



## Supporting Information

for

### Selective hydrolysis of $\alpha$ -oxo ketene *N,S*-acetals in water: switchable aqueous synthesis of $\beta$ -keto thioesters and $\beta$ -keto amides

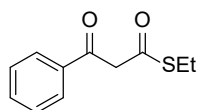
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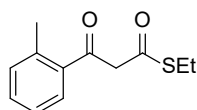
### Analytic data and copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of compounds 2 and 3

|                                                                                    |     |
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| 1. Spectroscopic Data of compound <b>2</b>                                         | S1  |
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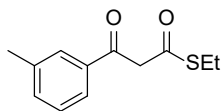
## 1. Spectroscopic Data of compound **2**



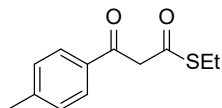
**S-Ethyl 3-oxo-3-phenylpropanethioate (2a)** [1,2]: colorless liquid. Keto/enol 5:4. Yield: 91% (47.3 mg),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  for keto-**2a**: 7.97 (dd,  $J_1 = 8.6$  Hz,  $J_2 = 1.4$  Hz, 2 H), 7.60 (t,  $J = 7.4$  Hz, 1 H), 7.49 (t,  $J = 8.0$  Hz, 2 H), 4.21 (s, 2 H), 2.97-2.91 (m, 2 H), 1.27 (t,  $J = 7.4$  Hz, 3 H); for enol-**2a**: 13.2 (s, 1 H), 7.79 (dd,  $J_1 = 8.6$  Hz,  $J_2 = 1.5$  Hz, 2 H), 7.49 (t,  $J = 8.0$  Hz, 1 H), 7.42 (t,  $J = 8.2$  Hz, 2 H), 6.09 (s, 1H), 3.03-2.98 (m, 2 H), 1.32 (t,  $J = 7.4$  Hz, 3 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  for keto-**2a**: 192.4, 192.2, 134.0, 131.8, 129.0 (2 C), 126.5 (2 C), 54.1, 24.2, 14.6; for enol-**2a**: 195.2, 168.9, 136.2, 133.3, 128.9 (2 C), 128.8 (2 C), 97.4, 23.0, 15.1.



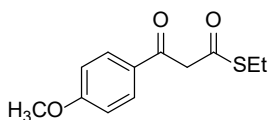
**S-Ethyl 3-oxo-3-(o-tolyl)propanethioate (2b)** [2]: colorless liquid. Keto/enol 5:4. Yield: 89% (49.4 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  for keto-**2b**: 7.69 (d,  $J = 7.8$  Hz, 1 H), 7.40 (t,  $J = 7.8$  Hz, 2 H), 7.34-7.28 (m, 1 H), 4.16 (s, 2 H), 2.95-2.90 (m, 2 H), 2.54 (s, 3 H), 1.25 (t,  $J = 7.4$  Hz, 3 H); for enol-**2b**: 13.1 (s, 1 H), 7.34-7.19 (m, 4 H), 5.71 (s, 1H), 3.03-2.97 (m, 2 H), 2.47 (s, 3 H), 1.34 (t,  $J = 7.4$  Hz, 3 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  for keto-**2b**: 192.5, 192.2, 139.7, 136.4, 132.4, 131.3, 129.6, 125.9, 56.4, 24.1, 21.7, 14.6; for enol-**2b**: 195.1, 172.4, 137.0, 133.9, 132.3, 130.5, 128.6, 125.9, 101.6, 23.0, 20.7, 15.0.



**S-Ethyl 3-oxo-3-(*m*-tolyl)propanethioate (2c)** [2]: colorless liquid. Keto/enol 5:4. Yield: 88% (48.8 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  for keto-**2c**: 7.77 (s, 1 H), 7.44 (d,  $J = 7.8$  Hz, 1 H), 7.40 (d,  $J = 7.5$  Hz, 1 H), 7.34-7.29 (m, 1 H), 4.19 (s, 2 H), 2.96-2.91 (m, 2 H), 2.41 (s, 3 H), 1.26 (t,  $J = 7.4$  Hz, 3 H); for enol-**2c**: 13.2 (s, 1 H), 7.60 (s, 1 H), 7.58 (d,  $J = 7.8$  Hz, 1 H), 7.37 (d,  $J = 7.5$  Hz, 1 H), 7.34-7.29 (m, 1 H), 6.07 (s, 1H), 3.03-2.97 (m, 2 H), 2.39 (s, 3 H), 1.32 (t,  $J = 7.4$  Hz, 3 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  for keto-**2c**: 192.5, 192.3, 138.8, 134.7, 132.6, 129.4, 128.8, 126.2, 54.1, 24.1, 21.5, 14.6; for enol-**2c**: 195.1, 169.1, 138.5, 136.2, 133.0, 129.4, 128.6, 127.1, 97.3, 23.0, 21.5, 15.1.

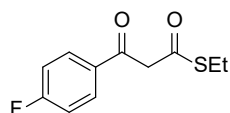


**S-Ethyl 3-oxo-3-(*p*-tolyl)propanethioate (2d)** [1,2]: colorless liquid. Keto/enol 5:3. Yield: 90% (50.0 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  for keto-**2d**: 7.87 (d,  $J = 8.0$  Hz, 2 H), 7.28 (d,  $J = 8.3$  Hz, 2 H), 4.18 (s, 2 H), 2.96-2.90 (m, 2 H), 2.42 (s, 3 H), 1.26 (t,  $J = 7.4$  Hz, 3 H); for enol-**2d**: 13.2 (s, 1 H), 7.68 (d,  $J = 8.3$  Hz, 2 H), 7.22 (d,  $J = 8.1$  Hz, 2 H), 6.06 (s, 1 H), 3.02-2.97 (m, 2 H), 2.39 (s, 3 H), 1.33 (t,  $J = 7.4$  Hz, 3 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  for keto-**2d**: 195.0, 191.7, 145.0, 133.8, 129.6 (2 C), 129.1 (2 C), 54.2, 24.2, 21.9, 14.6; for enol-**2d**: 192.5, 169.2, 142.4, 130.3, 129.5 (2 C), 126.5 (2 C), 96.8, 23.0, 21.7, 15.1.

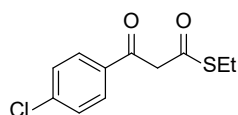


**S-Ethyl 3-(4-methoxyphenyl)-3-oxopropanethioate (2e)** [1,2]: colorless liquid. Keto/enol 3:1. Yield: 91% (54.1 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  for keto-**2e**: 7.95 (d,  $J = 8.9$  Hz, 2 H), 6.94 (d,  $J = 8.5$  Hz, 2 H), 4.16 (s, 2 H), 3.87 (s, 3 H), 2.95-2.90 (m, 2 H), 1.26 (t,  $J = 7.4$  Hz, 3 H); for enol-**2e**: 13.3 (s, 1 H), 7.75 (d,  $J = 8.9$  Hz, 2 H), 6.92 (d,  $J = 8.5$  Hz, 2 H), 6.01 (s, 1 H), 3.85 (s, 3 H),

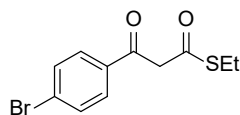
3.02-2.97 (m, 2 H), 1.33 (t,  $J = 7.4$  Hz, 3 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  for keto-**2e**: 192.6, 190.5, 164.2, 131.4 (2 C), 128.3, 114.1 (2 C), 55.6, 54.0, 24.1, 14.5; for enol-**2e**: 194.7, 169.0, 162.6, 129.2 (2 C), 125.2, 114.1 (2 C), 96.0, 55.5, 23.0, 15.1.



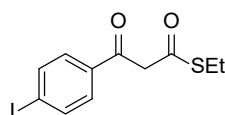
**S-Ethyl 3-(4-fluorophenyl)-3-oxopropanethioate (2f)**: colorless liquid. Keto/enol 4:3. Yield: 90% (50.9 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  for keto-**2f**: 8.02-7.98 (m, 2 H), 7.15 (t,  $J = 8.6$  Hz, 2 H), 4.18 (s, 2 H), 2.96-2.90 (m, 2 H), 1.26 (t,  $J = 7.4$  Hz, 3 H); for enol-**2f**: 13.3 (s, 1 H), 7.81-7.77 (m, 2 H), 7.10 (t,  $J = 8.6$  Hz, 2 H), 6.02 (s, 1 H), 3.02-2.97 (m, 2 H), 1.33 (t,  $J = 7.4$  Hz, 3 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  for keto-**2f**: 192.2, 190.5, 166.3 (d,  $J = 254.7$  Hz), 132.6 (d,  $J = 2.9$  Hz), 131.7 (d,  $J = 9.6$  Hz, 2 C), 116.1 (d,  $J = 21.9$  Hz, 2 C), 54.2, 24.2, 14.5; for enol-**2f**: 195.2, 167.8, 165.0 (d,  $J = 21.1$  Hz), 129.2 (d,  $J = 3.0$  Hz), 128.8 (d,  $J = 8.8$  Hz, 2 C), 115.9 (d,  $J = 21.9$  Hz, 2 C), 97.1, 23.1, 15.0. HRMS Calcd for  $\text{C}_{11}\text{H}_{12}\text{FO}_2\text{S}^+$ :  $([\text{M}+\text{H}]^+)$  227.0537; Found: 227.0539.



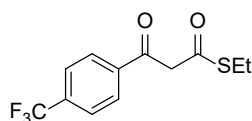
**S-Ethyl 3-(4-chlorophenyl)-3-oxopropanethioate (2g)** [1,2]: colorless liquid. Keto/ enol = 5:2. Yield: 92% (55.7 mg).  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ , 400 MHz)  $\delta$  for keto-**2g**: 7.96 (d,  $J = 8.6$  Hz, 2 H), 7.61 (d,  $J = 8.6$  Hz, 2 H), 4.46 (s, 2 H), 2.88-2.83 (m, 2 H), 1.16 (t,  $J = 7.4$  Hz, 3 H); for enol-**2g**: 13.2 (s, 1 H), 7.90 (d,  $J = 8.7$  Hz, 2 H), 7.53 (d,  $J = 8.6$  Hz, 2 H), 6.47 (s, 1H), 2.99-2.93 (m, 2 H), 1.24 (t,  $J = 7.4$  Hz, 3 H).  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ , 100 MHz) for keto-**2g**: 192.6, 192.0, 138.8, 134.5, 130.4 (2 C), 128.9 (2 C), 53.5, 23.2, 14.5; for enol-**2g**: 194.9, 166.2, 135.7, 131.1, 128.9 (2 C), 128.2 (2 C), 97.5, 22.5, 14.8.



**S-Ethyl 3-(4-bromophenyl)-3-oxopropanethioate (2h)** [1,2]: slight yellow oil. Keto/ enol = 2:5. Yield: 90% (64.4 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  for keto-**2h**: 7.75 (d,  $J$  = 8.6 Hz, 2 H), 7.55 (d,  $J$  = 8.6 Hz, 2 H), 4.10 (s, 2 H), 2.89-2.83 (m, 2 H), 1.19 (t,  $J$  = 7.4 Hz, 3 H); for enol-**2h**: 13.1 (s, 1 H), 7.57 (d,  $J$  = 7.9 Hz, 2 H), 7.48 (d,  $J$  = 8.6 Hz, 2 H), 5.98 (s, 1 H), 2.96-2.90 (m, 2 H), 1.26 (t,  $J$  = 7.4 Hz, 3 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  for keto-**2h**: 192.1, 191.0, 134.9, 132.3 (2 C), 130.5 (2 C), 129.4, 54.1, 23.2, 14.5; for enol-**2h**: 195.3, 167.6, 132.0 (2 C), 128.0 (3 C), 126.3, 97.5, 23.2, 15.0.

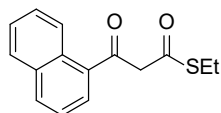


**S-Ethyl 3-(4-iodophenyl)-3-oxopropanethioate (2i)**: colorless crystal, m.p. 46-47 °C. Keto/enol 1:7. Yield: 91% (76.0 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  for keto-**2i**: 7.85 (d,  $J$  = 8.6 Hz, 2 H), 7.67 (d,  $J$  = 8.6 Hz, 2 H), 4.16 (s, 2 H), 2.96-2.91 (m, 2 H), 1.25 (t,  $J$  = 7.4 Hz, 3 H); for enol-**2i**: 13.2 (s, 1 H), 7.77 (d,  $J$  = 8.5 Hz, 2 H), 7.50 (d,  $J$  = 8.6 Hz, 2 H), 6.06 (s, 1H), 3.03-2.97 (m, 2 H), 1.33 (t,  $J$  = 7.4 Hz, 3 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  for keto-**2i**: 192.1, 191.5, 138.3 (2 C), 135.4, 130.3 (2 C), 102.3, 54.1, 24.3, 14.6; for enol-**2i**: 195.3, 167.8, 138.0 (2 C), 132.6, 128.0 (2 C), 98.6, 97.5, 23.2, 15.0. HRMS Calcd for  $\text{C}_{11}\text{H}_{12}\text{IO}_2\text{S}^+$ : ( $[\text{M}+\text{H}]^+$ ) 334.9597; Found: 334.9598.

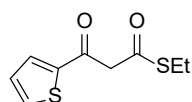


**S-Ethyl 3-oxo-3-(4-(trifluoromethyl)phenyl)propanethioate (2j)** [1]: colorless crystal, m.p. 29-30 °C. Keto/enol 1:2. Yield: 91% (62.8 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  for keto-**2j**: 8.08 (d,  $J$  = 8.2 Hz, 2 H), 7.75 (d,  $J$  = 8.3 Hz, 2 H), 4.23 (s, 2 H), 2.97-2.92 (m, 2 H), 1.27 (t,  $J$  = 7.4 Hz, 3 H); for enol-**2j**: 13.2 (s, 1 H), 7.89 (d,  $J$  = 8.2 Hz, 2 H), 7.68 (d,  $J$  = 8.3 Hz, 2 H), 6.11 (s, 1 H), 3.05-2.99 (m, 2 H), 1.34 (t,  $J$  = 7.4 Hz, 3 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  for

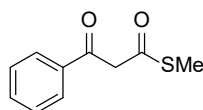
keto-**2j**: 191.9, 191.3, 138.7, 135.25 (q,  $J = 21.6$  Hz), 129.3 (2 C), 126.00 (q,  $J = 3.6$  Hz), 123.60 (q,  $J = 271.0$  Hz), 54.3, 24.3, 14.5; for enol-**2j**: 195.6, 167.8, 136.6, 133.17 (q,  $J = 32.5$  Hz), 126.8 (2 C), 125.74 (q,  $J = 3.8$  Hz), 123.85 (q,  $J = 270.7$  Hz), 98.6, 23.2, 15.0.



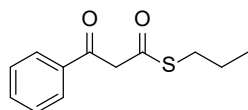
**S-Ethyl 3-(naphthalen-1-yl)-3-oxopropanethioate (2k)**: colorless liquid. Keto/enol 1:1. Yield: 88% (56.8 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  for keto-**2k**: 8.78 (d,  $J = 8.3$  Hz, 1 H), 7.96 (d,  $J = 8.4$  Hz, 1 H), 7.88 (d,  $J = 8.4$  Hz, 2 H), 7.63 (t,  $J = 8.4$  Hz, 1 H), 7.58-7.46 (m, 2 H), 4.33 (s, 2 H), 2.96-2.91 (m, 2 H), 1.25 (t,  $J = 7.4$  Hz, 3 H); for enol-**2k**: 13.4 (s, 1 H), 8.38 (d,  $J = 8.2$  Hz, 1 H), 8.03 (d,  $J = 8.2$  Hz, 1 H), 7.93 (d,  $J = 8.4$  Hz, 1 H), 7.67 (t,  $J = 7.2$  Hz, 1 H), 7.58-7.46 (m, 3 H), 6.06 (s, 1H), 3.03-2.97 (m, 2 H), 1.33 (t,  $J = 7.4$  Hz, 3 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  for keto-**2k**: 195.1, 192.5, 134.0, 133.8, 132.0, 130.5, 129.5, 128.6, 127.1, 126.8, 126.0, 125.0, 56.7, 24.2, 14.6; for enol-**2k**: 195.4, 171.6, 134.0, 131.1, 130.4, 128.6 (2 C), 127.1 (2 C), 126.4, 125.6, 124.3, 102.6, 23.1, 15.1. HRMS Calcd for  $\text{C}_{15}\text{H}_{15}\text{O}_2\text{S}^+$ :  $([\text{M}+\text{H}]^+)$  259.0787; Found: 259.0789.



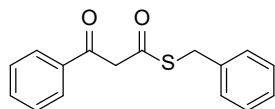
**S-Ethyl 3-oxo-3-(thiophen-2-yl)propanethioate (2l)** [1,2]: colorless liquid. Keto/enol 7:1. Yield: 92% (49.2 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  for keto-**2l**: 7.78 (dd,  $J_1 = 7.8$  Hz,  $J_2 = 1.1$  Hz, 1 H), 7.71 (dd,  $J_1 = 7.7$  Hz,  $J_2 = 1.1$  Hz, 1 H), 7.16 (dd,  $J_1 = 4.9$  Hz,  $J_2 = 3.8$  Hz, 1 H), 4.13 (s, 2 H), 2.97-2.91 (m, 2 H), 1.27 (t,  $J = 7.4$  Hz, 3 H); for enol-**2l**: 13.2 (s, 1 H), 7.60 (dd,  $J_1 = 7.8$  Hz,  $J_2 = 1.1$  Hz, 1 H), 7.50 (dd,  $J_1 = 7.7$  Hz,  $J_2 = 1.1$  Hz, 1 H), 7.11 (dd,  $J_1 = 4.9$  Hz,  $J_2 = 3.8$  Hz, 1 H), 5.97 (s, 1H), 3.02-2.98 (m, 2 H), 1.33 (t,  $J = 7.4$  Hz, 3 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  for keto-**2l**: 191.8, 184.4, 143.5, 135.3, 133.9, 128.5, 54.9, 24.3, 14.5; for enol-**2l**: 194.8, 163.9, 137.0, 130.3, 128.8, 128.3, 96.5, 23.1, 15.1.



**S-Methyl 3-oxo-3-phenylpropanethioate (2m)** [2]: slight yellow oil. Keto:enol = 6:5. Yield: 89% (43.2 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  for keto-**2m**: 7.95 (d,  $J=8.3\text{Hz}$ , 2 H), 7.57 (t, 1 H), 7.45 (t, 2 H), 4.22 (s, 2 H), 2.33 (s, 3 H); for enol-**2m**: 13.2 (br, 1 H), 7.77 (d,  $J=8.3\text{Hz}$ , 2 H), 7.45 (t, 1 H), 7.40 (t, 2 H), 6.10 (s, 1 H), 2.38 (s, 3 H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  for keto-**2m**: 192.5, 191.9, 135.9, 133.8, 128.8 (2 C), 126.4 (2 C), 53.7, 12.2; for enol-**2m**: 195.2, 168.6, 132.8, 131.7, 128.8 (2 C), 128.6 (2 C), 97.1, 11.1.

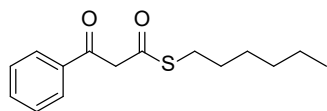


**S-Propyl 3-oxo-3-phenylpropanethioate (2n)** [2]: slight yellow oil. Keto:enol = 6:5. Yield: 90% (50.0 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  for keto-**2n**: 7.96 (d,  $J=7.6\text{ Hz}$ , 2 H), 7.59 (t, 1 H), 7.48 (t, 2 H), 4.22 (s, 2 H), 2.91 (t, 2 H), 1.62-1.60 (m, 2 H), 0.96 (t, 3 H); for enol-**2n**: 13.2 (br, 1 H), 7.78 7.96 (d,  $J=7.5\text{ Hz}$ , 2 H), 7.48 (t, 1 H), 7.42 (t, 2 H), 6.09 (s, 1 H), 2.97 (t, 2 H), 1.69-1.67 (m, 2 H), 1.02 (t, 3 H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  for keto-**2n**: 192.5, 192.20, 136.1, 133.9, 128.9 (2 C), 126.5 (2 C), 54.1, 31.6, 22.8, 13.4; for enol-**2n**: 195.2, 168.8, 133.0, 131.7, 128.9 (2 C), 128.7(2 C), 97.4, 30.5, 23.2, 13.5.



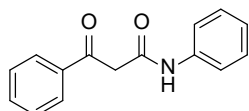
**S-Benzyl 3-oxo-3-phenylpropanethioate (2o)** [2]: slight yellow oil, Keto:enol=5:7. Yield: 90% (60.8 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  for keto-**2o**: 7.94 (d,  $J=8.2\text{ Hz}$ , 2 H), 7.58 (t, 1 H), 7.47 (t, 2 H), 7.35 (d,  $J=8.2\text{ Hz}$ , 2 H), 7.32-7.30 (m, 3 H), 4.22 (s, 2 H), 4.17 (s, 2 H); for enol-**2o**: 13.2 (s, 1 H), 7.77 (d,  $J=8.2\text{ Hz}$ , 2 H), 7.47 (t, 1 H), 7.41 (t, 2 H), 7.28 (d,  $J=8.2\text{ Hz}$ , 2 H), 7.27 (t, 1 H), 7.24 (t, 2 H), 6.08 (s, 1 H), 4.24 (s, 2 H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  for keto-**2o**: 194.1, 191.7, 136.9, 136.0, 132.9, 129.0 (4 C), 128.9 (2 C), 127.6,

126,5 (2 C), 53.7, 34.0; for enol-**2o**: 191.9, 169.3, 137.6, 134.0, 131.9, 128.8 (6 C), 127.4, 126,5 (2 C), 96.9, 32.7. HRMS Calcd for C<sub>16</sub>H<sub>15</sub>O<sub>2</sub>S<sup>+</sup>: ([M+H]<sup>+</sup>) 271.0787; Found: 271.0772.

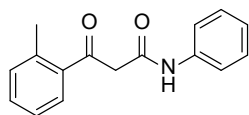


**S-Hexyl 3-oxo-3-phenylpropanethioate (2p)** [2]: slight yellow oil. Keto:enol=21:20. Yield: 88% (58.1 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ for keto-**2p**: 7.96 (d, *J*=8.3 Hz, 2 H), 7.58 (t, 1 H), 7.47 (t, 2 H), 4.21 (s, 2 H), 2.92 (t, 2 H), 1.58-1.55 (m, 2 H), 1.41-1.39 (m, 2 H), 1.35-1.31 (m, 2 H), 1.28-1.25 (m, 2 H), 0.87 (t, 3 H); for enol-**2p**: 13.2 (br, 1 H), 7.78 (d, *J*=8.3 Hz, 2 H), 7.47 (t, 1 H), 7.41 (t, 2 H), 6.09 (s, 1 H), 2.99 (t, 2 H), 1.67-1.62 (m, 2 H), 1.35-1.32 (m, 2 H), 1.35-1.31 (m, 2 H), 1.28-1.25 (m, 2 H), 0.90 (t, 3 H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ for keto-**2p**: 192.4, 192.1, 133.9, 133.0, 128.9 (2 C), 126.4 (2 C), 54.1, 31.4, 29.8, 29.3, 28.6, 22.6, 14.1; for enol-**2p**: 195.2, 168.7, 136.1, 131.7, 128.8 (2 C), 128.7 (2 C), 97.4, 31.3, 29.7, 28.6, 28.5, 22.6, 14.1.

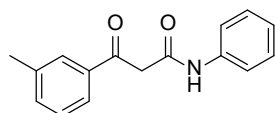
## 2. Spectroscopic Data of compound 3



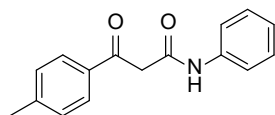
**3-Oxo-N,3-diphenylpropanamide (3a)** [3]: white solid, m.p. 106-107 °C. Keto/enol 3:1. Yield: 90% (53.8 mg). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz) δ for keto-**3a**: 10.19 (s, 1 H), 8.39 (dd, *J*<sub>1</sub> = 8.5 Hz, *J*<sub>2</sub> = 1.3 Hz, 2 H), 7.67 (t, *J* = 7.5 Hz, 1 H), 7.56 (d, *J* = 8.0 Hz, 3 H), 7.52 (d, *J* = 7.4 Hz, 1 H), 7.30 (t, *J* = 8.2 Hz, 2 H), 7.05 (t, *J* = 7.4 Hz, 1 H), 4.13 (s, 2 H); for enol-**3a**: 14.4 (s, 1 H), 10.21 (s, 1 H), 7.74 (dd, *J*<sub>1</sub> = 7.8 Hz, *J*<sub>2</sub> = 2.8 Hz, 2 H), 7.61 (d, *J* = 8.0 Hz, 3 H), 7.56 (d, *J* = 8.0 Hz, 1 H), 7.33 (t, *J* = 7.8 Hz, 3 H), 7.09 (d, *J* = 7.2 Hz, 1 H), 5.98 (s, 1 H). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 100 MHz) δ for keto-**3a**: 194.6, 165.3, 139.0, 136.3, 133.6, 128.8 (4 C), 128.4 (2 C), 123.4, 119.0 (2 C), 48.1; for enol-**3a**: 194.6, 165.3, 139.0, 136.3, 131.1, 128.5 (4 C), 125.3 (2 C), 123.4, 119.6 (2 C), 89.8.



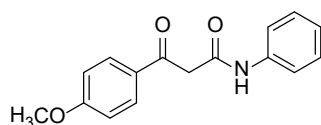
**3-Oxo-N-phenyl-3-o-tolylpropanamide (3b)** [3]: white solid, m.p. 81-82 °C. Keto/enol 2:1. Yield: 88% (55.7 mg). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz) δ for keto-**3b**: 10.15 (s, 1 H), 7.86 (d, *J* = 7.7 Hz, 1 H), 7.56 (d, *J* = 8.3 Hz, 2 H), 7.44 (d, *J* = 7.5 Hz, 1 H), 7.34 (t, *J* = 8.6 Hz, 2 H), 7.29 (t, *J* = 8.4 Hz, 2 H), 7.04 (t, *J* = 7.5 Hz, 1 H), 4.07 (s, 2 H), 2.44 (s, 3 H); for enol-**3b**: 14.21 (s, 1 H), 10.14 (s, 1 H), 7.61 (d, *J* = 8.0 Hz, 2 H), 7.45 (d, *J* = 7.5 Hz, 1 H), 7.34 (t, *J* = 8.6 Hz, 2 H), 7.29 (t, *J* = 8.4 Hz, 2 H), 7.08 (t, *J* = 7.3 Hz, 1 H), 5.53 (s, 1 H), 2.43 (s, 3 H). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 100 MHz) δ for keto-**3b**: 197.9, 165.3, 139.0, 137.8, 136.9, 131.8 (2 C), 129.3, 128.8 (2 C), 125.9, 123.4, 119.2 (2 C), 50.6, 20.9; for enol-**3b**: 172.1, 170.4, 138.4, 135.7, 134.8, 131.0 (2 C), 129.9, 128.0 (2 C), 126.0, 123.6, 119.6 (2 C), 94.0, 20.3.



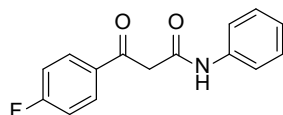
**3-Oxo-N-phenyl-3-m-tolylpropanamide (3c)** [3]: colorless liquid. Keto/enol 3:1. Yield: 87% (55.0 mg). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz) δ for keto-**3c**: 10.17 (s, 1 H), 7.81 (s, 1 H), 7.80 (d, *J* = 8.4 Hz, 1 H), 7.57 (d, *J* = 7.6 Hz, 2 H), 7.47 (d, *J* = 7.5 Hz, 1 H), 7.34 - 7.29 (m, 3 H), 7.04 (t, *J* = 7.6 Hz, 1 H), 4.11 (s, 2 H), 2.38 (s, 3 H); for enol-**3c**: 14.31 (s, 1 H), 10.14 (s, 1 H), 7.61 (d, *J* = 7.9 Hz, 3 H), 7.57 (d, *J* = 7.6 Hz, 1 H), 7.44 (d, *J* = 7.4 Hz, 3 H), 7.36 (d, *J* = 7.6 Hz, 1 H), 7.09 (t, *J* = 7.4 Hz, 1 H), 5.97 (s, 1 H), 2.37 (s, 3 H). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 100 MHz) δ for keto-**3c**: 194.7, 165.4, 139.0, 138.2, 136.3, 134.2, 128.8 (2 C), 128.7 (2 C), 125.7, 123.4, 119.0 (2 C), 48.1, 20.9; for enol-**3c**: 170.6, 168.8, 138.5, 138.1, 133.7, 131.7, 128.9 (2 C), 128.8, 125.8, 123.6, 122.5, 119.6 (2 C), 89.8, 21.0.



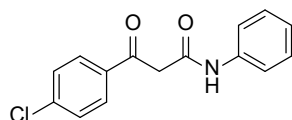
**3-Oxo-*N*-phenyl-3-*p*-tolylpropanamide (3d)** [3]: colorless liquid. Keto/enol 16:1. Yield: 89% (56.3 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  9.35 (s, 1 H), 7.93 (d,  $J$  = 8.2 Hz, 2 H), 7.58 (d,  $J$  = 7.6 Hz, 2 H), 7.35 - 7.30 (m, 4 H), 7.12 (t,  $J$  = 7.4 Hz, 1 H), 4.09 (s, 2 H), 2.44 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  196.3, 164.0, 145.7, 137.8, 133.8, 129.8 (2 C), 129.1 (2 C), 128.9 (2 C), 124.6, 120.3 (2 C), 45.4, 21.9.



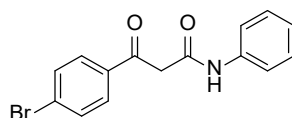
**3-(4-Methoxyphenyl)-3-oxo-*N*-phenylpropanamide (3e)** [3]: colorless liquid. Keto/ enol = 29:1. Yield: 86% (57.9 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  9.40 (s, 1 H), 8.02 (d,  $J$  = 8.8 Hz, 2 H), 7.58 (d,  $J$  = 7.7 Hz, 2 H), 7.33 (t,  $J$  = 8.2 Hz, 2 H), 7.11 (t,  $J$  = 7.4 Hz, 1 H), 6.97 (d,  $J$  = 8.9 Hz, 2 H), 4.05 (s, 2 H), 3.89 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  195.0, 164.7, 161.1, 137.8, 131.3 (2 C), 129.2, 129.1 (2 C), 124.6, 120.3 (2 C), 114.3 (2 C), 55.8, 45.2.



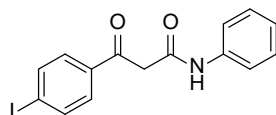
**3-(4-Fluorophenyl)-3-oxo-*N*-phenylpropanamide (3f)** [3]: white solid, m.p. 112-113 °C. Keto/enol 8:1. Yield: 90% (57.8 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  9.17 (s, 1 H), 8.04 (dd,  $J_1$  = 8.3 Hz,  $J_2$  = 5.4 Hz, 2 H), 7.57 (d,  $J$  = 7.9 Hz, 2 H), 7.33 (t,  $J$  = 7.7 Hz, 2 H), 7.18 (t,  $J$  = 8.0 Hz, 2 H), 7.13 (d,  $J$  = 7.5 Hz, 1 H), 4.08 (s, 2 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  194.9, 166.6 (d,  $J$  = 255.7 Hz), 163.7, 137.6, 132.6 (d,  $J$  = 2.9 Hz), 131.6 (d,  $J$  = 9.6 Hz, 2 C), 129.2 (2 C), 124.8, 120.3 (2 C), 116.4 (d,  $J$  = 22.0 Hz, 2 C), 45.9.



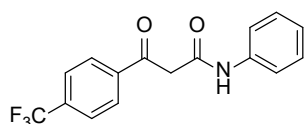
**3-(4-Chlorophenyl)-3-oxo-N-phenylpropanamide (3g)** [3]: white solid, m.p. 129-130 °C. Keto/enol 8:1. Yield: 88% (60.1 mg). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 9.10 (s, 1 H), 7.99 (d, *J* = 8.6 Hz, 2 H), 7.57 (d, *J* = 7.8 Hz, 2 H), 7.50 (d, *J* = 8.6 Hz, 2 H), 7.34 (t, *J* = 8.1 Hz, 2 H), 7.13 (d, *J* = 7.4 Hz, 1 H), 4.08 (s, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 195.3, 163.4, 141.2, 137.6, 134.5, 130.2 (2 C), 129.5 (2 C), 129.2 (2 C), 124.8, 120.3 (2 C), 45.9.



**3-(4-Bromophenyl)-3-oxo-N-phenylpropanamide (3h)** [3]: white solid, m.p. 146-147 °C. Keto/enol 6:1. Yield: 89% (57.2 mg). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 9.09 (s, 1 H), 7.90 (d, *J* = 8.4 Hz, 2 H), 7.67 (d, *J* = 8.4 Hz, 2 H), 7.57 (d, *J* = 7.8 Hz, 2 H), 7.34 (t, *J* = 8.0 Hz, 2 H), 7.13 (d, *J* = 7.4 Hz, 1 H), 4.08 (s, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 195.5, 163.4, 141.2, 137.6, 134.9, 132.5 (2 C), 130.3 (2 C), 129.2 (2 C), 124.8, 120.3 (2 C), 45.9.

