Supporting information

Polymer supported Pd catalyzed thioesters synthesis *via* carbonylation of aryl halides under phosphine free condition

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NMR Data of carbonylation products

S-Phenyl benzothioate (Table 4, entry 1)
Colorless crystals, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.06-8.04 (m, 2H), 7.64-7.44 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 190.1, 136.7, 135.1, 133.7, 129.5, 129.3, 128.8, 127.5, 127.4.

S-Phenyl 4-methylbenzothioate (Table 4, entry 2)
Colorless crystals, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.94 (d, J = 8.4 Hz, 2H), 7.54-7.44 (m, 5H), 7.29 (d, J = 8.4 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 189.7, 144.6, 135.1, 134.1, 129.4, 129.2, 127.6, 21.7.

***S*-Phenyl 3-methylbenzothioate (Table 4, entry 3)**
Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.86-7.85 (m, 2H), 7.54-7.36 (m, 7H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 190.2, 138.7, 136.7, 135.1, 134.4, 129.5, 129.2, 128.6, 127.7, 127.5, 124.7, 21.3.

***S*-Phenyl 2-methylbenzothioate (Table 4, entry 4)**
Colorless crystals, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 (dd, J = 7.6 Hz, J = 0.8 Hz, 1H), 7.55-7.41 (m, 6H), 7.32 (d, J = 7.6 Hz, 1H), 7.28 (d, J = 8.0 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 192.1, 137.4, 136.8, 134.9, 132.0, 131.7, 129.4, 129.2, 128.6, 128.2, 125.8, 20.8.

S-Phenyl 4-methoxybenzothioate (Table 4, entry 5)
Colorless crystals, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.02 (d, J = 9.2 Hz, 2H), 7.54-7.44 (m, 5H), 6.97 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 188.5, 164.0, 135.2, 129.7, 129.4, 129.3, 129.1, 127.6, 113.9, 55.5.

***S*-Phenyl 3-methoxybenzothioate (Table 4, entry 6)**
Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.67 (d, J = 9.2 Hz, 1H), 7.54-7.45 (m, 6H), 7.40 (t, J = 8.4 Hz, 1H), 7.16 (dd, J = 8.4 Hz, J = 0.4 Hz,1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 190.0, 159.8, 138.0,135.0, 129.7, 129.5, 129.2, 127.4, 120.1, 120.0, 111.8, 55.5.

S-Phenyl 2-methoxybenzothioate (Table 4, entry 7)
Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.86 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.55-7.42 (m, 6H), 7.03 (t, J = 7.2 Hz, 2H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 189.1, 158.2, 134.9, 134.1, 129.9, 129.3, 129.1, 128.8, 126.3, 120.5, 112.1, 56.0.

S-Phenyl 2,4-dimethoxybenzothioate (Table 4, entry 8)
Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.91 (d, J = 8.8 Hz, 1H), 7.53-7.42 (m, 5H), 6.55 (dd, J = 8.8 Hz, J = 2.0 Hz, 1H), 6.51 (d, J = 2.0 Hz, 1H), 3.96 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 187.4,164.8, 160.5, 135.1, 132.2, 129.12, 129.07, 129.0, 119.2, 105.2, 98.7, 55.8, 55.6.

***S*-Phenyl thiophene-2-carbothioate (Table 4, entry 9)**
Orange crystals, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.92 (dd, J = 4.0 Hz, J = 1.2 Hz, 1H), 7.67 (dd, J = 5.2 Hz, J = 1.2 Hz, 1H), 7.56-7.43 (m, 5H), 7.16 (dd, J = 4.8 Hz, J = 3.6 Hz,

1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 182.0, 141.4, 135.0, 133.2, 131.6, 129.6, 129.2, 128.0, 126.9.

_S_-Phenyl 3,4-dimethoxybenzothioate(Table 4, entry 10)
Colorless crystals, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.75 (dd, *J* = 8.4 Hz, *J* = 2.0 Hz, 1H), 7.53-7.44 (m, 6H), 6.92 (d, *J* = 8.4 Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 188.7, 153.7, 149.0, 135.1, 129.5, 129.4, 129.2, 127.6, 122.0, 110.3, 109.7, 56.1, 56.0.

S-Phenyl 3,4,5-trimethoxybenzothioate(Table 4, entry 11)
Orange oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.53-7.45 (m, 5H), 7.29 (s, 2H), 3.93 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 189.2, 153.2, 142.2, 134.8, 131.7, 129.5, 129.2, 127.4, 104.8, 61.0, 56.3.

_S_-Phenyl 4-(*tert*-butyl)benzothioate(Table 4, entry 12)
Colorless crystals, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.98 (d, *J* = 8.4 Hz, 2H), 7.54-7.44 (m, 7H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 189.6, 157.5, 135.1, 134.0, 129.4, 129.2, 127.6, 127.4, 125.7, 35.2, 31.1.

_S_-Phenyl naphthalene-2-carbothioate (Table 4, entry 13)
Colorless crystals, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.55 (d, J = 8.4 Hz, 1H), 8.23 (d, J = 7.2 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.63-7.50 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 192.2, 134.9, 134.7, 133.8, 133.3, 129.6, 129.4, 129.3, 128.4, 128.3, 128.1, 128.0, 126.7, 125.3,124.5.

_S_-Phenyl-indole-3-carbothioate (Table 4, entry 14)
Colorless crystals, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.64 (br. s, 1H), 8.28-8.24 (m, 1H), 8.10 (d, *J* = 3.2 Hz, 1H), 7.59-7.56 (m, 2H), 7.49-7.41 (m, 4H), 7.32-7.28 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 183.1, 136.1, 135.3, 130.4, 129.2, 129.1, 127.7, 124.9, 123.9, 122.9, 121.9, 116.8, 111.5.

_S_-(4-Methoxyphenyl) 4-methoxybenzothioate (Table 4, entry 15)
Colorless crystals, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.01 (d, *J*= 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J*= 8.8 Hz, 2H), 3.87 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 189.5, 163.9, 160.7, 136.7, 129.7, 129.4, 118.2, 114.9, 113.9, 55.5, 55.4.

_S_-(3-Methoxyphenyl) 4-methoxybenzothioate (Table 4, entry 16)
Colorless crystals, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.01 (d, J= 9.2 Hz, 2H), 7.36 (t, J = 8.0 Hz, 1H), 7.11 (ddd, J = 7.6 Hz, J = 1.6 Hz, J= 0.8 Hz, 1H), 7.07 (dd, J = 2.4 Hz, J = 1.6 Hz, 1H), 6.99 (ddd, , J = 8.0 Hz, J = 2.4 Hz, J = 0.8 Hz, 1H), 6.96 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H) 3.83(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 188.5, 164.0, 159.9, 129.9, 129.7, 129.4, 128.5, 127.4, 120.2, 115.6, 113.9, 55.5, 55.4.

_S_-(2,6-Dimethylphenyl) 4-methoxybenzothioate (Table 4, entry 17)
Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.07 (d, J = 8.8 Hz, 2H), 7.27 (dd, J = 8.8 Hz, J = 6.4 Hz, 1H), 7.20 (d, J = 7.6 Hz, 2H), 6.98 (d, J =8.8 Hz, 2H), 3.89 (s, 3H), 2.41 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 187.6, 163.8, 143.3, 129.83, 129.78, 128.3, 126.9, 113.8, 55.6, 22.6.

***S*-Phenyl 4-(trifluoromethyl)benzothioate (Table 4, entry 18)**
Colorless crystals, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.13 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.54-7.47 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 189.3, 139.4, 135.0, 134.9 (q, *J*C-F = 32.7 Hz), 129.9, 129.4, 127.8, 126.6, 125.9 (q, *J*C-F = 3.7 Hz), 123.5 (q, *J*C-F = 272.7 Hz).

***S*-Phenyl 3-chlorobenzothioate (Table 4, entry 19)**
Colorless crystals, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.99 (s, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.53-7.42 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 189.0, 138.2, 135.03, 135.00, 133.5, 130.0, 129.7, 129.3, 127.5, 126.8, 125.6.

S-Phenyl 4-chlorobenzothioate (Table 4, entry 20)
Colorless crystals, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.97 (d, *J* = 8.8 Hz, 2H), 7.53-7.46 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 189.0, 140.1, 135.04, 134.96, 129.7, 129.3, 129.1, 128.8, 126.9.

S-Phenyl 4-bromobenzothioate (Table 4, entry 21)
Colorless crystals, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.90 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.53-7.46 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 189.2, 135.4, 135.0, 132.0, 129.7, 129.3, 128.9, 128.7, 126.9.

***S*-phenyl 4-nitrobenzothioate (Table 4, entry 22)**
Yellow crystals, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.34 (d, *J* = 8.9 Hz, 2H), 8.18 (d, *J* = 8.9 Hz, 2H), 7.54-7.48 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 188.8, 150.7, 141.3, 134.9, 130.1, 129.5, 128.5, 126.1, 124.0.

S-phenyl 4-acetylbenzothioate (Table 4, entry 23)

Colorless crystals, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (d, *J* = 8.7 Hz, 2H), 8.05 (d, *J* = 8.6 Hz, 2H), 7.53-7.46 (m, 5H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.2, 189.6, 140.6, 139.9, 135.0, 129.8 129.4, 128.6, 127.7, 126.8, 26.9.

^{1}H NMR spectra of compounds

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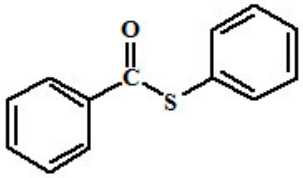

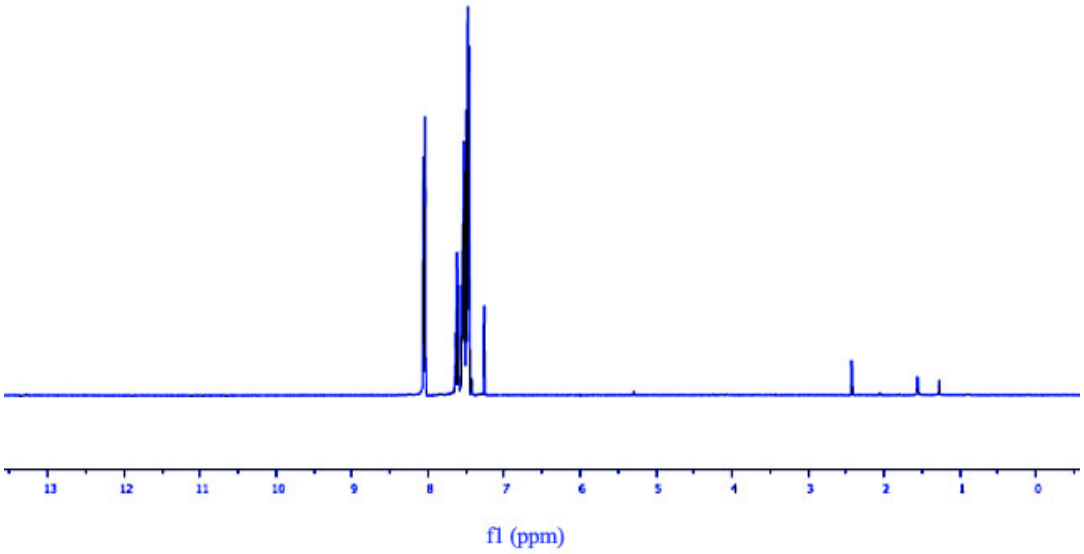

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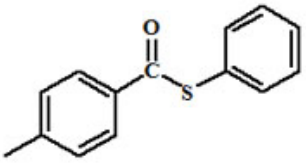

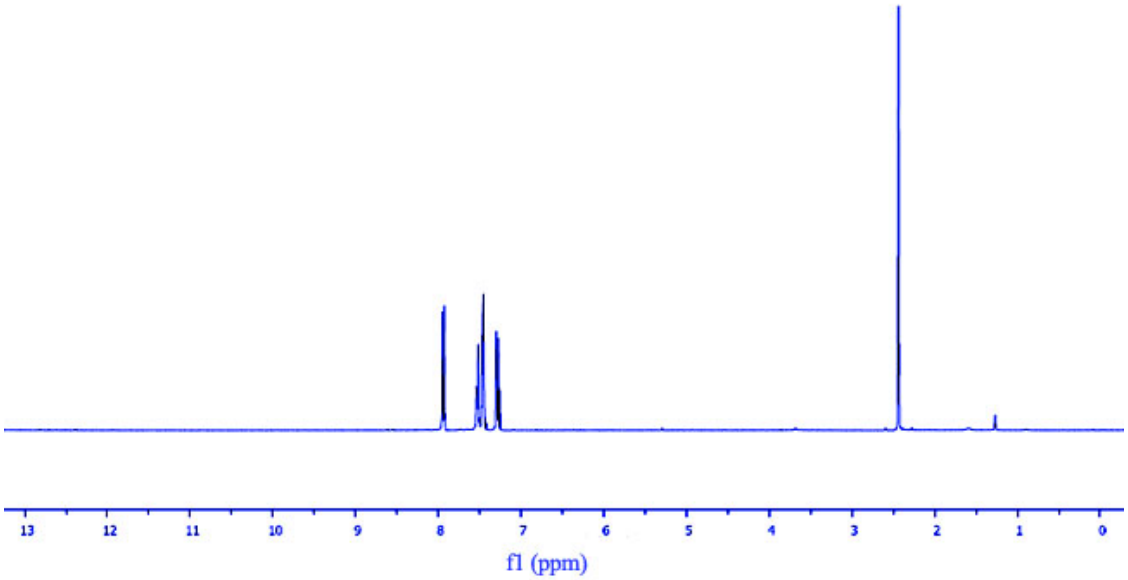

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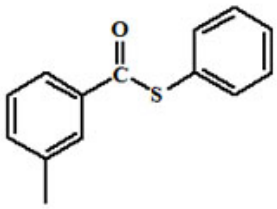

