Supplementary Information

Iridium-CNP complex catalyzed cross-coupling of primary alcohols and secondary alcohols by borrowing hydrogen strategy

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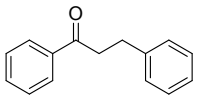
General information

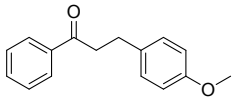
All the obtained products were characterized by melting points (mp), ^{1}H NMR spectra and ^{13}C NMR spectra. Melting points were measured on an BÙCHIB-545 microscopy digital melting point apparatus and are uncorrected; NMR spectra were obtained on Bruker Advance 400 and -300; Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF_{254}), and visualization was effected at 254 nm; All the reagents were purchased from commercial sources (J&KChemic, TCI, Fluka, Acros, SCRC), and used without further purification.

Typical procedure for the synthesis of 5a.

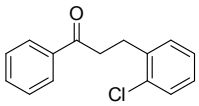
Catalyst **3b** (2 mol%, 0.02 mmol), benzyl alcohol (1.1 mmol), Phenylethanol (1 mmol), Caesium carbonate (1 mmol), and toluene (2 mL) was added to a Schlenk tube. The mixture was heated under 110 ^{o}C for 16 h and then cooled to room temperature. The resulting solution was directly purified by column chromatography with petroleum ether/ethyl acetate (10:1) as eluent to give 1, 3-diphenylpropan-1-one (**5a)** as a white solid (yield: 89%).



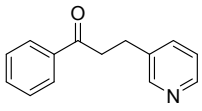
1, 3-diphenylpropan-1-one (**5a).** Yield 89%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.26 -7.20 (m, 2H), 7.20-7.17 (m, 2H), 7.13 (t, *J* = 7.0 Hz, 1H), 3.23 (t, *J* = 5.3 Hz, 2H), 3.00 (t, *J* = 5.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.26, 141.31, 136.89, 133.07, 128.76-128.34 (m), 128.06, 126.15, 40.46, 30.15, 29.71.



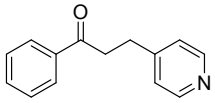
3-(4-methoxyphenyl)-1-phenylpropan-1-one (**5b**). Yield 97%; white solid; IR (neat): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.93 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 6.91-6.84 (m, 2H), 3.81 (s, 3H), 3.33-3.26 (m, 2H), 3.10-2.99 (m, 2H).



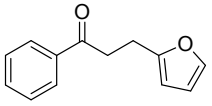
3-(2-chlorophenyl)-1-phenylpropan-1-one (**5c**). Yield 81%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-7.97 (m, 2H), 7.62-7.56 (m, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.39 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.34 (dd, *J* = 7.2, 1.9 Hz, 1H), 7.21 (pd, *J* = 7.3, 1.7 Hz, 2H), 3.38-3.31 (m, 2H), 3.25-3.17 (m, 2H).



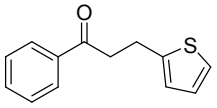
1-phenyl-3-(pyridin-3-yl)propan-1-one (**5d**). Yield 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.46 (d, *J* = 3.8 Hz, 1H), 8.01-7.92 (m, 2H), 7.63-7.54 (m, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.23 (dd, *J* = 7.7, 4.9 Hz, 1H), 3.33 (dd, *J* =7.4 Hz, 2H), 3.09 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.47, 149.97, 147.69, 136.67, 136.06, 133.27, 128.69, 128.01, 123.39, 39.77, 27.14.



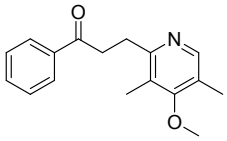
1-phenyl-3-(pyridin-4-yl)propan-1-one (**5e**). Yield 82%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 2H), 7.87 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.52-7.47 (m, 1H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.10 (t, *J* = 7.0 Hz, 2H), 3.30-3.20 (m, 2H), 3.00 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.23, 150.35, 149.79, 136.58, 133.35, 128.72, 128.00, 123.96, 38.85, 29.18.



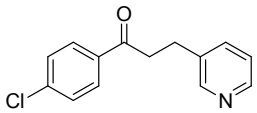
3-(furan-2-yl)-1-phenylpropan-1-one (**5f**). Yield: 78%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.98 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 3.3 Hz, 1H), 6.33-6.28 (m, 1H), 6.08 (d, *J* = 3.1 Hz, 1H), 3.36 (dd, *J* = 9.2, 5.8 Hz, 2H), 3.16 -3.10 (m, 2H).



1-phenyl-3-(thiophen-2-yl)propan-1-one (**5g**).Yield:74%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.3 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.15 (d, *J* = 4.2 Hz, 1H), 6.95 (dd, *J* = 5.0, 3.5 Hz, 1H), 5.91 (q, *J* = 6.6 Hz, 1H), 3.43-3.37 (m, 2H), 3.36-3.30 (m, 2H).

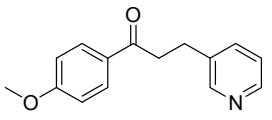


3-(4-methoxy-3,5-dimethylpyridin-2-yl)-1-phenylpropan-1-one (**5h**). Yield: 69%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.03 (d, *J* = 7.2 Hz, 2H), 7.58-7.52 (m, 1H), 7.45 (d, *J* = 7.6 Hz, 2H), 3.74 (s, 3H), 3.50 (t, *J* = 7.3 Hz, 2H), 3.17 (t, *J* = 7.3 Hz, 2H), 2.28 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.95, 163.69, 158.55, 148.69, 137.11, 132.91, 128.52, 128.16, 124.28, 123.96, 59.88, 36.69, 28.89, 13.20, 11.16.

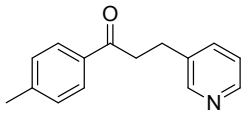


1-(4-chlorophenyl)-3-(pyridin-3-yl)propan-1-one (**5i**). Yield: 73%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 1.8 Hz, 1H), 8.40-8.35 (m, 1H), 7.85-7.77 (m, 2H), 7.51-7.48 (m, 1H), 7.38-7.33 (m, 2H), 7.16-7.11 (m, 1H), 3.20 (t, *J* = 7.4 Hz, 2H), 3.00 (t, *J* = 7.4 Hz,

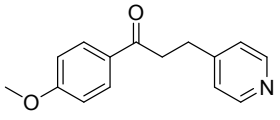
2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.20, 149.89, 147.71, 139.75, 136.44, 136.09, 134.93, 129.64-128.80 (m), 123.43, 39.73, 27.03.



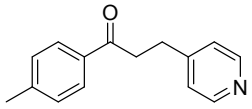
1-(4-methoxyphenyl)-3-(pyridin-3-yl)propan-1-one (**5j**). Yield: 81%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 1.7 Hz, 1H), 8.38 (dd, *J* = 4.7, 1.2 Hz, 1H), 7.91-7.83 (m, 2H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.14 (dd, *J* = 7.7, 4.8 Hz, 1H), 6.88-6.83 (m, 2H), 3.19 (t, *J* = 7.5 Hz, 2H), 3.00 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.02, 163.61, 149.96, 147.62, 136.80, 136.06, 130.28, 129.77, 123.36, 113.81, 55.49, 39.41, 27.31.



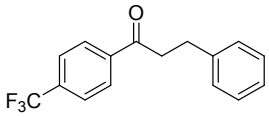
3-(pyridin-3-yl)-1-(p-tolyl)propan-1-one (**5k**). Yield: 79%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 1.8 Hz, 1H), 8.45 (dd, *J* = 4.8, 1.4 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.62-7.56 (m, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.21 (dd, *J* = 7.7, 4.8 Hz, 1H), 3.29 (t, *J* = 7.5, 2H), 3.07 (t, *J* = 7.5 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.17, 149.97, 147.65, 144.13, 136.74, 136.10, 134.15, 129.37, 128.14, 123.40, 39.68, 27.19, 21.68.



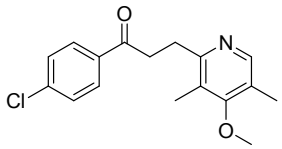
1-(4-methoxyphenyl)-3-(pyridin-4-yl)propan-1-one (**5l**). Yield: 82%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 5.9 Hz, 2H), 7.87 (d, *J* = 8.9 Hz, 2H), 7.12 (d, *J* = 5.8 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 3.80 (s, 3H), 3.21 (t, *J* = 7.5 Hz, 2H), 3.00 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.80, 163.65, 150.47, 149.86, 130.30, 129.67, 123.91, 113.83, 55.52, 38.52, 29.35.



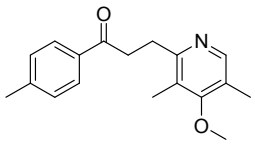
3-(pyridin-4-yl)-1-(p-tolyl)propan-1-one (**5m**). Yield: 78%; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.38 (d, *J* = 4.6 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 5.8 Hz, 2H), 3.21 (t *J* = 7.4 Hz, 2H), 2.95 (t, *J* = 7.4 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 197.73, 149.64, 144.16, 134.24, 129.29, 127.97, 38.64, 29.69, 21.34.



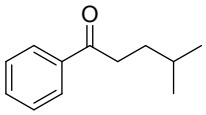
3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one (**5n**) Yield: 58%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.2 Hz, 2H), 7.74 (t, *J* = 7.0 Hz, 2H), 7.37-7.31 (m, 2H), 7.30-7.28 (m, 2H), 7.27 (s, 1H), 3.39-3.33 (m, 2H), 3.12 (t, *J* = 7.6 Hz, 2H).



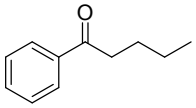
1-(4-chlorophenyl)-3-(4-methoxy-3,5-dimethylpyridin-2-yl)propan-1-one (**5o**). Yield: 63%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.89 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 3.67 (s, 3H), 3.39 (t, *J* = 7.2 Hz, 2H), 3.09 (t, *J* = 7.2 Hz, 2H), 2.20 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.80, 163.65, 150.47, 149.86, 130.30, 129.67, 123.91, 113.83, 55.52, 38.52, 29.35.



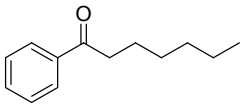
3-(4-methoxy-3,5-dimethylpyridin-2-yl)-1-(p-tolyl)propan-1-one (**5p**). Yield: 73%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.21-7.14 (m, 2H), 3.67 (s, 3H), 3.39 (t, *J* = 7.4 Hz, 2H), 3.09 (t, *J* = 7.3 Hz, 2H), 2.33 (s, 3H), 2.20 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.56, 163.66, 158.72, 148.72, 143.64, 134.60, 129.20, 128.28, 124.27, 123.92, 59.87, 36.63, 28.98, 21.66, 13.21, 11.16.



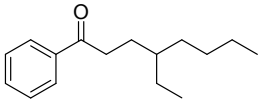
4-methyl-1-phenylpentan-1-one (**5q**). Yield: 46%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.96 (m, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.52-7.46 (m, 2H), 3.05-2.95 (m, 2H), 1.70 -1.62 (m, 3H), 1.00-0.93 (m, 6H)



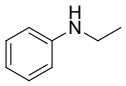
1-phenylpentan-1-one (**5r**). Yield: 31%;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.97 (m, 2H), 7.61- 7.54 (m, 1H), 7.53-7.44 (m, 2H), 3.00 (t, *J* = 7.4 Hz, 2H), 1.82-1.68 (m, 2H), 0.97-0.84 (m, 5H);



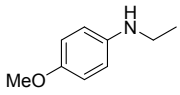
1-phenylheptan-1-one (**5s**). Yield: 62%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.96 (m, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 2.99 (t, *J* = 7.4 Hz, 2H), 1.80 -1.70 (m, 2H), 1.40-1.27 (m, 4H), 0.97-0.86 (m, 5H);



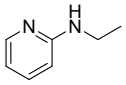
4-ethyl-1-phenyloctan-1-one (**5t**). Yield: 59%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.97 (m, 2H), 7.61-7.55 (m, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 3.01-2.93 (m, 2H), 1.72 (td, *J* = 8.8, 5.7 Hz, 2H), 1.35-1.26 (m, 6H), 0.95-0.86 (m, 7H).



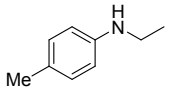
N-ethylaniline (**7a**) (Yield: 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.8 Hz, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 2H), 3.55 (s, 1H), 3.19 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 129.2, 117.2, 112.7, 38.4, 14.9.



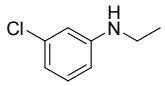
N-ethyl-4-methoxyaniline (**7b**) (Yield: 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.69 (d, *J* = 8.8 Hz, 2H), 6.48 (d, *J* = 8.8 Hz, 2H), 3.64 (s, 3H), 3.18-2.94 (m, 3H), 1.13 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 142.8, 114.9, 114.1, 55.8, 39.4, 15.0.



N-ethylpyridin-2-amine (**7c**) (Yield: 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.47-7.32 (m, 1H), 6.63-6.45 (m, 1H), 6.42-6.26 (m, 1H), 3.84-2.57 (m, 3H), 1.26-1.19 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 148.0, 137.4, 112.5, 106.3, 36.8, 14.7.



