Synthesis and Characterization of Bisoxazolines- and Pybox-Copper(II) Complexes and Their Application in the Coupling of α-Carbonyls with Functionalized Amines

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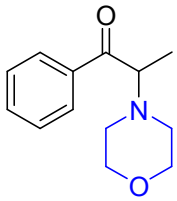
General procedure for the synthesis α-amination of ketones and esters

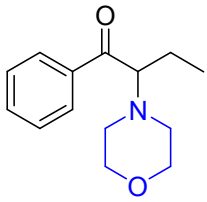
[Cu] 1 (25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO (0.1 - 0.5 mL), then appropriate ketone (0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of second amine (1.5 mmol, 3.0 equiv). The reaction was stirred for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the products.

1. Experimental Data for Products of α-Amination



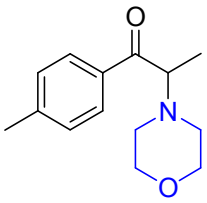
2-Morpholino-1-phenylpropan-1-one (**1a**):[1]

[Cu] 1(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO (0.5 mL), then propiophenone (67 μL, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of morpholine (130 μL, 1.5 mmol, 3.0 equiv). The reaction was stirred at room temperature for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (105mg, 96% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, J = 7.20 Hz, 2H), 7.49 (t, J = 7.20 Hz 1H), 7.40 (t, J = 7.20 Hz, 2H), 4.00 (q, J = 6.75 Hz, 1H), 3.63 (m, 4H), 2.52 (m, 4H), 1.22 (d, J = 6.75 Hz, 3H).



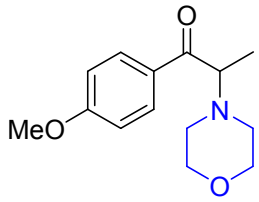
2-Morpholino-1-phenylbutan-1-one (**2a**):[2]

[Cu] 1(25mg, 0.05mmol, 0.1equiv) was dissolved in DMSO (0.5 mL), then Butyrophenone(75 µL, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of morpholine (130 µL, 1.5 mmol, 3.0 equiv). The reaction was stirred at room temperature for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (110 mg, 94% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, J = 7.20 Hz, 2H), 7.54 (t, J = 7.20 Hz, 1H), 7.43 (t, J = 7.20 Hz 2H), 3.99 (q, J = 4.80 Hz, 1H), 3.63 (m, 4H), 2.59 (m, 4H), 1.88 (m, 1H), 1.74 (m, 1H), 0.84 (t, J = 7.53 Hz, 3H).



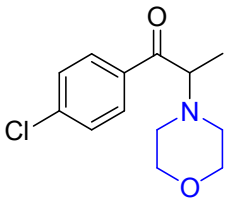
1-(1-p-tolyl)-2-morpholinopropan-1-one (**3a**):

[Cu] 1(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO (0.1 mL), then 4-Methylpropiophenone (75 µL, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of morpholine (130 µL, 1.5 mmol, 3.0 equiv). The reaction was stirred at room temperature for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (110 mg, 94% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, J = 7.90 Hz, 2H), 7.19 (d, J = 7.89 Hz, 2H), 3.99 (m ,1H), 3.63 (m, 4H), 2.54 (m, 4H), 2.35 (s, 3H), 1.22 (d, J = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.19, 144.24, 133.86, 129.44, 129.20, 67.40, 64.92, 50.43, 21.96, 12.36. HRMS (APCI) Calcd. for $C_{14}H_{19}NO_2$ $[M + H]^+$ 234.1489, found 234.1483.



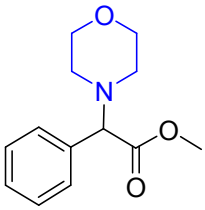
1-(4-Methoxyphenyl)-2-morpholinopropan-1-one (**4a**):[1]

[Cu] **1**(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO (0.1 mL), then 4-Methoxypropiophenone (82 mg, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of morpholine (130 µL, 1.5 mmol, 3.0 equiv). The reaction was stirred at room temperature for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (116mg, 93% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, J = 8.70 Hz, 2H), 6.99 (d, J = 8.70 Hz, 2H), 3.96 (q, J = 6.90 Hz, 1H), 3.82 (s, 3H), 3.64 (m, 4H), 2.54 (m, 4H), 1.24 (d, J = 6.90 Hz, 3H).



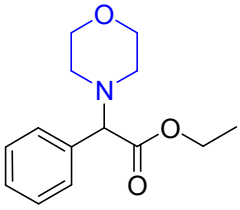
1-(4-chlorophenyl)-2-morpholinopropan-1-one (**5a**):

[Cu] **1**(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO (0.5 mL), then 4-chloropropiophenone (84mg, 0.5mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of morpholine (130 µL, 1.5 mmol, 3.0 equiv). The reaction was stirred at 10℃ for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (123 mg, 97% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, J = 8.10 Hz, 2H), 7.41 (d, J = 8.10 Hz, 2H), 4.00 (q, J = 6.90 Hz, 1H), 3.66 (m, 4H), 2.57 (m, 4H), 1.29 (d, J = 6.90 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.29, 139.79, 134.60, 130.70, 129.06, 67.39, 65.36, 50.23, 11.49. HRMS (APCI) Calcd. for $C_{13}H_{16}ClNO_2$ $[M + H]^+$ 254.0942, found 254.0940.



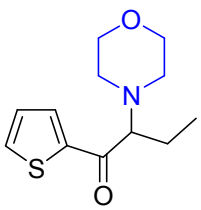
Methyl 2-morpholino-2-phenylacetate (**6a**):[1]

[Cu] 1(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO (0.1 mL), then Methyl phenylacetate (71 μL, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of morpholine (130 μL, 1.5 mmol, 3.0 equiv). The reaction was stirred at 50℃ for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the pale yellow liquid (81 mg, 69% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (m, 2H), 7.24 (m, 3H), 3.90 (s, 1H), 3.64 (m, 4H), 3.60 (s, 3H), 2.37 (m, 4H).



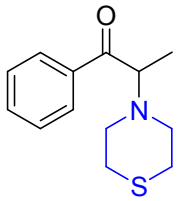
Ethyl 2-morpholino-2-phenylacetate (**7a**):

[Cu] 1(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO (0.1 mL), then Eethyl phenylacetate (80 μL, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of morpholine (130 μL, 1.5 mmol, 3.0 equiv). The reaction was stirred at 50℃ for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the pale yellow liquid (81 mg, 65% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (m, 2H), 7.24 (m, 3H), 4.07 (m, 2H), 3.88 (s, 1H), 3.65 (m, 4H), 2.38 (m, 4H), 1.12 (t, J = 7.05 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.52, 135.75, 129.18, 128.91, 128.76, 74.83, 67.12, 61.28, 51.91, 14.41. HRMS (APCI) Calcd. for $C_{14}H_{19}NO_3$ $[M + H]^+$ 250.1438, found 250.1440.



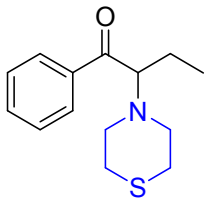
2-morpholino-1-(thiophen-2-yl)butan-1-one (**8a**):

[Cu] 1 (25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO (0.5 mL), then 2-Butyrylthiophene (72 µL, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of morpholine (130 µL, 1.5 mmol, 3.0 equiv). The reaction was stirred at room temperature for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (111 mg, 93% Yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, J = 3.50 Hz, 1H), 7.57 (d, J = 3.50 Hz, 1H), 7.07 (t, J = 3.5, Hz, 1H), 3.64 (m, 4H), 3.51 (m, 1H), 2.61 (m, 2H), 2.54 (m, 2H), 1.75 (m, 2H), 0.94 (t, J = 4.25 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.30, 142.76, 133.97, 132.85, 127.74, 73.04, 67.03, 50.59, 20.48, 10.90. HRMS (APCI) Calcd. for $C_{12}H_{17}NO_2S$ $[M + H]^+$ 240.1053, found 240.1051.



1-Phenyl-2-thiomorpholinopropan-1-one (**9a**):[1]

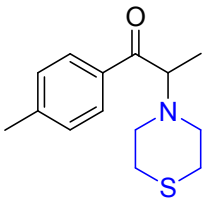
[Cu] 1(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO (0.5 mL), then propiophenone (67 µL, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of Thiomorpholine(150 µL, 1.5 mmol, 3.0 equiv). The reaction was stirred at room temperature for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (106mg, 90% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J = 7.20 Hz, 2H), 7.47 (t, J = 7.20 Hz, 1H), 7.37 (t, J = 7.20 Hz, 2H), 4.09 (q, J = 6.60 Hz, 1H), 2.80 (m, 4H), 2.52 (m, 4H), 1.19 (d, J = 6.60 Hz, 3H).



phenyl-2-thiomorpholinobutan-1-one (**10a**):

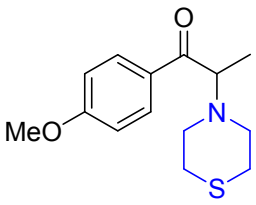
[Cu] 1(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO (0.5 mL), then Butyrophenone (75 µL, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of Thiomorpholine (150 µL, 1.5 mmol, 3.0 equiv). The reaction was stirred at room

temperature for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (111mg, 89% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, J = 7.23 Hz, 2H), 7.54 (t, J = 7.25 Hz, 1H), 7.43 (t, J = 7.24 Hz, 2H), 3.93 (m, 1H), 2.88 (m, 4H), 2.56 (m, 4H), 1.87 (m, 1H), 1.69 (m, 1H), 0.86 (t, J =7.35 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.62, 137.66, 133.23, 128.82, 128.77, 70.94, 52.28, 28.85, 18.91, 11.64. HRMS (APCI) Calcd. for $C_{14}H_{19}NOS$ $[M + H]^+$ 250.1260, found 250.1261.



2-thiomorpholino-1-p-tolylpropan-1-one (**11a**):

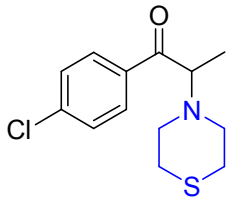
[Cu] **1**(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO (0.1 mL), then 4-Methylpropiophenone (75 µL, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of Thiomorpholine(150 µL, 1.5 mmol, 3.0 equiv). The reaction was stirred at room temperature for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (102 mg, 82% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, J = 8.10 Hz, 2H), 7.15 (d, J = 8.10 Hz, 2H), 4.03 (m, 1H), 2.77 (m, 4H), 2.50 (m, 4H), 2.32 (s, 3H), 1.15 (d, J = 6.90 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.45, 143.45, 133.45, 128.80, 128.78, 64.76, 51.37, 28.17, 21.45, 9.89. HRMS (APCI) Calcd. for $C_{14}H_{19}NOS$ $[M + H]^+$ 250.1260, found 250.1256.



1-(4-methoxyphenyl)-2-thiomorpholinopropan-1-one (**12a**):

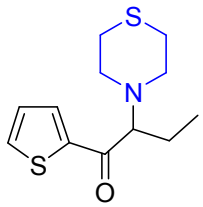
[Cu] **1**(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO (0.1 mL), then 4-Methoxypropiophenone (82 mg, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of Thiomorpholine(150 µL, 1.5 mmol, 3.0 equiv). The reaction was stirred at room temperature for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the

yellow liquid (106 mg, 80% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, J = 9.00 Hz, 2H), 6.89 (d, J = 9.00 Hz, 2H), 4.05 (q, J = 6.60 Hz, 1H), 3.84 (s, 3H), 2.83 (m, 4H), 2.57 (m, 4H), 1.21 (d, J = 6.60 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.80, 163.54, 131.51, 129.35, 113.67, 65.23, 55.67, 51.83, 28.63, 10.39. HRMS (APCI) Calcd. for $C_{14}H_{19}NO_2S$ $[M + H]^+$ 266.1209, found 266.1213.



1-(4-chlorophenyl)-2-thiomorpholinopropan-1-one (**13a**):

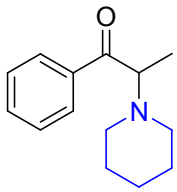
[Cu] **1**(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO (0.5 mL), then 4-chloropropiophenone (84 mg, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of Thiomorpholine(150 μL, 1.5 mmol, 3.0 equiv). The reaction was stirred at 10℃ for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (99 mg, 74% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, J = 8.40 Hz, 2H), 7.39 (d, J = 8.40 Hz, 2H), 4.05 (q, J = 6.90 Hz, 1H), 2.81 (m, 4H), 2.58 (m, 4H), 1.22 (d, J = 6.90 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.15, 139.58, 134.72, 130.81, 128.94, 65.78, 51.83, 28.68, 9.77. HRMS (APCI) Calcd. for $C_{13}H_{16}ClNOS$ $[M + H]^+$ 270.0714, found 270.0712.



2-thiomorpholino-1-(thiophen-2-yl)butan-1-one (**14a**):

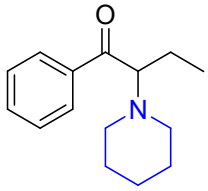
[Cu] **1**(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO (0.5 mL), then 2-Butyrylthiophene(72 μL, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of Thiomorpholine(150 μL, 1.5 mmol, 3.0 equiv). The reaction was stirred at room temperature for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (107 mg, 84% Yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, J = 4.00 Hz, 1H), 7.58 (d, J = 4.00 Hz, 1H),

7.08 (t, J = 4.00 Hz, 1H), 3.61 (m, 1H), 2.89 (m, 4H), 2.62 (m, 4H), 1.83 (m, 1H), 1.69 (m, 1H), 0.88 (t, J = 5.00 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.09, 142.19, 133.01, 132.08, 126.93, 72.67, 51.51, 27.54, 18.45, 10.77. HRMS (APCI) Calcd. for $C_{12}H_{17}NOS_2$ $[M + H]^+$ 256.0824, found 256.0823.



1-Phenyl-2-(piperidin-1-yl)propan-1-one (**15a**):[1]

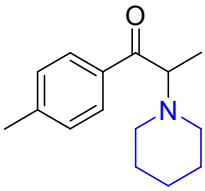
[Cu] 1(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO (0.5 mL), then propiophenone (67 µL, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of piperidine(149 µL, 1.5 mmol, 3.0 equiv). The reaction was stirred at room temperature for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (103 mg, 95% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (m, 2H), 7.51(m, 1H), 7.43 (m, 2H), 4.13 (q, J = 6.90 Hz, 1H), 2.56 (m, 4H), 1.54 (m, 4H), 1.40 (m, 2H), 1.26 (d, J = 6.90 Hz, 3H).



1-phenyl-2-(piperidin-1-yl)butan-1-one (**16a**):

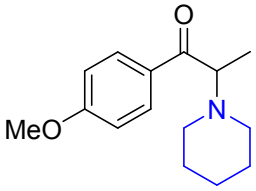
[Cu] 1(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMF(0.5 mL), then Butyrophenone(75 µL, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of piperidine(149 µL, 1.5 mmol, 3.0 equiv). The reaction was stirred at room temperature for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (110 mg, 95% Yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 7.00 Hz, 2H), 7.50(d, J =7.00 Hz, 1H), 7.42 (m, J = 7.00 Hz, 2H), 3.89 (q, J = 7.50 Hz, 1H), 2.57 (m, 2H), 2.49 (m, 2H), 1.87 (m, 1H), 1.70 (m, 1H), 1.49 (m, 4H), 1.36 (m, 2H), 0.83 (t, J = 7.50 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.41, 137.87, 132.78, 128.61, 128.43, 70.58, 51.03, 26.52, 24.57, 19.49, 11.29. HRMS (APCI) Calcd. for $C_{15}H_{21}NO$ [M +

H]$^+$ 232.1696, found 232.1696.



2-(piperidin-1-yl)-1-p-tolylpropan-1-one (**17a**):

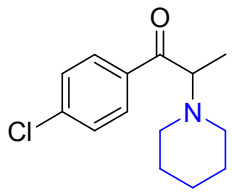
[Cu] **1**(25mg, 0.05mmol, 0.1equiv) was dissolved in DMSO (0.1 mL), then 4-Methylpropiophenone (75µL, 0.5mmol, 1.0equiv) was added. This was stirred for 10 minutes at room temperature before the addition of piperidine(149µL, 1.5mmol, 3.0equiv). The reaction was stirred at room temperature for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (109mg, 94% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, J = 8.10 Hz, 2H), 7.16 (d, J = 8.10 Hz, 2H), 4.06 (q, J = 6.90 Hz, 1H), 2.49 (m, 4H), 2.32 (s, 3H), 1.49 (m, 4H), 1.34 (m, 2H), 1.20 (d, J = 6.90 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.48, 143.75, 133.88, 129.08, 129.05, 64.82, 50.80, 26.16, 24.35, 21.72, 11.84, 11.79. HRMS (APCI) Calcd. for $C_{15}H_{21}NO$ [M + H]$^+$ 232.1696, found 232.1696.



1-(4-methoxyphenyl)-2-(piperidin-1-yl)propan-1-one (**18a**):

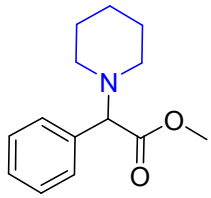
[Cu] **1**(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO (0.1 mL), then 4-Methoxypropiophenone (82 mg, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of piperidine(149 µL, 1.5 mmol, 3.0 equiv). The reaction was stirred at room temperature for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (114 mg, 92% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, J = 8.70 Hz, 2H), 6.90 (d, J = 8.70 Hz, 2H), 4.00 (q, J = 6.90 Hz, 1H), 3.85 (s, 3H), 2.52 (m, 4H), 1.51 (m, 4H), 1.41 (m, 2H), 1.24 (d, J = 6.90 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.98, 163.59, 131.62, 129.82, 113.74, 65.50, 55.76, 51.18, 26.67, 24.78, 11.94. HRMS (APCI) Calcd. for $C_{15}H_{21}NO_2$ [M + H]$^+$ 248.1645, found

248.1647.



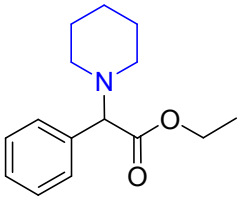
1-(4-chlorophenyl)-2-(piperidin-1-yl)propan-1-one (**19a**):

[Cu] 1(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO (0.1 mL), then 4-chloropropiophenone (84 mg, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of piperidine(149 μL, 1.5 mmol, 3.0 equiv). The reaction was stirred at 10℃ for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (122 mg, 97% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, J = 8.40 Hz, 2H), 7.39 (d, J = 8.40 Hz, 2H), 4.01 (q, J = 6.90 Hz, 1H), 2.51 (m, 4H), 1.51 (m, 4H), 1.39 (m, 2H), 1.23 (d, J = 6.90 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.04, 139.42, 134.98, 130.88, 128.86, 65.85, 50.95, 26.58, 24.63, 10.82. HRMS (APCI) Calcd. for $C_{14}H_{18}ClNO$ $[M + H]^+$ 252.1150, found 252.1150.



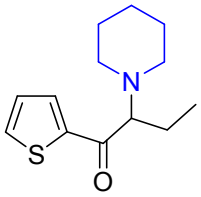
methyl 2-phenyl-2-(piperidin-1-yl)acetate (**20a**):[2]

[Cu] 1(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO (0.1 mL), then Methyl phenylacetate (71 μL, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of piperidine(149 μL, 1.5 mmol, 3.0 equiv). The reaction was stirred at 50℃ for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (101 mg, 87% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (m, 2H), 7.23 (m, 3H), 3.90 (s, 1H), 3.59 (s, 3H), 2.29 (m, 4H), 1.51 (m, 4H), 1.35 (m, 2H).



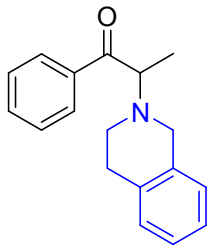
Ethyl 2-(piperidin-1-yl)-2-phenylacetate (**21a**):

[Cu] 1(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO (0.1 mL), then Eethyl phenylacetate (80 μL, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of piperidine(149 μL, 1.5 mmol, 3.0 equiv). The reaction was stirred at 50℃ for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (104 mg, 84% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (m, 2H), 7.23 (m, 3H), 4.06 (m, 2H), 3.87 (s, 1H), 2.31 (m, 4H), 1.50 (m, 4H), 1.35 (m, 2H), 1.11 (t, J = 7.20 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.06, 136.65, 129.08, 128.65, 128.34, 75.23, 60.94, 52.62, 26.06, 24.64, 14.39. HRMS (APCI) Calcd. for $C_{15}H_{21}NO_2$ $[M + H]^+$ 248.1645, found 248.1643.



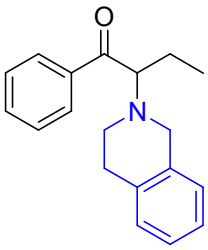
2-(piperidin-1-yl)-1-(thiophen-2-yl)butan-1-one (**22a**)

[Cu] 1(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO (0.5 mL), then 2-Butyrylthiophene(72 μL, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of piperidine(149 μL, 1.5 mmol, 3.0 equiv). The reaction was stirred at room temperature for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (110 mg, 93% Yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, J = 4.00 Hz, 1H), 7.56 (d, J = 4.00 Hz, 1H), 7.09 (t, J =4.00 Hz, 1H), 3.53 (m, 1H), 2.59 (m, 2H), 2.50 (m, 2H), 1.82 (m, 1H), 1.74 (m, 1H), 1.55 (m, 4H), 1.39 (m, 2H), 0.86 (t, J = 7.50 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.49, 143.32, 133.97, 133.08, 127.82, 73.85, 51.66, 26.52, 24.79, 20.54, 11.71. HRMS (APCI) Calcd. for $C_{13}H_{19}NOS$ $[M + H]^+$ 238.1260, found 238.1257.



2-(3,4-Dihydroisoquinolin-2(1H)-yl)-1-phenylpropan-1-one (**23a**):[1]

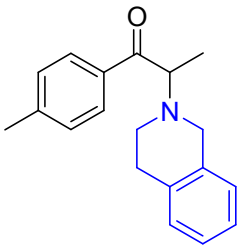
[Cu] 1(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO (0.5 mL), then propiophenone (67 µL, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of 1,2,3,4,-Tetrahydroisoquinoline(188 µL, 1.5 mmol, 3.0 equiv). The reaction was stirred at room temperature for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (125 mg, 94% Yield). ^{1}H NMR (300MHz, $CDCl_3$) δ 8.06 (m, 2H), 7.46 (m, 1H), 7.35 (m, 2H), 6.99 (m, 4H), 4.24 (q, J = 6.90 Hz, 1H), 3.81 (d, J = 15.0 Hz, 1H), 3.76 (d , J = 15.0 Hz, 1H), 2.77 (m, 4H), 1.31 (d, J = 6.90 Hz, 3H).



2-(3,4-dihydroisoquinolin-2(1H)-yl)-1-phenylbutan-1-one (**24a**):

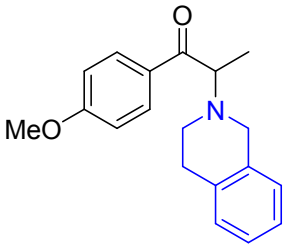
[Cu] 1(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO (0.5 mL), then Butyrophenone(75 µL, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of 1,2,3,4,-Tetrahydroisoquinoline(188 µL, 1.5 mmol, 3.0 equiv). The reaction was stirred at room temperature for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (133 mg, 95% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (m, 2H), 7.43 (m, 1H), 7.33 (m, 2H), 6.96 (m, 4H), 4.06 (q, J = 4.80 Hz, 1H), 3.80 (d, J = 15.0 Hz, 1H), 3.72 (d, J = 15.0 Hz, 1H), 2.80 (m, 2H), 2.72 (m, 2H), 1.92 (m, 1H), 1.75 (m, 1H), 0.82 (d, J = 7.20 Hz, 3H). ^{13}C NMR (75MHz, $CDCl_3$) δ 200.59, 137.84, 135.45, 135.00, 133.45, 129.19, 129.07, 128.99, 126.97, 126.44, 125.97, 70.12, 52.76, 47.70, 30.27, 19.89, 11.68. HRMS (APCI) Calcd. for $C_{19}H_{21}NO$ $[M + H]^+$ 280.1696, found

280.1695.



2-(3,4-dihydroisoquinolin-2(1H)-yl)-1-p-tolylpropan-1-one (**25a**):

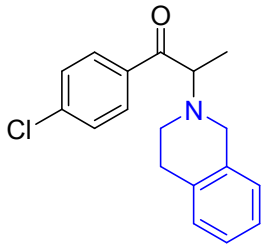
[Cu] **1**(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO (0.1 mL), then 4-Methylpropiophenone (75 µL, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of 1,2,3,4,-Tetrahydroisoquinoline(188 µL, 1.5 mmol, 3.0 equiv). The reaction was stirred at room temperature for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (130 mg, 93% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (m, 2H), 7.13 (m, 2H), 6.97 (m, 4H), 4.19 (q, J = 6.90 Hz, 1H), 3.80 (d, J = 14.7 Hz, 1H), 3.70 (d, J = 14.7 Hz, 1H), 2.75 (m, 4H), 2.29 (s, 3H), 1.28 (d, J = 6.90 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.57, 144.09, 135.16, 134.78, 133.99, 129.42, 129.35, 126.87, 126.29, 125.84, 64.39, 52.38, 47.51, 29.91, 21.97, 11.98. HRMS (APCI) Calcd. for $C_{19}H_{21}NO$ $[M + H]^+$ 280.1696, found 280.1696.



2-(3,4-dihydroisoquinolin-2(1H)-yl)-1-(4-methoxyphenyl)propan-1-one (**26a**):

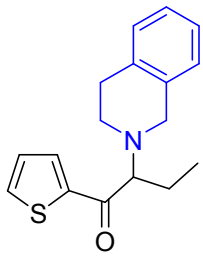
[Cu] **1**(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO(0.1 mL), then 4-Methoxypropiophenone (82 mg, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of 1,2,3,4,-Tetrahydroisoquinoline(188 µL, 1.5 mmol, 3.0 equiv). The reaction was stirred at room temperature for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (136 mg, 92% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (m, 2H), 6.98 (m, 4H), 6.90 (m, 2H), 4.15 (q, J = 6.90 Hz, 1H), 3.80 (d, J = 14.7 Hz, 1H), 3.79 (s, 3H), 3.75 (m, 2H),

2.76 (m, 4H), 1.28 (d, J = 6.90 Hz, 3H). ^{13}C NMR (125 MHz, CDCl3) δ 199.46, 163.65, 135.16, 134.76, 131.61, 129.37, 128.97, 126.86, 126.27, 125.82, 113.81, 64.55, 55.67, 52.39, 47.52, 29.90, 11.99. HRMS (APCI) Calcd. for $C_{19}H_{21}NO_2$ $[M + H]^+$ 296.1645, found 296.1643.