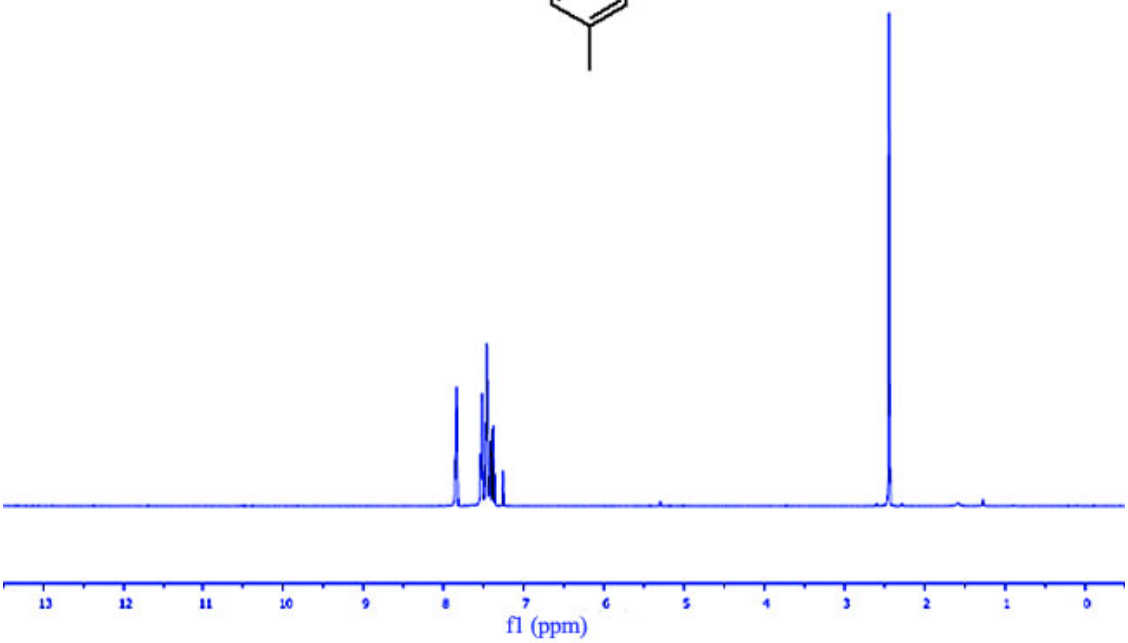

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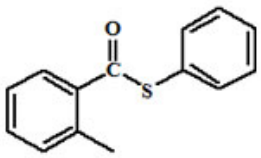

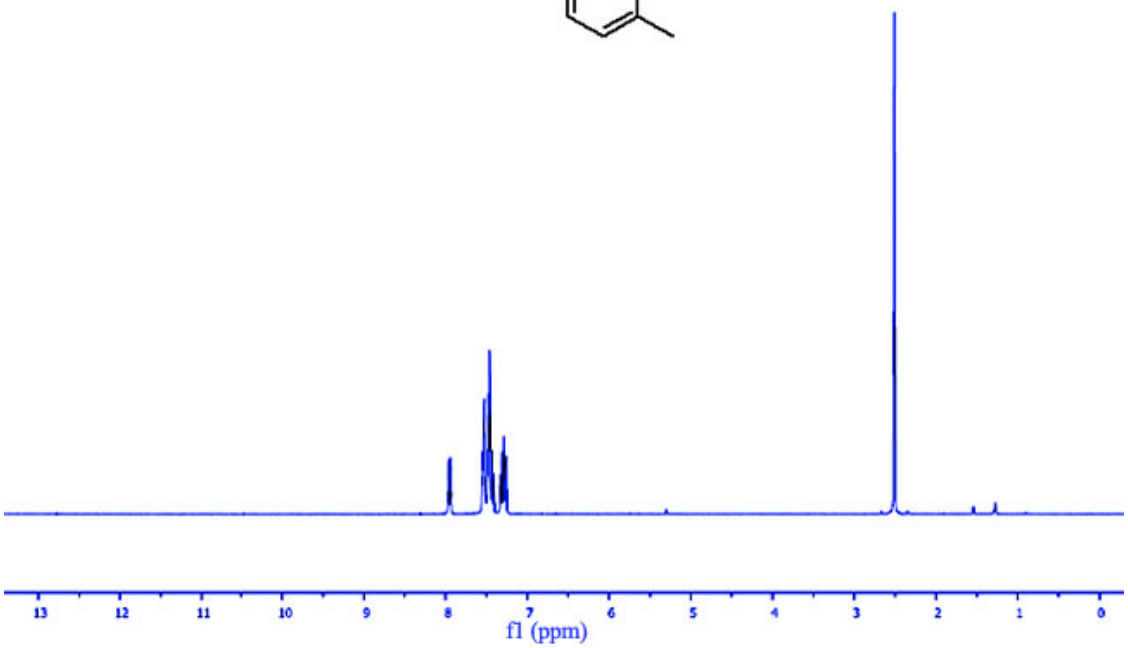

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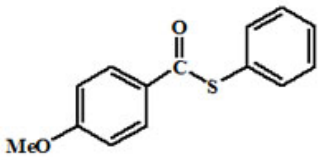

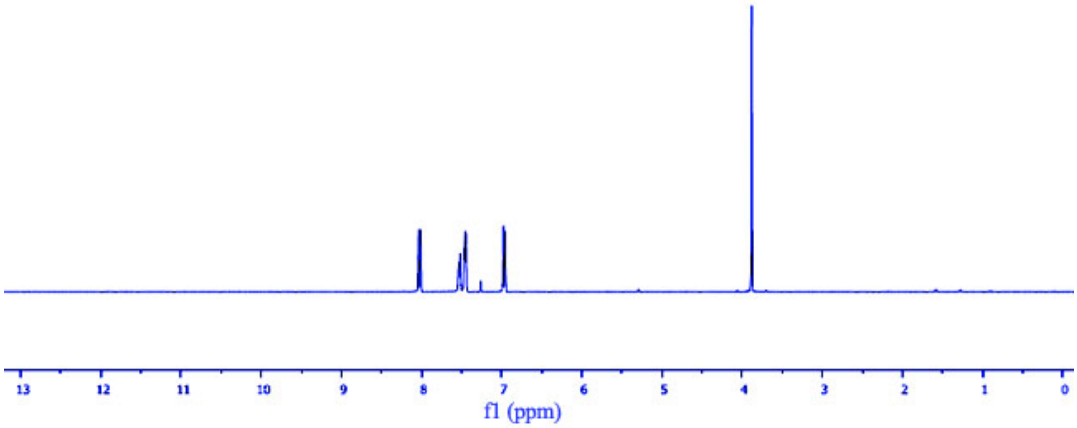

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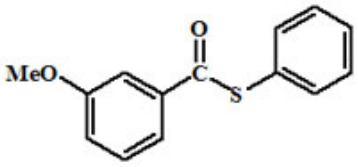

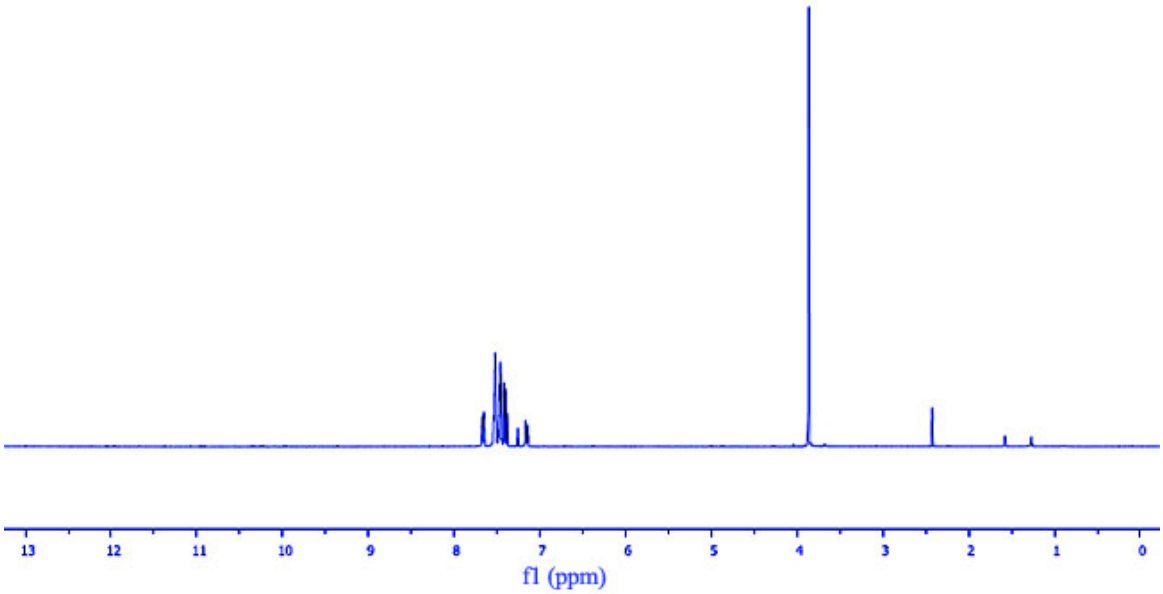

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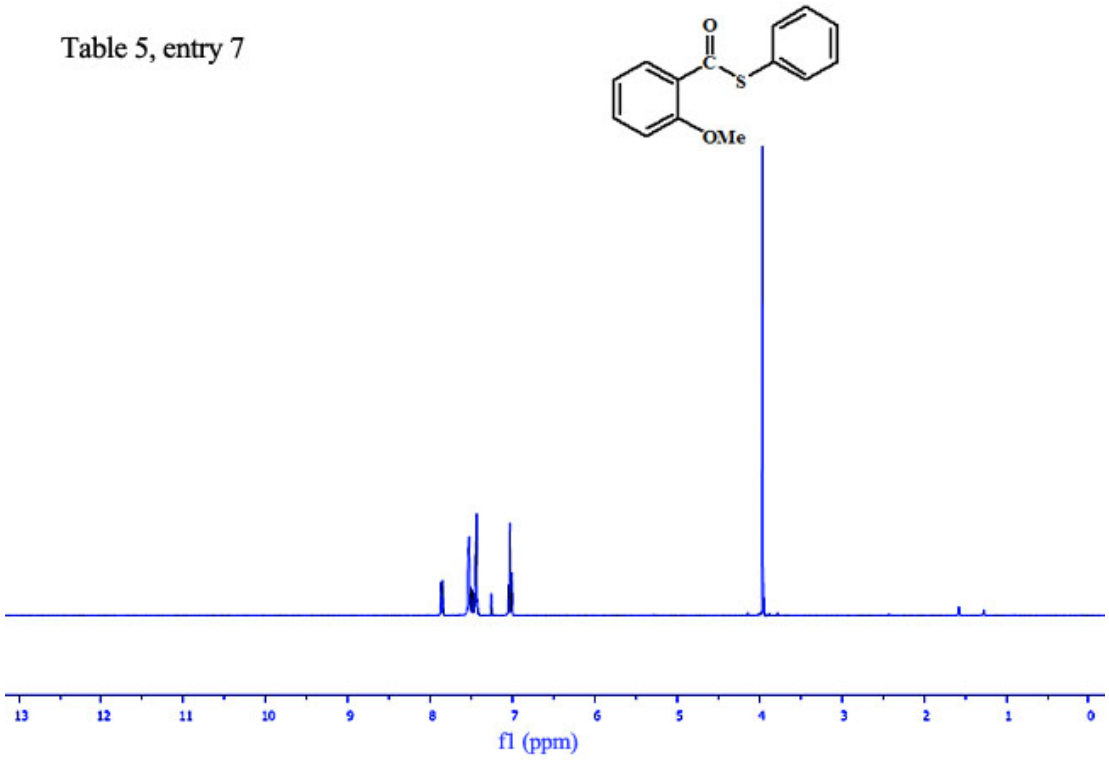

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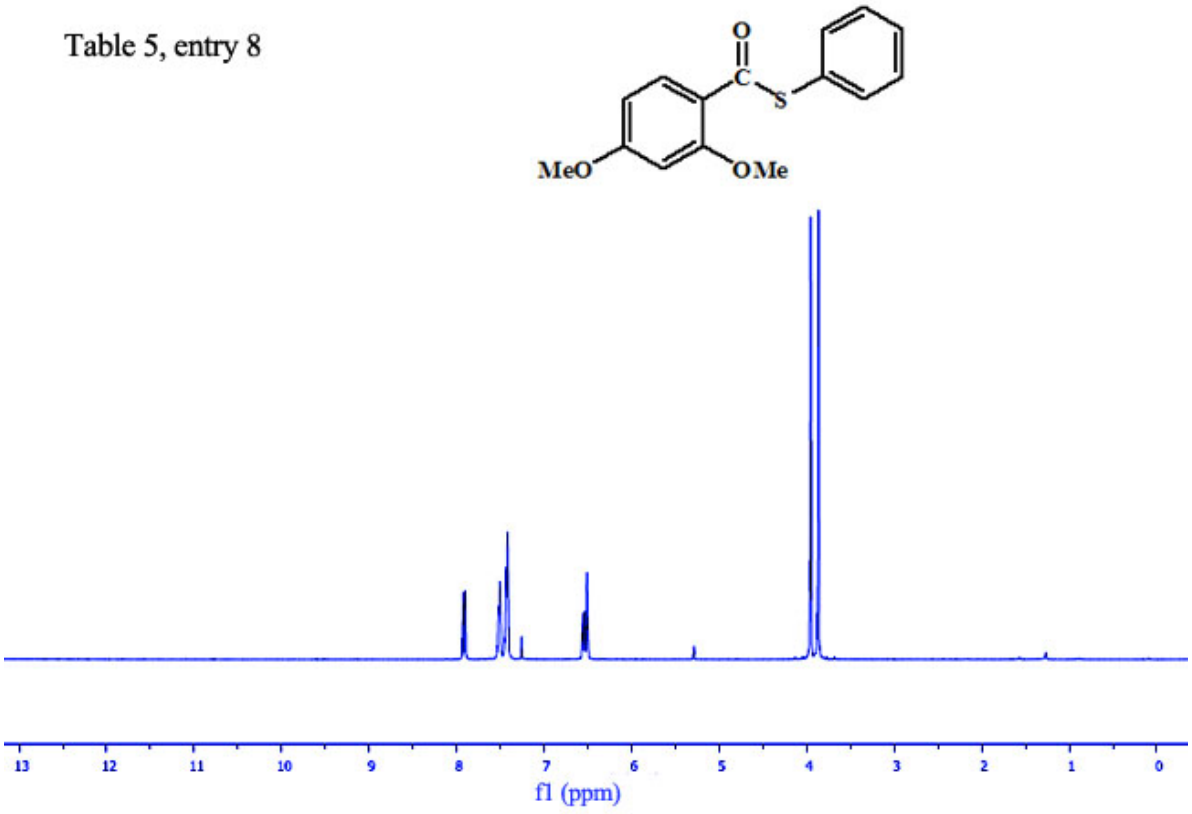

