Supporting Information

Direct α-Acyloxylation of Organic Sulfides with the Hypervalent (Diacyloxyiodo)benzene/Tetra-*n*-Butylammonium Bromide (TBAB) Reagent Combination

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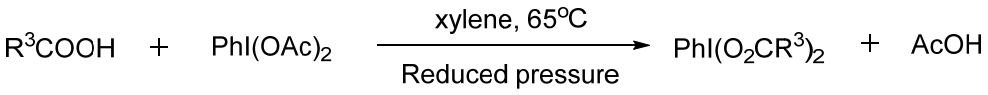
1. General information

Unless otherwise noted, all reagents were purchased from commercial sources and used without further purification. The reaction solvent, DCM was dried by refluxing over CaH_2, and freshly distilled prior to use. All reactions were monitored by TLC and visualized by UV lamp (254 nm)/or by staining with a solution of 10 g phosphomolybdic acid and 100 mL EtOH followed by heating. Flash column chromatography was performed using 230-400 mesh silica gel. ^{1}H NMR (400 MHz) and ^{13}C NMR (150 MHz) spectra were obtained on Bruker AV-400 instrument. Chemical shifts for ^{1}H NMR spectra were reported in δ ppm referenced to an internal $SiMe_4$ standard. The abbreviations s, brs, d, t, q and m stand for the resonance multiplicity singlet, broad singlet, doublet, triplet, quartet and multiplet, respectively. HR-ESI-MS spectra were recorded on a Bruker Esquire LC mass spectrometer using electrospray ionization. GC-MS (EI) spectra were recorded on an Agilent Technologies 7890A GC-MS system.

2. Preparation of Substrates

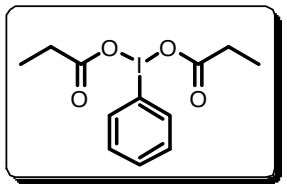
2.1 General procedure for the preparation of Hypervalent Iodine(III) Reagents[1]



To a round-bottom flask, $PhI(OAc)_2$ (3.22g, 10 mmol, 1.0 eq.) and R^3COOH (22 mmol, 2.2 eq.) were dissolved in m-xylene (50 mL) and the flask was heated in 65 ºC under reduced pressure (about 30-50 Torr.) using a diaphragm pump. When the xylene was removed, petroleum ether (PE) was used to wash the solid for 3 times and the white solid was filtered and dried in vacuum. Product $PhI(O_2CR^3)_2$ was obtained and could be used directly in the following reaction.

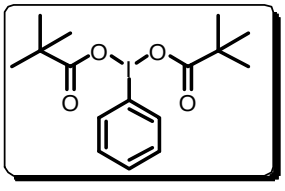
2.1.1 Characterization of Hypervalent Iodine(III) Reagents

Iodobenzene dipropionate(3a)



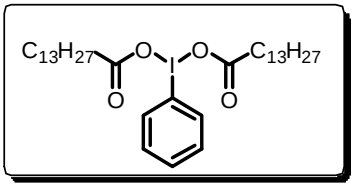
Following the general procedure. White solid, 63% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.07 (d, J = 7.8 Hz, 2H; H_{Ar}), 7.57 (t, J = 7.2 Hz, 1H; H_{Ar}), 7.48 (t, J = 7.2 Hz, 2H; H_{Ar}), 2.26 (q, J = 7.2 Hz, 4H; CH_2), 1.06 (t, J = 7.8 Hz, 6H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ179.6 (CO), 134.9 (C_{Ar}), 131.7 (C_{Ar}), 131.0 (C_{Ar}), 121.8 (C_{Ar}), 27.6 (CH_2), 10.0 (CH_3).

Iodobenzene Dipivalate(3b)



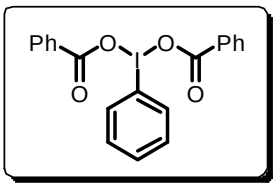
Following the general procedure. White solid, 65% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00 (d, J = 8.4 Hz, 2H; H_{Ar}), 7.54 (t, J = 7.2 Hz, 1H; H_{Ar}), 7.46 (t, J = 7.8 Hz, 2H; H_{Ar}), 1.10 (s, 18H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ183.7 (CO), 134.3 (C_{Ar}), 131.4 (C_{Ar}), 130.7 (C_{Ar}), 122.1 (C_{Ar}), 39.1 (C), 27.8 (CH_3).

Iodobenzene ditetradecanoate(3c)



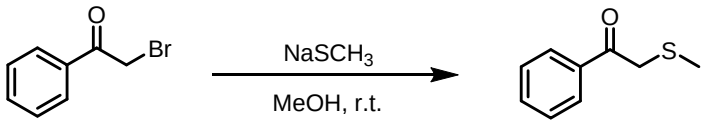
Following the general procedure. White solid, 65% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.07 (d, J = 8.4 Hz, 2H; H_{Ar}), 7.57 (t, J = 7.2 Hz, 1H; H_{Ar}), 7.48 (t, J = 7.8 Hz, 2H; H_{Ar}), 2.24 (t, J = 7.5 Hz, 4H; CH_2), 1.55–1.51 (m, 4H; CH_2), 1.25–1.22 (m, 40H; CH_2), 0.88 (t, J = 7.2 Hz, 6H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 179.1 (CO), 135.0 (C_{Ar}), 131.7 (C_{Ar}), 131.0 (C_{Ar}), 121.9 (C_{Ar}), 130.2 (C_{Ar}), 34.2 (CH_2), 32.1 (CH_2), 29.8 (CH_2), 29.78 (2CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.36 (CH_2), 25.8 (CH_2), 22.8 (CH_2), 14.3 (CH_3).

Iodobenzene Dibenzoate(3d)



Following the general procedure. White solid, 77% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.24 (d, J = 7.8 Hz, 2H; H_{Ar}), 7.94 (d, J = 8.4 Hz, 4H; H_{Ar}), 7.62 (t, J = 7.2 Hz, 1H; H_{Ar}), 7.55 (t, J = 7.8 Hz, 2H; H_{Ar}), 7.50 (t, J = 7.2 Hz, 2H; H_{Ar}), 7.37 (t, J = 7.8 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.4 (CO), 135.0 (C_{Ar}), 132.6 (C_{Ar}), 131.8 (C_{Ar}), 131.1 (C_{Ar}), 130.2 (C_{Ar}), 130.2 (C_{Ar}), 128.3 (C_{Ar}), 122.4 (C_{Ar}).

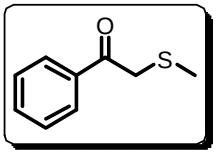
2.2 General procedure for preparation of organic thioether[2]



2-bromo-1-arylethanone (10 mmol) was added in portions to a solution of $NaSCH_3$ (12 mmol, 1.2 eq.) in methanol (50 mL). Within a few minutes the solution turned orange. After the addition was completed, the mixture was stirred at room temperature for 15 min and water was then added to the mixture. The product was extracted with dichloromethane, the organic layer was dried over Na_2SO_4, filtered and evaporated in vacuo. The residue was purified by flash chromatography (petroleum ether : CH_2Cl_2 = 5:1) to afford the desired product.

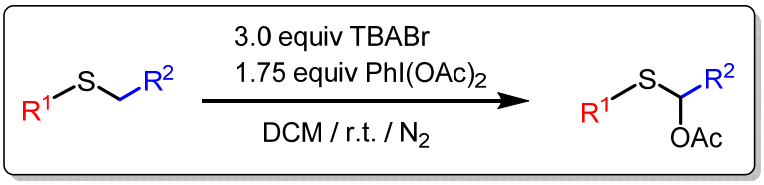
2.2.1 Characterization of organic thioether

2-(methylthio)-1-phenylethan-1-one(1t)



Colorless oil, 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.0 Hz, 2H; H_{Ar}), 7.57 (t, J = 8.0 Hz, 1H; H_{Ar}), 7.46 (t, J = 8.0 Hz, 2H; H_{Ar}), 3.76 (s, 2H; CH_2), 2.13 (s, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 194.1 (CO), 135.3 (C_{Ar}), 133.4 (C_{Ar}), 128.8 (C_{Ar}), 128.2 (C_{Ar}), 39.1 (CH_2), 16.0 (CH_3);

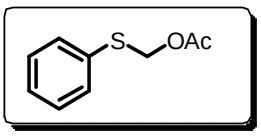
3. General procedure for α-oxyalkylation of thioether



A solution of thioether 1a (0.5 mmol), tetrabutylammonium bromideand (TBABr, 1.5mmol, 3.0 equiv) and $PhI(OAc)_2$ (1.75 equiv) in dichloromethane (2 mL) was stirred in sealed tube at room temperature for 6 h under nitrogen atmosphere. The reaction was then concentrated in vacuum and purified by column chromatography using petroleum ether/ethyl acetate to afford corresponding products.

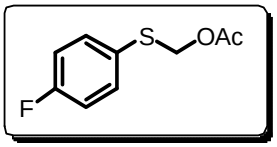
3.1 Characterization of α-Acetoxysulfide

(phenylthio)methyl acetate(2a)



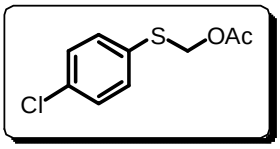
Light yellow oil, 60 mg (66% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 8.0 Hz, 2H; H_{Ar}), 7.24-7.18 (m, 3H; H_{Ar}), 5.33 (s, 2H; CH_2), 2.02 (s, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.4 (CO), 134.8 (C_{Ar}), 130.4 (C_{Ar}), 129.2 (C_{Ar}), 127.5 (C_{Ar}), 68.1 (CH_2), 21.2 (CH_3); GC-MS (EI): *m/z* (%): 182, 152, 123, 110, 77, 65, 43 (100), 28.

((4-fluorophenyl)thio)methyl acetate(2b)



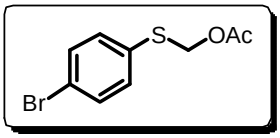
Colorless oil, 80 mg (80% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 8.0 Hz, 2H; H_{Ar}), 7.02 (t, J = 8.0 Hz, 2H; H_{Ar}), 5.33 (s, 2H; CH_2), 2.09 (s, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.3 (CO), 162.7 (d, J = 246.3 Hz; C_{Ar}), 133.6 (d, J = 8.2 Hz; C_{Ar}), 129.6 (d, J = 3.4 Hz; C_{Ar}), 116.3 (d, J = 21.9 Hz; C_{Ar}), 68.9 (CH_2), 21.1 (CH_3); GC-MS (EI): *m/z* (%): 200, 170, 141, 128, 83.1, 43 (100); HRMS (ES+) exact mass calculated for $[M+Na]^+$ ($C_9H_9FO_2S$) requires ***m/z*** 223.0205, found ***m/z*** 223.0204.

((4-chlorophenyl)thio)methyl acetate(2c)



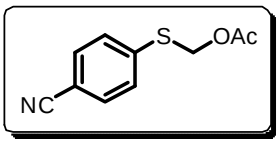
Light yellow oil, 79 mg (73% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 7.28 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 5.37 (s, 2H; CH_2), 2.09 (s, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.3 (CO), 133.7 (C_{Ar}), 133.3 (C_{Ar}), 131.8 (C_{Ar}), 129.3 (C_{Ar}), 68.0 (CH_2), 21.1 (CH_3); GC-MS (EI): *m/z* (%): 216, 186, 157, 144, 108, 73, 43 (100), 28.

((4-bromophenyl)thio)methyl acetate(2d)



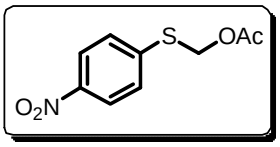
Light yellow oil, 74 mg (55% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 7.30 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 5.37 (s, 2H; CH_2), 2.09 (s, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.2 (CO), 134.0 (C_{Ar}), 132.2 (C_{Ar}), 131.9 (C_{Ar}), 121.6 (C_{Ar}), 67.8 (CH_2), 21.1 (CH_3); GC-MS (EI): *m/z* (%): 260, 230, 188, 122, 108, 43 (100), 28.

((4-cyanophenyl)thio)methyl acetate(2e)



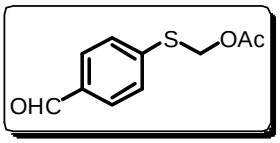
White solid, 33 mg (32% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 7.47 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 5.48 (s, 2H; CH_2), 2.10 (s, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.1 (CO), 142.4 (C_{Ar}), 132.6 (C_{Ar}), 128.3 (C_{Ar}), 118.6 (C_{Ar}), 110.0 (CN), 65.7 (CH_2), 21.0 (CH_3); GC-MS (EI): *m/z* (%): 207, 177, 148, 134, 90, 73, 43 (100), 28.

((4-nitrophenyl)thio)methyl acetate(2f)



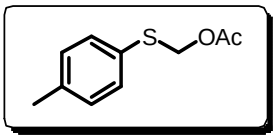
Yellow solid, 39 mg (34% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 7.51 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 5.52 (s, 2H; CH_2), 2.12 (s, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.1 (CO), 146.2 (C_{Ar}), 144.9 (C_{Ar}), 127.8 (C_{Ar}), 124.2 (C_{Ar}), 65.5 (CH_2), 21.0 (CH_3); GC-MS (EI): *m/z* (%): 227, 297, 168, 121, 108, 96, 58, 43 (100), 28.

((4-formylphenyl)thio)methyl acetate(2g)



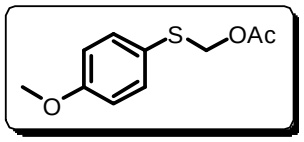
Colorless oil, 35 mg (33% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.95 (s, 1H; CHO), 7.80 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 7.52 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 5.51 (s, 2H; CH_2), 2.11 (s, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 191.3 (CHO), 170.2 (CO), 143.9 (C_{Ar}), 134.5 (C_{Ar}), 130.3 (C_{Ar}), 127.9 (C_{Ar}), 65.8 (CH_2), 21.1 (CH_3); GC-MS (EI): *m/z* (%): 210, 180, 138, 109, 73, 65, 51, 43 (100), 28.

(p-tolylthio)methyl acetate(2h)



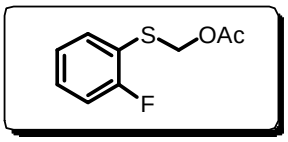
Light yellow oil, 74 mg (55% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 7.11 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 5.36 (s, 2H; CH_2), 2.34 (s, 3H; CH_3), 2.09 (s, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.4 (CO), 137.7 (C_{Ar}), 131.2 (C_{Ar}), 131.0 (C_{Ar}), 130.0 (C_{Ar}), 68.8 (CH_2), 21.2 ($2CH_3$); GC-MS (EI): *m/z* (%): 196, 166, 137, 124 (100), 91, 77, 65, 43.

((4-methoxyphenyl)thio)methyl acetate(2i)



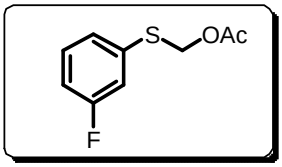
Colorless oil, 49 mg (46% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 6.86 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 5.28 (s, 2H; CH_2), 3.79 (s, 3H; OCH_3), 2.08 (s, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.4 (CO), 159.9 (C_{Ar}), 134.1 (C_{Ar}), 124.8 (C_{Ar}), 114.8 (C_{Ar}), 69.7 (CH_2), 55.4 (OCH_3), 21.1 (CH_3); GC-MS (EI): *m/z* (%): 212, 182, 140 (100), 125, 77, 43, 28; HRMS (ES+) exact mass calculated for $[M+Na]^+$ ($C_{10}H_{12}O_3S$) requires ***m/z*** 235.0405, found ***m/z*** 235.0397.

((2-fluorophenyl)thio)methyl acetate(2j)



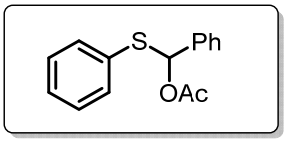
Light yellow oil, 78 mg (78% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (t, *J* = 8.0 Hz, 1H; H_{Ar}), 7.45-7.42 (m, 1H; H_{Ar}), 7.29-7.22 (m, 2H; H_{Ar}), 5.52 (s, 2H; CH_2), 2.23 (s, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.3 (CO), 161.6 (d, *J* = 244.9 Hz; C_{Ar}), 133.6 (C_{Ar}), 130.0 (d, *J* = 8.0 Hz; C_{Ar}), 124.8 (d, *J* = 3.7 Hz; C_{Ar}), 121.2 (d, *J* = 17.7 Hz; C_{Ar}), 116.0 (d, *J* = 22.5 Hz; C_{Ar}), 67.1 (d, *J* = 2.3 Hz; CH_2), 21.0 (CH_3); GC-MS (EI): *m/z* (%): 200, 170, 128, 83, 57, 43 (100), 28; HRMS (ES+) exact mass calculated for $[M+Na]^+$ ($C_9H_9FO_2S$) requires ***m/z*** 223.0205, found ***m/z*** 223.0198.

((3-fluorophenyl)thio)methyl acetate(2k)



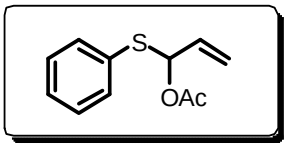
Light yellow oil, 64 mg (64% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.30 (m, 1H; H_{Ar}), 7.24-7.20 (m, 2H; H_{Ar}), 7.00 (t, *J* = 8.0 Hz, 1H; H_{Ar}), 5.47 (s, 2H; CH_2), 2.16 (s, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.3 (CO), 162.8 (d, *J* = 250.2 Hz; C_{Ar}), 137.2 (d, *J* = 7.8 Hz; C_{Ar}), 130.5 (d, *J* = 8.4 Hz; C_{Ar}), 125.3 (d, *J* = 3.0 Hz; C_{Ar}), 116.6 (d, *J* = 33.0 Hz; C_{Ar}), 114.2 (d, *J* = 21.0 Hz; C_{Ar}), 67.4 (CH_2), 21.1 (CH_3); GC-MS (EI): *m/z* (%): 200, 170, 128, 83, 57, 43 (100), 28; HRMS (ES+) exact mass calculated for $[M+Na]^+$ ($C_9H_9FO_2S$) requires ***m/z*** 223.0205, found ***m/z*** 223.0199.

phenyl(phenylthio)methyl acetate(2l)



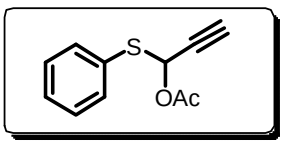
Light yellow oil, 55 mg (43% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.29 (m, 10H; H_{Ar}), 7.15 (s, 1H; CH), 2.08 (s, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.6 (CO), 137.3 (C_{Ar}), 134.1 (C_{Ar}), 132.0 (C_{Ar}), 129.0 (C_{Ar}), 128.8 (C_{Ar}), 128.7 (C_{Ar}), 128.6 (C_{Ar}), 126.6 (C_{Ar}), 81.3 (CH), 21.2 (CH_3); GC-MS (EI): *m/z* (%): 258, 199, 165, 149, 110 (100), 77, 43, 28; HRMS (ES+) exact mass calculated for $[M+Na]^+$ ($C_{15}H_{14}O_2S$) requires ***m/z*** 281.0612, found ***m/z*** 281.0606.

1-(phenylthio)allyl acetate(2m)



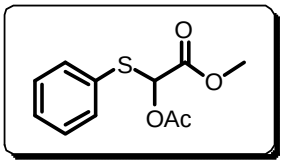
Light yellow oil, 34 mg (33% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31 (d, *J* = 7.8 Hz, 2H; H_{Ar}), 7.26 (t, *J* = 7.8 Hz, 2H; H_{Ar}), 7.19 (t, *J* = 7.6 Hz, 1H; H_{Ar}), 6.45 (d, *J* = 15.0 Hz, 1H; CH), 5.78-5.74 (m, 1H; =CH), 4.52 (d, *J* = 6.6 Hz, 2H; $=CH_2$), 1.99 (s, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.8 (CO), 134.1 (C_{Ar}), 130.7 (C_{Ar}), 129.8 (=C), 129.4 (C_{Ar}), 127.5 (C_{Ar}), 124.8 (=C), 64.5 (CH), 21.1 (CH_3); GC-MS (EI): *m/z* (%): 208, 165, 147, 110 (100), 77, 59, 43, 28.

1-(phenylthio)prop-2-yn-1-yl acetate(2n)



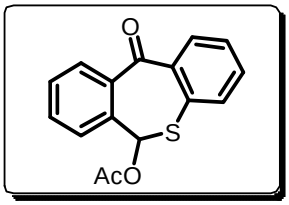
Light yellow oil, 99 mg (96 yield %); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57(d, *J* = 8.0 Hz, 2H; H_{Ar}), 7.37-7.36 (m, 3H; H_{Ar}), 6.59 (s, 1H; CH), 2.67 (s, 1H; ≡CH), 2.10 (s, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.0 (CO), 134.9 (C_{Ar}), 130.4 (C_{Ar}), 129.4 (C_{Ar}), 129.1 (C_{Ar}), 77.4 (≡C), 77.0 (≡C), 68.6 (CH), 21.0 (CH_3); GC-MS (EI): *m/z* (%): 206, 152, 110 (100), 65, 43, 28.

methyl 2-acetoxy-2-(phenylthio)acetate(2o)



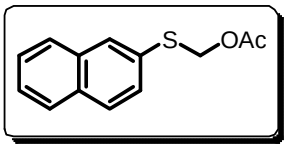
Light yellow oil, 42 mg (35% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 7.35-7.33 (m, 3H; H_{Ar}), 6.21 (s, 1H; CH), 3.67 (s, 3H; OCH_3), 2.17 (s, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.8 (CO), 166.5 (CO), 134.4 (C_{Ar}), 130.0 (C_{Ar}), 129.5 (C_{Ar}), 129.2 (C_{Ar}), 76.8 (CH), 52.9 (CH_3), 20.9 (CH_3); GC-MS (EI): *m/z* (%): 240, 181, 152, 139, 121, 110, 77, 65, 43 (100), 28.

11-oxo-6,11-dihydrodibenzo[b,e]thiepin-6-yl acetate(2p)



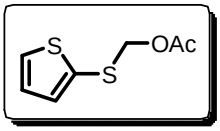
White solid, 103 mg (72% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.0 Hz, 1H; H_{Ar}), 7.59 (d, *J* = 8.0 Hz, 1H; H_{Ar}), 7.50-7.45 (m, 1H; H_{Ar}), 7.43-7.36 (m, 2H; H_{Ar}), 7.34-7.23 (m, 3H; H_{Ar}), 6.86 (s, 1H; CH), 1.97 (s, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.1 (CO), 168.8 (CO), 139.9 (C_{Ar}), 135.9 (C_{Ar}), 135.6 (C_{Ar}), 133.8 (C_{Ar}), 132.8 (C_{Ar}), 131.8 (C_{Ar}), 131.6 (C_{Ar}), 129.4 (C_{Ar}), 129.2 (C_{Ar}), 128.5 (C_{Ar}), 125.9 (C_{Ar}), 124.5 (C_{Ar}), 75.9 (CH), 21.0 (CH_3); GC-MS (EI): *m/z* (%): 284, 242, 213 (100), 197, 181, 152, 77, 43; HRMS (ES+) exact mass calculated for $[M+Na]^+$ ($C_{16}H_{12}O_3S$) requires ***m/z*** 307.0405, found ***m/z*** 307.0396.

(naphthalen-2-ylthio)methyl acetate(2q)



Light yellow solid, 78 mg (69% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (s, 1H; H_{Ar}), 7.83-7.79 (m, 3H; H_{Ar}), 7.55-7.47 (m, 3H; H_{Ar}), 5.52 (s, 2H; CH_2), 2.13 (s, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.4 (CO), 133.7 (C_{Ar}), 132.4 (C_{Ar}), 132.0 (C_{Ar}), 129.0 (C_{Ar}), 128.9 (C_{Ar}), 127.8 (C_{Ar}), 127.8 (C_{Ar}), 127.5 (C_{Ar}), 126.8 (C_{Ar}), 126.3 (C_{Ar}), 68.0 (CH_2), 21.2 ($2CH_3$); GC-MS (EI): *m/z* (%): 232, 173, 160 (100), 128, 115, 43, 28.

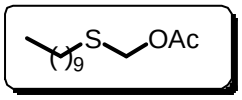
(thiophen-2-ylthio)methyl acetate(2r)



Light yellow oil, 50 mg (53% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-6.97 (m, 3H; 3CH), 5.17 (s, 2H; CH_2), 2.13 (s, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.2 (CO), 135.6 (CH), 132.9 (CH), 130.8 (CH), 116.0 (CH), 70.4 (CH_2), 21.2 (CH_3);GC-MS (EI): *m/z* (%): 188, 158, 116,

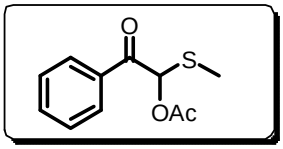
71, 57, 43 (100), 28.

