Supporting Information

S-Acetylation of thiols mediated by triflic acid: a novel route to thioesters

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Characterization Data:

S-phenyl thioacetate (Table 2, entry 1) was obtained as yellow oil (89%); ^{1}H NMR: (600 MHz, C_6D_6): δ (ppm) = 1.85 (s, 3H), 6.94-7.07 (m, 3H), 7.28-7.38 (m, 2H); ^{13}C NMR: (151 MHz, C_6D_6): δ (ppm) = 29.3, 128.5, 128.9, 129.0, 134.4, 191.8; MS (EI) m/z (rel. int.): 152 (M^+, 15%), 109 (100), 84 (5), 65 (15), 51 (5).

S-(4-fluorophenyl) thioacetate (Table 2, entry 2) was obtained as yellow oil (85%); ^{1}H NMR: (600 MHz, C_6D_6): δ (ppm) = 1.82 (s, 3H), 6.66 (t, *J* = 8.6 Hz, 2H), 7.01-7.13 (m, 2H); ^{13}C NMR: (151 MHz, C_6D_6): δ (ppm) = 29.1, 116.1 (d, *J* = 22.1 Hz), 123.6 (d, *J* = 3.6 Hz), 136.5 (d, *J* = 8.4 Hz), 163.3 (d, *J* = 249.3 Hz), 191.7; MS (EI) m/z (rel. int.): 170 (M^+, 5%), 127 (100), 108 (10), 83 (30), 57 (20).

S-(4-chlorophenyl) thioacetate (Table 2, entry 3) was obtained as yellow oil (90%); ^{1}H NMR: (600 MHz, C_6D_6): δ (ppm) = 1.79 (s, 3H), 6.91-6.98 (m, 2H), 6.98-7.04 (m, 2H); ^{13}C NMR: (151 MHz, C_6D_6): δ (ppm) = 29.2, 126.7, 129.2, 135.4, 135.6, 191.2; MS (EI) m/z (rel. int.): 185 (M^+, 10%), 143 (100), 108 (10).

S-(4-bromophenyl) thioacetate (Table 2, entry 4) was obtained as pale-yellow solid (93%); ^{1}H NMR: (600 MHz, C_6D_6): δ (ppm) = 1.79 (s, 3H), 6.90-6.95 (m, 2H), 7.09-7.14 (m, 2H); ^{13}C NMR: (151 MHz, C_6D_6): δ (ppm) = 29.2, 123.7, 127.3, 132.1, 135.8, 191.0; MS (EI) m/z (rel. int.): 229 (M^+, 15%), 189 (100), 109 (50), 81 (10), 69 (15).

S-(4-methylphenyl) thioacetate (Table 2, entry 5) was obtained as pale-yellow oil (89%); ^{1}H NMR: (600 MHz, C_6D_6): δ (ppm) = 1.88 (s, 3H), 1.98 (s, 3H), 6.84-6.90 (m, 2H), 7.23-7.32 (m, 2H); ^{13}C NMR: (151 MHz, C_6D_6): δ (ppm) = 20.7, 29.3, 125.1, 129.8, 134.4, 139.1, 192.2; MS (EI) m/z (rel. int.): 166 (M^+, 5%), 124 (100), 91 (50).

S-(3-methoxyphenyl) thioacetate (Table 2, entry 6) was obtained as yellow oil (90%); ^{1}H NMR: (600 MHz, C_6D_6): δ (ppm) = 1.87 (s, 3H), 3.20 (s, 3H), 6.84-6.69 (ddd, *J* = 8.1, 2.6, 1.2 Hz, 1H), 6.92-7.05 (m, 2H), 7.07 (dd, *J* = 2.6, 1.6 Hz, 1H); ^{13}C NMR: (151 MHz, C_6D_6): δ (ppm) = 29.3, 54.5, 115.4, 119.6, 126.5, 129.4, 129.8, 160.1, 191.8; MS (EI) m/z (rel. int.): 182 (M^+, 10%), 139 (100), 125 (25), 95 (10).

S-(3-methylphenyl) thioacetate (Table 2, entry 7) was obtained as yellow oil (89%); ^{1}H NMR: (600 MHz, C_6D_6): δ (ppm) = 1.88 (s, 3H), 1.97 (s, 3H), 6.80-6.87 (m, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 7.17-7.28 (m, 2H); ^{13}C NMR: (151 MHz, C_6D_6): δ (ppm) = 20.7, 29.3, 128.2, 128.8, 129.8, 131.5, 135.1, 138.7, 192.0; MS (EI) m/z (rel. int.): 166 (M^+, 20%), 124 (100), 91 (50).

S-(2-methylphenyl) thioacetate (Table 2, entry 8) was obtained as pale-yellow oil (92%); ^{1}H NMR: (600 MHz, C_6D_6): δ (ppm) = 1.86 (s, 3H), 2.23 (s, 3H), 6.90-6.96 (m, 1H), 6.96-7.05 (m, 2H), 7.38 (dd, *J* = 7.6, 1.2 Hz, 1H); ^{13}C NMR: (151 MHz, C_6D_6): δ (ppm) = 20.4, 29.3, 126.4, 128.0, 129.8, 130.6, 135.9, 141.9, 191.4; MS (EI) m/z (rel. int.): 166 (M^+, 10%), 124 (100), 91 (50).

S-(2-chlorophenyl) thioacetate (Table 2, entry 9) was obtained as pale-yellow oil (91%); ^{1}H NMR: (600 MHz, C_6D_6): δ (ppm) = 1.83 (s, 3H), 6.68-6.79 (m, 2H), 7.11-7.15 (m, 1H), 7.27-7.34 (m, 1H); ^{13}C NMR: (151 MHz, C_6D_6): δ (ppm) = 29.2, 126.9, 127.9, 130.0, 130.7, 137.0, 138.4, 190.0; MS (EI) m/z (rel. int.): 185 (M^+, 30%), 143 (100), 108 (50).

S-(2-methoxyphenyl) thioacetate (Table 2, entry 10) was obtained as pale-yellow oil (90%); ^{1}H NMR: (600 MHz, C_6D_6): δ (ppm) = 1.92 (s, 3H), 3.25 (s, 3H), 6.46 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.74 (ddd, *J* = 8.5, 7.1, 0.9 Hz, 1H), 6.98-7.11 (m, 1H), 7.42 (dd, *J* = 7.6, 1.7 Hz, 1H); ^{13}C NMR: (151 MHz, C_6D_6): δ (ppm) = 29.2, 55.0, 111.3, 116.9, 120.7, 131.2, 136.8, 159.5, 191.4; MS (EI) m/z (rel. int.): 182 (M^+, 10%), 170 (5), 140 (100), 125 (30), 97 (10).

S-naphthalene-2-yl thioacetate (Table 2, entry 11) was obtained as pale-yellow solid (89%); ^{1}H NMR: (600 MHz, C_6D_6): δ (ppm) = 1.90 (s, 3H), 7.16-7.22 (m, 2H), 7.40-7.53 (m, 4H), 7.86 (dd, *J* = 1.6, 0.8 Hz, 1H); ^{13}C NMR: (151 MHz, C_6D_6): δ (ppm) = 29.4, 125.9, 126.3, 126.8, 127.9, 128.0, 128.7, 131.1, 133.4, 133.7, 134.3, 192.0; MS (EI) m/z (rel. int.): 202 (M^+, 10%), 159 (100), 115 (30).

S-octyl thioacetate (Table 2, entry 12) was obtained as yellow oil (92%); ^{1}H NMR: (600 MHz, C_6D_6): δ (ppm) = 0.87 (t, *J* = 7.3 Hz, 3H), 1.10-1.25 (m, 10H), 1.39-1.48 (m, 2H), 1.90 (s, 3H), 2.77 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR: (151 MHz, C_6D_6): δ (ppm) = 14.0, 22.7, 28.7, 28.9, 29.1, 29.2, 29.7, 29.8, 31.8, 193.9; MS (EI) m/z (rel. int.): 188 (M^+, 25%), 145 (100), 69 (70), 55 (45).

Methyl 2-(acetylthio)acetate (Table 2, entry 13) was obtained as pale-orange oil (80%); ^{1}H NMR: (600 MHz, C_6D_6): δ (ppm) = 1.74 (s, 3H), 3.24 (s, 3H), 3.39 (s, 2H); ^{13}C NMR: (151 MHz, C_6D_6): δ (ppm) = 29.1, 30.8, 51.7, 168.3, 192.4; MS (EI) m/z (rel. int.): 148 (M^+, 10%), 125 (50), 105 (100), 74 (60), 45 (90).

S-(4-chlorobenzyl) thioacetate (Table 2, entry 14) was obtained as pale-yellow oil (89%); ^{1}H NMR: (600 MHz, C_6D_6): δ (ppm) = 1.78 (s, 3H), 3.74 (s, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR: (151 MHz, C_6D_6): δ (ppm) = 29.4, 32.3, 128.5, 130.1, 132.9, 136.6, 193.1; MS (EI) m/z (rel. int.): 200 (M^+, 15%), 156 (30), 127 (100), 89 (25).

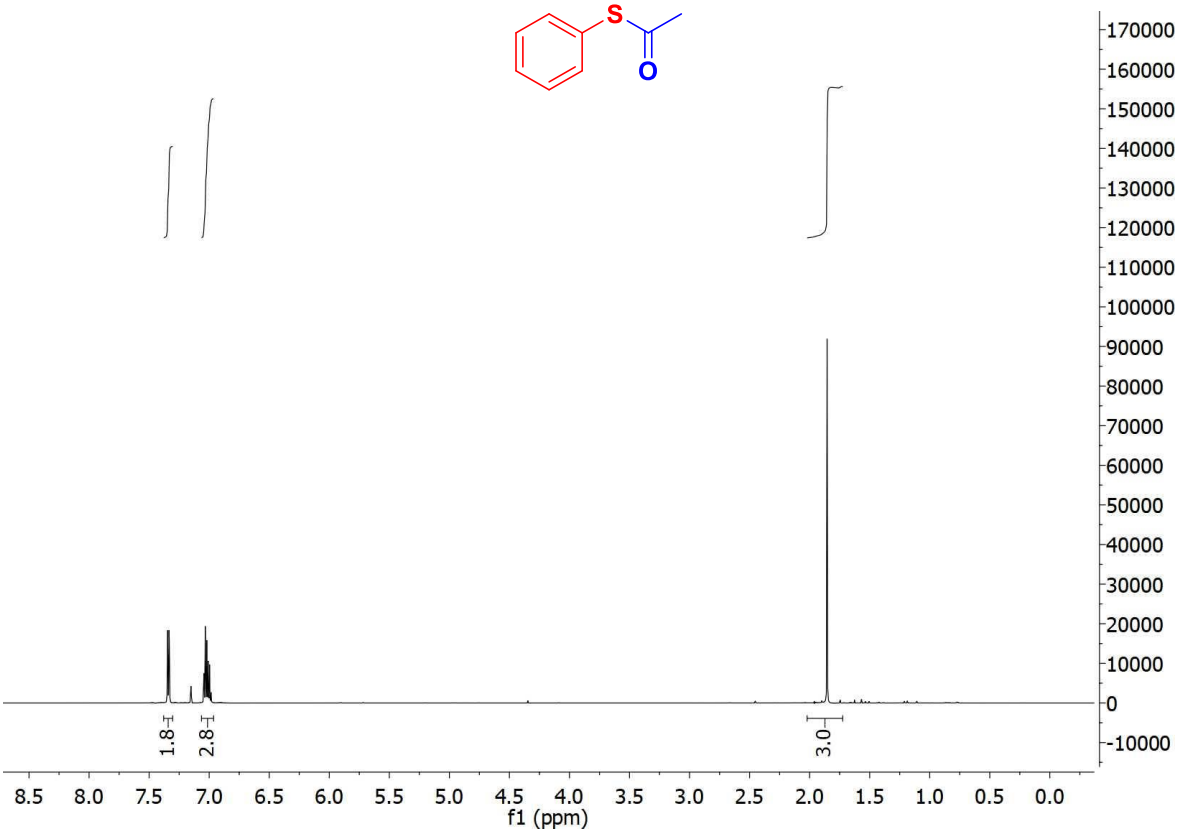
S-cyclohexyl thioacetate (Table 2, entry 15) was obtained as pale-yellow oil (85%); ^{1}H NMR: (600 MHz, C_6D_6): δ (ppm) = 0.96-1.49 (m, 8H), 1.74-1.87 (m, 2H), 1.89 (s, 3H), 3.52-3.66 (m, 1H); ^{13}C NMR: (151 MHz, C_6D_6): δ (ppm) = 25.4, 25.8, 30.0, 32.9, 42.3, 193.7; MS (EI) m/z (rel. int.): 158 (M^+, 50%), 113 (60), 67 (100), 55 (60).

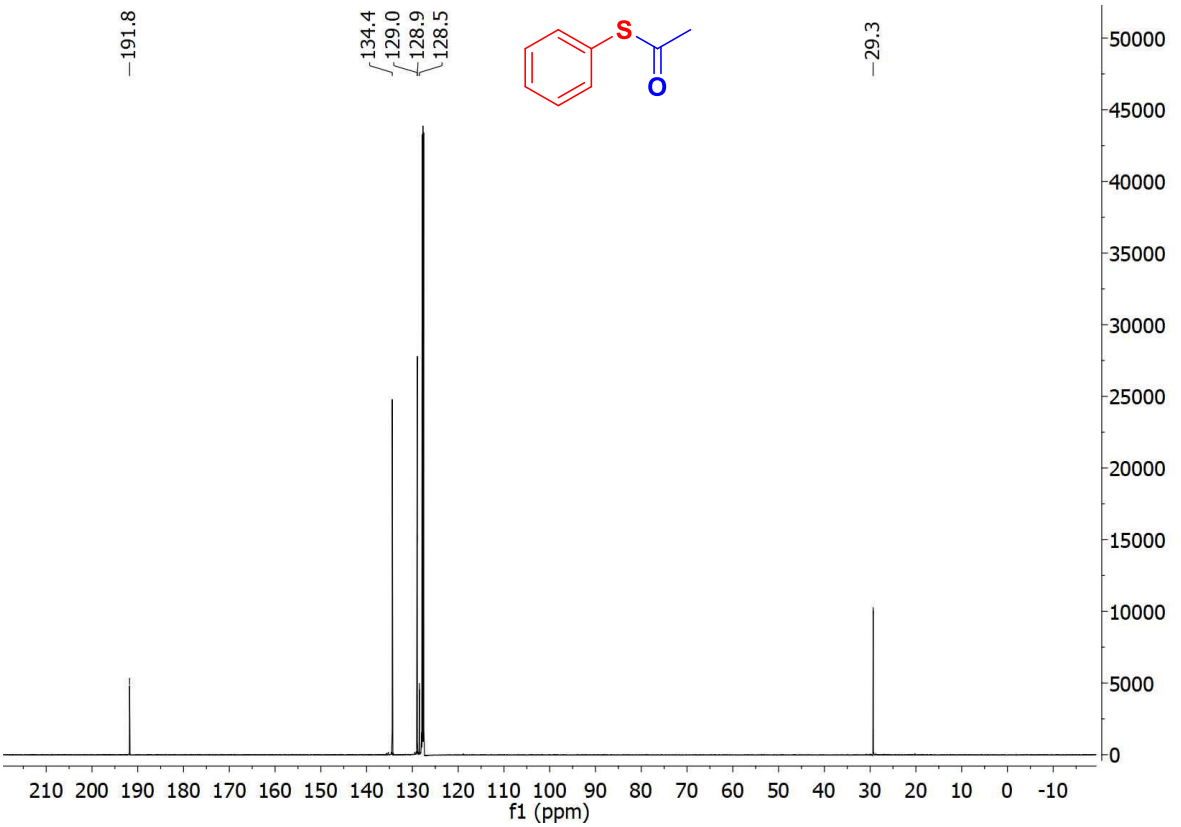
S-(2-fluorophenyl) thioacetate (Table 2, entry 16) was obtained as pale-yellow oil (88%); ^{1}H NMR: (400 MHz, C_6D_6): δ (ppm) = 1.79 (s, 3H), 6.61-6.72 (m, 1H), 6.73-6.80 (m, 1H), 6.81-6.87 (m, 1H), 7.15-7.25 (m, 1H); ^{13}C NMR: (101 MHz, C_6D_6): δ (ppm) = 29.0, 115.8 (d, *J* = 8.8 Hz), 116.0 (d, *J* = 12.9 Hz), 124.3 (d, *J* = 3.9 Hz), 131.7 (d, *J* = 8.1 Hz), 136.5, 162.3 (d, *J* = 249.1 Hz), 190.0; MS (EI) m/z (rel. int.): 170 (M^+, 35%), 127 (100), 108 (20), 83 (25), 57 (15).

