

# Supporting Information

## Lewis- and Brønsted-Acid Cooperative Catalytic

### Radical Coupling of Aldehydes and Azodicarboxylate

Hong-Bo Zhang, Yao Wang, Yun Gu and Peng-Fei Xu\*

State Key Laboratory of Applied Organic Chemistry & Department of Chemistry, Lanzhou  
University, Lanzhou 730000, P. R. China  
Fax: (+86) 931-8915557, E-mail: xupf@lzu.edu.cn

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## 1. General Information

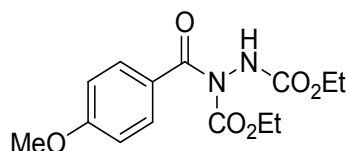
Chemicals and solvents were either purchased from commercial suppliers or purified by standard procedures as specified in *Purification of Laboratory Chemicals*, 4th Ed (Armarego, W. L. F.; Perrin, D. D. Butterworth Heinemann: 1997). All reactions were carried out in carousel tubes (15 cm × 2 cm) equipped with an octagon-shaped magnetic stirrer bar (12.7 mm × 3 mm). All reactions were monitored by thin-layer chromatography (TLC) on pre-coated silica gel plates (254 μm). Flash column chromatography was carried out with (200–300 mesh) silica gel. <sup>1</sup>H NMR spectra were recorded at 400 MHz and <sup>13</sup>C NMR at 100 MHz on Bruker AM-400 spectrometers at ambient temperature in CDCl<sub>3</sub>. HRMS were performed on Bruker maXis 4G mass instrument (ESI) or Thermo ORBITRAP ELITE (ESI). IR spectra were recorded using Nicolet NEXUS 670 FT-IR instrument.

## 2. General Procedure for the functionalization of aldehyde with DEAD

Azodicarboxylate (0.2 mmol), CoCO<sub>3</sub> (2.4 mg, 0.02 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (0.2 mL) were added to a test tube, the aldehyde (0.24 mmol) was then added to the mixture. After that, 8 μL solution of TFA (50 μL) and CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) mixture was added to the reaction mixture. The reaction mixture was stirred at 300 rpm at 21 °C in a stoppered carousel tube for the time specified below. The solvent was removed *in vacuo* and the product was purified as specified below.

## 3. Analytical Data

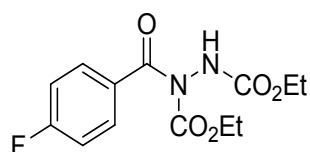
### Diethyl-2-yl 1-(4-methoxybenzoyl)hydrazine-1,2-dicarboxylate 2a



The reaction was stirred for 12 h. Purification by column chromatography (20% EtOAc/Petrol) gave diethyl-2-yl 1-(4-methoxybenzoyl)hydrazine-1,2-dicarboxylate as a colorless oil (57.0 mg, 0.18 mmol, 92%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.73-7.71 (m, 2H), 7.33 (br s, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 4.25 (q, *J* = 7.0 Hz, 2H), 4.17 (q, *J* = 7.0 Hz, 2H), 3.85 (s, 3H), 1.31-1.27 (t, *J* = 7.2 Hz, 3H), 1.14-1.11

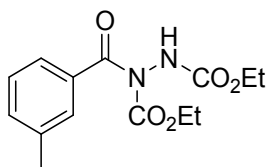
(t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.3, 163.0, 155.6, 153.4, 131.1, 126.4, 113.5, 63.7, 62.4, 55.3, 14.2, 13.8; IR (thin film) 3312, 2984, 2938, 1743, 1704, 1606, 1578  $\text{cm}^{-1}$ ; HRMS (FTMS) calculated for  $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_6$   $[\text{M}+\text{H}]^+$  311.1238, found 311.1231.

### Diethyl 1-(4-fluorobenzoyl)hydrazine-1,2-dicarboxylate 2b



The reaction was stirred for 12 h. Purification by column chromatography (20% EtOAc/Petrol) gave diethyl 1-(4-fluorobenzoyl)hydrazine-1,2-dicarboxylate as a colorless oil (56.0 mg, 0.18 mmol, 94%):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (m, 2H), 7.37 (br s, 1H), 7.12-7.08 (m, 2H), 4.25 (q,  $J = 7.0$  Hz, 2H), 4.17 (q,  $J = 7.0$  Hz, 2H), 1.31-1.27 (t,  $J = 7.2$  Hz, 3H), 1.14-1.11 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.9, 166.2, 163.7, 155.6 (d,  $J_{\text{C-F}} = 230$  Hz), 132.0 (d,  $J_{\text{C-F}} = 8$  Hz), 130.9 (d,  $J_{\text{C-F}} = 9$  Hz), 115.4 (d,  $J_{\text{C-F}} = 22$  Hz), 64.0, 62.6, 14.2, 13.7; IR (thin film) 3315, 2985, 2938, 1746, 1714, 1603, 1508  $\text{cm}^{-1}$ ; HRMS (FTMS) calculated for  $\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}_5\text{F}$   $[\text{M}+\text{Na}]^+$  321.0857, found 321.0853.

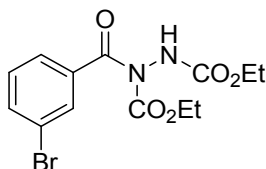
### Diethyl 1-(3-methylbenzoyl)hydrazine-1,2-dicarboxylate 2c



The reaction was stirred for 12 h. Purification by column chromatography (20% EtOAc/petrol) gave diethyl 1-(3-methylbenzoyl)hydrazine-1,2-dicarboxylate as a colorless oil (54.1 mg, 0.18 mmol, 92%):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (m, 2H), 7.33-7.27 (m, 3H), 4.29 (q,  $J = 7.0$  Hz, 2H), 4.21 (q,  $J = 7.0$  Hz, 2H), 2.37 (s, 3H), 1.31-1.27 (t,  $J = 7.2$  Hz, 3H), 1.08-1.05 (t,  $J = 7.2$  Hz

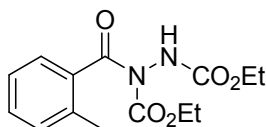
,3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.1, 155.6, 153.4, 137.9, 134.7, 132.7, 128.5, 127.9, 125.2, 63.7, 62.5, 21.1, 14.2, 13.6; IR (thin film) 3312, 2984, 2937, 1745, 1711  $\text{cm}^{-1}$ ; HRMS (FTMS) calculated for  $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_5$   $[\text{M}+\text{H}]^+$  295.1288, found 295.1284.

#### Diethyl 1-(3-bromobenzoyl)hydrazine-1,2-dicarboxylate 2d



The reaction was stirred for 12 h. Purification by column chromatography (20% EtOAc/petrol) gave diethyl 1-(3-bromobenzoyl)hydrazine-1,2-dicarboxylate as a colorless oil (66.8 mg, 0.18 mmol, 93%):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (s, 1H), 7.65-7.60 (m, 2H), 7.31-7.27 (m, 2H), 4.29 (q,  $J = 7.0$  Hz, 2H), 4.21 (q,  $J = 7.0$  Hz, 2H), 1.31-1.27 (t,  $J = 7.2$  Hz, 3H), 1.08-1.05 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.5, 155.6, 153.0, 136.6, 134.7, 130.8, 129.6, 126.5, 122.0, 64.1, 62.5, 14.3, 13.7; IR (thin film) 3313, 2984, 2938, 1747, 1714  $\text{cm}^{-1}$ ; HRMS (FTMS) calculated for  $\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}_5\text{Br}$   $[\text{M}+\text{H}]^+$  359.0237, found 359.0236.

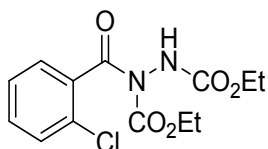
#### Diethyl 1-(2-methylbenzoyl)hydrazine-1,2-dicarboxylate 2e



The reaction was stirred for 12 h. Purification by column chromatography (20% EtOAc/Petrol) gave diethyl 1-(2-methylbenzoyl)hydrazine-1,2-dicarboxylate as a colorless oil (47 mg, 0.16 mmol, 80%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37-7.31 (m, 2H), 7.26-7.18 (m, 2H), 7.06 (br s, 1H), 4.25 (q,  $J = 7.0$  Hz, 2H), 4.10 (q,  $J = 7.0$  Hz, 2H), 2.40 (s, 3H), 1.33-1.29 (t,  $J = 7.2$  Hz, 3H), 1.04-1.01 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.0, 155.5, 152.8, 135.7, 135.3, 130.3, 130.1, 126.3, 125.3, 64.0, 62.7, 19.1, 14.3, 13.6; IR (thin film) 3310, 2985, 2936, 1744, 1711,  $\text{cm}^{-1}$ ; HRMS (FTMS) calculated for  $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_5$   $[\text{M}+\text{H}]^+$  295.1288,

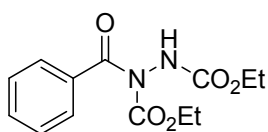
found 295.1281.

### Diethyl 1-(2-chlorobenzoyl)hydrazine-1,2-dicarboxylate 2f



The reaction was stirred for 12 h. Purification by column chromatography (20% EtOAc/Petrol) gave diethyl 1-(2-chlorobenzoyl)hydrazine-1,2-dicarboxylate as a colorless oil (48.5 mg, 0.15 mmol, 77%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45-7.26 (m, 4H), 6.96 (br s, 1H), 4.25 (q,  $J = 7.0$  Hz, 2H), 4.10 (q,  $J = 7.0$  Hz, 2H), 1.33-1.29 (t,  $J = 7.2$  Hz, 3H), 1.04-1.01 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.4, 155.2, 152.2, 135.7, 131.0, 130.2, 129.3, 127.9, 126.7, 64.2, 62.8, 14.3, 13.7; IR (thin film) 3308, 2984, 2930, 1743, 1717  $\text{cm}^{-1}$ ; HRMS (FTMS) calculated for  $\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}_6\text{Cl}$   $[\text{M}+\text{H}]^+$  315.0742, found 315.0734.

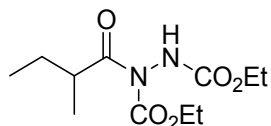
### Diethyl-2-yl 1-benzoylhydrazine-1,2-dicarboxylate 2g



The reaction was stirred for 12 h. Purification by column chromatography (20% EtOAc/Petrol) gave diethyl-2-yl 1-benzoylhydrazine-1,2-dicarboxylate as a colorless oil (52.6 mg, 0.18 mmol, 94%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69-7.68 (m, 2H), 7.53-7.39 (m, 3H), 7.24 (br s, 1H), 4.29 (q,  $J = 7.0$  Hz, 2H), 4.21 (q,  $J = 7.0$  Hz, 2H), 1.31-1.27 (t,  $J = 7.2$  Hz, 3H), 1.08-1.05 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.1, 155.6, 153.4, 134.8, 131.9, 130.1, 128.4, 128.1, 128.0, 63.9, 62.5, 14.3, 14.1; IR (thin film) 3310, 2985, 1743, 1712, 1601, 1508  $\text{cm}^{-1}$ ; HRMS (FTMS) calculated for  $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_5$   $[\text{M}+\text{H}]^+$  281.1132, found

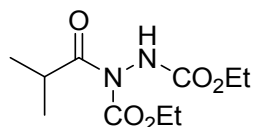
281.1130.

