Supporting information

Metabolism of the Selective Matrix Metalloproteinase-9 Inhibitor (*R*)-ND-336

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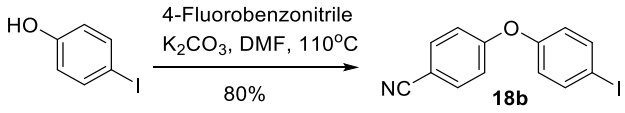
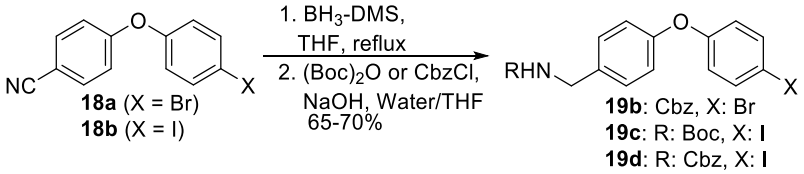
S1. Experimental details



4-(4-Iodophenoxy)benzonitrile (18b) [856704-55-7]. To a round-bottom flask containing DMF (10 mL) under an argon atmosphere were added 4-fluorobenzonitrile (1.00 g, 8.26 mmol), 4-iodophenol (1.82 g, 8.26 mmol) and K_2CO_3 (1.37 g, 9.9 mmol). The mixture was heated to 110 °C for 15 h (reaction was complete by TLC). The mixture was diluted with water (40 mL) and washed with Et_2O (2 × 20 mL). The combined Et_2O extract was washed with brine and dried over anhydrous Na_2SO_4. The suspension was filtered and the filtrate was evaporated to dryness. The residue was purified by silica-gel chromatography (9:1 hexanes:EtOAc) to give the desired product1**8b** (2.1 g, 6.54 mmol, 80%) as an off-white-colored solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.08, 155.01, 139.37, 134.36, 122.52, 118.77, 118.28, 106.54, 88.60; HRMS (ESI$^+$) *m/z* calcd for $C_{13}H_8INNaO$ $(M+Na)^+$ 343.9543, found 343.9550.



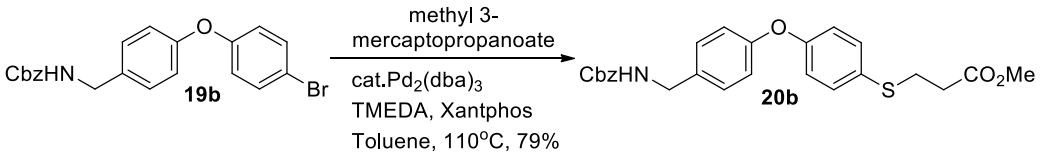
Synthesis of compounds 19b–19d. To a round-bottom flask containing anhydrous THF (20 mL) under an argon atmosphere was added the respective starting materials (**18a**, X = Br: 1.7 g, 6.2 mmol or **18b**, X = I: 2.0 g, 6.2 mmol). A solution of $BH_3 \cdot SMe_2$ (1 M in THF, 7.45 mL, 1.2 equiv.) was added. The mixture was refluxed for 12 h, at which time the reaction had reached completion. It was cooled to room temperature and methanolic HCl (5 mL, 3 M HCl in MeOH) was added slowly. The solvent was evaporated *in vacuo*. The resulting solid was triturated with Et_2O (10 mL) to give the product as the HCl salt. The crude product was carried forward to protection without further purification. The entire solid HCl salt was suspended in dry THF (20 mL). To this stirred mixture were added sequentially 2 M aq NaOH (5 mL), and Boc_2O (1.6 g, 7.43 mmol) or CbzCl (1.27 g, 7.43 mmol). The mixture was stirred at room temperature for 15 h. The reaction mixture was washed with Et_2O (2 × 20 mL). The combined Et_2O layer were washed with brine and dried over anhydrous Na_2SO_4. The suspension was filtered. The filtrate was concentrated to dryness *in*

vacuo. The resulting crude was purified by silica-gel chromatography (2:8 hexanes/EtOAc) to afford the product (**19b**, *N*-Cbz protection with X = Br: 1.66 g, 4.03 mmol, 65%; **19c**, *N*-Boc protection with X = I: 1.8 g, 4.23 mmol, 68%; **19d**, *N*-Cbz protection with X = I: 2.0 g, 4.35 mmol, 70%).

Benzyl 4-(4-bromophenoxy)benzylcarbamate (19b, $C_{21}H_{18}BrNO_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.8 Hz, 2H), 7.32–7.23 (m, 5H), 7.19 (d, *J* = 7.9 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 5.07 (s, 2H), 5.00 (s, 1H), 4.29 (d, *J* = 5.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.48, 156.12, 136.42, 133.85, 132.72, 129.16, 128.58, 128.23, 128.19, 120.40, 119.22, 115.73, 66.95, 44.56; HRMS (ESI$^+$) *m/z* calcd for $C_{21}H_{19}BrNO_3$ $(M+H)^+$ 412.0543, found 412.0543.

***tert*-Butyl 4-(4-iodophenoxy)benzylcarbamate (19c, $C_{18}H_{20}INO_3$).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.9 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 6.68 (d, *J* = 8.9 Hz, 2H), 4.78 (br s, 1H), 4.29 (d, *J* = 5.9 Hz, 2H), 1.39 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.47, 155.76, 138.66, 134.49, 129.06, 120.75, 119.3, 85.92, 44.08, 28.43; HRMS (ESI$^+$) *m/z* calcd for $C_{18}H_{21}INO_3$ $(M+H)^+$ 448.0380, found 448.0377.

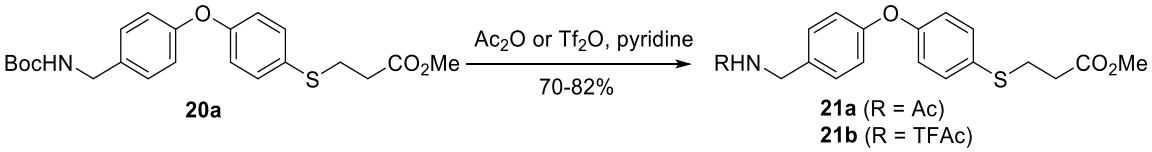
Benzyl 4-(4-iodophenoxy)benzylcarbamate (19d, $C_{21}H_{18}INO_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.9 Hz, 2H), 7.37–7.23 (m, 5H), 7.19 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 6.68 (d, *J* = 8.9 Hz, 2H), 5.07 (s, 1H), 5.00 (br s, 1H), 4.29 (d, *J* = 5.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.37, 155.94, 138.69, 136.42, 133.93, 129.16, 128.58, 128.23, 128.19, 120.80, 119.33, 86.01, 66.95, 44.56; HRMS (ESI$^+$) *m/z* calcd for $C_{21}H_{18}INNaO_3$ $(M+Na)^+$ 482.0224, found 482.0239.



Synthesis of 20b. $Pd(dba)_3$ (0.1 mmol) and Xantphos (0.2 mmol) were suspended in a round-bottom flask with toluene (20 mL) under an argon atmosphere. Compound **19b** (1.6 g, 3.9 mmol) was added, followed by methyl 3-mercaptopropanoate (648 mg, 4.0 mmol) and DIPEA (1.154 g, 8.93 mmol). The reaction mixture was refluxed overnight, at which time the reaction had reached completion. The mixture was cooled to room temperature and filtered through Celite. The Celite plug was washed with toluene. The combined toluene solution was evaporated. The residue was

purified by silica-gel chromatography (8:2 hexanes/EtOAc) to give the product as an off-white-colored solid (**20b**, 1.4 g, 3.10 mmol, 79%).

Methyl 3-((4-(4-((((benzyloxy)carbonyl)amino)methyl)phenoxy)phenyl)thio)propanoate (20b, $C_{25}H_{25}NO_5S$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.22 (m, 6H), 7.24–7.16 (m, 3H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 5.07 (s, 2H), 5.00 (br s, 1H), 4.30 (d, *J* = 5.9 Hz, 2H), 3.62 (s, 3H), 3.04 (t, *J* = 7.4 Hz, 2H), 2.54 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.22, 156.82, 156.15, 133.75, 133.31, 129.14, 128.57, 128.22, 128.18, 119.33, 119.24, 66.94, 51.87, 44.57, 34.34, 30.44; HRMS (ESI$^+$) *m/z* calcd for $C_{25}H_{26}NO_5S$ $(M+H)^+$ 452.1526, found 452.1523.



20a

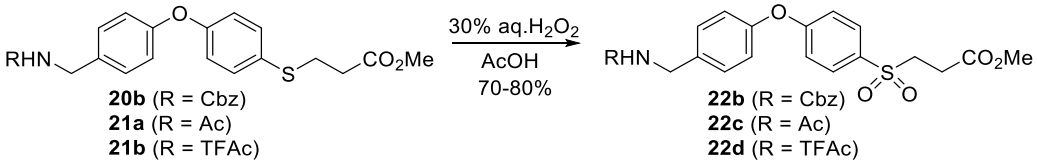
21a (R = Ac)
21b (R = TFAc)

Synthesis of compounds 21a and 21b. A solution of **20a** (150 mg, 0.34 mmol) in 10:1 CH_2Cl_2/TFA (5.5 mL) was stirred overnight. The solvents were removed by evaporation. To the resulting residue were added respectively Ac_2O (34 mg, 0.33 mmol) in pyridine (2 mL), or trifluoroacetic anhydride (70 mg, 0.33 mmol) in pyridine (2 mL). The reaction was stirred at room temperature for 6 h, at which time the reaction had reached completion. The solvents were removed by evaporation. The residue was purified by silica-gel chromatography (7:3 hexanes/EtOAc) to give the products as an off-white solids (**21a**, *N*-Ac: 91 mg, 0.25 mmol, 70%; **21b**, *N*-TFAc: 122 mg, 0.29 mmol, 82%).

Methyl 3-((4-(4-(acetamidomethyl)phenoxy)phenyl)thio)propanoate (21a, $C_{19}H_{21}NO_4S$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.69 (br s, 1H), 4.35 (d, *J* = 5.8 Hz, 2H), 3.62 (s, 3H), 3.04 (t, *J* = 7.4 Hz, 2H), 2.54 (t, *J* = 7.4 Hz, 2H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.22, 169.89, 156.76, 156.20, 133.56, 133.30, 129.45, 128.68, 119.34, 119.26, 51.87, 43.18, 34.33, 30.42, 23.35; HRMS (ESI$^+$) *m/z* calcd for $C_{19}H_{22}NO_4S$ $(M+H)^+$ 360.1264, found 360.1276.

Methyl 3-((4-(4-((2,2,2-trifluoroacetamido)methyl)phenoxy)phenyl)thio)propanoate (21b, $C_{19}H_{18}F_3NO_4S$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.7 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.59 (br s, 1H), 4.44 (d, *J* = 5.8 Hz, 2H), 3.61 (s, 3H), 3.04 (t, *J* = 7.4 Hz, 2H), 2.54 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.23,

157.12 (J = 36 Hz), 157.02, 156.31, 133.20, 130.92, 129.71, 129.16, 115.86 (q, J = 286 Hz), 119.57, 119.36, 51.88, 43.37, 34.31, 30.32; HRMS (ESI$^+$) *m/z* calcd for $C_{19}H_{19}F_3NO_4S$ $(M+H)^+$ 414.0981, found 414.0965.



20b (R = Cbz)
21a (R = Ac)
21b (R = TFAc)

22b (R = Cbz)
22c (R = Ac)
22d (R = TFAc)

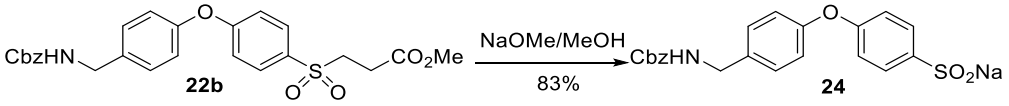
Synthesis of 22b–22d. To a round-bottom flask containing anhydrous acetic acid (10 mL) under an argon atmosphere was added the respective starting materials (**20b**, 1.0 g, 2.21 mmol; **21a**, 70 mg, 0.19 mmol; **21b**, 70mg, 0.17 mmol) To this solution was added 30% H_2O_2 (2 mL). The mixture was stirred at room temperature overnight, at which time the reaction had reached completion. The solvent was removed by evaporation. The residue was taken up into EtOAc (2 × 20 mL). The combined EtOAc solution was washed sequentially with sat. $NaHCO_3$ and brine, and the organic layer was dried over anhydrous Na_2SO_4. The mixture was filtered and the filtrate was concentrated to dryness. The residue was purified by silica-gel chromatography (6:4 hexanes/EtOAc) to give the product as an off-white solid (**22b**, R = Cbz, 846 g, 1.75 mmol, 79%; **22c**, R = Ac, 61 g, 0.155 mmol, 80%; **22d**, R = TFAc, 53 g, 0.118 mmol, 70%).

Methyl 3-((4-(4-((((benzyloxy)carbonyl)amino)methyl)phenoxy)phenyl)sulfonyl)propanoate (22b, $C_{25}H_{25}NO_7S$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.71 (m, 2H), 7.35–7.23 (m, 7H), 7.06–6.88 (m, 4H), 5.08 (br s, 2H), 4.34 (d, J = 6.0 Hz, 2H), 3.59 (s, 3H), 3.35 (t, J = 7.5 Hz, 2H), 2.69 (t, J = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.53, 162.77, 156.48, 154.10, 136.34, 135.59, 131.87, 130.54, 129.44, 128.60, 128.28, 128.21, 120.68, 117.69, 67.04, 52.38, 51.72, 44.49, 27.73; HRMS (ESI$^+$) *m/z* calcd for $C_{25}H_{26}NO_7S$ $(M+H)^+$ 484.1424, found 484.1452.

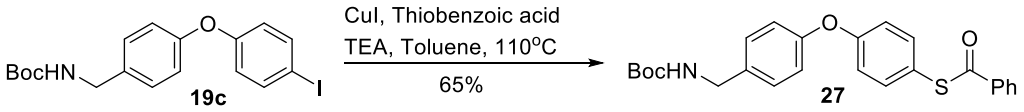
Methyl 3-((4-(4-(acetamidomethyl)phenoxy)phenyl)sulfonyl)propanoate (22c, $C_{19}H_{21}NO_6S$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.7 Hz, 2H), 7.19 (d, J = 8.5 Hz, 2H), 6.90 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 5.75 (br s, 1H), 4.34 (d, J = 5.7 Hz, 2H), 3.61 (s, 1H), 3.03 (t, J = 7.4 Hz, 2H), 2.54 (t, J = 7.4 Hz, 2H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.22, 169.92, 156.76, 156.19, 133.57, 133.29, 129.45, 128.67, 119.34, 119.25, 51.87, 43.17, 34.33, 30.42, 23.34; HRMS (ESI$^+$) *m/z* calcd for $C_{19}H_{22}NO_6S$ $(M+H)^+$ 392.1162, found 392.1143.

Methyl 3-((4-(4-((2,2,2-trifluoroacetamido)methyl)phenoxy)phenyl)sulfonyl)propanoate (22d, $C_{19}H_{18}F_3NO_6S$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.9 Hz, 2H), 7.29 (d, J = 8.5

Hz, 2H), 7.02 (d, J = 5.0 Hz, 2H), 7.00 (d, J = 4.8 Hz, 2H), 6.74 (br s, 1H), 4.48 (d, J = 5.9 Hz, 2H), 3.60 (s, 1H), 3.35 (t, J = 7.5 Hz, 2H), 2.69 (t, J = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.50, 162.43, 157.25 (q, J = 37 Hz), 154.84, 132.91, 132.17, 130.58, 130.03, 120.86, 117.93, 115.86 (J = 287 Hz), 52.39, 51.70, 43.24, 27.70; HRMS (ESI$^+$) *m/z* calcd for $C_{19}H_{19}F_3NO_6S$ $(M+H)^+$ 446.0880, found 446.0872.

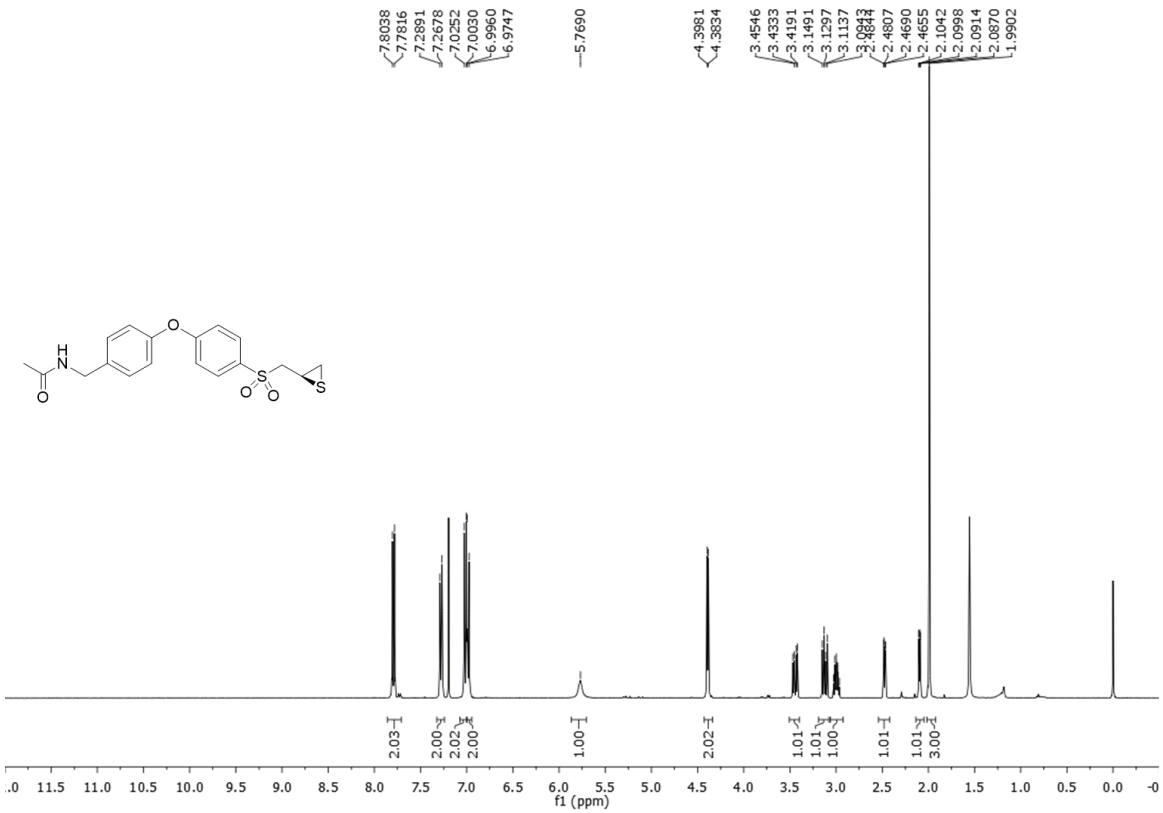


Synthesis of the sodium salt of sulfinic acid (24). To a round-bottom flask containing **22b** (500 mg, 1.03 mmol) in methanol (5 mL) under an atmosphere of argon was added NaOMe (56 mg, 1.03 mmol). The reaction mixture was stirred overnight at room temperature, at which time the reaction had reached completion. The solvent was evaporated to dryness. The solid was triturated with two portions of Et_2O (20 mL, discarded) and collected by filtration. Formation of the sulfinate salt **24** was confirmed by LC-MS analysis.