(decylthio)methyl acetate(2s)



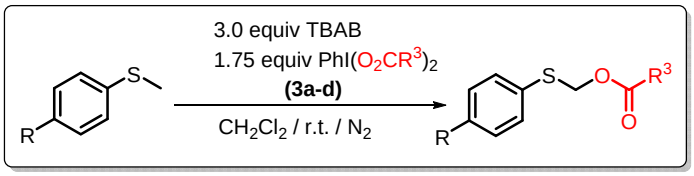
Light yellow oil, 39 mg (32% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.14 (s, 2H; CH_2), 2.66 (t, *J* = 7.6 Hz, 2H; CH_2), 2.08 (s, 3H; CH_3), 1.66-1.58 (m, 2H; CH_2), 1.26 (m, 14H; CH_2), 0.87 (t, *J* = 7.2 Hz, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.8 (CO), 66.8 (CH_2), 32.5 (CH_2), 32.0 (CH_2), 29.89 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.8 (CH_2), 22.8 (CH_2), 21.2 (CH_3), 14.2 (CH_3); GC-MS (EI): *m/z* (%): 246, 216, 185, 171, 157, 143, 129, 115, 101, 87, 73, 65, 43 (100), 29.

1-(methylthio)-2-oxo-2-phenylethyl acetate(2t)



Light yellow oil, 65 mg (58% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 7.57 (t, *J* = 8.0 Hz, 1H; H_{Ar}), 7.45 (t, *J* = 8.0 Hz, 2H; H_{Ar}), 6.83 (s, 1H; CH), 2.19 (s, 3H; CH_3), 2.08 (s, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 188.8 (CO), 170.2 (CO), 133.8 (C_{Ar}), 133.8 (C_{Ar}), 128.7 (C_{Ar}), 128.7 (C_{Ar}), 75.2 (CH), 20.8 (CH_3), 11.6 (CH_3); GC-MS (EI): *m/z* (%): 224, 196, 178, 137, 121, 105 (100), 77, 43; HRMS (ES+) exact mass calculated for $[M+Na]^+$ ($C_{11}H_{12}O_3S$) requires ***m/z*** 247.0405, found ***m/z*** 247.0399.

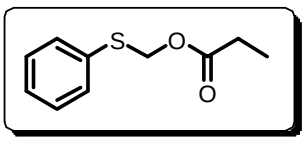
4. Scope of hypervalent iodine (III) reagents derivatives



A solution of thioanisole 1a (0.5 mmol), tetrabutylammonium bromideand (TBABr, 1.5mmol, 3.0 equiv) and $PhI(O_2CR^3)_2$ (1.75 equiv) in DCM (2 mL) was stirred in sealed tube at room temperature for 8 h under nitrogen atmosphere. The reaction was then concentrated in vacuum and purified by column chromatography using petroleum ether/ethyl acetate to afford corresponding products.

4.1 Characterization of the product

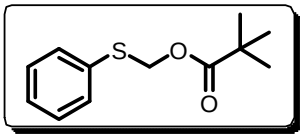
(phenylthio)methyl propionate(3aa)



Light yellow solid, 54 mg (55% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.0 Hz, 2H;

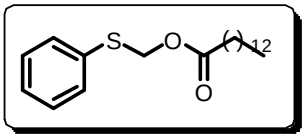
H_{Ar}), 7.25-7.18 (m, 3H; H_{Ar}), 5.35 (s, 2H; CH_2), 2.30 (q, *J* = 8.0 Hz, 2H; CH_2), 1.08 (t, *J* = 8.0 Hz, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 173.9 (CO), 134.9 (C_{Ar}), 130.5 (C_{Ar}), 129.2 (C_{Ar}), 127.5 (C_{Ar}), 68.0 (CH_2), 27.8 (CH_2), 9.0 (CH_3); GC-MS (EI): *m/z* (%): 196, 166, 123, 110, 77, 57 (100), 29; HRMS (ES+) exact mass calculated for $[M+Na]^+$ ($C_{10}H_{12}O_2S$) requires ***m/z*** 219.0456, found ***m/z*** 219.0446.

(phenylthio)methyl pivalate(3ab)



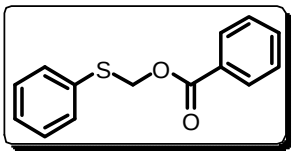
Light yellow solid, 90 mg (80% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 7.24-7.19 (m, 3H; H_{Ar}), 5.33 (s, 2H; CH_2), 1.13 (s, 9H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 177.8 (CO), 135.0 (C_{Ar}), 130.7 (C_{Ar}), 129.2 (C_{Ar}), 127.5 (C_{Ar}), 68.3 (CH_2), 38.9 (C), 27.1 (CH_3); GC-MS (EI): *m/z* (%): 224, 194, 123, 110, 85, 57 (100), 41, 28; HRMS (ES+) exact mass calculated for $[M+Na]^+$ ($C_{12}H_{16}O_2S$) requires ***m/z*** 247.0769, found ***m/z*** 247.0760.

(phenylthio)methyl tetradecanoate(3ac)



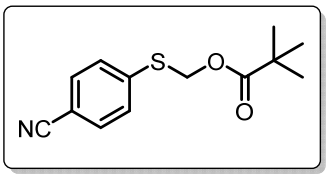
Light yellow solid, 103 mg (59% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 7.36-7.27 (m, 3H; H_{Ar}), 5.44 (s, 2H; CH_2), 2.36 (t, *J* = 8.0 Hz, 2H; CH_2), 1.66-1.60 (m, 2H; CH_2), 1.34-1.27 (m, 20H; CH_2), 0.90 (t, *J* = 8.0 Hz, 3H; CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 173.1 (CO), 134.9 (C_{Ar}), 130.3 (C_{Ar}), 129.1 (C_{Ar}), 127.3 (C_{Ar}), 67.8 (CH_2), 34.4 (CH_2), 32.0 (CH_2), 29.7 (CH_2), 29.72 ($2CH_2$), 29.66 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 24.9 (CH_2), 22.8 (CH_2), 14.2 (CH_3); GC-MS (EI): *m/z* (%): 350, 211 (100), 123, 95, 71, 43, 27.

(phenylthio)methyl benzoate(3ad)



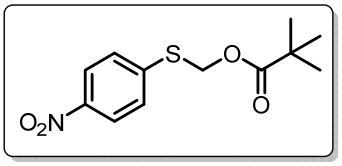
Light yellow oil, 89 mg (77% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 7.6 Hz, 2H; H_{Ar}), 7.61-7.54 (m, 3H; H_{Ar}), 7.46 (t, *J* = 8.0 Hz, 2H; H_{Ar}), 7.38-7.34 (m, 3H; H_{Ar}), 5.69 (s, 2H; CH_2); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.9 (CO), 134.8 (C_{Ar}), 133.4 (C_{Ar}), 130.7 (C_{Ar}), 129.8 (C_{Ar}), 129.7 (C_{Ar}), 129.2 (C_{Ar}), 128.5 (C_{Ar}), 127.5 (C_{Ar}), 68.9 (CH_2); GC-MS (EI): *m/z* (%): 244, 214, 123, 105 (100), 77, 51.

((4-cyanophenyl)thio)methyl pivalate (3eb)



Light yellow oil, 50 mg (40% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 7.47 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 5.47 (s, 2H; CH_2), 1.17 (s, 9H; $3CH_3$); ^{13}C NMR (150 MHz, $CDCl_3$): δ 177.4 (CO), 142.5 (C_{Ar}), 132.5 (C_{Ar}), 128.2 (C_{Ar}), 118.5 (C_{Ar}), 109.9 (CN), 65.7 (CH_2), 38.9 (C), 26.9 (CH_3); GC-MS (EI): *m/z* (%): 249, 219 204, 191, 176, 163, 148, 134, 85, 75, 57(100), 41, 29.

((4-nitrophenyl)thio)methyl pivalate(3fb)



Light yellow oil, 65 mg (51% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 7.51 (d, *J* = 8.0 Hz, 2H; H_{Ar}), 5.52 (s, 2H; CH_2), 1.19 (s, 9H; $3CH_3$); ^{13}C NMR (150 MHz, $CDCl_3$): δ 177.5 (CO), 146.2 (C_{Ar}), 145.2 (C_{Ar}), 127.8 (C_{Ar}), 124.2 (C_{Ar}), 65.5 (CH_2), 39.0 (C), 27.0 (CH_3); GC-MS (EI): *m/z* (%): 269, 253, 239,168, 121, 85, 77, 69, 57(100), 41, 29.

5. Mechanism detecting experiment

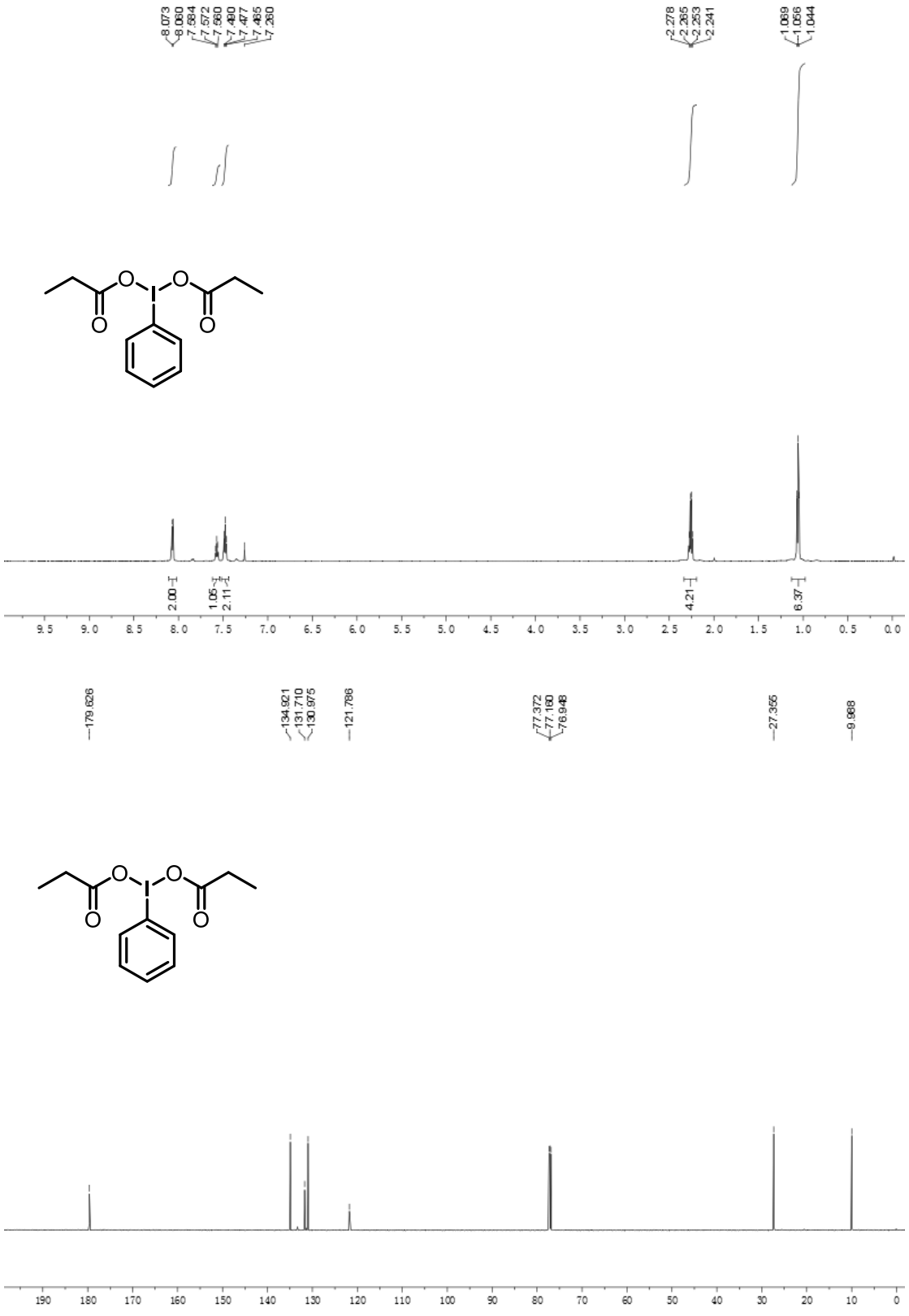
A solution of thioanisole 1a (0.1 mmol), tetrabutylammonium bromideand (TBABr, 0.3mmol, 3.0 equiv) and $PhI(OAc)_2$ (1.75 equiv) was added in $CDCl_3$ (0.4 mL). From the ^{13}C NMR, we can clearly observe the existing of the AcOH, which can strongly prove the rationality of the mechanism.

6. References

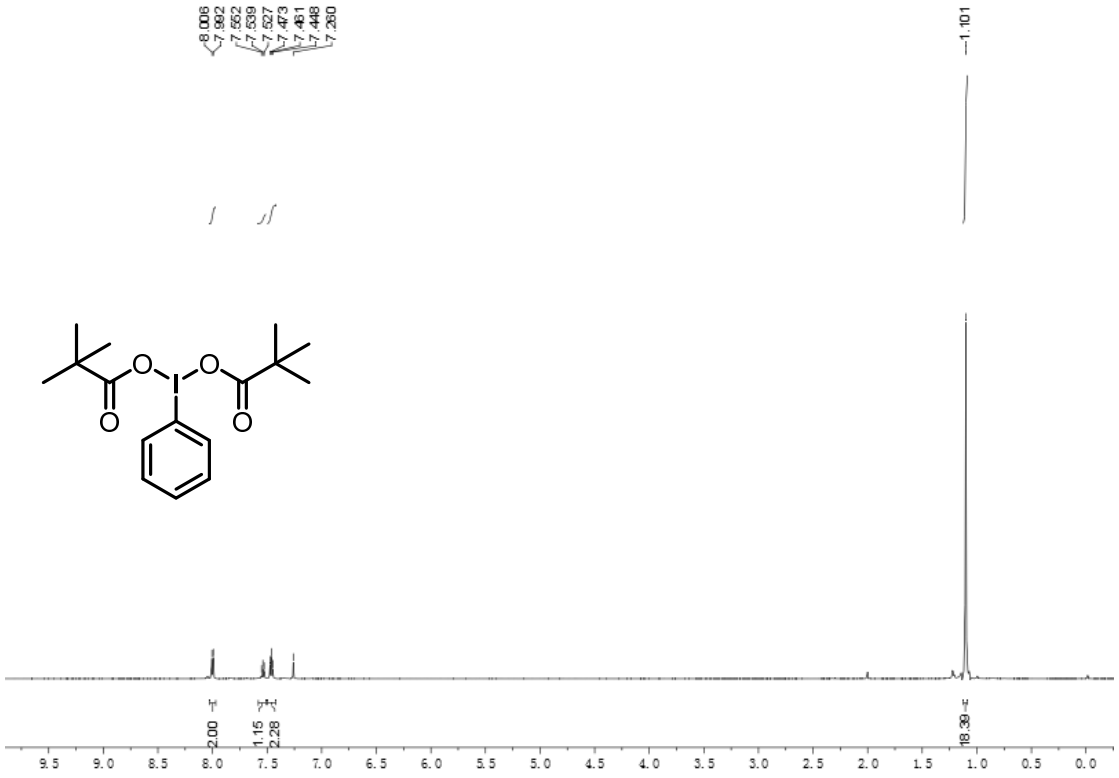
1. Wang, Y.; Zhang, L.; Yang, Y.; Zhang, P.; Du, Z.; Wang, C. *J. Am. Chem. Soc.* **2013**, *135*, 18048–18051.
2. Su, Q.; Zhao, Z.; Xu, F.; Lou, P.; Zhang, K.; Xie, D.; Shi, L.; Cai, Q.; Peng, Z.; An, D. Eur. J. Org. Chem. **2013**, 1551–1557.

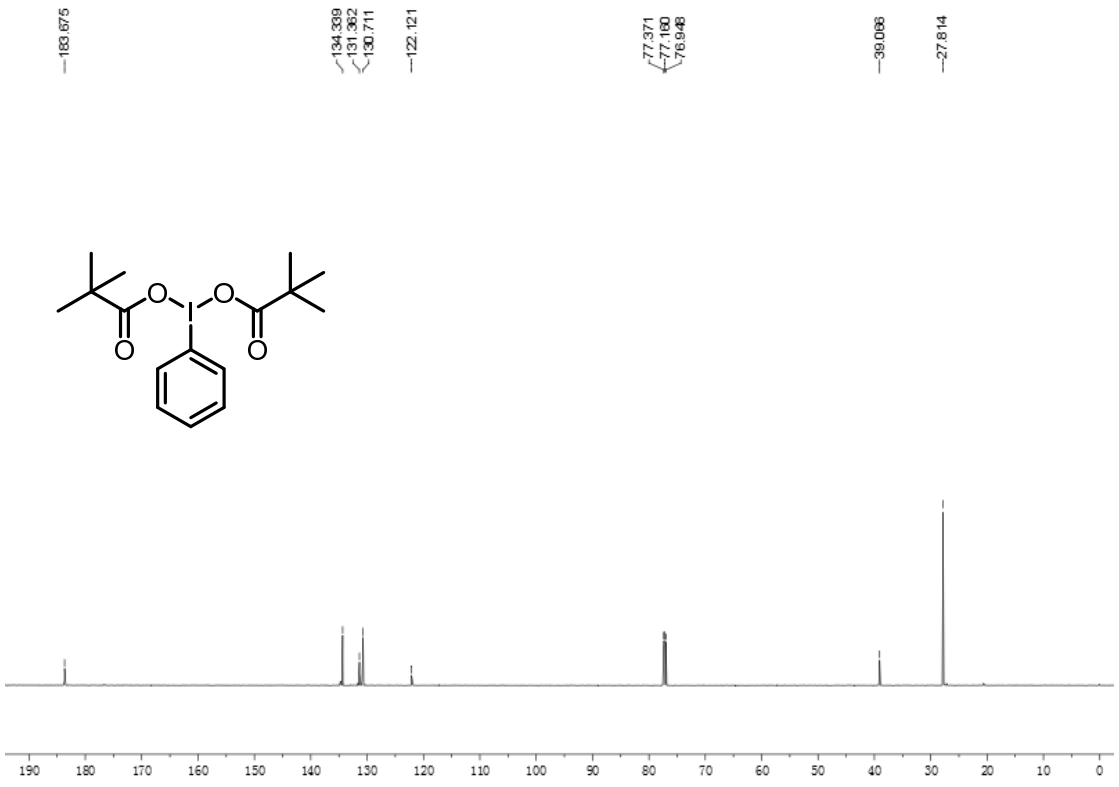
7. NMR Spectra for all the compounds

Iodobenzene dipropionate(3a)

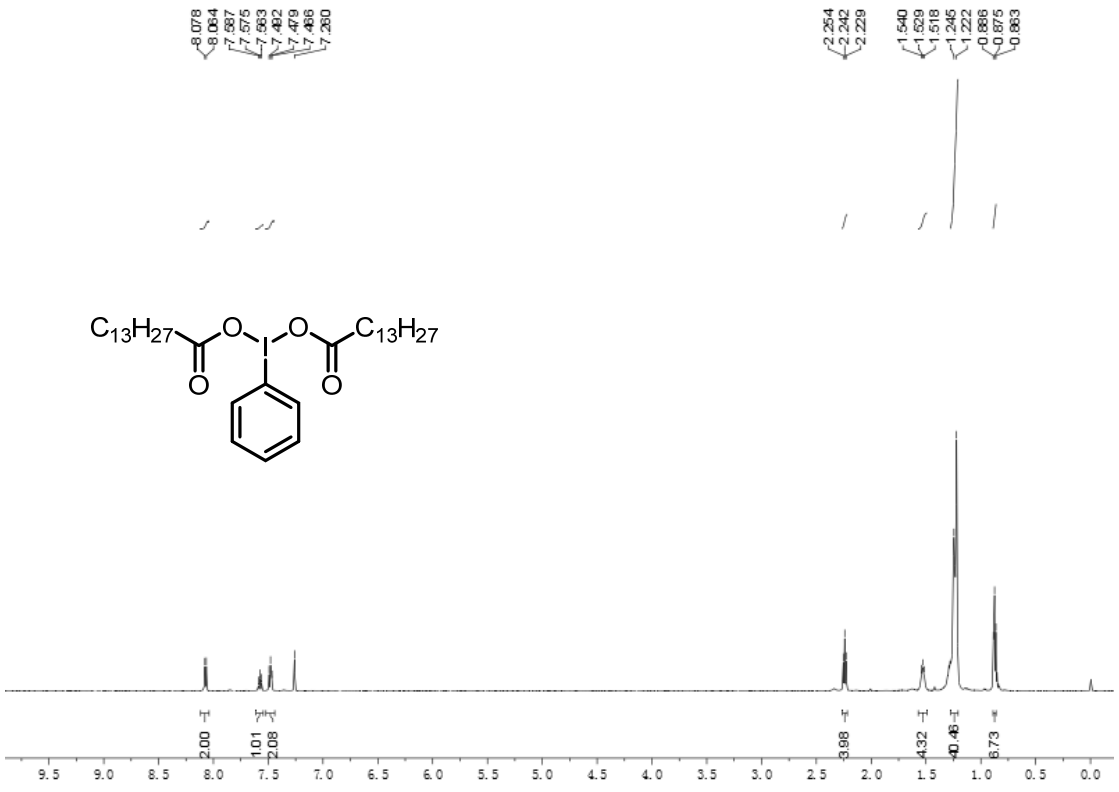


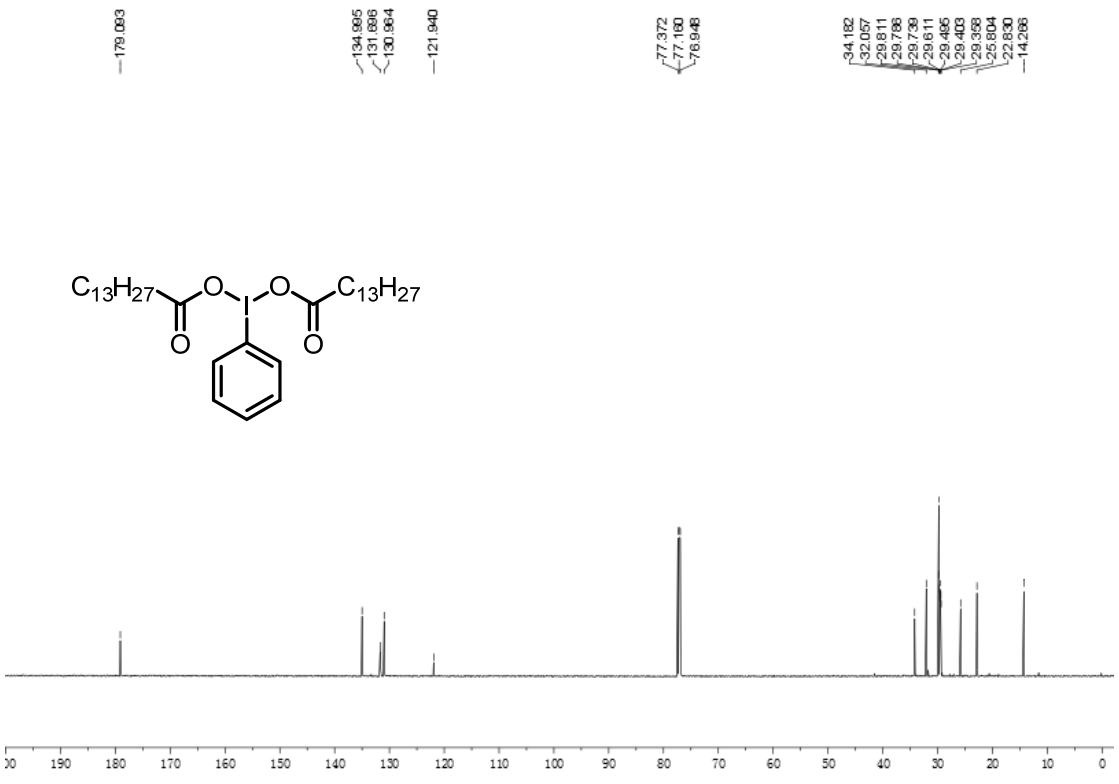
Iodobenzene Dipivalate(3b)



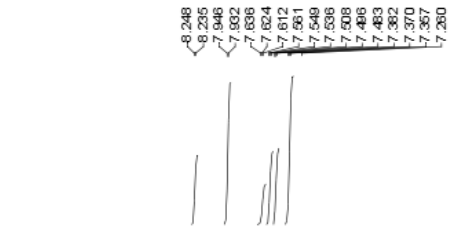


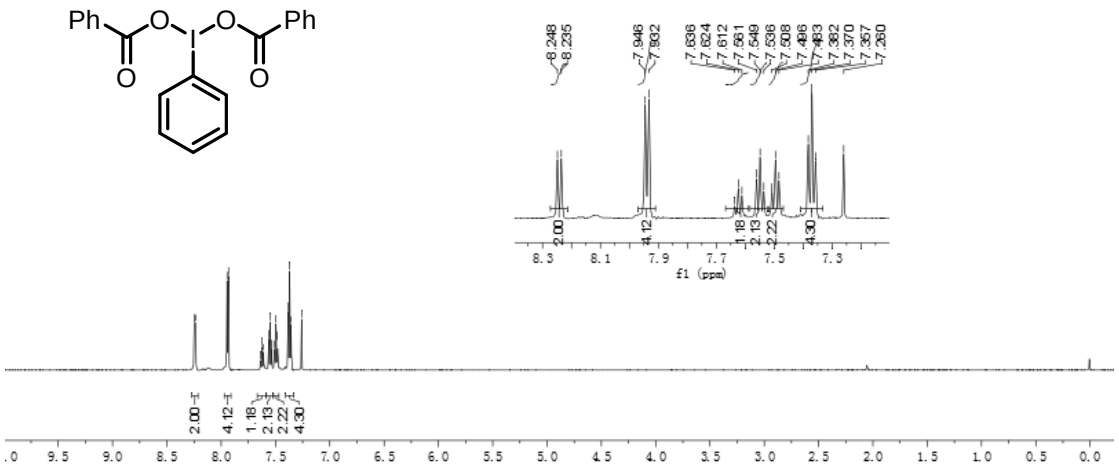
Iodobenzene ditetradecanoate(3c)