**Diethyl-2-yl 1-2-methylbutanoyl hydrazine-1,2-dicarboxylate 2h**



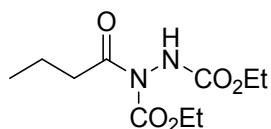
The reaction was stirred for 12 h. Purification by column chromatography (20% EtOAc/Petrol) gave diethyl-2-yl 1-2-methylbutanoyl hydrazine-1,2-dicarboxylate as a colorless oil (50 mg, 0.19 mmol, 96%):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.92 (br s, 1H), 4.31 (q,  $J = 7.2$  Hz, 2H), 4.21 (q,  $J = 7.2$  Hz, 2H), 3.52-3.50 (m, 1H), 1.80 (doublet of quintets,  $J = 14.5, 7.2$  Hz, 1H), 1.46 (doublet of quintets,  $J = 14.5, 7.0$  Hz, 1H), 1.35-1.28 (m, 6H), 1.19 (t,  $J = 7.0$  Hz, 3H), 0.93 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  177.7, 155.6, 153.1, 63.8, 62.4, 40.8, 26.9, 16.7, 14.3, 14.1, 11.5; IR (thin film) 3315, 2978, 2938, 1786, 1746  $\text{cm}^{-1}$ ; HRMS (FTMS) calculated for  $\text{C}_{11}\text{H}_{20}\text{N}_2\text{O}_5$   $[\text{M}+\text{H}]^+$  261.1445, found 261.1444

**Diethyl 1-(2-methylpropanoyl)hydrazine-1,2-dicarboxylate 2i**



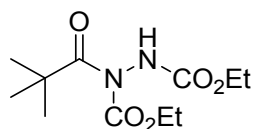
The reaction was stirred for 12 h. Purification by column chromatography (20% EtOAc/petrol) gave diethyl 1-(2-methylpropanoyl)hydrazine-1,2-dicarboxylate as a colorless oil (46.7 mg, 0.19 mmol, 95%):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.90 (br s, 1H), 4.29 (q,  $J = 7.0$  Hz, 2H), 4.21 (q,  $J = 7.0$  Hz, 2H), 3.65 (m,  $J = 6.8$  Hz, 1H), 1.35-1.28 (m, 6H), 1.20 (d,  $J = 6.8$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  178.2, 155.6, 153.0, 63.8, 62.4, 34.2, 19.1, 18.8, 14.3, 14.0; IR (thin film) 3316, 2983, 2938, 1787, 1746  $\text{cm}^{-1}$ ; HRMS (FTMS) calculated for  $\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_5$   $[\text{M}+\text{H}]^+$  247.1288, found 247.1288.

**Diethyl 1-butanoylhydrazine-1,2-dicarboxylate 2j**



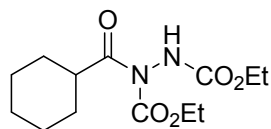
The reaction was stirred for 12 h. Purification by column chromatography (20% EtOAc/petrol) gave diethyl 1-butanoylhydrazine-1,2-dicarboxylate as a colorless oil (47.2 mg, 0.19 mmol, 96%):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.03 (br s, 1H), 4.28 (q,  $J = 7.0$  Hz, 2H), 4.21 (q,  $J = 7.0$  Hz, 2H), 2.90-2.80 (m, 2H), 1.68 (sextet,  $J = 7.2$  Hz, 2H), 1.35-1.20 (m, 6H), 0.97 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.7, 155.6, 153.1, 63.7, 62.4, 38.7, 17.9, 14.2, 14.0, 13.5; IR (thin film) 3317, 2970, 2877, 1787, 1748  $\text{cm}^{-1}$ ; HRMS (FTMS) calculated for  $\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_5$   $[\text{M}+\text{H}]^+$  247.1288, found 247.1286

#### Diethyl 1-(2,2-dimethylpropanoyl)hydrazine-1,2-dicarboxylate 2k



The reaction was stirred for 12 h. Purification by column chromatography (20% EtOAc/petrol) gave diethyl 1-(2,2-dimethylpropanoyl)hydrazine-1,2-dicarboxylate as a colorless oil (48.9 mg, 0.18 mmol, 94%):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.04 (br s, 1H), 4.32 (q,  $J = 7.0$  Hz, 2H), 4.23 (q,  $J = 7.0$  Hz, 2H), 1.36-1.32 (m, 15H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  180.0, 156.0, 154.0, 64.0, 62.6, 42.0, 27.3, 27.0, 14.3, 14.0; IR (thin film) 3301, 2982, 2938, 1780, 1740,  $\text{cm}^{-1}$ ; HRMS (FTMS) calculated for  $\text{C}_{11}\text{H}_{20}\text{N}_2\text{O}_5$   $[\text{M}+\text{Na}]^+$  283.1264, found 283.1258.

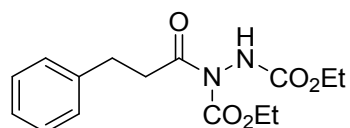
#### Diethyl 1-cyclohexylhydrazine-1,2-dicarboxylate 2l



The reaction was stirred for 12 h. Purification by column chromatography (20% EtOAc/petrol) gave diethyl 1-cyclohexylhydrazine-1,2-dicarboxylate as a colorless oil (53.8 mg, 0.18 mmol, 94%):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.88 (br s,

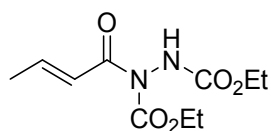
1H), 4.31 (q,  $J = 7.0$  Hz, 2H), 4.21 (q,  $J = 7.0$  Hz, 2H), 3.38 (t,  $J = 7.2$  Hz, 1H), 1.93 (m, 2H), 1.80 (m, 2H), 1.70 (doublet of quintets, 1H), 1.50 (m, 2H), 1.40-1.28 (doublet of quintets, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  177.0, 155.6, 153.1, 63.7, 62.4, 43.9, 29.3, 25.7, 25.5, 14.3, 14.0; IR (thin film) 3316, 2983, 2933, 2856, 1785, 1743  $\text{cm}^{-1}$ ; HRMS (FTMS) calculated for  $\text{C}_{13}\text{H}_{22}\text{N}_2\text{O}_5$   $[\text{M}+\text{H}]^+$  287.1601, found 287.1597.

#### Diethyl 1-(3-phenylpropanoyl)hydrazine-1,2-dicarboxylate 2m



The reaction was stirred for 12 h. Purification by column chromatography (20% EtOAc/petrol) gave diethyl 1-(3-phenylpropanoyl)hydrazine-1,2-dicarboxylate as a colorless oil (59.1 mg, 0.19 mmol, 96%):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (d,  $J = 15.6$  Hz, 1H), 7.38-7.60 (m, 6H), 6.97 (br s, 1H), 4.33 (q,  $J = 7.0$  Hz, 2H), 4.23 (q,  $J = 7.0$  Hz, 2H), 1.38-1.30 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.6, 155.5, 153.4, 146.2, 134.6, 132.0, 130.5, 128.8, 128.4, 128.0, 118.6, 64.2, 62.6, 14.3, 14.1; IR (thin film) 3625, 3316, 2983, 1788, 1746,  $\text{cm}^{-1}$ ; HRMS (FTMS) calculated for  $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_5$   $[\text{M}+\text{H}]^+$  309.1445, found 309.1440.

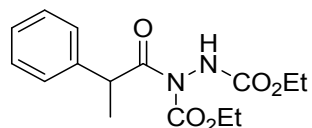
#### (E)-diethyl 1-(but-2-enoyl)hydrazine-1,2-dicarboxylate 2n



The reaction was stirred for 12 h. Purification by column chromatography (20% EtOAc/petrol) gave (E)-diethyl 1-(but-2-enoyl)hydrazine-1,2-dicarboxylate as a colorless oil (46.4 mg, 0.19 mmol, 95%):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.14 (m, 1H), 6.90 (m, 2H), 4.29 (q,  $J = 7.0$  Hz, 2H), 4.21 (q,  $J = 7.0$  Hz, 2H), 1.94 (d,  $J = 7.2$  Hz, 3H), 1.36-1.29 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.6, 155.6, 153.3, 146.6, 123.1, 63.9, 62.5, 18.5, 14.3, 14.1; IR (thin film) 3308, 2984, 2939, 1745  $\text{cm}^{-1}$ ; HRMS (FTMS) calculated for  $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_5$   $[\text{M}+\text{H}]^+$  245.1132, found 245.1133.

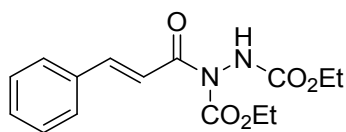


### Diethyl 1-(2-phenylpropanoyl)hydrazine-1,2-dicarboxylate 2o



The reaction was stirred for 12 h. Purification by column chromatography (20% EtOAc/Petrol) gave diethyl 1-(2-phenylpropanoyl)hydrazine-1,2-dicarboxylate as a colorless oil (31.4 mg, 0.10 mmol, 51%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30-7.17 (m, 5H), 6.86 (br s, 1H), 4.29 (q,  $J = 7.0$  Hz, 2H), 4.22 (q,  $J = 7.0$  Hz, 2H), 3.24-2.97 (m, 4H), 1.33-1.26 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.9, 155.5, 153.1, 140.5, 128.4, 128.3, 126.1, 63.9, 62.5, 38.6, 30.5, 14.3, 14.1, IR (thin film) 3308, 2983, 2936, 1744, 1603  $\text{cm}^{-1}$ ; HRMS (FTMS) calculated for  $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_5$   $[\text{M}+\text{Na}]^+$  331.1264, found 331.1256.

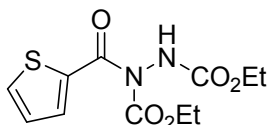
### Diethyl 1-cinnamoylhydrazine-1,2-dicarboxylate 2p



The reaction was stirred for 12 h. Purification by column chromatography (20% EtOAc/Petrol) gave diethyl 1-cinnamoylhydrazine-1,2-dicarboxylate as a colorless oil (31.8 mg, 0.10 mmol, 52%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83-7.79 (d,  $J = 8.5$  Hz, 1H), 7.60-7.56 (m, 3H), 7.41-7.38 (m, 3H), 6.97 (br s, 1H), 4.29 (q,  $J = 7.0$  Hz, 2H), 4.21 (q,  $J = 7.0$  Hz, 2H), 1.38-1.29 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.5, 155.6, 153.4, 146.21, 134.6, 132.0, 130.5, 128.8, 128.4, 128.1,

118.6, 64.0, 62.6, 14.3, 14.1; IR (thin film) 3306, 2984, 2937, 1743, 1621  $\text{cm}^{-1}$ ;  
HRMS (FTMS) calculated for  $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_5$   $[\text{M}+\text{H}]^+$  307.1288, found 307.1281.