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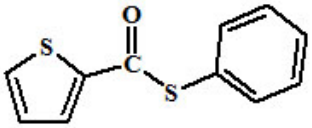

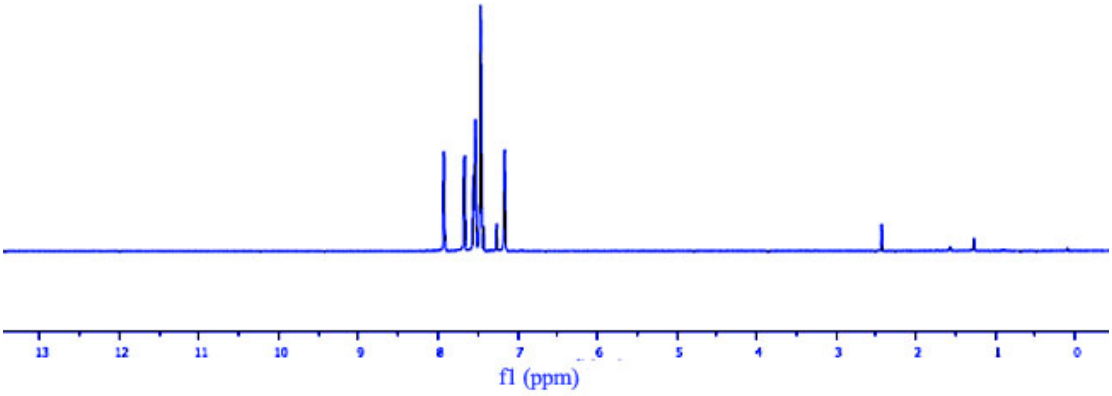

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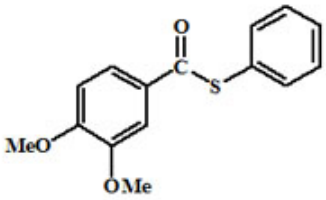

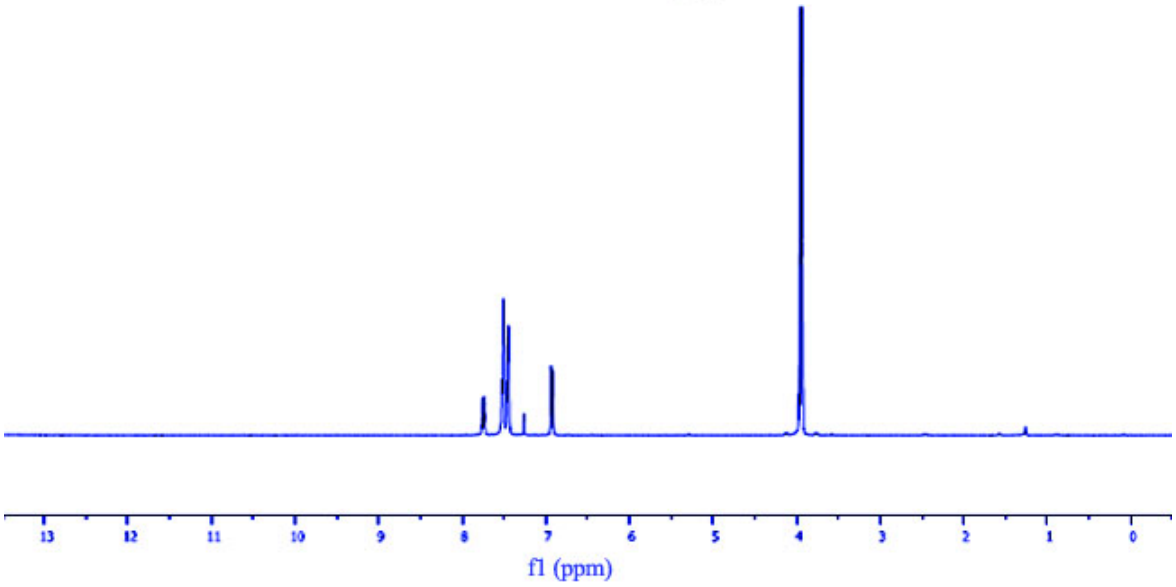

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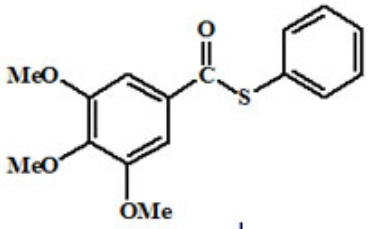

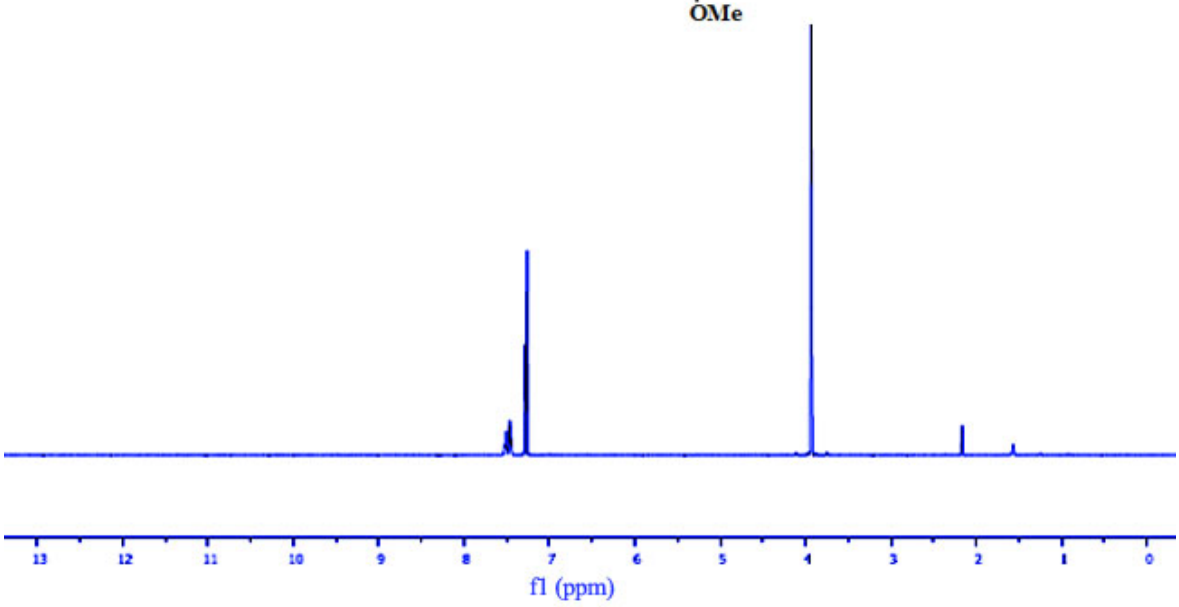

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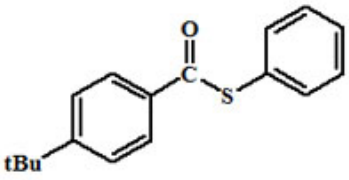

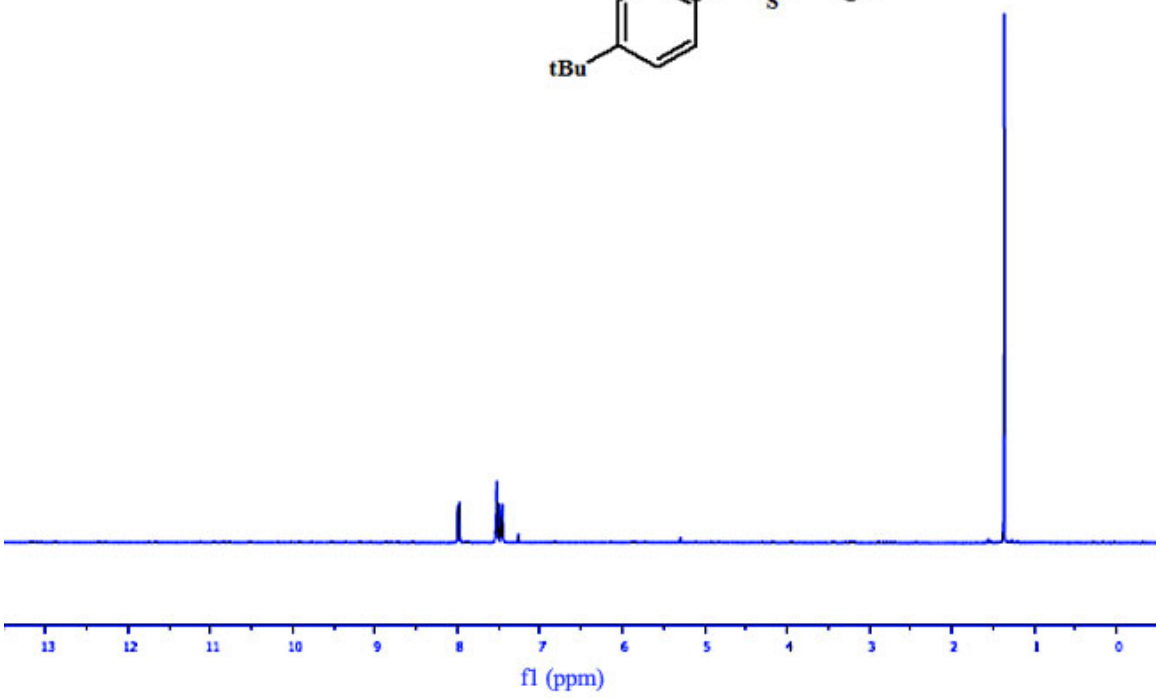

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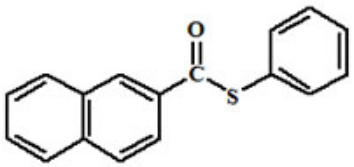

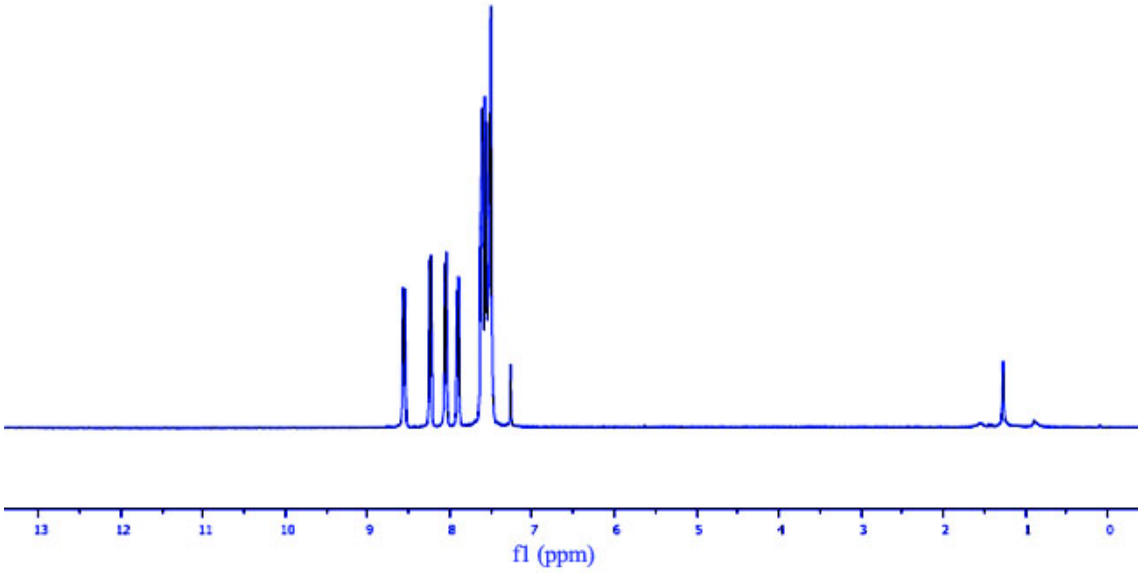

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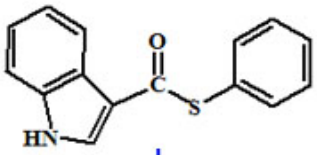

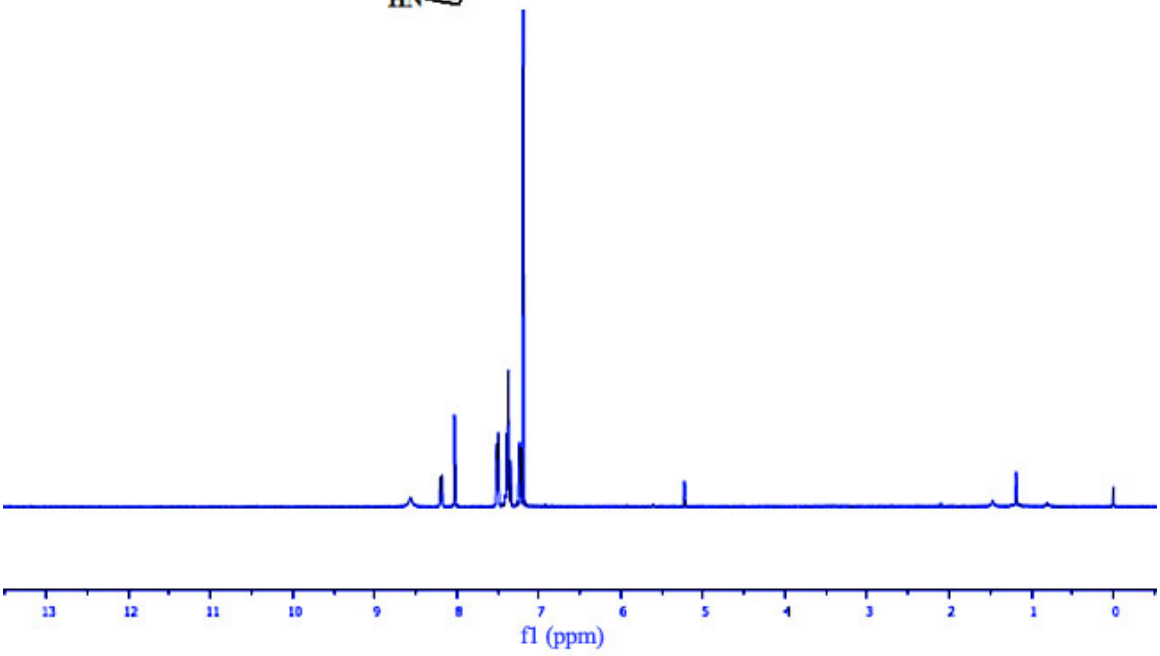

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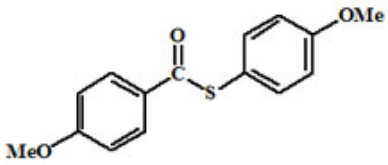

