Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

for

Electrosynthesis of enaminones directly from methyl ketones and amines with nitromethane as a carbon source

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General remarks:

NMR spectra were recorded on 300MHz or 400 MHz (75 MHz or 100 MHz for ^{13}C NMR) Bruker NMR spectrometer with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in parts per million (ppm, δ scale) downfield from TMS at 0.00 ppm and referenced to the $CDCl_3$ at 7.26 ppm (for ^1H NMR) or 77.16 ppm (for ^{13}C NMR). HRMS was recorded on a Micromass UK LTD GCT spectrometer. Melting points were determined on a melting point apparatus and are uncorrected. All reagents were commercially available and were used without further purification.

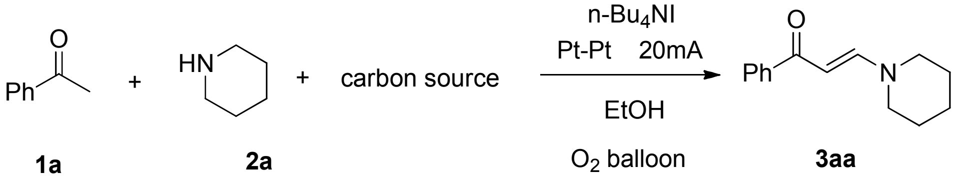
General procedure for the reaction

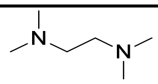
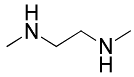
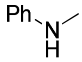
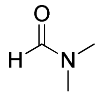
The reaction was carried out using an undivided cell (20 mL) equipped with a platinum plate cathode (1.3 cm* 1.3 cm), a platinum plate anode (1.3 cm* 1.3 cm) and a magnetic stirring bar. The distance between cathode and anode was 3 cm. Methyl ketone (0.5 mmol), MeOH (8 mL), CF_3CH_2OH (1 mmol), amine (2 mmol), KI (1 mmol) and $MeNO_2$ (1mL) were added in sequence, and the total solution volume was almost 10 mL. The constant current electrolysis (20 mA) was carried out at room temperature under 1 atm of oxygen atmosphere (O_2 balloon). After the reaction was finished, the solvent was removed under reduced pressure. The resulting crude product was purified with flash chromatography (Hex: EtOAc = 3:1-1:1) to give enaminone as a yellow solid or pale yellow oil.

Optimization of the carbon source

In this part, some common carbon sources were screened. However, only nitromethane could be employed as an ideal carbon source, while others failed to give the corresponding product. The results were shown as below.

Table S1.Screening the proper carbon source

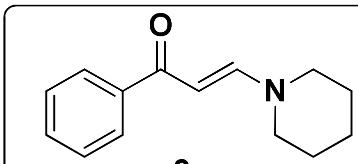


Entry[a]	Carbon Source	Yield[b]
1		0
2		0
3		0
4		0
5	CH_3NO_2	41
6	$EtNO_2$	0

[a] Reaction condition: **1a** (0.5 mmol), **2a** (2 mmol), *n*-Bu_4NI (1 mmol), EtOH (8 mL), carbon source (1 mL), platinum sheet as an anode and a cathode in an undivided cell, at a constant current of 20 mA for 7 hours, room temperature. [b] Isolated yield.

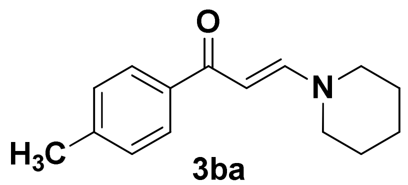
Characterization of the products

For the ^{1}HNMR, the peaks of hydrogens on the piperidine cycle should be multiplet, however, in most cases, they were shown as a single peak. For the ^{13}CNMR, the chemical shift of carbons on the piperidine cycle should be different, however, in some cases, only one carbon was found even if the concentration of the sample in $CDCl_3$ was increased. These phenomena were in accordance with the references.



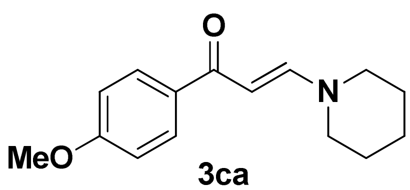
3aa

pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.2 Hz, 2H), 7.78 (d, *J* = 12.5 Hz, 1H), 7.49 – 7.34 (m, 3H), 5.82 (d, *J* = 12.4 Hz, 1H), 3.56 – 3.23 (m, 4H), 1.77 – 1.54 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.20, 153.30, 140.82, 130.90, 128.20, 127.53, 91.32, 55.05 (brs, NCH_2), 46.74 (brs, NCH_2), 26.21(brs), 24.13. MS (EI) *m/z* 215 (M^+); IR(KBr) 1210, 1280, 1371, 1446, 1541, 1639, 2937cm^{-1}; mp90-91°C. [S1,3]



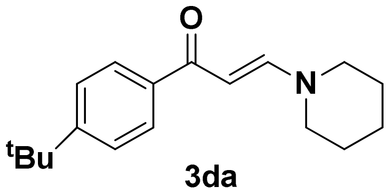
3ba

pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 5.83 (d, *J* = 12.5 Hz, 1H), 3.37 (m, 4H), 2.39 (s, 3H), 1.67 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.89, 153.16, 141.25, 137.97, 128.86, 127.60, 91.14, 55.48 (brs), 46.27 (brs), 25.86 (brs), 24.11, 21.54. MS (EI) *m/z* 229 (M^+); IR(KBr) 768, 1206, 1368, 1447, 1546, 1641, 2857, 2938cm^{-1}; mp120-121°C. [S2]



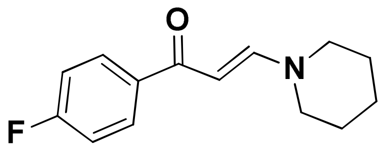
3ca

pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.75 (m, 2H), 7.77 (d, *J* = 12.5 Hz, 1H), 6.92 – 6.89 (m, 2H), 5.81 (d, *J* = 5.6 Hz, 1H), 3.85 (s, 3H), 3.39 – 3.33 (m, 4H), 1.70 – 1.63 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.85, 161.97, 152.93, 133.33, 129.46, 113.58, 90.79, 54.99, 24.12. HRMS calc. $C_{15}H_{19}NO_2$ (M^+): 245.1416, Found: 245.1419. IR(KBr) 778, 1167, 1213, 1252, 1448, 1546, 1601, 1639, 2855, 2937 cm^{-1}; mp125-126°C.



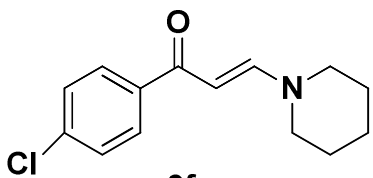
3da

pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.82 (m, 2H), 7.77 (d, *J* = 12.5 Hz, 1H), 7.43 – 7.41 (m, 2H), 5.82 (d, *J* = 12.5 Hz, 1H), 3.36 (s, 4H), 1.67 (s, 6H), 1.33 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 188.92, 154.27, 153.02, 138.04, 127.38, 125.11, 91.30, 55.00 (brs)，47.20 (brs)，34.93, 31.32, 25.98 (brs)，24.13. HRMS calc. $C_{18}H_{25}NO$ (M^+): 271.1936, Found: 271.1941. IR(KBr) 762, 1207, 1640, 2938cm^{-1}; mp111-112^{o}C.



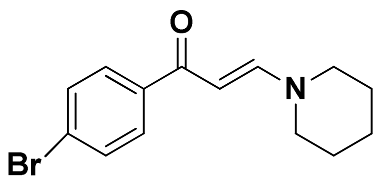
3ea

pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.88 (m, 2H), 7.78 (d, *J* = 12.4 Hz, 1H), 7.07 (t, *J* = 8.7 Hz, 2H), 5.77 (d, *J* = 12.4 Hz, 1H), 3.37 (s, 4H), 1.67 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 187.57, 164.58 (d, *J* = 250.5 Hz), 153.36, 136.97 (d, *J* = 3.0 Hz), 129.79 (d, *J* = 8.8 Hz), 115.08 (d, *J* = 21.5 Hz), 90.77, 55,01(brs), 46.51 (brs), 25.90 (brs)，24.12. HRMS calc. $C_{14}H_{16}FNO$ (M^+): 233.1216, Found: 233.1222. IR(KBr) 1213, 1446, 1538, 1595, 1638, 2852, 2940cm^{-1}; mp114-115^{o}C.



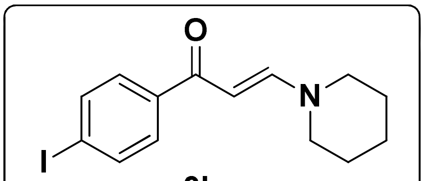
3fa

pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.79 (m, 3H), 7.37 (d, *J* = 8.6 Hz, 2H), 5.77 (d, *J* = 12.4 Hz, 1H), 3.38 (br, 4H), 1.68 (m, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 187.60, 153.50, 139.14, 136.95, 128.99, 128.42, 90.79, 24.12. MS (EI) *m/z* 249 (M^+); IR(KBr) 1446, 1540, 1631, 2935cm^{-1}; mp127-128^{o}C. [S2]



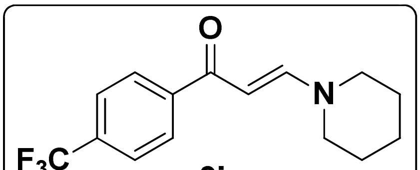
3ga

pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.74 (m, 3H), 7.55 – 7.52 (m, 2H), 5.76 (d, *J* = 12.4 Hz, 1H), 3.38 (br, 1H), 1.68 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.67, 153.50, 139.58, 131.37, 129.19, 125.48, 90.74, 55.29, 46.67, 26.53, 25.12, 24.10. HRMS calc. $C_{14}H_{16}BrNO$ (M^+): 293.0415, Found: 293.0417. IR(KBr) 1447, 1540, 1634, 2938, 3021cm^{-1}; mp133-134^{o}C.



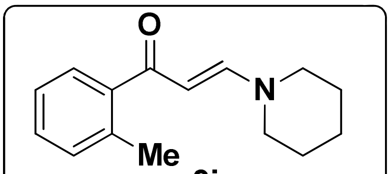
3ha

pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 16.1, 10.3 Hz, 3H), 7.61 (d, *J* = 8.1 Hz, 2H), 5.75 (d, *J* = 12.4 Hz, 1H), 3.47–3.26 (m, 4H), 1.79–1.56 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.82, 153.48, 140.13, 137.35, 129.21, 97.86, 90.65, 55.17, 46.35, 26.63, 24.82, 24.07. HRMS calc. $C_{14}H_{16}INO$ (M^+): 341.0277, Found: 341.0282. IR(KBr) 762, 881, 1446, 1541, 1571, 1634, 2853, 2938cm^{-1}; mp111-112°C.



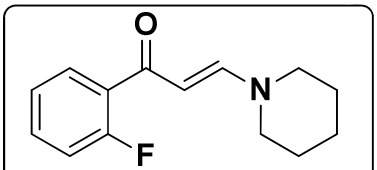
3ia

pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.82 (d, *J* = 12.4 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 5.78 (d, *J* = 12.4 Hz, 1H), 3.39 (m, 4H), 1.69 (m, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 187.63, 153.82, 144.00, 132.30 (q, *J* = 32 Hz), 127.80, 124.12 (d, *J* = 270 Hz), 125.23 (q, *J* = 3.7 Hz), 91.05, 55.38, 46.58, 26.52, 25.04, 24.07. HRMS calc. $C_{15}H_{16}F_3NO$ (M^+): 283.1184, Found: 283.1187. IR(KBr) 1333, 1546, 1641, 2853, 2972 cm^{-1}; mp124-125°C.



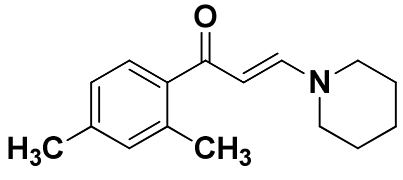
3ja

pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.3 Hz, 1H), 7.25 – 7.13 (m, 3H), 5.46 (d, *J* = 12.8 Hz, 1H), 3.29 (m, 4H), 2.40 (s, 3H), 1.65 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.98, 153.81, 142.36, 135.43, 130.73, 128.71, 127.17, 125.30, 96.98, 24.09, 19.92. HRMS calc. $C_{15}H_{19}NO$ (M^+): 229.1467, Found: 229.1471. IR(KBr) 767, 1210, 1368, 1447, 1546, 1640, 2858, 2938cm^{-1}; mp75-76°C.



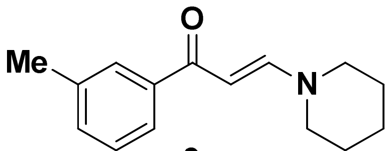
3ka

pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.72 (m, 2H), 7.44 – 7.31 (m, 1H), 7.17 (td, *J* = 7.6, 1.0 Hz, 1H), 7.06 (ddd, *J* = 10.5, 8.4, 0.9 Hz, 1H), 5.71 (d, *J* = 12.6 Hz, 1H), 3.34 (m, 4H), 1.65 (m, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 186.38, 161.25 (d, *J* = 250 Hz), 153.27, 131.65 (d, *J* = 8.5 Hz), 130.47 (d, *J* = 3.3 Hz), 129.51 (d, *J* = 14.2 Hz), 124.10 (d, *J* = 3.5 Hz), 116.04 (d, *J* = 23.7 Hz), 95.74, 55.17, 46.46, 26.46, 24.91, 24.02. HRMS calc. $C_{14}H_{16}FNO$ (M^+): 233.1216, Found: 233.1220. IR(KBr) 1212, 1446, 1538, 1638, 2852, 2941cm^{-1}; mp 87-88°C.



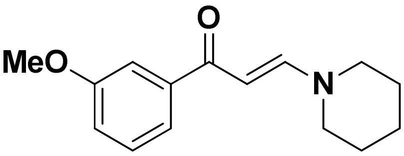
3la

pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 10.7 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.05 – 6.93 (m, 2H), 5.44 (d, *J* = 12.8 Hz, 1H), 3.37 – 3.19 (m, 4H), 2.38 (s, 3H), 2.32 (s, 3H), 1.64 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.88, 153.71, 139.37, 138.64, 135.62, 131.57, 127.42, 125.89, 96.82, 77.48, 77.16, 76.84, 55.02, 45.89, 26.17, 24.98, 24.08, 21.29, 19.99. HRMS calc. $C_{16}H_{21}NO$ (M^+): 243.1623, Found: 243.1626. IR(KBr) 766, 1206, 1447, 1546, 1638, 2856, 2940cm^{-1}; mp125-126^{o}C.



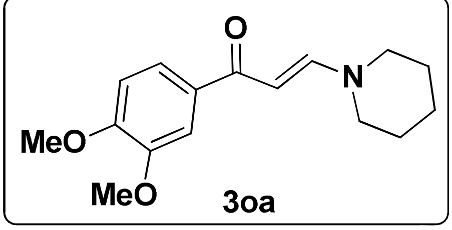
3ma

pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 12.5 Hz, 1H), 7.73 – 7.58 (m, 2H), 7.38 – 7.14 (m, 2H), 5.81 (d, *J* = 12.5 Hz, 1H), 3.37 (s, 4H), 2.39 (s, 3H), 1.67 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.36, 152.96, 149.94, 147.73, 135.40, 122.54, 107.97, 107.62, 101.43, 90.78, 25.72，24.10. HRMS calc. $C_{15}H_{19}NO$ (M^+): 229.1467, Found: 229.1470. IR(KBr) 768, 1206, 1368, 1447, 1546, 1641, 2857, 2938cm^{-1}; mp113-114^{o}C.



3na

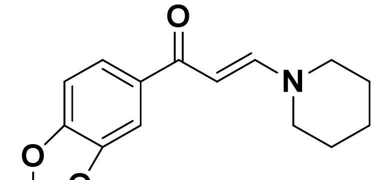
pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 12.5 Hz, 1H), 7.51 – 7.40 (m, 2H), 7.35 – 7.23 (m, 1H), 7.03 – 6.93 (m, 1H), 5.79 (d, *J* = 12.5 Hz, 1H), 3.85 (s, 3H), 3.36 (m, 4H), 1.64 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.84, 159.64, 153.30, 142.35, 129.09, 119.93, 117.14, 112.31, 91.36, 55.46, 54.95, 46.39, 24.09. HRMS calc. $C_{15}H_{19}NO_2$ (M^+): 245.1416, Found: 245.1420. IR(KBr) 778, 1213, 1252, 1448, 1546, 1639, 2855, 2937cm^{-1}; mp116-118^{o}C.



3oa

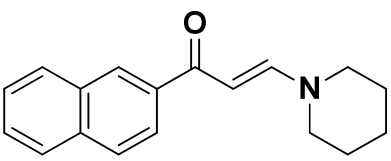
pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 12.5 Hz, 1H), 7.47 (d, *J* = 1.9 Hz, 1H), 7.41 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 5.75 (d, *J* = 12.5 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.29 (s, 4H), 1.59 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.81, 152.92, 151.55, 148.77, 133.70, 120.95, 110.58, 109.99, 90.71, 56.05， 56.04, 25.89, 24.13. HRMS calc. $C_{16}H_{21}NO_3$ (M^+):

275.1521, Found: 275.1527. IR(KBr) 778, 1168, 1213, 1448, 1546, 1601, 1637, 2855, 2936cm^{-1}; mp136-137^{o}C.



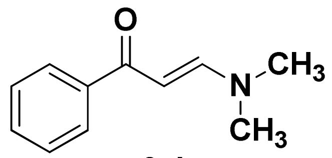
3pa

pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 12.4 Hz, 1H), 7.47 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.42 (d, *J* = 1.6 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.00 (s, 2H), 5.75 (d, *J* = 12.4 Hz, 1H), 3.35 (m, 4H), 1.66 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.44, 153.04, 149.98, 147.75, 135.40, 122.58, 108.01, 107.66, 101.47, 90.77, 25.81, 24.13. HRMS calc. $C_{15}H_{17}NO_3$ (M^+): 259.1208, Found: 259.1211; mp127-128^{o}C.



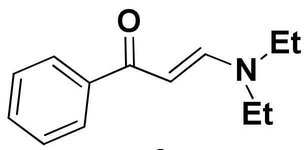
3qa

pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.07 – 7.77 (m, 5H), 7.59 – 7.41 (m, 2H), 5.99 (d, *J* = 12.4 Hz, 1H), 3.42 (s, 4H), 1.69 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.82, 153.20, 138.12, 134.76, 132.88, 129.20, 127.83, 127.76, 127.69, 127.17, 126.24, 124.73, 91.44, 24.08. HRMS calc. $C_{18}H_{19}NO$ (M^+): 265.1467, Found: 265.1472. IR(KBr) 1209, 1280, 1446, 1541, 1638, 2937cm^{-1}; mp110-111^{o}C.



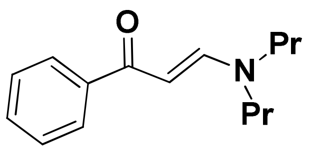
3ab

pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.85 (m, 2H), 7.80 (d, *J* = 12.4 Hz, 1H), 7.49 – 7.37 (m, 3H), 5.72 (d, *J* = 12.4 Hz, 1H), 3.13 (s, 3H), 2.93 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 188.88, 154.44 , 140.63, 131.00, 128.23, 127.60, 92.35,44.85,37.36. MS (EI) *m/z* 175 (M^+); IR(KBr) 760, 1206, 1465, 1640, 2968cm^{-1}; mp89-90^{o}C. [S3]



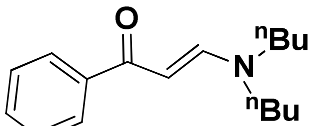
3ac

pale yellow foam; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89-7.81 (m, 3H), 7.45 – 7.37 (m, 3H), 5.77 (d, *J* = 12.5 Hz, 1H), 3.33 (q, *J* = 7.1 Hz, 4H), 1.24 (t, *J* = 7.1 Hz, 7H).^{13}C NMR (101 MHz, $CDCl_3$) δ 188.92, 152.51, 140.93, 130.87, 128.22, 127.59, 91.89, 50.69, 42.97, 14.92, 11.70. MS (EI) *m/z* 203 (M^+); IR(KBr) 762, 1050, 1281, 1365, 1465, 1546, 1639, 2855, 2968cm^{-1}. [S1]



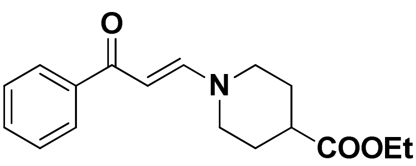
3ad

pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89-7.86 (m, 3H), 7.43-7.40 (m, 3H), 5.75 (d, J = 12.4 Hz, 1H), 3.23 (br, 4H), 1.68-1.66 (m, 4H), 0.95 – 0.85 (m, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 189.00, 153.63, 140.86, 130.85, 128.19, 127.54, 91.89, 58.32, 50.46, 22.54, 19.78, 11.61, 11.09. HRMS calc. $C_{15}H_{21}NO$ (M^+): 231.1623, Found: 231.1629. IR(KBr) 760, 1048, 1280, 1365, 1462, 1548, 1640, 2870, 2968cm^{-1}.