S-(2,5-dichlorophenyl) thioacetate (Table 2, entry 17) was obtained as pale-yellow oil (90%); ^{1}H NMR: (400 MHz, C_6D_6): δ (ppm) = 1.75 (s, 3H), 6.64 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.78 (d, *J* = 8.6 Hz, 1H), 7.34 (d, *J* = 2.5 Hz, 1H), 7.15-7.25 (m, 1H); ^{13}C NMR: (101 MHz, C_6D_6): δ (ppm) = 29.2, 129.5, 130.6, 130.8, 132.4, 136.3, 136.6, 189.2; MS (EI) m/z (rel. int.): 220 (M^+, 5%), 176 (100), 67 (25), 57 (35).

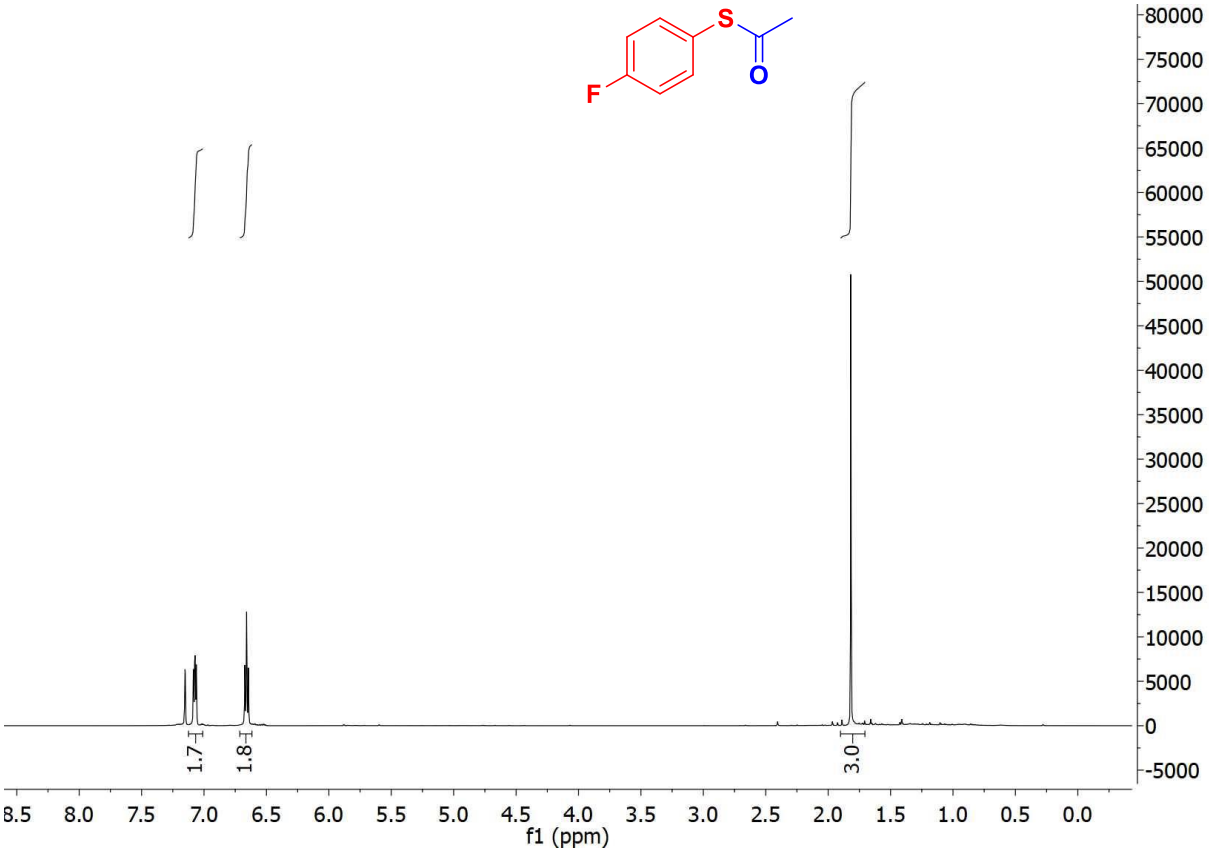
^{1}H and ^{13}C Spectra of Products:

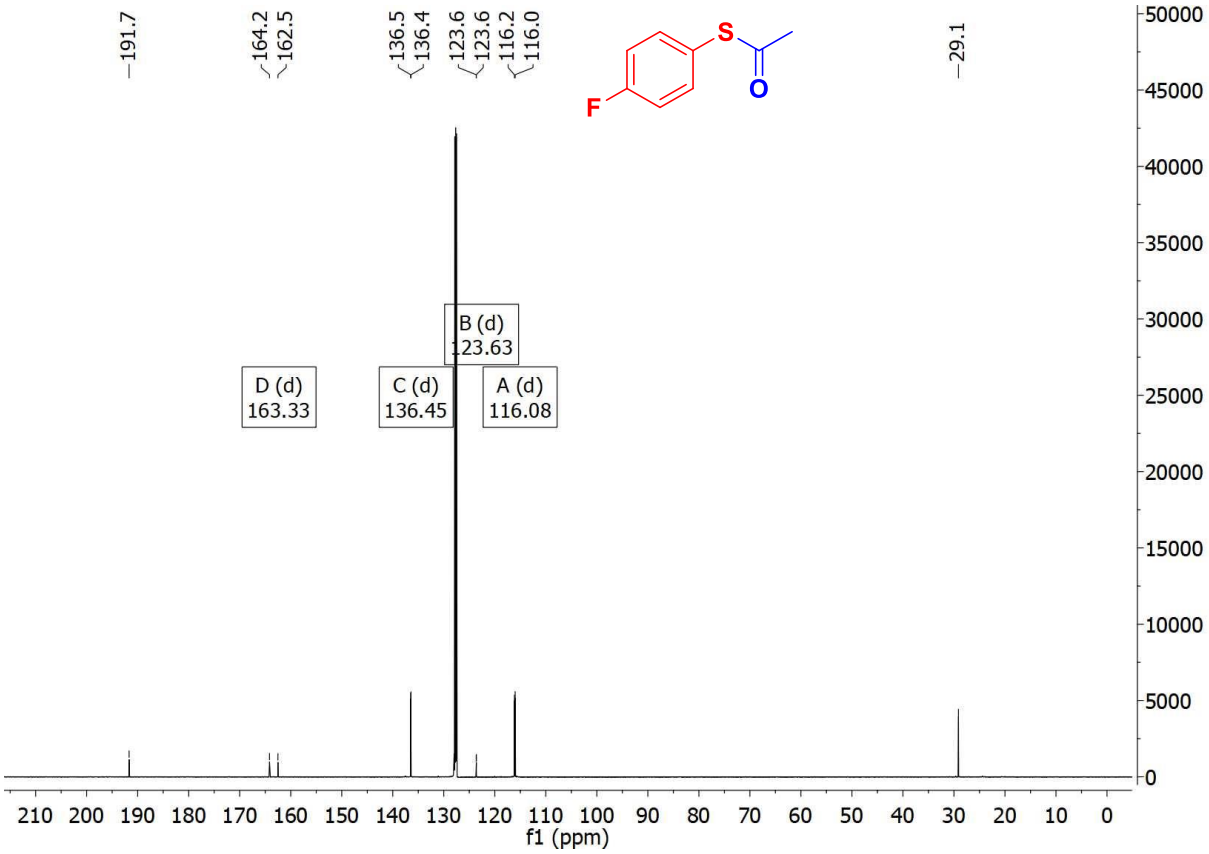
S-phenyl thioacetate (Table 2, entry 1)



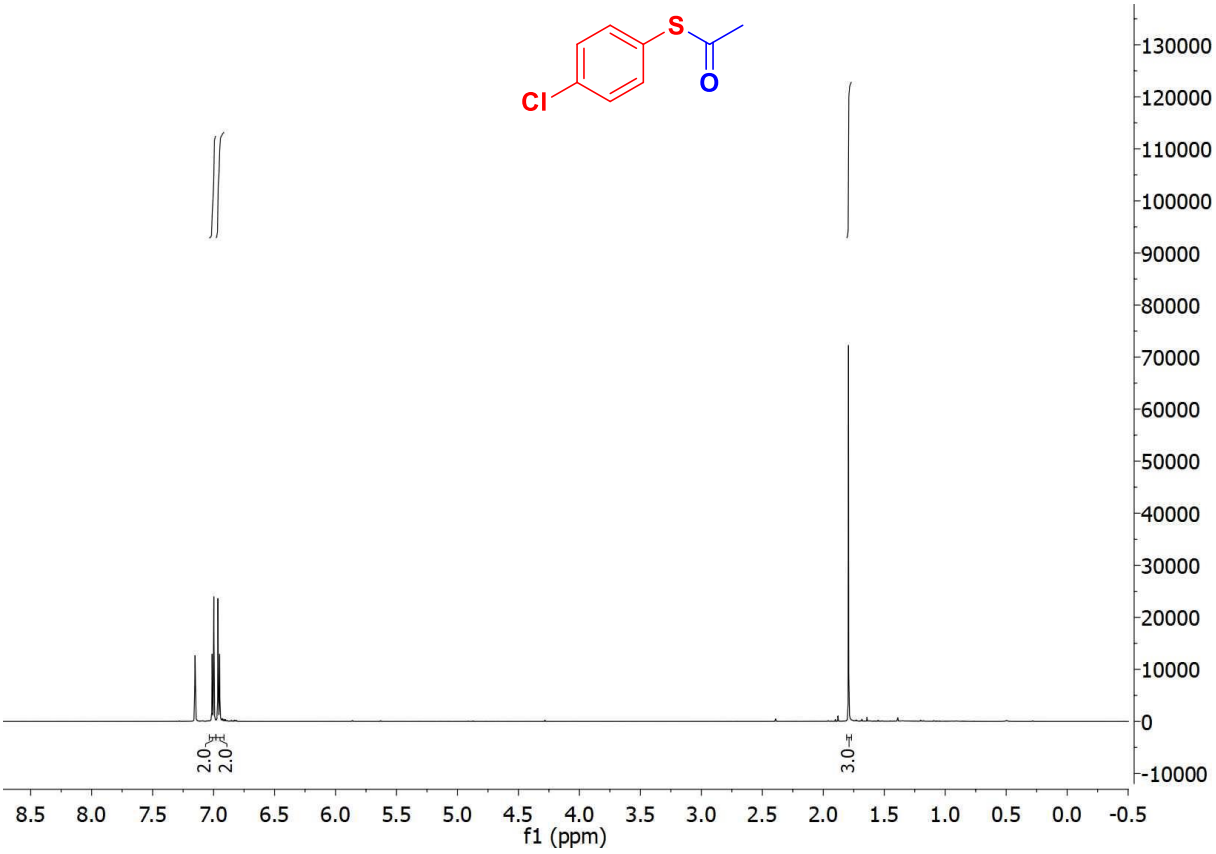


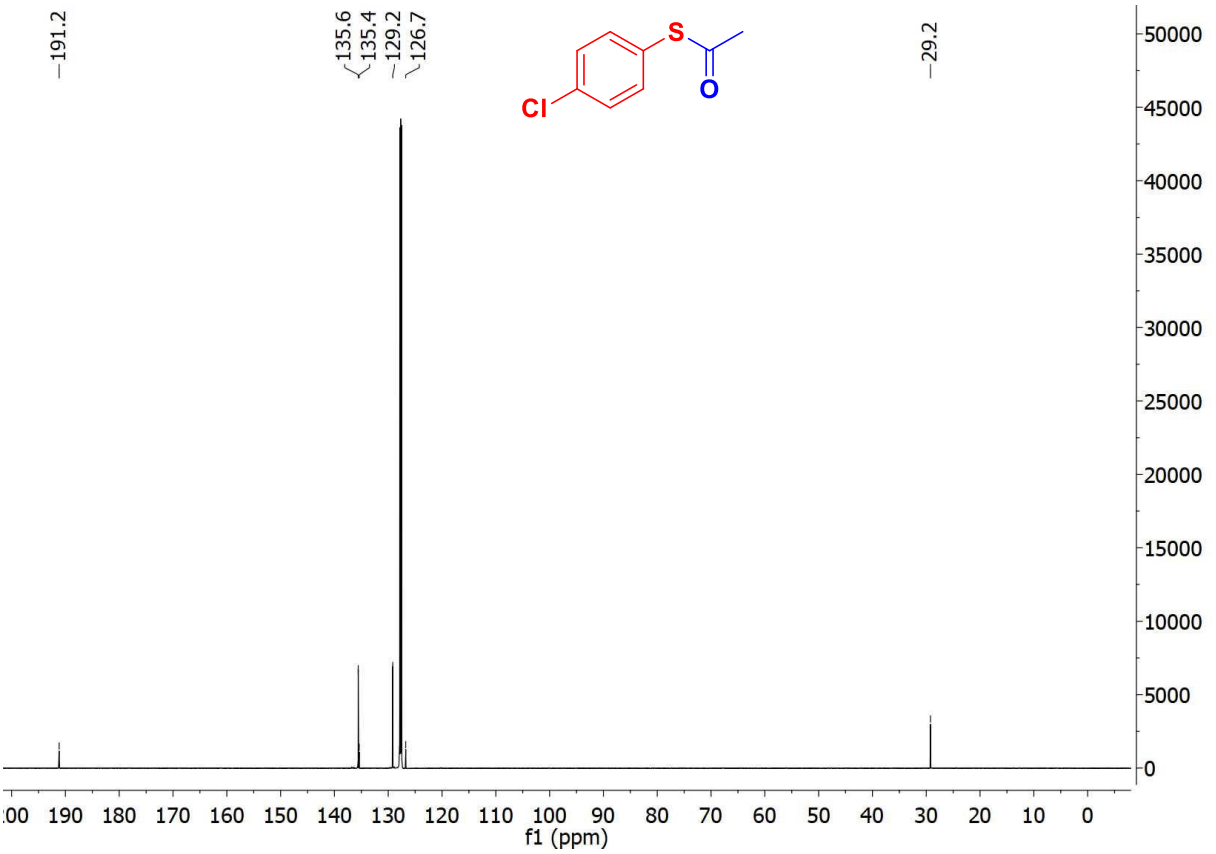
S-(4-fluorophenyl) thioacetate (Table 2, entry 2)