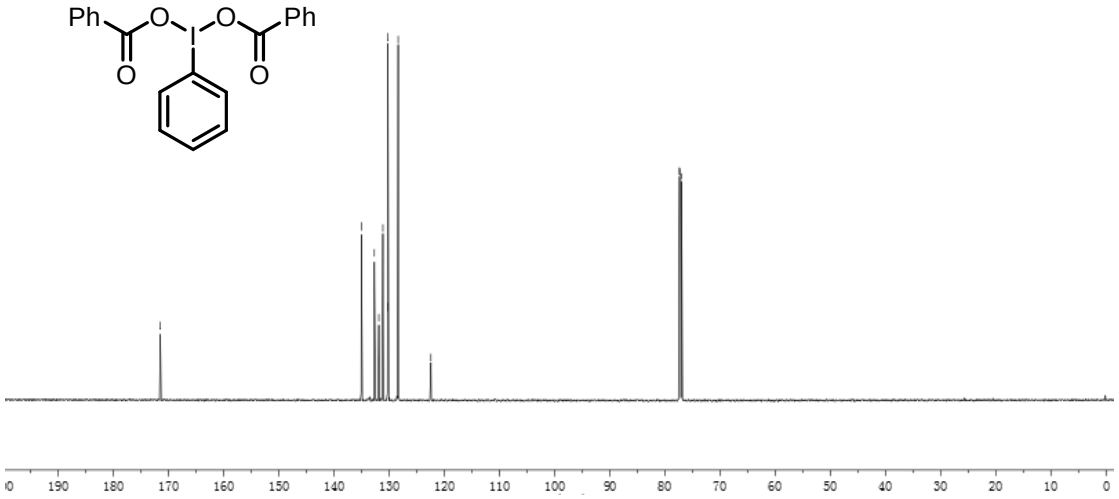




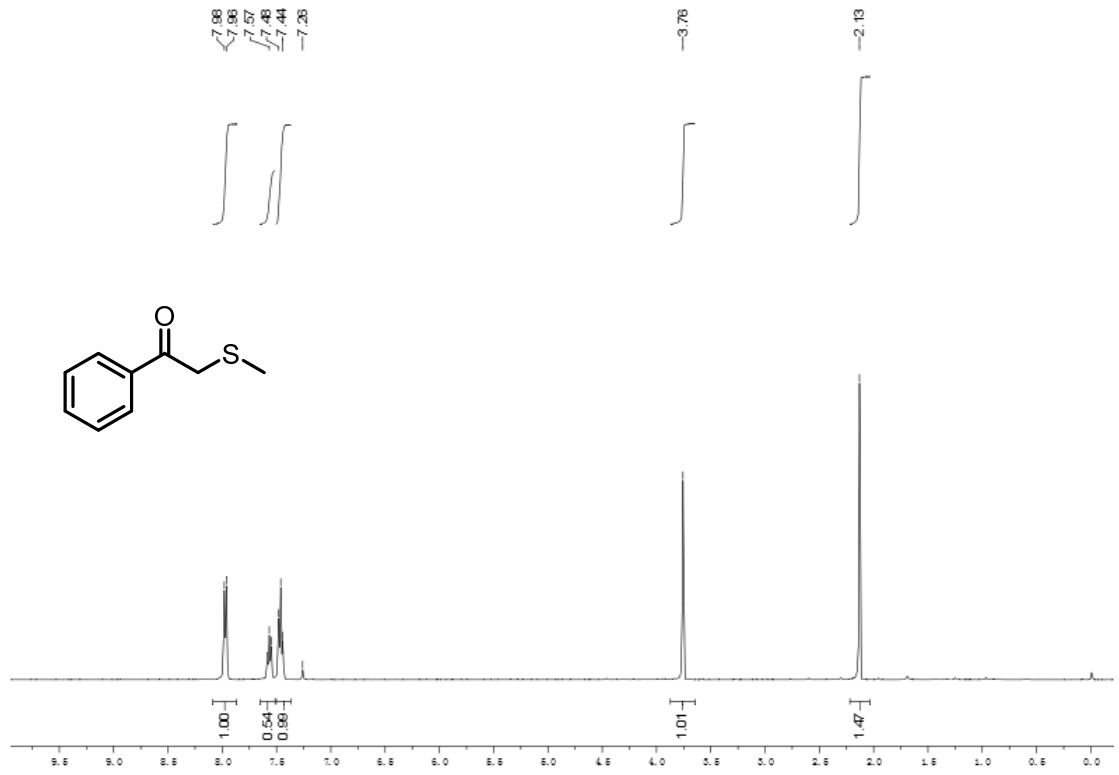
Iodobenzene Dibenzoate(3d)

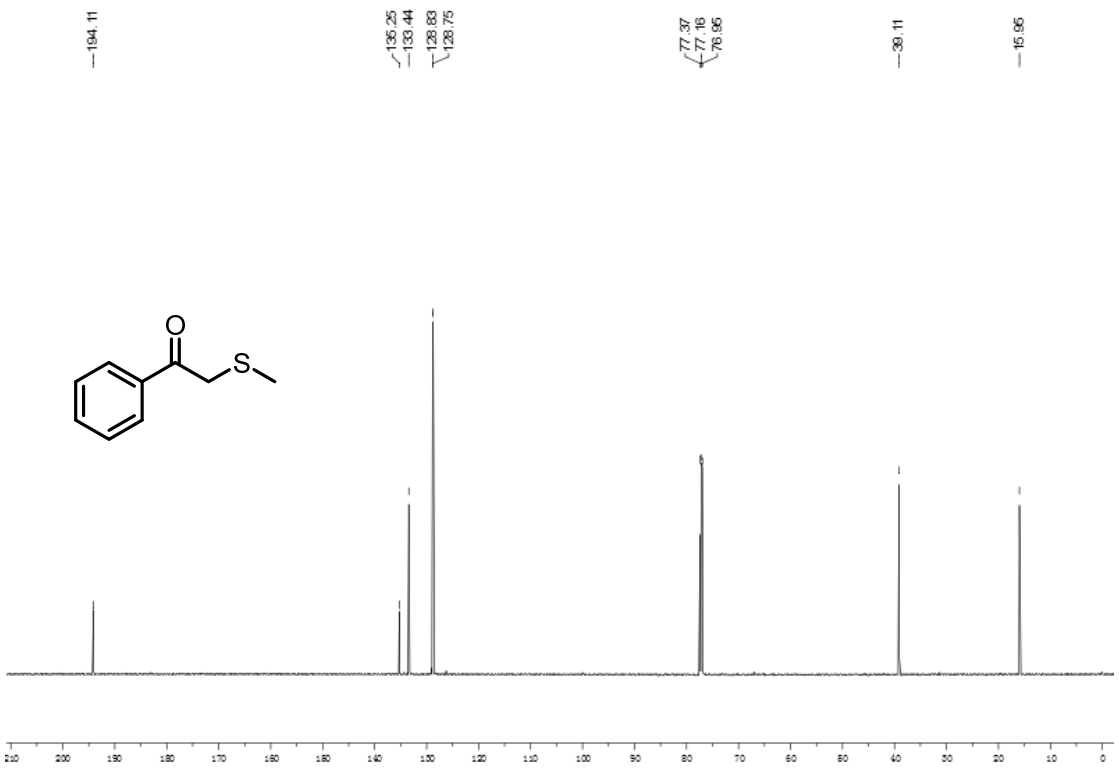




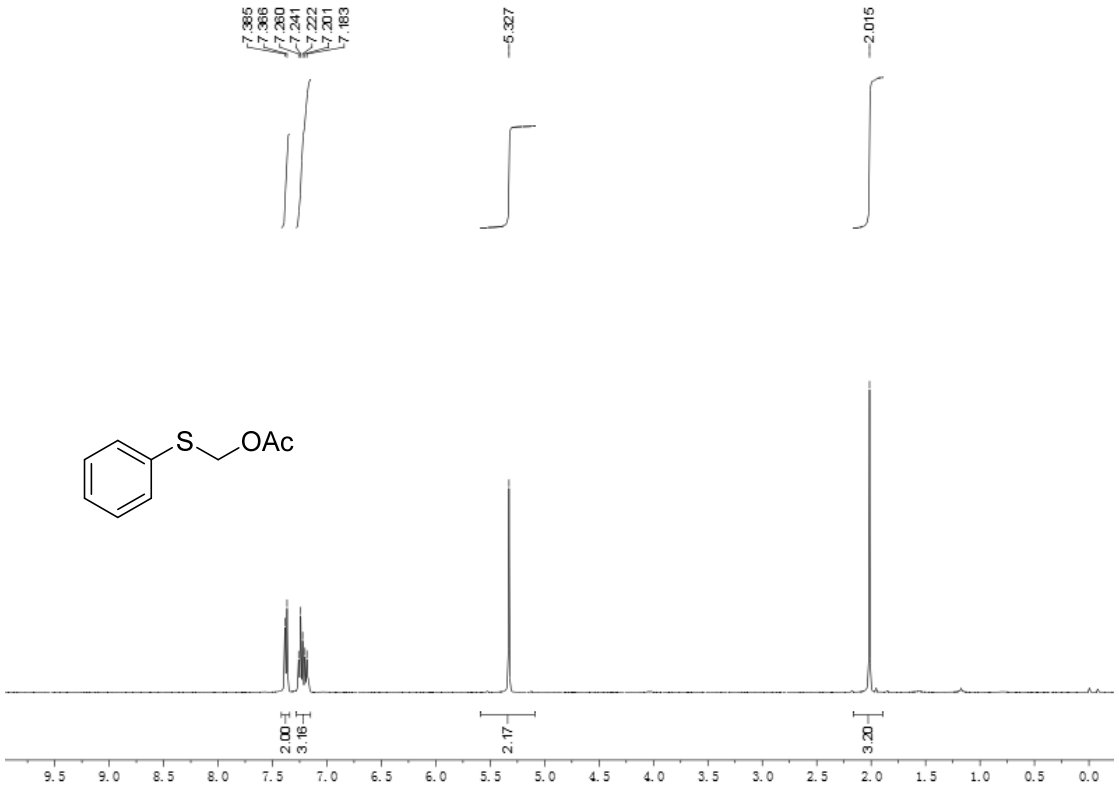


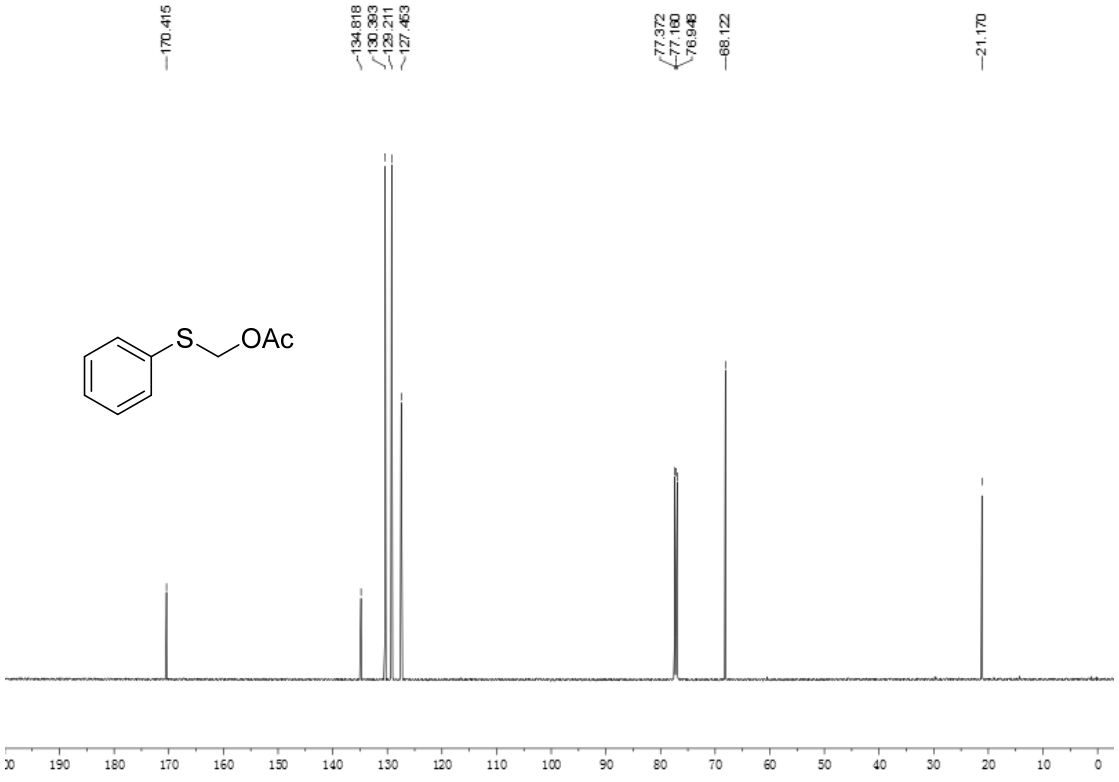
2-(methylthio)-1-phenylethan-1-one(1v)



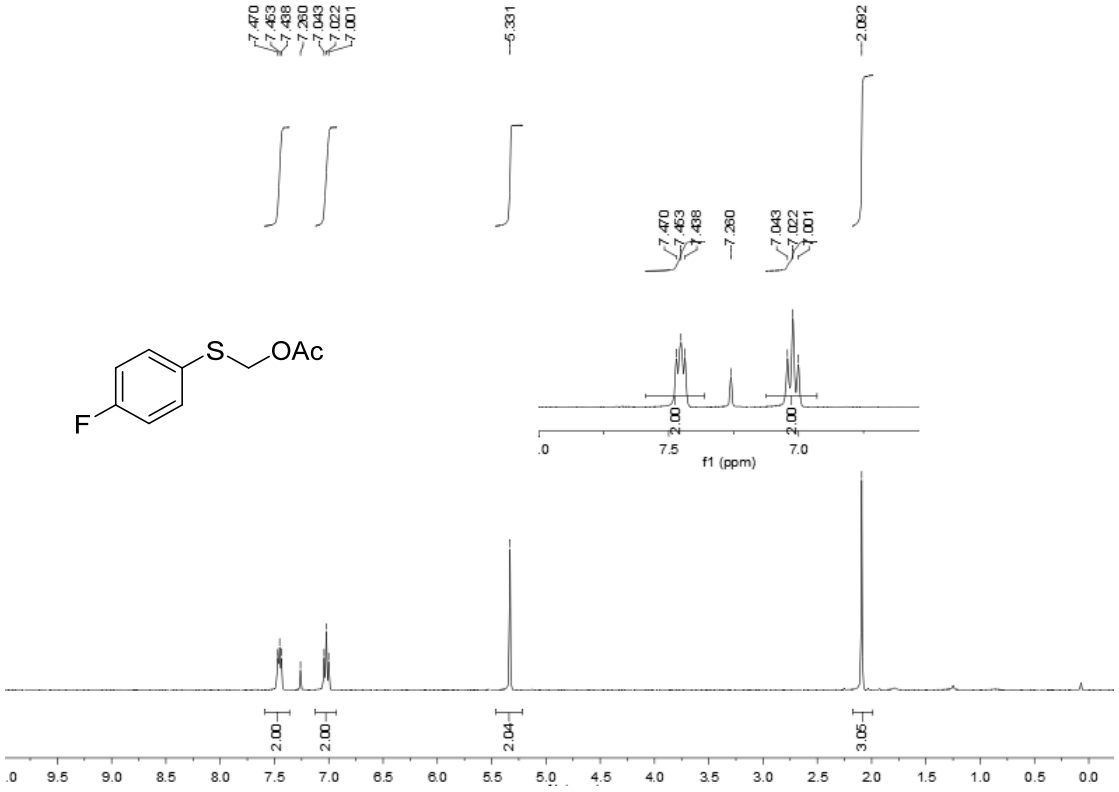


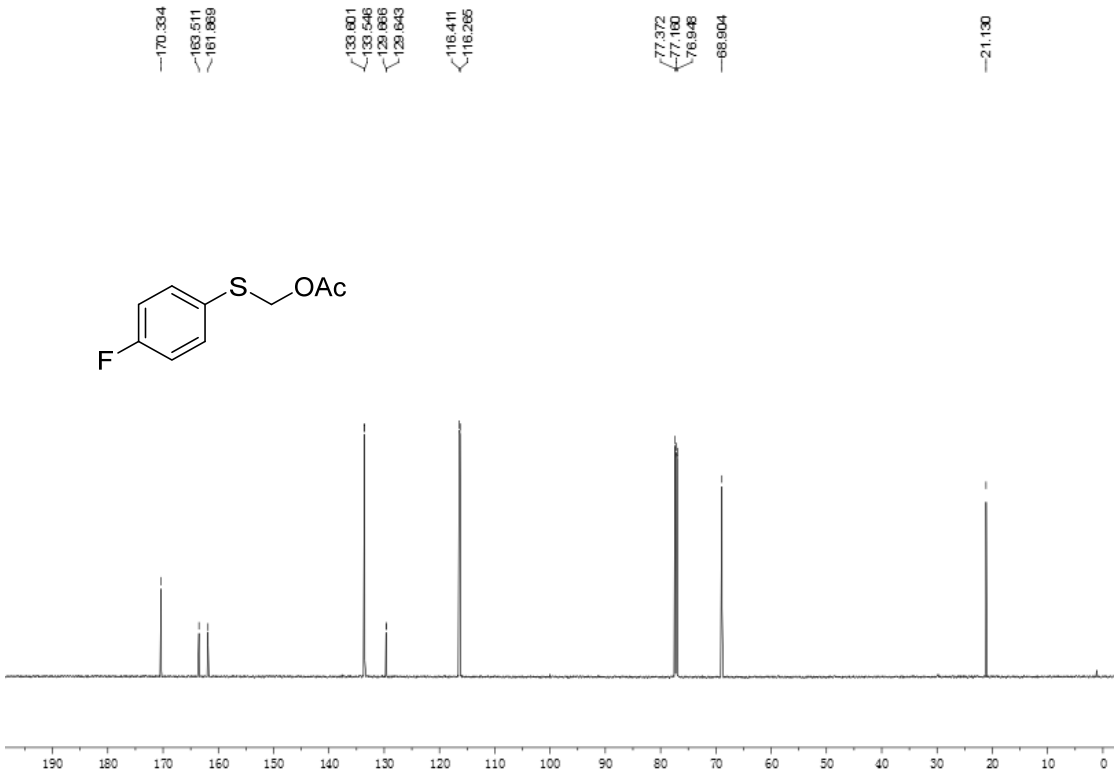
(phenylthio)methyl acetate(2a)



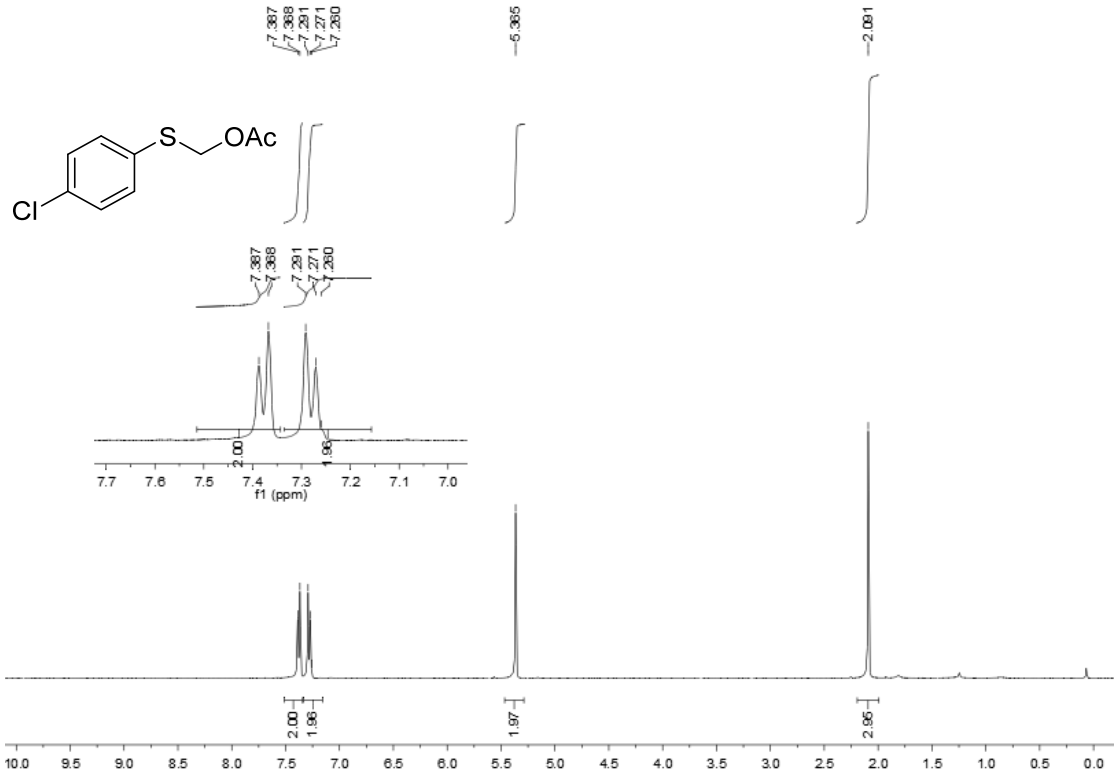


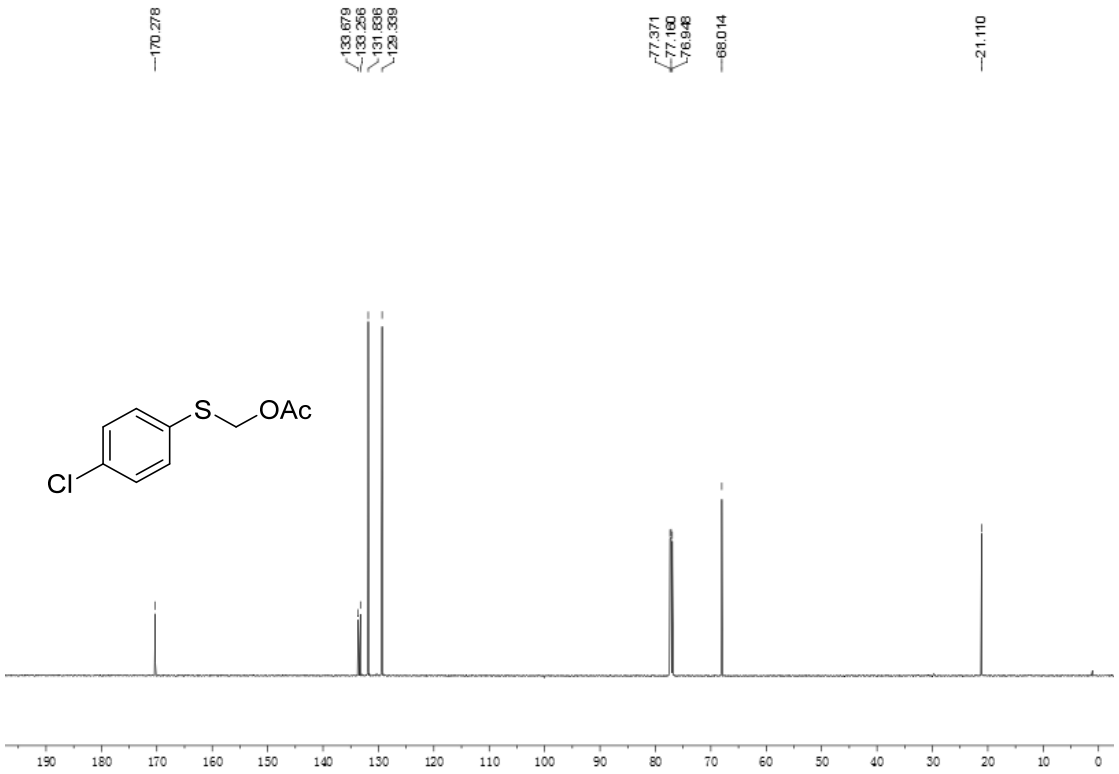
((4-fluorophenyl)thio)methyl acetate(2b)



