

Supporting information for
Direct oxidative coupling of thiols and benzylic ethers *via*
C(sp³)-H activation and C-O cleavage to lead thioesters

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1 Experimental

1.1 General

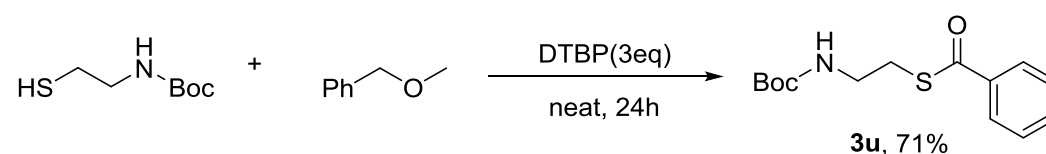
All commercial materials were used without further purification. DTBP used is of 100% purity. Special attention is needed when using DTBP as it is flammable. All known compounds are identified by appropriate technique such as ^1H NMR, ^{13}C NMR and compared with previously reported data. All unknown compounds are characterized by ^1H 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. ^1H 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 \times 320 μm \times 0.25 μm , carrier gas: H_2 , FID detection).

1.2 Experimental Procedure

General procedure for synthesis of thioesters

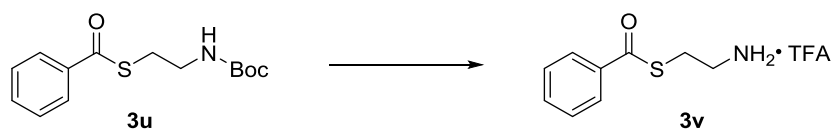
A 5 ml vial sealed tube was charged with thiols or thiophenol (1.3 mmol), benzylic ether (1 mmol) and DTBP (3 mmol) which was stirred at 120 $^\circ\text{C}$ for 24 h. Upon completion, the reaction mixture was then cooled, extracted with ethyl acetate, and dried over anhydrous Na_2SO_4 . After filtration, 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).

*The synthesis of S-(2-((tert-butoxycarbonyl)amino)ethyl) benzothioate **3u***



A mixture of tert-butyl (2-mercaptoethyl)carbamate (1.3 mmol), benzyl methyl ether (1 mmol) and DTBP (3 mmol) was stirred at 120 $^\circ\text{C}$ for 24 h. Upon completion, the reaction mixture was then cooled, extracted with ethyl acetate, washed with water (3 \times 10 mL), 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) **3u** (200 mg, 71%).

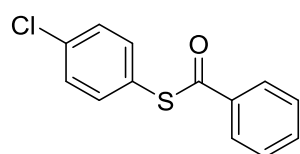
*The synthesis of S-(2-((2,2,2-trifluoroacetyl)-1H-imidazol-4-yl)ethyl) benzothioate **3v***



Compounds **3v** (1.0 mmol) was added of dry trifluoroacetic acid (TFA) (2 mL) at 0 °C. The solution was stirred at room temperature for 16 h and then evaporated to dryness. Crystallization of the residue from hexanes-EtOAc afforded pure **3v** as a light brown solid (0.283 g, 96%).

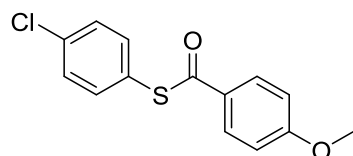
2. Characterization Data

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



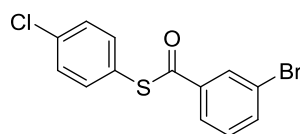
Chemical Formula: $\text{C}_{13}\text{H}_9\text{ClOS}$
Exact Mass: 248.01
Elemental Analysis: C, 62.78; H, 3.65; Cl, 14.25; O, 6.43; S, 12.89

S-(4-chlorophenyl) benzothioate **3a**. ^1H NMR (500 MHz, CDCl_3) 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) 188.7, 135.3, 135.0, 132.9, 128.5, 127.8, 126.5, 124.9. MS (ESI) m/z : 248.



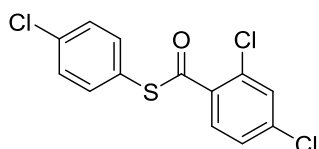
Chemical Formula: $\text{C}_{14}\text{H}_{11}\text{ClO}_2\text{S}$
Exact Mass: 278.02
Elemental Analysis: C, 60.32; H, 3.98; Cl, 12.72; O, 11.48; S, 11.50

S-(4-chlorophenyl) 4-methoxybenzothioate **3b**. ^1H 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.



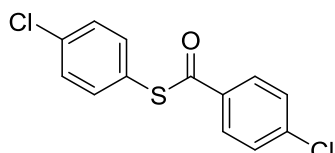
Chemical Formula: $\text{C}_{13}\text{H}_8\text{BrClOS}$
Exact Mass: 325.92
Elemental Analysis: C, 47.66; H, 2.46; Br, 24.39; Cl, 10.82; O, 4.88; S, 9.79

S-(4-chlorophenyl) 3-bromobenzothioate **3c**. ^1H 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.



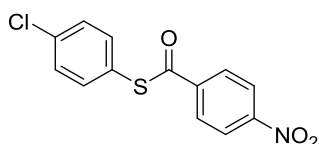
Chemical Formula: C₁₃H₇Cl₃OS
 Exact Mass: 315.93
 Elemental Analysis: C, 49.16; H, 2.22; Cl, 33.48; O, 5.04; S, 10.09

S-(4-chlorophenyl) 2,4-dichlorobenzothioate **3d**. ¹H NMR (500 MHz, CDCl₃) 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). ¹³C NMR (126 MHz, CDCl₃) 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.



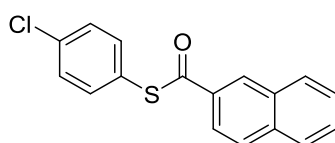
Chemical Formula: C₁₃H₈Cl₂OS
 Exact Mass: 281.97
 Elemental Analysis: C, 55.14; H, 2.85; Cl, 25.04; O, 5.65; S, 11.32

S-(4-chlorophenyl) 4-chlorobenzothioate **3e**. ¹H NMR (500 MHz, CDCl₃) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.45 (s, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 187.52, 139.34, 135.28, 133.71, 128.61, 128.39, 128.18, 127.87, 124.43. MS (ESI) *m/z*: 282.



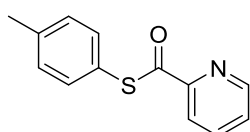
Chemical Formula: C₁₃H₈ClNO₃S
 Exact Mass: 292.99
 Elemental Analysis: C, 53.16; H, 2.75; Cl, 12.07; N, 4.77; O, 16.34; S, 10.92

S-(4-chlorophenyl) 4-nitrobenzothioate **3f**. ¹H NMR (500 MHz, CDCl₃) δ 8.35 (d, *J* = 8.7 Hz, 2H), 8.17 (d, *J* = 8.7 Hz, 2H), 7.46 (s, 4H). ¹³C NMR (126 MHz, CDCl₃) 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: C₁₇H₁₁ClOS
 Exact Mass: 298.02
 Elemental Analysis: C, 68.34; H, 3.71; Cl, 11.86; O, 5.35; S, 10.73

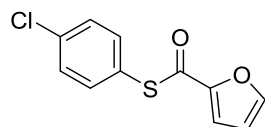
S-(4-chlorophenyl) naphthalene-2-carbothioate **3g**. ¹H NMR (500 MHz, CDCl₃) δ 8.54 (d, *J* = 8.3 Hz, 1H), 8.23 (d, *J* = 7.2 Hz, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.71 – 7.45 (m, 7H). ¹³C NMR (126 MHz, CDCl₃) δ 190.62, 135.17, 135.05, 133.32, 132.88, 132.57, 128.59, 128.35, 127.44, 127.28, 127.15, 125.83, 124.22, 123.48. MS (ESI) *m/z*: 298.



Chemical Formula: C₁₂H₈ClNOS
 Exact Mass: 249.00
 Elemental Analysis: C, 57.72; H, 3.23; Cl, 14.20; N, 5.61; O, 6.41; S, 12.84

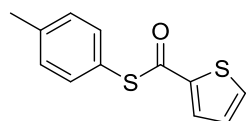
S-(4-chlorophenyl) pyridine-2-carbothioate **3h**. ¹H NMR (500 MHz, CDCl₃) δ 8.73

(d, $J = 4.4$ Hz, 1H), 7.94 (d, $J = 7.8$ Hz, 1H), 7.86 (d, $J = 7.6$ Hz, 1H), 7.53 (dd, $J = 6.9, 5.3$ Hz, 1H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.26 (d, $J = 7.8$ Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 191.38, 150.79, 148.17, 138.67, 136.40, 133.89, 129.09, 127.08, 123.59, 119.79, 20.40. MS (ESI) m/z : 249



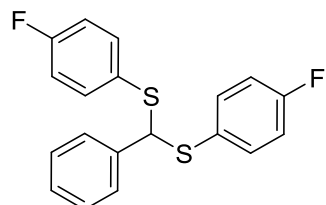
Chemical Formula: $\text{C}_{11}\text{H}_7\text{ClO}_2\text{S}$
 Exact Mass: 237.99
 Elemental Analysis: C, 55.35; H, 2.96; Cl, 14.85; O, 13.41; S, 13.43

S-(4-chlorophenyl) furan-2-carbothioate **3i**. ^1H NMR (500 MHz, CDCl_3) δ 7.65 (s, 1H), 7.44 (s, 4H), 7.28 (d, $J = 3.1$ Hz, 1H), 6.60 (d, $J = 1.6$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 177.15, 149.12, 145.70, 135.38, 135.16, 128.55, 123.69, 115.57, 111.56. MS (ESI) m/z : 238



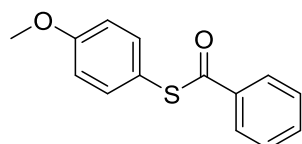
Chemical Formula: $\text{C}_{11}\text{H}_7\text{ClOS}_2$
 Exact Mass: 253.96
 Elemental Analysis: C, 51.86; H, 2.77; Cl, 13.92; O, 6.28; S, 25.17

S-(4-chlorophenyl) thiophene-2-carbothioate **3j**. ^1H NMR (500 MHz, CDCl_3) δ 7.90 (d, $J = 3.8$ Hz, 1H), 7.66 (d, $J = 4.9$ Hz, 1H), 7.40 (d, $J = 8.1$ Hz, 2H), 7.26 (d, $J = 2.5$ Hz, 2H), 7.17 – 7.12 (m, 1H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 181.50, 140.51, 138.97, 134.00, 132.04, 130.48, 129.10, 126.96, 122.39, 20.37. MS (ESI) m/z : 254.



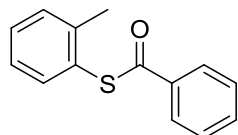
(phenylmethylene)bis((4-fluorophenyl)sulfane)
 Chemical Formula: $\text{C}_{19}\text{H}_{14}\text{F}_2\text{S}_2$
 Exact Mass: 344.0
 Elemental Analysis: C, 66.26; H, 4.10; F, 11.03; S, 18.62

(Phenylmethylene)bis((4-fluorophenyl)sulfane) **3k'**. ^1H NMR (500 MHz, CDCl_3) δ 7.35 – 7.28 (m, 4H), 7.28 – 7.22 (m, 5H), 6.98 – 6.90 (m, 4H), 5.24 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 163.99, 162.01, 139.39, 135.95, 135.89, 129.21, 128.57, 128.26, 127.92, 116.15, 115.98, 77.38, 77.12, 76.87, 62.23. ^{19}F NMR (470 MHz, CDCl_3) δ -112.62. MS (ESI) m/z : 344.



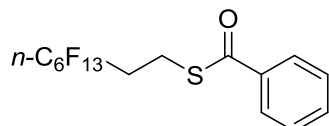
Chemical Formula: $\text{C}_{14}\text{H}_{12}\text{O}_2\text{S}$
 Exact Mass: 244.06
 Elemental Analysis: C, 68.83; H, 4.95; O, 13.10; S, 13.12

S-(4-methoxyphenyl) benzothioate **3l**. ^1H 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



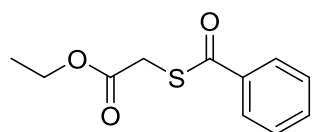
Chemical Formula: C₁₄H₁₂OS
 Exact Mass: 228.06
 Elemental Analysis: C, 73.65; H, 5.30; O, 7.01; S, 14.04

S-(*o*-tolyl) benzothioate **3m**. ¹H NMR (500 MHz, CDCl₃) 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). ¹³C 188.7, 141.7, 135.8, 132.6, 129.9, 129.3, 127.8, 126.6, 125.7. MS (ESI) *m/z*: 228.



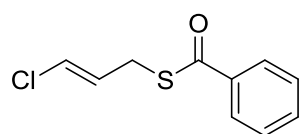
Chemical Formula: C₁₅H₉F₁₃OS
 Exact Mass: 484.02
 Elemental Analysis: C, 37.20; H, 1.87; F, 51.00; O, 3.30; S, 6.62

S-1H,1H,2H,2H-perfluorooctyl benzothioate **3o**. ¹H NMR (500 MHz, CDCl₃) 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). ¹³C NMR (126 MHz, CDCl₃) δ, 189.8, 135.5, 132.8, 127.8, 126.3, 30.8, 19.1. ¹⁹F NMR (470 MHz, CDCl₃) δ -126.2, -123.4, -122.9, -121.9, -114.5, -80.9. MS (ESI) *m/z*: 484.



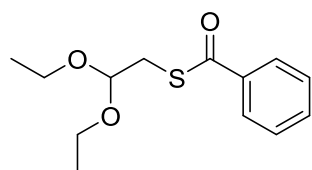
Chemical Formula: C₁₁H₁₂O₃S
 Exact Mass: 224.05
 Elemental Analysis: C, 58.91; H, 5.39; O, 21.40; S, 14.30

Ethyl 2-(benzoylthio)acetate **3p**. ¹H NMR (500 MHz, CDCl₃) 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). ¹³C NMR (126 MHz, CDCl₃) δ 189.1, 167.8, 135.2, 132.8, 127.7, 126.4, 60.9, 30.5, 13.1. MS (ESI) *m/z*: 224.



Chemical Formula: C₁₀H₉ClOS
 Exact Mass: 212.00
 Elemental Analysis: C, 56.47; H, 4.26; Cl, 16.67; O, 7.52; S, 15.08

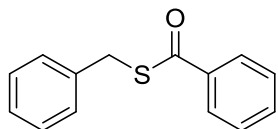
(*E*)-*S*-3-chloroallyl benzothioate **3q**. ¹H NMR (500 MHz, CDCl₃) δ 7.97 (d, *J* = 7.5 Hz, 1H), 7.62-7.59 (t, *J* = 7.5 Hz), 7.50-7.46 (t, *J* = 7.0 Hz, 2H), 6.34-6.31 (dt, *J* = 13.5, 1.0 Hz, 1H), 6.04-6.00 (dt, *J* = 13.0, 8.0 Hz, 1H), 3.75-3.73 (dd, *J* = 7.5, 1.5 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 189.8, 135.7, 132.6, 127.7, 127.5, 126.3, 120.6, 28.0. MS (ESI) *m/z*: 212.



Chemical Formula: C₁₃H₁₈O₃S
 Exact Mass: 254.10
 Elemental Analysis: C, 61.39; H, 7.13; O, 18.87; S, 12.60

S-(2,2-diethoxyethyl) benzothioate **3r**. ¹H NMR (500 MHz, CDCl₃) δ 1.25-1.27 (t, *J* =

7.0 Hz, 6H), 3.33 (d, $J = 5.5$ Hz, 2H), 3.61-3.65 (m, 2H), 3.72-3.78 (m, 2H), 4.62 (t, $J = 5.5$ Hz, 1H), 7.48-7.49 (t, $J = 7.5$ Hz, 2H), 7.58-7.61 (t, $J = 7.5$ Hz, 1H), 8.01 (d, $J = 7.5$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 14.2, 31.3, 81.6, 100.5, 126.3, 127.6, 128.0, 132.5, 135.9, 190.6. MS (ESI) m/z : 254.