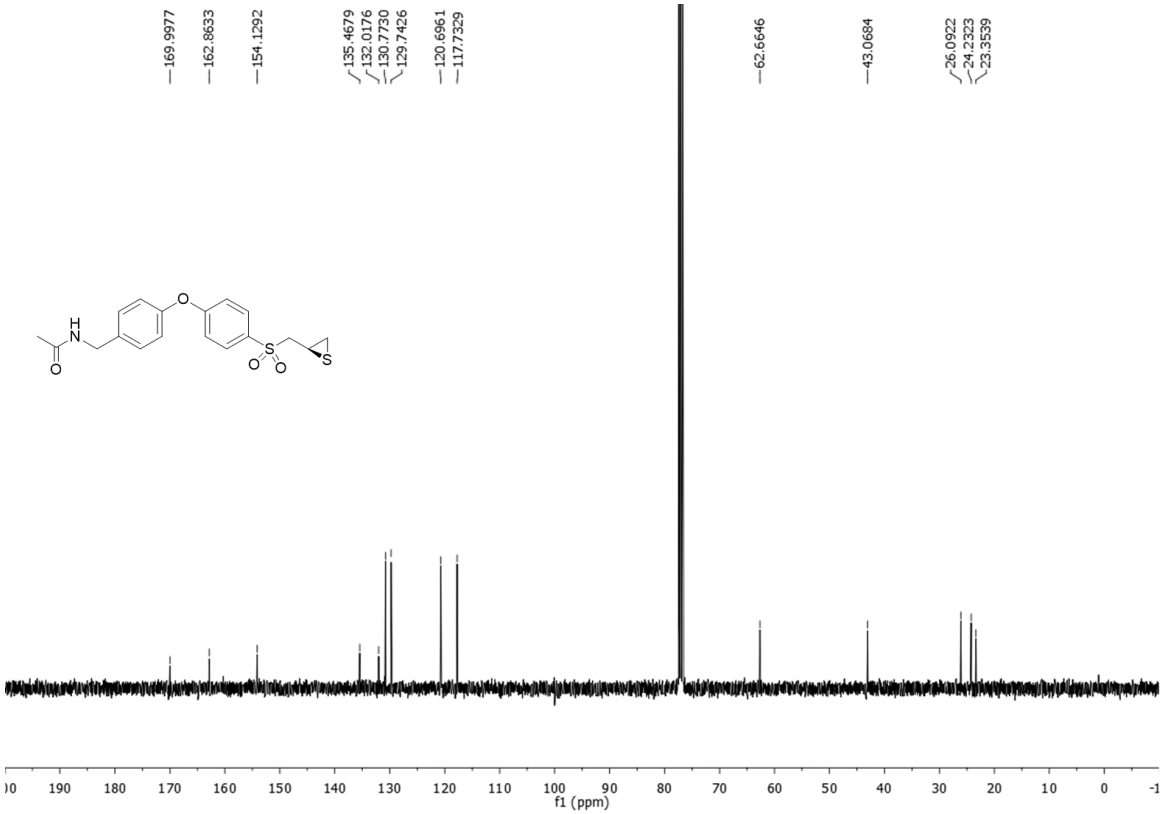


S-(4-(4-(((*tert*-Butoxycarbonyl)amino)methyl)phenoxy)phenyl) benzothioate (27, $C_{25}H_{25}NO_4S$). To a dry flask under an atmosphere of argon were added sequentially toluene (20 mL), CuI (15 mg, 0.08 mmol), 1,10-phenanthroline (29 mg, 0.16 mmol), **19c** (1.0 g, 2.35 mmol), thiobenzoic acid (663 g, 4.8 mmol), and DIPEA (1.033 g, 8 mmol). The reaction mixture was stirred at 100 °C overnight, at which time the reaction had reached completion. The mixture was cooled to room temperature and filtered through Celite. The Celite plug was washed with toluene. The combined toluene portion was evaporated to dryness. The residue was purified by silica-gel chromatography (8:2 hexanes/EtOAc) to give **27** as an off-white solid (1.13 g, 2.59 mmol, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, J = 8.3, 1.2 Hz, 2H), 7.55 (tt, J = 7.4, 1.2 Hz, 1H), 7.43 (d, J = 7.9 Hz, 2H), 7.37 (tt, J = 8.8, 2.9 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 6.97 (tt, J = 8.7, 2.8 Hz, 4H), 4.79 (br s, 1H), 4.25 (d, J = 5.6 Hz, 2H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.67, 159.01, 155.89, 155.36, 136.78, 136.55, 133.72, 129.11, 128.79, 127.50, 120.62, 119.96, 118.86, 44.12, 28.44; HRMS (ESI$^+$) *m/z* calcd for $C_{25}H_{25}NNaO_4S$ $(M+H)^+$ 458.1396, found 458.1392.**S2. The ^{1}H and ^{13}C NMR Spectra of compounds**

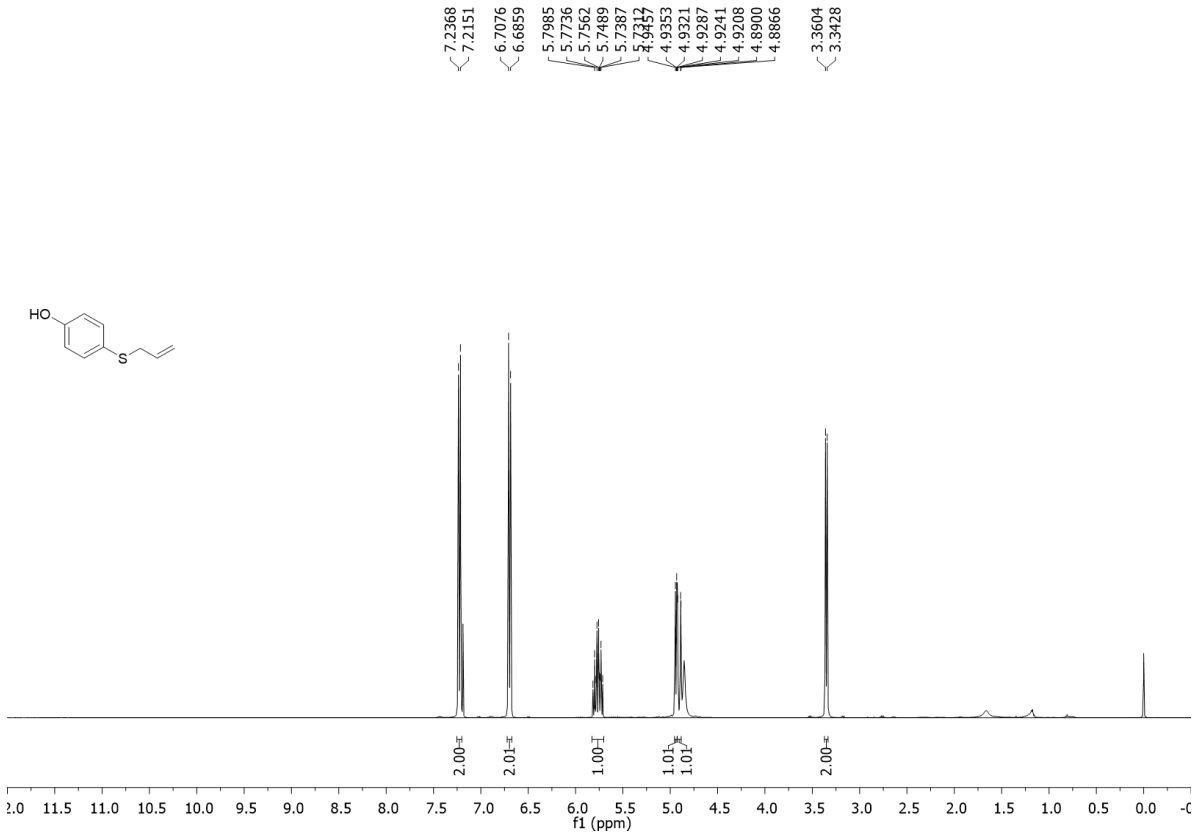
^{1}H NMR ($CDCl_3$) of (*R*)-*N*-(4-(4-((thiiran-2-ylmethyl)sulfonyl)phenoxy)benzyl)acetamide (9, M1)



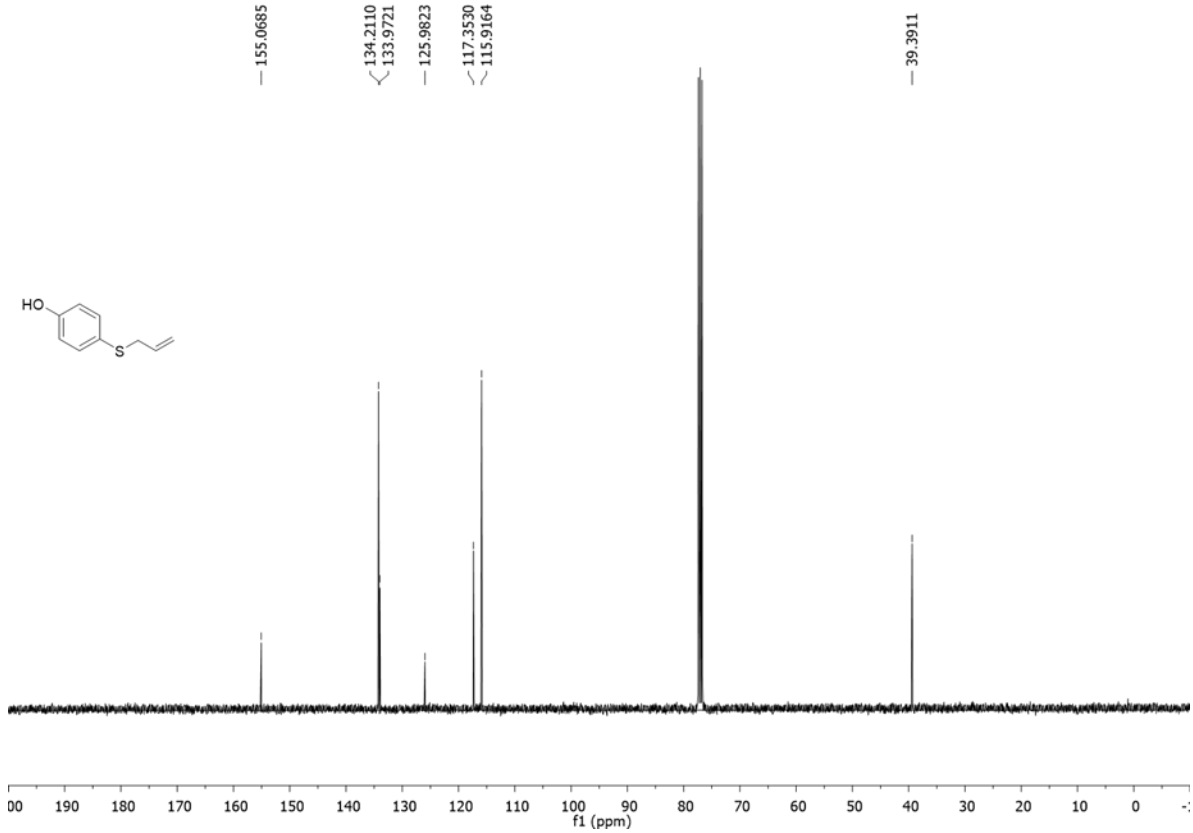
^{13}C NMR ($CDCl_3$) of (*R*)-*N*-(4-(4-((thiiran-2-ylmethyl)sulfonyl)phenoxy)benzyl)acetamide (9, M1)



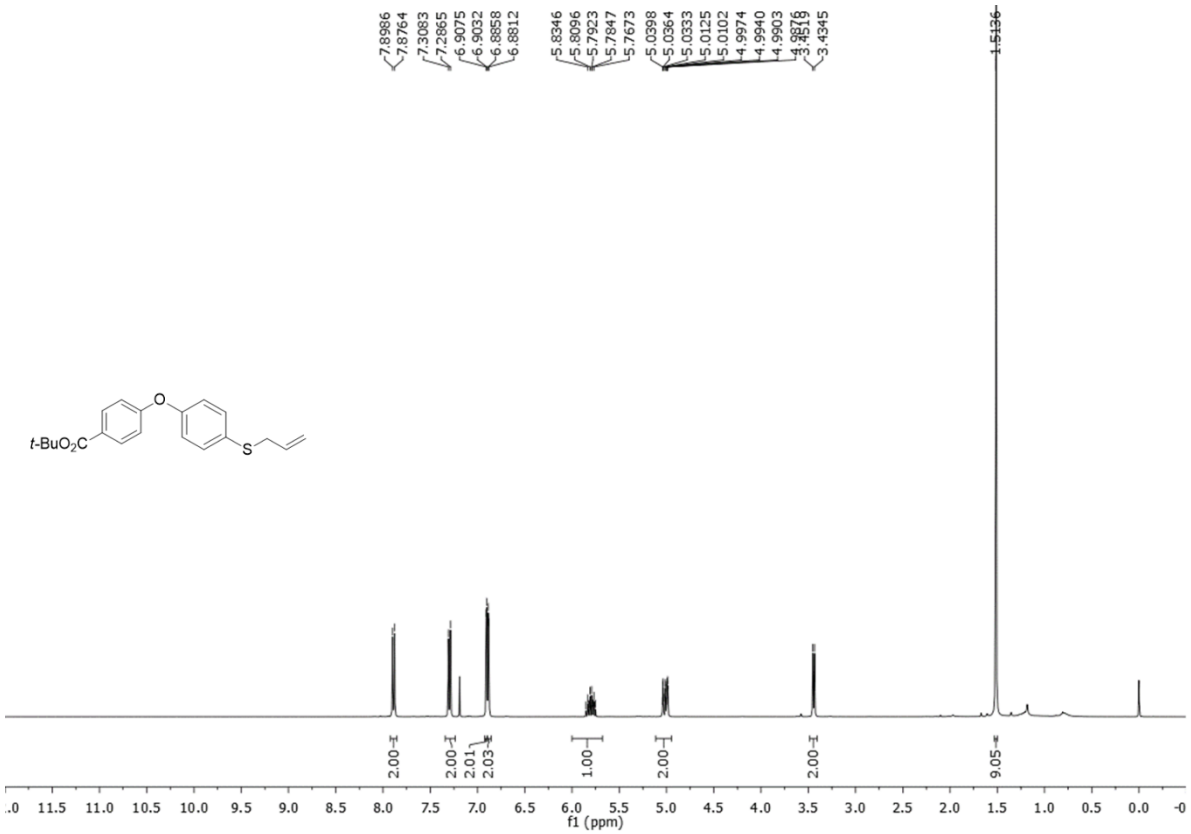
^{1}H NMR ($CDCl_3$) of 4-(Allylthio)phenol (14)



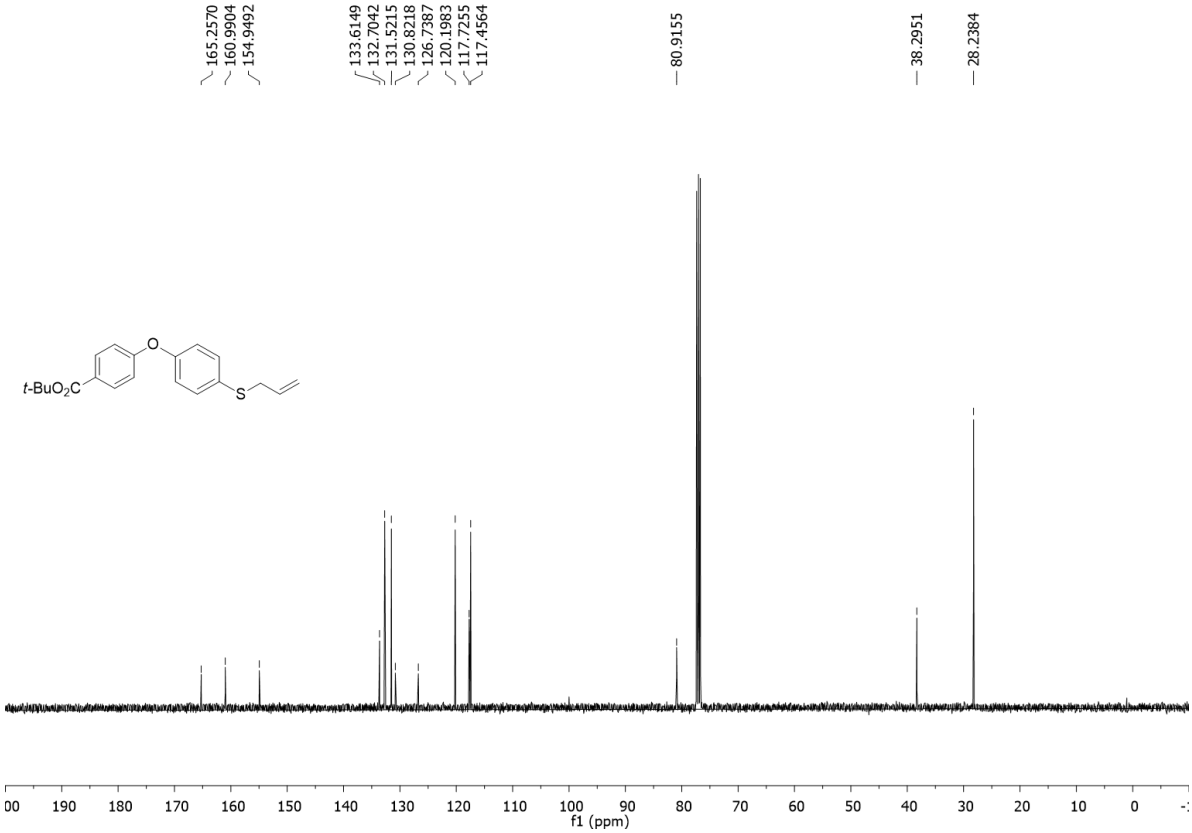
^{13}C NMR ($CDCl_3$) of 4-(Allylthio)phenol (14)



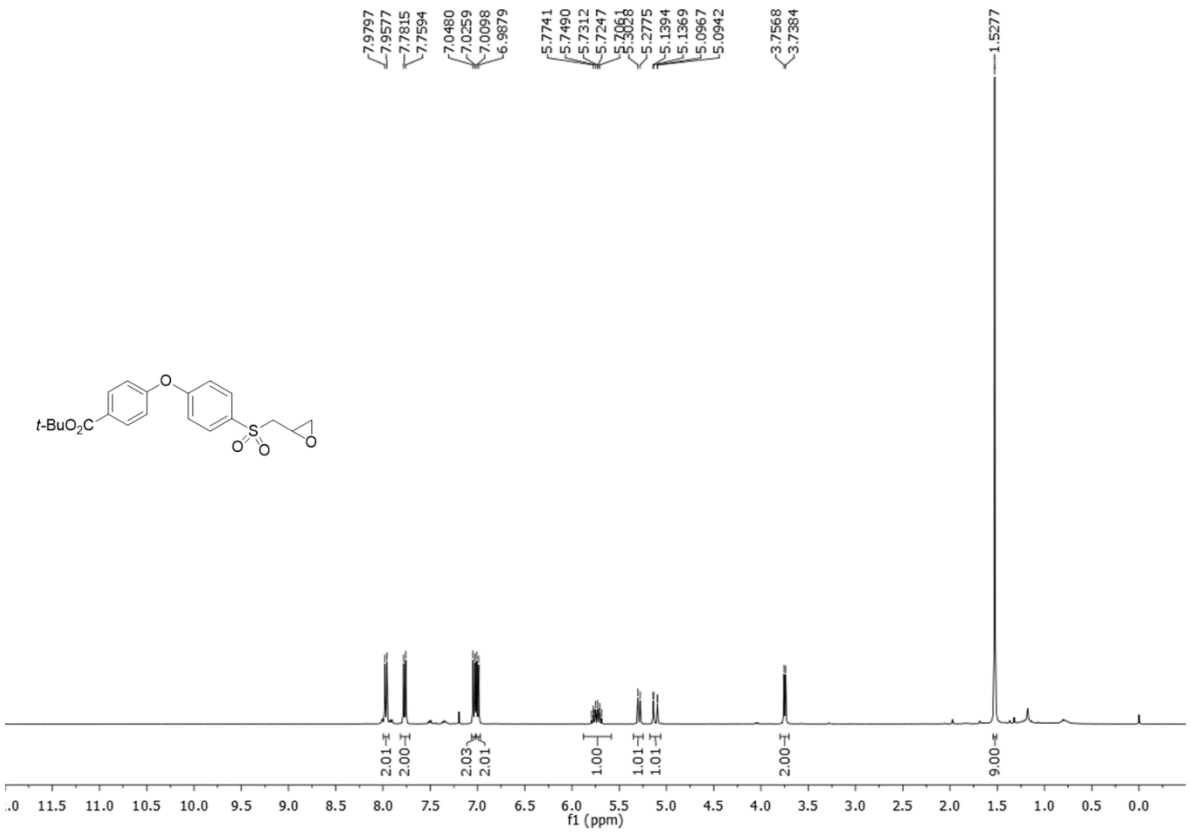
^{1}H NMR ($CDCl_3$) of *tert*-Butyl 4-(4-(allylthio)phenoxy)benzoate (15)



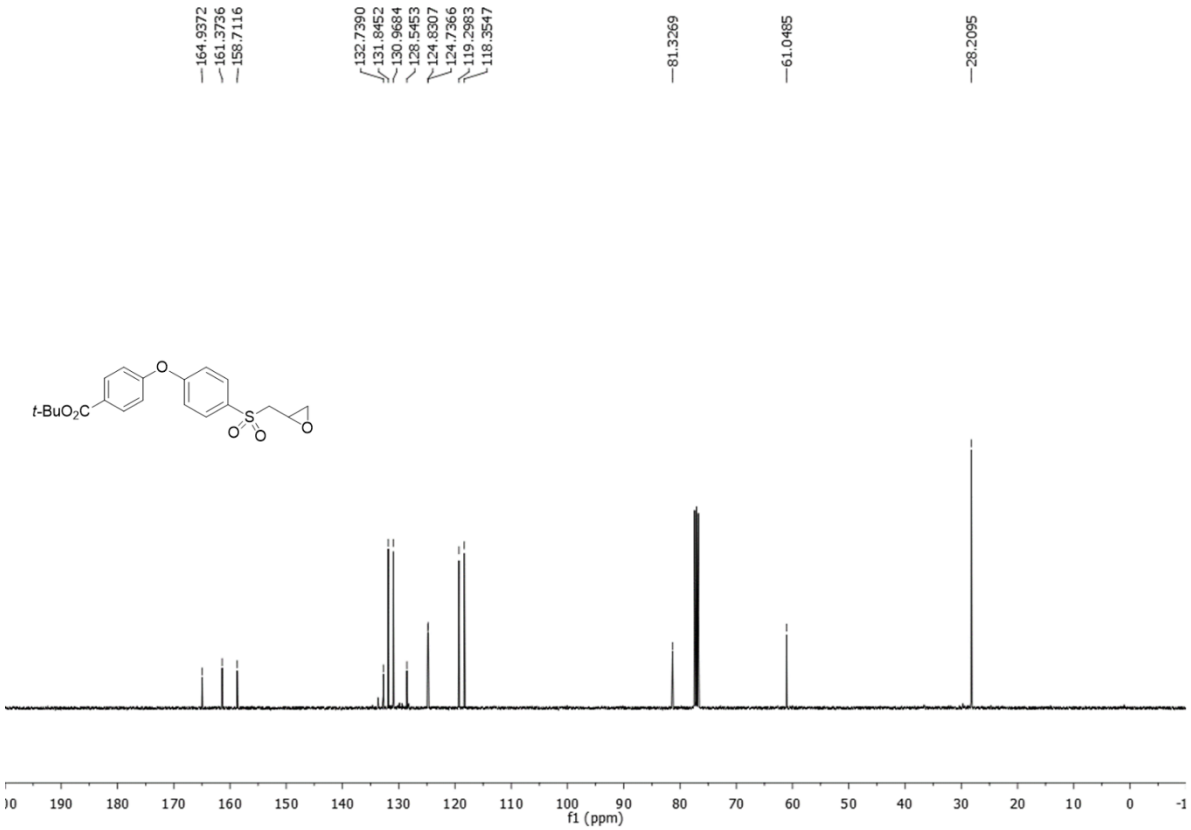
^{13}C NMR ($CDCl_3$) of *tert*-Butyl 4-(4-(allylthio)phenoxy)benzoate (15)