#### Diethyl 1-(thiophene-2-carbonyl)hydrazine-1,2-dicarboxylate 2q

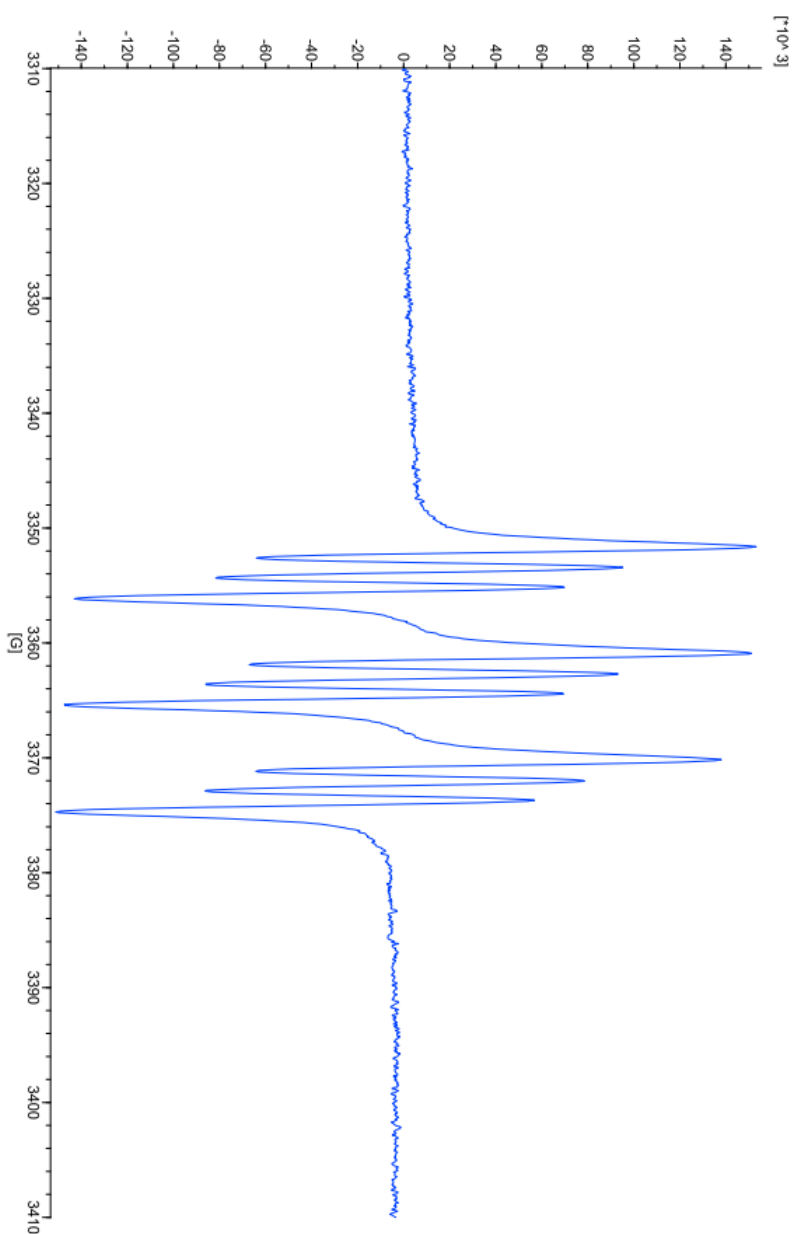


The reaction was stirred for 12 h. Purification by column chromatography (20% EtOAc/Petrol) gave diethyl 1-(thiophene-2-carbonyl)hydrazine-1,2-dicarboxylate as a colorless oil (44.0 mg, 0.15 mmol, 77%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J = 2.8$  Hz, 1H), 7.66 (d,  $J = 22$  Hz, 1H), 7.28-7.11 (m, 1H), 4.30-4.26 (m, 4H) 1.34-1.27 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.9, 135.7, 133.8, 127.2, 64.2, 62.9, 13.9; IR (thin film) 3497, 3301, 2985, 2937, 1768, 1517  $\text{cm}^{-1}$ ;  
HRMS (FTMS) calculated for  $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_5\text{S}$   $[\text{M}+\text{H}]^+$  287.0696, found 287.0689.

#### 4. EPR Experiment and Spectra

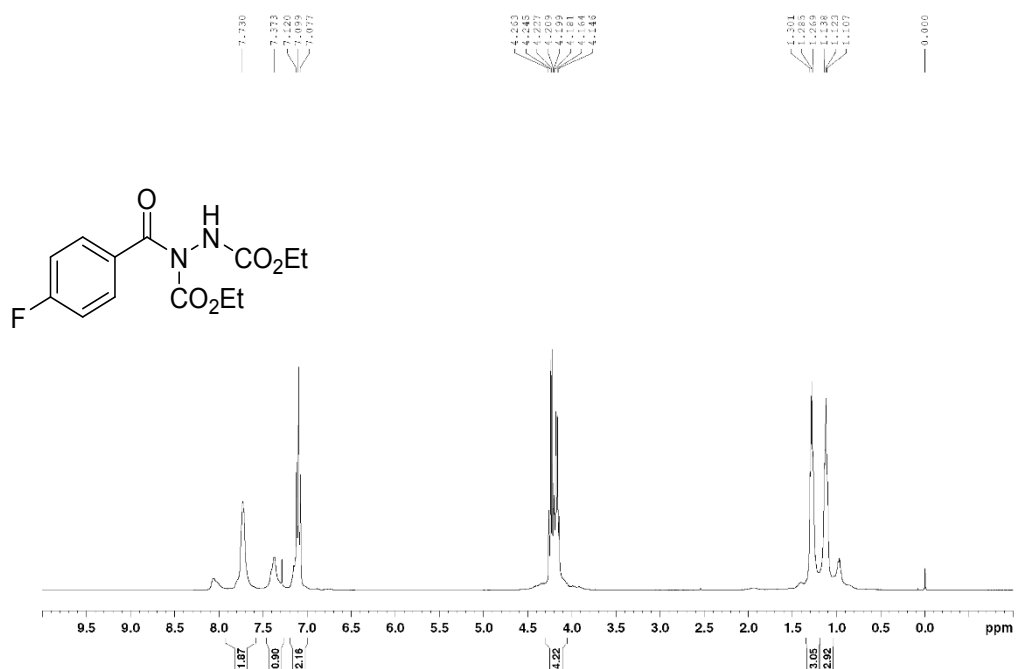
The EPR experiment was performed as following procedure. Diethyl azodicarboxylate (34.8 mg, 0.2 mmol),  $\text{CoCO}_3$  (2.4 mg, 0.02 mmol) and  $\text{CH}_2\text{Cl}_2$  (0.2 mL) were added to a test tube, the 2-methylbutanal (26  $\mu\text{L}$ , 0.24 mmol) was then added to the mixture. After that, 8  $\mu\text{L}$  solution of TFA (50  $\mu\text{L}$ ) and  $\text{CH}_2\text{Cl}_2$  (0.5 mL) mixture was added to the reaction mixture. The reaction mixture was stirred at 300 rpm at 21  $^\circ\text{C}$  in a stoppered carousel tube. After 5 minutes, extract upper clear liquid to EPR experiment.

## **EPR Spectra**

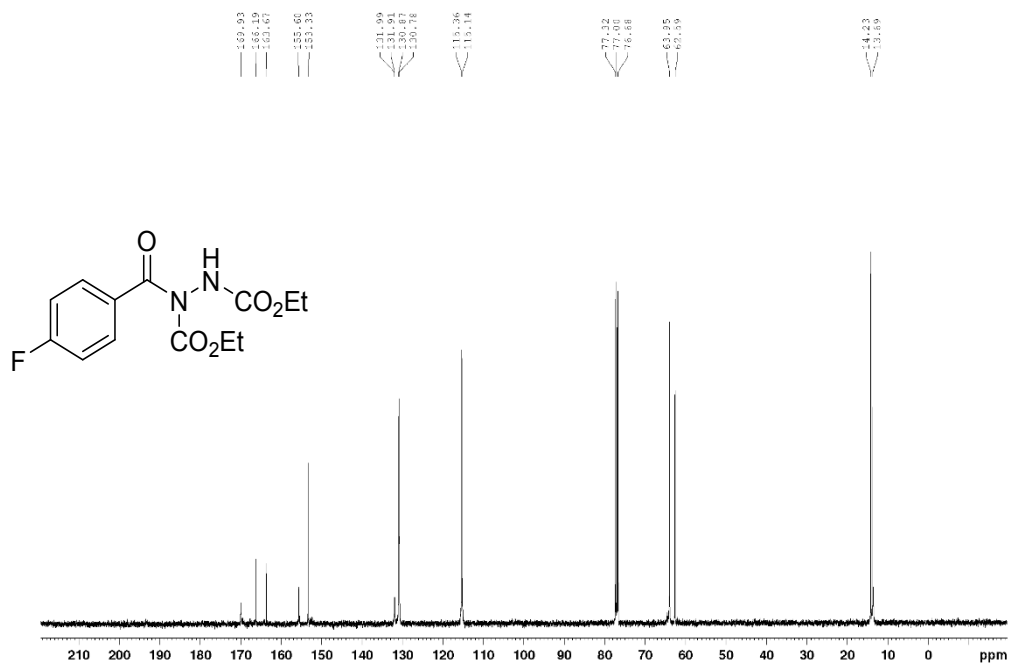


Parameter List	
Operator:	Administrator
Resonator:	c:\jhs0525lic.ca
Acqu. Date:	07/03/2013
# of Scans:	1
Field	
Center Field:	3360.000 G
Sweep Width:	100.000 G
Resolution:	1500 points
Microwave	
Frequency:	9.448 GHz
Power:	25.250 mW
Receiver	
Receiver Gain:	2.00e+003
Phase:	0.00 deg
Harmonic:	1
Mod. Frequency:	100.00 KHz
Mod. Amplitude:	0.50 G
Signal Channel	
Conversion:	40.000 ms
Time Constant:	40.960 ms
Sweep Time:	60.000 s

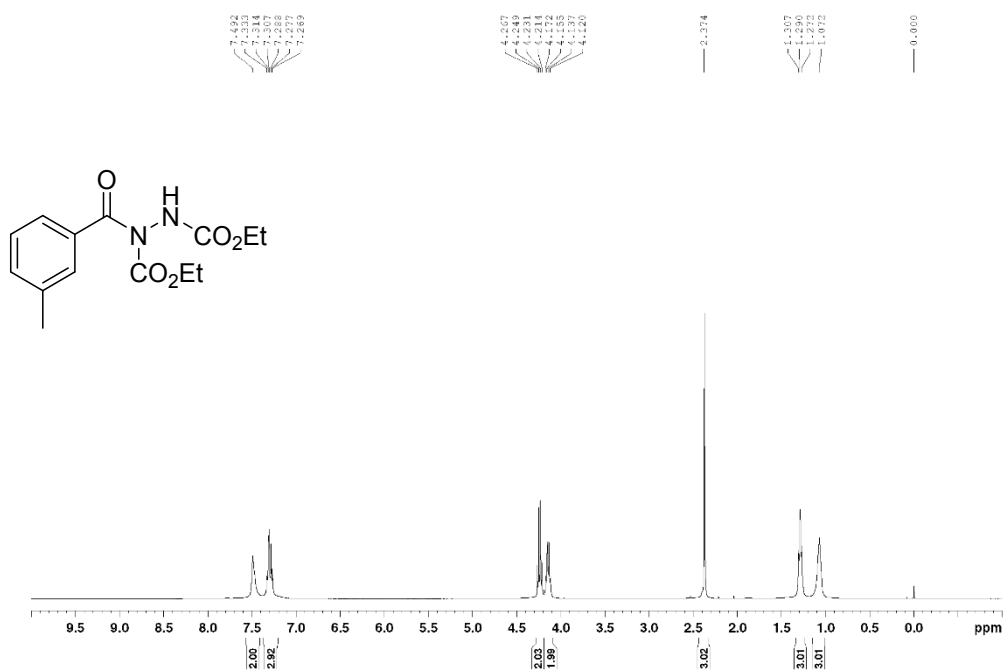




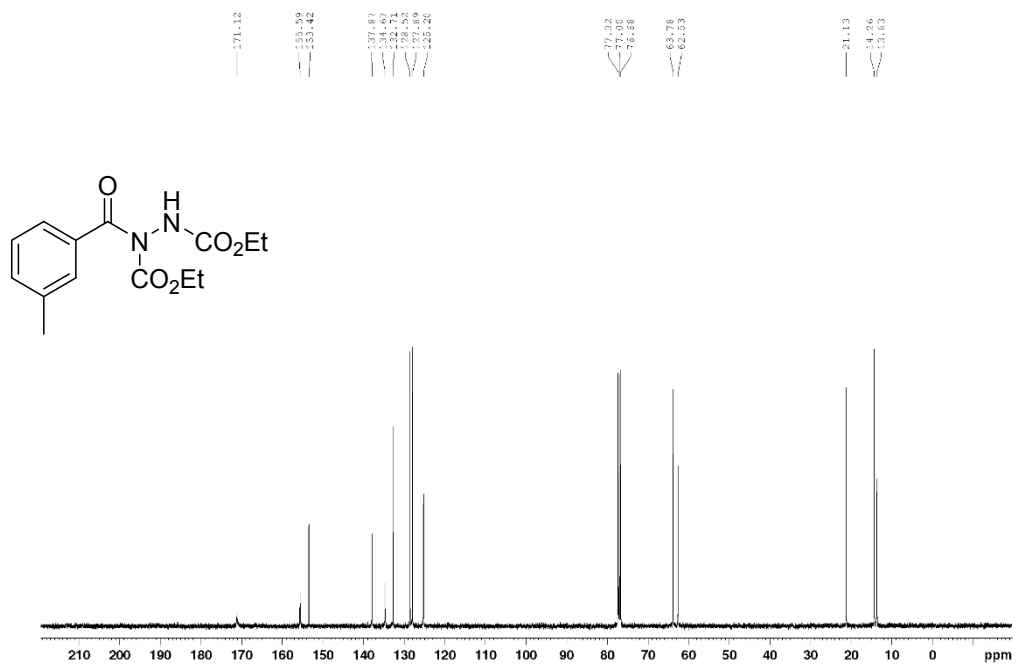
**<sup>13</sup>C NMR spectrum of compound 2b (CDCl<sub>3</sub>, 100 MHz)**