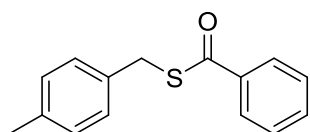


Chemical Formula: $\text{C}_{14}\text{H}_{12}\text{OS}$

Exact Mass: 228.06

Elemental Analysis: C, 73.65; H, 5.30; O, 7.01; S, 14.04

S-benzyl benzothioate **3s**. ^1H NMR (500 MHz, CDCl_3) δ 8.01 – 7.91 (m, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.44 (t, $J = 7.8$ Hz, 2H), 7.38 (d, $J = 7.3$ Hz, 2H), 7.32 (t, $J = 7.5$ Hz, 2H), 7.25 (t, $J = 7.3$ Hz, 1H), 4.32 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 190.32, 136.49, 135.82, 132.46, 128.00, 127.66, 126.33, 32.36. MS (ESI) m/z : 228.



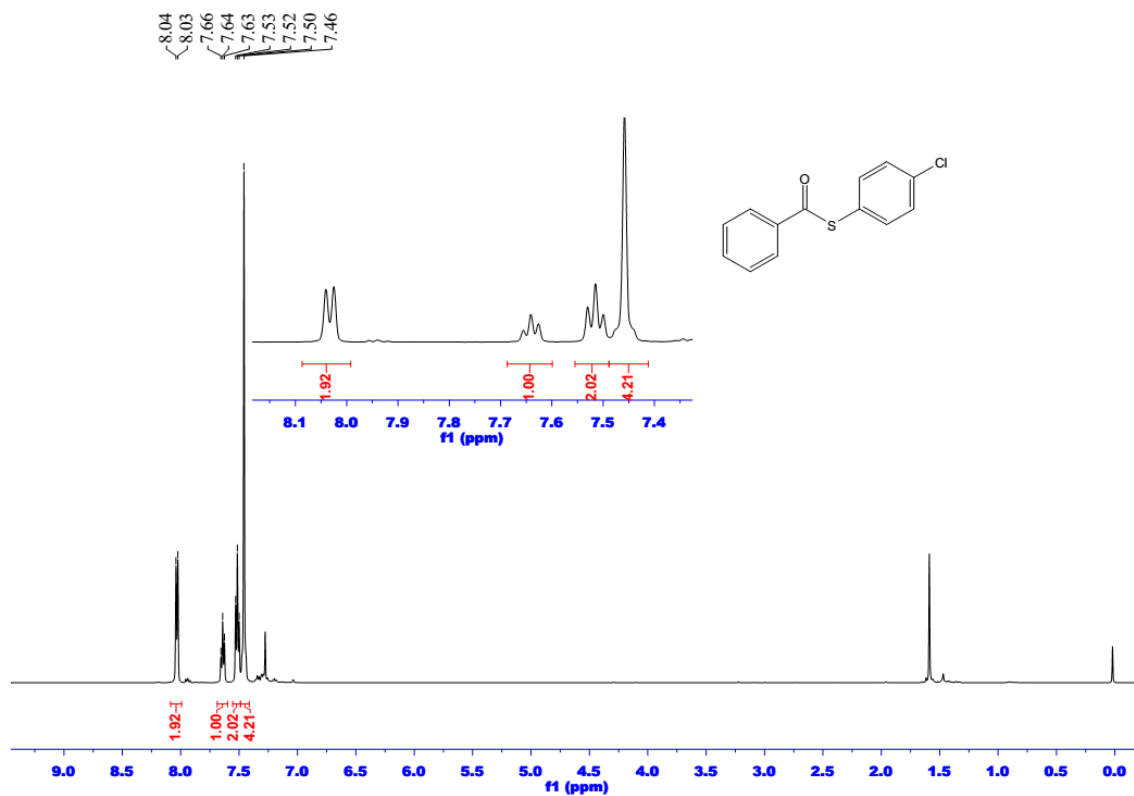
Chemical Formula: $\text{C}_{15}\text{H}_{14}\text{OS}$

Exact Mass: 242.08

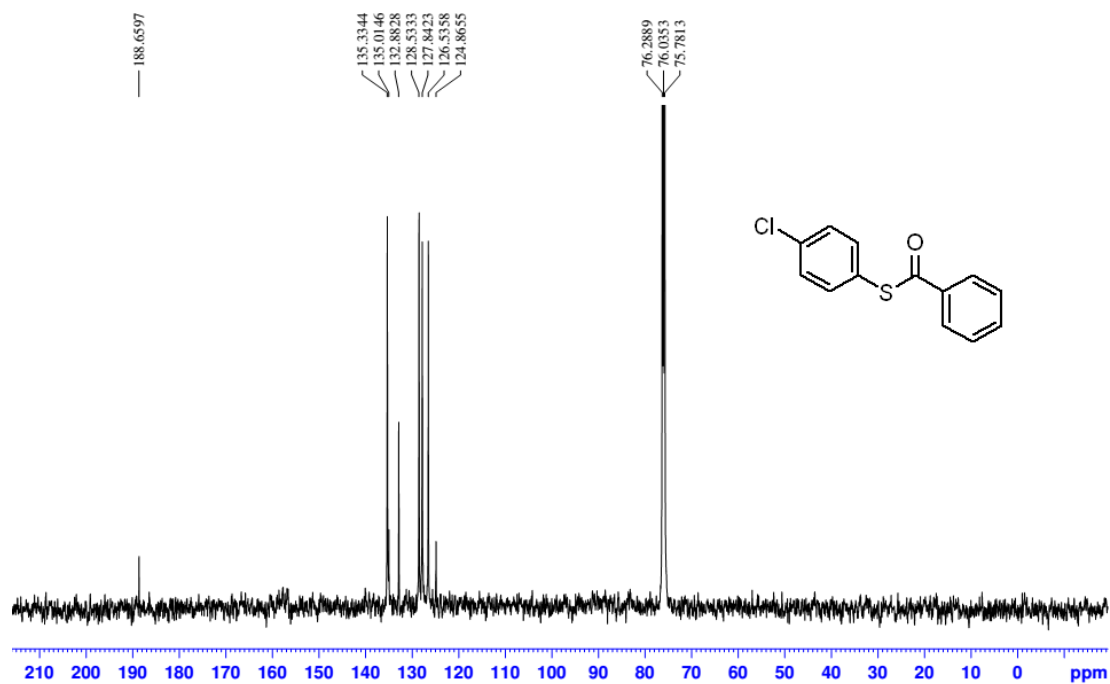
Elemental Analysis: C, 74.34; H, 5.82; O, 6.60; S, 13.23

S-4-methylbenzyl benzothioate **3t**. ^1H NMR (500 MHz, CDCl_3) δ 8.01-7.99 (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, 136.1, 135.9, 133.4, 132.4, 128.4, 127.9, 127.6, 126.3, 32.1, 20.2. MS (ESI) m/z : 242.

3. NMR Spectra of All Products



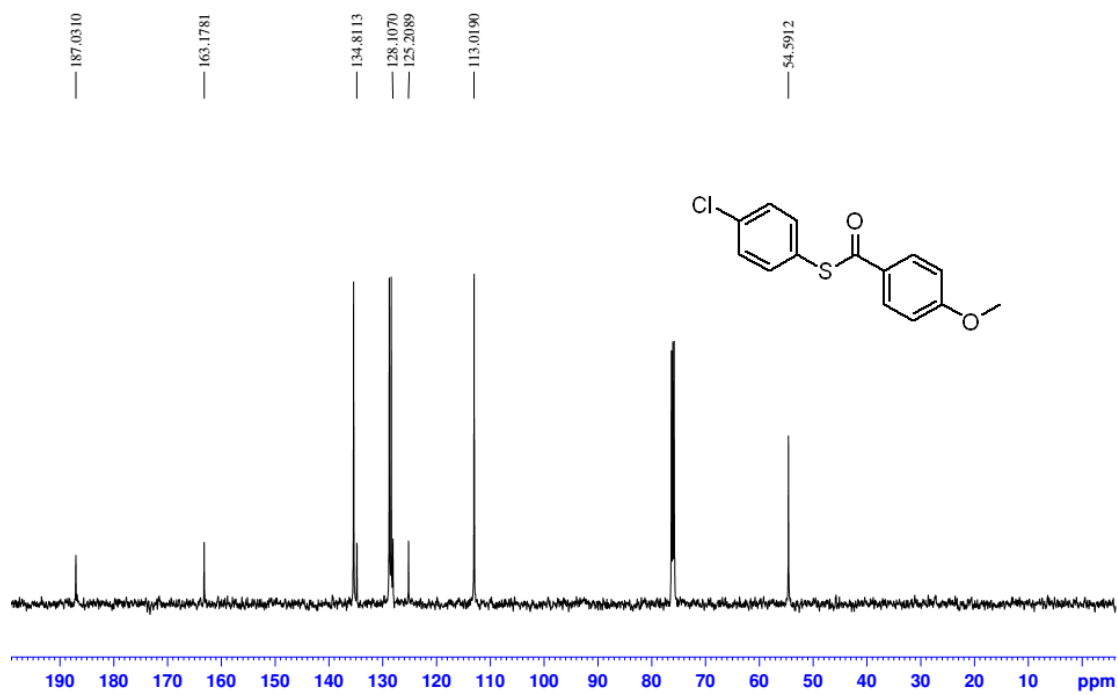
^1H NMR spectrum (500 MHz, CDCl_3) of **3a**



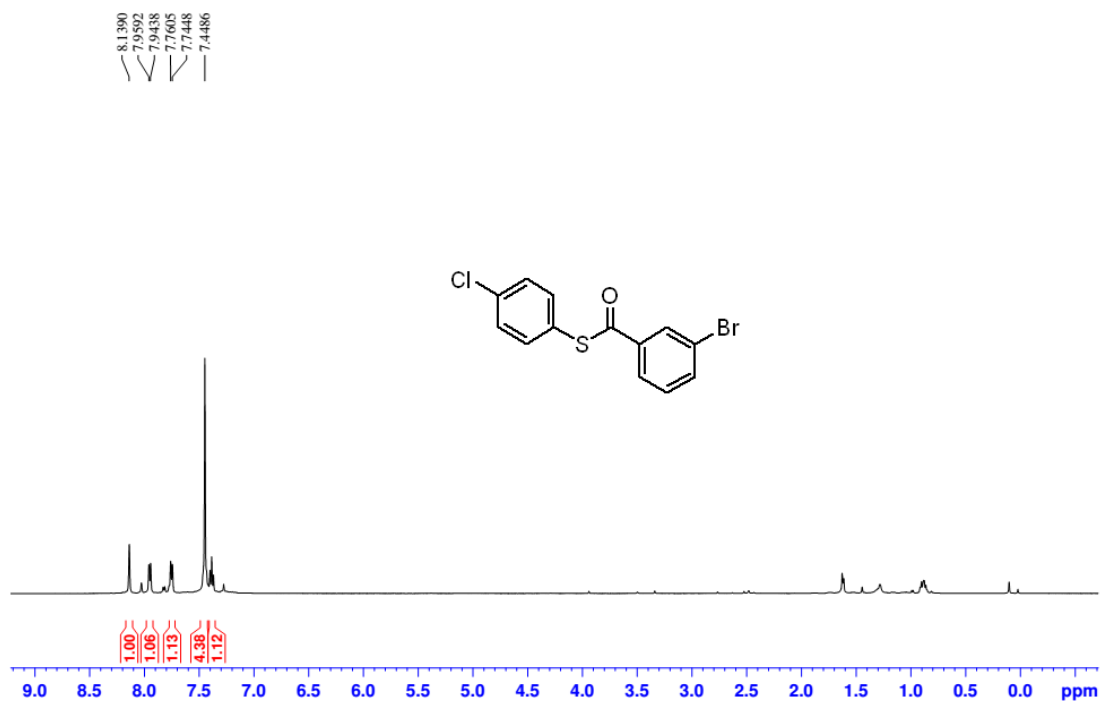
^{13}C NMR spectrum (125 MHz, CDCl_3) of **3a**



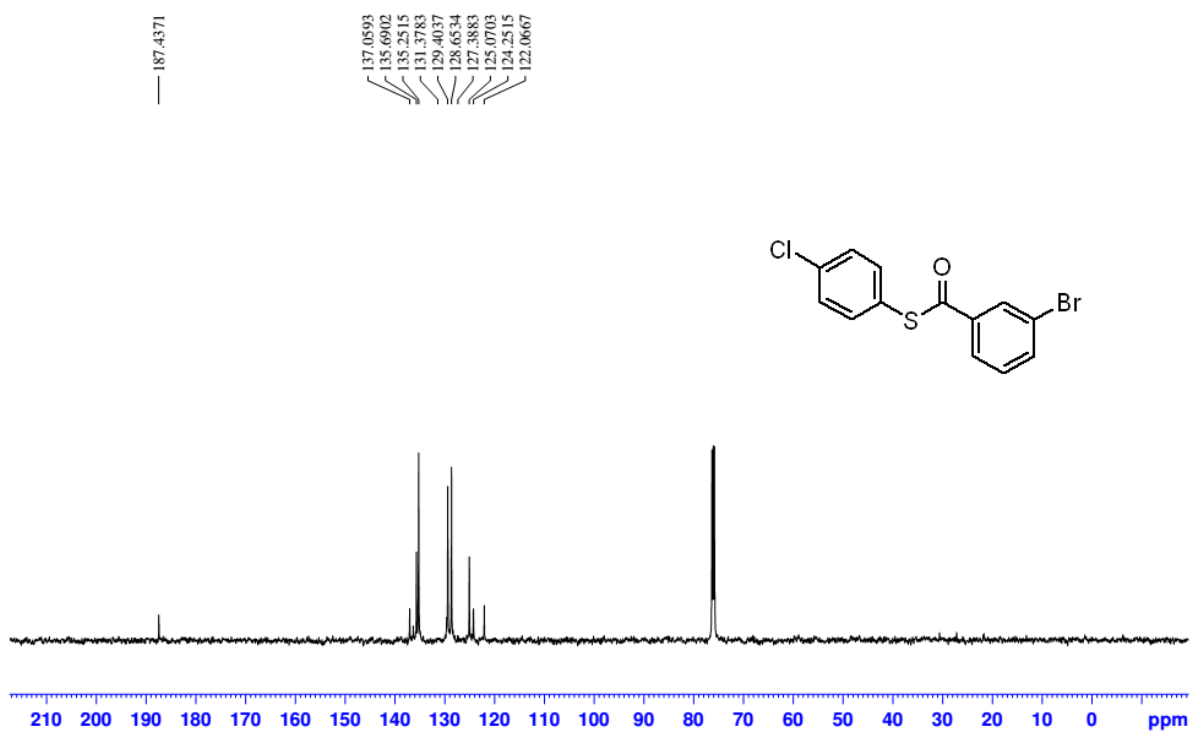
¹H NMR spectrum (500 MHz, CDCl₃) of **3b**