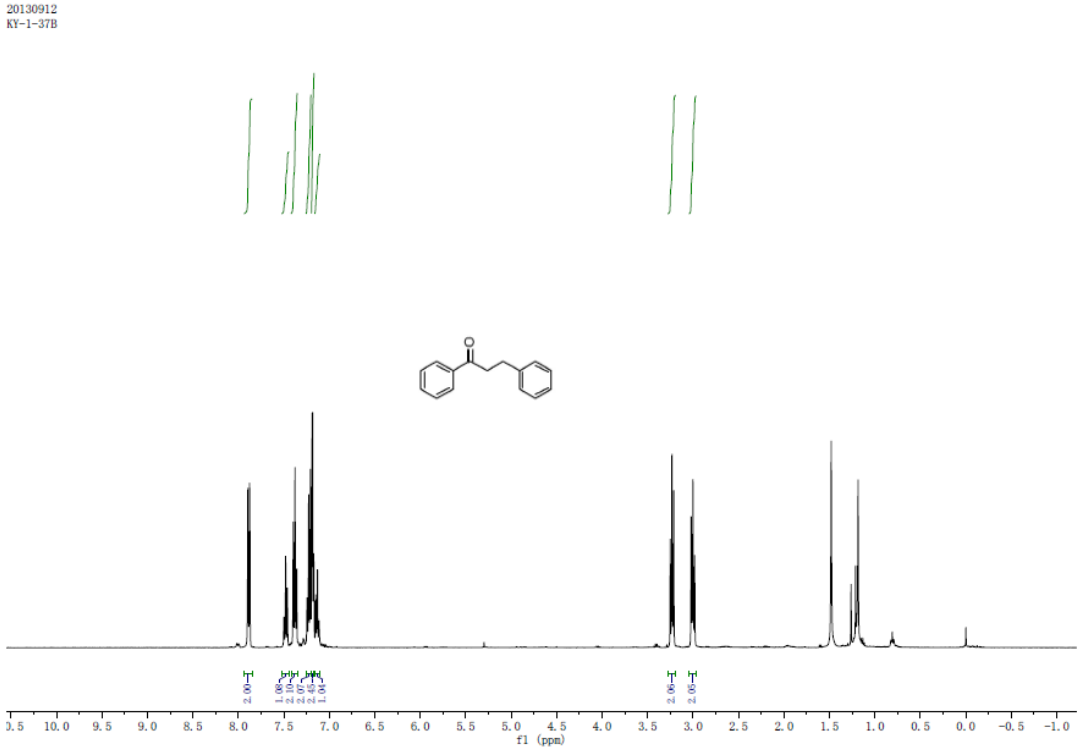
N-ethyl-4-methylaniline (**7d**) (Yield: 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.1 Hz, 2H), 6.57 (d, *J* = 8.3 Hz, 2H), 3.16 (q, *J* = 7.1 Hz, 2H), 2.27 (s, 3H), 1.41-1.15 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 129.7, 126.4, 113.0, 38.8, 20.3, 14.9.



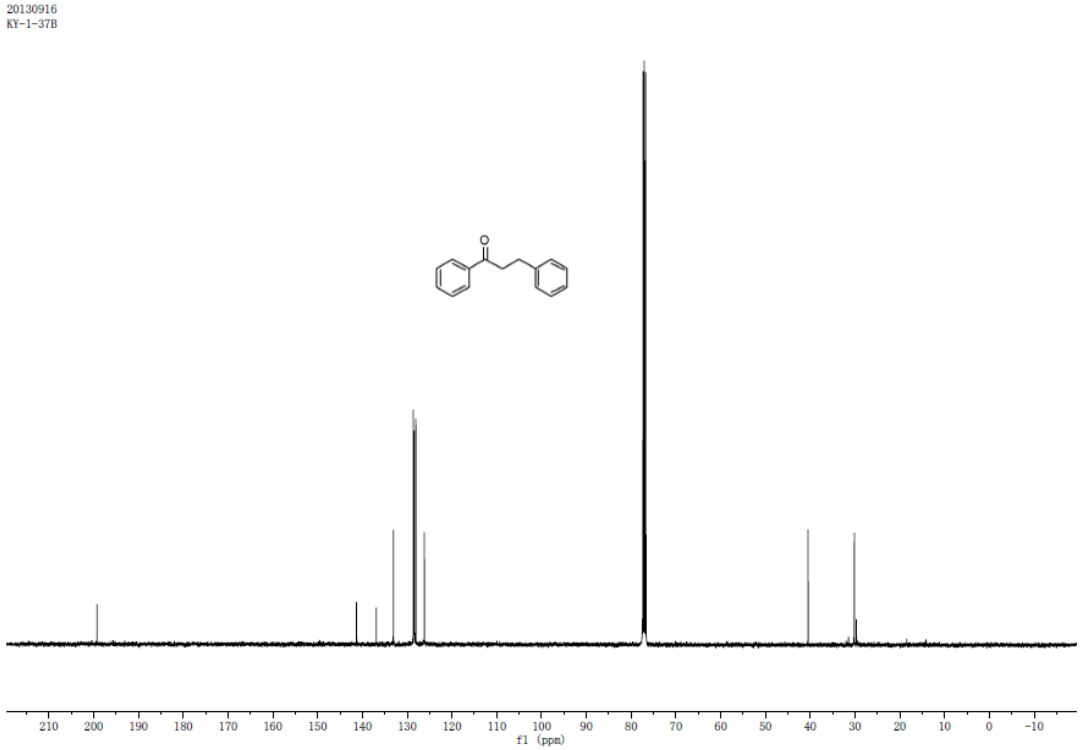
3-chloro-N-ethylaniline (**7e**) (Yield: 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (t, *J* = 8.0 Hz, 1H), 6.67 (dd, *J* = 7.9, 0.9 Hz, 1H), 6.59 (s, 1H), 6.48 (dd, *J* = 8.2, 2.0 Hz, 1H), 3.65 (s, 1H), 3.16 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 135.0, 130.1, 116.9, 112.2, 111.0, 38.3, 14.7.