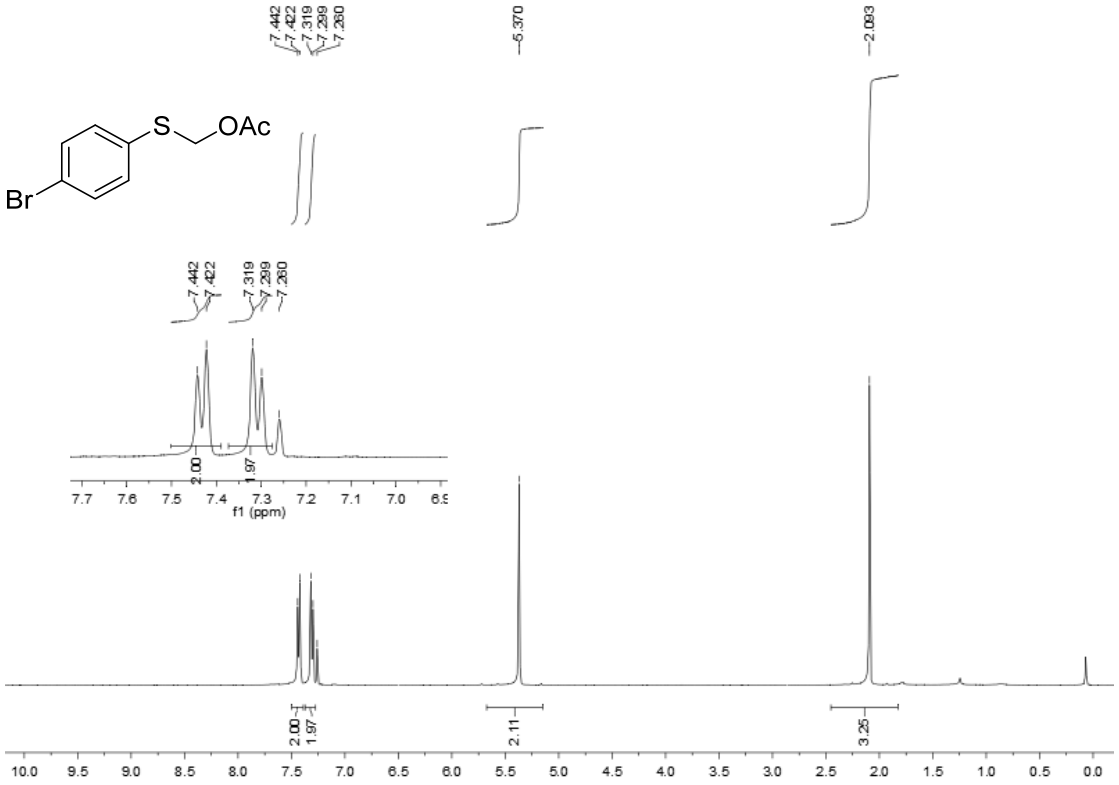


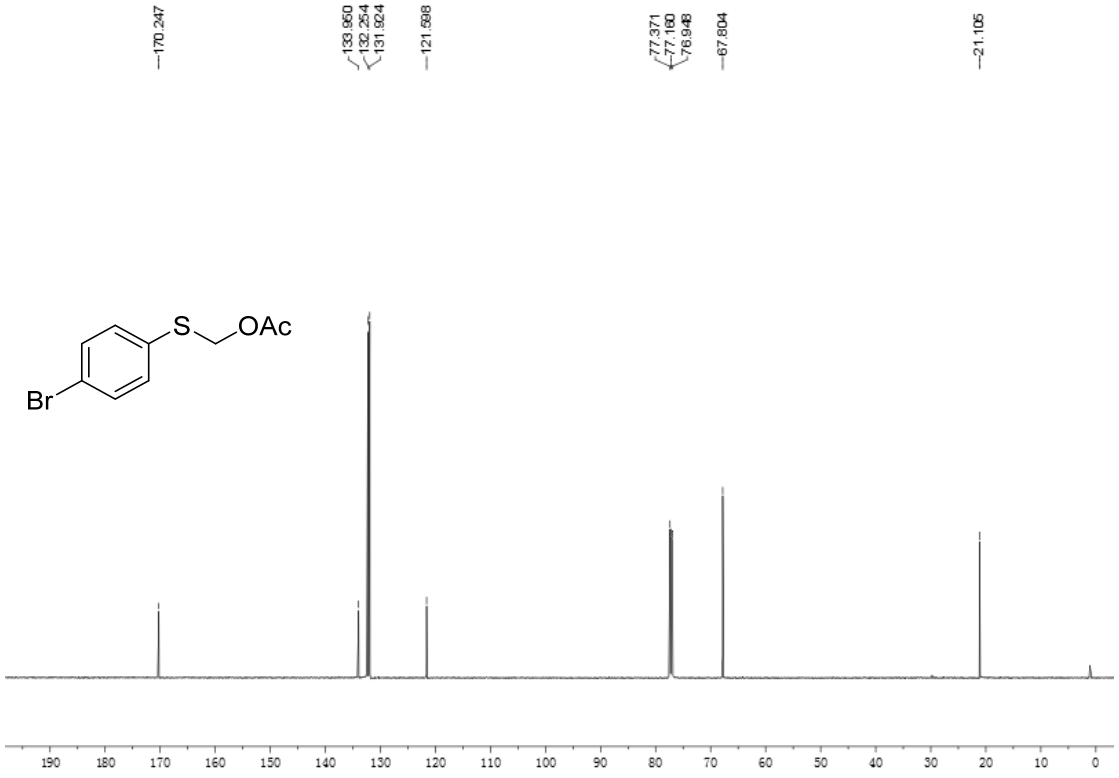
((4-chlorophenyl)thio)methyl acetate(2c)



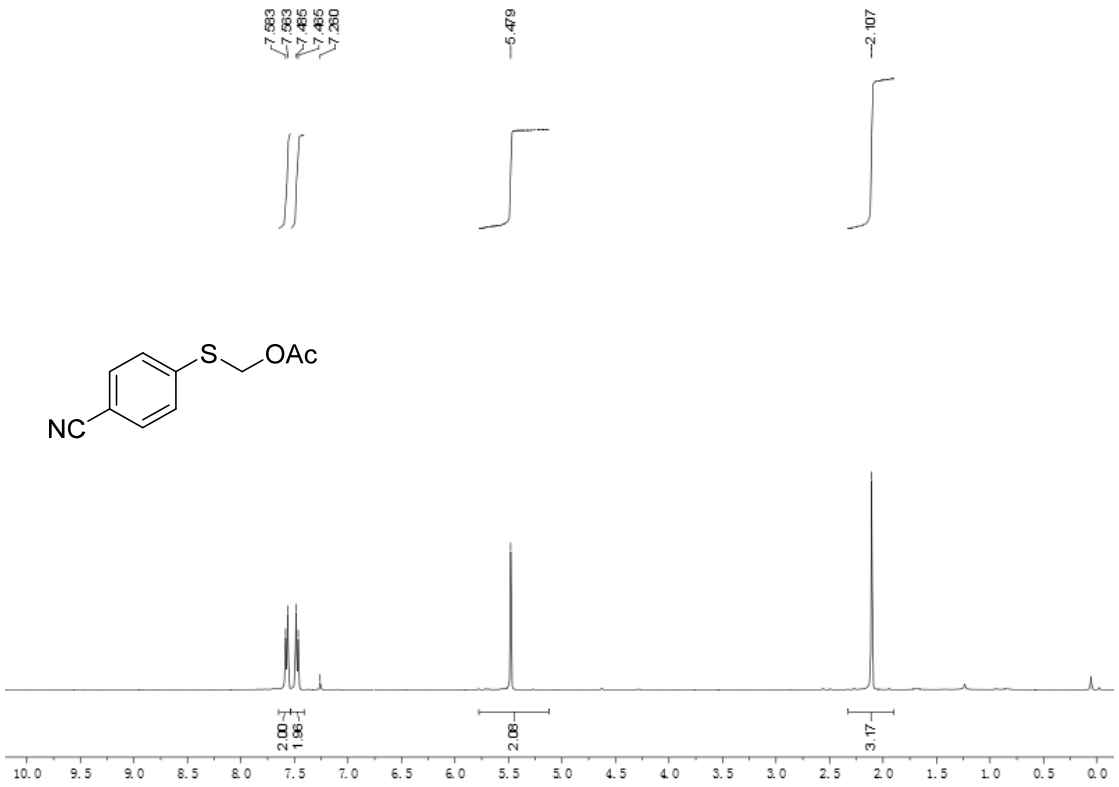


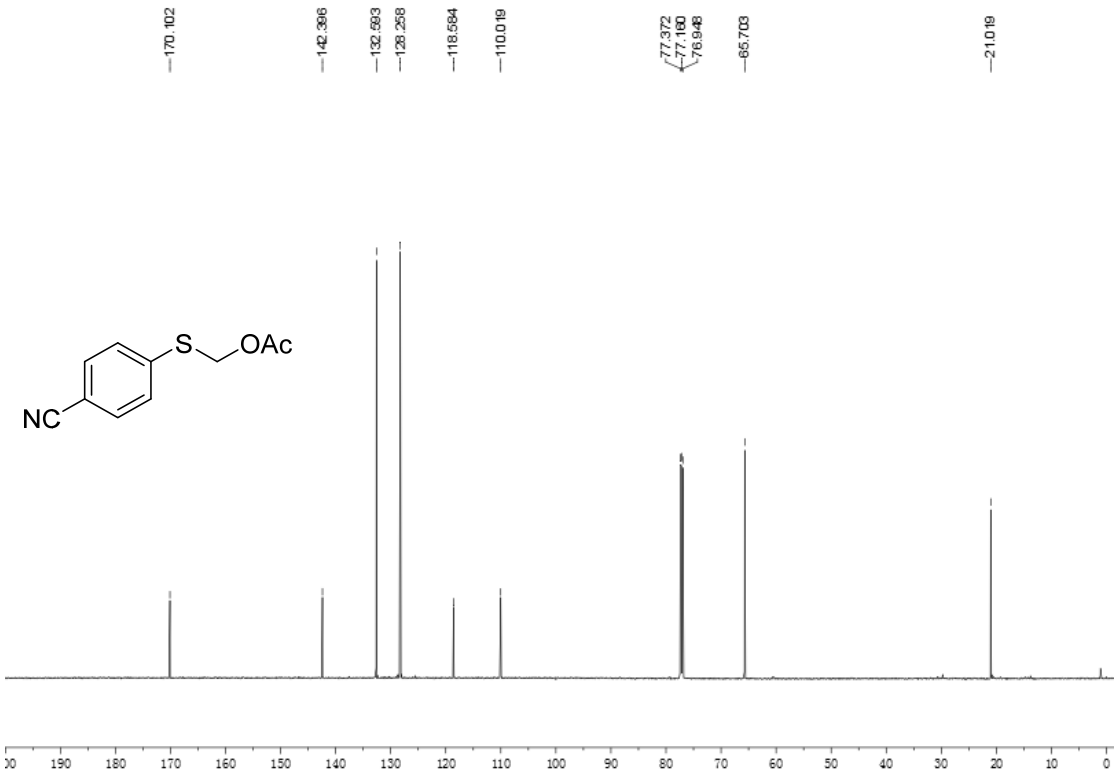
((4-bromophenyl)thio)methyl acetate(2d)



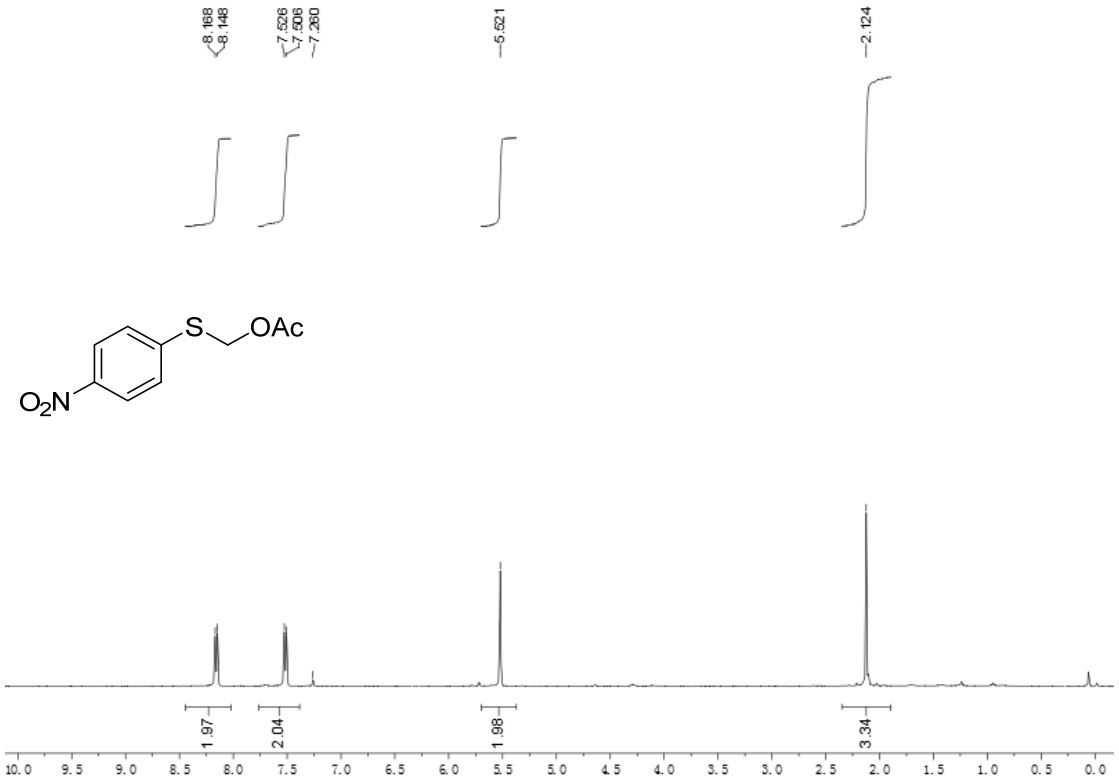


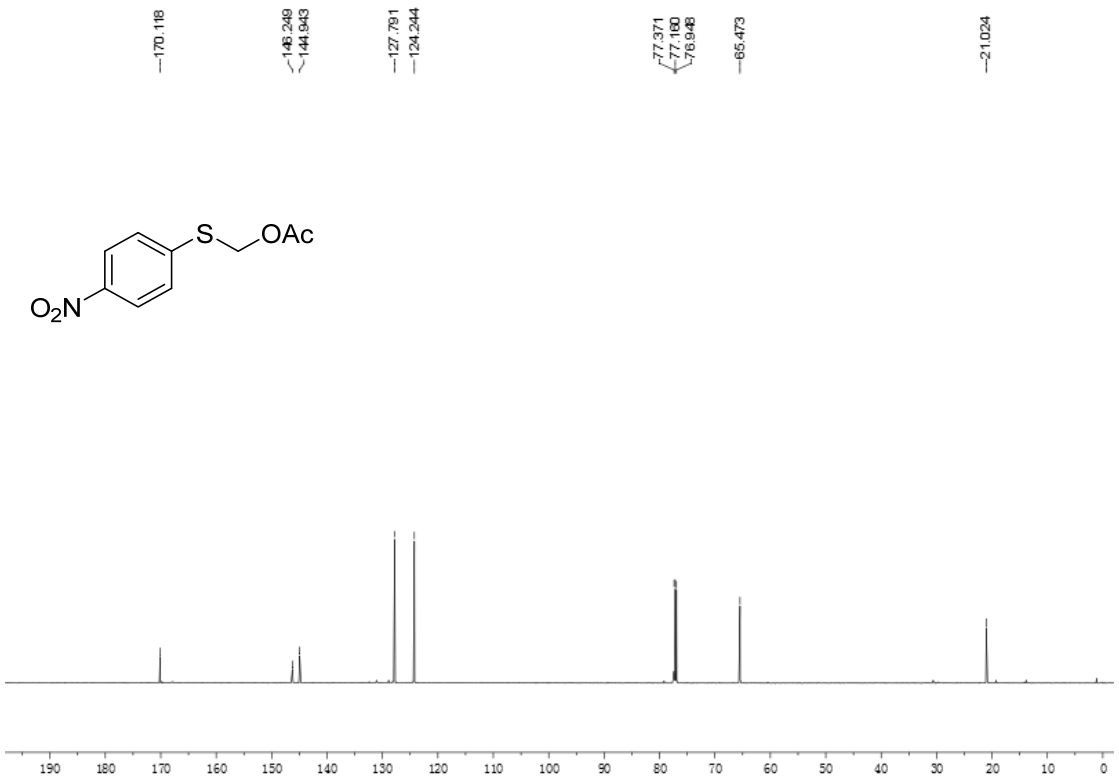
((4-cyanophenyl)thio)methyl acetate(2e)



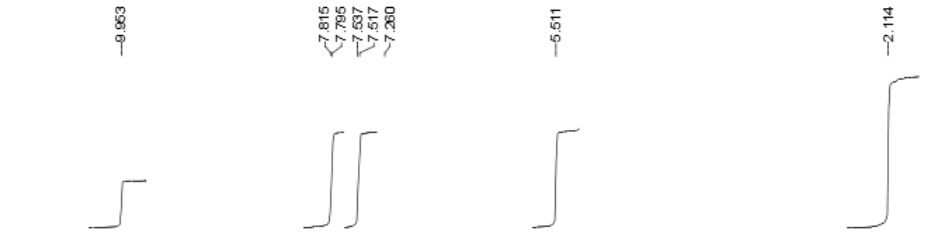


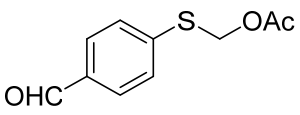
((4-nitrophenyl)thio)methyl acetate(2f)

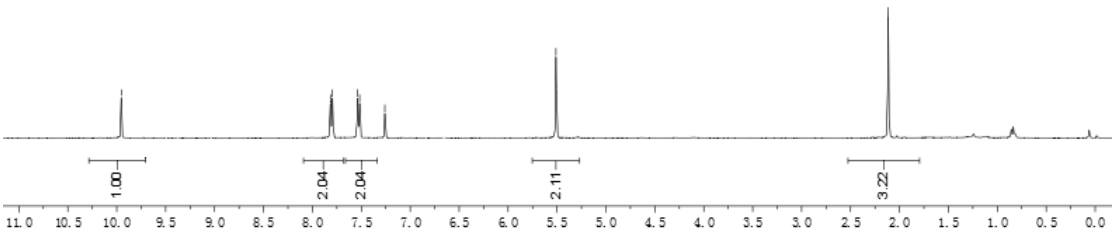


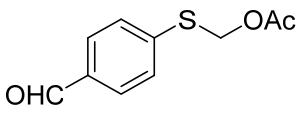


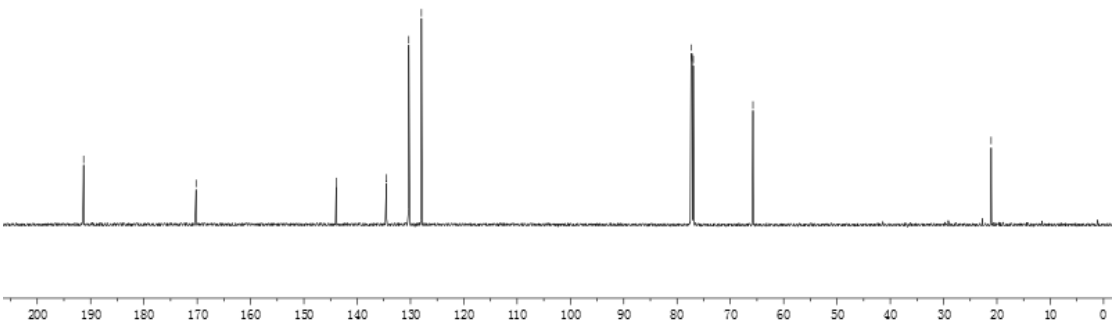
((4-formylphenyl)thio)methyl acetate(2g)