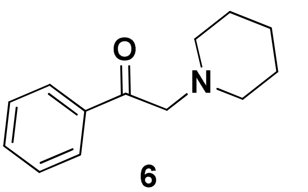
3ae

pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.82 (m, 3H), 7.45-7.43 (m, 3H), 5.76 (d, J = 12.4 Hz, 1H), 3.28 (s, 4H), 1.63 (br, 4H), 1.38 (br, 4H), 0.98 (br, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 13C NMR (101 MHz, CDCl3) δ 188.82, 153.41 , 140.92 , 130.80, 128.17, 127.53, 91.85, 56.36, 48.56, 31.43, 28.52, 20.41, 19.87， 13.85. MS (EI) *m/z* 259 (M^+); IR(KBr) 762, 1049, 1204, 1285, 1460, 1549, 1640, 2872, 2956cm^{-1}. [S1]



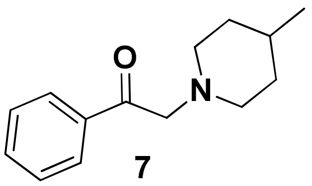
3af

pale yellow foam; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 8.1, 1.5 Hz, 2H), 7.75 (d, J = 12.5 Hz, 1H), 7.45 – 7.40 (m, 3H), 5.85 (d, J = 12.6 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.66 (d, J = 12.4 Hz, 2H), 3.18 (br, 2H), 2.60-2.53 (m, 1H), 2.03 – 1.99 (m, 2H), 1.85 – 1.75(m, 2H), 1.27 (t, J = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 189.32, 173.80, 153.00, 140.49, 131.08, 128.23, 127.54, 92.05, 60.89, 40.49, 27.76, 14.26. HRMS calc. $C_{17}H_{21}NO_3$ (M^+): 287.1521, Found: 287.1525. IR(KBr) 990, 1195, 1640, 1710, 2940, 2961cm^{-1}.



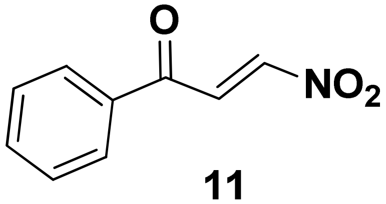
6

pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.99 (m, 2H), 7.57-7.53 (m, 1H), 7.45 (t, J = 7.8 Hz, 2H), 3.81 (s, 2H), 2.58 (m, 4H), 1.66 (dt, J = 11.3, 5.6 Hz, 4H), 1.46 (dt, J = 11.5, 5.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.83, 136.33, 133.24, 128.59, 128.27, 65.26, 54.88, 25.82, 24.05.



7

pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 7.3 Hz, 1H), 7.28 (t, *J* = 7.7 Hz, 2H), 3.63 (s, 2H), 2.82 (d, *J* = 10.9 Hz, 2H), 1.98 (t, *J* = 10.9 Hz, 2H), 1.47 (d, *J* = 9.1 Hz, 2H), 1.22 (dd, *J* = 14.6, 6.6 Hz, 3H), 0.79 (d, *J* = 5.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.73, 136.23, 133.16, 128.52, 128.18, 64.85, 54.26, 34.06, 30.40, 21.87.



11

yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 13.2 Hz, 1H), 8.02 – 8.00 (m, 2H), 7.72 – 7.68 (m, 2H), 7.59 – 7.55 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.15, 148.28, 136.02, 135.00, 129.78, 129.37, 129.07. IR(KBr) 721, 796, 945, 1014, 1450, 1533, 1620, 1672, 2924cm^{-1}; mp102-103°C.

Detection of the reaction intermediates

The reaction conditions were the same as the general procedure as shown in page S2. For the GC-MS analysis of the reaction mixture, small samples were taken with a syringe at different reaction times and then were diluted with EtOAc. The results showed that phenacyl iodine **5** and tertiary amine **6** were generated as the reaction continues. After 6h, these two intermediates were consumed almost entirely. However, intermediate **11** can't be detected by GC-MS even if the reaction mixture was rapidly cooling by liquid nitrogen. The main reason may due to the high reaction rate between intermediate **11** and piperidine. The control experiment showed that this reaction was completed in less than 5 minutes (Scheme 3, eq 4 in the main text).

The GC-MS spectra at different reaction stage (t= 1h, 6h) are shown as below:

Retention time for intermediates and product:

Acetophenone **1a** t=3.40 min; Phenacyl iodine **5** t=4.72 min; tertiary amine **6** t=5.27 min; enaminon **3aa** t=8.40 min.

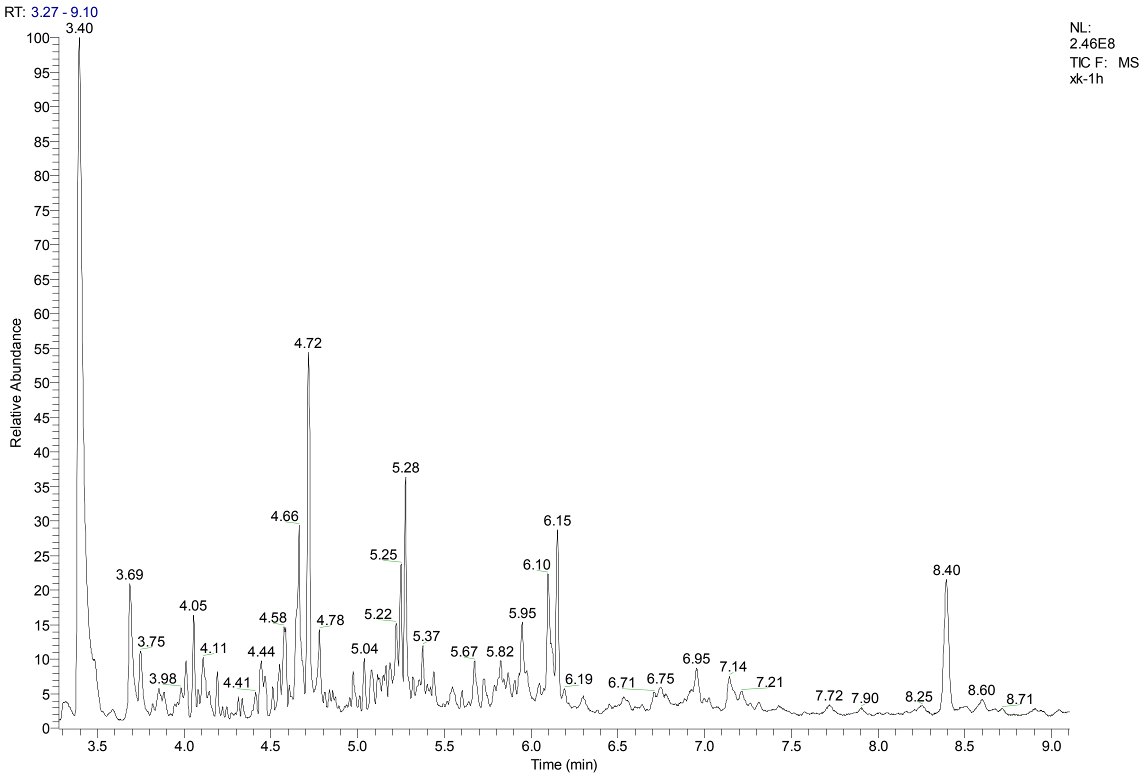


Fig 1. GC spectrum for reaction mixture at 1h

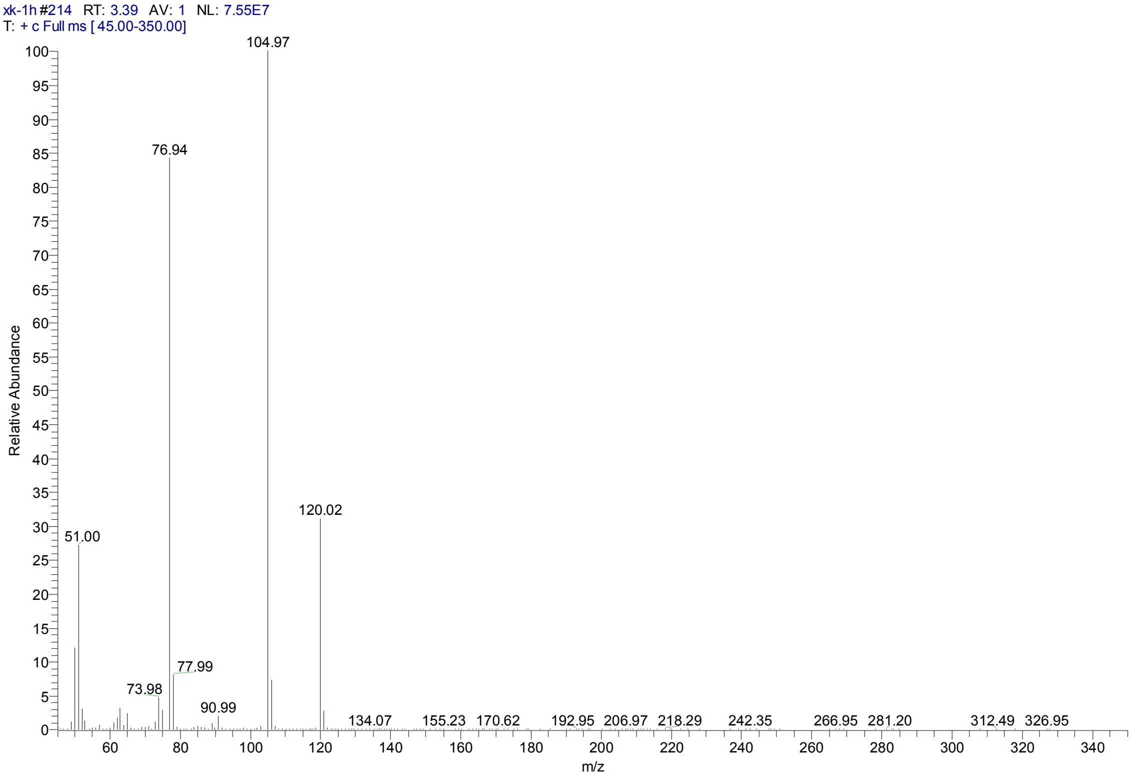


Fig 2. MS spectrum for substance with retention time at 3.39 min

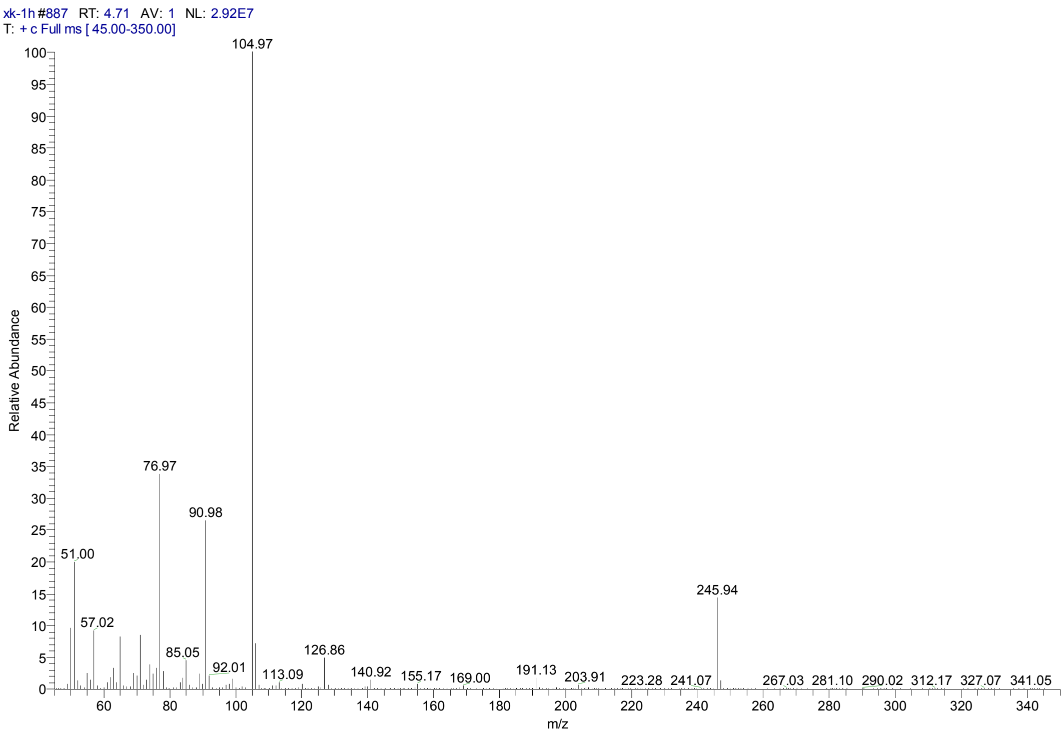


Fig 3. MS spectrum for substance with retention time at 4.72 min (compound **5**)

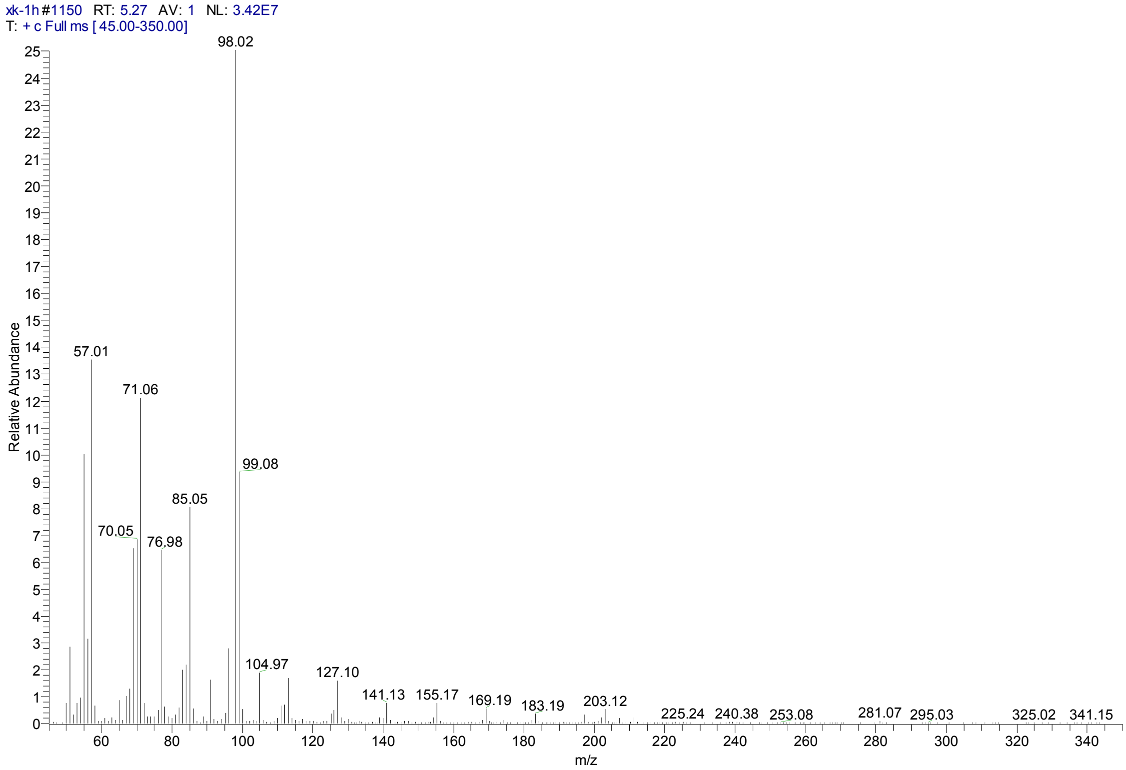


Fig 4. MS spectrum for substance with retention time at 5.27 min (compound **6**)

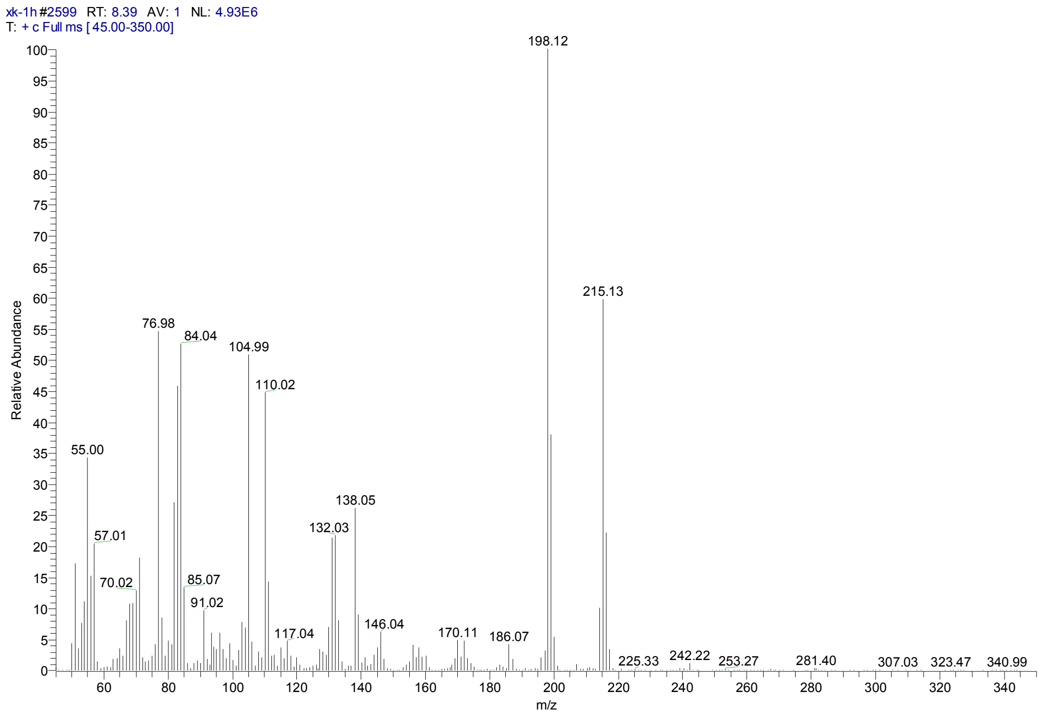


Fig 5. MS spectrum for substance with retention time at 8.39 min (compound **3aa**)

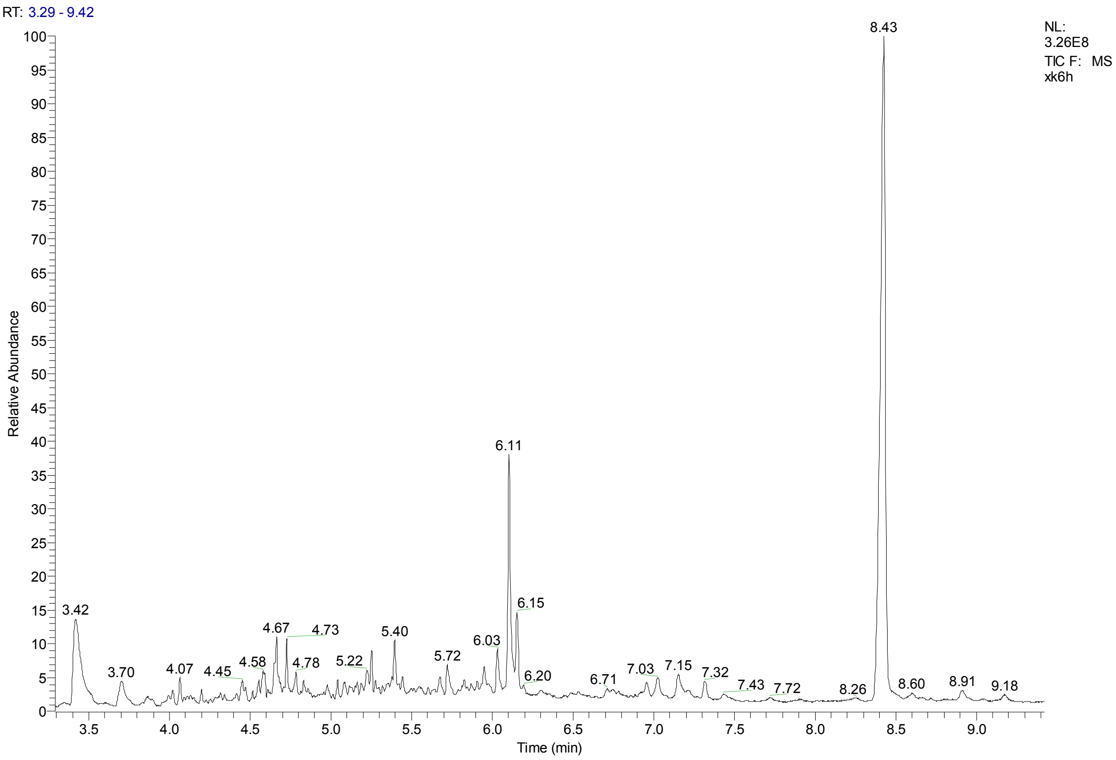


Fig 6. GC spectrum for reaction mixture at 6h

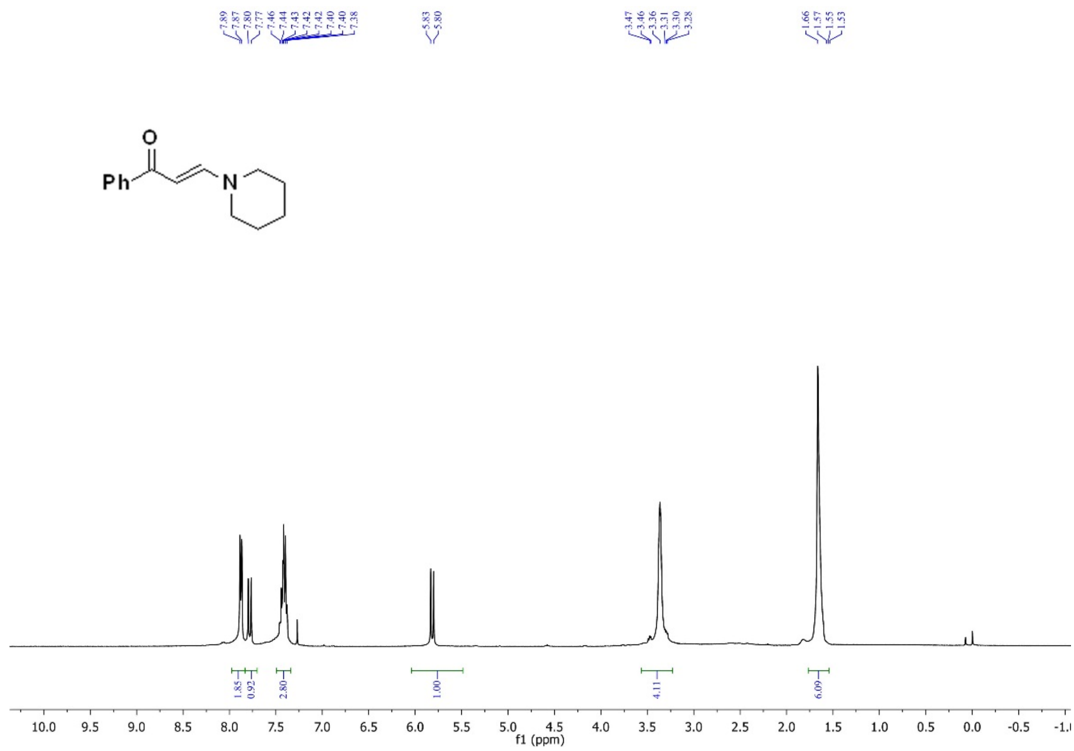
Reference:

S1. S. Ueno, R. Shimizu and R. Kuwano, Angew. Chem. Int. Ed., 2009, **48**, 4543.

