Annulation of *a*-Bromocinnamaldehydes to Access 3-Formyl-imidazo[1,2-a]pyridines and Pyrimidines under Transition-Metal-Free Conditions

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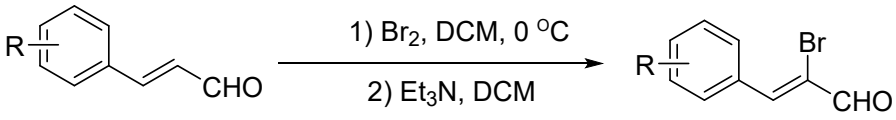
A. General method

Melting points were investigated using a melting point instrument and are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained on a 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, chloroform is solvent with TMS as the internal standard unless otherwise noted. High resolution mass spectra (HRMS) (TOF) were measured using an electrospray ionization (ESI) mass spectrometry. Silica gel (300-400 mesh) was used for flash column chromatograph, eluting (unless otherwise stated) with ethyl acetate/petroleum ether (PE) (60-90 ºC) mixture.

B. Preparation of starting materials

The route toward α-bromocinnamaldehyde:



Method： Following a known procedure,[1] substituted α-bromocinnamaldehydes were synthesized. All are known compounds and their spectral data were in good with the corresponding literature values.

To a solution of cinnamaldehyde (20.0 g, 151 mmol) in DCM (200 mL) was added Br_2 (9.4 mL, 183 mmol, 1.2 equiv.) at 0 ºC. The reaction mixture was stirred for 15 min, followed by the addition of Et_3N (36.0 mL, 258 mmol, 1.7 equiv.). After stirring for an additional 15 min, the reaction mixture was diluted with DCM and washed sequentially with a 10% $NaHSO_3$ solution, H_2O, and brine. The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated to yield orange oil.

C. General procedure for the synthesis of 3-formyl-imidazo[1,2-a]pyridines

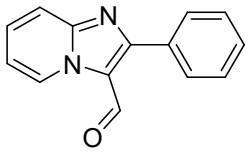
A mixture of *a*-bromocinnamaldehyde (0.2 mmol), 2-aminopyridine (0.2 mmol) in DMF (1.5 mL) was stirred in a preheated oil bath at 100 ºC for 10 h in a sealed tube under 1 atm of oxygen. After the reaction was finished, water (5 mL) was added and the solution was extracted with ethyl acetate (3×5 mL), and the combined extract was dried with anhydrous $MgSO_4$. Solvent was removed, and the residue was separated by column chromatography to give the pure sample.

D. General procedure for the synthesis of pyrimidines

A mixture of *a*-bromocinnamaldehyde (0.2 mmol), benzimidamide (0.2 mmol), sodium hydroxide (0.2 mmol) in DMF (1.5 mL) was stirred in a preheated oil bath at 100 ºC for 10 h in a sealed tube. After the reaction was finished, water (5 mL) was added and the solution was extracted with ethyl acetate (3×5 mL), and the combined extract was dried with anhydrous $MgSO_4$. Solvent was removed, and the residue was separated by column chromatography to give the pure sample.

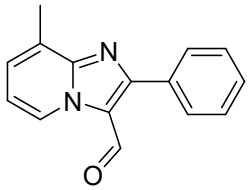
E. Analytical data

2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3a)[2]



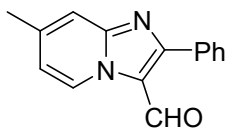
Yellow solid; mp = 143-144 °C; R_f = 0.24 (petroleum ether / ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): 10.01 (s, 1H), 9.59 (d, *J* = 6.8 Hz, 1H), 7.81 – 7.76 (m, 2H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.54 – 7.44 (m, 4H), 7.05 (t, *J* = 6.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.3, 158.0, 147.5, 132.2, 130.2, 129.6, 128.7, 128.6, 120.5, 117.2, 115.1.

8-methyl-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3b)[2]



Yellow solid; mp = 132-133 °C; R_f = 0.49 (petroleum ether / ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.03 (s, 1H), 9.52 (d, *J* = 6.8 Hz, 1H), 7.85 – 7.80 (m, 2H), 7.55 – 7.49 (m, 3H), 7.37 (d, *J* = 7.1 Hz, 1H), 7.03 (t, *J* = 6.9 Hz, 1H), 2.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.6, 157.9, 147.9, 132.6, 129.9, 129.9, 129.9, 129.9, 129.9, 129.6, 129.4, 128.8, 128.8, 127.6, 126.5, 121.1, 115.3, 17.0.

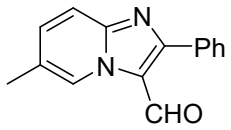
7-methyl-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3c)[3]



White solid; mp = 161-162 °C; R_f = 0.26 (petroleum ether / ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.99 (s, 1H), 9.49 (d, *J* = 6.9 Hz, 1H), 7.80 (dd, *J* = 7.5,

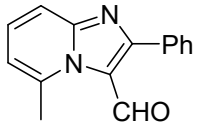
1.9 Hz, 2H), 7.54 – 7.48 (m, 4H), 6.93 (d, *J* = 7.0 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.0, 158.4, 148.1, 142.1, 132.4, 129.7, 129.6, 128.7, 127.8, 120.4, 117.5, 116.0, 21.6.

6-methyl-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3d)[2]



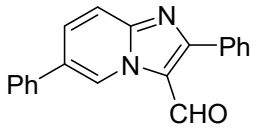
Yellow solid; mp = 116-117 °C; R_f = 0.25 (petroleum ether / ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.97 (s, 1H), 9.41 (s, 1H), 7.77 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.63 (d, *J* = 9.0 Hz, 1H), 7.50 – 7.43 (m, 3H), 7.36 (dd, *J* = 9.1, 1.5 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.3, 158.0, 146.5, 133.1, 132.4, 129.6, 129.5, 128.7, 126.6, 125.3, 120.4, 116.4, 18.2.

5-methyl-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3e)



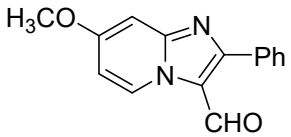
Brown solid; mp = 113-114 °C; R_f = 0.25 (petroleum ether / ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.83 (s, 1H), 7.84 – 7.79 (m, 2H), 7.65 (d, *J* = 8.7 Hz, 1H), 7.51 (ddd, *J* = 7.1, 3.7, 2.0 Hz, 4H), 6.90 (d, *J* = 7.0 Hz, 1H), 2.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.6, 161.8, 150.3, 141.3, 132.8, 131.0, 130.2, 129.7, 128.6, 122.9, 116.5, 115.0, 23.1. HRMS (ESI): calcd. for $C_{15}H_{13}N_2O$ $[M + H]^+$ 237.1022, found 237.1034.

2,6-diphenylimidazo[1,2-a]pyridine-3-carbaldehyde (3f)[4]



Yellow solid; mp = 173-174 °C; R_f = 0.46 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ =10.09 (s, 1H), 9.90 – 9.87 (m, 1H), 7.86 – 7.82 (m, 4H), 7.65 – 7.62 (m, 2H), 7.54 – 7.47 (m, 5H), 7.44 – 7.40 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.5, 158.5, 146.8, 136.3, 132.3, 130.6, 129.8, 129.7, 129.2, 128.8, 128.3, 127.1, 126.1, 120.9, 117.1.

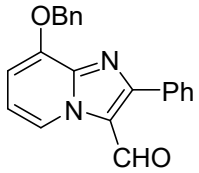
7-methoxy-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3g)



White solid; mp = 178-179 °C; R_f = 0.25 (petroleum ether / ethyl acetate = 3:1); ^{1}H

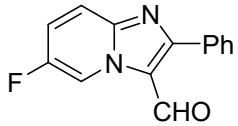
NMR (400 MHz, $CDCl_3$): δ = 9.94 (s, 1H), 9.44 (d, J = 7.5 Hz, 1H), 7.83 – 7.78 (m, 2H), 7.54 – 7.48 (m, 3H), 7.06 (d, J = 2.5 Hz, 1H), 6.77 (dd, J = 7.5, 2.6 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.7, 161.7, 158.9, 150.1, 132.4, 129.7, 129.6, 129.3, 128.8, 120.4, 109.0, 100.0, 95.6, 55.8. HRMS (ESI): calcd. for $C_{15}H_{13}N_2O_2$ $[M + H]^+$ 253.0972, found 253.0981.

8-(benzyloxy)-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3h)[5]



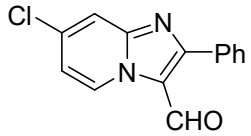
Brown solid; mp = 127-128 °C; R_f = 0.56 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.05 (s, 1H), 9.25 (dd, J = 6.7, 0.9 Hz, 1H), 7.89 – 7.84 (m, 2H), 7.53 – 7.47 (m, 5H), 7.40 – 7.32 (m, 3H), 6.95 – 6.91 (m, 1H), 6.89 –6.84 (m, 1H), 5.45 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.8, 157.4, 147.5, 142.0, 135.7, 132.3, 130.1, 129.7, 128.7, 128.7, 128.3, 127.2, 121.5, 115.2, 109.6, 71.2.

6-fluoro-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3i)[5]



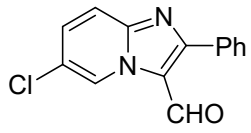
Yellow solid; mp = 150-151 °C; R_f = 0.45 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.06 (s, 1H), 9.67 – 9.64 (m, 1H), 7.82 – 7.74 (m, 3H), 7.56 – 7.47 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.6, 158.5 (d, J = 3 Hz), 154.4 (d, J = 239 Hz), 154.1, 132.0, 129.9, 129.6, 128.9, 121.6 (d, J = 25 Hz), 117.6 (d, J = 8 Hz), 116.2, 115.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -135.16.

7-chloro-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3j)[5]



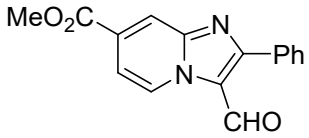
Brown solid; mp = 174-175 °C; R_f = 0.41 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.05 (s, 1H), 9.58 (d, J = 7.2 Hz, 1H), 7.83 – 7.77 (m, 3H), 7.54 (dd, J = 5.0, 1.8 Hz, 3H), 7.10 (dd, J = 7.3, 2.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.6, 158.8, 147.8, 137.0, 131.9, 130.1, 129.7, 129.0, 120.7, 116.7, 116.5.

6-chloro-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3k)[2]



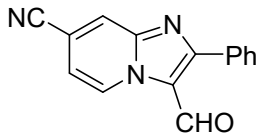
Yellow solid; mp = 166-167 °C; R_f = 0.55 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.07 (s, 1H), 9.74 (dd, J = 2.0, 0.7 Hz, 1H), 7.83 – 7.79 (m, 2H), 7.74 (d, J = 9.4 Hz, 1H), 7.56 – 7.52 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.7, 158.3, 146.0, 131.9, 131.5, 130.0, 129.7, 129.7, 129.0, 126.7, 123.5, 120.8, 117.6.

methyl 3-formyl-2-phenylimidazo[1,2-a]pyridine-7-carboxylate (3l)



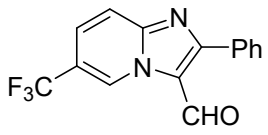
Yellow solid; mp = 134-135 °C; R_f = 0.49 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.10 (s, 1H), 9.64 (d, J = 7.1 Hz, 1H), 8.44 (s, 1H), 7.81 (dd, J = 6.4, 2.8 Hz, 2H), 7.68 – 7.64 (m, 1H), 7.54 – 7.49 (m, 3H), 3.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.0, 164.7, 158.9, 146.8, 131.9, 131.2, 130.0, 129.7, 128.9, 128.3, 121.2, 119.3, 114.3, 52.9. HRMS (ESI): calcd. for $C_{16}H_{13}N_2O_3$ $[M + H]^+$ 281.0921, found 281.0923.

3-formyl-2-phenylimidazo[1,2-a]pyridine-7-carbonitrile (3m)



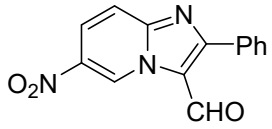
Yellow solid; mp = 174-175 °C; R_f = 0.53 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.16 (s, 1H), 9.75 (dd, J = 7.1, 0.9 Hz, 1H), 8.18 – 8.15 (m, 1H), 7.85 – 7.81 (m, 2H), 7.59 – 7.55 (m, 3H), 7.29 – 7.26 (m, 1H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.3, 159.2, 145.5, 131.3, 130.5, 129.8, 129.3, 129.1, 122.9, 121.3, 116.6, 115.4, 113.0. HRMS (ESI): calcd. for $C_{15}H_{10}N_3O$ $[M + H]^+$ 248.0818, found 248.0829.

2-phenyl-6-(trifluoromethyl)imidazo[1,2-a]pyridine-3-carbaldehyde (3n)[4]



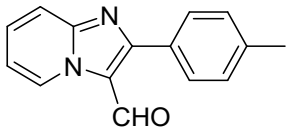
Yellow solid; mp = 163-164 °C; R_f = 0.60 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.11 (s, 1H), 10.02 (s, 1H), 7.88 (d, J = 9.3 Hz, 1H), 7.82 (dd, J = 6.6, 2.9 Hz, 2H), 7.71 (dd, J = 9.4, 1.8 Hz, 1H), 7.56 – 7.49 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.9 (d, J = 3 Hz), 159.1, 147.4, 131.6 (d, J = 2 Hz), 130.2 (d, J = 1 Hz), 129.7, 129.0 (d, J = 2 Hz), 127.6 (q, J = 5 Hz), 126.1, 123.0 (q, J = 270 Hz), 121.0, 119.4 (q, J = 35 Hz), 118.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -61.86.

6-nitro-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde (3o)



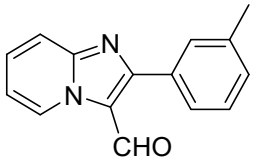
Brown solid; mp = 173-174 °C; R_f = 0.36 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.68 (d, J = 1.9 Hz, 1H), 10.19 (s, 1H), 8.34 (dd, J = 9.8, 2.2 Hz, 1H), 7.87 (dd, J = 9.5, 5.2 Hz, 3H), 7.61 – 7.55 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.1, 160.3, 147.7, 138.8, 131.2, 130.7, 129.8, 129.2, 128.2, 124.2, 121.6, 117.1. HRMS (ESI): calcd. for $C_{14}H_{10}N_3O_3$ $[M + H]^+$ 268.0717, found 268.0722.

2-(*p*-tolyl)imidazo[1,2-a]pyridine-3-carbaldehyde (3p)[4]



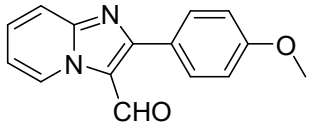
Brown solid; mp = 162-163 °C; R_f = 0.35 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.05 (s, 1H), 9.66 – 9.62 (m, 1H), 7.81 – 7.77 (m, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.59 – 7.53 (m, 1H), 7.33 (d, J = 7.9 Hz, 2H), 7.10 (t, J = 6.9 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.6, 158.4, 147.7, 140.0, 130.3, 129.6, 129.6, 128.7, 120.5, 117.3, 115.1, 21.4.

2-(*m*-tolyl)imidazo[1,2-a]pyridine-3-carbaldehyde (3q)[5]



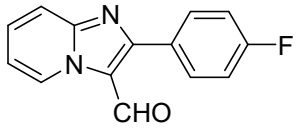
Yellow solid; mp = 120-121 °C; R_f = 0.37 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.04 (s, 1H), 9.62 (d, J = 6.8 Hz, 1H), 7.77 (d, J = 8.9 Hz, 1H), 7.65 (s, 1H), 7.59 – 7.51 (m, 2H), 7.39 (t, J = 7.6 Hz, 1H), 7.30 (d, J = 7.6 Hz, 1H), 7.09 (t, J = 6.7 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.5, 158.4, 147.6, 138.6, 132.1, 130.5, 130.3, 130.2, 128.7, 128.6, 126.9, 120.6, 117.3, 115.1, 21.3.

2-(4-methoxyphenyl)imidazo[1,2-a]pyridine-3-carbaldehyde (3r)[2]



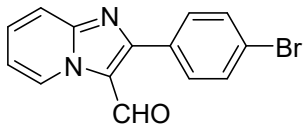
Yellow solid; mp = 168-169 °C; R_f = 0.2 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.03 (s, 1H), 9.65 – 9.61 (m, 1H), 7.77 (dt, J = 9.5, 2.9 Hz, 3H), 7.55 (ddd, J = 8.8, 7.0, 1.3 Hz, 1H), 7.09 (td, J = 6.9, 1.1 Hz, 1H), 7.06 – 7.02 (m, 2H), 3.87 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.4, 161.0, 158.1, 147.7, 131.1, 130.3, 128.7, 124.7, 120.4, 117.1, 115.0, 114.3, 55.3.

2-(4-fluorophenyl)imidazo[1,2-a]pyridine-3-carbaldehyde (3s)[4]



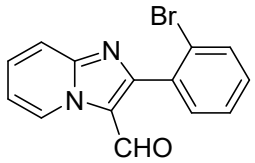
Yellow solid; mp = 170-171 °C; R_f = 0.32 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.03 (s, 1H), 9.67 – 9.63 (m, 1H), 7.84 – 7.78 (m, 3H), 7.60 (ddd, J = 8.8, 7.0, 1.3 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.14 (td, J = 6.9, 1.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.1, 163.8 (d, J = 249 Hz), 157.2, 147.6, 131.6 (d, J = 9 Hz), 130.5, 128.7, 128.5 (d, J = 3 Hz), 120.6, 117.3, 116.0 (d, J = 22 Hz), 115.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -110.77.

2-(4-bromophenyl)imidazo[1,2-a]pyridine-3-carbaldehyde (3t)[2]



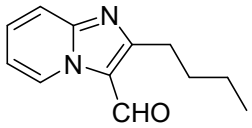
Brown solid; mp = 175-176 °C; R_f = 0.36 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.04 (s, 1H), 9.65 (d, J = 6.8 Hz, 1H), 7.80 (d, J = 9.0 Hz, 1H), 7.72 – 7.65 (m, 4H), 7.60 (ddd, J = 8.8, 7.0, 1.3 Hz, 1H), 7.14 (td, J = 6.9, 1.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.1, 156.9, 147.7, 132.1, 131.3, 131.2, 130.6, 128.8, 124.5, 120.7, 117.5, 115.5.

2-(2-bromophenyl)imidazo[1,2-a]pyridine-3-carbaldehyde (3u)



Brown solid; mp = 154-155 °C; R_f = 0.28 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.71 (s, 1H), 9.54 (dt, J = 6.8, 1.1 Hz, 1H), 7.77 (dt, J = 9.0, 1.0 Hz, 1H), 7.68 (dd, J = 8.0, 1.1 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.40 (td, J = 7.5, 1.2 Hz, 1H), 7.31 (td, J = 7.7, 1.8 Hz, 1H), 7.11 (td, J = 6.9, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.1, 156.7, 147.3, 133.3, 133.1, 132.3, 130.8, 130.0, 128.4, 127.2, 123.2, 120.9, 117.5, 115.4. HRMS (ESI): calcd. for $C_{14}H_{10}BrN_2O$ $[M + H]^+$ 300.9971, found 300.9983.

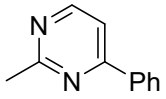
2-butylimidazo[1,2-a]pyridine-3-carbaldehyde (3v)



Yellow oil; R_f = 0.30 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.01 (s, 1H), 9.54-9.52 (m, 1H), 7.70-7.68 (m, 1H), 7.53-7.49 (m, 1H), 7.08-7.04 (m, 1H), 3.03 (t, J = 7.6 Hz, 2H), 1.85-1.82 (m, 2H), 1.47-1.41 (m, 2H), 0.96

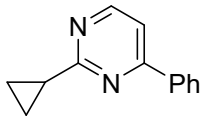
(t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.0, 161.5, 147.8, 130.0, 128.5, 120.9, 116.8, 114.8, 32.2, 27.7, 22.5, 13.8. HRMS (ESI): calcd. for $C_{12}H_{15}N_2O$ $[M + H]^+$ 203.1179, found 203.1187.

2-methyl-4-phenylpyrimidine (4a)[6]



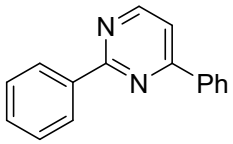
Yellow oil liquid; R_f = 0.41 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.67 (d, J = 5.3 Hz, 1H), 8.10 – 8.04 (m, 2H), 7.52 – 7.49 (m, 4H), 2.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.4, 164.1, 157.4, 136.9, 130.8, 128.9, 127.2, 114.0, 26.3.

2-cyclopropyl-4-phenylpyrimidine (4b)[6]



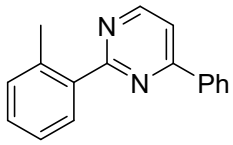
Yellow oil liquid; R_f = 0.53 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (d, J = 5.3 Hz, 1H), 8.07 (ddd, J = 5.6, 3.0, 1.5 Hz, 2H), 7.52 – 7.46 (m, 3H), 7.44 (d, J = 5.3 Hz, 1H), 2.32 (ddd, J = 8.2, 4.7, 3.4 Hz, 1H), 1.22 (dt, J = 4.5, 3.1 Hz, 2H), 1.11 – 1.06 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.1, 163.5, 157.2, 137.0, 130.7, 128.8, 127.1, 113.4, 18.3, 10.7.

2,4-diphenylpyrimidine (4c)[6]



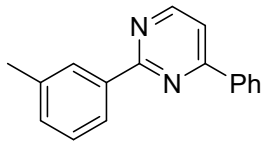
Yellow solid; mp = 63-65 °C; R_f = 0.44 (petroleum ether / ethyl acetate = 9:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.85 (d, J = 5.3 Hz, 1H), 8.59 (dd, J = 7.3, 2.3 Hz, 2H), 8.24 (dd, J = 6.5, 3.1 Hz, 2H), 7.61 (d, J = 5.3 Hz, 1H), 7.58 – 7.50 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.6, 163.9, 157.8, 137.8, 136.9, 131.0, 130.7, 128.9, 128.5, 128.3, 127.2, 114.5.

4-phenyl-2-(*o*-tolyl)pyrimidine (4d)[6]



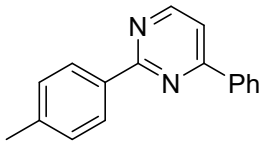
Yellow oil liquid; R_f = 0.32 (petroleum ether / ethyl acetate = 9:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.90 (d, J = 5.3 Hz, 1H), 8.25 – 8.17 (m, 2H), 7.98 (dd, J = 7.5, 1.6 Hz, 1H), 7.65 (d, J = 5.3 Hz, 1H), 7.55 (p, J = 3.8, 3.2 Hz, 3H), 7.43 – 7.33 (m, 3H), 2.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6, 163.5, 157.5, 138.3, 137.4, 136.9, 131.3, 130.9, 130.6, 129.4, 128.9, 127.2, 125.9, 113.8, 21.4.

4-phenyl-2-(*m*-tolyl)pyrimidine (4e)[6]



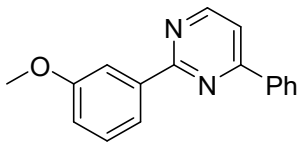
Yellow solid; mp = 60-61 °C; R_f = 0.45 (petroleum ether / ethyl acetate = 9:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.84 (d, J = 5.3 Hz, 1H), 8.43 – 8.36 (m, 2H), 8.26 – 8.20 (m, 2H), 7.60 (d, J = 5.3 Hz, 1H), 7.58 – 7.51 (m, 3H), 7.42 (t, J = 7.9 Hz, 1H), 7.33 (d, J = 7.5 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.7, 163.9, 157.8, 138.1, 137.8, 137.0, 131.5, 130.9, 128.9, 128.8, 128.5, 127.2, 125.5, 114.5, 21.5.

4-phenyl-2-(*p*-tolyl)pyrimidine (4f)[6]



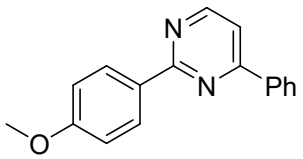
Yellow oil liquid; R_f = 0.44 (petroleum ether / ethyl acetate = 9:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (d, J = 5.3 Hz, 1H), 8.49 (d, J = 8.2 Hz, 2H), 8.23 (dd, J = 6.5, 3.1 Hz, 2H), 7.59 – 7.51 (m, 4H), 7.33 (d, J = 8.1 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.6, 163.7, 157.7, 140.9, 137.0, 135.1, 130.9, 130.8, 129.3, 128.9, 128.7, 128.2, 127.2, 114.2, 21.5.

2-(3-methoxyphenyl)-4-phenylpyrimidine (4g)[6]



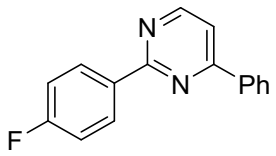
Yellow oil liquid; R_f = 0.6 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.84 (d, J = 5.3 Hz, 1H), 8.25 – 8.19 (m, 3H), 8.15 (dd, J = 2.5, 1.5 Hz, 1H), 7.61 (d, J = 5.3 Hz, 1H), 7.56 – 7.52 (m, 3H), 7.44 (t, J = 7.9 Hz, 1H), 7.07 (ddd, J = 8.2, 2.7, 0.9 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.4, 163.8, 159.9, 157.8, 139.3, 136.9, 131.0, 129.5, 128.9, 127.2, 120.9, 117.0, 114.6, 113.0, 55.4.

2-(4-methoxyphenyl)-4-phenylpyrimidine (4h)[6]



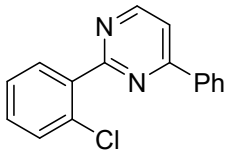
Yellow oil liquid; R_f = 0.49 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (d, J = 5.3 Hz, 1H), 8.58 – 8.52 (m, 2H), 8.25 – 8.16 (m, 2H), 7.56 – 7.50 (m, 4H), 7.05 – 7.00 (m, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.3, 163.7, 161.8, 157.7, 137.1, 130.8, 130.5, 129.9, 128.8, 127.1, 113.8, 113.8, 55.3.

2-(4-fluorophenyl)-4-phenylpyrimidine (4i)[6]



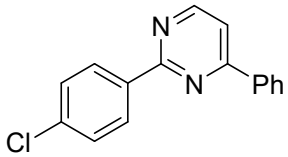
Yellow solid; mp = 68-69 °C; R_f = 0.61 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (d, J = 5.3 Hz, 1H), 8.62 – 8.56 (m, 2H), 8.25 – 8.18 (m, 2H), 7.60 (d, J = 5.3 Hz, 1H), 7.55 (dd, J = 5.0, 1.7 Hz, 3H), 7.23 – 7.15 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.7 (d, J = 249 Hz), 163.9, 163.6, 157.8, 136.8, 134.0 (d, J = 3 Hz), 131.0, 130.3 (d, J = 9 Hz), 128.9, 127.1, 115.4 (d, J = 22 Hz), 114.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -110.43.

