# Supporting Information

## Reusable Brønsted Acidic Ionic Liquid Efficiently Catalyzed *N*-Formylation and *N*-Acylation of Amines

Chun Li,[†] Mengna Wang,[†] Xunhua Lu, Ling Zhang, Jian Jiang, and Lin Zhang*

School of Pharmaceutical Sciences, Guizhou Medical University, No. 9 Beijing Road, Guiyang 550004, People's Republic of China

*Fax: +86-0851-88416166. Email: gmulinzhang@163.com

[†]C. Li and M. Wang contributed equally to this work

The supporting information contains 84 pages and 6 figures.

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## Ⅰ General information

All reactions were carried out under normal conditions and no any stringent conditions were used. Commercially available compounds were used without further purification. Melting points were uncorrected and determined in an open capillary tube. NMR experiments were recorded in DMSO-$d_6$ and $CDCl_3$ on a JEOL NMR 400 MHz spectrometer using TMS as an internal standard. High-resolution mass spectra (HRMS) were obtained on a Bruker MicroQTOFII instrument using electrospray ionization (ESI) techniques.

## Ⅱ The determination of the acidity of BAILs

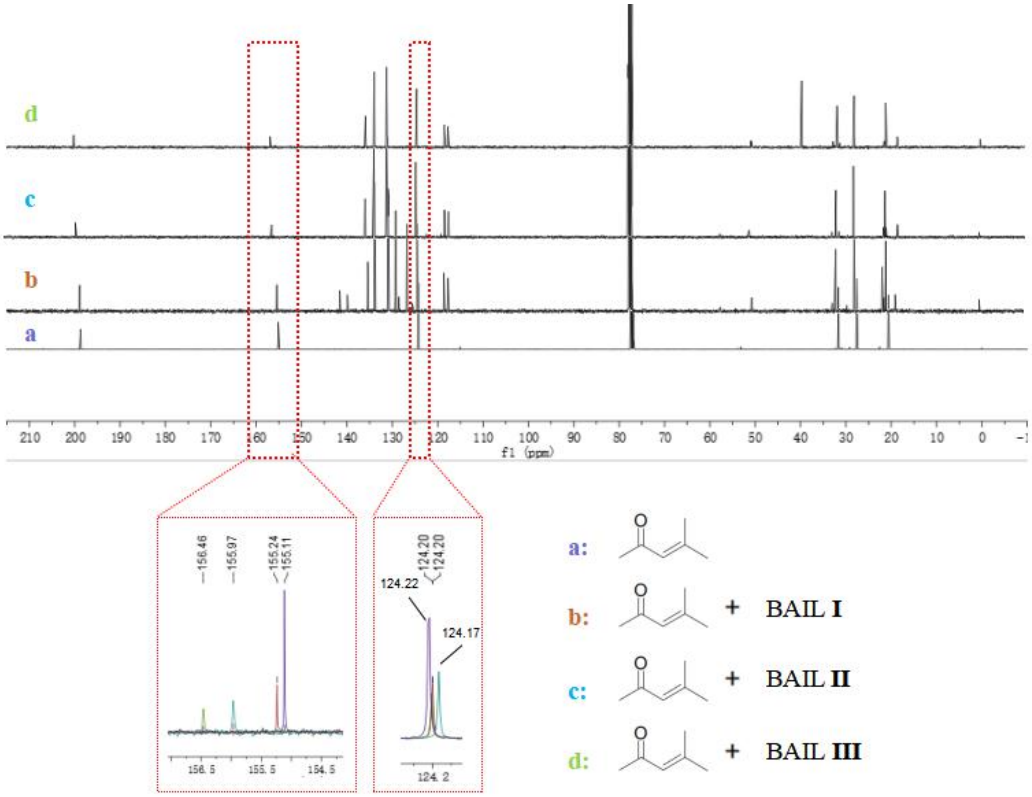



**Figure S1**. Determination of acidity of BAILs in $^{13}C$ NMR experiments on the mixture of mesityl oxide and BAIL (2:1) in $CDCl_3$ at 25 ℃. (a) pure mesityl oxide; (b) mesityl oxide + BAIL Ⅰ; (c) mesityl oxide + BAIL Ⅱ; (d)mesityl oxide + BAIL Ⅲ.

## Ⅲ Mechanistic Studies

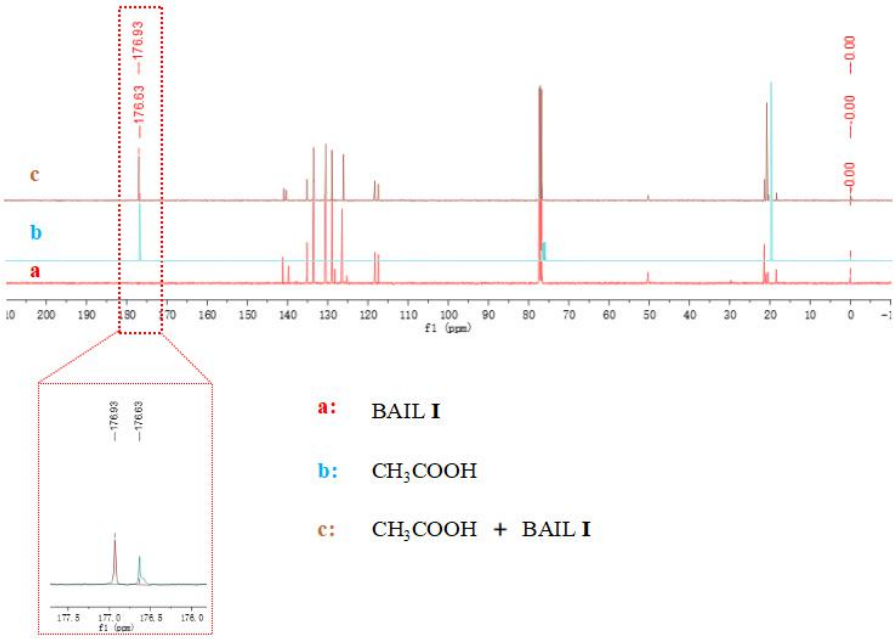



**Figure S2**. The ***C***=O signal in $CH_3COOH$ in $^{13}C$ NMR experiments on the mixture of $CH_3COOH$ and BAIL Ⅰ (6:1) in $CDCl_3$ at 25 ℃. (a) BAIL Ⅰ; (b) $CH_3COOH$; (c) $CH_3COOH$ + BAIL Ⅰ ( mix at 80 ℃ for 20 h).

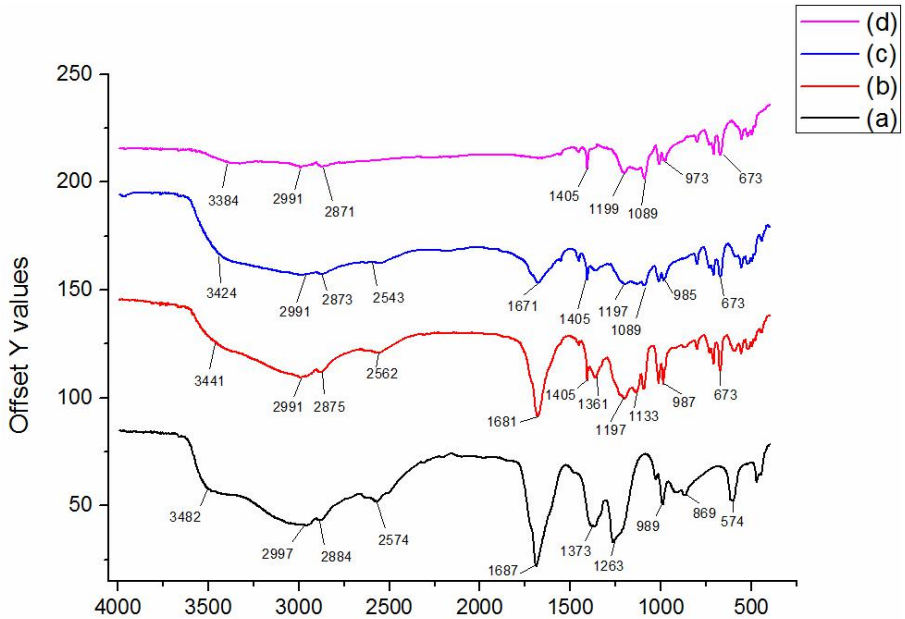



**Figure S3**. The FTIR spectrum. (a) $CH_3COOH$; (b) BAIL Ⅰ /$CH_3COOH$ = 1/60 (mix at 80 ℃ for 20 h); (c) BAIL Ⅰ /$CH_3COOH$ = 1/6 (mix at 80 ℃ for 20 h); (d) BAIL Ⅰ.

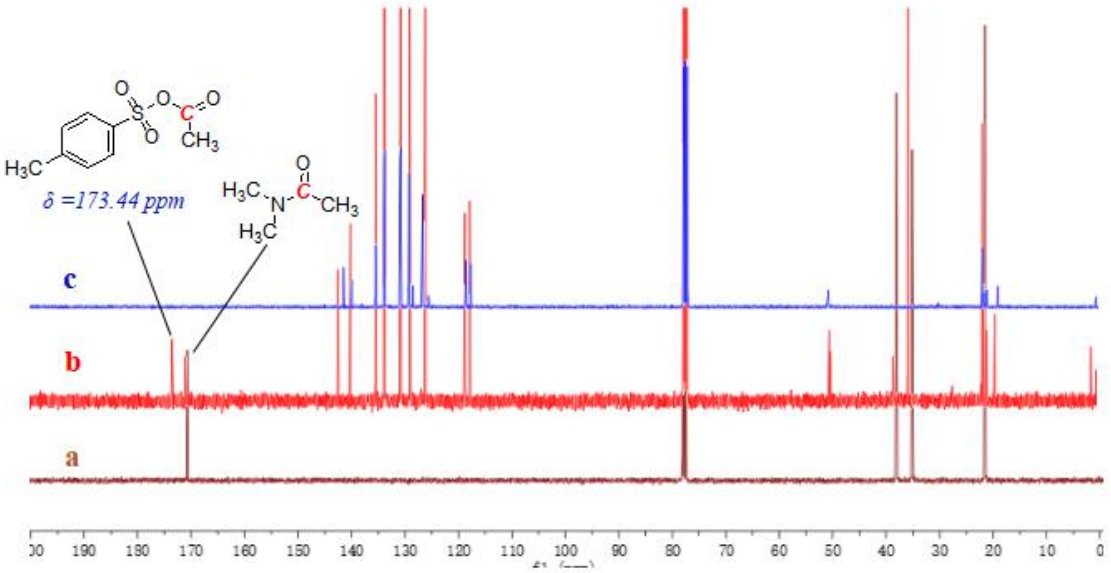



**Figure S4**. The ***C***=O signal in $^{13}C$ NMR experiments on the mixture of DMA and BAIL Ⅰ (6:1) in $CDCl_3$ at 25 ℃. (a) DMA; (b) DMA/BAIL Ⅰ = 6/1 (mix at 140 ℃ for 20 h); (c) BAIL Ⅰ.

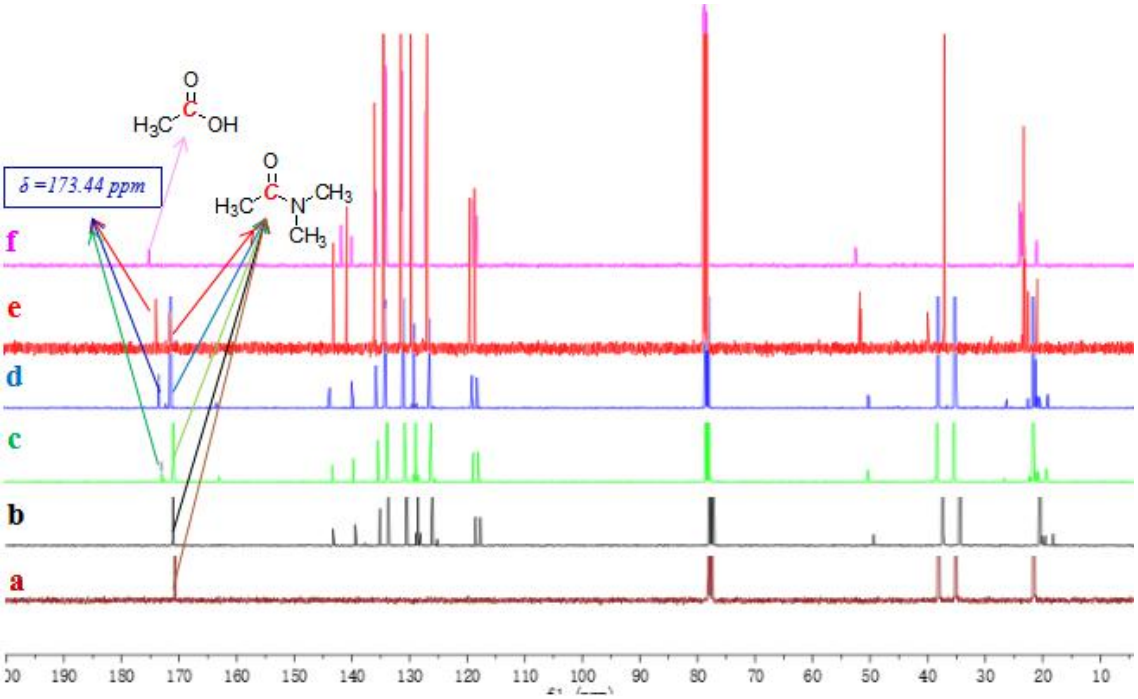



**Figure S5**. The ***C***=O signal in $^{13}C$ NMR experiments in $CDCl_3$ at 25 ℃. (a) DMA; (b) DMA and BAIL Ⅰ (mix at rt for 20 h); (c) DMA and BAIL Ⅰ (mix at rt 80 ℃r 20 h); (d) DMA and BAIL Ⅰ (mix at 120 ℃ for 20 h). (e) DMA and BAIL Ⅰ (mix at 140 ℃ for 20 h); (f) $CH_3COOH$ and BAIL Ⅰ (mix at 140 ℃ for 20 h).

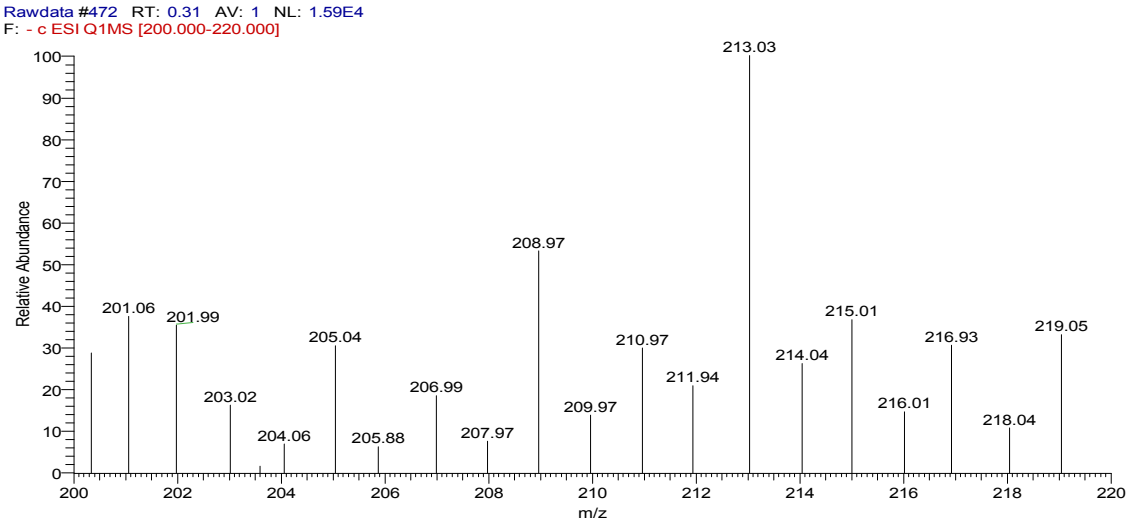



**Figure S6**. Mass spectrometric analysis on DMA/BAIL Ⅰ = 6/1 (mix at 140 ℃ for 20 h).

## Ⅳ General procedure for *N*-formylation of amines using formic acid

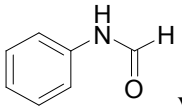
To a round-bottom flask were added amine (1.0 mmol, 1.0 equiv), HCOOH (184.1 mg, 4.0 mmol, 4.0 equiv) and BAIL Ⅰ (111 mg, 0.2 mmol, 0.2 equiv). The mixture was vigorously stirred at 80 °C for 20 h and the progress of the reaction was monitored by TLC visualized with UV short wavelengths followed by iodine or ninhydrin stain. Upon completion, the mixture was diluted with EtOAc (10 mL) and filtered. The filtrate was washed with 1 M hydrochloric acid (3 × 5 mL). The EtOAc layer was dried over anhydrous $Na_2SO_4$ and concentrated under vacuum to obtain pure *N*-formyl amine without column purification.

## Ⅴ General procedure for *N*-formylation of amines using DMF

To a round bottomed flask were added amine (1.0 mmol, 1.0 equiv), DMF (438.5 mg, 6.0 mmol, 6.0 equiv) and BAIL Ⅰ (111 mg, 0.2 mmol, 0.2 equiv). The mixture was vigorously stirred at 140 °C for 20 h and the progress of the reaction was monitored by TLC visualized with UV short wavelengths followed by iodine or ninhydrin stain. Upon completion, the mixture was diluted with EtOAc (10 mL) and filtered. The filtrate was

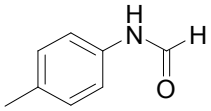
washed with 1 M hydrochloric acid (3 × 5 mL). The EtOAc layer was dried over anhydrous $Na_2SO_4$ and concentrated under vacuum to obtain pure *N*-formylamine without column purification.

***N*-phenyl-formamide(2a)** [1]



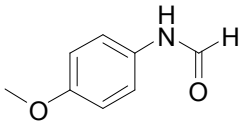
yellow solid, m.p. 47～48 ℃; the product was obtained in the form of 2 rotamers with a ratio of 3:1. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 10.20 (s, 0.75H), 10.17 (s, 0.25H), 8.82 (d, $J$ = 4.0 Hz, 0.25H), 8.32 (d, $J$ = 2.0 Hz, 0.75H), 7.64 (d, $J$ = 4.0 Hz, 1.5H), 7.31～7.35 (m, 2H), 7.22 (d, $J$ = 4.0 Hz, 0.5H), 7.06～7.11 (m, 1H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 163.04 (minor), 160.10 (major), 138.85 (minor), 138.78 (major), 129.89 (minor), 129.36 (major), 124.16 (minor), 124.12 (major), 119.69 (major), 118.09 (minor); HRMS: [M+Na$^+$] calcd for $C_7H_7NONa$ 144.0425, found 144.0424.

***N*-*p*-tolyl-formamide(2b)** [1]



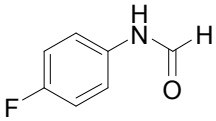
white solid, m.p. 47～49 ℃; the product was obtained in the form of 2 rotamers with a ratio of 3:1. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 10.08 (s, 0.75H), 10.03 (s, 0.25H), 8.72 (d, $J$ = 6.0 Hz, 0.25H), 8.25 (d, $J$ = 1.0 Hz, 0.75H), 7.49 (d, $J$ = 4.0 Hz, 1.5H), 7.12 (d, $J$ = 4.0 Hz, 2H), 7.08 (d, $J$ = 4.0 Hz, 0.5H), 2.25 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 162.94 (minor), 159.81 (major), 136.26, 133.21 (minor), 133.03 (major), 130.27 (minor), 129.70 (major), 119.61 (major), 118.19 (minor), 20.92 (major), 20.79 (minor); HRMS: [M+Na$^+$] calcd for $C_8H_9NONa$ 158.0582, found 158.0580.

***N*-(4-methoxy-phenyl)-formamide(2c)** [1]



white solid, m.p. 79～80 ℃; the product was obtained in the form of 2 rotamers with a ratio of 3:1. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 10.02 (s, 0.75H), 9.96 (d, $J$ = 6.0 Hz, 0.25H), 8.61 (d, $J$ = 6.0 Hz, 0.25H), 8.22 (d, $J$ = 1.0 Hz,, 0.75H), 7.52 (d, $J$ = 4.0 Hz, 1.5H), 7.12 (d, $J$ = 4.0 Hz, 0.5H)，6.87～6.92 (m, 2H), 3.72 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 163.05 (minor), 159.53 (major), 156.49 (minor), 155.88 (major), 131.95 (major), 131.76 (minor), 121.08 (major), 120.17 (minor), 115.08 (minor), 114.44 (major), 55.72 (minor), 55.63 (major); HRMS: [M+Na$^+$] calcd for $C_8H_9O_2NNa$ 174.0531, found 174.0528.

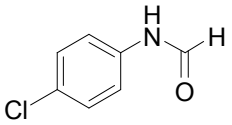
***N*-(4-fluoro-phenyl)-formamide(2d)** [2]



white solid, m.p. 62～64 ℃; the product was obtained in the form of 2 rotamers

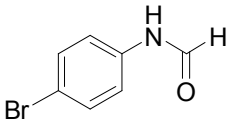
with a ratio of 3:1. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 10.24 (s, 0.75H), 10.15 (d, $J$ = 6.0 Hz, 0.25H), 8.72 (d, $J$ = 6.0 Hz, 0.25H), 8.27 (d, $J$ = 4.0 Hz, 0.75H), 7.62 (m, 1.5H), 7.22～7.25 (m, 0.5H), 7.14～7.19 (m, 2H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 163.16 (minor), 160.43 (minor), 159.95 (major), 159.80 (major), 158.05 (minor), 157.41 (major), 135.26 (minor), 135.23 (minor), 135.17 (major), 135.14 (major), 121.40 (major), 121.33 (major), 120.01 (minor), 119.93 (minor), 116.59 (minor), 116.37 (minor), 116.02 (major), 115.80 (major); HRMS: [M+Na$^+$] calcd for $C_7H_6FNONa$ 162.0331, found 162.0324.

***N*-(4-chloro-phenyl)-formamide(2e)** [1]



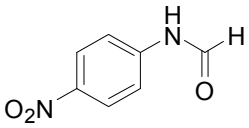
white solid, m.p. 100～102 ℃; the product was obtained in the form of 2 rotamers with a ratio of 4:1. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 10.33 (s, 0.8H), 10.24 (d, $J$ = 4.0 Hz, 0.2H), 8.81 (d, $J$ = 6.0 Hz, 0.2H), 8.31 (d, $J$ = 1.0 Hz, 0.8H), 7.62-7.66 (m, 1.6H), 7.36～7.40 (m, 2H)，7.24 (d, $J$ = 4.0 Hz, 0.4H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 163.01 (minor), 160.19 (major), 137.90 (minor), 137.65 (major), 129.70 (minor), 129.24 (major), 127.96 (minor), 127.65 (major), 121.19 (major), 119.46 (minor); HRMS: [M+Na$^+$] calcd for $C_7H_6ClNONa$ 178.0036, found 178.0036.

***N*-(4-bromo-phenyl)-formamide(2f)** [2]



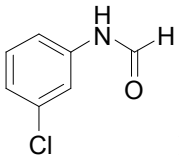
white solid, m.p. 113～115 ℃; the product was obtained in the form of 2 rotamers with a ratio of 4:1. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 10.33 (s, 0.8H), 10.23 (d, $J$ = 4.0 Hz, 0.2H), 8.81 (d, $J$ = 6.0 Hz, 0.2H), 8.31 (d, $J$ = 1.0 Hz,, 0.8H), 7.58 (d, $J$ = 4.0 Hz, 1.6H), 7.51 (m, 2H)，7.18 (d, $J$ = 4.0 Hz, 0.4H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 162.95 (minor), 160.22 (major), 138.32 (minor), 138.04 (major), 132.59 (minor), 132.14 (major), 121.55 (major), 119.80 (minor), 115.86 (minor), 115.63 (major); HRMS: [M+Na$^+$] calcd for $C_7H_6BrNONa$ 221.9530, found 221.9514.

***N*-(4-nitro-phenyl)-formamide(2g)** [1]



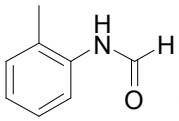
light yellow solid, m.p. 196～198 ℃; the product was obtained in the form of 2 rotamers with a ratio of 3:1. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 10.84 (s, 0.75H), 10.74 (s, 0.25H), 9.09 (s, 0.25H), 8.44 (s, 0.75H), 8.25 (d, $J$ = 4.0 Hz, 2H), 7.85 (d, $J$ = 4.0 Hz, 1.5H)，7.45 (d, $J$ = 4.0 Hz, 0.5H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 163.31 (minor), 161.01 (major), 145.48 (minor), 144.72 (major), 143.09 (major), 143.00 (minor), 125.98 (minor), 125.59 (major), 119.51 (major), 117.07 (minor); HRMS: [M+Na$^+$] calcd for $C_7H_6O_3N_2Na$ 189.0276, found 189.0278.

***N*-(3-chloro-phenyl)-formamide(2h)** [3]



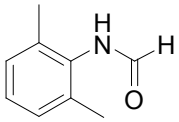
light yellow solid, m.p. 56～58 ℃; the product was obtained in the form of 2 rotamers with a ratio of 3:1. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 10.39 (s, 0.75H), 10.26 (d, $J$ = 4.0 Hz, 0.25H), 8.86 (d, $J$ = 4.0 Hz, 0.25H), 8.32(d, $J$ = 1.0 Hz, 0.75H), 7.81 (m, 0.75H), 7.46 (d, $J$ = 4.0 Hz, 0.75H), 7.33～7.38 (m, 1H), 7.32 (m, 0.25H), 7.18 (d, $J$ = 4.0 Hz, 0.25H), 7.12～7.15 (m, 1H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 163.08 (minor), 160.46 (major), 140.56 (minor), 140.09 (major), 134.26 (minor), 133.62 (major), 131.48 (minor), 131.06 (major), 123.82 (major), 123.65 (minor), 119.18 (major), 118.00 (major), 117.34 (major), 116.24 (major); HRMS: [M+Na$^+$] calcd for $C_7H_6ClNONa$ 178.0036, found 178.0027.

***N*-*o*-tolyl-formamide(2i)** [4]



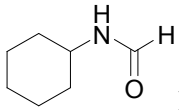
light yellow solid, m.p. 56～57 ℃; the product was obtained in the form of 2 rotamers with a ratio of 7:3. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 9.73 (d, $J$ = 4.0 Hz, 0.3H), 9.55 (s, 0.7H), 8.42 (d, $J$ = 8.0 Hz, 0.3H), 8.30 (d, $J$ = 2.0 Hz, 0.7H), 7.73～7.75 (m, 0.7H), 7.20～7.23 (m, 1.3H)，7.14～7.18 (m, 1H), 7.09～7.13 (m, 0.3H), 7.03～7.07(m, 0.7H), 2.24 (s, 0.9H), 7.23 (s, 2.1H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 164.08 (minor), 160.26 (major), 136.69 (minor), 136.13 (major), 131.26 (minor), 130.85 (major), 130.80 (minor), 129.74 (major), 127.22 (minor), 126.57 (major), 125.76 (minor), 125.10 (major), 123.30 (major), 122.32 (minor), 18.29 (major), 18.15 (minor); HRMS: [M+H$^+$] calcd for $C_8H_{10}NO$ 136.0762, found 136.0765.

***N*-(2,6-dimethyl-phenyl)-formamide(2j)** [5]



white solid, m.p. 158～159 ℃; the product was obtained in the form of 2 rotamers with a ratio of 5:1. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 9.44 (s, 0.83H), 9.28 (d, $J$ = 6.0 Hz, 0.17H), 8.25 (s, 0.83H), 7.98 (d, $J$ = 6.0 Hz, 0.17H), 7.10～7.14 (m, 0.5H), 7.04～7.09 (m, 2.5H)，2.22 (s, 1H), 2.15 (s, 5H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 165.14 (minor), 159.81 (major), 135.43 (minor), 135.19 (major), 134.95 (minor), 134.50 (major), 128.76 (minor), 128.18 (major), 127.26 (minor), 127.03 (major), 18.86 (minor), 18.75 (major); HRMS: [M+H$^+$] calcd for $C_9H_{12}NO$ 150.0919, found 150.0918.

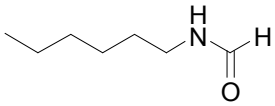
***N*-cyclohexyl-formamide(2k)** [3]



light yellow oil; The product was obtained in the form of 2 rotamers with a ratio of 9:1. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 7.95 (d, $J$ = 6.0 Hz, 0.9H), 7.87 (s, 0.9H), 7.70-7.75 (m, 0.1H), 7.49-7.60 (m, 0.9H), 3.52～3.57 (m, 0.9H), 3.11-3.19 (m, 0.1H), 1.59～1.68 (m, 4H), 1.49 (d, $J$ = 4.0

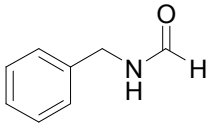
Hz, 1H), 1.08～1.23 (m, 5H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 163.93 (minor), 160.44 (major), 50.68 (minor), 46.54 (major), 34.72 (minor), 32.84 (major), 25.66 (major), 25.35 (minor), 25.09 (minor), 24.88 (major); HRMS: [M+H$^+$] calcd for $C_7H_{14}NO$ 128.1075, found 128.1078.

***N*-hexyl-formamide(2l)** [3]



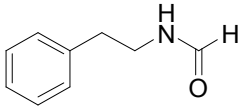
light yellow oil; the product was obtained in the form of 2 rotamers with a ratio of 9:1. $^1$H NMR (DMSO-$d_6$, 400 MHz) δ = 7.99 (s, 1.8H), 7.94 (s, 0.1H), 7.91 (s. 0.1H), 3.04～3.09 (m, 2H), 1.36～1.41 (m, 2H), 1.25～1.30 (m, 6H), 0.86 (m, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 164.97 (minor), 161.38 (major), 41.38 (minor), 37.58 (major), 31.50 (major), 31.43 (minor), 29.53, 26.60 (major), 26.11 (minor), 22.63, 14.43; HRMS: [M+H$^+$] calcd for $C_7H_{16}NO$ 130.1232, found 130.1234.

***N*-benzyl-formamide(2m)** [4]



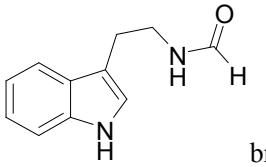
light yellow solid, 62～63 ℃; the product was obtained in the form of 2 rotamers with a ratio of 9:1. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 8.53 (s, 1H), 8.16 (s, 0.9H), 8.14 (d, $J$ = 6.0 Hz, 0.1H), 7.33～7.37 (m, 2H), 7.26-7.30 (m, 3H), 4.32 (d, $J$ = 2.0 Hz, 2H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 165.44 (minor), 161.56 (major), 140.19 (minor), 139.52 (major), 128.97 (minor), 128.86 (major), 127.82 (major), 127.60 (minor), 127.57 (minor), 127.40 (minor), 45.08 (minor), 41.25 (major); HRMS: [M+Na$^+$] calcd for $C_8H_9NONa$ 158.0582, found 158.0577.

***N*-phenethyl-formamide(2n)** [6]



light yellow oil; the product was obtained in the form of 2 rotamers with a ratio of 9:1. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 8.06 (s, 0.9H), $\delta$ = 8.01 (s, 0.9H), 7.79 (d, $J$ = 6.0 Hz, 0.1H), 7.75 (s, 0.1H), 7.28～7.31 (m, 2H), 7.19～7.23 (m, 3H), 3.31～3.36 (m, 2H), 2.72～2.75 (m, 2H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 164.90 (minor), 161.53 (major), 139.74 (major), 139.24 (minor), 129.37 (minor), 129.11 (major), 128.82, 126.69 (minor), 126.62 (major), 42.96 (minor), 39.20 (major), 37.62 (minor), 35.50 (major); HRMS: [M+Na$^+$] calcd for $C_9H_{11}NONa$ 172.0738, found 172.0736.

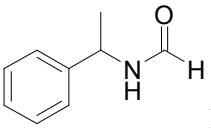
***N*-[2-(1*H*-indol-3-yl)-ethyl]-formamide(2o)** [7]



brown oil; the product was obtained in the form of 2 rotamers with a ratio of 9:1. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ =10.83 (s, 1H), 8.08 (s, 0.9H), 8.04 (s, 0.9H), 7.83 (d, $J$ = 6.0 Hz, 0.1H), 7.75 (d, $J$ = 4.0 Hz, 0.1H), 7.54 (d, $J$ = 4.0 Hz, 1H), 7.35 (d, $J$ = 4.0 Hz, 1H), 7.17 (d, $J$ = 2.0 Hz, 0.9H), 7.15 (d, $J$ = 1.0 Hz, 0.1H), 7.05～7.09 (m, 1H), 6.97～7.01 (m, 1H), 3.34～3.39 (m, 2H), 2.83～2.87 (m, 2H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 164.95 (minor), 161.60 (major), 136.77,

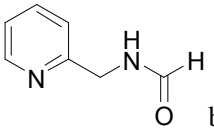
127.68, 127.63 (minor), 123.57 (minor), 123.23 (major), 121.46 , 118.79 (major), 118.78, 118.74, 112.09 (major), 112.09, 111.90(major), 111.55 (minor), 42.28 (minor), 38.56 (major), 27.72 (minor), 25.62 (major); HRMS: [M+Na$^+$] calcd for $C_{11}H_{12}N_2ONa$ 211.0847, found 211.0839.

***N*-(1-phenyl-ethyl)-formamide(2p)** [7]



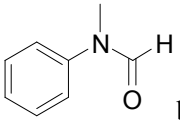
light yellow oil; the product was obtained in the form of 2 rotamers with a ratio of 9:1. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 8.54 (d, $J$ = 2.0 Hz, 0.9H), 8.28 ～8.33(m, 0.1H), 8.09 (d, $J$ = 4.0 Hz, 0.1H), 8.04 (s, 0.9H), 7.31～7.35 (m, 4H), 7.21～7.26 (m, 1H), 4.96～5.03 (m, 0.9H), 4.65～4.73 (m, 0.1H), 1.41 (d, $J$ = 4.0 Hz, 0.3H), 1.36 (d, $J$ = 4.0 Hz, 2.7H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 164.47 (minor), 160.57 (major), 145.22 (minor), 144.62 (major), 128.93 (minor), 128.80 (major), 127.41 (minor), 127.25 (major), 126.44 (major), 126.37 (minor), 51.27 (minor), 47.05 (major), 23.91 (minor), 22.93 (major); HRMS: [M+Na$^+$] calcd for $C_9H_{11}NONa$ 172.0738, found 172.0736.

**N-pyridin-2-ylmethyl-formamide(2q)** [7]



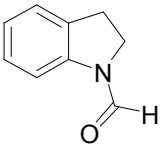
brown oil; the product was obtained in the form of 2 rotamers with a ratio of 9:1. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 8.59 (s, 1H), 8.51 (d, $J$ = 4.0 Hz, 1H), 8.18 (s, 0.9H), 8.14 (s, 0.1H), 7.75～7.79 (m, 1H), 7.31 (d, $J$ = 4.0 Hz, 1H), 7.26～7.29 (m, 1H), 4.40 (d, $J$ = 2.0 Hz, 1H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 165.86 (minor), 161.82 (major), 159.23 (minor), 158.46 (major), 149.61 (minor), 149.41 (major), 137.44 (minor), 137.30 (major), 122.94 (minor), 122.73 (major), 121.74 (minor), 121.65 (major), 46.99 (minor), 43.30 (major); HRMS: [M+Na$^+$] calcd for $C_7H_8N_2ONa$ 159.0534, found 159.0539.

***N*-methyl-*N*-phenyl-formamide(2r)** [3]



brown oil; the product was obtained in the form of 2 rotamers with a ratio of 9:1. .m.p. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 8.53 (s, 0.9H), 8.35 (s, 0.1H), 7.49 (d, $J$ = 4.0 Hz, 0.2H), 7.40～7.44 (m, 2H), 7.33 (d, $J$ = 4.0 Hz, 1.8H), 7.23～7.27 (m, 1H), 3.21 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 163.06 (minor), 162.55 (major), 142.56 (major), 140.95 (minor), 129.91 (major), 129.17 (minor), 126.09 (major), 125.89 (minor), 123.53 (minor), 121.99 (major), 36.61 (minor), 31.50 (major); HRMS: [M+Na$^+$] calcd for $C_8H_9NONa$ 158.0582, found 158.0577.

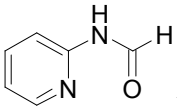
**2,3-dihydro-indole-1-carbaldehyde(2s)** [7]



light yellow solid, 62～64 ℃; The product was obtained in the form of 2 rotamers with a ratio of 3:1. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 9.07 (s, 0.75H), 8.51 (s, 0.25H), 7.94 (d, $J$ = 4.0 Hz,

0.25H), 7.46 (d, $J$ = 4.0 Hz, 0.75H), 7.30 (d, $J$ = 4.0 Hz, 1H), 7.18～7.22 (m, 1H), 7.03～7.07 (m, 1H), 4.13～4.17 (m, 0.5H), 3.91～3.96 (m, 1.5H), 3.10～3.15 (m, 2H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 160.62 (minor), 158.88 (major), 141.75 (minor), 141.68 (major), 133.15 (minor), 132.23 (major), 127.80 (major), 127.52 (minor), 126.31 (major), 125.63 (minor), 124.56 (major), 124.13 (minor), 115.98 (minor), 110.35 (major), 46.95 (minor), 44.63 (major), 27.67 (minor), 27.08 (major); HRMS: [M+Na$^+$] calcd for $C_9H_9NONa$ 170.0582, found 170.0582.

***N*-pyridin-2-yl-formamide(2t)** [4]



white solid, m.p. 70～71 ℃; the product was obtained in the form of 2 rotamers with a ratio of 1:1. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 10.60 (s, 1H), 9.30 (d, $J$ = 4.0 Hz, 0.5H), 8.34 (s, 1H), 8.26 (d, $J$ = 1.0 Hz 0.5H), 8.07 (d, $J$ = 4.0 Hz, 0.5H), 7.73～7.82 (m, 1H), 7.08～7.13 (m, 1H), 6.94(s, $J$ = 4.0 Hz, 0.5H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 162.66, 160.64, 152.16, 151.55, 148.69, 148.58, 139.25, 138.86, 120.30, 119.76, 114.30, 111.85; HRMS: [M+Na$^+$] calcd for $C_6H_6N_2ONa$ 145.0378, found 145.0379.

## Ⅵ General procedure A: *N*-acylation of amines using HAc

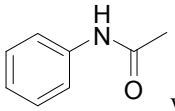
To a round bottomed flask were added amine (1.0 mmol, 1.0 equiv), HAc (240.2 mg, 4.0 mmol, 4.0 equiv) and BAIL Ⅰ (111 mg, 0.2 mmol, 0.2 equiv). The mixture was vigorously stirred at given temperature for 20 h and the progress of the reaction was monitored by TLC visualized with UV short wavelengths followed by iodine or ninhydrin stain. After completion, the mixture was diluted with EtOAc (10 mL) and filtered. The filtrate was washed with 1 M hydrochloric acid (3 × 5 mL). The EtOAc layer was dried over anhydrous $Na_2SO_4$ and concentrated under vacuum to obtain pure acetamide without column purification.

## Ⅶ General procedure B: *N*-acylation of amines using DMA

To a round bottomed flask were added amine (1.0 mmol, 1.0 equiv), DMA (522.7 mg, 6.0 mmol, 6.0 equiv) and BAIL Ⅰ (111 mg, 0.2 mmol, 0.2 equiv). The mixture was vigorously stirred at 140 °C for 20 h and the progress of the reaction was monitored by TLC visualized with UV short wavelengths followed by iodine or ninhydrin stain. After completion, the mixture was diluted with EtOAc (10 mL), then filtered the precipitate formed and filtrate was washed with 1 M hydrochloric acid (3 X 5 mL). The EtOAc layer

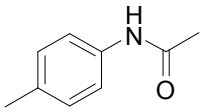
was dried over anhydrous $Na_2SO_4$ and concentrated under vacuum to obtain afforded pure acetamide without column purification.

***N*-phenyl-acetamide(3a)** [1]



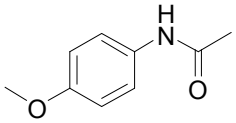
white solid, mp: 113～114 ℃. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 9.92 (s, 1H), 7.58 (d, $J$ = 4.0 Hz, 2H), 7.27～7.31 (m, 2H), 7.01～7.04 (m, 1H), 2.05 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 168.77, 139.86, 129.17, 123.47 , 119.49, 24.52 ; HRMS: [M+Na$^+$] calcd for $C_8H_9NNaO$ 158.0582, found 158.0585.

***N*-*p*-tolyl-acetamide(3b)** [1]



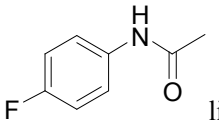
white solid, mp: 150～152 ℃. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 9.83 (s, 1H), 7.47 (d, $J$ = 4.0 Hz, 2H), 7.09 (d, $J$ = 4.0 Hz, 2H), 2.25 (s, 3H), 2.03 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 168.51, 137.37, 132.31, 129.53, 119.51, 24.45, 20.93; HRMS: [M+Na$^+$] calcd for $C_9H_{11}NNaO$ 172.0738, found 172.0736.

***N*-(4-methoxy-phenyl)-acetamide(3c)** [8]



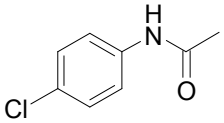
white solid, mp: 126～128 ℃. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 9.77 (s, 1H), 7.48 (d, $J$ = 4.0 Hz, 2H), 6.87 (d, $J$ = 4.0 Hz, 2H), 3.72 (s, 3H), 2.01 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 168.22, 155.52, 133.06, 121.04, 114.29, 55.64, 24.32; HRMS: [M+Na$^+$] calcd for $C_9H_{11}NNaO_2$ 188.0687, found 188.0678.

***N*-(4-fluoro-phenyl)-acetamide(3d)** [9]



light yellow solid, mp: 150～152 ℃. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 9.98 (s, 1H), 7.60 (d, $J$ = 4.0 Hz, 2H), 7.13 (d, $J$ = 4.0 Hz, 2H), 2.05 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 168.66, 158.33 (d, $^1J_{CF}$ = 238.0 Hz), 136.25 (d, $^4J_{CF}$ = 2.0 Hz), 121.19 (d, $^3J_{CF}$ = 8.0 Hz), 115.69 (d, $^2J_{CF}$ = 22.0 Hz), 24.37; HRMS: [M+Na$^+$] calcd for $C_8H_8FNNaO$ 176.0488, found 176.0492.

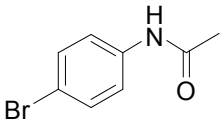
***N*-(4-chloro-phenyl)-acetamide(3e)** [2]



light yellow solid, mp: 176～178℃. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 10.06 (s, 1H), 7.62 (d, $J$ = 6.0 Hz, 2H), 7.35 (d, $J$ = 4.0 Hz, 2H), 2.05 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 168.95, 138.79, 129.08, 127.00, 120.98, 24.51; HRMS: [M+Na$^+$] calcd for $C_8H_8ClNNaO$ 192.0192,

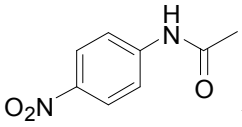
found 192.0182.

***N*-(4-bromo-phenyl)-acetamide(3f)** [2]



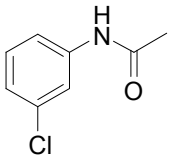
yellow solid, mp: 167～169℃. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 10.07 (s, 1H), 7.57 (d, $J$ = 4.0 Hz, 2H), 7.46 (d, $J$ = 6.0 Hz, 2H), 2.05 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 168.97, 139.21, 131.97, 121.38, 115.00, 24.54; HRMS: [M+Na$^+$] calcd for $C_8H_8BrNNaO$ 235.9687, 237.9666, found 235.9690, 237.9689.

