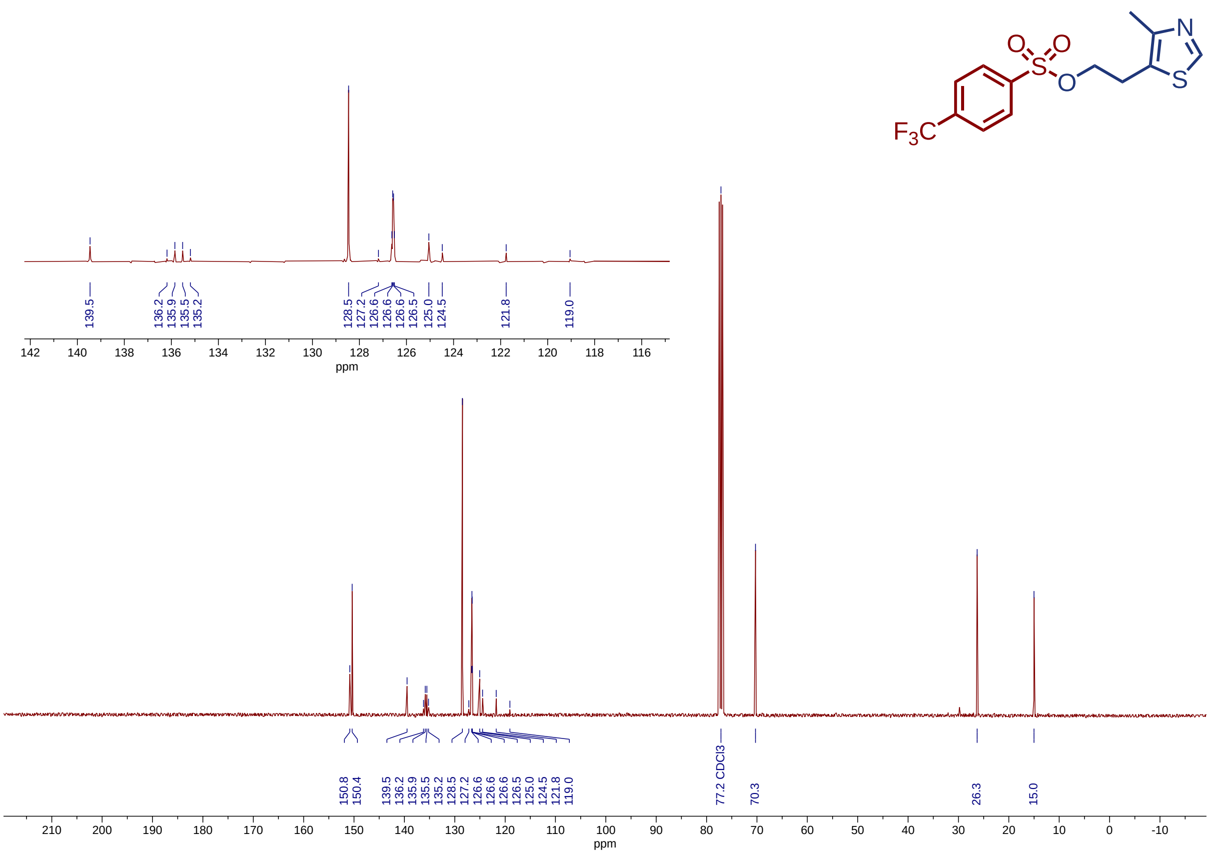
^{19}F NMR Spectrum for Compound **6i** (376 MHz, $CDCl_3$)



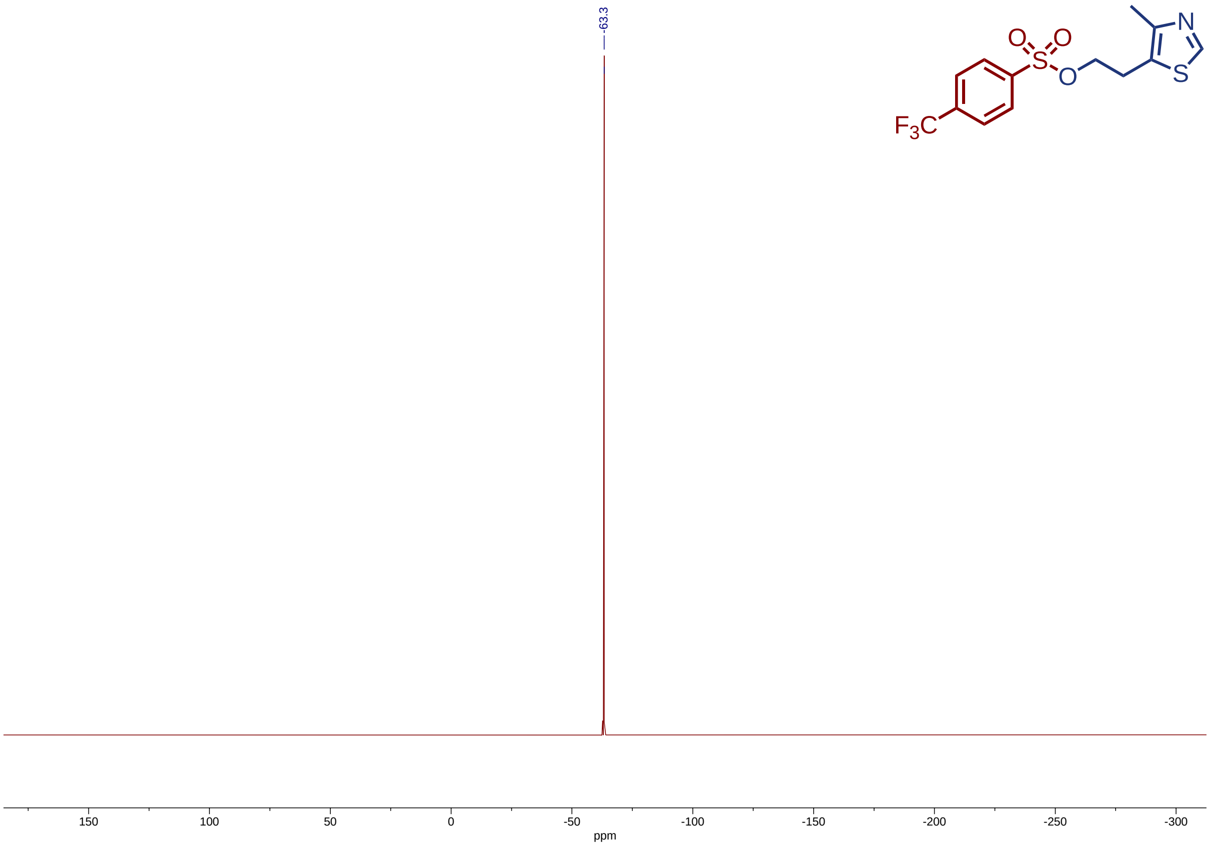
^{1}H NMR Spectrum for Compound **6j** (400 MHz, $CDCl_3$)



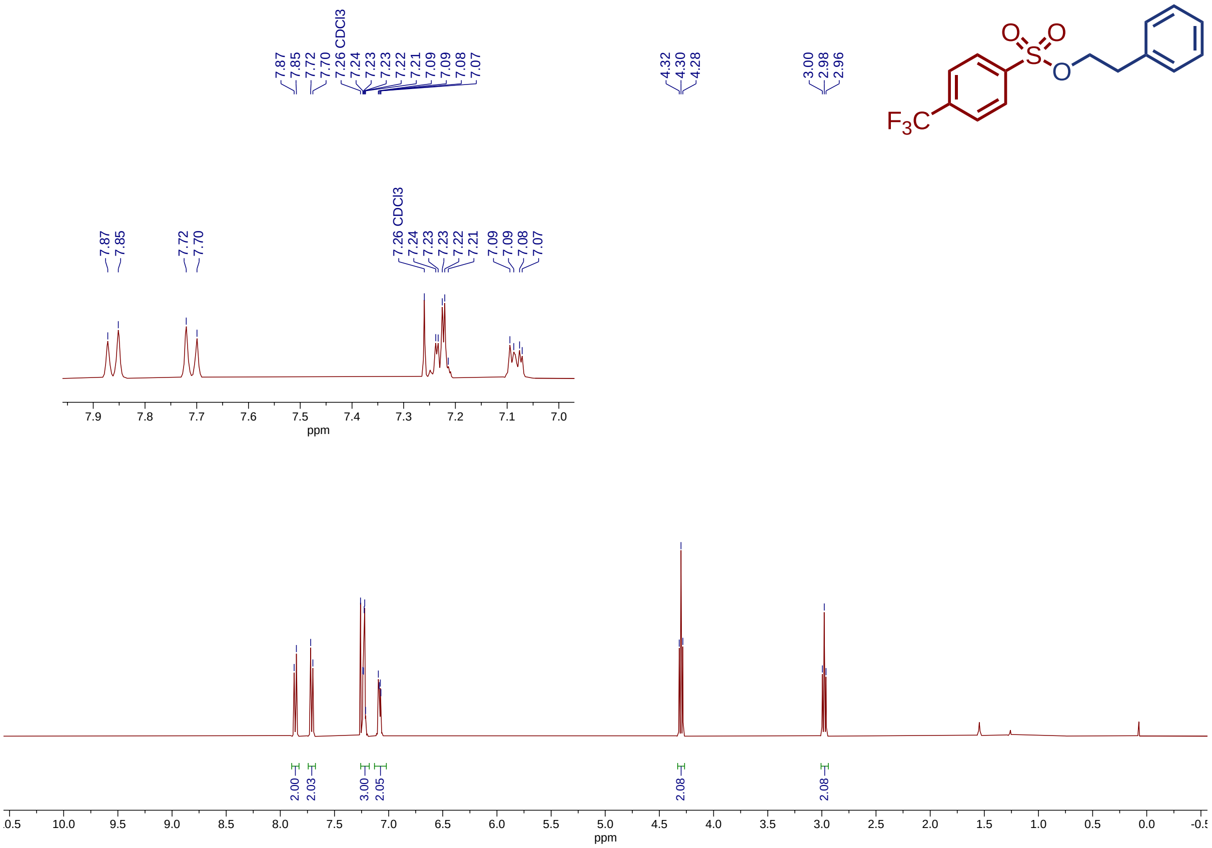
^{13}C NMR Spectrum for Compound **6j** (101 MHz, $CDCl_3$)



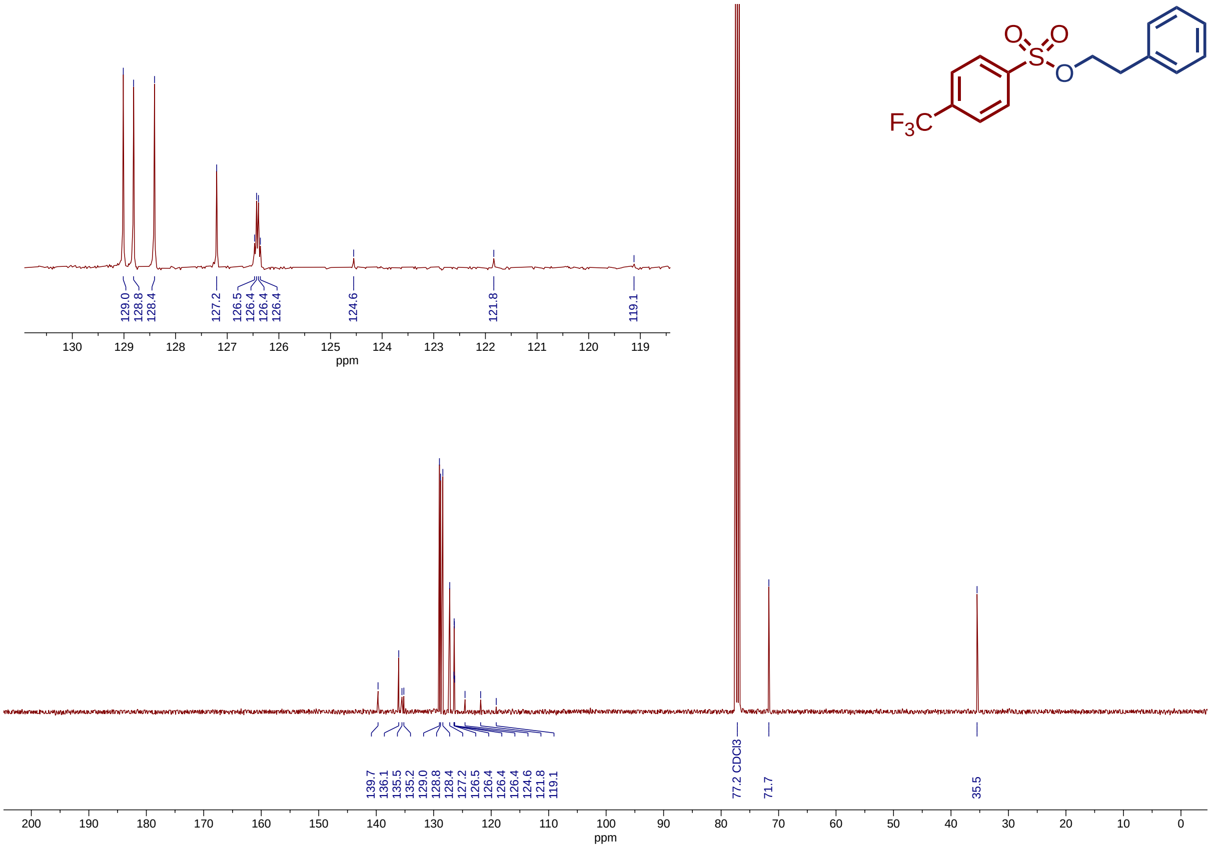
^{19}F NMR Spectrum for Compound **6j** (376 MHz, $CDCl_3$)



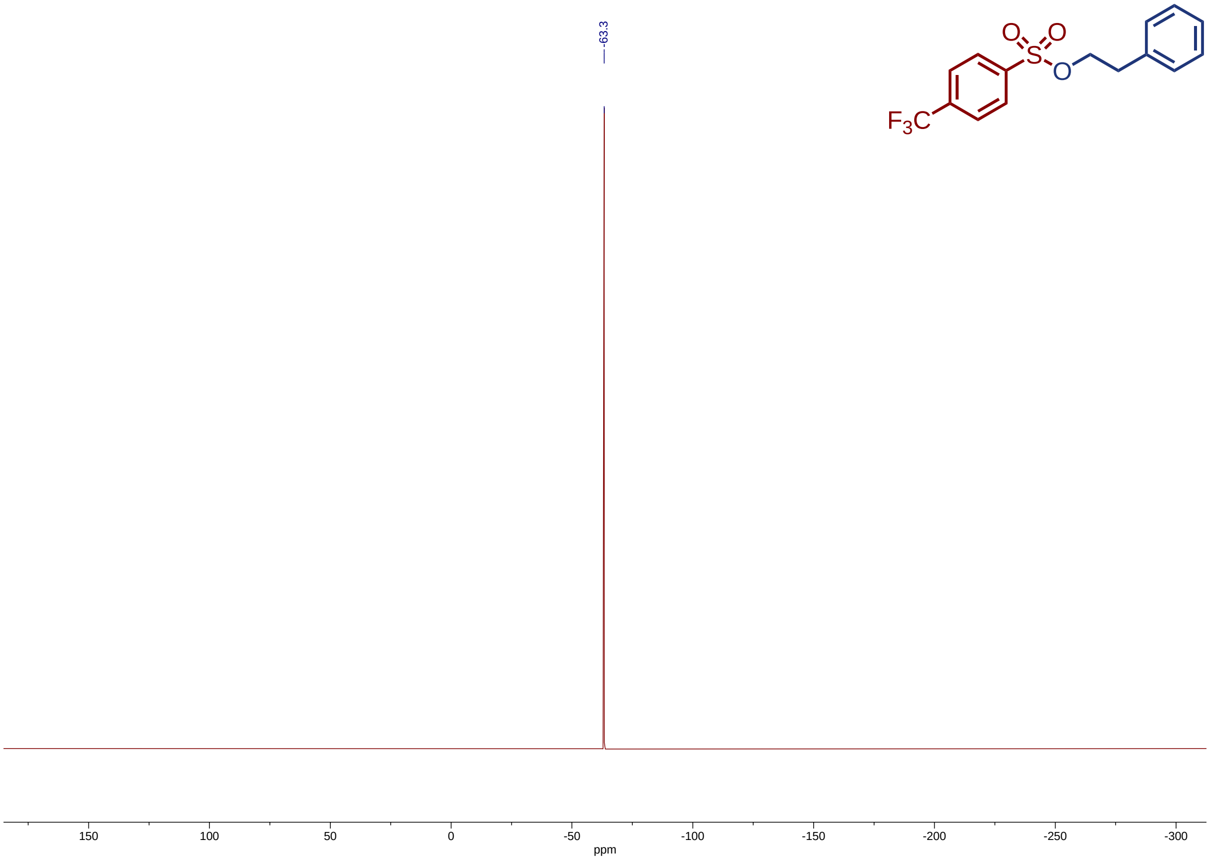
^{1}H NMR Spectrum for Compound **6k** (400 MHz, $CDCl_3$)



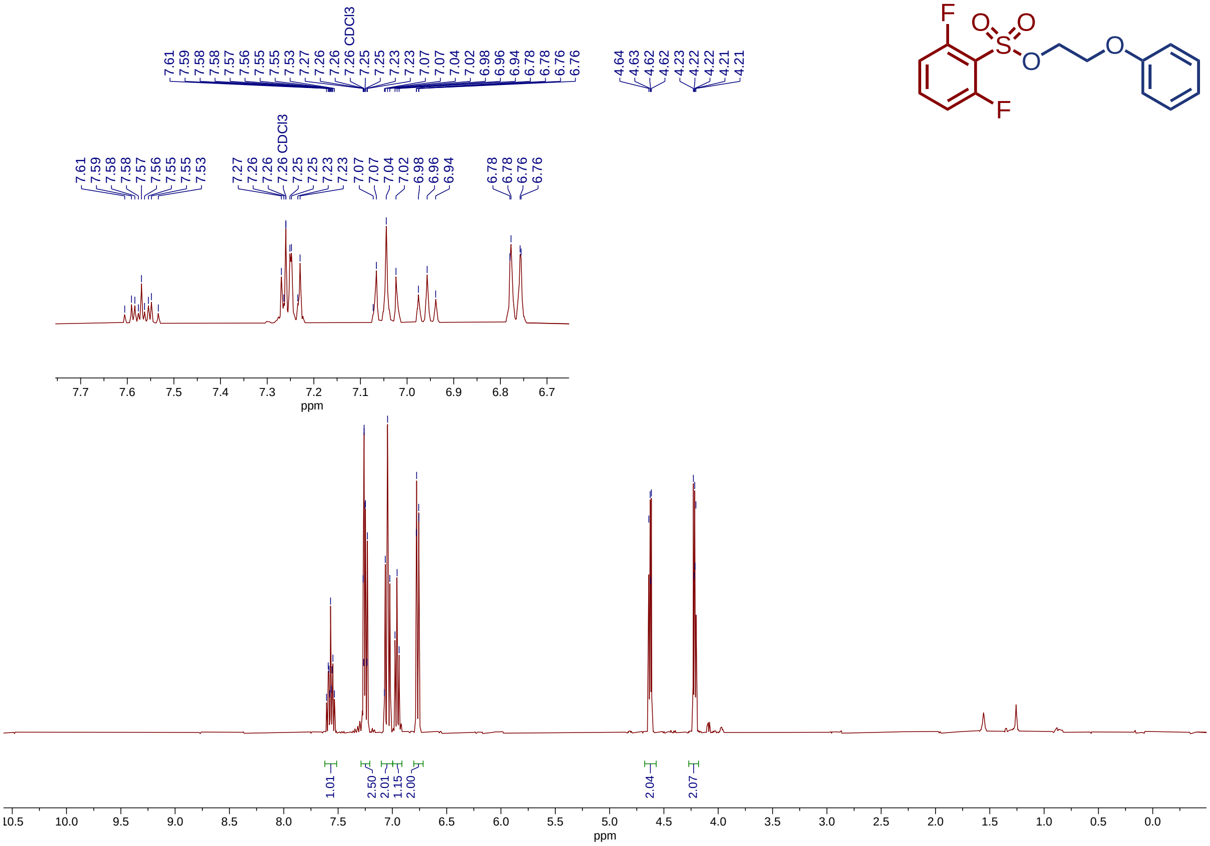
^{13}C NMR Spectrum for Compound **6k** (101 MHz, $CDCl_3$)



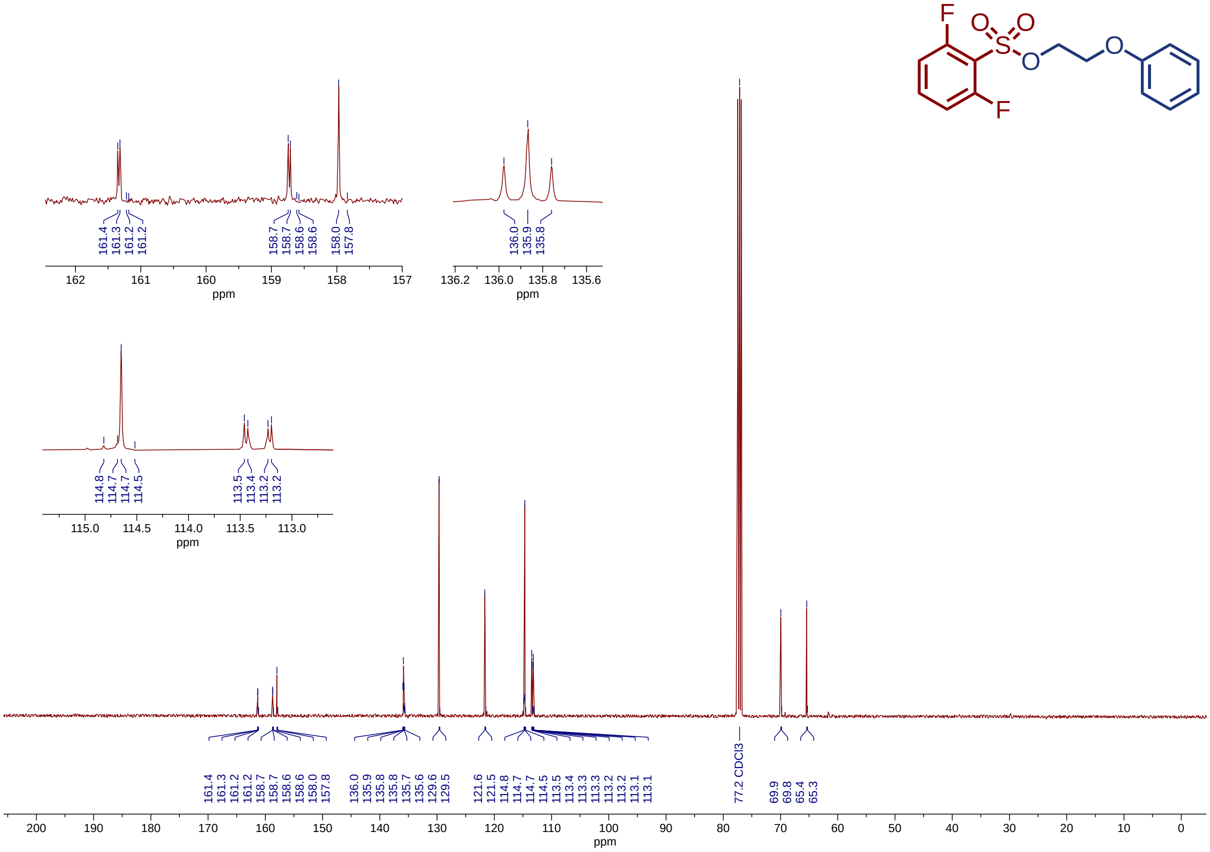
^{19}F NMR Spectrum for Compound **6k** (376 MHz, $CDCl_3$)



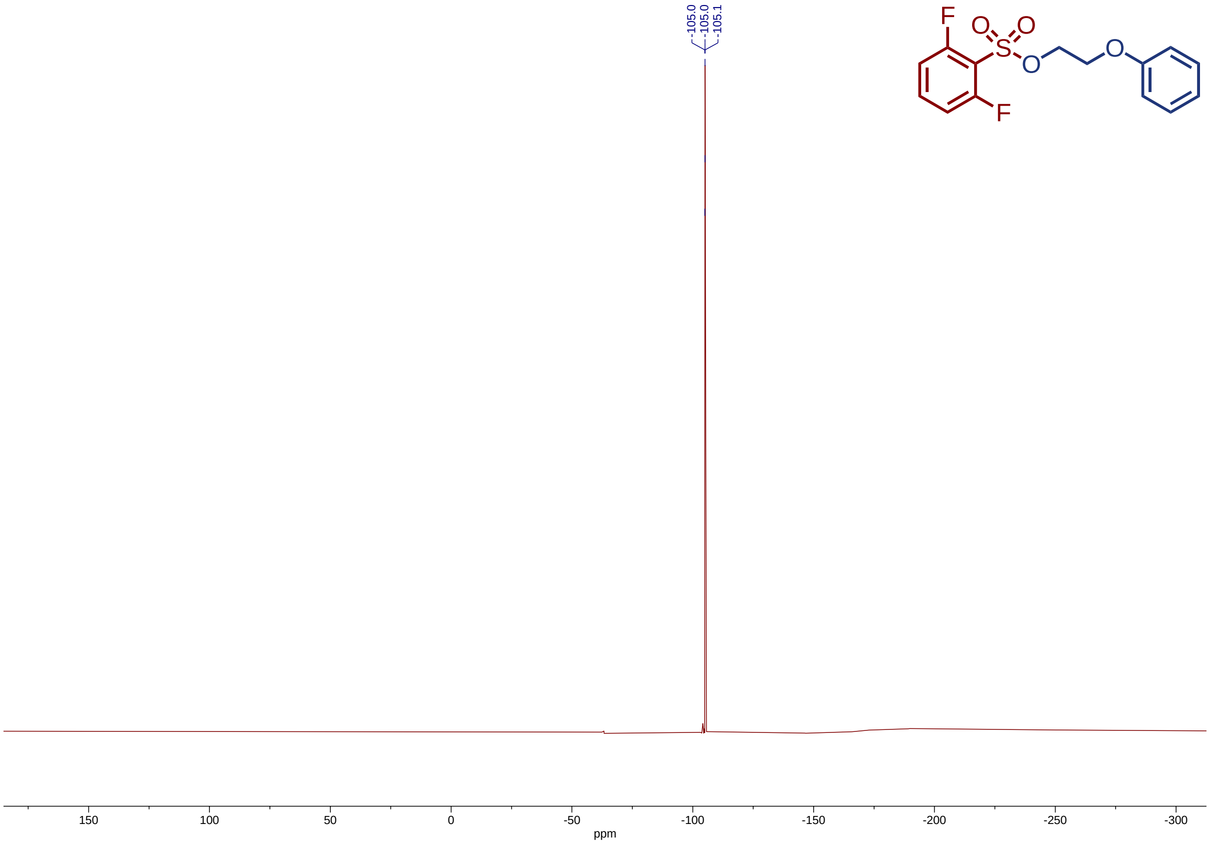
^{1}H NMR Spectrum for Compound **6l** (400 MHz, $CDCl_3$)



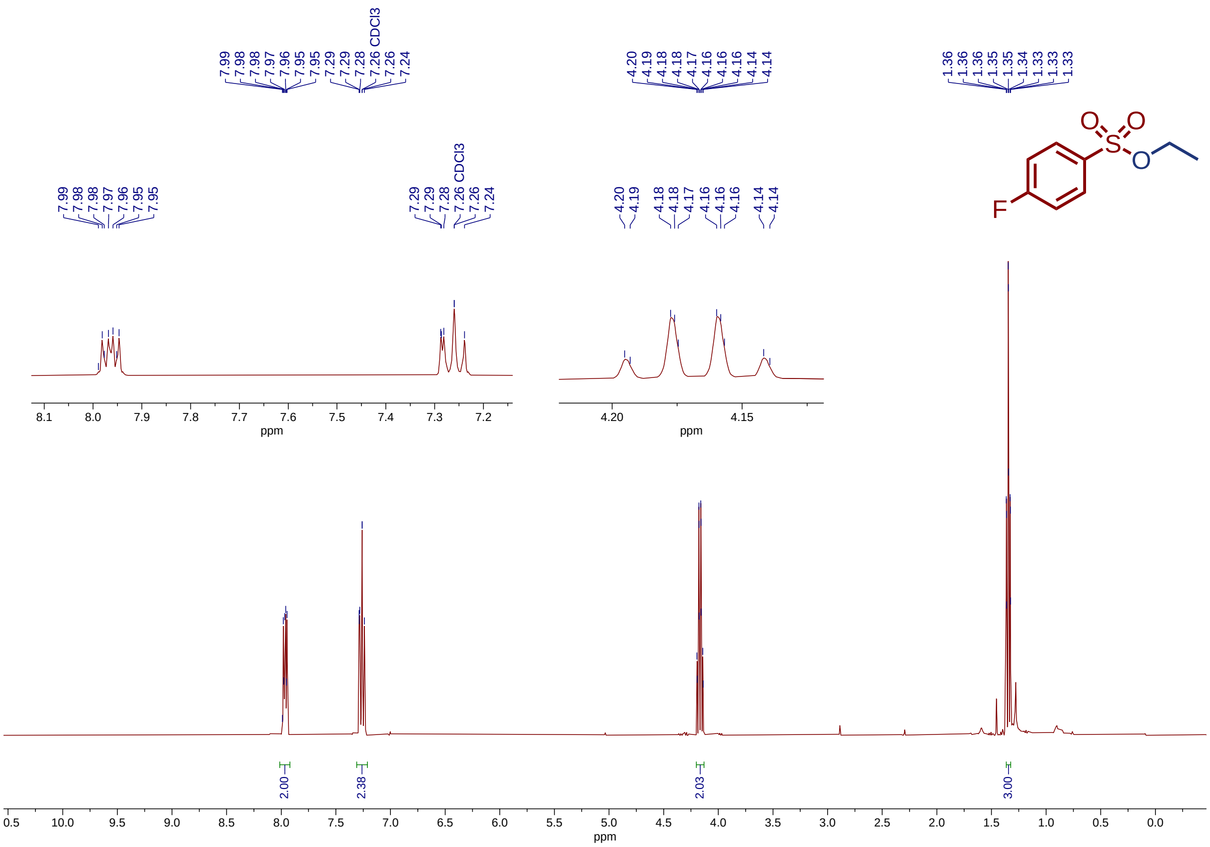
^{13}C NMR Spectrum for Compound **6l** (101 MHz, CDCl$_3$)



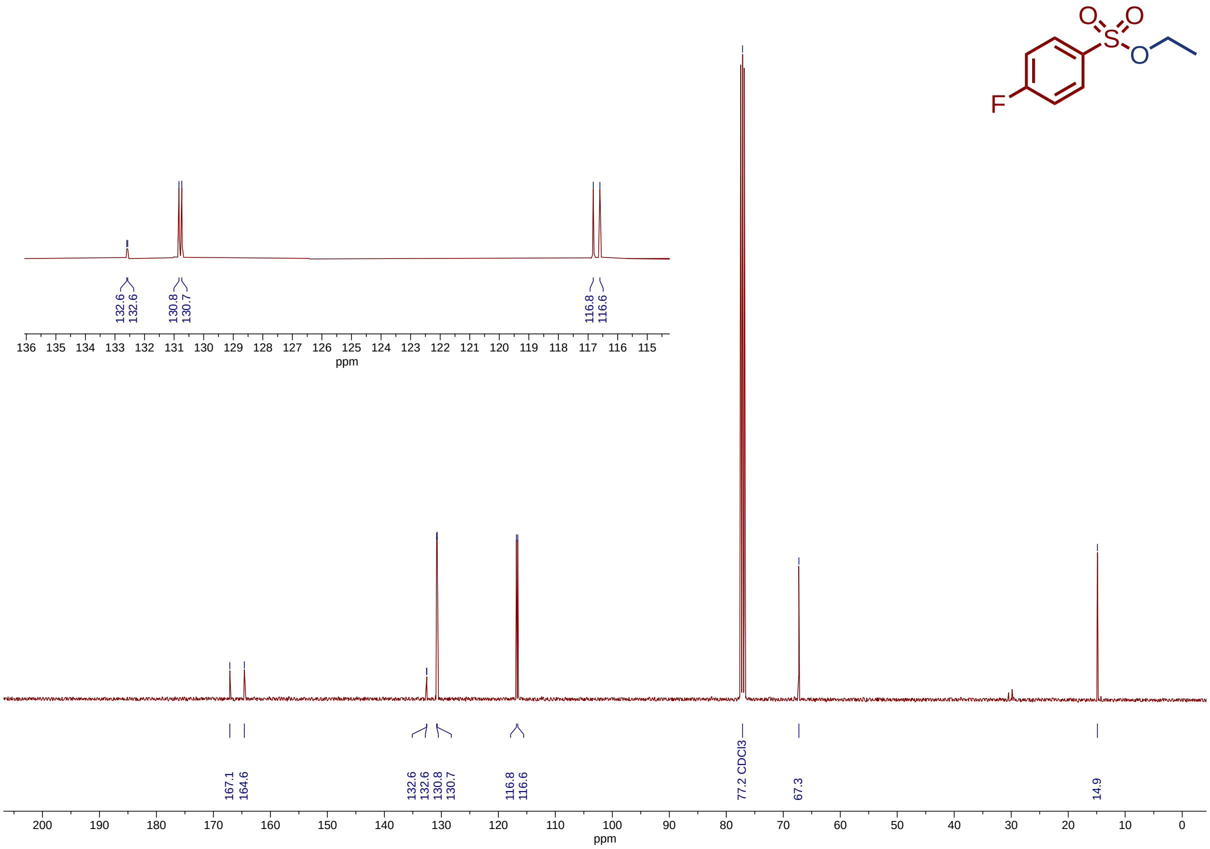
^{19}F NMR Spectrum for Compound **6l** (376 MHz, CDCl$_3$)



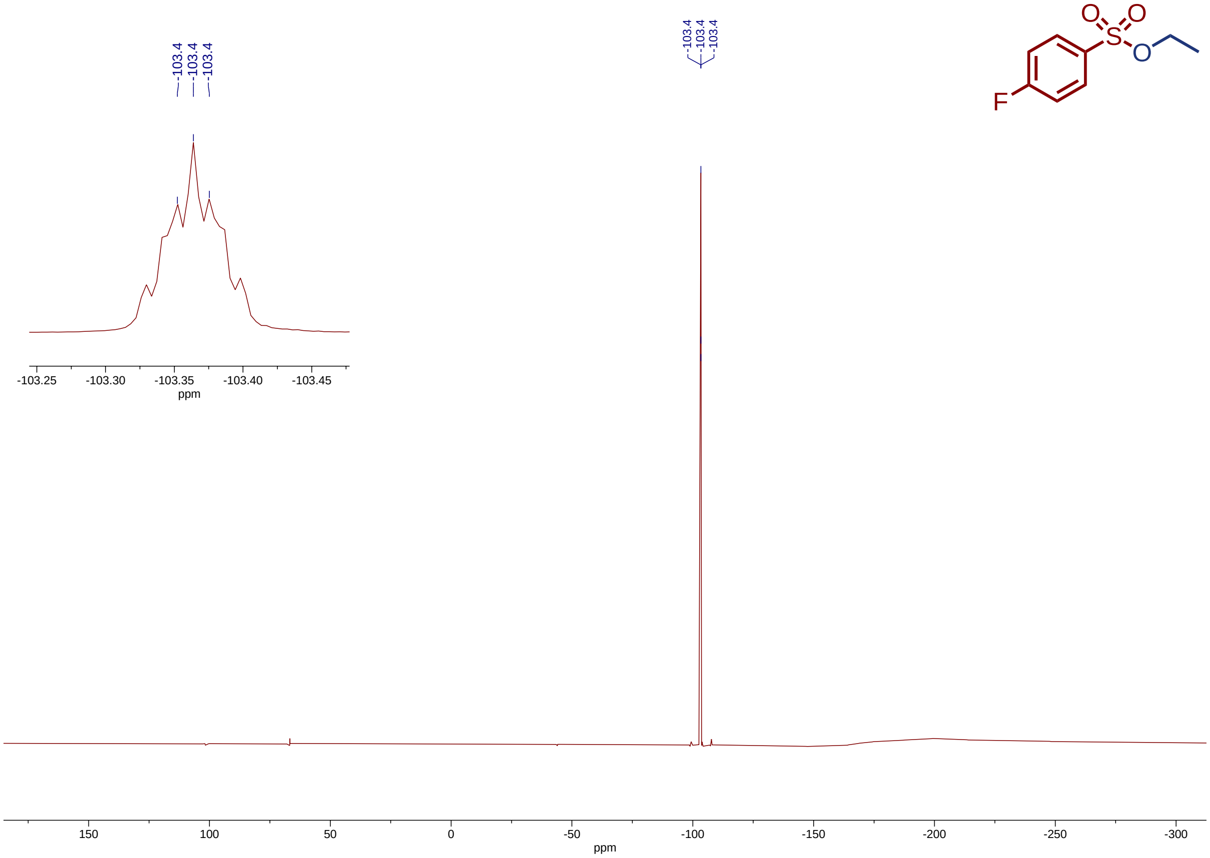
^{1}H NMR Spectrum for Compound **6m** (400 MHz, CDCl$_3$)



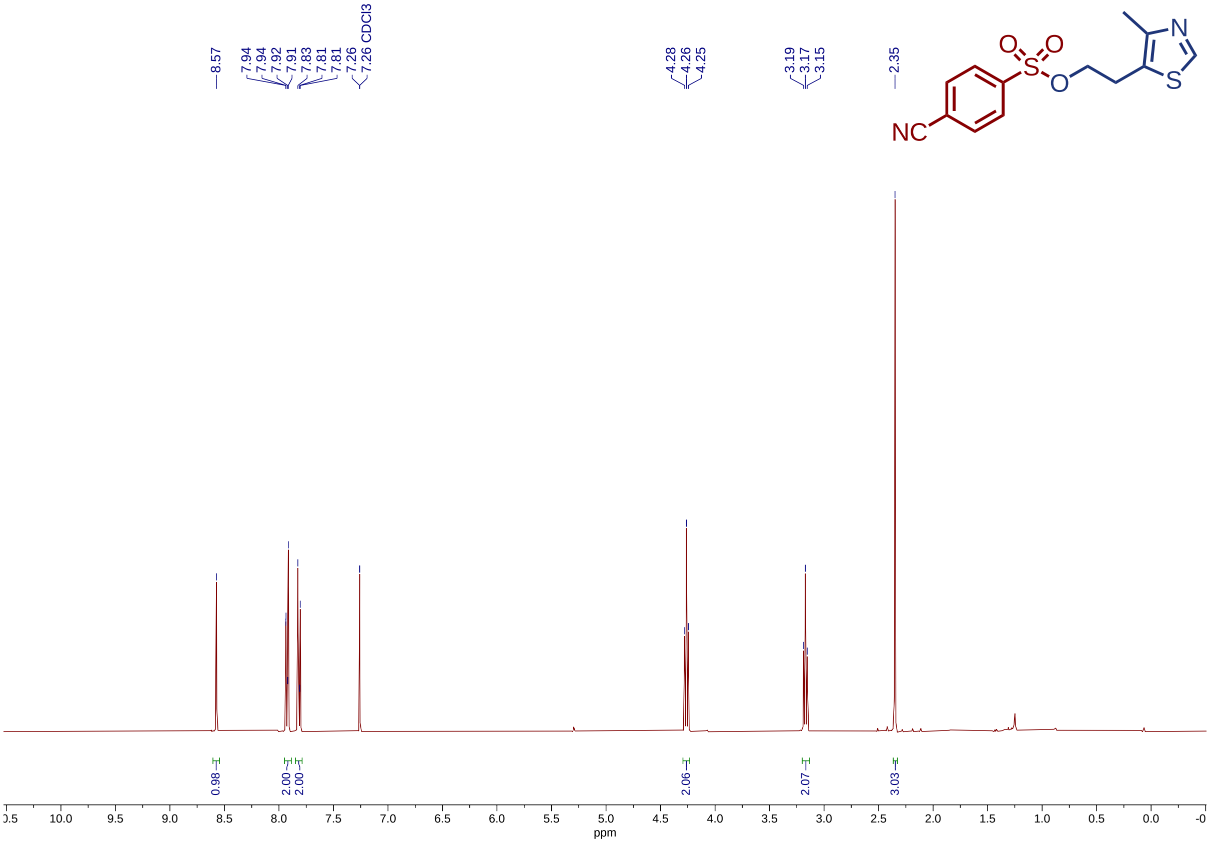
^{13}C NMR Spectrum for Compound **6m** (101 MHz, CDCl$_3$)



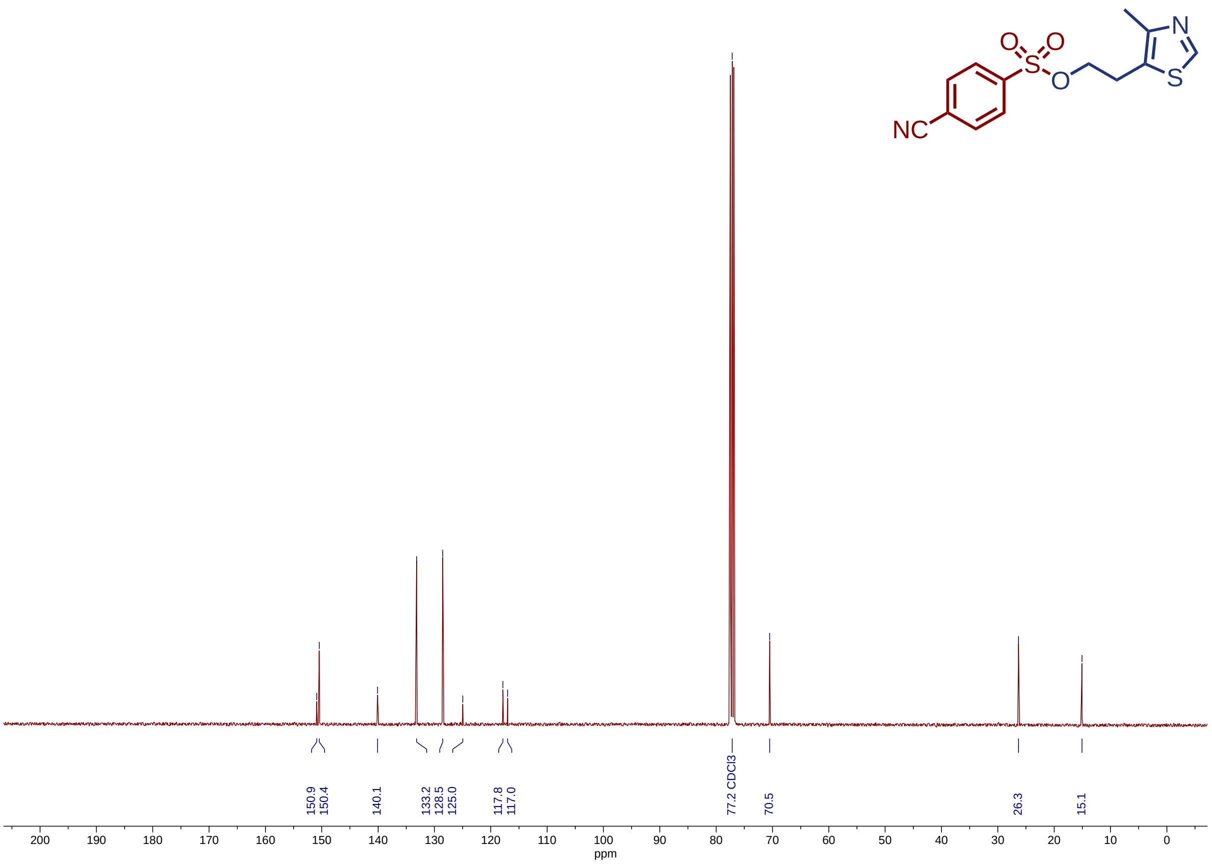
^{19}F NMR Spectrum for Compound **6m** (376 MHz, CDCl$_3$)



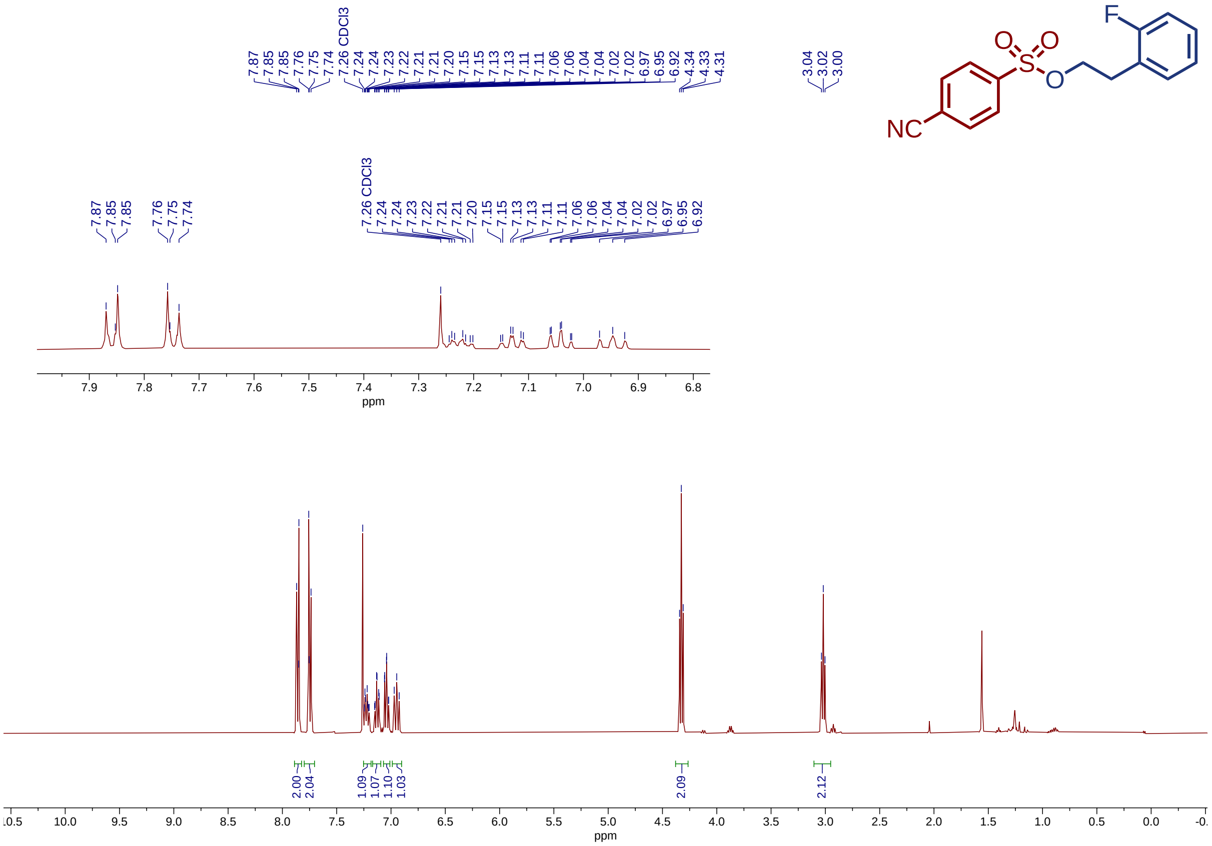
^{1}H NMR Spectrum for Compound **6n** (400 MHz, CDCl$_3$)



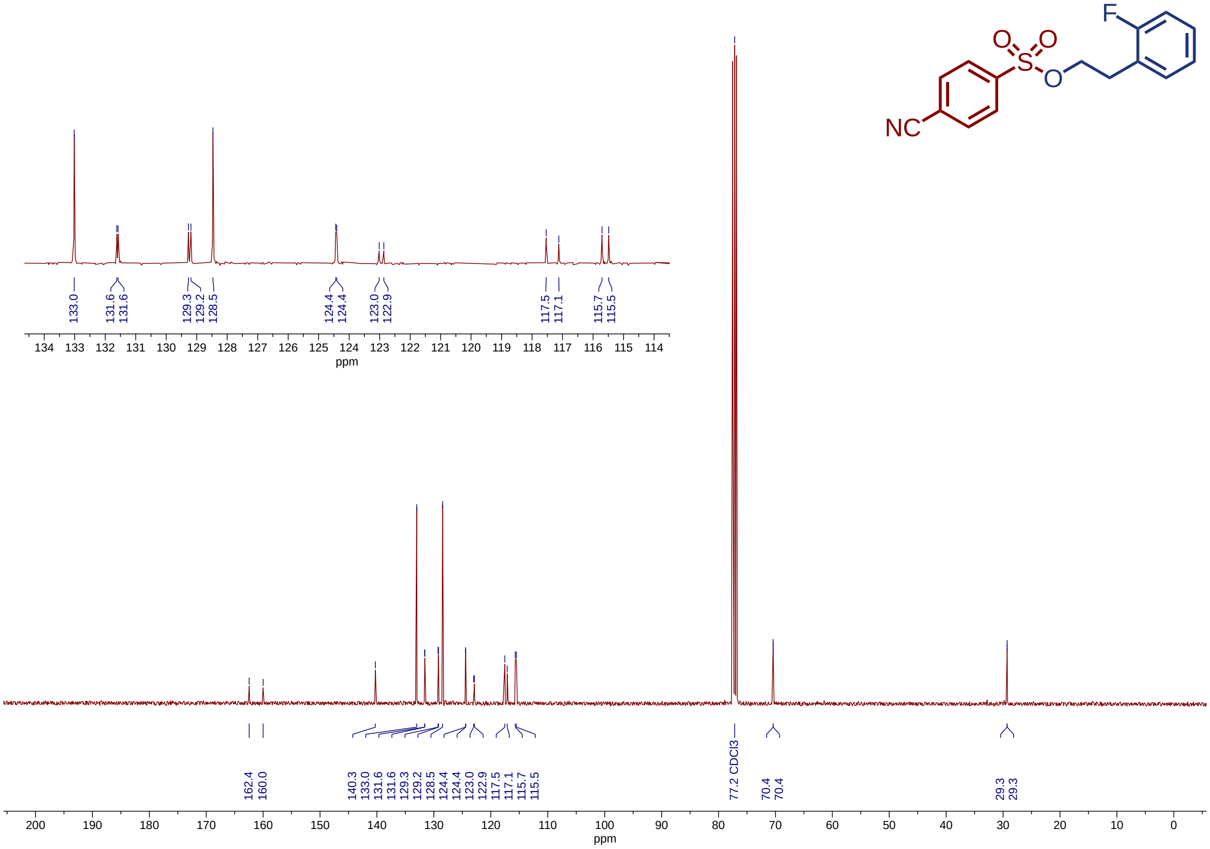
^{13}C NMR Spectrum for Compound **6n** (101 MHz, CDCl$_3$)



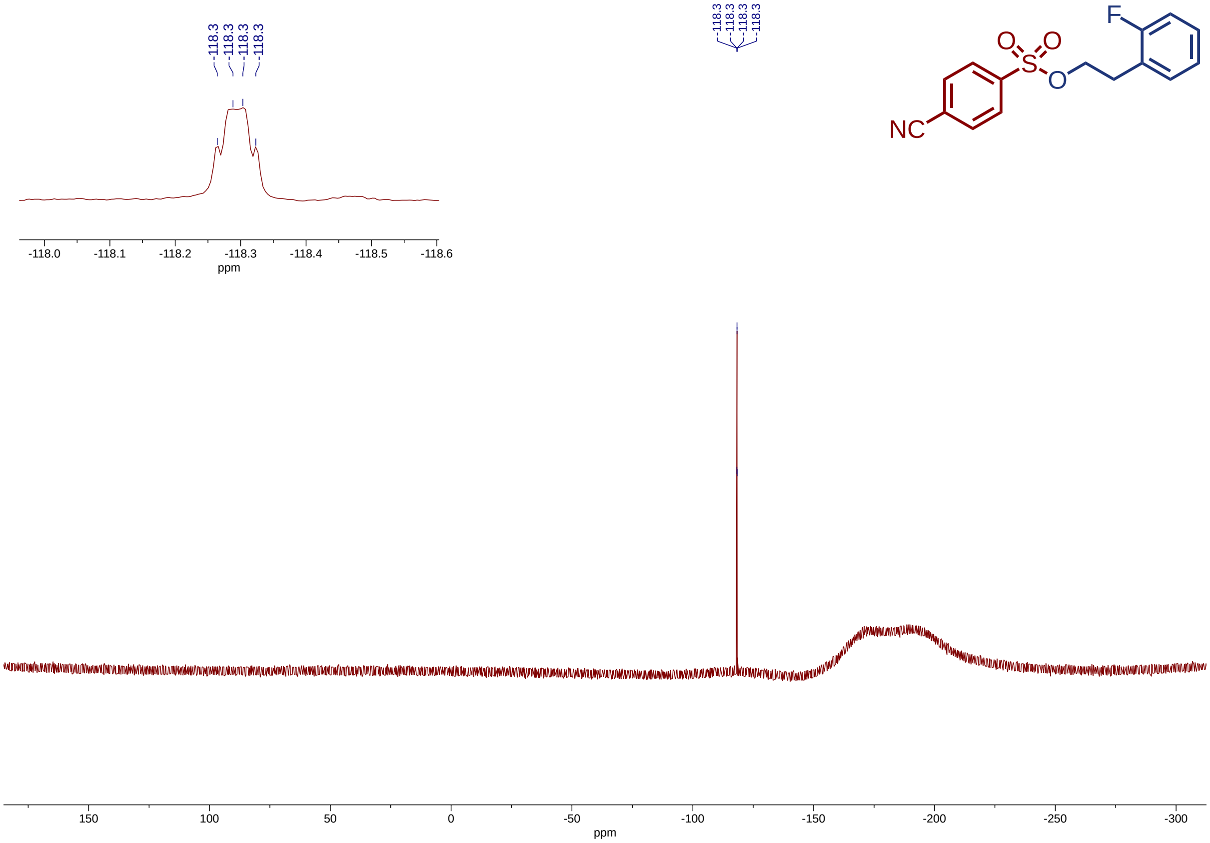
^{1}H NMR Spectrum for Compound **6o** (400 MHz, CDCl$_3$)



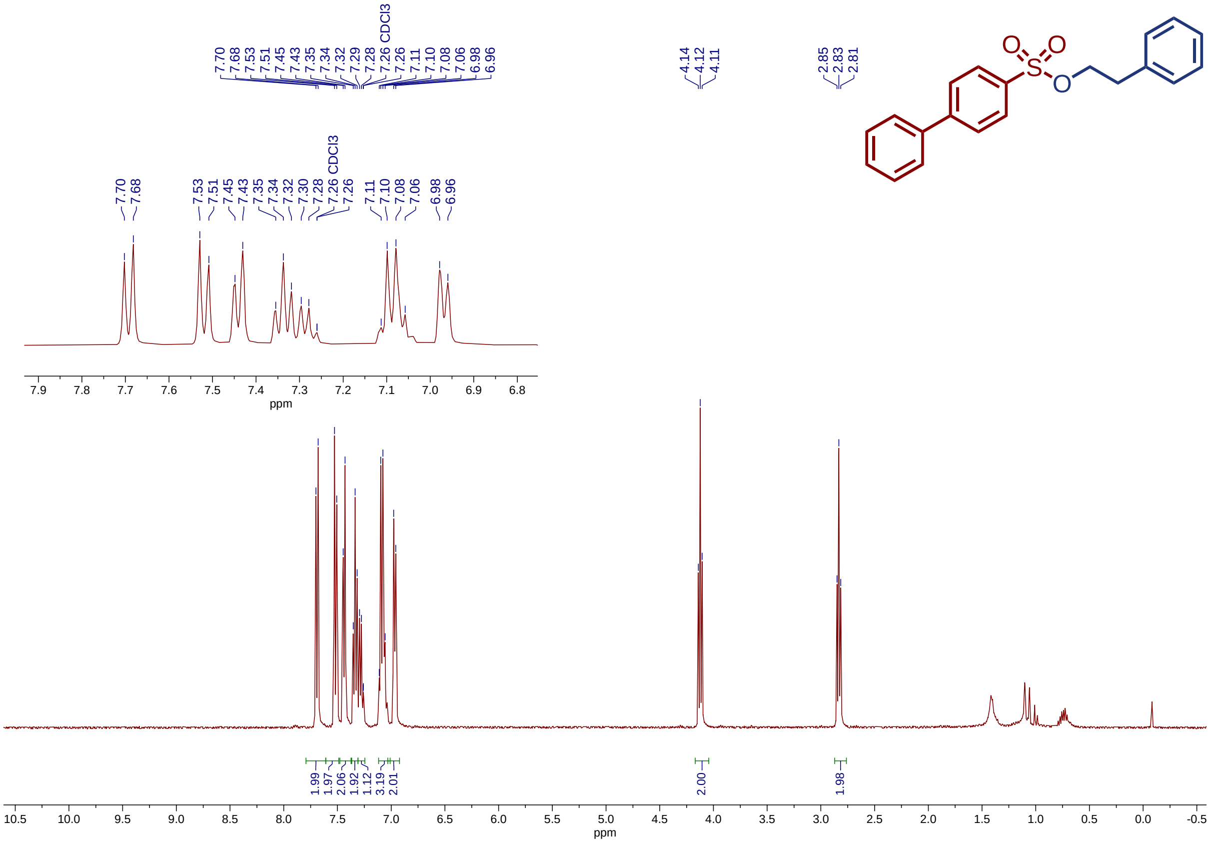
^{13}C NMR Spectrum for Compound **6o** (101 MHz, $CDCl_3$)



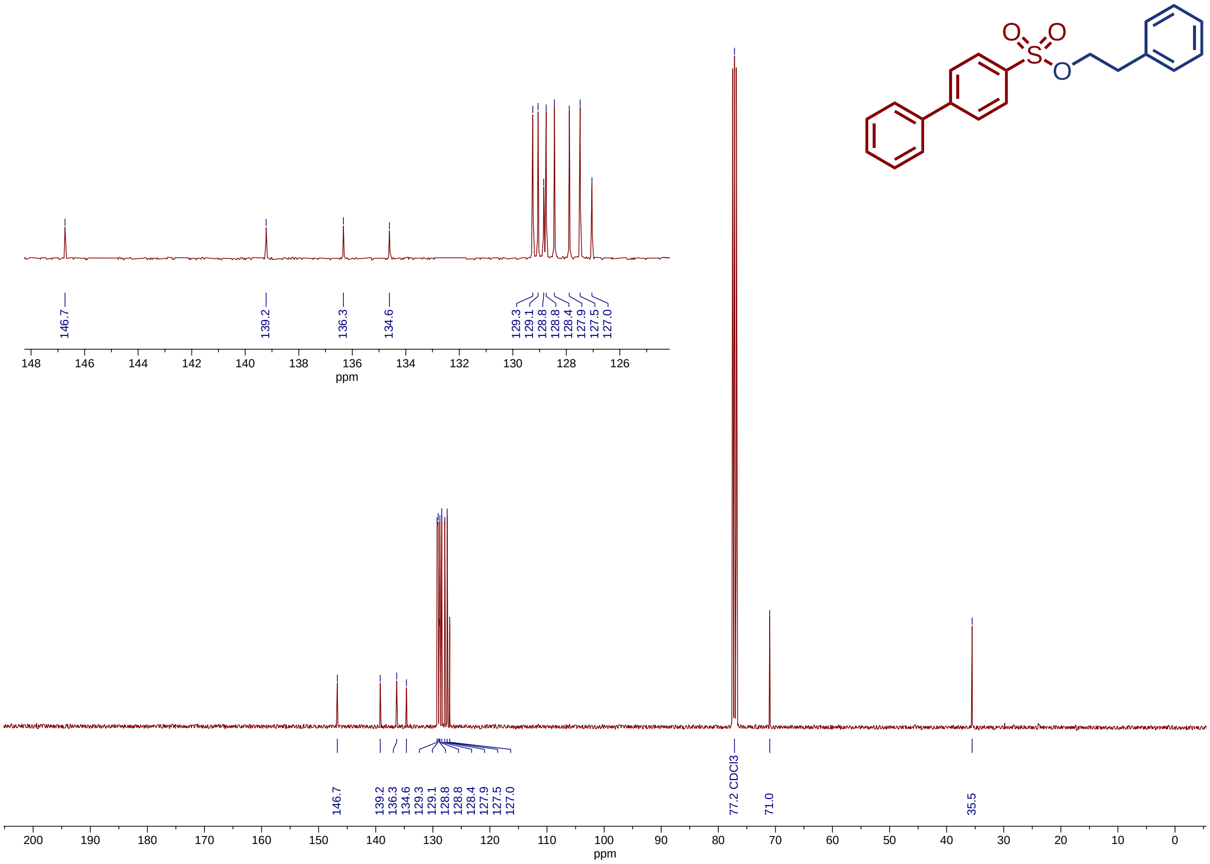
^{19}F NMR Spectrum for Compound **6o** (376 MHz, $CDCl_3$)



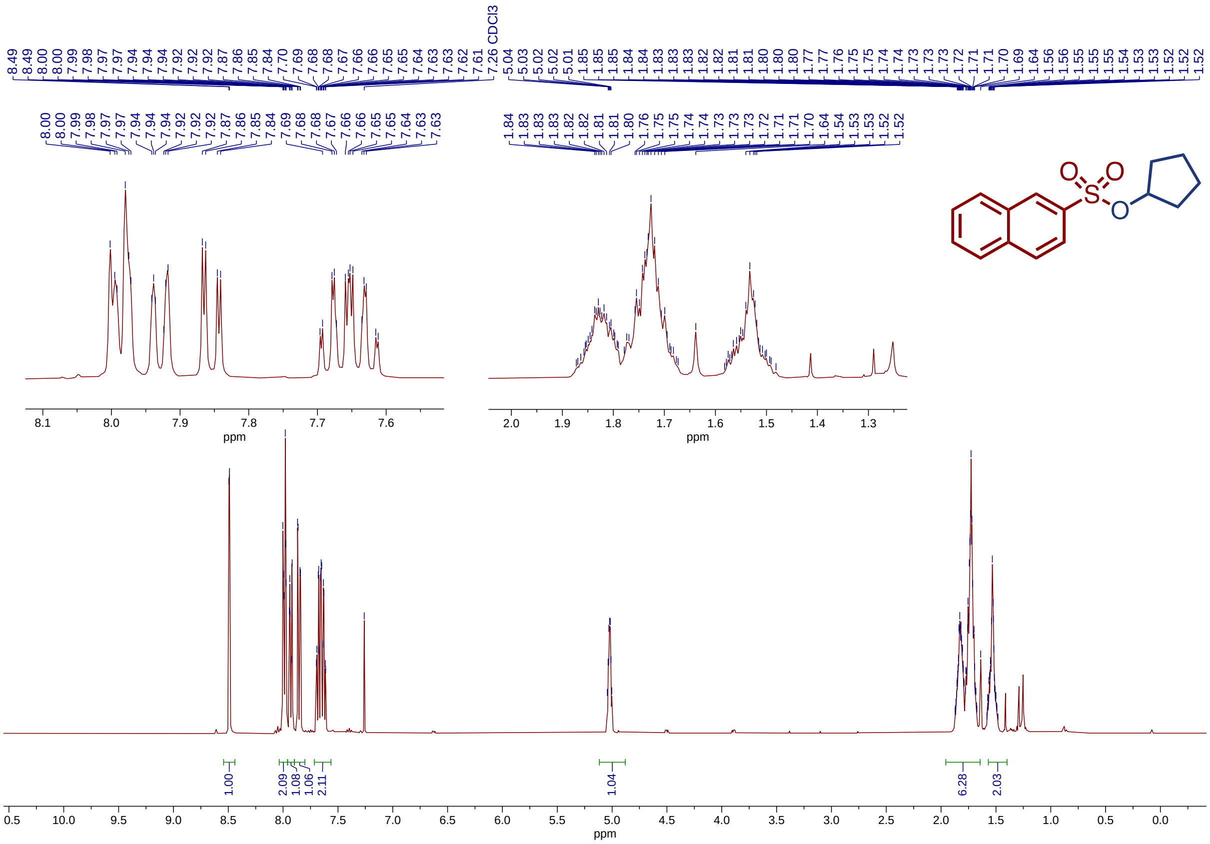
^{1}H NMR Spectrum for Compound **6p** (400 MHz, $CDCl_3$)



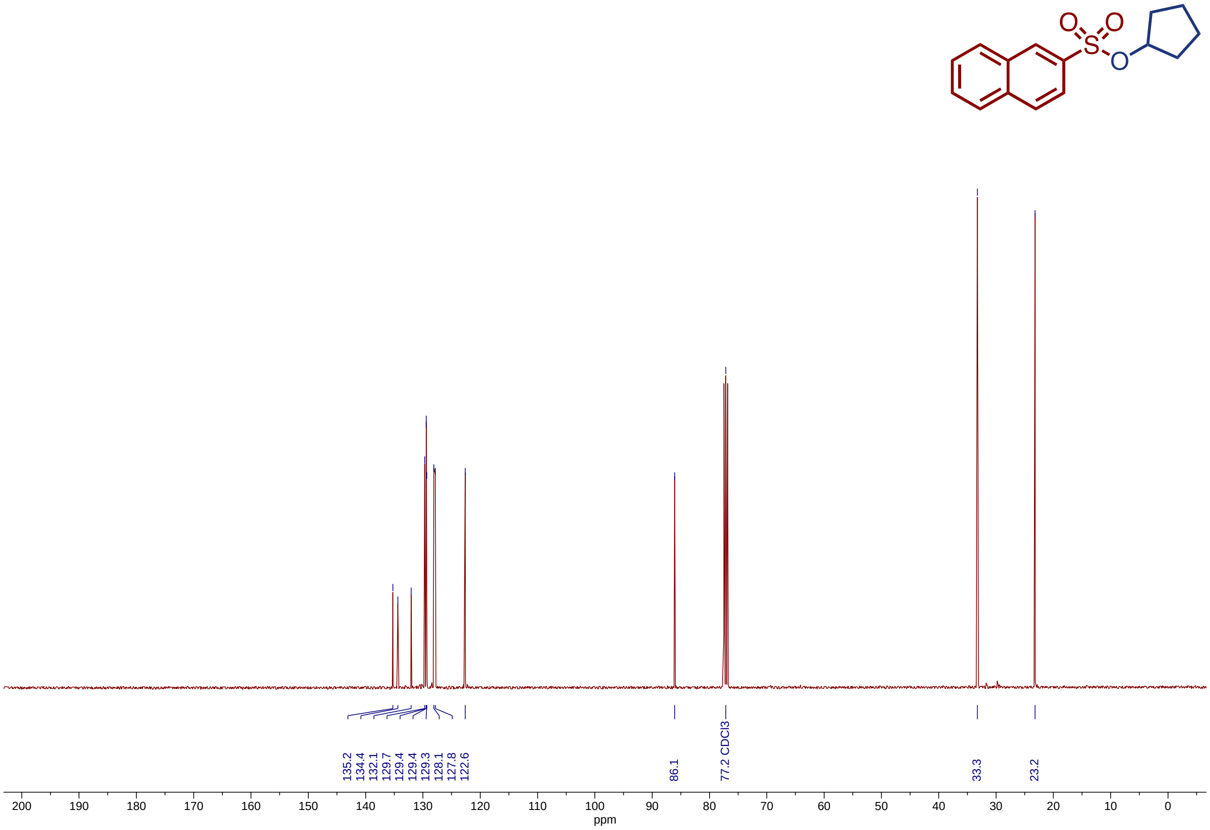
^{13}C NMR Spectrum for Compound **6p** (101 MHz, $CDCl_3$)



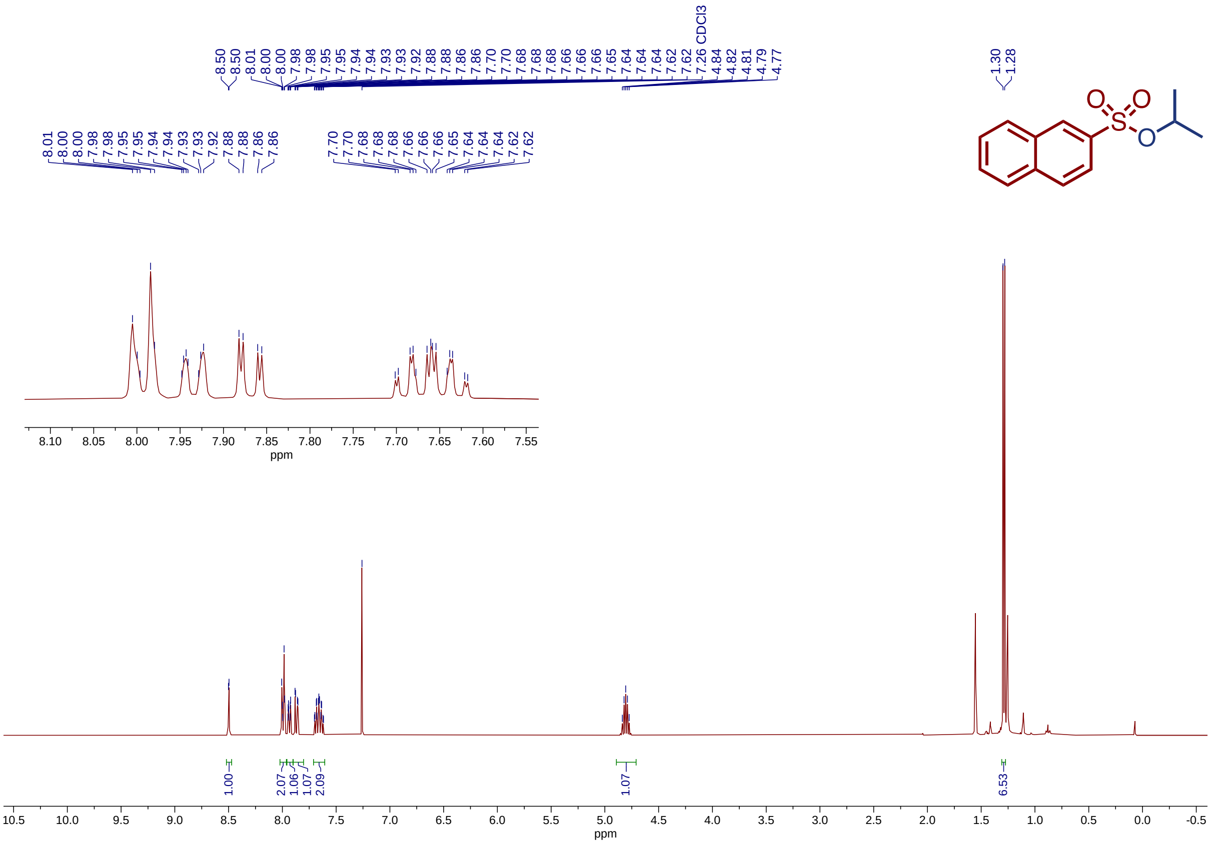
^{1}H NMR Spectrum for Compound **6q** (400 MHz, $CDCl_3$)



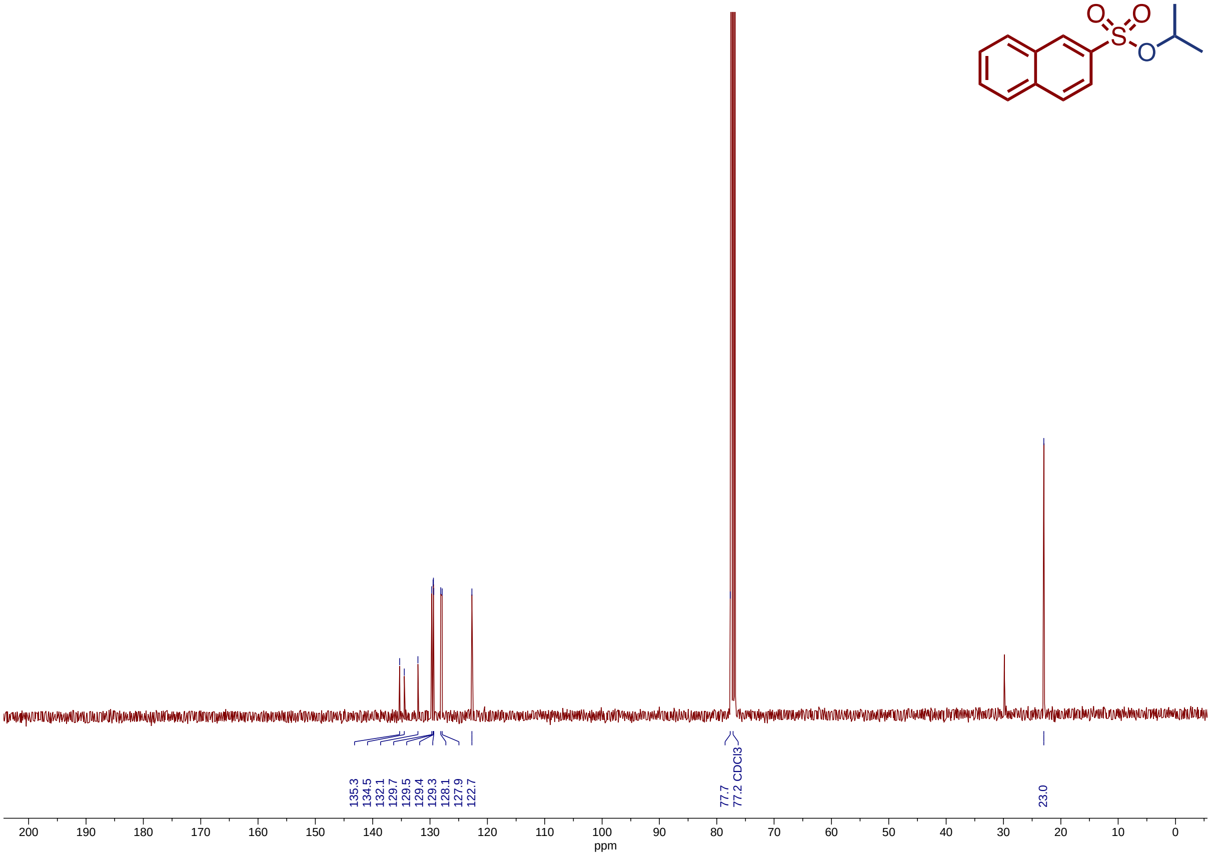
^{13}C NMR Spectrum for Compound **6q** (101 MHz, $CDCl_3$)



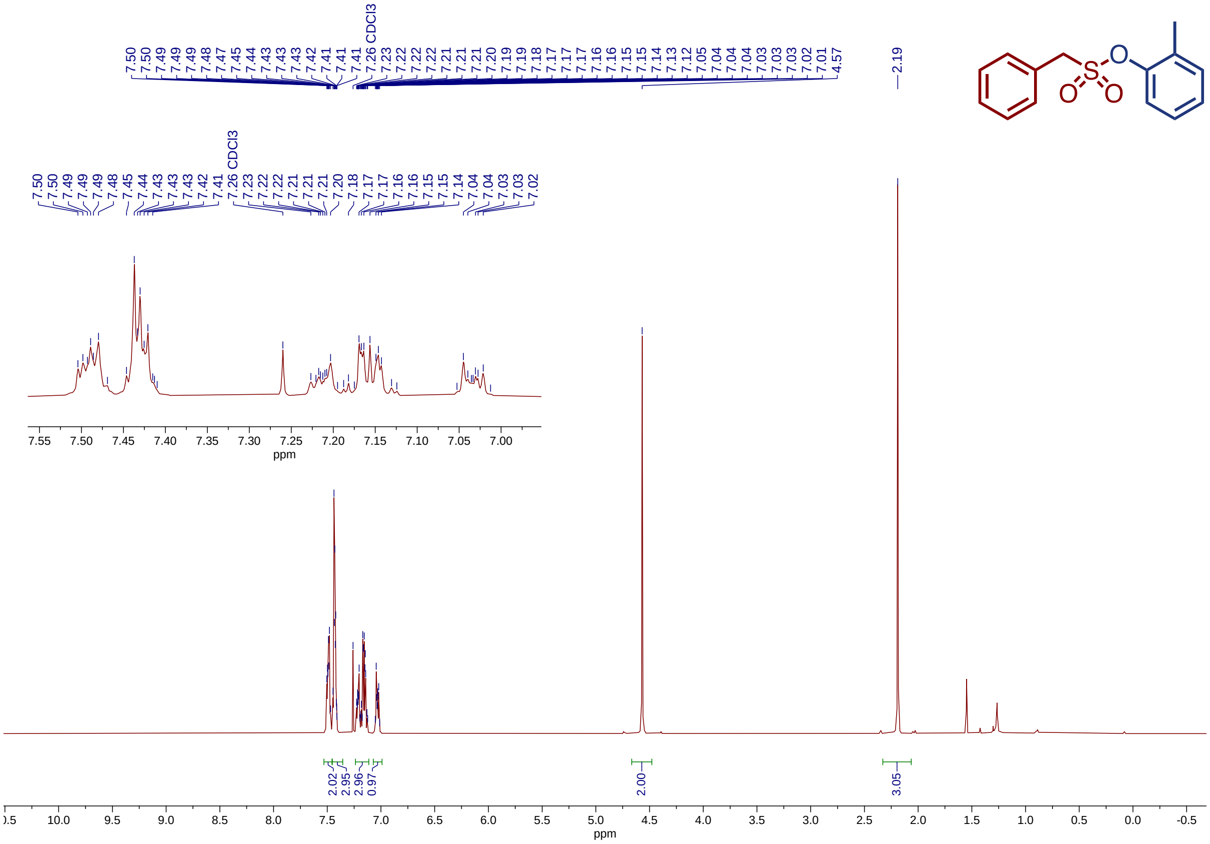
^{1}H NMR Spectrum for Compound **6r** (400 MHz, $CDCl_3$)



