Electronic Supplementary Information

Amide-assisted α-C(sp^3)–H acyloxyation of organic sulfides to access α-acyloxy sulfides

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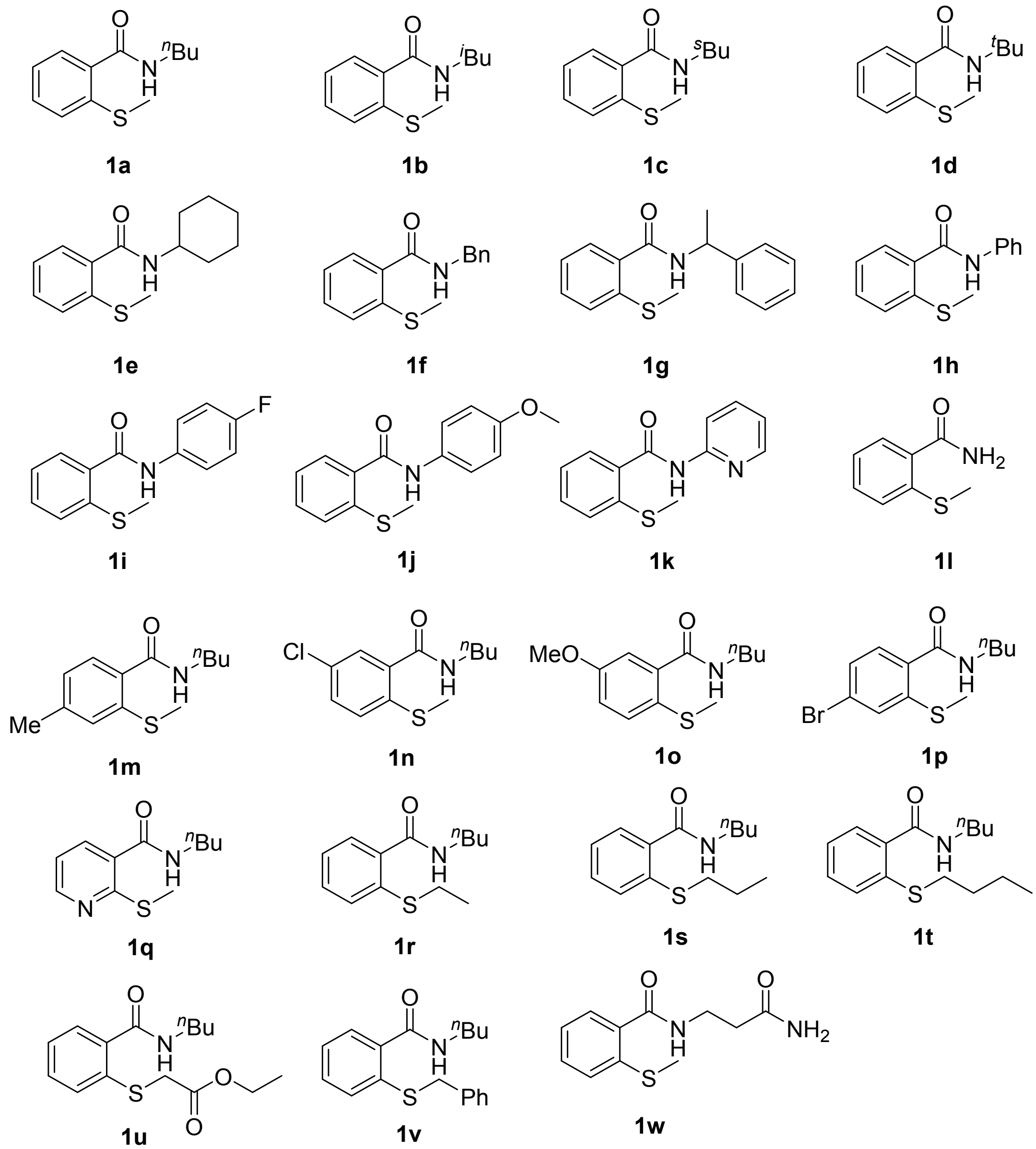
I. General Information

All the solvents and commercially available reagents were purchased and used directly. Thin layer chromatography (TLC) was performed on EMD precoated plates (silica gel 60 F254, Art 5715) and visualized by fluorescence quenching under UV light. Column chromatography was performed on EMD Silica Gel 60 (200–300 Mesh) using a forced flow of 0.5–1.0 bar. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AVANCE Ⅲ–300 or 400 spectrometer. ^{1}H NMR data was reported as: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR data was reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). Mass (HRMS) analysis was obtained using Agilent 6200 Accurate-Mass TOF LC/MS system with Electrospray Ionization (ESI). Melting points were measured by an X4-A microscopic melting point apparatus.

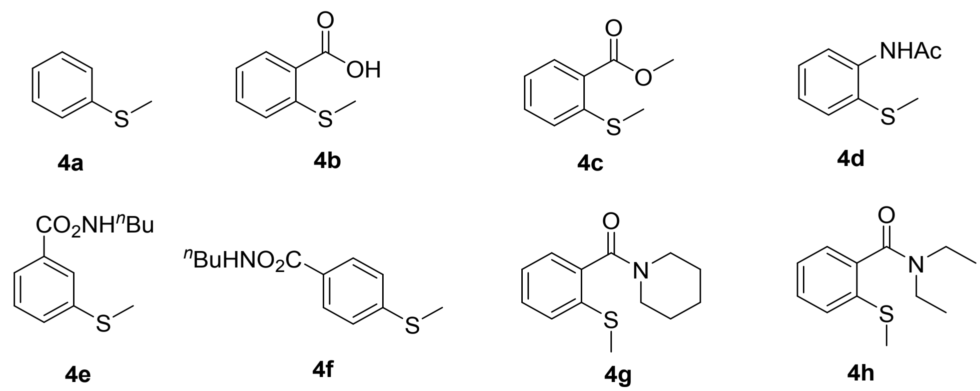
II. Experimental Section

1. Starting materials:



Scheme S1. 2-Alkylthiobenzamide **1**

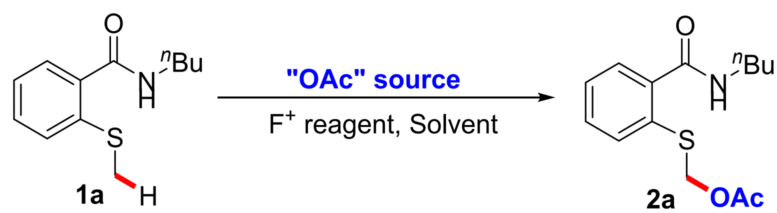
2-Alkylthiobenzamides (**1a-k** and **1m-w**) were prepared from commercial 2-(methylthio)benzoic acid (2.0 mmol) and the corresponding amines (3.0 mmol) in DCM at room temperature according to the reported procedure.[1] 2-Alkylthiobenzamide (**1l**) was prepared from commercial 2-(methylthio)benzoic acid (2.0 mmol) and the corresponding ammonium hydroxide (1.5 mL) according to the reported procedure.[2]



Scheme S2. Aryl methyl sulfide **4**

Aryl methyl sulfides (**4a-d**) were purchased from Energy-chemical, Adamas-beta®, TCI, J&K@, Sigma-Aldrich, Chemieliva Pharmaceutical or Enamine. Aryl methyl sulfides (**4e-h**) were prepared from commercial methylthiobenzoic acids (2.0 mmol) and corresponding amines (3.0 mmol) in DCM at room temperature according to the reported procedure.[1]

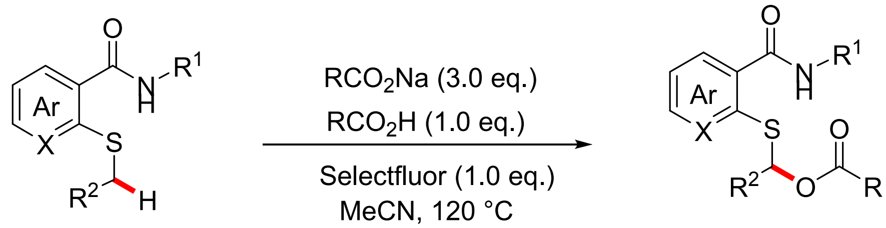
2. Optimization of the reaction conditions



A 30 mL Schlenk tube was charged with *N*-butyl-2-(methylthio)benzamide **1a** (0.2 mmol), electrophilic fluorinating reagent (0.1 ~ 0.4 mmol), "OAc" source (0.2 ~ 1.2 mmol) and solvent (2.0 mL). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo, and the crude product was analyzed by ^1H NMR in

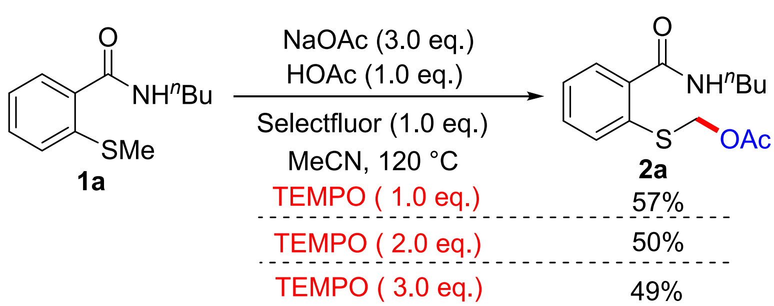
$CDCl_3$. Yields are based on **1a**, determined by crude ^1H NMR using dibromomethane as the internal standard. And the residue was purified by flash chromatography on silica gel to yield the product **2a**.

3. General procedure for the scope study

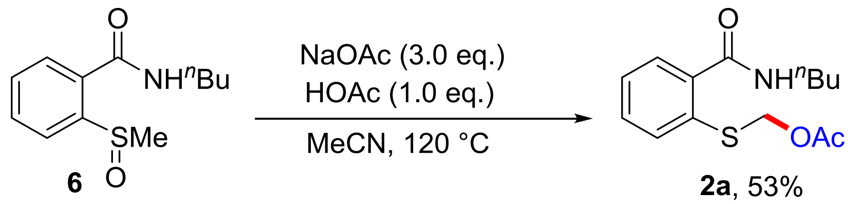


A 30 mL Schlenk tube was charged with 2-alkylthiobenzamides **1** (0.2 mmol), Selectfluor (0.2 mmol, 70.9 mg), carboxylic acid sodium salt (0.6mmol), carboxylic acid (0.2 mmol) and MeCN (2.0 mL). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the desired products **2** and **3**.

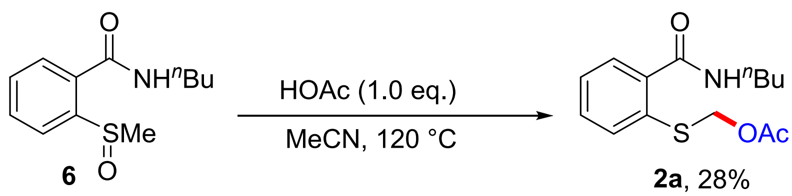
4. Mechanistic studies



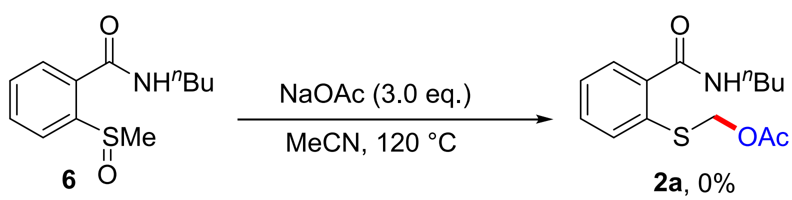
A 30 mL Schlenk tube was charged with *N*-butyl-2-(methylthio)benzamide **1a** (0.2 mmol), TEMPO (0.2 ~ 0.6 mmol), Selectfluor (0.2 mmol, 70.9 mg), NaOAc (0.6 mmol, 49.2 mg), HOAc (0.2 mmol, 11.4 μL) and MeCN (2.0 mL). The tube was then sealed and stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The crude product was purified by flash chromatography on silica gel to yield the product **2a**.



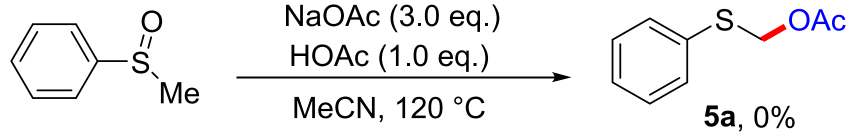
A 30 mL Schlenk tube was charged with *N*-butyl-2-(methylsulfinyl)benzamide **6** (0.2 mmol), NaOAc (0.6 mmol, 49.2 mg), HOAc (0.2 mmol, 11.4 μL) and MeCN (2.0 mL). The tube was then sealed and stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The crude product was purified by flash chromatography on silica gel to yield the product **2a** (29.8 mg, 53%).



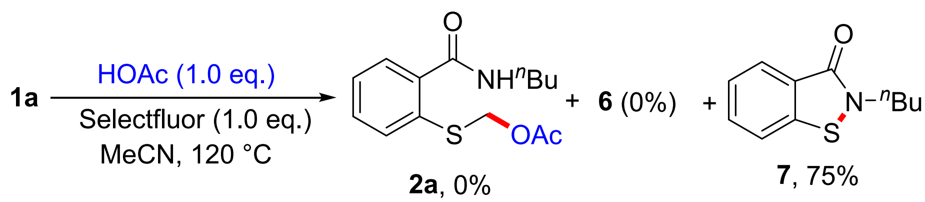
A 30 mL Schlenk tube was charged with *N*-butyl-2-(methylsulfinyl)benzamide **6** (0.2 mmol), HOAc (0.2 mmol, 11.4 μL) and MeCN (2.0 mL). The tube was then sealed and stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The crude product was purified by flash chromatography on silica gel to yield the product **2a** (15.7 mg, 28%).



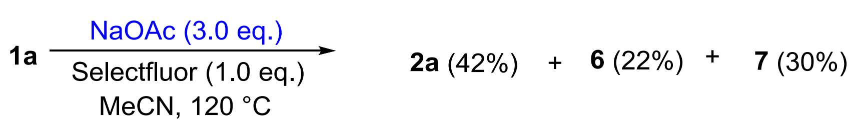
A 30 mL Schlenk tube was charged with *N*-butyl-2-(methylsulfinyl)benzamide **6** (0.2 mmol), NaOAc (0.6 mmol, 49.2 mg) and MeCN (2.0 mL). The tube was then sealed and stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. No desired product **2a** was detected by GC-MS and ^{1}H NMR.



A 30 mL Schlenk tube was charged with (methylsulfinyl)benzene (0.2 mmol), NaOAc (0.6 mmol, 49.2 mg), HOAc (0.2 mmol, 11.4 μL) and MeCN (2.0 mL). The tube was then sealed and stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. No desired product **5a** was detected by GC-MS and ^{1}H NMR.

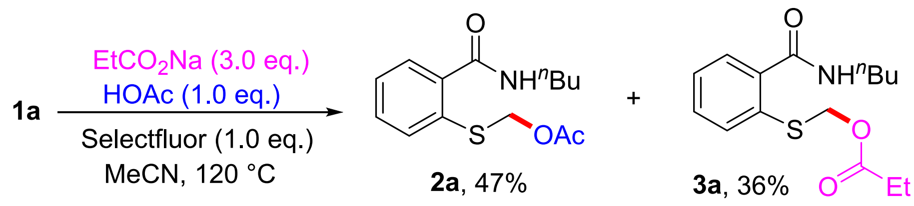


A 30 mL Schlenk tube was charged with *N*-butyl-2-(methylthio)benzamide **1a** (0.2 mmol), Selectfluor (0.2 mmol, 70.9 mg), HOAc (0.2 mmol, 11.4 μL) and MeCN (2.0 mL). The tube was then sealed and stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The crude product was purified by flash chromatography on silica gel, cyclic product **7** (31.1 mg, 75%) was isolated.

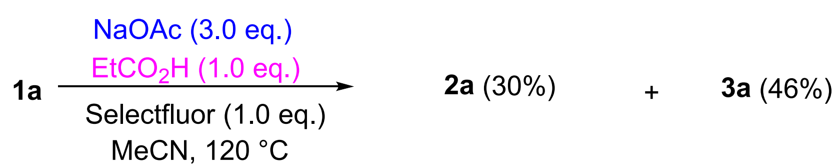


A 30 mL Schlenk tube was charged with *N*-butyl-2-(methylthio)benzamide **1a** (0.2 mmol), Selectfluor (0.2 mmol, 70.9 mg), NaOAc (0.6 mmol, 49.2 mg) and MeCN (2.0 mL). The tube was then sealed and stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The crude product was purified by flash chromatography on silica gel to yield the desired product

2a (23.6 mg, 42%), *N*-butyl-2-(methylsulfinyl)benzamide **6** (10.5 mg, 22%) and cyclic product **7** (12.4 mg, 30%).

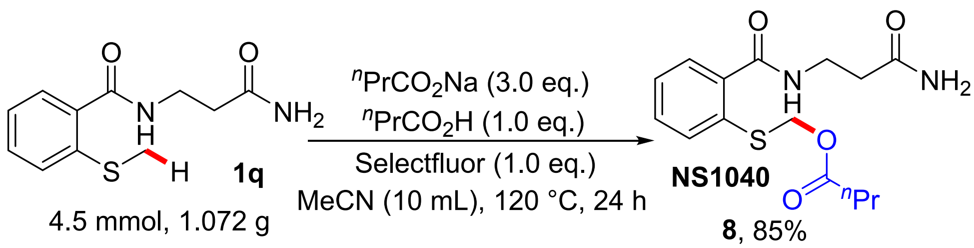


A 30 mL Schlenk tube was charged with *N*-butyl-2-(methylthio)benzamide **1a** (0.2 mmol), Selectfluor (0.2 mmol, 70.9 mg), $EtCO_2Na$ (0.6 mmol, 57.6 mg), HOAc (0.2 mmol, 11.4 µL) and MeCN (2.0 mL). The tube was then sealed and stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The crude product was analyzed by ^1H NMR. Yields are based on **1a**, determined by crude ^1H NMR using dibromomethane as the internal standard. The desired products **2a** and **3a** were analyzed by crude ^1H NMR.



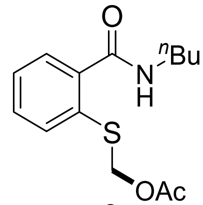
A 30 mL Schlenk tube was charged with *N*-butyl-2-(methylthio)benzamide **1a** (0.2 mmol), Selectfluor (0.2 mmol, 70.9 mg), NaOAc (0.6 mmol, 49.2 mg), $EtCO_2H$ (0.2 mmol, 15.0 µL) and MeCN (2.0 mL). The tube was then sealed and stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The crude product was analyzed by ^1H NMR. Yields are based on **1a**, determined by crude ^1H NMR using dibromomethane as the internal standard. The desired products **2a** and **3a** were analyzed by crude ^1H NMR.

5. The gram-scale reaction for the synthesis of NS1040



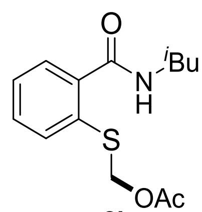
A 100 mL Schlenk tube was charged with *N*-(3-amino-3-oxopropyl)-2-(methylthio)benzamide **1q** (1.072 g, 4.5 mmol), Selectfluor (4.5 mmol, 1.595 g), *n*-$PrCO_2Na$ (1.486 g, 13.5 mmol), *n*-$PrCO_2H$ (411.3 µL ,4.5 mmol) and MeCN (10.0 mL). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The residue was then diluted with DCM (15 mL). Next, the diluted solution was washed with saturated $NaHCO_3$ solution (3 × 5 mL), and the aqueous layer was extracted with DCM (3 × 5 mL). The combined organic layers were washed with H_2O (3 × 5 mL) and brine (5 mL), then dried over anhydrous Na_2SO_4 and concentrated in vacuo. Finally, the solid was washed with *n*-hexane (5 mL) to yield the desired product **8** (1.241 g, 85%).

6. Data of compounds



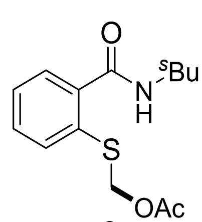
2a

Yellow oil, 49.5 mg, yield: 88%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H), 7.33 – 7.20 (m, 2H), 6.22 (br, 1H), 5.32 (s, 2H), 3.36 (q, J = 7.2 Hz, 2H), 2.01 (s, 3H), 1.55 – 1.50 (m, 2H), 1.38 – 1.31 (m, 2H), 0.89 (t, J = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.26, 168.02, 138.40, 132.38, 131.77, 130.64, 128.49, 127.72, 68.00, 39.83, 31.54, 21.00, 20.19, 13.77. HRMS (ESI, *m/z*): calcd. for $C_{14}H_{20}NO_3S$ $[M+H]^+$: 282.1158, found: 282.1154.



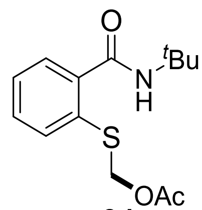
2b

Yellow oil, 34.3 mg, yield: 61%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H), 7.35 – 7.20 (m, 2H), 6.25 (br, 1H), 5.32 (s, 2H), 3.20 (t, J = 6.4 Hz, 2H), 2.01 (s, 3H), 1.87 – 1.78 (m, 1H), 0.92 (d, J = 6.7 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.25, 168.10, 138.45, 132.40, 131.73, 130.65, 128.49, 127.71, 67.98, 47.43, 28.56, 21.03, 20.28. HRMS (ESI, *m/z*): calcd. for $C_{14}H_{20}NO_3S$ $[M+H]^+$: 282.1158, found: 282.1155.



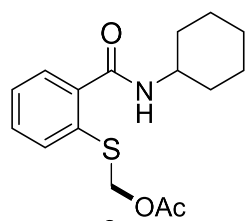
2c

White solid, 29.8 mg, yield: 53%, m.p. 93 – 95 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 2H), 7.35 – 7.20 (m, 2H), 5.90 (br, 1H), 5.33 (s, 2H), 4.09 – 3.99 (m, 1H), 2.02 (s, 3H), 1.53 – 1.48 (m, 2H), 1.16 (d, J = 6.7 Hz, 3H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.26, 167.44, 138.70, 132.34, 131.65, 130.55, 128.37, 127.68, 68.02, 47.37, 29.69, 21.04, 20.35, 10.49. HRMS (ESI, *m/z*): calcd. for $C_{14}H_{20}NO_3S$ $[M+H]^+$: 282.1158, found: 282.1157.



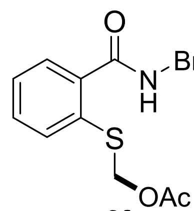
2d

Yellow oil, 33.7 mg, yield: 60%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.41 (m, 2H), 7.31 – 7.20 (m, 2H), 5.88 (br, 1H), 5.33 (s, 2H), 2.02 (s, 3H), 1.39 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.28, 167.43, 139.49, 132.09, 131.50, 130.33, 128.21, 127.64, 67.97, 52.11, 28.79, 21.06. HRMS (ESI, *m/z*): calcd. for $C_{14}H_{20}NO_3S$ $[M+H]^+$: 282.1158, found: 282.1158.



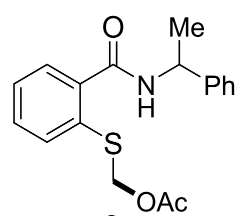
2e

White solid, 35.1 mg, yield: 57 %, m.p. 105 – 107 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 2H), 7.35 – 7.20 (m, 2H), 6.02 (br, 1H), 5.33 (s, 2H), 3.96 – 3.86 (m, 1H), 2.02 – 1.95 (m, 5H), 1.71 – 1.54 (m, 3H), 1.38 – 1.28 (m, 2H), 1.23 – 1.11 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.26, 167.11, 138.60, 132.30, 131.71, 130.56, 128.46, 127.71, 68.01, 48.90, 33.02, 25.55, 24.84, 21.05. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{22}NO_3S$ [M+H]$^+$: 308.1315, found: 308.1310.



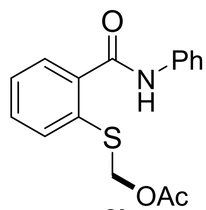
2f

White solid, 51.7 mg, yield: 82%, m.p. 86 – 87 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 2H), 7.33 – 7.19 (m, 7H), 6.54 (br, 1H), 5.28 (s, 2H), 4.54 (d, *J* = 5.7 Hz, 2H), 1.92 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.23, 167.94, 138.08, 137.84, 132.57, 132.00, 130.86, 128.78, 128.57, 128.02, 127.80, 127.67, 68.12, 44.19, 20.91. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{18}NO_3S$ [M+H]$^+$: 316.1002, found: 316.0996.



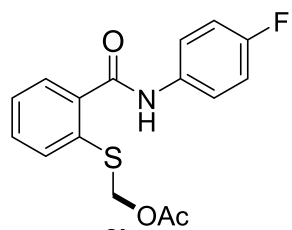
2g

White solid, 49.4 mg, yield: 75%, m.p. 81 – 83 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.44 (m, 2H), 7.33 – 7.19 (m, 7H), 6.56 (br, 1H), 5.30 – 5.20 (m, 3H), 1.93 (s, 3H), 1.51 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.26, 167.11, 142.84, 138.22, 132.39, 131.98, 130.74, 128.72, 128.62, 127.79, 127.49, 126.37, 68.07, 49.50, 21.69, 20.95. HRMS (ESI, *m/z*): calcd. for $C_{18}H_{20}NO_3S$ [M+H]$^+$: 330.1158, found: 330.1154.



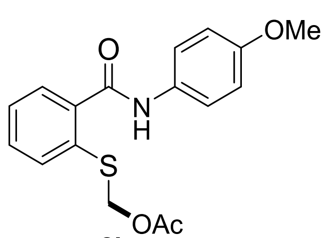
2h

Brown solid, 36.1 mg, yield: 60%, m.p. 106 – 107 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (br, 1H), 7.65 – 7.54 (m, 4H), 7.37– 7.25 (m, 4H), 7.18 – 7.04 (m, 1H), 5.29 (s, 2H), 1.89 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.33, 165.97, 138.43, 137.81, 132.90, 132.14, 131.19, 129.15, 129.11, 128.31, 124.72, 120.08, 68.32, 20.89. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{15}NNaO_3S$ $[M+Na]^+$: 324.0665, found: 324.0665.



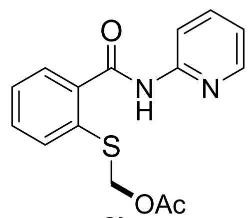
2i

White solid, 40.2 mg, yield: 63%, m.p. 116 – 118 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 (br, 1H), 7.65 – 7.50 (m, 4H), 7.41 – 7.29 (m, 2H), 6.99 – 6.94 (m, 2H), 5.30 (s, 2H), 1.90 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.29, 165.91, 159.59 (d, J = 244.0 Hz), 138.15, 133.81, 132.92, 132.09, 131.31, 129.17, 128.34, 121.89 (d, J = 7.8 Hz), 115.75 (d, J = 22.5 Hz), 68.28, 20.89. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{15}FNO_3S$ $[M+H]^+$: 320.0751, found: 320.0741.