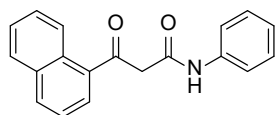


**3-(4-Iodophenyl)-3-oxo-N-phenylpropanamide (3i)** [3]: white solid, m.p. 163-164 °C. Keto/enol 5:1. Yield: 91% (83.0 mg). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 9.10 (s, 1 H), 7.89 (d, *J* = 8.4 Hz, 2 H), 7.73 (d, *J* = 8.5 Hz, 2 H), 7.56 (d, *J* = 7.9 Hz, 2 H), 7.33 (t, *J* = 8.0 Hz, 2 H), 7.13 (d, *J* = 7.4 Hz, 1 H), 4.06 (s, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 195.9, 163.4, 138.5 (2 C), 137.9, 135.4, 130.2 (2 C), 129.2 (2 C), 124.8, 120.3 (2 C), 103.0, 45.8.

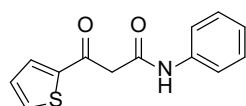


**3-Oxo-N-phenyl-3-(4-(trifluoromethyl)phenyl)propanamide (3j)** [3]: white solid, m.p. 110-111 °C. Keto/enol 6:5. Yield: 83% (63.8 mg). <sup>1</sup>H NMR

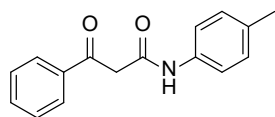
(DMSO- $d_6$ , 600 MHz)  $\delta$  for keto-**3j**: 10.24 (s, 1H), 8.20 (d,  $J$  = 8.1 Hz, 2 H), 7.93 (t,  $J$  = 8.1 Hz, 2 H), 7.57 (d,  $J$  = 7.7 Hz, 2 H), 7.31 (t,  $J$  = 7.8 Hz, 2 H), 7.05 (t,  $J$  = 7.4 Hz, 1 H), 4.22 (s, 2 H); for enol-**3j**: 14.39 (s, 1 H), 10.33 (s, 1H), 7.93 (d,  $J$  = 8.1 Hz, 2H), 7.87 (d,  $J$  = 8.3 Hz, 2 H), 7.63 (d,  $J$  = 7.9 Hz, 2 H), 7.35 (d,  $J$  = 7.8 Hz, 2 H), 7.10 (t,  $J$  = 7.4 Hz, 1 H), 6.10 (s, 1H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 151 MHz)  $\delta$  for keto-**3j**: 194.2, 165.0, 138.9, 138.2, 132.8 (q,  $J$  = 32.0 Hz), 129.2 (2 C), 128.8 (2 C), 125.8 (q,  $J$  = 3.6 Hz, 2 C), 123.8 (q,  $J$  = 272.5 Hz), 123.5, 119.1 (2 C), 48.7; for enol-**3j**: 170.2, 166.7, 139.5, 137.6, 130.7 (q,  $J$  = 32.0 Hz), 128.9 (2 C), 126.1 (2 C), 125.8 (q,  $J$  = 3.6 Hz, 2 C), 123.9 (q,  $J$  = 272.5 Hz), 123.8, 119.7 (2 C), 91.7.



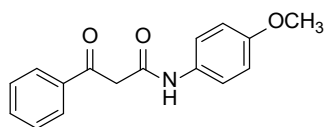
**3-(Naphthalen-1-yl)-3-oxo-N-phenylpropanamide (3k)** [3]: white solid, m.p. 164-165 °C. Keto/enol 5:1. Yield: 86% (62.2 mg).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  9.08 (s, 1 H), 8.63 (d,  $J$  = 8.5 Hz, 2 H), 7.98 (d,  $J$  = 7.6 Hz, 2 H), 7.83 (d,  $J$  = 8.1 Hz, 1 H), 7.59-7.44 (m, 4 H), 7.27 (t,  $J$  = 7.2 Hz, 2 H), 7.05 (d,  $J$  = 7.3 Hz, 1 H), 4.13 (s, 2 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  199.9, 163.9, 137.7, 134.6, 134.1, 129.8, 129.2 (2 C), 128.9, 128.8, 127.0, 125.7, 125.6, 125.1, 124.7, 124.6, 120.3 (2 C), 49.5.



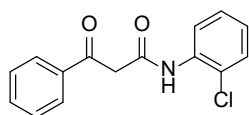
**3-Oxo-N-phenyl-3-(thiophen-2-yl)propanamide (3l)** [3]: colorless liquid. Keto/enol 25:1. Yield: 85% (52.1 mg).  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz)  $\delta$  10.26 (s, 1 H), 8.06-8.03 (m, 2 H), 7.57 (d,  $J$  = 7.9 Hz, 2 H), 7.32 (m, 3 H), 7.05 (t,  $J$  = 7.4 Hz, 1 H), 4.08 (s, 2 H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$  187.3, 164.8, 143.5, 138.9, 135.7, 134.6, 128.9, 128.8 (2 C), 123.5, 119.1 (2 C), 48.3.



**3-Oxo-3-phenyl-N-p-tolylpropanamide (3m)** [3]: white solid, m.p. 131-132 °C. Keto/ enol = 3:1. Yield: 90% (56.9 mg). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz) δ for keto-**3m**: 10.11 (s, 1 H), 8.00 (dd, *J*<sub>1</sub> = 8.5 Hz, *J*<sub>2</sub> = 1.3 Hz, 2 H), 7.66 (t, *J* = 7.5 Hz, 1 H), 7.55 (t, *J* = 7.8 Hz, 2 H), 7.46 (d, *J* = 8.4 Hz, 2 H), 7.09 (d, *J* = 8.3 Hz, 2 H), 4.12 (s, 2 H), 2.24 (s, 3 H); for enol-**3m**: 14.42 (s, 1 H), 10.13 (s, 1 H), 7.75-7.73 (m, 2 H), 7.51-7.49 (m, 5 H), 7.14 (d, *J* = 7.5 Hz, 2 H), 5.97 (s, 1 H), 2.43 (s, 3 H). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 100 MHz) δ for keto-**3m**: 194.6, 165.0, 136.5, 136.3, 133.5, 132.3, 129.1 (2 C), 128.8 (2 C), 128.3 (2 C), 119.0 (2 C), 48.0, 20.4; for enol-**3m**: 170.4, 168.5, 135.8, 133.7, 132.6, 130.9, 129.3 (2 C), 128.8 (2 C), 125.3 (2 C), 119.6 (2 C), 89.8, 20.4.

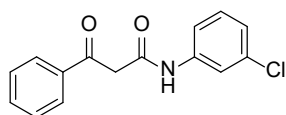


**N-(4-Methoxyphenyl)-3-oxo-3-phenylpropanamide (3n)** [3]: white solid, m.p. 129-130 °C. Keto/enol 3:1. Yield: 87% (58.5 mg). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz) δ for keto-**3n**: 10.06 (s, 1 H), 8.00 (dd, *J*<sub>1</sub> = 8.5 Hz, *J*<sub>2</sub> = 1.3 Hz, 2 H), 7.66 (t, *J* = 7.4 Hz, 1 H), 7.56 (d, *J* = 7.8 Hz, 2 H), 7.48 (dd, *J*<sub>1</sub> = 7.0 Hz, *J*<sub>2</sub> = 2.0 Hz, 2 H), 6.87 (d, *J*<sub>1</sub> = 7.0 Hz, *J*<sub>2</sub> = 2.0 Hz, 2 H), 4.10 (s, 2 H), 3.71 (s, 3 H); for enol-**3n**: 14.44 (s, 1 H), 10.08 (s, 1 H), 7.75-7.72 (m, 2 H), 7.54-7.50 (m, 5 H), 6.92 (d, *J* = 8.8 Hz, 2 H), 5.94 (s, 1 H), 3.73 (s, 3 H). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 100 MHz) δ for keto-**3n**: 194.6, 164.7, 155.3, 136.3, 133.5, 132.1, 128.8 (2 C), 128.4 (2 C), 120.6 (2 C), 113.9 (2 C), 55.1, 47.9; for enol-**3n**: 170.1, 168.2, 155.6, 133.8, 131.4, 130.9, 128.8 (2 C), 125.2 (2 C), 121.2 (2 C), 114.0 (2 C), 89.8, 55.2.

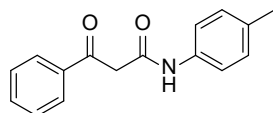


**N-(2-Chlorophenyl)-3-oxo-3-phenylpropanamide (3o)** [3]: white solid, m.p. 139-140 °C. Keto/enol 3:1. Yield: 85% (58.0 mg). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400

MHz)  $\delta$  for keto-**3o**: 9.85 (s, 1 H), 8.01 (d,  $J = 7.4$  Hz, 2 H), 7.83 (d,  $J = 7.4$  Hz, 1 H), 7.67 (d,  $J = 7.4$  Hz, 1 H), 7.55 (t,  $J = 7.8$  Hz, 2 H), 7.49 (td,  $J_1 = 8.0$  Hz,  $J_2 = 1.2$  Hz, 2 H), 7.18 (td,  $J_1 = 8.8$  Hz,  $J_2 = 1.0$  Hz, 1 H), 4.26 (s, 2 H); for enol-**3o**: 14.20 (s, 1 H), 9.76 (s, 1 H), 7.78-7.75 (m, 4 H), 7.37 (d,  $J = 7.3$  Hz, 1 H), 7.32 (td,  $J_1 = 8.5$  Hz,  $J_2 = 1.0$  Hz, 3 H), 7.23 (t,  $J = 7.3$  Hz, 1 H), 6.25 (s, 1 H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$  for keto-**3o**: 194.6, 165.9, 136.2, 134.8, 133.6, 129.5, 128.8 (2 C), 128.3 (2 C), 127.5, 126.1, 125.4, 125.3, 47.5; for enol-**3o**: 171.1, 169.0, 134.1, 133.5, 131.6, 129.6, 128.9 (2 C), 128.3 (2 C), 127.5, 126.6, 125.6 (2 C), 89.6.

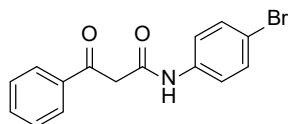


**N-(3-Chlorophenyl)-3-oxo-3-phenylpropanamide (3p)** [3]: white solid, m.p. 117-118 °C. Keto/enol 3:1. Yield: 87% (59.4 mg).  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz)  $\delta$  for keto-**3p**: 10.38 (s, 1 H), 8.01 (dd,  $J_1 = 8.5$  Hz,  $J_2 = 1.3$  Hz, 2 H), 7.80 (d,  $J = 2.4$  Hz, 1 H), 7.67 (dt,  $J_1 = 7.4$  Hz,  $J_2 = 1.2$  Hz, 1 H), 7.55 (t,  $J = 7.8$  Hz, 2 H), 7.52 (t,  $J = 7.8$  Hz, 1 H), 7.33 (t,  $J = 8.0$  Hz, 1 H), 7.13-7.10 (m, 1 H), 4.16 (s, 2 H); for enol-**3p**: 14.16 (s, 1 H), 10.38 (s, 1 H), 7.83 (t,  $J = 2.4$  Hz, 1 H), 7.76-7.74 (m, 2 H), 7.45 (d,  $J = 8.2$  Hz, 1 H), 7.41-7.39 (m, 3 H), 7.35 (d,  $J = 8.0$  Hz, 1 H), 7.15-7.12 (m, 1 H), 5.96 (s, 1 H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$  for keto-**3p**: 194.4, 165.8, 140.3, 136.2, 133.6, 133.1, 130.5, 128.8 (2 C), 128.3 (2 C), 123.1, 118.5, 117.4, 48.1; for enol-**3p**: 170.8, 169.2, 139.9, 133.5, 133.2, 130.6, 130.5, 128.9 (2 C), 125.4 (2 C), 123.3, 119.0, 118.0, 89.7.

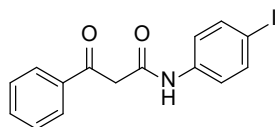


**N-(4-Chlorophenyl)-3-oxo-3-phenylpropanamide (3q)** [3]: white solid, m.p. 160-161 °C. Keto/enol 3:1. Yield: 90% (61.4 mg).  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz)  $\delta$  for keto-**3q**: 10.32 (s, 1 H), 7.99 (dd,  $J_1 = 8.5$  Hz,  $J_2 = 1.3$  Hz, 2 H), 7.64 (d,  $J = 7.3$  Hz, 1 H), 7.60 (d,  $J = 8.8$  Hz, 2 H), 7.56 (d,  $J = 7.9$  Hz, 2 H), 7.35 (d,  $J = 8.8$  Hz, 2 H), 4.15 (s, 2 H); for enol-**3q**: 14.24 (s, 1 H), 10.32 (s, 1

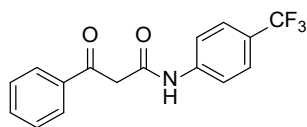
H), 7.75 (dd,  $J_1 = 7.9$  Hz,  $J_2 = 2.4$  Hz, 2 H), 7.67 (d,  $J = 7.4$  Hz, 2 H), 7.53-7.50 (m, 3 H), 7.39 (d,  $J = 8.9$  Hz, 2 H), 5.96 (s, 1 H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$  for keto-**3q**: 194.5, 165.5, 137.9, 136.2, 133.6, 128.8 (3 C), 128.7 (2 C), 128.3 (2 C), 120.5 (2 C), 48.0; for enol-**3q**: 170.6, 169.0, 137.4, 133.5, 131.1, 128.9 (2 C), 126.9 (2 C), 125.3 (2 C), 121.1 (2 C), 104.5, 89.7.



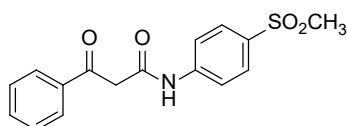
**N-(4-Bromophenyl)-3-oxo-3-phenylpropanamide (3r)** [3]: white solid, m.p. 176-177 °C. Keto/enol 3:1. Yield: 84% (66.6 mg).  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz)  $\delta$  for keto-**3r**: 10.32 (s, 1 H), 8.00 (d,  $J = 7.5$  Hz, 2 H), 7.66 (t,  $J = 7.2$  Hz, 1 H), 7.60-7.47 (m, 6 H), 4.15 (s, 2 H); for enol-**3r**: 14.24 (s, 1 H), 10.32 (s, 1 H), 7.75 (d,  $J = 7.2$  Hz, 2 H), 7.60-7.47 (m, 7 H), 5.96 (s, 1 H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$  for keto-**3r**: 194.4, 165.5, 138.3, 136.2, 133.6, 131.6 (2 C), 128.8 (2 C), 128.3 (2 C), 120.9 (2 C), 114.9, 48.1; for enol-**3r**: 170.6, 169.0, 137.8, 133.5, 131.7 (2 C), 131.1, 128.8 (2 C), 125.4 (2 C), 121.5 (2 C), 115.3, 89.7.



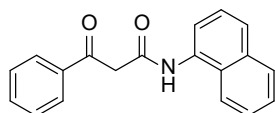
**N-(4-Iodophenyl)-3-oxo-3-phenylpropanamide (3s)** [3]: white solid, m.p. 179-180 °C. Keto/enol 3:1. Yield: 86% (78.5 mg).  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz)  $\delta$  for keto-**3s**: 10.29 (s, 1 H), 7.99 (dd,  $J_1 = 8.5$  Hz,  $J_2 = 1.2$  Hz, 2 H), 7.67 (d,  $J = 8.5$  Hz, 1 H), 7.64 (d,  $J = 8.7$  Hz, 2 H), 7.56 (d,  $J = 7.8$  Hz, 1 H), 7.51 (t,  $J = 7.1$  Hz, 1 H), 7.42 (d,  $J = 8.7$  Hz, 2 H), 4.14 (s, 2 H); for enol-**3s**: 14.24 (s, 1 H), 10.29 (s, 1 H), 7.74 (dd,  $J_1 = 7.9$  Hz,  $J_2 = 2.3$  Hz, 1 H), 7.67 (d,  $J = 8.5$  Hz, 1 H), 7.64 (d,  $J = 8.7$  Hz, 2 H), 7.56 (d,  $J = 7.8$  Hz, 2 H), 7.51 (t,  $J = 7.1$  Hz, 2 H), 7.45 (d,  $J = 8.5$  Hz, 1 H), 5.96 (s, 1 H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz)  $\delta$  for keto-**3s**: 194.4, 165.5, 137.4 (2 C), 136.2, 133.6, 128.8 (2 C), 128.3 (2 C), 125.3, 121.2 (2 C), 86.8, 48.1; for enol-**3s**: 170.6, 169.0, 138.3, 137.5 (2 C), 133.5, 131.1, 128.8 (2 C), 125.3 (2 C), 121.7 (2 C), 89.8, 87.2.



**3-Oxo-3-phenyl-N-(4-(trifluoromethyl)phenyl)propanamide (3t)** [3]: white solid, m.p. 165-166 °C. Keto/enol 3:1. Yield: 89% (68.3 mg). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz) δ for keto-**3t**: 10.55 (s, 1 H), 8.00 (d, *J* = 7.6 Hz, 2 H), 7.84-7.76 (m, 2 H), 7.71-7.66 (m, 3 H), 7.57 (d, *J* = 7.6 Hz, 2 H), 4.20 (s, 2 H); for enol-**3t**: 14.16 (s, 1 H), 10.55 (s, 1 H), 7.84-7.76 (m, 3 H), 7.71-7.66 (m, 3 H), 7.54-7.51 (m, 3 H), 6.00 (s, 1 H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 100 MHz) δ for keto-**3t**: 194.42, 166.12, 142.49, 136.15, 133.69, 133.55 (q, *J* = 29.0 Hz), 128.84 (2 C), 128.37 (2 C), 126.15 (q, *J* = 3.7 Hz), 125.44, 124.35 (q, *J* = 269.5 Hz), 118.90 (2 C), 48.1; for enol-**3t**: 171.03, 169.51, 142.10, 133.55 (q, *J* = 29.0 Hz), 131.32, 128.92 (2 C), 128.37 (2 C), 126.15 (q, *J* = 3.7 Hz), 124.35 (q, *J* = 269.5 Hz), 123.56, 123.24, 119.46 (2 C), 89.73.

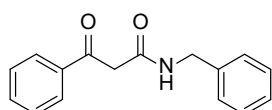


**N-(4-(Methylsulfonyl)phenyl)-3-oxo-3-phenylpropanamide (3u)** [3b]: white solid, m.p. 118-119 °C. Keto/enol 3:1. Yield: 82% (65.0 mg). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz) δ for keto-**3u**: 10.63 (s, 1 H), 8.01-7.50 (m, 7 H), 6.63 (d, *J* = 7.0 Hz, 1 H), 6.07 (s, 1 H), 4.22 (s, 2 H), 3.15 (s, 3 H); for enol-**3u**: 14.12 (s, 1 H), 10.63 (s, 1 H), 8.01-7.50 (m, 7 H), 6.63 (d, *J* = 7.0 Hz, 1 H), 6.07 (s, 1 H), 6.02 (s, 1 H), 3.01 (s, 3 H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 100 MHz) δ for keto-**3u**: 194.4, 166.3, 153.5, 143.4, 134.8, 133.7, 128.9 (2 C), 128.4 (2 C), 128.3 (2 C), 118.8, 112.7, 48.2, 43.8; for enol-**3u**: 171.1, 169.7, 143.0, 136.1, 134.9, 133.4, 131.4, 128.9 (2 C), 125.8 (2 C), 125.5 (2 C), 119.3, 89.8, 44.5.



**N-(Naphthalen-1-yl)-3-oxo-3-phenylpropanamide (3v)** [3]: white solid, m.p. 173-174 °C. Keto/enol 3:1. Yield: 89% (64.3 mg). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz) δ for keto-**3v**: 10.19 (s, 1 H), 8.17 (d, *J* = 7.7 Hz, 1 H), 8.08 (d, *J* = 7.5 Hz,

2 H), 7.94 (d,  $J = 7.4$  Hz, 1 H), 7.78-7.67 (m, 3 H), 7.60-7.47 (m, 5 H), 4.33 (s, 2 H); for enol-**3v**: 14.44 (s, 1 H), 10.19 (s, 1 H), 8.17 (d,  $J = 7.7$  Hz, 1 H), 8.08 (d,  $J = 7.5$  Hz, 1 H), 7.94 (d,  $J = 7.4$  Hz, 1 H), 7.78-7.67 (m, 3 H), 7.60-7.47 (m, 6 H), 6.31 (s, 1 H);  $^{13}\text{C}$  NMR (DMSO- $\text{d}_6$ , 100 MHz)  $\delta$  for keto-**3v**: 194.9, 166.1, 136.3, 133.6, 133.3, 128.8 (2 C), 128.3 (2 C), 128.1, 126.4, 125.9, 125.6 (2 C), 125.3 (2 C), 122.7, 121.4, 47.8; for enol-**3v**: 171.4, 168.8, 133.7, 131.0, 128.8, 128.2 (2 C), 127.6 (2 C), 126.0, 125.9, 125.6 (2 C), 125.4, 126.1, 125.3 (2 C), 122.5, 89.6.

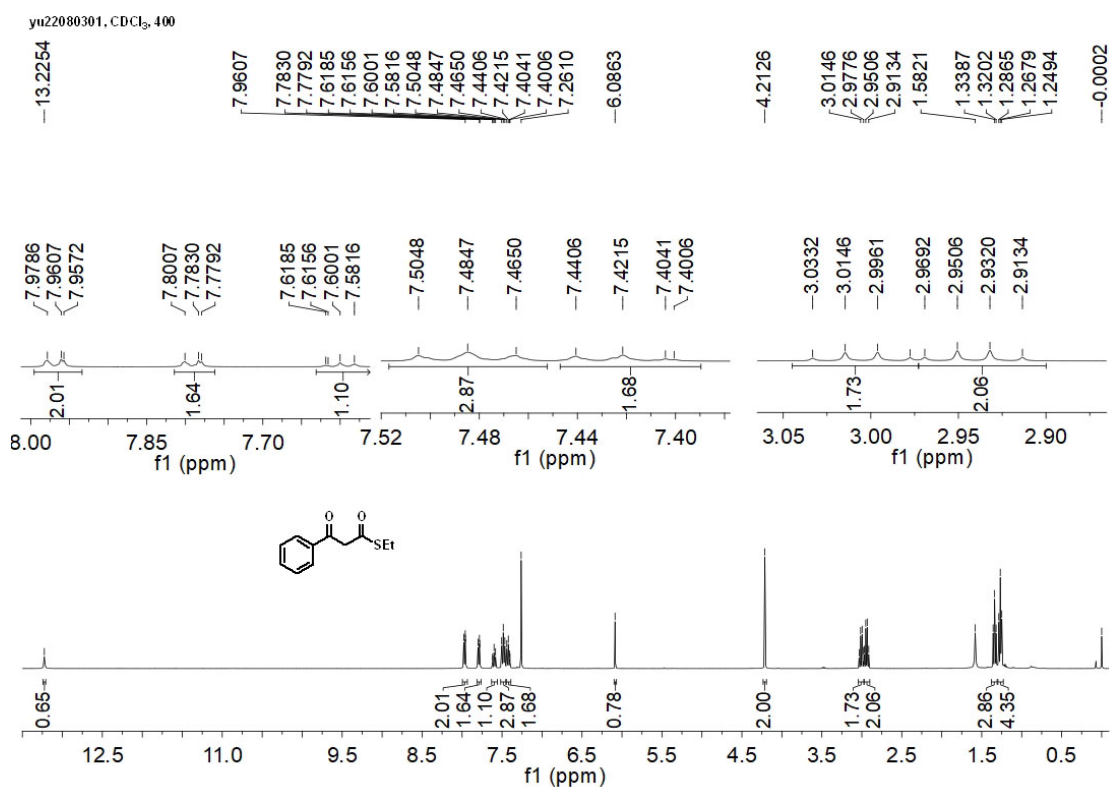


**N-Benzyl-3-oxo-3-phenylpropanamide (3w)** [3]: colorless liquid. Keto/enol 3:1. Yield: 80% (50.6 mg).  $^1\text{H}$  NMR (DMSO- $\text{d}_6$ , 400 MHz)  $\delta$  for keto-**3w**: 8.63 (s, 1 H), 7.97 (d,  $J = 7.4$  Hz, 2 H), 7.70-7.68 (m, 1 H), 7.65 (t,  $J = 7.4$  Hz, 1 H), 7.53 (t,  $J = 7.6$  Hz, 2 H), 7.48-7.46 (m, 1 H), 7.35-7.22 (m, 5 H), 4.30 (d,  $J = 5.8$  Hz, 2 H); for enol-**3w**: 14.68 (s, 1 H), 8.63 (s, 1 H), 7.70-7.68 (m, 1 H), 7.48-7.46 (m, 1 H), 7.35-7.22 (m, 8 H), 5.83 (s, 1 H), 4.40 (d,  $J = 5.8$  Hz, 2 H);  $^{13}\text{C}$  NMR (DMSO- $\text{d}_6$ , 100 MHz)  $\delta$  for keto-**3w**: 194.8, 166.3, 139.2, 136.3, 133.5, 128.7 (2 C), 128.4 (2 C), 128.3 (2 C), 127.2 (2 C), 125.2, 46.9, 42.2; for enol-**3w**: 171.7, 167.5, 138.9, 133.9, 133.5, 128.7 (2 C), 128.4 (2 C), 127.4 (2 C), 127.0, 126.8 (2 C), 89.0, 41.9.

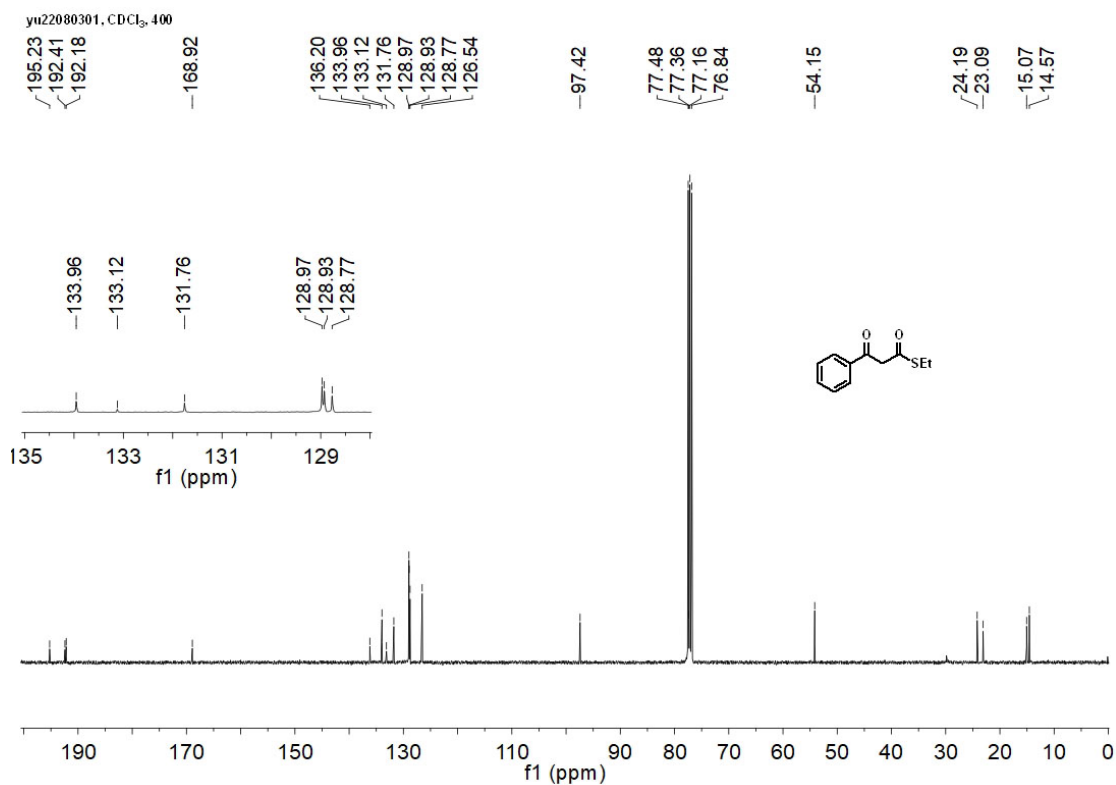
### 3. References

- [1] Xu, Q.; Zheng, B. H.; Pan, L.; Liu, Q.; Li, Y. F. *Eur. J. Org. Chem.* **2019**, 2019, 3704–3710.
- [2] Qi, F.; Yu, H. F.; Wang, Y. N.; Lv, Y.; Li, Y. X.; Han, L.; Wang, R.; Feng, X. N. *Synthetic. Commun.* **2017**, 47(23), 2220–2224.
- [3] Li, L. L.; Jiang, C. X.; Peng, T. T.; Zhang, N. N.; Jia, J.; Yu, H. F.; Zhao, X. B. *Synthetic Commun.* **2023**, 54(4), 312-320.