2-(2-chlorophenyl)-4-phenylpyrimidine (4j)[6]



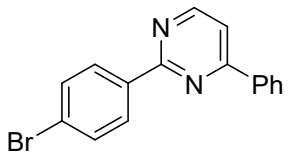
Yellow oil liquid; R_f = 0.44 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.91 (d, J = 5.3 Hz, 1H), 8.19 (ddd, J = 5.6, 3.0, 1.5 Hz, 2H), 7.90 – 7.85 (m, 1H), 7.69 (d, J = 5.3 Hz, 1H), 7.56 – 7.49 (m, 4H), 7.43 – 7.37 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.5, 164.0, 157.6, 137.8, 136.6, 132.9, 131.8, 131.1, 130.7, 130.4, 129.0, 127.3, 126.8, 114.7.

2-(4-chlorophenyl)-4-phenylpyrimidine (4k)[6]



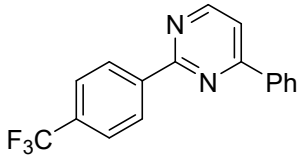
Yellow solid; mp = 109-110 °C; R_f = 0.61 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (d, J = 5.3 Hz, 1H), 8.56 – 8.50 (m, 2H), 8.25 – 8.18 (m, 2H), 7.61 (d, J = 5.3 Hz, 1H), 7.57 – 7.52 (m, 3H), 7.50 – 7.46 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.9, 163.6, 157.8, 136.9, 136.7, 136.3, 131.1, 129.6, 129.0, 128.7, 127.2, 114.7.

2-(4-bromophenyl)-4-phenylpyrimidine (4l)[6]



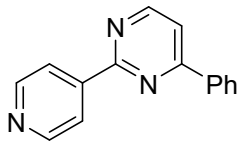
Yellow solid; mp = 99-100 °C; R_f = 0.61 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (d, J = 5.3 Hz, 1H), 8.49 – 8.43 (m, 2H), 8.23 – 8.17 (m, 2H), 7.67 – 7.59 (m, 3H), 7.54 (p, J = 3.8, 3.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.9, 163.7, 157.8, 136.8, 136.7, 131.7, 131.1, 129.9, 128.9, 127.2, 125.5, 114.7.

4-phenyl-2-(4-(trifluoromethyl)phenyl)pyrimidine (4m)[7]



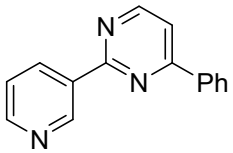
Yellow solid; mp = 106-107 °C; R_f = 0.60 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.86 (d, J = 5.3 Hz, 1H), 8.70 (d, J = 8.1 Hz, 2H), 8.26 – 8.18 (m, 2H), 7.77 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 5.3 Hz, 1H), 7.59 – 7.53 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.1, 163.2, 157.9, 141.1, 136.5, 132.2 (q, J = 32 Hz), 131.1, 129.0, 128.5, 127.2, 125.4 (q, J = 4 Hz), 124.1 (q, J = 270 Hz), 115.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.65.

4-phenyl-2-(pyridin-4-yl)pyrimidine (4n)[6]



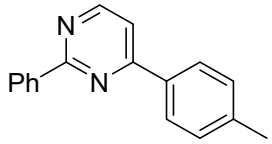
Yellow solid; mp = 97-98 °C; R_f = 0.24 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.87 (d, J = 5.3 Hz, 1H), 8.79 (d, J = 5.7 Hz, 2H), 8.44 – 8.37 (m, 2H), 8.21 (ddd, J = 5.5, 3.0, 1.5 Hz, 2H), 7.69 (d, J = 5.3 Hz, 1H), 7.58 – 7.50 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.2, 162.6, 158.0, 150.4, 145.1, 136.3, 131.3, 129.0, 127.2, 122.1, 115.9.

4-phenyl-2-(pyridin-3-yl)pyrimidine (4o)[6]



Brown solid; mp = 78-81 °C; R_f = 0.24 (petroleum ether / ethyl acetate = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.77 (d, J = 1.6 Hz, 1H), 8.85 (d, J = 5.3 Hz, 1H), 8.82 (dt, J = 8.0, 1.9 Hz, 1H), 8.73 (dd, J = 4.8, 1.6 Hz, 1H), 8.24 – 8.19 (m, 2H), 7.65 (d, J = 5.3 Hz, 1H), 7.57 – 7.53 (m, 3H), 7.46 – 7.41 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.0, 162.8, 158.0, 151.3, 149.9, 136.5, 135.6, 133.3, 131.2, 129.0, 127.2, 123.3, 115.1.

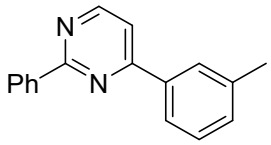
2-phenyl-4-(*p*-tolyl)pyrimidine (4p)[7]



Yellow solid; mp = 106-107 °C; R_f = 0.67 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (d, J = 5.3 Hz, 1H), 8.62 – 8.55 (m, 2H), 8.20 – 8.08 (m, 2H), 7.57 (d, J = 5.3 Hz, 1H), 7.52 (dq, J = 8.5, 2.8, 2.2 Hz, 3H), 7.34 (d, J = 7.9 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.5, 163.8, 157.7, 141.4,

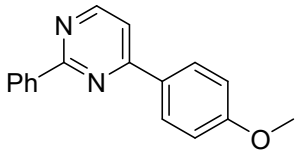
138.0, 134.2, 130.6, 129.6, 128.5, 128.3, 127.1, 114.2, 21.5.

2-phenyl-4-(*m*-tolyl)pyrimidine (4q)[7]



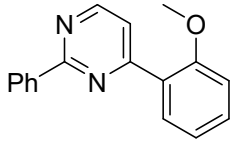
Yellow oil liquid; R_f = 0.70 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.83 (d, J = 5.3 Hz, 1H), 8.63 – 8.55 (m, 2H), 8.05 (s, 1H), 8.01 (d, J = 7.7 Hz, 1H), 7.59 (d, J = 5.3 Hz, 1H), 7.56 – 7.50 (m, 3H), 7.43 (t, J = 7.6 Hz, 1H), 7.35 (d, J = 7.5 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.5, 164.0, 157.7, 138.6, 137.9, 136.9, 131.7, 130.6, 128.8, 128.5, 128.3, 127.8, 124.3, 114.6, 21.5.

4-(4-methoxyphenyl)-2-phenylpyrimidine (4r)[7]



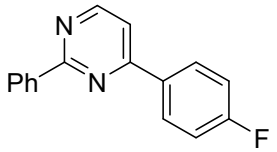
Yellow solid; mp = 87-89 °C; R_f = 0.50 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = ^{1}H NMR (400 MHz, Chloroform-d) δ 8.78 (d, J = 5.3 Hz, 1H), 8.57 (dd, J = 7.5, 2.3 Hz, 2H), 8.25 – 8.18 (m, 2H), 7.57 – 7.48 (m, 4H), 7.08 – 7.02 (m, 2H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.4, 163.3, 162.1, 157.5, 138.0, 133.3, 130.6, 129.4, 128.7, 128.5, 128.2, 114.3, 113.6, 55.4.

4-(2-methoxyphenyl)-2-phenylpyrimidine (4s)[7]



Yellow solid; mp = 112-113 °C; R_f = 0.50 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.80 (d, J = 5.3 Hz, 1H), 8.57 – 8.50 (m, 2H), 8.35 (d, J = 2.6 Hz, 1H), 7.85 (d, J = 5.3 Hz, 1H), 7.58 – 7.48 (m, 4H), 6.91 (d, J = 8.8 Hz, 1H), 3.90 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.4, 161.0, 157.3, 157.1, 137.8, 134.1, 133.7, 130.6, 128.5, 128.2, 128.1, 119.5, 113.6, 113.3, 55.9.

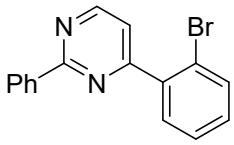
4-(4-fluorophenyl)-2-phenylpyrimidine (4t)[7]



Yellow solid; mp = 55-56 °C; R_f = 0.63 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.83 (d, J = 5.3 Hz, 1H), 8.62 – 8.52 (m, 2H), 8.28 – 8.19 (m, 2H), 7.59 – 7.48 (m, 4H), 7.26 – 7.19 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.6 (d, J = 249 Hz), 164.5, 162.7, 157.8, 137.7, 133.0 (d, J = 3 Hz), 130.7, 129.2 (d, J = 9

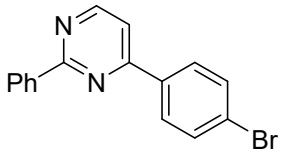
Hz), 128.5, 128.2, 115.9 (d, J = 21 Hz), 114.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -109.47.

4-(2-bromophenyl)-2-phenylpyrimidine (4u)[7]



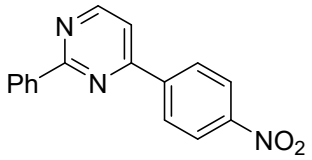
Yellow solid; mp = 61-62 °C; R_f = 0.54 (petroleum ether / ethyl acetate = 9:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.87 (d, J = 5.1 Hz, 1H), 8.57 – 8.49 (m, 2H), 7.71 (ddd, J = 12.6, 7.9, 1.4 Hz, 2H), 7.56 (d, J = 5.1 Hz, 1H), 7.52 – 7.45 (m, 4H), 7.33 (td, J = 7.7, 1.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.4, 164.6, 157.0, 139.1, 137.6, 133.7, 131.6, 130.8, 130.8, 128.5, 128.3, 127.7, 121.5, 119.3.

4-(4-bromophenyl)-2-phenylpyrimidine (4v)[7]



Yellow solid; mp = 104-105 °C; R_f = 0.57 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.84 (d, J = 5.3 Hz, 1H), 8.60 – 8.53 (m, 2H), 8.14 – 8.06 (m, 2H), 7.69 – 7.63 (m, 2H), 7.56 – 7.50 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.7, 162.7, 158.0, 137.6, 135.8, 132.1, 130.8, 128.7, 128.5, 128.3, 125.6, 114.2.

4-(4-nitrophenyl)-2-phenylpyrimidine (4w)[7]



Yellow solid; mp = 155-156 °C; R_f = 0.32 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.94 (d, J = 5.2 Hz, 1H), 8.61 – 8.54 (m, 2H), 8.39 (s, 4H), 7.65 (d, J = 5.2 Hz, 1H), 7.57 – 7.49 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.0, 161.4, 158.6, 149.3, 142.8, 137.2, 131.1, 128.6, 128.3, 128.1, 124.1, 115.1.

F. Reference

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G. Copies of ^{1}H and ^{13}C NMR spectra

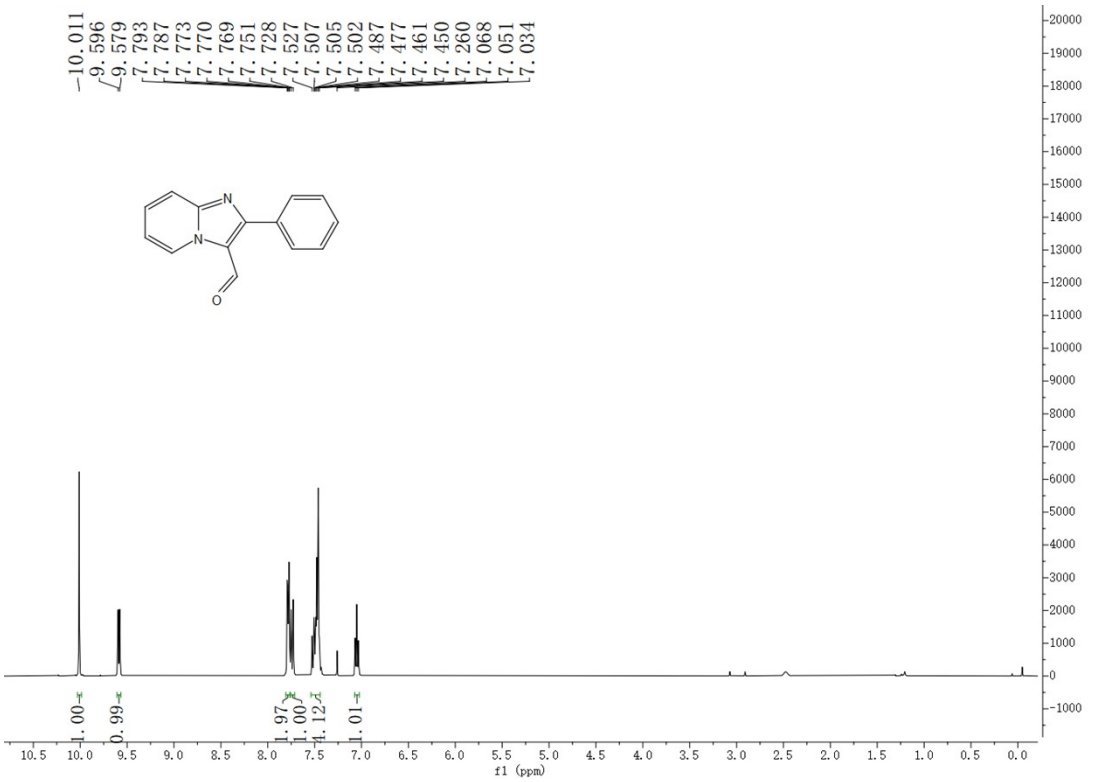

Figure S1. ^{1}H NMR Spectrum of 3a (400 MHz, $CDCl_3$)

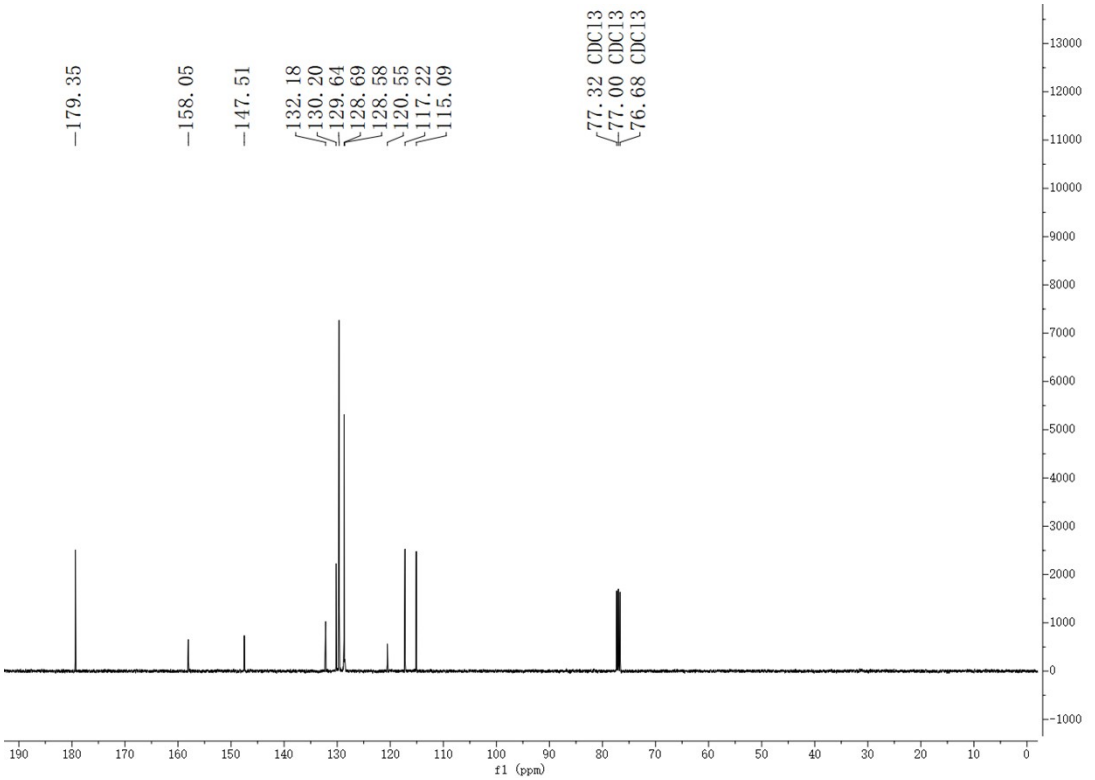

Figure S2. ^{13}C NMR Spectrum of 3a (100 MHz, $CDCl_3$)

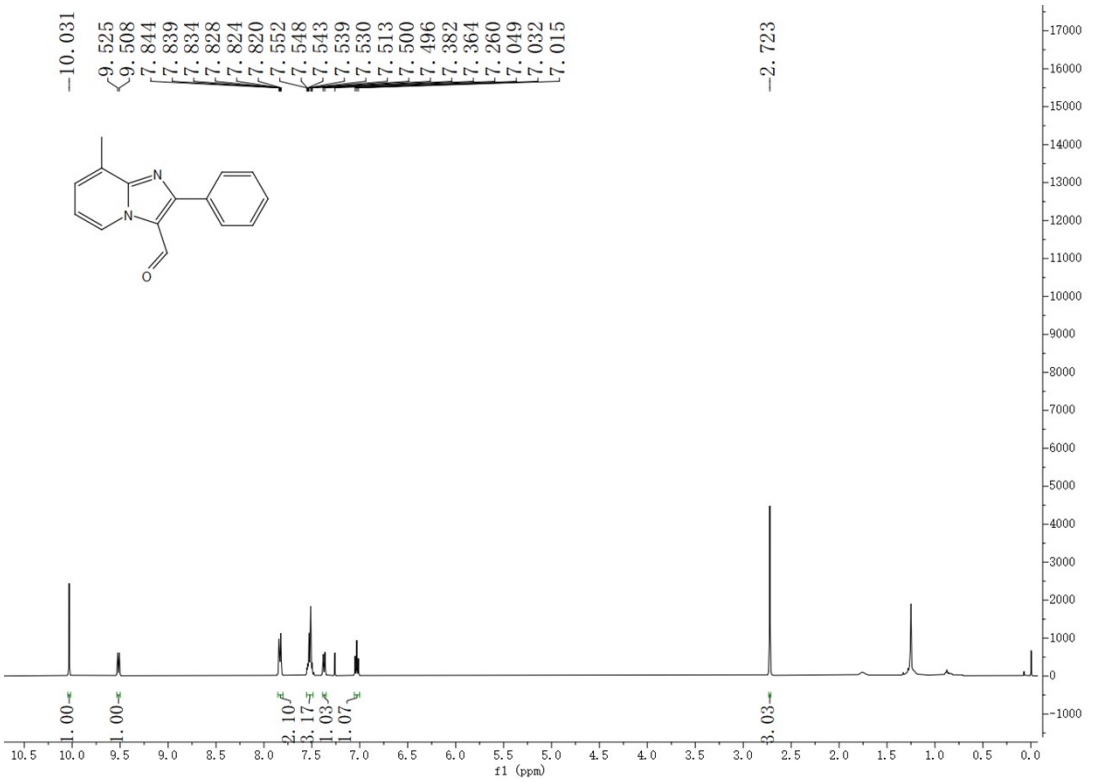

Figure S3. ^{1}H NMR Spectrum of 3b (400 MHz, $CDCl_3$)

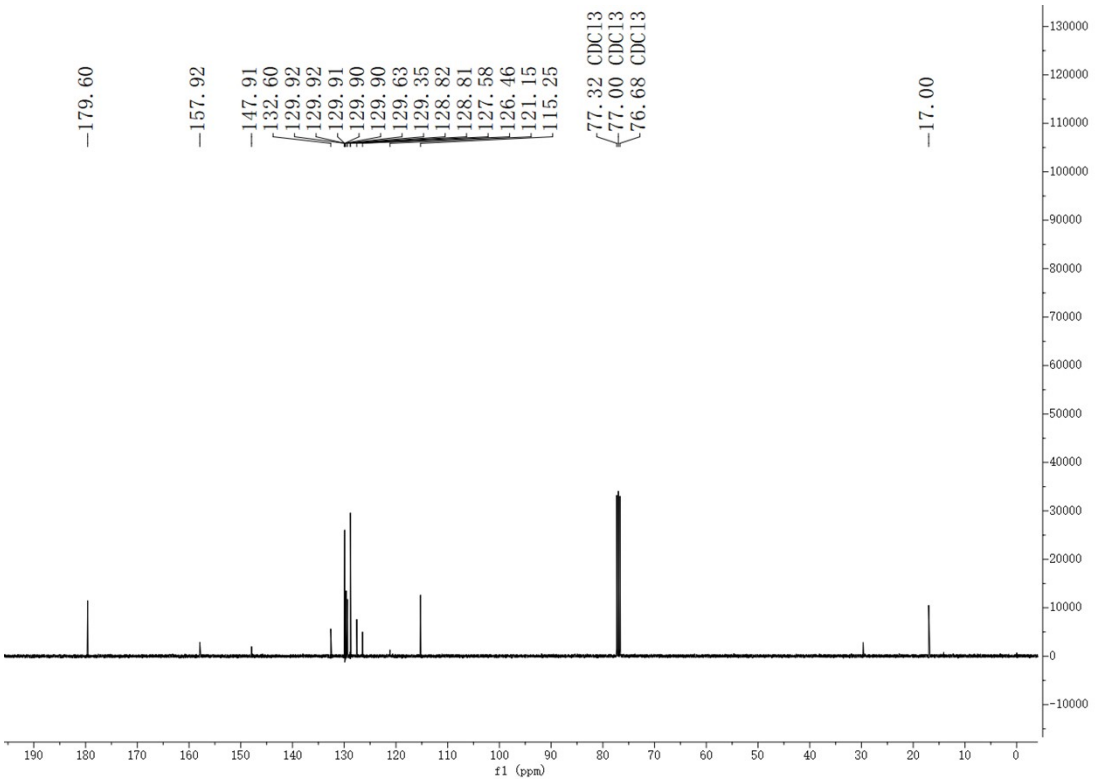

Figure S4. ^{13}C NMR Spectrum of 3b (100 MHz, $CDCl_3$)

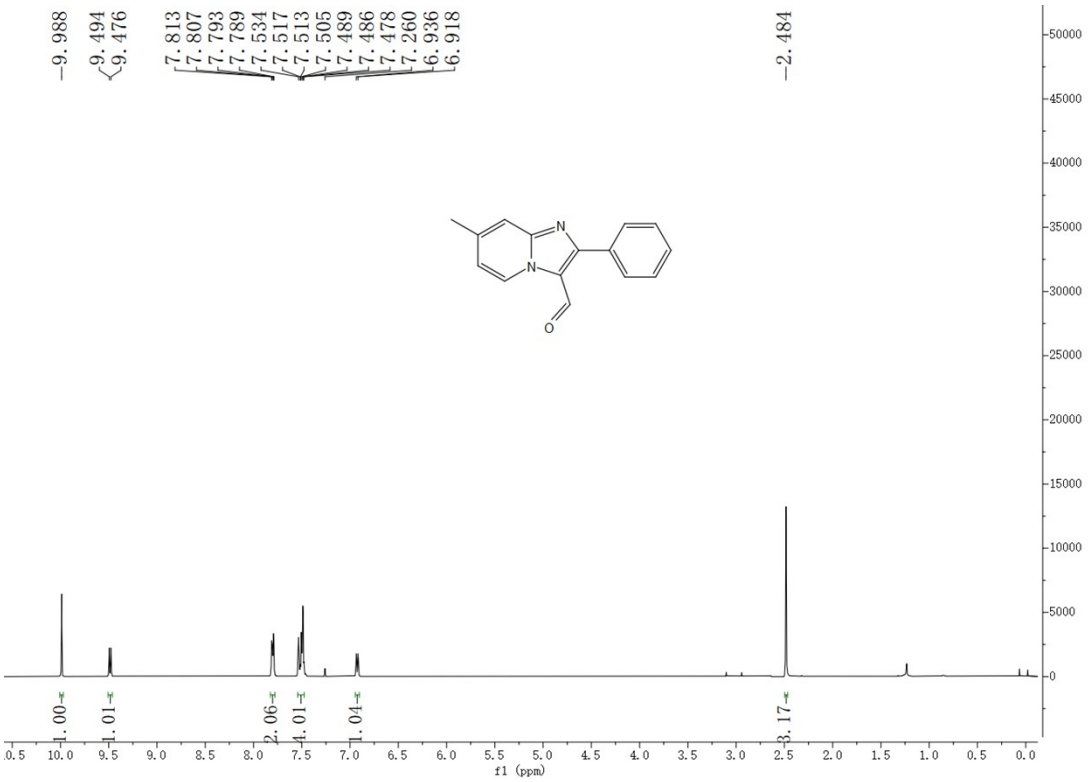

Figure S5. ^{1}H NMR Spectrum of 3c (400 MHz, $CDCl_3$)

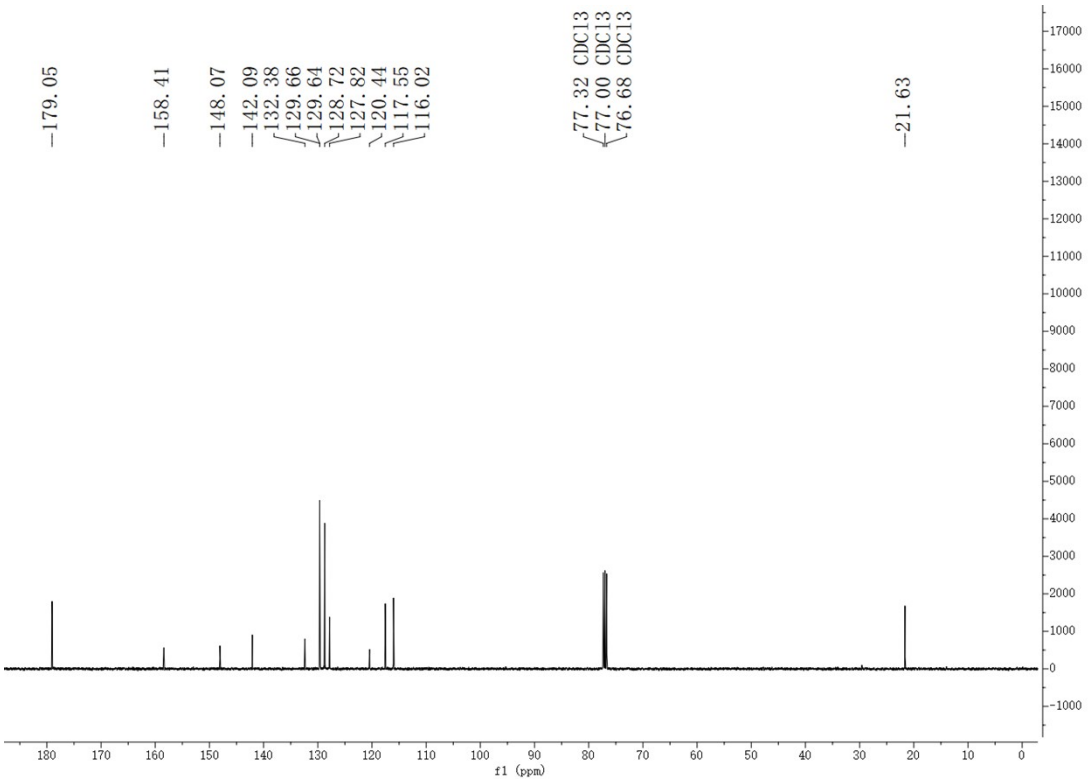

Figure S6. ^{13}C NMR Spectrum of 3c (100 MHz, $CDCl_3$)