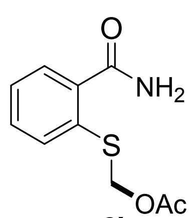
2j

White solid, 47.7 mg, yield: 72%, m.p. 106 – 108 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (br, 1H), 7.70 – 7.65 (m, 1H), 7.63 – 7.58 (m, 1H), 7.55 – 7.51 (m, 2H), 7.46 – 7.34 (m, 2H), 6.89 – 6.84 (m, 2H), 5.36 (s, 2H), 3.79 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.32, 165.81, 156.65, 138.44, 132.68, 132.21, 131.06, 130.94, 129.05, 128.18, 121.88, 114.20, 68.28, 55.52, 20.92. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{17}NNaO_4S$ $[M+Na]^+$: 354.0770, found: 354.0763.



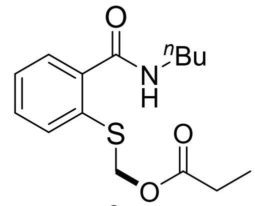
2k

White solid, 28.4 mg, yield: 47%, m.p. 131 – 133 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.85 (br, 1H), 8.31 (d, *J* = 8.5 Hz, 1H), 7.65 – 7.55 (m, 4H), 7.42 – 7.25 (m, 2H), 6.87 – 6.83 (m, 1H), 5.32 (s, 2H), 1.97 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.22, 166.77, 151.61, 147.44, 138.60, 138.04, 133.43, 131.83, 131.27, 128.50, 127.77, 119.90, 114.53, 68.02, 20.98. HRMS (ESI, *m/z*): calcd. for $C_{15}H_{15}N_2O_3S$ $[M+H]^+$: 303.0798, found: 303.0796.



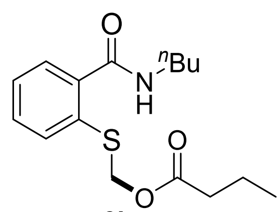
2l

White solid, 24.8 mg, yield: 55%, m.p. 98 – 100 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 – 7.64 (m, 2H), 7.49 – 7.35 (m, 2H), 6.43 (br, 1H), 6.08 (br, 1H), 5.43 (s, 2H), 2.12 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ170.22, 169.73, 136.60, 132.97, 132.02, 131.34, 129.02, 127.77, 67.94, 21.00. HRMS (ESI, *m/z*): calcd. for $C_{10}H_{11}NaNO_3S$ $[M+Na]^+$: 248.0352, found: 248.0342.



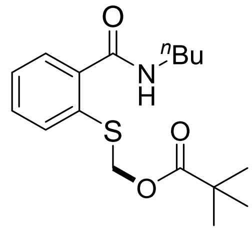
3a

Yellow oil, 49.0 mg, yield: 83%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.34 – 7.21 (m, 2H), 6.30 (br, 1H), 5.33 (s, 2H), 3.35 (q, *J* = 6.6 Hz, 2H), 2.32 – 2.25 (m, 2H), 1.54 – 1.49 (m, 2H), 1.35 – 1.33 (m, 2H), 1.05 (t, *J* = 7.6 Hz, 3H), 0.88 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.67, 167.02, 137.23, 131.50, 130.62, 129.58, 127.43, 126.59, 66.81, 38.80, 30.50, 26.56, 19.16, 12.76, 7.84. HRMS (ESI, *m/z*): calcd. for $C_{15}H_{22}NO_3S$ $[M+H]^+$: 296.1315, found: 296.1311.



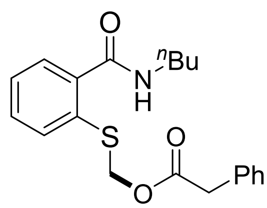
3b

Yellow oil, 49.5 mg, yield: 80%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.34 – 7.20 (m, 2H), 6.23 (br, 1H), 5.33 (s, 2H), 3.39 – 3.32 (m, 2H), 2.26 – 2.21 (m, 2H), 1.58 – 1.53 (m, 4H), 1.39 – 1.30 (m, 2H), 0.91 – 0.83 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.88, 168.01, 138.22, 132.61, 131.53, 130.59, 128.45, 127.57, 67.73, 39.82, 36.10, 31.55, 20.20, 18.24, 13.79, 13.60. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{24}NO_3S$ $[M+H]^+$: 310.1471, found: 310.1466.



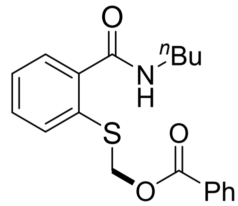
3c

Yellow oil, 48.5 mg, yield: 75%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.34 – 7.20 (m, 2H), 6.22 (br, 1H), 5.34 (s, 2H), 3.40 – 3.33 (m, 2H), 1.55 – 1.48 (m, 2H), 1.38 – 1.31 (m, 2H), 1.11 (s, 9H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.67, 168.02, 138.02, 132.82, 131.42, 130.52, 128.43, 127.48, 67.87, 39.84, 38.85, 31.56, 26.98, 20.21, 13.80. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{26}NO_3S$ $[M+H]^+$: 324.1628, found: 324.1627.



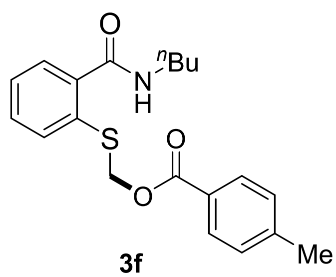
3d

White solid, 64.3 mg, yield: 90%, m.p. 90 – 92 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.41 (m, 1H), 7.31 – 7.15 (m, 8H), 6.06 (br, 1H), 5.33 (s, 2H), 3.57 (s, 2H), 3.33 (q, J = 6.2 Hz, 2H), 1.54 – 1.45 (m, 2H), 1.36 – 1.27 (m, 2H), 0.87 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.74, 168.03, 138.51, 133.37, 132.14, 131.93, 130.53, 129.34, 128.66, 128.30, 127.68, 127.26, 68.34, 41.37, 39.82, 31.56, 20.20, 13.81. HRMS (ESI, *m/z*): calcd. for $C_{20}H_{24}NO_3S$ $[M+H]^+$: 358.1471, found: 358.1468.



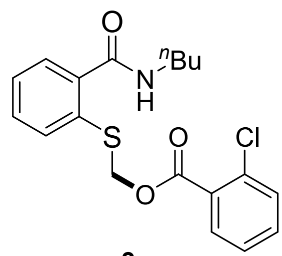
3e

White solid, 48.8 mg, yield: 71%, m.p. 96 – 97 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 – 7.94 (m, 2H), 7.59 – 7.49 (m, 3H), 7.40 – 7.27 (m, 4H), 6.17 (br, 1H), 5.60 (s, 2H), 3.34 – 3.27 (m, 2H), 1.49 – 1.44 (m, 2H), 1.34 – 1.26 (m, 2H), 0.85 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.98, 165.84, 138.51, 133.50, 132.39, 132.18, 130.71, 129.80, 129.46, 128.60, 128.54, 127.87, 68.89, 39.85, 31.51, 20.19, 13.76. HRMS (ESI, *m/z*): calcd. for $C_{19}H_{22}NO_3S$ $[M+H]^+$: 344.1315, found: 344.1308.



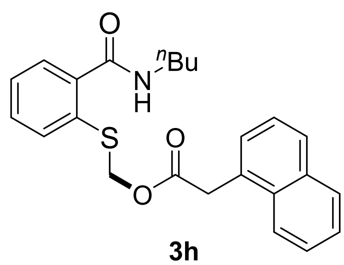
3f

White solid, 45.0 mg, yield: 63%, m.p. 101 – 103 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 – 7.82 (m, 2H), 7.59 – 7.50 (m, 2H), 7.33 – 7.16 (m, 4H), 6.19 (br, 1H), 5.57 (s, 2H), 3.30 (q, J = 6.6 Hz, 2H), 2.34 (s, 3H), 1.49 – 1.44 (m, 2H), 1.31 – 1.29 (m, 2H), 0.85 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.95, 165.88, 144.34, 138.50, 132.42, 132.22, 130.70, 129.84, 129.26, 128.62, 127.84, 126.69, 68.74, 39.85, 31.51, 21.75, 20.20, 13.78. HRMS (ESI, *m/z*): calcd. for $C_{20}H_{24}NO_3S$ $[M+H]^+$: 358.1471, found: 358.1468.



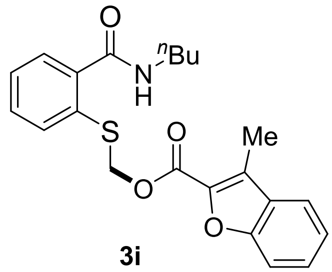
3g

White solid, 52.9 mg, yield: 70%, m.p. 193 – 194 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.50 – 7.48 (m, 1H), 7.39 – 7.19 (m, 5H), 6.12 (br, 1H), 5.61 (s, 2H), 3.34 (q, *J* = 6.6 Hz, 2H), 1.57 – 1.46 (m, 2H), 1.35 – 1.28 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.93, 163.72, 137.31, 133.02, 132.06, 131.44, 130.72, 130.21, 129.69, 128.07, 127.39, 126.71, 125.68, 68.16, 38.81, 30.49, 19.14, 12.73. HRMS (ESI, *m/z*): calcd. for $C_{19}H_{21}ClNO_3S$ $[M+H]^+$: 378.0925, found: 378.0920.



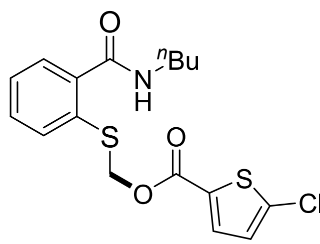
3h

White solid, 65.2 mg, yield: 80%, m.p. 110 – 111 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 – 7.71 (m, 3H), 7.42 – 7.32 (m, 5H), 7.19 – 7.05 (m, 3H), 5.91 (br, 1H), 5.32 (s, 2H), 4.03 (s, 2H), 3.34 – 3.27 (m, 2H), 1.49 – 1.42 (m, 2H), 1.34 – 1.27 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.74, 168.02, 138.32, 133.81, 131.98, 131.69, 130.41, 129.93, 128.74, 128.24, 128.19, 128.17, 127.55, 126.52, 125.89, 125.53, 123.78, 68.30, 39.80, 39.23, 31.53, 20.18, 13.80. HRMS (ESI, *m/z*): calcd. for $C_{24}H_{26}NO_3S$ $[M+H]^+$:408.1628, found: 408.1629.



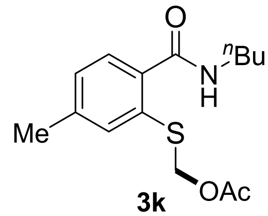
3i

White solid, 55.6 mg, yield: 70%, m.p. 106 – 108 °C.[1]H NMR (300 MHz, $CDCl_3$) δ 7.72 – 7.28 (m, 8H), 6.31 (br, 1H), 5.74 (s, 2H), 3.42 (q, *J* = 6.8 Hz, 2H), 2.57 (s, 3H), 1.60 – 1.52 (m, 2H), 1.42 – 1.35 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.05, 159.59, 154.56, 140.06, 138.99, 132.49, 131.96, 130.71, 128.89, 128.51, 128.30, 128.05, 127.21, 123.38, 121.30, 112.23, 69.21, 39.89, 31.54, 20.20, 13.76, 9.51. HRMS (ESI, *m/z*): calcd. for $C_{22}H_{24}NO_4S$ $[M+H]^+$: 398.1421, found: 398.1416.



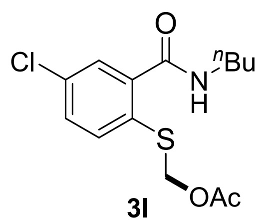
3j

White solid, 59.9 mg, yield: 78%, m.p. 107 – 108 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 3H), 7.36 – 7.24 (m, 2H), 6.87 (d, *J* = 4.1 Hz, 1H), 6.15 (br, 1H), 5.52 (s, 2H), 3.36 – 3.29 (m, 2H), 1.52 – 1.47 (m, 2H), 1.36 – 1.28 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.00, 160.31, 138.72, 138.34, 133.86, 132.33, 132.06, 130.95, 130.68, 128.44, 128.01, 127.54, 69.22, 39.86, 31.55, 20.21, 13.80. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{19}ClNO_3S_2$ $[M+H]^+$: 384.0489, found: 384.0481.



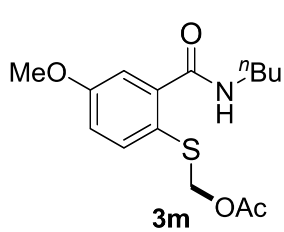
3k

Yellow oil, 42.5 mg, yield: 72%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, J = 7.8 Hz, 1H), 7.31 (s, 1H), 7.08 – 7.05 (m, 1H), 6.29 (br, 1H), 5.31 (s, 2H), 3.39 – 3.32 (m, 2H), 2.31 (s, 3H), 2.02 (s, 3H), 1.55 – 1.50 (m, 2H), 1.38 – 1.31 (m, 2H), 0.88 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.23, 166.87, 139.99, 134.43, 131.58, 130.89, 127.77, 127.59, 67.16, 38.78, 30.54, 20.29, 19.99, 19.19, 12.76. HRMS (ESI, *m/z*): calcd. for $C_{15}H_{22}NO_3S$ $[M+H]^+$: 296.1315, found: 296.1311.



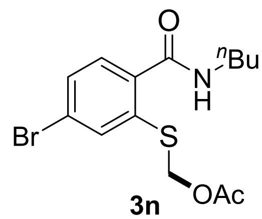
3l

Yellow oil, 42.3 mg, yield: 67%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H), 7.31 – 7.28 (m, 1H), 6.24 (br, 1H), 5.29 (s, 2H), 3.39 – 3.33 (m, 2H), 2.02 (s, 3H), 1.55 – 1.50 (m, 2H), 1.39 – 1.30 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.16, 166.60, 139.88, 134.11, 133.44, 130.70, 130.65, 128.66, 67.94, 39.93, 31.49, 21.00, 20.19, 13.79. HRMS (ESI, *m/z*): calcd. for $C_{14}H_{19}ClNO_3S$ $[M+H]^+$: 316.0769, found: 316.0761.



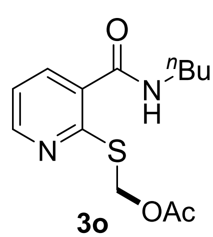
3m

Yellow oil, 48.5 mg, yield: 78%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 1H), 7.13 – 7.12 (m, 1H), 6.87 – 6.84 (m, 1H), 6.53 (br, 1H), 5.20 (s, 2H), 3.75 (s, 3H), 3.40 – 3.32 (m, 2H), 1.99 (s, 3H), 1.61 – 1.48 (m, 2H), 1.41 – 1.29 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.24, 167.69, 160.10, 141.45, 136.66, 120.89, 116.79, 114.25, 69.55, 55.55, 39.85, 31.49, 20.99, 20.22, 13.77. HRMS (ESI, *m/z*): calcd. for $C_{15}H_{21}NO_4S$ $[M+H]^+$: 312.1264, found: 312.1262.



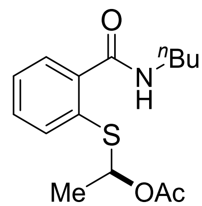
3n

Red solid, 36.6 mg, yield: 51%, m.p. 96 – 98 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 – 7.72 (m, 1H), 7.47 – 7.41 (m, 2H), 6.22 (br, 1H), 5.40 (s, 2H), 3.51 – 3.35 (m, 2H), 2.12 (s, 3H), 1.64 – 1.54 (m, 2H), 1.48 – 1.35 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.12, 167.01, 136.71, 134.89, 133.74, 130.64, 129.88, 124.63, 67.43, 39.91, 31.51, 20.97, 20.19, 13.76. HRMS (ESI, *m/z*): calcd. for $C_{14}H_{18}BrNO_3S$ $[M+H]^+$: 360.0264, found: 360.0260.



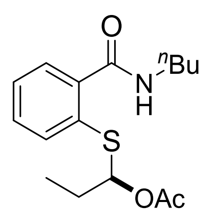
3o

White solid, 46.9 mg, yield: 83%, m.p. 173 – 174 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.49 – 8.47 (m, 1H), 7.74 – 7.72 (m, 1H), 7.08 – 7.04 (m, 1H), 6.15 (br, 1H), 5.81 (s, 2H), 3.38 – 3.34 (m, 2H), 2.00 (s, 3H), 1.54 – 1.53 (m, 2H), 1.36 – 1.34 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.72, 165.01, 152.96, 149.49, 135.29, 129.19, 119.04, 61.30, 38.92, 30.41, 20.04, 19.14, 12.73. HRMS (ESI, *m/z*): calcd. for $C_{13}H_{19}N_2O_3S$ $[M+H]^+$: 283.1111, found: 283.1108.



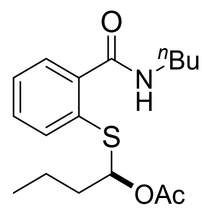
3p

Yellow oil, 29.5 mg, yield: 50%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 – 7.55 (m, 1H), 7.48 – 7.45 (m, 1H), 7.32 – 7.29 (m, 2H), 6.55 (br, 1H), 6.16 (q, *J* = 6.5 Hz, 1H), 3.46 – 3.31 (m, 2H), 1.91 (s, 3H), 1.56 – 1.36 (m, 7H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.94, 167.99, 140.54, 135.67, 130.21, 129.11, 128.90, 128.56, 76.88, 39.79, 31.56, 21.08, 21.01, 20.24, 13.80. HRMS (ESI, *m/z*): calcd. for $C_{15}H_{22}NO_3S$ $[M+H]^+$: 296.1315, found: 296.1318.



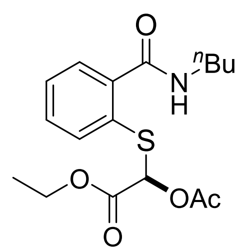
3q

Yellow oil, 29.7 mg, yield: 48%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 1H), 7.50 – 7.46 (m, 1H), 7.33 – 7.26 (m, 2H), 6.55 (br, 1H), 6.01 (t, *J* = 6.5 Hz, 1H), 3.49 – 3.29 (m, 2H), 1.91 (s, 3H), 1.87 – 1.69 (m, 2H), 1.59 – 1.49 (m, 2H), 1.43 – 1.31 (m, 2H), 0.97 – 0.87 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.10, 168.02, 140.68, 135.80, 130.17, 129.13, 128.85, 128.58, 81.97, 39.79, 31.58, 28.14, 20.96, 20.25, 13.79, 10.25. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{23}NO_3S$ $[M+H]^+$: 310.1471, found: 310.1465.



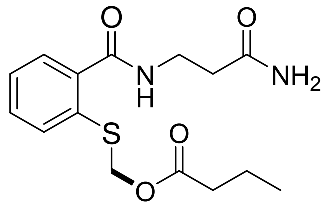
3r

Yellow oil, 23.9 mg, yield: 37%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 1H), 7.57 – 7.52 (m, 1H), 7.41 – 7.32 (m, 2H), 6.64 (br, 1H), 6.16 (t, *J* = 6.6 Hz, 1H), 3.56 – 3.37 (m, 2H), 1.97 (s, 3H), 1.85 – 1.78 (m, 2H), 1.64 – 1.57 (m, 2H), 1.51 – 1.38 (m, 4H), 1.00 – 0.90 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.08, 168.02, 140.70, 135.86, 130.15, 129.12, 128.88, 128.58, 80.43, 39.78, 36.80, 31.59, 20.95, 20.25, 19.08, 13.79, 13.53. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{25}NO_3S$ $[M+H]^+$: 324.1628, found: 324.1623.



3s

Yellow oil, 45.9 mg, yield: 65%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 2H), 7.33 – 7.30 (m, 2H), 6.54 (br, 1H), 6.22 (s, 1H), 4.07 – 4.00 (m, 2H), 3.42 – 3.35 (m, 2H), 2.10 (s, 3H), 1.58 – 1.51 (m, 2H), 1.41 – 1.34 (m, 2H), 1.09 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.68, 167.63, 166.09, 140.43, 135.02, 130.38, 129.30, 129.20, 127.82, 76.90, 62.56, 39.91, 31.49, 20.77, 20.25, 13.88, 13.80. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{24}NO_5S$ $[M+H]^+$: 354.1370, found: 354.1370.



8

Yellow solid, 1.241 g, yield: 85%, m.p. 135 – 137 °C (known compound[3]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 1H), 7.49 – 7.21 (m, 3H), 7.06 (br, 1H), 6.30 (br, 1H), 5.85 (br, 1H), 5.38 (s, 2H), 3.67 (q, *J* = 5.9 Hz, 2H), 2.57 (t, *J* = 5.8 Hz, 2H), 2.33 (t, *J* = 7.4 Hz, 2H), 1.64 (q, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.18, 173.10, 168.48, 137.56, 133.35, 130.83, 130.77, 127.97, 127.30, 67.51, 36.13, 35.84, 34.76, 18.26, 13.63.

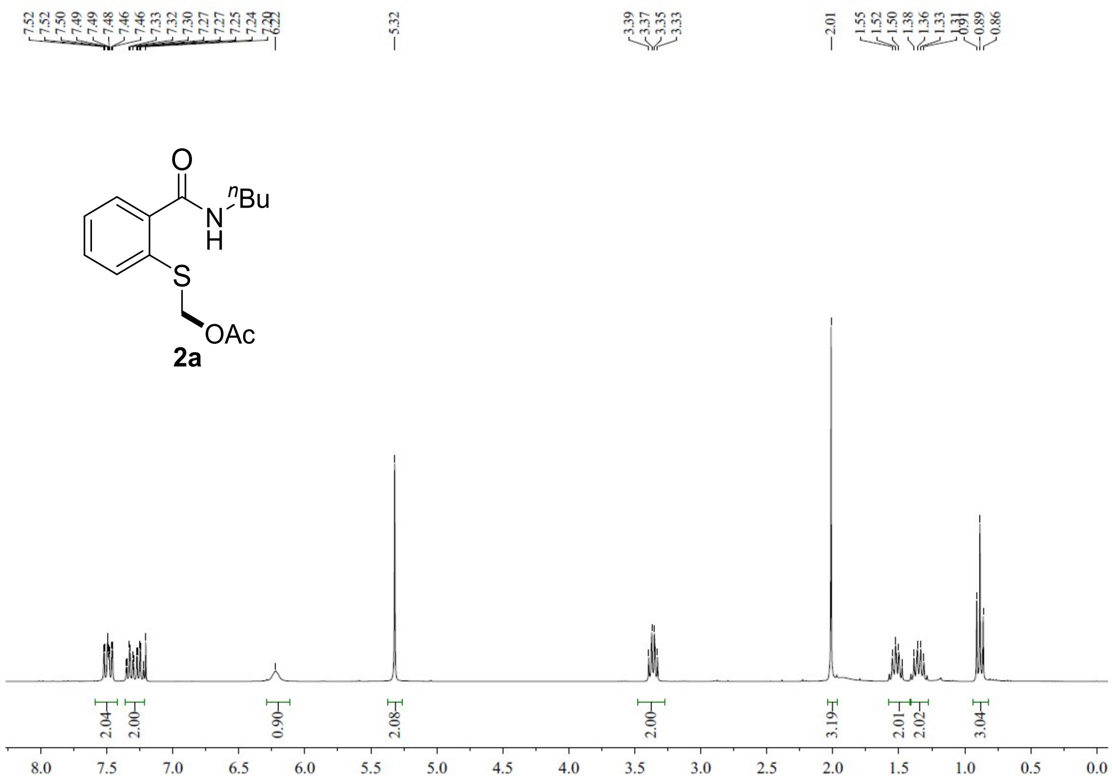
III. References and notes:

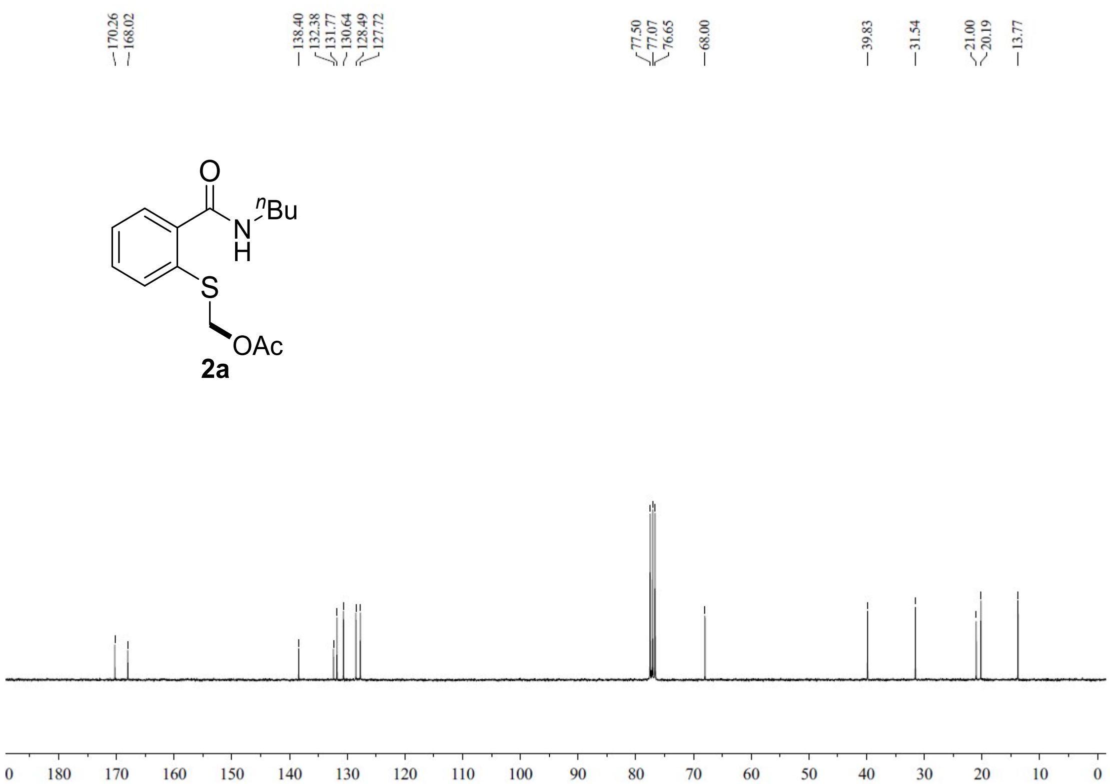
(1) Y. Naro, M. Thomas, M. D. Stephens, C. M. Connelly and A. Deiters, *Bioorg. Med. Chem. Lett.,* 2015, **25**, 4793.