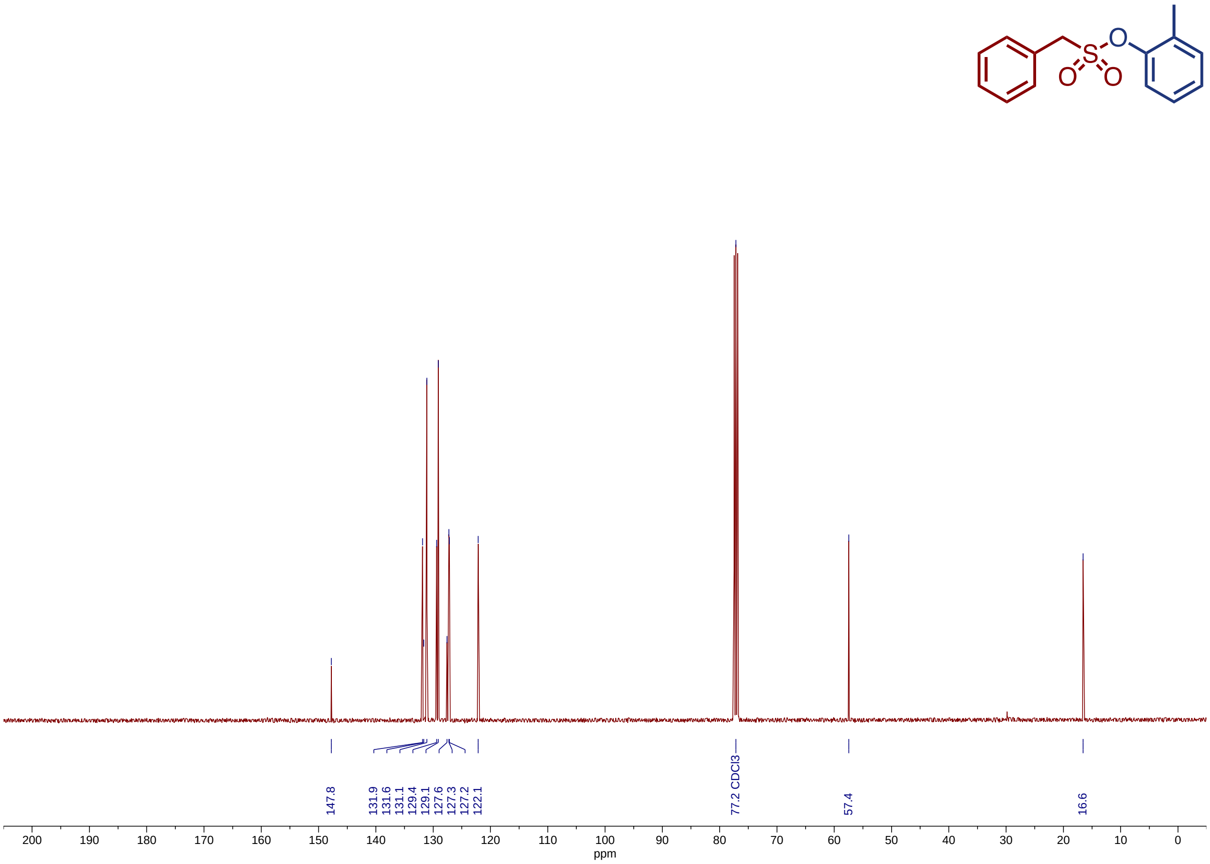
^{13}C NMR Spectrum for Compound **6r** (101 MHz, $CDCl_3$)



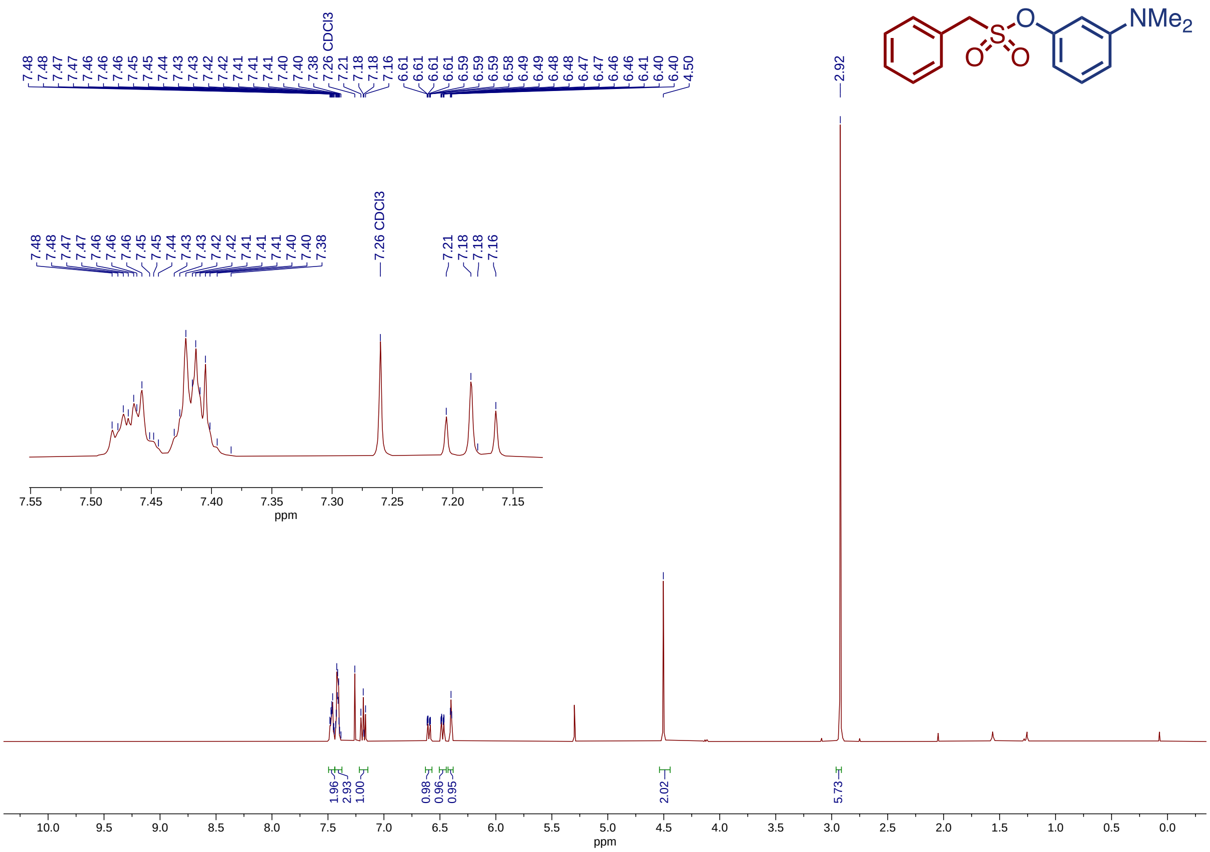
^{1}H NMR Spectrum for Compound **7a** (400 MHz, $CDCl_3$)



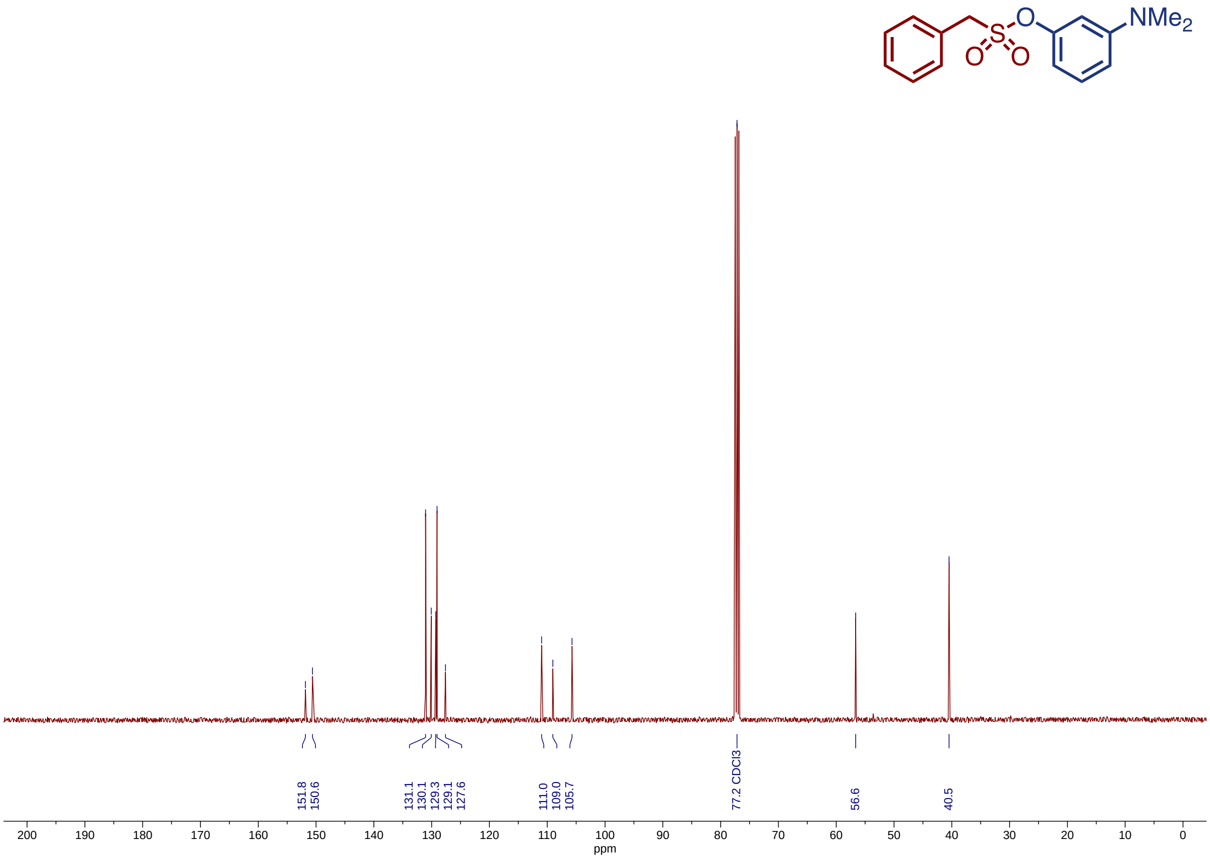
^{13}C NMR Spectrum for Compound **7a** (101 MHz, $CDCl_3$)



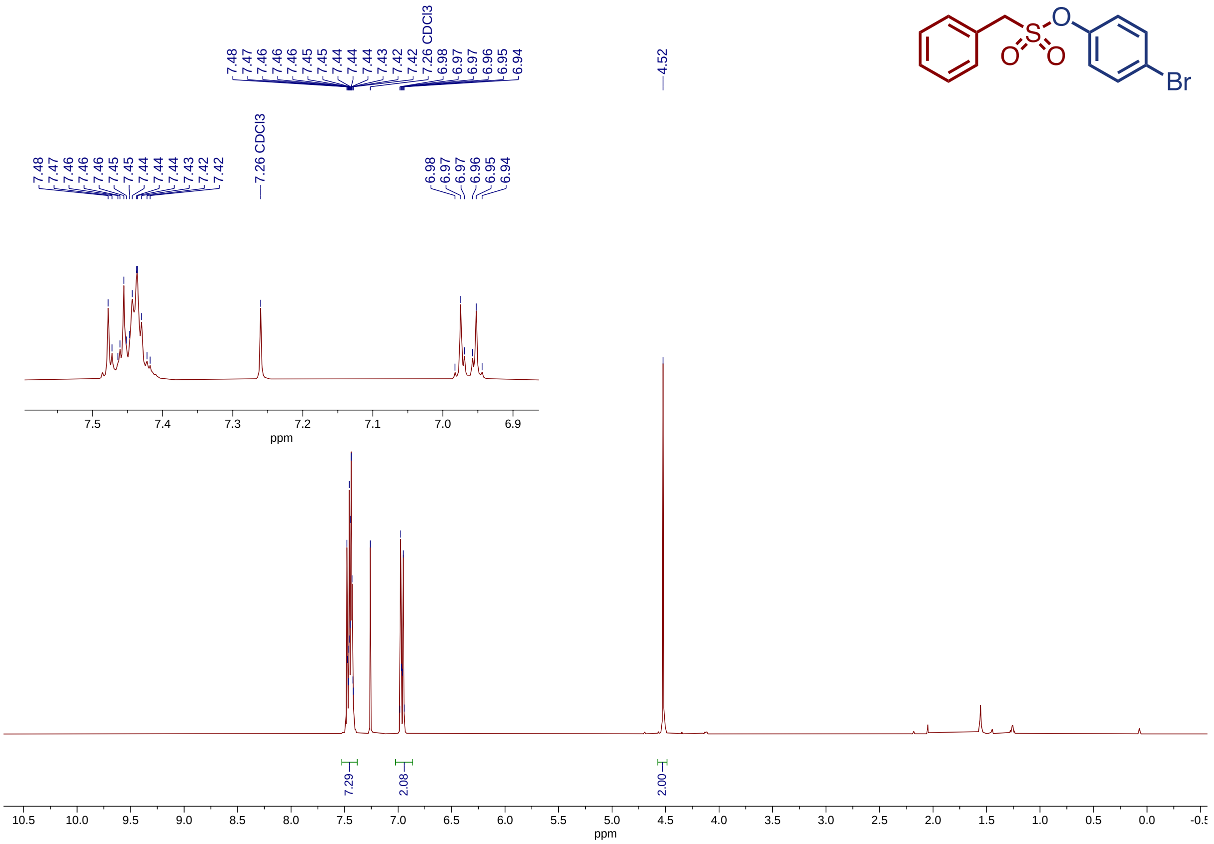
^{1}H NMR Spectrum for Compound **7b** (400 MHz, $CDCl_3$)



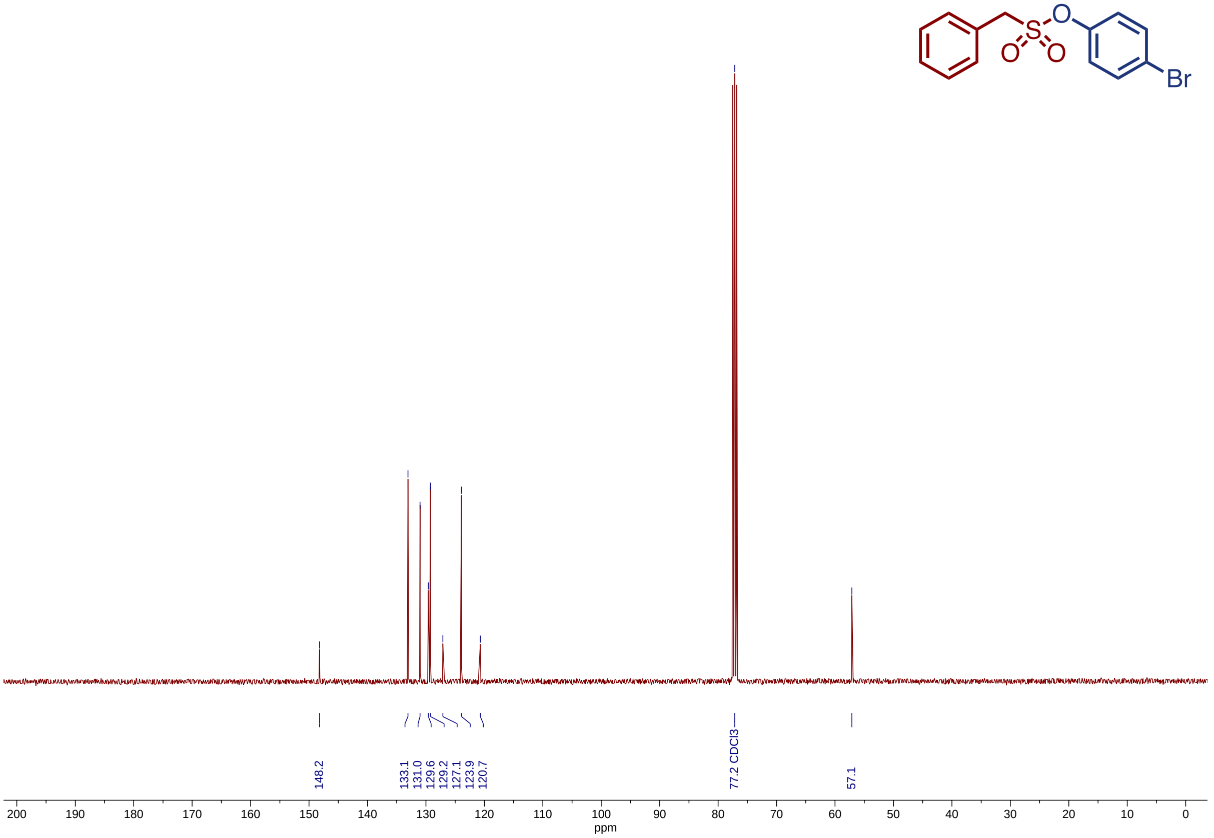
^{13}C NMR Spectrum for Compound **7b** (101 MHz, $CDCl_3$)



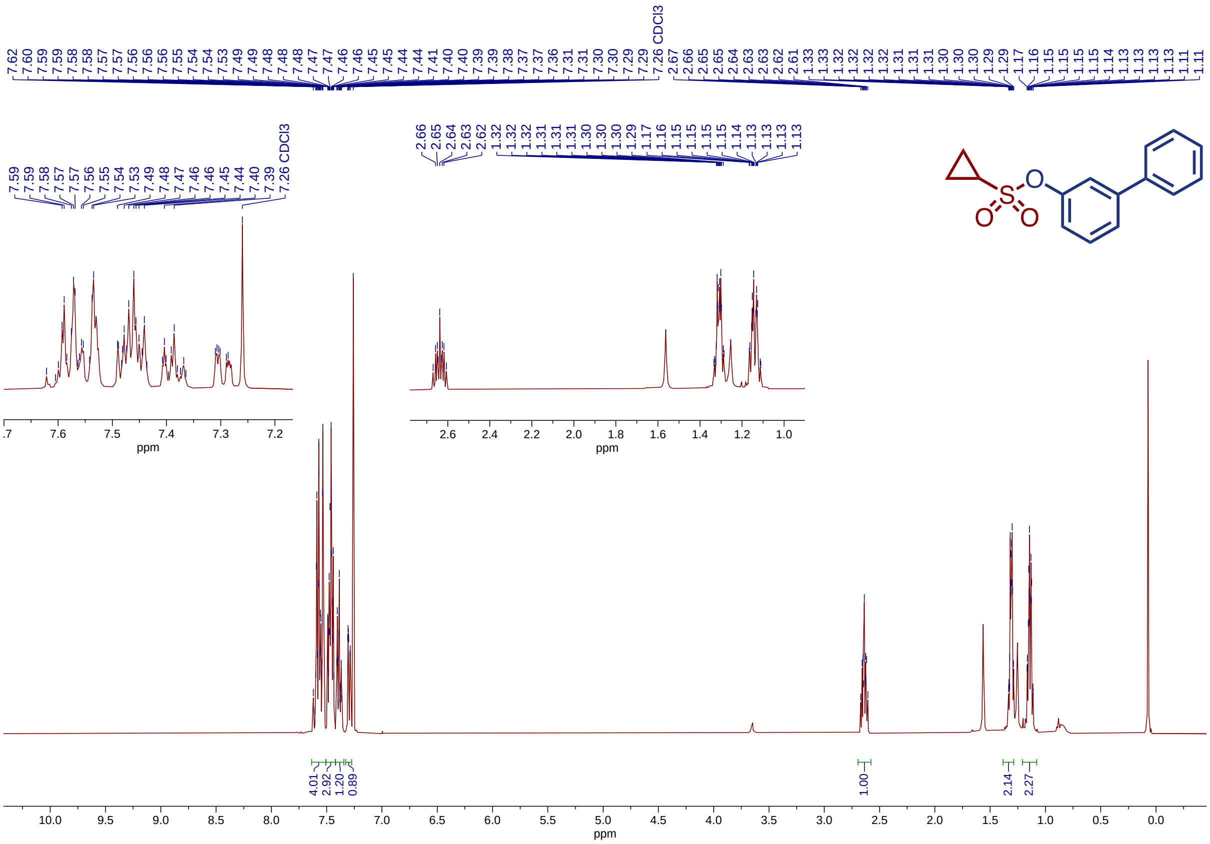
^{1}H NMR Spectrum for Compound **7c** (400 MHz, $CDCl_3$)



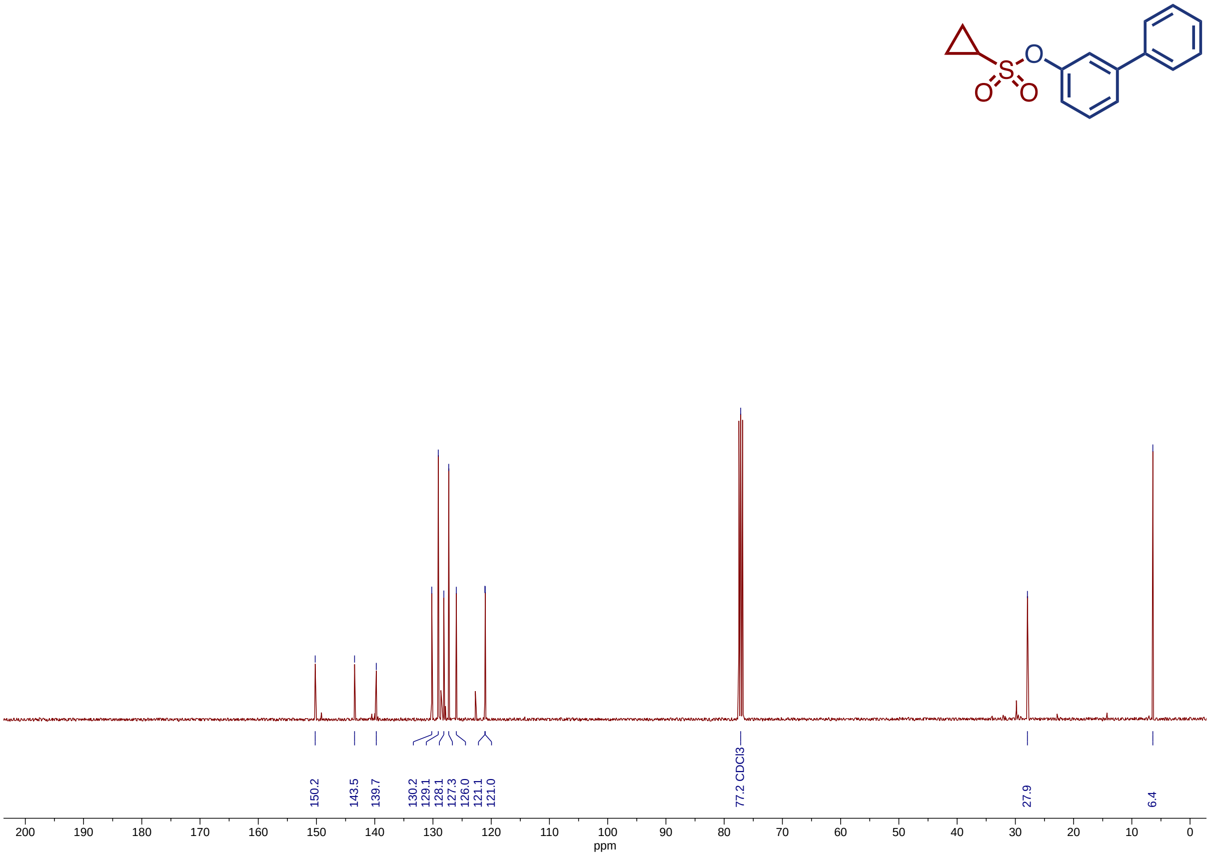
^{13}C NMR Spectrum for Compound **7c** (101 MHz, $CDCl_3$)



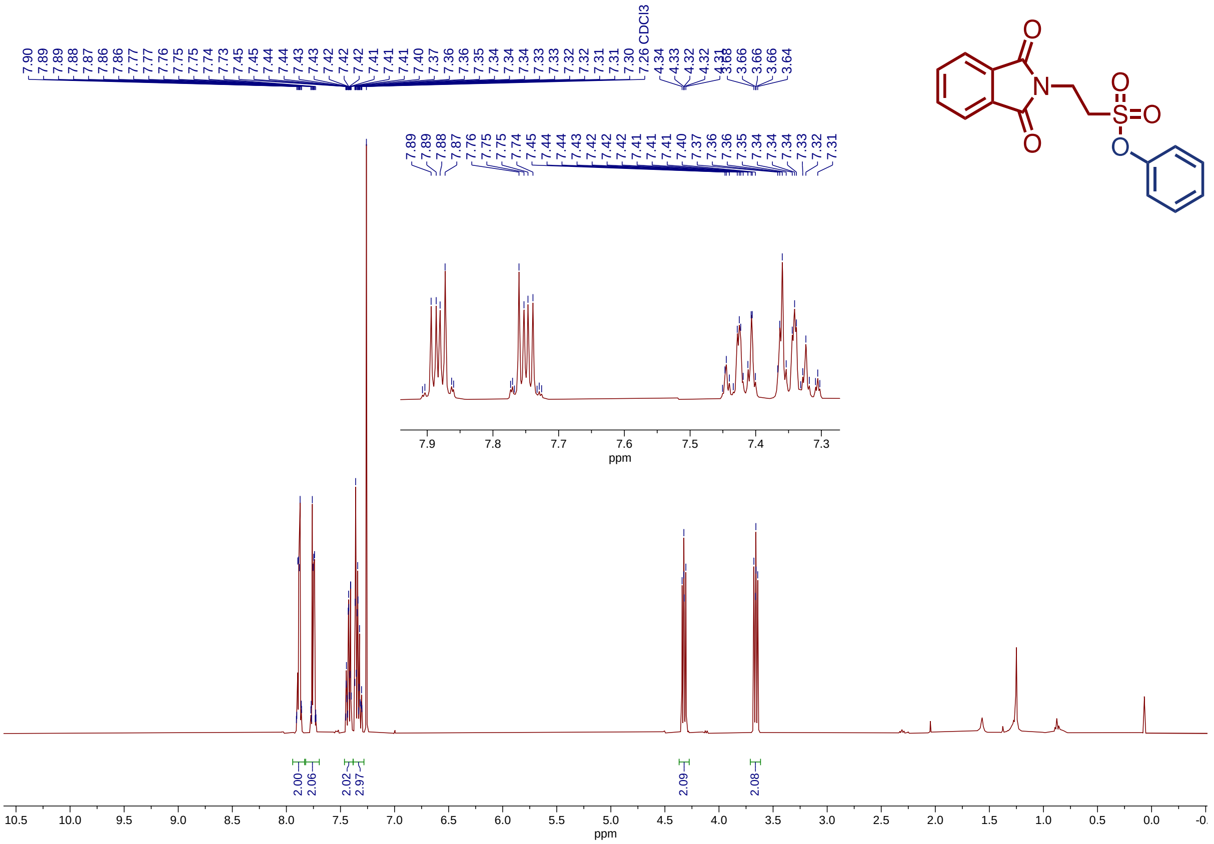
^{1}H NMR Spectrum for Compound **7d** (400 MHz, $CDCl_3$)



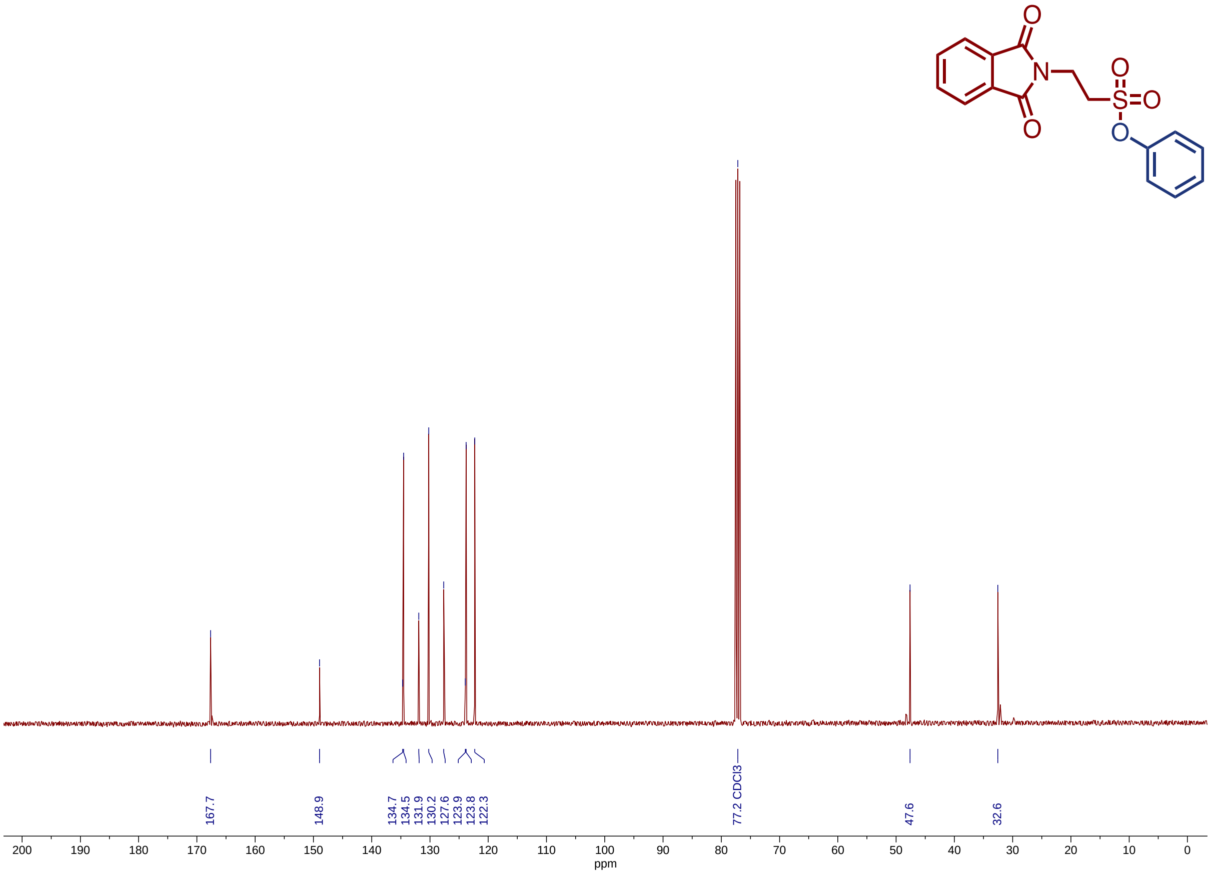
^{13}C NMR Spectrum for Compound **7d** (101 MHz, $CDCl_3$)



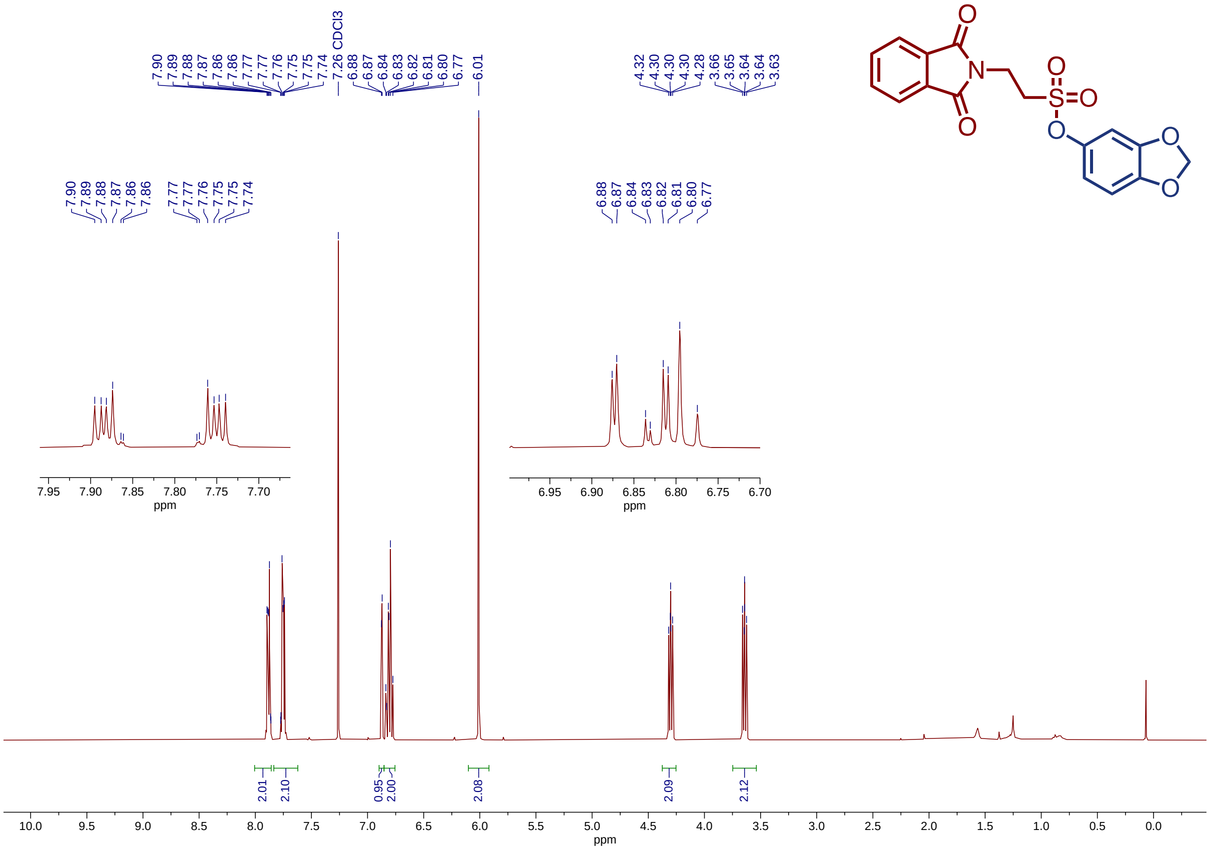
^{1}H NMR Spectrum for Compound **7e** (400 MHz, CDCl$_3$)



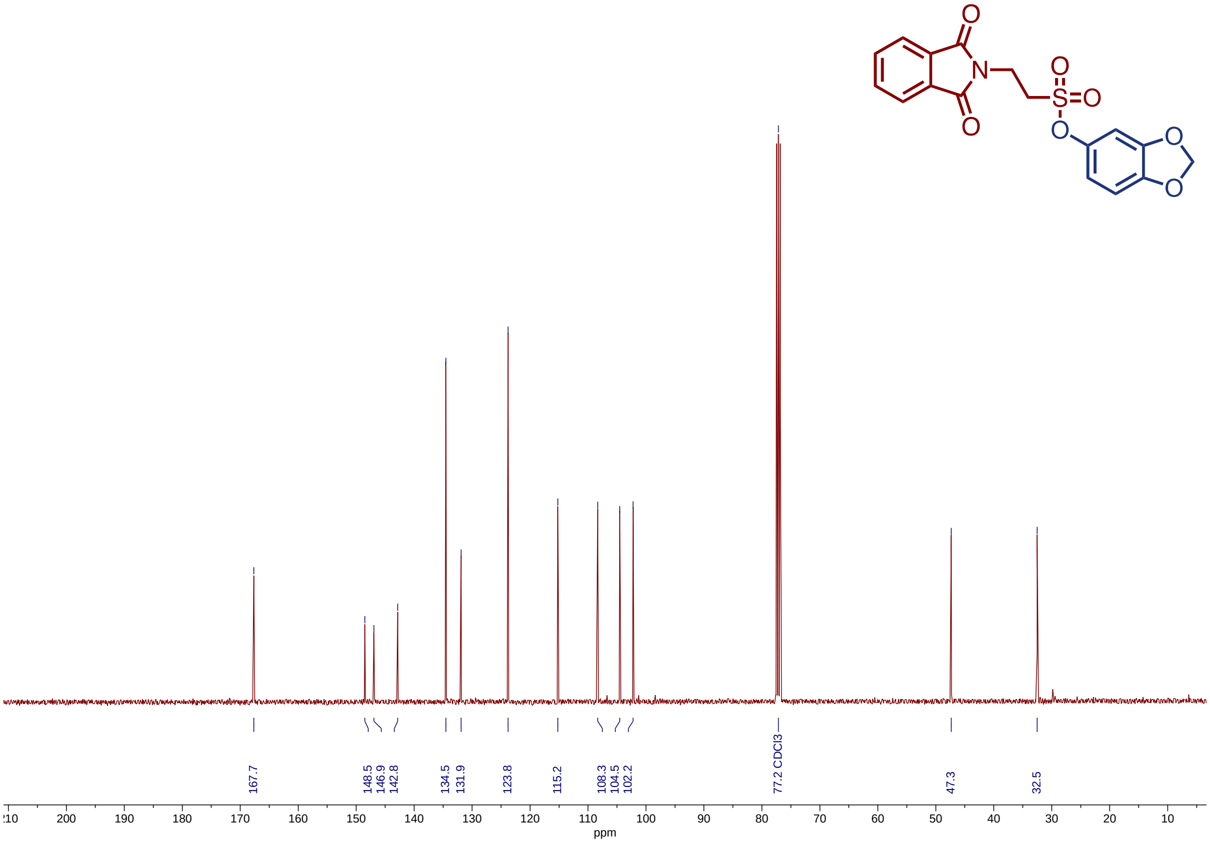
^{13}C NMR Spectrum for Compound **7e** (101 MHz, CDCl$_3$)



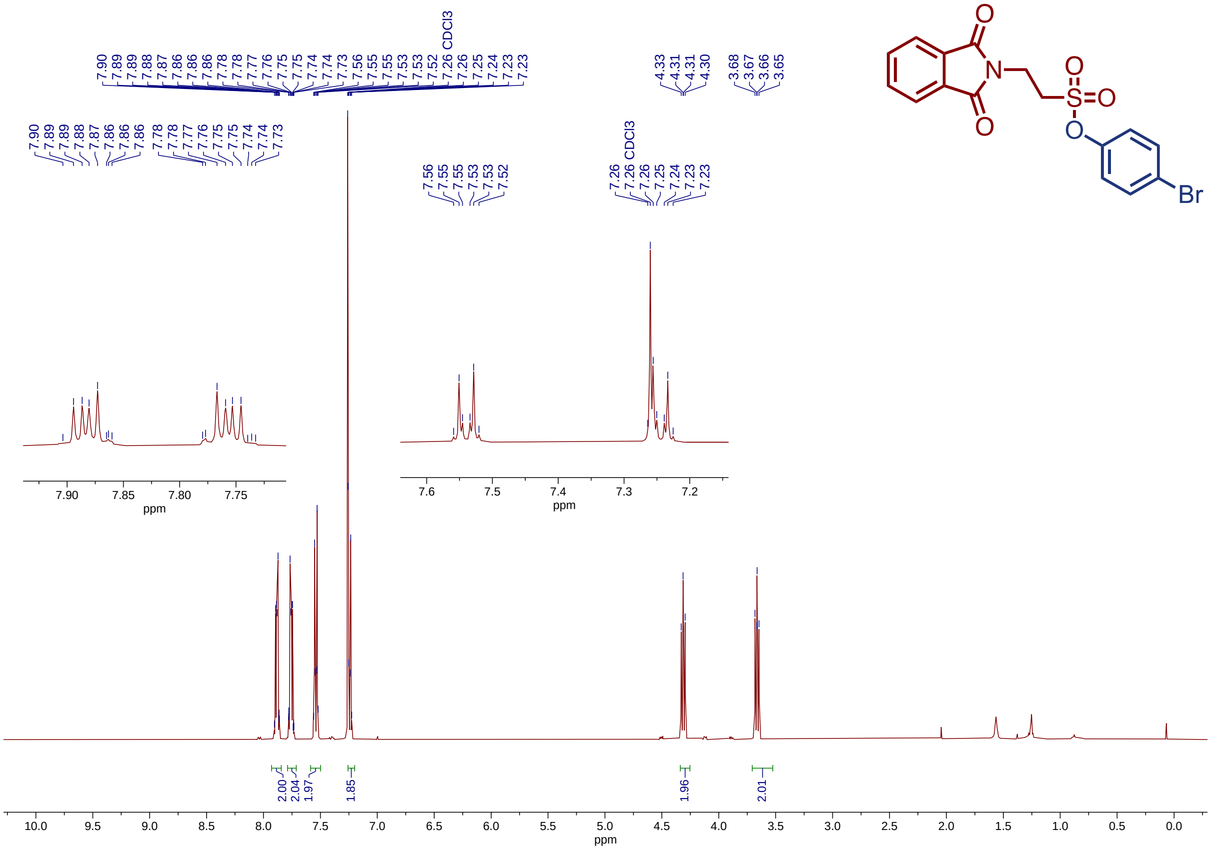
^{1}H NMR Spectrum for Compound **7f** (400 MHz, $CDCl_3$)



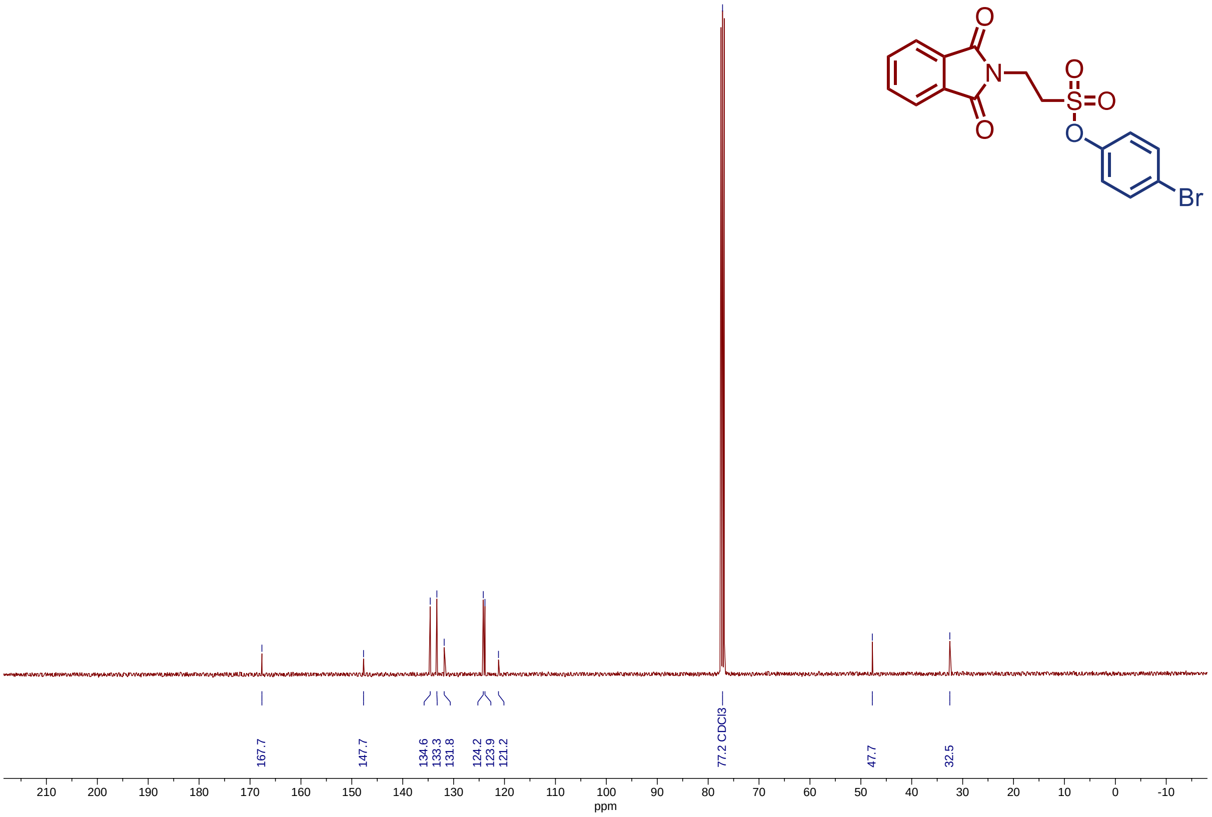
^{13}C NMR Spectrum for Compound **7f** (101 MHz, $CDCl_3$)



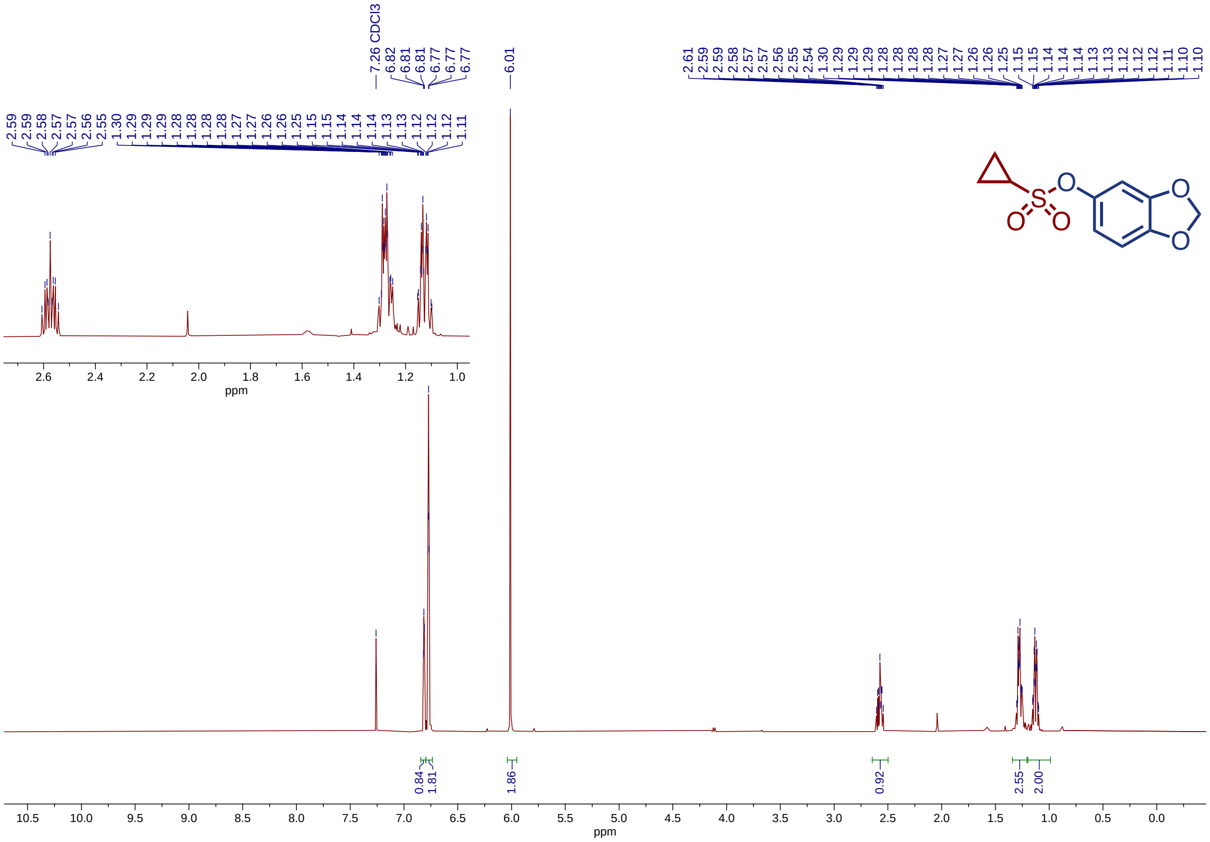
^{1}H NMR Spectrum for Compound **7g** (400 MHz, CDCl$_3$)



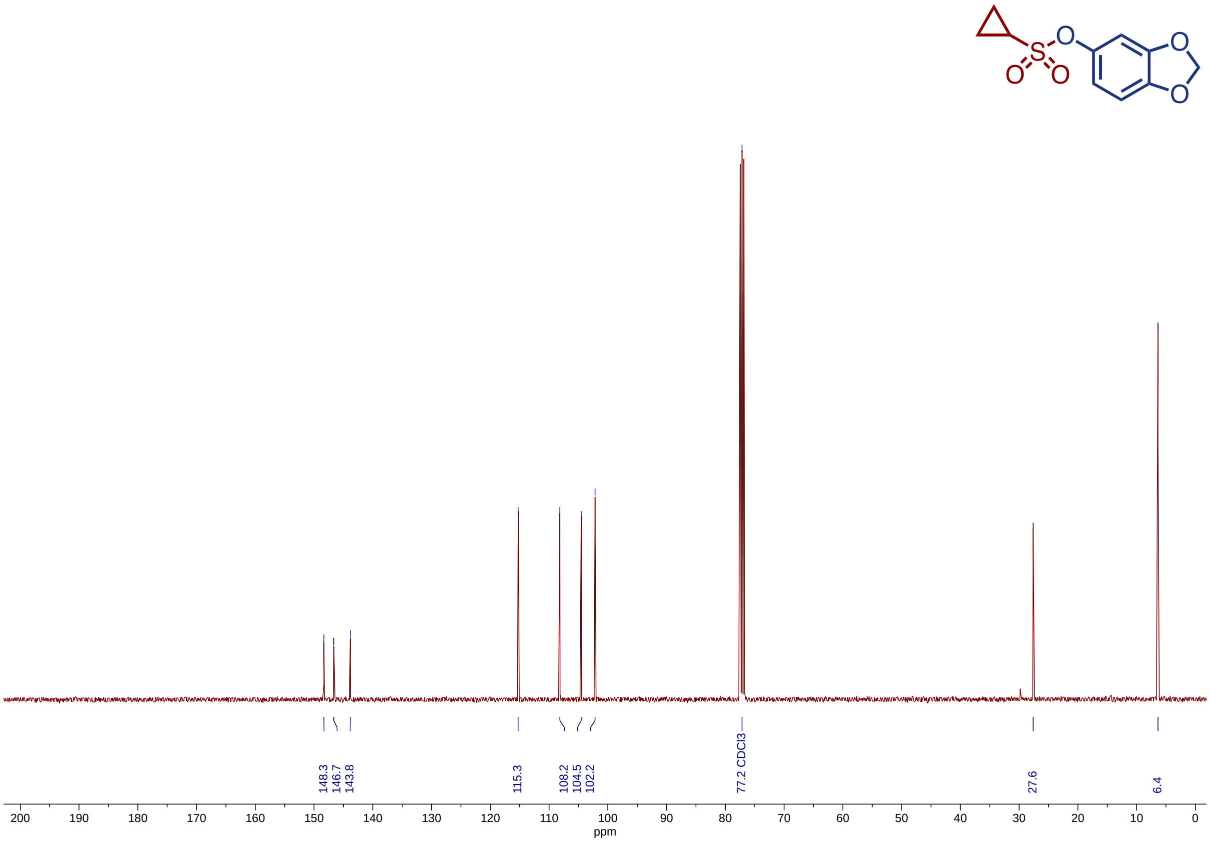
^{13}C NMR Spectrum for Compound **7g** (101 MHz, CDCl$_3$)



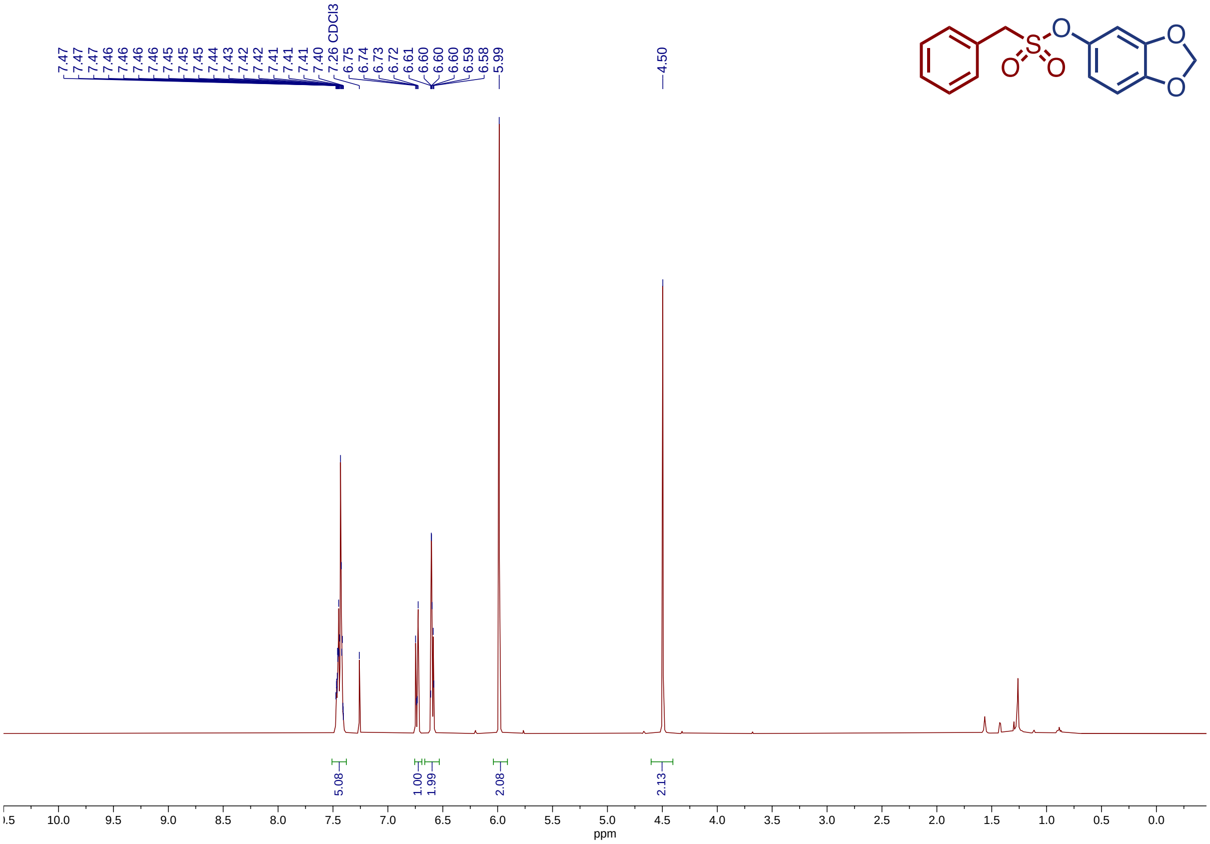
^1H NMR Spectrum for Compound **7h** (400 MHz, $CDCl_3$)



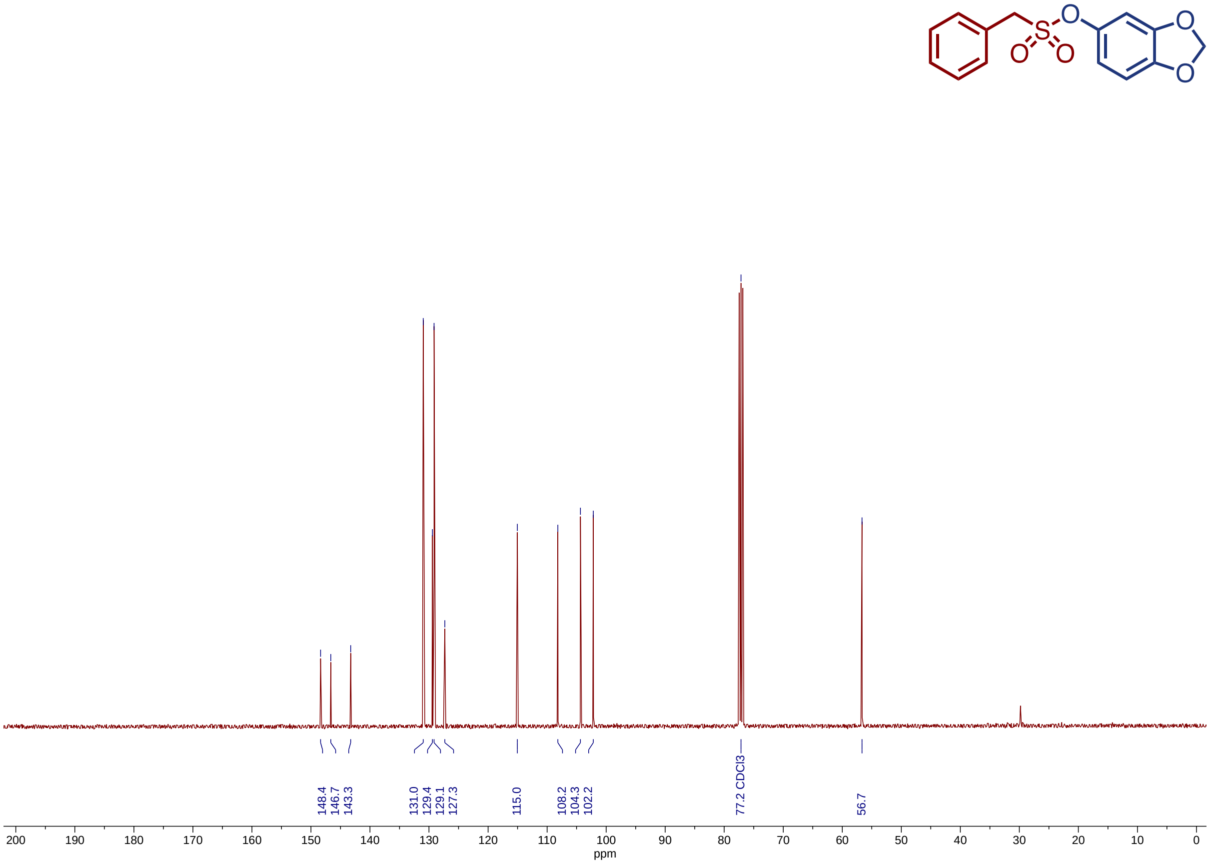
^{13}C NMR Spectrum for Compound **7h** (101 MHz, $CDCl_3$)



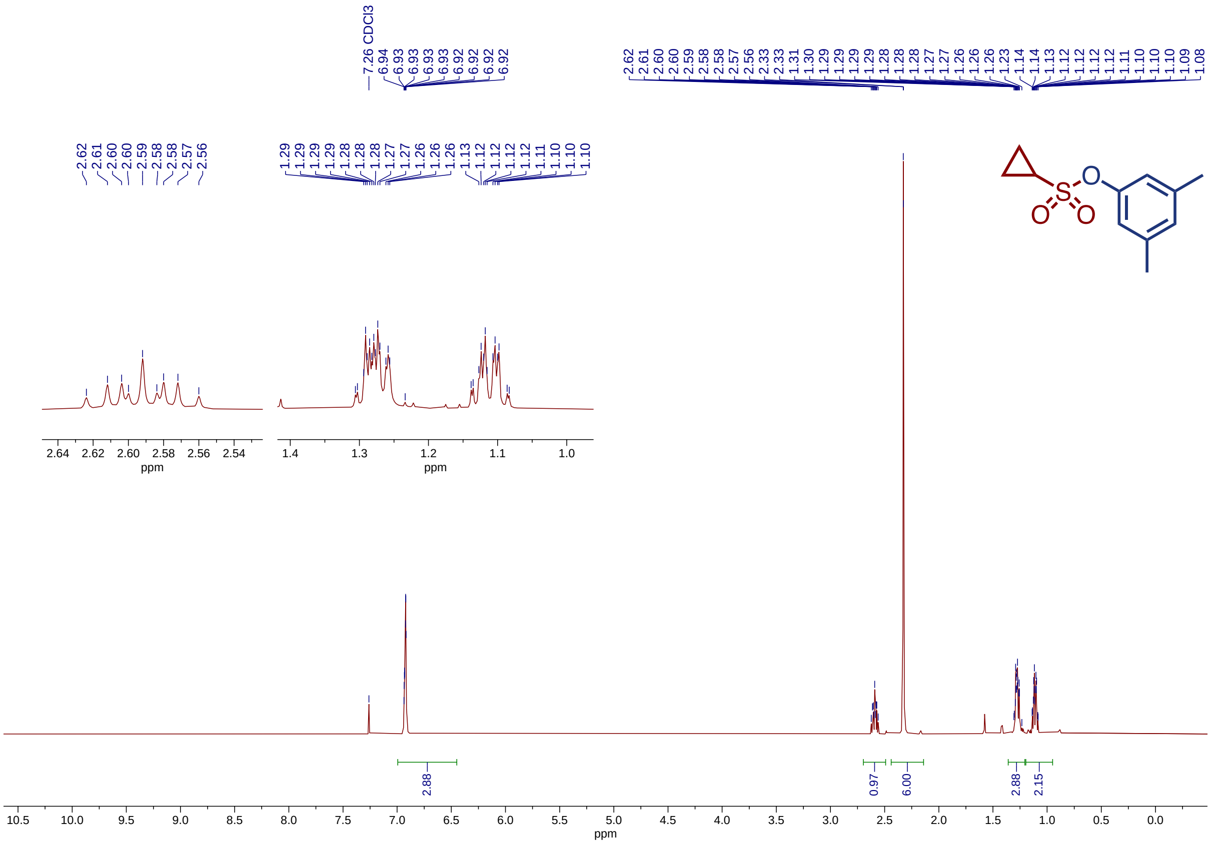
^{1}H NMR Spectrum for Compound **7i** (400 MHz, CDCl$_3$)



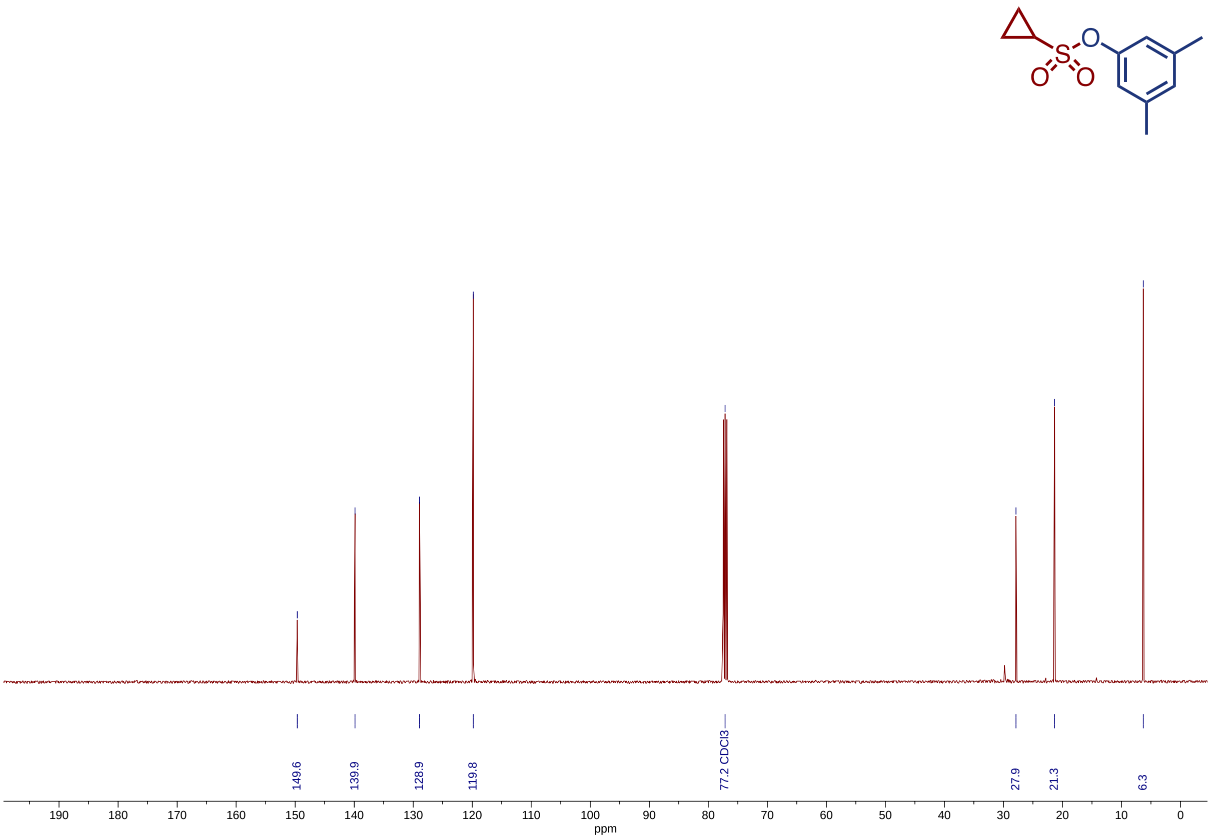
^{13}C NMR Spectrum for Compound **7i** (101 MHz, CDCl$_3$)



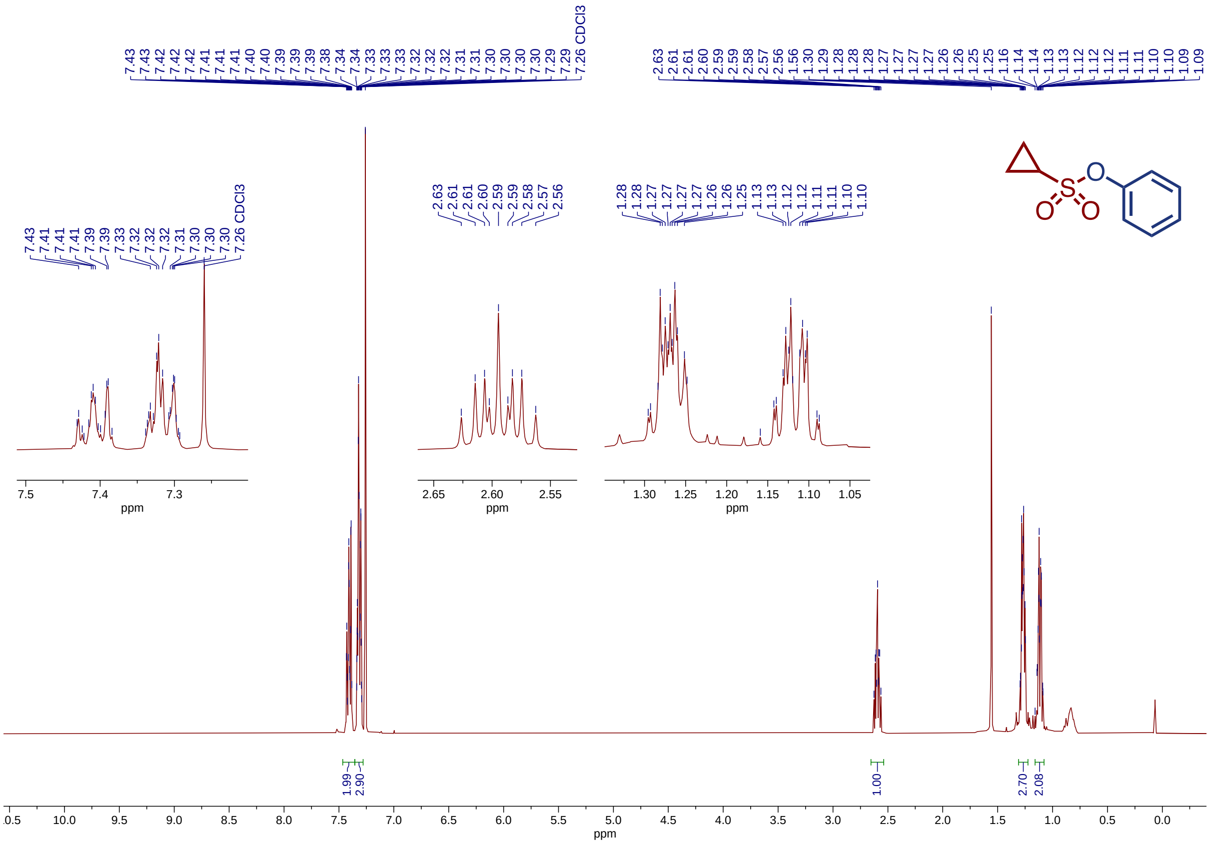
^{1}H NMR Spectrum for Compound **7j** (400 MHz, CDCl$_3$)



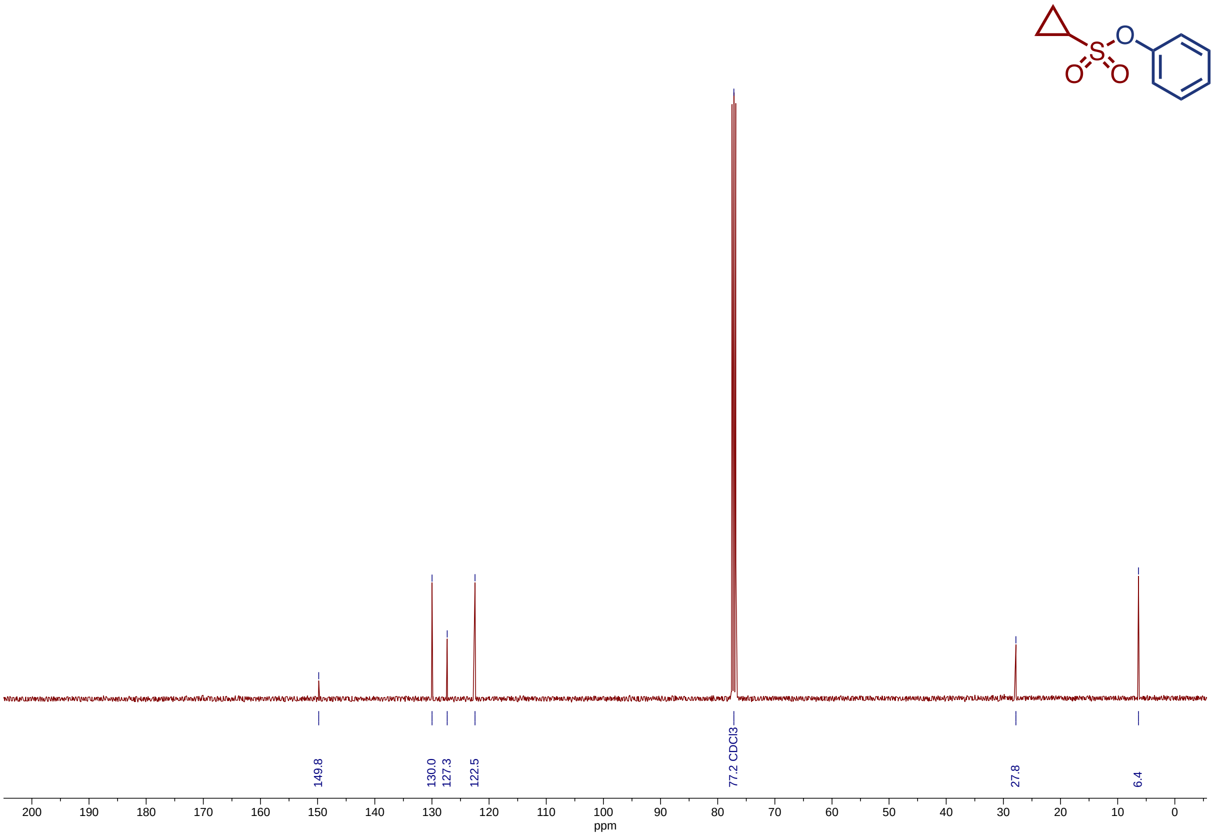
^{13}C NMR Spectrum for Compound **7j** (101 MHz, CDCl$_3$)



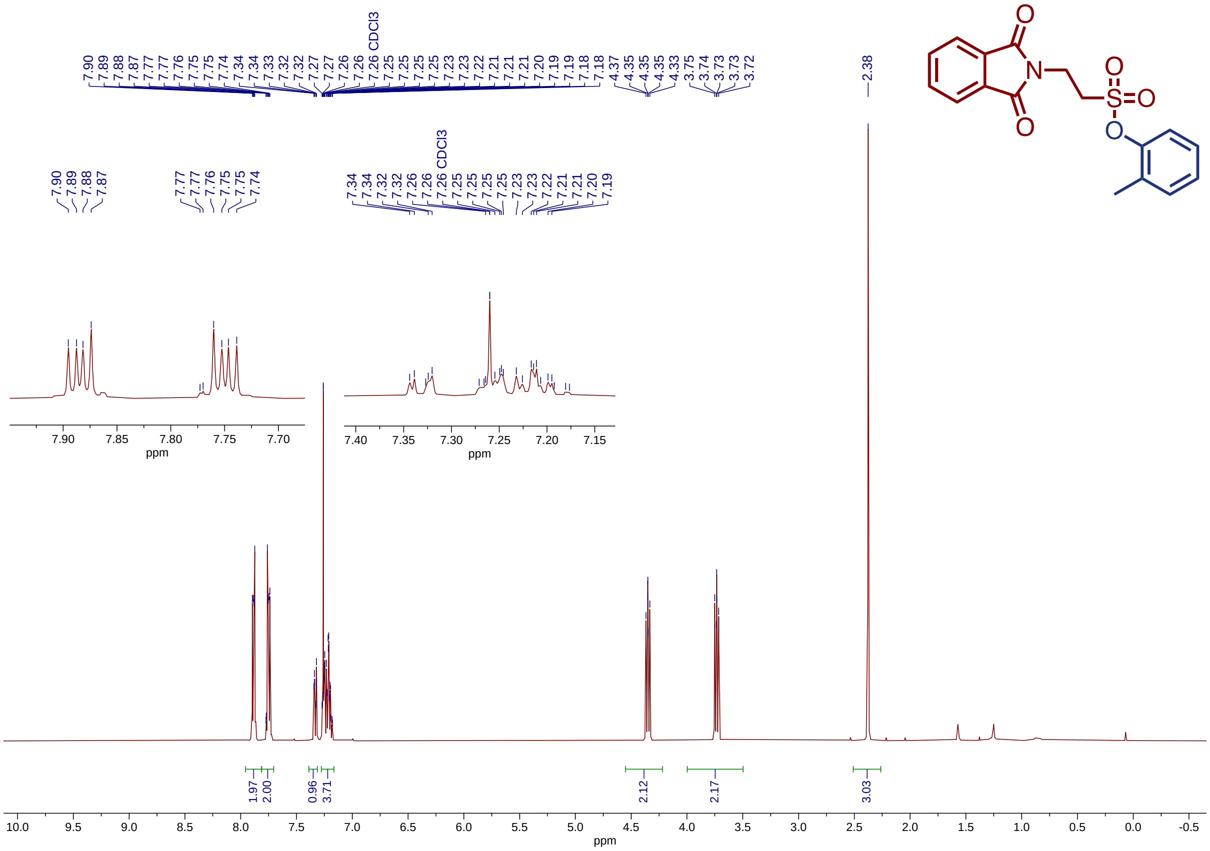
^{1}H NMR Spectrum for Compound **7k** (400 MHz, CDCl$_3$)



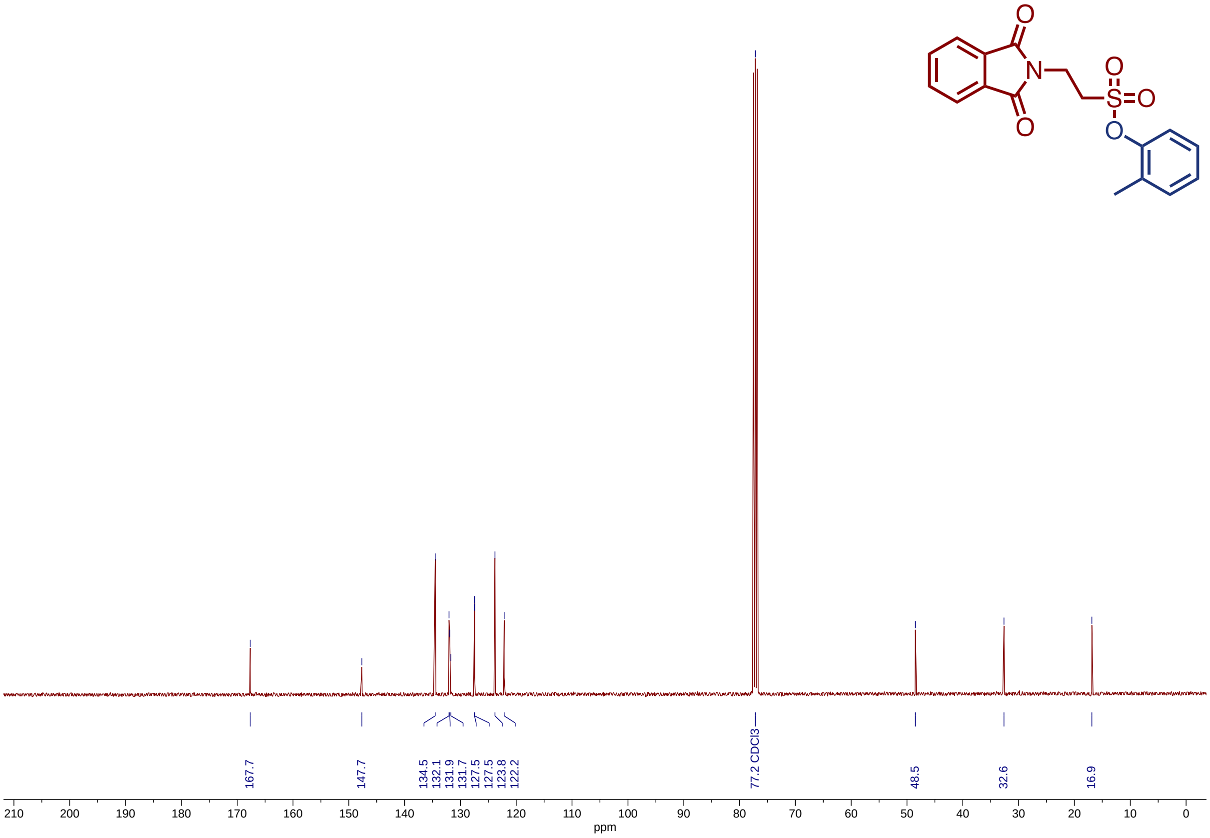
^{13}C NMR Spectrum for Compound **7k** (101 MHz, CDCl$_3$)



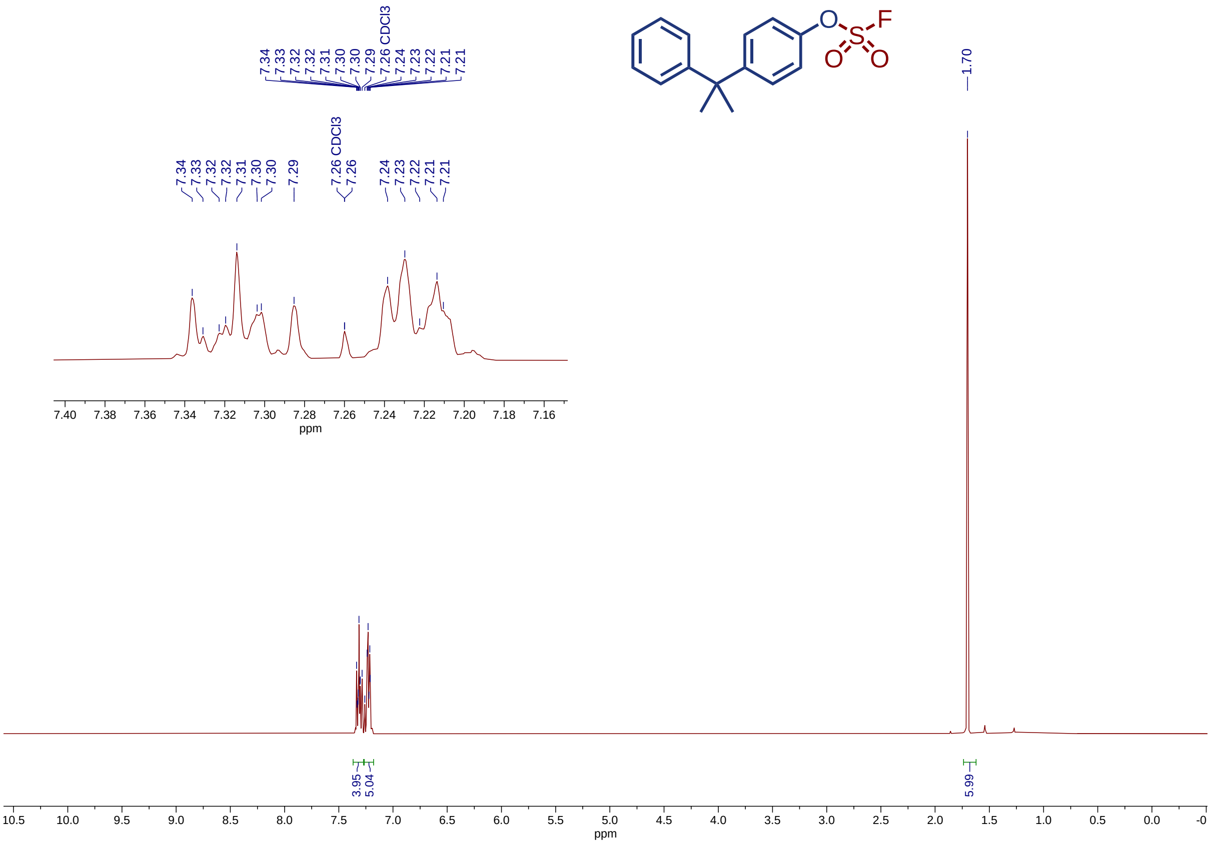
^{1}H NMR Spectrum for Compound **7l** (400 MHz, CDCl$_3$)