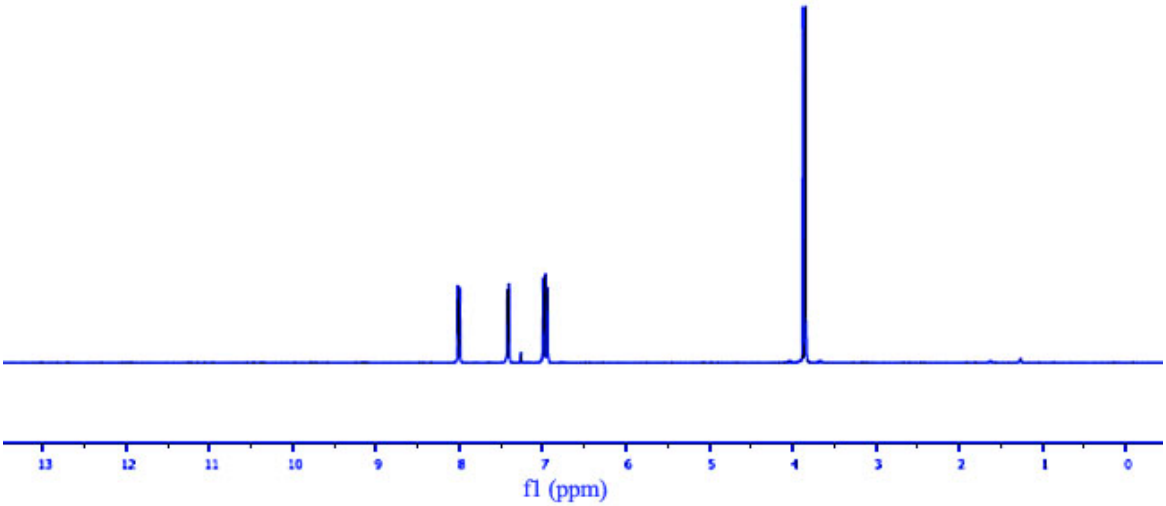

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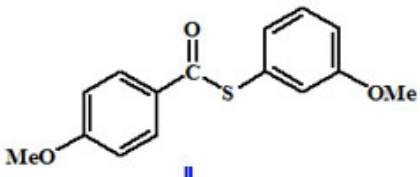

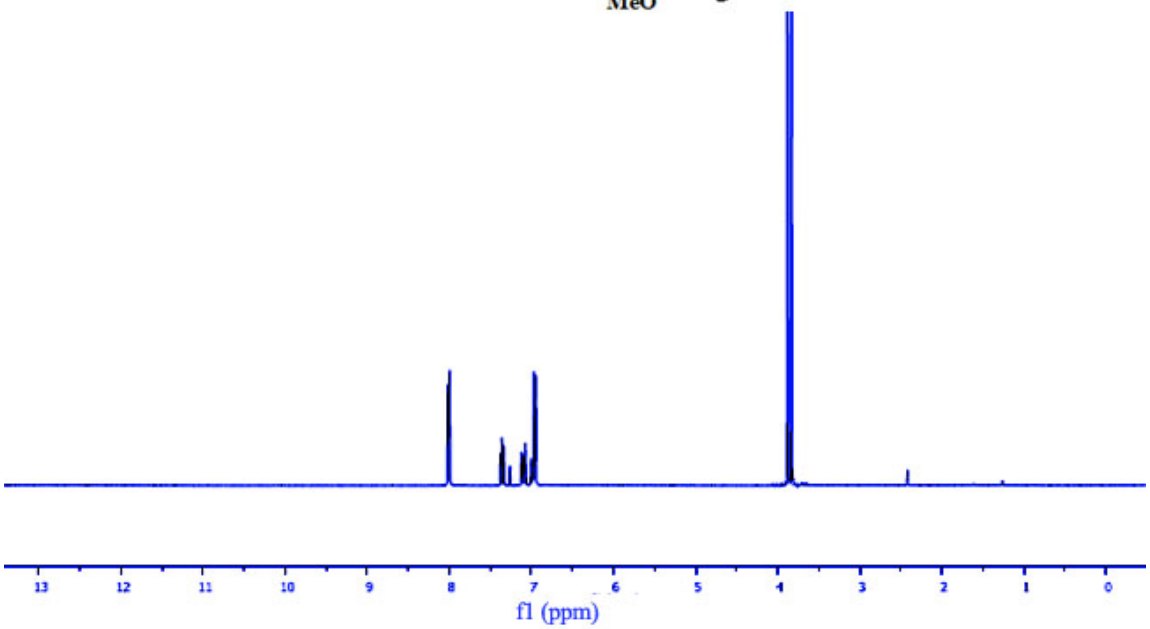

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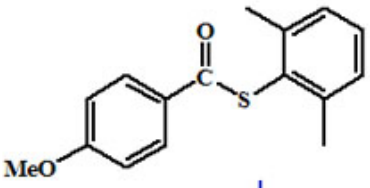

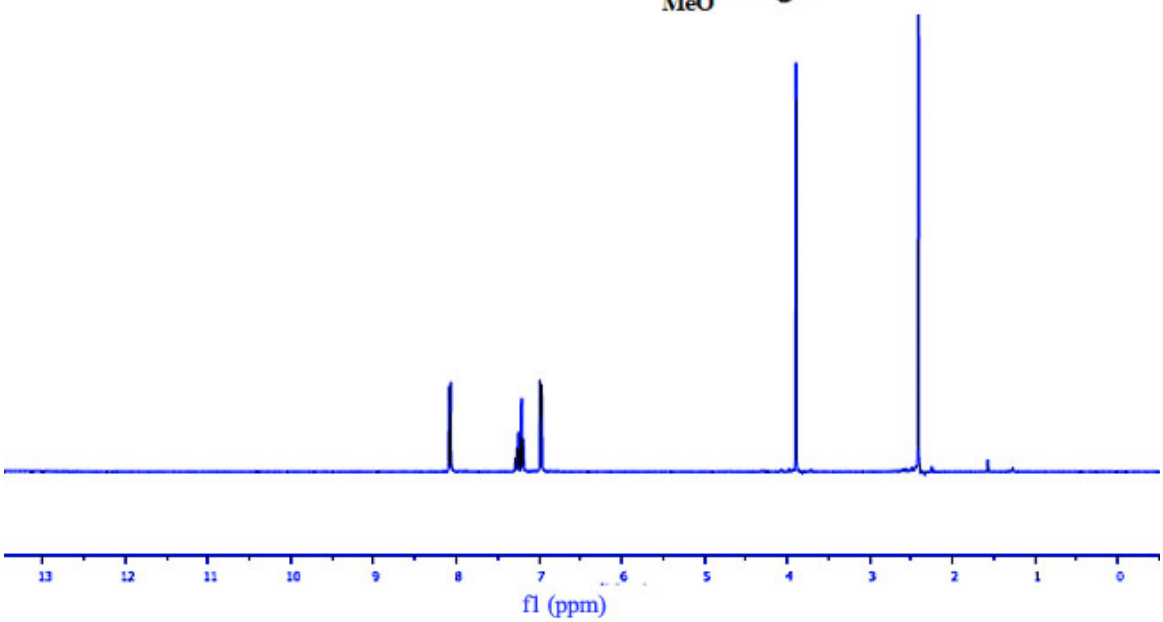

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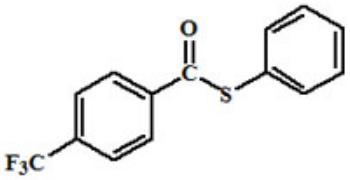

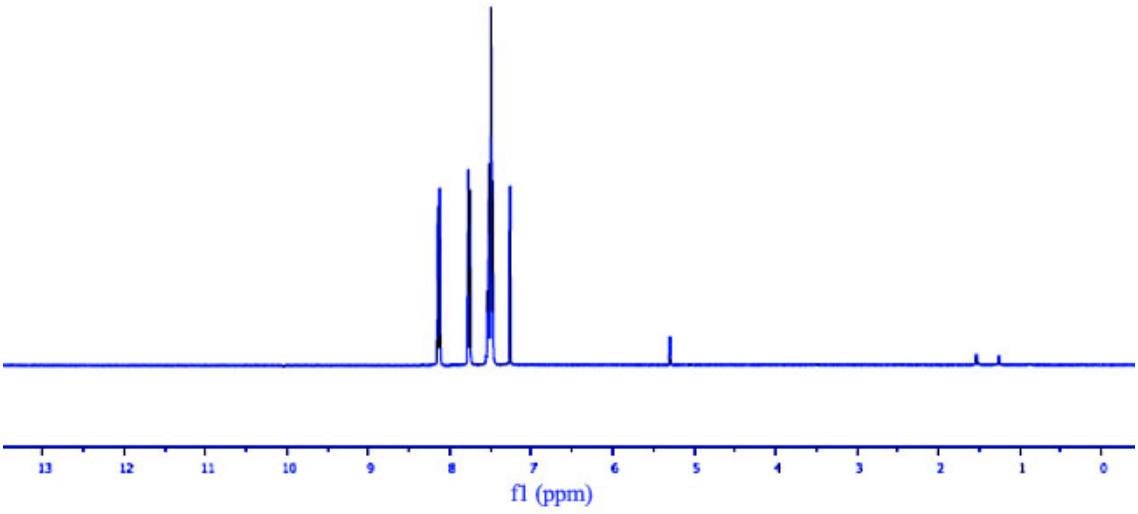

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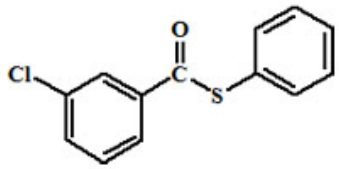

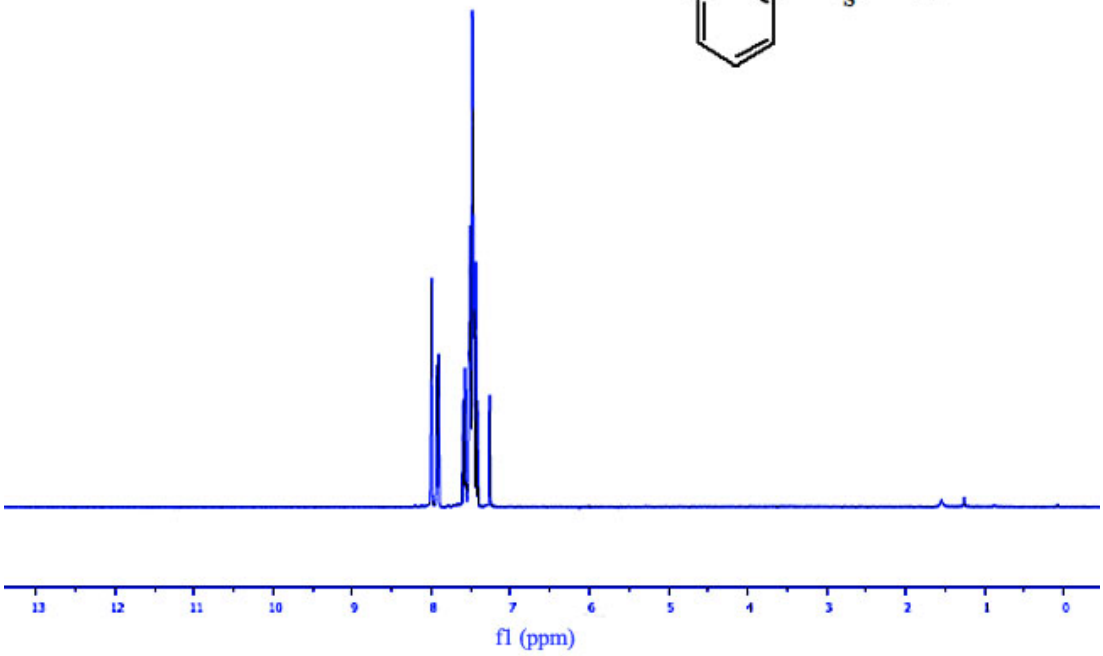

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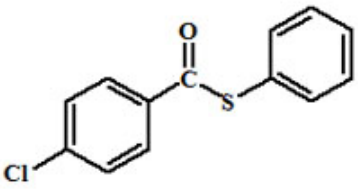