1-(4-chlorophenyl)-2-(3,4-dihydroisoquinolin-2(1H)-yl)propan-1-one (**27a**):

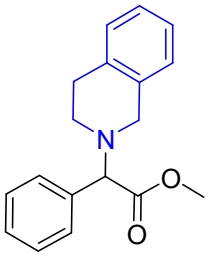
[Cu] **1**(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO (0.5 mL), then 4-chloropropiophenone (84 mg, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of 1,2,3,4,-Tetrahydroisoquinoline(188 μL, 1.5 mmol, 3.0 equiv). The reaction was stirred at 10℃ for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (130 mg, 87% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (m, 2H), 7.27 (m, 2H), 6.97 (m, 4H), 4.14 (q, J = 6.90 Hz, 1H), 3.77 (d, J = 14.7 Hz, 1H), 3.69 (d, J = 14.7 Hz, 1H), 2.72 (m, 4H), 1.28 (d, J = 6.90 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.61, 139.61, 134.91, 134.64, 130.85, 129.05, 128.98, 126.87, 126.43, 125.94, 64.94, 52.23, 47.38, 29.89, 11.02. HRMS (APCI) Calcd. for $C_{18}H_{16}ClNO$ $[M + H]^+$ 300.1150, found 300.1144.



2-(3,4-dihydroisoquinolin-2(1H)-yl)-1-(thiophen-2-yl)butan-1-one (**28a**):

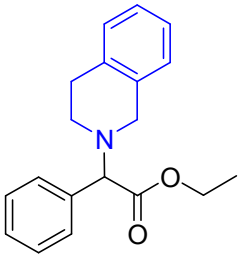
[Cu] **1**(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO(0.5 mL), then 2-Butyrylthiophene(72 μL, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of 1,2,3,4,-Tetrahydroisoquinoline(188 μL, 1.5 mmol, 3.0 equiv). The reaction was stirred at room temperature for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (127 mg, 89%

Yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (m, 1H), 7.57 (m, 1H), 7.11 (m, 4H), 7.01 (m, 1H), 3.96 (m, 1H), 3.83 (m, 2H), 2.90 (m, 4H), 1.98 (m, 1H), 1.92 (m, 1H), 0.96 (d, J = 7.50 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.03, 143.28, 135.02, 134.73, 134.32, 133.30, 129.03, 128.08, 126.86, 126.39, 125.90, 72.71, 52.84, 48.03, 29.77, 20.93, 11.58. HRMS (APCI) Calcd. for $C_{17}H_{19}NOS$ [M + H]$^{+}$ 286.1260, found 286.1263.



Methyl 2-(3,4-dihydroisoquinolin-2(1H)-yl)-2-phenylacetate (**29a**):

[Cu] 1(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO(0.5 mL), then Methyl phenylacetate (71 μL, 0.5 mmol, 1.0 equiv)was added. This was stirred for 10 minutes at room temperature before the addition of 1,2,3,4,-Tetrahydroisoquinoline(188 μL, 1.5 mmol, 3.0 equiv). The reaction was stirred at 50℃ for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow liquid (121 mg, 86% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (m, 2H), 7.37 (m, 3H), 7.10 (m, 3H), 6.95 (m, 1H), 4.25 (s, 1H), 3.74 (s, 3H), 3.70 (m, 2H), 2.82 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.45, 136.36, 134.58, 129.16, 129.05, 128.86, 127.04, 126.57, 126.06, 73.91, 54.26, 52.51, 48.72, 29.20. HRMS (APCI) Calcd. for $C_{18}H_{19}NO_2$ [M + H]$^{+}$ 282.1489, found 282.1487.



Ethyl 2-(3,4-dihydroisoquinolin-2(1H)-yl)-2-phenylacetate (**30a**):

[Cu] 1(25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMSO(0.5 mL), then Eethyl phenylacetate (80 μL, 0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of 1,2,3,4,-Tetrahydroisoquinoline(188 μL, 1.5 mmol, 3.0 equiv). The reaction was stirred at 50℃ for 10 hours, after which the crude reaction mixture was loaded directly onto a

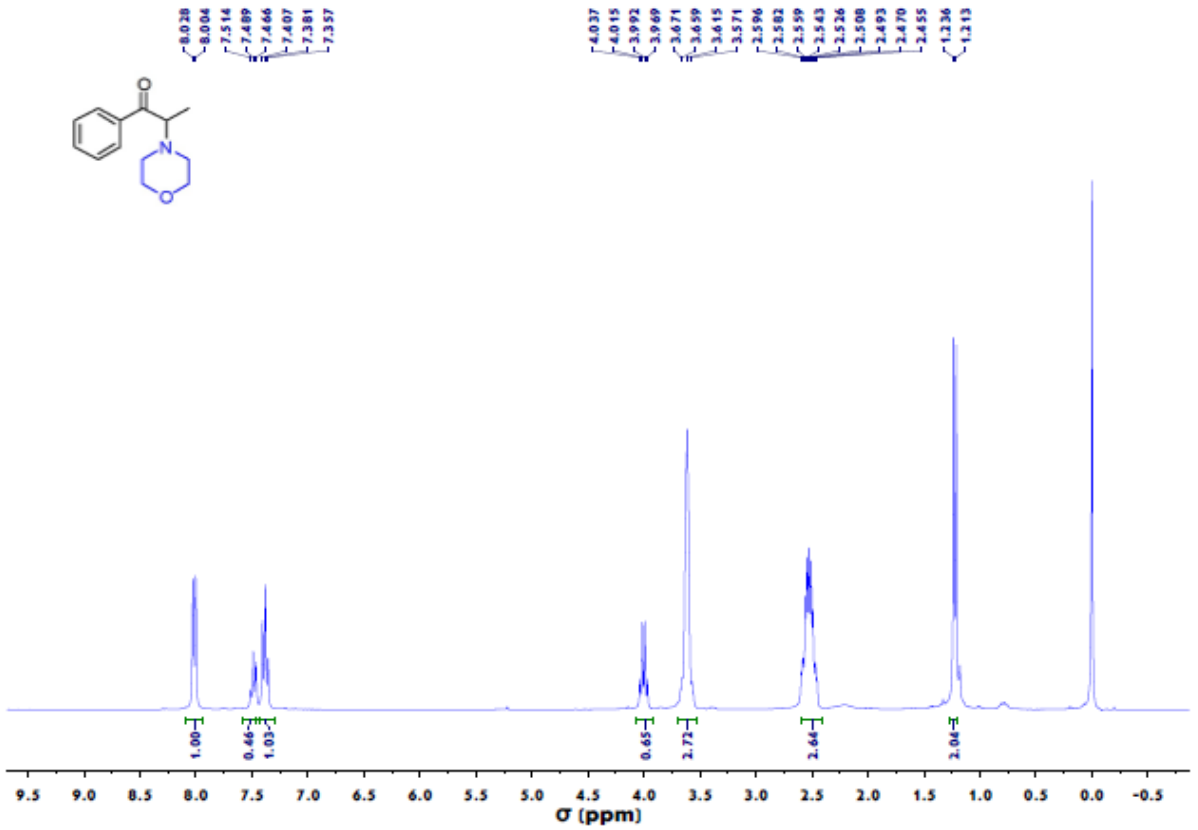
column of silica gel and purified by column chromatography to give the yellow liquid (119 mg, 81% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (m, 2H), 7.37 (m, 3H), 7.10 (m, 3H), 6.94 (m, 1H), 4.19 (m, 2H), 4.18 (s, 1H), 3.70 (m, 2H), 2.80 (m, 4H), 1.24 (t, J = 7.08 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.79, 136.33, 134.56, 134.48, 129.00, 128.89, 128.82, 128.59, 126.88, 126.38, 125.82, 73.77, 61.18, 54.01, 48.55, 29.06, 14.37. HRMS (APCI) Calcd. for $C_{19}H_{21}NO_2$ $[M + H]^+$ 296.1645, found 296.1647.

References

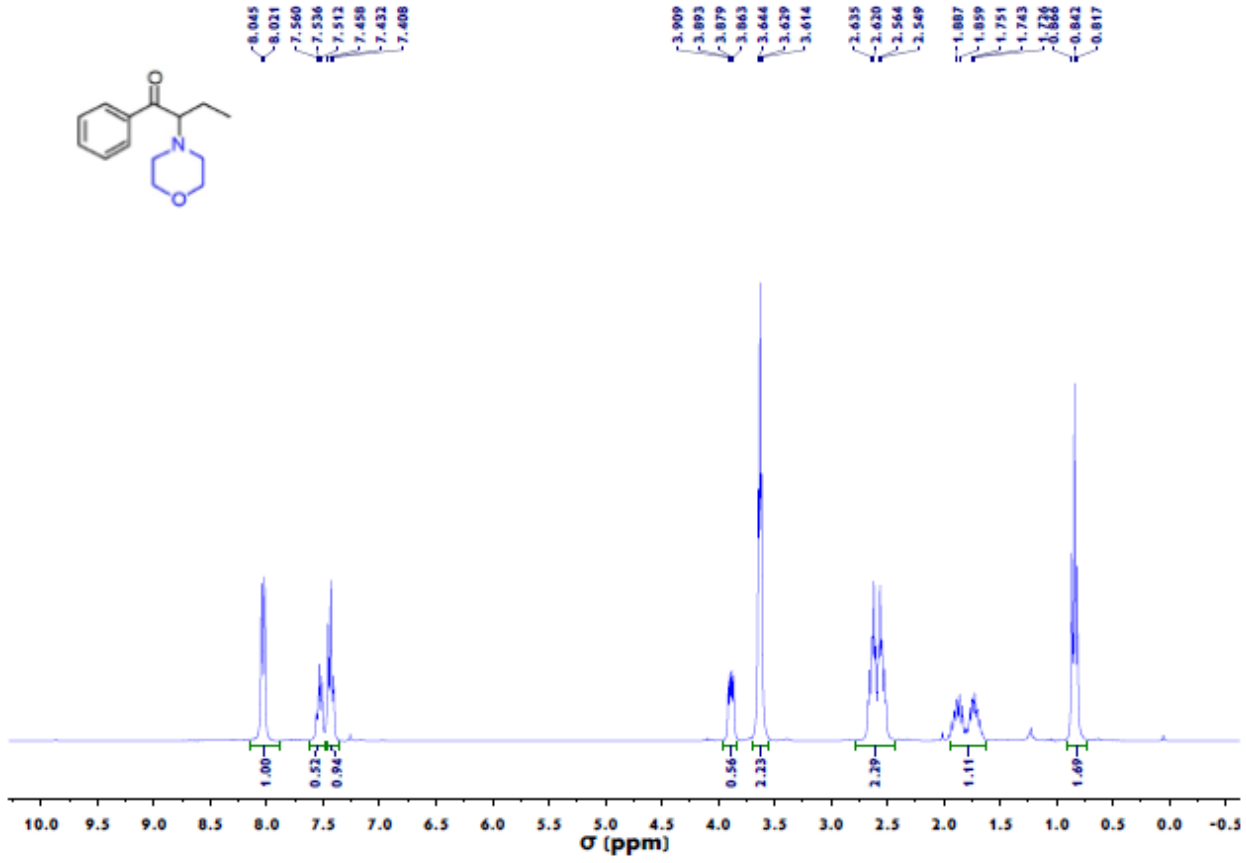
1 R. W. Evans, J. R. Zbieg, S. Zhu, W. Li and D. W. C. MacMillan, *J. Am. Chem. Soc.,* 2013, **135**, 16074-16077.

2 M. Lamani and K. R. Prabhu, *Chem. Eur. J.,* 2012, **18**, 14638-14642.

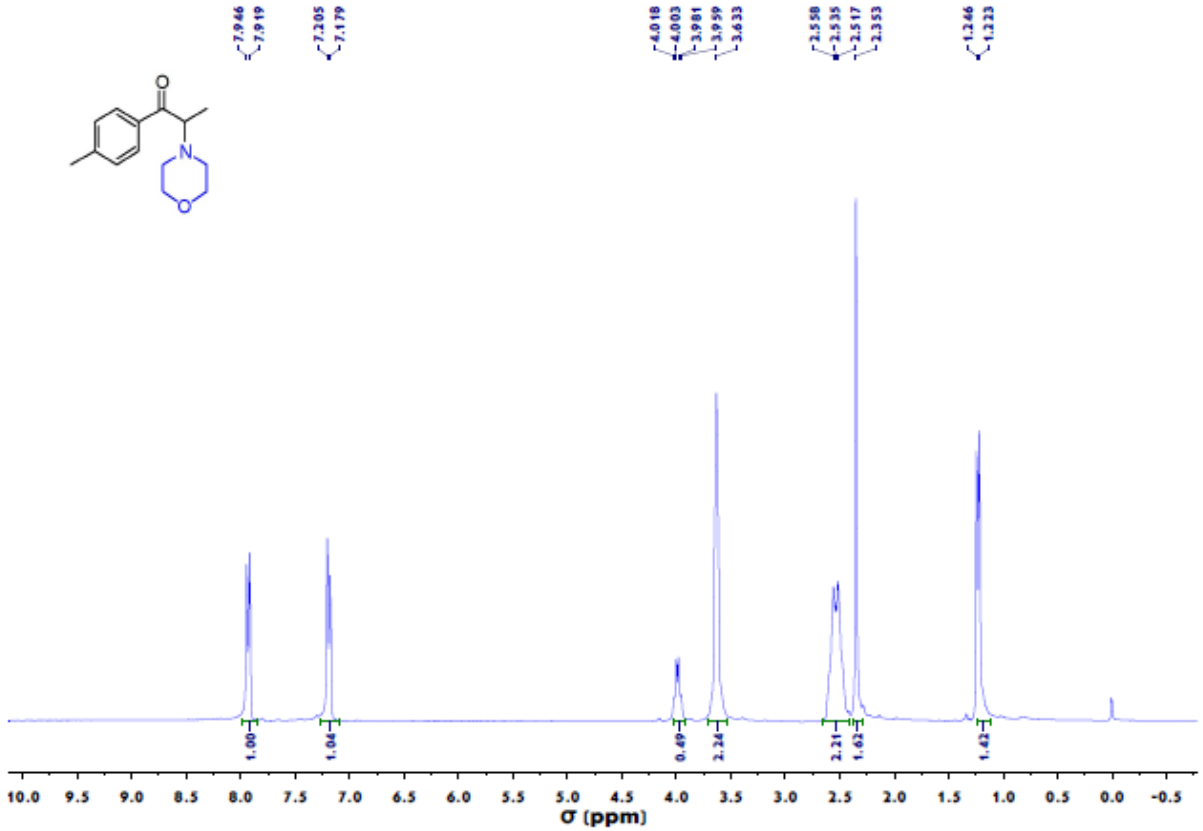
3 T. Miura, M. Morimoto and M. Murakami, *Org. Lett.,* 2012, **14**, 5214-5217.