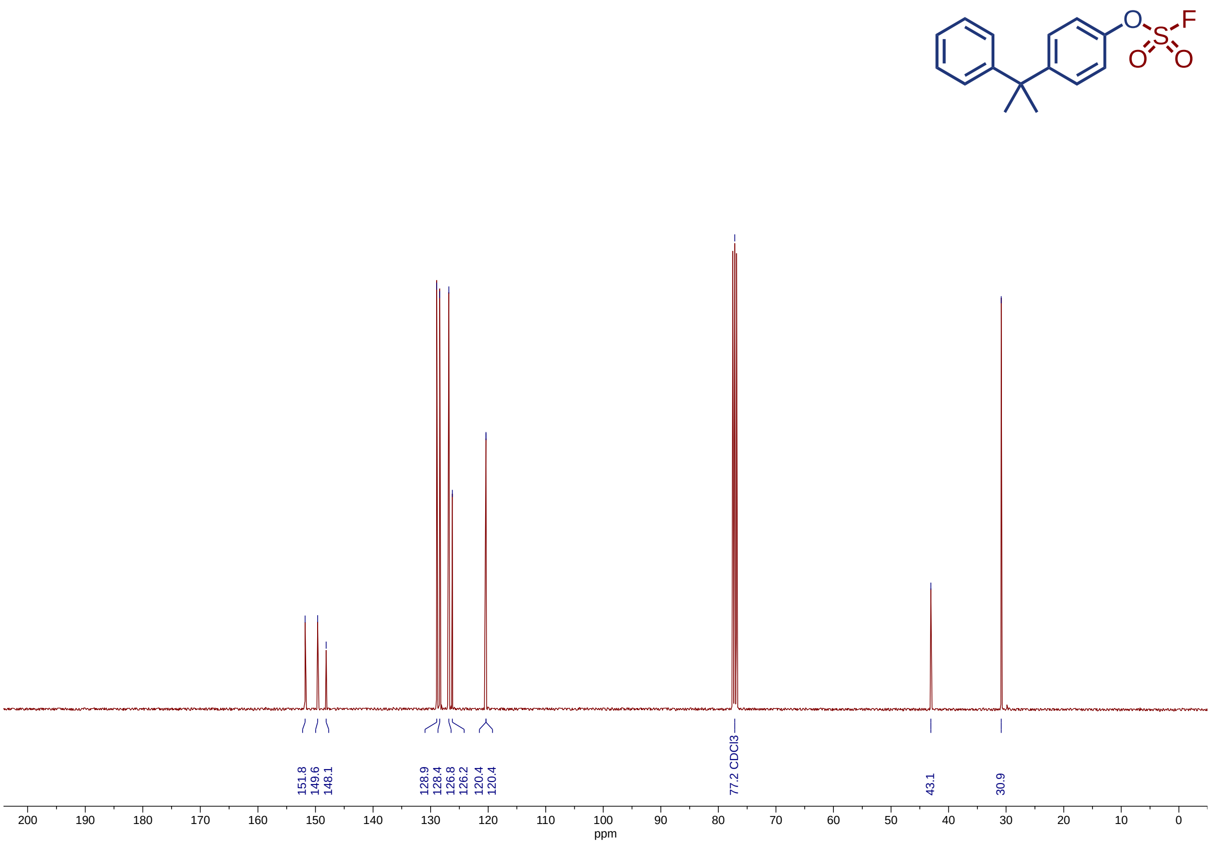
^{13}C NMR Spectrum for Compound **7l** (101 MHz, CDCl$_3$)



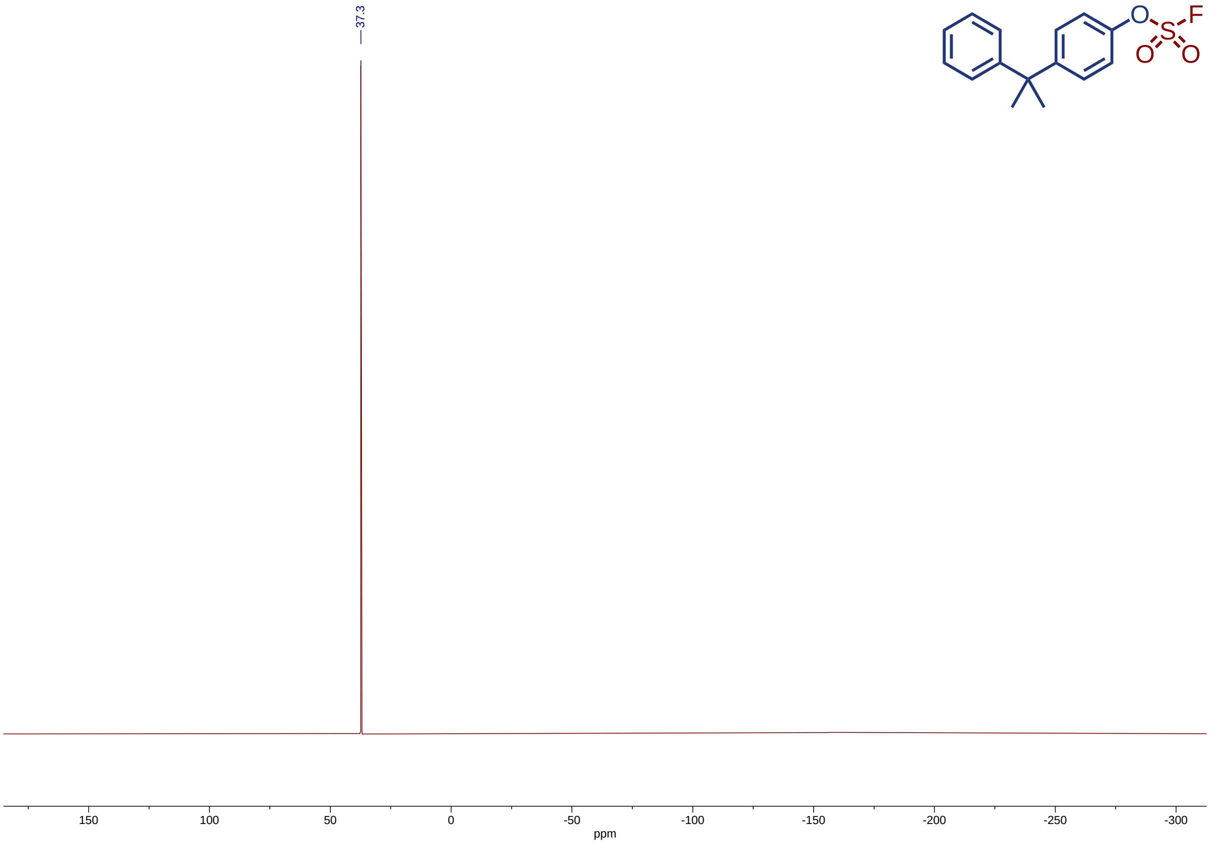
^1H NMR Spectrum for Compound **8a** (400 MHz, $CDCl_3$)



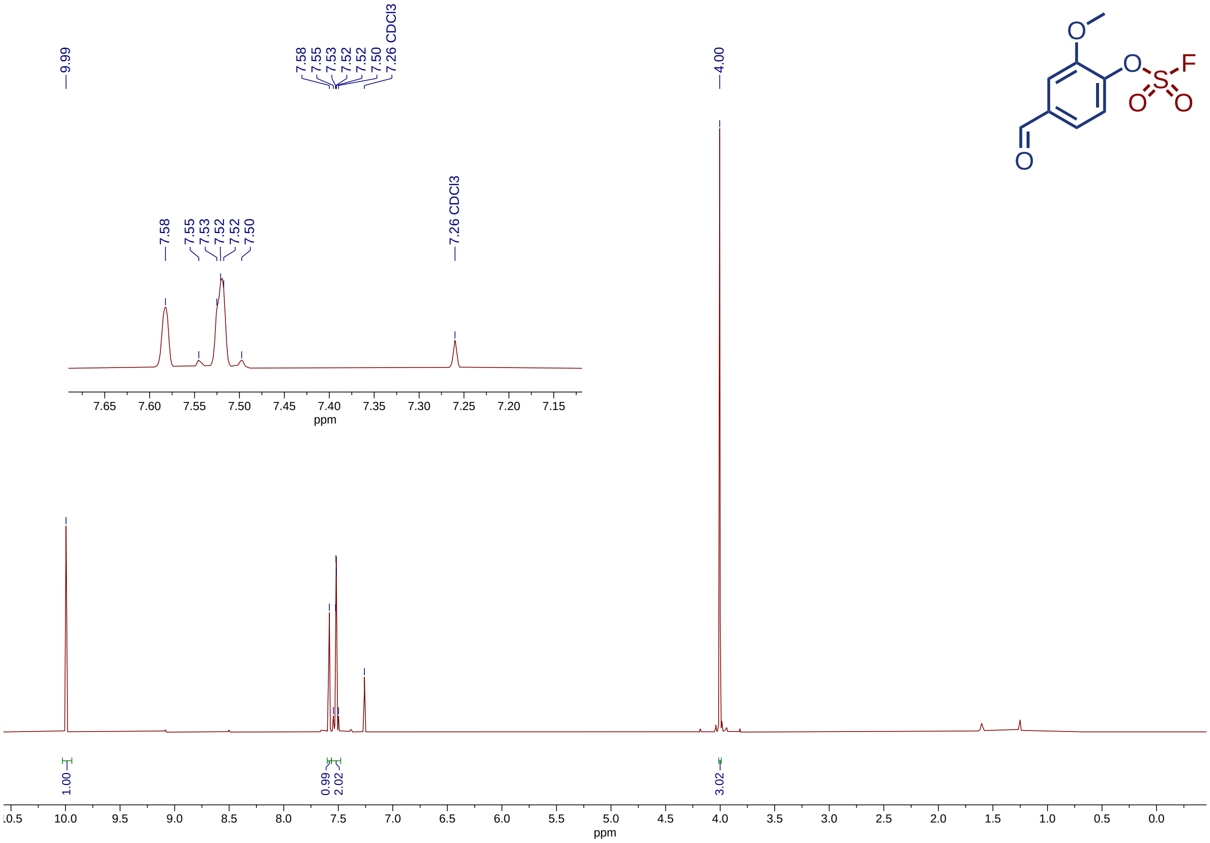
^{13}C NMR Spectrum for Compound **8a** (101 MHz, $CDCl_3$)



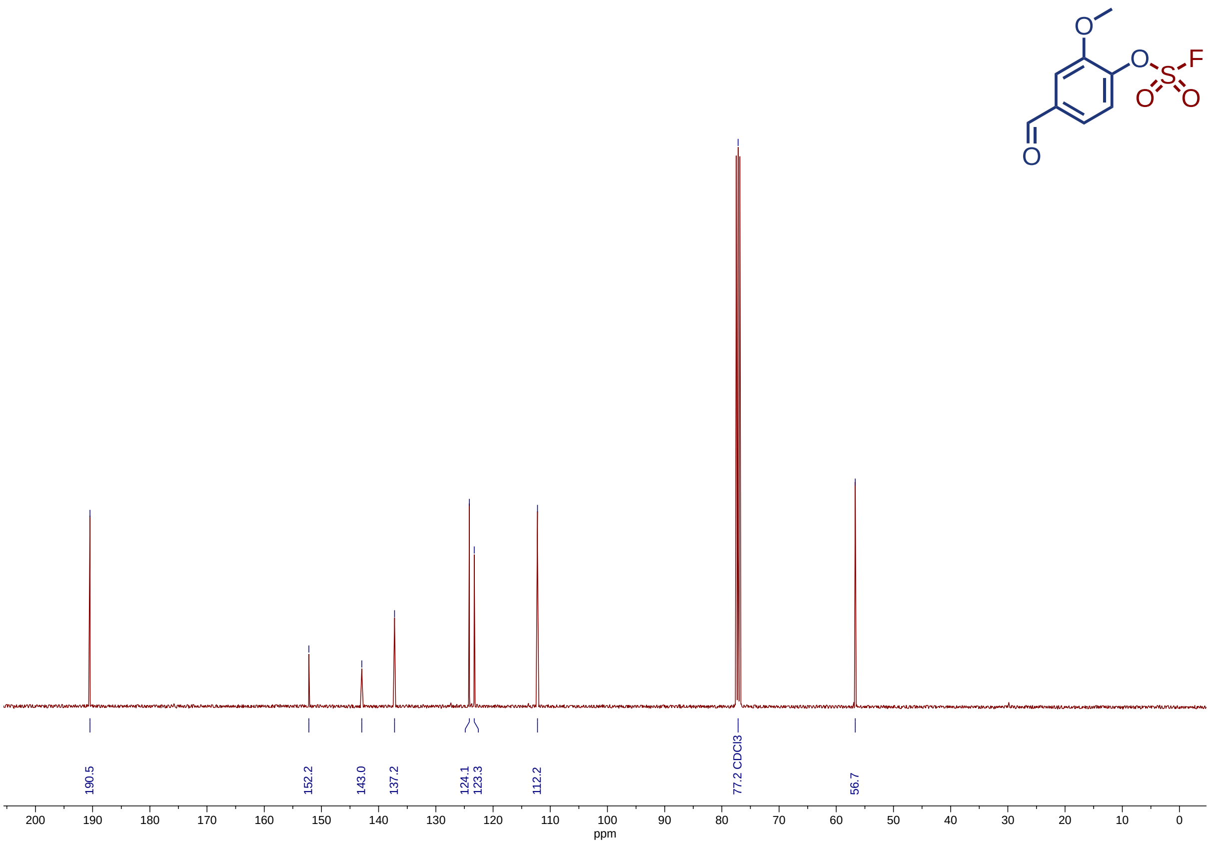
^{19}F NMR Spectrum for Compound **8a** (376 MHz, $CDCl_3$)



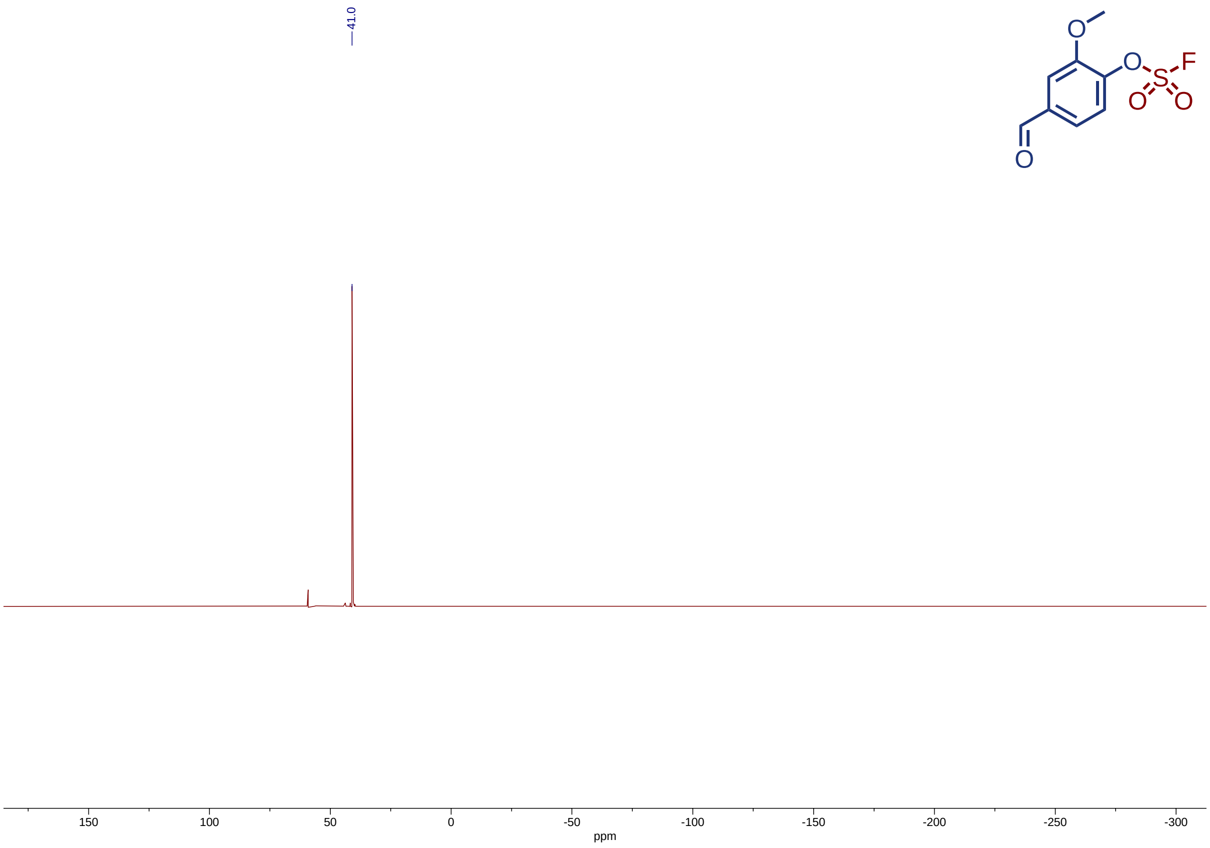
^{1}H NMR Spectrum for Compound **8b** (400 MHz, $CDCl_3$)



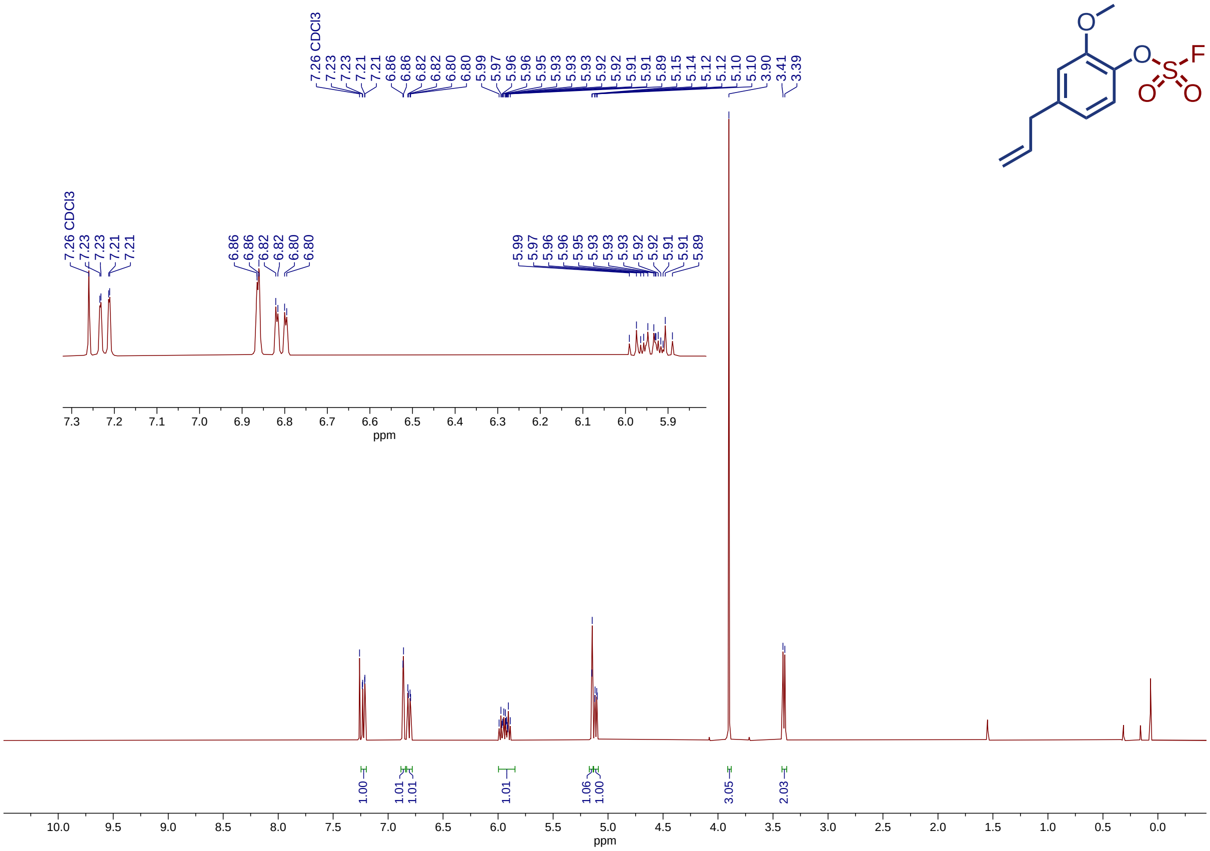
^{13}C NMR Spectrum for Compound **8b** (101 MHz, CDCl$_3$)



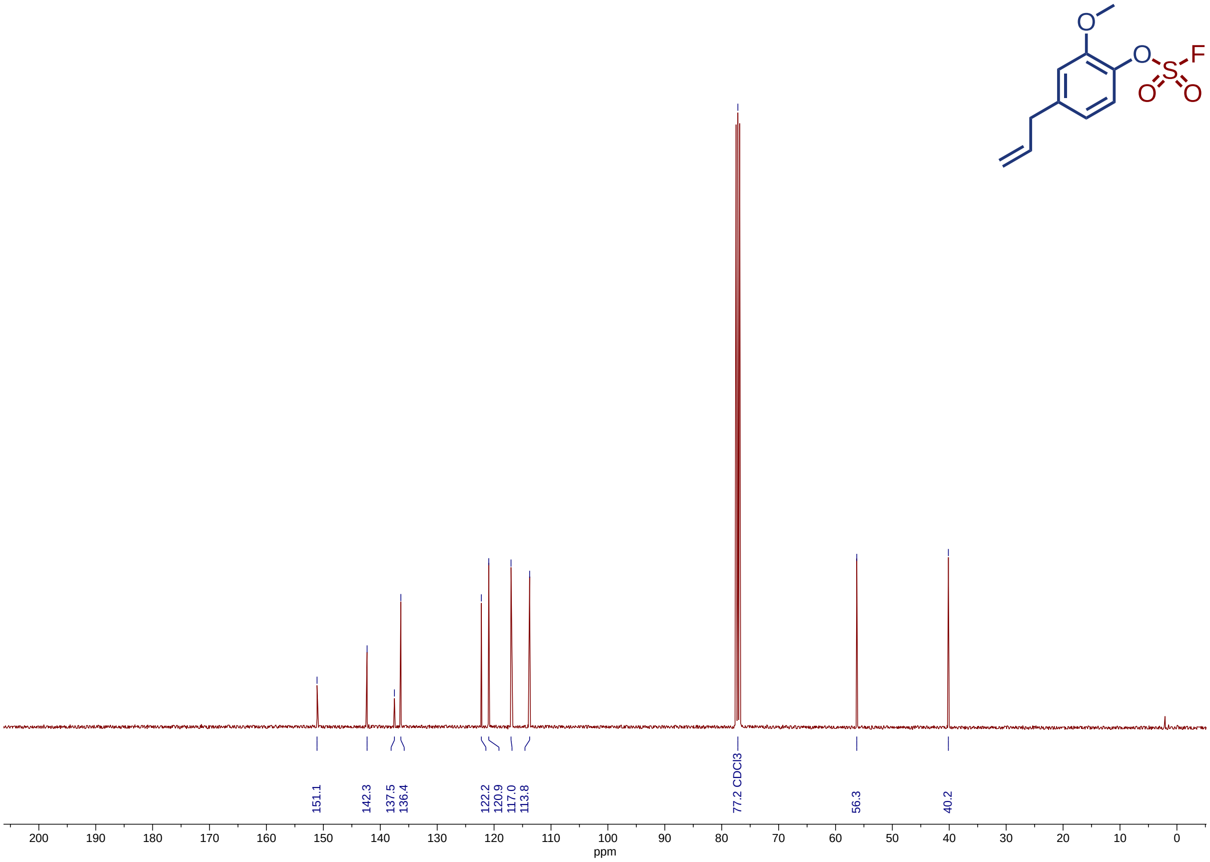
^{19}F NMR Spectrum for Compound **8b** (376 MHz, CDCl$_3$)



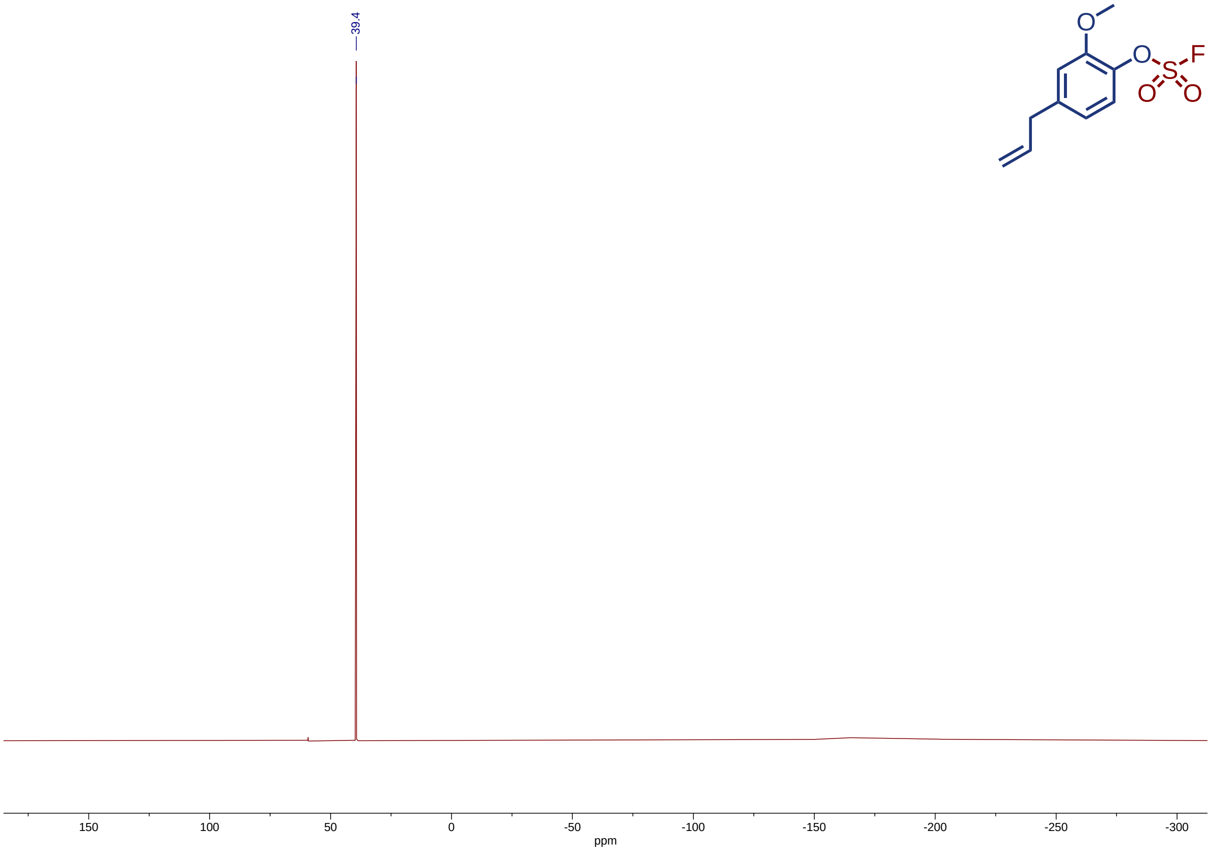
^{1}H NMR Spectrum for Compound **8c** (400 MHz, $CDCl_3$)



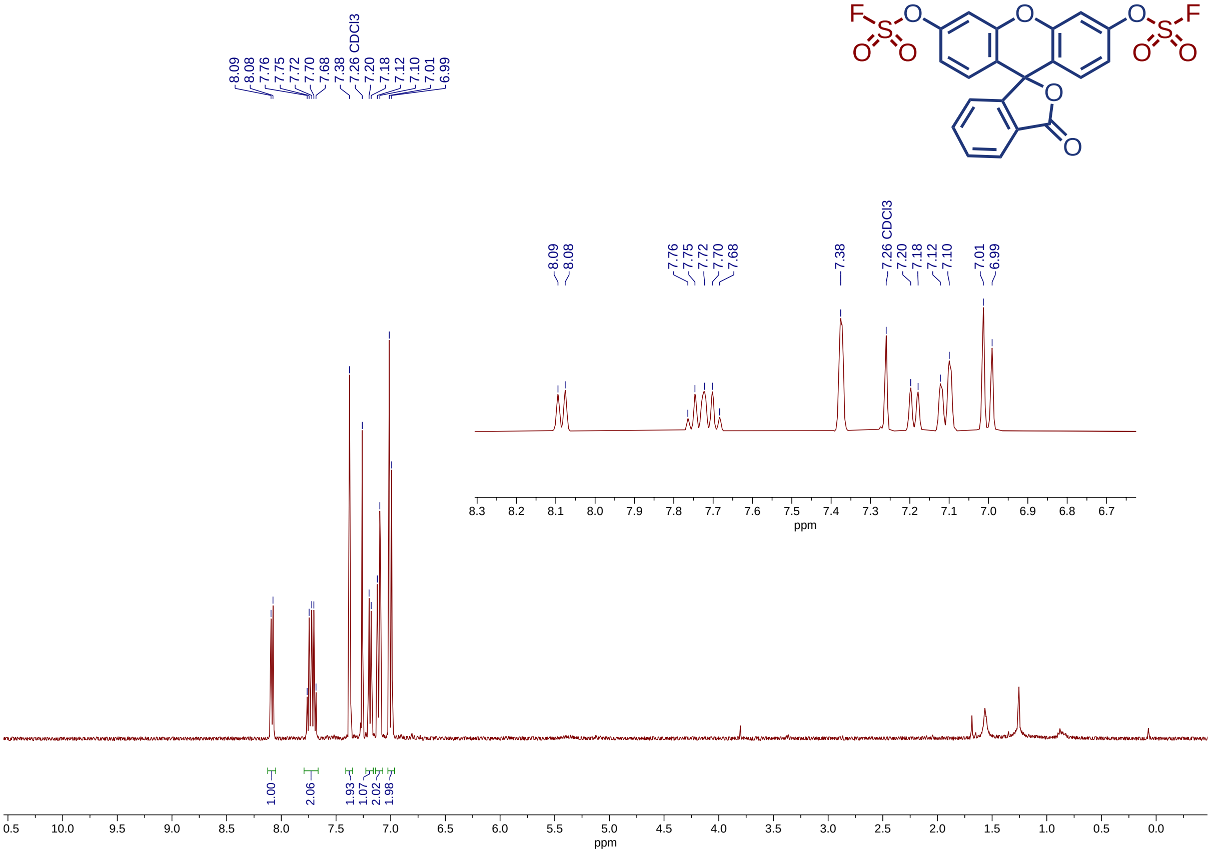
^{13}C NMR Spectrum for Compound **8c** (101 MHz, $CDCl_3$)



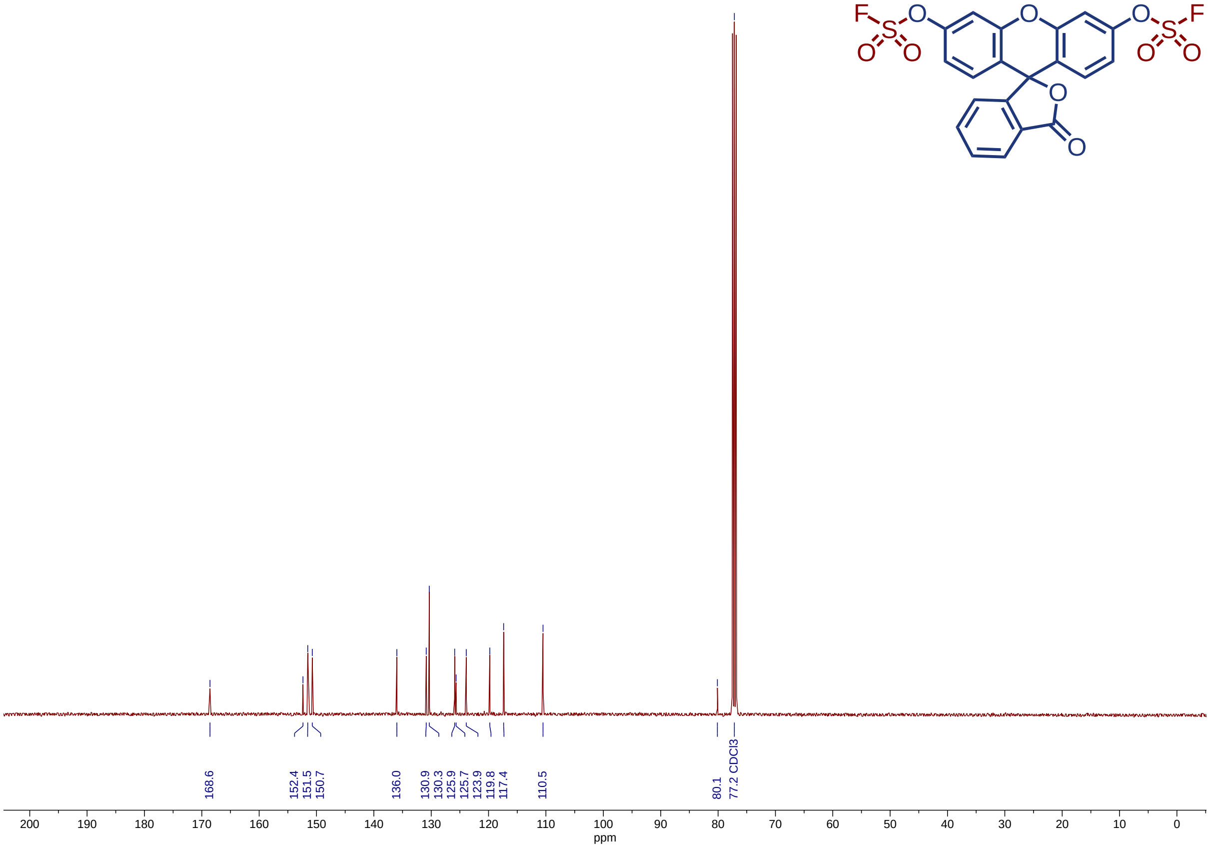
^{19}F NMR Spectrum for Compound **8c** (376 MHz, CDCl$_3$)



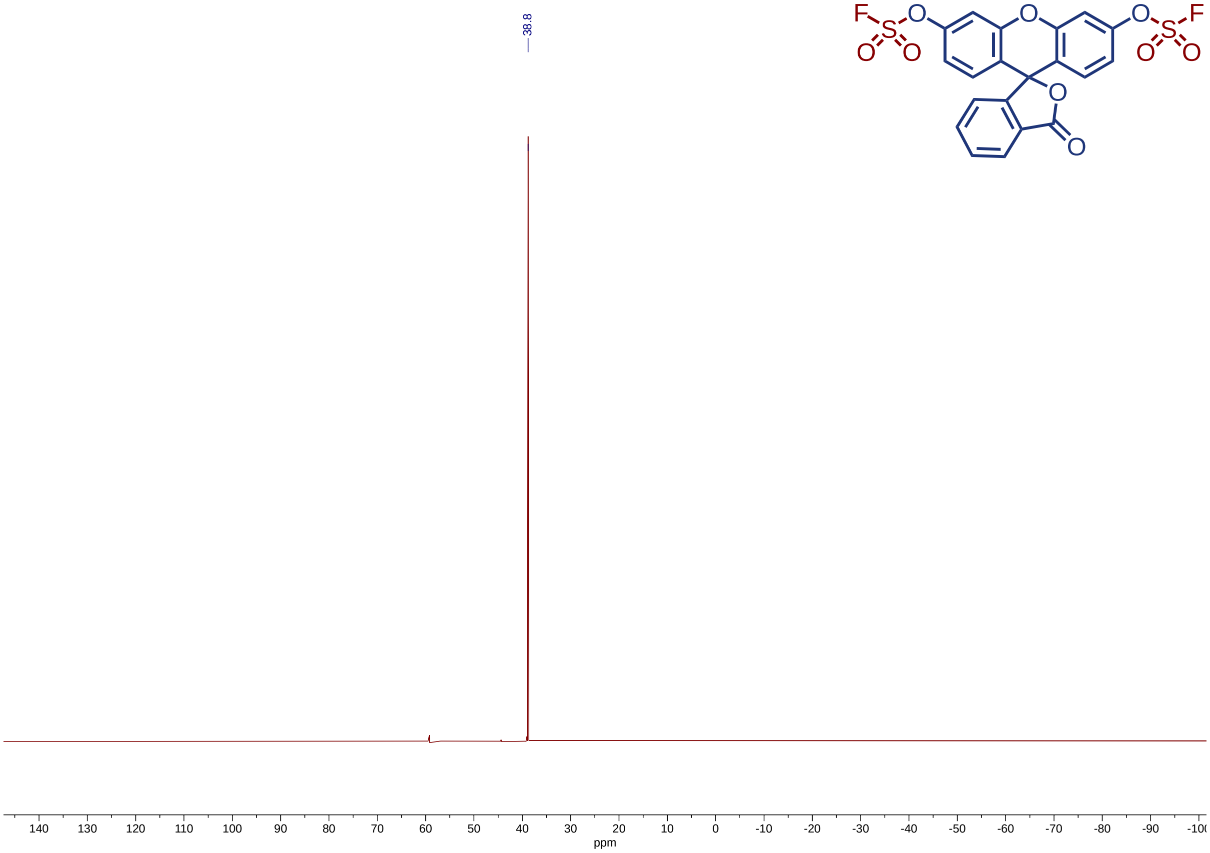
^{1}H NMR Spectrum for Compound **8d** (400 MHz, CDCl$_3$)



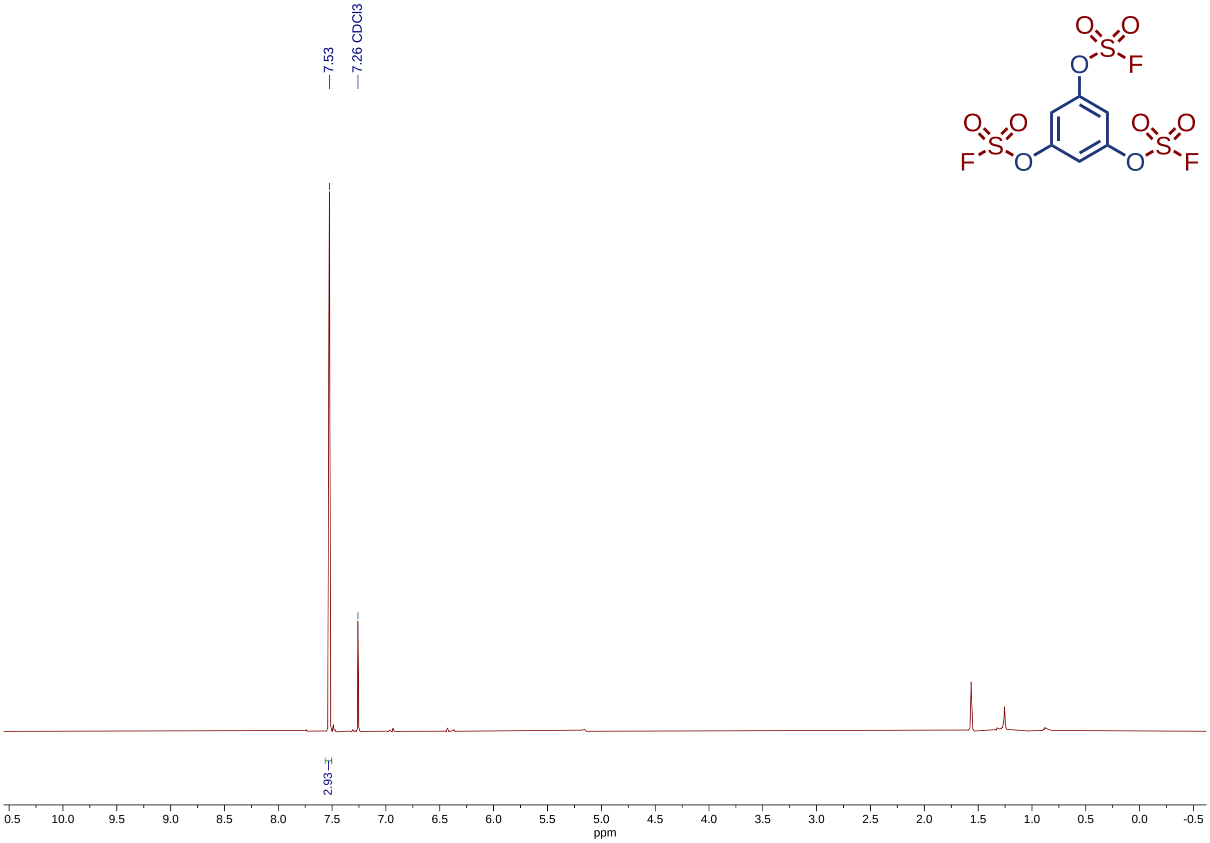
^{13}C NMR Spectrum for Compound **8d** (101 MHz, $CDCl_3$)



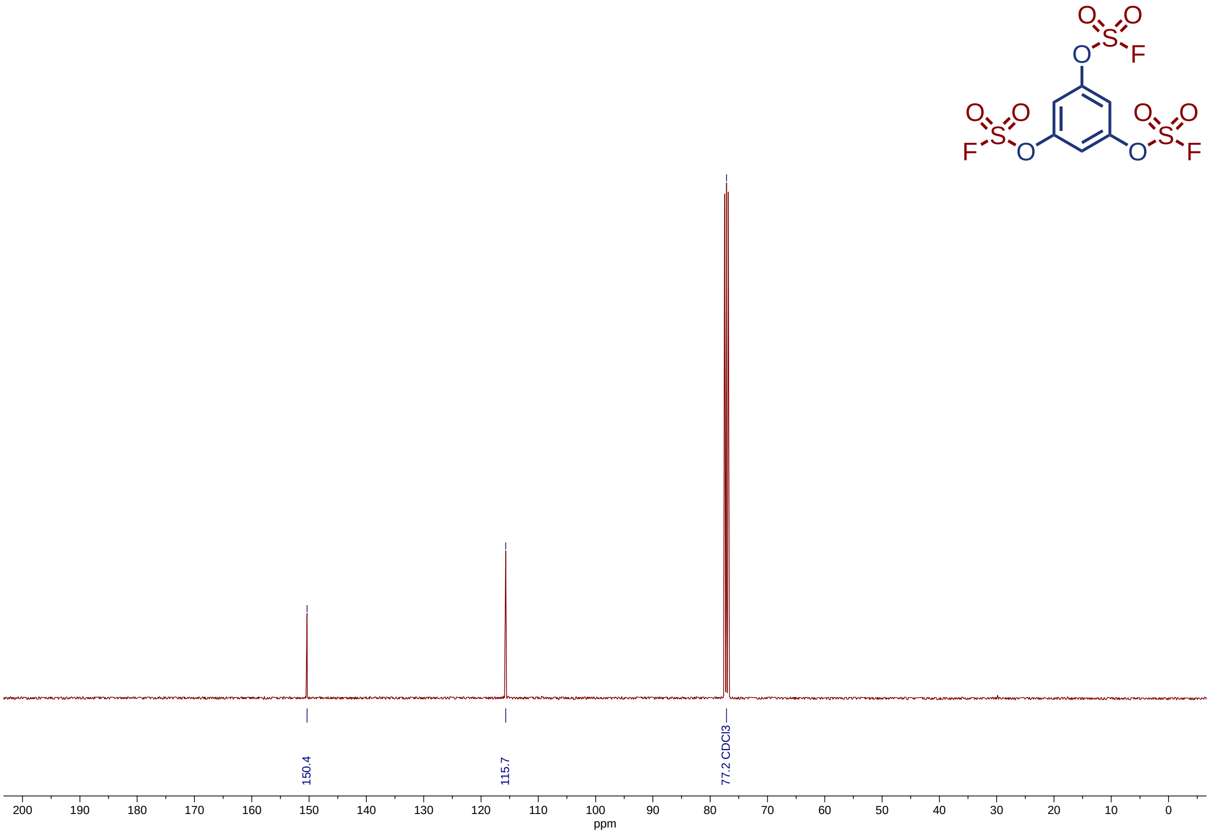
^{19}F NMR Spectrum for Compound **8d** (376 MHz, $CDCl_3$)



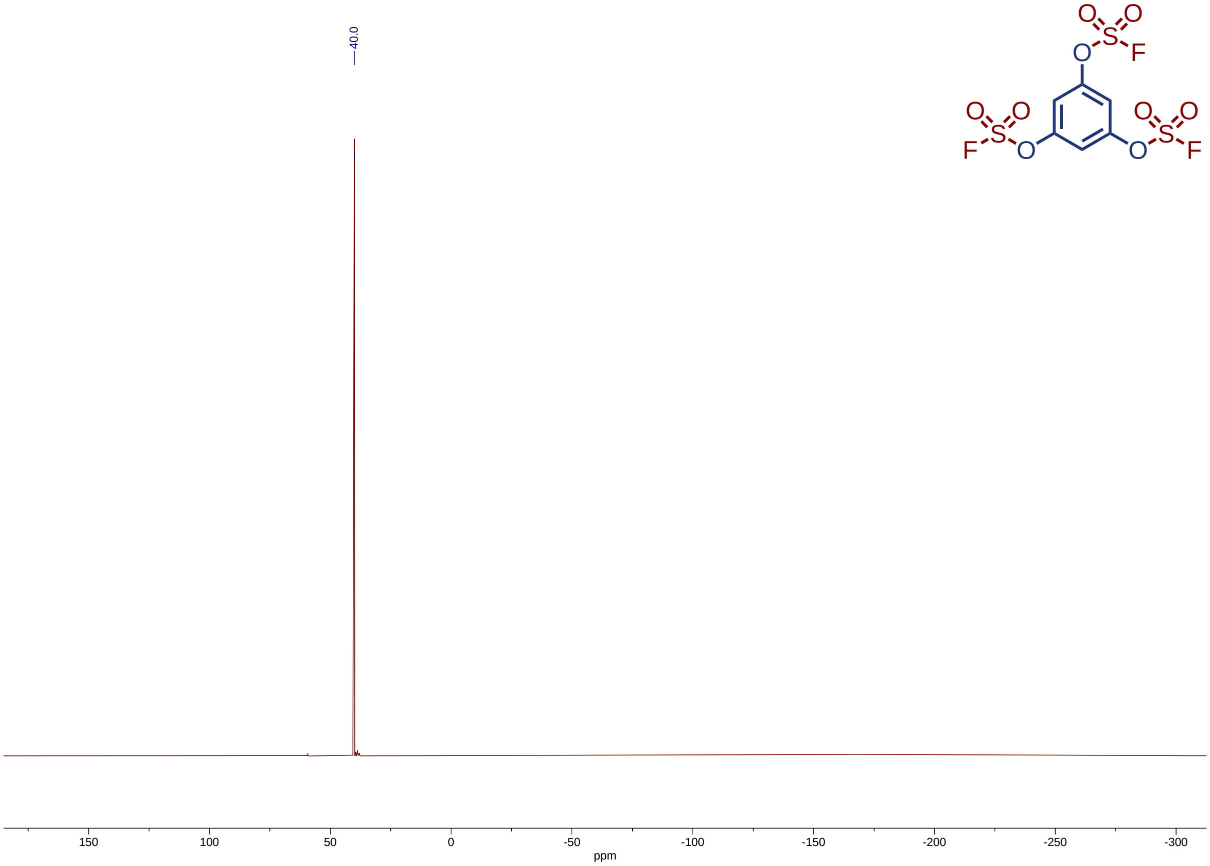
^{1}H NMR Spectrum for Compound **8e** (400 MHz, $CDCl_3$)



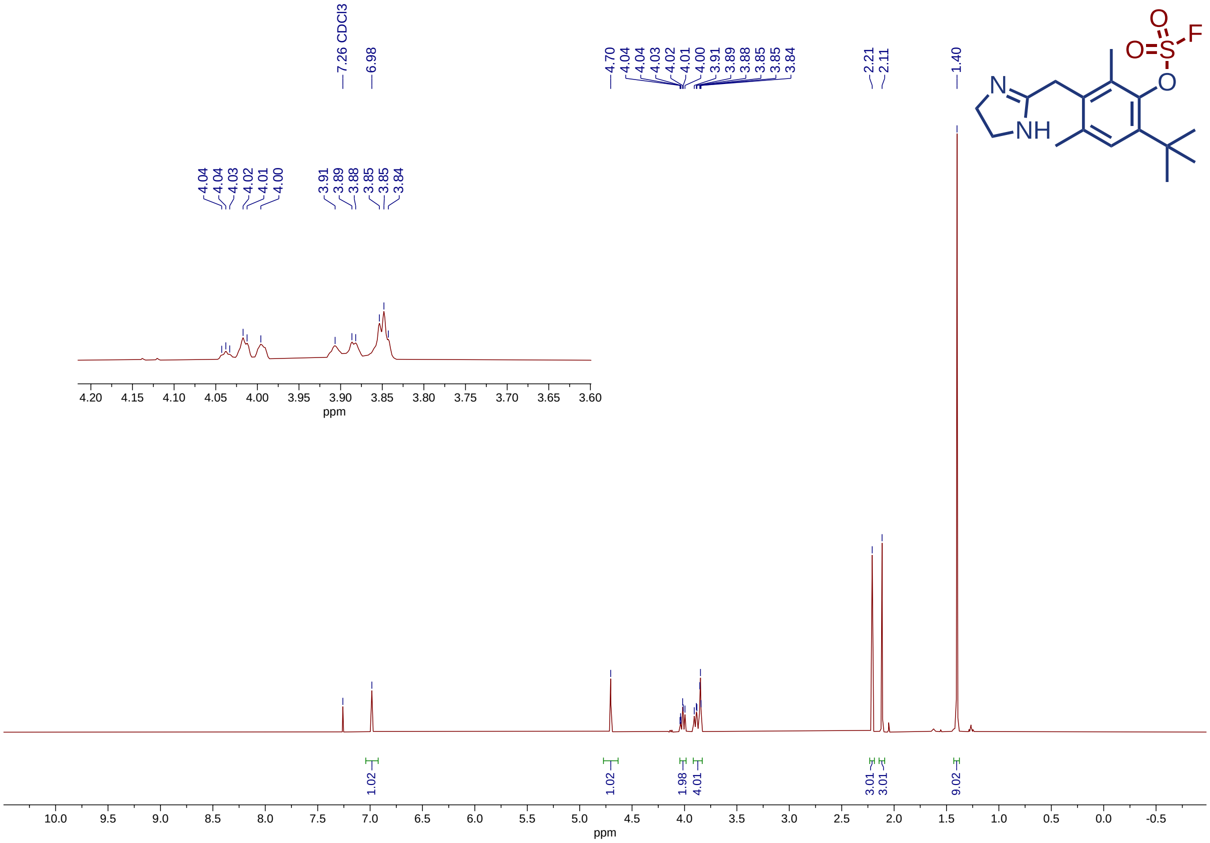
^{13}C NMR Spectrum for Compound **8e** (101 MHz, $CDCl_3$)



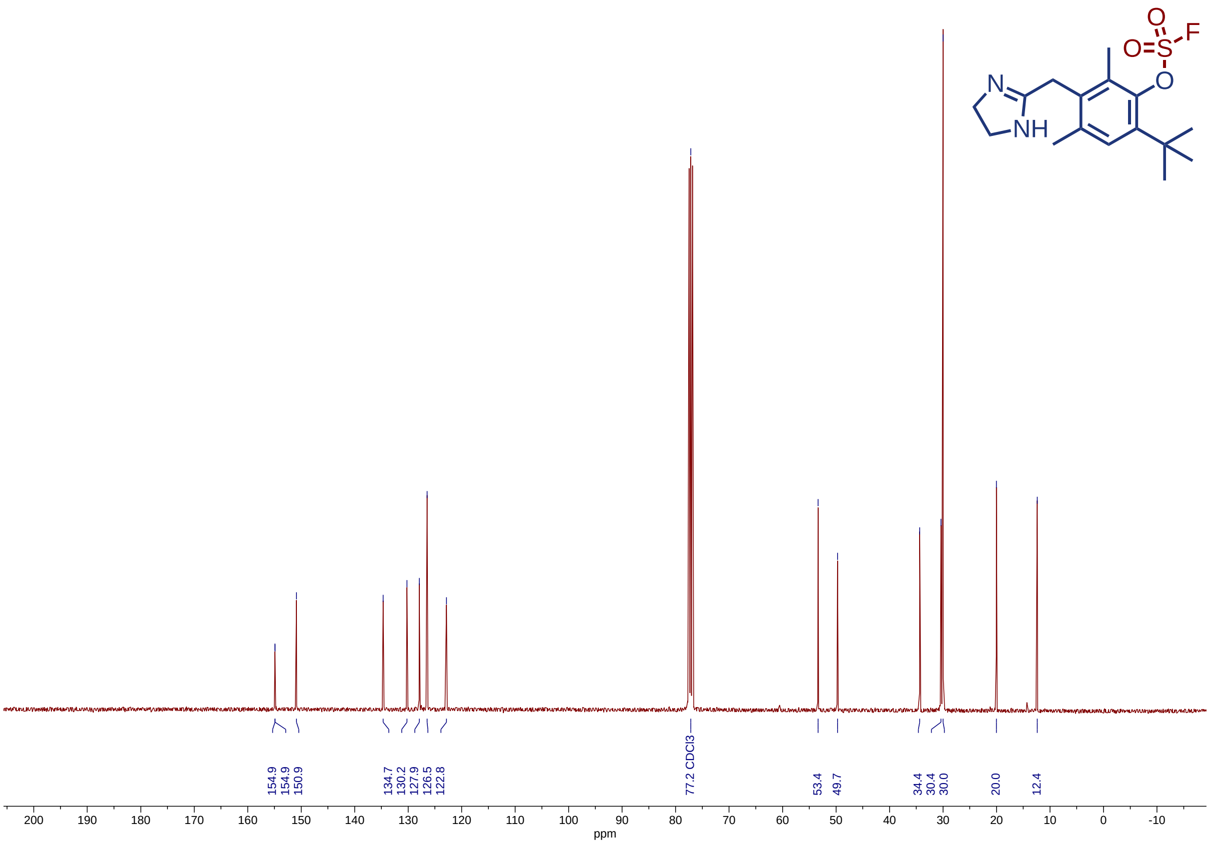
^{19}F NMR Spectrum for Compound **8e** (376 MHz, CDCl$_3$)



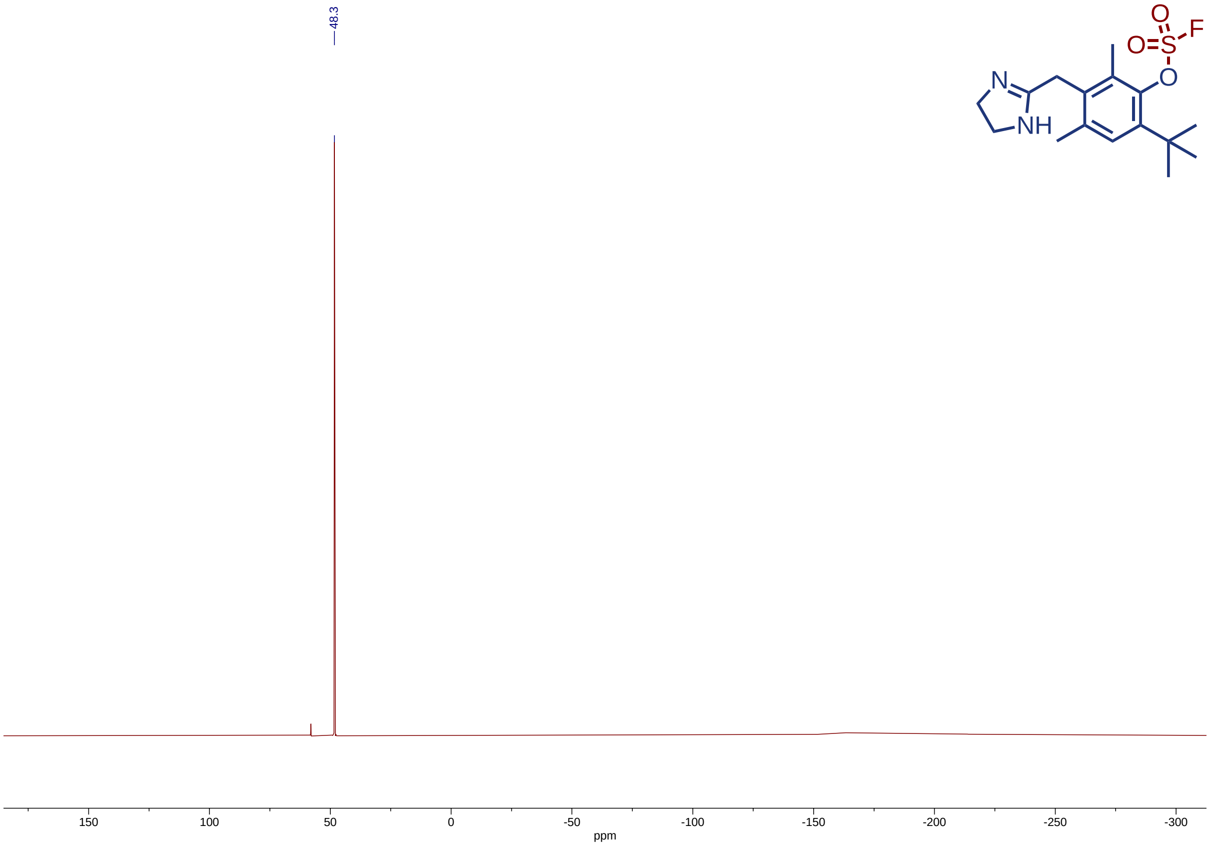
^{1}H NMR Spectrum for Compound **8f** (400 MHz, CDCl$_3$)



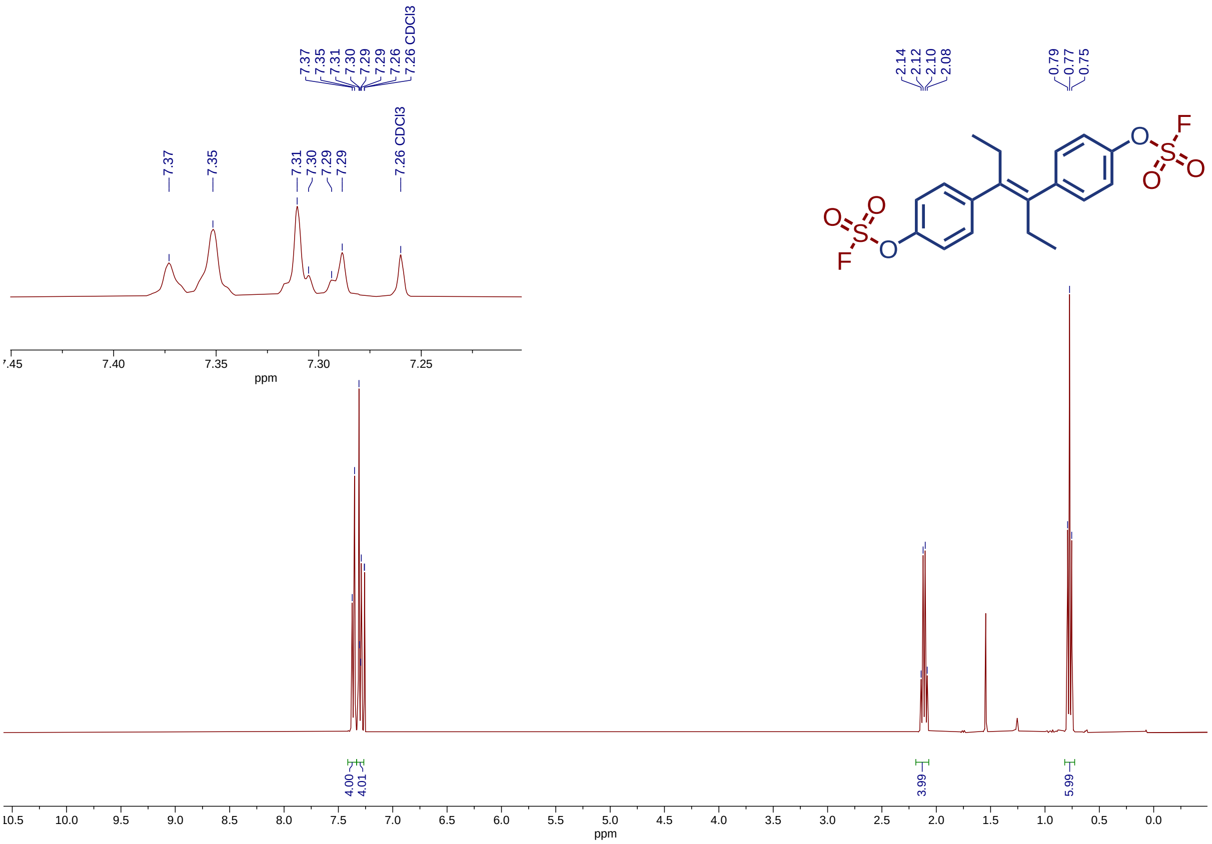
^{13}C NMR Spectrum for Compound **8f** (101 MHz, $CDCl_3$)



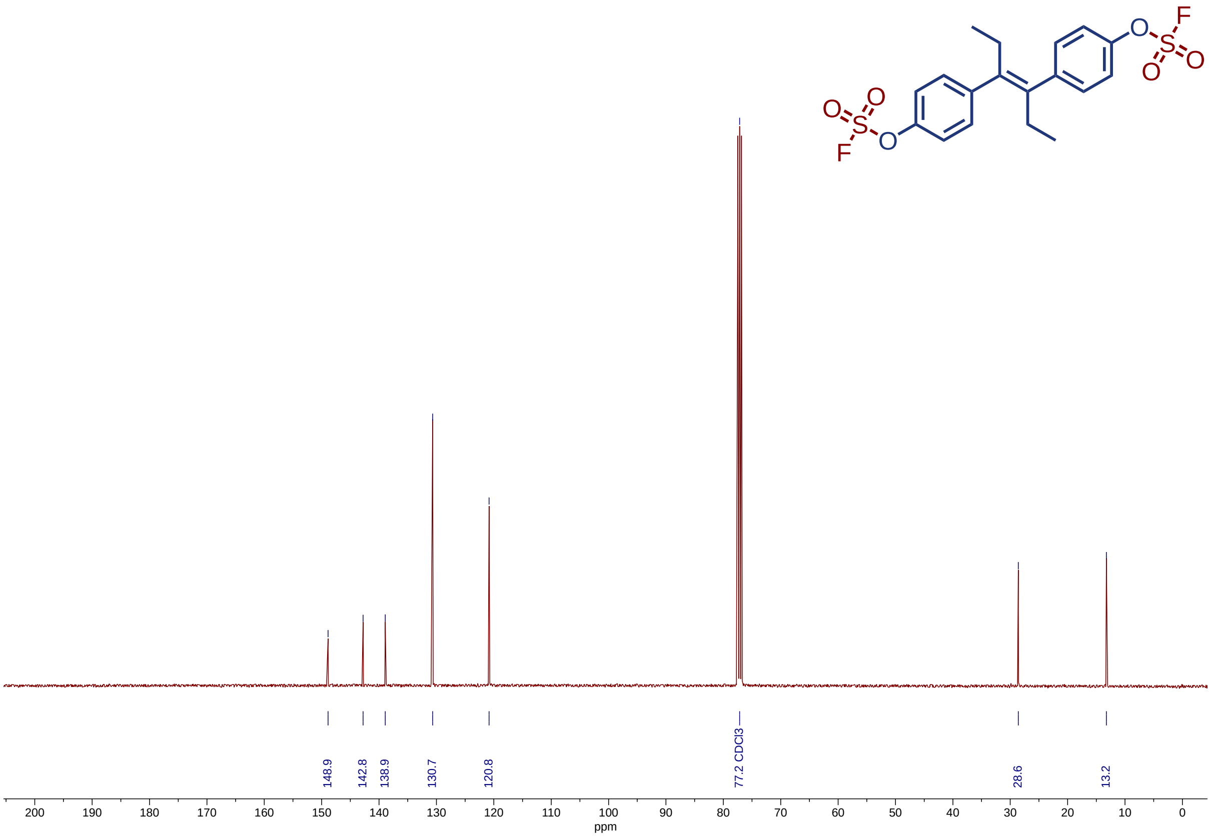
^{19}F NMR Spectrum for Compound **8f** (376 MHz, $CDCl_3$)



^{1}H NMR Spectrum for Compound **8g** (400 MHz, $CDCl_3$)

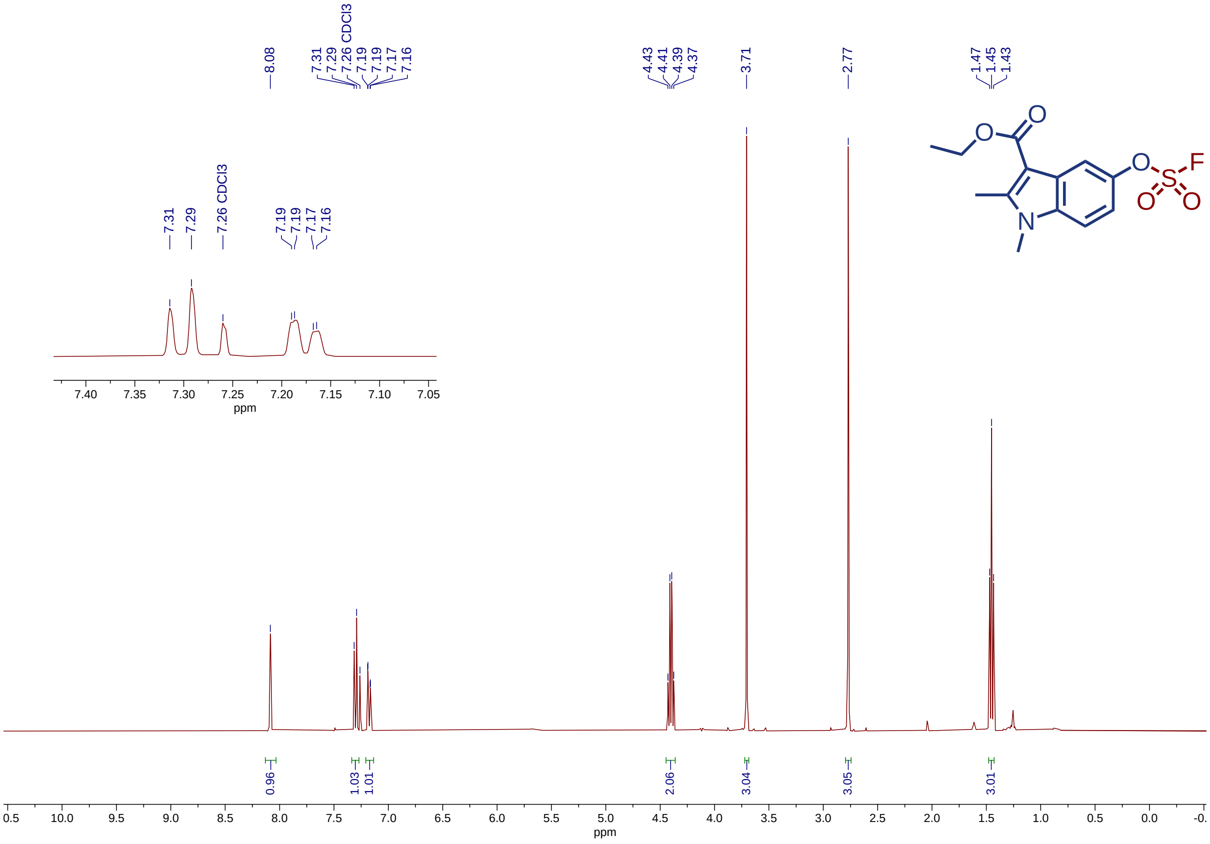


^{13}C NMR Spectrum for Compound **8g** (101 MHz, $CDCl_3$)

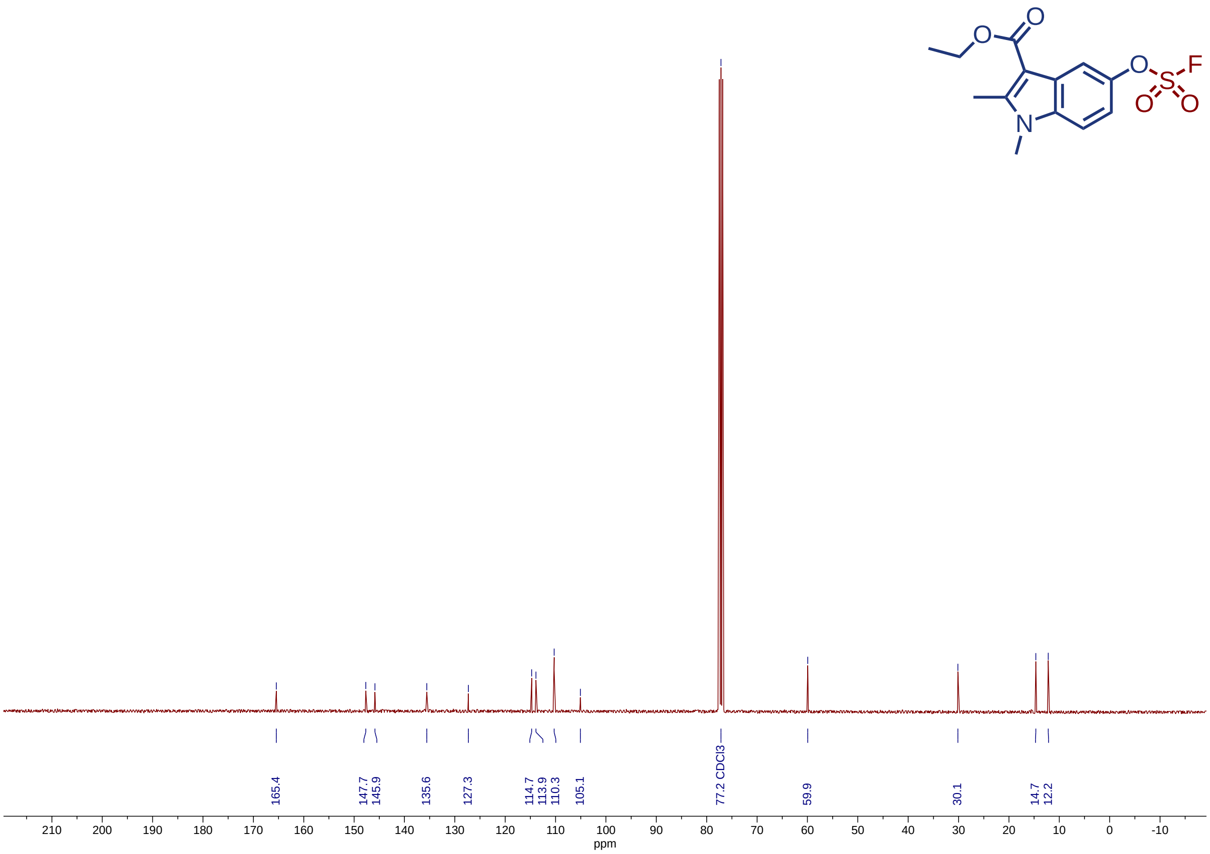


^{19}F NMR Spectrum for Compound **8g** (376 MHz, CDCl$_3$)

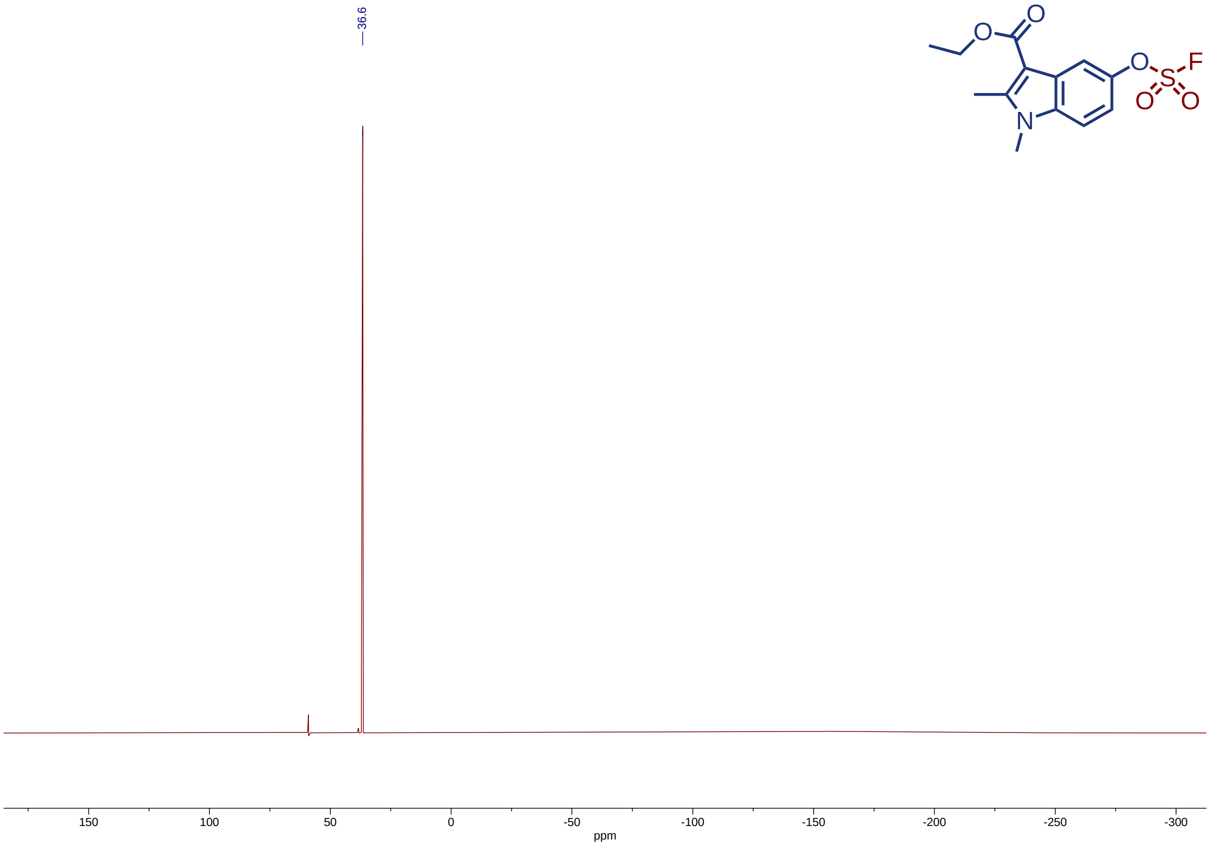
^{1}H NMR Spectrum for Compound **8h** (400 MHz, CDCl$_3$)



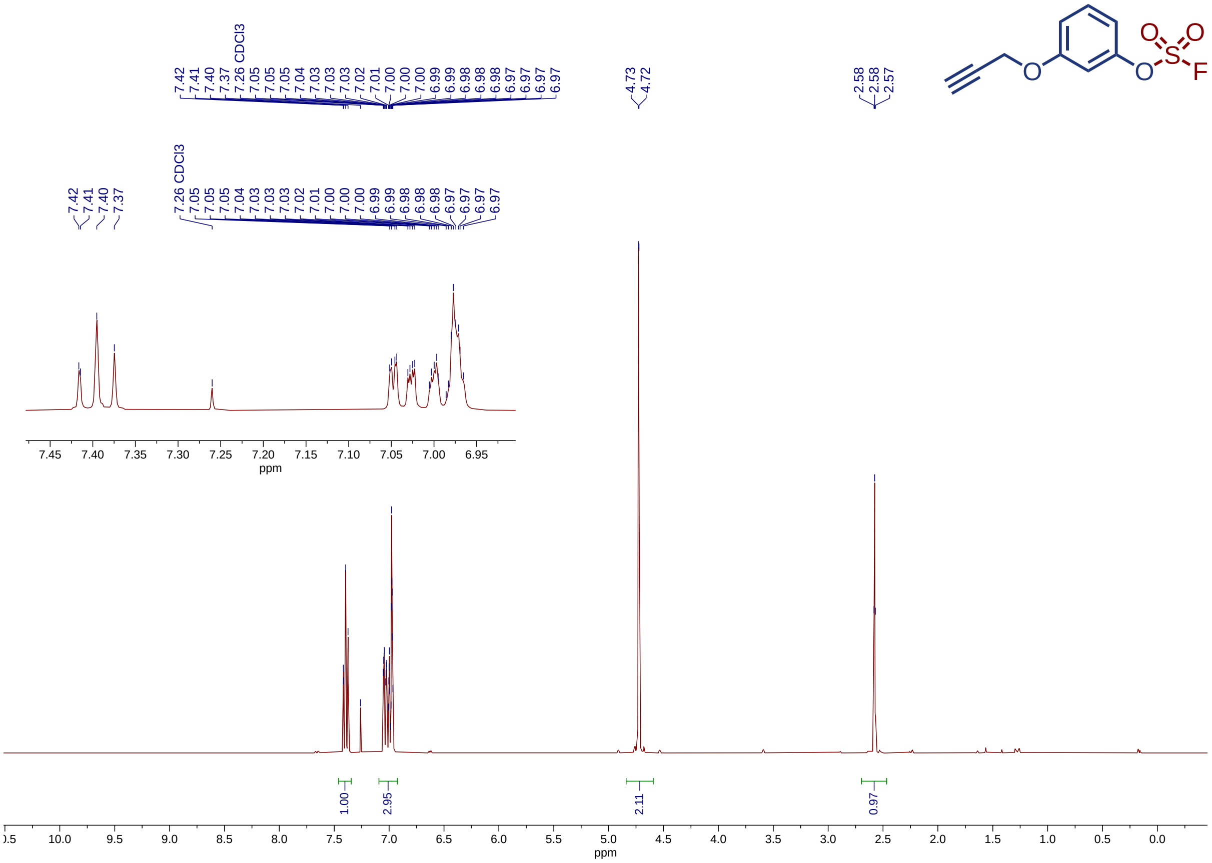
^{13}C NMR Spectrum for Compound **8h** (101 MHz, $CDCl_3$)