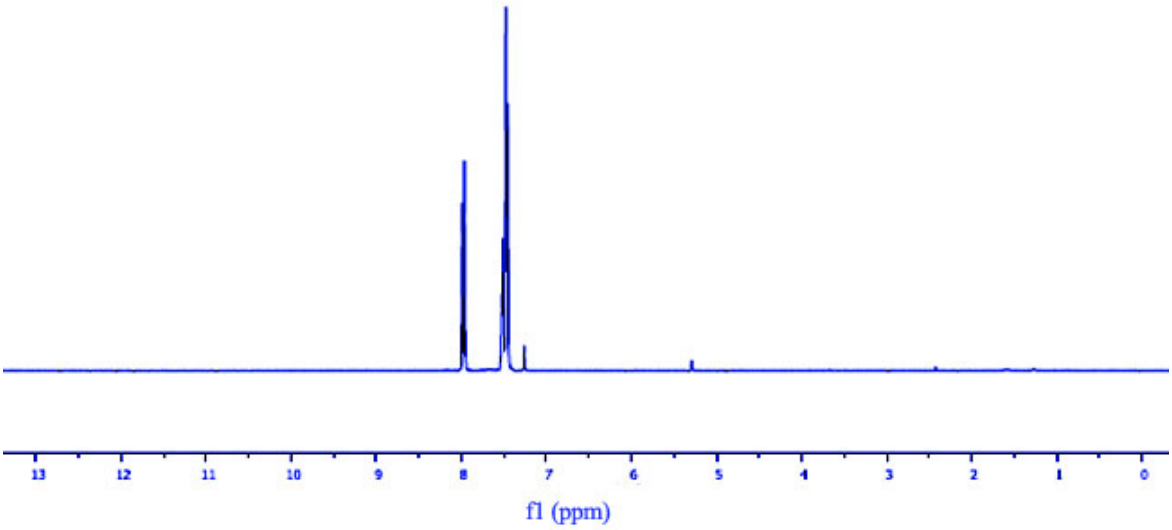

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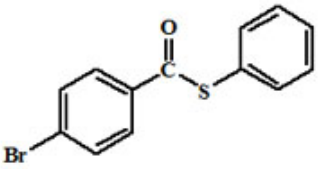

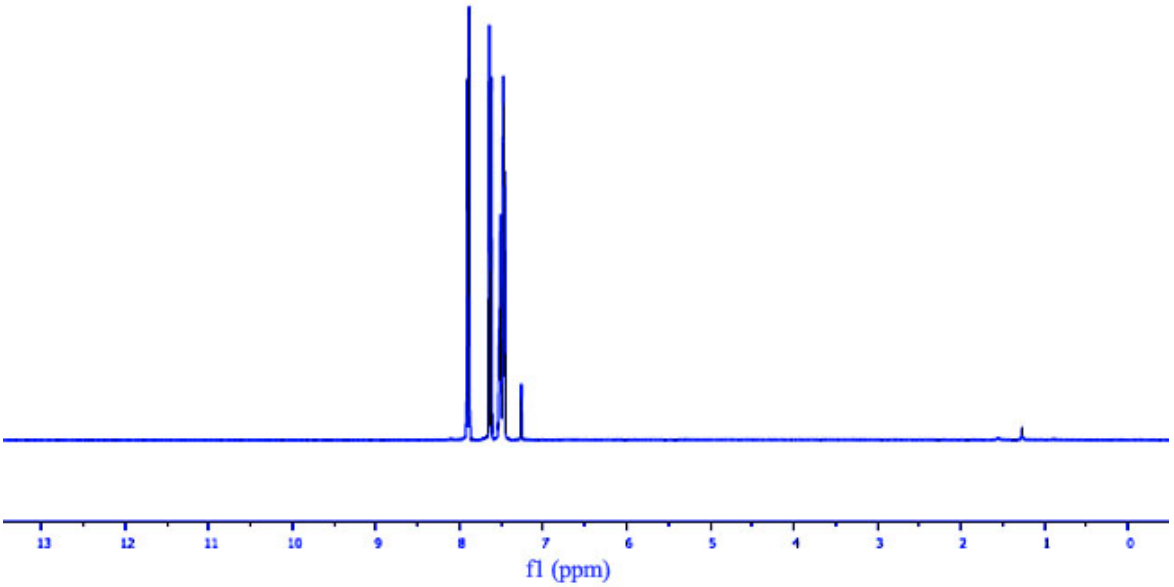

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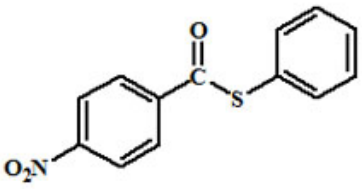

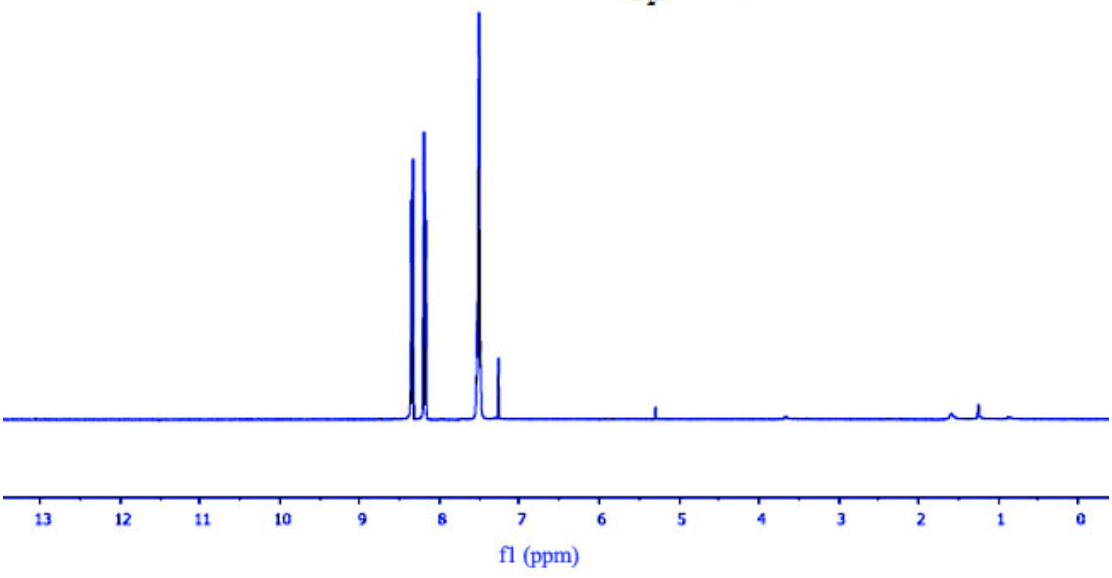

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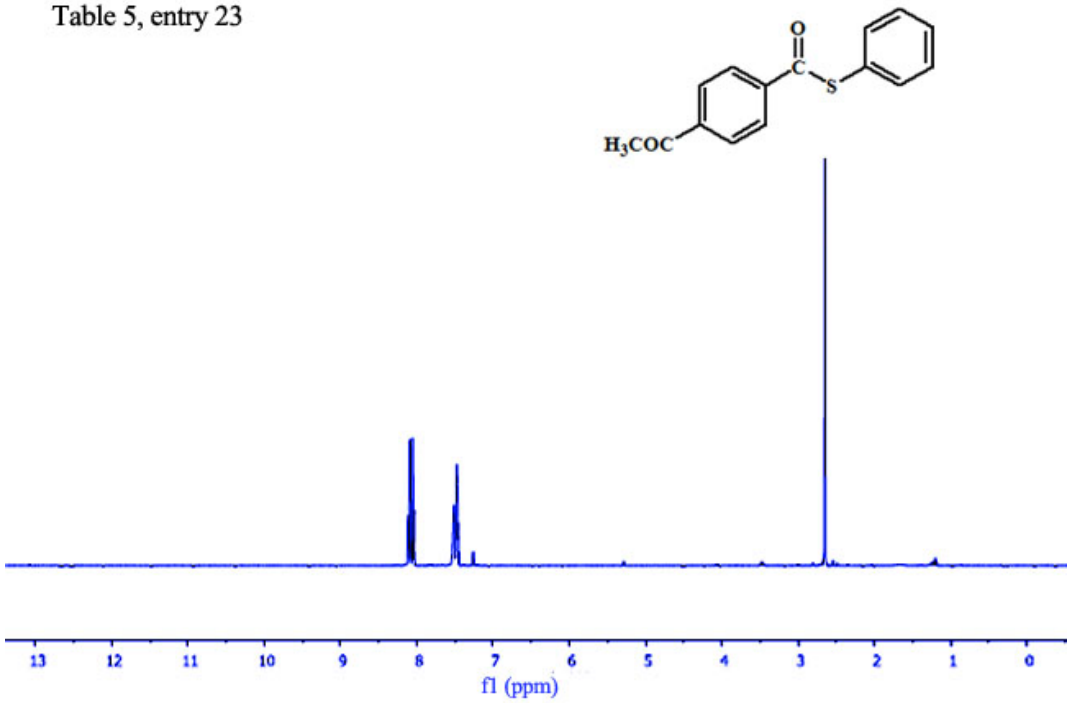

^{13}C NMR spectra of compounds

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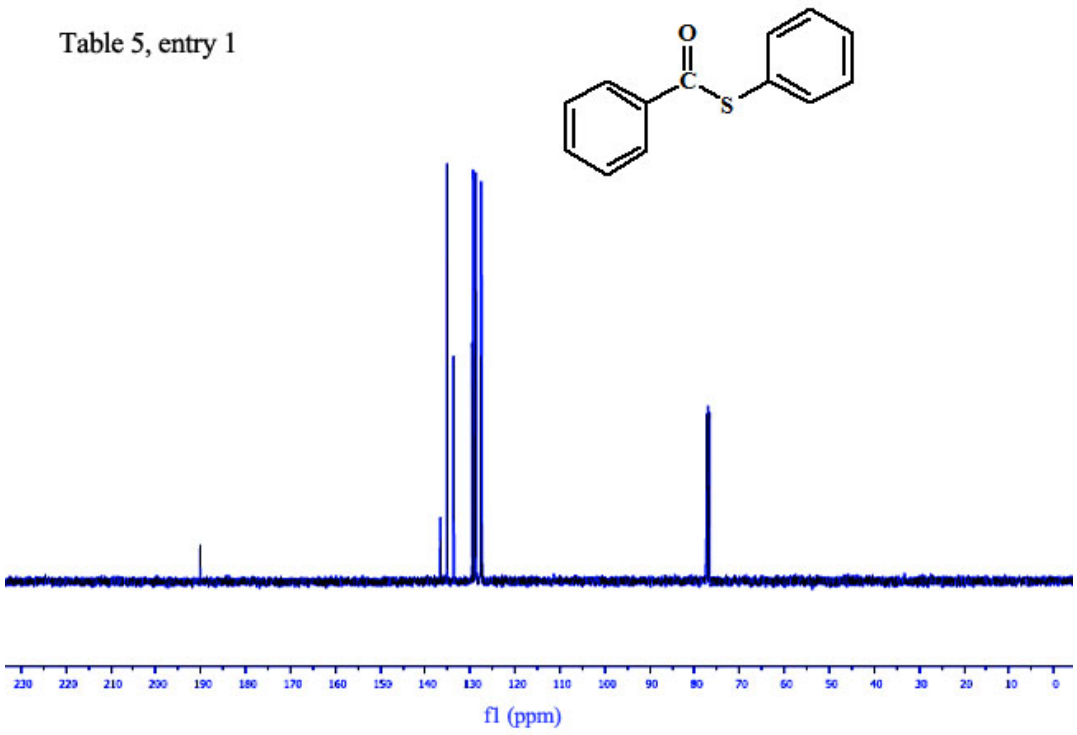

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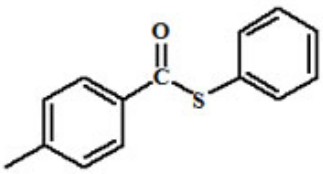

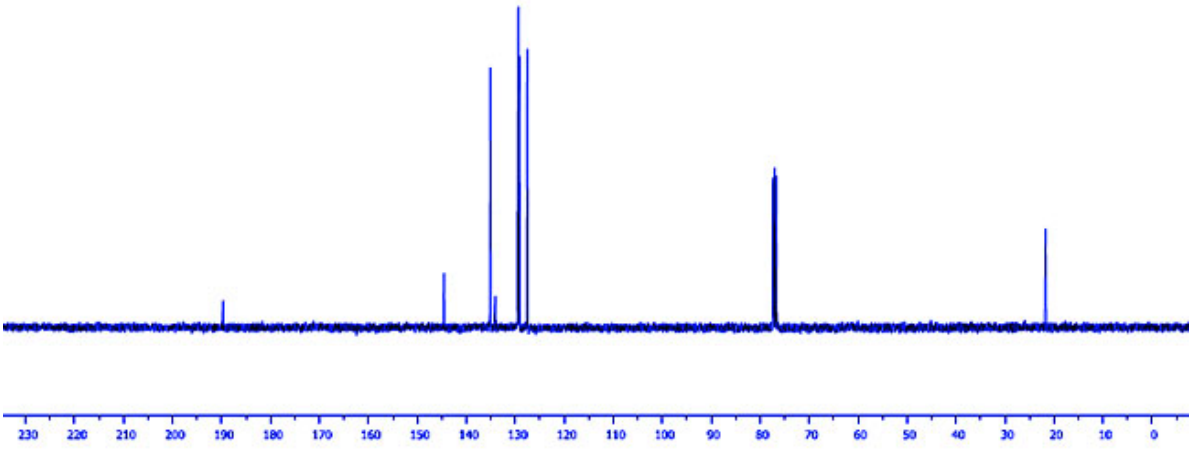

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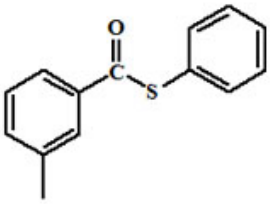

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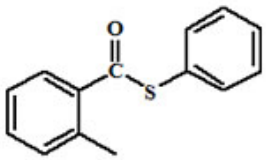