Selected NMR spectra of the obtained compounds

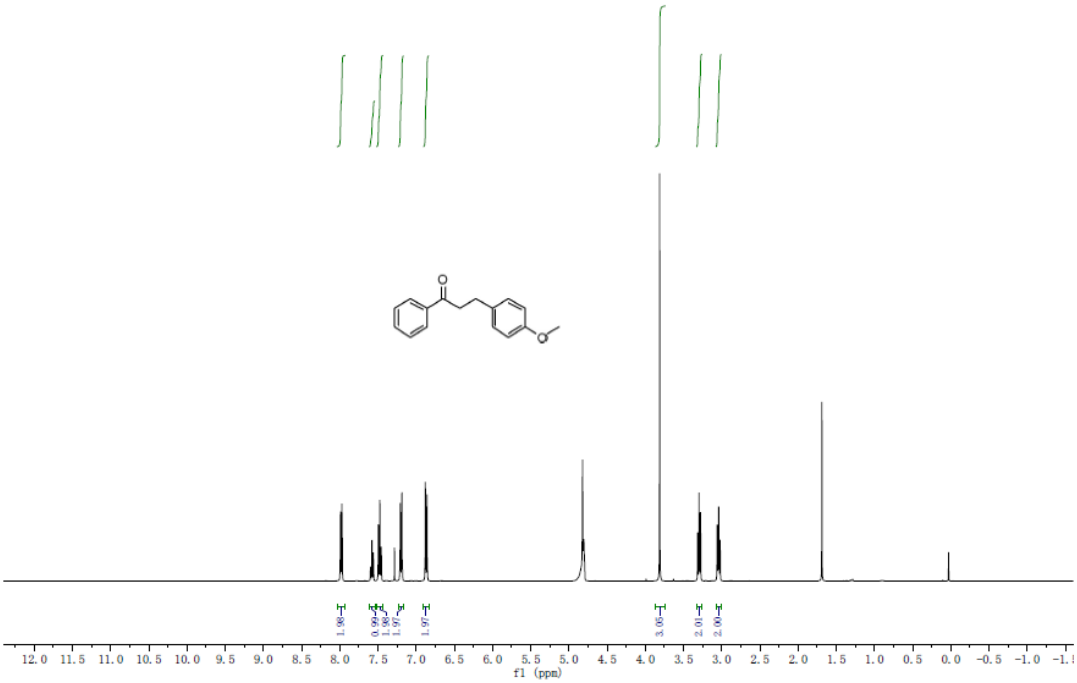
^{1}H NMR of **5a**



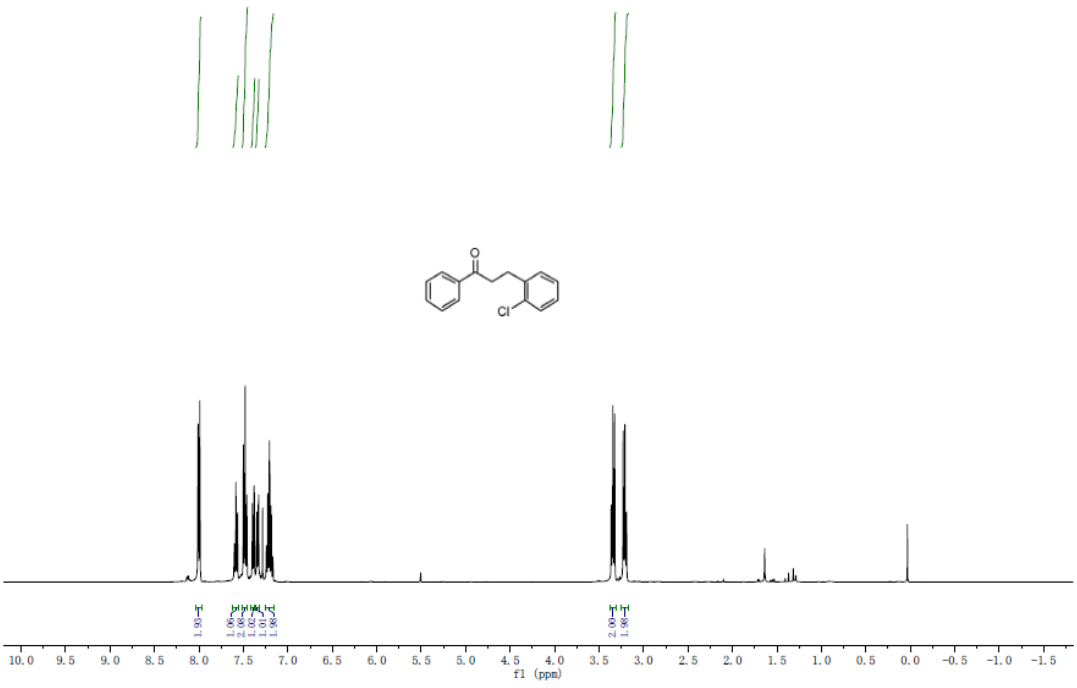
^{13}C NMR of **5a**



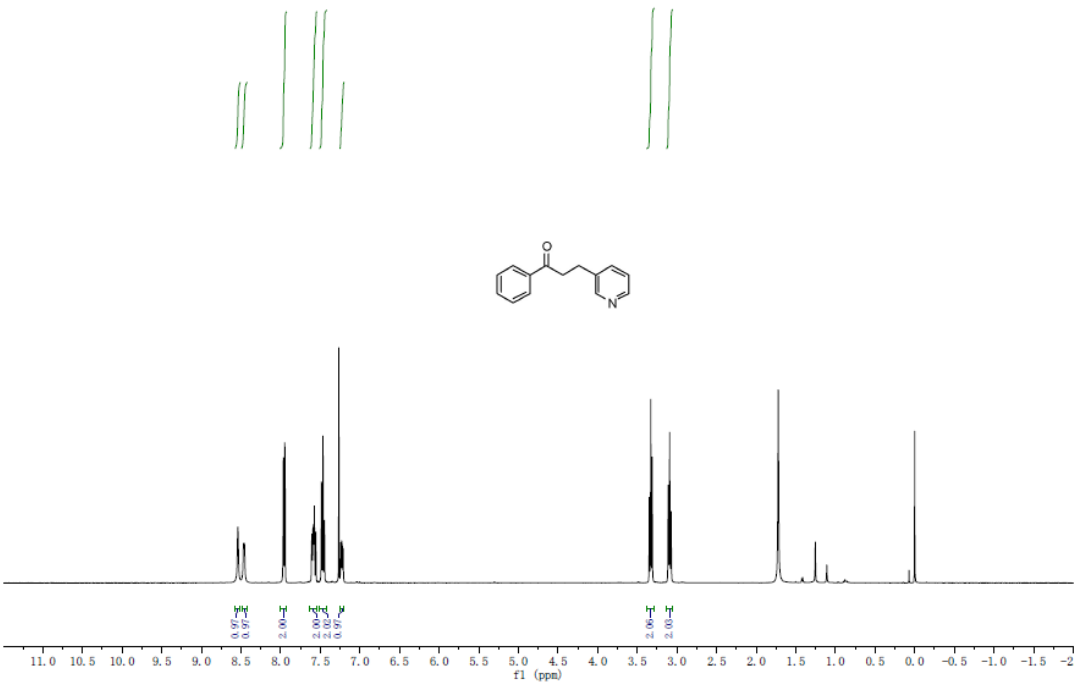
^{1}H NMR of **5b**



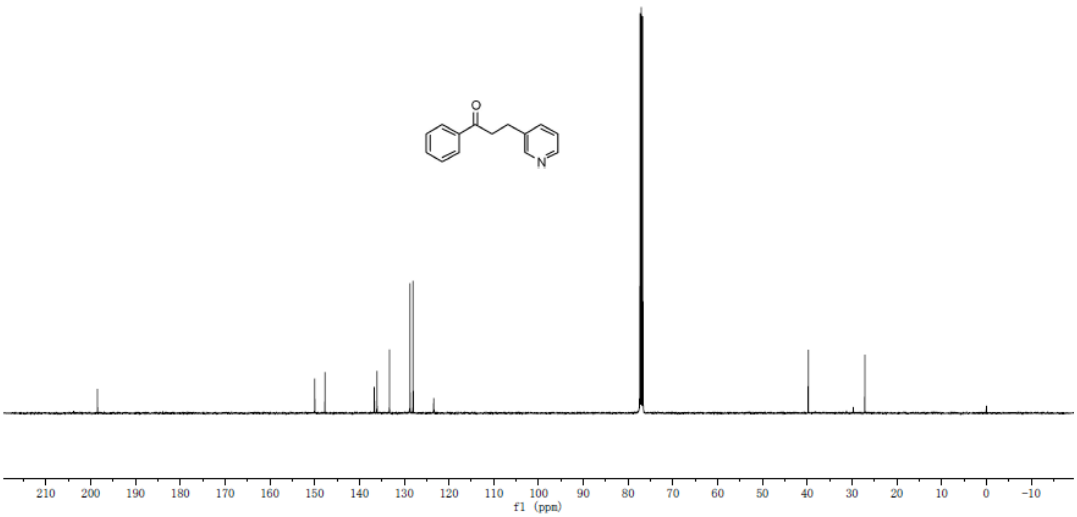
^{1}H NMR of **5c**



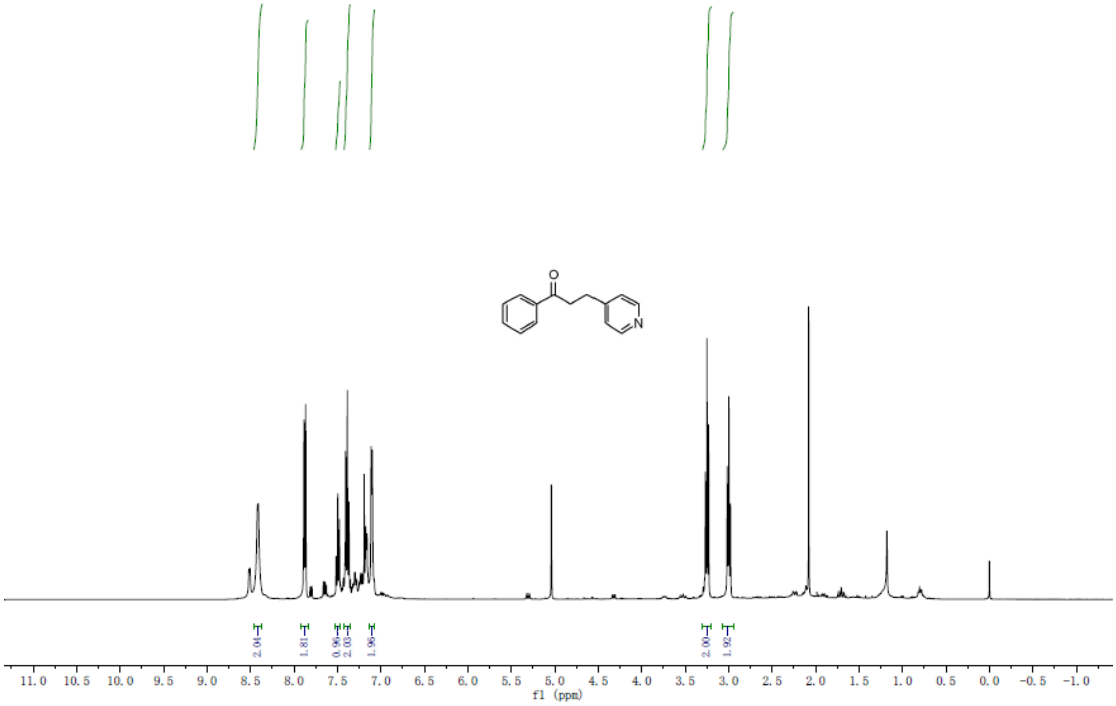
^{1}H NMR of **5d**



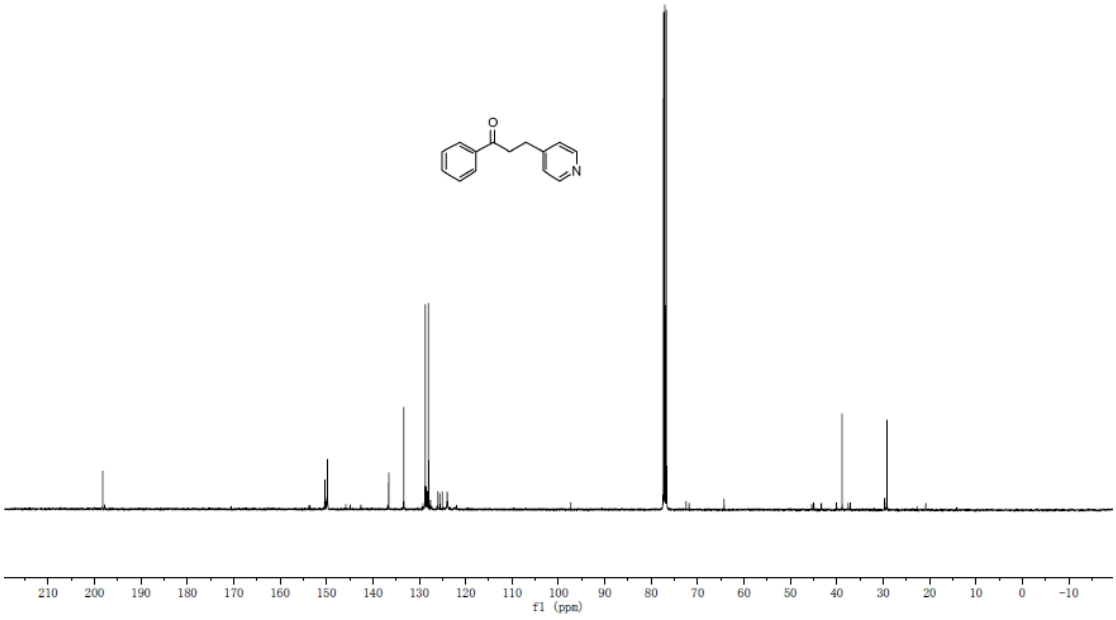
^{13}C NMR of **5d**