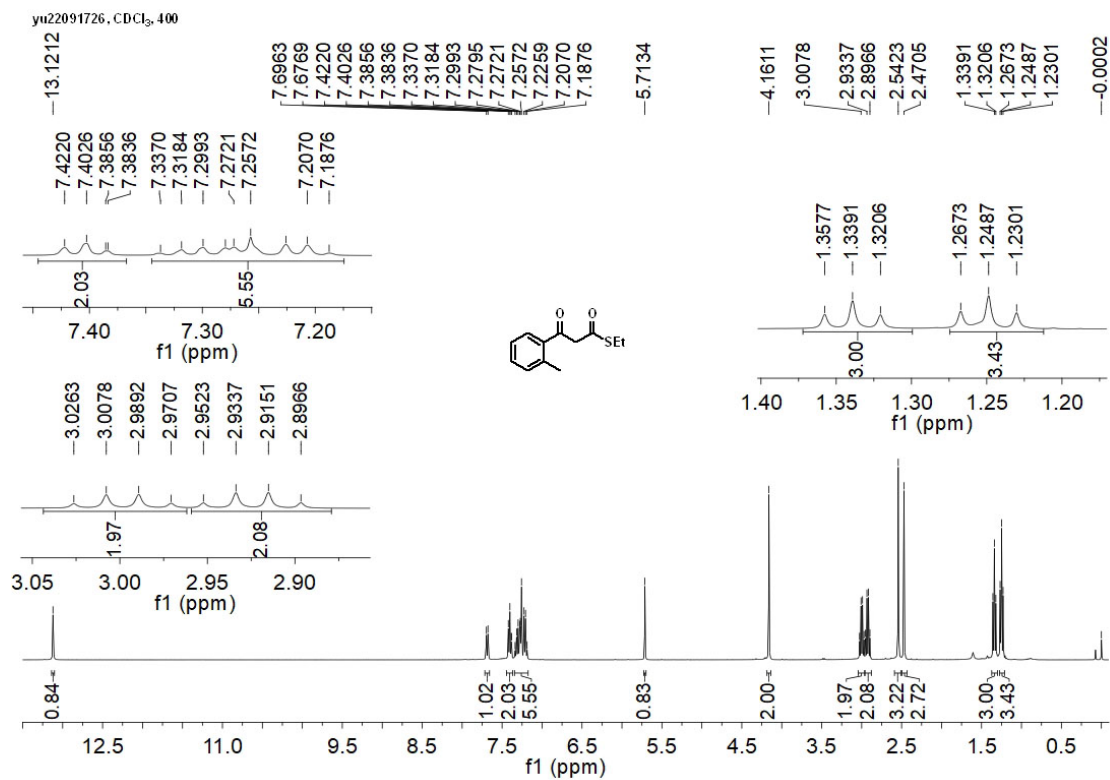
#### 4. Copies of $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 2