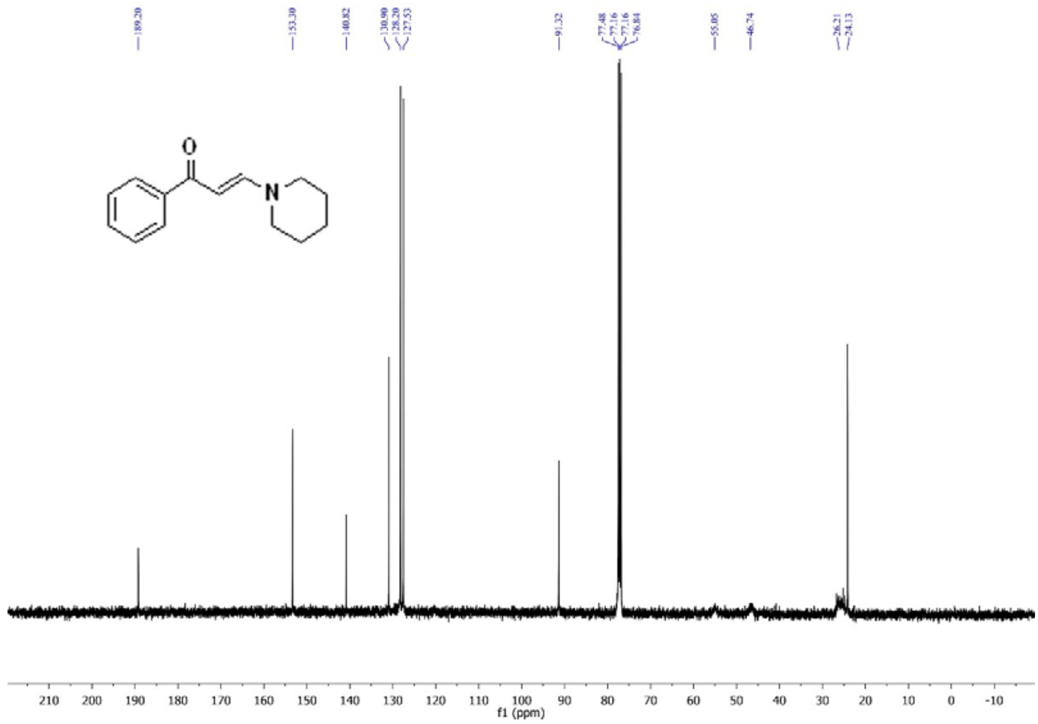
S2. S. Almazroa, M. H. Elnagdi and A. M. Salah El-Din, J. Heterocyclic Chem., 2004, **41**, 267.

S3. D. Yu, Y. N. Sum, A. C. C. Ean, M. P. Chin and Y. Zhang, Angew. Chem. Int. Ed., 2013, **52**, 5125.

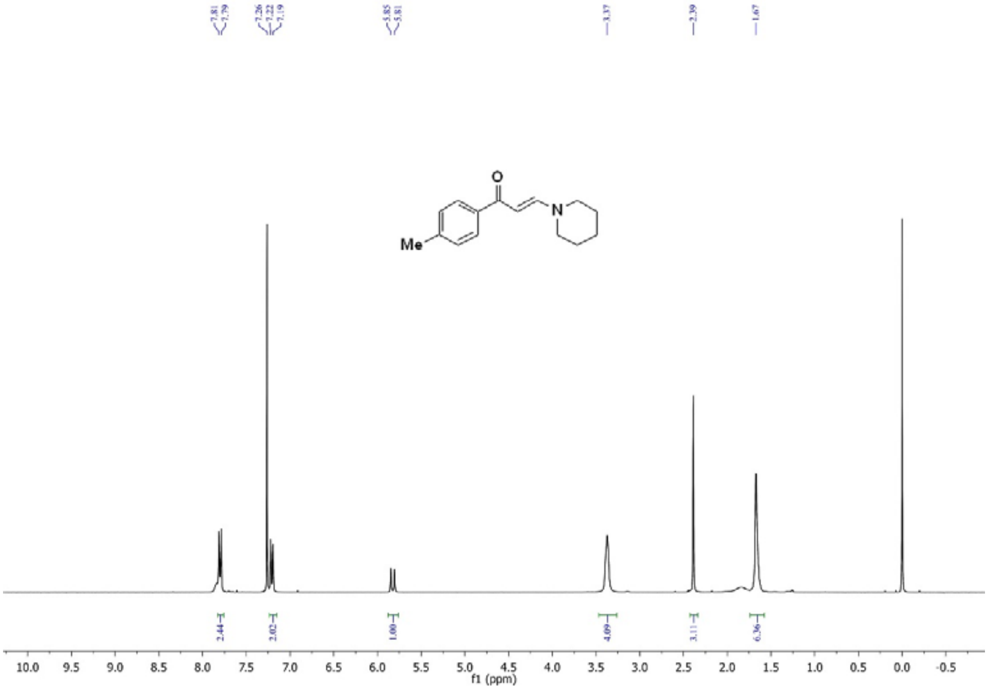
^{1}H NMR of **3aa** ($CDCl_3$, 400MHz)



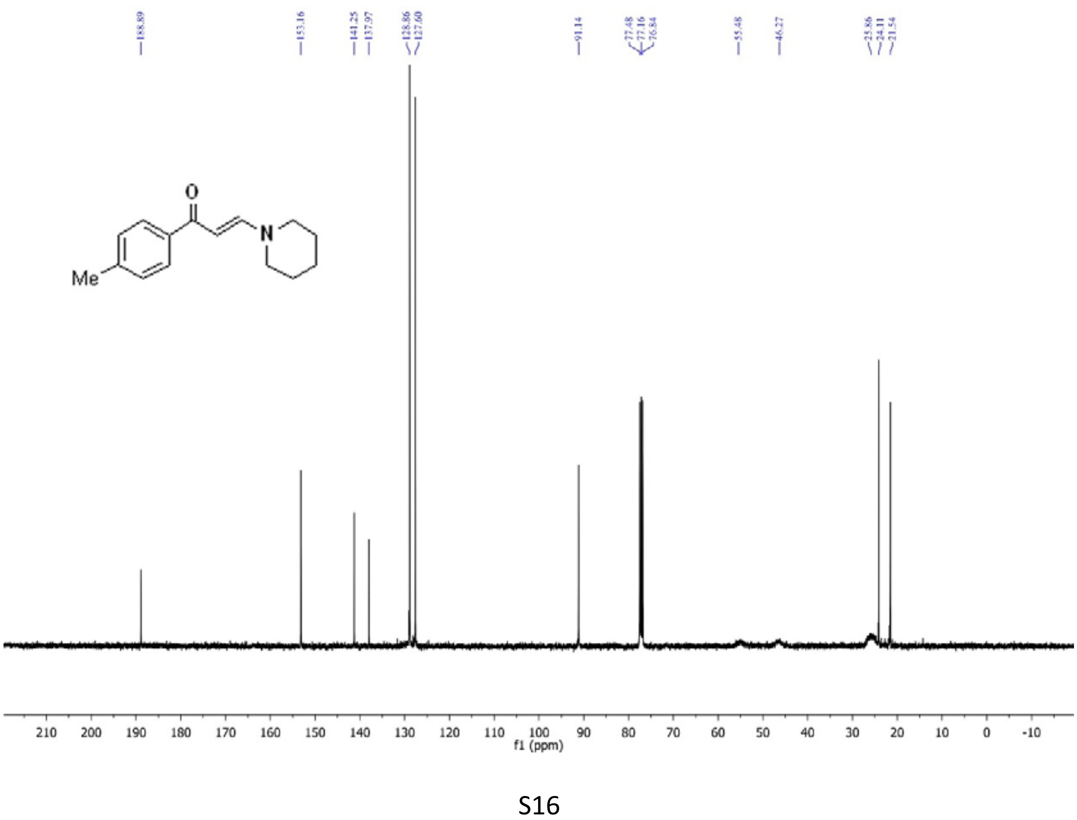
^{13}C NMR of **3aa** ($CDCl_3$, 100MHz)



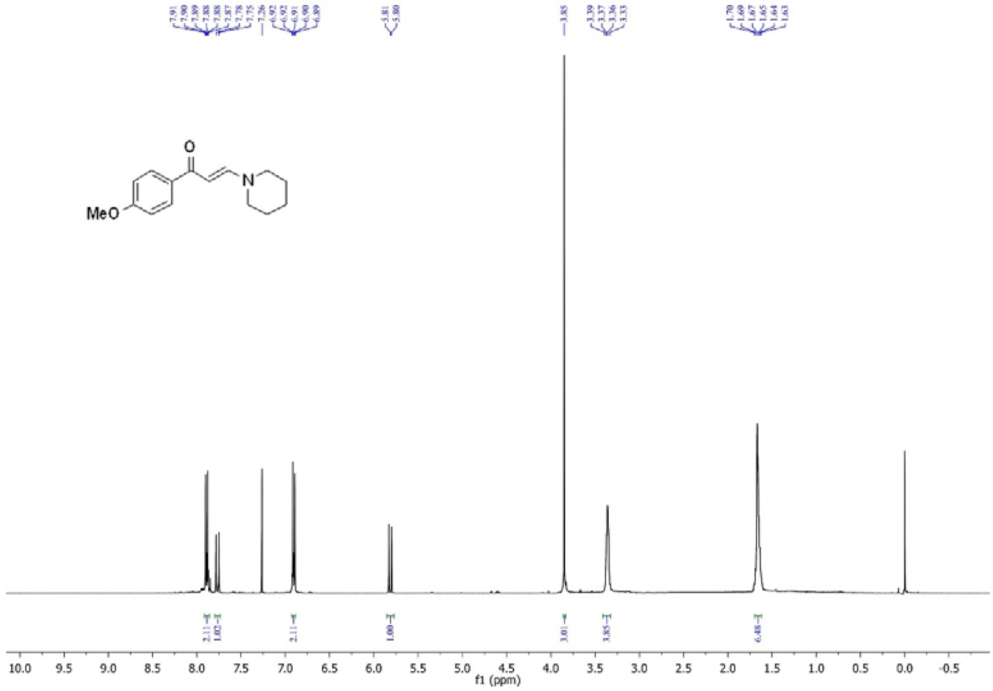
[1]HNMR of **3ba** ($CDCl_3$, 300MHz)



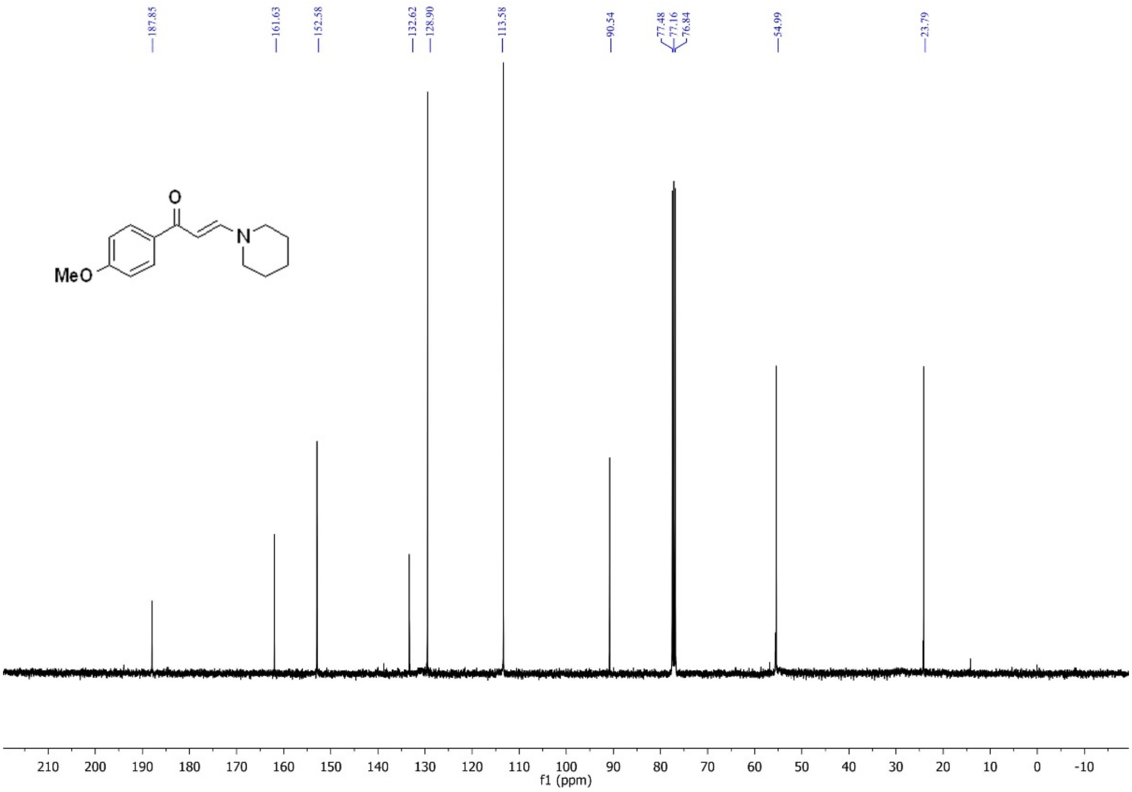
[13]CNMR of **3ba** ($CDCl_3$, 100MHz)



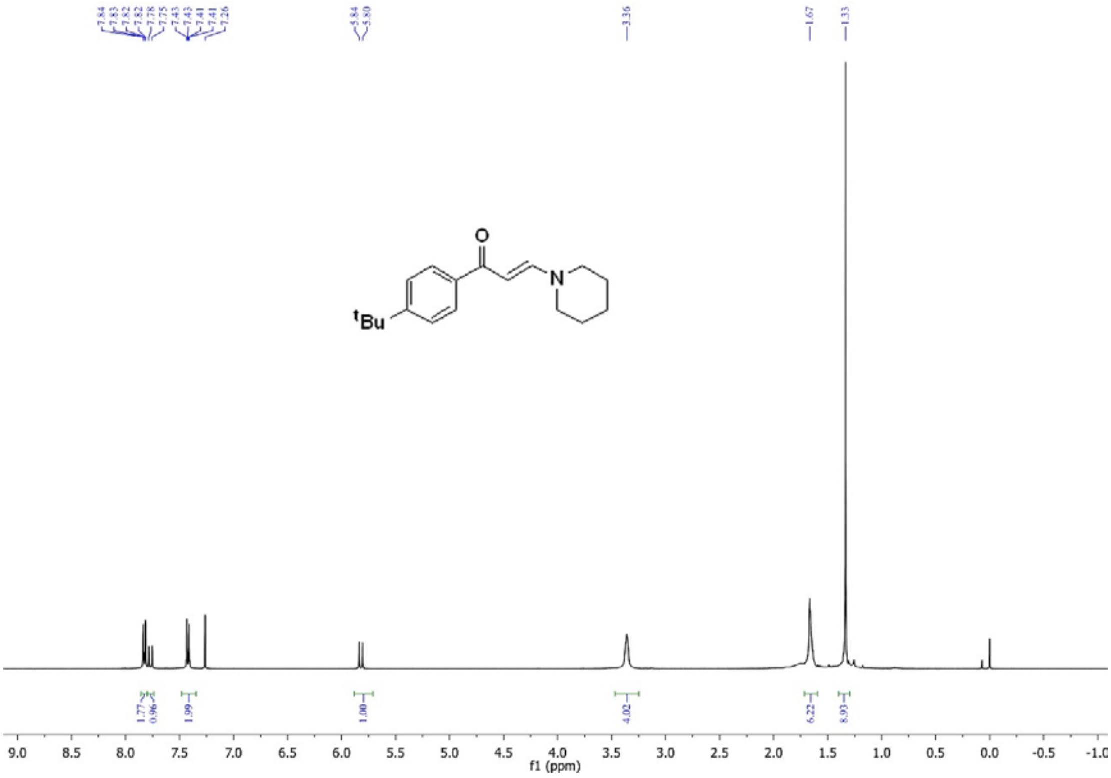
[1]H NMR of **3ca** ($CDCl_3$, 400MHz)



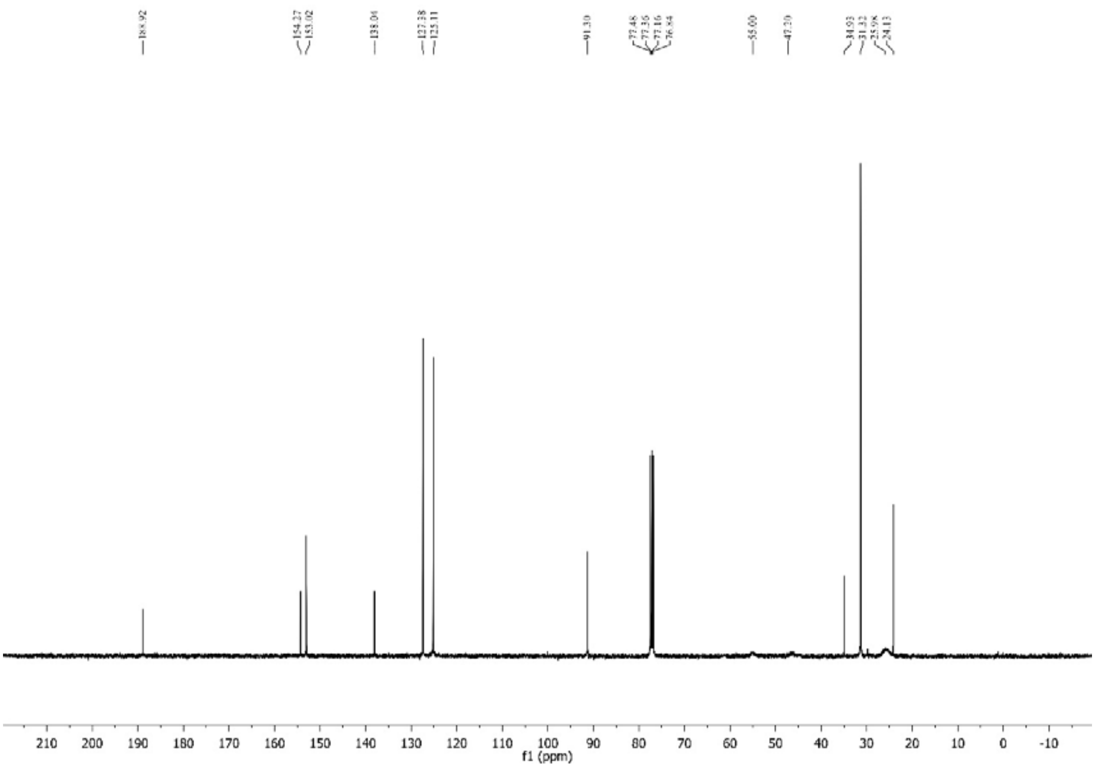
[13]C NMR of **3ca** ($CDCl_3$, 100MHz)