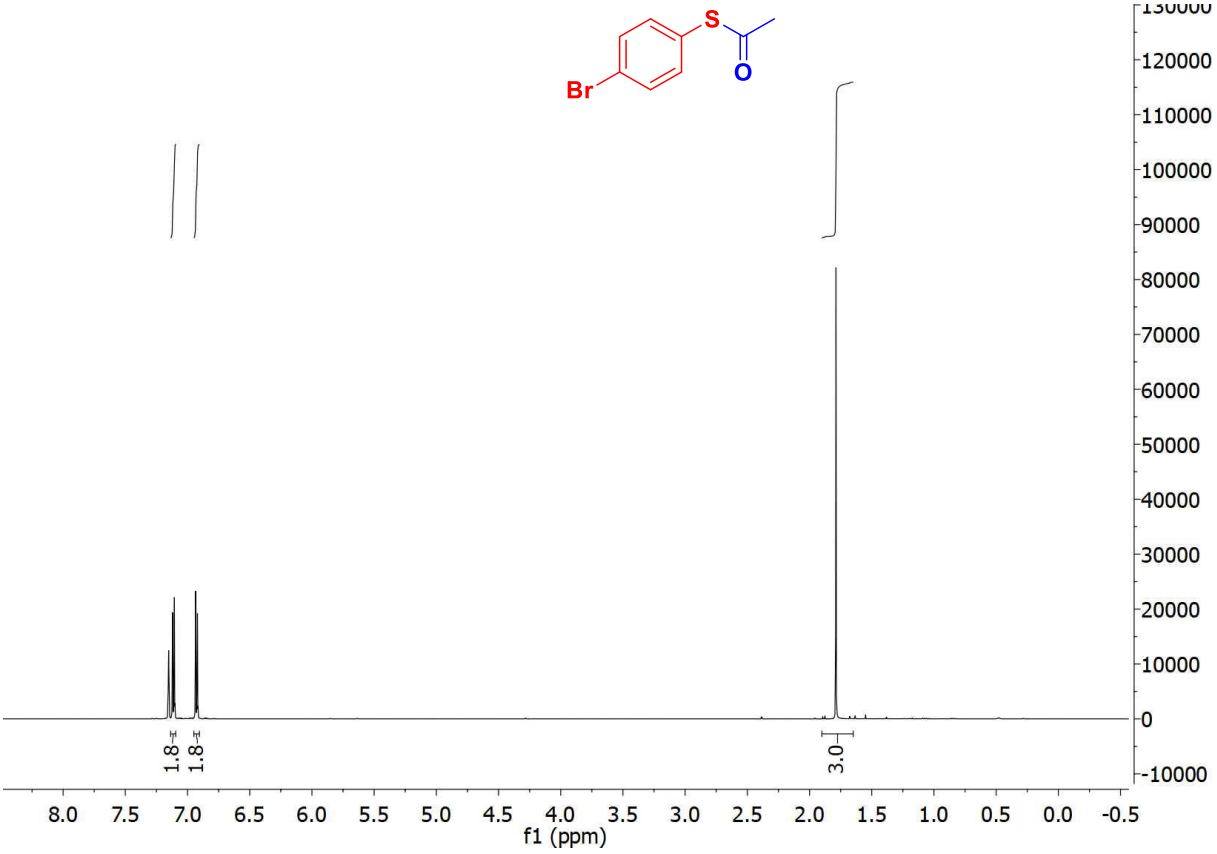


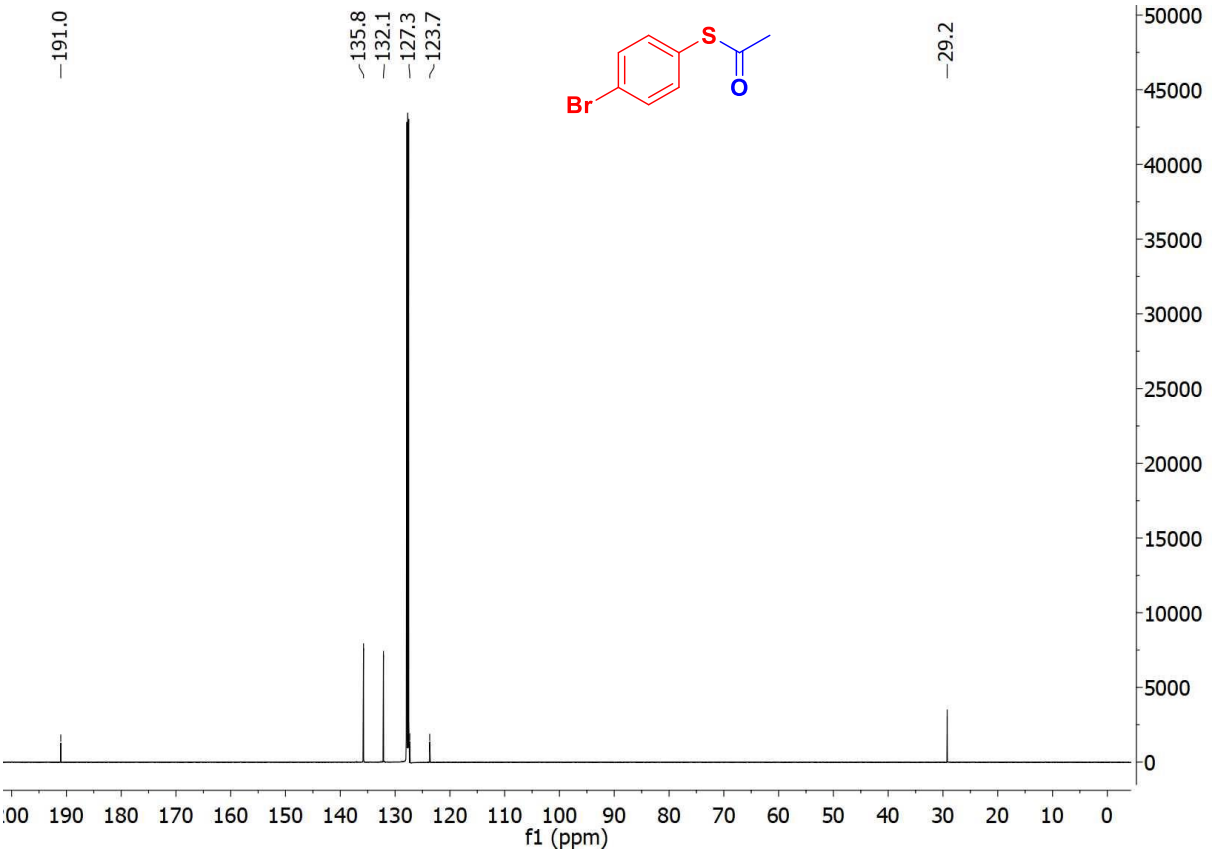
S-(4-chlorophenyl) thioacetate (Table 2, entry 3)



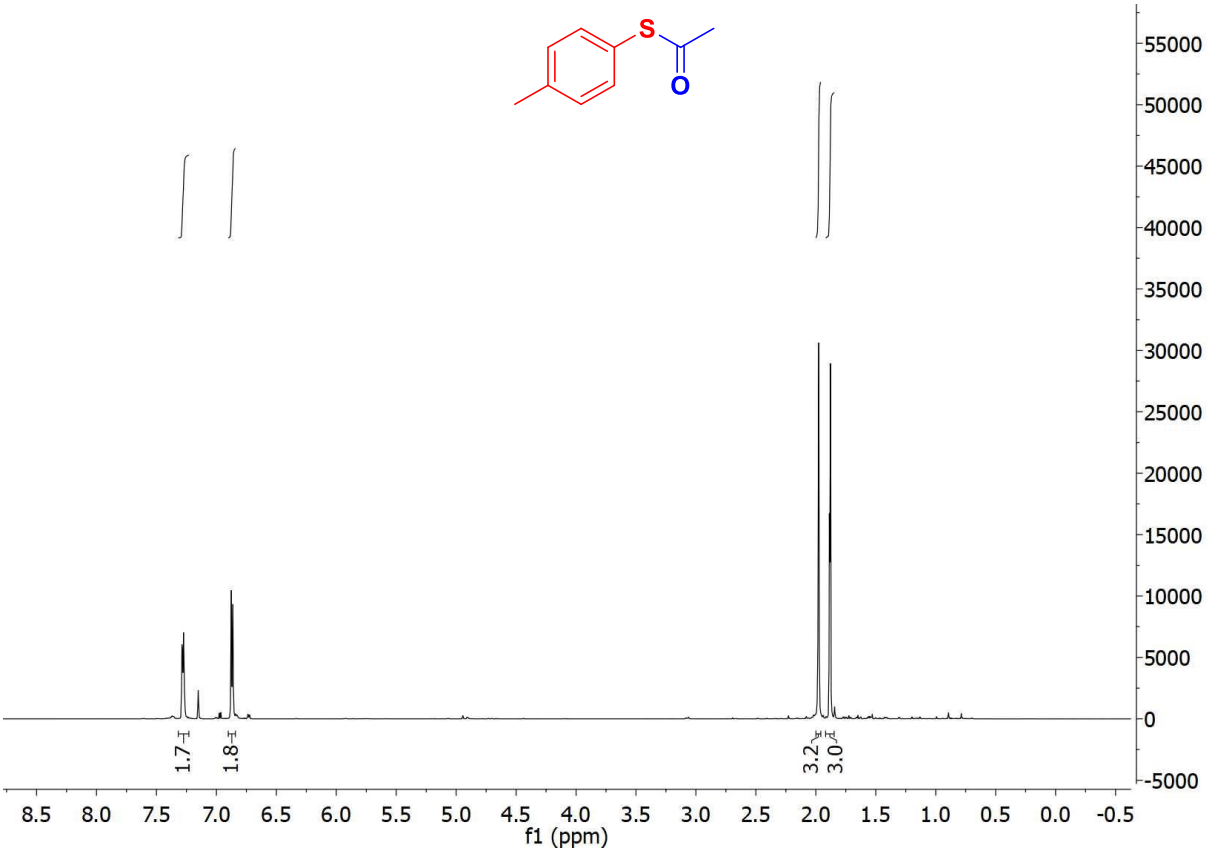


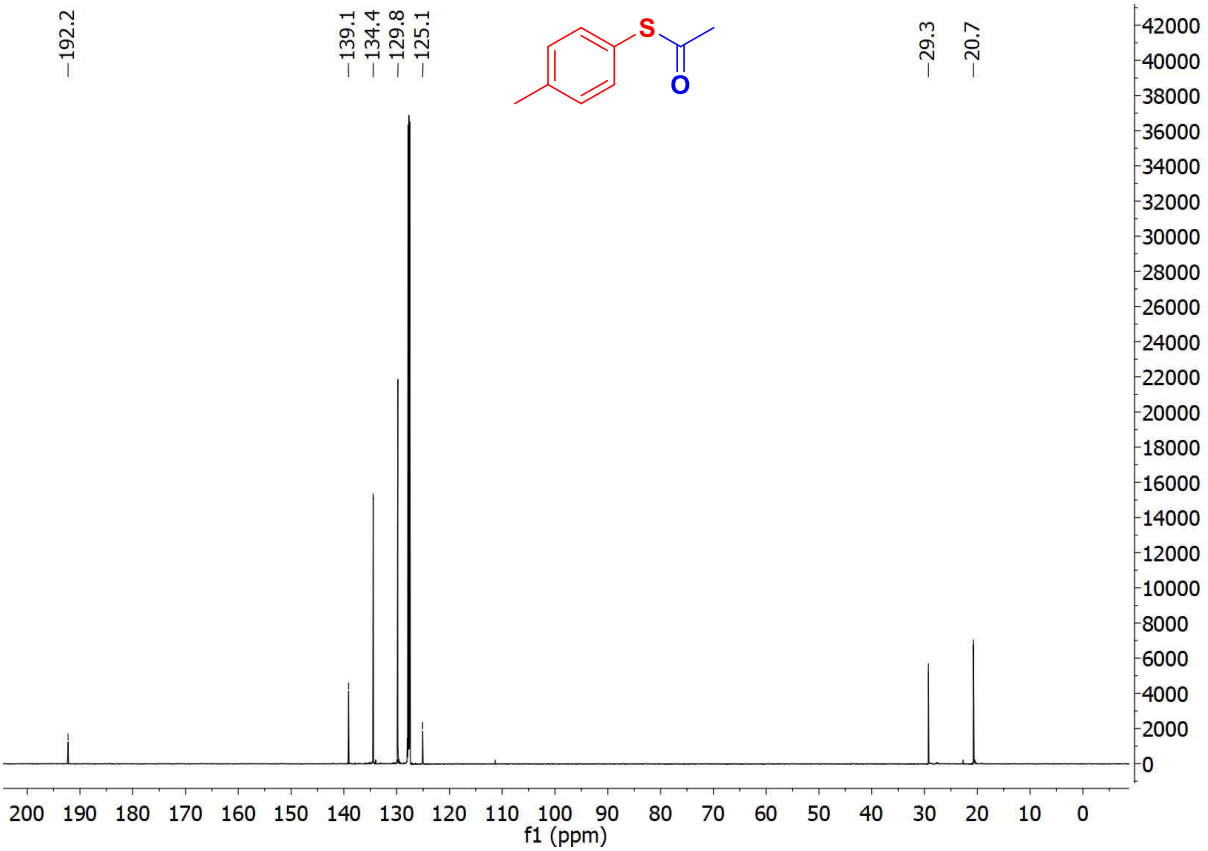
S-(4-bromophenyl) thioacetate (Table 2, entry 4)