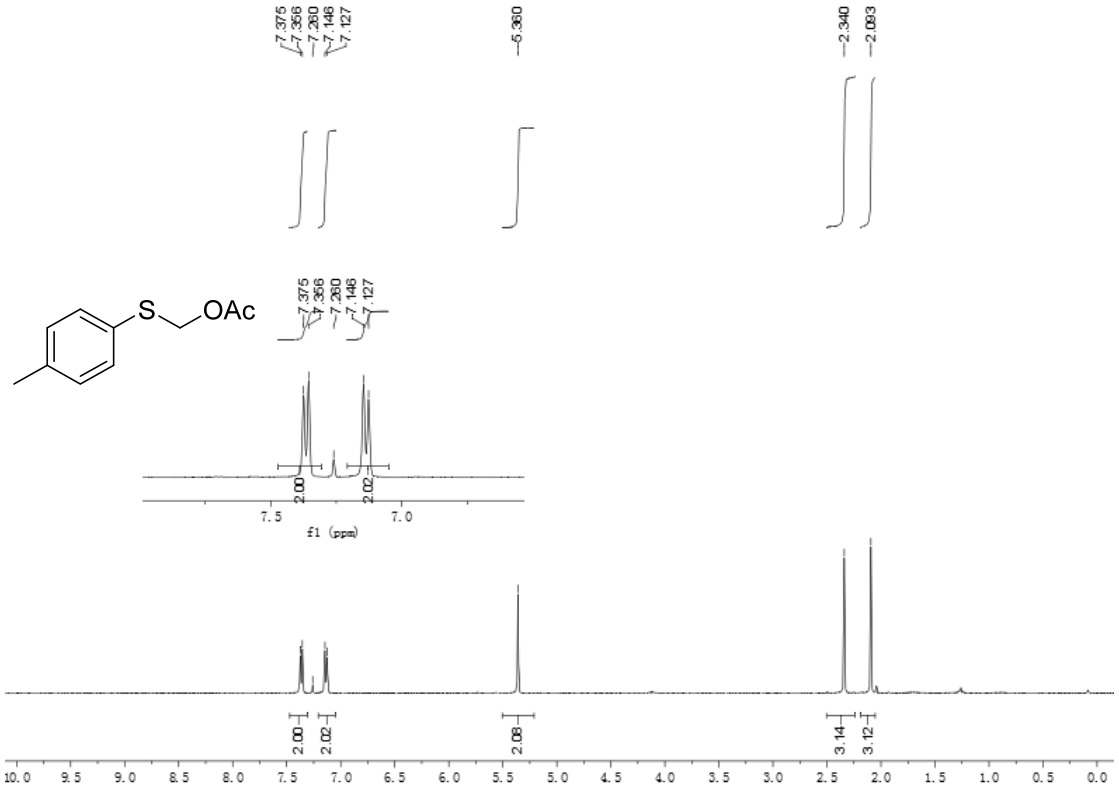


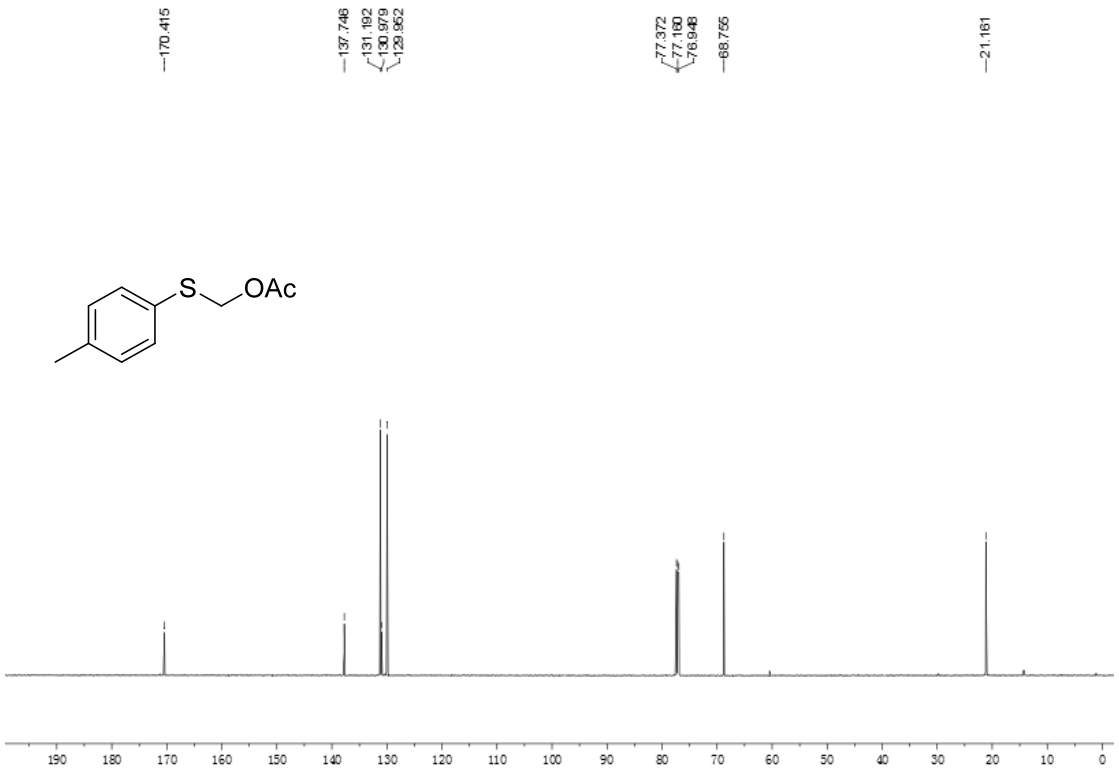




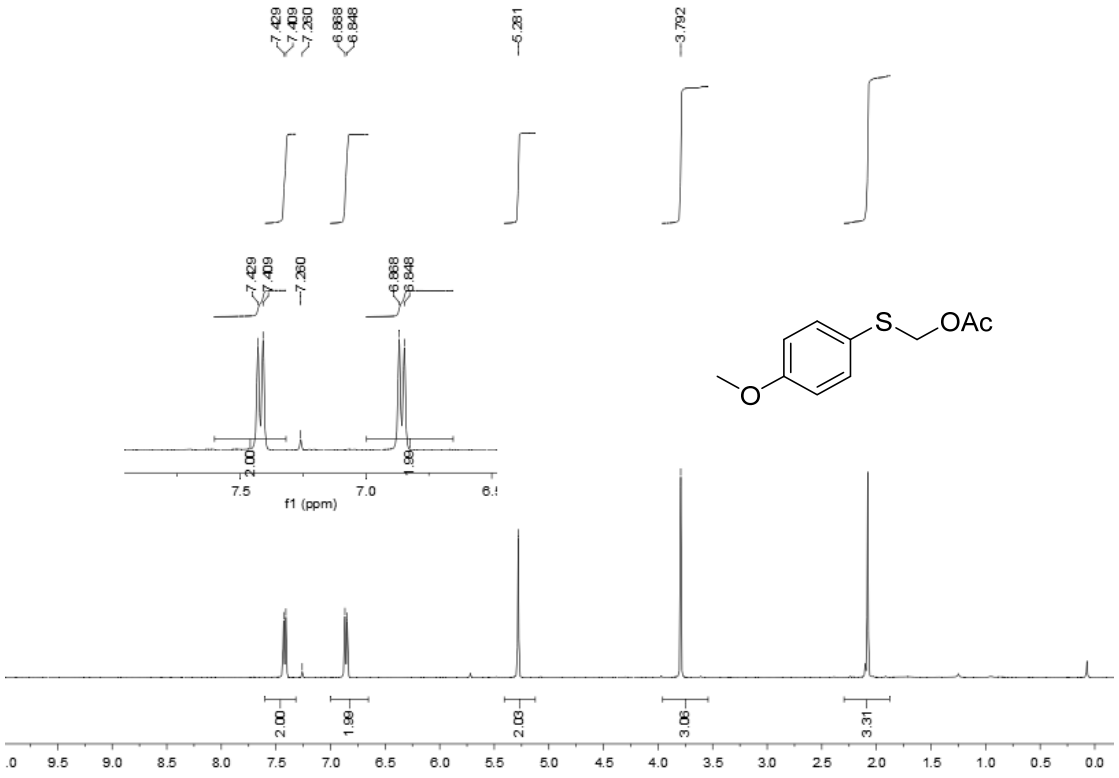


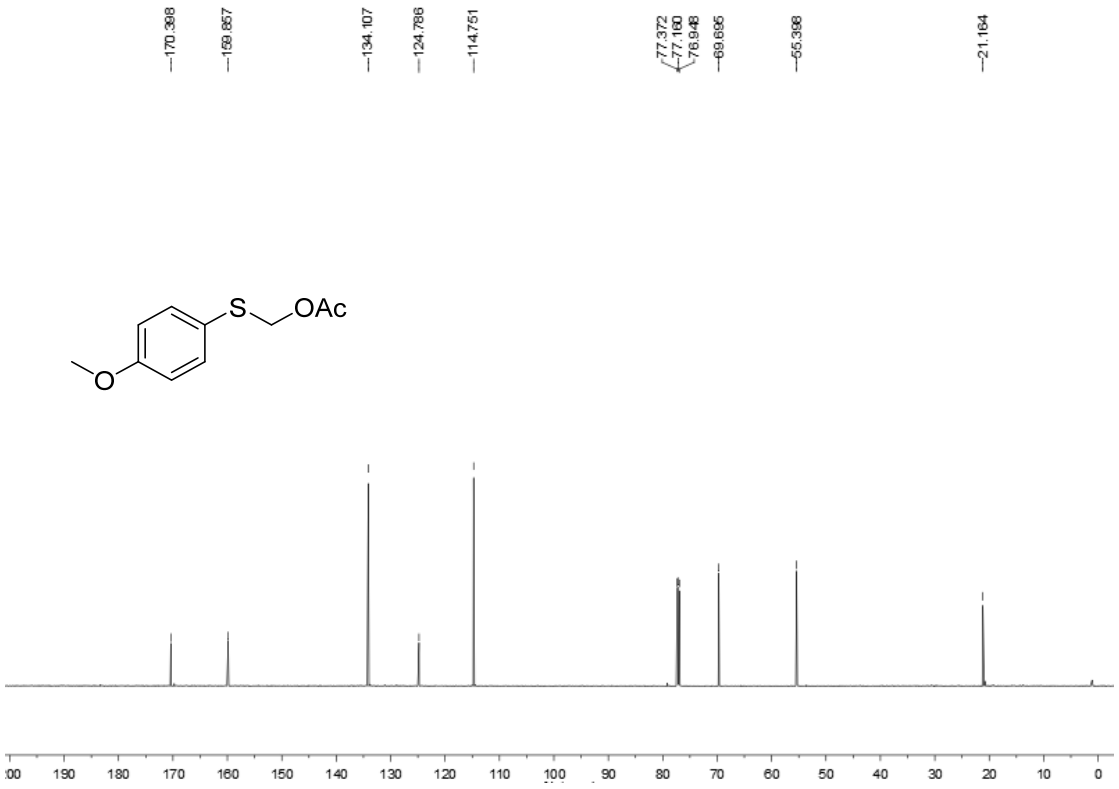
(p-tolylthio)methyl acetate(2h)



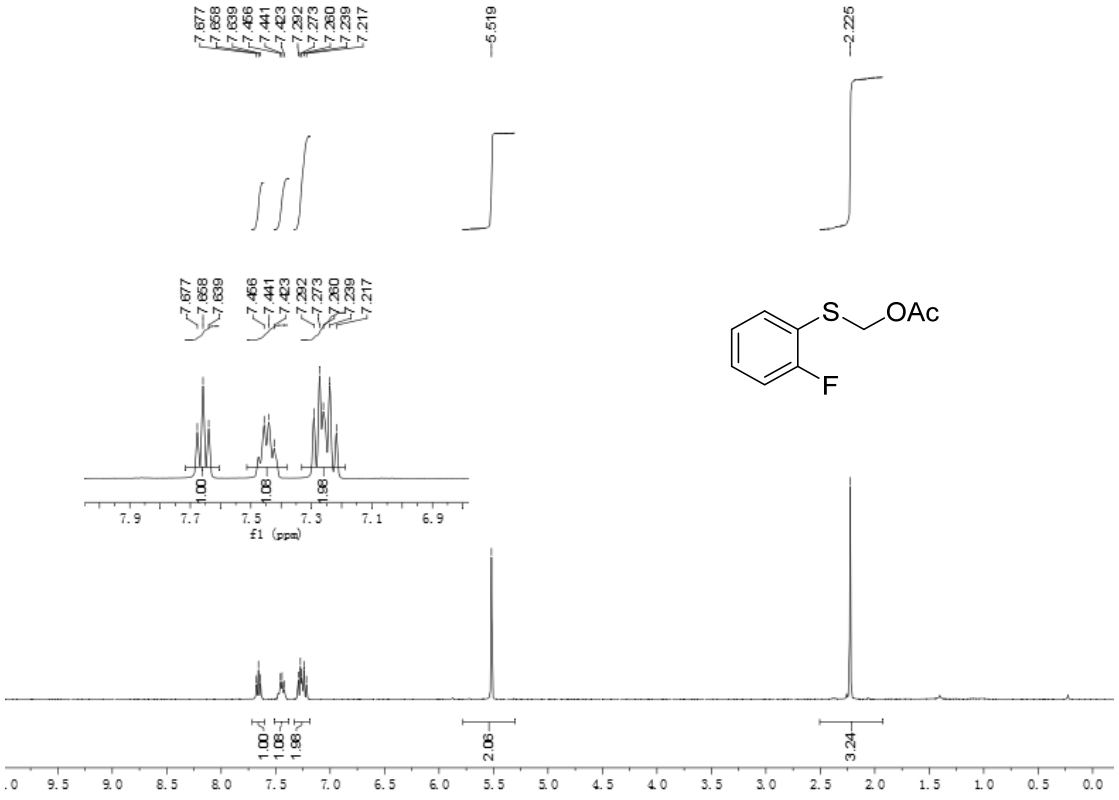


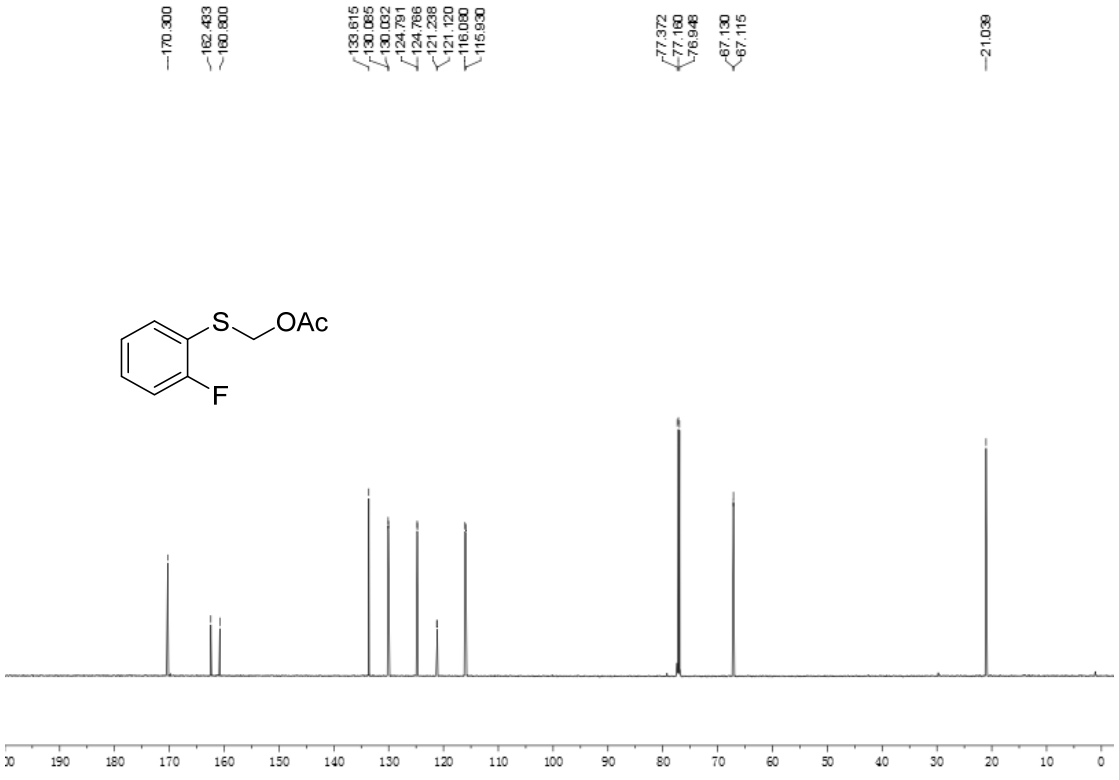
((4-methoxyphenyl)thio)methyl acetate(2i)



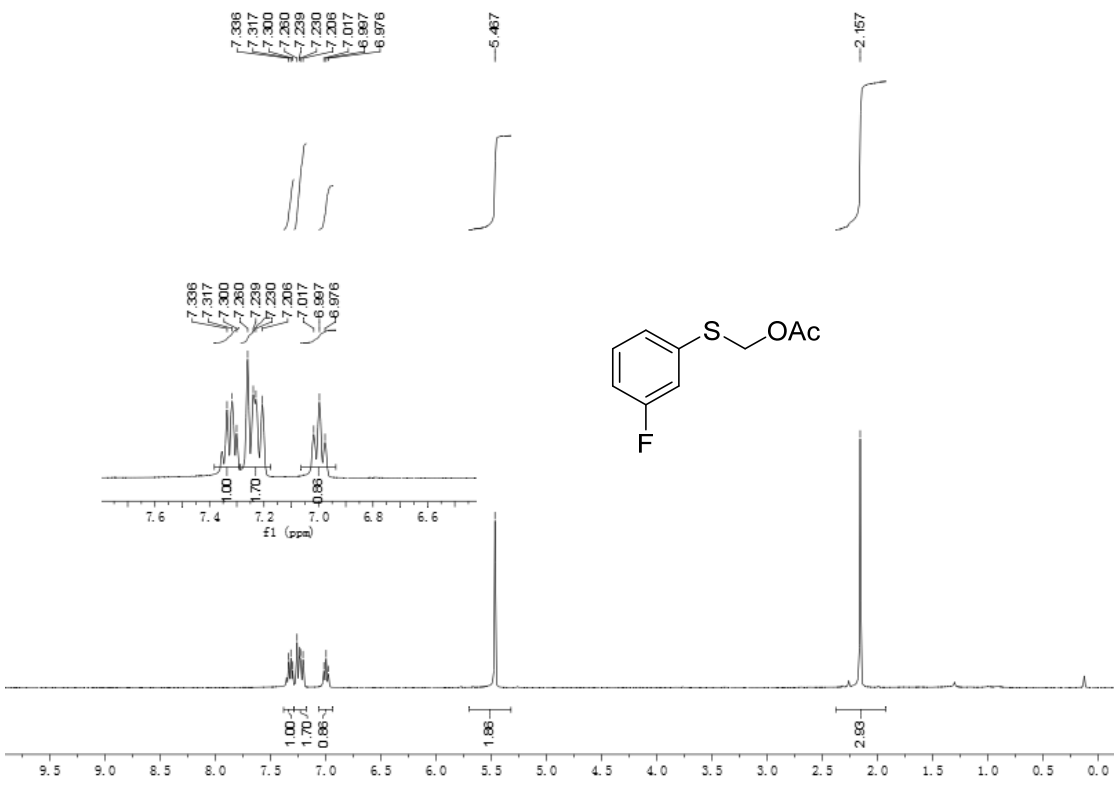


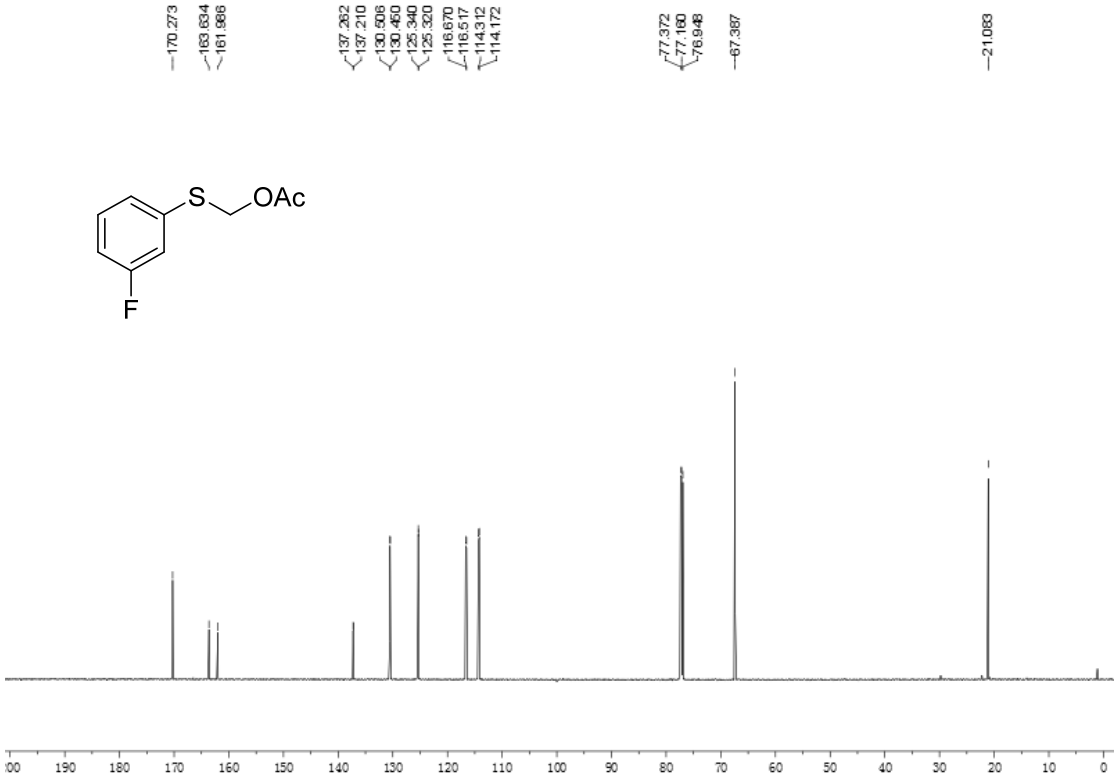
((2-fluorophenyl)thio)methyl acetate(2j)



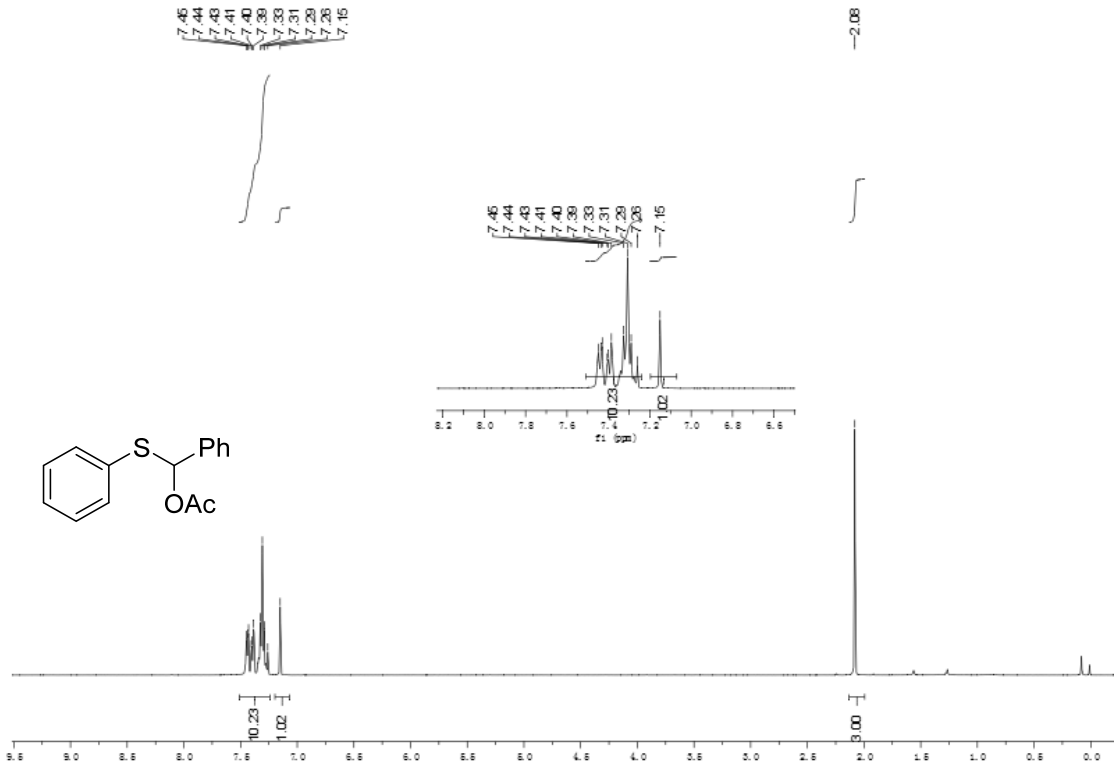


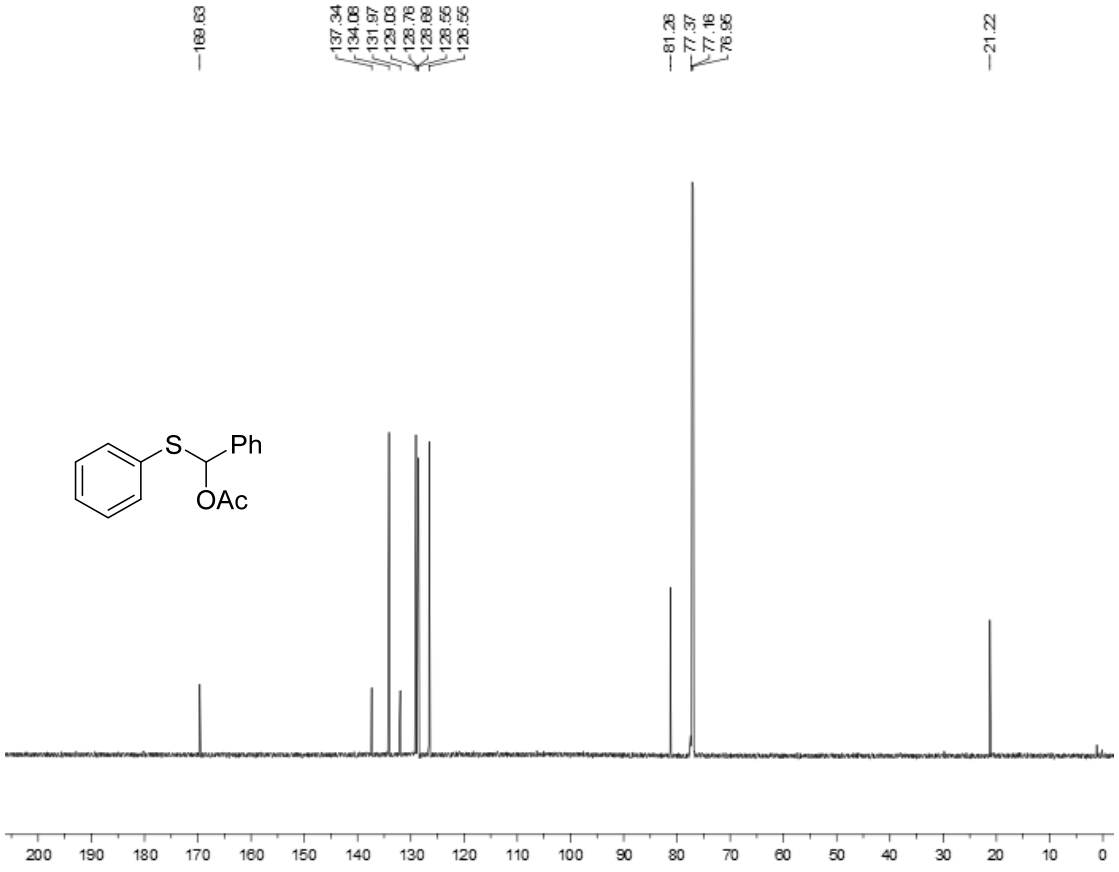
((3-fluorophenyl)thio)methyl acetate(2k)