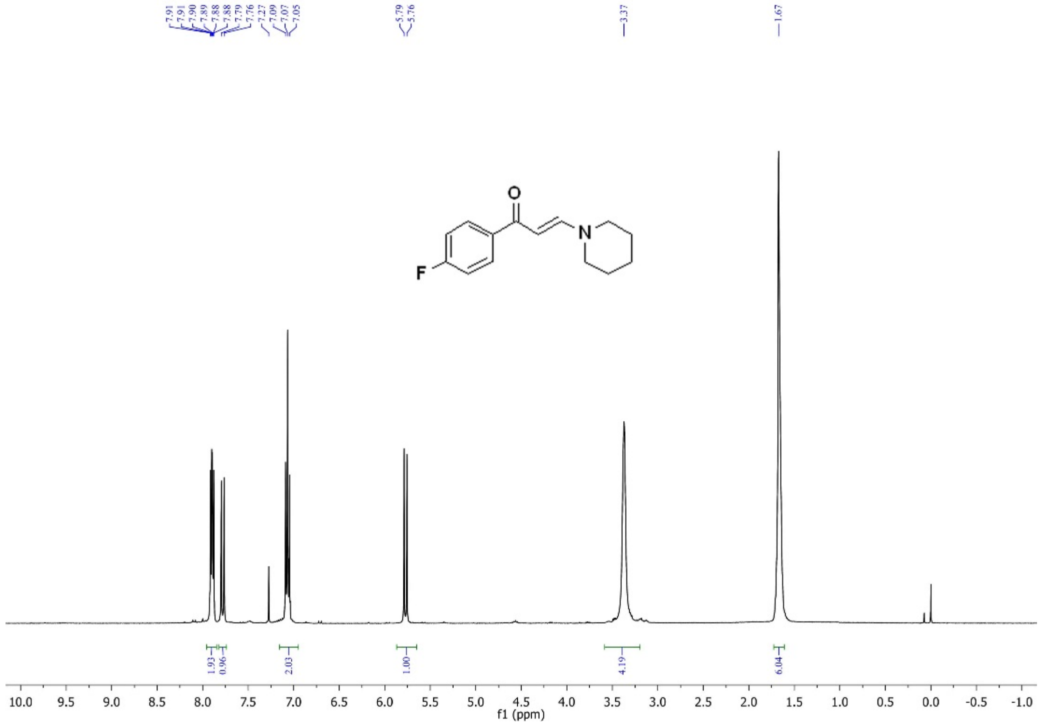
^{1}H NMR of **3da** ($CDCl_3$, 400MHz)



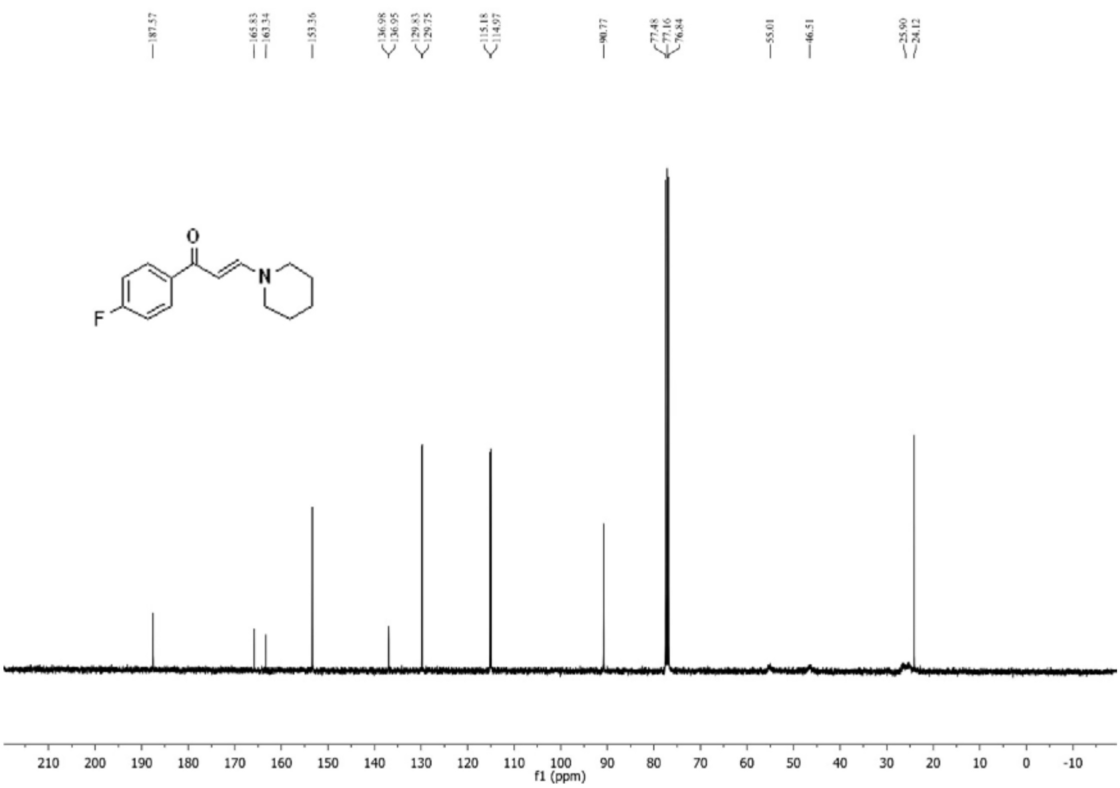
^{13}C NMR of **3da** ($CDCl_3$, 100MHz)



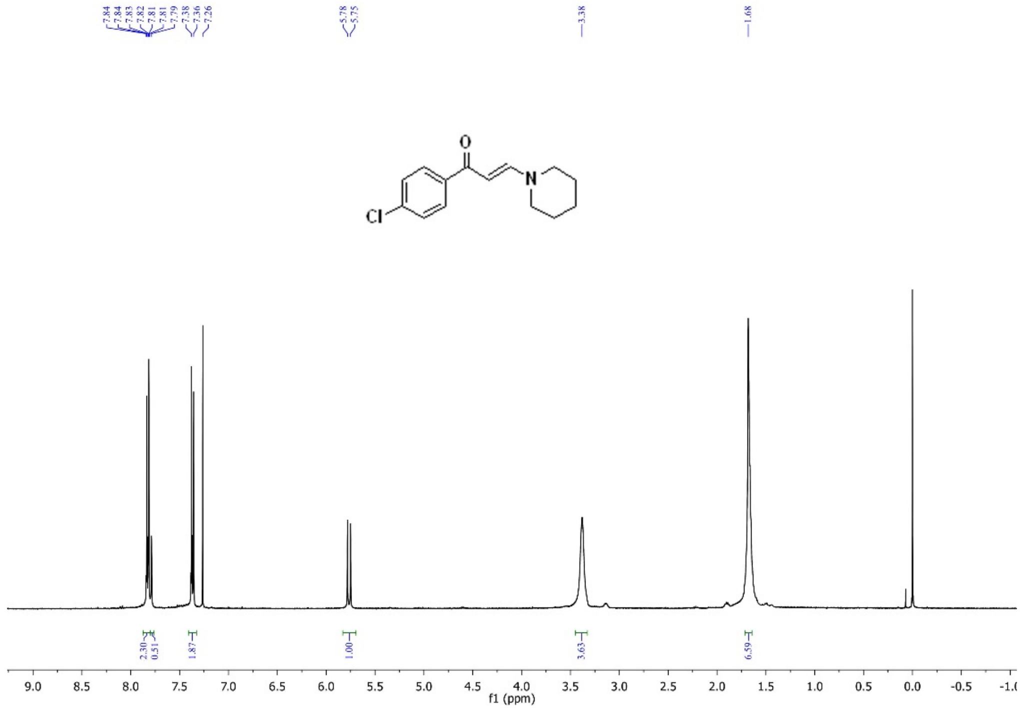
[1]H NMR of **3ea** ($CDCl_3$, 400MHz)



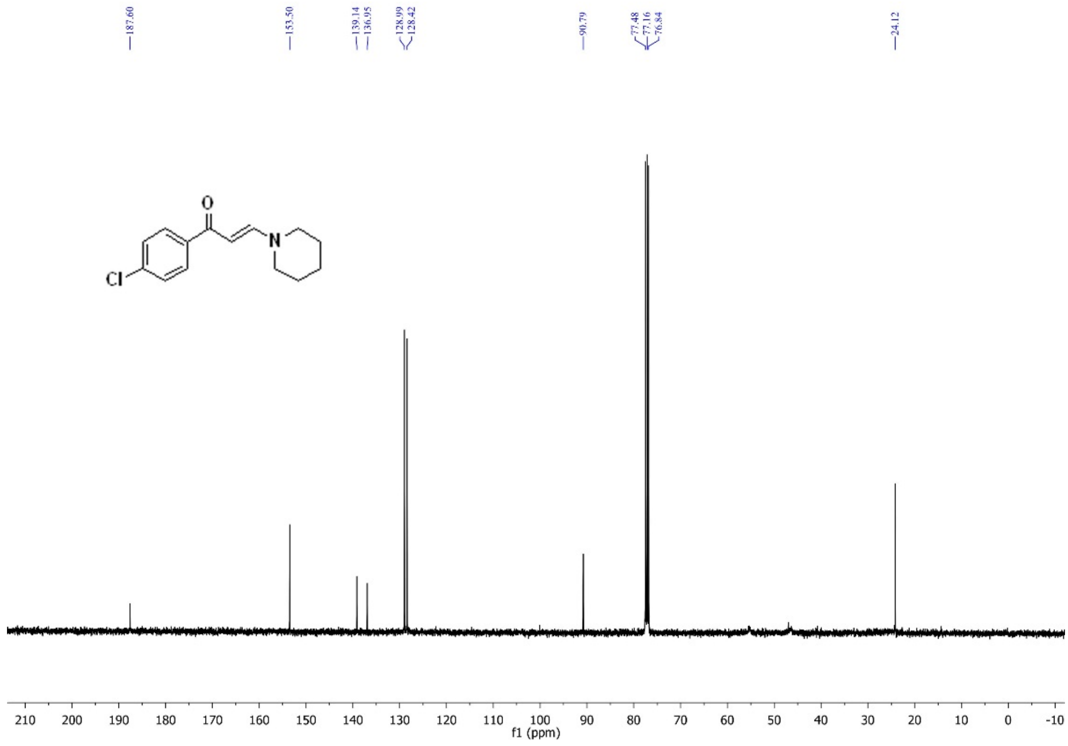
[13]C NMR of **3ea** ($CDCl_3$, 100MHz)



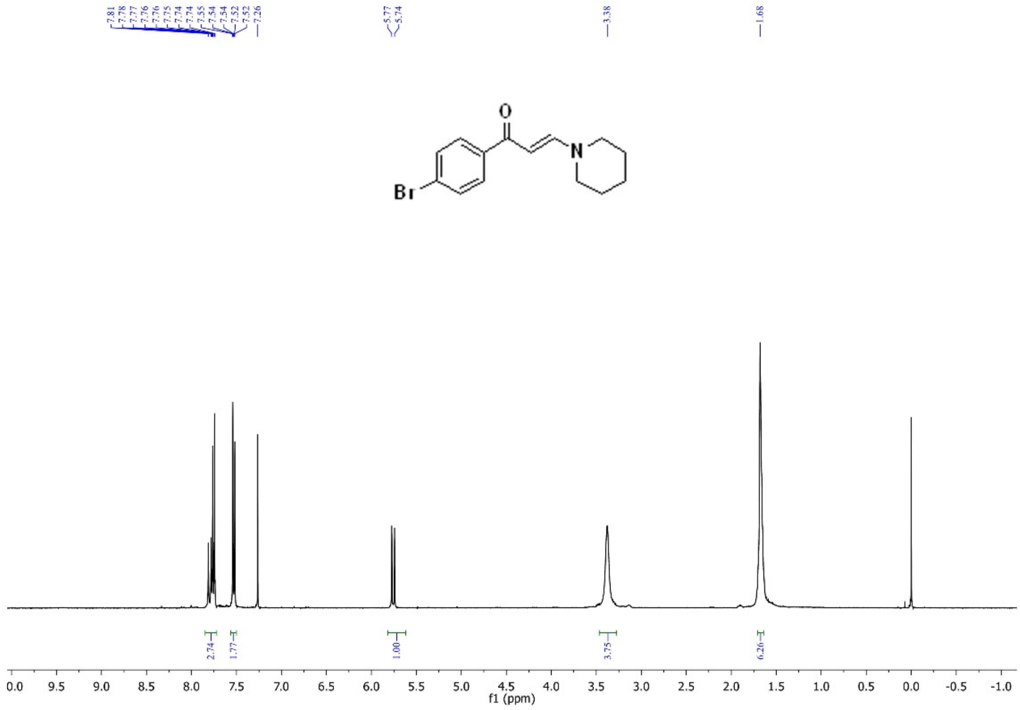
[1]H NMR of **3fa** ($CDCl_3$, 400MHz)



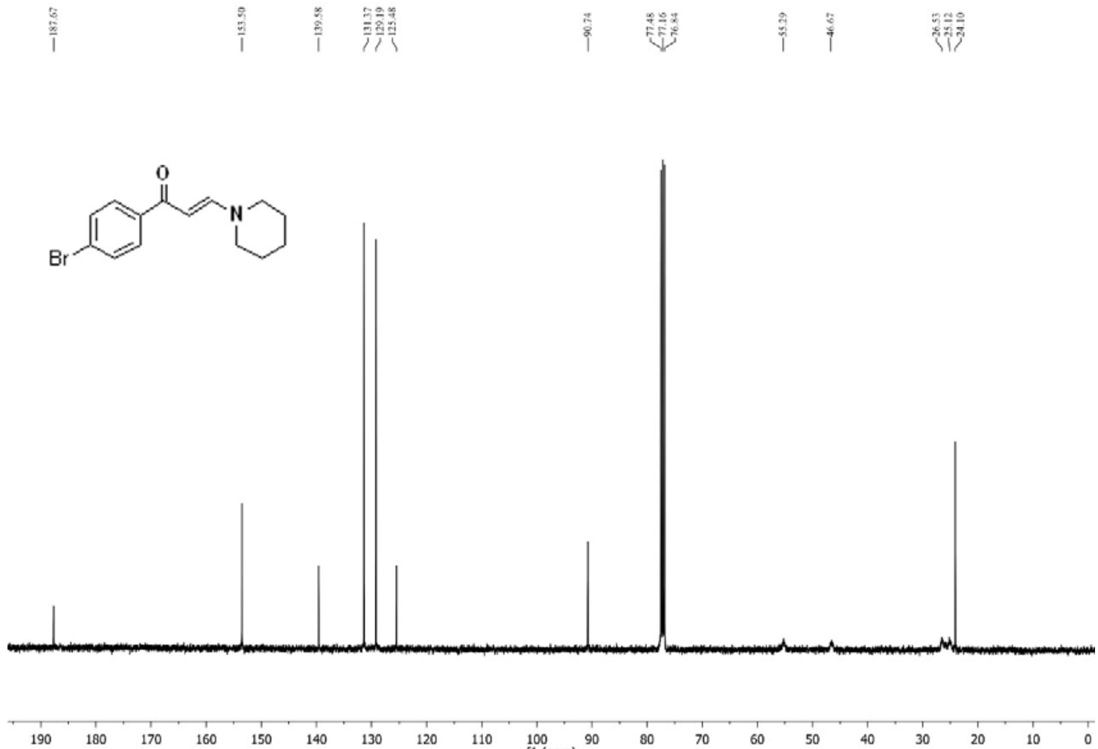
[13]C NMR of **3fa** ($CDCl_3$, 100MHz)



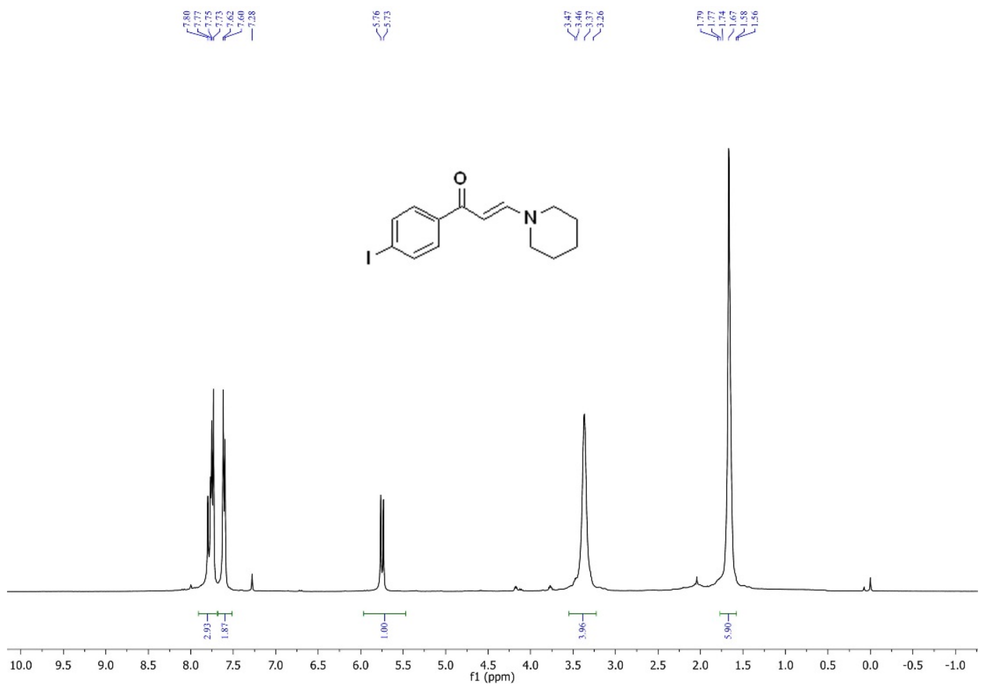
[1]H NMR of **3ga** ($CDCl_3$, 400MHz)



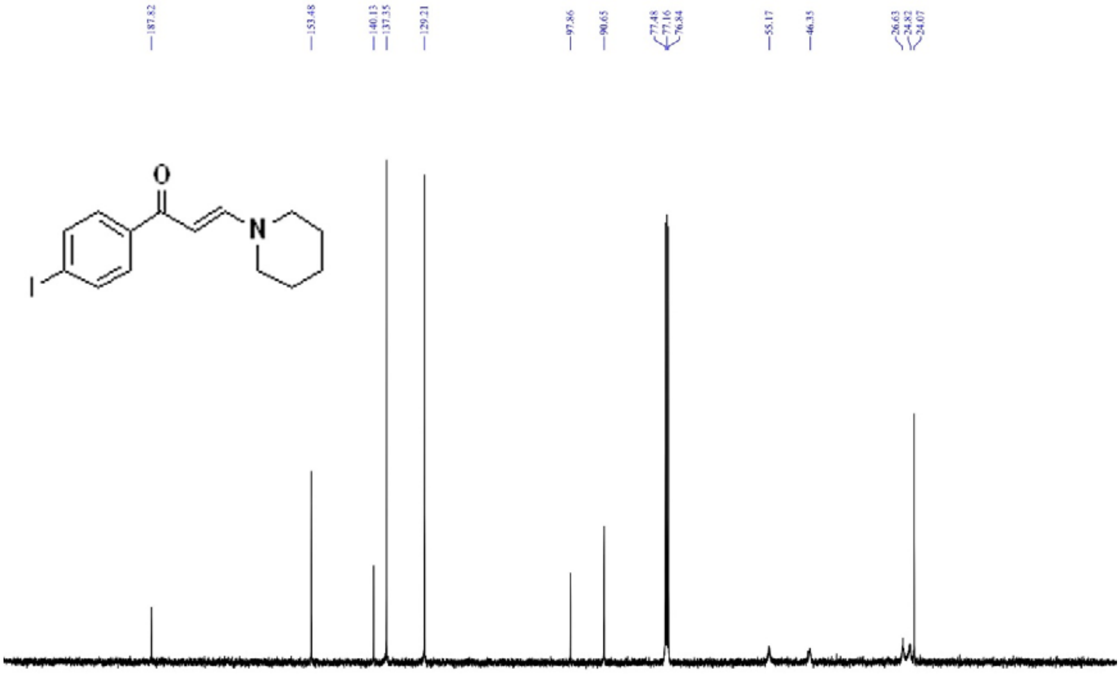
[13]C NMR of **3ga** ($CDCl_3$, 100MHz)