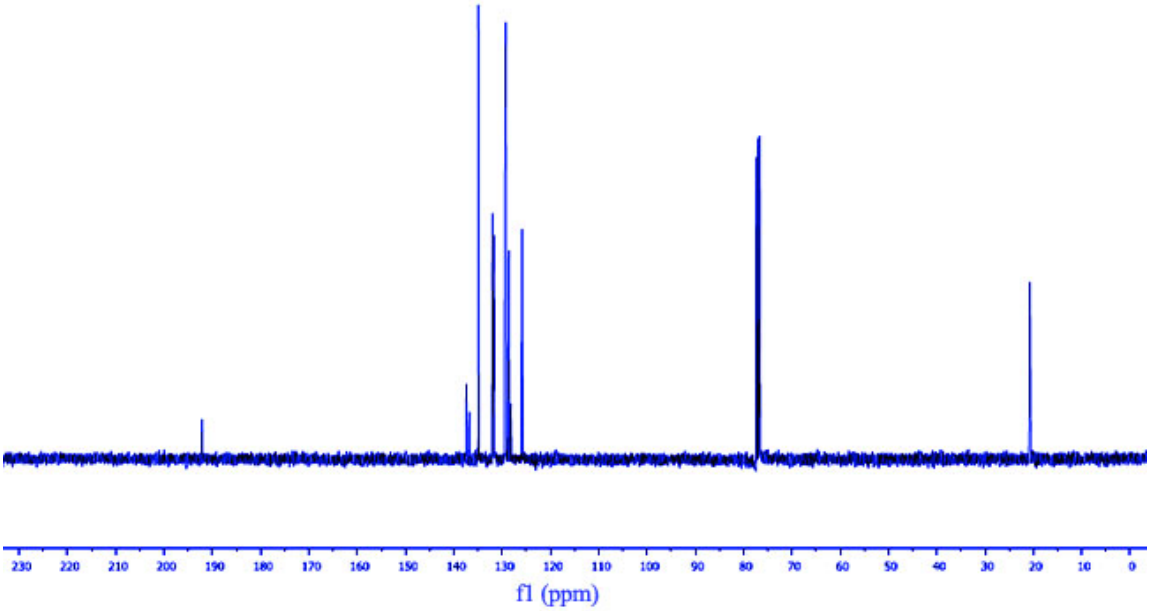

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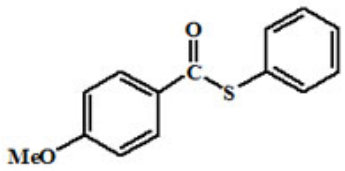

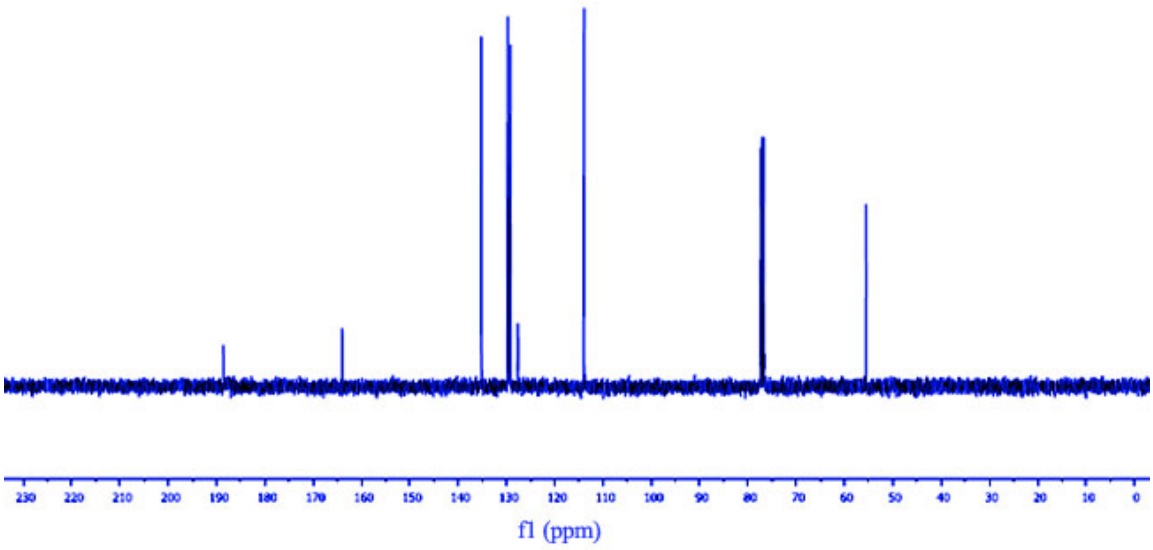

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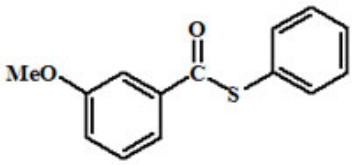

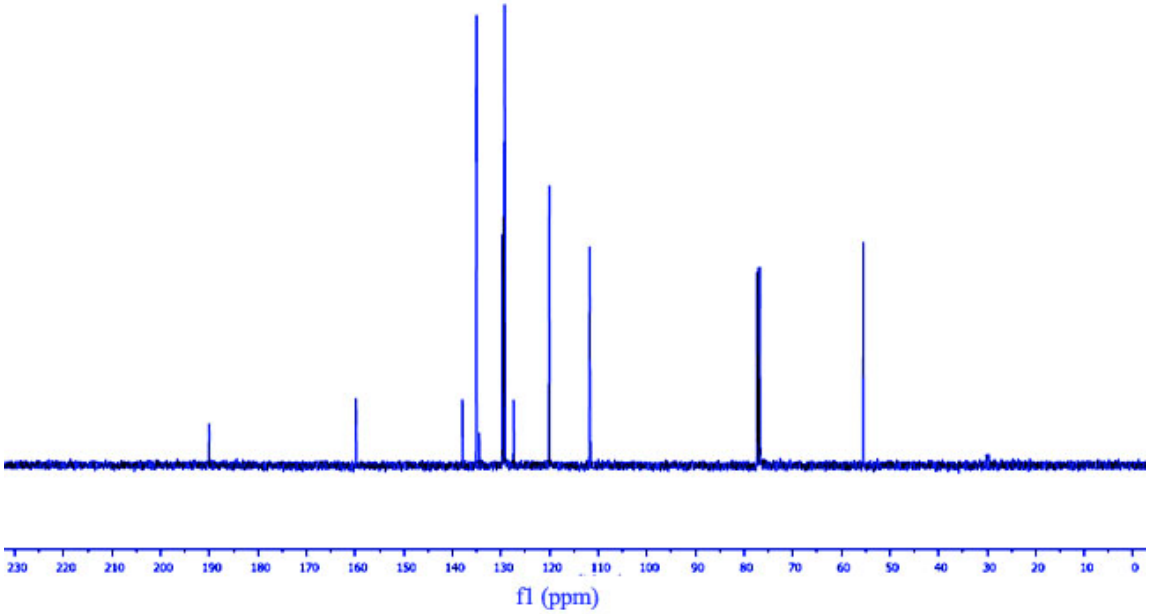

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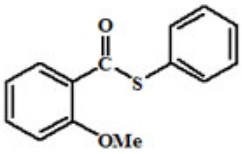

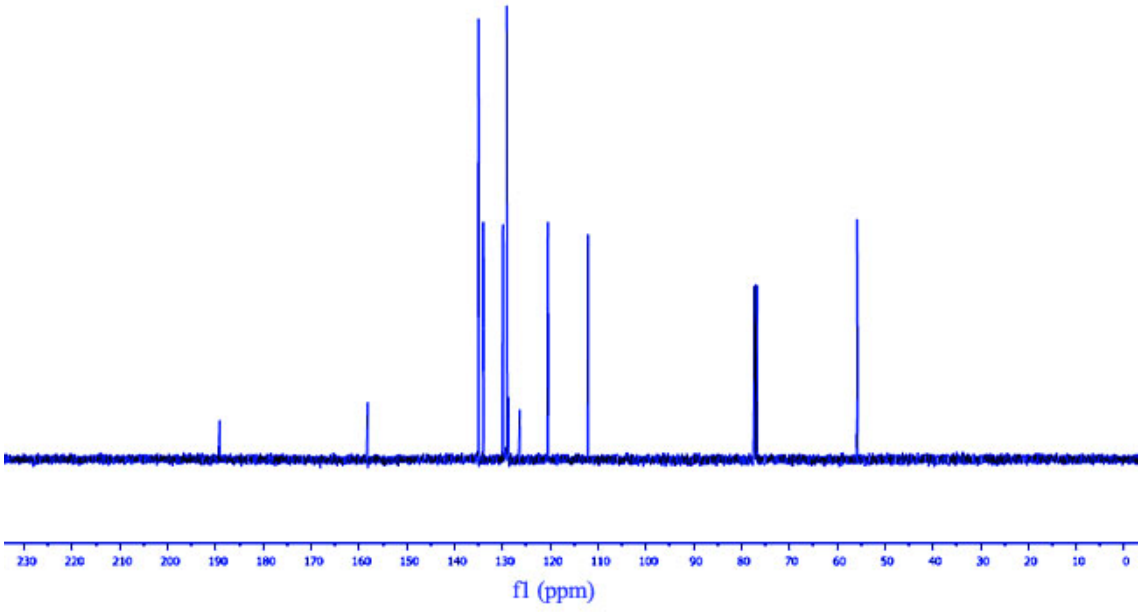

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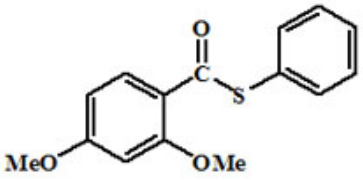

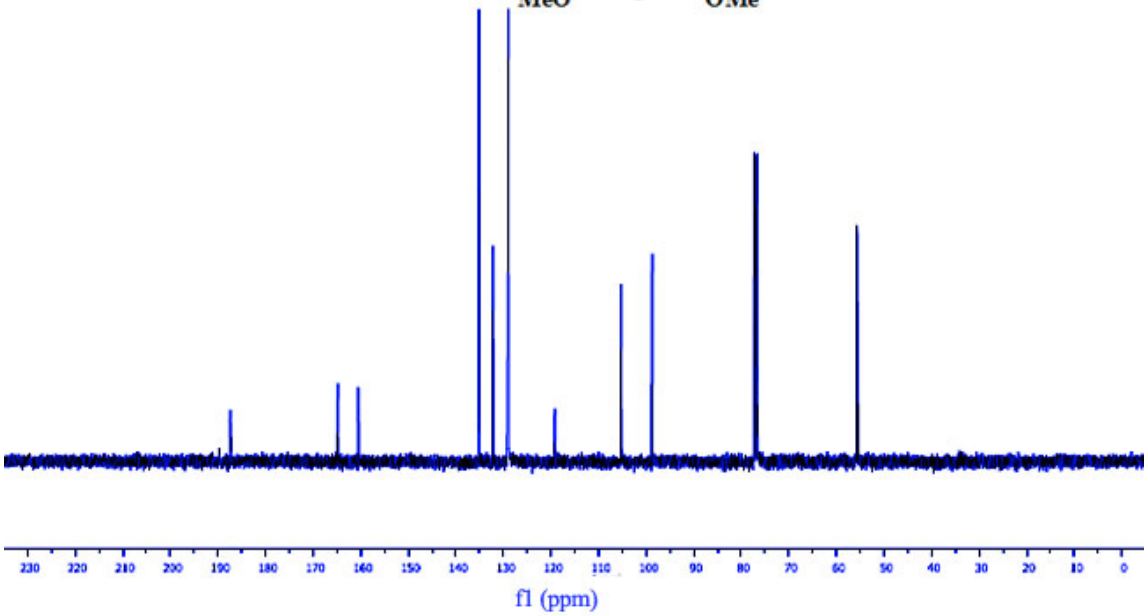

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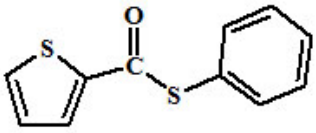

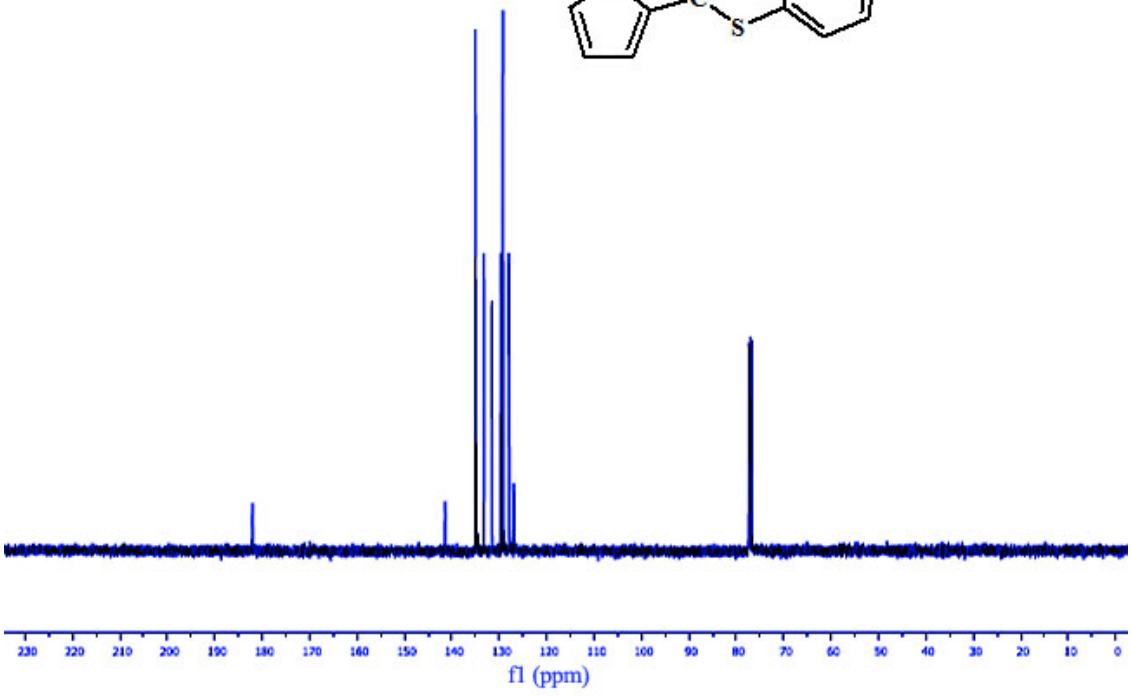

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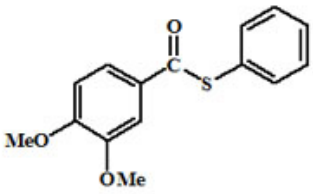

