Supporting information for

Selective approach to thioesters and thioethers via sp^3 C-H activation of methylarenes

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1 Experimental

1.1 General

Melting points are uncorrected. All commercial materials were used without further purification. Thiols were synthesized according to the literature [22]; TBHP used was 70% TBHP in water. All known compounds are identified by appropriate technique such as ^{1}H NMR, ^{13}C NMR and compared with previously reported data. All unknown compounds are characterized by ^{1}H NMR, ^{13}C NMR, MS and elemental analyses. Analytical thin-layer chromatography are performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm), and the plates are visualized by exposure to ultraviolet light. GC-MS analyses were performed on an Agilent 7890A-5975C instrument (Column: DB-5 MS). Mass spectra are taken on a Finnigan TSQ Quantum - MS instrument in the electrospray ionization (ESI) mode. ^{1}H NMR and ^{13}C NMR spectra are recorded on an AVANCE 500 Bruker spectrometer operating at 500 MHz and 125 MHz in $CDCl_3$, respectively, and chemical shifts are reported in ppm. Elemental analyses are performed on a Yanagimoto MT3CHN recorder. GC analyses are performed on an Agilent 7890A instrument (Column: Agilent 19091J-413: 30 m × 320 μm × 0.25 μm, carrier gas: H_2, FID detection.

1.2 Experimental Procedure

General procedure for synthesis of thioesters

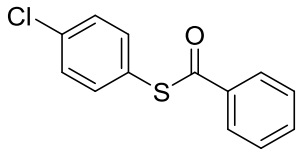
A 5 ml vial with condenser was charged with toluene (1.5 mmol), $FeBr_2$ (0.01mmol), TBHP(1.5 mmol), 2% wt. SDS /H_2O (2 ml), thiol (thiophenol)(0.5mmol) was then added in a dropwise (in portion for solids) at 100^{o}C. The reaction mixture was stirred at 100 ^{o}C for 24h. Upon competition, The reaction mixture was then cooled, extracted with ethyl acetate, and dried over anhydrous Na_2SO_4. After filtration, the organic solutions were concentrated and the residue was purified by column chromatography on silica gel to give the pure product (hexane/ethyl acetate=20/1).

General procedure for synthesis of thioethers

A mixture of toluene (1.5 mmol), $Pd(OAc)_2$ (0.05 mmol), TBHP(1.5 mmol) thiol (thiophenol)(0.5mmol) was introduced in a pressure reactor. The suspension was stirred at 115^{o}C for 24 h under 1 atm of oxygen. After this, the pressure was released and the mixture was extracted with ethyl acetate, and dried over anhydrous Na_2SO_4. After filtration, the organic solutions were concentrated and the residue was purified by column chromatography on silica gel to give the pure product (hexane/ethyl acetate=50/1).

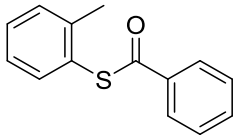
2. Characterization Data

All the products were known compounds, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and MS datas were given as below.



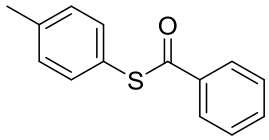
Chemical Formula: $C_{13}H_9ClOS$
Exact Mass: 248.01
Elemental Analysis: C, 62.78; H, 3.65; Cl, 14.25; O, 6.43; S, 12.89

S-(4-chlorophenyl) benzothioate **3a**. ^{1}H NMR (500 MHz, $CDCl_3$) 1H NMR (500 MHz, CDCl3) δ 8.03 (d, *J* = 7.8 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.46 (s, 4H).^{13}C NMR (125 MHz, $CDCl_3$) δ13C NMR (126 MHz, CDCl3) δ 188.7, 135.3, 135.0, 132.9, 128.5, 127.8, 126.5, 124.9. MS (ESI) *m*/*z*: 248



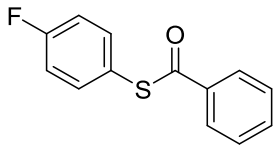
Chemical Formula: $C_{14}H_{12}OS$
Exact Mass: 228.06
Elemental Analysis: C, 73.65; H, 5.30; O, 7.01; S, 14.04

S-(o-tolyl) benzothioate **3b**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.4 Hz, 2H), 7.61 (d, *J* = 7.4 Hz, 1H), 7.54 -7.47 (m, 3H), 7.38 (d, *J* = 6.4 Hz, 2H), 7.30-7.24 (m, 1H), 2.41 (s, 3H). ^{13}C 188.7, 141.7, 135.8, 132.6,129.9, 129.3, 127.8, 126.6, 125.7. MS (ESI) *m*/*z*: 228.



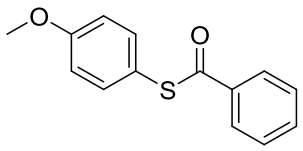
Chemical Formula: $C_{14}H_{12}OS$
Exact Mass: 228.06
Elemental Analysis: C, 73.65; H, 5.30; O, 7.01; S, 14.04

S-(p-tolyl) benzothioate **3c**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.5, 139.9, 136.8, 135.1, 133.8, 130.2, 128.9, 127.5, 123.9, 21.5. MS (ESI) *m*/*z*: 228.



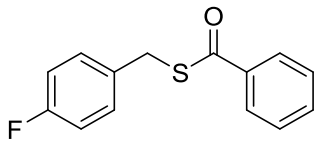
Chemical Formula: $C_{13}H_9FOS$
Exact Mass: 232.04
Elemental Analysis: C, 67.22; H, 3.91; F, 8.18; O, 6.89; S, 13.80

S-(4-fluorophenyl) benzothioate **3d**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (m, 2H), 7.43 (m, 1H), 7.30 (m, 4H), 7.04 – 6.92 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.9, 164.5, 162.6, 137.2, 137.2, 136.3, 133.9, 128.9, 127.4, 122.7, 116.6, 116.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ -111.0. MS (ESI) *m*/*z*: 232.



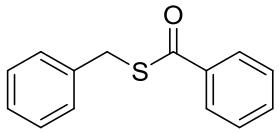
Chemical Formula: $C_{14}H_{12}O_2S$
Exact Mass: 244.06
Elemental Analysis: C, 68.83; H, 4.95; O, 13.10; S, 13.12

S-(4-methoxyphenyl) benzothioate **3e**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.57 – 7.50 (m, 1H), 7.45 – 7.35 (m, 4H), 6.94 (d, *J* = 8.7 Hz, 2H), 3.73 (d, *J* = 27.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.0, 160.9, 136.7, 133.7, 128.9, 127.5, 118.0, 115.1, 55.5. MS (ESI) *m*/*z*: 244



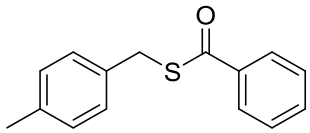
Chemical Formula: $C_{14}H_{11}FOS$
Exact Mass: 246.05
Elemental Analysis: C, 68.27; H, 4.50; F, 7.71; O, 6.50; S, 13.02

S-4-fluorobenzyl benzothioate **3f**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00-7.98 (m, 2H), 7.61-7.58 (m, 1H), 7.49-7.46 (m, 2H),. 7.39-7.36 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.04-7.00 (m, 2H), 4.31 (s, 2H),^{13}C NMR (126 MHz, $CDCl_3$) δ190.2, 162.0, 160.1, 135.7, 132.6, 132.4, 129.7, 129.6, 127.7, 126.3, 114.6, 114.4, 31.6. MS (ESI) *m*/*z*: 246.



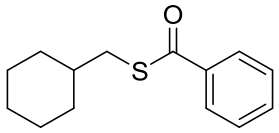
Chemical Formula: $C_{14}H_{12}OS$
Exact Mass: 228.06
Elemental Analysis: C, 73.65; H, 5.30; O, 7.01; S, 14.04

S-benzyl benzothioate **3g**. ^{1}H NMR (500 MHz, $CDCl_3$) δ8.02-8.00 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.61-7.58 (m, 1H), 7.49-7.46 (m, 2H), 7.43-7.41 (m, 2H), 7.37-7.34 (m, 2H), 7.31-7.27 (m, 1H), 4.36 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.3, 136.5, 135.8, 132.5, 128.0, 127.7, 126.3, 32.4. MS (ESI) *m*/*z*: 228.



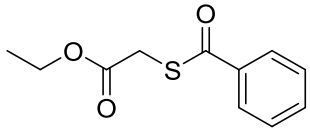
Chemical Formula: $C_{15}H_{14}OS$
Exact Mass: 242.08
Elemental Analysis: C, 74.34; H, 5.82; O, 6.60; S, 13.23

S-4-methylbenzyl benzothioate **3h**. ^{1}H NMR (500 MHz, $CDCl_3$) δ8.01-7.99 (m, 2H), 7.61-7.57 (m, 1H), 7.48-7.45 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.5 Hz, 2H), 4.32 (s, 2H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.5,136.1135.9, 133.4, 132.4, 128.4, 127.9, 127.6, 126.3, 32.1, 20.2. MS (ESI) *m*/*z*: 242.



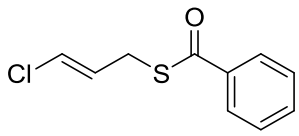
Chemical Formula: $C_{14}H_{18}OS$
Exact Mass: 234.11
Elemental Analysis: C, 71.75; H, 7.74; O, 6.83; S, 13.68

S-cyclohexylmethyl benzothioate **3i**. ^{1}H NMR (500 MHz, $CDCl_3$) δ8.00 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.59-7.56 (t, *J* = 7.5 Hz, 1H), 3.01 (d, *J* = 6.5 Hz, 2H), 1.90-1.87 (m, 2H),1.77-1.73 (m, 2H), 1.61-1.54 (m, 1H), 1.69-1.66 (m, 1H), 1.31-1.16 (m, 3H), 1.09-1.01 (m, 2H),. ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.2, 136.3, 132.2, 127.6, 126.2, 37.1, 34.9, 31.6, 25.3, 25.0. MS (ESI) *m*/*z*: 234.



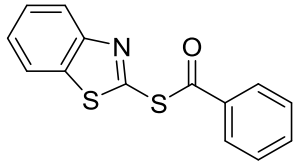
Chemical Formula: $C_{11}H_{12}O_3S$
Exact Mass: 224.05
Elemental Analysis: C, 58.91; H, 5.39; O, 21.40; S, 14.30

Ethyl 2-(benzoylthio)acetate **3k**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.63-7.60 (t, *J* = 7.5 Hz, 1H),7.50-7.47 (t, *J* = 7.5 Hz, 2H), 4.27-4.23 (q, *J* = 7.0 Hz, 2H), 3.90 (s, 2H), 1.33-1.31 (t, *J* = 7.0 Hz, 3H),. ^{13}C NMR (126 MHz, $CDCl_3$) δ189.1, 167.8, 135.2, 132.8, 127.7, 126.4, 60.9, 30.5, 13.1. MS (ESI) *m*/*z*: 224.



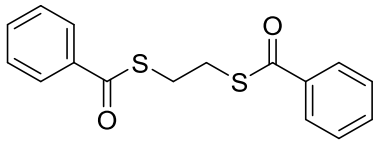
Chemical Formula: $C_{10}H_9ClOS$
Exact Mass: 212.00
Elemental Analysis: C, 56.47; H, 4.26; Cl, 16.67; O, 7.52; S, 15.08

(*E*)-*S*-3-chloroallyl benzothioate **3m**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.5 Hz, 1H), 7.62-7.59 (t, *J* = 7.5 Hz), 7.50-7.46 (t, *J* = 7.0 Hz, 2H), 6.34-6.31 (dt, *J* = 13.5, 1.0 Hz, 1H), 6.04-6.00 (dt, *J* = 13.0, 8.0 Hz, 1H), 3.75-3.73 (dd, *J* = 7.5, 1.5 Hz, 2H),. ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.8, 135.7, 132.6, 127.7, 127.5, 126.3, 120.6, 28.0. MS (ESI) *m*/*z*: 212.



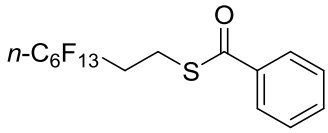
Chemical Formula: $C_{14}H_9NOS_2$
Exact Mass: 271.01
Elemental Analysis: C, 61.97; H, 3.34; N, 5.16; O, 5.90; S, 23.63

S-(benzo[d]thiazol-2-yl) benzothioate **3n**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.90 (m, 1H), 7.86 (dd, *J* = 7.4, 1.1 Hz, 2H), 7.82 – 7.74 (m, 1H), 7.50 (ddd, *J* = 11.8, 8.3, 3.0 Hz, 1H), 7.40 – 7.31 (m, 3H), 7.29 (qd, *J* = 6.9, 1.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.8, 157.8, 151.7, 136.1, 135.4, 134.8, 129.2, 127.7, 126.4, 125.7, 123.00, 121.3. MS (ESI) *m*/*z*: 271.



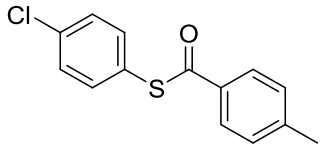
Chemical Formula: $C_{16}H_{14}O_2S_2$
Exact Mass: 302.04
Elemental Analysis: C, 63.55; H, 4.67; O, 10.58; S, 21.21

S,*S'*-ethane-1,2-diyl dibenzothioate **3o**. ^{1}H NMR (500 MHz, $CDCl_3$) δ8.00 (d, *J* = 8.0 Hz, 4H), 7.62-7.59 (t, *J* = 7.5 Hz, 2H), 7.50-7.47 (t, *J* = 7.0 Hz, 4H), 3.39 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.3, 135.8, 132.6, 127.7, 126.3, 28.0. MS (ESI) *m*/*z*: 302.



Chemical Formula: $C_{15}H_9F_{13}OS$
Exact Mass: 484.02
Elemental Analysis: C, 37.20; H, 1.87; F, 51.00; O, 3.30; S, 6.62

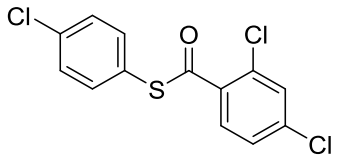
S-1*H*,1*H*,2*H*,2*H*-perfluorooctyl benzothioate **3p**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99-7.97 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.64-7.60 (t, *J* = 7.5 Hz, 1H), 7.51-7.48 (t, *J* = 7.5 Hz, 2H), 3.33-3.30 (m, 2H), 2.57-2.47 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ, 189.8, 135.5,132.8, 127.8, 126.3, 30.8, 19.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ -126.2, -123.4, -122.9, -121.9, -114.5, -80.9. MS (ESI) *m*/*z*: 484.



Chemical Formula: $C_{14}H_{11}ClOS$
Exact Mass: 262.02
Elemental Analysis: C, 64.00; H, 4.22; Cl, 13.49; O, 6.09; S, 12.20

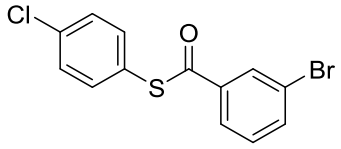
S-(4-chlorophenyl) 4-methylbenzothioate **4a**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.43 (q, *J* = 8.6 Hz, 4H), 7.28 (d, *J* = 7.9 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.13, 143.90, 135.36, 134.84, 132.83, 128.51, 128.45,

126.61, 125.15, 20.76. MS (ESI) *m*/*z*: 262.



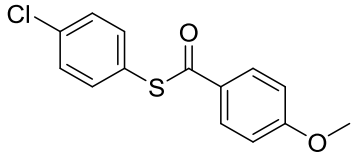
Chemical Formula: $C_{13}H_7Cl_3OS$
Exact Mass: 315.93
Elemental Analysis: C, 49.16; H, 2.22; Cl, 33.48; O, 5.04; S, 10.09

S-(4-chlorophenyl) 2,4-dichlorobenzothioate **4b**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 1H), 7.52 (s, 1H), 7.46 (s, 4H), 7.37 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.64, 137.44, 135.42, 134.92, 134.01, 131.36, 130.03, 129.18, 128.72, 126.22, 124.50. MS (ESI) *m*/*z*: 316.



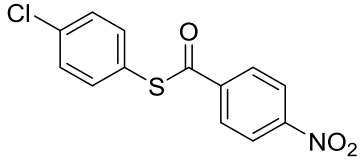
Chemical Formula: $C_{13}H_8BrClOS$
Exact Mass: 325.92
Elemental Analysis: C, 47.66; H, 2.46; Br, 24.39; Cl, 10.82; O, 4.88; S, 9.79

S-(4-chlorophenyl) 3-bromobenzothioate **4c**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.45 (s, 5H), 7.39 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.44, 137.06, 135.69, 135.25, 131.38, 129.41, 128.66, 127.39, 125.07, 124.26, 122.07. MS (ESI) *m*/*z*: 326.



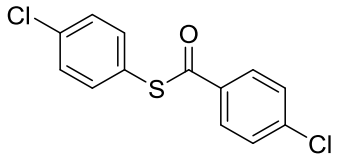
Chemical Formula: $C_{14}H_{11}ClO_2S$
Exact Mass: 278.02
Elemental Analysis: C, 60.32; H, 3.98; Cl, 12.72; O, 11.48; S, 11.50

S-(4-chlorophenyl) 4-methoxybenzothioate **4d**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.5 Hz, 2H), 7.53 – 7.36 (m, 4H), 6.97 (d, *J* = 8.5 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.03, 163.18, 135.43, 134.81, 128.79, 128.43, 128.11, 125.21, 113.02, 76.36, 76.11, 75.85, 54.59. MS (ESI) *m*/*z*: 278



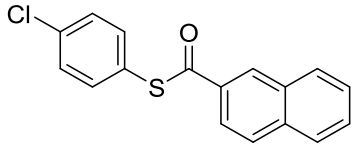
Chemical Formula: $C_{13}H_8ClNO_3S$
Exact Mass: 292.99
Elemental Analysis: C, 53.16; H, 2.75; Cl, 12.07; N, 4.77; O, 16.34; S, 10.92

S-(4-chlorophenyl) 4-nitrobenzothioate **4f**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.7 Hz, 2H), 8.17 (d, *J* = 8.7 Hz, 2H), 7.46 (s, 4H).^{13}C NMR (126 MHz, $CDCl_3$) δ 187.36, 149.79, 139.98, 135.61, 135.14, 128.81, 127.55, 123.66, 123.09. MS (ESI) *m*/*z*: 293



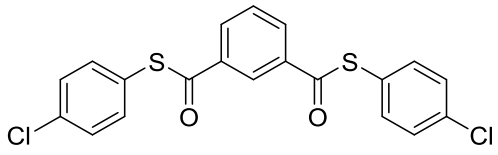
Chemical Formula: $C_{13}H_8Cl_2OS$
Exact Mass: 281.97
Elemental Analysis: C, 55.14; H, 2.85; Cl, 25.04; O, 5.65; S, 11.32

S-(4-chlorophenyl) 4-chlorobenzothioate **4g** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.45 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.52, 139.34, 135.28, 133.71, 128.61, 128.39, 128.18, 127.87, 124.43. MS (ESI) *m*/*z*: 282



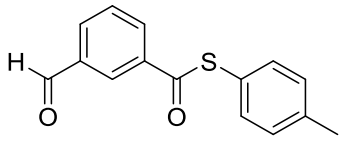
Chemical Formula: $C_{17}H_{11}ClOS$
Exact Mass: 298.02
Elemental Analysis: C, 68.34; H, 3.71; Cl, 11.86; O, 5.35; S, 10.73

S-(4-chlorophenyl) naphthalene-2-carbothioate **4j**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.3 Hz, 1H), 8.23 (d, *J* = 7.2 Hz, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.71 – 7.45 (m, 7H).^{13}C NMR (126 MHz, $CDCl_3$) δ 190.62, 135.17, 135.05, 133.32, 132.88, 132.57, 128.59, 128.35, 127.44, 127.28, 127.15, 125.83, 124.22, 123.48. MS (ESI) *m*/*z*: 298



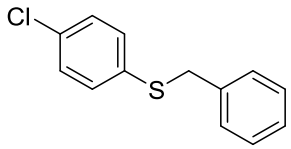
Chemical Formula: $C_{20}H_{12}Cl_2O_2S_2$
Exact Mass: 417.97
Elemental Analysis: C, 57.29; H, 2.88; Cl, 16.91; O, 7.63; S, 15.29

S,S-bis(4-chlorophenyl) benzene-1,3-bis(carbothioate) **4k**
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.25 (d, *J* = 7.7 Hz, 2H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.48 (s, 8H), 7.28 (s, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 187.83, 136.06, 135.36, 135.25, 131.23, 128.69, 128.57, 125.47, 124.15. MS (ESI) *m*/*z*: 418.



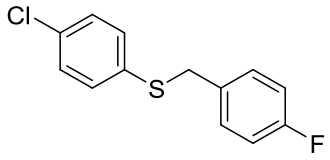
Chemical Formula: $C_{15}H_{12}O_2S$
Exact Mass: 256.06
Elemental Analysis: C, 70.29; H, 4.72; O, 12.48; S, 12.51

S-(p-tolyl) 3-formylbenzothioate **4k'** ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.12 (s, 1H), 8.51 (s, 1H), 8.26 (d, *J* = 7.7 Hz, 1H), 8.16 (d, *J* = 7.5 Hz, 1H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.47 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.01, 187.85, 136.27, 135.81, 135.37, 135.25, 133.00, 131.84, 128.70, 127.86, 124.10. MS (ESI) *m*/*z*: 256.



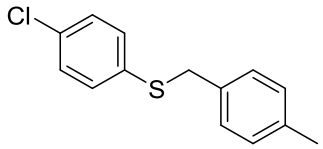
Chemical Formula: $C_{13}H_{11}ClS$
Exact Mass: 234.03
Elemental Analysis: C, 66.52; H, 4.72; Cl, 15.10; S, 13.66

Benzyl(4-chlorophenyl)sulfane **5a**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 4H), 7.23 (s, 4H), 4.09 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.16, 133.74, 131.50, 130.44, 127.99, 127.84, 127.60, 126.36, 38.34. MS (ESI) *m*/*z*: 234.



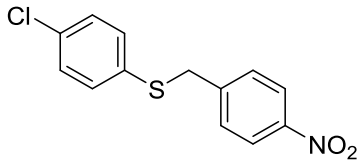
Chemical Formula: $C_{13}H_{10}ClFS$
Exact Mass: 252.02
Elemental Analysis: C, 61.78; H, 3.99; Cl, 14.03; F, 7.52; S, 12.69

(4-Chlorophenyl)(4-fluorobenzyl)sulfane **5b**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (dd, J = 5.9, 4.7 Hz, 6H), 6.97 (t, J = 8.6 Hz, 2H), 4.04 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.04, 160.08, 133.40, 131.98, 131.70, 130.65, 129.46, 129.40, 128.06, 114.54, 114.36, 37.62. ^{19}F NMR (470 MHz, $CDCl_3$) δ -114.8. MS (ESI) *m*/*z*: 252.



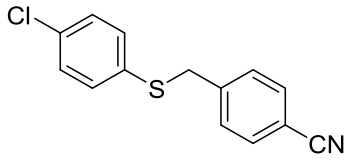
Chemical Formula: $C_{14}H_{13}ClS$
Exact Mass: 248.04
Elemental Analysis: C, 67.59; H, 5.27; Cl, 14.25; S, 12.89

(4-Chlorophenyl)(4-methylbenzyl)sulfane **5c**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (s, 4H), 7.16 (d, J = 7.9 Hz, 2H), 7.09 (d, J = 7.8 Hz, 2H), 4.05 (s, 2H), 2.32 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 136.02, 134.04, 132.97, 131.27, 130.16, 128.28, 127.95, 127.72, 37.93, 20.15. MS (ESI) *m*/*z*: 248.



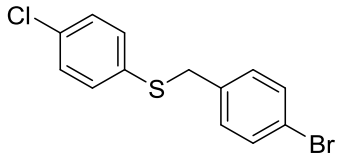
Chemical Formula: $C_{13}H_{10}ClNO_2S$
Exact Mass: 279.01
Elemental Analysis: C, 55.82; H, 3.60; Cl, 12.67; N, 5.01; O, 11.44; S, 11.46

(4-Chlorophenyl)(4-nitrobenzyl)sulfane **5d**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.20 (q, *J* = 8.6 Hz, 4H), 4.10 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.13, 144.15, 132.53, 131.97, 131.44, 128.59, 128.26, 122.77, 76.34, 76.09, 75.84, 38.13. MS (ESI) *m*/*z*: 279.



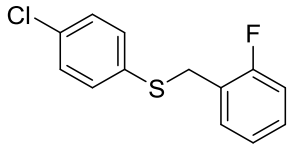
Chemical Formula: $C_{14}H_{10}ClNS$
Exact Mass: 259.02
Elemental Analysis: C, 64.74; H, 3.88; Cl, 13.65; N, 5.39; S, 12.34

4-(((4-Chlorophenyl)thio)methyl)benzonitrile **5e**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.5 Hz, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.19 (d, *J* = 10.7 Hz, 4H), 4.06 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.03, 132.41, 132.16, 131.32, 128.50, 128.22, 117.67, 110.16, 76.37, 76.12, 75.86, 38.38. MS (ESI) *m*/*z*: 259.



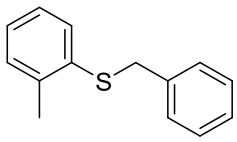
Chemical Formula: $C_{13}H_{10}BrClS$
Exact Mass: 311.94
Elemental Analysis: C, 49.78; H, 3.21; Br, 25.48; Cl, 11.30; S, 10.22

(4-Bromobenzyl)(4-chlorophenyl)sulfane **5f**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, J = 8.3 Hz, 2H), 7.20 (q, J = 8.7 Hz, 4H), 7.11 (d, J = 8.2 Hz, 2H), 4.00 (s, 2H)； ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.33, 133.03, 131.87, 130.81, 130.66, 129.47, 128.09, 120.23, 37.87. MS (ESI) *m*/*z*: 312.



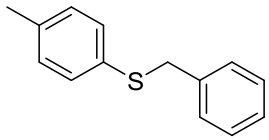
Chemical Formula: $C_{13}H_{10}ClFS$
Exact Mass: 252.02
Elemental Analysis: C, 61.78; H, 3.99; Cl, 14.03; F, 7.52; S, 12.69

(4-Bromobenzyl)(4-chlorophenyl)sulfane **5g**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27–7.20 (m, 6H), 7.08 – 7.01 (m, 2H), 4.12 (s, 2H). ^{13}C NMR (126 MHz, CDCl3) δ 160.78, 158.82, 133.13, 131.93, 131.10, 129.84, 128.19, 128.13, 128.05, 123.17, 114.59, 114.42, 31.49. MS (ESI) *m*/*z*: 252.



benzyl(*o*-tolyl)sulfane
Chemical Formula: $C_{14}H_{14}S$
Exact Mass: 214.08
Elemental Analysis: C, 78.46; H, 6.58; S, 14.96

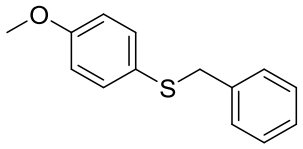
Benzyl(o-tolyl)sulfane **5i**. ^{1}H NMR (500 MHz, CDCl3) δ 7.56 (dt, J = 14.5, 7.0 Hz, 6H), 7.44 – 7.38 (m, 2H), 4.31 (s, 2H), 2.63 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 137.04, 136.65, 135.31, 129.44, 128.27, 128.12, 128.05, 127.93, 127.85, 127.69, 126.54, 125.83, 125.40, 37.54, 19.69. MS (ESI) *m*/*z*: 214.



Chemical Formula: $C_{14}H_{14}S$
Exact Mass: 214.08
Elemental Analysis: C, 78.46; H, 6.58; S, 14.96

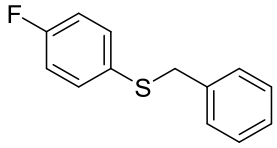
Benzyl(p-tolyl)sulfane **5j**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 6H), 7.23 (t, *J* = 7.5 Hz, 2H), 4.24 (s, 2H), 2.47 (d, *J* = 5.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.08, 135.62, 131.94, 129.81, 128.91, 128.13, 127.70, 126.34, 38.88, 20.32. MS

(ESI) *m*/*z*: 214.



