Supporting Information

N-Bromosuccinimide Promoted and Base Switchable One Pot Synthesis of *α*-Imido and *α*-Amino Ketones from Styrenes

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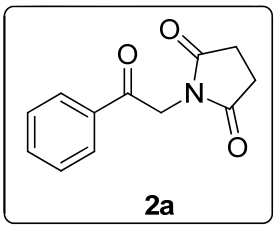
General

All chemicals were of reagent grade quality, purchased commercially from TCI-Chemicals, Sigma-Aldrich, or Spectrochem, and used without further purification except NBS. NBS was recrystallized from water using literature procedure. Purification by column chromatography was performed on Merck chromatographic silica gel (100-200 mesh). TLC analyses were performed using Merck silica gel 60 F_{254} precoated aluminium plates. NMR spectra were recorded on Bruker Avance III (500MHz), or Varian Mercury (300 MHz) instruments; chemical shifts, given in ppm, are relative to Me_4Si as the internal standard or to the residual solvent peak. HR-MS data were obtained using a Thermo-Scientific Bruker Daltonik GmbH, Germany Impact II UHR-ToF Mass Spectrometer ESI (Electron Spray Ionization).

General procedure for the synthesis of *α*-imido ketones (2): *N*-Bromosuccinimide (2.0 mmole) was added to the flask containing styrene (1.0 mmole) and H_2O (1.0 mL) at room temperature under nitrogen atmosphere. Reaction flask was immersed in oil bath and temperature was raised to 80 ^oC. Reaction mixture was stirred at 80 °C for 1.2 hr (when *N*-bromophthalimide and 1,3-dibromo-5,5-dimethylhydantoin was used, reaction mixture was heated for 2.0 hr). The reaction mixture was then cooled to room temperature and diluted with 2 mL acetone followed by addition of DBU (3.0 mmole) and further stirred for additional 45 min at room temperature. After completion of reaction (checked by TLC), acetone was evaporated in vaccuo and crude product was extracted with ethyl acetate (3 x 20 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vaccuo. The crude product was purified by silica gel column chromatography with hexane–ethyl acetate (7:3) to give *α*-imido ketones.

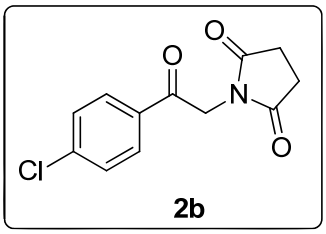
General procedure for *α*-amino ketones synthesis (3): *N*-Bromosuccinimide (2.0 mmole) was added to the flask containing styrene (1.0 mmole) and H_2O (1.0 mL) at room temperature under nitrogen atmosphere. Reaction flask was immersed in oil bath and temperature was raised to 80 ^oC. Reaction mixture was stirred at 80 °C for 1.2 hr. The reaction mixture was then cooled to room temperature and diluted with 2 mL acetone followed by addition of amine (2.0 mmole) and further stirred for 2-6 hr at room temperature. After completion of reaction (checked by TLC), acetone was evaporated in vaccuo and crude product was extracted with ethyl acetate (3 x 20 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vaccuo. The crude product was purified by silica gel column chromatography with hexane–ethyl acetate to give *α*-amino ketones.

Spectral data:



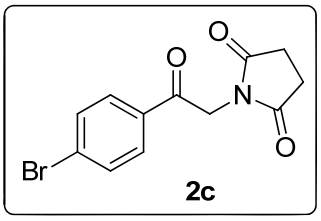
2a

1-(2-Oxo-2-phenylethyl)pyrrolidine-2,5-dione (2a)[1]: white solid, R_f = 0.3 (ethyl acetate:hexane, 4:6), FTIR (neat) ν (cm^{-1}): 1768, 1690, 1592, 1446, 1418; ^1H NMR (500 MHz, $CDCl_3$): δ 2.87 (s, 4H), 4.95 (s, 2H), 7.48-7.53 (m, 2H), 7.63 (tt, J = 1.22, 7.48 Hz, 1H), 7.97 (dd, J = 1.07, 8.54 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 28.3, 44.7, 128.1, 128.9, 134.1, 134.2, 176.7, 190.2; HRMS (ESI, m/z) calcd for $C_{12}H_{11}NNaO_3$ = 240.0637 $[M + Na]^+$, found 240.0634.



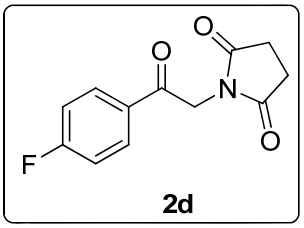
2b

1-(2-(4-Chlorophenyl)-2-oxoethyl)pyrrolidine-2,5-dione (2b)[1]: white solid, R_f = 0.3 (ethyl acetate:hexane, 4:6); ^1H NMR (300 MHz, $CDCl_3$): δ 2.86 (s, 4H), 4.90 (s, 2H), 7.48 (d, J = 8.57 Hz, 2H), 7.91 (d, J = 8.57 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 28.3, 44.6, 129.2, 129.4, 132.6, 140.6, 176.6, 189.1; HRMS (ESI, m/z) calcd for $C_{12}H_{10}ClNNaO_3$ = 274.0247 $[M + Na]^+$, found 274.0244.



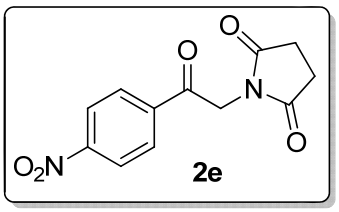
2c

1-(2-(4-Bromophenyl)-2-oxoethyl)pyrrolidine-2,5-dione (2c)[1]: white solid, R_f = 0.3 (ethyl acetate:hexane, 4:6); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.87 (s, 4H), 4.90 (s, 2H), 7.65 (d, J = 8.58 Hz, 2H), 7.83 (d, J = 8.58 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 28.3, 44.6, 129.4, 129.5, 132.2, 133.0, 176.6, 189.4; HRMS (ESI, m/z) calcd for $C_{12}H_{10}BrNNaO_3$ = 317.9742 $[M + Na]^+$, found 317.9736.



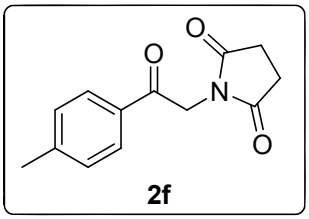
2d

1-(2-(4-Fluorophenyl)-2-oxoethyl)pyrrolidine-2,5-dione (2d)[2]: white solid, R_f = 0.3 (ethyl acetate:hexane, 4:6); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.87 (s, 4H), 4.91 (s, 2H), 7.15-7.21 (m, 2H), 7.98-8.03 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 28.3, 44.5, 116.1 (d, $J_{C\text{-}F}$ = 21.8 Hz), 126.0, 130.8 (d, $J_{C\text{-}F}$ = 9.08 Hz), 130.75, 166.2 (d, $J_{C\text{-}F}$ = 257.0 Hz), 176.6, 188.7; HRMS (ESI, m/z) calcd for $C_{12}H_{10}FNNaO_3$ = 258.0542 $[M + Na]^+$, found 258.0540.



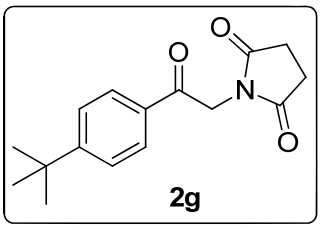
2e

1-(2-(4-nitrophenyl)-2-oxoethyl)pyrrolidine-2,5-dione (2e)[1]: red solid, R_f = 0.3 (ethyl acetate:hexane, 4:6); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.90 (s, 4H), 4.98 (s, 2H), 8.15 (d, J = 8.09 Hz, 2H), 8.37 (d, J = 7.93 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 28.3, 44.9, 124.1, 129.2, 138.7, 150.8, 176.5, 189.2; HRMS (ESI, m/z) calcd for $C_{12}H_{10}N_2NaO_5$ = 285.0487 $[M + Na]^+$, found 285.0483.



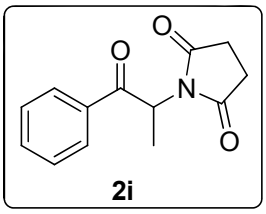
2f

1-(2-Oxo-2-(*p*-tolyl)ethyl)pyrrolidine-2,5-dione (2f)[1]: white solid, R_f = 0.3 (ethyl acetate:hexane, 4:6); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.44 (s, 3H), 2.87 (s, 4H), 4.93 (s, 2H), 7.30 (d, J = 8.09 Hz, 2H), 7.87 (d, J = 8.09 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.8, 28.3, 44.6, 128.2, 129.5, 131.8, 145.1, 176.6, 189.8; HRMS (ESI, m/z) calcd for $C_{13}H_{13}NNaO_3$ = 254.0793 $[M + Na]^+$, found 254.0787.



2g

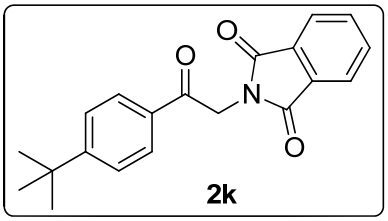
1-(2-(4-(*tert*-Butyl)phenyl)-2-oxoethyl)pyrrolidine-2,5-dione (2g): white solid, R_f = 0.3 (ethyl acetate:hexane, 4:6); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.35 (s, 9H), 2.86 (s, 4H), 4.93 (s, 2H), 7.52 (d, J = 8.79 Hz, 2H), 7.91 (d, J = 8.79 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 28.3, 31.0, 35.2, 44.6, 125.8, 128.0, 131.8, 158.0, 176.7, 189.8; HRMS (ESI, m/z) calcd for $C_{16}H_{19}NNaO_3$ = 296.1263 $[M + Na]^+$, found 296.1263.



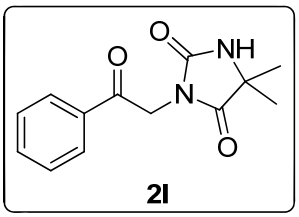
2i

1-(1-Oxo-1-phenylpropan-2-yl)pyrrolidine-2,5-dione (2i)[1]: white solid, R_f = 0.3 (ethyl acetate:hexane, 4:6); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.55 (d, J = 7.15 Hz, 3H), 2.50-2.65 (m, 4H), 5.41 (q, J = 7.15 Hz, 1H), 7.30-7.40 (m, 2H), 7.47 (tt, J = 1.43, 7.15, Hz, 1H), 7.67 (dd,

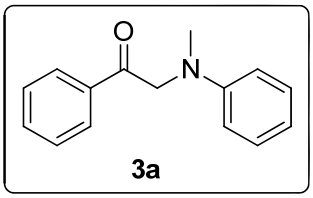
J = 1.43, 7.15, Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.0, 28.1, 51.6, 127.8, 128.7, 133.0, 135.2, 176.3, 195.9; HRMS (ESI, m/z) calcd for $C_{13}H_{13}NNaO_3$ = 254.0793 $[M + Na]^+$, found 254.0790.



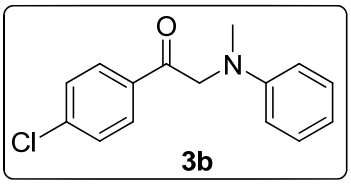
2-(2-(4-(*tert*-Butyl)phenyl)-2-oxoethyl)isoindoline-1,3-dione (2k): white solid, R_f = 0.3 (ethyl acetate:hexane, 4:6); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.36 (s, 9H), 5.12 (s, 2H), 7.54 (d, *J* = 8.70 Hz, 2H), 7.96 (d, *J* = 8.70 Hz, 2H), 7.73-7.77 (m, 2H), 7.88-7.92 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 31.0, 35.3, 44.1, 123.5, 125.8, 128.1, 131.8, 132.3, 134.1, 157.9, 167.9, 190.6; HRMS (ESI, m/z) calcd for $C_{20}H_{19}NNaO_3$ = 344.1263 $[M + Na]^+$, found 344.1259.



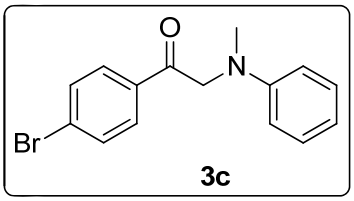
5,5-Dimethyl-3-(2-oxo-2-phenylethyl)imidazolidine-2,4-dione (2l)[1]**:** white solid, R_f = 0.3 (ethyl acetate:hexane, 4:6); FTIR (neat) ν (cm^{-1}): 3351, 2925, 1758, 1694, 1448; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.54 (s, 6H), 4.93 (s, 2H), 6.10 (br s, 1H), 7.48-7.53 (m, 2H), 7.60-7.67 (m, 1H), 7.97 (dd, *J* = 1.22, 8.39 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.0, 44.4, 59.4, 128.1, 128.9, 134.0, 134.3, 156.0, 177.3, 190.8; HRMS (ESI, m/z) calcd for $C_{13}H_{14}N_2NaO_3$ = 269.0902 $[M + Na]^+$, found 269.0903.



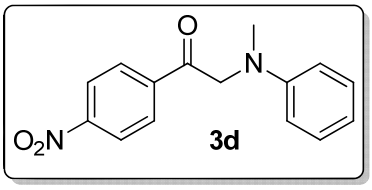
2-(Methyl(phenyl)amino)-1-phenylethanone (3a)[3]: Yellow oil, R_f = 0.5 (ethyl acetate:hexane, 1:9); FTIR (neat) ν (cm^{-1}): 1690, 1594, 1504, 1448; ^1H NMR (300 MHz, $CDCl_3$): δ 3.05 (s, 3H), 4.72 (s, 2H), 6.63 (d, J = 8.11 Hz, 2H), 6.59-6.71 (m, 1H), 7.10-7.21 (m, 2H), 7.40-7.48 (m, 2H), 7.56 (tt, J = 1.43, 7.15, Hz, 1H), 7.94 (dd, J = 1.43, 7.15 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 39.5, 58.9, 112.2, 117.1, 127.8, 128.8, 129.2, 133.5, 135.4, 149.2, 196.5; HRMS (ESI, m/z) calcd for $C_{15}H_{16}NO$ = 226.1232 $[M + H]^+$, found 226.1232.



1-(4-Chlorophenyl)-2-(methyl(phenyl)amino)ethanone (3b)[4]: Yellow solid, R_f = 0.5 (ethyl acetate:hexane, 1:9); ^1H NMR (500 MHz, $CDCl_3$): δ 3.10 (s, 3H), 4.74 (s, 2H), 6.68 (dd, J = 1.22, 8.85 Hz, 2H), 6.72-6.77 (m, 1H), 7.20-7.25 (m, 2H), 7.48 (d, J = 8.85 Hz, 2H), 7.94 (d, J = 8.85 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 39.5, 59.0, 112.3, 117.3, 129.1, 129.2 (2 carbons), 133.7, 134.0, 149.1, 195.5; HRMS (ESI, m/z) calcd for $C_{15}H_{15}ClNO$ = 260.0842 $[M + H]^+$, found 260.0839.

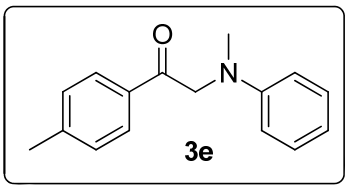


1-(4-Bromophenyl)-2-(methyl(phenyl)amino)ethanone (3c)[3]: Yellow solid, R_f = 0.5 (ethyl acetate:hexane, 1:9); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.09 (s, 3H), 4.73 (s, 2H), 6.68 (dd, J = 0.92, 8.85 Hz, 2H), 6.72-6.77 (m, 1H), 7.23 (dd, J = 7.32, 8.85Hz, 2H) 7.65 (d, J = 6.71 Hz, 2H) 7.86 (d, J = 6.71 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 39.6, 59.0, 112.3, 117.3, 128.7, 129.2, 129.3, 132.1, 149.0, 195.7; HRMS (ESI, m/z) calcd for $C_{15}H_{15}BrNO$ = 304.0337 $[M + H]^+$, found 304.0334.



3d

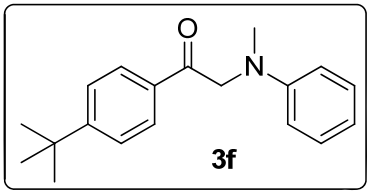
2-(methyl(phenyl)amino)-1-(4-nitrophenyl)ethanone (3d): red solid, R_f = 0.5 (ethyl acetate:hexane, 1:9); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.12 (s, 3H), 4.80 (s, 2H), 6.70-6.73 (m, 2H), 6.79 (tt, J = 0.92, 7.32 Hz, 1H), 7.26 (dd, J = 1.68, 7.17 Hz, 2H) 8.14 (d, J = 9.00 Hz, 2H) 8.34 (d, J = 8.85 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 39.6, 59.6, 112.5, 117.7, 124.0, 128.9, 129.3, 139.8, 148.8, 150.5, 195.7; HRMS (ESI, m/z) calcd for $C_{15}H_{15}N_2O_3$ = 271.1083 $[M + H]^+$, found 271.1083.



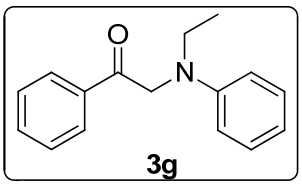
3e

2-(Methyl(phenyl)amino)-1-(*p*-tolyl)ethanone (3e)[3]: Yellow oil, R_f = 0.5 (ethyl acetate:hexane, 1:9); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.43 (s, 3H), 3.09 (s, 3H), 4.74 (s, 2H), 6.67 (dd, J = 0.96, 8.85 Hz, 2H), 6.69-6.75 (m, 1H), 7.20 (dd, J = 7.32, 8.85 Hz, 2H), 7.29 (d, J = 7.93 Hz, 2H), 7.89 (d, J = 8.24 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.7, 39.5, 58.8,

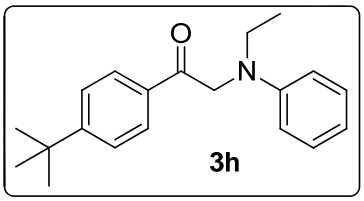
112.2, 117.0, 127.9, 129.1, 129.4, 132.9, 144.4, 149.2, 196.1; HRMS (ESI, m/z) calcd for $C_{16}H_{18}NO$ = 240.1388 $[M + H]^+$, found 240.1381.



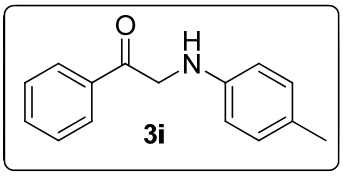
1-(4-(*tert*-Butyl)phenyl)-2-(methyl(phenyl)amino)ethanone (3f): Yellow solid, R_f = 0.5 (ethyl acetate:hexane, 1:9); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29 (s, 9H), 3.04 (s, 3H), 4.69 (s, 2H), 6.57-6.68 (m, 1H), 6.61 (d, J = 8.58 Hz, 2H), 7.10-7.20 (m, 2H), 7.45 (d, J = 8.58 Hz, 2H), 7.88 (d, J = 8.58 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 31.1, 35.2, 39.6, 58.9, 112.2, 117.0, 125.7, 127.8, 129.2, 132.9, 149.2, 157.3, 196.1; HRMS (ESI, m/z) calcd for $C_{19}H_{24}NO$ = 282.1858 $[M + H]^+$, found 282.1860.



2-(Ethyl(phenyl)amino)-1-phenylethanone (3g)[5]: Yellow solid, R_f = 0.6 (ethyl acetate:hexane, 1:9); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.17 (t, J = 7.15 Hz, 3H), 3.45 (q, J = 7.15 Hz, 2H), 4.68 (s, 2H), 6.56 (d, J = 8.11 Hz, 2H), 6.63 (t, J = 7.15 Hz, 1H), 7.08-7.17 (m, 2H), 7.40-7.49 (m, 2H), 7.50-7.60 (m, 1H), 7.92-7.99 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 12.5, 46.1, 56.7, 112.1, 116.7, 127.8, 128.8, 129.2, 133.5, 135.4, 148.0, 196.5; HRMS (ESI, m/z) calcd for $C_{16}H_{18}NO$ = 240.1388 $[M + H]^+$, found 240.1386.

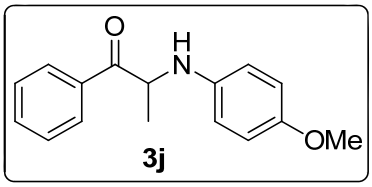


1-(4-(*tert*-Butyl)phenyl)-2-(ethyl(phenyl)amino)ethanone (3h): Yellow solid, R_f = 0.6 (ethyl acetate:hexane, 1:9); ^{1}H NMR (500 MHz, $CDCl_3$) : δ 1.25 (t, J = 7.02 Hz, 3H), 1.39 (s, 9H), 3.53 (q, J = 7.02 Hz, 2H), 4.75 (s, 2H), 6.64 (dd, J = 0.92, 8.85 Hz, 2H), 6.68-6.74 (m, 1H), 7.18-7.23 (m, 2H), 7.54 (d, J = 8.70 Hz, 2H), 7.99 (d, J = 8.70 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 12.5, 31.1, 35.2, 46.1, 56.6, 112.1, 116.6, 125.7, 127.8, 129.2, 132.9, 148.1, 157.3, 196.1; HRMS (ESI, m/z) calcd for $C_{20}H_{26}NO$ = 296.2014 $[M + H]^+$, found 296.2012.



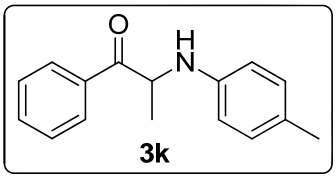
3i

1-Phenyl-2-(*p*-tolylamino)ethanone (3i)[6]: Yellow oil, R_f = 0.4 (ethyl acetate:hexane, 1:9); ^{1}H NMR (300 MHz, $CDCl_3$) : δ 2.19 (s, 3H), 4.54 (s, 2H), 6.57 (d, J = 8.11 Hz, 2H), 6.97 (d, J = 8.11 Hz, 2H), 7.41-7.48 (m, 2H), 7.52-7.59 (m, 1H), 7.92-7.97 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.4, 50.7, 113.2, 127.0, 127.7, 128.9, 129.9, 133.8, 135.0, 144.9, 195.3; HRMS (ESI, m/z) calcd for $C_{15}H_{16}NO$ = 226.1232 $[M + H]^+$, found 226.1233.

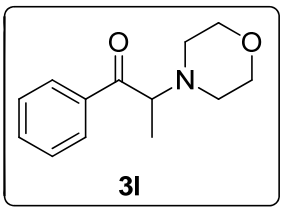


3j

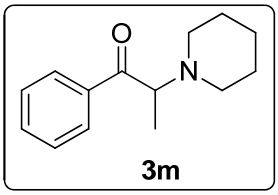
2-((4-methoxyphenyl)amino)-1-phenylpropan-1-one (3j)[7]: Red oil, R_f = 0.4 (ethyl acetate:hexane, 1:9); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.46 (d, J = 7.15 Hz, 3H), 3.72 (s, 3H), 5.06 (q, J = 7.15 Hz, 1H), 6.61-6.68 (m, 2H), 6.72-6.79 (m, 2H), 7.46-7.54 (m, 2H), 7.57-7.62 (m, 1H), 7.97-8.03 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 19.7, 54.5, 55.7, 114.9, 115.2, 128.4, 128.8, 133.6, 134.8, 140.8, 152.5, 201.2; HRMS (ESI, m/z) calcd for $C_{16}H_{18}NNaO_2$ = 256.1338 $[M + Na]^+$, found 256.1339.



1-Phenyl-2-(*p*-tolylamino)propan-1-one (3k)[7]: Brown solid, R_f = 0.3 (ethyl acetate:hexane, 1:9); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.50 (d, J = 7.02 Hz, 3H), 2.26 (s, 3H), 5.14 (q, J = 7.02 Hz, 1H), 6.64 (d, J = 8.54 Hz, 2H), 7.02 (d, J = 8.54 Hz, 2H), 7.51-7.56 (m, 2H), 7.64 (tt, J = 7.32, 1.22 Hz, 1H), 8.02-8.06 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 19.6, 20.4, 53.7, 113.7, 127.2, 128.4, 128.8, 129.8, 133.5, 134.8, 144.2, 201.9; HRMS (ESI, m/z) calcd for $C_{16}H_{18}NO$ = 240.1388 $[M + H]^+$, found 240.1386.

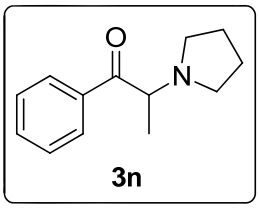


2-Morpholino-1-phenylpropan-1-one (3l)[7]: Yellow oil, R_f = 0.2 (ethyl acetate:hexane, 2:8); FTIR (neat) v (cm^{-1}): 1681, 1588, 1449; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.31 (d, J = 6.70 Hz, 3H), 2.54-2.67 (m, 4H), 3.65-3.73 (m, 4H), 4.08 (q, J = 6.70 Hz, 1H), 7.44-7.48 (m, 2H), 7.57 (tt, J = 7.32, 1.22 Hz, 1H), 8.10 (dd, J = 1.22, 8.24 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 11.6, 50.1, 64.8, 67.1, 128.4, 128.8, 133.0, 136.8, 200.2; HRMS (ESI, m/z) calcd for $C_{13}H_{18}NO_2$ = 220.1338 $[M + H]^+$, found 220.1339.



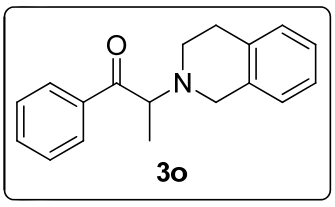
1-Phenyl-2-(piperidin-1-yl)propan-1-one (3m)[7]: Yellow solid, R_f = 0.3 (ethyl acetate:hexane, 2:8); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.26 (d, J = 6.87 Hz, 3H), 1.41 (dd, J =

5.80, 11.75 Hz, 2H), 1.50-1.58 (m, 4H), 2.46-2.60 (m, 4H), 4.09 (q, J = 6.87 Hz, 1H), 7.41-7.47 (m, 2H), 7.50-7.58 (m, 1H), 8.11 (dd, J = 1.07, 8.24 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 11.2, 24.4, 26.3, 50.7, 65.0, 128.2, 128.9, 132.7, 136.5, 201.1; HRMS (ESI, m/z) calcd for $C_{14}H_{20}NO$ = 218.1545 $[M + H]^+$, found 218.1541.