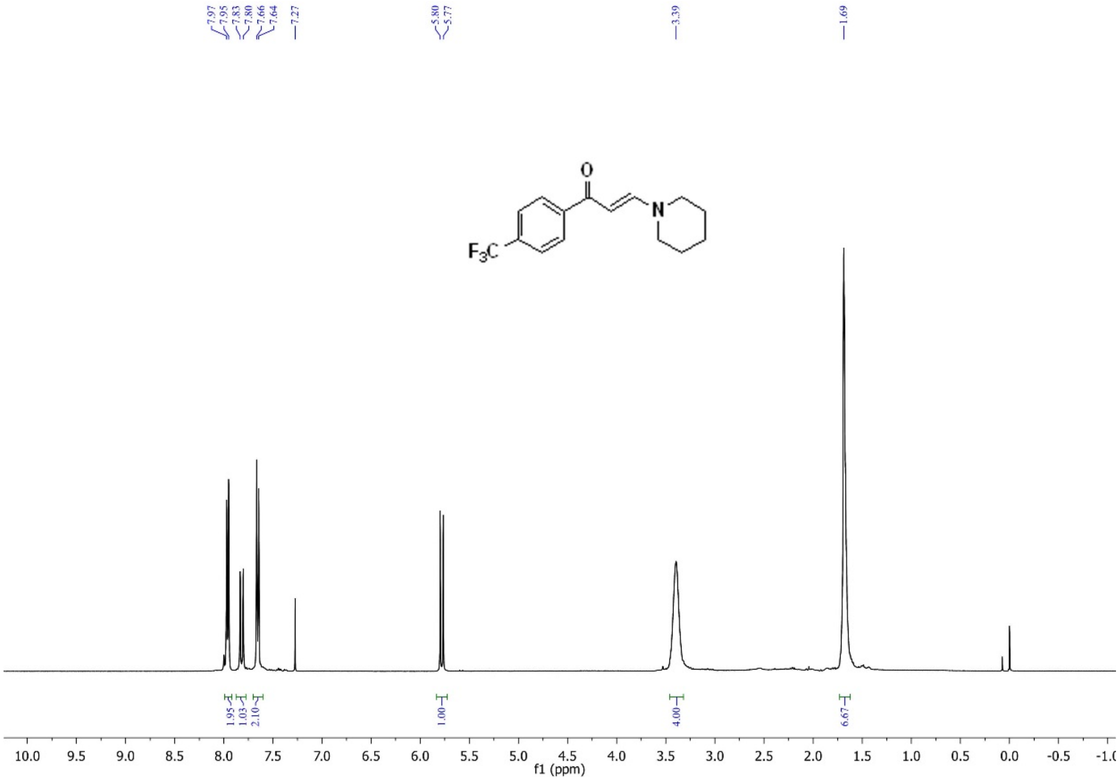
^{1}H NMR of **3ha** ($CDCl_3$, 400MHz)



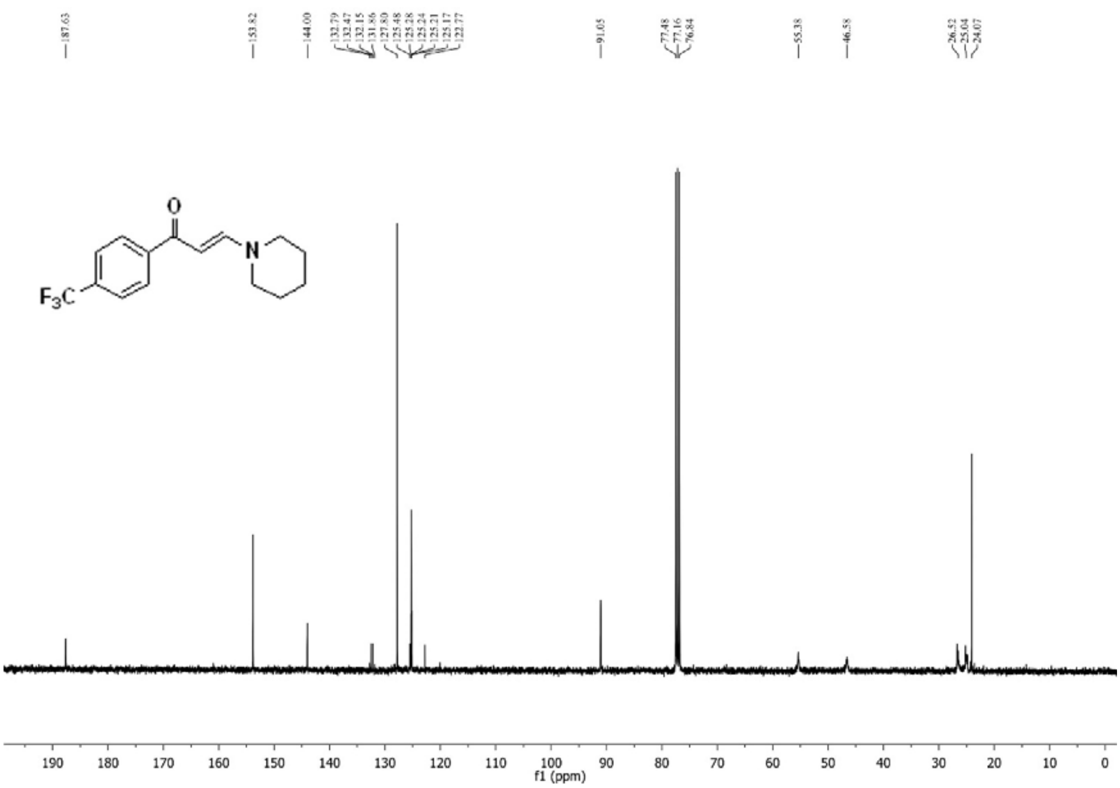
^{13}C NMR of **3ha** ($CDCl_3$, 100MHz)



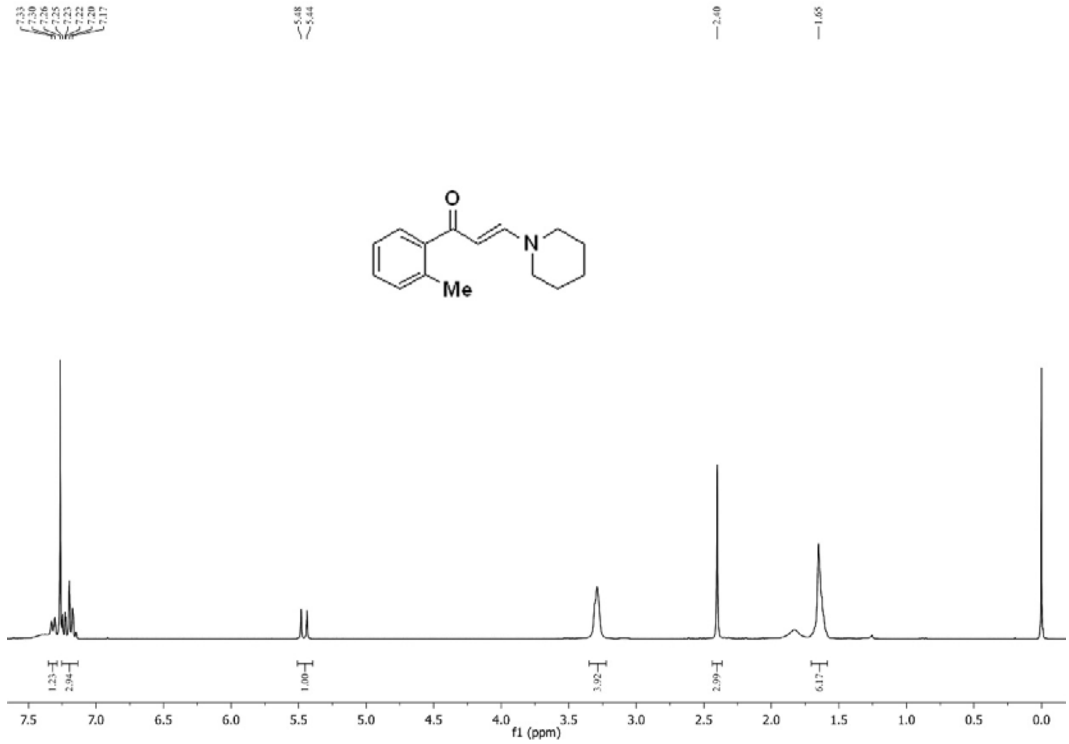
^{1}H NMR of **3ia** ($CDCl_3$, 400MHz)



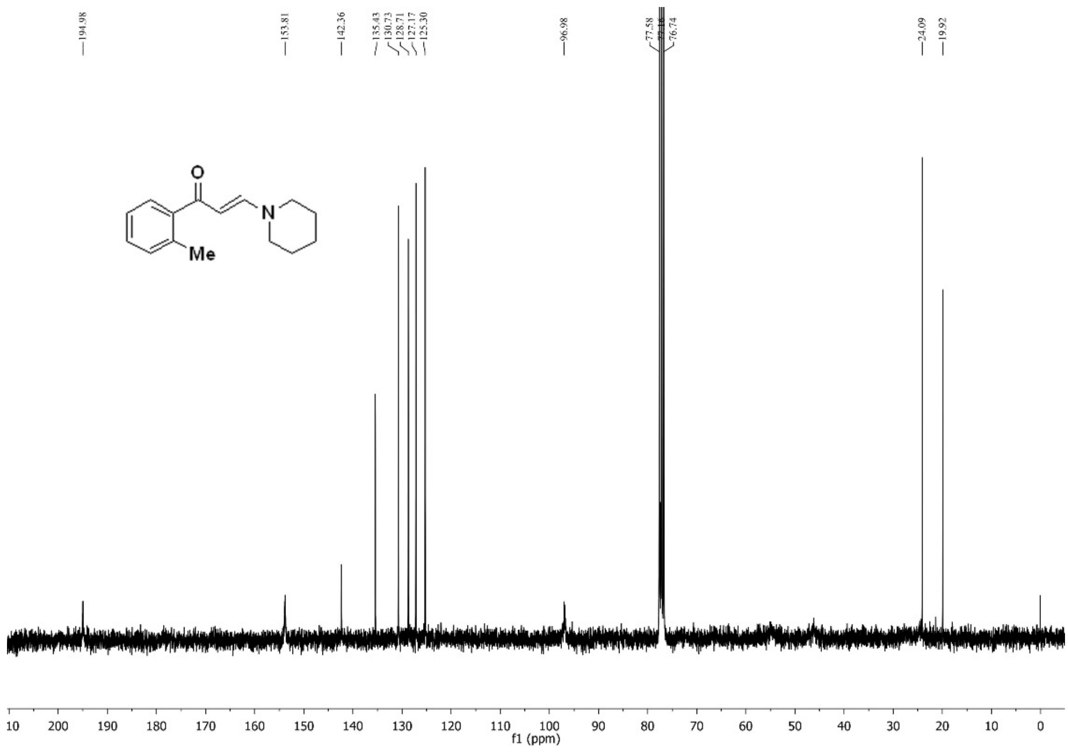
^{13}C NMR of **3ia** ($CDCl_3$, 100MHz)



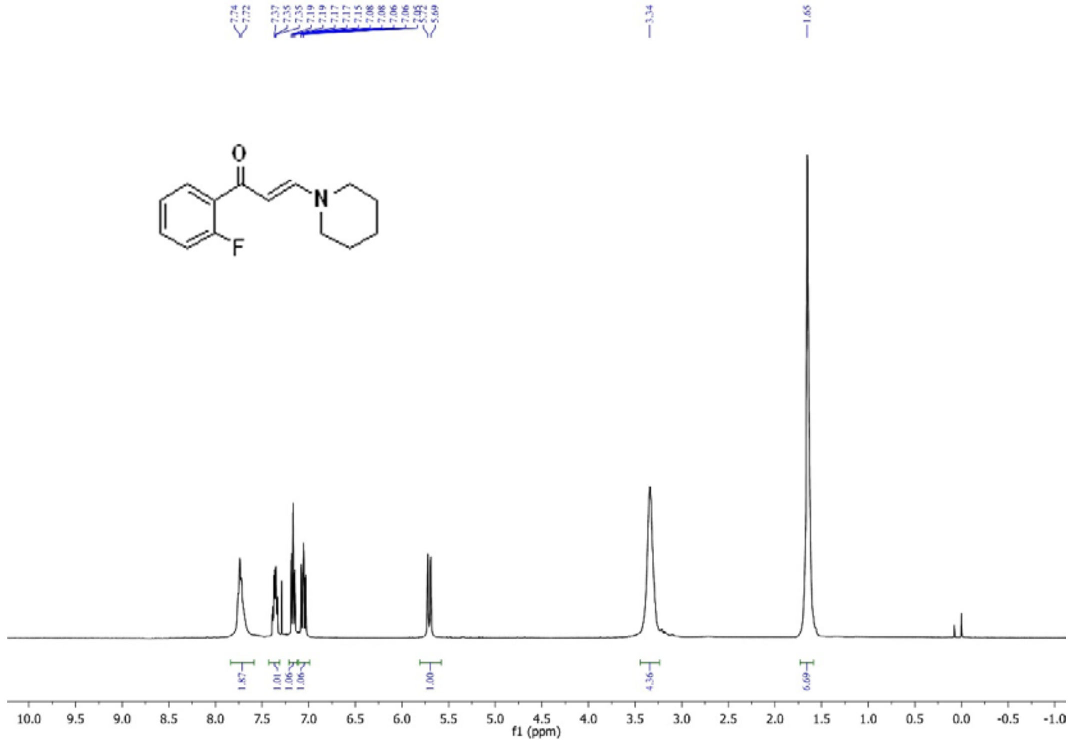
[1]H NMR of **3ja** ($CDCl_3$, 300MHz)



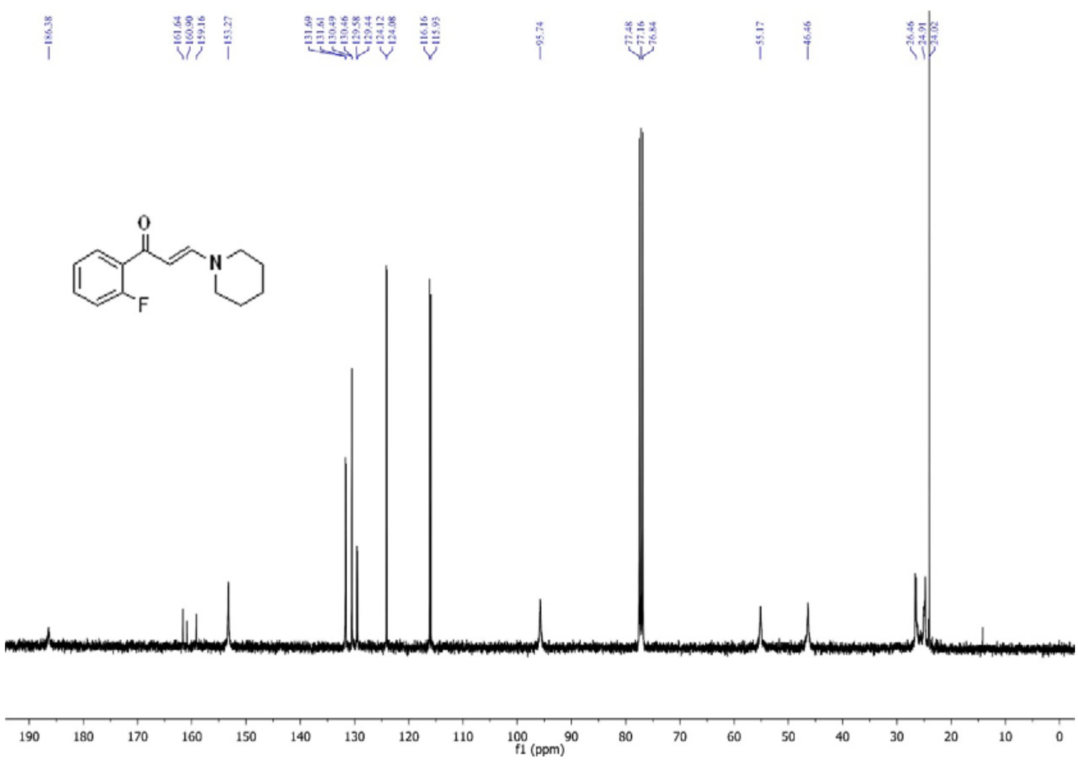
[13]C NMR of **3ja** ($CDCl_3$, 75MHz)



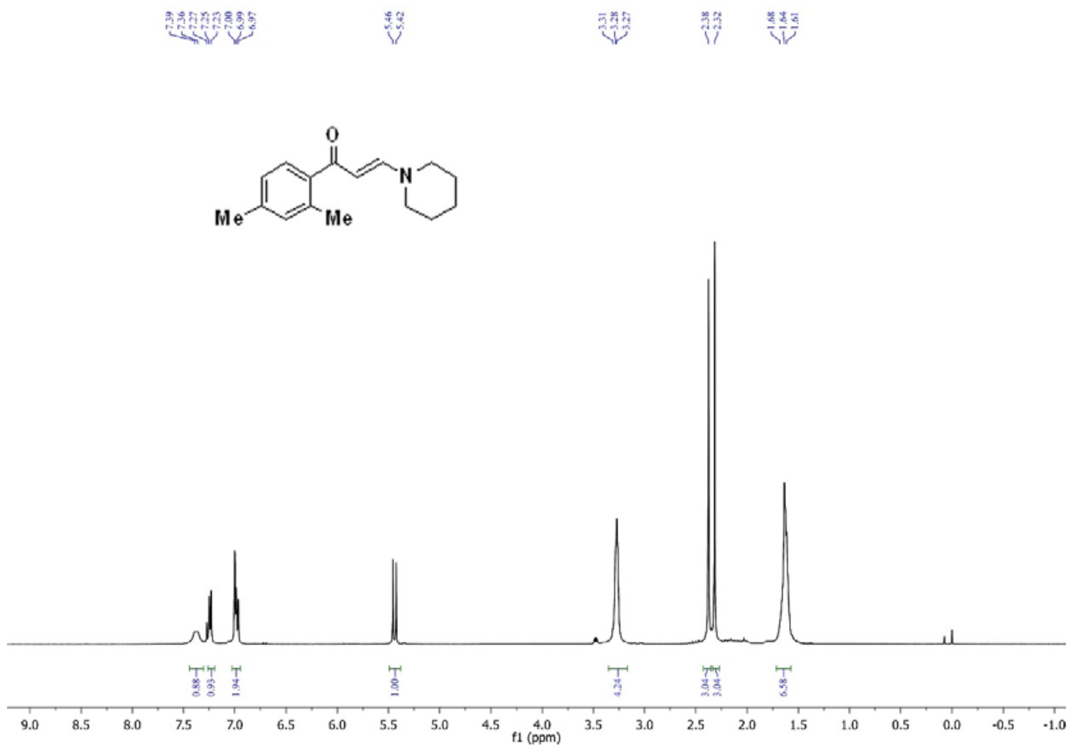
^{1}HNMR of **3ka** ($CDCl_3$, 400MHz)



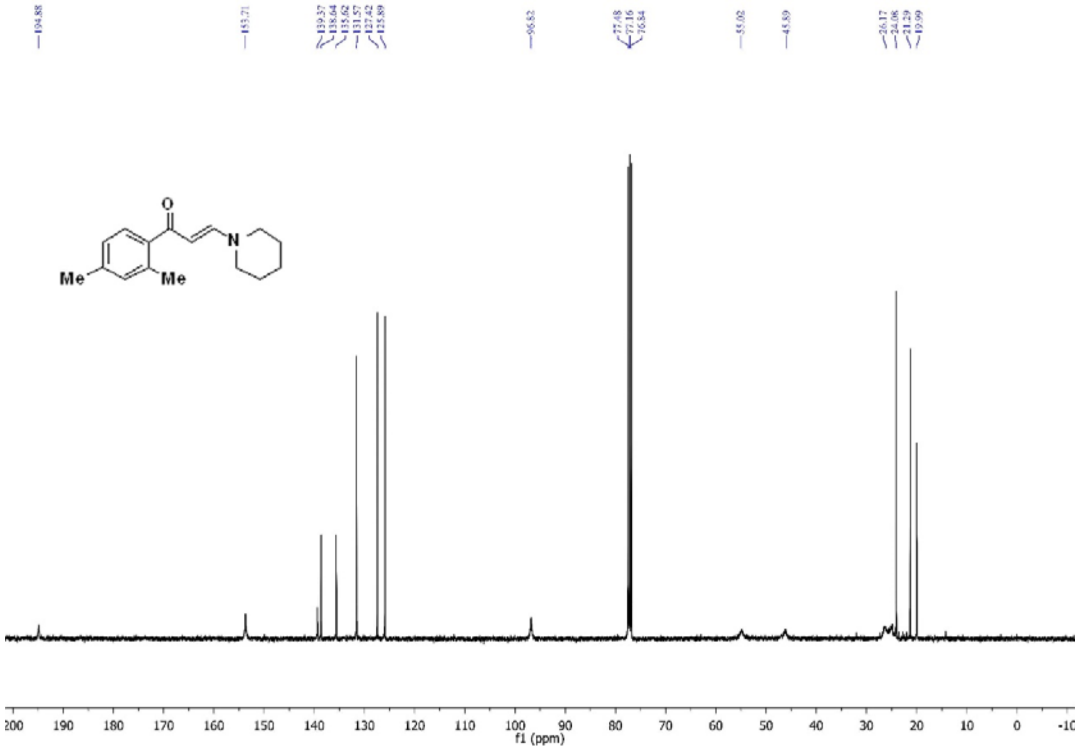
^{13}CNMR of **3ka** ($CDCl_3$, 100MHz)