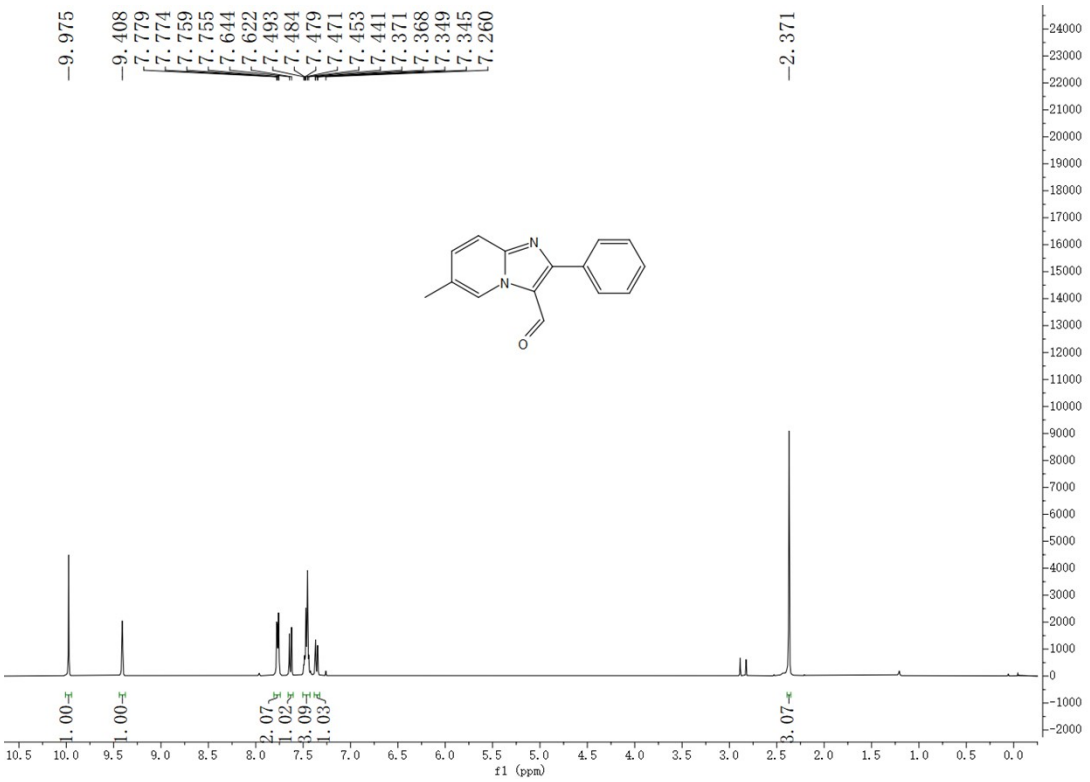

Figure S7. ^{1}H NMR Spectrum of 3d (400 MHz, $CDCl_3$)

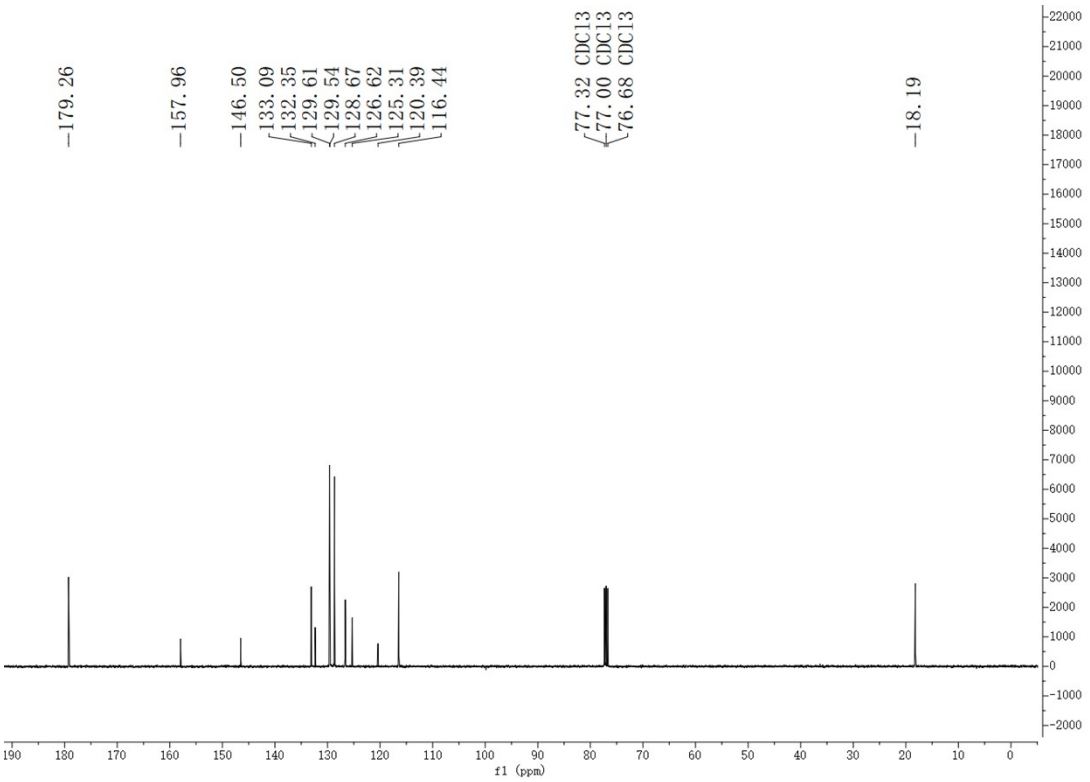

Figure S8. ^{13}C NMR Spectrum of 3d (100 MHz, $CDCl_3$)

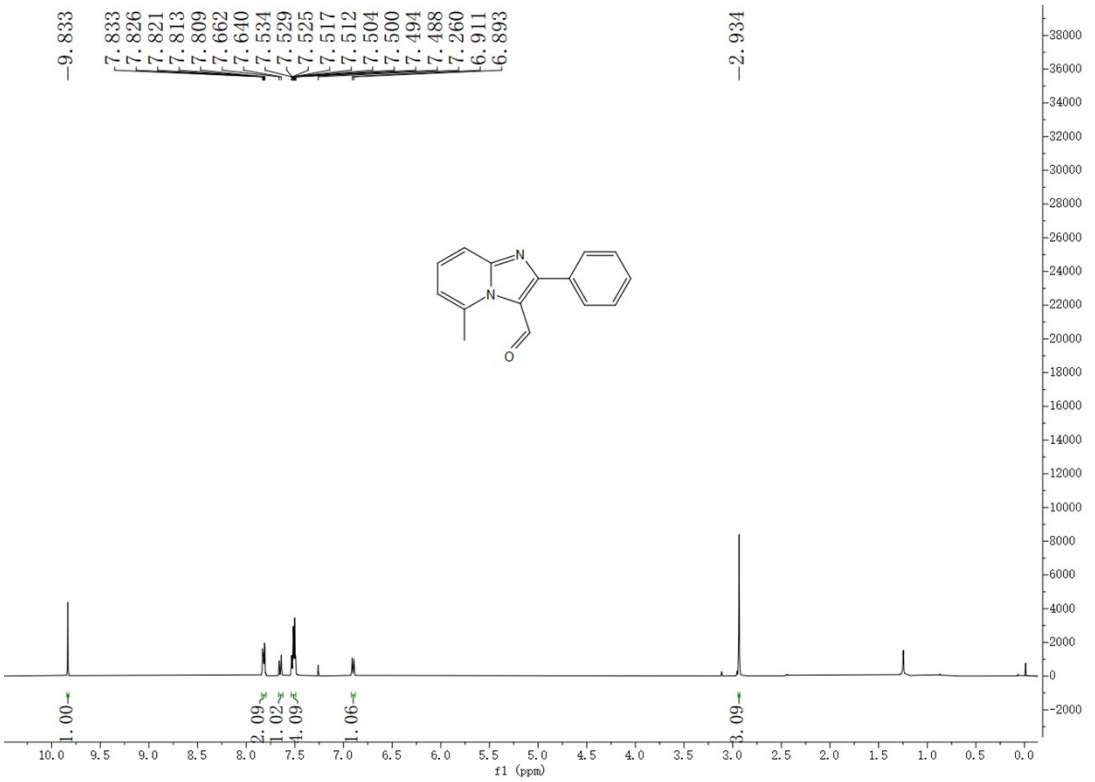

Figure S9. ^{1}H NMR Spectrum of 3e (400 MHz, $CDCl_3$)

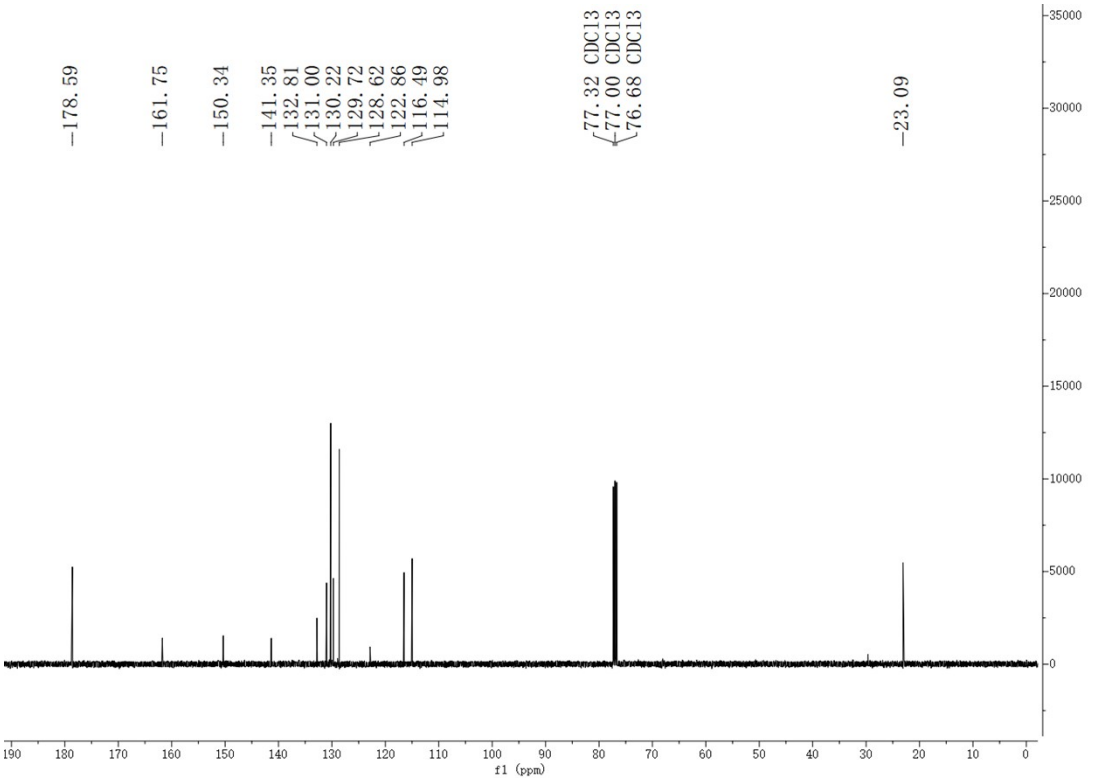

Figure S10. ^{13}C NMR Spectrum of 3e (100 MHz, $CDCl_3$)

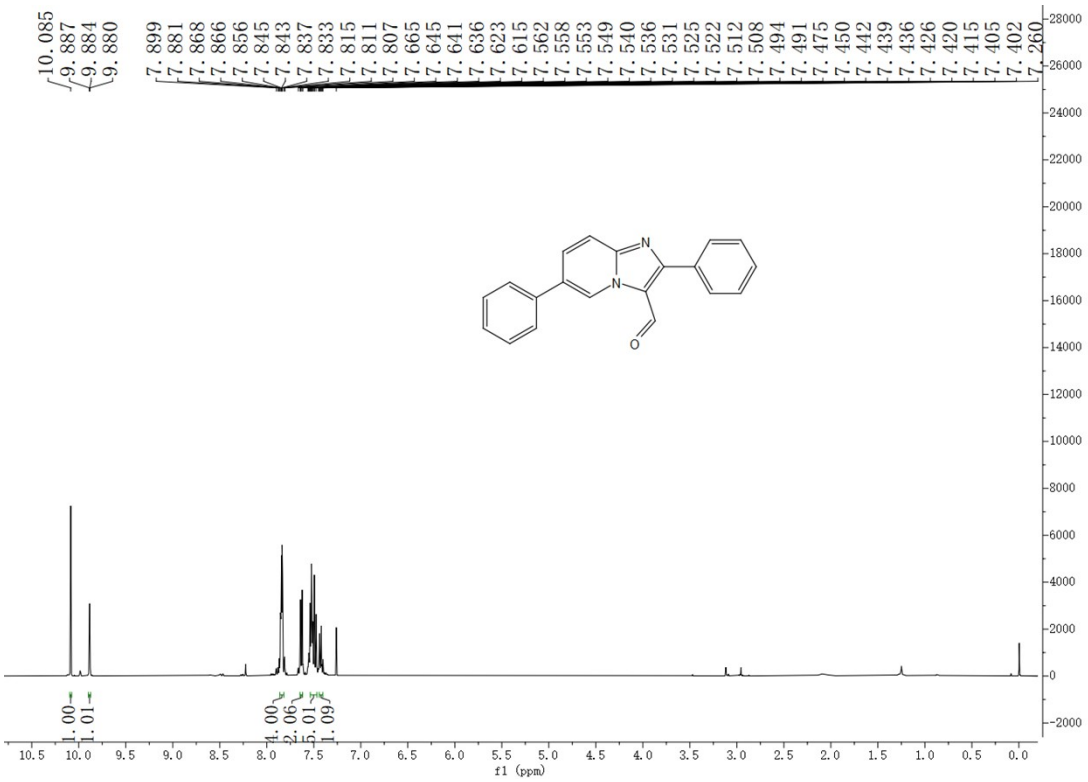

Figure S11. ^{1}H NMR Spectrum of 3f (400 MHz, $CDCl_3$)

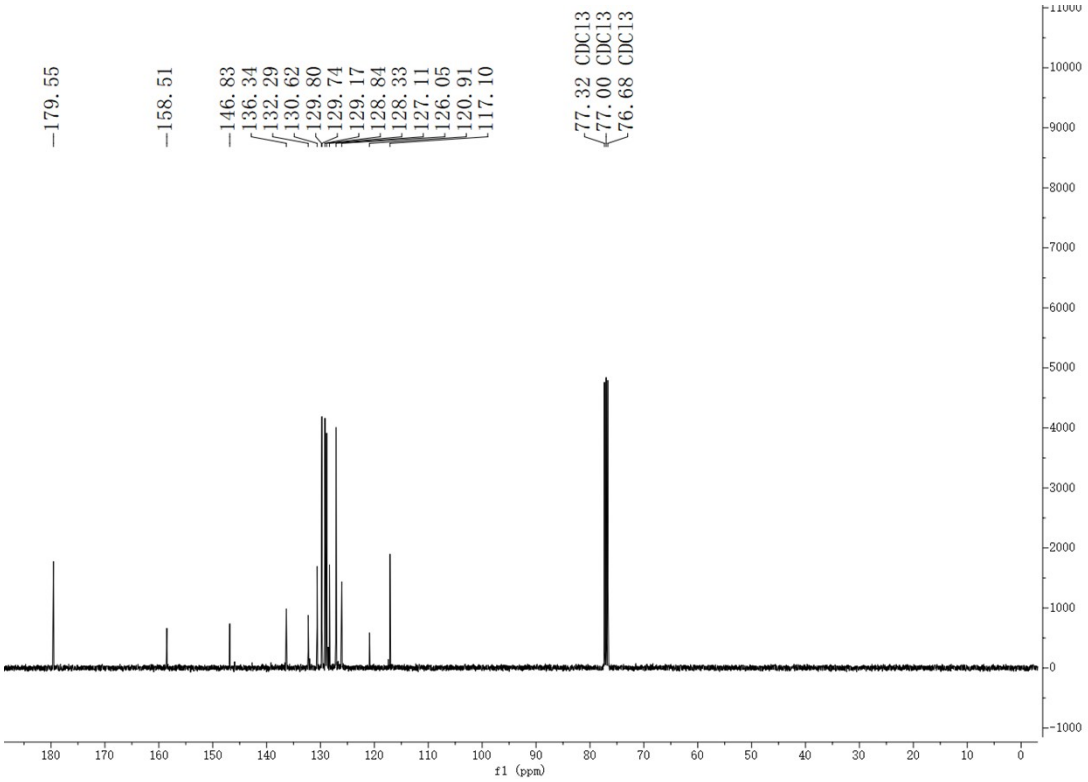

Figure S12. ^{13}C NMR Spectrum of 3f (100 MHz, $CDCl_3$)

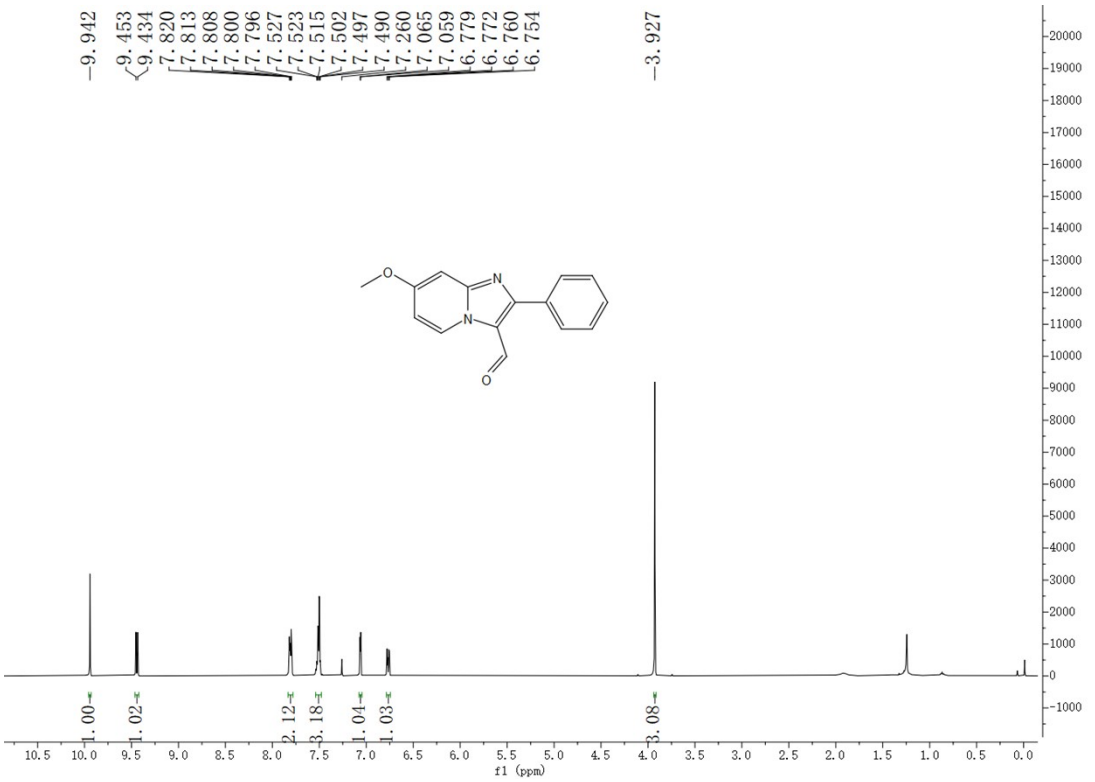

Figure S13. ^{1}H NMR Spectrum of 3g (400 MHz, $CDCl_3$)

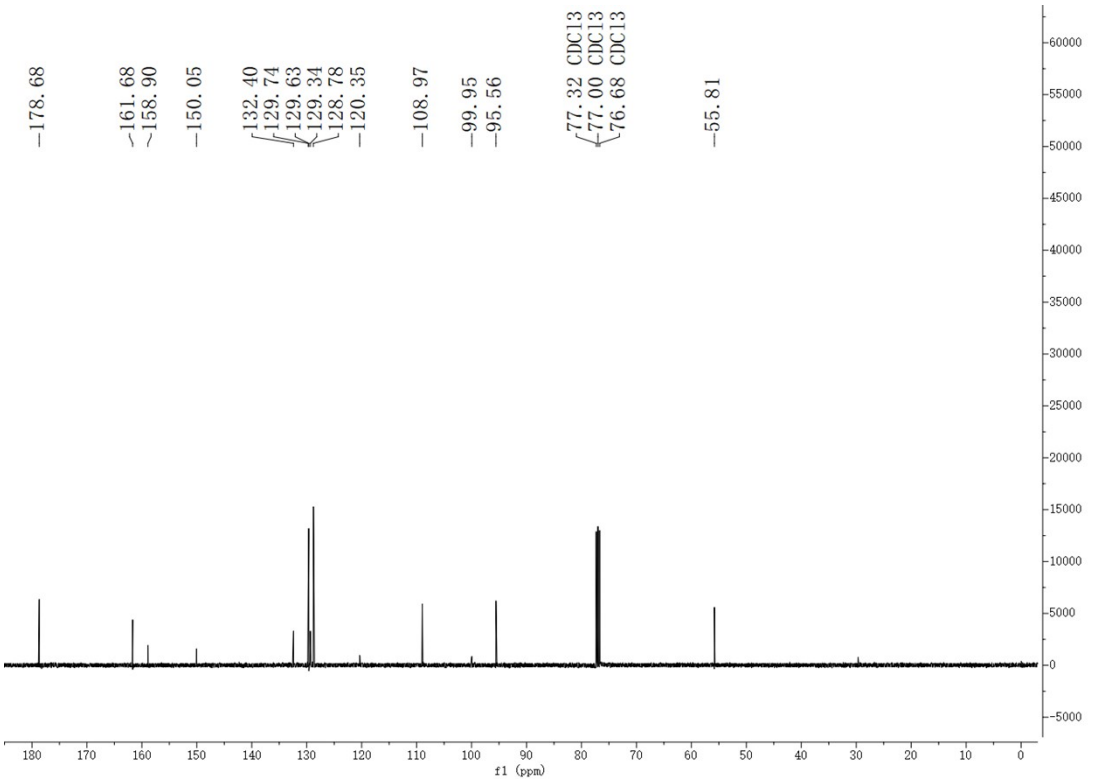

Figure S14. ^{13}C NMR Spectrum of 3g (100 MHz, $CDCl_3$)

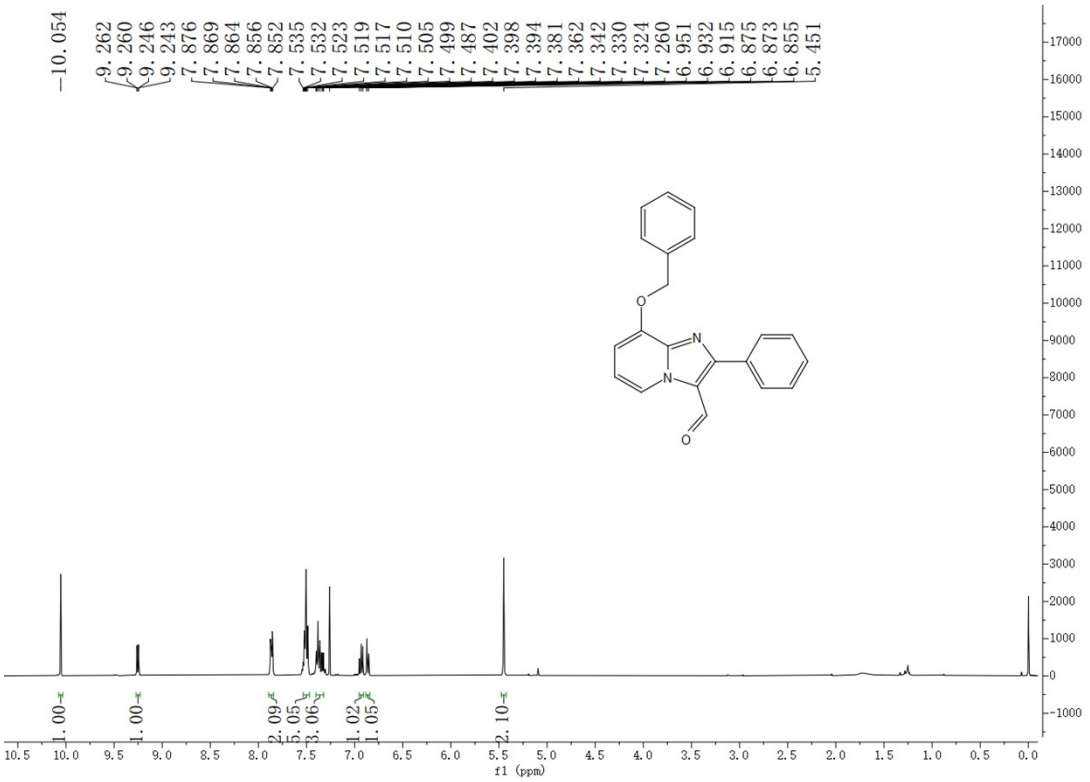

Figure S15. ^{1}H NMR Spectrum of 3h (400 MHz, $CDCl_3$)