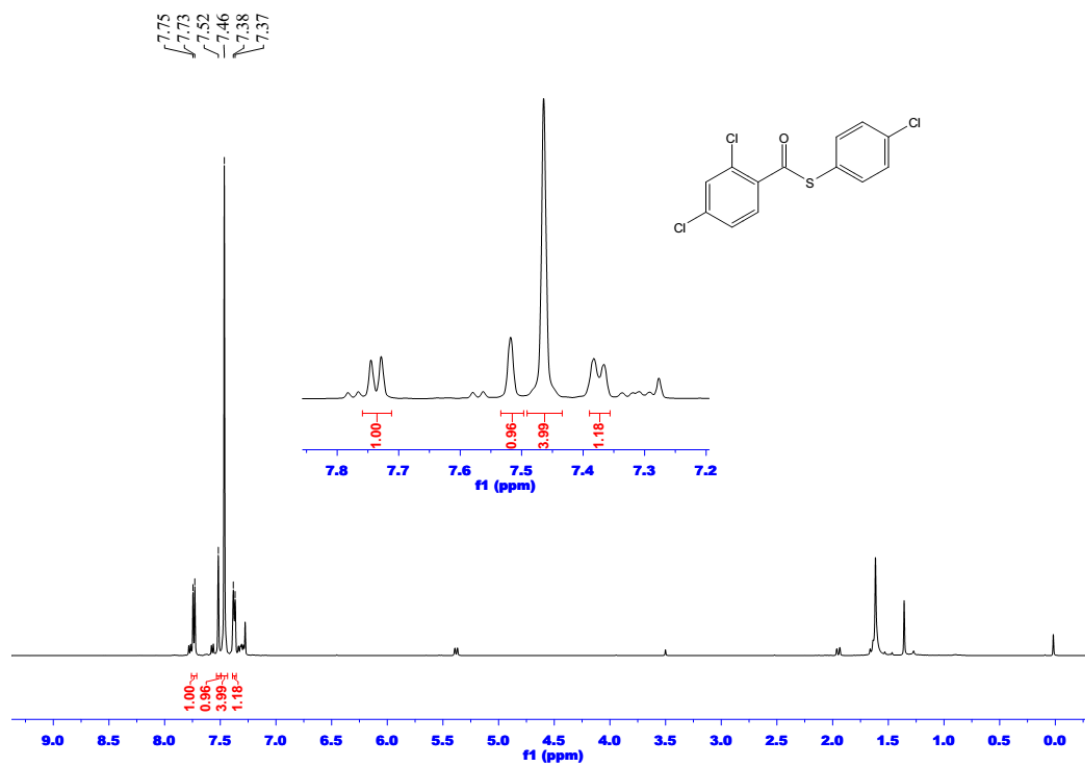
¹³C NMR spectrum (125 MHz, CDCl₃) of **3b**



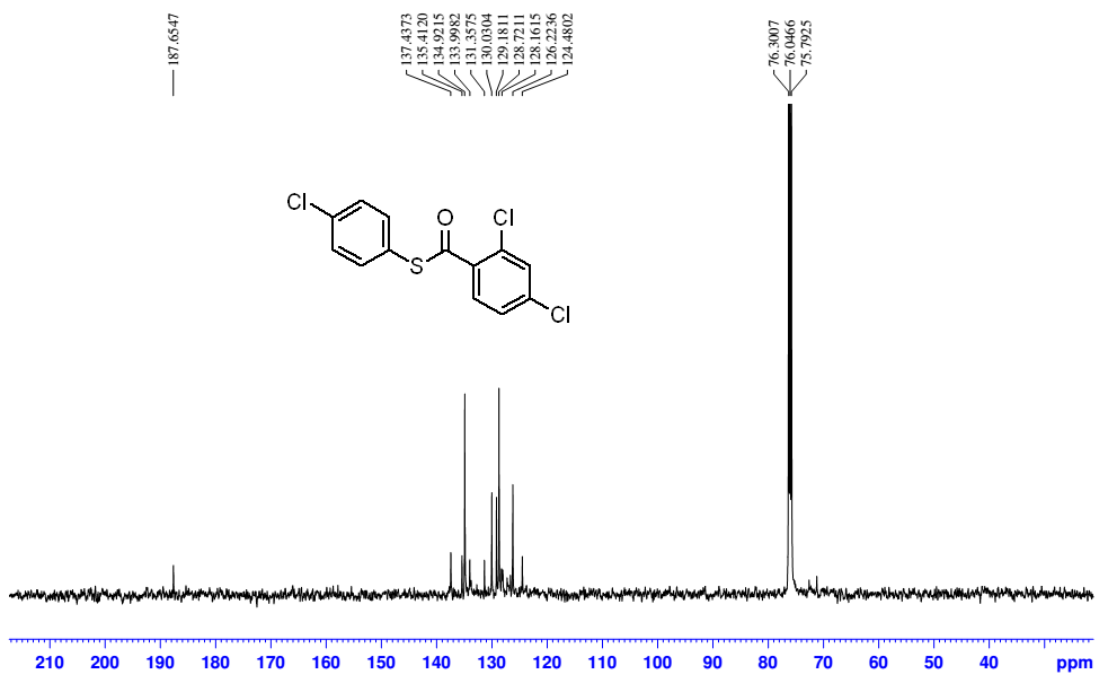
¹H NMR spectrum (500 MHz, CDCl₃) of **3c**



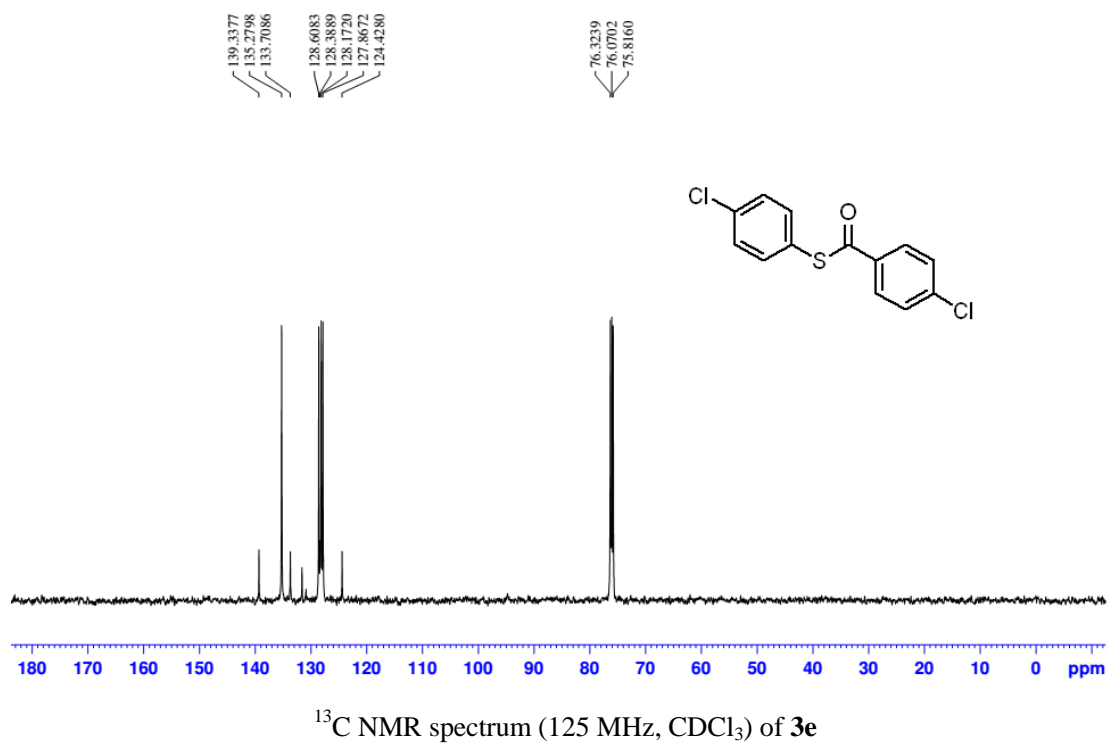
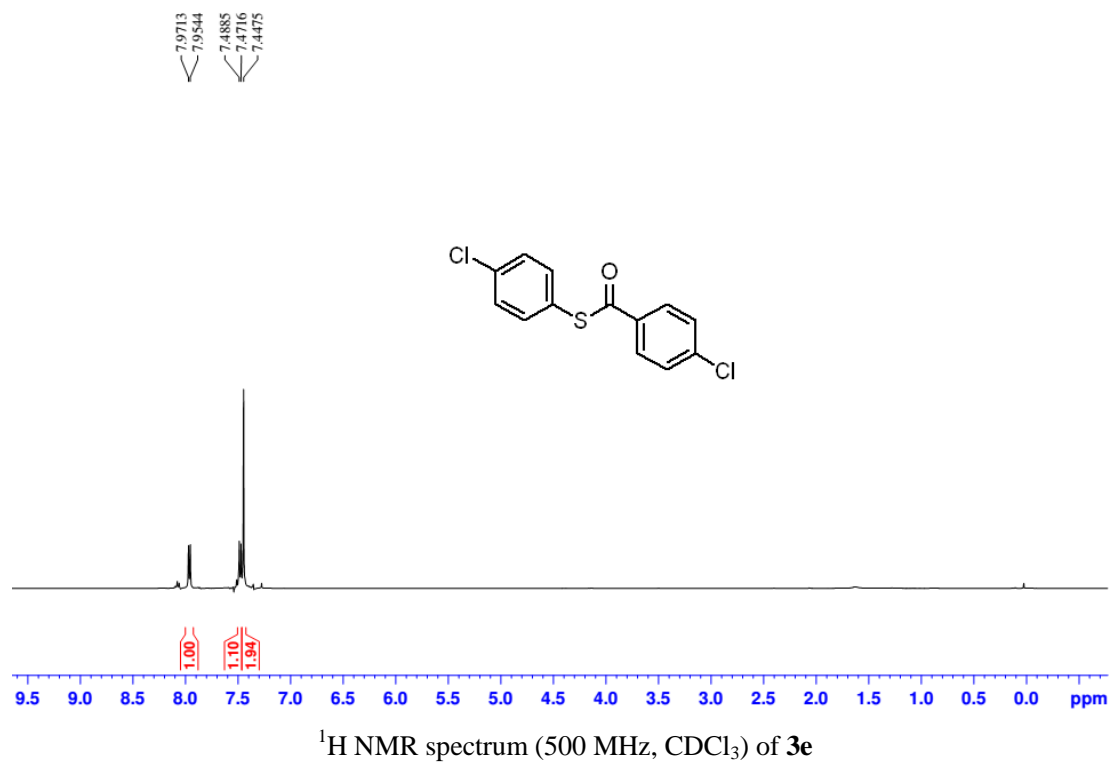
¹³C NMR spectrum (125 MHz, CDCl₃) of **3c**