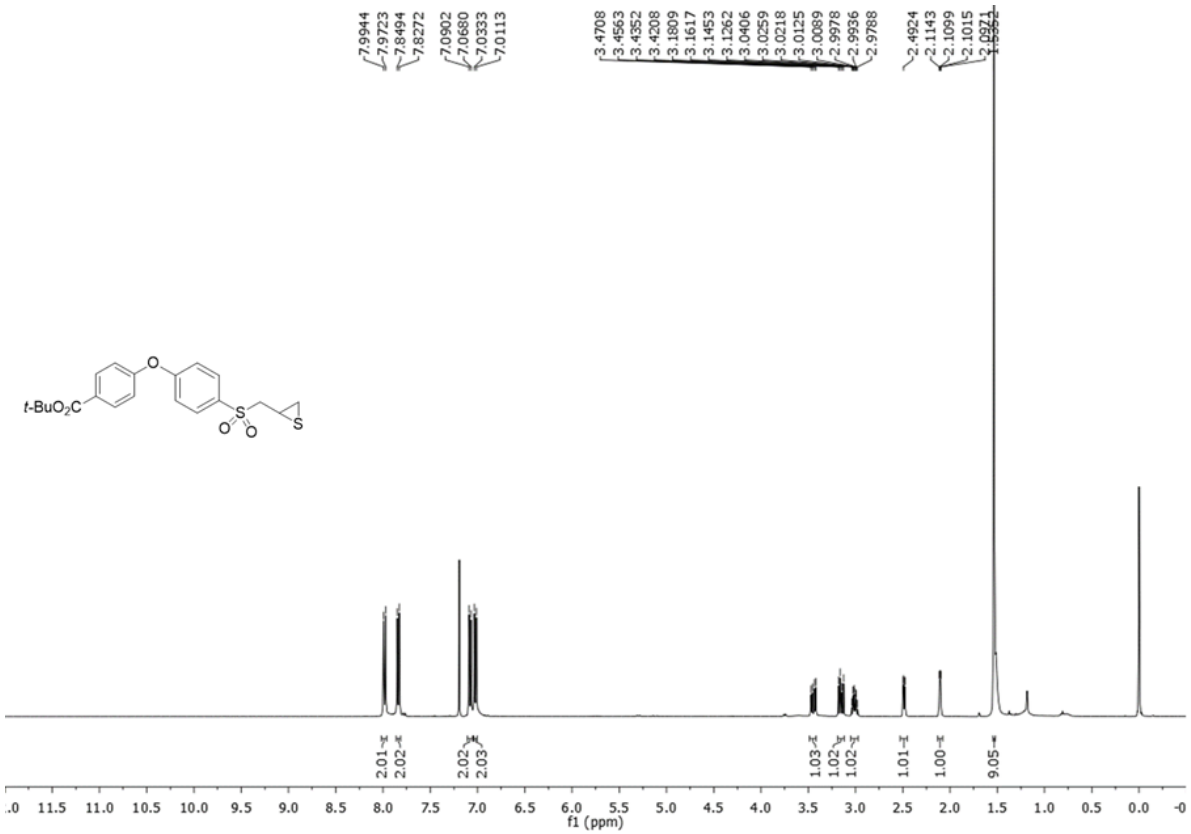
^{1}H NMR ($CDCl_3$) of *tert*-Butyl 4-(4-((oxiran-2-ylmethyl)sulfonyl)phenoxy)benzoate (16)



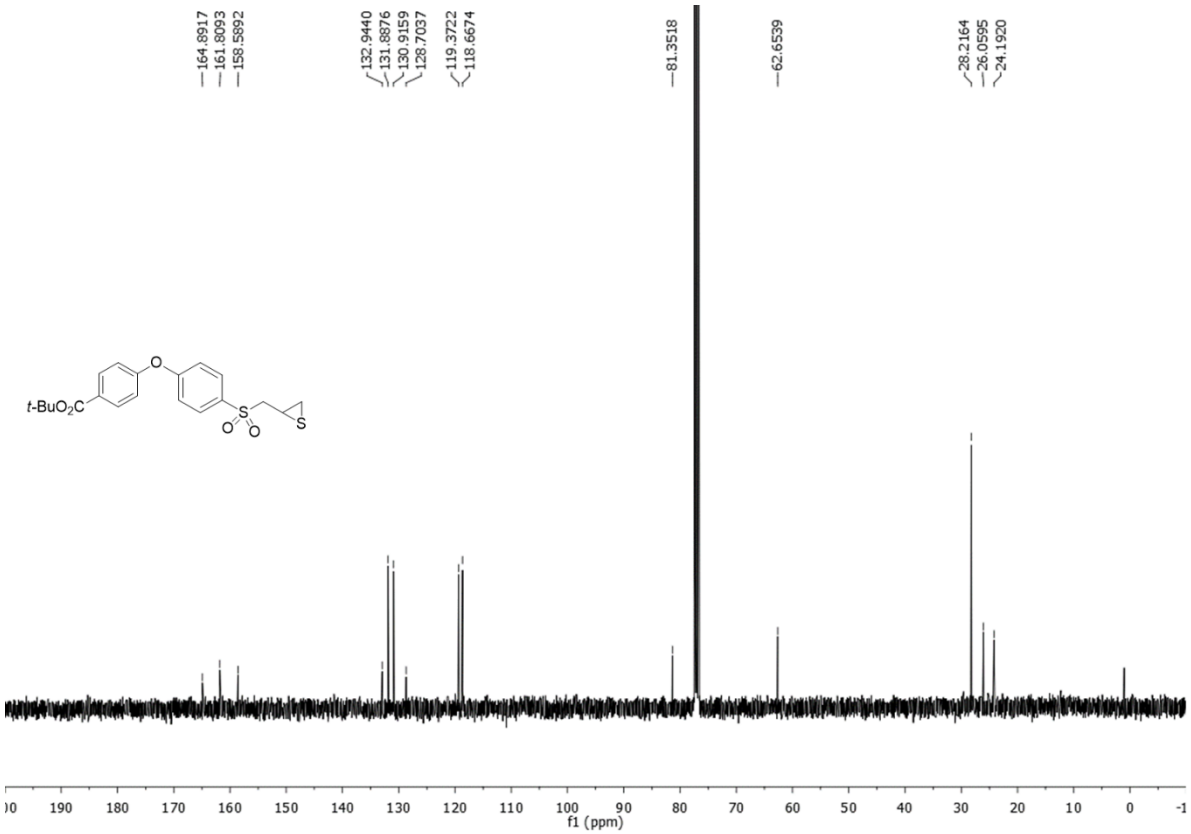
^{13}C NMR ($CDCl_3$) of *tert*-Butyl 4-(4-((oxiran-2-ylmethyl)sulfonyl)phenoxy)benzoate (16)



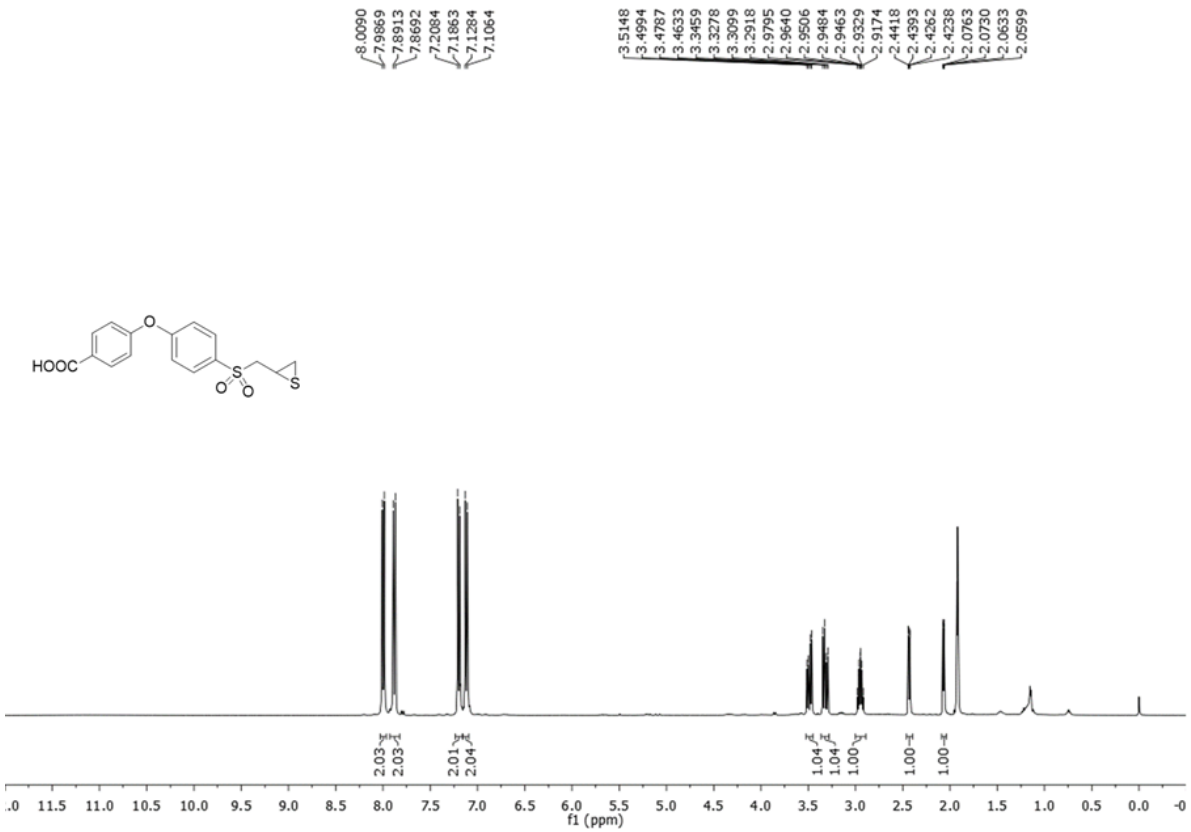
^{1}H NMR ($CDCl_3$) of *tert*-Butyl 4-(4-((thiiran-2-ylmethyl)sulfonyl)phenoxy)benzoate (17)



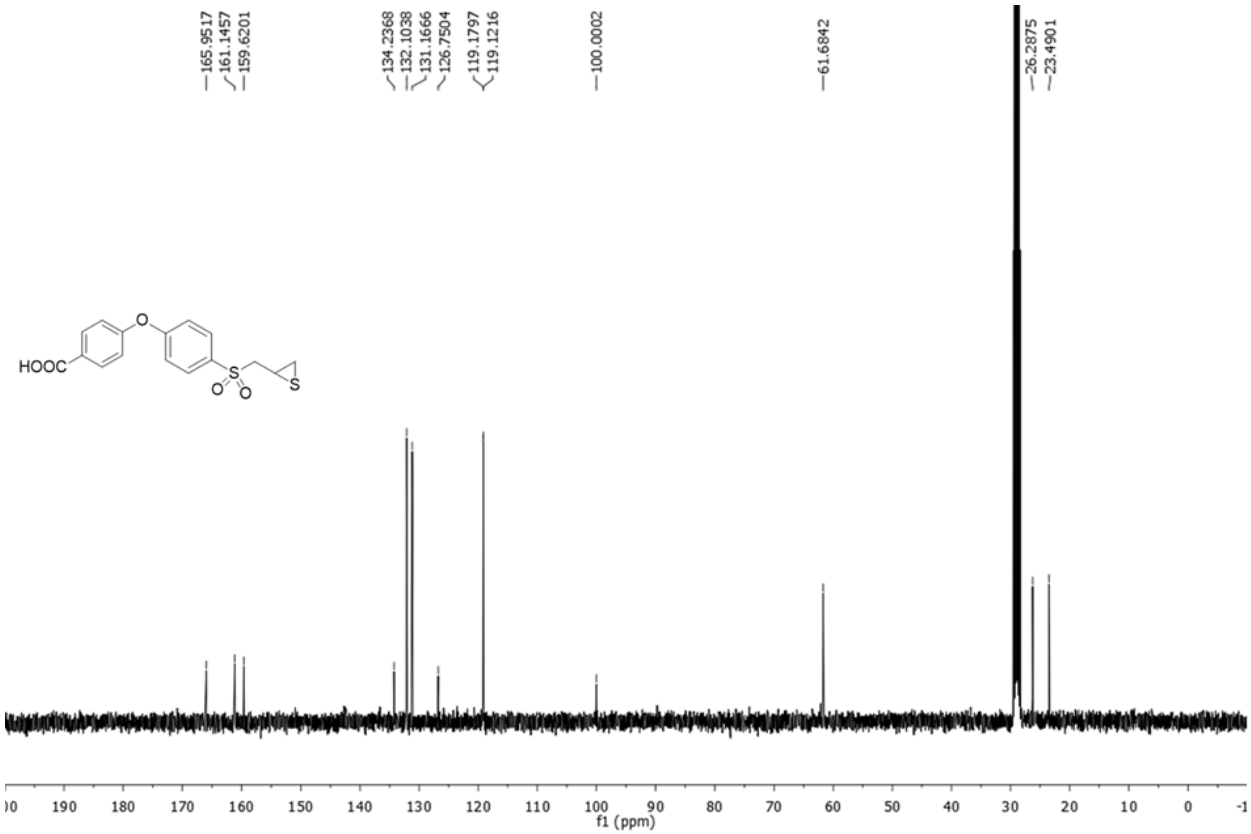
^{13}C NMR ($CDCl_3$) of *tert*-Butyl 4-(4-((thiiran-2-ylmethyl)sulfonyl)phenoxy)benzoate (17)



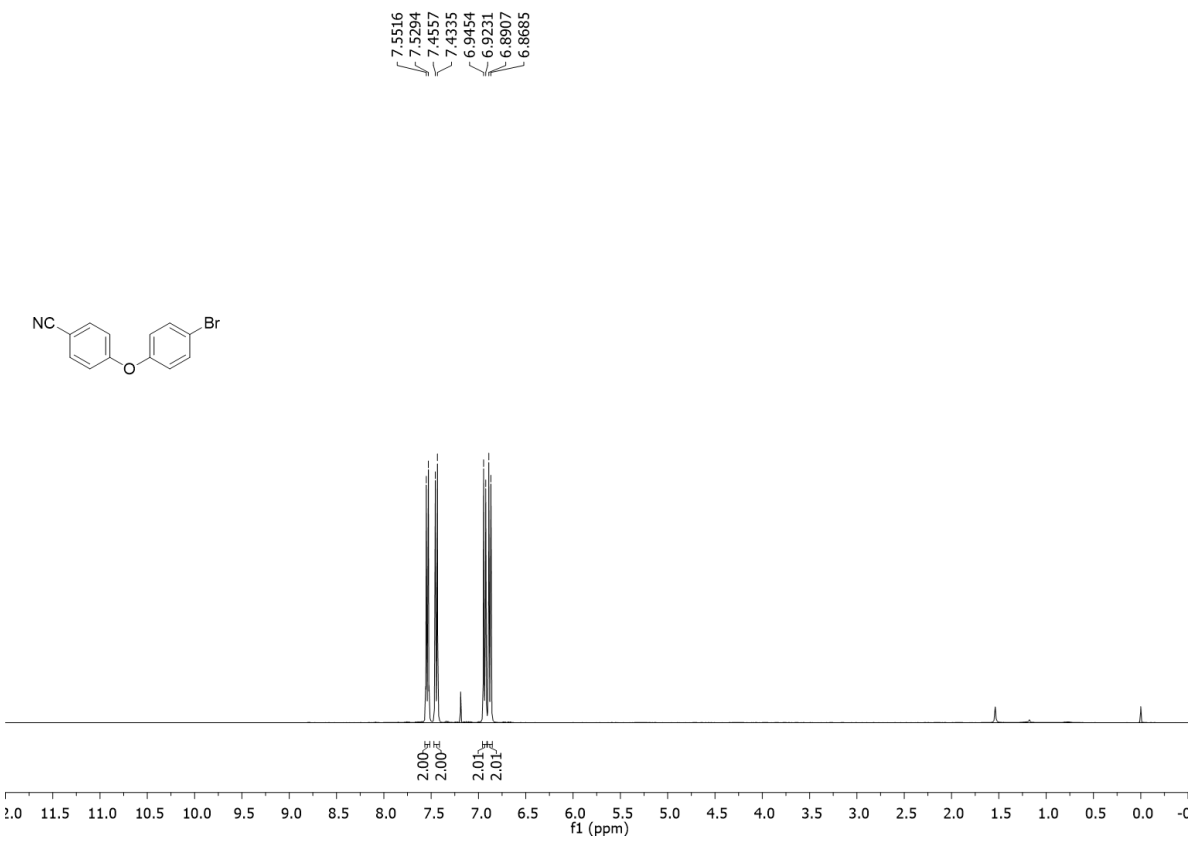
^{1}H NMR ($CDCl_3$) of 4-(4-((Thiiran-2-ylmethyl)sulfonyl)phenoxy)benzoic acid (7, M3)



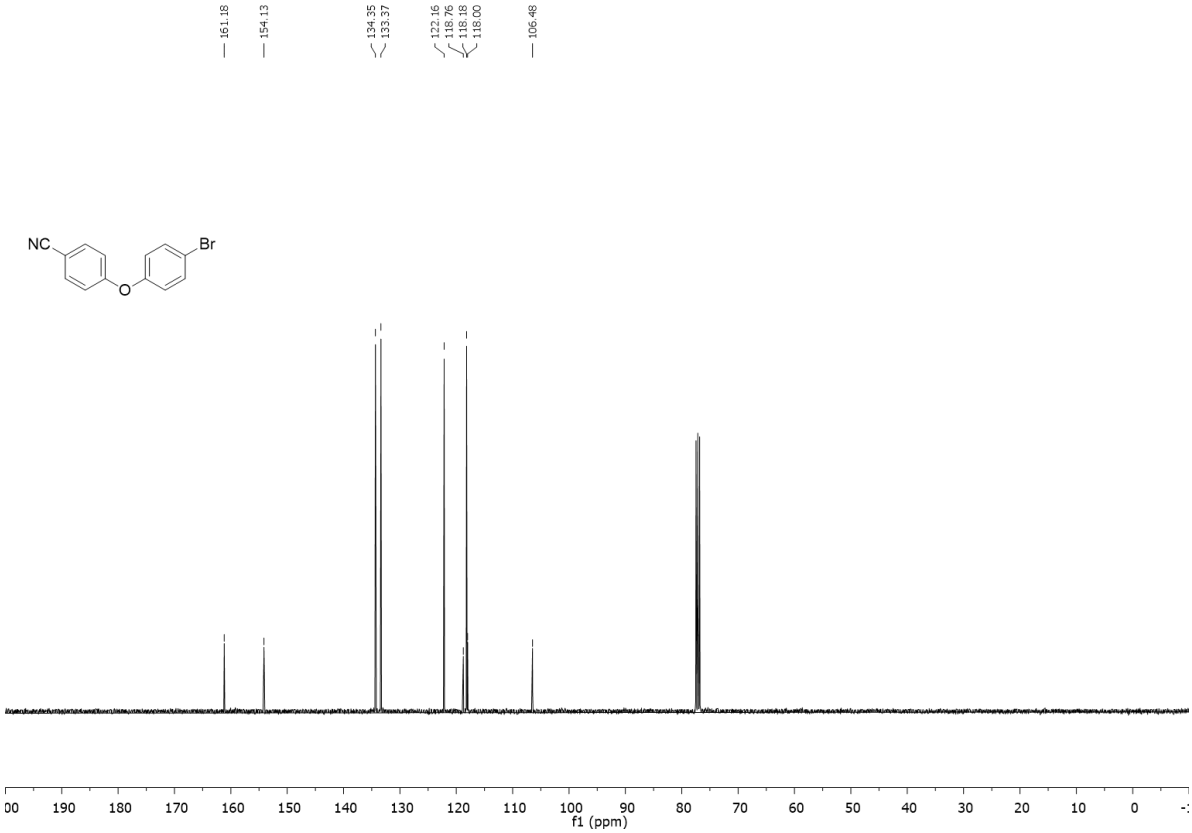
^{13}C NMR ($CDCl_3$) of 4-(4-((Thiiran-2-ylmethyl)sulfonyl)phenoxy)benzoic acid (7, M3)