***N*-(4-nitro-phenyl)-acetamide(3g)** [10]



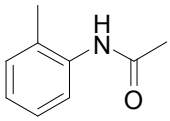
yellow solid, mp: 210～213 ℃. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 10.55(s, 1H), 8.21 (d, $J$ = 4.0 Hz, 2H), 7.83 (d, $J$ = 6.0 Hz, 2H), 2.13 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 169.86, 145.97, 142.50, 125.48, 119.05, 24.75; HRMS: [M+Na$^+$] calcd for $C_8H_8N_2NaO_3$ 203.0433, found 203.0428.

***N*-(3-chloro-phenyl)-acetamide(3h)** [2]



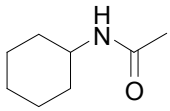
yellow solid, mp: 75～76 ℃. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 10.12 (s, 1H), 7.82 (s, 1H), 7.43 (d, $J$ = 4.0 Hz, 1H), 7.29～7.33 (m, 1H), 7.07 (d, $J$ = 4.0 Hz, 2H), 2.07 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 169.18, 141.27, 133.56, 130.81, 123.16, 118.94, 117.79, 24.54; HRMS: [M+Na$^+$] calcd for $C_8H_8ClNNaO$ 192.0192, found 192.0188.

***N*-*o*-tolyl-acetamide(3i)** [11]



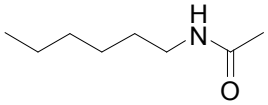
white solid, mp: 98～100 ℃. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 9.28 (s, 1H), 7.39 (d, $J$ = 4.0 Hz, 1H), 7.19 (d, $J$ = 4.0 Hz, 1H), 7.12～7.16 (m, 2H), 7.04～7.07 (m, 2H), 2.19 (s, 3H), 2.05 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 168.65, 137.01, 132.02, 130.73, 126.36, 125.50, 125.47, 23.79, 18.40; HRMS: [M+Na$^+$] calcd for $C_9H_{11}NNaO$ 172.0738, found 172.0732.

***N*-cyclohexyl-acetamide(3k)** [9]



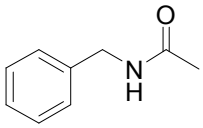
light yellow oil; $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 7.70 (d, $J$ = 4.0 Hz, 1H), 3.45-3.52(m, 1H), 1.76 (s, 3H), 1.64～1.72 (m, 4H), 1.06～1.28 (m, 6H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 168.49, 47.85, 35.05, 25.76, 25.13, 23.27; HRMS: [M+H$^+$] calcd for $C_8H_{14}NNaO$ 164.1051, found 164.1045.

***N*-hexyl-acetamide(3l)** [9]



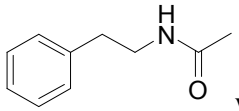
light yellow oil; $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 7.80(s, 1H), 2.97～3.02(m, 2H), 1.78 (s, 3H), 1.24～1.36 (m, 8H), 0.85～0.87 (m, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 169.35, 39.00, 31.54, 29.64, 26.66, 23.11, 22.60, 14.44; HRMS: [M+H$^+$] calcd for $C_8H_{17}NNaO$ 166.1208, found 166.1202.

***N*-benzyl-acetamide(3m)** [9]



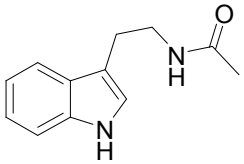
white solid, mp: 60～62℃.$^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 8.33 (s, 1H), 7.30～7.33 (m, 2H), 7.21～7.25 (m, 3H), 4.24 (d, $J$ = 2.0 Hz, 2H), 1.87(s, 3H), 2.07 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 169.63, 140.14, 128.78, 127.78, 127.24, 42.63, 23.09; HRMS: [M+Na$^+$] calcd for $C_9H_{11}NNaO$ 172.0738, found 172.0732.

***N*-phenethyl-acetamide(3n)** [12]



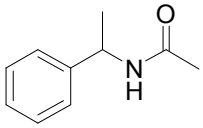
white solid, mp: 52～54℃. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ =7.93 (s, 1H), 7.28～7.32 (m, 2H), 7.19～7.22 (m, 3H), 3.24～3.26 (m, 2H), 2.70～2.73(m, 2H), 1.08 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 169.57, 140.06, 129.11, 128.82, 126.56, 40.74, 35.75, 23.13; HRMS: [M+Na$^+$] calcd for $C_{10}H_{13}NNaO$ 186.0895, found 186.0888.

***N*-[2-(1*H*-indol-3-yl)-ethyl]-acetamide(3o)** [13]



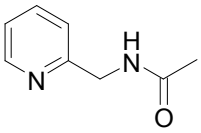
brown solid, mp: 75～77℃. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ =10.81 (s, 1H), 7.93～7.95 (m, 1H), 7.53 (d, $J$ = 4.0 Hz, 1H), 7.34 (d, $J$ = 4.0 Hz, 1H), 7.14 (d, $J$ = 2.0 Hz, 1H), 7.05～7.09 (m, 1H), 6.96～7.00 (m, 1H), 3.30～3.35(m, 2H), 2.80～2.84(m, 2H), 1.81(s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 169.54, 136.75, 127.76, 123.10, 121.42, 118.74, 112.40, 111.88, 60.29, 25.77, 23.24, 21.29; HRMS: [M+Na$^+$] calcd for $C_{12}H_{14}N_2NaO$ 225.1004, found 225.0989.

***N*-(1-phenyl-ethyl)-acetamide(3p)** [14]



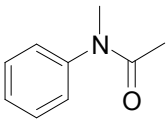
white solid, mp: 99～101℃. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ =8.36 (s, 1H), 7.31～7.33 (m, 4H), 7.21～7.24 (m, 1H), 4.89～4.96 (m, 1H), 1.86(s, 3H), 1.35(d, $J$ = 2.0 Hz, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 168.79, 145.35, 128.72, 127.05, 126.49, 48.30, 23.17, 23.03; HRMS: [M+Na$^+$] calcd for $C_{10}H_{13}NNaO$ 186.0895, found 186.0882.

***N*-pyridin-2-ylmethyl-acetamide(3q)** [15]



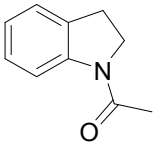
white solid, mp: 58～59℃. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ =8.50 (d, $J$ = 2.0 Hz, 1H), 8.44 (s, 1H), 7.73～7.77 (m, 1H), 7.24～7.29 (m, 2H), 4.35 (d, $J$ = 4.0 Hz, 2H), 1.91 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 169.94, 159.24, 149.33, 137.19, 122.57, 121.54, 44.73, 23.07; HRMS: [M+Na$^+$] calcd for $C_8H_{10}N_2NaO$ 173.0691, found 173.0684.

***N*-methyl-*N*-phenyl-acetamide(3r)** [14]



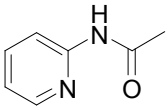
white solid, mp: 98～100 ℃. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 7.43～7.47 (m, 2H), 7.33～7.35 (m, 3H), 3.14 (s, 3H), 1.75 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 169.46, 144.90, 130.10, 127.91, 127.60, 37.05, 22.73; HRMS: [M+Na$^+$] calcd for $C_9H_{11}NNaO$ 172.0738, found 172.0732.

**1-(2,3-Dihydro-indol-1-yl)-ethanone(3s)** [16]



light yellow solid, 101～103℃. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ =8.06 (d, $J$ = 4.0 Hz, 1H), 7.22(d, $J$ = 4.0 Hz, 1H), 7.12～7.16(m, 1H), 6.97～7.00 (m, 1H), 4.04～4.09 (m, 2H), 3.11～3.15 (m, 2H), 2.15 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 169.01, 143.42, 132.22, 127.42, 125.28, 123.54, 116.30, 48.61, 27.87, 24.52; HRMS: [M+Na$^+$] calcd for $C_{10}H_{11}NNaO$ 184.0738, found 184.0732.

***N*-pyridin-2-yl-acetamide(3t)** [9]



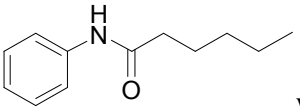
white solid, m.p. 69～71℃. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ =10.47 (s, 1H), 8.29 (d, $J$ = 2.0 Hz, 1H), 8.06 (d, $J$ = 4.0 Hz, 1H), 7.73～7.78 (m, 1H), 7.06～7.09 (m, 1H), 2.09 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 169.80, 152.64, 148.41, 138.61, 119.72, 113.83, 24.43; HRMS: [M+Na$^+$] calcd for $C_7H_8N_2NaO$ 159.0534, found 159.0528.

## Ⅷ General procedure for the amidation of carboxylic acids with amines

To a round bottomed flask were added amine (1.0 mmol, 1.0 equiv), carboxylic acids (reference to Table 5 in main article) and BAIL Ⅰ (111 mg, 0.2 mmol, 0.2 equiv). After warming to the given temperature, the mixture became a viscous liquid, which was vigorously stirred for 20 h. The progress of the reaction was monitored by TLC visualized with UV short wavelengths followed by iodine or ninhydrin stain. After

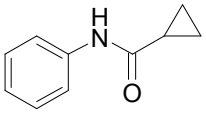
completion, the mixture was diluted with EtOAc (10 mL)and filtered. The filtrate was washed with 1 M hydrochloric acid (3 × 5 mL). The EtOAc layer was dried over anhydrous $Na_2SO_4$ and concentrated under vacuum to obtain pure product without column purification.

**Hexanoic acid phenylamide(4a)** [17]



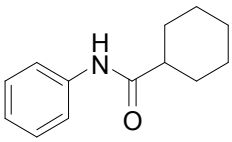
white solid, mp: 95～97 ℃. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 9.88 (s, 1H), 7.60 (d, $J$ = 4.0 Hz, 2H), 7.26～7.30 (m, 2H), 7.01～7.03 (m, 1H), 7.27～7.31 (m, 2H), 1.55～1.63 (m, 2H), 1.23～1.34 (m, 4H), 0.86～0.89 (m, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 171.75, 139.88, 129.14, 123.39 , 119.47, 36.89, 31.43, 25.34, 22.45, 14.41 ; HRMS: [M+Na$^+$] calcd for $C_{12}H_{17}NNaO$ 214.1208, found 214.1202.

**Cyclopropanecarboxylic acid phenylamide(4b)** [11]



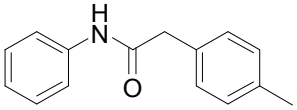
white solid, mp: 108～110 ℃. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 10.11 (s, 1H), 7.55 (d, $J$ = 4.0 Hz, 2H), 7.22～7.25 (m, 2H), 6.95～6.99 (m, 1H), 1.70～1.75(m, 1H), 0.73-～0.76 (m, 4H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 172.11, 139.90, 129.19, 123.39 , 119.47, 15.05, 7.64; HRMS: [M+Na$^+$] calcd for $C_{10}H_{11}NNaO$ 184.0738, found 184.0729.

**Cyclohexanecarboxylic acid phenylamide(4c)** [11]



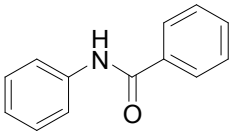
white solid, mp: 140～142 ℃. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 9.81 (s, 1H), 7.60 (d, $J$ = 4.0 Hz, 2H), 7.25～7.29 (m, 2H), 6.99～7.02 (m, 1H), 2.28～2.35(m, 1H), 1.74～1.81 (m, 4H), 1.36～1.45(m, 2H), 1.16～1.31(m, 4H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 174.79, 140.02, 129.12, 123.33 , 119.49, 45.36, 29.65, 25.91, 25.76; HRMS: [M+Na$^+$] calcd for $C_{13}H_{17}NNaO$ 226.1208, found 226.1195.

***N*-Phenyl-2-p-tolyl-acetamide(4d)** [18]



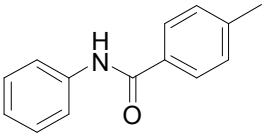
white solid, mp: 149～151 ℃. $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 10.10 (s, 1H), 7.59 (d, $J$ = 4.0 Hz, 2H), 7.26～7.30 (m, 2H), 7.22 (d, $J$ = 4.0 Hz, 2H), 7.12 (d, $J$ = 4.0 Hz, 2H), 7.01～7.04 (m, 1H), 3.58 (s, 2H), 2.27 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 169.78, 139.78, 136.05, 133.46, 129.47, 129.38, 129.22, 123.68, 119.58, 43.48, 21.18; HRMS: [M+Na$^+$] calcd for $C_{15}H_{15}NNaO$ 248.1051, found 248.1039.

***N*-Phenyl-benzamide(4e)** [17]



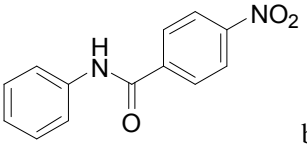
white solid, mp: 161～163 ℃. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 10.26 (s, 1H), 7.96 (d, $J$ = 6.0 Hz, 2H), 7.78 (d, $J$ = 4.0 Hz, 2H), 7.58～7.62(m, 1H), 7.52～7.55(m, 2H), 7.34～7.37 (m, 2H), 7.08～7.12 (m, 1H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 166.08, 139.69, 135.51, 132.08, 129.14, 128.92, 128.18, 124.18, 120.86; HRMS: [M+Na$^+$] calcd for $C_{13}H_{11}NNaO$ 220.0738, found 220.0733.

**4-Methyl-*N*-phenyl-benzamide(4f)** [19]



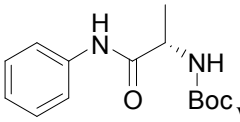
white solid, mp: 146～148 ℃. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 10.16 (s, 1H), 7.88 (d, $J$ = 4.0 Hz, 2H), 7.78 (d, $J$ = 4.0 Hz, 2H), 7.33～7.36 (m, 4H), 7.07～7.11 (m, 1H), 2.39 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 165.83, 142.05, 139.73, 132.58, 129.40, 129.07, 128.18, 124.03, 120.82, 21.52; HRMS: [M+Na$^+$] calcd for $C_{14}H_{13}NNaO$ 234.0895, found 234.0889.

**4-Nitro-*N*-phenyl-benzamide(4g)** [20]



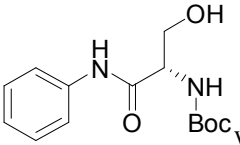
brown solid, mp: 146～148 ℃. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 10.83 (s, 1H), 8.37 (d, $J$ = 6.0 Hz, 2H), 8.20 (d, $J$ = 4.0 Hz, 2H), 7.79 (d, $J$ = 4.0 Hz, 2H), 7.36～7.40 (m, 2H), 7.13～7.16 (m, 1H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 164.39, 149.62, 141.13, 139.22, 129.73, 129.22, 124.67, 124.05, 120.97, ; HRMS: [M+Na$^+$] calcd for $C_{13}H_{10}N_2NaO_3$ 265.0589, found 265.0582.

**Compound (4h)**



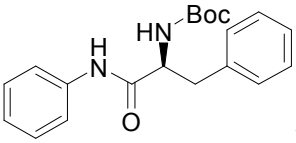
white solid, mp: 144～147 ℃. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 9.90 (s, 1H), 7.59 (d, $J$ = 4.0 Hz, 2H), 7.28～7.32 (m, 2H), 7.02～7.06 (m, 2H), 4.08～4.15 (m, 1H), 1.38 (s, 9H), 1.25 (d, $J$ = 2.0 Hz, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 172.32, 155.65, 139.56, 129.15, 123.60, 119.58, 78.48, 50.88, 28.68, 18.50; HRMS: [M+Na$^+$] calcd for $C_{14}H_{20}N_2NaO_3$ 287.1372, found 287.1367.

**Compound (4i)**



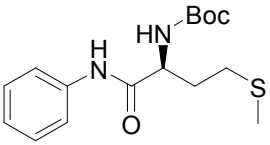
white solid, mp: 85-87 ℃. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ = 9.96 (s, 1H), 7.62 (d, $J$ = 4.0 Hz, 2H), 7.28～7.32 (m, 2H), 7.02～7.06 (m, 2H), 6.79 (d, $J$ = 4.0 Hz, 2H), 4.94～4.97 (m, 1H), 3.60～3.64 (m, 2H), 1.39 (s, 9H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 169.97, 155.74, 139.52, 129.19, 123.72, 119.65, 78.73, 62.33, 57.88, 28.69; HRMS: [M+Na$^+$] calcd for $C_{14}H_{20}N_2NaO_4$ 303.1321, found 303.1318.

**Compound (4j)**



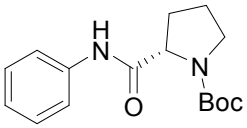
white solid, mp: 117-119 ℃. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ =10.03(s, 1H), 7.55 (d, $J$ = 4.0 Hz, 2H), 7.22～7.30 (m, 6H), 7.11～7.17 (m, 2H), 6.99～7.03 (m, 1H), 4.27～4.29 (m, 1H), 2.77～2.96 (m, 2H), 1.27 (s, 9H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 171.38, 155.96, 139.47, 138.51, 129.78, 129.26, 128.57, 126.81, 123.81, 119.75, 78.59, 57.11, 37.95, 28.68; HRMS: [M+Na$^+$] calcd for $C_{20}H_{24}N_2NaO_3$363.1685, found 363.1679.

**Compound (4k)**



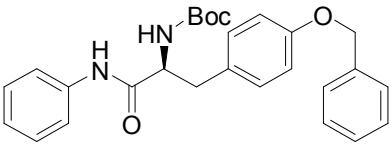
white solid, mp: 104-107℃. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ =10.00(s, 1H), 7.60(d, $J$ = 4.0 Hz, 2H), 7.29～7.33 (m, 2H), 7.18 (d, $J$ = 4.0 Hz, 2H), 7.03～7.07 (m, 1H), 4.12～4.17 (m, 1H), 2.46～2.53 (m, 2H), 2.05 (s, 3H), 1.84～1.92 (m, 2H), 1.38 (s, 9H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 171.40, 155.06, 139.48, 129.23, 123.76, 119.73, 78.64, 54.90, 32.06, 30.33, 28.71, 15.15; HRMS: [M+Na$^+$] calcd for $C_{16}H_{24}N_2NaO_3S$ 347.1405, found 347.1418.

**Compound (4l)**



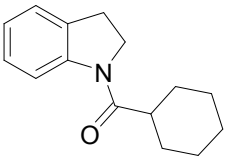
white solid, mp: 181～183 ℃. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ =9.98(s, 1H), 7.60(d, $J$ = 4.0 Hz, 2H), 7.28～7.30 (m, 2H), 7.02～7.06 (m, 1H), 4.17～4.27 (m, 1H), 3.32～3.41 (m, 2H), 1.76～2.22 (m, 4H), 1.27～1.40 (m, 9H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 172.01, 153.67, 139.60, 129.23, 123.71, 119.74, 78.98, 60.88, 47.08, 31.52, 28.46, 23.93; HRMS: [M+Na$^+$] calcd for $C_{16}H_{22}N_2NaO_3$ 313.1528, found 313.1520.

**Compound (4m)**



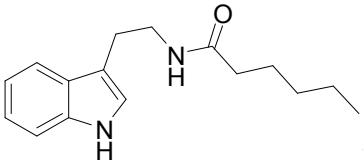
white solid, mp: 161～163 ℃. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ =10.05(s, 1H), 7.59(d, $J$ = 4.0 Hz, 2H), 7.37～7.45 (m, 4H), 7.29～7.34 (m, 3H), 7.24 (d, $J$ = 4.0 Hz, 2H), 7.11 (d, $J$ = 6.0 Hz, 1H), 7.03～7.07 (m, 1H), 6.93 (d, $J$ = 4.0 Hz, 2H), 5.06 (s, 2H), 4.22～4.28 (m, 1H), 2.76～2.93 (m, 2H), 1.32(s, 9H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 171.45, 157.43, 155.96, 139.47, 137.70, 130.77, 130.60, 129.25, 128.92, 128.28, 128.18, 123.77, 119.72, 114.84, 78.56, 69.60, 57.35, 37.06, 28.68.; HRMS: [M+Na$^+$] calcd for $C_{27}H_{30}N_2NaO_4$ 469.2103, found 469.2098.

**Compound (4n)** [21]



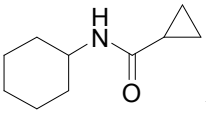
white solid, mp:128-130 ℃. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ =8.10 (d, $J$ = 4.0 Hz, 1H), 7.21 (d, $J$ = 4.0 Hz, 1H), 7.10～7.14 (m, 1H), 6.95～6.98 (m, 1H), 4.12～4.16 (m, 2H), 3.10～3.15 (m, 2H), 2.51～2.56 (m, 1H), 1.65～1.81 (m, 5H), 1.18～1.45 (m, 5H), 2.03～2.07 (m, 2H), 1.48～1.51 (m, 2H), 1.20～1.28 (m, 4H), 0.83～0.87 (m, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 174.39, 143.66, 132.37, 127.31, 125.16, 123.51, 116.71, 47.82, 43.11, 29.14, 27.88, 26.00, 25.65; HRMS: [M+H$^+$] calcd for $C_{15}H_{20}N_2O$ 230.1545, found 230.1542.

**Compound (4o)** [22]



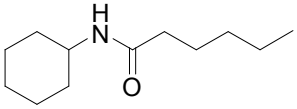
yellow solid, mp: 88-90 ℃. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ =10.80 (s, 1H), 7.87 (s, 1H), 7.53 (d, $J$ = 4.0 Hz, 1H), 7.33 (d, $J$ = 6.0 Hz, 1H), 7.13 (s, 1H), 7.04～7.08 (m, 1H), 6.96～6.99 (m, 1H), 3.30～3.36 (m, 2H), 2.79～2.83 (m, 2H), 2.03～2.07 (m, 2H), 1.48～1.51 (m, 2H), 1.20～1.28 (m, 4H), 0.83～0.87 (m, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 172.47, 136.71, 127.73, 123.02, 121.34, 118.72, 118.64, 112.38, 111.81, 39.89, 35.94, 31.40, 25.76, 25.47, 22.38, 14.34; HRMS: [M+H$^+$] calcd for $C_{16}H_{32}N_2O$ 259.1810, found 259.1811.

**Compound (4p)** [23]



white solid, mp: 140-142 ℃. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ =7.88 (d, $J$ = 4.0 Hz, 1H), 3.50～3.53 (m, 1H), 1.64～1.74 (m, 4H), 1.49～1.54 (m, 2H), 1.09～1.26 (m, 5H), 0.58～0.64 (m, 4H), 0.83～0.87 (m, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 171.78, 47.93, 33.11, 25.72, 25.09, 14.02, 6.49; HRMS: [M+H$^+$] calcd for $C_{10}H_{18}NO$ 168.1388, found 168.1387.

**Compound (4q)** [24]



white solid, mp: 68-70 ℃. $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ =7.60 (d, $J$ = 4.0 Hz, 1H), 3.47～3.52 (m, 1H), 1.99～2.03 (m, 2H), 1.64～1.72 (m, 4H), 1.43～1.56 (m, 3H), 1.08～1.28 (m, 9H), 0.83～0.87 (m, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ = 171.46, 47.68, 35.89, 33.01, 31.34, 25.73, 25.54, 25.09, 22.35, 14.33; HRMS: [M+H$^+$] calcd for $C_{12}H_{24}NO$ 198.1858, found 198.1856.

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# Ⅸ $^{1}$H and $^{13}$C-NMR Spectra of the synthesised products

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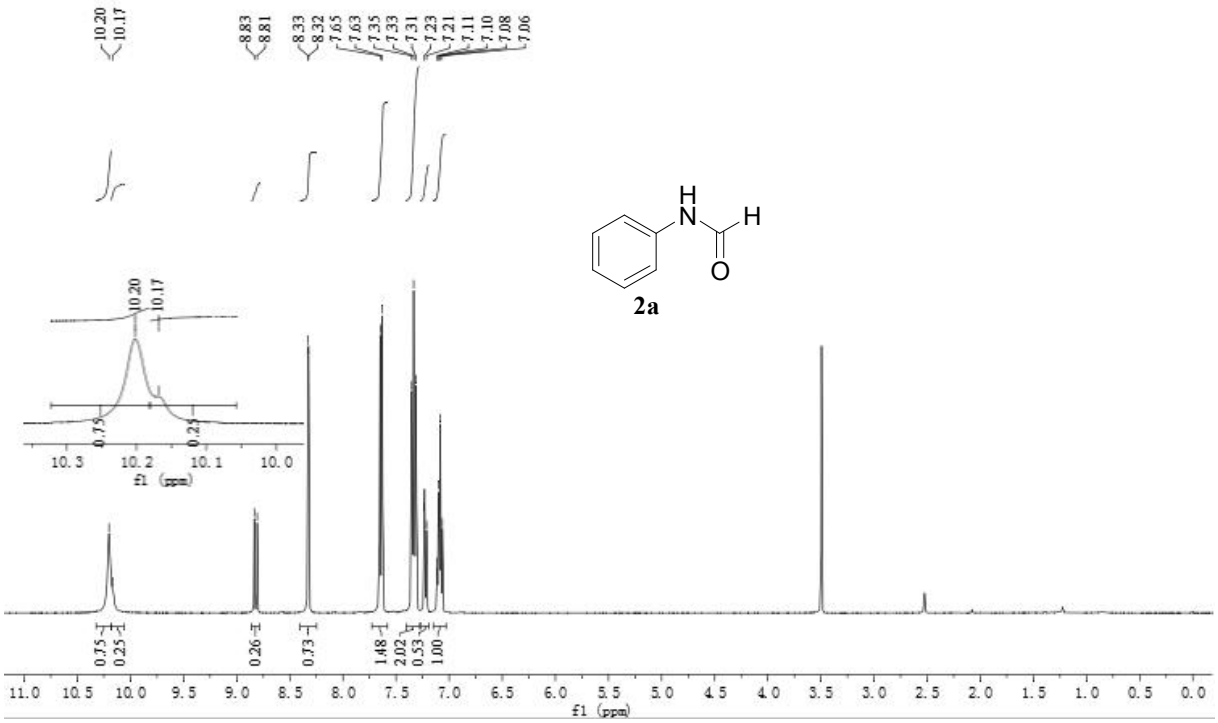


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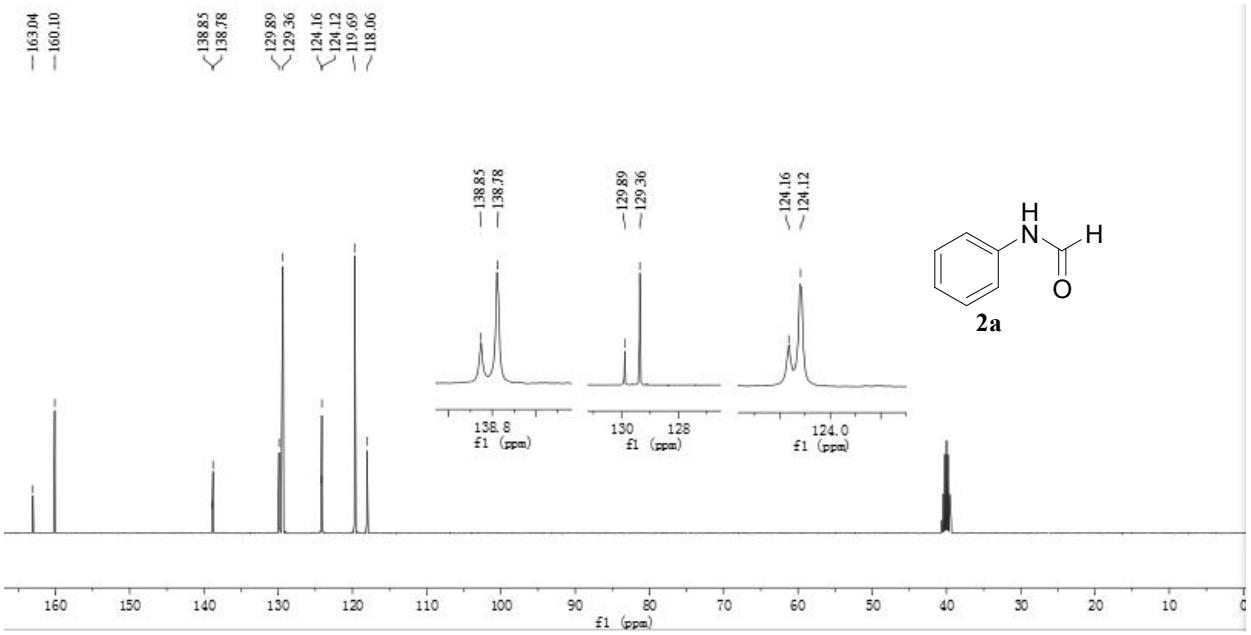
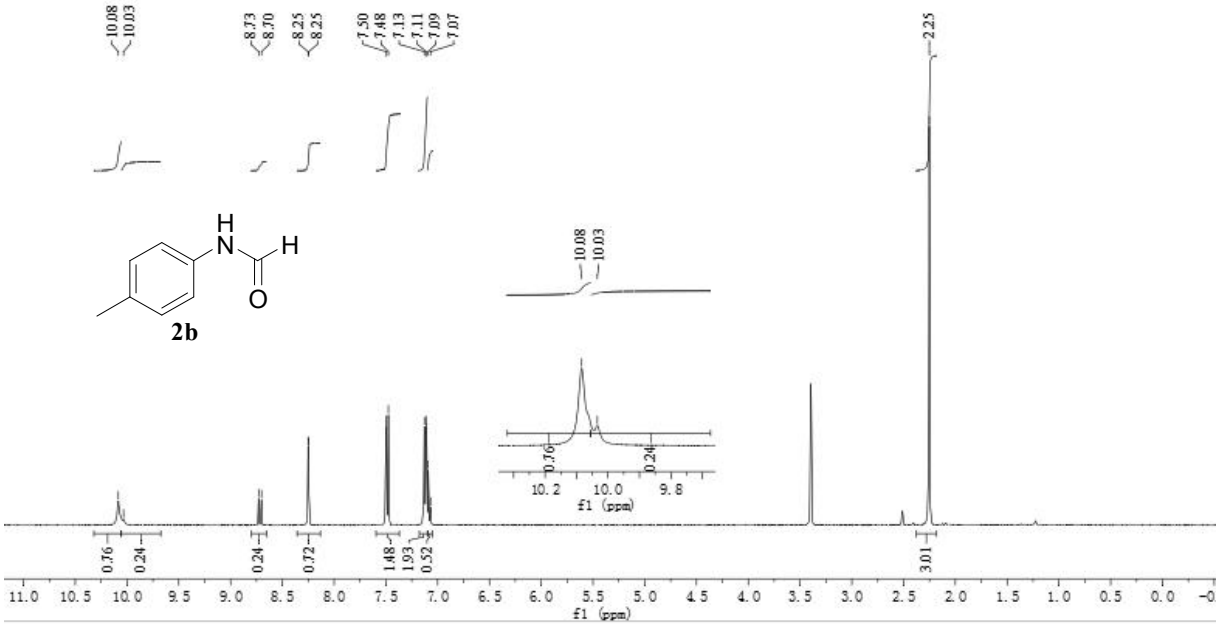


## $^{1}$H NMR spectra

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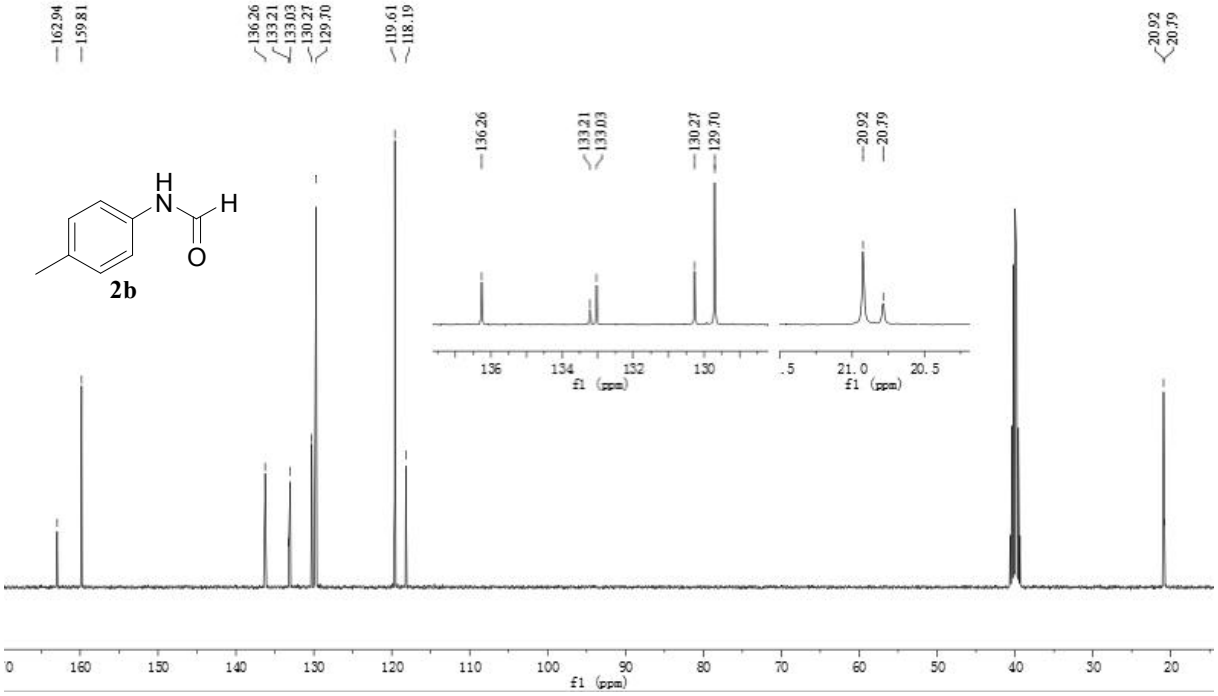

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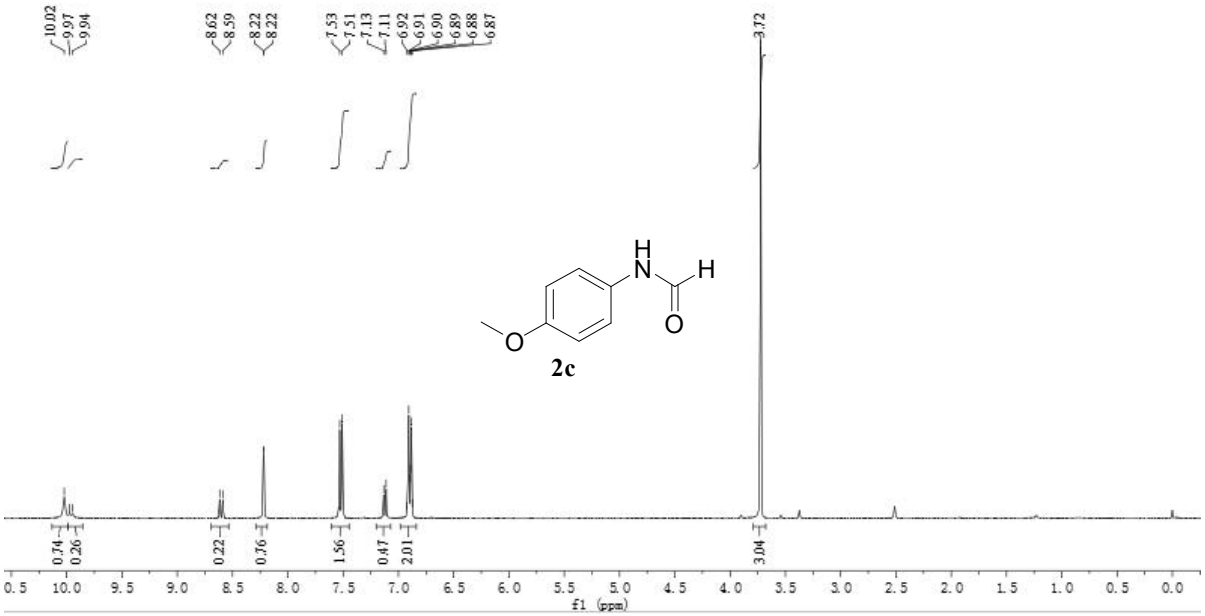


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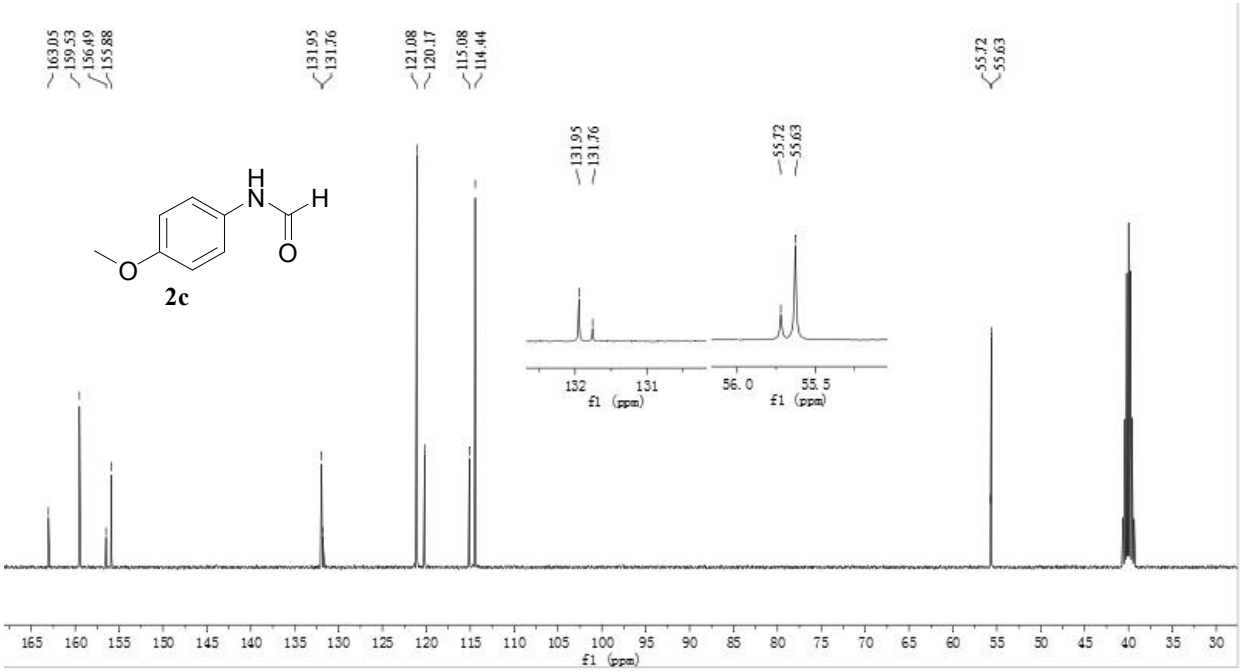

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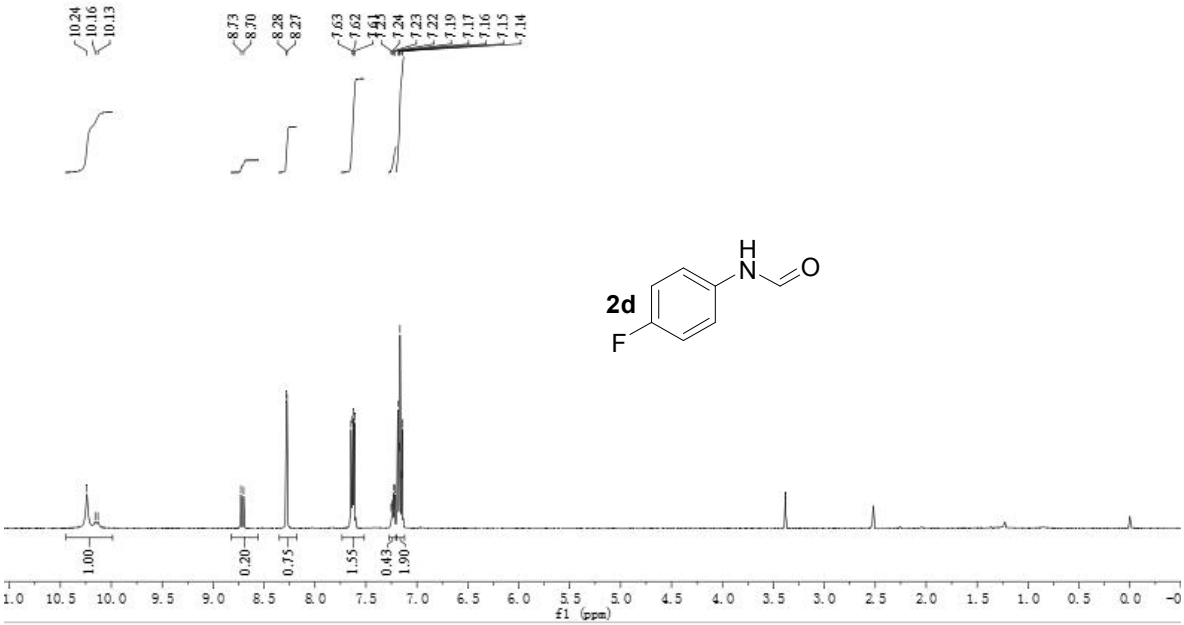


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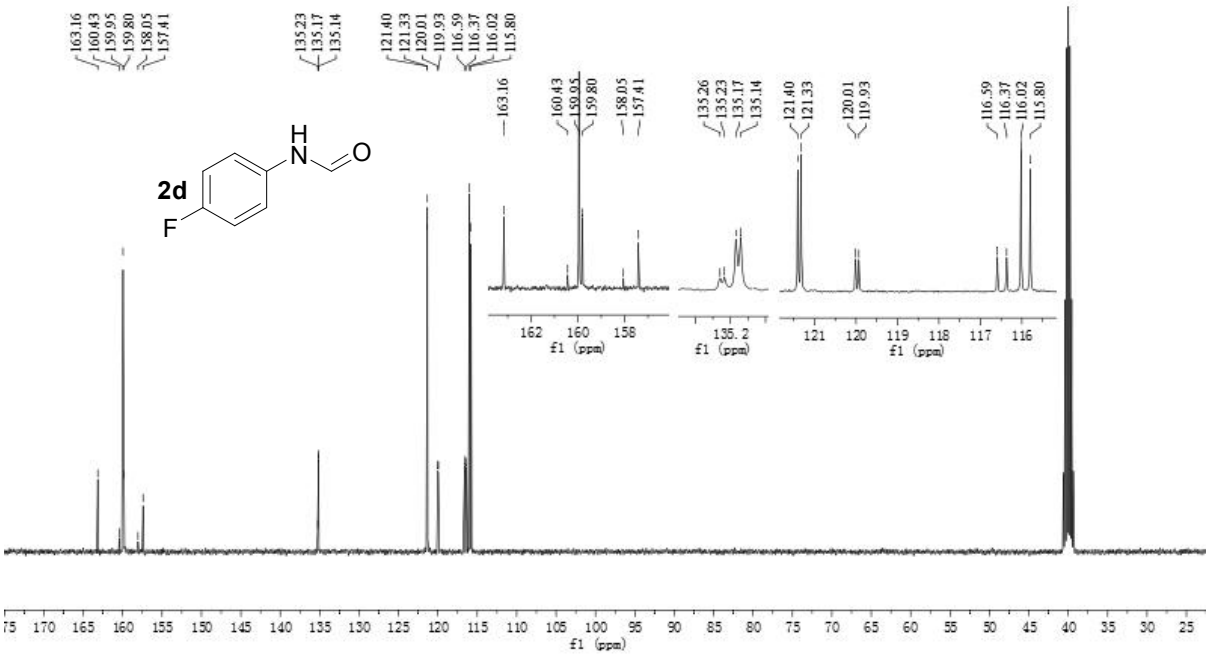