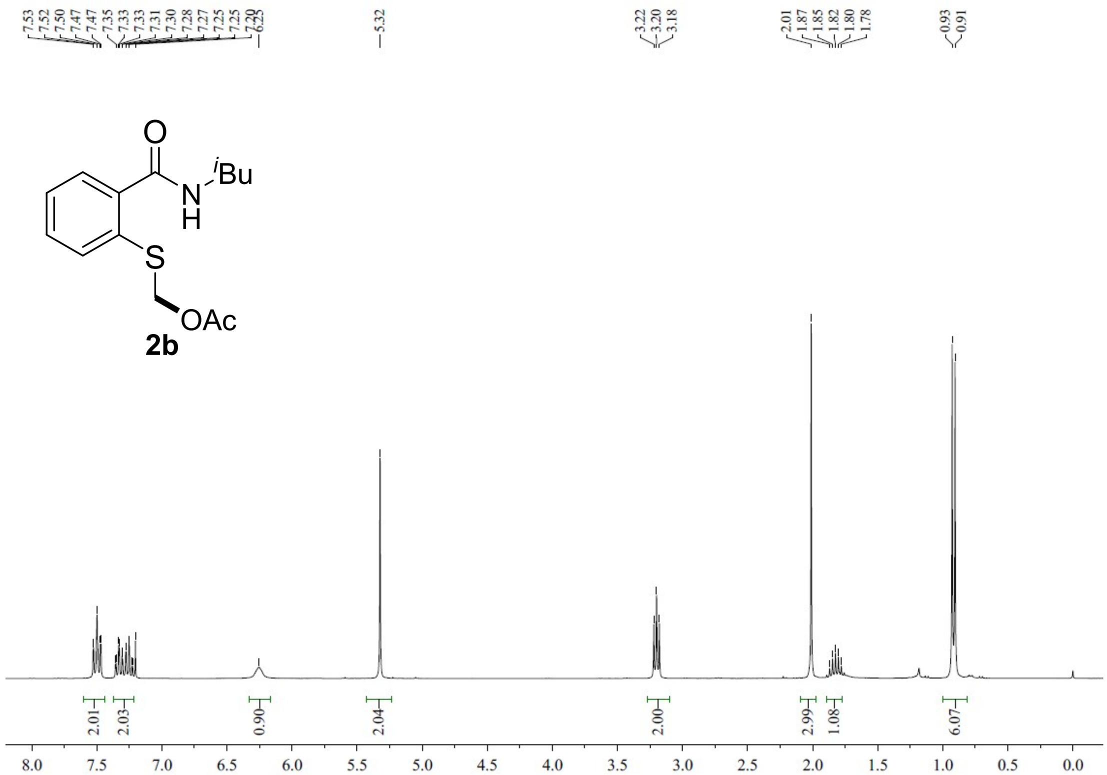
(2) G. Hallas and A. D. Towns, *Dyes Pigm.*, 1997, **35**, 219.

(3) L. Miller Jenkins, E. Paine and L. Deshmukh, *J. Am. Chem. Soc.*, 2019, **141**, 8327.

IV. ^{1}H and ^{13}C NMR Spectra



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0.93 0.91
O
N
H
iBu
S
OAc
2b
2.01 2.03 0.90 2.04 2.00 2.99 1.08 6.07
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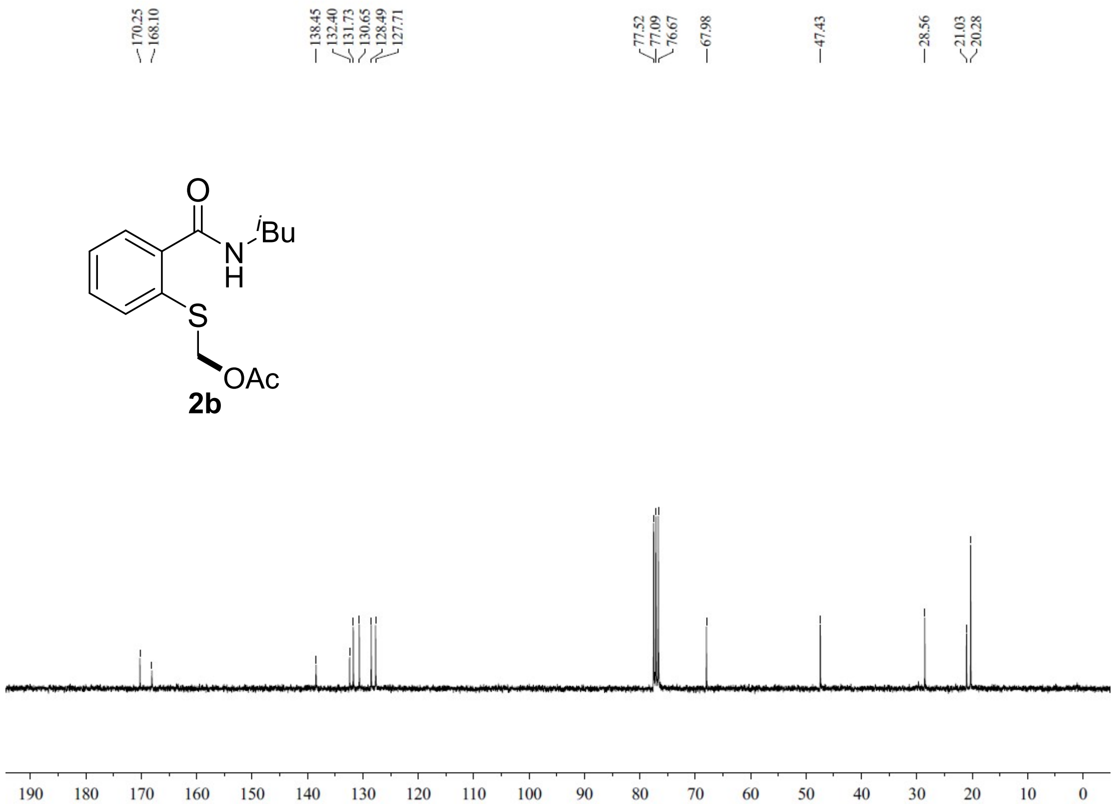
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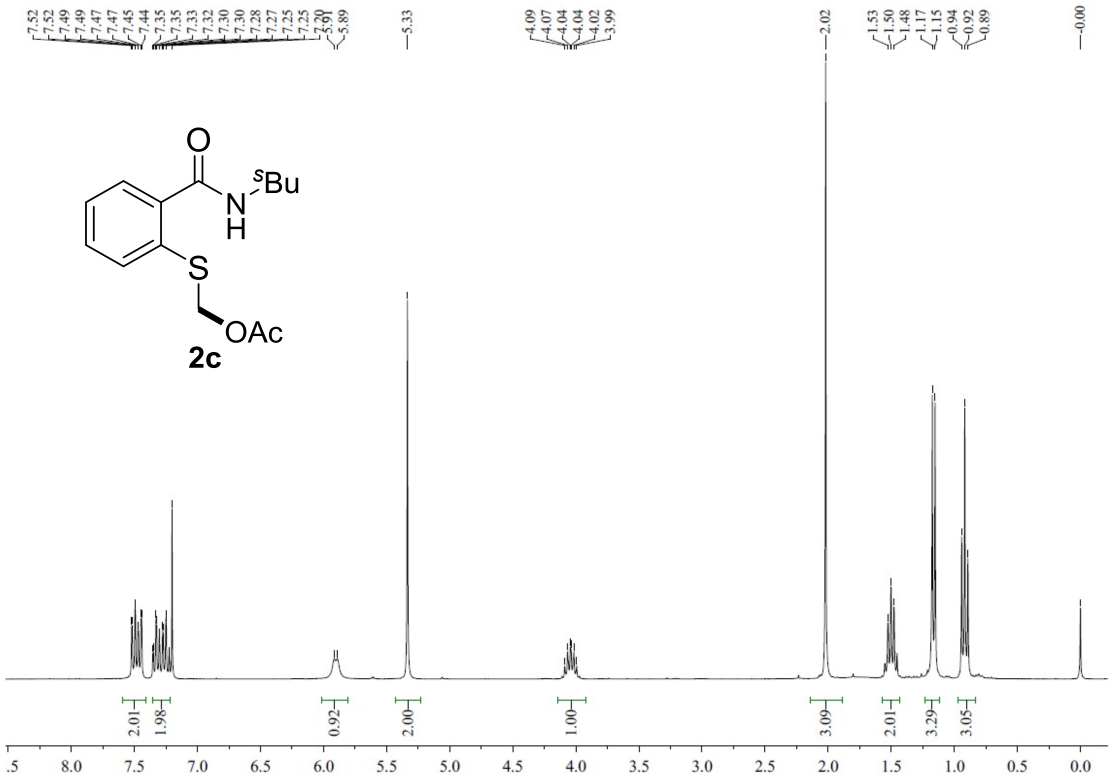
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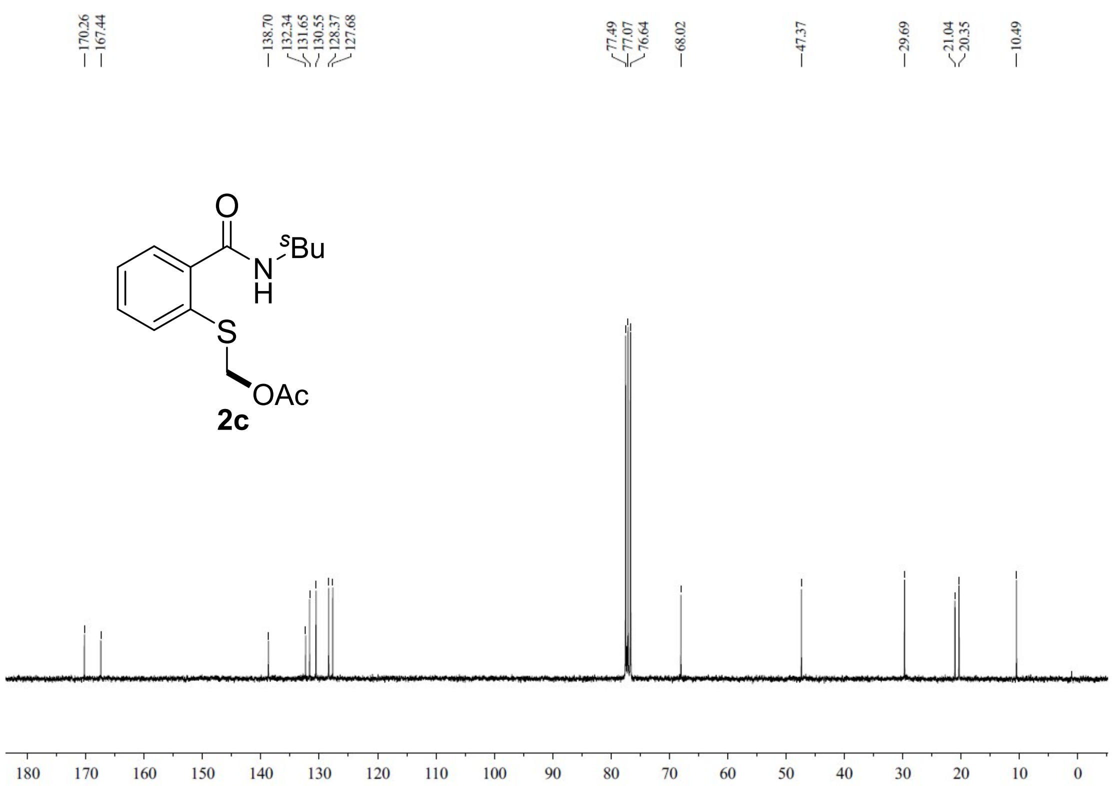
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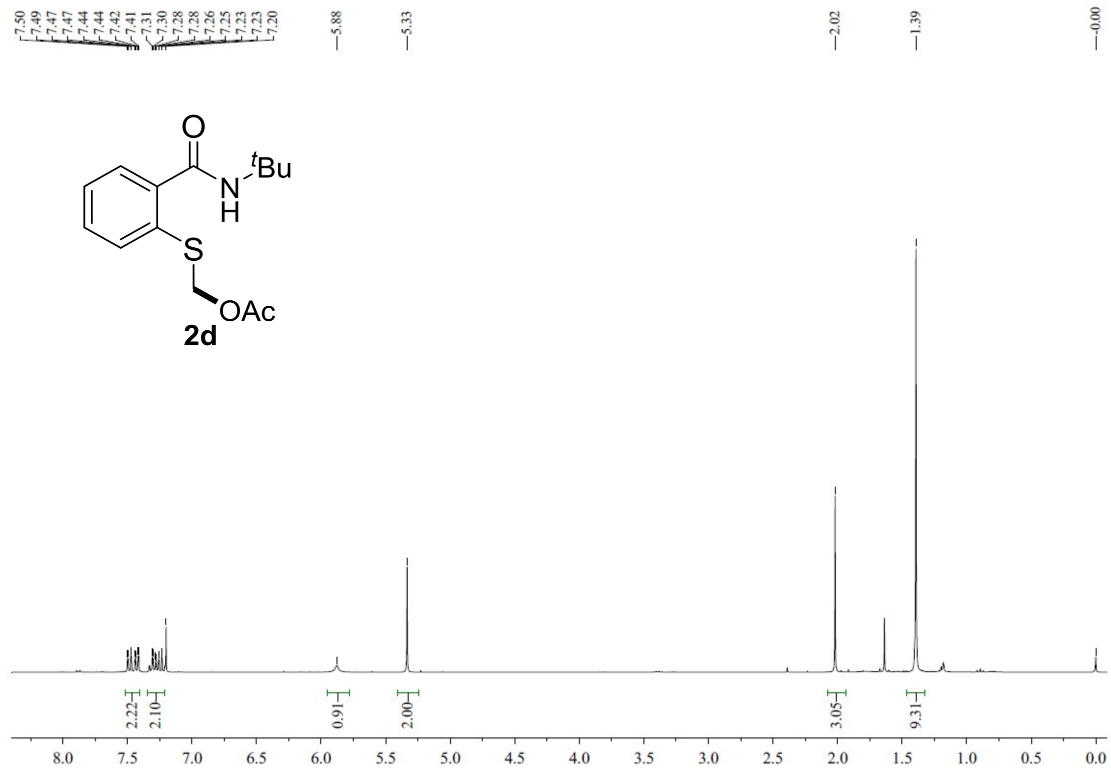
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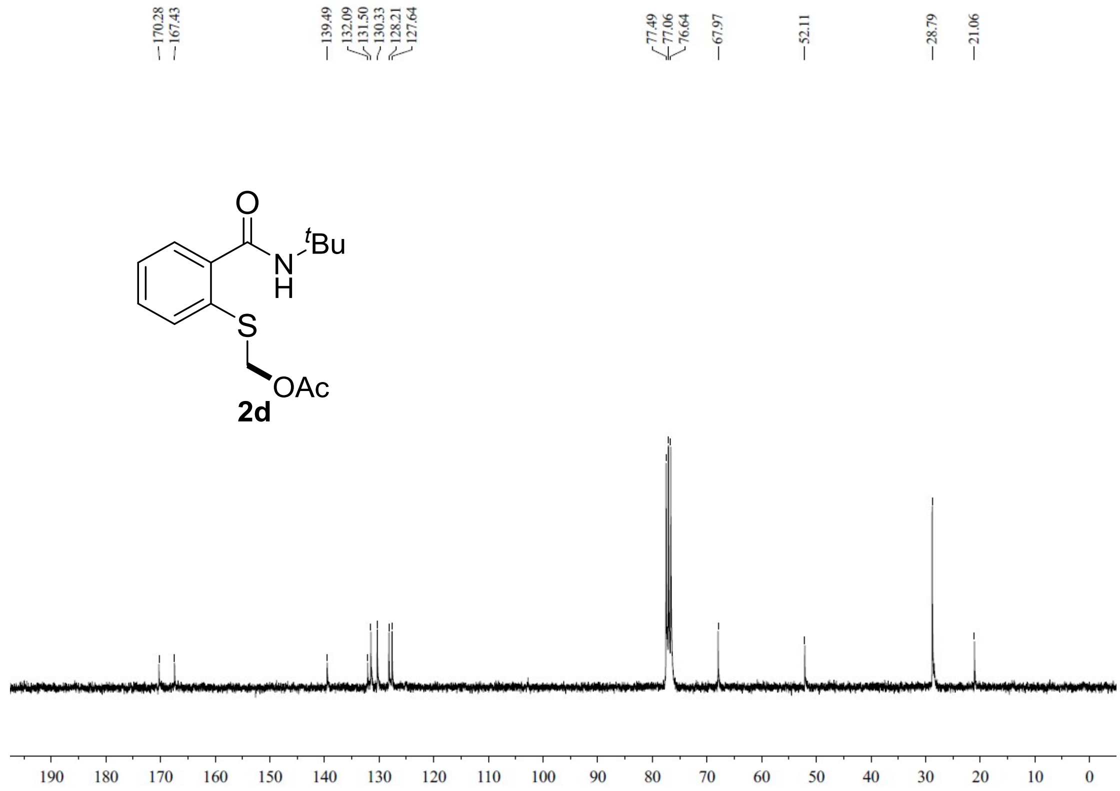
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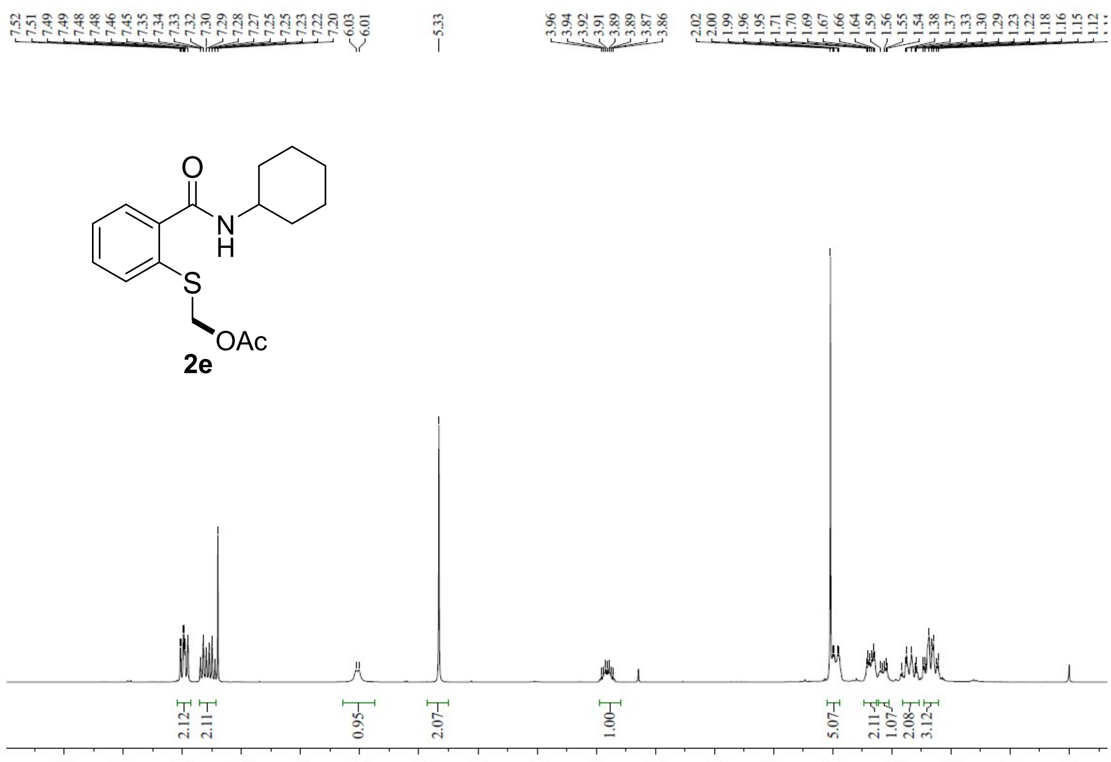
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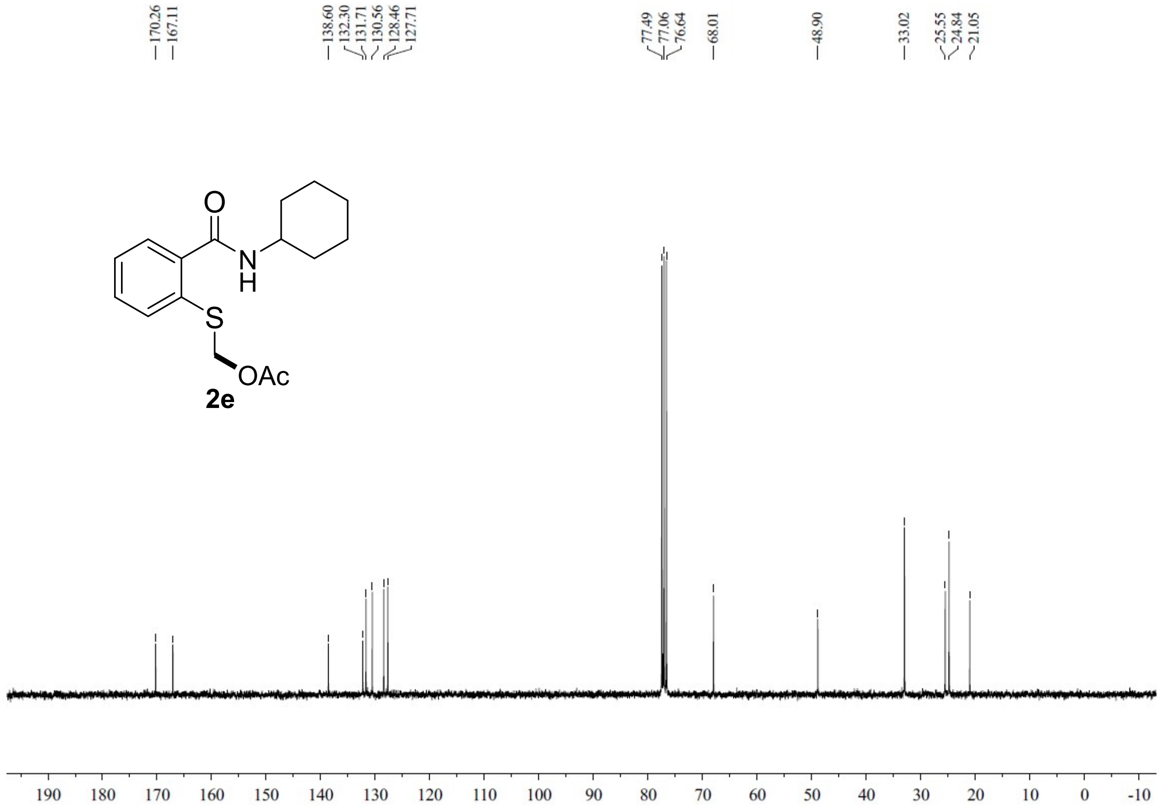
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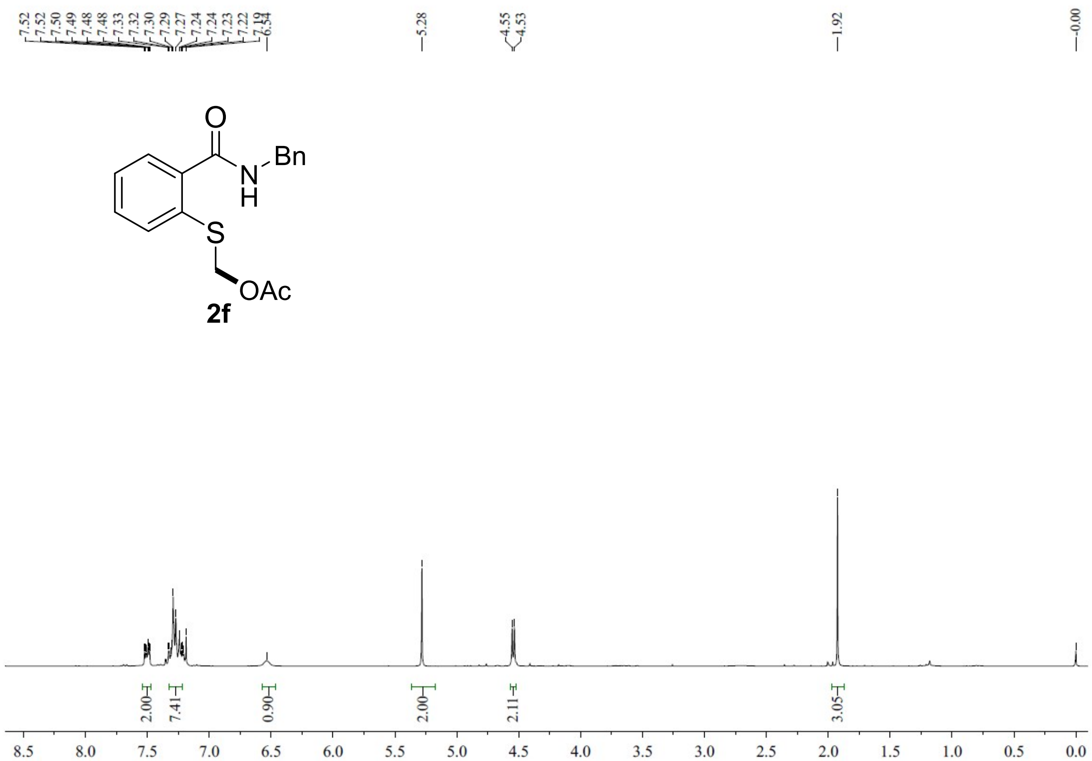
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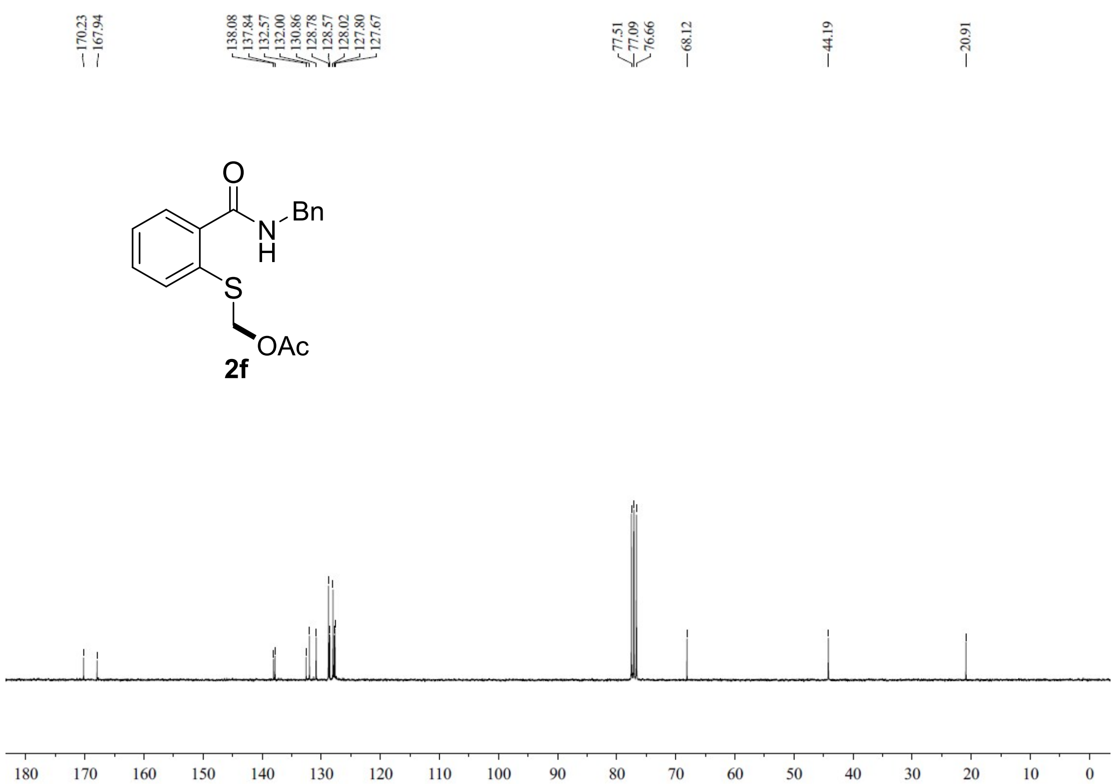
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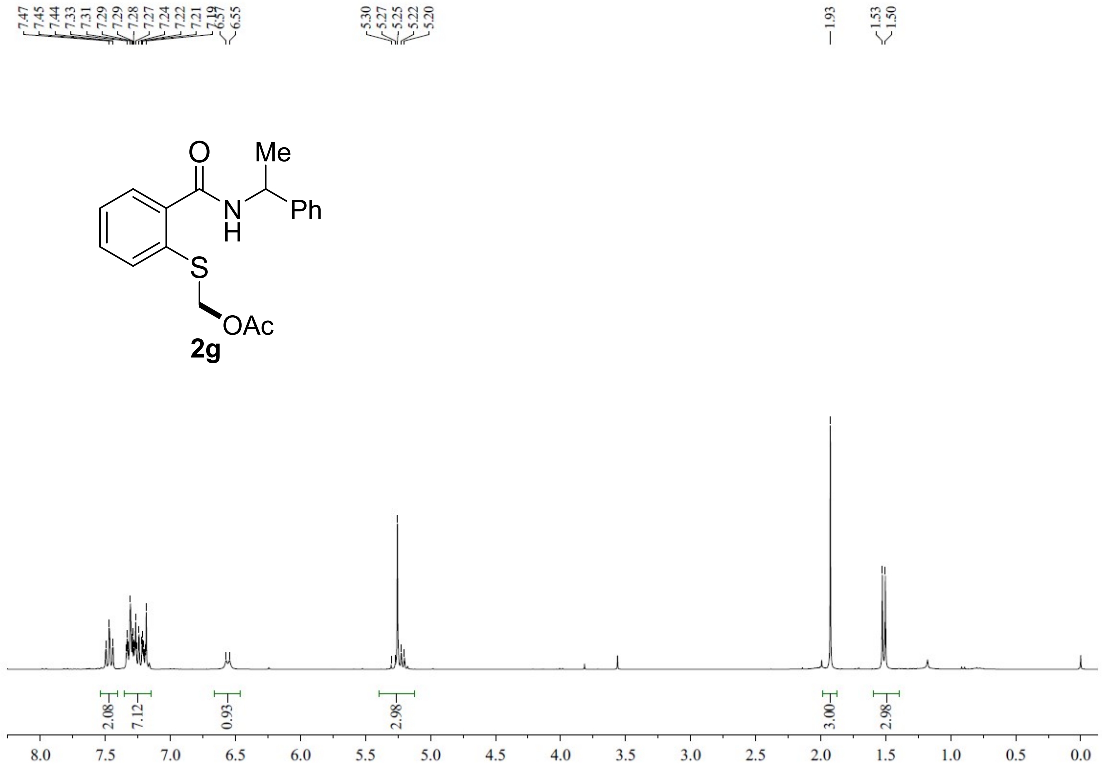
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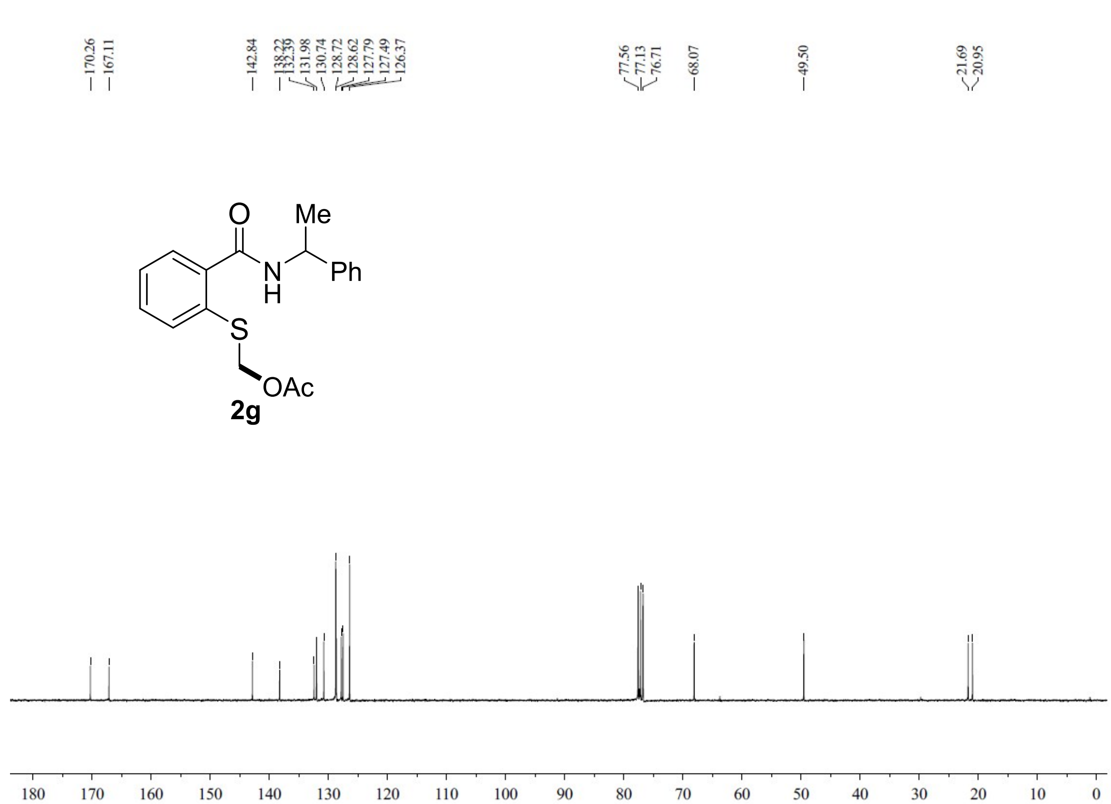
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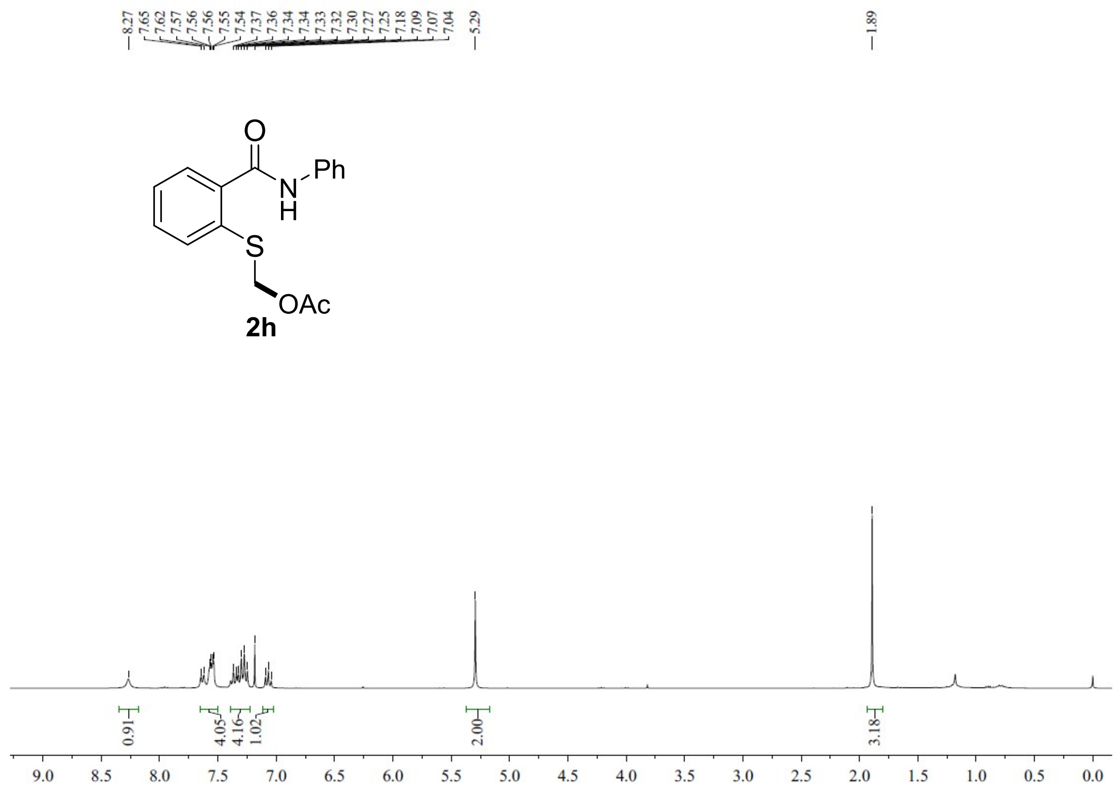
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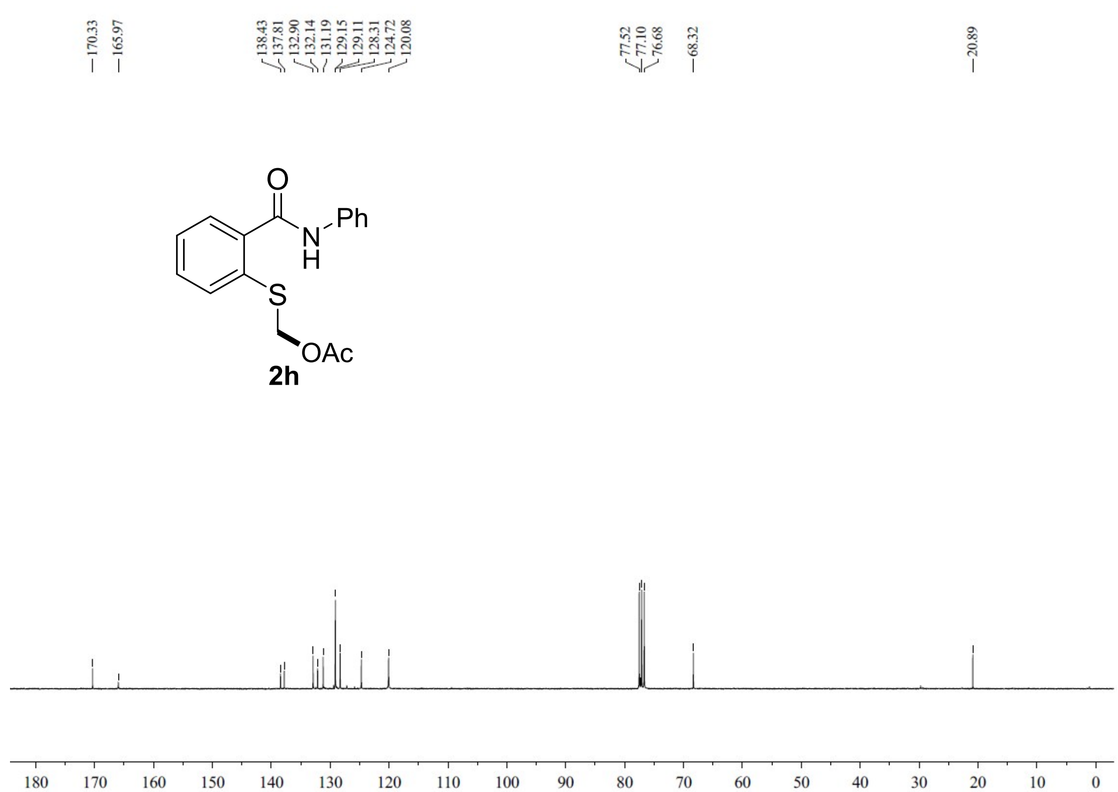
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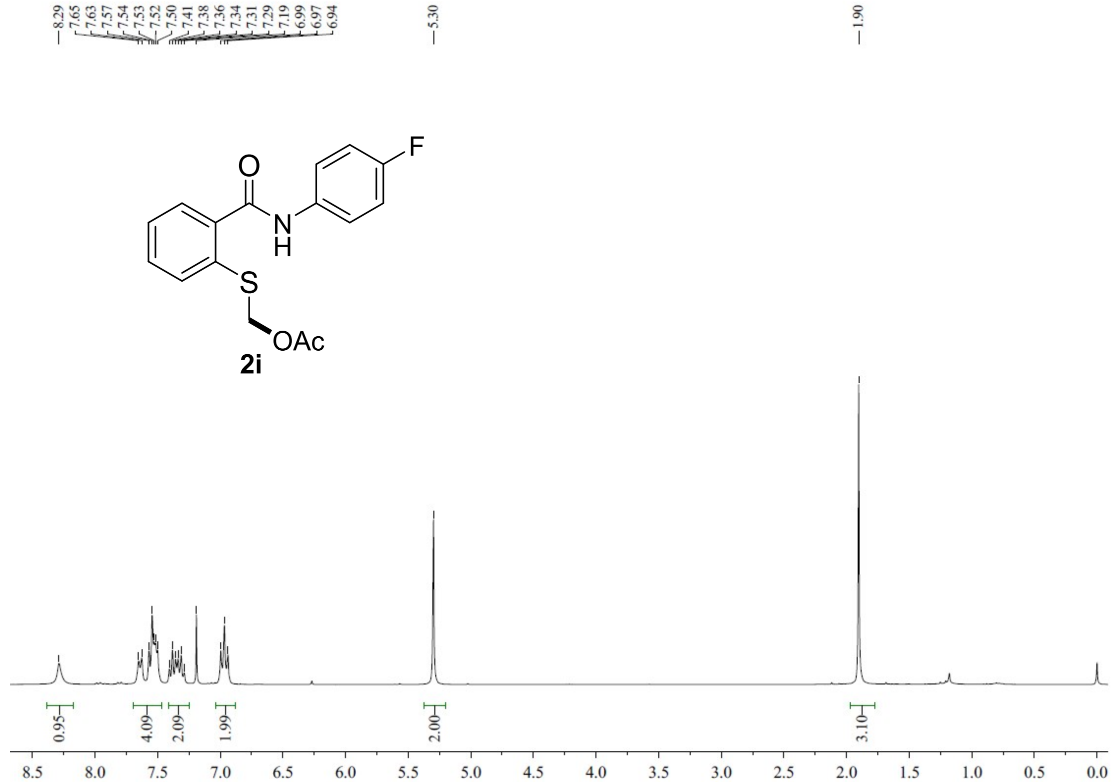
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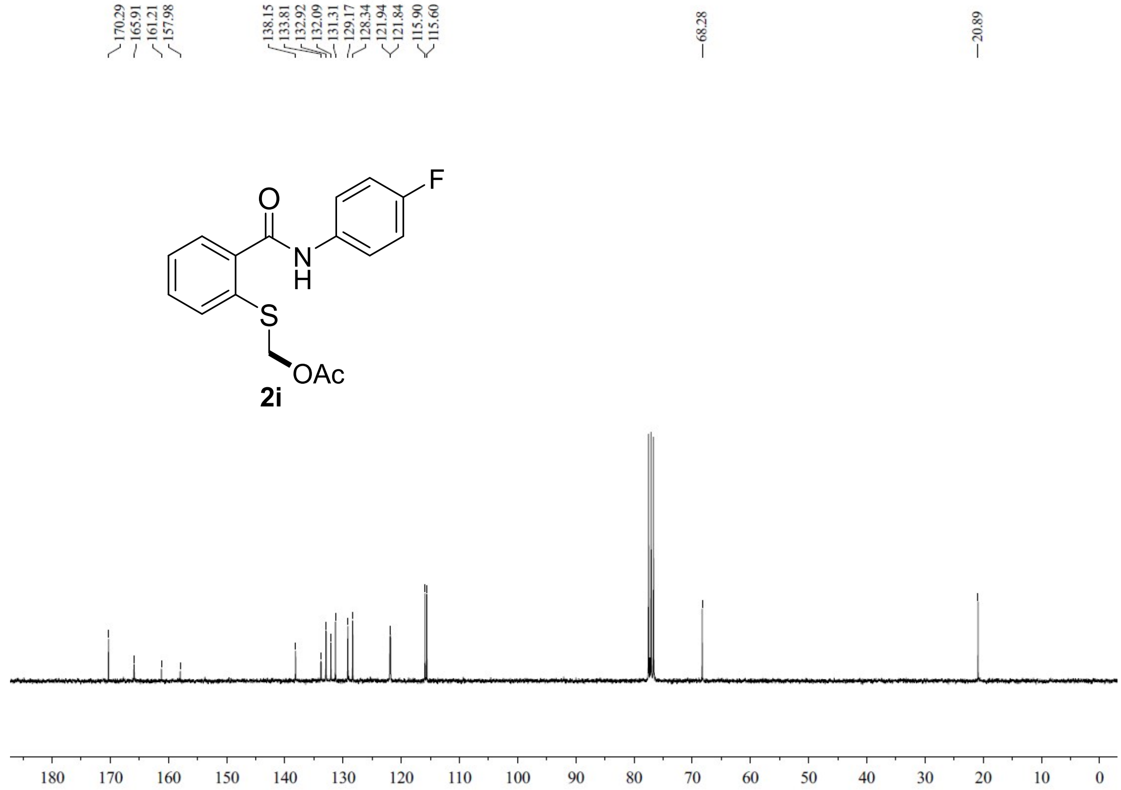
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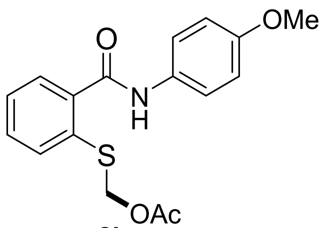