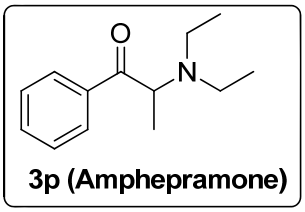
3n

1-Phenyl-2-(pyrrolidin-1-yl)propan-1-one (3n)[7]: Light brown liquid, R_f = 0.2 (ethyl acetate:hexane, 2:8); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38 (d, J = 6.85 Hz, 3H), 1.76-1.80 (m, 4H), 2.60-2.66 (m, 4H), 3.99 (q, J = 6.85 Hz, 1H), 7.41-7.46 (m, 2H), 7.54 (tt, J = 1.96, 7.34 Hz, 1H), 8.09 (dd, J = 1.47, 7.09 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.4, 23.4, 51.2, 64.5, 128.4, 128.6, 132.9, 135.9, 200.1; HRMS (ESI, m/z) calcd for $C_{13}H_{18}NO$ = 204.1388 $[M + H]^+$, found 204.1390.

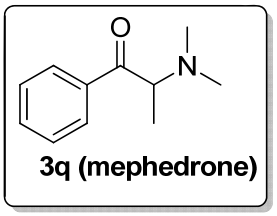


3o

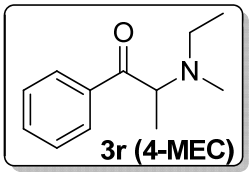
2-(3,4-Dihydroisoquinolin-2(1*H*)-yl)-1-phenylpropan-1-one (3o)[7]: Yellow oil, R_f = 0.4 (ethyl acetate:hexane, 2:8); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.32 (d, J = 6.68 Hz, 3H), 2.72-2.83 (m, 4H), 3.74 (d, J = 14.78 Hz, 1H), 3.85 (d, J = 14.78 Hz, 1H), 4.24 (q, J = 6.68 Hz, 1H), 6.92-7.05 (m, 4H), 7.33-7.38 (m, 2H), 7.46 (tt, J = 1.91, 7.15 Hz, 1H), 8.04-8.0 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 11.3, 29.6, 47.1, 52.1, 64.2, 125.5, 126.0, 126.6, 128.4, 128.7, 128.9, 133.0, 134.5, 134.8, 136.2, 200.6; HRMS (ESI, m/z) calcd for $C_{18}H_{20}NO$ = 266.1545 $[M + H]^+$, found 266.1545.



2-(Diethylamino)-1-phenylpropan-1-one (3p)[7]: Light brown liquid, R_f = 0.3 (ethyl acetate:hexane, 1:9); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.03 (t, J = 7.02 Hz, 6H), 1.26 (d, J = 6.71 Hz, 3H), 2.53-2.69 (m, 4H), 4.40 (q, J = 6.71Hz, 1H), 7.42-7.47 (m, 2H), 7.52-7.57 (m, 1H), 8.12 (dd, J = 1.22, 8.54 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 10.1, 13.6, 44.2, 60.3, 128.1, 128.9, 132.5, 136.8, 202.0; HRMS (ESI, m/z) calcd for $C_{13}H_{20}NO$ = 206.1545 $[M + H]^+$, found 206.1544.

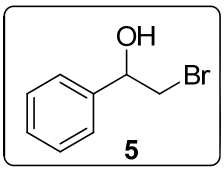


2-(dimethylamino)-1-phenylpropan-1-one (3q)[8]: yellow liquid, R_f = 0.3 (ethyl acetate:hexane, 2:8); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.28 (d, J = 6.71 Hz, 3H), 2.34 (s, 6H), 4.08 (q, J = 6.71 Hz, 1H), 7.45-7.48 (m, 2H) 7.55-7.59 (m, 1H), 8.08 (dd, J = 1.37, 8.54 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 11.1, 41.8, 64.2, 128.4, 128.7, 132.9, 136.3, 200.7; HRMS (ESI, m/z) calcd for $C_{16}H_{11}NO$ = 178.1232 $[M + H]^+$, found 178.1228.

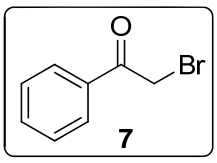


2-(ethyl(methyl)amino)-1-phenylpropan-1-one (3r): yellow liquid, R_f = 0.3 (ethyl acetate:hexane, 2:8); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.08 (t, J = 7.02 Hz, 3H), 1.26 (d, J =

7.02 Hz, 3H), 2.27 (s, 3H), 2.59 (q, *J* = 4.27 Hz, 2H), 4.25 (q, *J* = 6.71 Hz, 1H), 7.44-7.47 (m, 2H), 7.55 (tt, *J* = 1.83, 7.63 Hz, 1H), 8.09 (dd, J = 1.22, 7.02 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 10.0, 13.1, 37.2, 48.3, 62.7, 128.3, 128.8, 132.7, 136.5, 201.1.



2-Bromo-1-phenylethanol (**5**)**:** Colourless liquid, R_f = 0.3 (ethyl acetate:hexane, 1:9); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.67 (br s, 1H), 3.44-3.61 (m, 2H), 4.82-4.89 (m, 1H), 7.29-7.35 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 40.1, 73.8, 125.9, 128.4, 128.7, 140.2.



2-Bromo-1-phenylethanone (**7**)**:** Yellow liquid, R_f = 0.6 (ethyl acetate:hexane, 1:9); ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.49 (s, 2H), 7.41-7.46 (m, 2H), 7.50-7.57 (m, 1H), 7.92 (dd, *J* = 1.22, 8.24 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 30.9, 128.8, 128.9, 133.9, 191.3.

References.

1) Y. Wei. S. Lin, F. Liang. *Org. Lett*. 2012, **14**, 4202.

2) F. W. Short, L. M. Long. *J. Heterocyclic Chem*, 1969, **6**, 707.

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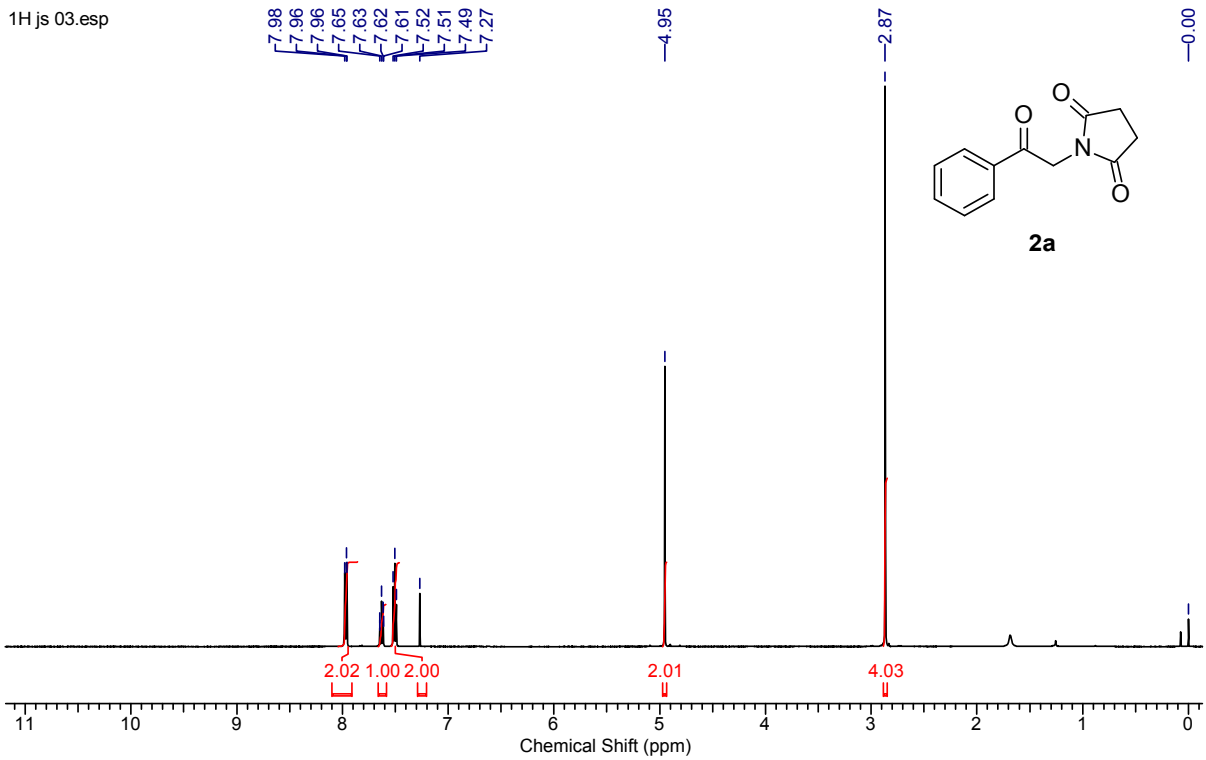
7) S. Guha, V. Rajeshkumar, S. S. Kotha, G. Sekar. *Org. Lett*. 2015, **17**, 406.

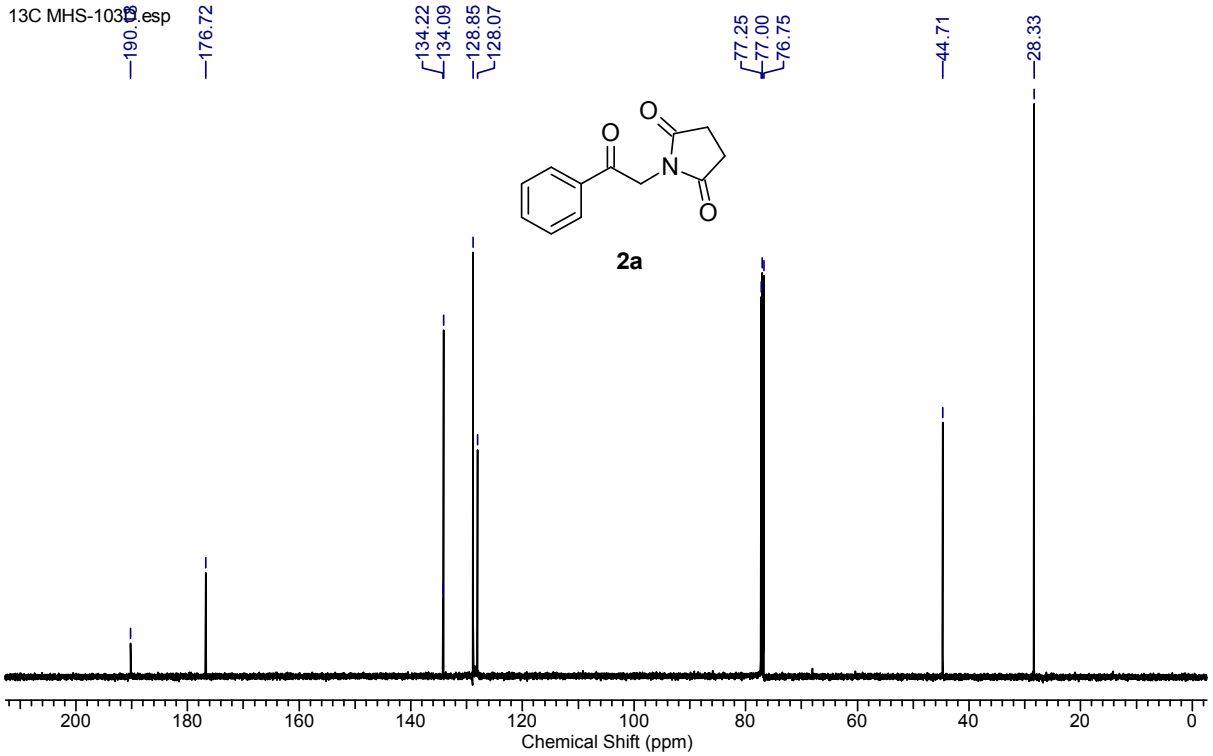
8) M. Fujita, T. Hiyama. *J. Org. Chem.*, 1988, **53**, 5405.

Copies of 1H and 13C NMR spectra:

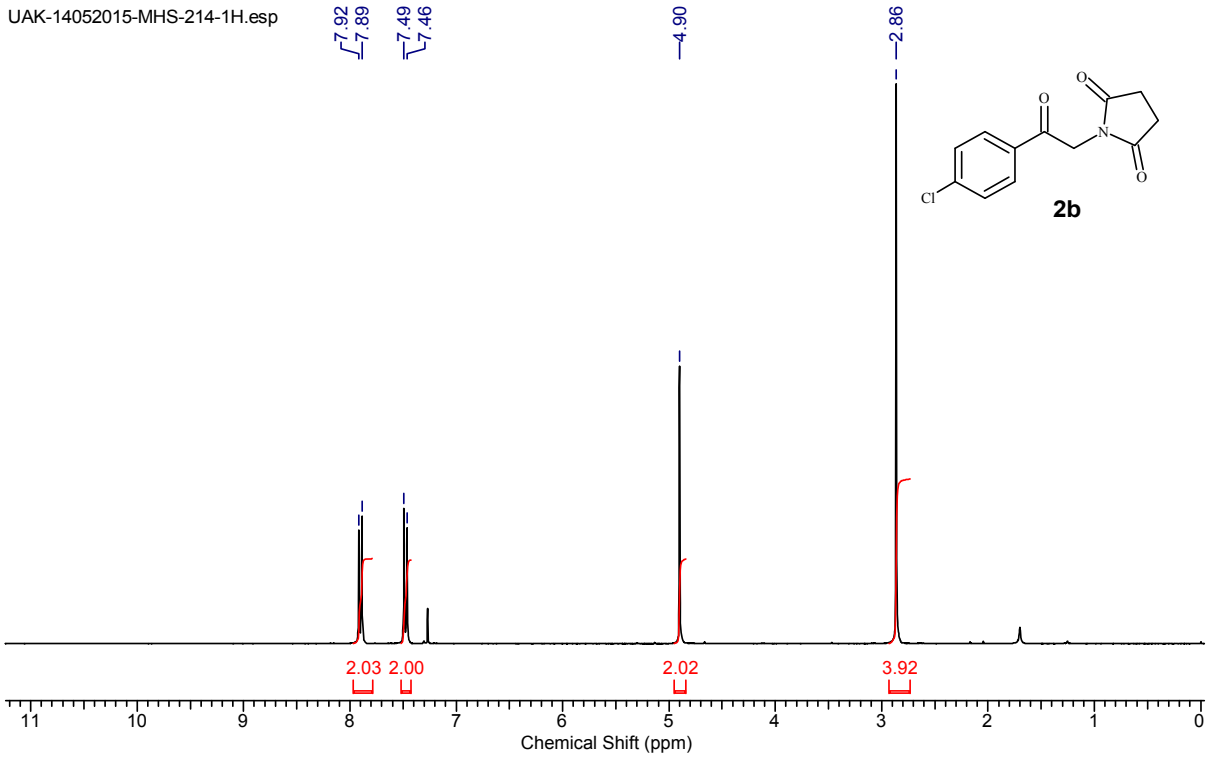
^{1}H NMR spectrum for compound **2a** ($CDCl_3$, 500 MHz)



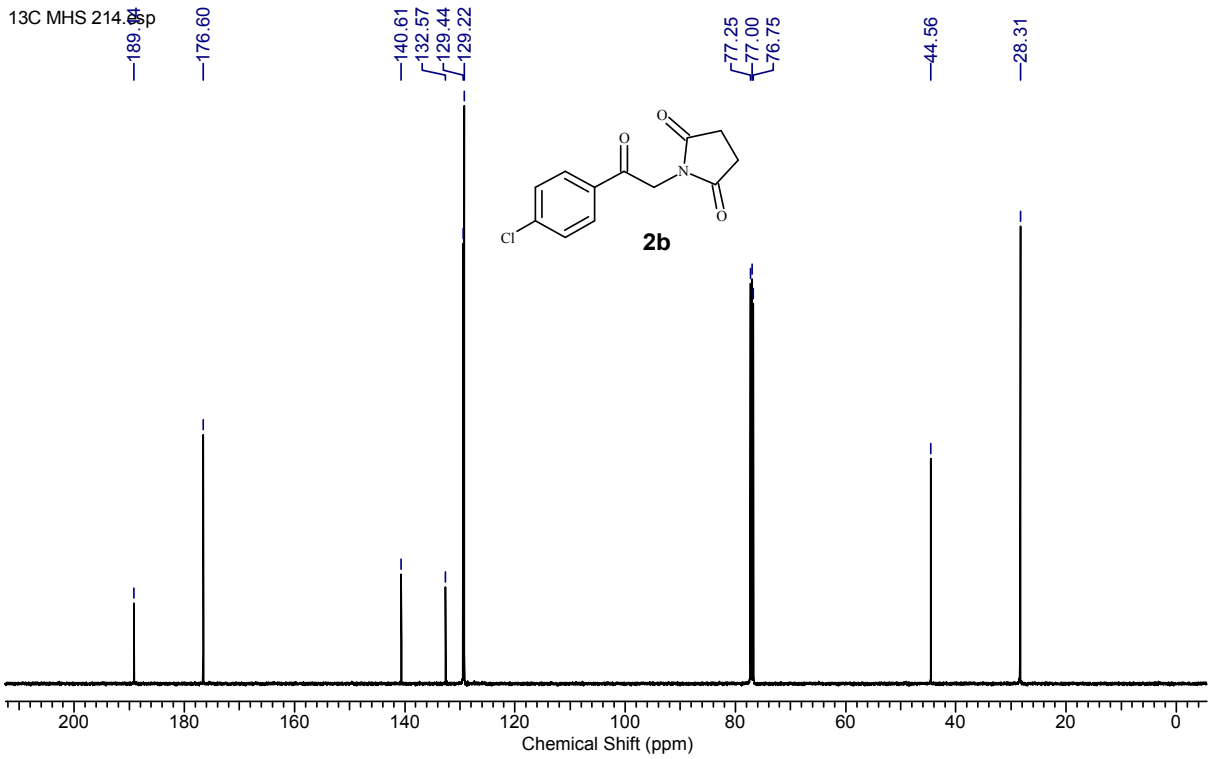
^{13}C NMR spectrum for compound **2a** ($CDCl_3$, 125 MHz)



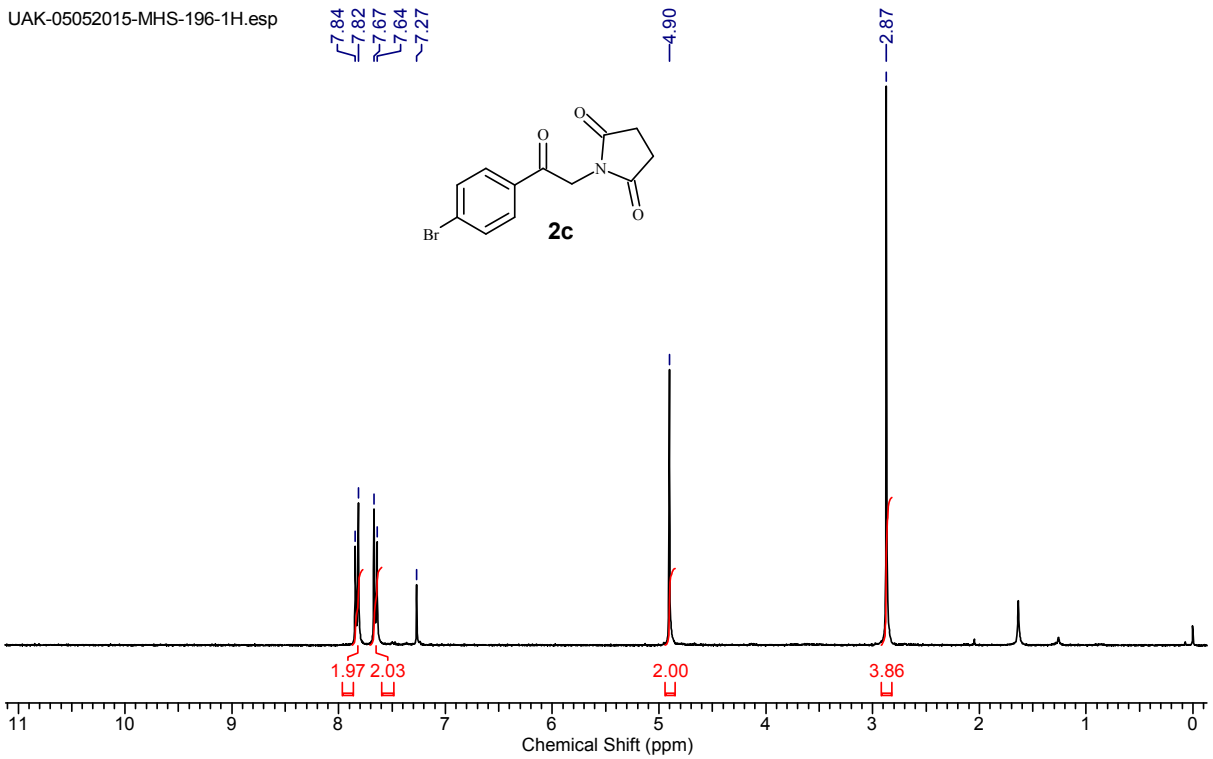
^{1}H NMR spectrum for compound **2b** ($CDCl_3$, 300 MHz)



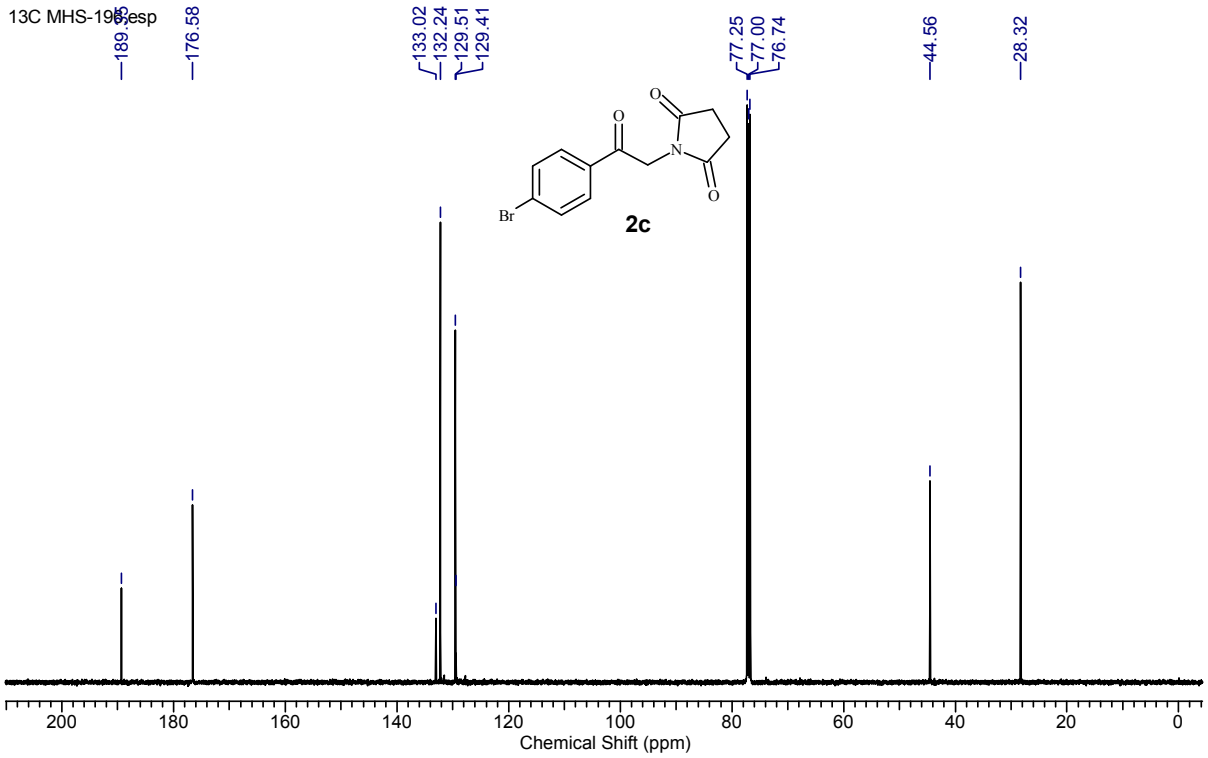
^{13}C NMR spectrum for compound **2b** ($CDCl_3$, 125 MHz)



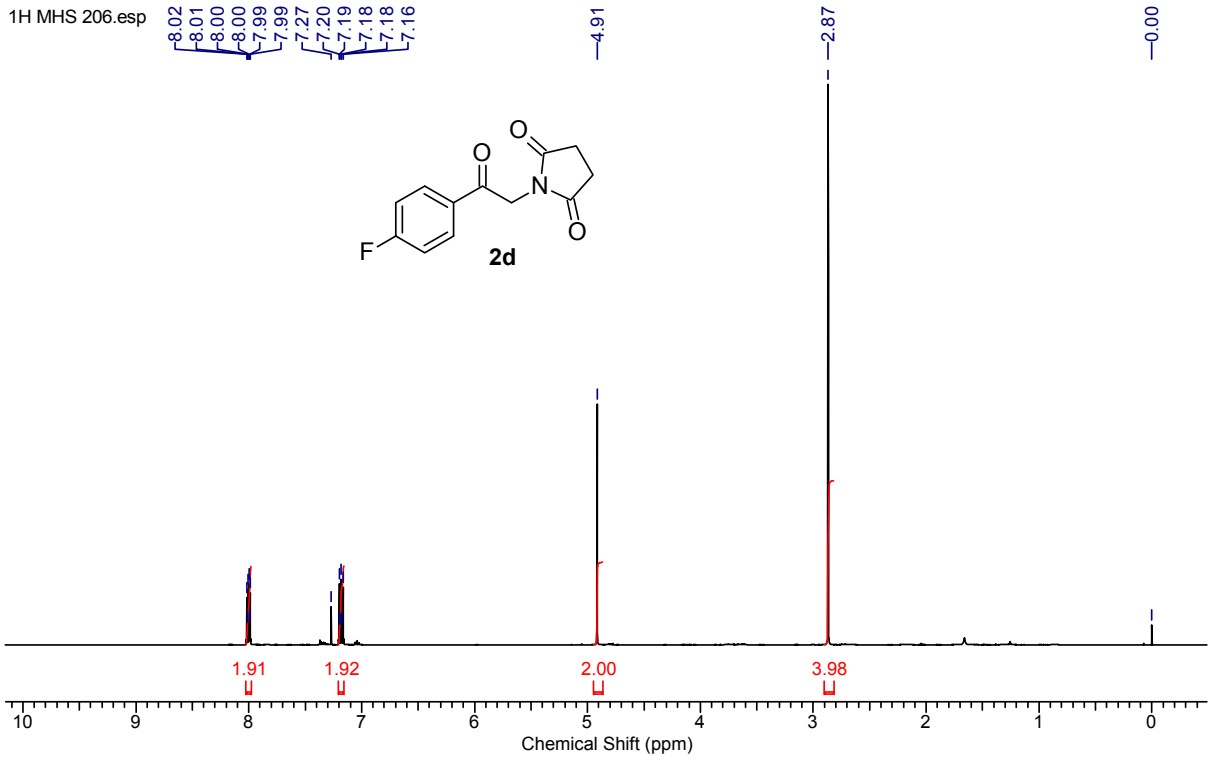
^{1}H NMR spectrum for compound **2c** ($CDCl_3$, 300 MHz)