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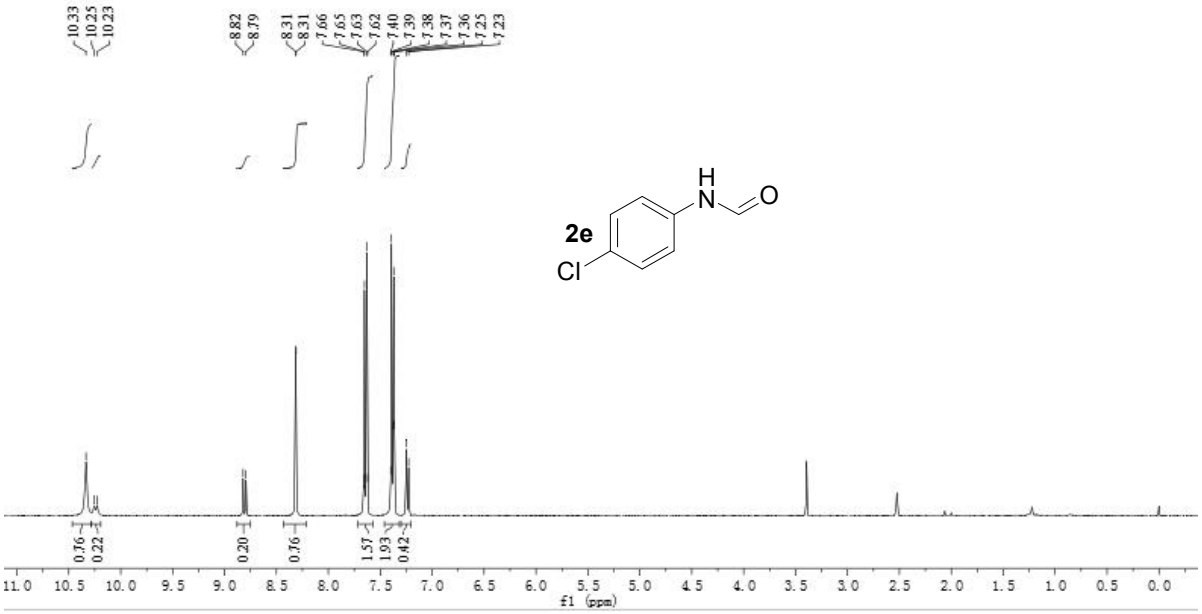


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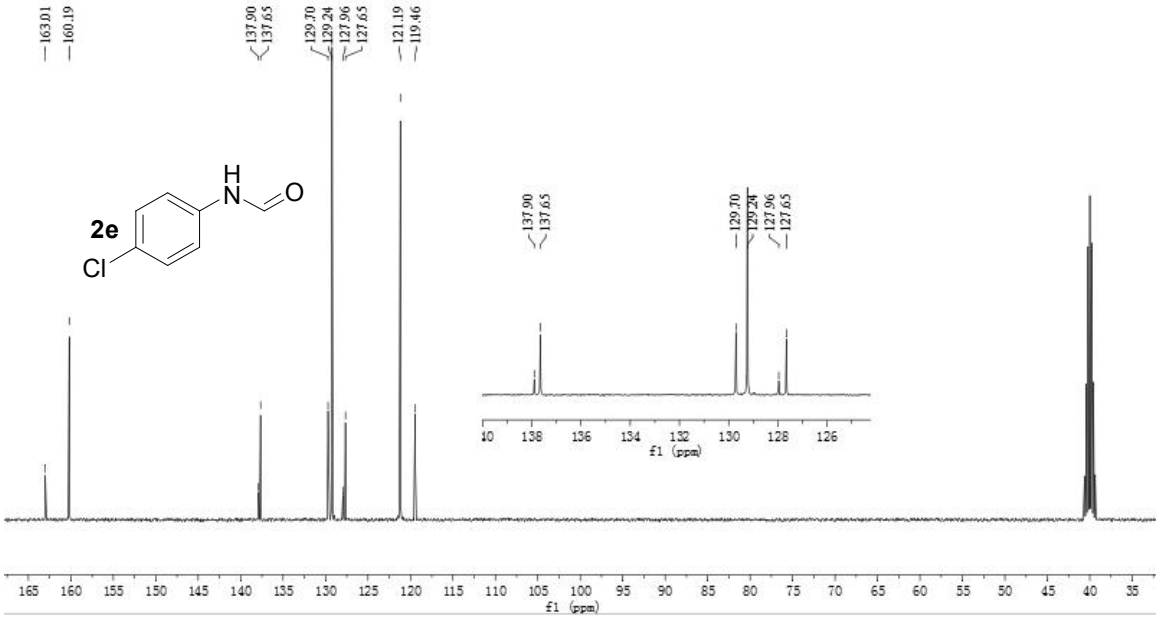

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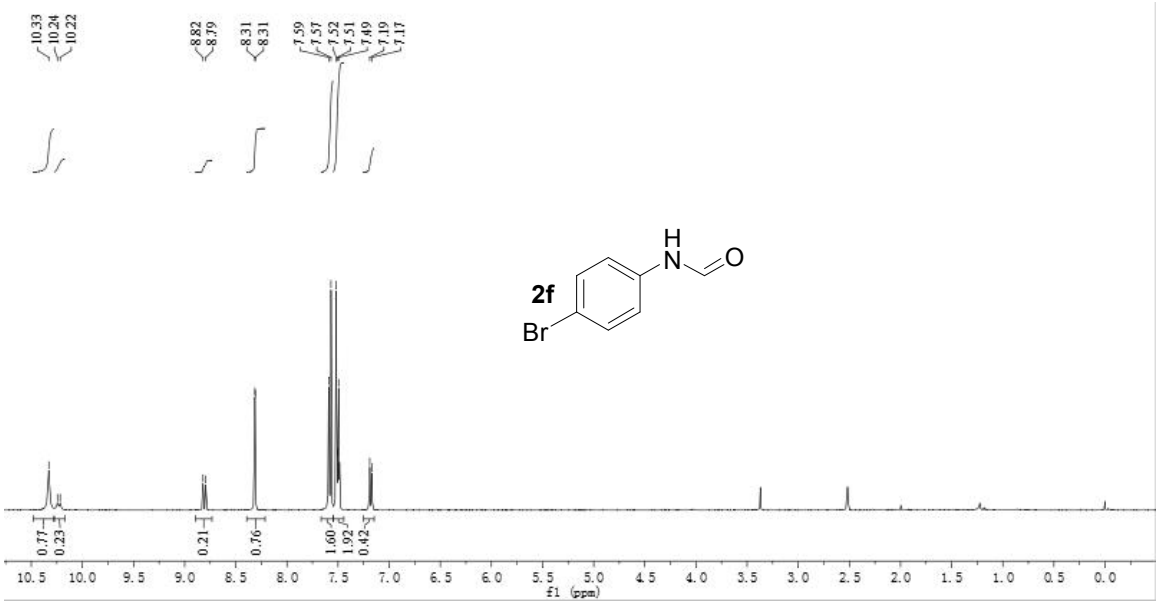


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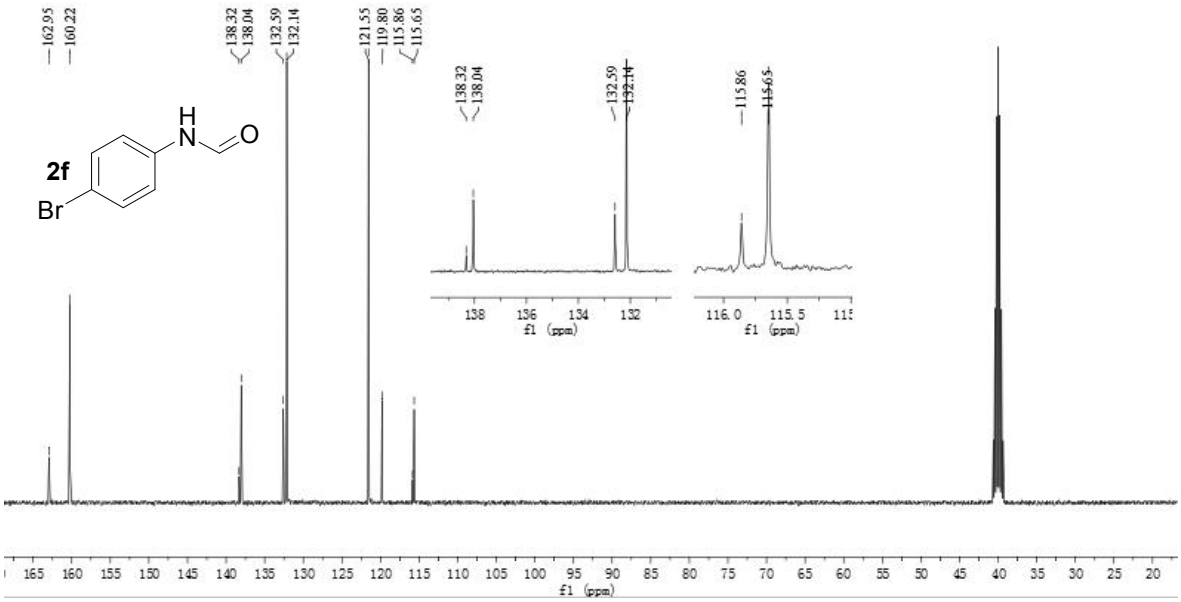

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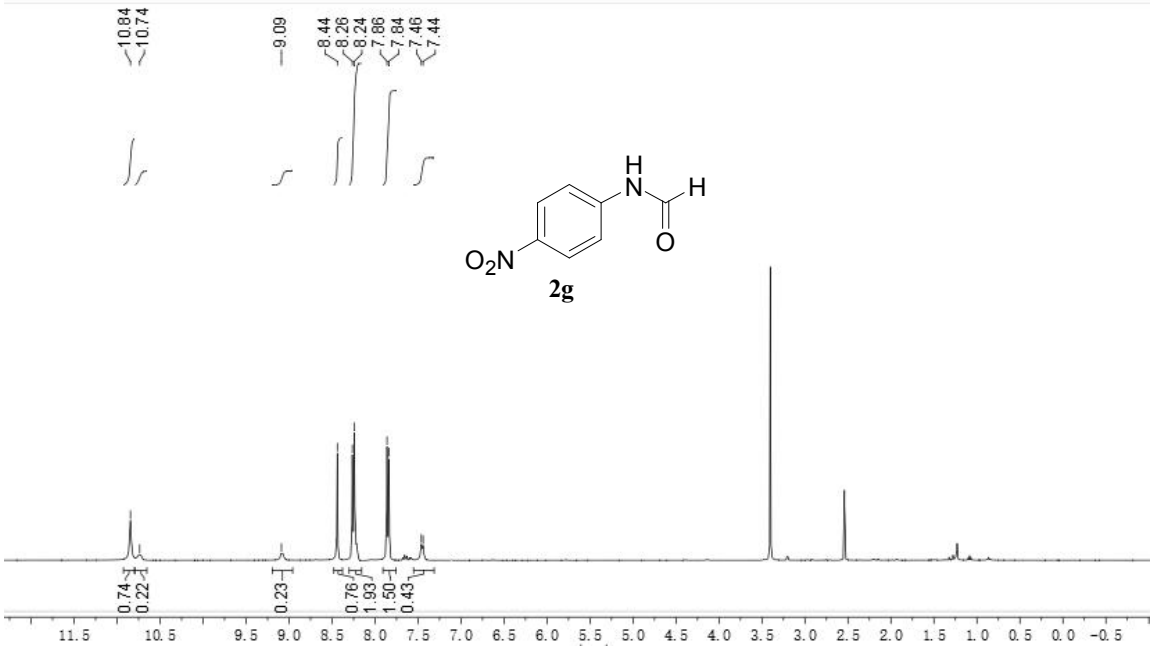


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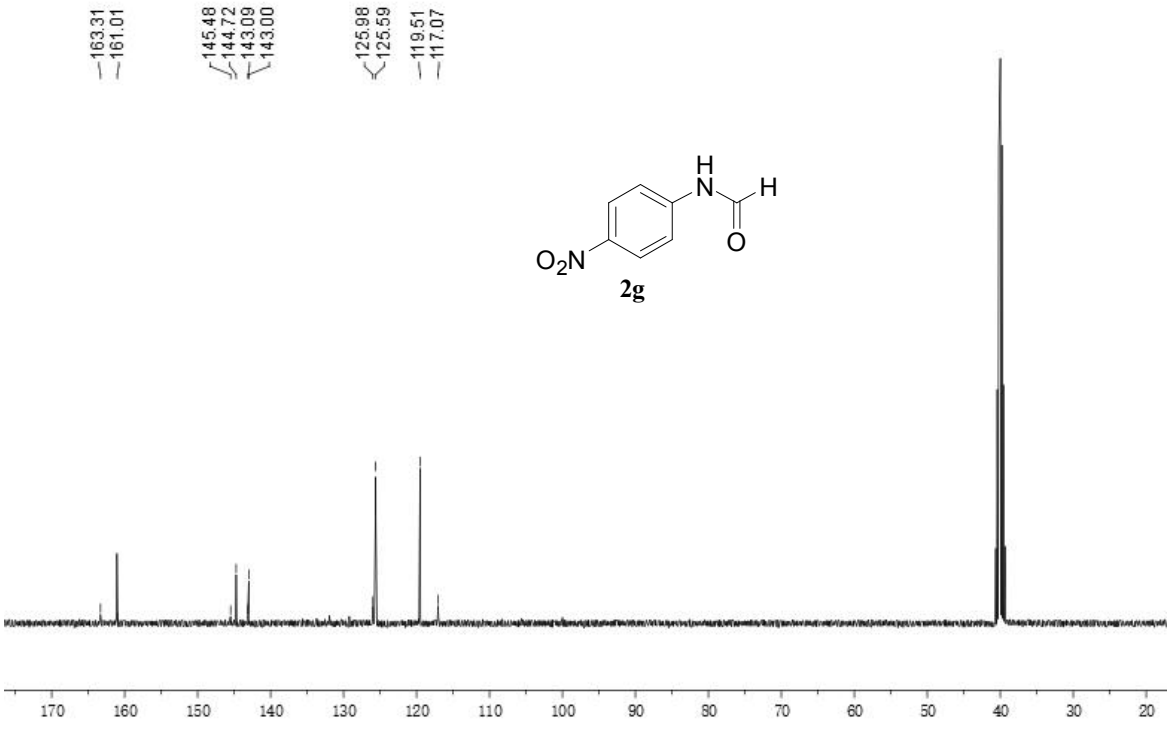

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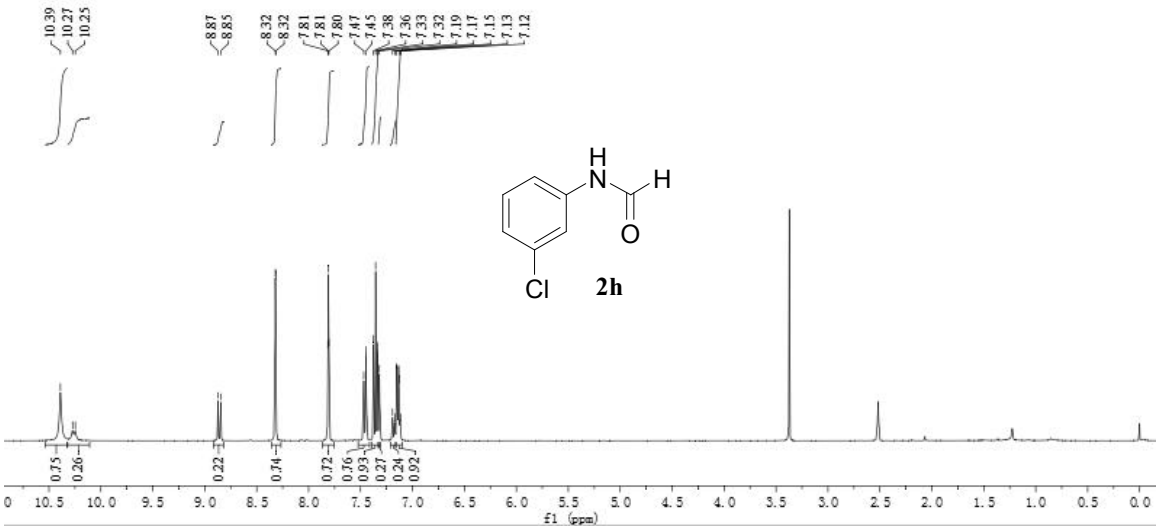


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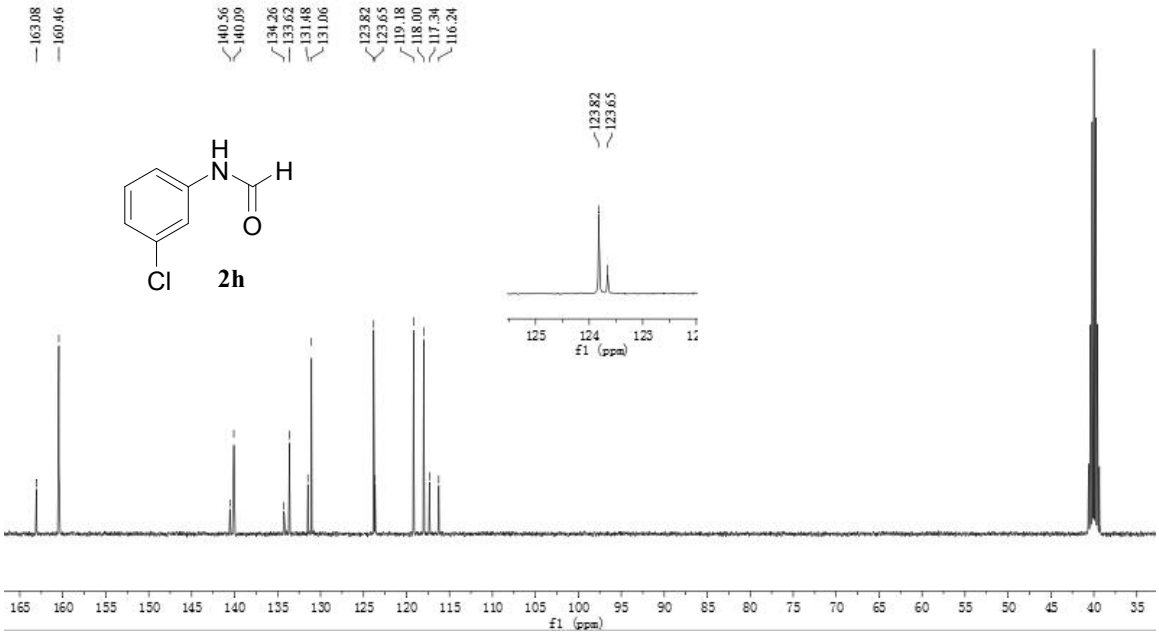

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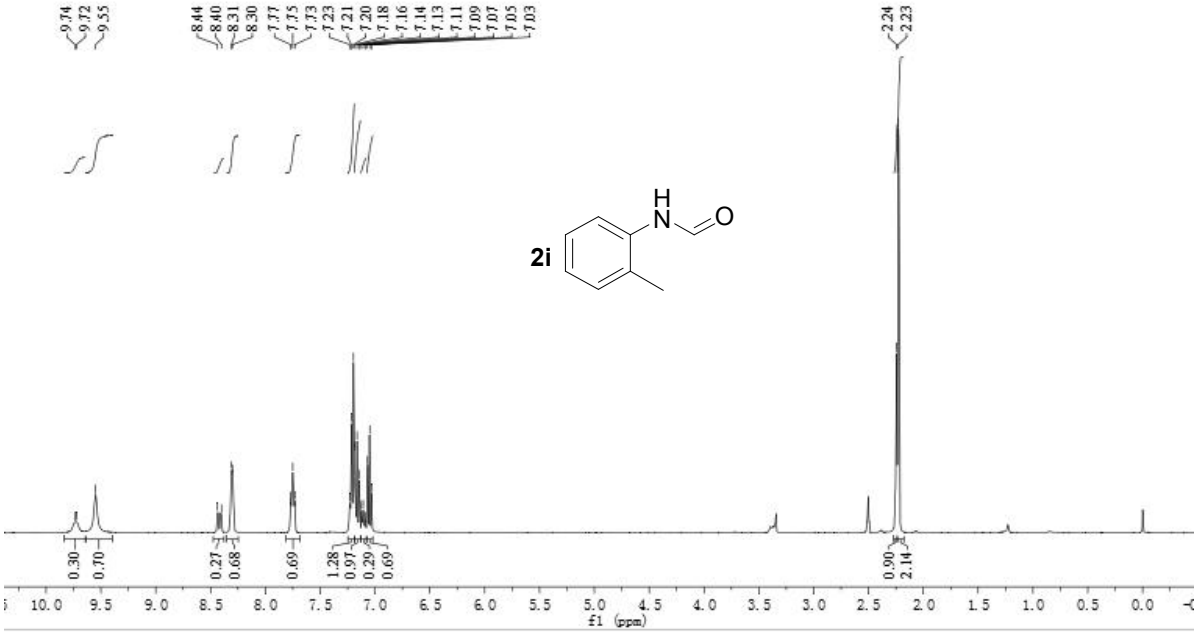


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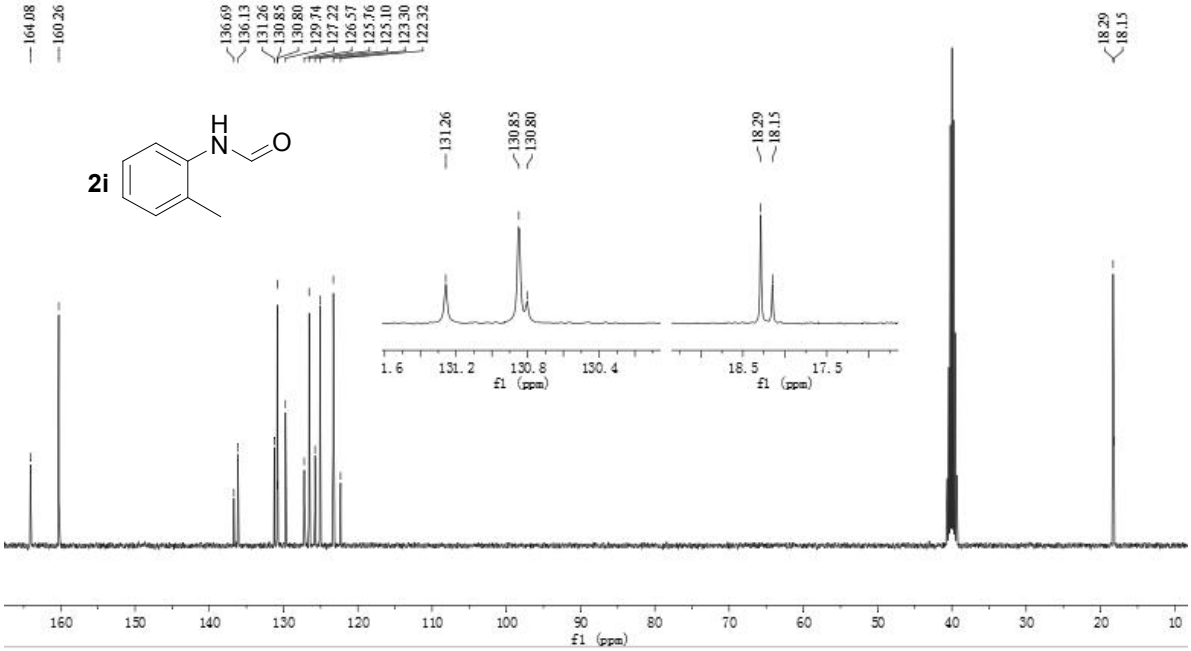

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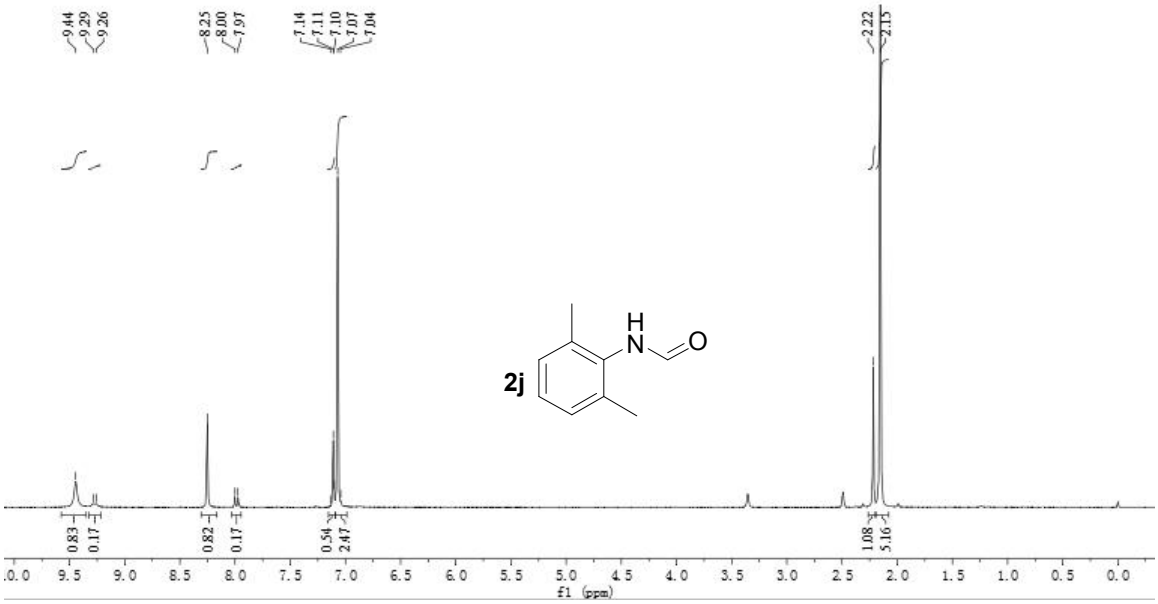


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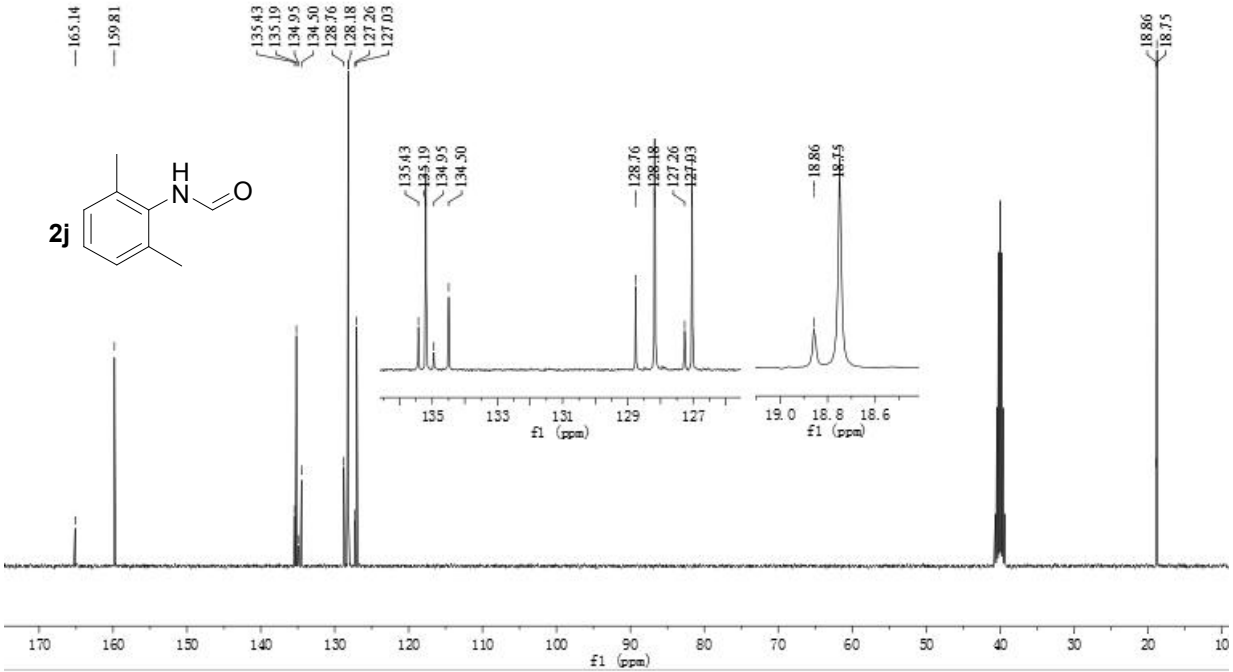

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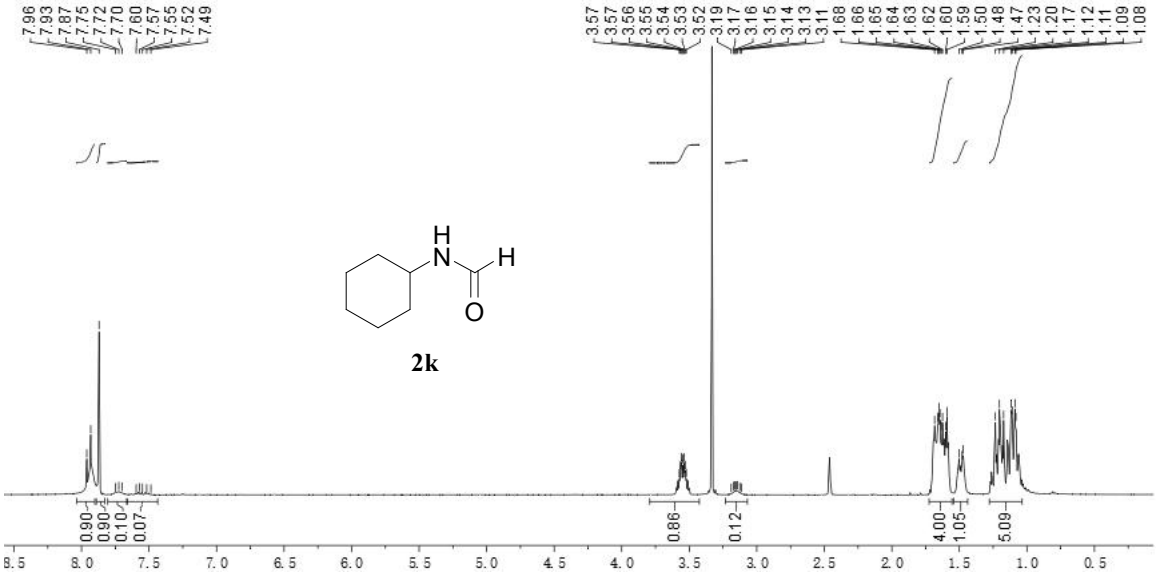
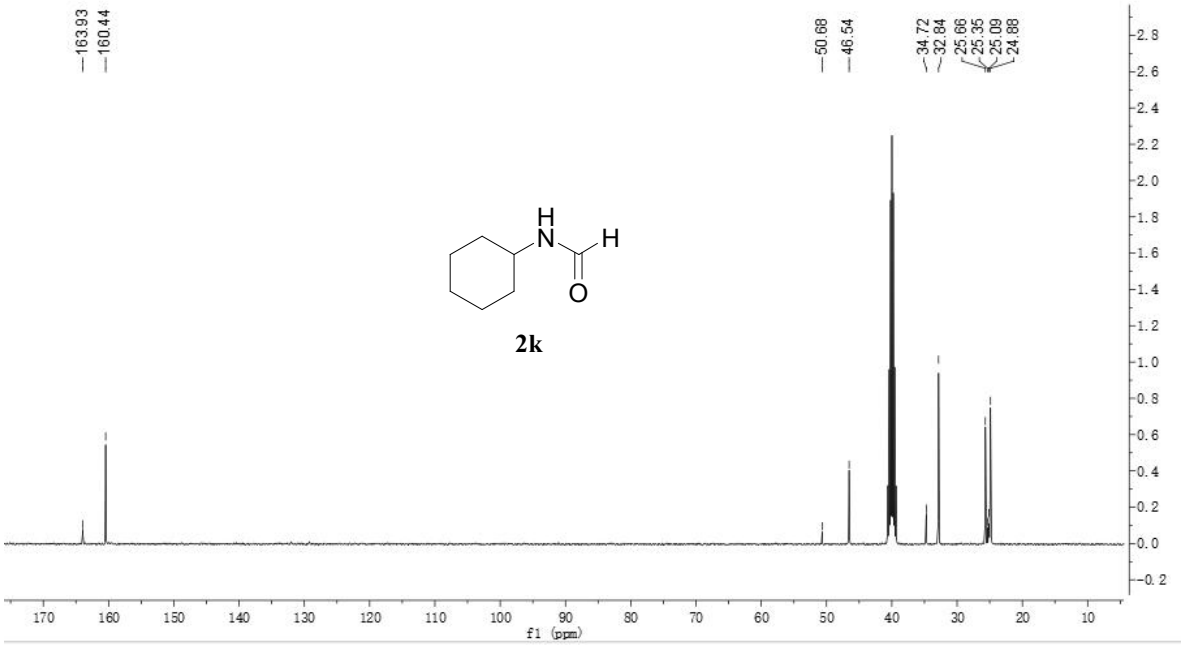
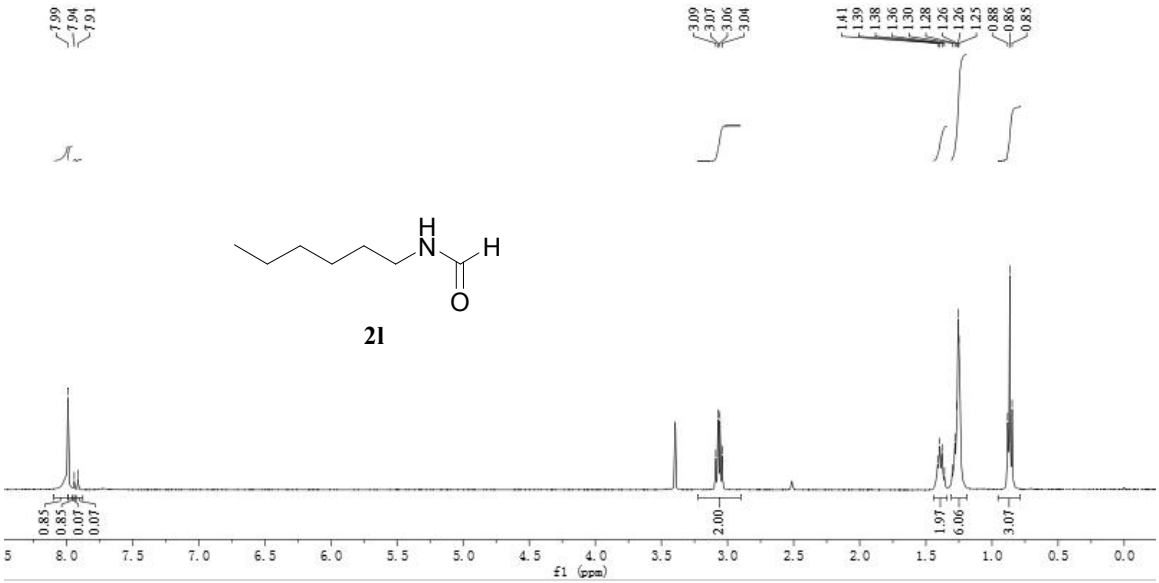