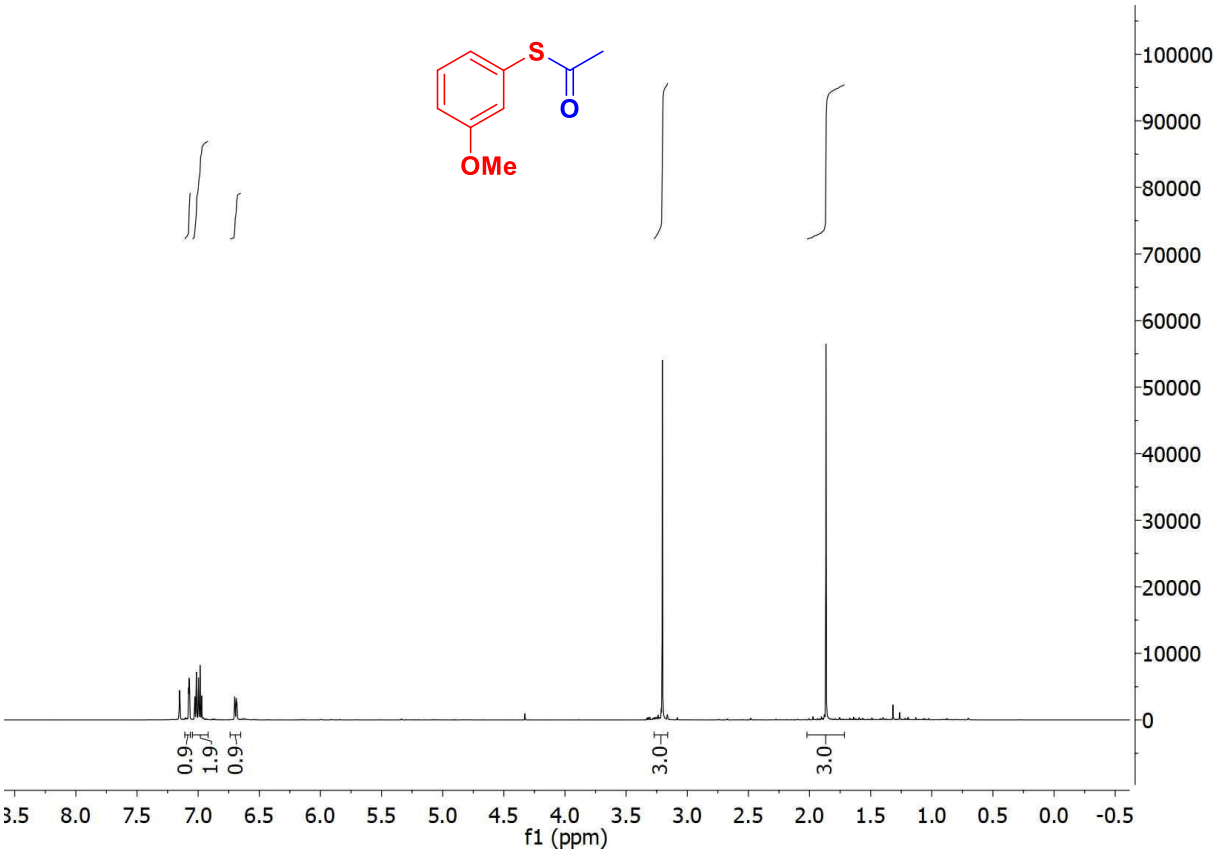


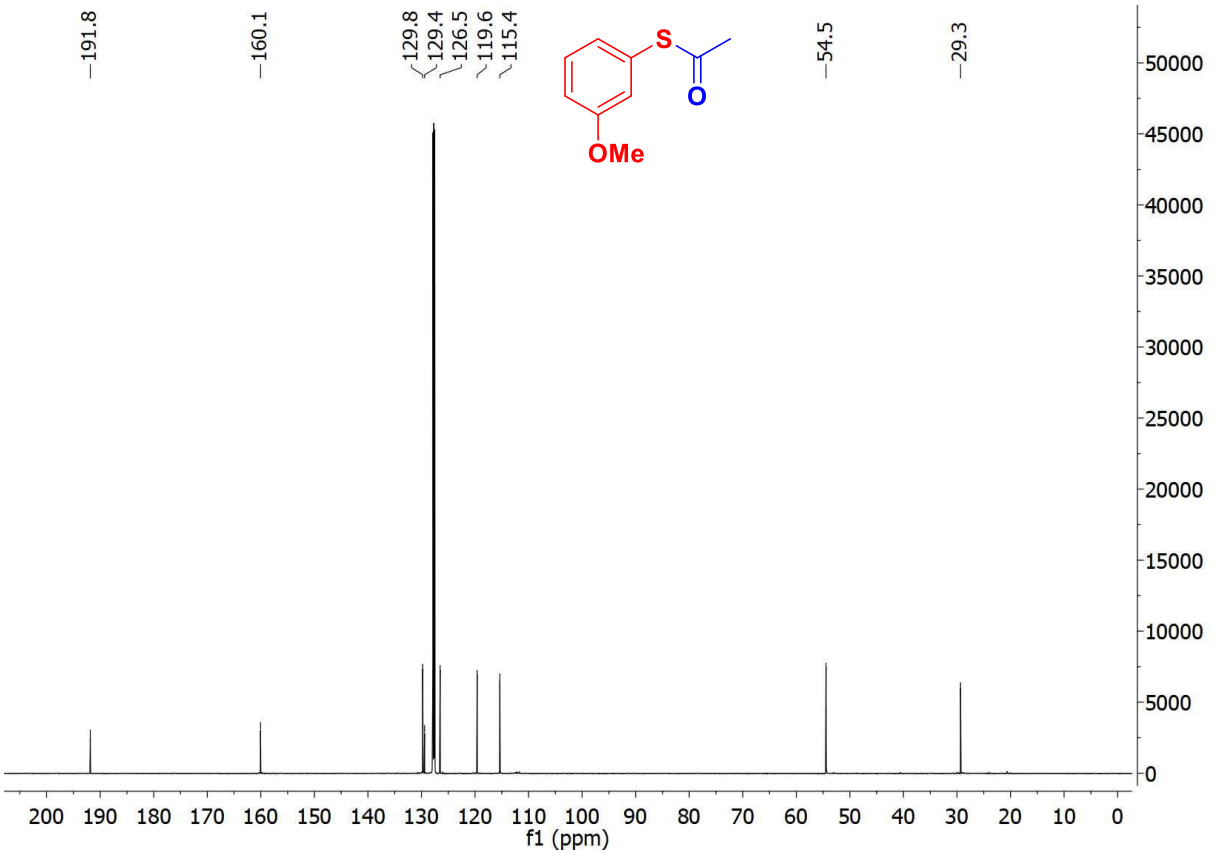
S-(4-methylphenyl) thioacetate (Table 2, entry 5)



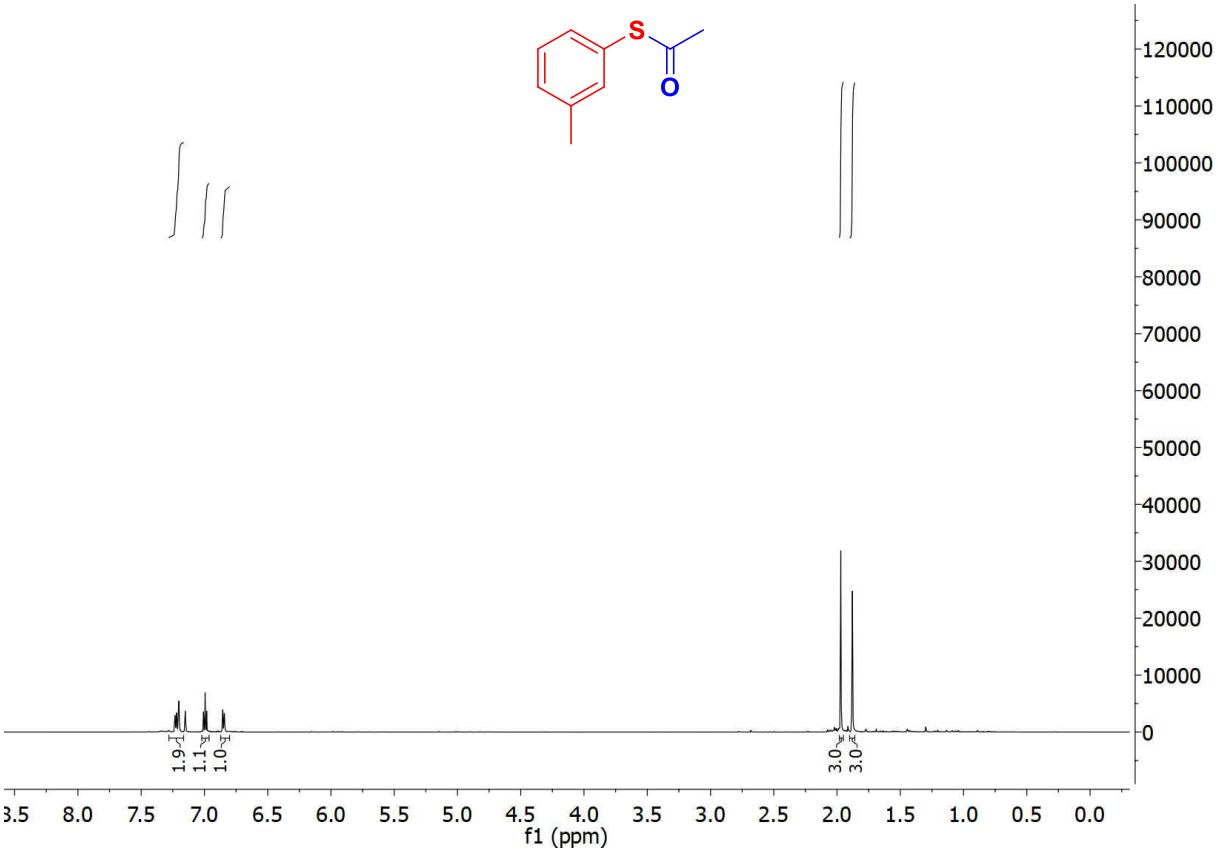


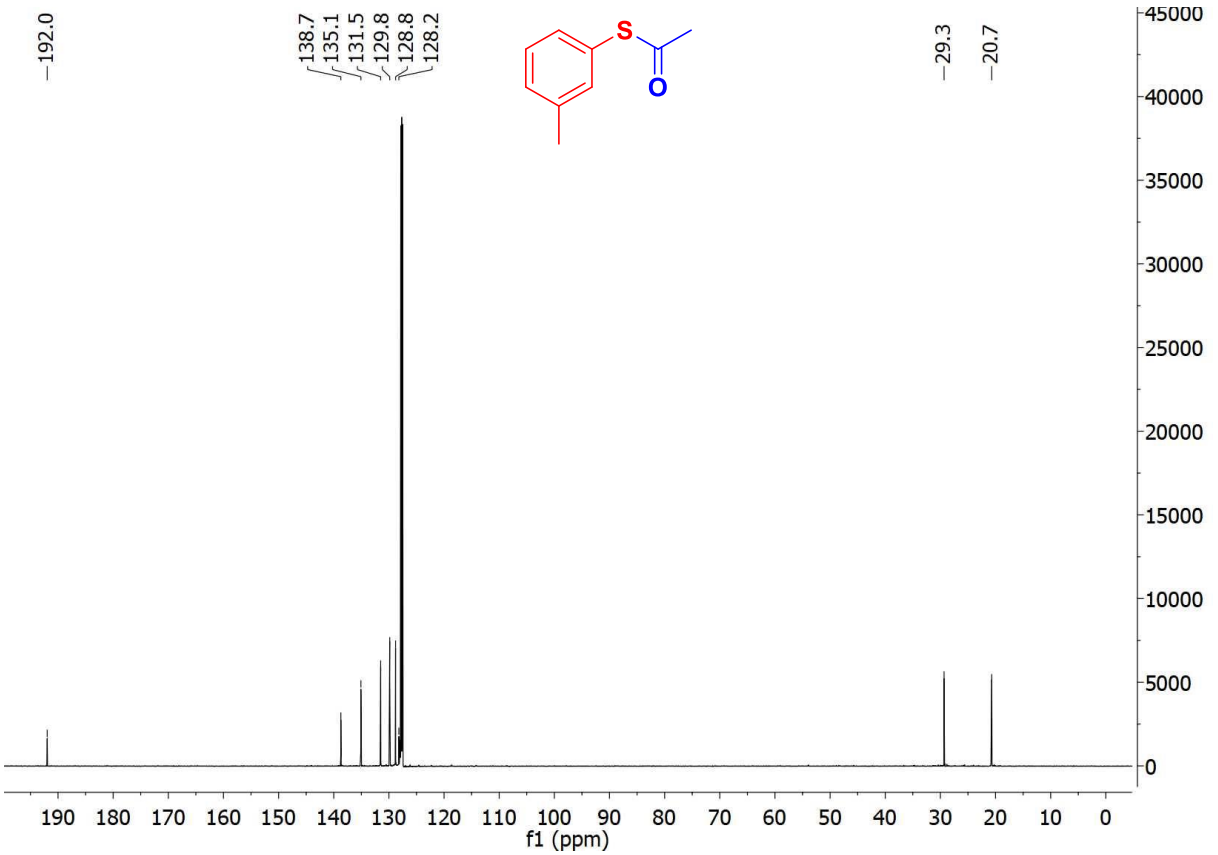
S-(3-methoxyphenyl) thioacetate (Table 2, entry 6)



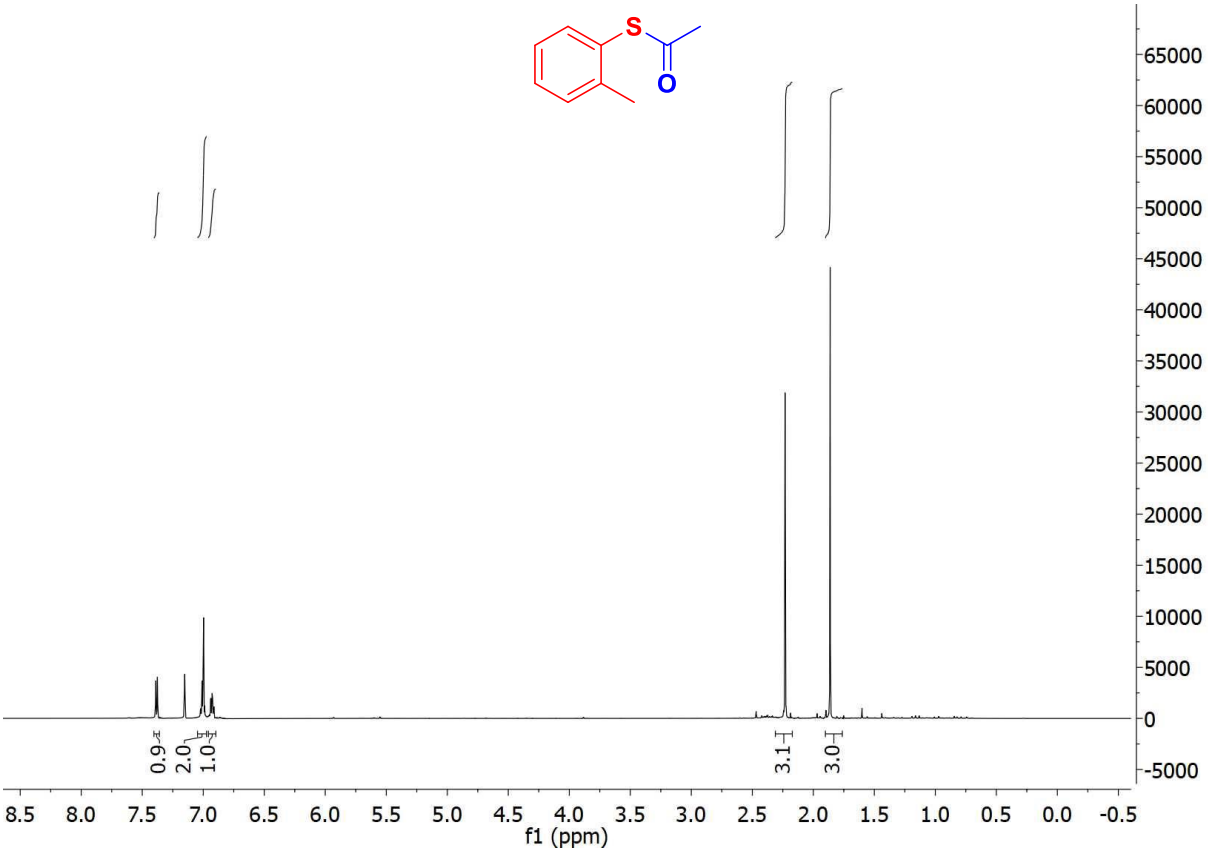


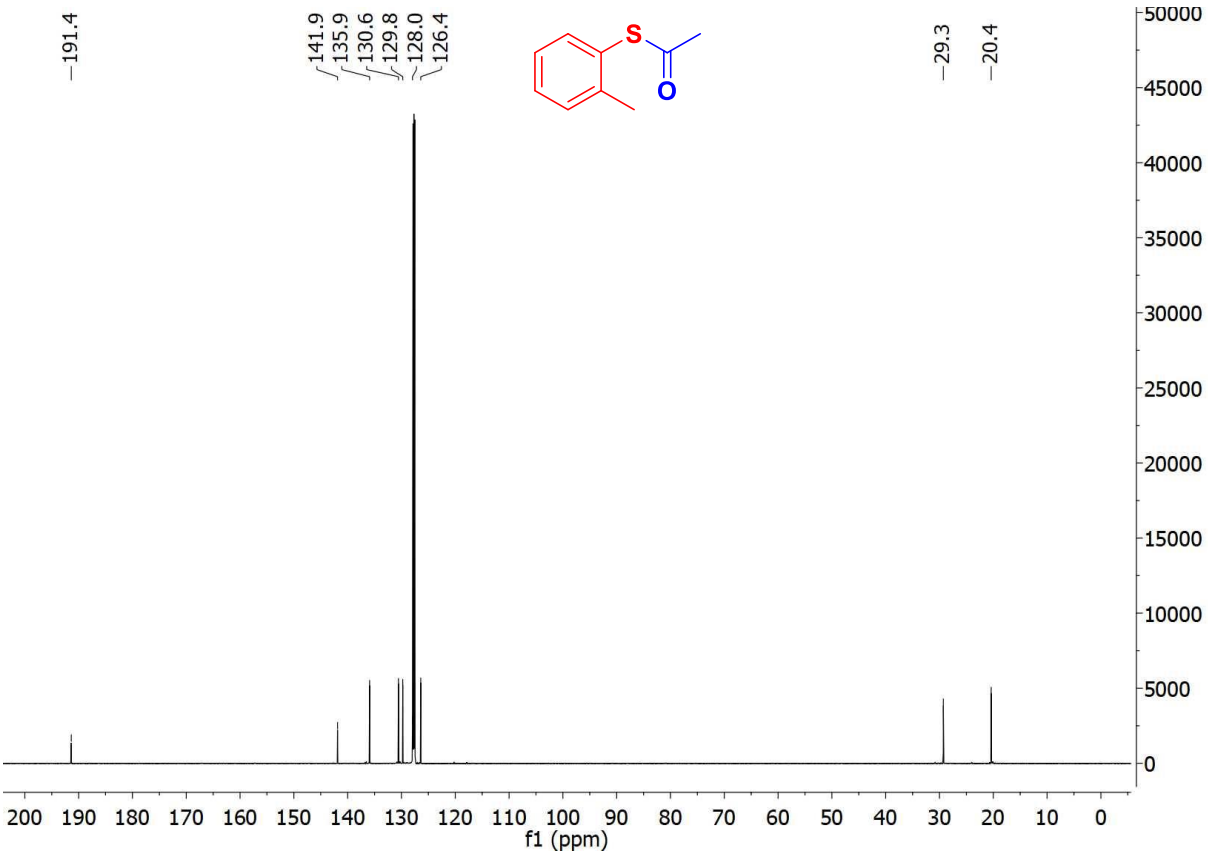
S-(3-methylphenyl) thioacetate (Table 2, entry 7)