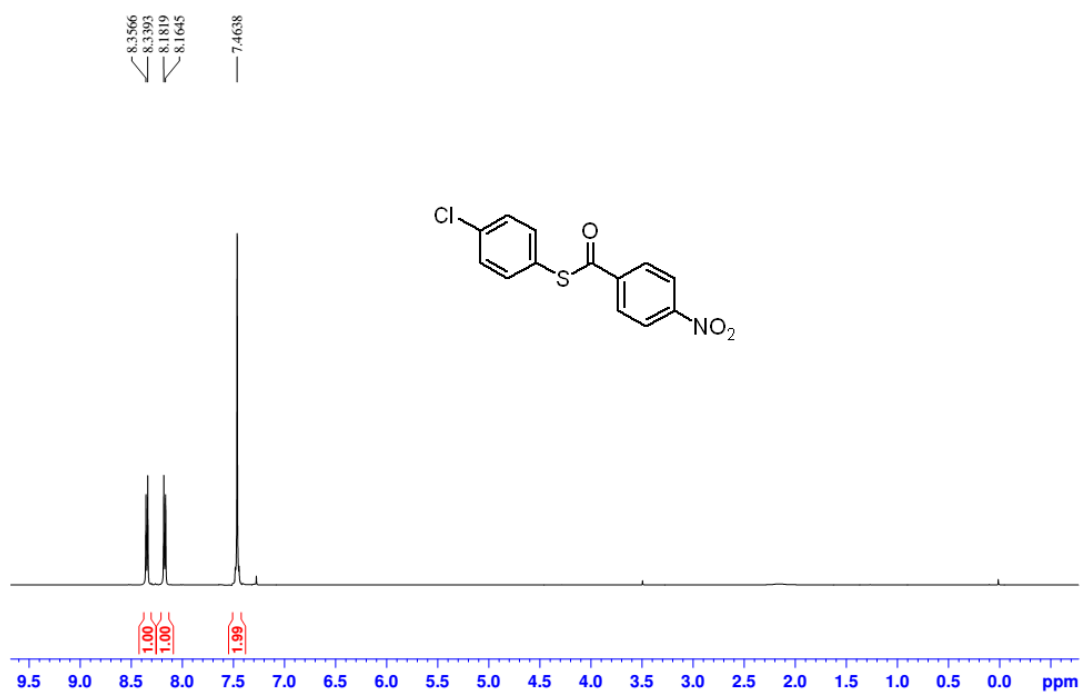


^1H NMR spectrum (500 MHz, CDCl_3) of **3d**

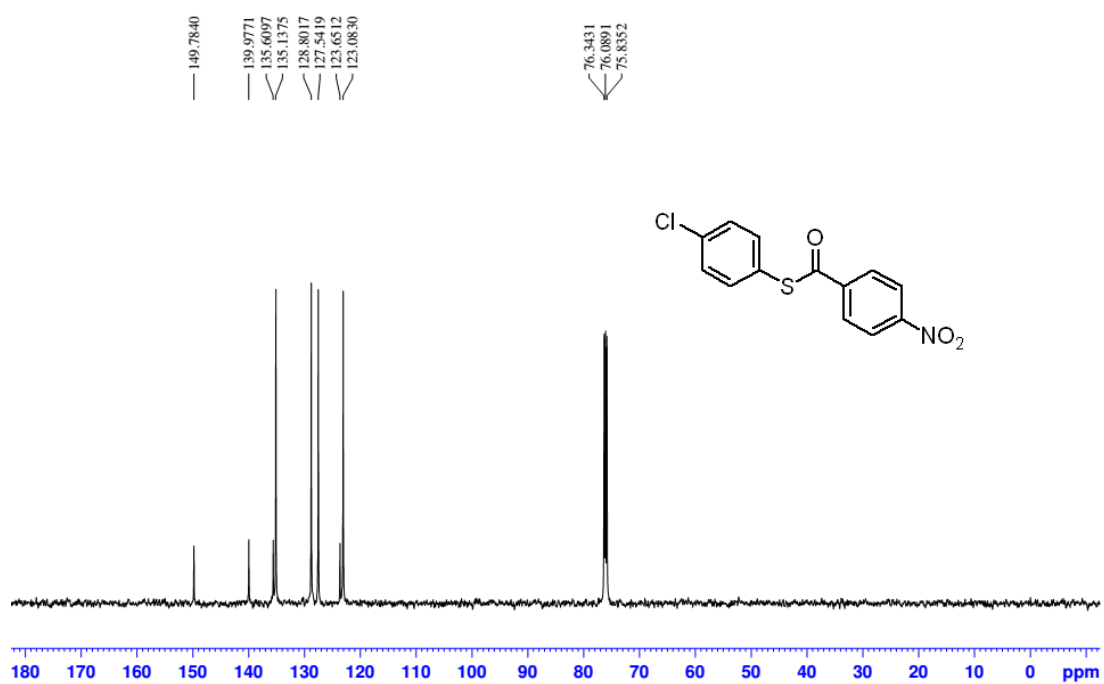


^{13}C NMR spectrum (125 MHz, CDCl_3) of **3d**

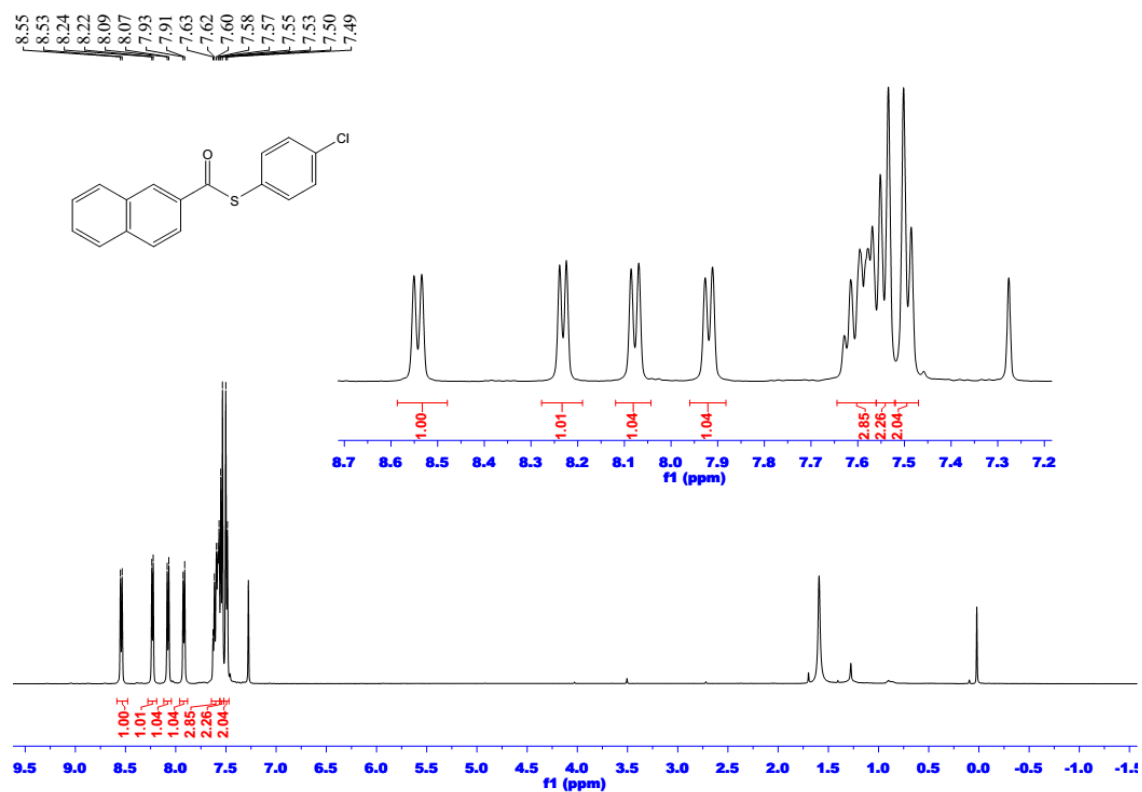




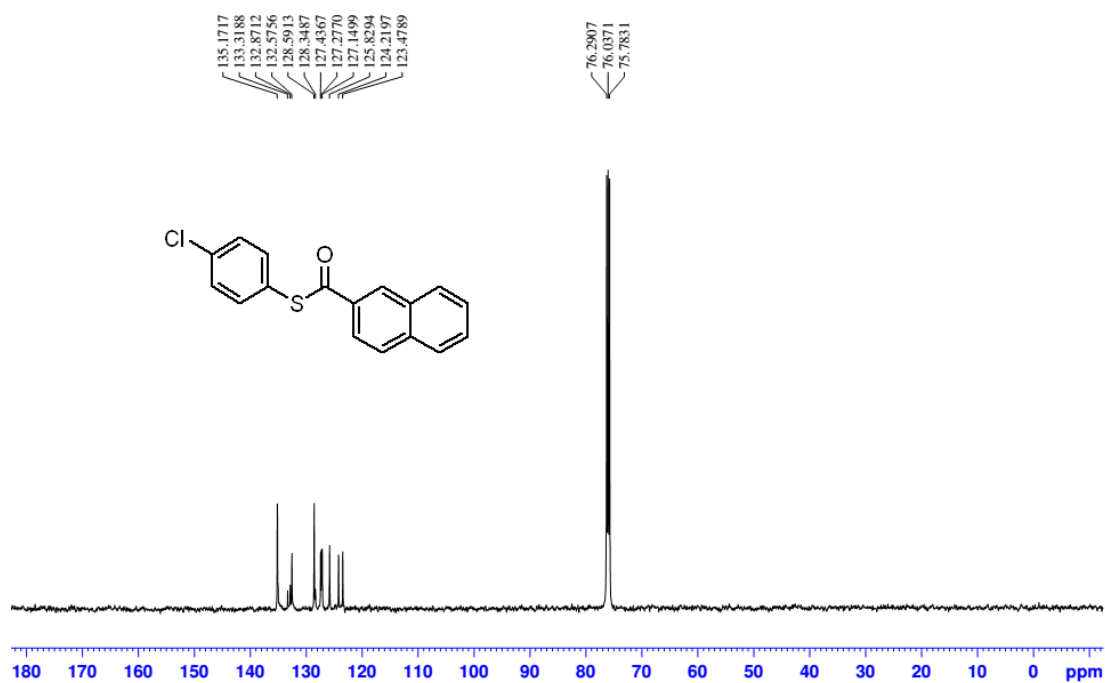
^1H NMR spectrum (500 MHz, CDCl_3) of **3f**



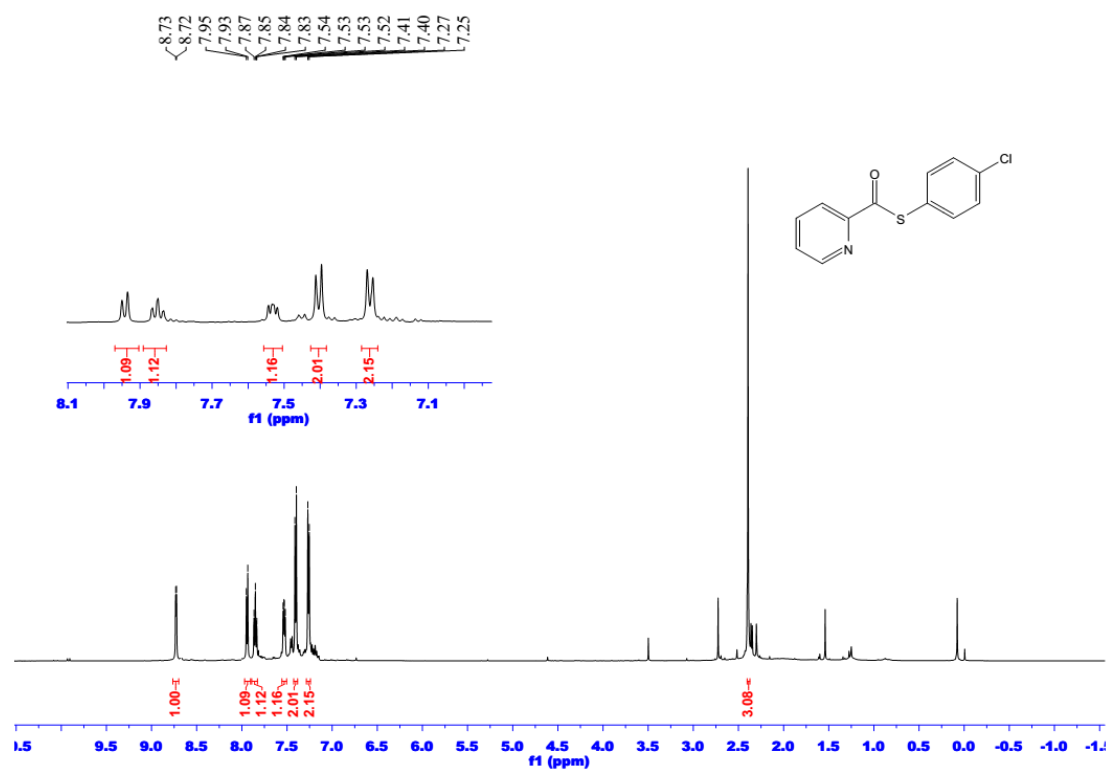
^{13}C NMR spectrum (125 MHz, CDCl_3) of **3f**



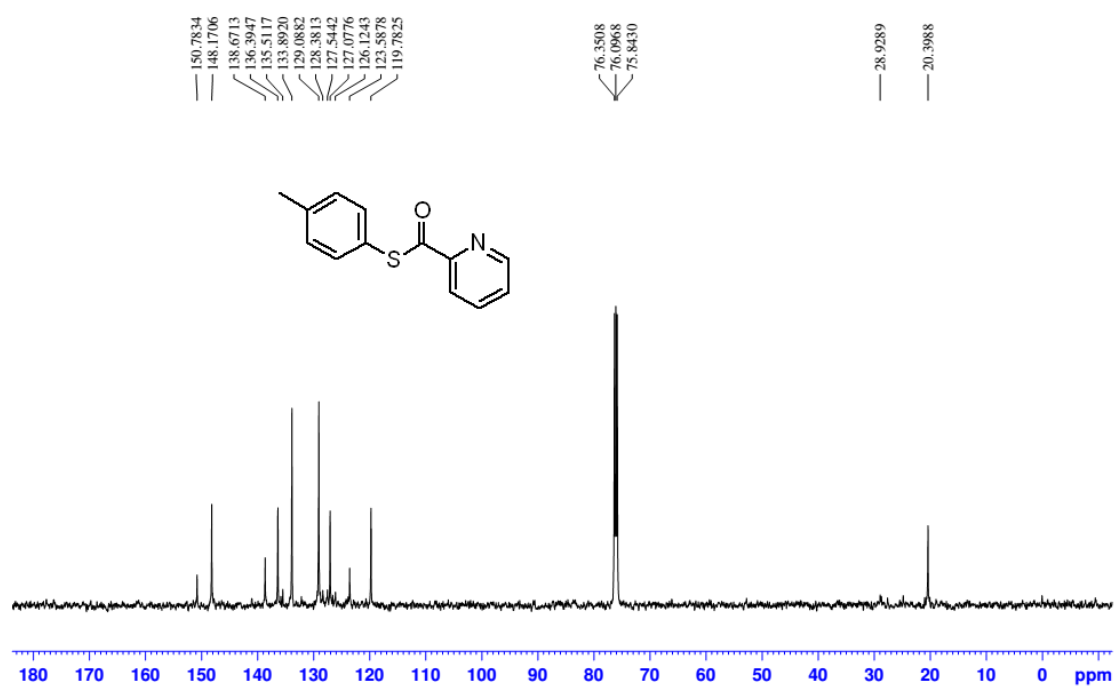
¹H NMR spectrum (500 MHz, CDCl₃) of **3g**



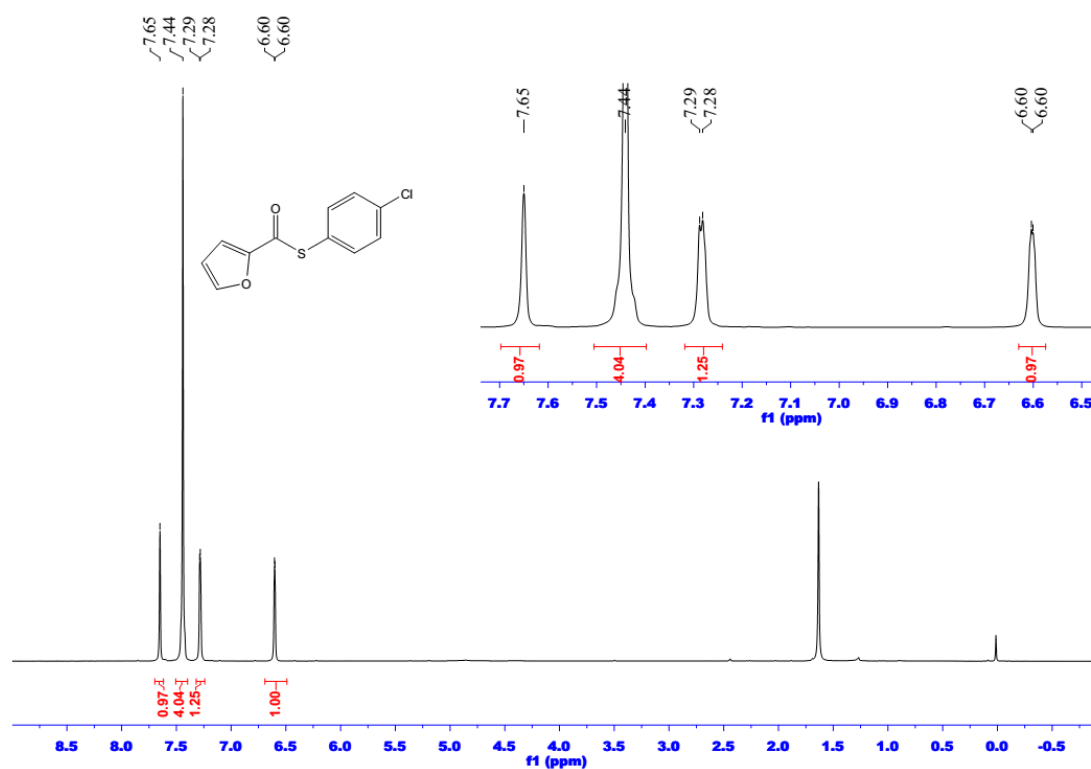
¹³C NMR spectrum (125 MHz, CDCl₃) of **3g**



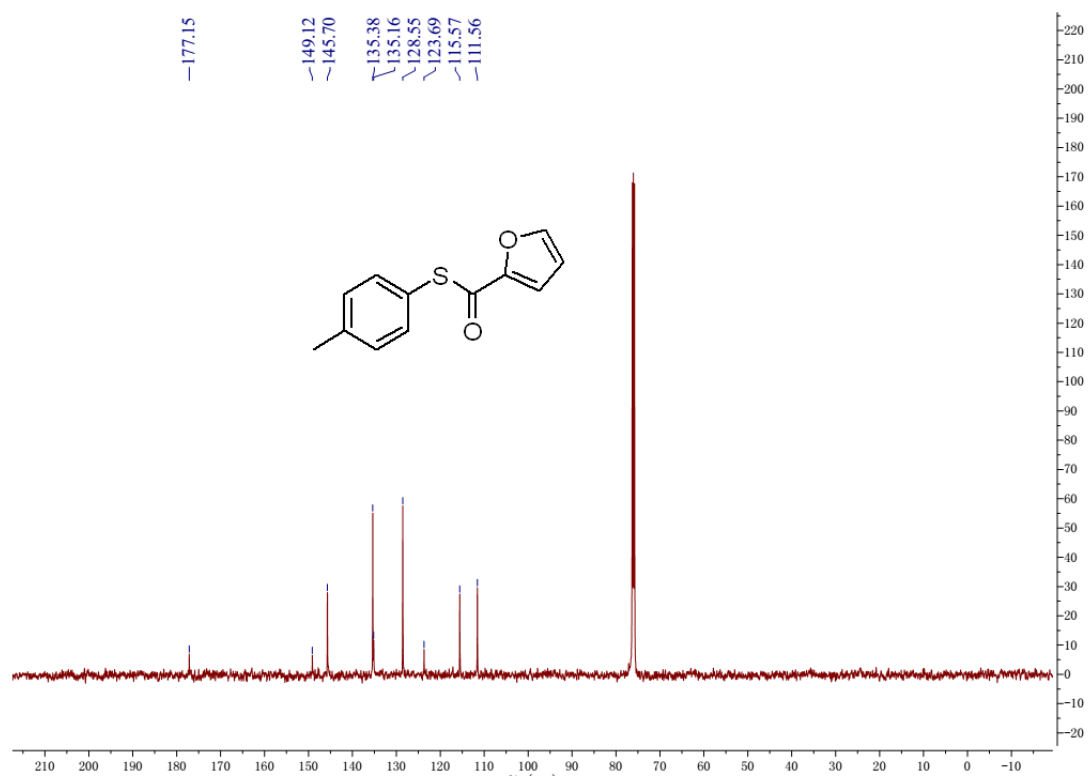
¹H NMR spectrum (500 MHz, CDCl₃) of **3h**