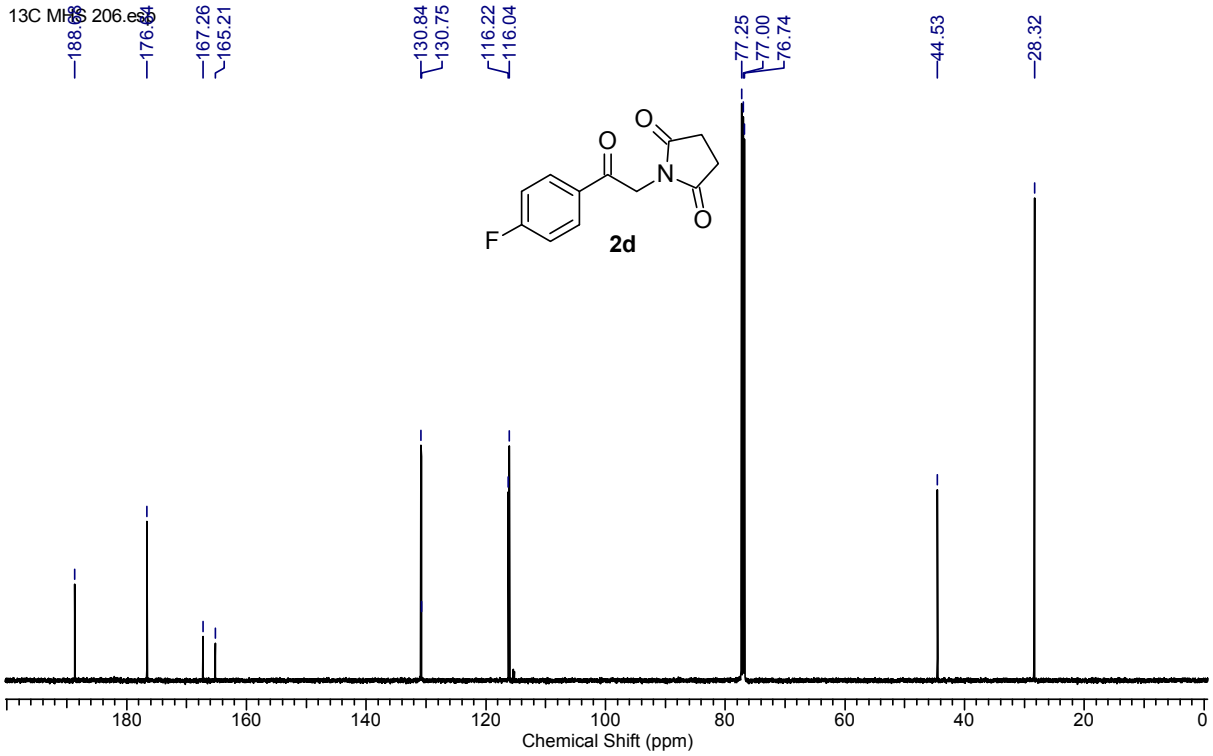
^{13}C NMR spectrum for compound **2c** ($CDCl_3$, 125 MHz)



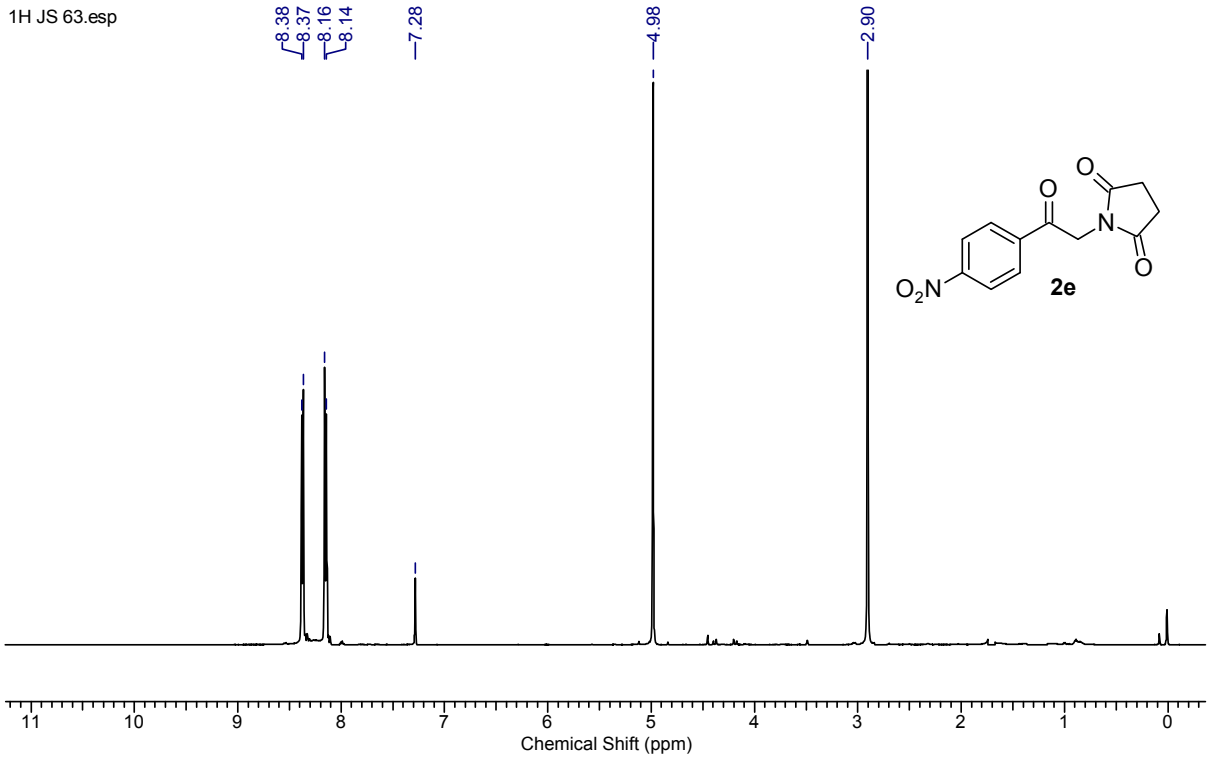
^{1}H NMR spectrum for compound **2d** ($CDCl_3$, 500 MHz)



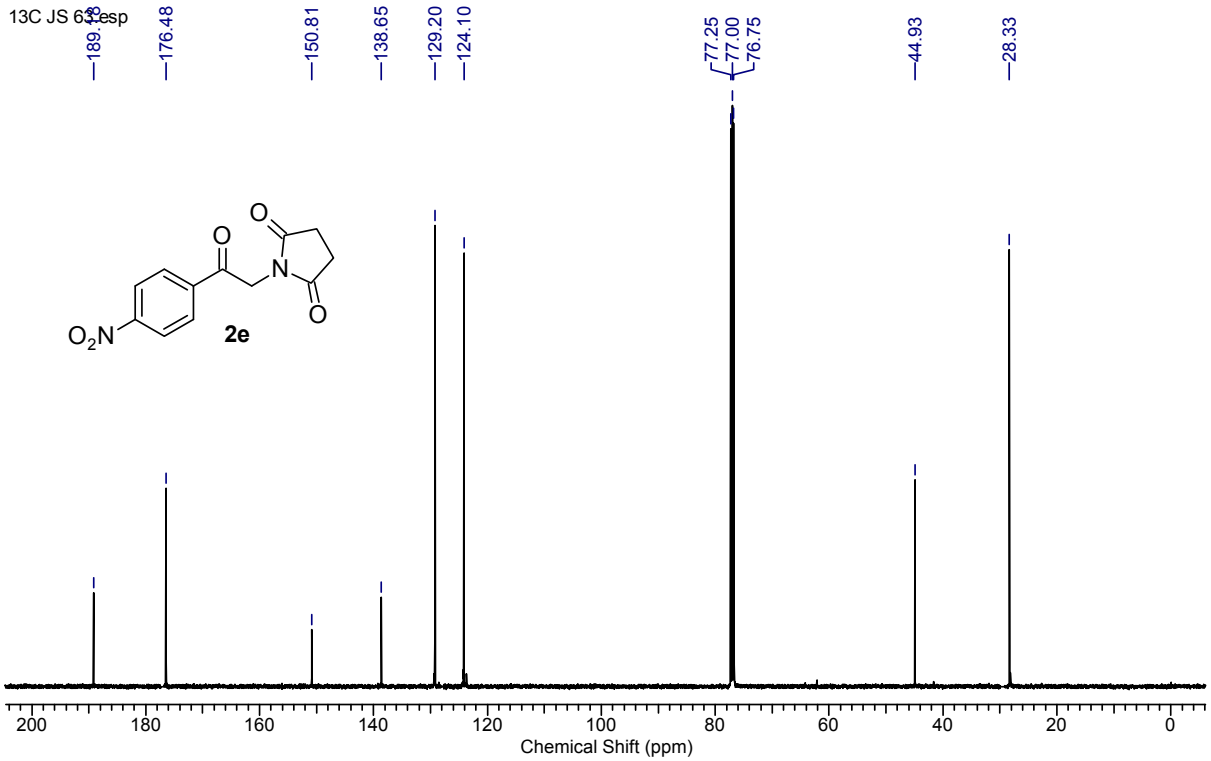
^{13}C NMR spectrum for compound **2d** ($CDCl_3$, 125 MHz)



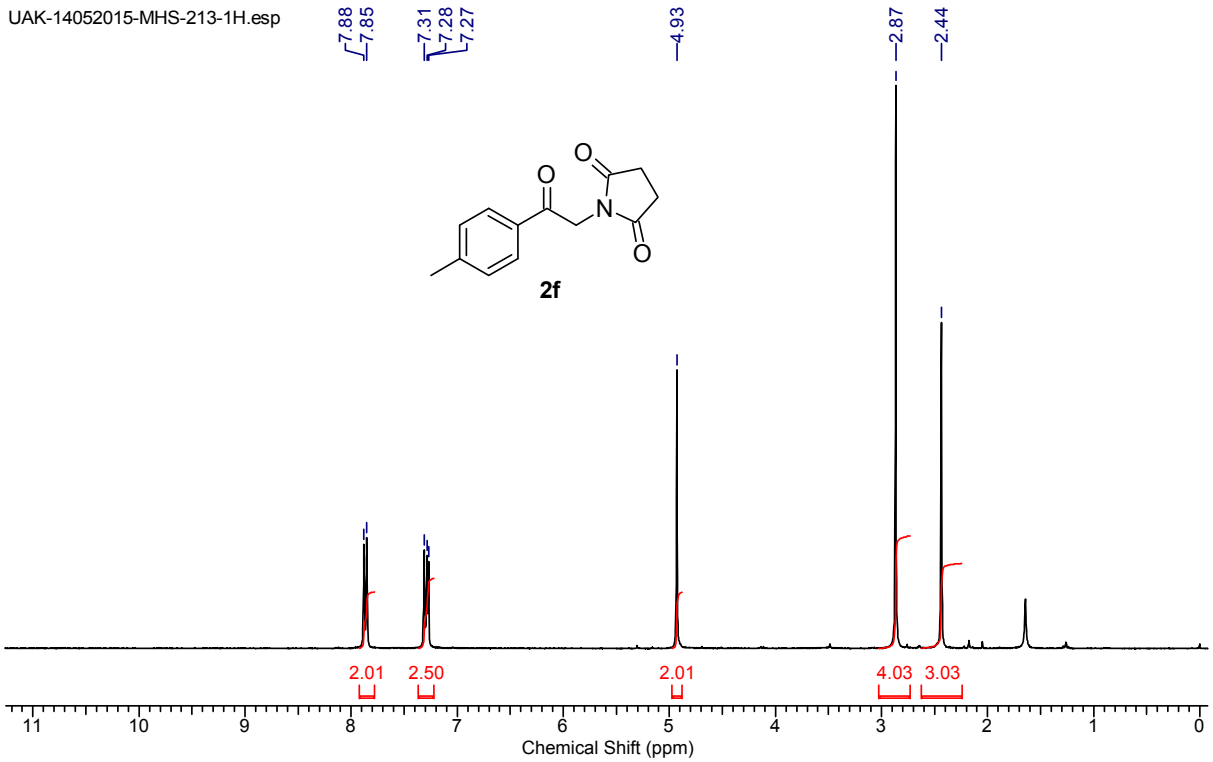
^{1}H NMR spectrum for compound **2e** ($CDCl_3$, 500 MHz)



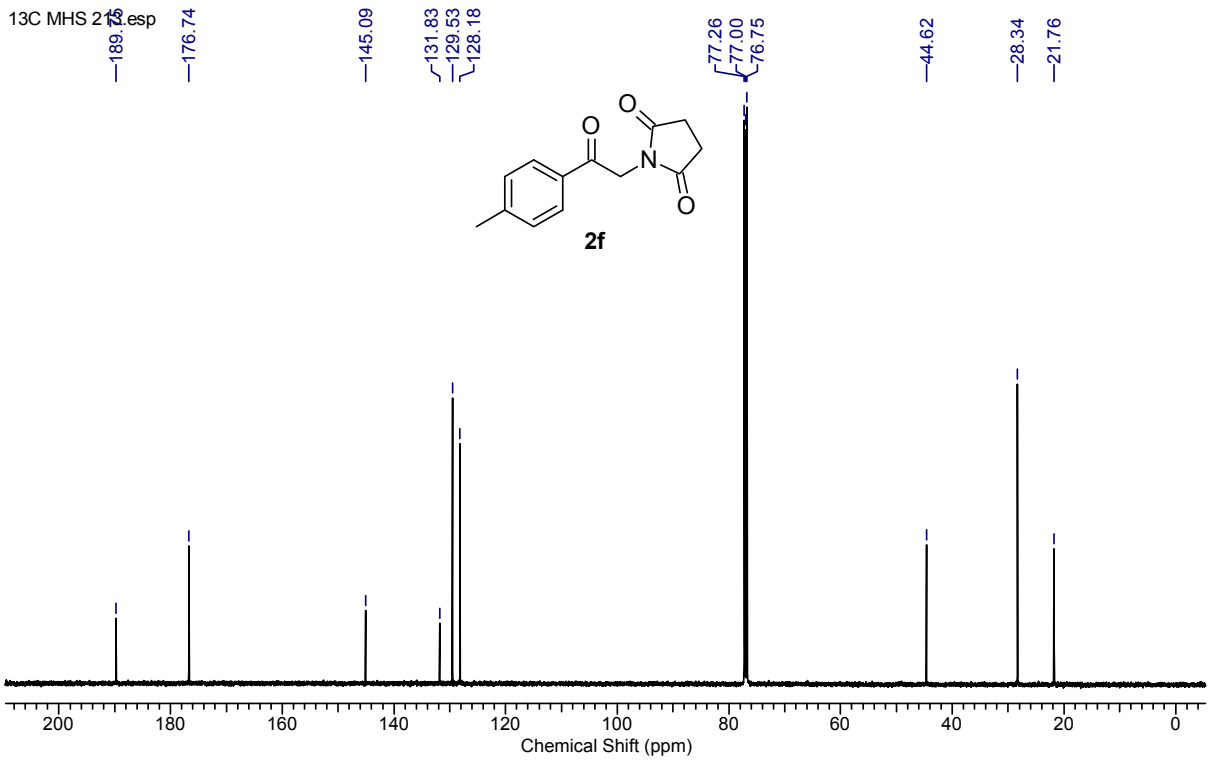
^{13}C NMR spectrum for compound **2e** ($CDCl_3$, 125 MHz)



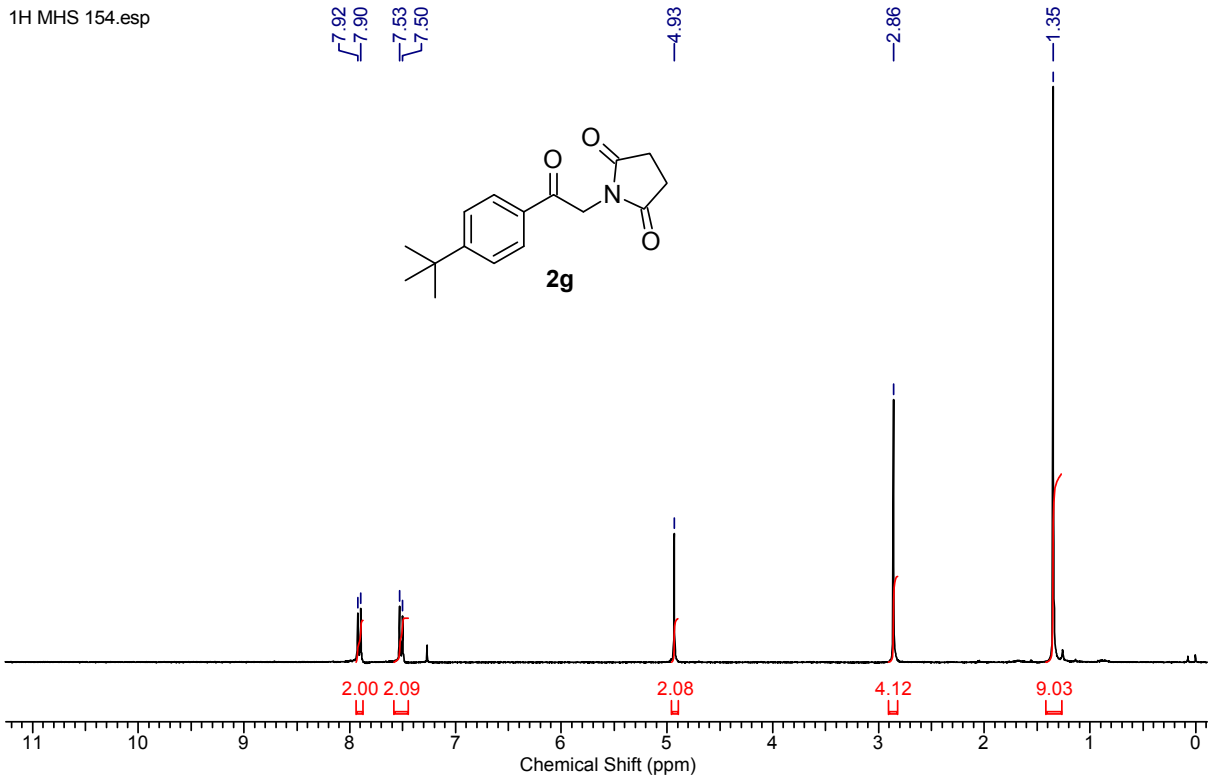
^{1}H NMR spectrum for compound **2f** ($CDCl_3$, 300 MHz)



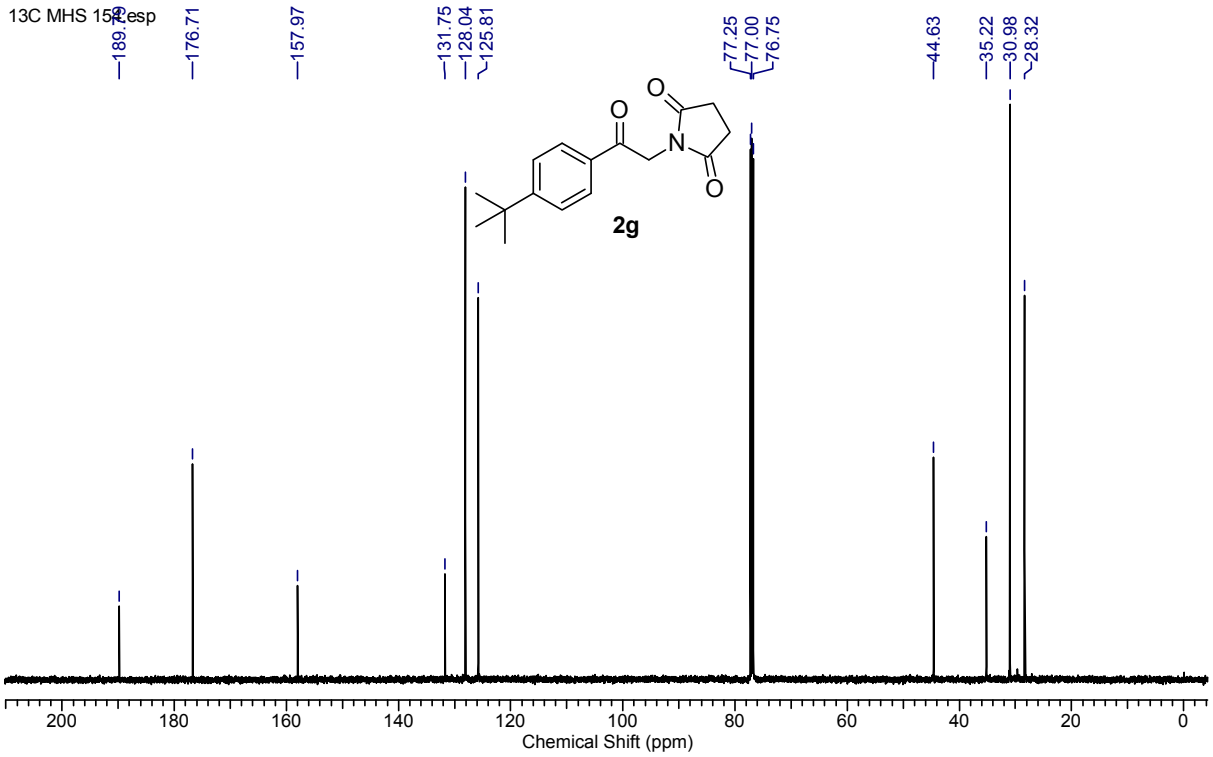
^{13}C NMR spectrum for compound **2f** ($CDCl_3$, 125 MHz)



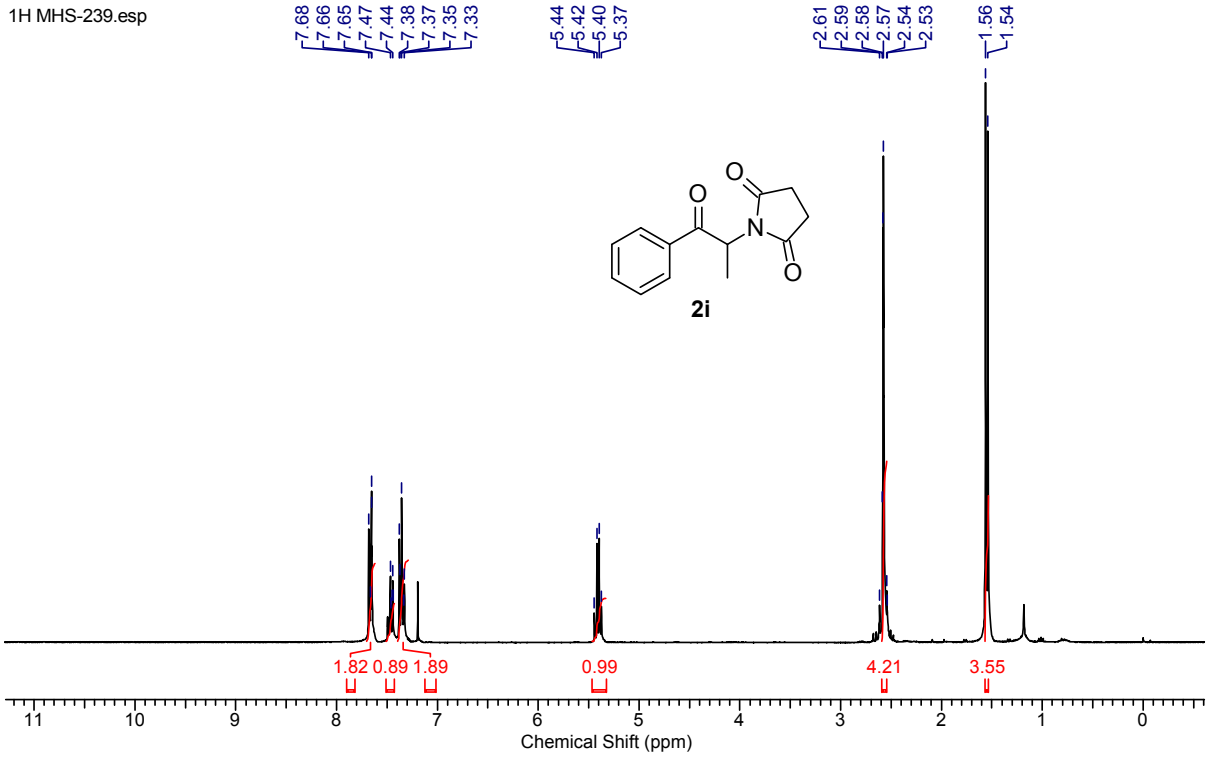
^{1}H NMR spectrum for compound **2g** ($CDCl_3$, 300 MHz)



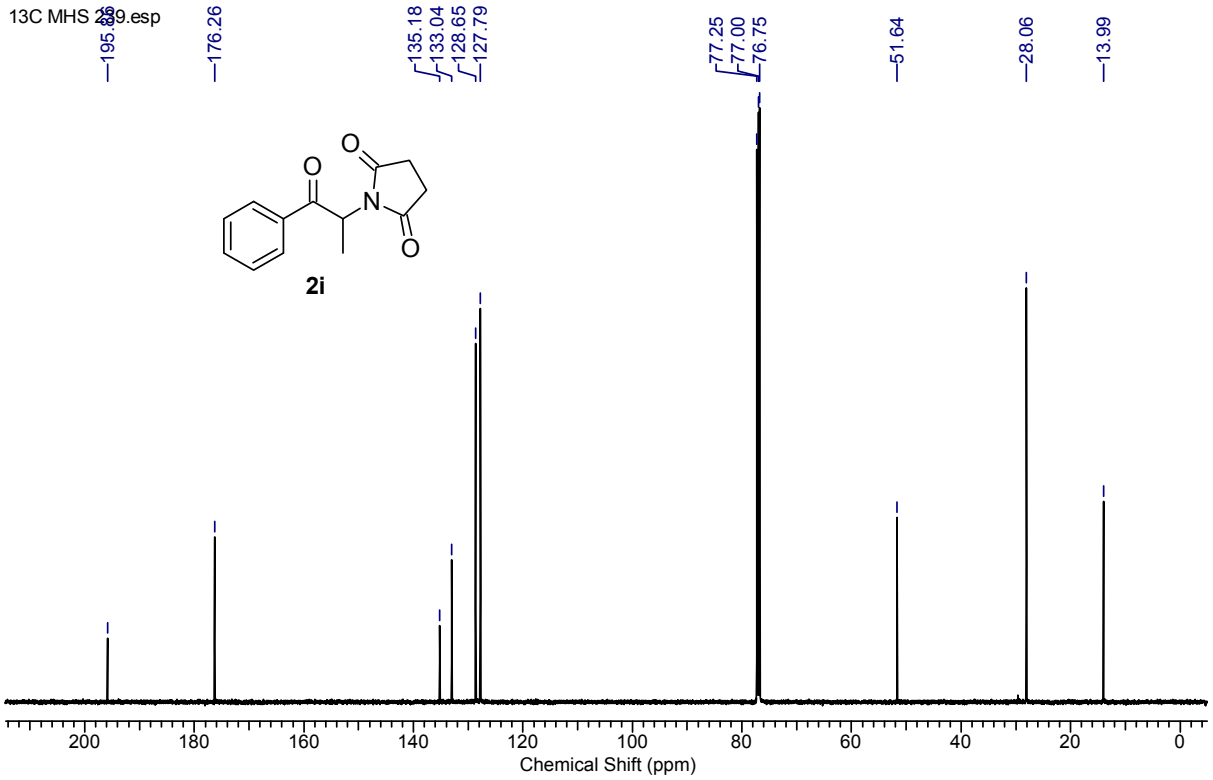
^{13}C NMR spectrum for compound **2g** ($CDCl_3$, 125 MHz)