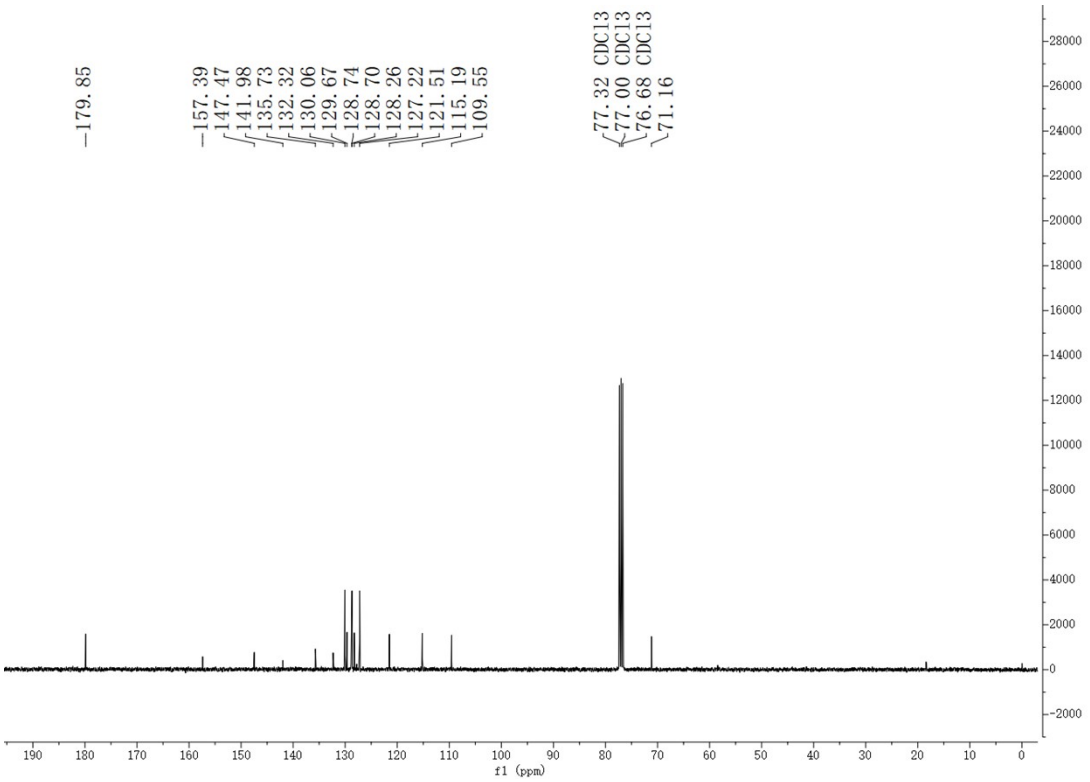

Figure S16. ^{13}C NMR Spectrum of 3h (100 MHz, $CDCl_3$)

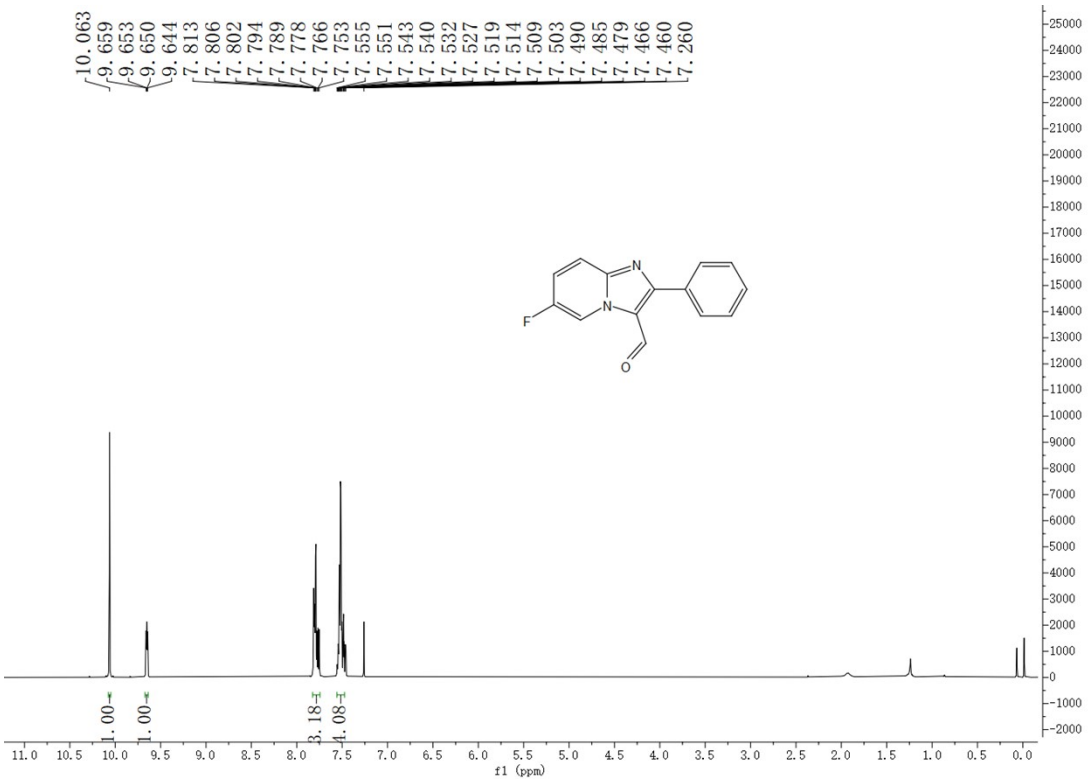

Figure S17. ^{1}H NMR Spectrum of 3i (400 MHz, $CDCl_3$)

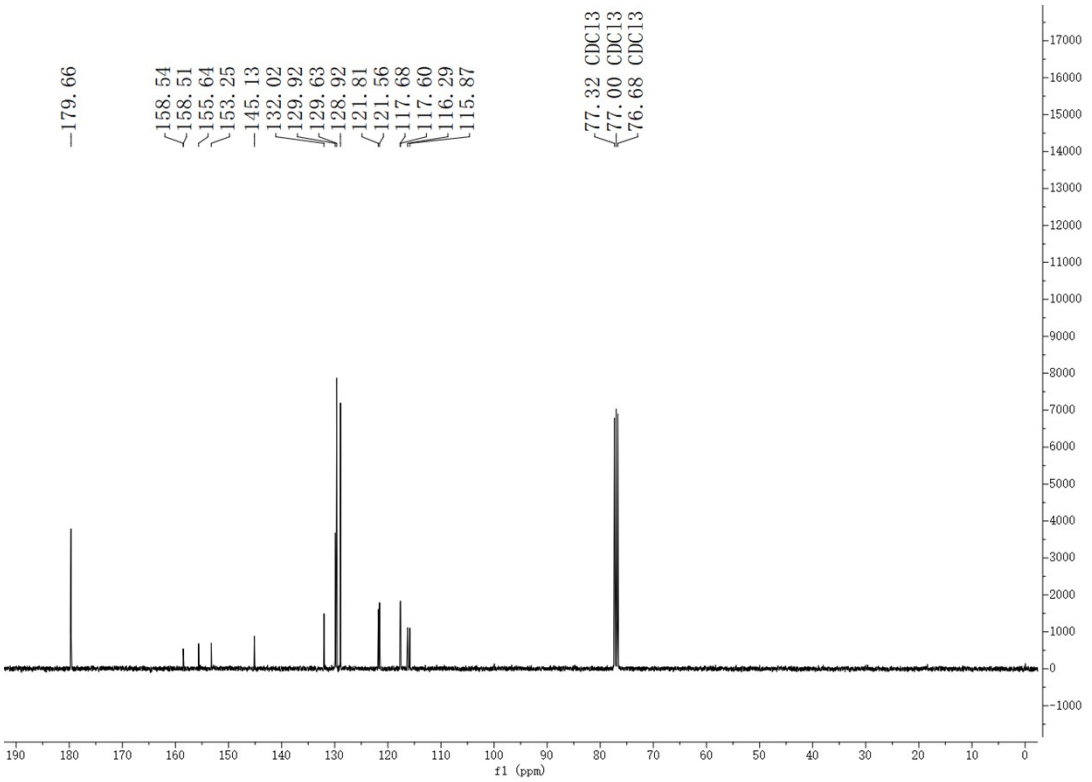

Figure S18. ^{13}C NMR Spectrum of 3i (100 MHz, $CDCl_3$)

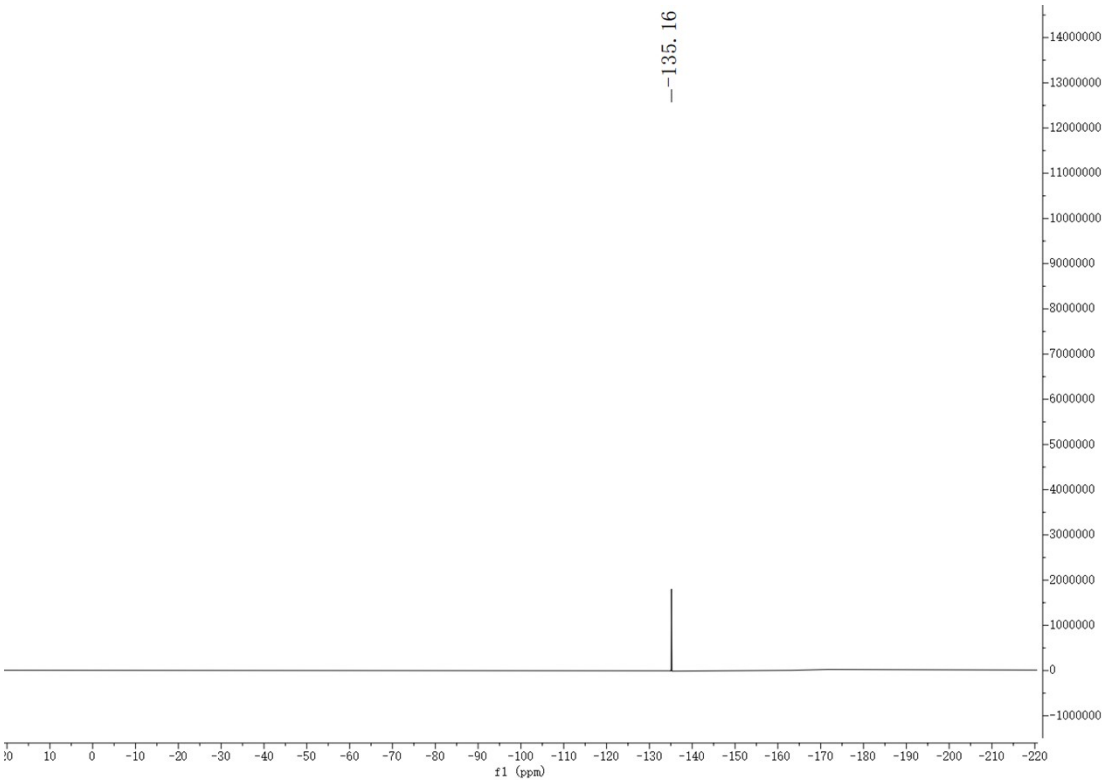

Figure S19. ^{19}F NMR Spectrum of 3i (376 MHz, $CDCl_3$)

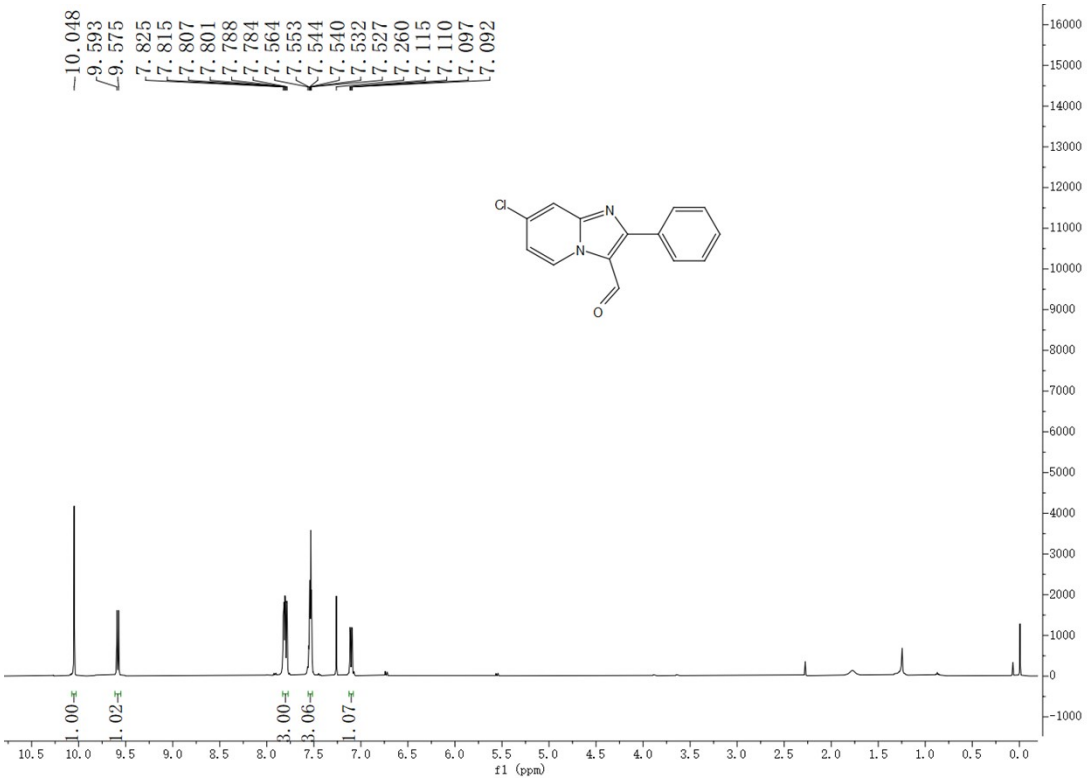

Figure S20. ^{1}H NMR Spectrum of 3j (400 MHz, $CDCl_3$)

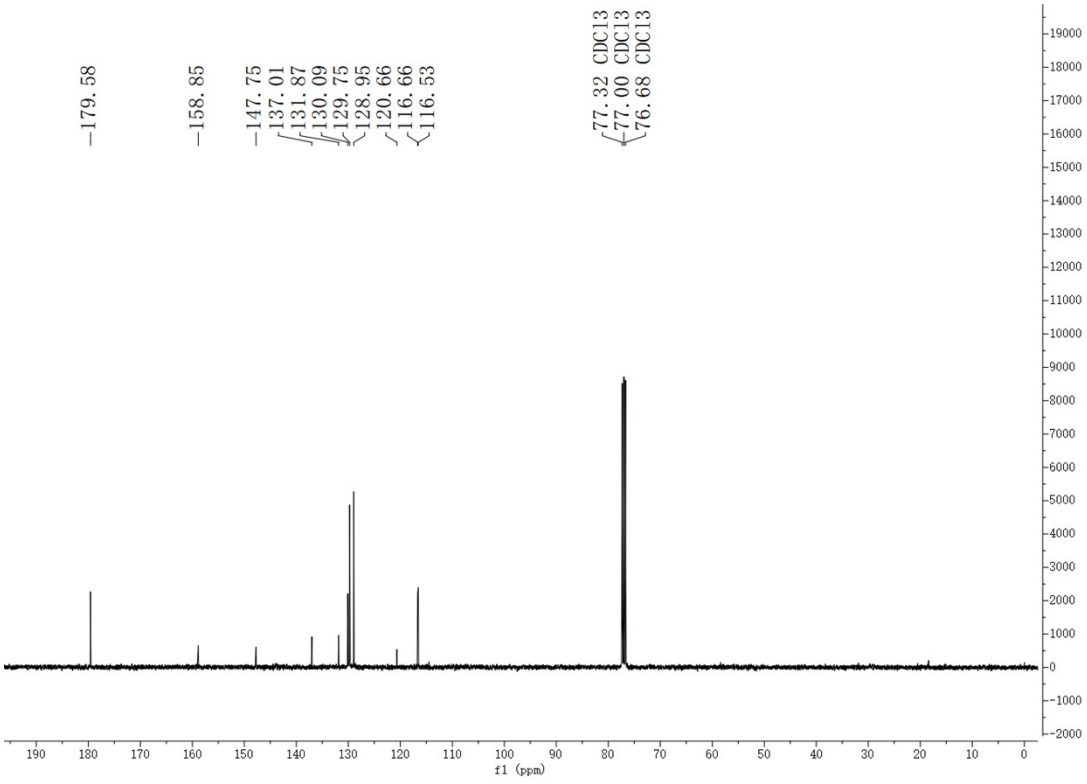

Figure S21. ^{13}C NMR Spectrum of 3j (100 MHz, $CDCl_3$)

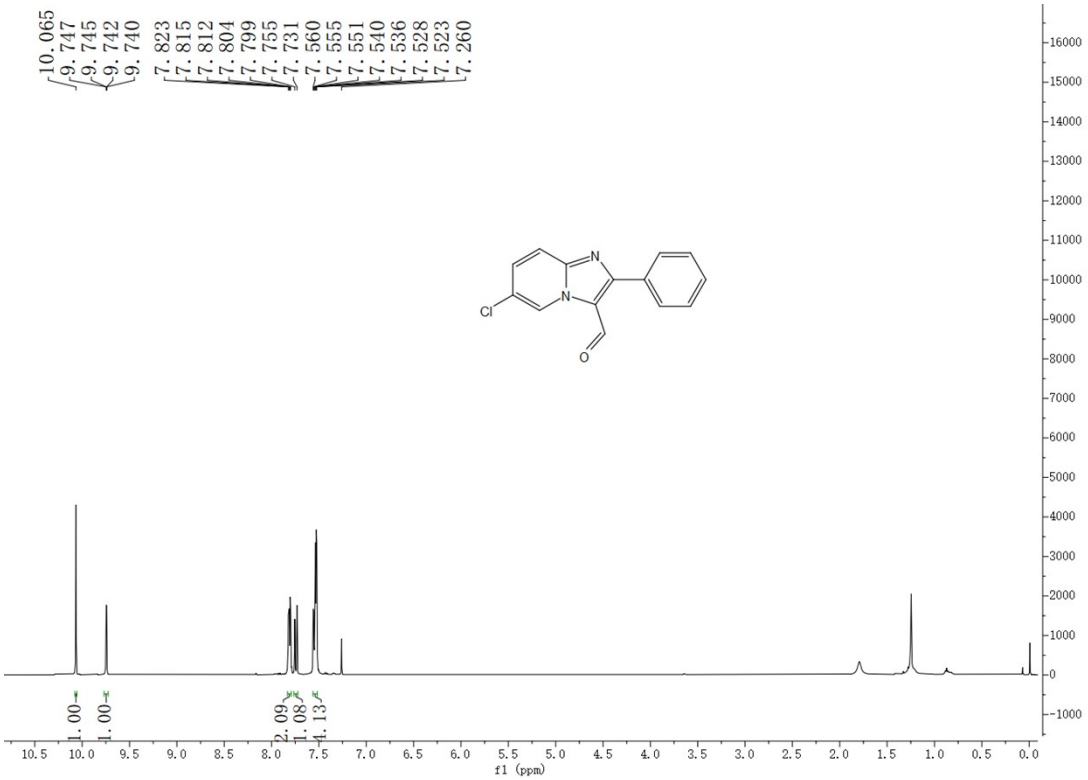

Figure S22. ^{1}H NMR Spectrum of 3k (400 MHz, $CDCl_3$)

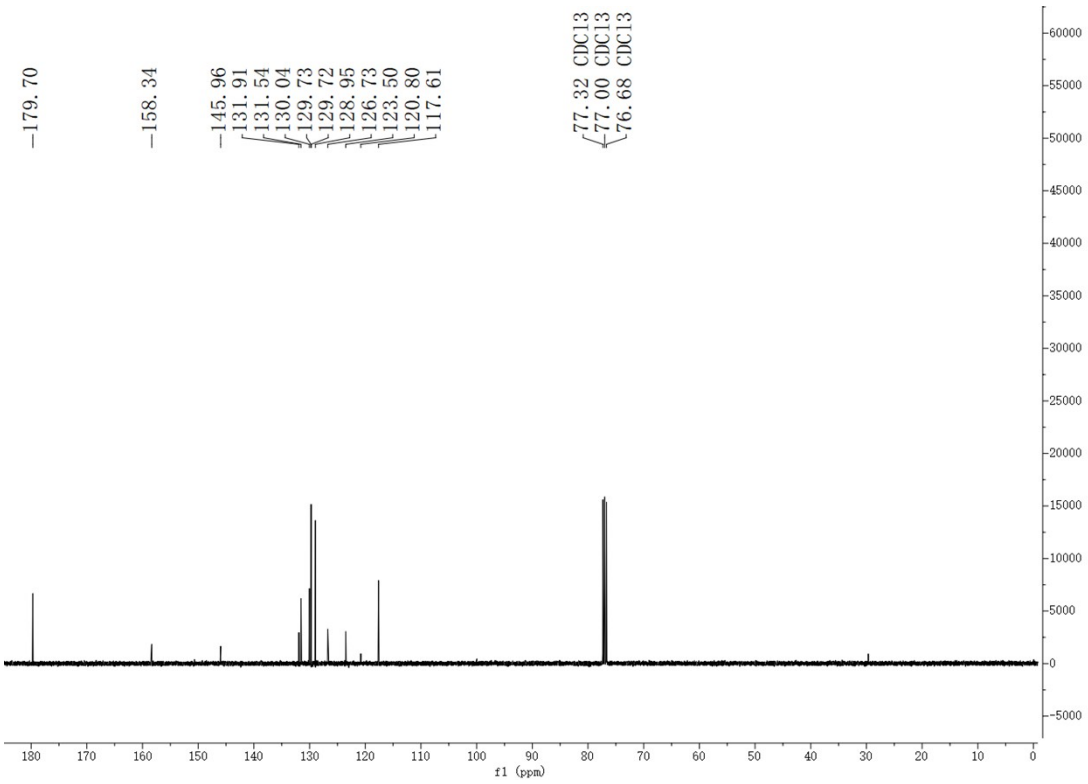

Figure S23. ^{13}C NMR Spectrum of 3k (100 MHz, $CDCl_3$)

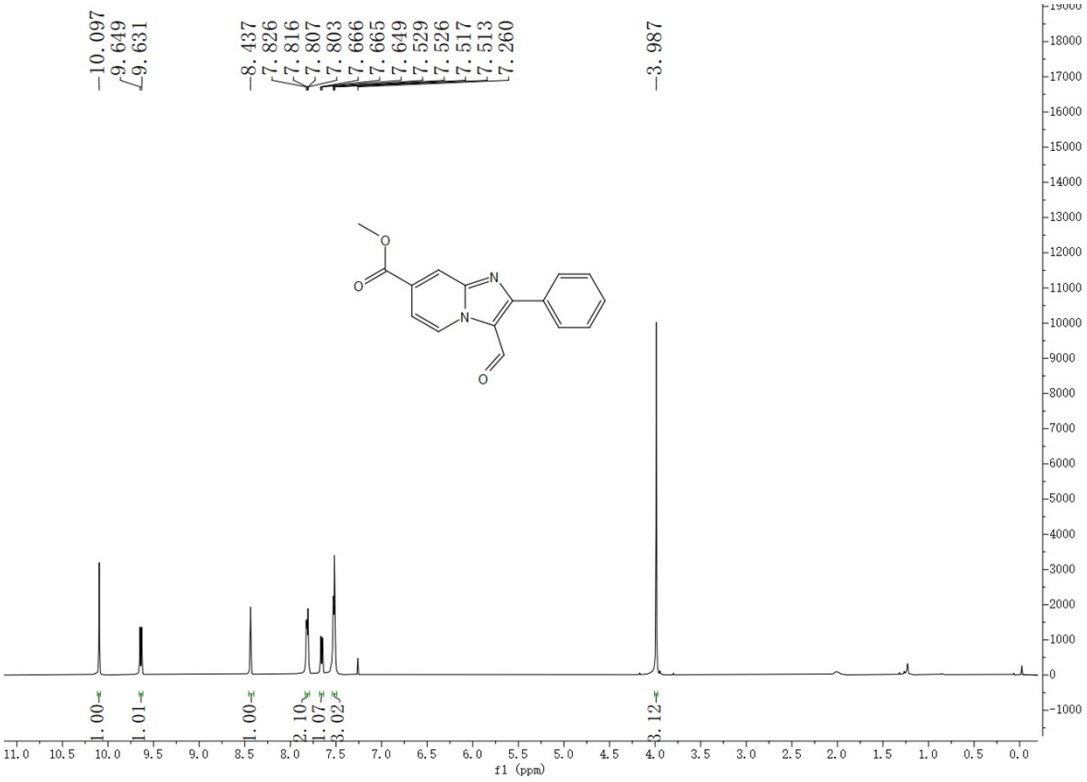

Figure S24. ^{1}H NMR Spectrum of 3l (400 MHz, $CDCl_3$)

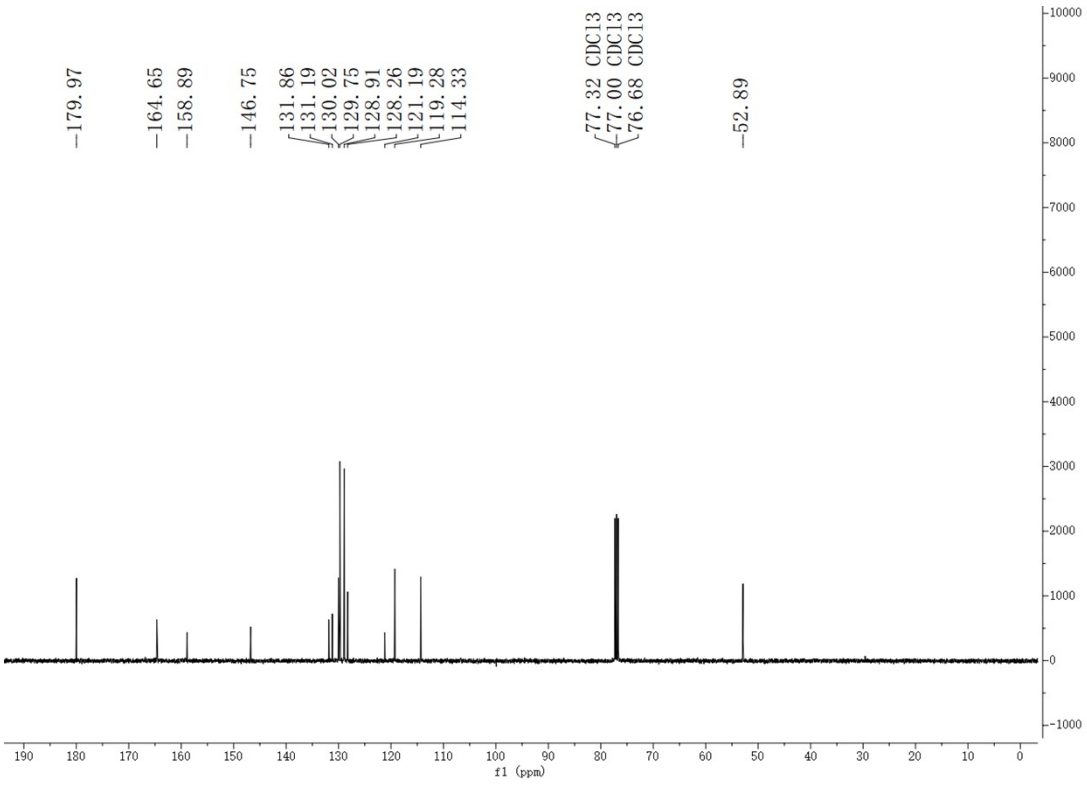

Figure S25. ^{13}C NMR Spectrum of 3l (100 MHz, $CDCl_3$)