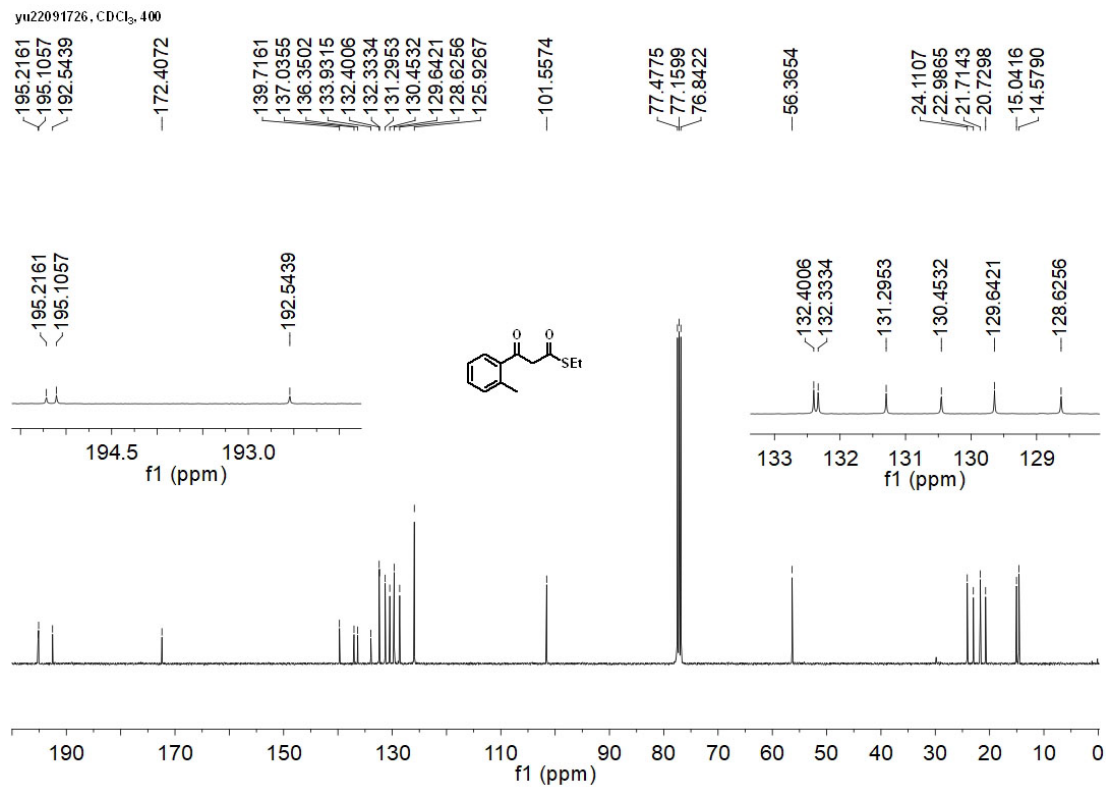
$^1\text{H}$  NMR of 2a



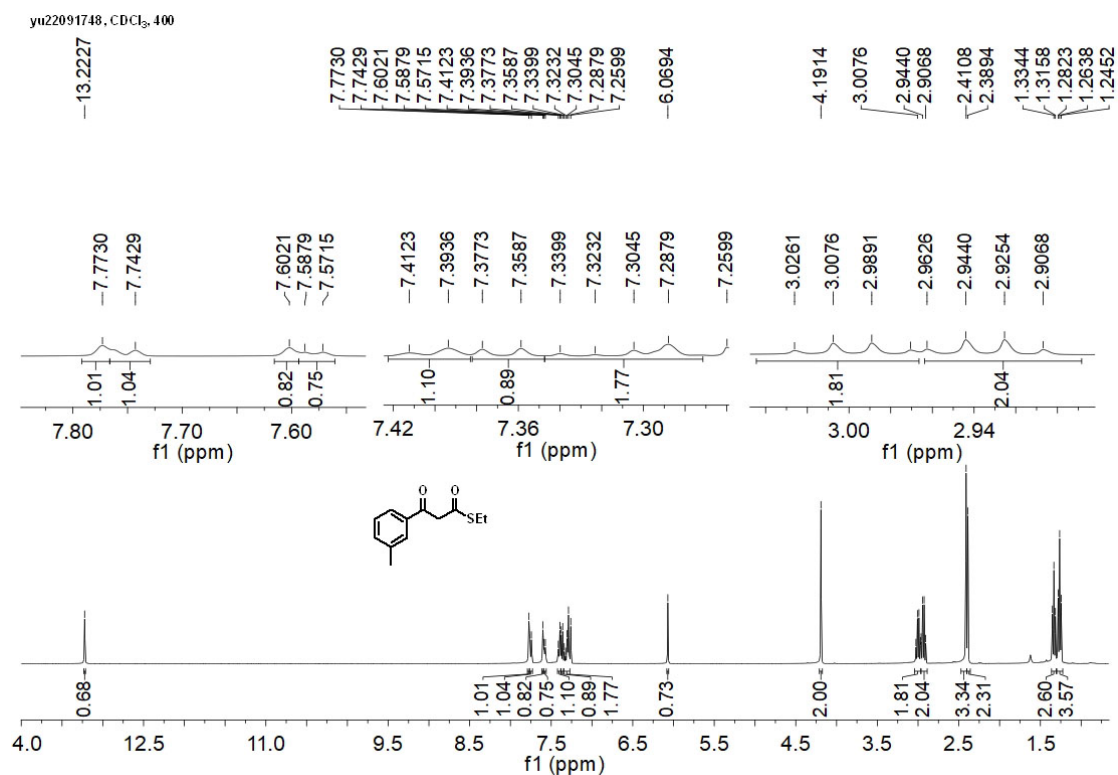
$^{13}\text{C}$  NMR of 2a



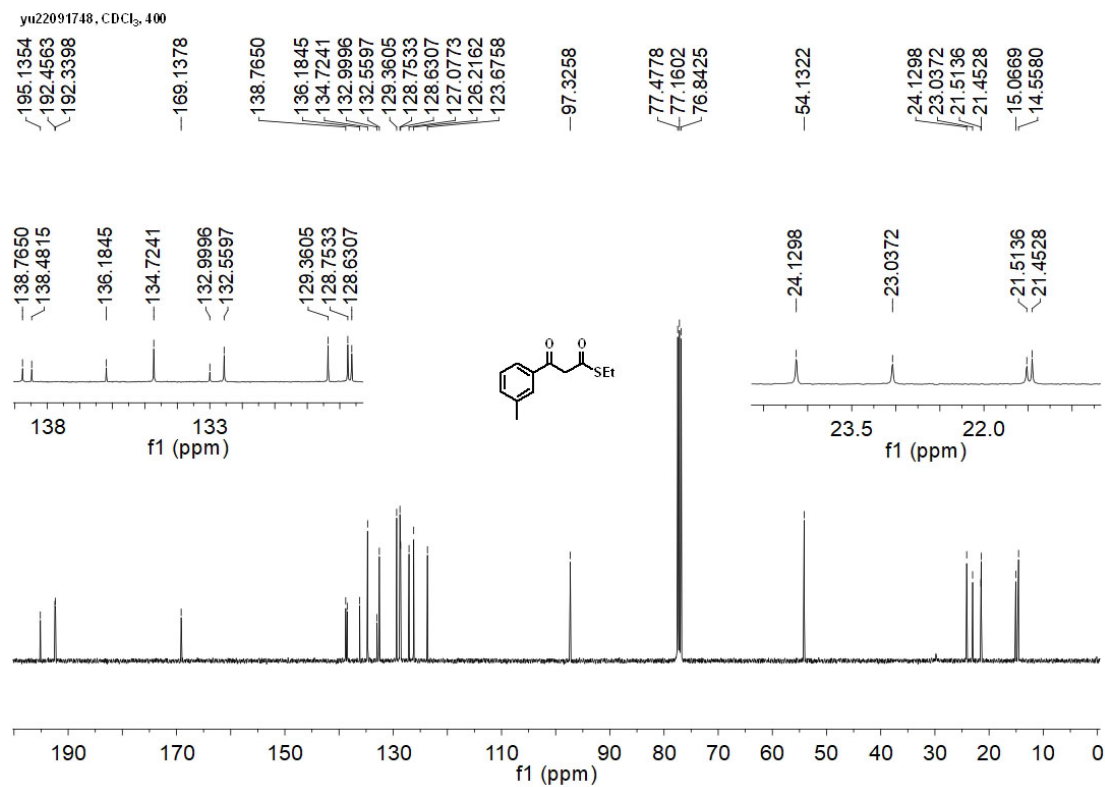
<sup>1</sup>H NMR of **2b**



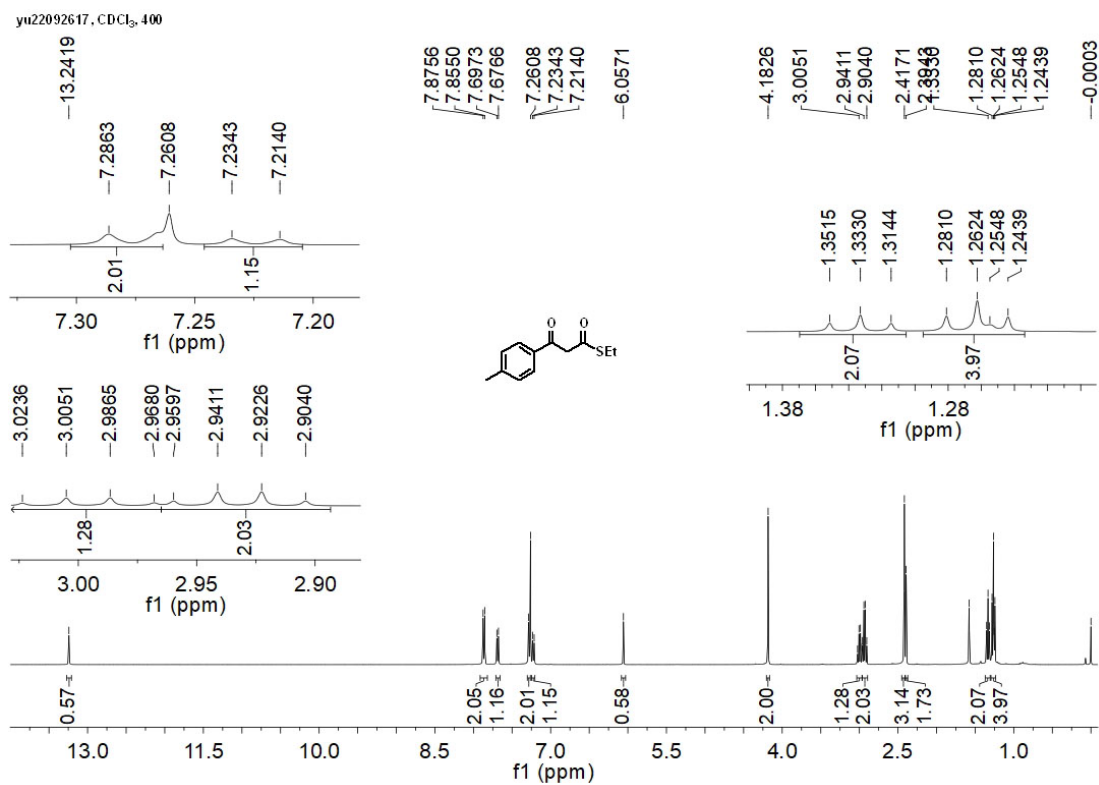
<sup>13</sup>C NMR of **2b**



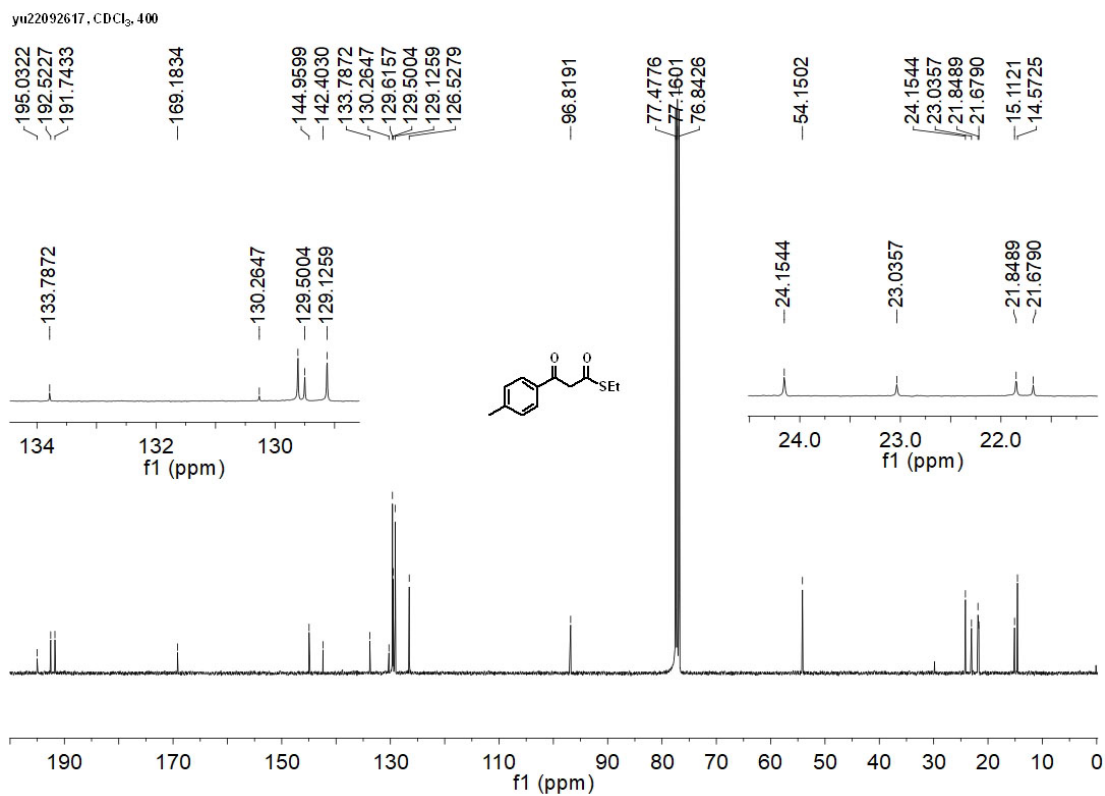
<sup>1</sup>H NMR of **2c**



<sup>13</sup>C NMR of **2c**

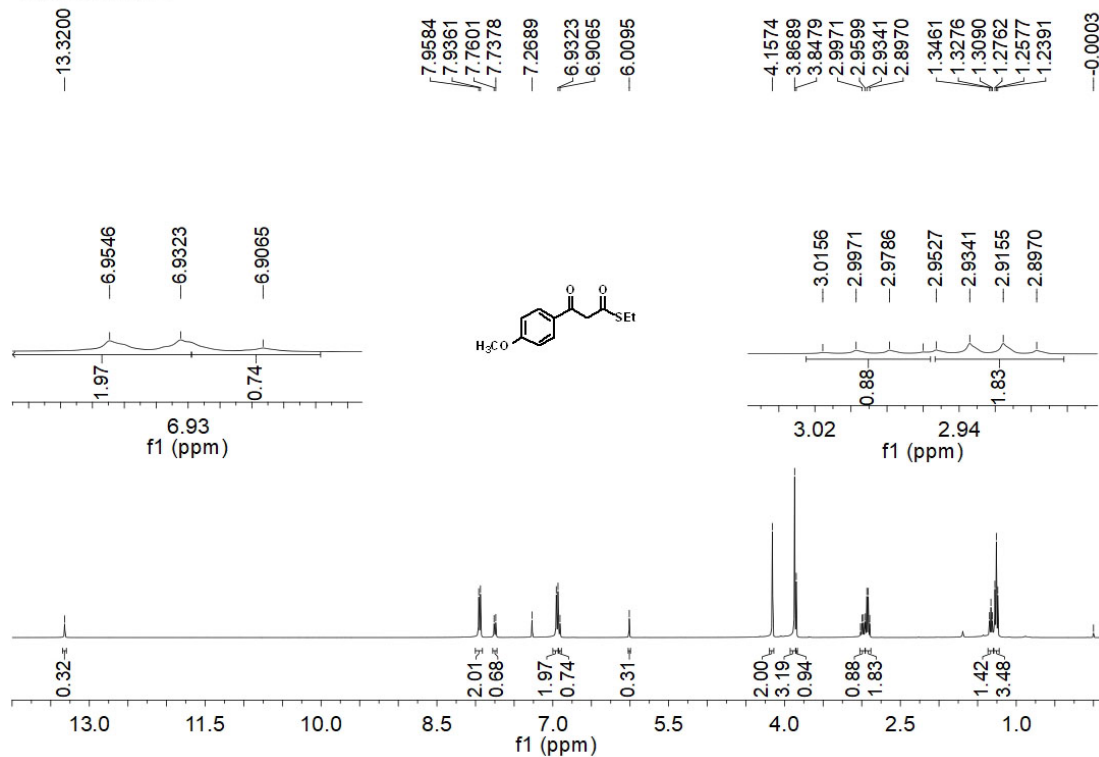


<sup>1</sup>H NMR of **2d**



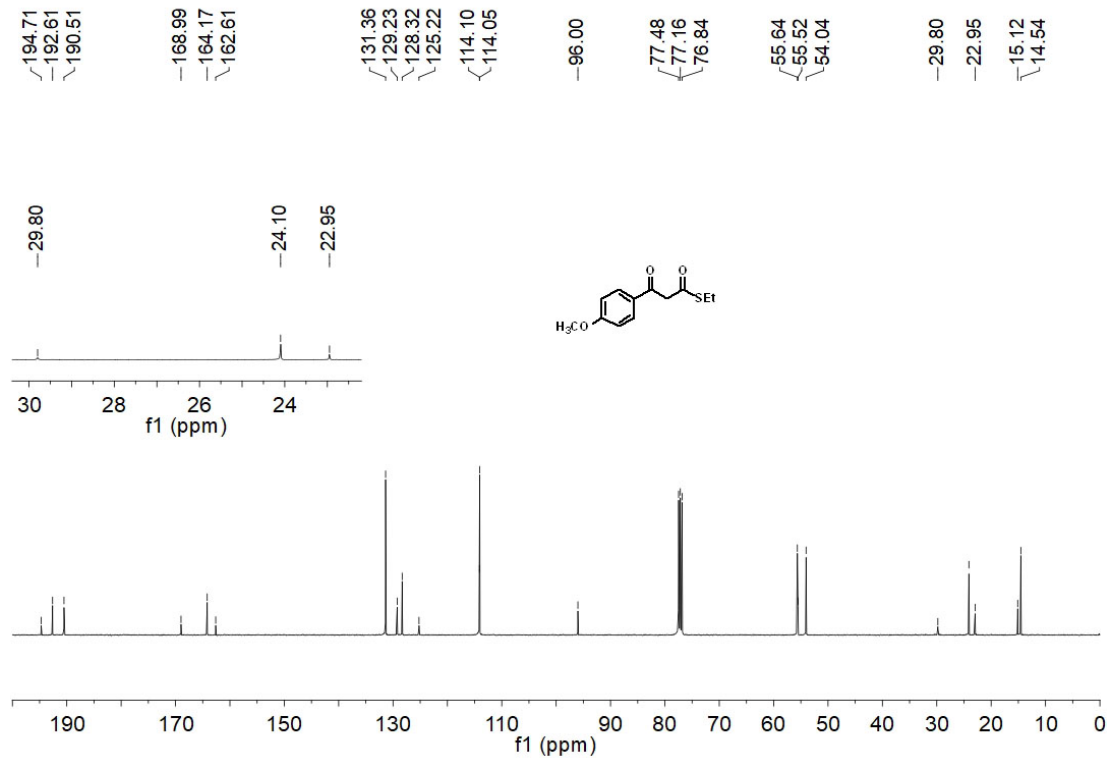
<sup>13</sup>C NMR of **2d**

yu22112708, CDCl<sub>3</sub>, 400

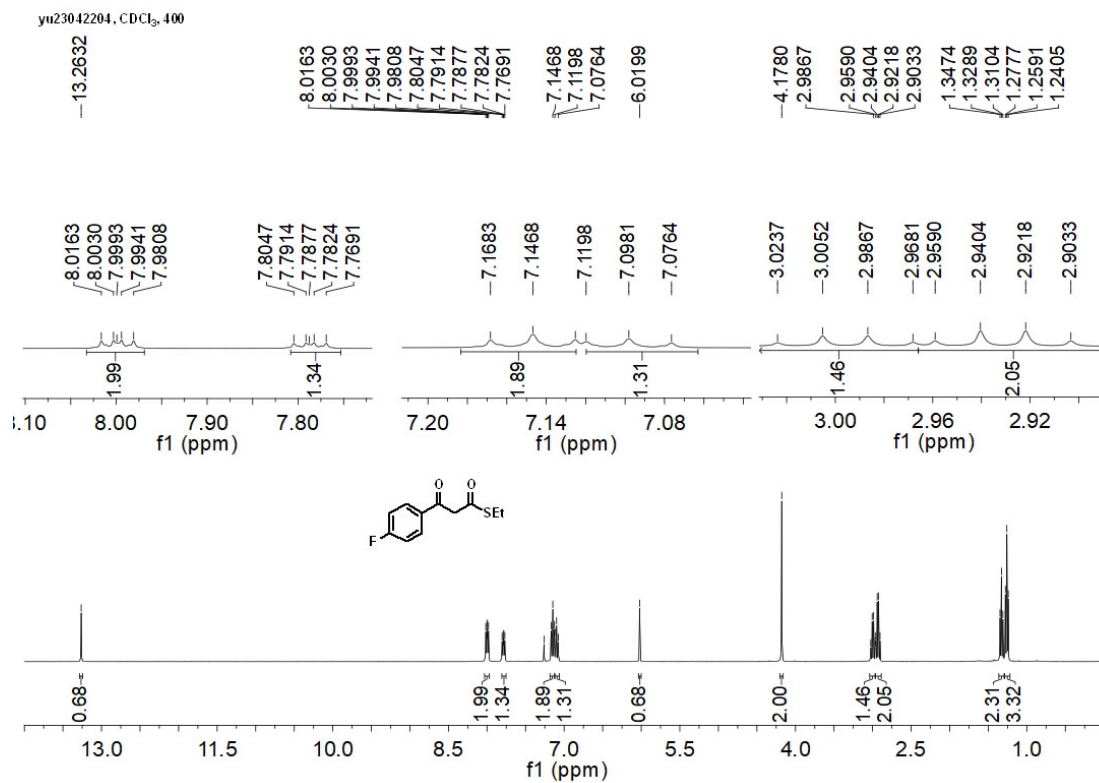


**<sup>1</sup>H NMR of 2e**

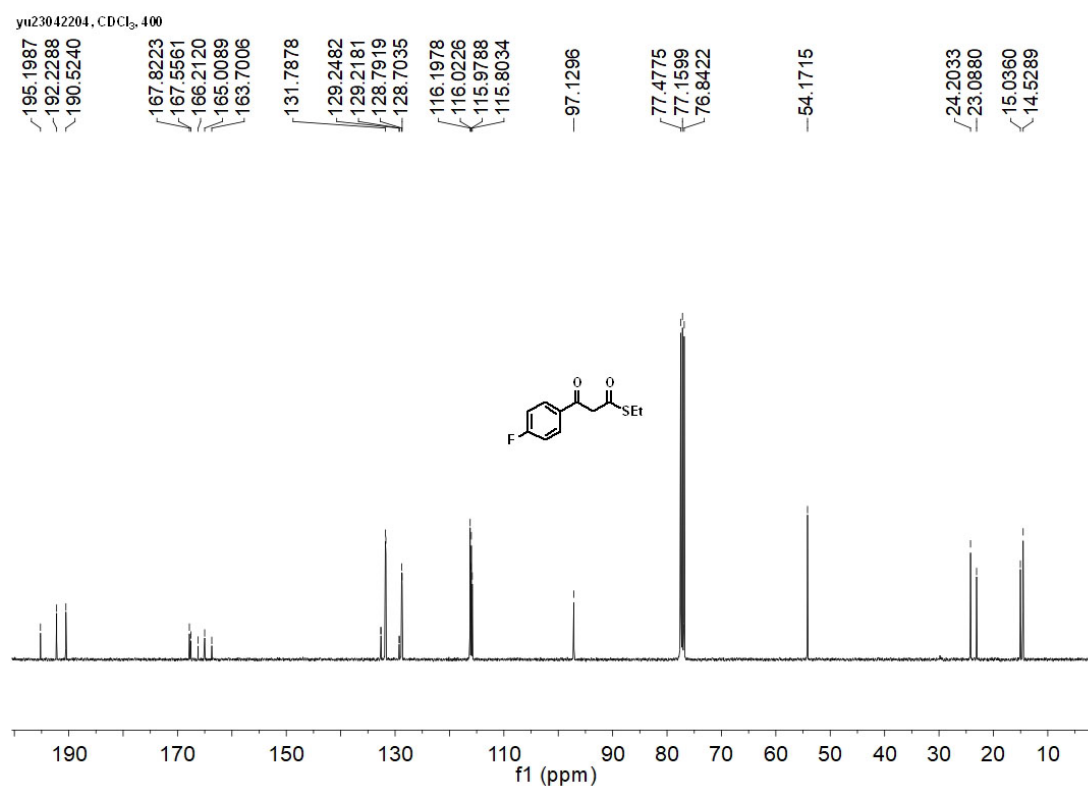
yu22112708, CDCl<sub>3</sub>, 400



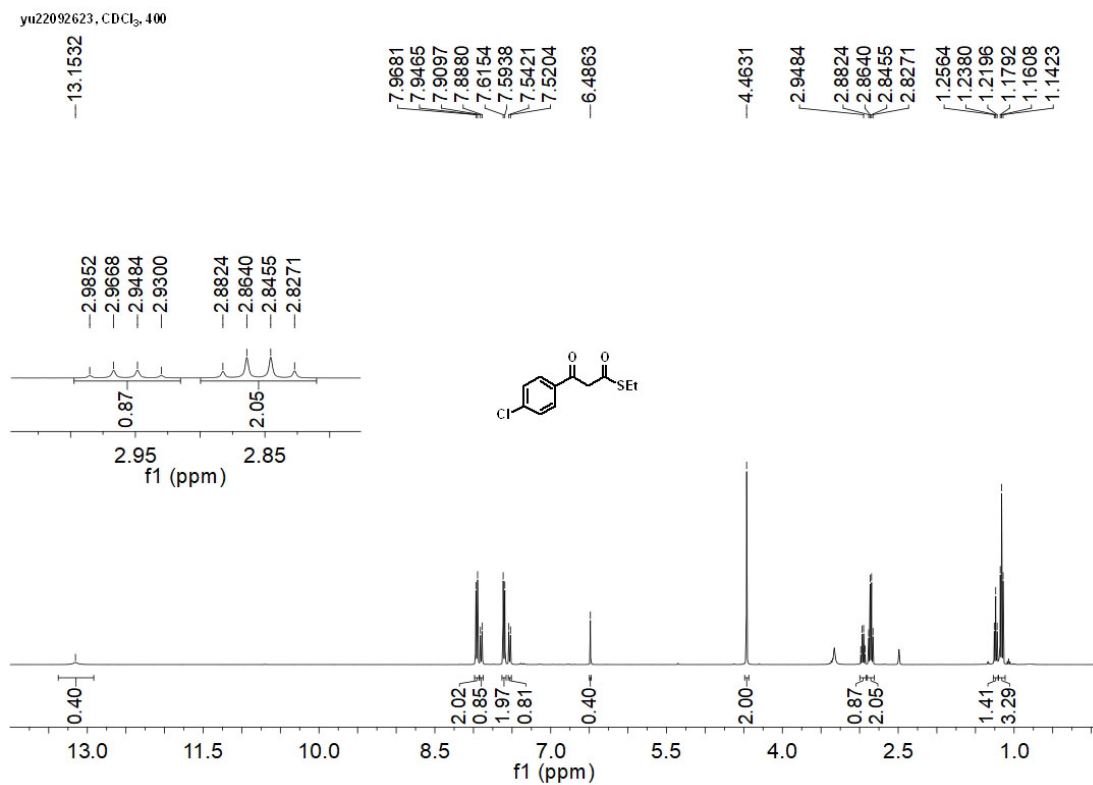
**<sup>13</sup>C NMR of 2e**



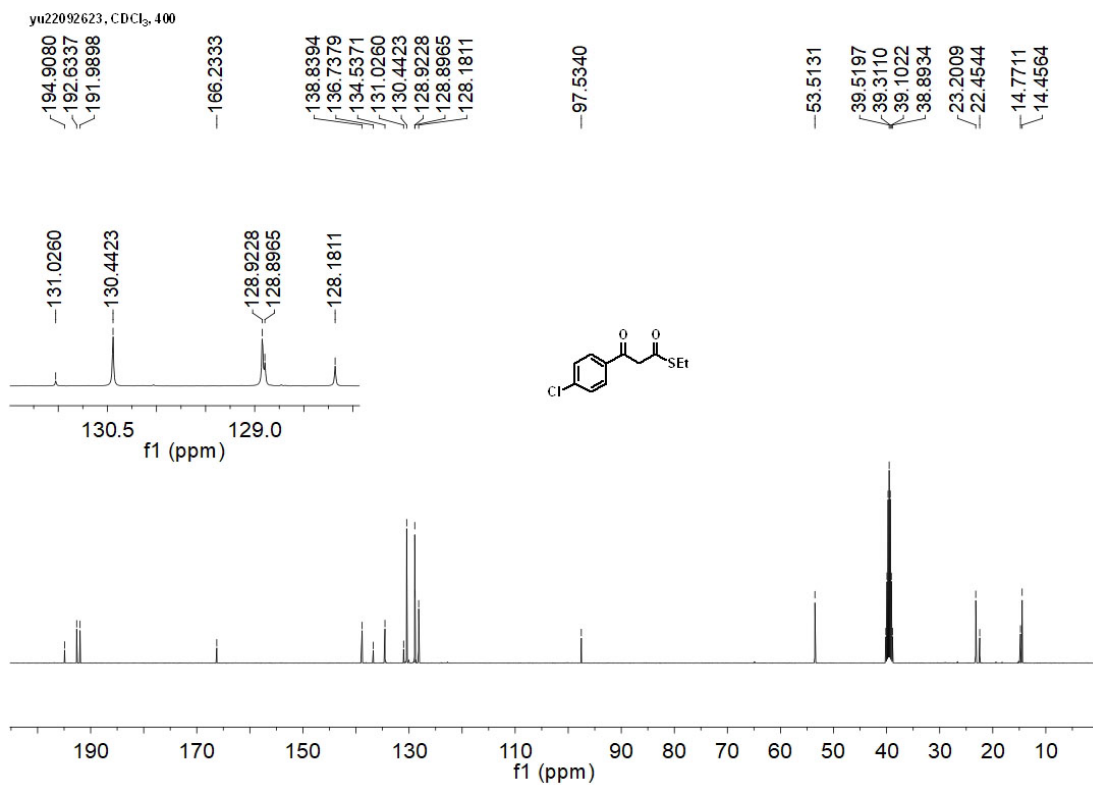
<sup>1</sup>H NMR of **2f**



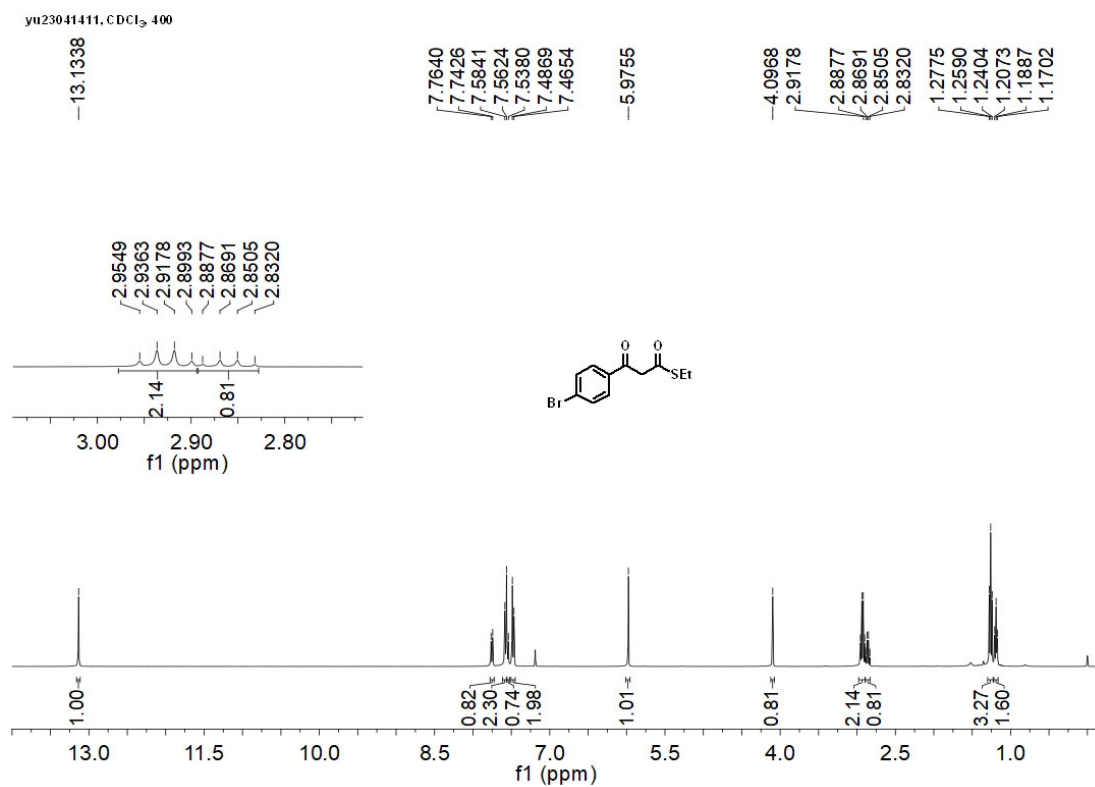
<sup>13</sup>C NMR of **2f**



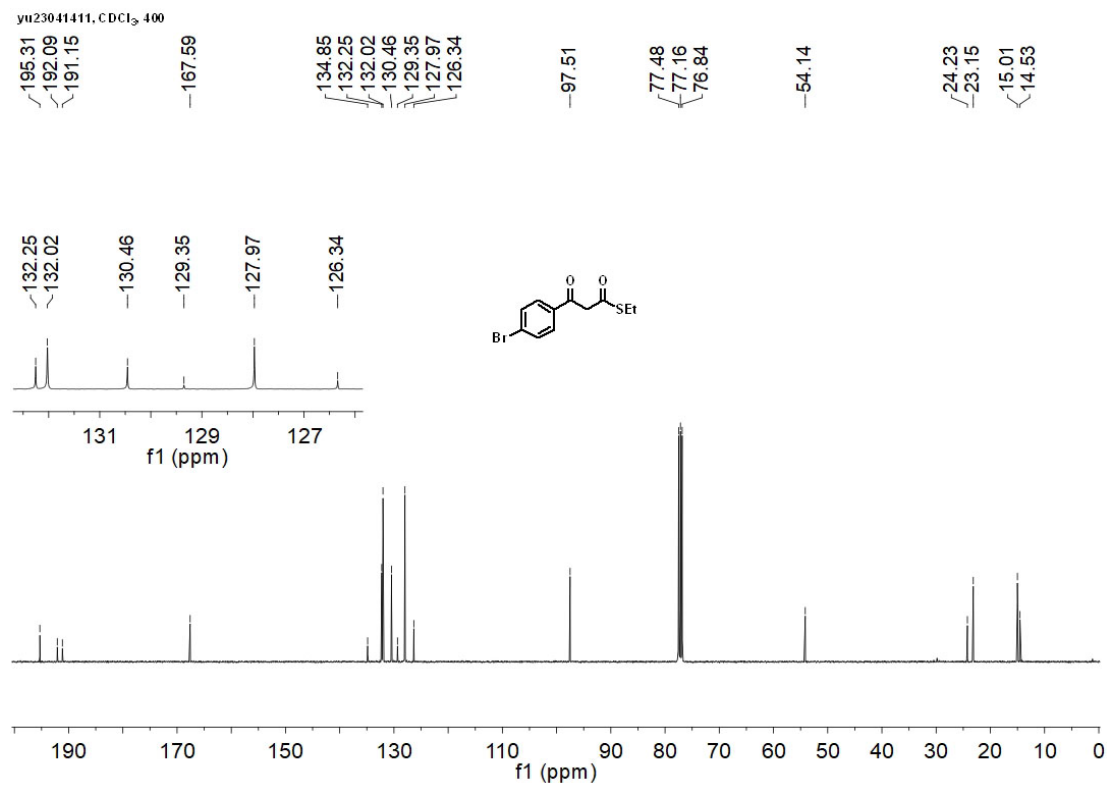
<sup>1</sup>H NMR of **2g**



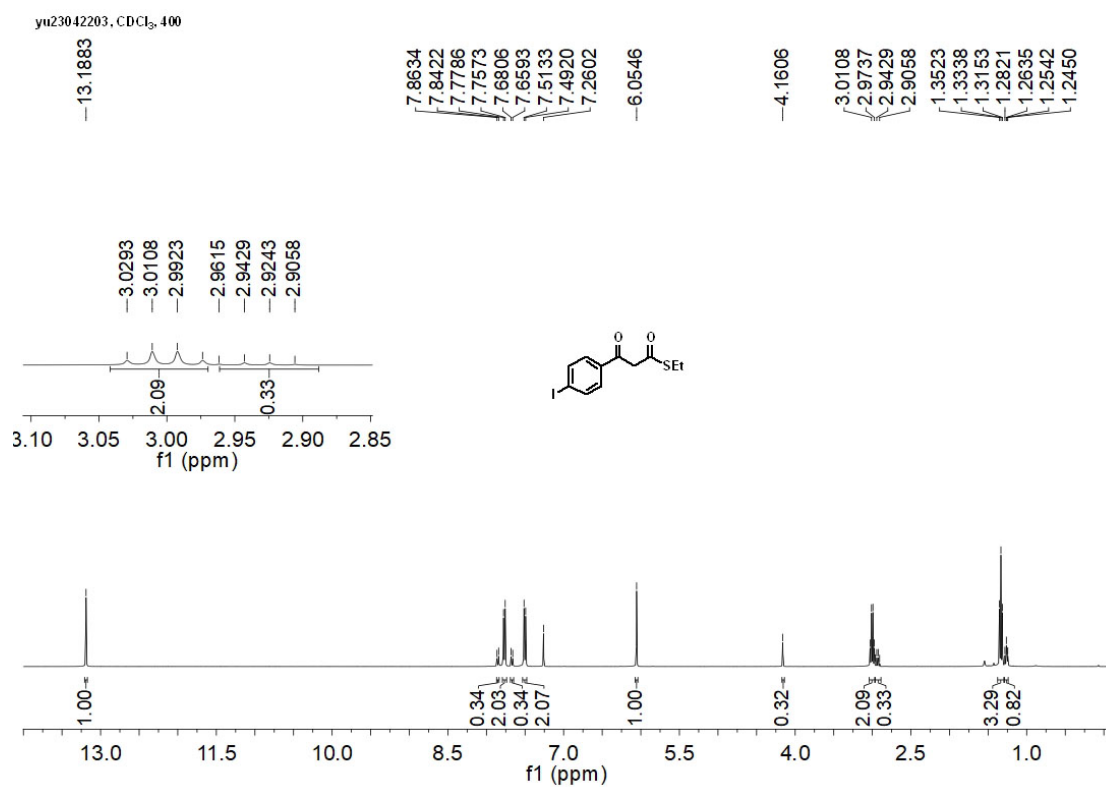
<sup>13</sup>C NMR of **2g**



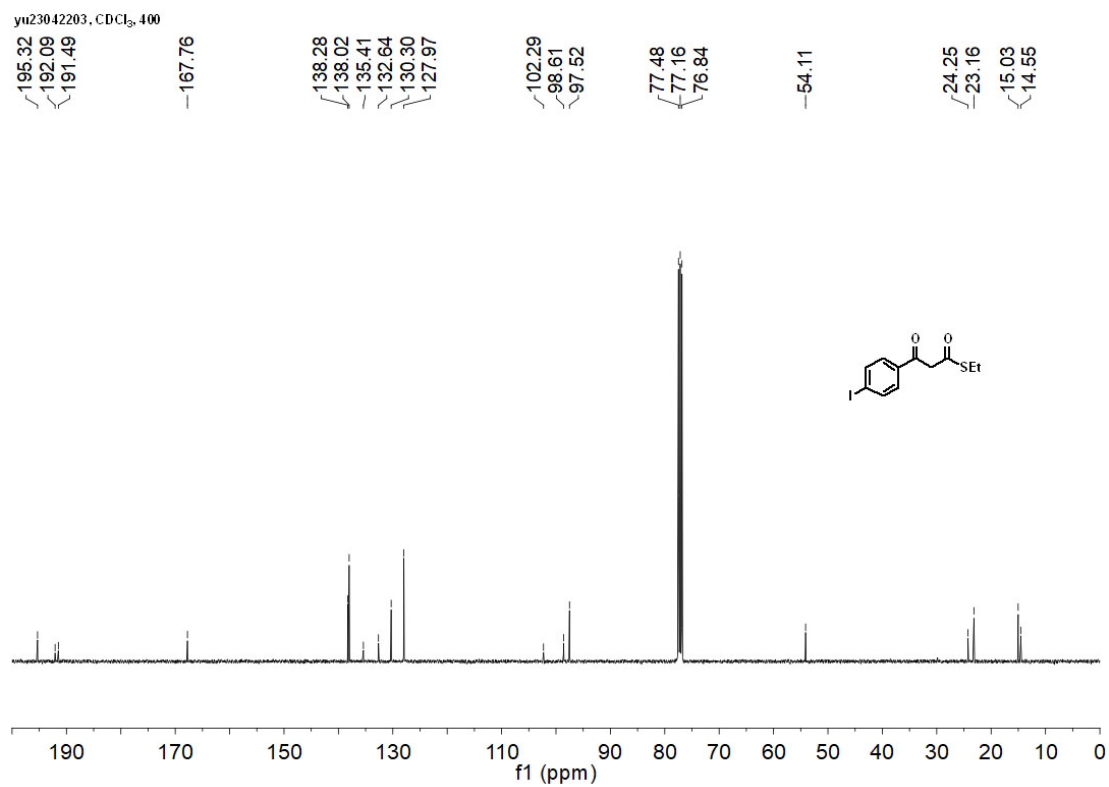
<sup>1</sup>H NMR of **2h**



<sup>13</sup>C NMR of **2h**

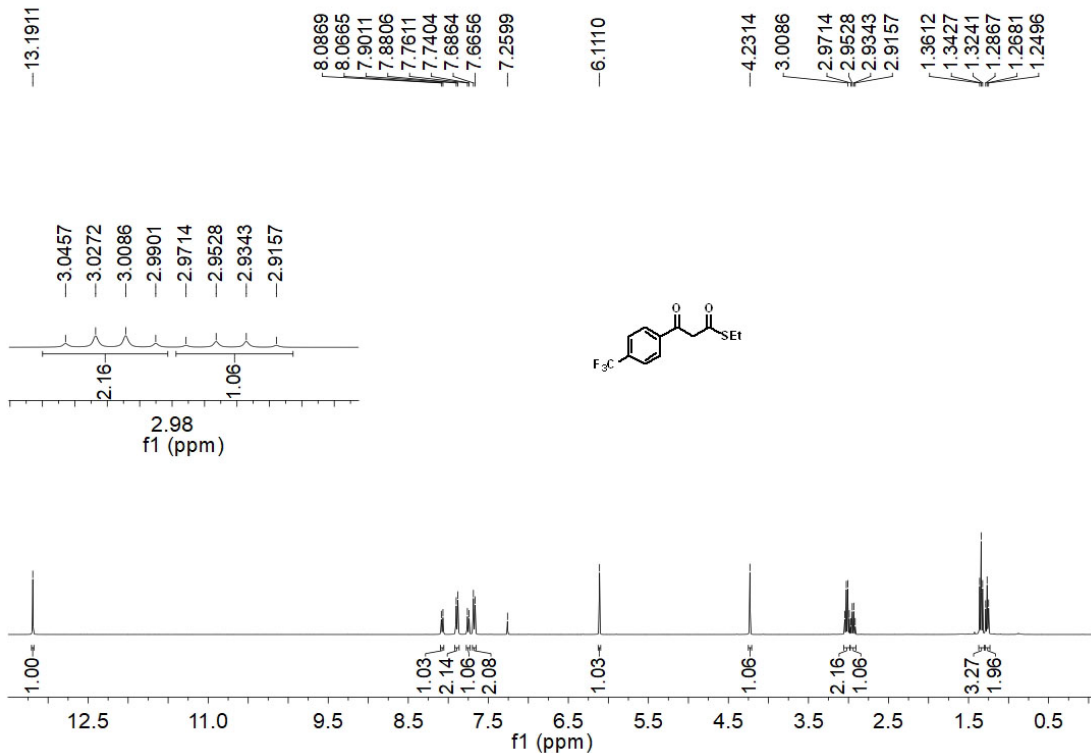


<sup>1</sup>H NMR of **2i**



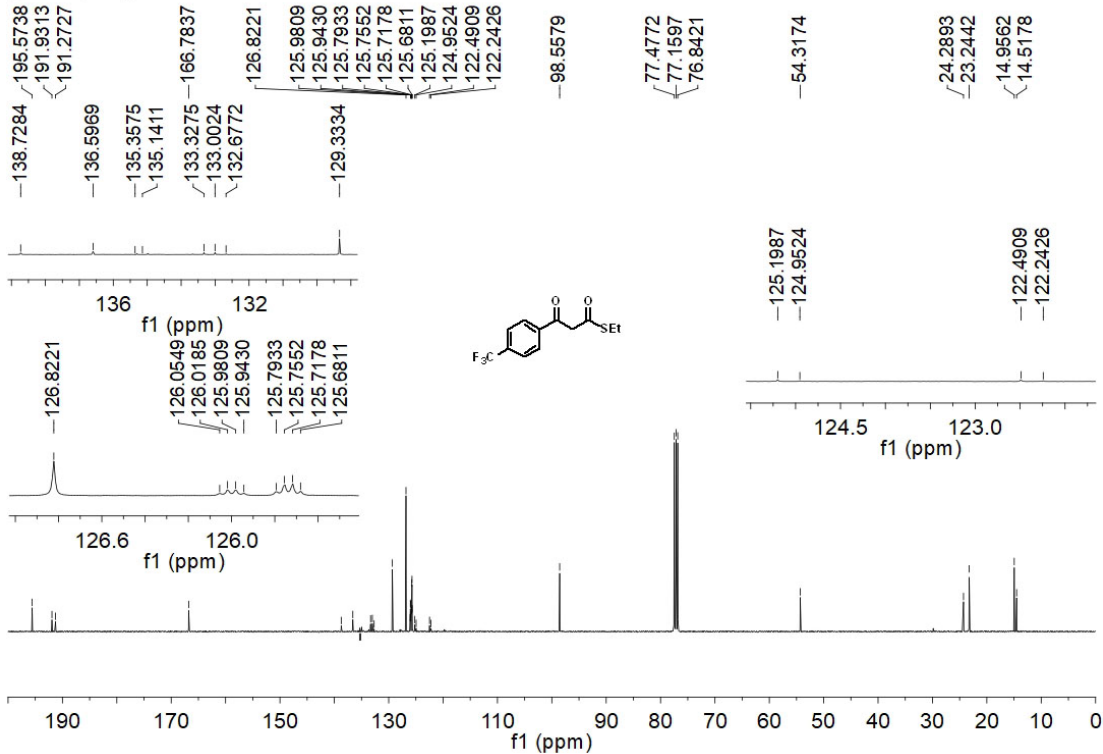
<sup>13</sup>C NMR of **2i**

yu23042201, CDCl<sub>3</sub>, 400

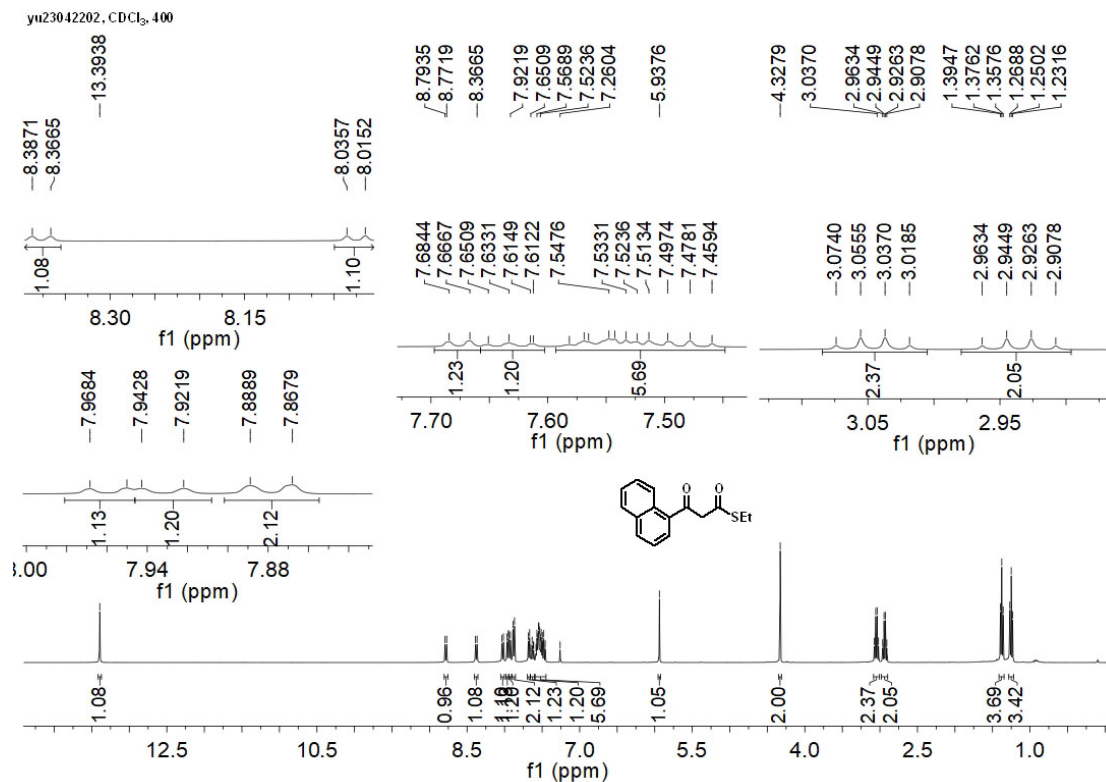