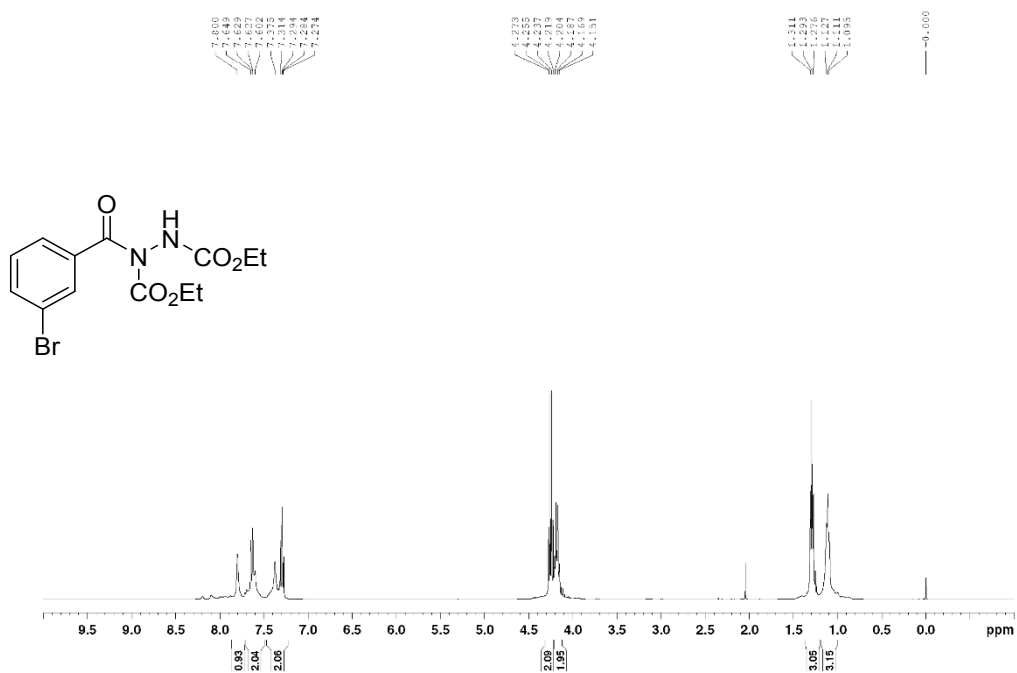
**<sup>1</sup>H NMR spectrum of compound 2c (CDCl<sub>3</sub>, 400 MHz)**



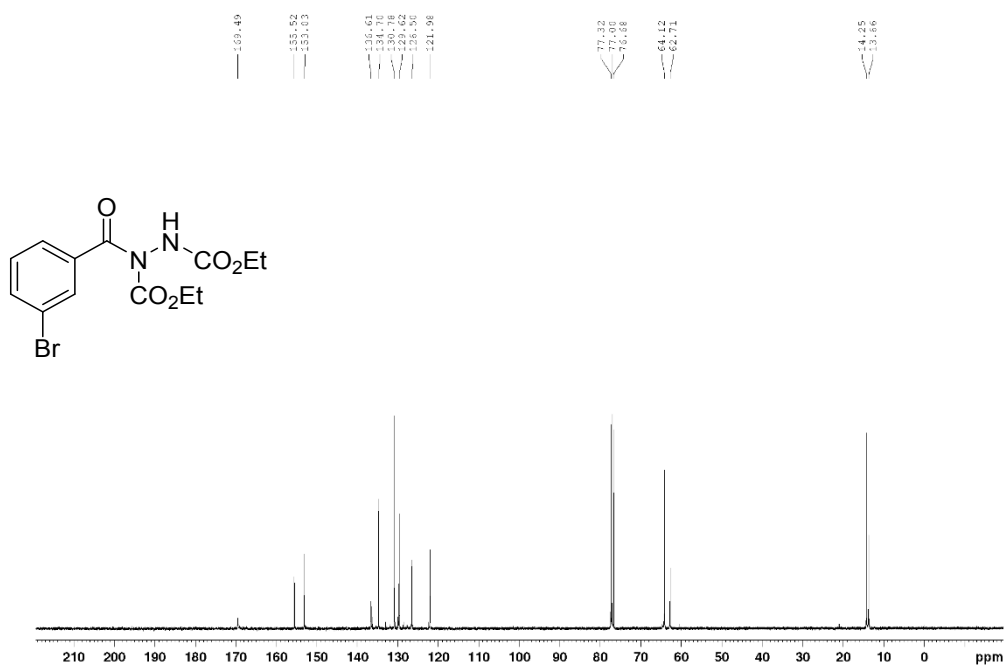
**<sup>13</sup>C NMR spectrum of compound 2c (CDCl<sub>3</sub>, 100 MHz)**



**<sup>1</sup>H NMR spectrum of compound 2d (CDCl<sub>3</sub>, 400 MHz)**



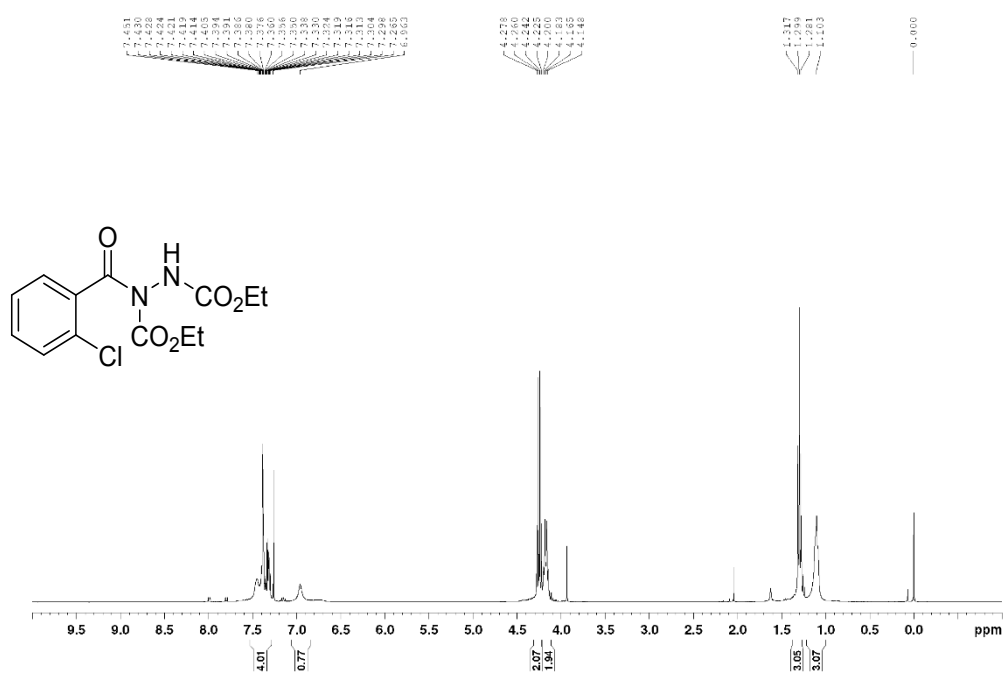
<sup>13</sup>C NMR spectrum of compound 2d (CDCl<sub>3</sub>, 100 MHz)



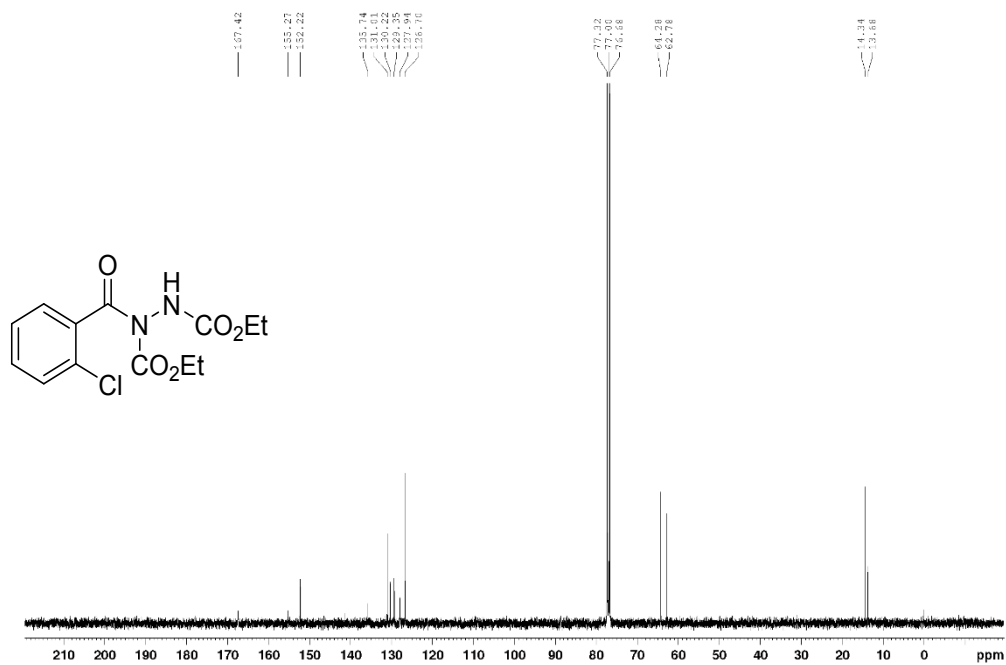
<sup>1</sup>H NMR spectrum of compound 2e (CDCl<sub>3</sub>, 400 MHz)