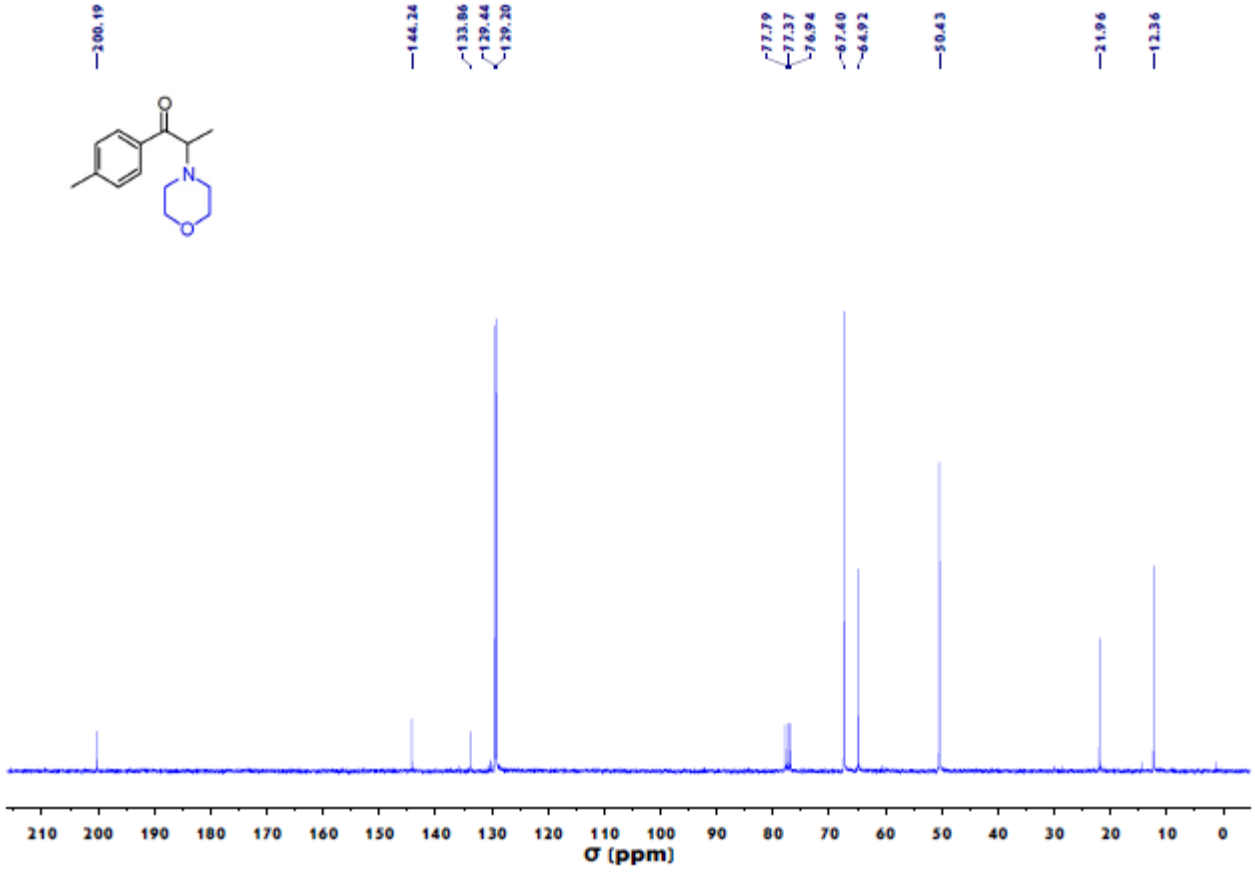
^{1}H NMR spectrum of **1a**



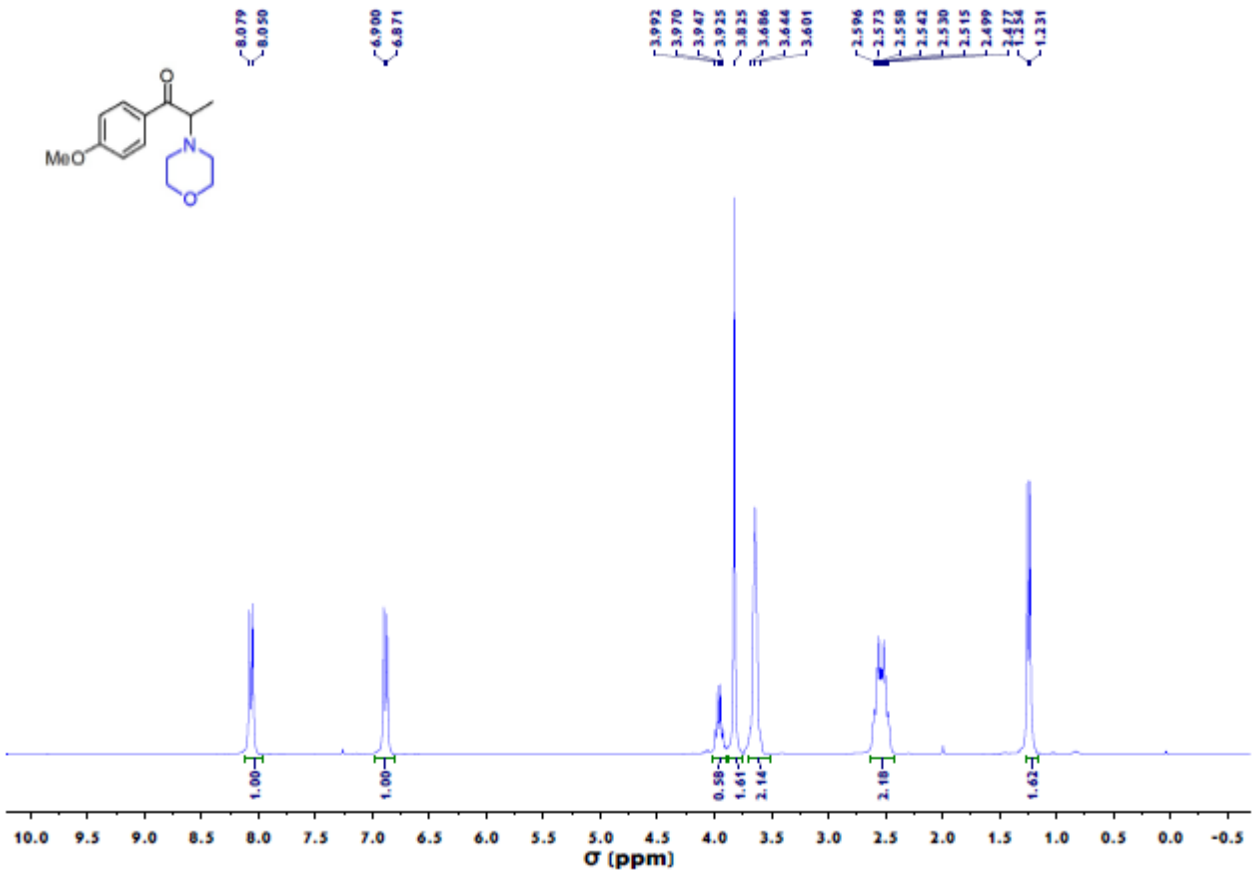
^{1}H NMR spectrum of **2a**



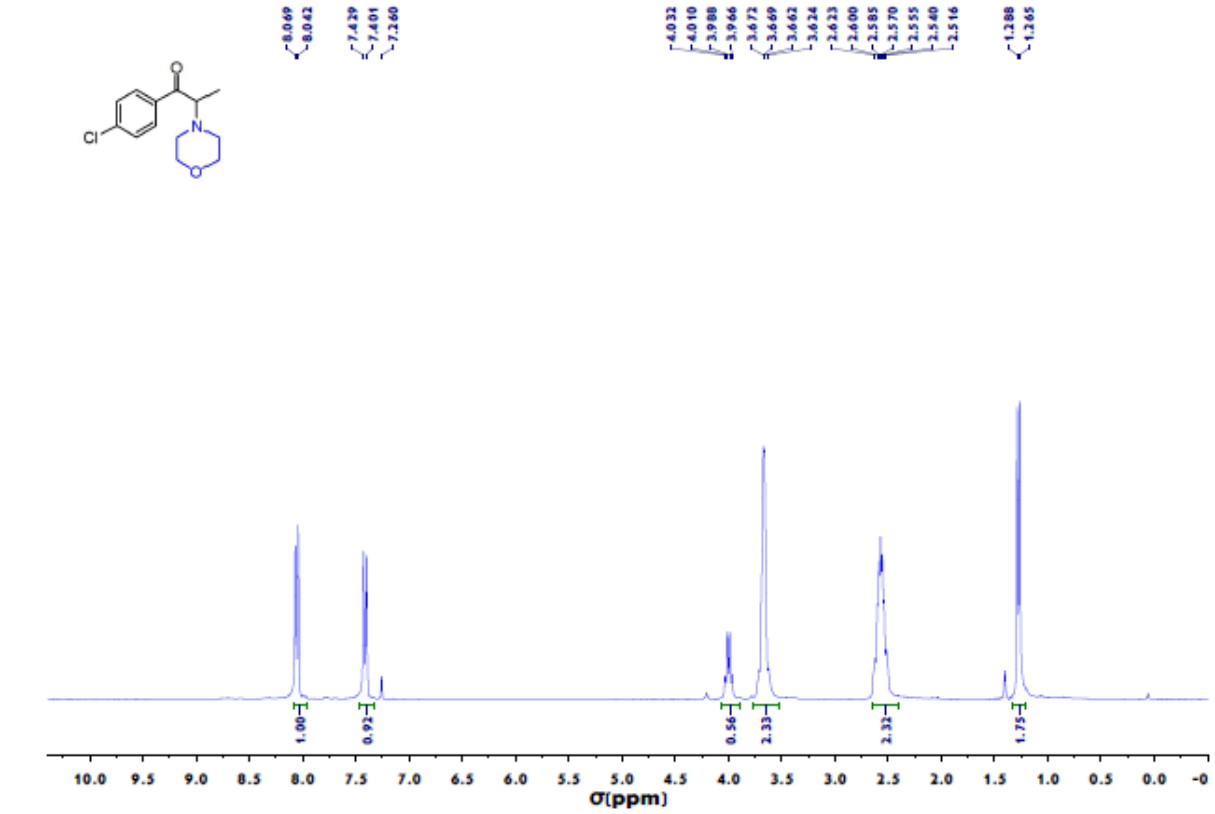
^{1}H NMR spectrum of **3a**



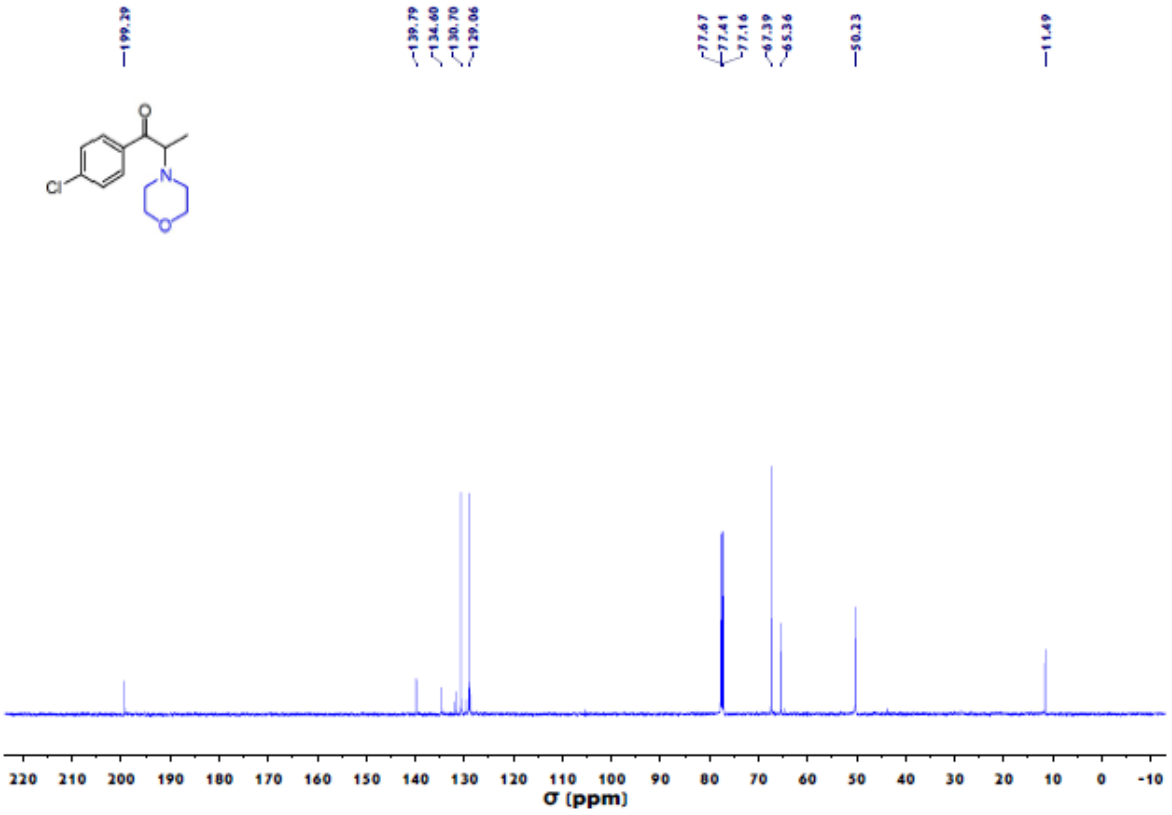
^{13}C NMR spectrum of **3a**



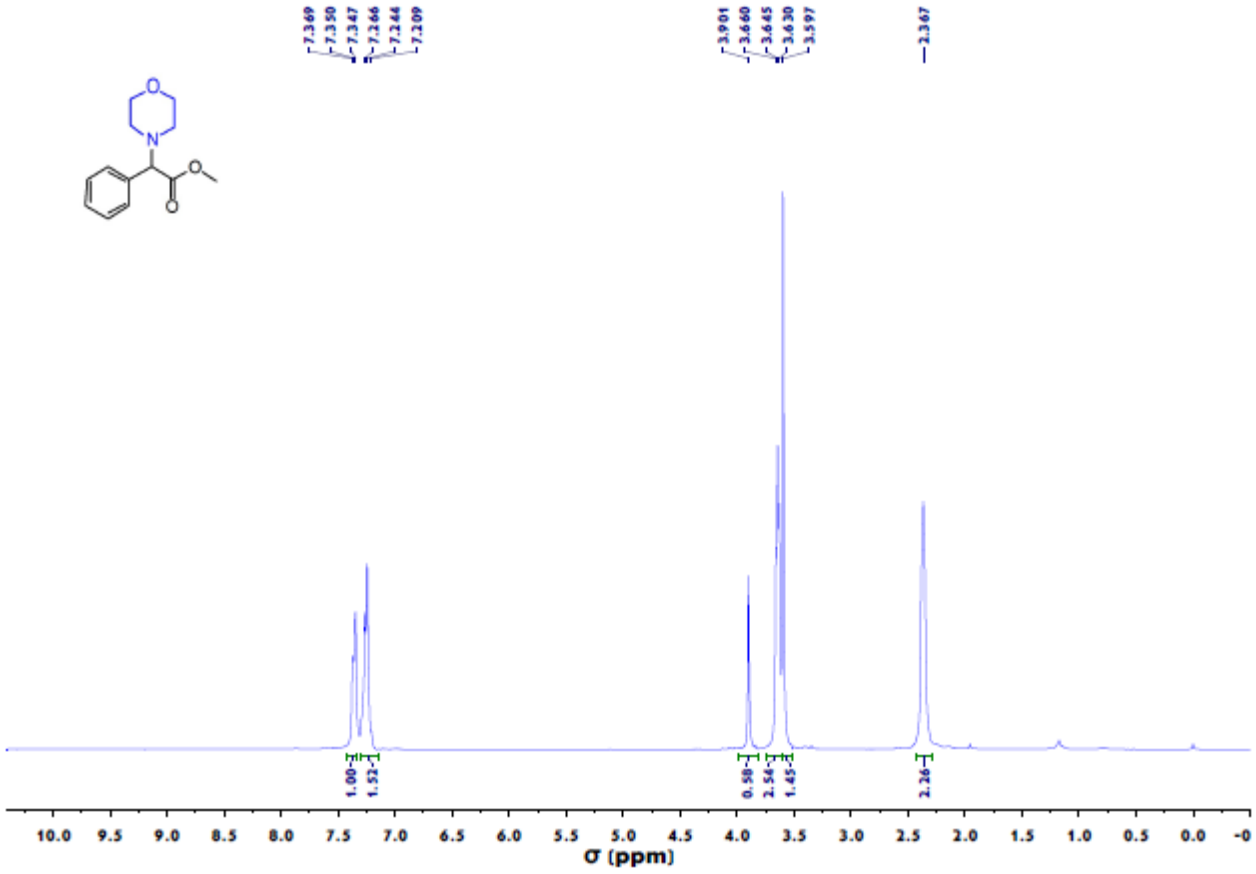
^{1}H NMR spectrum of **4a**



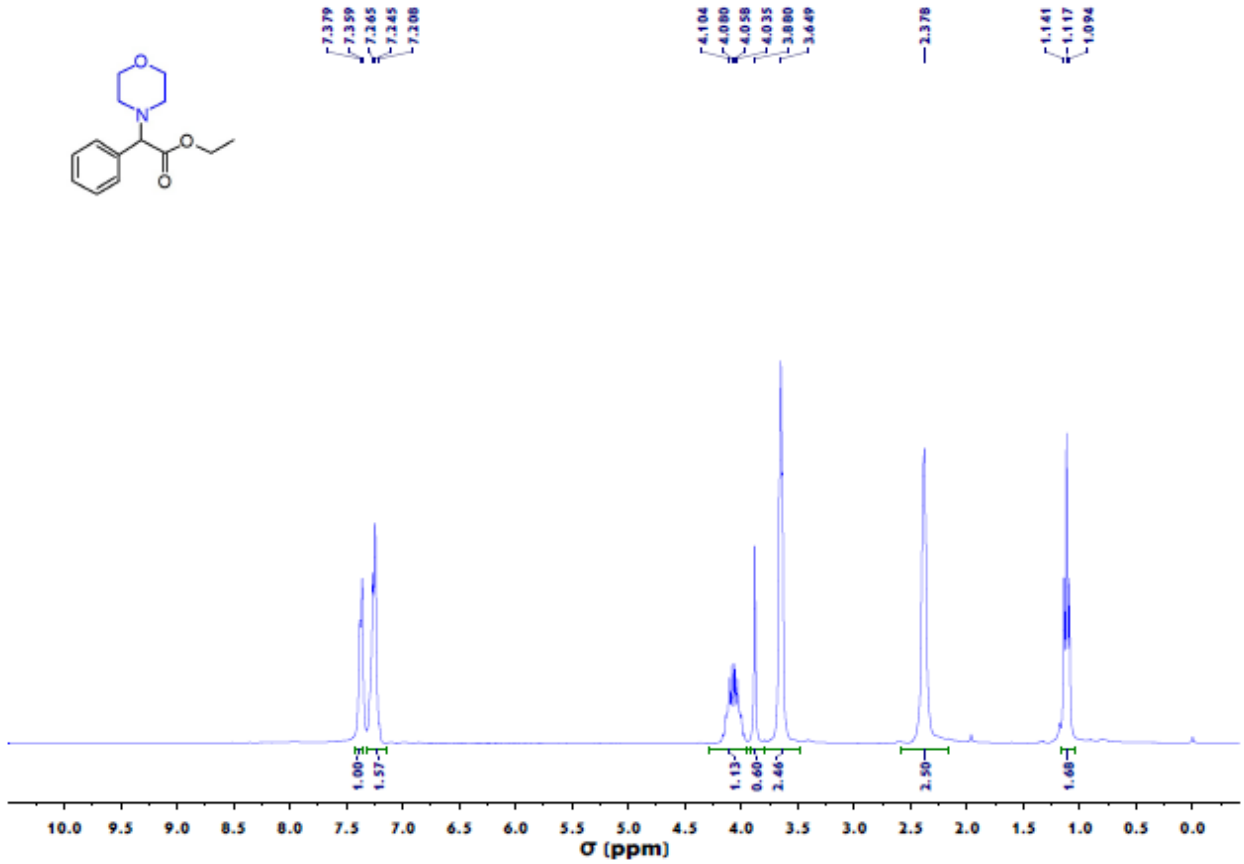
^{1}H NMR spectrum of **5a**



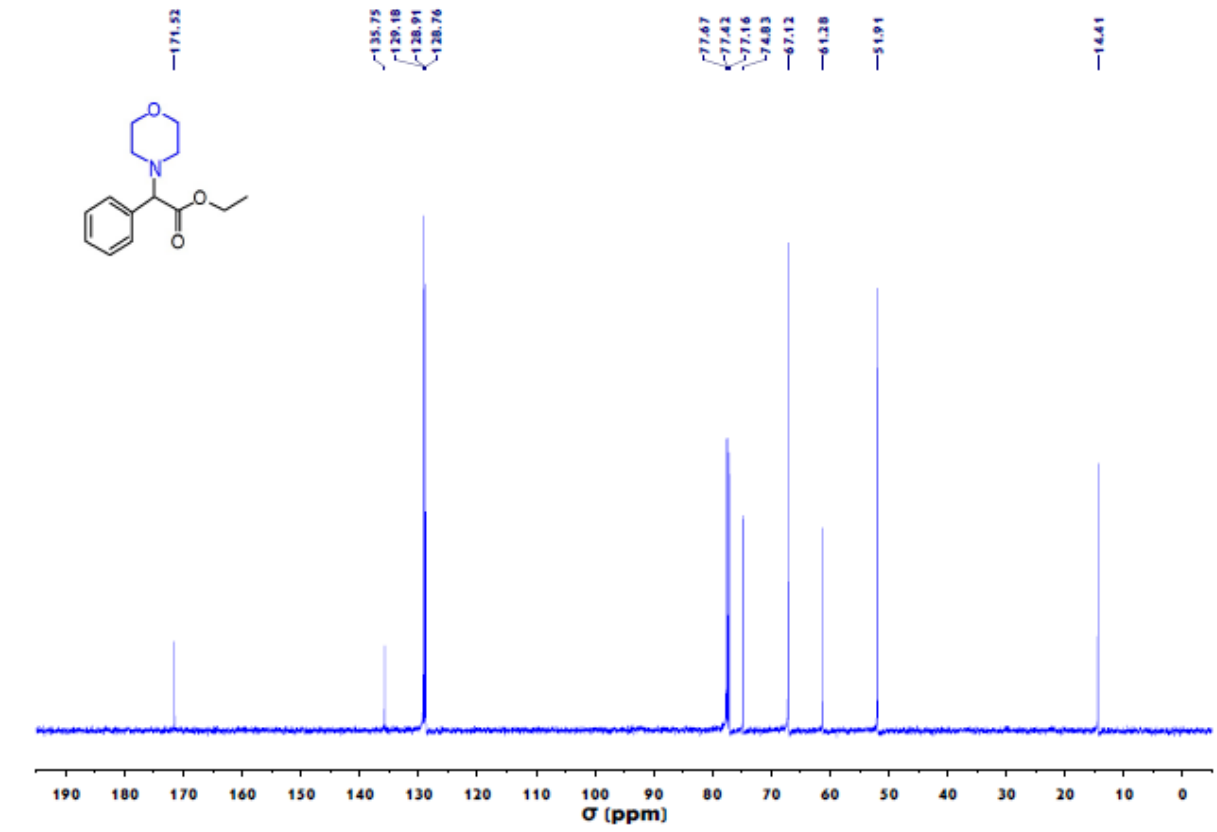
^{13}C NMR spectrum of **5a**



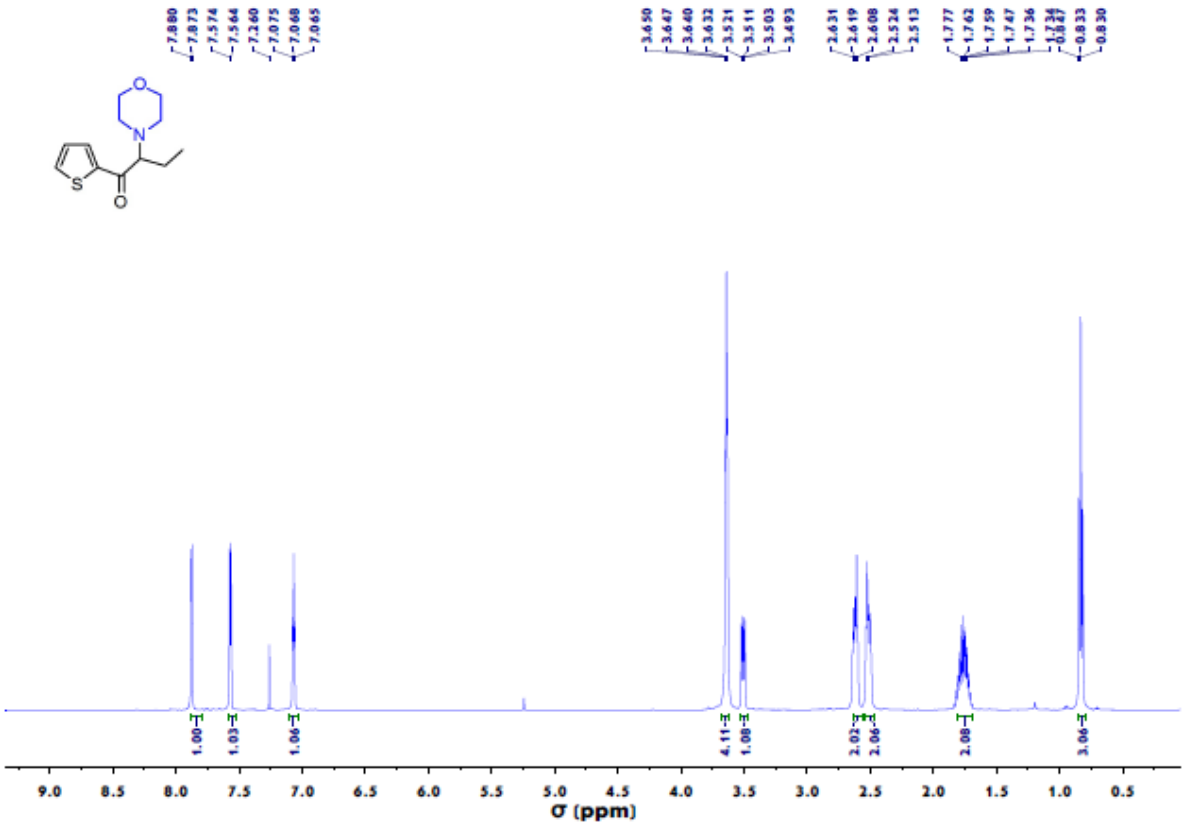
^{1}H NMR spectrum of **6a**



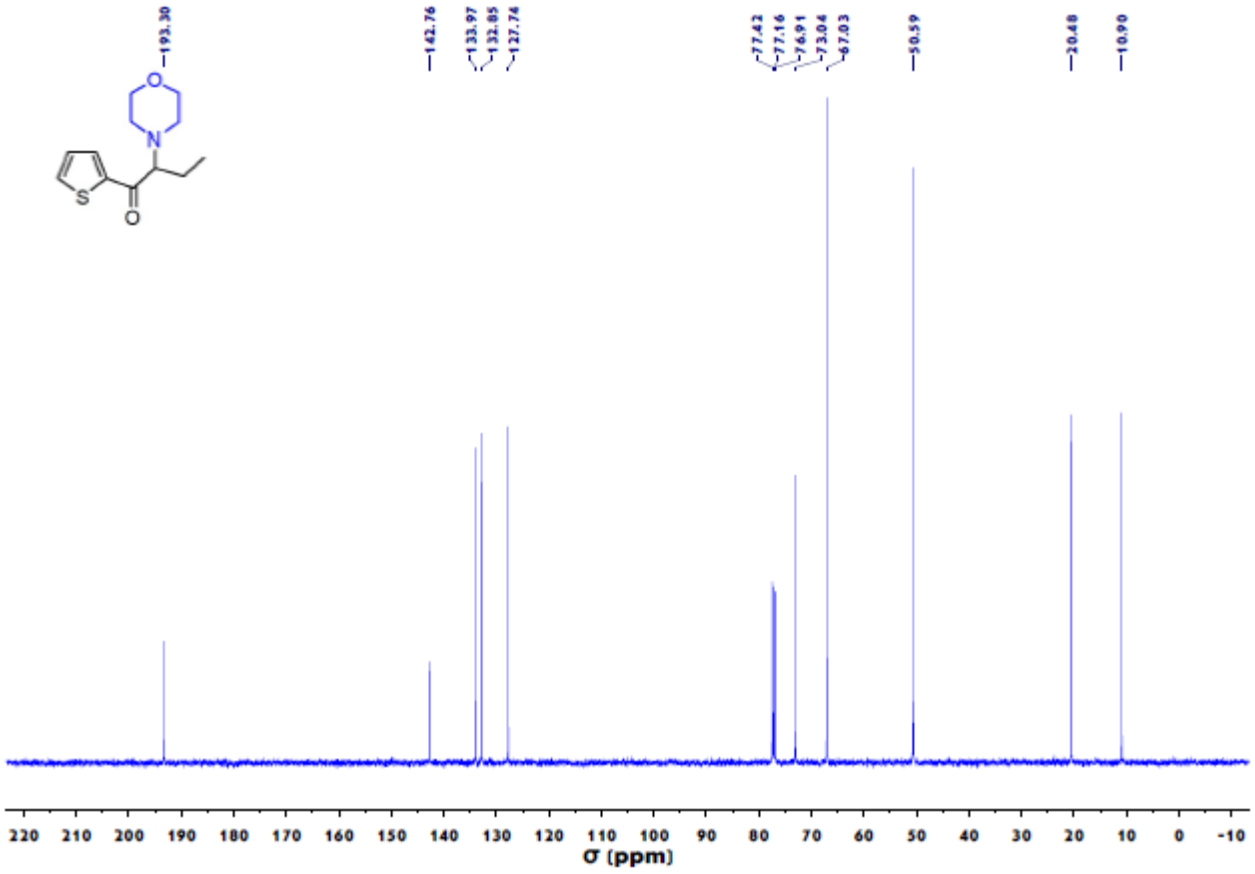
^{1}H NMR spectrum of **7a**



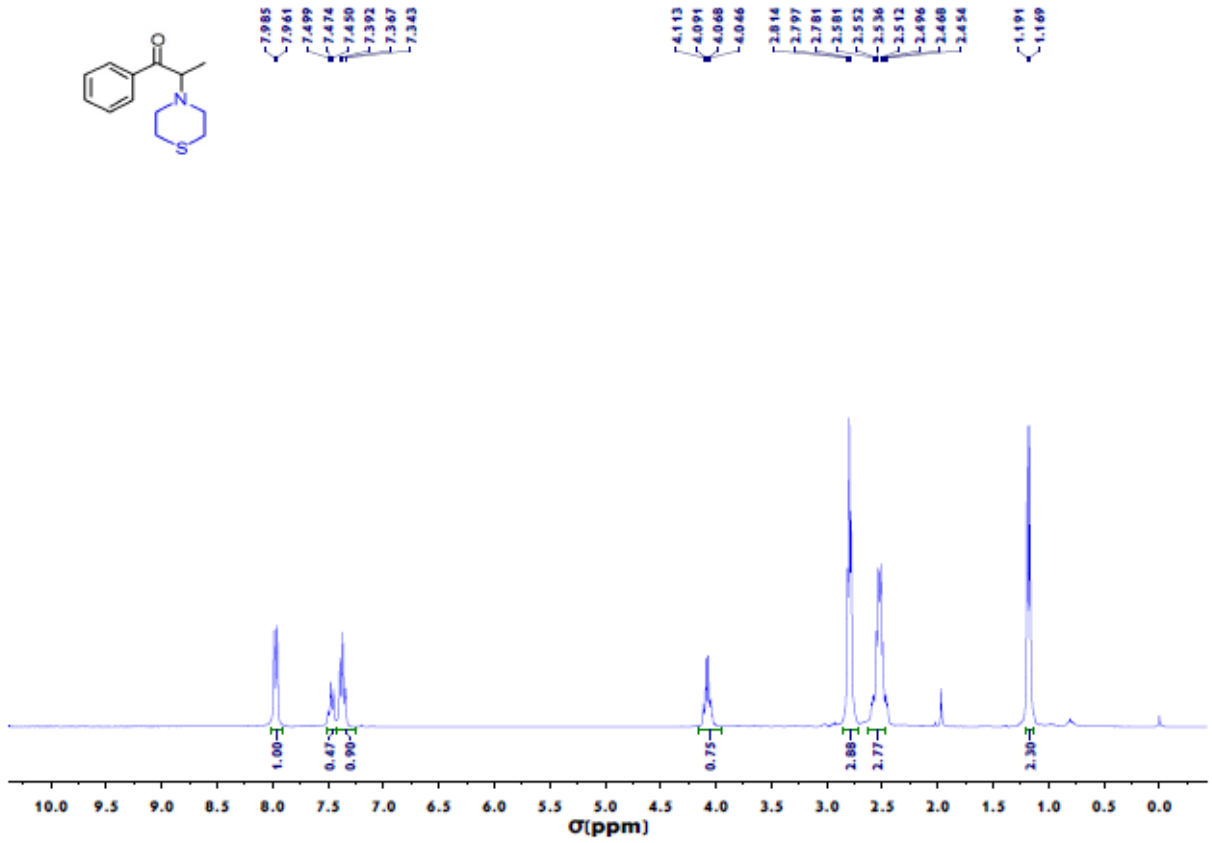
^{13}C NMR spectrum of **7a**



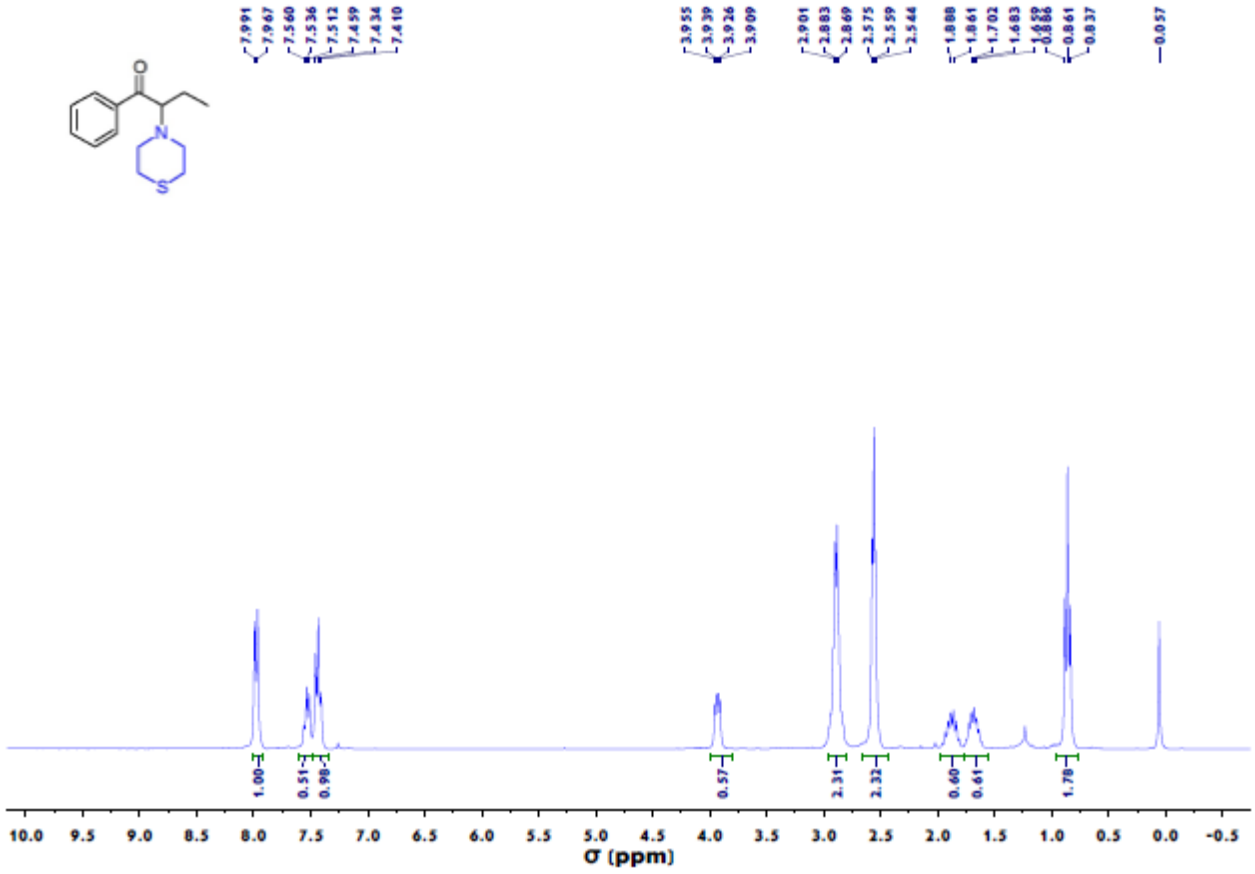
^{1}H NMR spectrum of **8a**



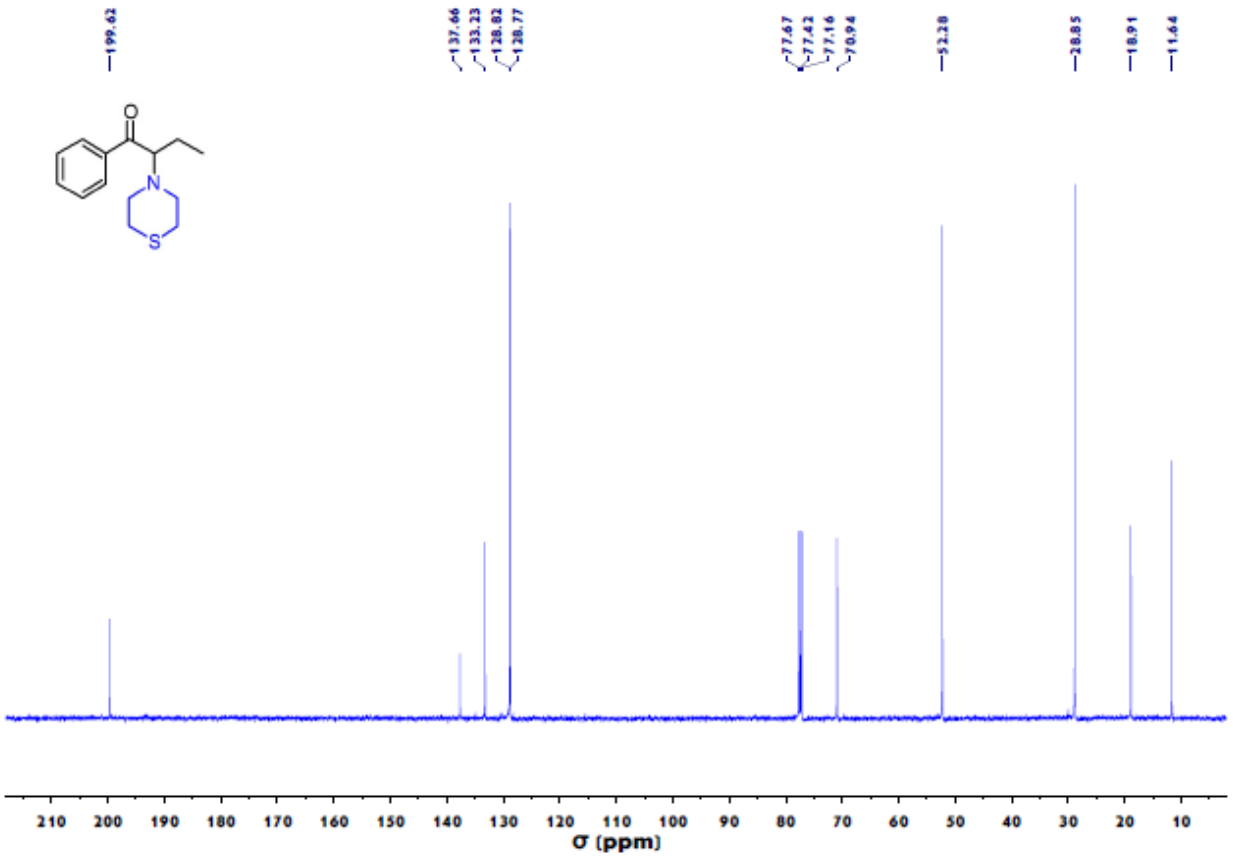
^{13}C NMR spectrum of **8a**



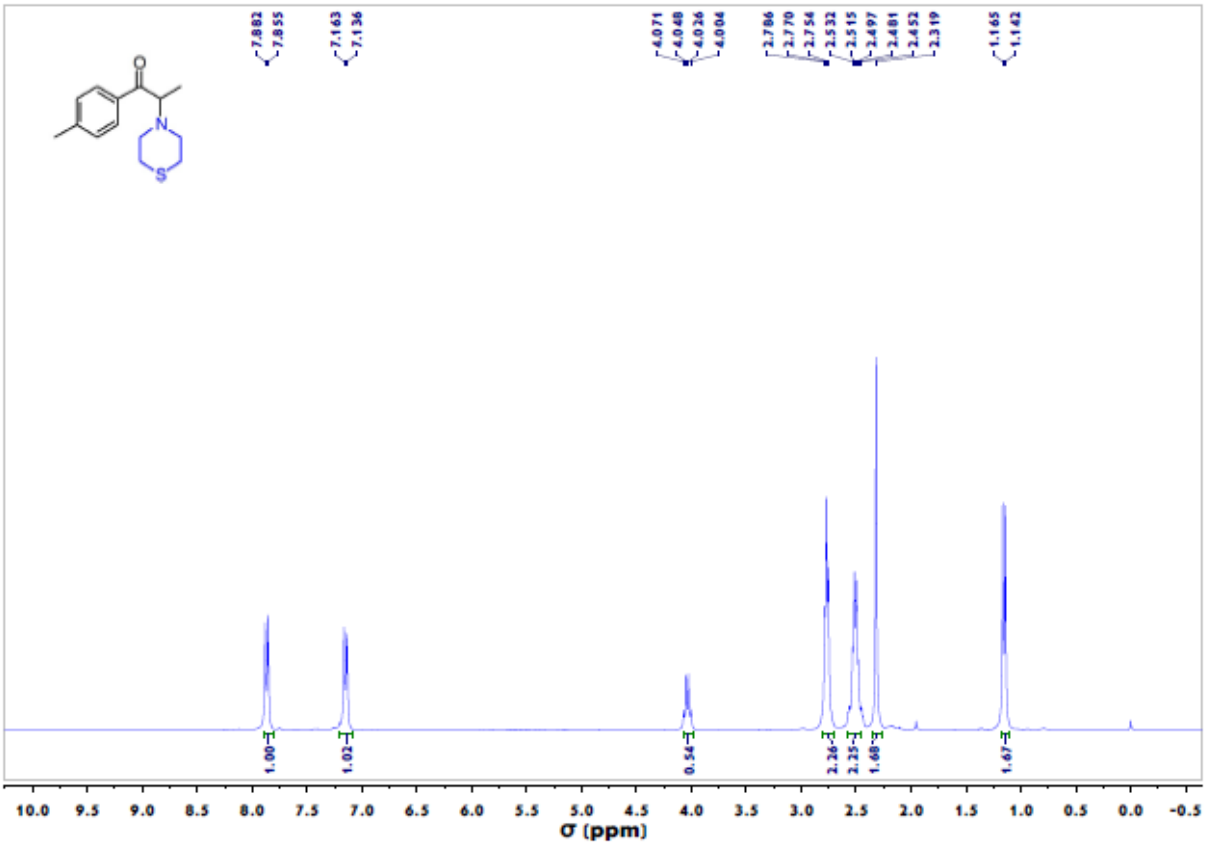
^{1}H NMR spectrum of **9a**



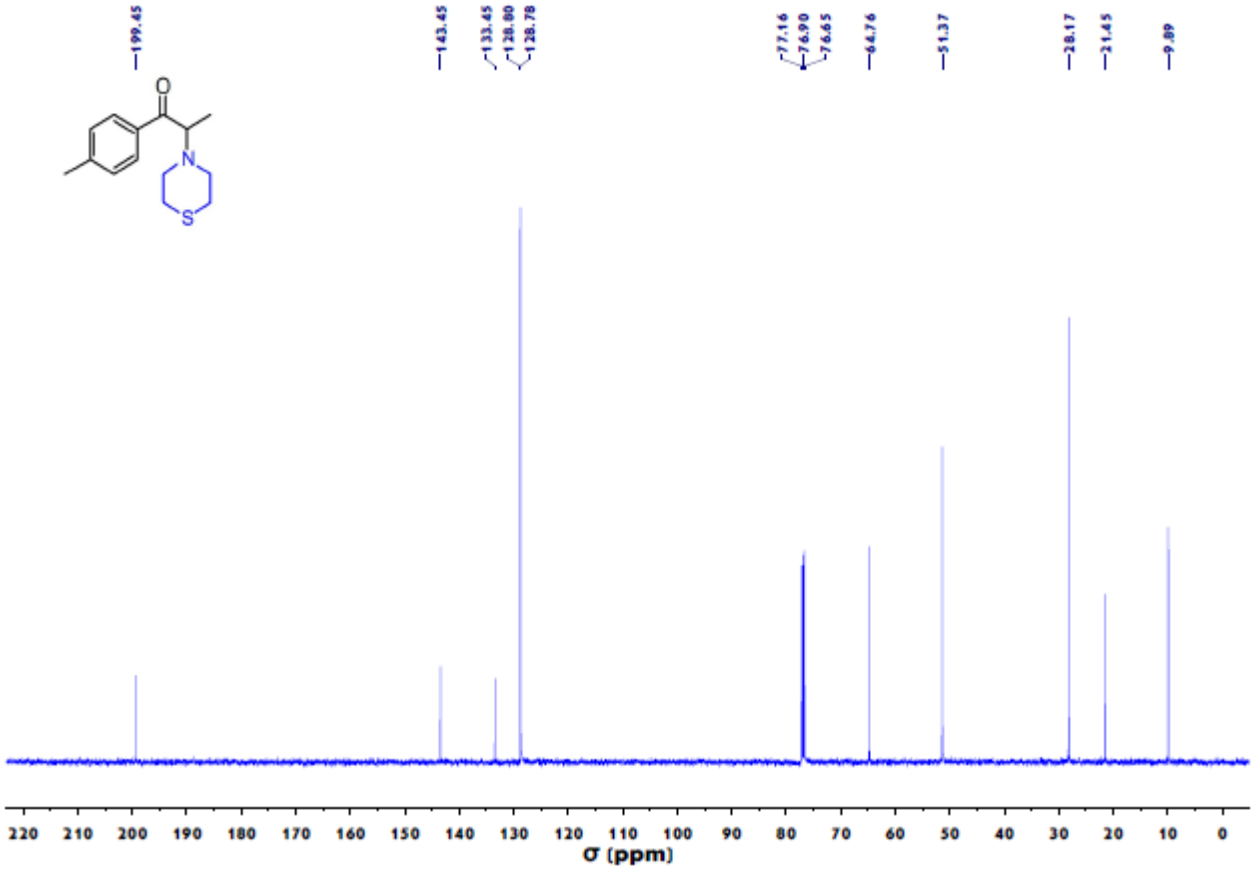