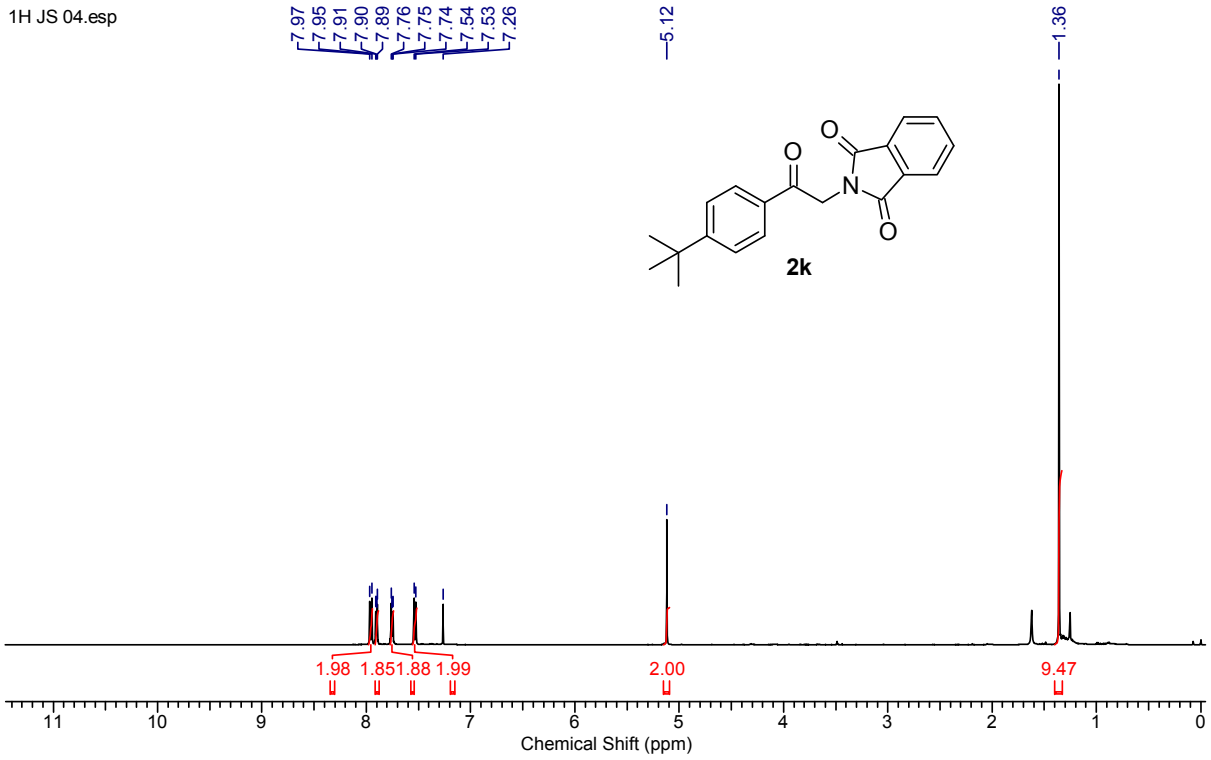
^{1}H NMR spectrum for compound **2i** ($CDCl_3$, 300 MHz)



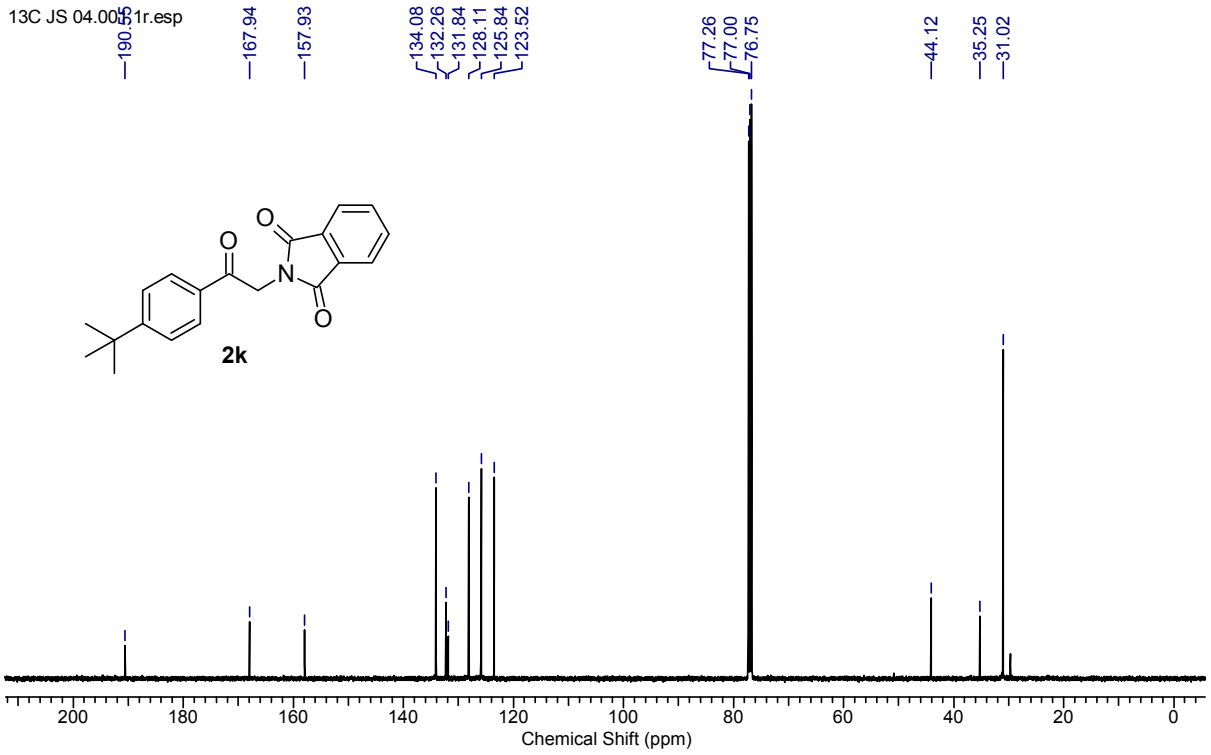
^{13}C NMR spectrum for compound **2i** ($CDCl_3$, 125 MHz)



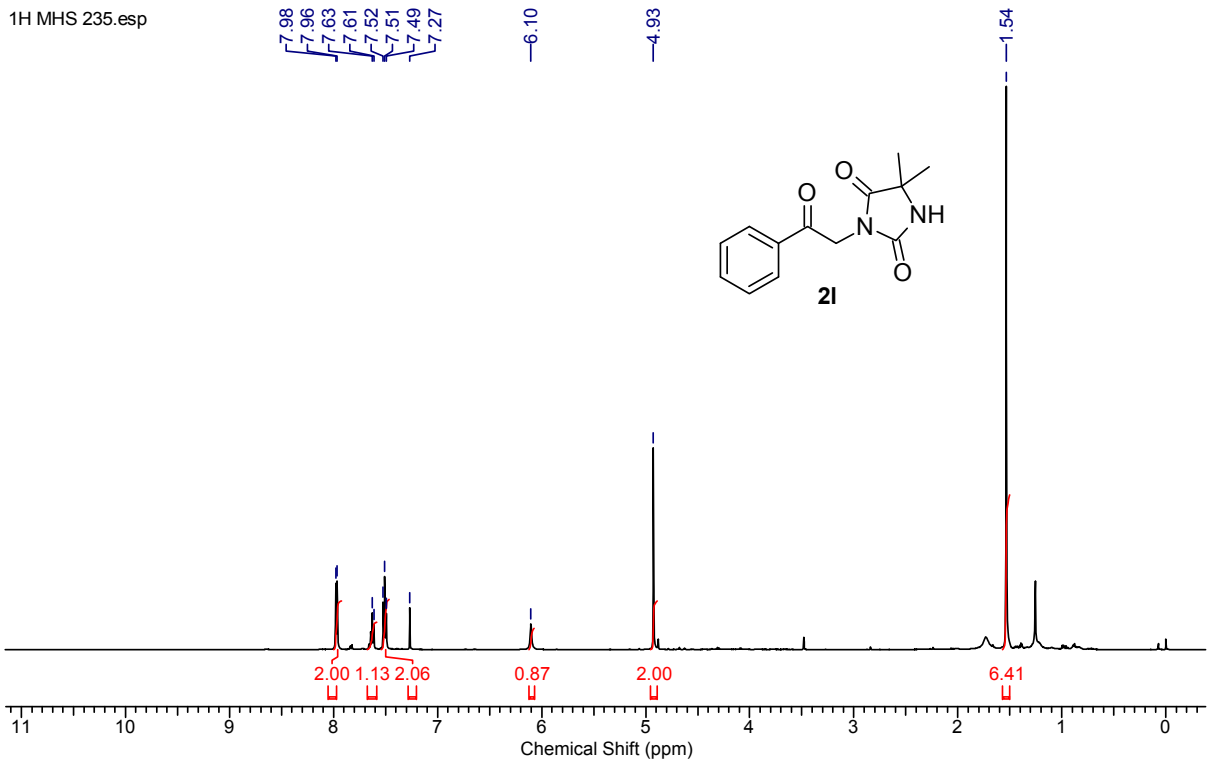
^{1}H NMR spectrum for compound **2k** ($CDCl_3$, 500 MHz)



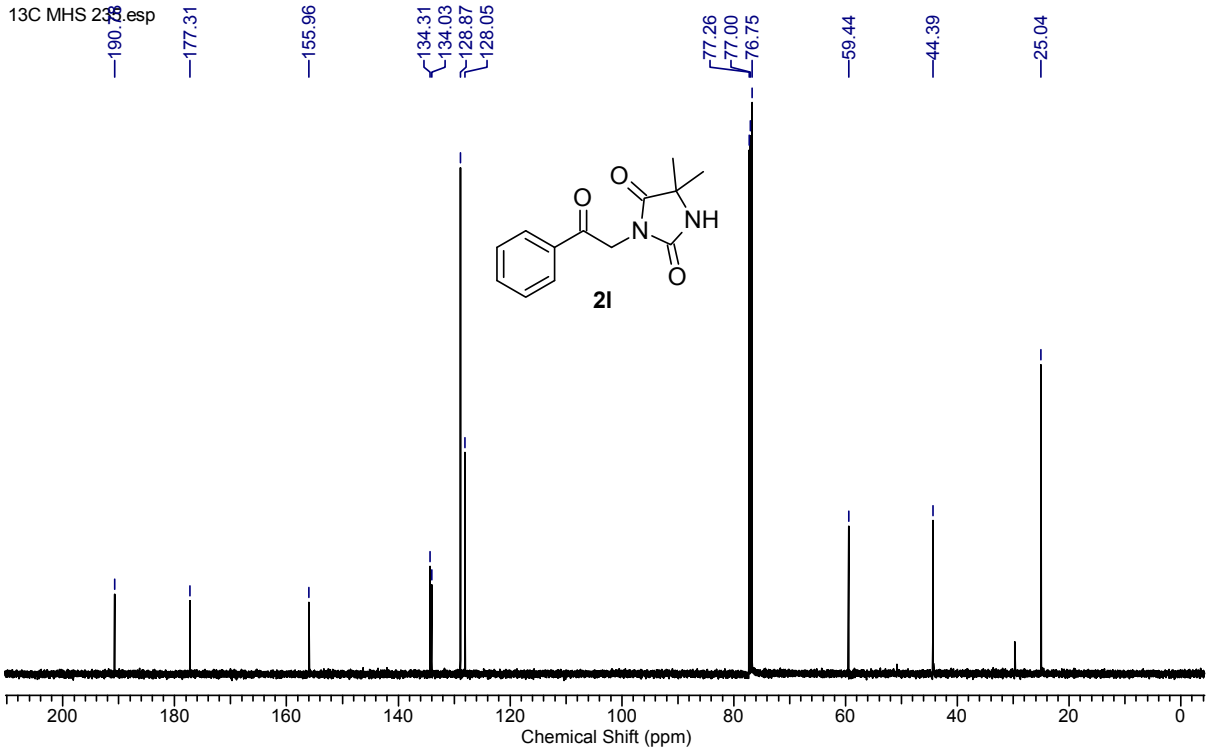
^{13}C NMR spectrum for compound **2k** ($CDCl_3$, 125 MHz)



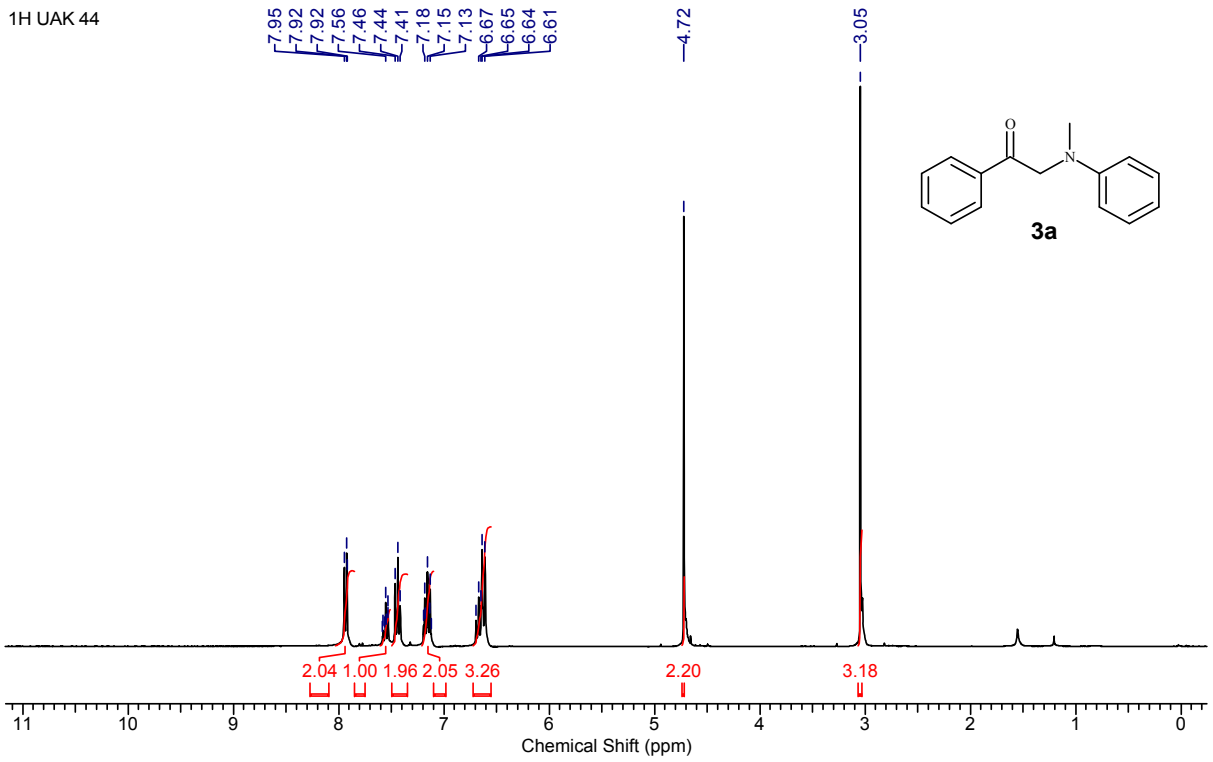
^{1}H NMR spectrum for compound **2l** ($CDCl_3$, 500 MHz)



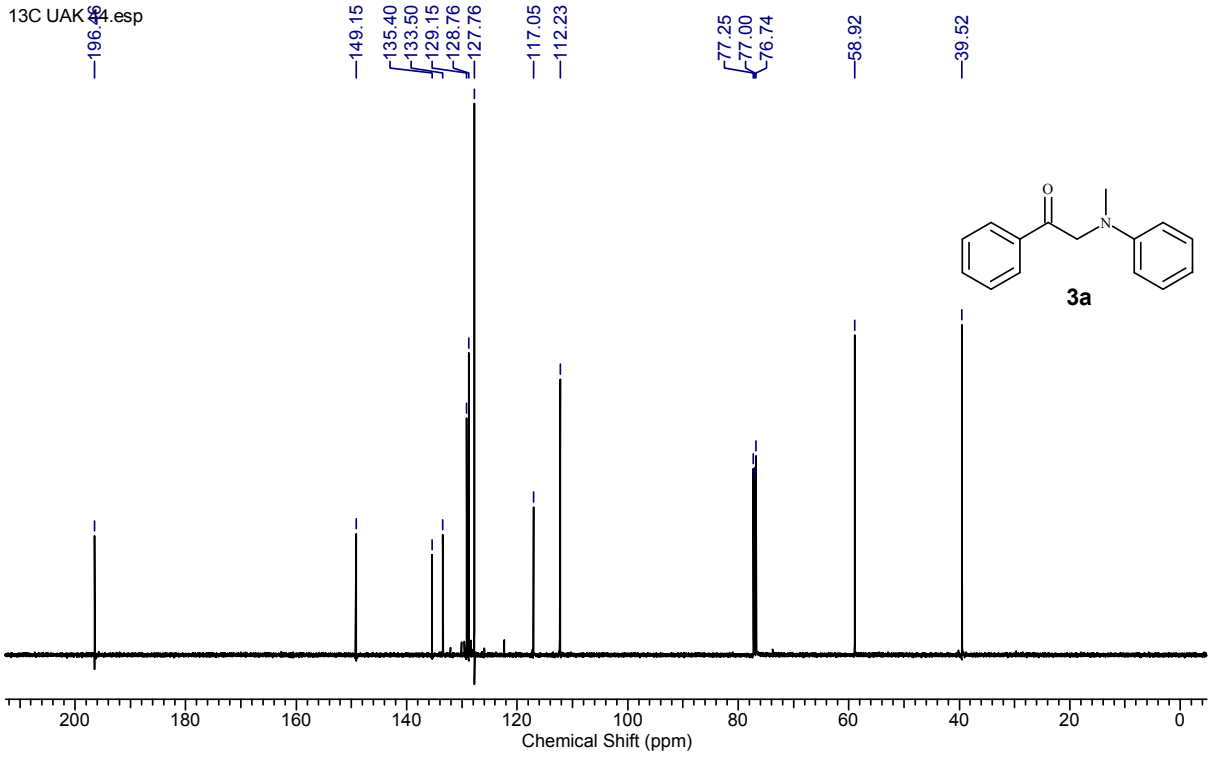
^{13}C NMR spectrum for compound **2l** ($CDCl_3$, 125 MHz)



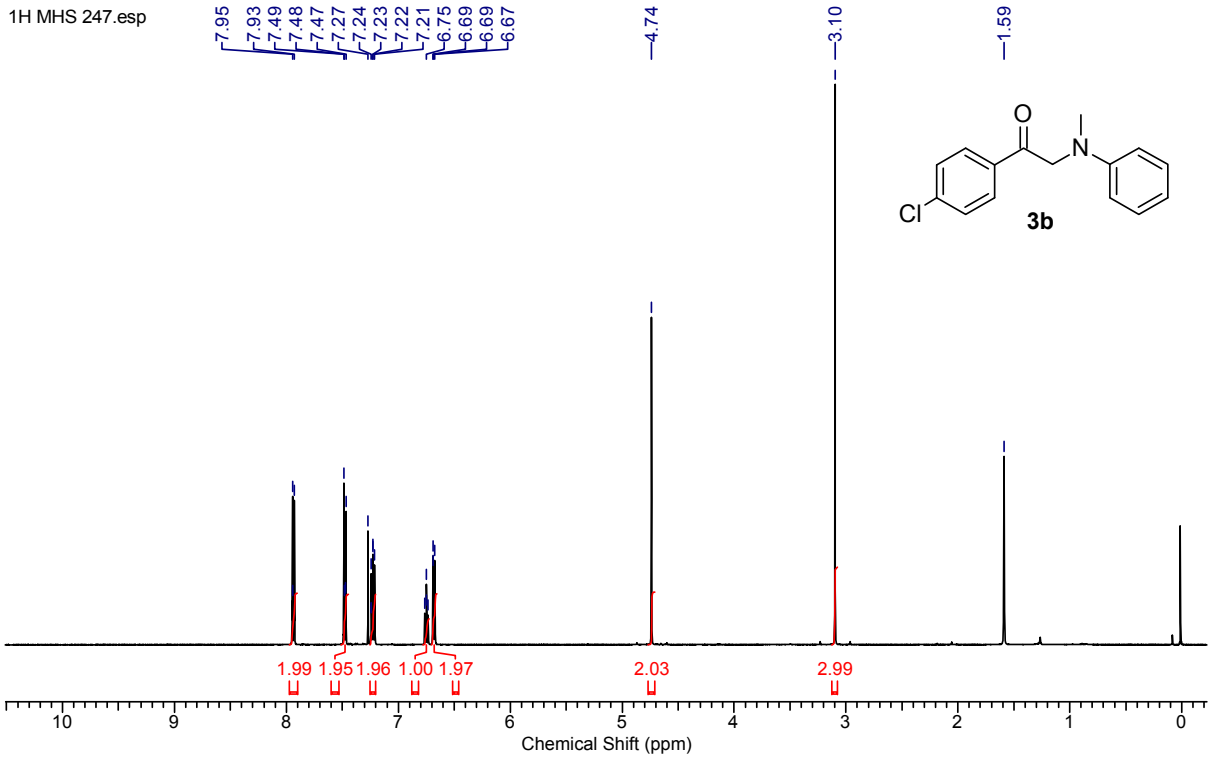
^{1}H NMR spectrum for compound **3a** ($CDCl_3$, 300 MHz)



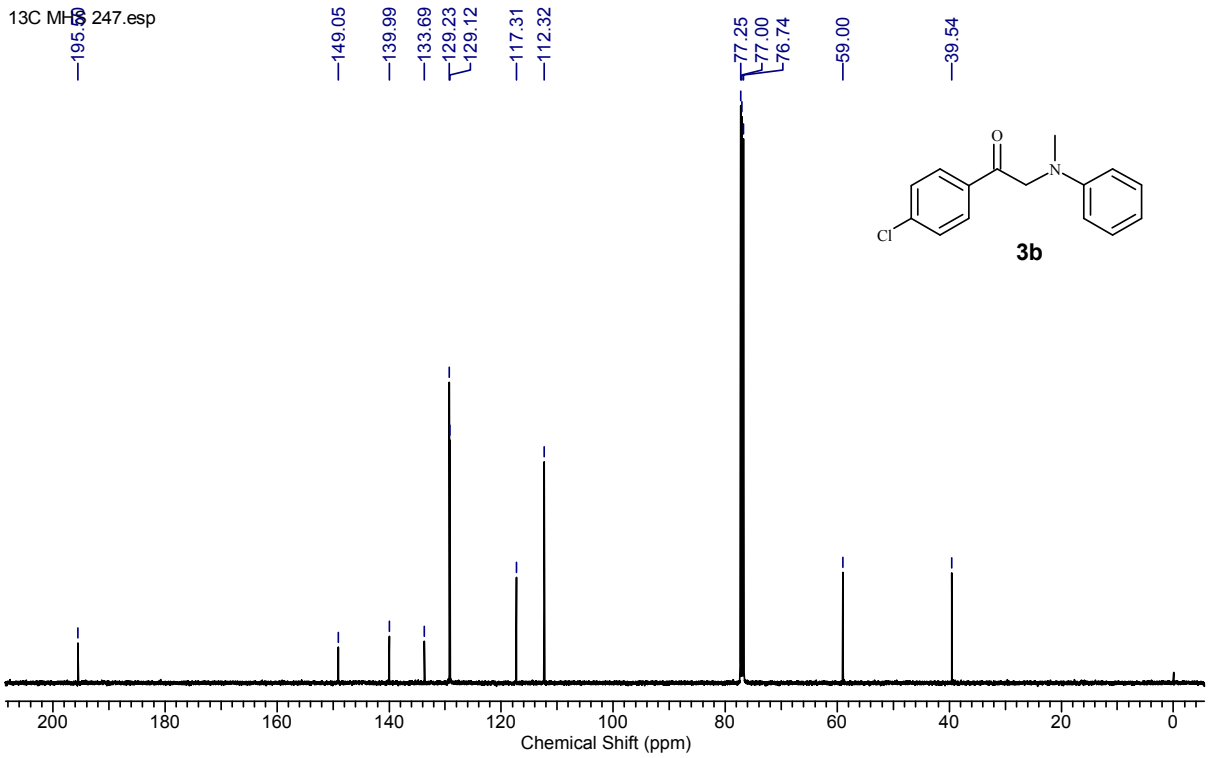
^{13}C NMR spectrum for compound **3a** ($CDCl_3$, 125 MHz)