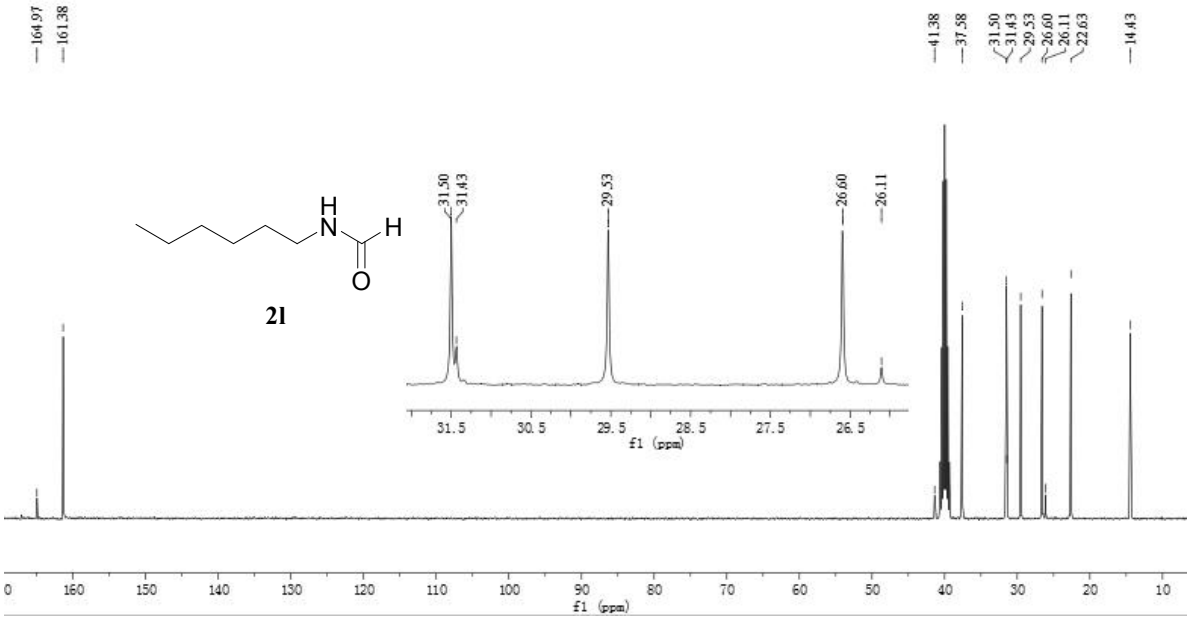

## $^{13}$C NMR spectra



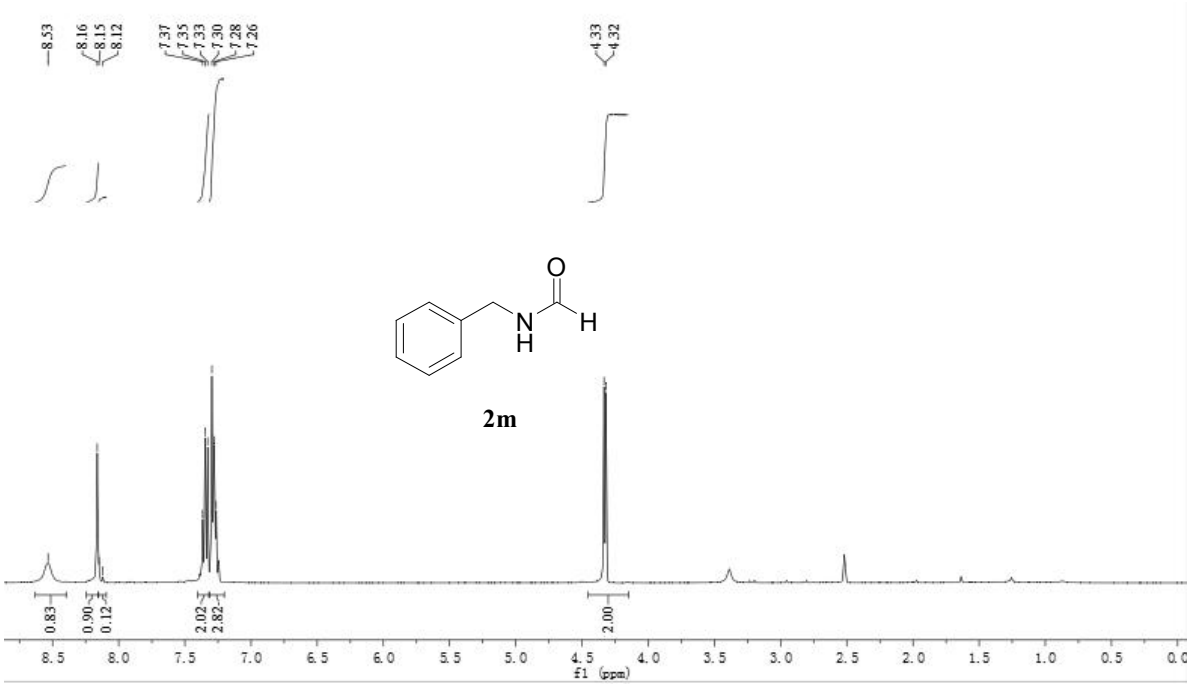
## $^{1}$H NMR spectra



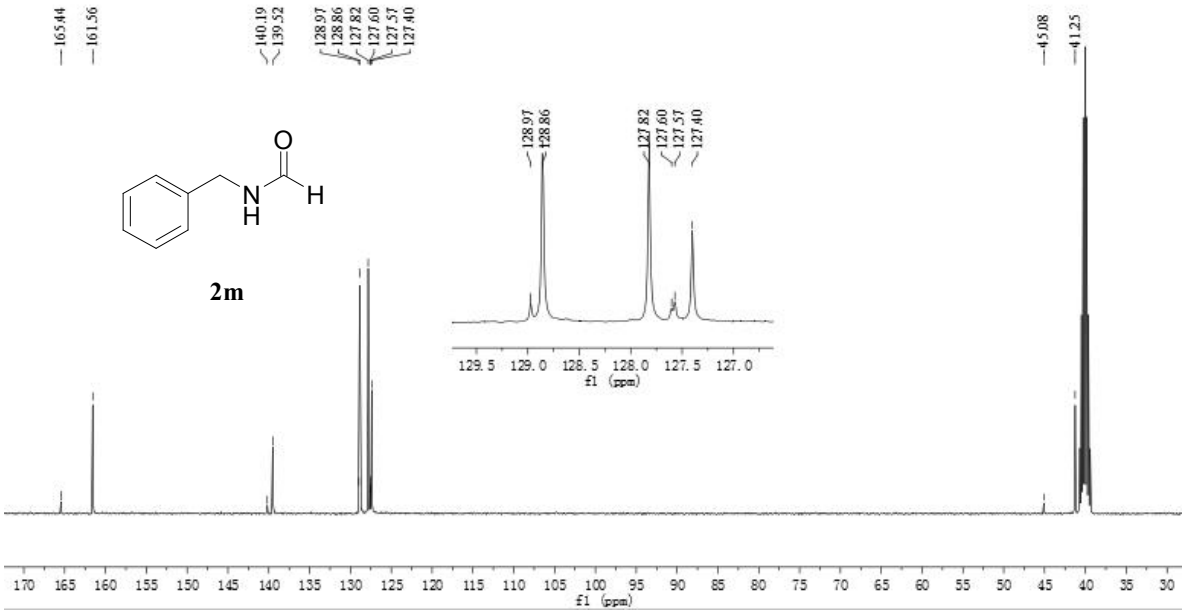

## $^{13}$C NMR spectra



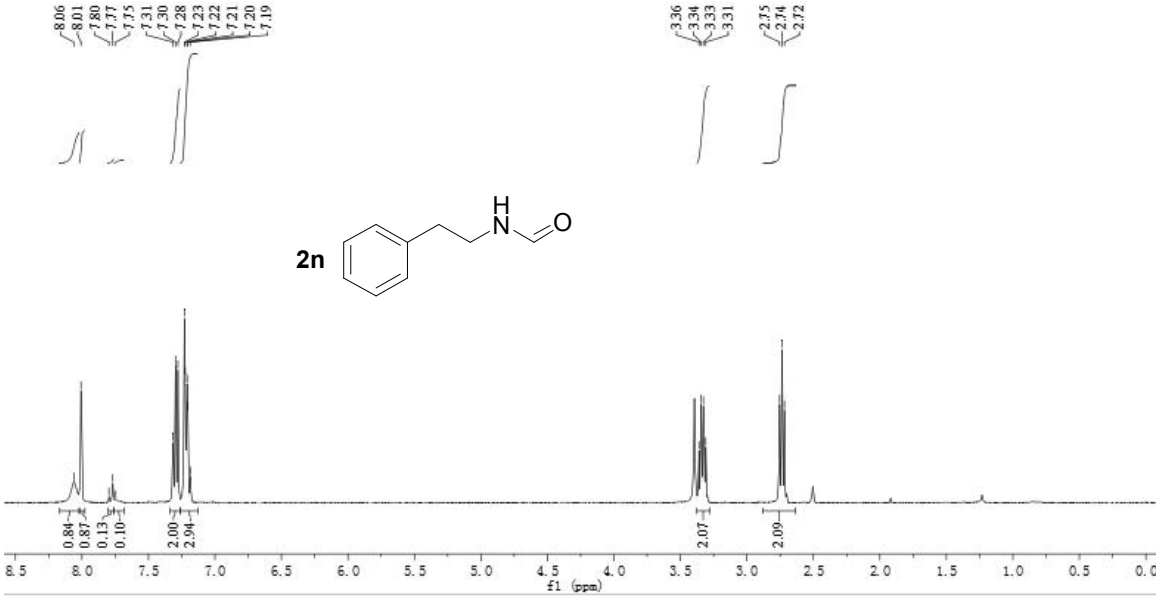
## $^{1}$H NMR spectra



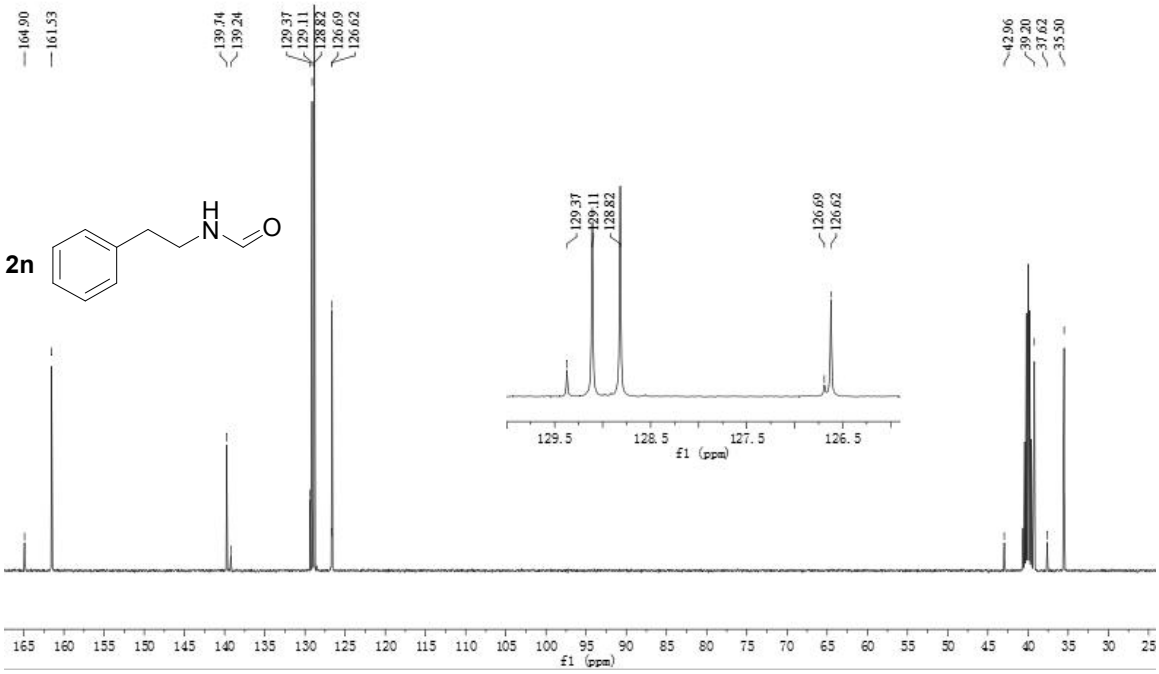

## $^{13}$C NMR spectra



## $^{1}$H NMR spectra




## $^{13}$C NMR spectra



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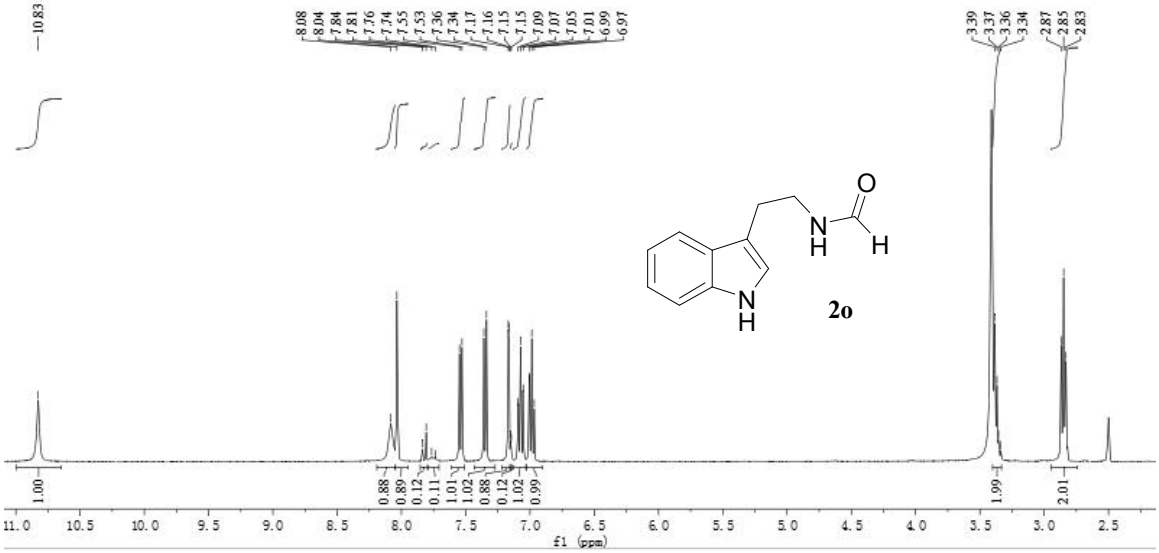
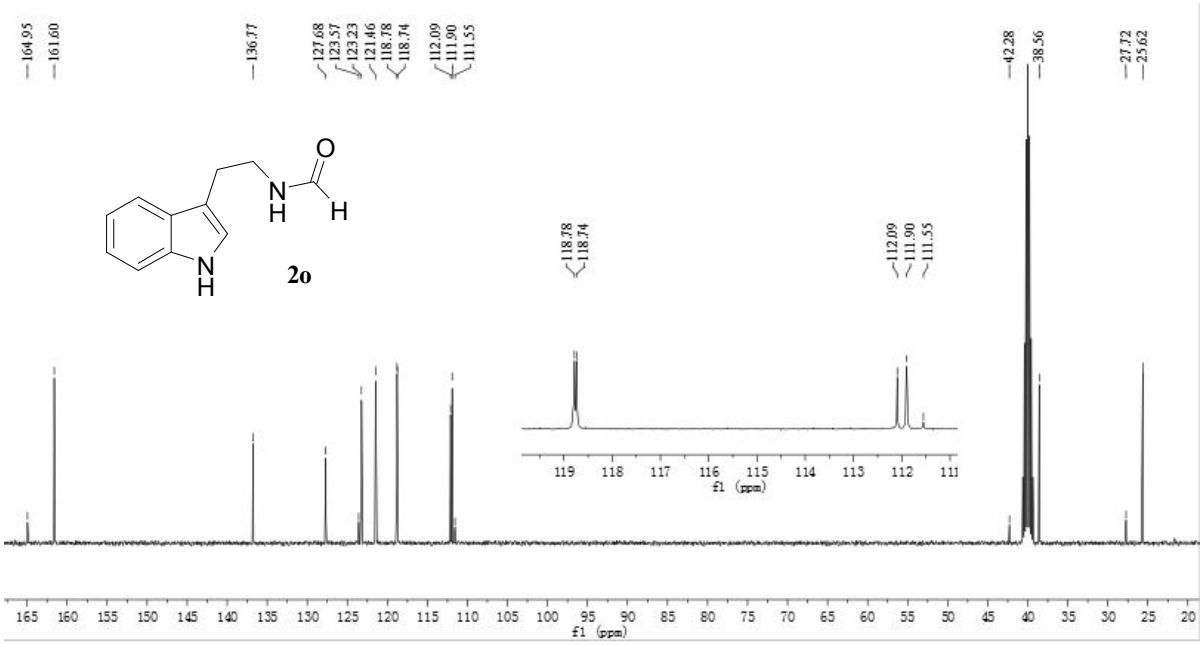



## $^{13}$C NMR spectra



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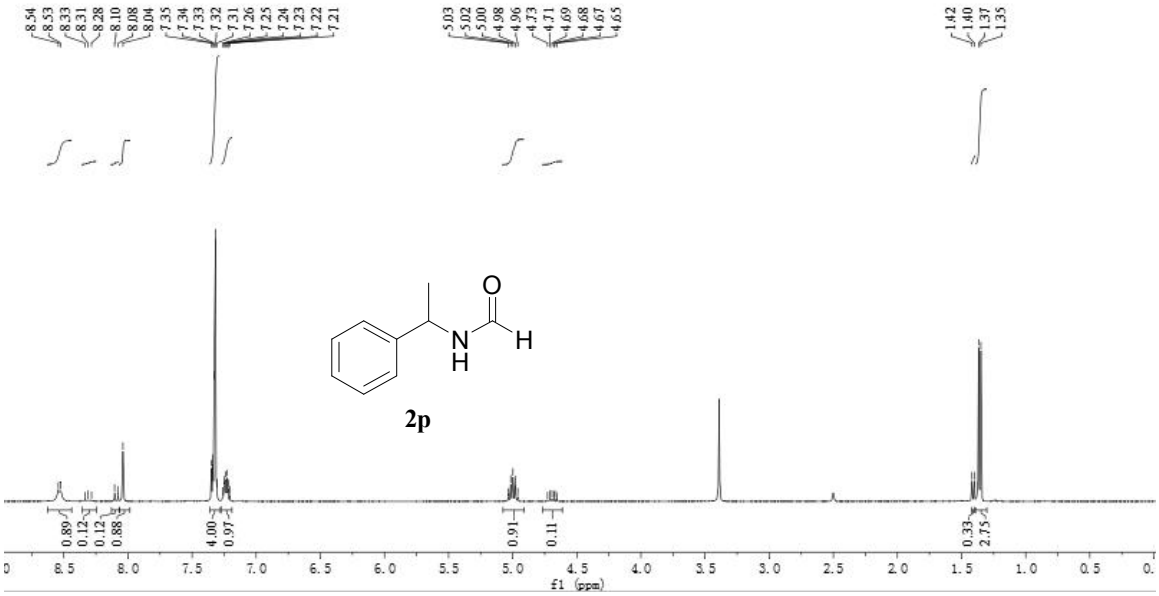
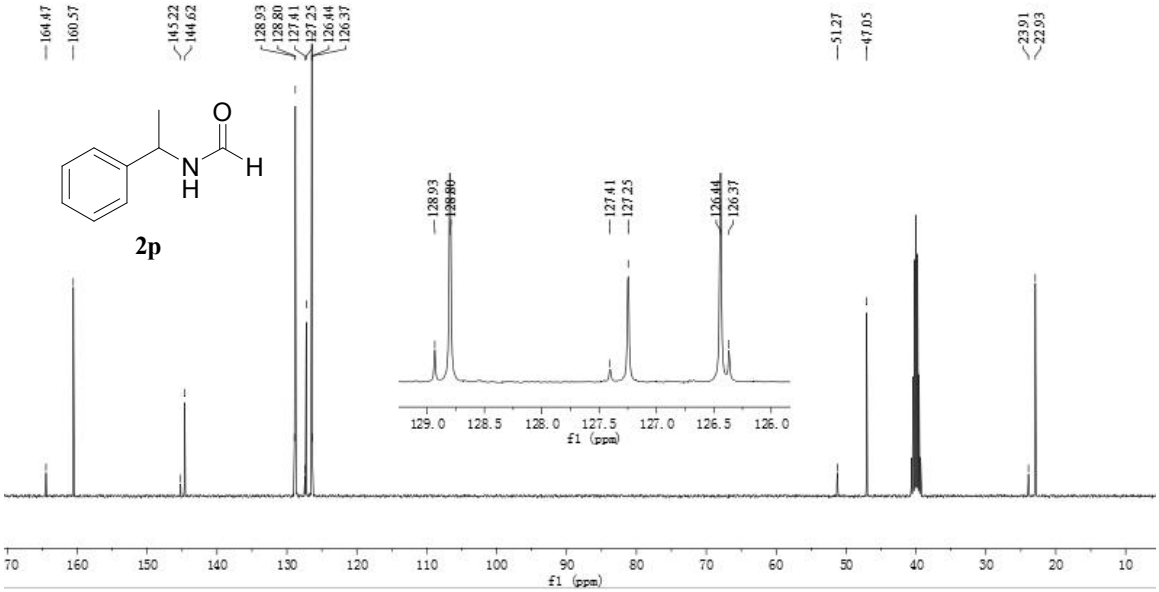
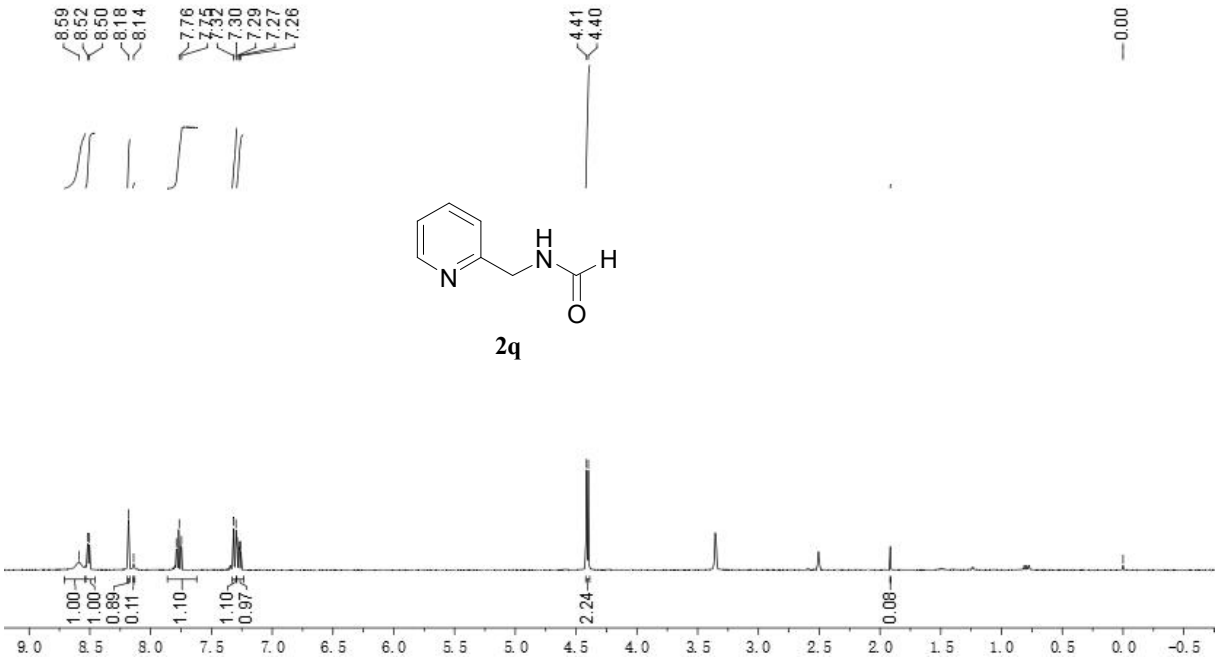


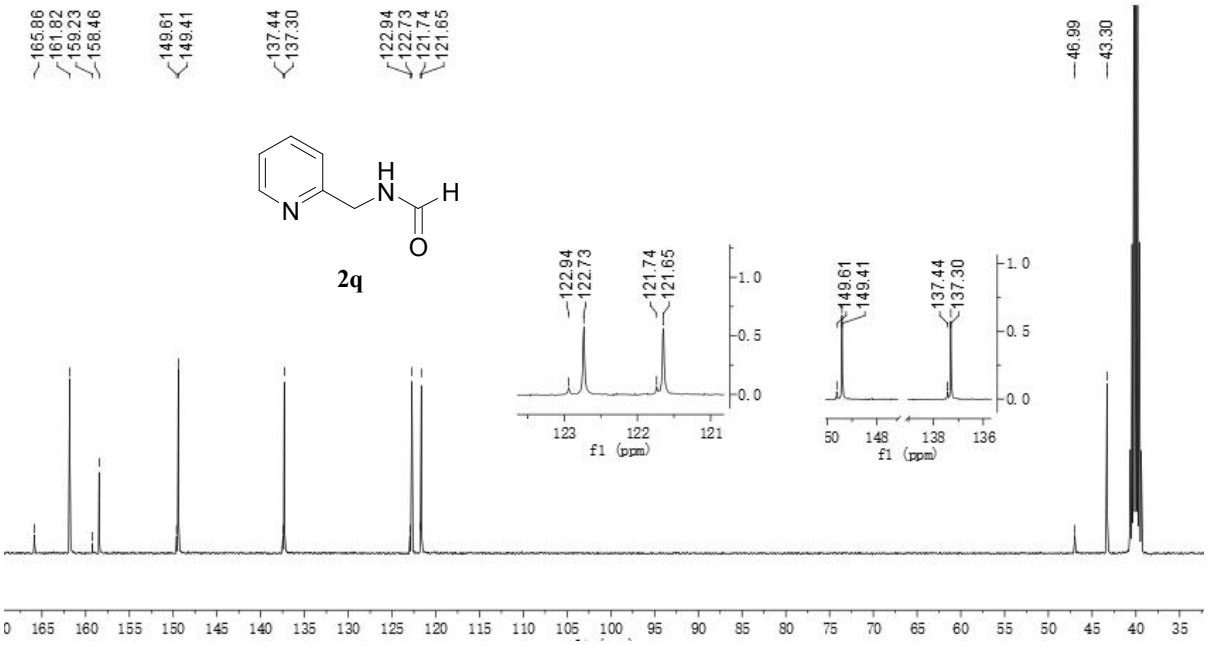

## $^{13}$C NMR spectra



## $^{1}$H NMR spectra




## $^{13}$C NMR spectra



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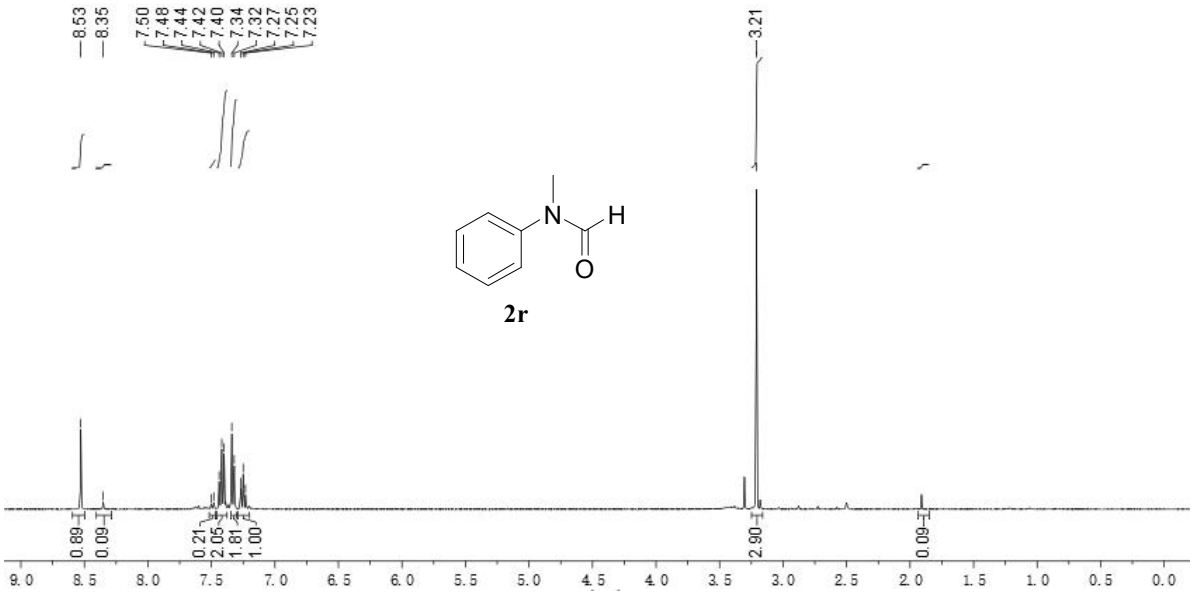
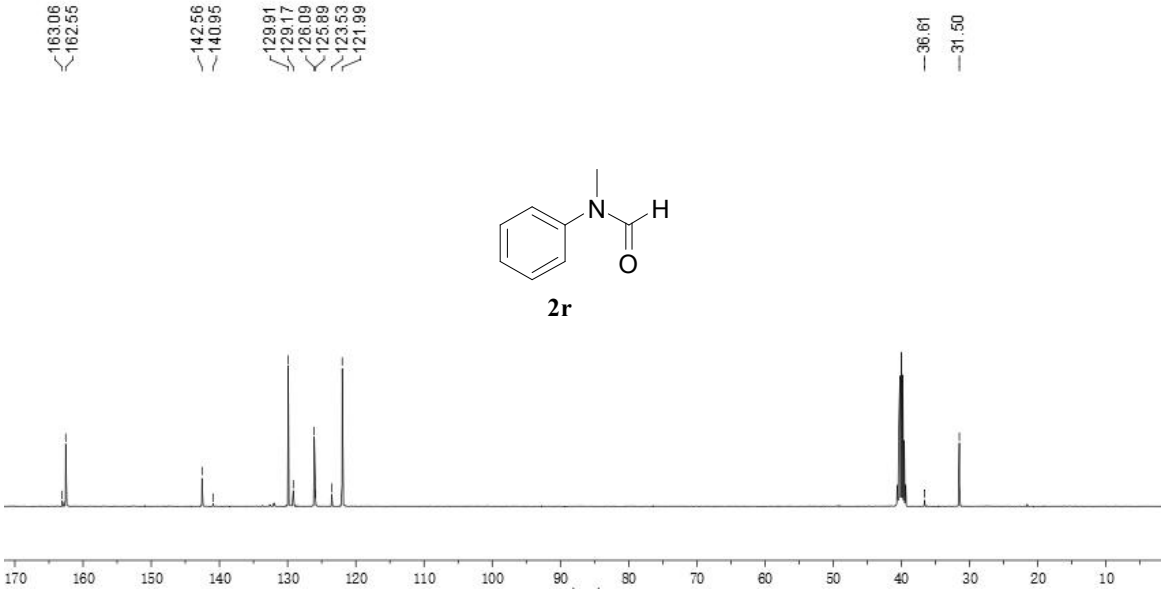



## $^{13}$C NMR spectra



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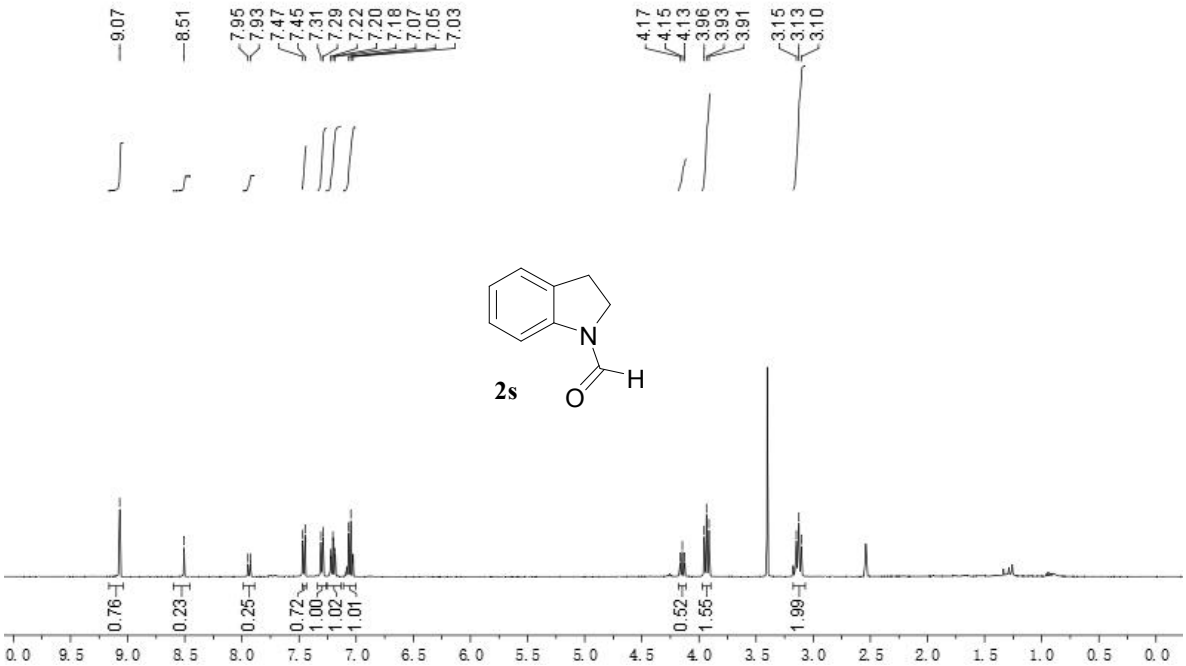


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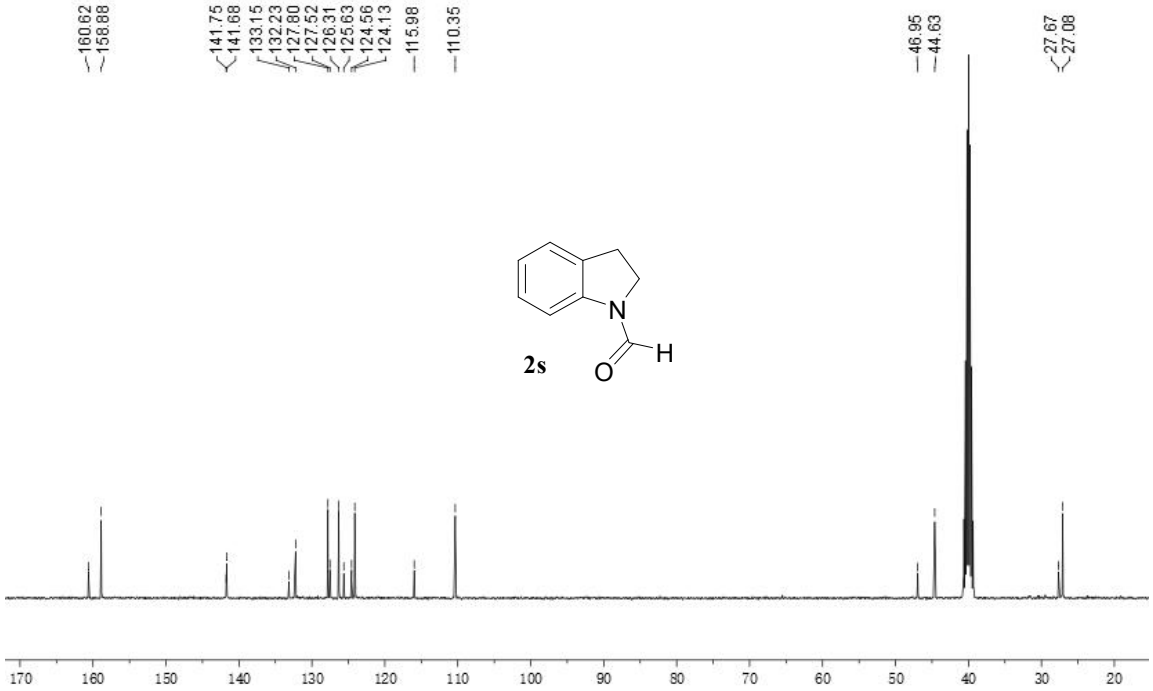

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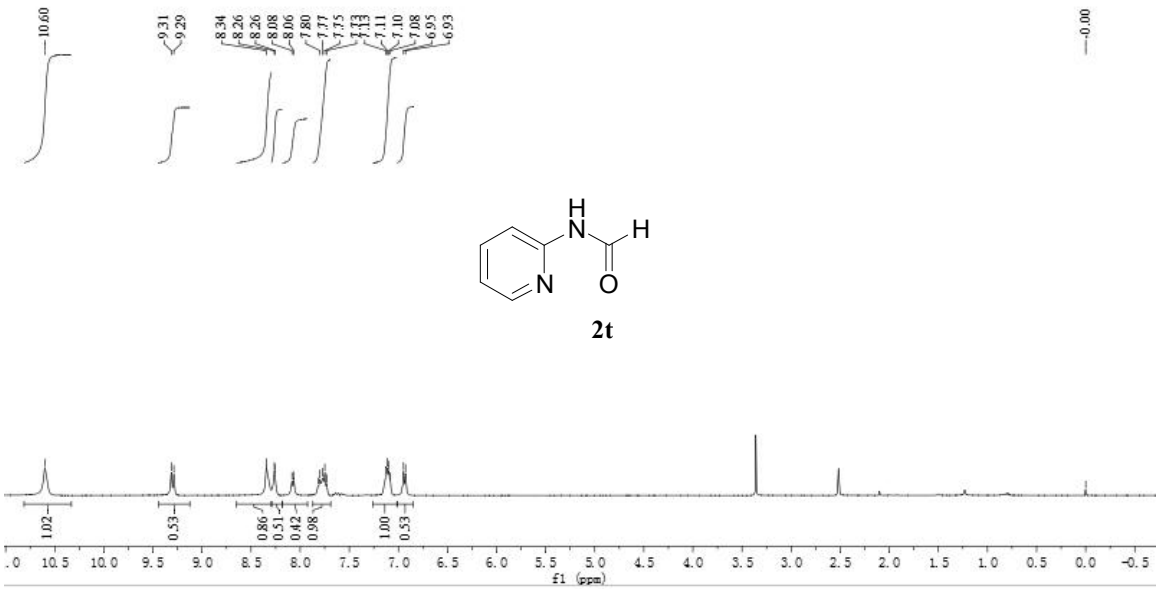


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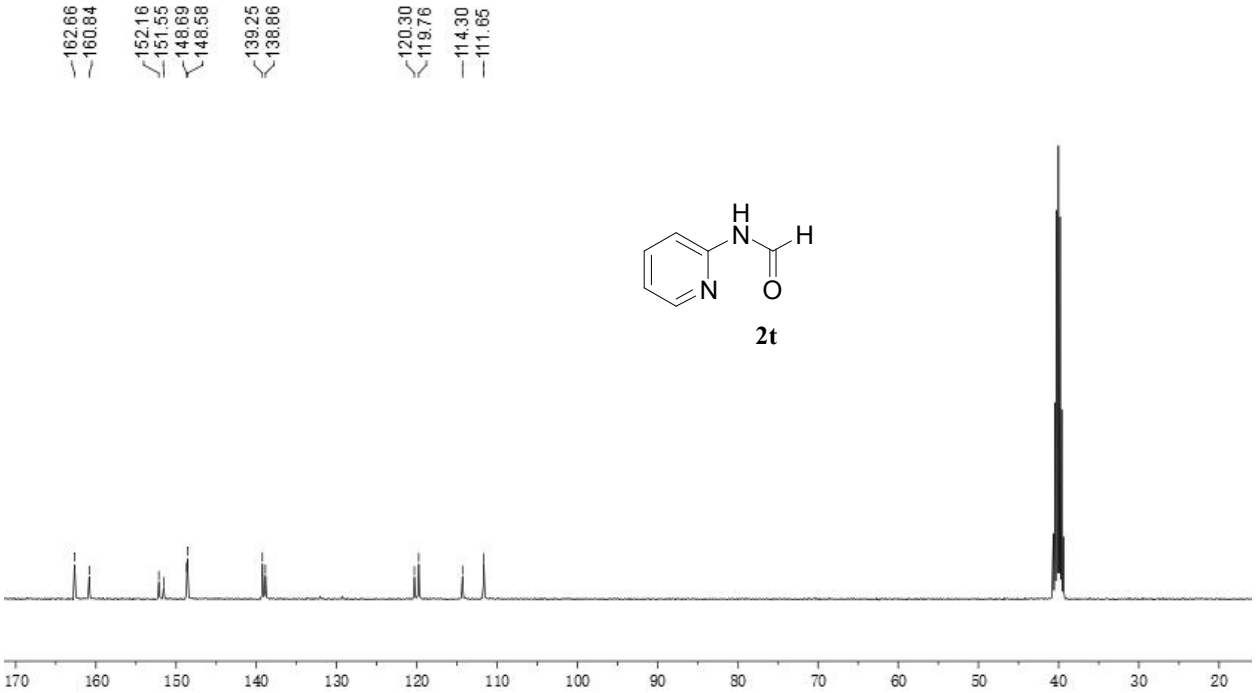

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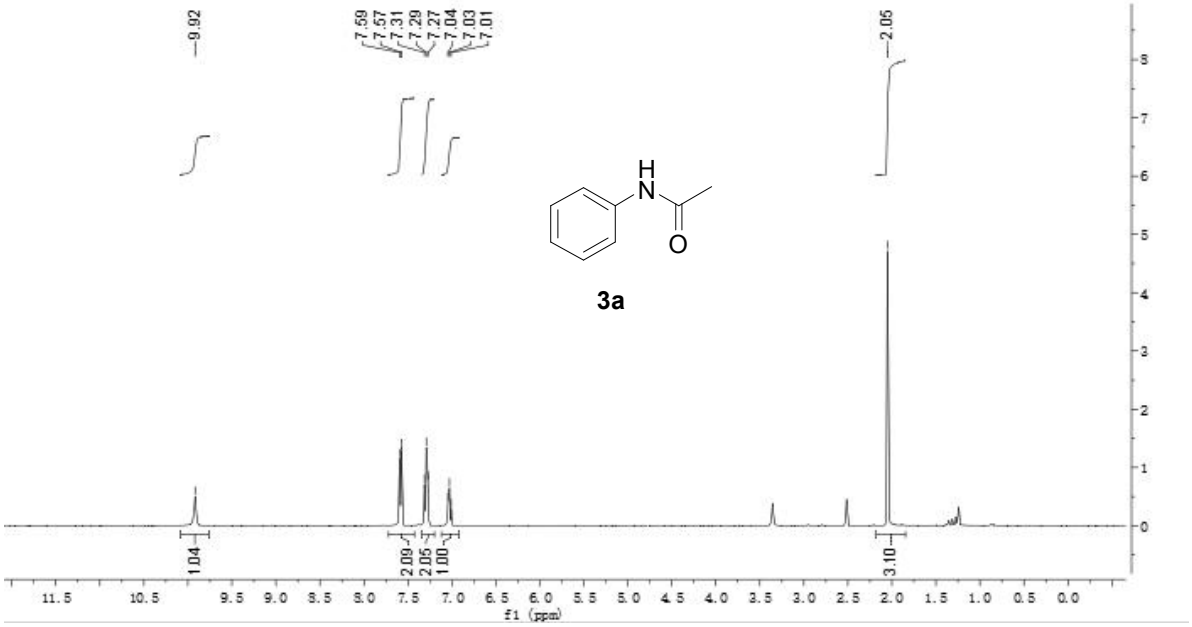


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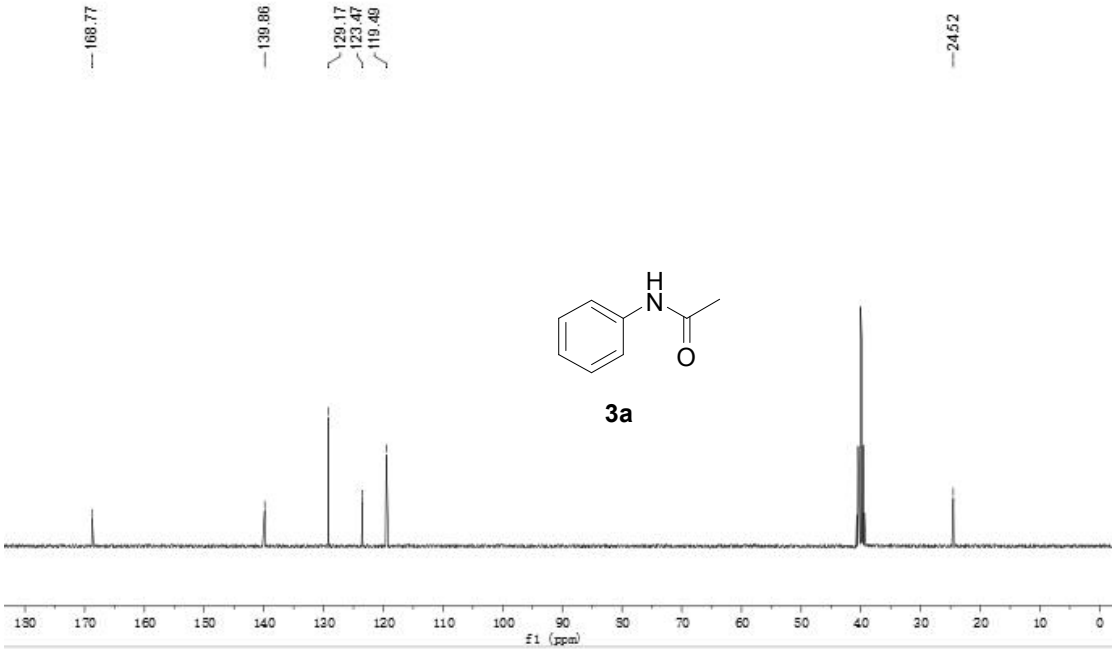

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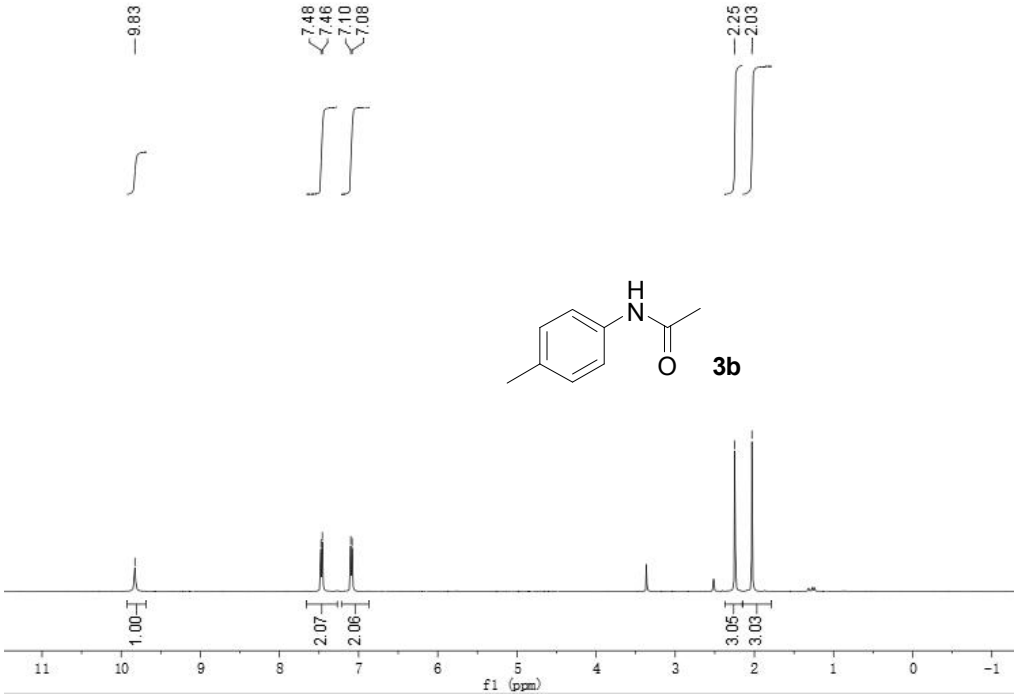


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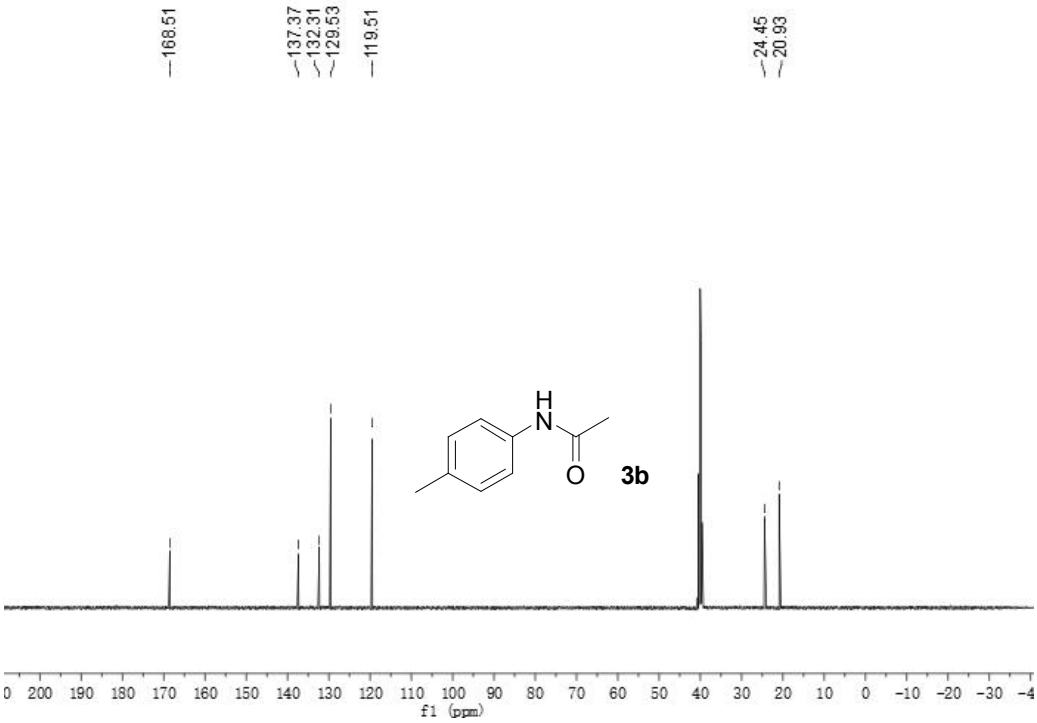

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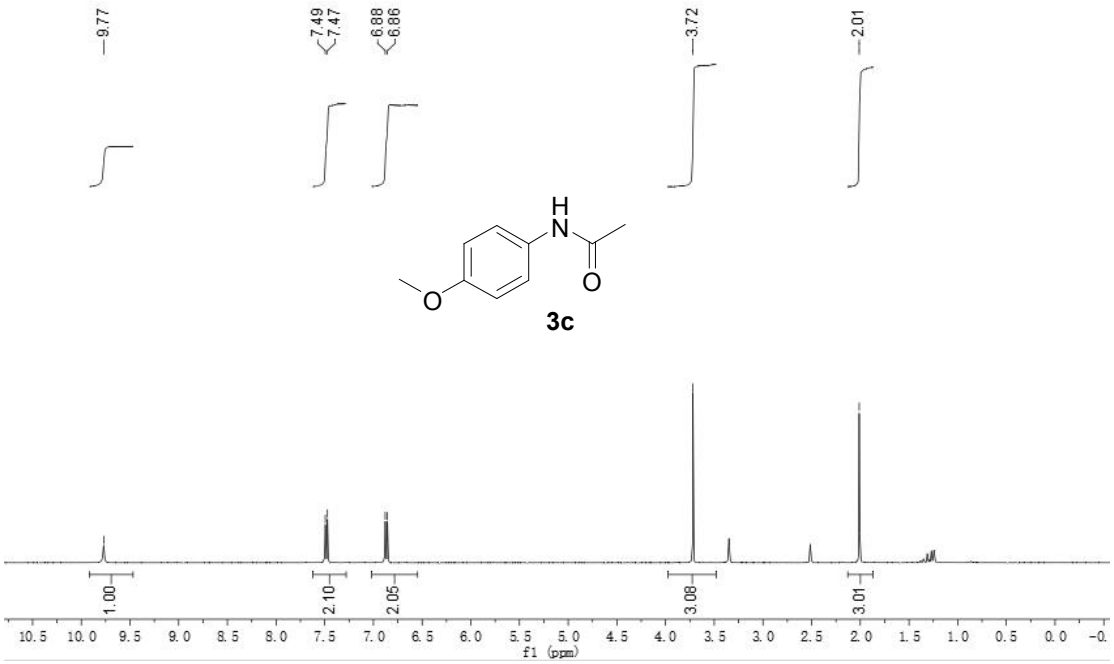