<sup>1</sup>H NMR of **2j**

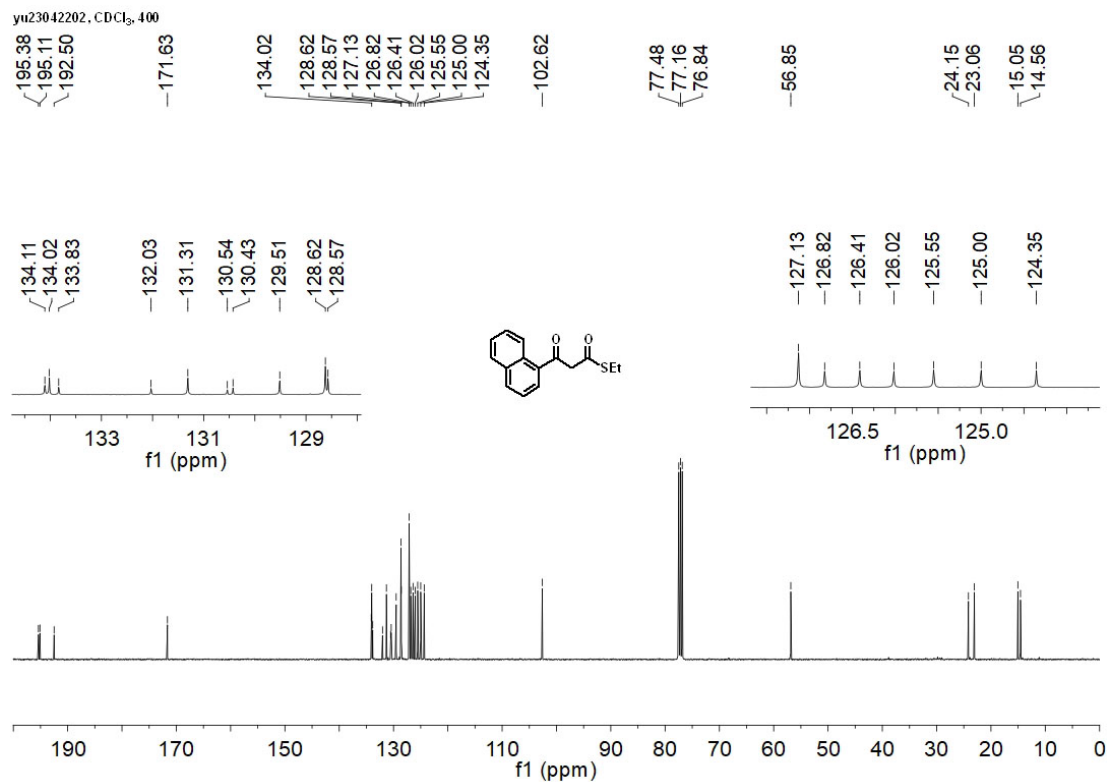
yu23042201, CDCl<sub>3</sub>, 400



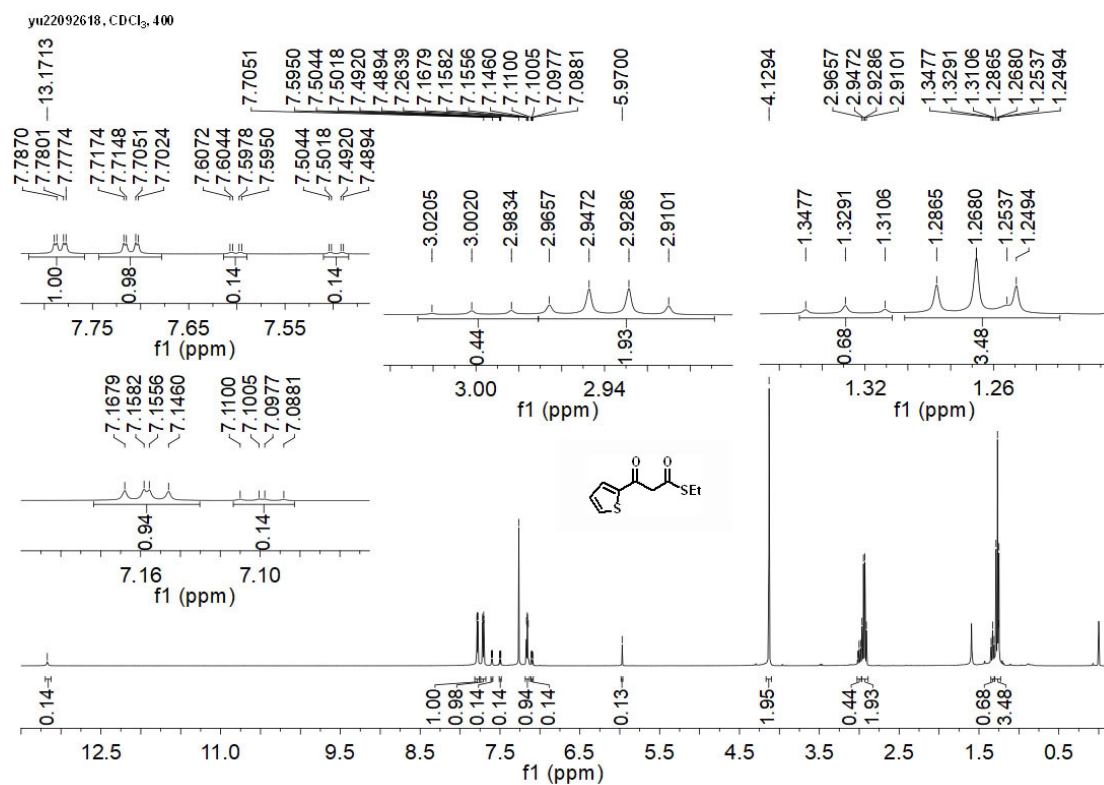
<sup>13</sup>C NMR of **2j**



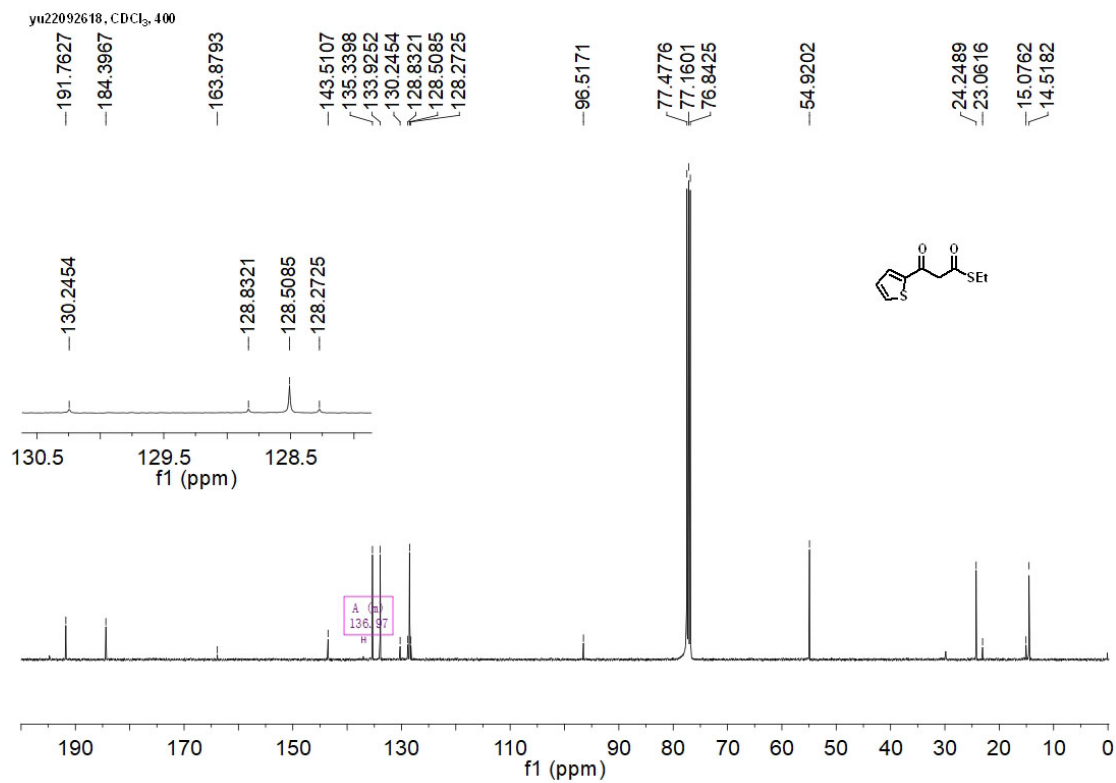
<sup>1</sup>H NMR of **2k**



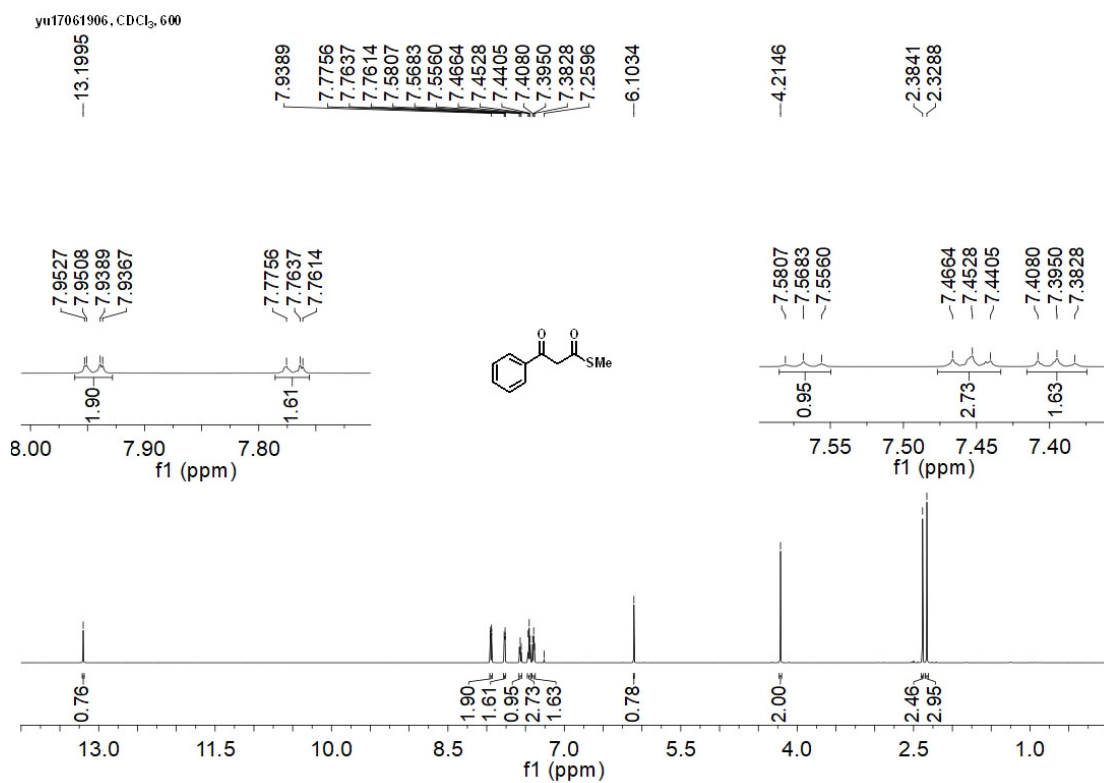
<sup>13</sup>C NMR of **2k**



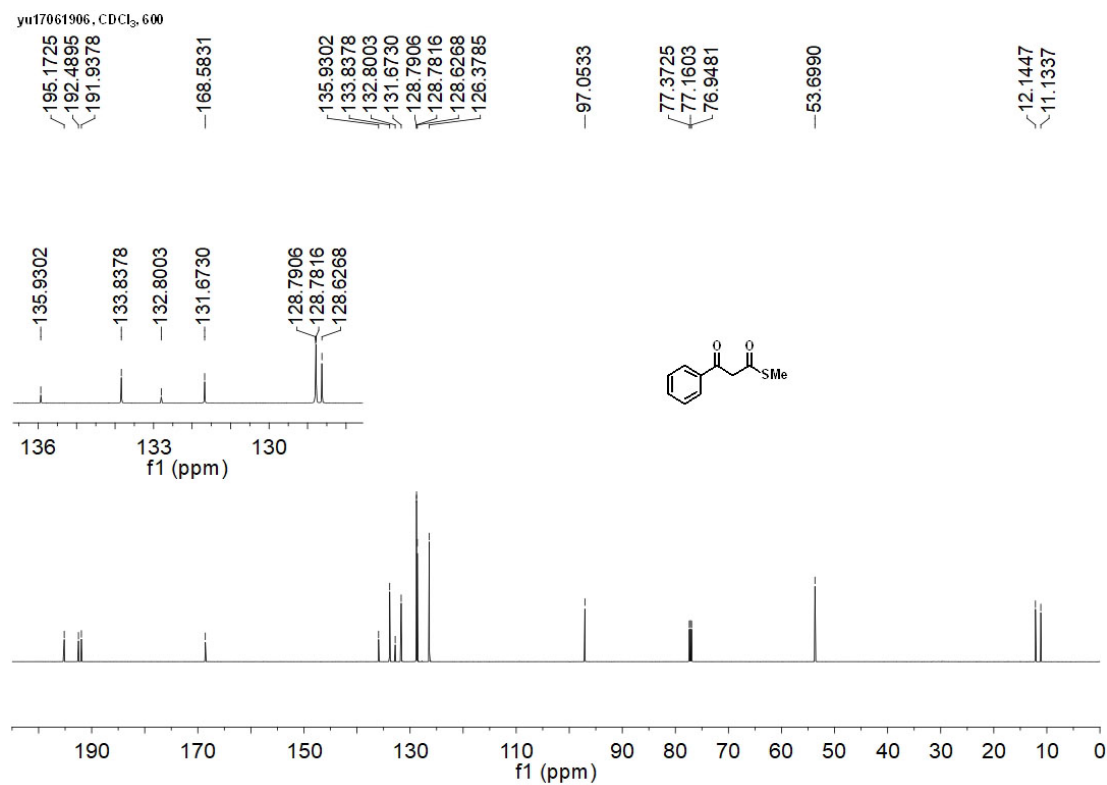
<sup>1</sup>H NMR of **2I**



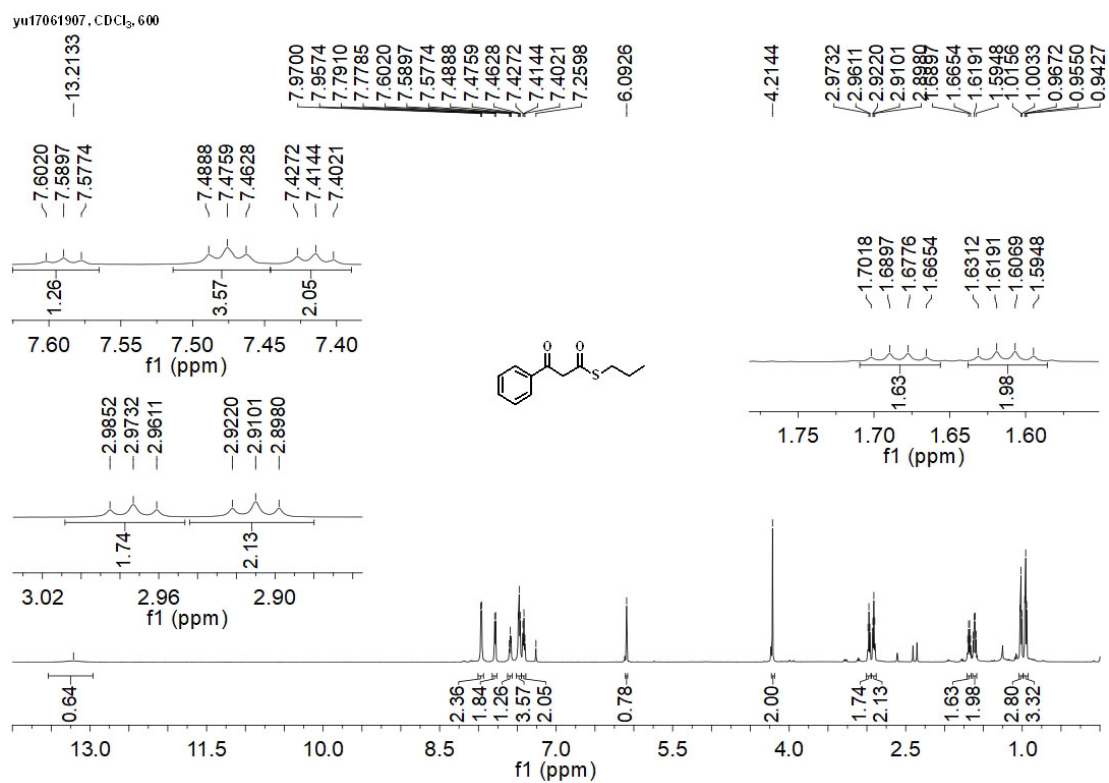
<sup>13</sup>C NMR of **2I**



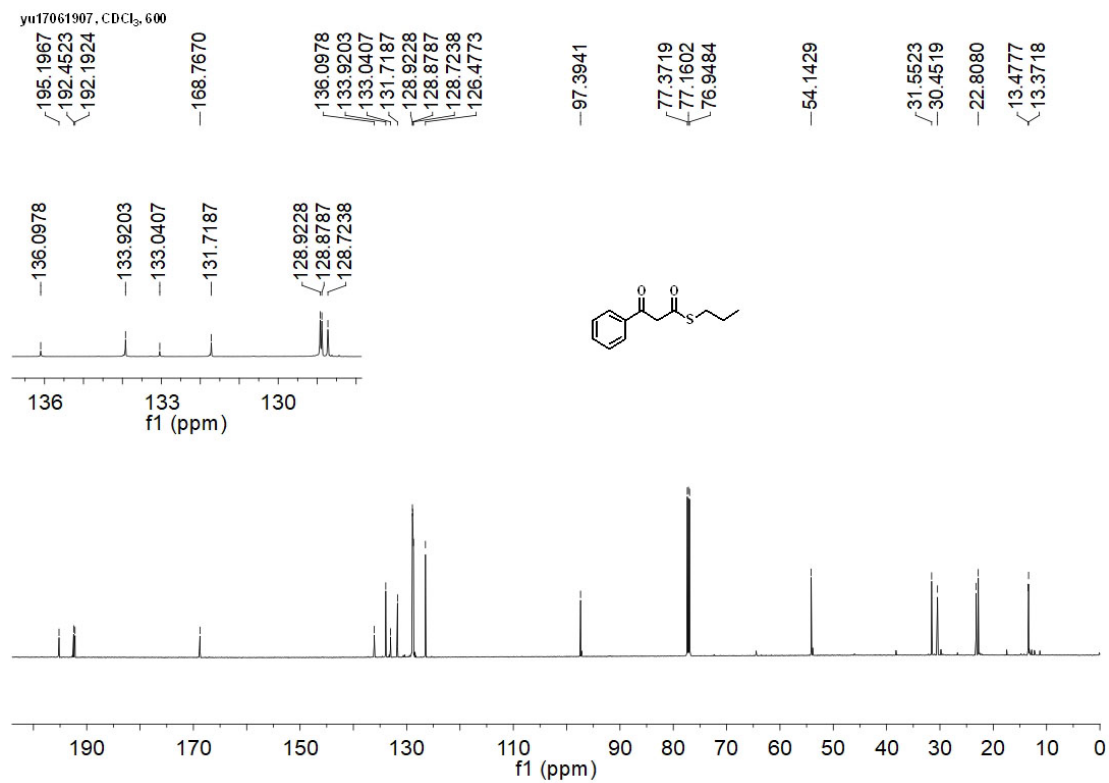
<sup>1</sup>H NMR of **2m**



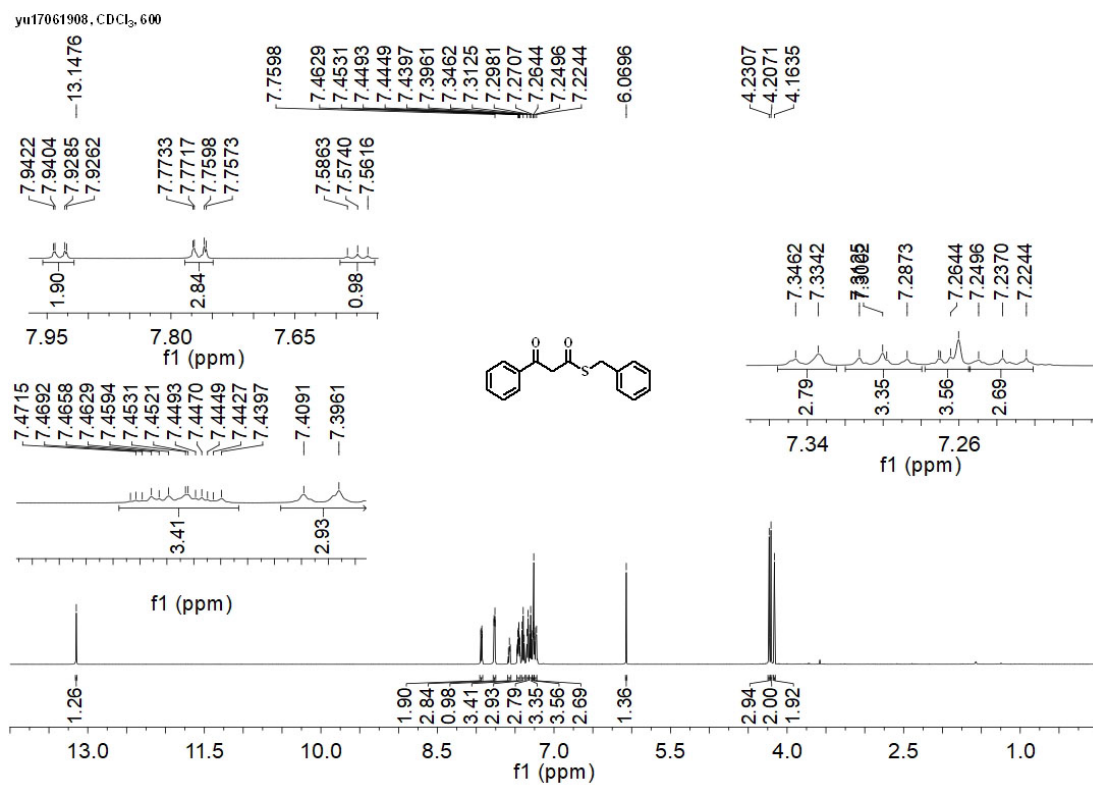
<sup>13</sup>C NMR of **2m**



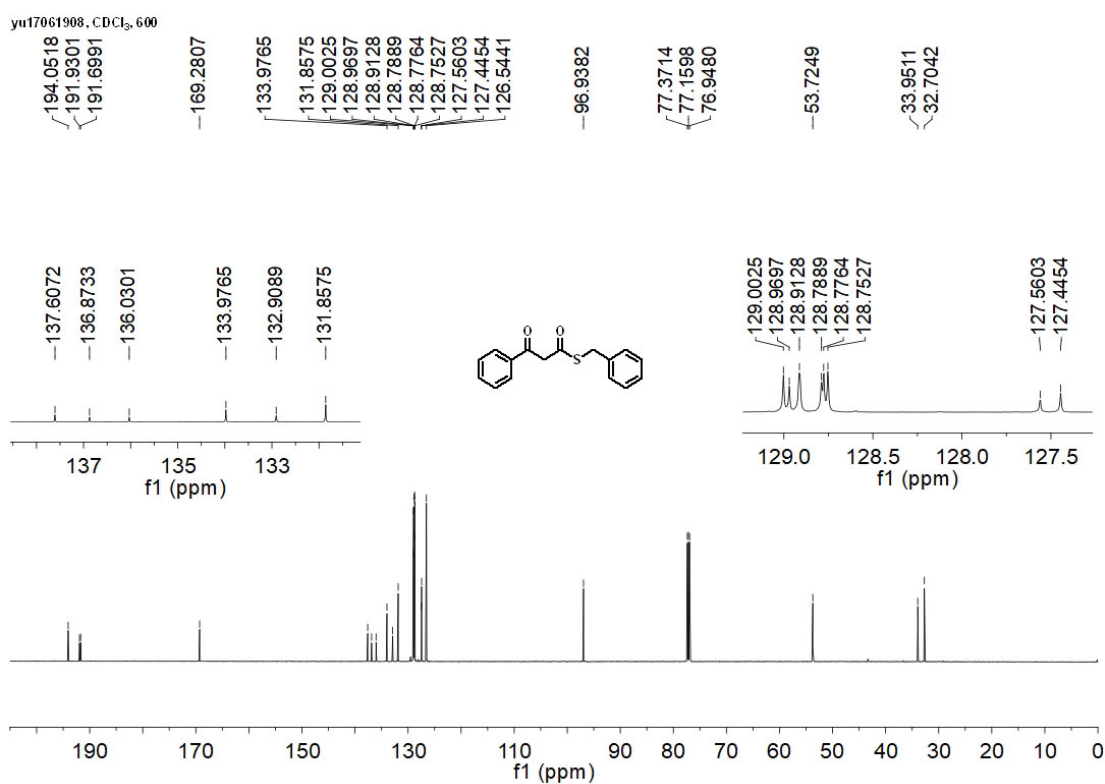
<sup>1</sup>H NMR of **2n**



<sup>13</sup>C NMR of **2n**

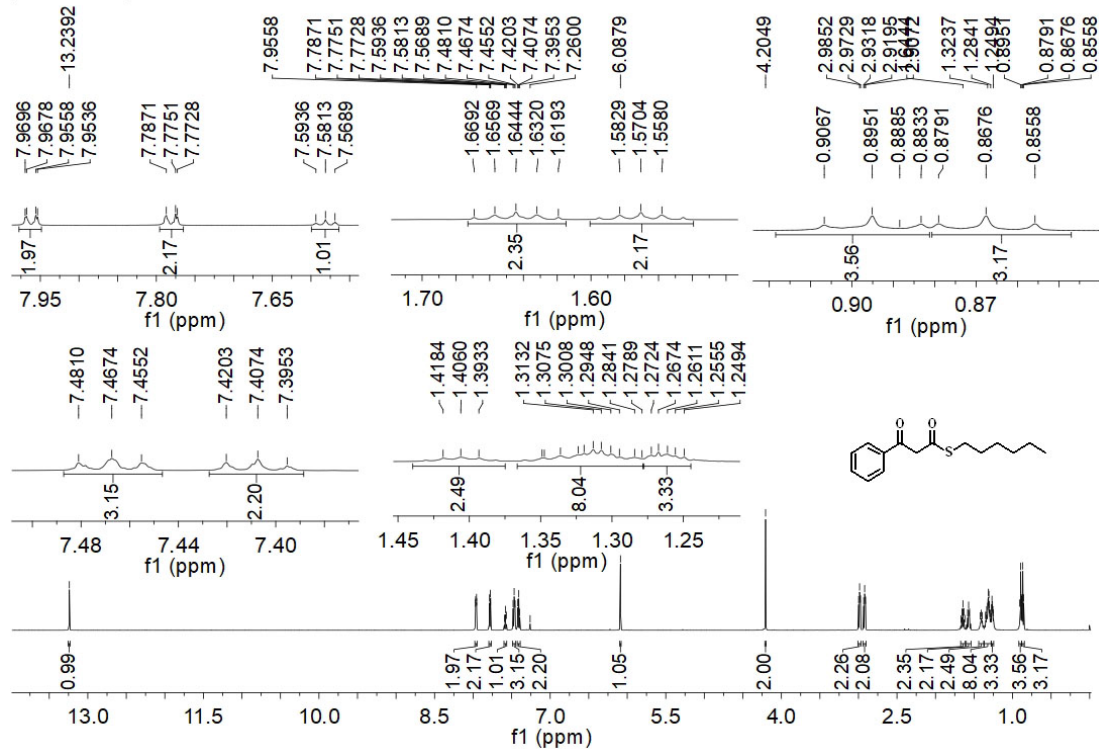


<sup>1</sup>H NMR of **2o**



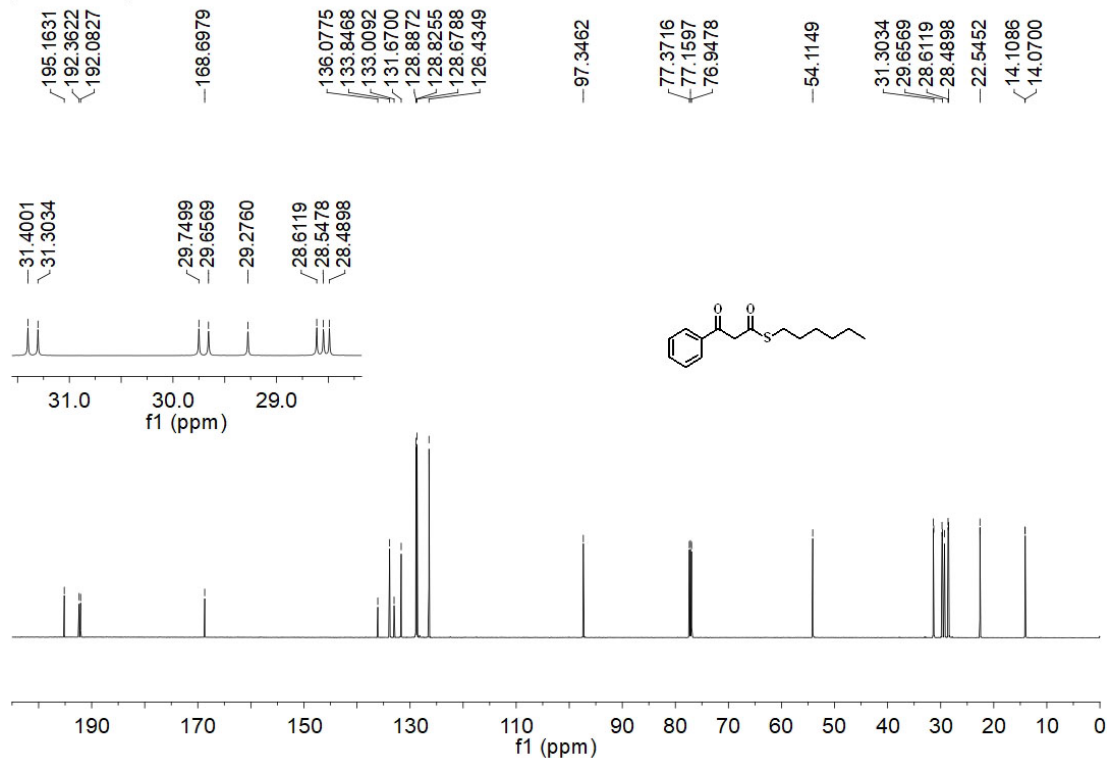
<sup>13</sup>C NMR of **2o**

yu17061905, CDCl<sub>3</sub>, 600



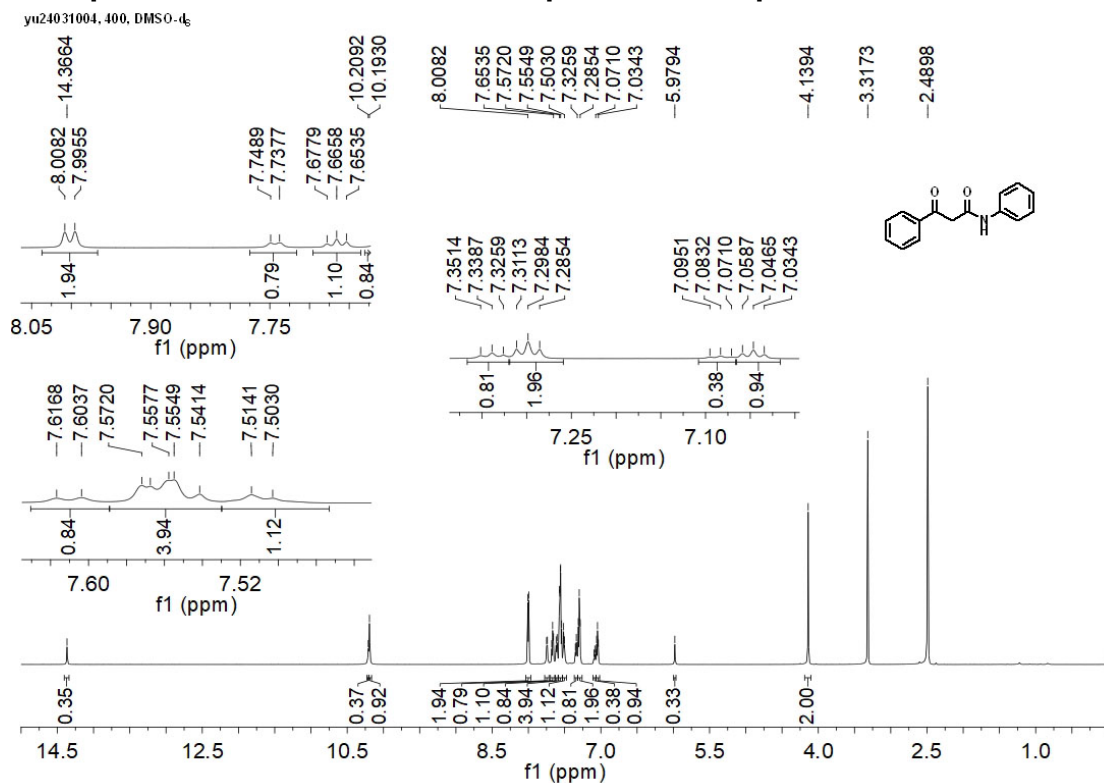
**<sup>1</sup>H NMR of 2p**

yu17061905, CDCl<sub>3</sub>, 600

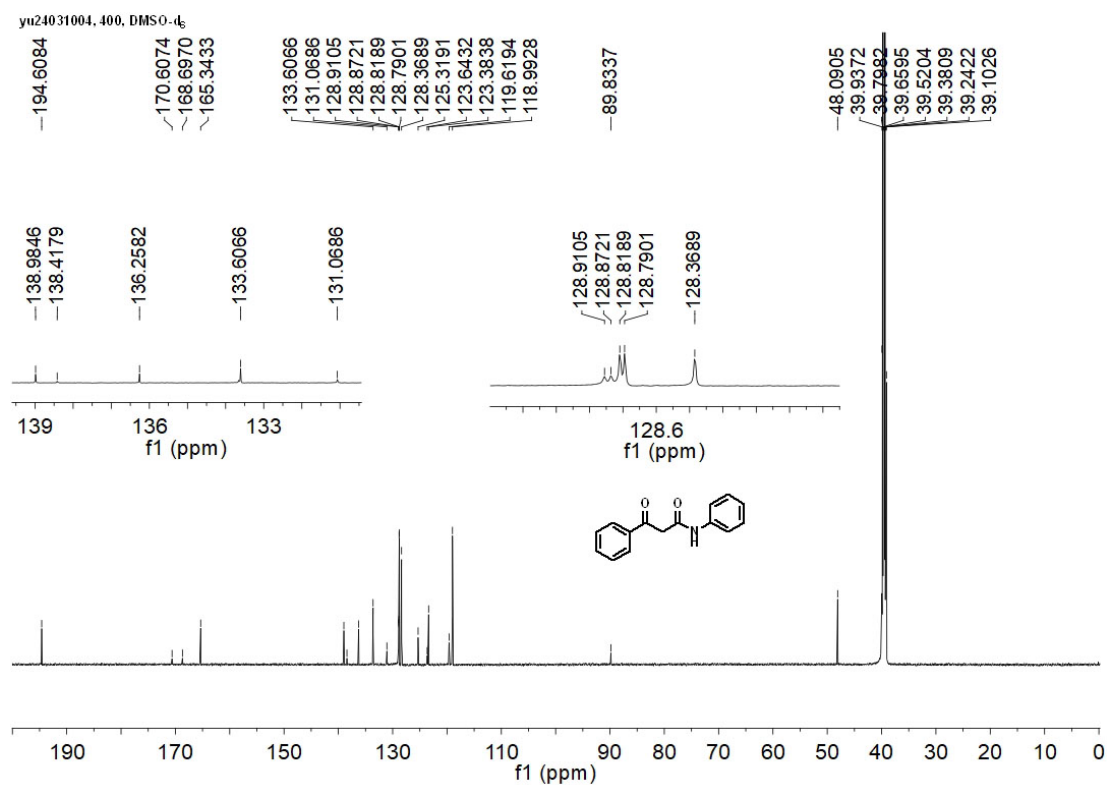


**<sup>13</sup>C NMR of 2p**

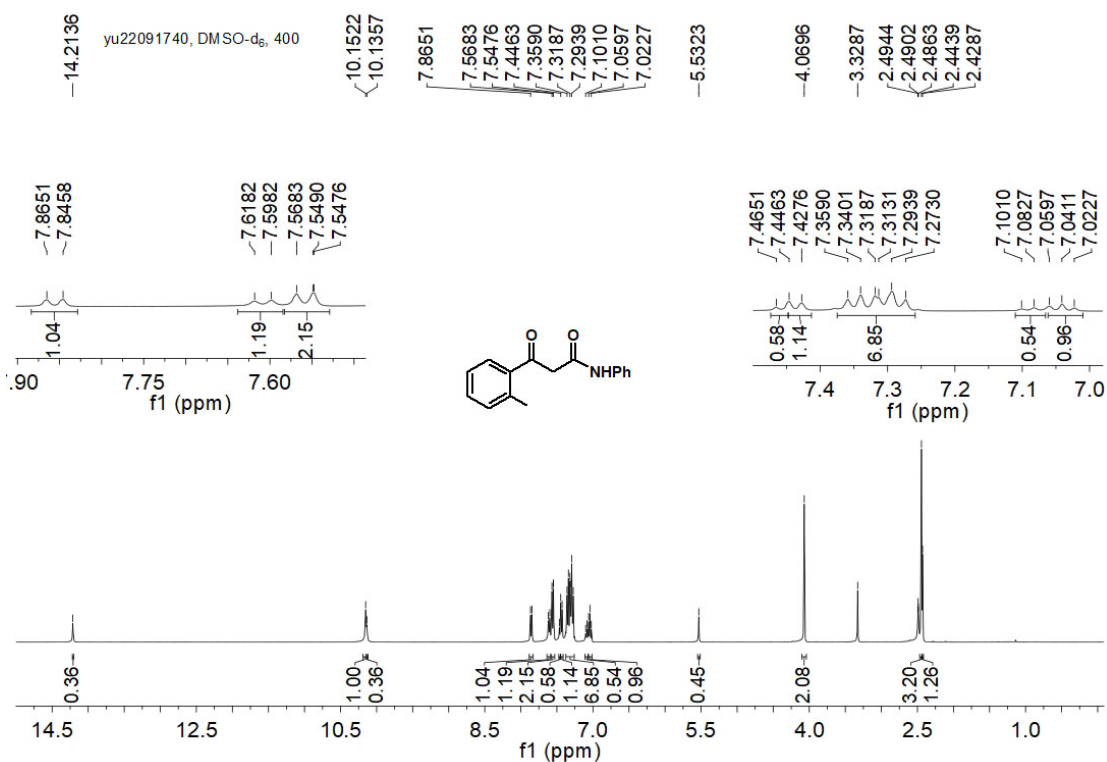
## 5. Copies of $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compound 3



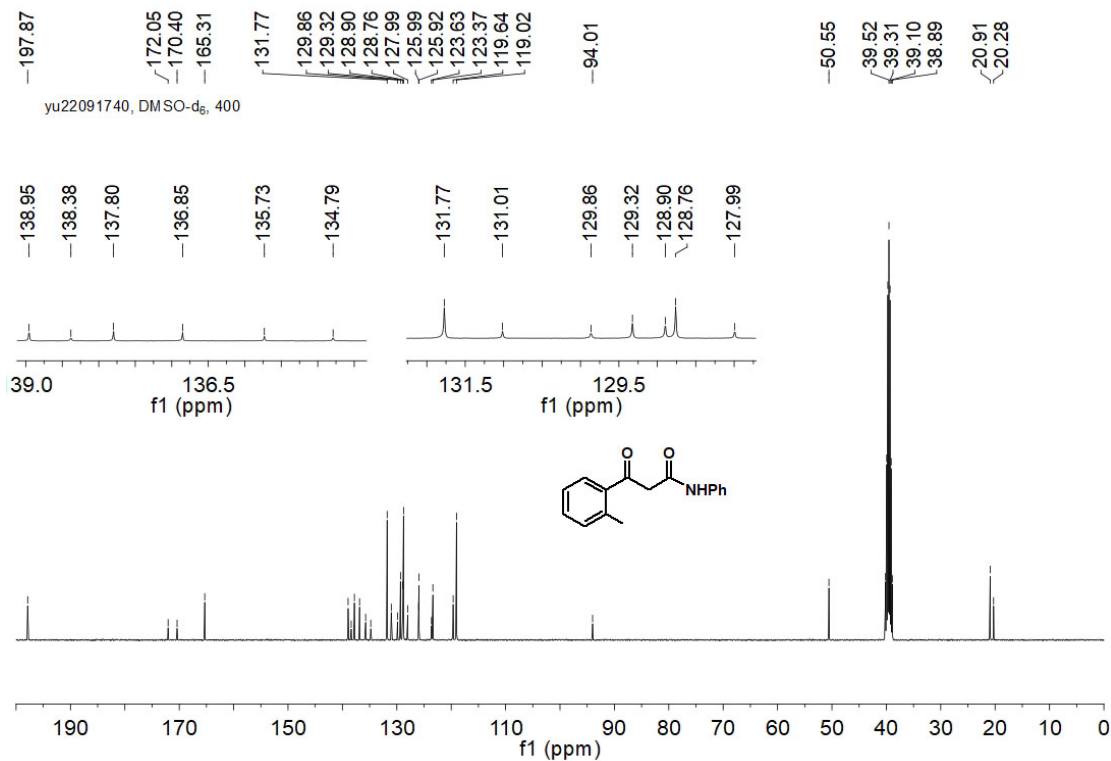
$^1\text{H}$  NMR of 3a



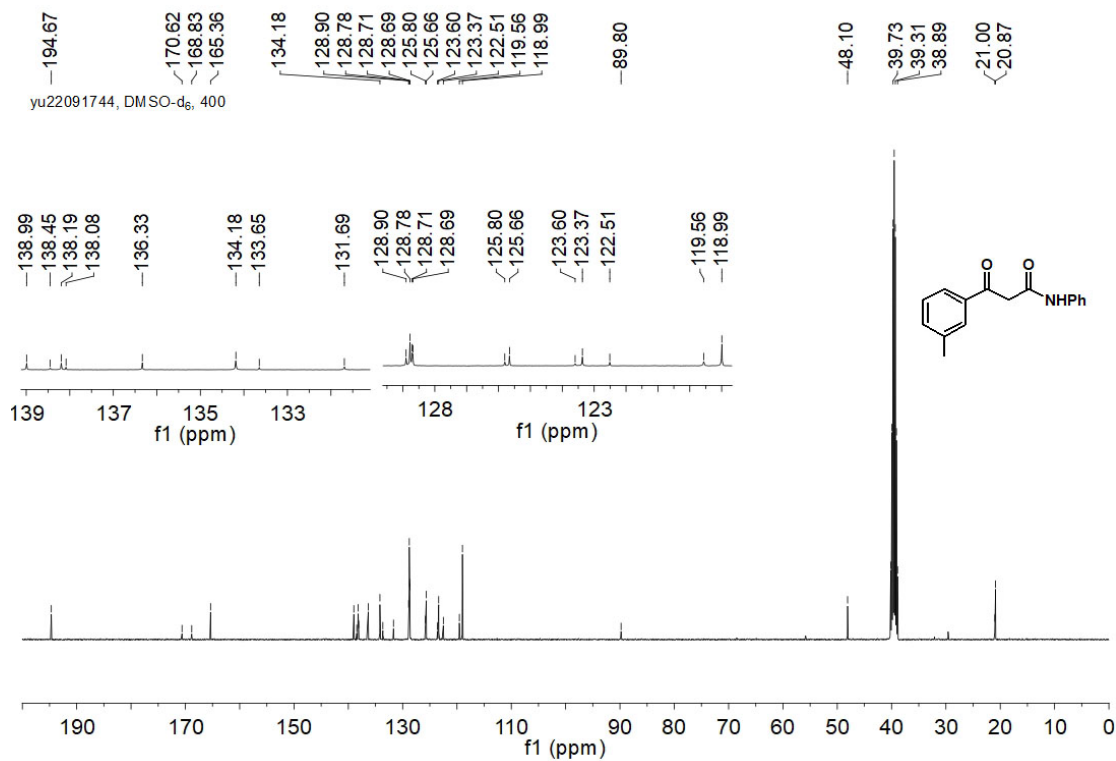
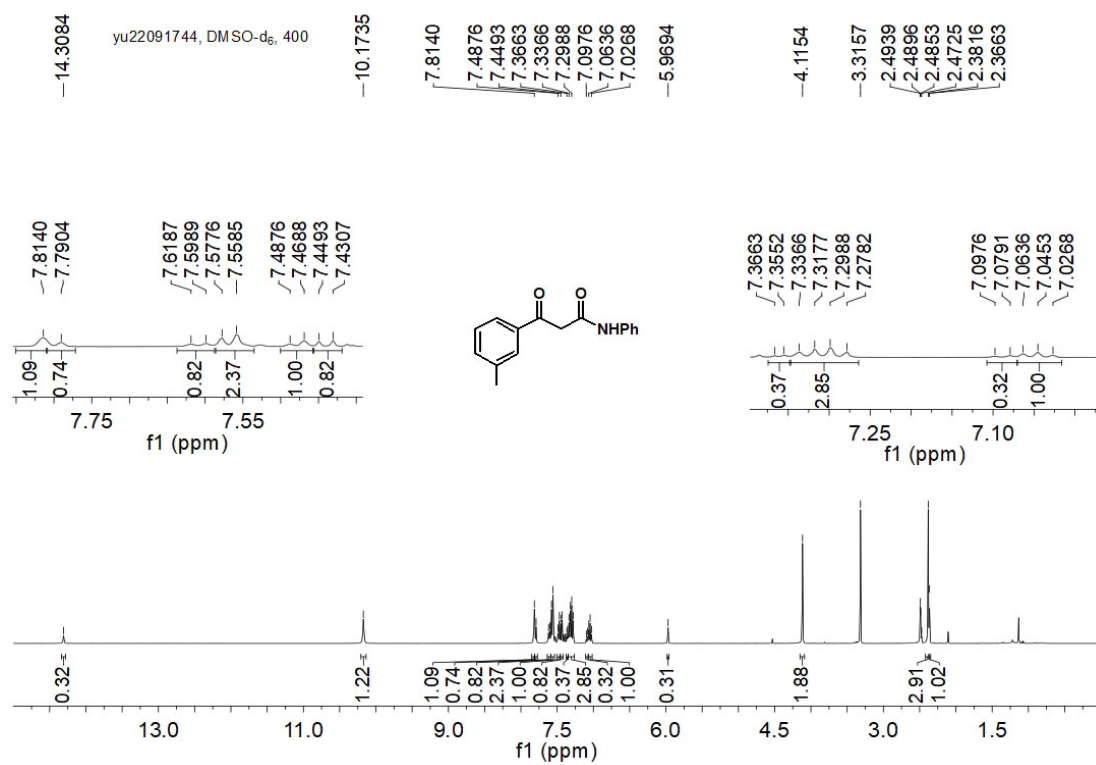
$^{13}\text{C}$  NMR of 3a