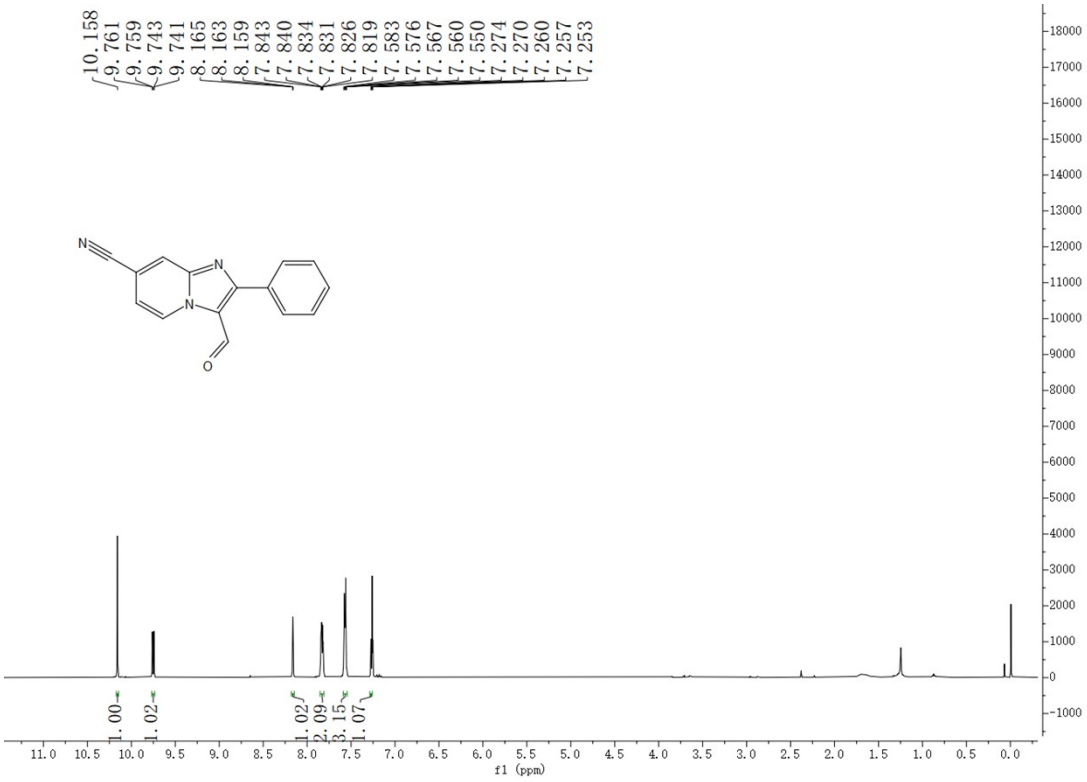

Figure S26. ^{1}H NMR Spectrum of 3m (400 MHz, $CDCl_3$)

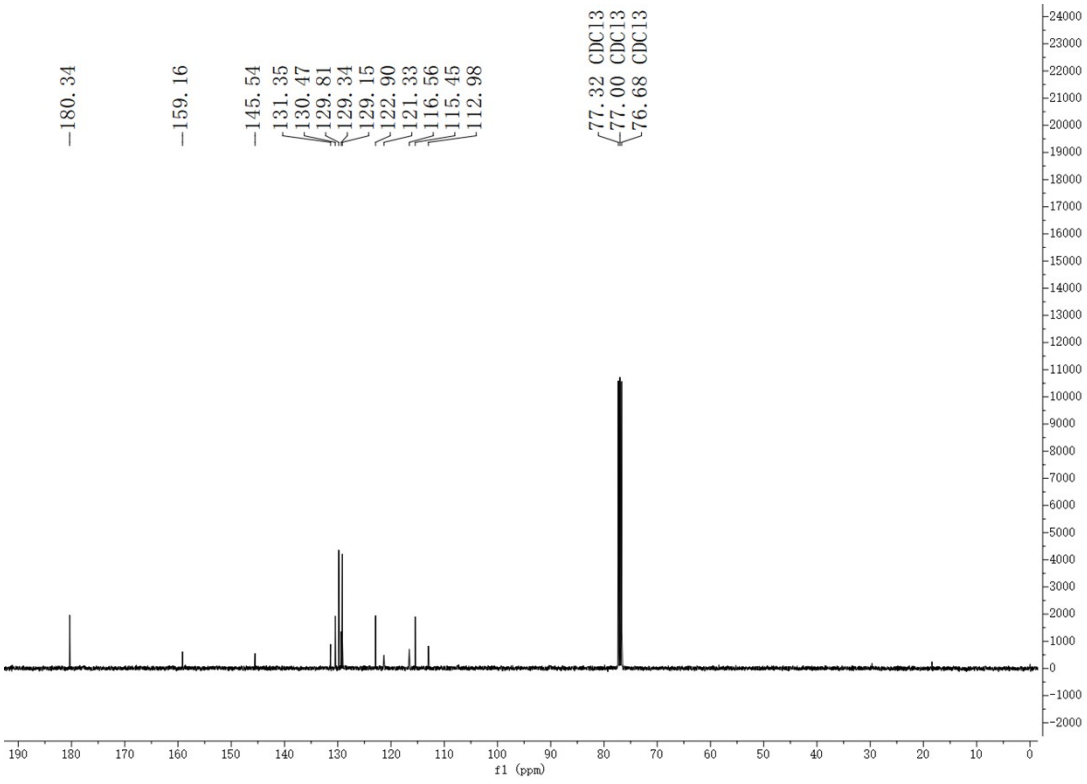

Figure S27. ^{13}C NMR Spectrum of 3m (100 MHz, $CDCl_3$)

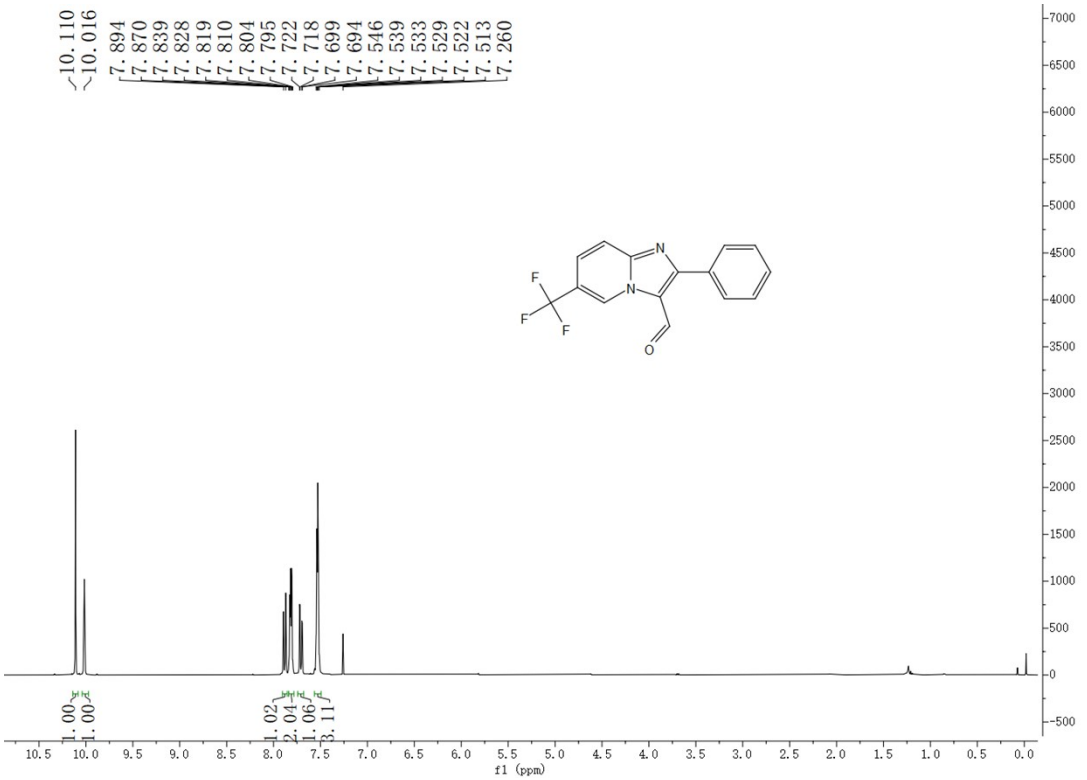

Figure S28. ^{1}H NMR Spectrum of 3n (400 MHz, $CDCl_3$)

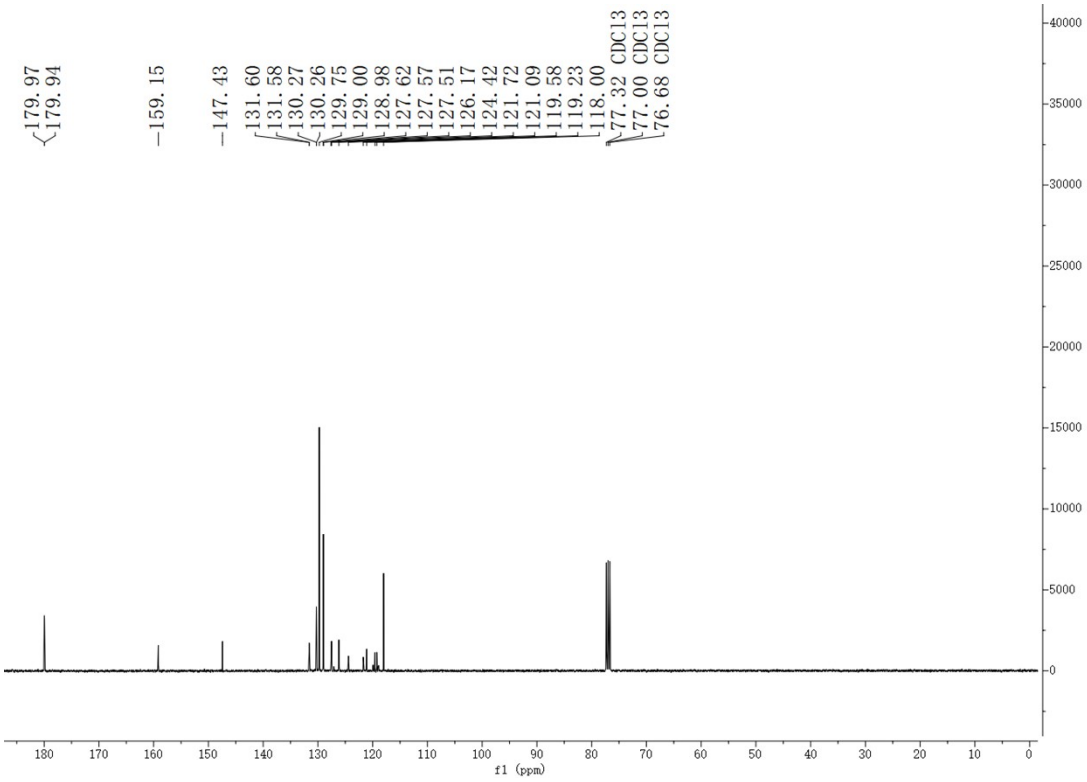

Figure S29. ^{13}C NMR Spectrum of 3n (100 MHz, $CDCl_3$)

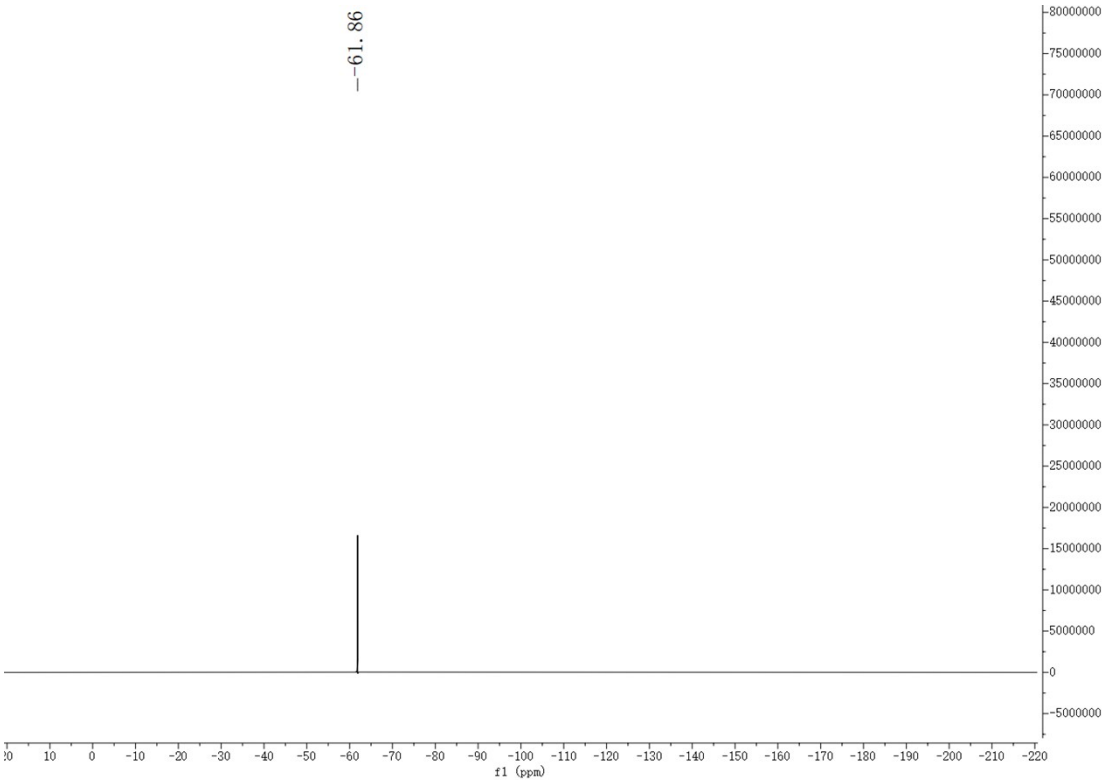

Figure S30. ^{19}F NMR Spectrum of 3n (376 MHz, $CDCl_3$)

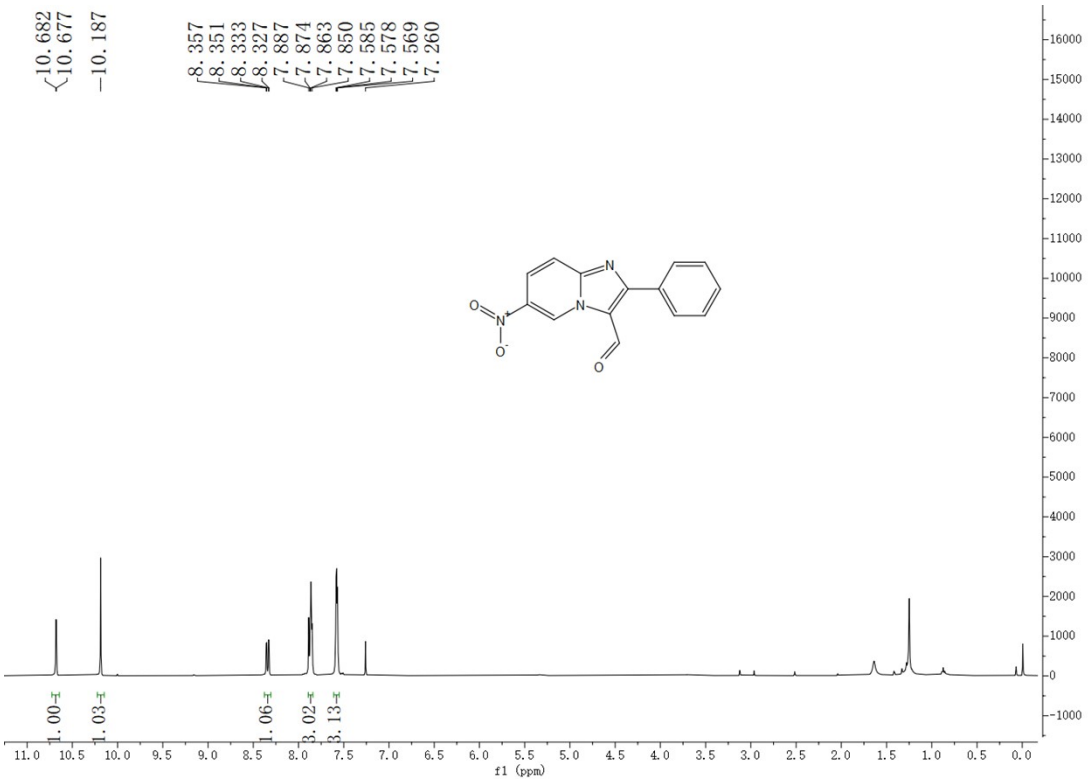

Figure S31. ^{1}H NMR Spectrum of 3o (400 MHz, $CDCl_3$)

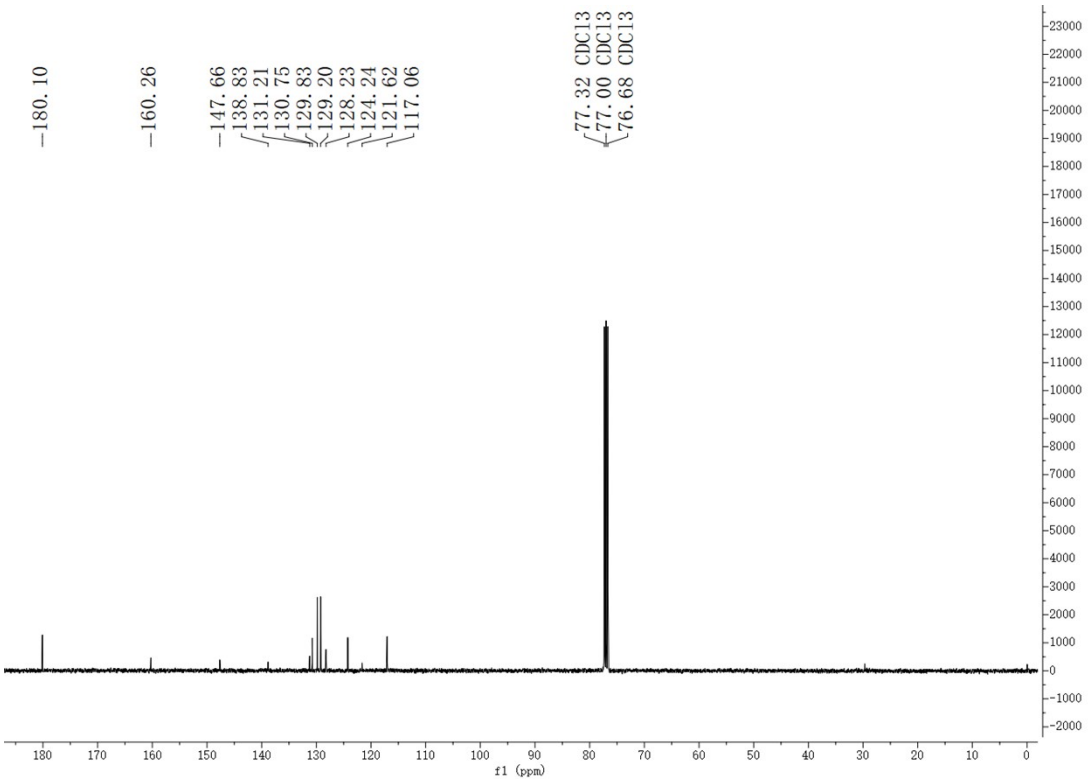

Figure S32. ^{13}C NMR Spectrum of 3o (100 MHz, $CDCl_3$)

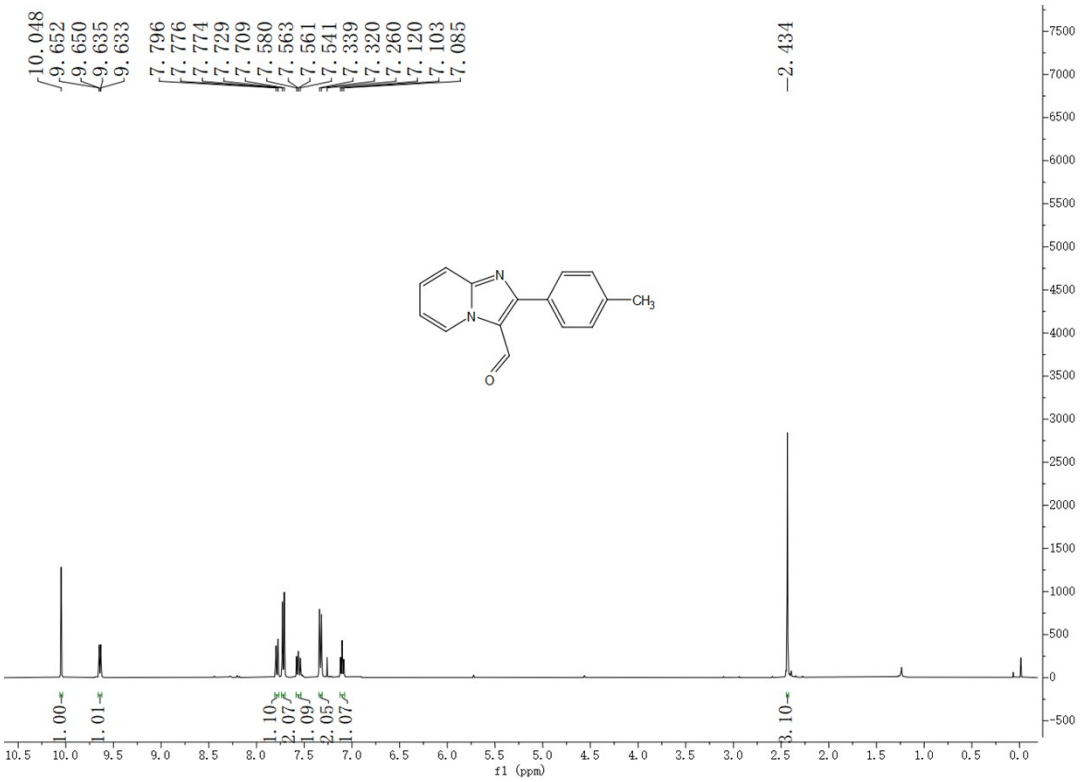

Figure S33. ^{1}H NMR Spectrum of 3p (400 MHz, $CDCl_3$)

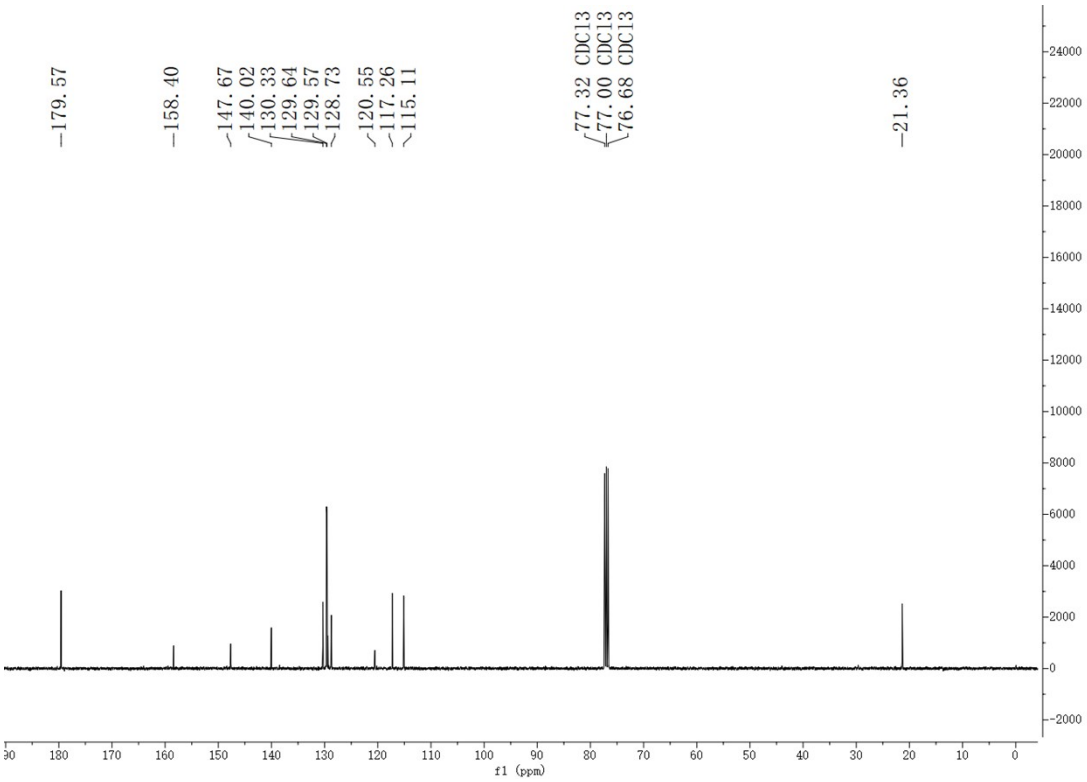

Figure S34. ^{13}C NMR Spectrum of 3p (100 MHz, $CDCl_3$)

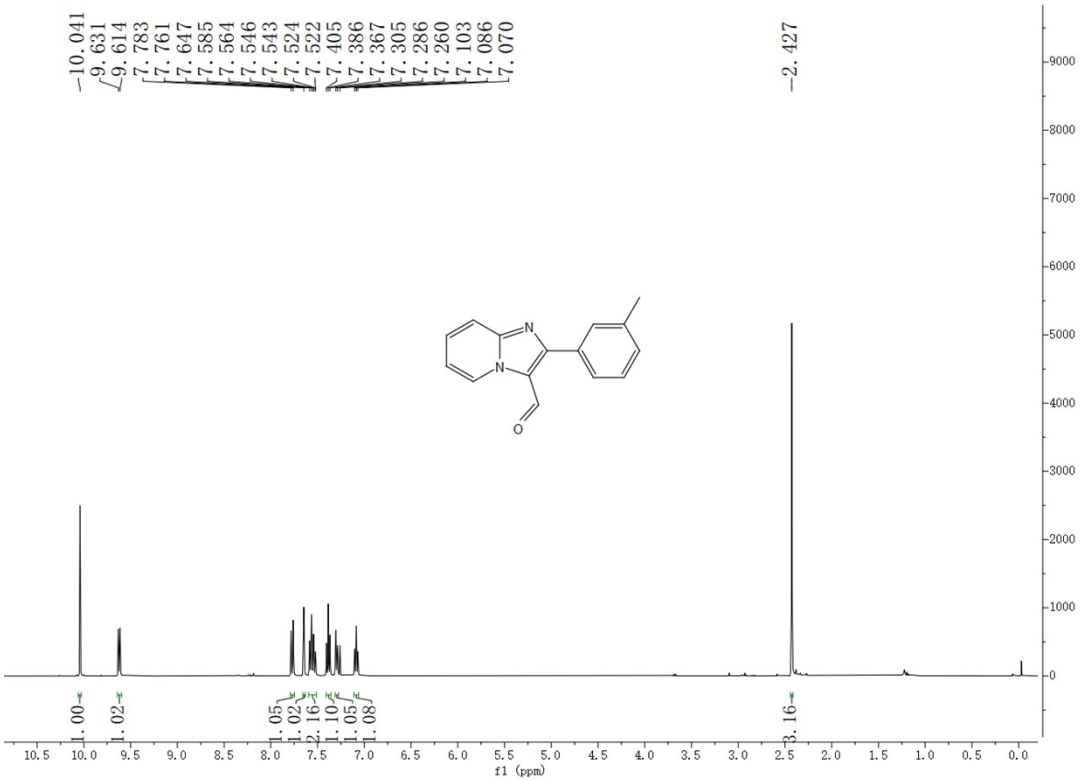

Figure S35. ^{1}H NMR Spectrum of 3q (400 MHz, $CDCl_3$)