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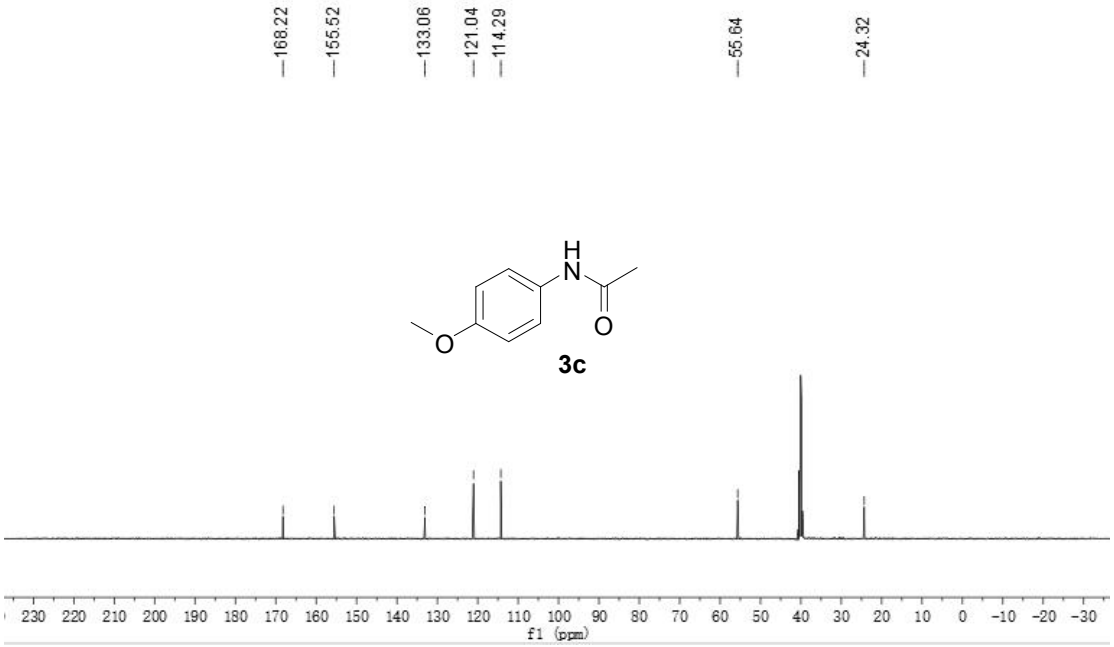

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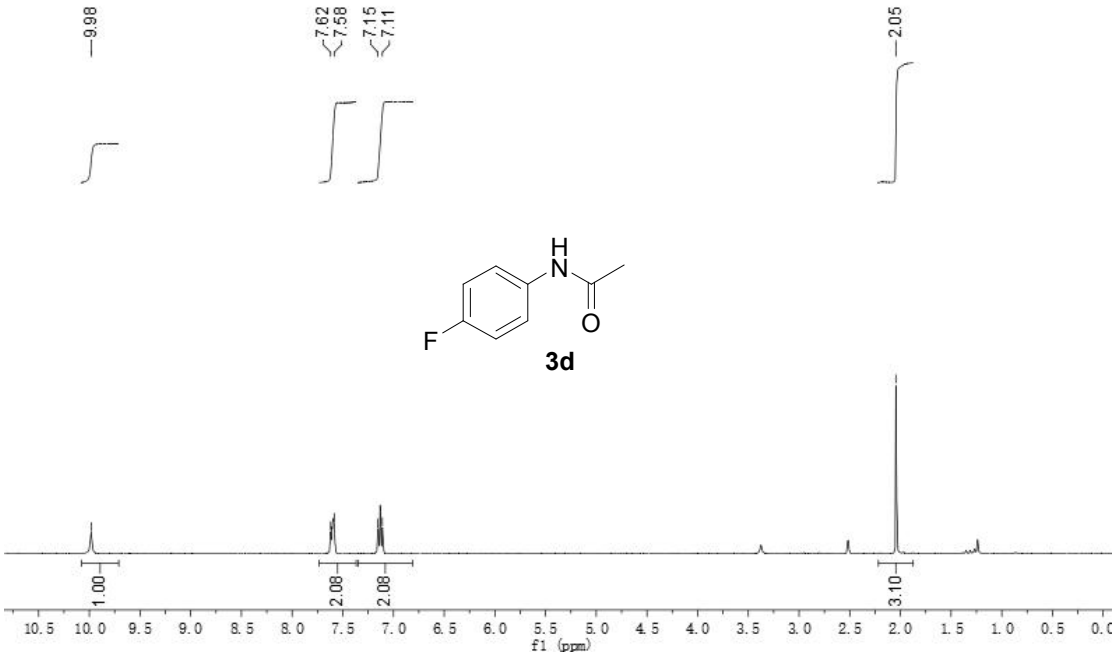


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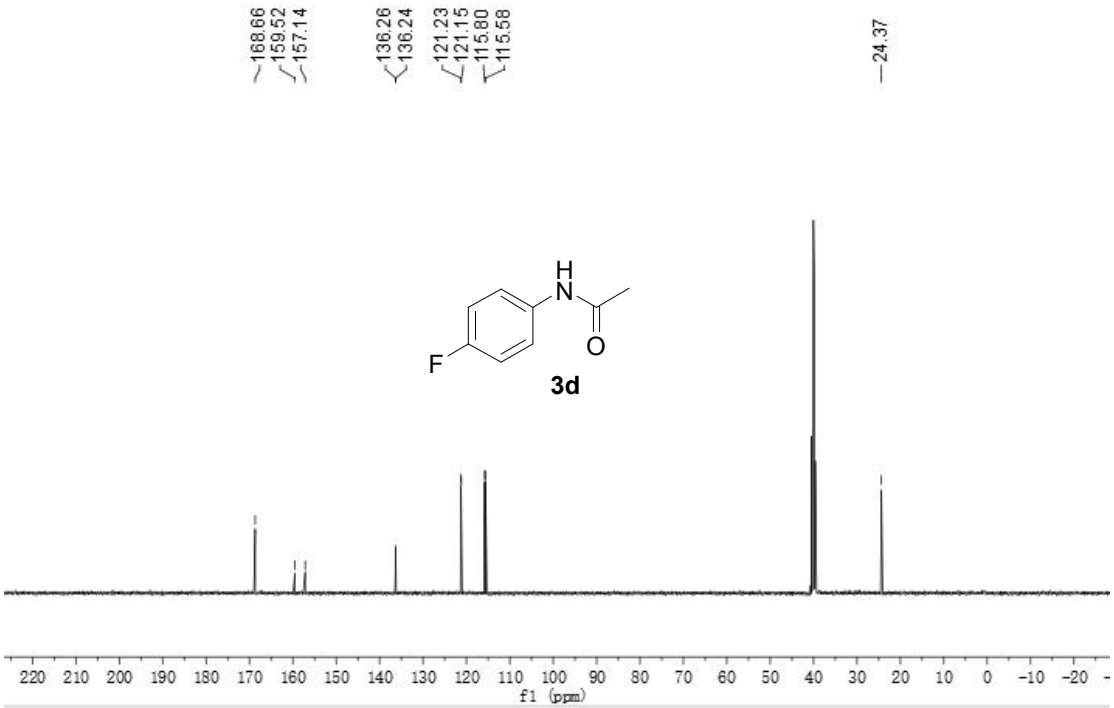

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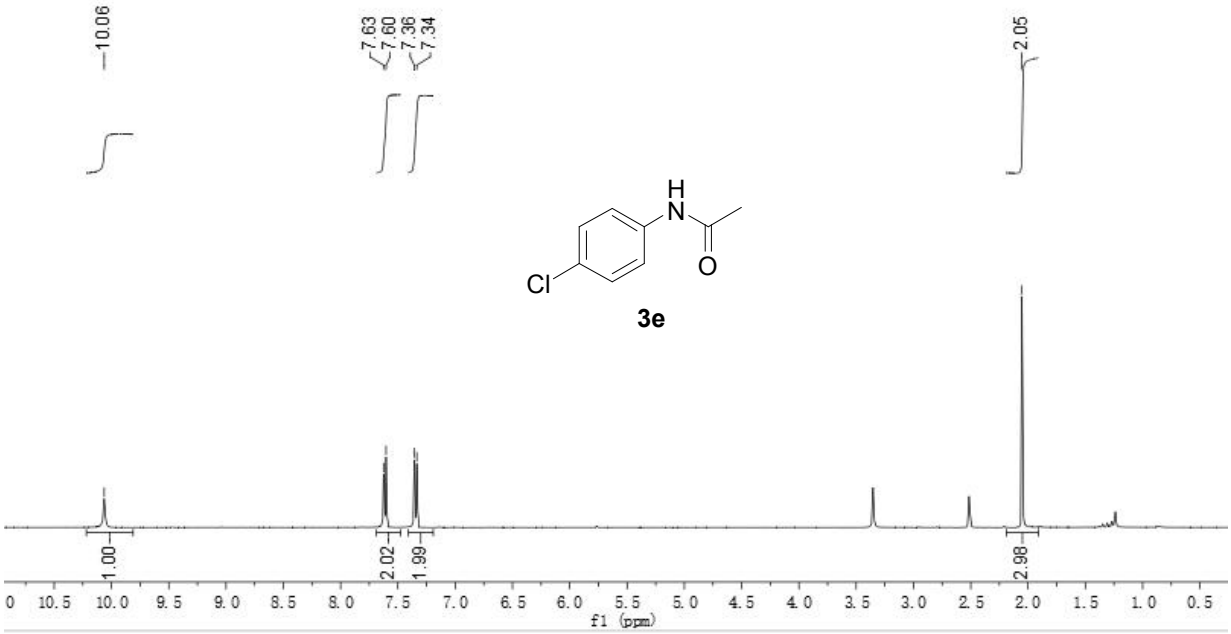


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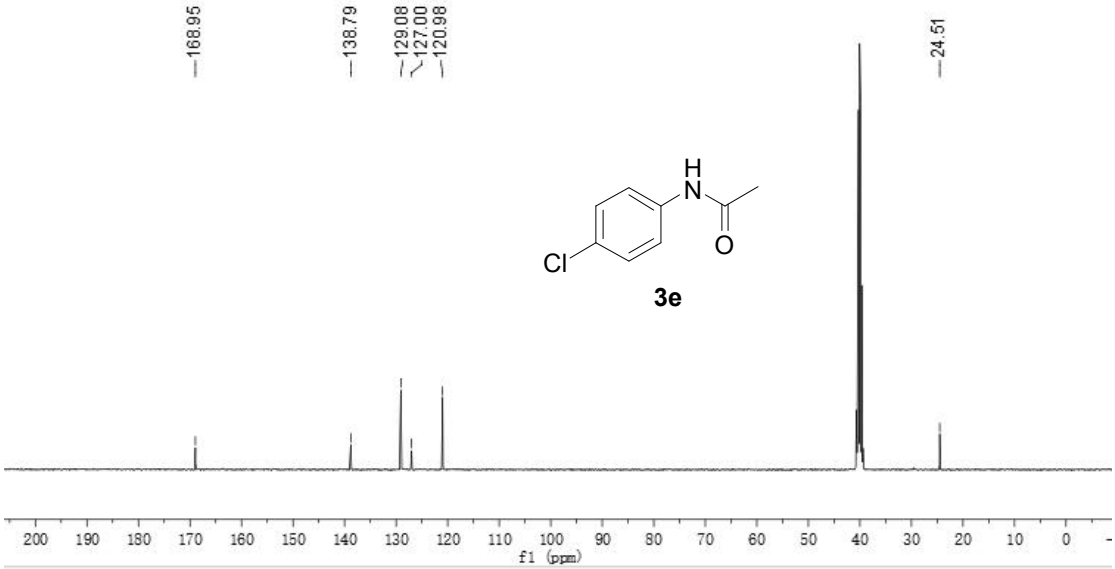

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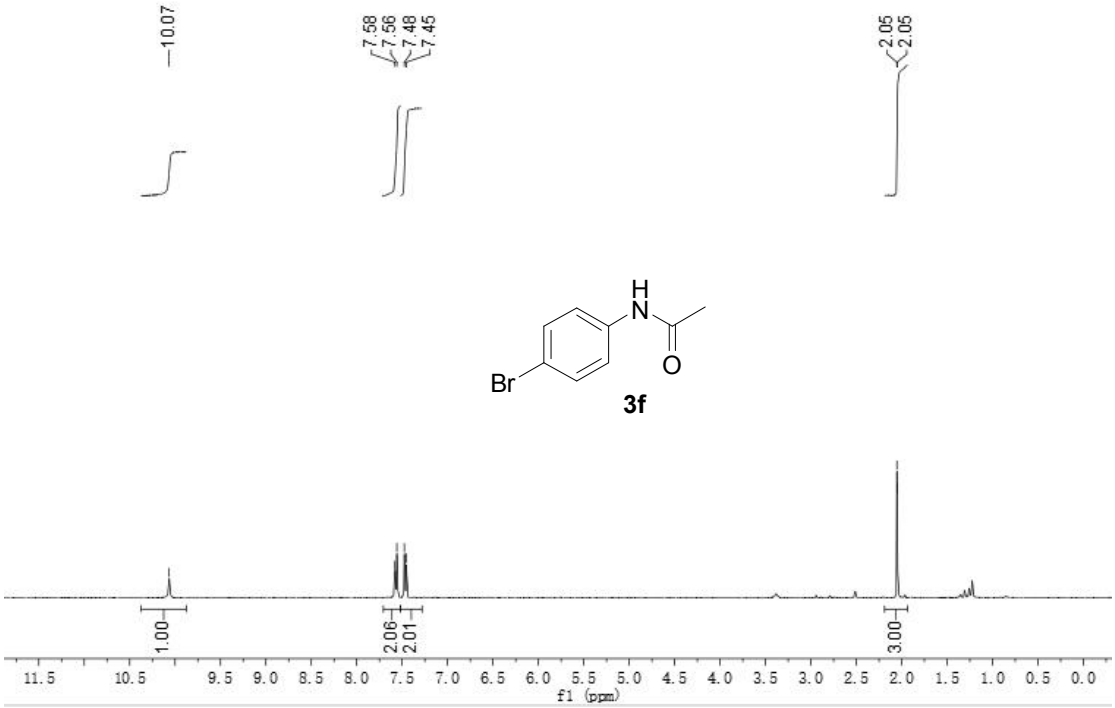


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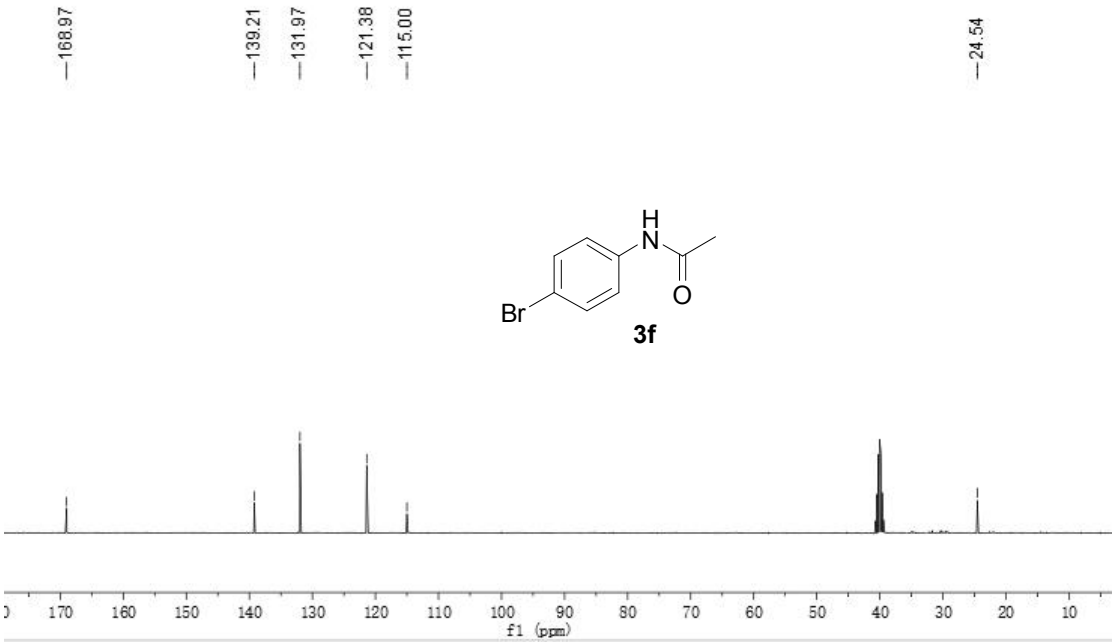

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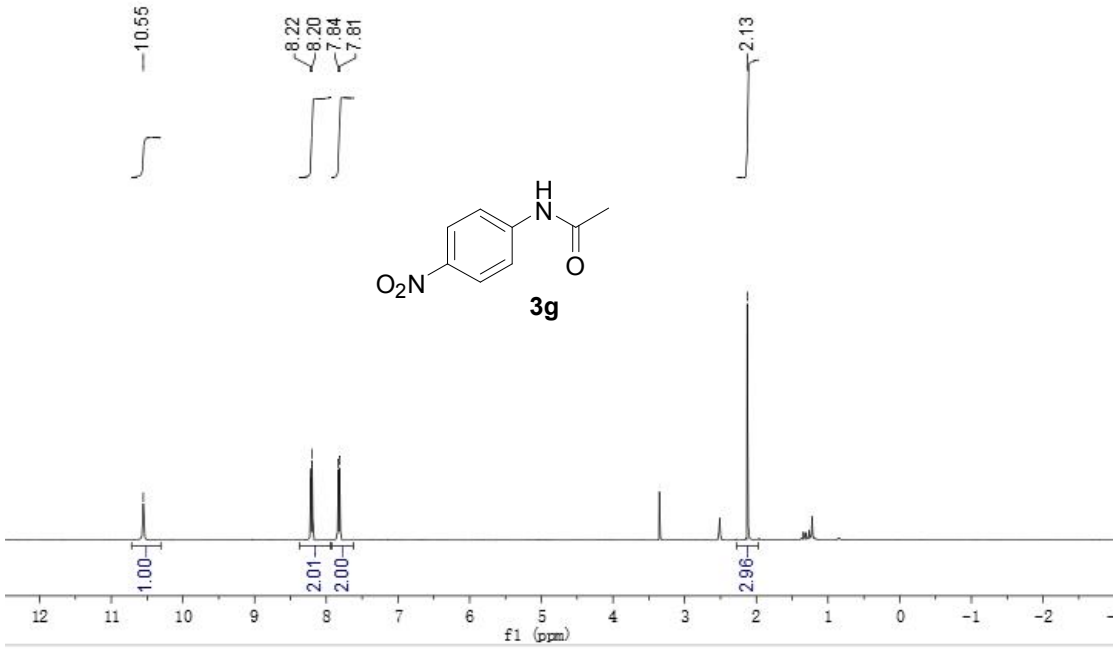


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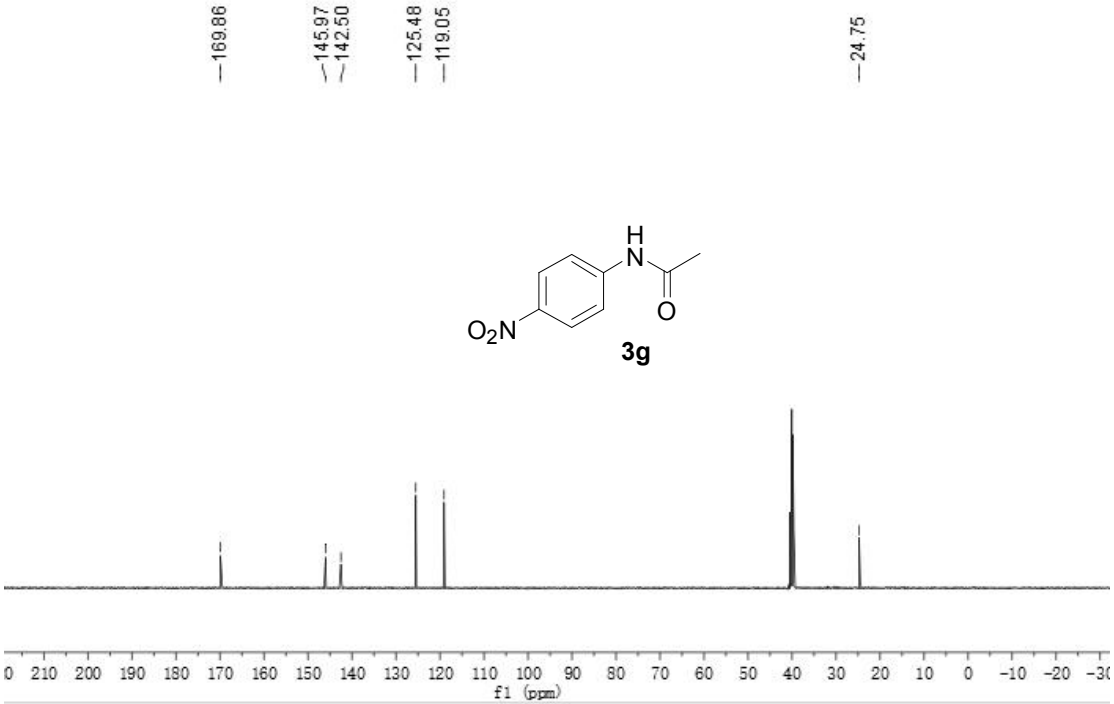

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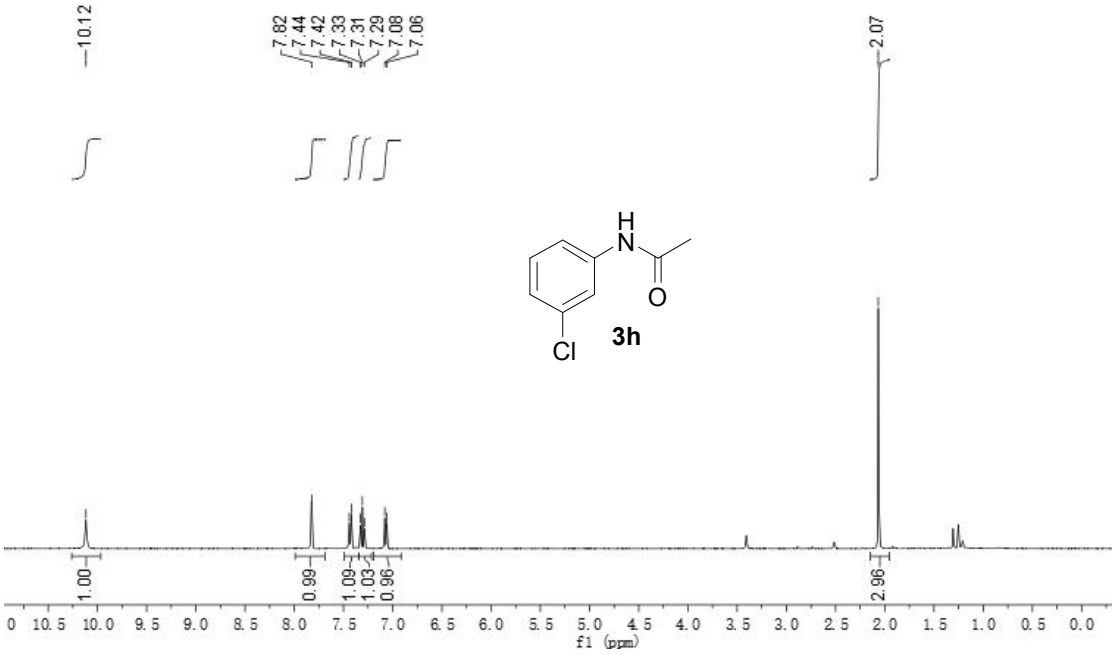


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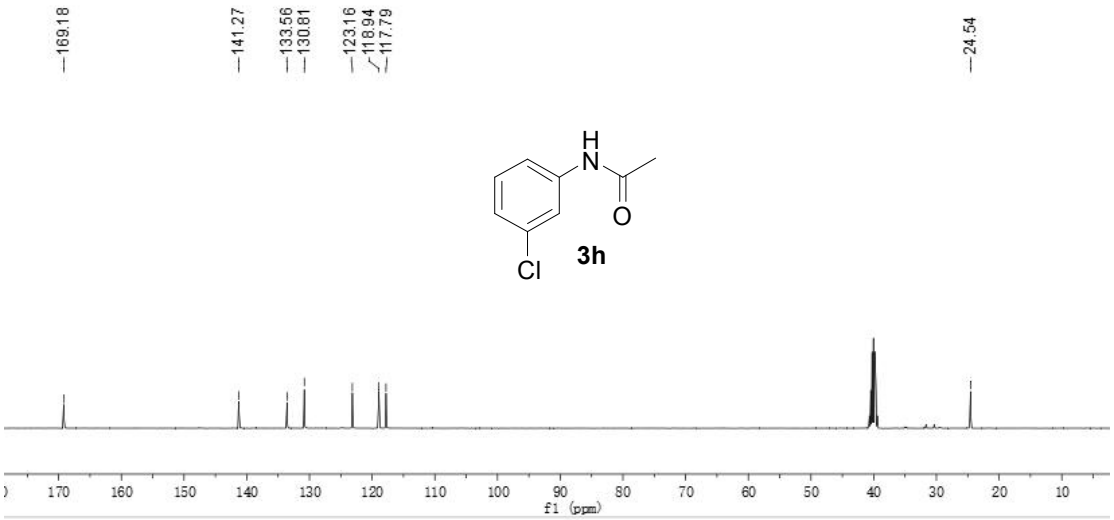

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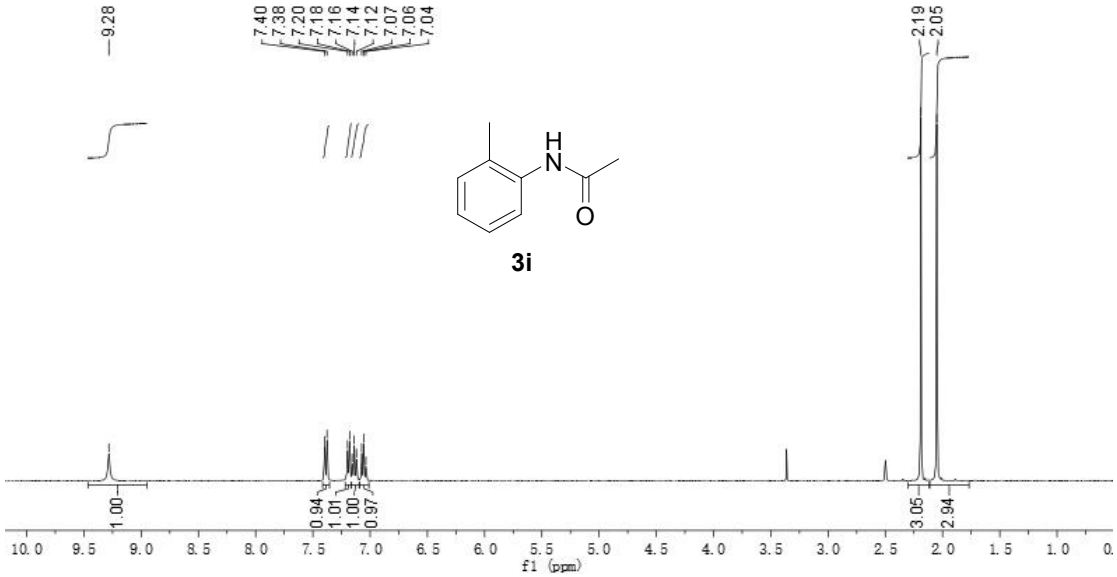


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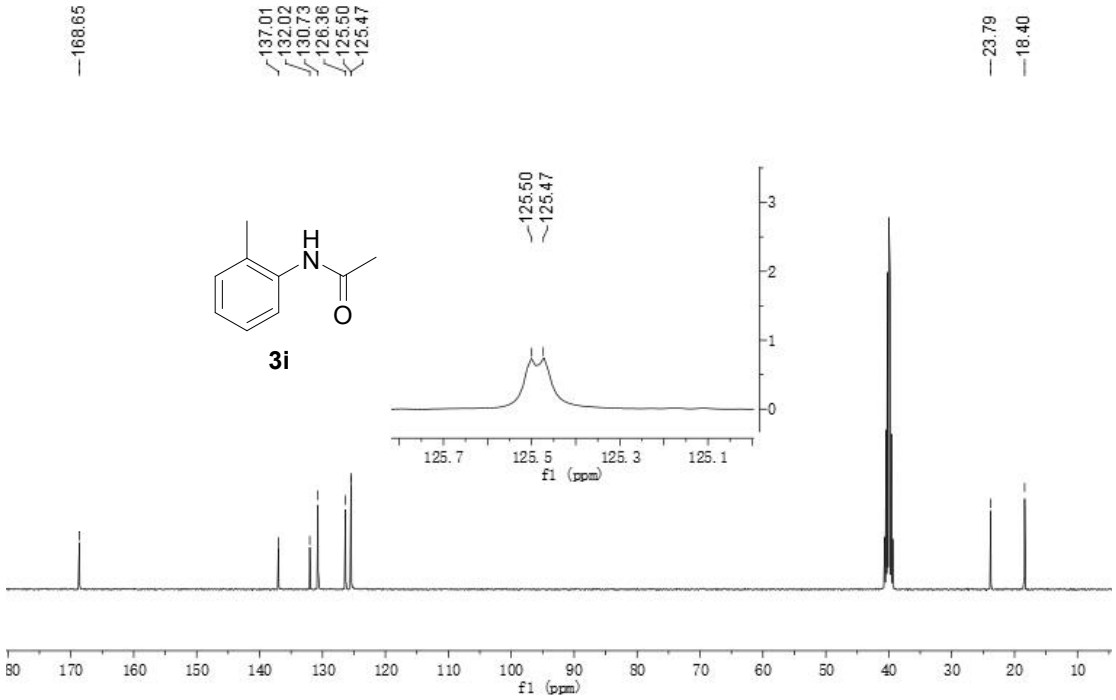

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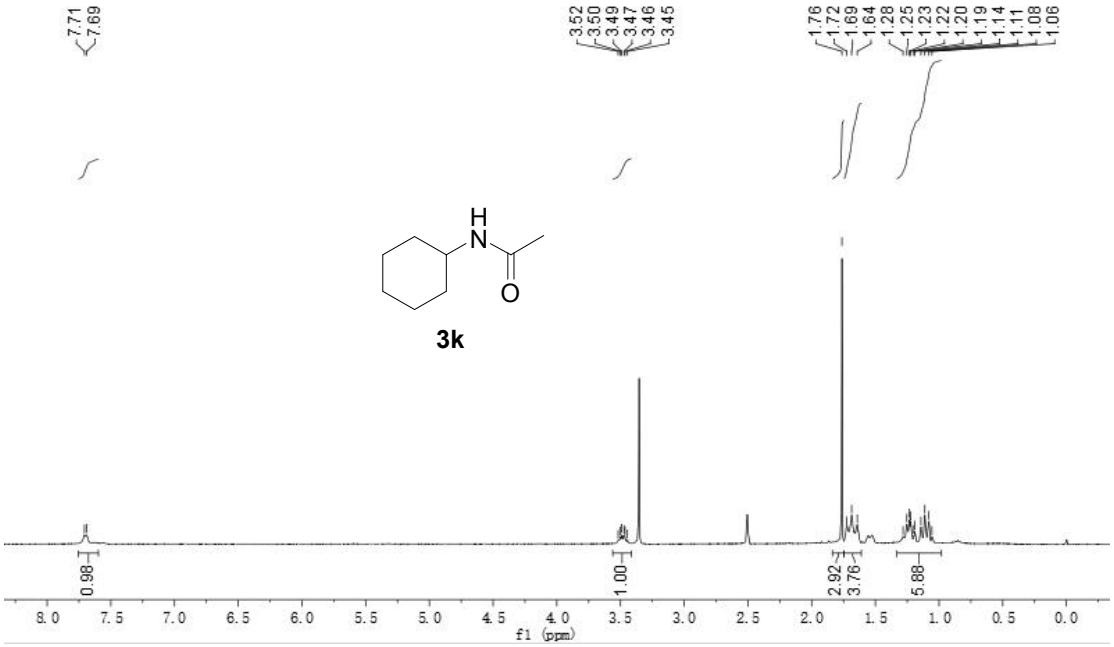


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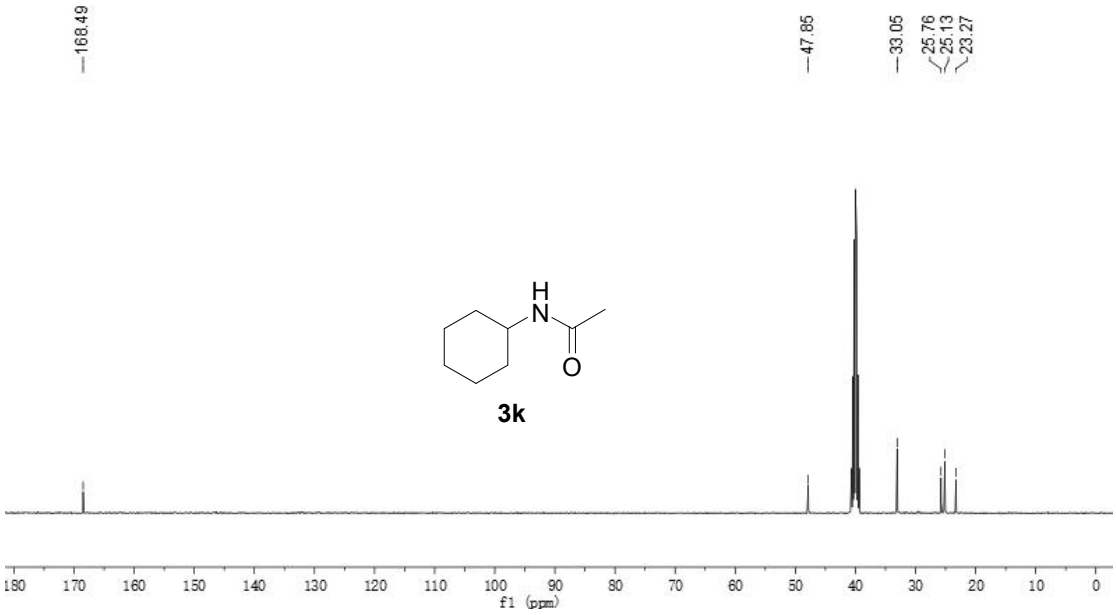

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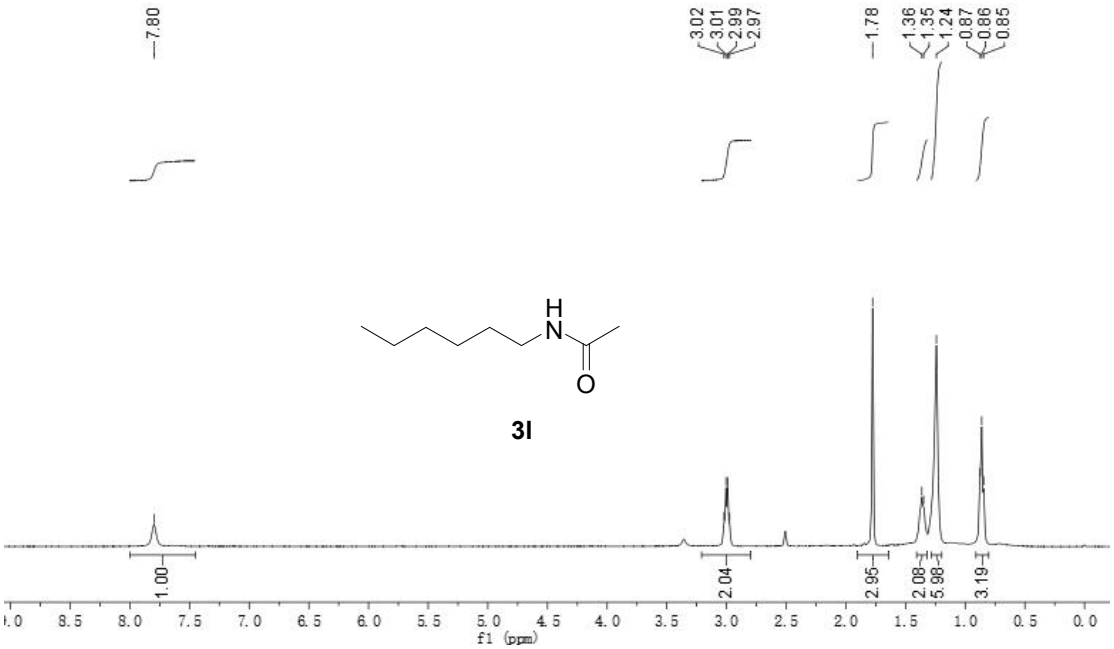


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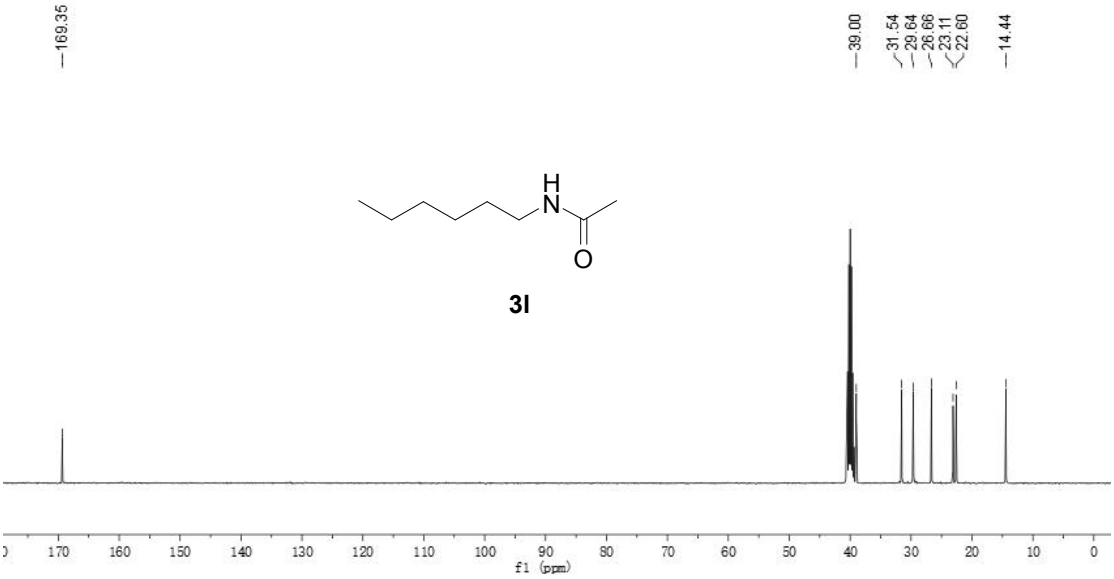

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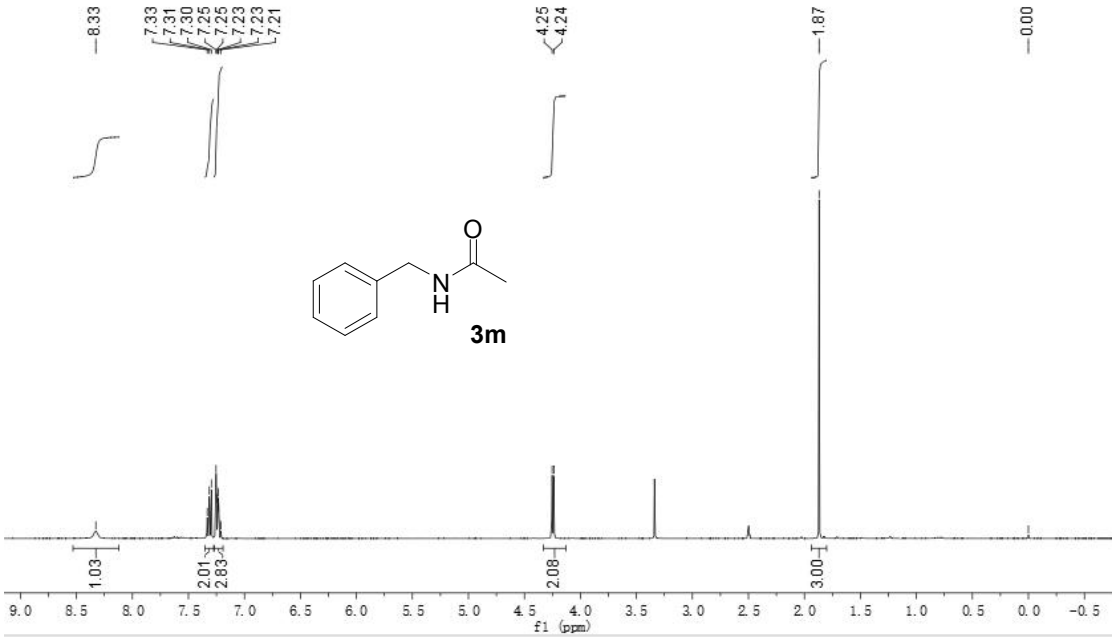


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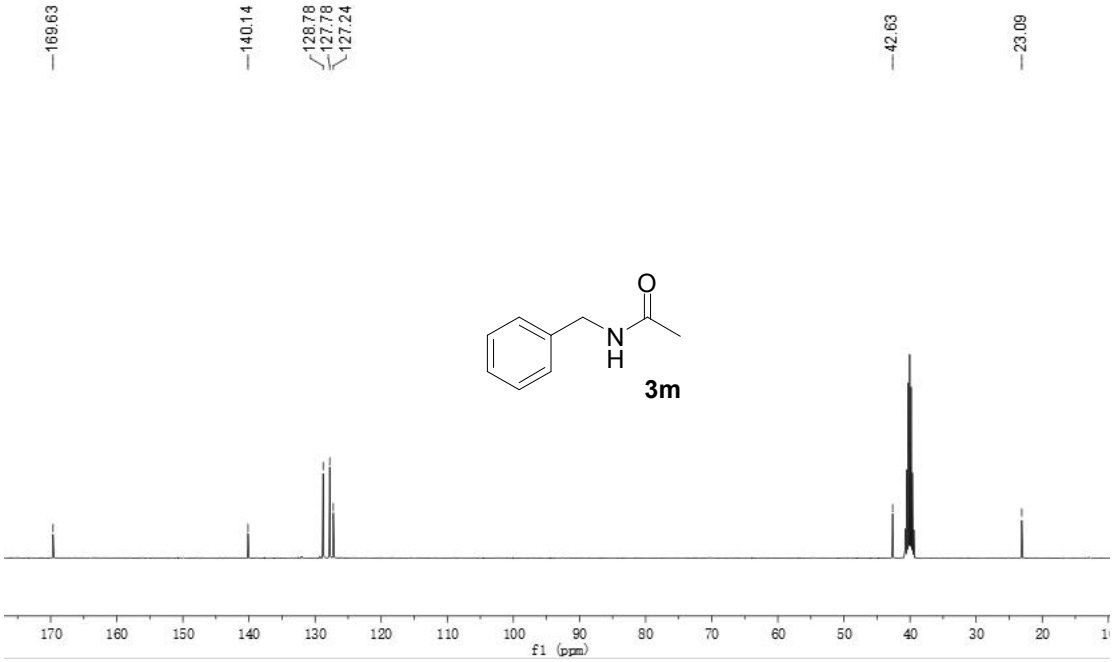