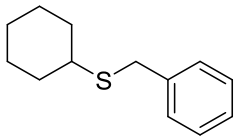
Chemical Formula: $C_{14}H_{14}OS$
Exact Mass: 230.08
Elemental Analysis: C, 73.01; H, 6.13; O, 6.95; S, 13.92

Benzyl(4-methoxyphenyl)sulfane **5k**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 14.3, 7.3 Hz, 4H), 7.28 (d, *J* = 7.1 Hz, 3H), 6.86 (d, *J* = 8.7 Hz, 2H), 4.06 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.31, 137.28, 133.08, 131.48, 128.04, 127.50, 125.26, 113.59, 54.35, 40.25. MS (ESI) *m*/*z*: 230.



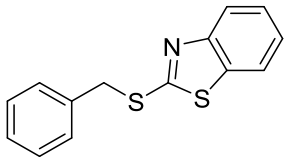
Chemical Formula: $C_{13}H_{11}FS$
Exact Mass: 218.06
Elemental Analysis: C, 71.53; H, 5.08; F, 8.70; S, 14.69

Benzyl(4-fluorophenyl)sulfane **5l**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 7H), 7.03 (t, *J* = 8.6 Hz, 2H), 4.12 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.17, 160.20, 136.71, 132.42, 132.37, 130.10, 128.04, 127.64, 126.37, 115.14, 114.97, 39.44. ^{19}F NMR (470 MHz, $CDCl_3$) δ -114.5. MS (ESI) *m*/*z*: 218.



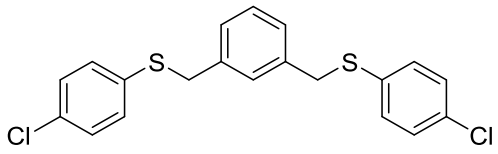
Chemical Formula: $C_{13}H_{18}S$
Exact Mass: 206.11
Elemental Analysis: C, 75.67; H, 8.79; S, 15.54

Benzyl(cyclohexyl)sulfane **5m**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.29 (m, 5H), 4.58 (s, 2H), 2.80 (dd, *J* = 9.4, 3.8 Hz, 1H), 2.02 (d, *J* = 12.0 Hz, 2H), 1.77 (dd, *J* = 9.1, 3.2 Hz, 2H), 1.68 – 1.58 (m, 1H), 1.44 – 1.19 (m, 5H). ^{13}C NMR (126 MHz, CDCl3) δ 136.58, 127.76, 127.64, 127.42, 76.60, 76.34, 76.09, 45.30, 37.52, 37.00, 25.43, 24.44. MS (ESI) *m*/*z*: 206.



Chemical Formula: $C_{14}H_{11}NS_2$
Exact Mass: 257.03
Elemental Analysis: C, 65.34; H, 4.31; N, 5.44; S, 24.91

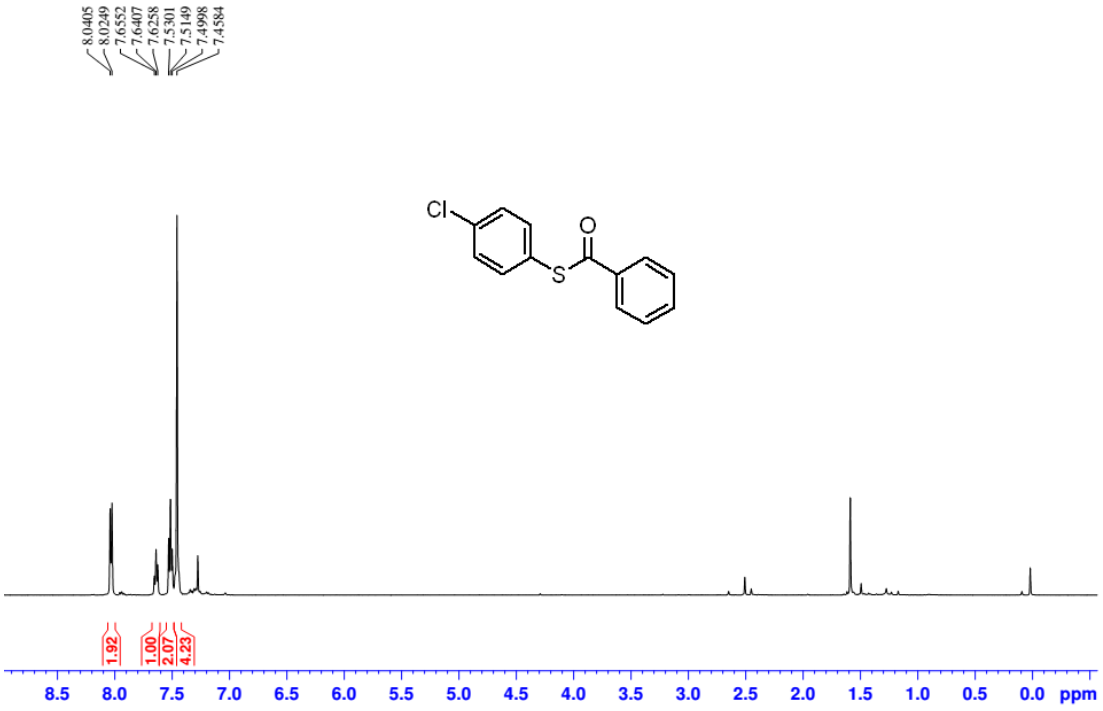
2-(benzylthio)benzo[d]thiazole **5o**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 7.4 Hz, 2H), 7.49 – 7.44 (m, 1H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.33 (dt, *J* = 13.5, 6.6 Hz, 2H), 4.66 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.58, 152.31, 135.32, 134.48, 128.29, 127.86, 126.91, 125.23, 123.44, 120.70, 120.18, 36.85. MS (ESI) *m*/*z*: 257.



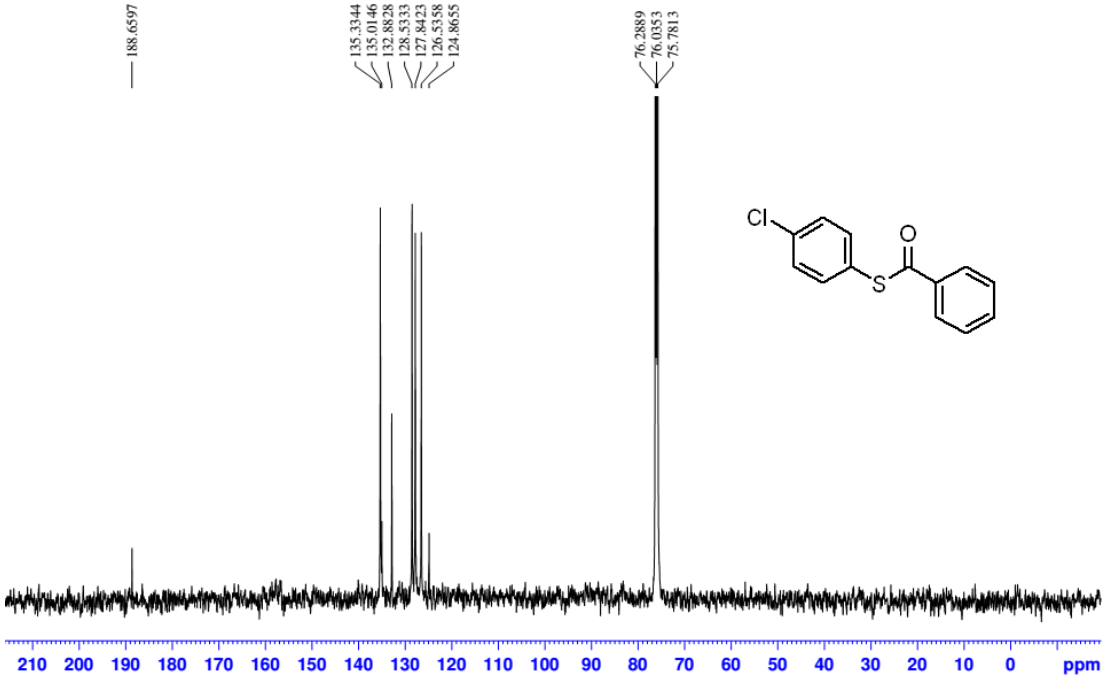
Chemical Formula: $C_{20}H_{16}Cl_2S_2$
Exact Mass: 390.01
Elemental Analysis: C, 61.38; H, 4.12; Cl, 18.12; S, 16.38

1,3-bis(((4-chlorophenyl)thio)methyl)benzene **5q**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.06 (m, 12H), 4.05 (s, 4H).^{13}C NMR (126 MHz, CDCl3) δ 135.33, 133.03, 131.87, 130.81, 130.66, 129.47, 128.09, 120.23, 37.87. MS (ESI) *m/z*: 390.

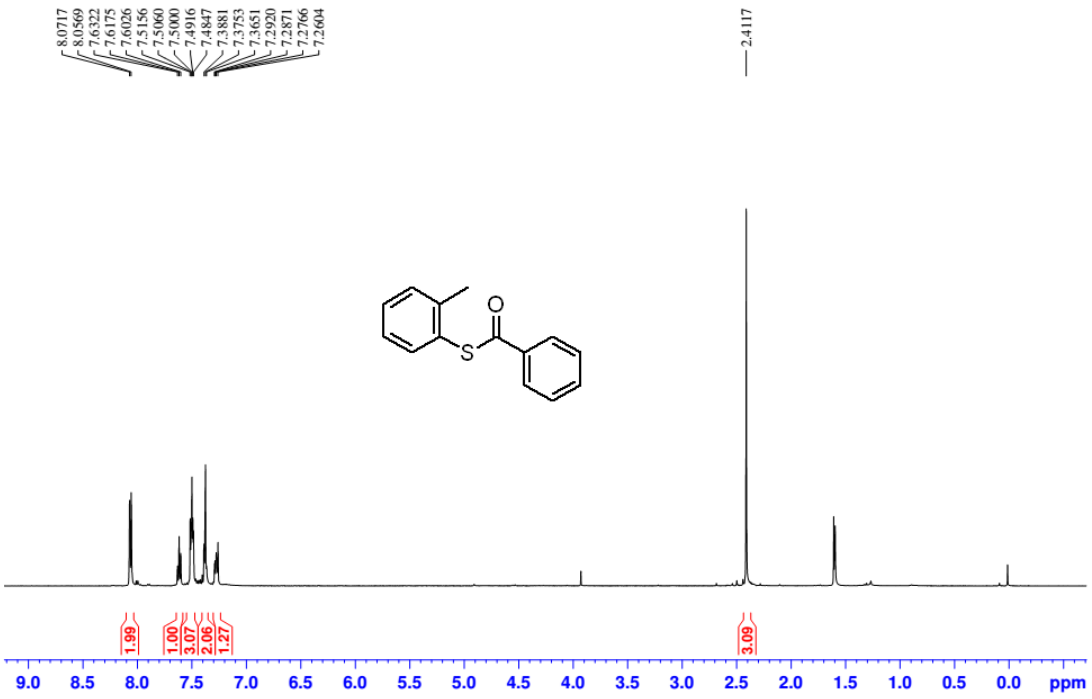
3. NMR Spectra of All Products



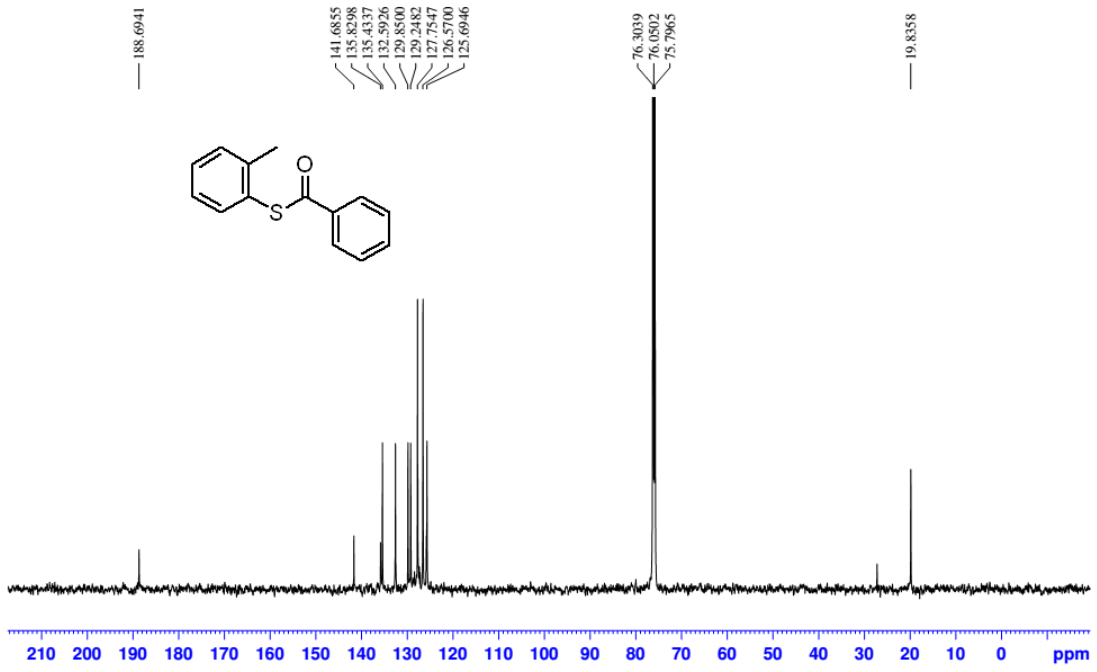
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3a**



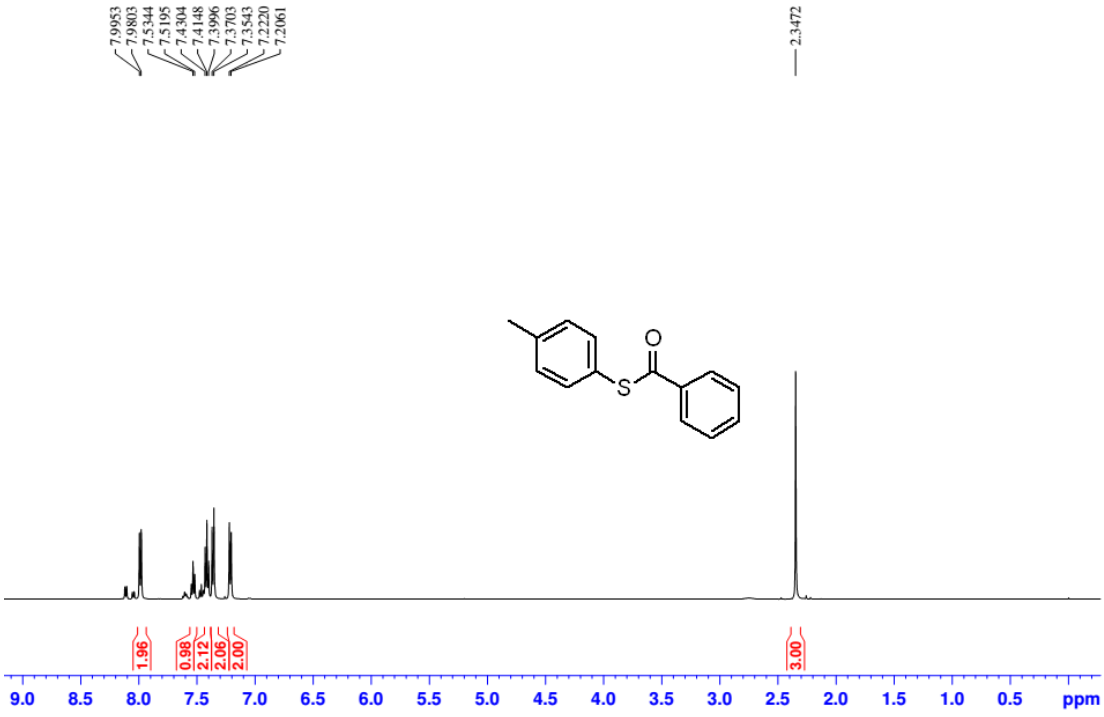
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3a**



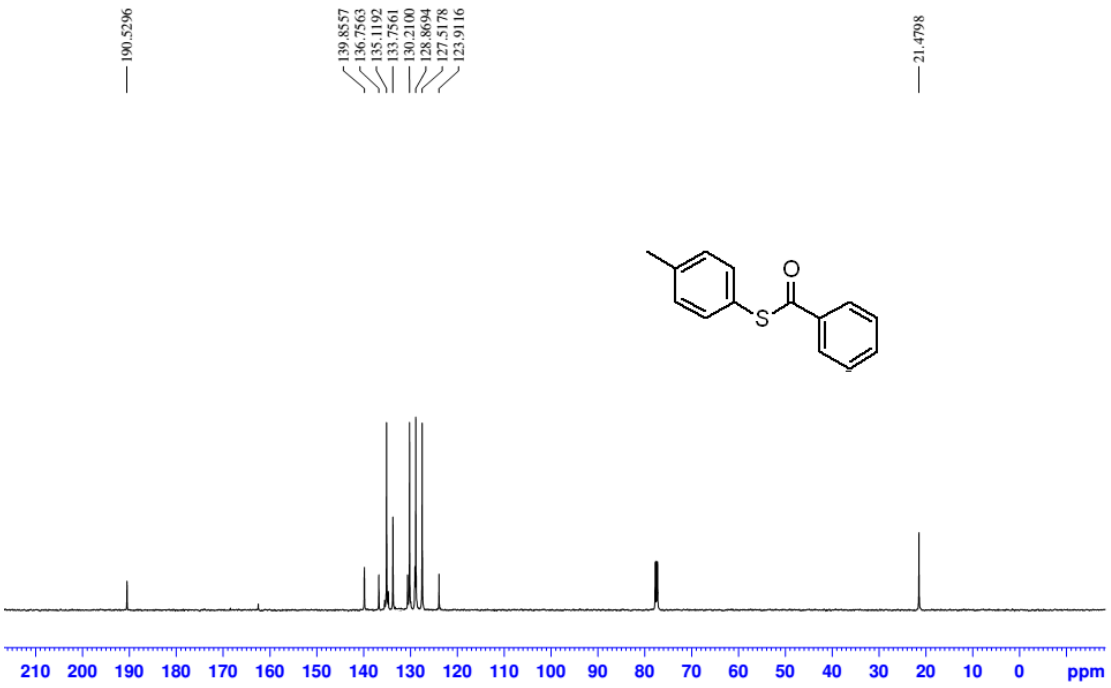
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3b**



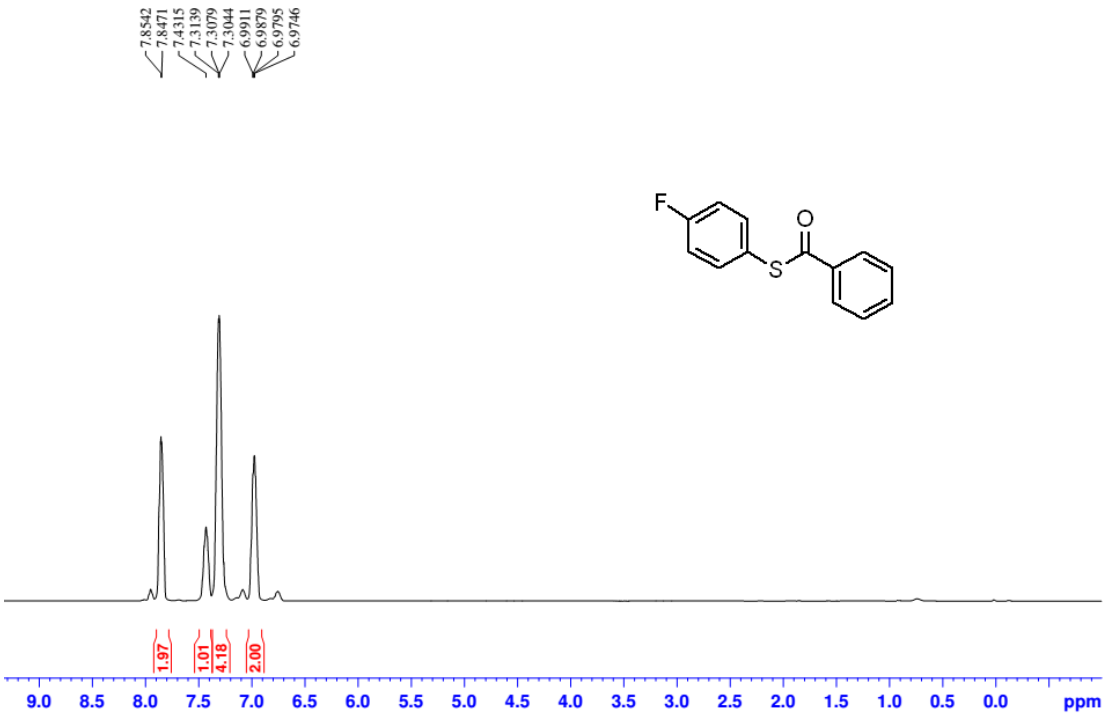
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3b**



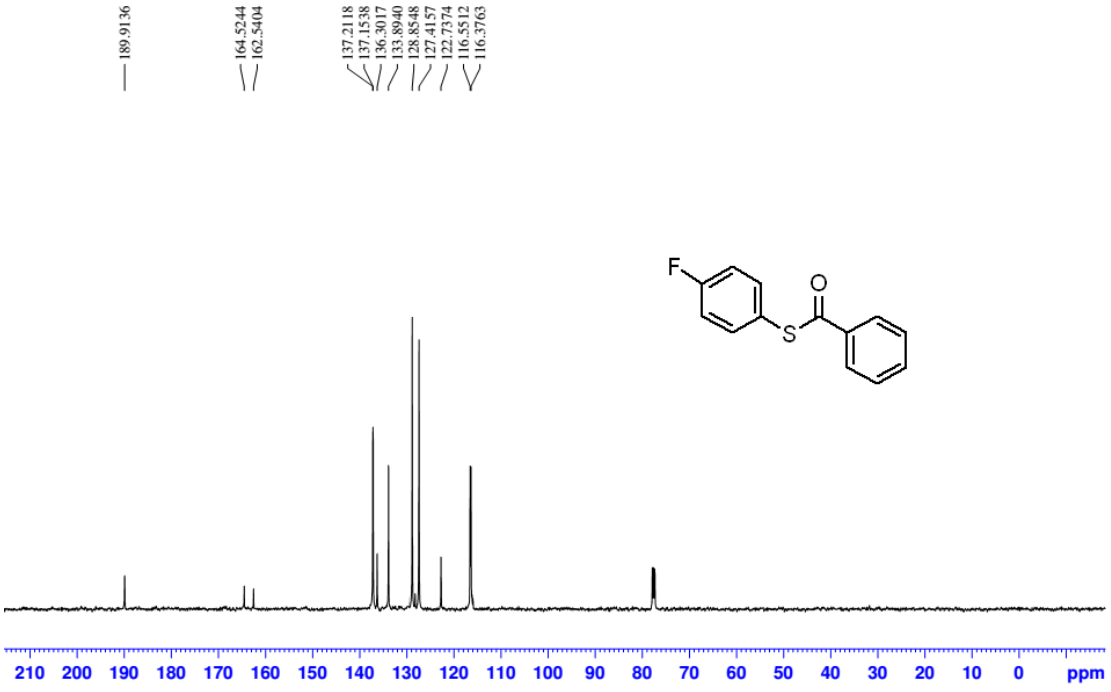
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3c**



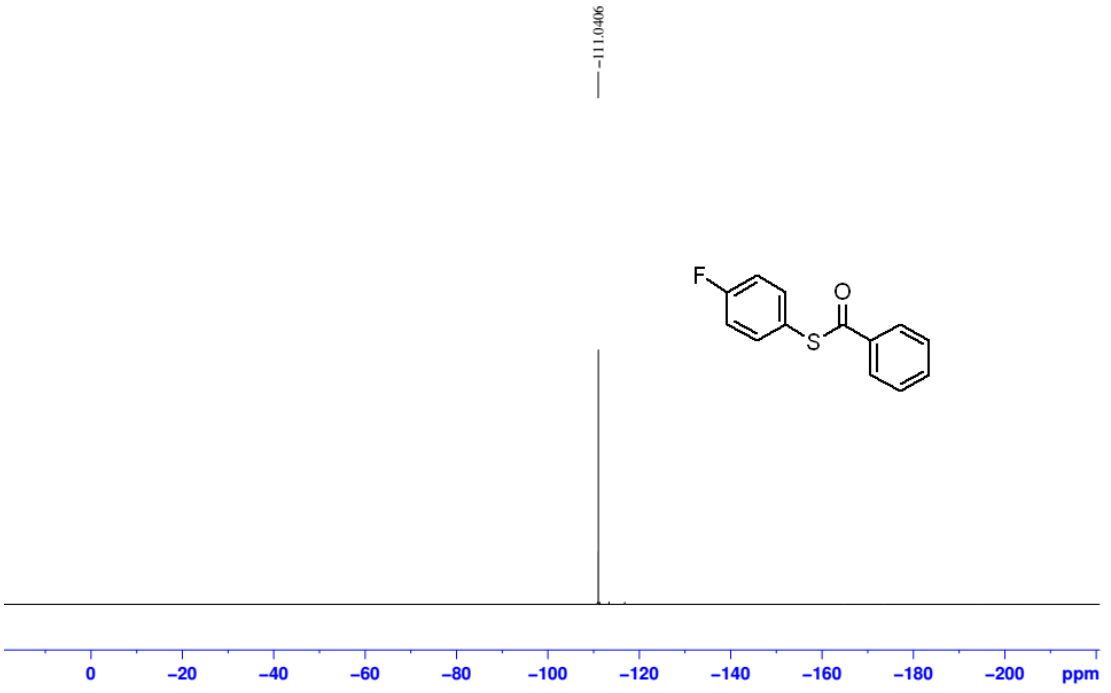
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3c**



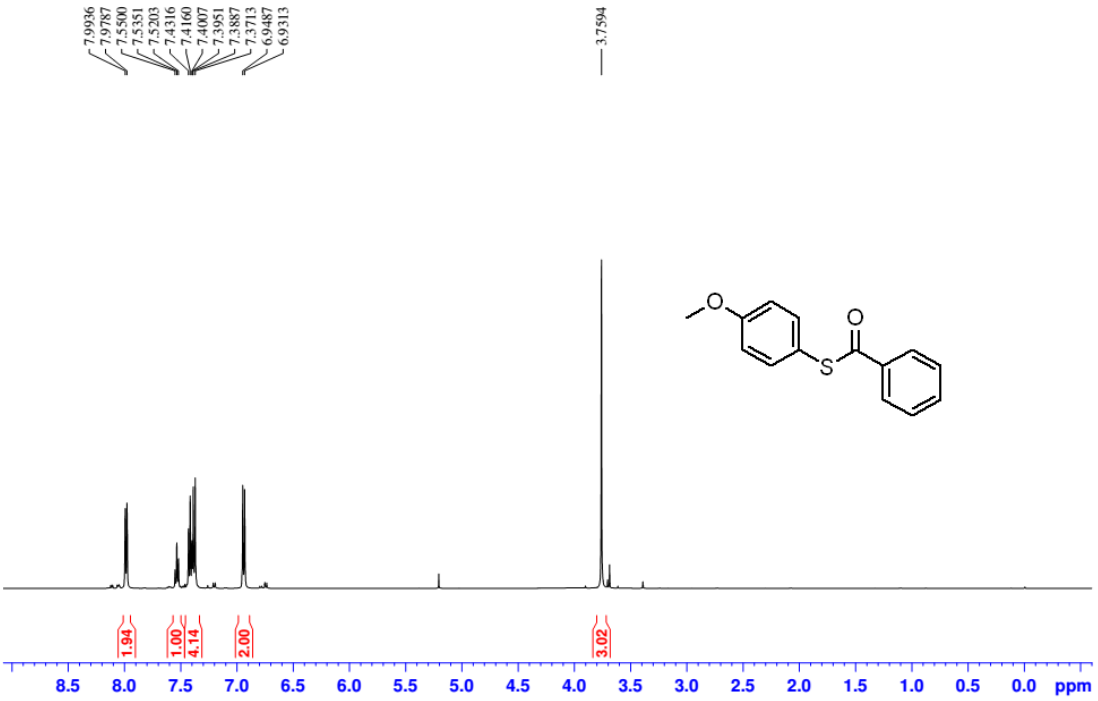
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3d**