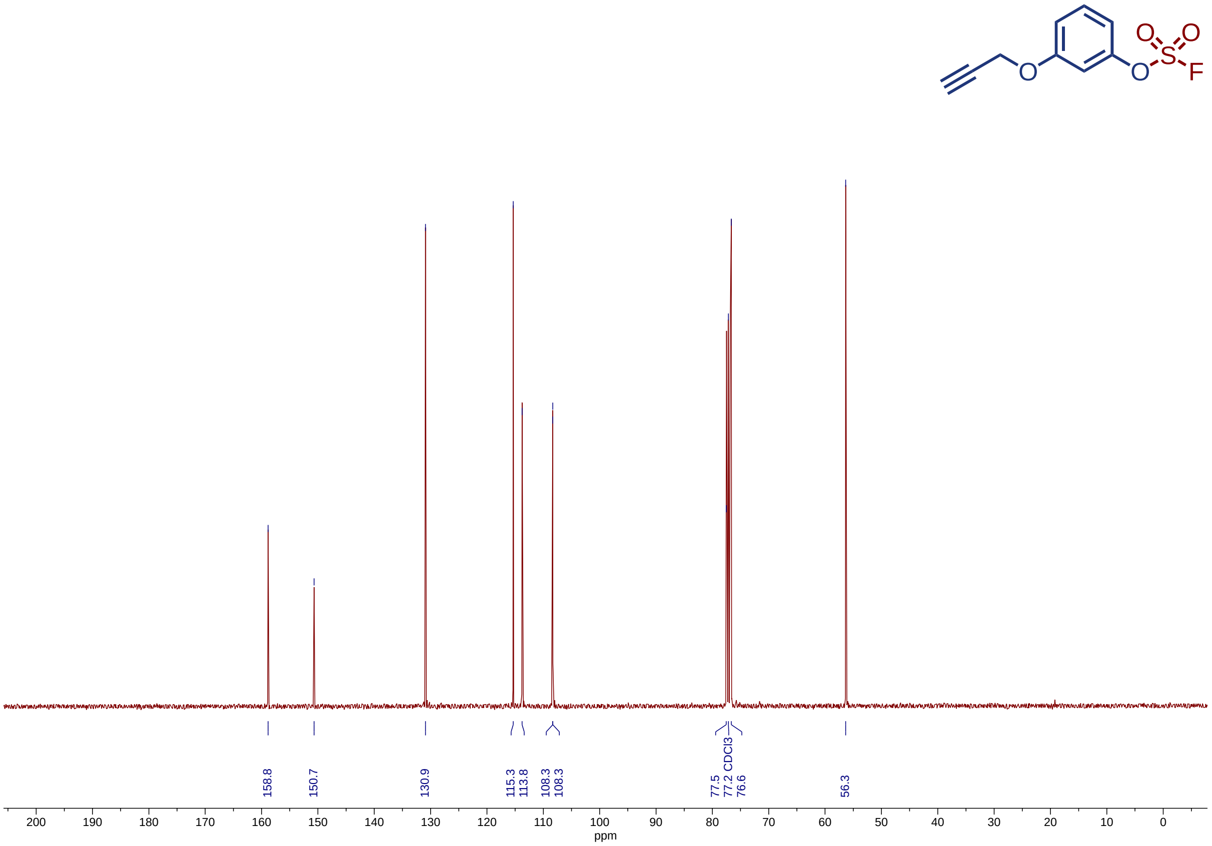
^{19}F NMR Spectrum for Compound **8h** (376 MHz, $CDCl_3$)



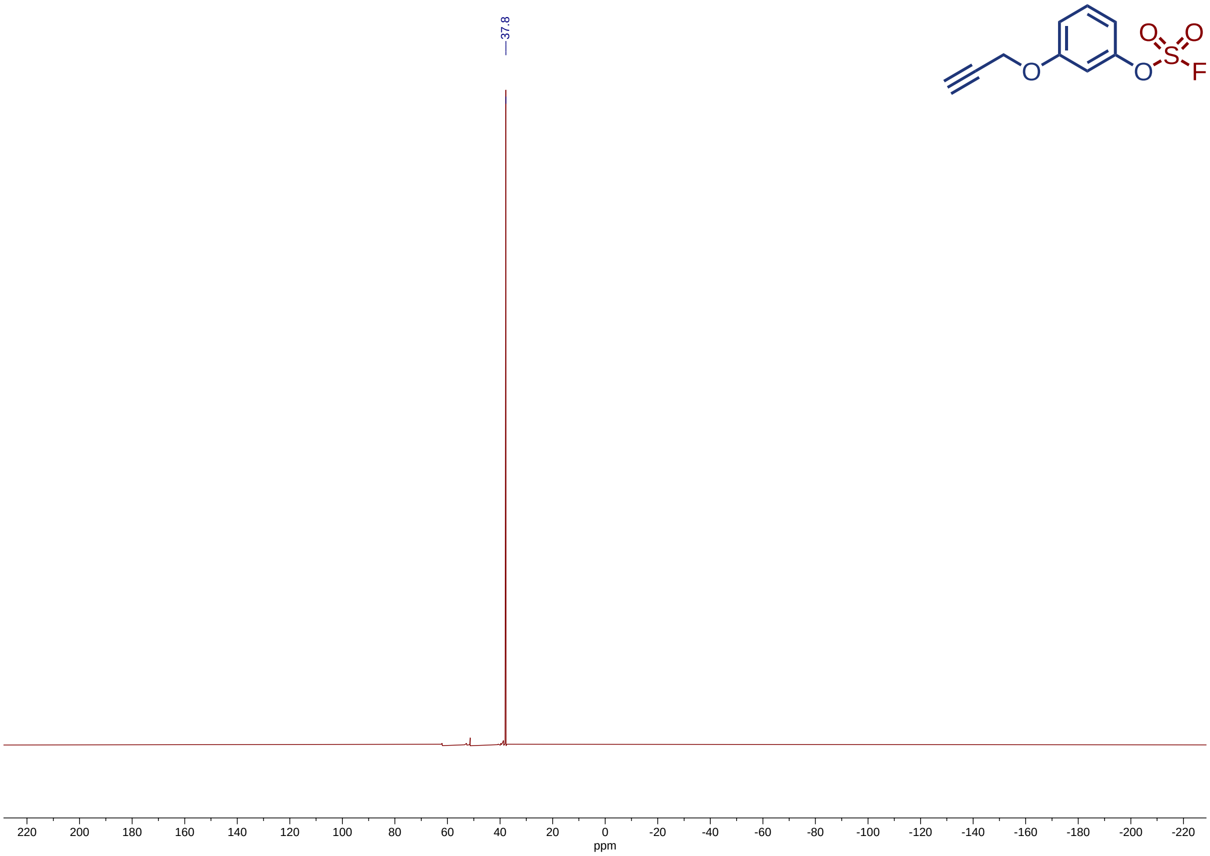
^{1}H NMR Spectrum for Compound **8i** (400 MHz, CDCl$_3$)



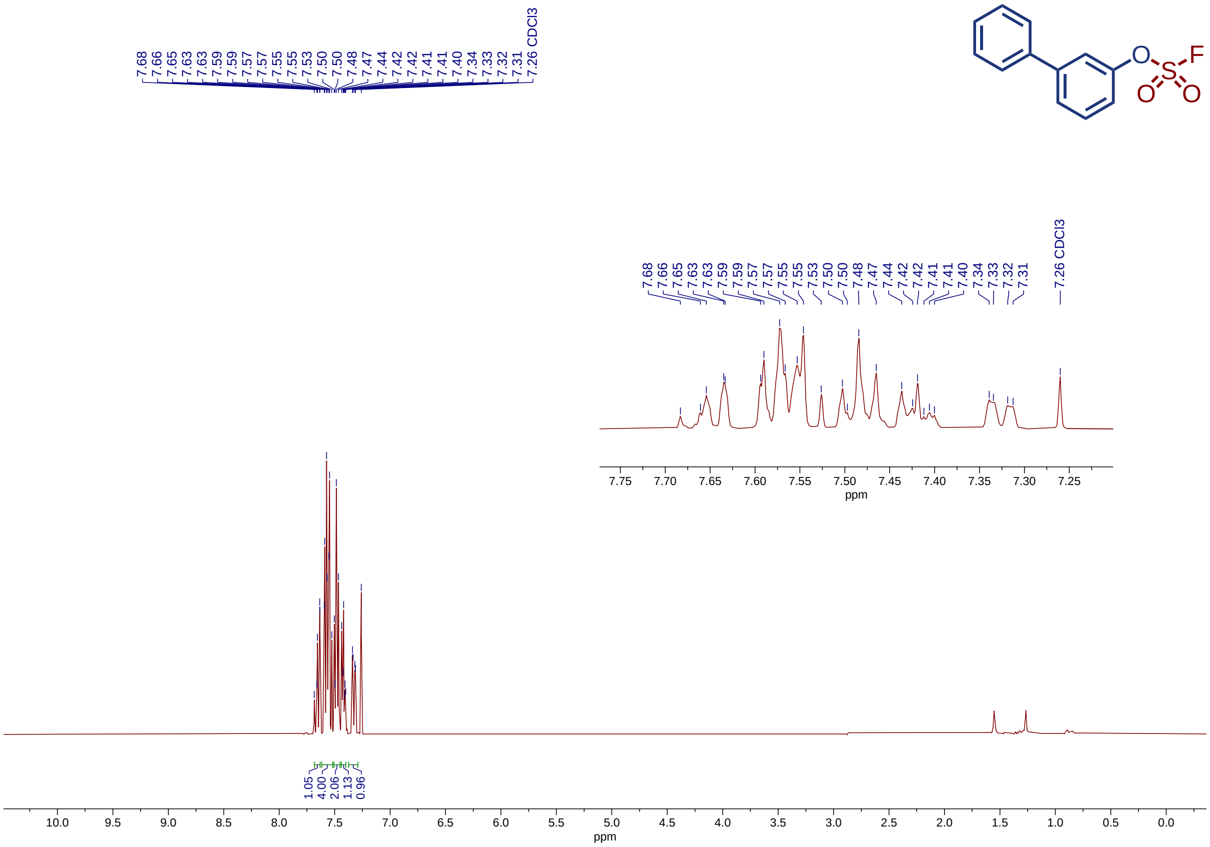
^{13}C NMR Spectrum for Compound **8i** (101 MHz, CDCl$_3$)



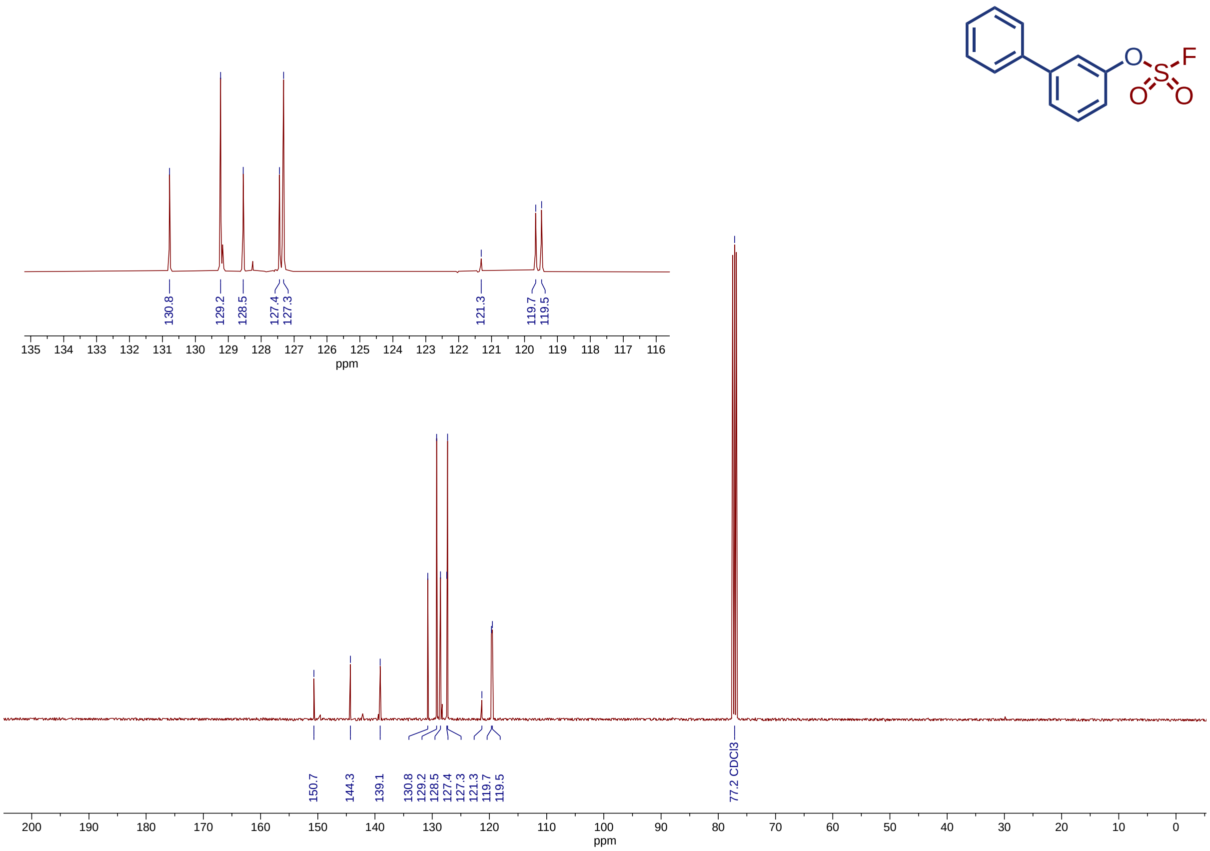
^{19}F NMR Spectrum for Compound **8i** (376 MHz, $CDCl_3$)



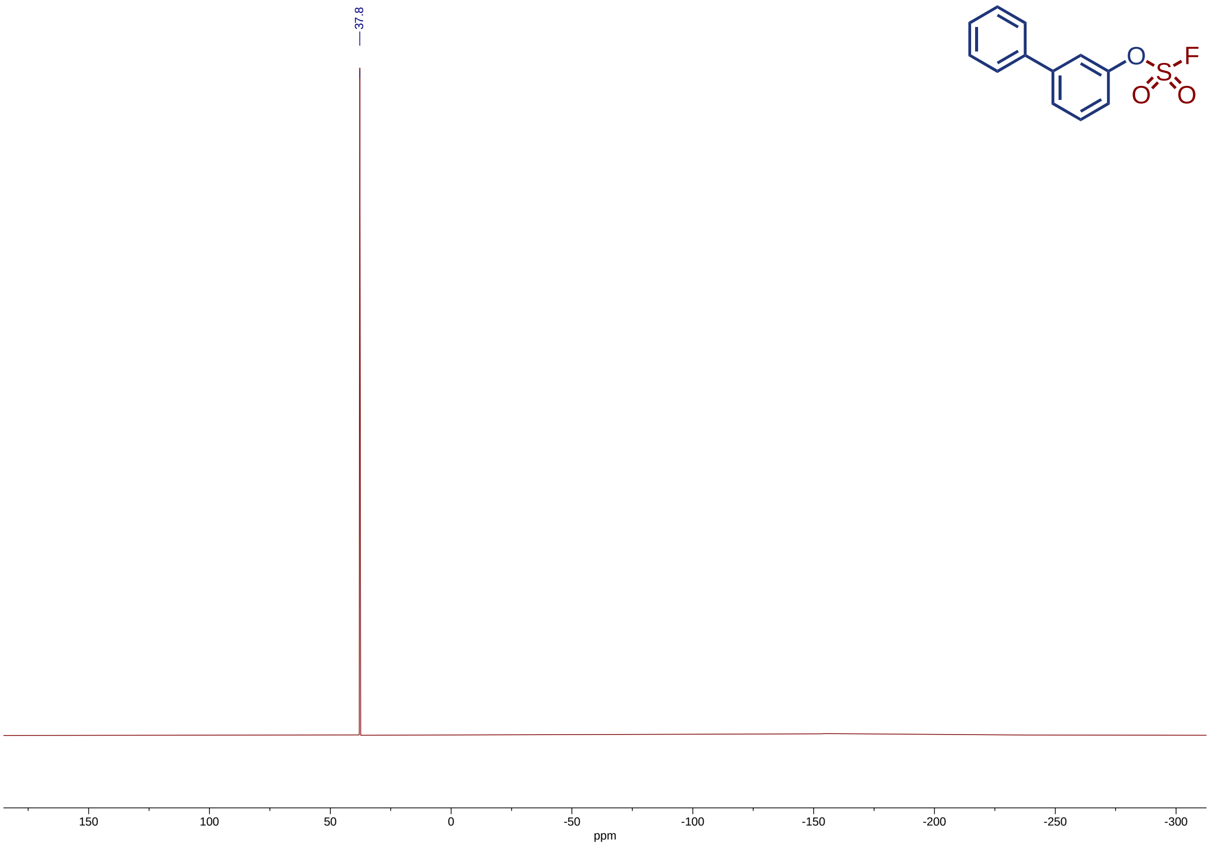
^{1}H NMR Spectrum for Compound **8j** (400 MHz, $CDCl_3$)



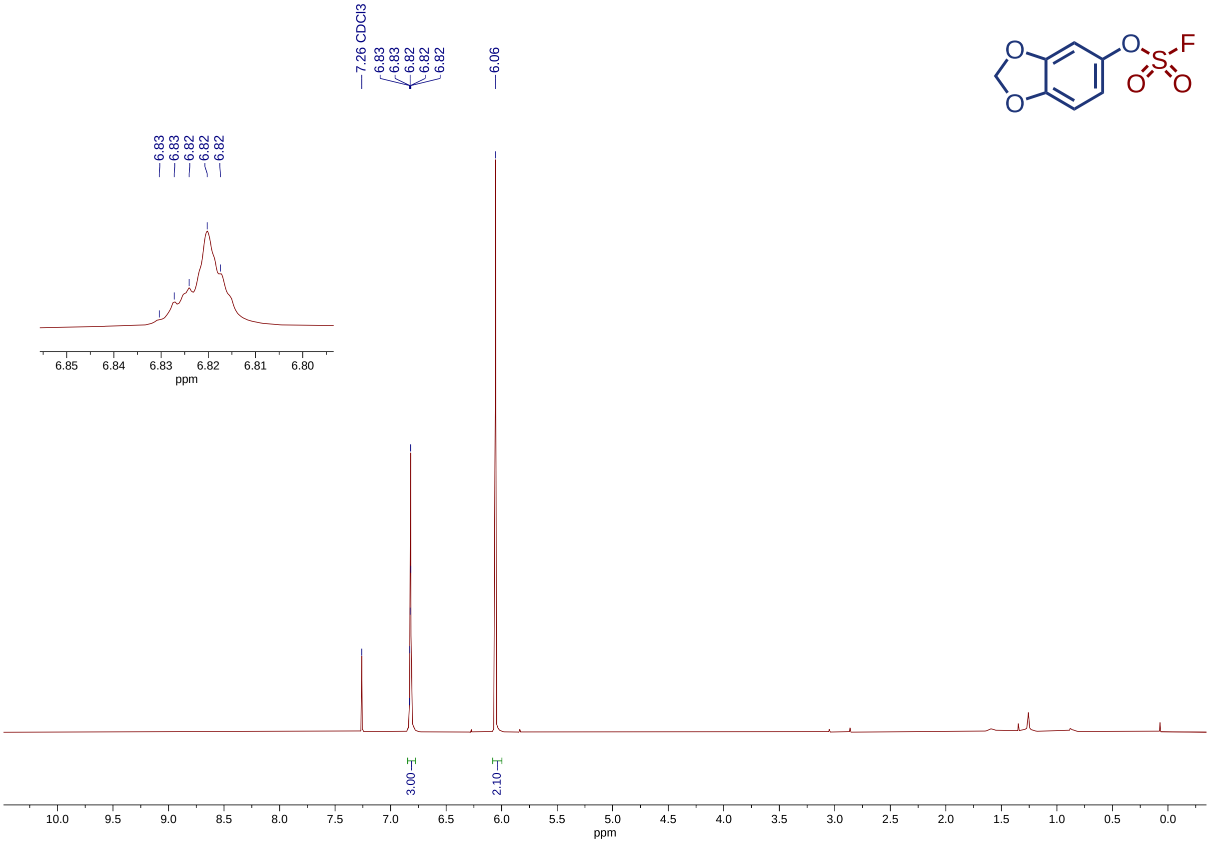
^{13}C NMR Spectrum for Compound **8j** (101 MHz, $CDCl_3$)



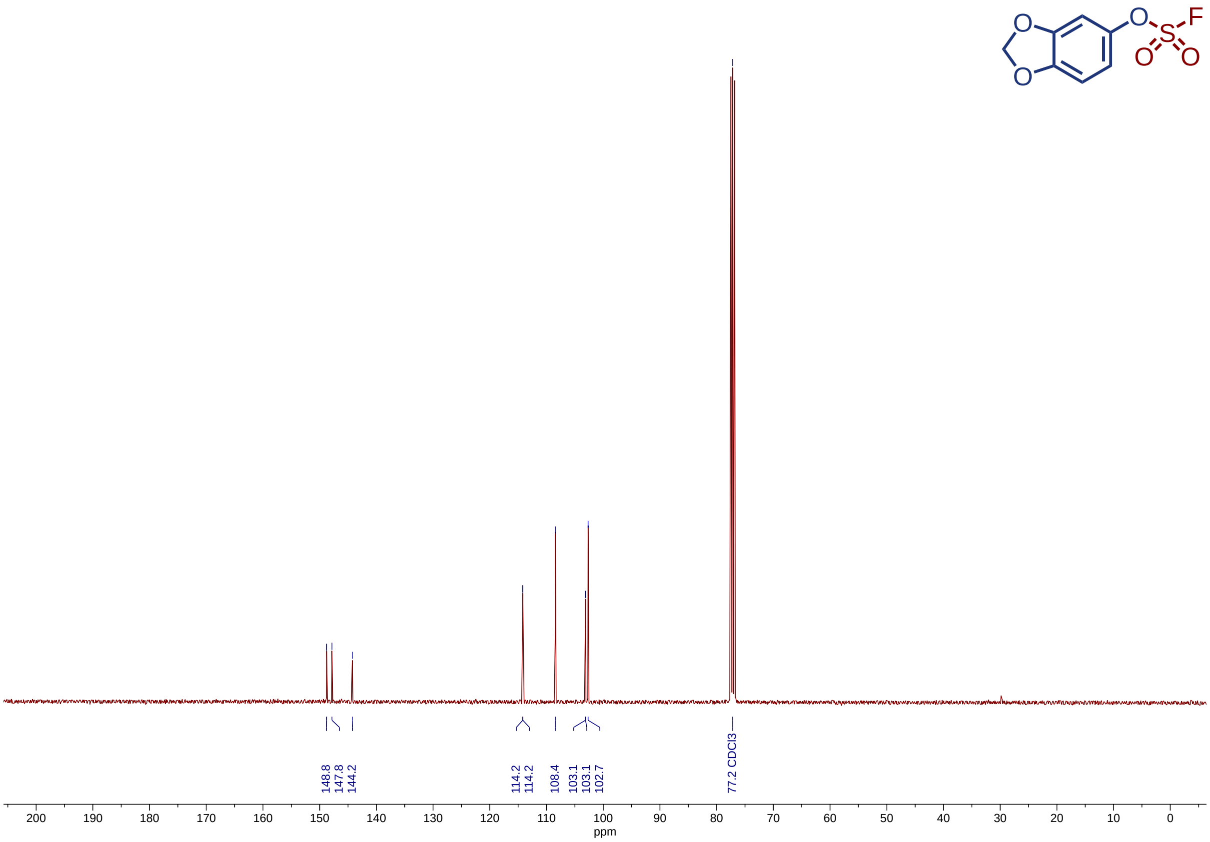
^{19}F NMR Spectrum for Compound **8j** (376 MHz, $CDCl_3$)



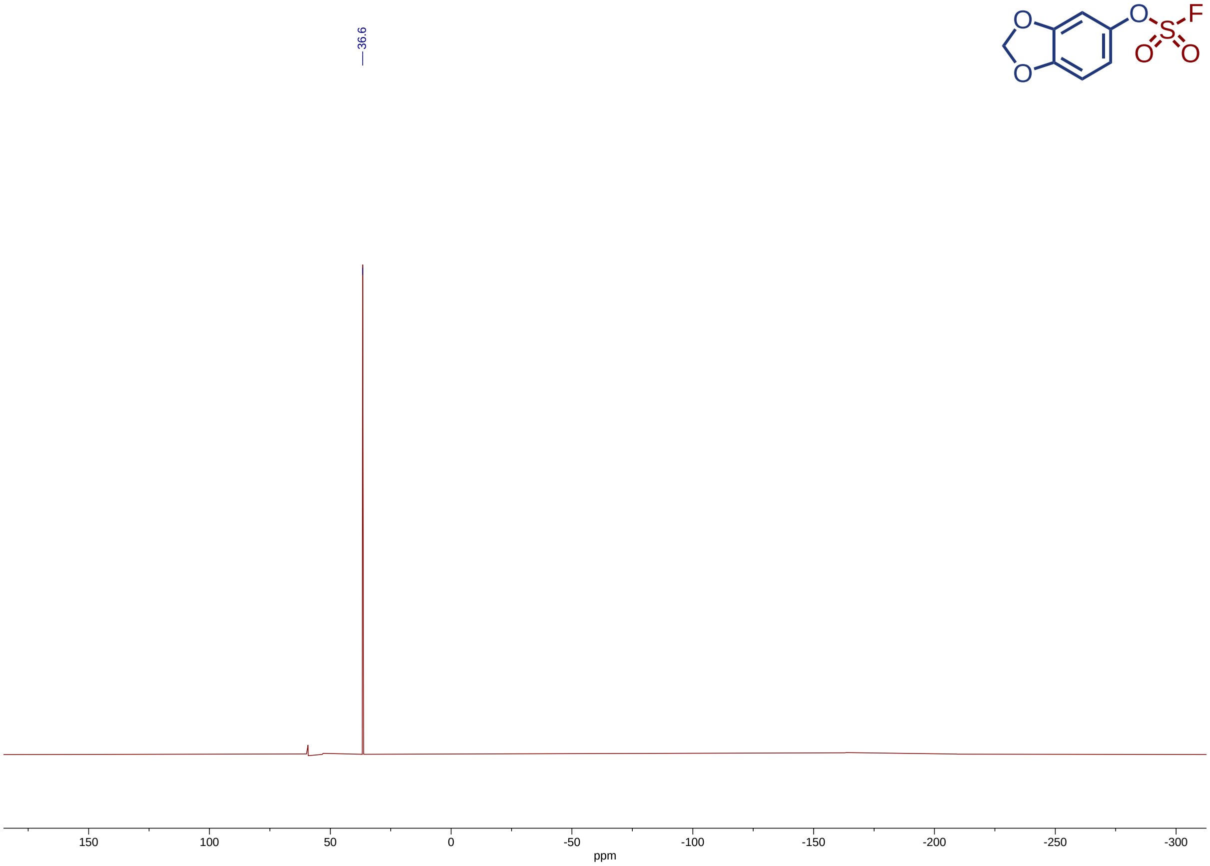
^{1}H NMR Spectrum for Compound **8k** (400 MHz, CDCl$_3$)



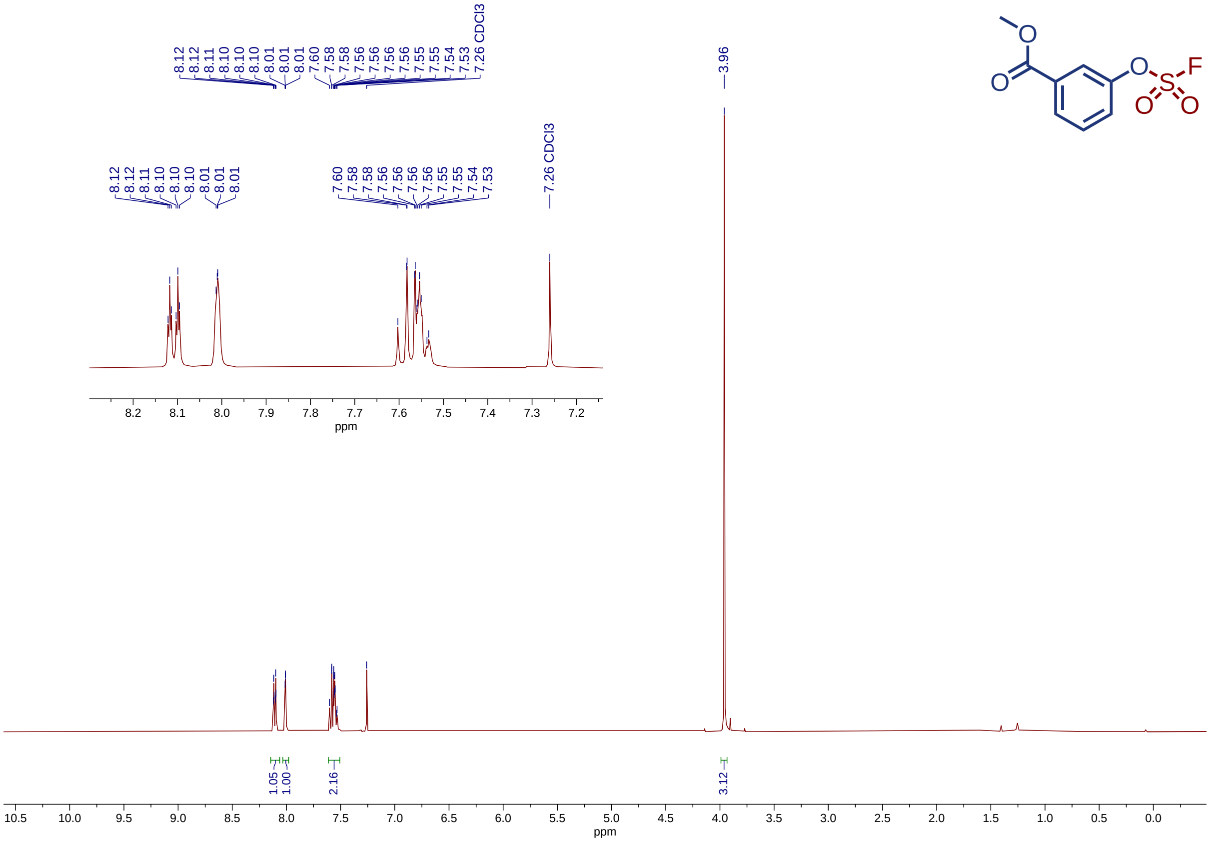
^{13}C NMR Spectrum for Compound **8k** (101 MHz, CDCl$_3$)



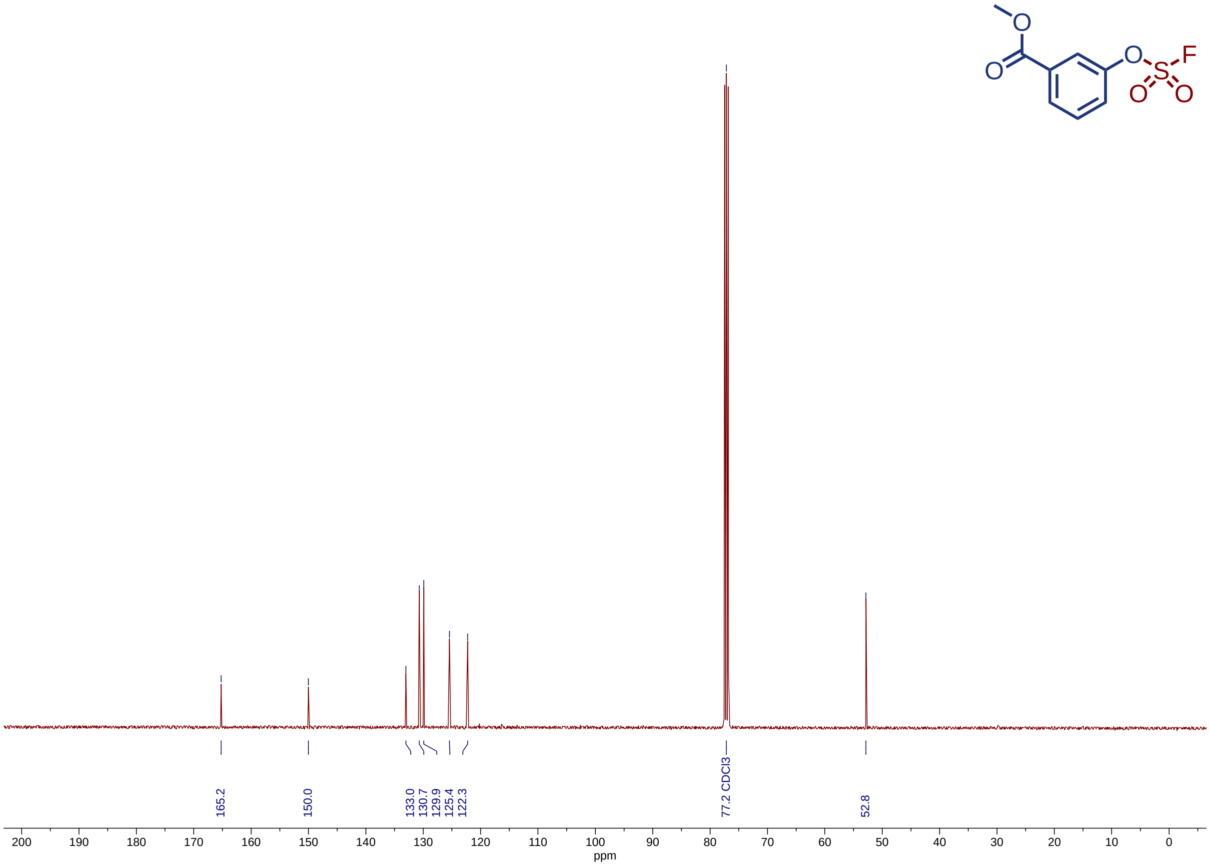
^{19}F NMR Spectrum for Compound **8k** (376 MHz, $CDCl_3$)



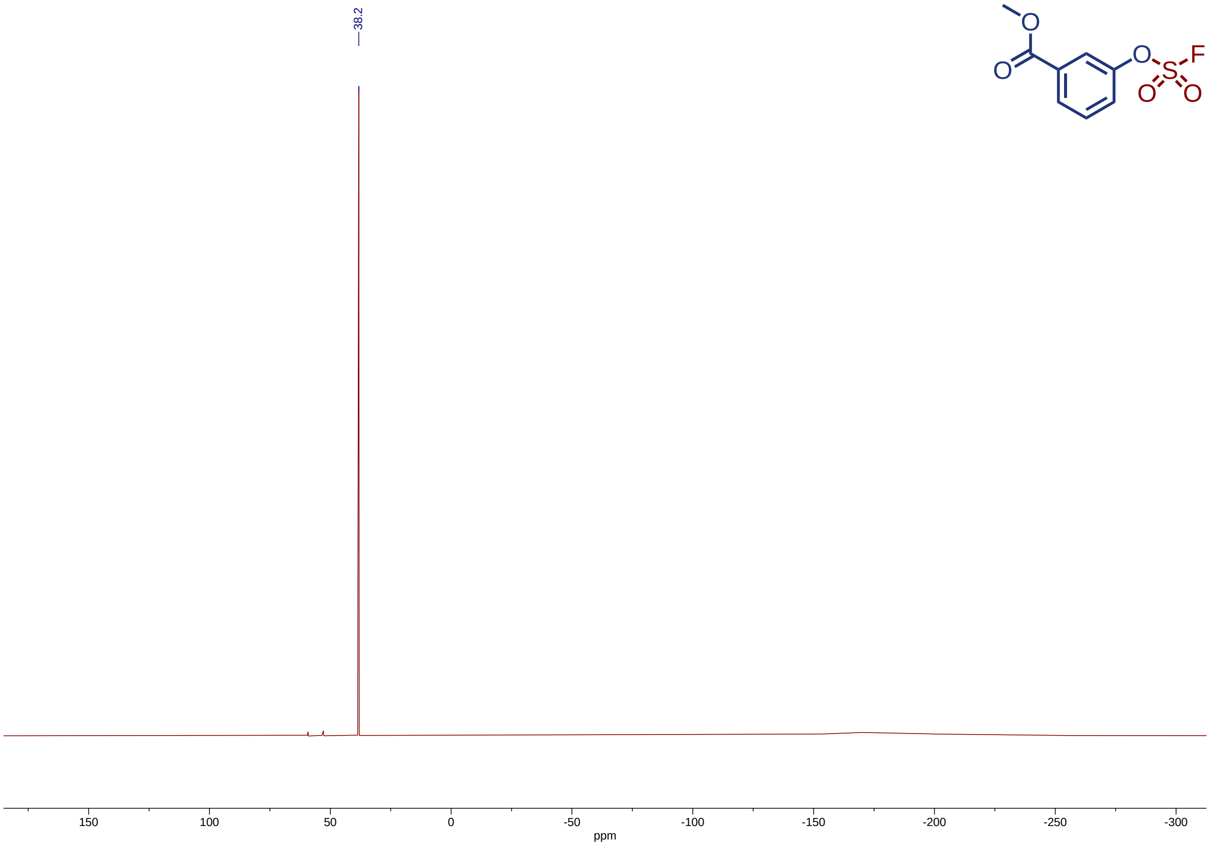
^{1}H NMR Spectrum for Compound **8l** (400 MHz, $CDCl_3$)



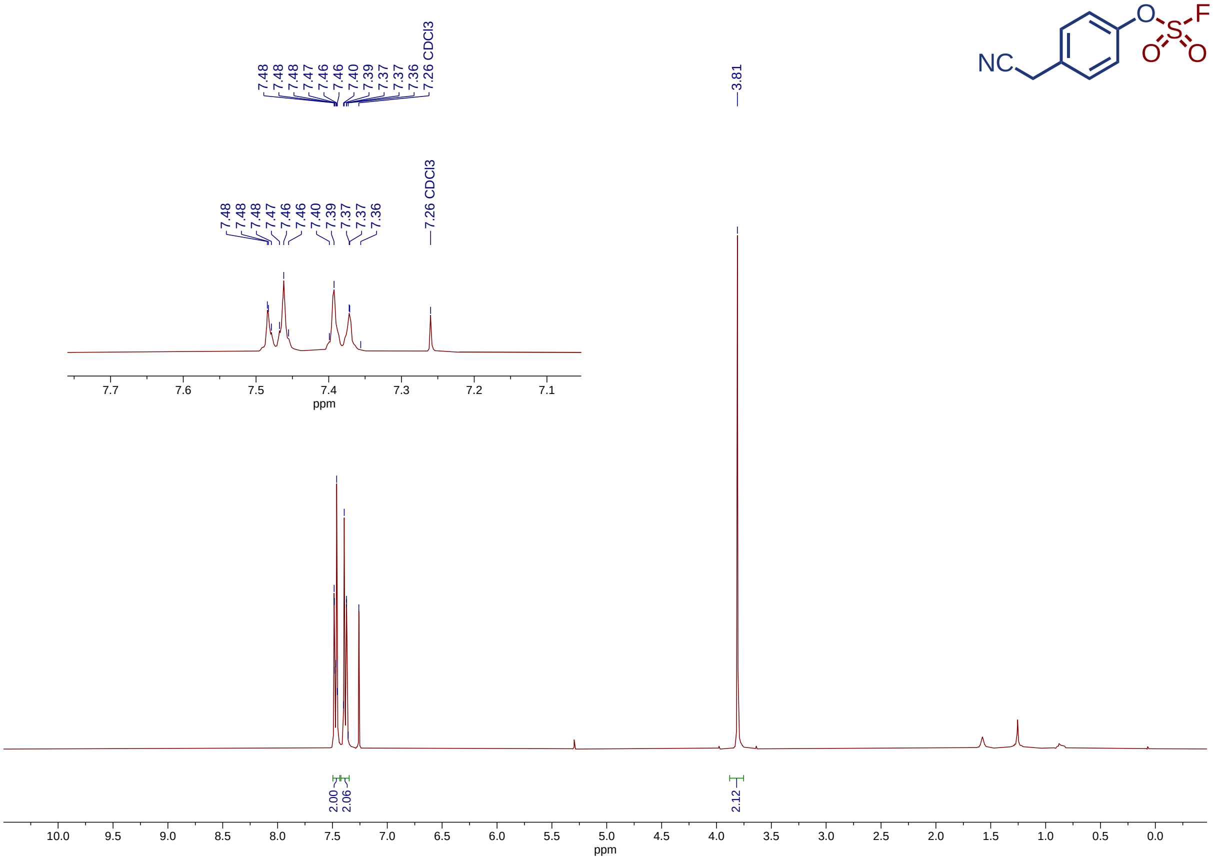
^{13}C NMR Spectrum for Compound **8l** (101 MHz, CDCl$_3$)



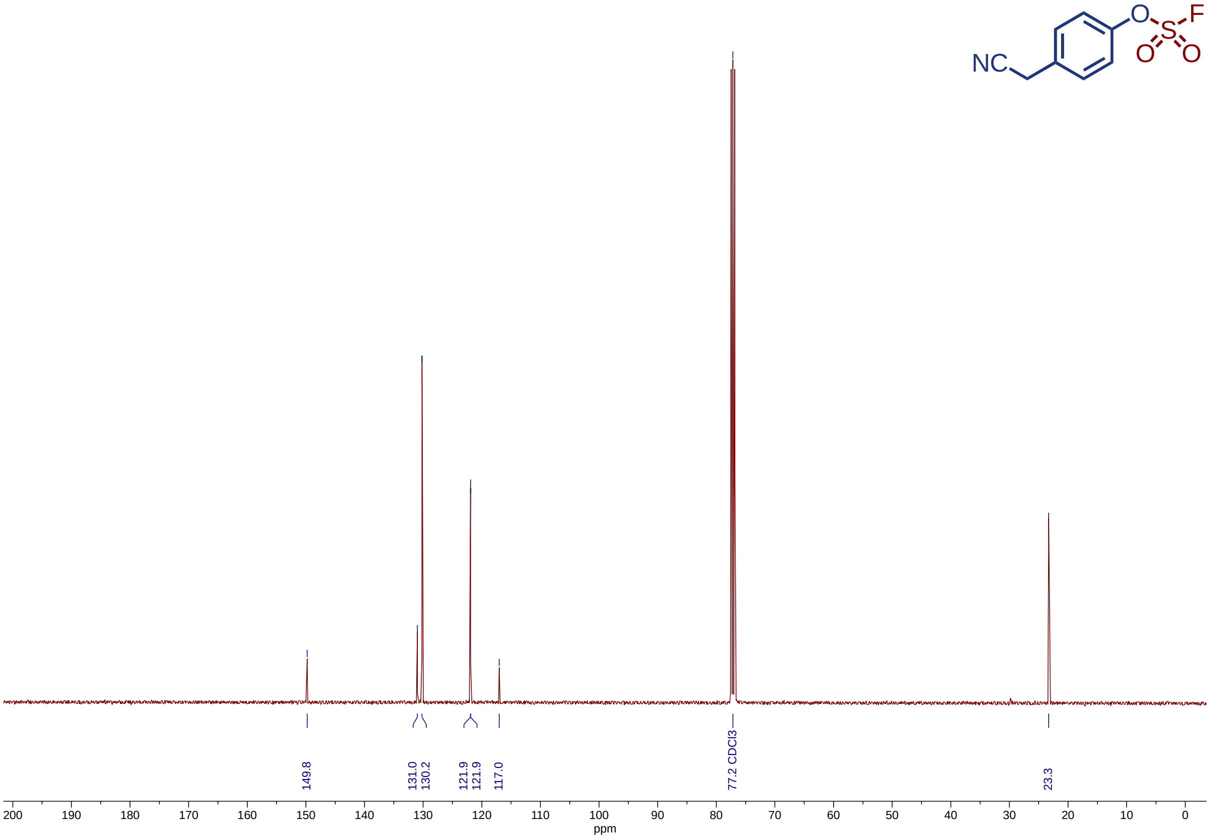
^{19}F NMR Spectrum for Compound **8l** (376 MHz, CDCl$_3$)



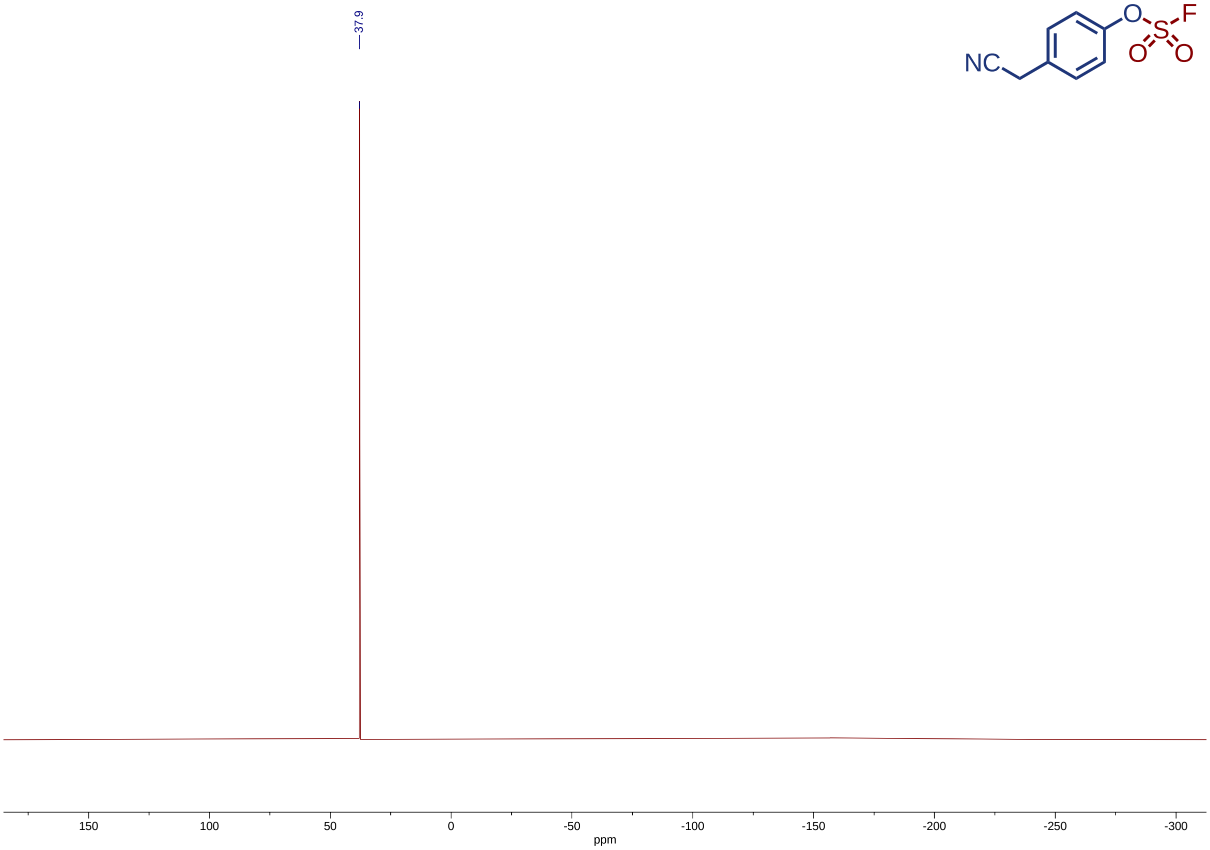
^{1}H NMR Spectrum for Compound **8m** (400 MHz, $CDCl_3$)



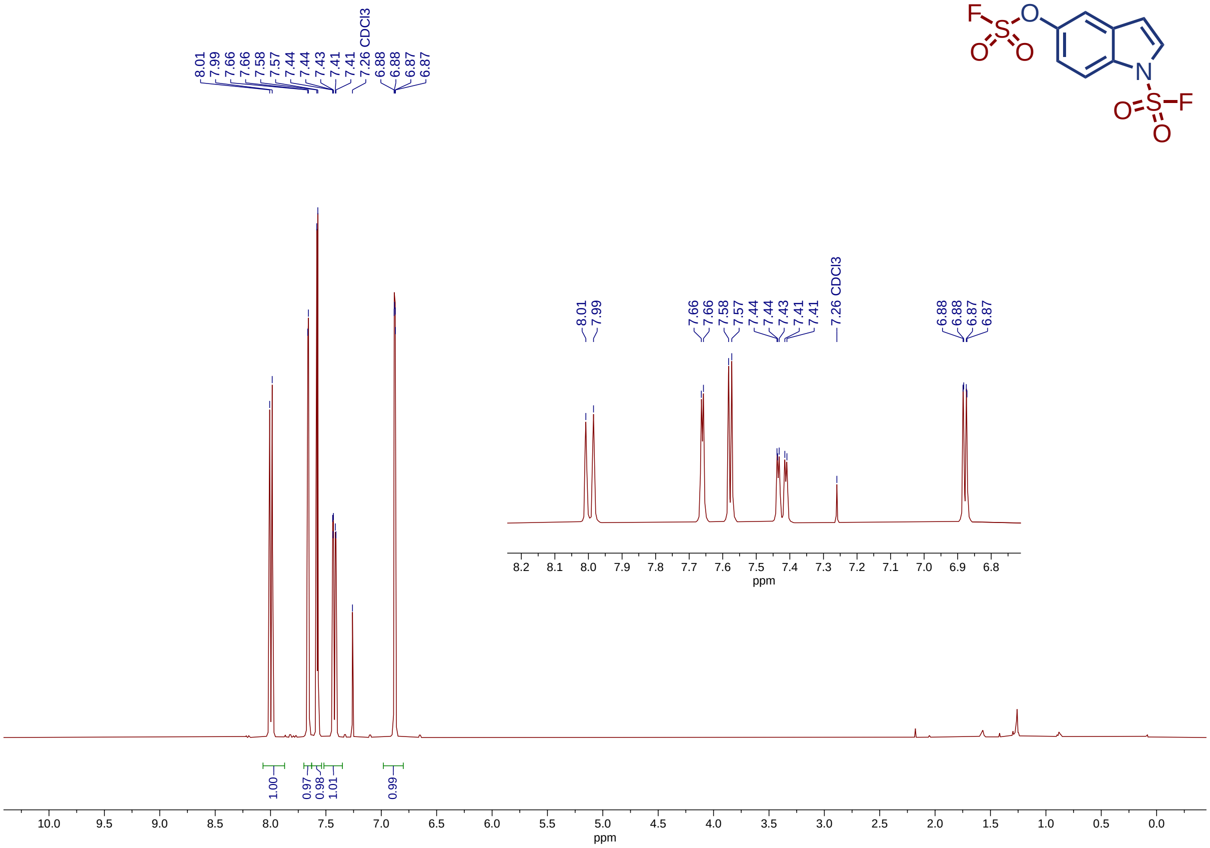
^{13}C NMR Spectrum for Compound **8m** (101 MHz, $CDCl_3$)



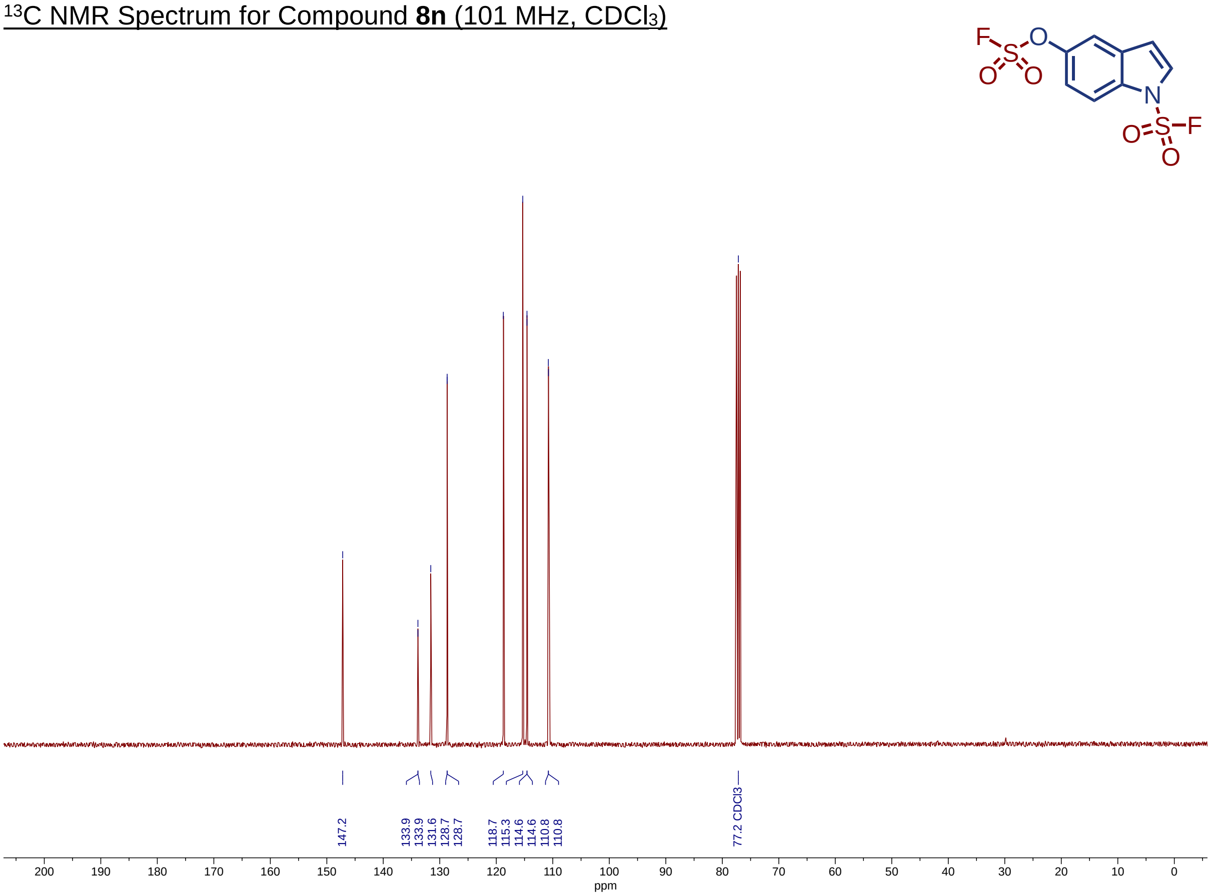
^{19}F NMR Spectrum for Compound **8m** (376 MHz, $CDCl_3$)



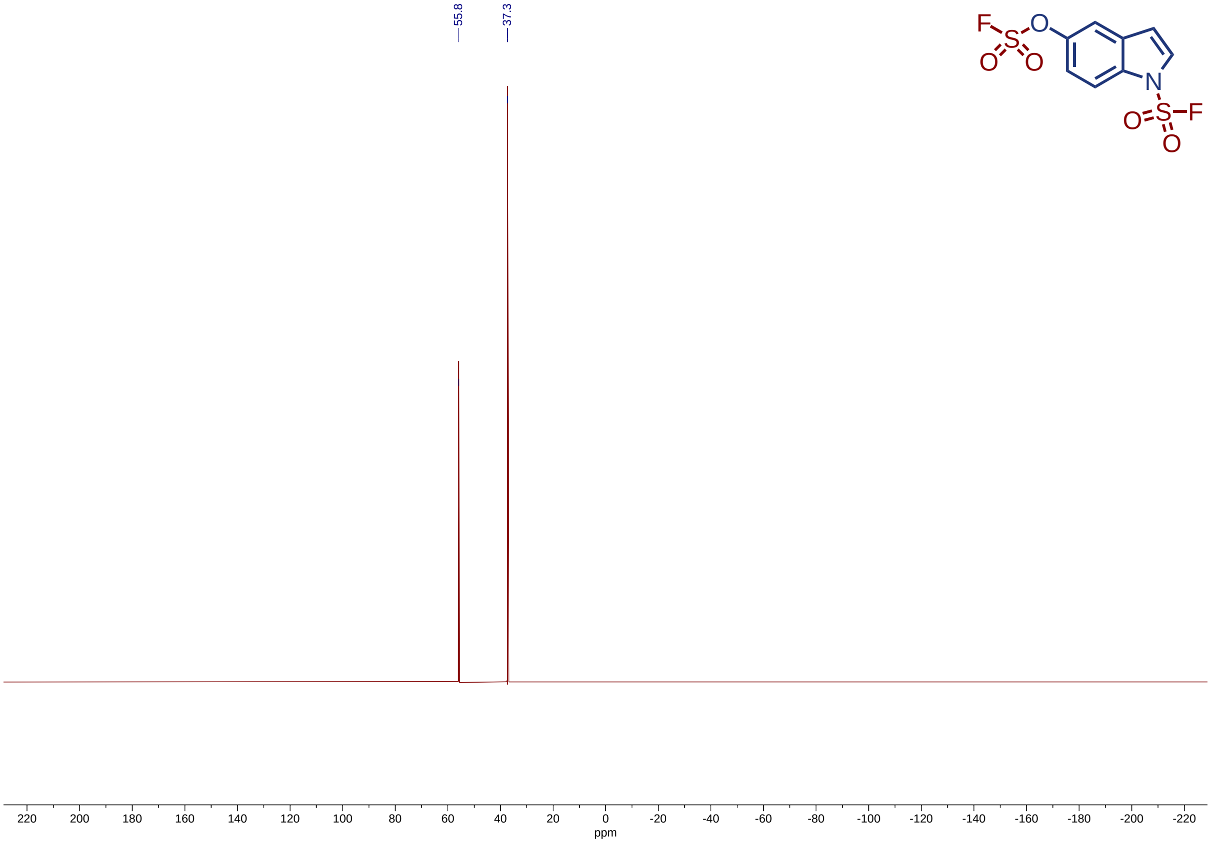
^{1}H NMR Spectrum for Compound **8n** (400 MHz, $CDCl_3$)



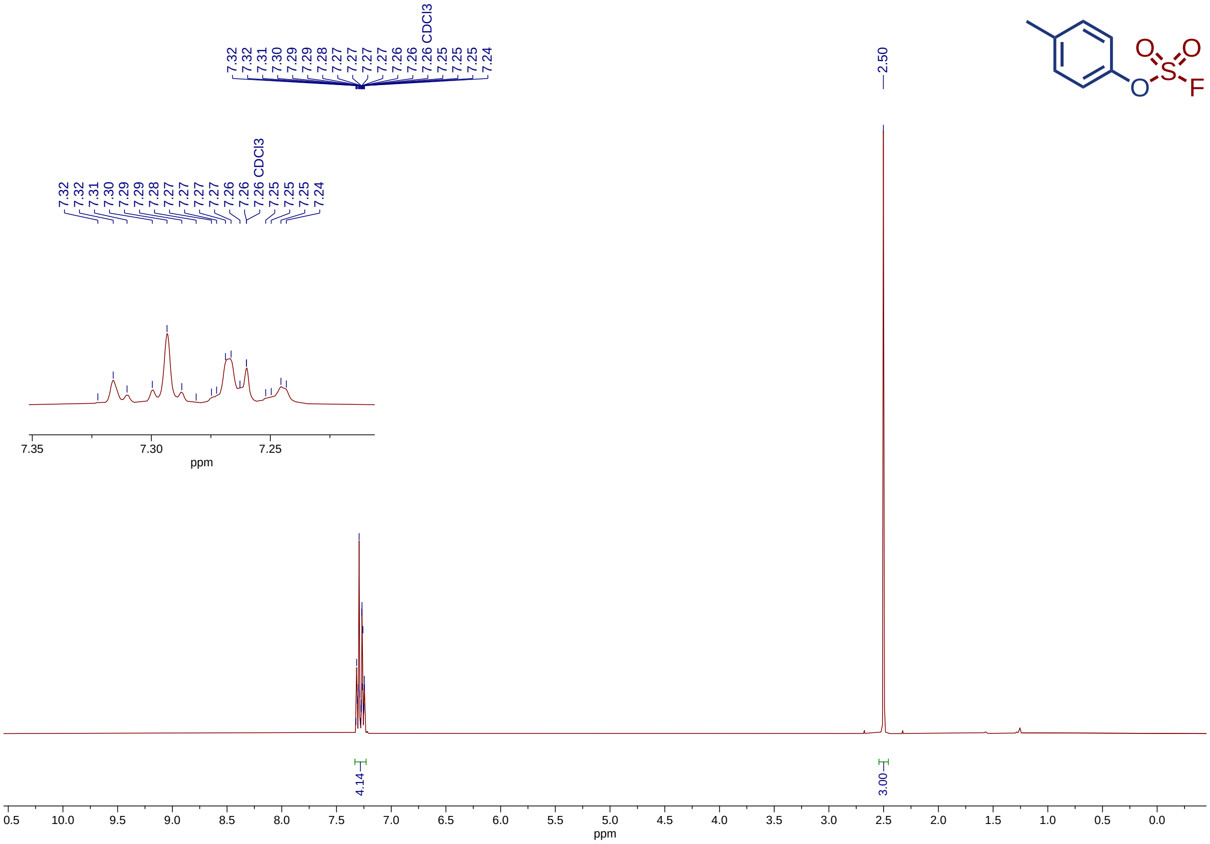
^{13}C NMR Spectrum for Compound **8n** (101 MHz, CDCl$_3$)



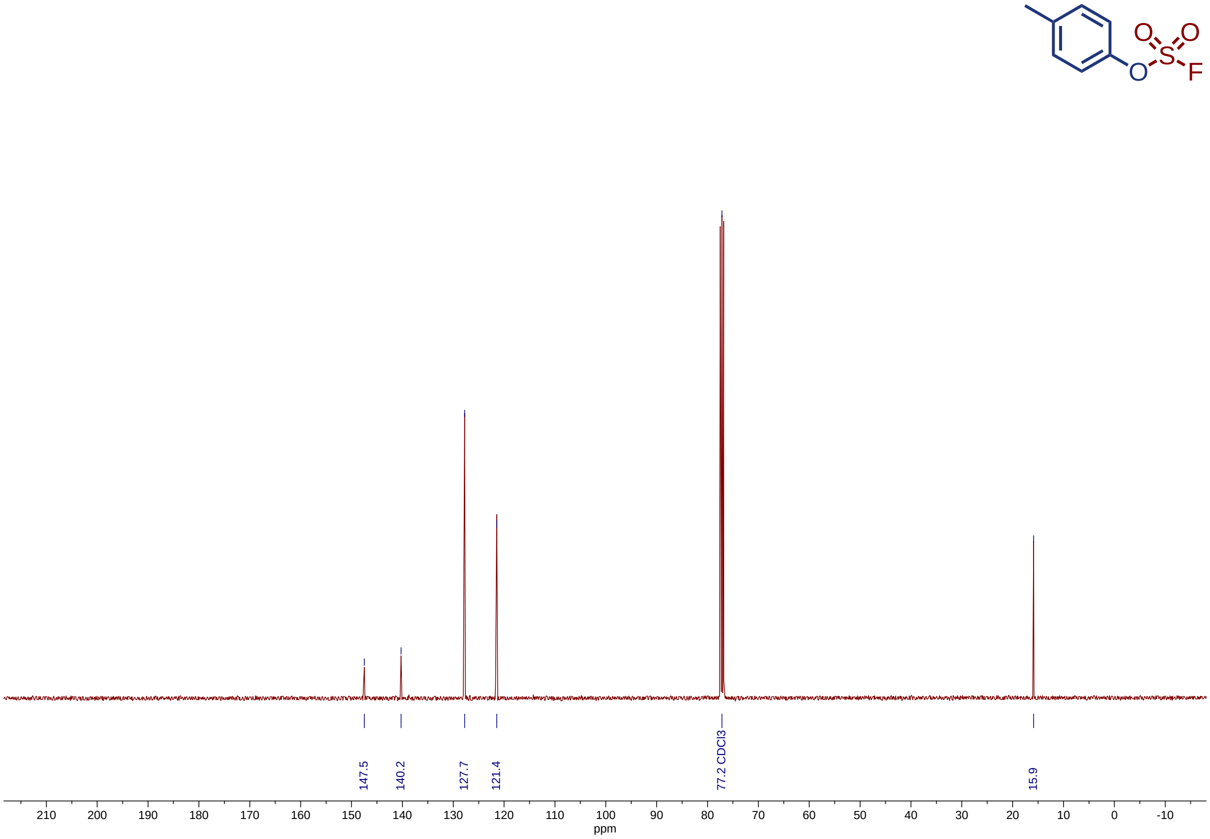
^{19}F NMR Spectrum for Compound **8n** (376 MHz, CDCl$_3$)



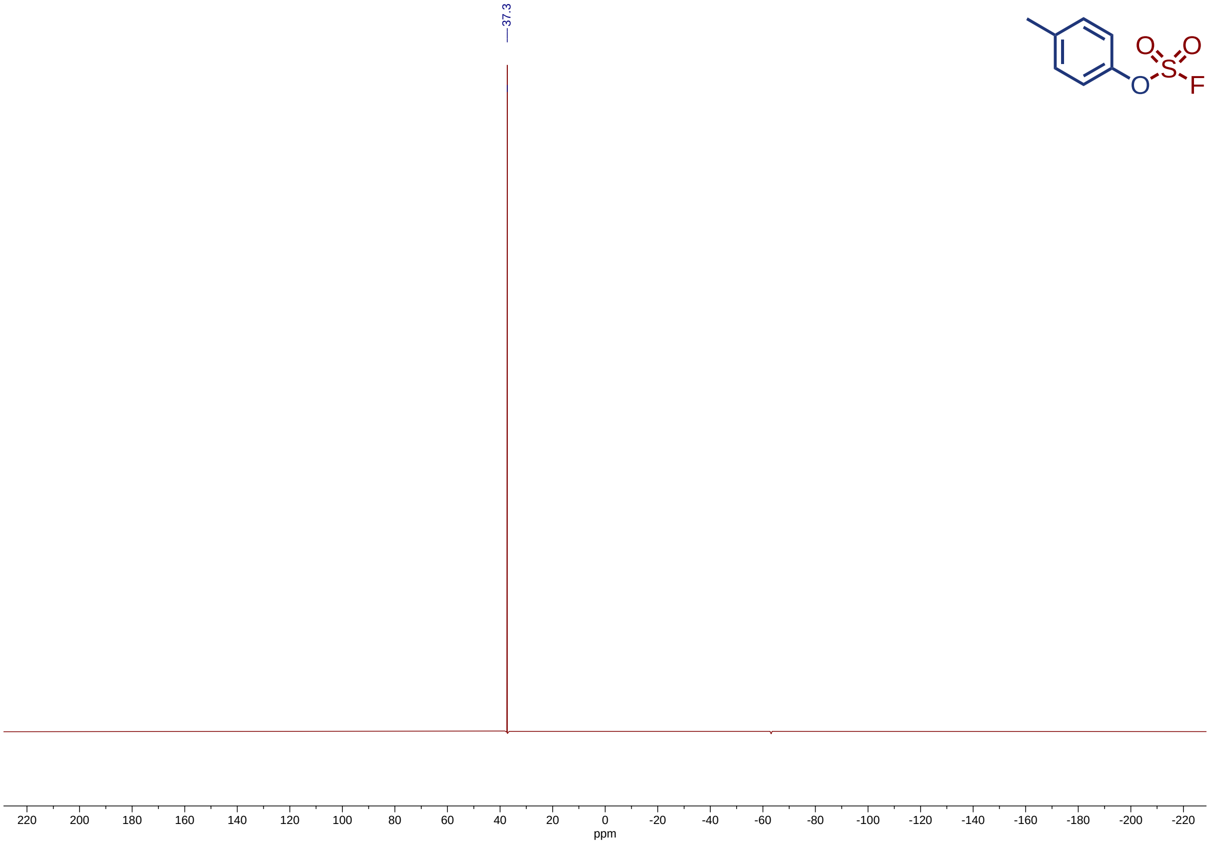
^{1}H NMR Spectrum for Compound **8o** (400 MHz, $CDCl_3$)



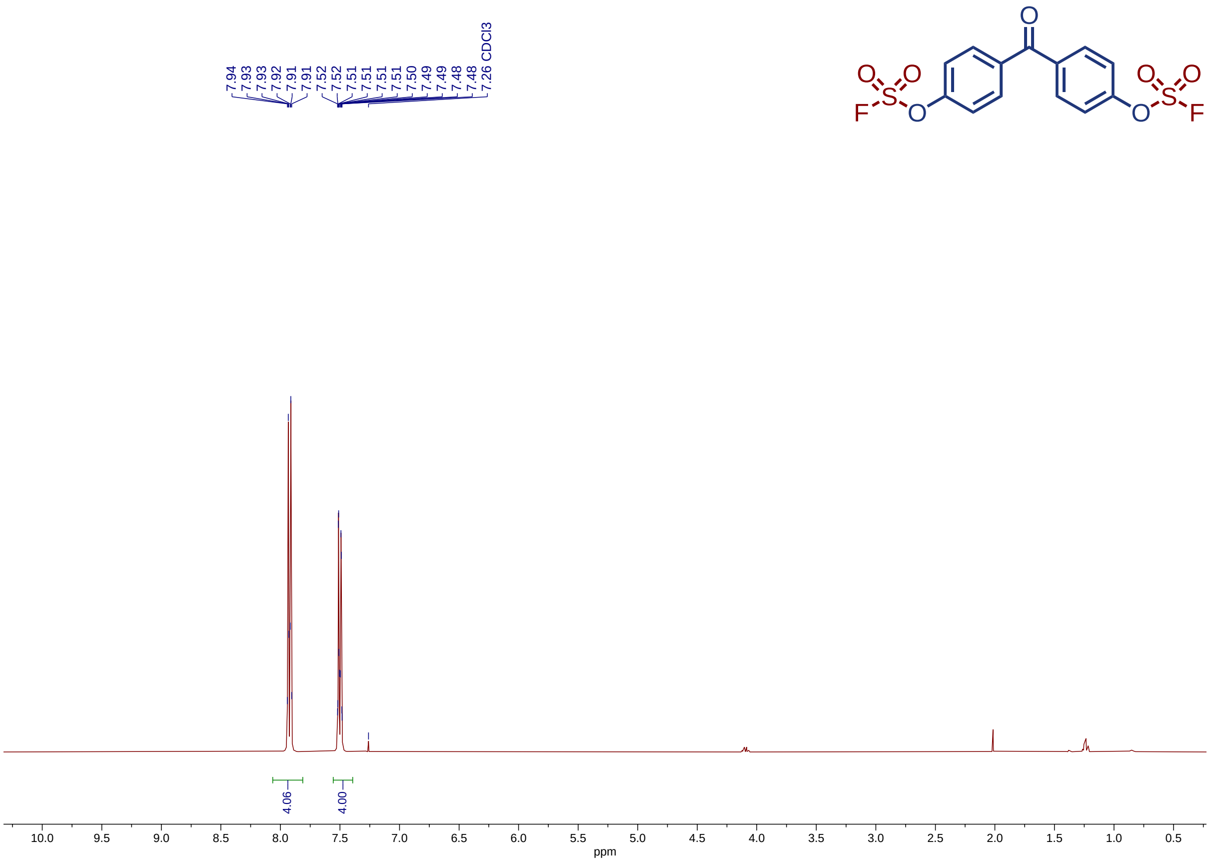
^{13}C NMR Spectrum for Compound **8o** (101 MHz, $CDCl_3$)



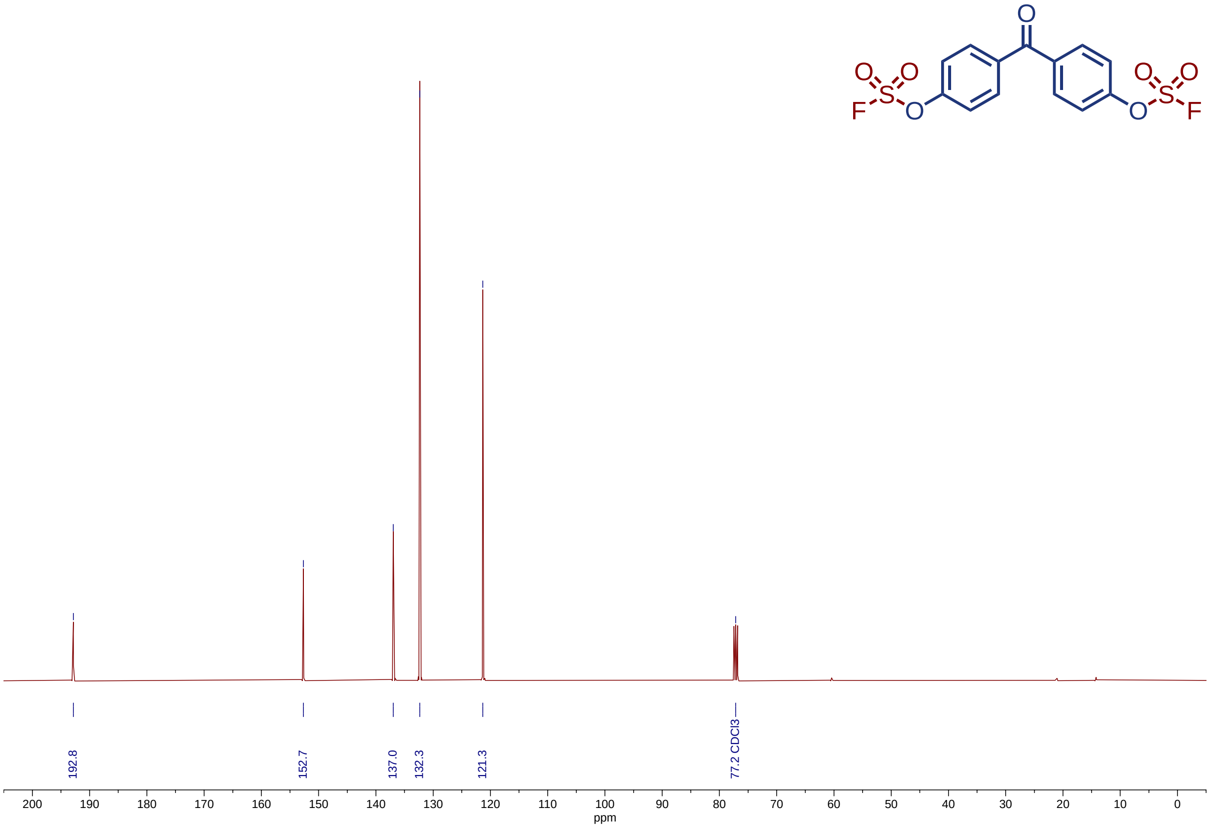
^{19}F NMR Spectrum for Compound **8o** (376 MHz, $CDCl_3$)



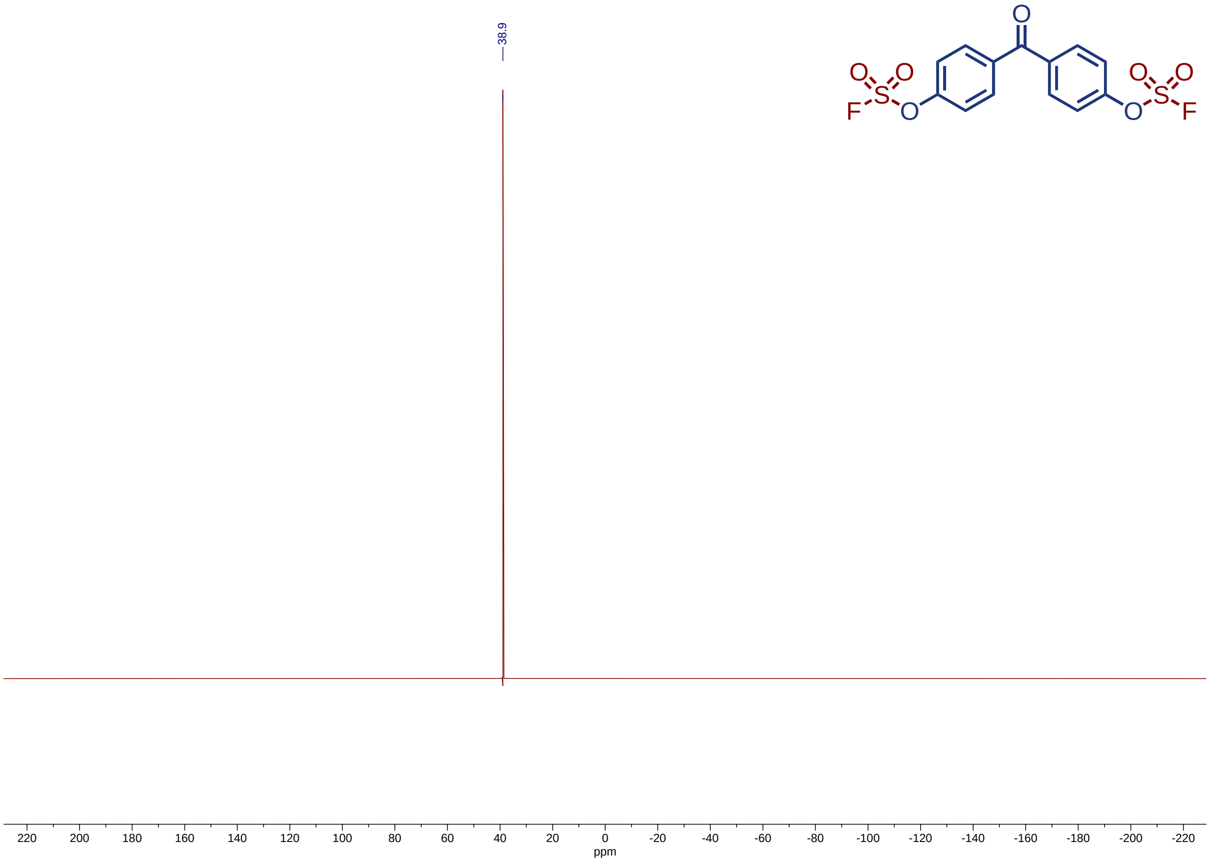
^{1}H NMR Spectrum for Compound **8p** (400 MHz, $CDCl_3$)



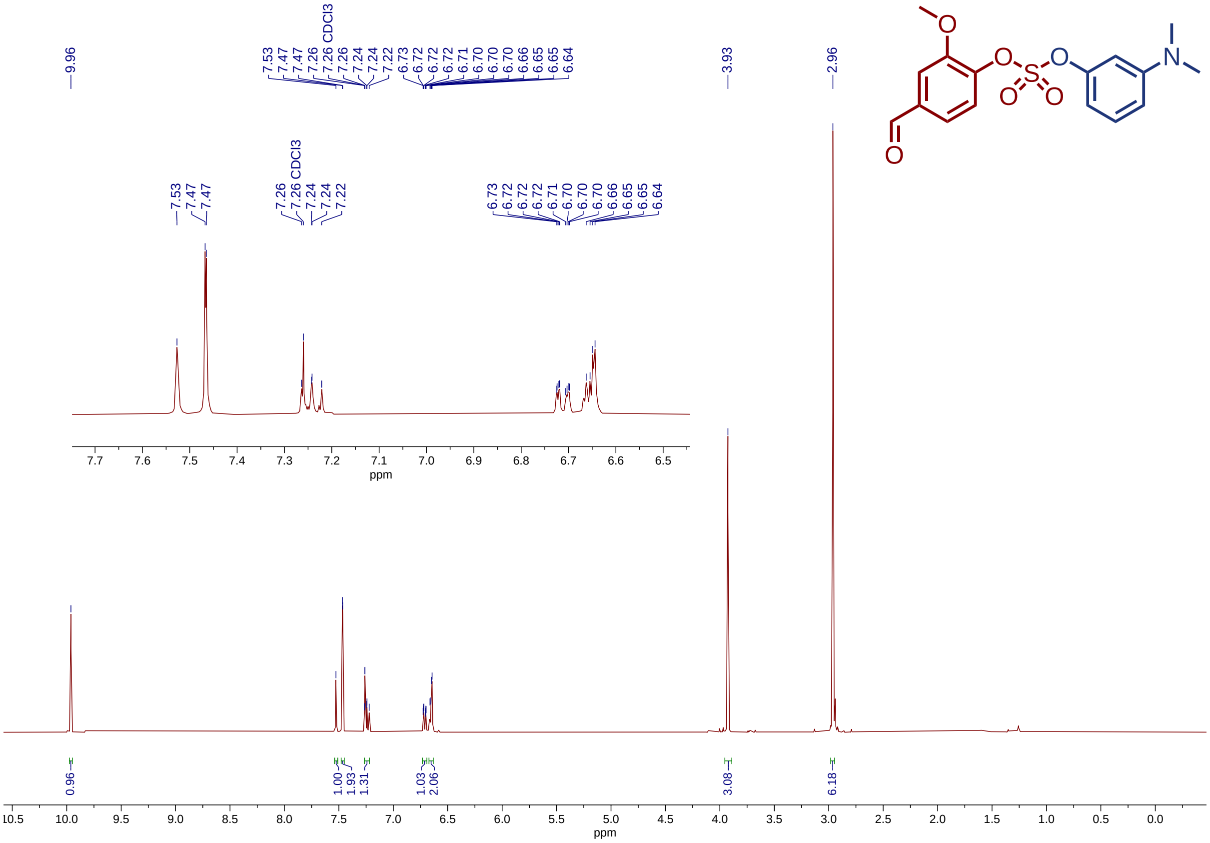
^{13}C NMR Spectrum for Compound **8p** (101 MHz, $CDCl_3$)