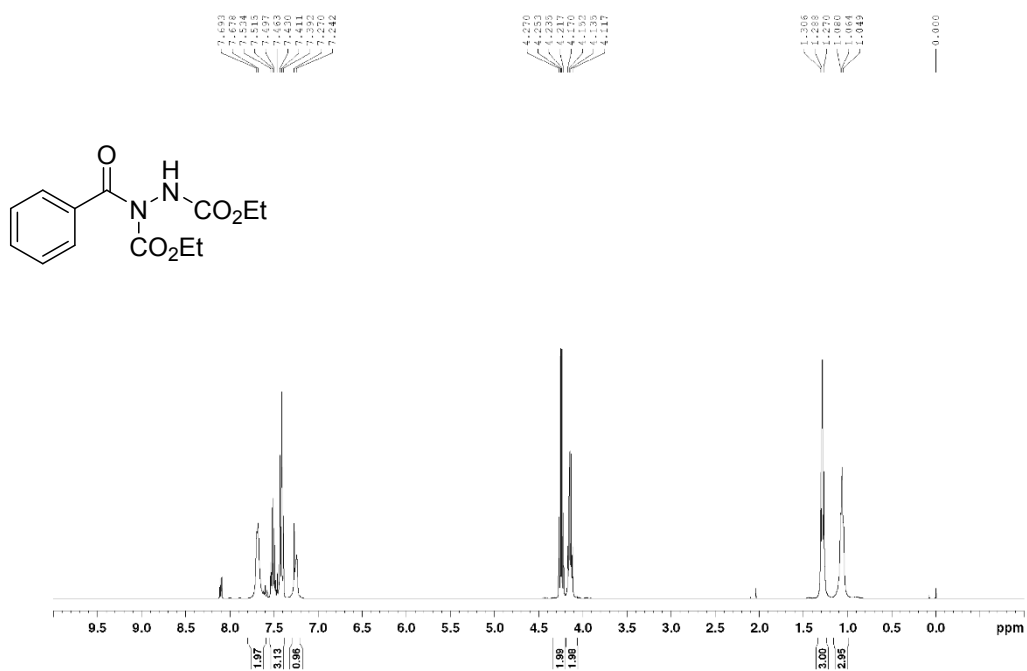




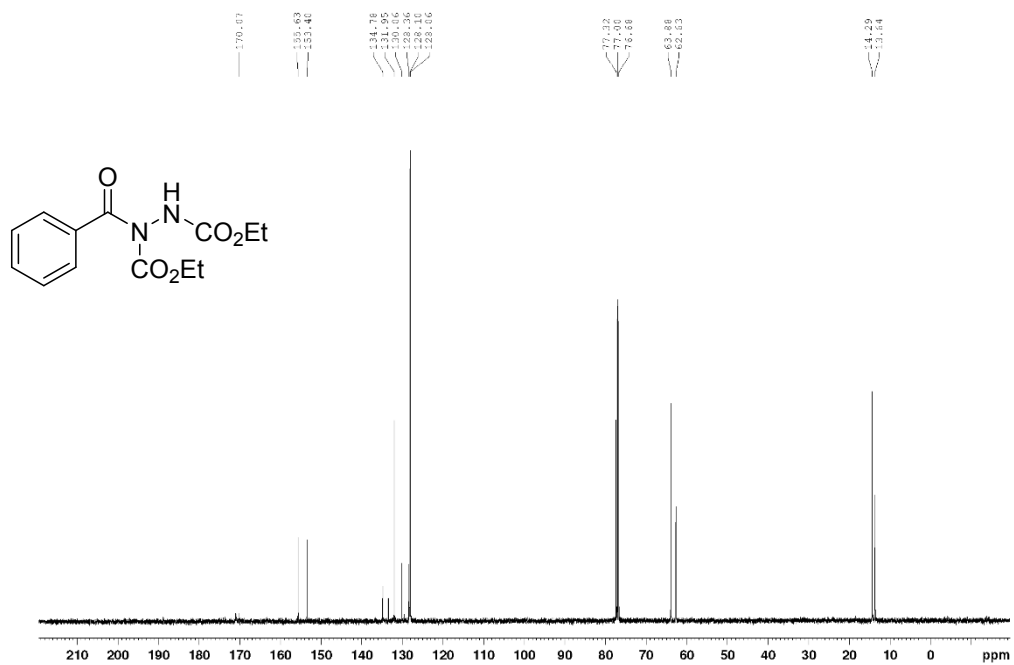
**<sup>13</sup>C NMR spectrum of compound 2f (CDCl<sub>3</sub>, 100 MHz)**



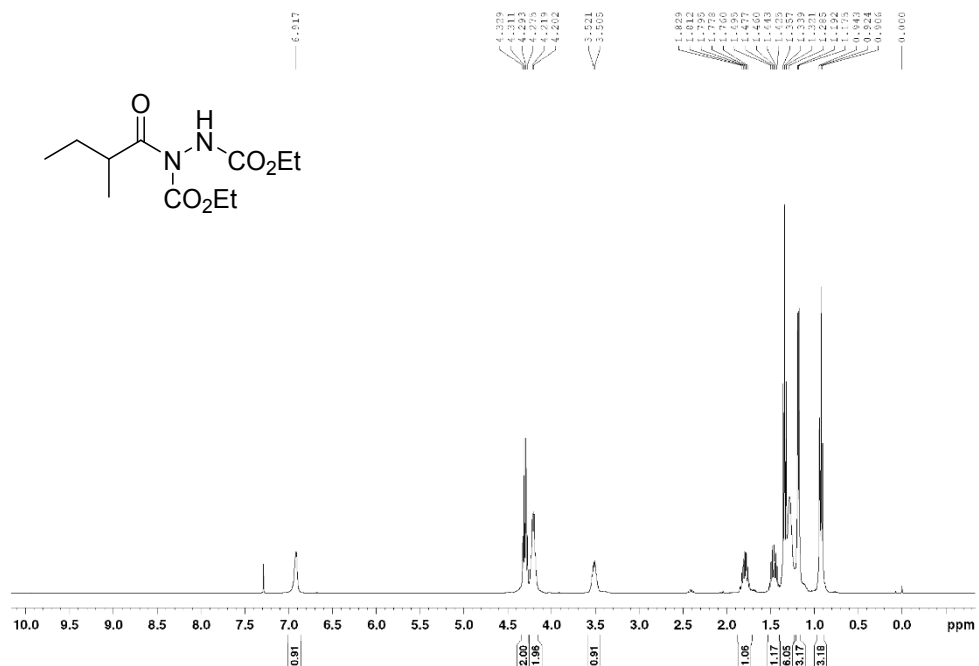
**<sup>1</sup>H NMR spectrum of compound 2g (CDCl<sub>3</sub>, 400 MHz)**



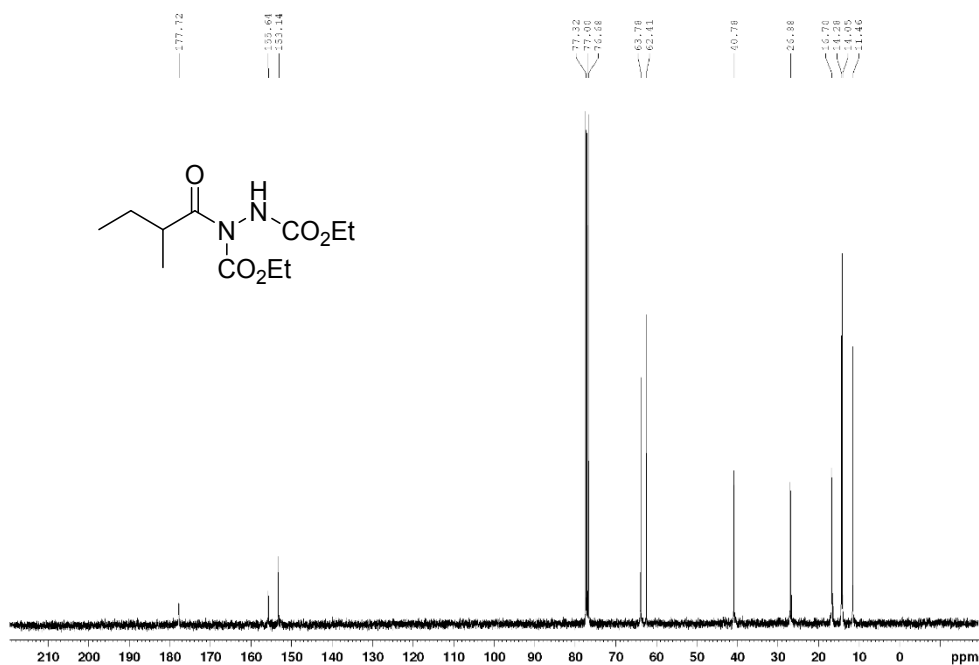
<sup>13</sup>C NMR spectrum of compound 2g (CDCl<sub>3</sub>, 100 MHz)



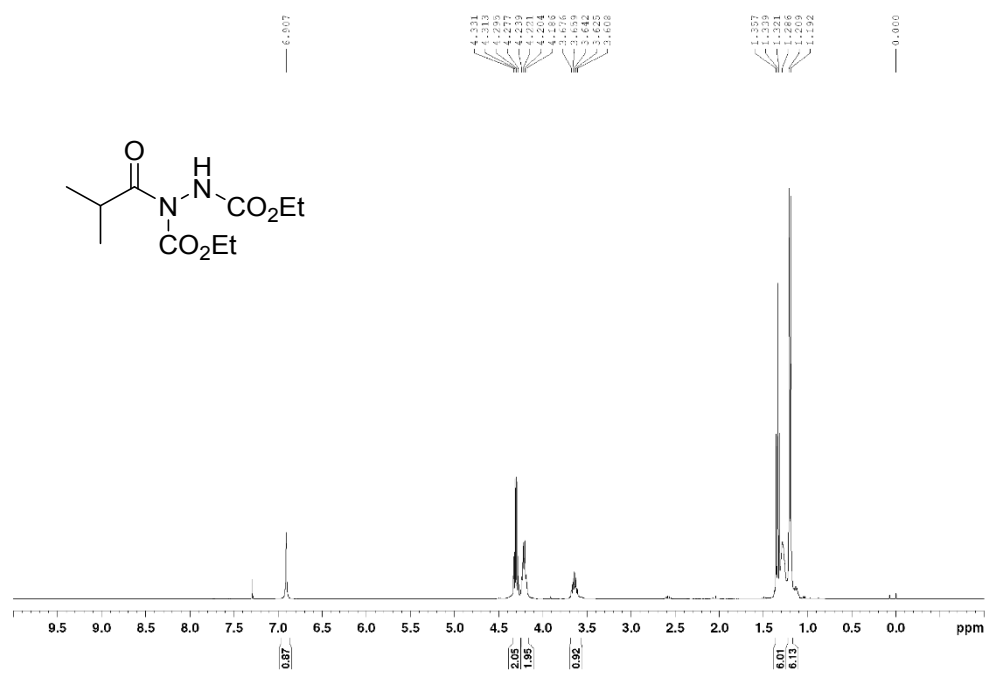
<sup>1</sup>H NMR spectrum of compound 2h (CDCl<sub>3</sub>, 400 MHz)



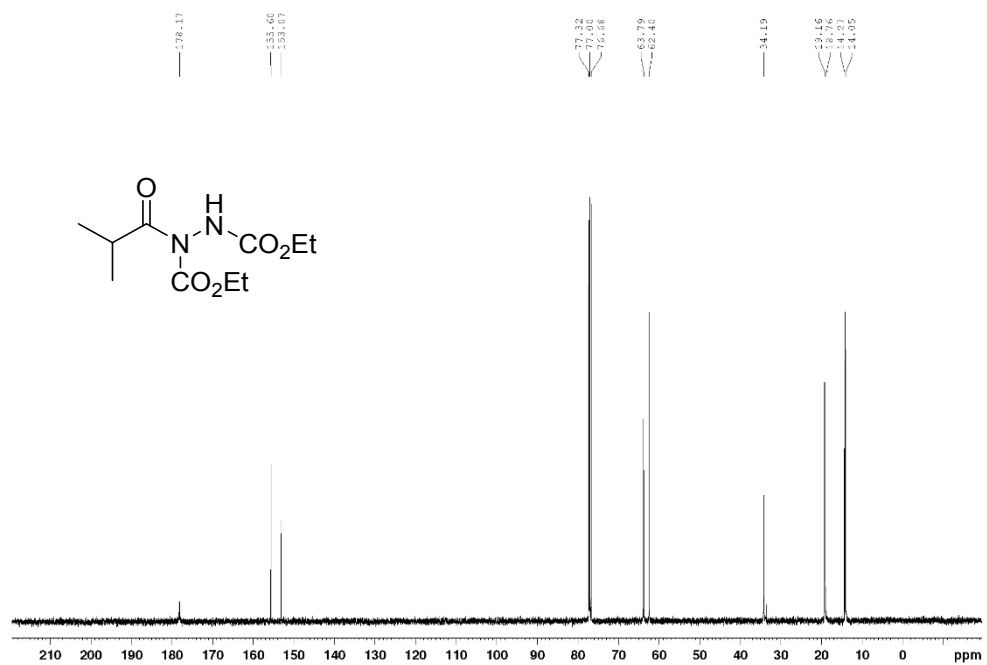
<sup>13</sup>C NMR spectrum of compound 2h (CDCl<sub>3</sub>, 100 MHz)