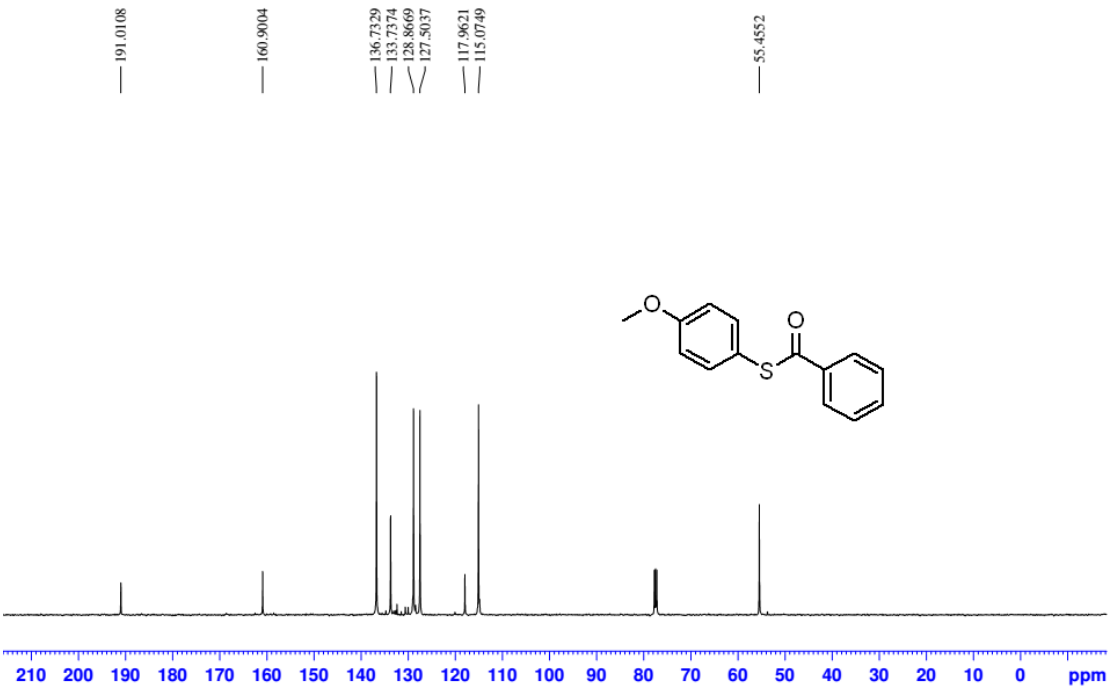
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3d**



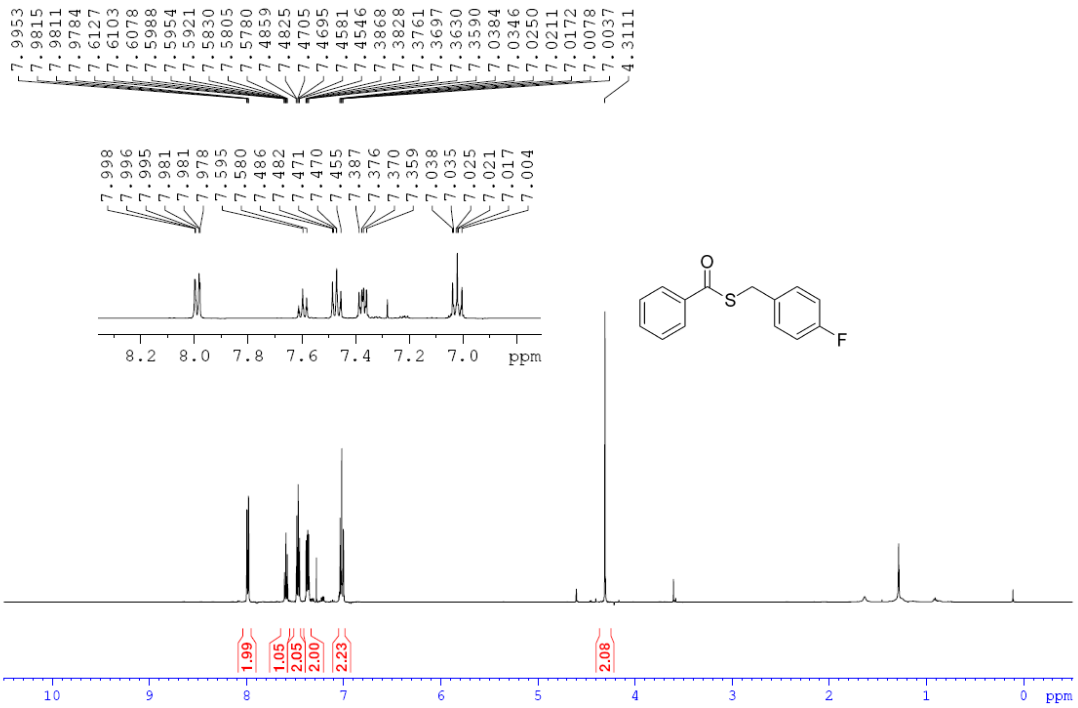
^{19}F NMR spectrum (470 MHz, $CDCl_3$) of **3d**



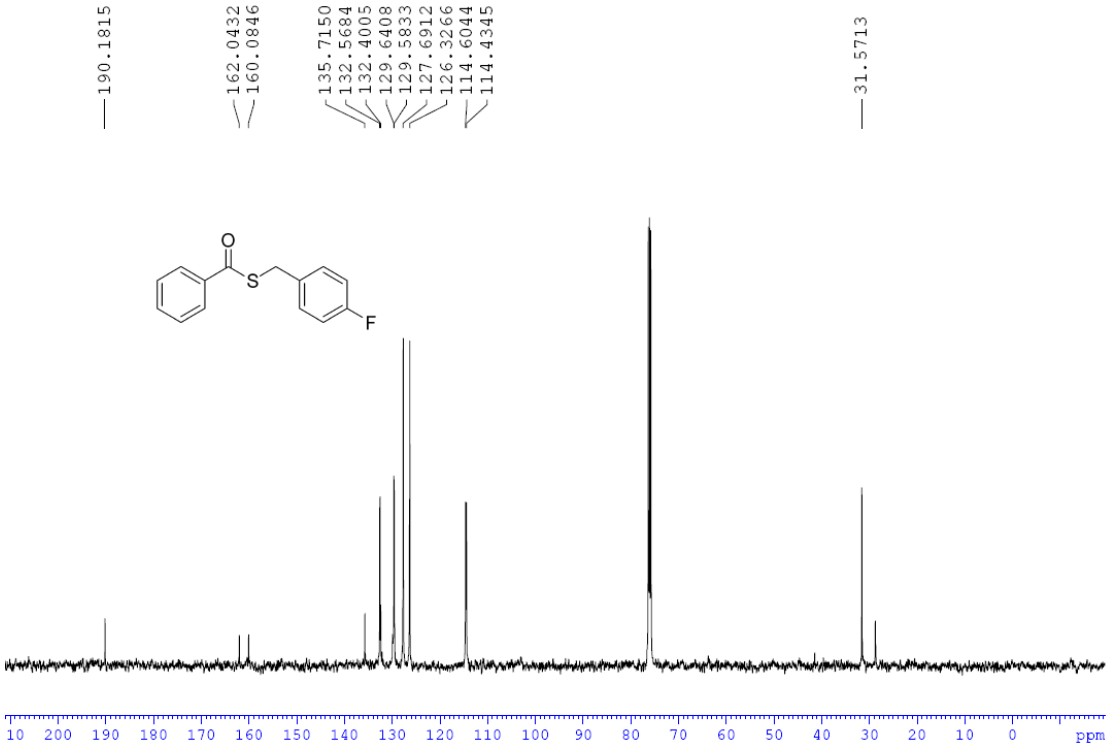
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3e**



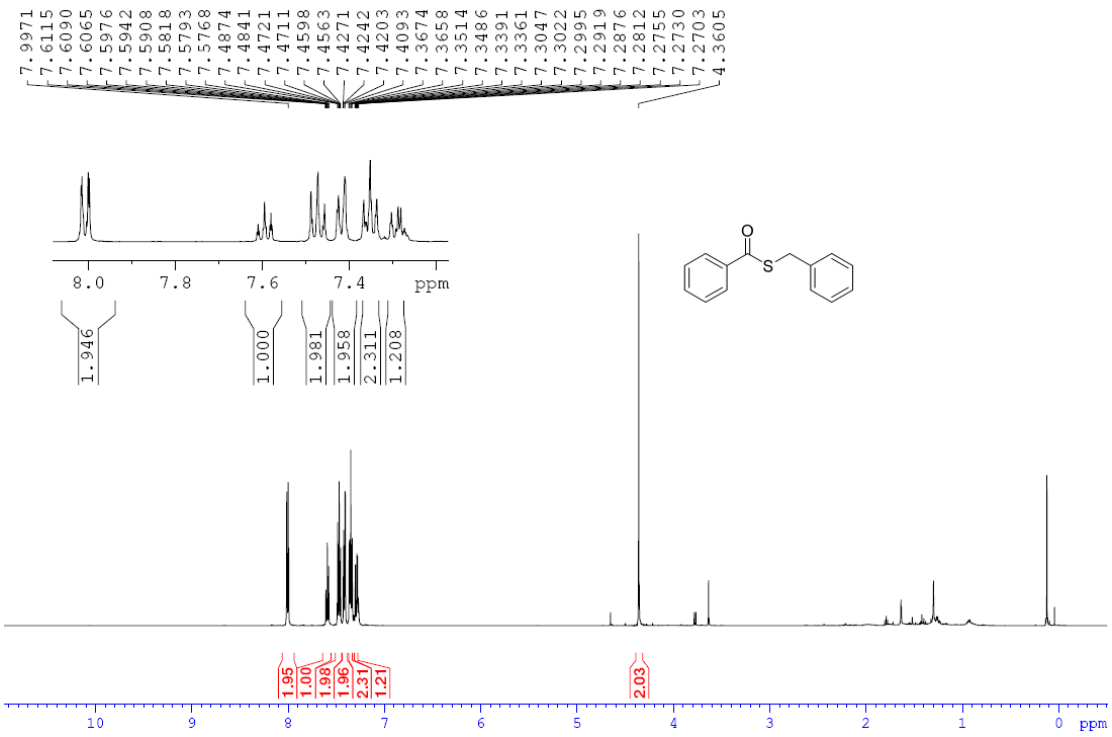
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3e**



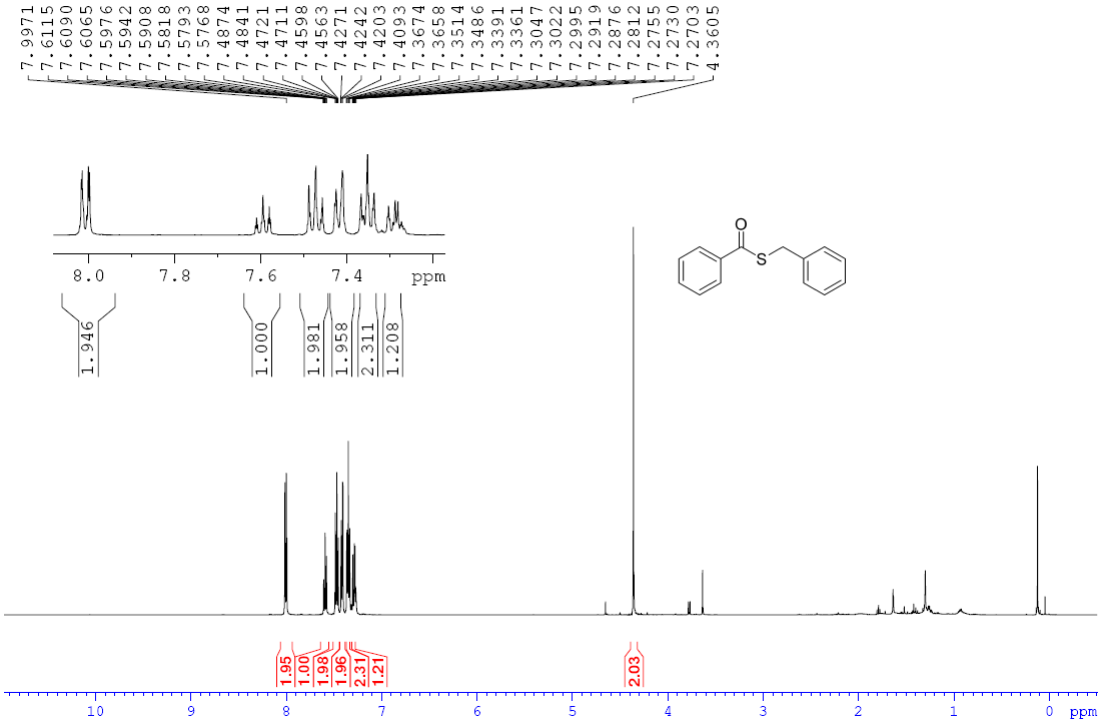
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3f**



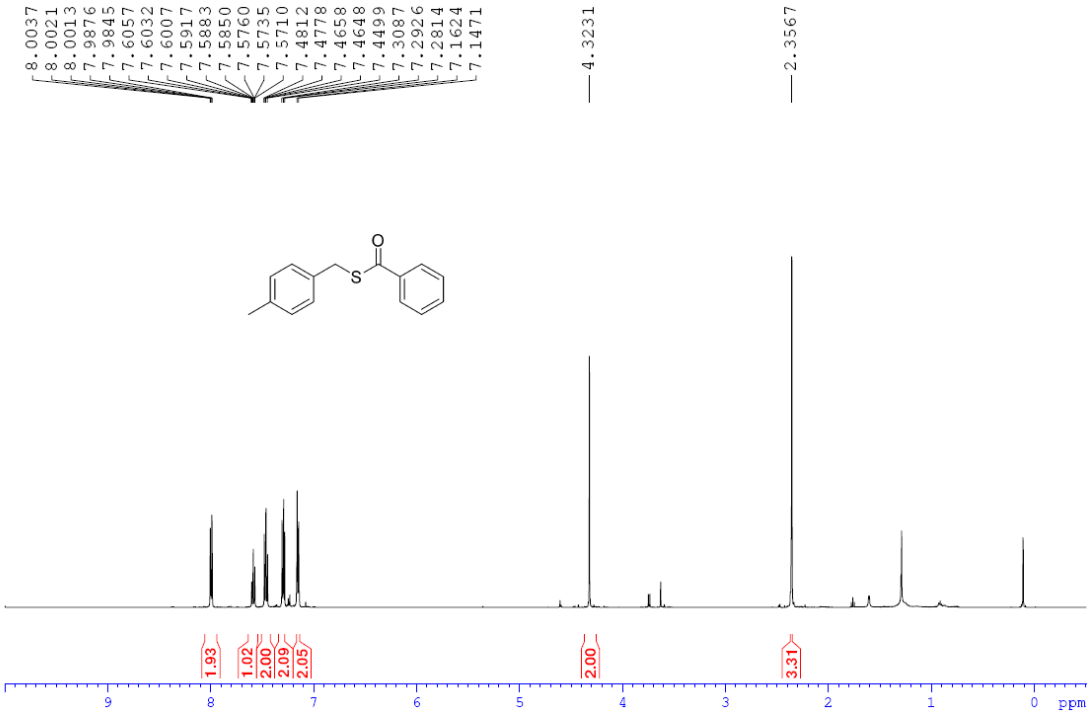
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3f**



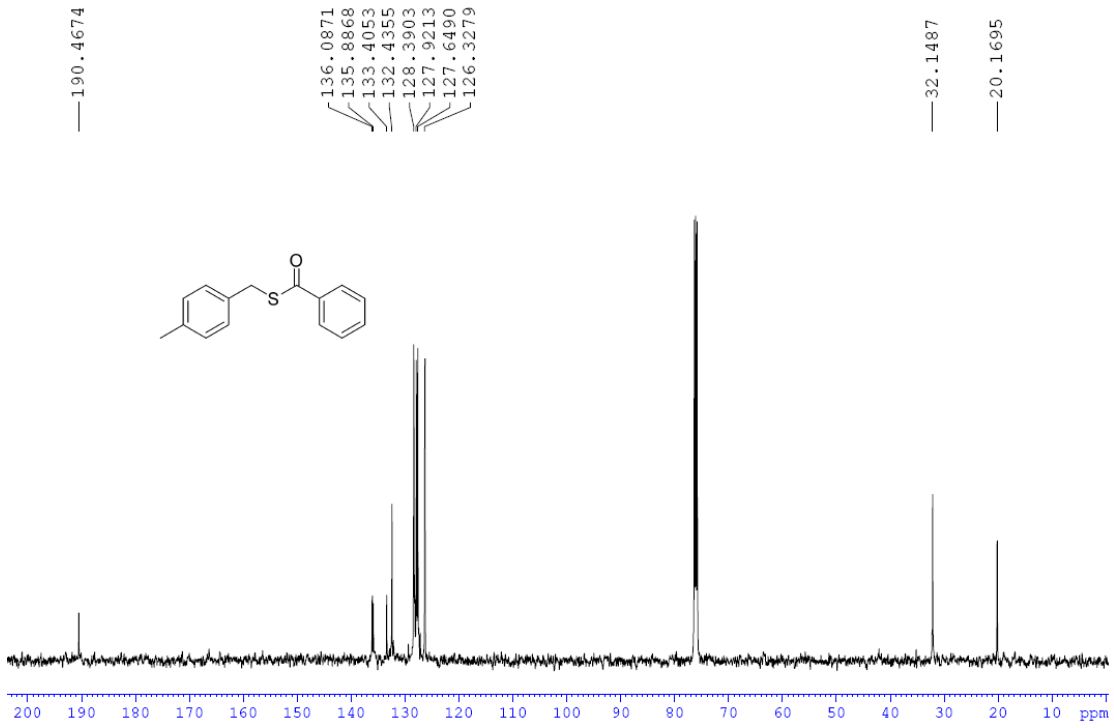
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3g**



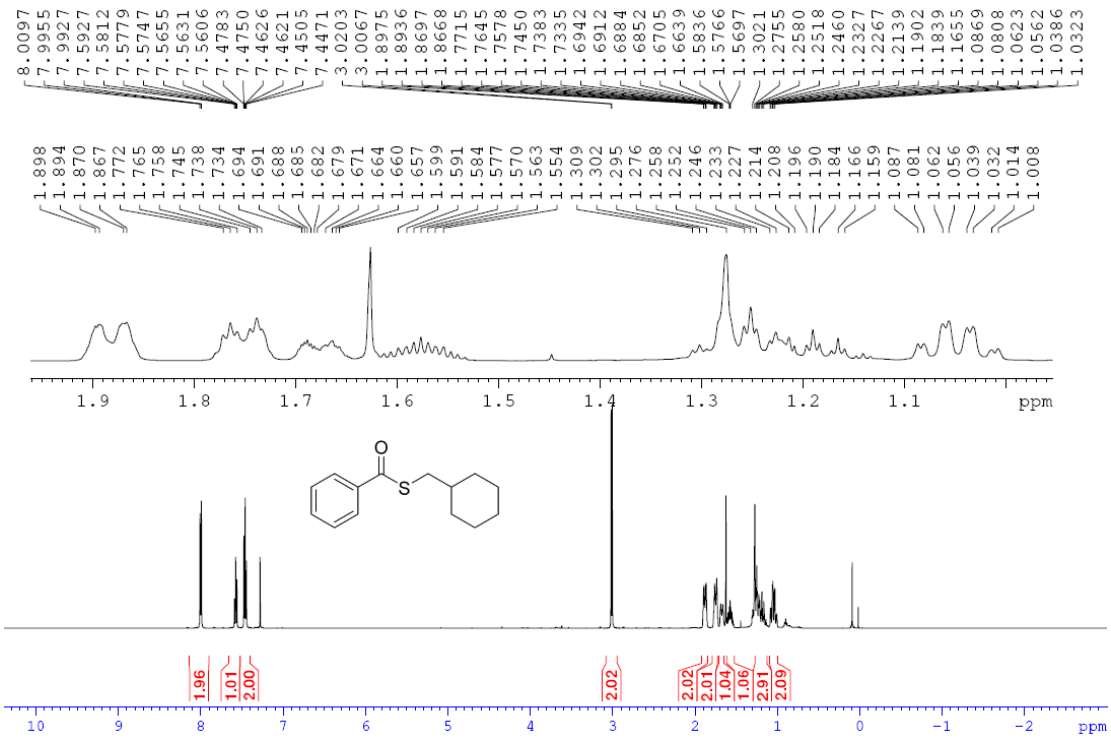
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3g**



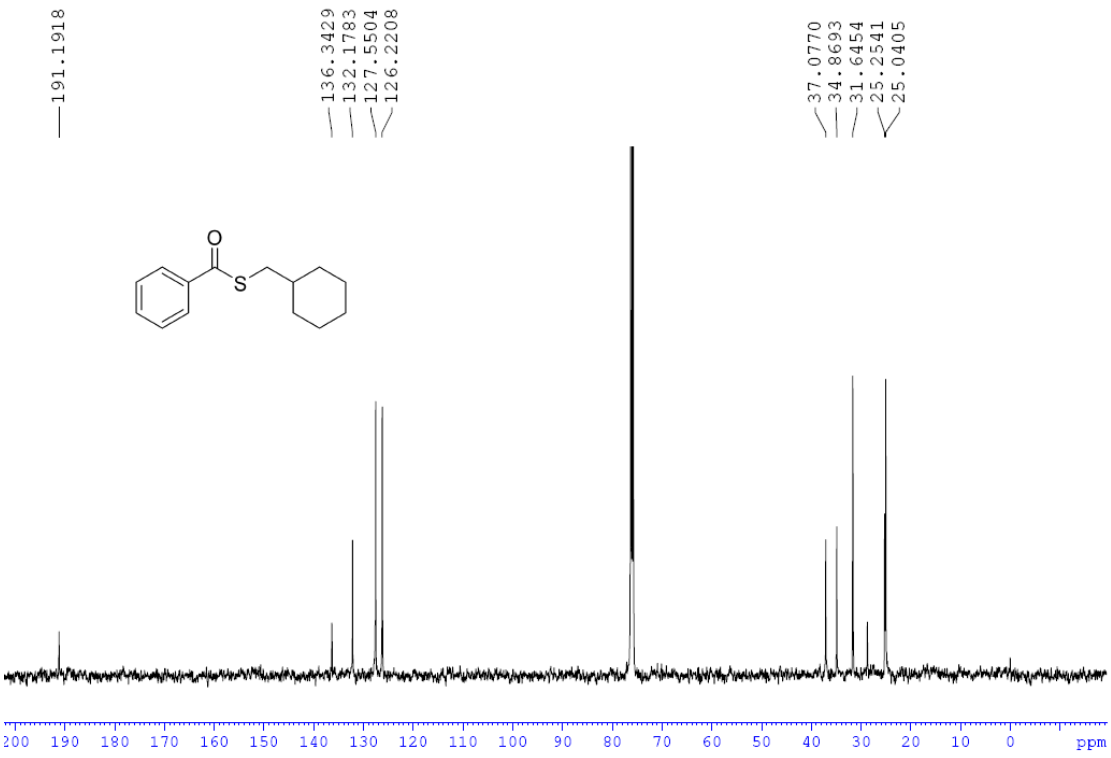
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3h**



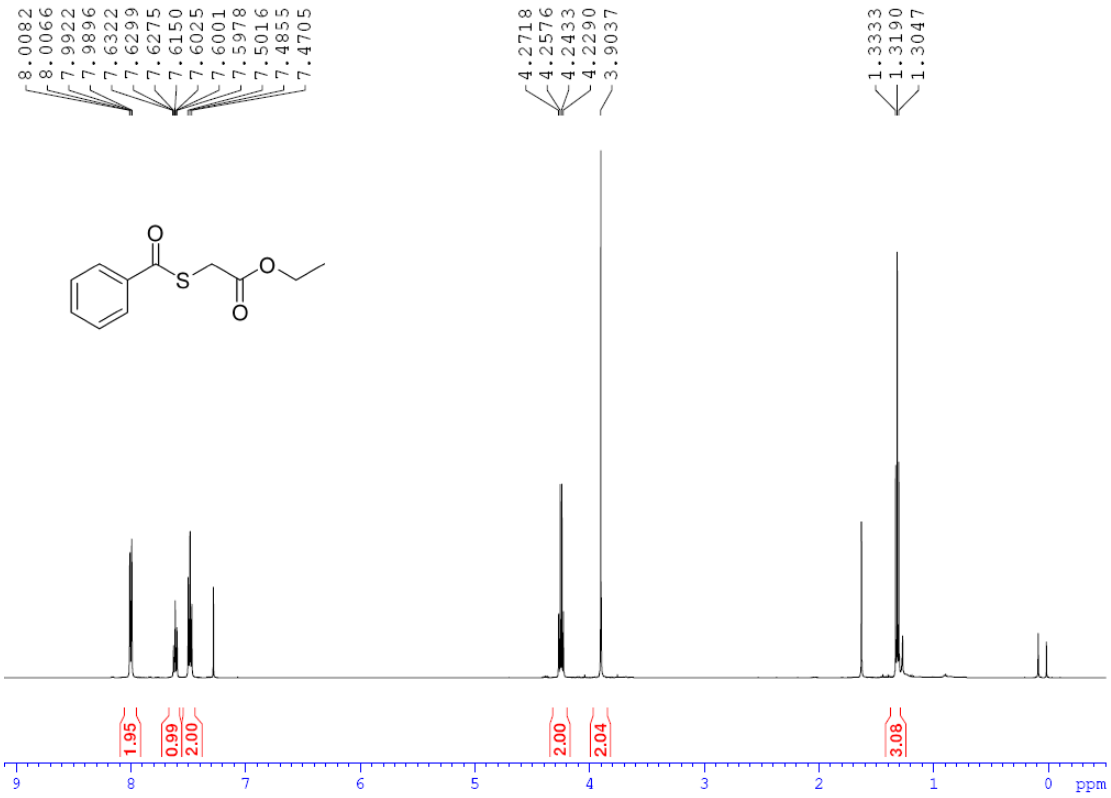
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **3h**



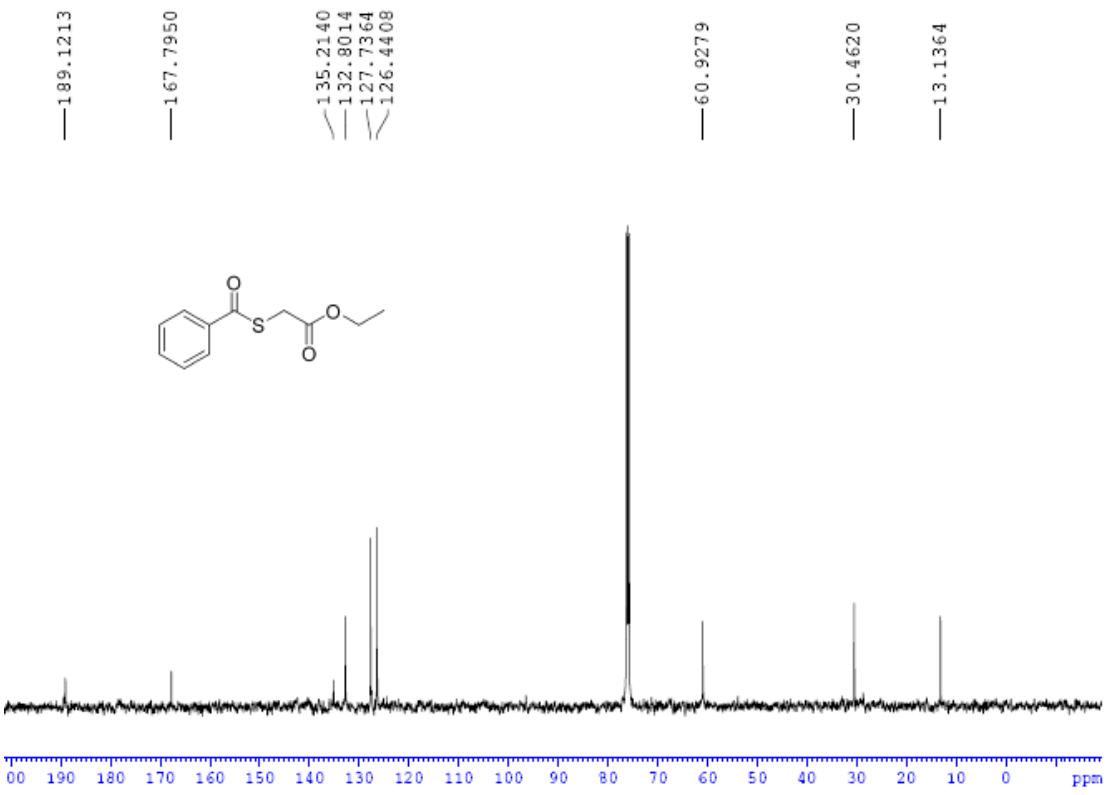
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3i**