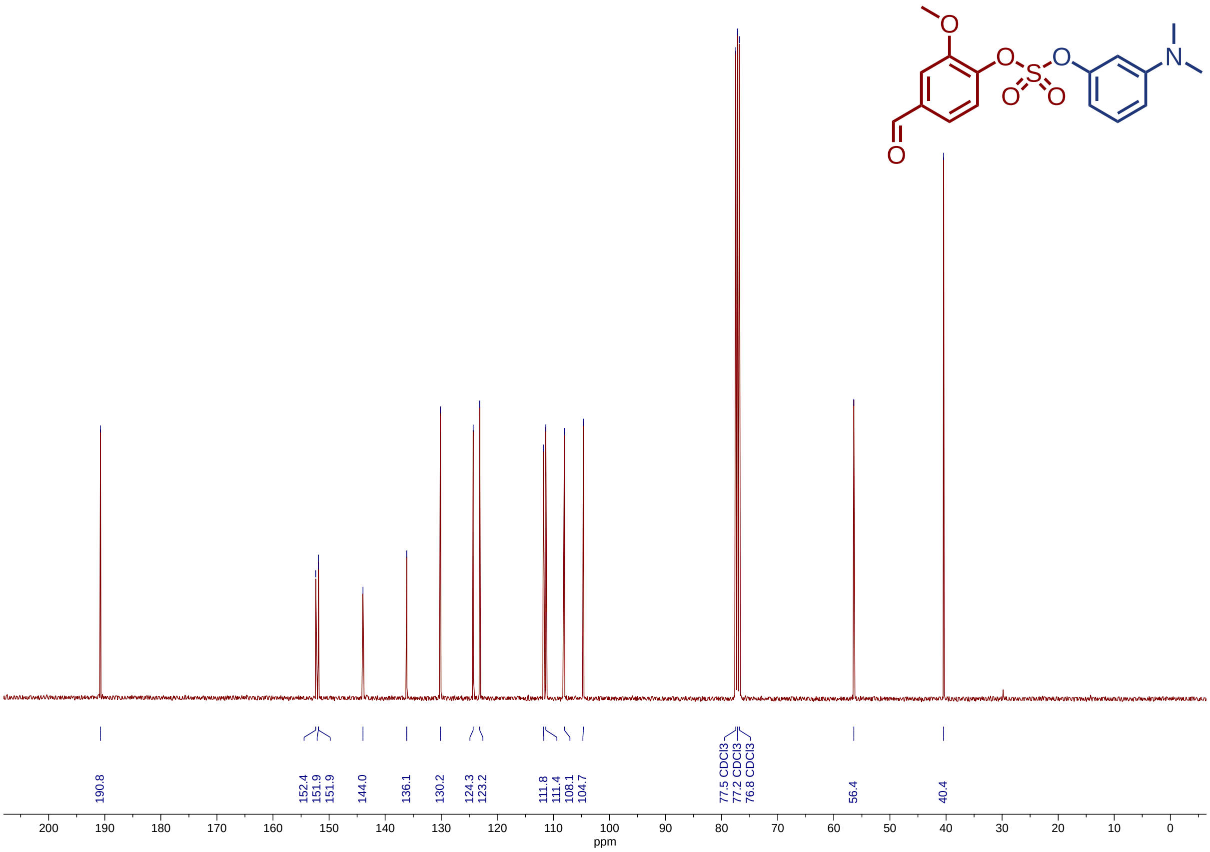
^{19}F NMR Spectrum for Compound **8p** (376 MHz, $CDCl_3$)



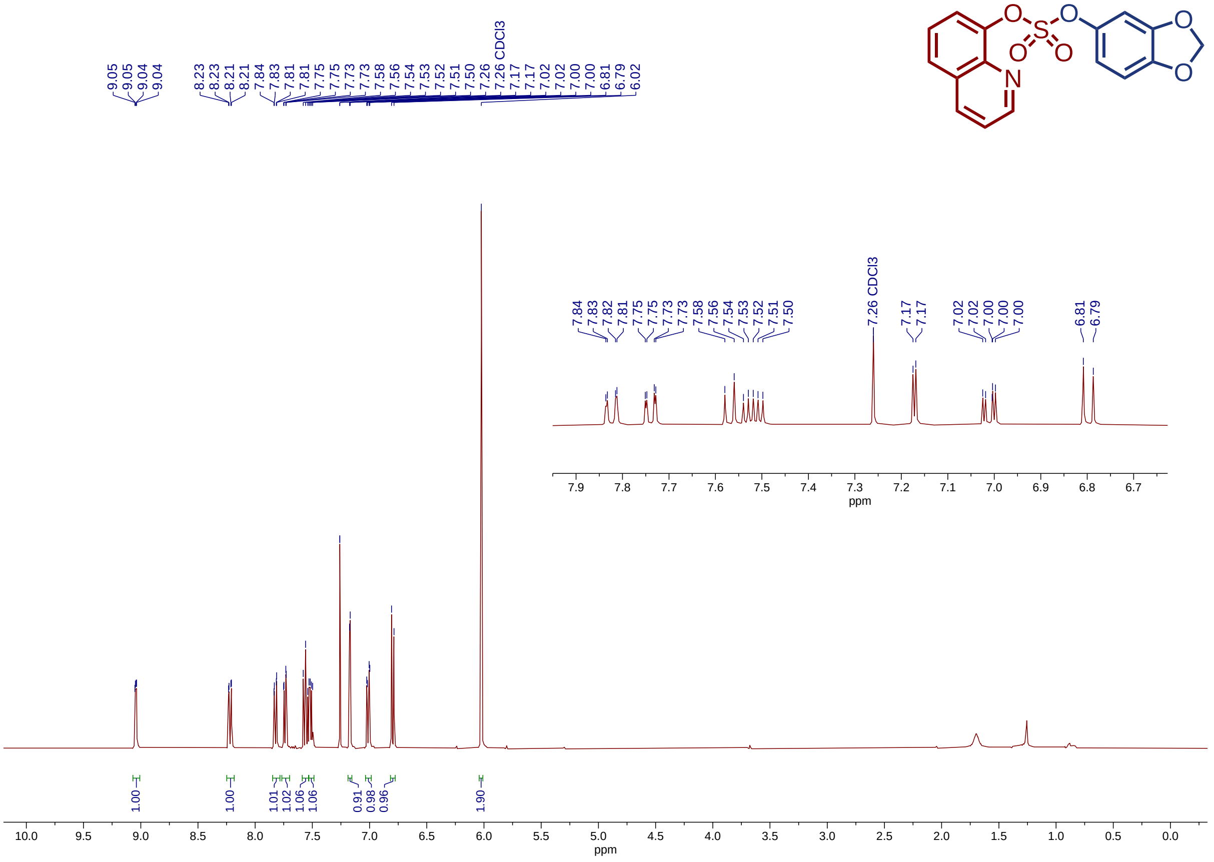
^{1}H NMR Spectrum for Compound **9a** (400 MHz, $CDCl_3$)



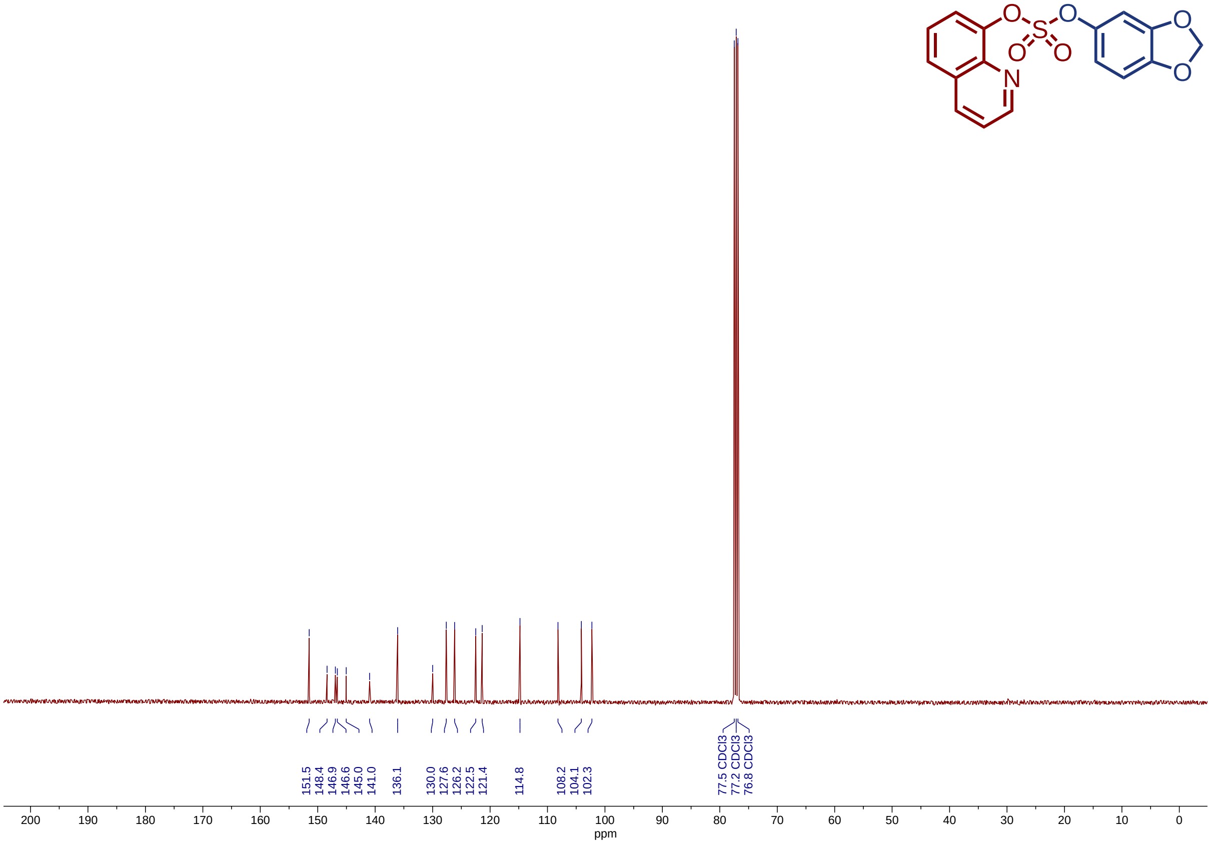
^{13}C NMR Spectrum for Compound **9a** (101 MHz, $CDCl_3$)



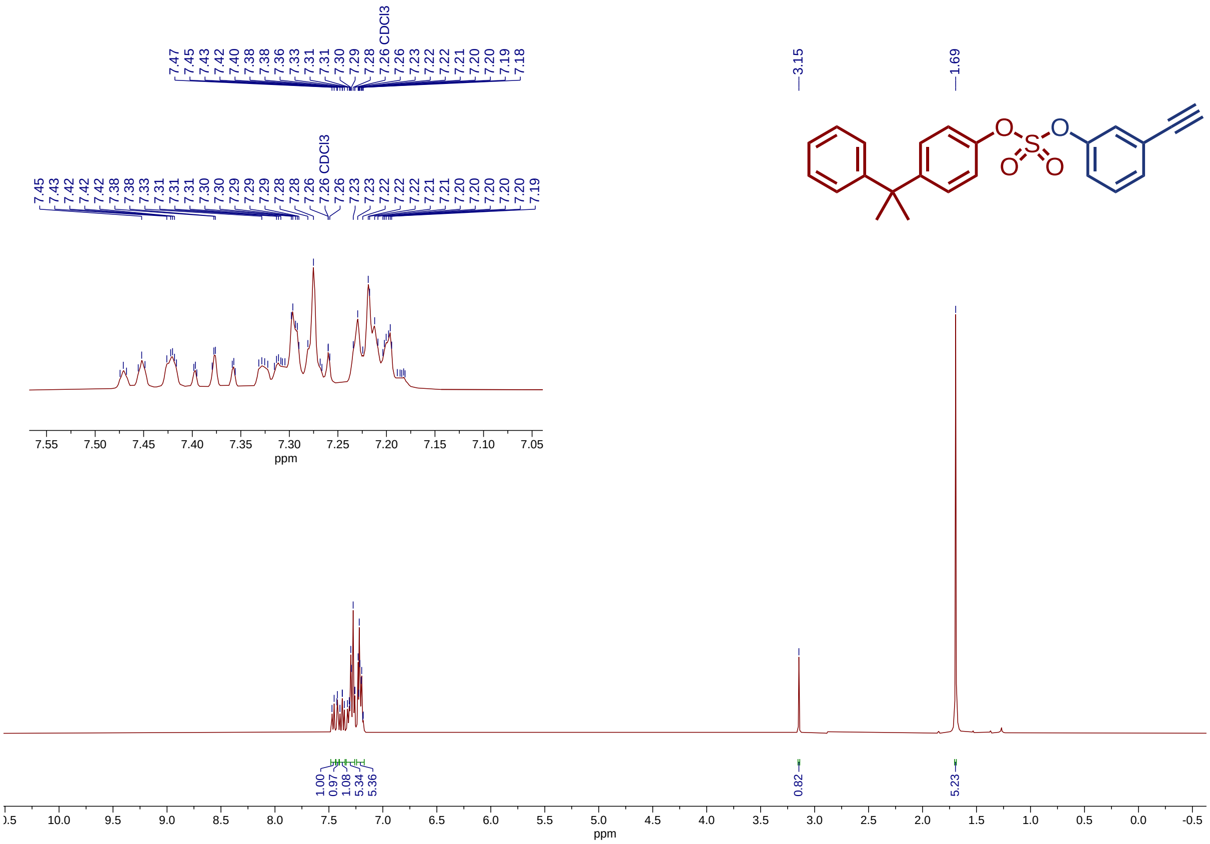
^{1}H NMR Spectrum for Compound **9b** (400 MHz, $CDCl_3$)



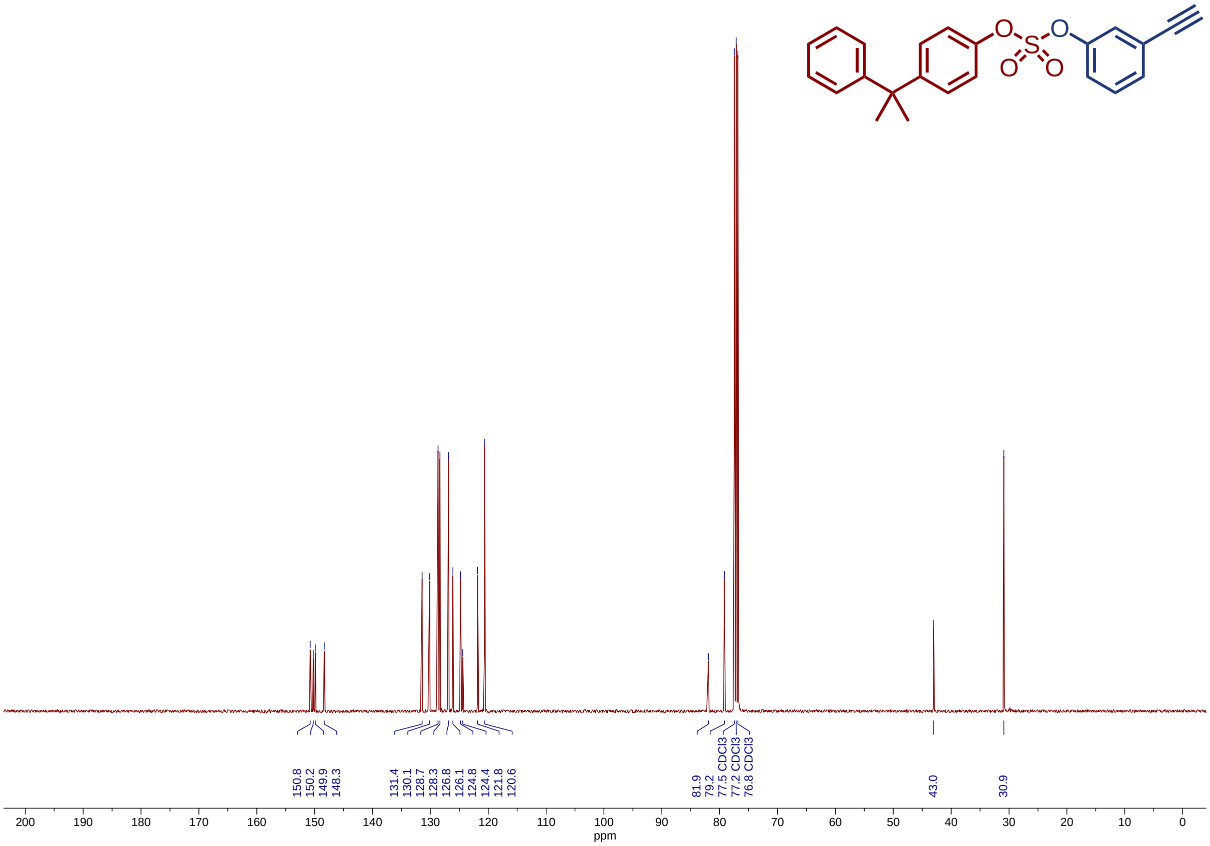
^{13}C NMR Spectrum for Compound **9b** (101 MHz, $CDCl_3$)



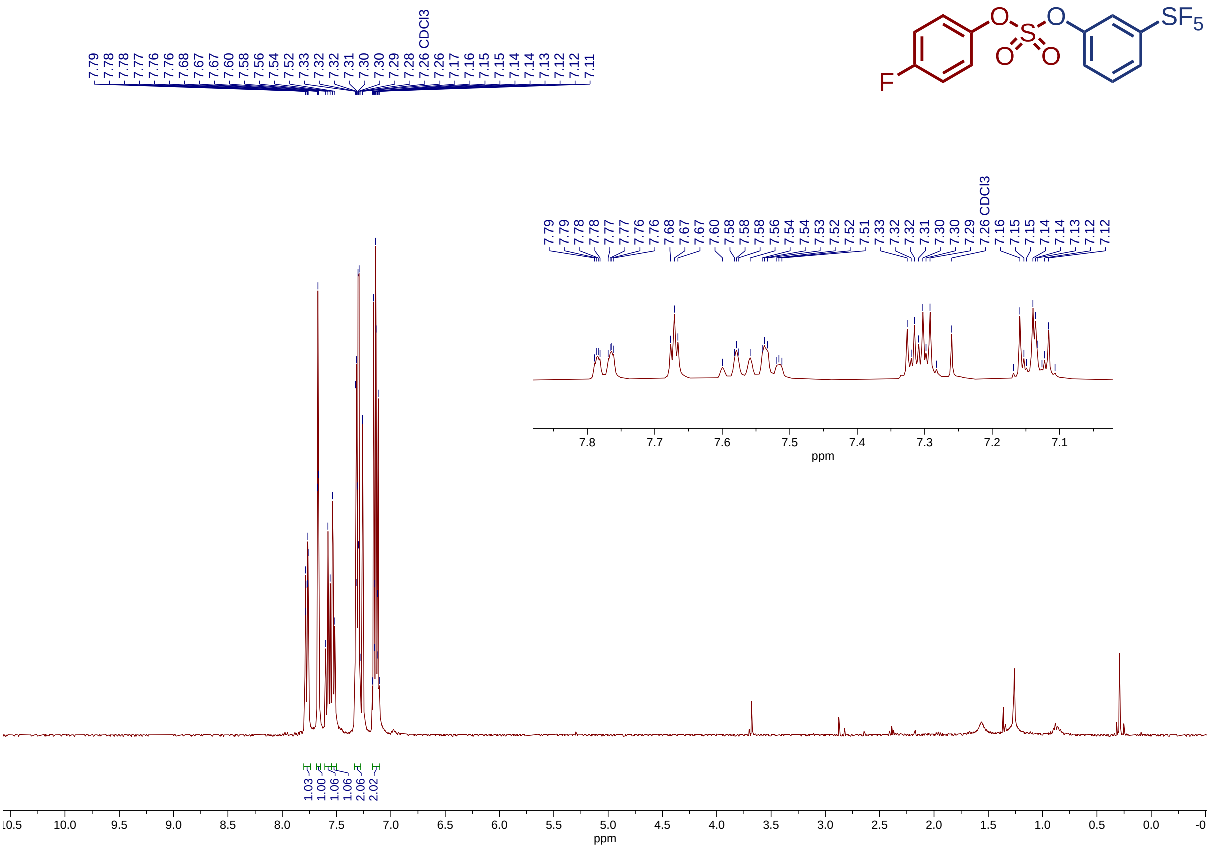
^{1}H NMR Spectrum for Compound **9c** (400 MHz, $CDCl_3$)



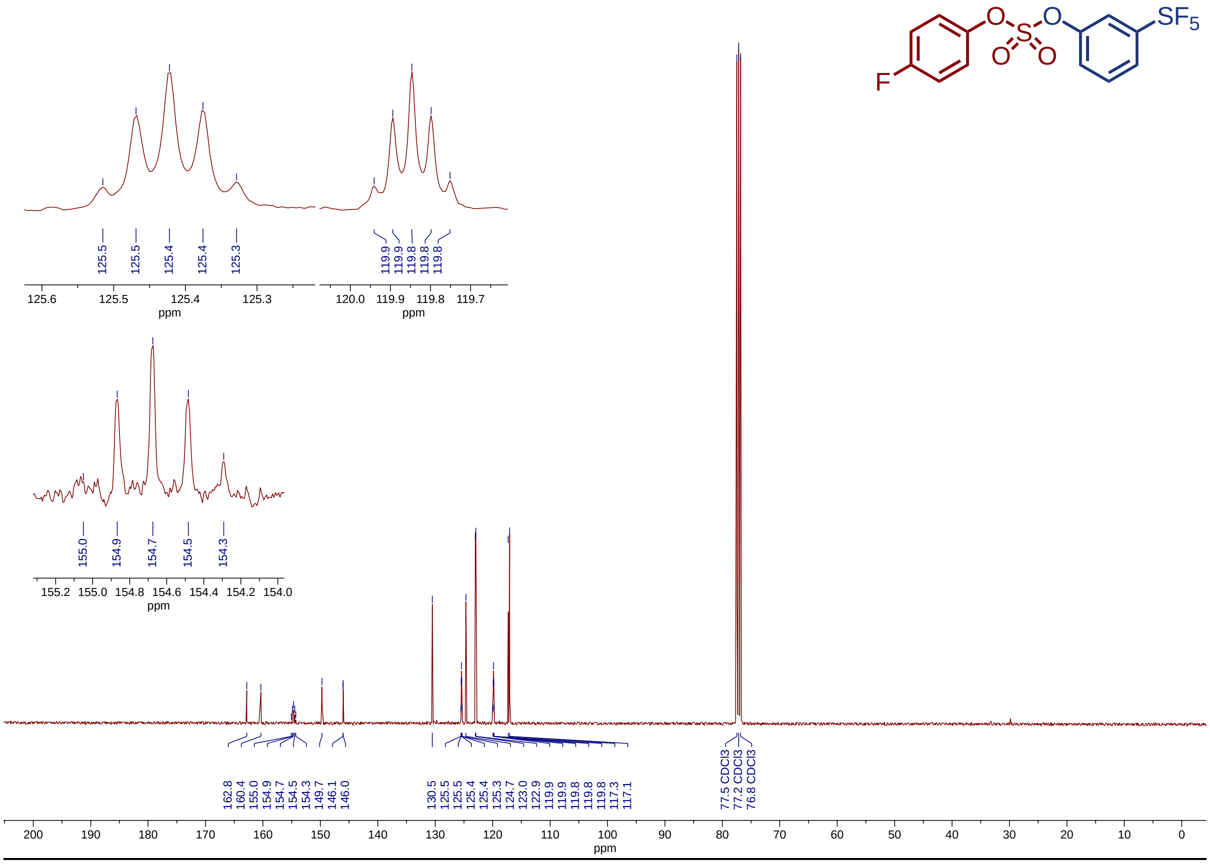
^{13}C NMR Spectrum for Compound **9c** (101 MHz, $CDCl_3$)



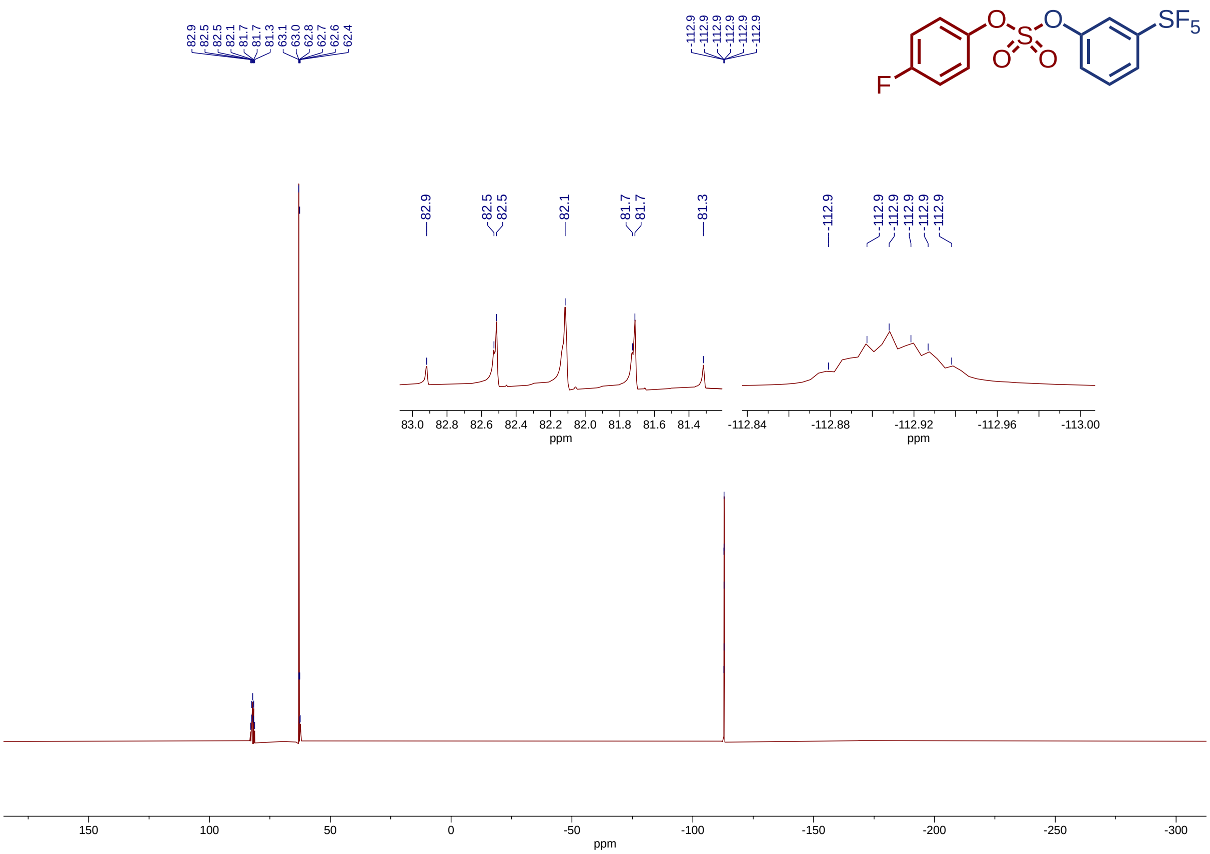
^{1}H NMR Spectrum for Compound **9d** (400 MHz, $CDCl_3$)



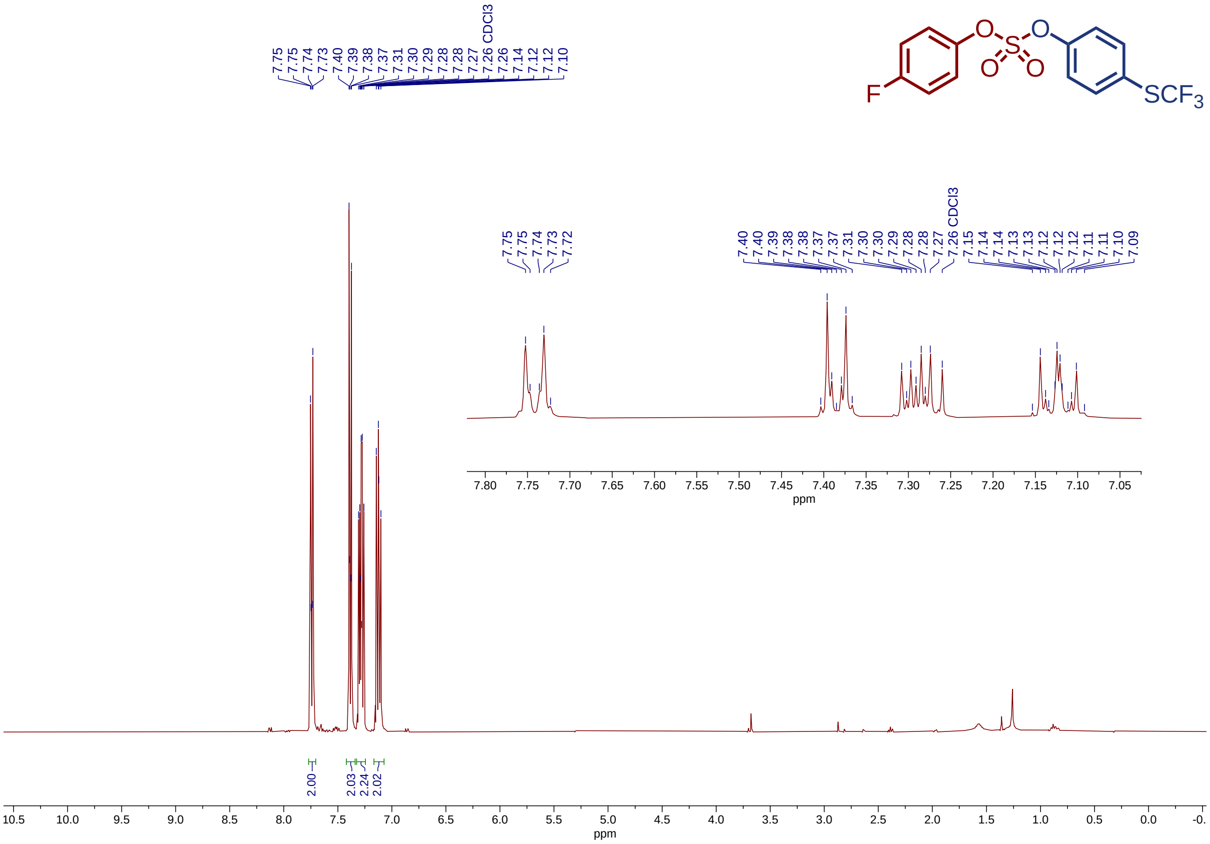
^{13}C NMR Spectrum for Compound **9d** (101 MHz, $CDCl_3$)



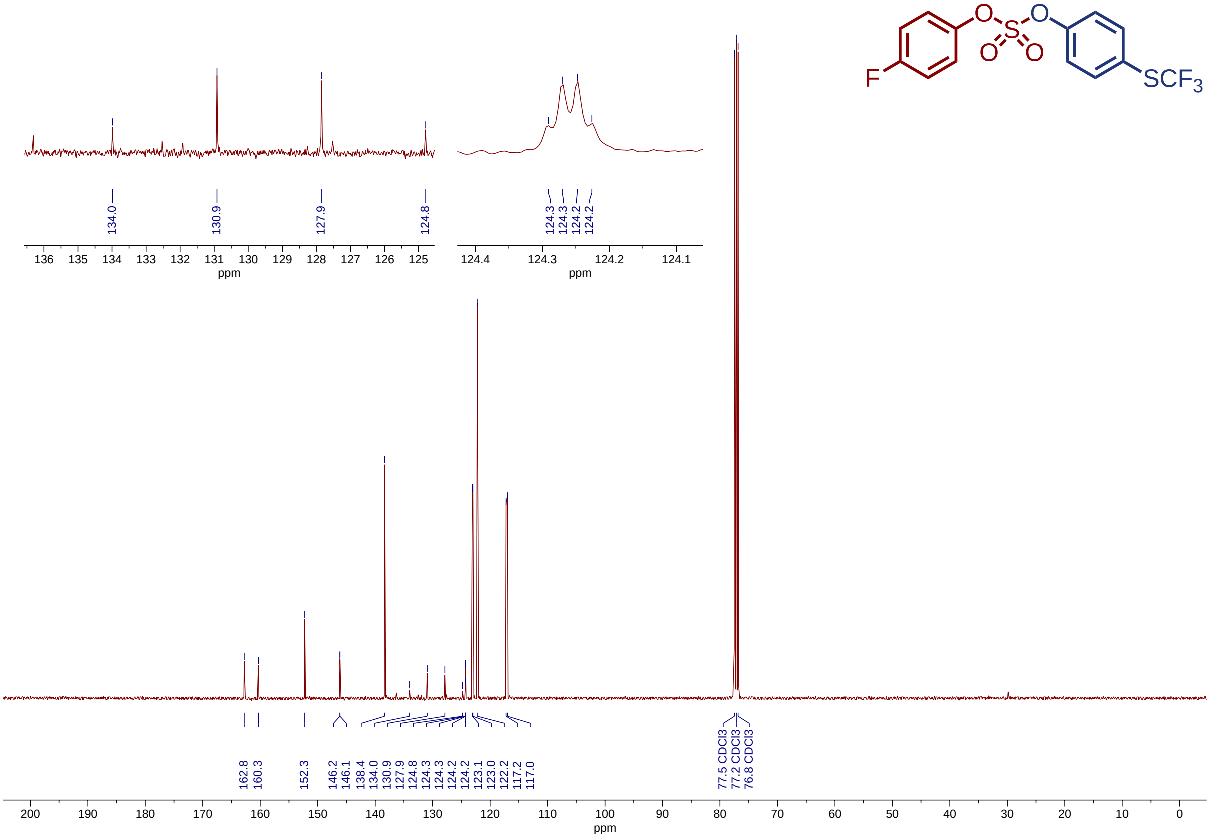
^{19}F NMR Spectrum for Compound **9d** (376 MHz, $CDCl_3$)



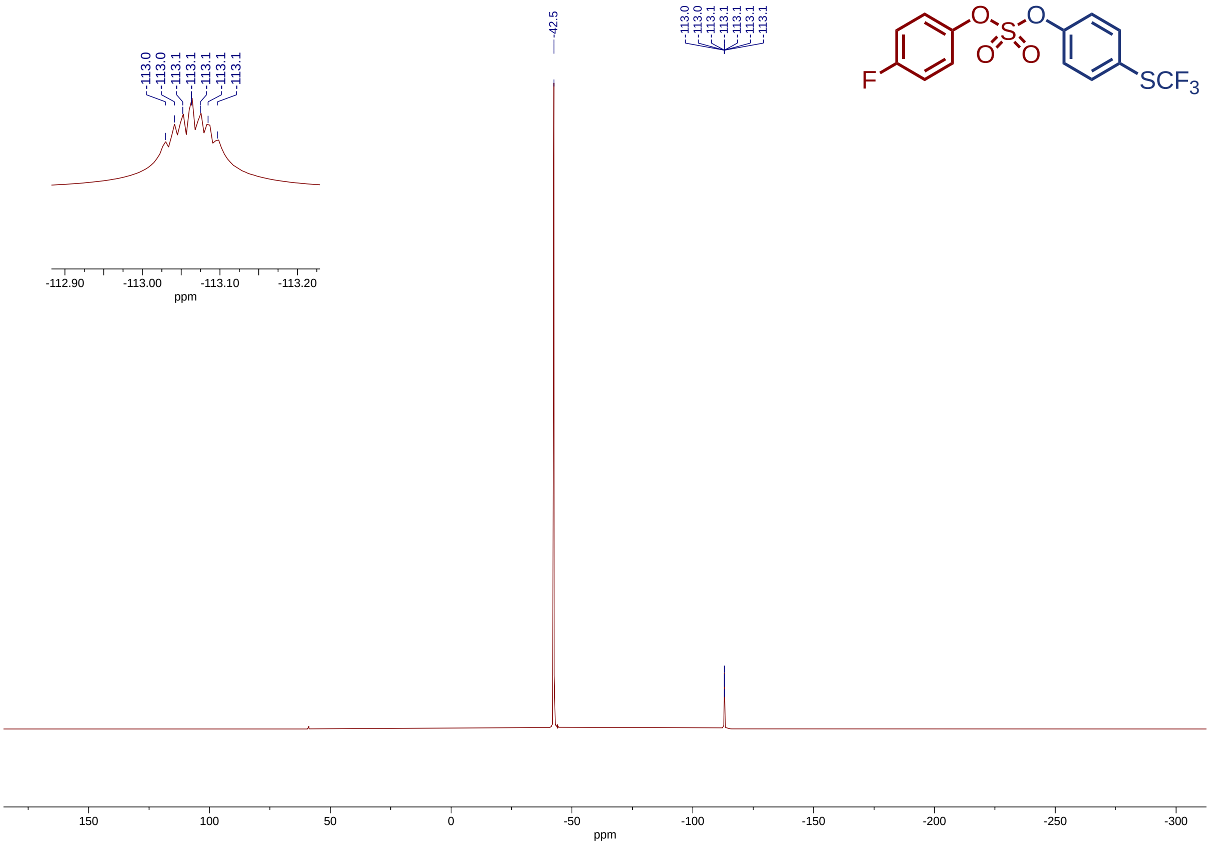
^{1}H NMR Spectrum for Compound **9e** (400 MHz, $CDCl_3$)



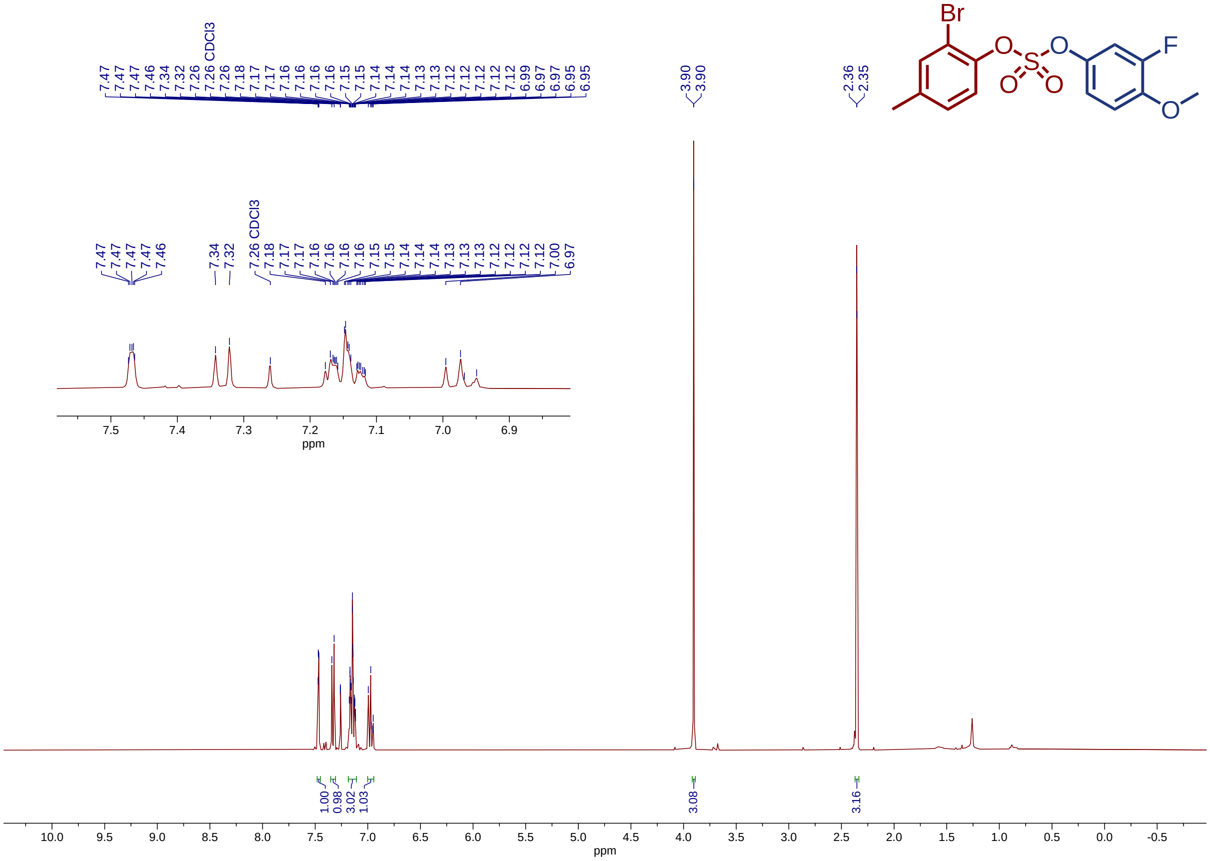
^{13}C NMR Spectrum for Compound **9e** (101 MHz, $CDCl_3$)



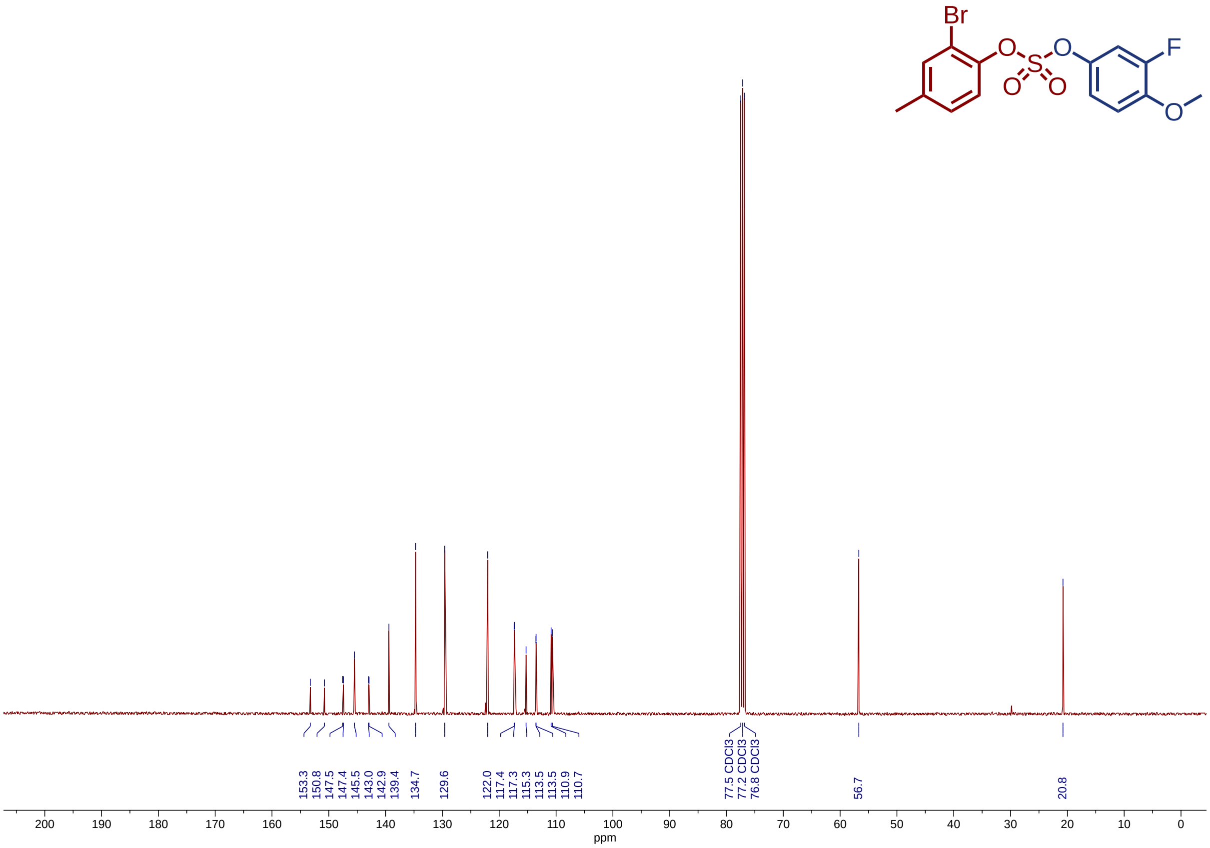
^{19}F NMR Spectrum for Compound **9e** (376 MHz, $CDCl_3$)



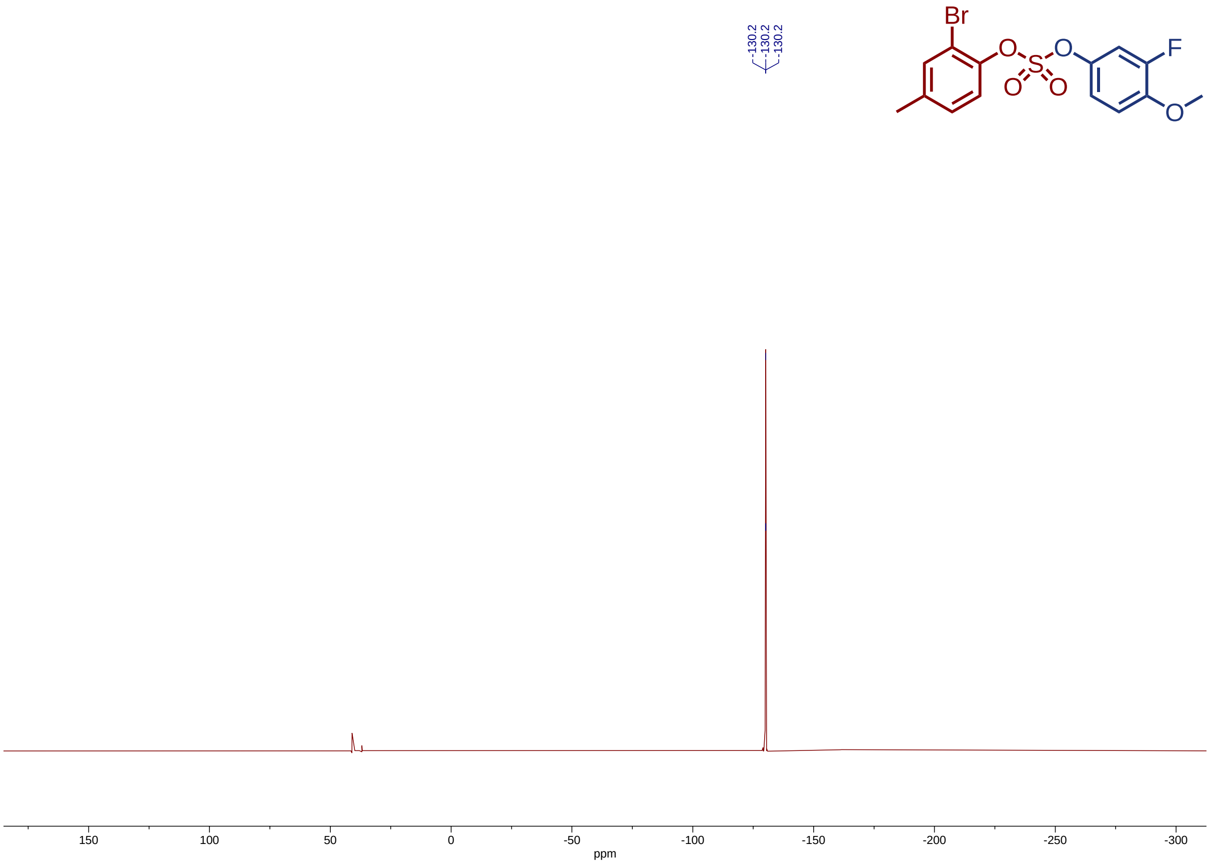
^{1}H NMR Spectrum for Compound **9f** (400 MHz, $CDCl_3$)



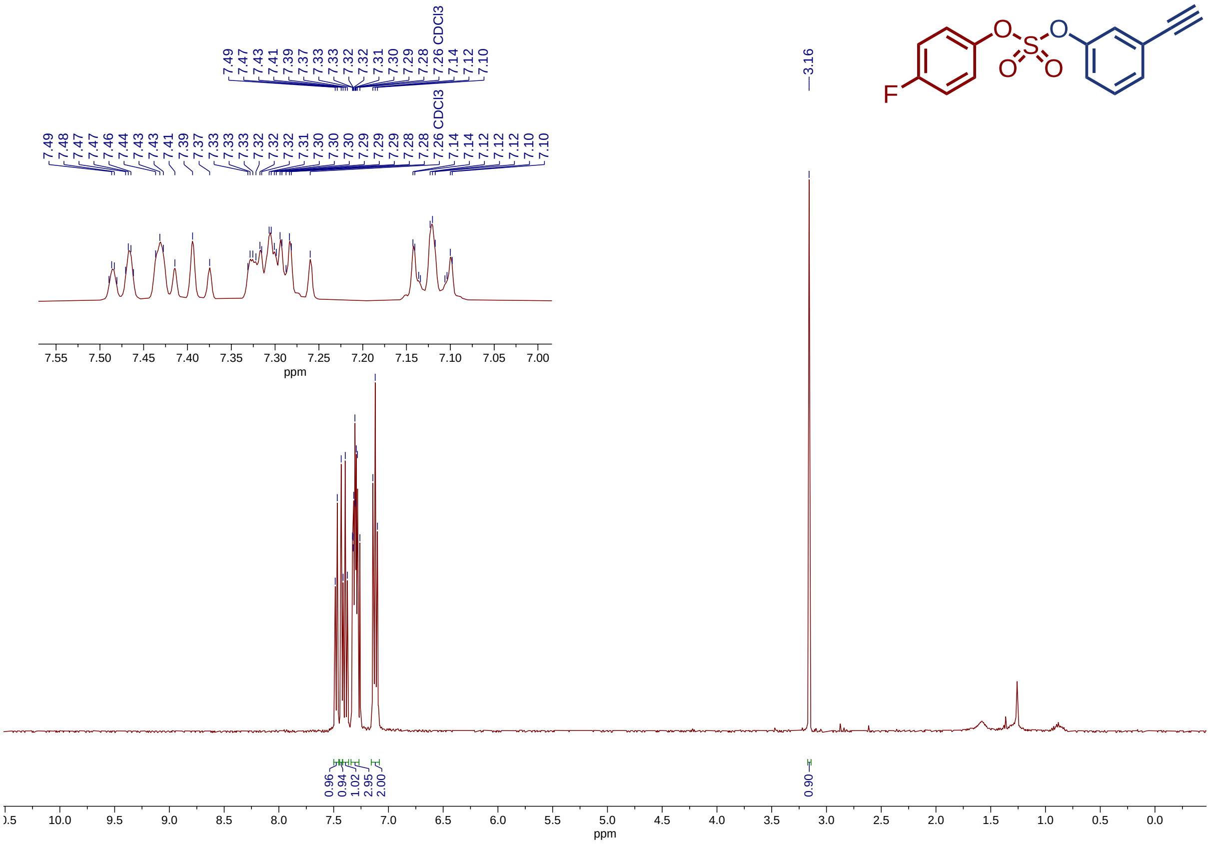
^{13}C NMR Spectrum for Compound **9f** (101 MHz, $CDCl_3$)



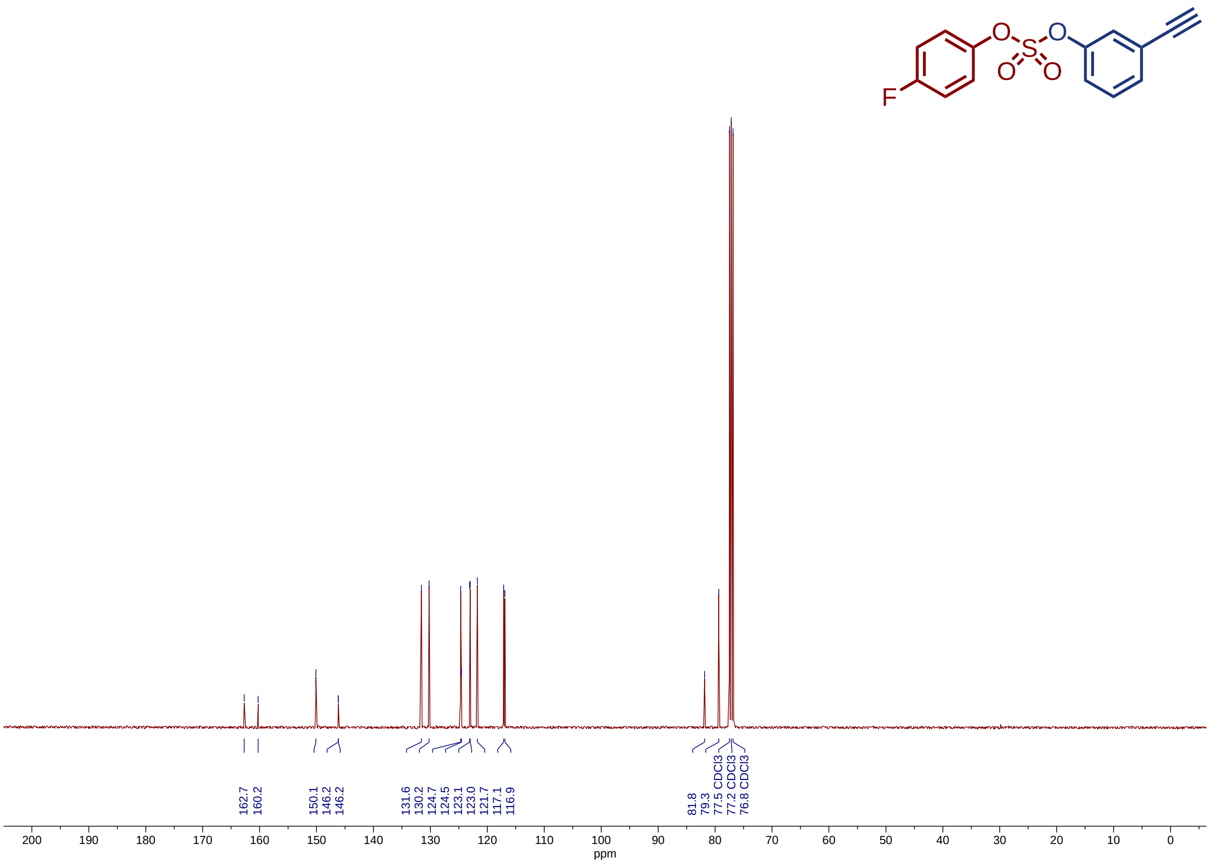
^{19}F NMR Spectrum for Compound **9f** (376 MHz, CDCl$_3$)



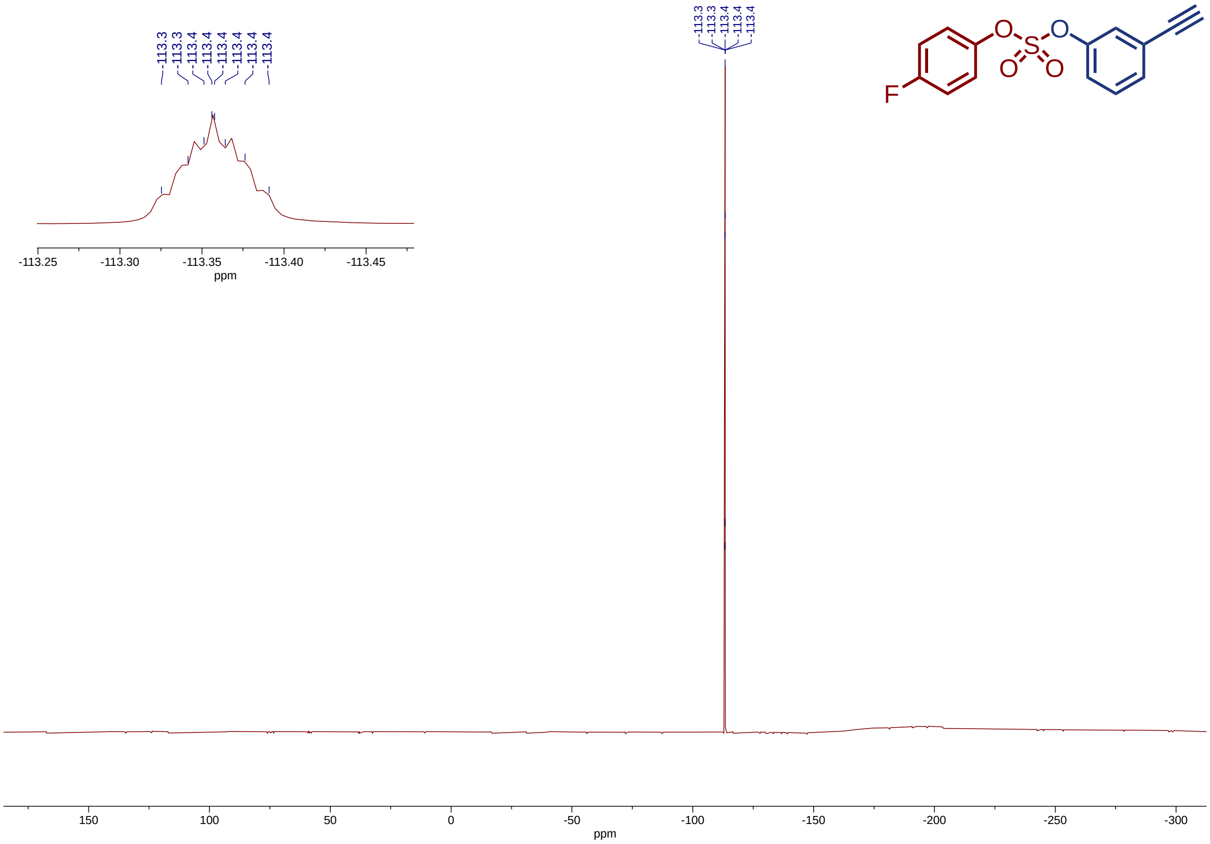
^{1}H NMR Spectrum for Compound **9g** (400 MHz, CDCl$_3$)



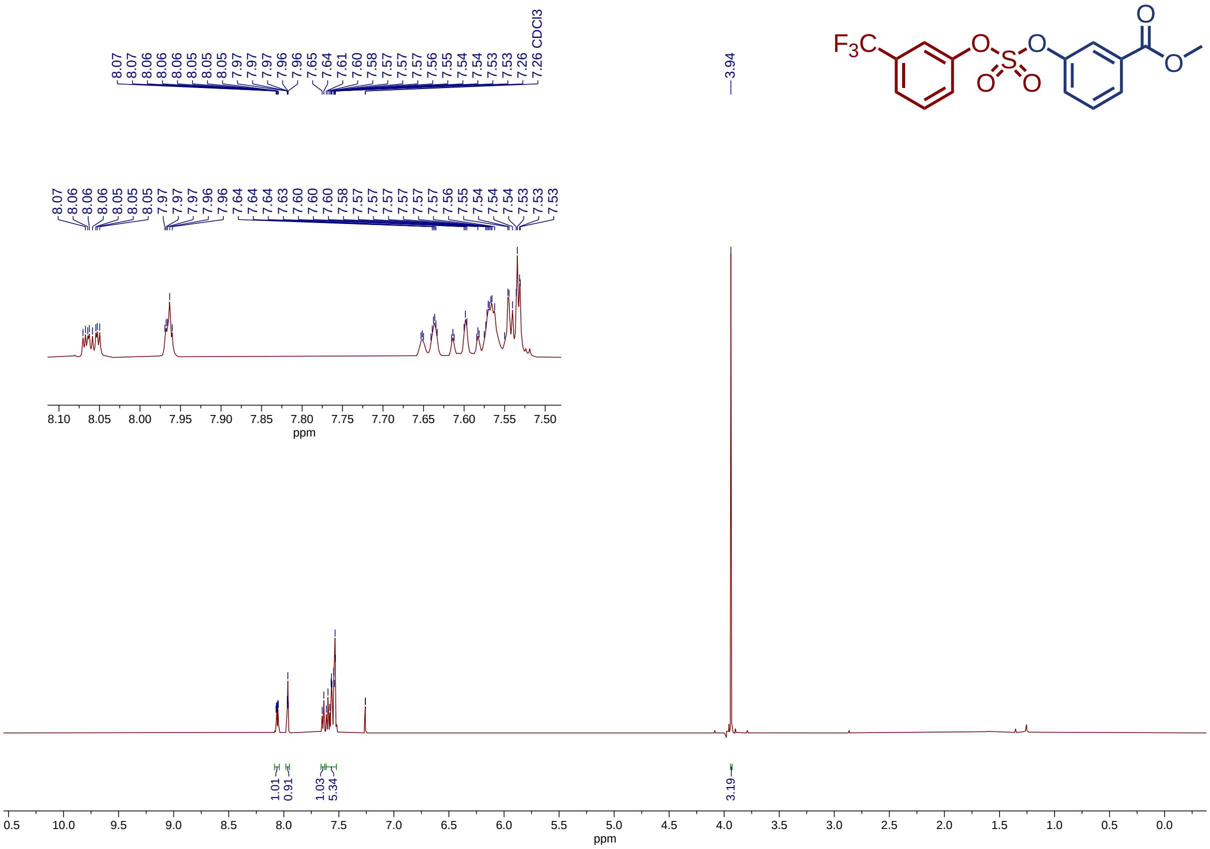
^{13}C NMR Spectrum for Compound **9g** (101 MHz, $CDCl_3$)



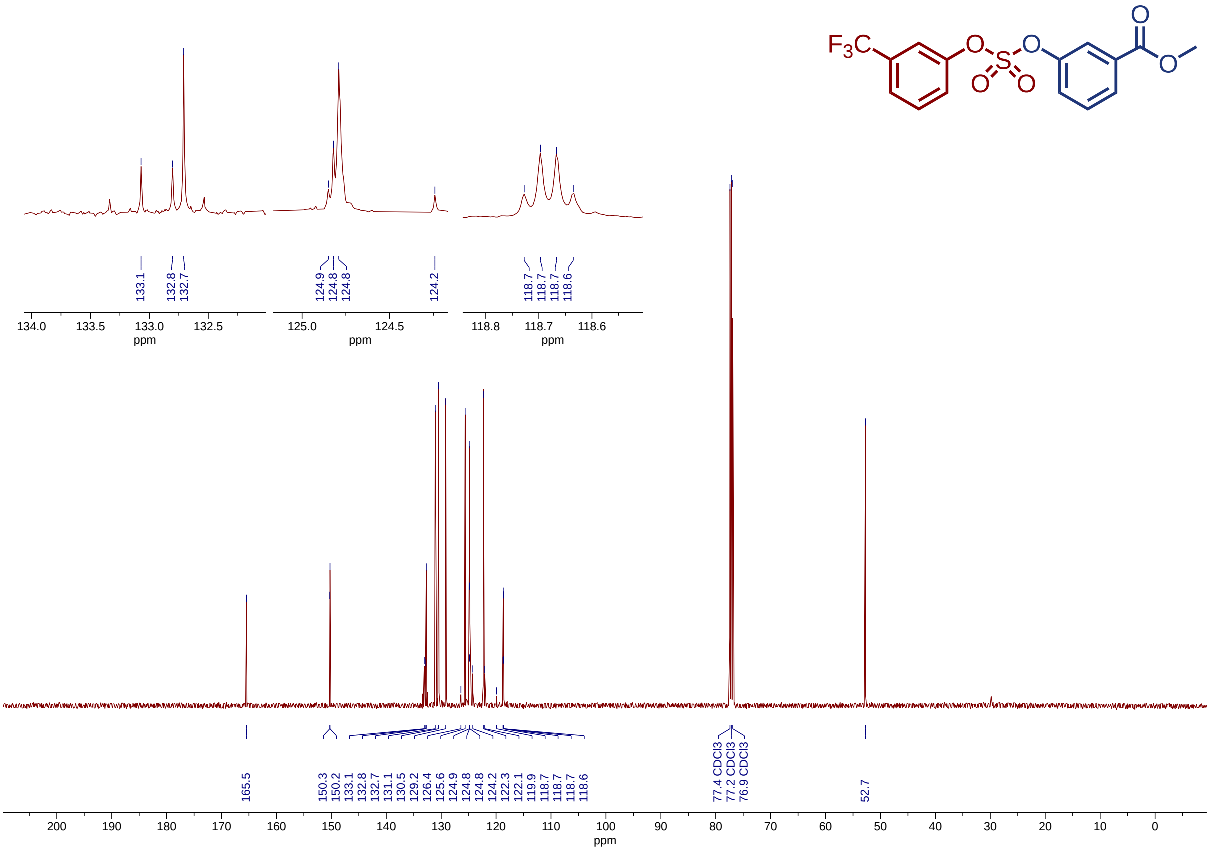
^{19}F NMR Spectrum for Compound **9g** (376 MHz, $CDCl_3$)



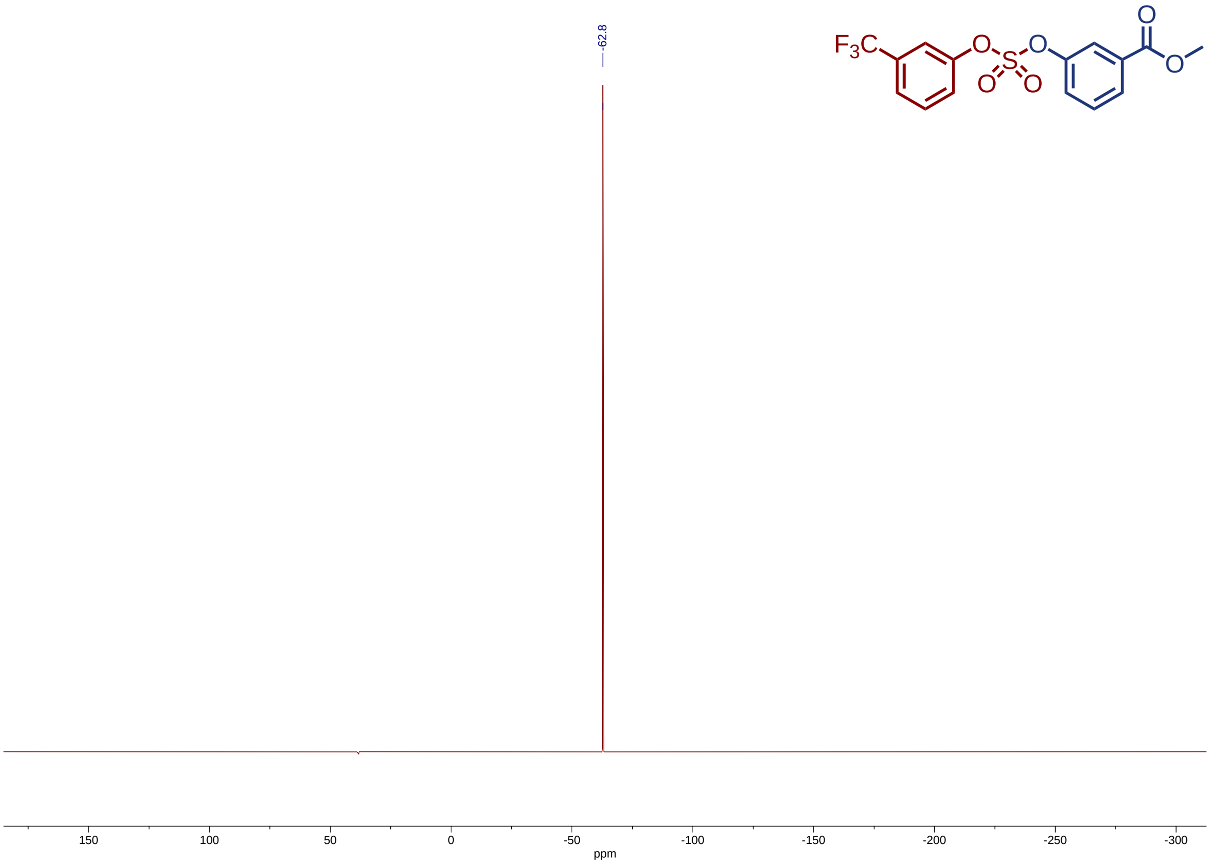
^{1}H NMR Spectrum for Compound **9h** (500 MHz, $CDCl_3$)



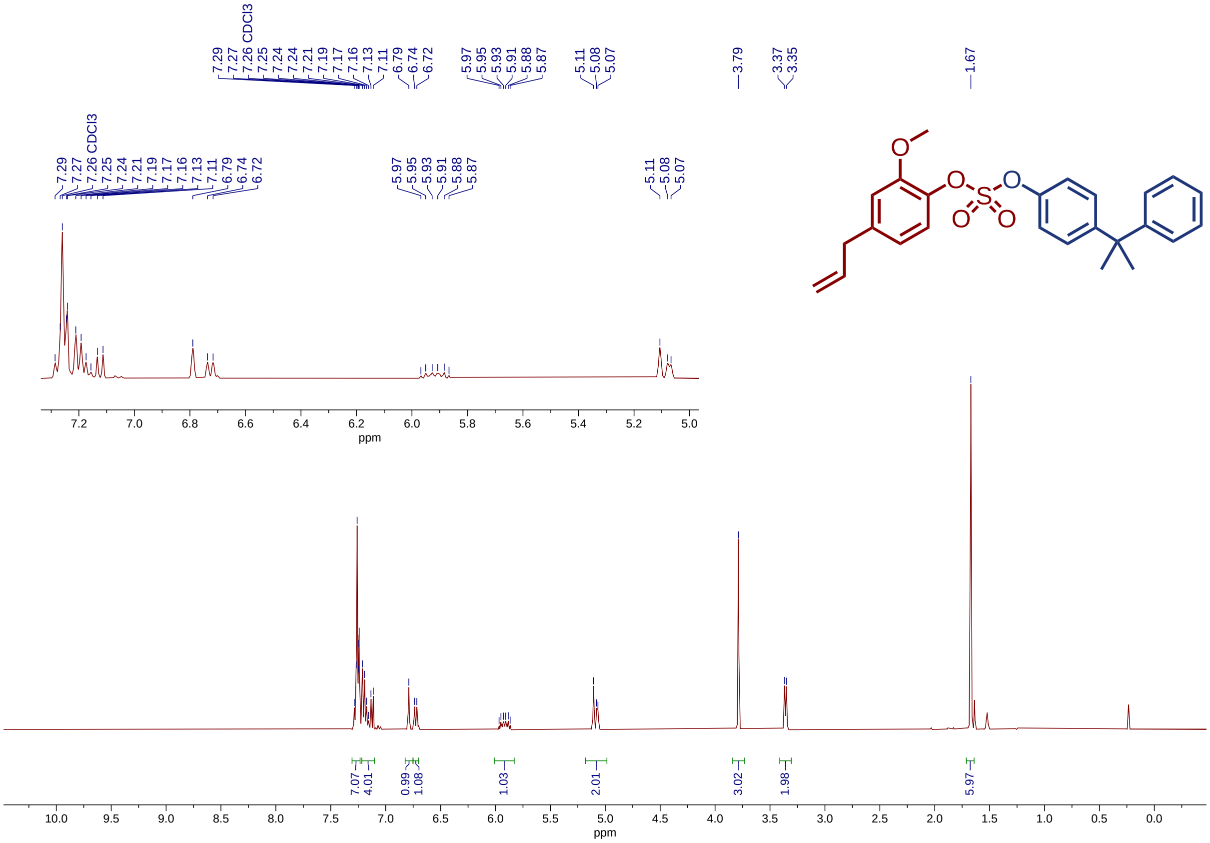
^{13}C NMR Spectrum for Compound **9h** (126 MHz, $CDCl_3$)



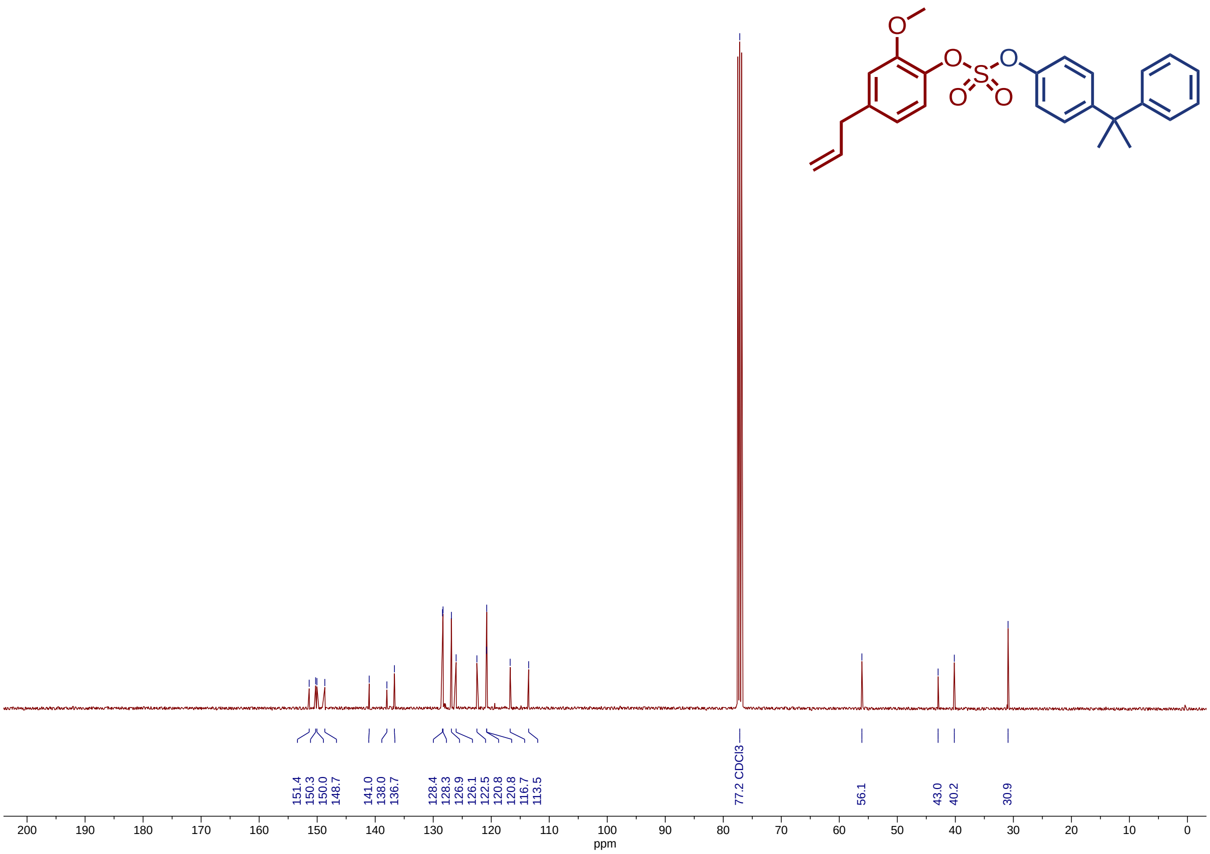
^{19}F NMR Spectrum for Compound **9h** (376 MHz, CDCl$_3$)



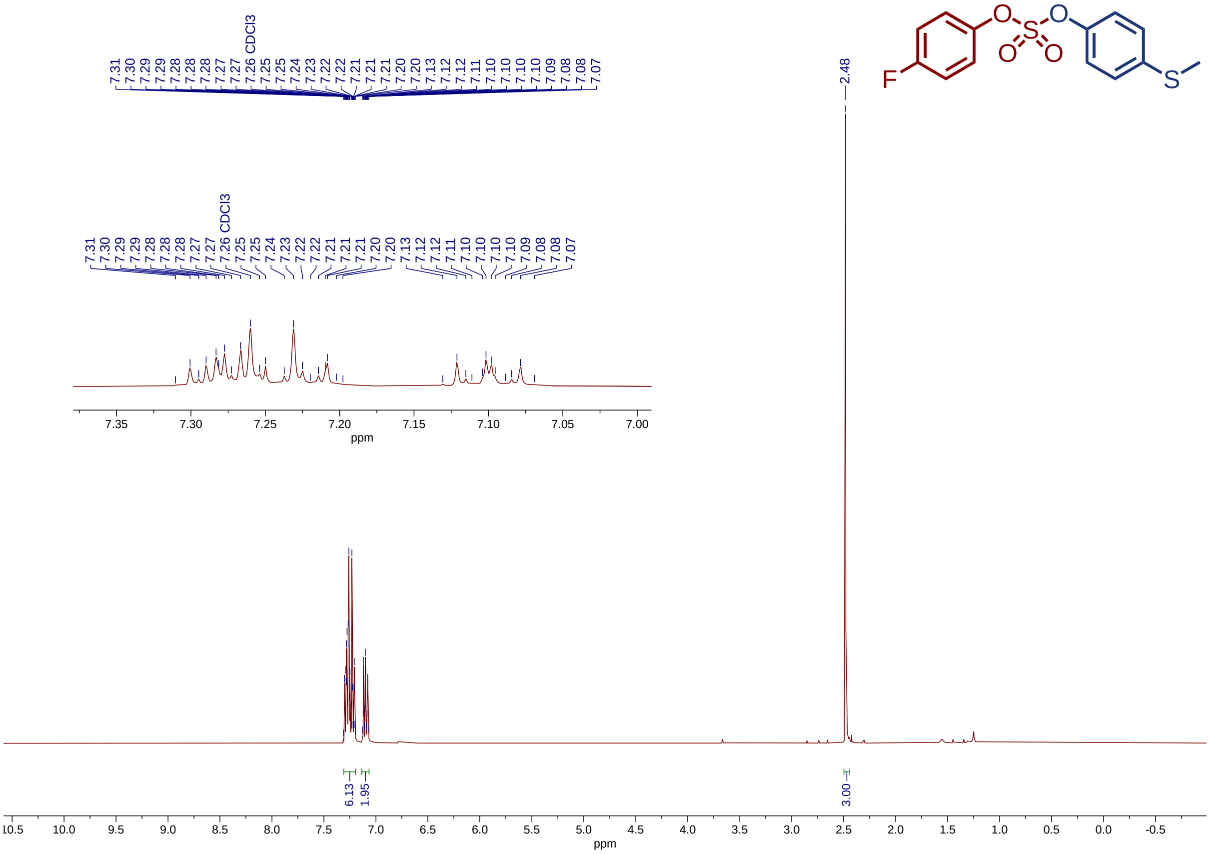
^{1}H NMR Spectrum for Compound **9i** (400 MHz, CDCl$_3$)