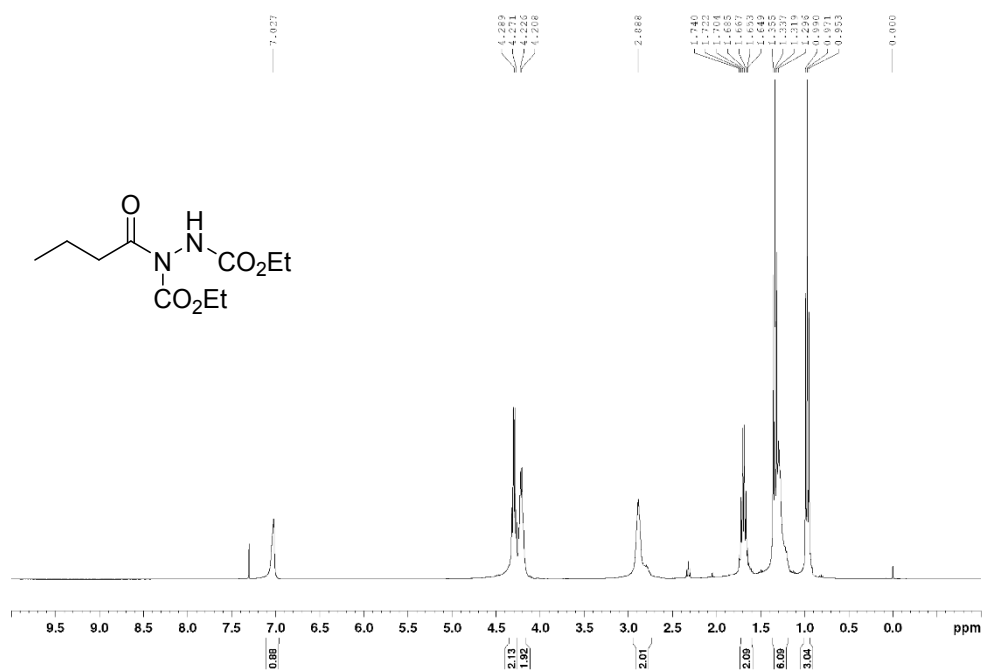
<sup>1</sup>H NMR spectrum of compound 2i (CDCl<sub>3</sub>, 400 MHz)



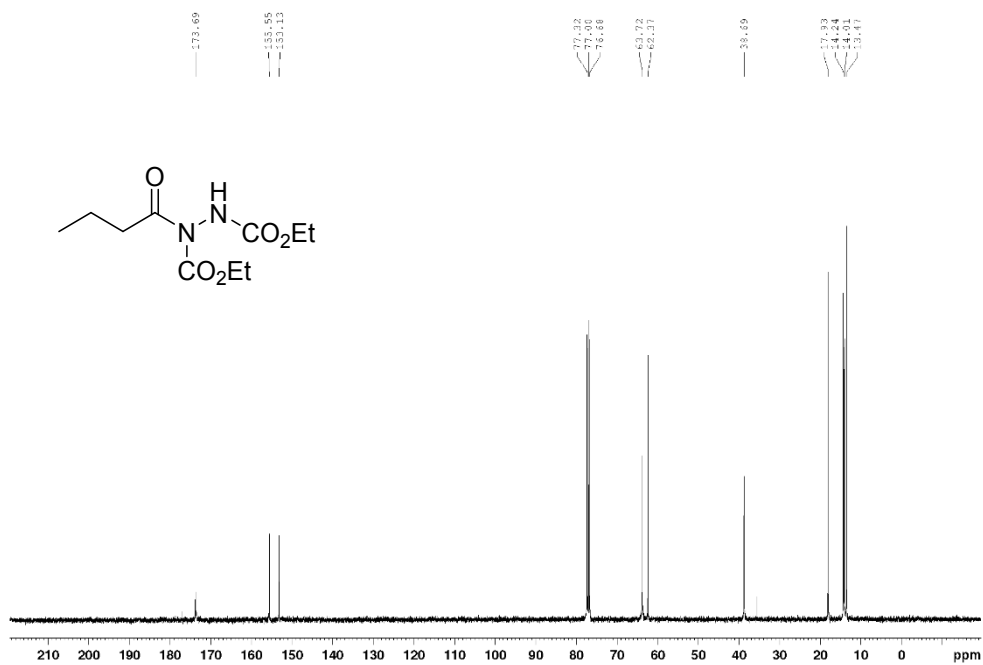
<sup>13</sup>C NMR spectrum of compound 2i (CDCl<sub>3</sub>, 100 MHz)



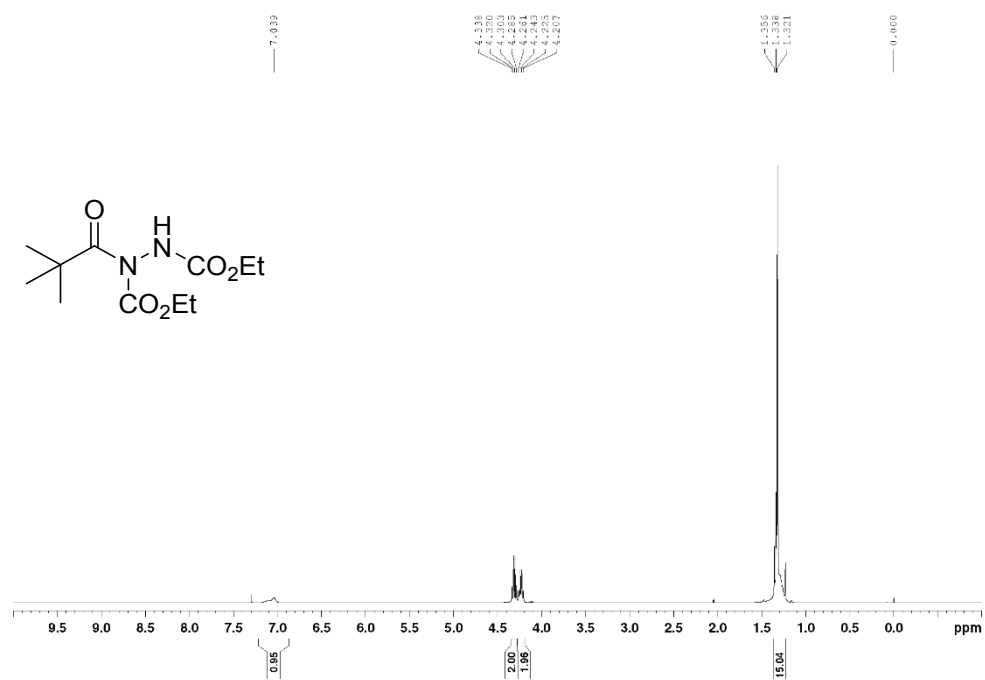
<sup>1</sup>H NMR spectrum of compound 2j (CDCl<sub>3</sub>, 400 MHz)



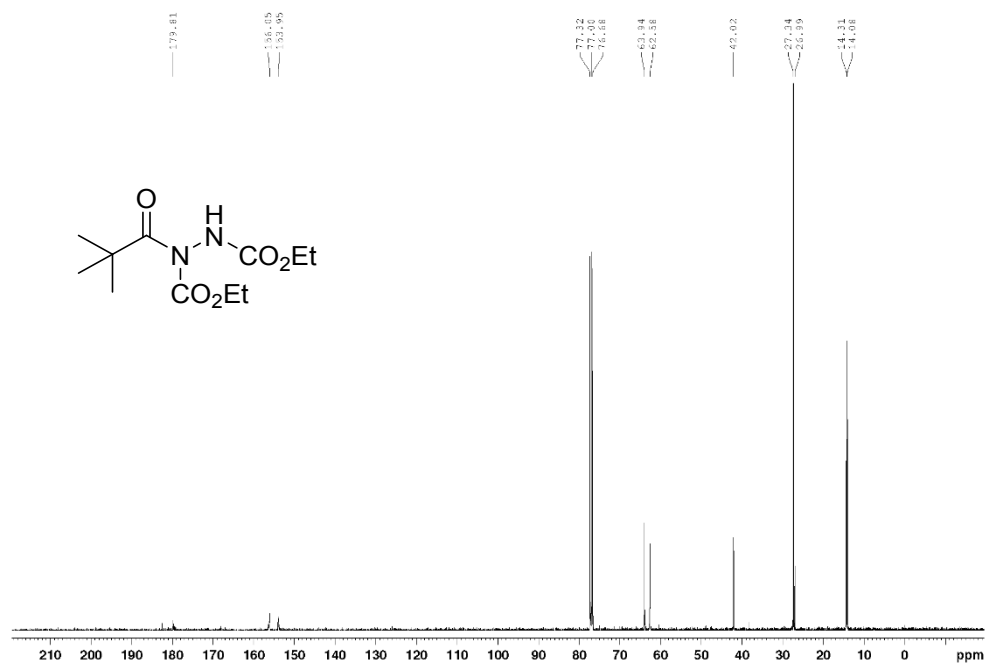
**<sup>13</sup>C NMR spectrum of compound 2j (CDCl<sub>3</sub>, 100 MHz)**



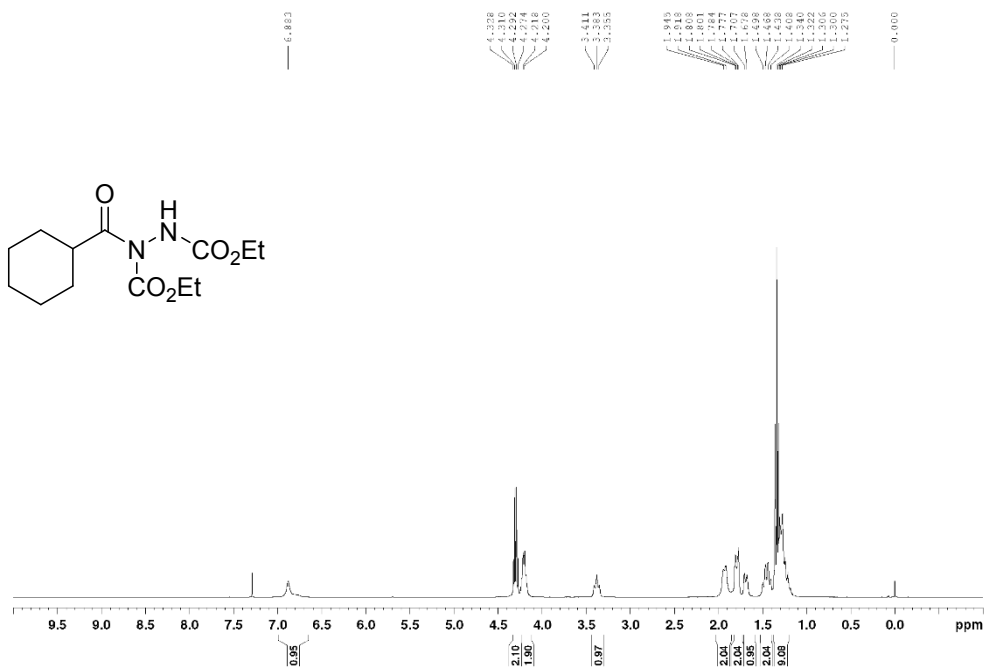
**<sup>1</sup>H NMR spectrum of compound 2k (CDCl<sub>3</sub>, 400 MHz)**