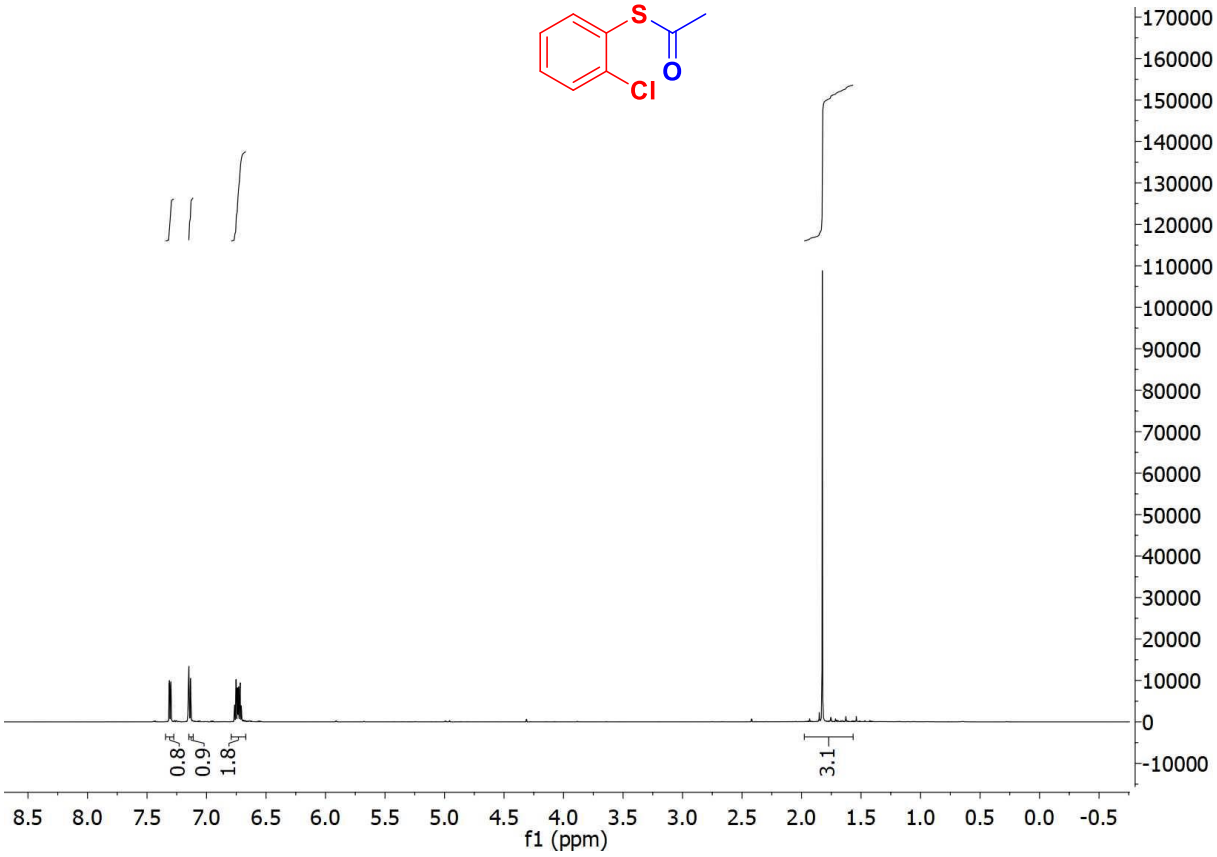


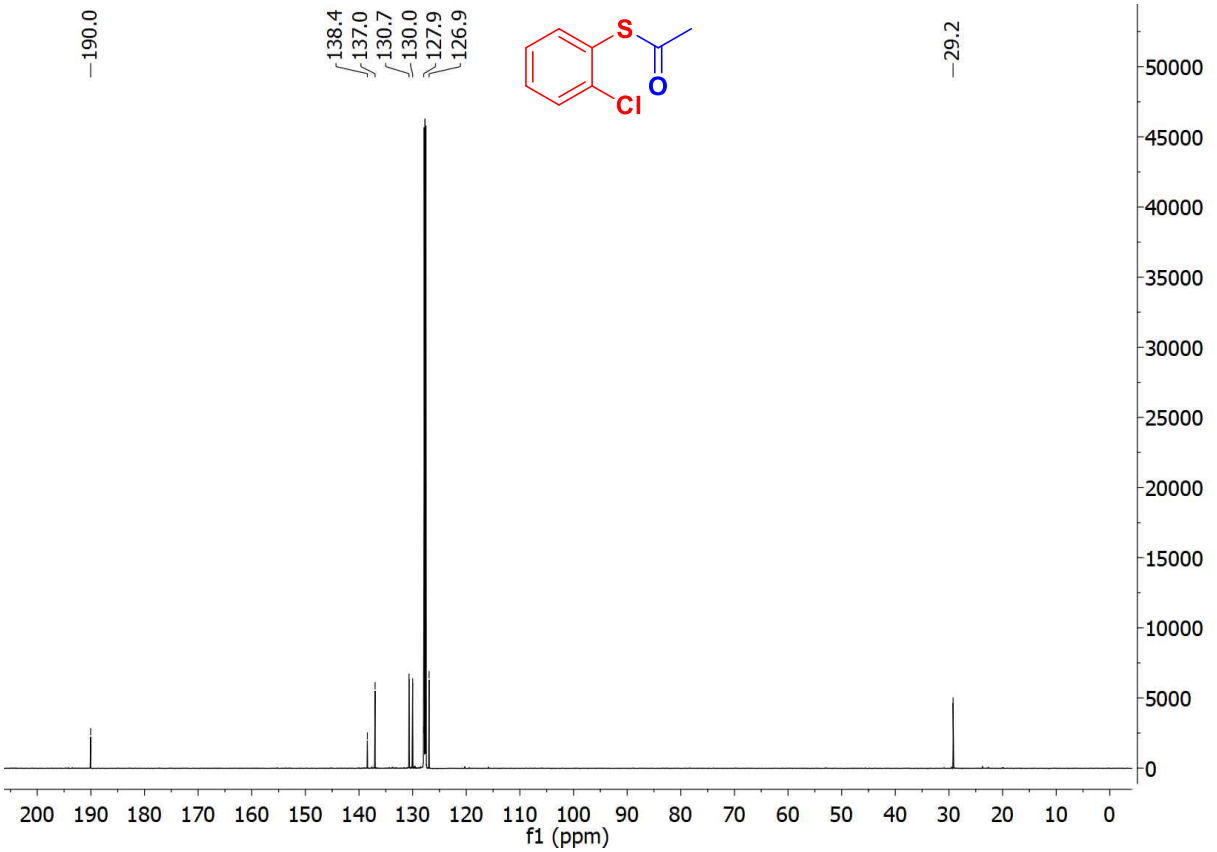
S-(2-methylphenyl) thioacetate (Table 2, entry 8)



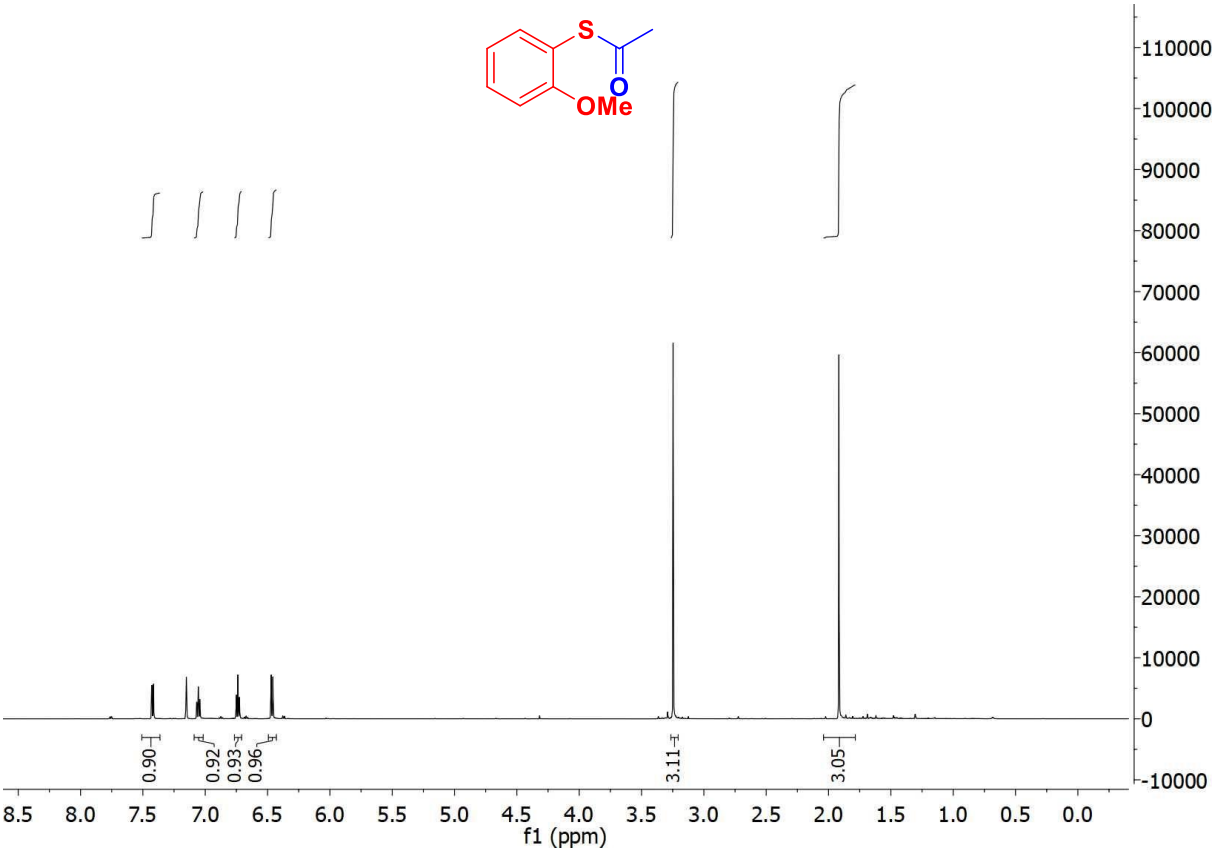


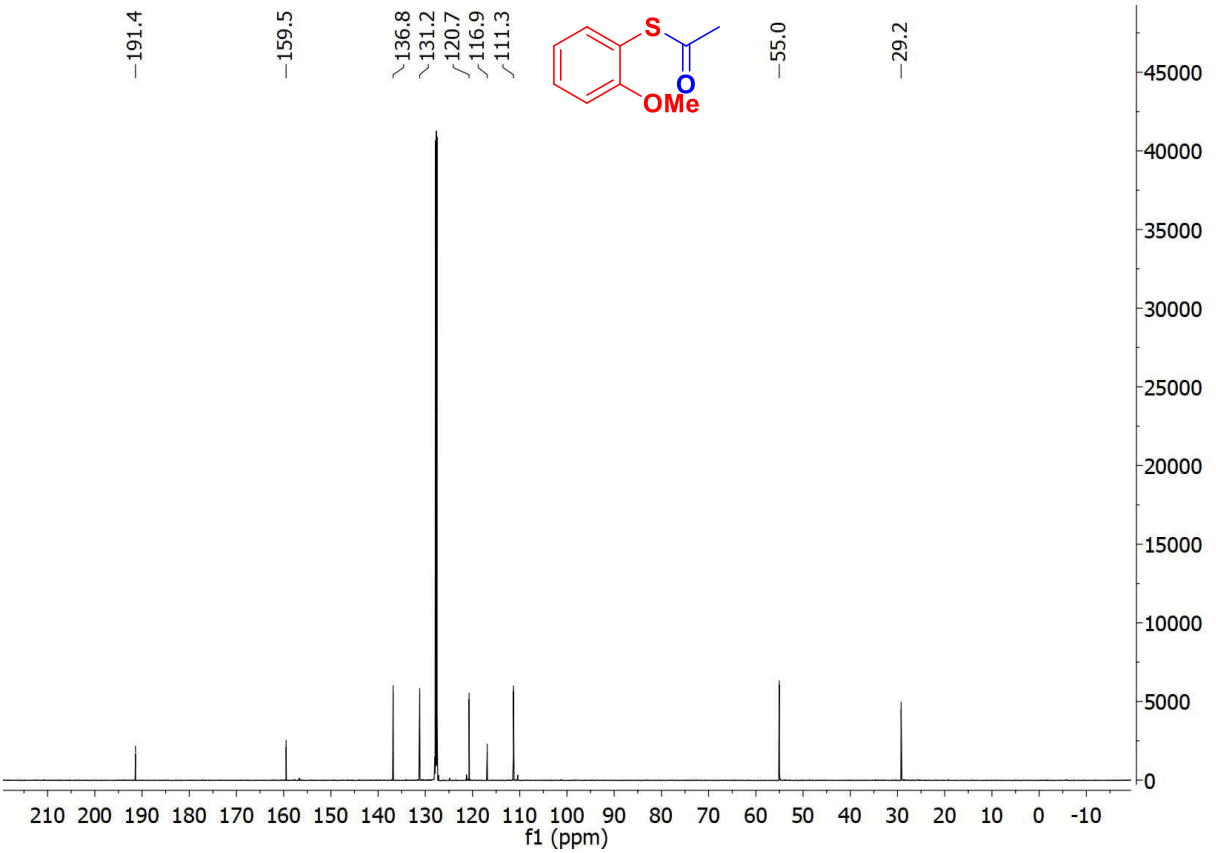
S-(2-chlorophenyl) thioacetate (Table 2, entry 9)