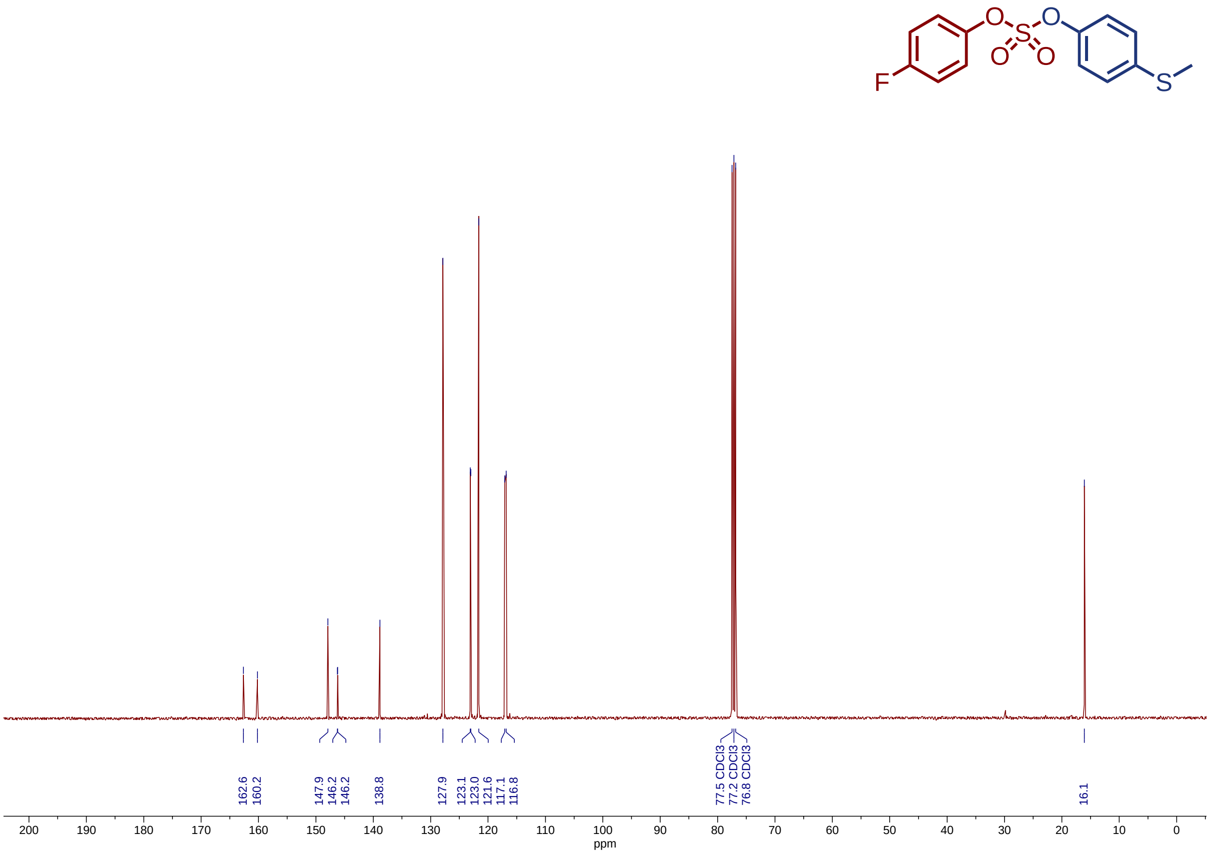
^{13}C NMR Spectrum for Compound **9i** (101 MHz, $CDCl_3$)



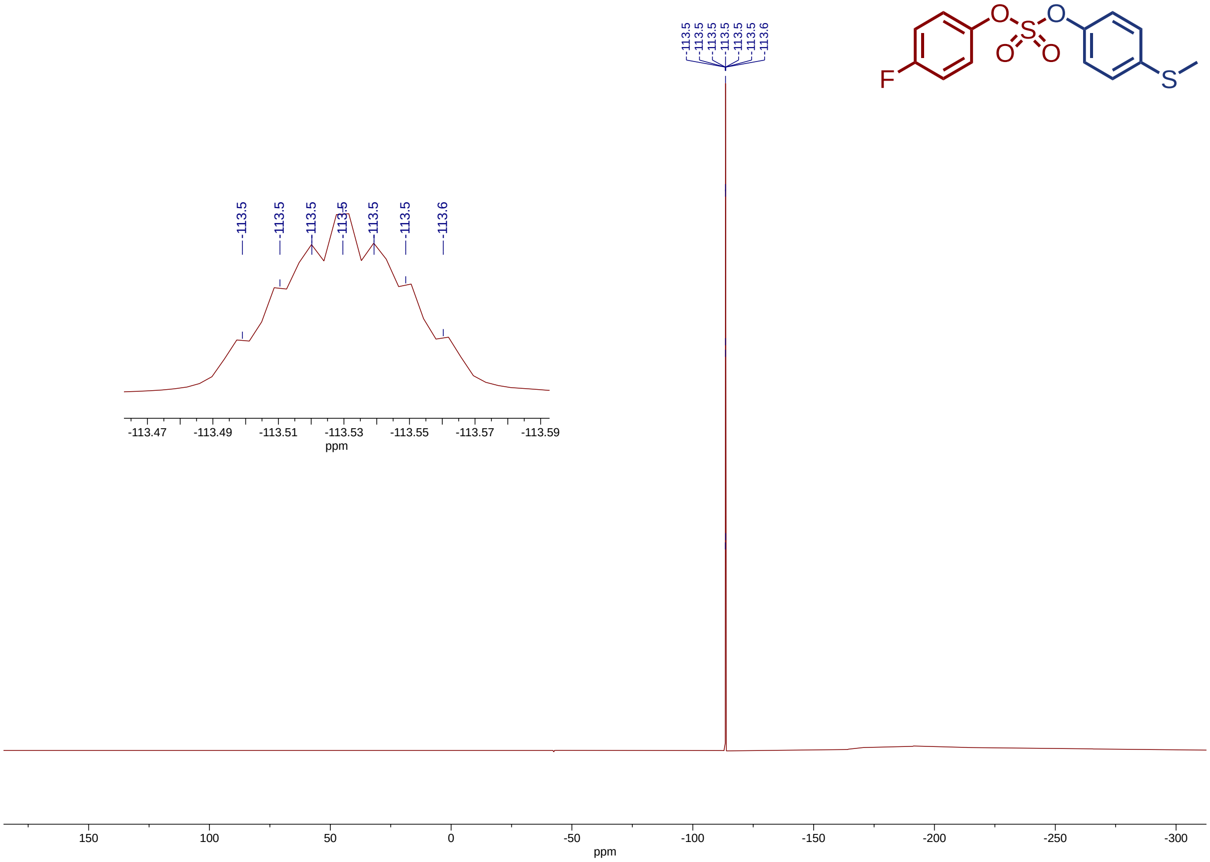
^{1}H NMR Spectrum for Compound **9j** (400 MHz, $CDCl_3$)



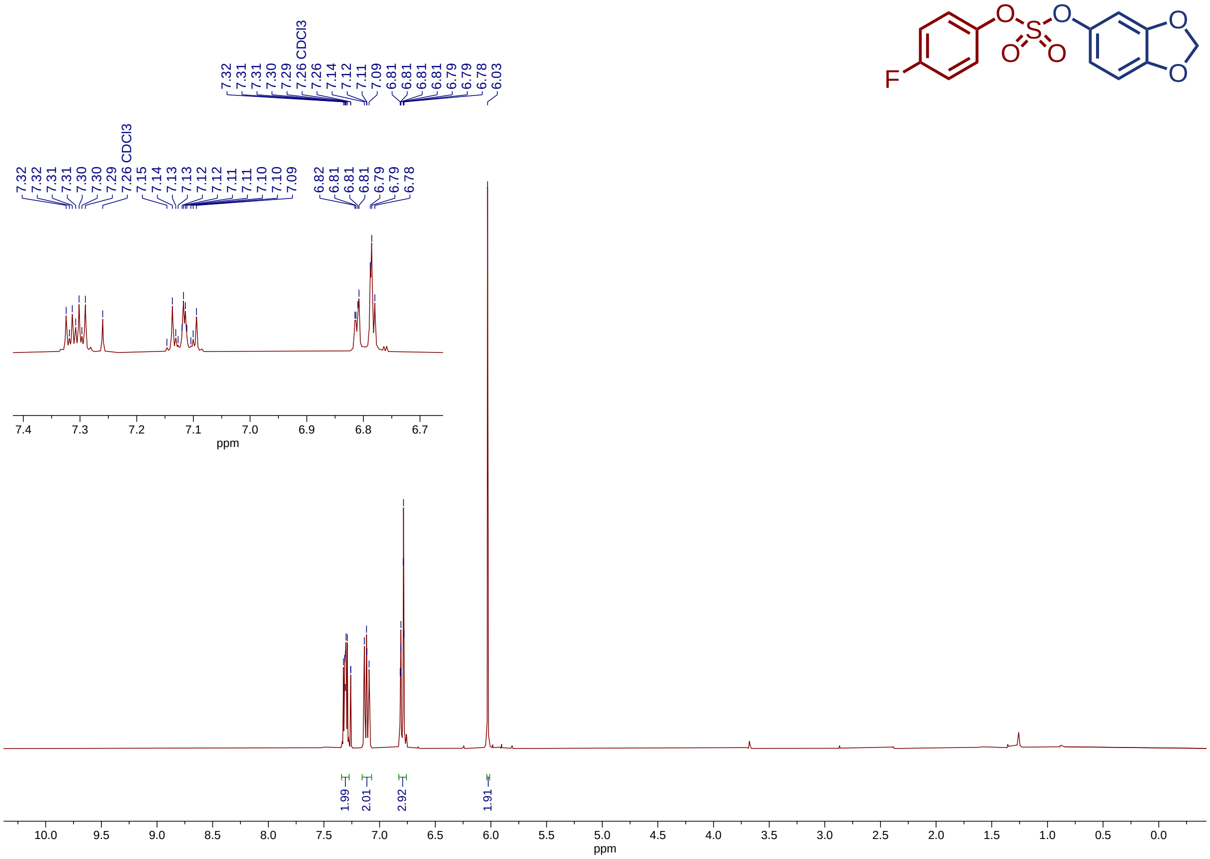
^{13}C NMR Spectrum for Compound **9j** (101 MHz, $CDCl_3$)



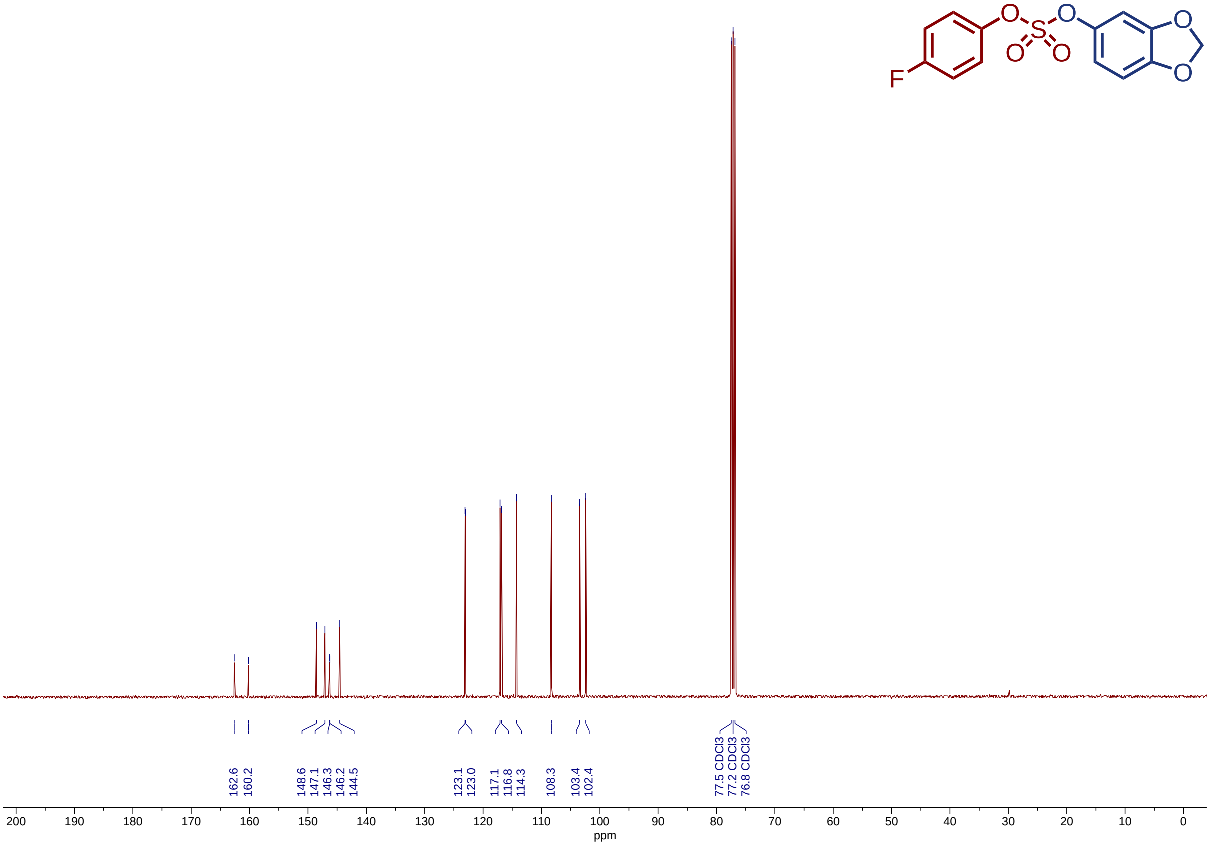
^{19}F NMR Spectrum for Compound **9j** (376 MHz, $CDCl_3$)



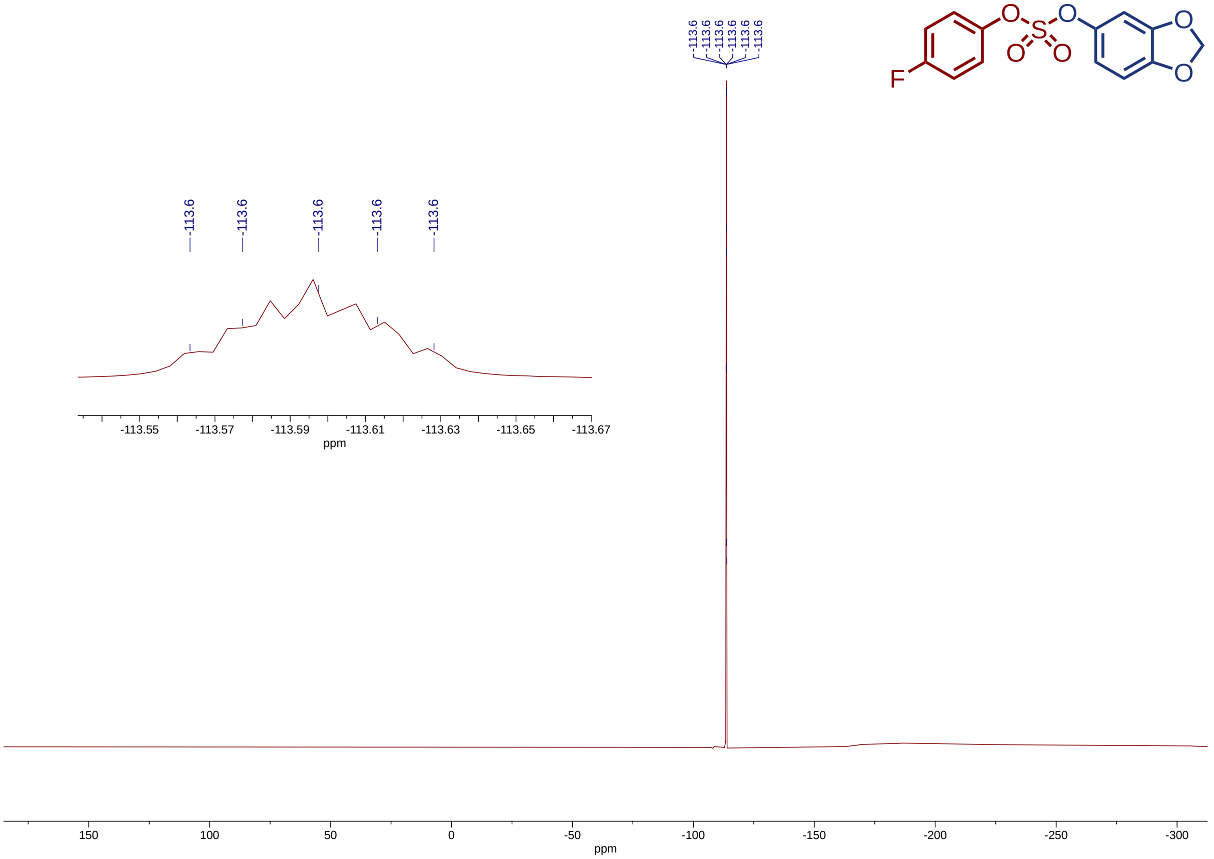
^{1}H NMR Spectrum for Compound **9k** (400 MHz, CDCl$_3$)



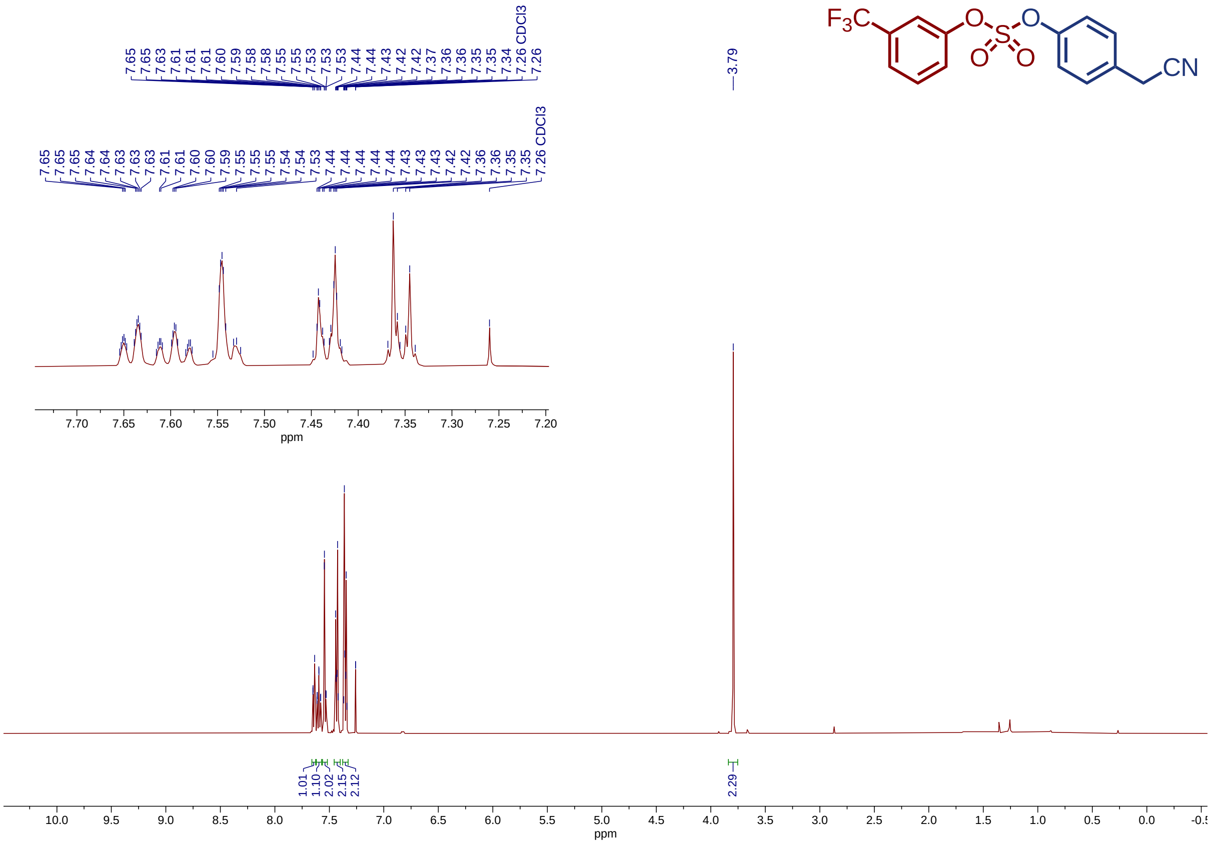
^{13}C NMR Spectrum for Compound **9k** (101 MHz, CDCl$_3$)



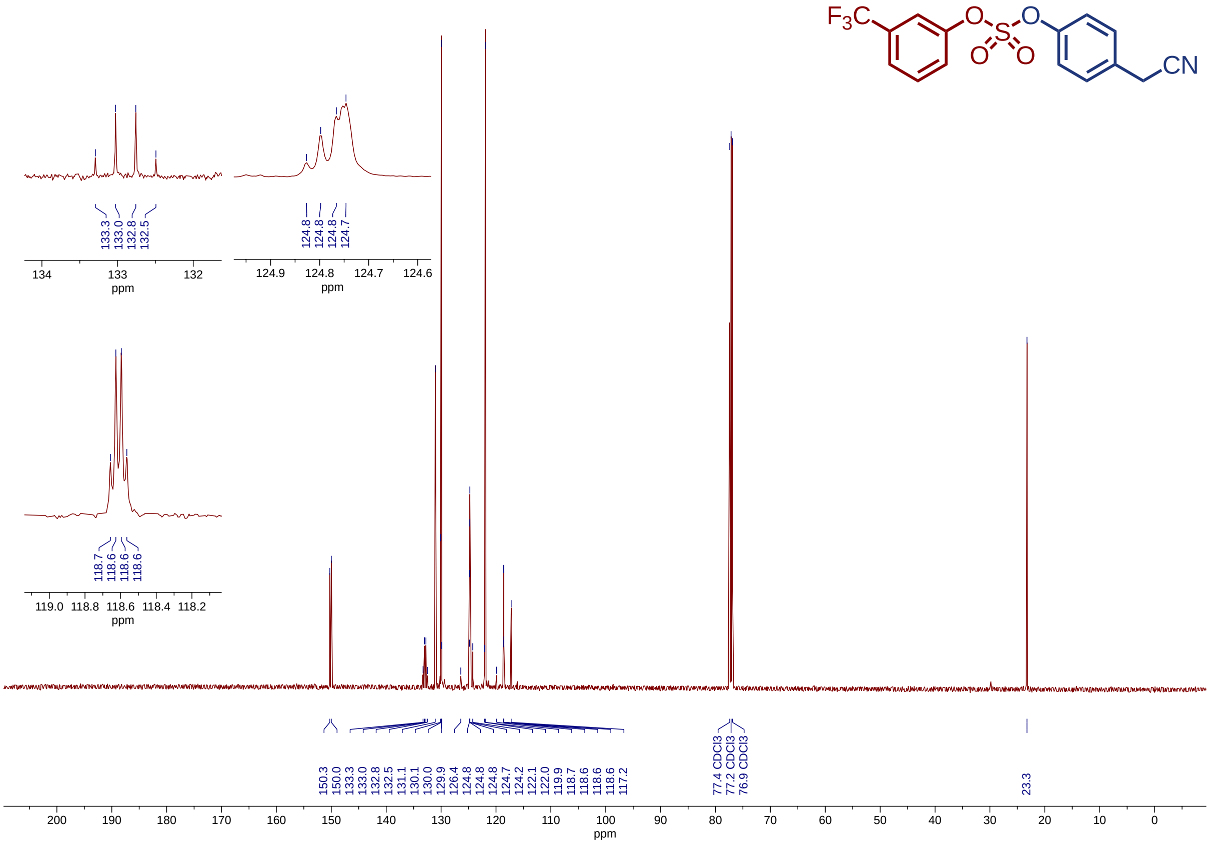
^{19}F NMR Spectrum for Compound **9k** (376 MHz, $CDCl_3$)



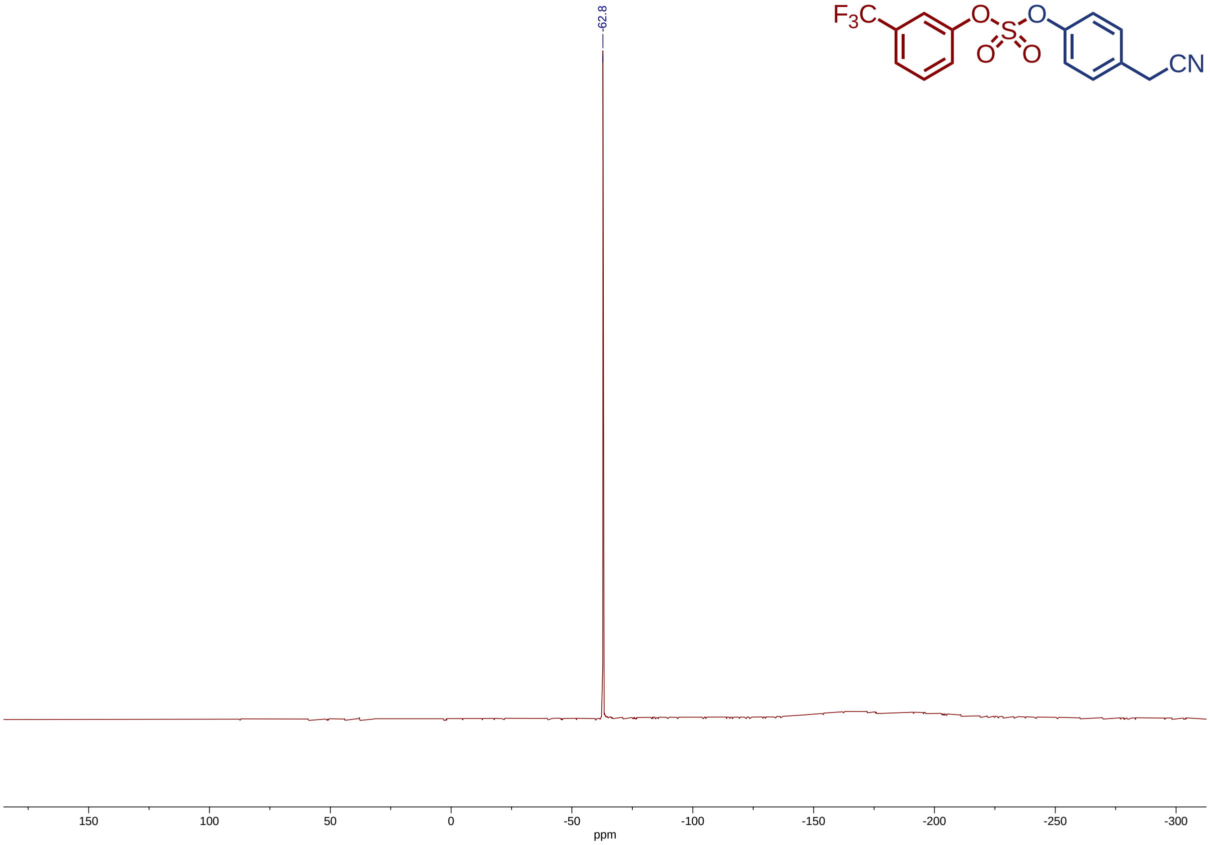
^{1}H NMR Spectrum for Compound **9l** (500 MHz, $CDCl_3$)



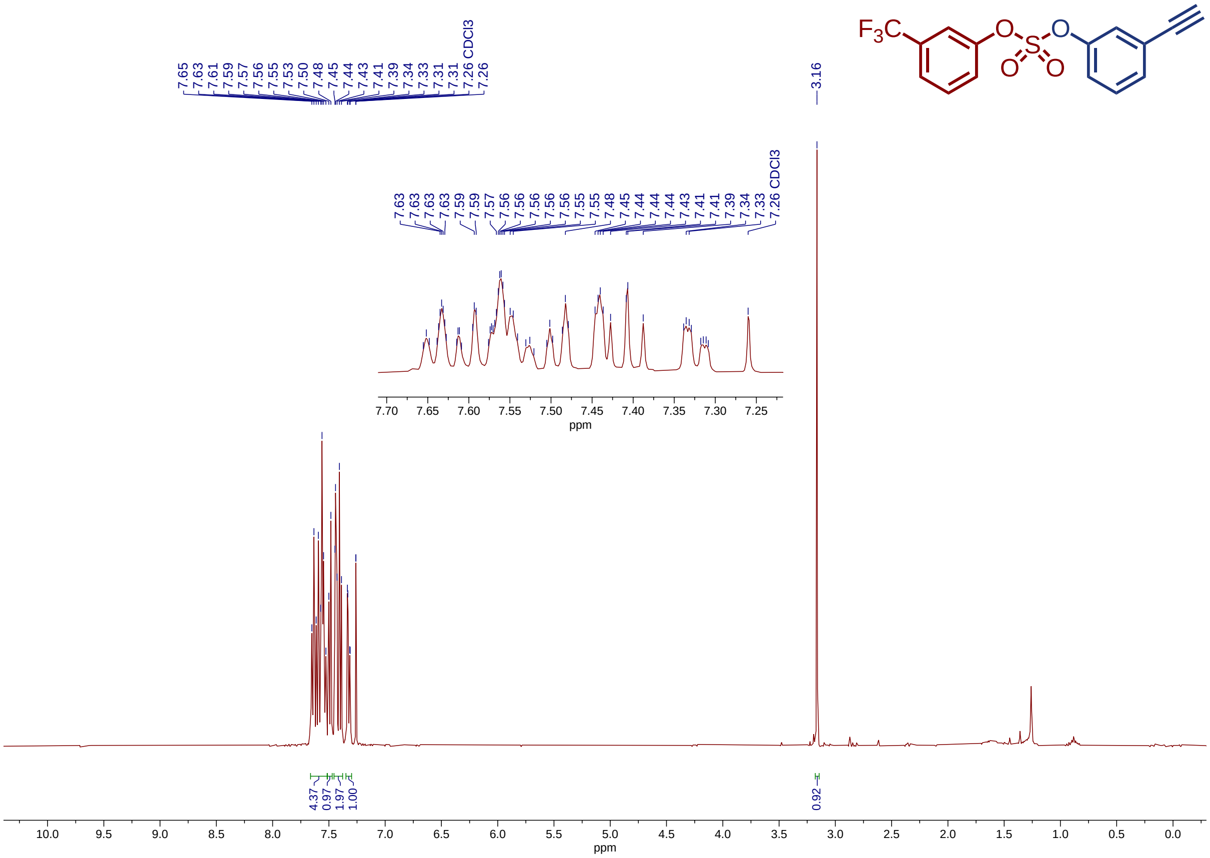
^{13}C NMR Spectrum for Compound **9l** (126 MHz, $CDCl_3$)



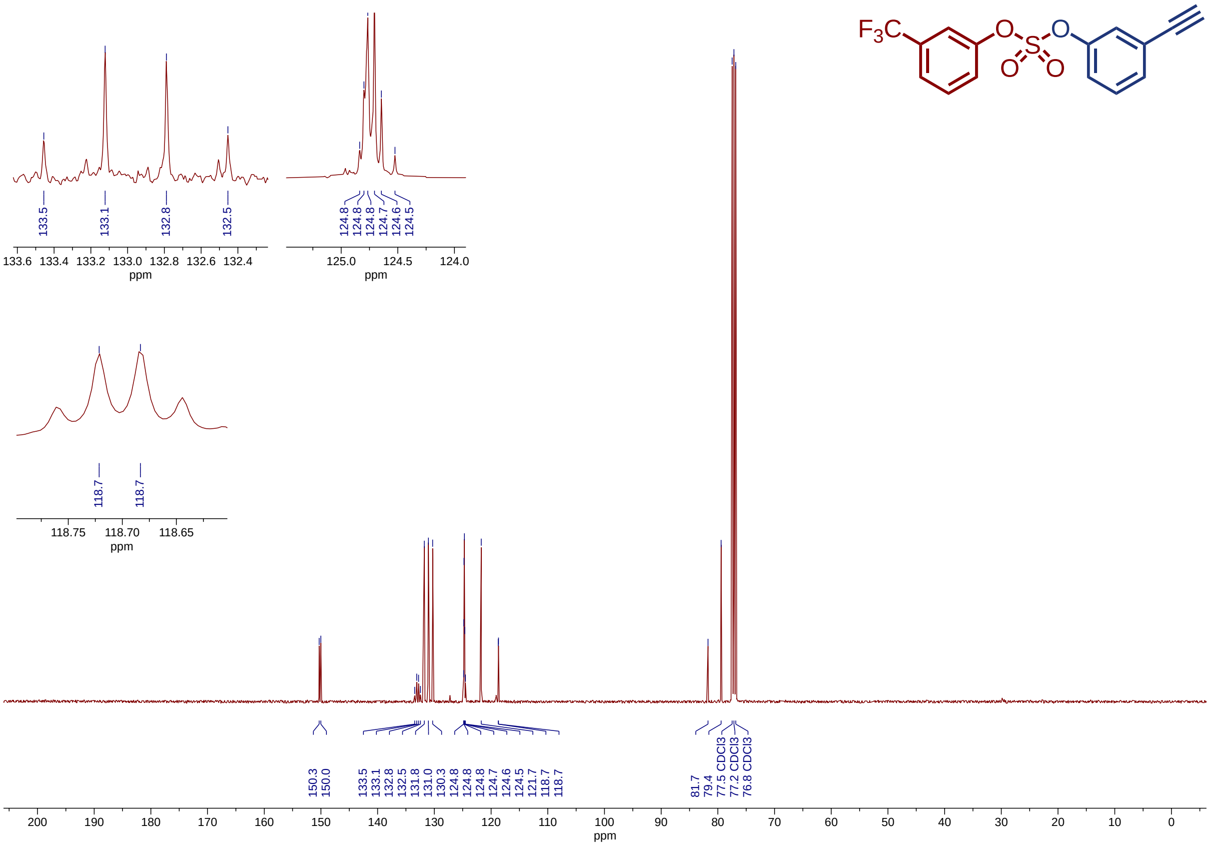
^{19}F NMR Spectrum for Compound **9l** (376 MHz, $CDCl_3$)



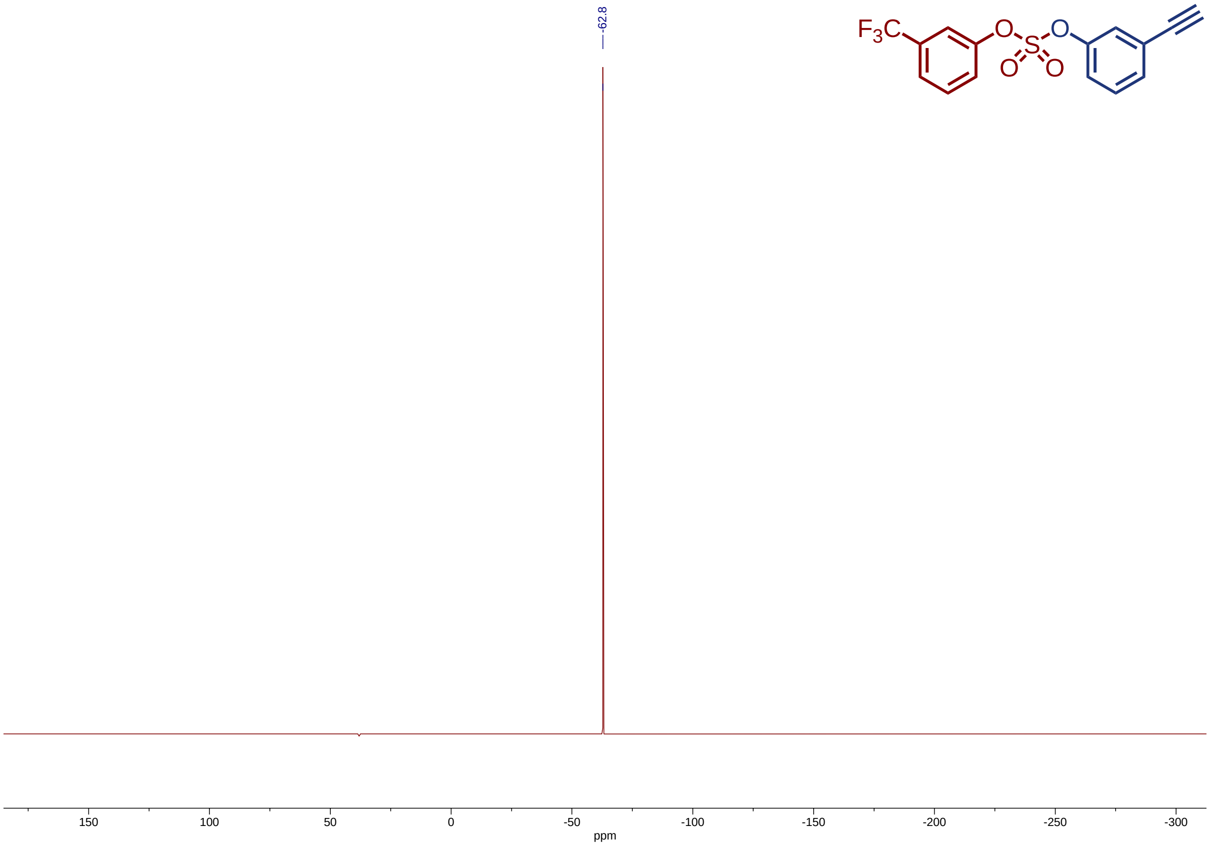
^{1}H NMR Spectrum for Compound **9m** (400 MHz, CDCl$_3$)



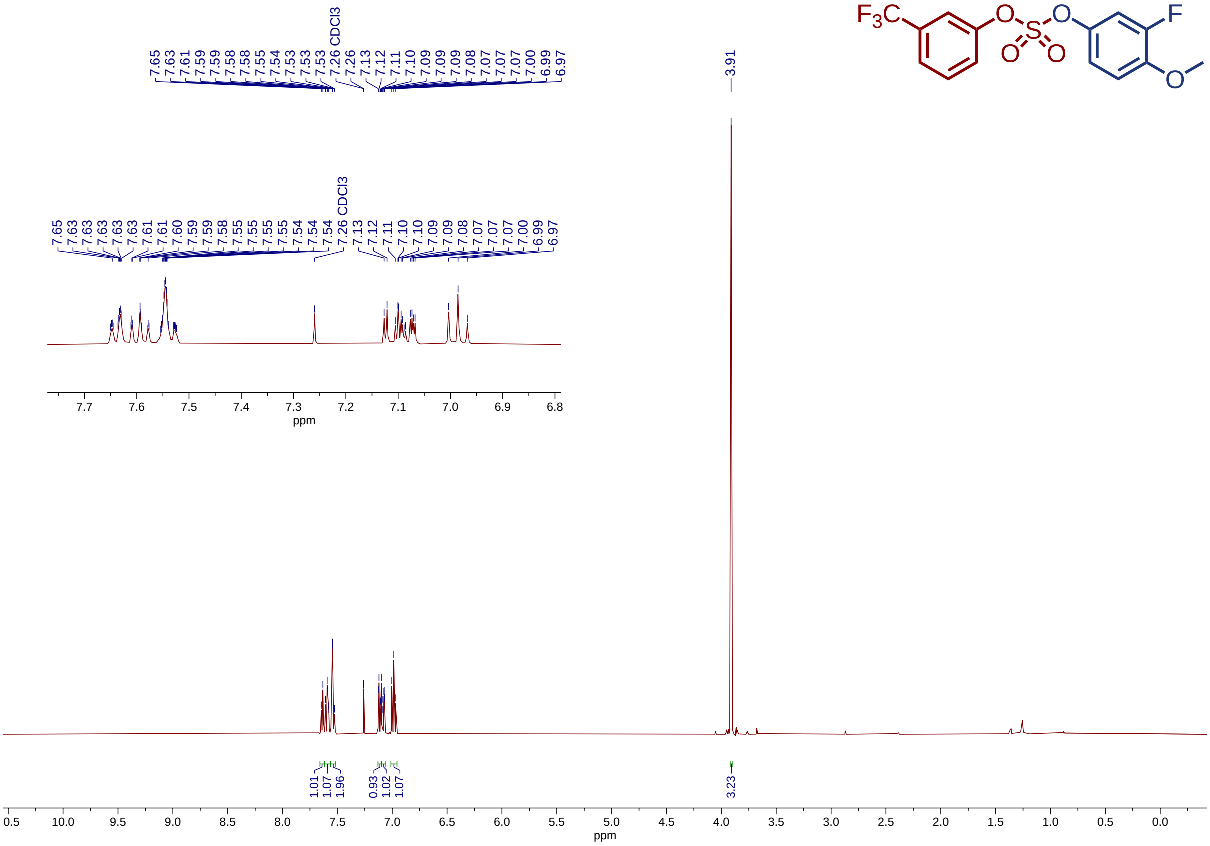
^{13}C NMR Spectrum for Compound **9m** (101 MHz, CDCl$_3$)



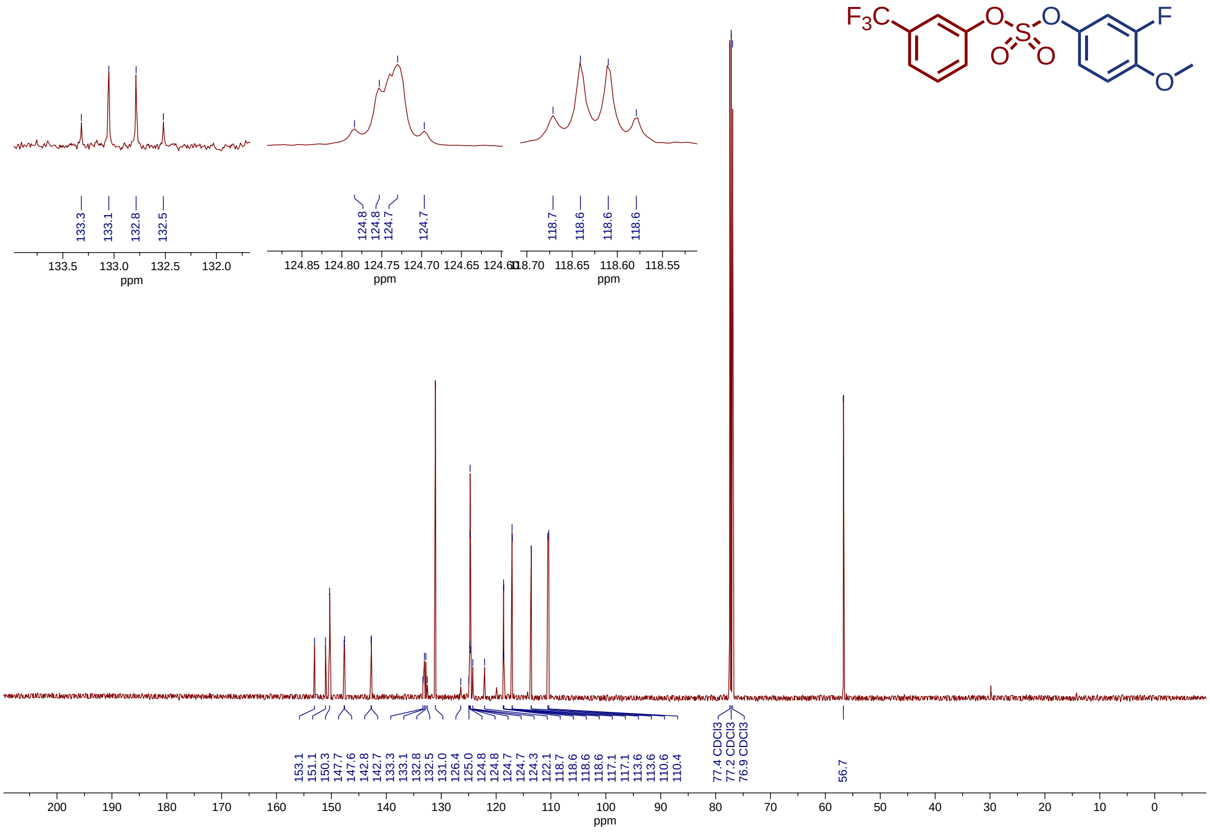
^{19}F NMR Spectrum for Compound **9m** (376 MHz, CDCl$_3$)



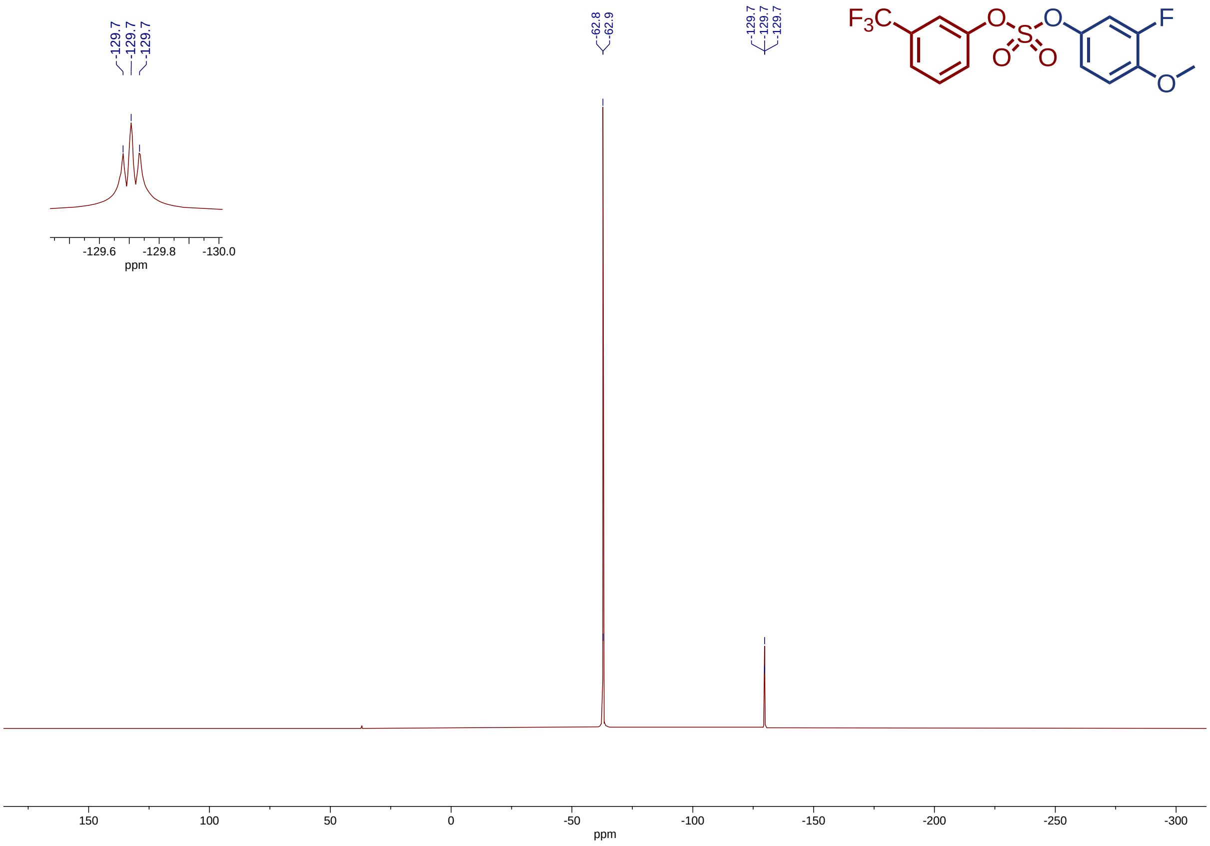
^{1}H NMR Spectrum for Compound **9n** (500 MHz, CDCl$_3$)



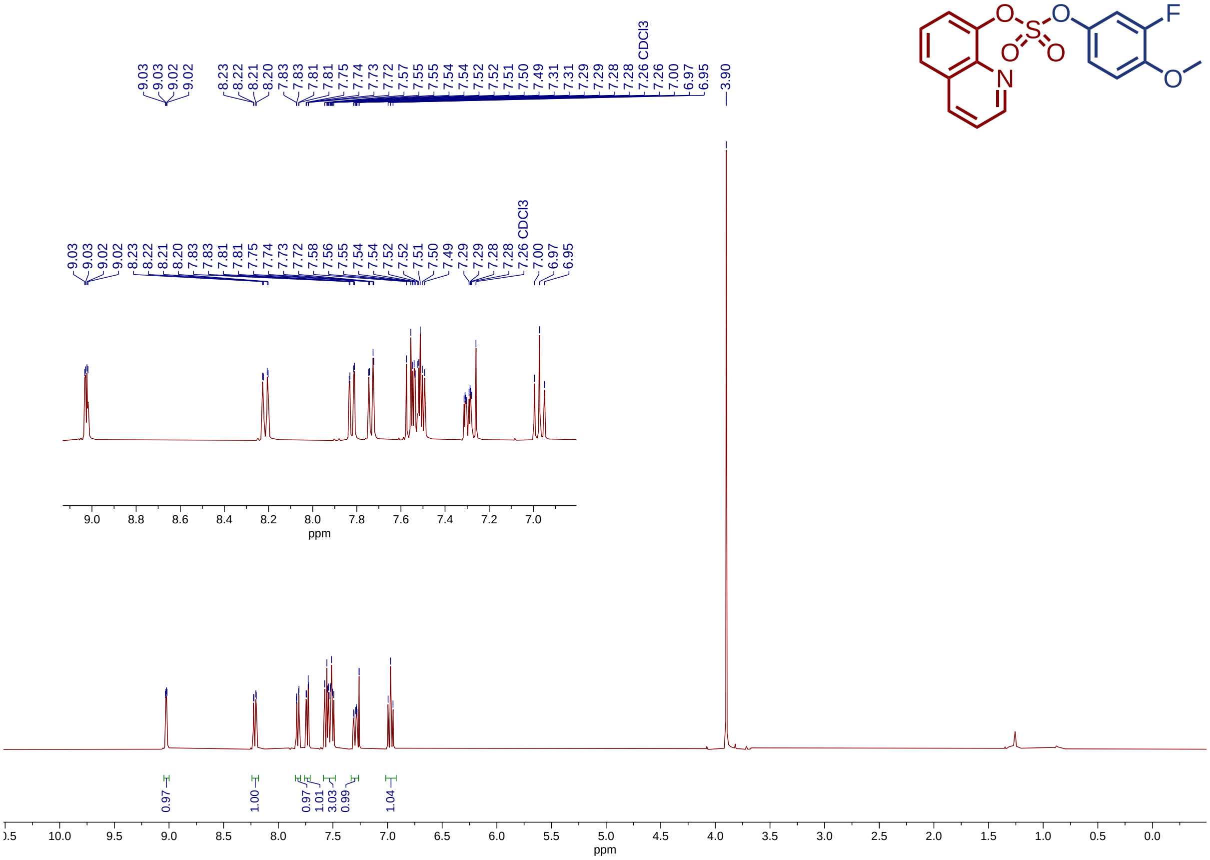
^{13}C NMR Spectrum for Compound **9n** (126 MHz, $CDCl_3$)



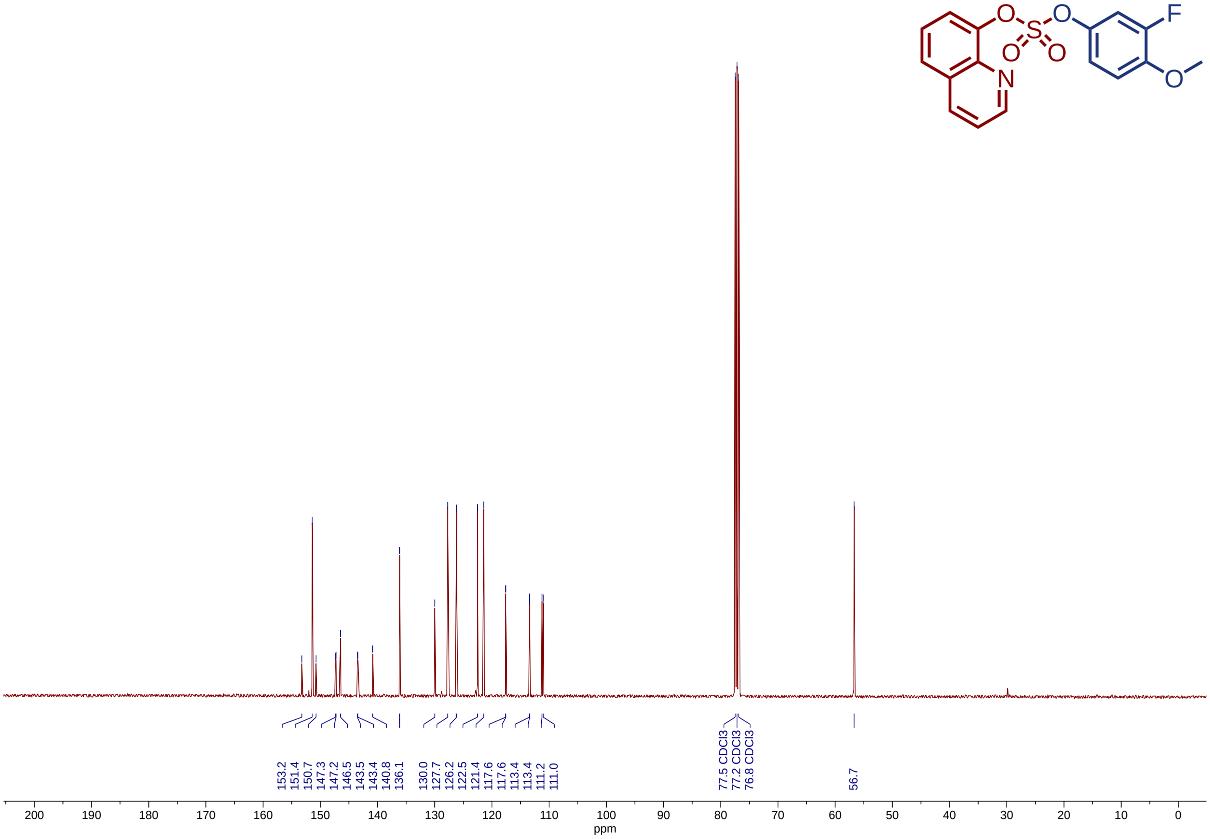
^{19}F NMR Spectrum for Compound **9n** (376 MHz, $CDCl_3$)



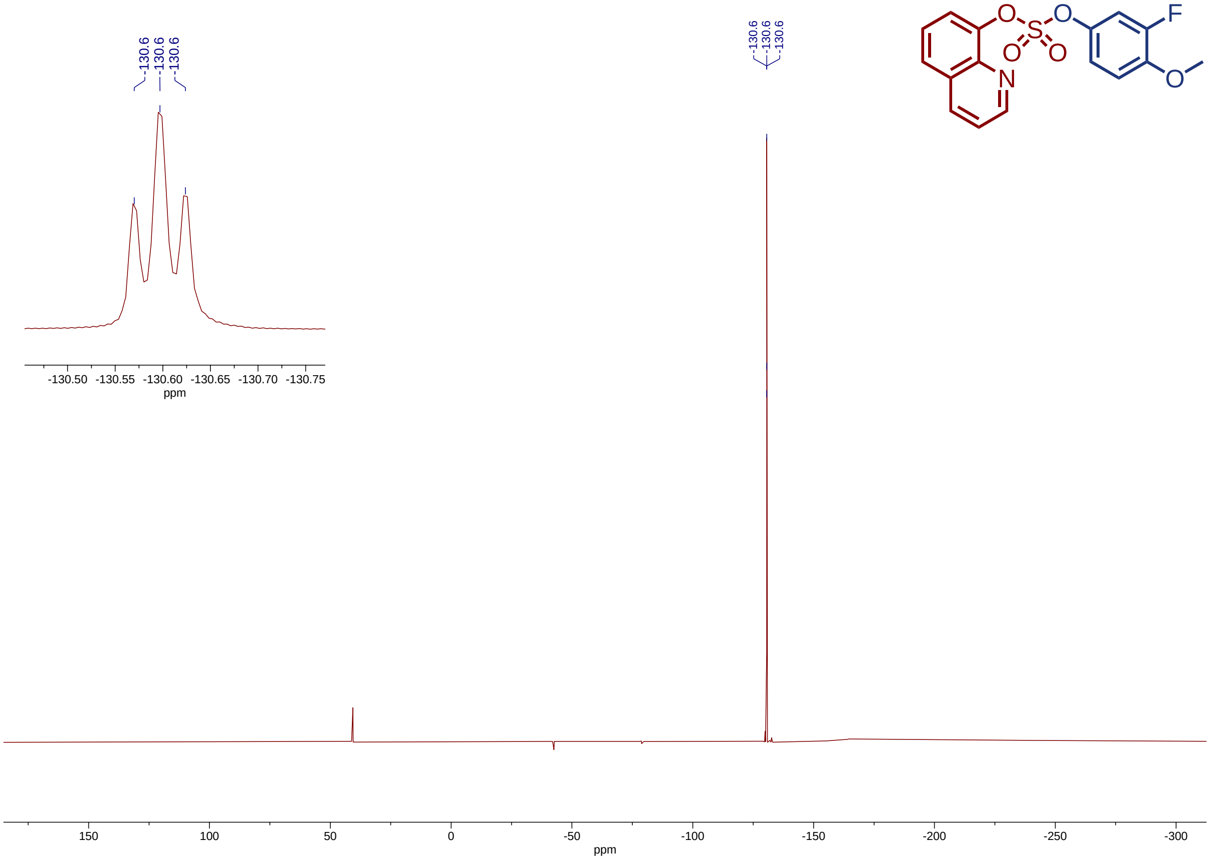
^{1}H NMR Spectrum for Compound **9o** (400 MHz, $CDCl_3$)



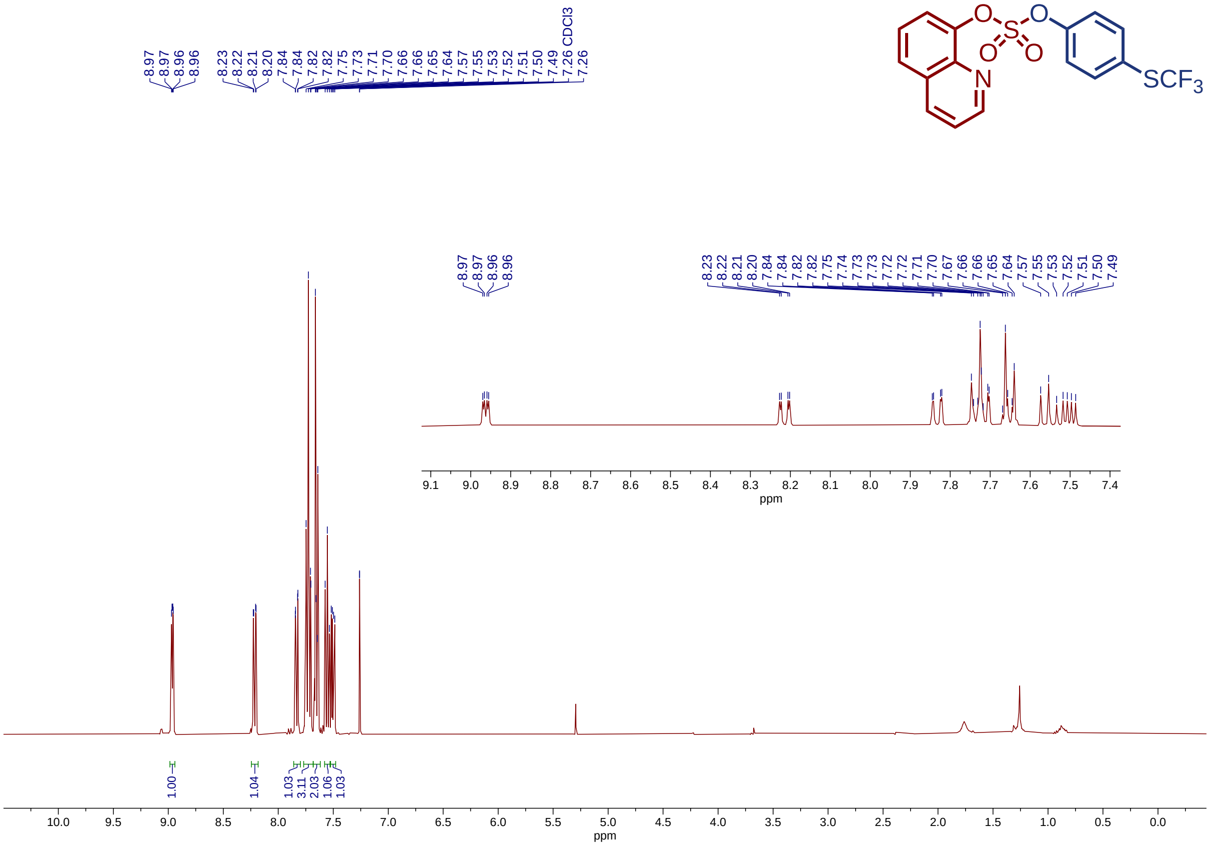
^{13}C NMR Spectrum for Compound **9o** (101 MHz, $CDCl_3$)



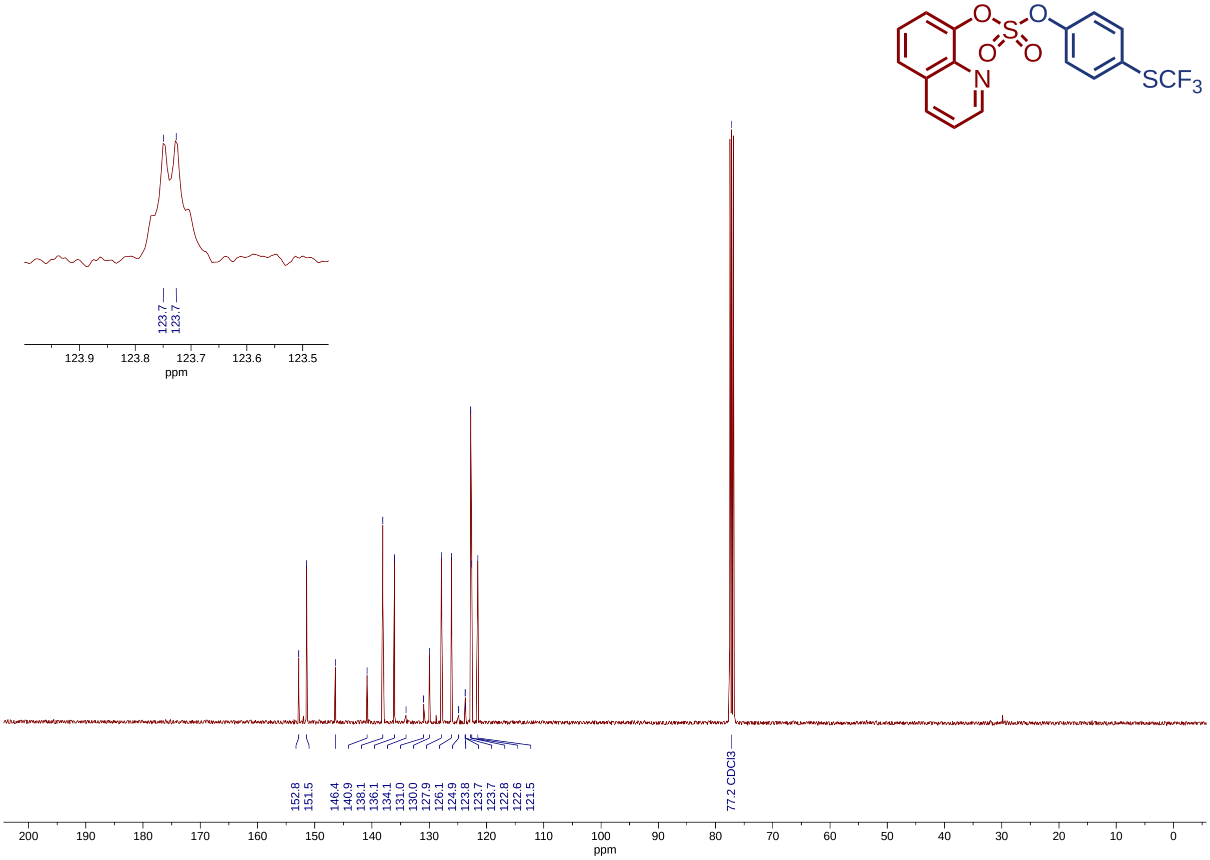
^{19}F NMR Spectrum for Compound **9o** (376 MHz, CDCl$_3$)



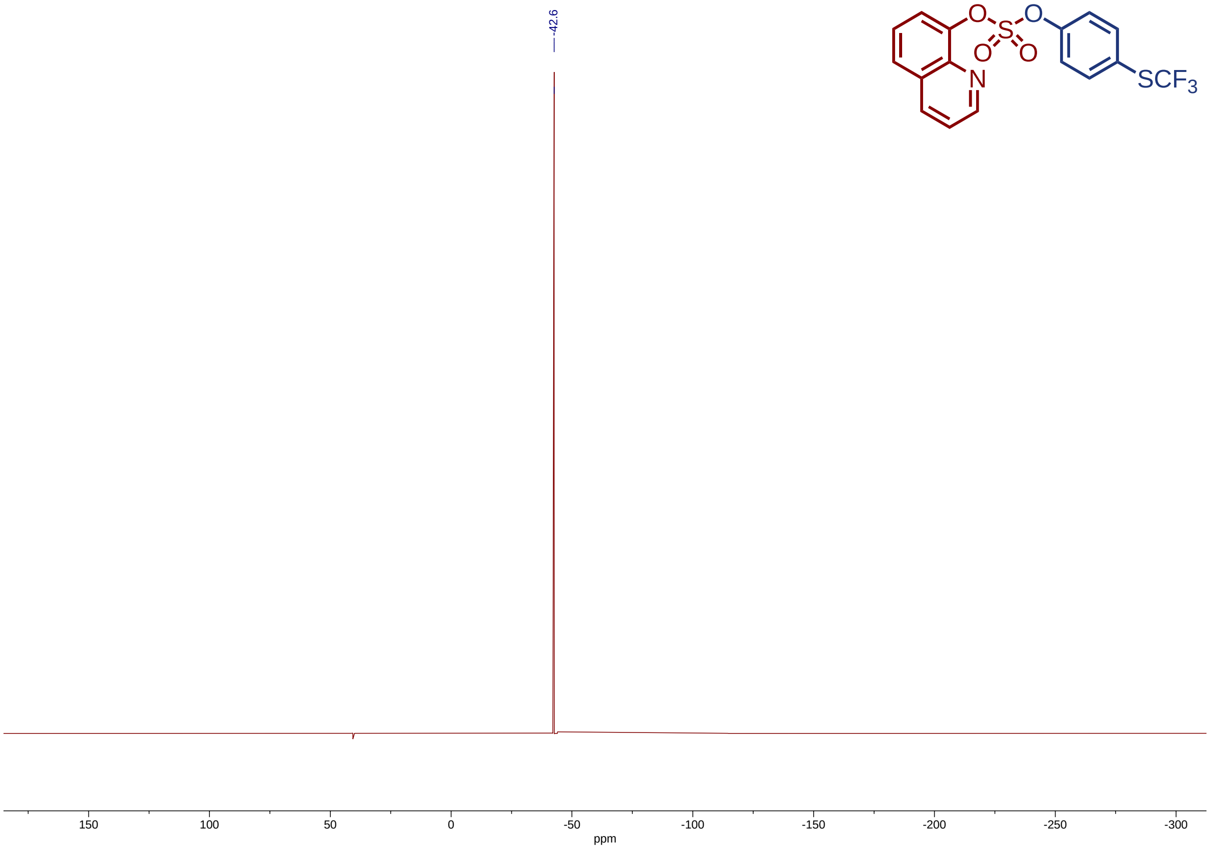
^{1}H NMR Spectrum for Compound **9p** (400 MHz, CDCl$_3$)



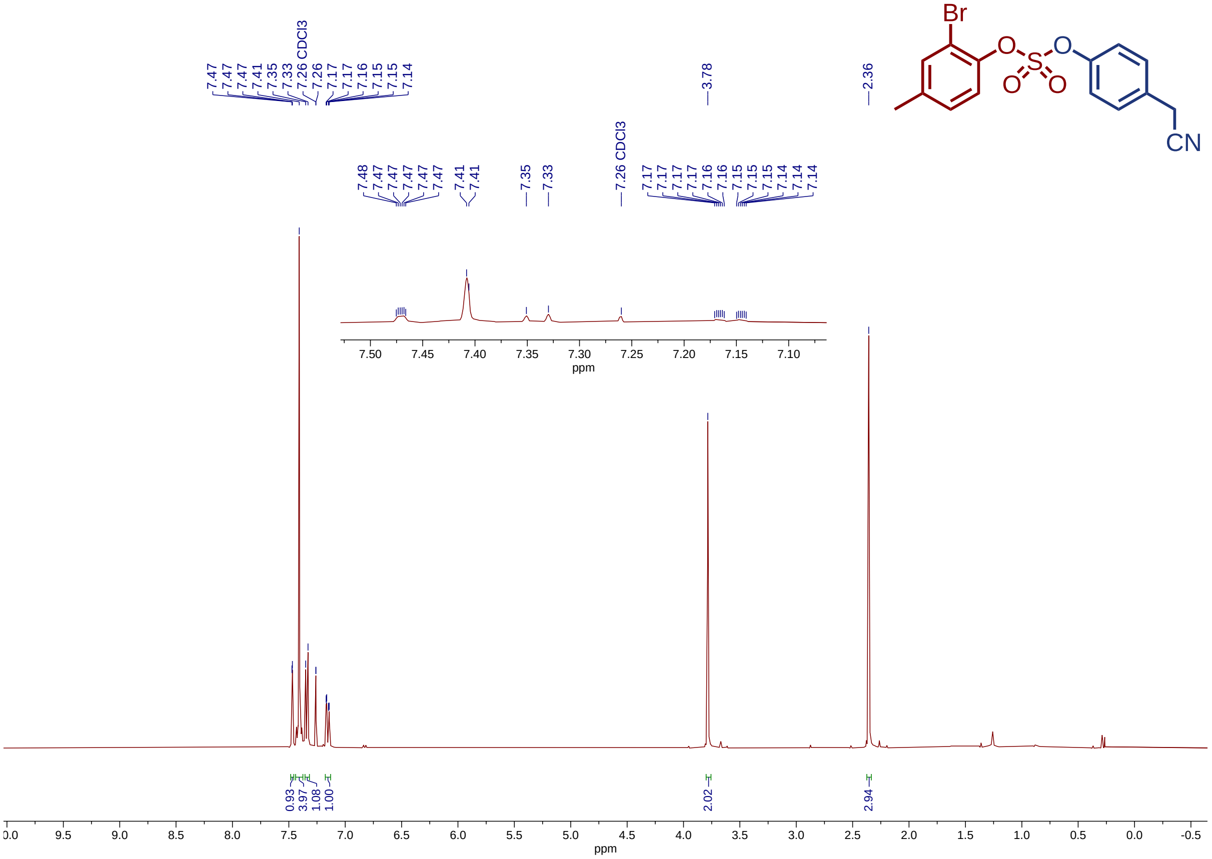
^{13}C NMR Spectrum for Compound **9p** (101 MHz, CDCl$_3$)



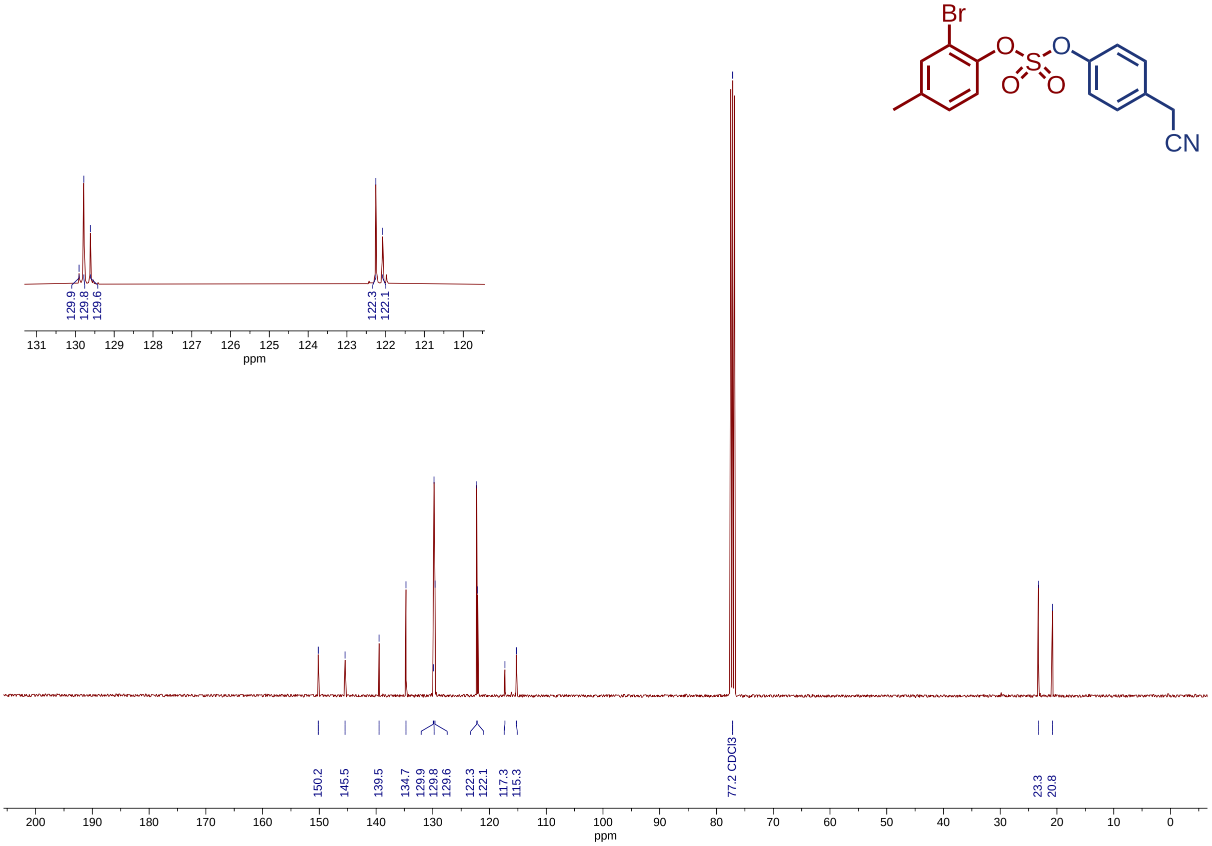
^{19}F NMR Spectrum for Compound **9p** (376 MHz, CDCl$_3$)



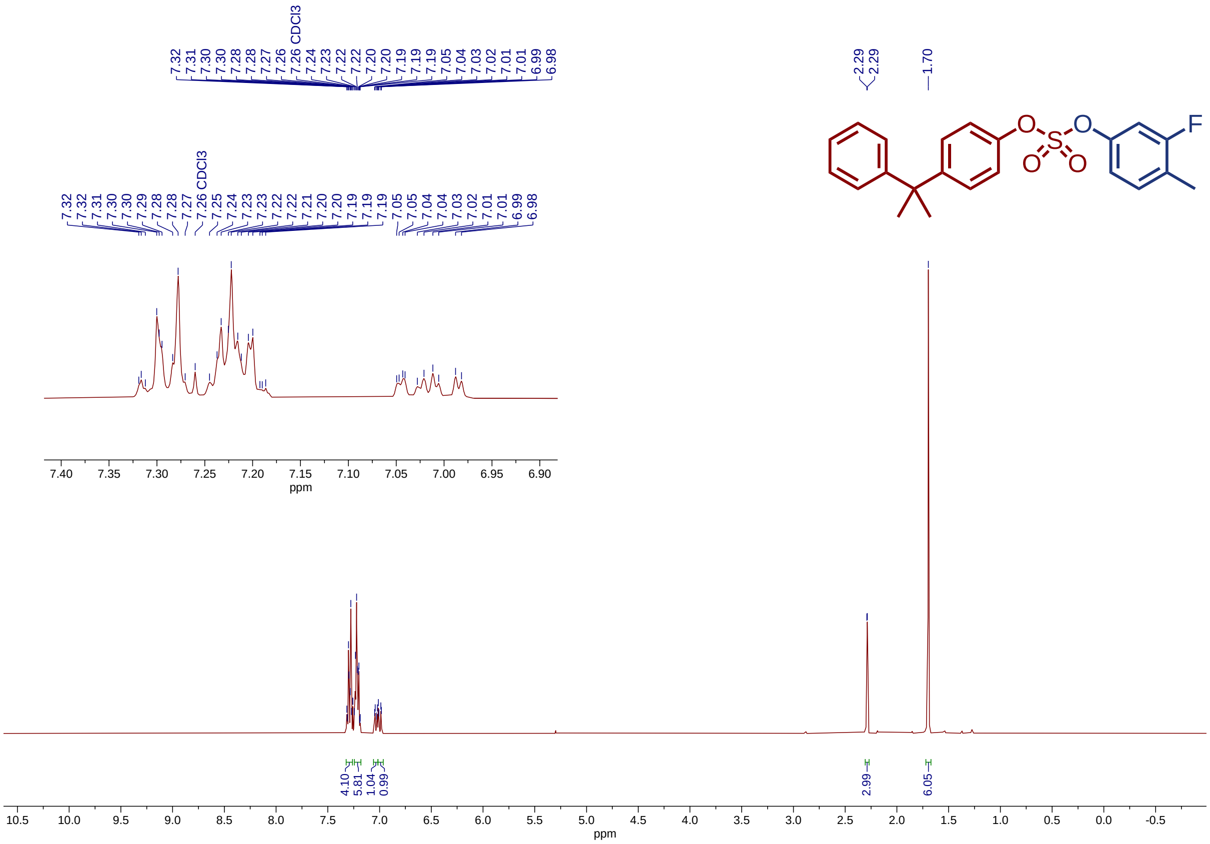
^{1}H NMR Spectrum for Compound **9q** (400 MHz, $CDCl_3$)



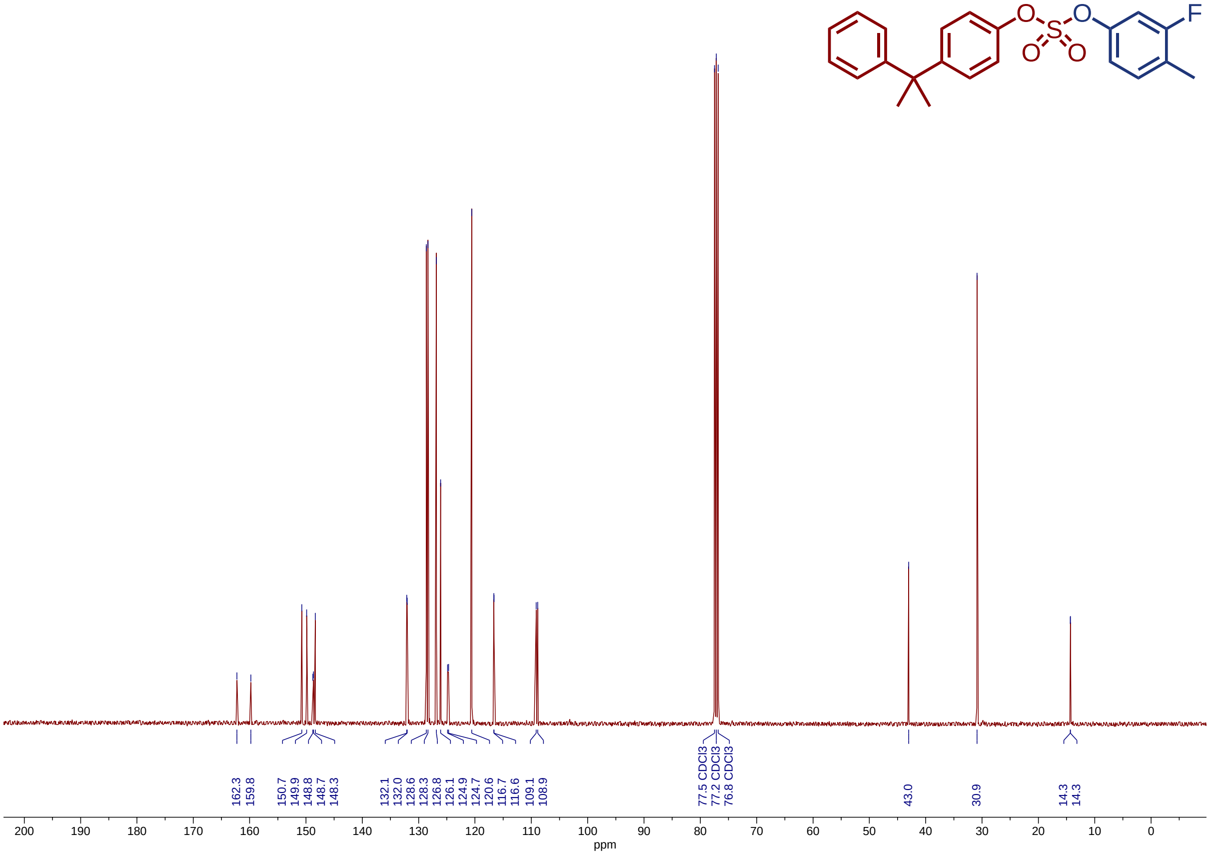
^{13}C NMR Spectrum for Compound **9q** (101 MHz, $CDCl_3$)