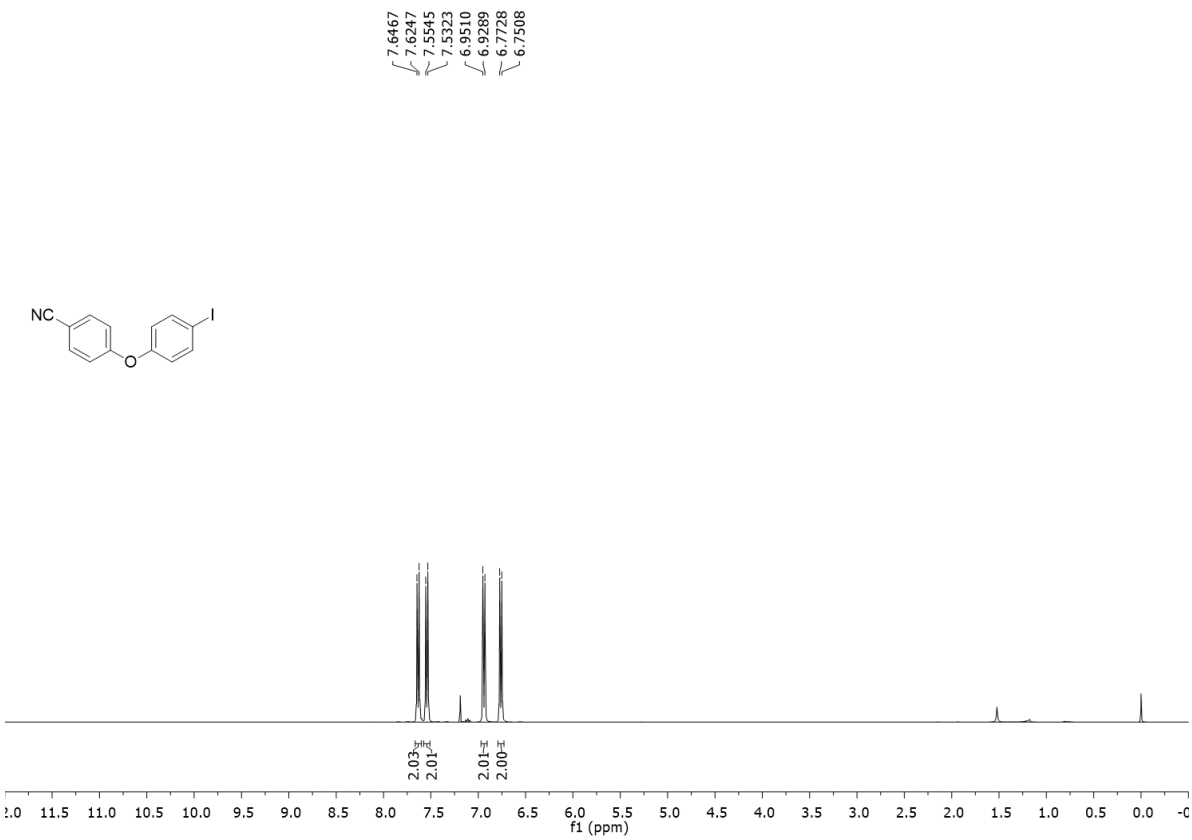
^{1}H NMR ($CDCl_3$) of 4-(4-Bromophenoxy)benzonitrile (18a)



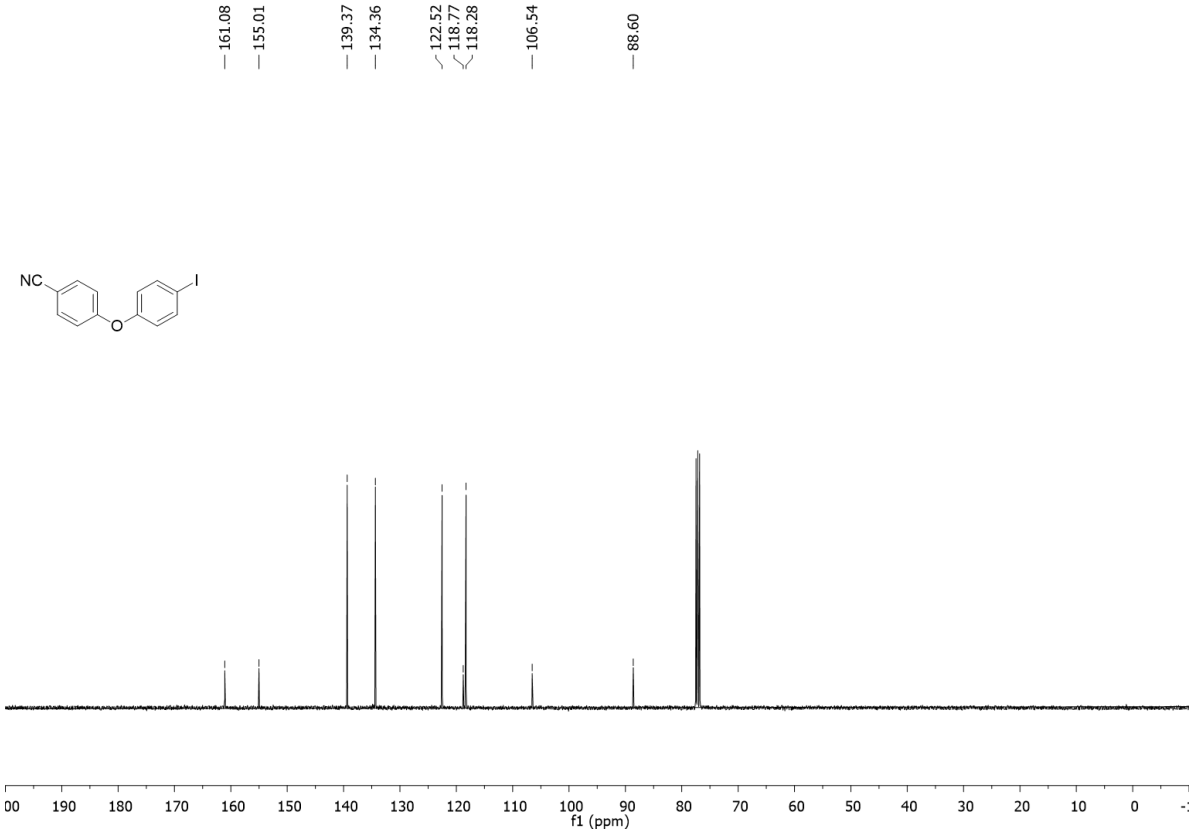
^{13}C NMR ($CDCl_3$) of 4-(4-Bromophenoxy)benzonitrile (18a)



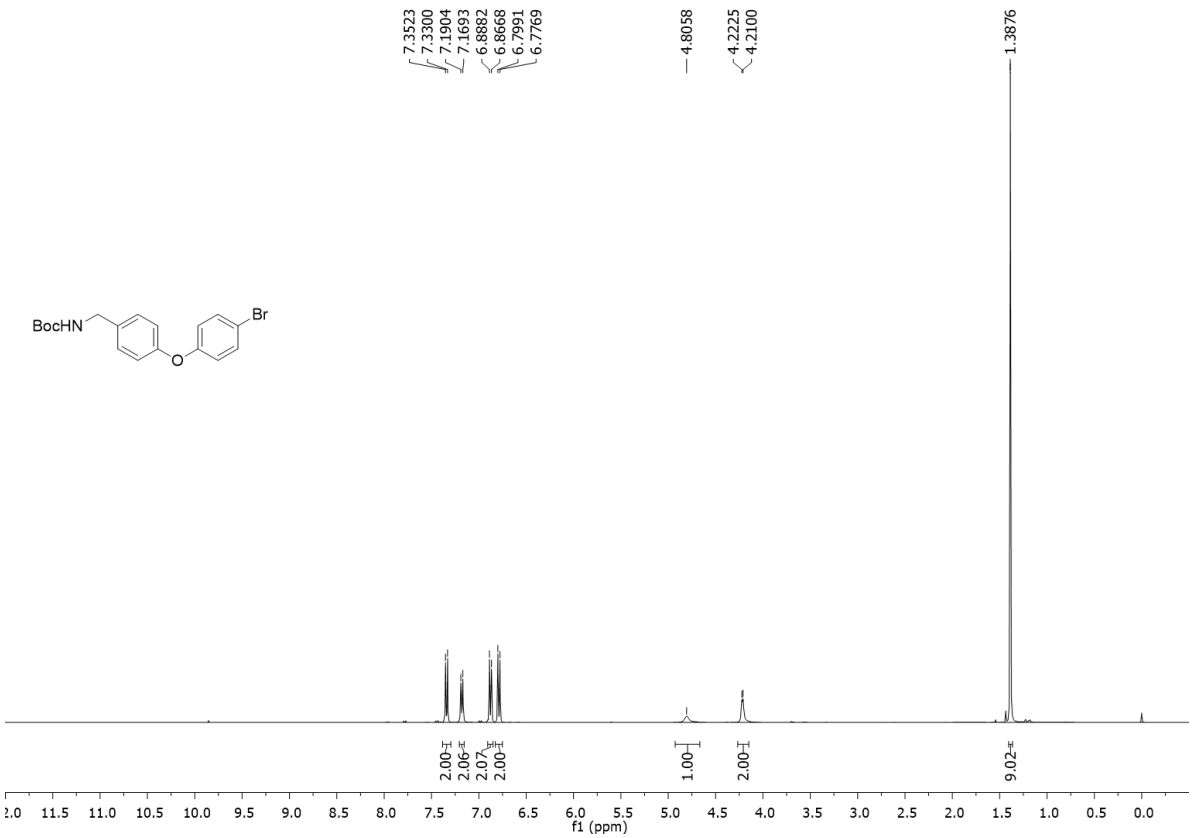
^{1}H NMR ($CDCl_3$) of 4-(4-Iodophenoxy)benzonitrile (18b)



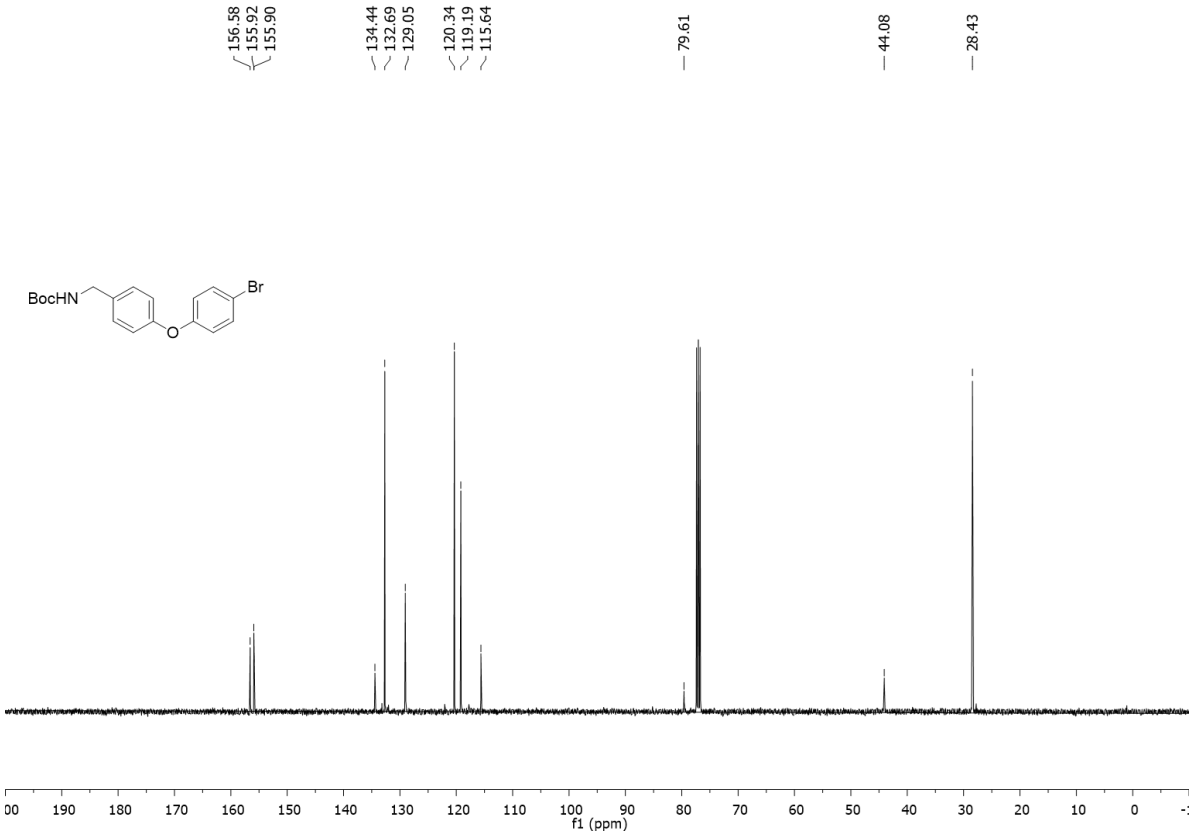
^{13}C NMR ($CDCl_3$) of 4-(4-Iodophenoxy)benzonitrile (18b)



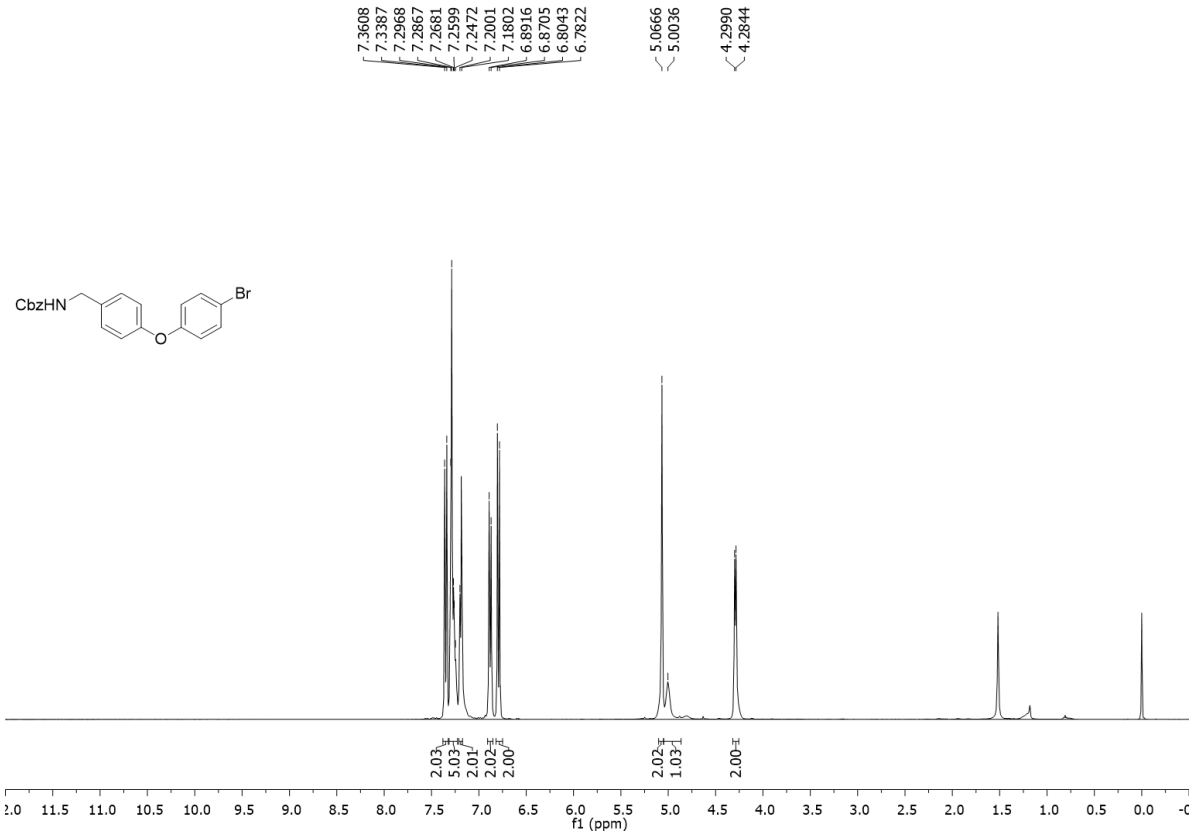
^{1}H NMR ($CDCl_3$) of *tert*-Butyl 4-(4-bromophenoxy)benzylcarbamate (19a)



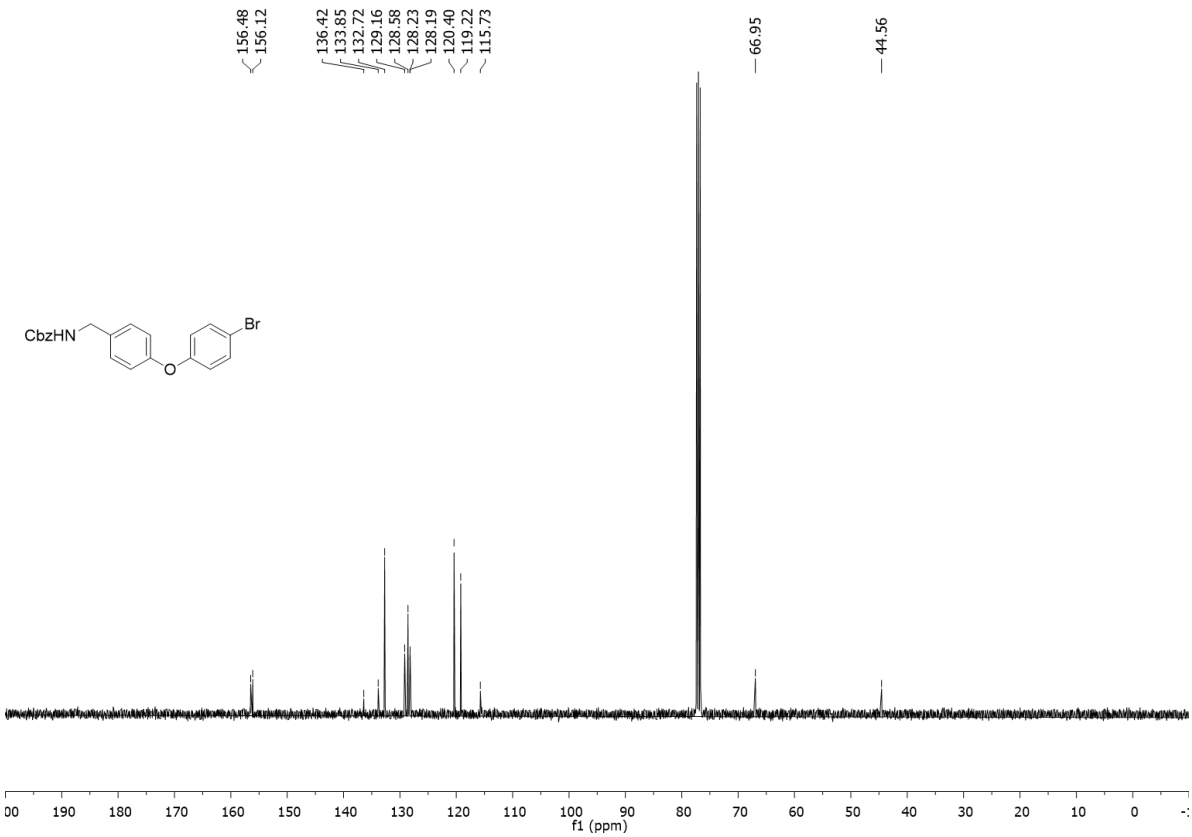
^{13}C NMR ($CDCl_3$) of *tert*-Butyl 4-(4-bromophenoxy)benzylcarbamate (19a)



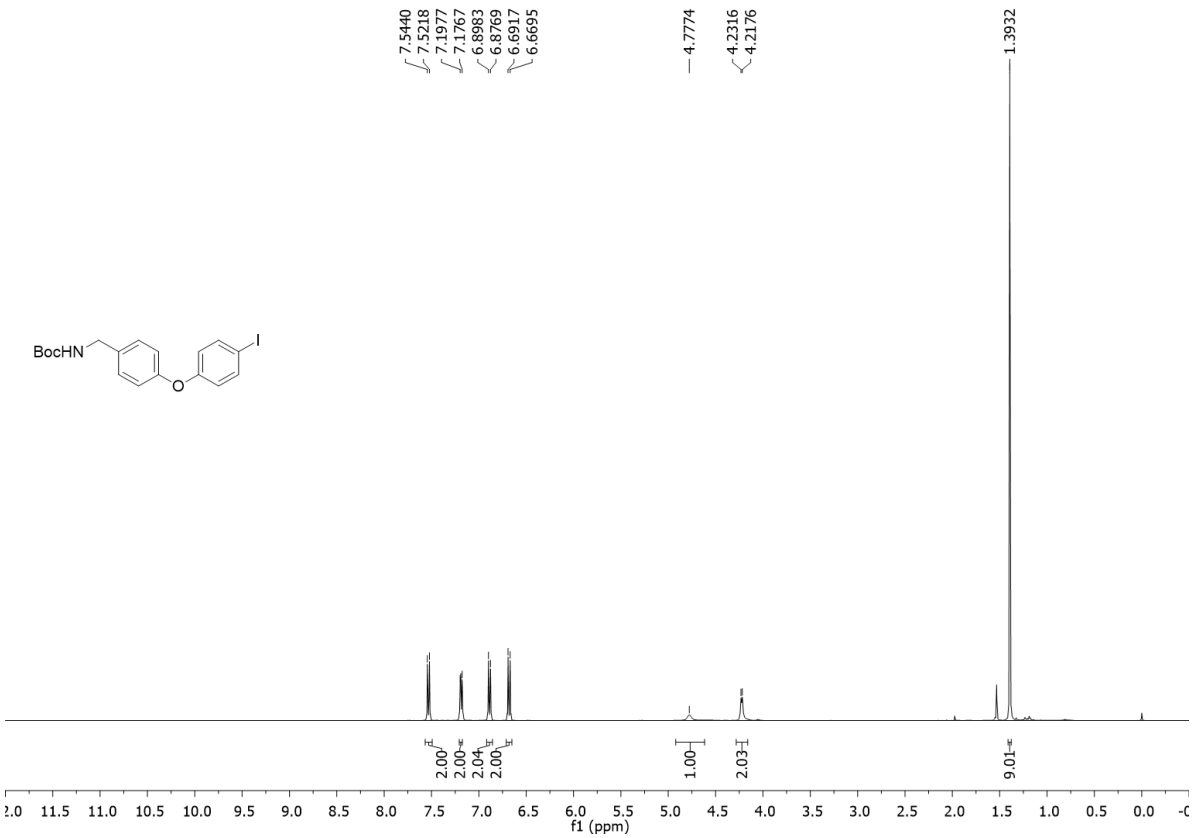
^{1}H NMR ($CDCl_3$) of Benzyl 4-(4-bromophenoxy)benzylcarbamate (19b)