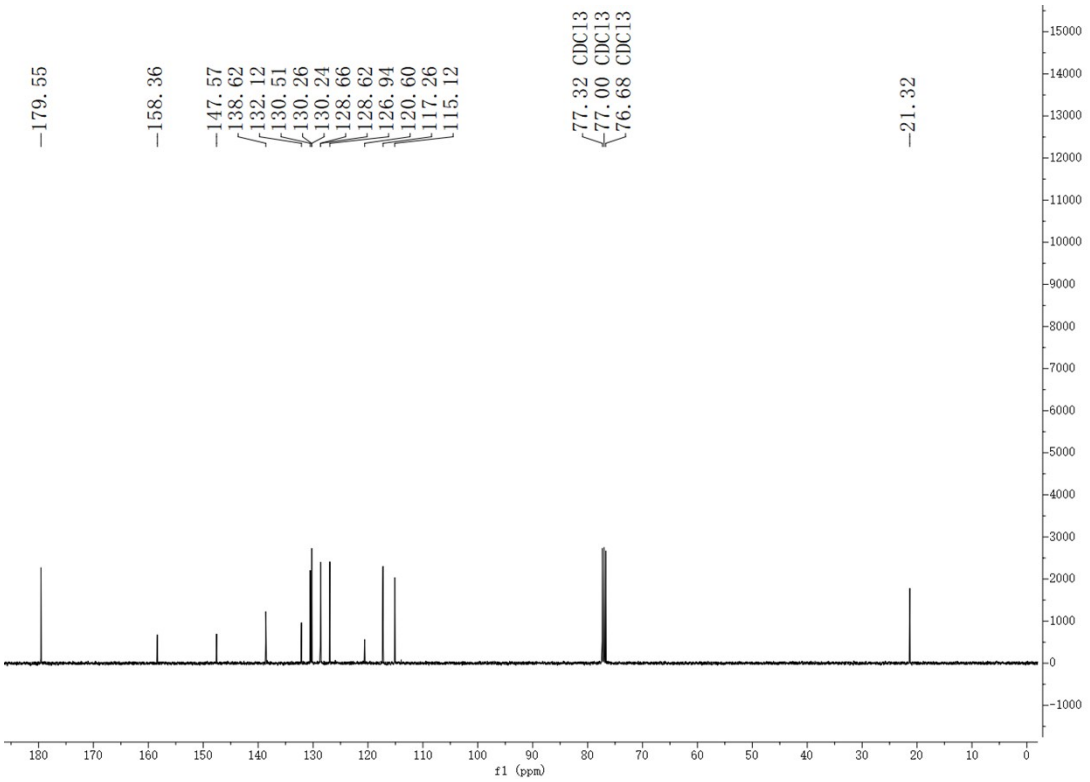

Figure S36. ^{13}C NMR Spectrum of 3q (100 MHz, $CDCl_3$)

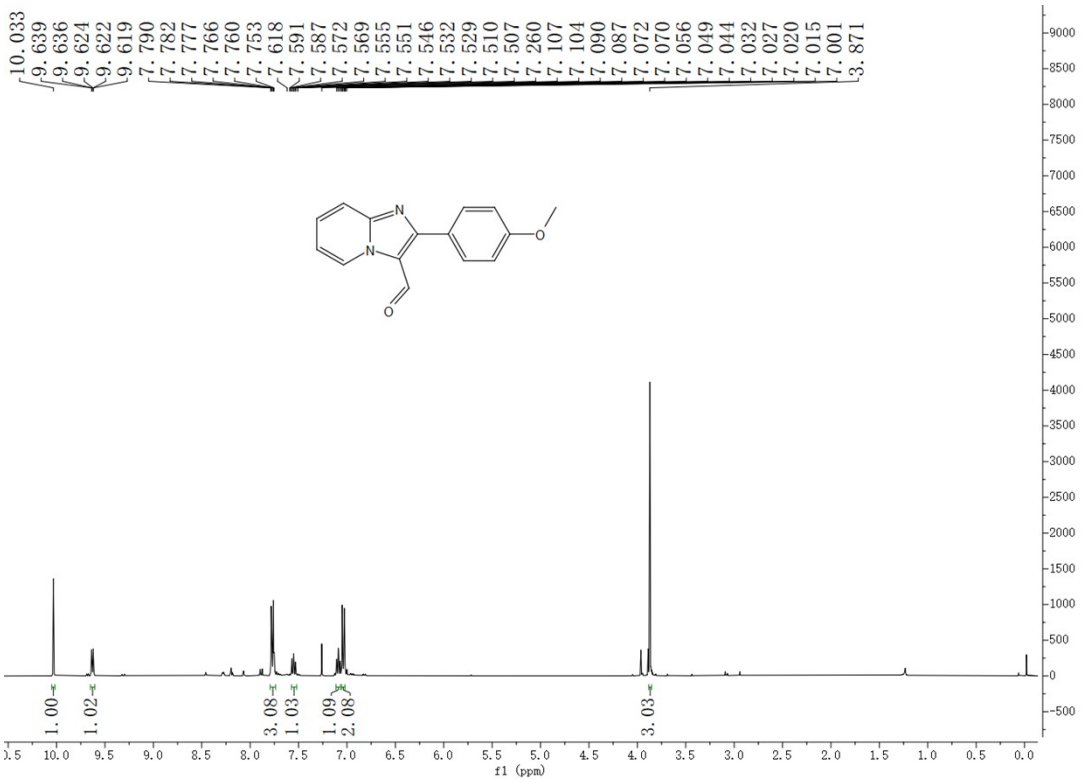

Figure S37. ^{1}H NMR Spectrum of 3r (400 MHz, $CDCl_3$)

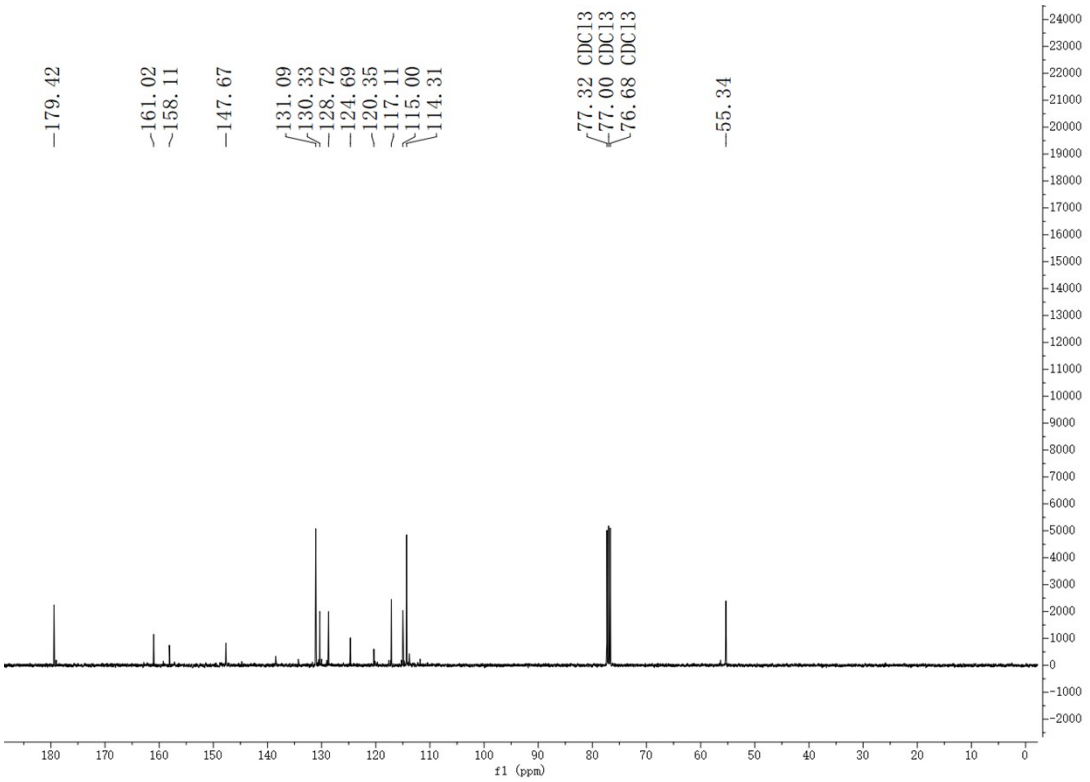

Figure S38. ^{13}C NMR Spectrum of 3r (100 MHz, $CDCl_3$)

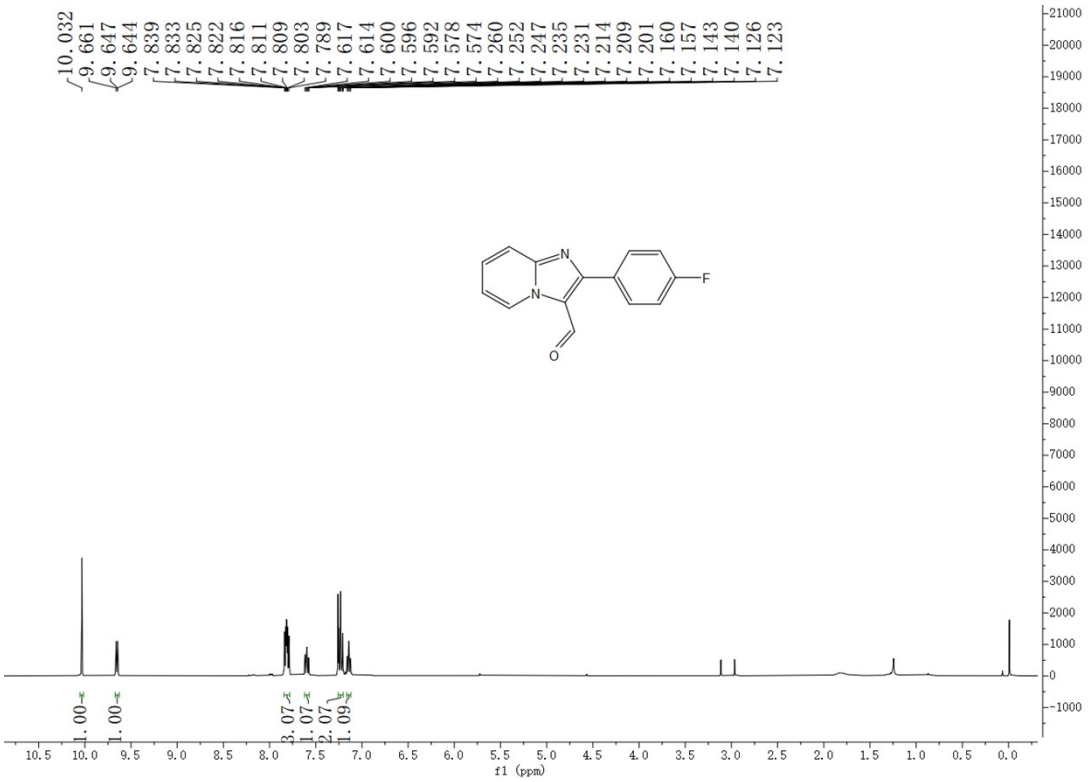

Figure S39. ^{1}H NMR Spectrum of 3s (400 MHz, $CDCl_3$)

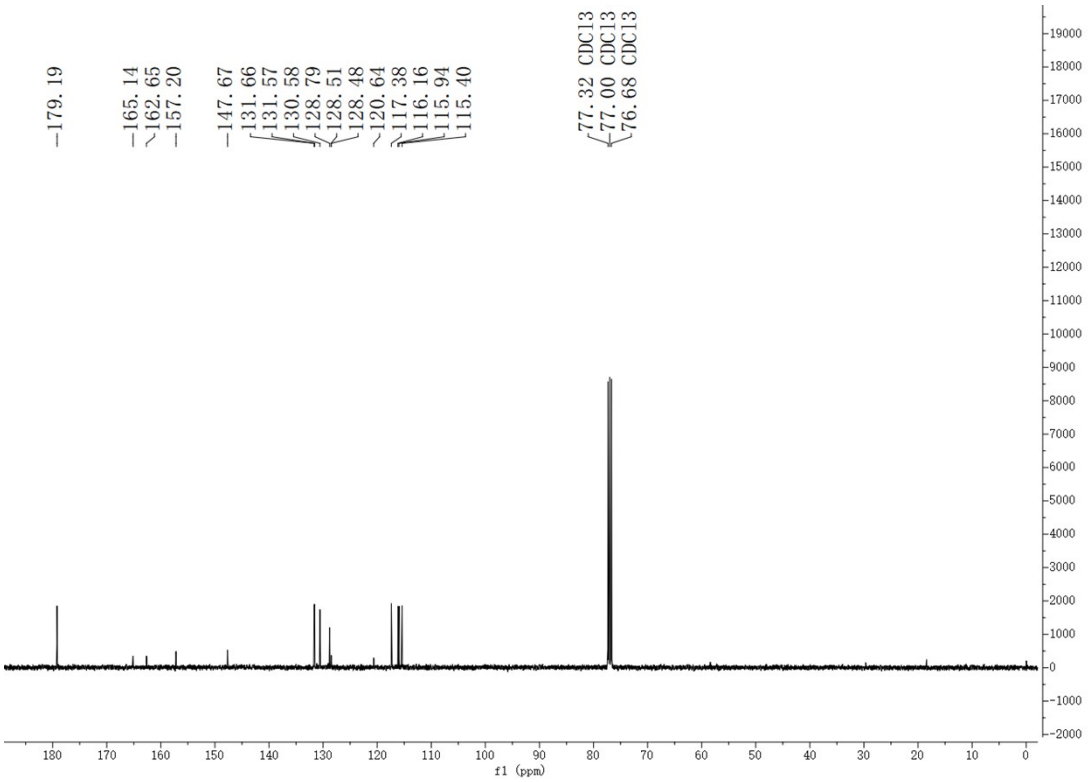

Figure S40. ^{13}C NMR Spectrum of 3s (100 MHz, $CDCl_3$)

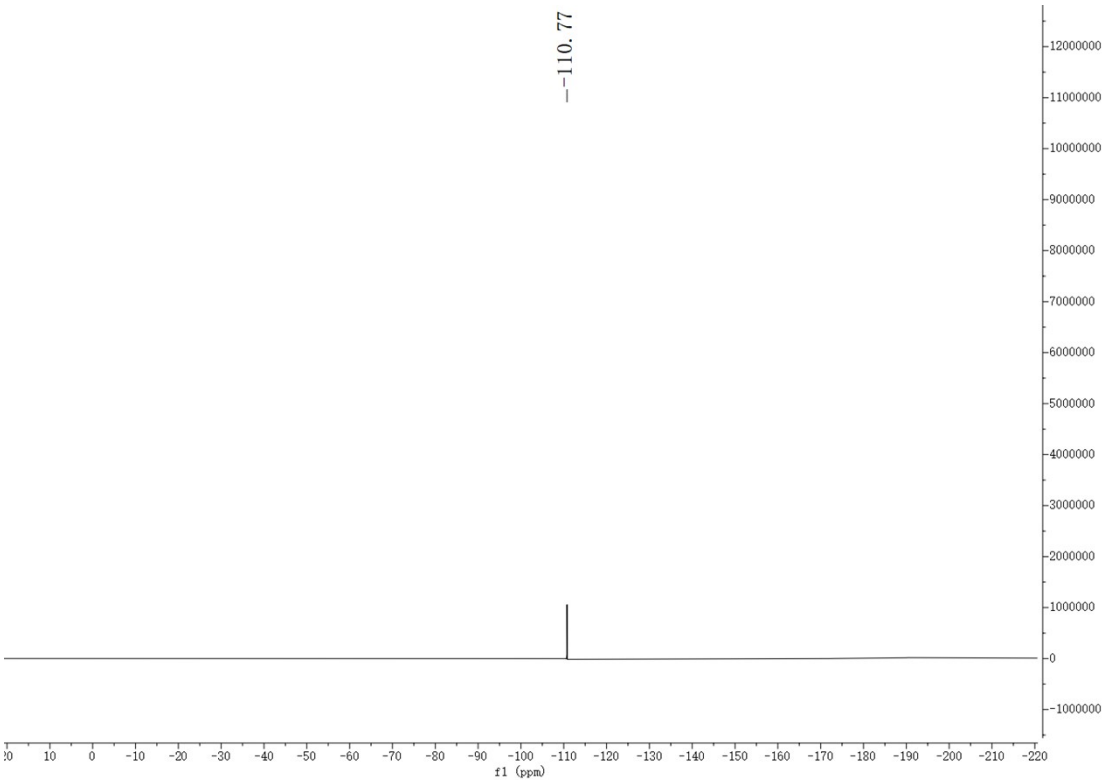

Figure S41. ^{19}F NMR Spectrum of 3s (376 MHz, $CDCl_3$)

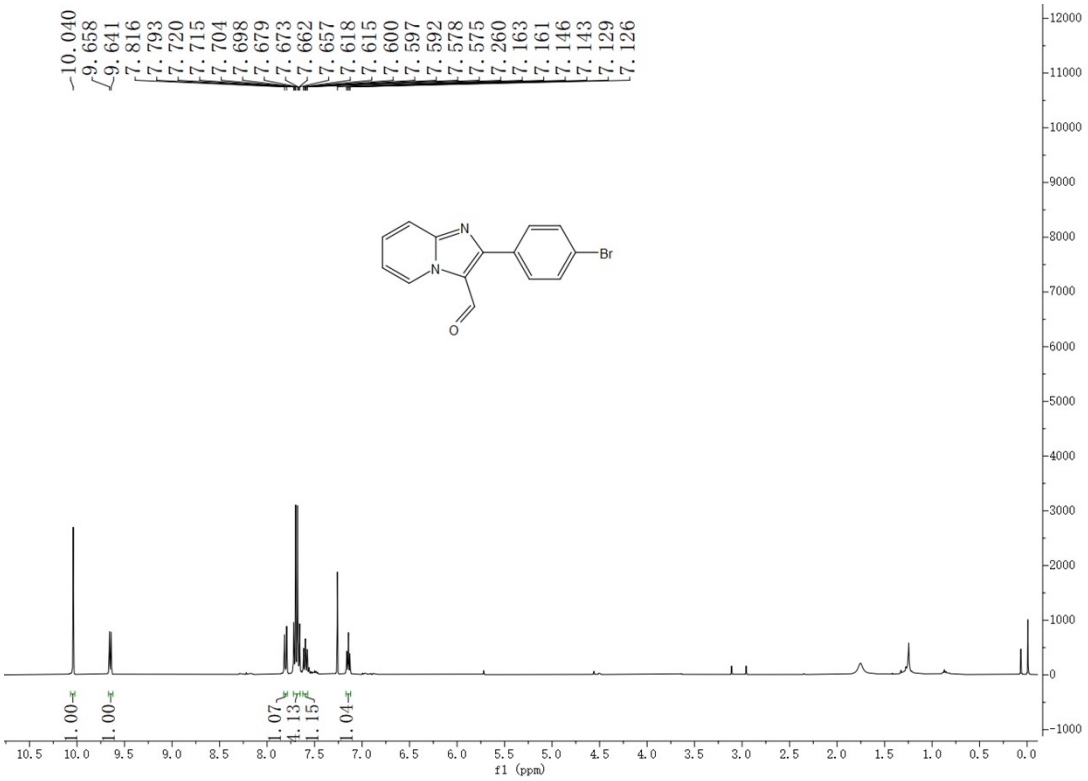

Figure S42. ^{1}H NMR Spectrum of 3t (400 MHz, $CDCl_3$)

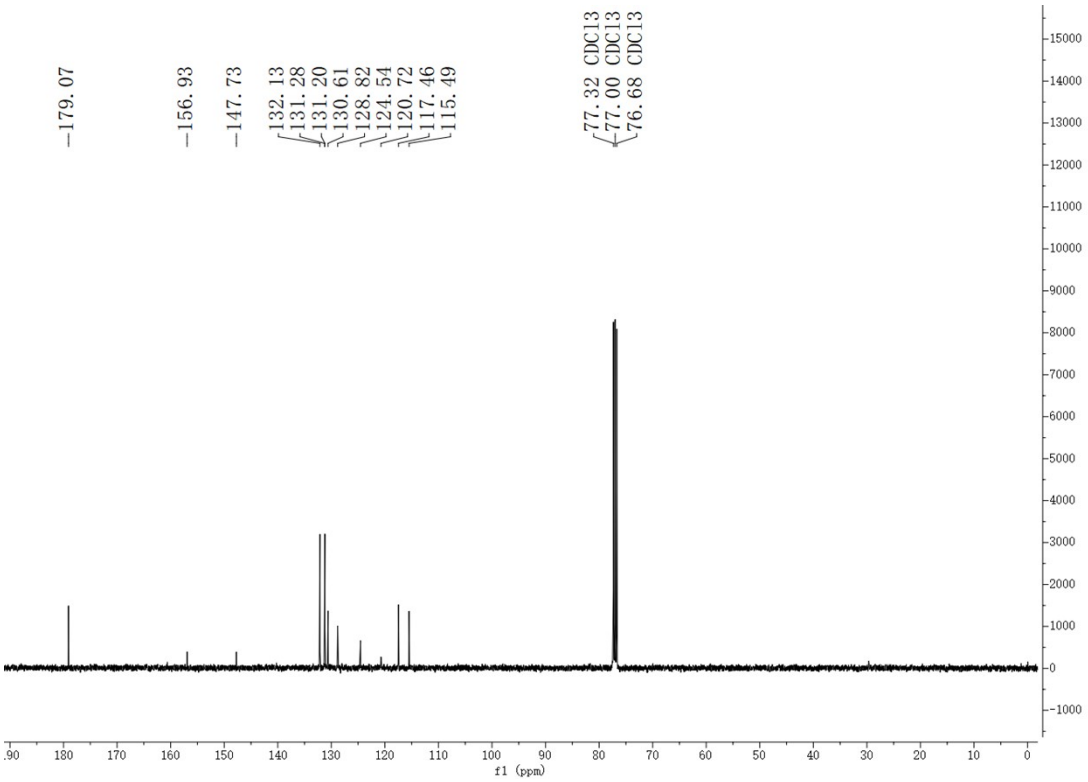

Figure S43. ^{13}C NMR Spectrum of 3t (100 MHz, $CDCl_3$)

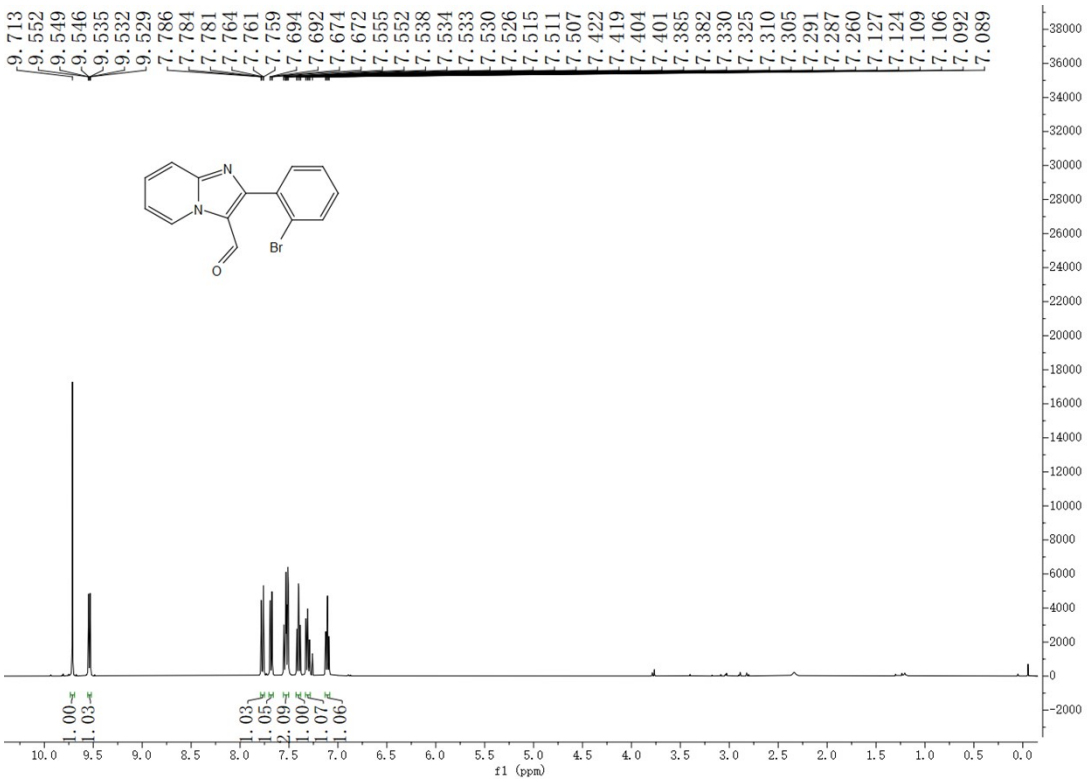

Figure S44. ^{1}H NMR Spectrum of 3u (400 MHz, $CDCl_3$)

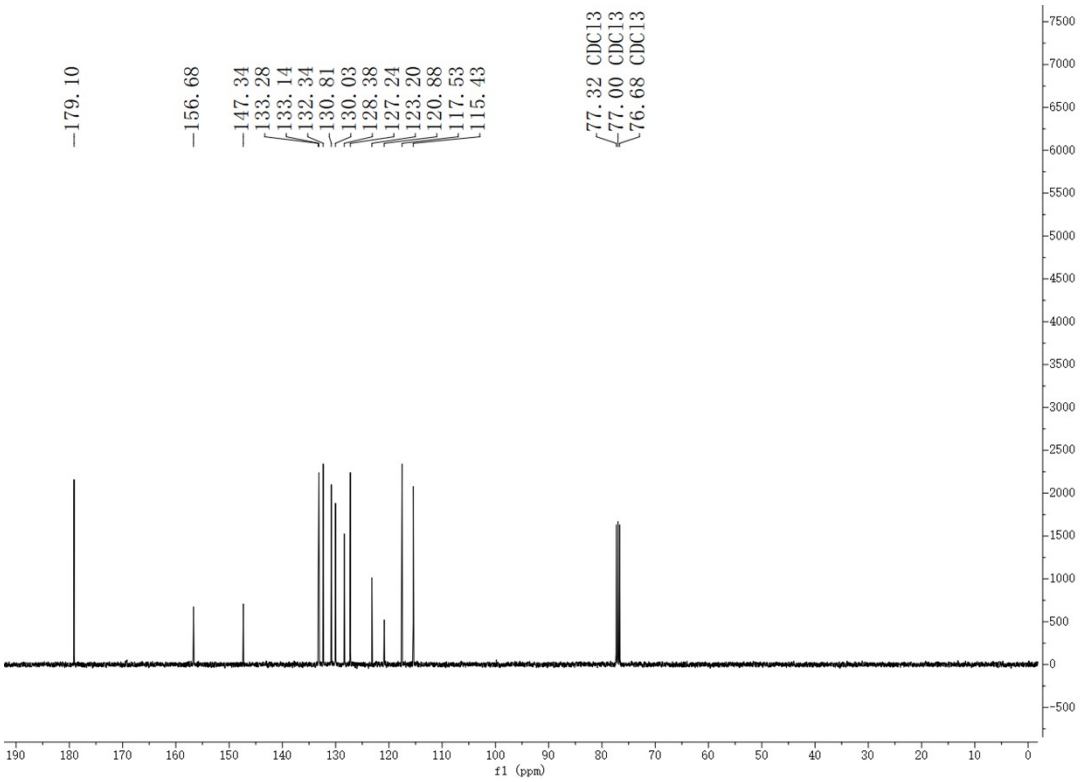

Figure S45. ^{13}C NMR Spectrum of 3u (100 MHz, $CDCl_3$)