^{1}H NMR spectrum of **10a**



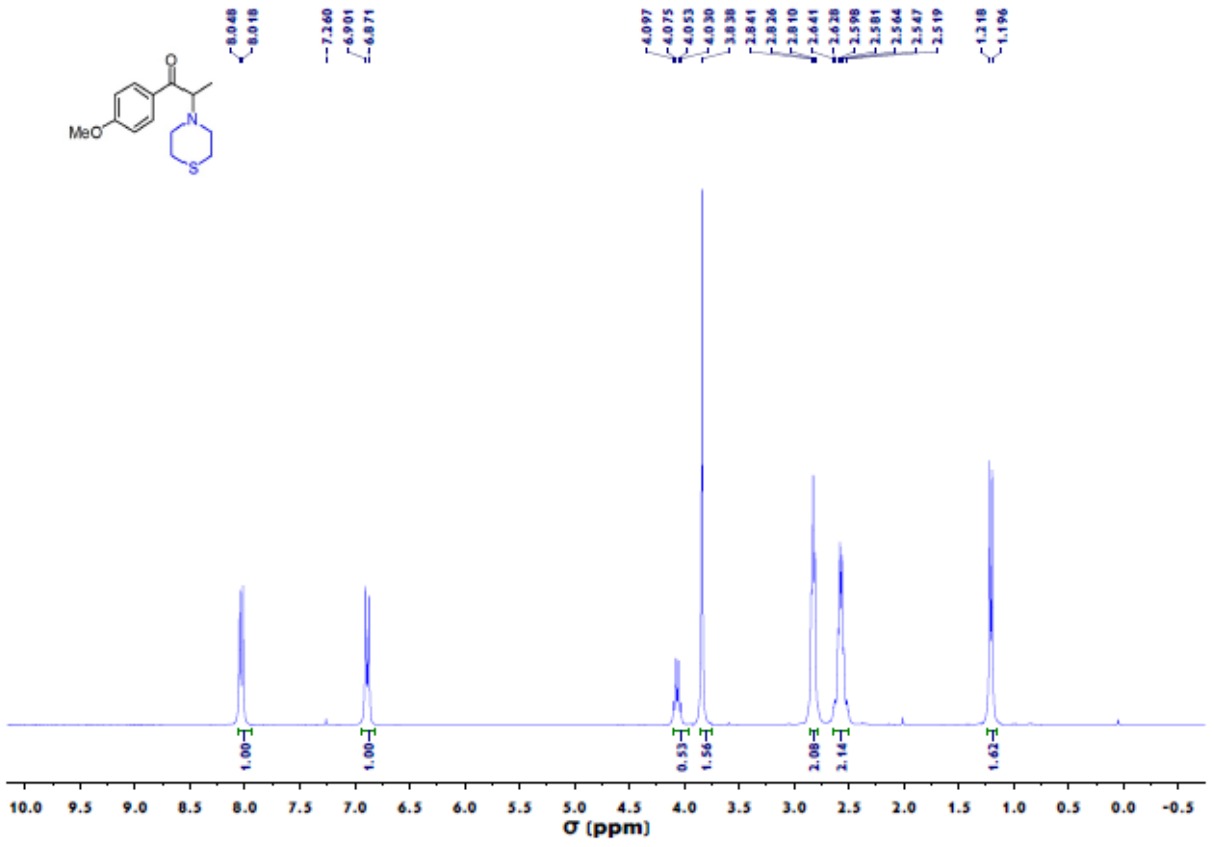
^{13}C NMR spectrum of **10a**



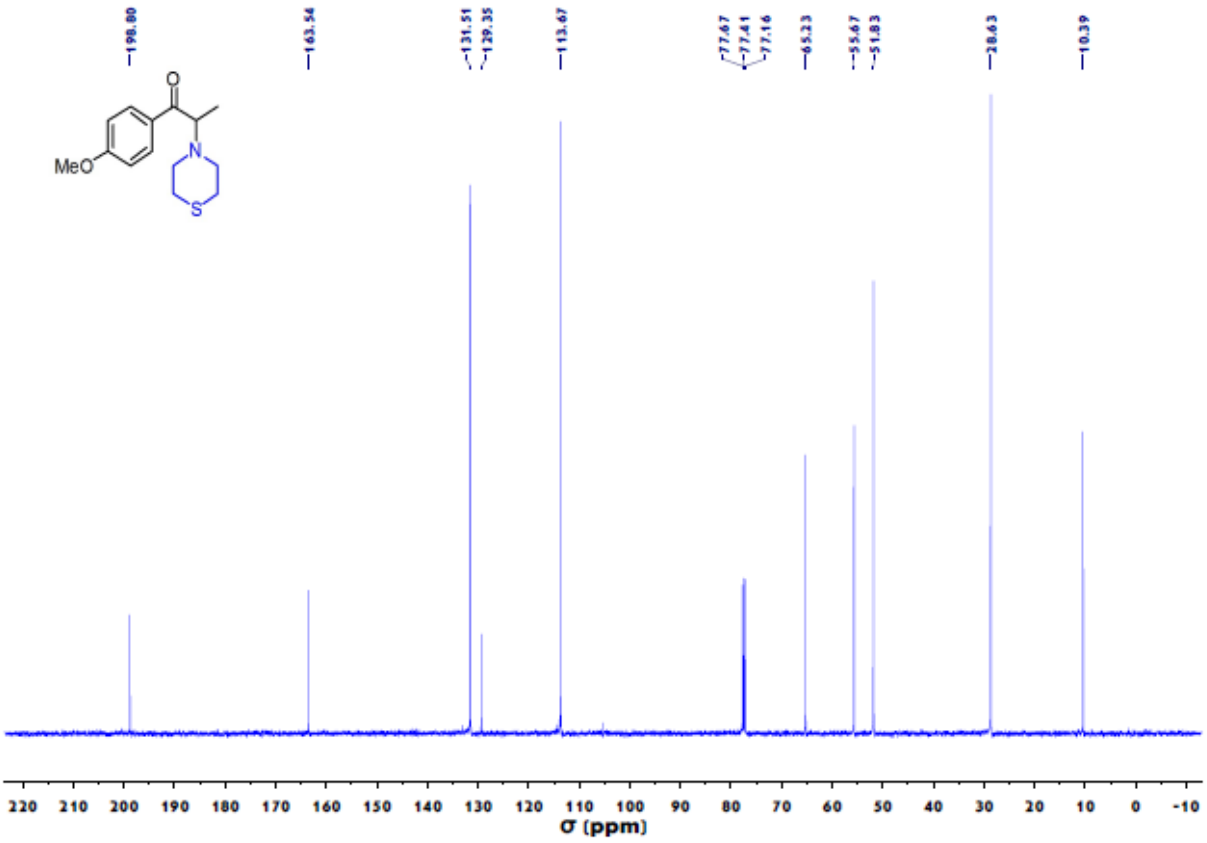
^{1}H NMR spectrum of **11a**



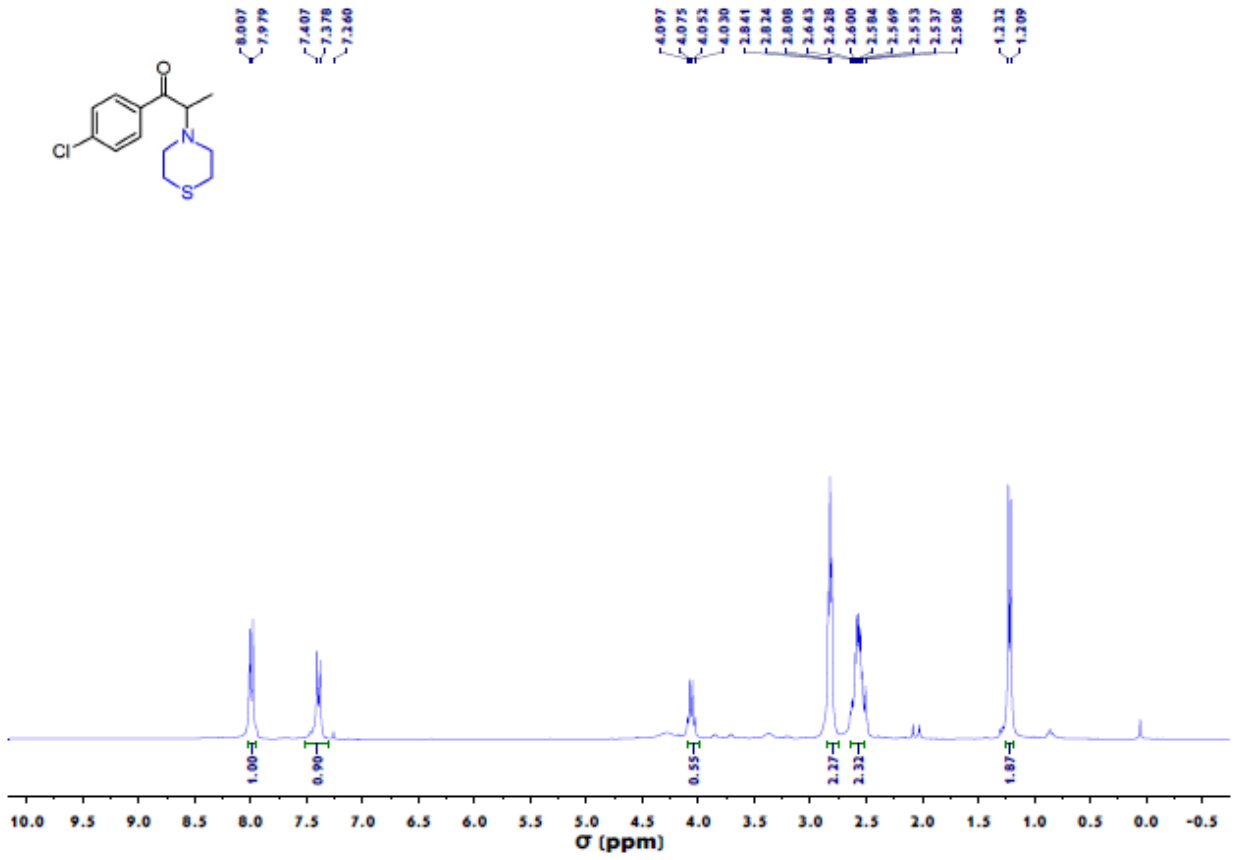
^{13}C NMR spectrum of **11a**



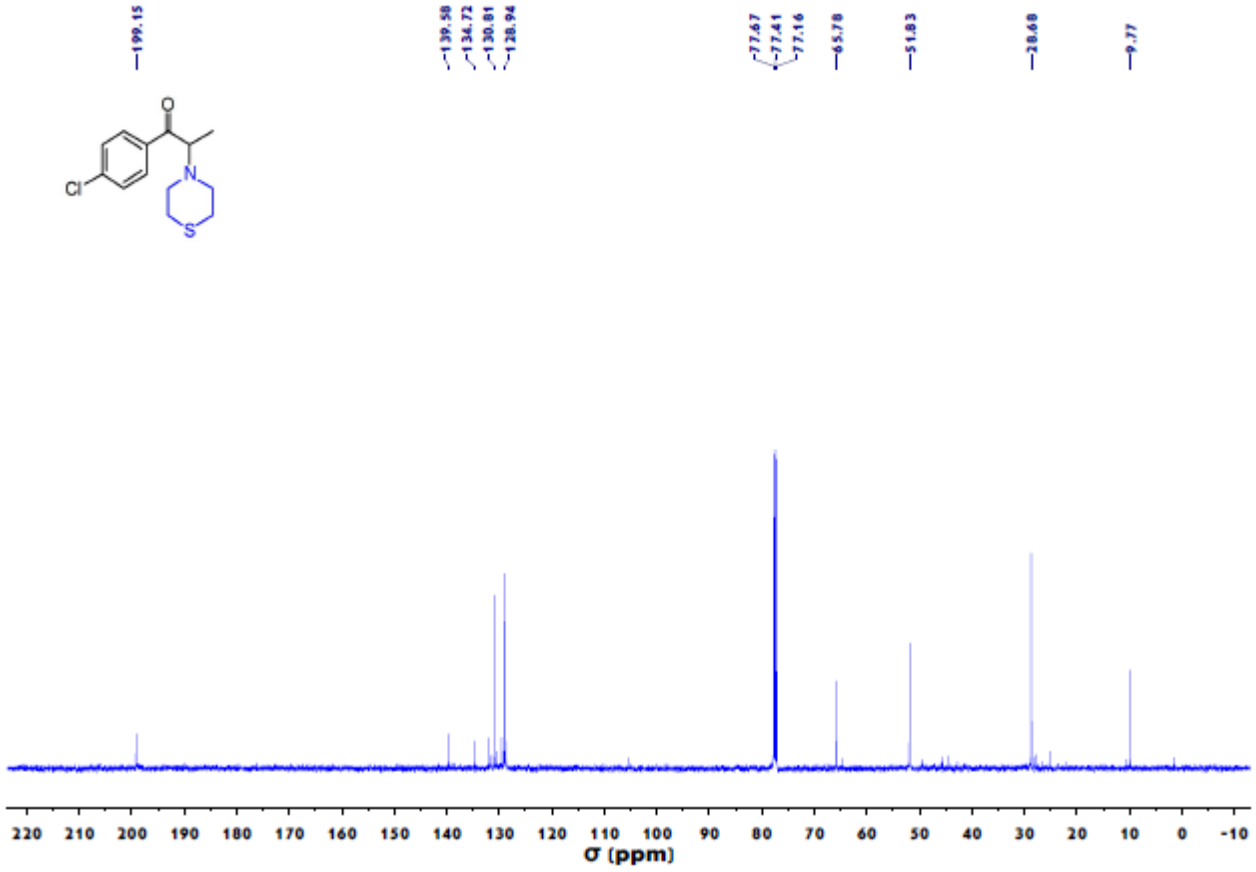
^{1}H NMR spectrum of **12a**



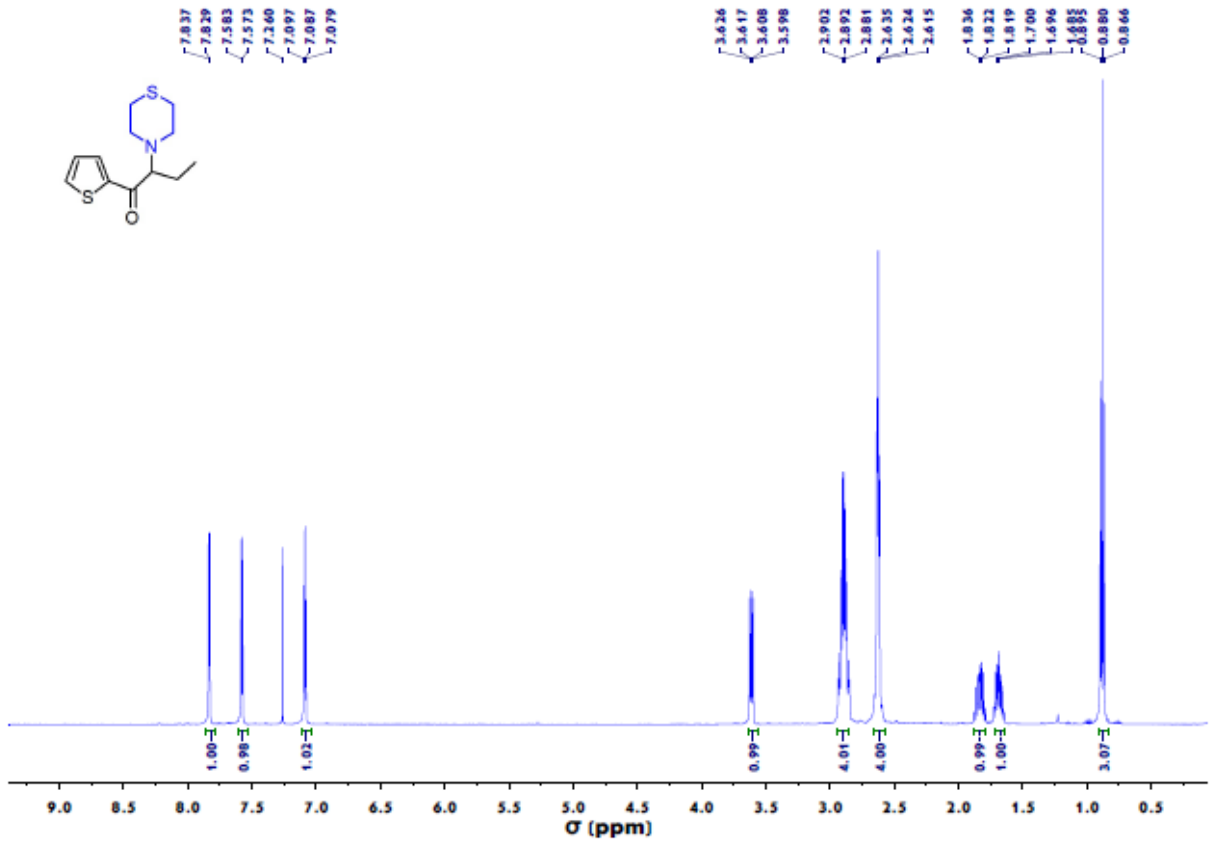
^{13}C NMR spectrum of **12a**



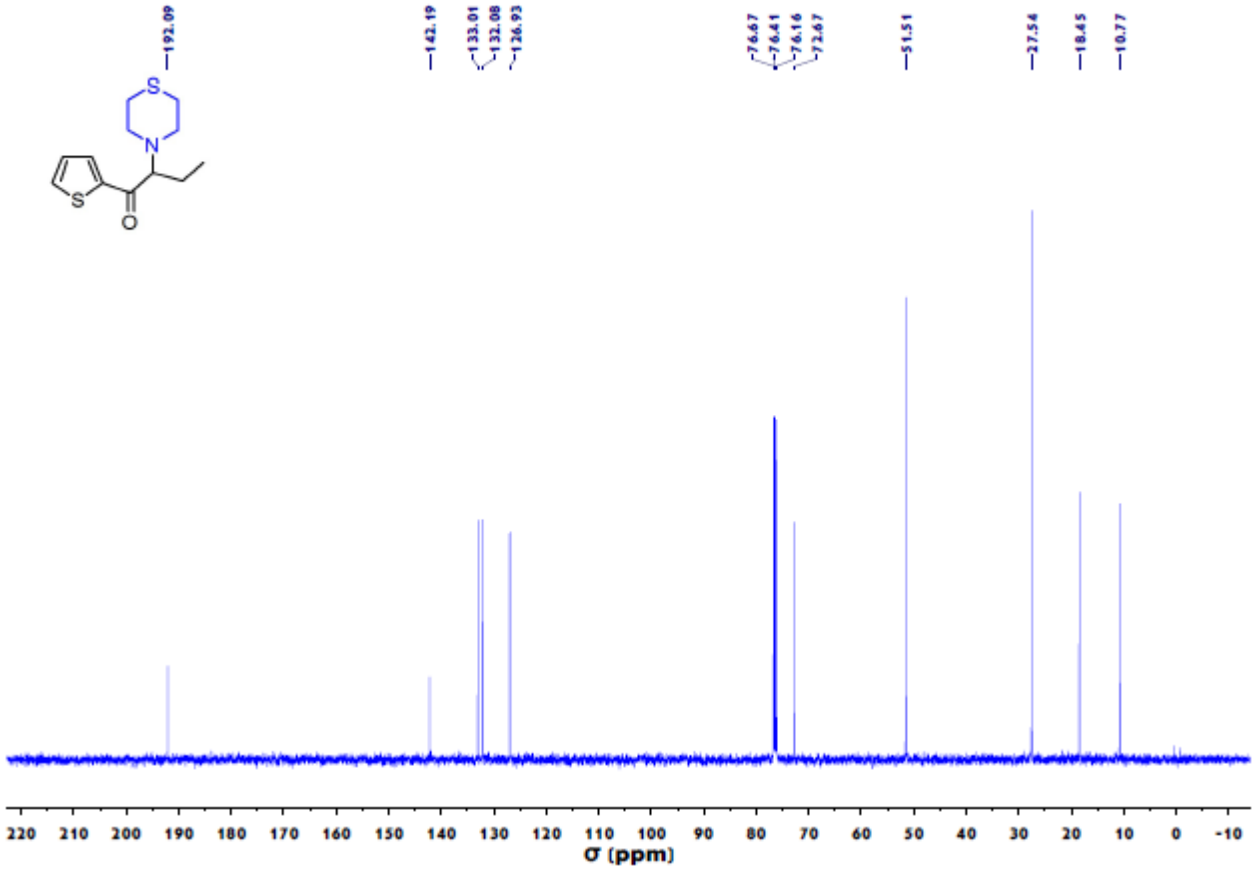
^{1}H NMR spectrum of **13a**



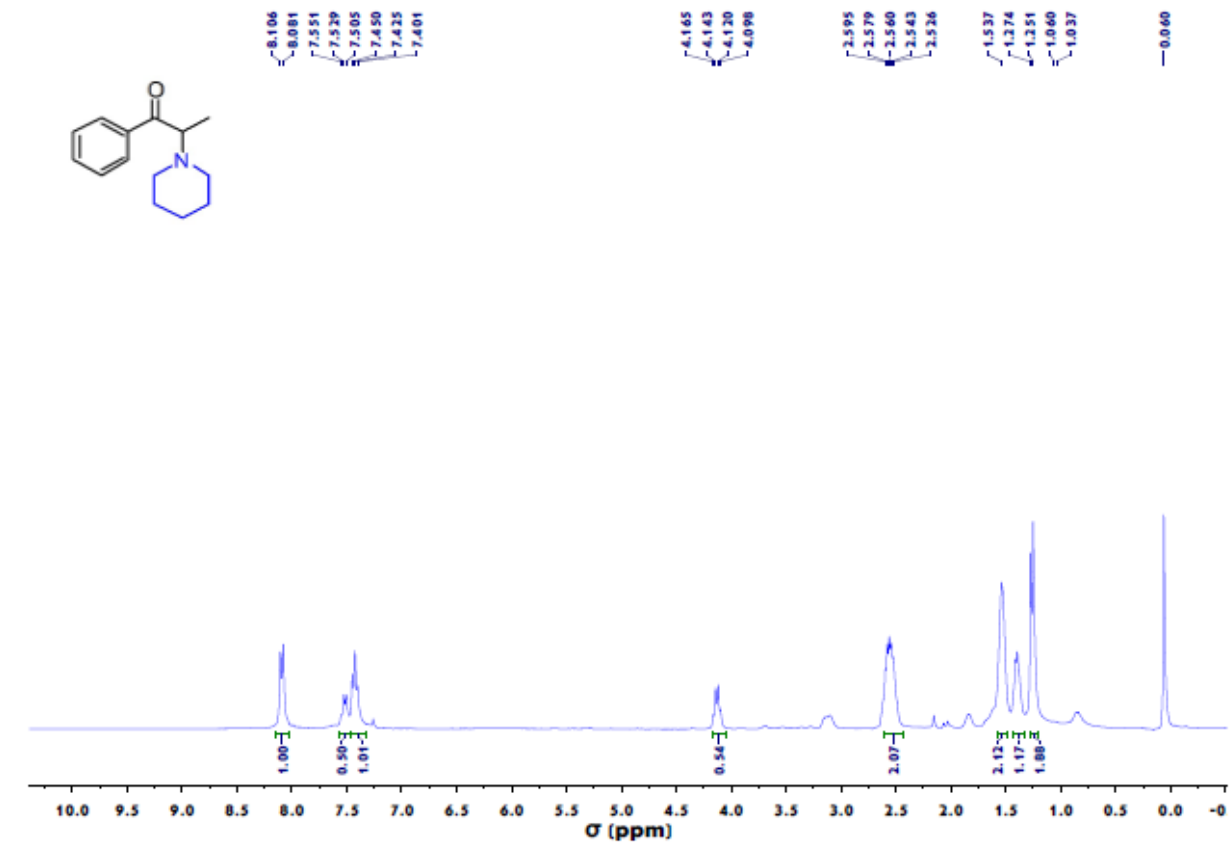
^{13}C NMR spectrum of **13a**



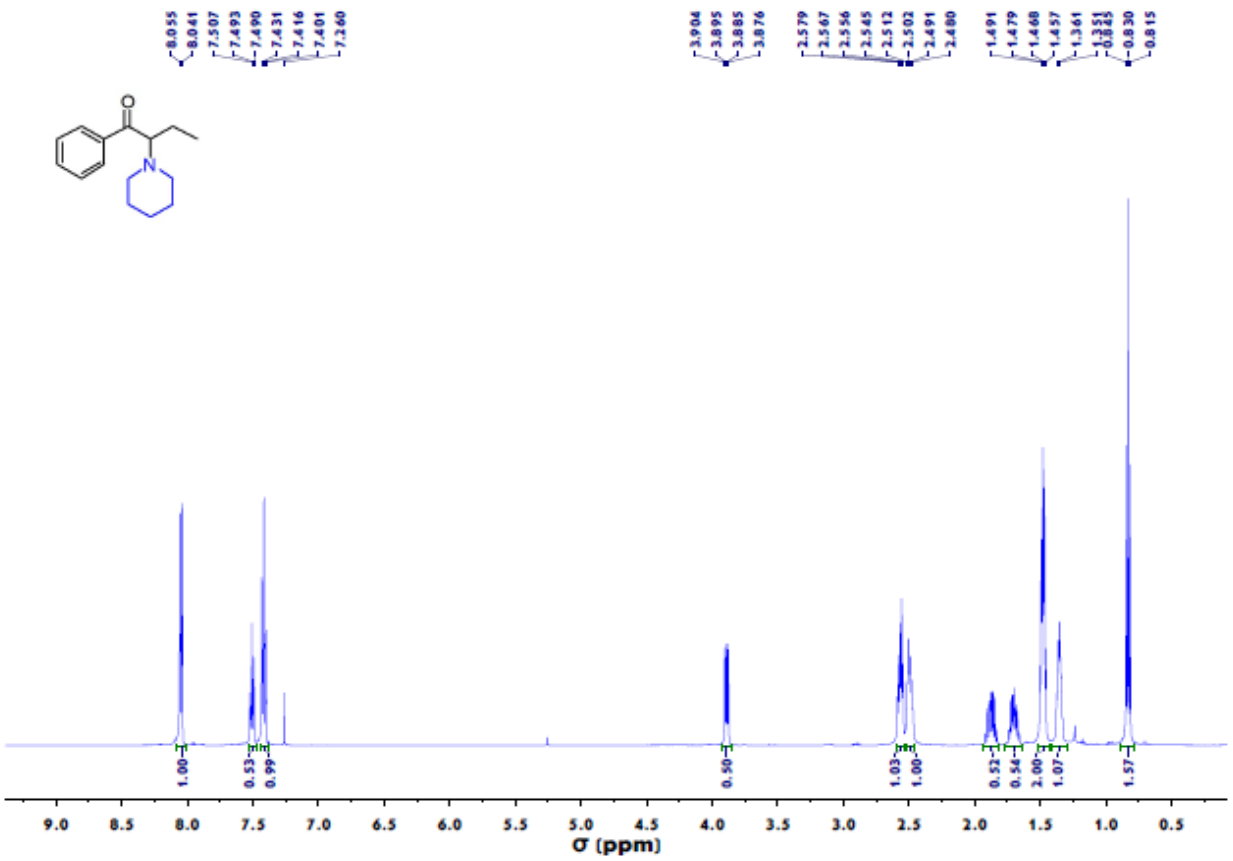
^{1}H NMR spectrum of **14a**



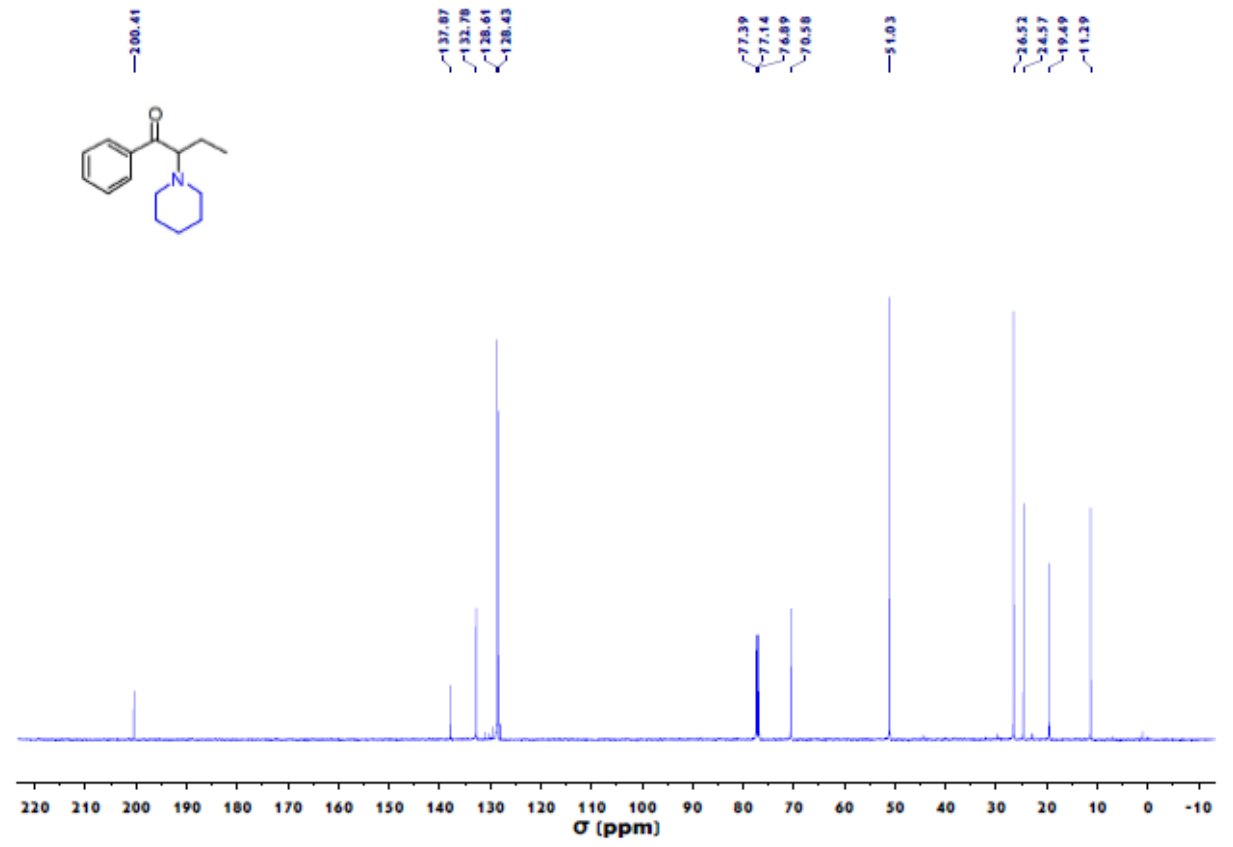
^{13}C NMR spectrum of **14a**



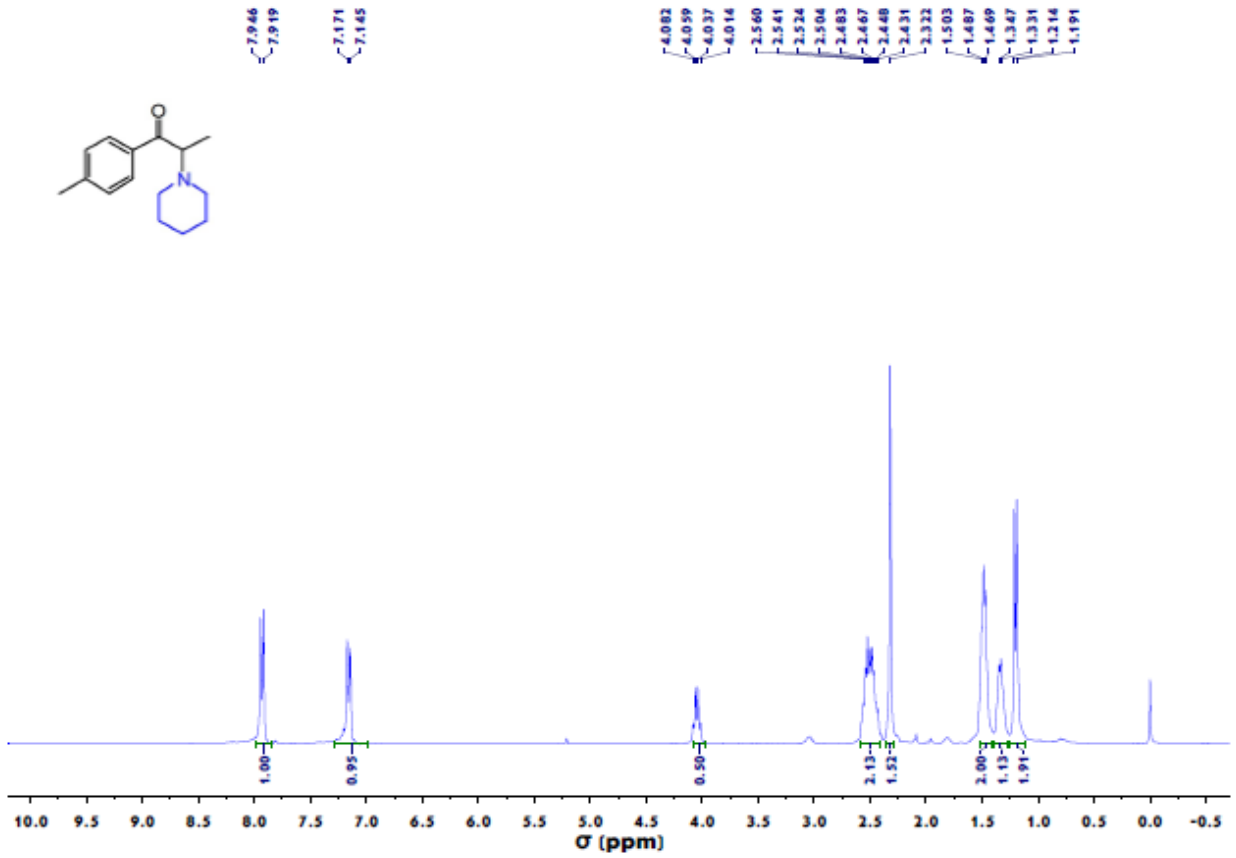
^{1}H NMR spectrum of **15a**



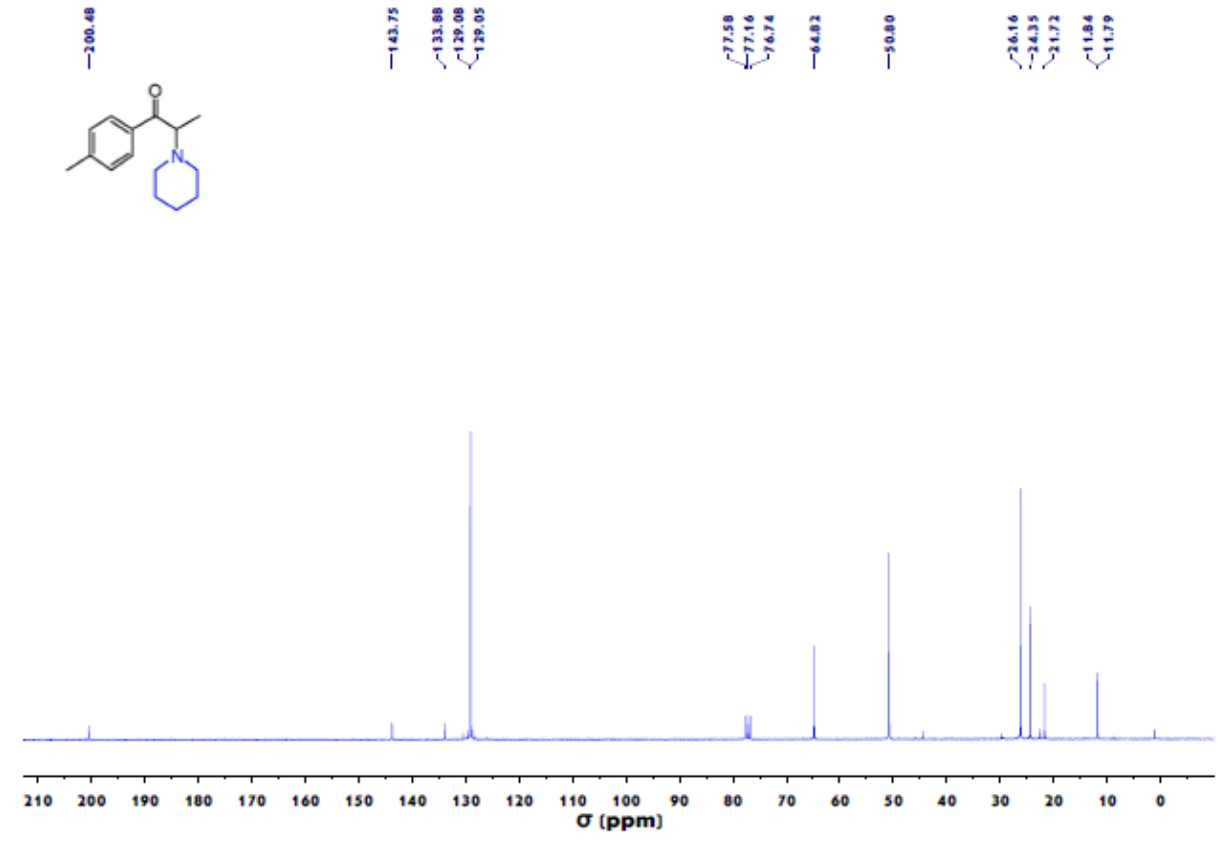
^{1}H NMR spectrum of **16a**



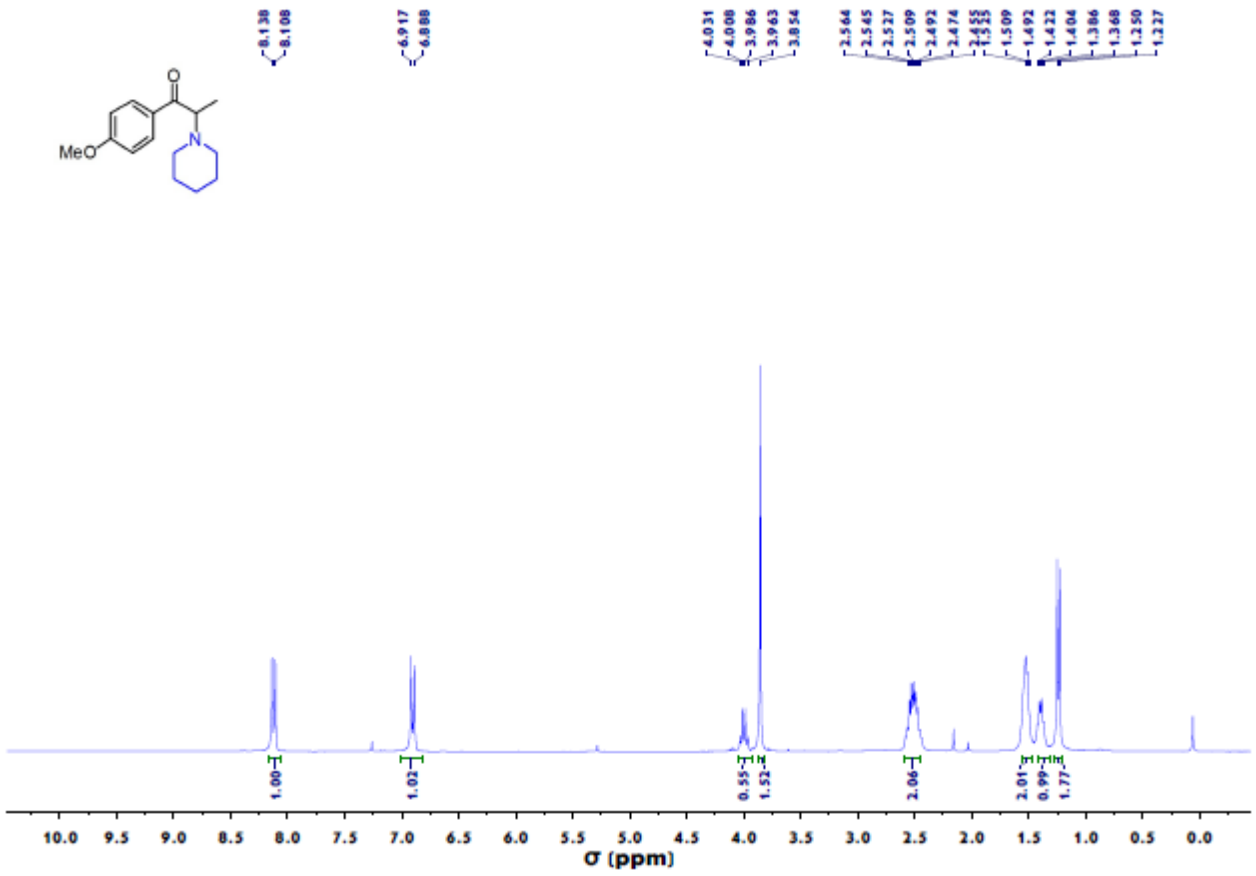
^{13}C NMR spectrum of **16a**



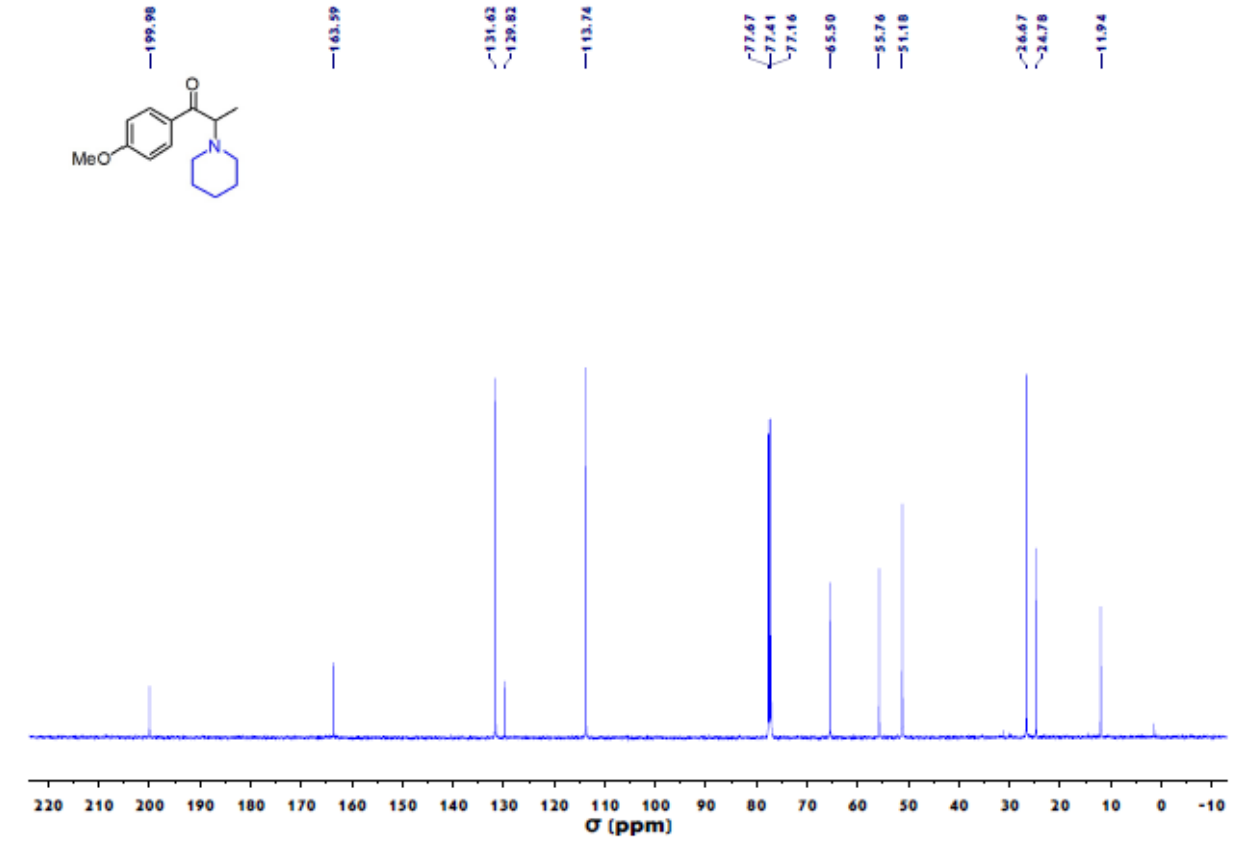
^{1}H NMR spectrum of **17a**