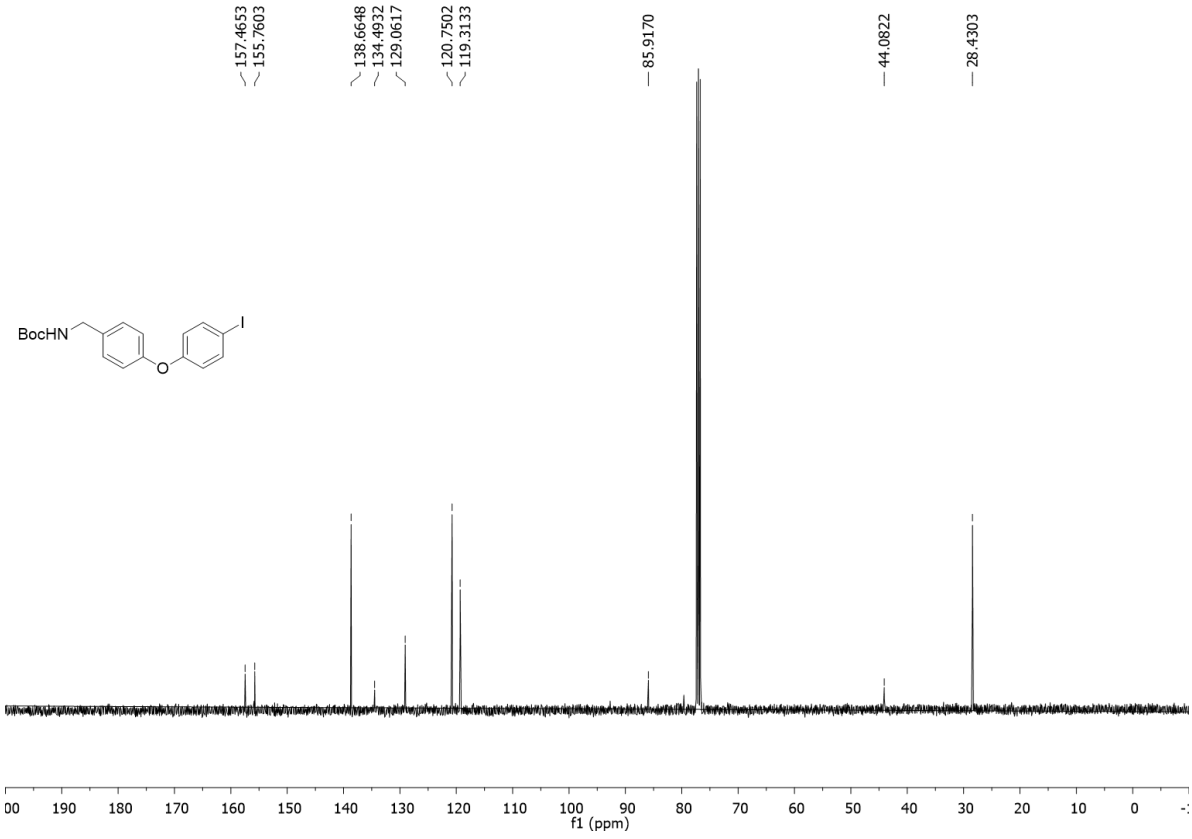
^{13}C NMR ($CDCl_3$) of Benzyl 4-(4-bromophenoxy)benzylcarbamate (19b)



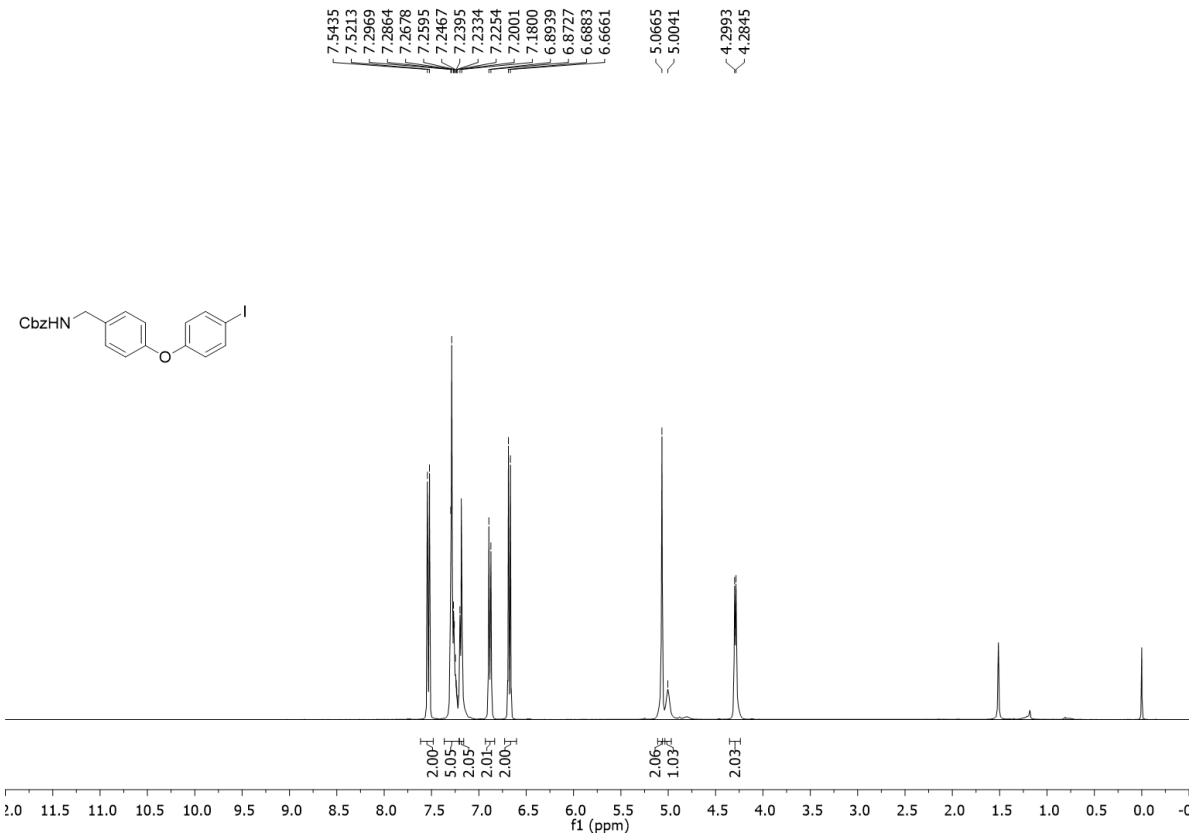
^{1}H NMR ($CDCl_3$) of *tert*-Butyl 4-(4-iodophenoxy)benzylcarbamate (19c)



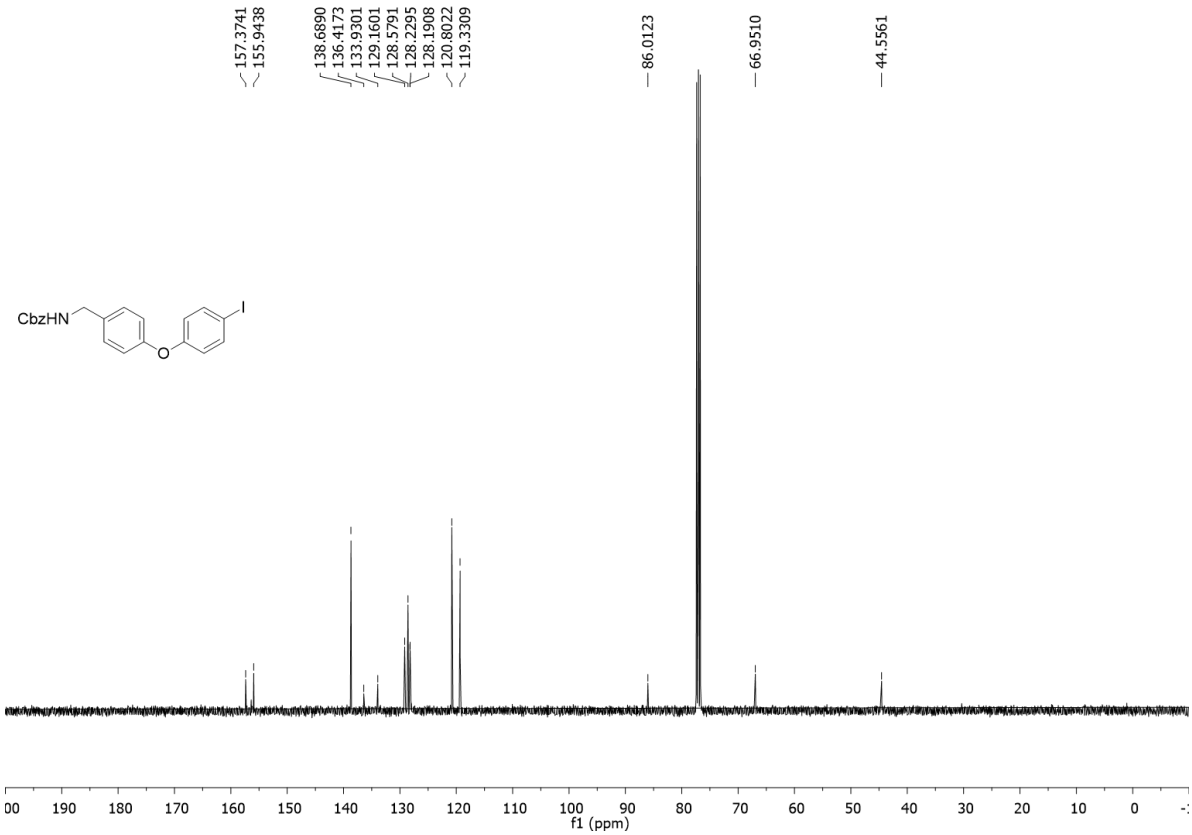
^{13}C NMR ($CDCl_3$) of *tert*-Butyl 4-(4-iodophenoxy)benzylcarbamate (19c)



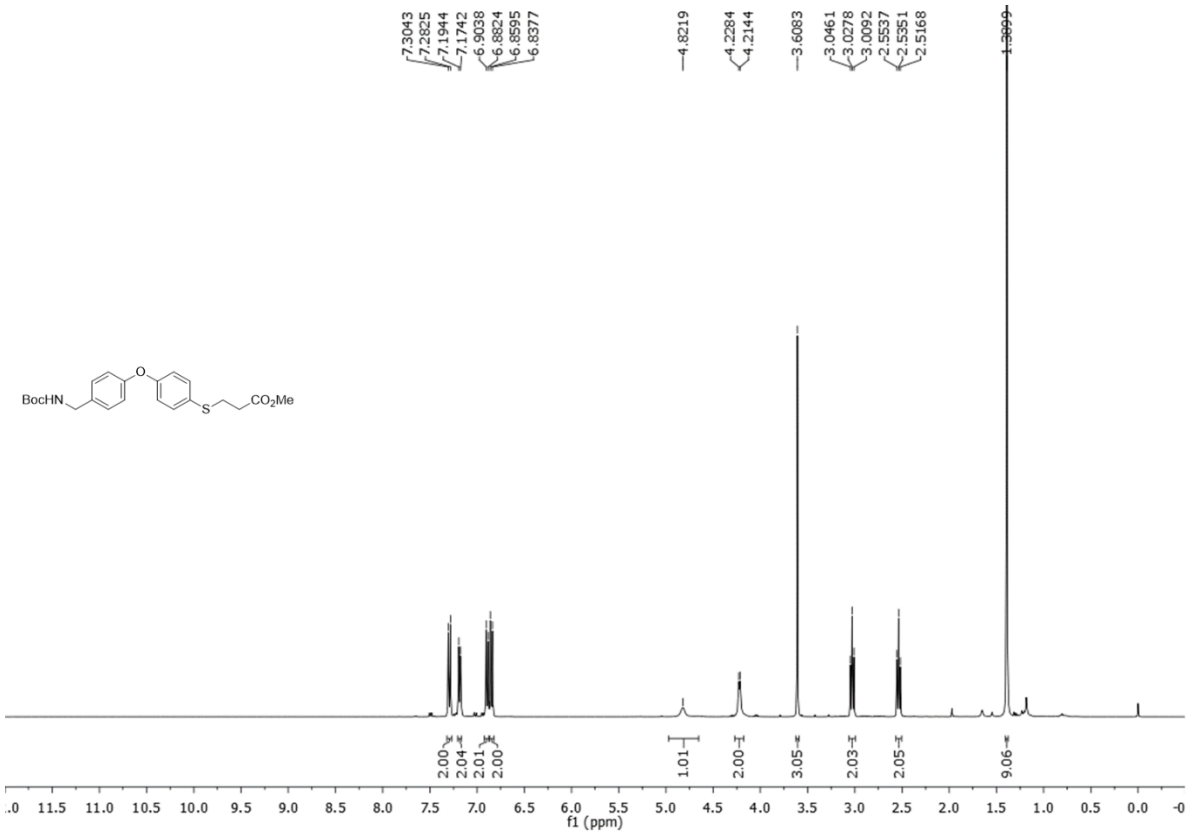
^{1}H NMR ($CDCl_3$) of Benzyl 4-(4-iodophenoxy)benzylcarbamate (19d)



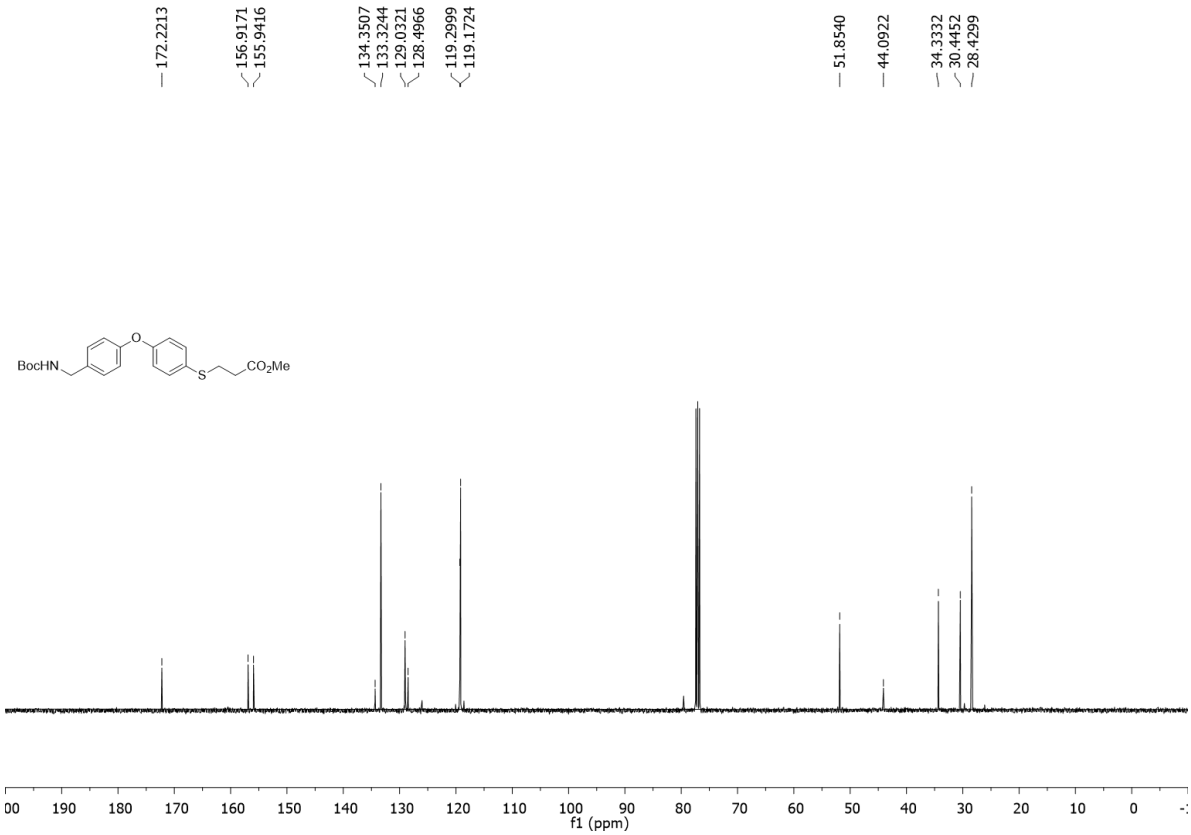
^{13}C NMR ($CDCl_3$) of Benzyl 4-(4-iodophenoxy)benzylcarbamate (19d)



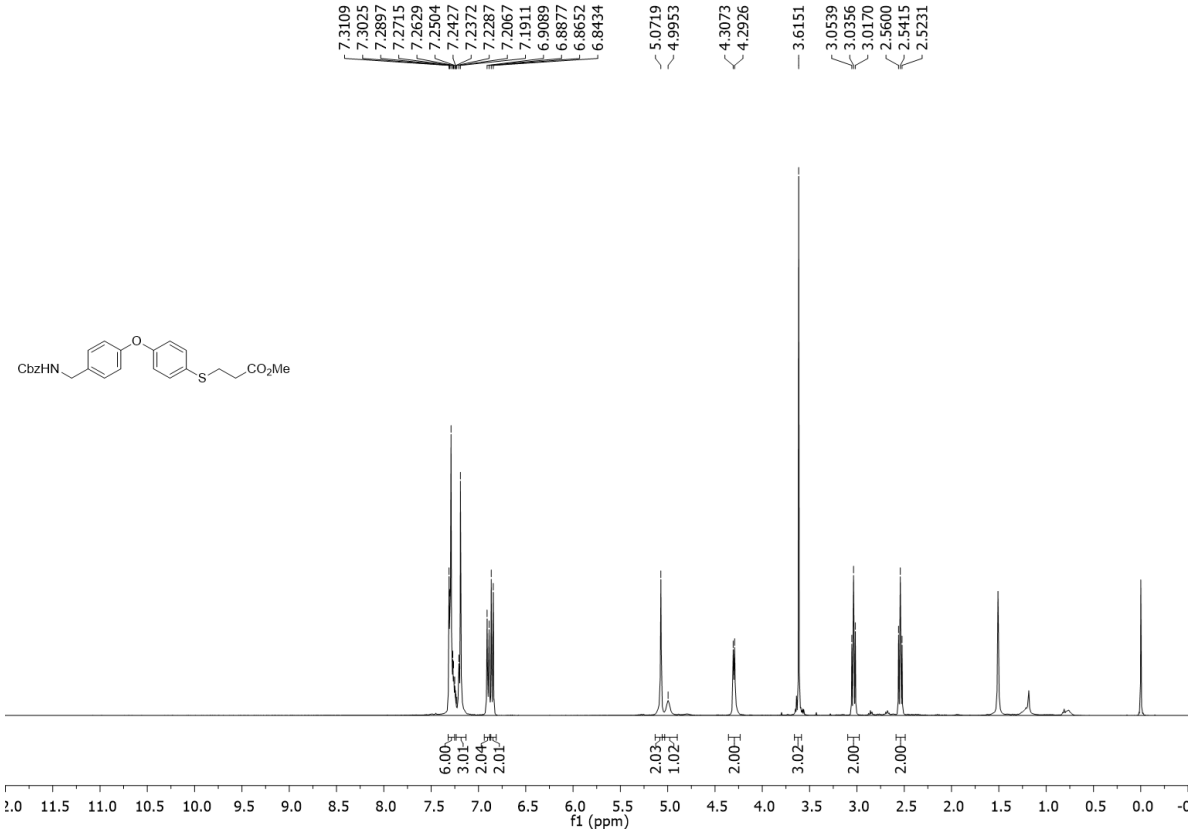
^{1}H NMR ($CDCl_3$) of Methyl 3-((4-(4-(((*tert*-butoxycarbonyl)amino)methyl)phenoxy)phenyl)thio)propanoate (20a)



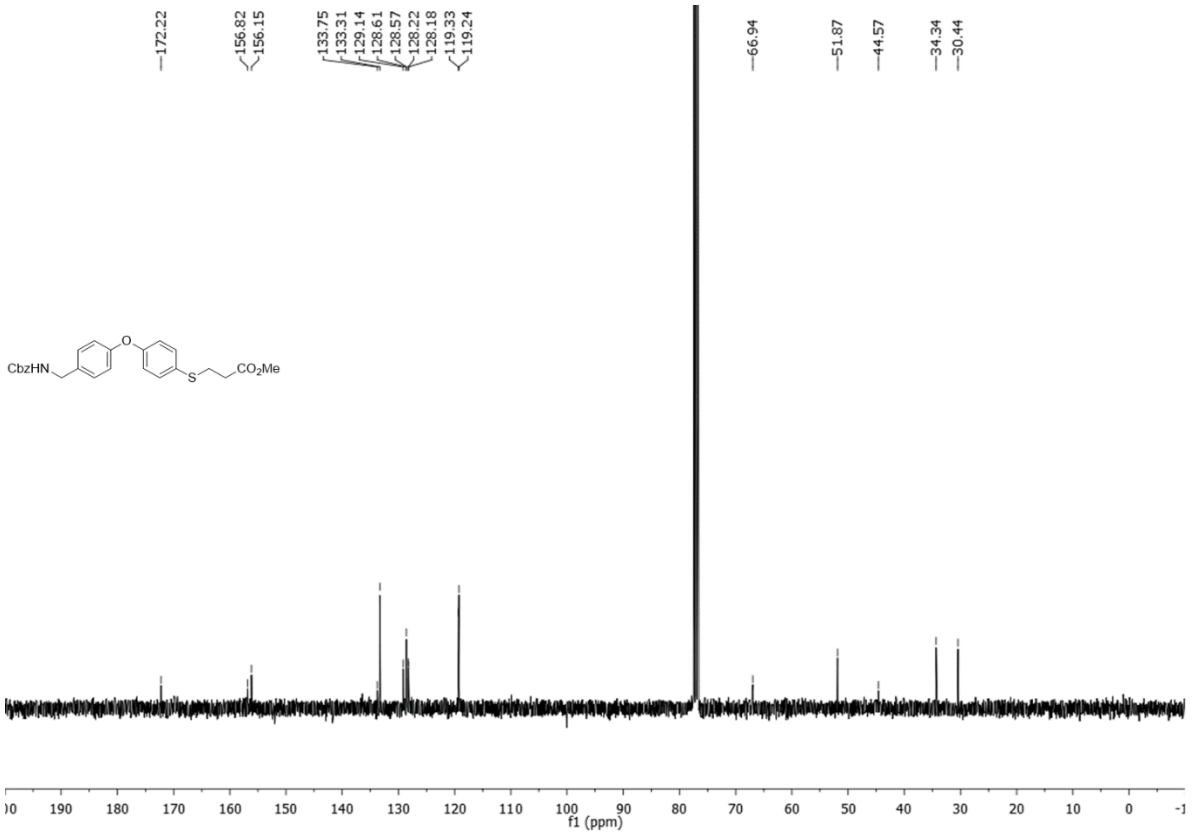
^{13}C NMR ($CDCl_3$) of Methyl 3-((4-(4-(((*tert*-butoxycarbonyl)amino)methyl)phenoxy)phenyl)thio)propanoate (20a)