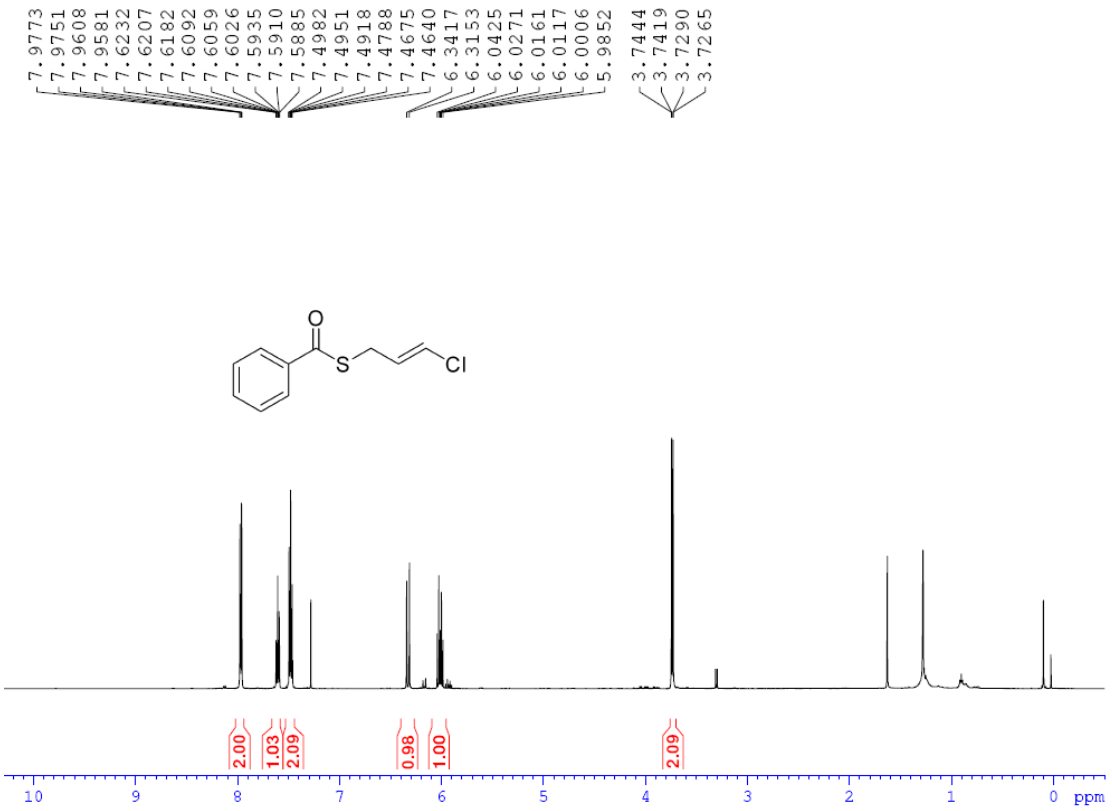
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3i**



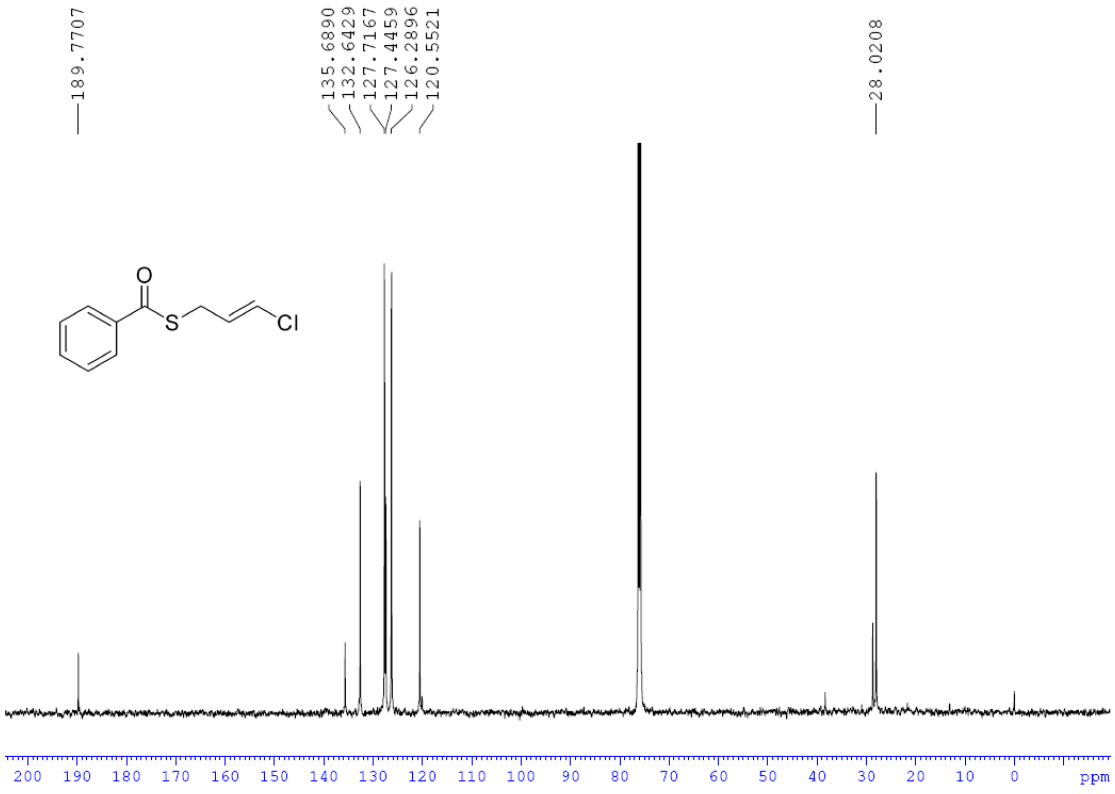
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3k**



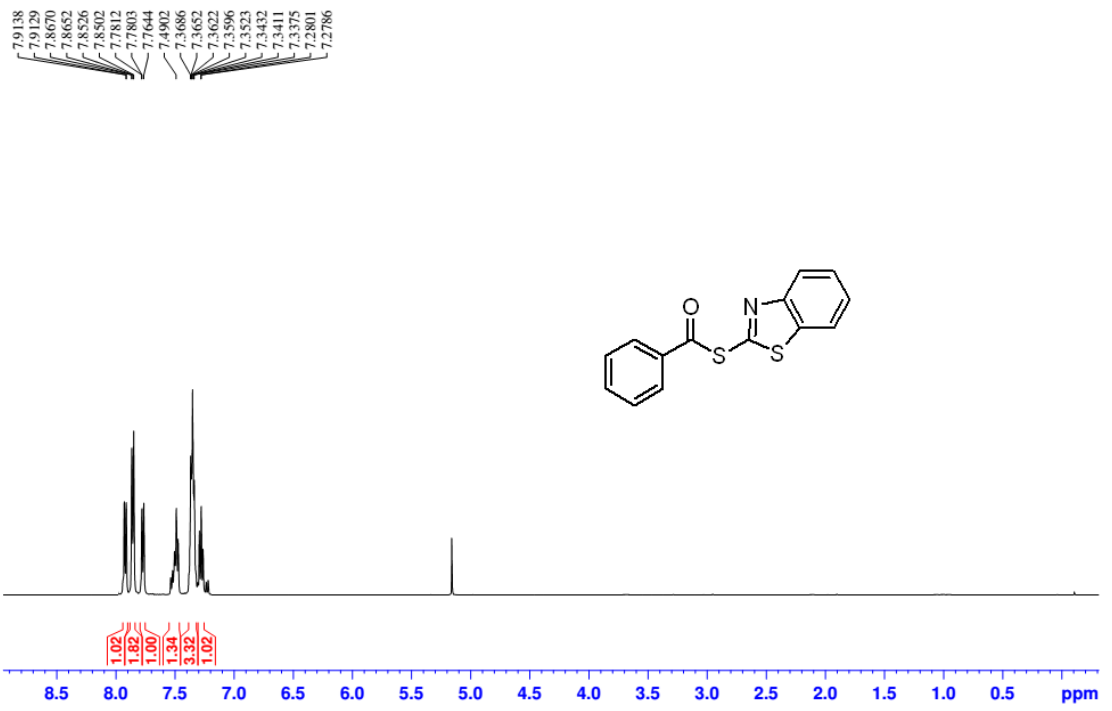
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3k**



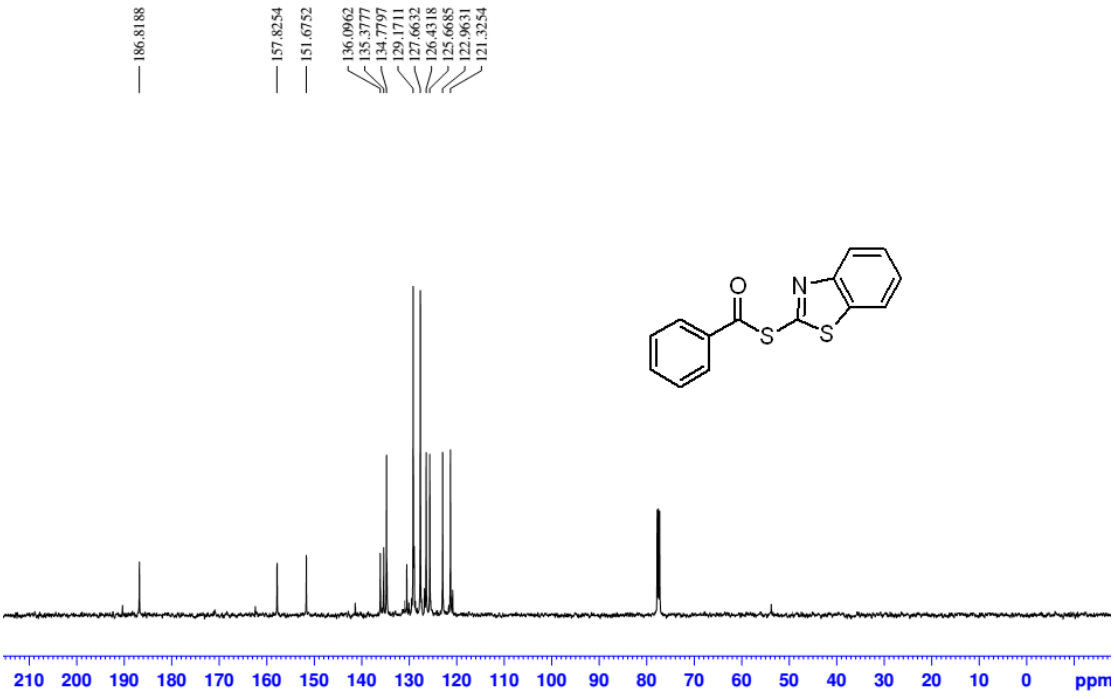
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3m**



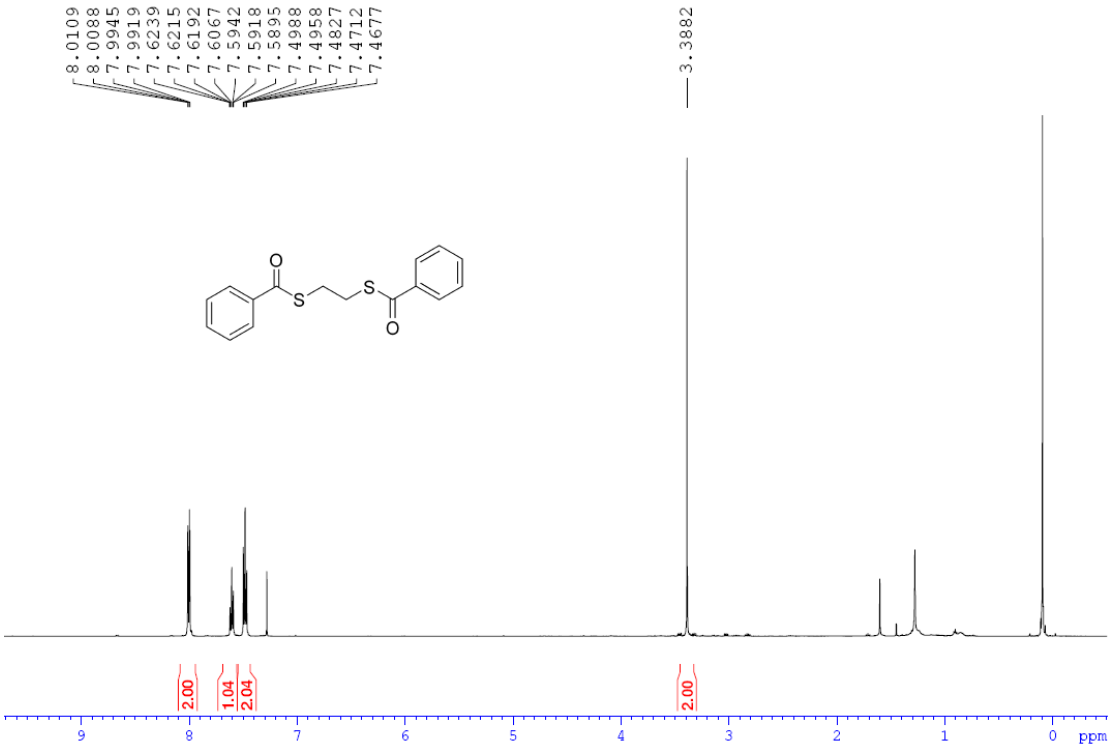
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3m**



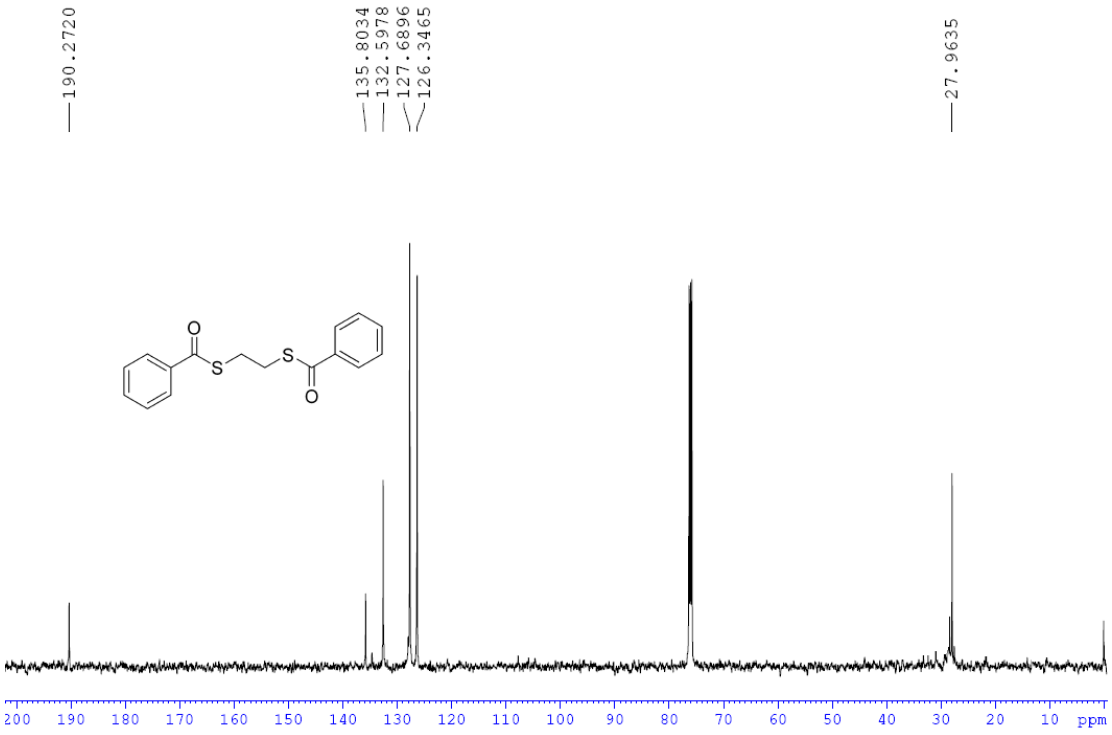
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3n**



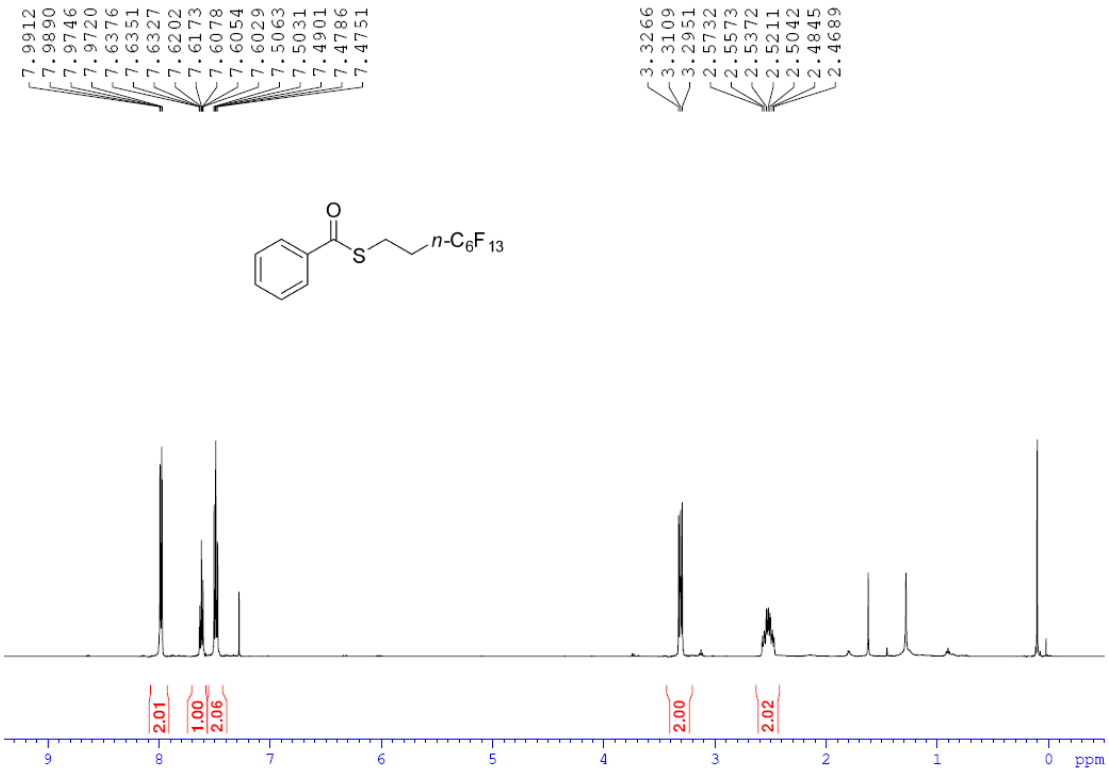
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3n**



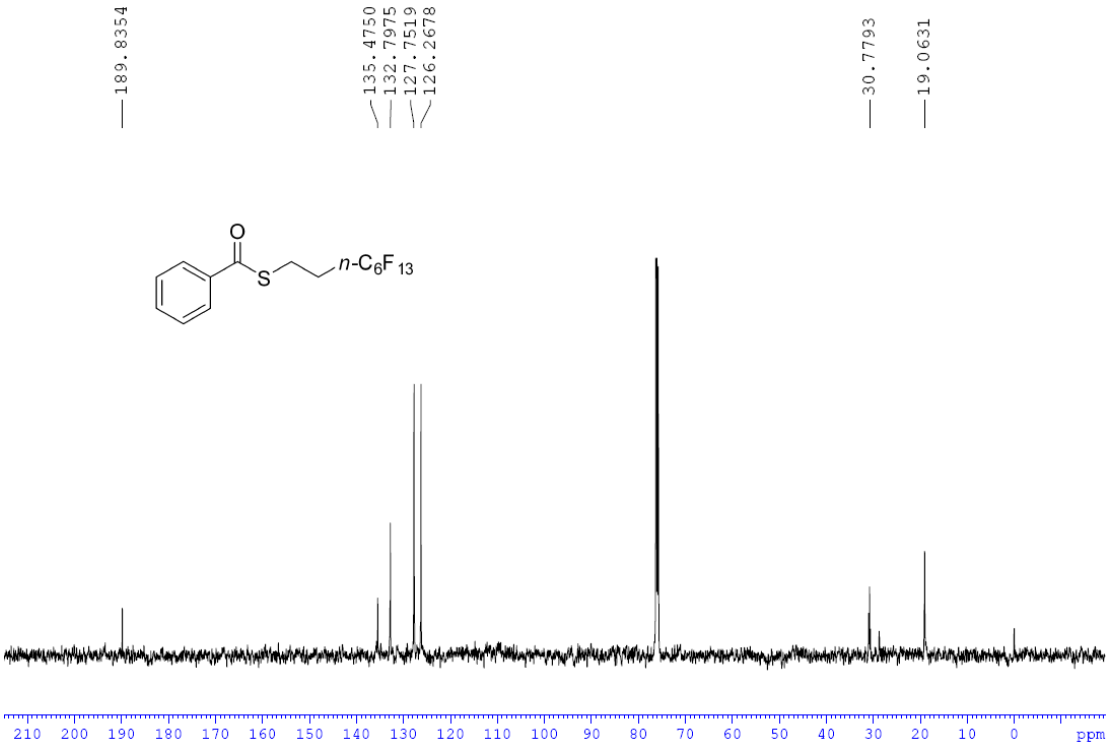
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3o**



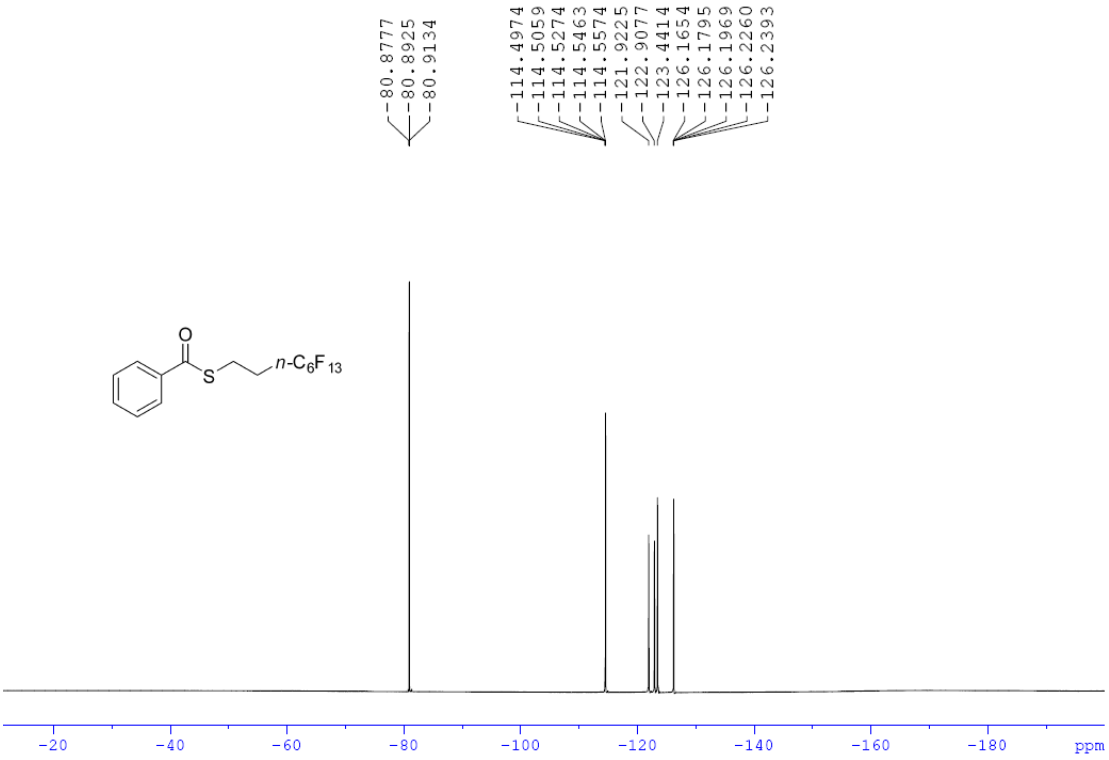
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3o**



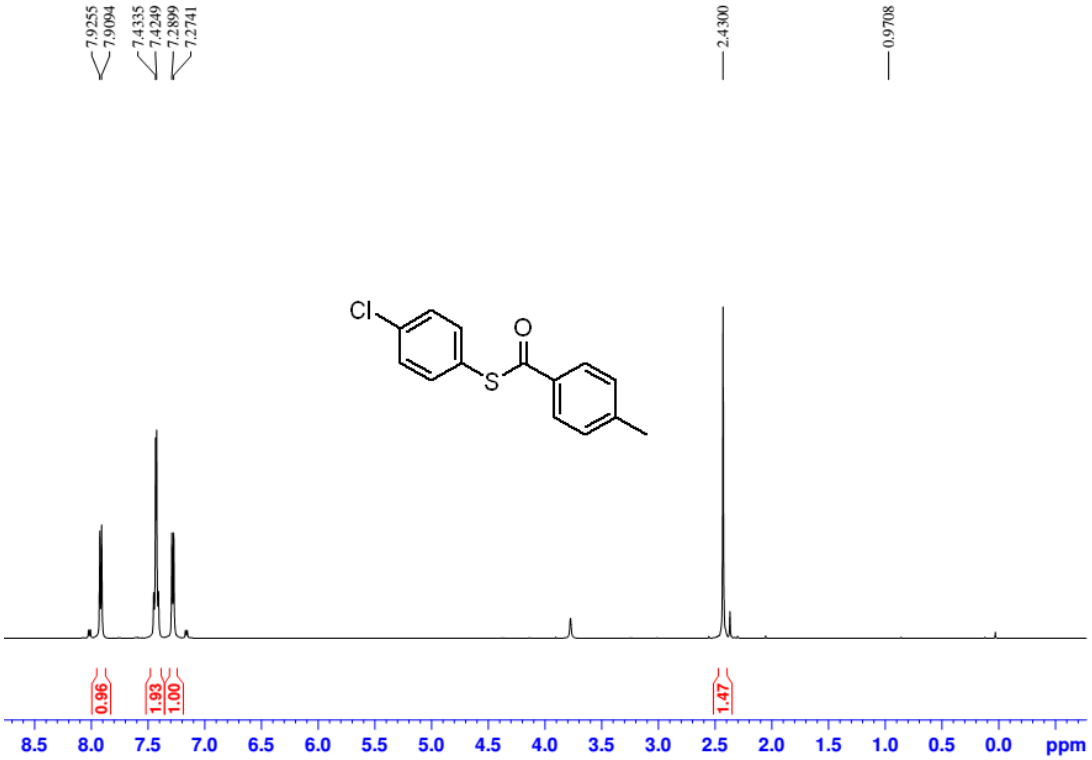
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3p**



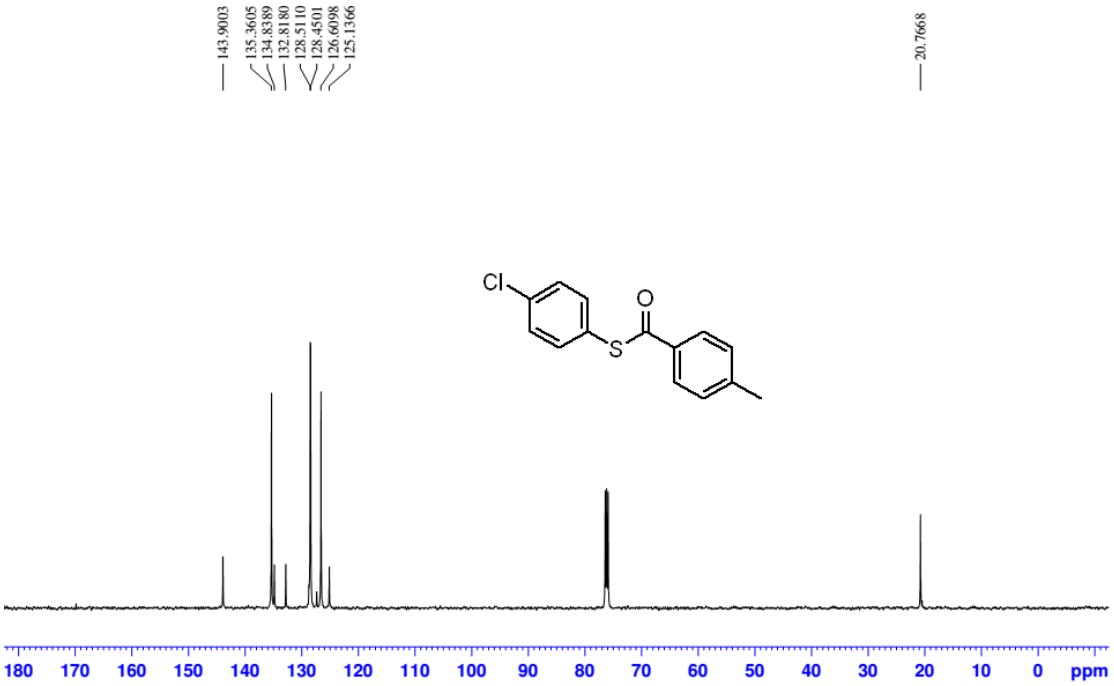
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3p**