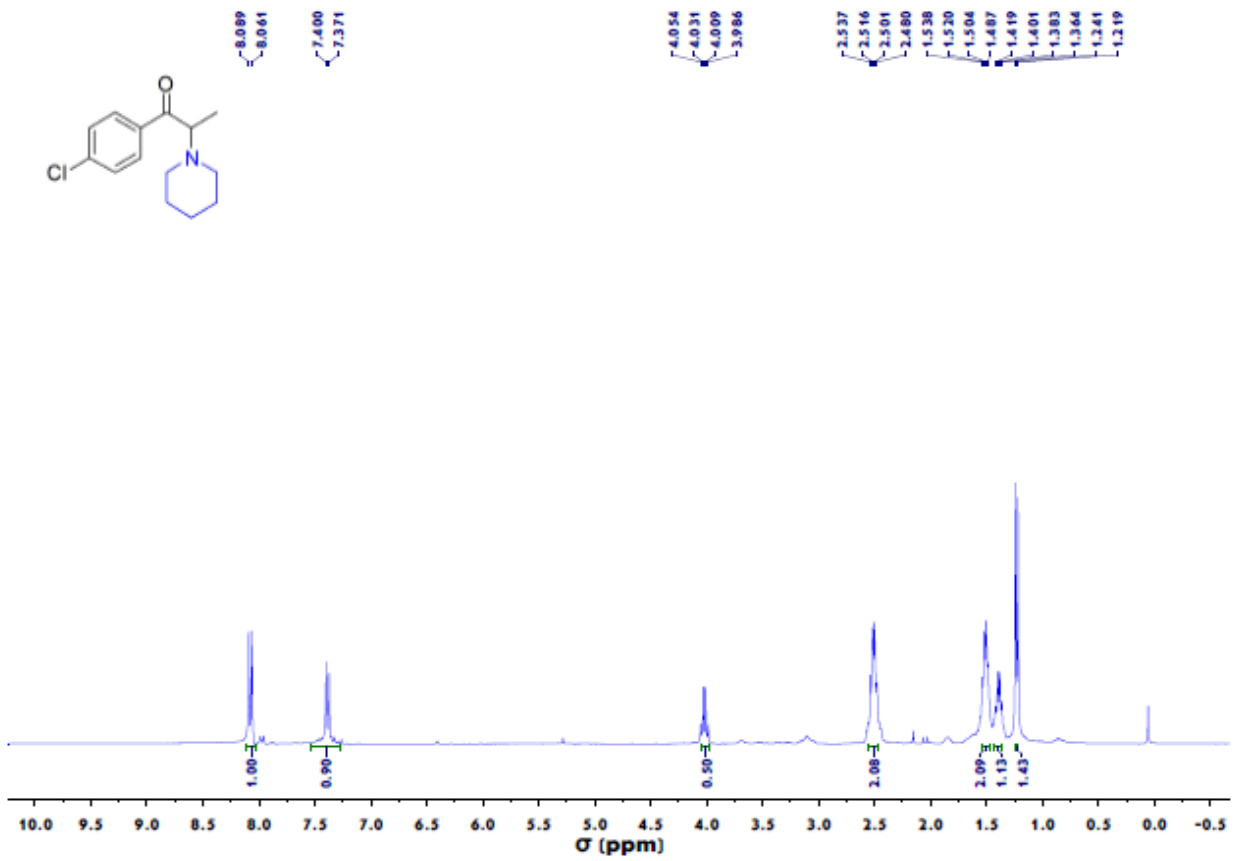
^{13}C NMR spectrum of **17a**



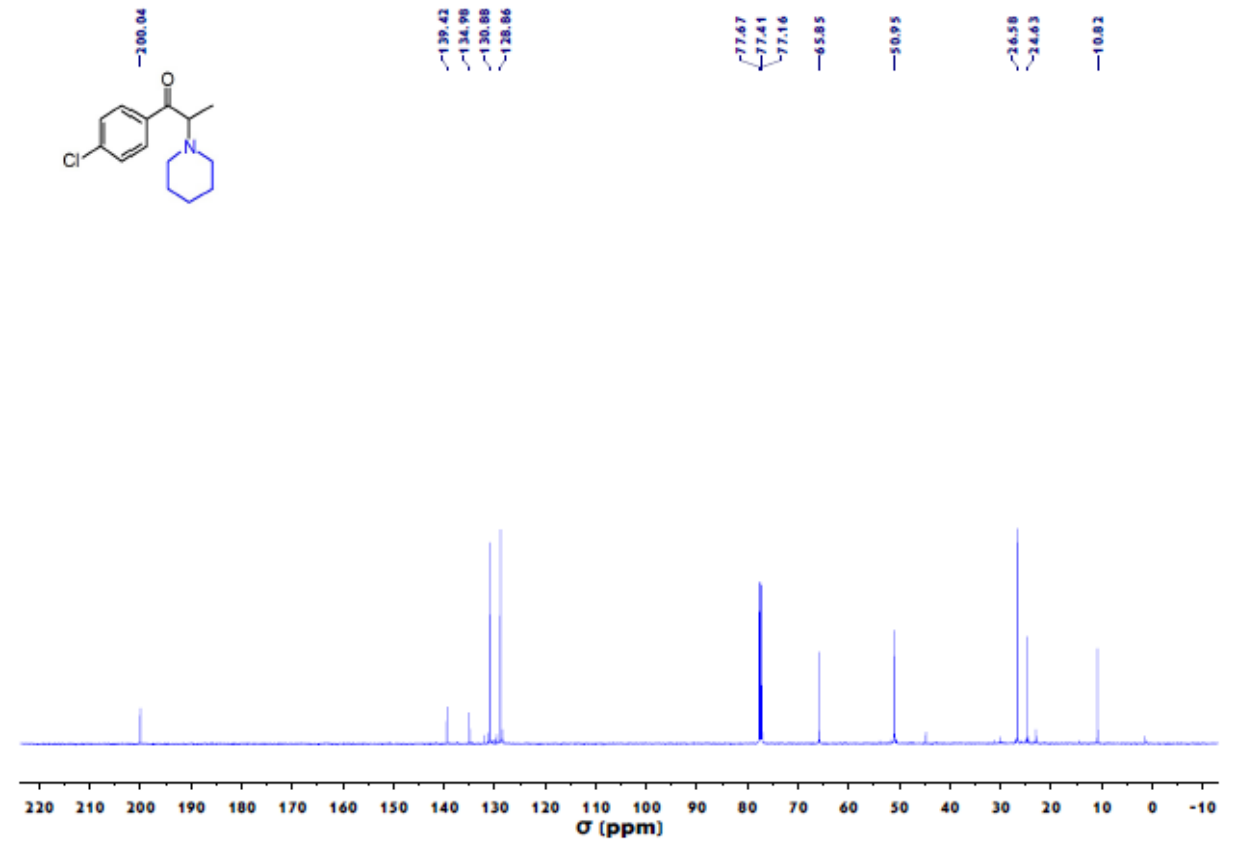
^{1}H NMR spectrum of **18a**



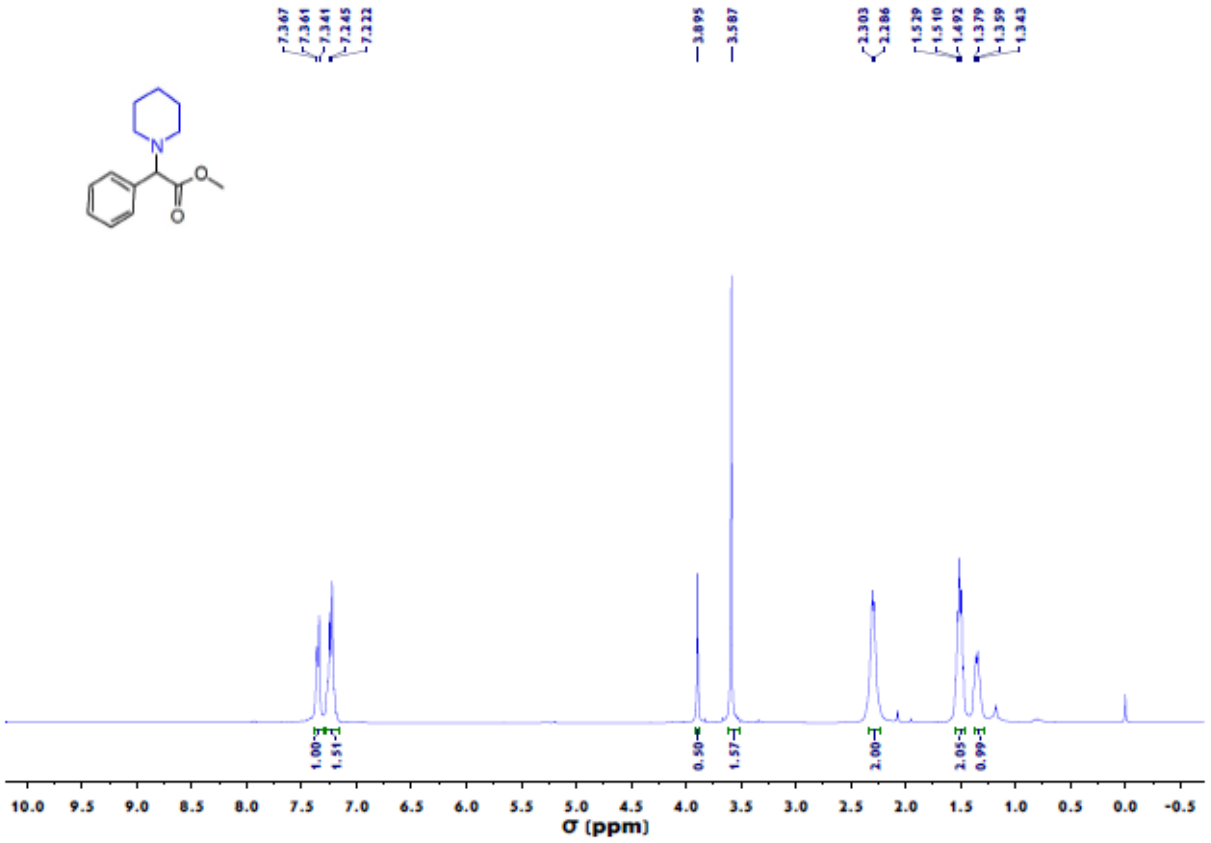
^{13}C NMR spectrum of **18a**



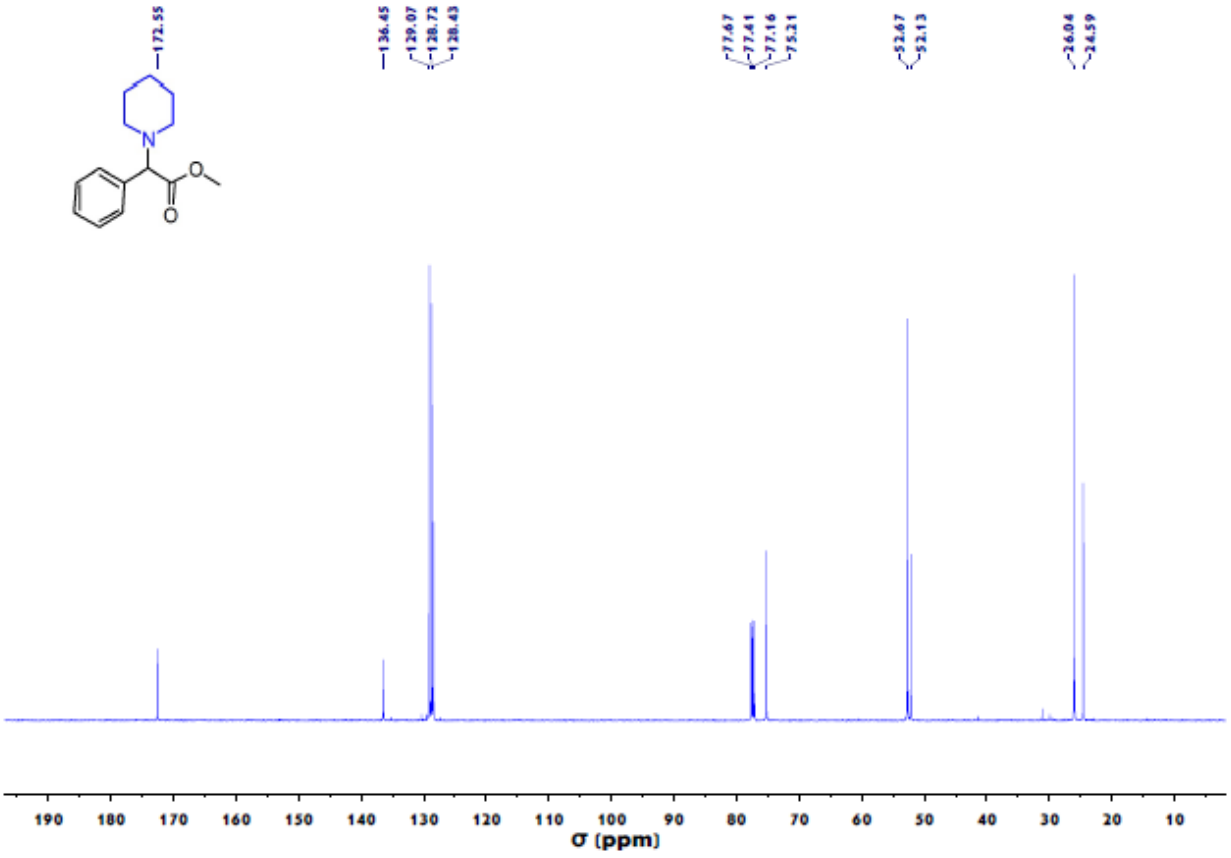
^{1}H NMR spectrum of **19a**



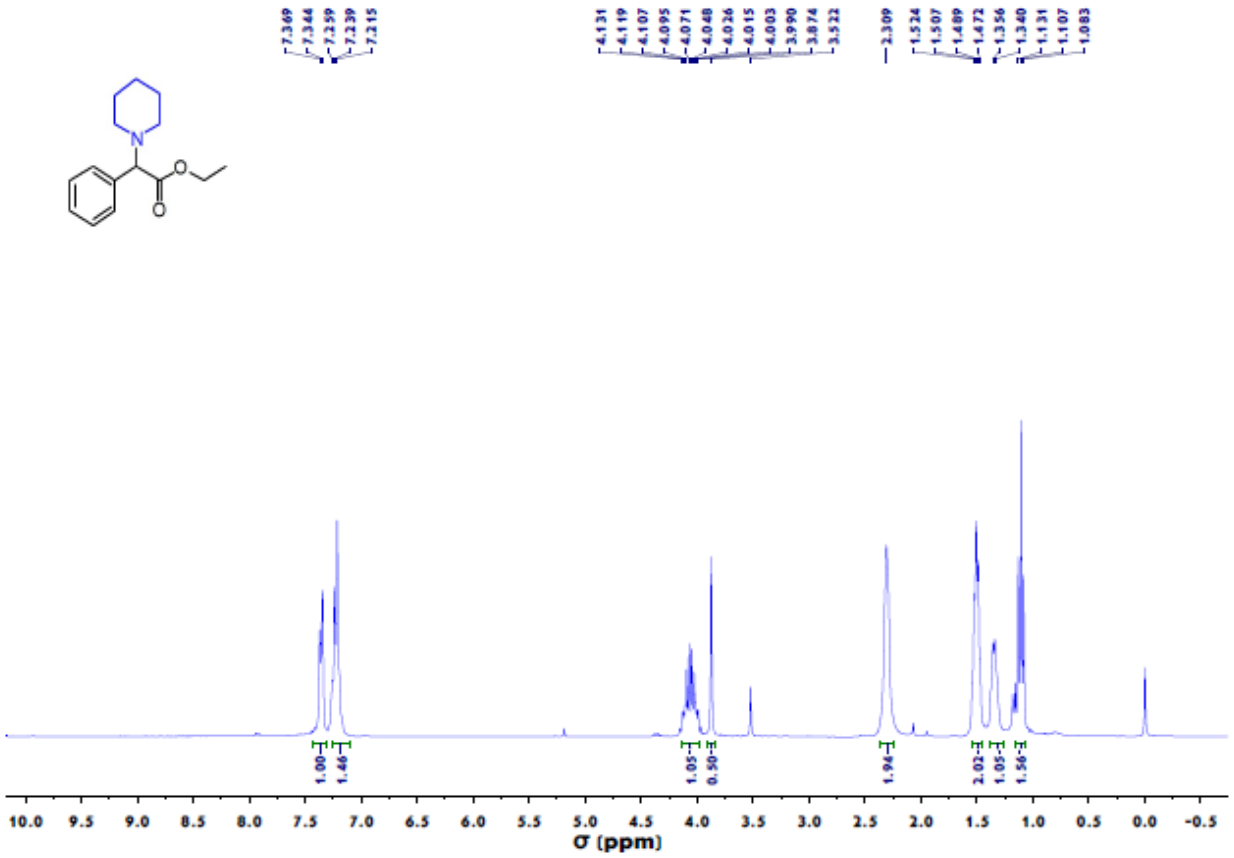
^{13}C NMR spectrum of **19a**



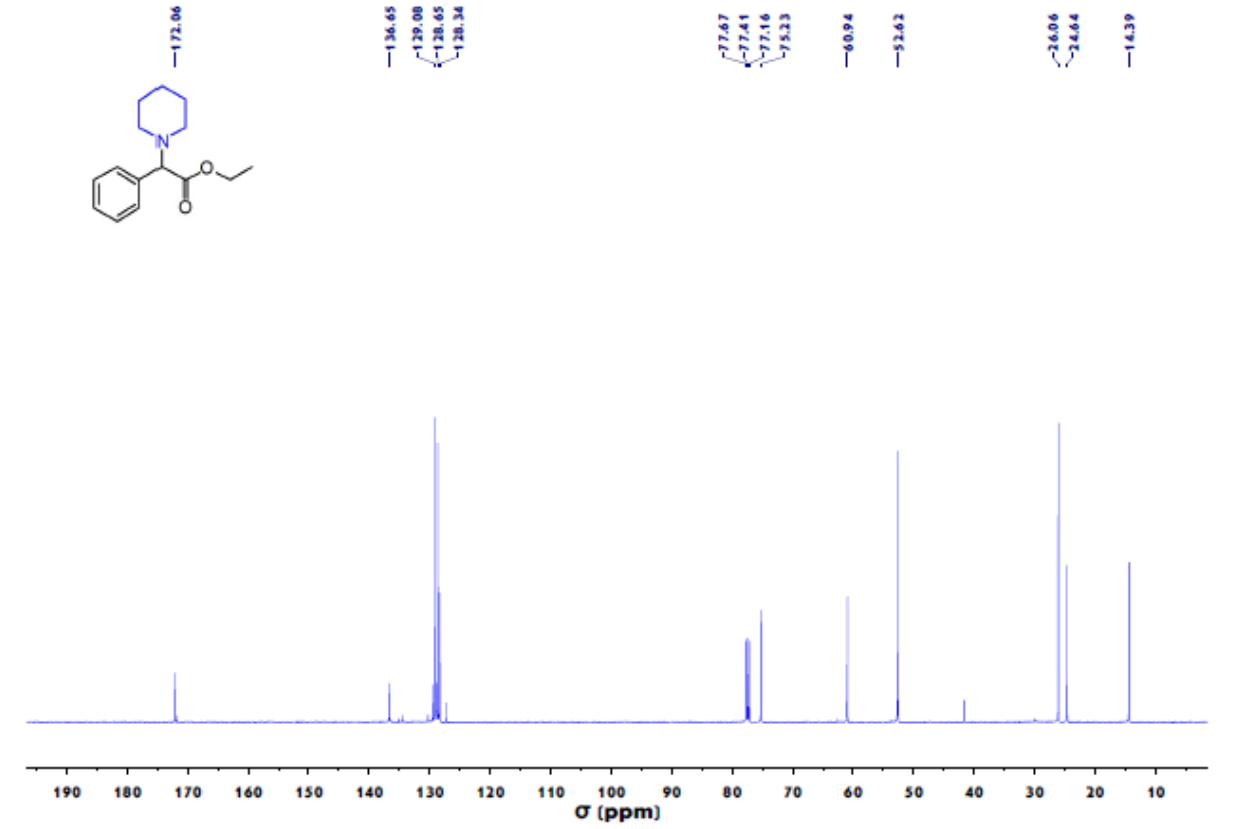
^{1}H NMR spectrum of **20a**



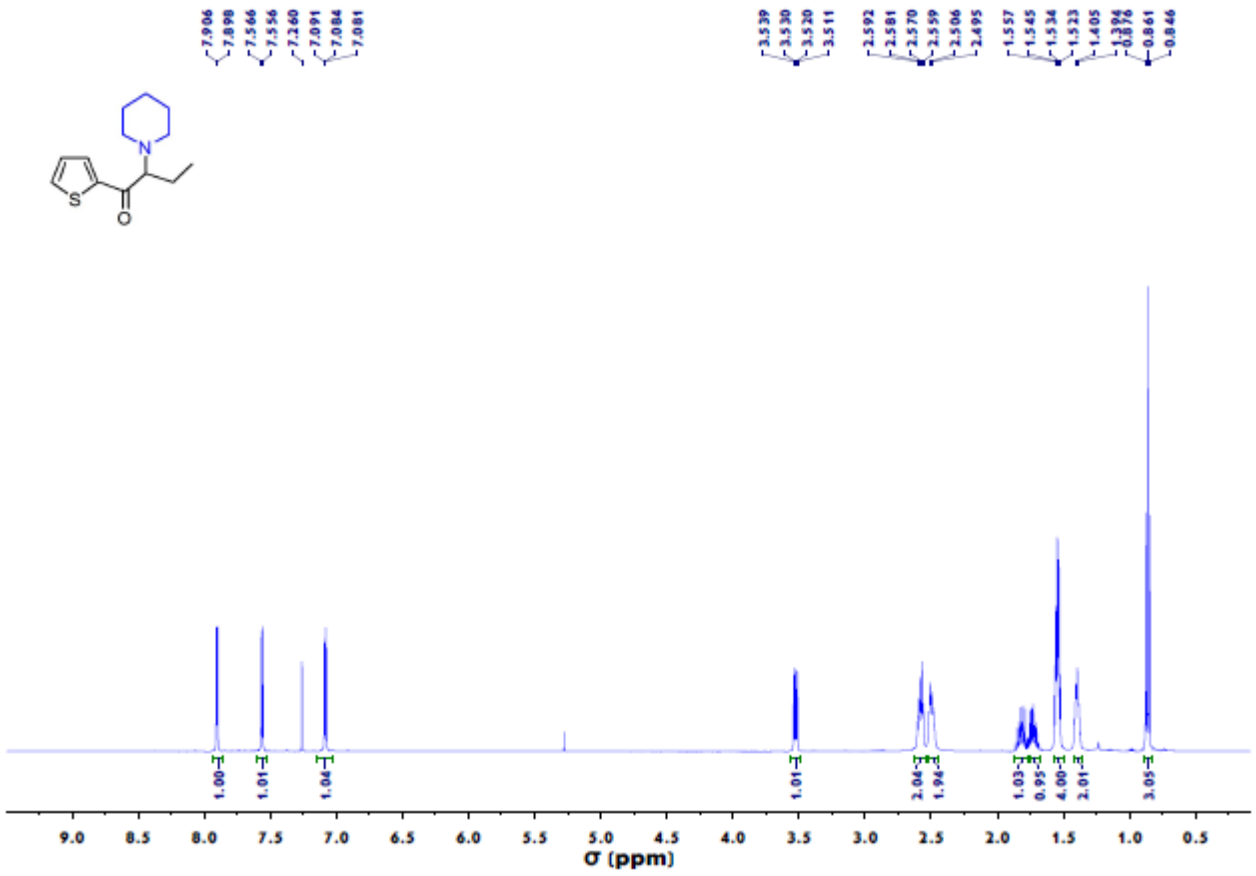
^{13}C NMR spectrum of **20a**



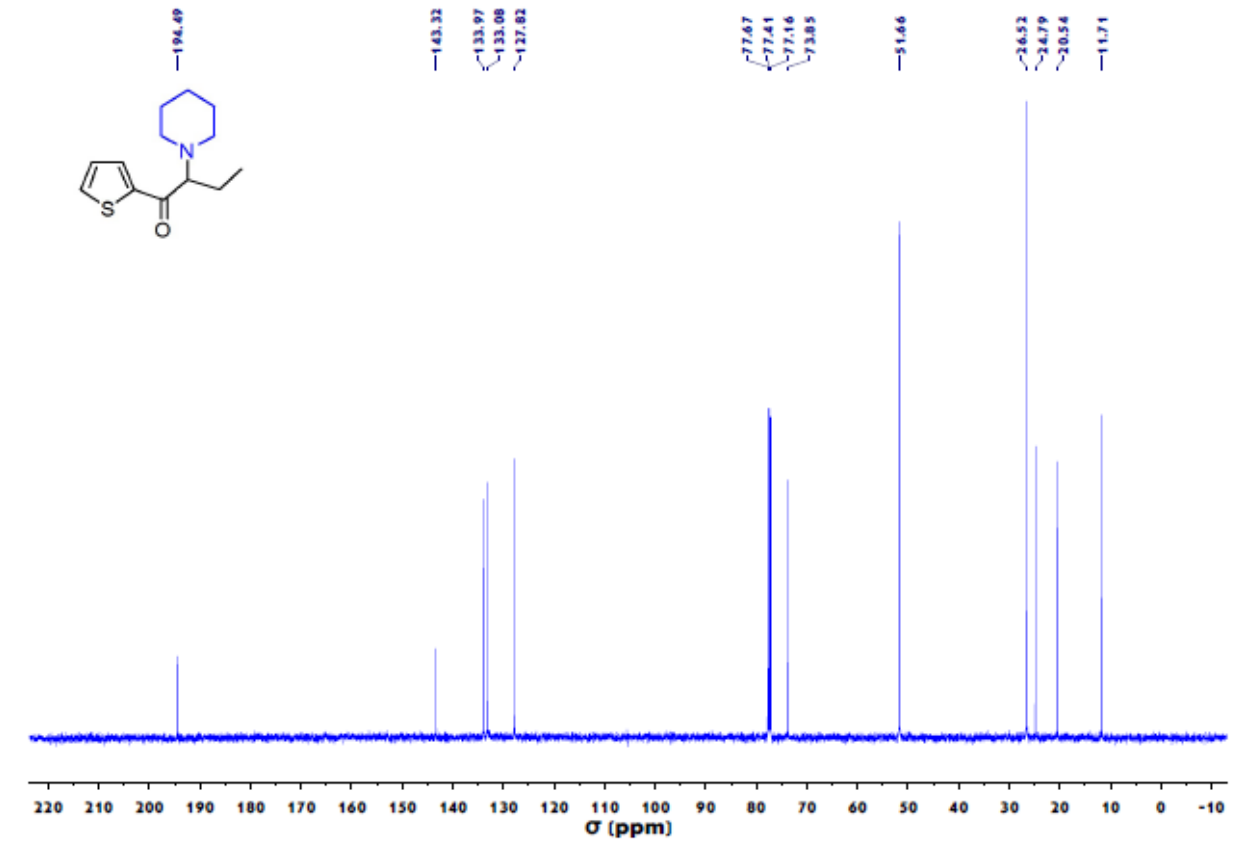
^{1}H NMR spectrum of **21a**



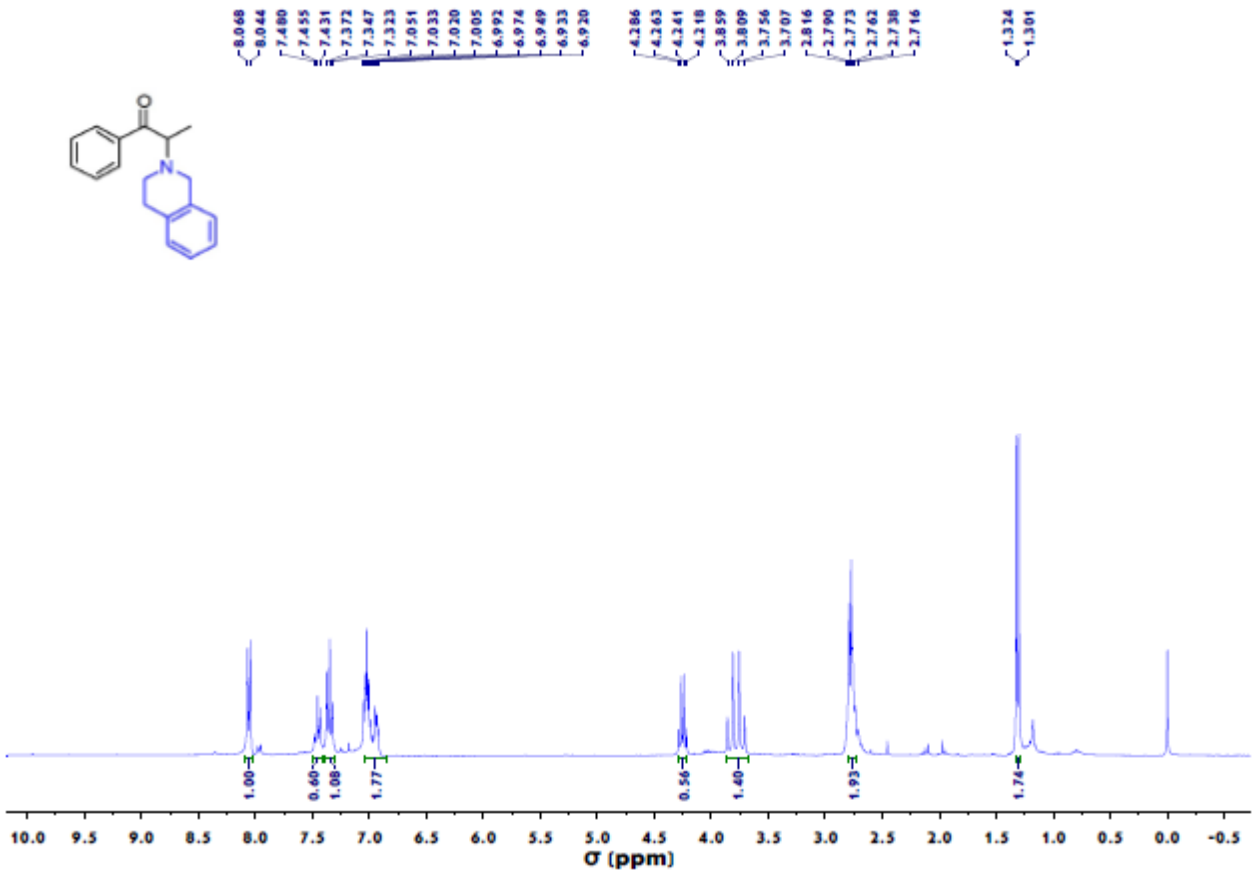
^{13}C NMR spectrum of **21a**



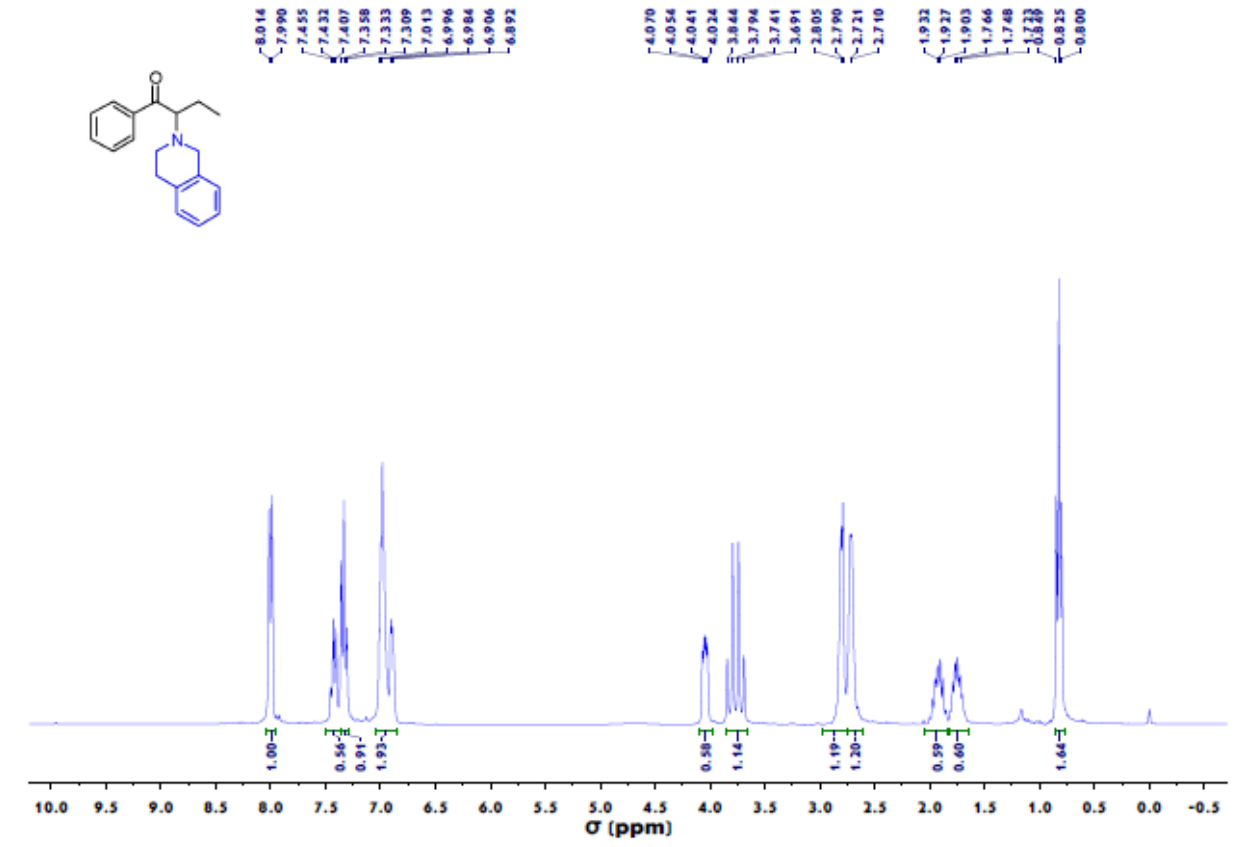
^{1}H NMR spectrum of **22a**



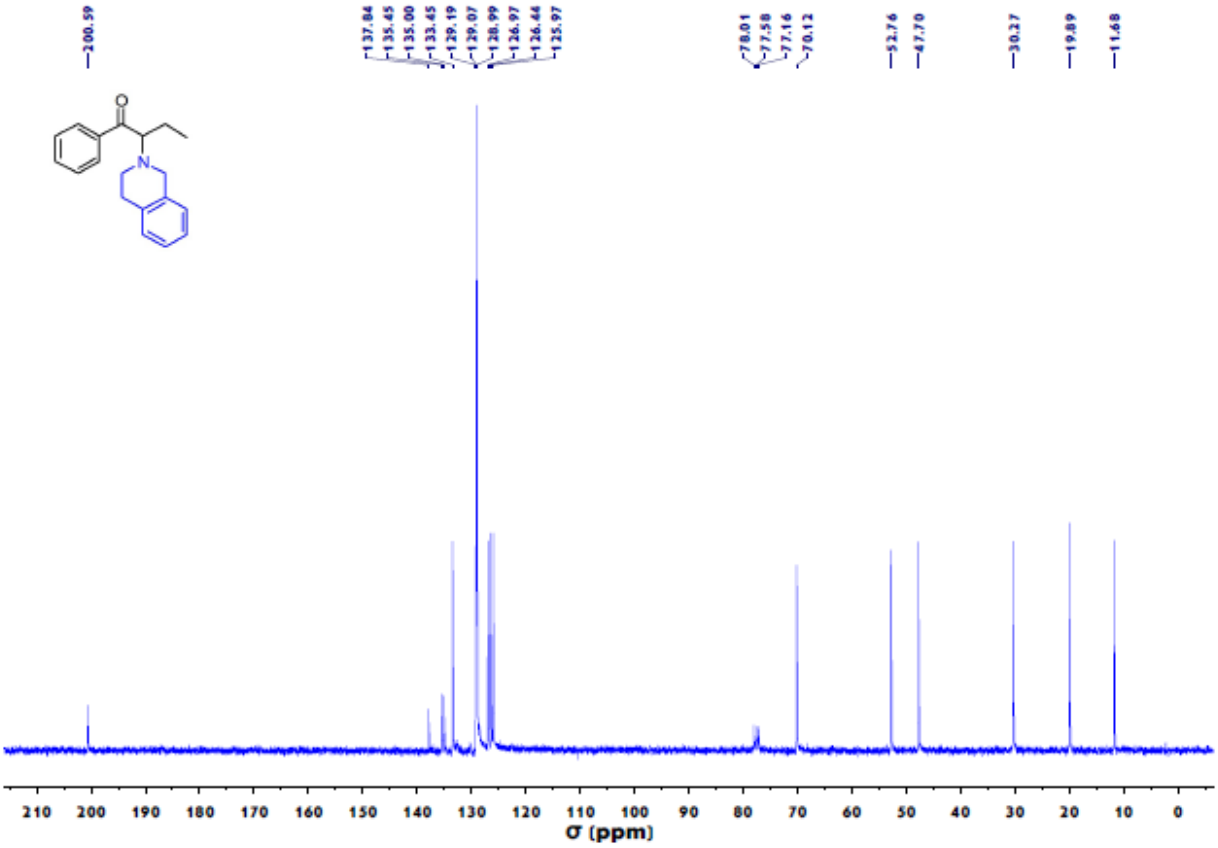
^{13}C NMR spectrum of **22a**



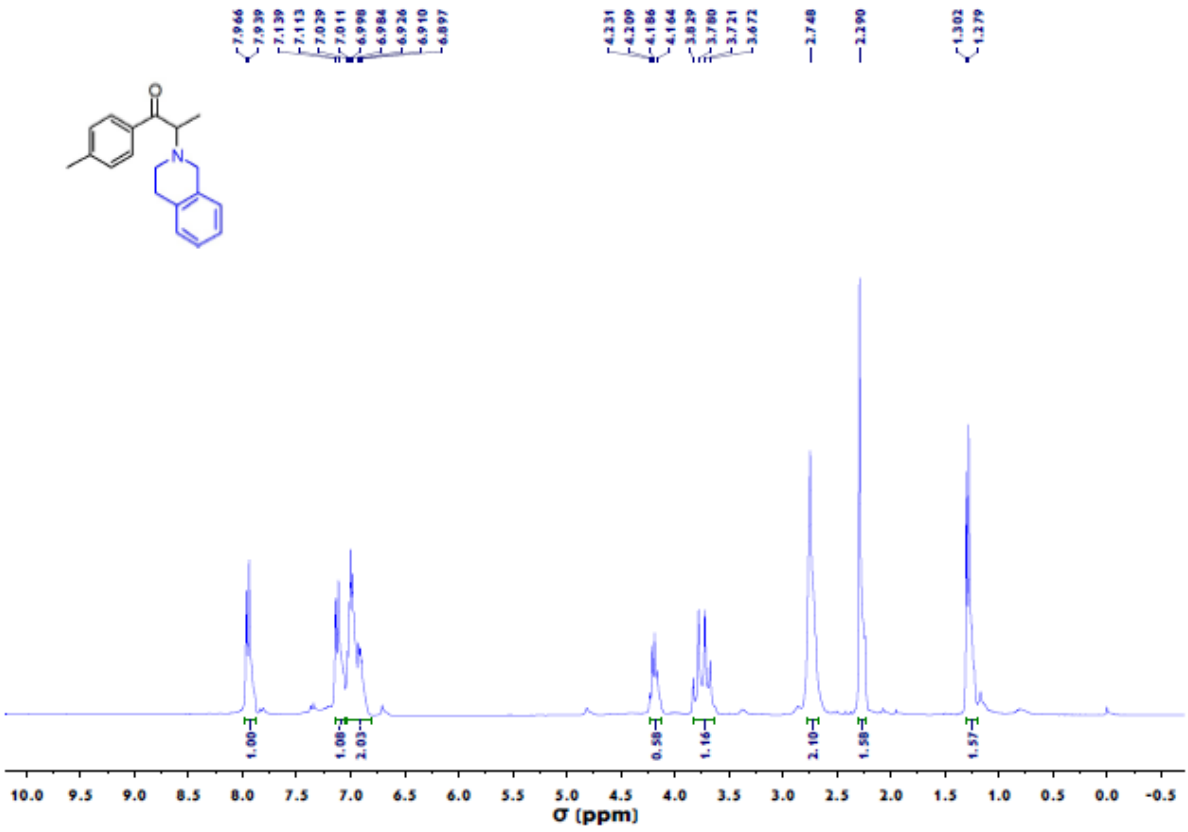
^{1}H NMR spectrum of **23a**



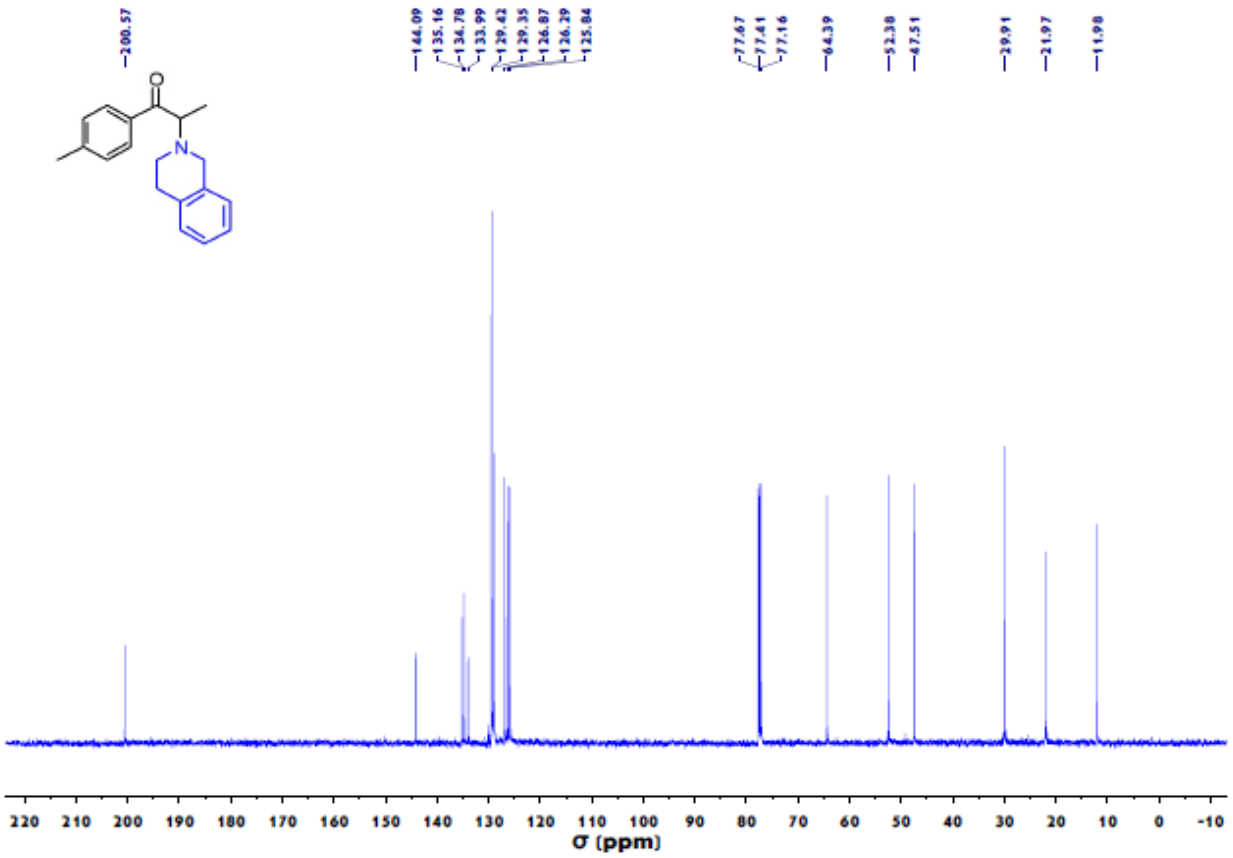
^{1}H NMR spectrum of **24a**



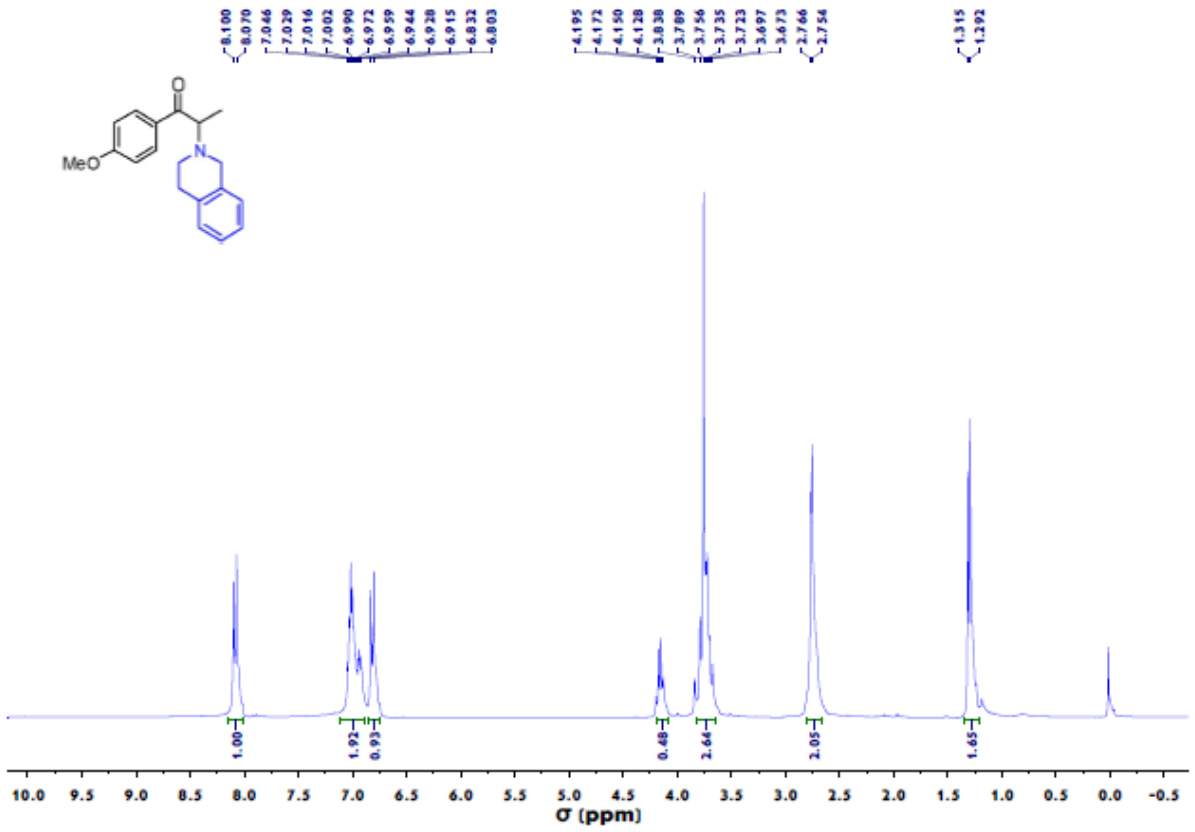