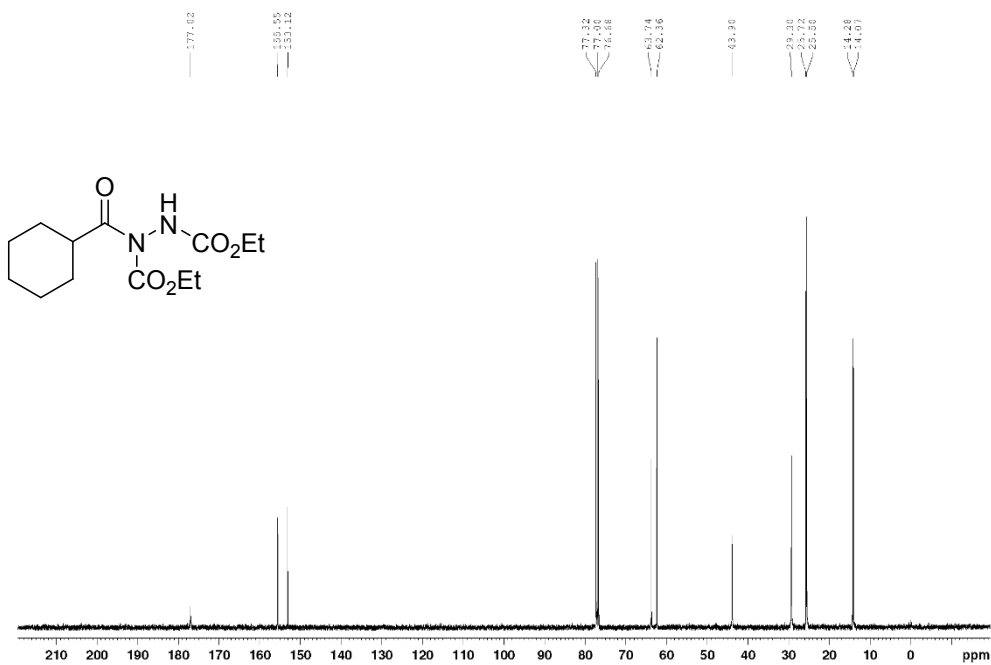
<sup>13</sup>C NMR spectrum of compound 2k (CDCl<sub>3</sub>, 100 MHz)



<sup>1</sup>H NMR spectrum of compound 2l (CDCl<sub>3</sub>, 400 MHz)

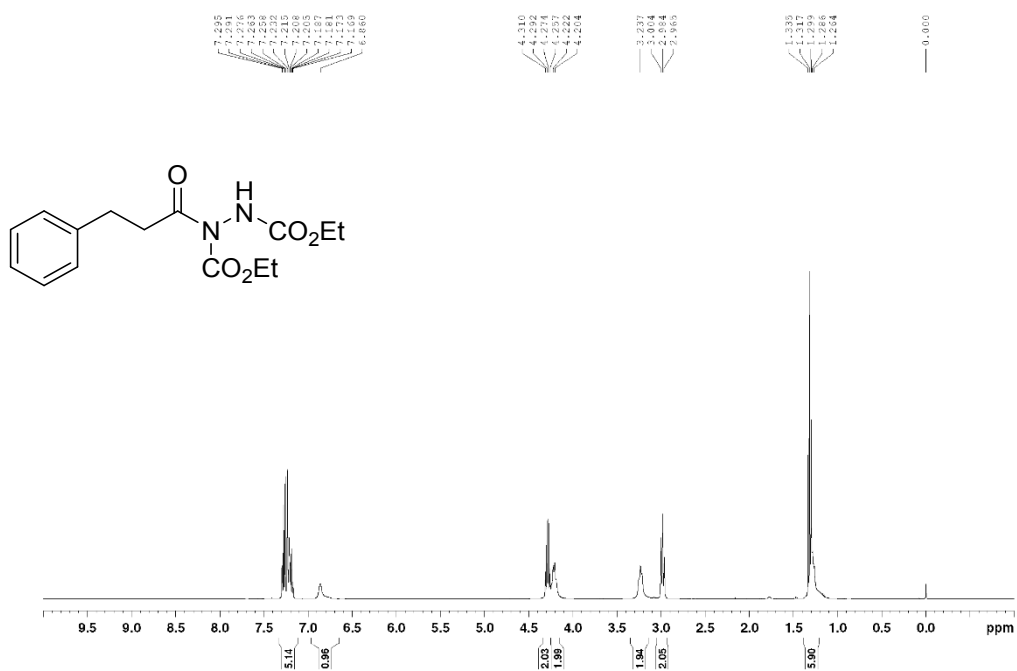


**<sup>13</sup>C NMR spectrum of compound 2l (CDCl<sub>3</sub>, 100 MHz)**

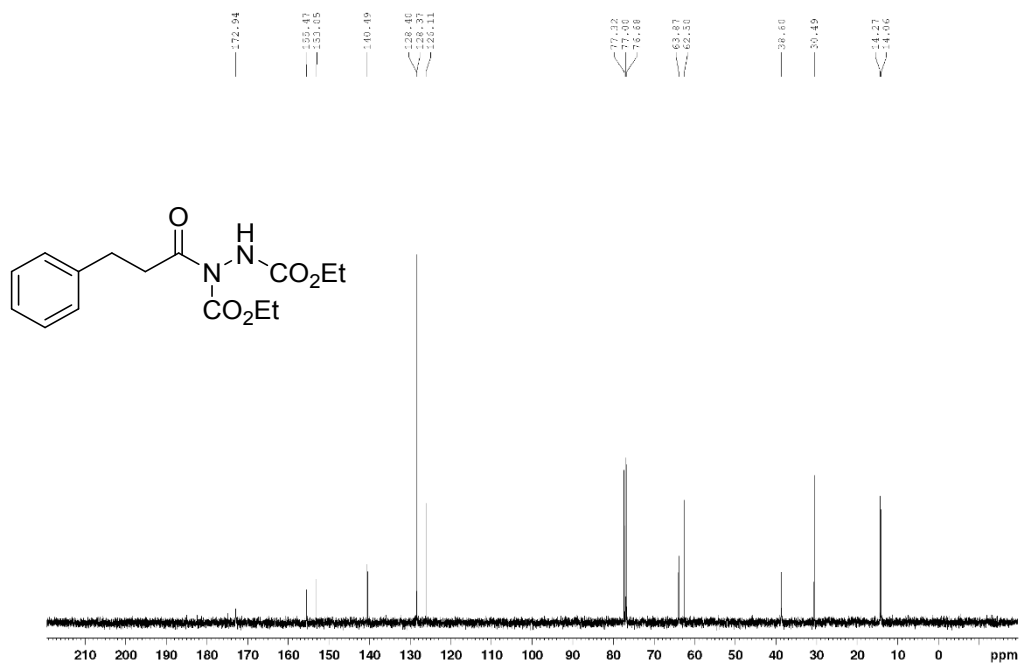


**<sup>1</sup>H NMR spectrum of compound 2m (CDCl<sub>3</sub>, 400 MHz)**

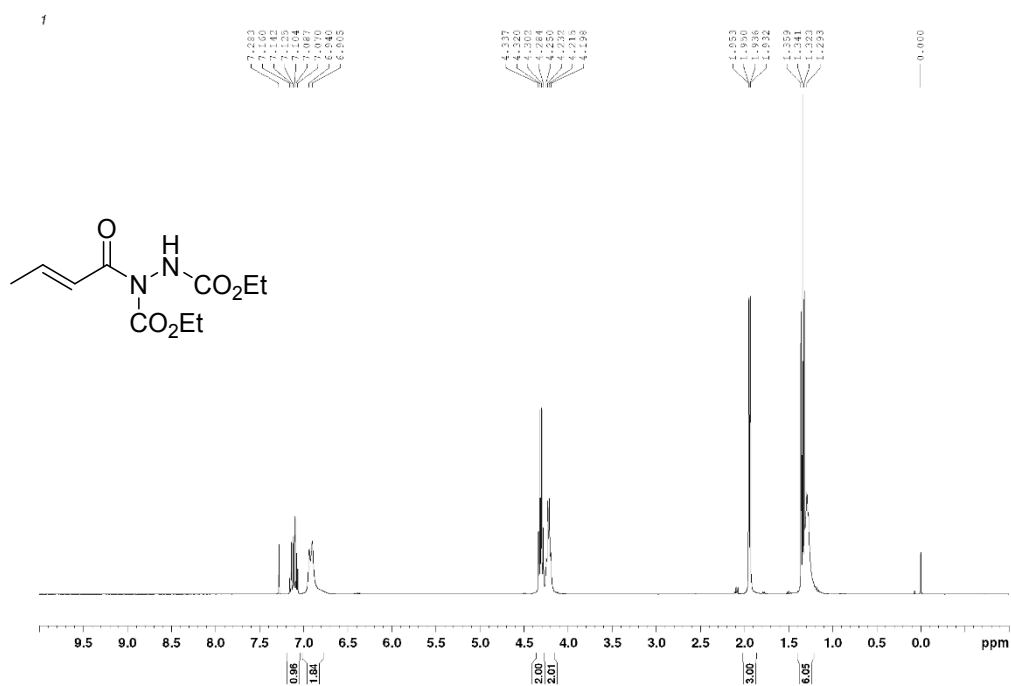




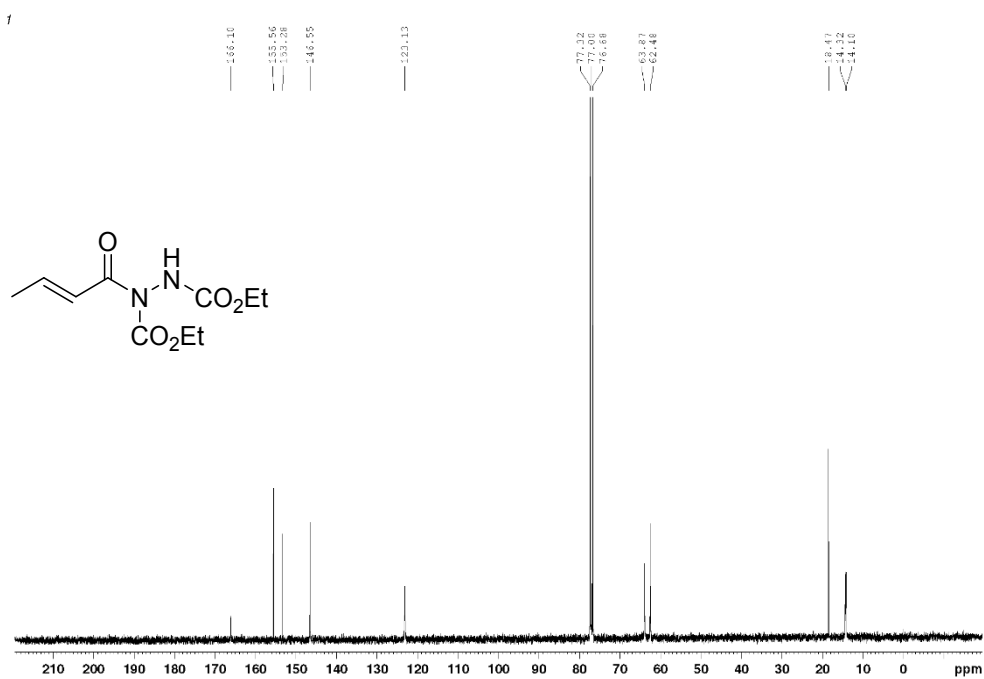
<sup>13</sup>C NMR spectrum of compound 2m (CDCl<sub>3</sub>, 100 MHz)