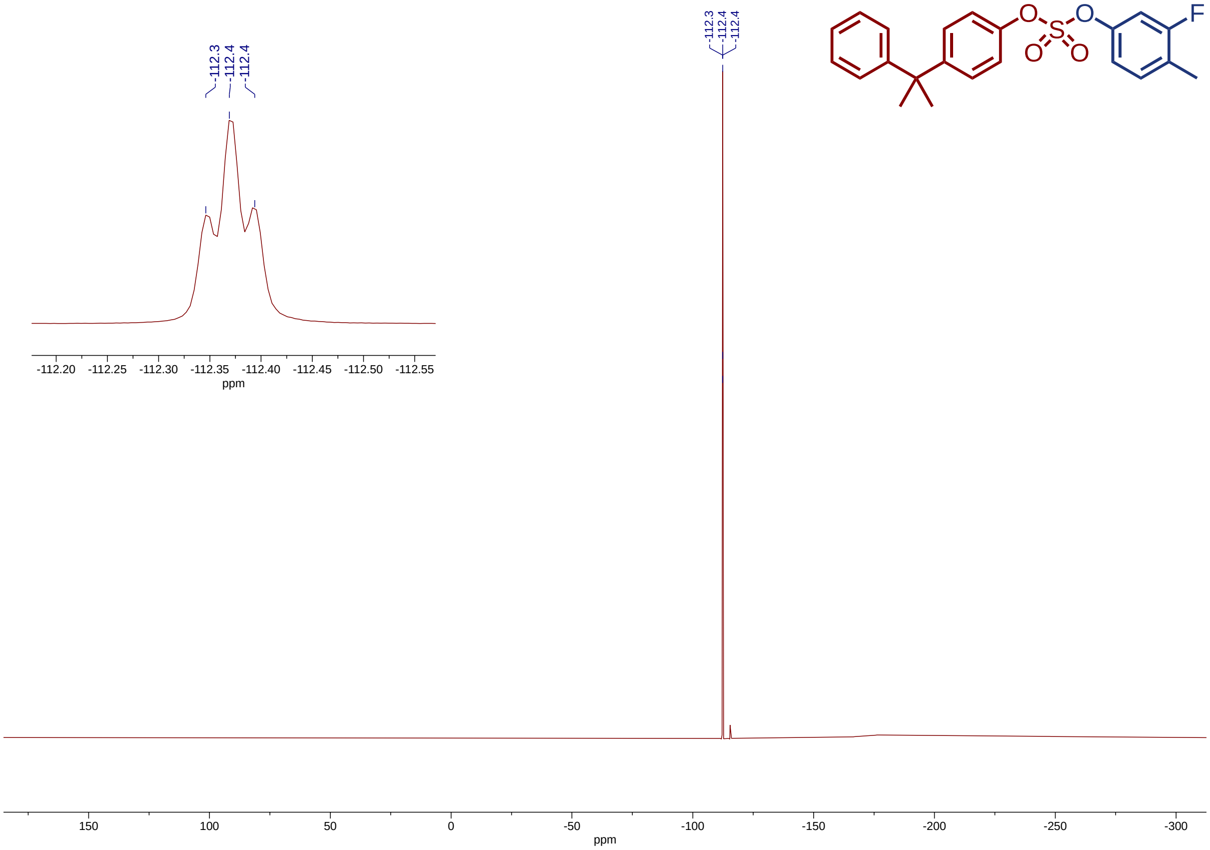
^{1}H NMR Spectrum for Compound **9r** (400 MHz, CDCl$_3$)



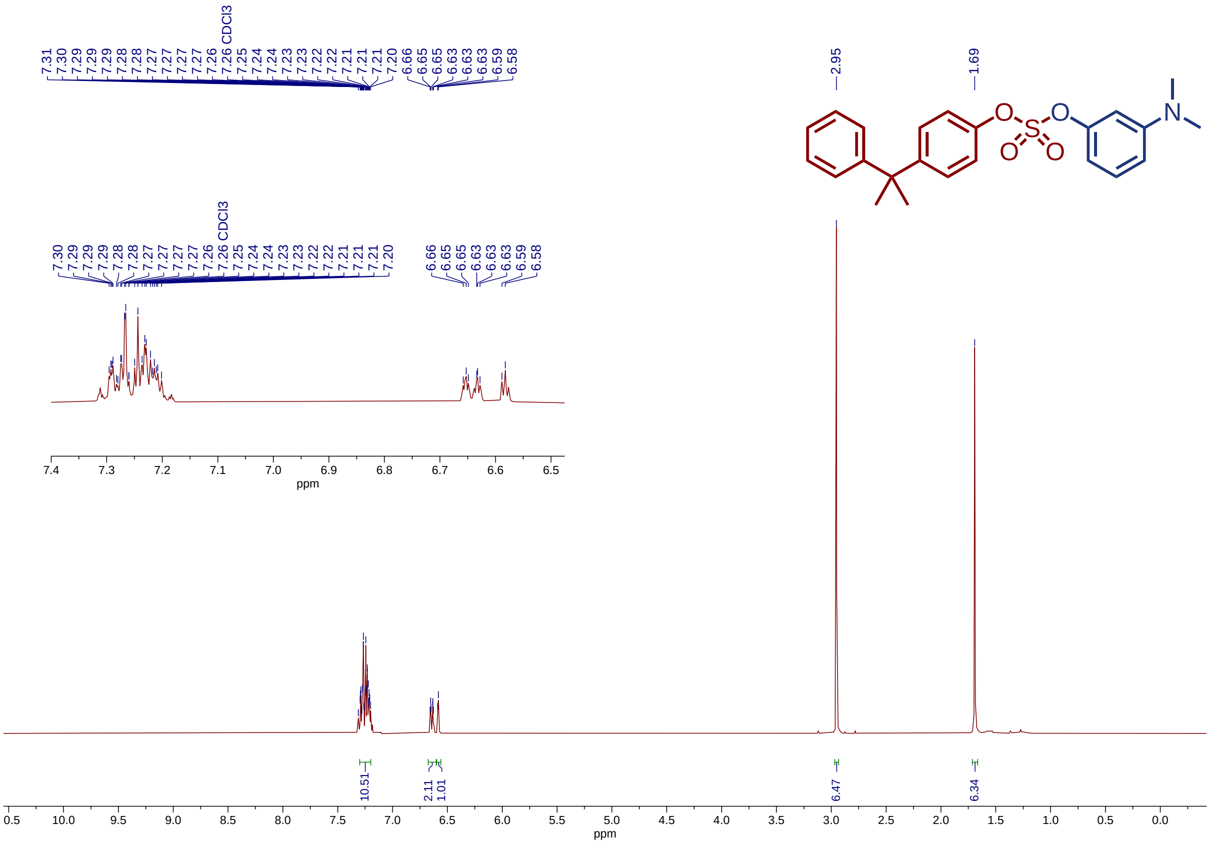
^{13}C NMR Spectrum for Compound **9r** (101 MHz, CDCl$_3$)



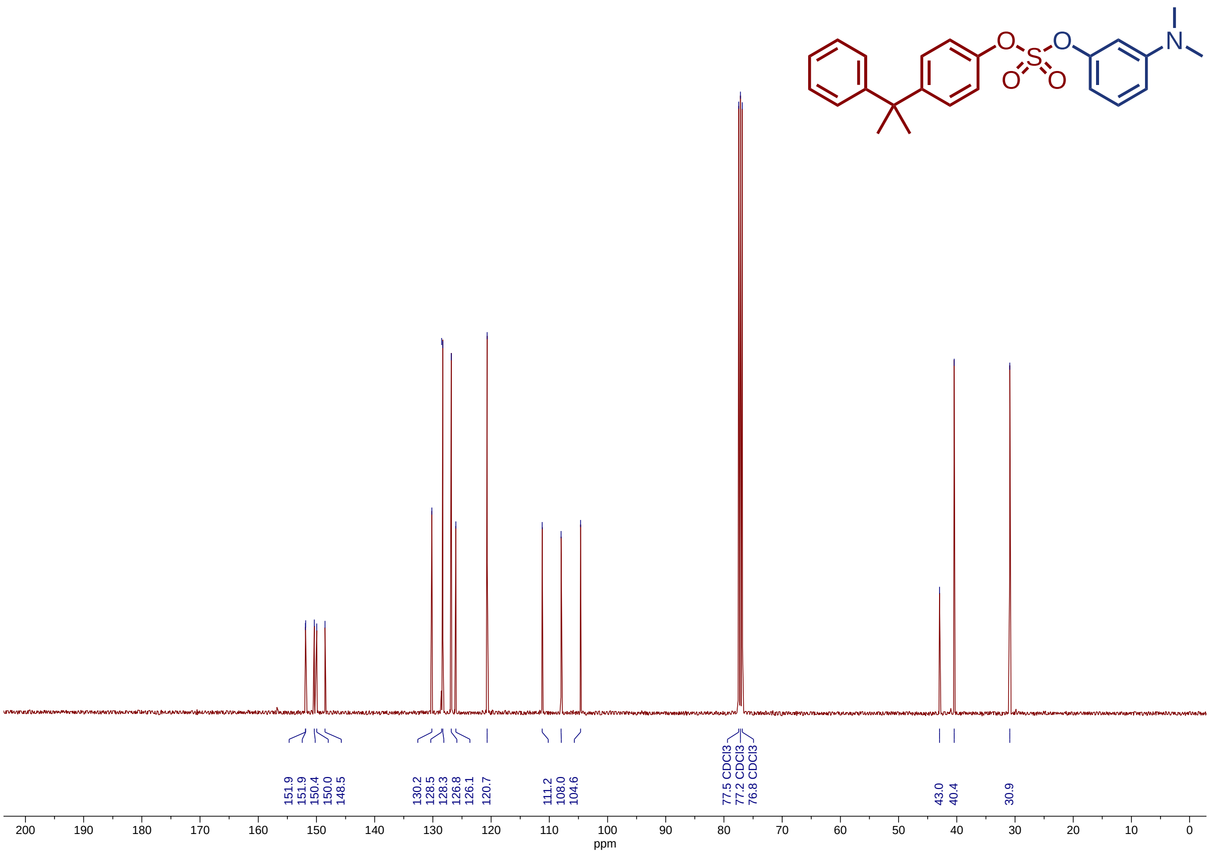
^{19}F NMR Spectrum for Compound **9r** (376 MHz, CDCl$_3$)



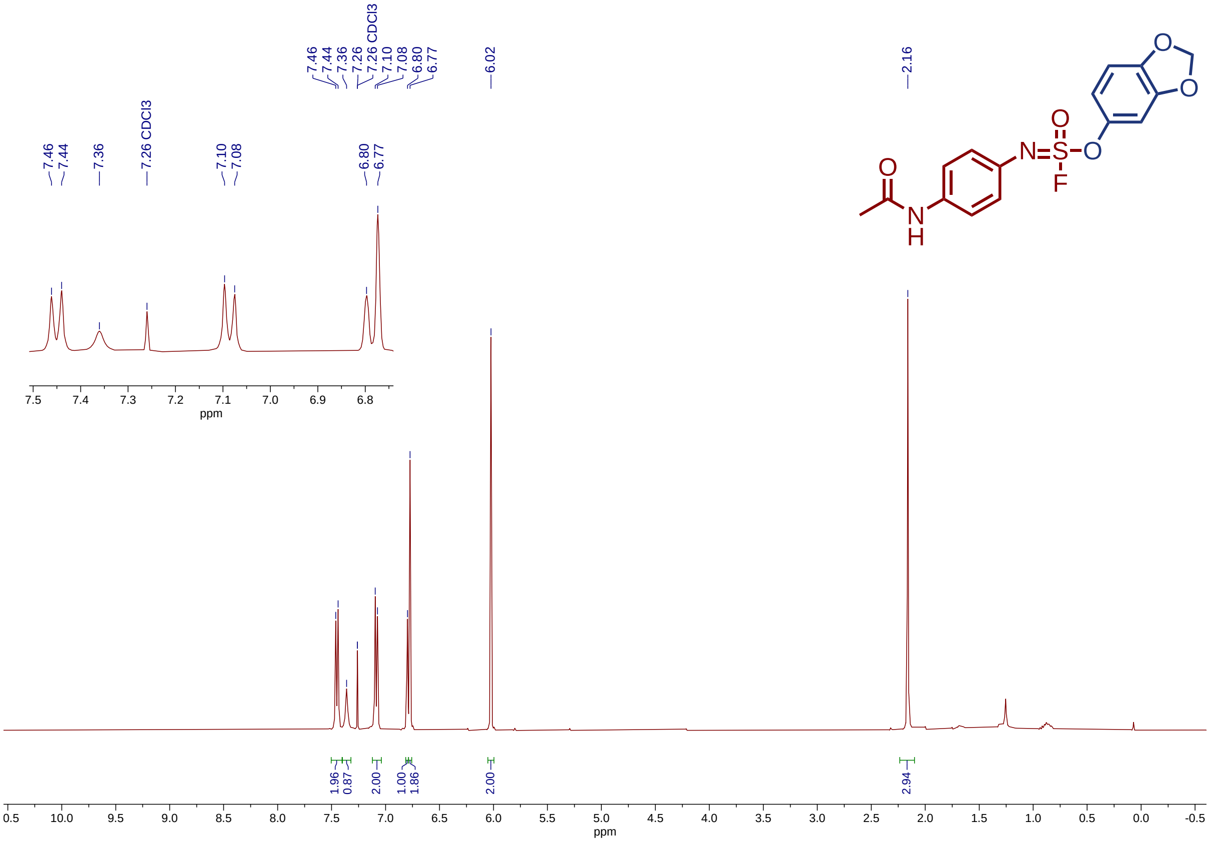
^{1}H NMR Spectrum for Compound **9s** (400 MHz, CDCl$_3$)



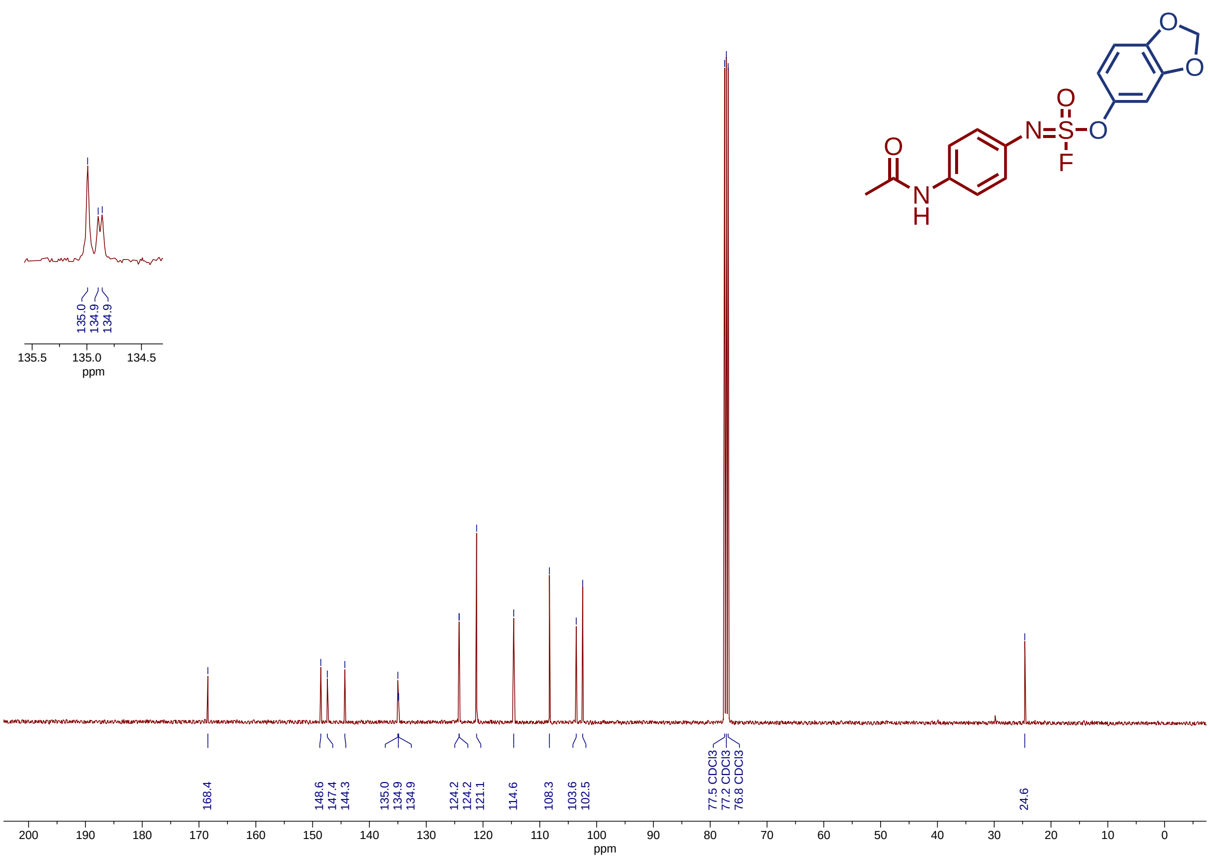
^{13}C NMR Spectrum for Compound **9s** (101 MHz, CDCl$_3$)



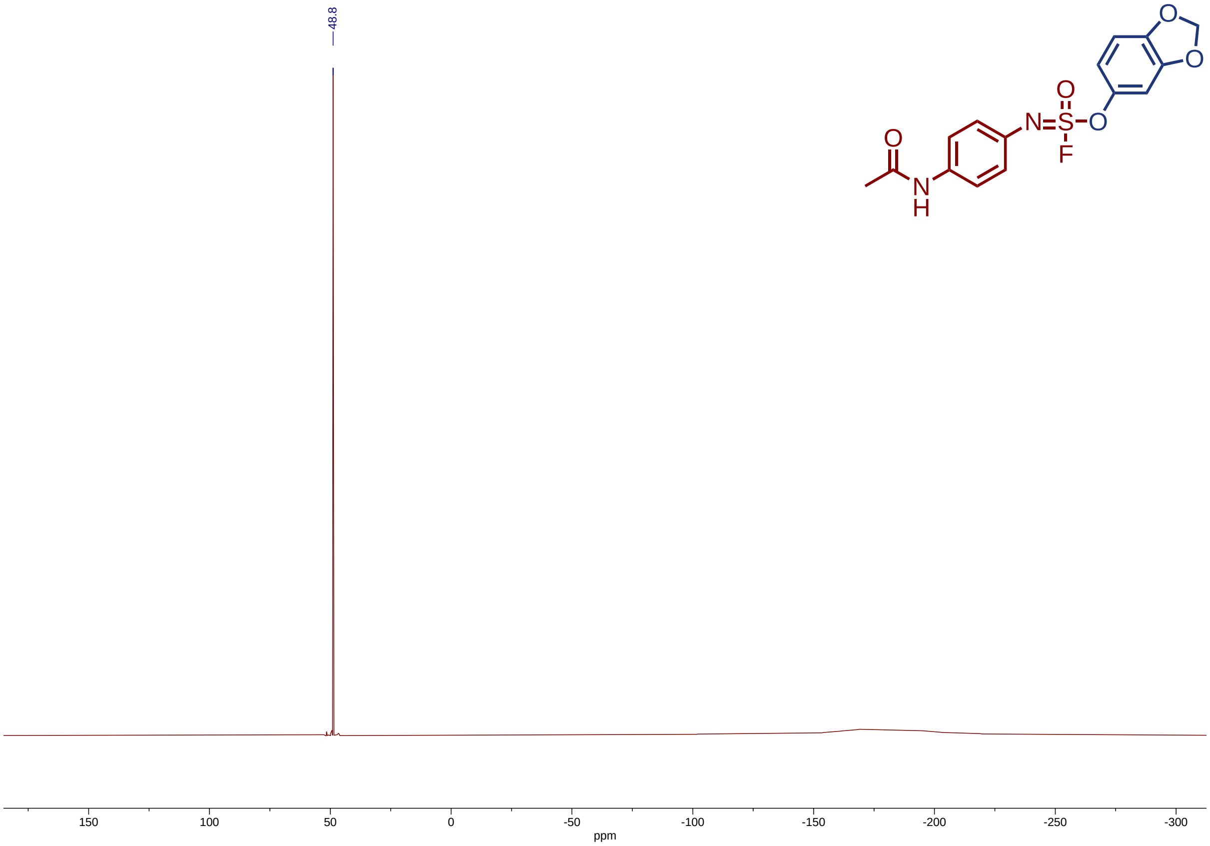
^{1}H NMR Spectrum for Compound **10a** (400 MHz, CDCl$_3$)



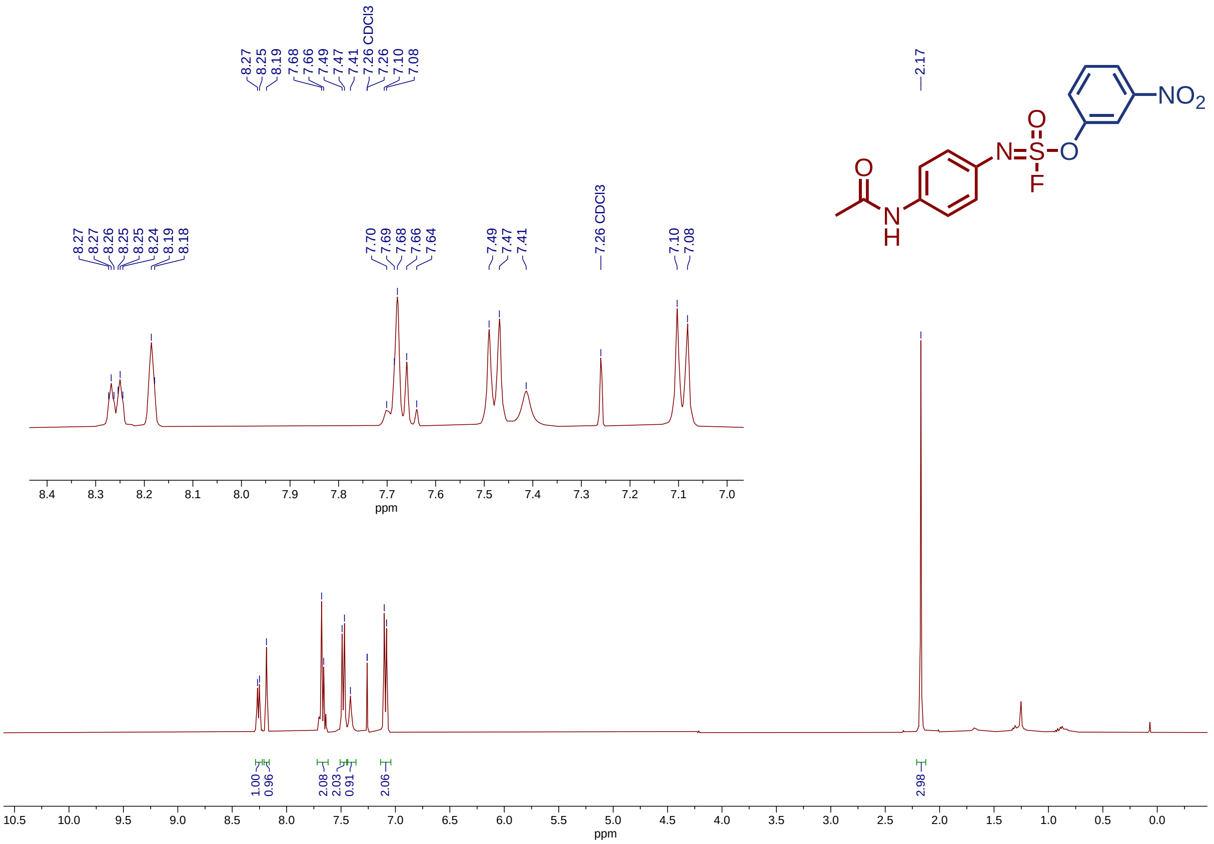
^{13}C NMR Spectrum for Compound **10a** (101 MHz, CDCl$_3$)



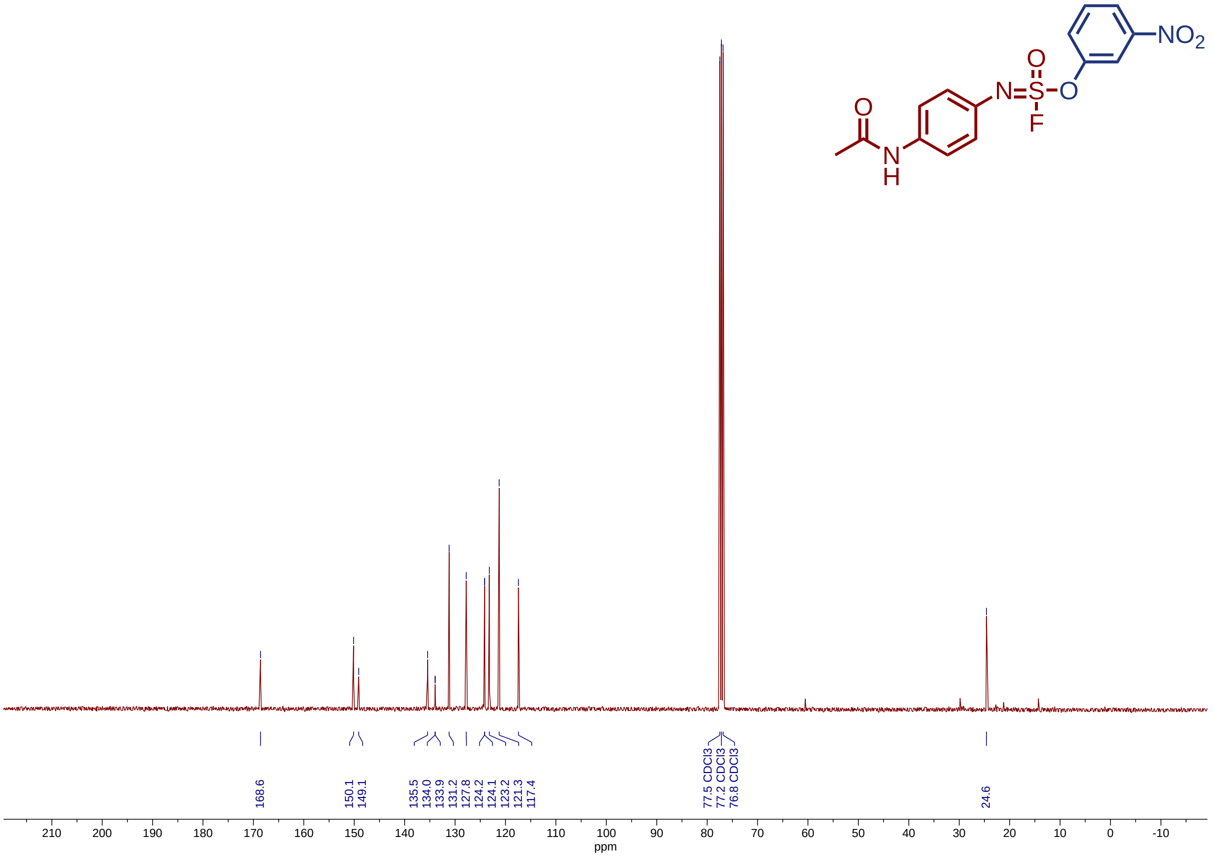
^{19}F NMR Spectrum for Compound **10a** (376 MHz, CDCl$_3$)



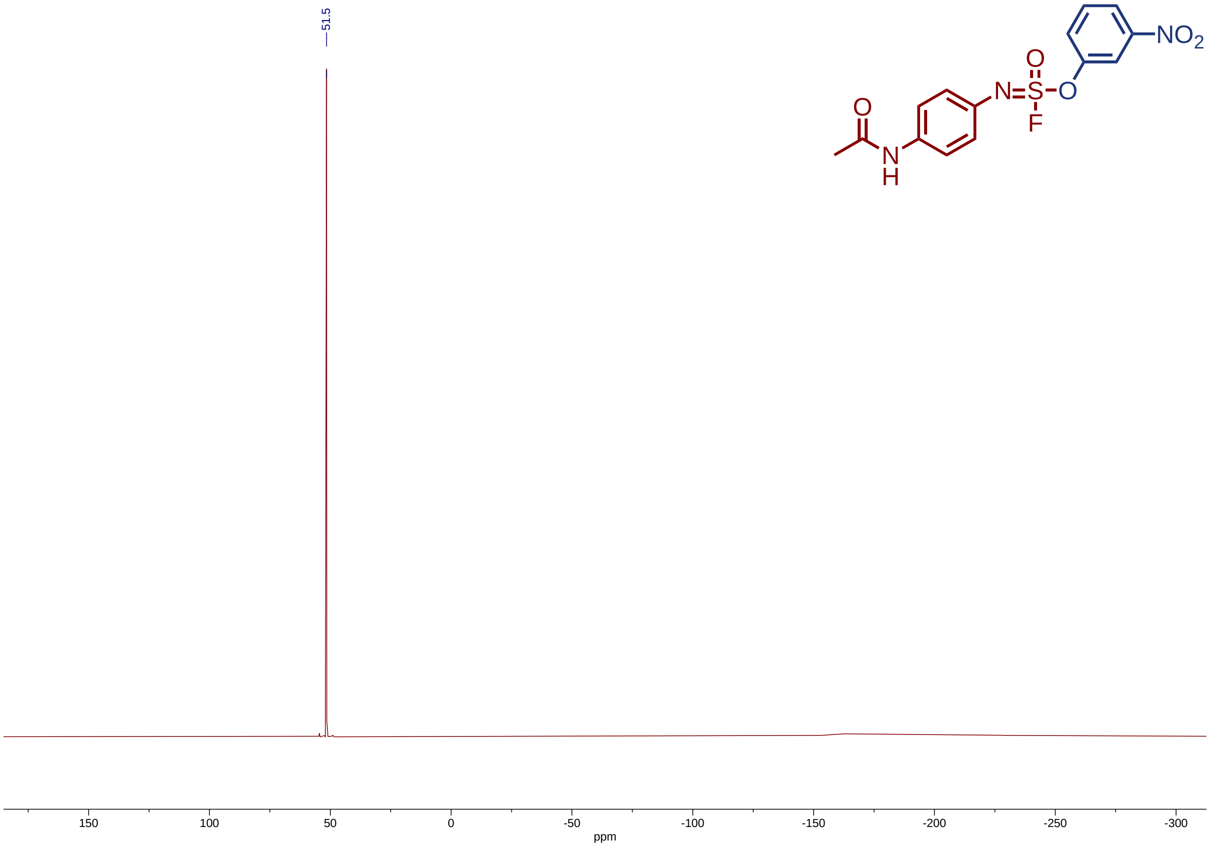
^{1}H NMR Spectrum for Compound **10b** (400 MHz, $CDCl_3$)



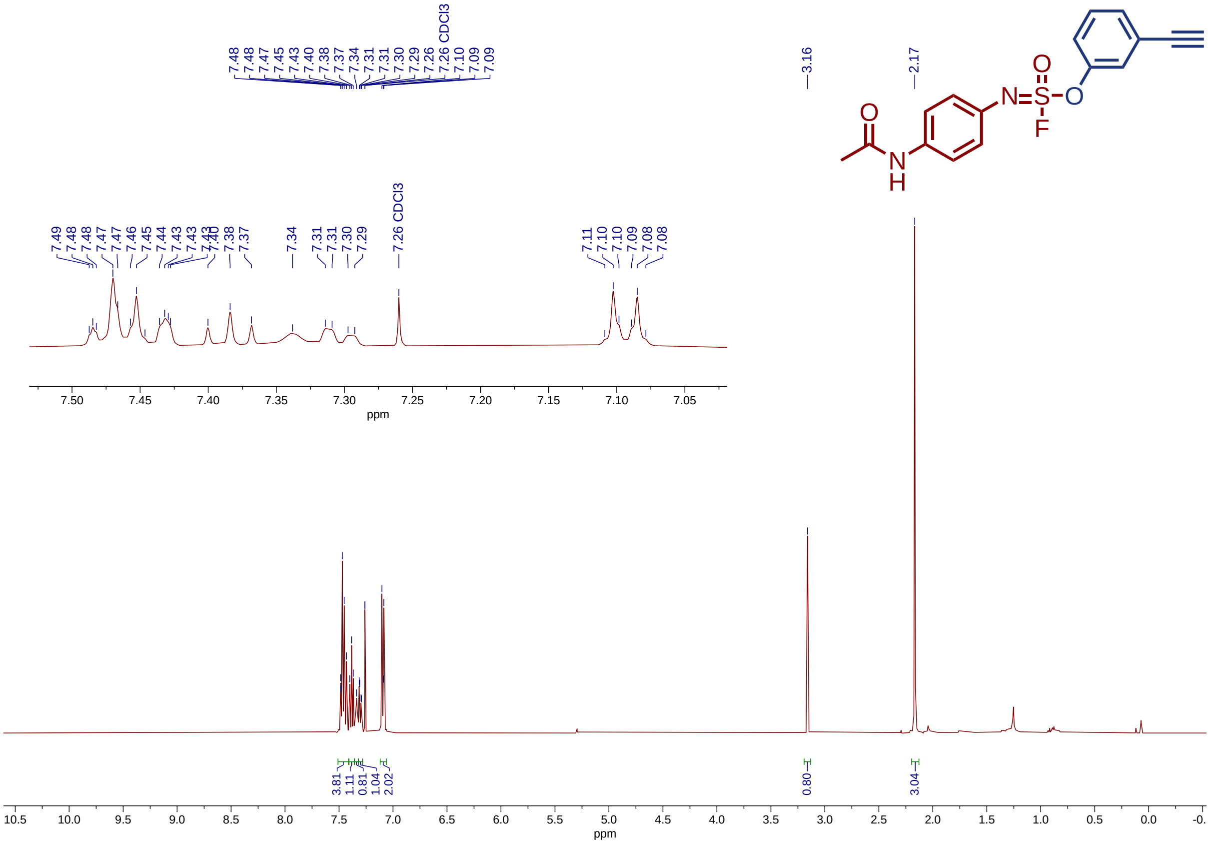
^{13}C NMR Spectrum for Compound **10b** (101 MHz, $CDCl_3$)



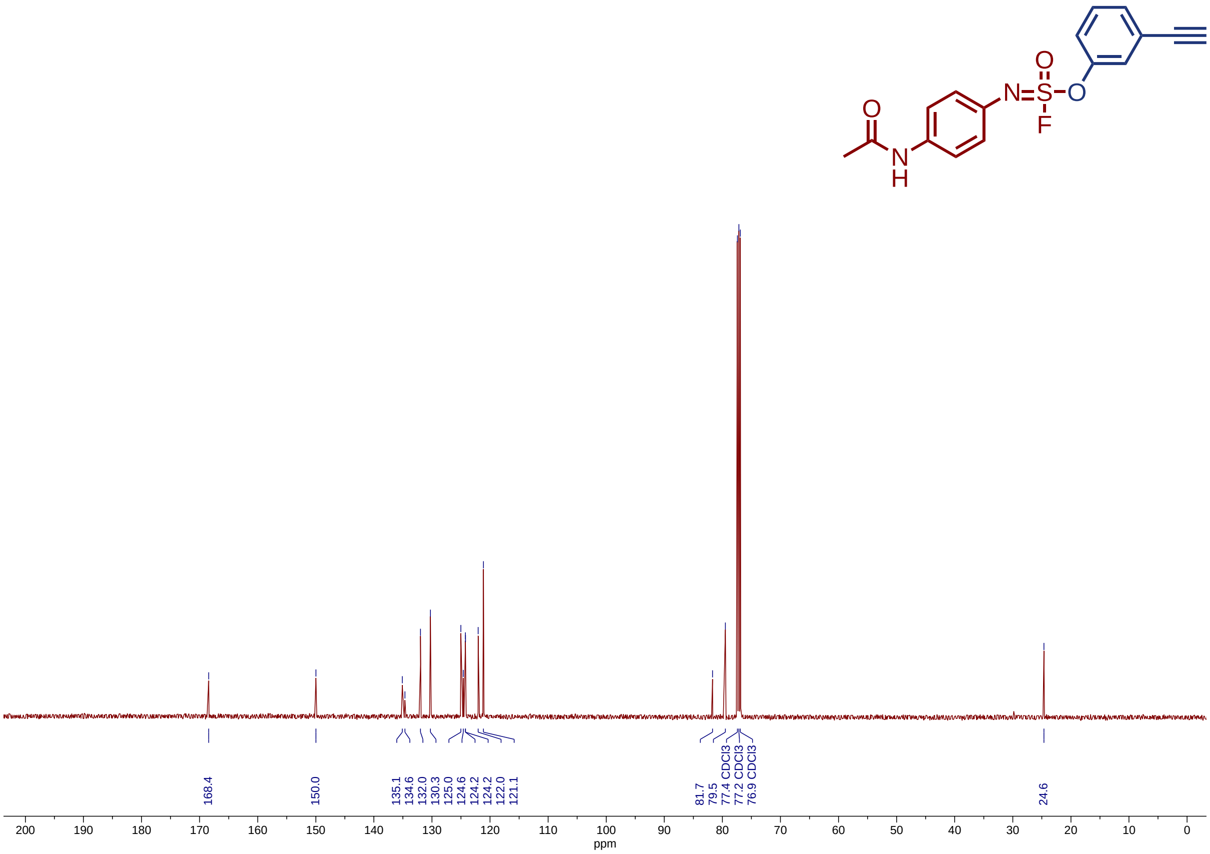
^{19}F NMR Spectrum for Compound **10b** (376 MHz, CDCl$_3$)



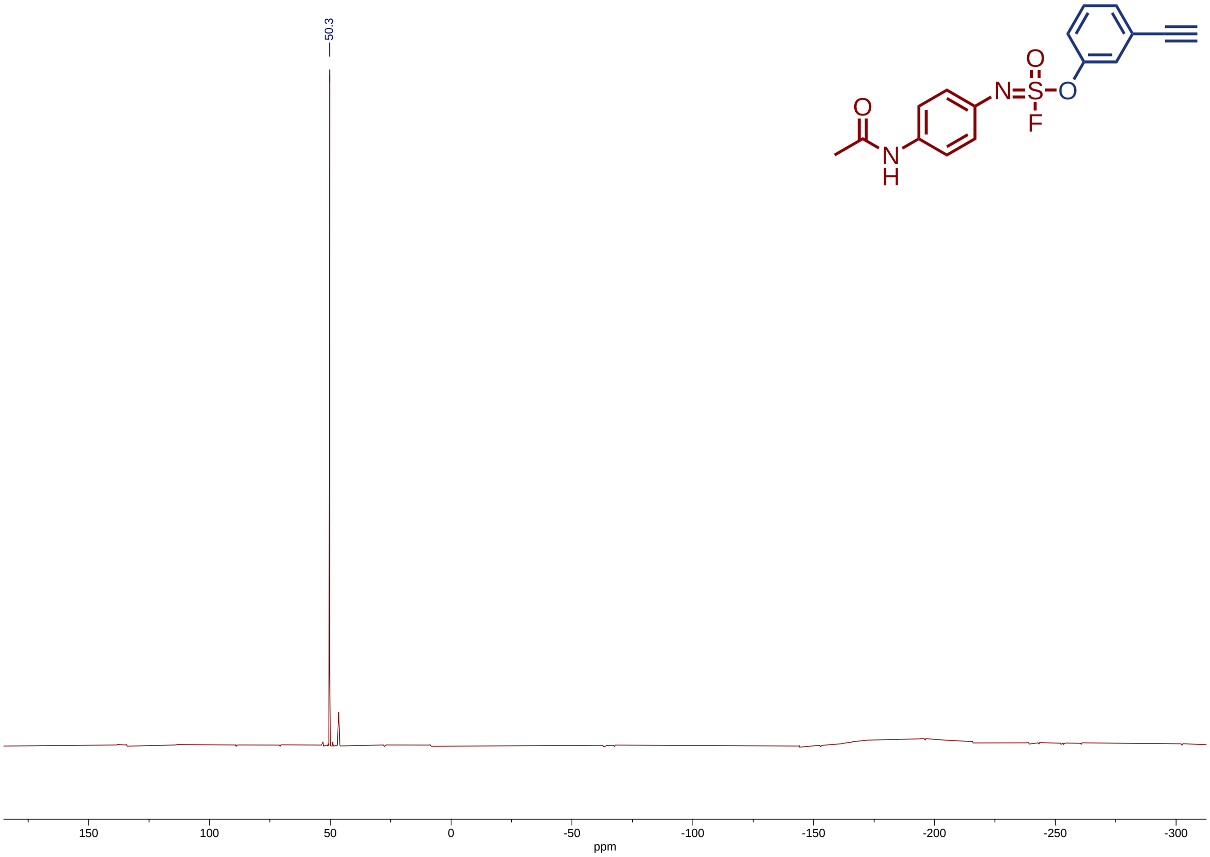
^{1}H NMR Spectrum for Compound **10c** (500 MHz, CDCl$_3$)



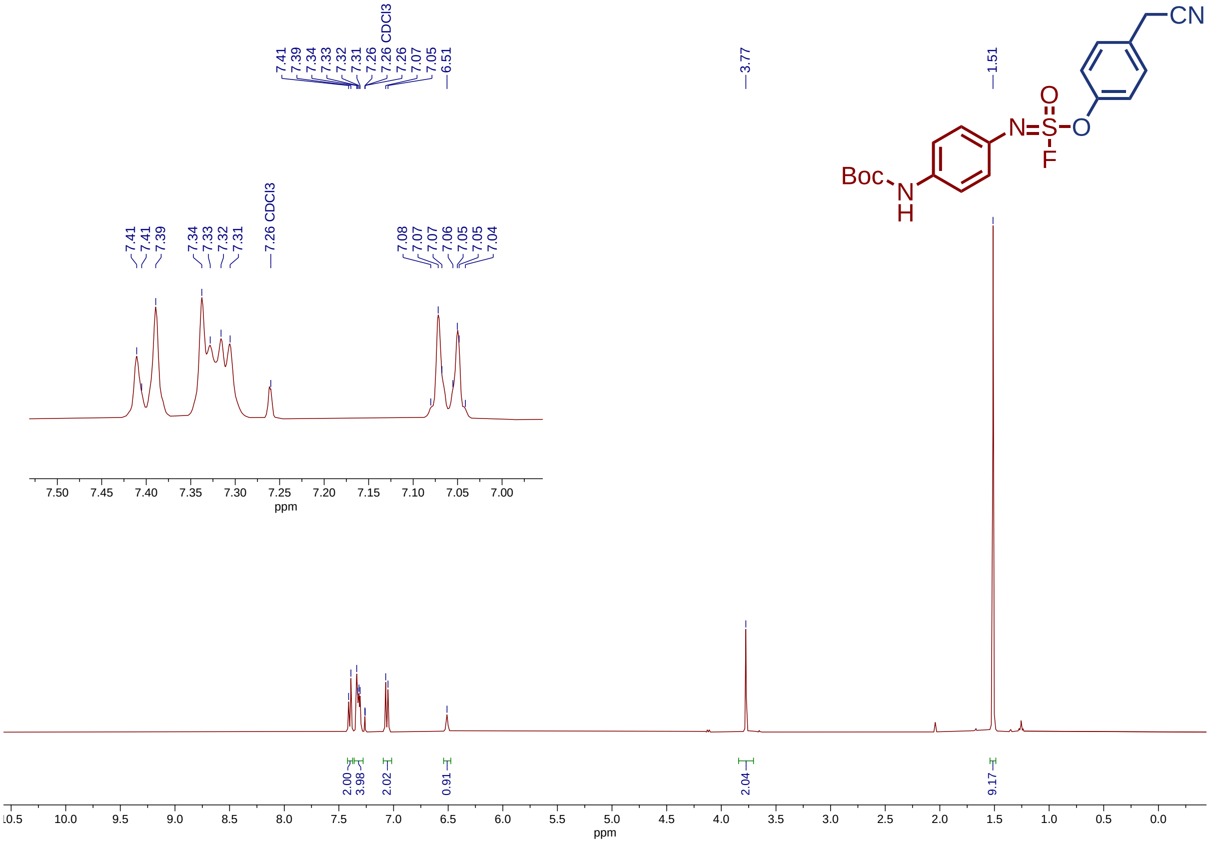
^{13}C NMR Spectrum for Compound **10c** (126 MHz, $CDCl_3$)



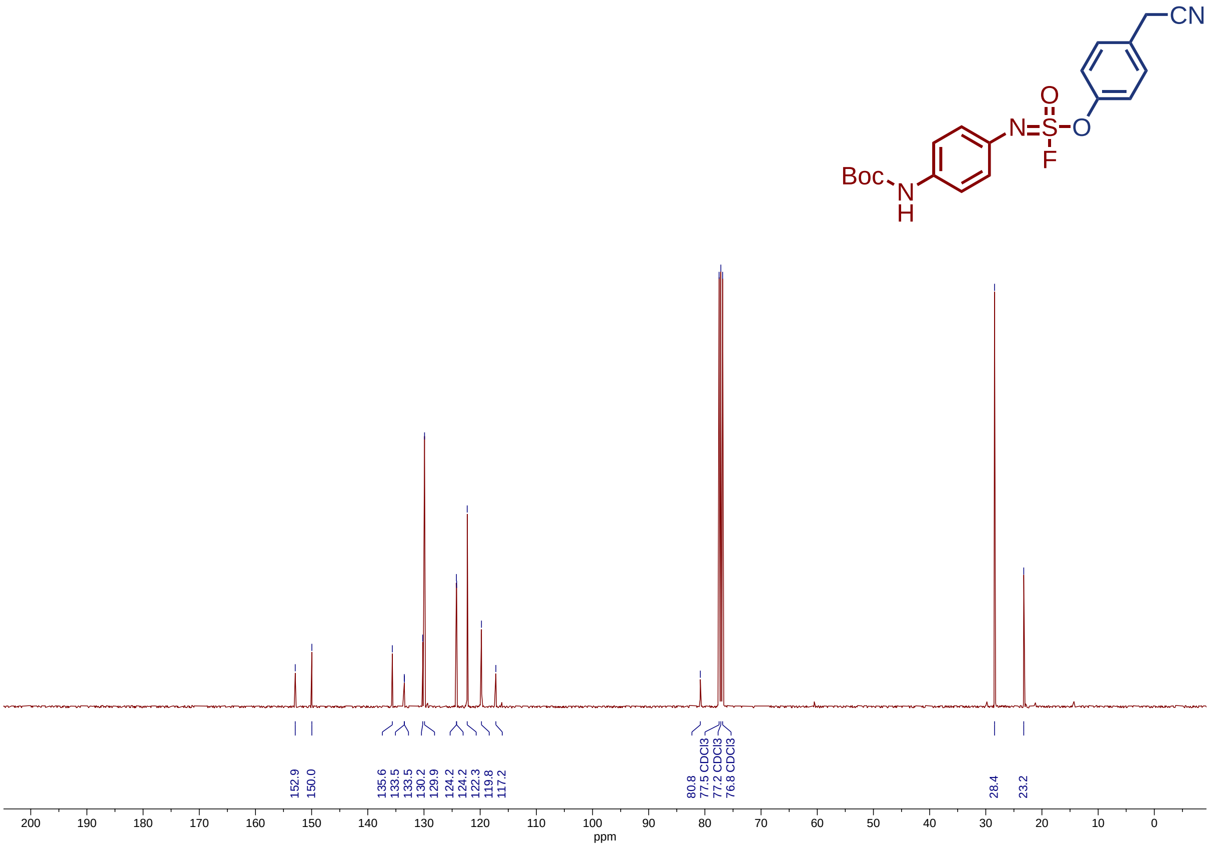
^{19}F NMR Spectrum for Compound **10c** (376 MHz, $CDCl_3$)



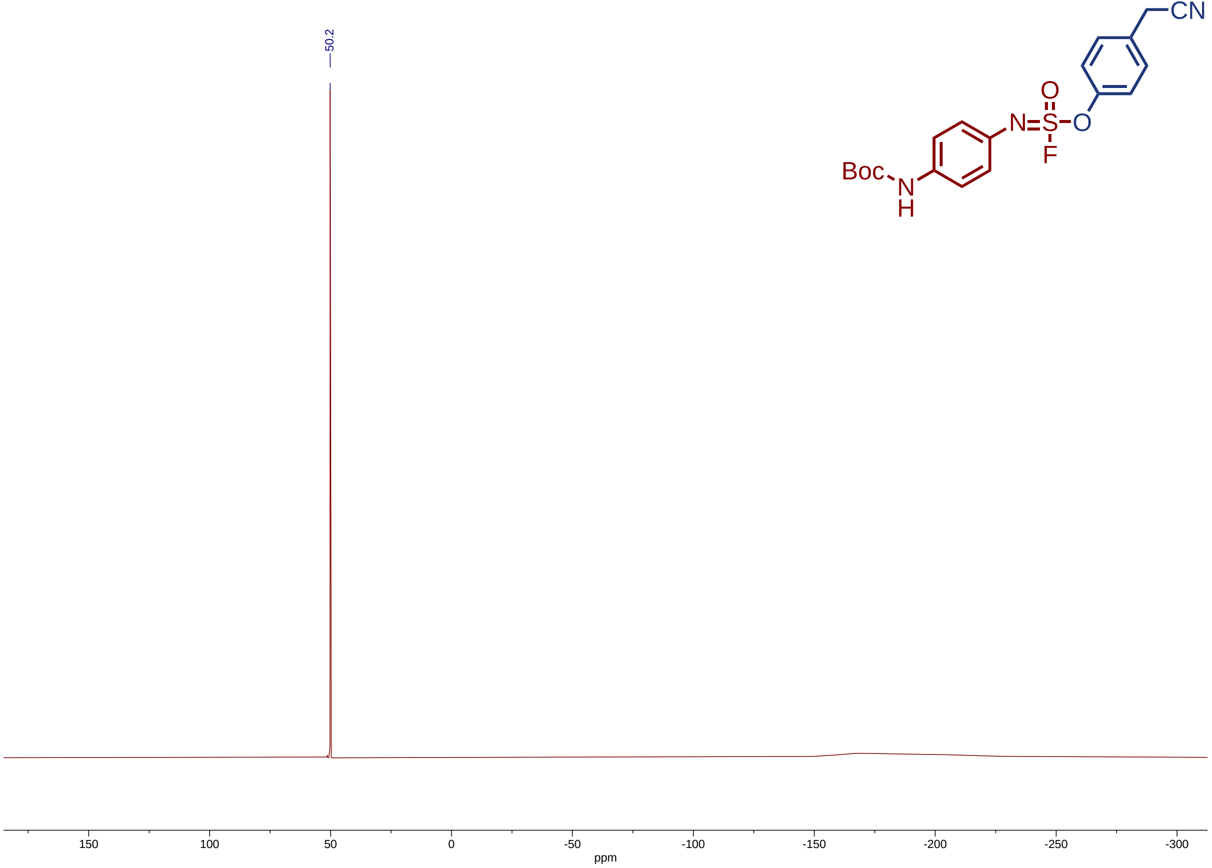
^{1}H NMR Spectrum for Compound **10d** (400 MHz, CDCl$_3$)



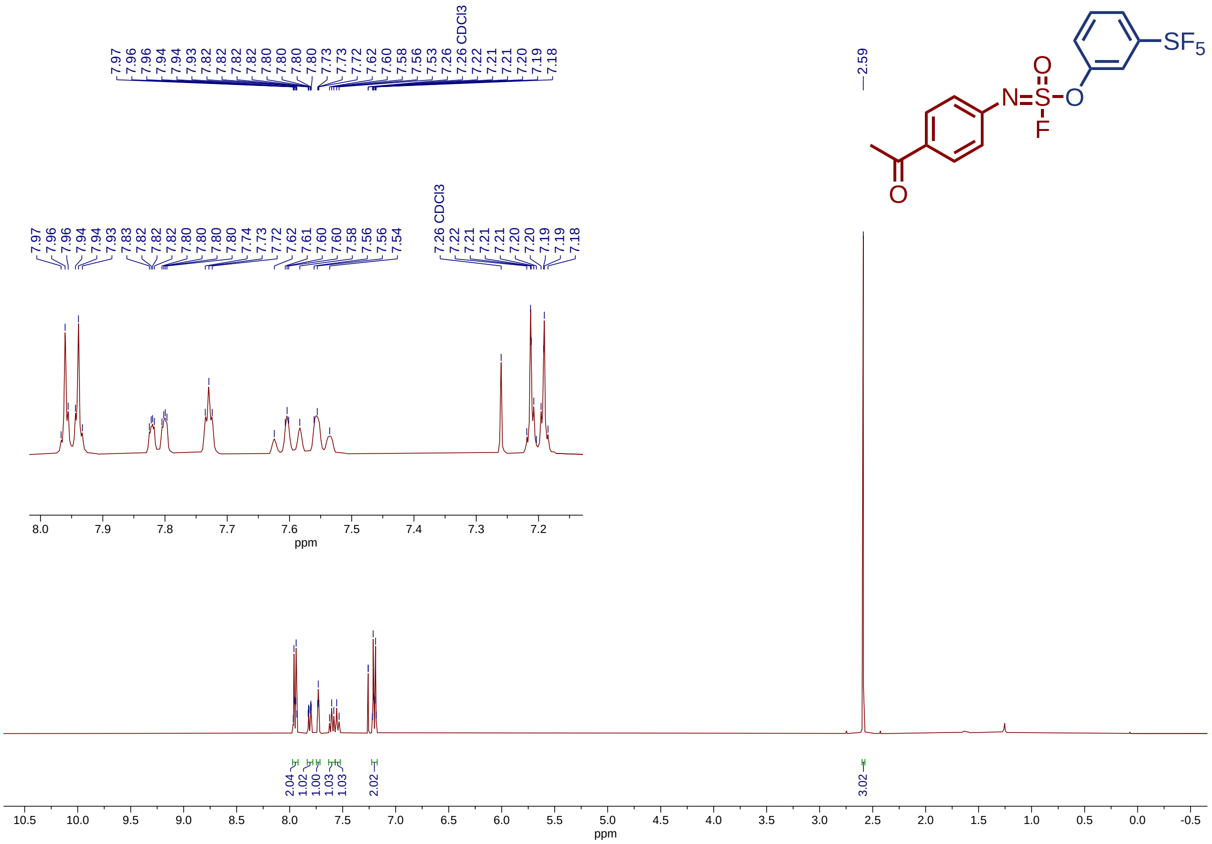
^{13}C NMR Spectrum for Compound **10d** (101 MHz, CDCl$_3$)



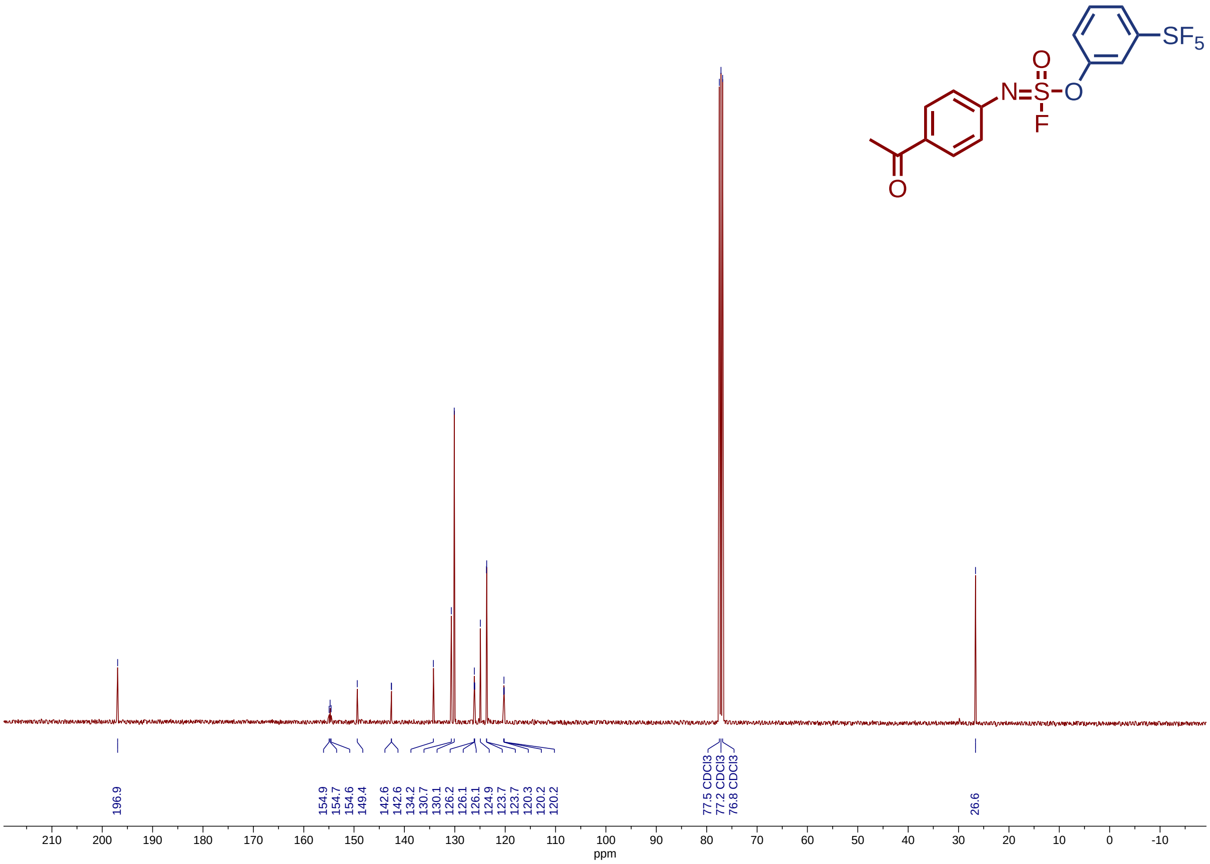
^{19}F NMR Spectrum for Compound **10d** (376 MHz, $CDCl_3$)



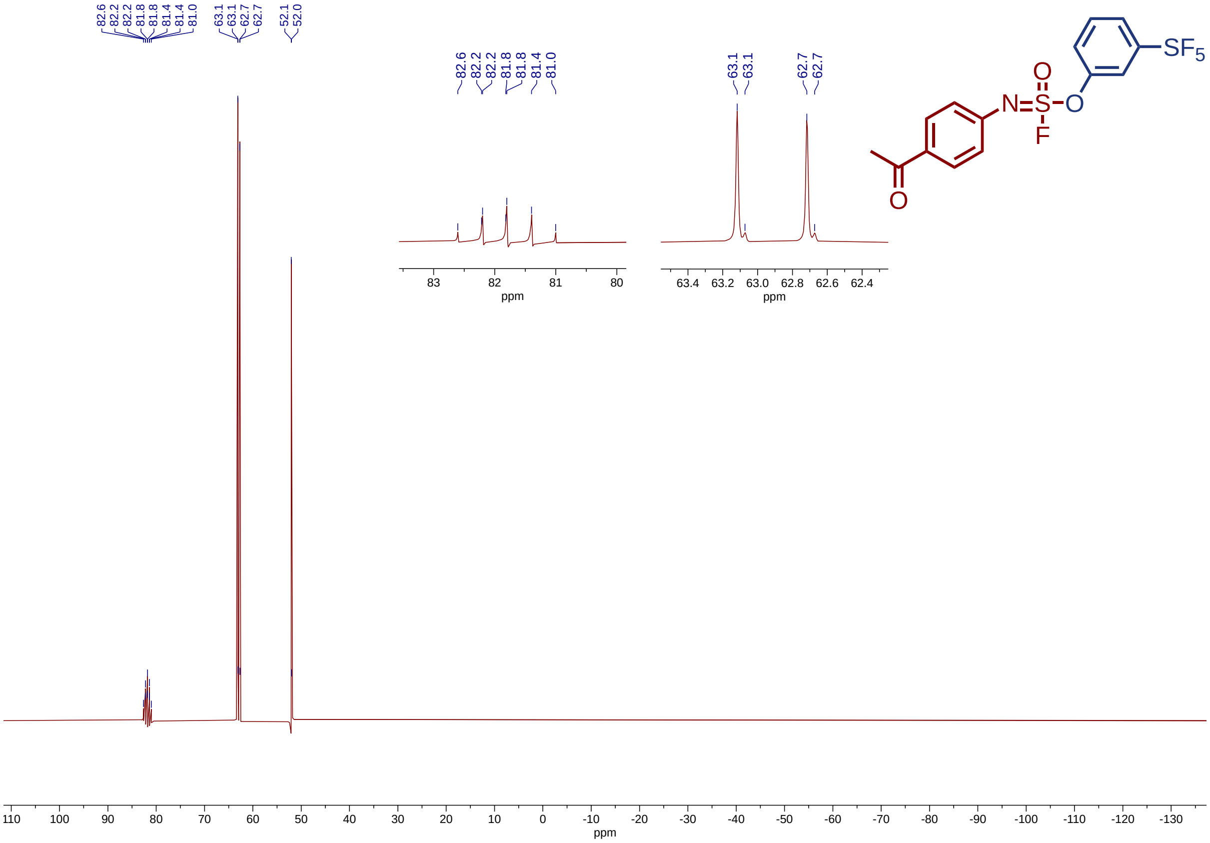
^{1}H NMR Spectrum for Compound **10e** (400 MHz, $CDCl_3$)



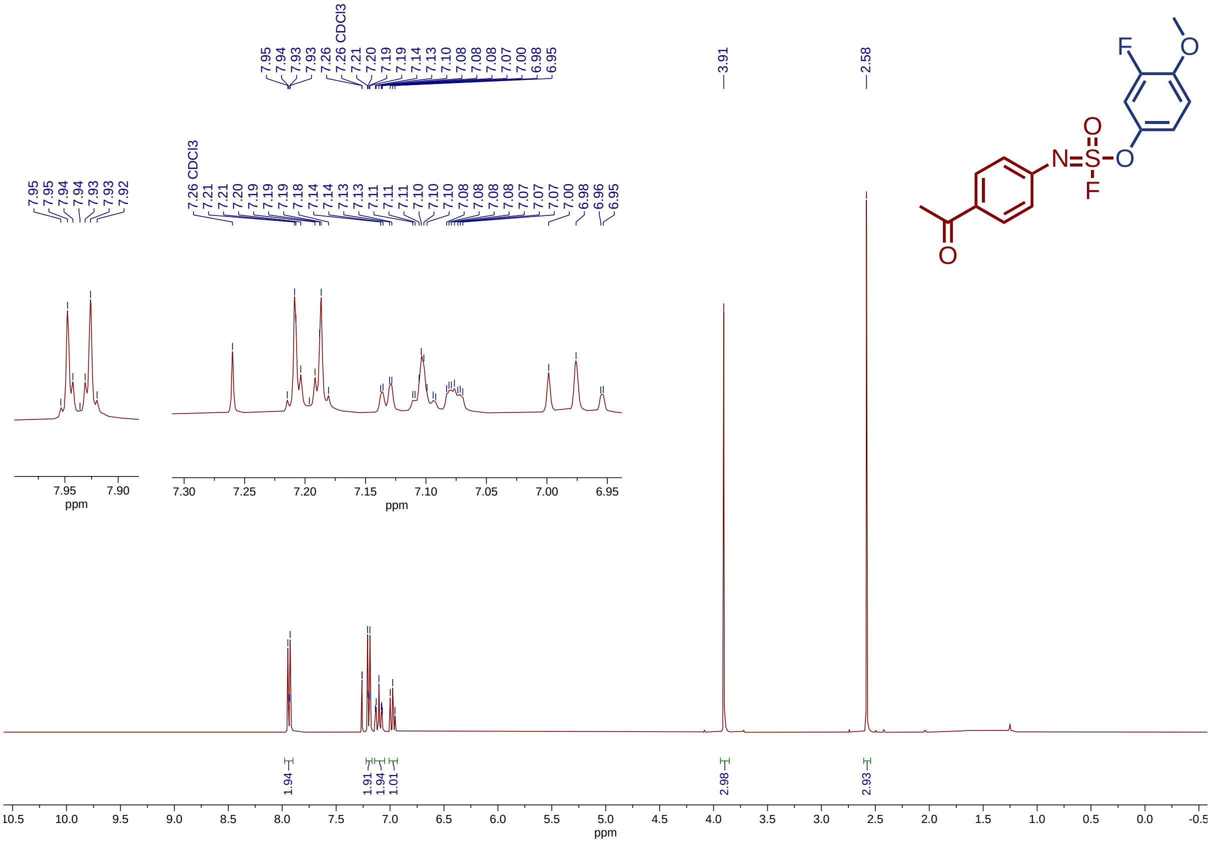
^{13}C NMR Spectrum for Compound **10e** (101 MHz, $CDCl_3$)



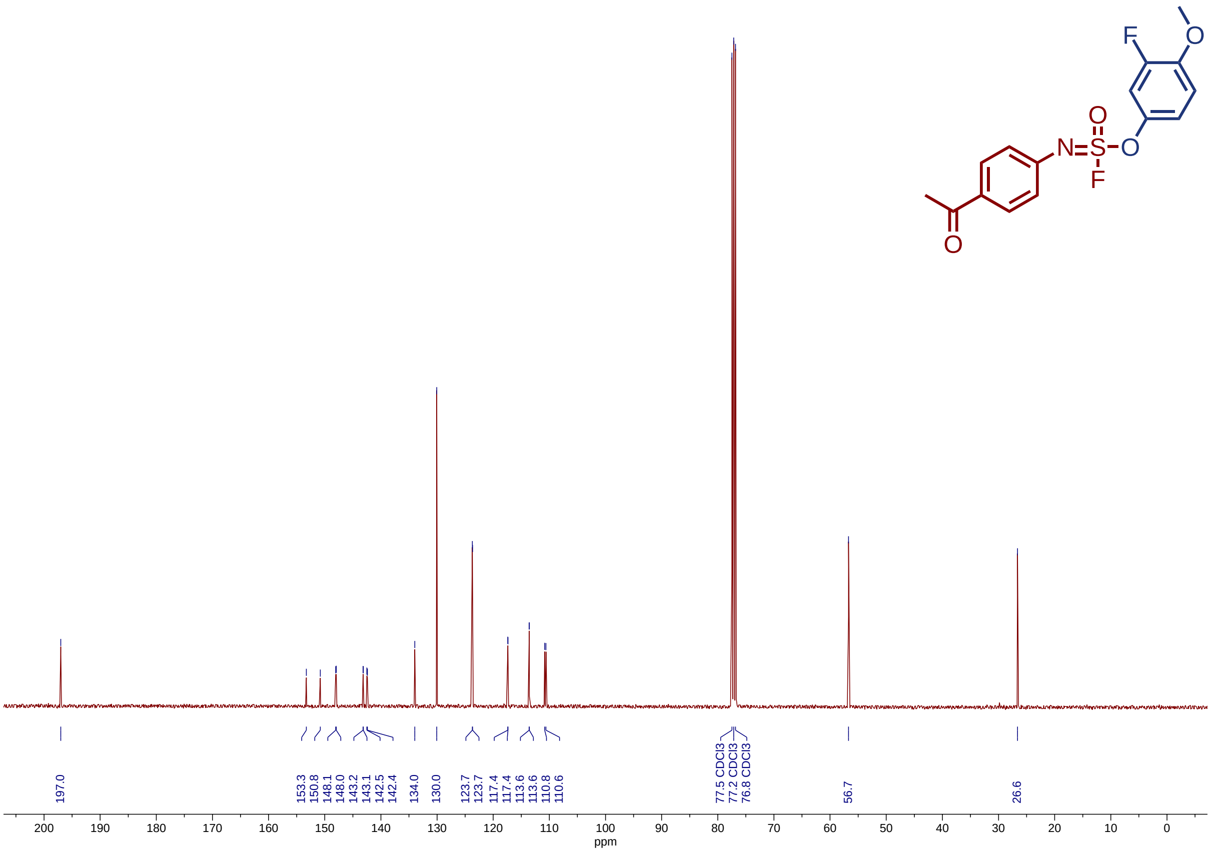
^{19}F NMR Spectrum for Compound **10e** (376 MHz, $CDCl_3$)



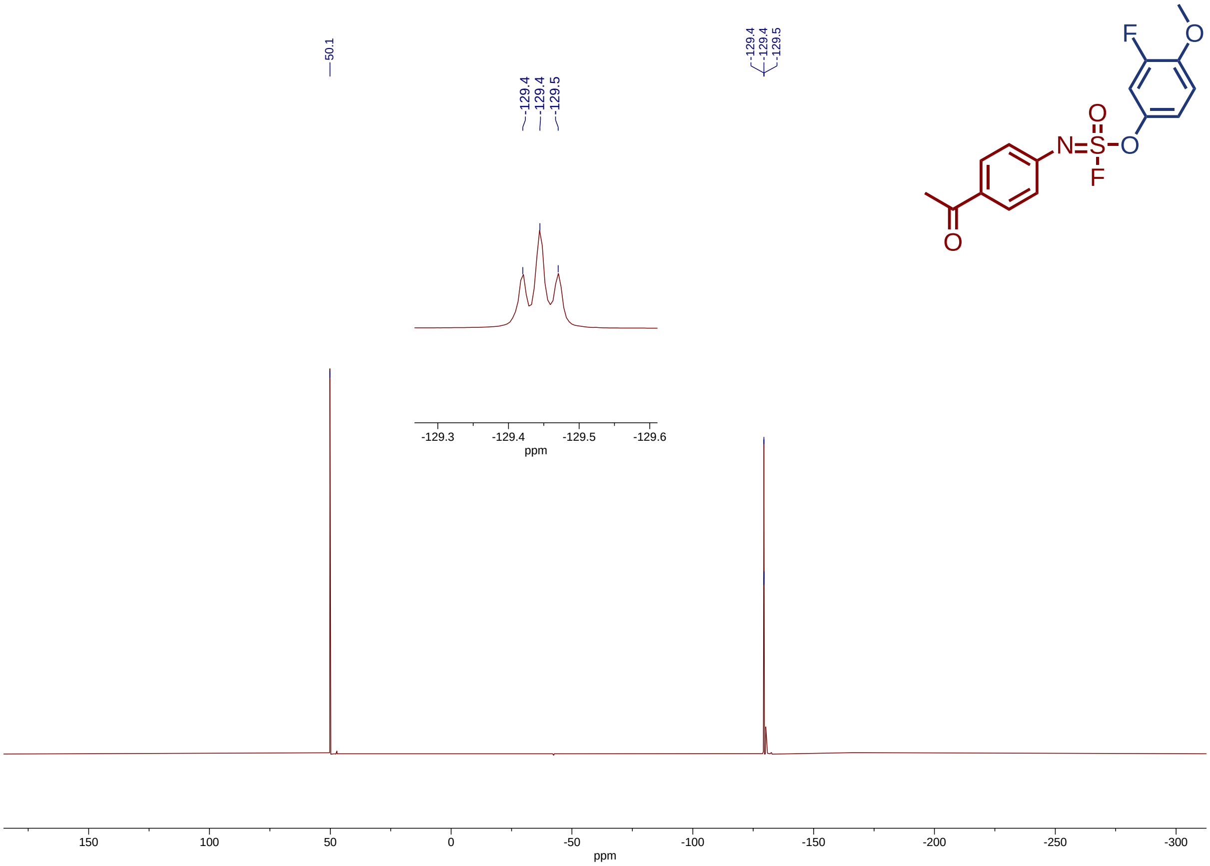
^{1}H NMR Spectrum for Compound **10f** (400 MHz, CDCl$_3$)



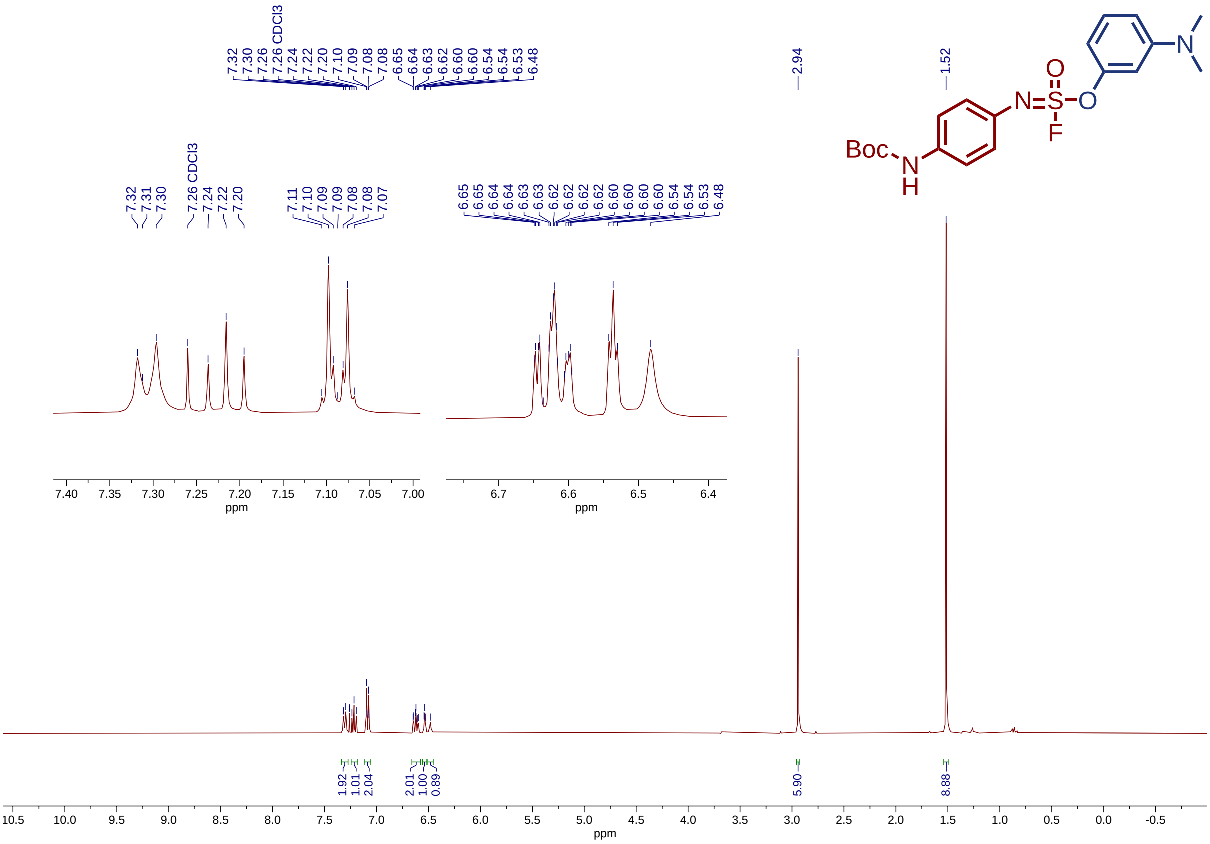
^{13}C NMR Spectrum for Compound **10f** (101 MHz, CDCl$_3$)



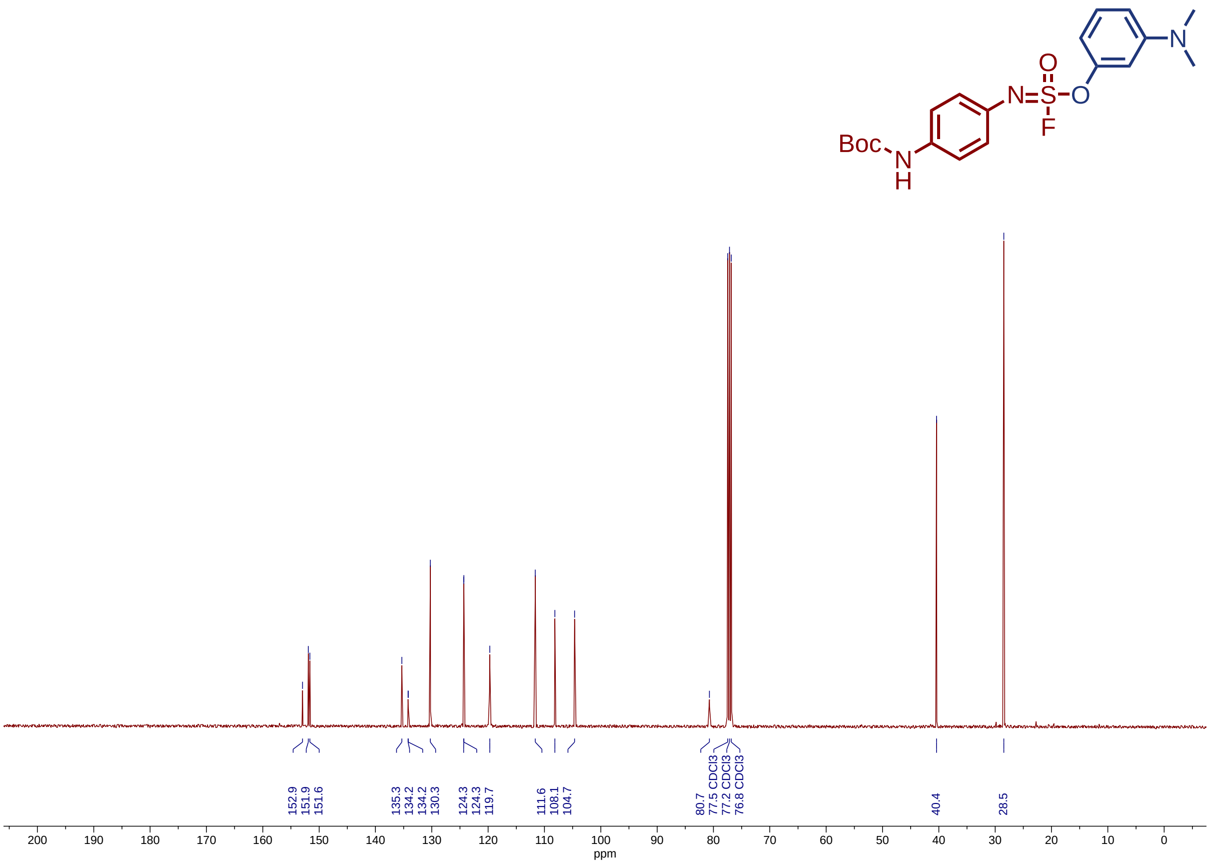
^{19}F NMR Spectrum for Compound **10f** (376 MHz, $CDCl_3$)