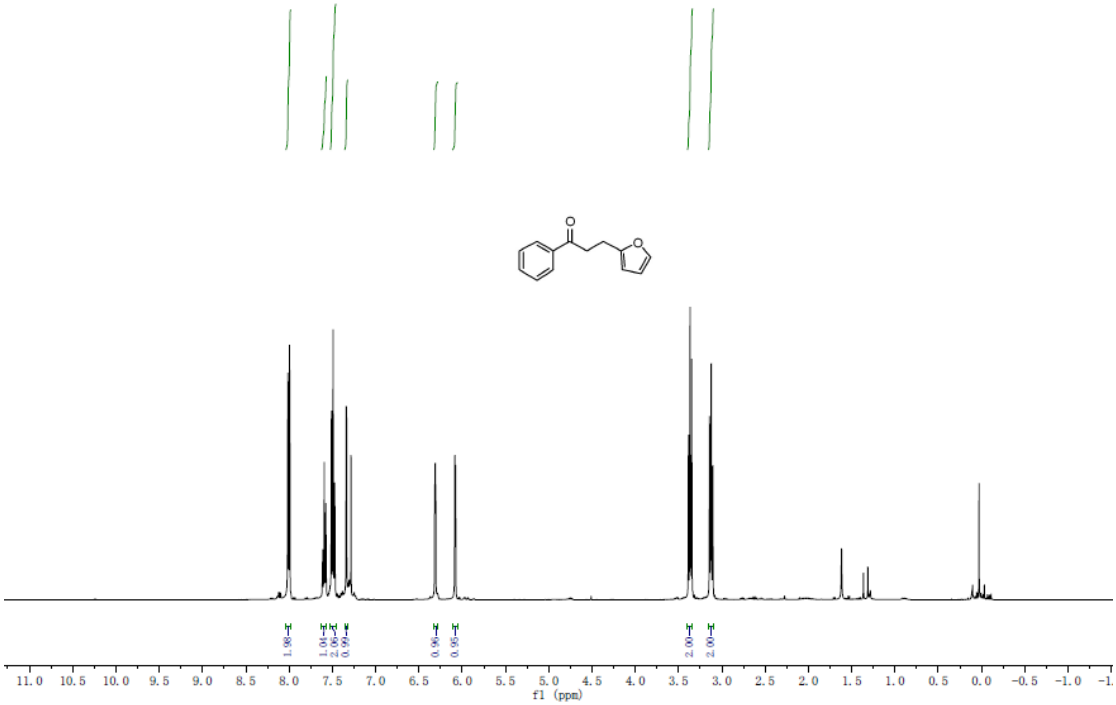
^{1}H NMR of **5e**



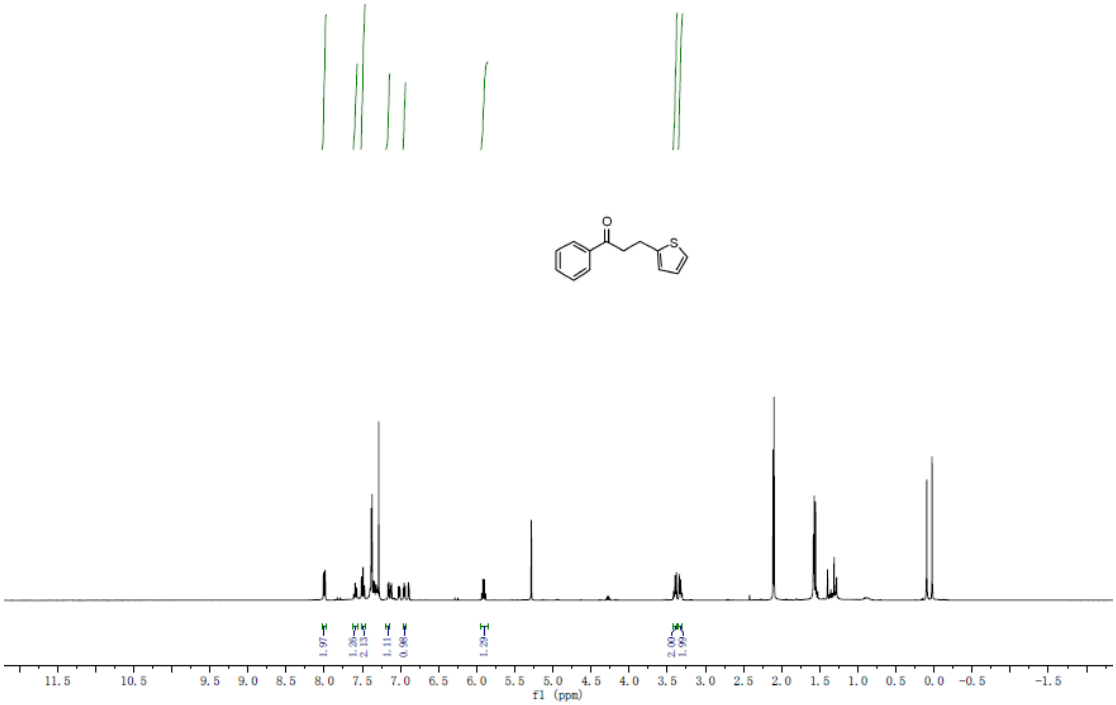
^{13}C NMR of **5e**



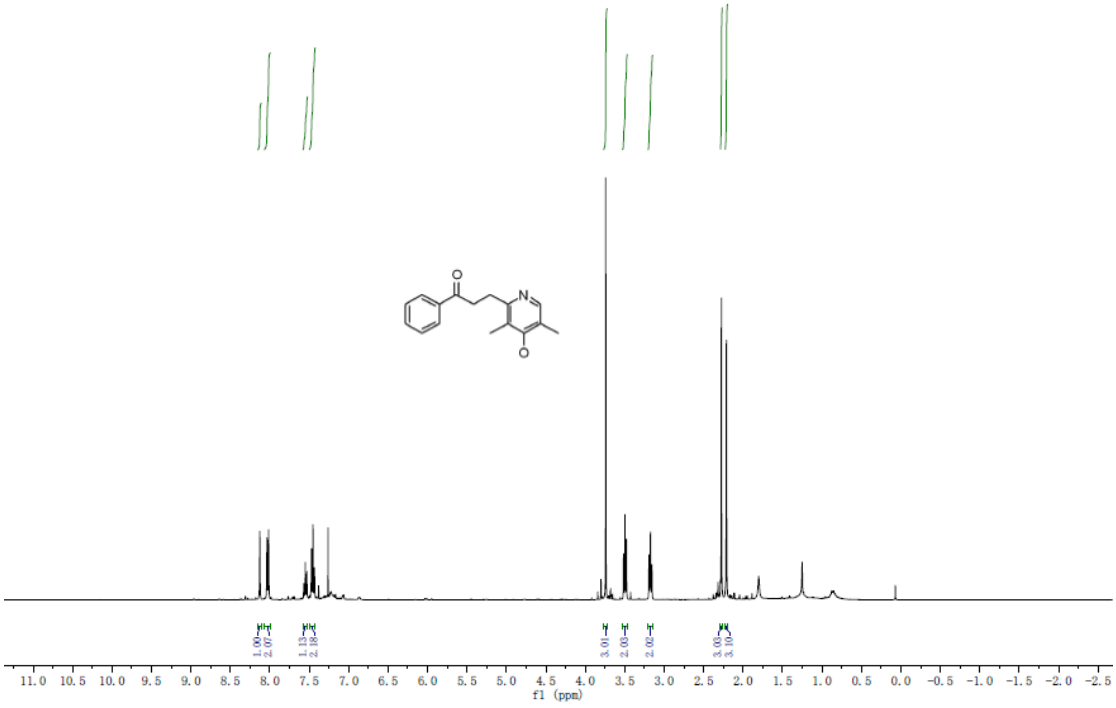
^{1}H NMR of **5f**



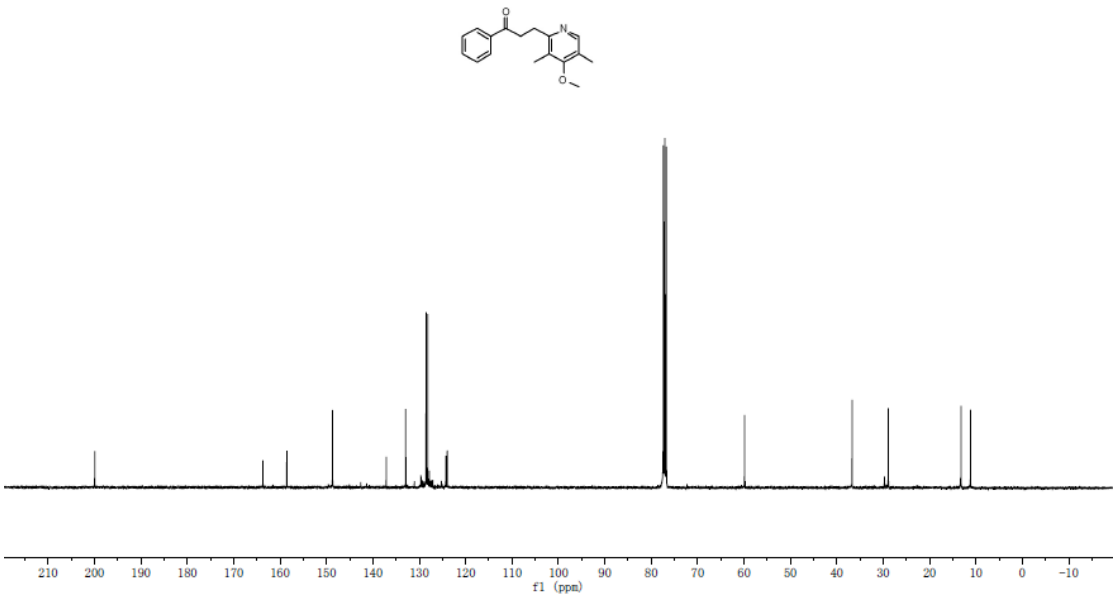
^{1}H NMR of **5g**



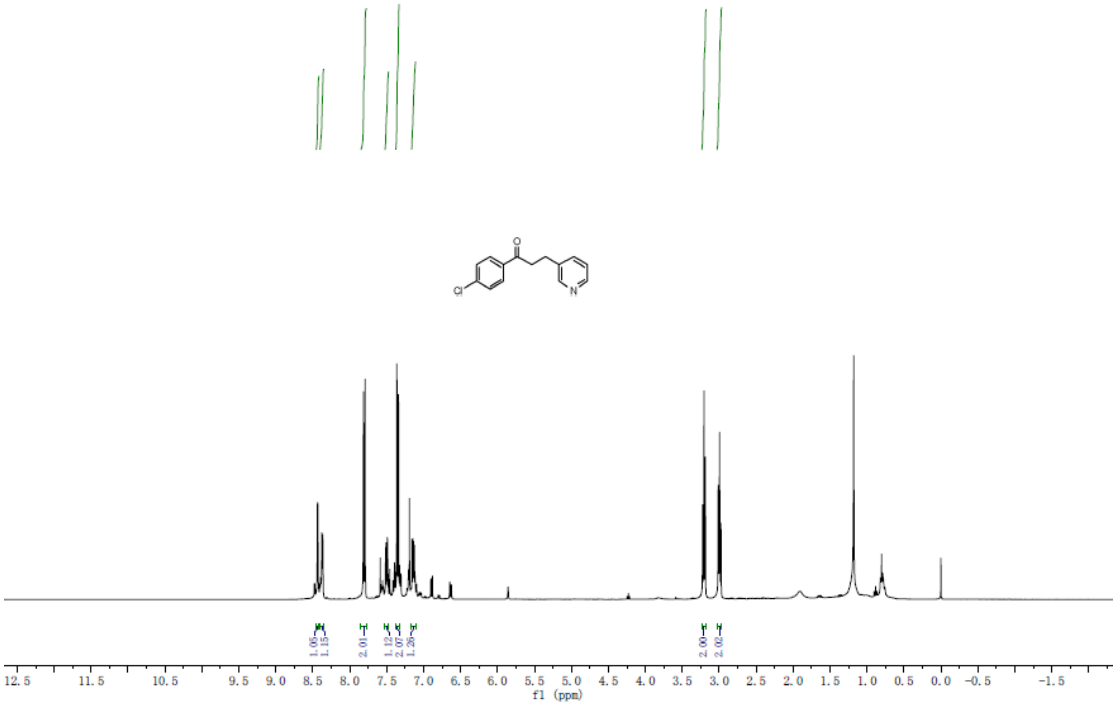
^{1}H NMR of **5h**



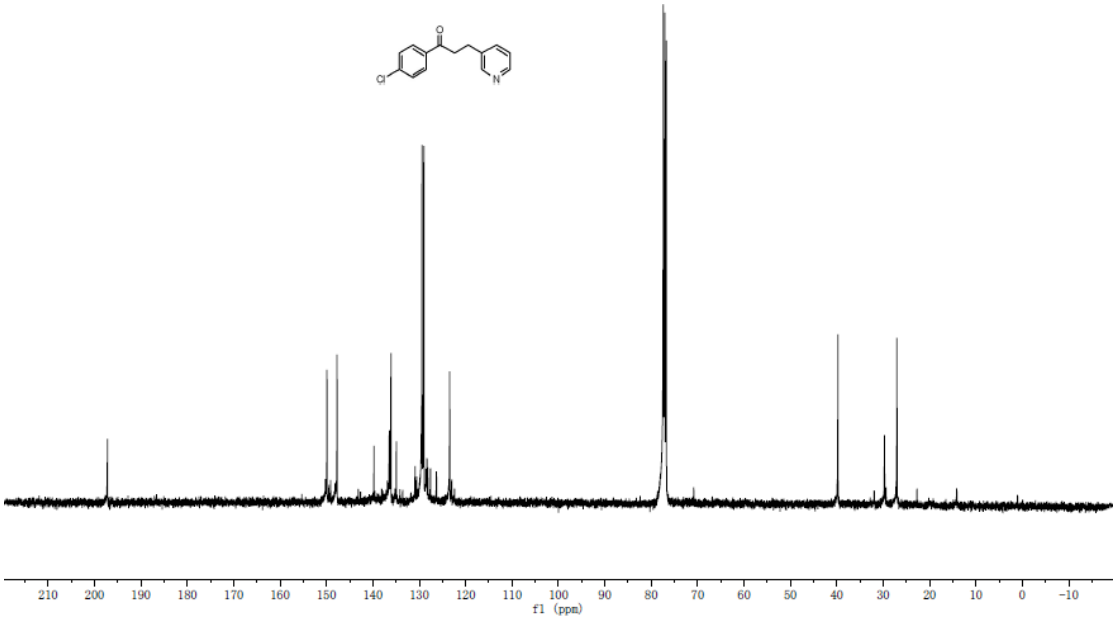
^{13}C NMR of **5h**



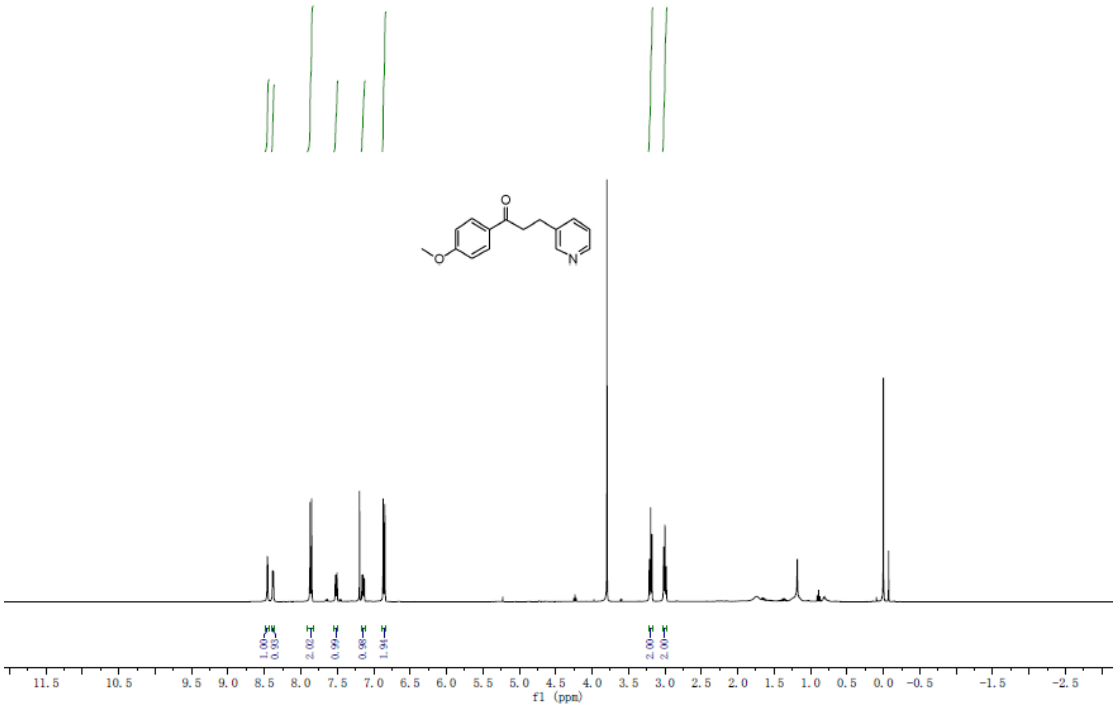
^{1}H NMR of **5i**