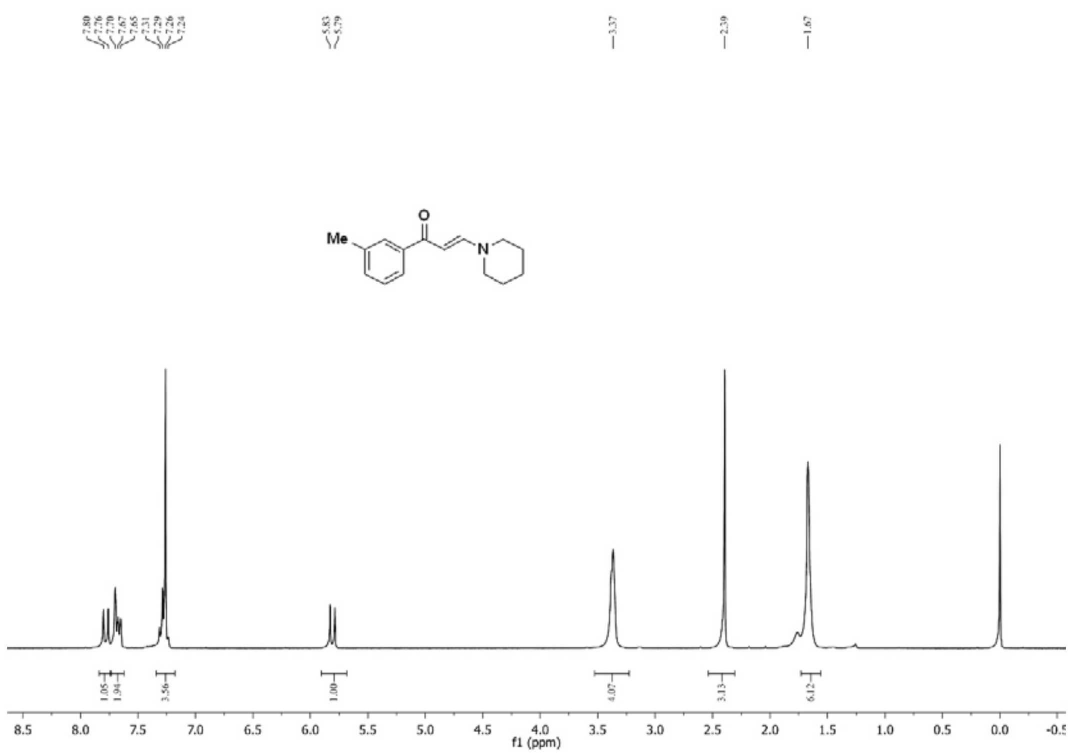
[1]HNMR of **3la** ($CDCl_3$, 400MHz)



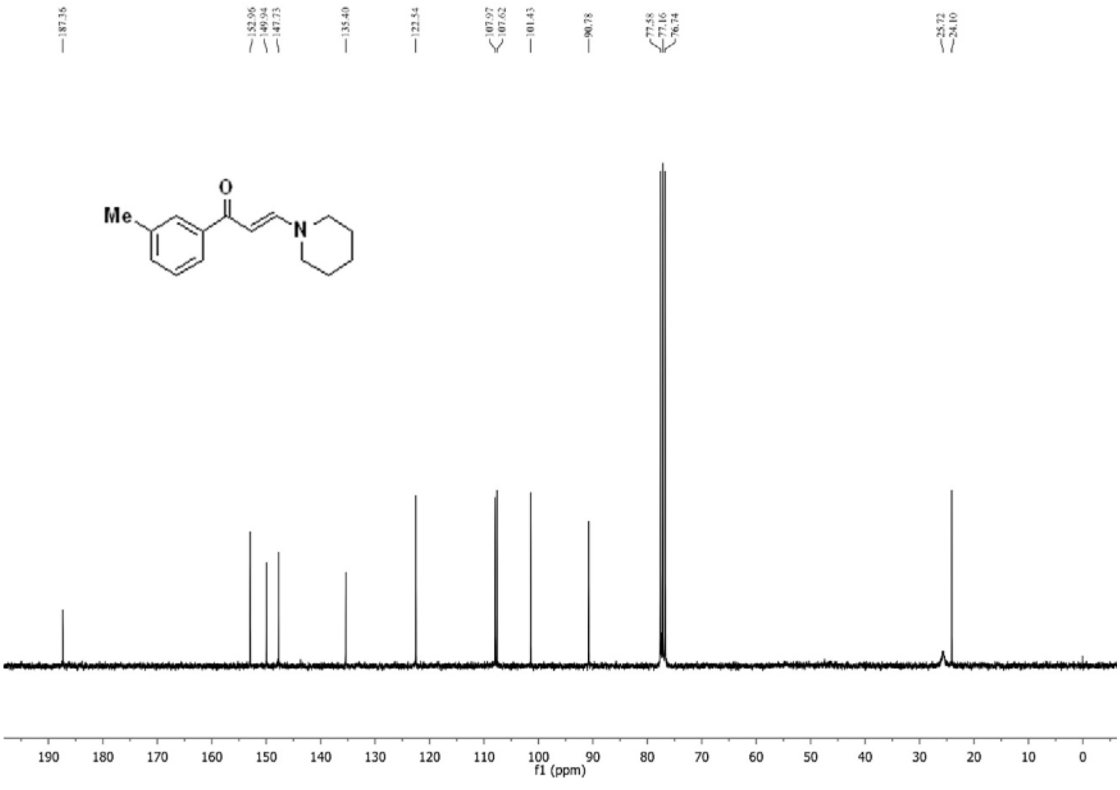
[13]C NMR of **3la** ($CDCl_3$, 100MHz)



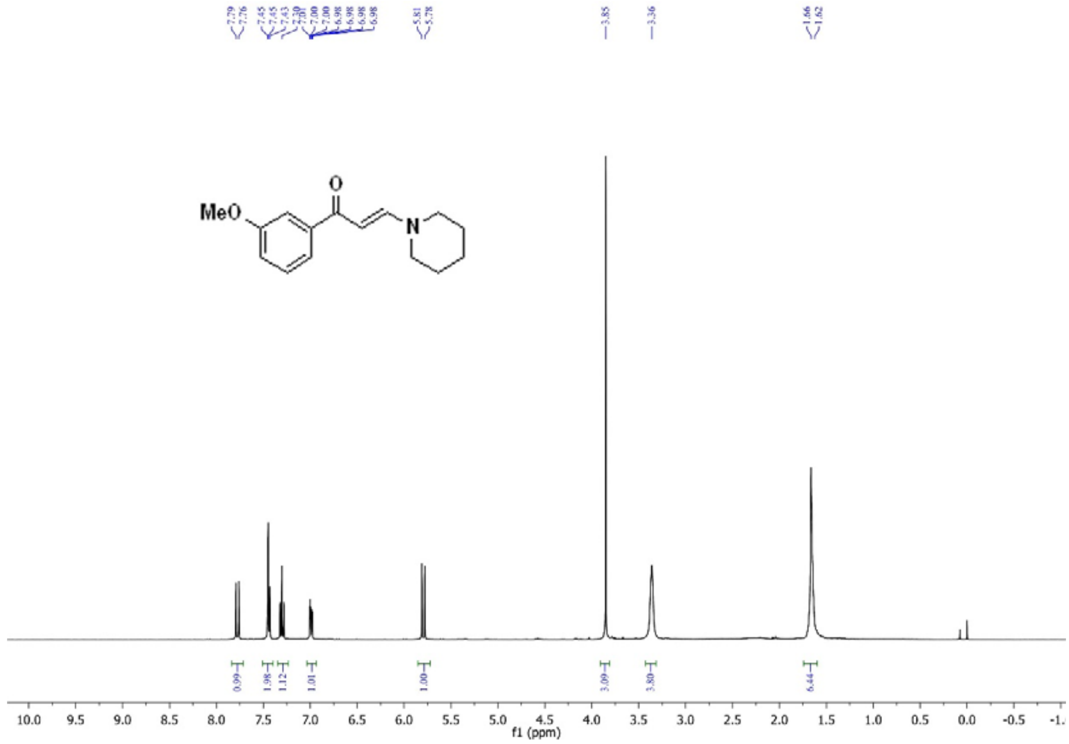
^{1}H NMR of **3ma** ($CDCl_3$, 300MHz)



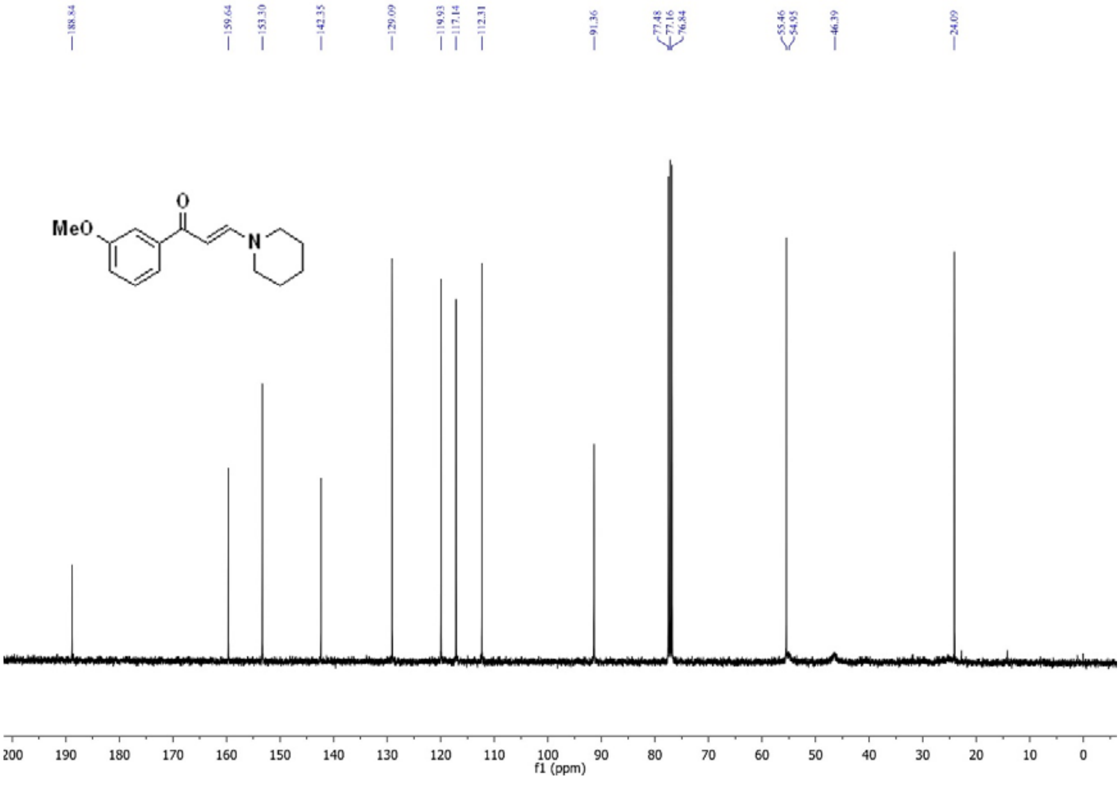
^{13}CNMR of **3ma** ($CDCl_3$, 75MHz)



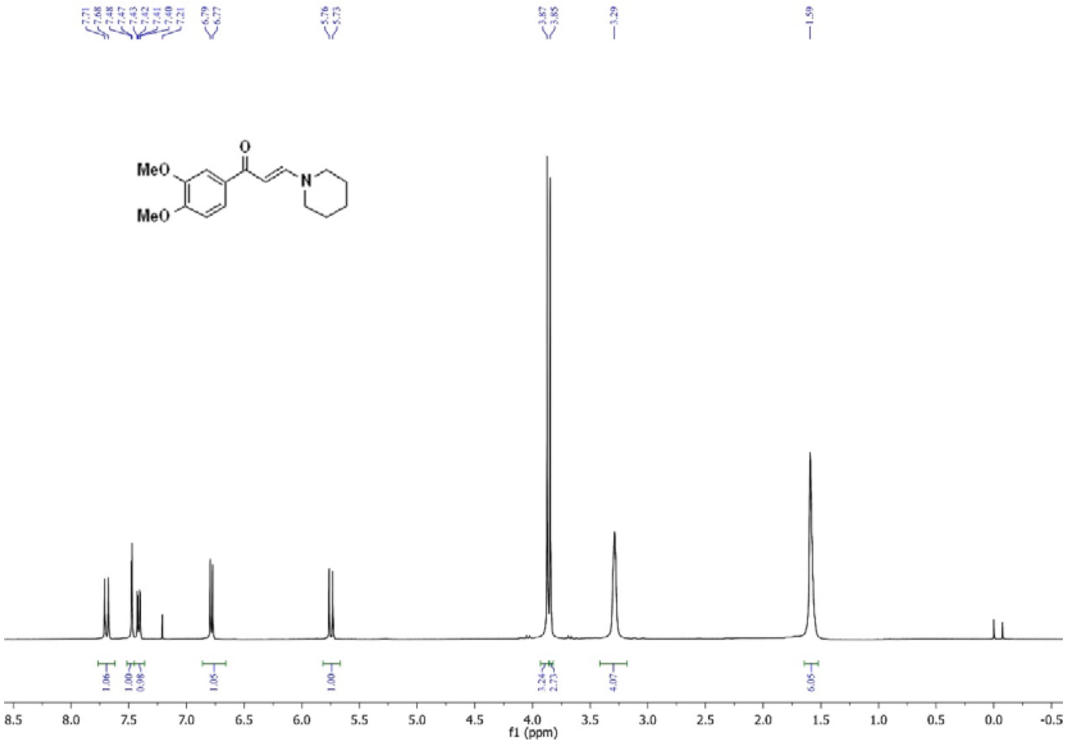
[1]HNMR of **3na** ($CDCl_3$, 400MHz)



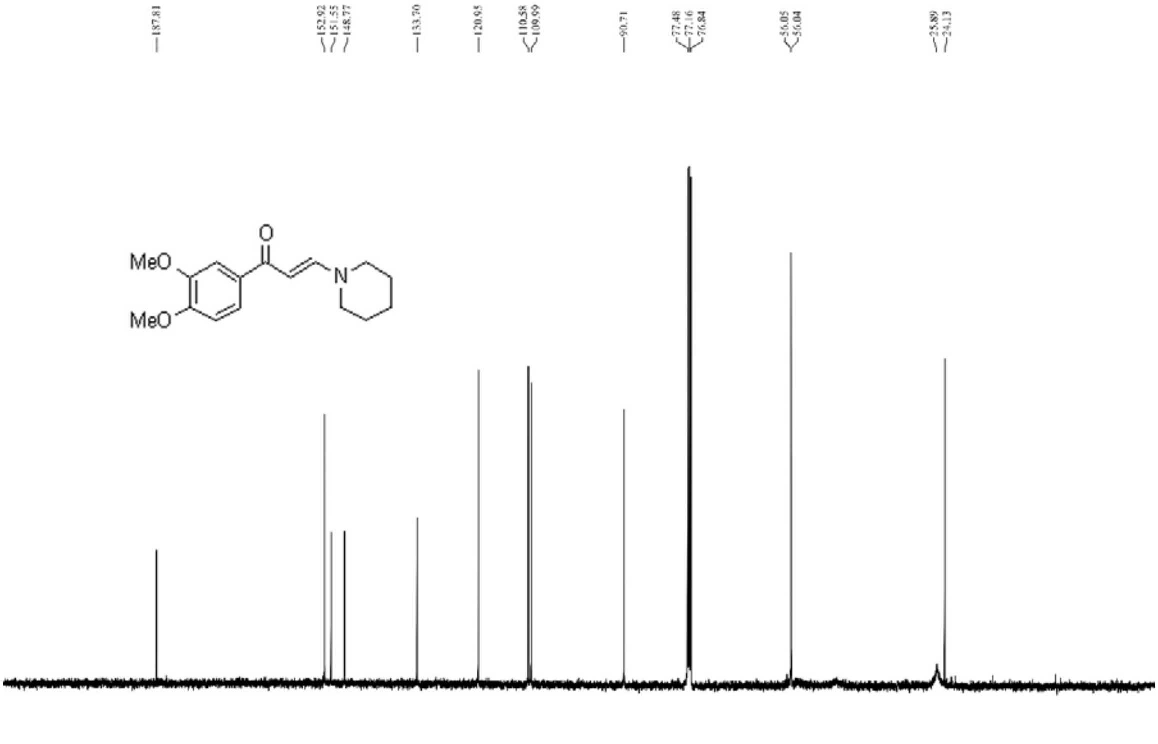
[13]C NMR of **3na** ($CDCl_3$, 100MHz)



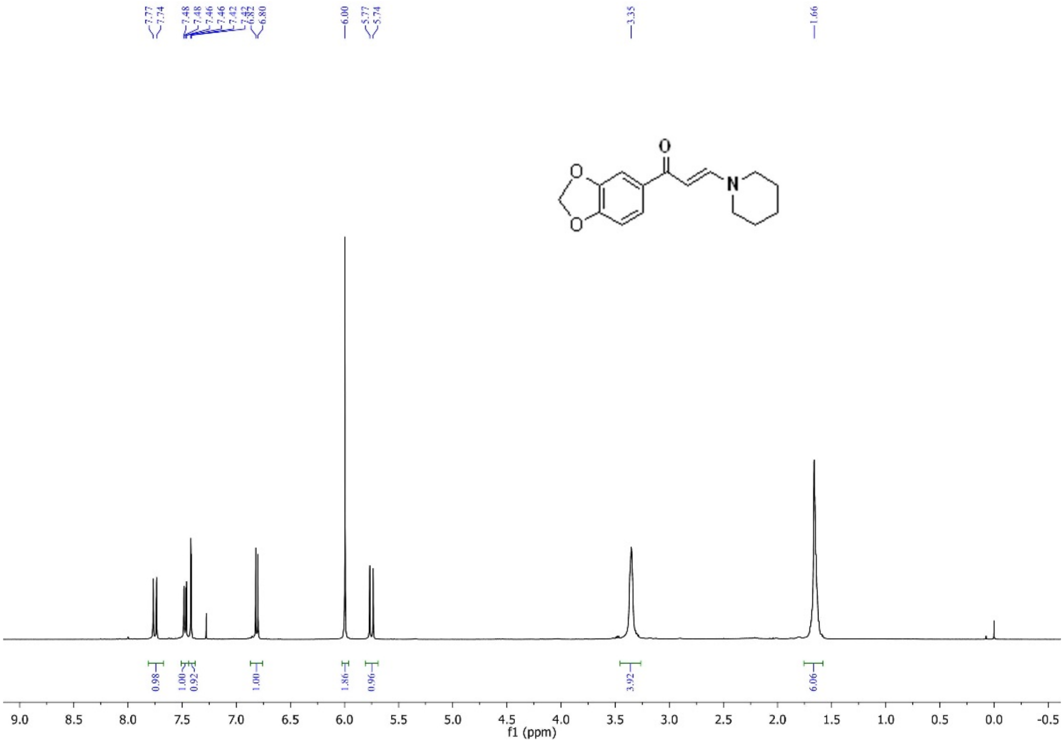
[1]H NMR of **3oa** ($CDCl_3$, 400MHz)