^{13}C NMR spectrum of **24a**



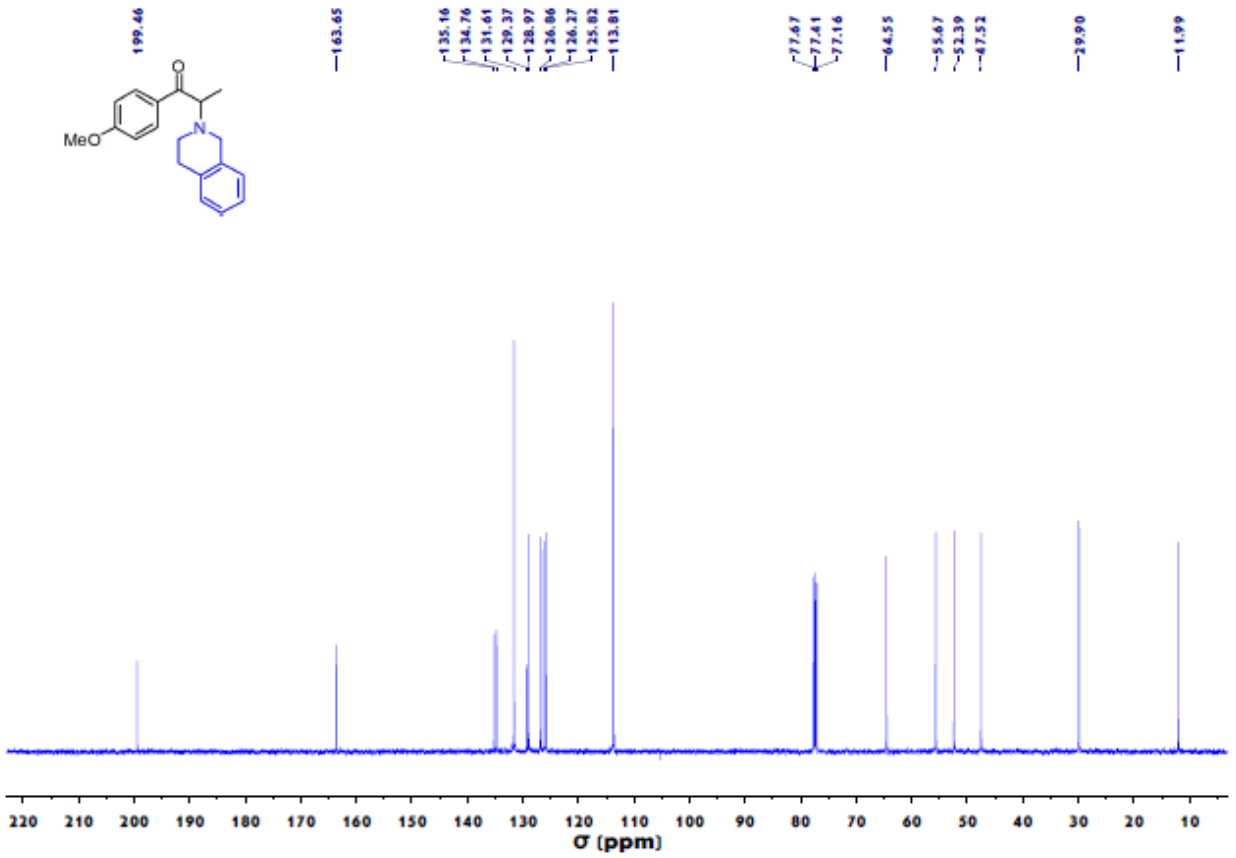
^{1}H NMR spectrum of **25a**



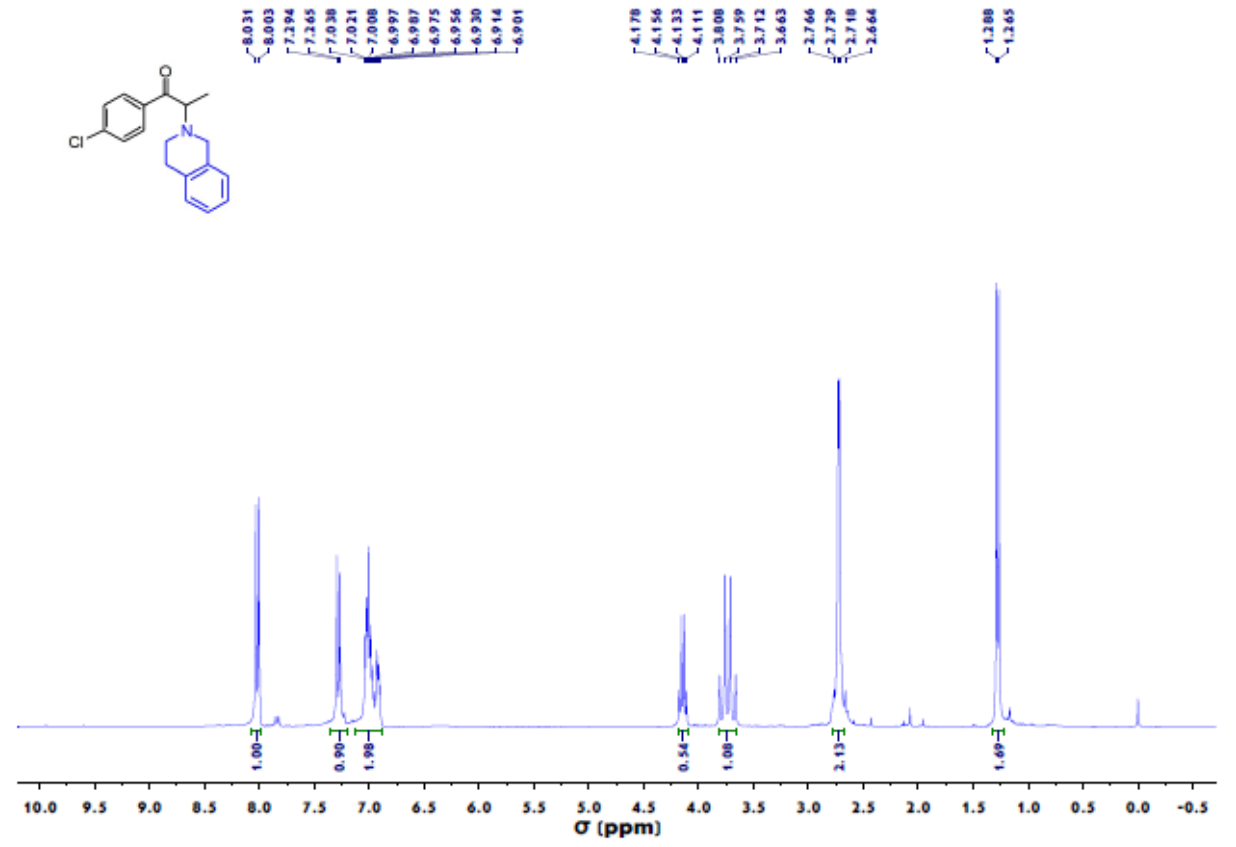
^{13}C NMR spectrum of **25a**



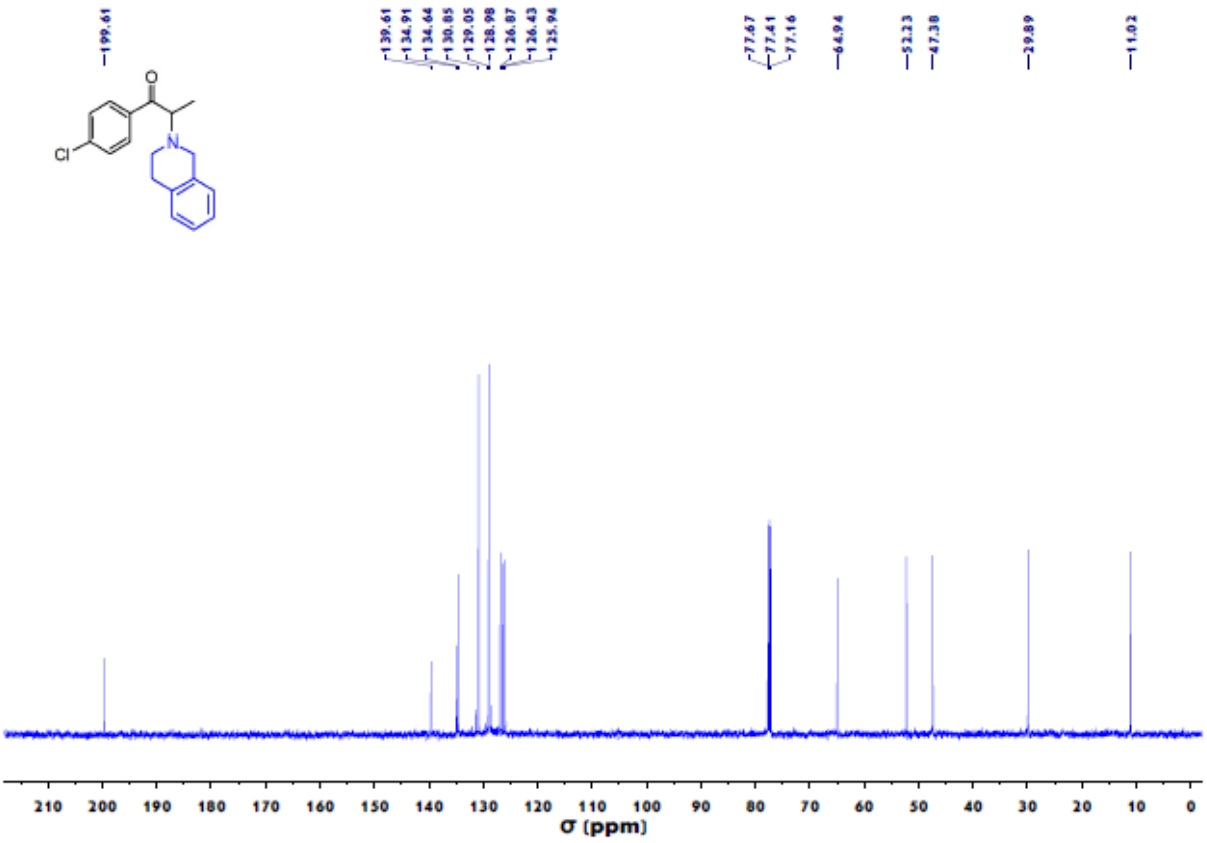
^{1}H NMR spectrum of **26a**



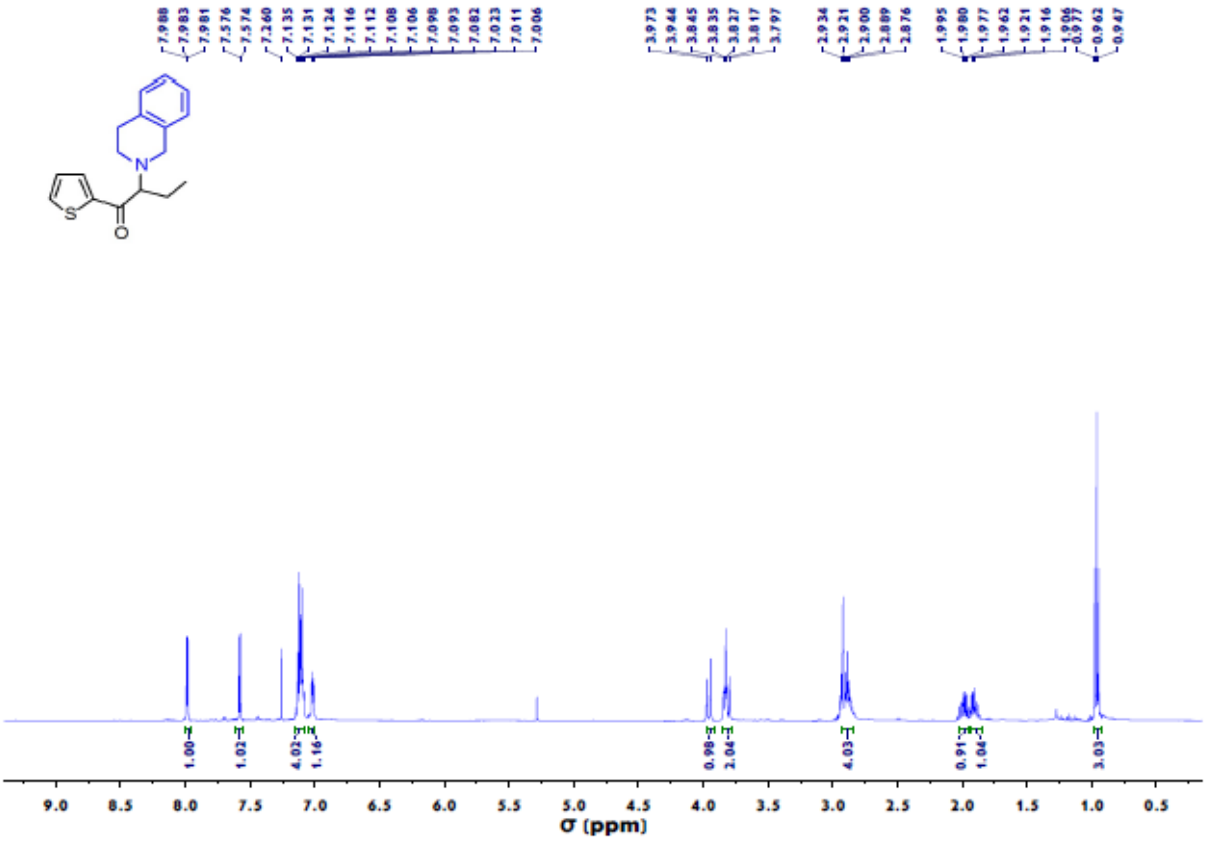
^{13}C NMR spectrum of **26a**



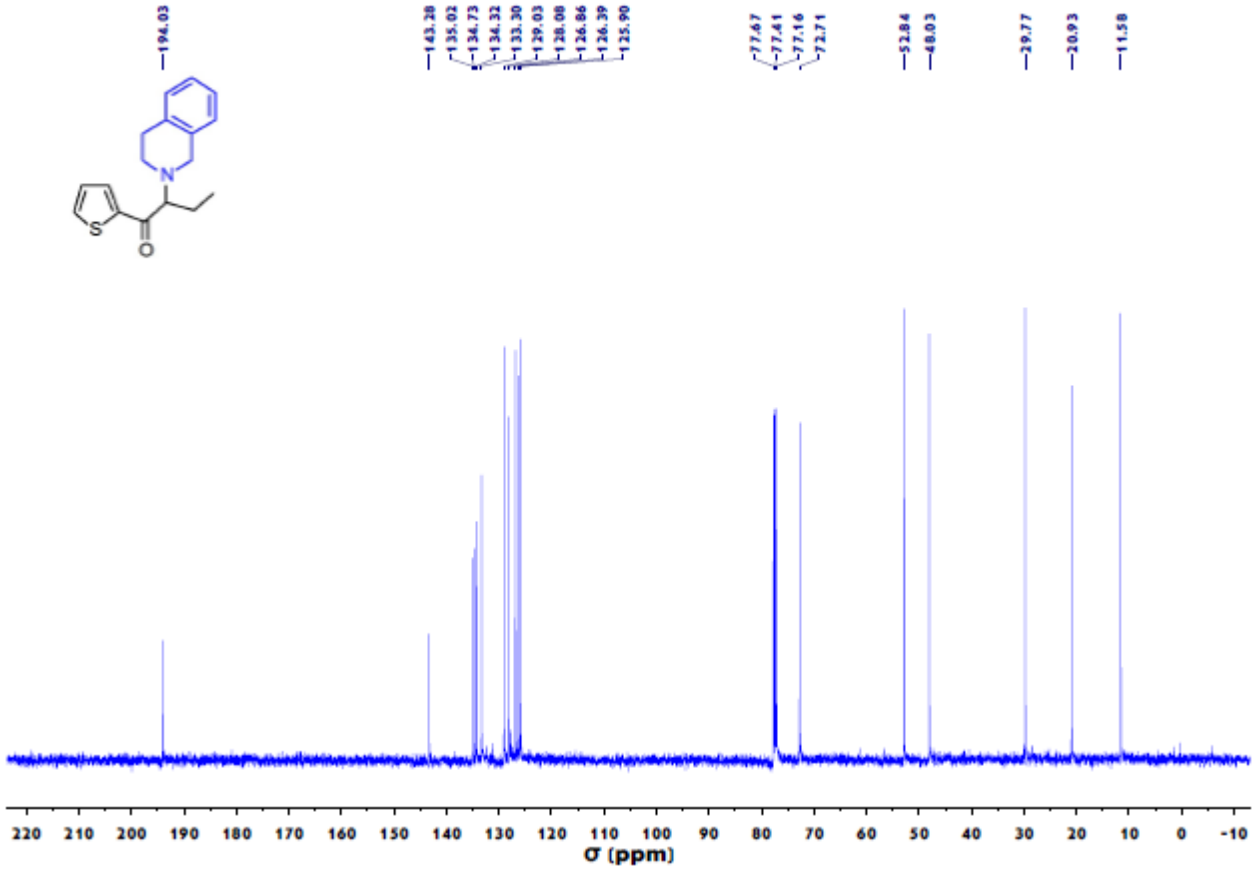
^{1}H NMR spectrum of **27a**



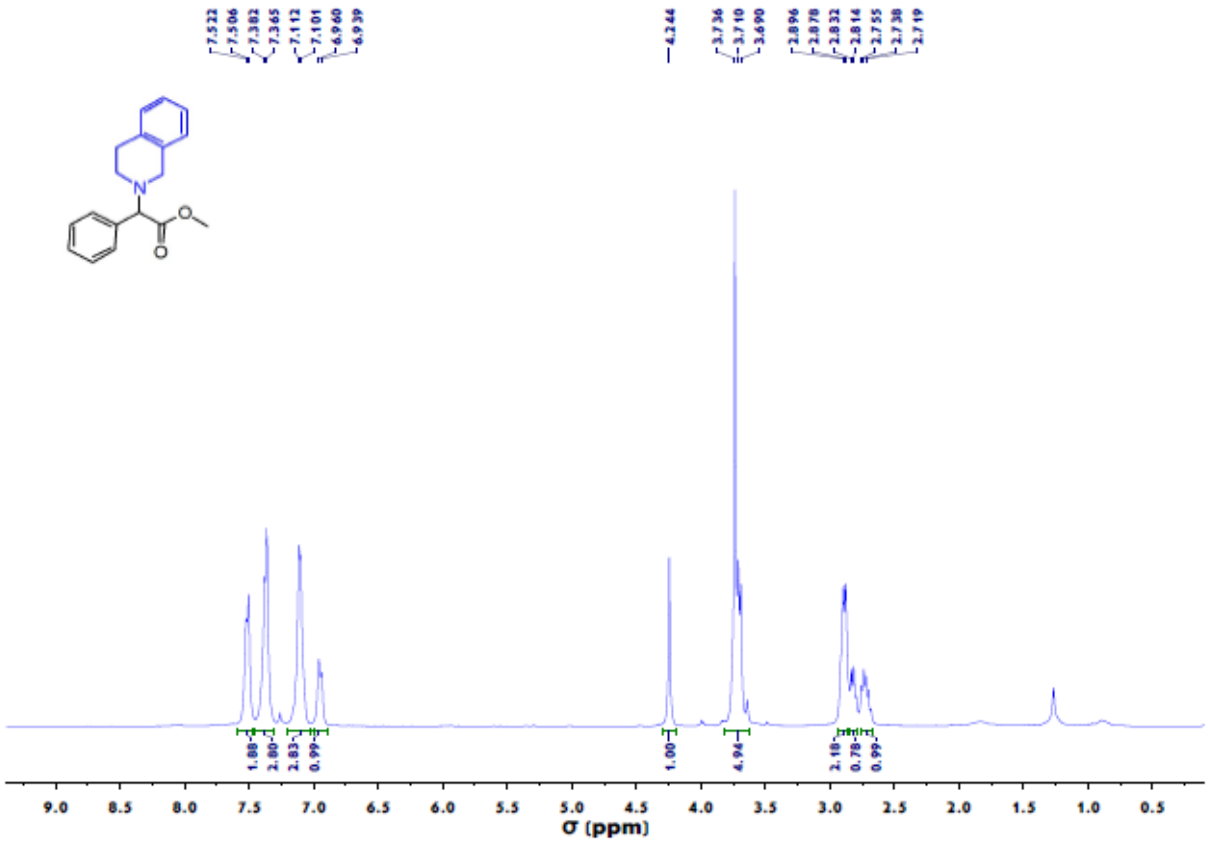
^{13}C NMR spectrum of **27a**



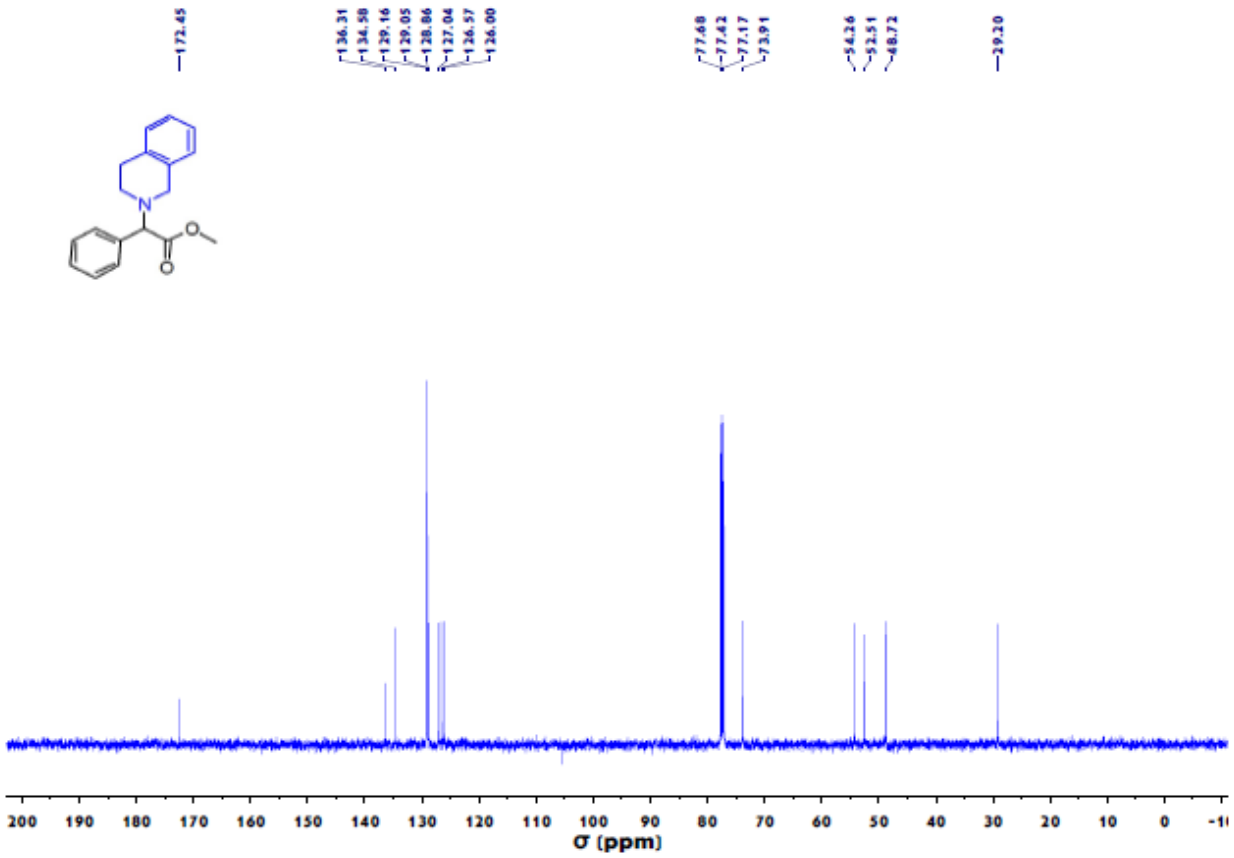
^{1}H NMR spectrum of **28a**



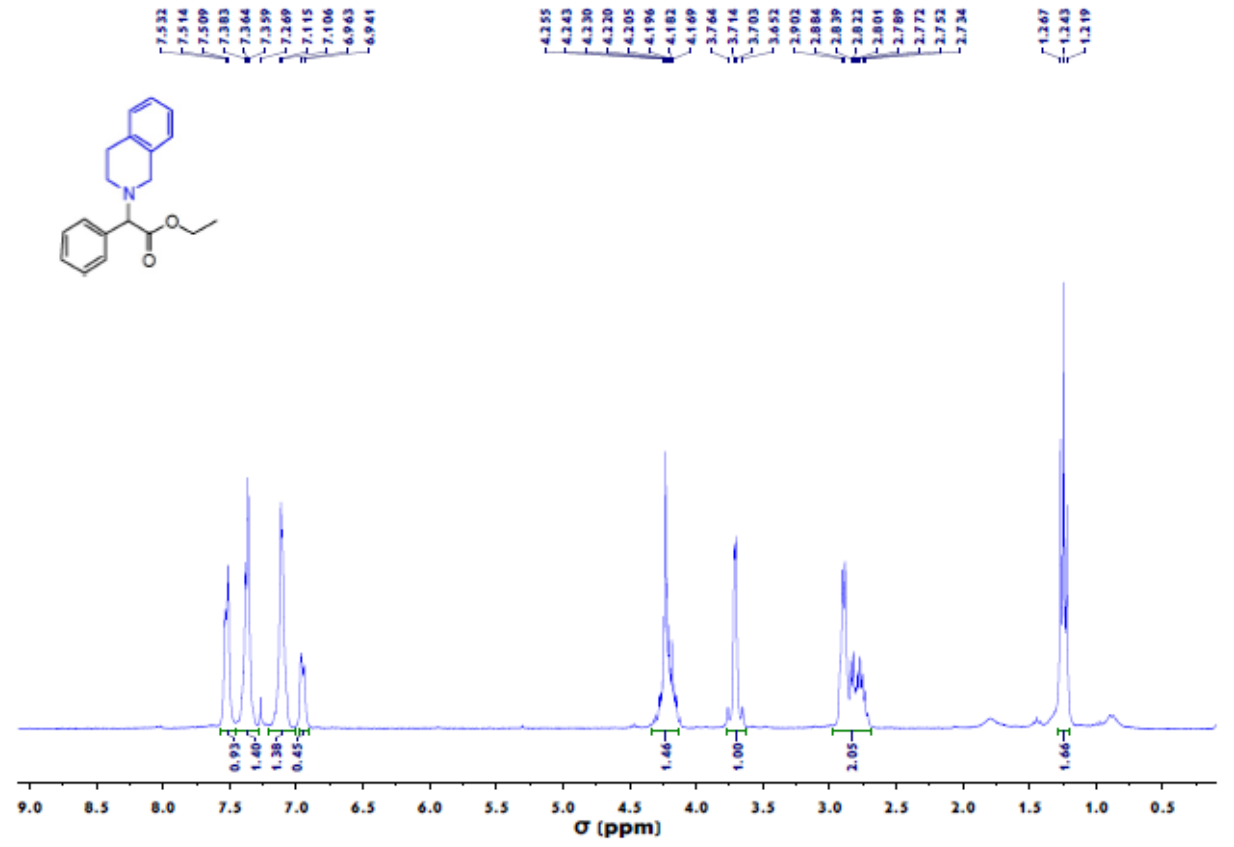
^{13}C NMR spectrum of **28a**



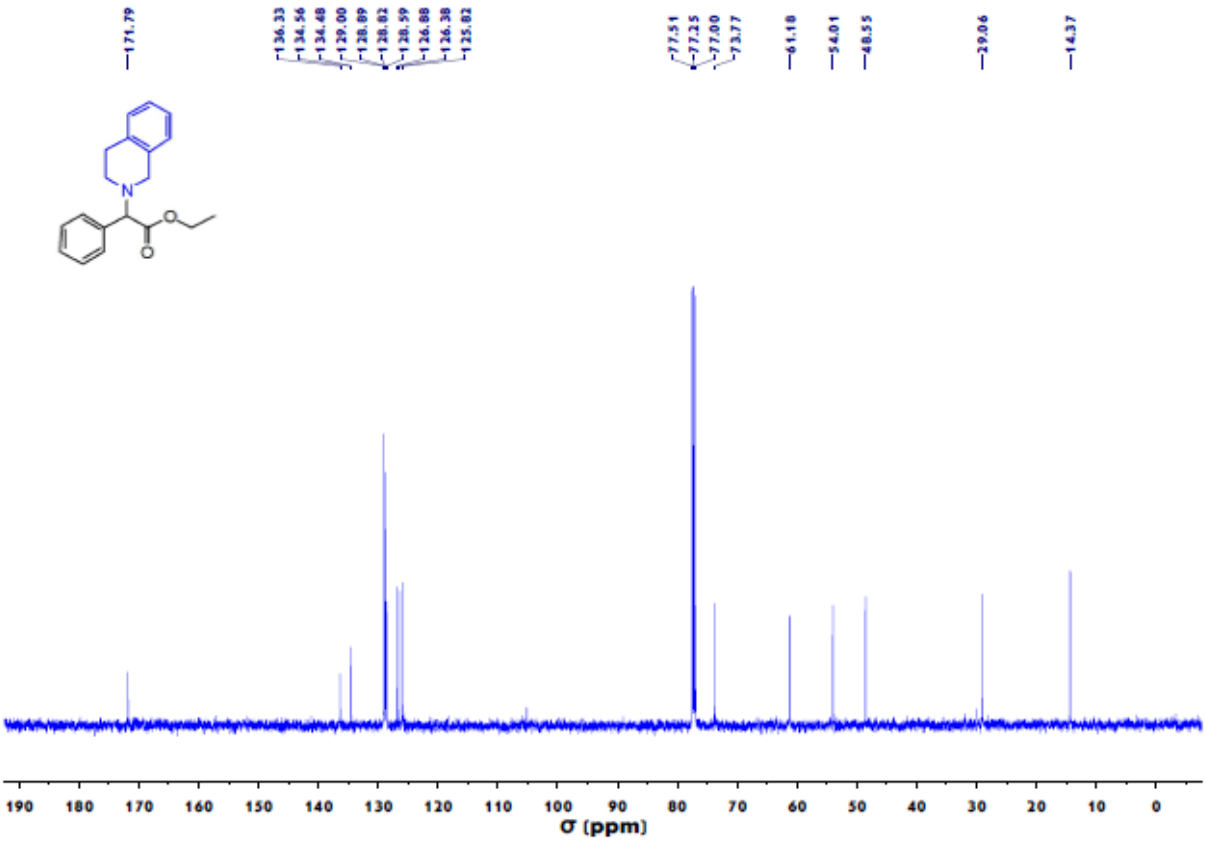
^{1}H NMR spectrum of **29a**



^{13}C NMR spectrum of **29a**



^{1}H NMR spectrum of **30a**



^{13}C NMR spectrum of **30a**

Table S1. Selected Bond Distances and Angles for [Cu] 1 and 3a

Bond distance (Å) in **1**			
Cu(1)-N(1)	2.0429(15)	Cu(1)-N(2)	2.1144(16)
Cu(1)-Cl(1)	2.2299(6)	Cu(1)-Cl(2)	2.2660(5)
Cu(1)-Cl(2A)	2.6241(6)		