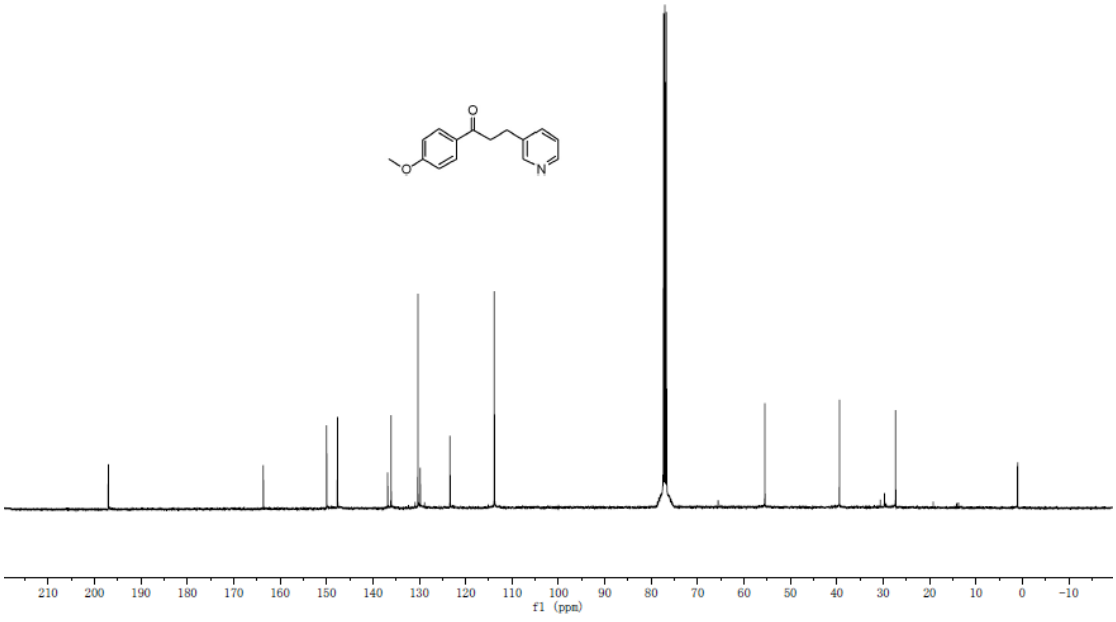
^{13}C NMR of **5i**



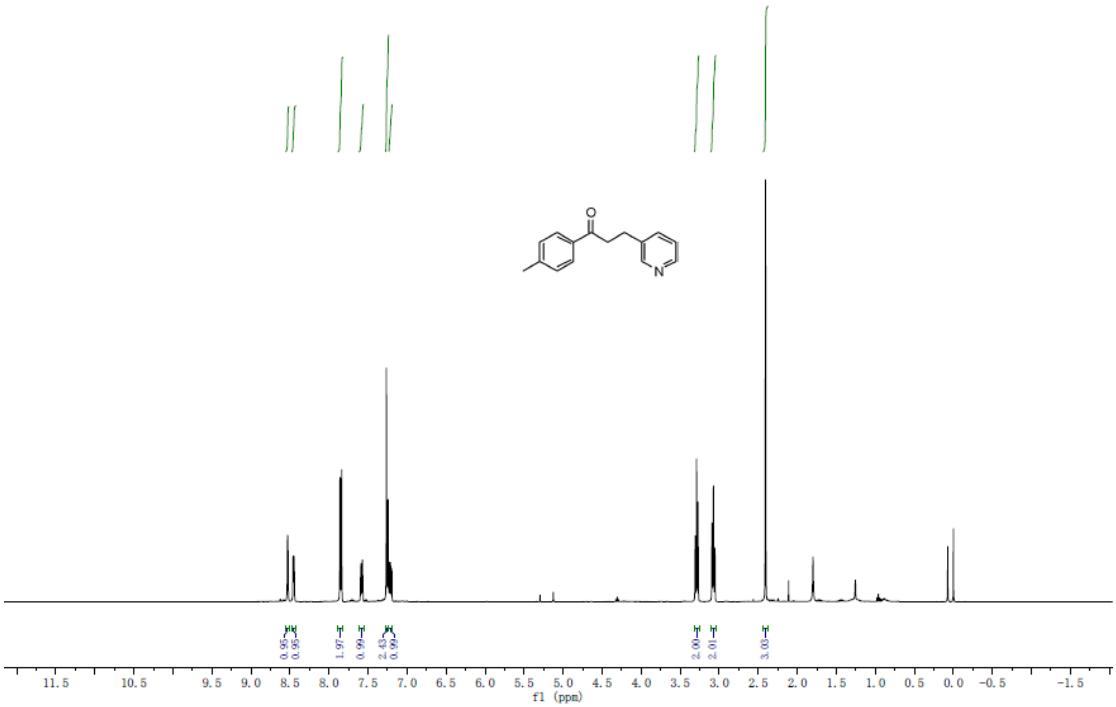
^{1}H NMR of **5j**



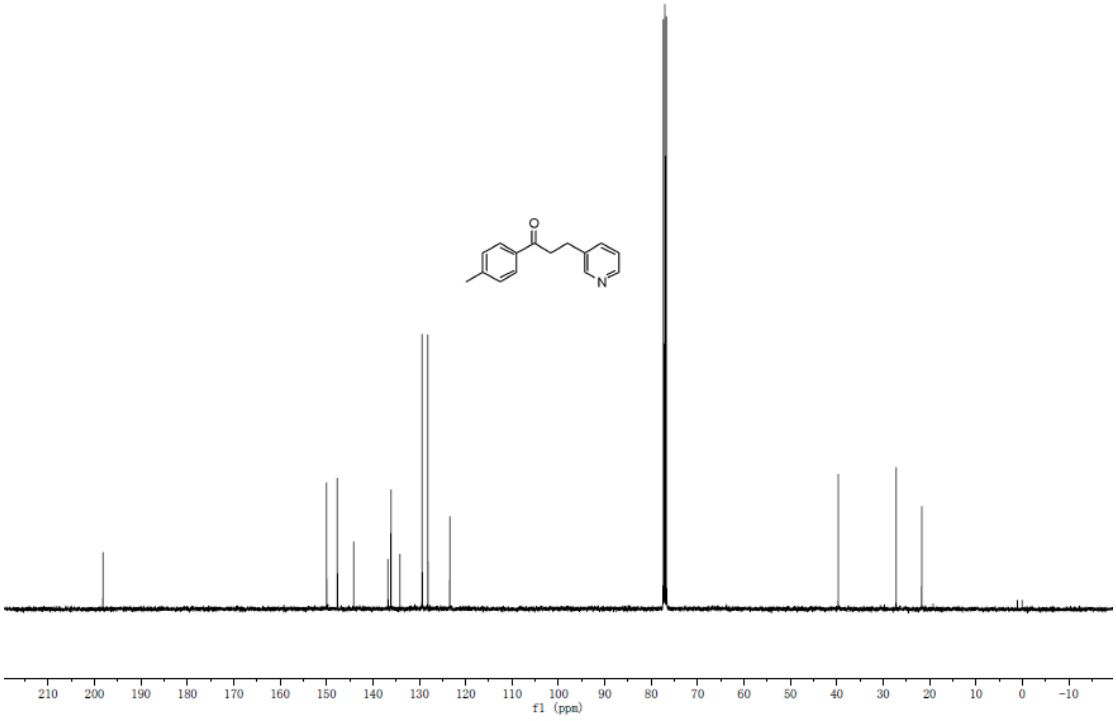
^{13}C NMR of **5j**



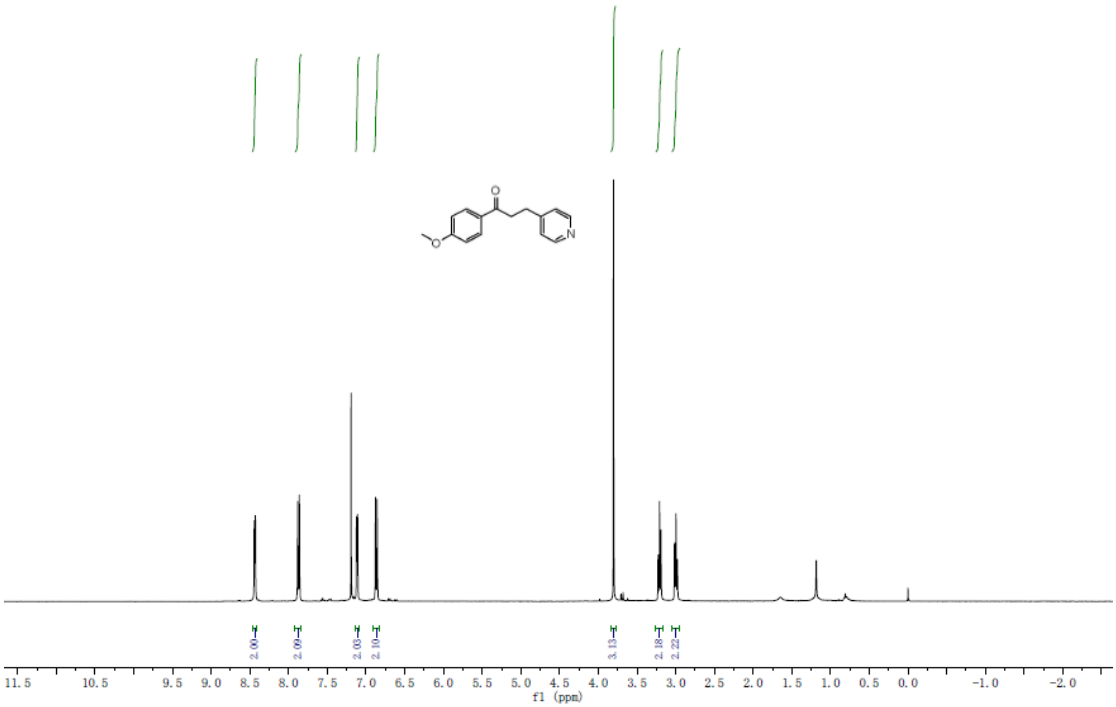
^{1}H NMR of **5k**



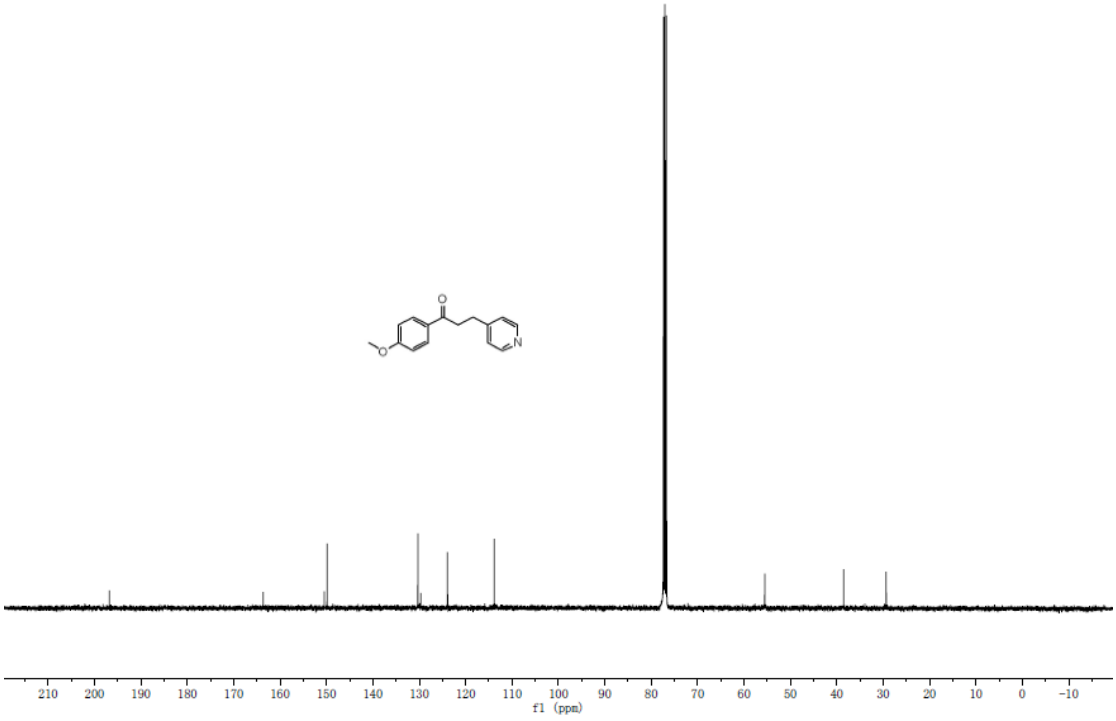
^{13}C NMR of **5k**



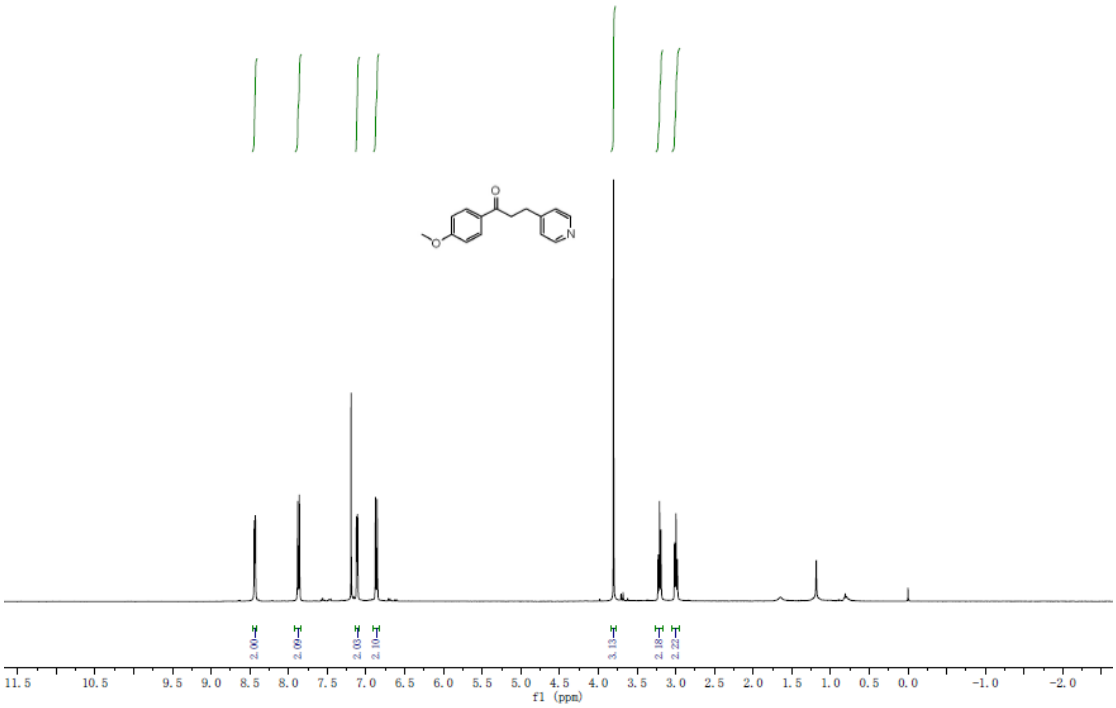
^{1}H NMR of **5l**



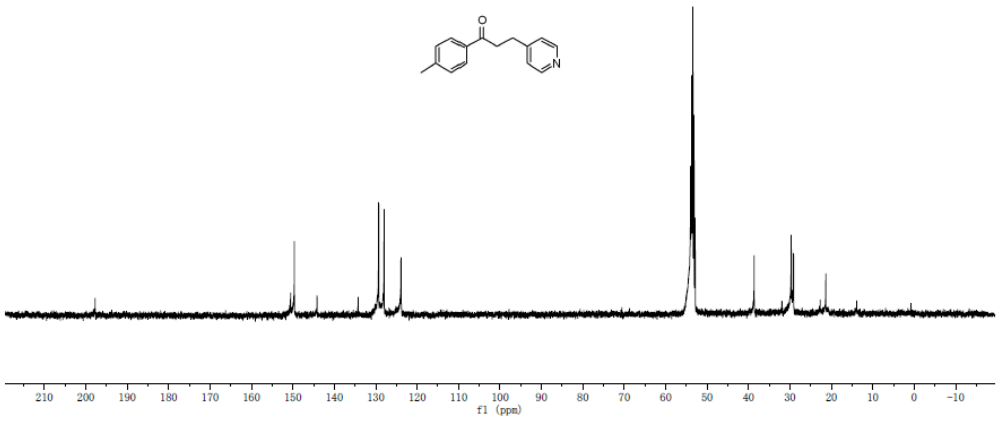