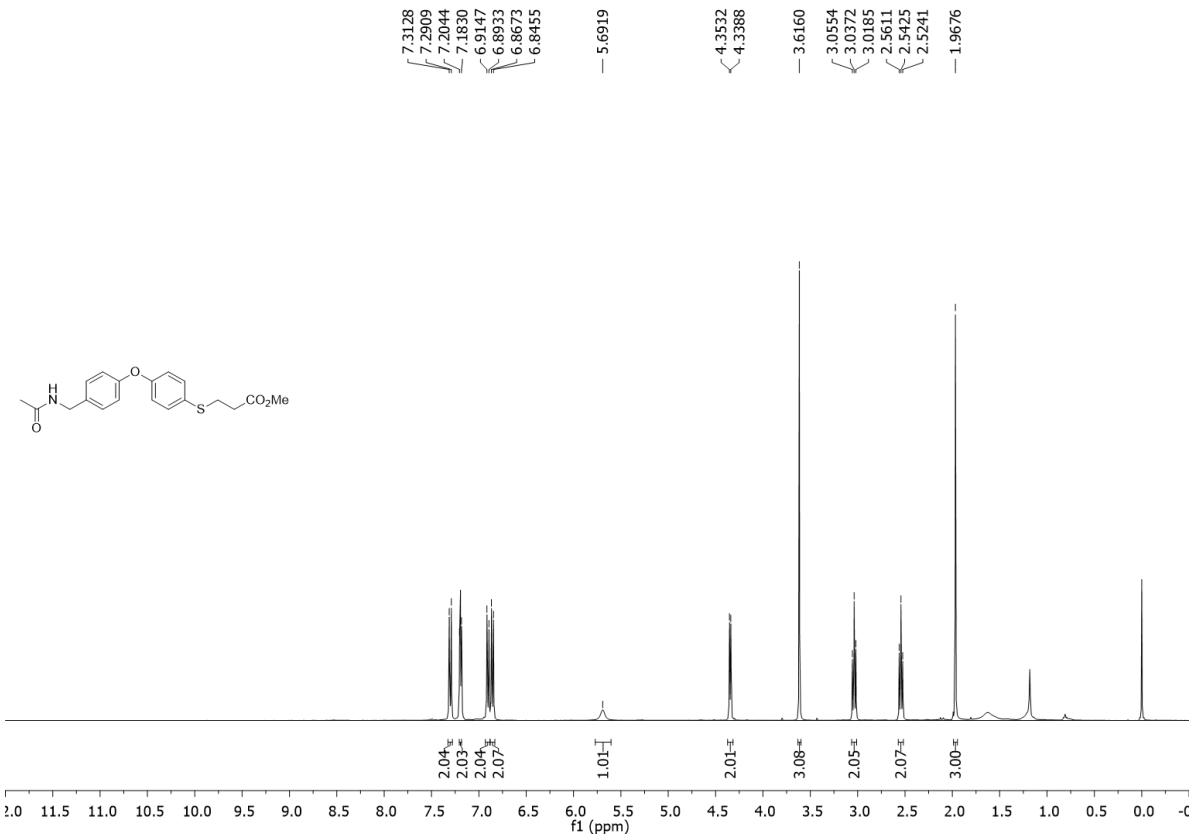
^{1}H NMR ($CDCl_3$) of Methyl 3-((4-(4-((((benzyloxy)carbonyl)amino)methyl)phenoxy)phenyl)thio)propanoate (20b)



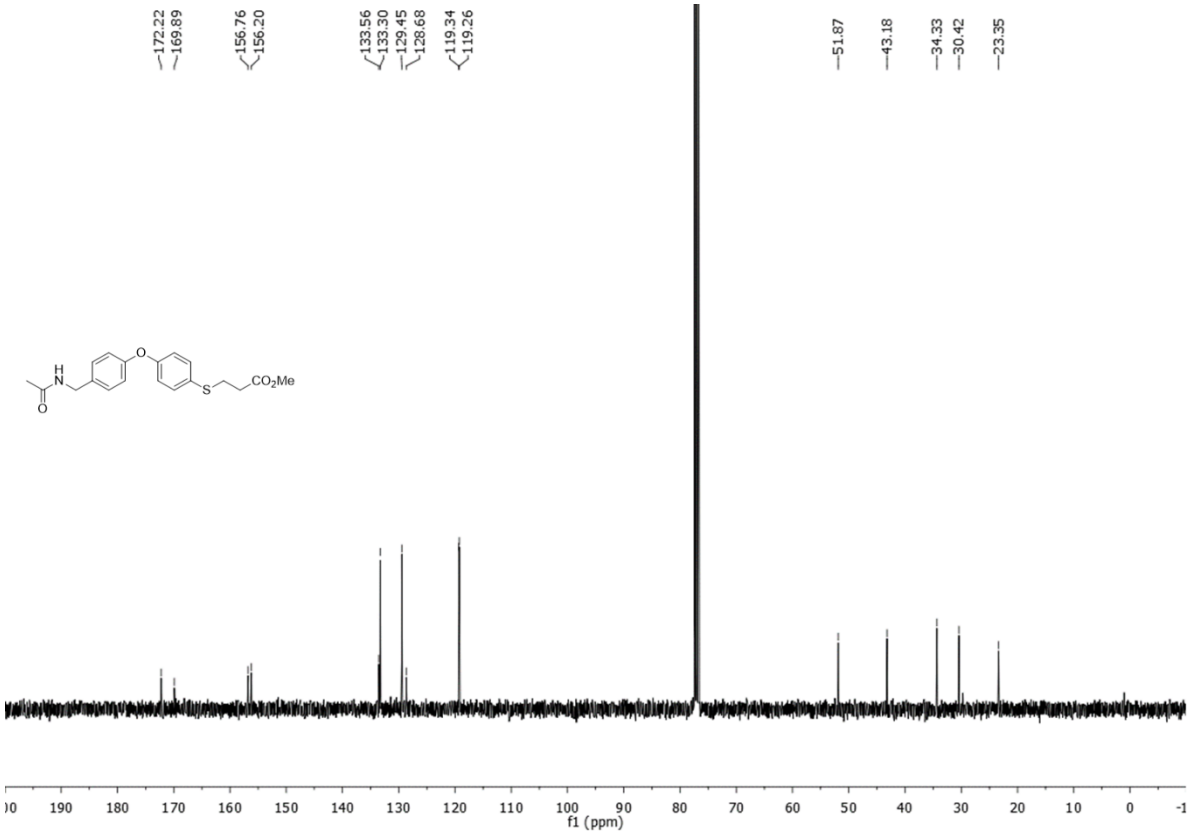
^{13}C NMR ($CDCl_3$) of Methyl 3-((4-(4-((((benzyloxy)carbonyl)amino)methyl)phenoxy)phenyl)thio)propanoate (20b)



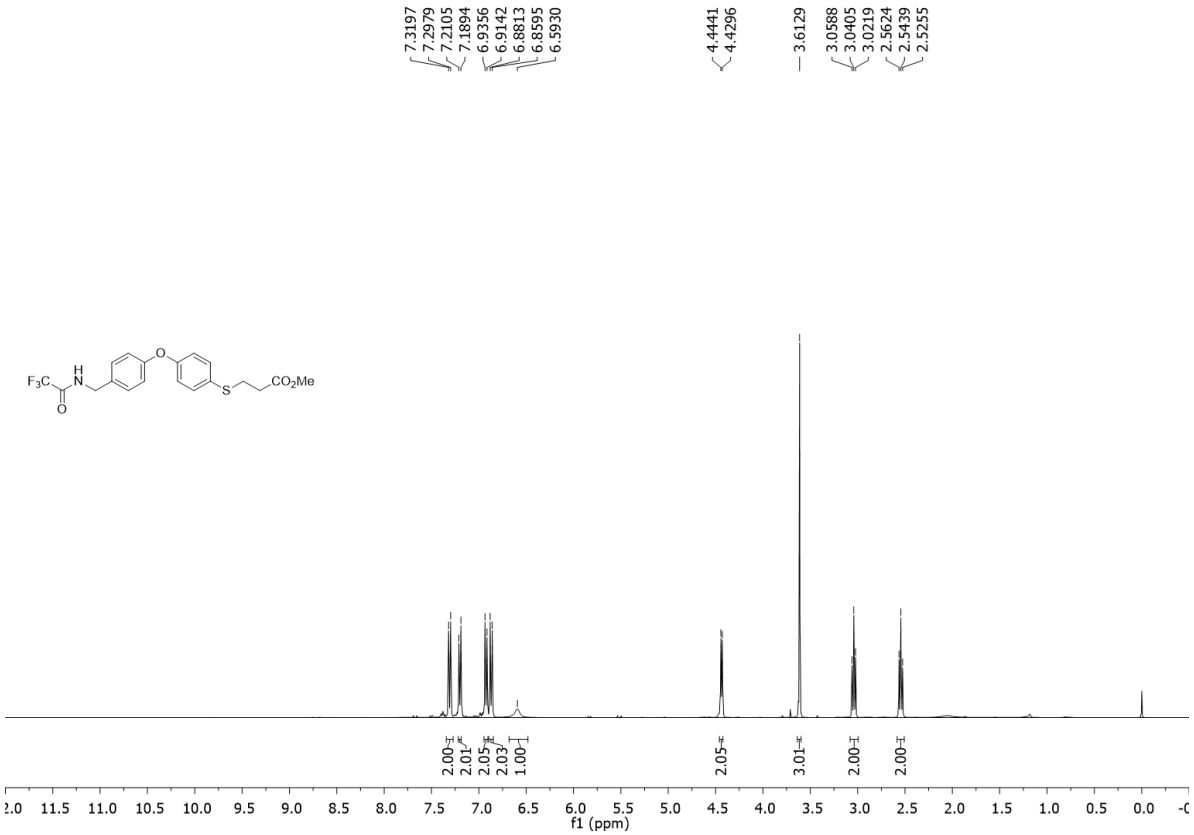
^{1}H NMR ($CDCl_3$) of Methyl 3-((4-(4-(acetamidomethyl)phenoxy)phenyl)thio)propanoate (21a)



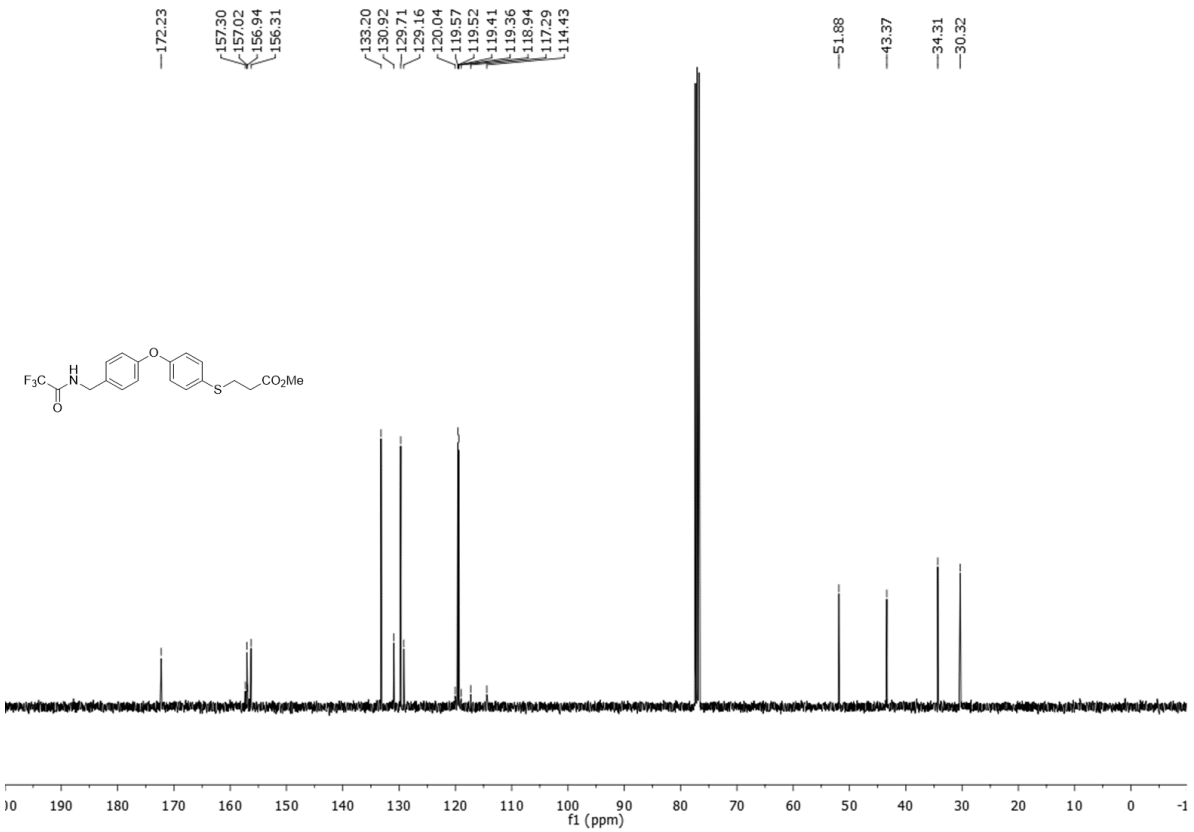
^{13}C NMR ($CDCl_3$) of Methyl 3-((4-(4-(acetamidomethyl)phenoxy)phenyl)thio)propanoate (21a)



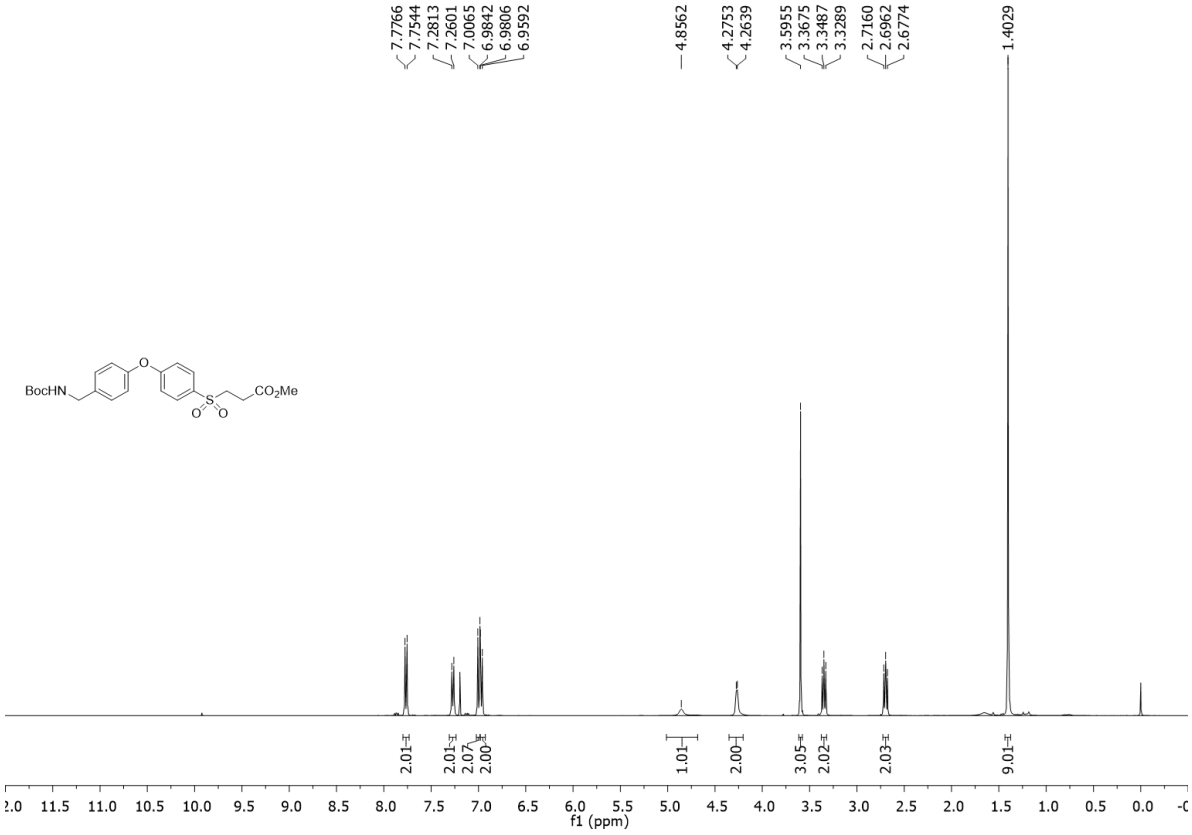
^{1}H NMR ($CDCl_3$) of Methyl 3-((4-(4-((2,2,2-trifluoroacetamido)methyl)phenoxy)phenyl)thio)propanoate (21b)



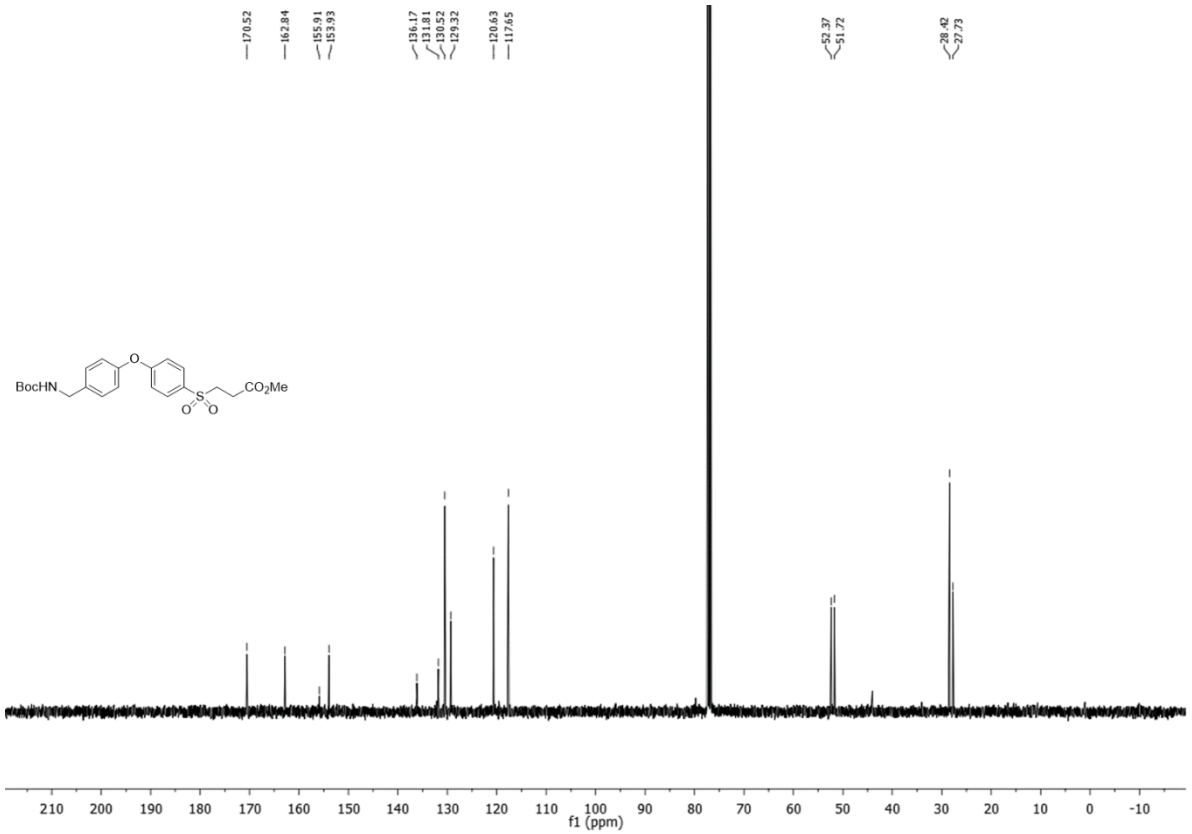
^{13}C NMR ($CDCl_3$) of Methyl 3-((4-(4-((2,2,2-trifluoroacetamido)methyl)phenoxy)phenyl)thio)propanoate (21b)