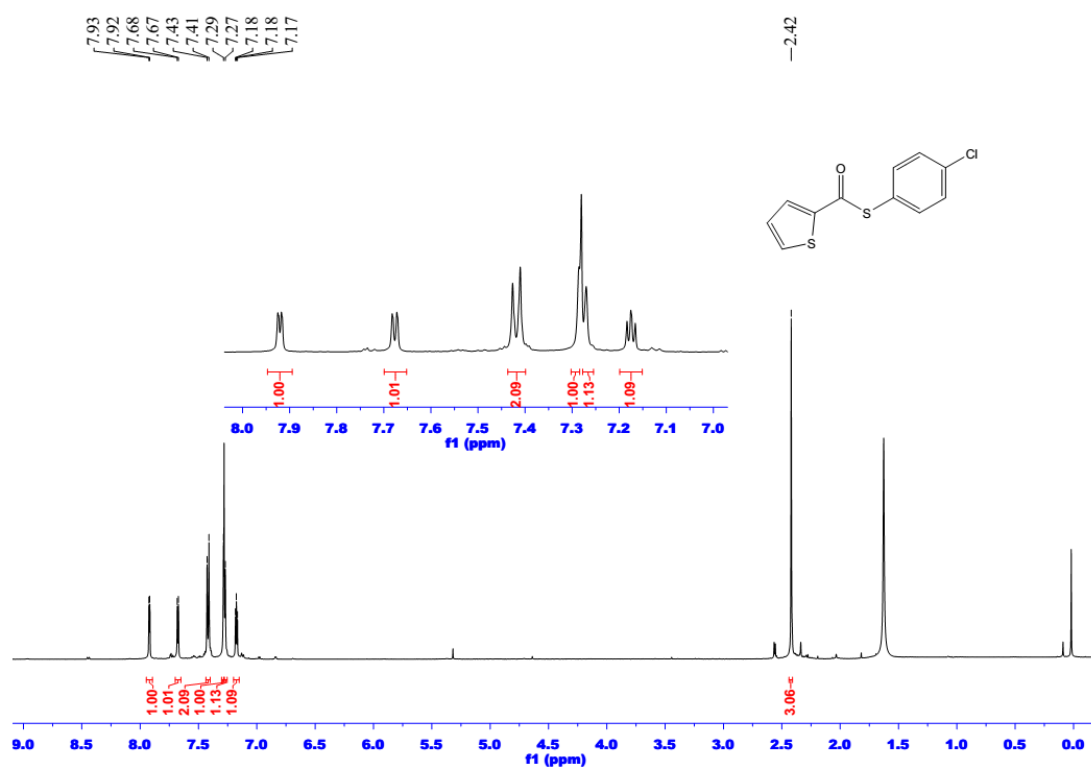
¹³C NMR spectrum (125 MHz, CDCl₃) of **3h**



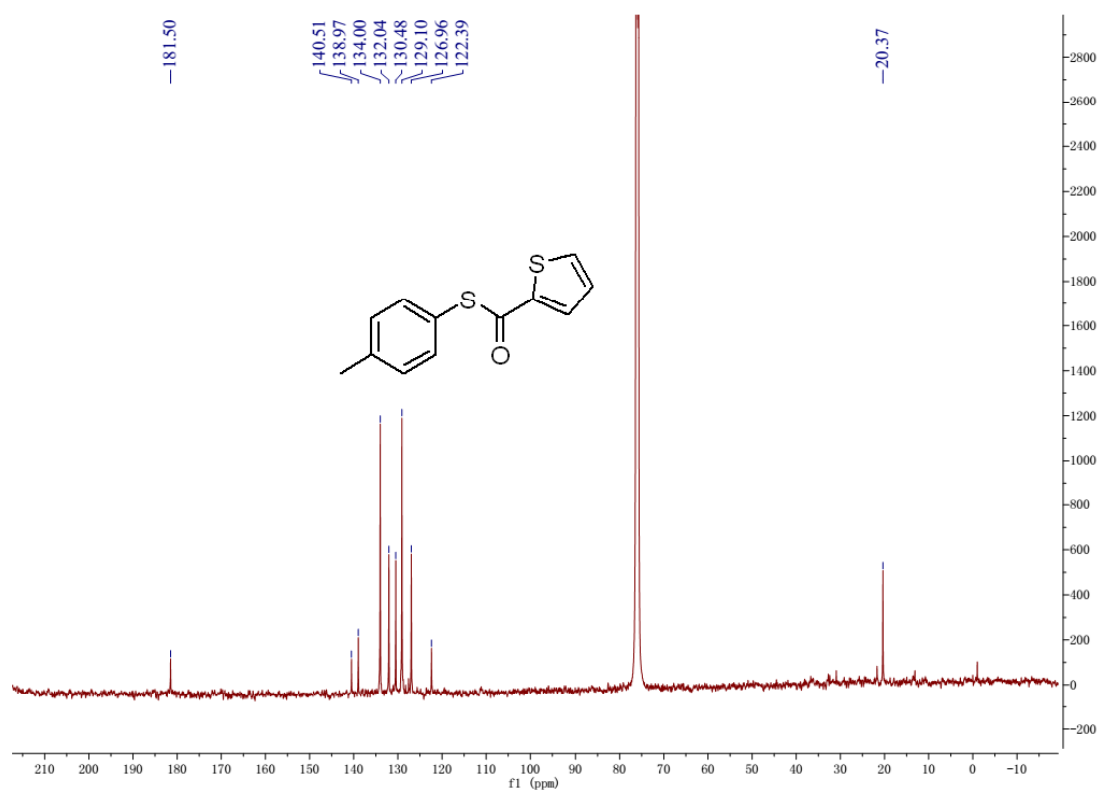
¹H NMR spectrum (500 MHz, CDCl₃) of **3i**



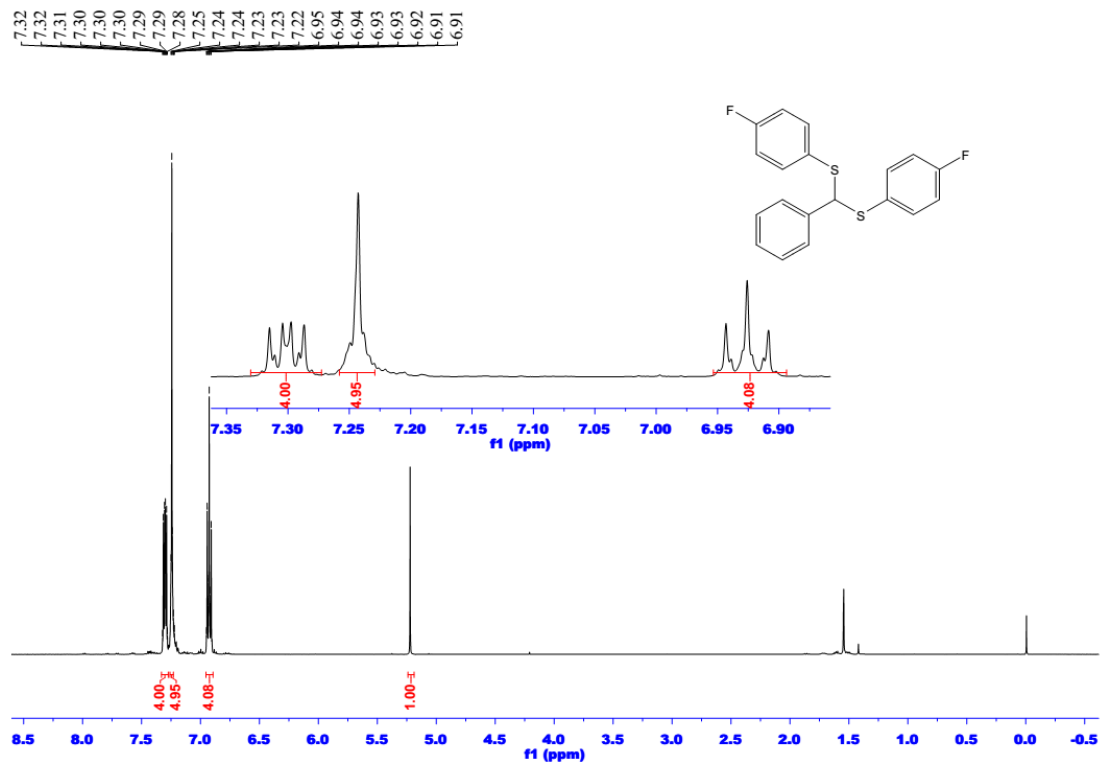
¹³C NMR spectrum (125 MHz, CDCl₃) of **3i**



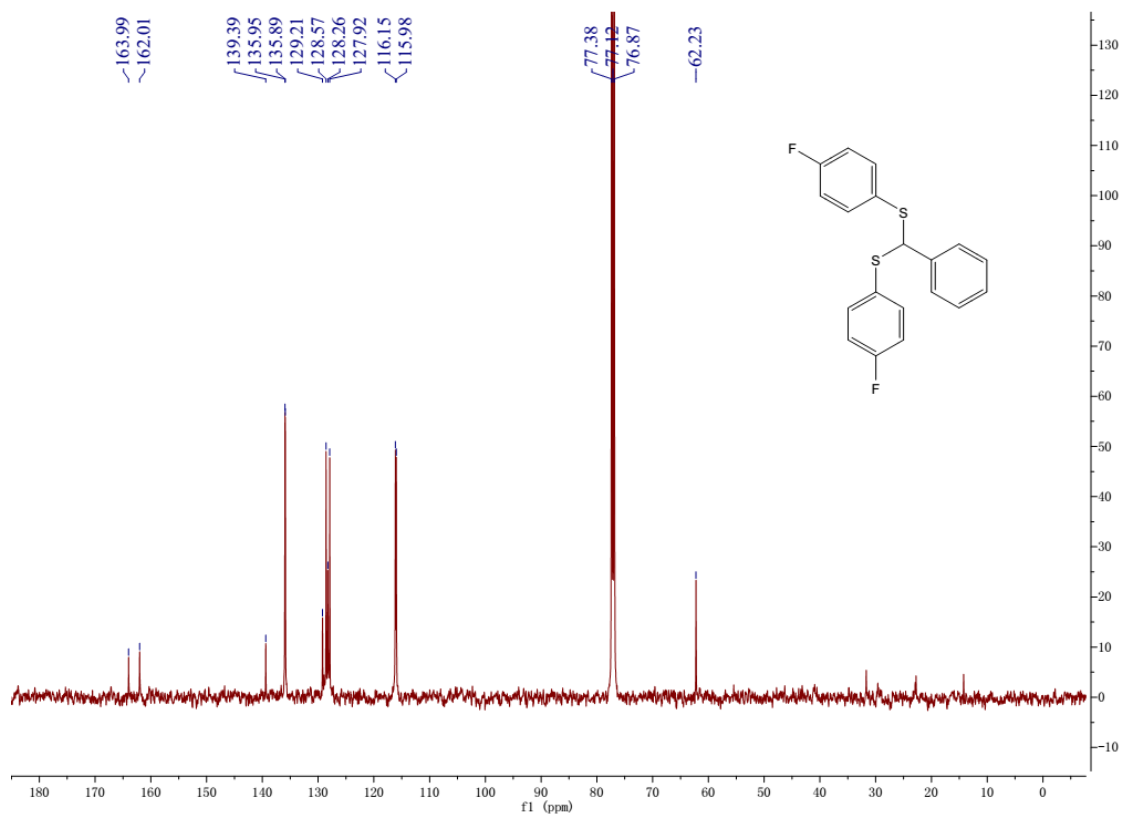
¹H NMR spectrum (500 MHz, CDCl₃) of **3j**



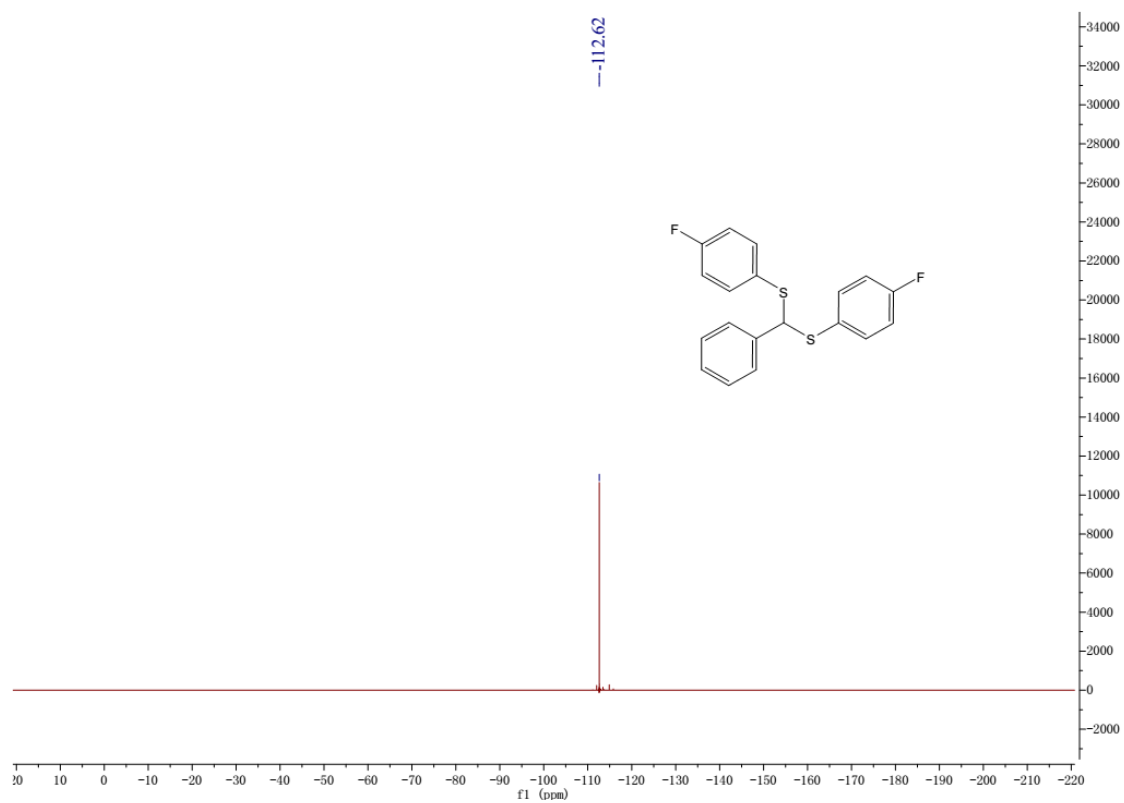
¹³C NMR spectrum (125 MHz, CDCl₃) of **3j**