^{13}C NMR of **5l**



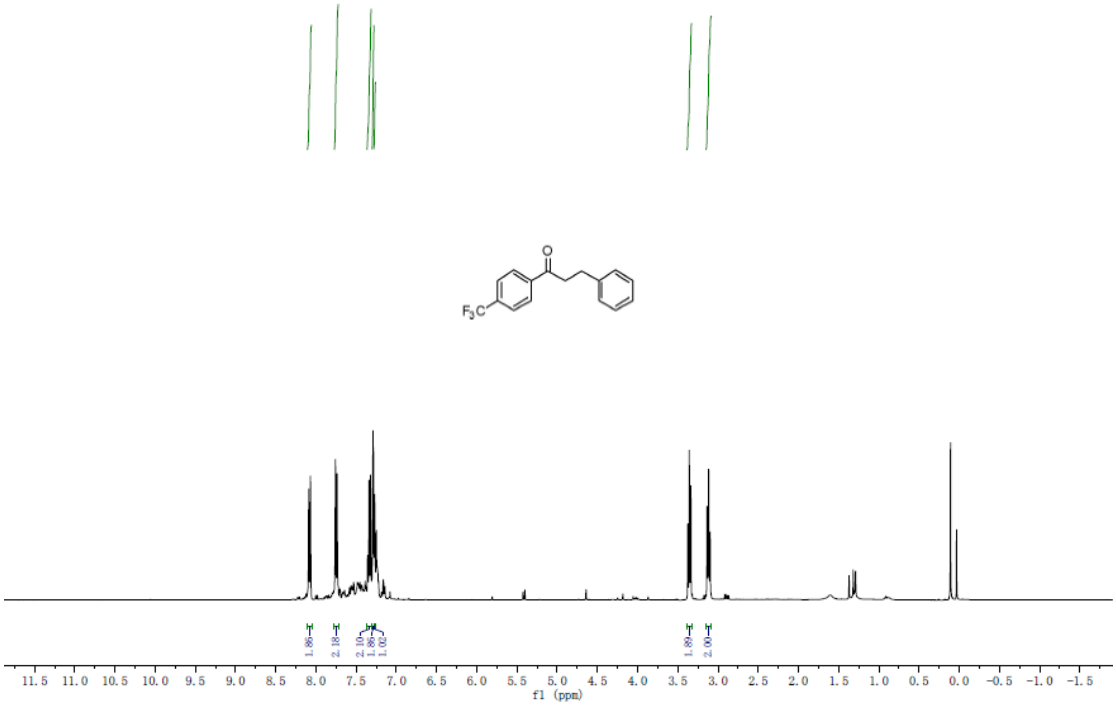
^{1}H NMR of **5m**



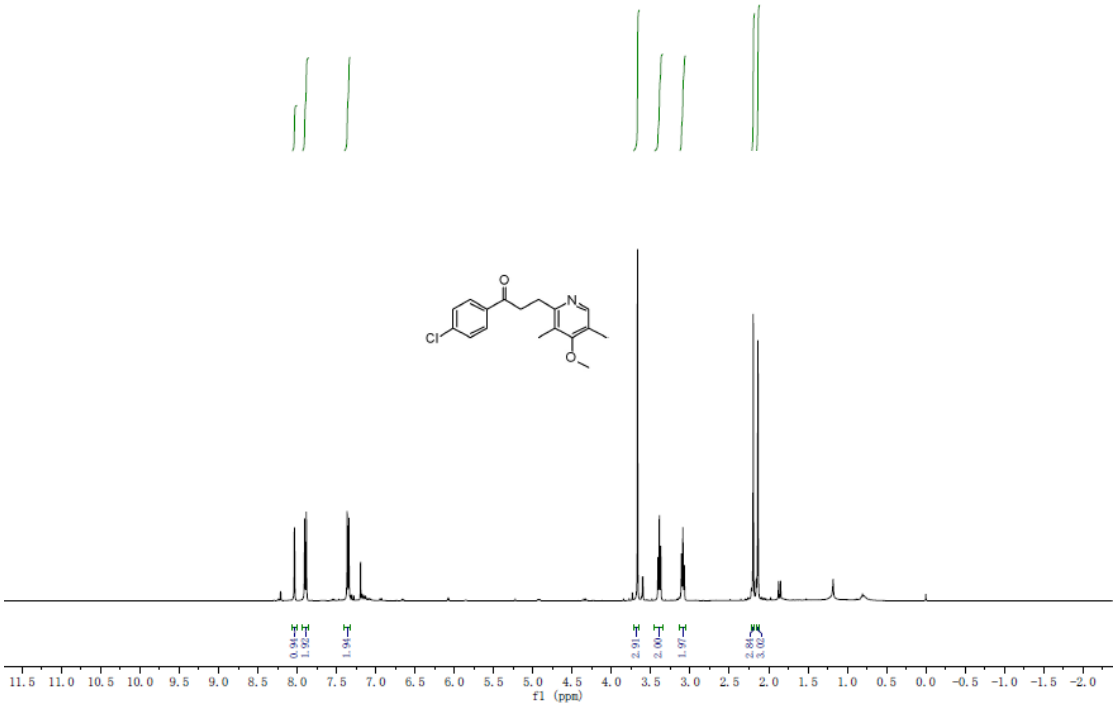
^{13}C NMR of **5m**



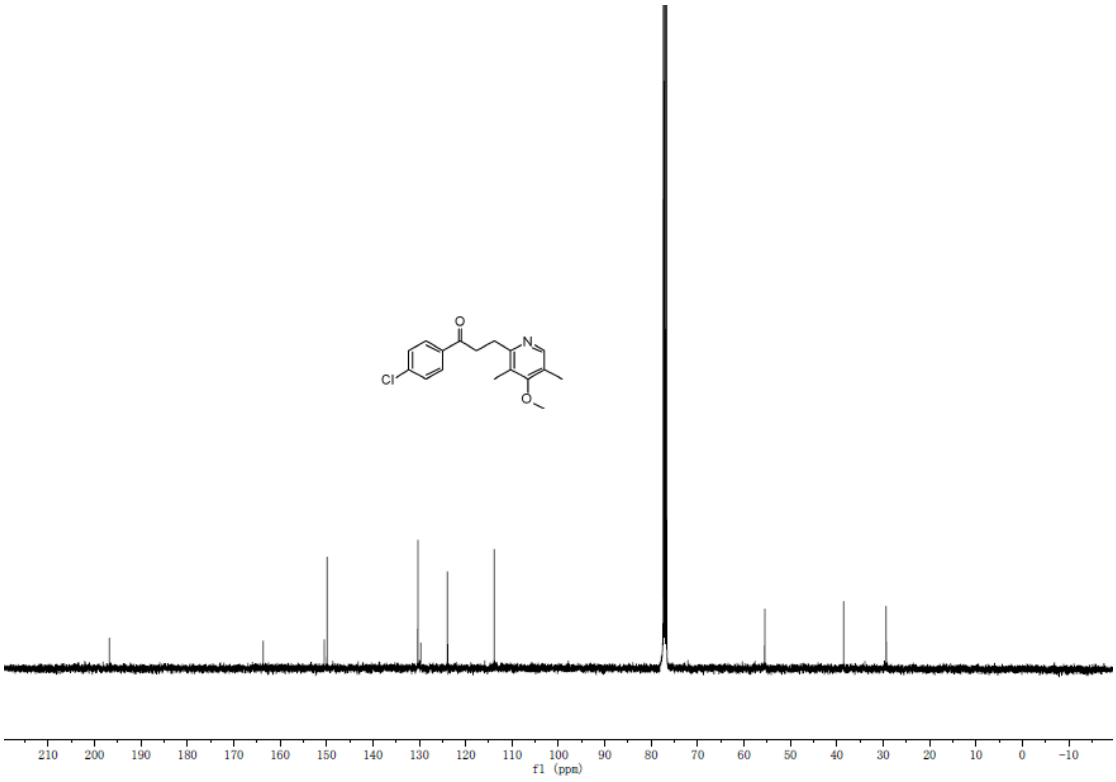
^{1}H NMR of **5n**



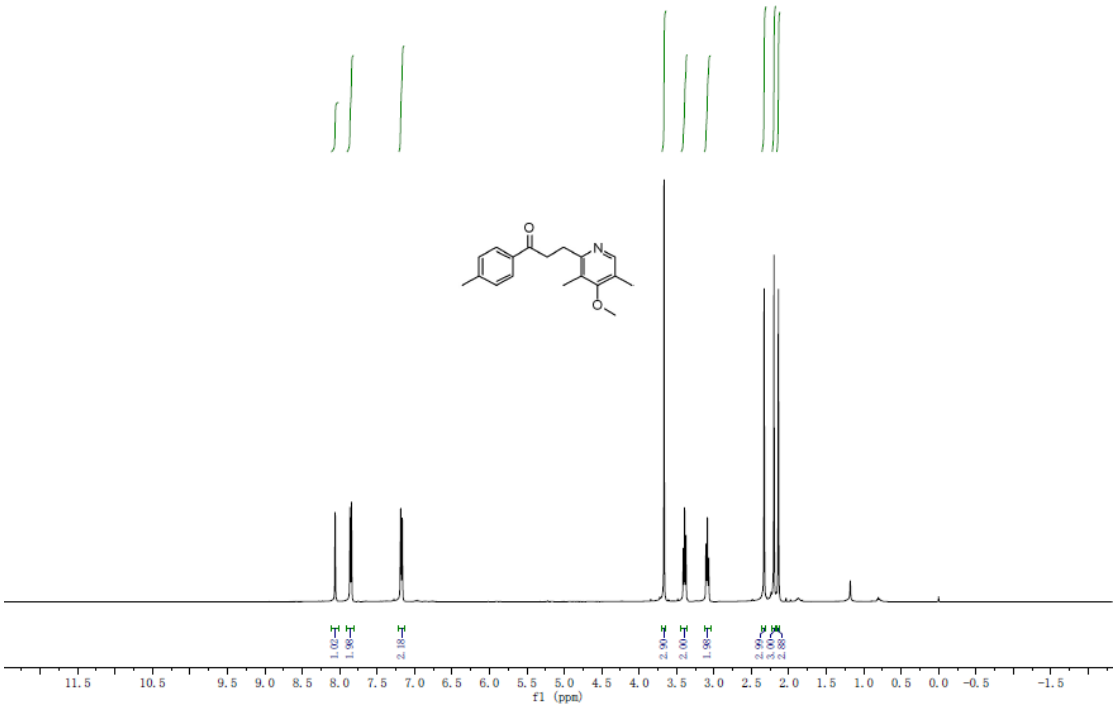
^{1}H NMR of **5o**



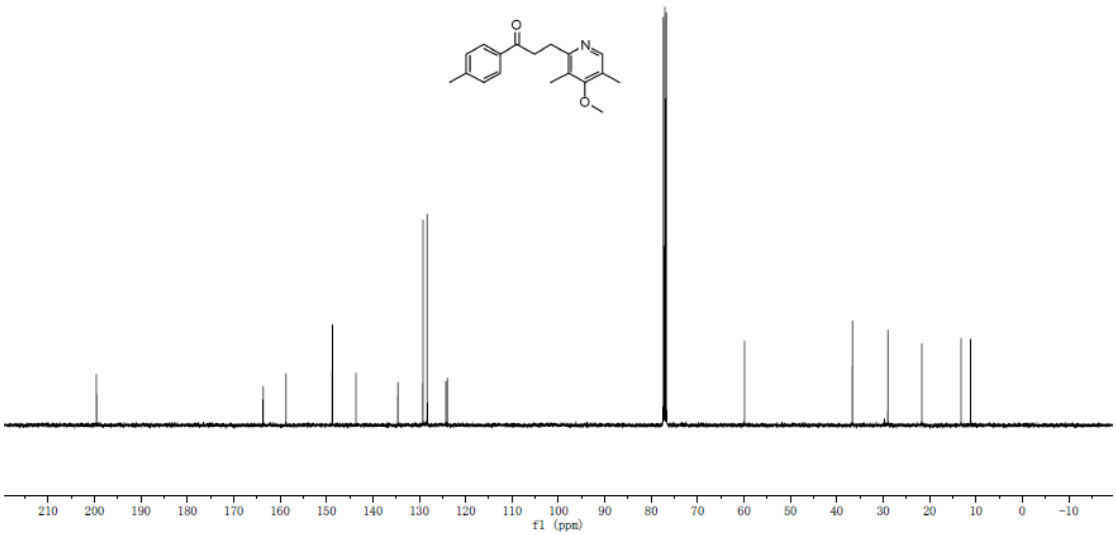
^{13}C NMR of **5o**



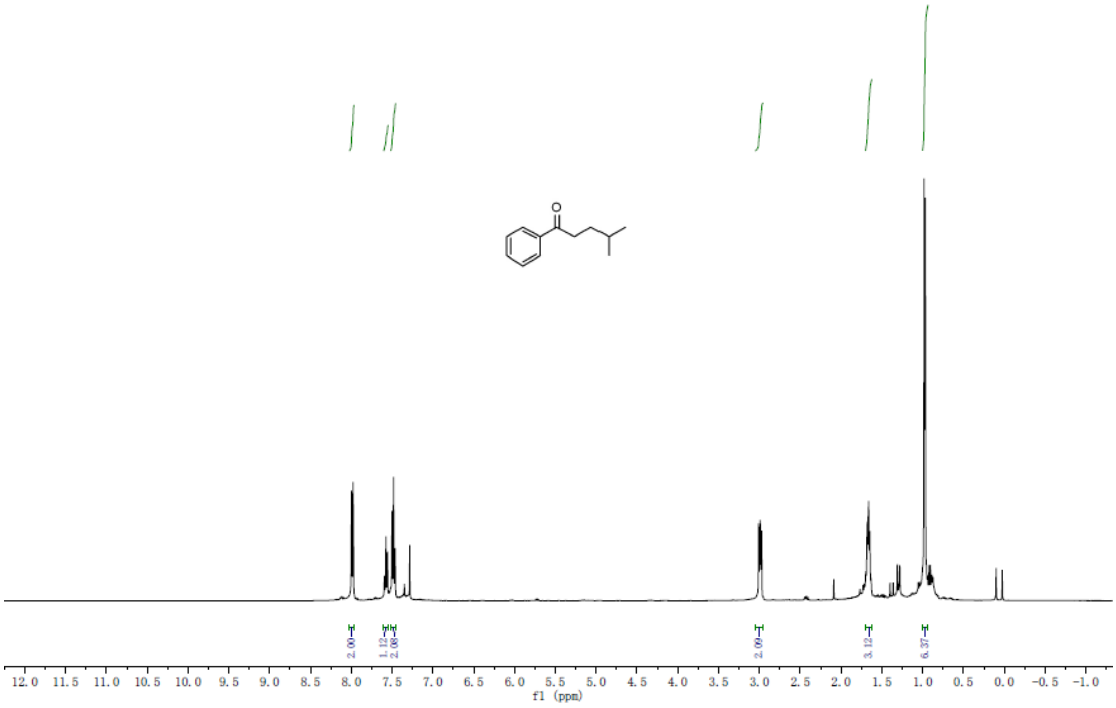
^{1}H NMR of **5p**



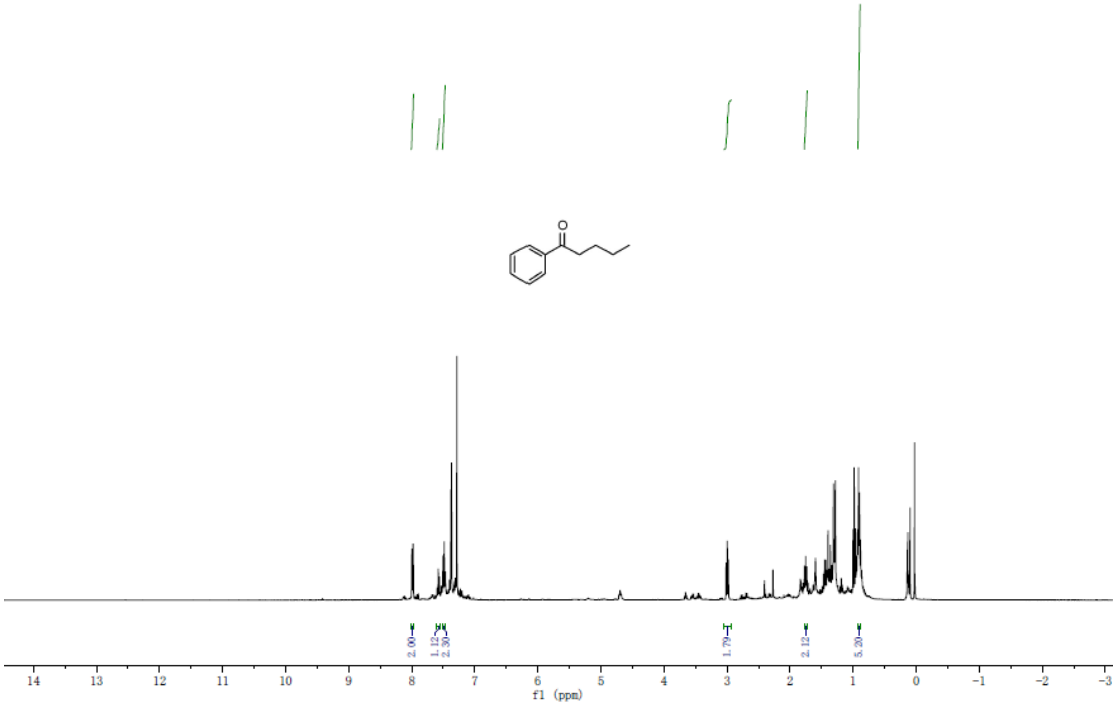