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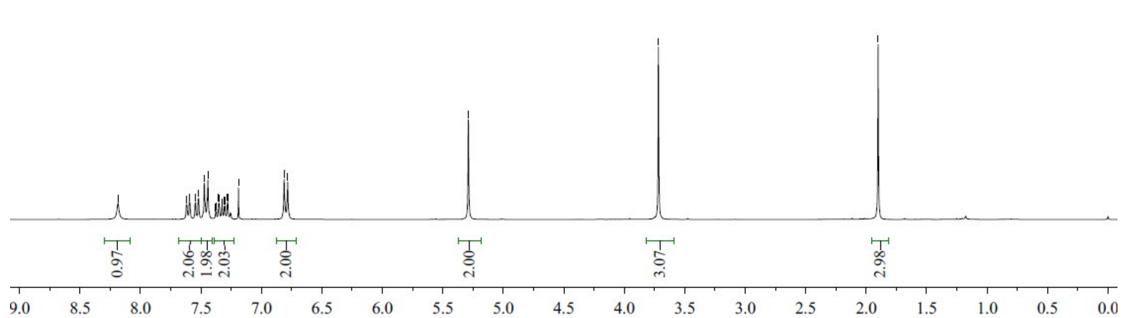

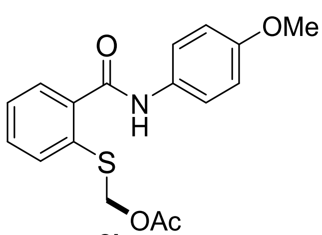

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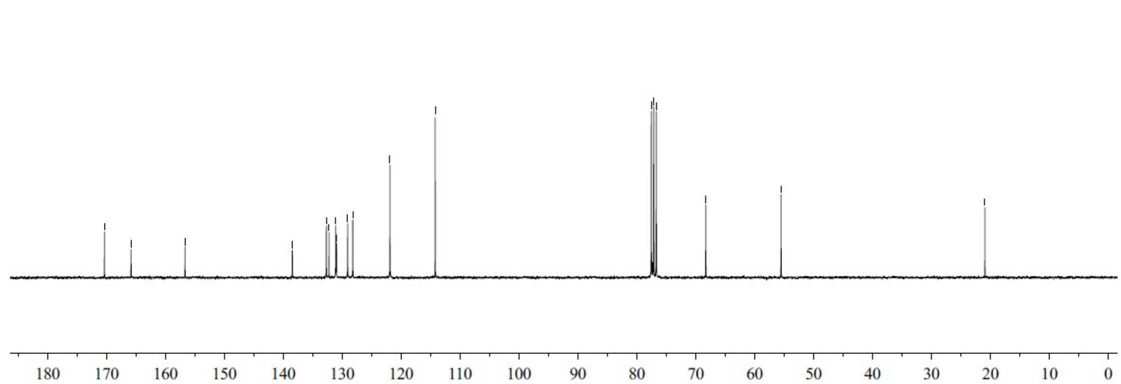