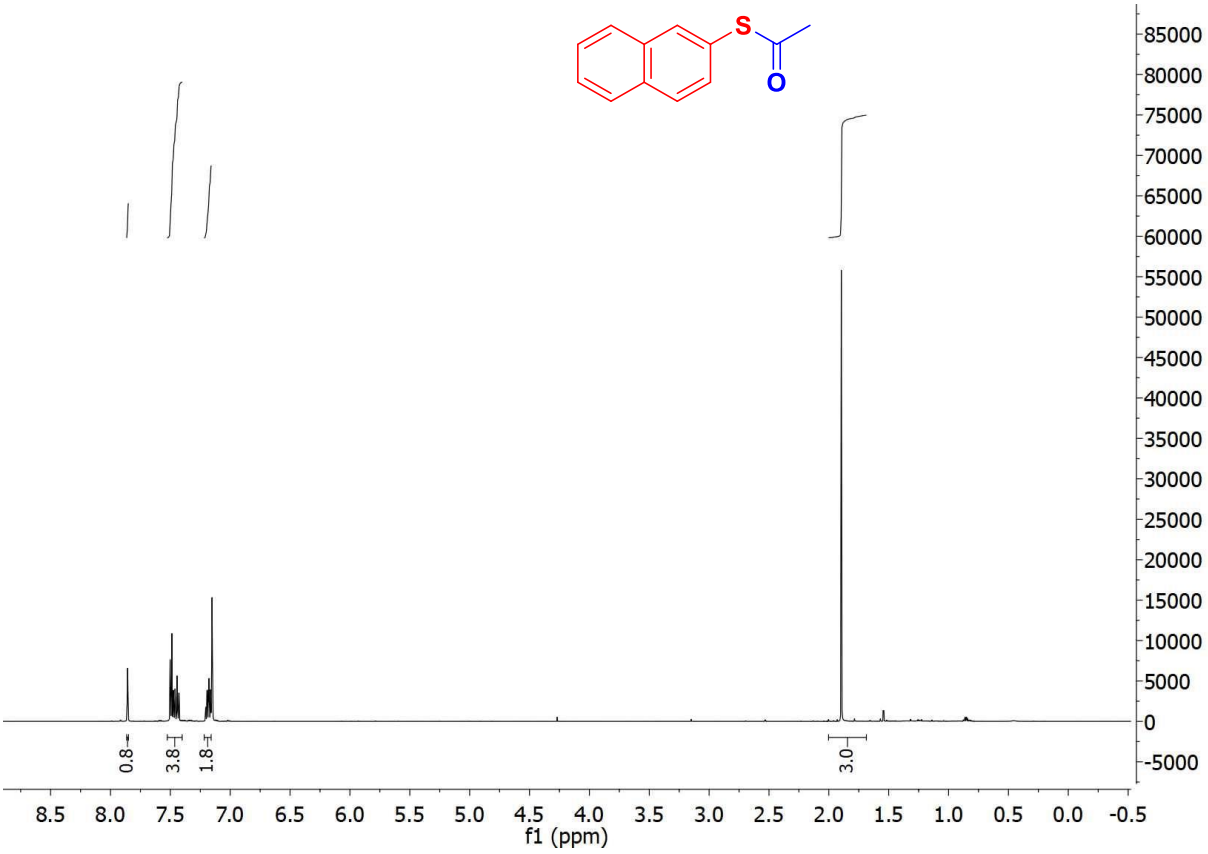


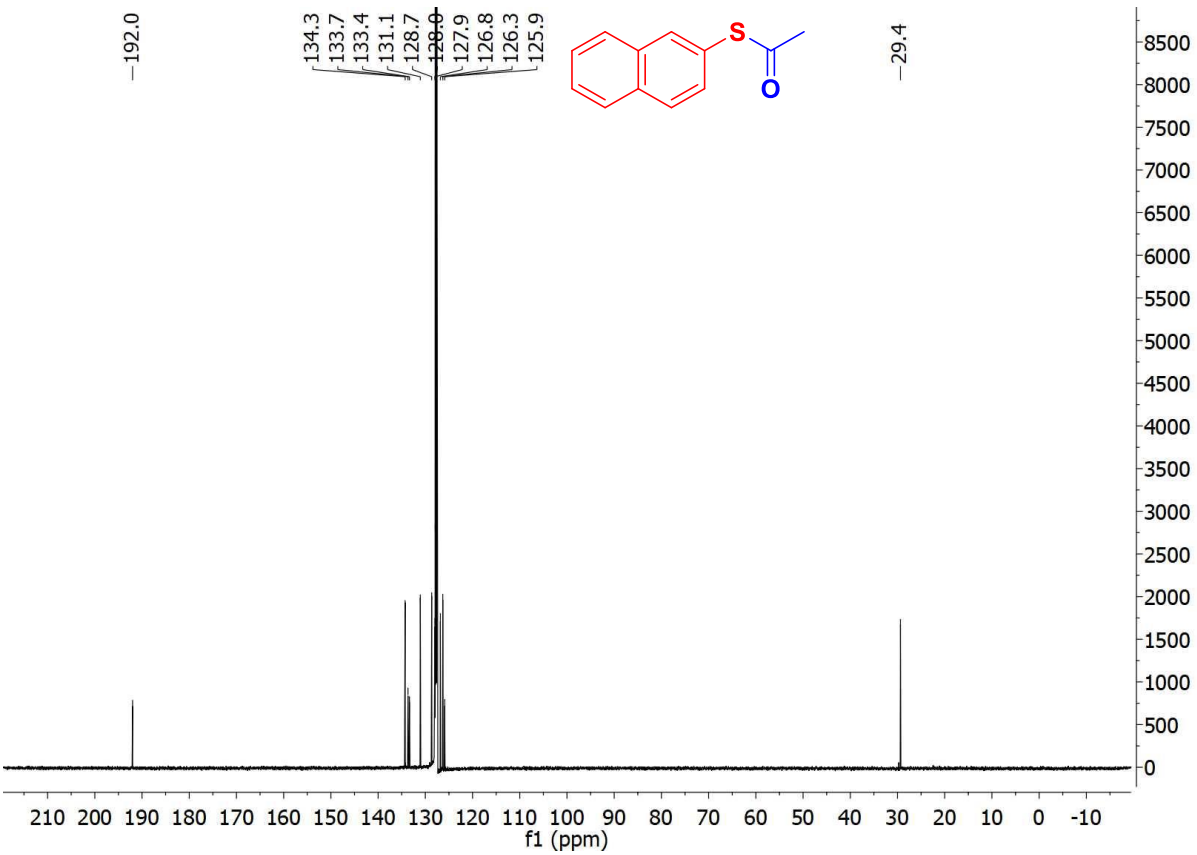
S-(2-methoxyphenyl) thioacetate (Table 2, entry 10)



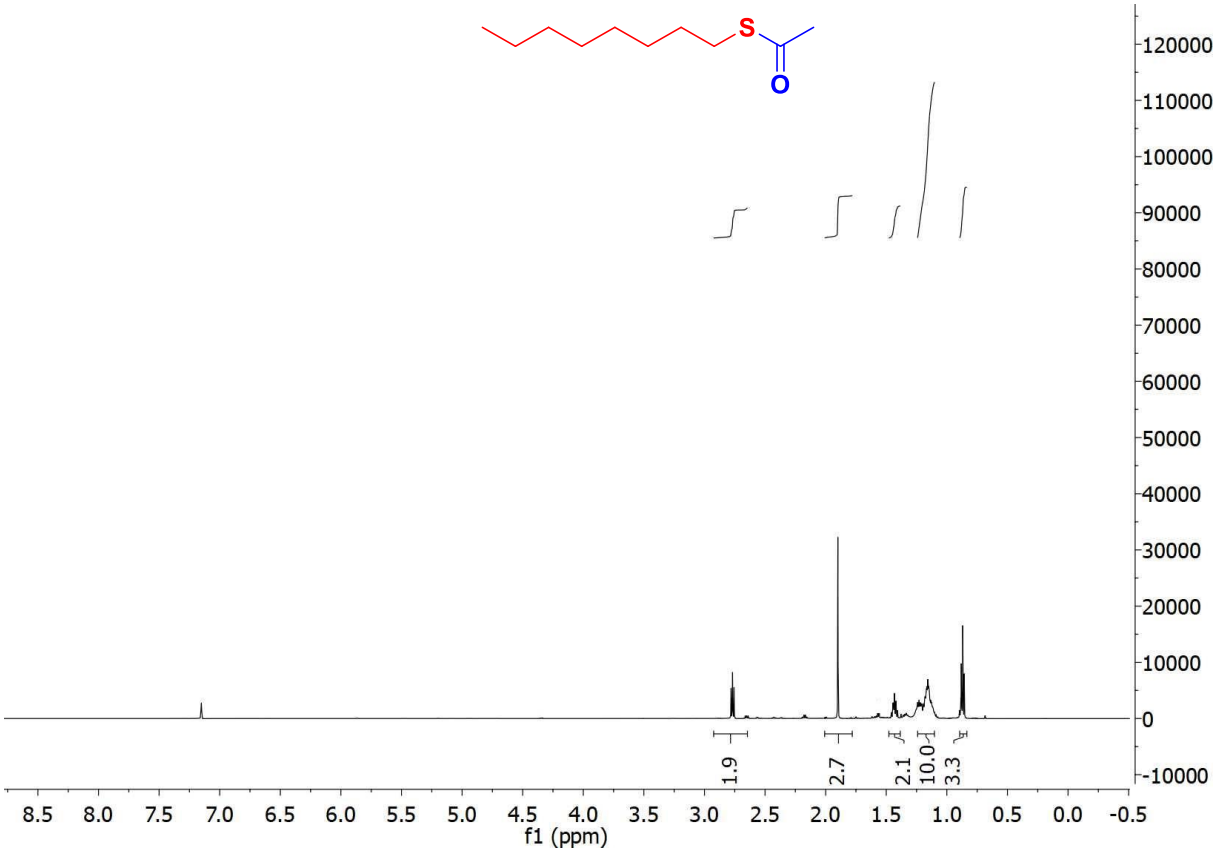


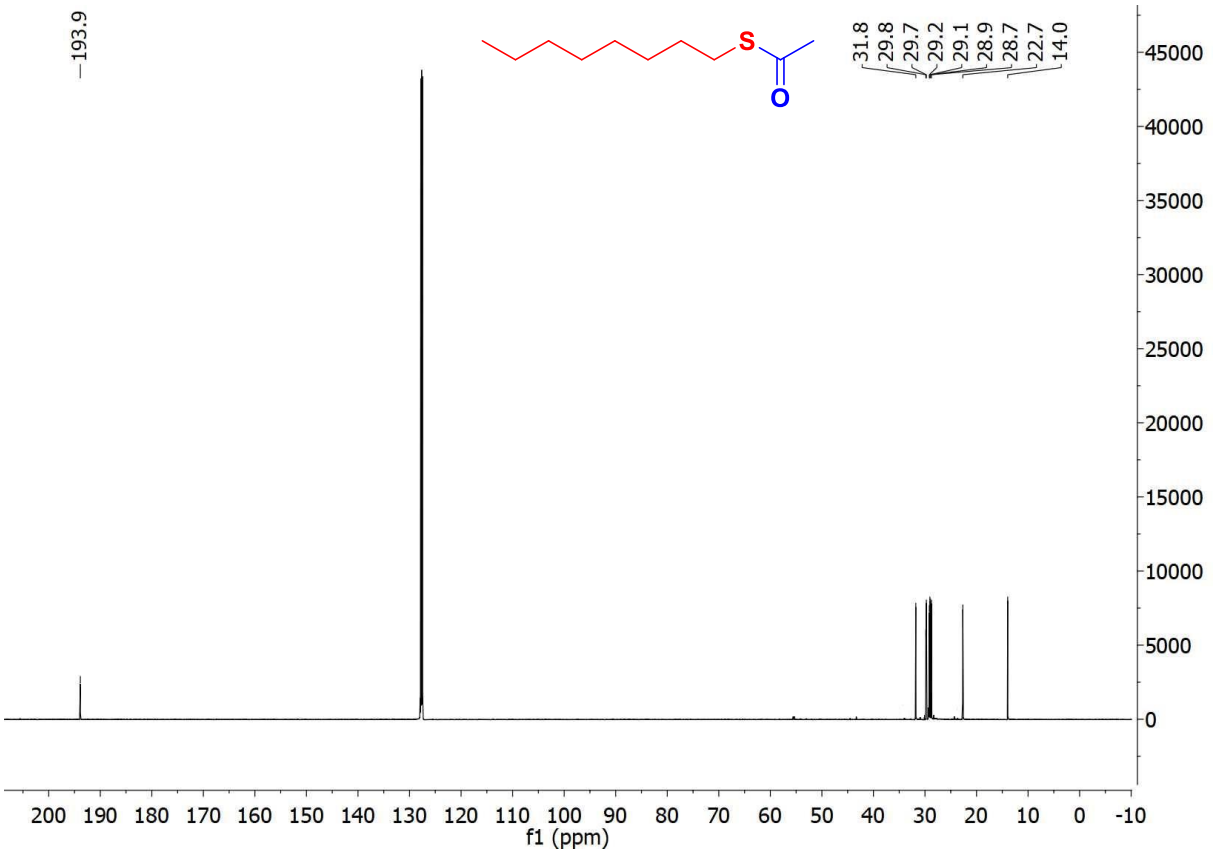
S-(naphthalene-2-yl) thioacetate (Table 2, entry 11)