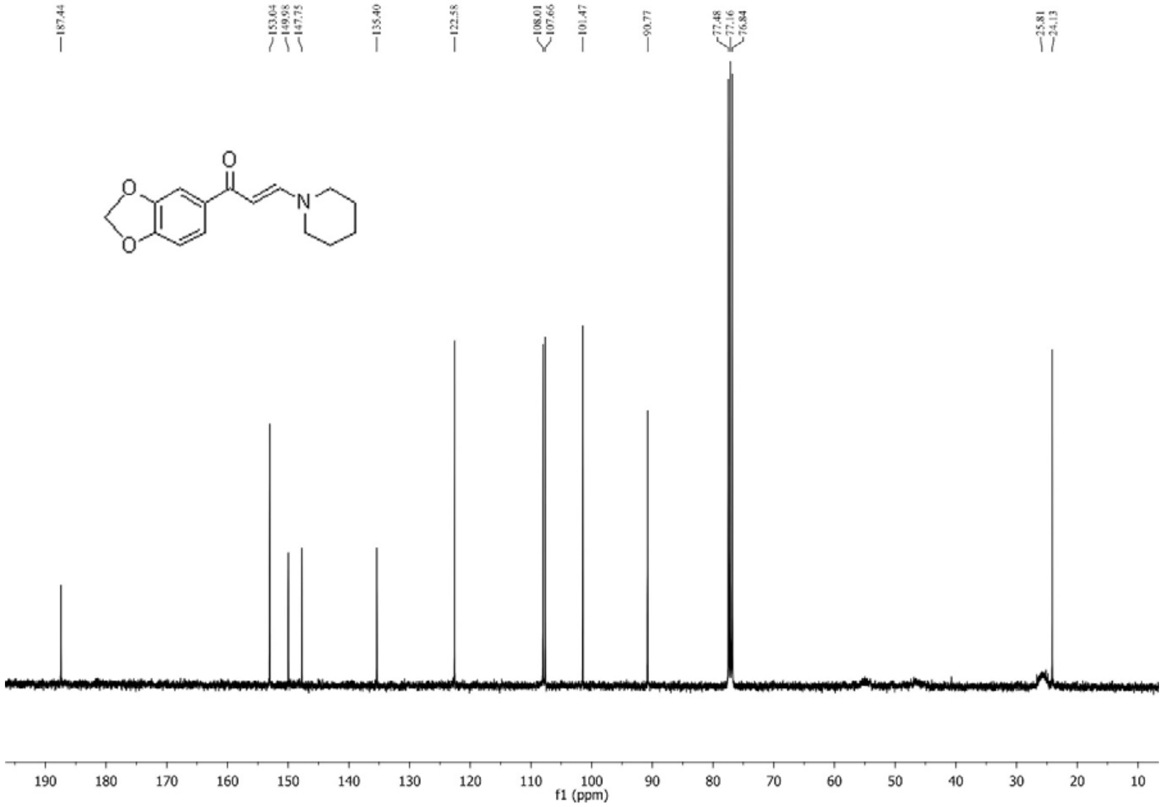
[13]C NMR of **3oa** ($CDCl_3$, 100MHz)



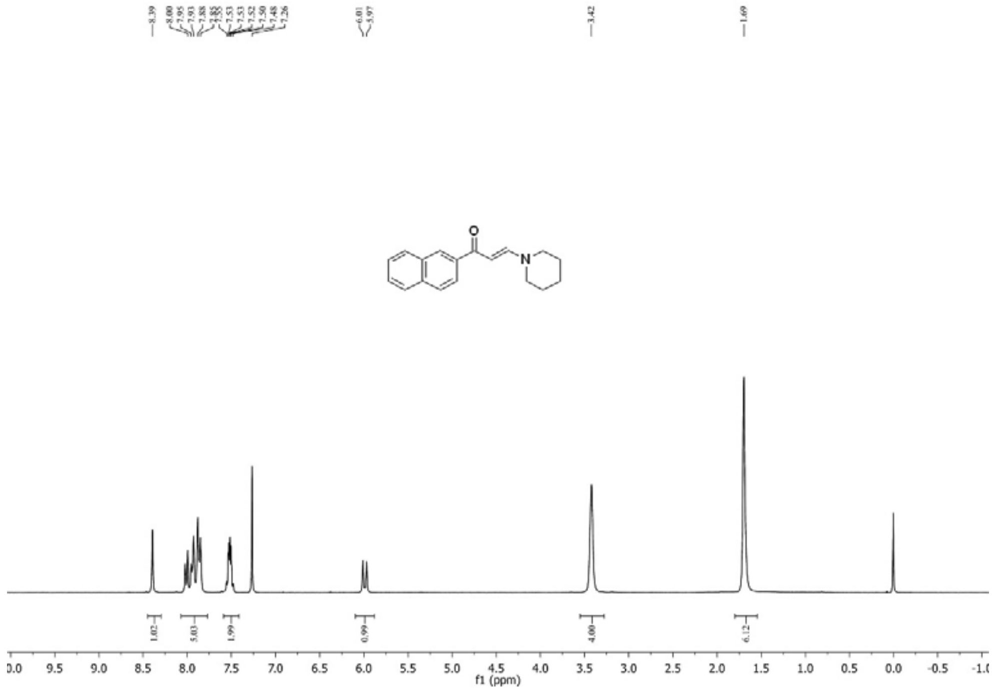
^{1}H NMR of **3pa** ($CDCl_3$, 400MHz)



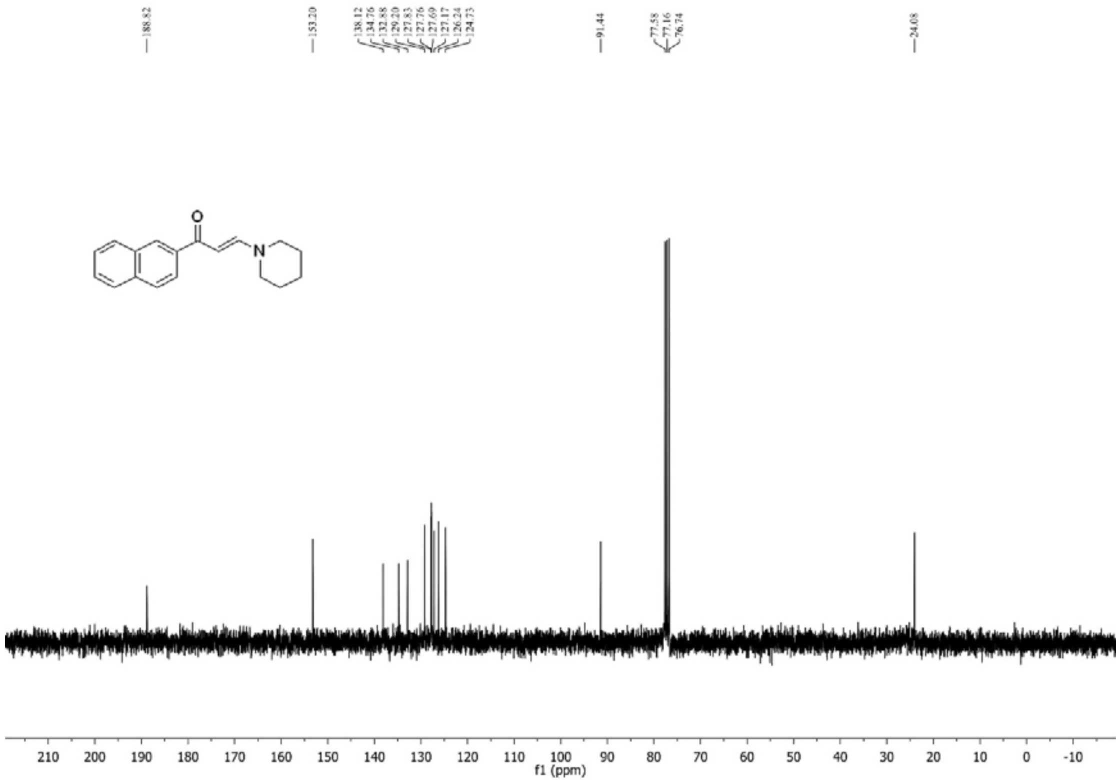
^{13}C NMR of **3pa** ($CDCl_3$, 100MHz)



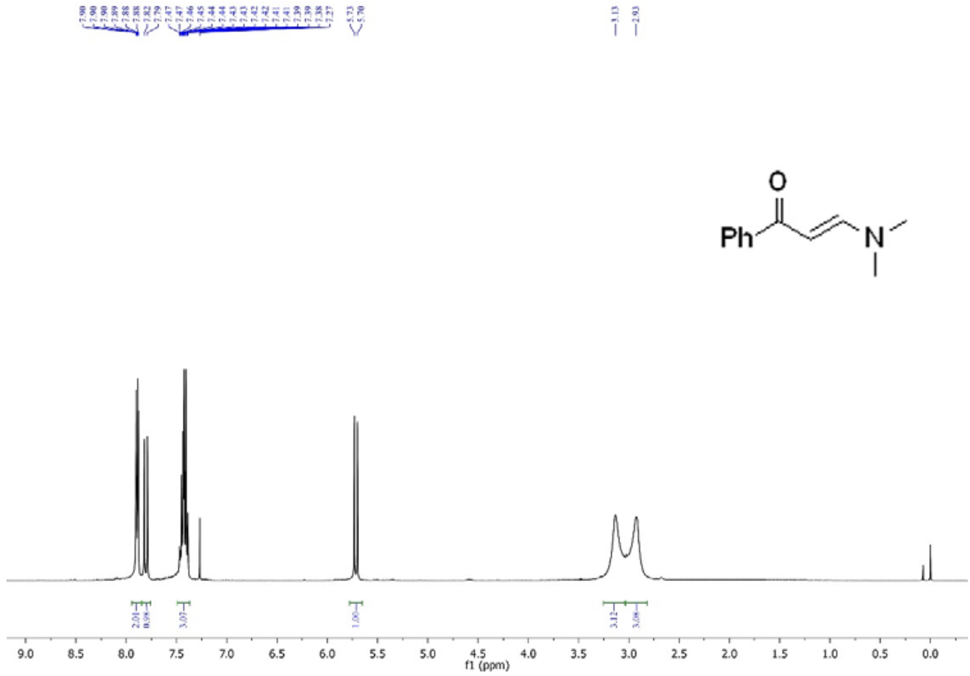
[1]H NMR of **3qa** ($CDCl_3$, 300MHz)



[13]C NMR of **3qa** ($CDCl_3$, 75MHz)

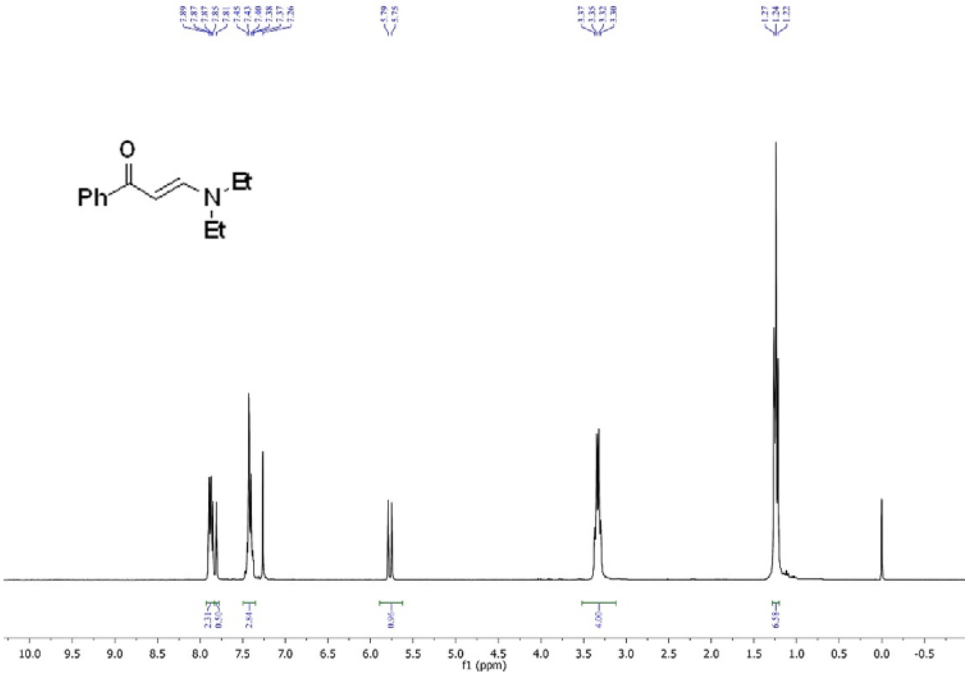


[1]H NMR of **3ab** ($CDCl_3$, 400MHz)

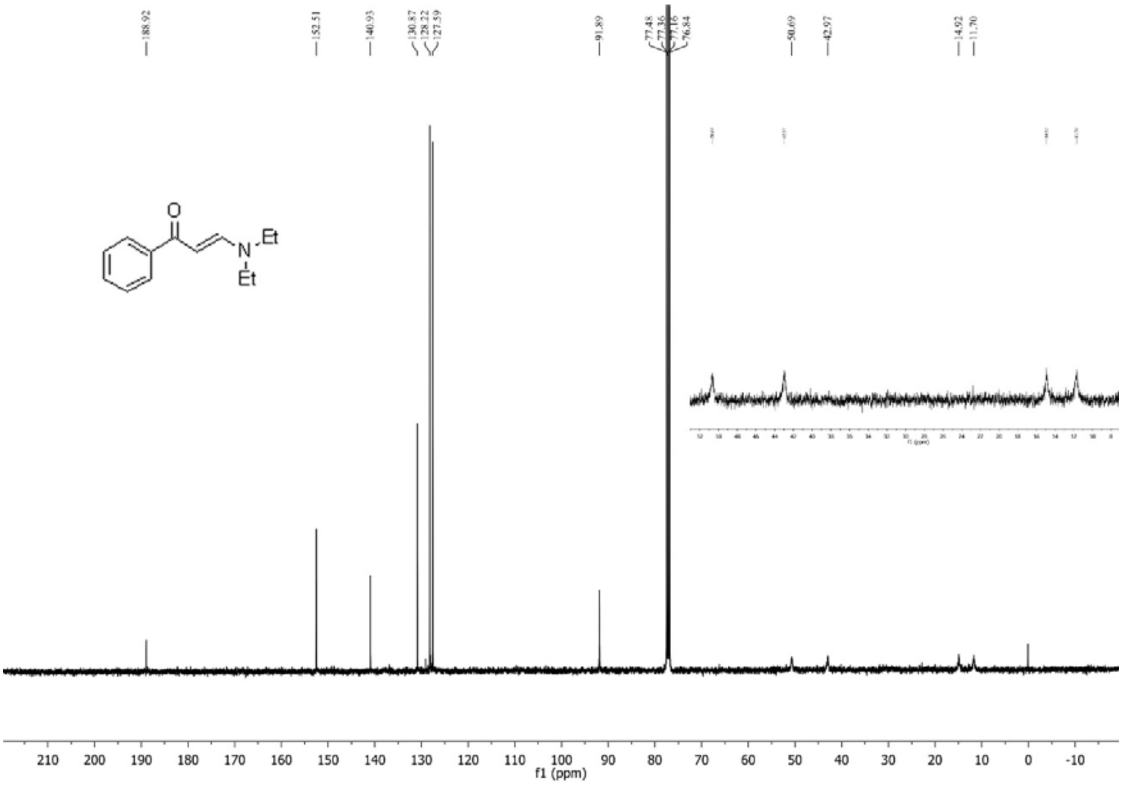


[13]C NMR of **3ab** ($CDCl_3$, 100MHz)

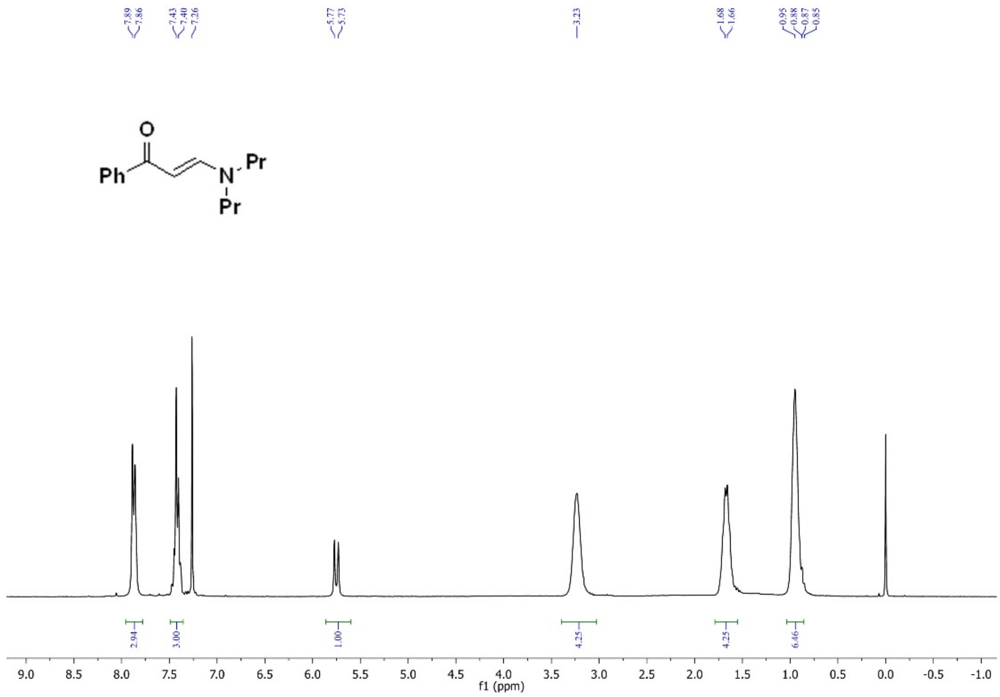
[1]H NMR of **3ac** ($CDCl_3$, 300MHz)



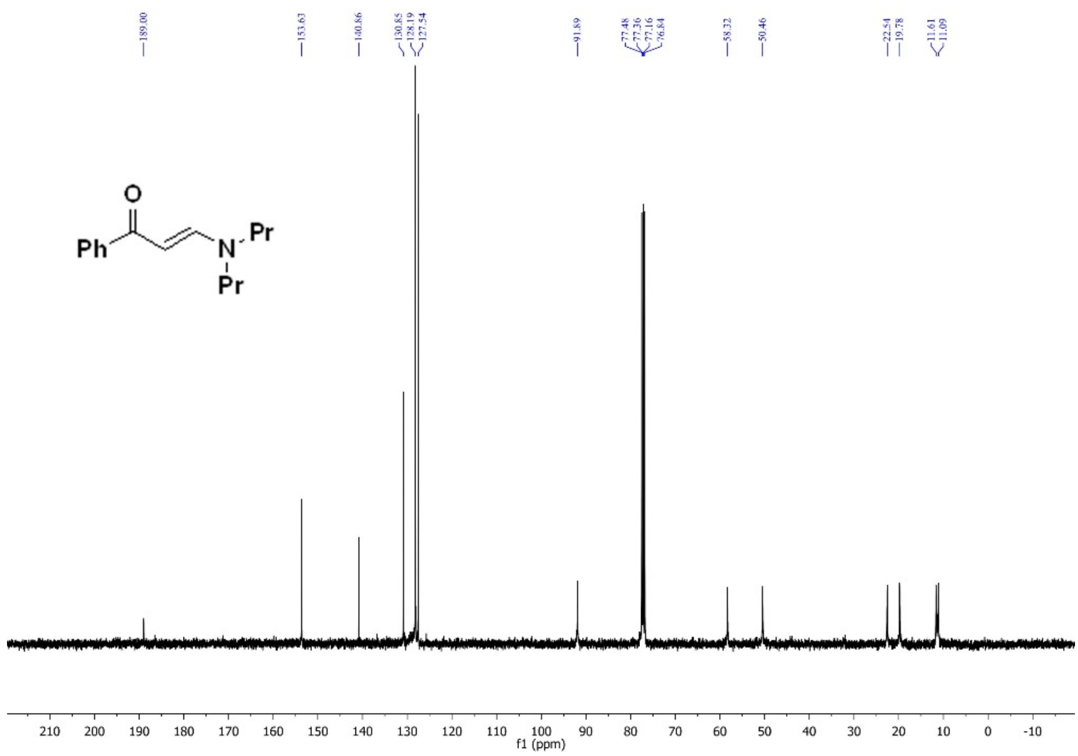
[13]C NMR of **3ac** ($CDCl_3$, 100MHz)



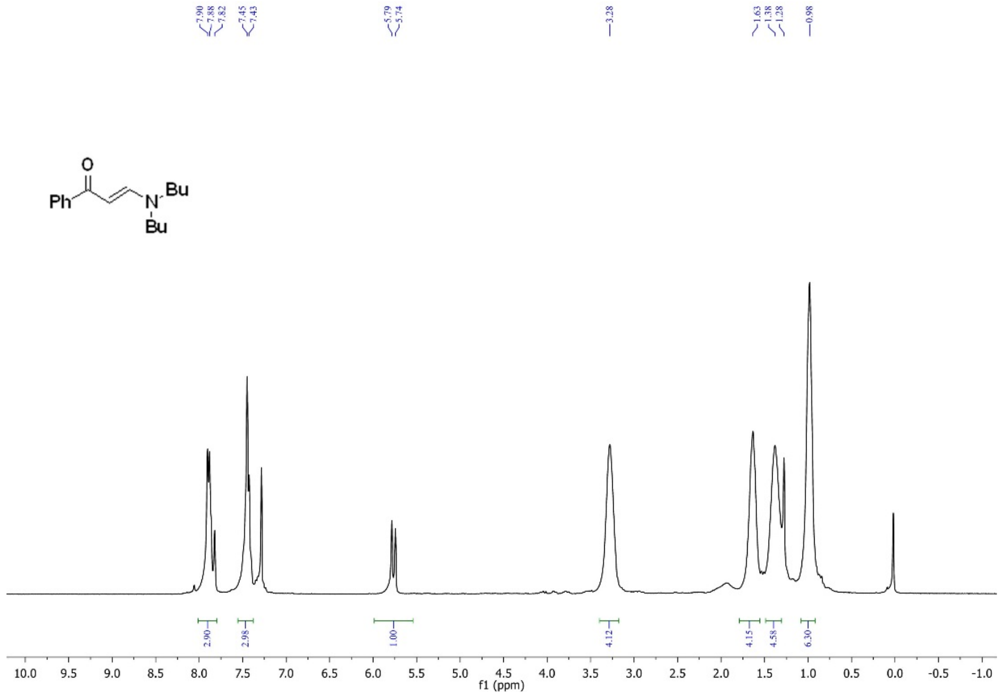
^{1}H NMR of **3ad** ($CDCl_3$, 300MHz)