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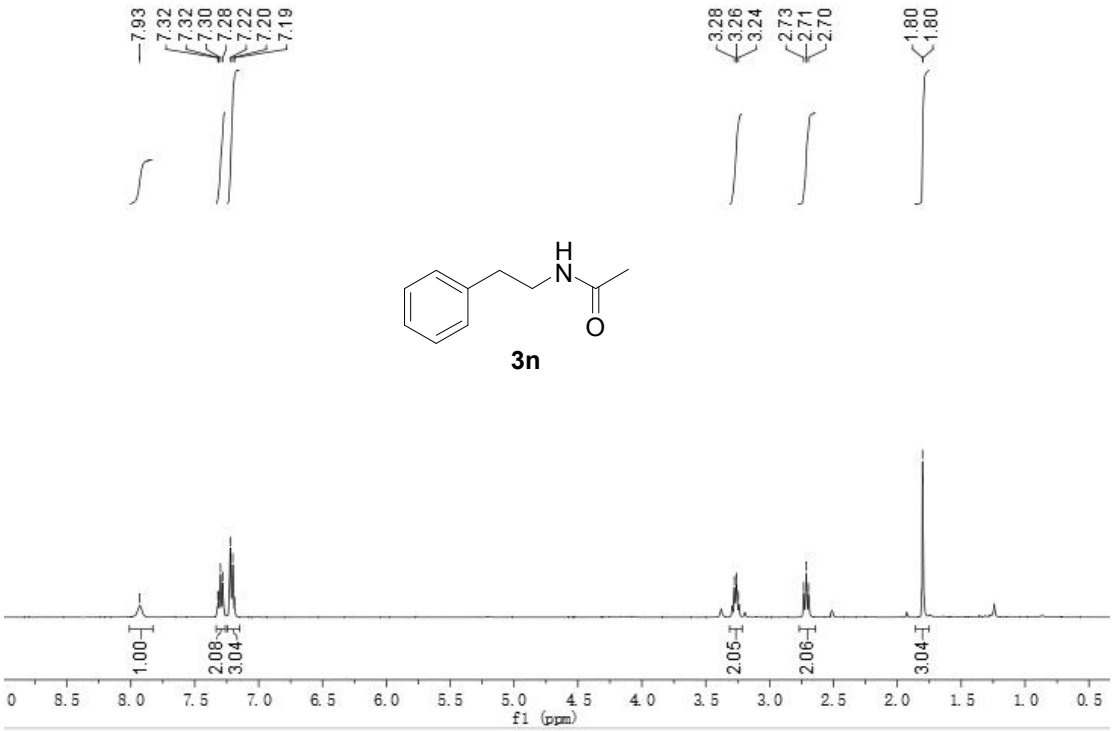


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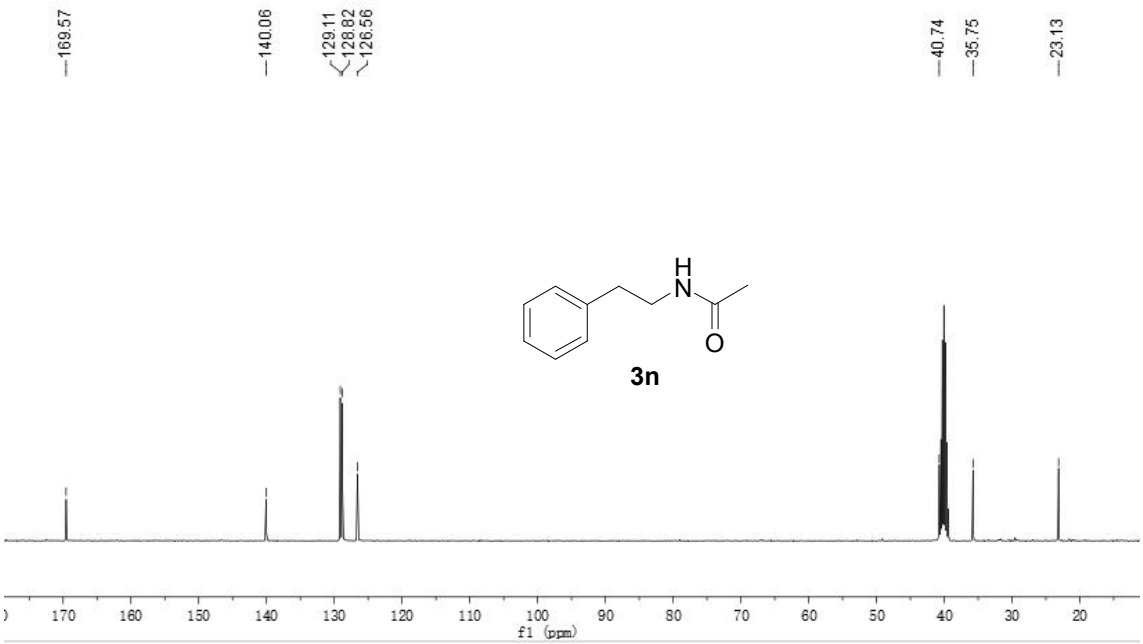

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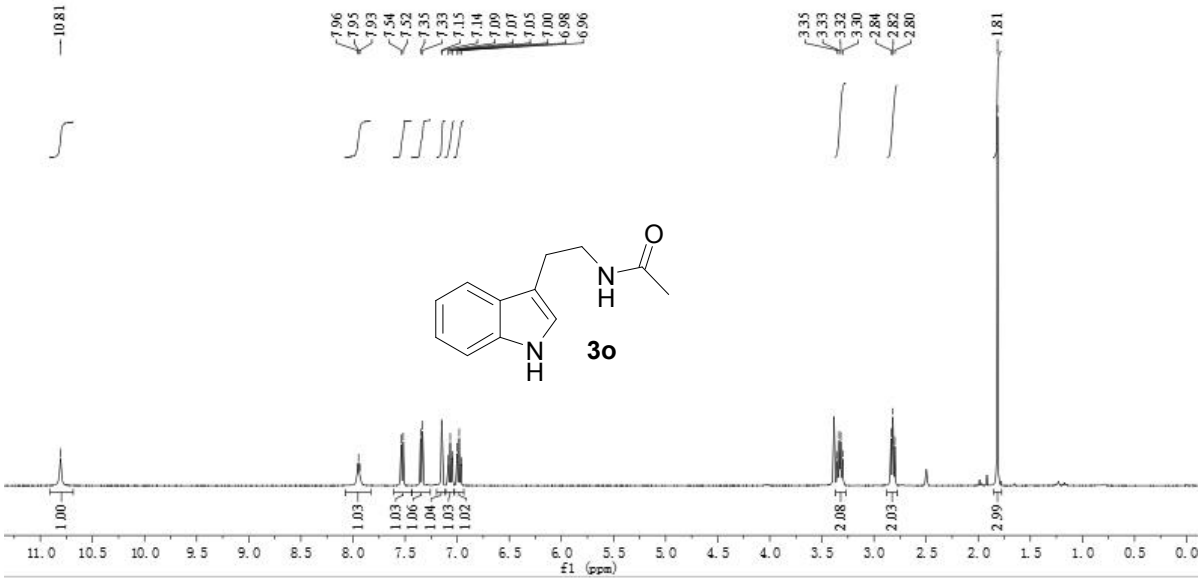


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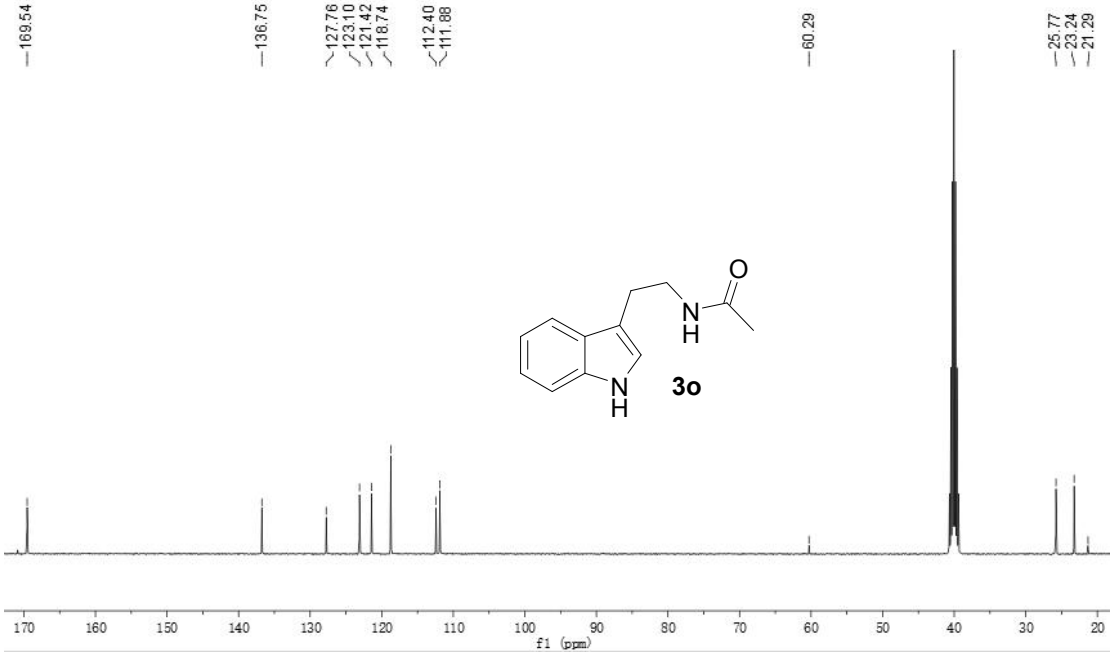

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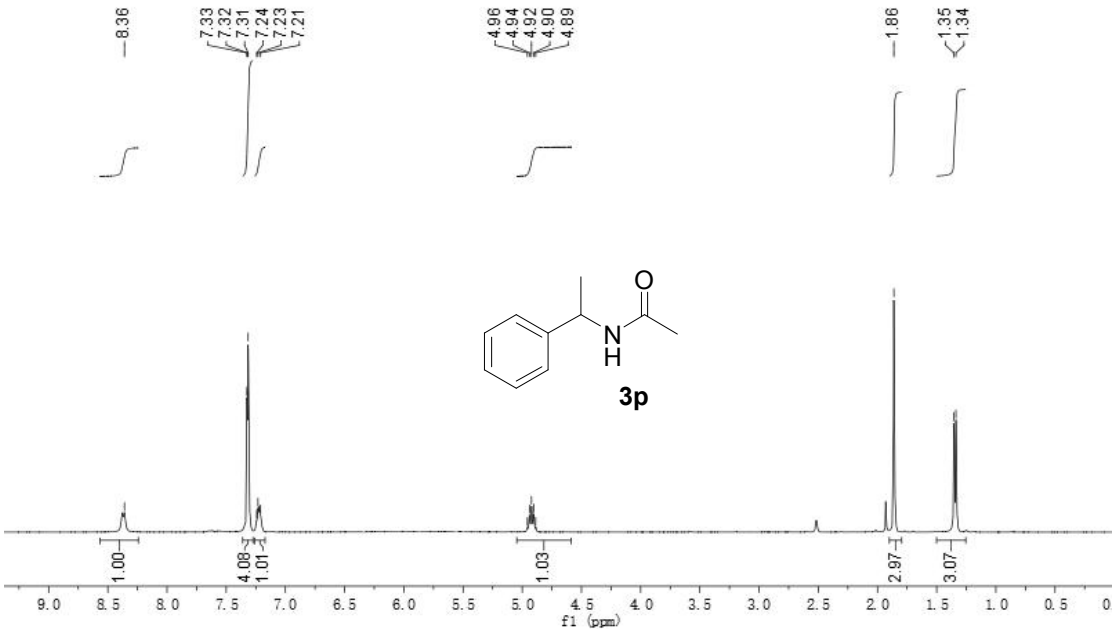


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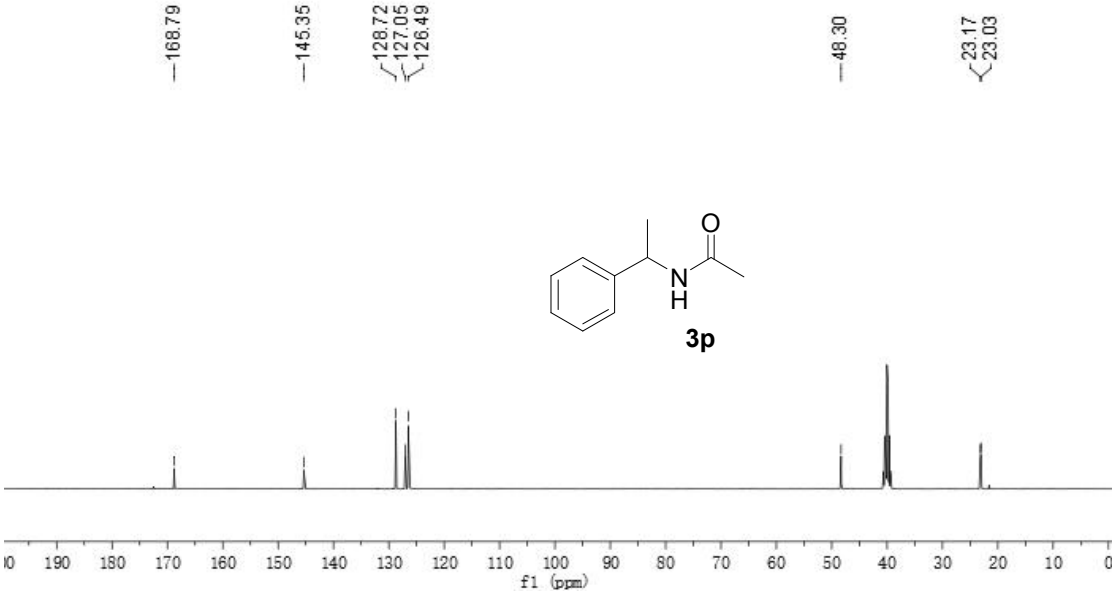

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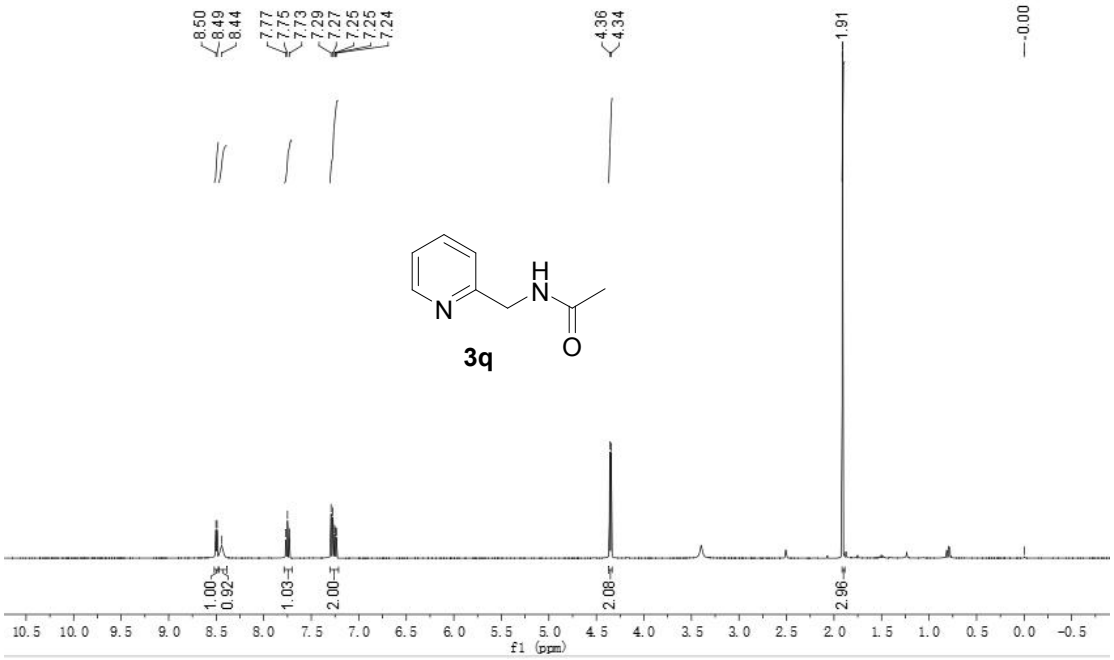


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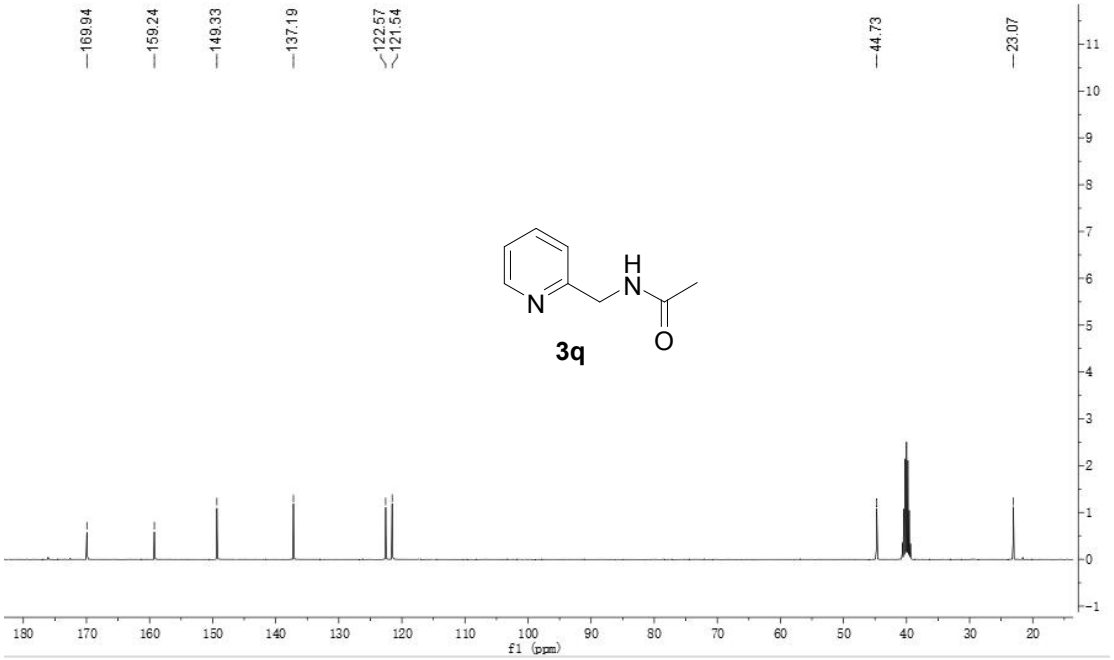

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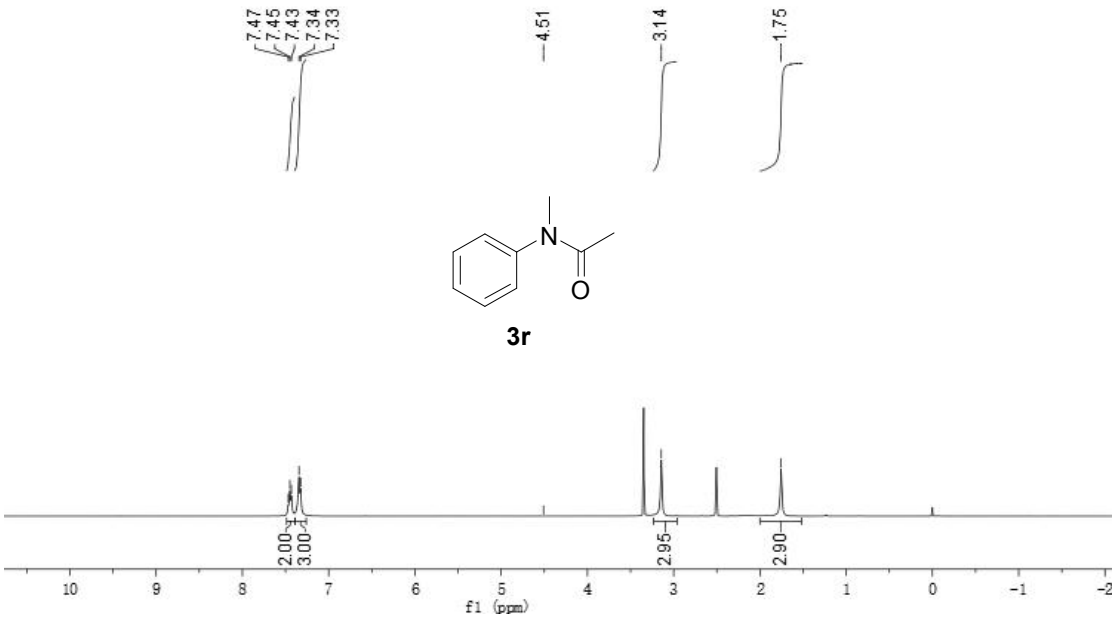


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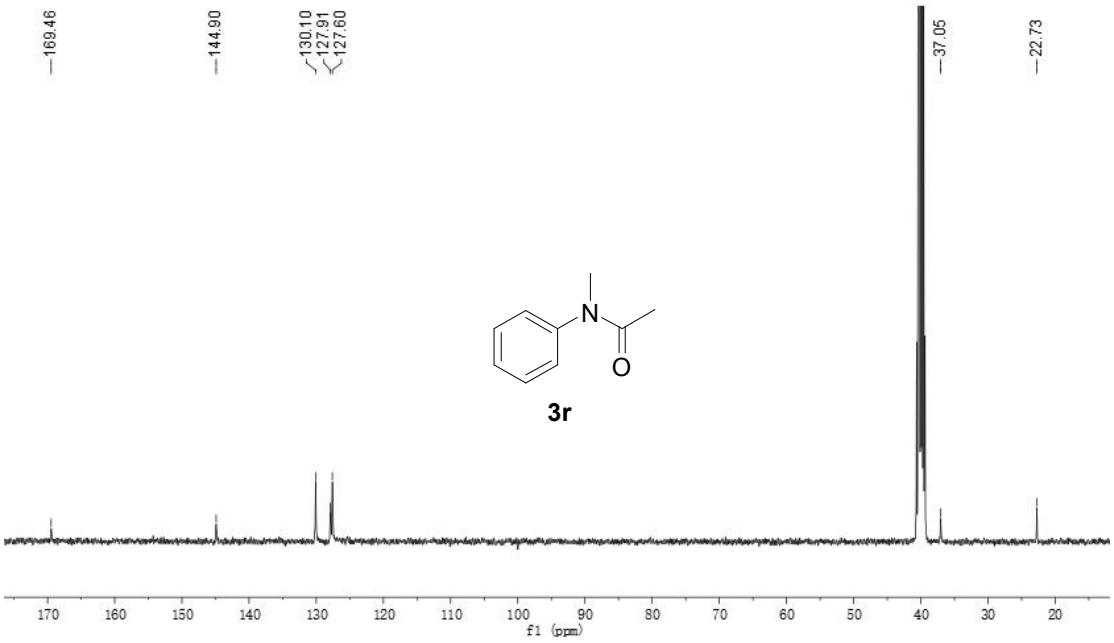
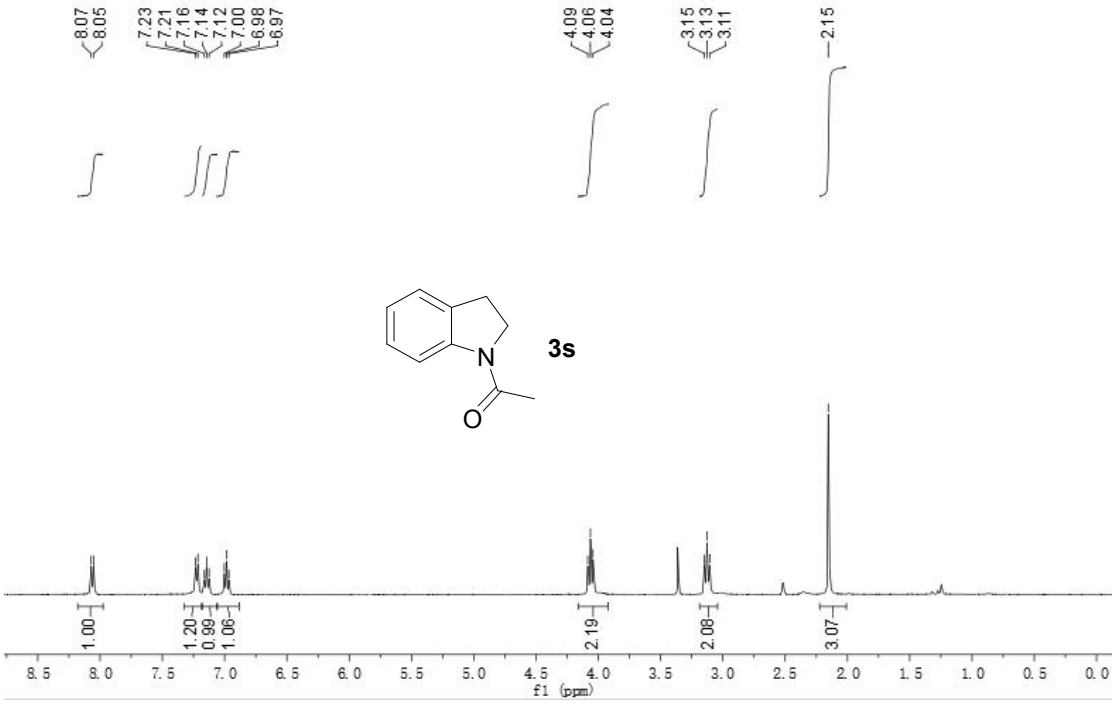
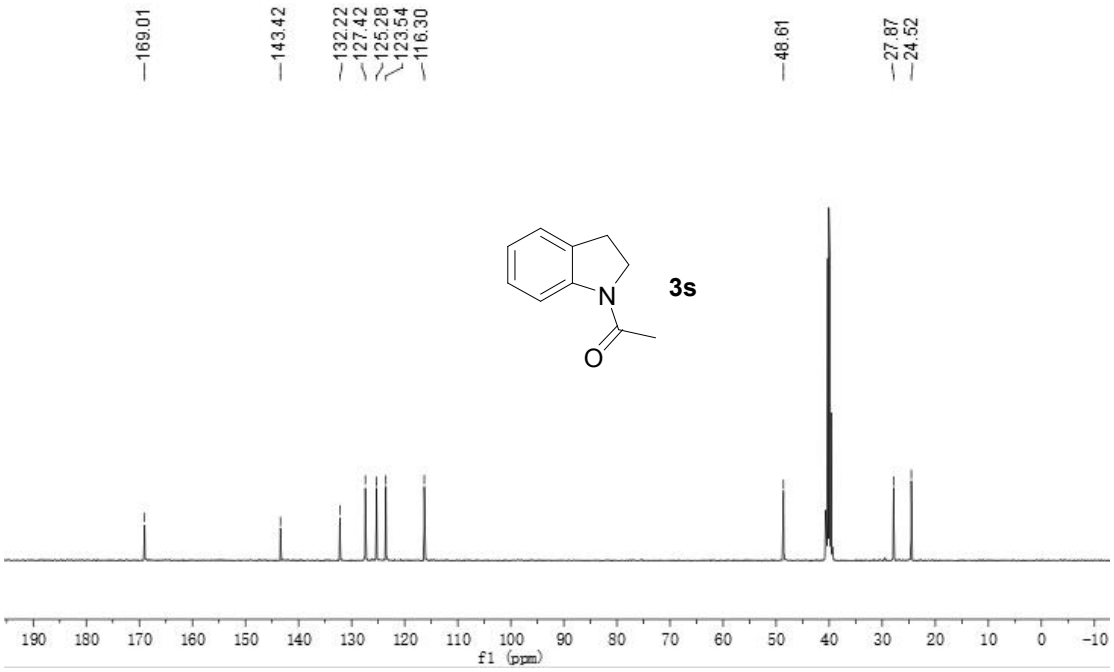