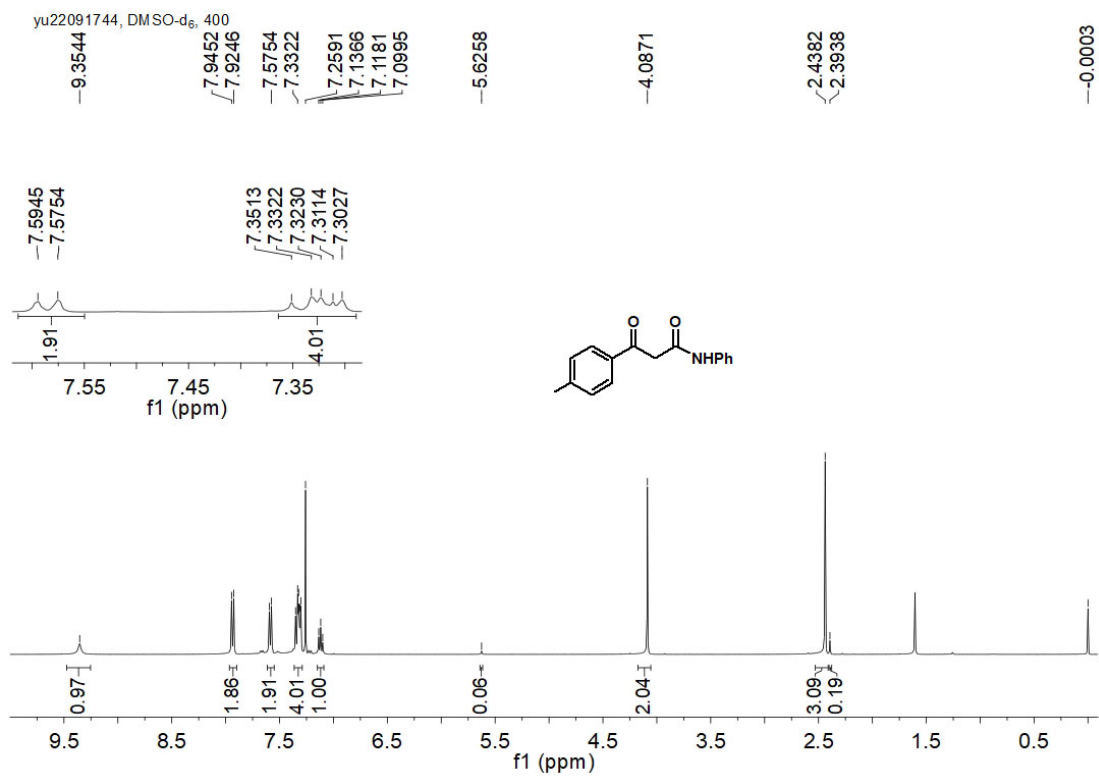


<sup>1</sup>H NMR of **3b**

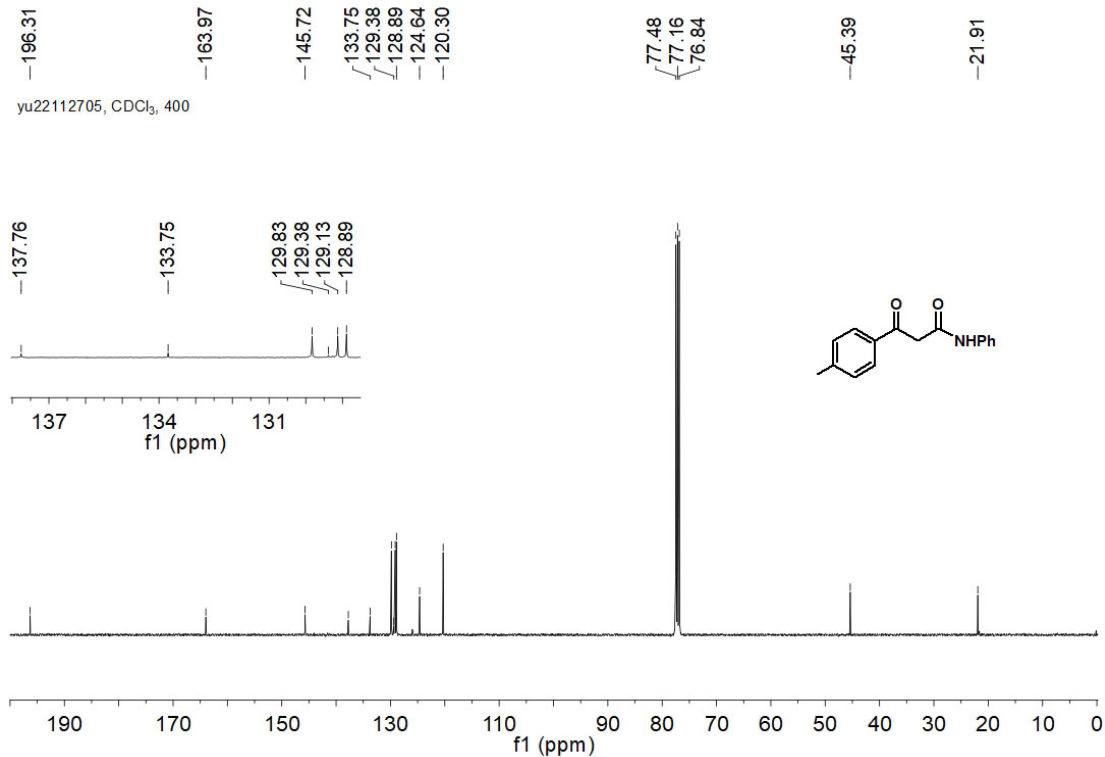


<sup>13</sup>C NMR of **3b**

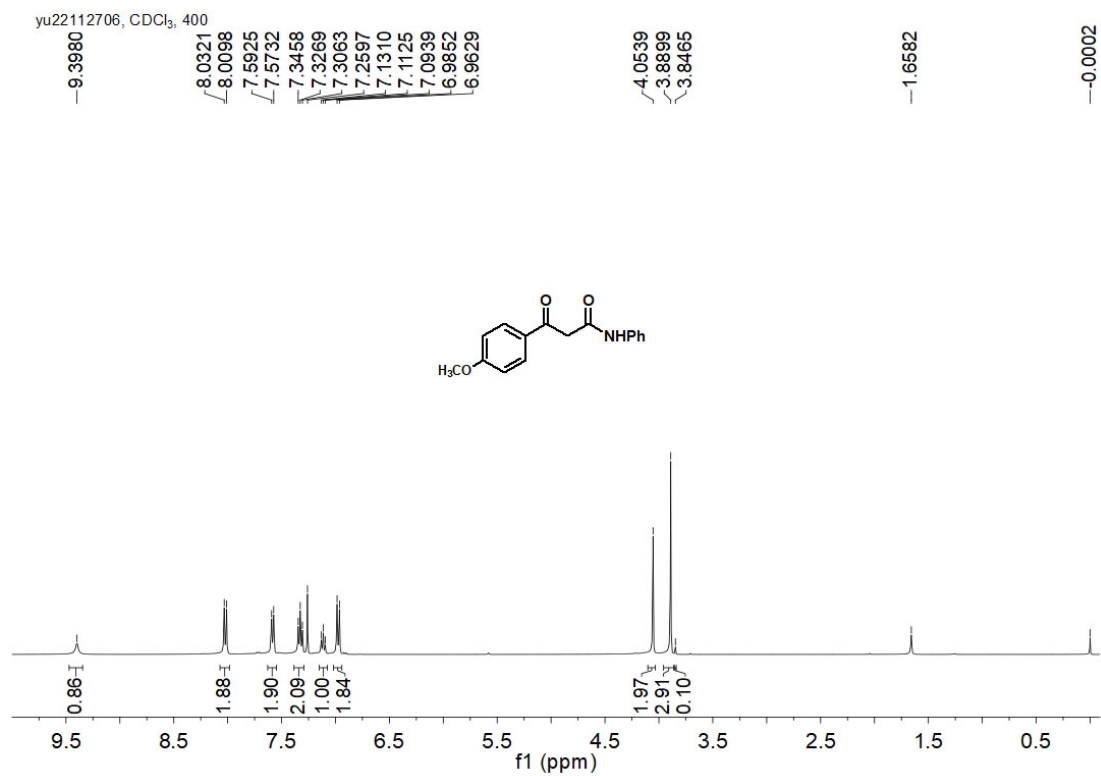




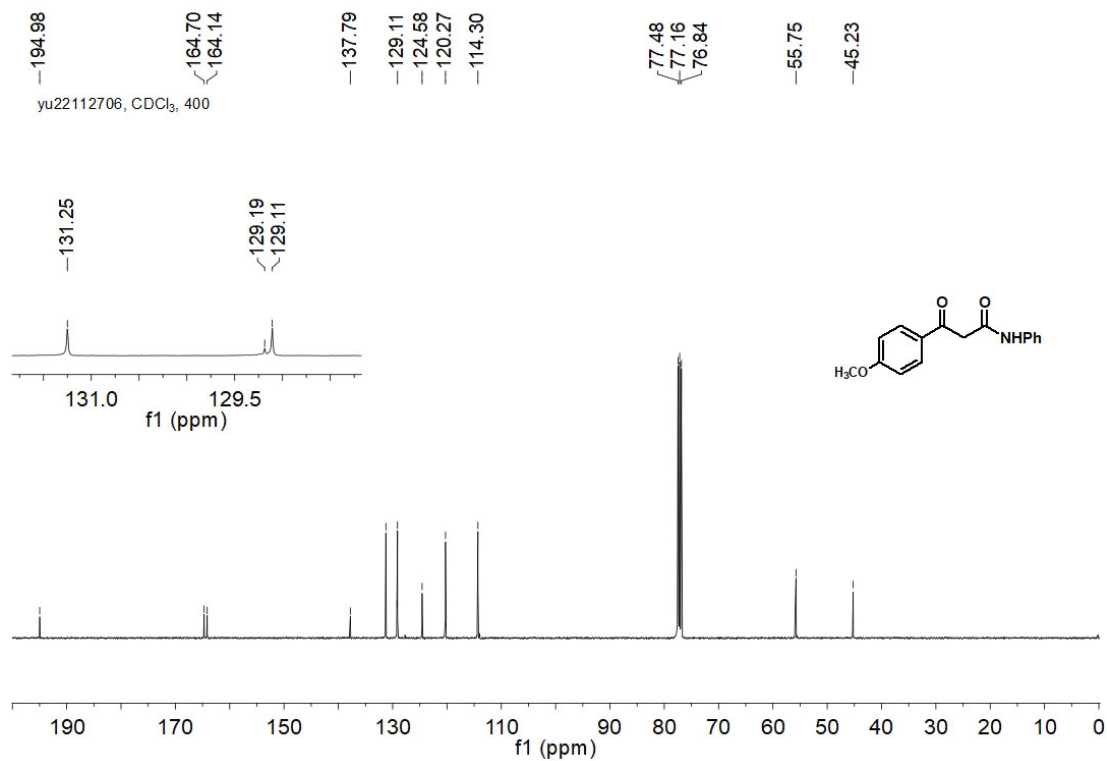
<sup>1</sup>H NMR of **3d**



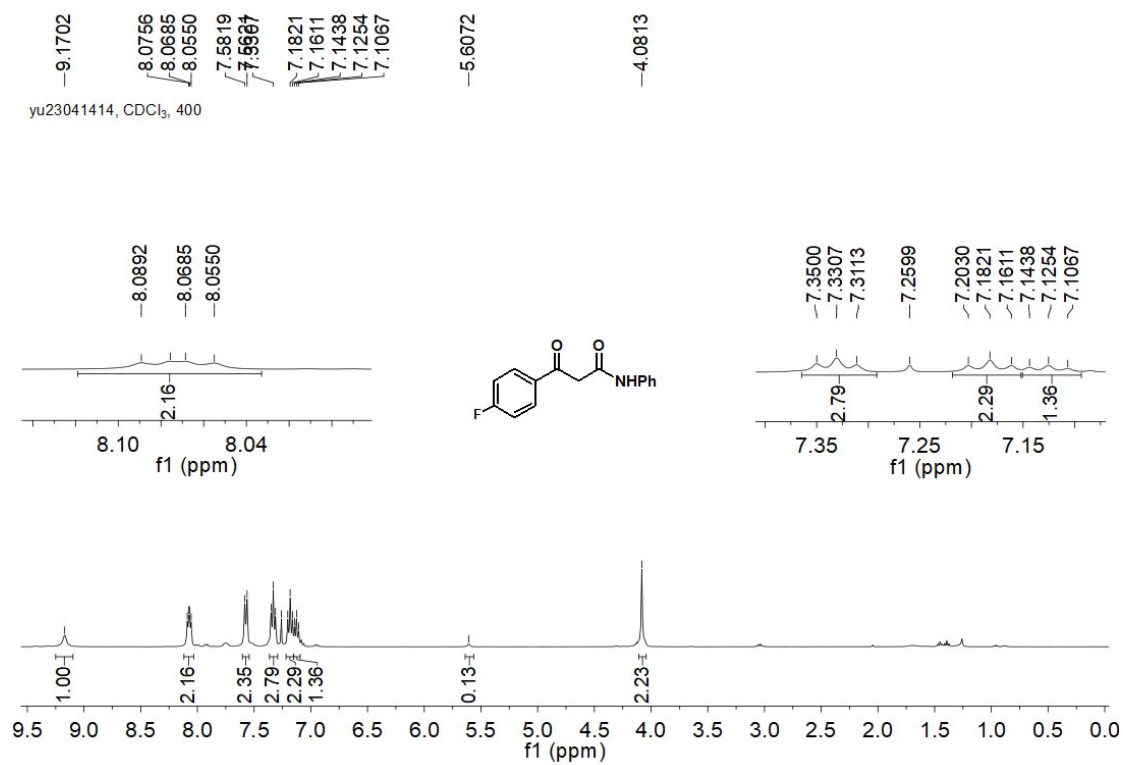
<sup>13</sup>C NMR of **3d**



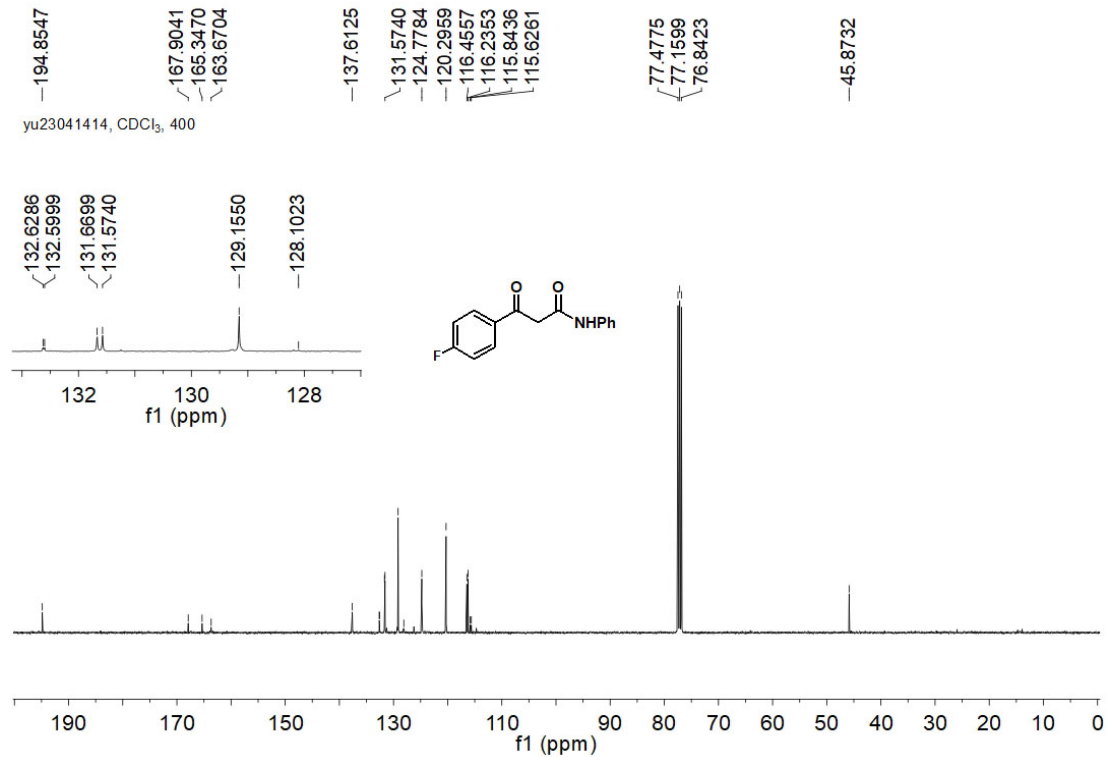
<sup>1</sup>H NMR of **3e**



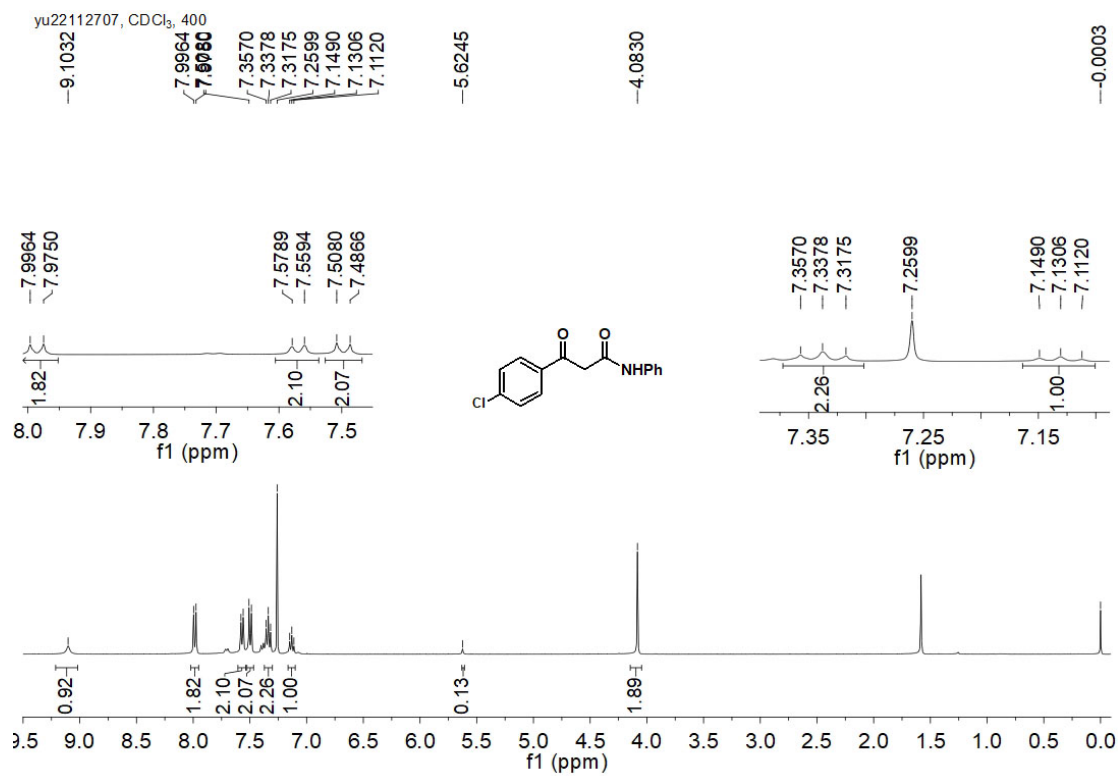
<sup>13</sup>C NMR of **3e**



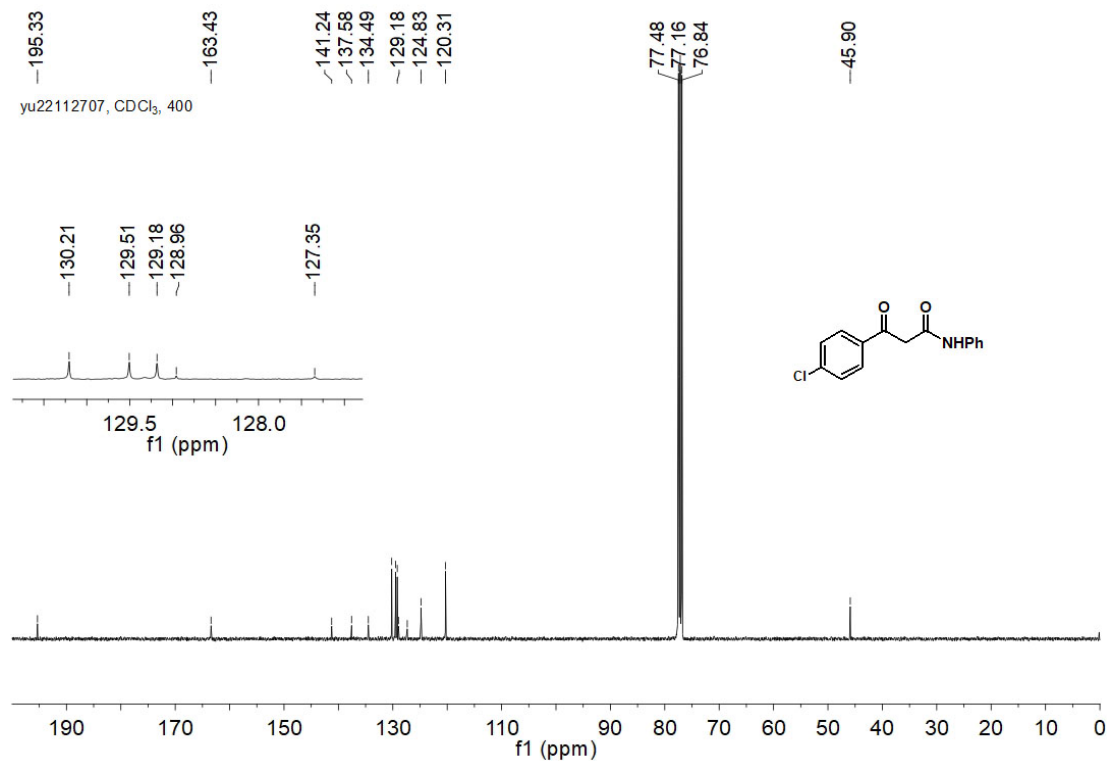
<sup>1</sup>H NMR of **3f**



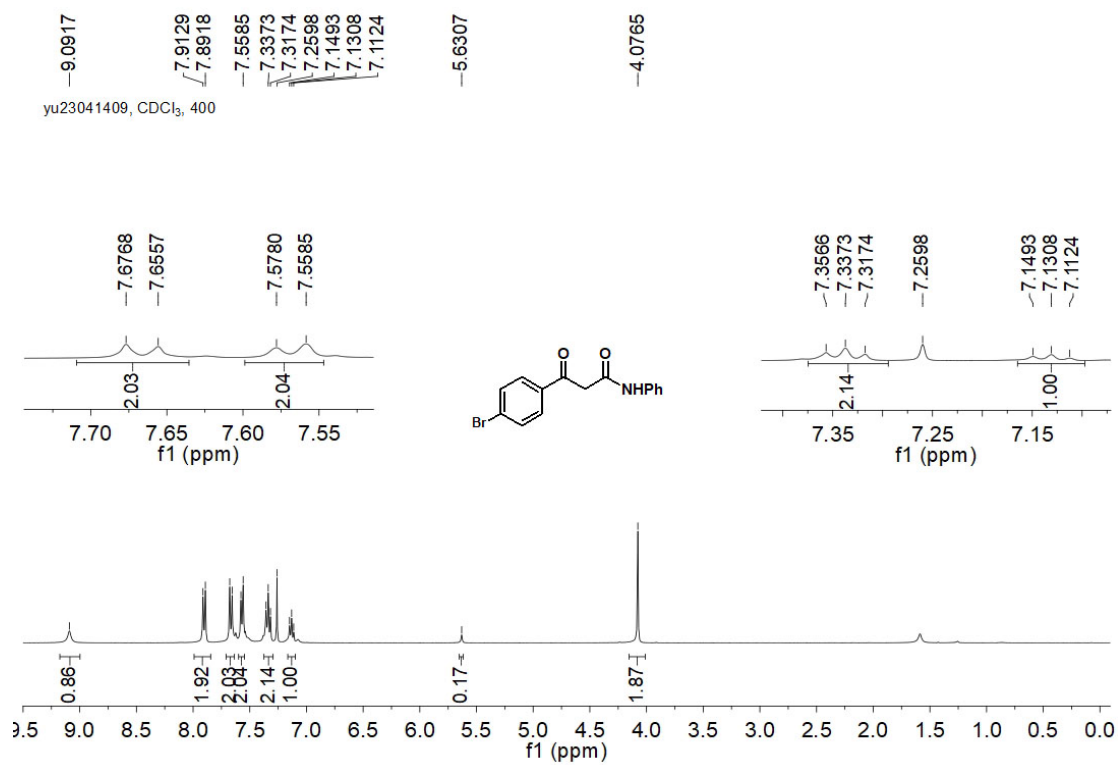
<sup>13</sup>C NMR of **3f**



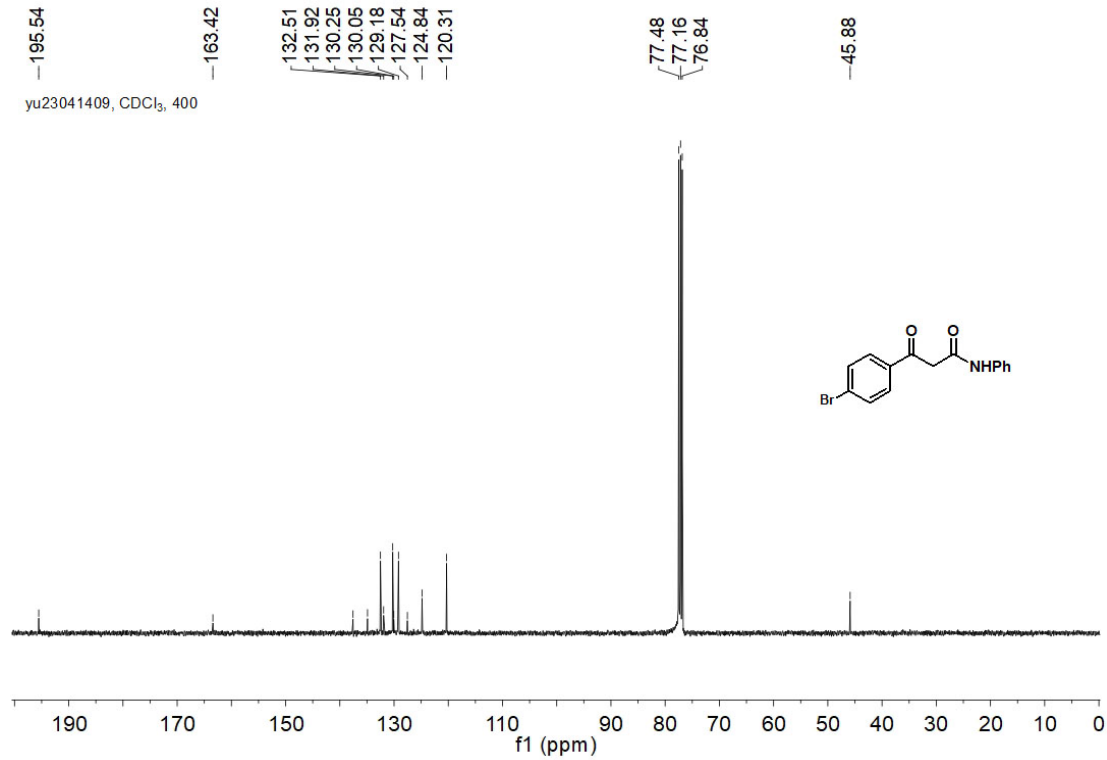
<sup>1</sup>H NMR of **3g**



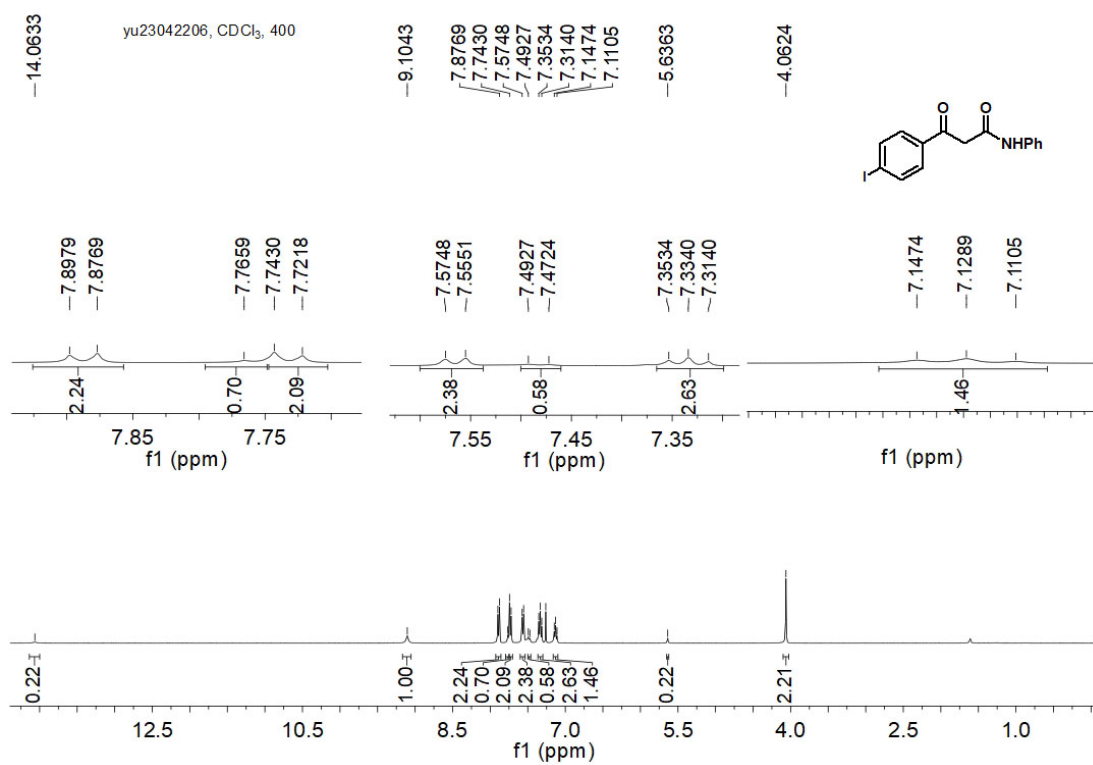
<sup>13</sup>C NMR of **3g**



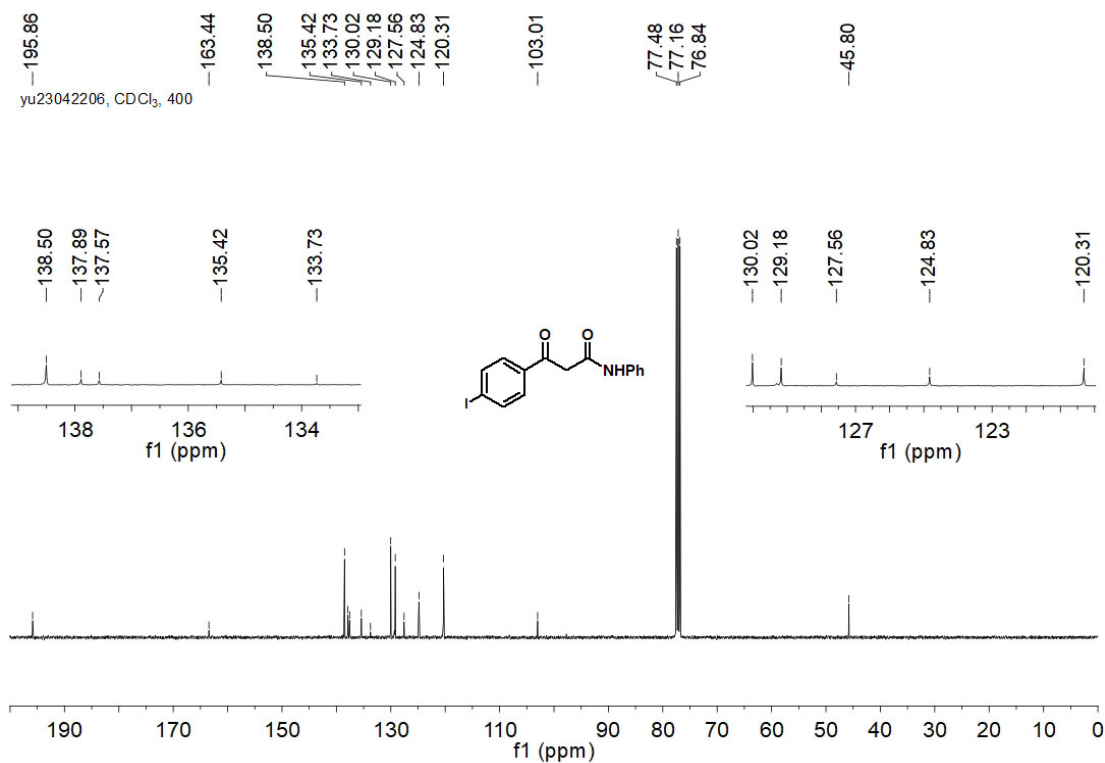
<sup>1</sup>H NMR of **3h**



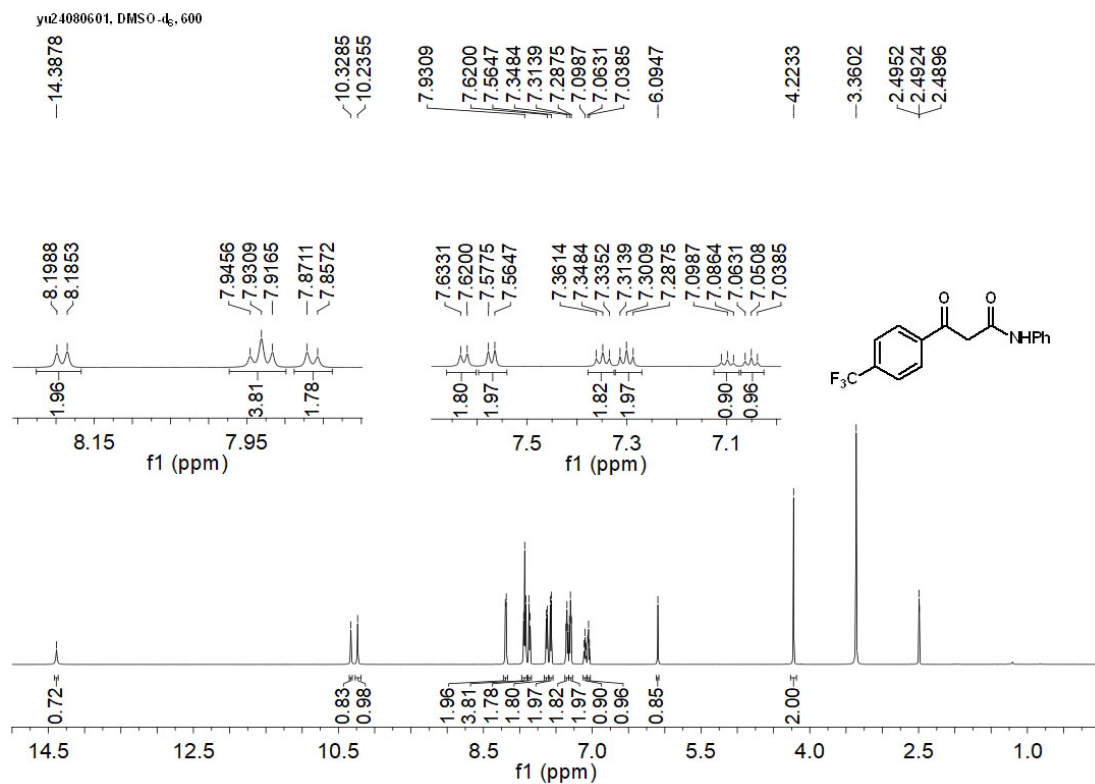
<sup>13</sup>C NMR of **3h**



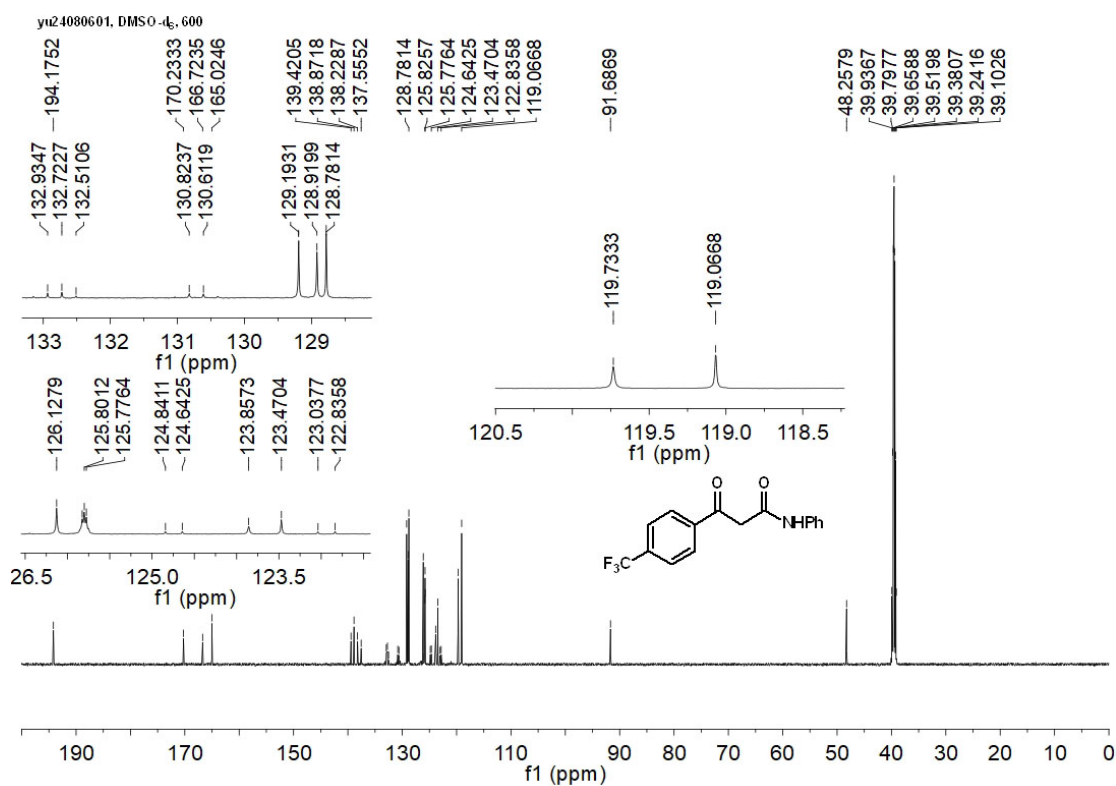