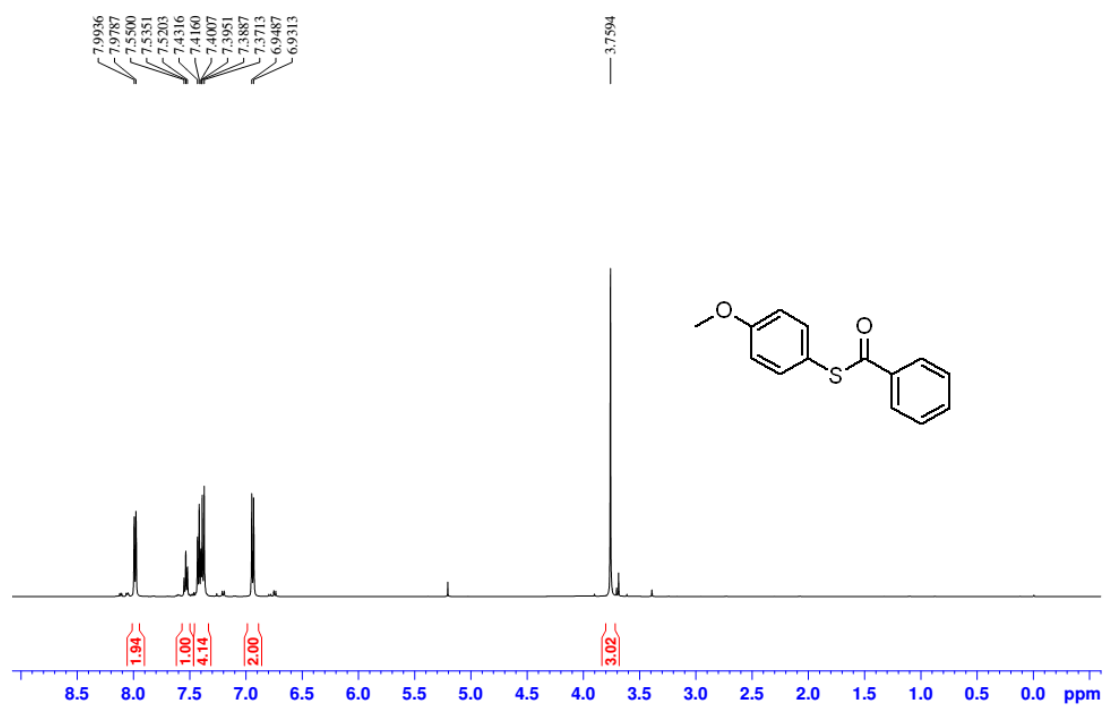


¹H NMR spectrum (500 MHz, CDCl₃) of **3k'**

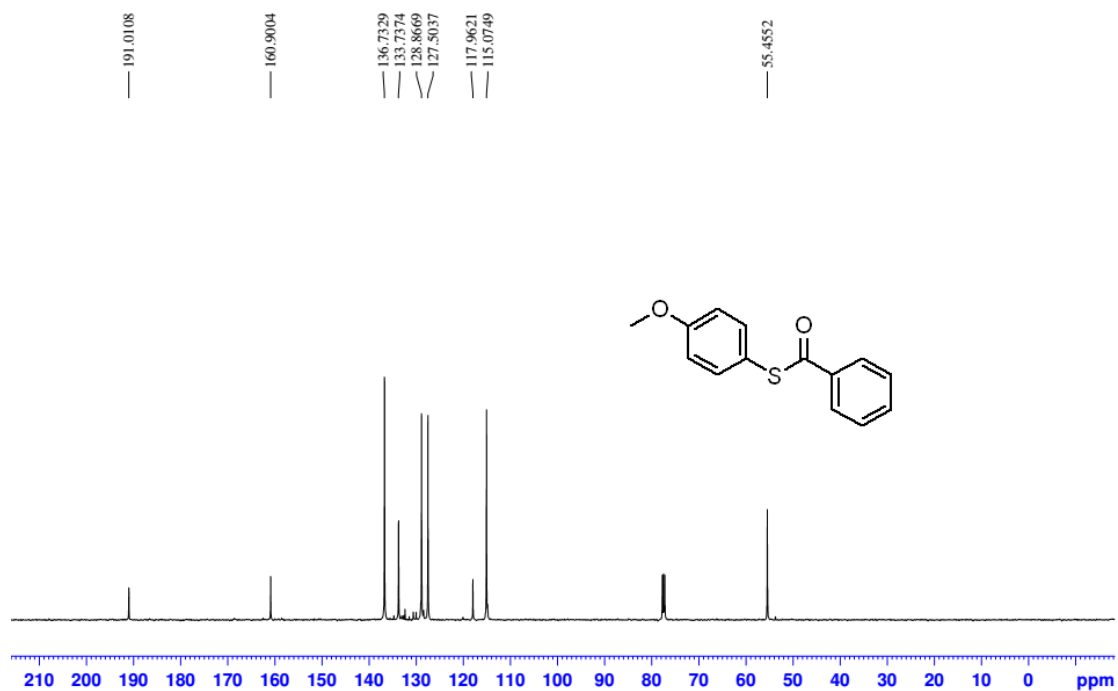


¹³C NMR spectrum (125 MHz, CDCl₃) of **3k'**

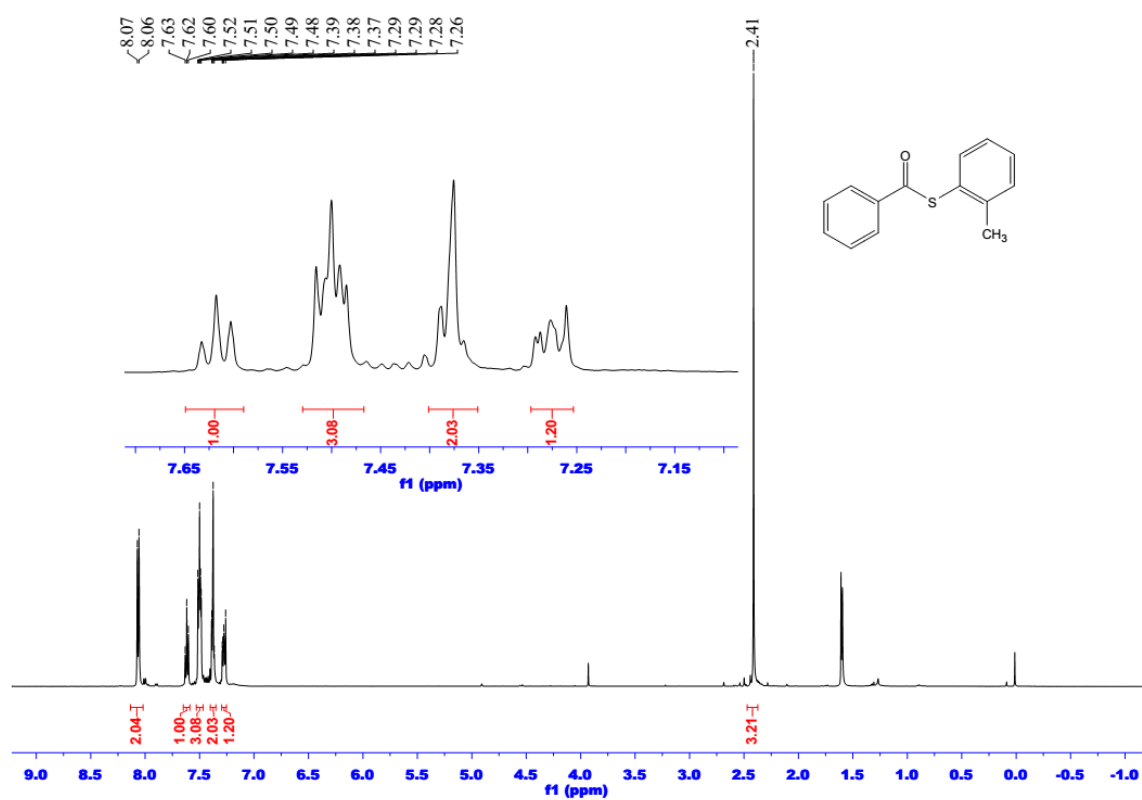




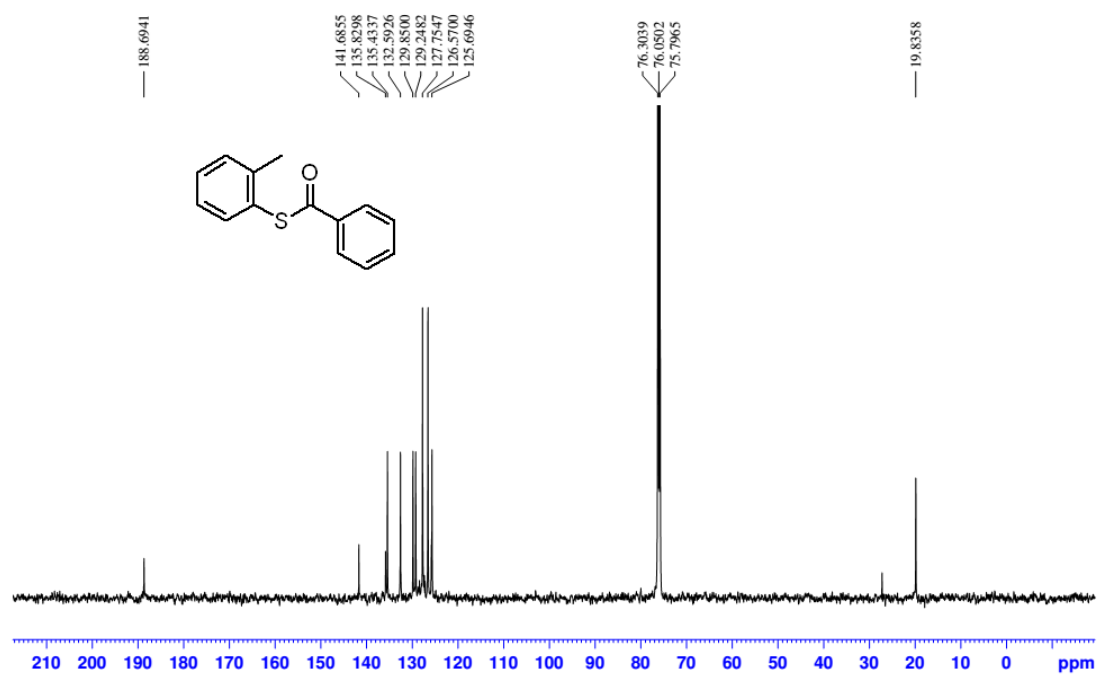
¹H NMR spectrum (500 MHz, CDCl₃) of **31**



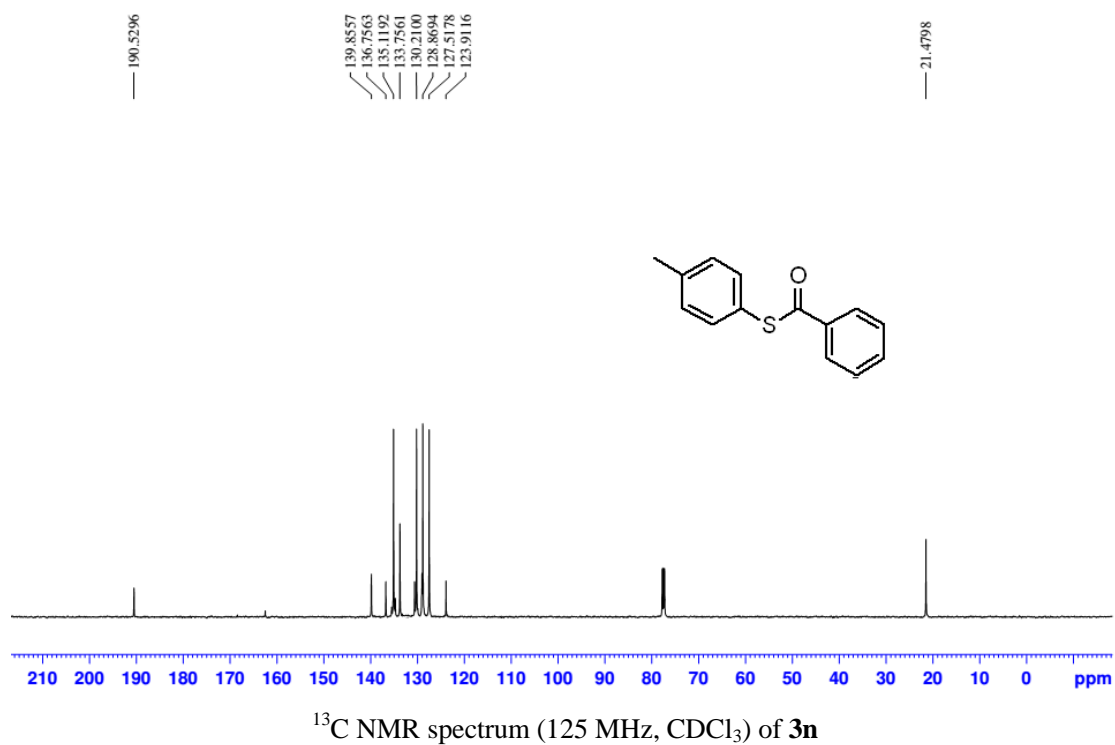
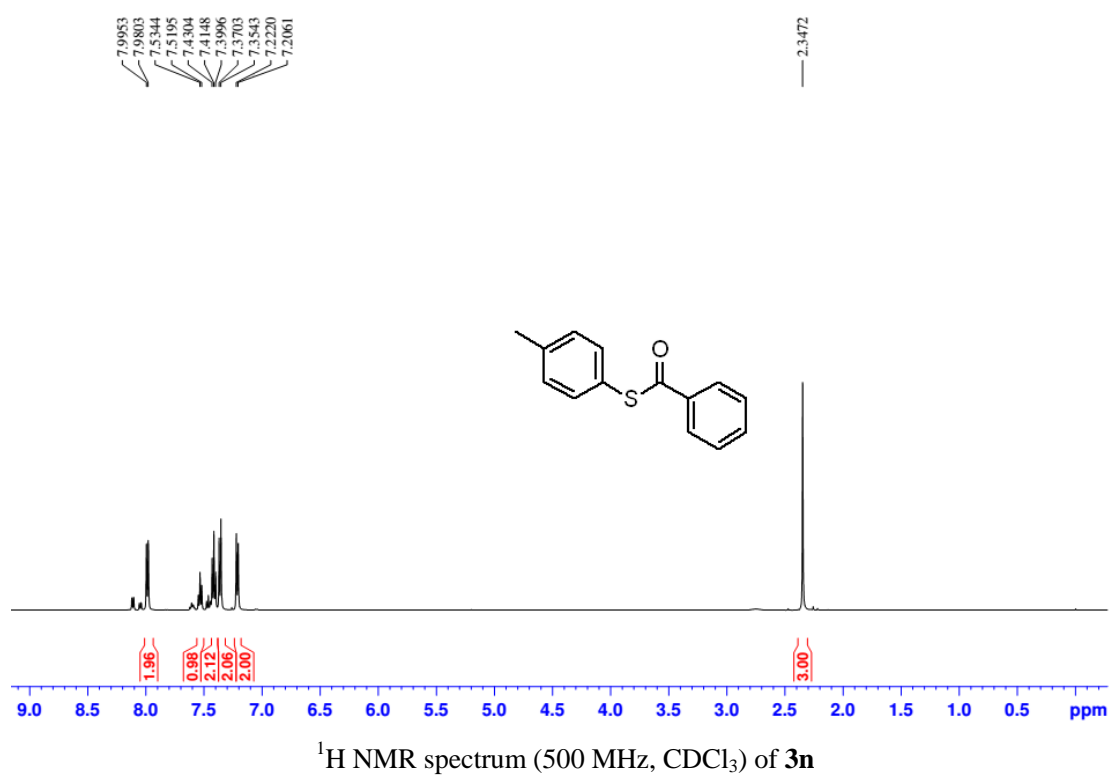
¹³C NMR spectrum (125 MHz, CDCl₃) of **31**