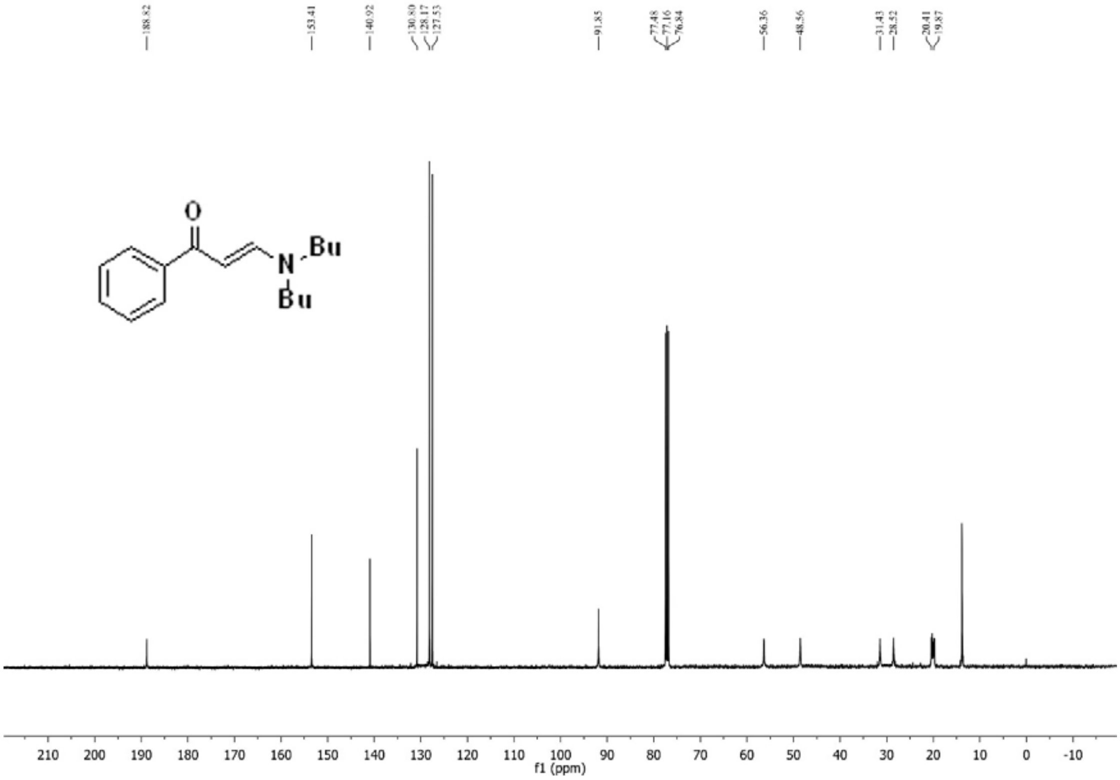
^{13}C NMR of **3ad** ($CDCl_3$, 75MHz)



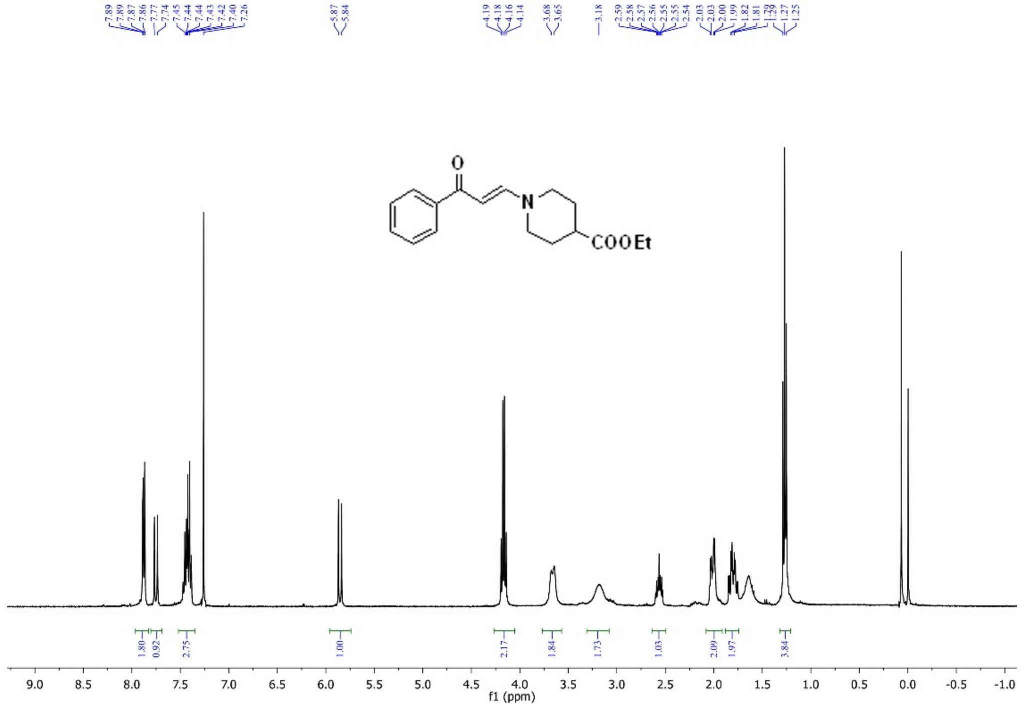
[1]H NMR of **3ae** ($CDCl_3$, 300MHz)



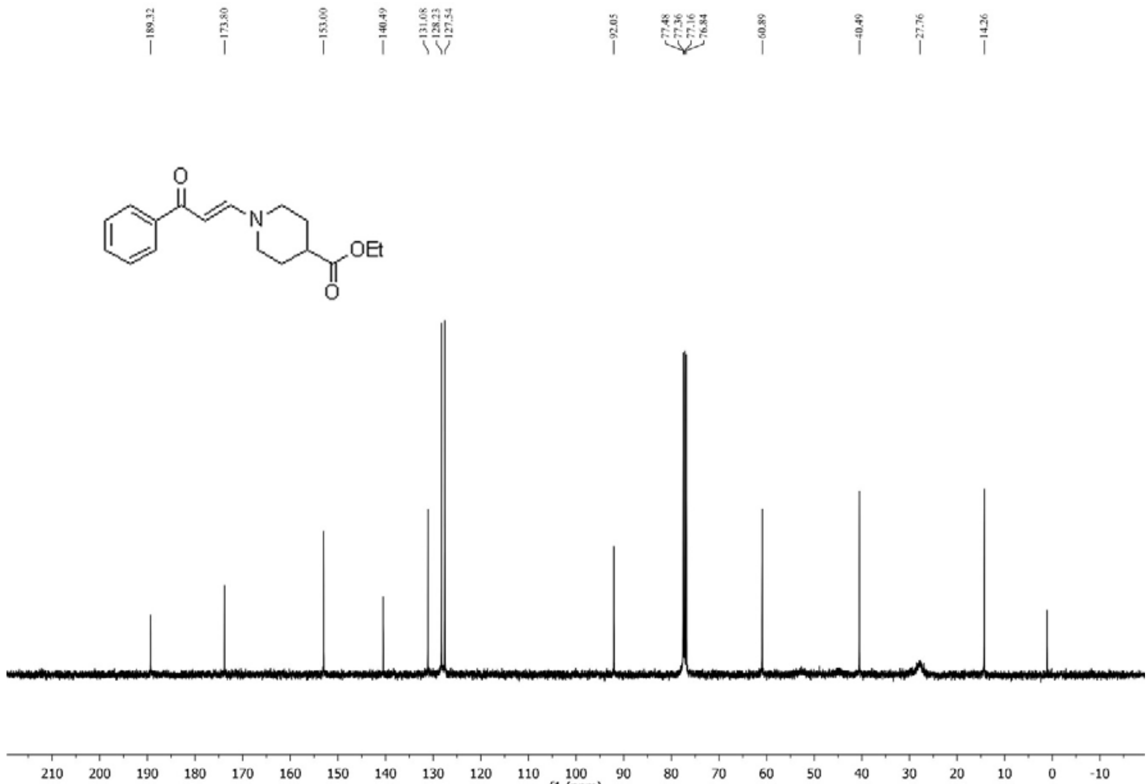
[13]C NMR of **3ae** ($CDCl_3$, 100MHz)



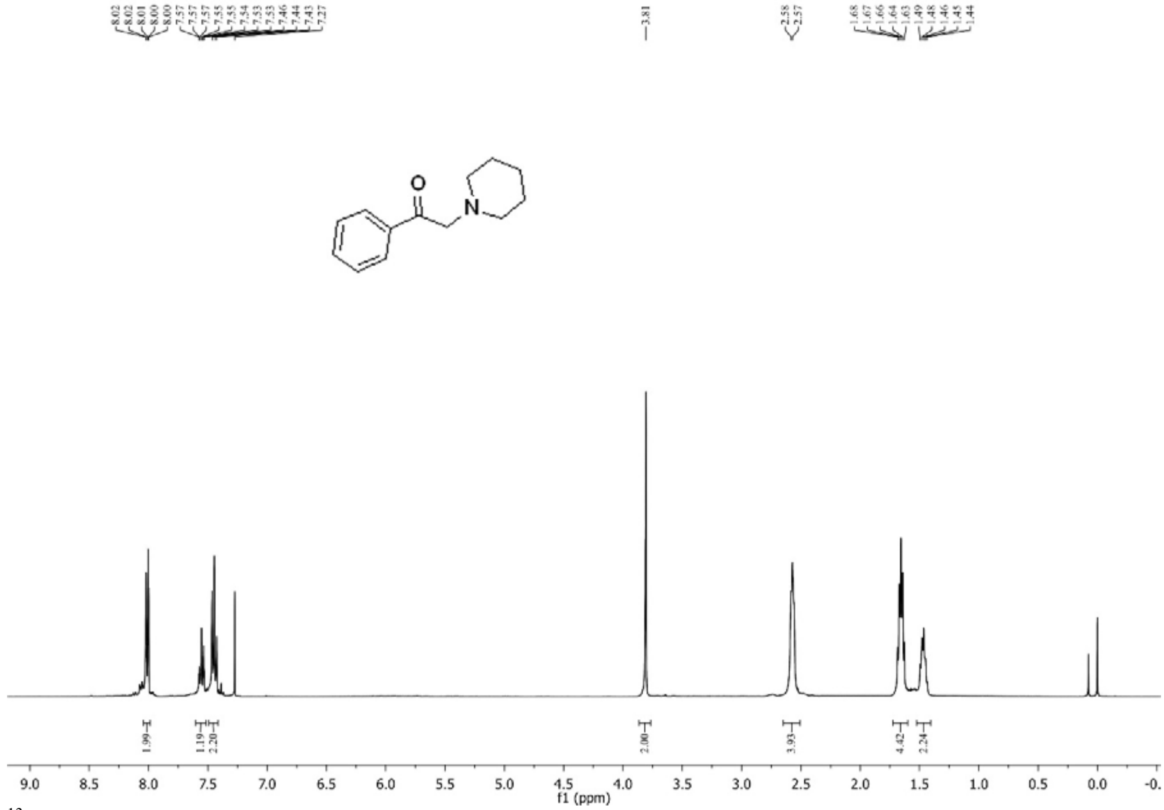
^{1}H NMR of **3af** ($CDCl_3$, 400MHz)



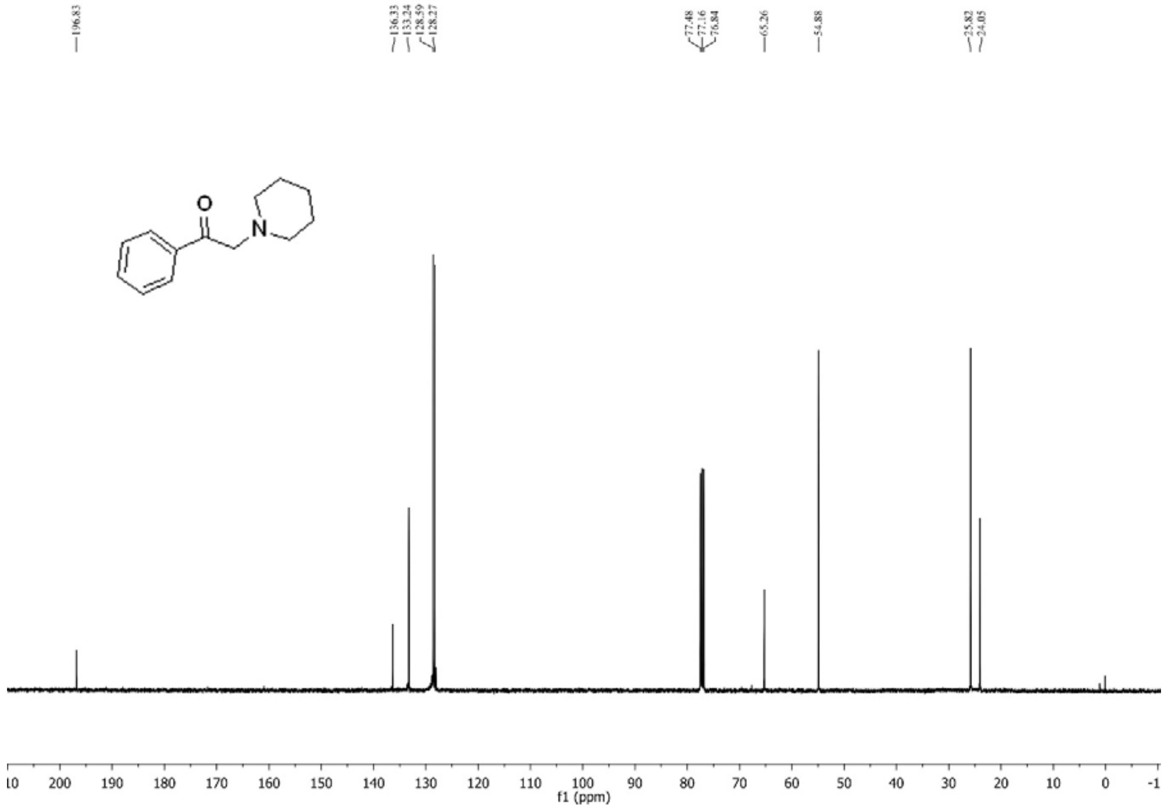
^{13}C NMR of **3af** ($CDCl_3$, 100MHz)



^{1}H NMR of **6** ($CDCl_3$, 400MHz)

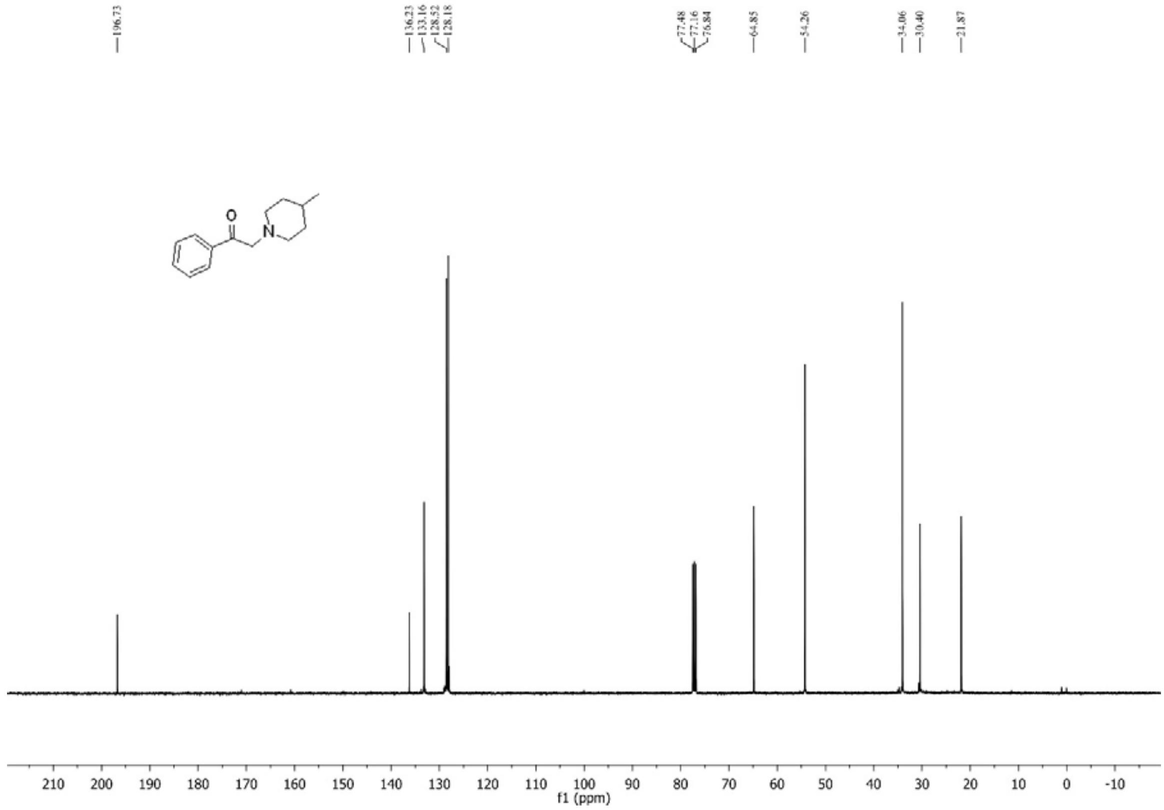


^{13}C NMR of **6** ($CDCl_3$, 100MHz)

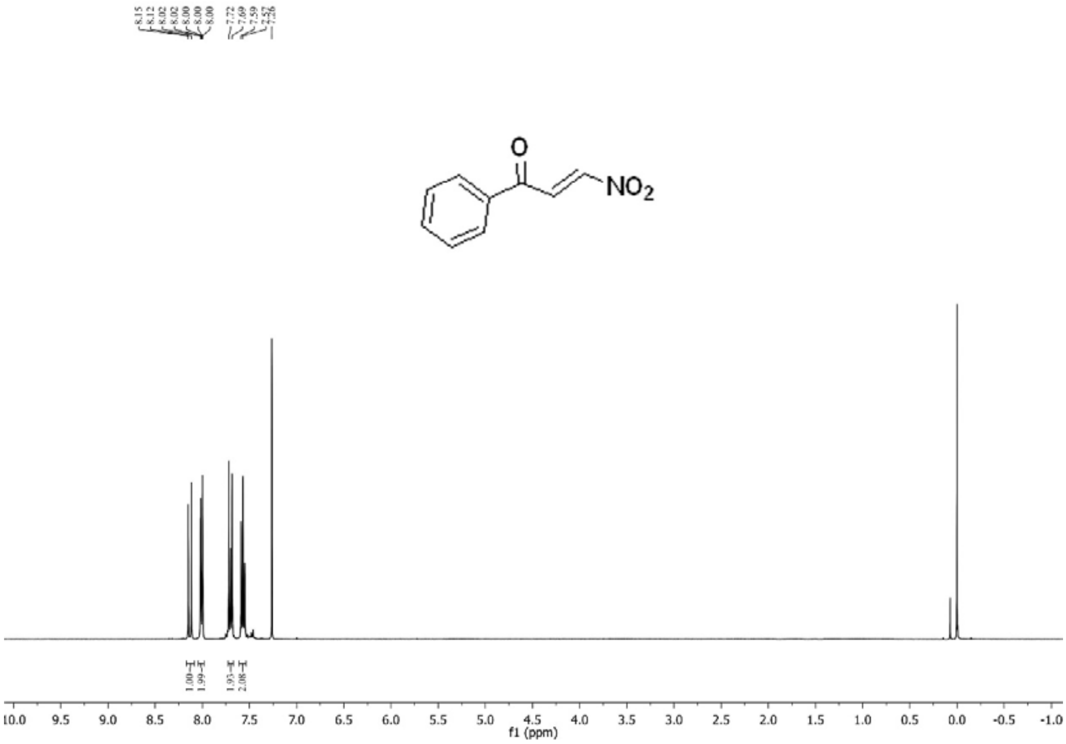


[1]H NMR of **7** ($CDCl_3$, 400MHz)

[13]C NMR of **7** ($CDCl_3$, 100MHz)



[1]HNMR of **11** ($CDCl_3$, 400MHz)



[13]CNMR of **11** ($CDCl_3$, 100MHz)