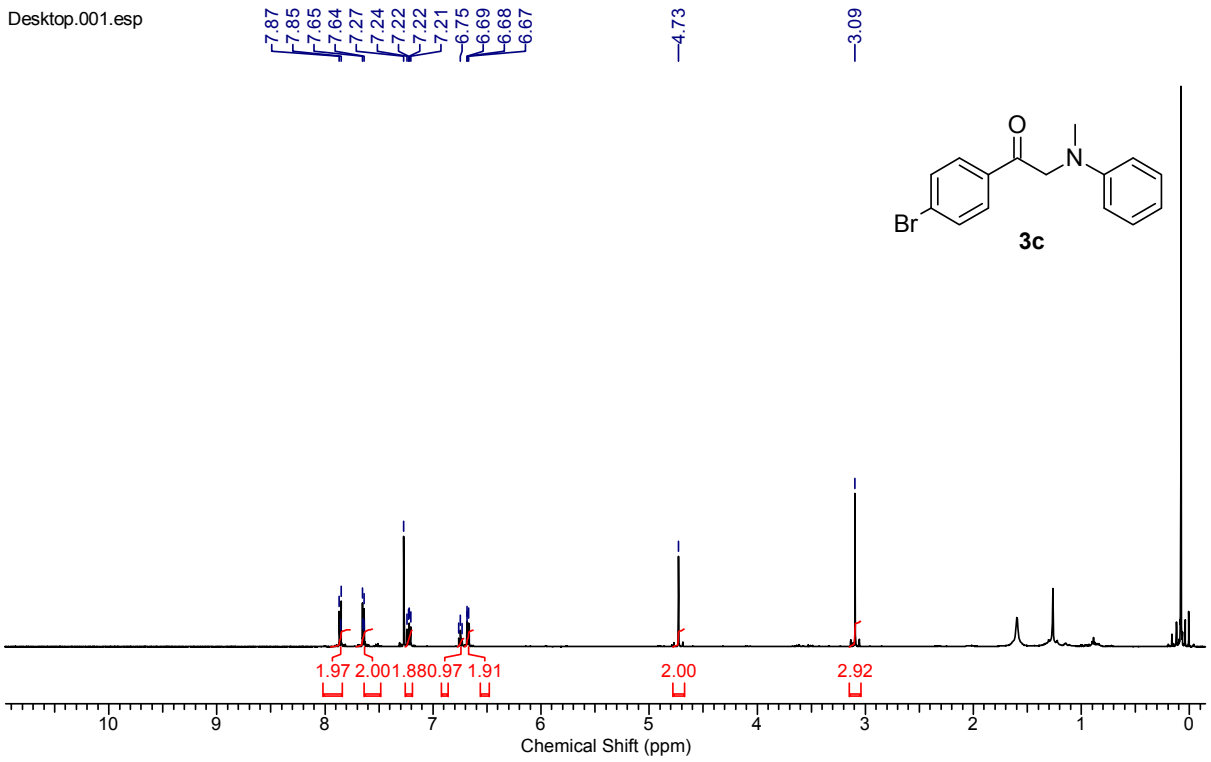
^{1}H NMR spectrum for compound **3b** ($CDCl_3$, 500 MHz)



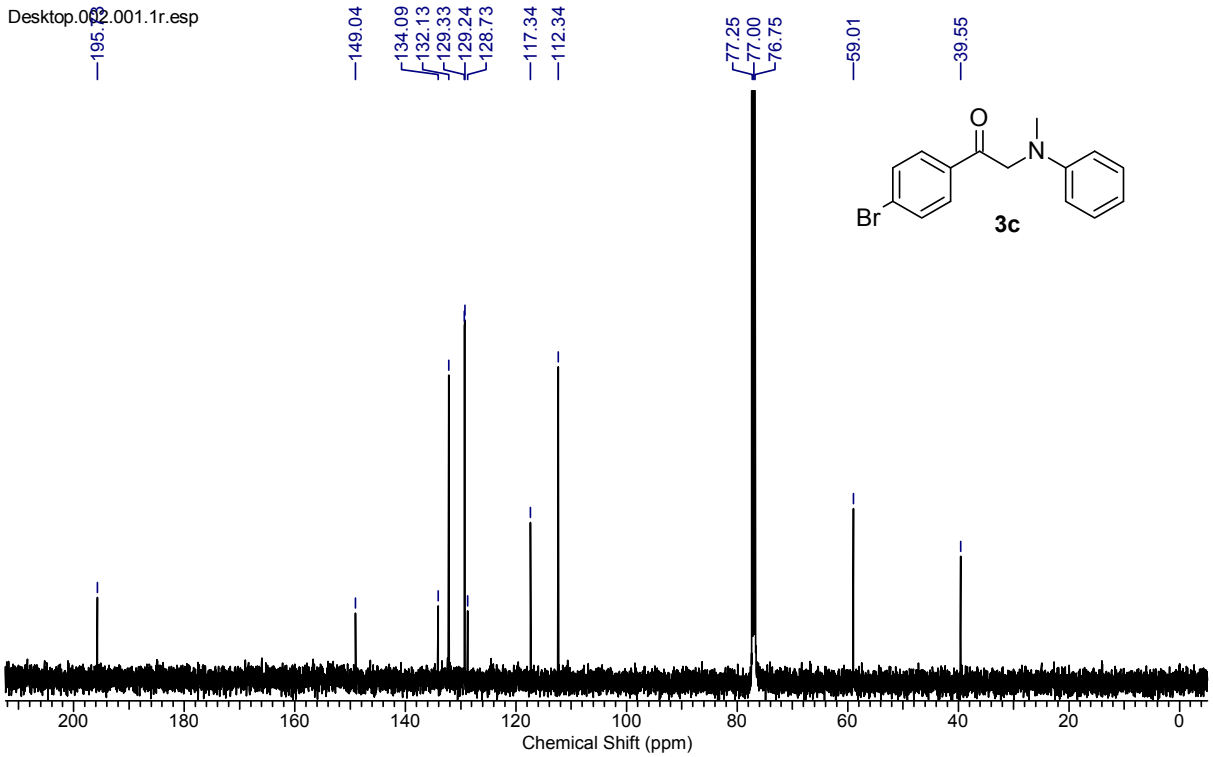
^{13}C NMR spectrum for compound **3b** ($CDCl_3$, 125 MHz)



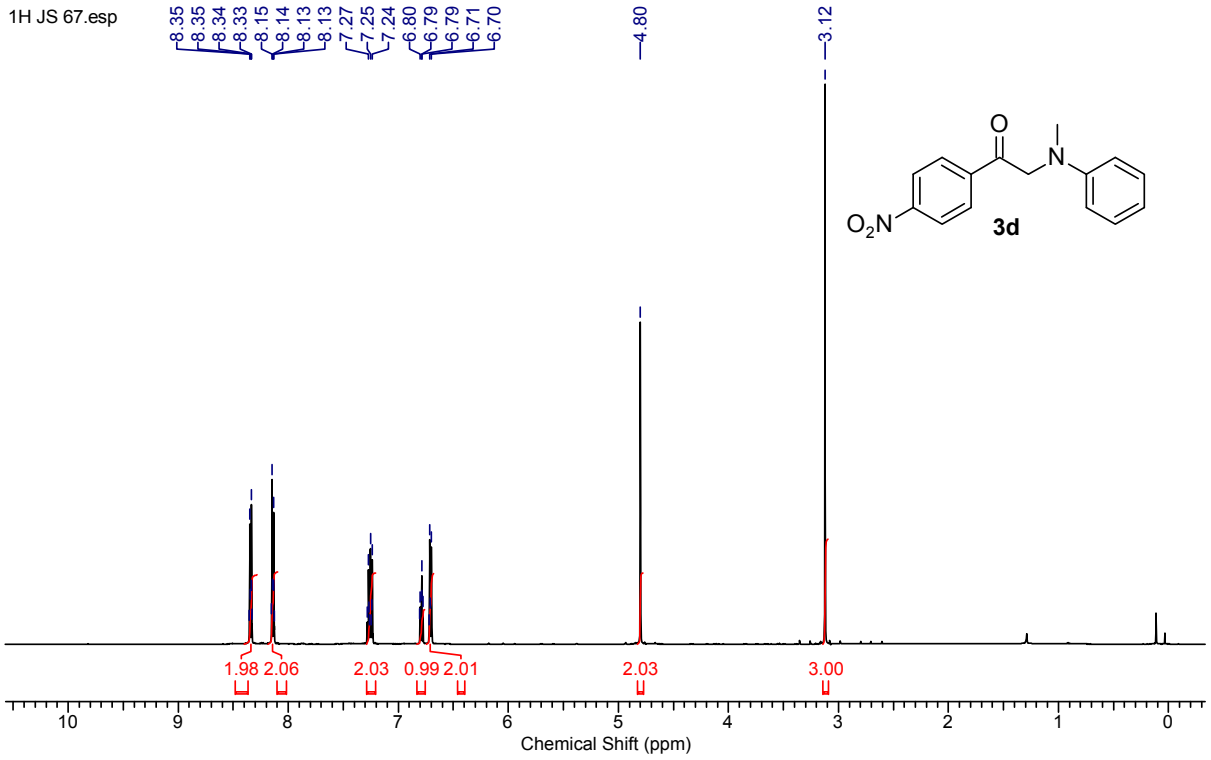
^{1}H NMR spectrum for compound **3c** ($CDCl_3$, 500 MHz)



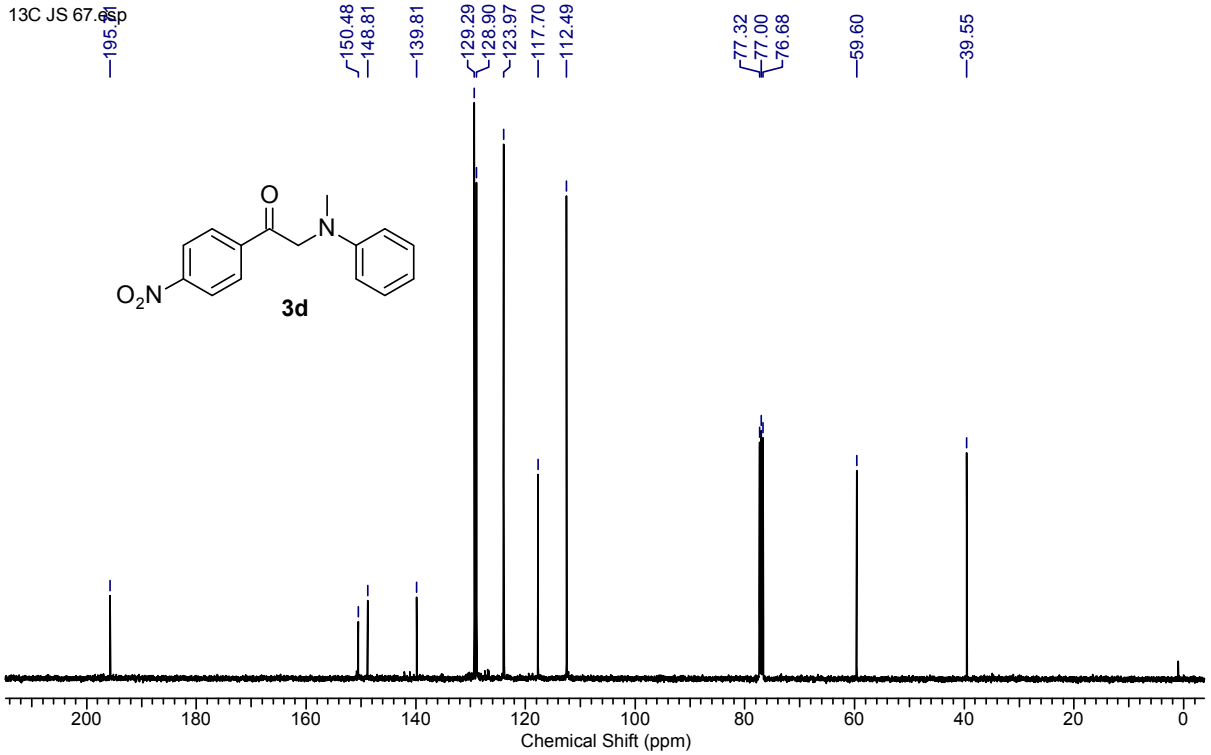
^{13}C NMR spectrum for compound **3c** ($CDCl_3$, 125 MHz)



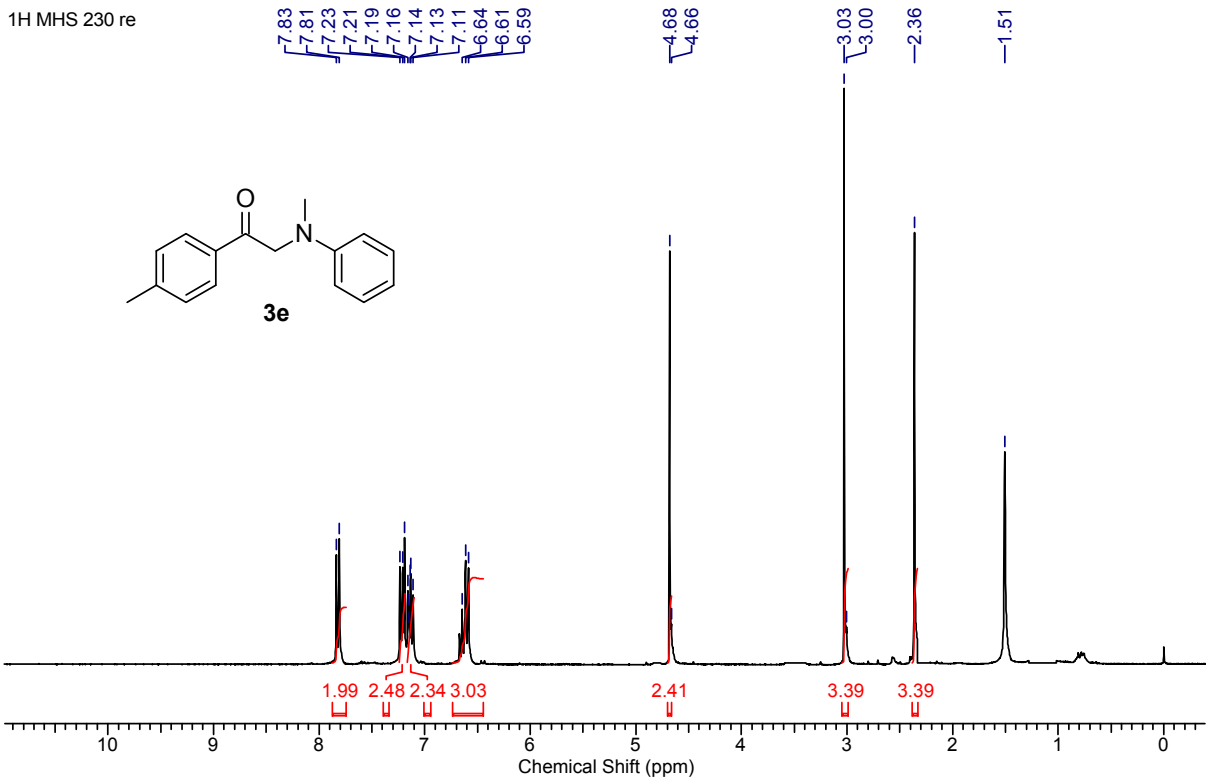
^{1}H NMR spectrum for compound **3d** ($CDCl_3$, 500 MHz)



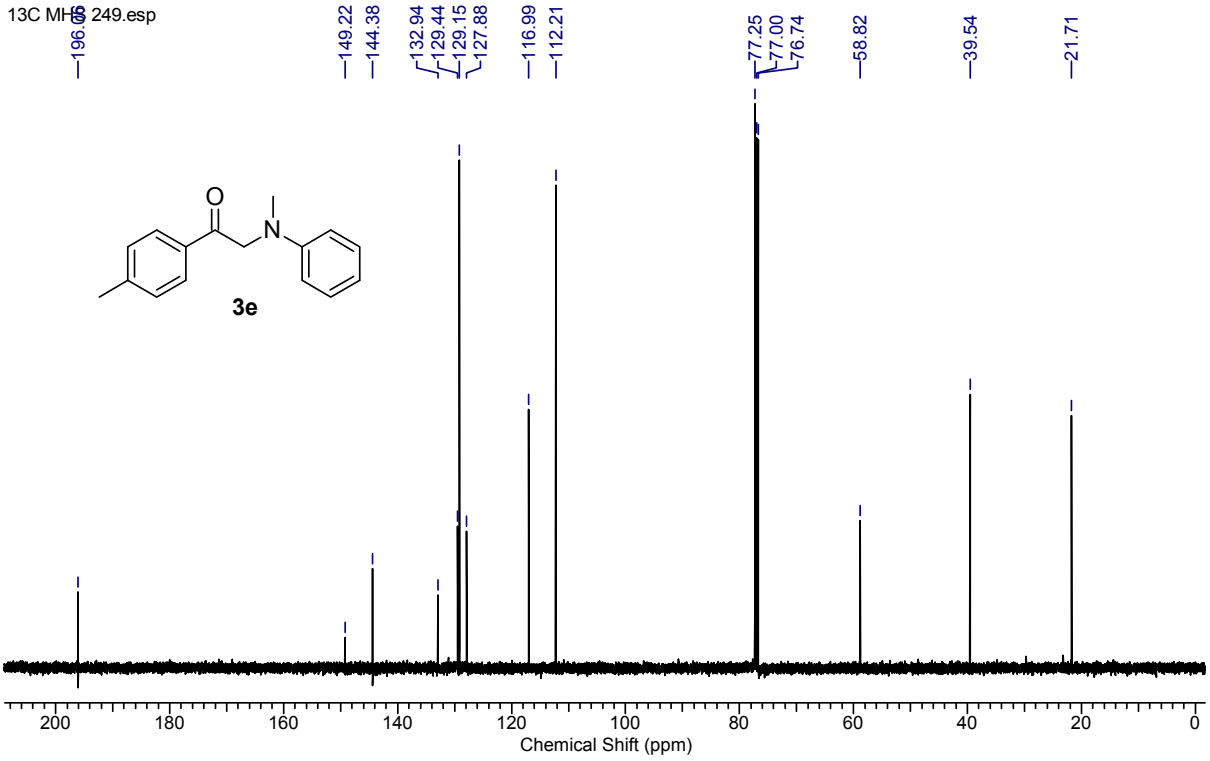
^{13}C NMR spectrum for compound **3d** ($CDCl_3$, 100 MHz)



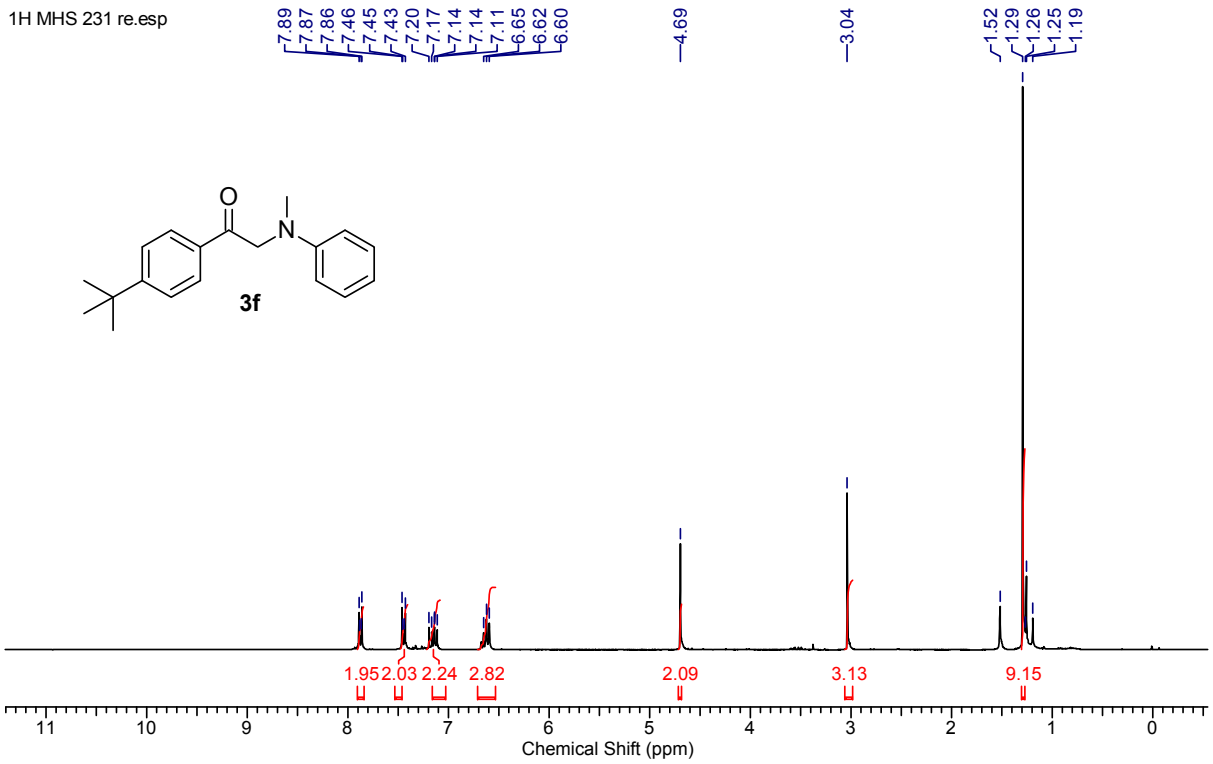
^{1}H NMR spectrum for compound **3e** ($CDCl_3$, 500 MHz)



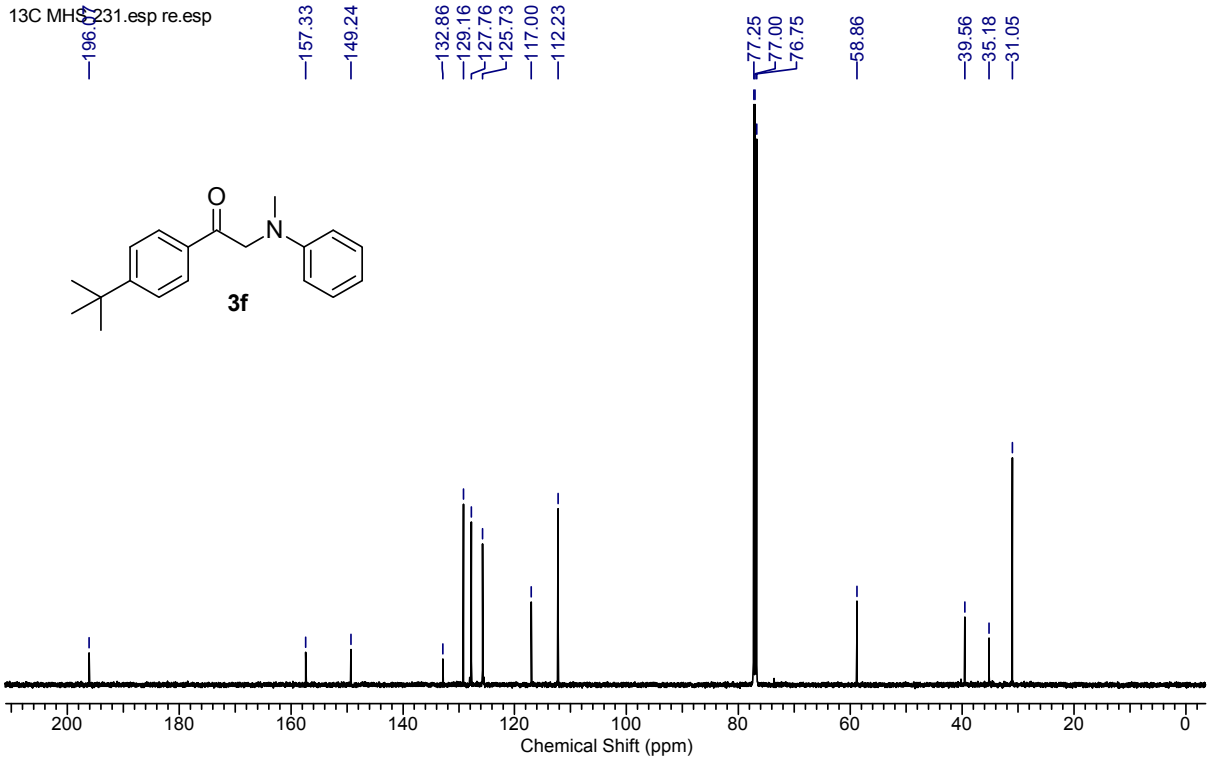
^{13}C NMR spectrum for compound **3e** ($CDCl_3$, 125 MHz)



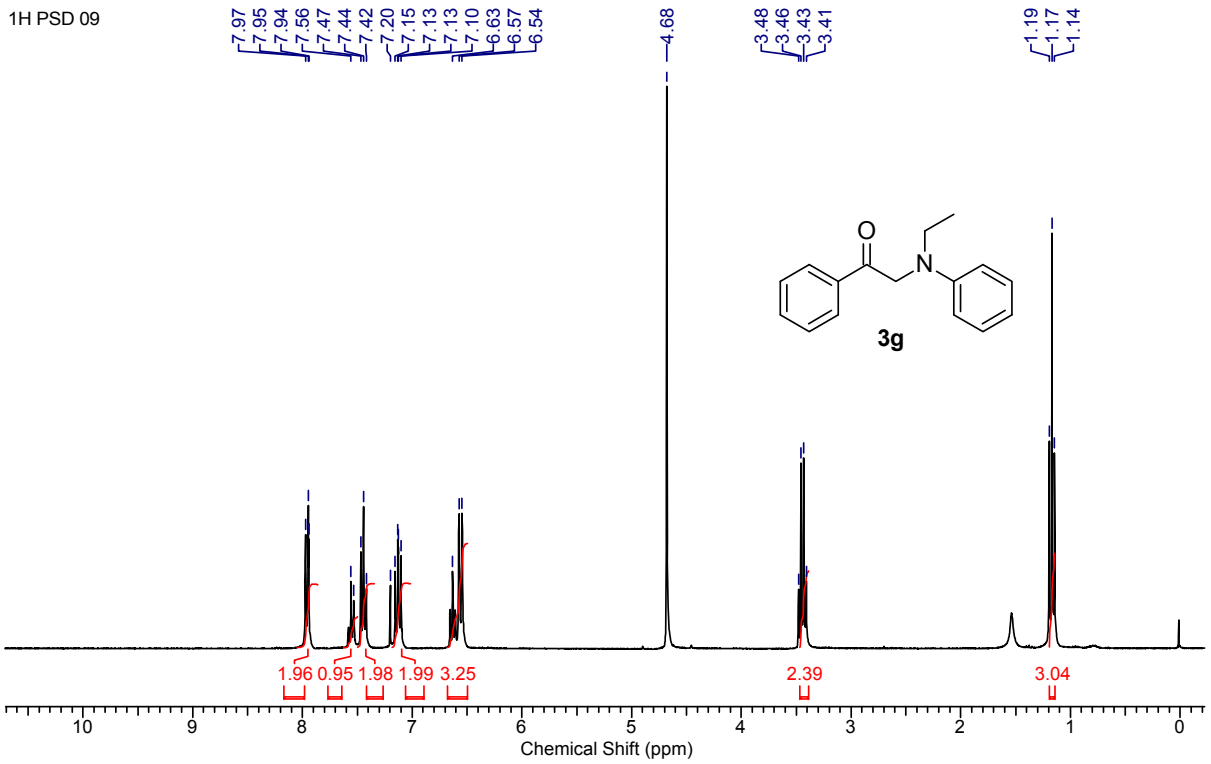
^{1}H NMR spectrum for compound **3f** ($CDCl_3$, 300 MHz)