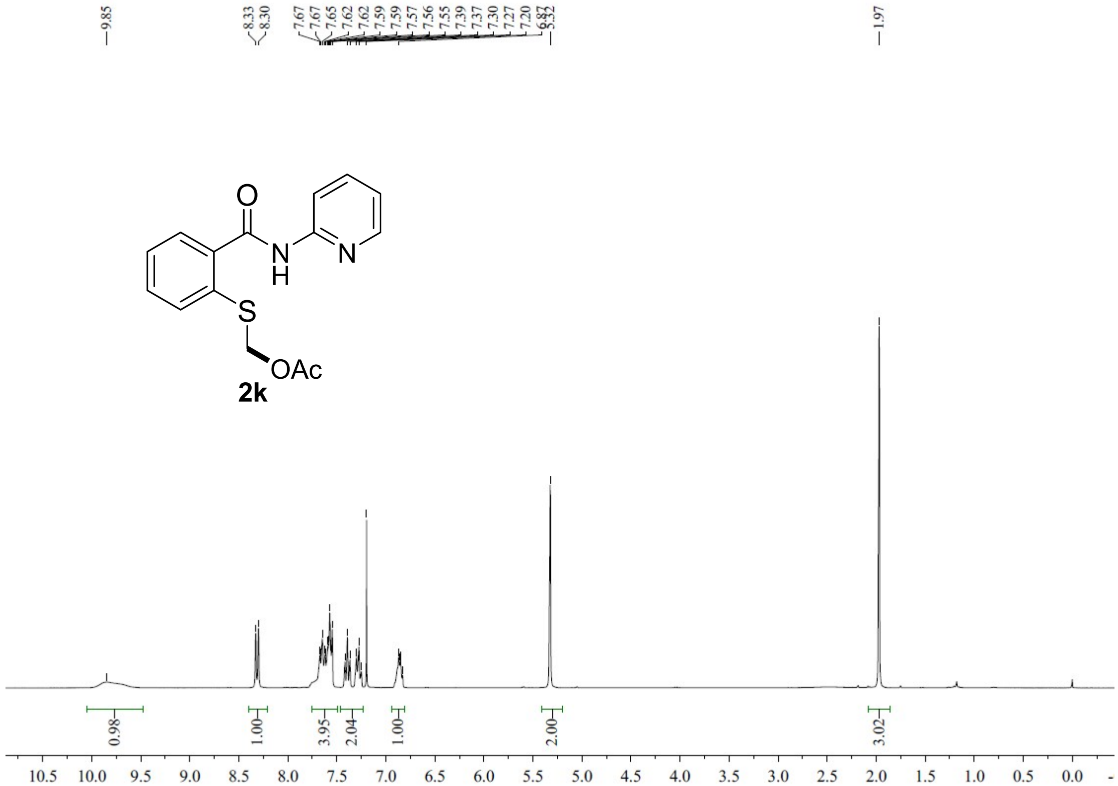
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H
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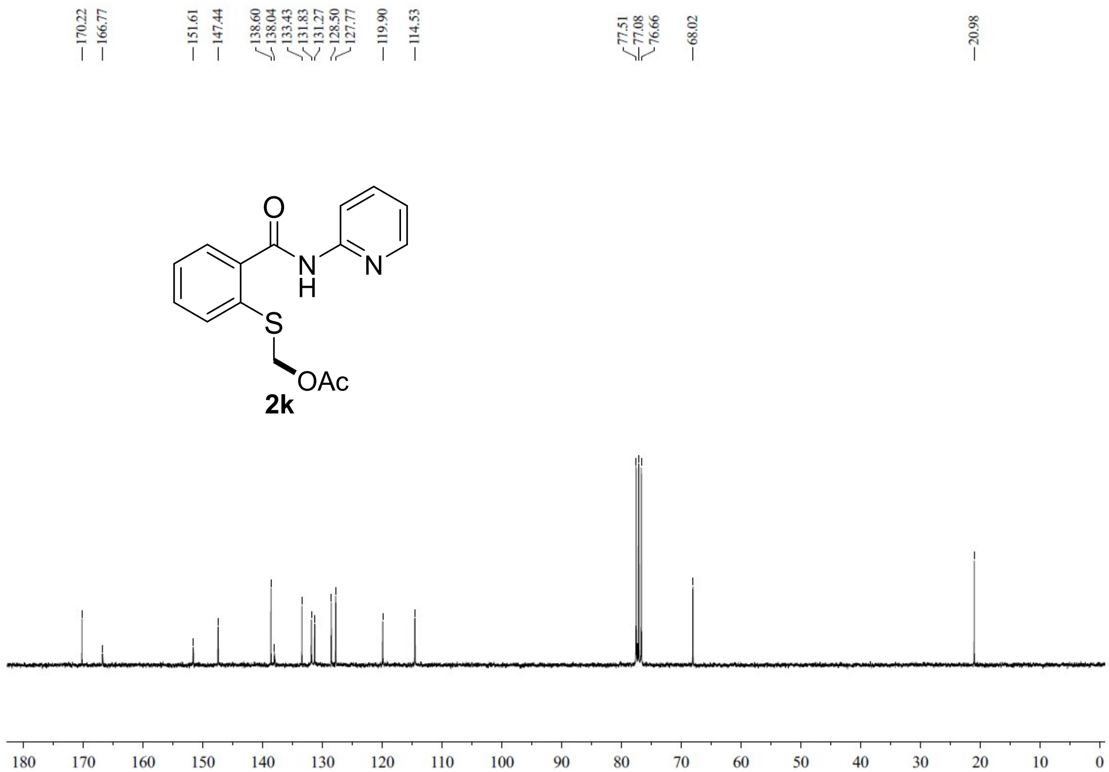
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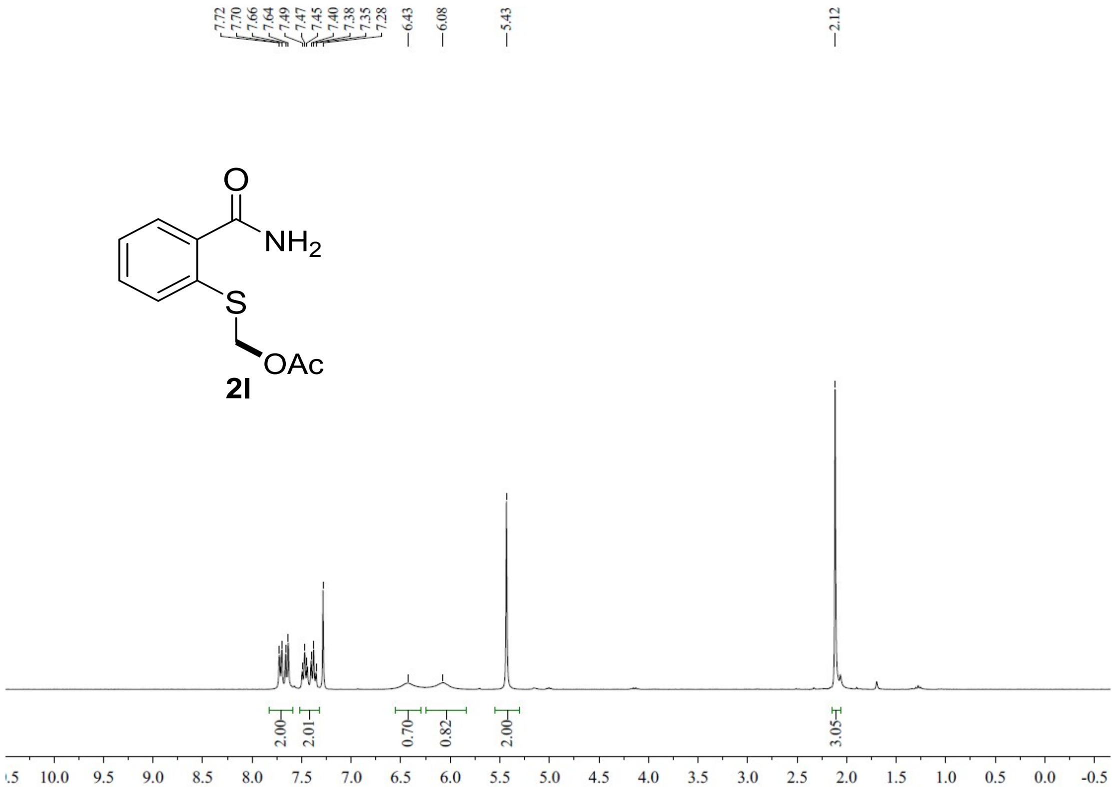
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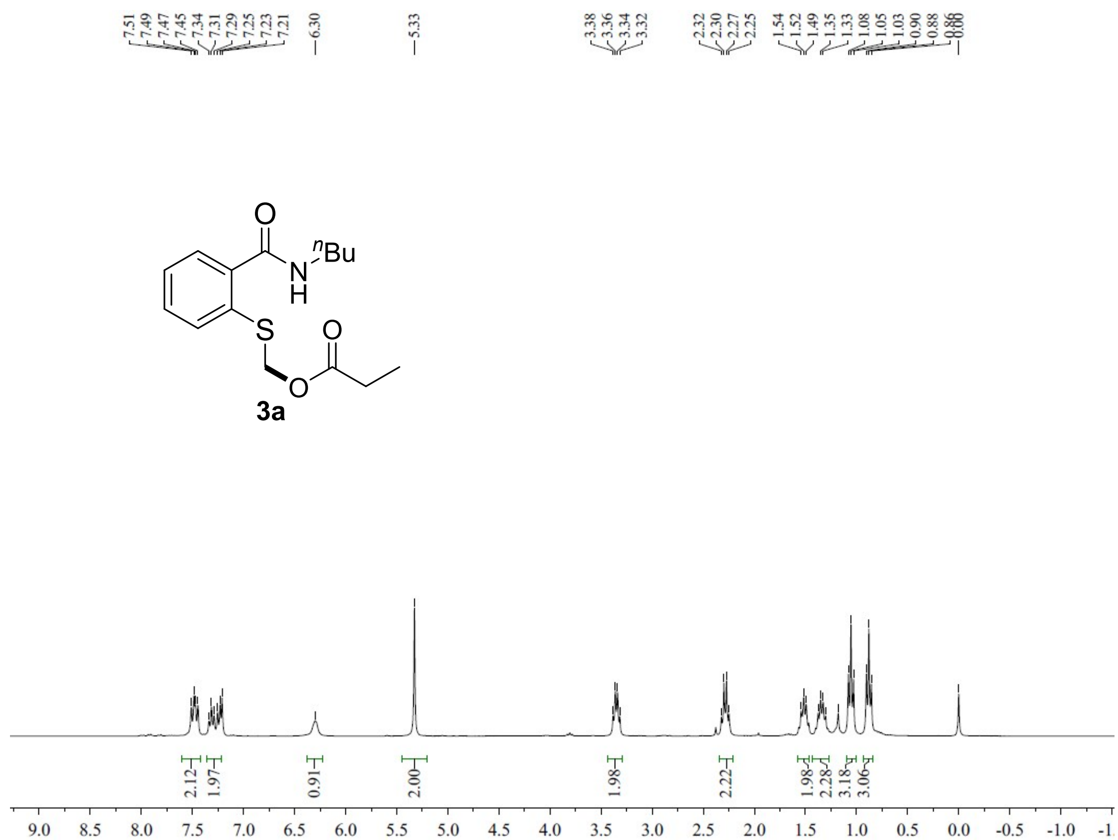
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O
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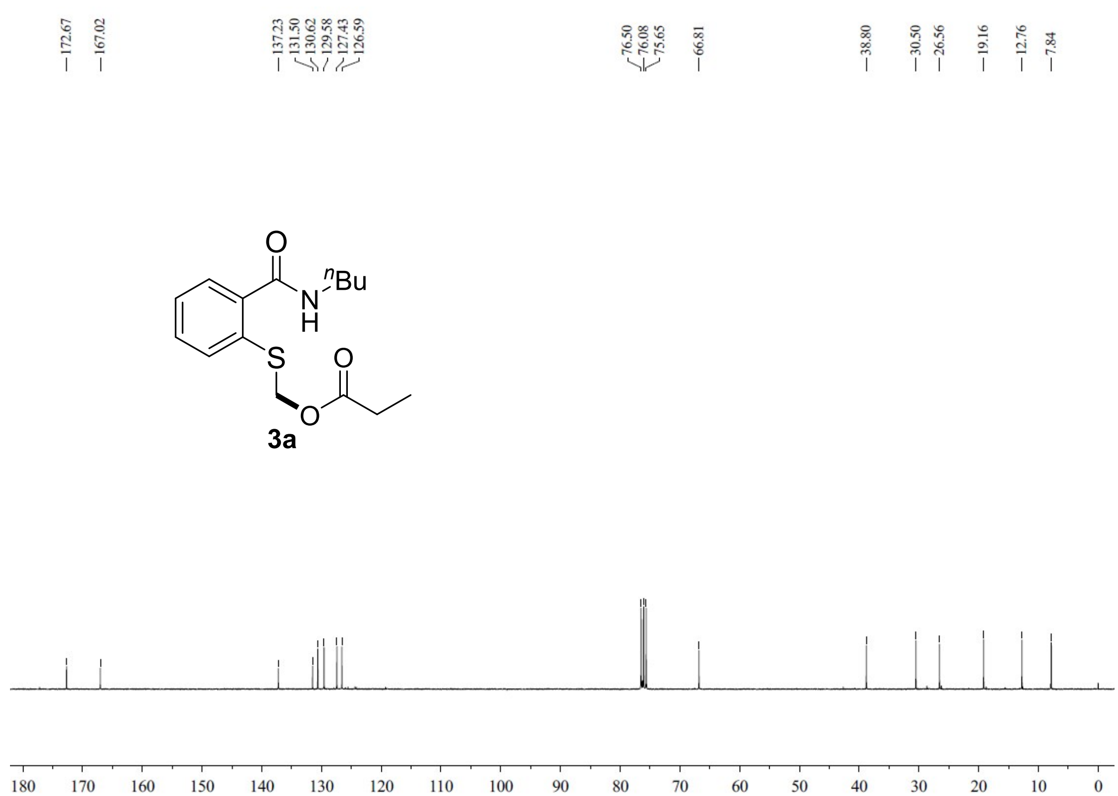
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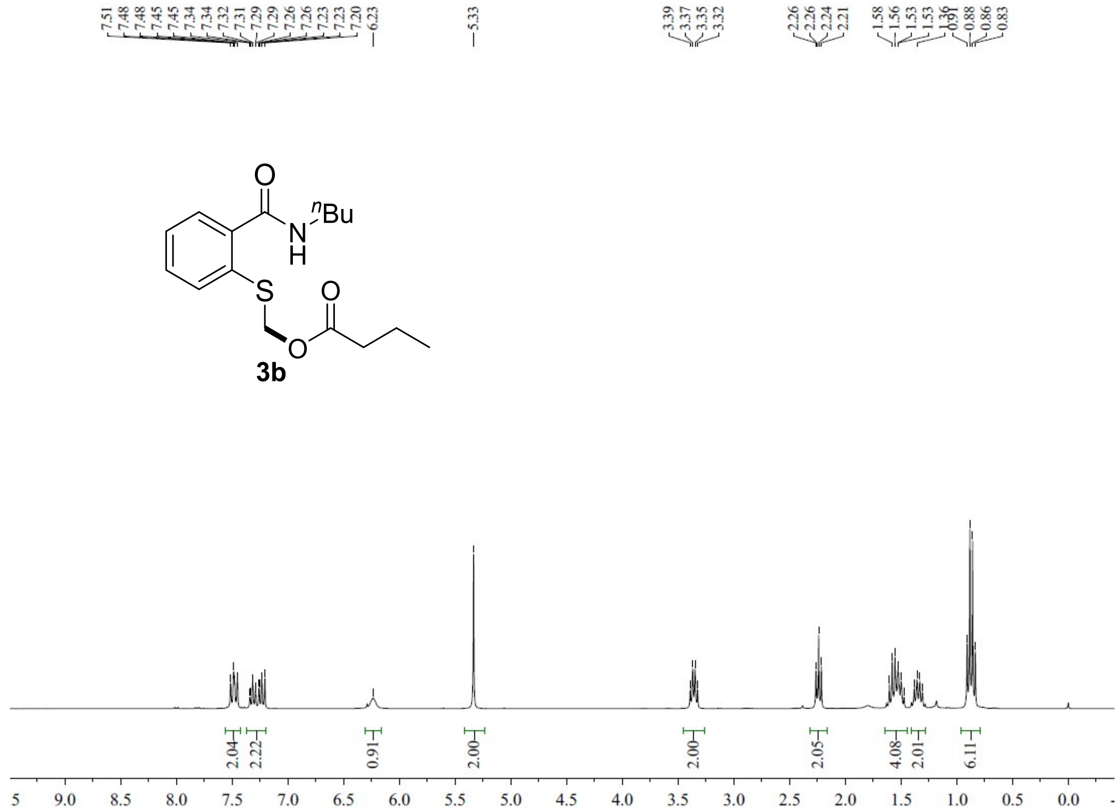

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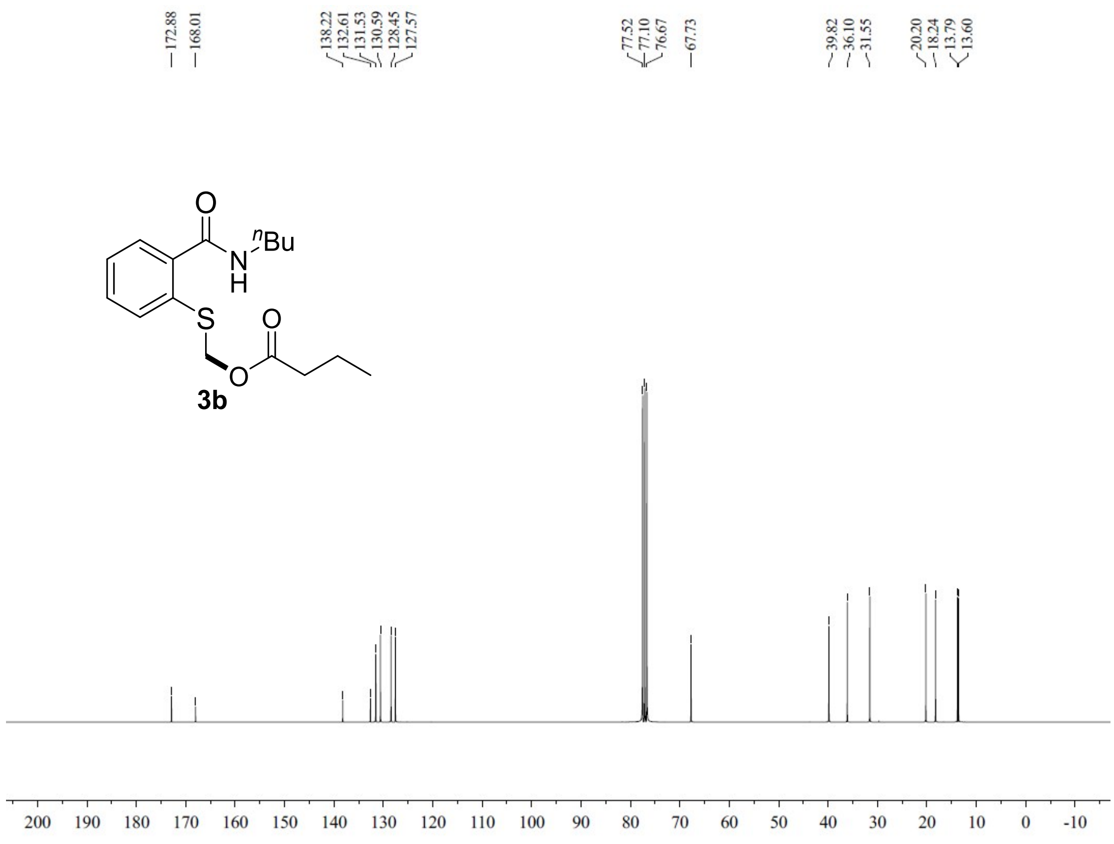

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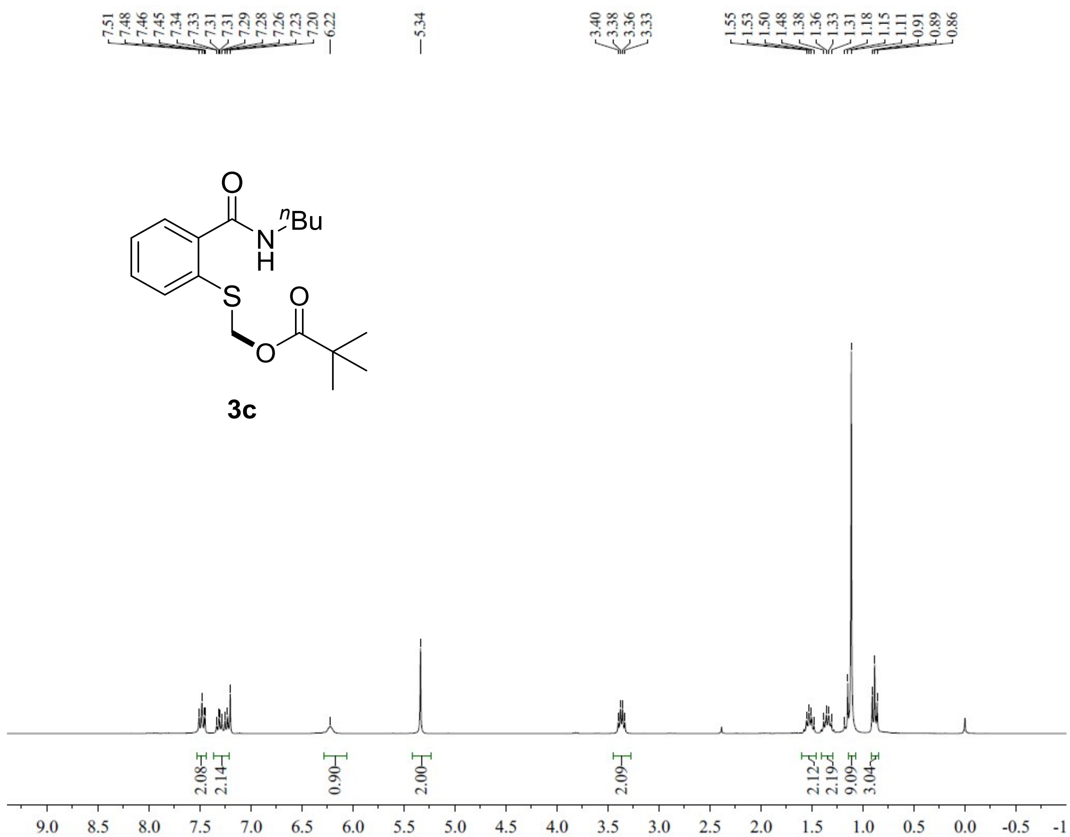
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5.34
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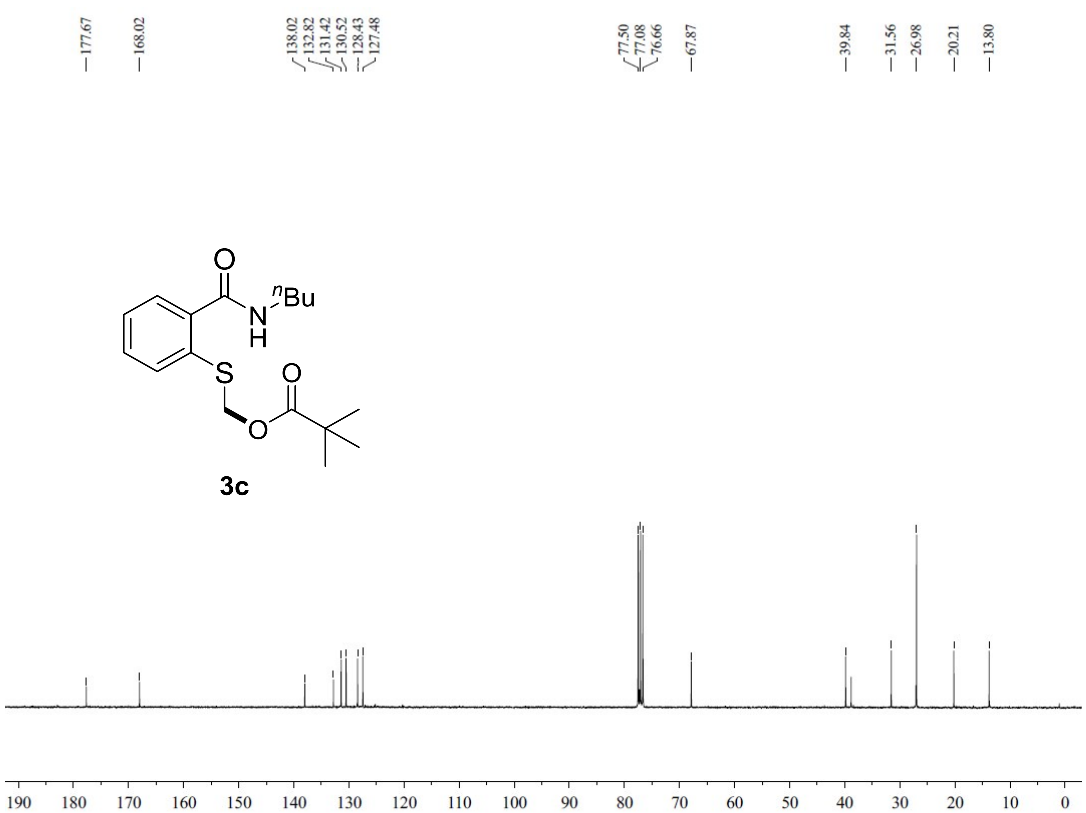
1.55 1.53 1.50 1.48 1.38 1.36 1.33 1.31 1.18 1.15 1.11 0.91 0.89 0.86
3c
2.08 2.14 0.90 2.00 2.09 2.12 2.19 9.09 3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1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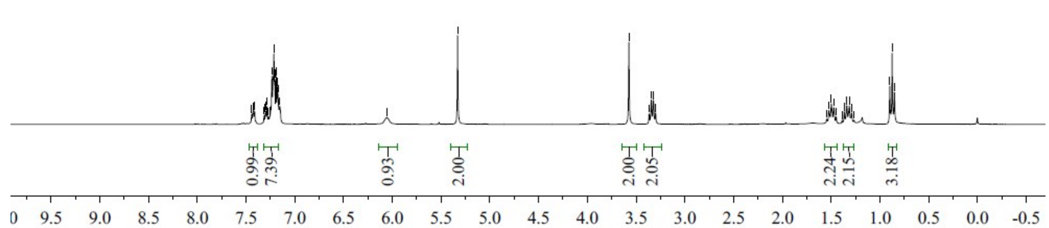
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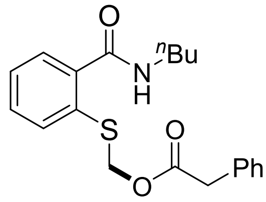
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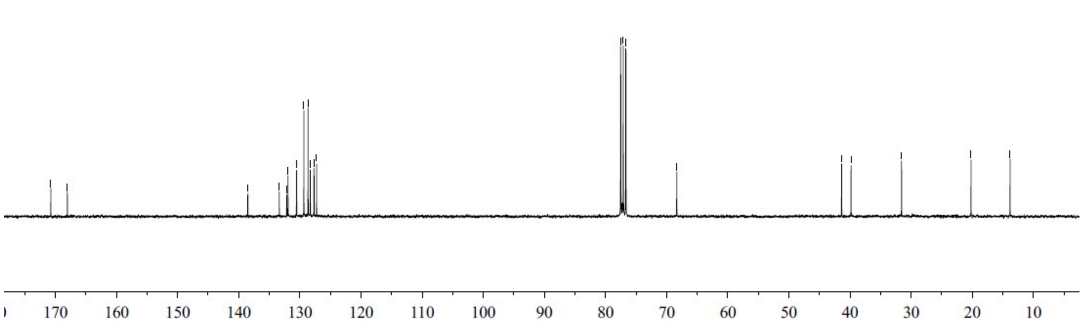
3d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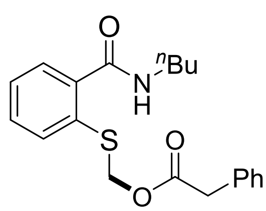
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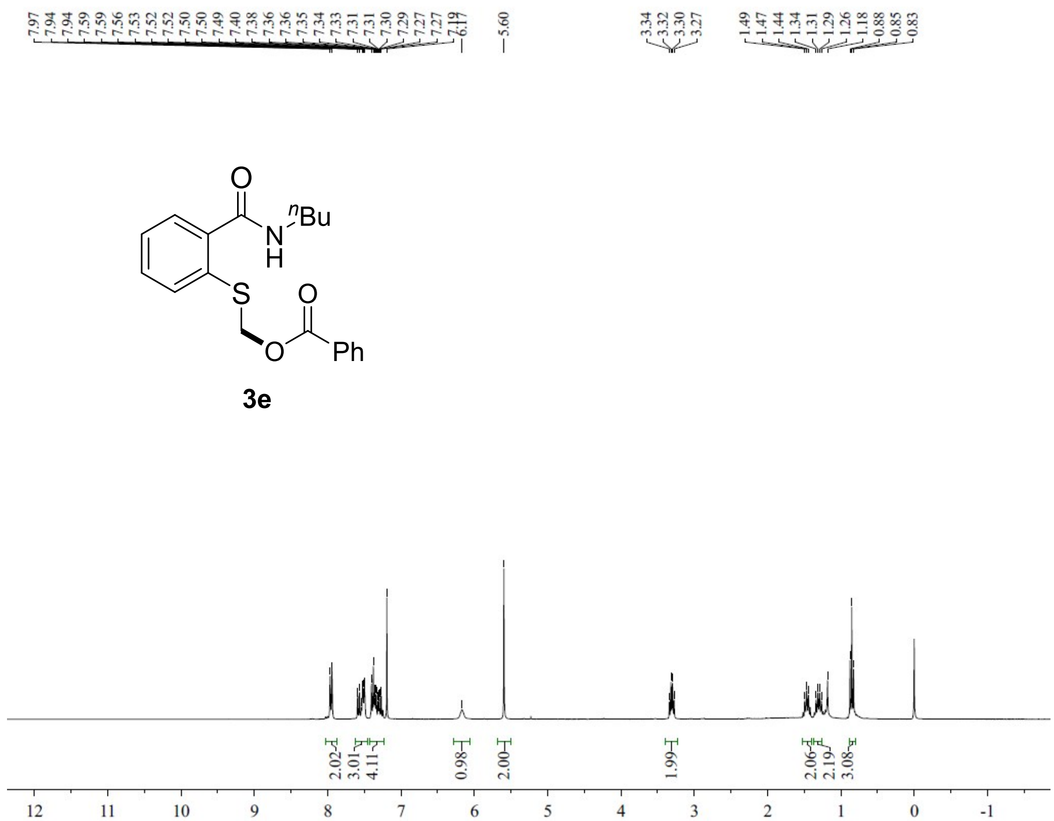
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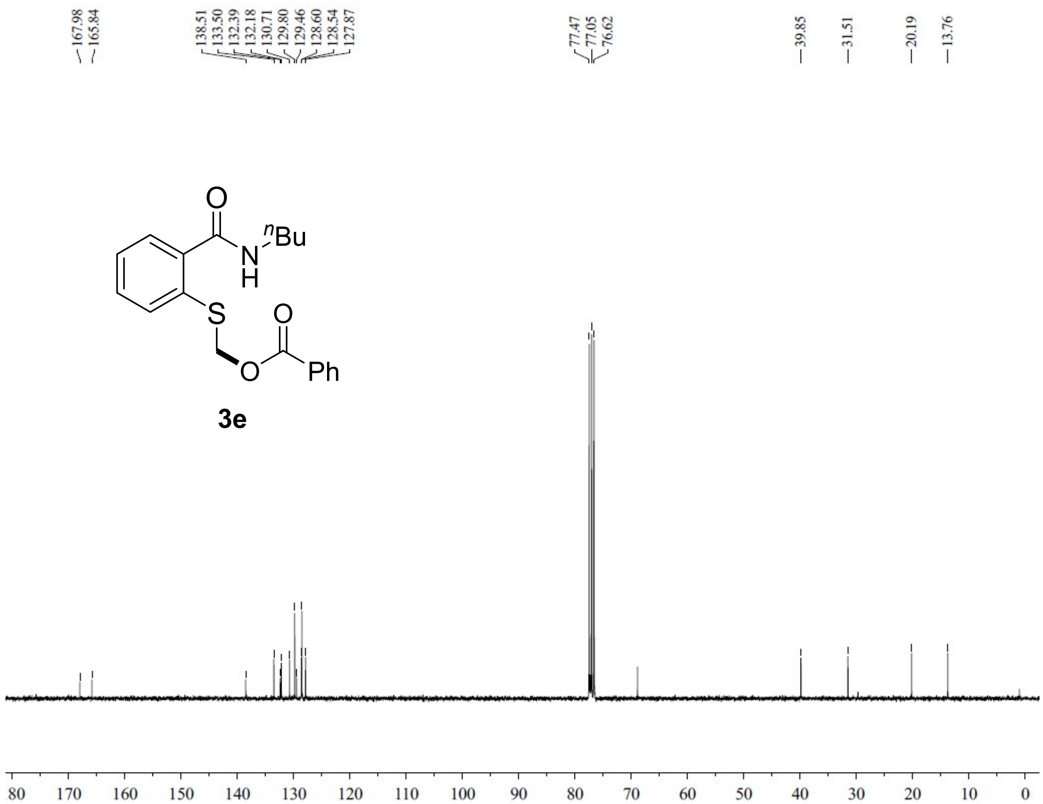
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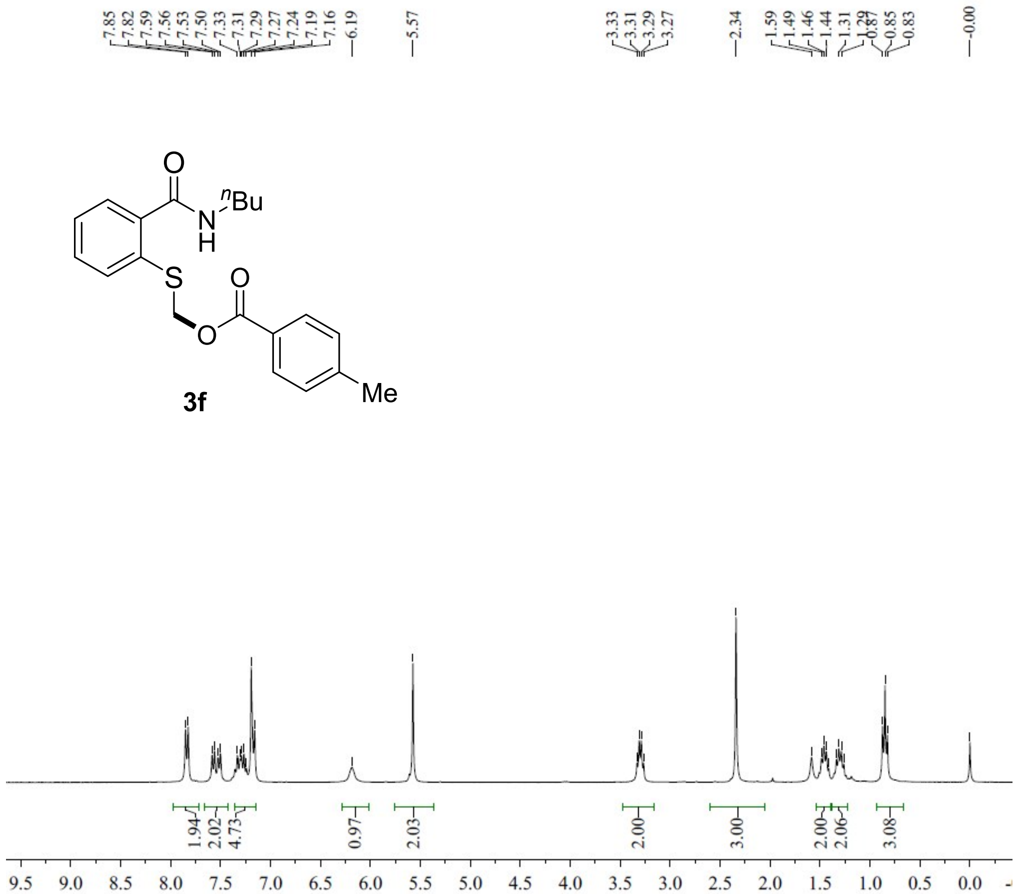
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1.59 1.49 1.46 1.44 1.31 1.29 0.87 0.85 0.83
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1.94 2.02 4.73 0.97 2.03 2.00 3.00 2.00 2.06 3.08
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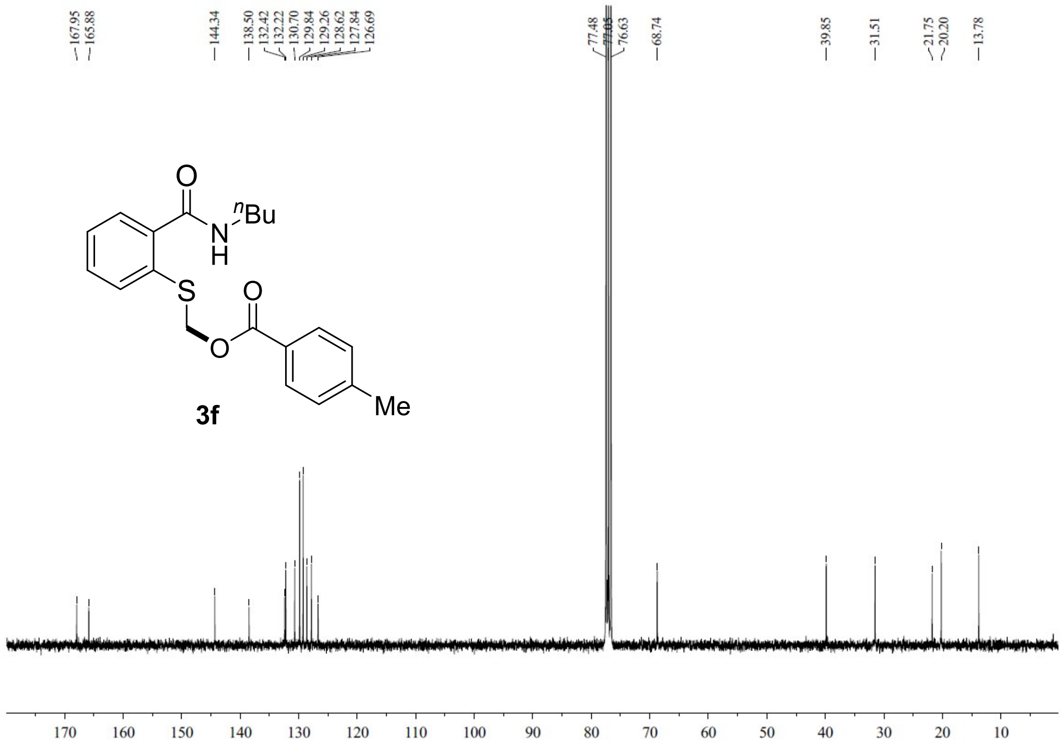
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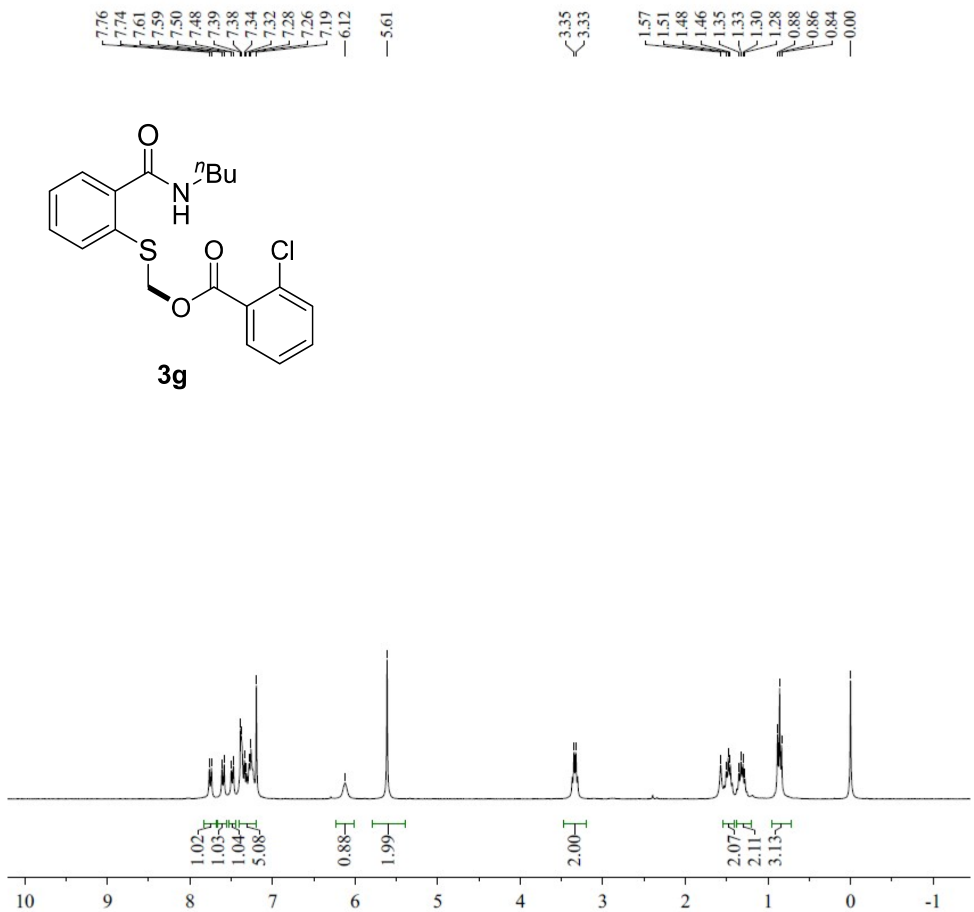