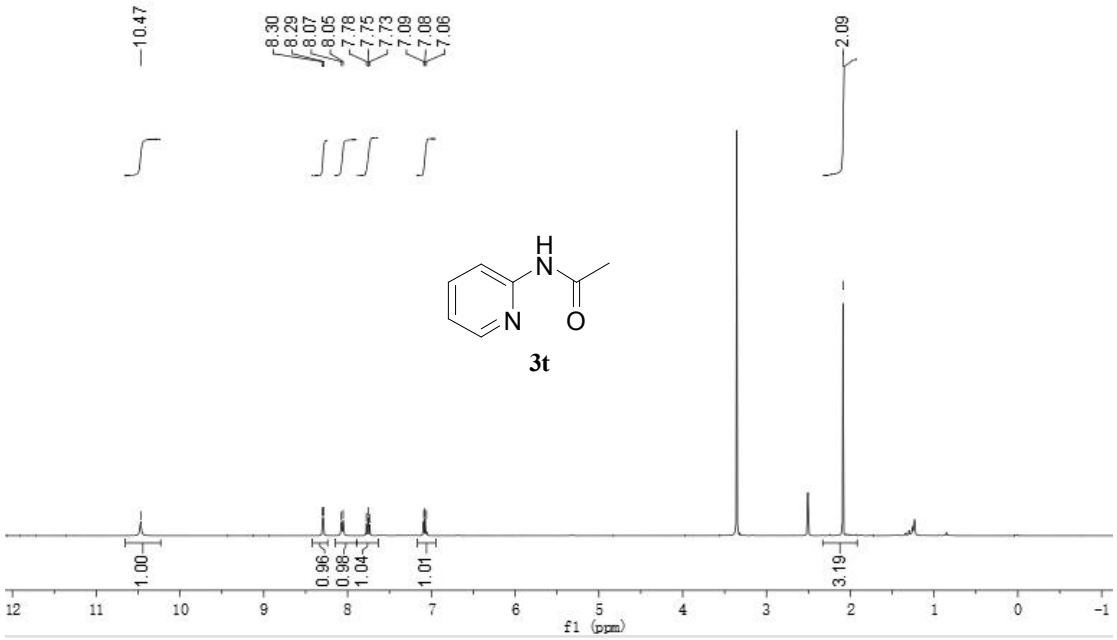
## $^{1}$H NMR spectra



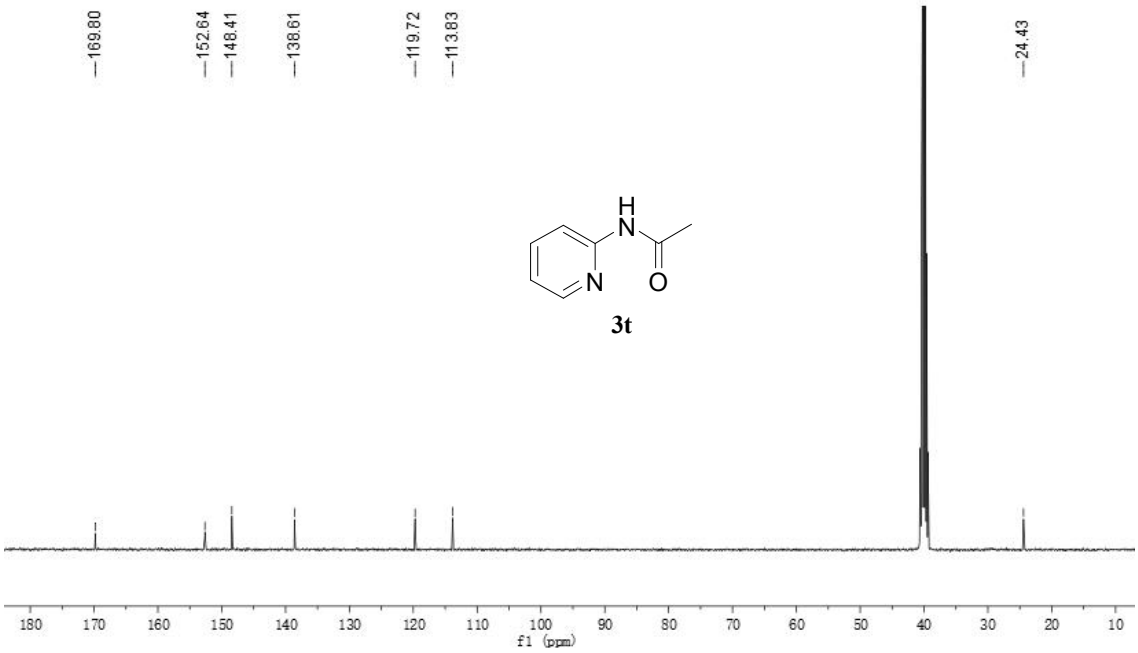

## $^{13}$C NMR spectra



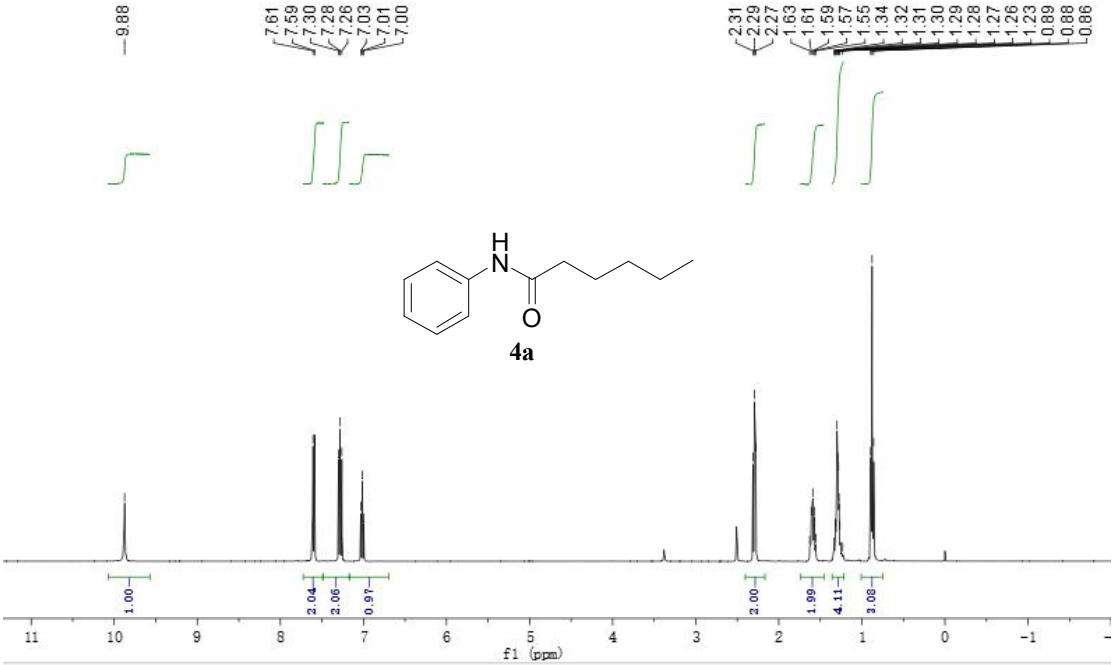
## $^{1}$H NMR spectra



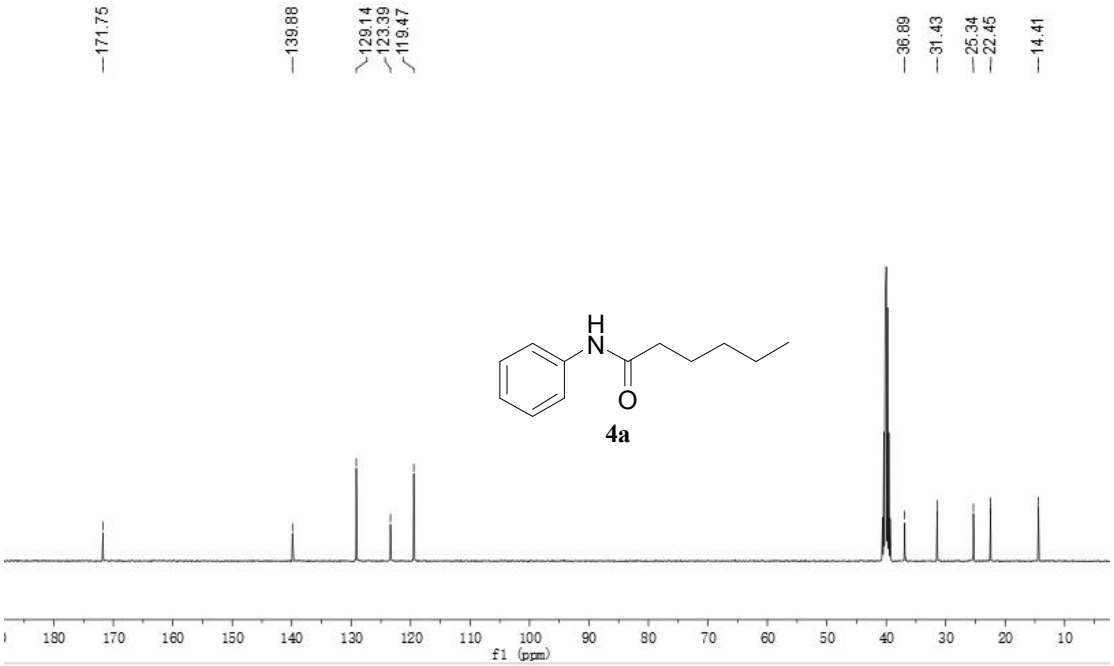

## $^{13}$C NMR spectra



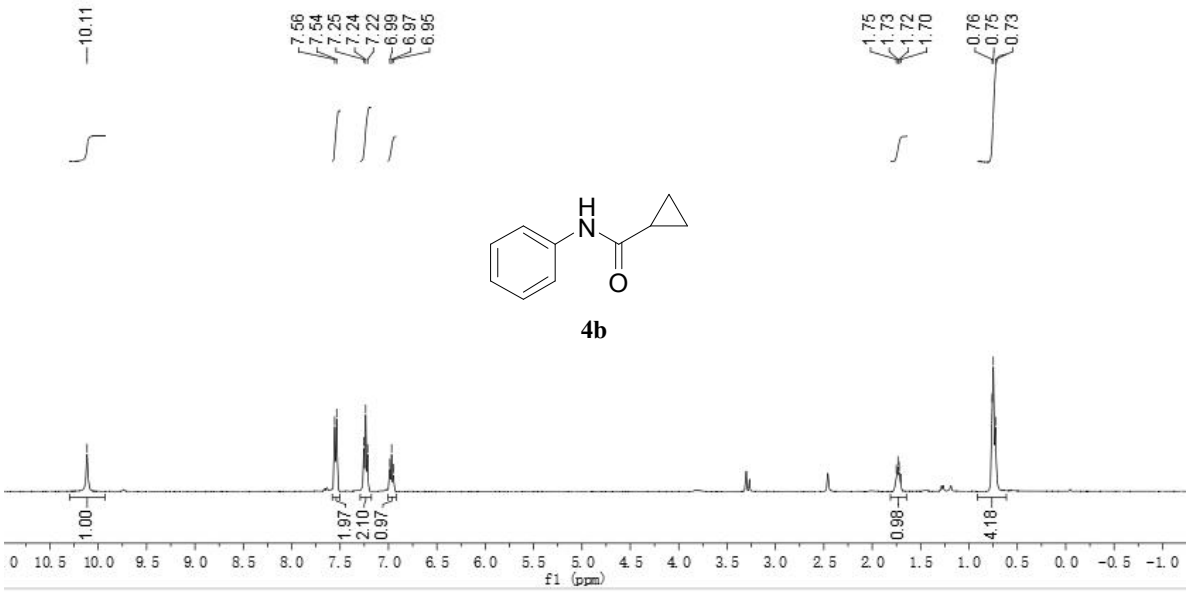
## $^{1}$H NMR spectra




## $^{13}$C NMR spectra

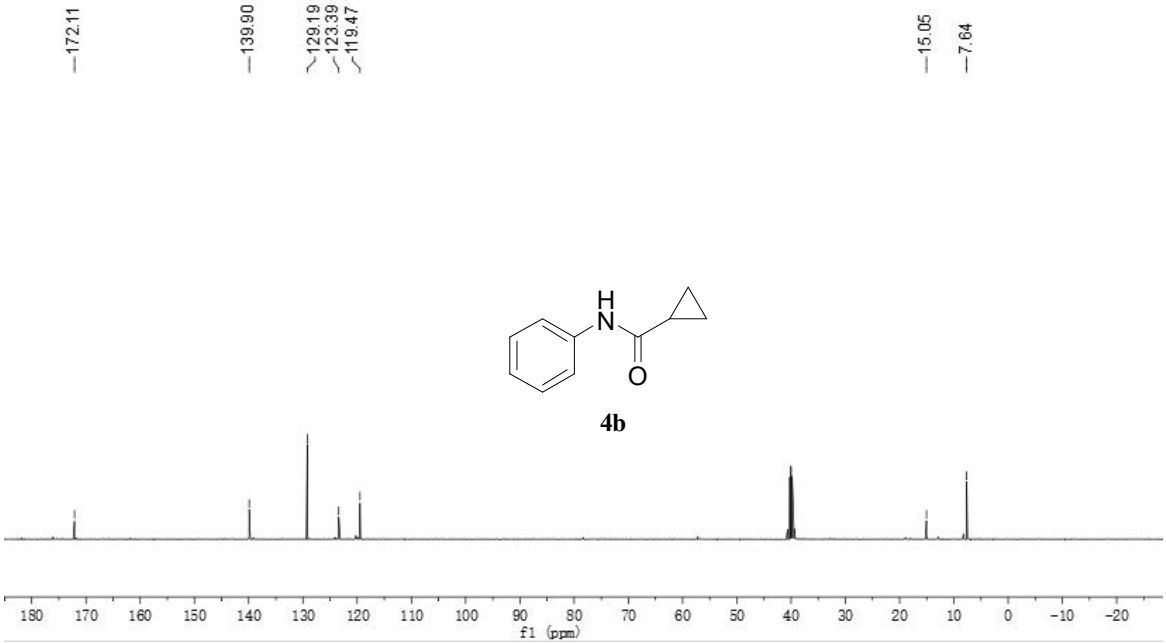


## $^{1}$H NMR spectra



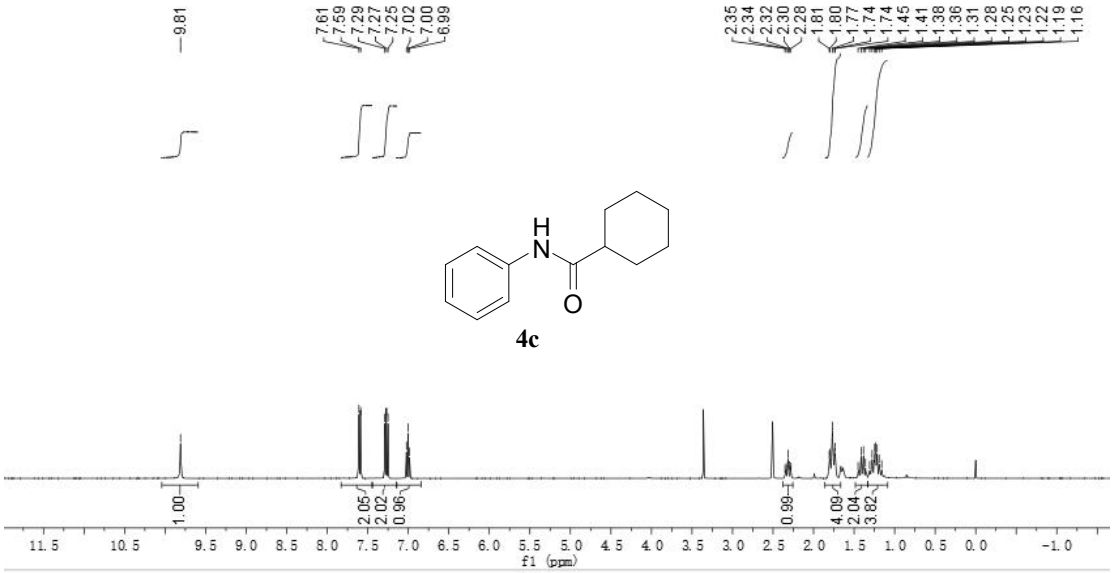

**4b**

## $^{13}$C NMR spectra

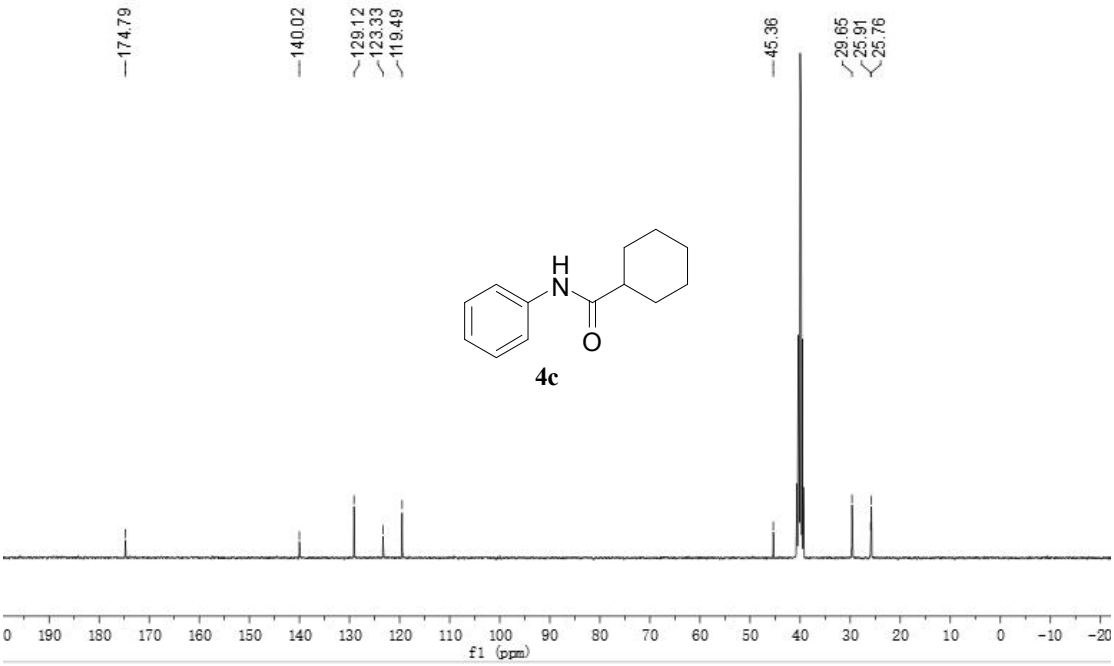



**4b**

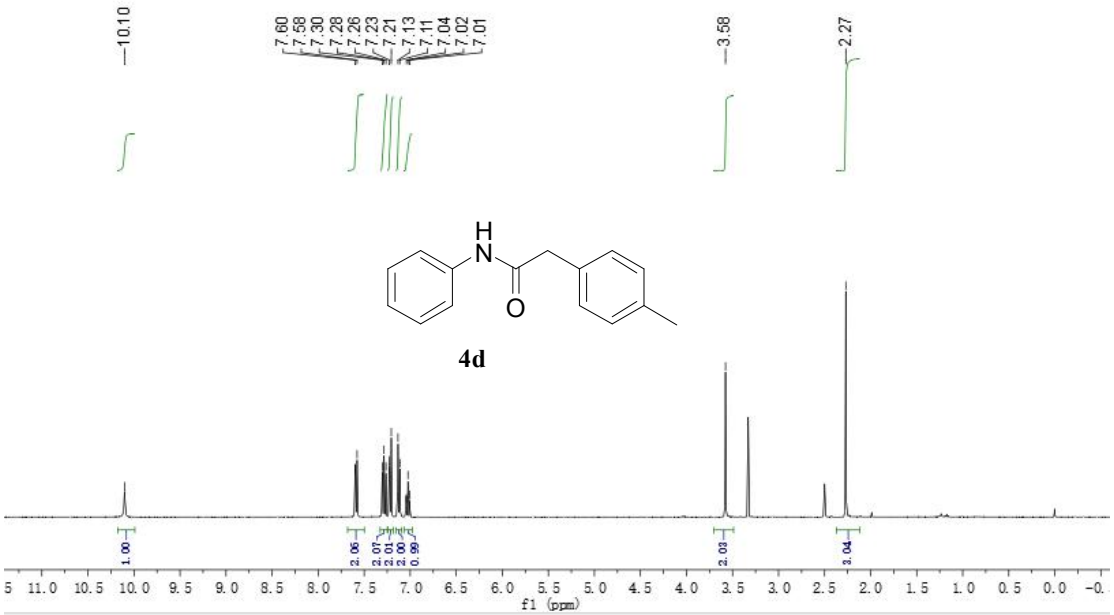
## $^{1}$H NMR spectra



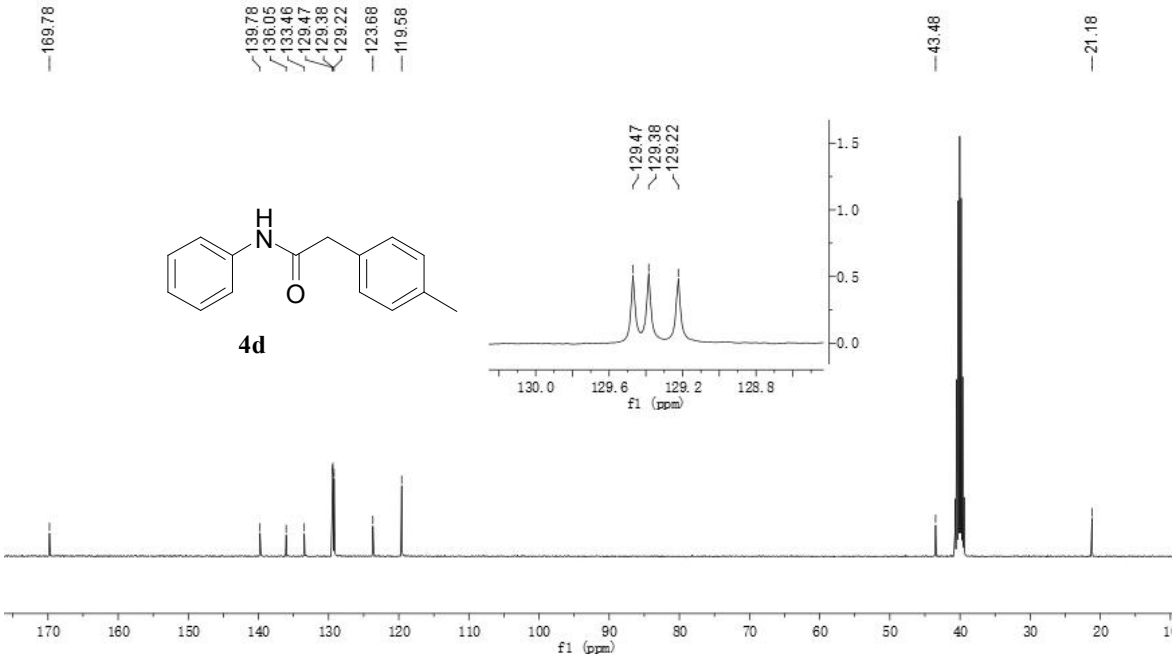

## $^{13}$C NMR spectra



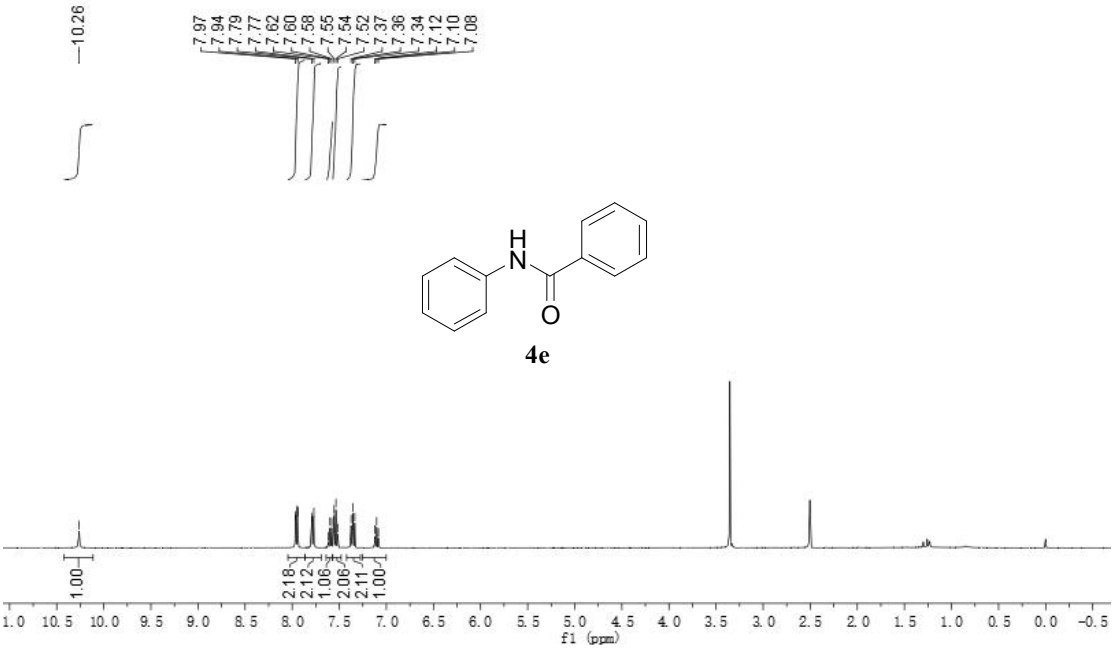
## $^{1}$H NMR spectra



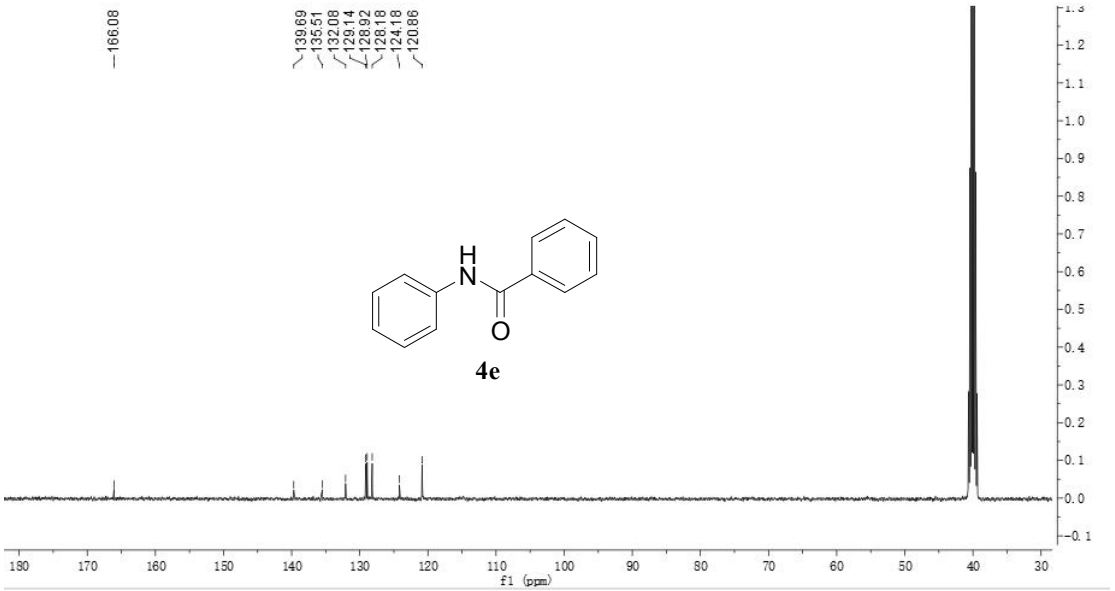

## $^{13}$C NMR spectra



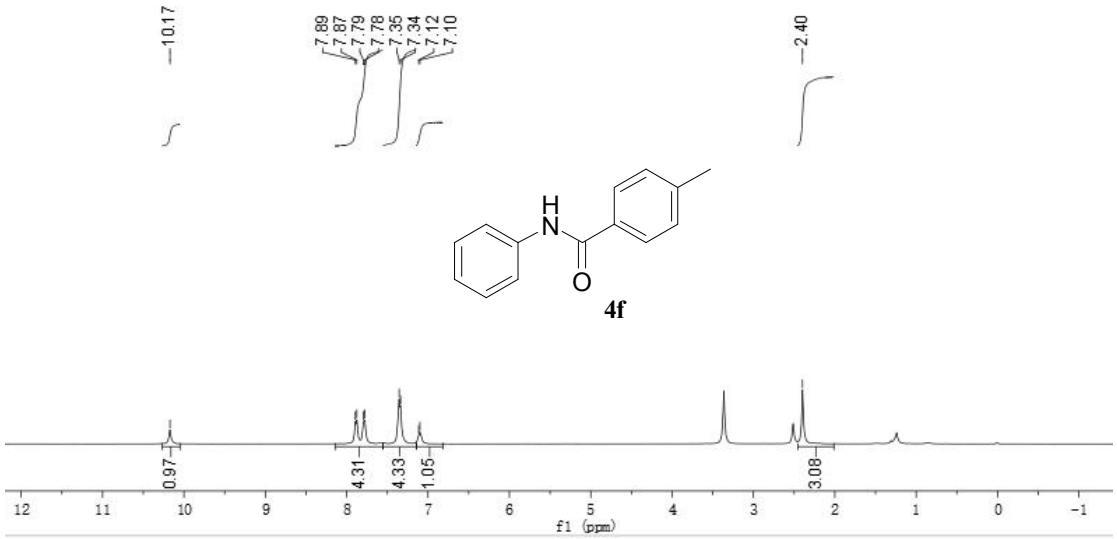
## $^{1}$H NMR spectra



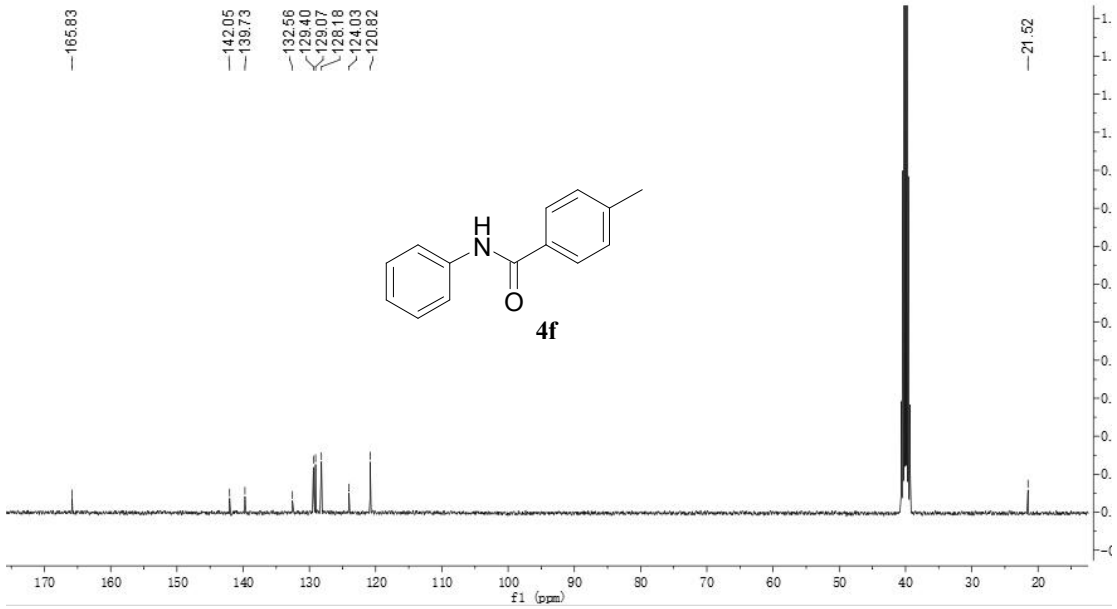

## $^{13}$C NMR spectra



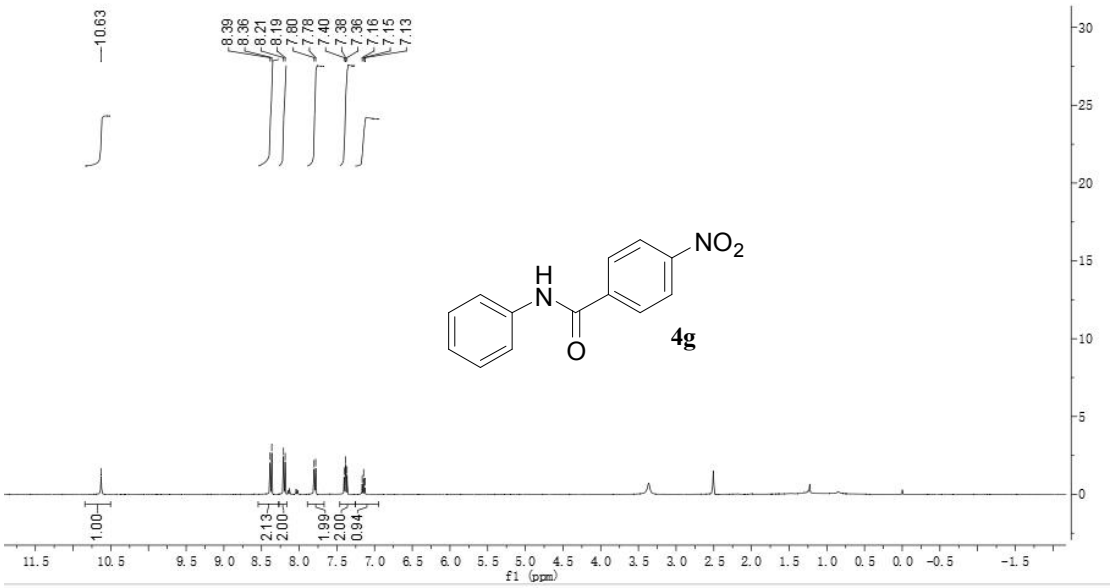
## $^{1}$H NMR spectra



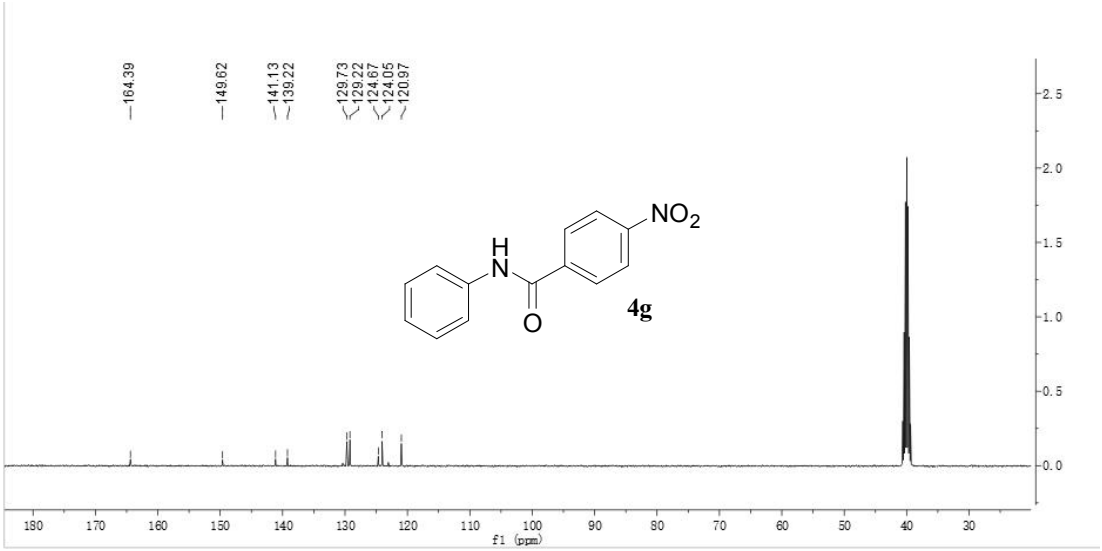

## $^{13}$C NMR spectra



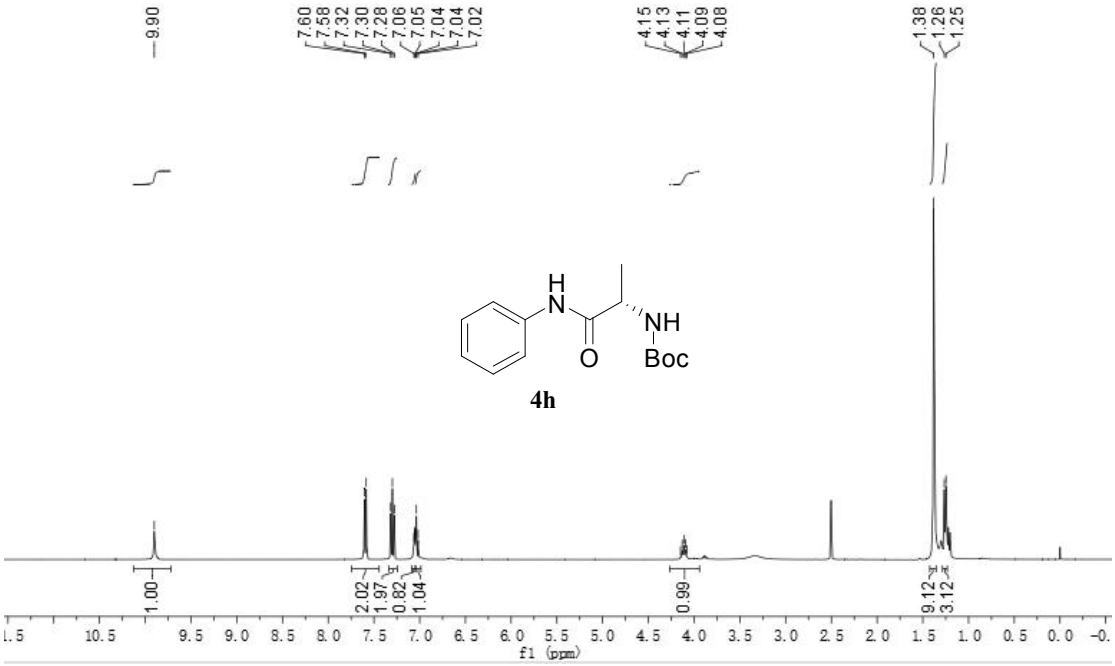
## $^{1}$H NMR spectra



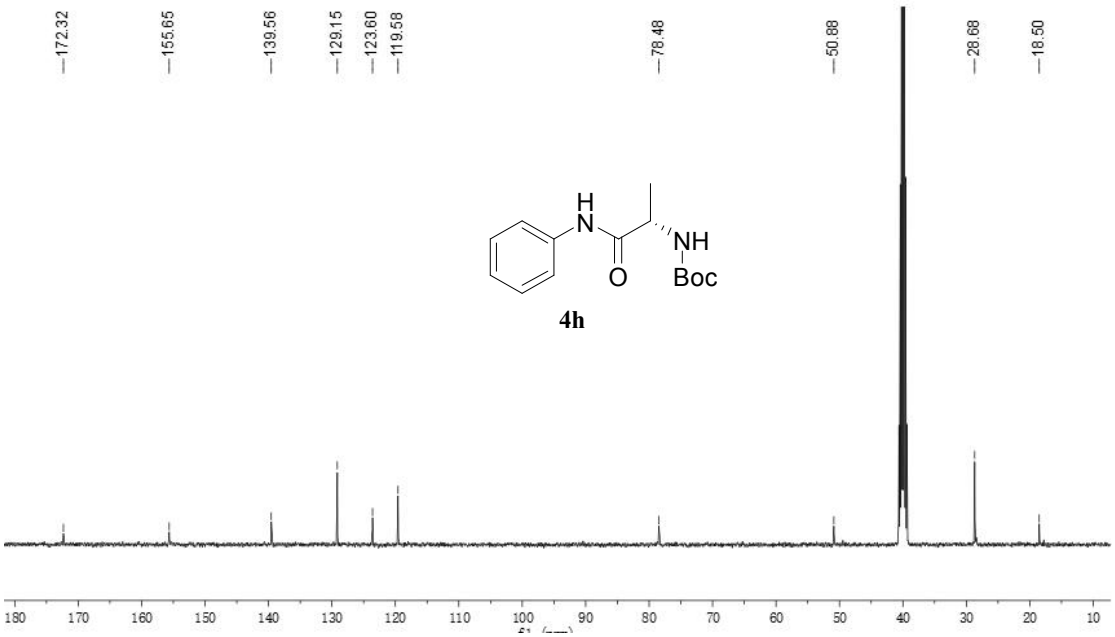

## $^{13}$C NMR spectra



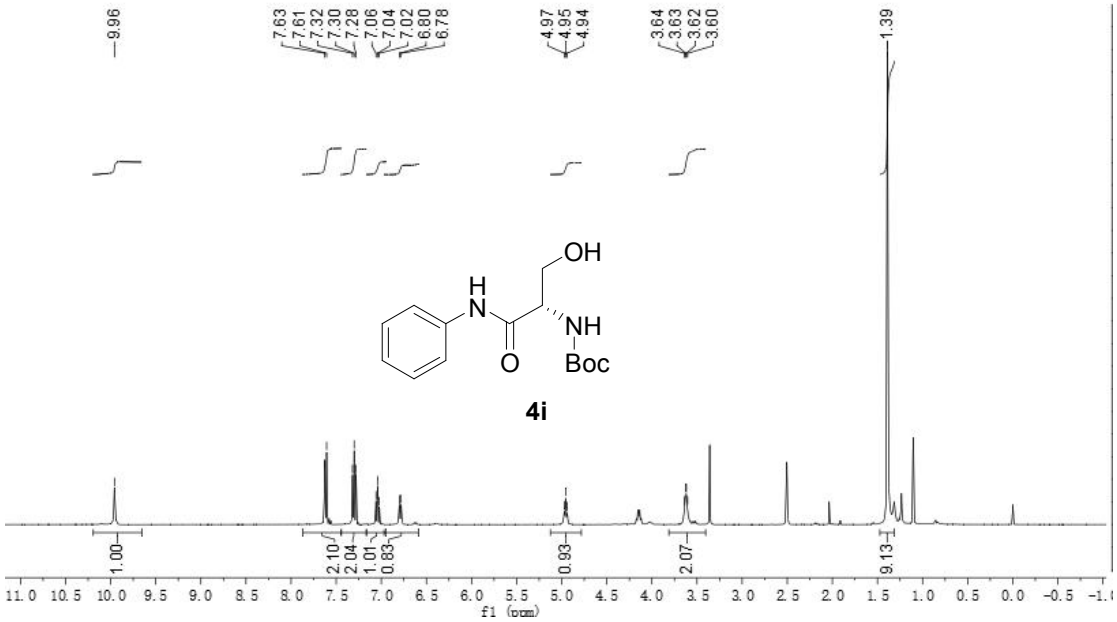
## $^{1}$H NMR spectra



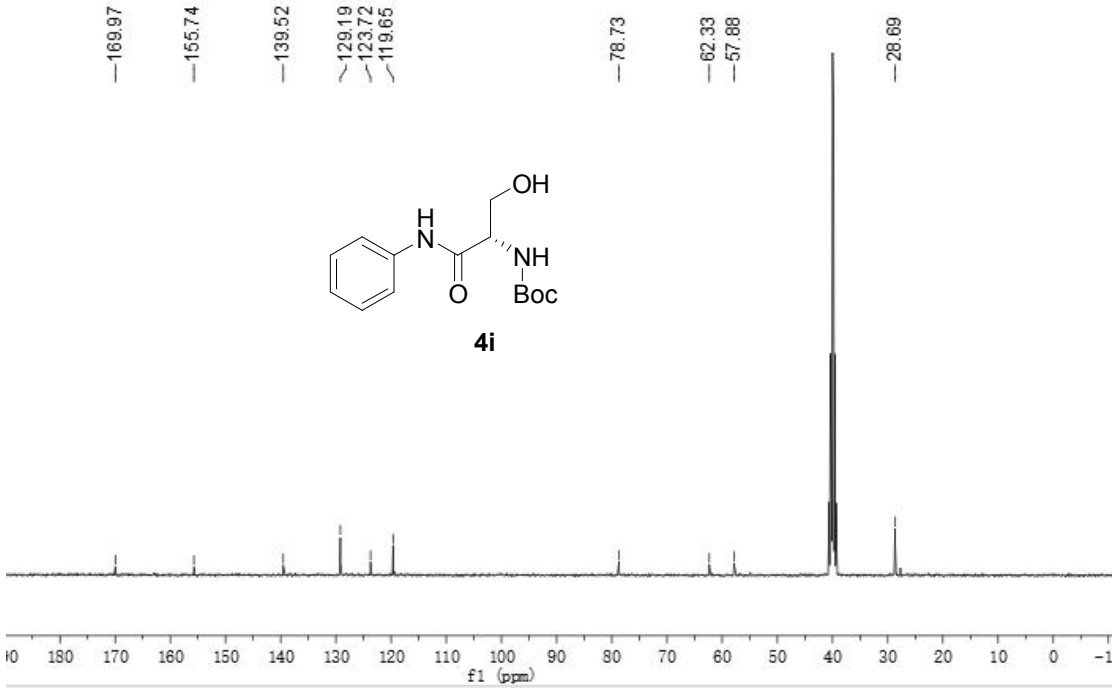

## $^{13}$C NMR spectra



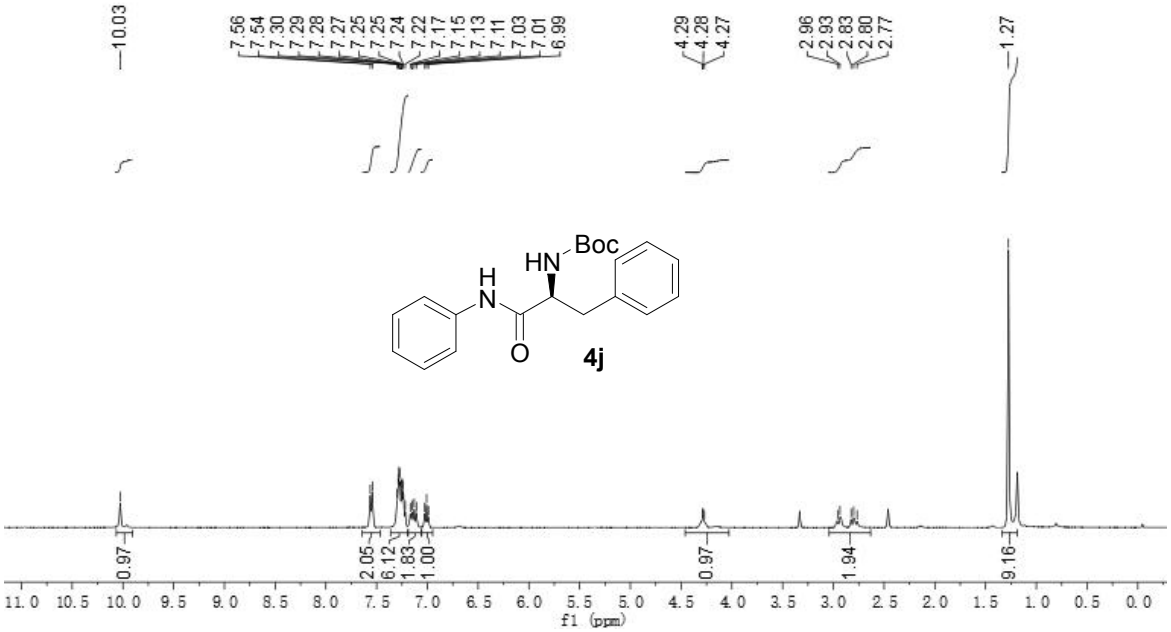
## $^{1}$H NMR spectra



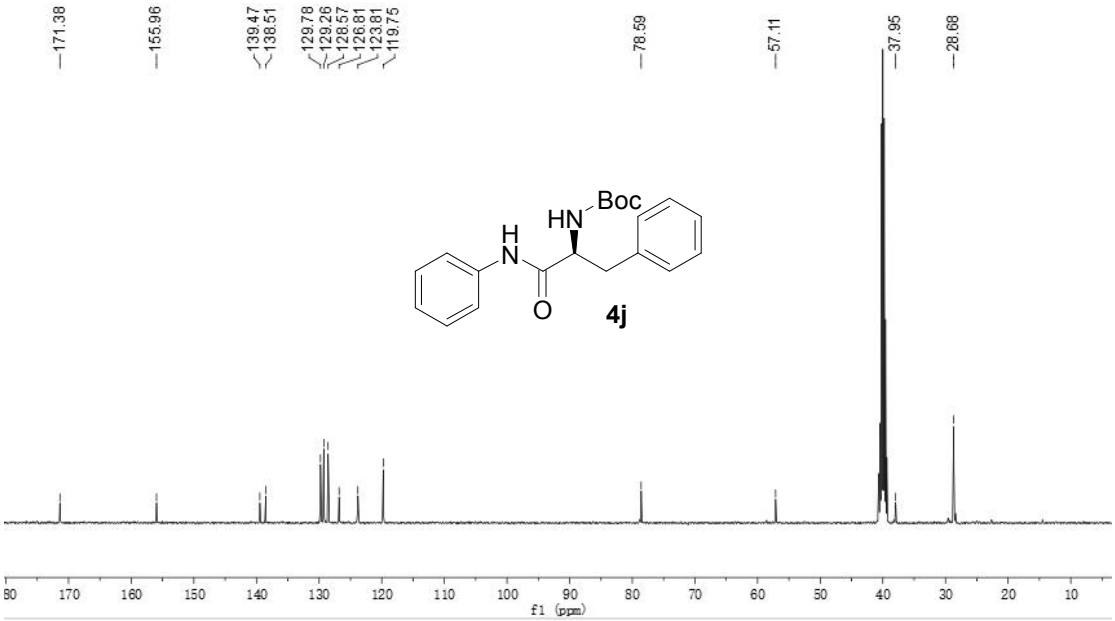

## $^{13}$C NMR spectra



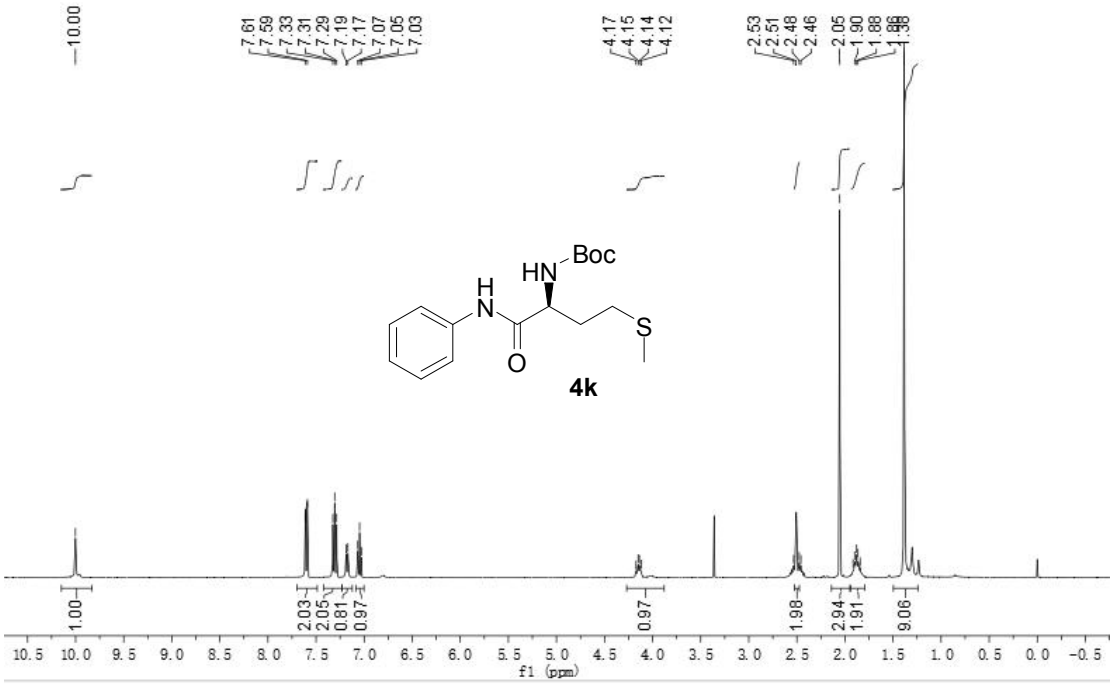
## $^{1}$H NMR spectra



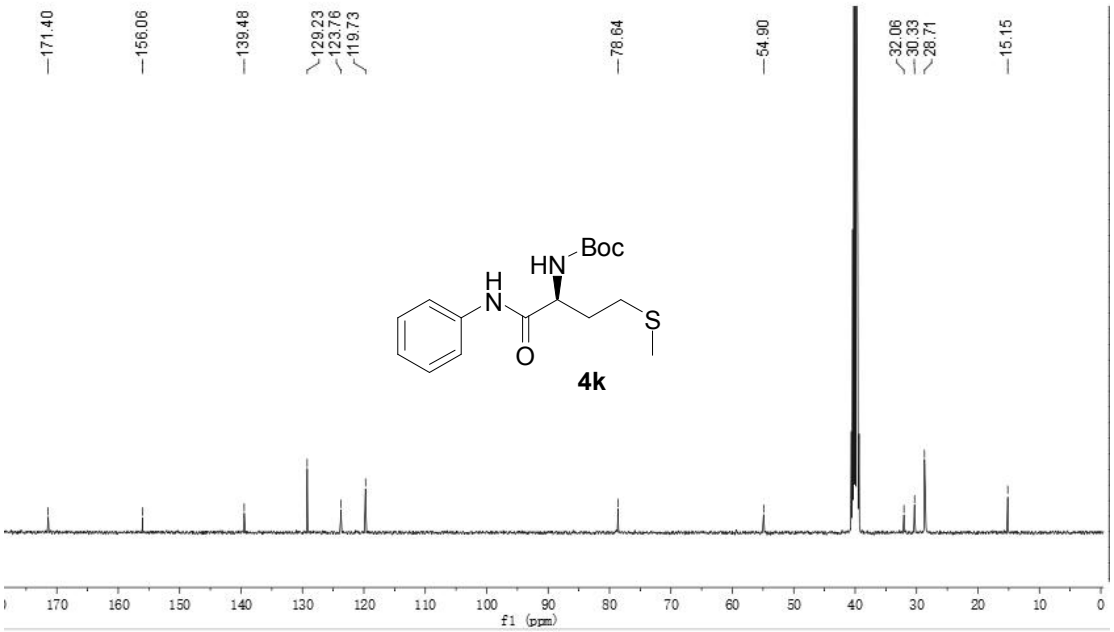

## $^{13}$C NMR spectra



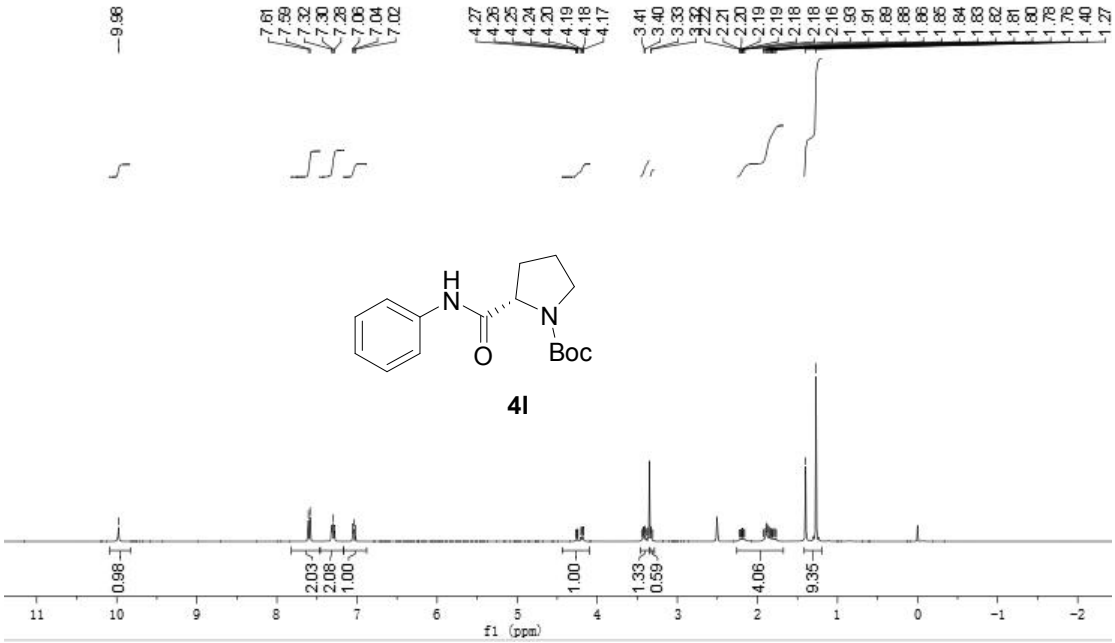
## $^{1}$H NMR spectra



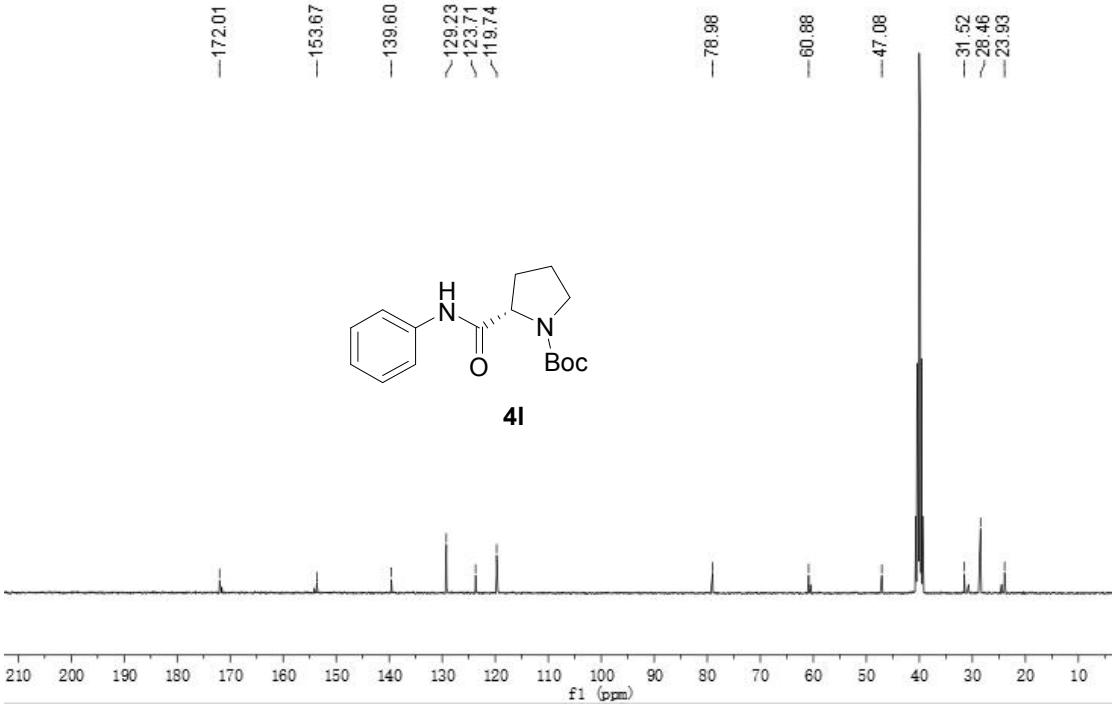

## $^{13}$C NMR spectra



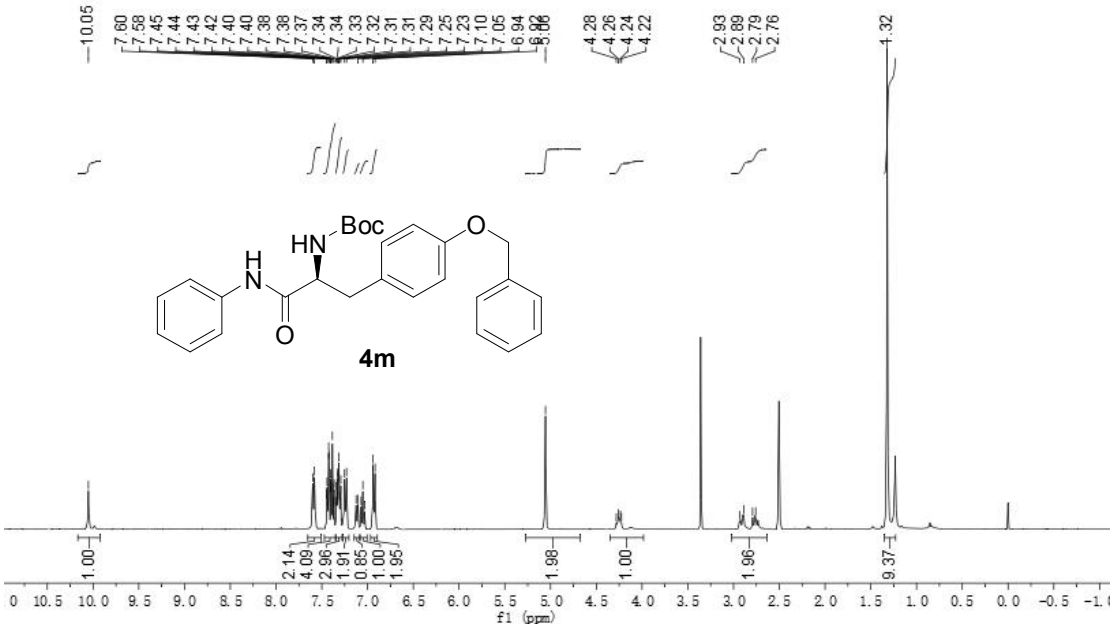
## $^{1}$H NMR spectra



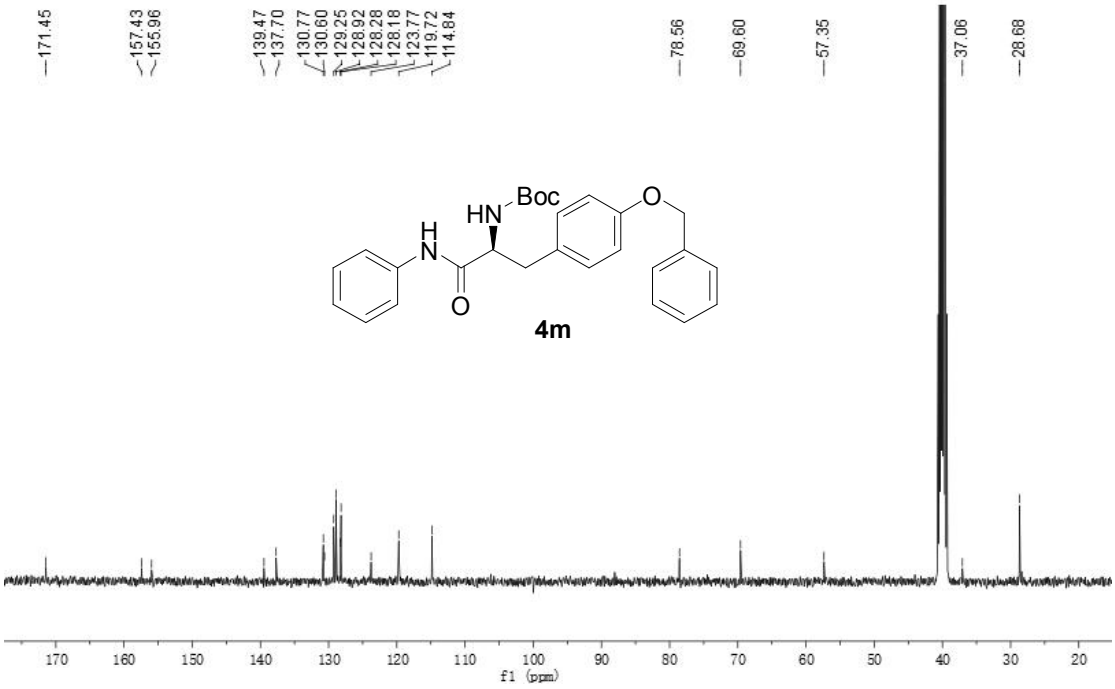

## $^{13}$C NMR spectra



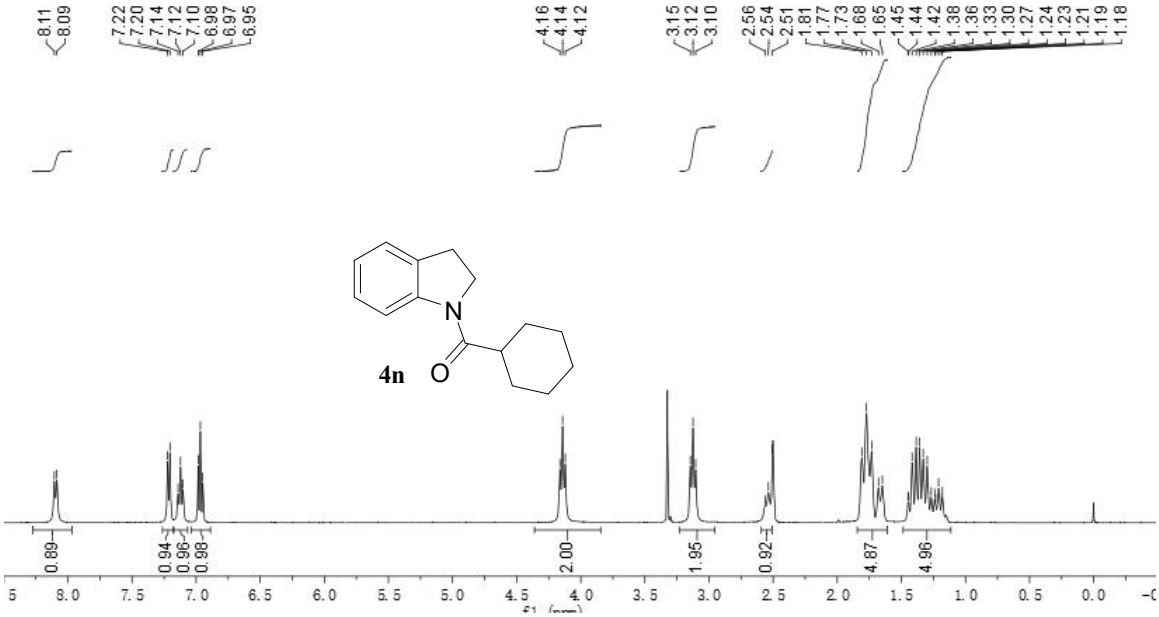
## $^{1}$H NMR spectra



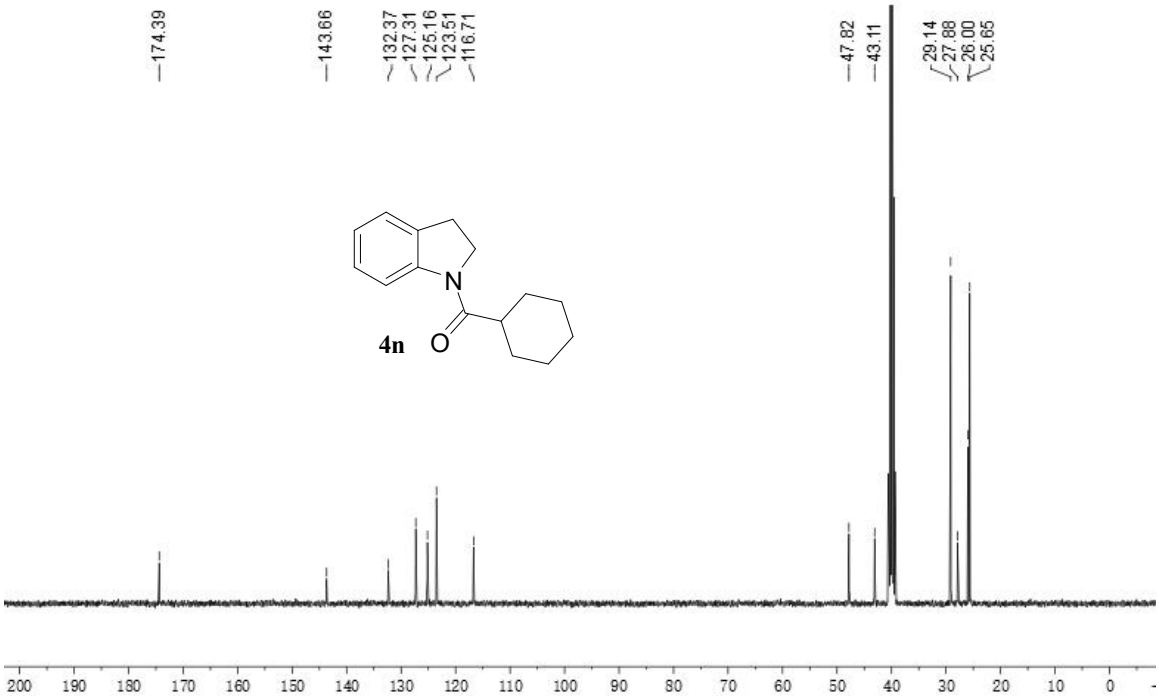

## $^{13}$C NMR spectra



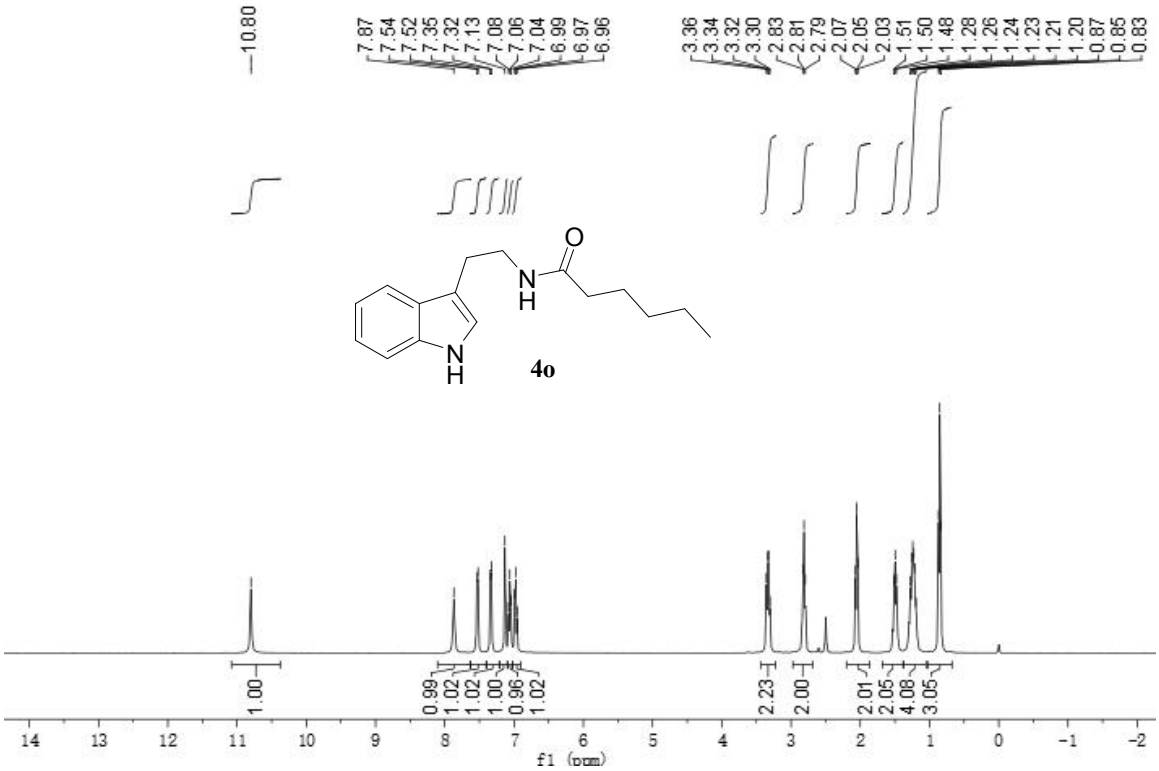
## $^{1}$H NMR spectra




## $^{13}$C NMR spectra

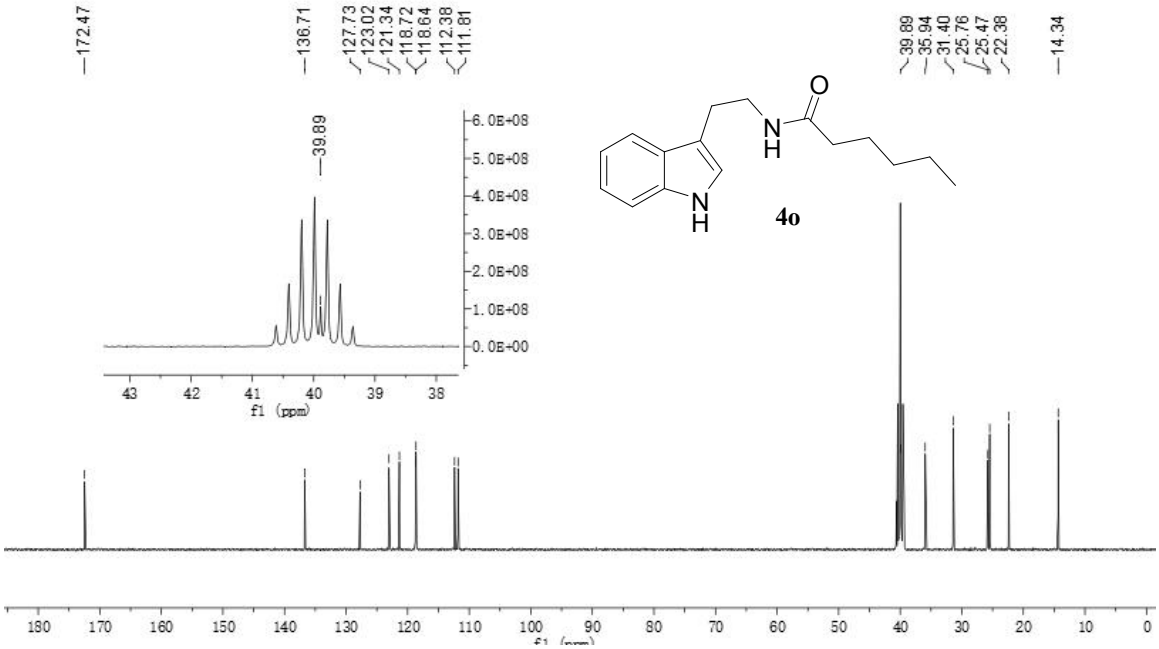


## $^{1}$H NMR spectra



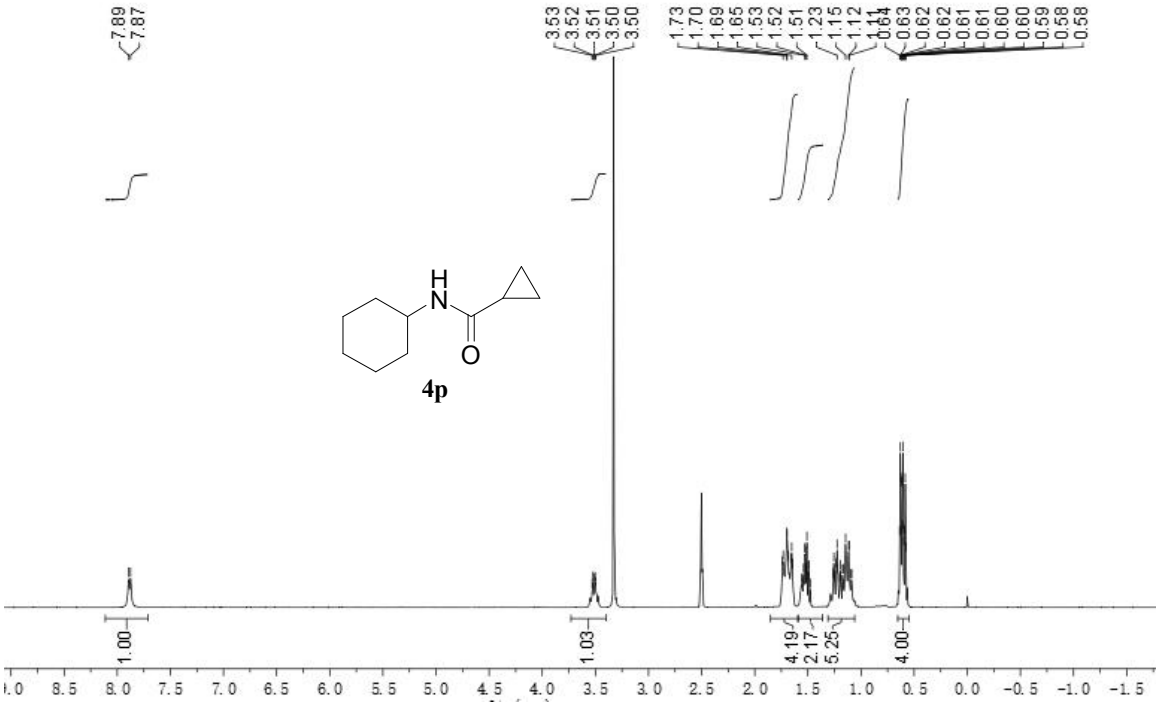

**4o**

## $^{13}$C NMR spectra

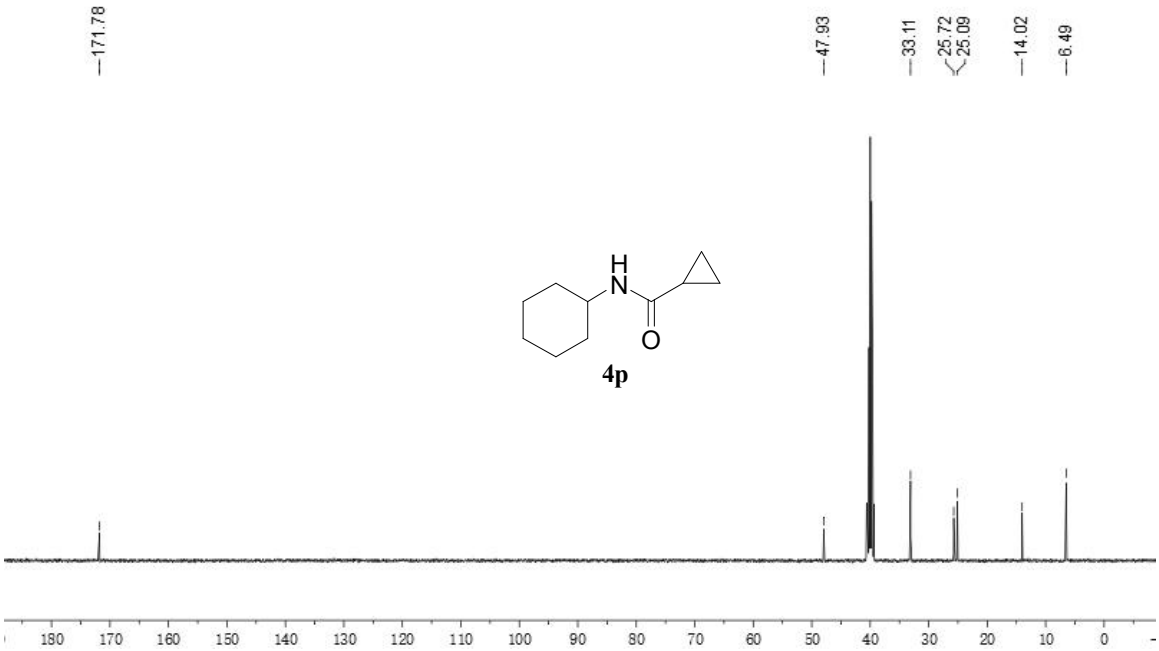



**4o**

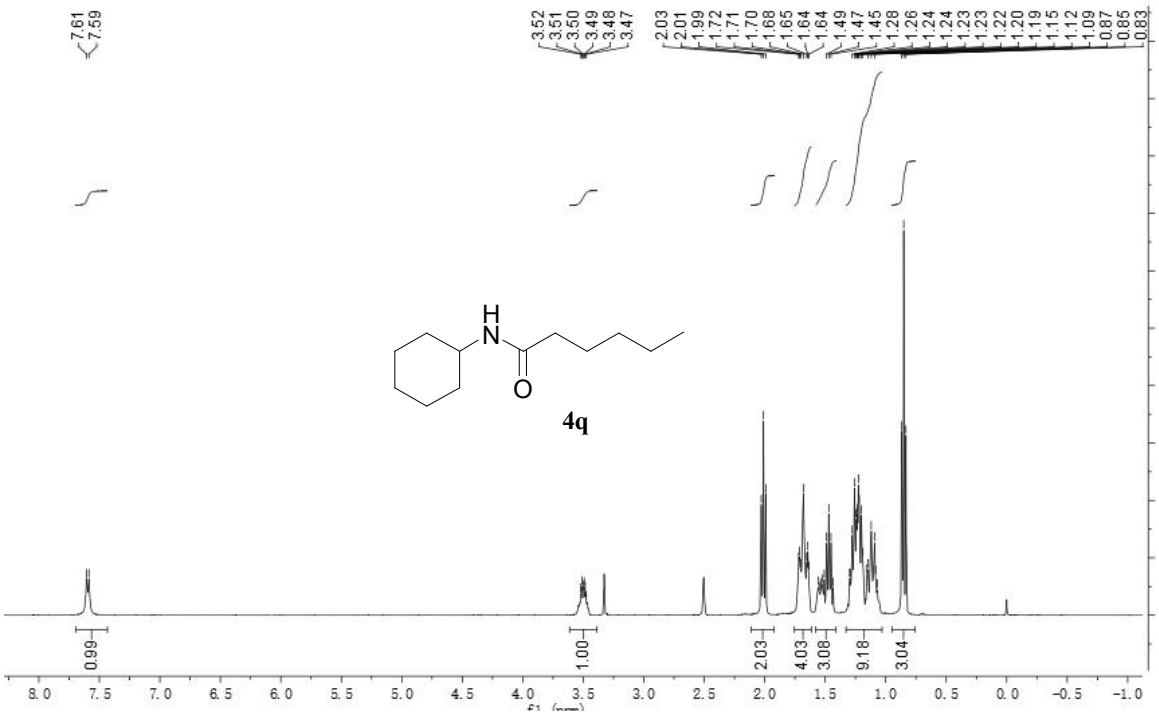
## $^{1}$H NMR spectra



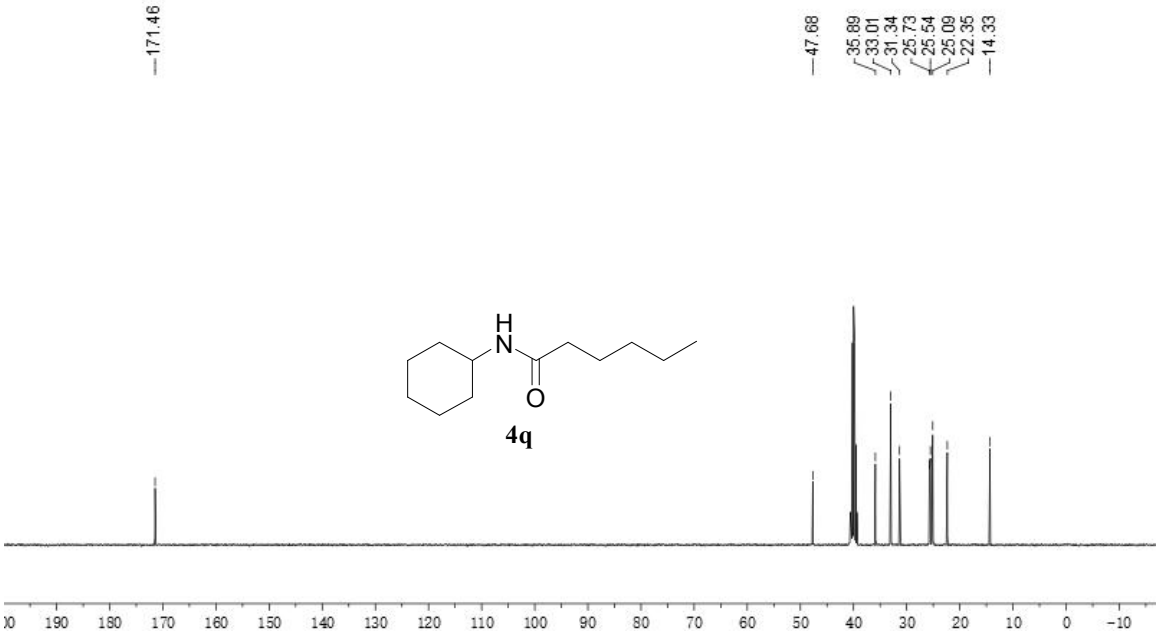

## $^{13}$C NMR spectra



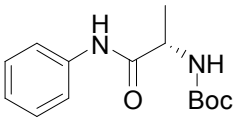
## $^{1}$H NMR spectra




## $^{13}$C NMR spectra



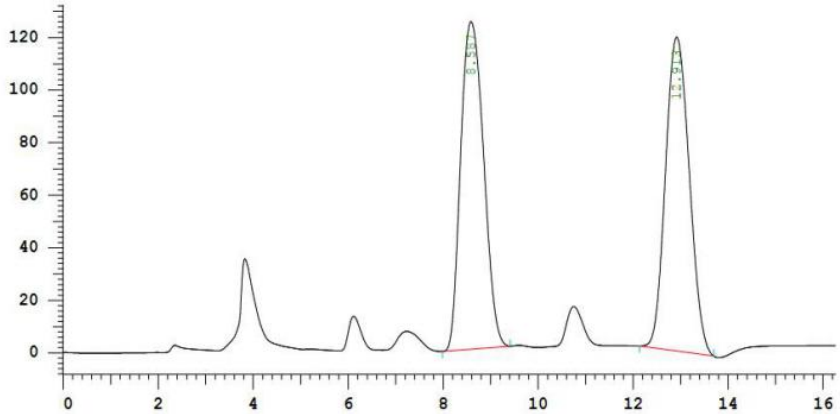
## X Chiral HPLC analysis



**(4h)**

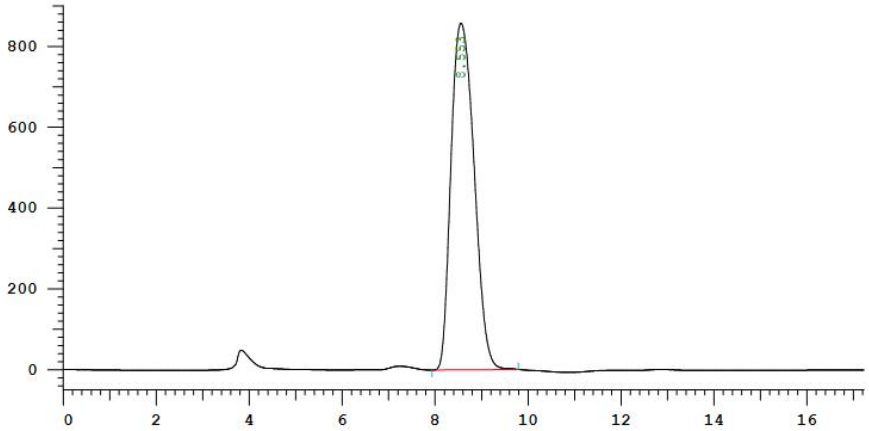
**HPLC Conditions: Column:** Chiralcel OD-H column; **Eluent**: Hexanes:*i*-propanol (90:10); **Flow rate**: 1.0 mL/min; **Detection**: UV210 nm.

**Racemic**

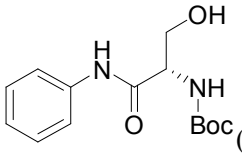



| No. | RT | Area | Area (%) | BC |
|---|---|---|---|---|
| 1 | 8.587 | 4178523 | 50.130 | BB |
| 2 | 12.913 | 4156822 | 49.870 | BB |
| | | 8335345 | 100.000 | |

**Chiral**



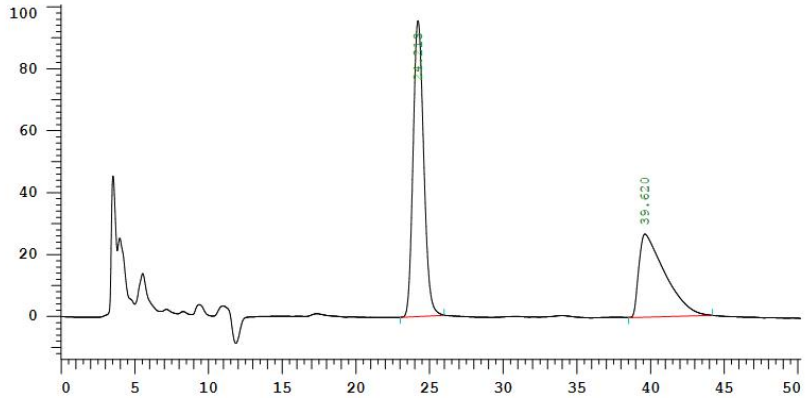