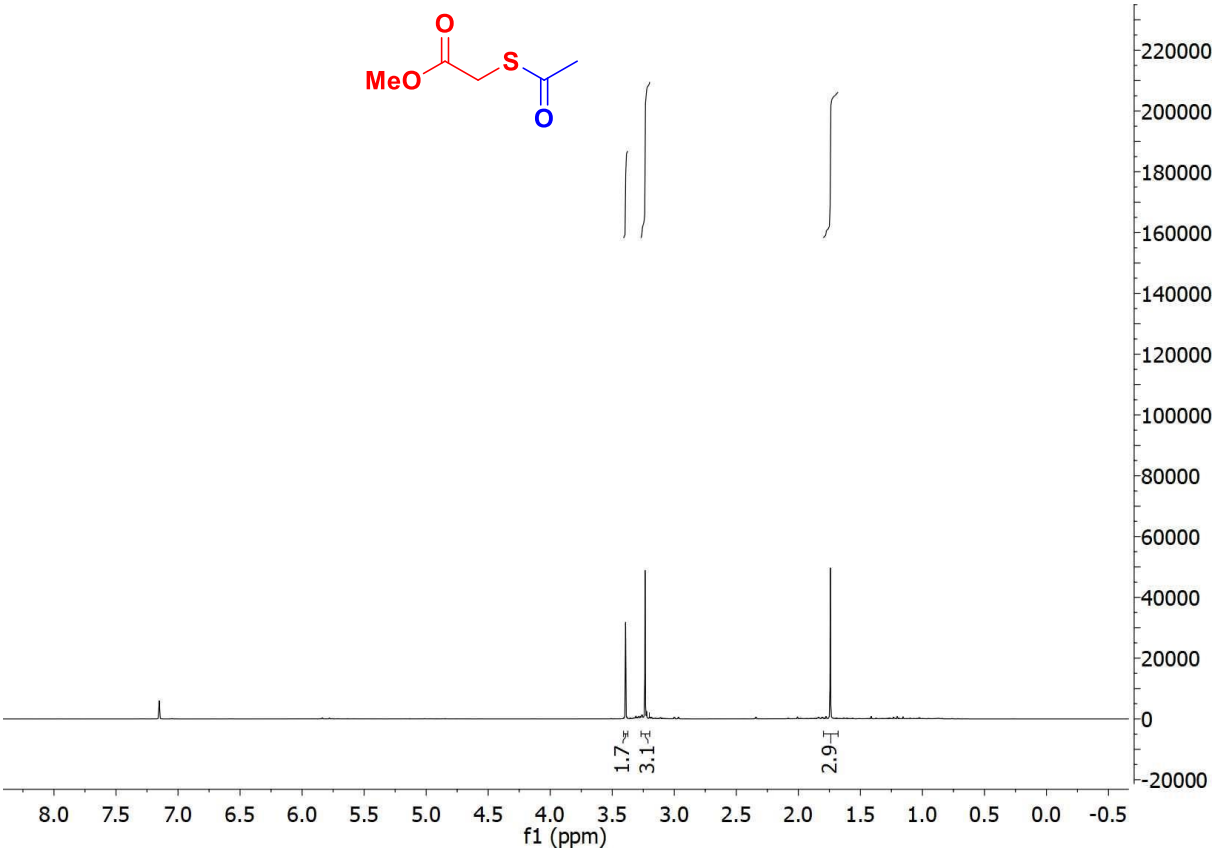


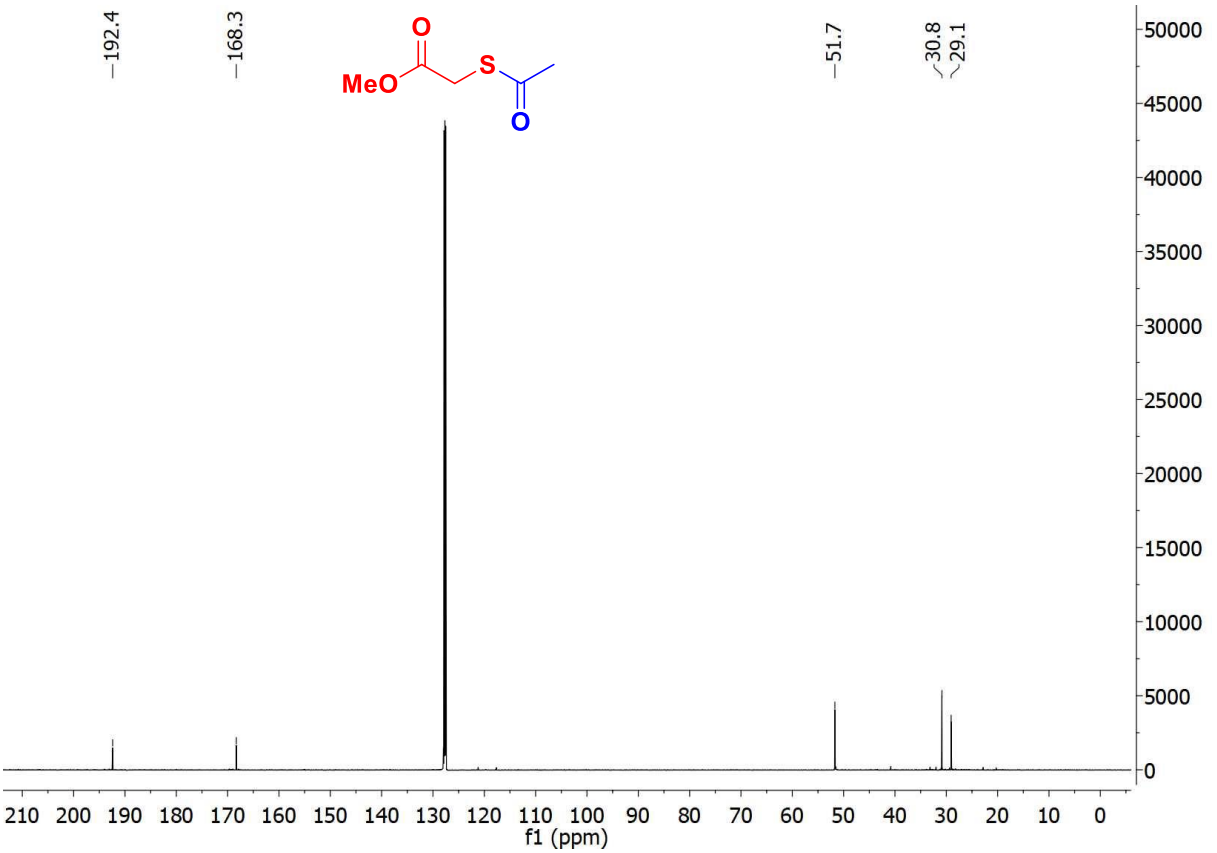
S-octyl thioacetate (Table 2, entry 12)



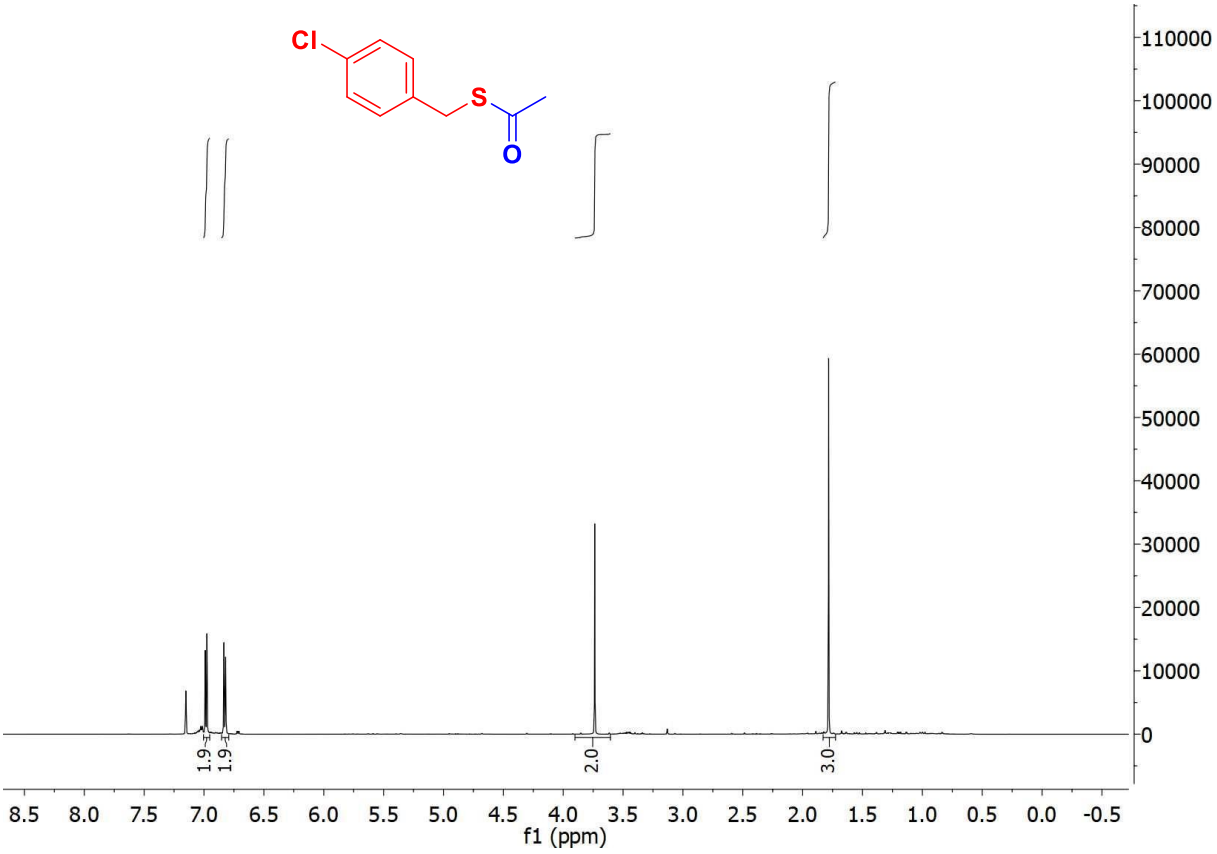


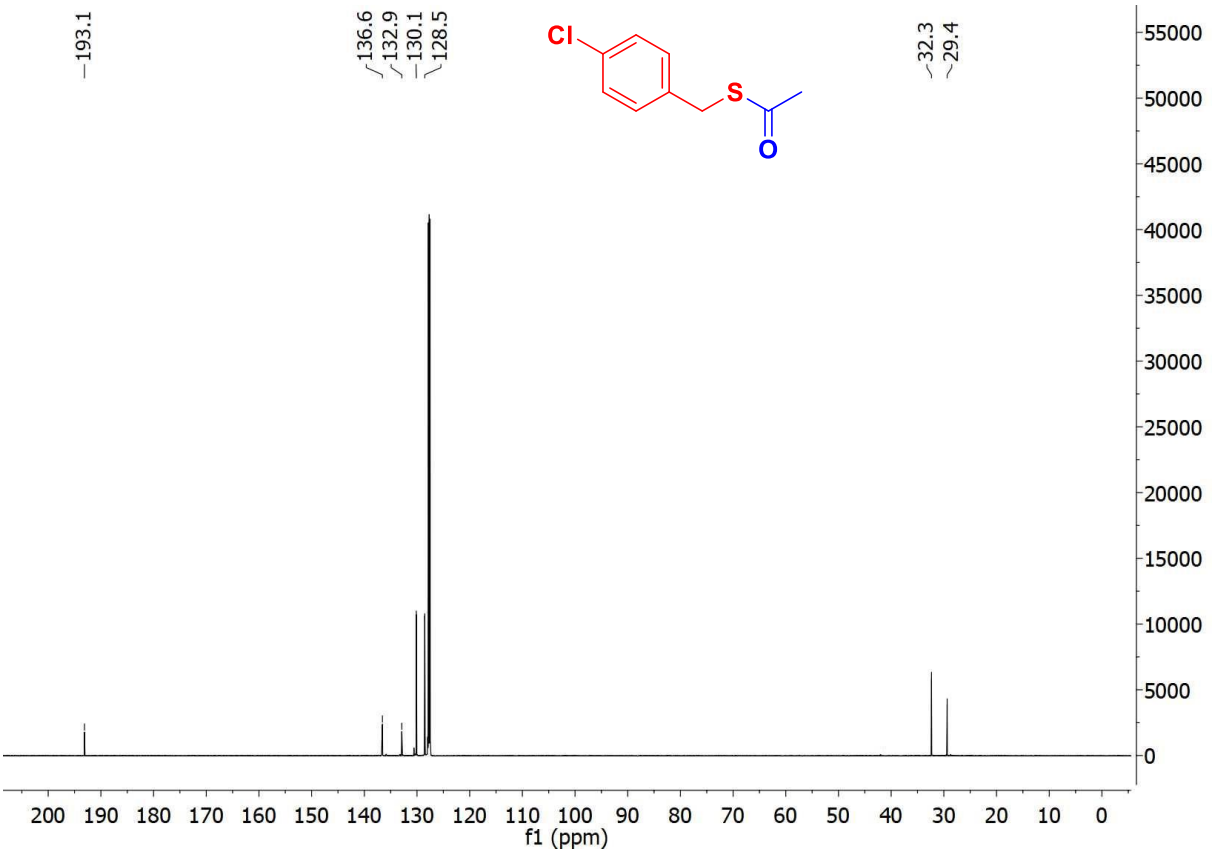
Methyl 2-(acetylthio)acetate (Table 2, entry 13)



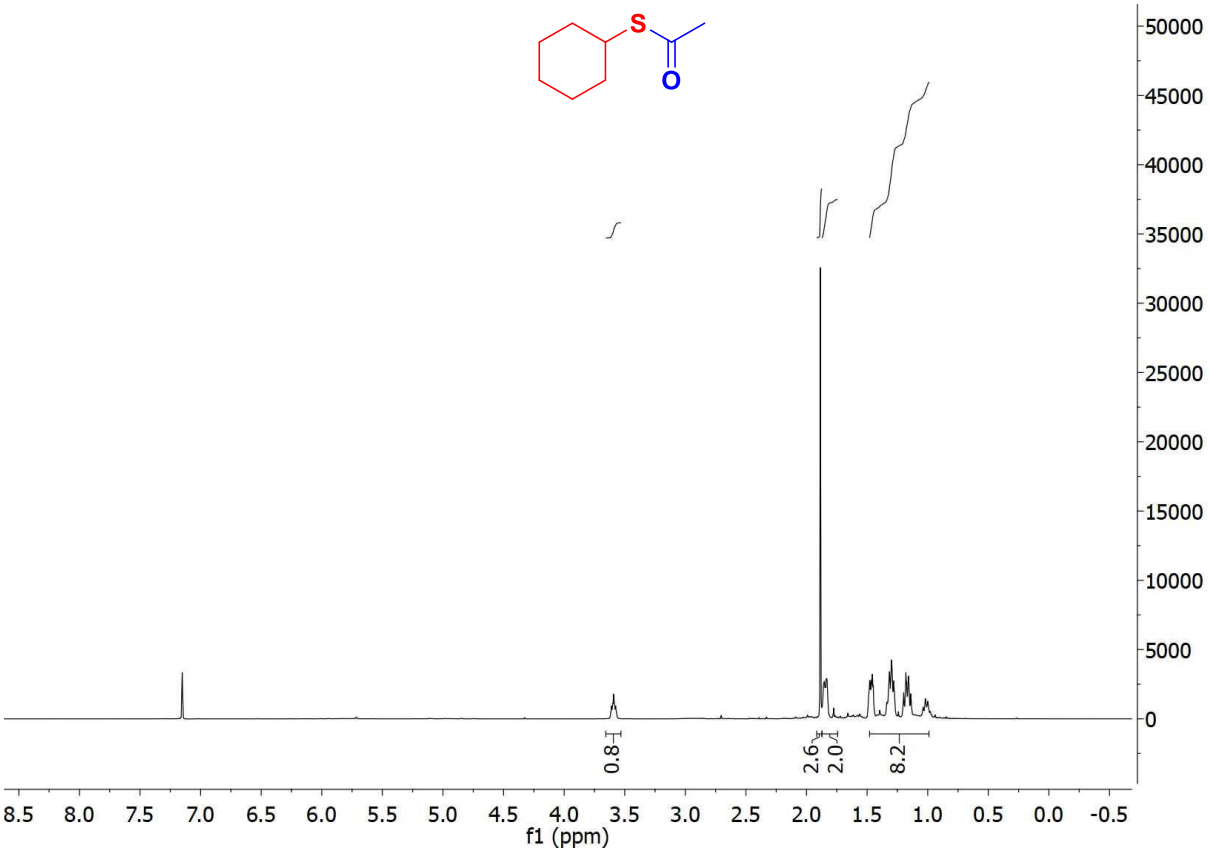


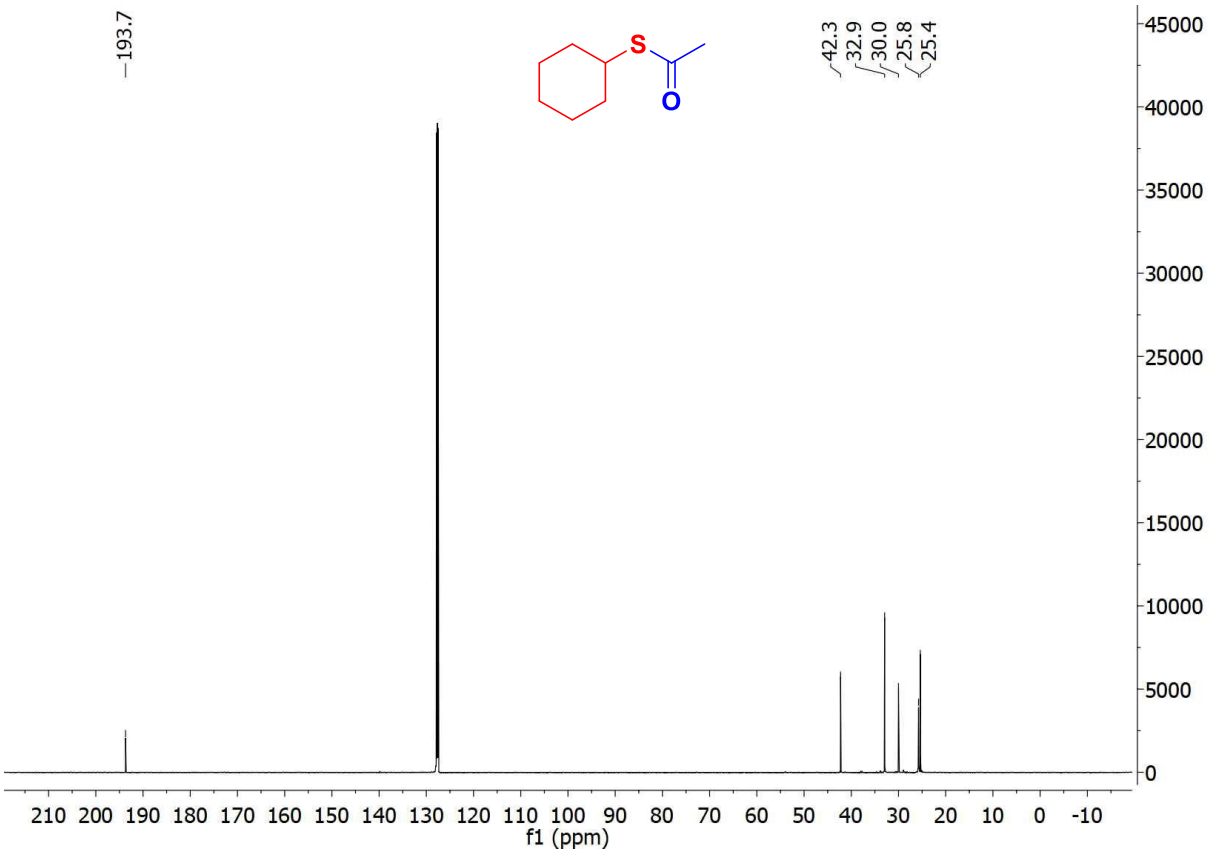
S-(4-chlorobenzyl) thioacetate (Table 2, entry 14)