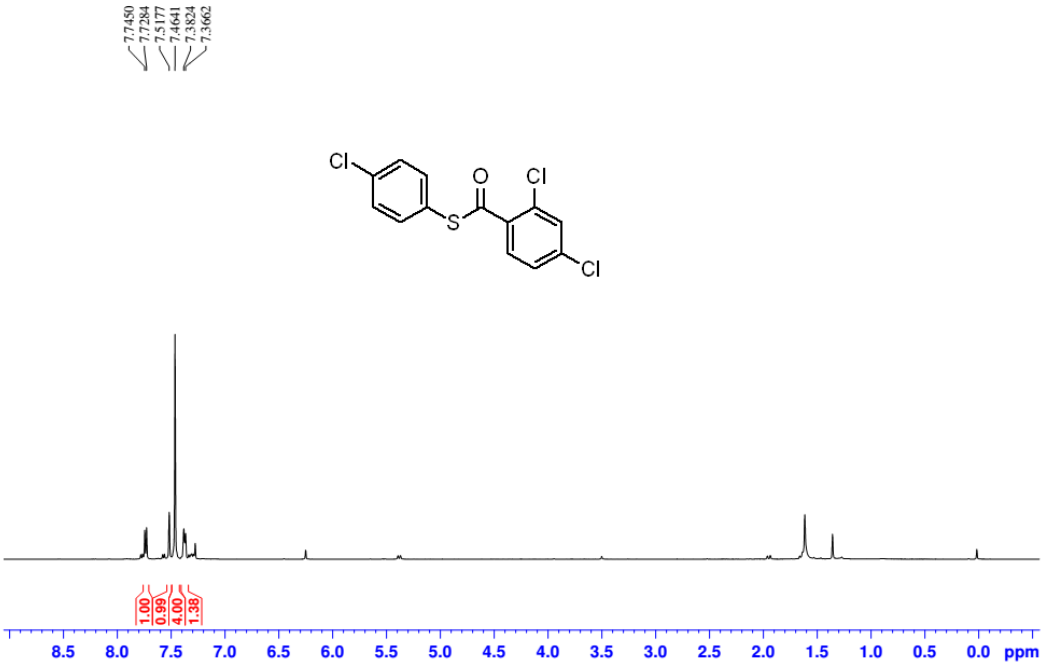
^{19}F NMR spectrum (470 MHz, $CDCl_3$) of **3p**



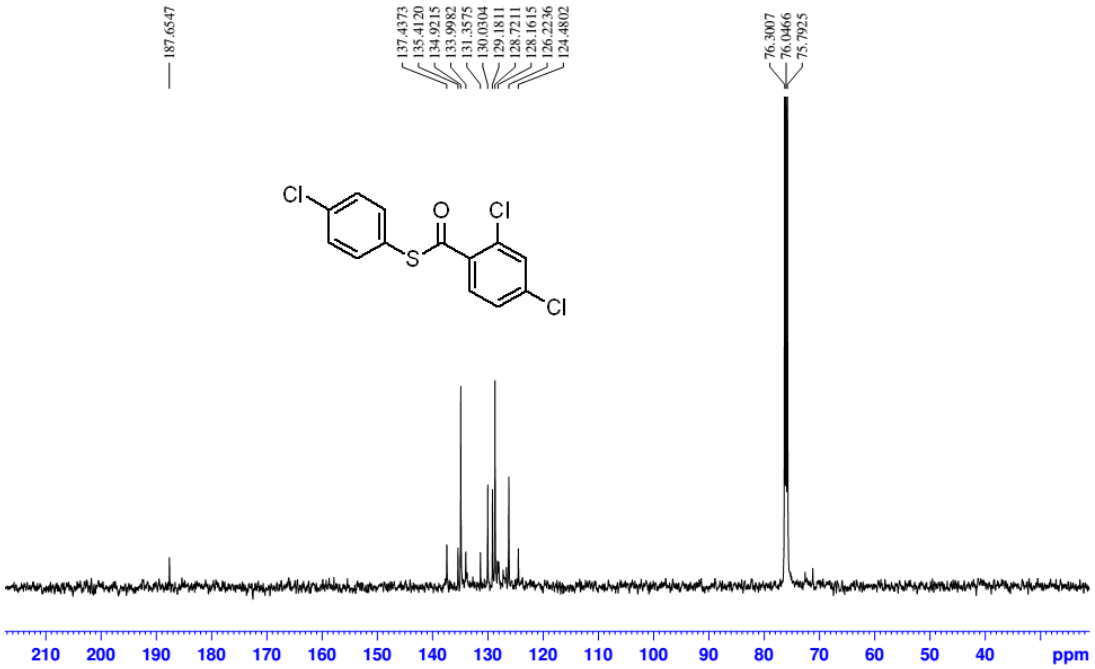
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4a**



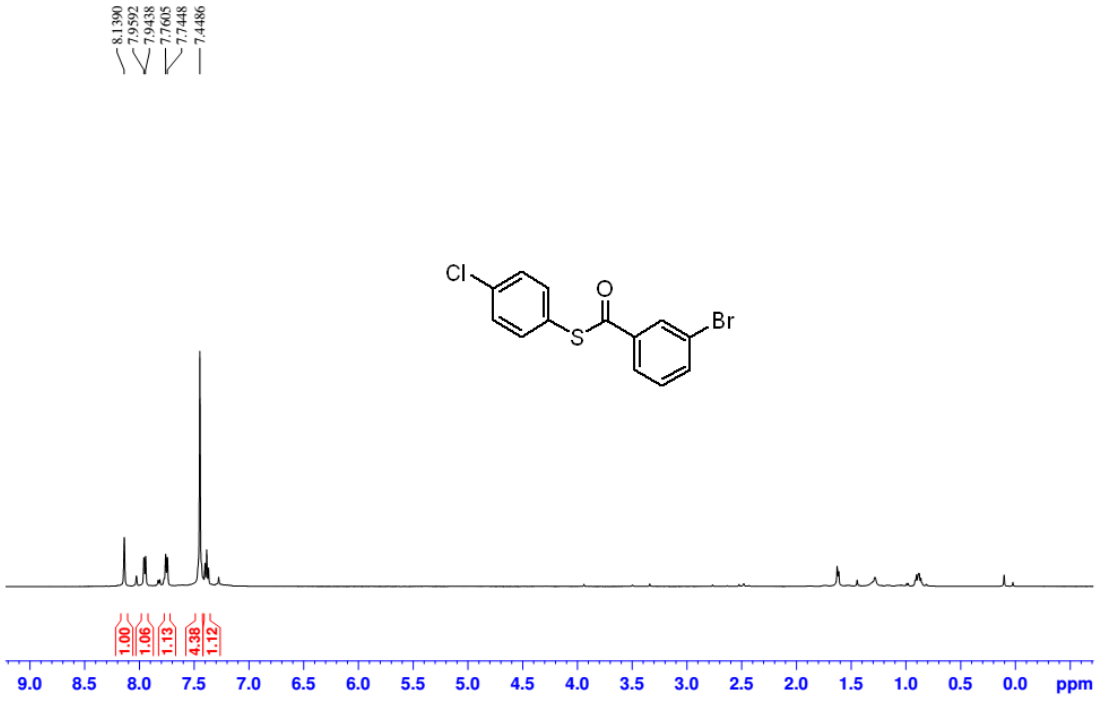
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **4a**



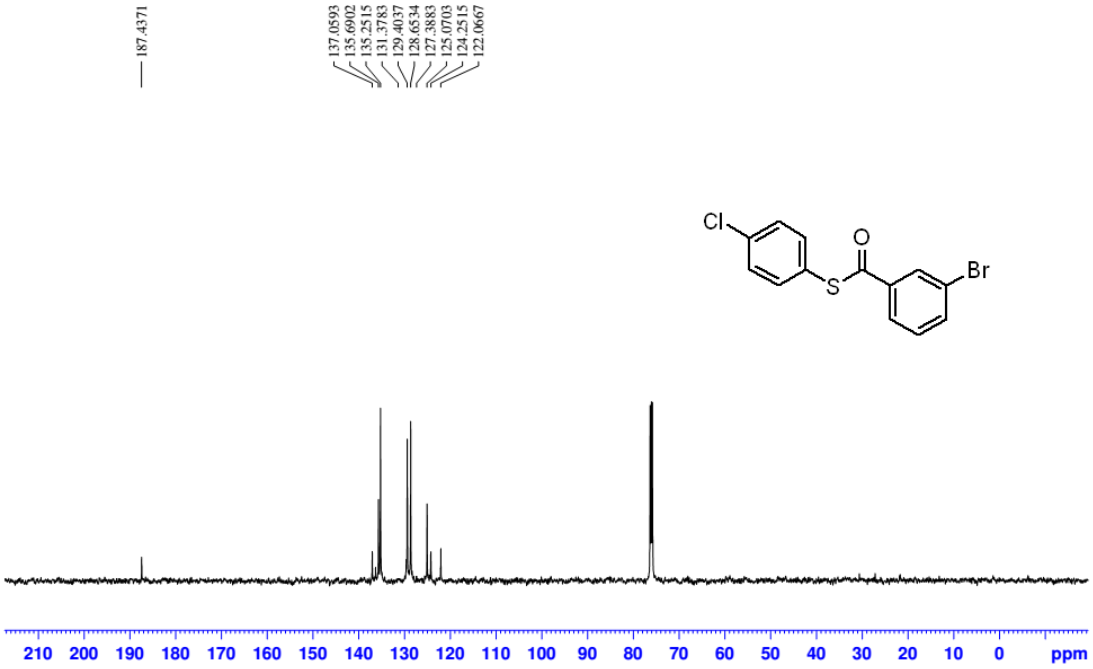
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4c**



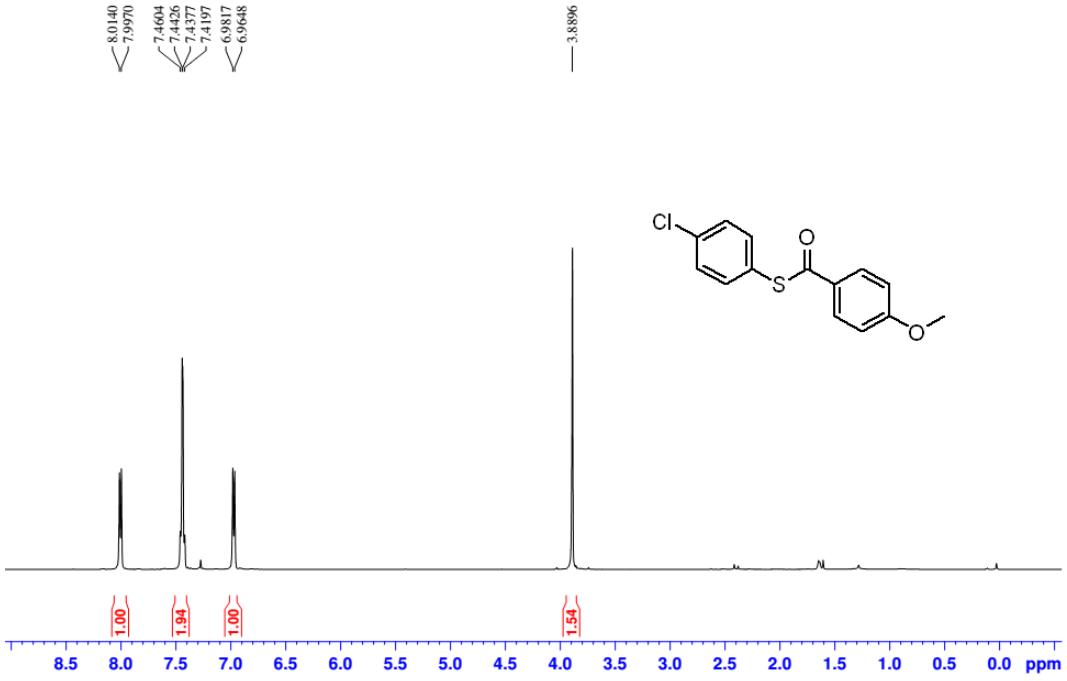
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **4c**



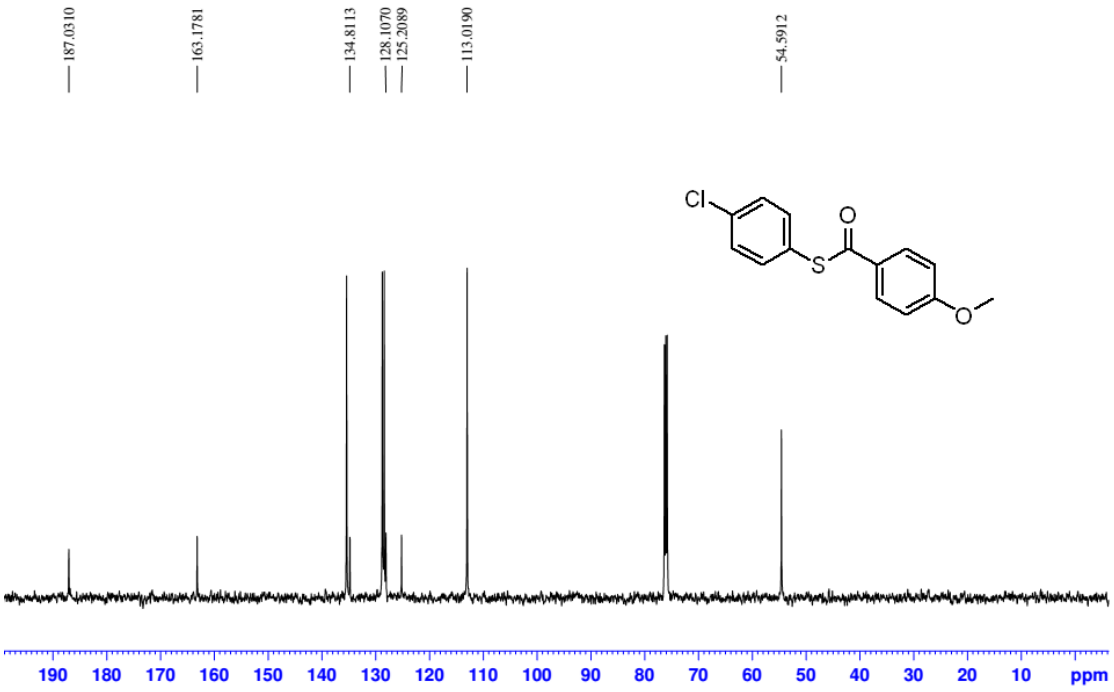
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4d**



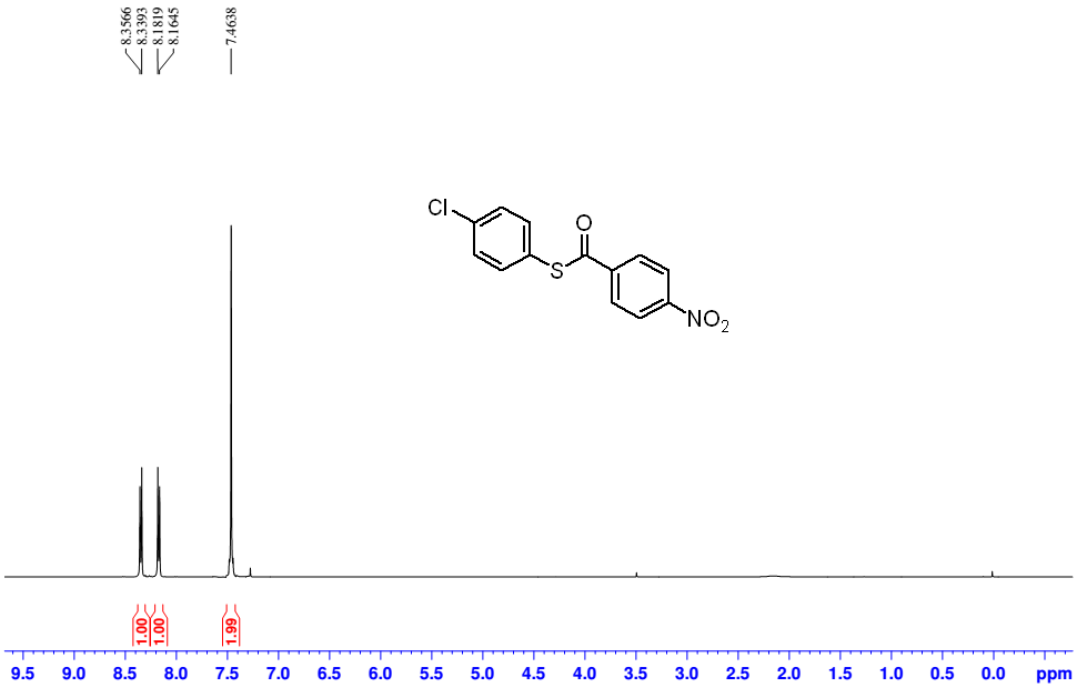
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **4d**



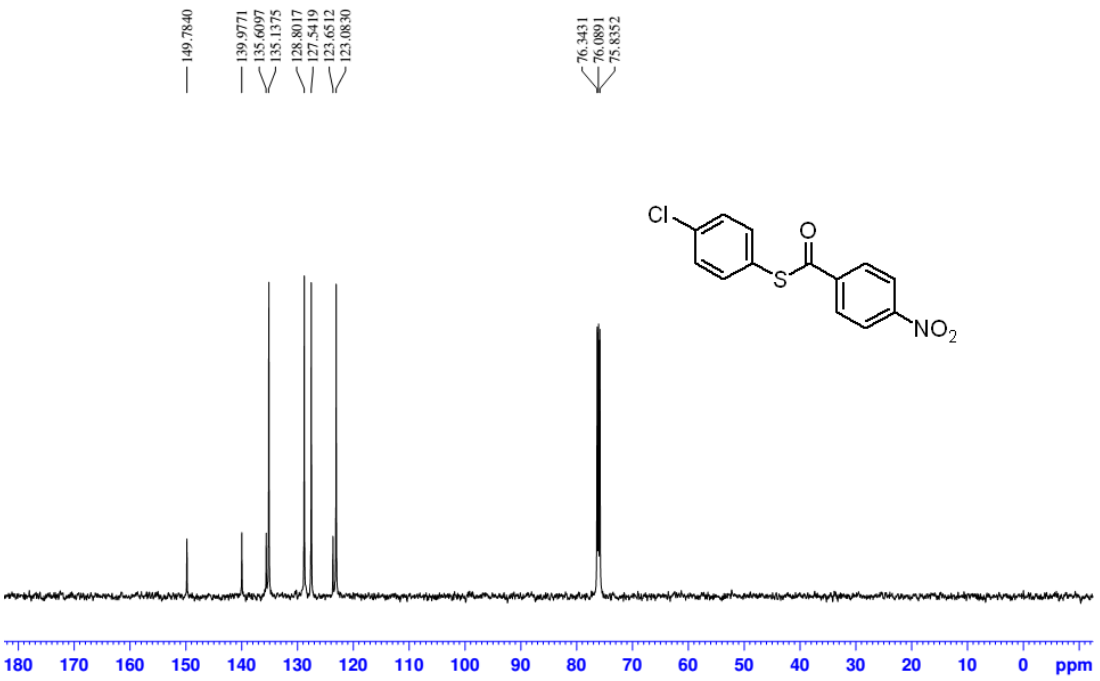
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4e**



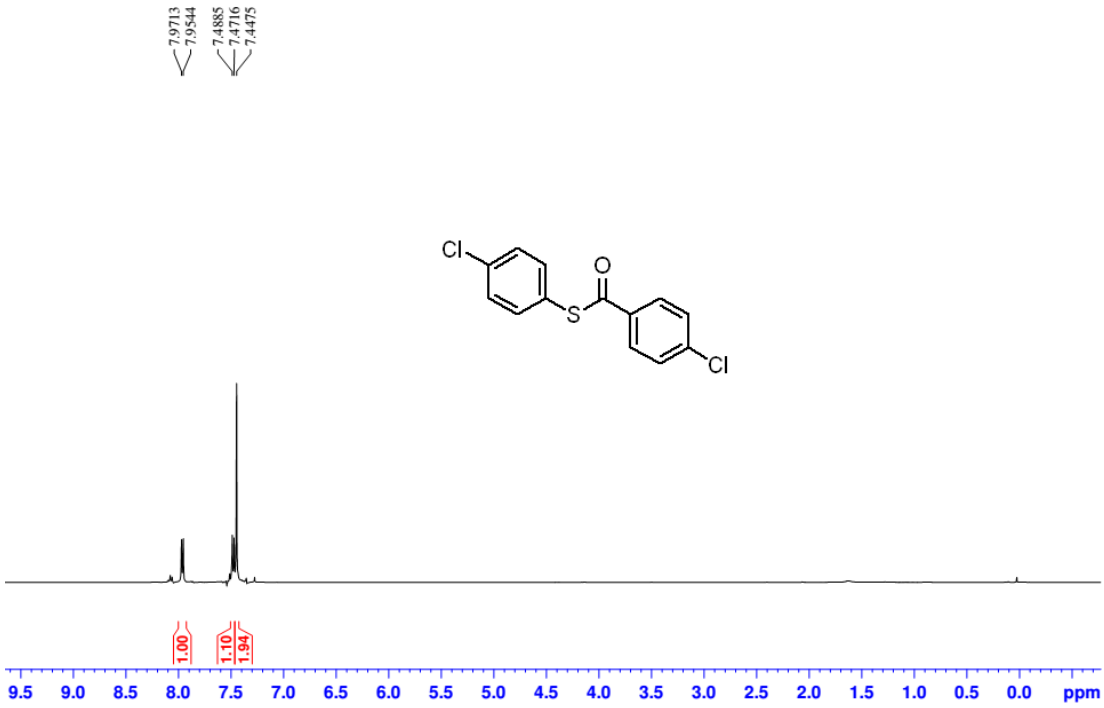
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **4e**



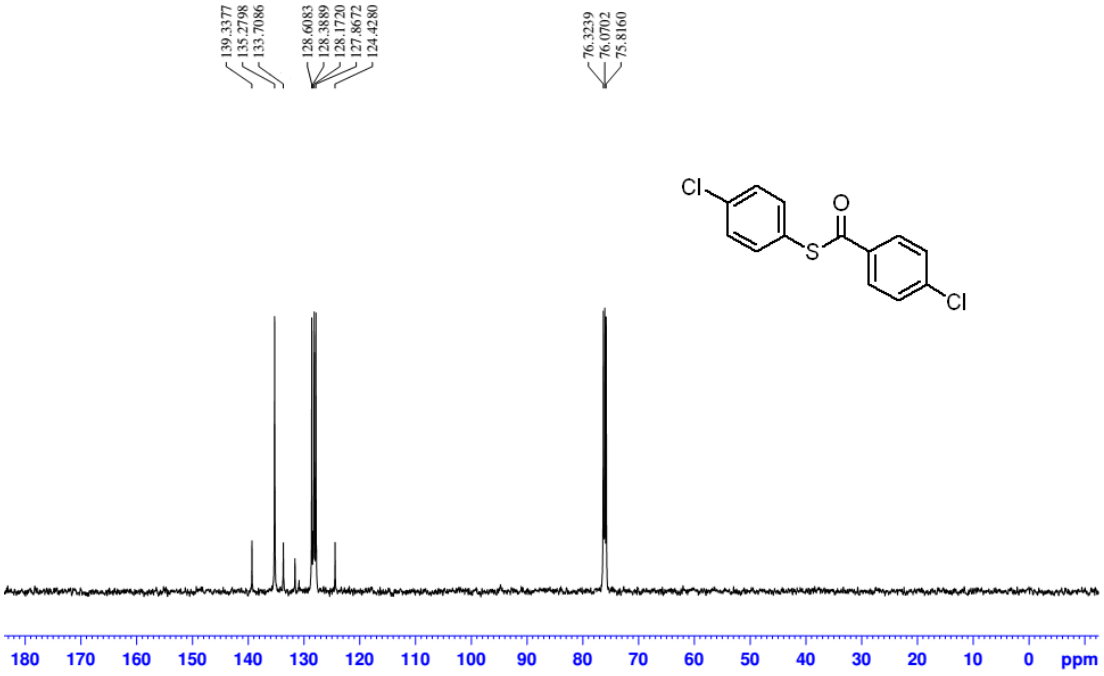
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4g**



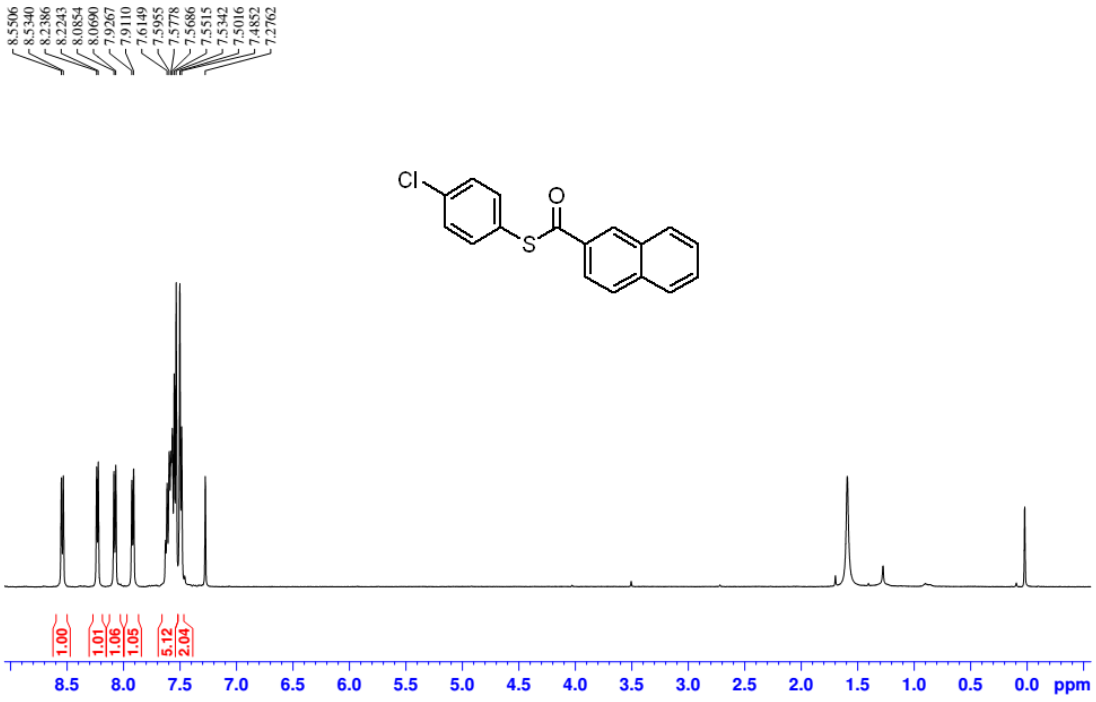
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **4g**