| No. | RT | Area | Area (%) | BC |
|---|---|---|---|---|
| 1 | 8.553 | 29595125 | 100.000 | BB |
| | | 29595125 | 100.000 | |



**(4i)**

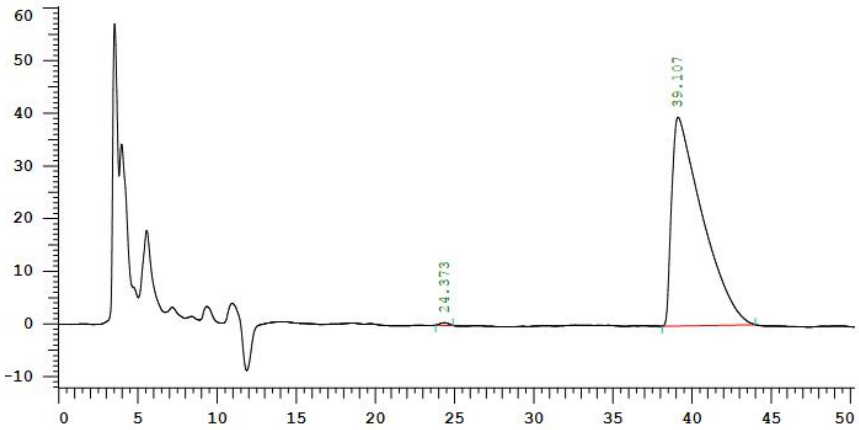
**HPLC Conditions: Column:** Chiralcel OD-H column; **Eluent**: Hexanes:*i*-propanol (90:10); **Flow rate**: 1.0 mL/min; **Detection**: UV210 nm.

**Racemic**

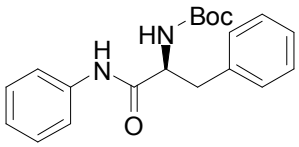



| No. | RT | Area | Area (%) | BC |
|---|---|---|---|---|
| 1 | 24.213 | 4722644 | 59.001 | BB |
| 2 | 39.620 | 3281766 | 40.999 | BB |
| | | 8004410 | 100.000 | |

**Chiral**



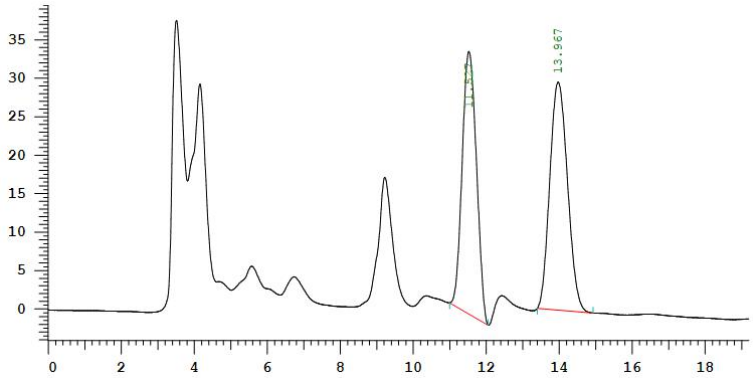

| No. | RT | Area | Area (%) | BC |
|---|---|---|---|---|
| 1 | 24.373 | 17487 | 0.326 | BB |
| 2 | 39.107 | 5344849 | 99.674 | BB |
| | | 5362336 | 100.000 | |



**(4j)**

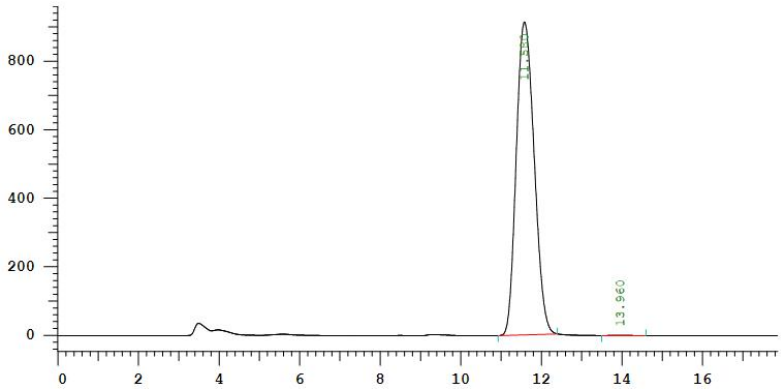
**HPLC Conditions: Column:** Chiralcel OD-H column; **Eluent**: Hexanes:*i*-propanol (90:10); **Flow rate**: 1.0 mL/min; **Detection**: UV210 nm.

**Racemic**

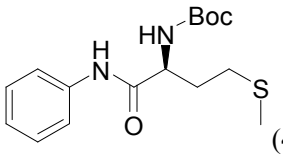



| No. | RT | Area | Area (%) | BC |
|---|---|---|---|---|
| 1 | 11.527 | 925536 | 48.054 | BB |
| 2 | 13.967 | 1000480 | 51.946 | BB |
| | | 1926016 | 100.000 | |

**Chiral**



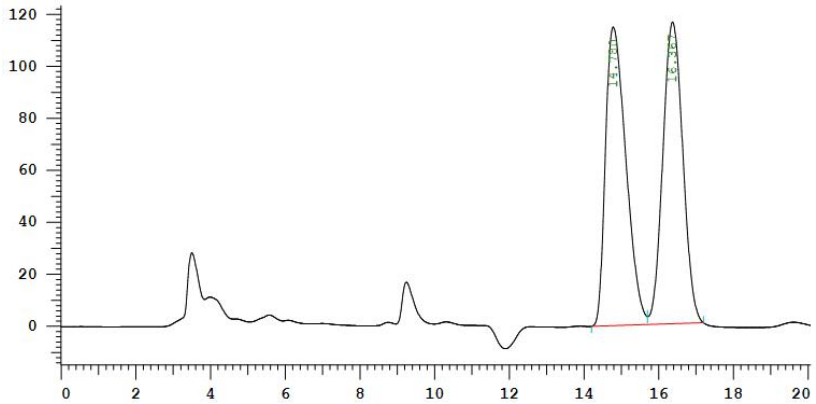

| No. | RT | Area | Area (%) | BC |
|---|---|---|---|---|
| 1 | 11.580 | 28135774 | 99.897 | BB |
| 2 | 13.960 | 28893 | 0.103 | BB |
| | | 28164667 | 100.000 | |



**(4k)**

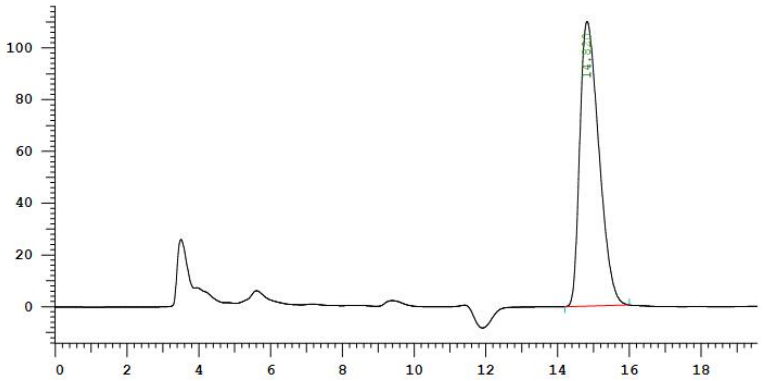
**HPLC Conditions: Column:** Chiralcel OD-H column; **Eluent**: Hexanes:*i*-propanol (90:10); **Flow rate**: 1.0 mL/min; **Detection**: UV210 nm.

**Racemic**

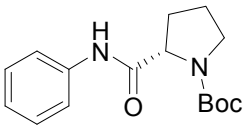


| No. | RT | Area | Area (%) | BC |
|---|---|---|---|---|
| 1 | 14.780 | 4365104 | 50.320 | BV |
| 2 | 16.367 | 4309513 | 49.680 | VB |
| | | 8674617 | 100.000 | |

**Chiral**



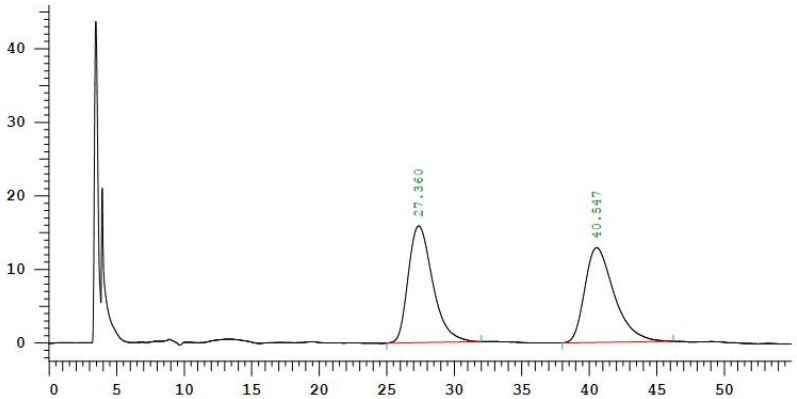
| No. | RT | Area | Area (%) | BC |
|---|---|---|---|---|
| 1 | 14.820 | 4065552 | 100.000 | BB |
| | | 4065552 | 100.000 | |



**(4m)**

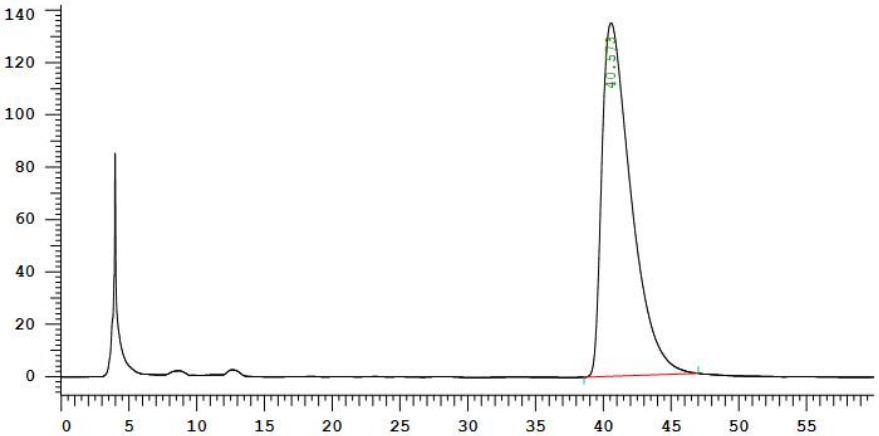
**HPLC Conditions: Column:** Chiralcel OD-H column; **Eluent**: Hexanes:*i*-propanol (99:1); **Flow rate**: 1.0 mL/min; **Detection**: UV210 nm.

**Racemic**

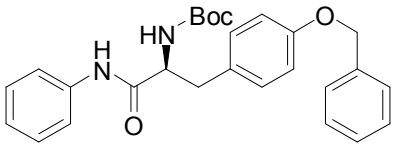



| No. | RT | Area | Area (%) | BC |
|---|---|---|---|---|
| 1 | 27.360 | 1990372 | 50.548 | BB |
| 2 | 40.547 | 1947212 | 49.452 | BB |
| | | 3937584 | 100.000 | |

**Chiral**



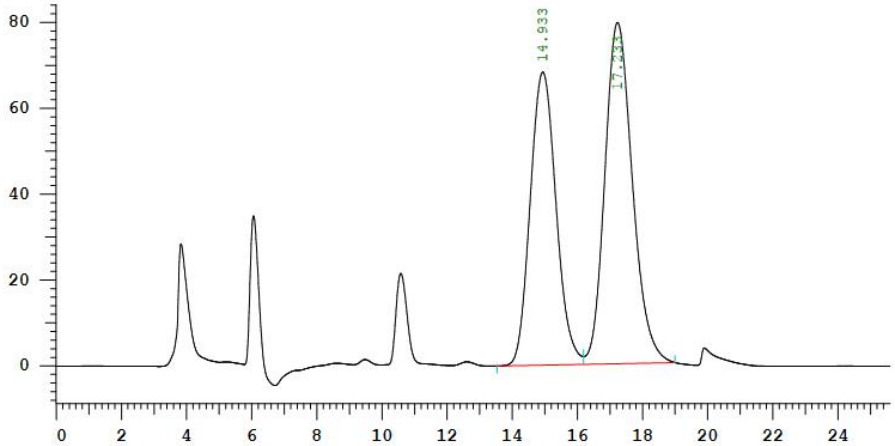

| No. | RT | Area | Area (%) | BC |
|---|---|---|---|---|
| 1 | 40.573 | 20123267 | 100.000 | BB |
| | | 20123267 | 100.000 | |




**(4m)**

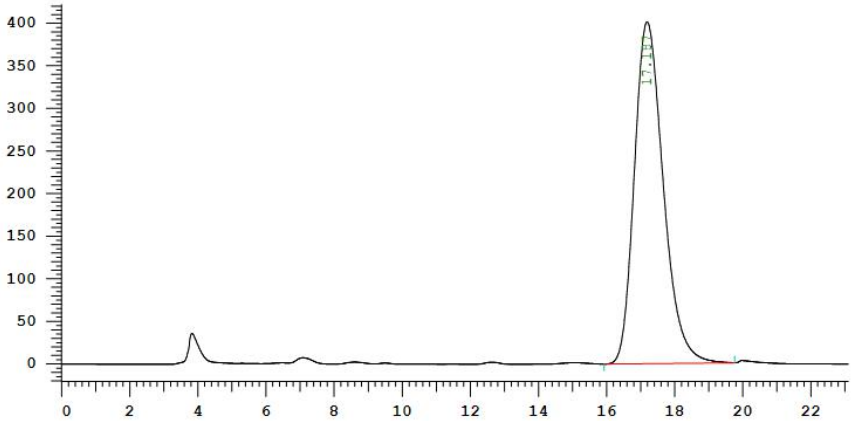
**HPLC Conditions: Column:** Chiralcel OD-H column; **Eluent**: Hexanes:*i*-propanol (99:1); **Flow rate**: 1.0 mL/min; **Detection**: UV210 nm.

**Racemic**




| No. | RT | Area | Area (%) | BC |
|---|---|---|---|---|
| 1 | 14.933 | 3760355 | 44.620 | BV |
| 2 | 17.233 | 4667166 | 55.380 | VB |
| | | 8427521 | 100.000 | |

**Chiral**




| No. | RT | Area | Area (%) | BC |
|---|---|---|---|---|
| 1 | 17.187 | 23649131 | 100.000 | BB |
| | | 23649131 | 100.000 | |