<sup>1</sup>H NMR of **3i**



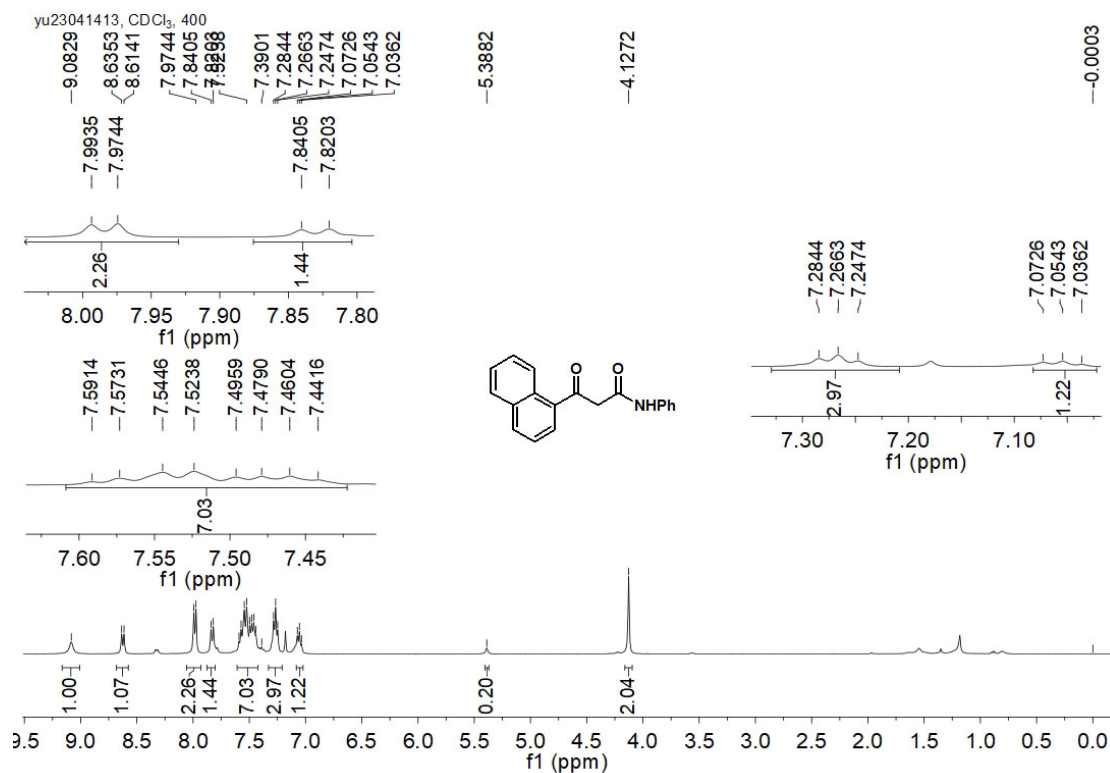
<sup>13</sup>C NMR of **3i**



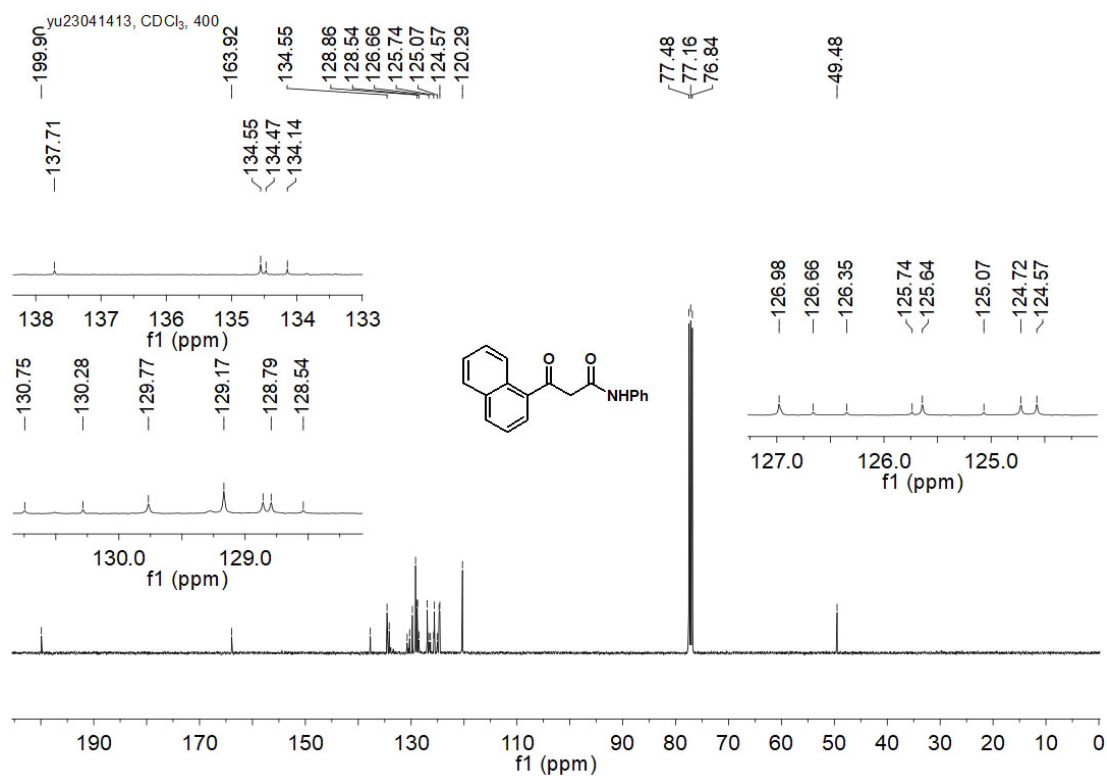
$^1\text{H}$  NMR of **3j**



$^{13}\text{C}$  NMR of **3j**

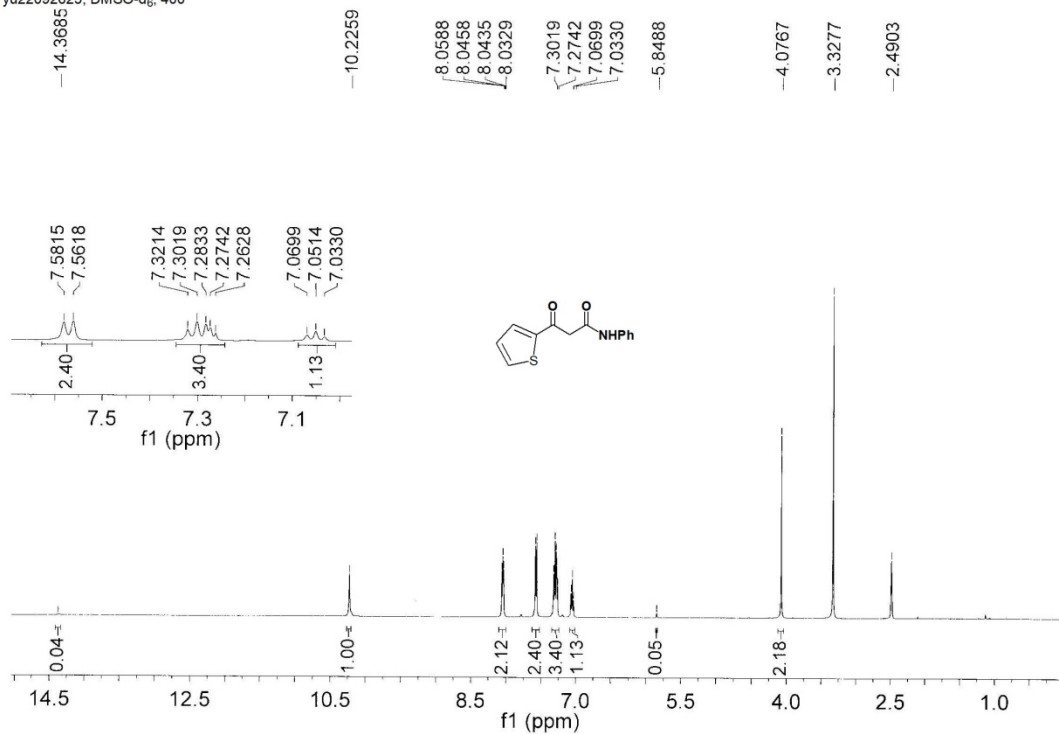


<sup>1</sup>H NMR of **3k**



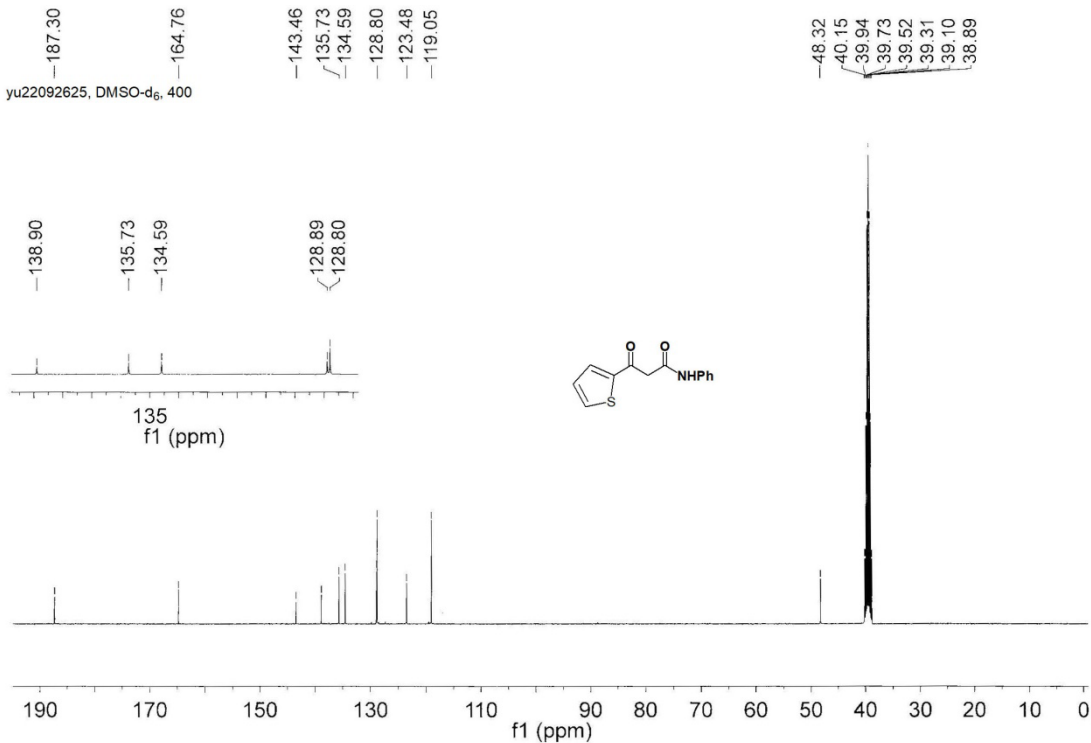
<sup>13</sup>C NMR of **3k**

yu22092625, DMSO-d<sub>6</sub>, 400

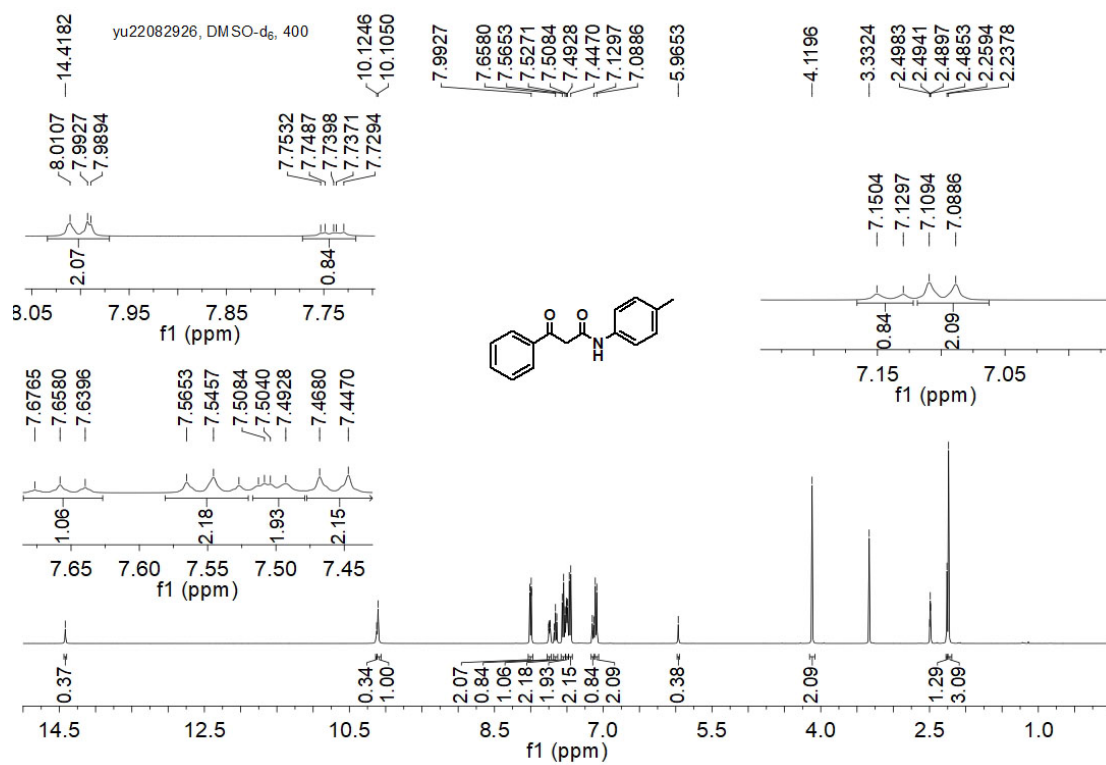


**<sup>1</sup>H NMR of 3I**

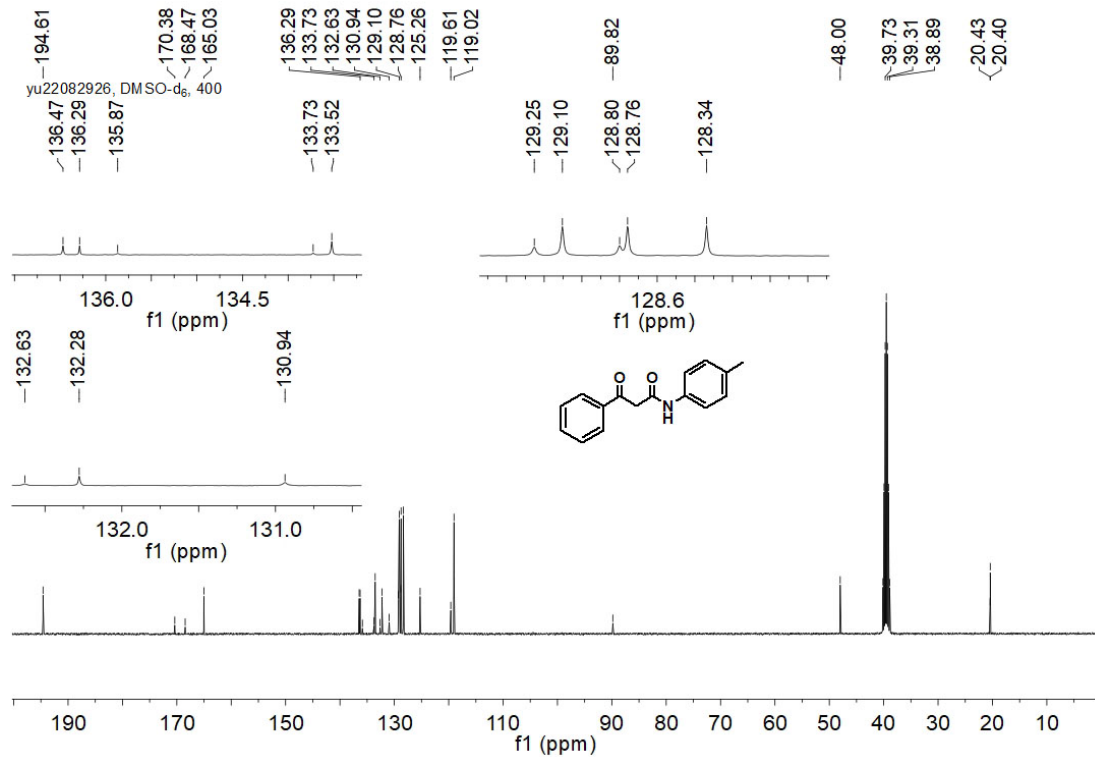
yu22092625, DMSO-d<sub>6</sub>, 400



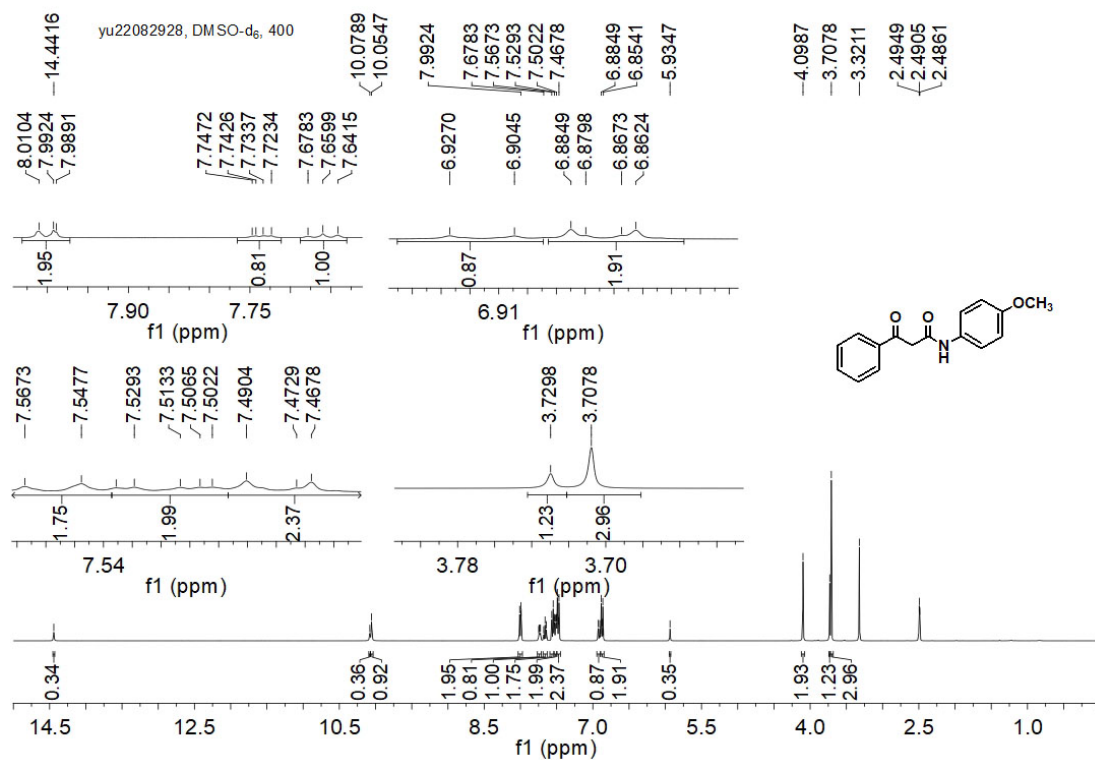
**<sup>13</sup>C NMR of 3I**



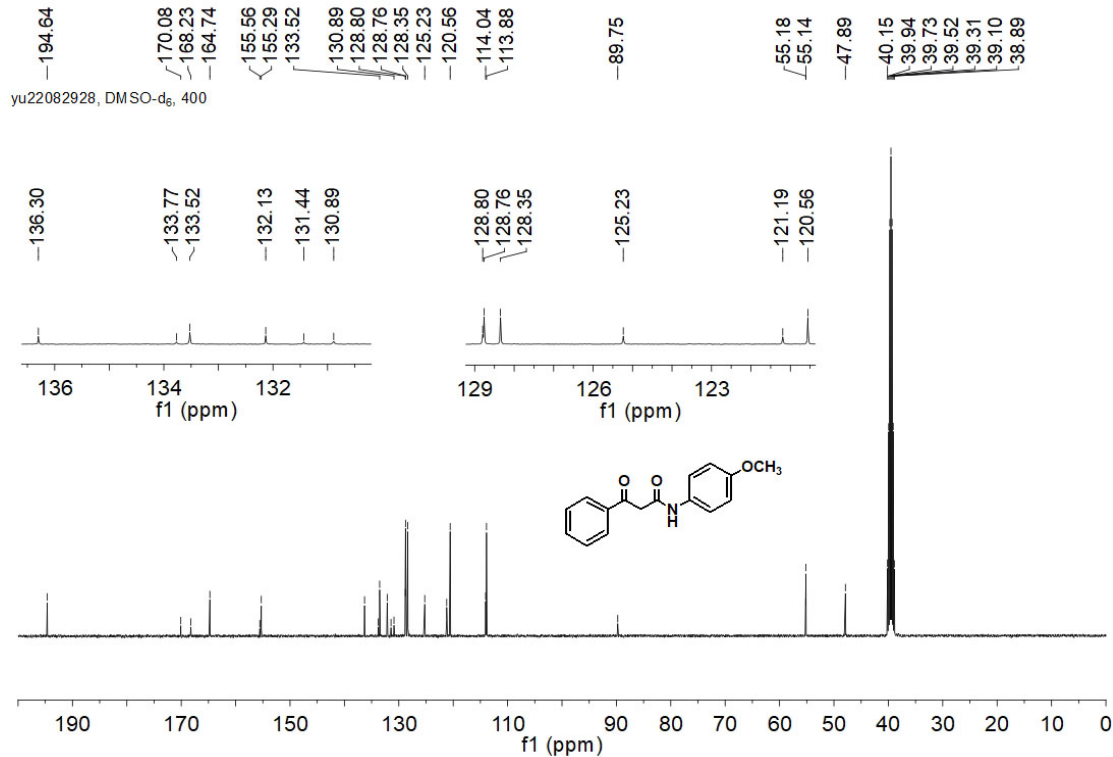
<sup>1</sup>H NMR of **3m**



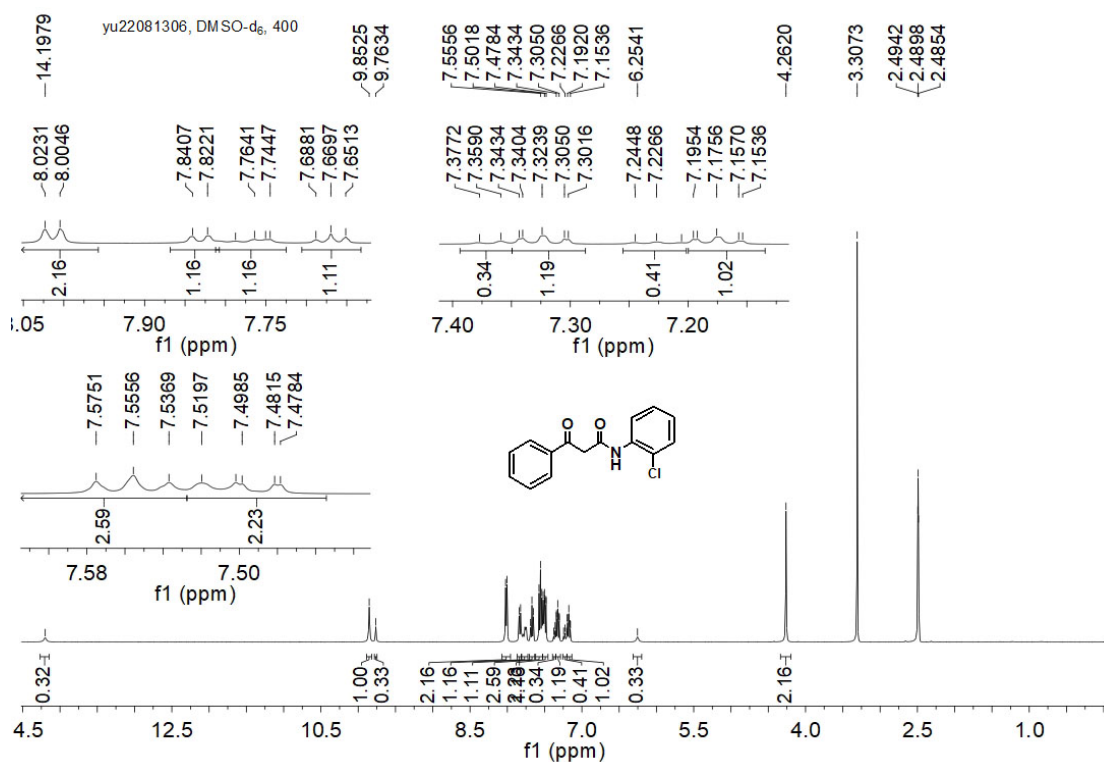
<sup>13</sup>C NMR of **3m**



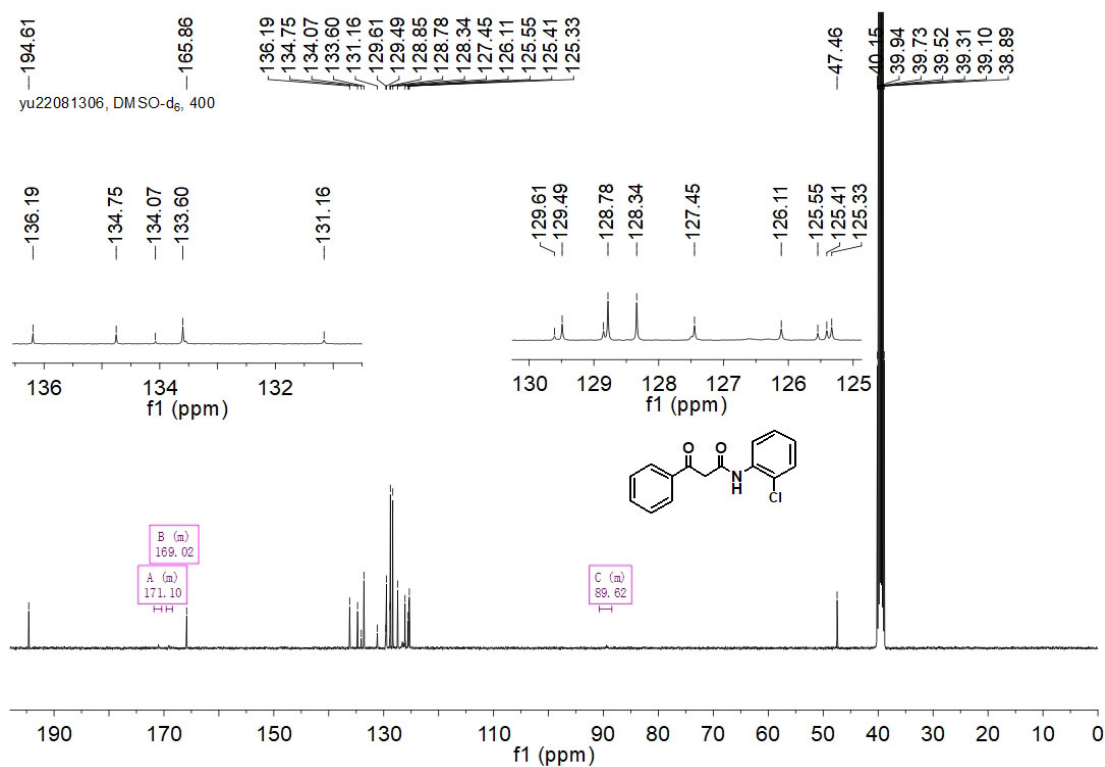
<sup>1</sup>H NMR of **3n**



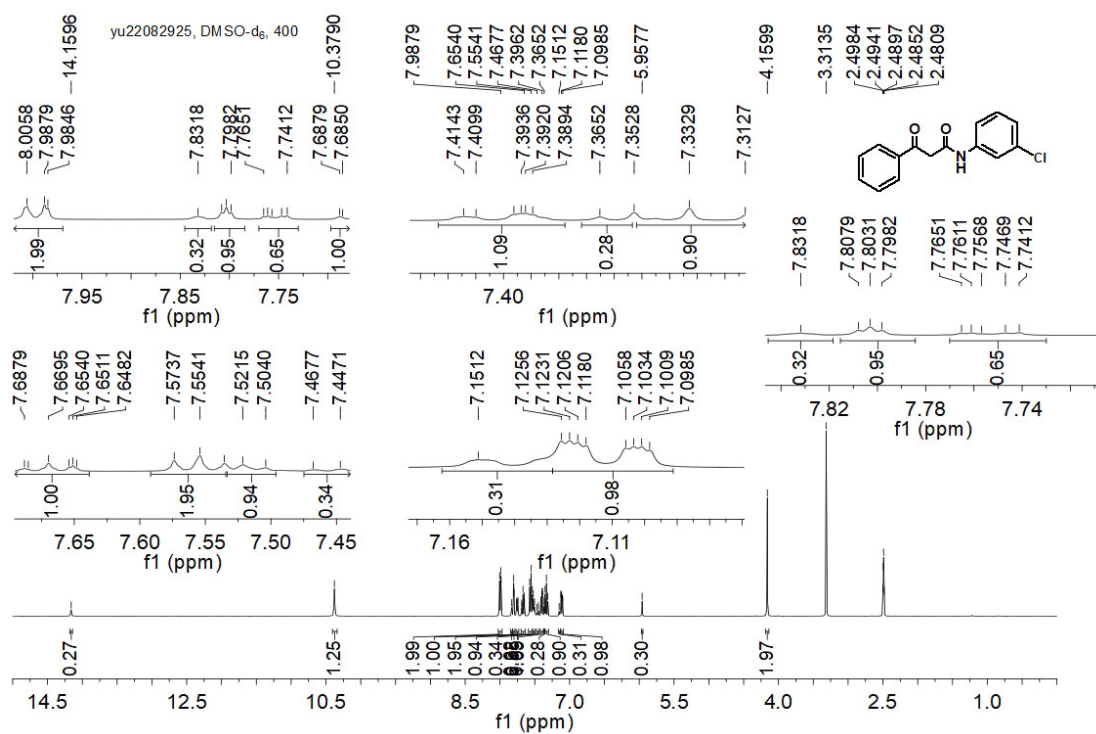
<sup>13</sup>C NMR of **3n**



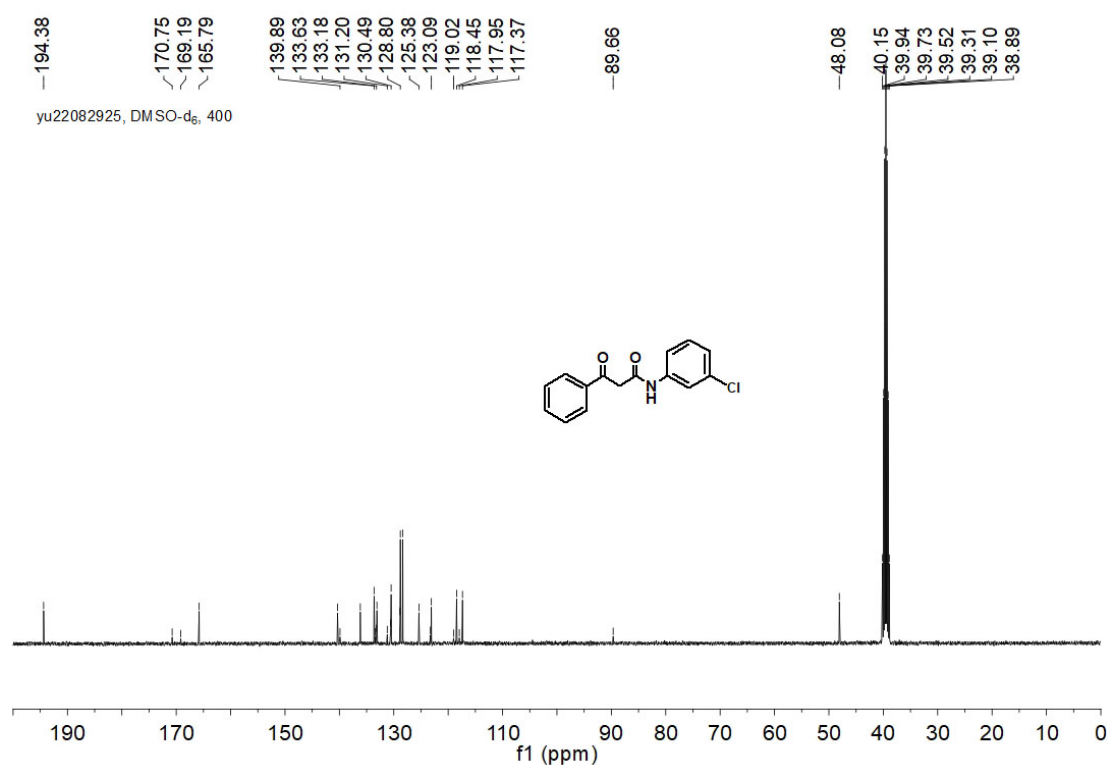
<sup>1</sup>H NMR of **3o**