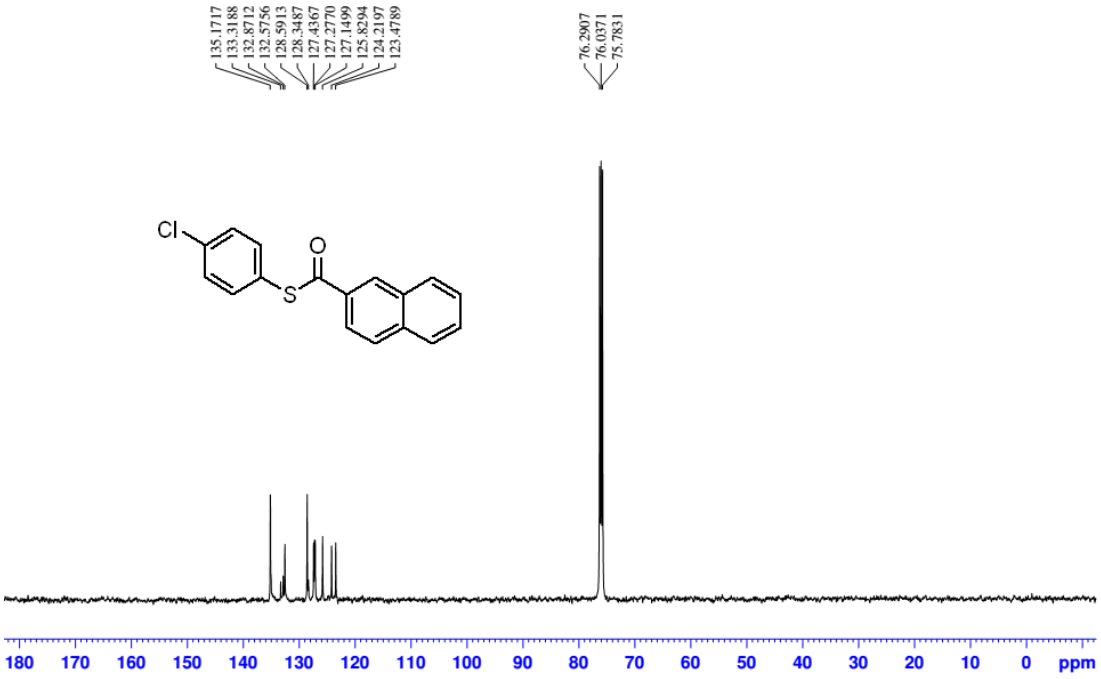
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4h**



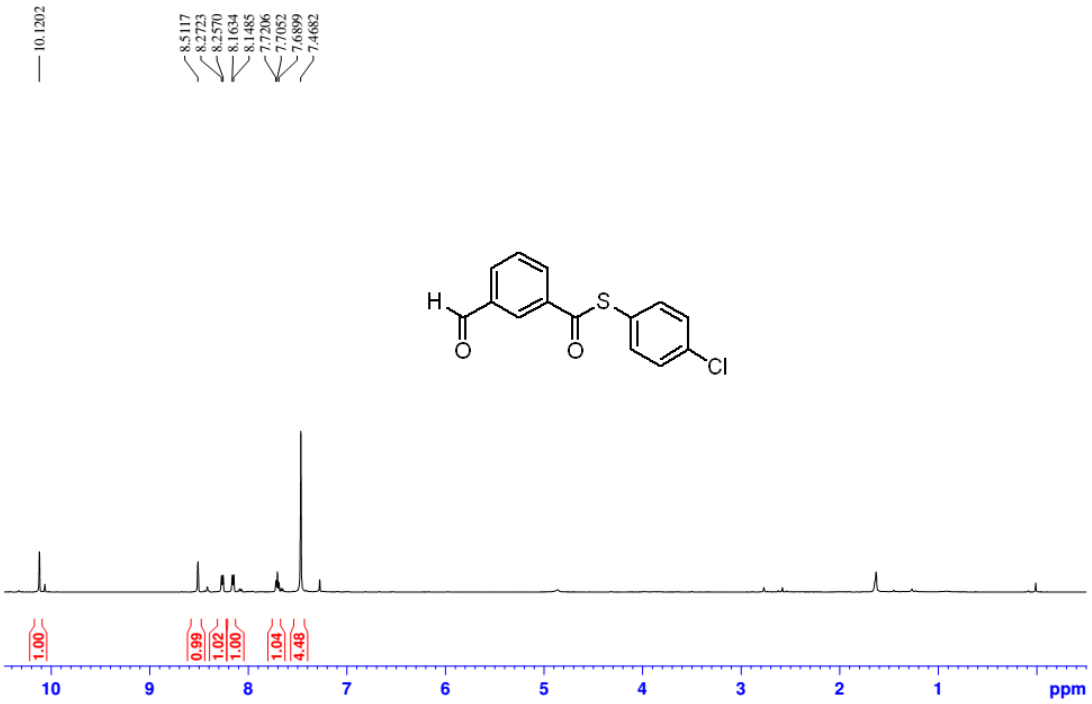
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **4h**



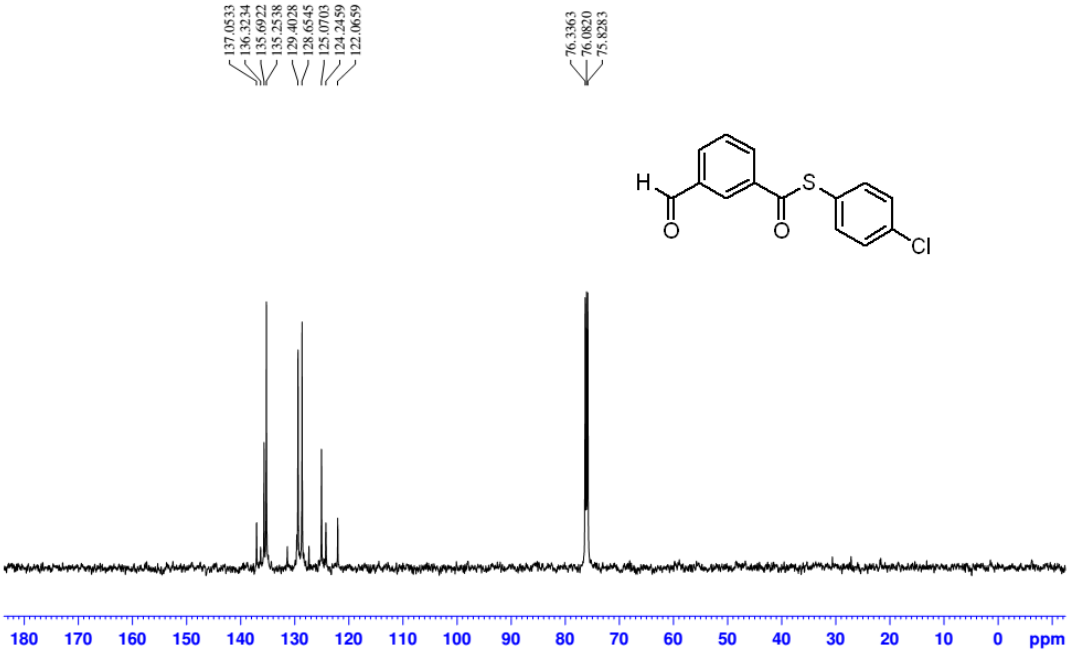
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4l**



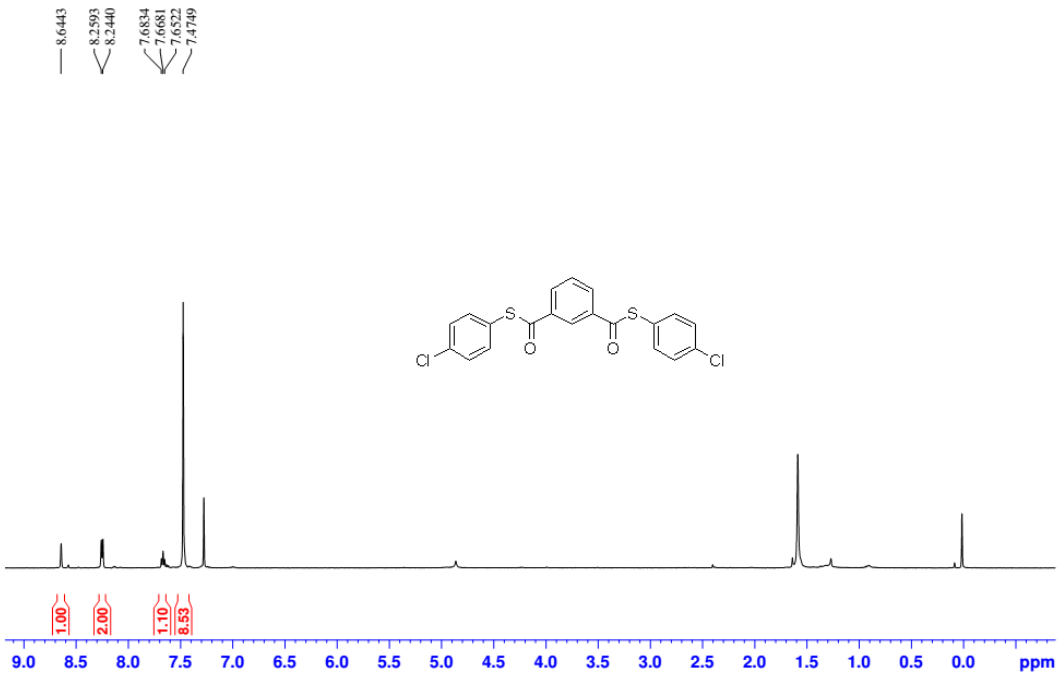
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **4l**



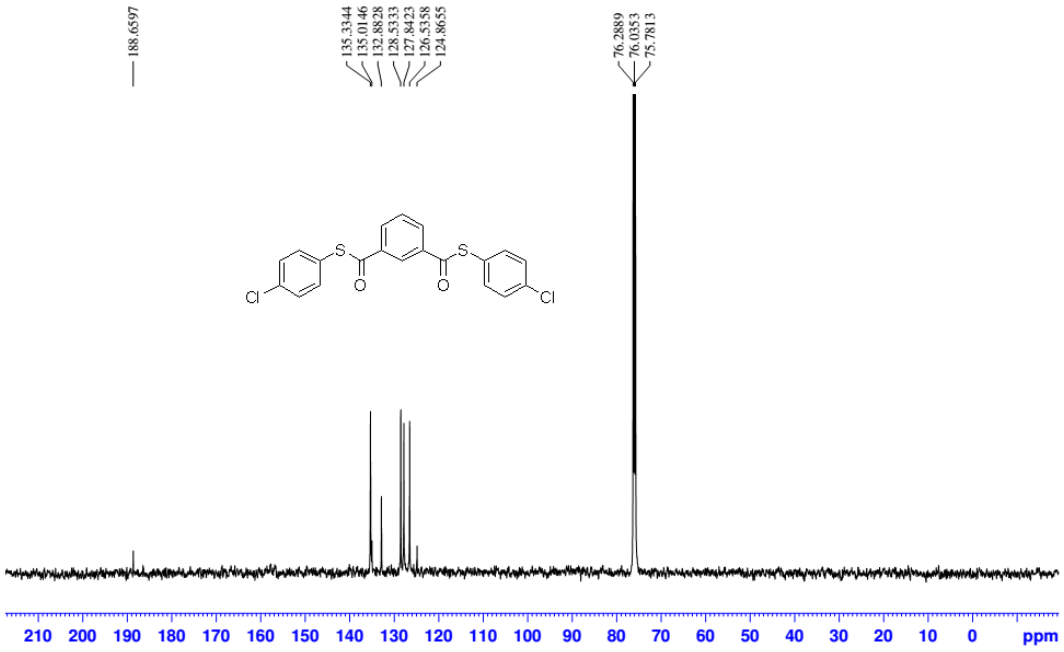
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4o'**



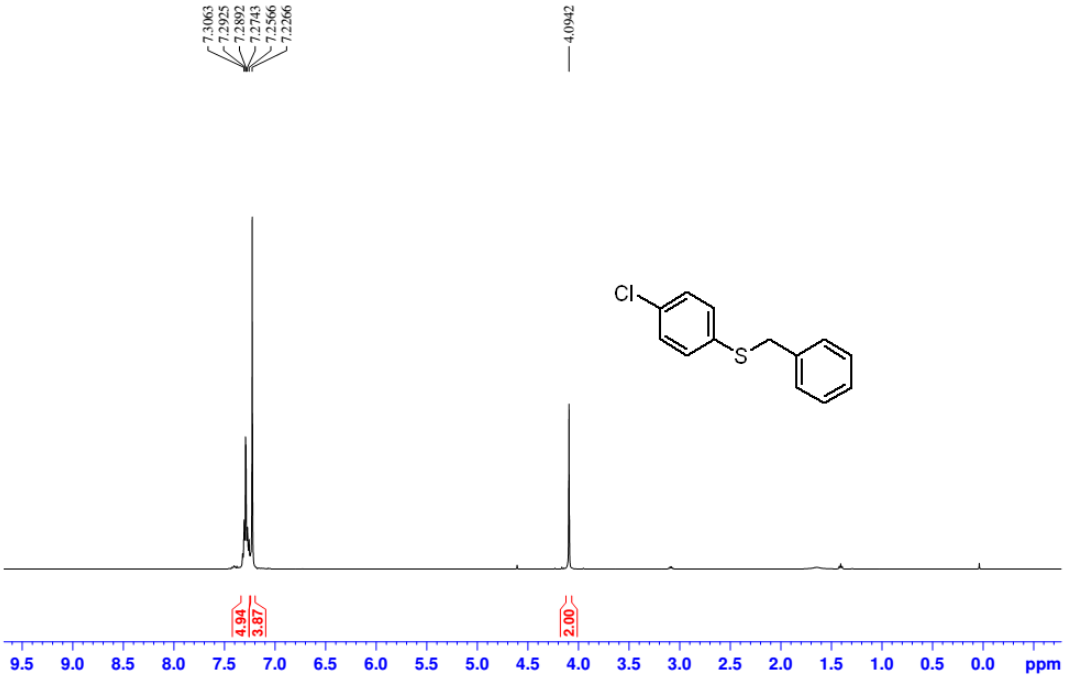
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **4o'**



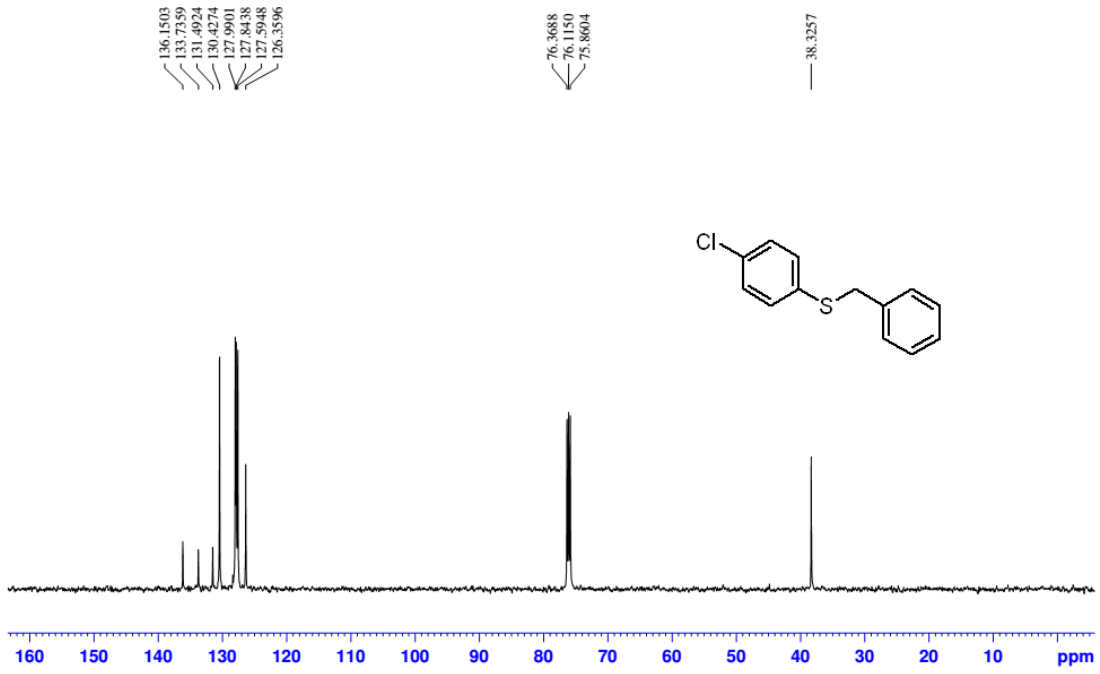
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4o**



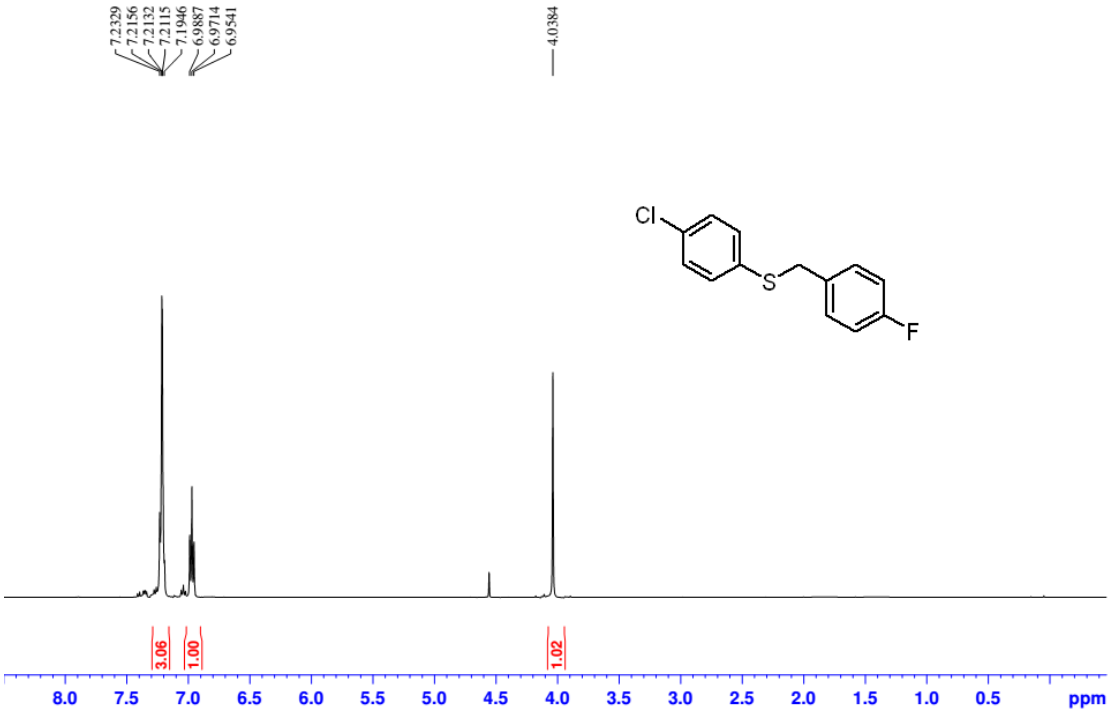
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **4o**



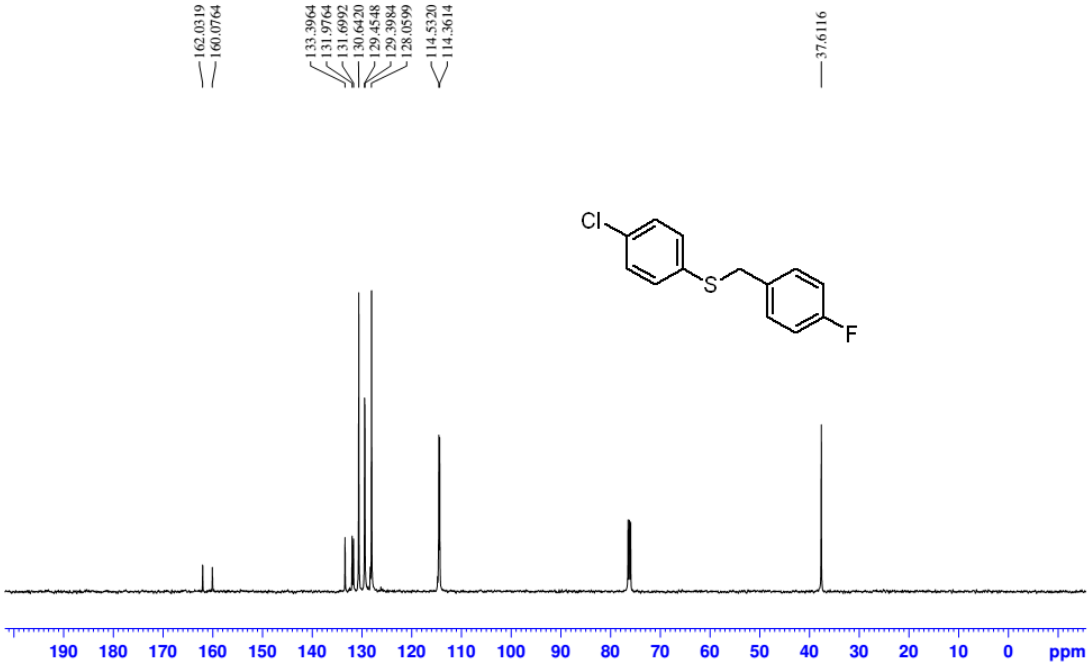
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **5a**



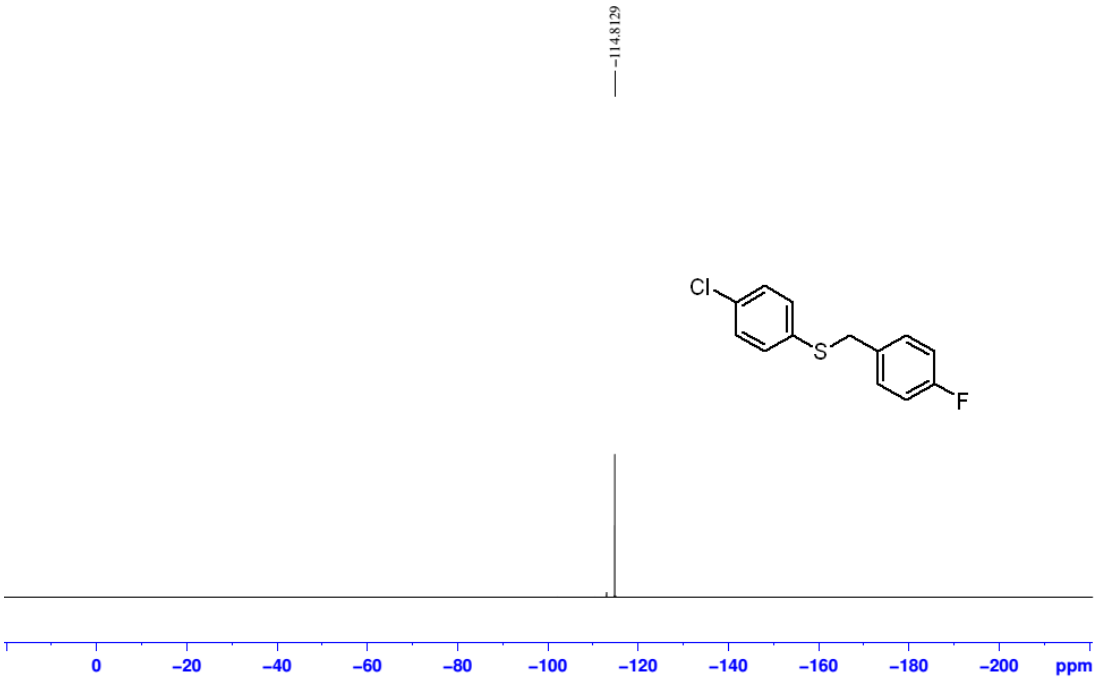
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **5a**、



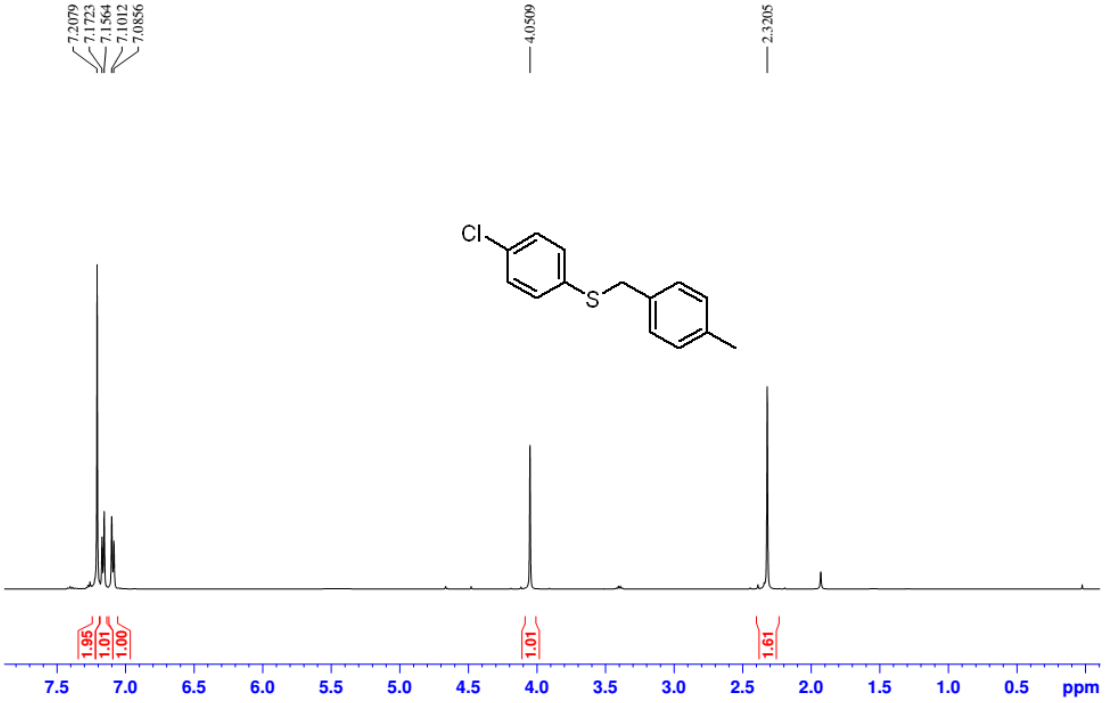
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **5b**



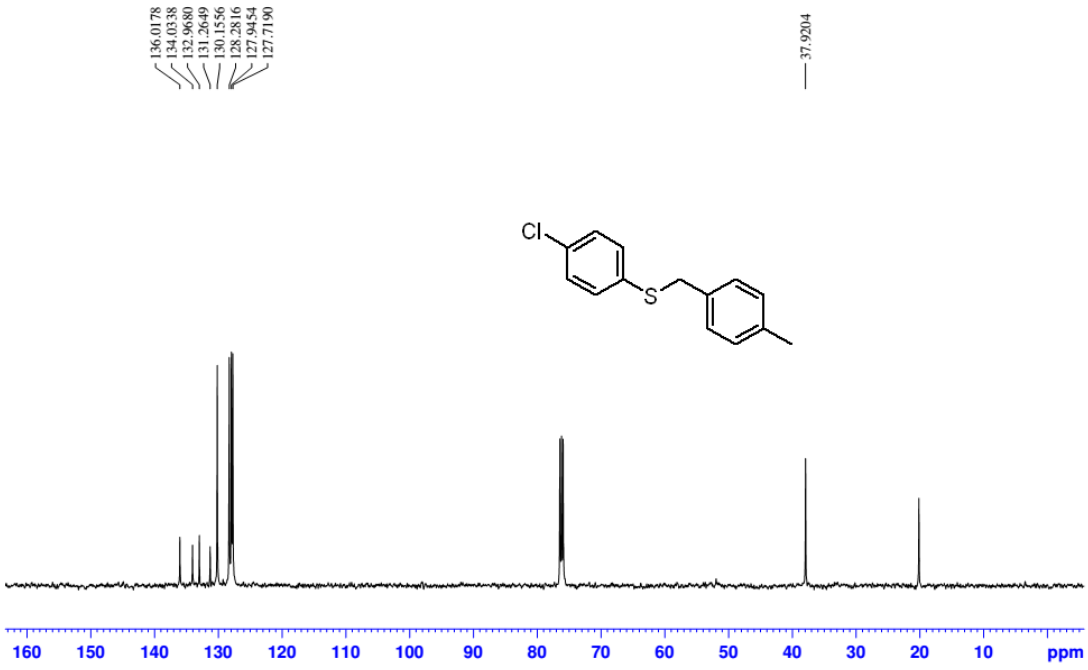
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **5b**