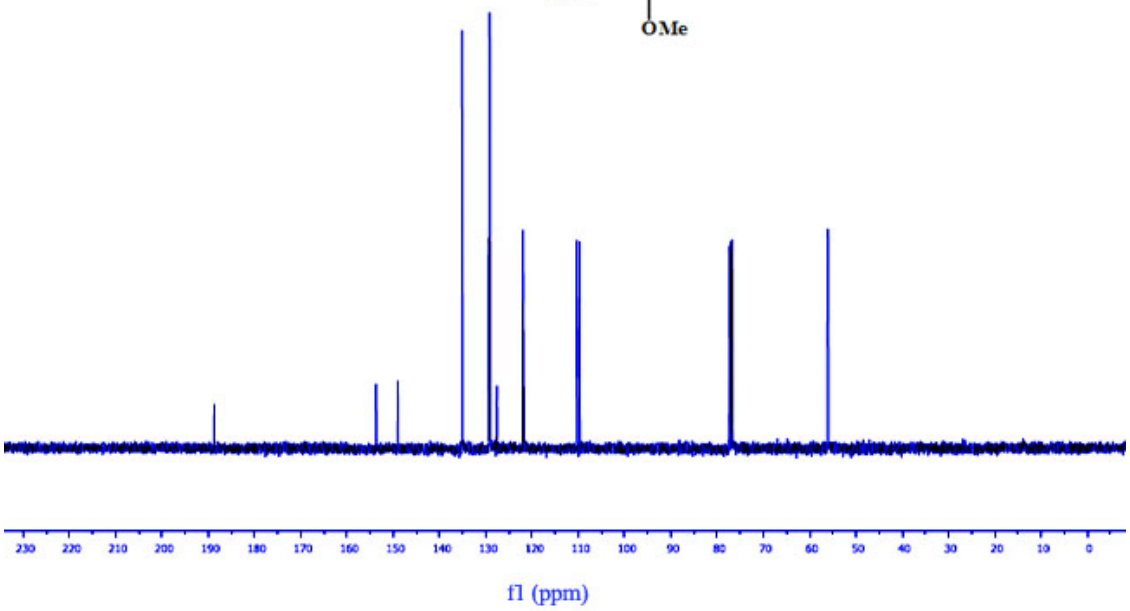

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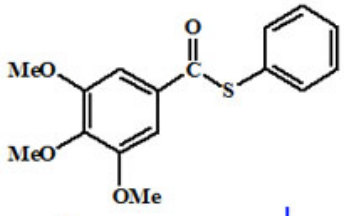

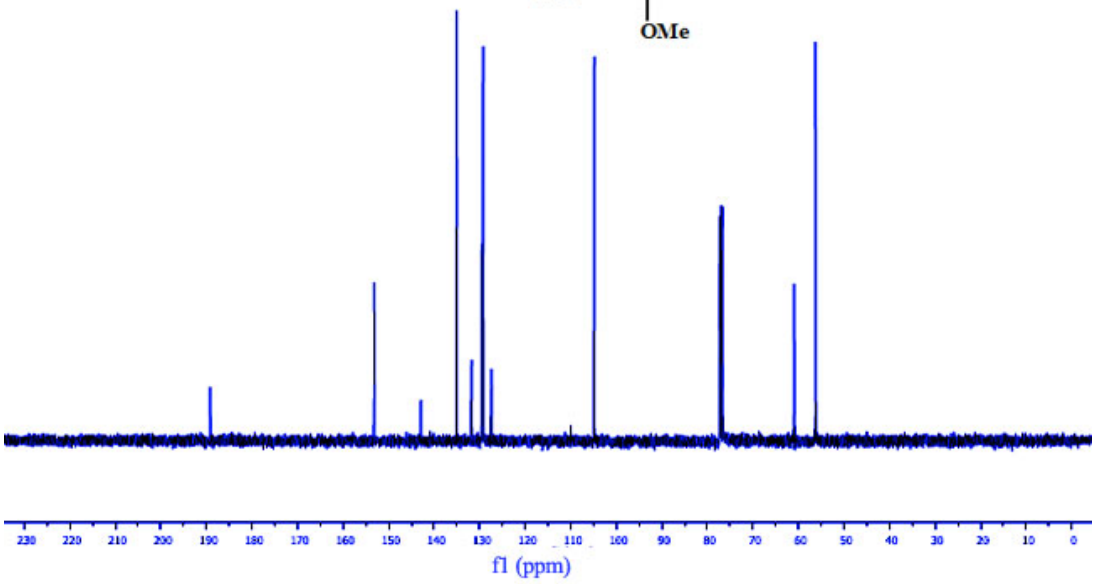

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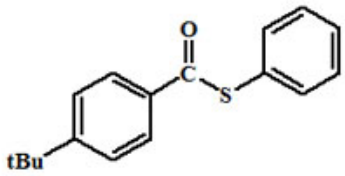

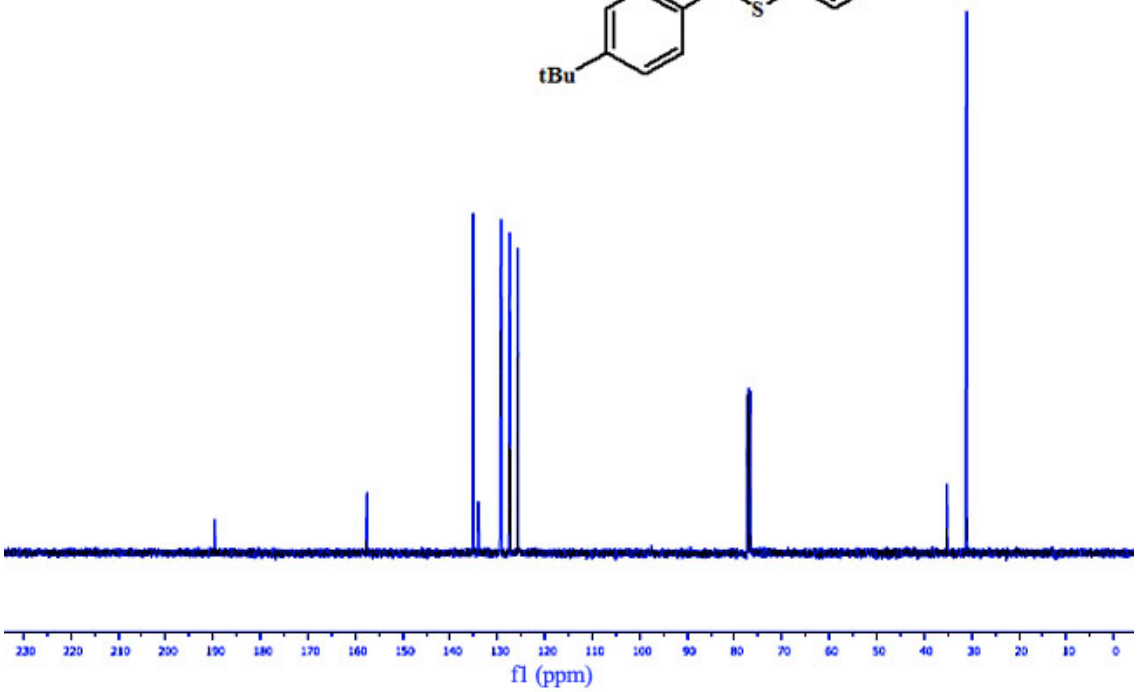

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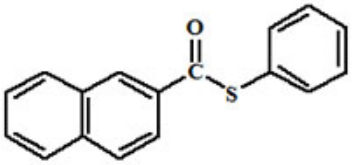

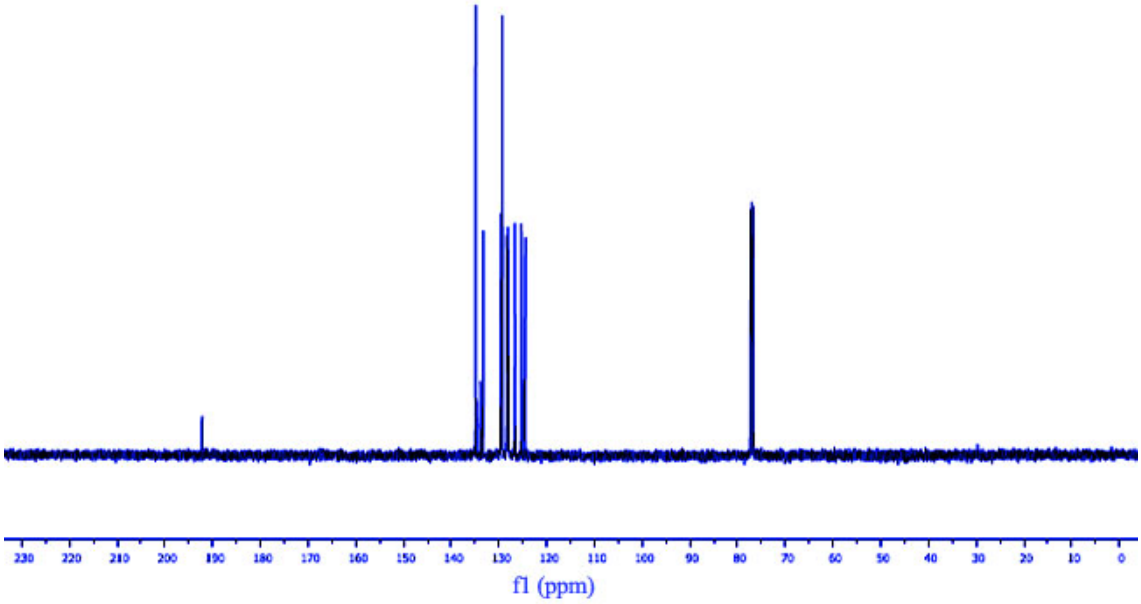

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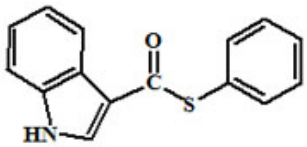

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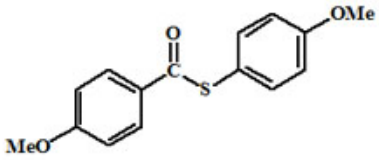

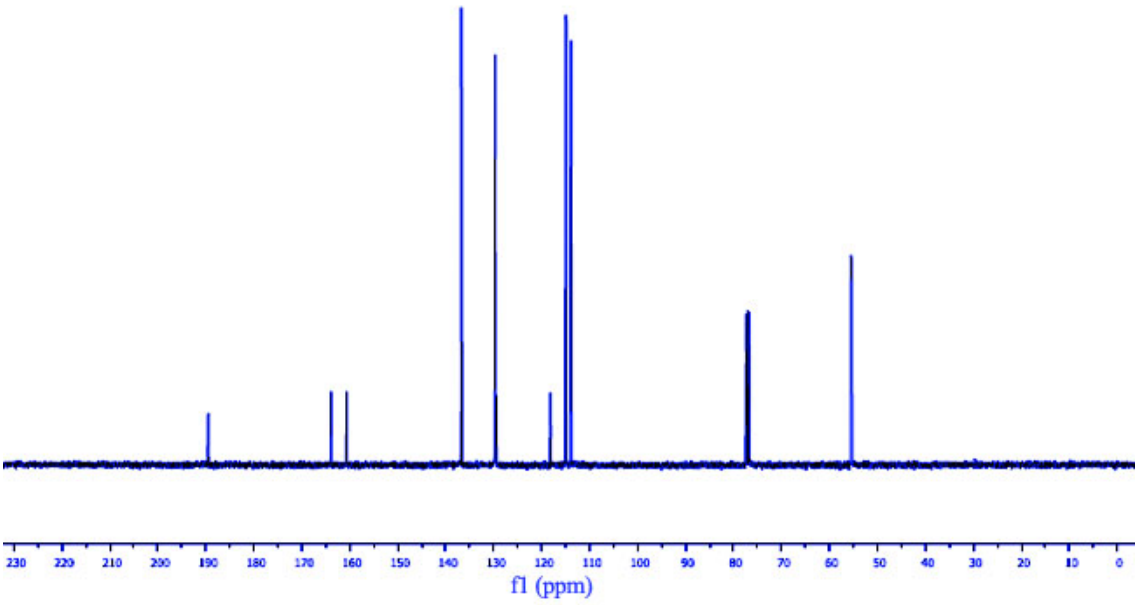

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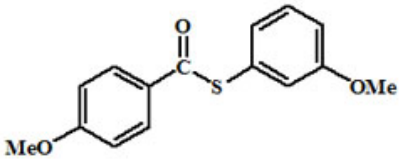

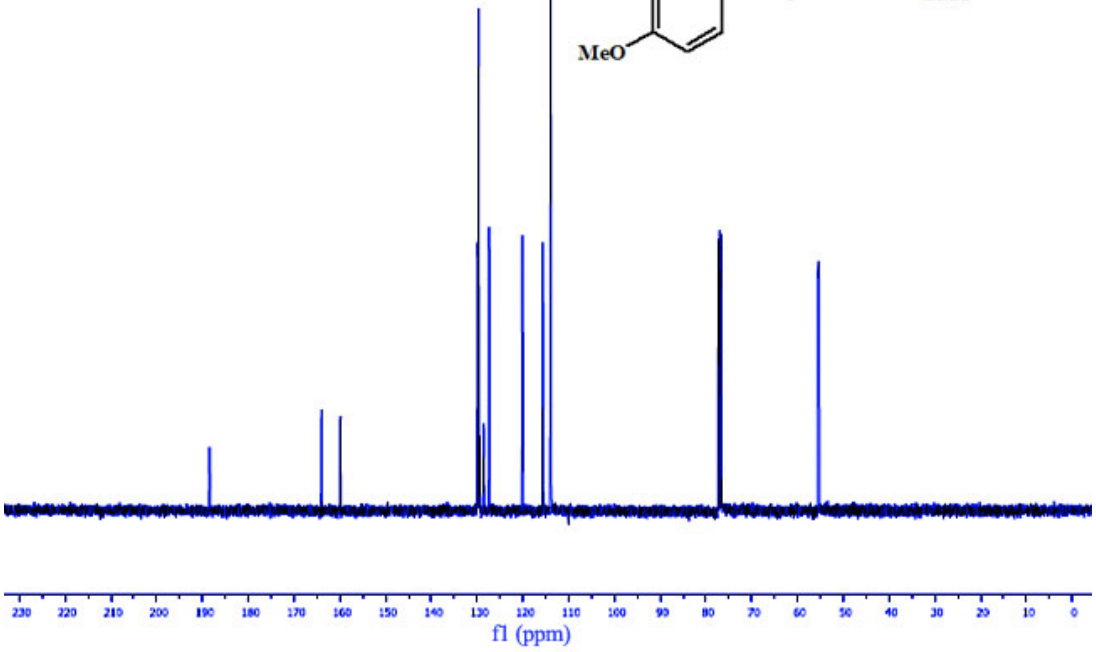

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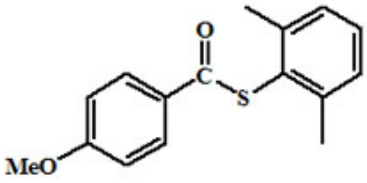