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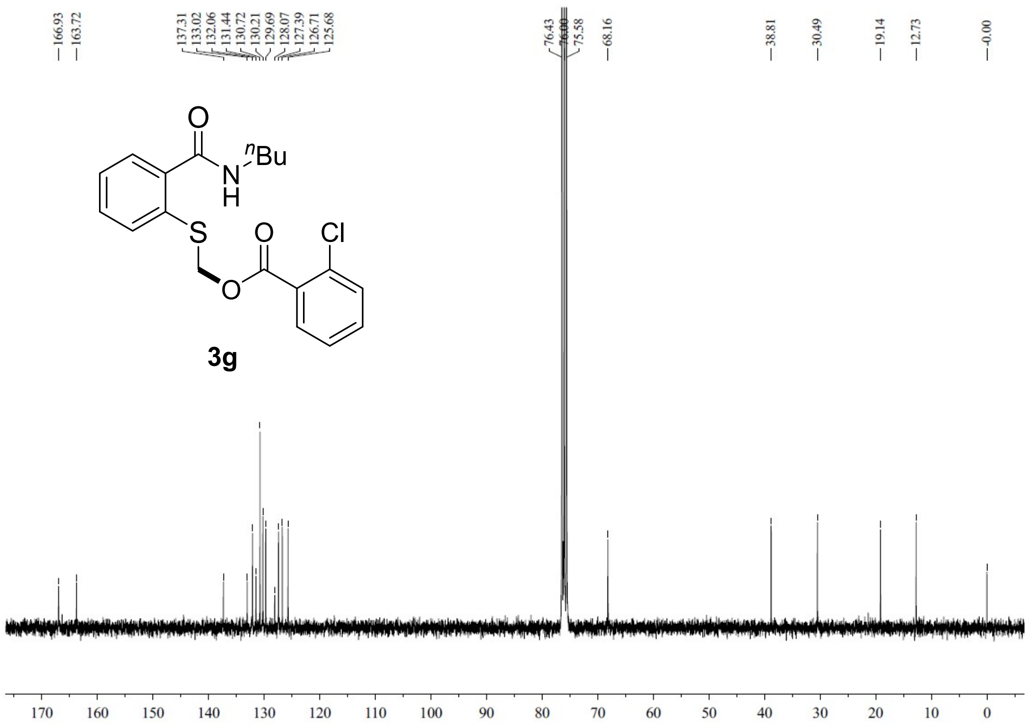

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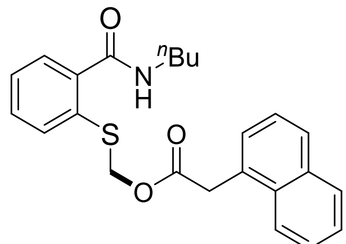

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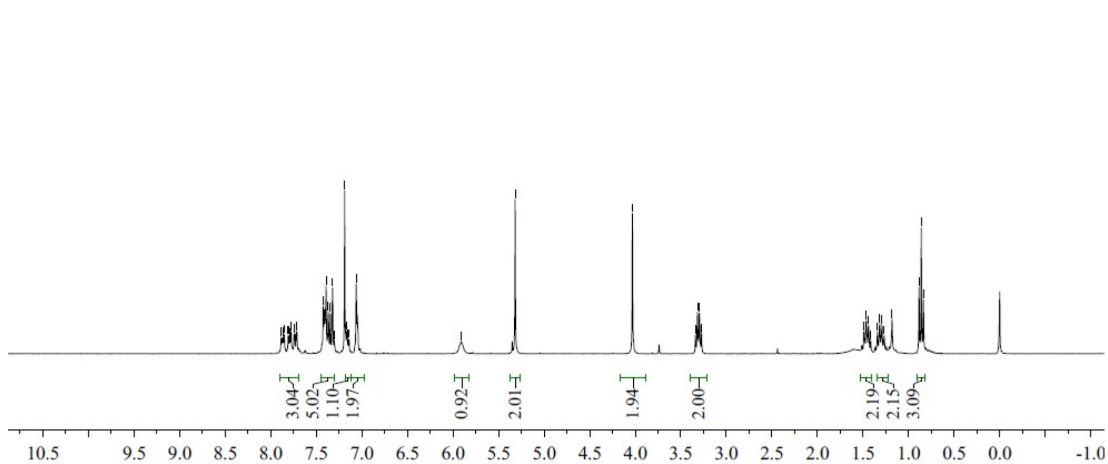

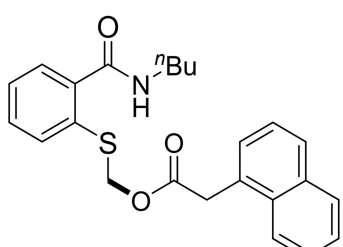

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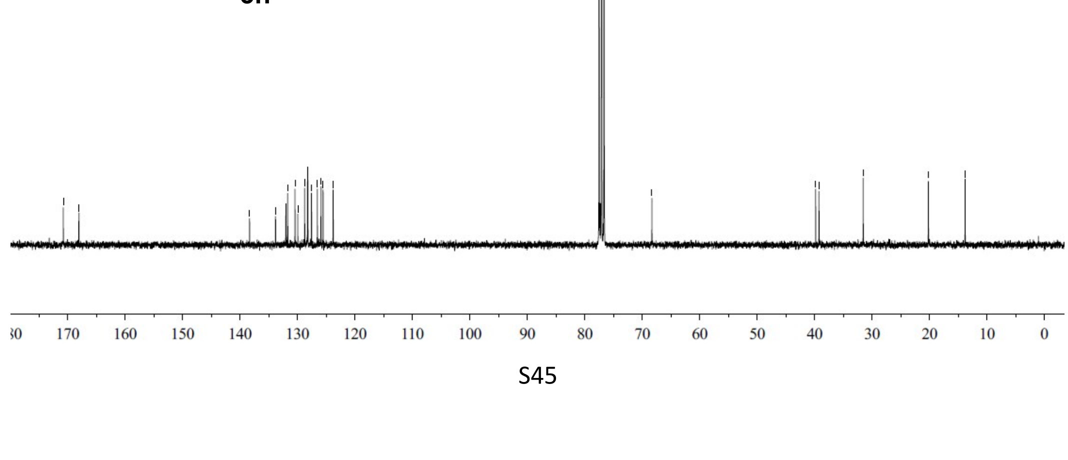

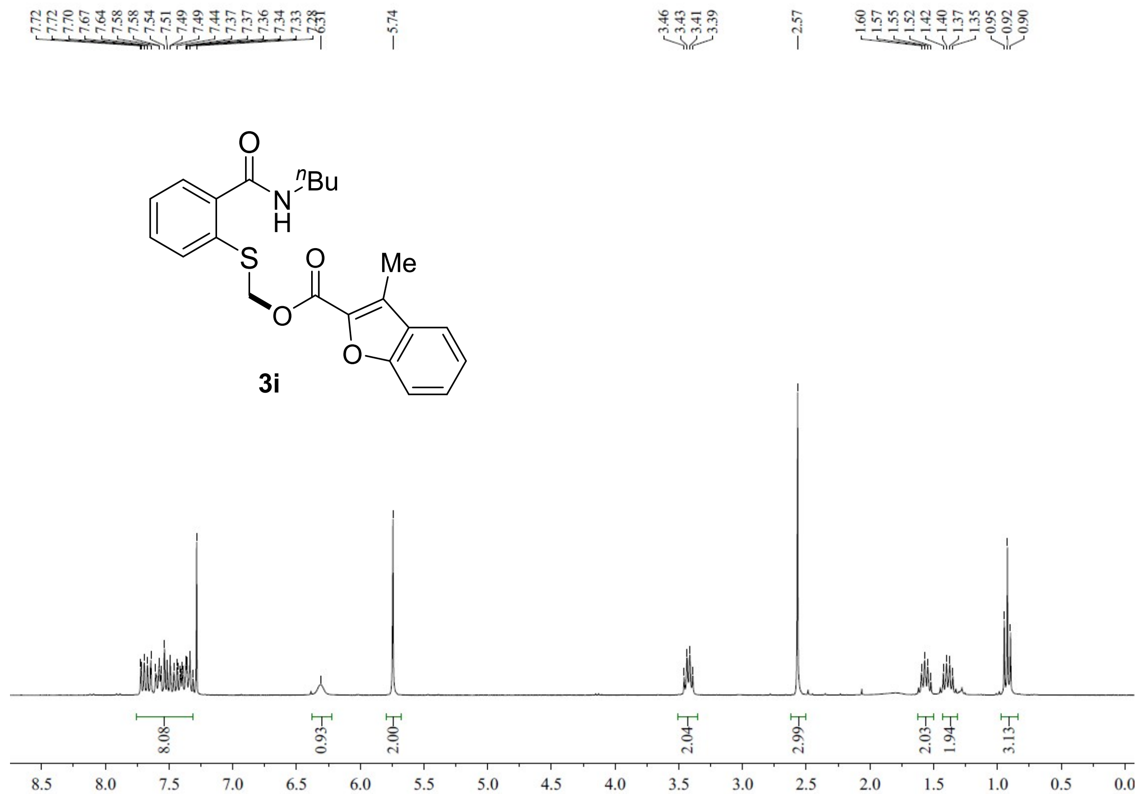

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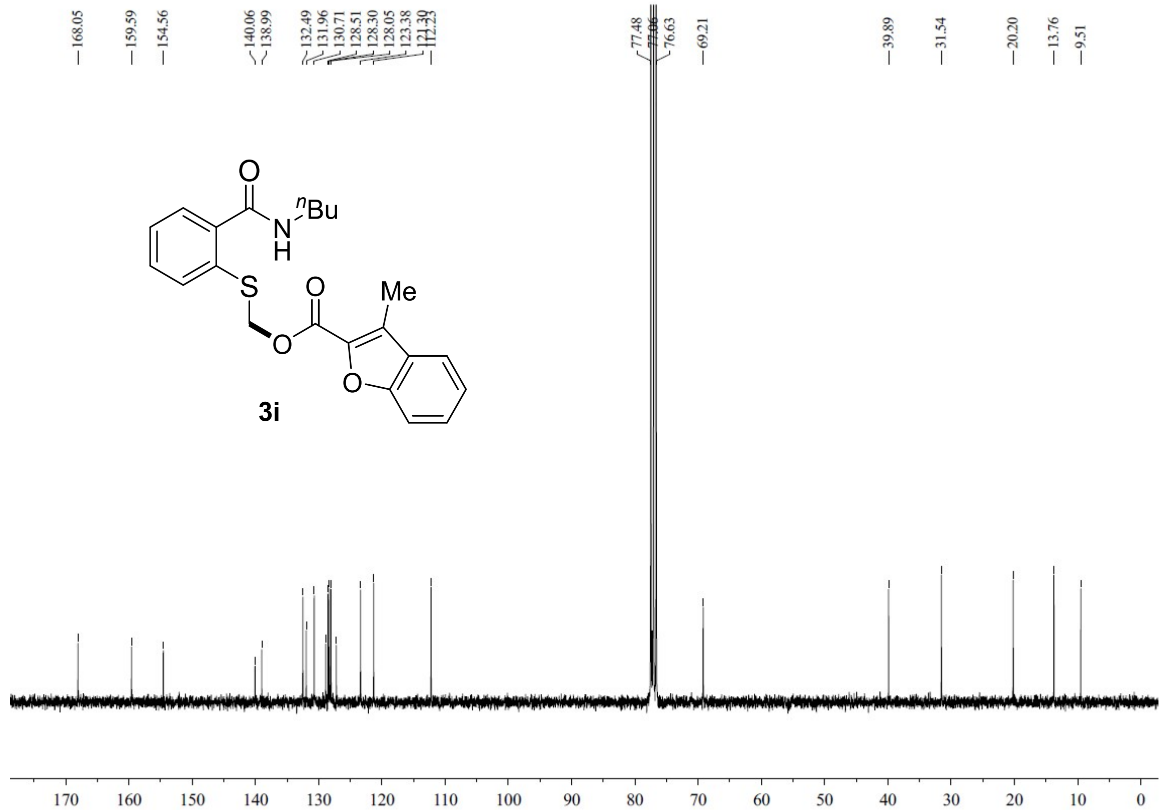

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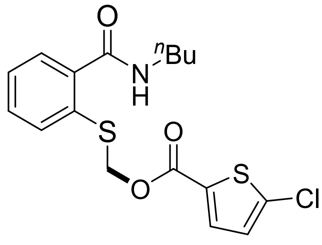

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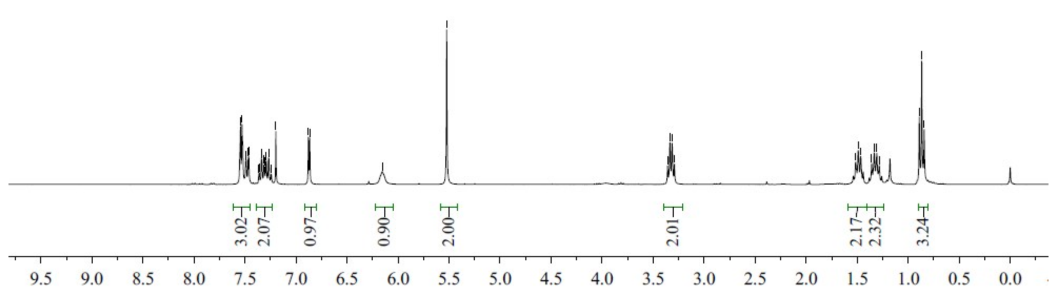

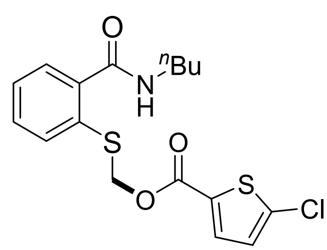

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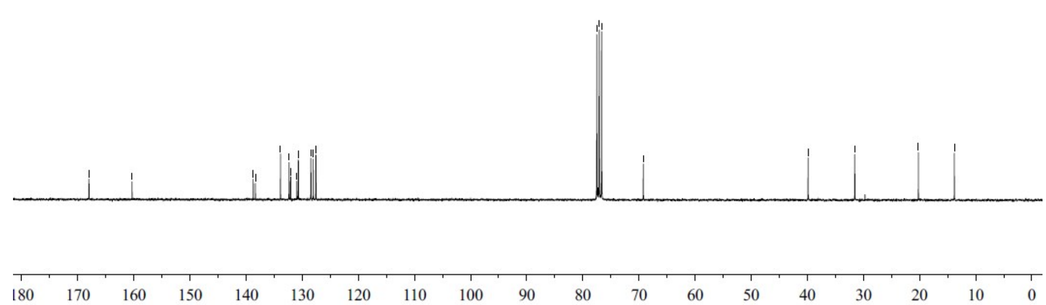