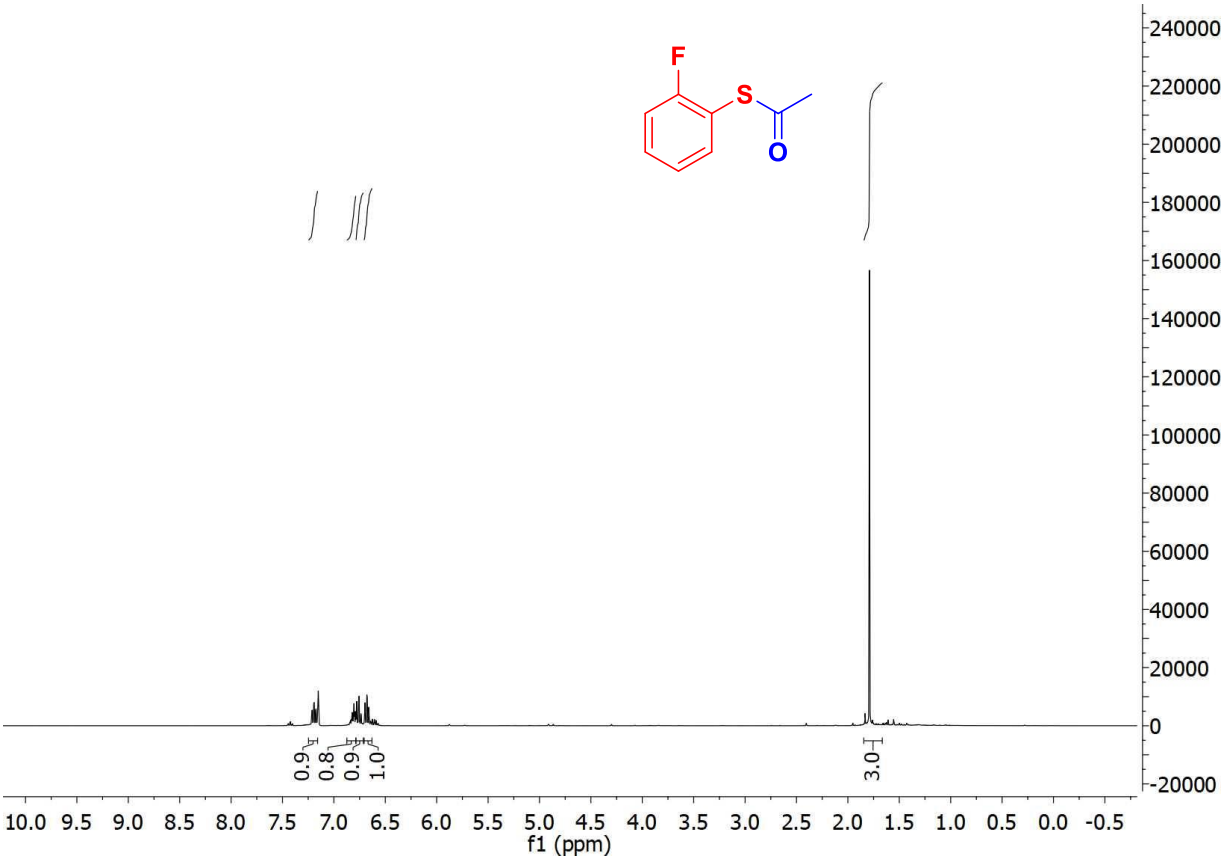


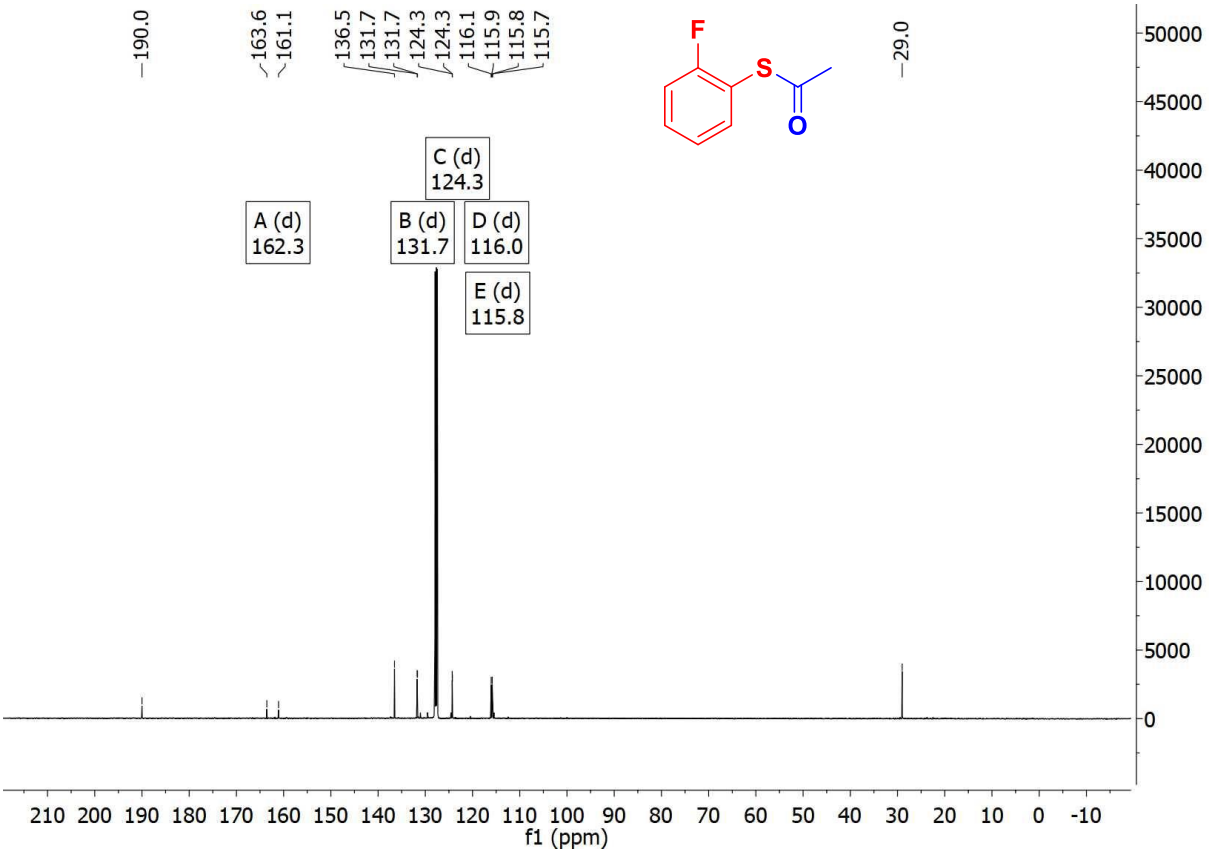
S-cyclohexyl thioacetate (Table 2, entry 15)



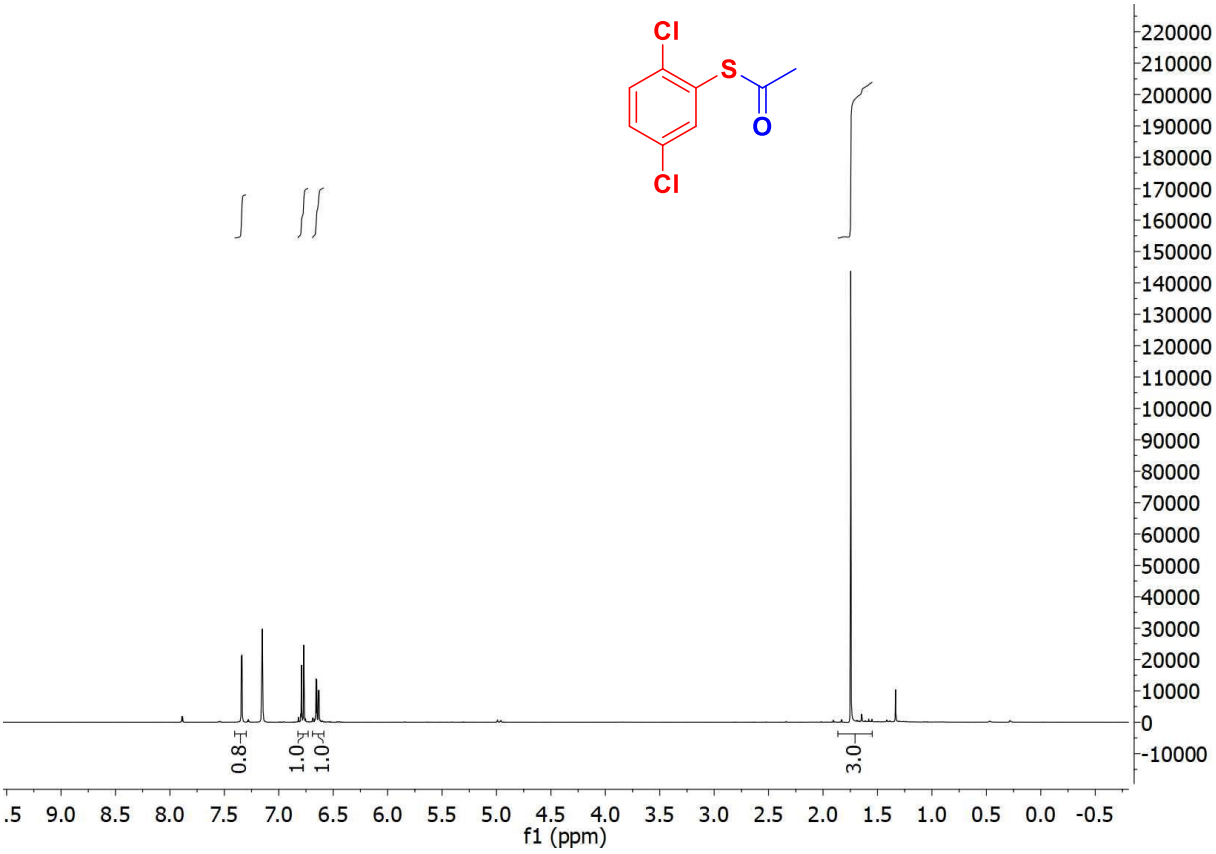


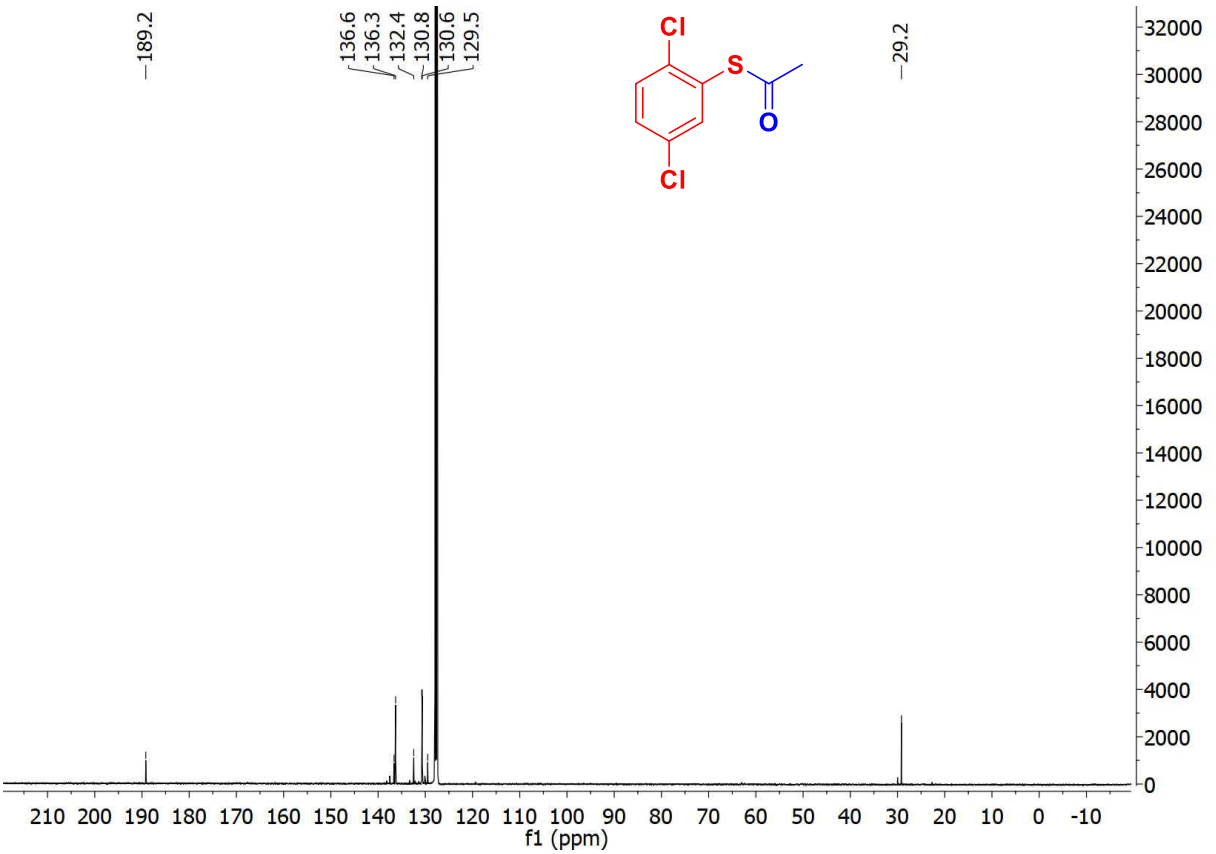
S-(2-fluorophenyl) thioacetate (Table 2, entry 16)





S-(2,5-dichlorophenyl) thioacetate (Table 2, entry 17)





Pictures of the column filled with Celite/Nafion® powder