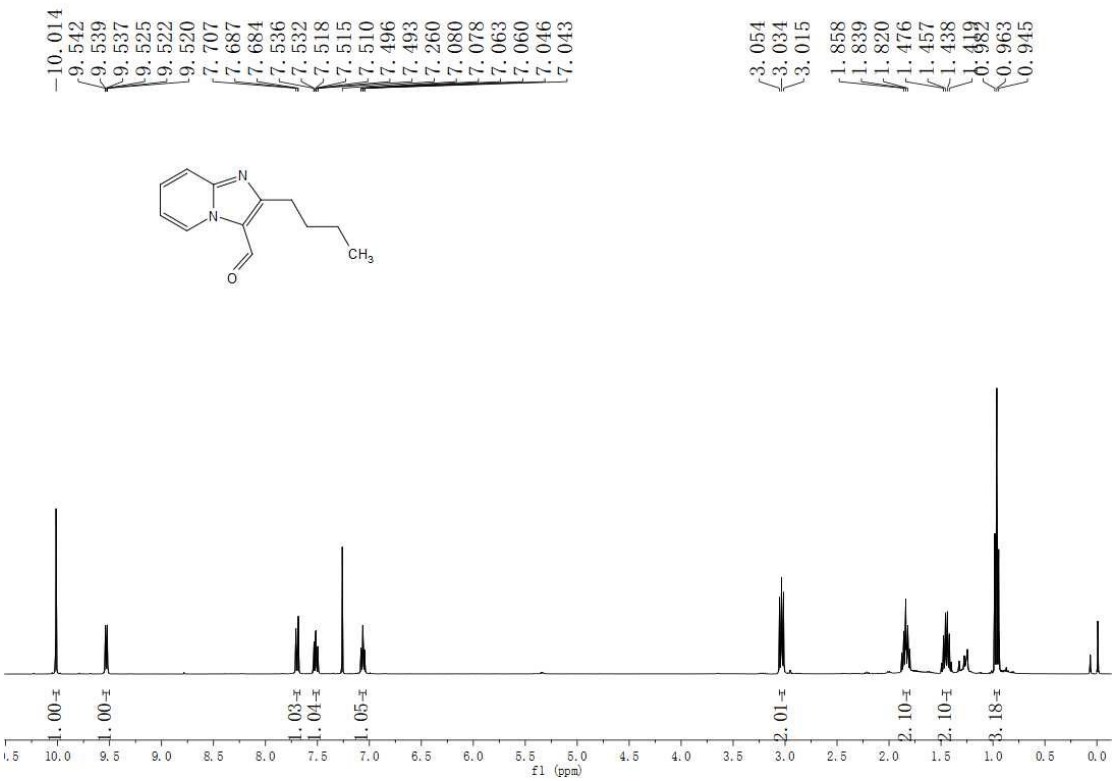

Figure S46. ^{1}H NMR Spectrum of 3v (400 MHz, $CDCl_3$)

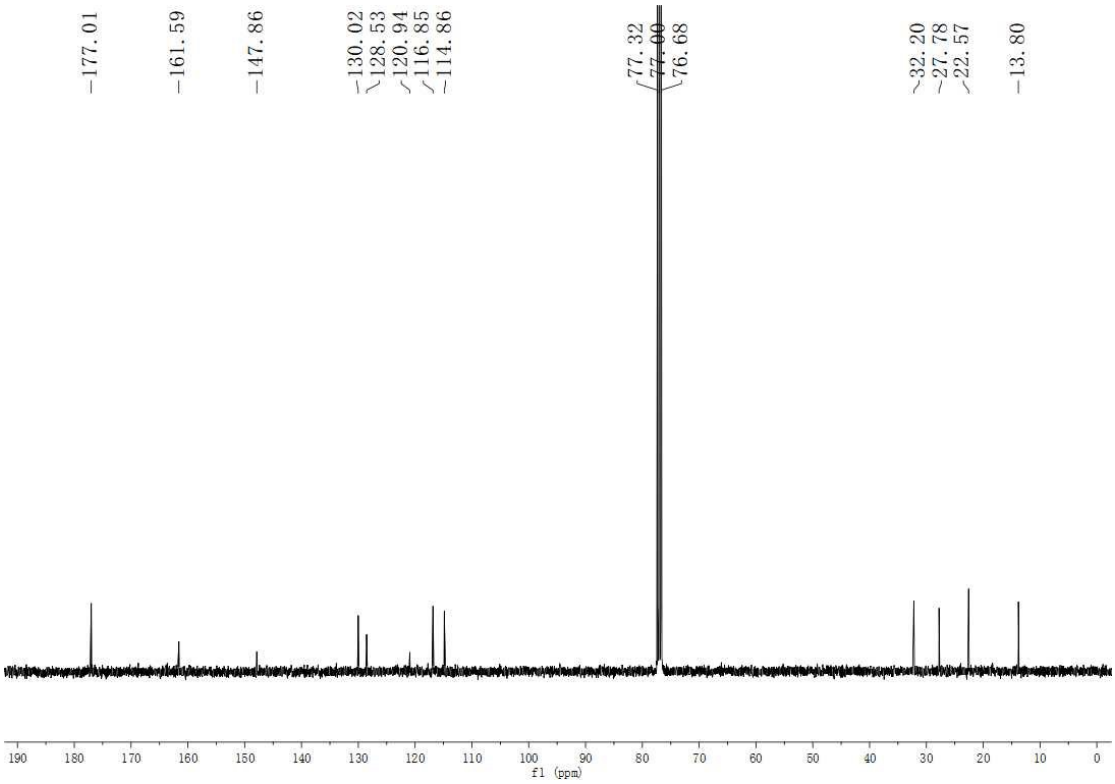

Figure S47. ^{1}H NMR Spectrum of 3v (400 MHz, $CDCl_3$)

Figure S48. ^{1}H NMR Spectrum of 4a (400 MHz, $CDCl_3$)

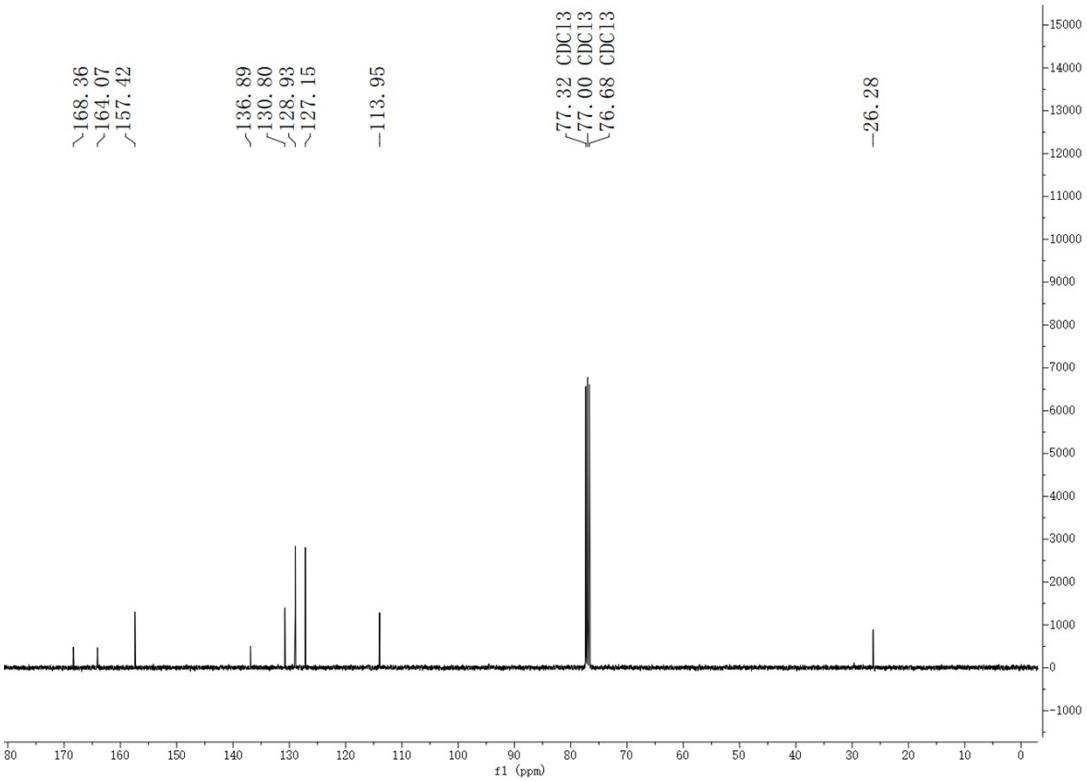

Figure S49. ^{13}C NMR Spectrum of 4a (100 MHz, $CDCl_3$)

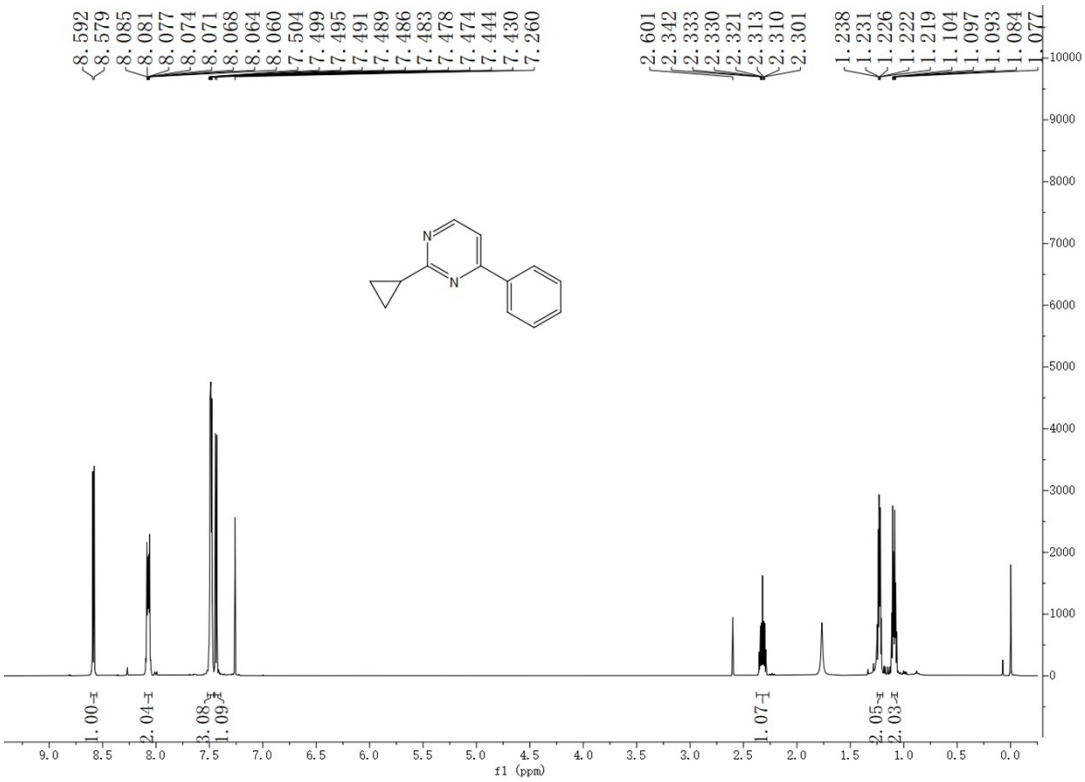

Figure S50. ^{1}H NMR Spectrum of 4b (400 MHz, $CDCl_3$)

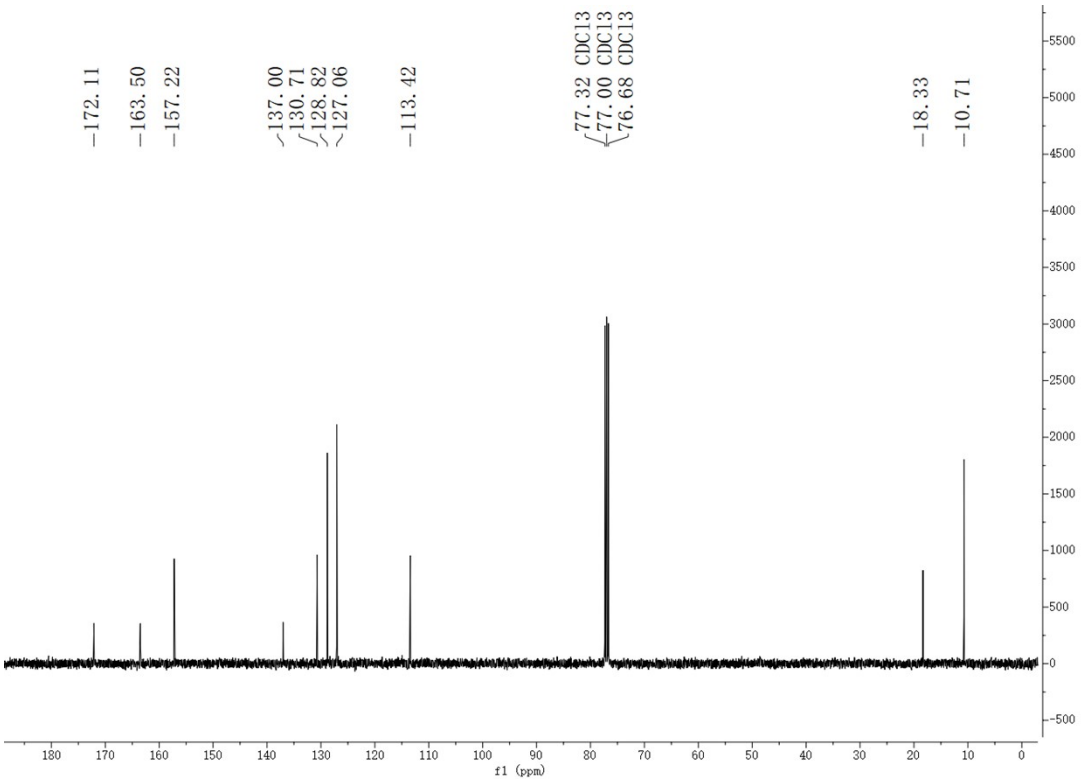

Figure S51. ^{13}C NMR Spectrum of 4b (100 MHz, $CDCl_3$)

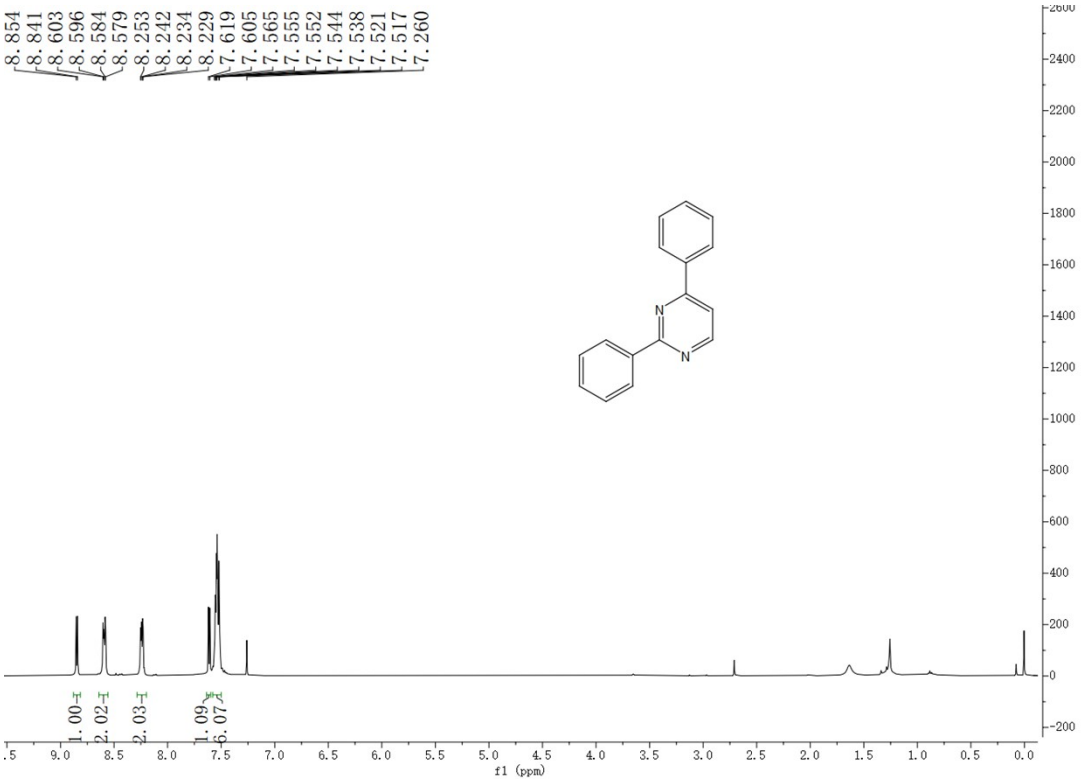

Figure S52. ^{1}H NMR Spectrum of 4c (400 MHz, $CDCl_3$)

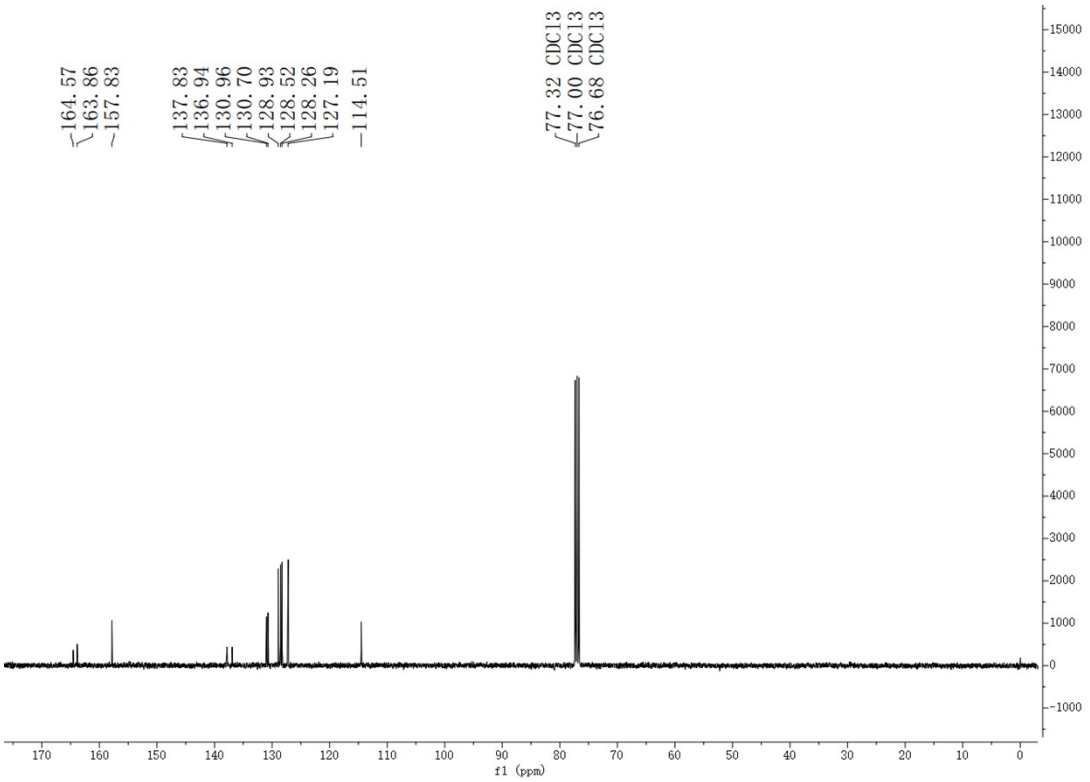

Figure S53. ^{13}C NMR Spectrum of 4c (100 MHz, $CDCl_3$)

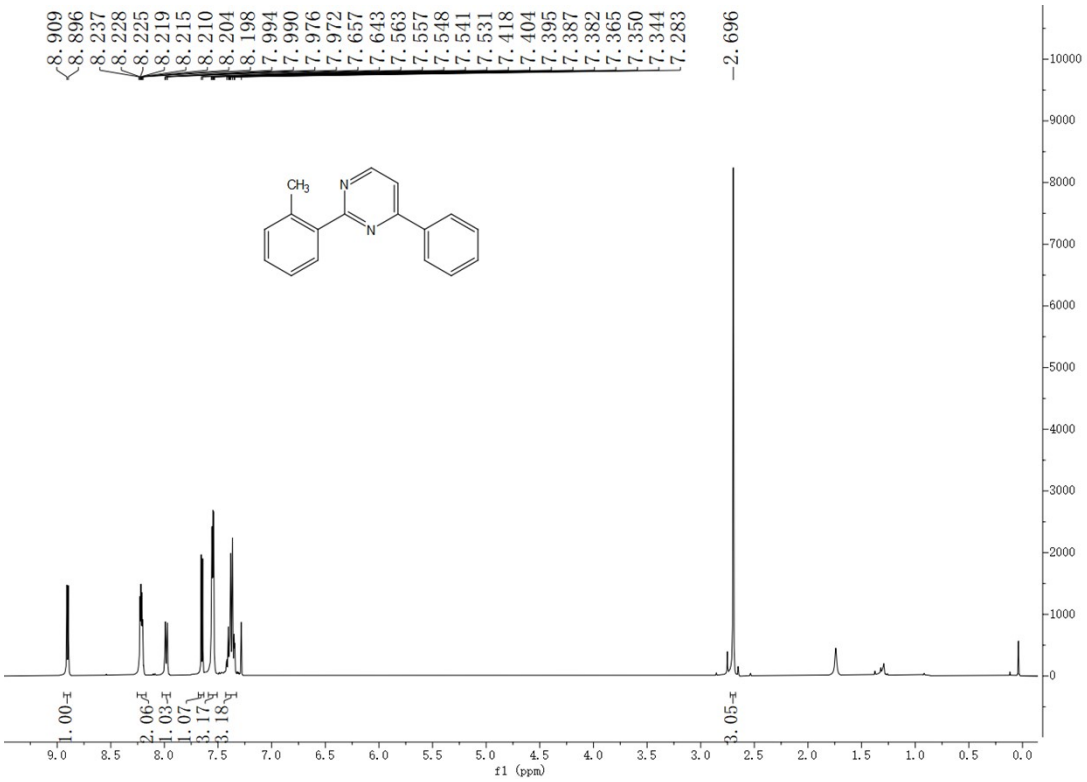

Figure S54. ^{1}H NMR Spectrum of 4d (400 MHz, $CDCl_3$)

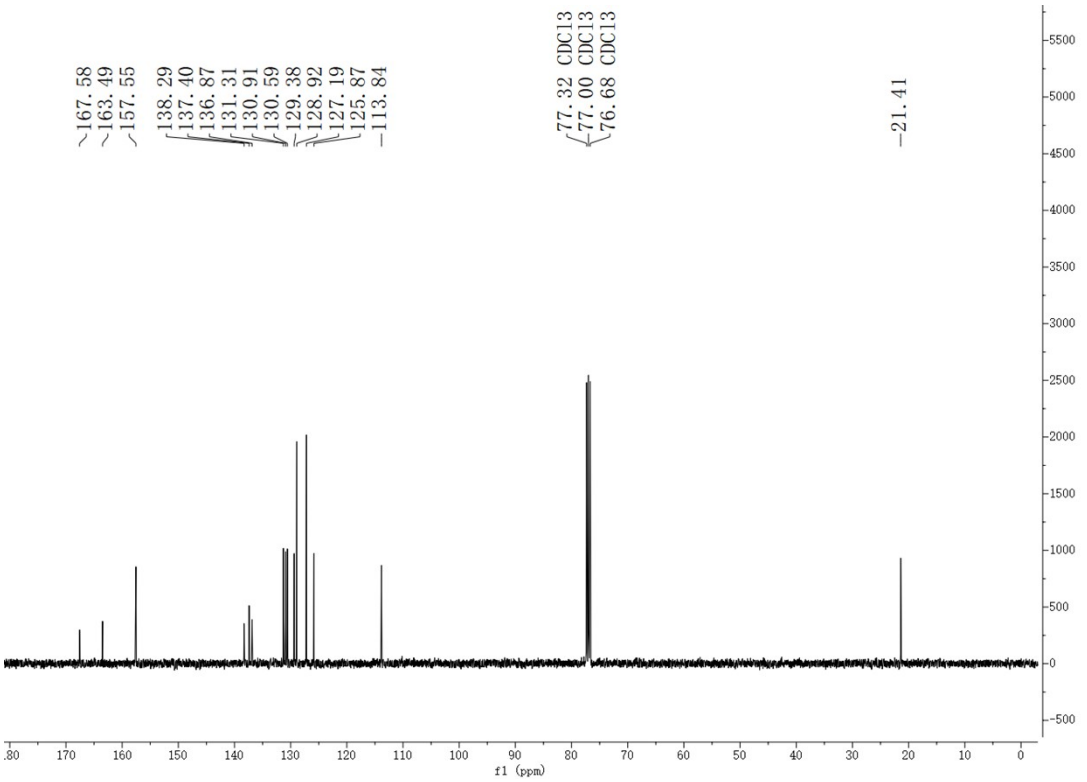

Figure S55. ^{13}C NMR Spectrum of 4d (100 MHz, $CDCl_3$)