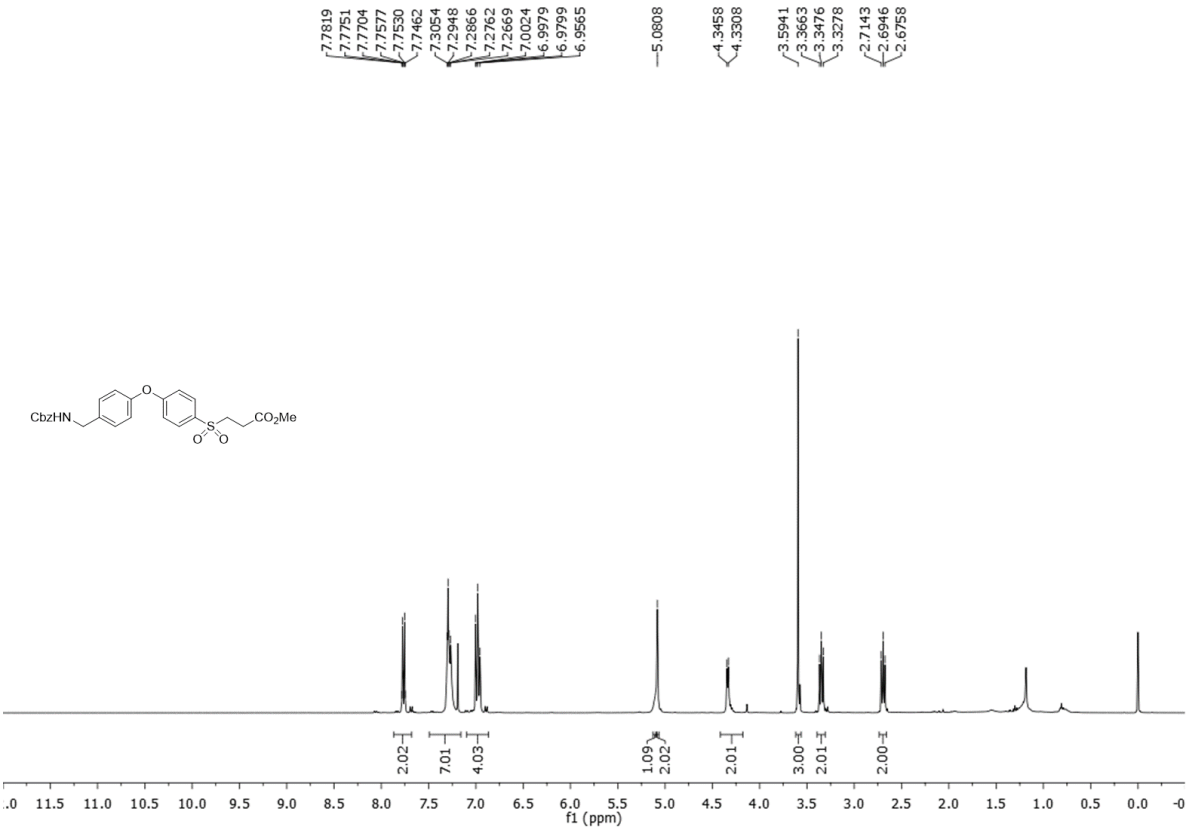
^{1}H NMR ($CDCl_3$) of Methyl 3-((4-(4-(((*tert*-butoxycarbonyl)amino)methyl)phenoxy)phenyl)sulfonyl)propanoate (22a)



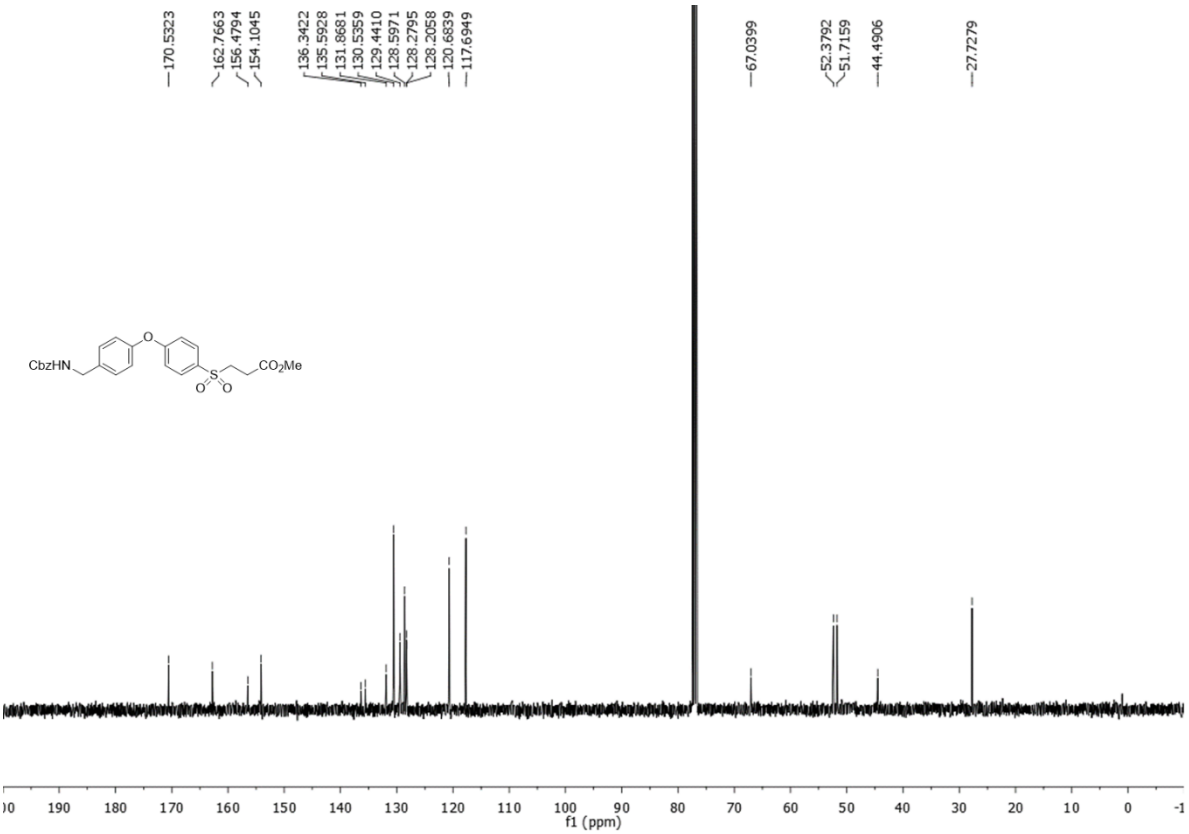
^{13}C NMR ($CDCl_3$) of Methyl 3-((4-(4-(((*tert*-butoxycarbonyl)amino)methyl)phenoxy)phenyl)sulfonyl)propanoate (22a)



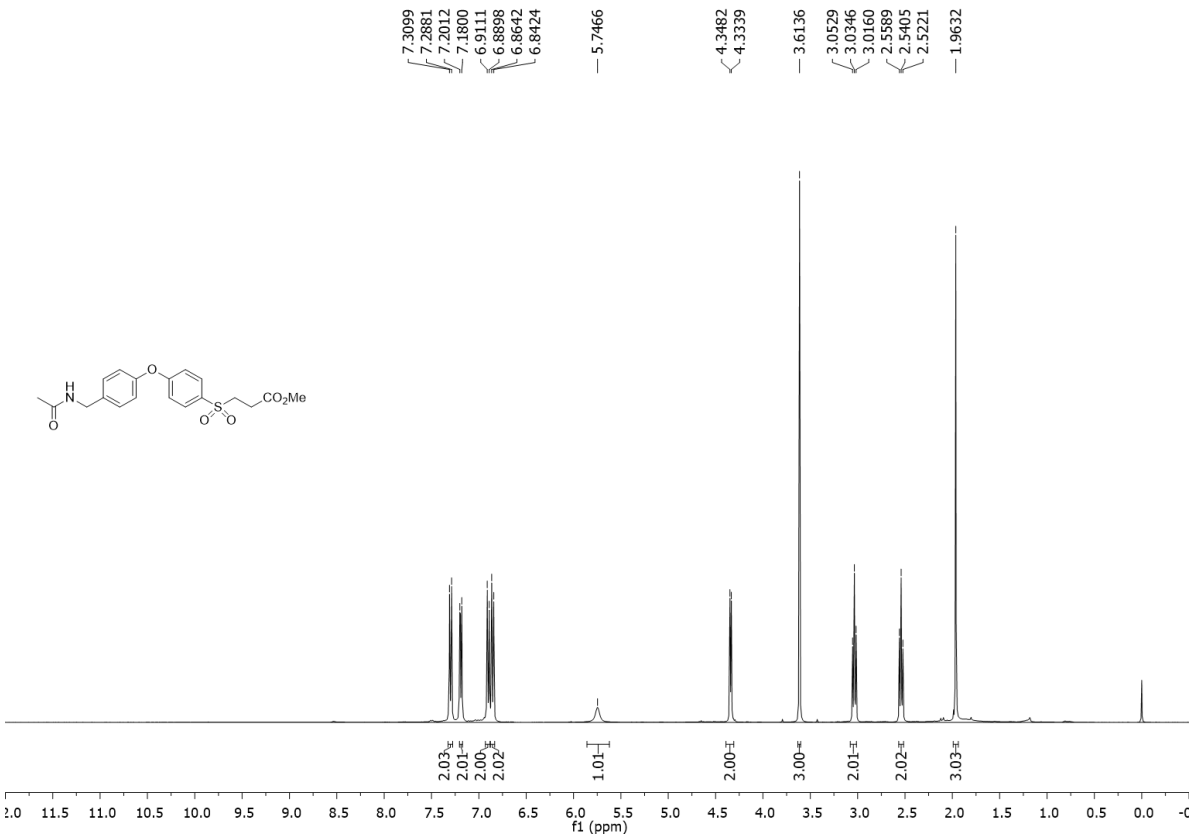
^{1}H NMR ($CDCl_3$) of Methyl 3-((4-(4-((((benzyloxy)carbonyl)amino)methyl)phenoxy)phenyl)sulfonyl)propanoate (22b)



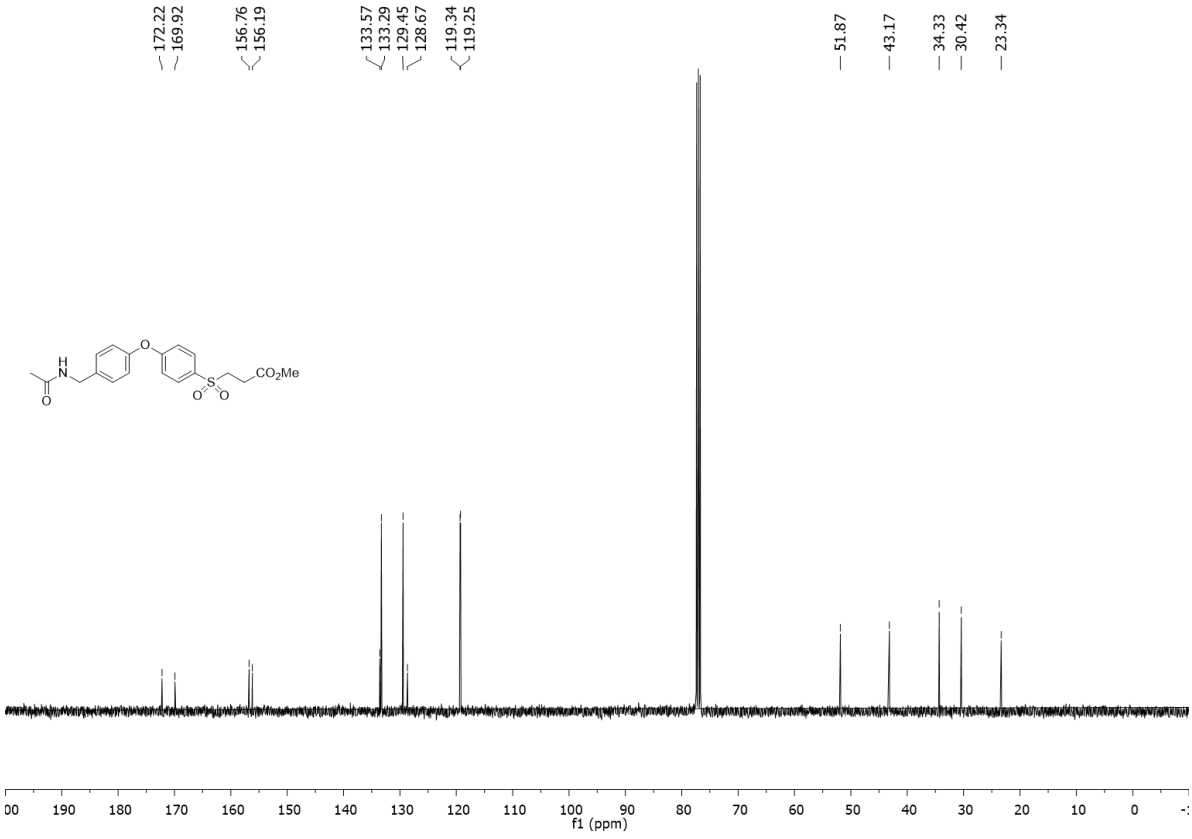
^{13}C NMR ($CDCl_3$) of Methyl 3-((4-(4-((((benzyloxy)carbonyl)amino)methyl)phenoxy)phenyl)sulfonyl)propanoate (22b)



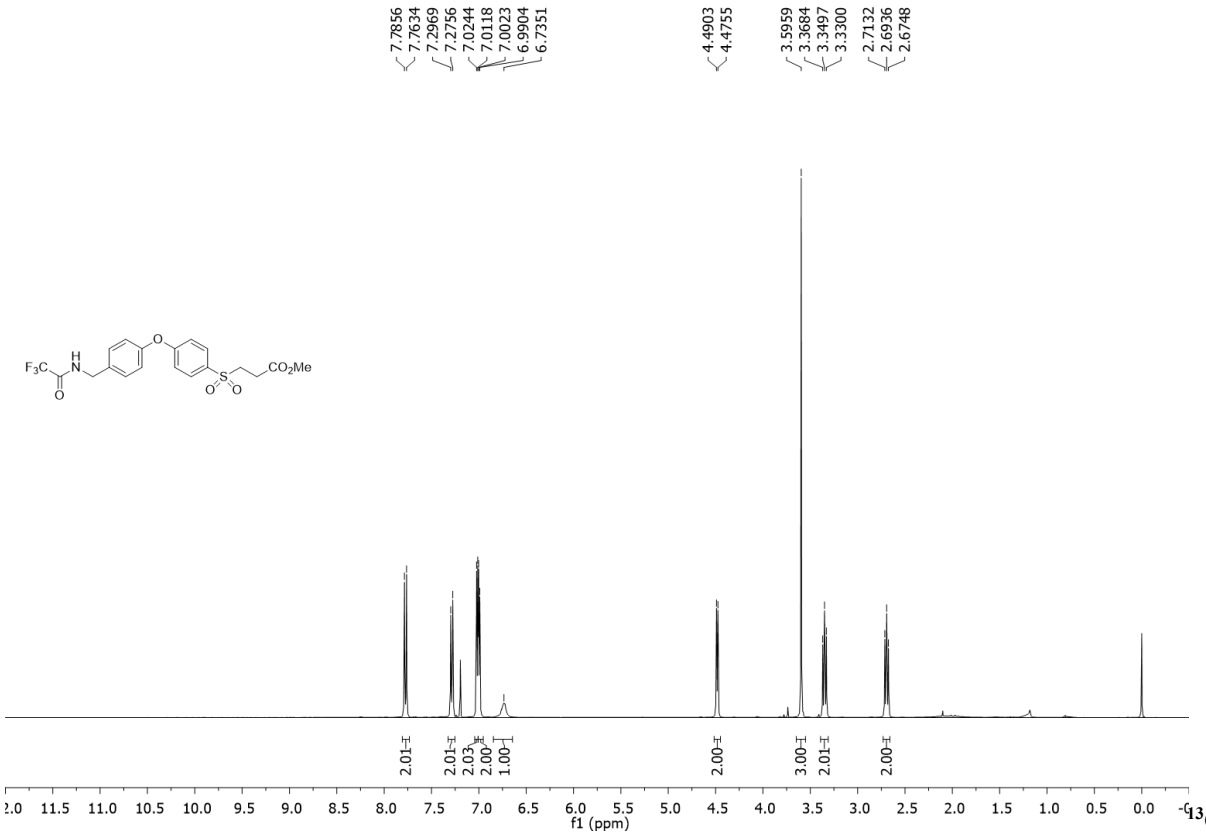
^{1}H NMR ($CDCl_3$) of Methyl 3-((4-(4-(acetamidomethyl)phenoxy)phenyl)sulfonyl)propanoate (22c)



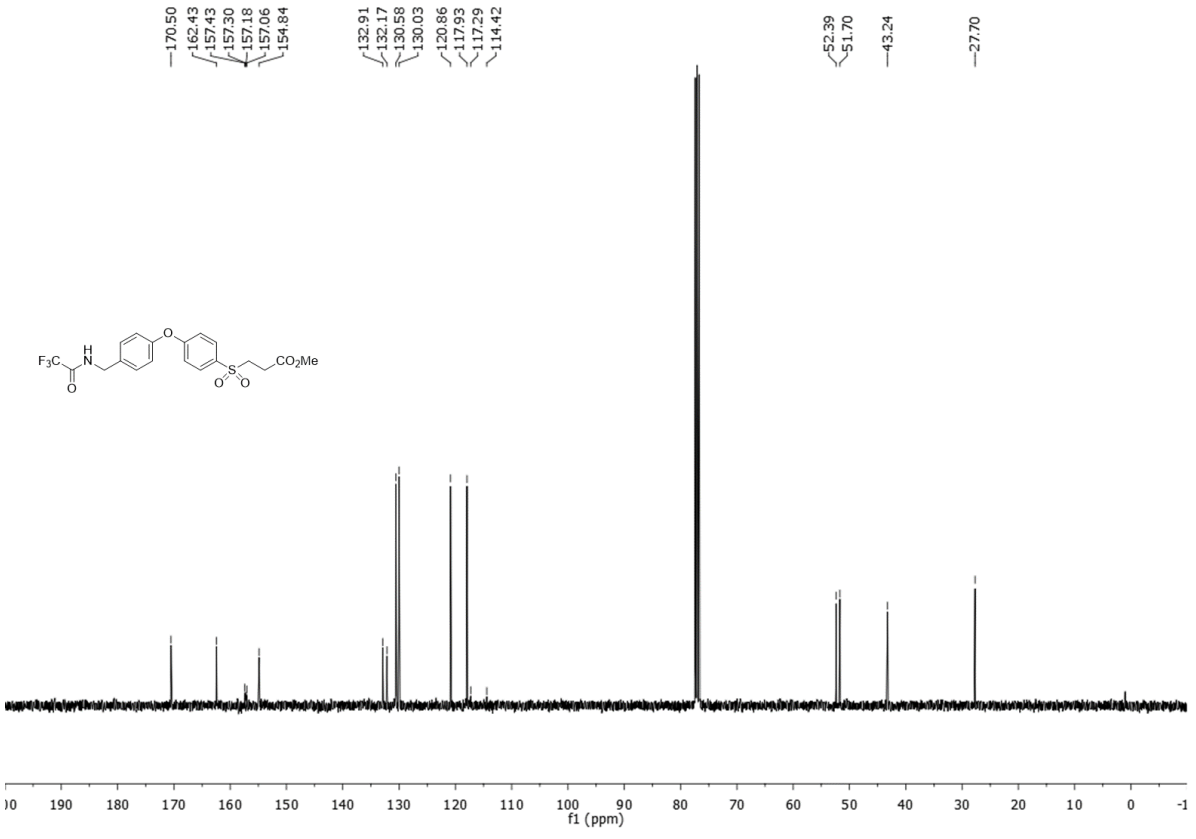
^{13}C NMR ($CDCl_3$) of Methyl 3-((4-(4-(acetamidomethyl)phenoxy)phenyl)sulfonyl)propanoate (22c)



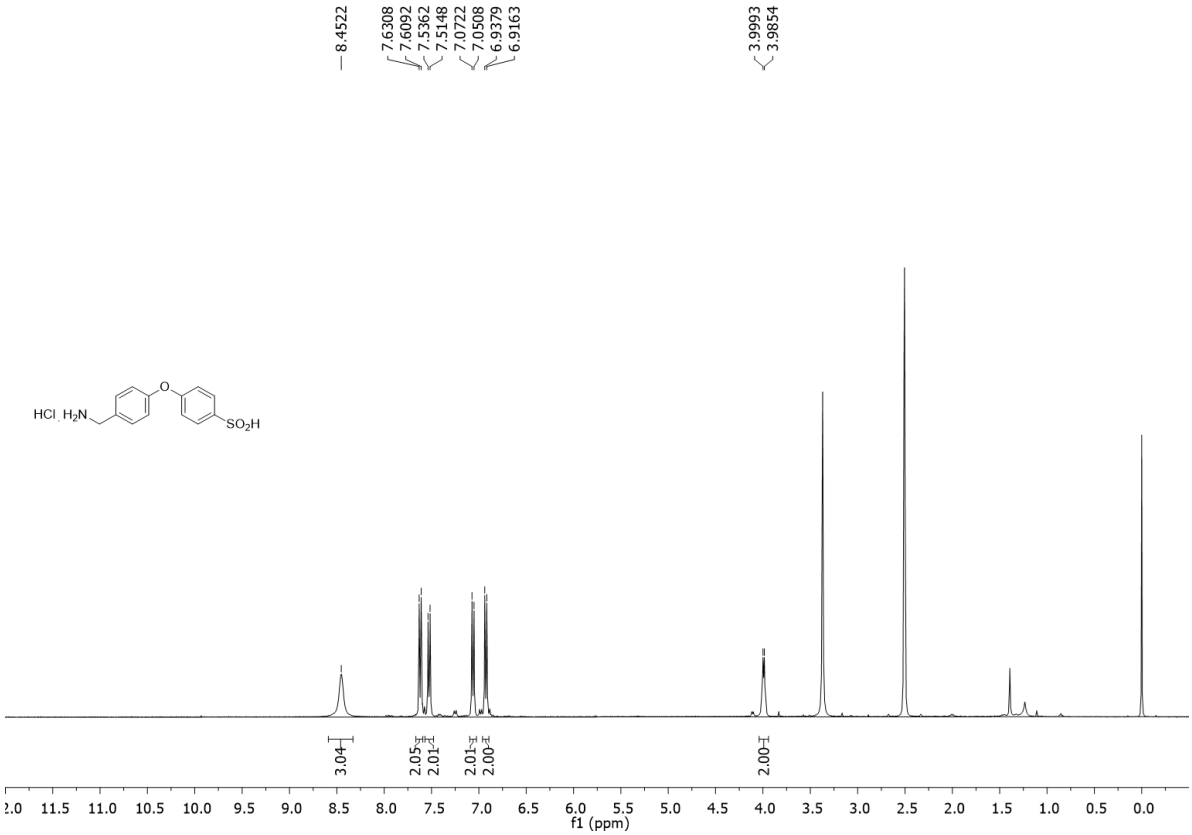
^{1}H NMR ($CDCl_3$) of Methyl 3-((4-(4-((2,2,2-trifluoroacetamido)methyl)phenoxy)phenyl)sulfonyl)propanoate (22d)