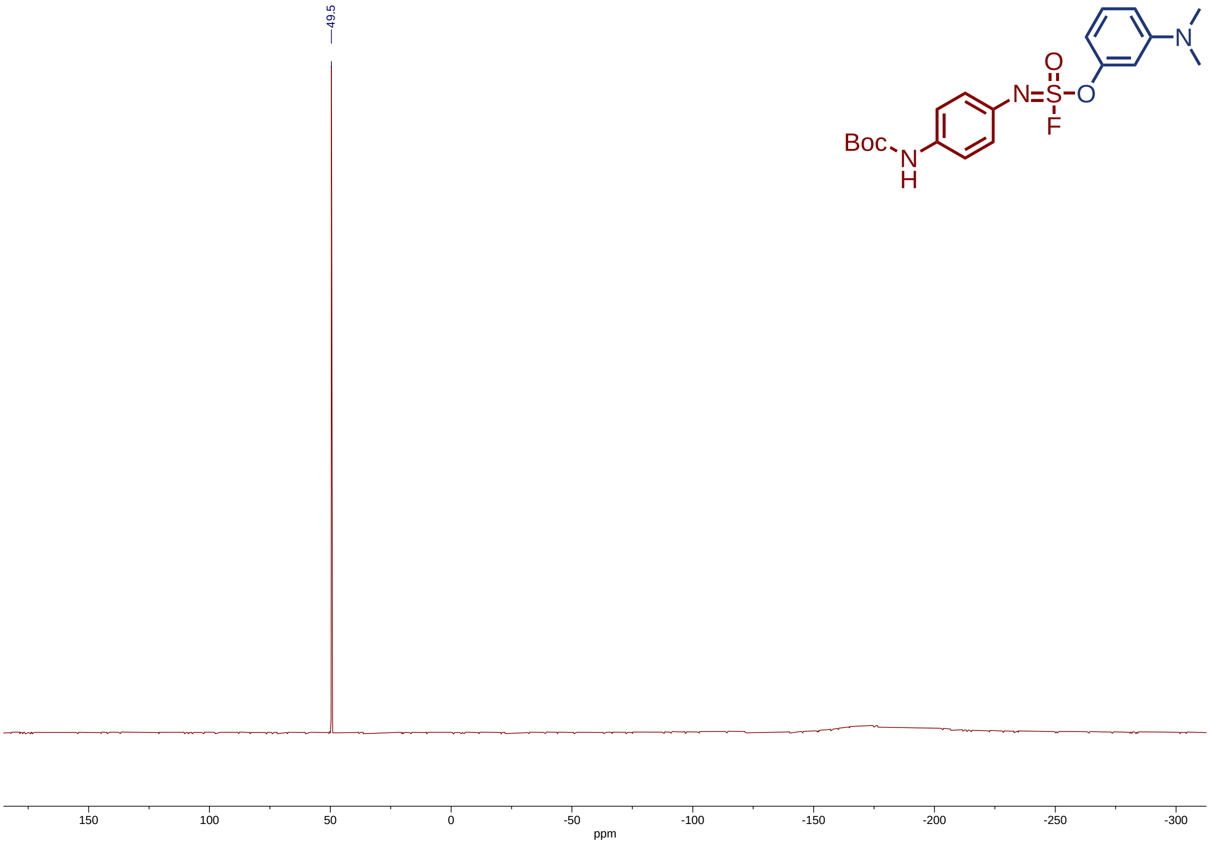
^{1}H NMR Spectrum for Compound **10g** (400 MHz, $CDCl_3$)



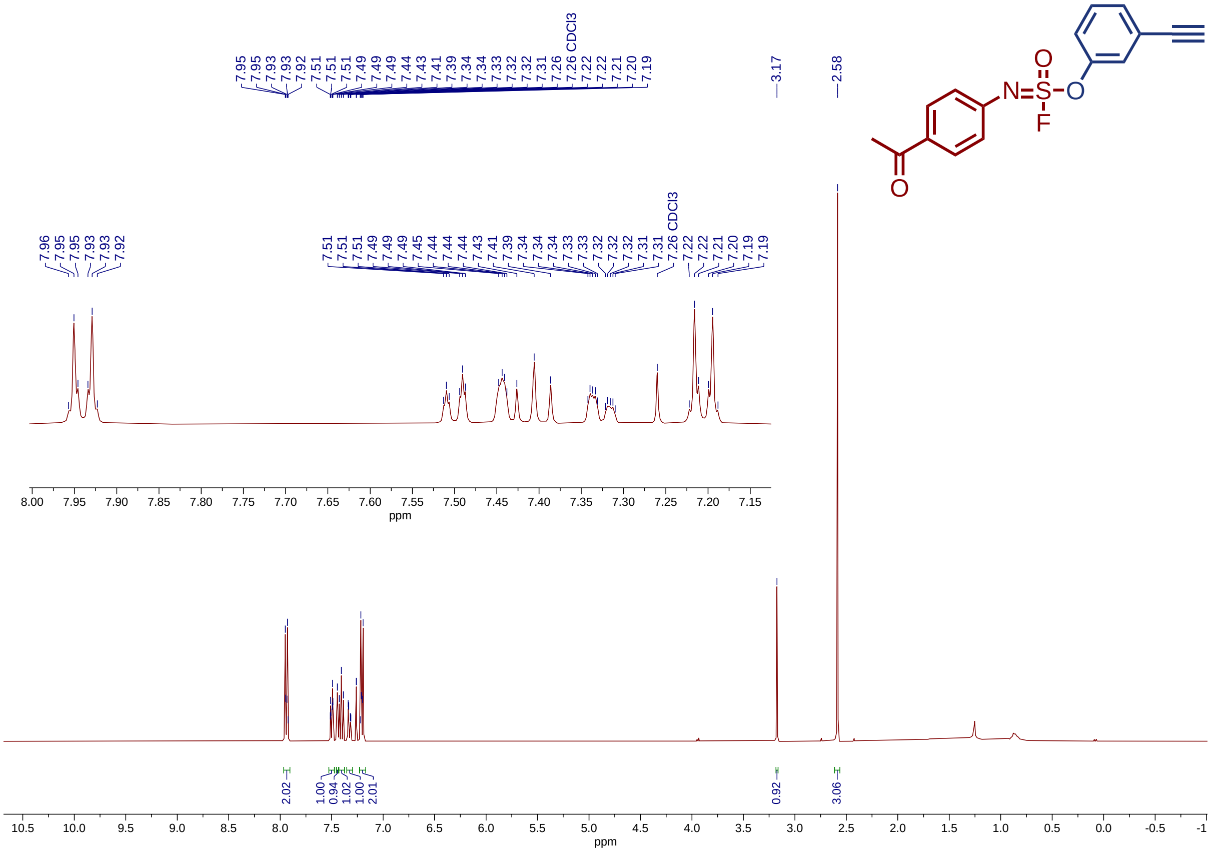
^{13}C NMR Spectrum for Compound **10g** (101 MHz, $CDCl_3$)



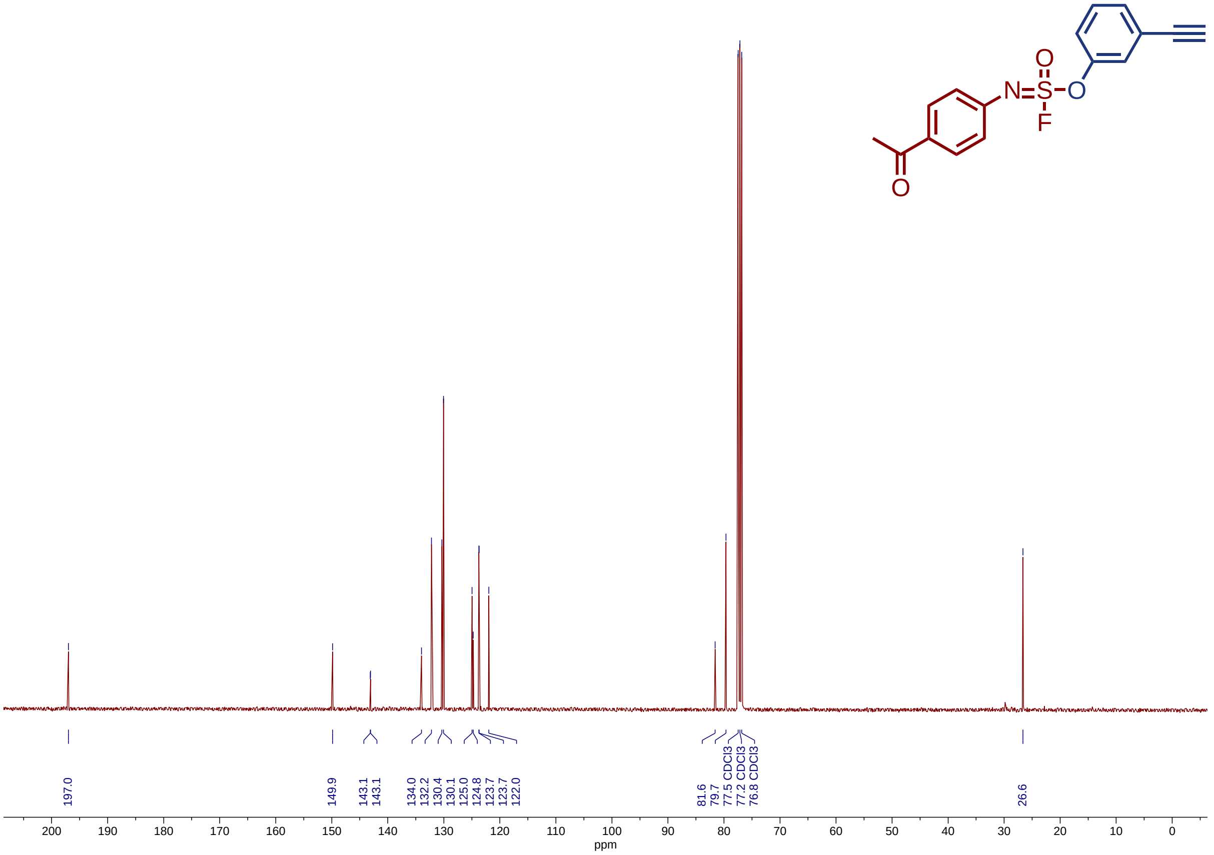
^{19}F NMR Spectrum for Compound **10g** (376 MHz, $CDCl_3$)



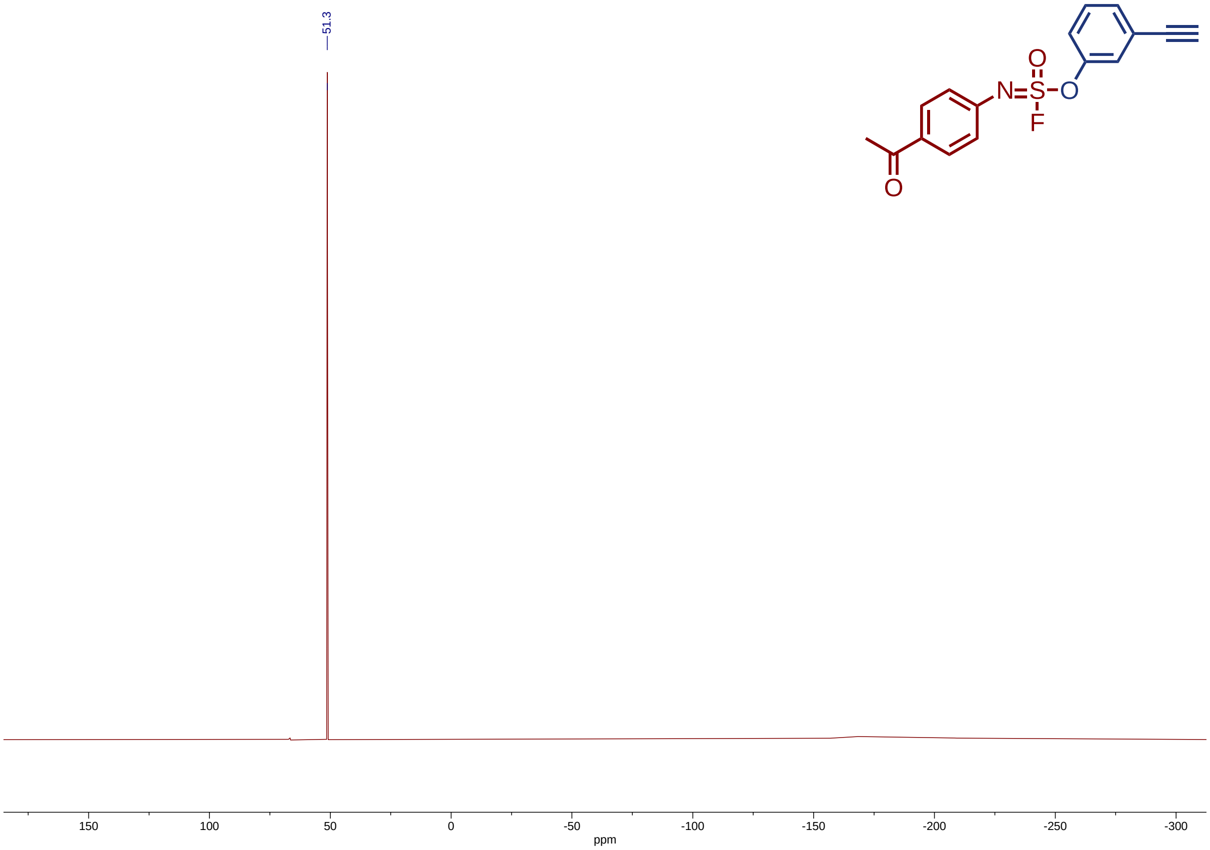
^{1}H NMR Spectrum for Compound **10h** (400 MHz, $CDCl_3$)



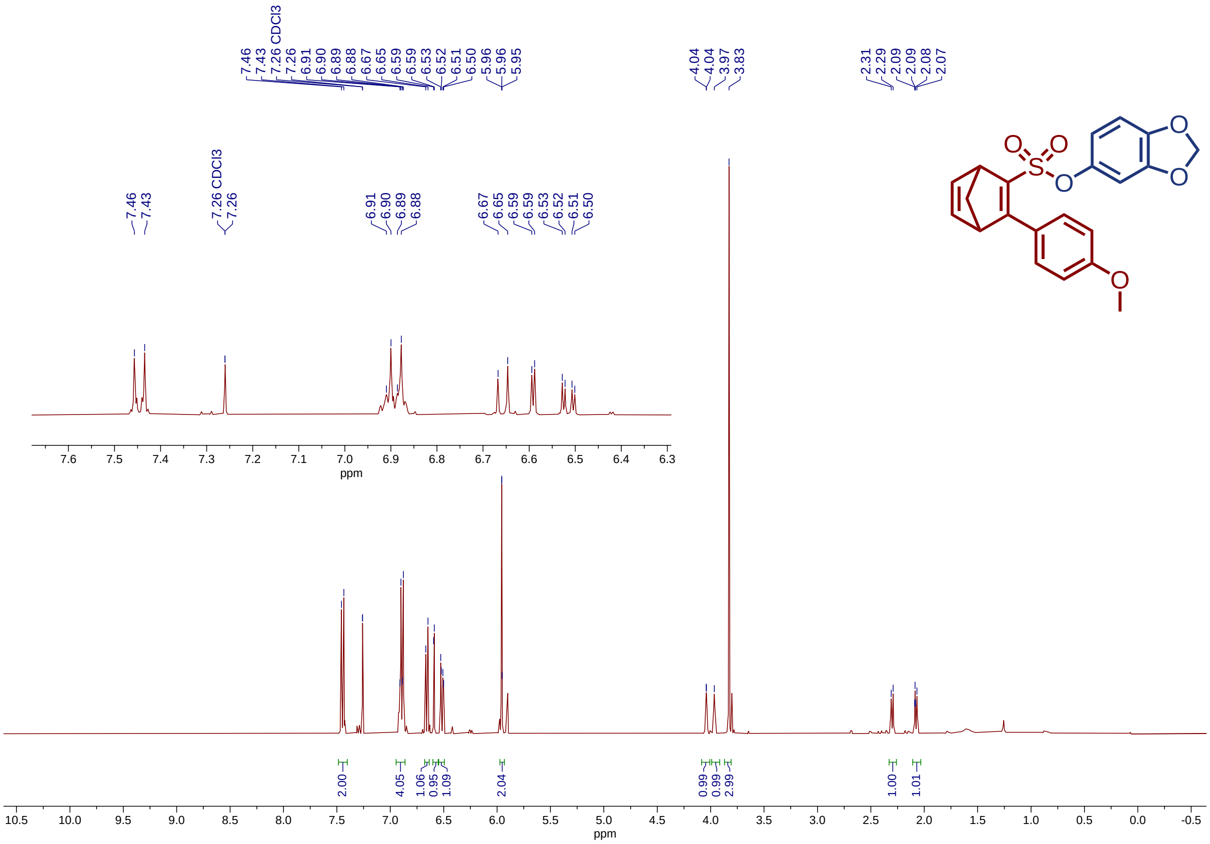
^{13}C NMR Spectrum for Compound **10h** (101 MHz, $CDCl_3$)



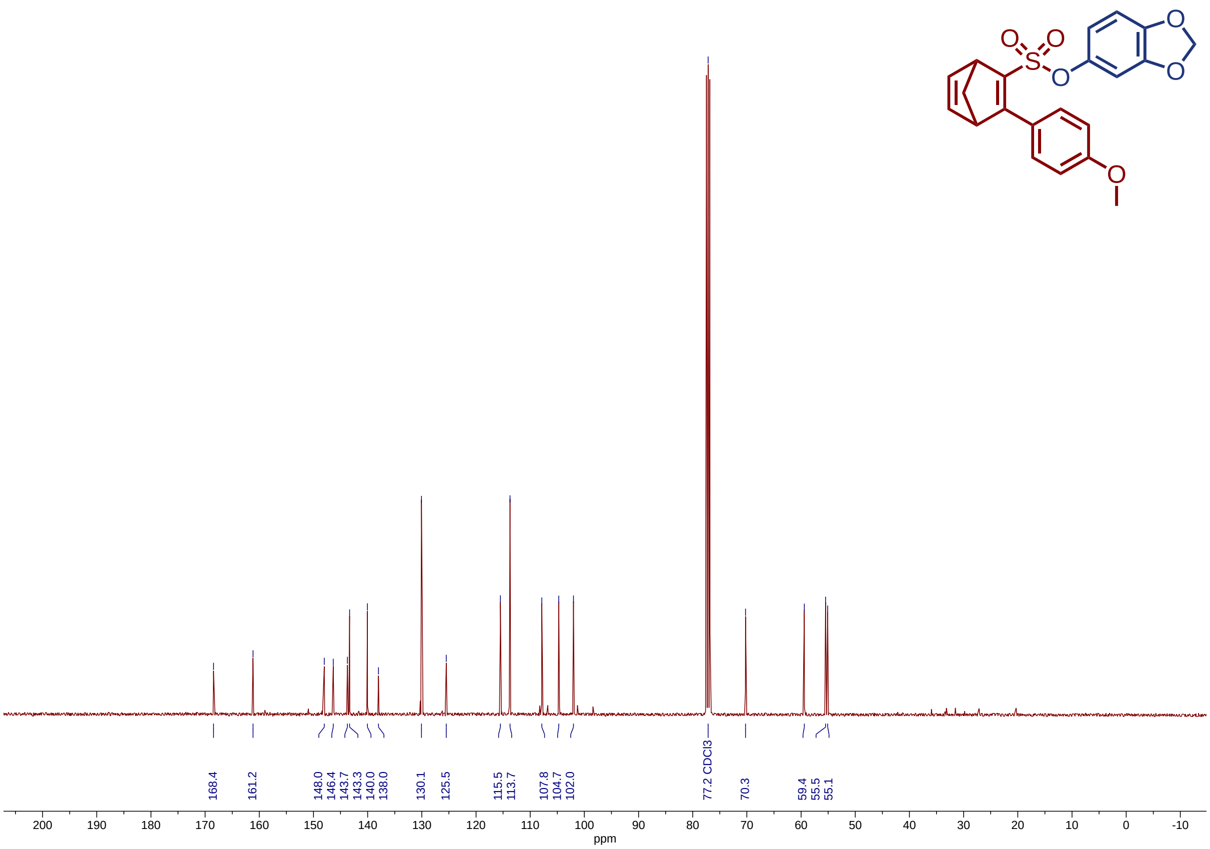
^{19}F NMR Spectrum for Compound **10h** (376 MHz, $CDCl_3$)



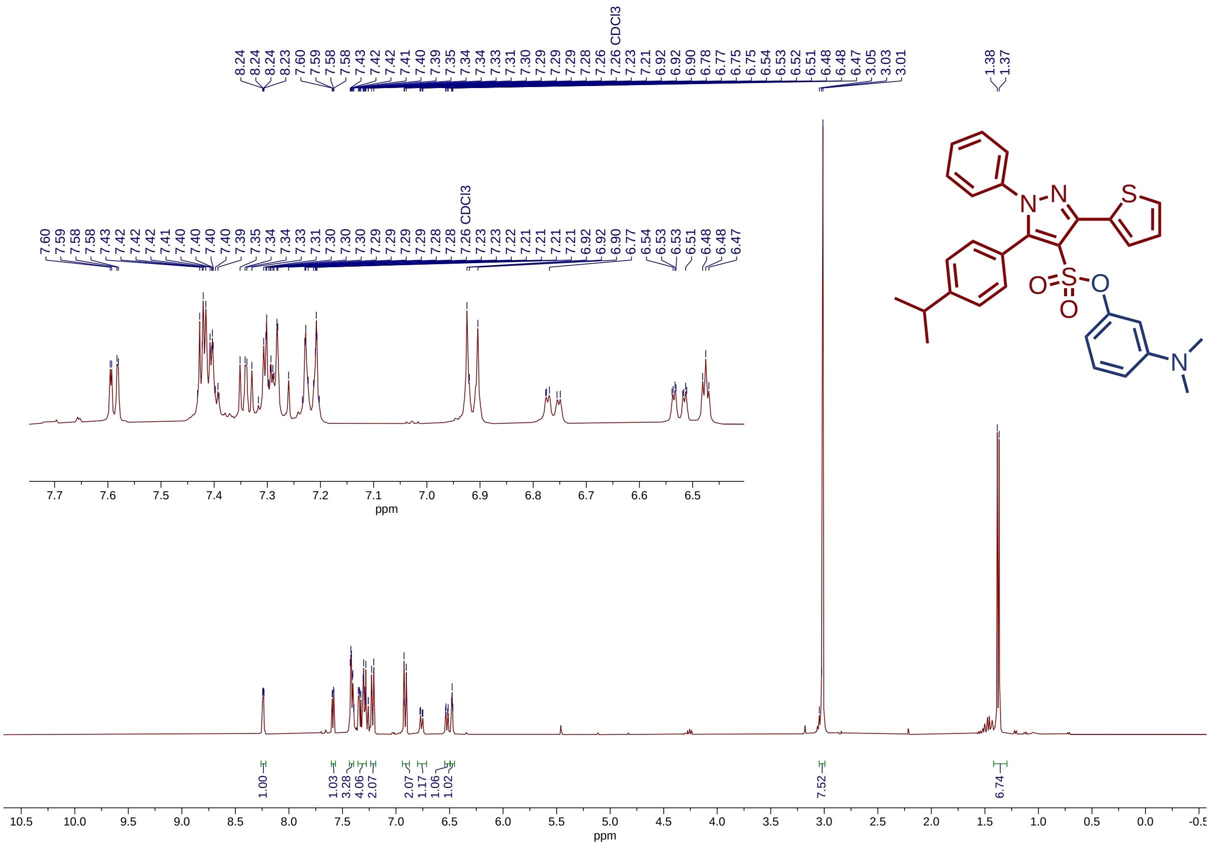
^{1}H NMR Spectrum for Compound **11a** (400 MHz, $CDCl_3$)



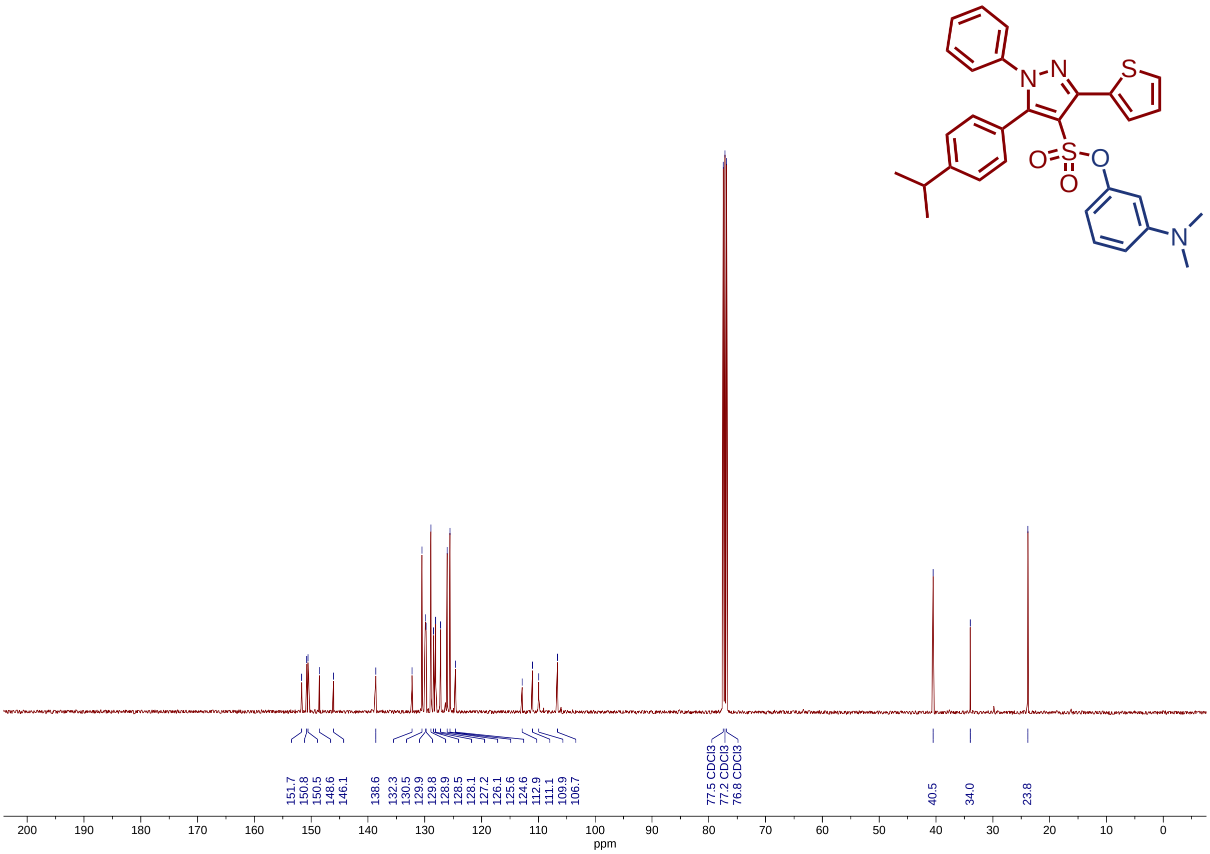
^{13}C NMR Spectrum for Compound **11a** (101 MHz, CDCl$_3$)



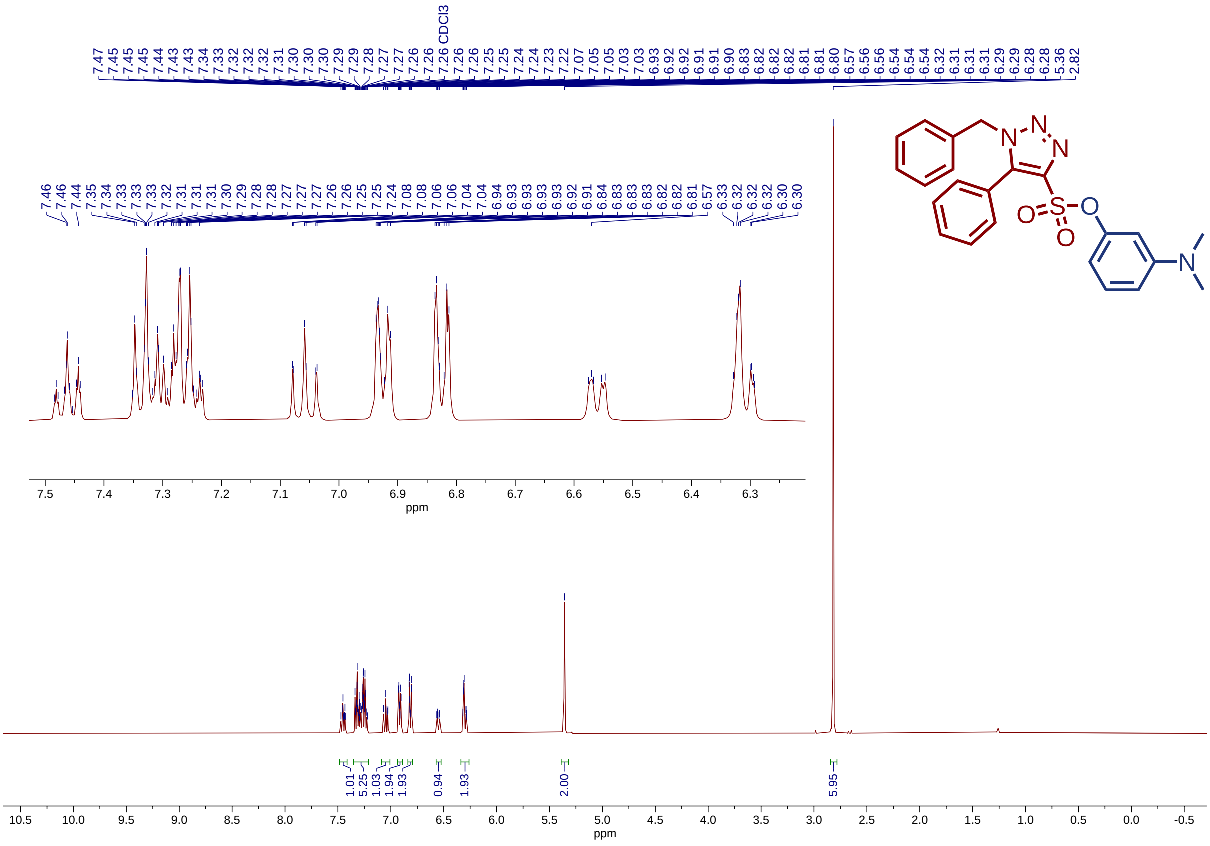
^{1}H NMR Spectrum for Compound **11b** (400 MHz, CDCl$_3$)



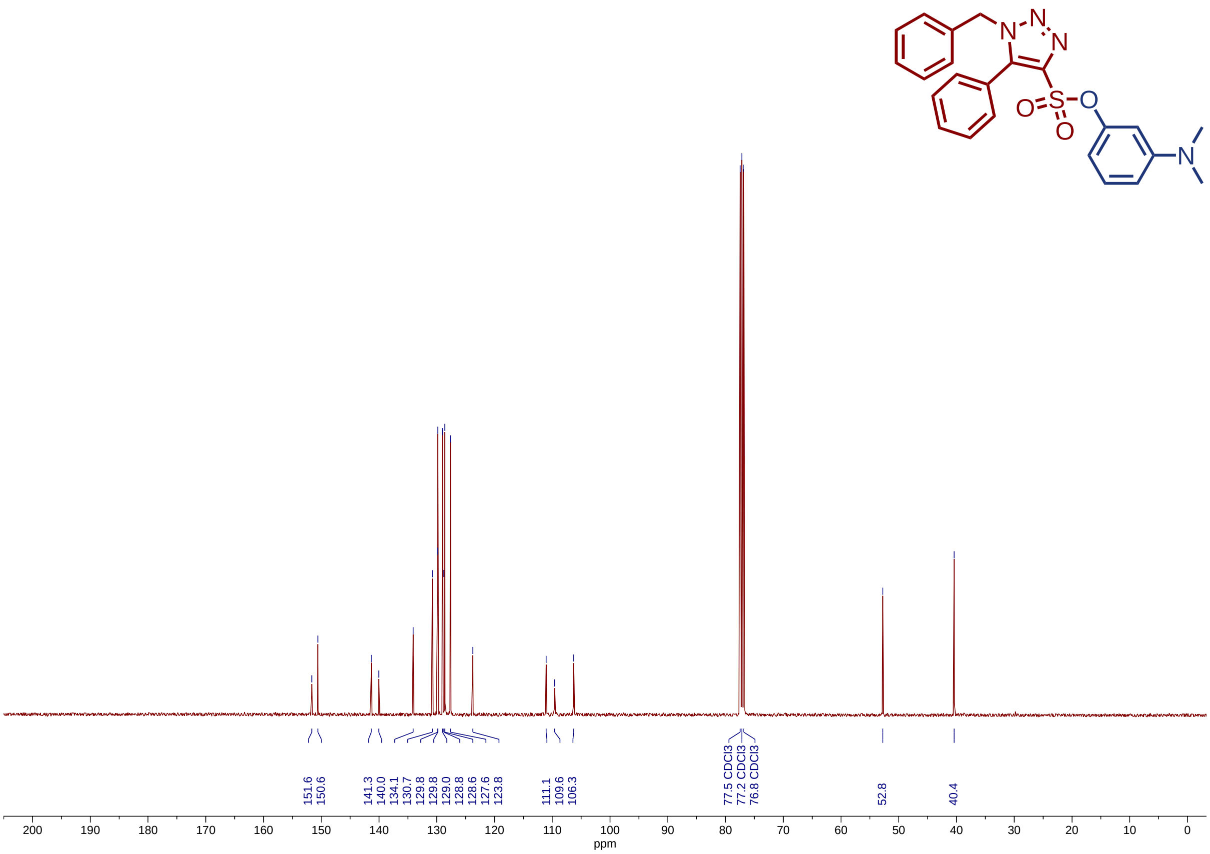
^{13}C NMR Spectrum for Compound **11b** (101 MHz, CDCl$_3$)



^{1}H NMR Spectrum for Compound **11c** (400 MHz, CDCl$_3$)

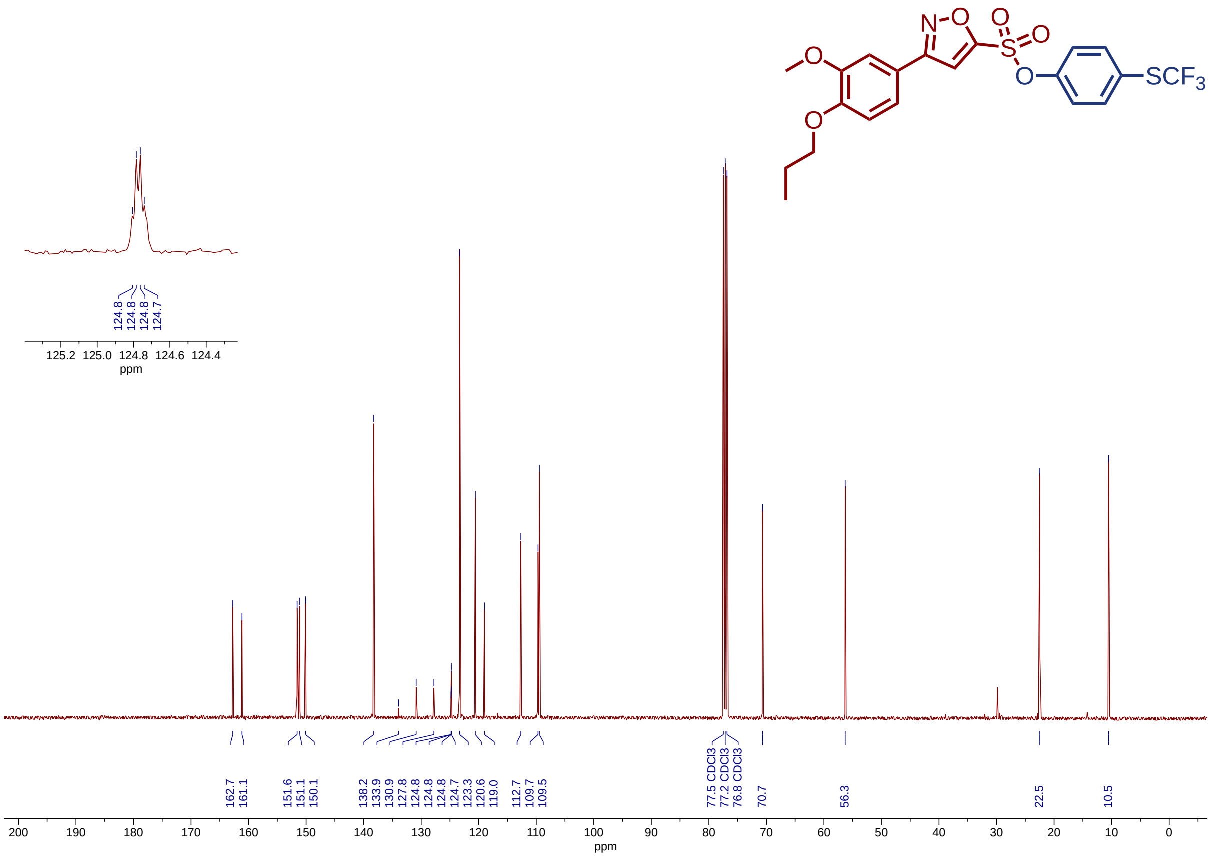


^{13}C NMR Spectrum for Compound **11c** (101 MHz, $CDCl_3$)



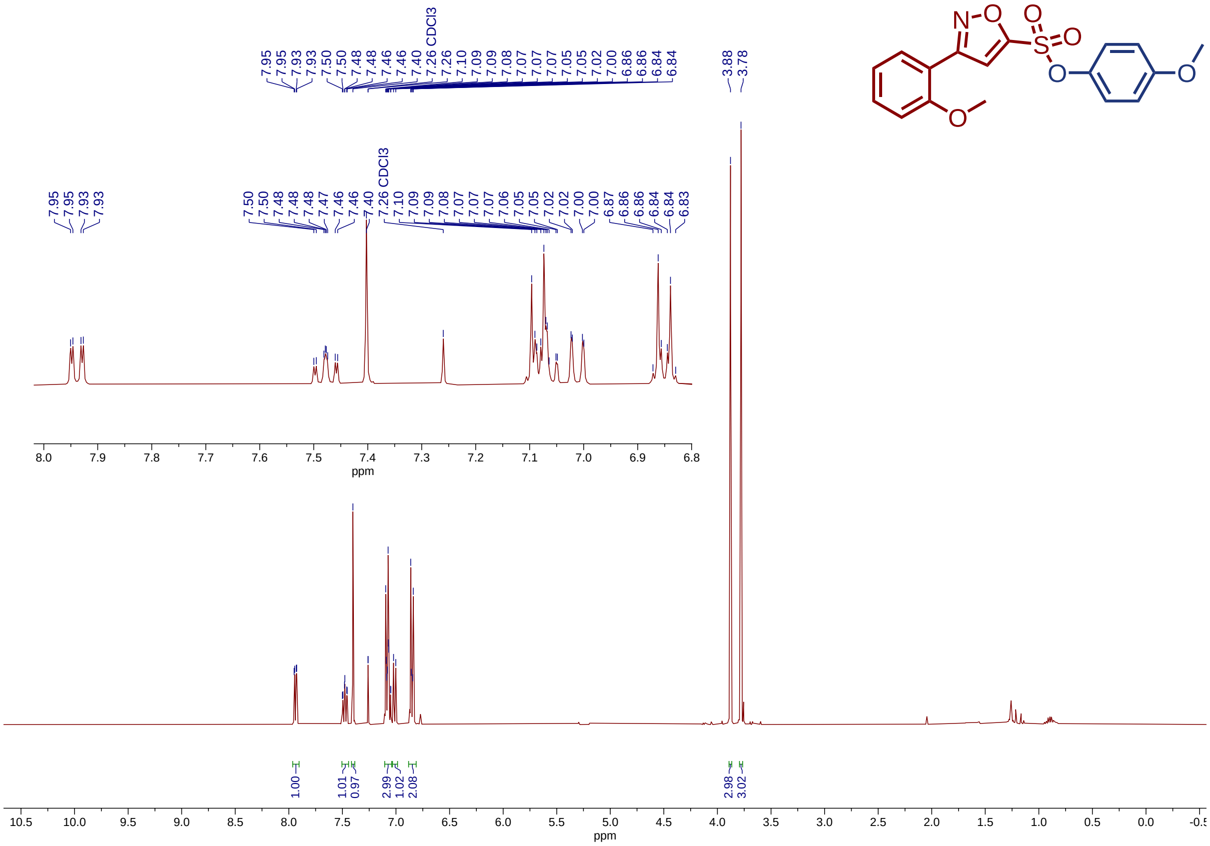
^{1}H NMR Spectrum for Compound **11d** (400 MHz, $CDCl_3$)

^{13}C NMR Spectrum for Compound **11d** (101 MHz, $CDCl_3$)

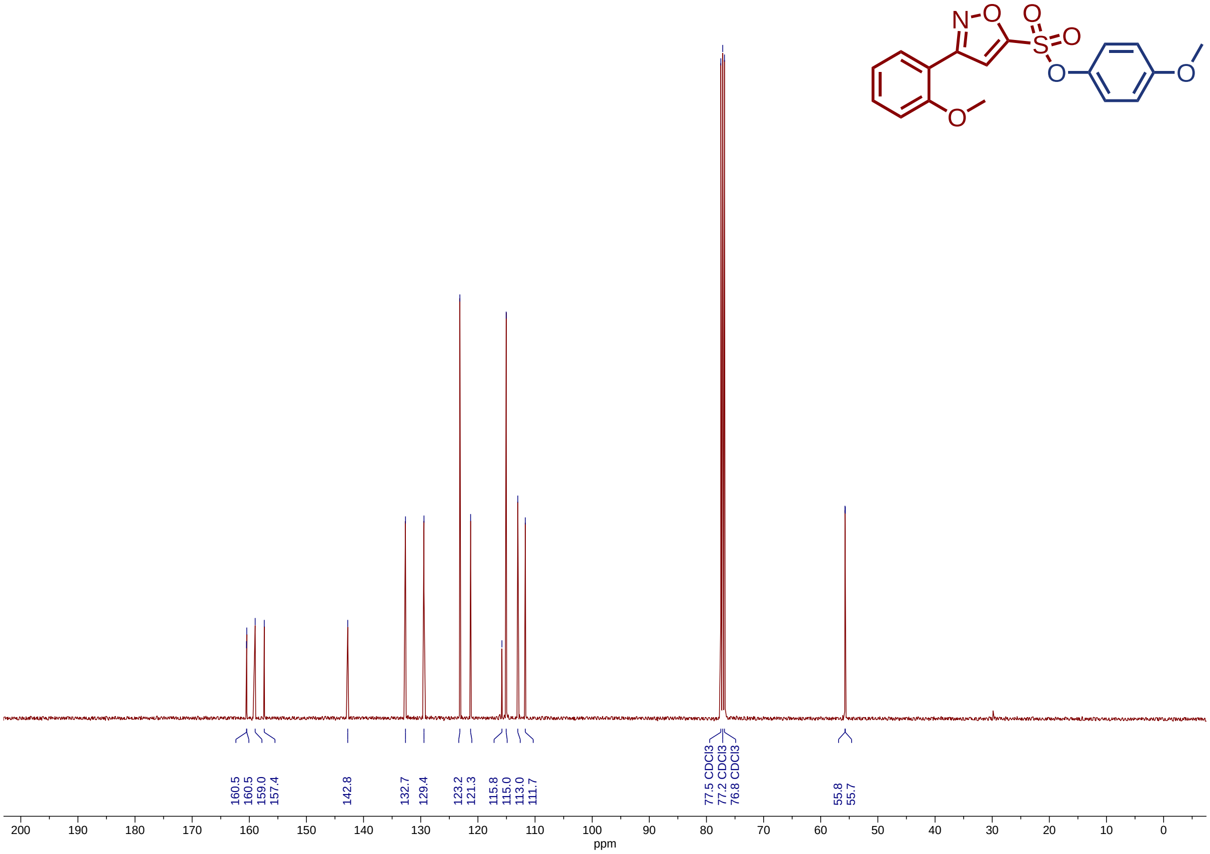


^{19}F NMR Spectrum for Compound **11d** (376 MHz, $CDCl_3$)

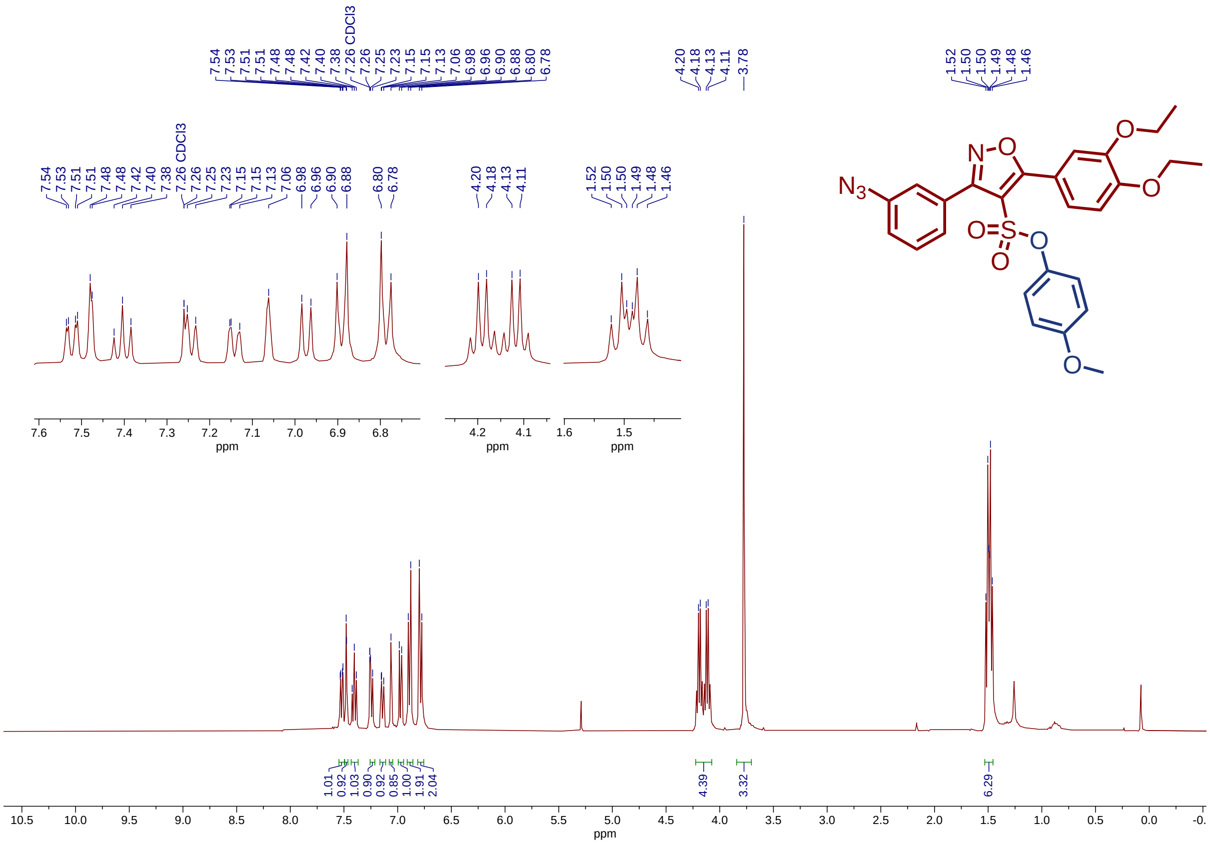
^{1}H NMR Spectrum for Compound **11e** (400 MHz, CDCl$_3$)



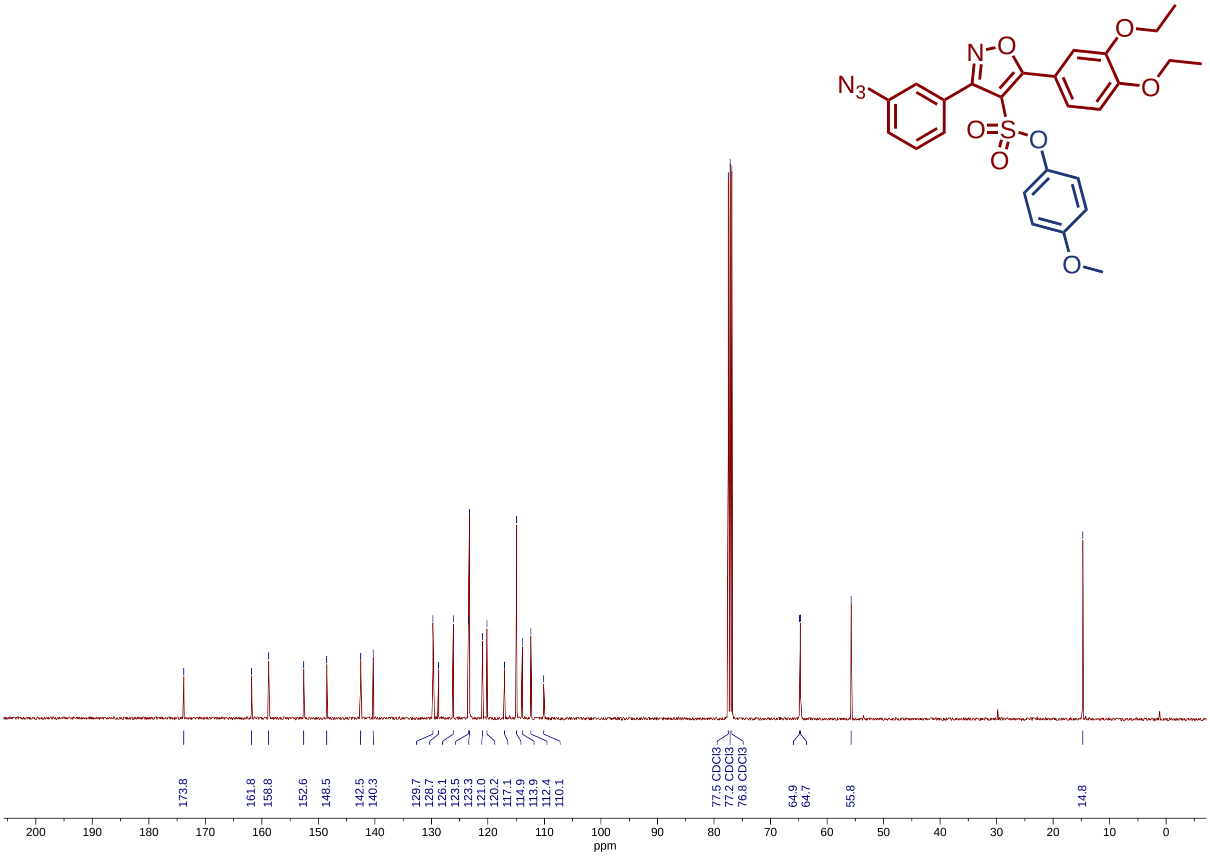
^{13}C NMR Spectrum for Compound **11e** (101 MHz, CDCl$_3$)



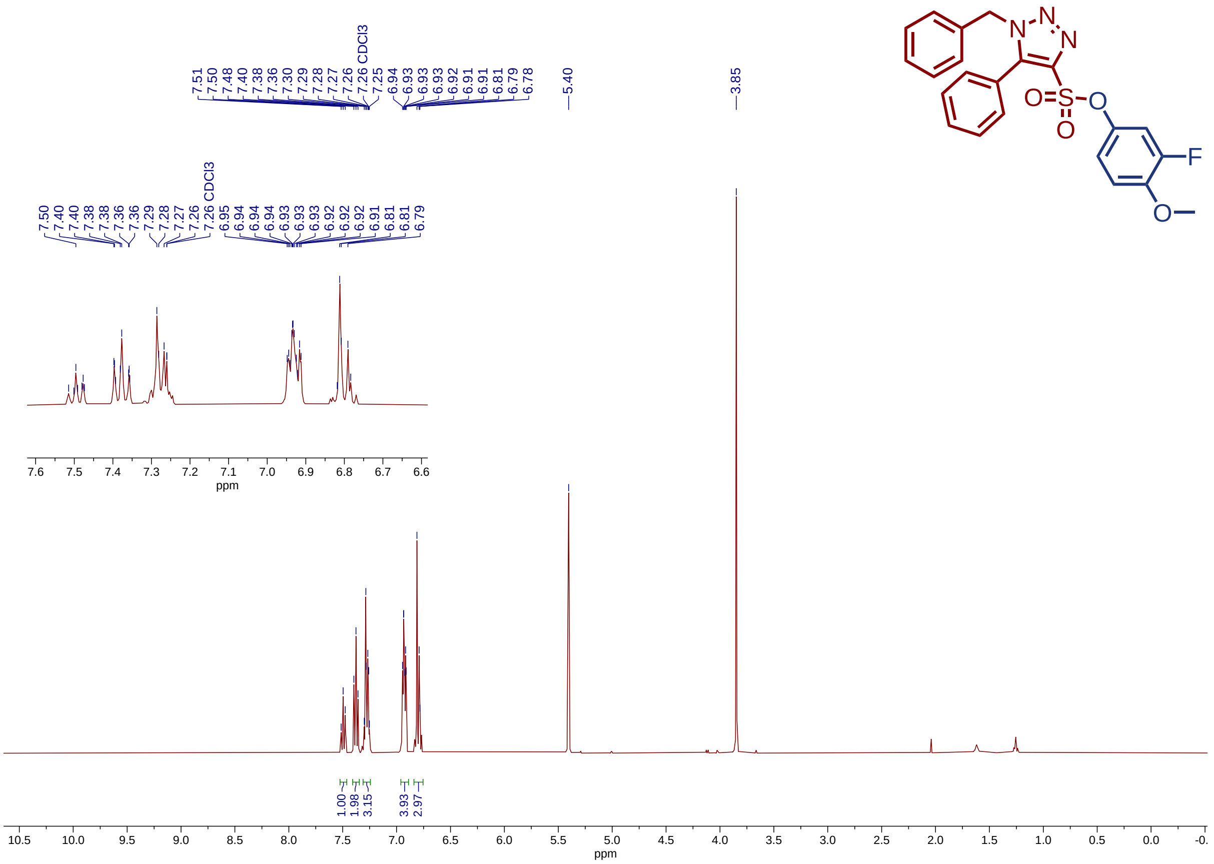
^{1}H NMR Spectrum for Compound **11f** (400 MHz, $CDCl_3$)



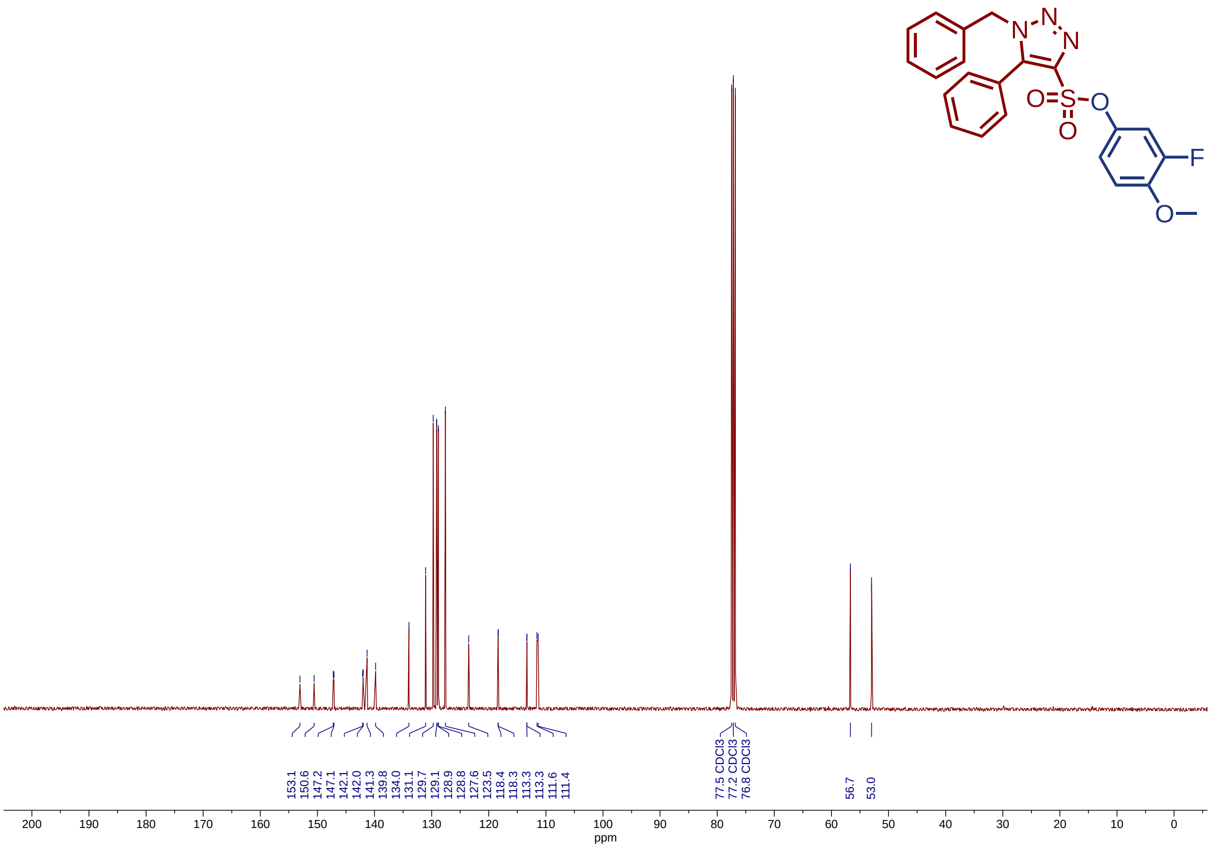
^{13}C NMR Spectrum for Compound **11f** (101 MHz, $CDCl_3$)



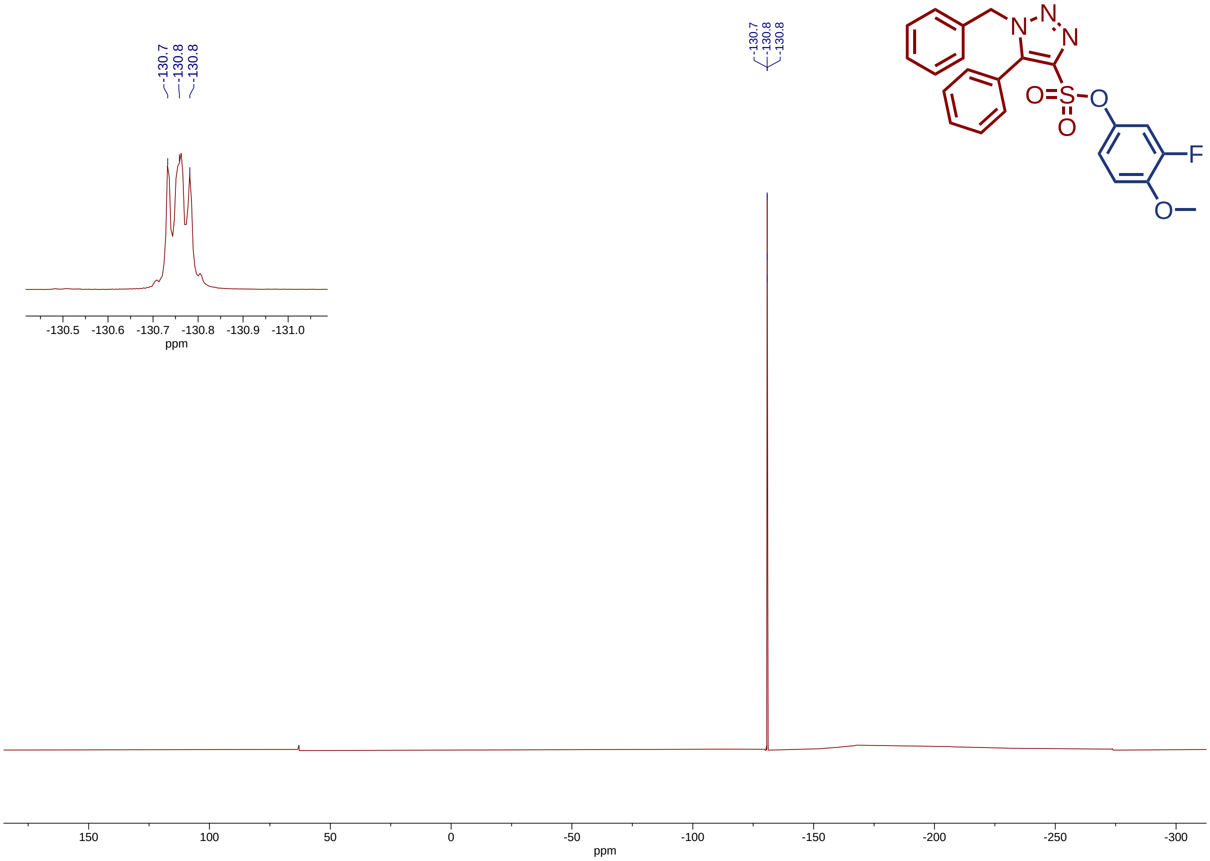
^{1}H NMR Spectrum for Compound **11g** (400 MHz, $CDCl_3$)



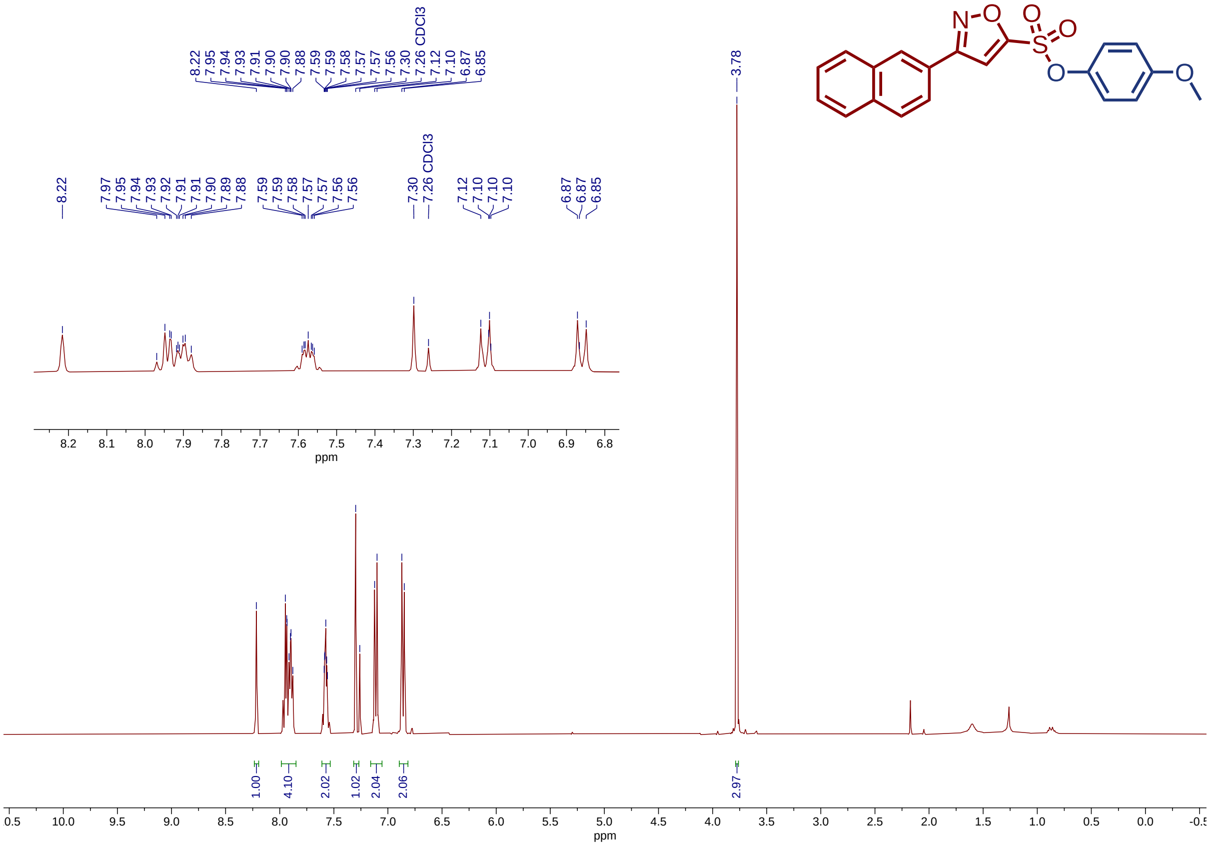
^{13}C NMR Spectrum for Compound **11g** (101 MHz, $CDCl_3$)



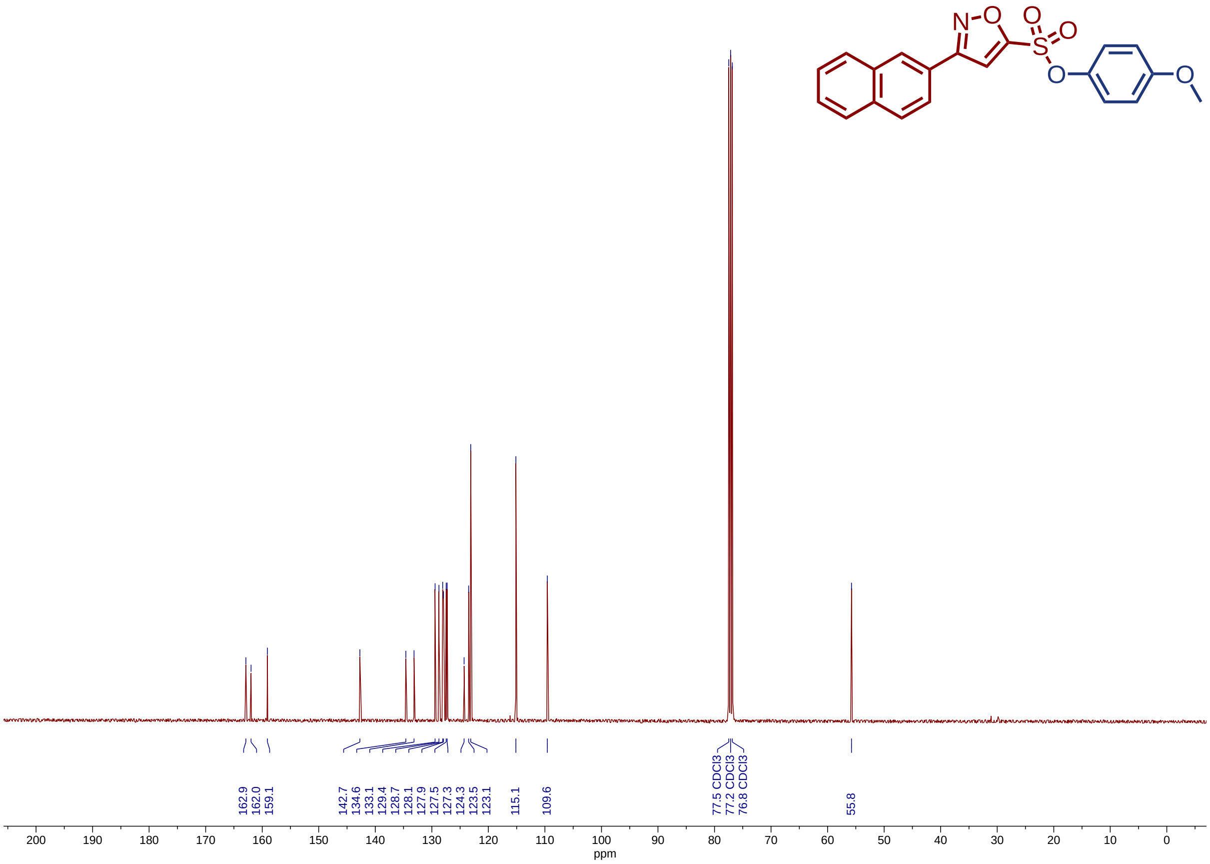
^{19}F NMR Spectrum for Compound **11g** (376 MHz, CDCl$_3$)



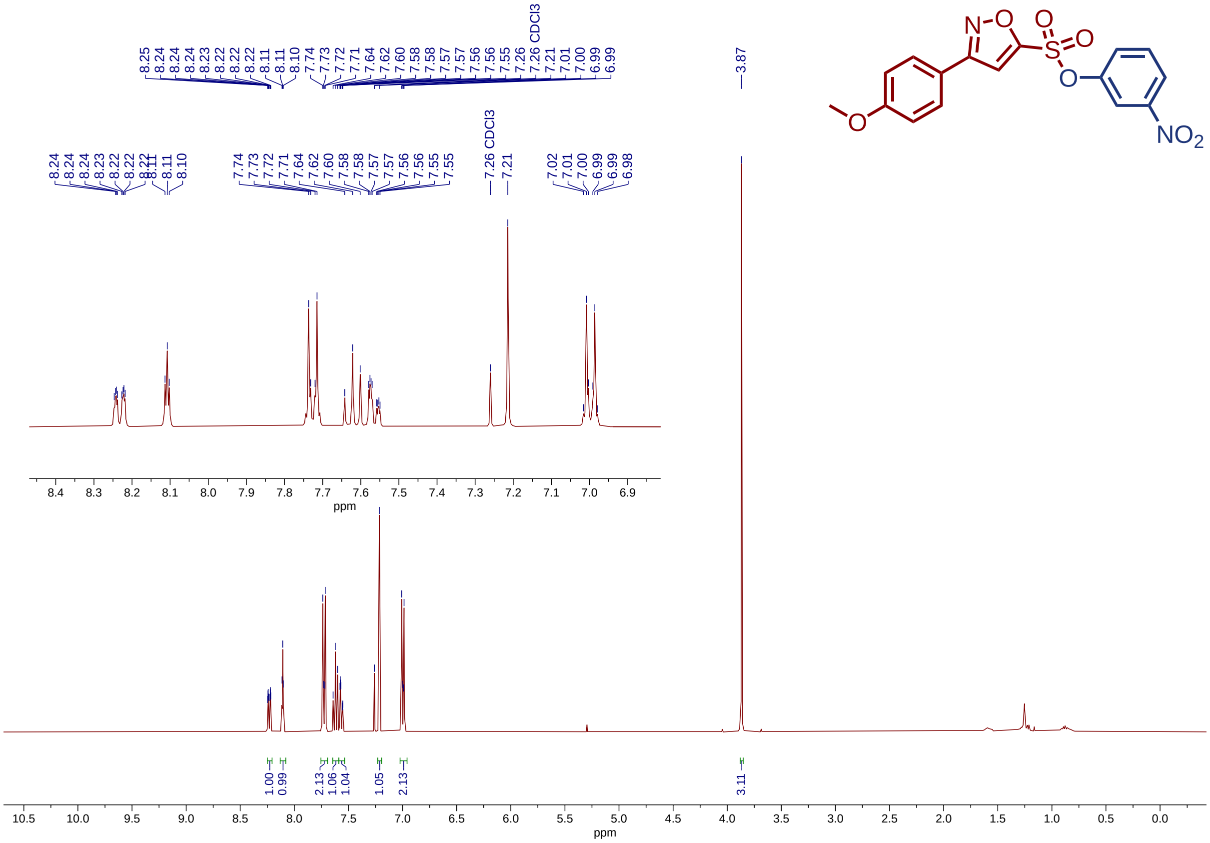
^{1}H NMR Spectrum for Compound **11h** (400 MHz, CDCl$_3$)



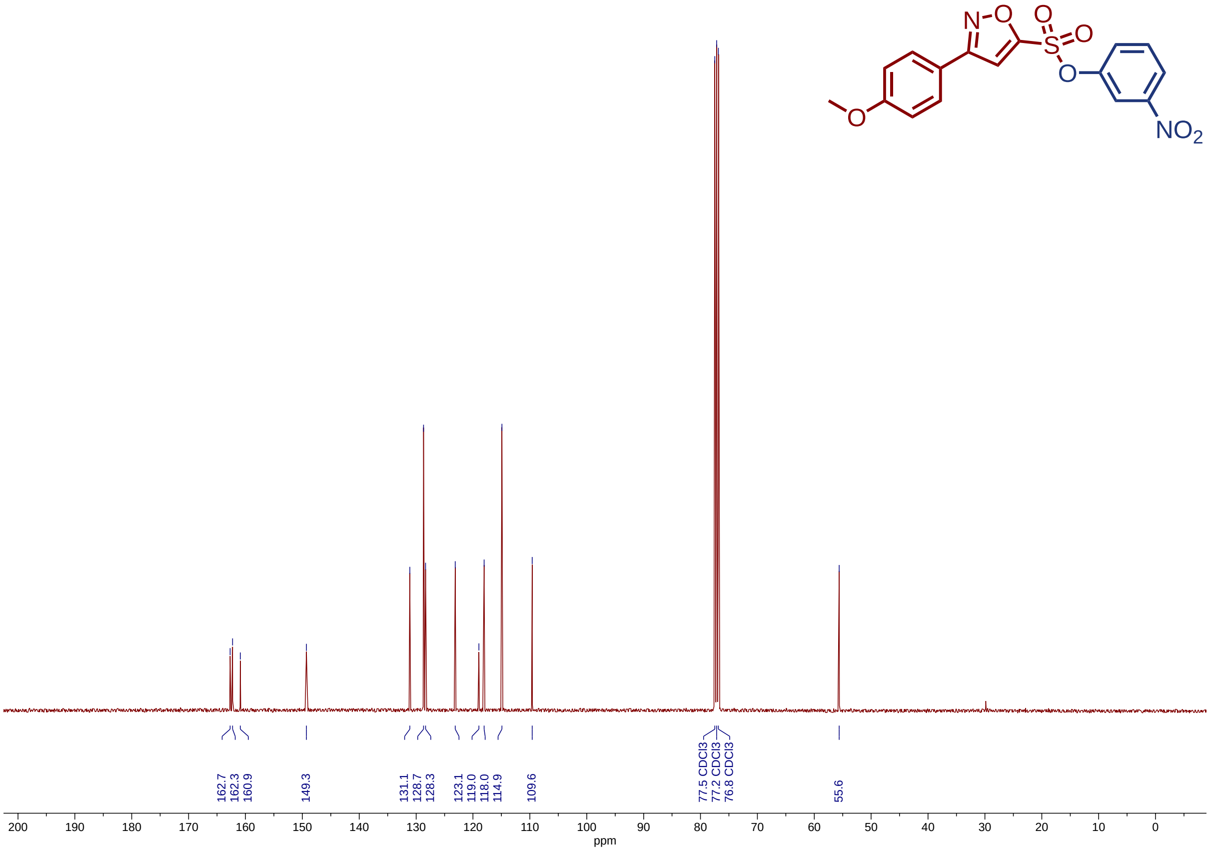
^{13}C NMR Spectrum for Compound **11h** (101 MHz, $CDCl_3$)



^{1}H NMR Spectrum for Compound **11i** (400 MHz, $CDCl_3$)



^{13}C NMR Spectrum for Compound **11i** (101 MHz, $CDCl_3$)



References

[1] R. Shang, D.-S. Ji, L. Chu, Y. Fu, L. Liu, *Angew. Chem. Int. Ed.* **2011**, *50*, 4470–4474; *Angew. Chem.* **2011**, *123,* 4562–4566.

[2] Z.-P. Che, J.-M. Yang, X.-J. Shan, Y.-E. Tian, S.-M. Liu, X.-M. Lin, J. Jiang, M. Hu, G.-Q. Chen, *J. Asian Nat. Prod. Res.* **2020**, *22*, 678–688.

[3] T. Agrawal, S. P. Cook, *Org. Lett.* **2013**, *15*, 96–99.

[4] D. A. Wilson, C. J. Wilson, C. Moldoveanu, A.-M. Resmerita, P. Corcoran, L. M. Hoang, B. M. Rosen, V. Percec, *J. Am. Chem. Soc.* **2010**, *132*, 1800–1801.

[5] H. Huang, Y. Wu, W. Zhang, C. Feng, B.-Q. Wang, W.-F. Cai, P. Hu, K.-Q. Zhao, S.-K. Xiang, *J. Org. Chem.* **2017**, *82*, 3094–3101.

[6] X. Wang, Y. Xu, F. Mo, G. Ji, D. Qiu, J. Feng, Y. Ye, S. Zhang, Y. Zhang, J. Wang, *J. Am. Chem. Soc.* **2013**, *135*, 10330–10333.

[7] X. Cheng, A. Takahashi, T. Oyama, *Polym. J.* **2010**, *42*, 86–94.

[8] W. E. Truce, L. W. Christensen, *J. Org. Chem.* **1970**, *35*, 3968–3970.

[9] T. Guo, G. Meng, X. Zhan, Q. Yang, T. Ma, L. Xu, K. B. Sharpless, J. Dong, *Angew. Chem. Int. Ed.* **2018**, *57*, 2605–2610; *Angew. Chem.* **2018**, *130*, 2635–2640.

[10] J. Dong, L. Krasnova, M. G. Finn, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2014**, *53*, 9430–9448; *Angew. Chem.* **2014**, *126*, 9584–9603.

[11] A. N. Butkevich, M. L. Bossi, G. Lukinavičius, S. W. Hell, *J. Am. Chem. Soc.* **2019**, *141*, 981–989.

[12] We suspect the reported value of -198 ppm in reference [11] could be an error due to a narrow scan range; our value of 38.8 is consistent with other fluorosulfates.

[13] C. Ma, C. Q. Zhao, X. T. Xu, Z. M. Li, X. Y. Wang, K. Zhang, T. S. Mei, *Org. Lett.* **2019**, *21*, 2464–2467.

[14] Y.-D. Kwon, M. H. Jeon, N. K. Park, J. K. Seo, J. Son, Y. H. Ryu, S. Y. Hong, J.-H. Chun, *Org. Lett.* **2020**, *22*, 5511–5516.

[15] C. Veryser, J. Demaerel, V. Bieliunas, P. Gilles, W. M. De Borggraeve, *Org. Lett.* **2017**, *19*, 5244–5247.

[16] HRMS could not be obtained with available methods.

[17] C. Liu, C. Yang, S. Hwang, S. L. Ferraro, J. P. Flynn, J. Niu, *Angew. Chem. Int. Ed.* **2020**, *59*, 18435–18441; *Angew. Chem.* **2020**, *132*, 18593–18599.

[18] J. Dong, K. B. Sharpless, L. Kwisnek, J. S. Oakdale, V. V. Fokin, *Angew. Chem. Int. Ed.* **2014**, *53*, 9466–9470; *Angew.Chem.* **2014**, *126*, 9620–9624.

[19] Integration in ^{1}H NMR spectrum = 7 due to $CDCl_3$ peak overlapping with signal.

[20] C. J. Smedley, M. C. Giel, A. Molino, A. S. Barrow, D. J. D. Wilson, J. E. Moses, *Chem. Comm.* **2018**, *54*, 6020–6023.

[21] C. J. Smedley, G. Li, A. S. Barrow, T. L. Gialelis, M.-C. Giel, A. Ottonello, Y. Cheng, S. Kitamura, D. W. Wolan, K. B. Sharpless, J. E. Moses, *Angew. Chem. Int. Ed.* **2020**, *59*, 12460–12469; *Angew.Chem.* **2020**, *132*, 12560–12569.