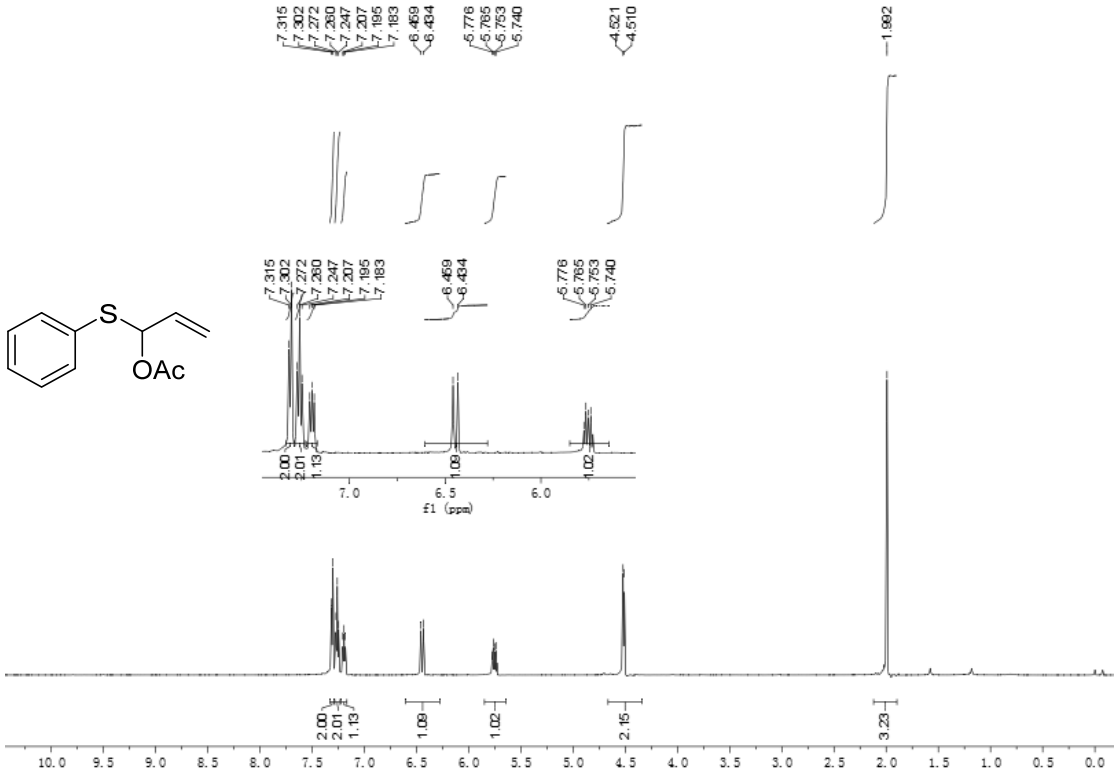


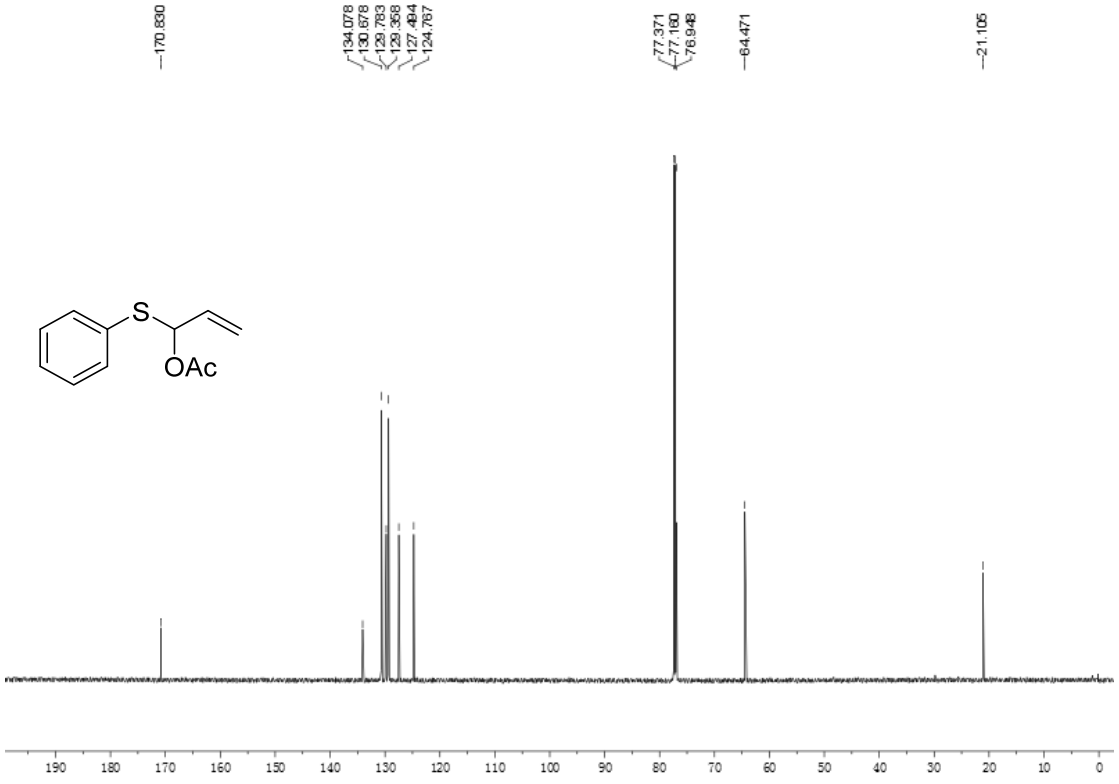
phenyl(phenylthio)methyl acetate(2l)



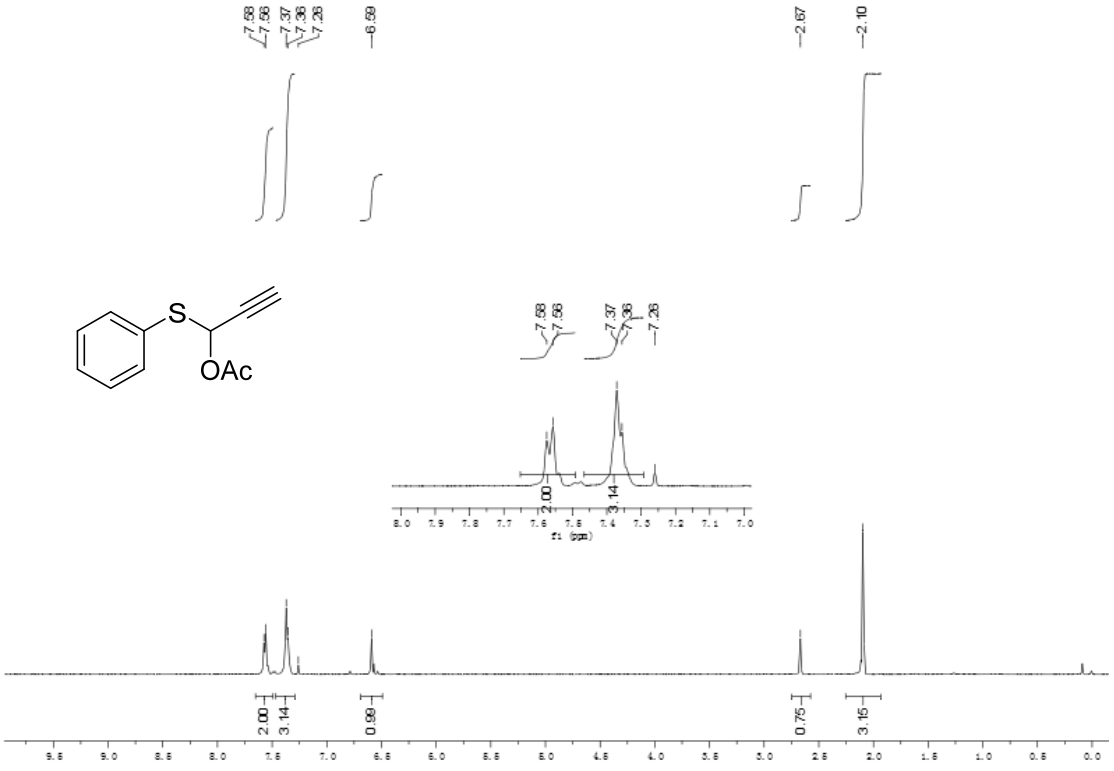


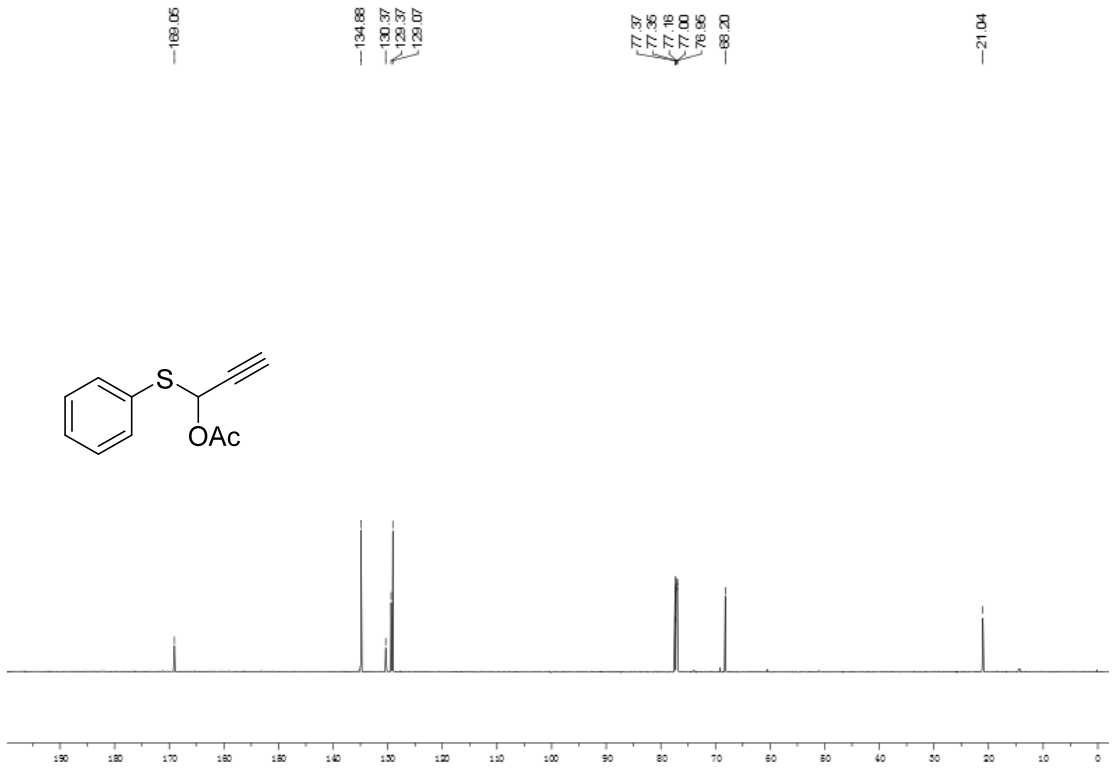
1-(phenylthio)allyl acetate(2m)



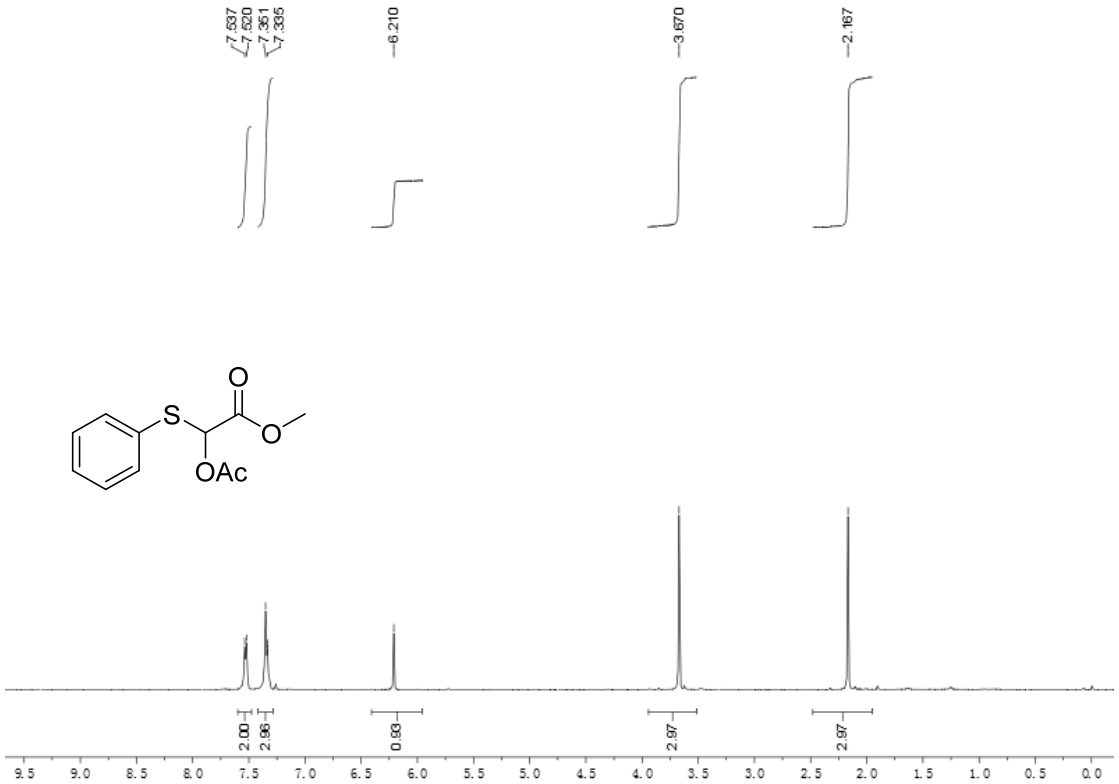


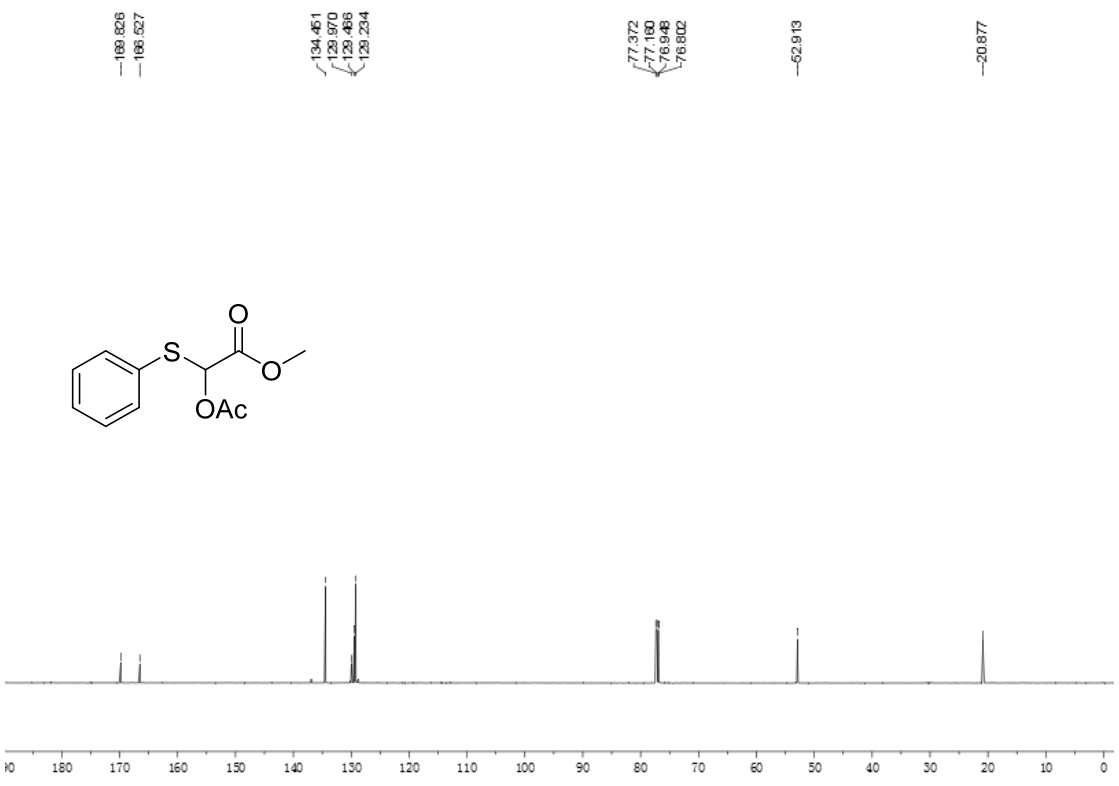
1-(phenylthio)prop-2-yn-1-yl acetate(2n)



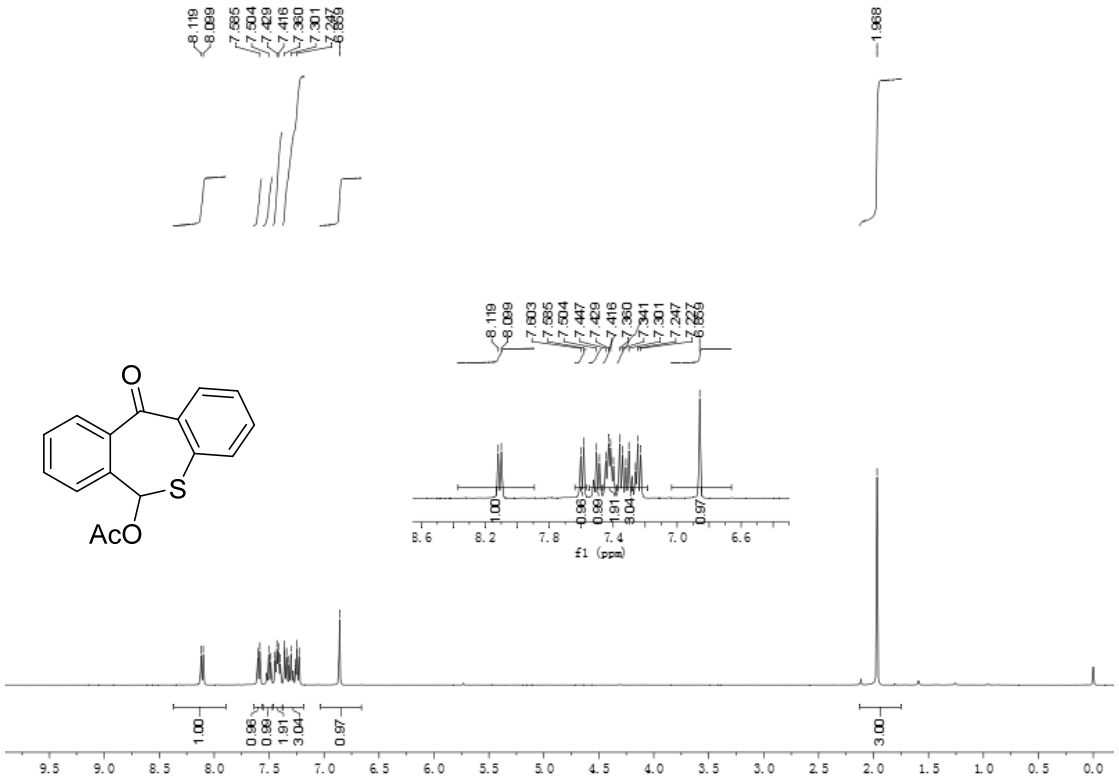


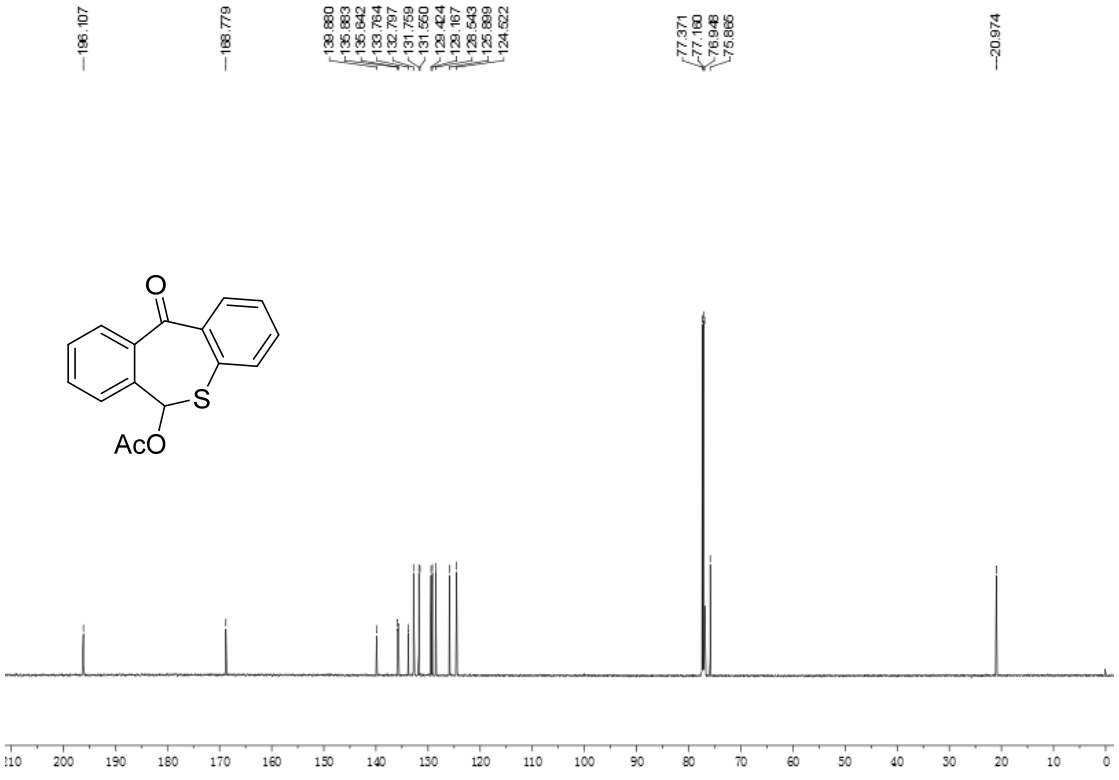
methyl 2-acetoxy-2-(phenylthio)acetate(2o)



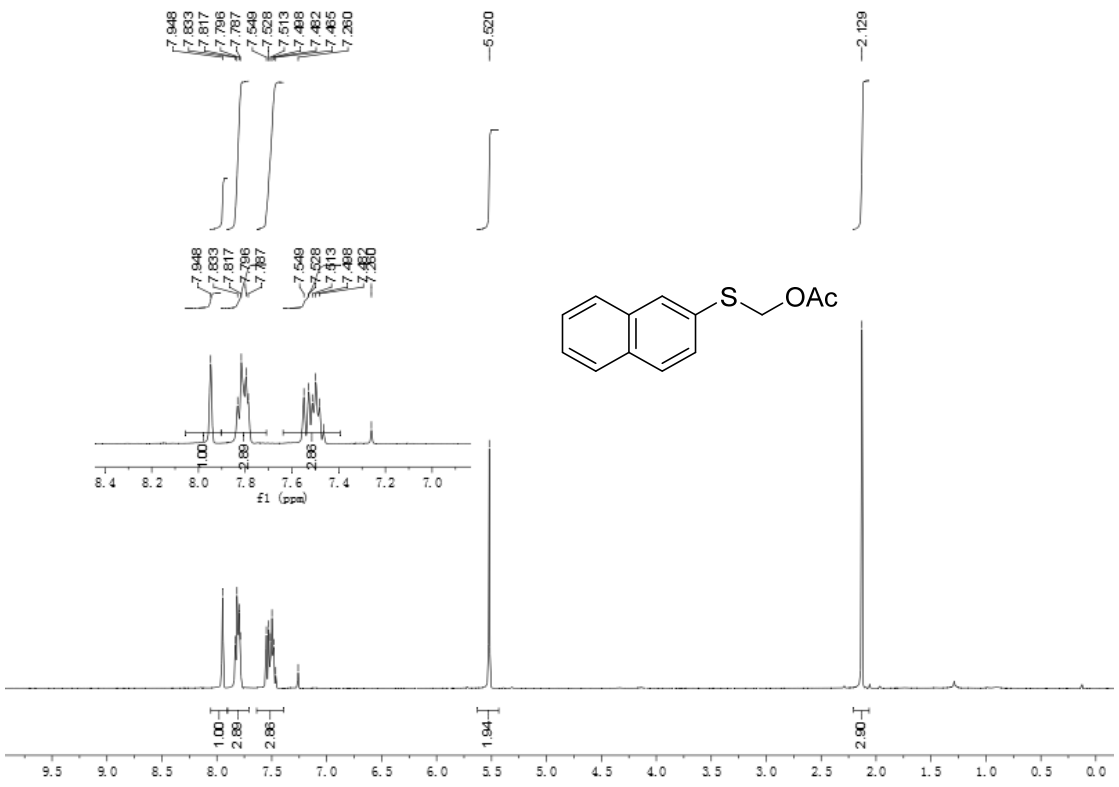


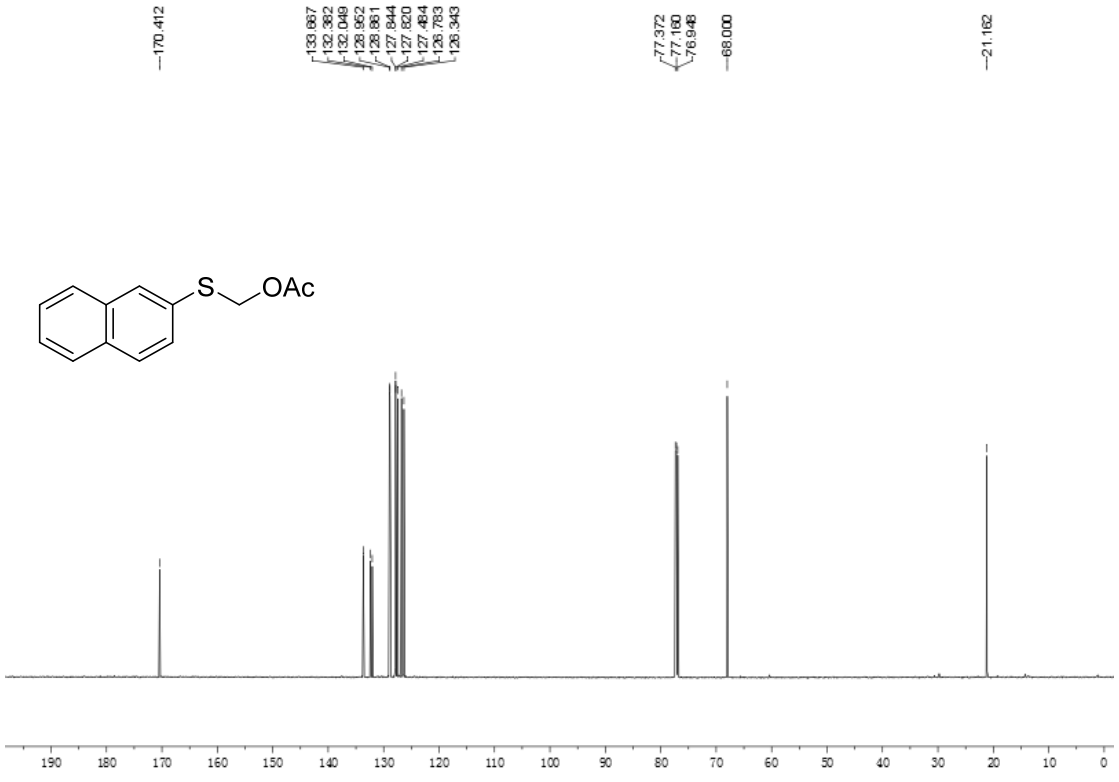
11-oxo-6,11-dihydrodibenzo[b,e]thiepin-6-yl acetate(2p)