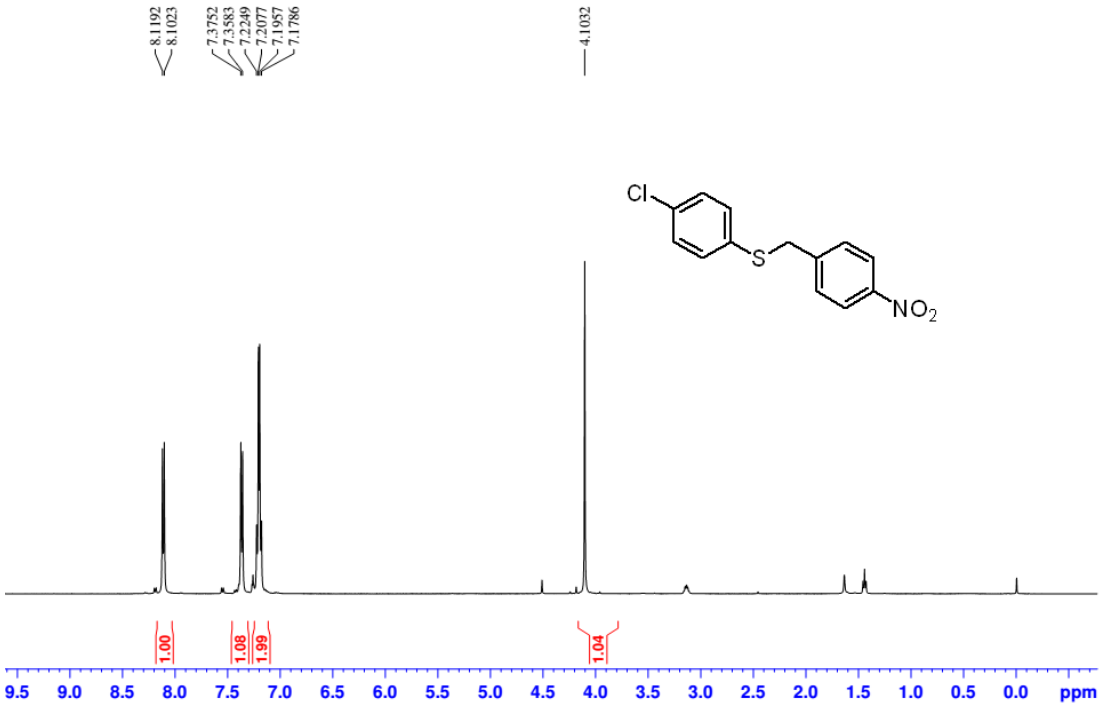
^{19} F NMR spectrum (470 MHz, $CDCl_3$) of **5b**



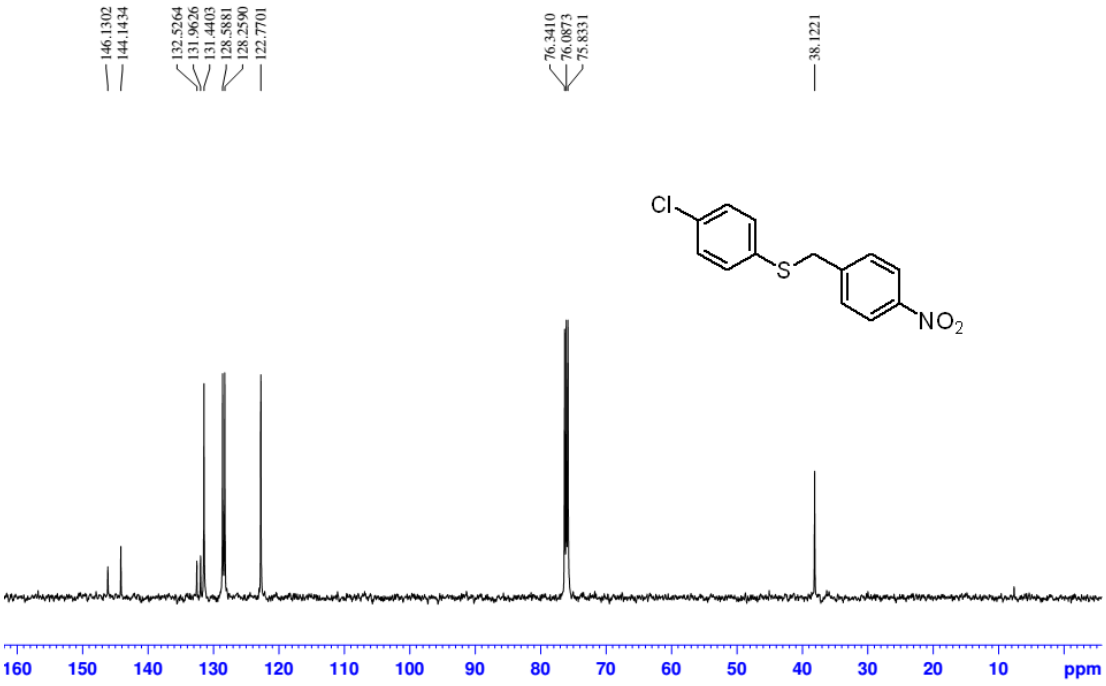
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **5c**



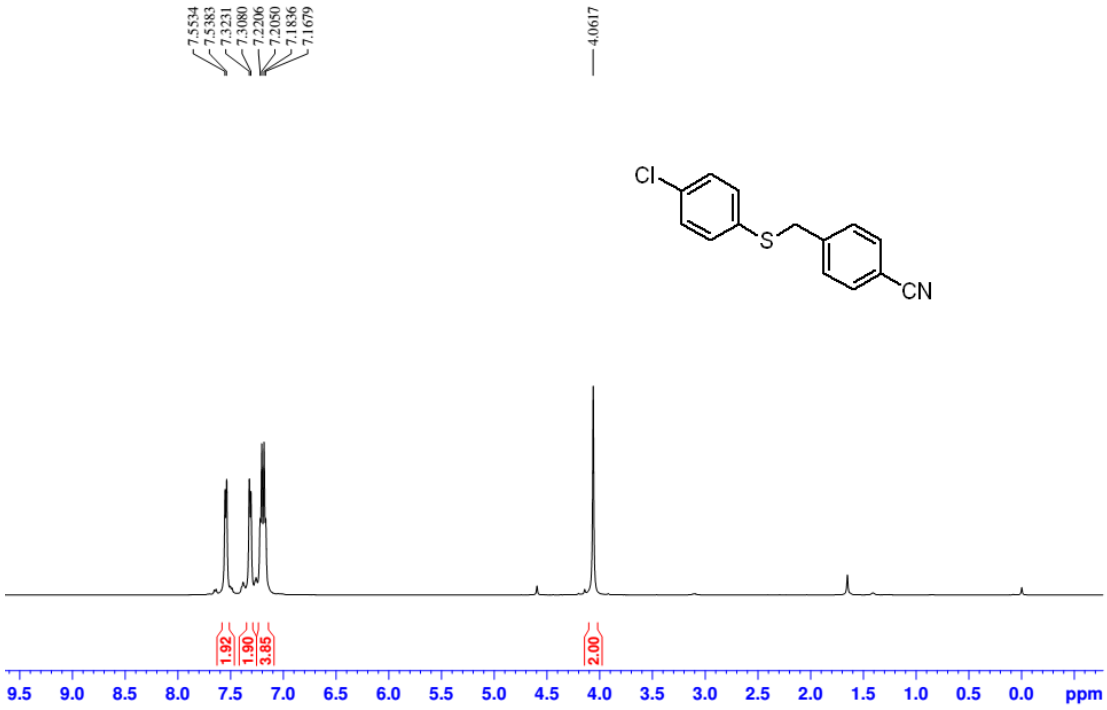
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **5c**



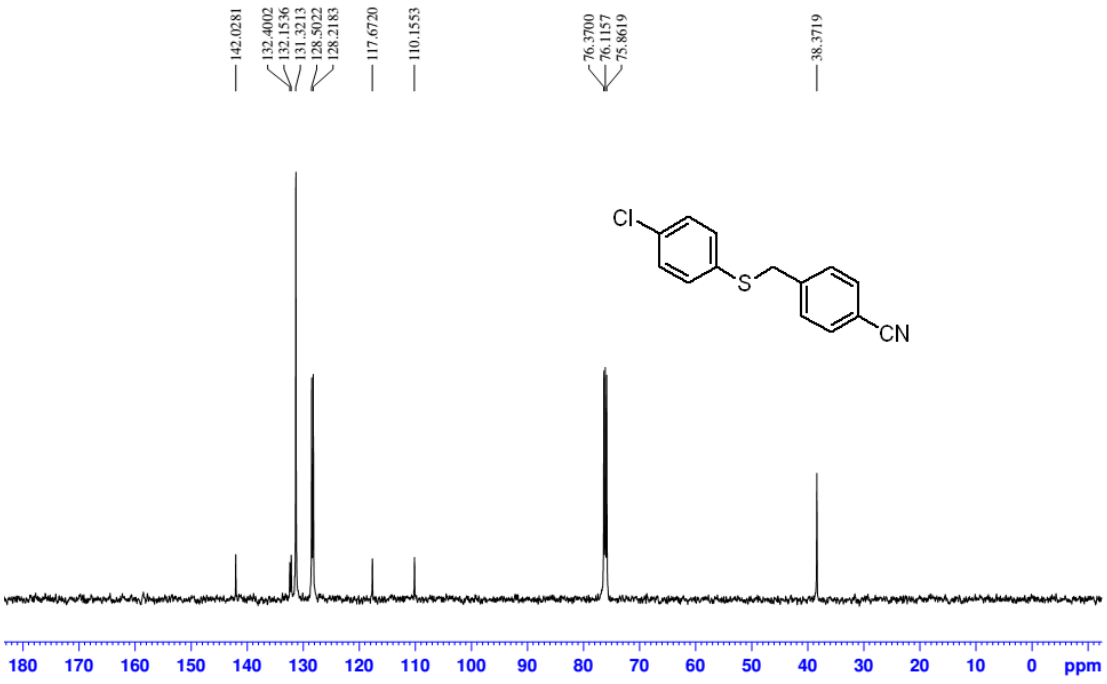
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **5d**



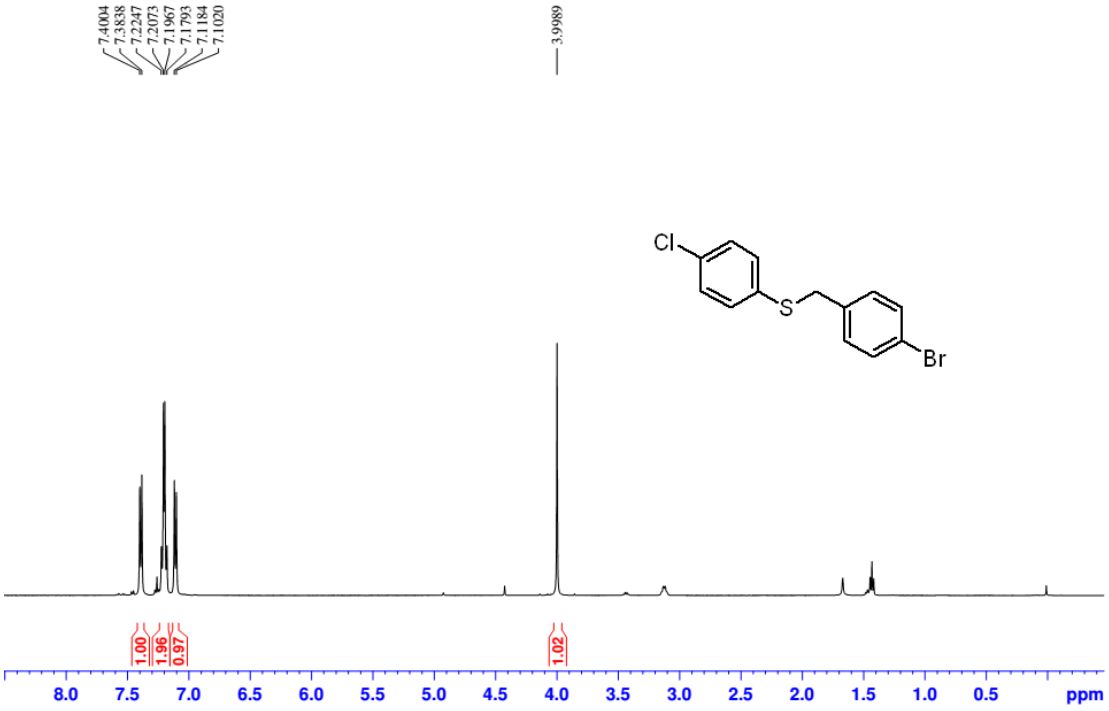
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **5d**



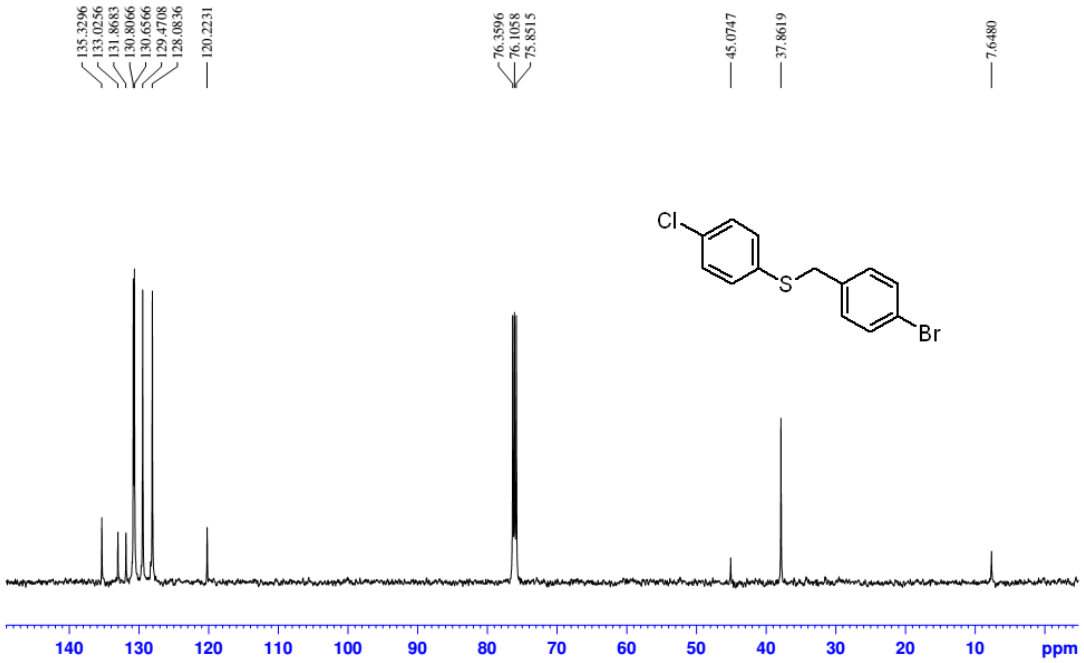
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **5e**



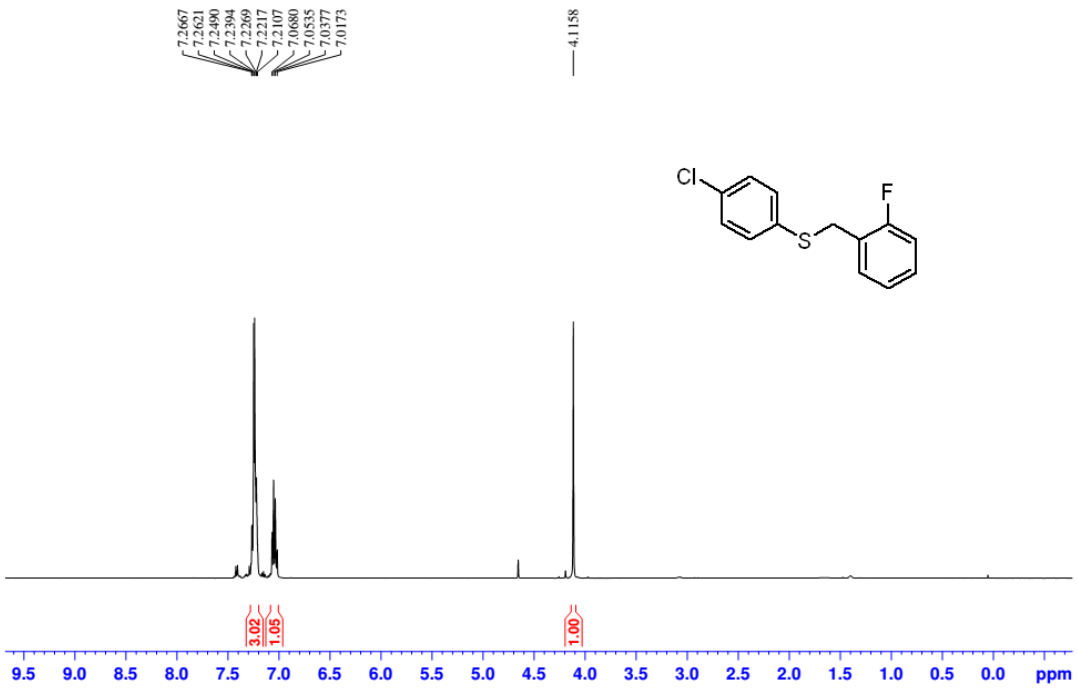
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **5e**



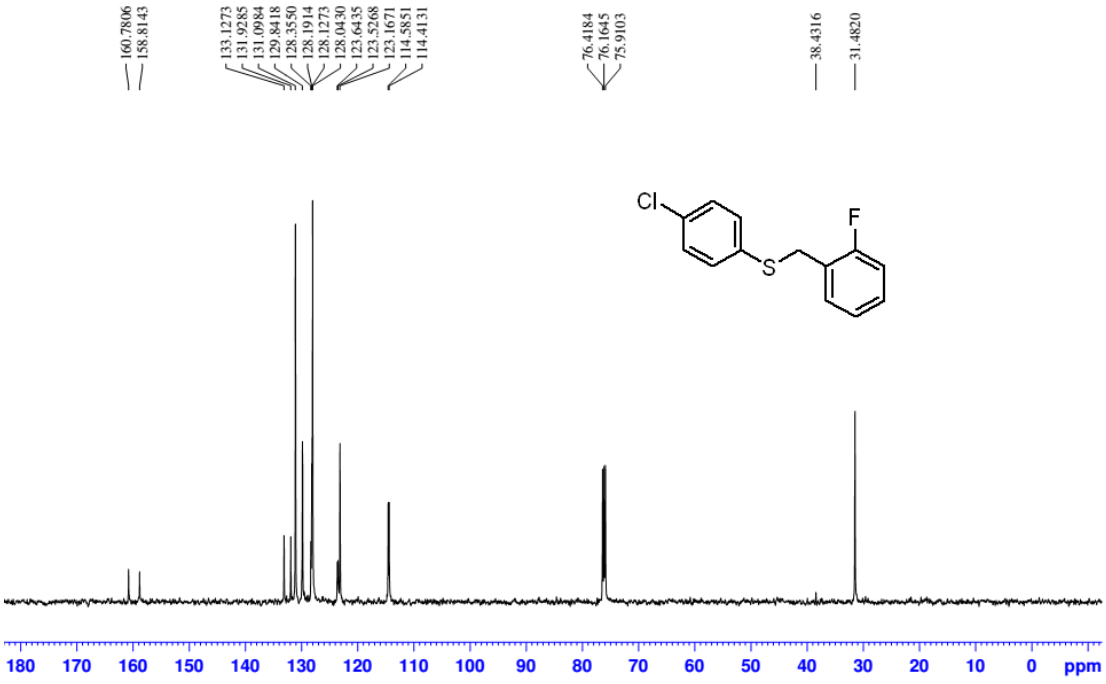
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **5f**



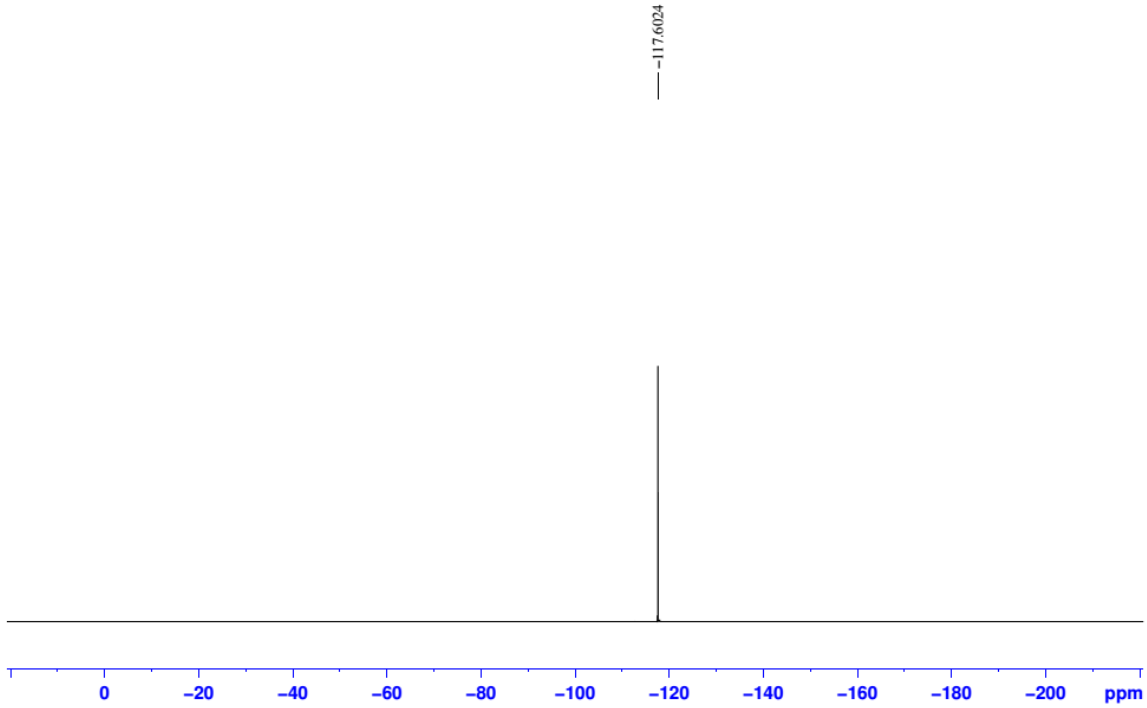
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **5f**



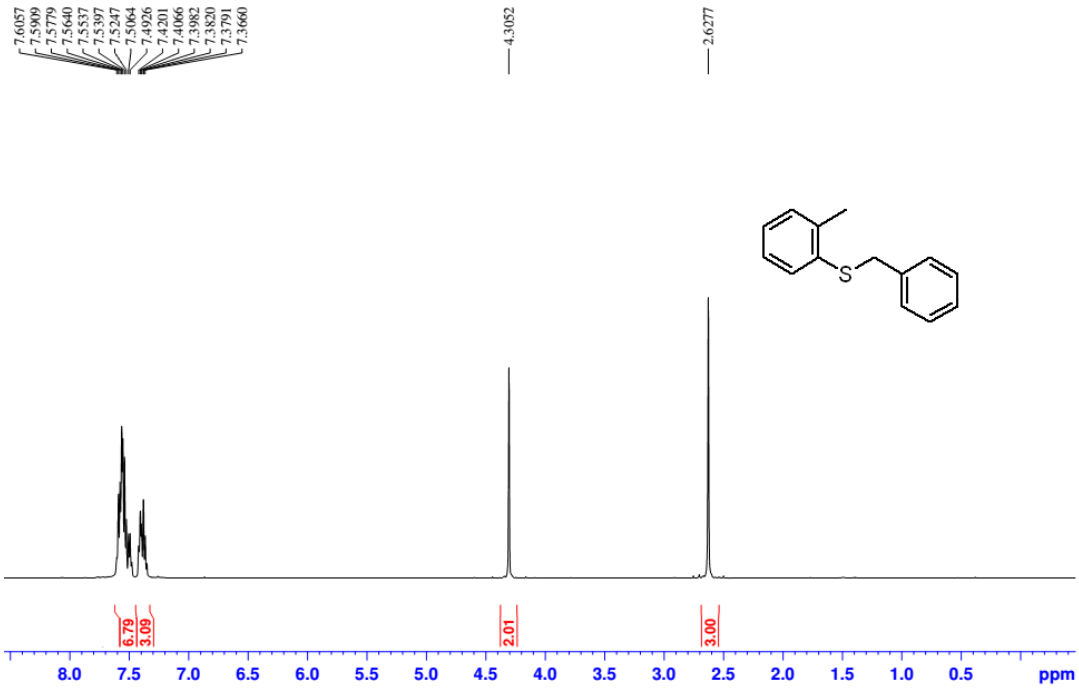
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **5g**



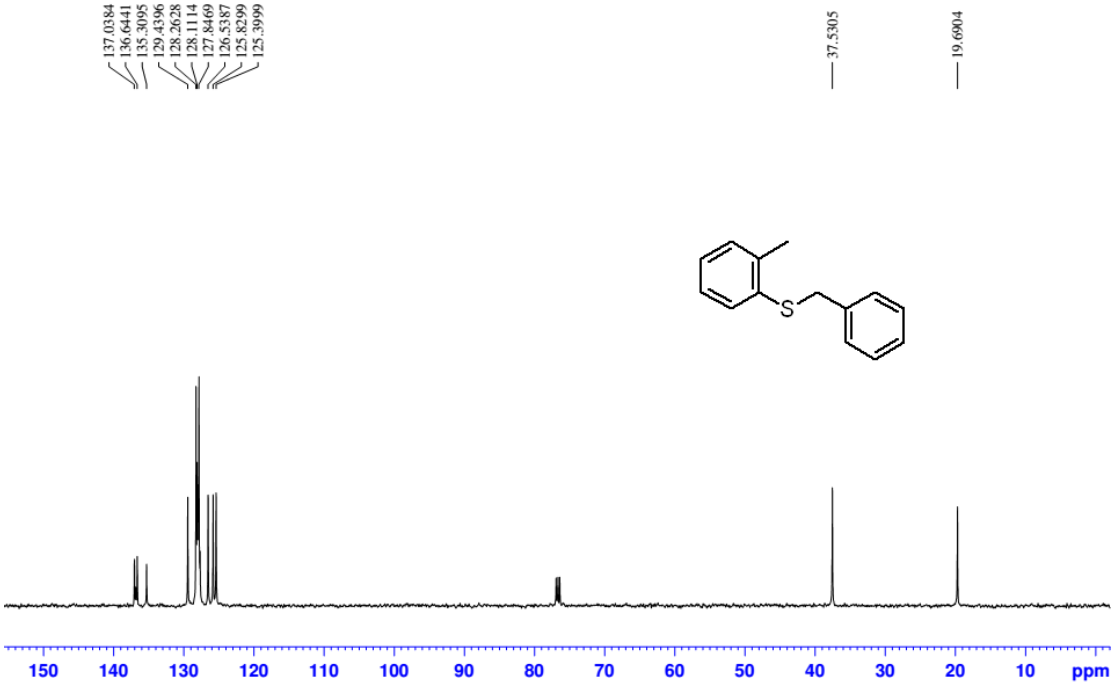
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **5g**



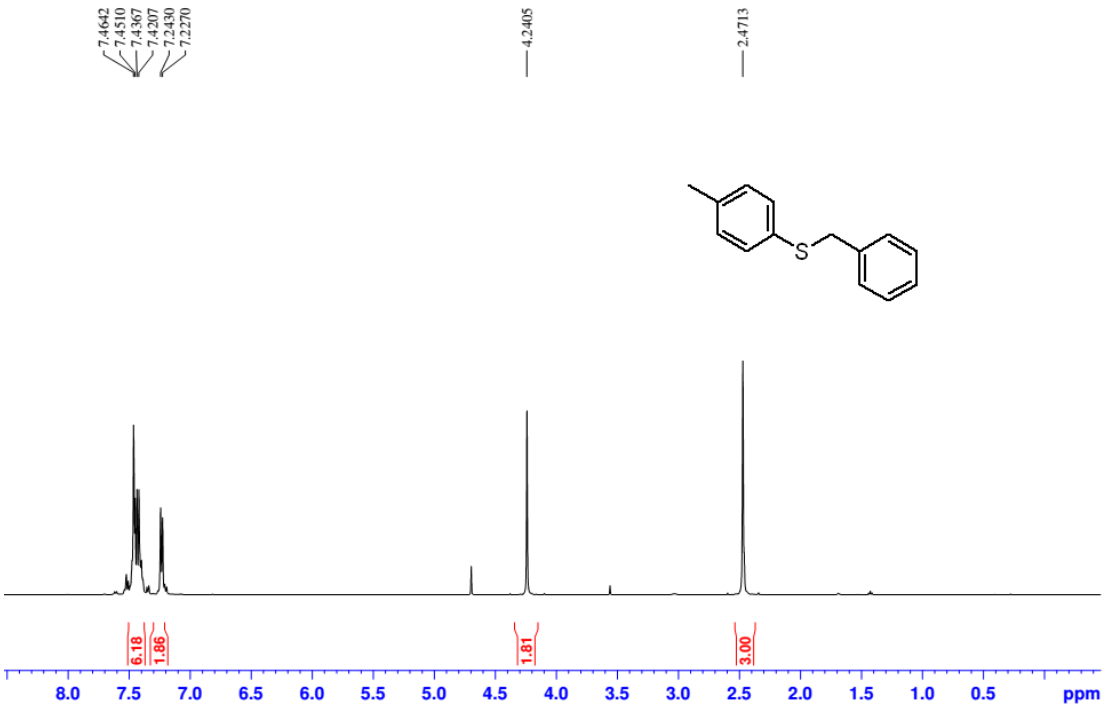
^{19} F NMR spectrum (470 MHz, $CDCl_3$) of **5g**