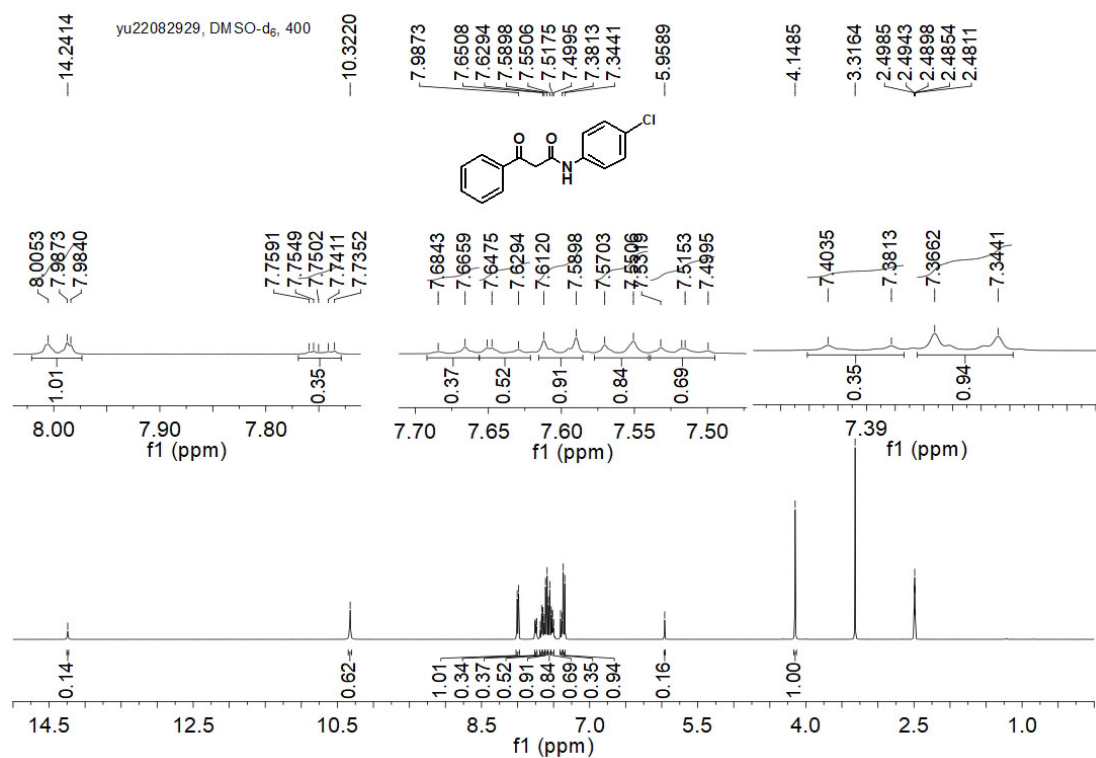
<sup>13</sup>C NMR of **3o**



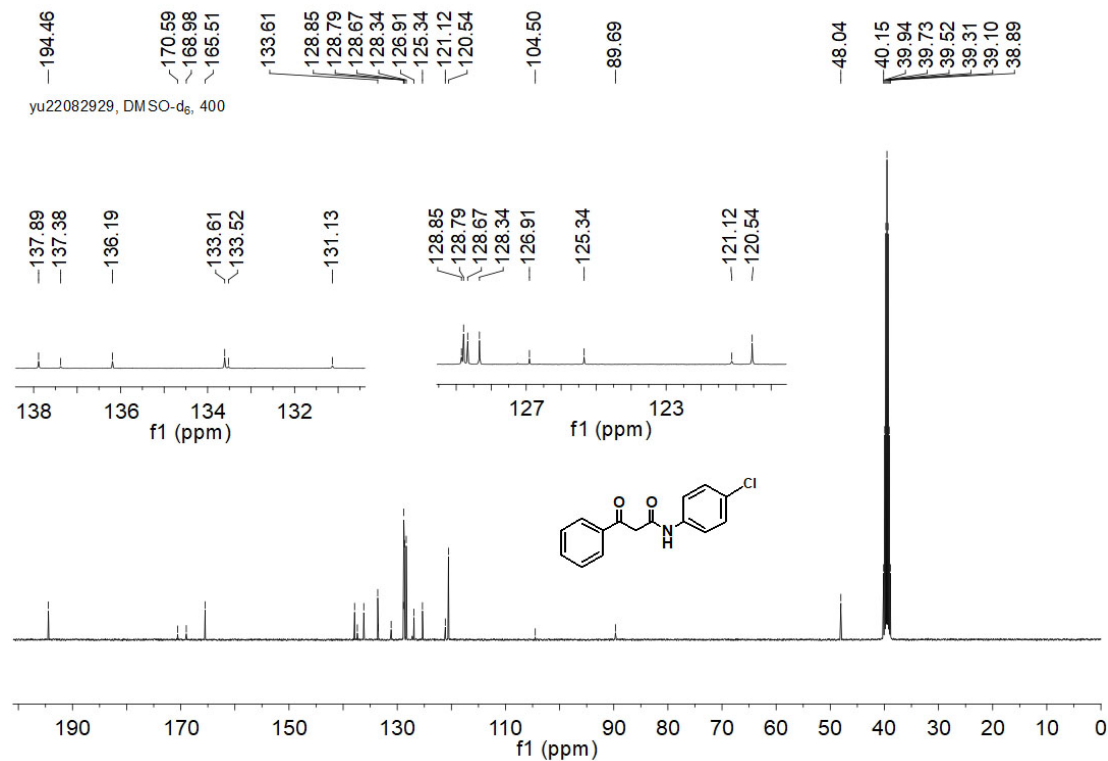
**<sup>1</sup>H NMR of 3p**



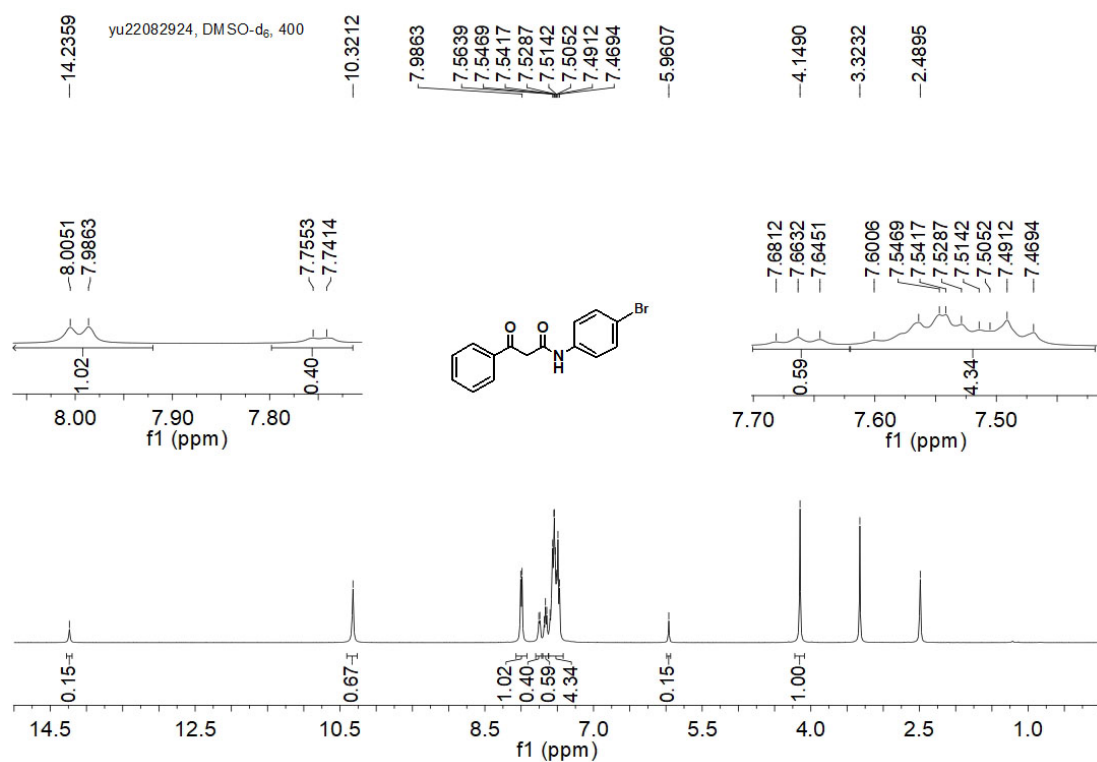
**<sup>13</sup>C NMR of 3p**



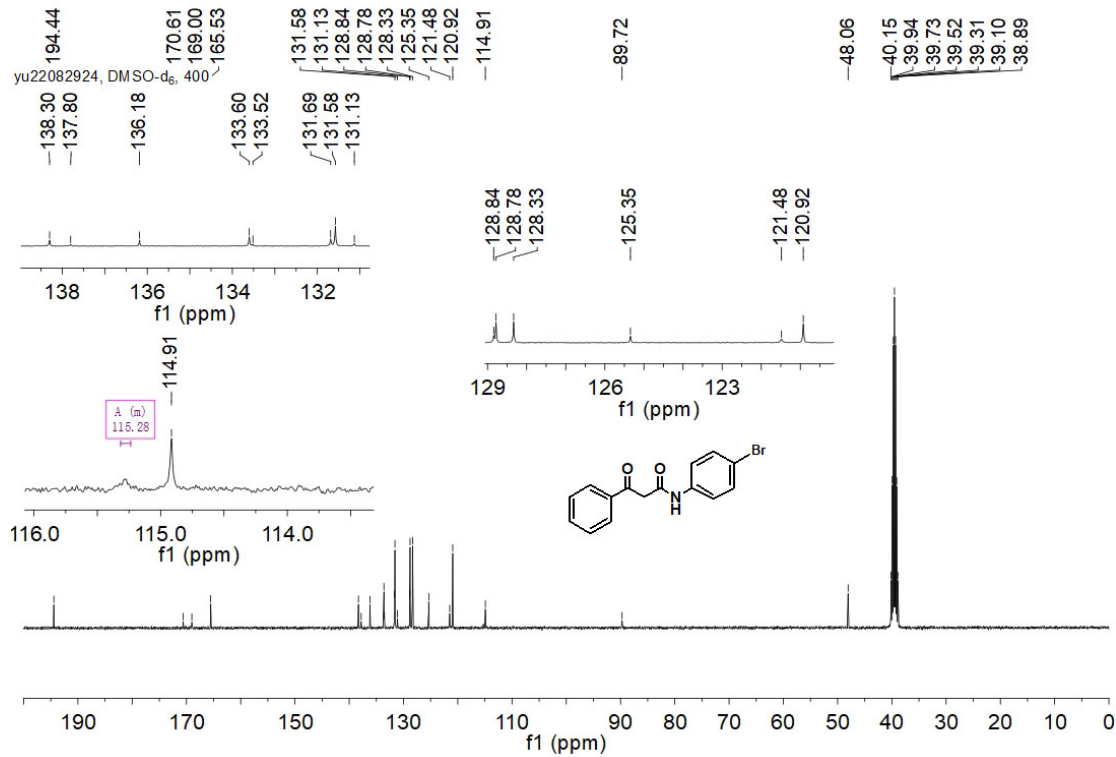
<sup>1</sup>H NMR of **3q**



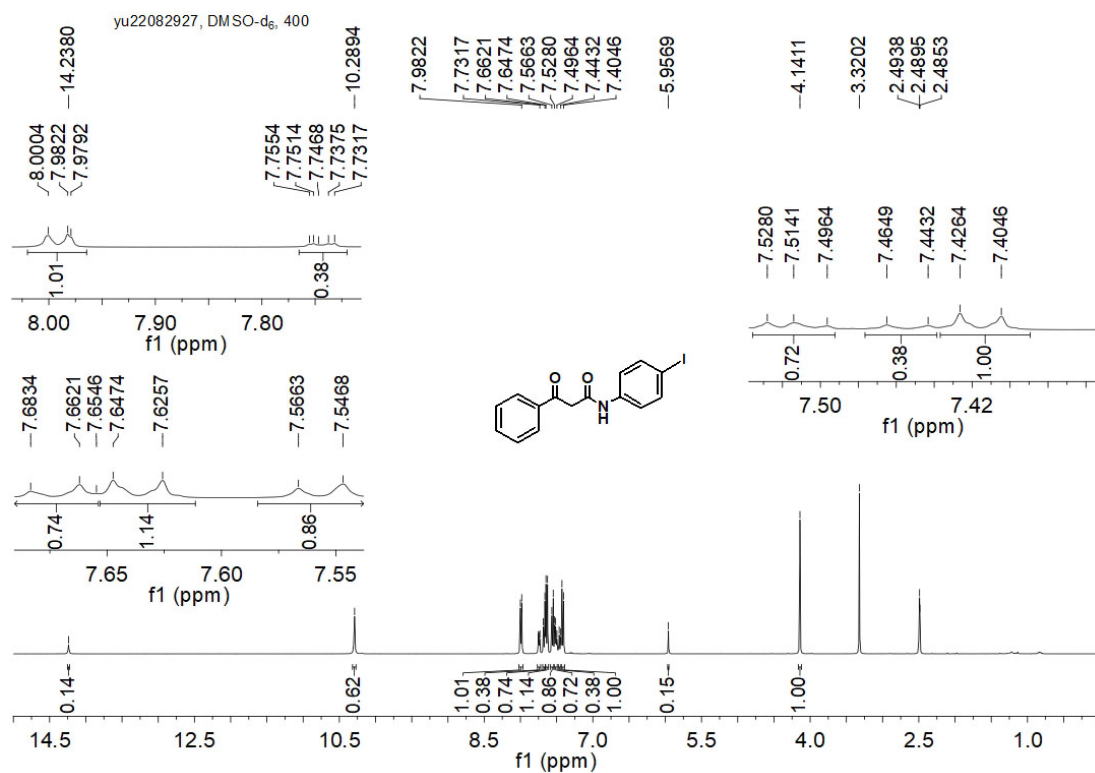
<sup>13</sup>C NMR of **3q**



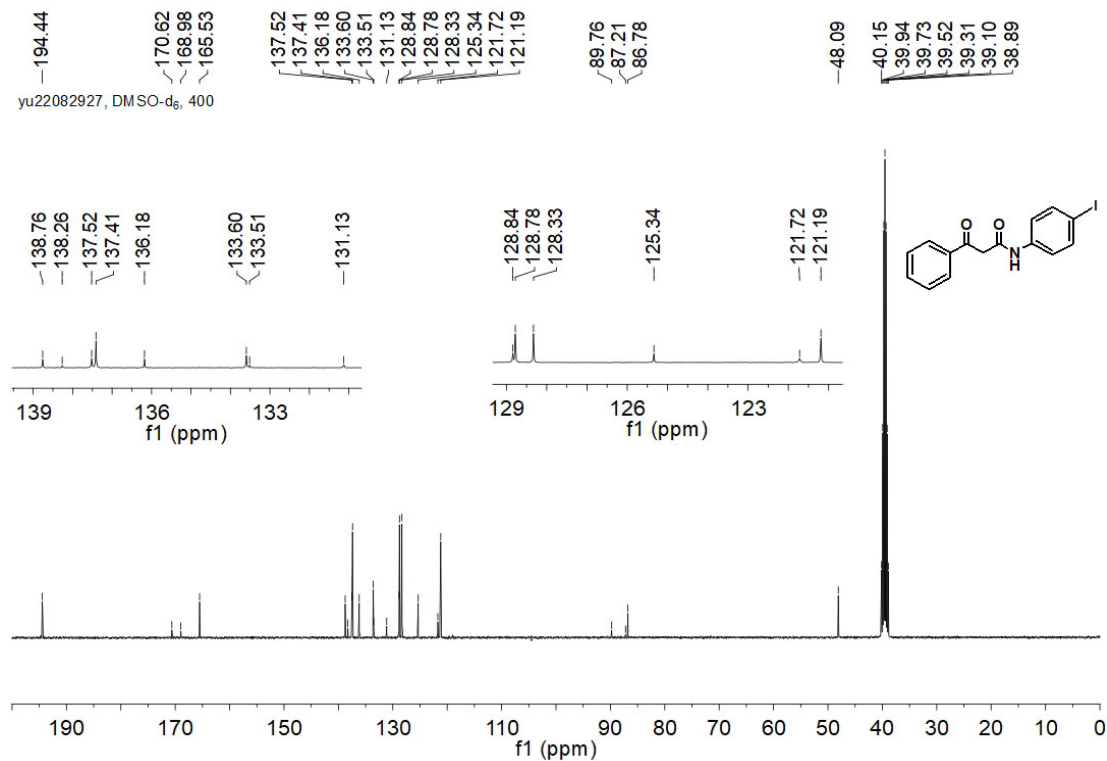
<sup>1</sup>H NMR of **3r**



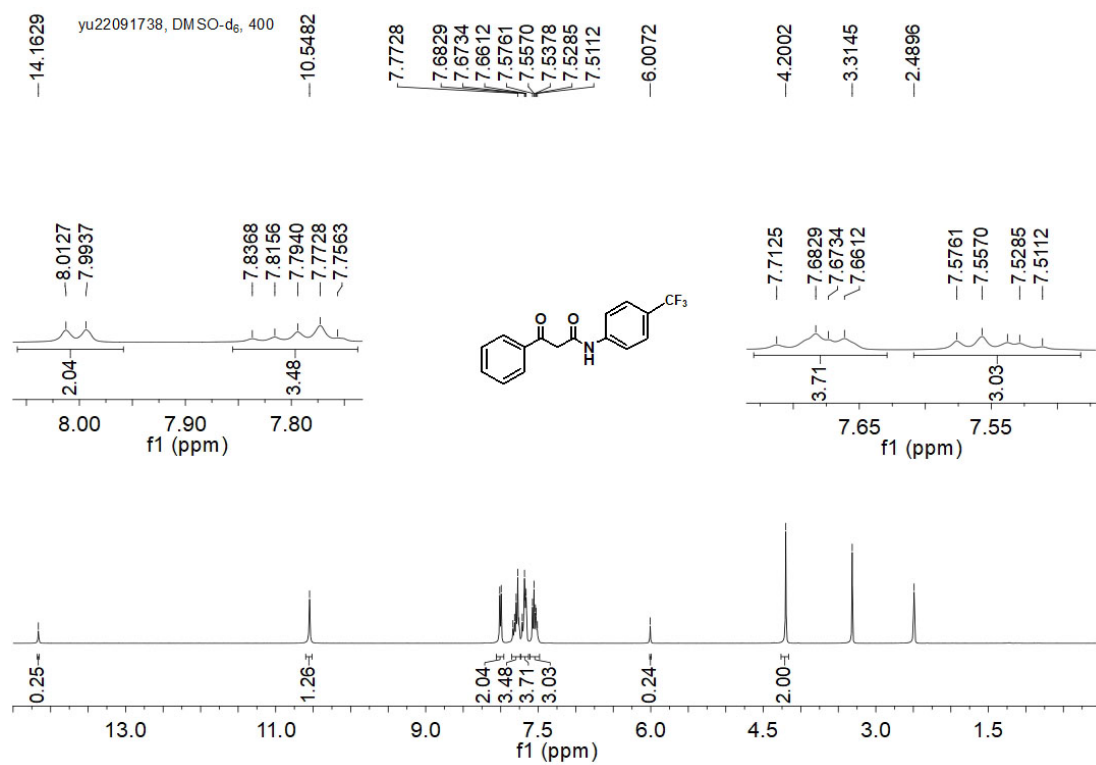
<sup>13</sup>C NMR of **3r**



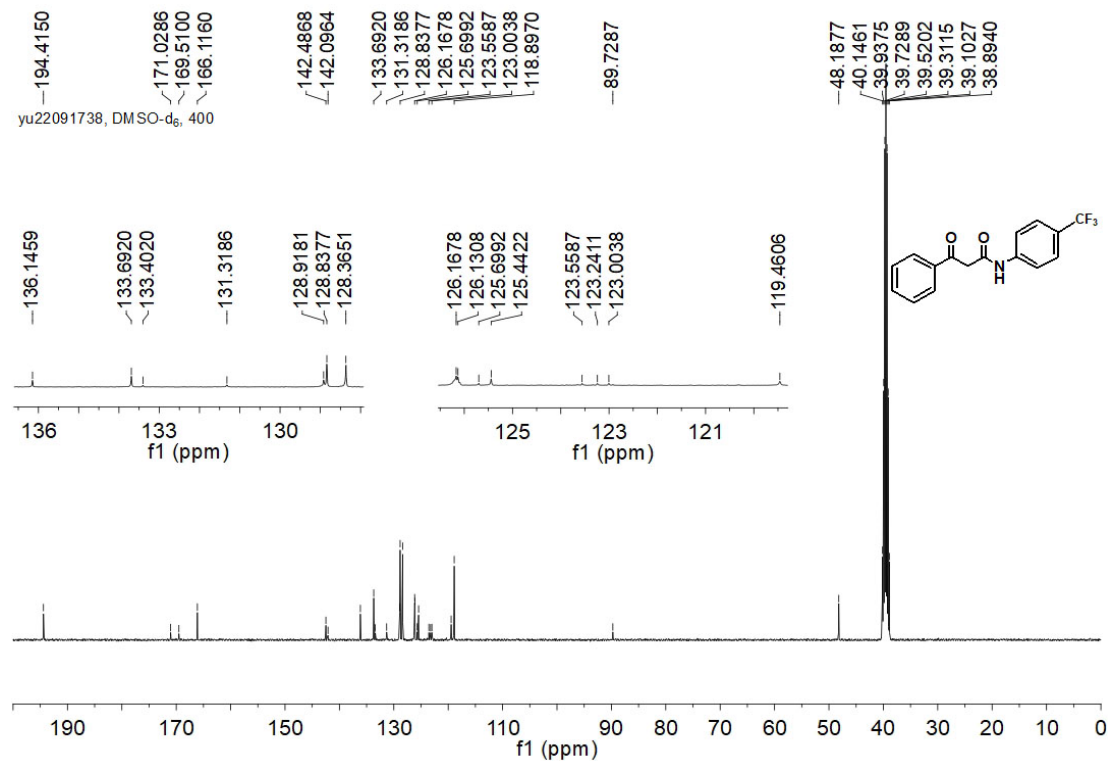
<sup>1</sup>H NMR of **3s**



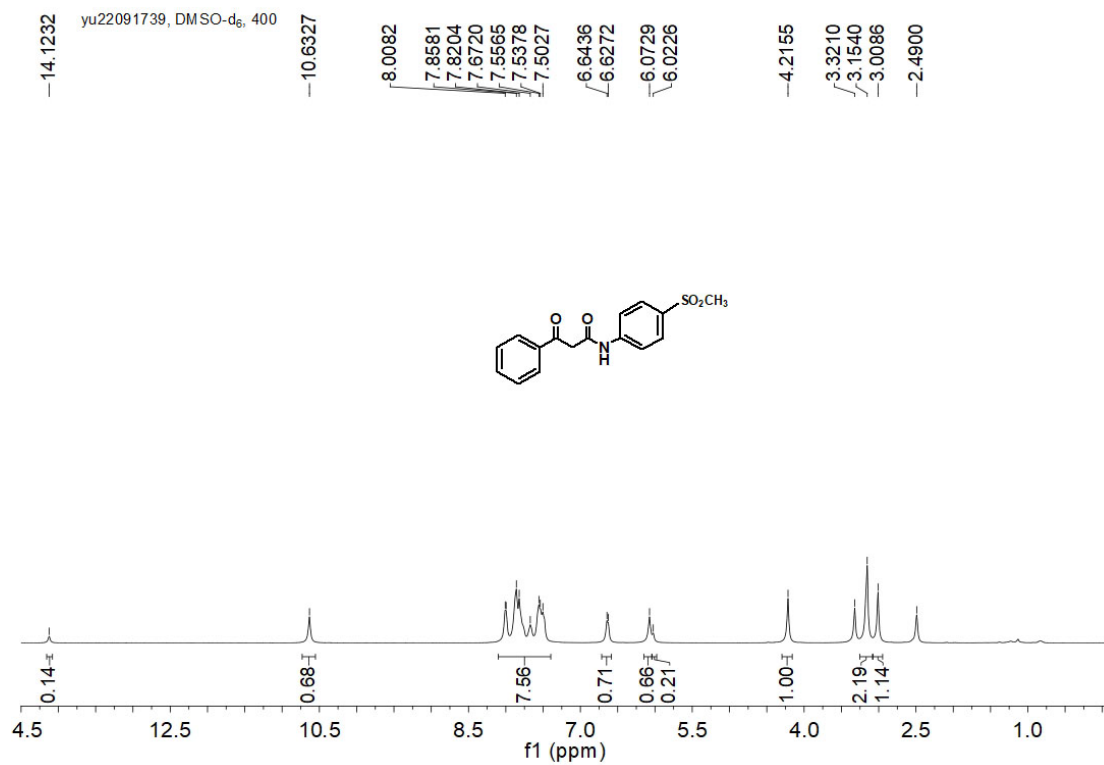
<sup>13</sup>C NMR of **3s**



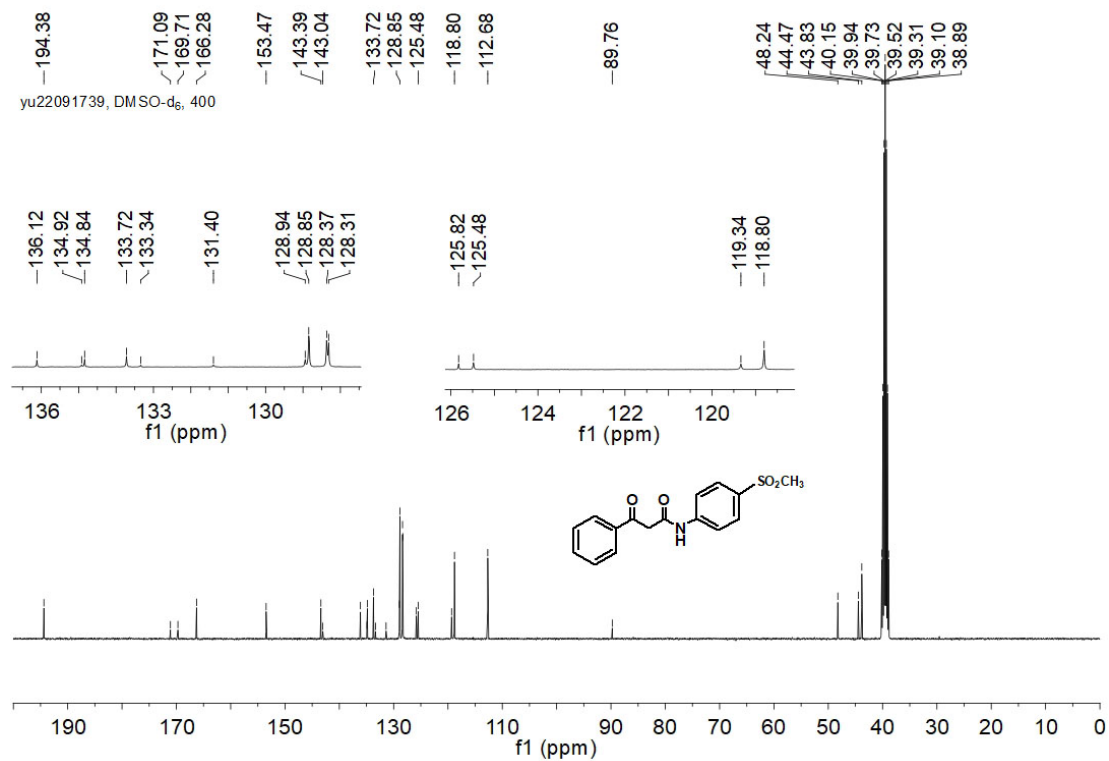
<sup>1</sup>H NMR of **3t**



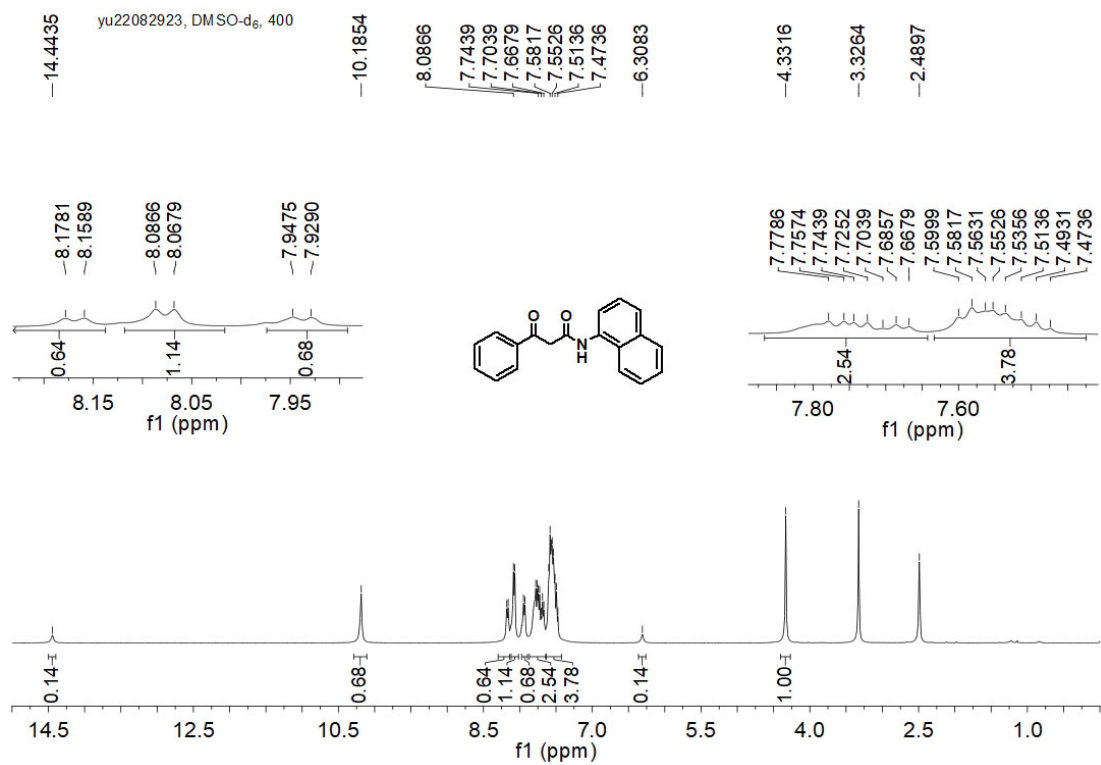
<sup>13</sup>C NMR of **3t**



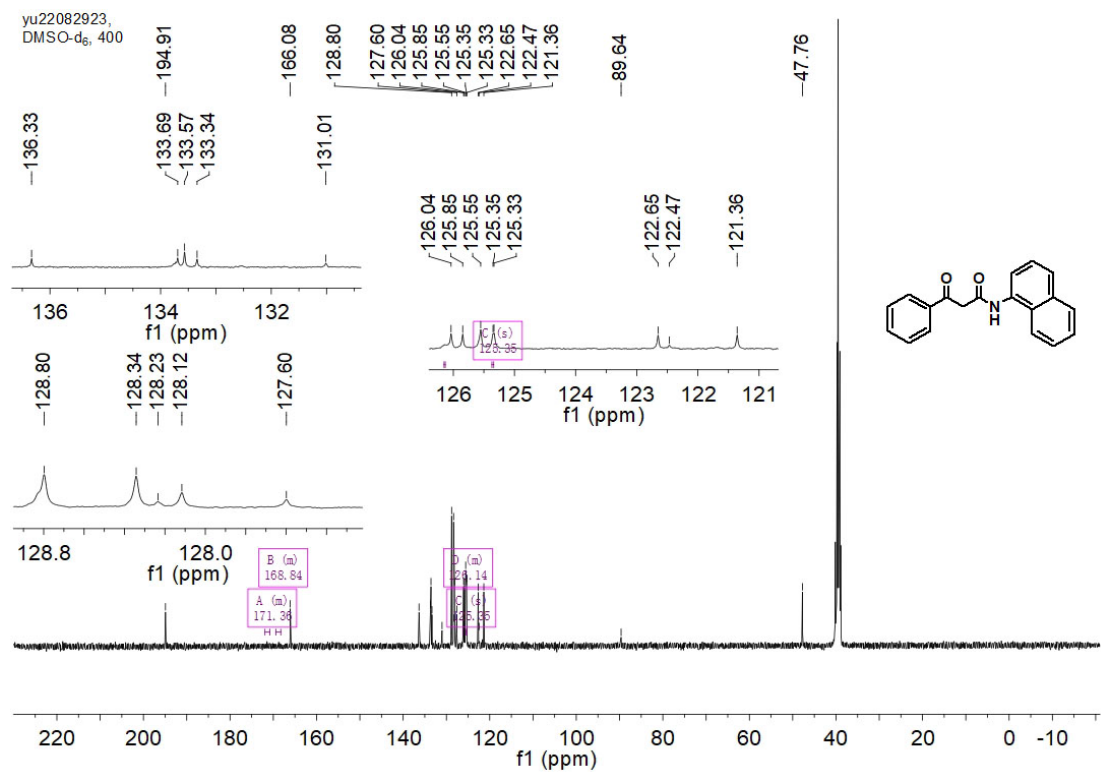
<sup>1</sup>H NMR of **3u**



<sup>13</sup>C NMR of **3u**



<sup>1</sup>H NMR of **3v**



<sup>13</sup>C NMR of **3v**