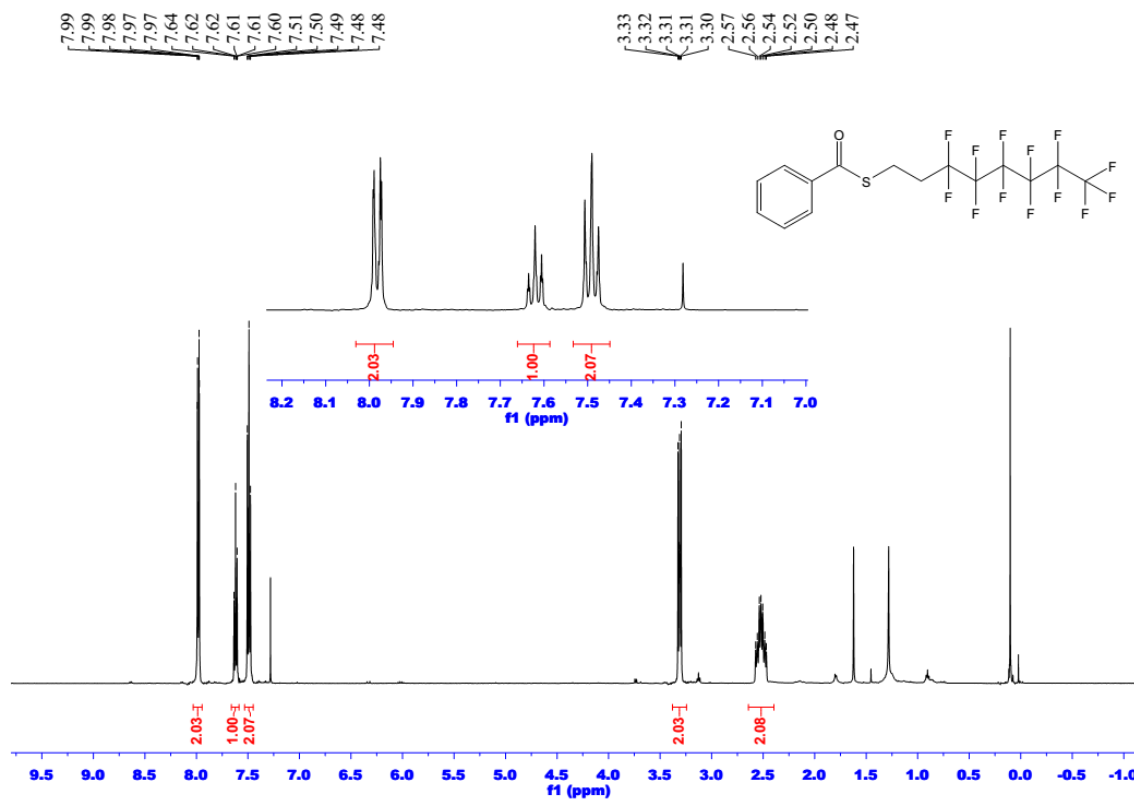


¹H NMR spectrum (500 MHz, CDCl₃) of **3m**

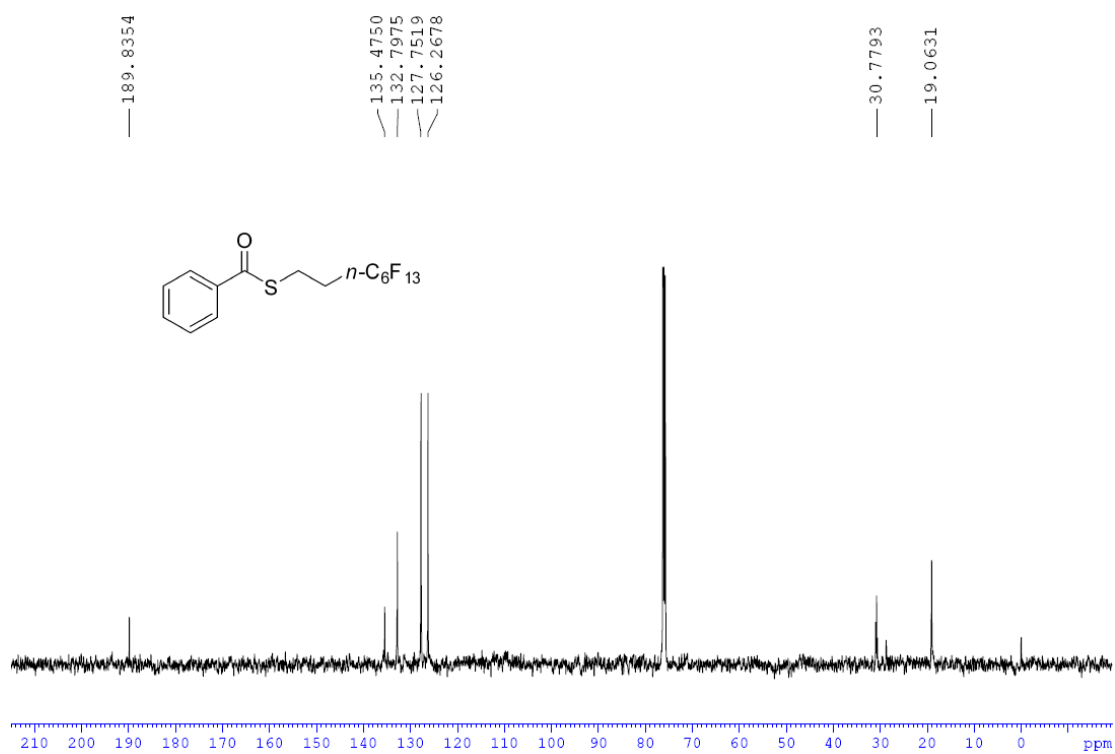


¹³C NMR spectrum (125 MHz, CDCl₃) of **3m**

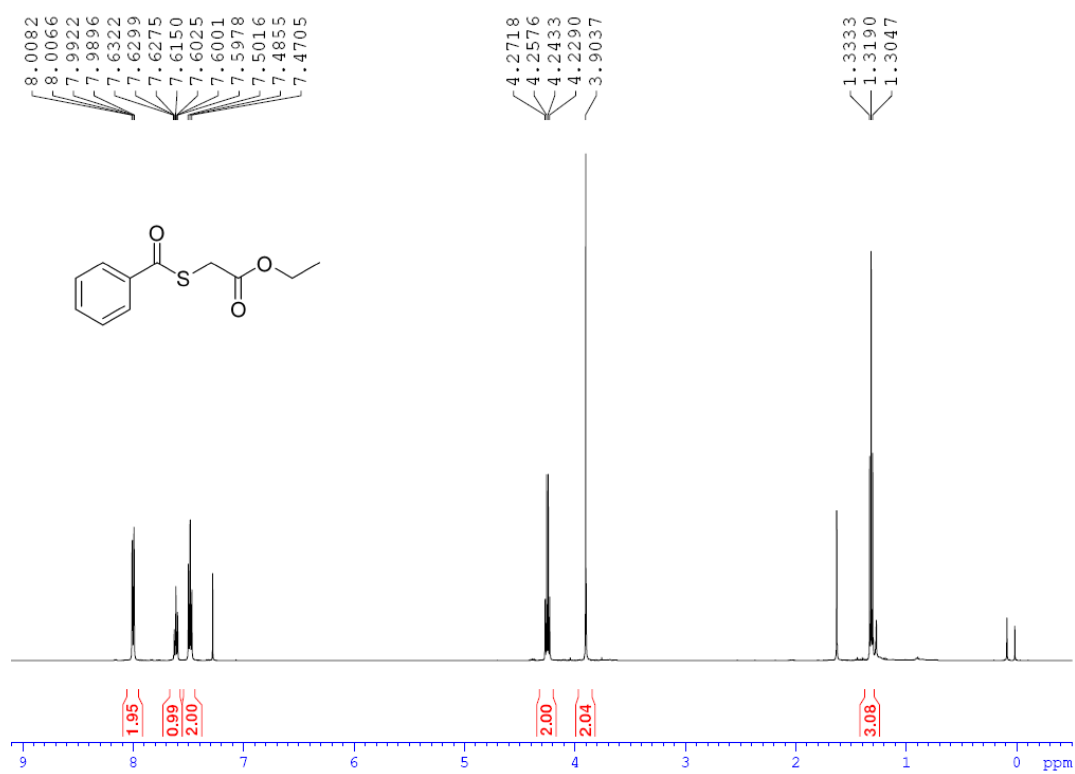




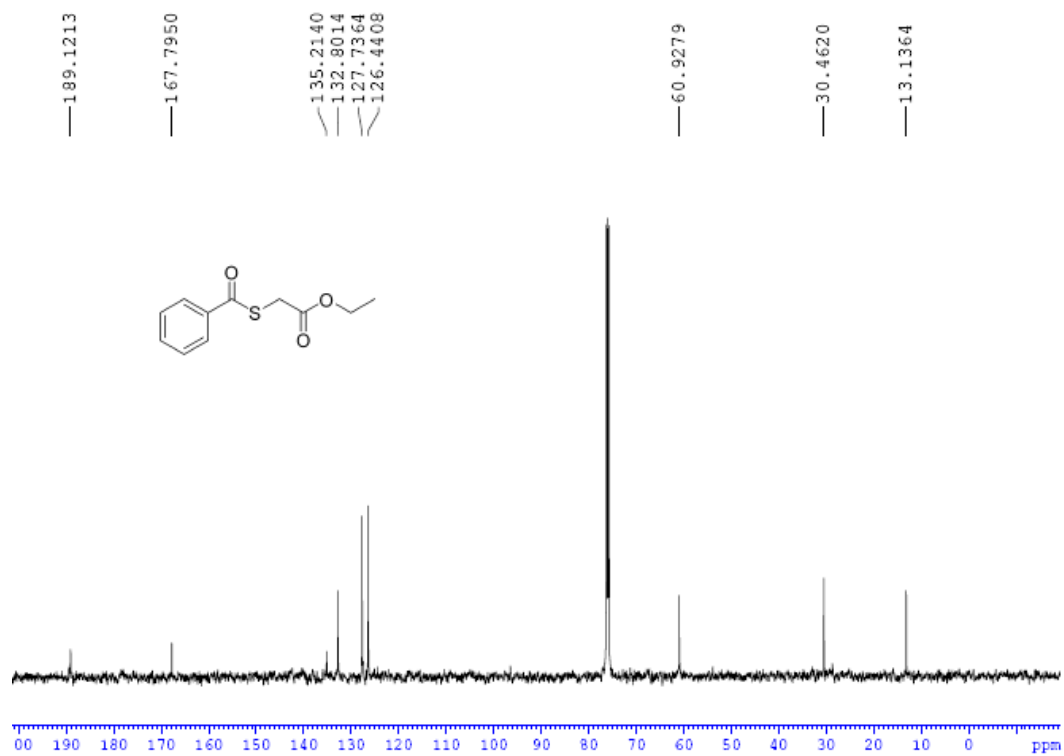
¹H NMR spectrum (500 MHz, CDCl₃) of **3o**



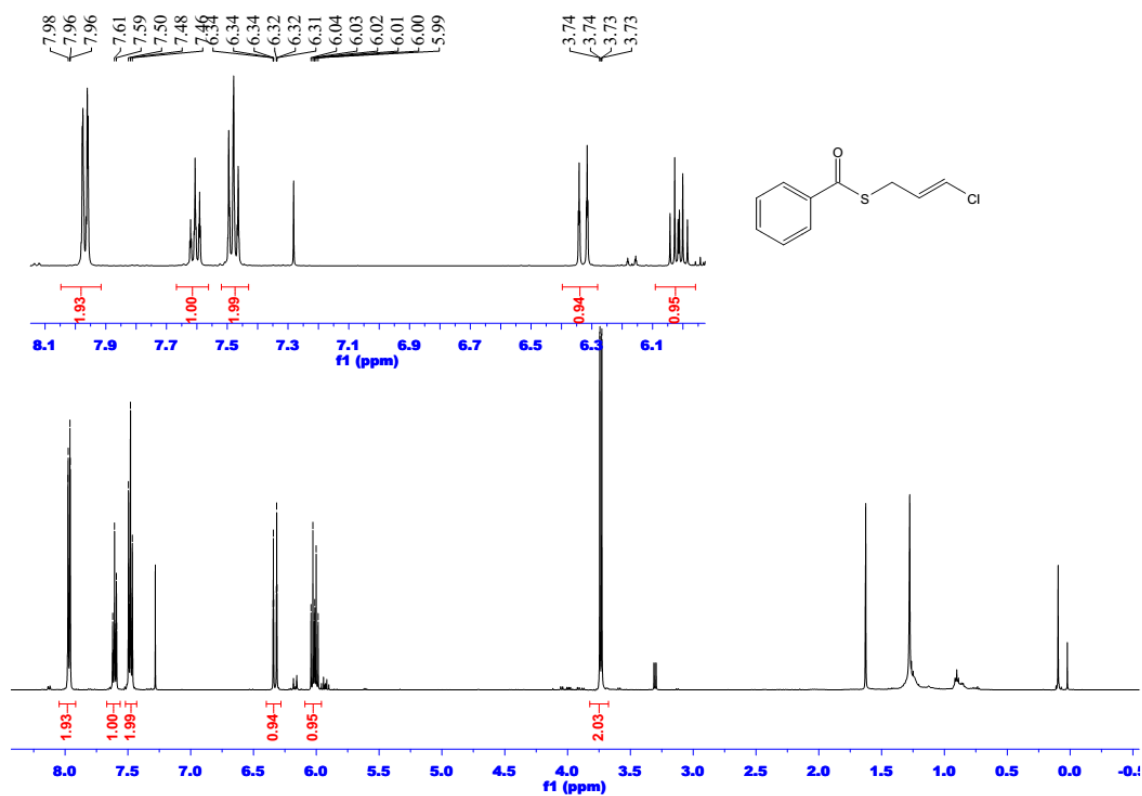
¹³C NMR spectrum (125 MHz, CDCl₃) of **3o**



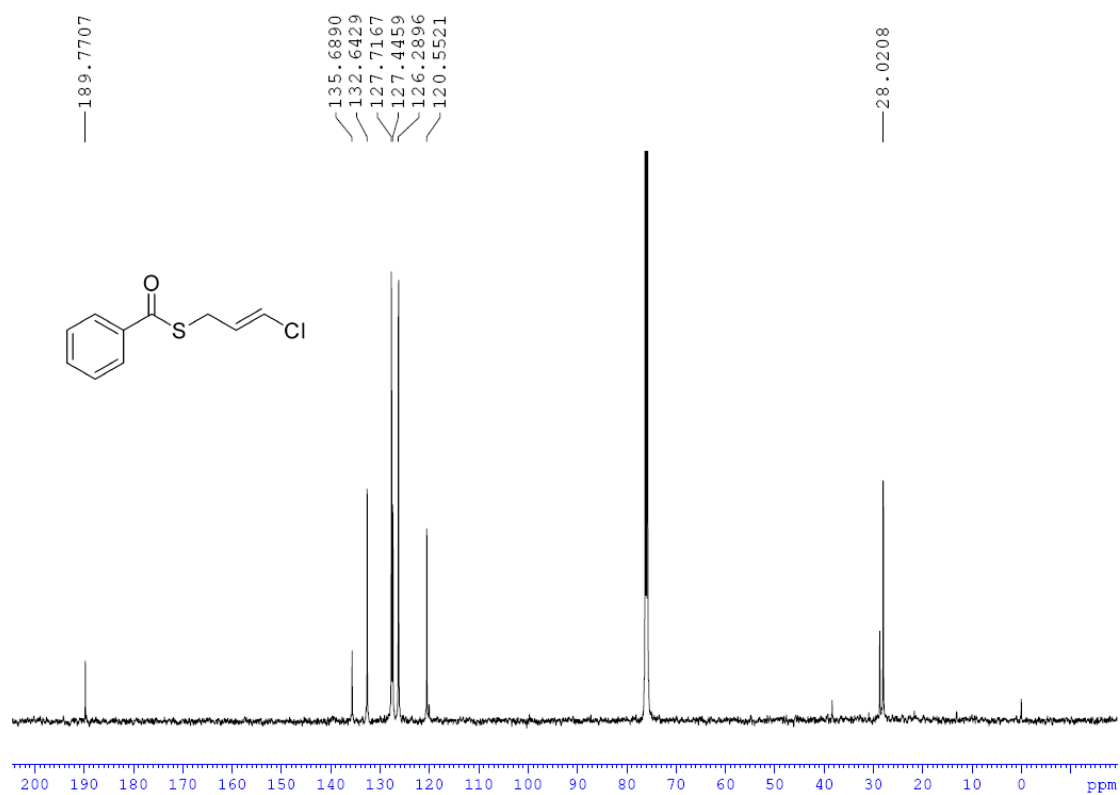
¹H NMR spectrum (500 MHz, CDCl₃) of **3p**