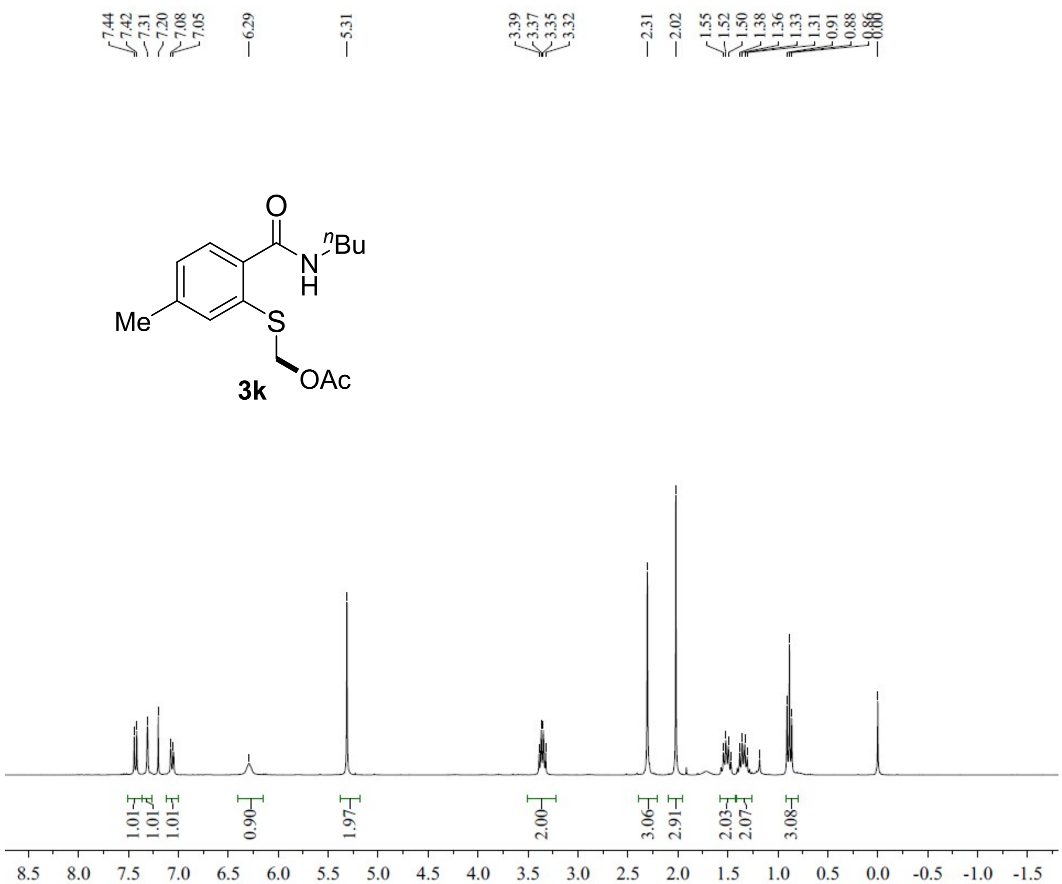
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1.31
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0.86
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1.01
1.01
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2.00
3.06
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2.03
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3.08
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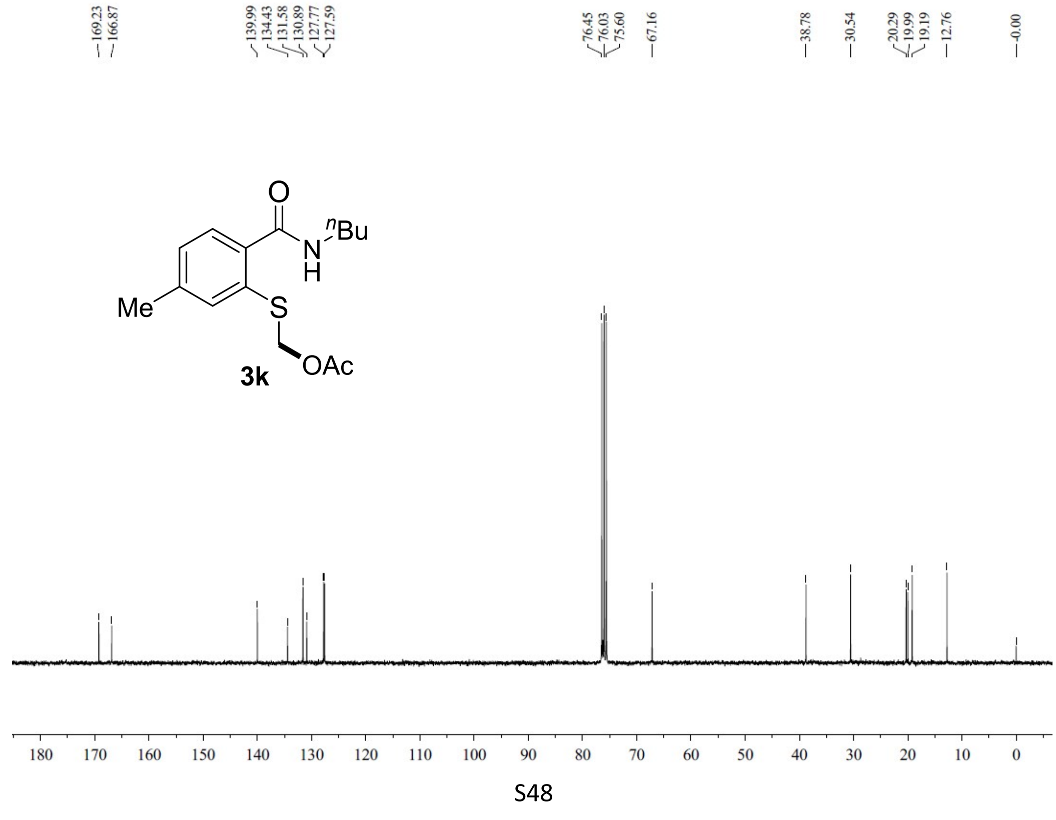
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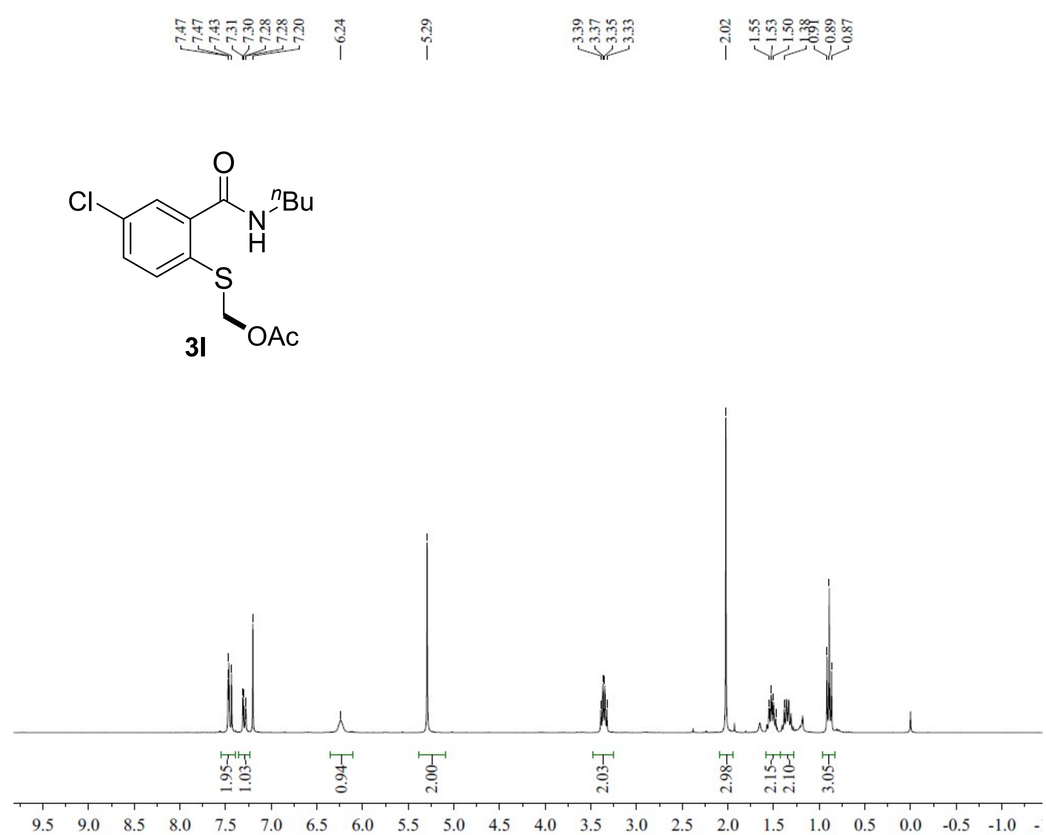
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1.50
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0.89
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3.05
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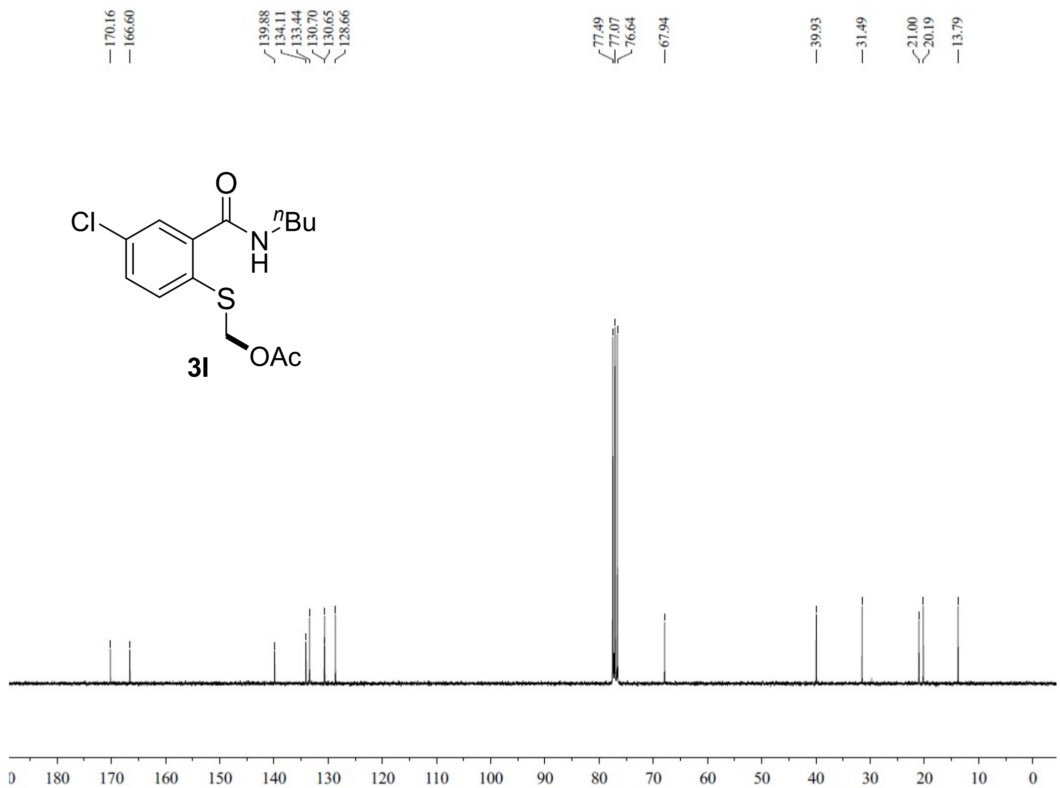
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31.49
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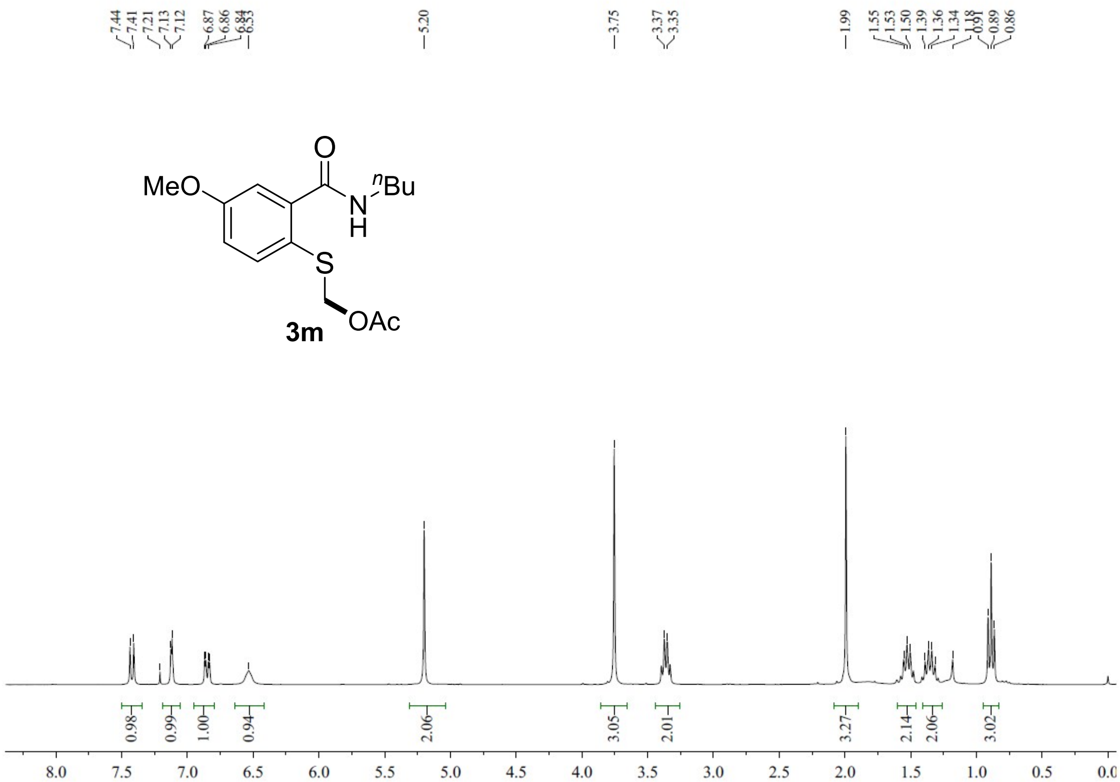
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MeO
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N
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0.98 0.99 1.00 0.94 2.06 3.05 2.01 3.27 2.14 2.06 3.02
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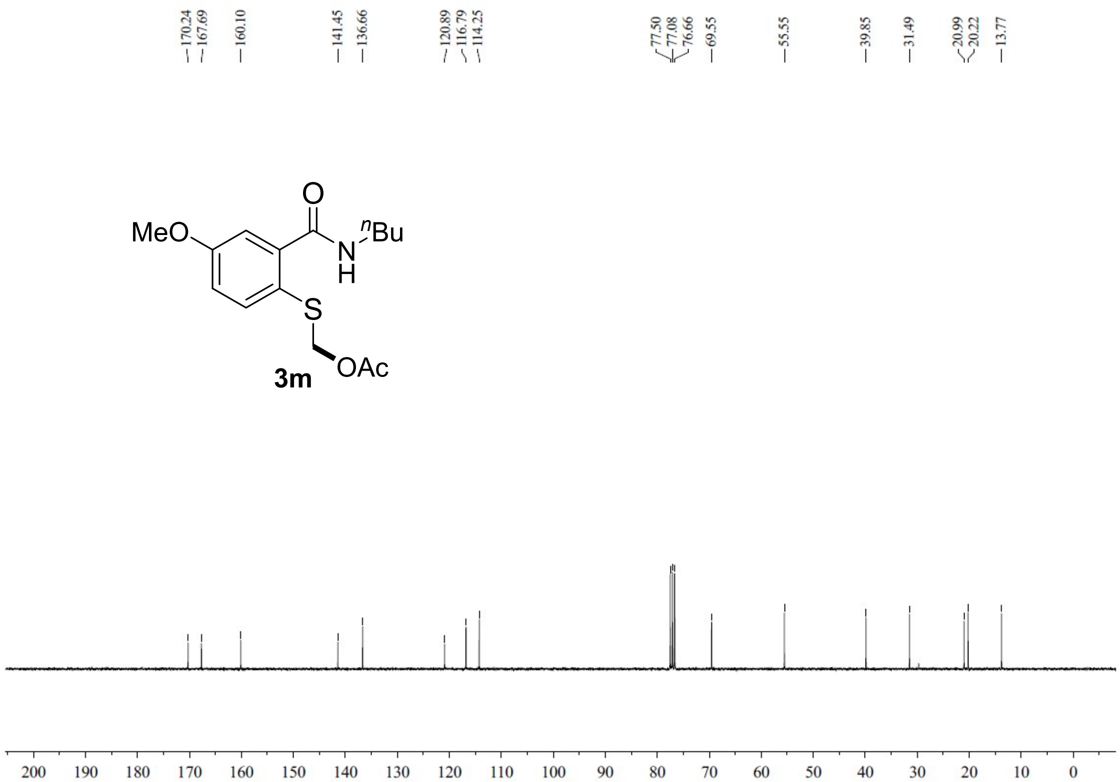
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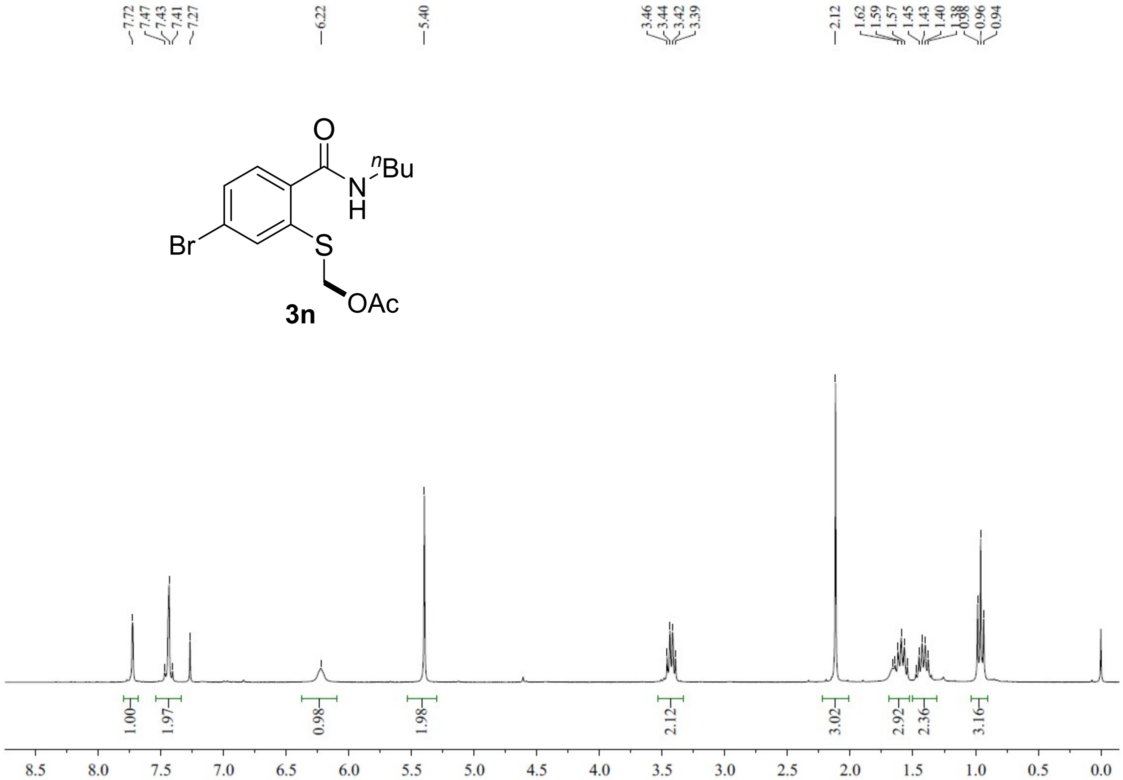
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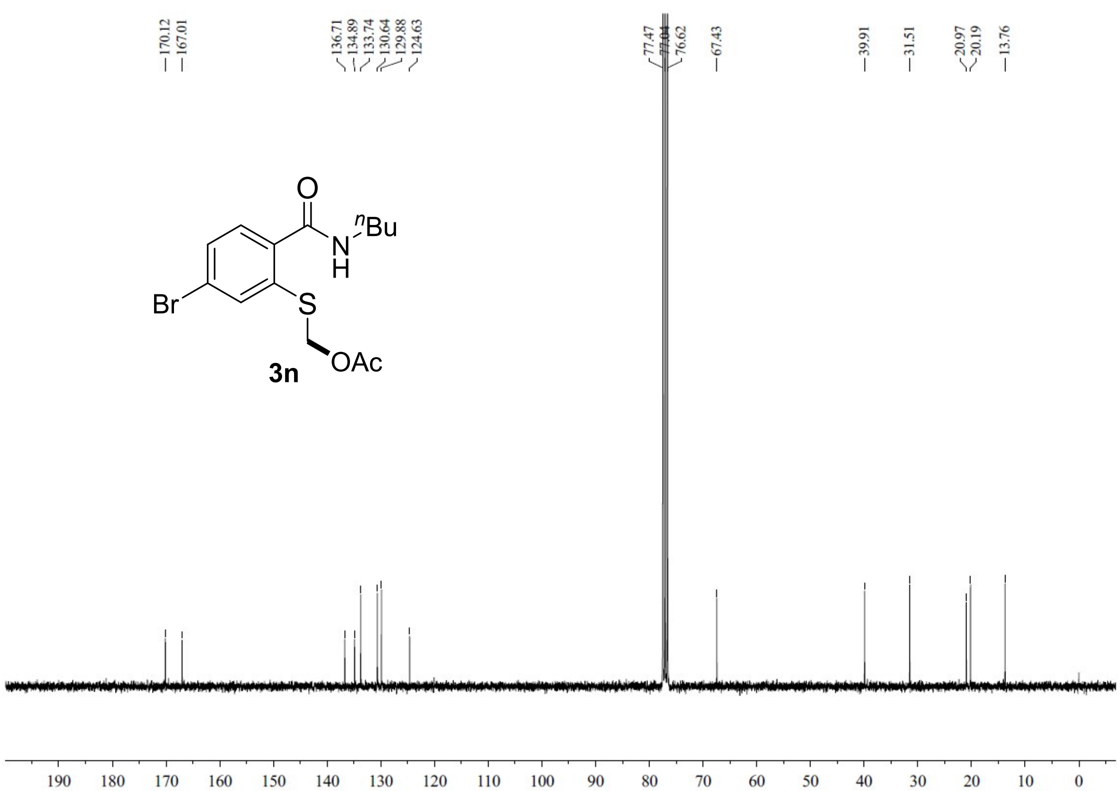
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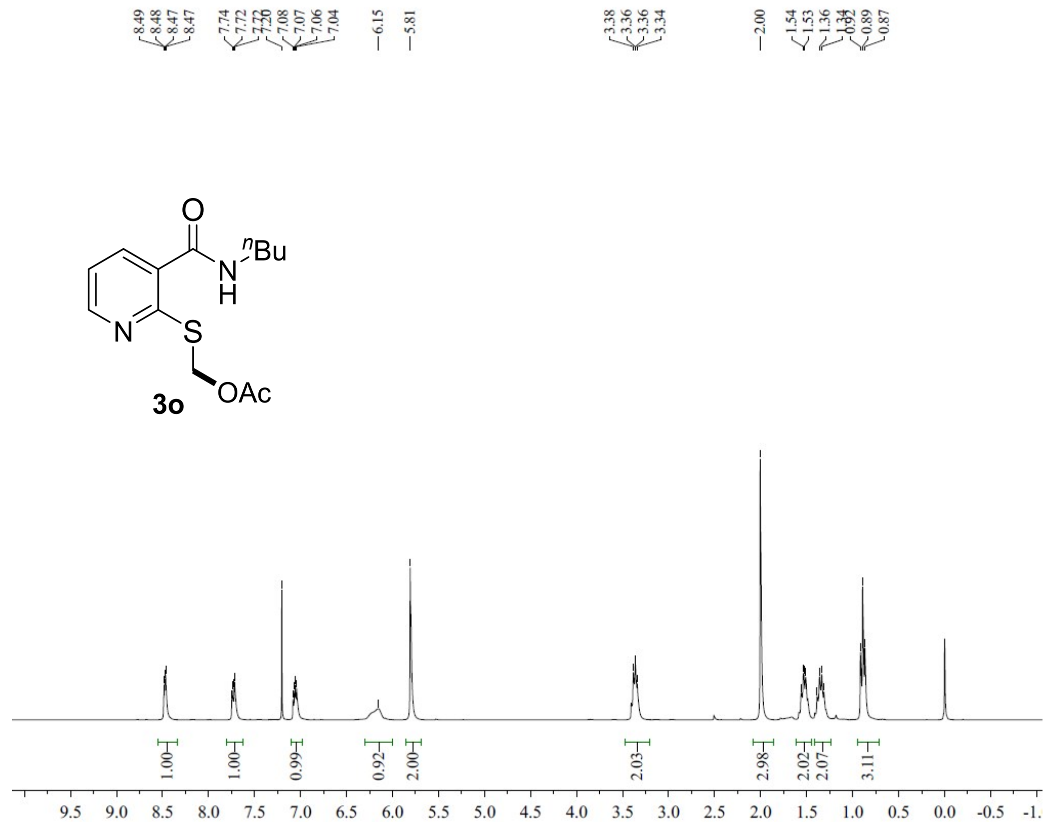
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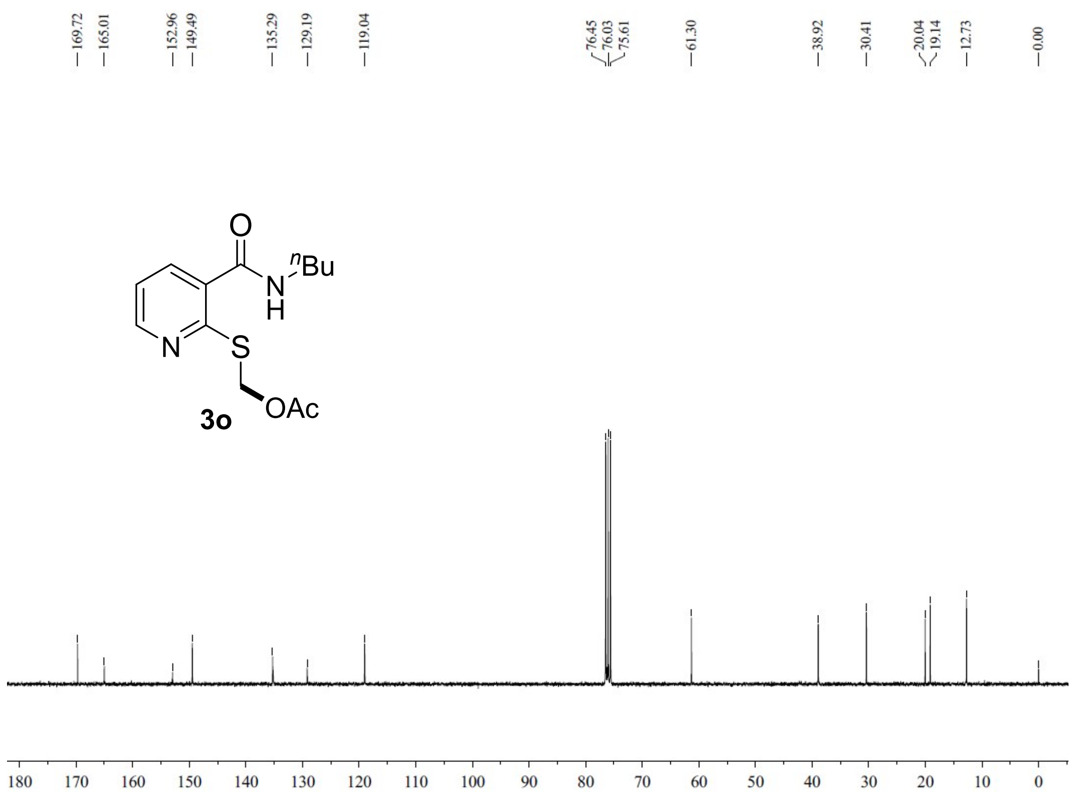
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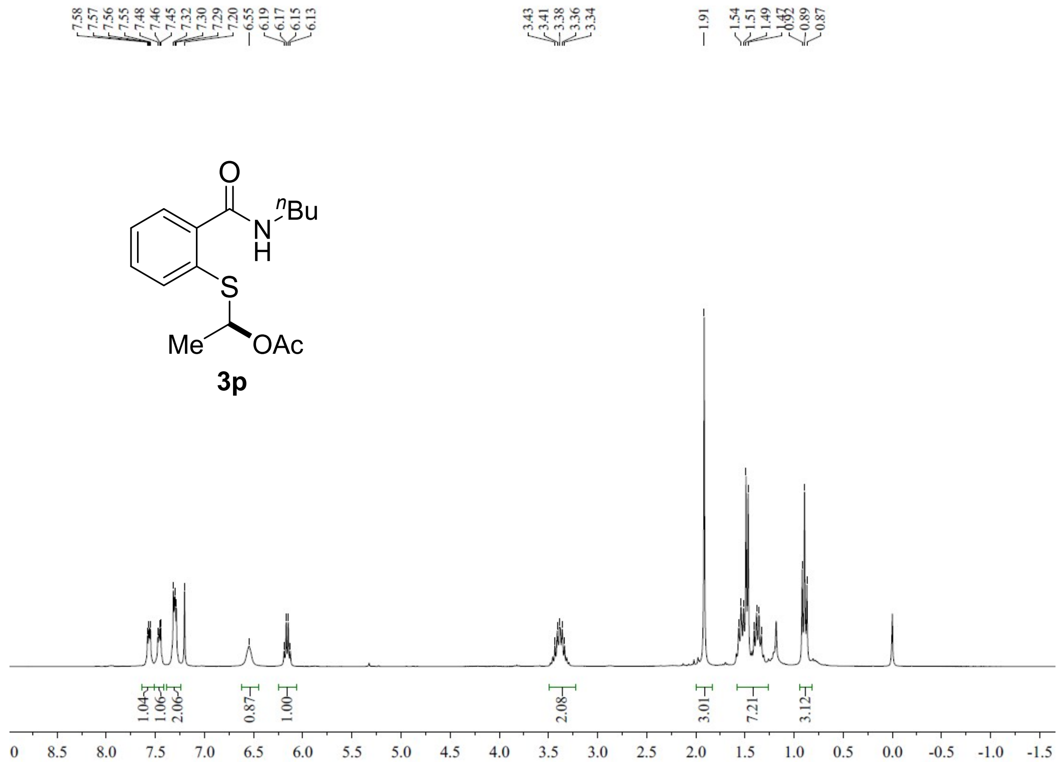
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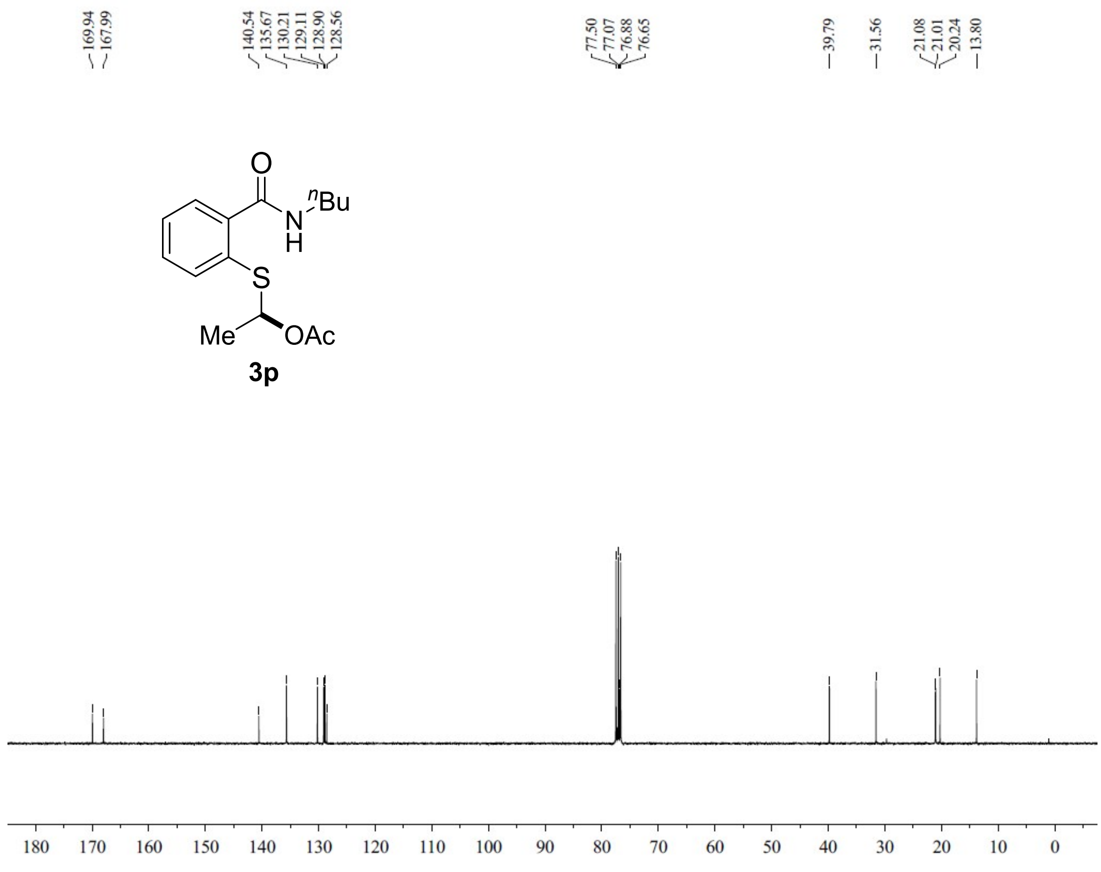
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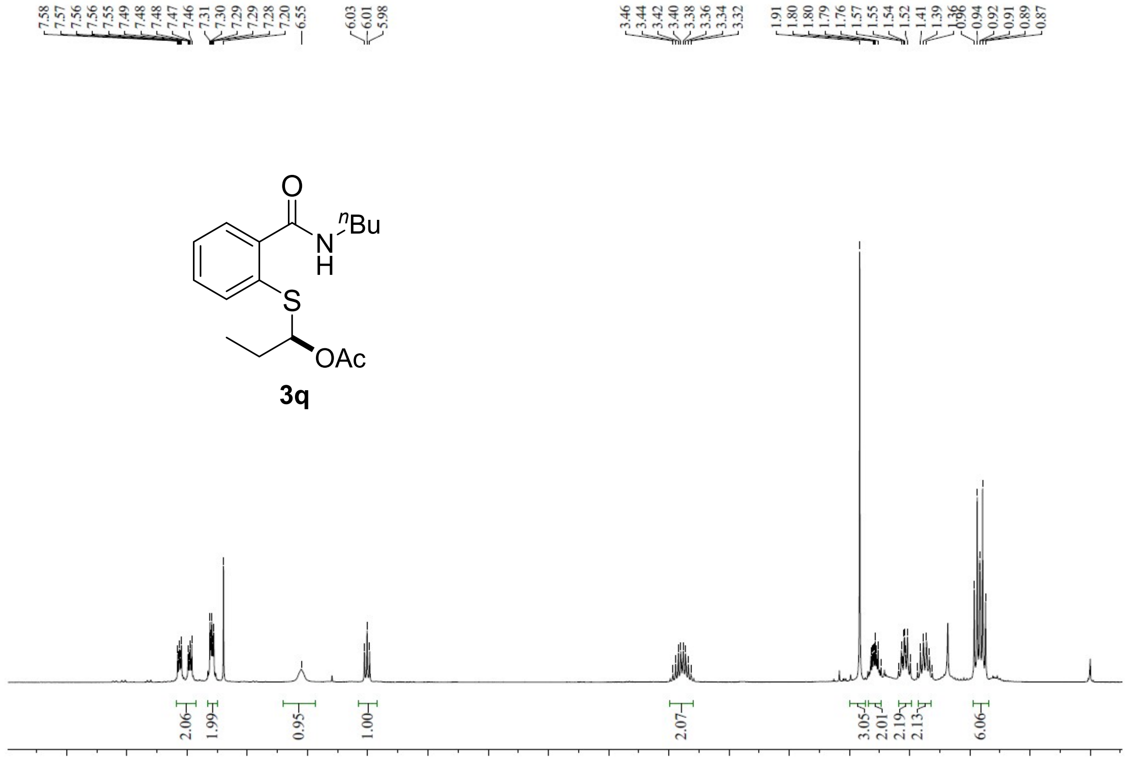
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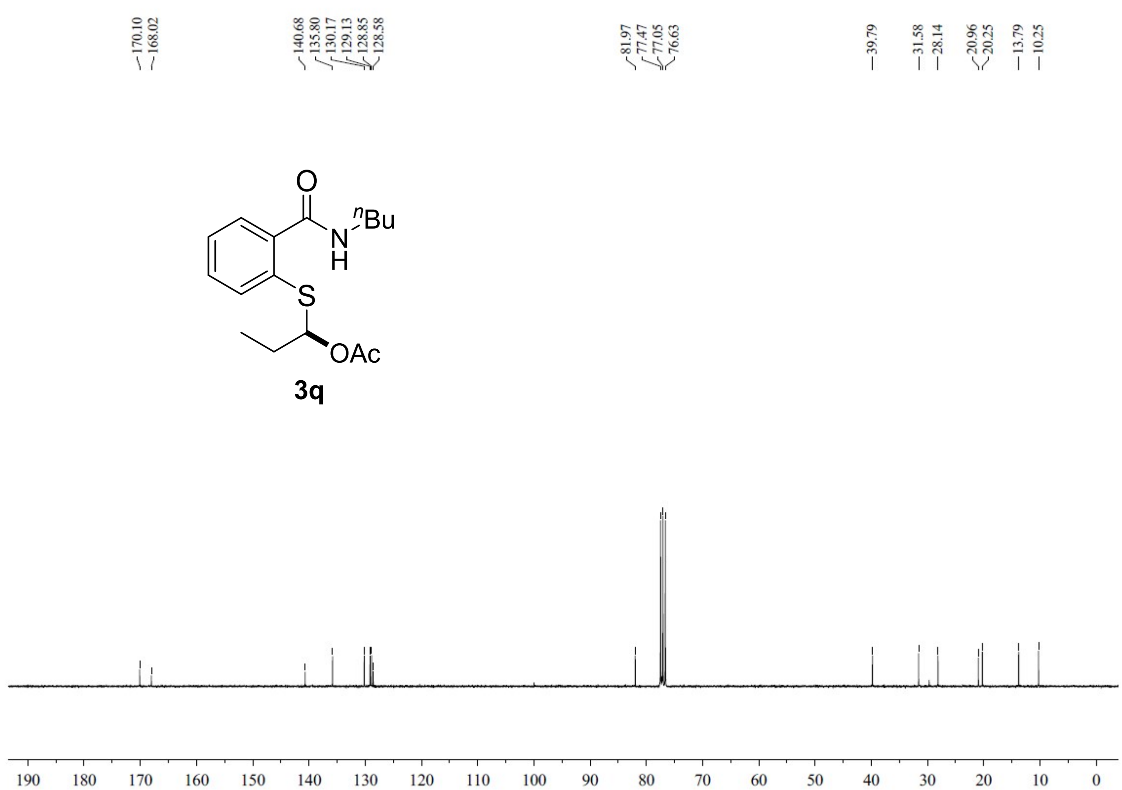
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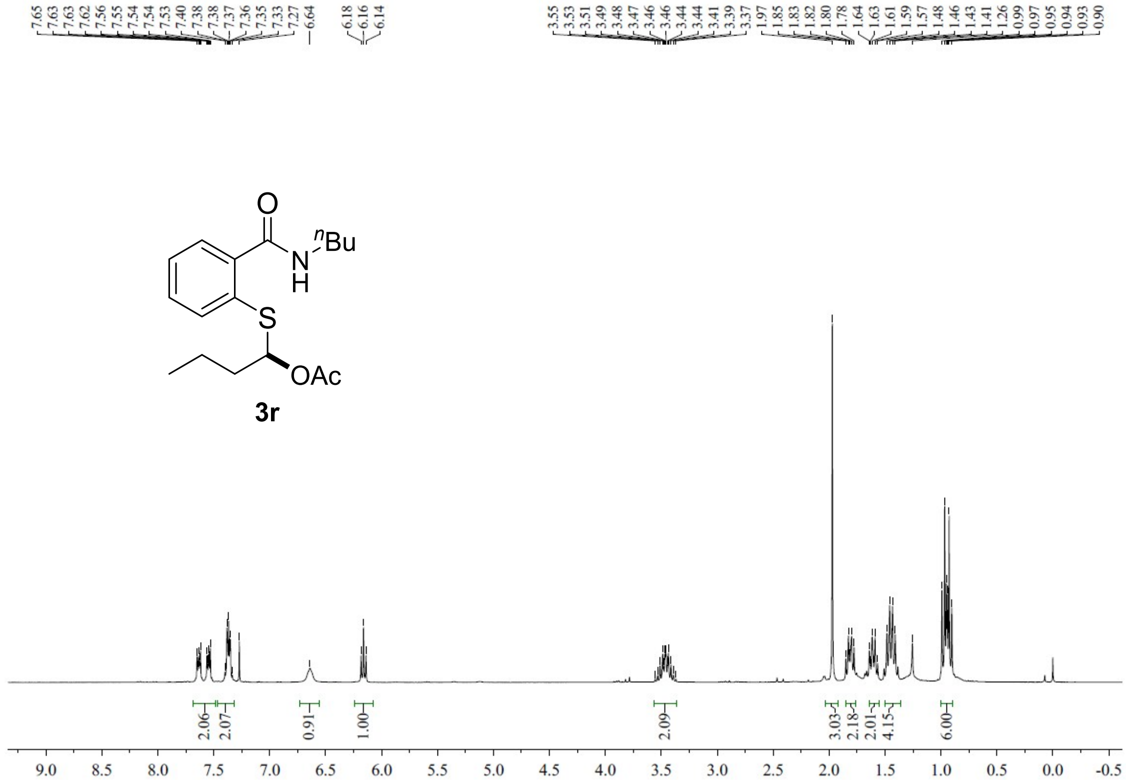
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1.00
2.09
3.03
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6.00
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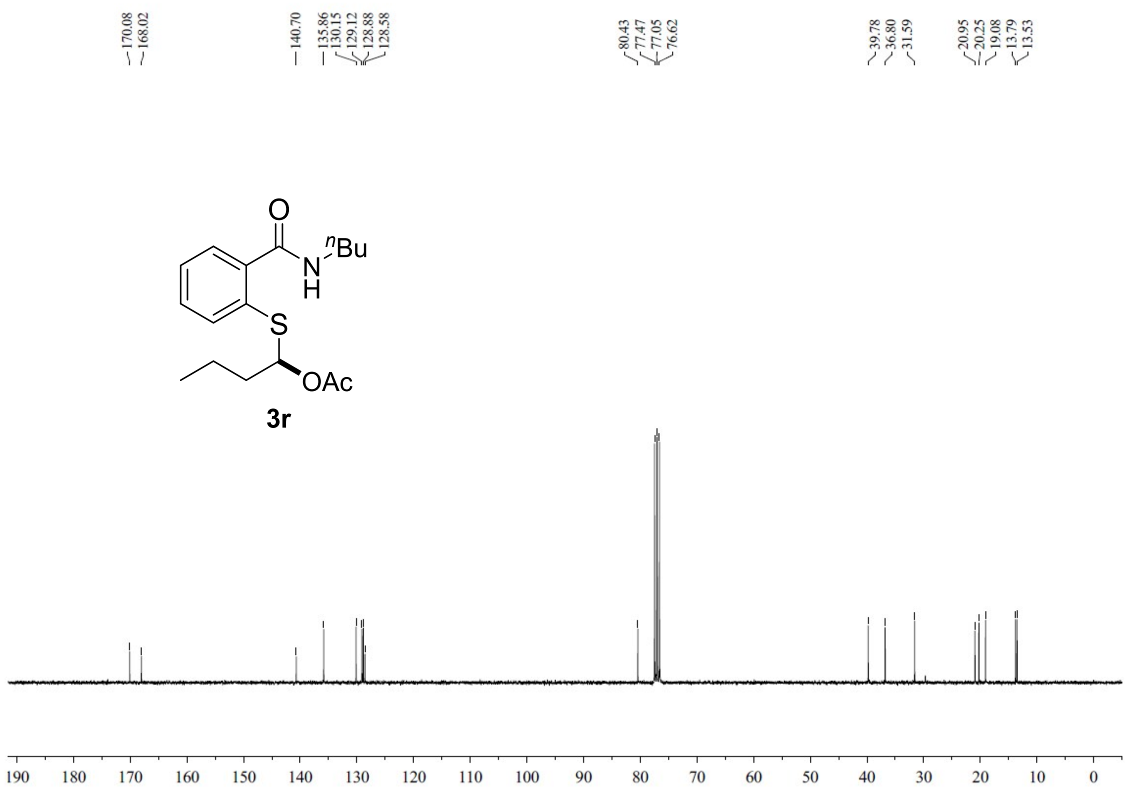
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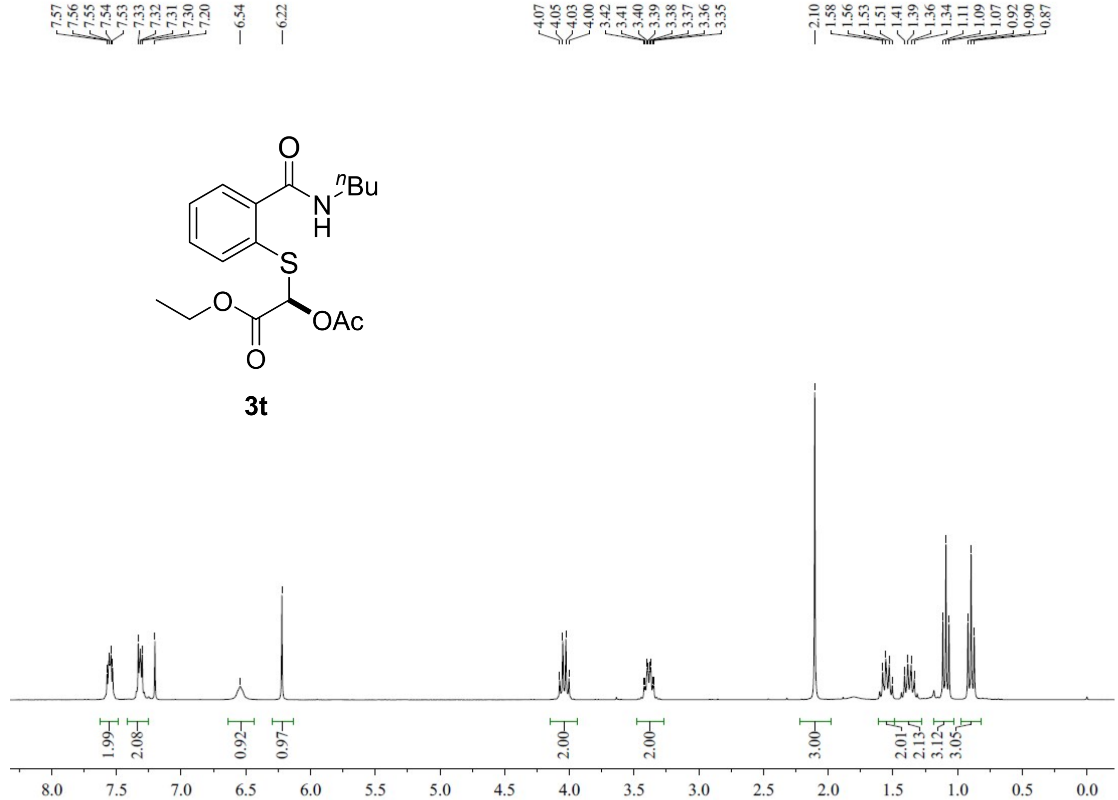