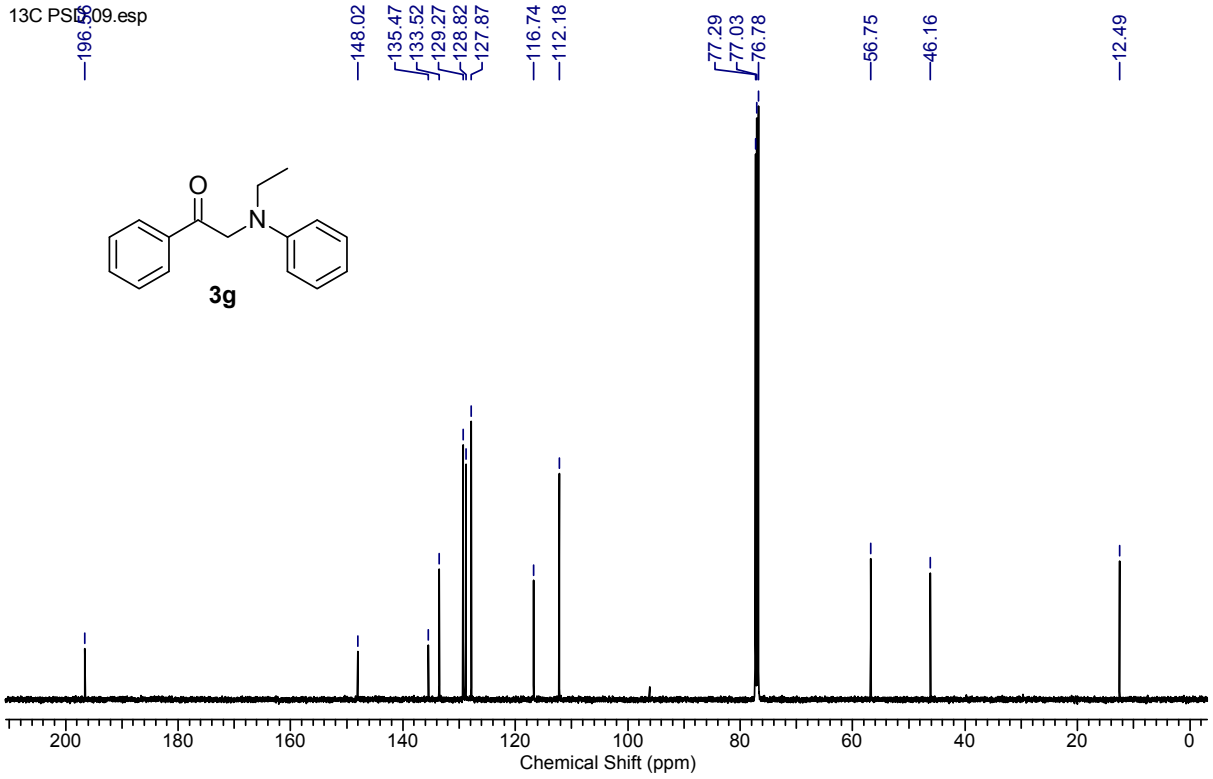
^{13}C NMR spectrum for compound **3f** ($CDCl_3$, 125 MHz)



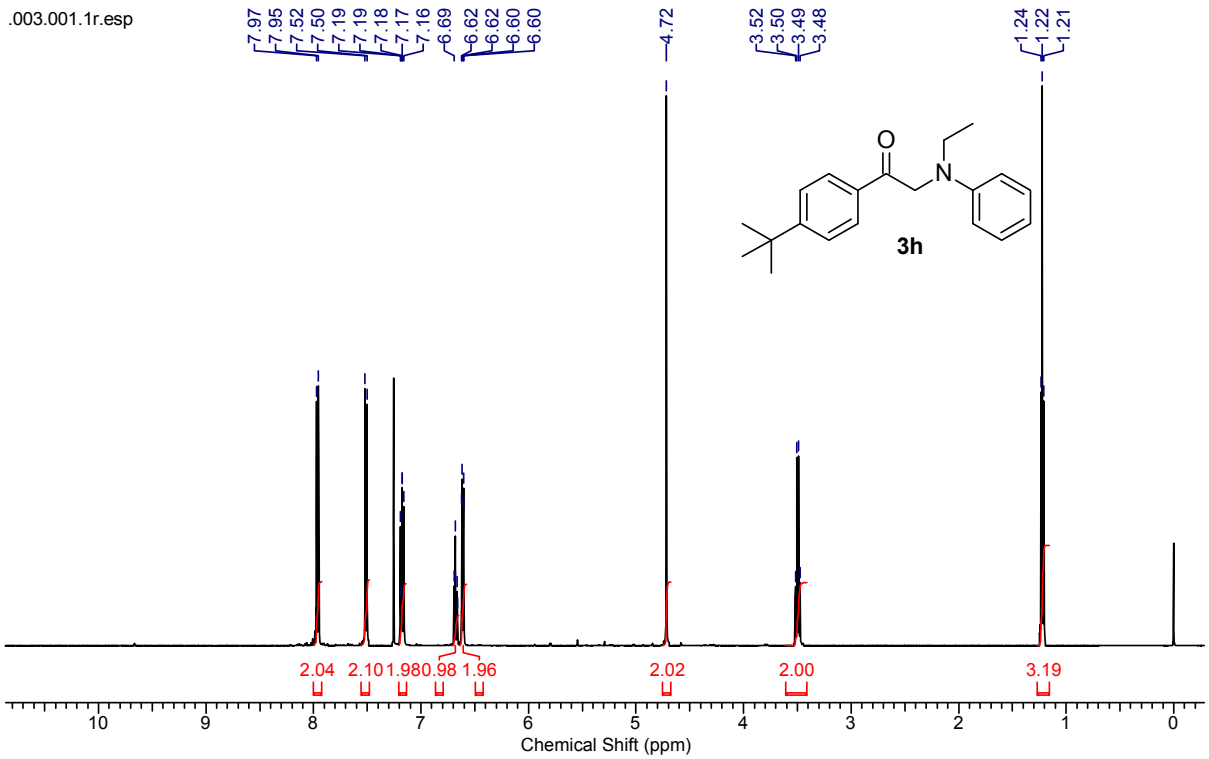
^{1}H NMR spectrum for compound **3g** ($CDCl_3$, 300 MHz)



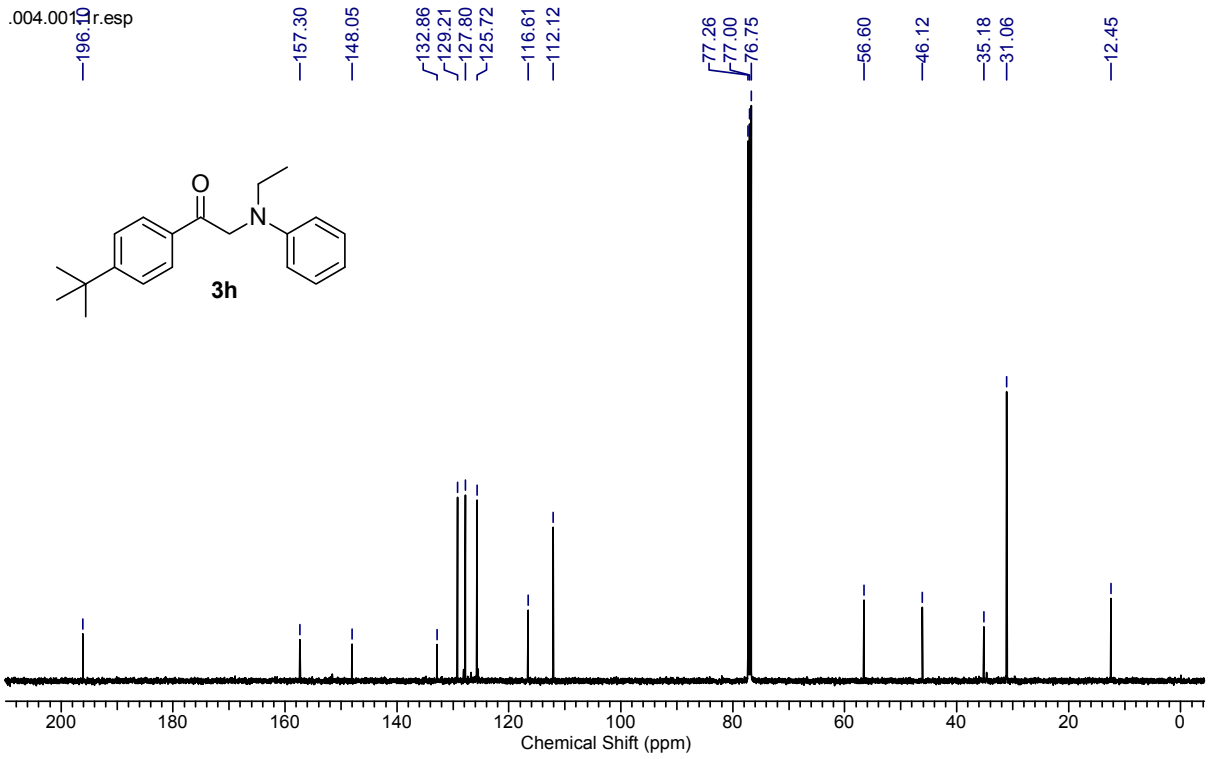
^{13}C NMR spectrum for compound **3g** ($CDCl_3$, 125 MHz)



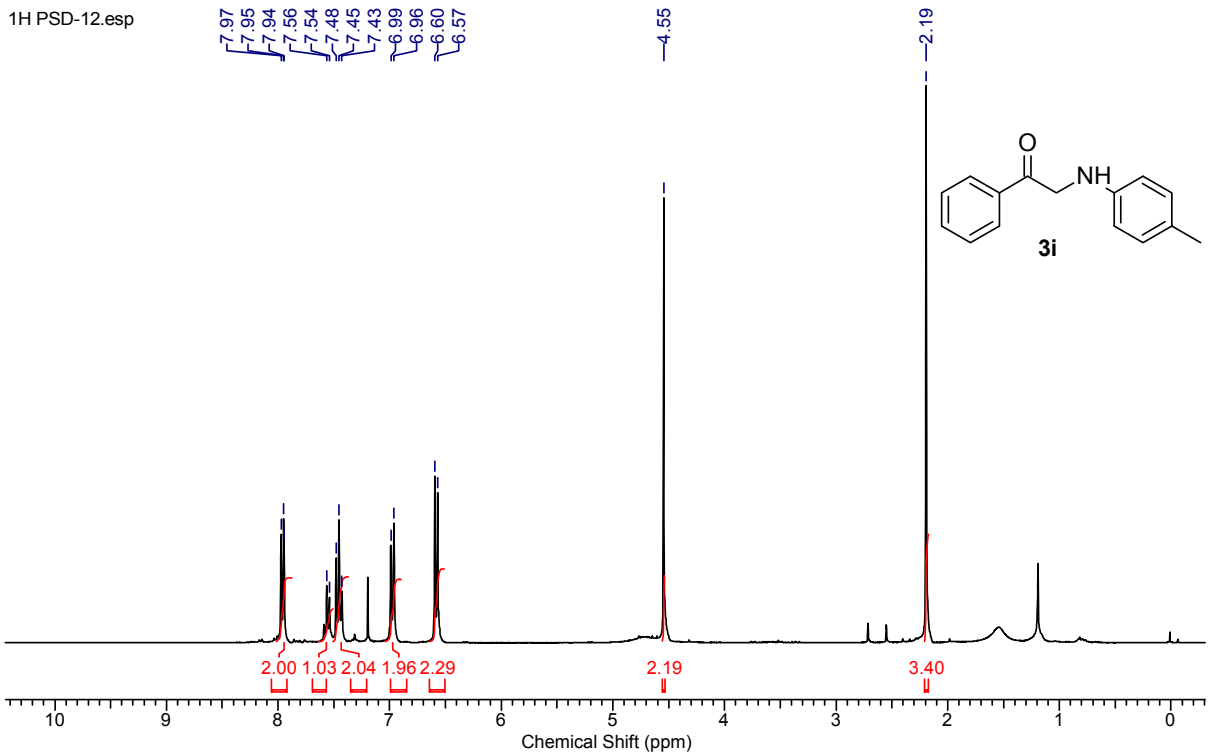
^{1}H NMR spectrum for compound **3h** ($CDCl_3$, 500 MHz)



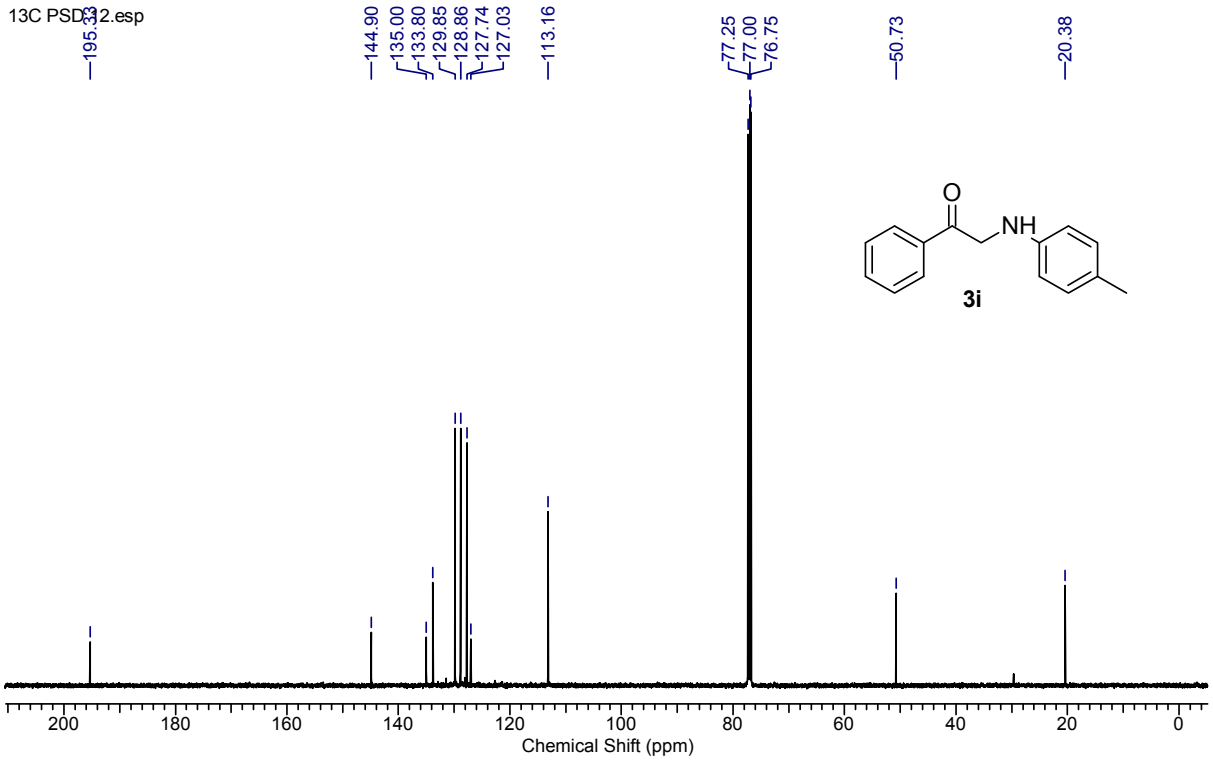
^{13}C NMR spectrum for compound **3h** ($CDCl_3$, 125 MHz)



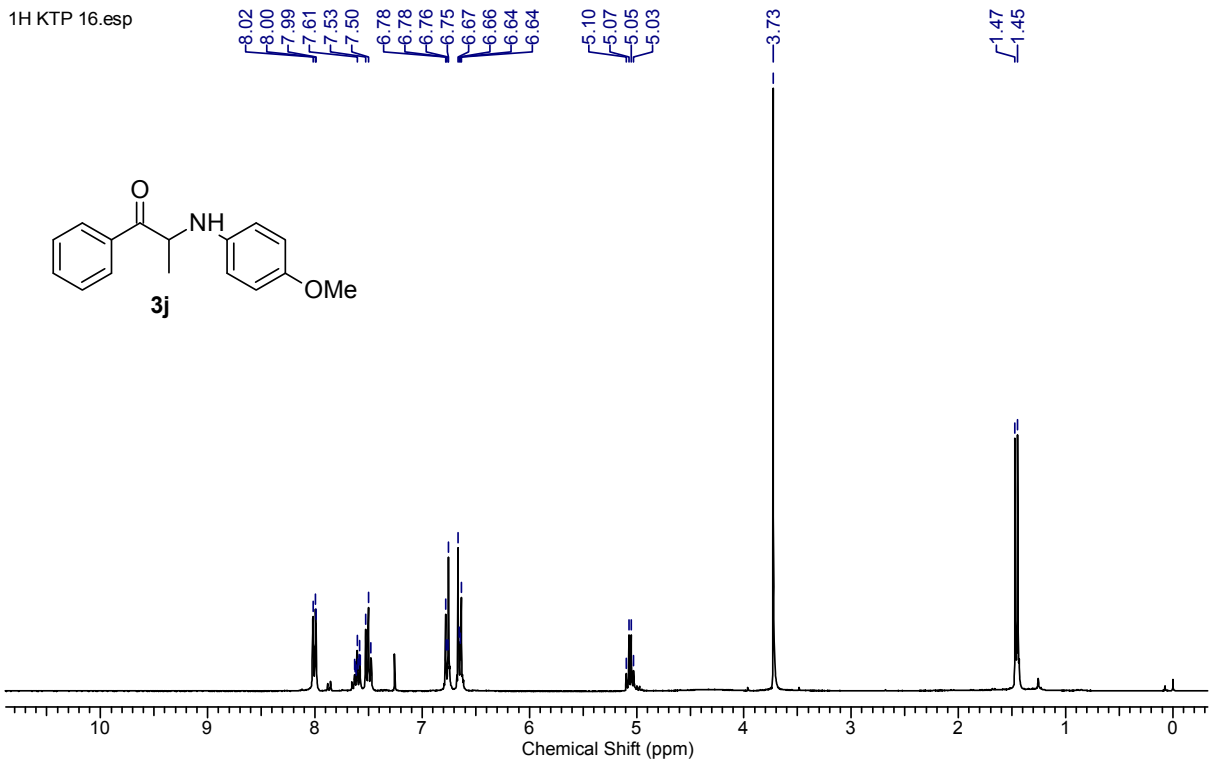
^{1}H NMR spectrum for compound **3i** ($CDCl_3$, 300 MHz)



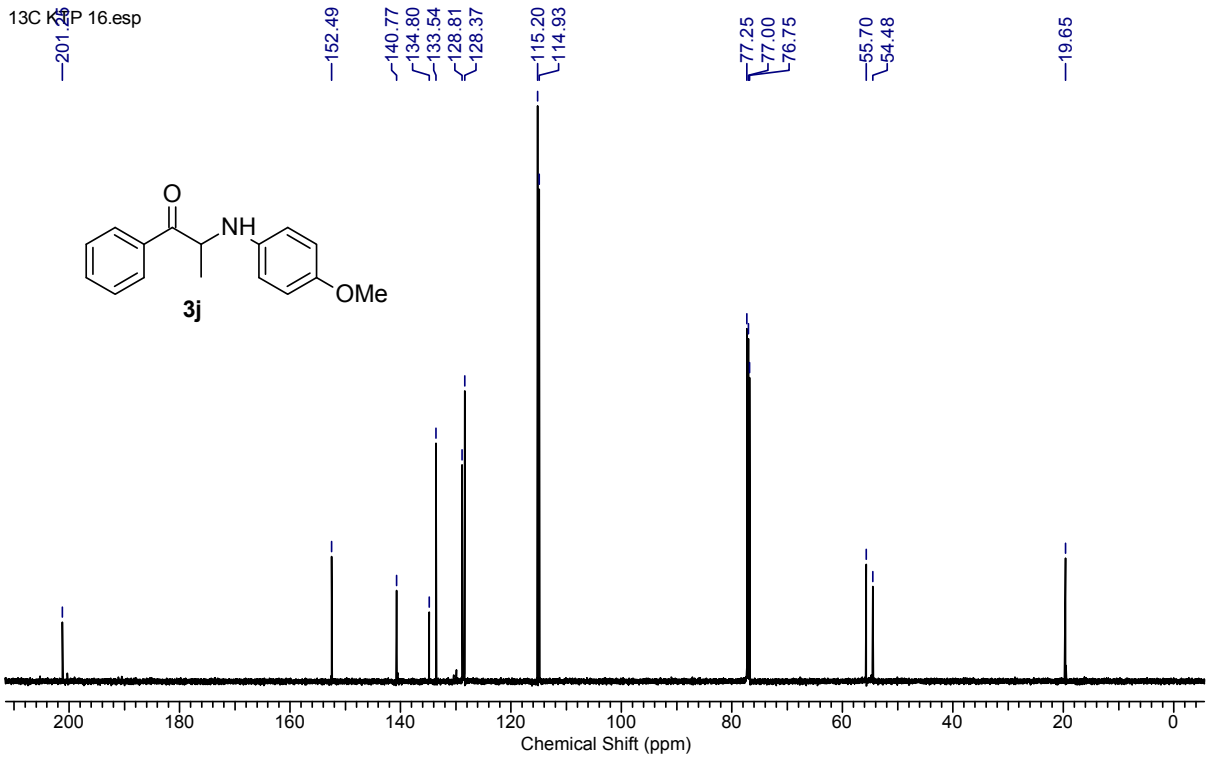
^{13}C NMR spectrum for compound **3i** ($CDCl_3$, 125 MHz)



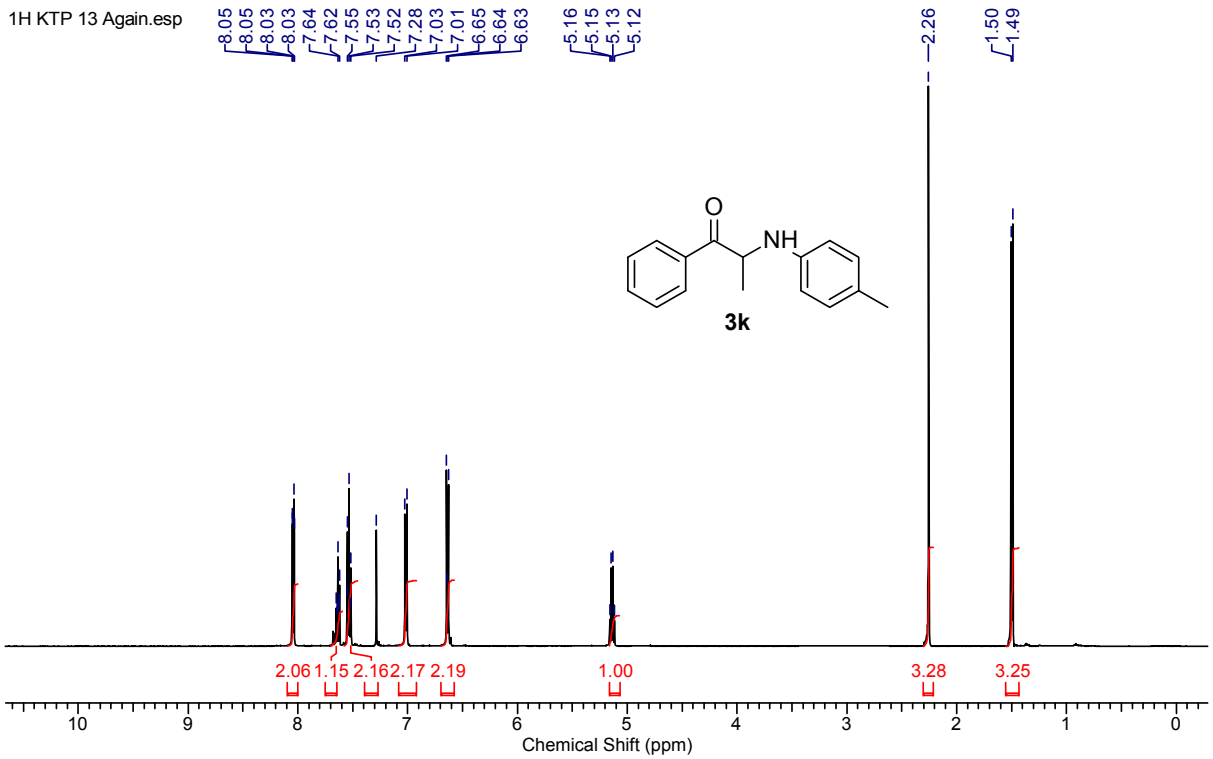
^{1}H NMR spectrum for compound **3j** ($CDCl_3$, 300 MHz)



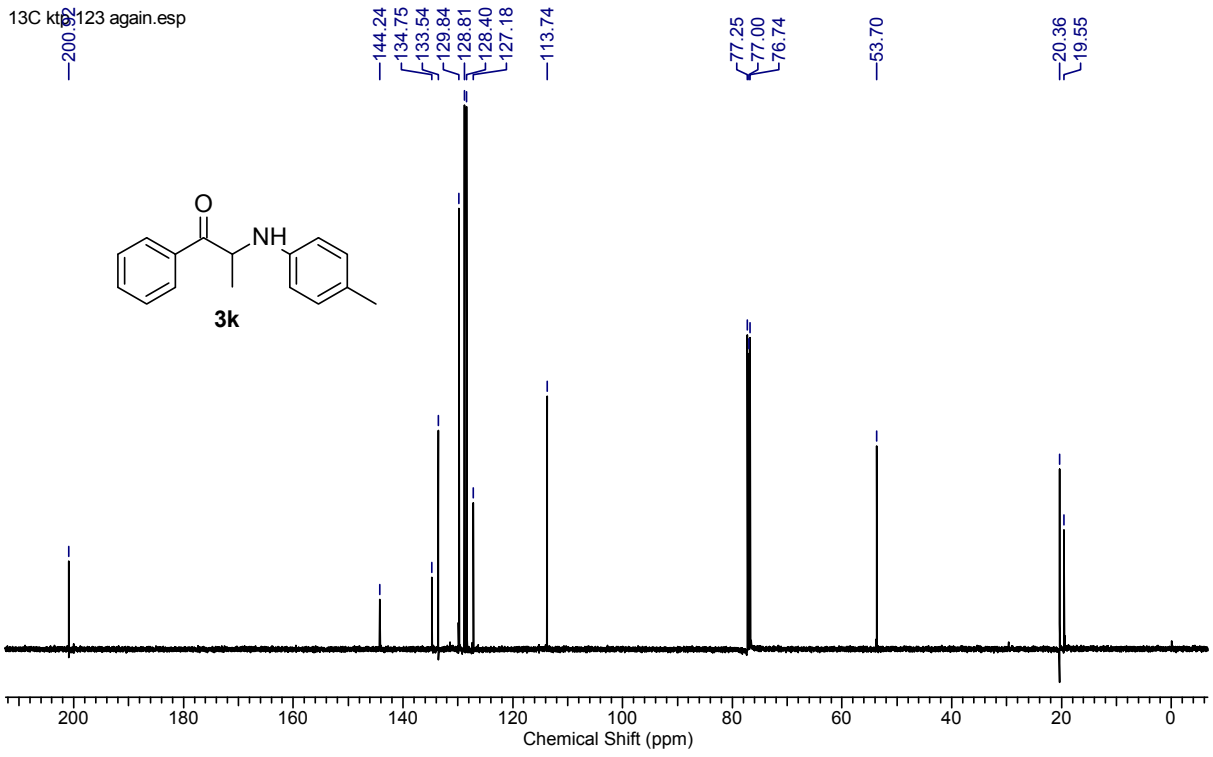
^{13}C NMR spectrum for compound **3j** ($CDCl_3$, 125 MHz)