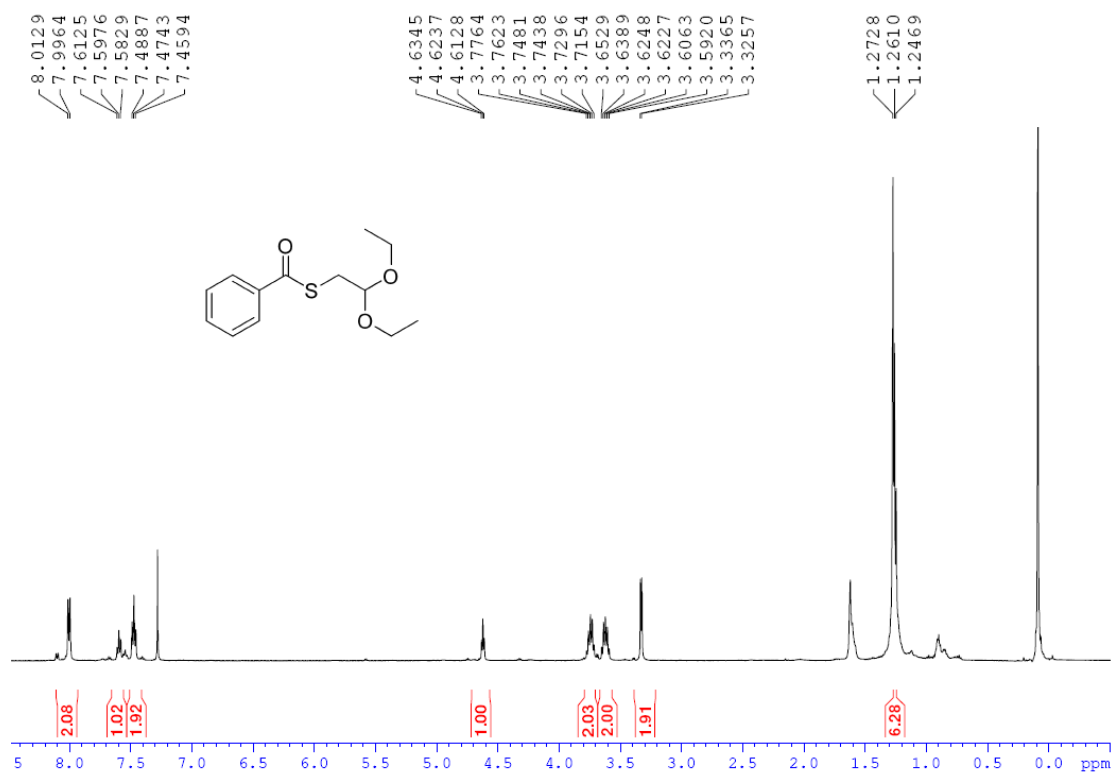
¹³C NMR spectrum (125 MHz, CDCl₃) of **3p**



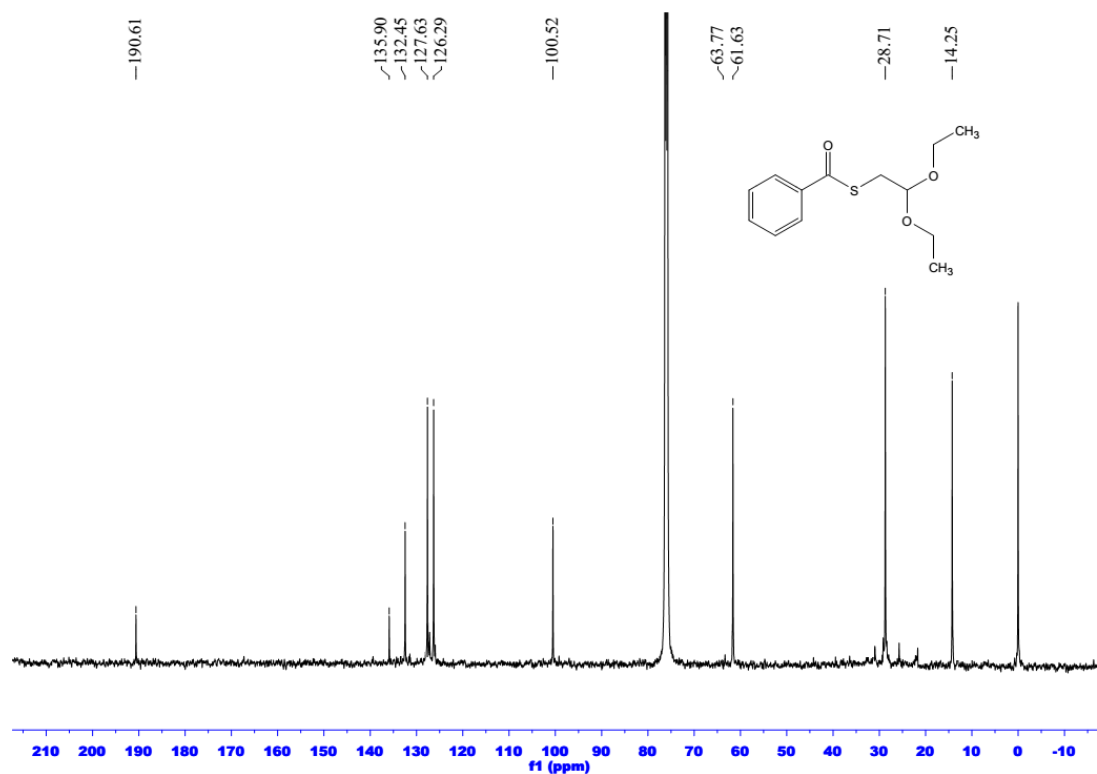
¹H NMR spectrum (500 MHz, CDCl₃) of **3q**



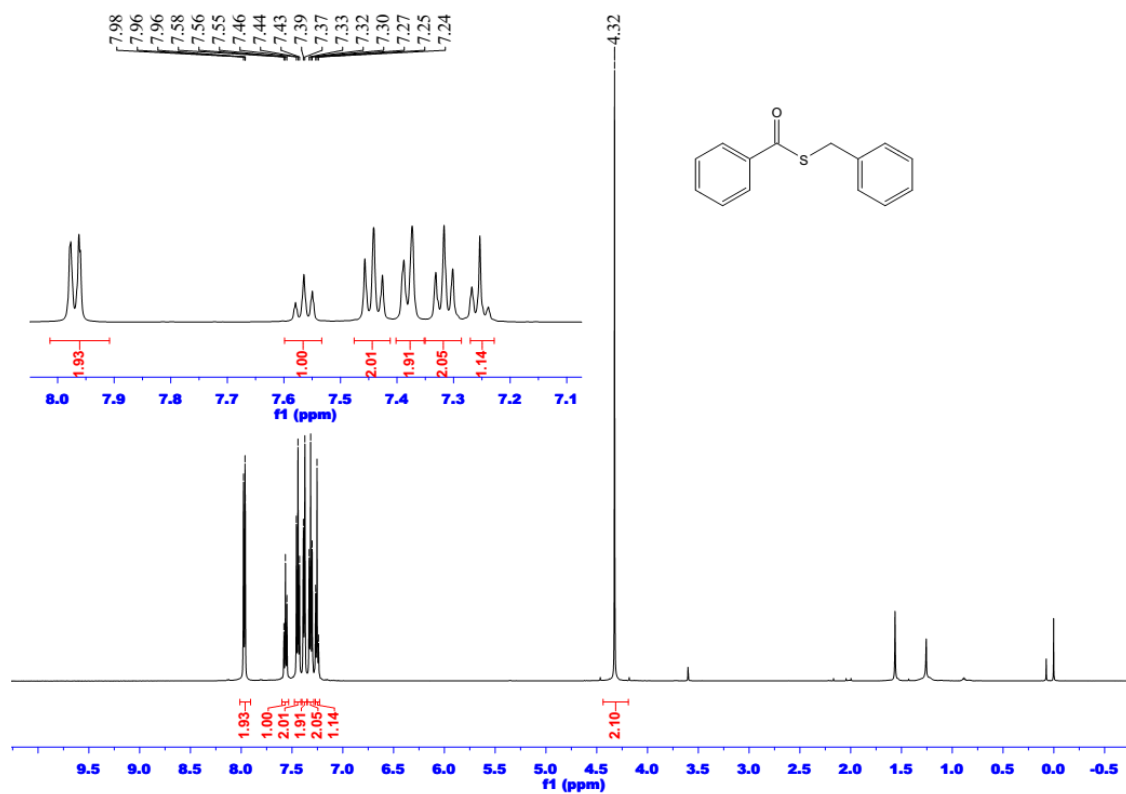
¹³C NMR spectrum (125 MHz, CDCl₃) of **3q**



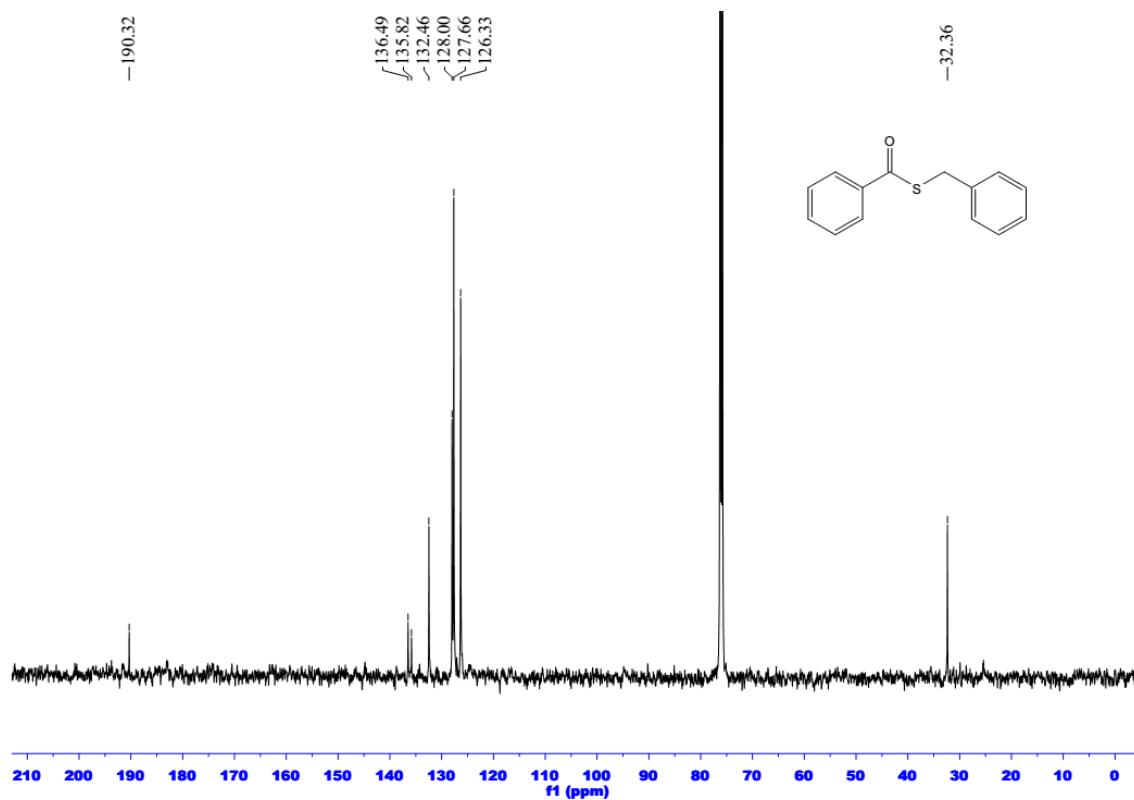
¹H NMR spectrum (500 MHz, CDCl₃) of **3r**



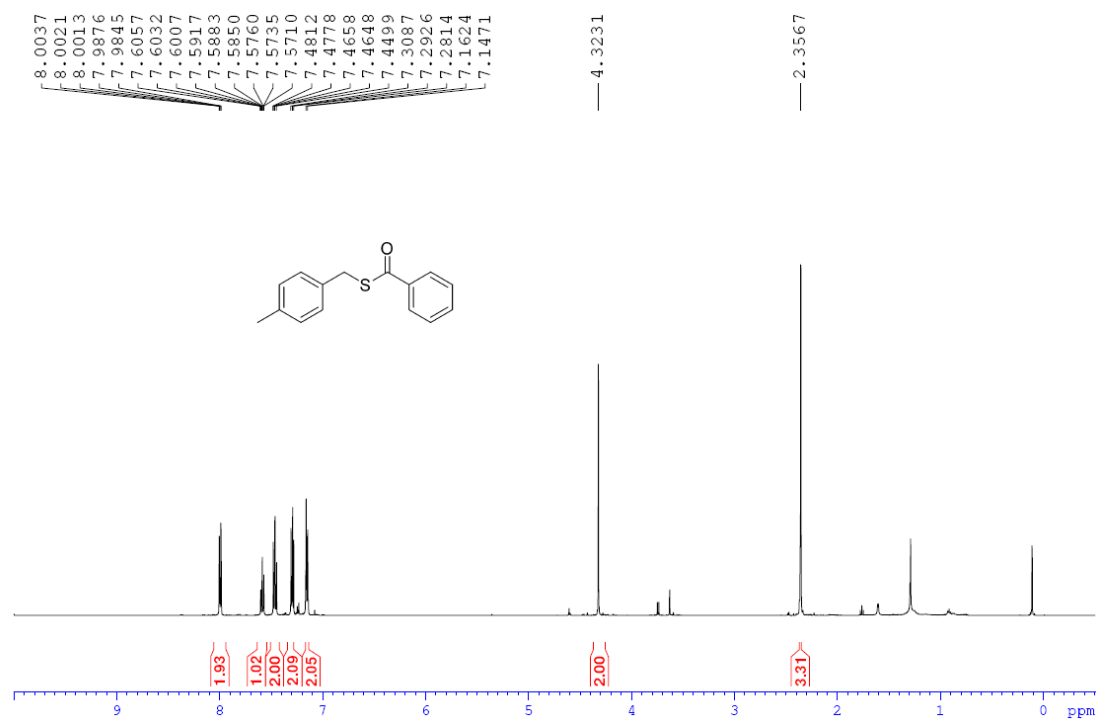
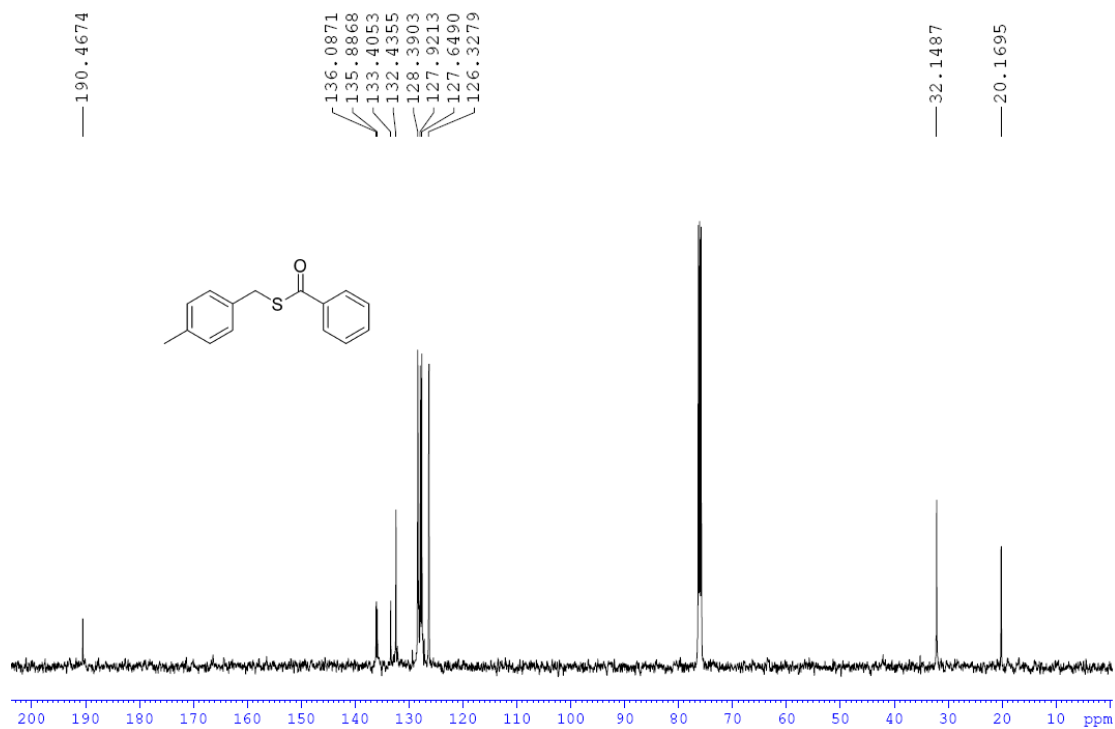
¹³C NMR spectrum (125 MHz, CDCl₃) of **3r**



¹H NMR spectrum (500 MHz, CDCl₃) of **3s**



¹³C NMR spectrum (1)

25 MHz, CDCl₃) of **3s**¹H NMR spectrum (500 MHz, CDCl₃) of **3t**¹³C NMR (125 MHz, CDCl₃) spectrum of **3t**