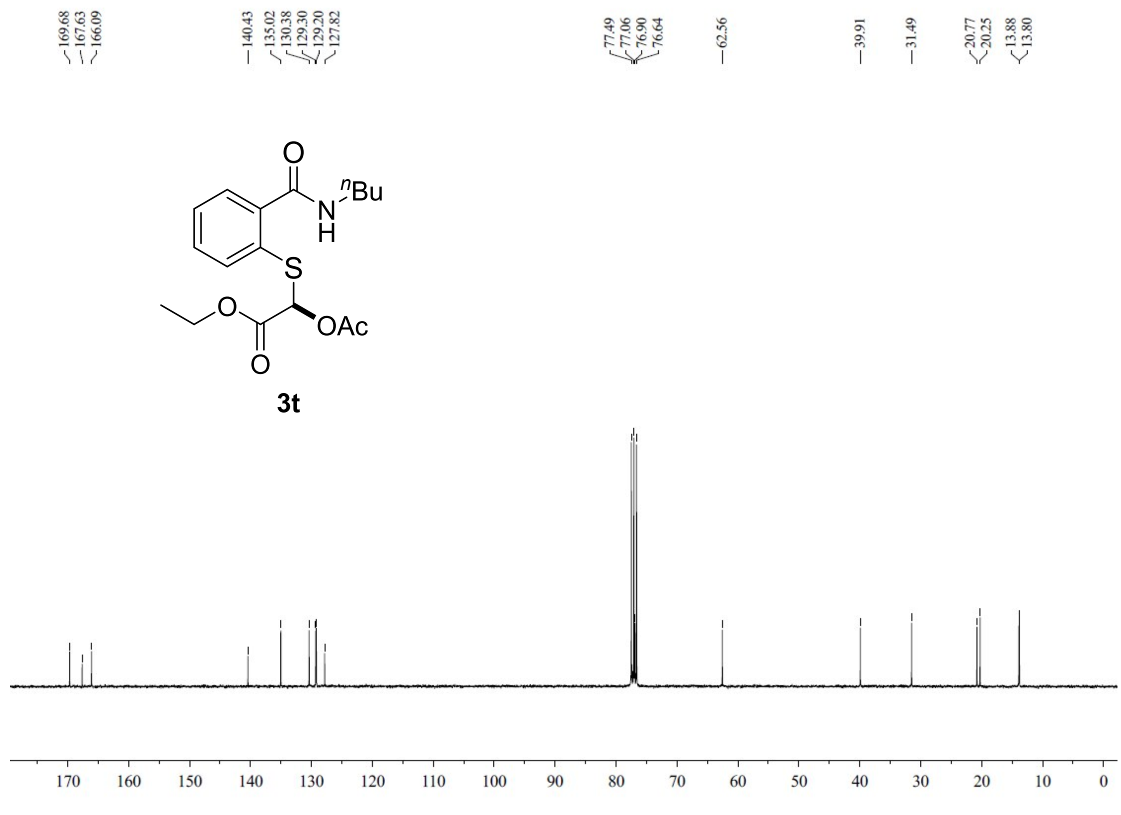

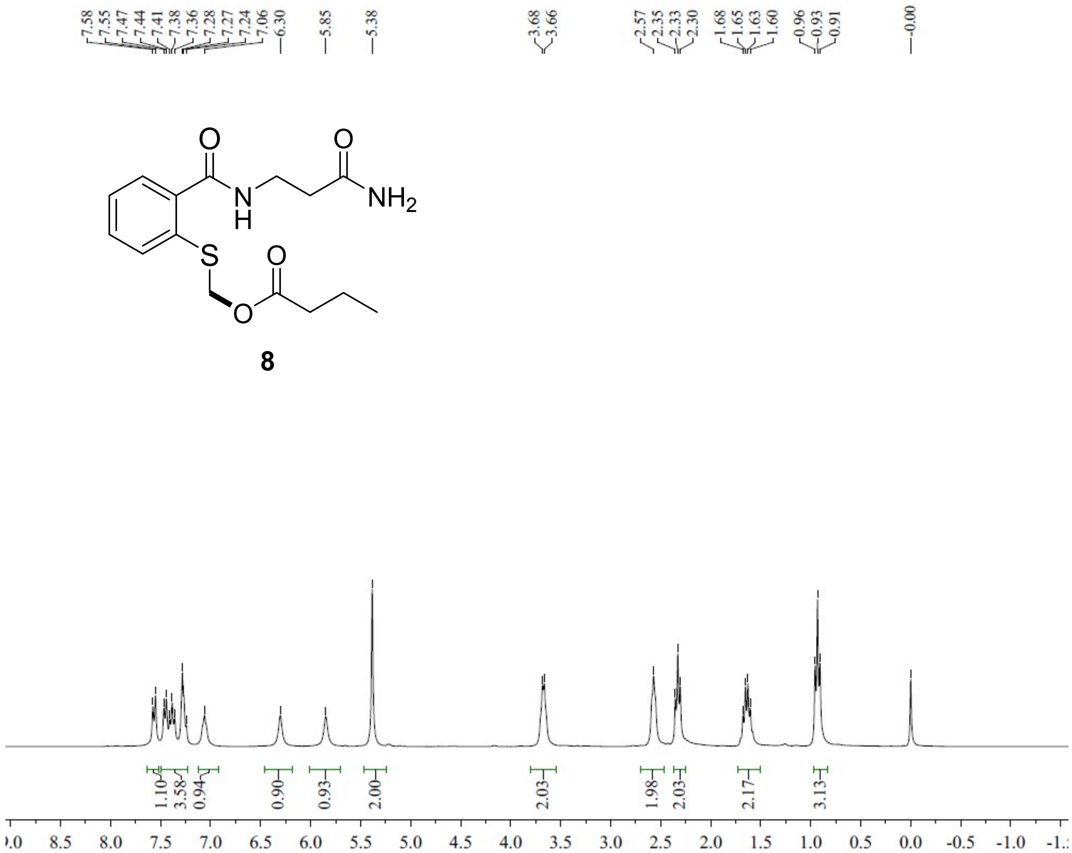
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O
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NH2
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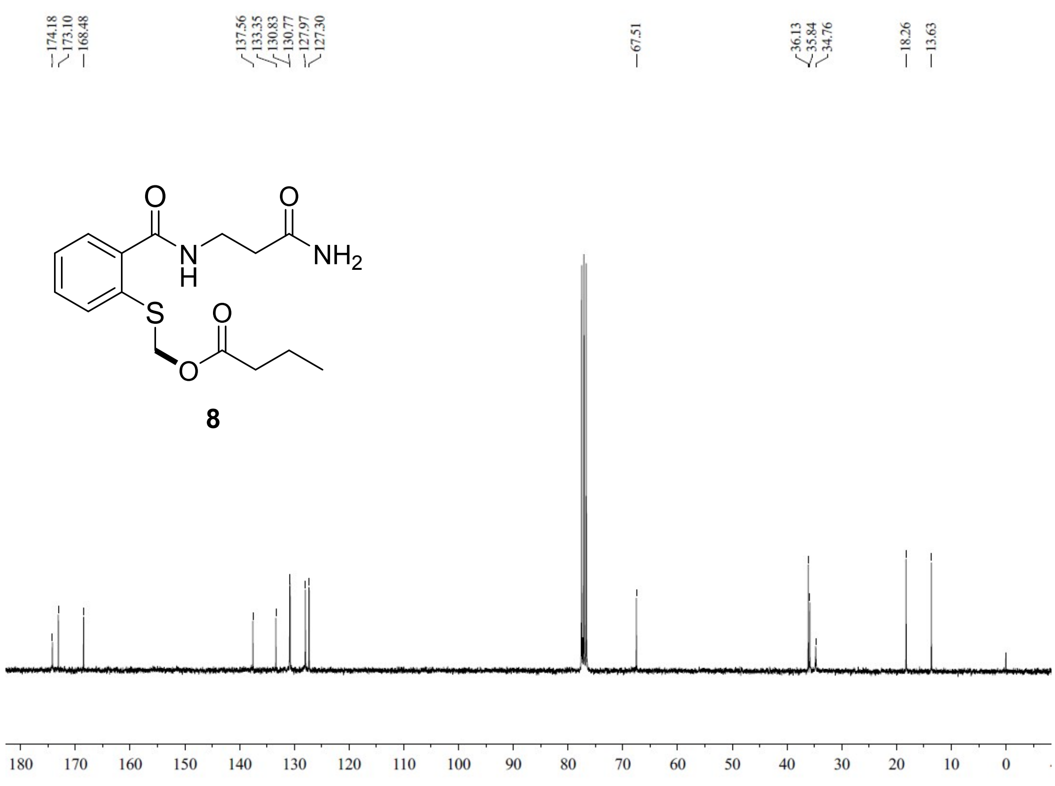
8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180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

8