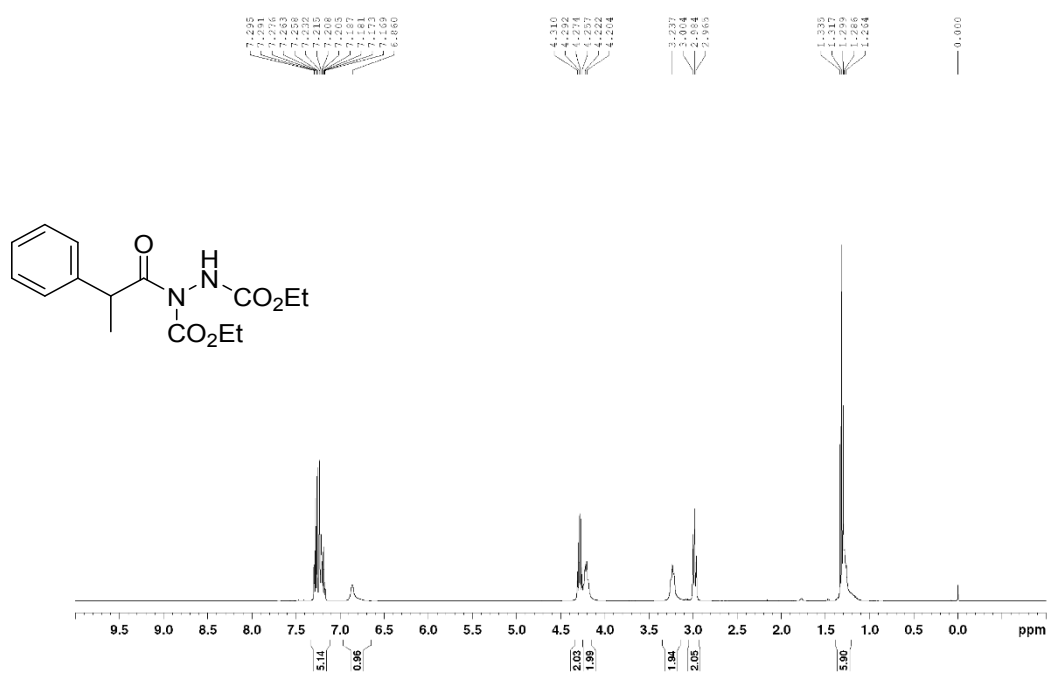
<sup>1</sup>H NMR spectrum of compound 2n (CDCl<sub>3</sub>, 400 MHz)



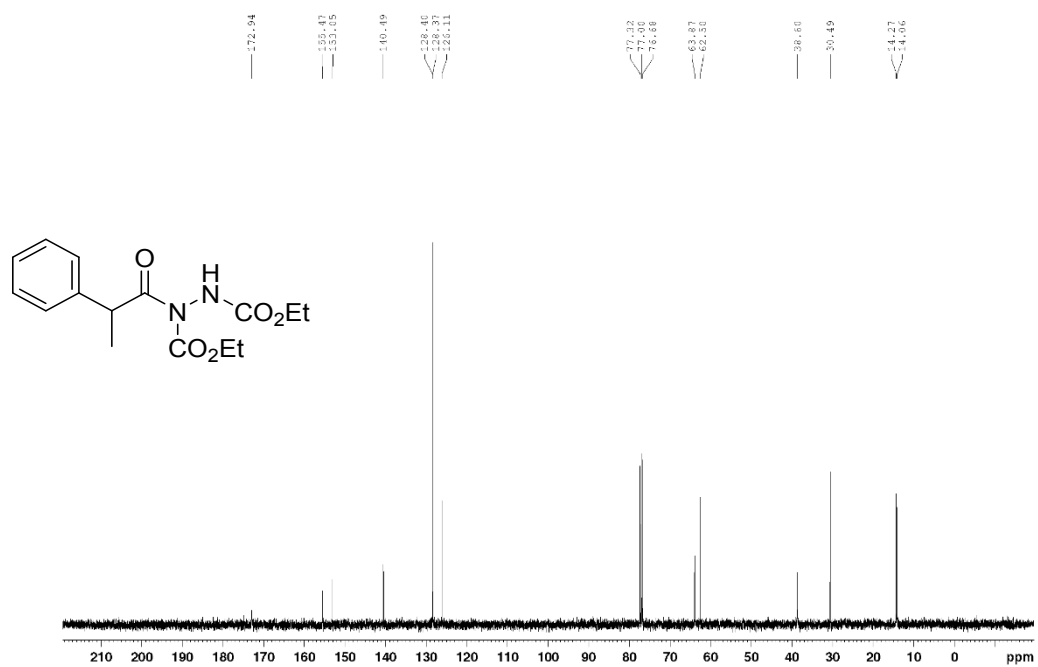
<sup>13</sup>C NMR spectrum of compound 2n (CDCl<sub>3</sub>, 100 MHz)



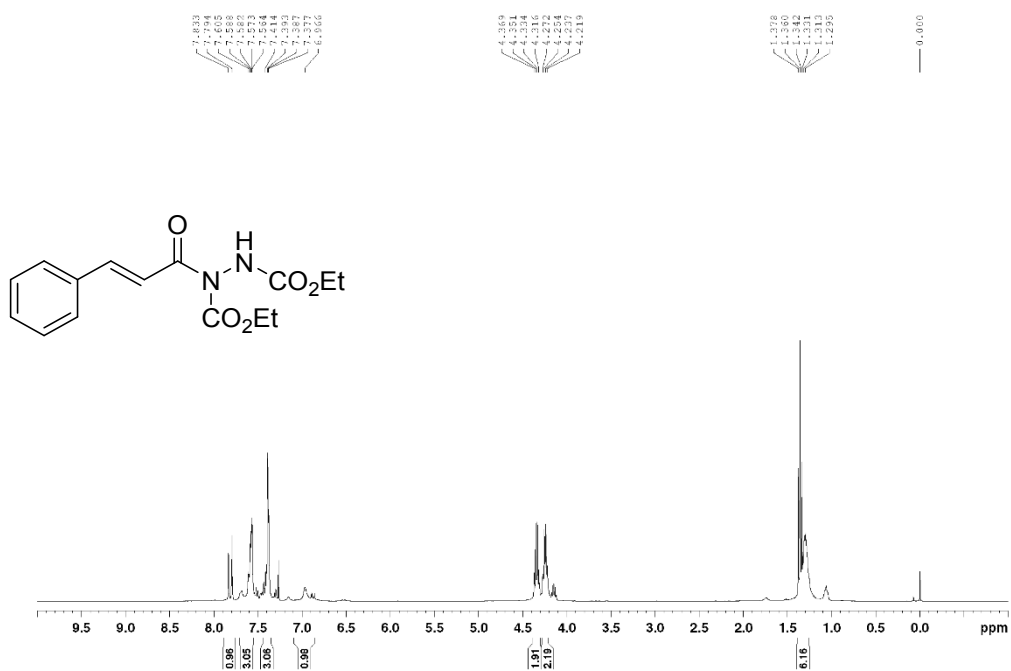
<sup>1</sup>H NMR spectrum of compound 2o (CDCl<sub>3</sub>, 400 MHz)



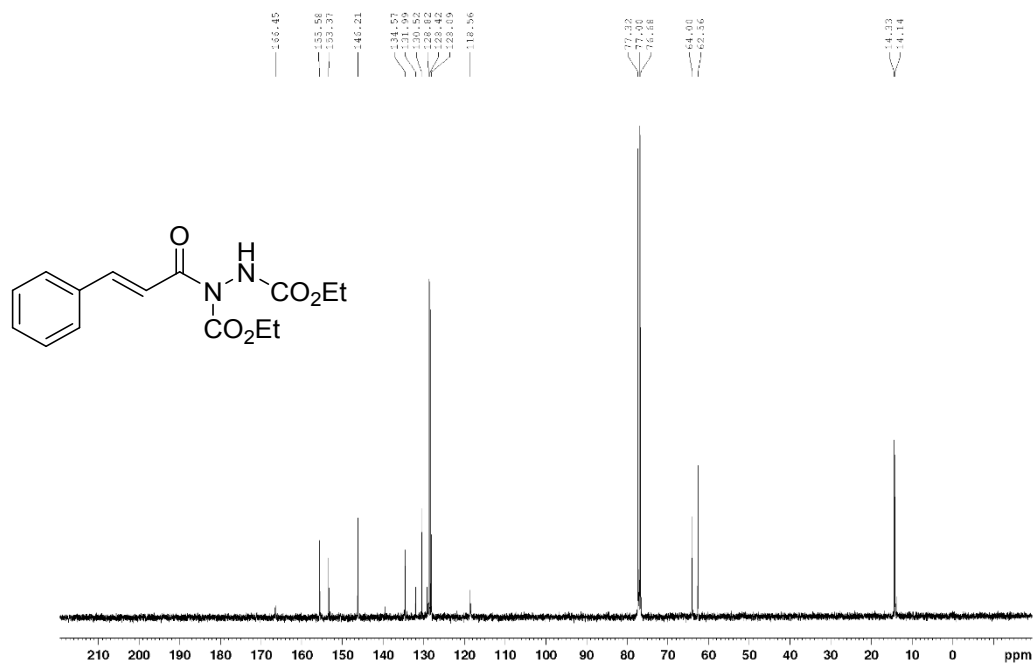
**<sup>13</sup>C NMR spectrum of compound 2o (CDCl<sub>3</sub>, 100 MHz)**



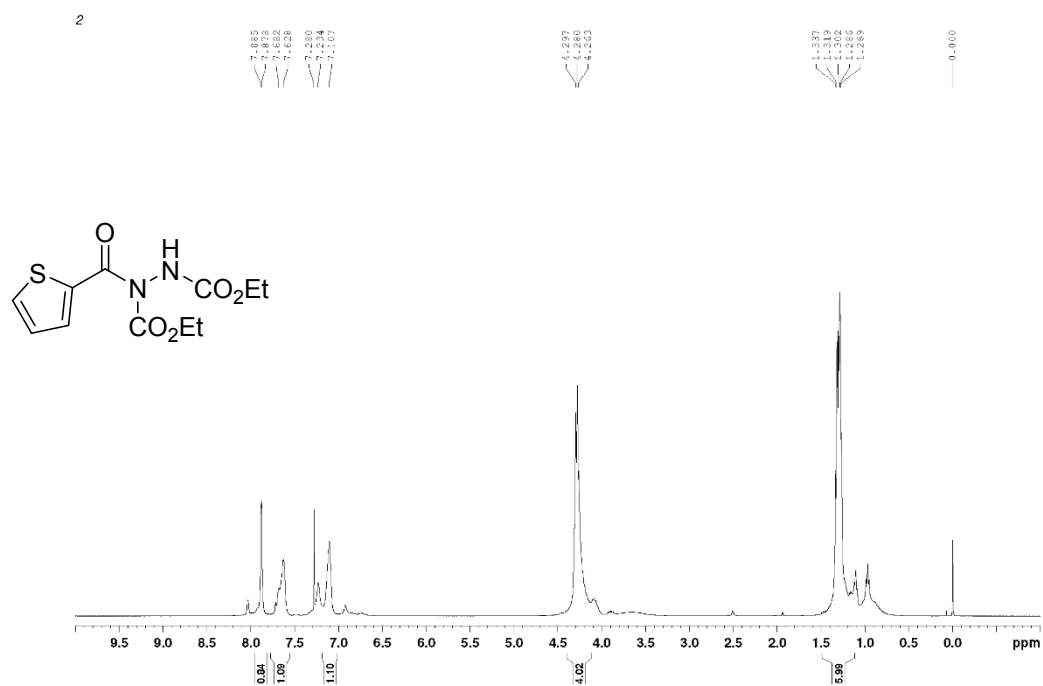
**<sup>1</sup>H NMR spectrum of compound 2p (CDCl<sub>3</sub>, 400 MHz)**



**<sup>13</sup>C NMR spectrum of compound 2p (CDCl<sub>3</sub>, 100 MHz)**



**<sup>1</sup>H NMR spectrum of compound 2q (CDCl<sub>3</sub>, 400 MHz)**



<sup>13</sup>C NMR spectrum of compound 2q (CDCl<sub>3</sub>, 100 MHz)