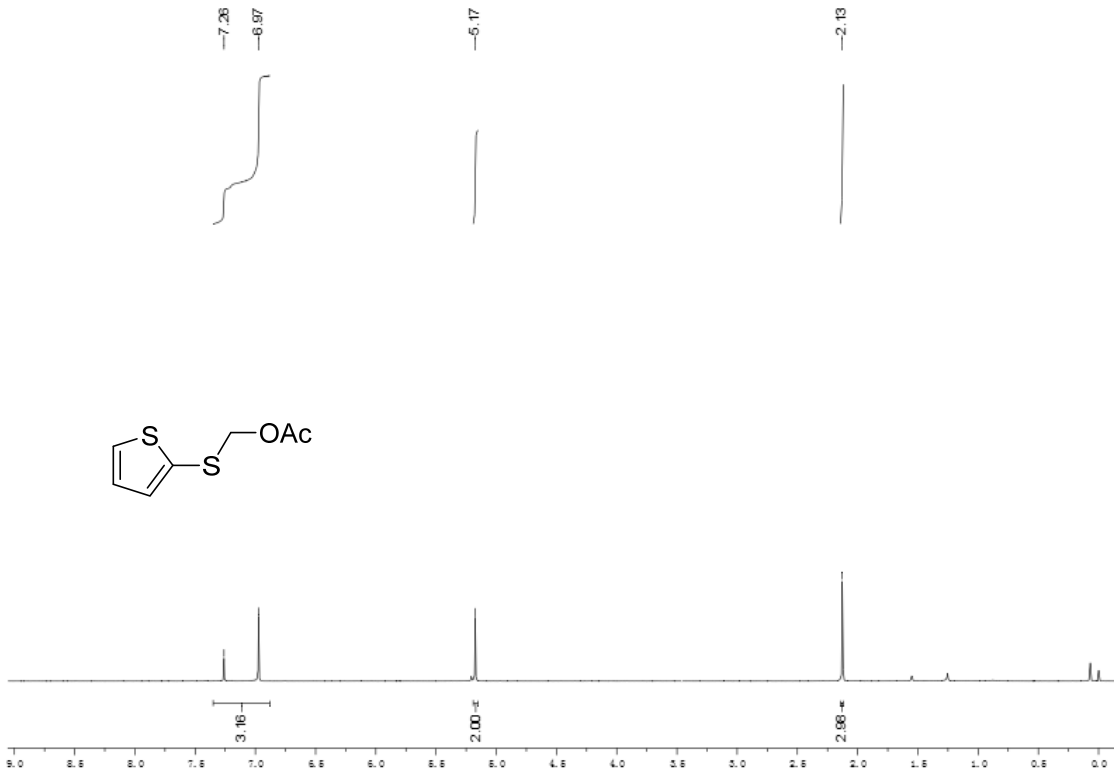


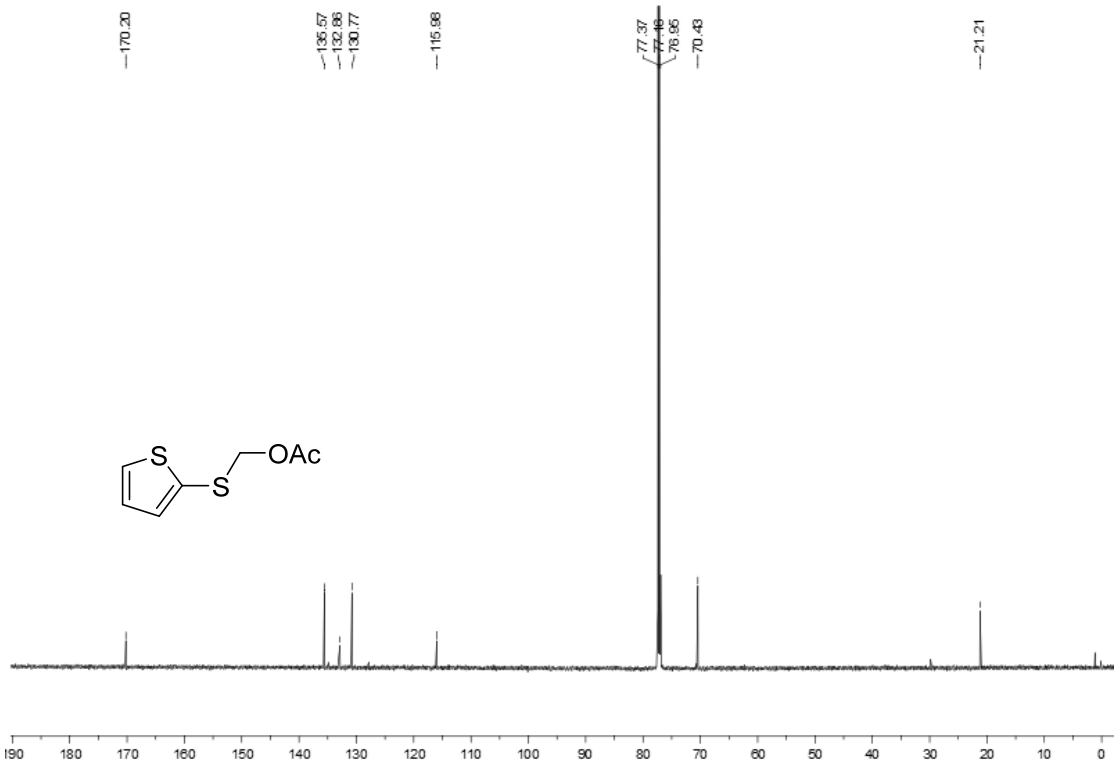
(naphthalen-2-ylthio)methyl acetate(2q)



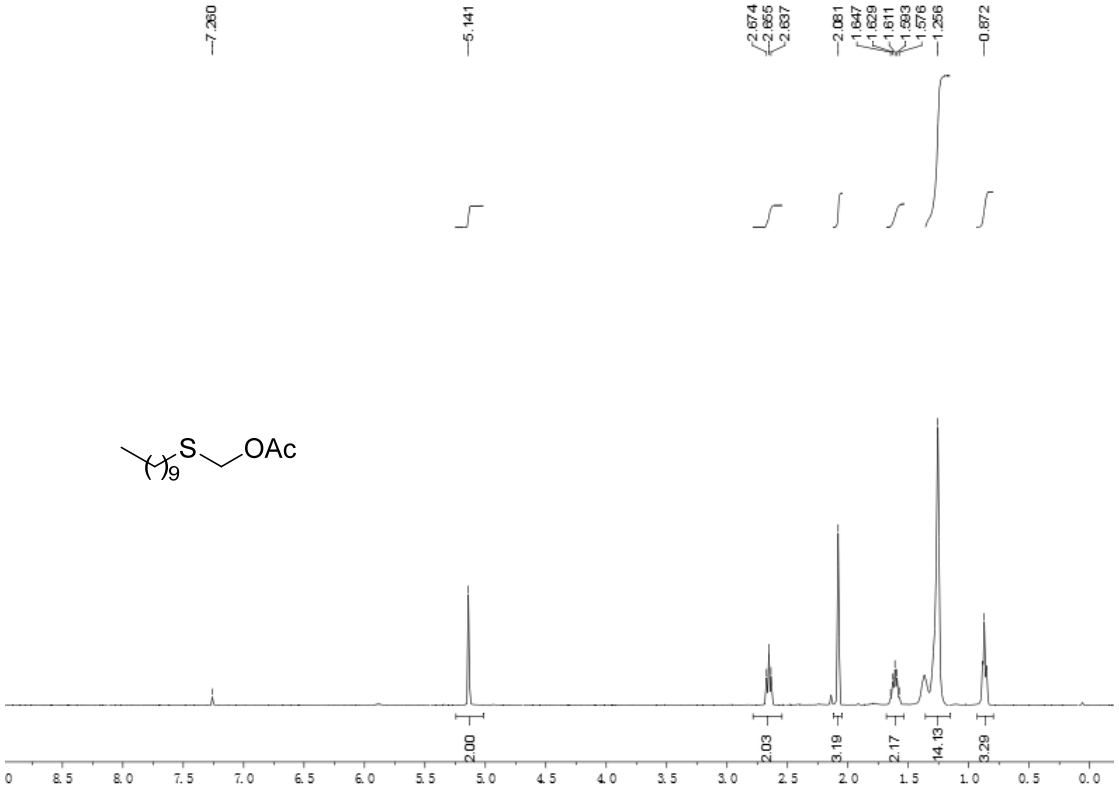


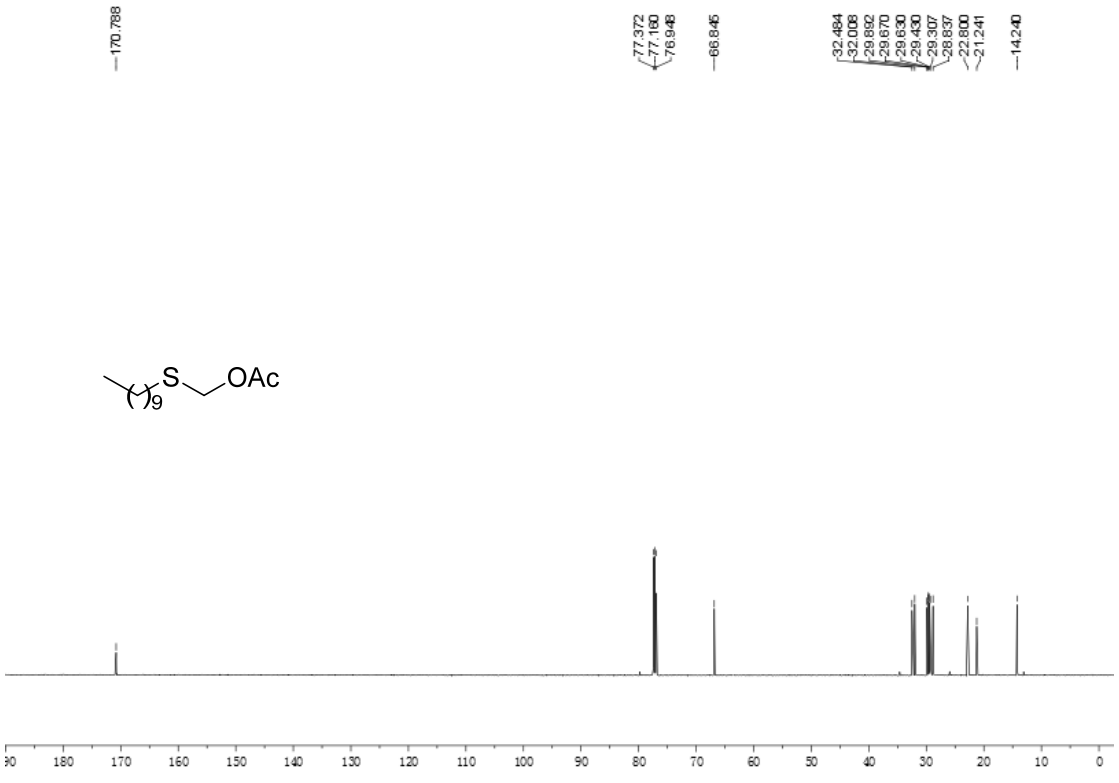
(thiophen-2-ylthio)methyl acetate(2r)



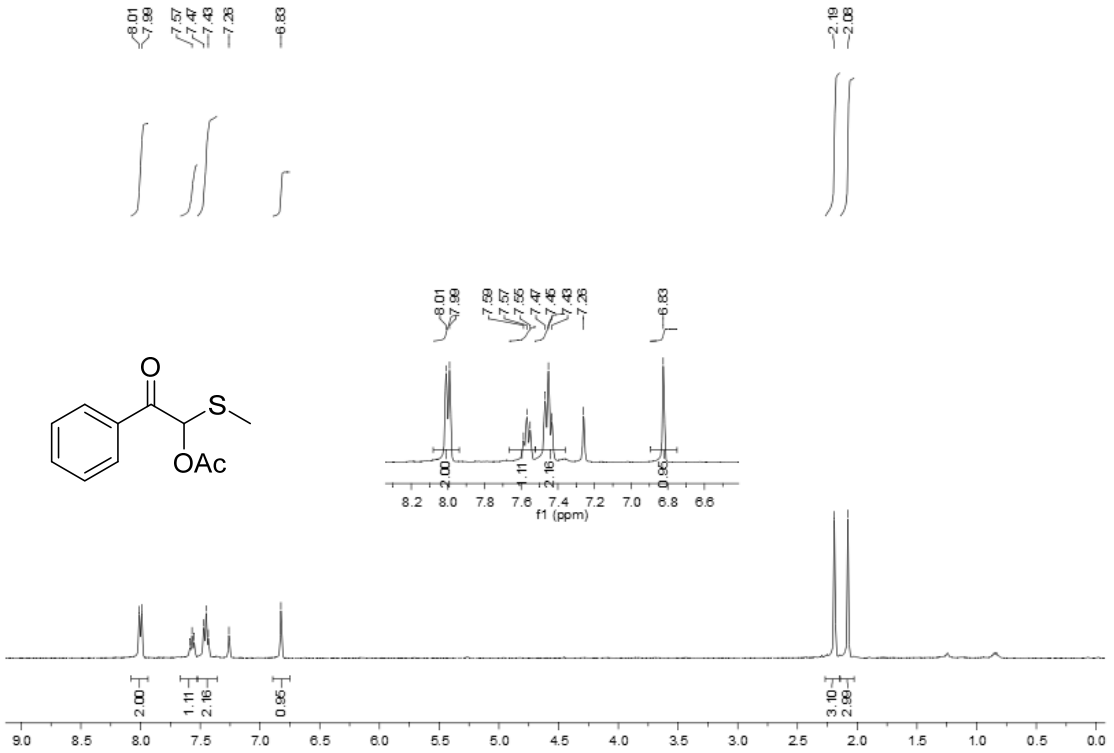


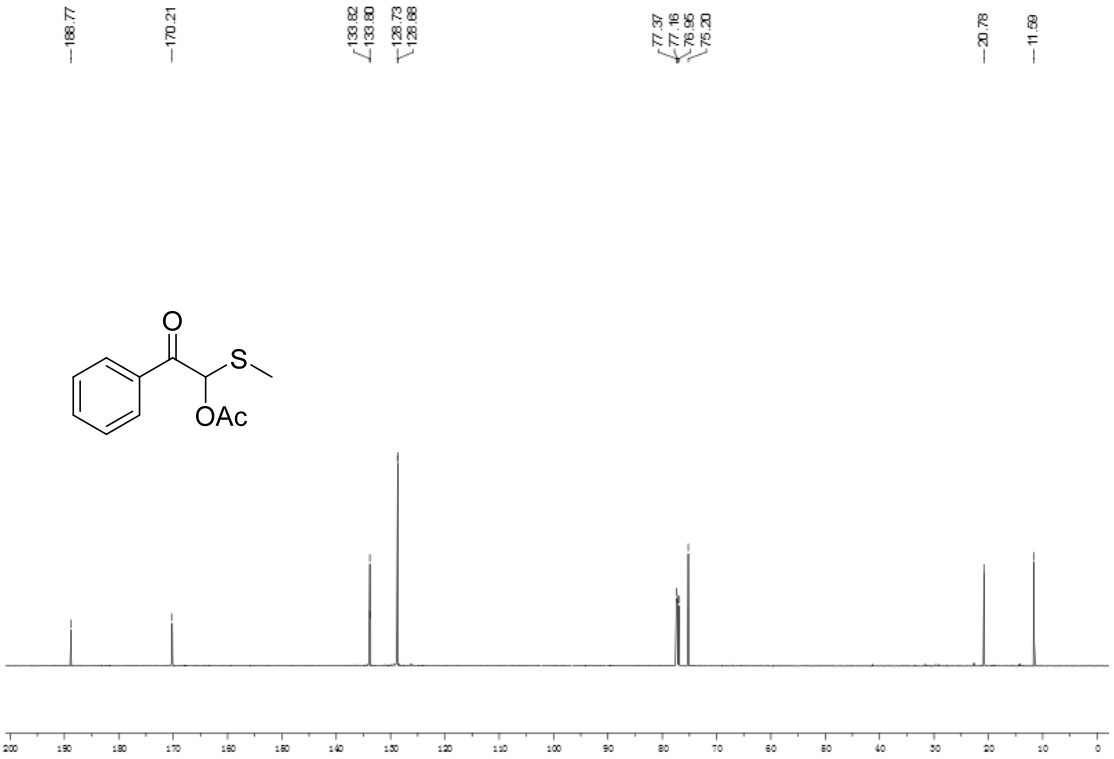
(decylthio)methyl acetate(2s)



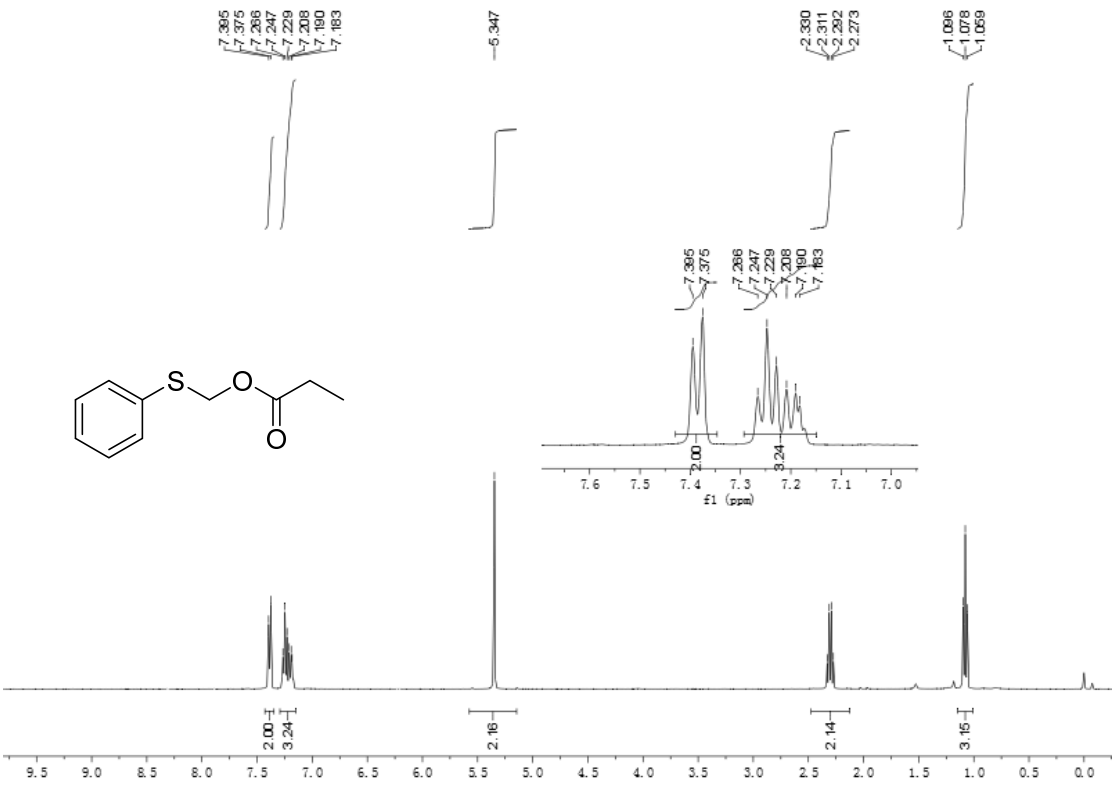


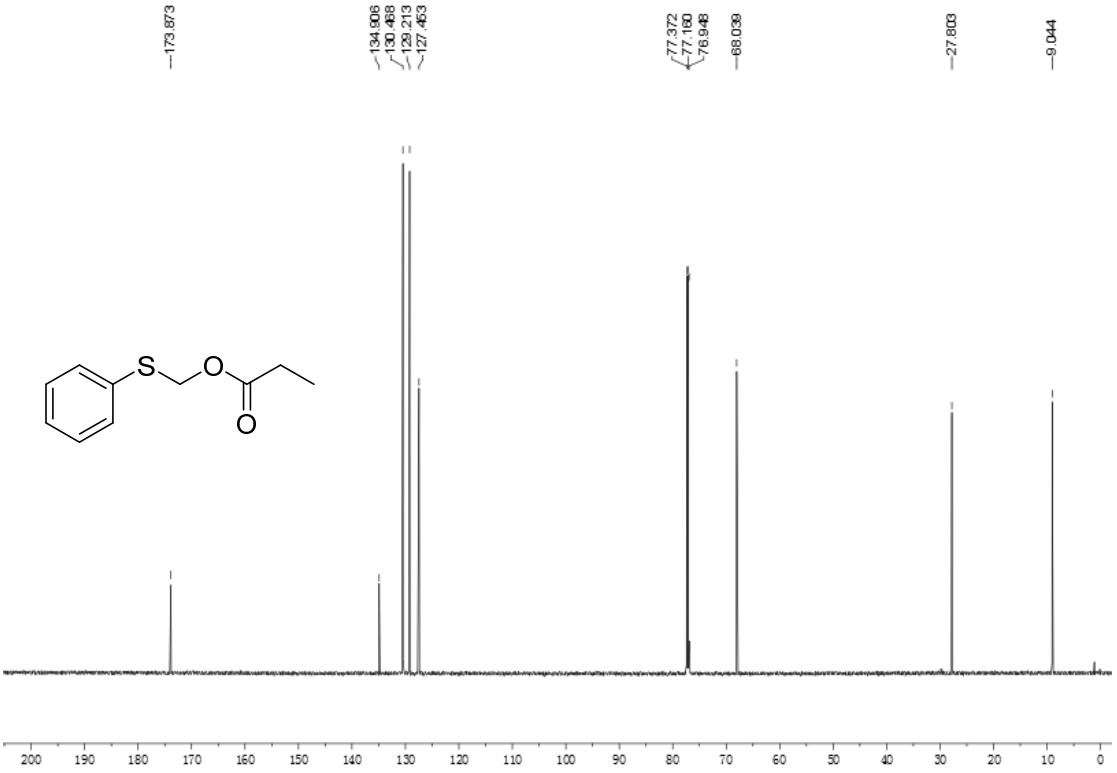
1-(methylthio)-2-oxo-2-phenylethyl acetate(2t)



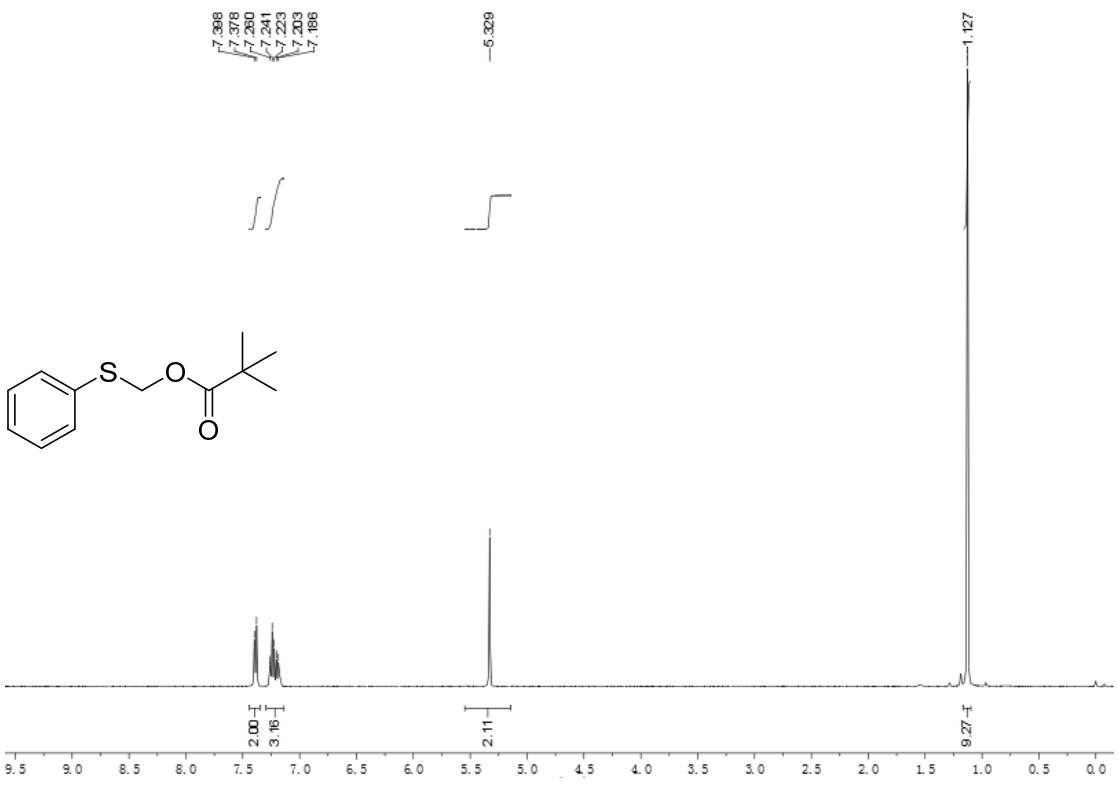


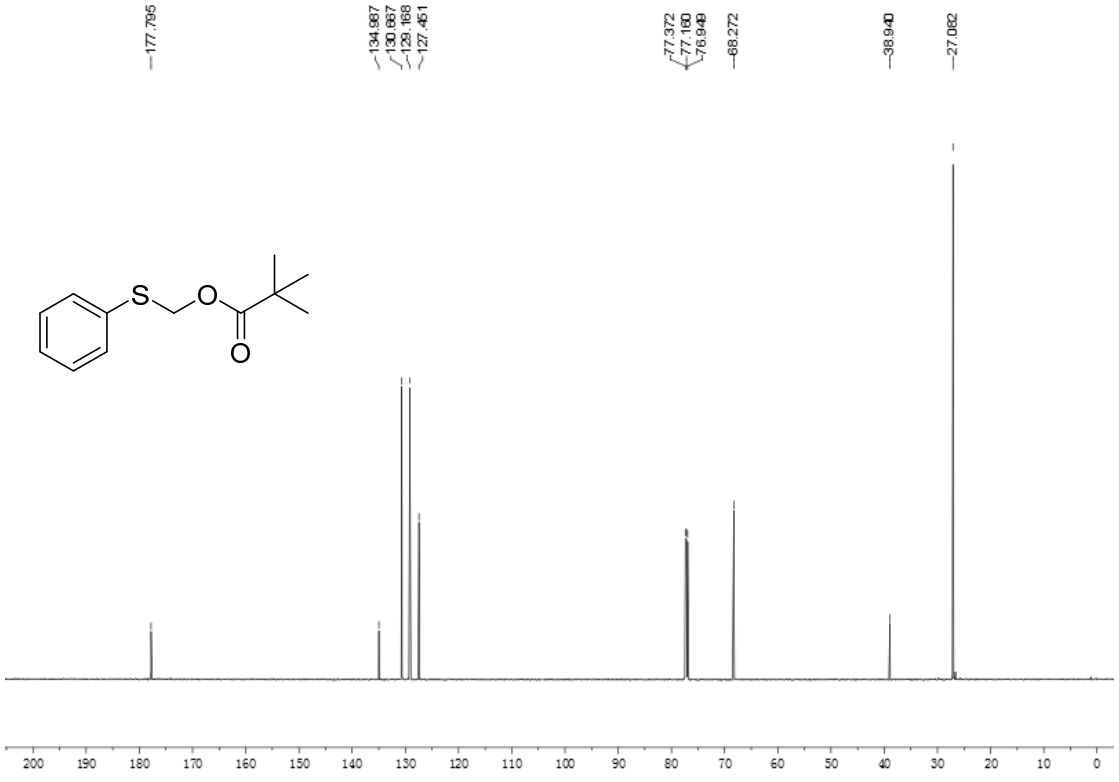
(phenylthio)methyl propionate(3aa)