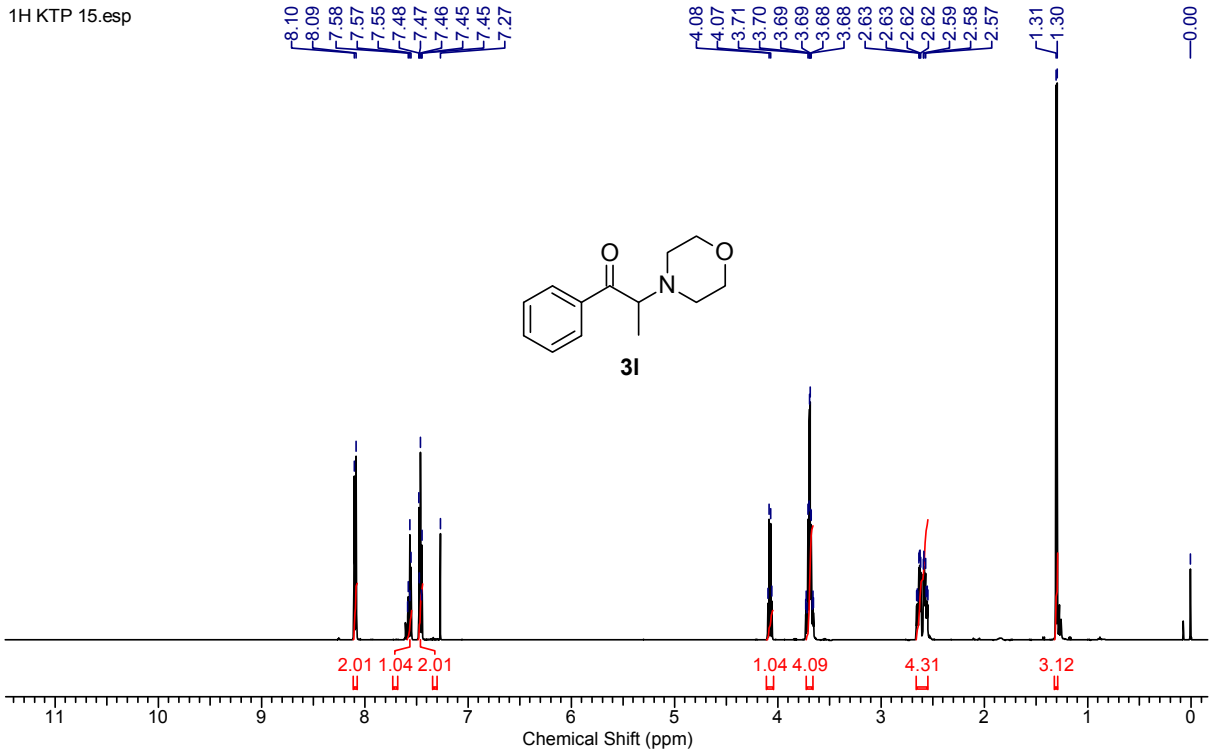
^{1}H NMR spectrum for compound **3k** ($CDCl_3$, 500 MHz)



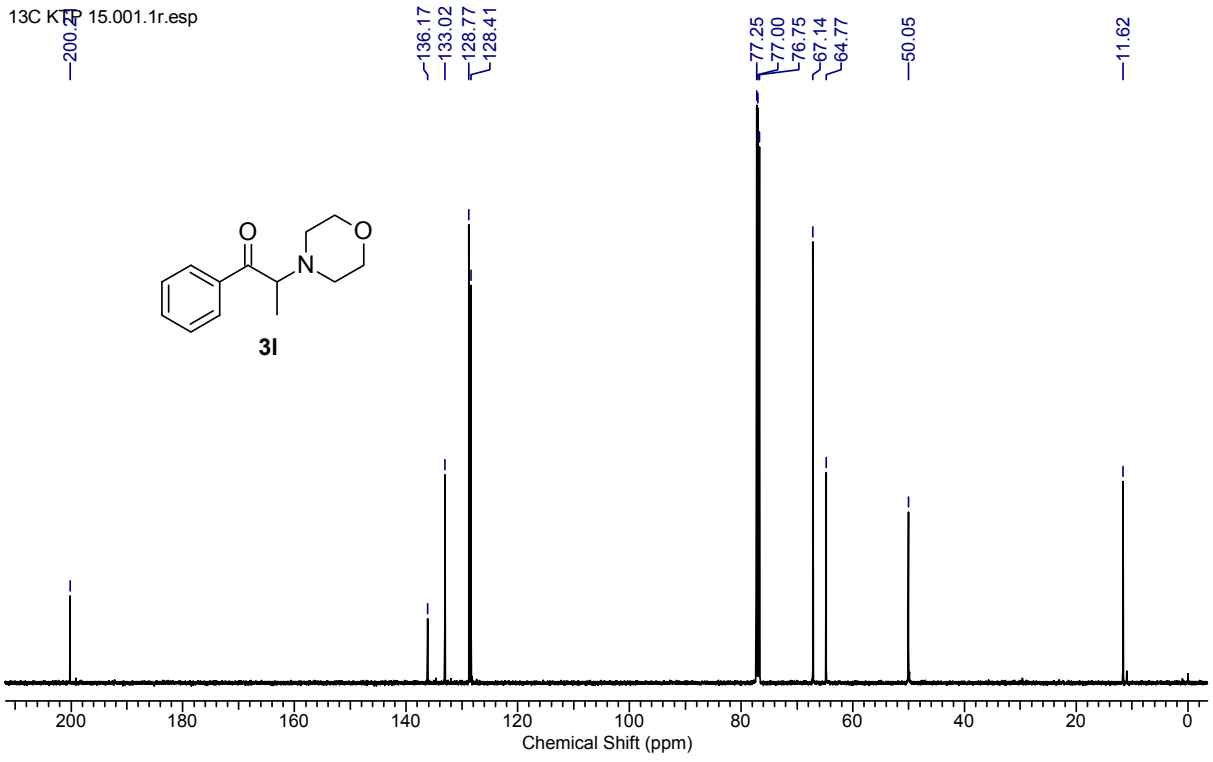
^{13}C NMR spectrum for compound **3k** ($CDCl_3$, 125 MHz)



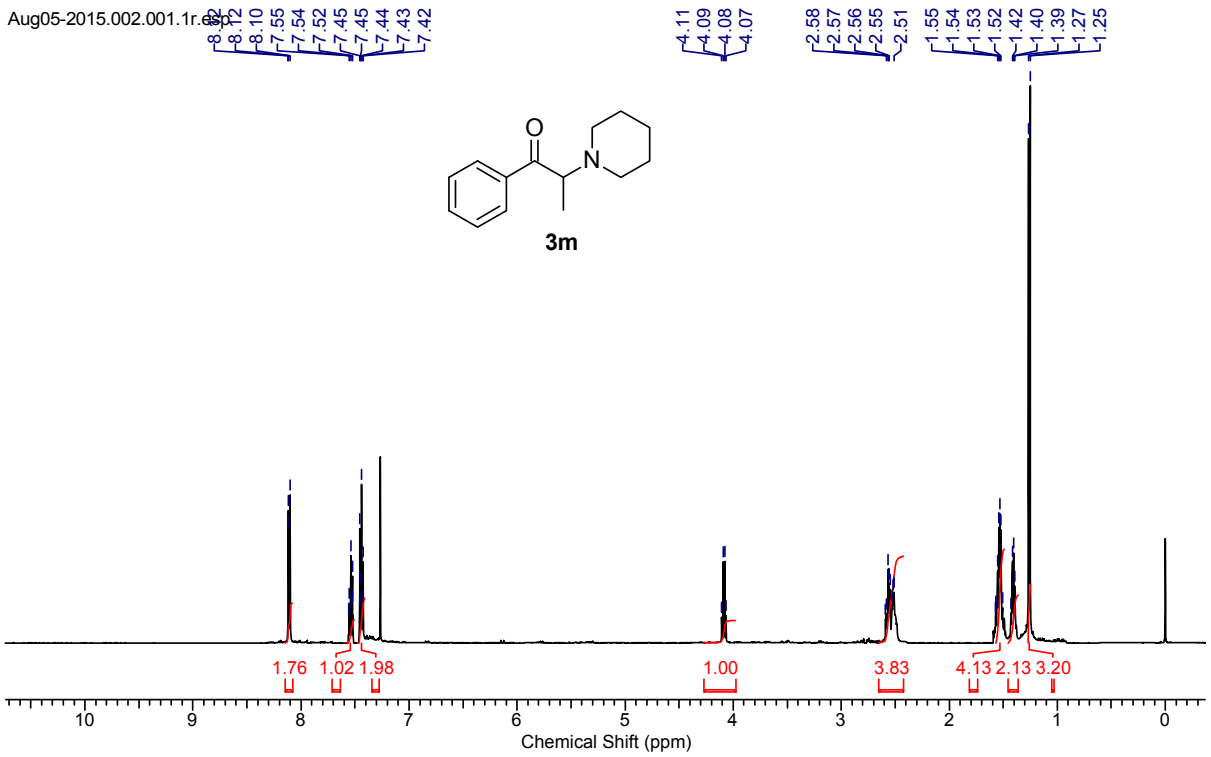
^{1}H NMR spectrum for compound **3l** ($CDCl_3$, 500 MHz)



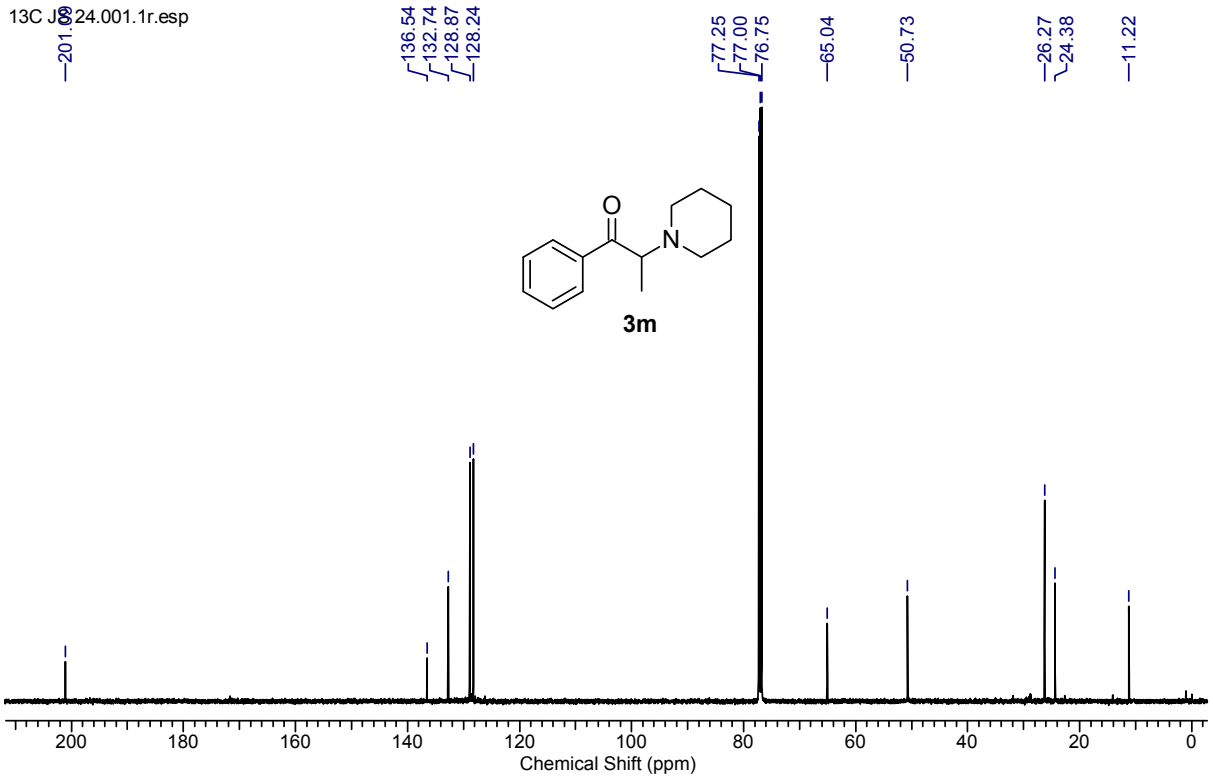
^{13}C NMR spectrum for compound **3l** ($CDCl_3$, 125 MHz)



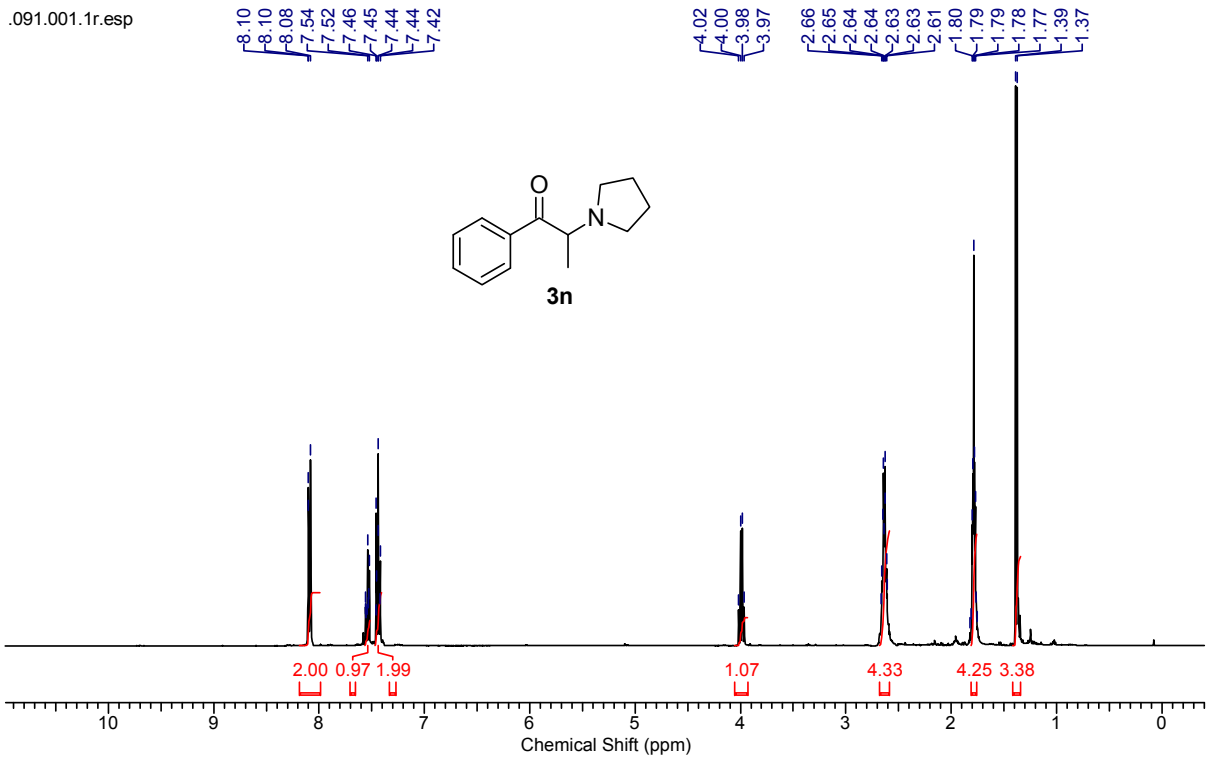
^{1}H NMR spectrum for compound **3m** ($CDCl_3$, 500 MHz)



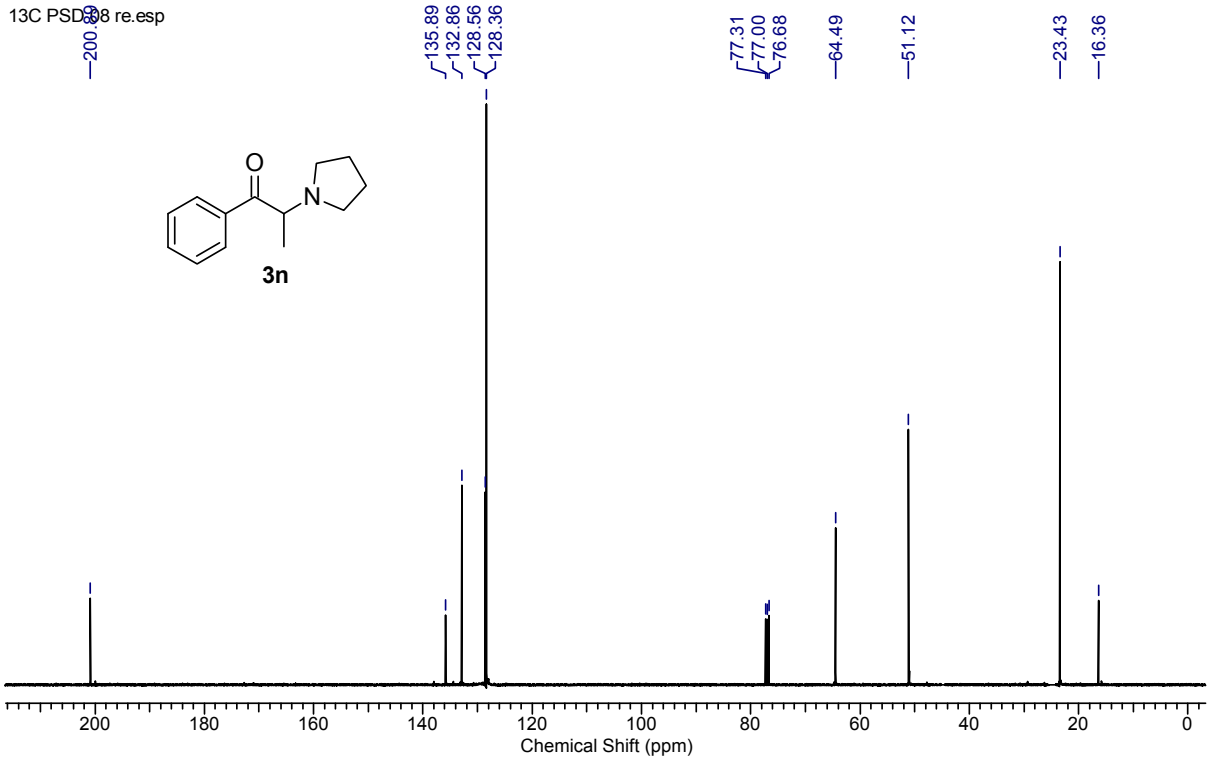
^{13}C NMR spectrum for compound **3m** ($CDCl_3$, 125 MHz)



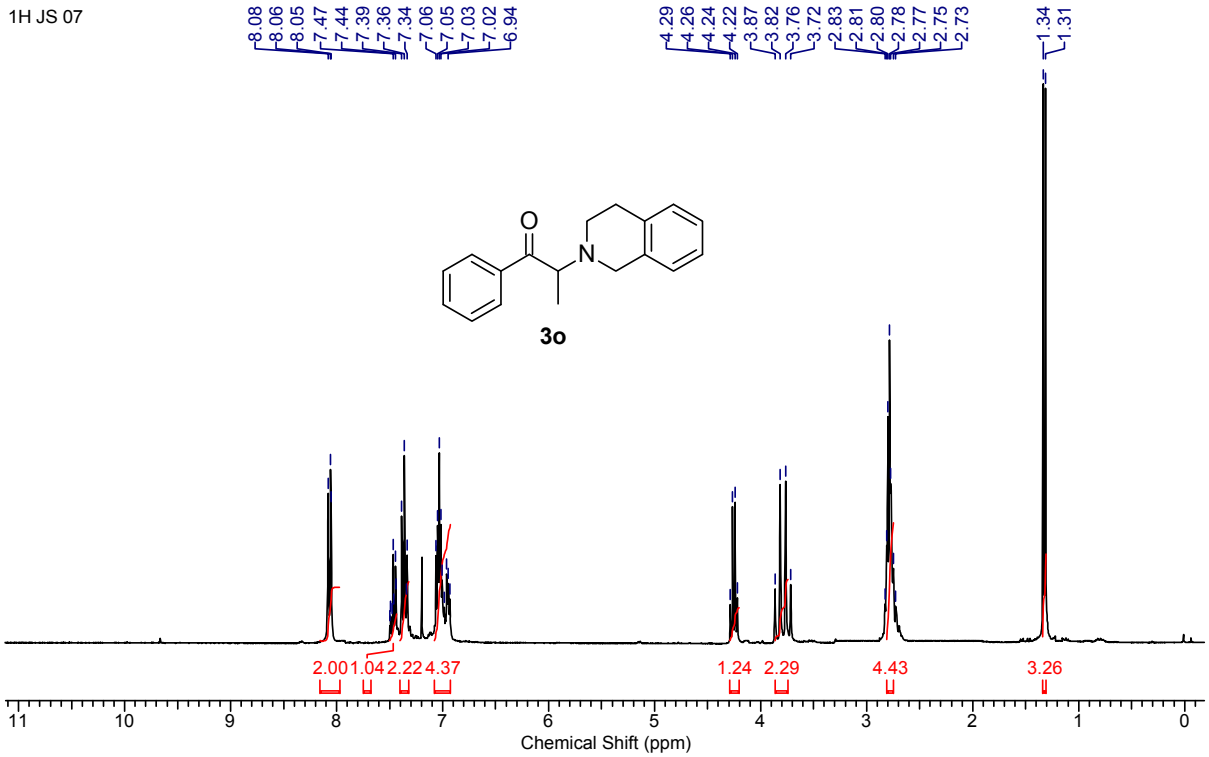
^{1}H NMR spectrum for compound **3n** ($CDCl_3$, 400 MHz)



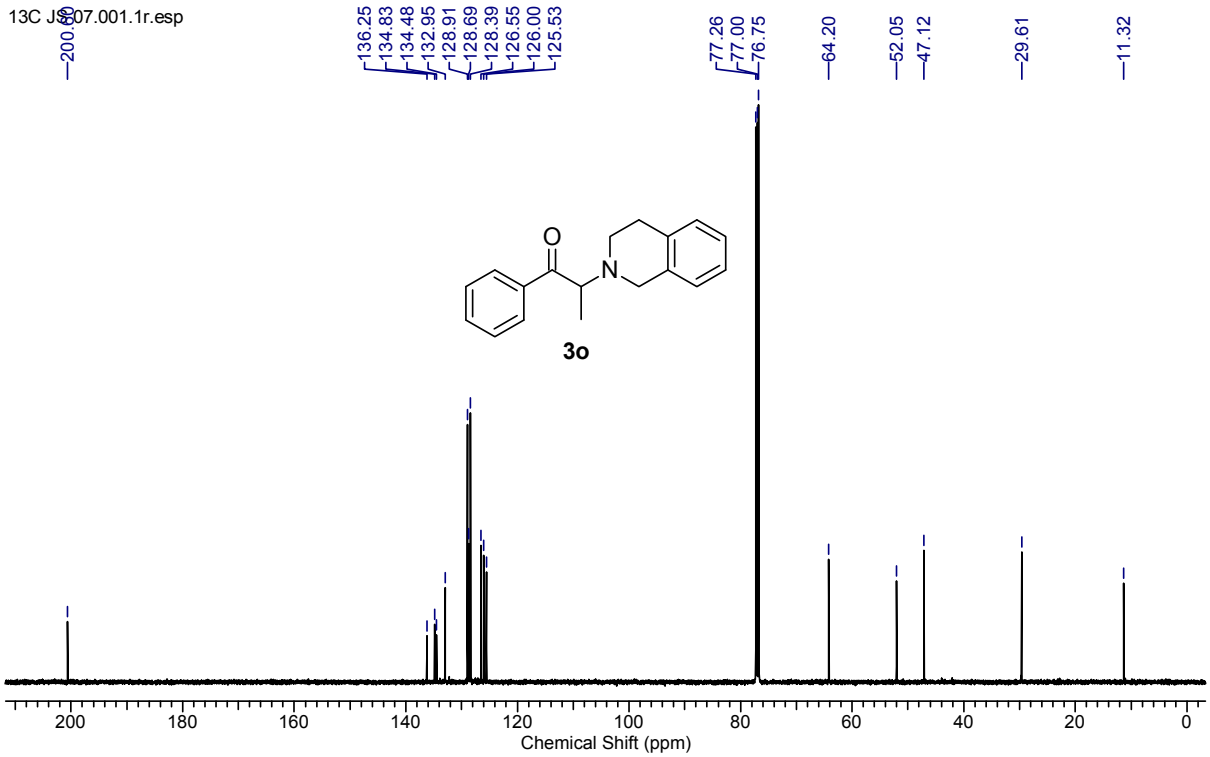
^{13}C NMR spectrum for compound **3n** ($CDCl_3$, 100 MHz)