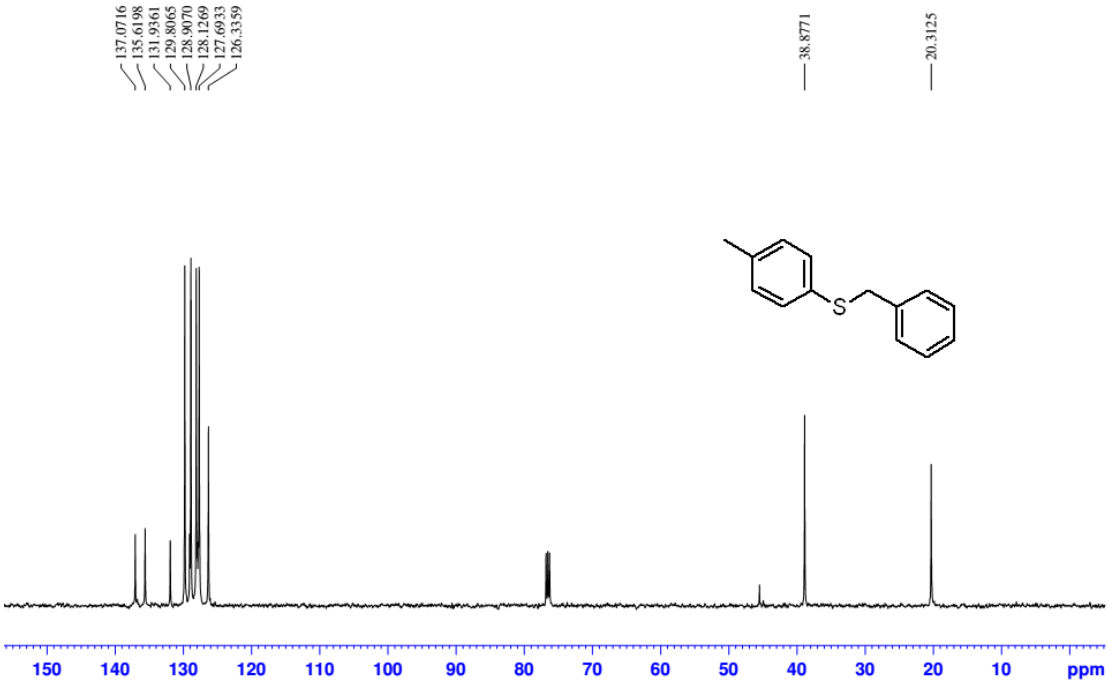
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **5i**



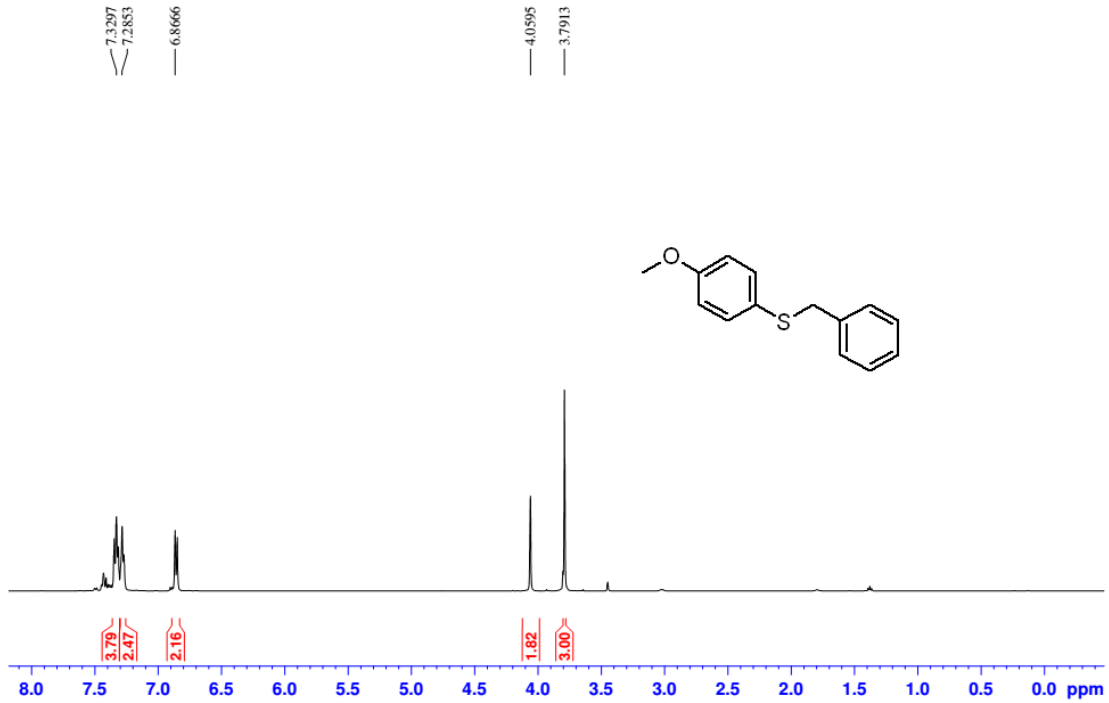
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **5i**



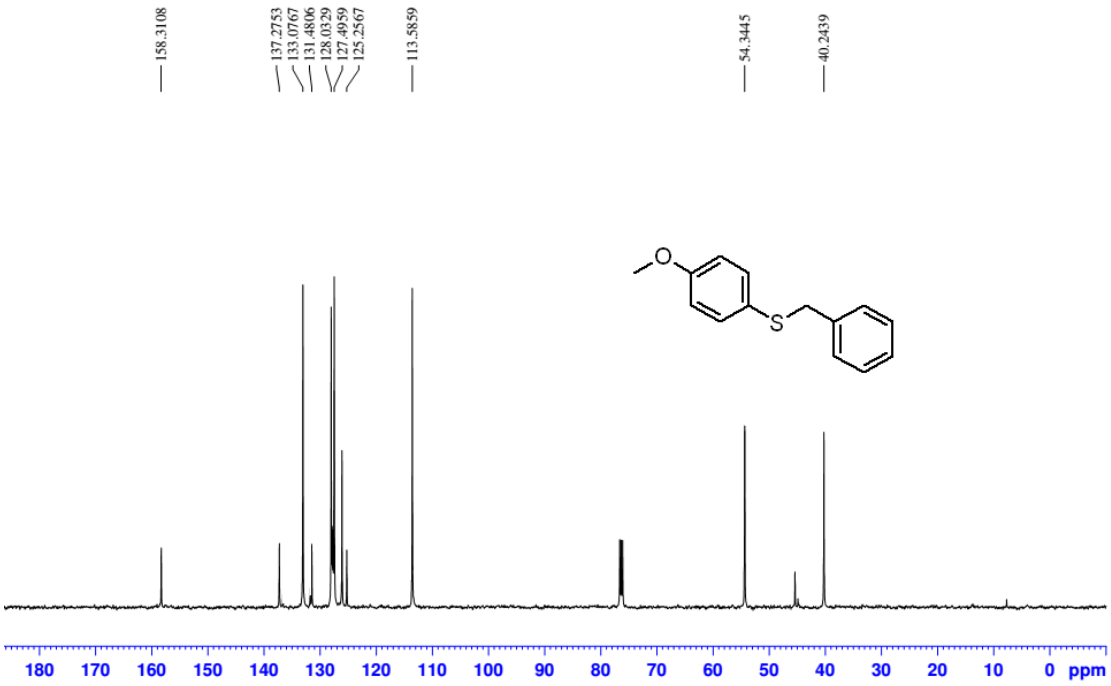
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **5j**



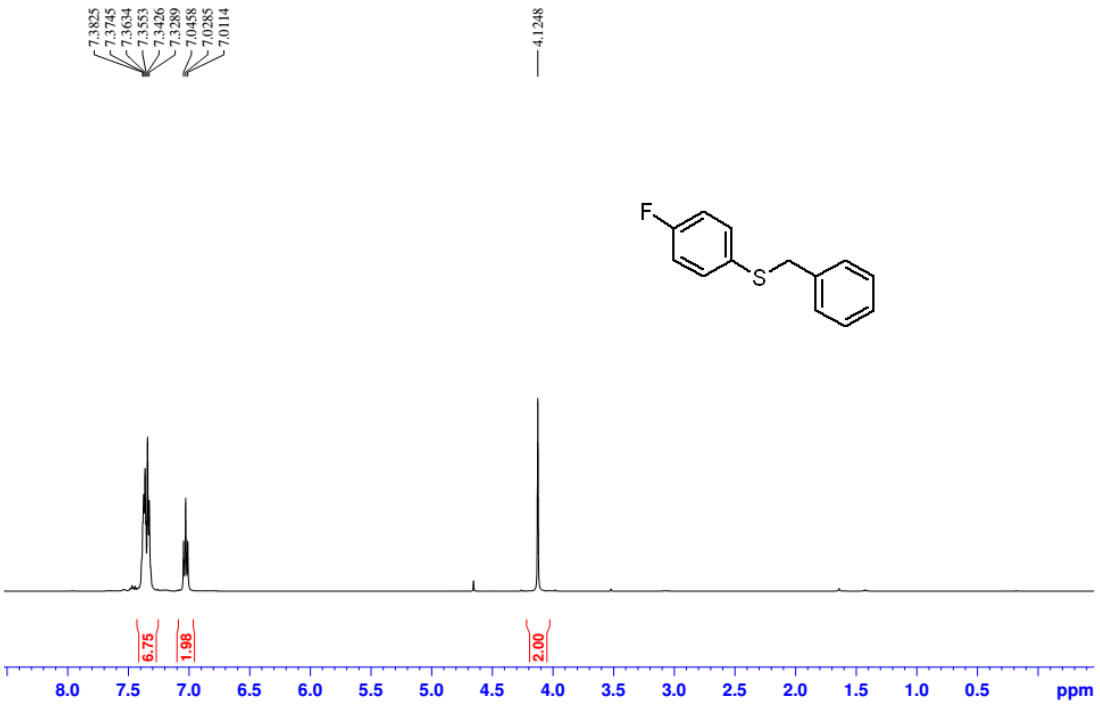
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **5j**



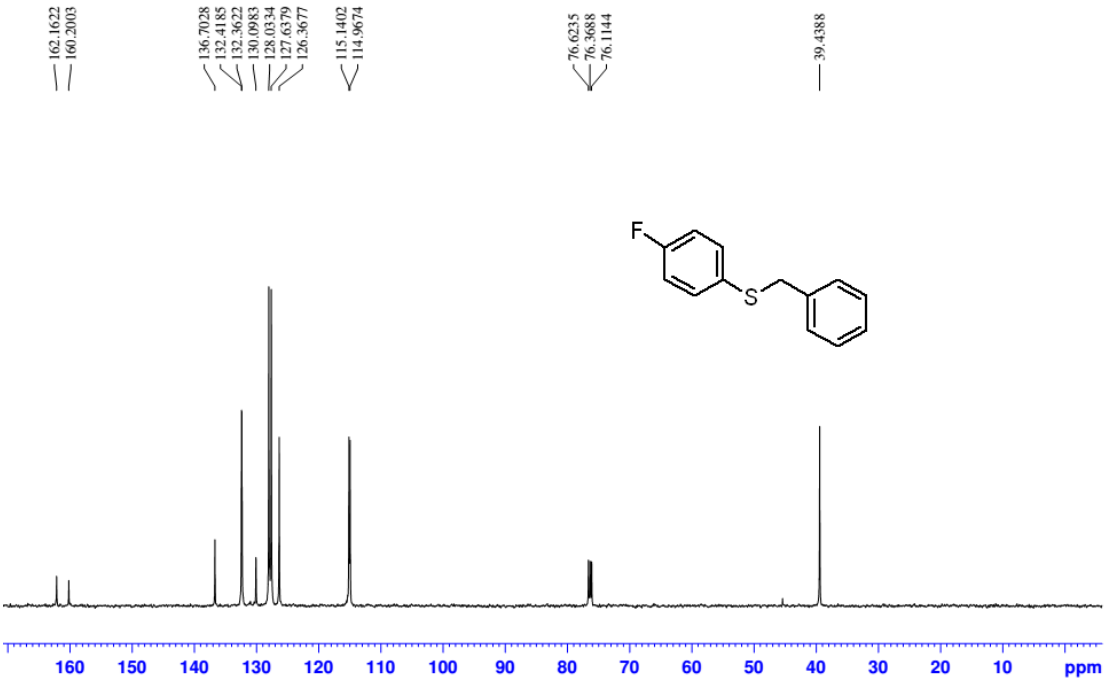
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **5k**



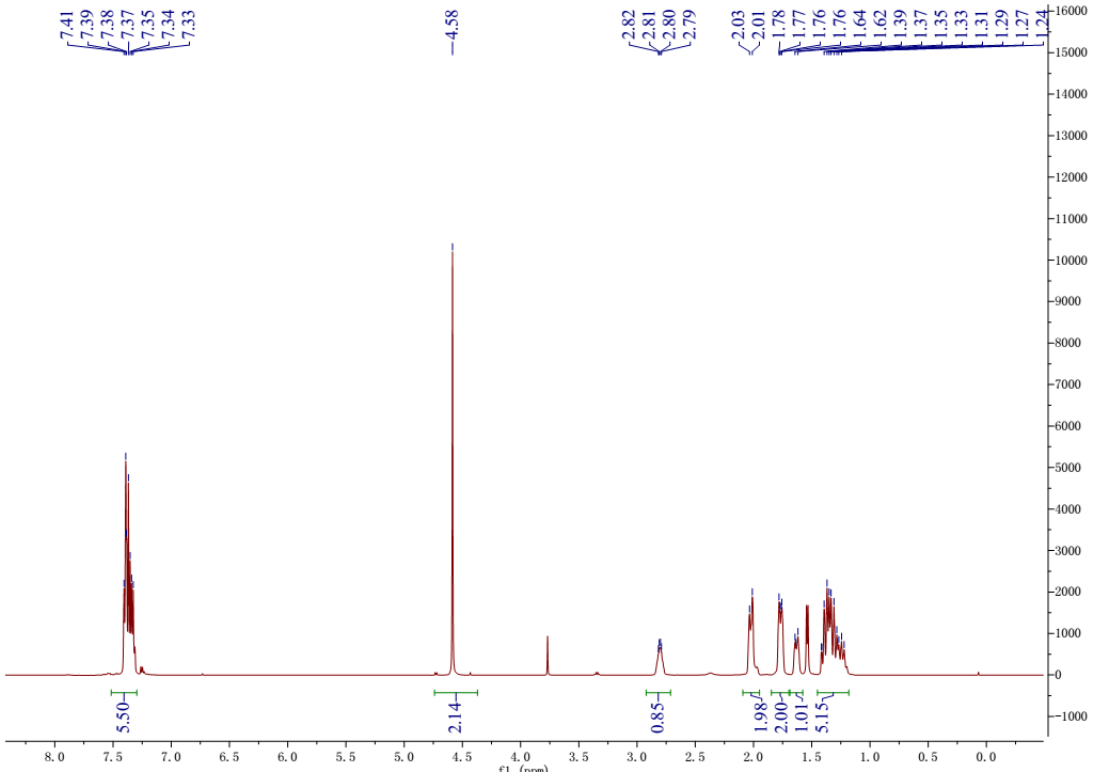
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **5k**



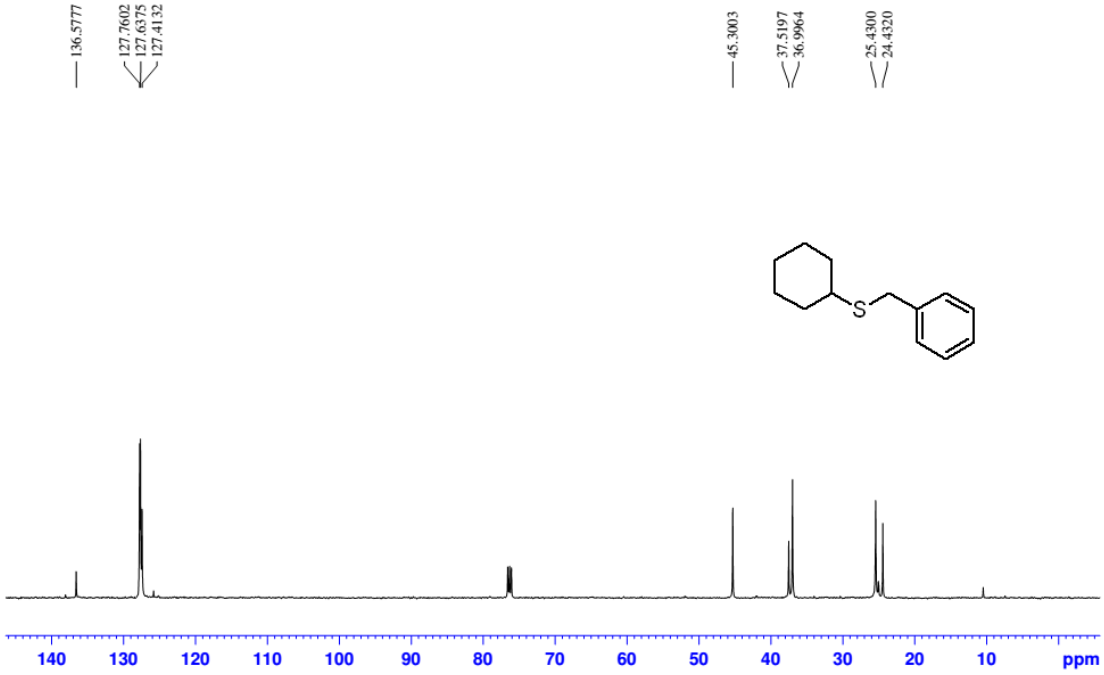
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **5l**



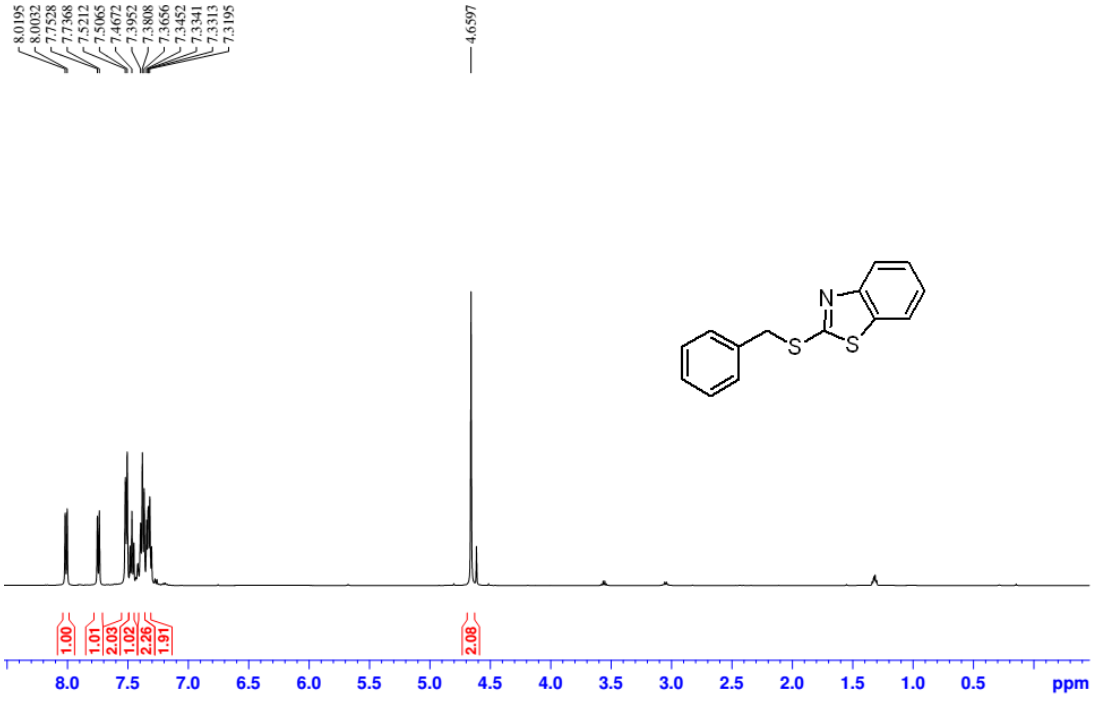
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **5l**



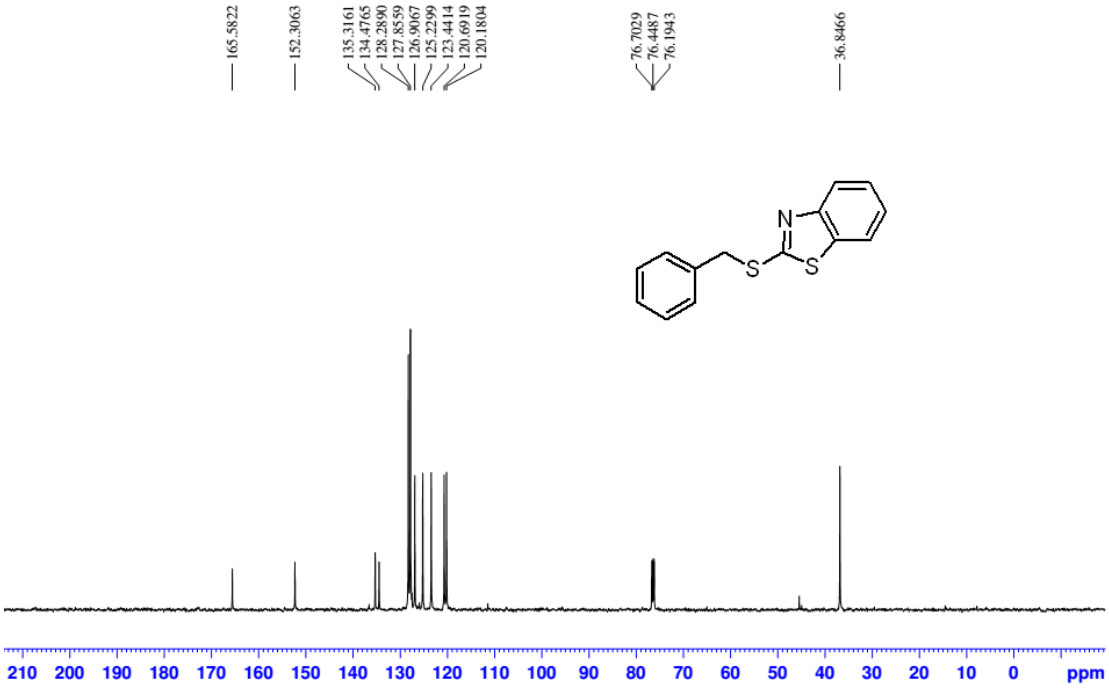
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **5m**



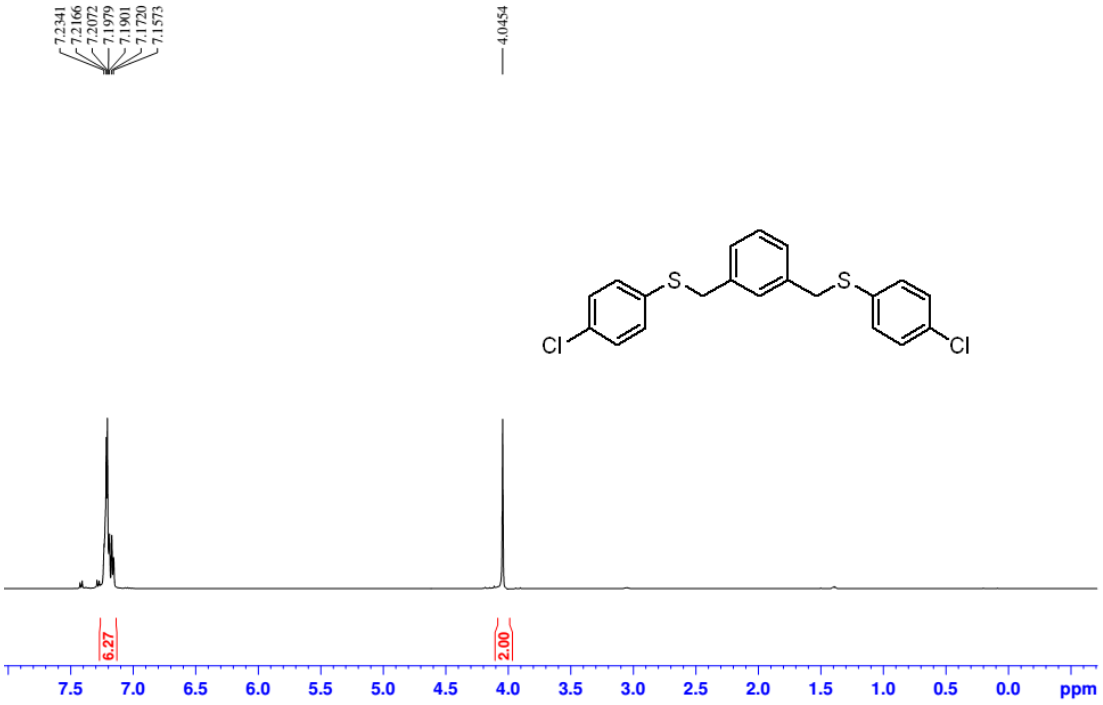
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **5m**



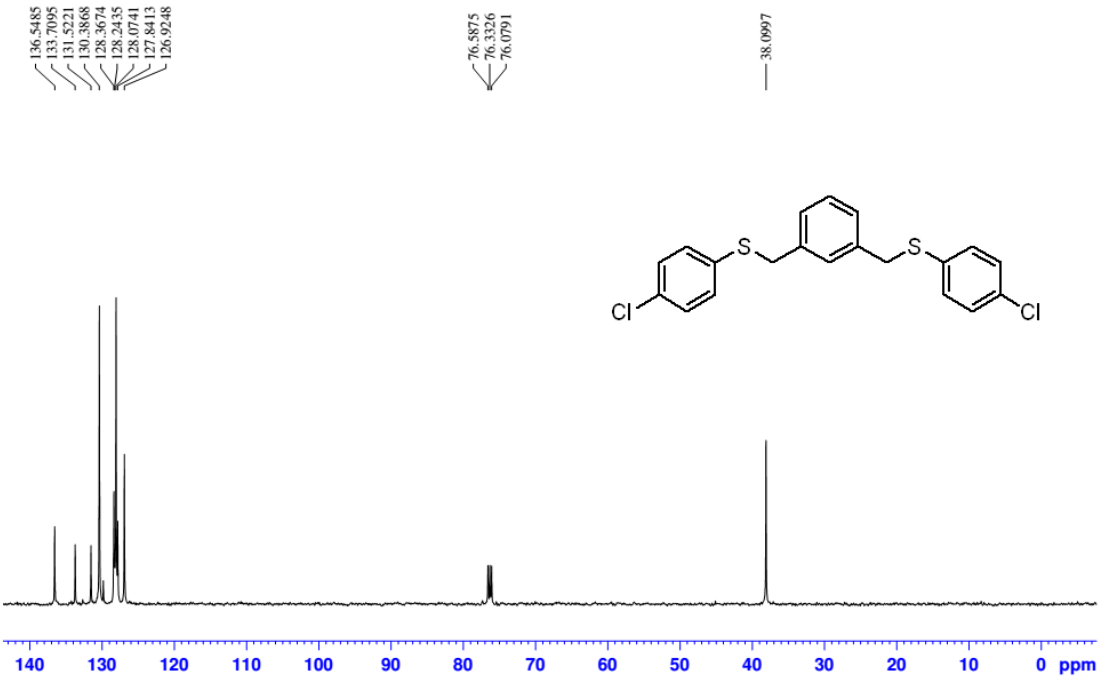
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **5p**



^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **5p**



^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **5q**



^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **5q**