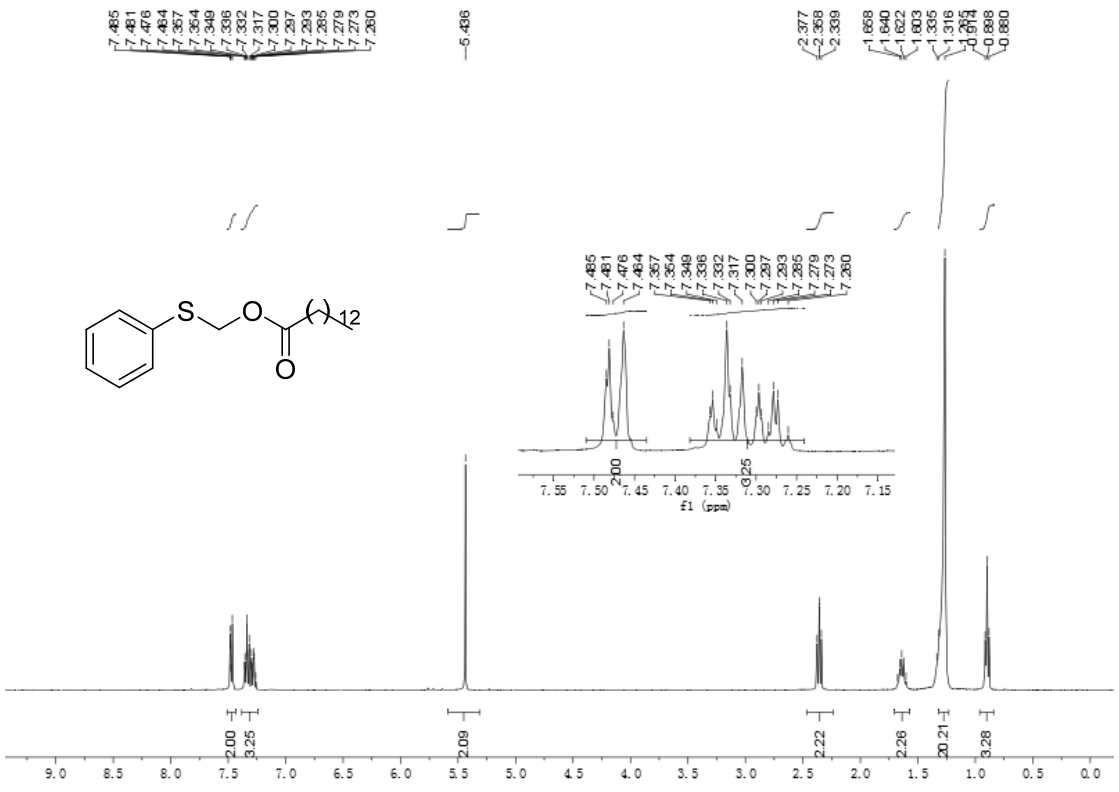


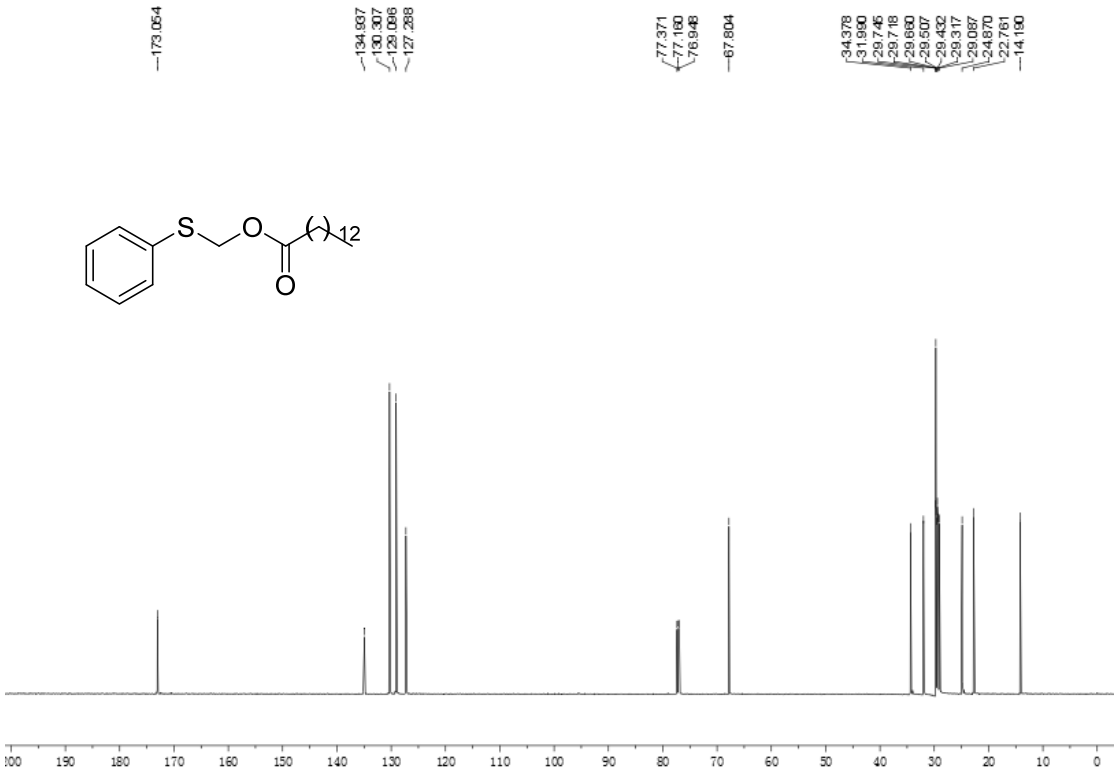
(phenylthio)methyl pivalate(3ab)



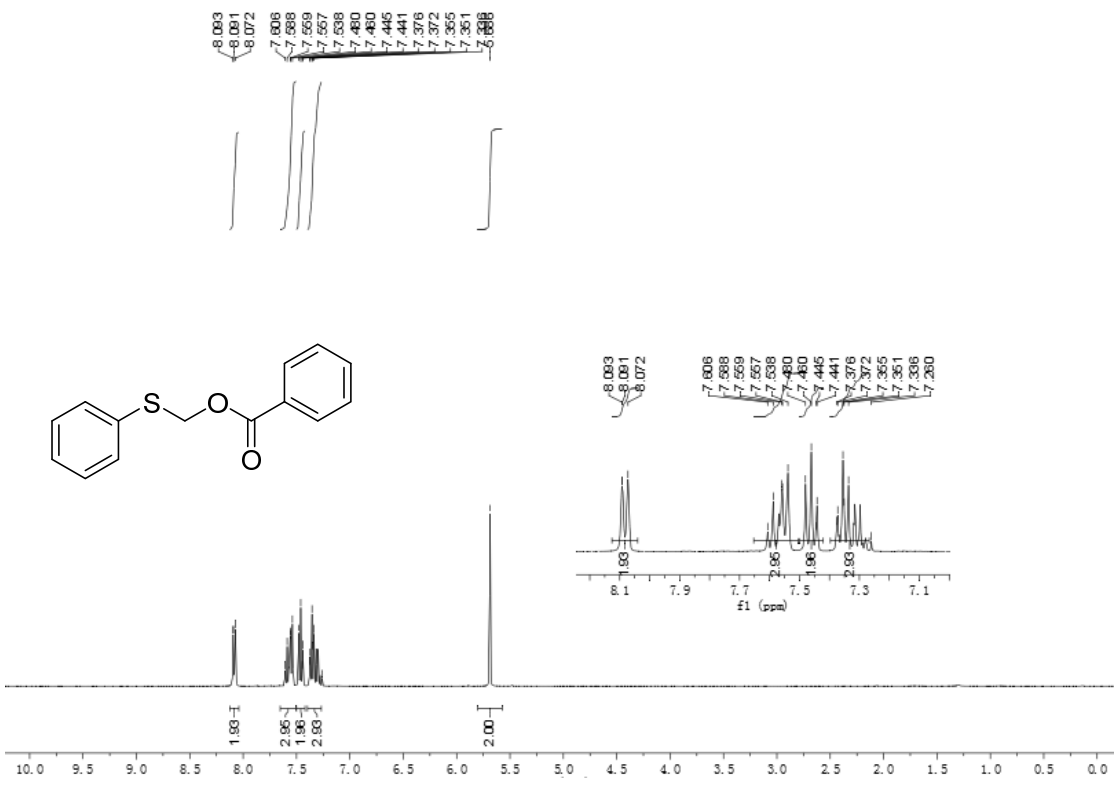


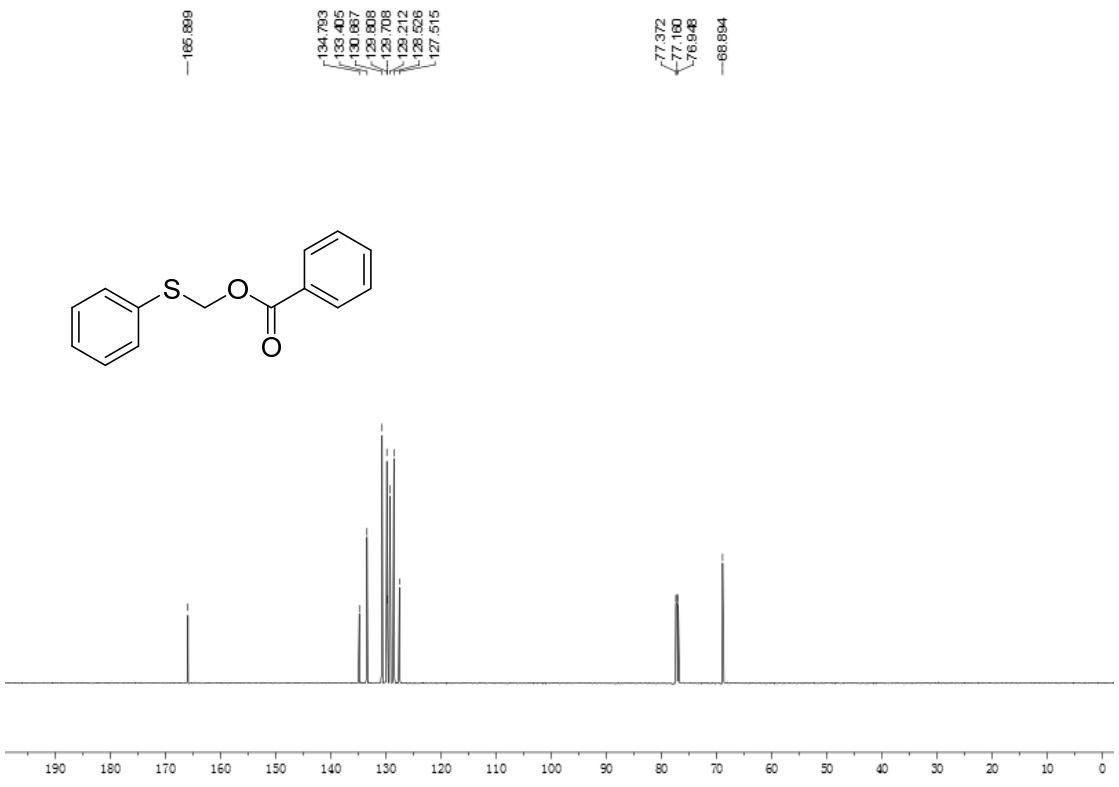
(phenylthio)methyl tetradecanoate(3ac)



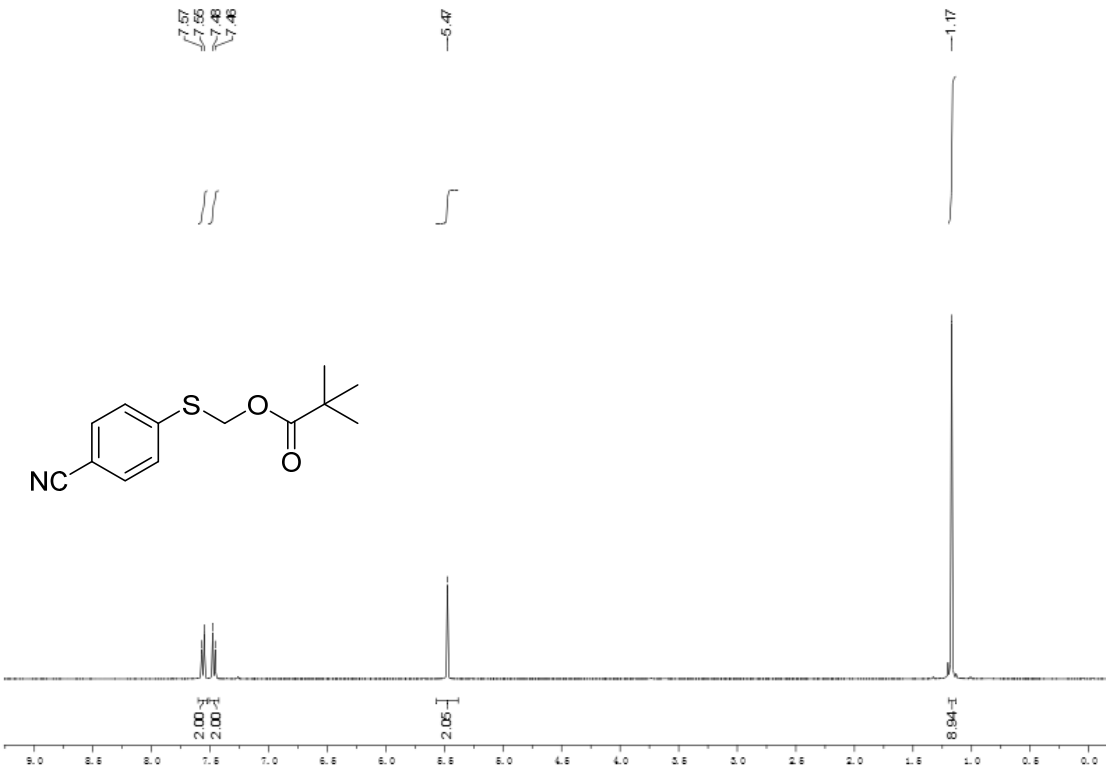


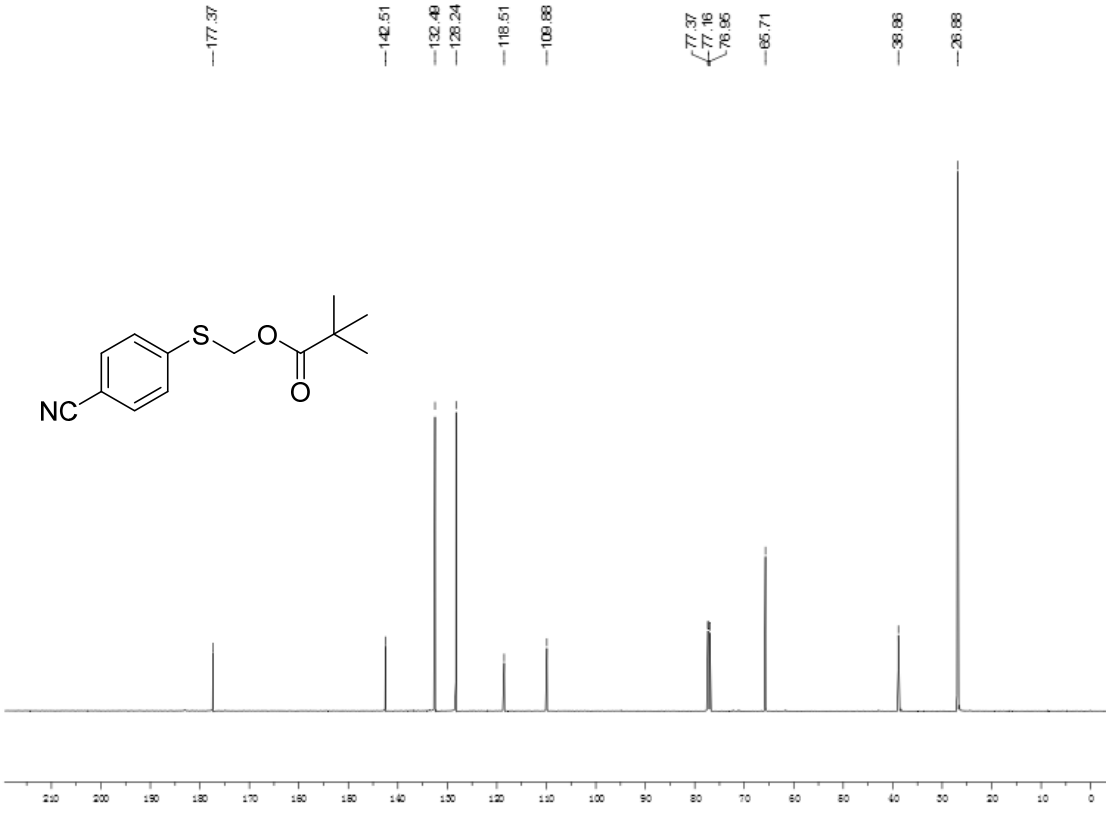
(phenylthio)methyl benzoate(3ad)



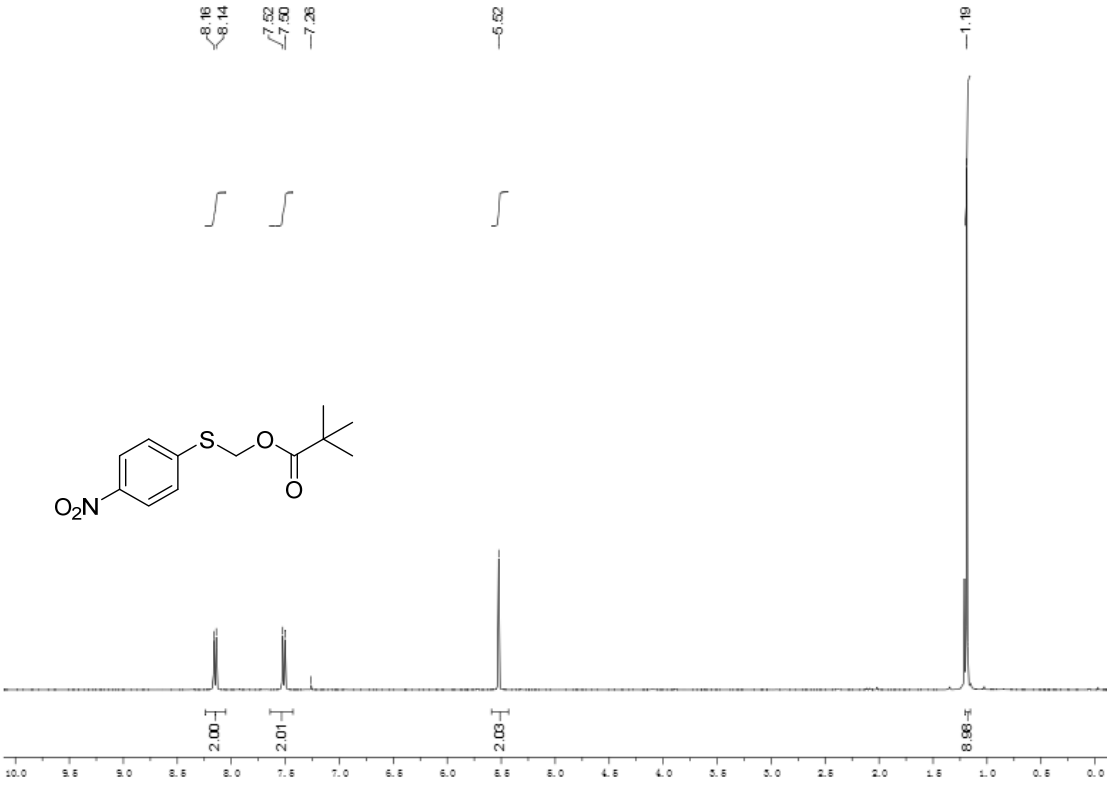


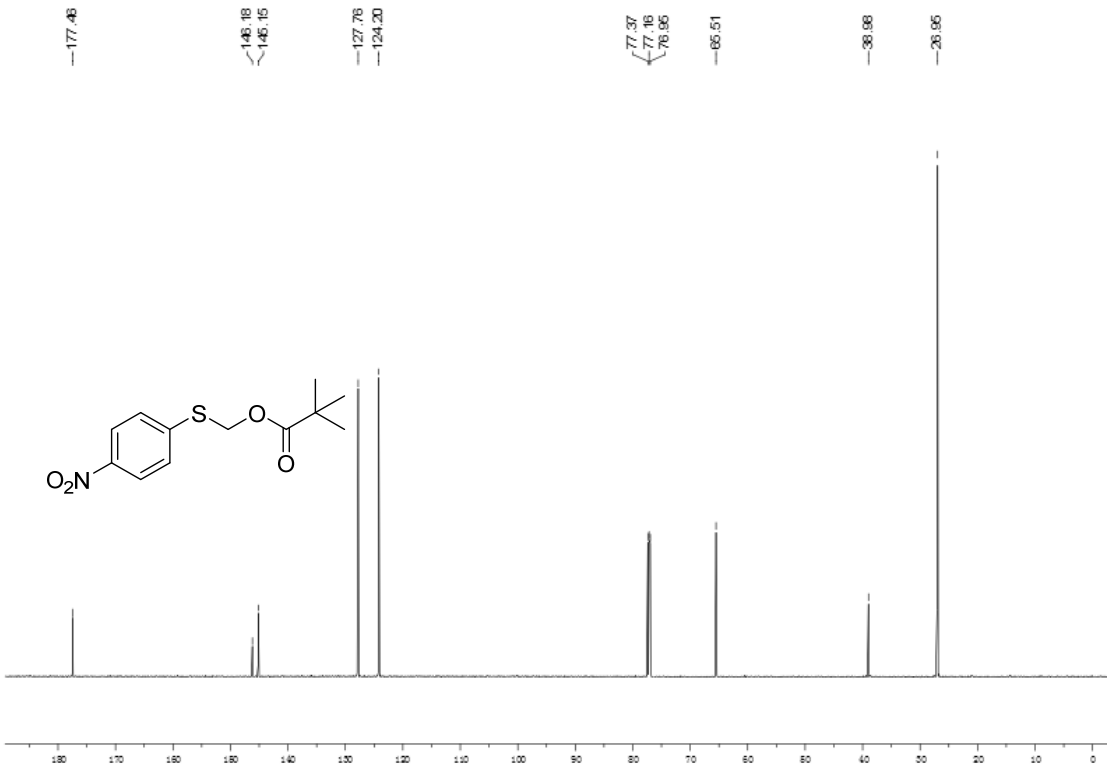
((4-cyanophenyl)thio)methyl pivalate (3eb)





((4-nitrophenyl)thio)methyl pivalate(3fb)





^{13}C NMR of mechanism detecting experiment