^{13}C NMR of **5p**



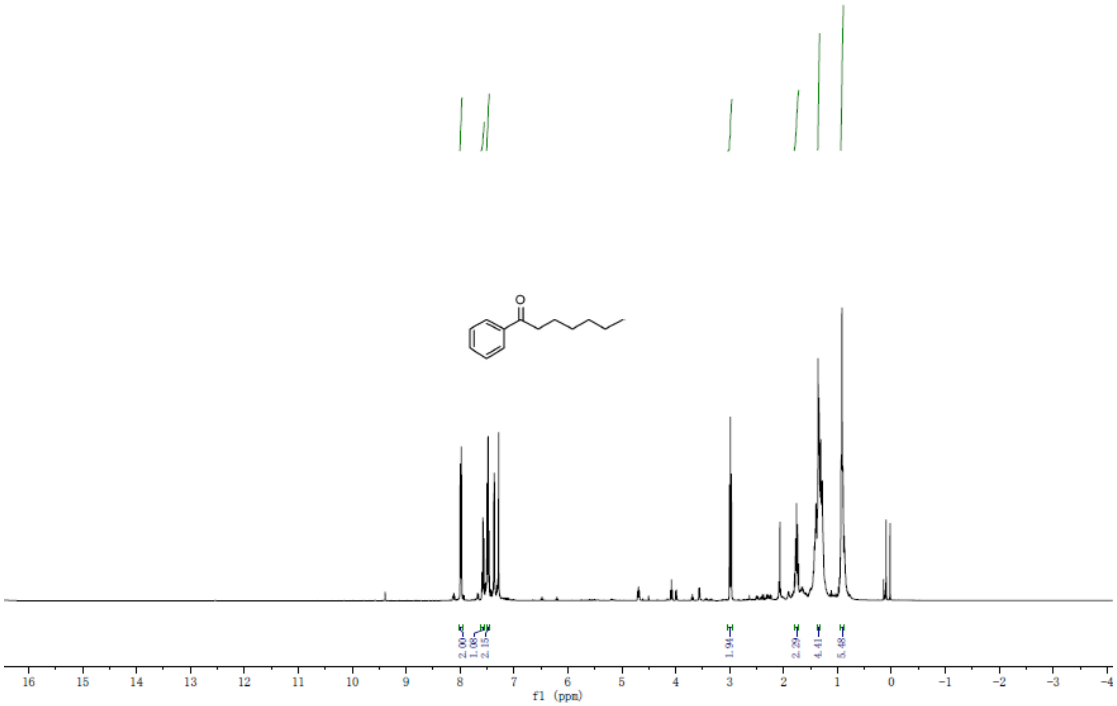
^{1}H NMR of **5q**



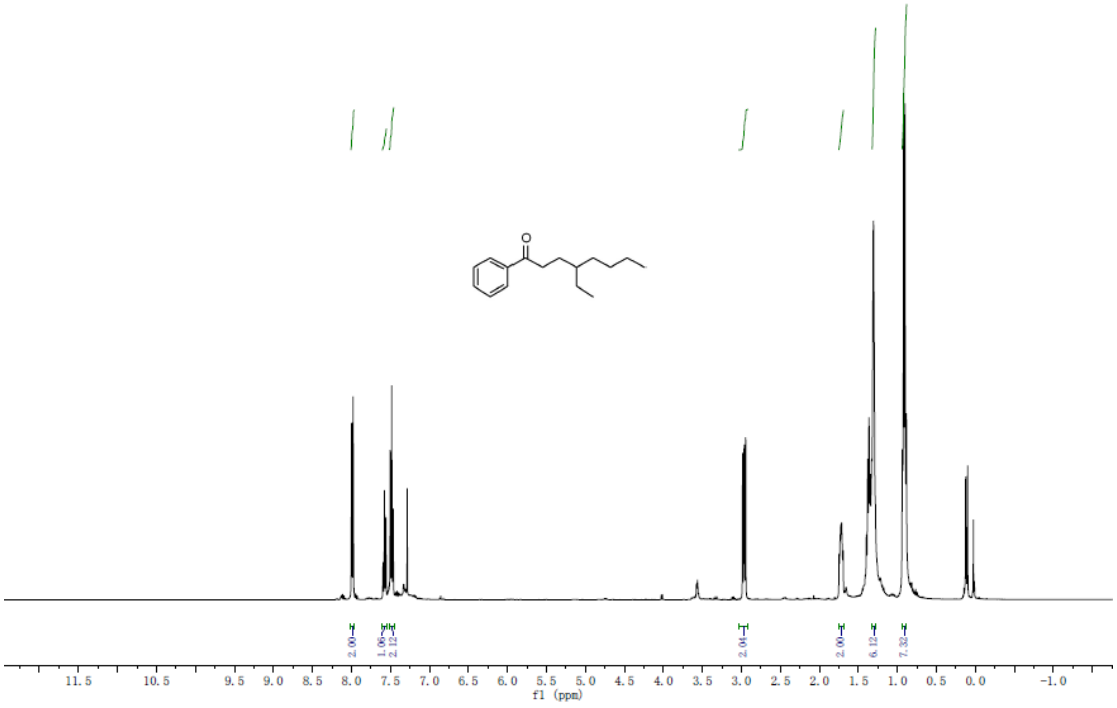
^{1}H NMR of **5r**



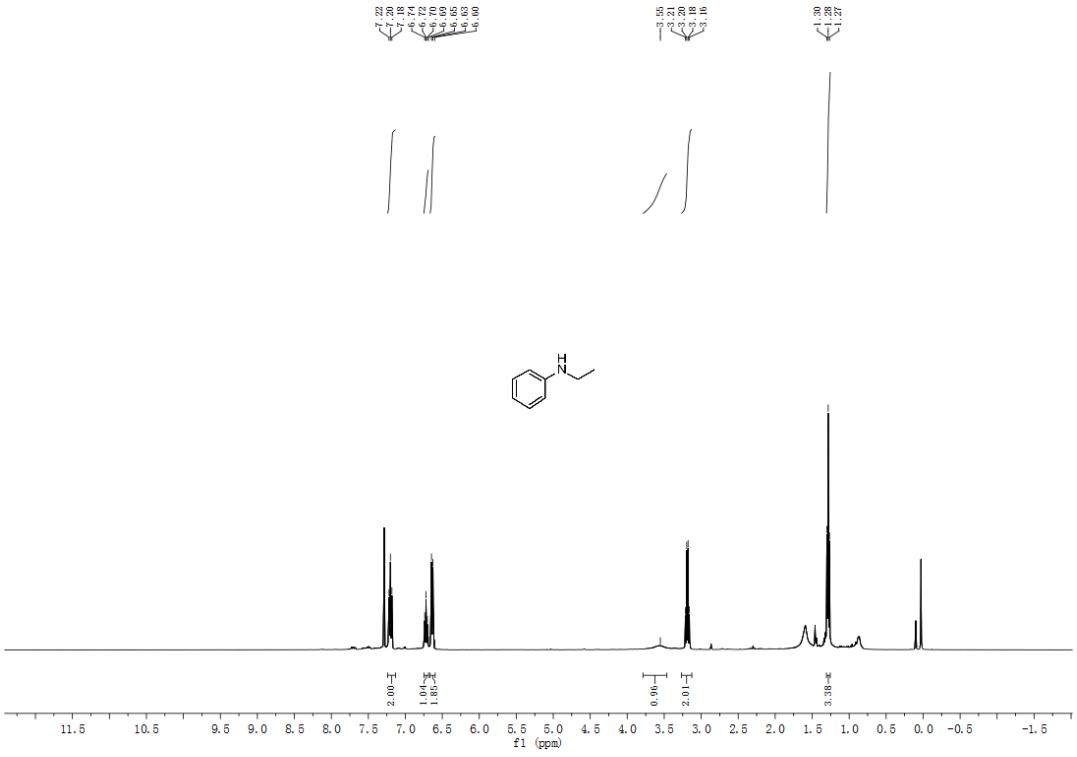
^{1}H NMR of **5s**



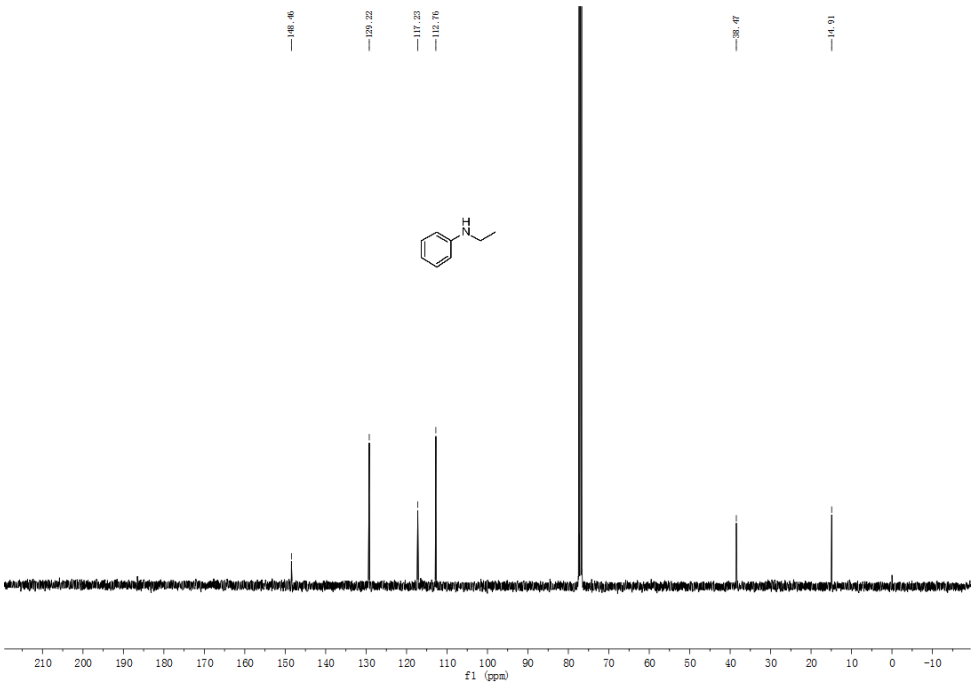
^{1}H NMR of **5t**



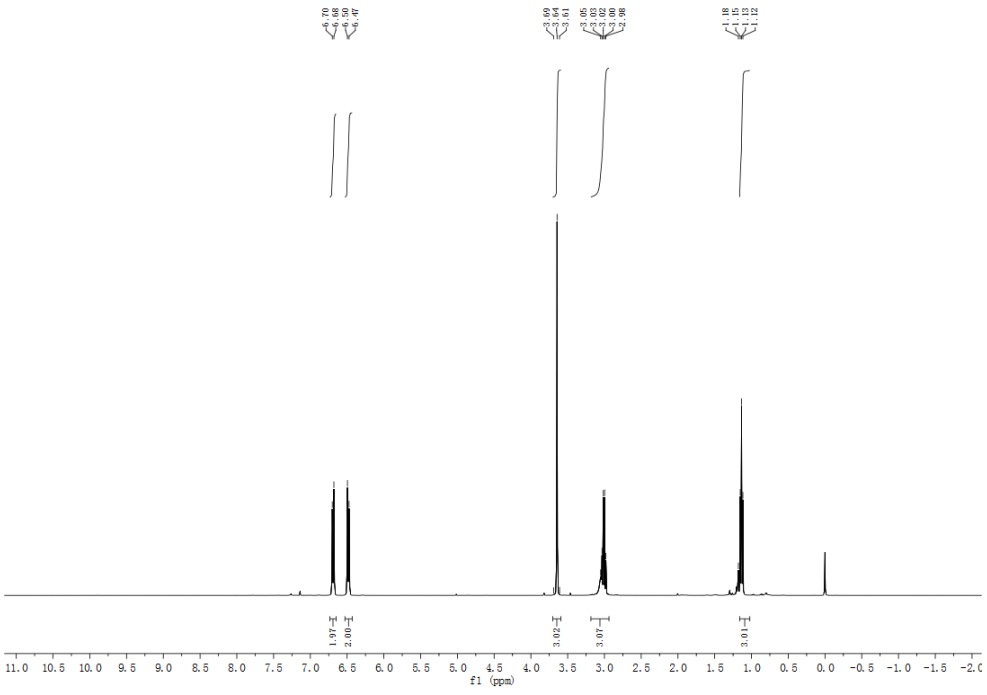
^{1}H NMR-spectra of **7a**



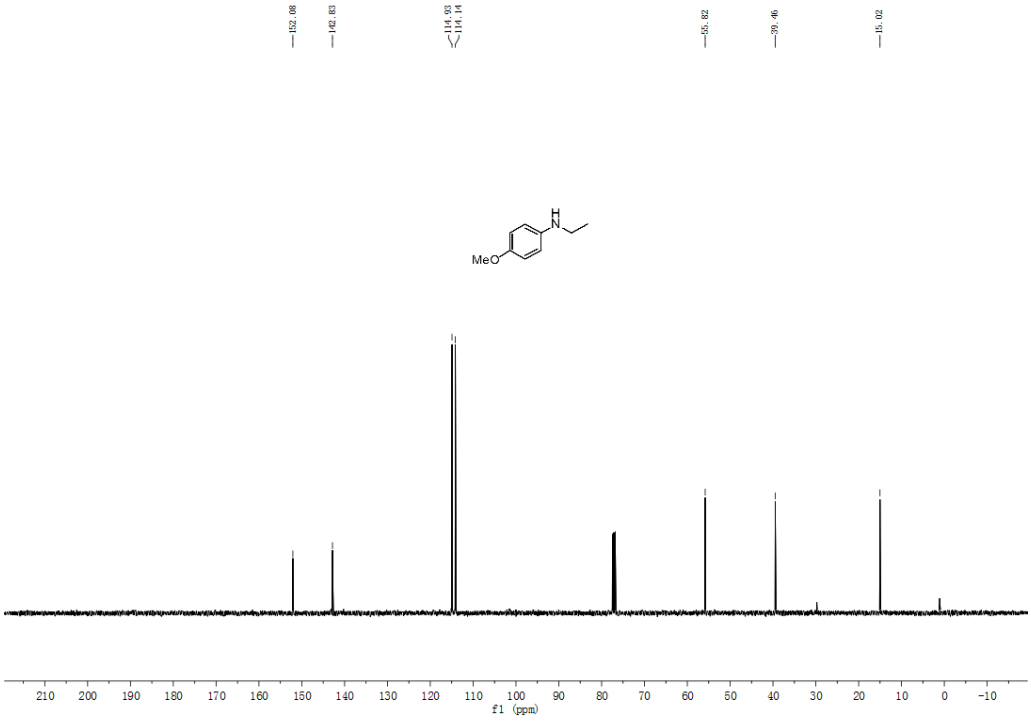
^{13}C NMR-spectra of **7a**