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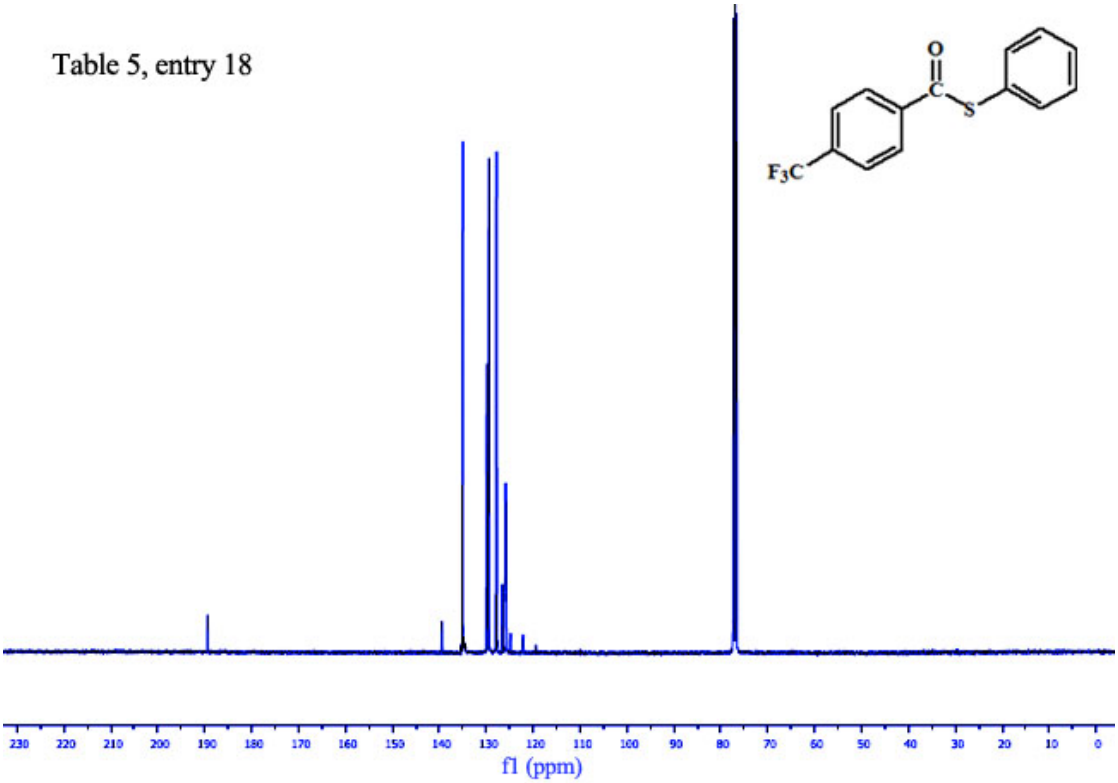

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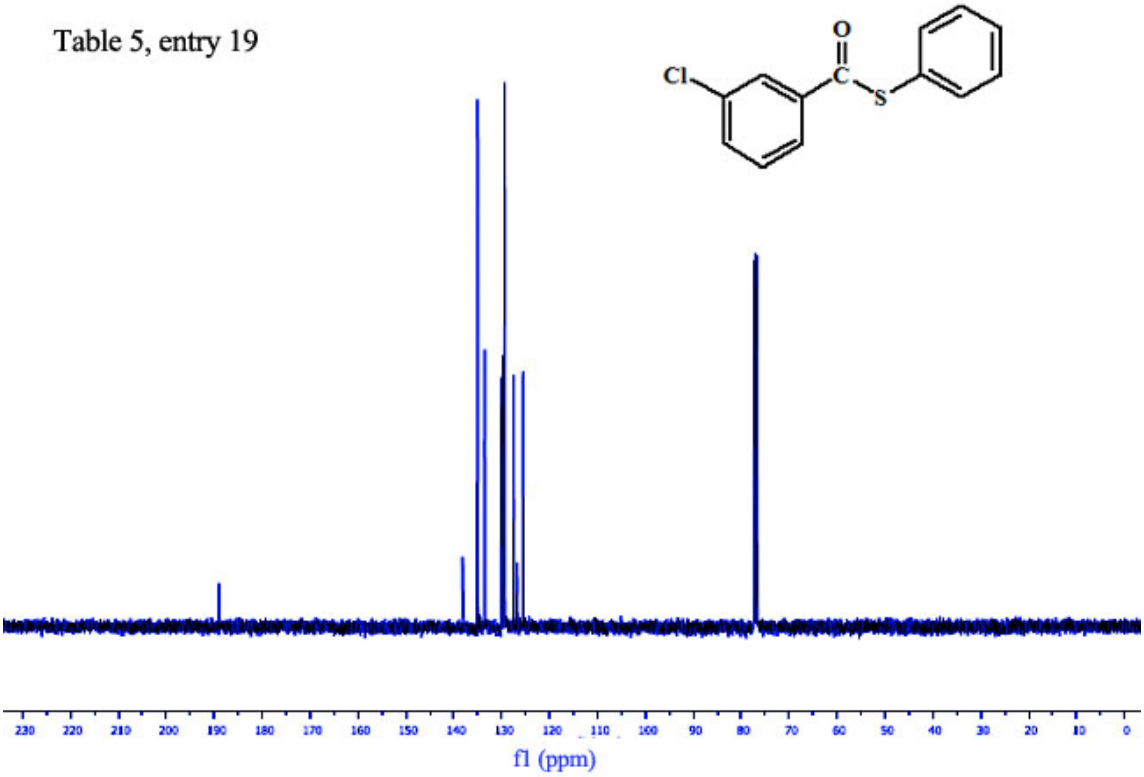

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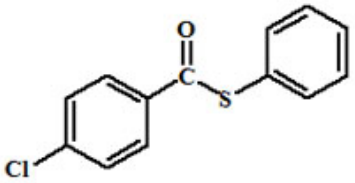

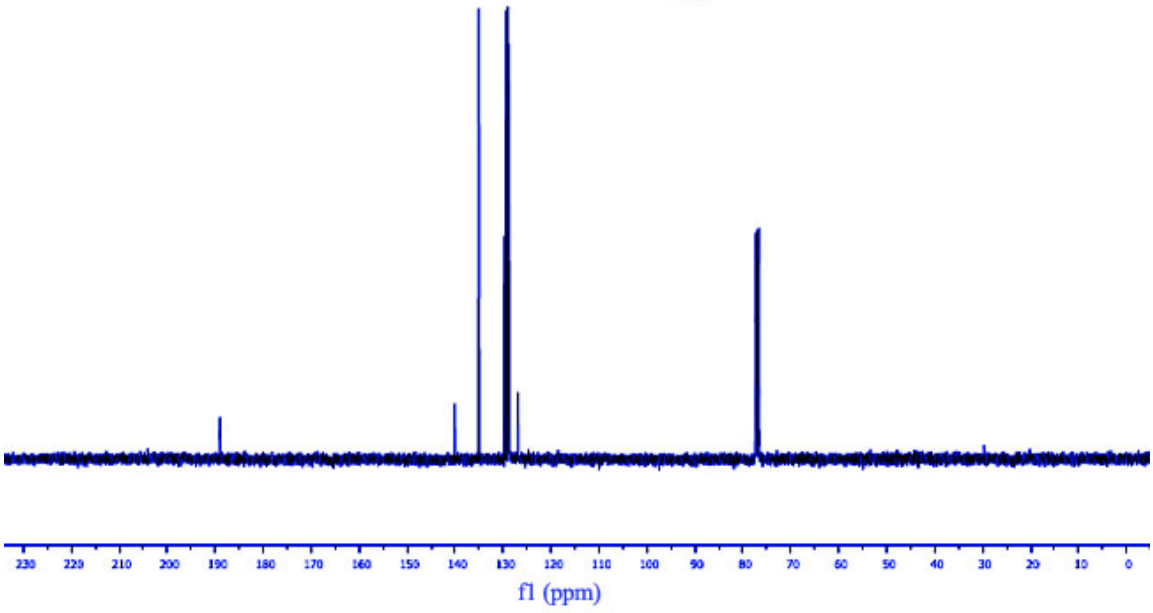

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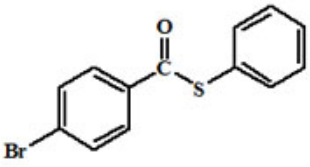

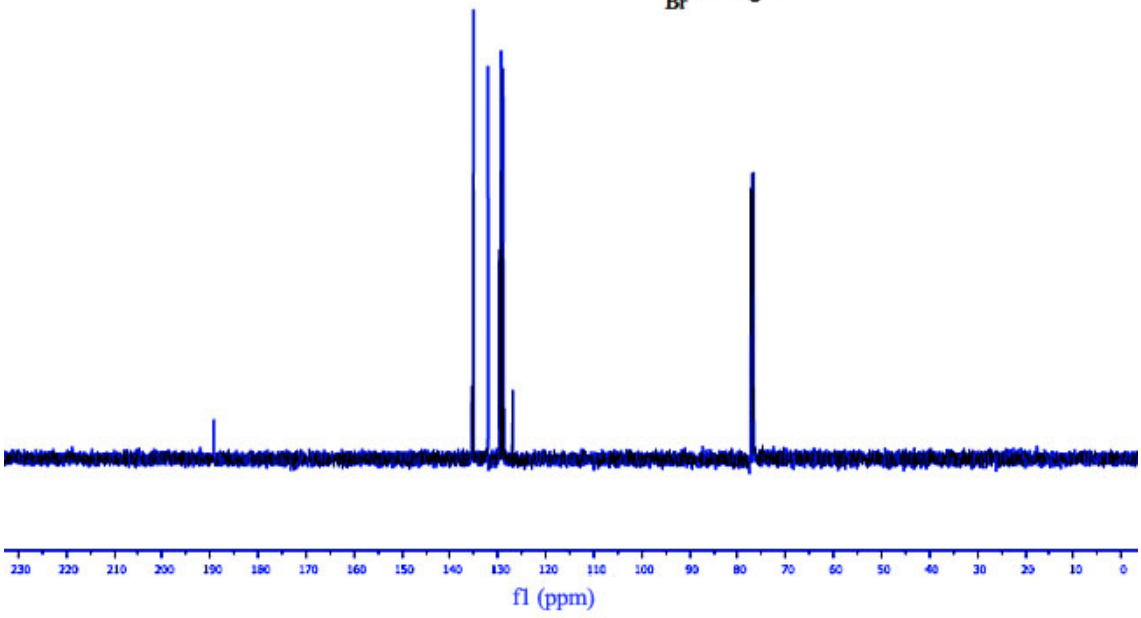

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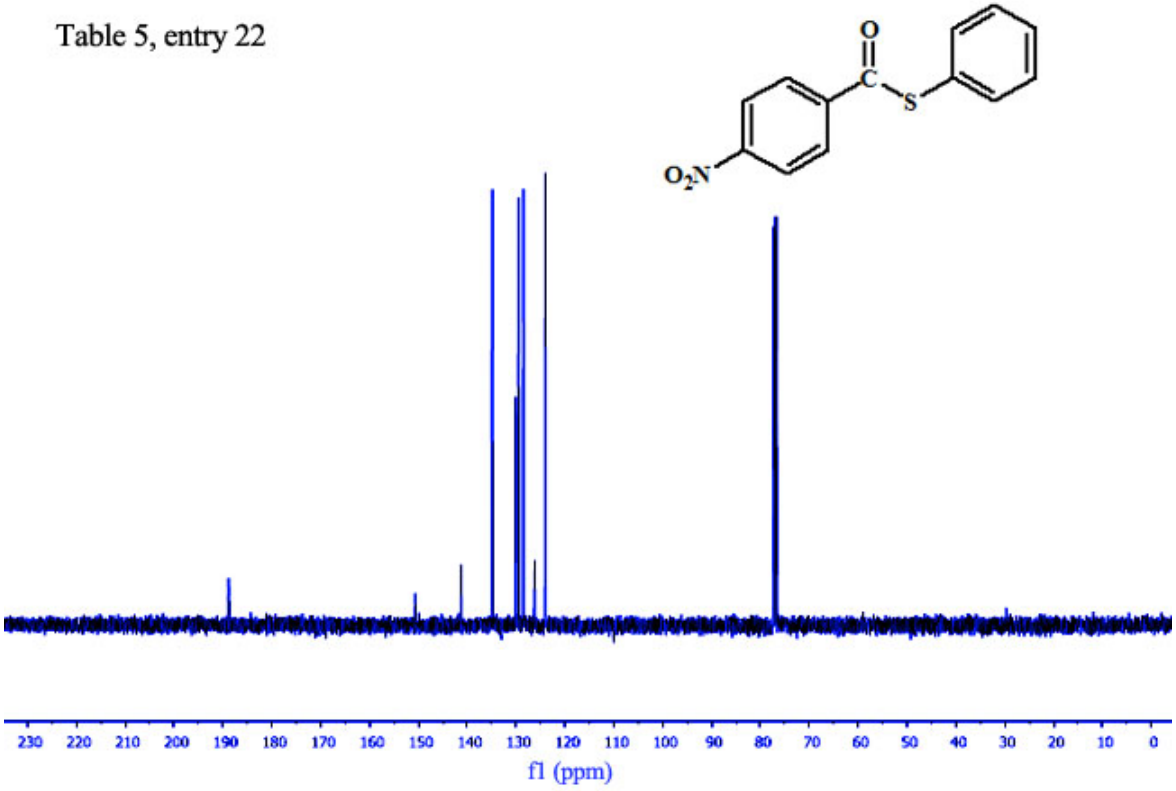

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