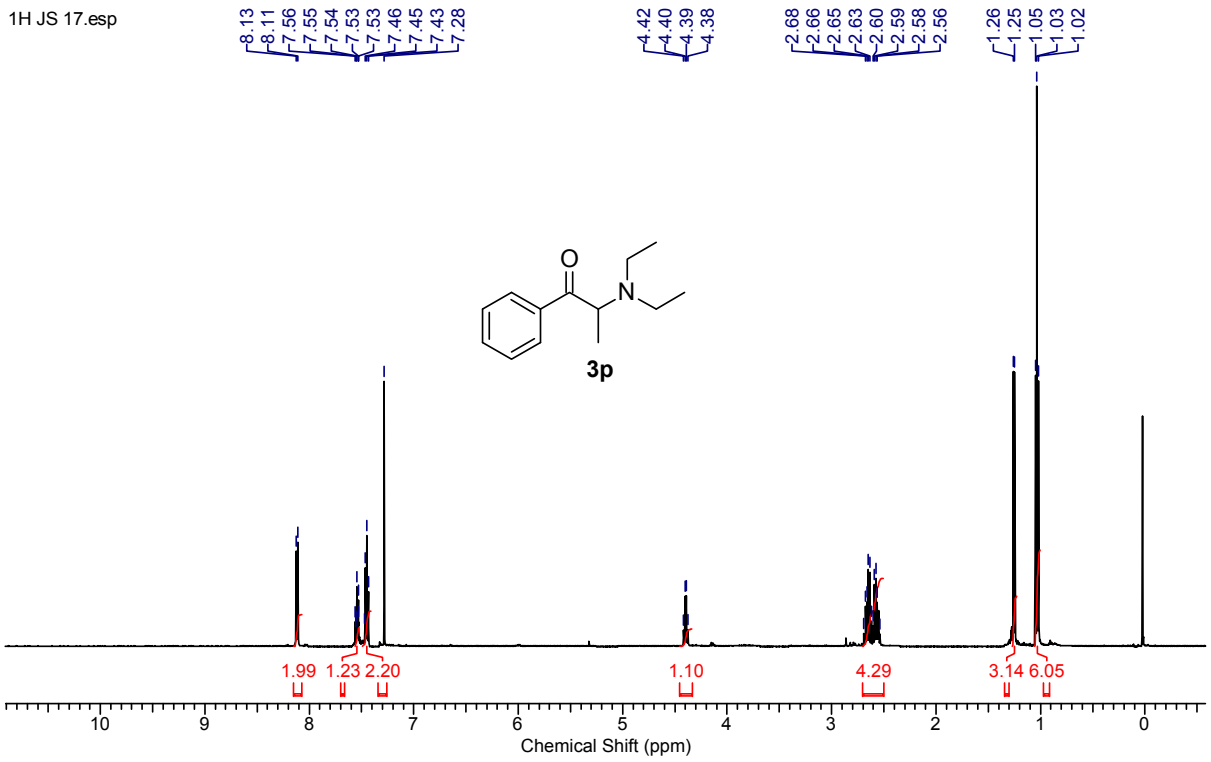
^{1}H NMR spectrum for compound **3o** ($CDCl_3$, 300 MHz)



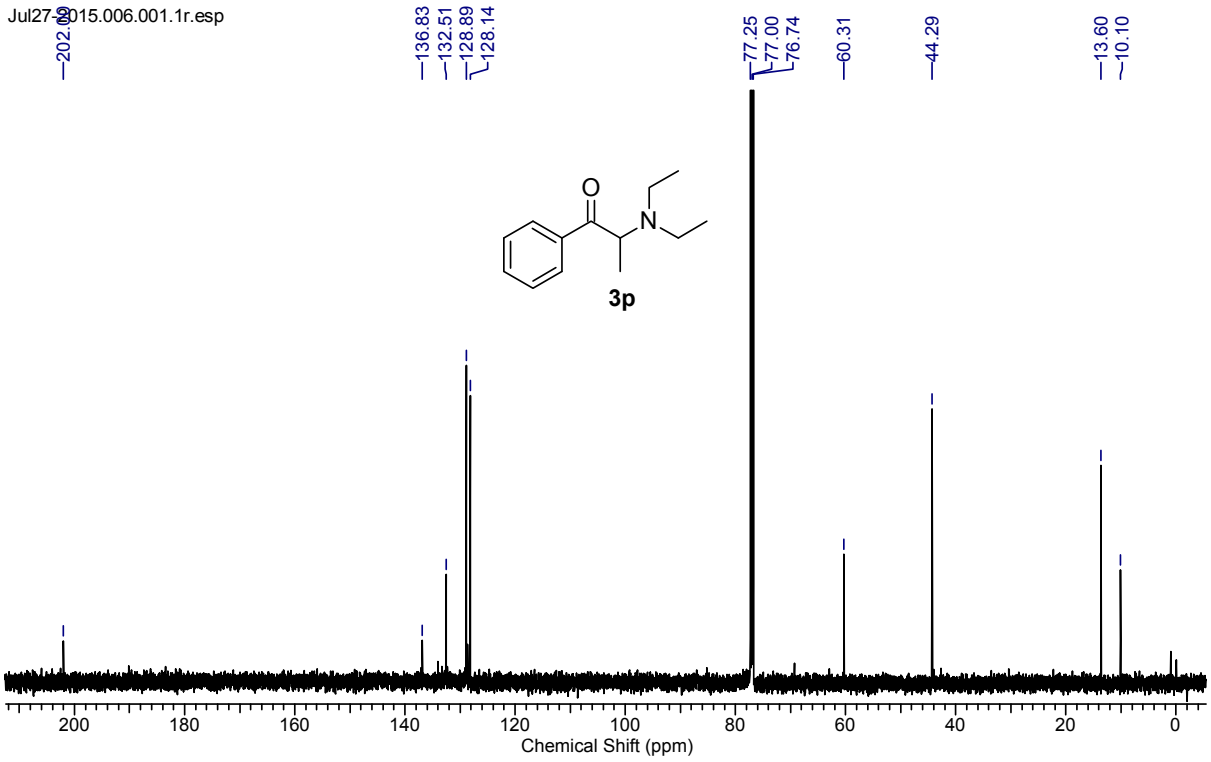
^{13}C NMR spectrum for compound **3o** ($CDCl_3$, 125 MHz)



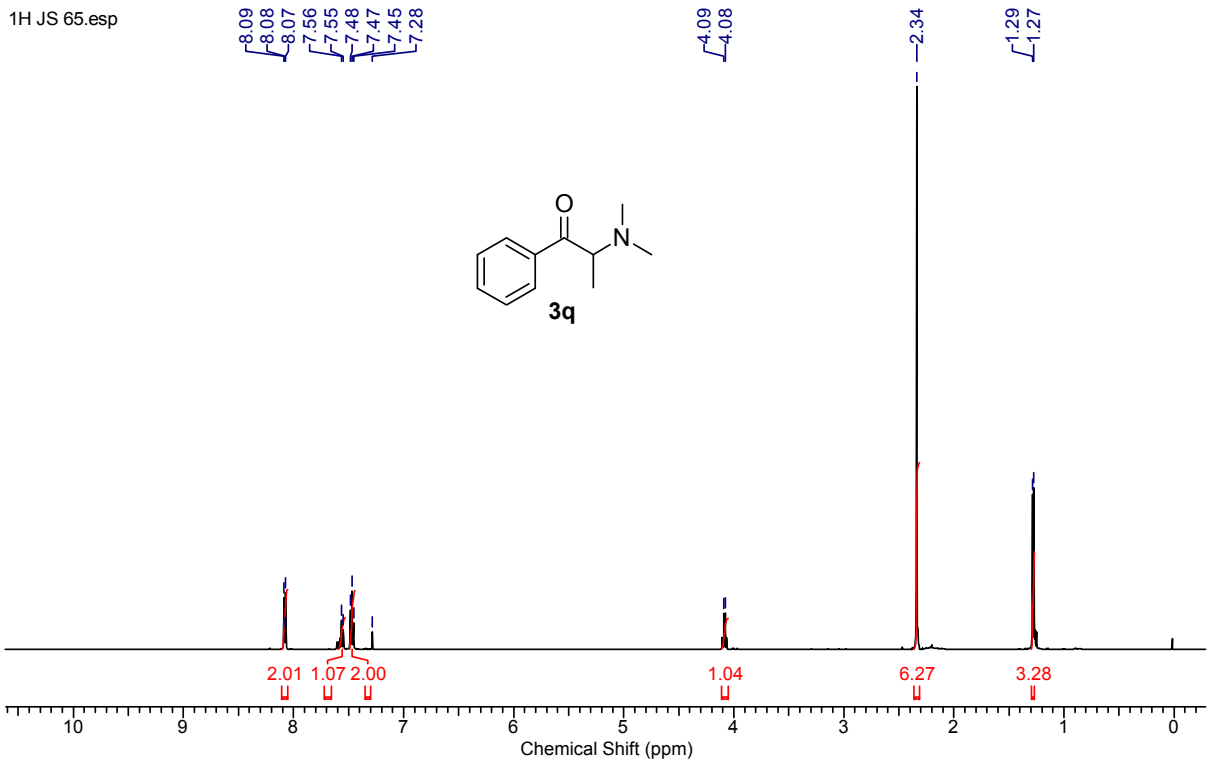
^{1}H NMR spectrum for compound **3p** ($CDCl_3$, 500 MHz)



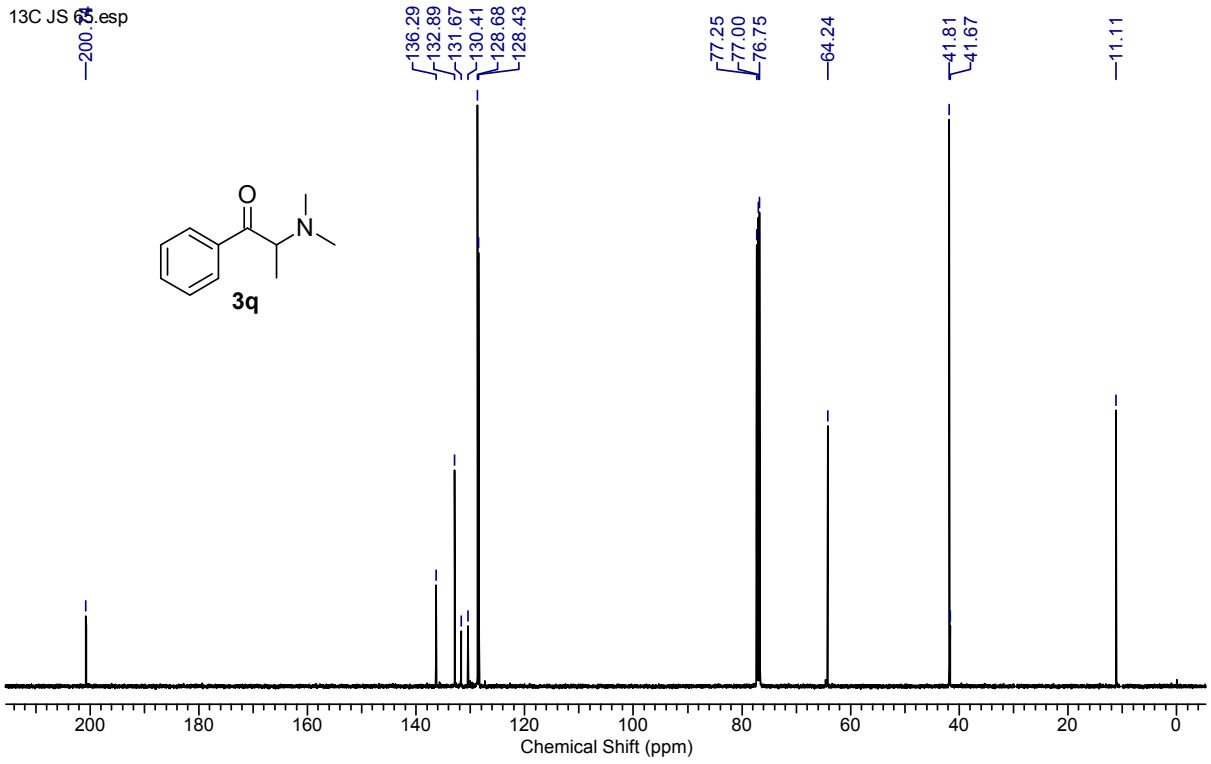
^{13}C NMR spectrum for compound **3p** ($CDCl_3$, 125 MHz)



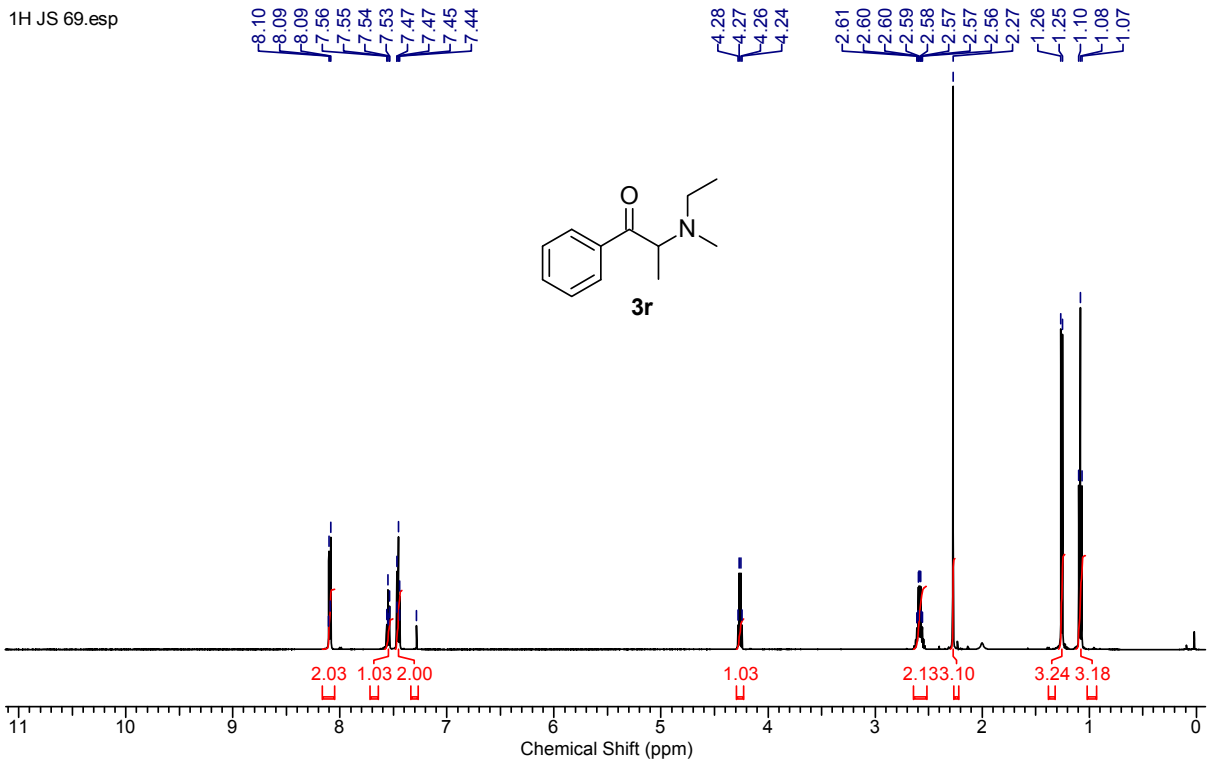
^{1}H NMR spectrum for compound **3q** ($CDCl_3$, 500 MHz)



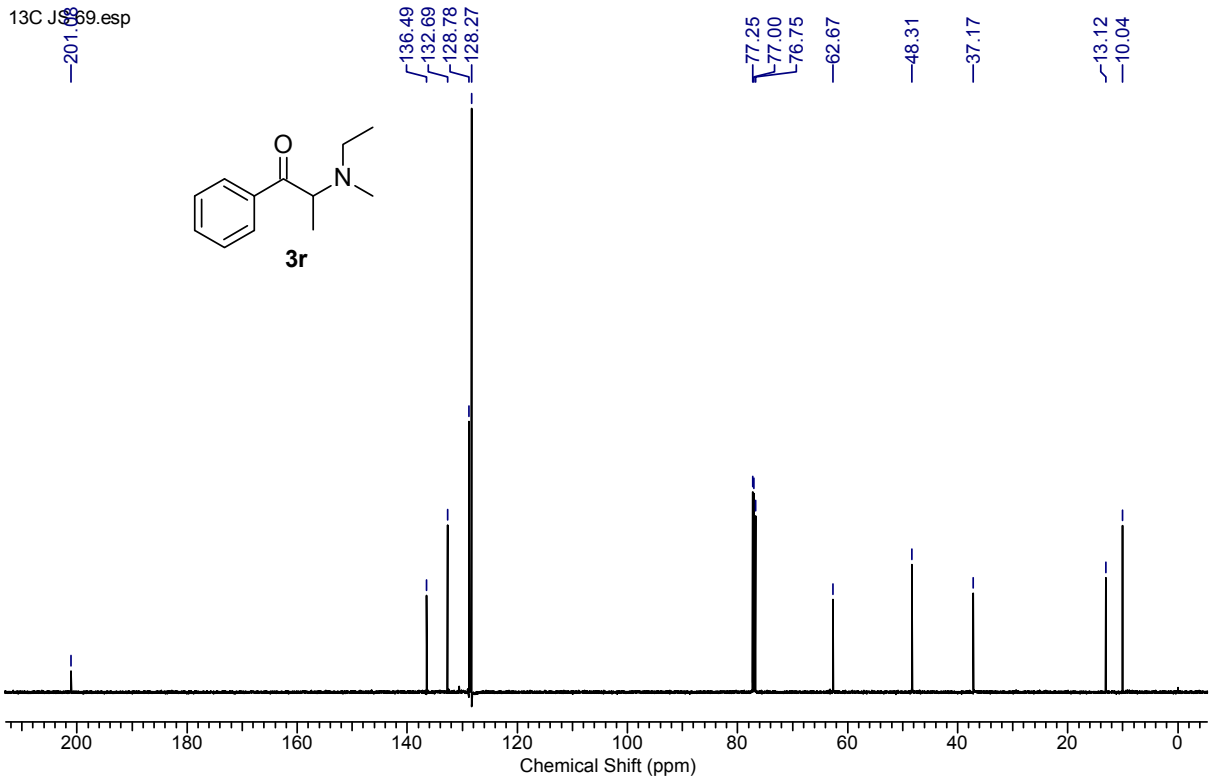
^{13}C NMR spectrum for compound **3q** ($CDCl_3$, 125 MHz)



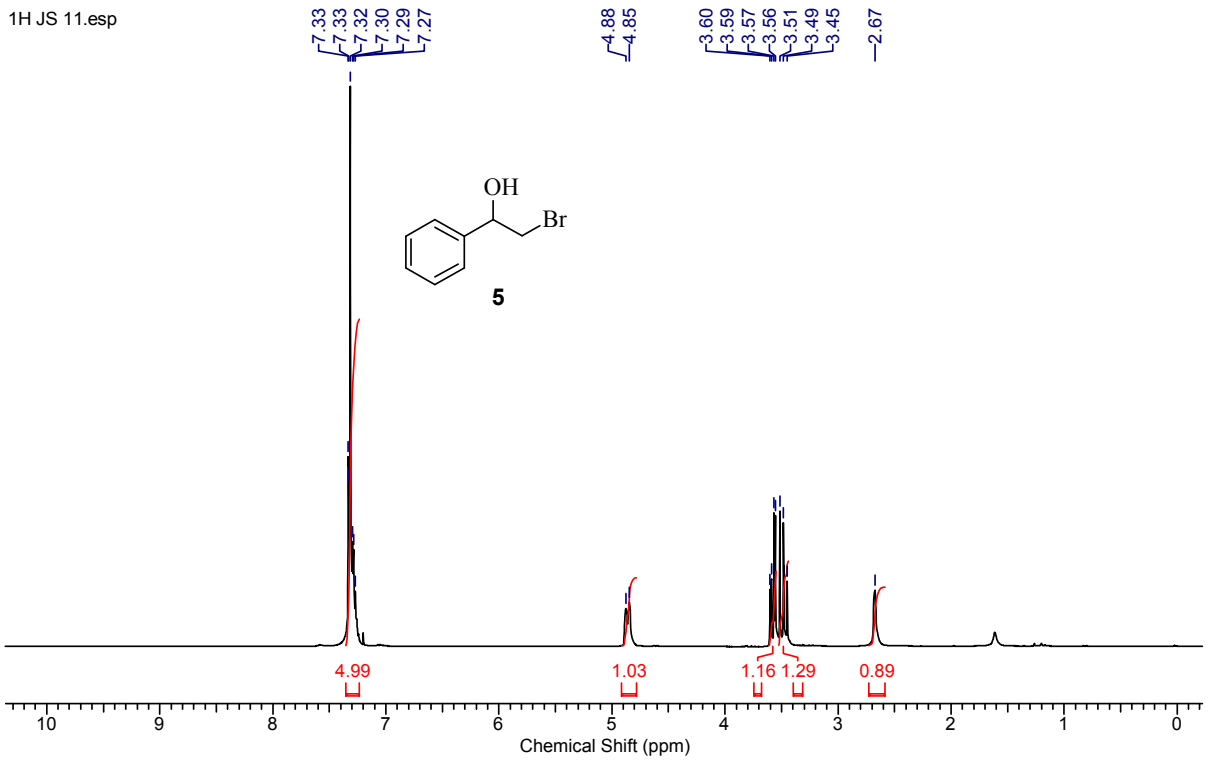
^{1}H NMR spectrum for compound **3r** ($CDCl_3$, 500 MHz



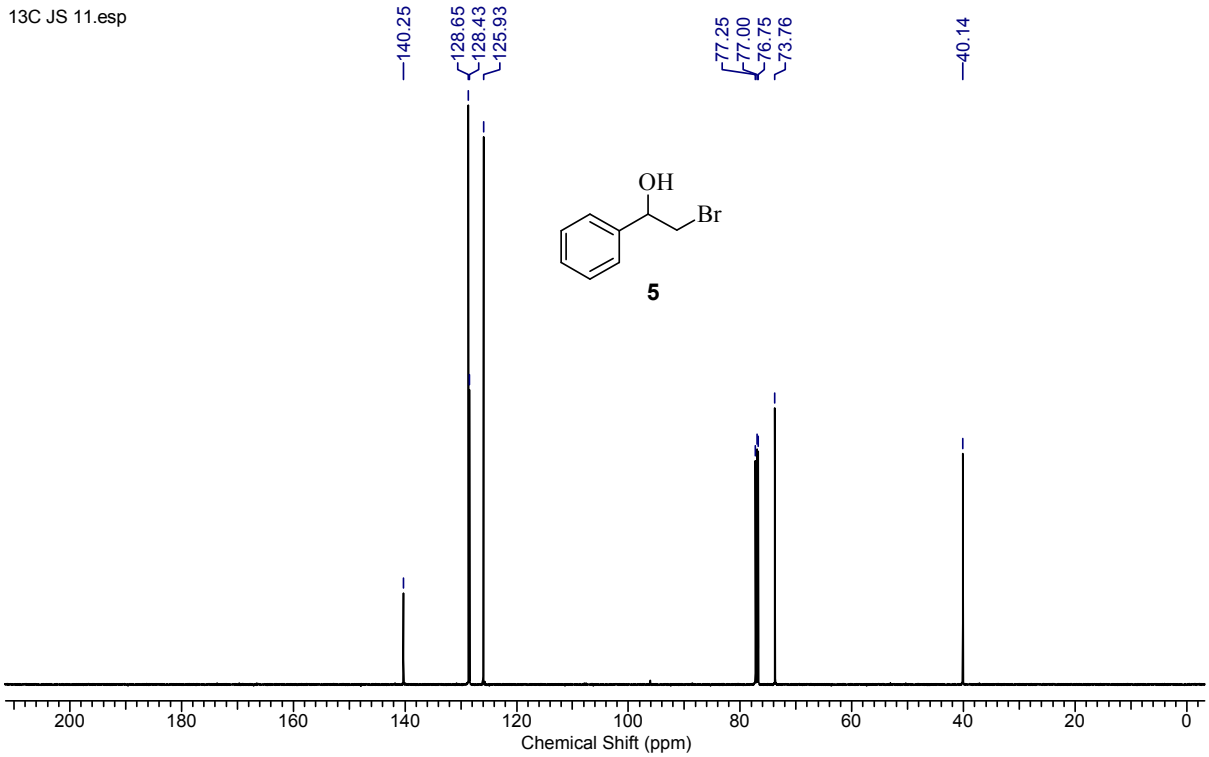
^{13}C NMR spectrum for compound **3r** ($CDCl_3$, 125 MHz)



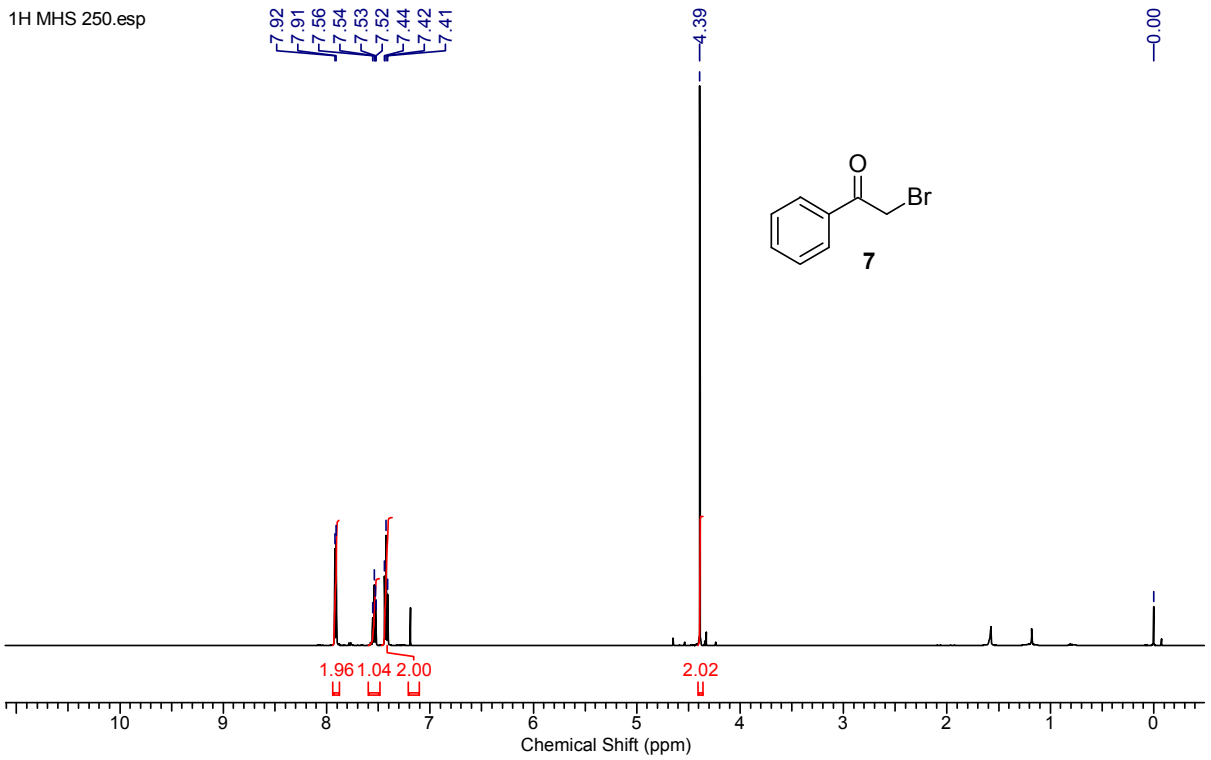
^{1}H NMR spectrum for compound **5** ($CDCl_3$, 300 MHz)



^{13}C NMR spectrum for compound **5** ($CDCl_3$, 125 MHz)



^{1}H NMR spectrum for compound **7** ($CDCl_3$, 500 MHz)



^{13}C NMR spectrum for compound **7** ($CDCl_3$, 125 MHz)