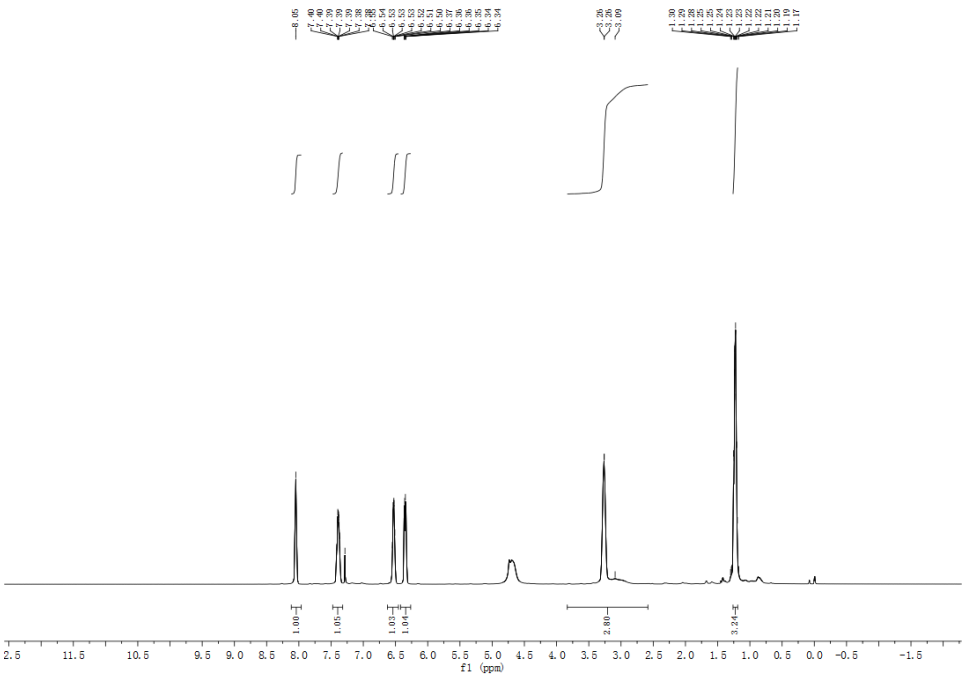
^{1}H NMR-spectra of **7b**



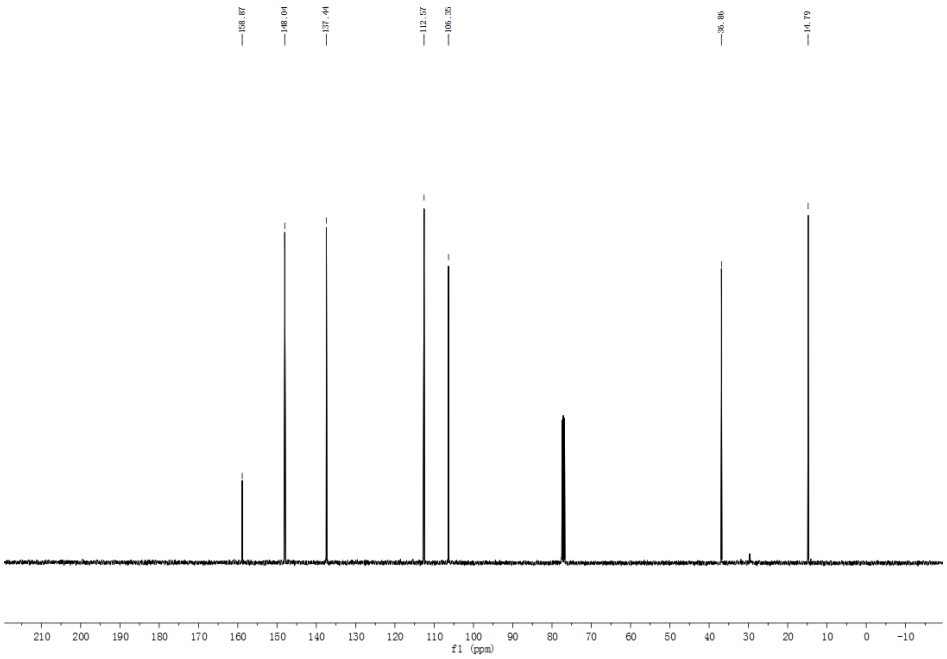
^{13}C NMR-spectra of **7b**



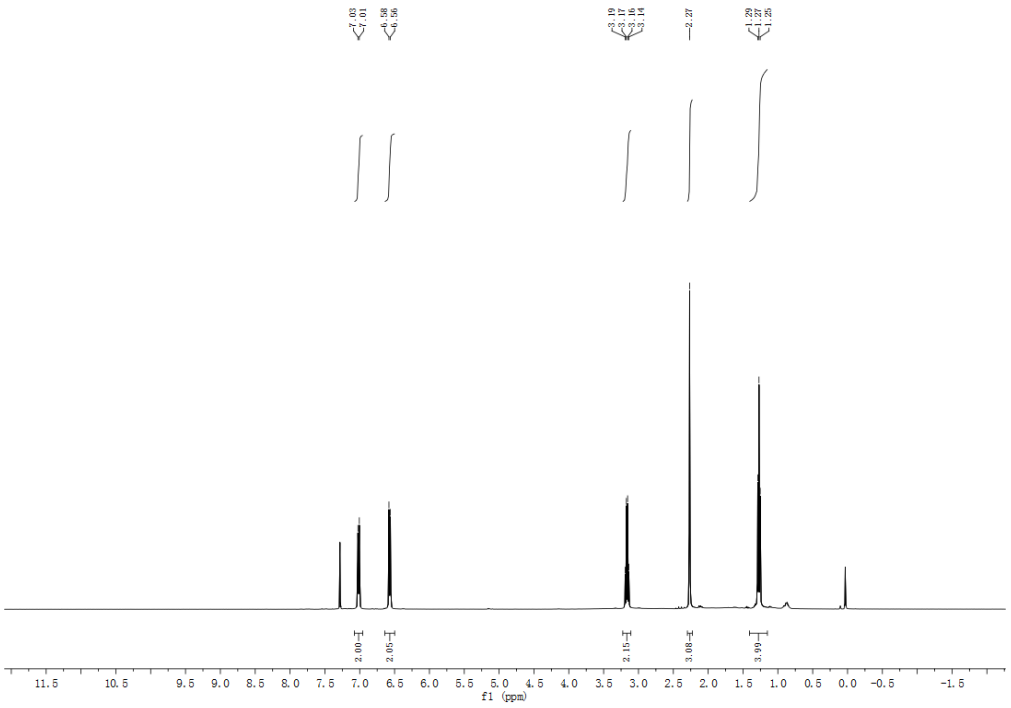
^{1}H NMR-spectra of **7c**



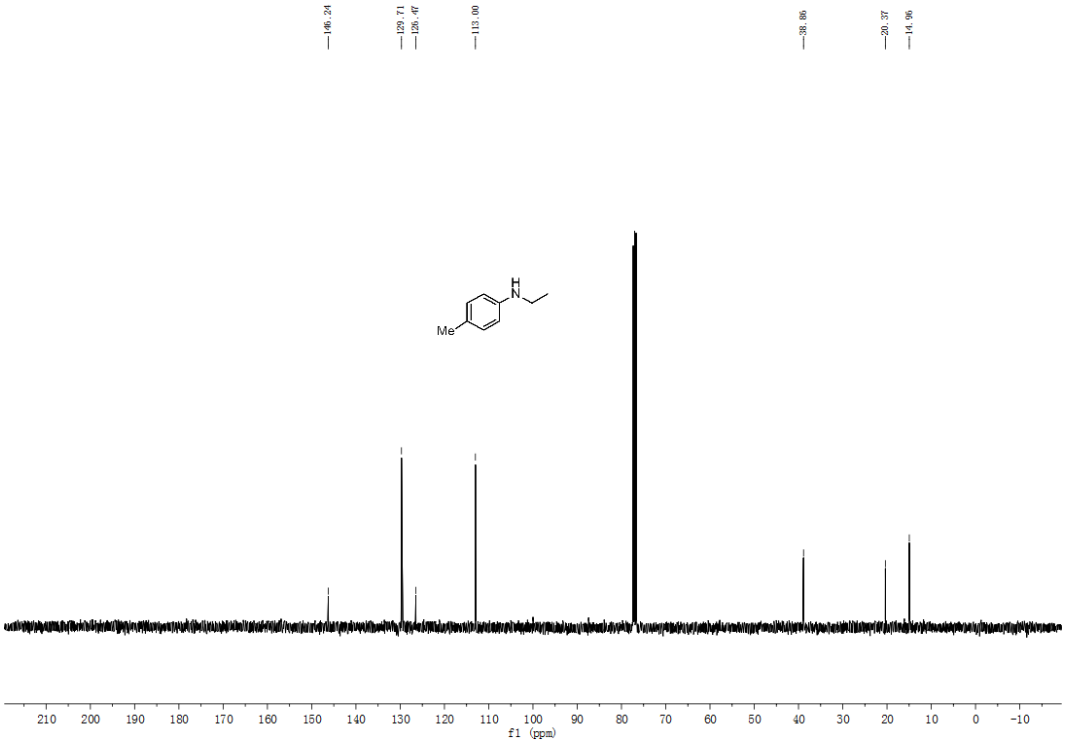
^{13}C NMR-spectra of **7c**



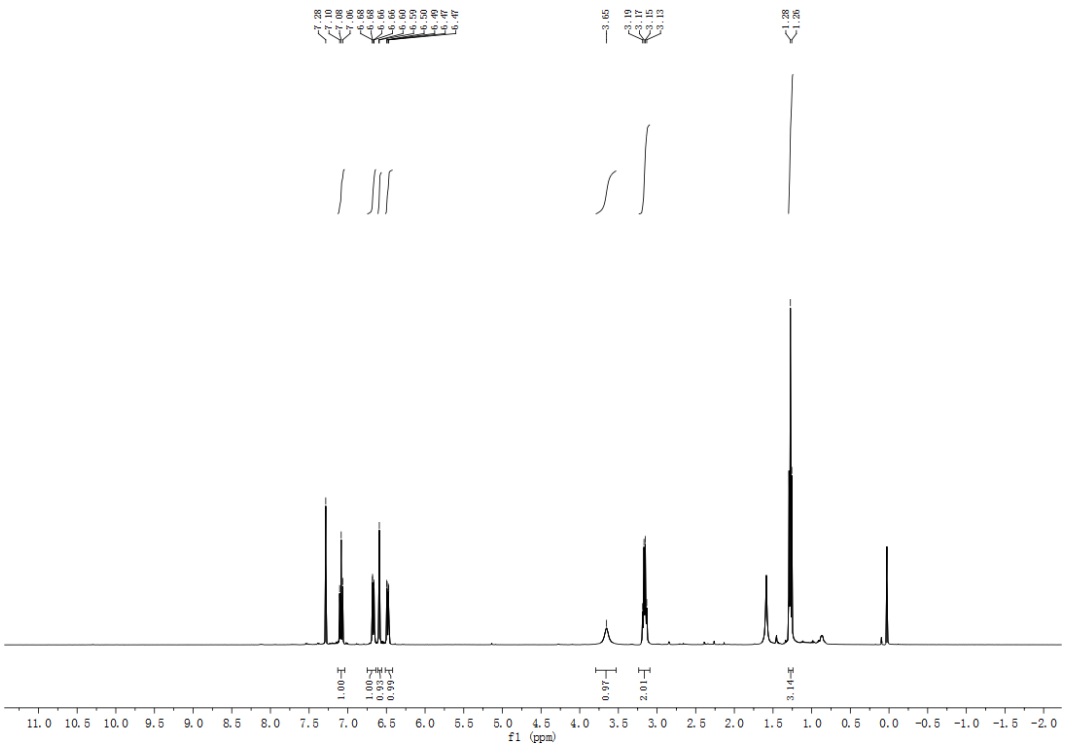
^{1}H NMR-spectra of **7d**



^{13}C NMR-spectra of **7d**



^{1}H NMR-spectra of **7e**



^{13}C NMR-spectra of **7e**