Bond angle (deg) in **1**			
N(1)-Cu(1)-N(2)	79.46(6)	N(1)-Cu(1)-Cl(1)	93.34(5)
N(1)-Cu(1)-Cl(2)	171.46(5)	N(1)-Cu(1)-Cl(2A)	87.53(5)
N(2)-Cu(1)-Cl(1)	139.85(5)	N(2)-Cu(1)-Cl(2)	95.75(4)
N(2)-Cu(1)-Cl(2A)	97.06(5)	Cl(1)-Cu(1)-Cl(2)	94.84(2)
Bond distance (Å) in **2**			
Cu(1)-N(1)	2.031(7)	Cu(1)-N(2)	2.116(6)
Cu(1)-Br(1)	2.3751(16)	Cu(1)-Br(2)	2.3712(17)
Bond angle (deg) in **2**			
N(1)-Cu(1)-N(2)	80.0(3)	N(1)-Cu(1)-Br(1)	94.73(18)
N(1)-Cu(1)-Br(2)	165.45(18)	N(2)-Cu(1)-Br(1)	149.39(18)
N(2)-Cu(1)-Br(2)	96.8(2)	Br(1)-Cu(1)-Br(2)	95.05(6)

Bond distance (Å) in **3**			
Cu(1)-N(1)	2.001(2)	Cu(1)-N(2)	2.102(2)
Cu(1)-N(3)	2.071(2)	Cu(1)-Br(1)	2.3686(5)
Cu(1)-Br(2)	2.5805(4)		
Bond angle (deg) in **3**			
N(1)-Cu(1)-N(2)	77.20(9)	N(1)-Cu(1)-N(3)	77.37(8)
N(1)-Cu(1)-Br(1)	151.67(6)	N(1)-Cu(1)-Br(2)	96.97(6)
N(2)-Cu(1)-N(3)	153.90(8)	N(2)-Cu(1)-Br(1)	100.41(6)
N(2)-Cu(1)-Br(2)	92.71(6)	N(3)-Cu(1)-Br(1)	99.15(6)
N(3)-Cu(1)-Br(2)	96.09(6)	Br(1)-Cu(1)-Br(2)	111.361(16)
Bond distance (Å) in **3a**			