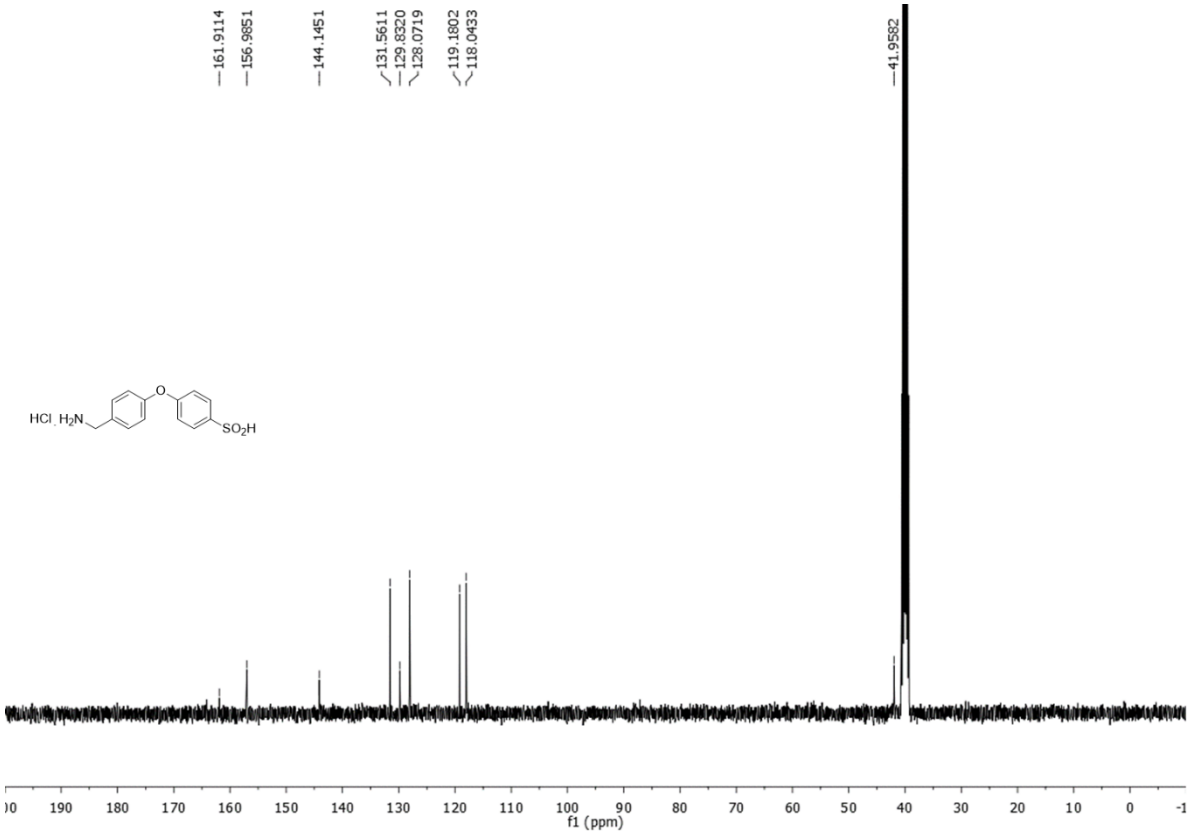
^{13}C NMR ($CDCl_3$) of Methyl 3-((4-(4-((2,2,2-trifluoroacetamido)methyl)phenoxy)phenyl)sulfonyl)propanoate (22d)



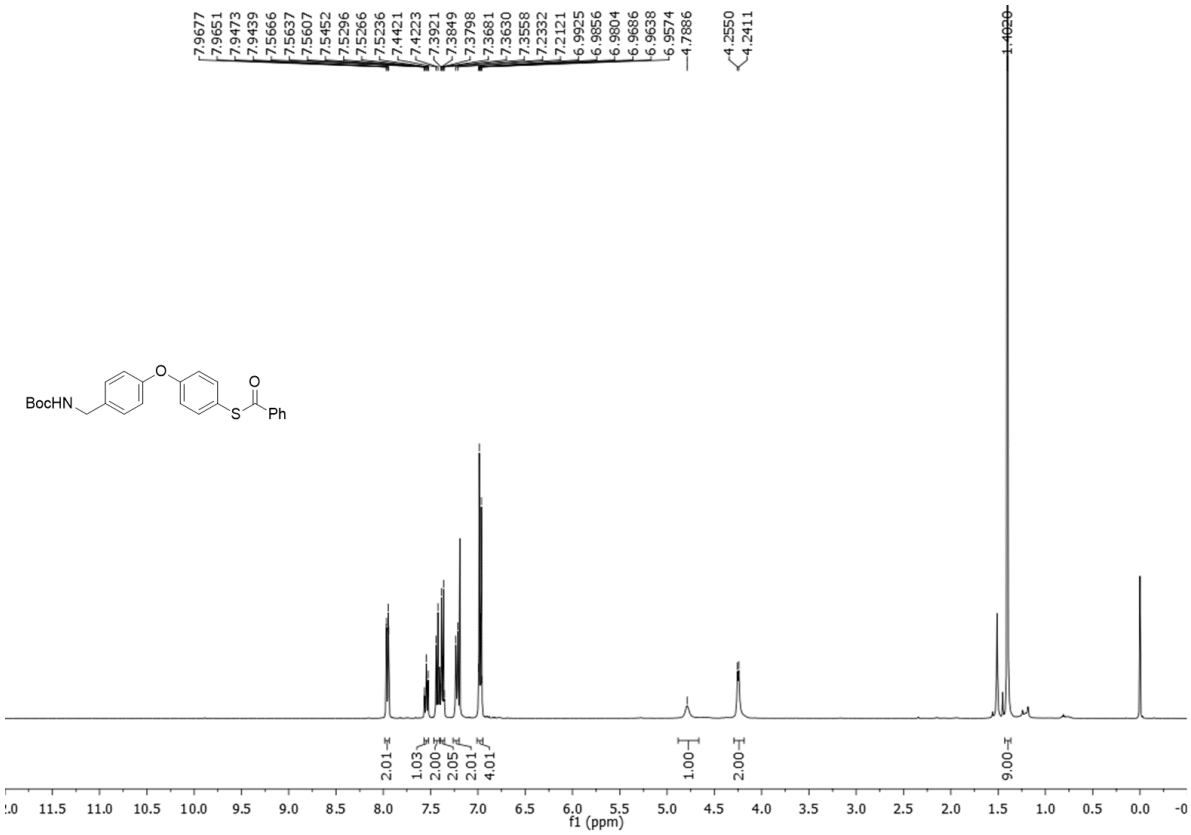
^{1}H NMR (DMSO-d_6) of 4-(4-(Aminomethyl)phenoxy)benzenesulfinic acid hydrochloride (6)



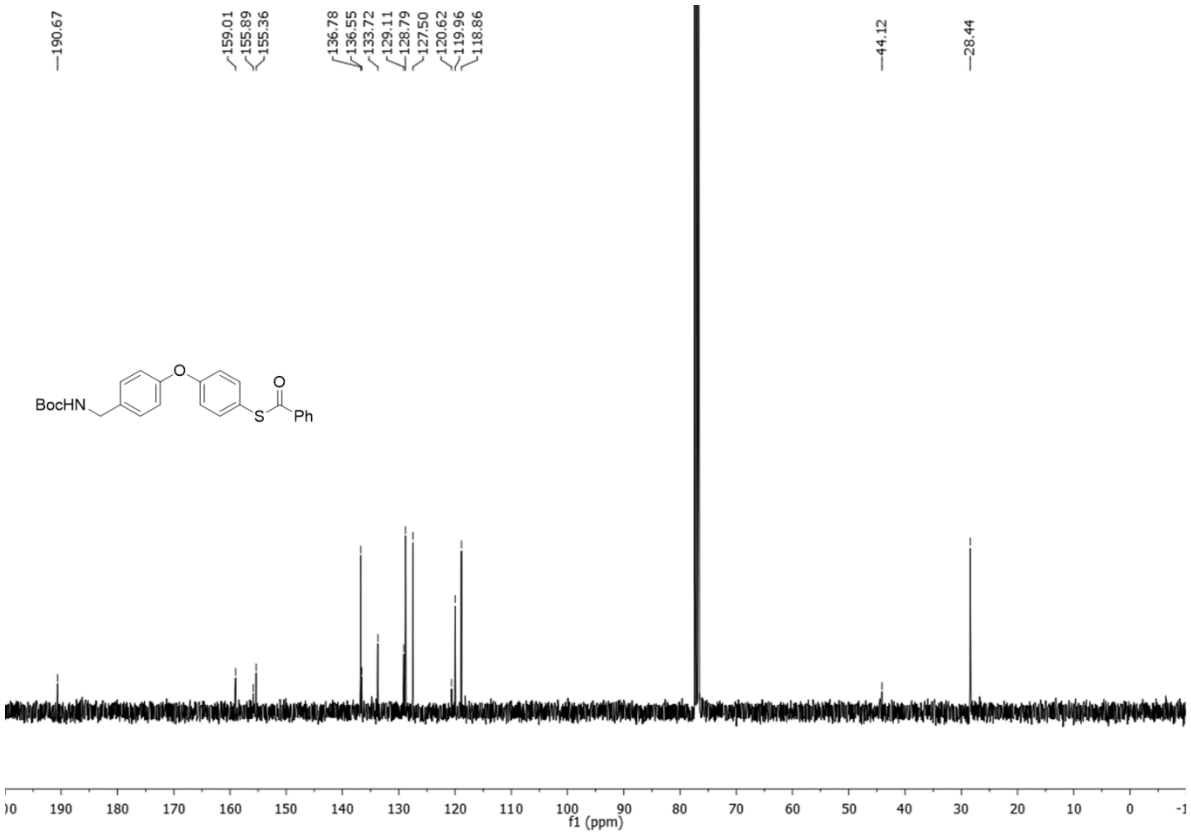
^{13}C NMR (DMSO-d_6) of 4-(4-(Aminomethyl)phenoxy)benzenesulfinic acid hydrochloride (6)



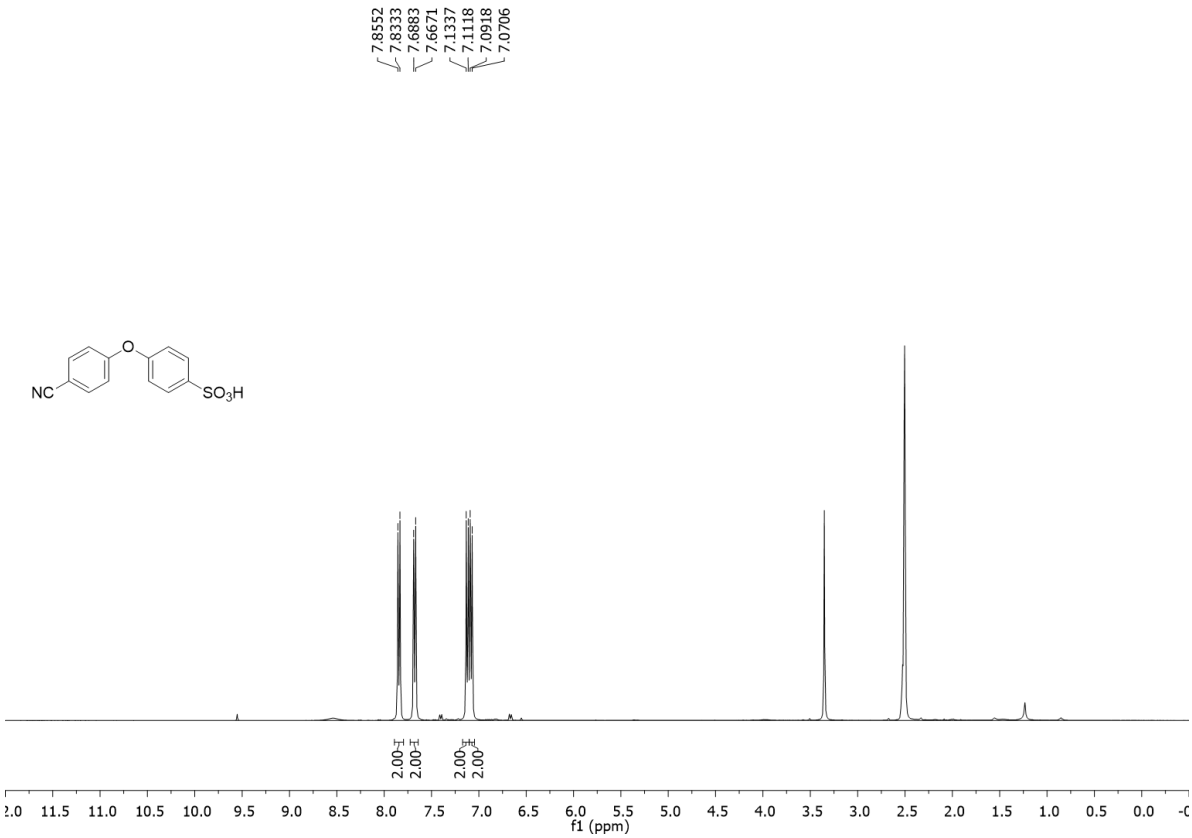
^{1}H NMR ($CDCl_3$) of S-(4-(4-(((*tert*-Butoxycarbonyl)amino)methyl)phenoxy)phenyl) benzothioate (27)



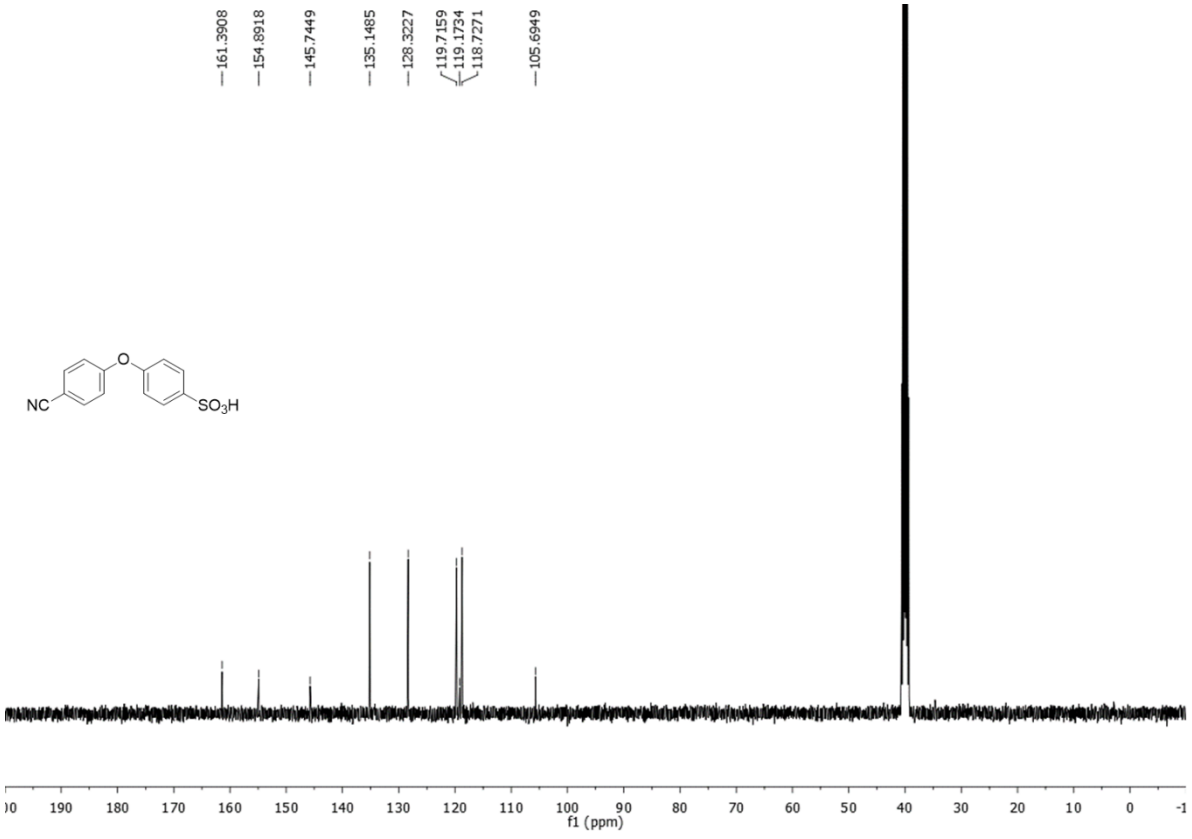
^{13}C NMR ($CDCl_3$) of S-(4-(4-(((*tert*-Butoxycarbonyl)amino)methyl)phenoxy)phenyl) benzothioate (27)



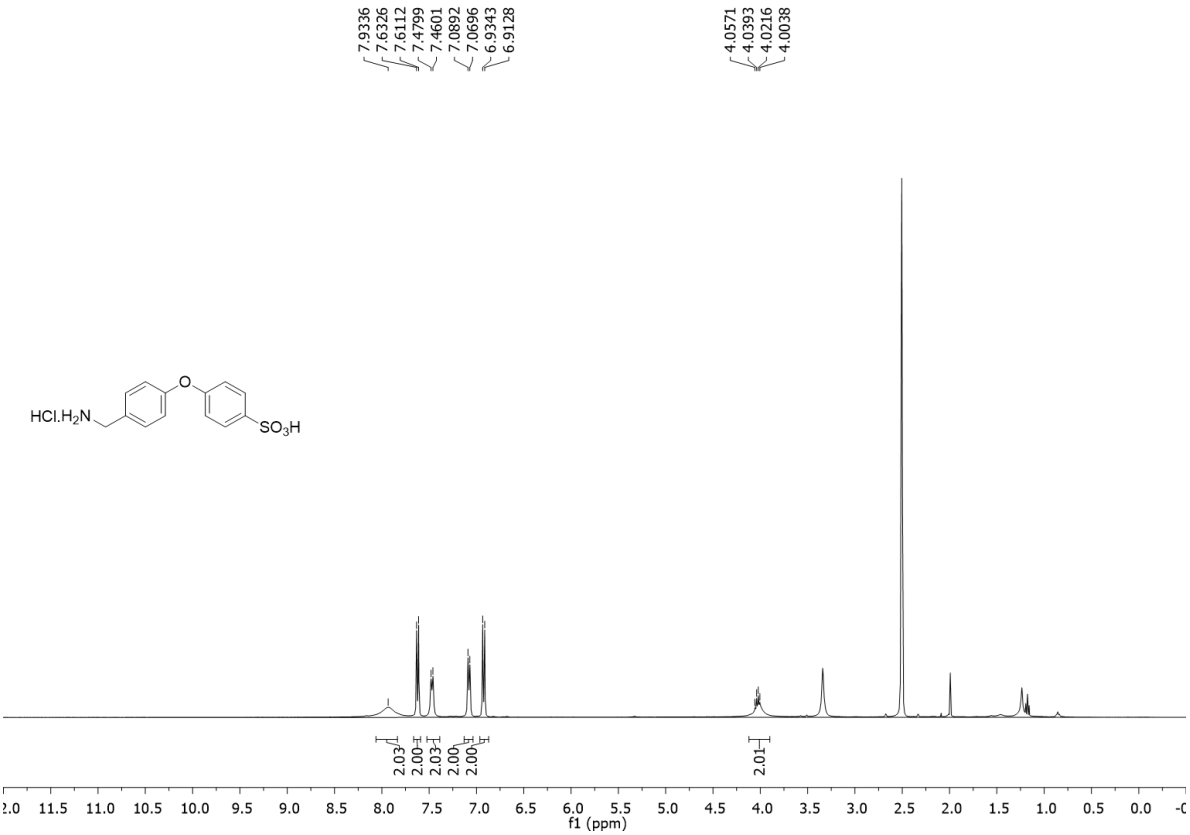
^{1}H NMR (DMSO-d_6) of 4-(4-Cyanophenoxy)benzenesulfonic acid (29)



^{13}C NMR (DMSO-d_6) of 4-(4-Cyanophenoxy)benzenesulfonic acid (29)



^{1}H NMR (DMSO-*d*$_6$) of 4-(4-(Aminomethyl)phenoxy)benzenesulfonic acid hydrochloride (12)



^{13}C NMR (DMSO-*d*$_6$) of 4-(4-(Aminomethyl)phenoxy)benzenesulfonic acid hydrochloride (12)