N(1)-C(1)	1.457(2)	N(1)-C(4)	1.456(2)
N(1)-C(5)	1.474(2)	C(1)-C(2)	1.508(3)
C(3)-C(4)	1.503(3)	C(5)-C(6)	1.523(2)
C(5)-C(14)	1.519(2)	C(6)-C(7)	1.491(3)
C(7)-C(8)	1.384(3)	C(7)-C(12)	1.384(2)
C(8)-C(9)	1.371(3)	C(9)-C(10)	1.381(3)
C(10)-C(11)	1.377(3)	C(10)-C(13)	1.508(3)
C(11)-C(12)	1.381(3)	O(1)-C(2)	1.415(2)
O(1)-C(3)	1.416(2)	O(2)-C(6)	1.219(2)
Bond angle (deg) in **3a**			
C(1)-N(1)-C(4)	110.02(14)	C(1)-N(1)-C(5)	114.28(13)
C(1)-C(2)-O(1)	111.21(16)	C(2)-C(1)-N(1)	109.65(15)
C(2)-O(1)-C(3)	109.72(14)	C(3)-C(4)-N(1)	109.85(15)
C(4)-N(1)-C(5)	112.27(14)	C(4)-C(3)-O(1)	111.50(16)
C(5)-C(6)-C(7)	119.81(16)	C(5)-C(6)-O(2)	120.18(18)
C(6)-C(7)-C(8)	118. 14(17)	C(6)-C(5)-N(1)	107.43(14)
C(6)-C(7)-C(12)	123.69(18)	C(6)-C(5)-C(14)	111.53(15)
C(7)-C(6)-O(2)	120.00(18)	C(7)-C(8)-C(9)	120.6(2)
C(7)-C(12)-C(11)	120.48(19)	C(8)-C(9)-C(10)	121.7(2)
C(8)-C(7)-C(12)	118.17(19)	C(9)-C(10)-C(11)	117.5(2)
C(9)-C(10)-C(13)	121.3(2)	C(10)-C(11)-C(12)	121.5(2)
C(11)-C(10)-C(13)	121.2(2)	C(14)-C(5)-N(1)	116.32(15)