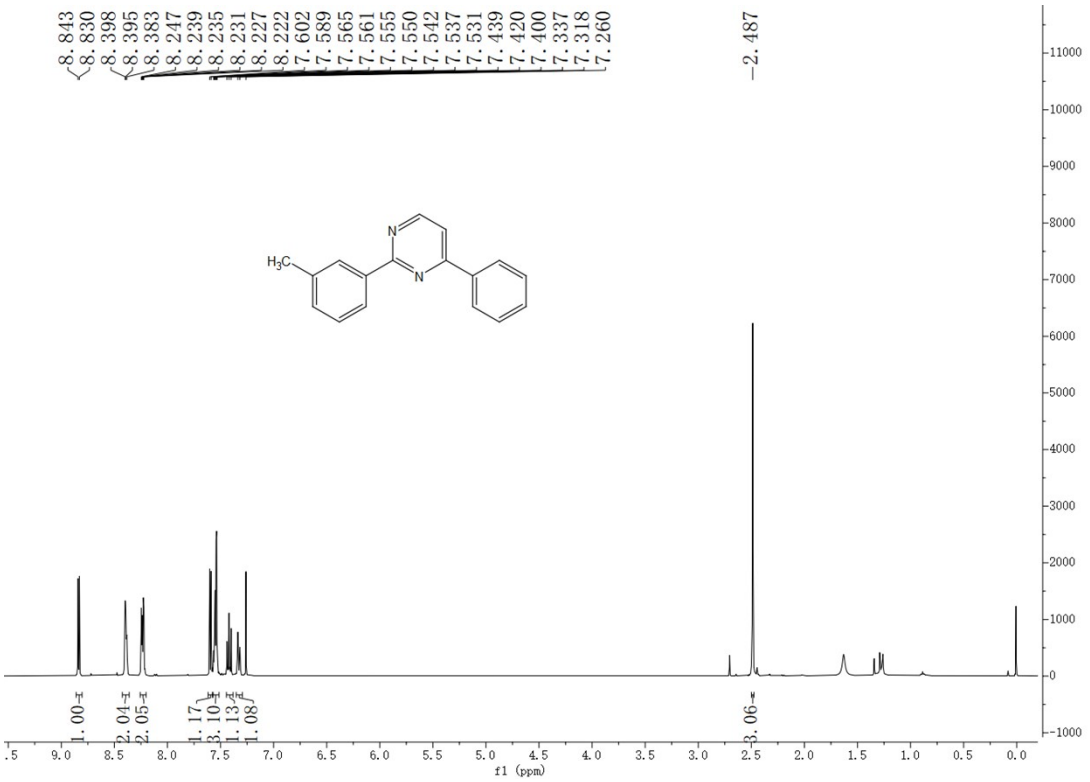

Figure S56. ^{1}H NMR Spectrum of 4e (400 MHz, $CDCl_3$)

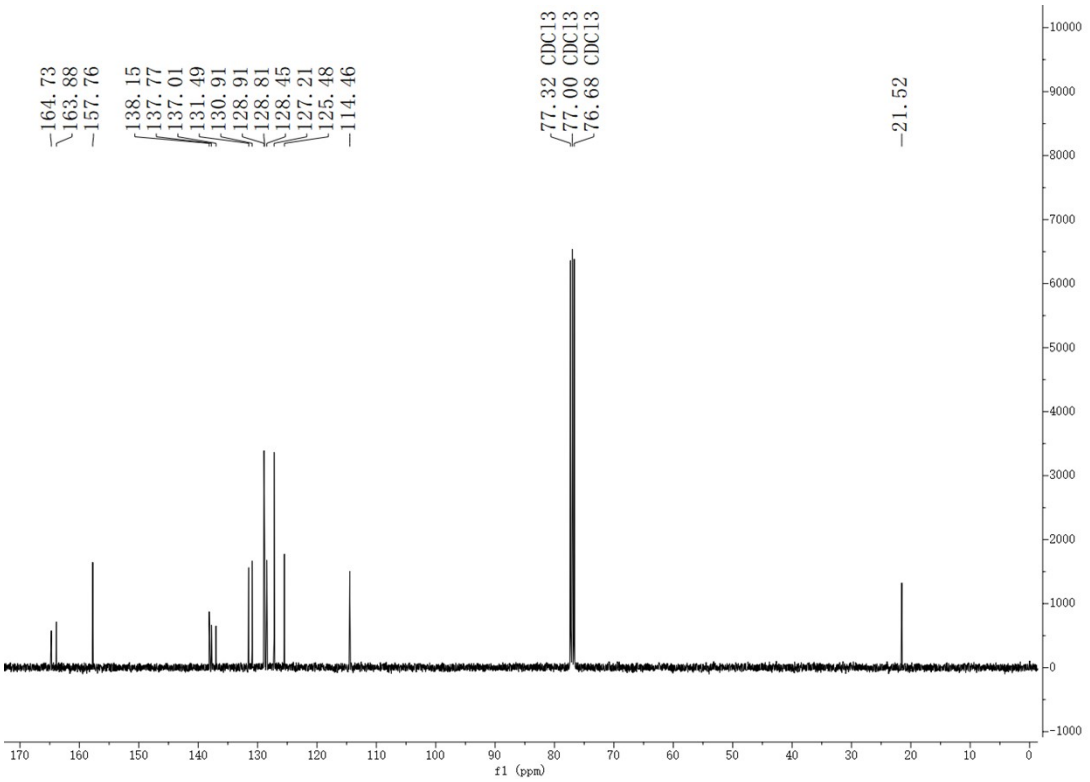

Figure S57. ^{13}C NMR Spectrum of 4e (100 MHz, $CDCl_3$)

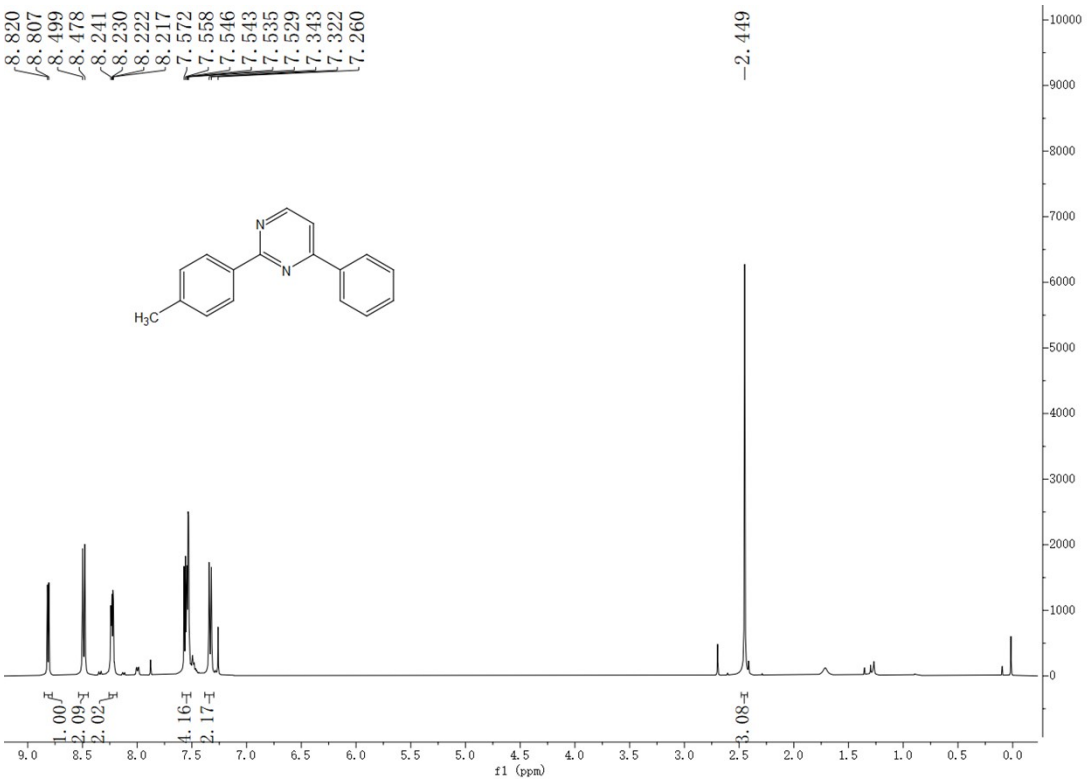

Figure S58. ^{1}H NMR Spectrum of 4f (400 MHz, $CDCl_3$)

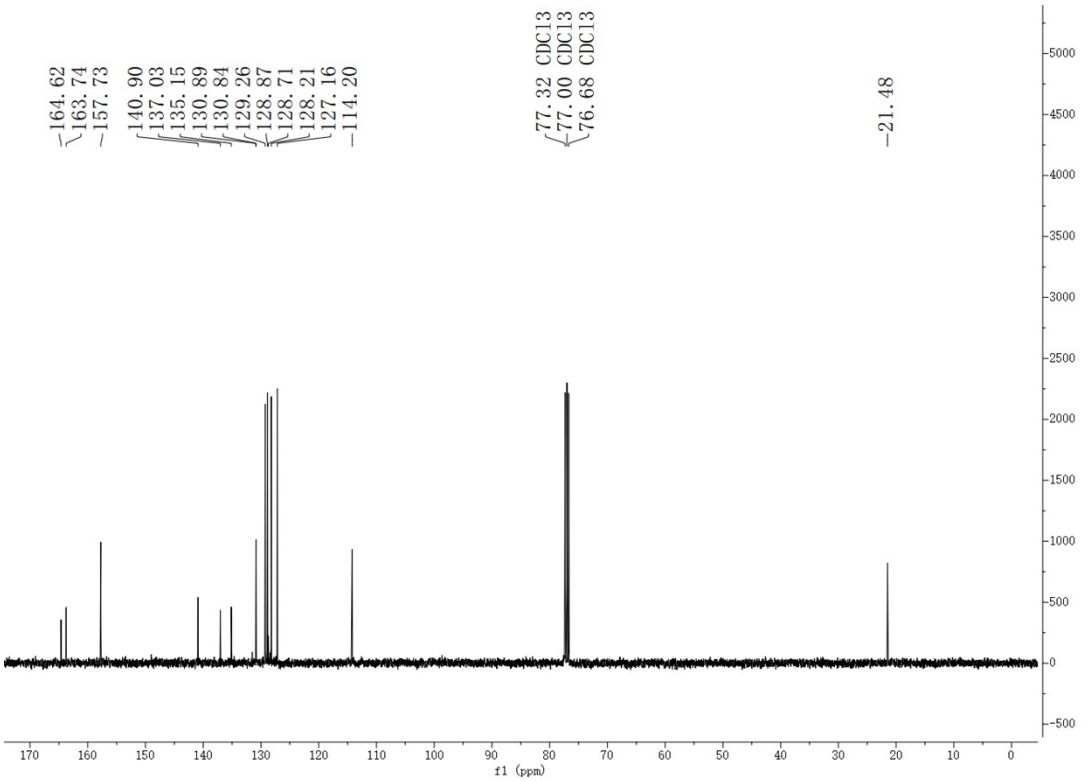

Figure S59. ^{13}C NMR Spectrum of 4f (100 MHz, $CDCl_3$)

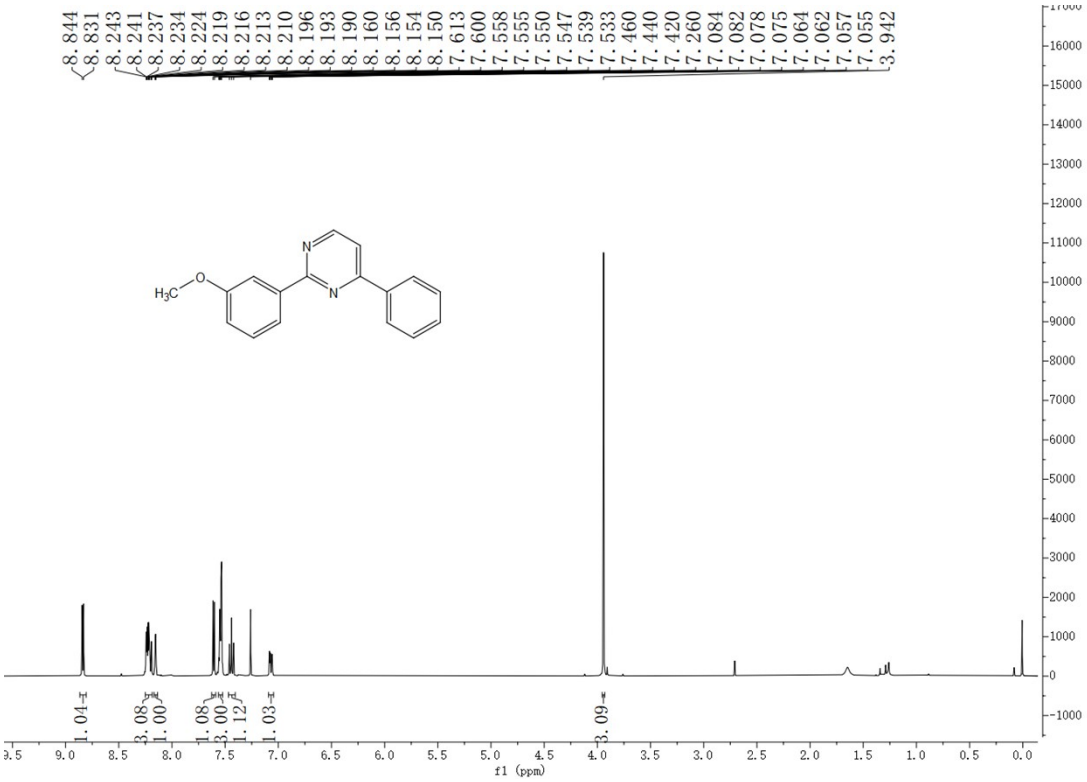

Figure S60. ^{1}H NMR Spectrum of 4g (400 MHz, $CDCl_3$)

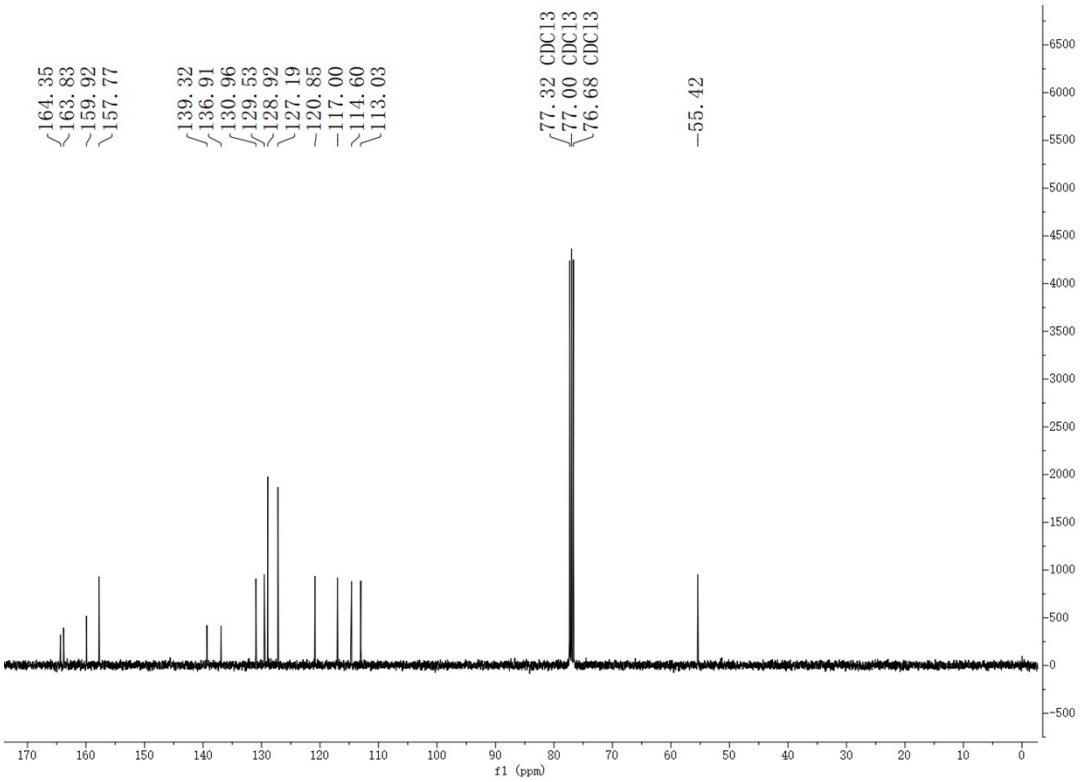

Figure S61. ^{13}C NMR Spectrum of 4g (100 MHz, $CDCl_3$)

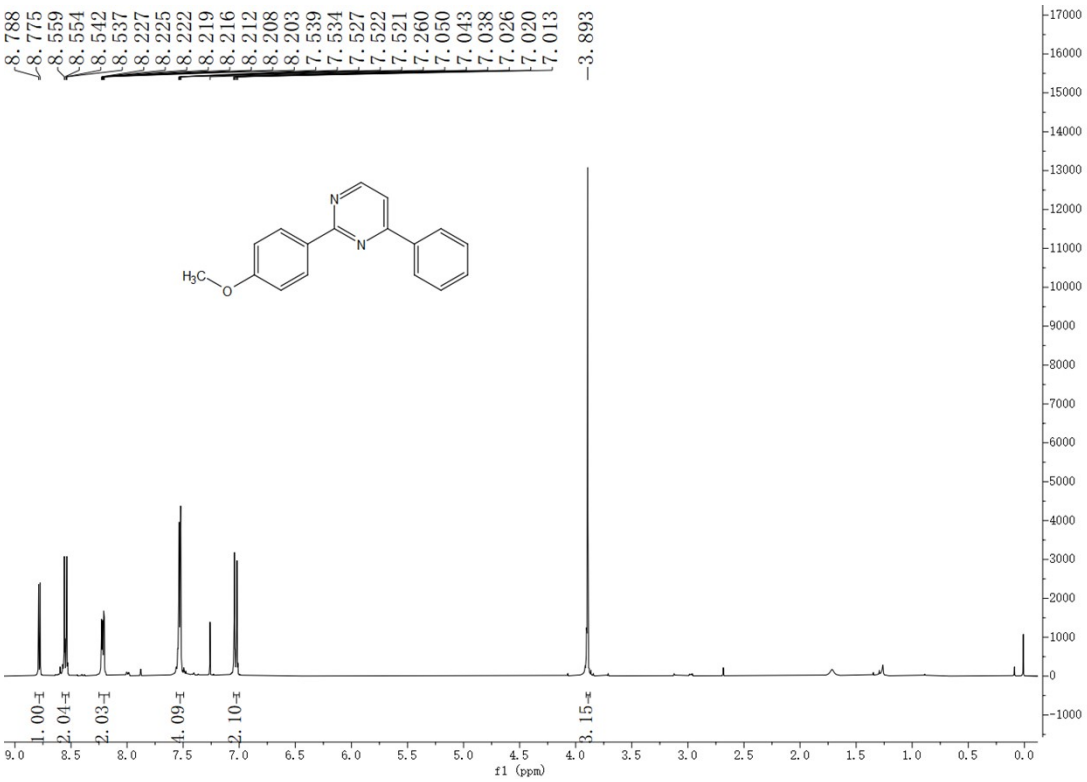

Figure S62. ^{1}H NMR Spectrum of 4h (400 MHz, $CDCl_3$)

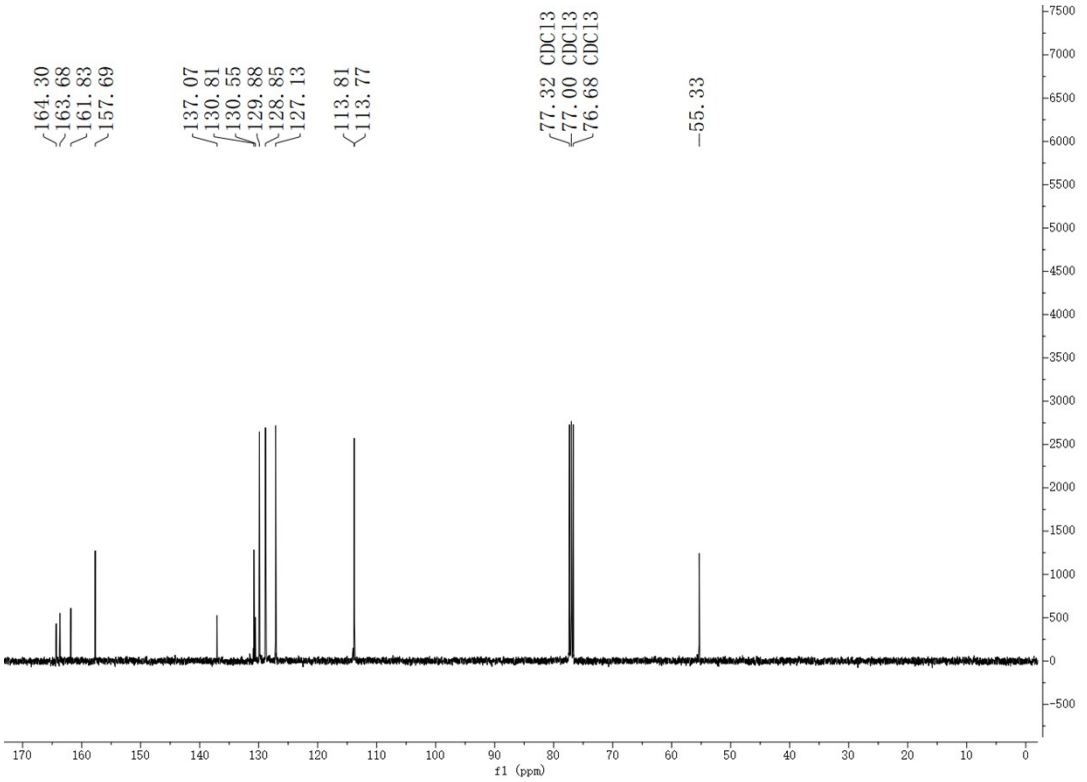

Figure S63. ^{13}C NMR Spectrum of 4h (100 MHz, $CDCl_3$)

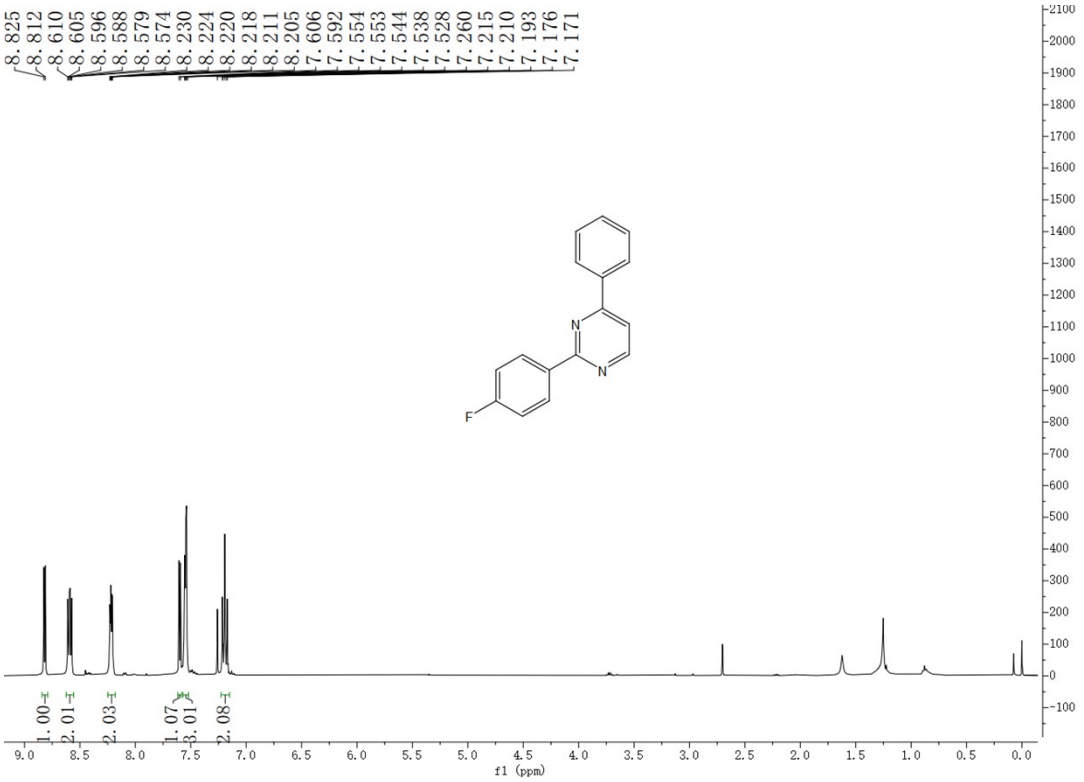

Figure S64. ^{1}H NMR Spectrum of 4i (400 MHz, $CDCl_3$)

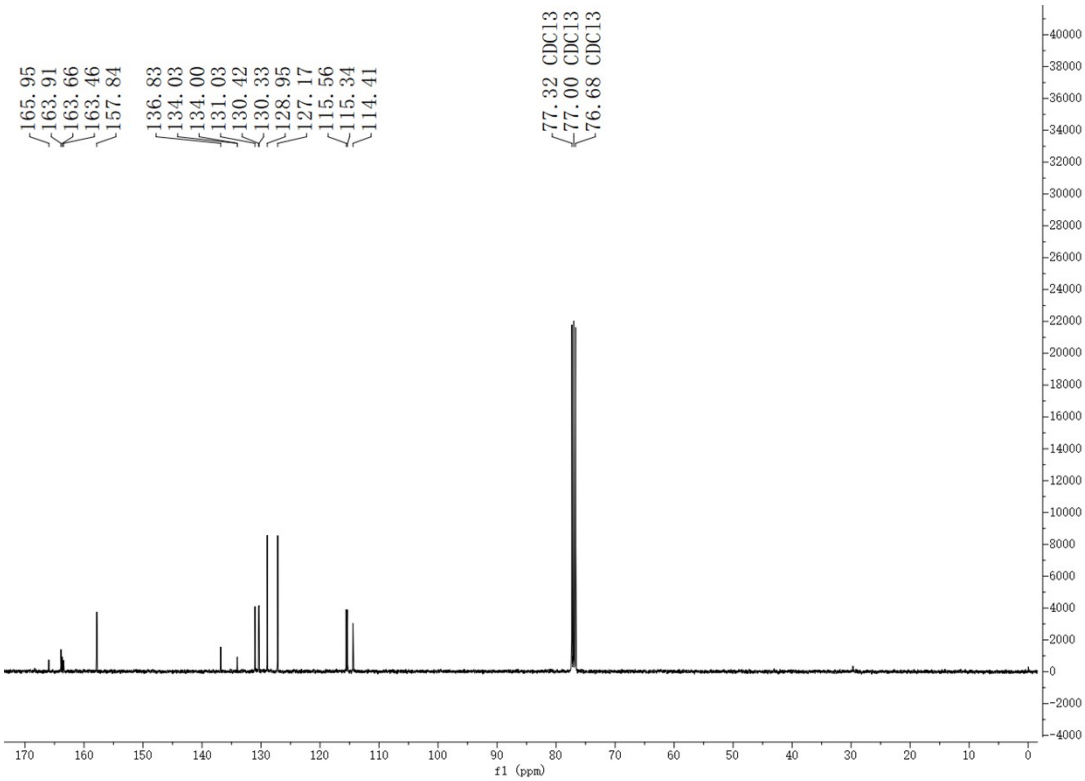

Figure S65. ^{13}C NMR Spectrum of 4i (100 MHz, $CDCl_3$)

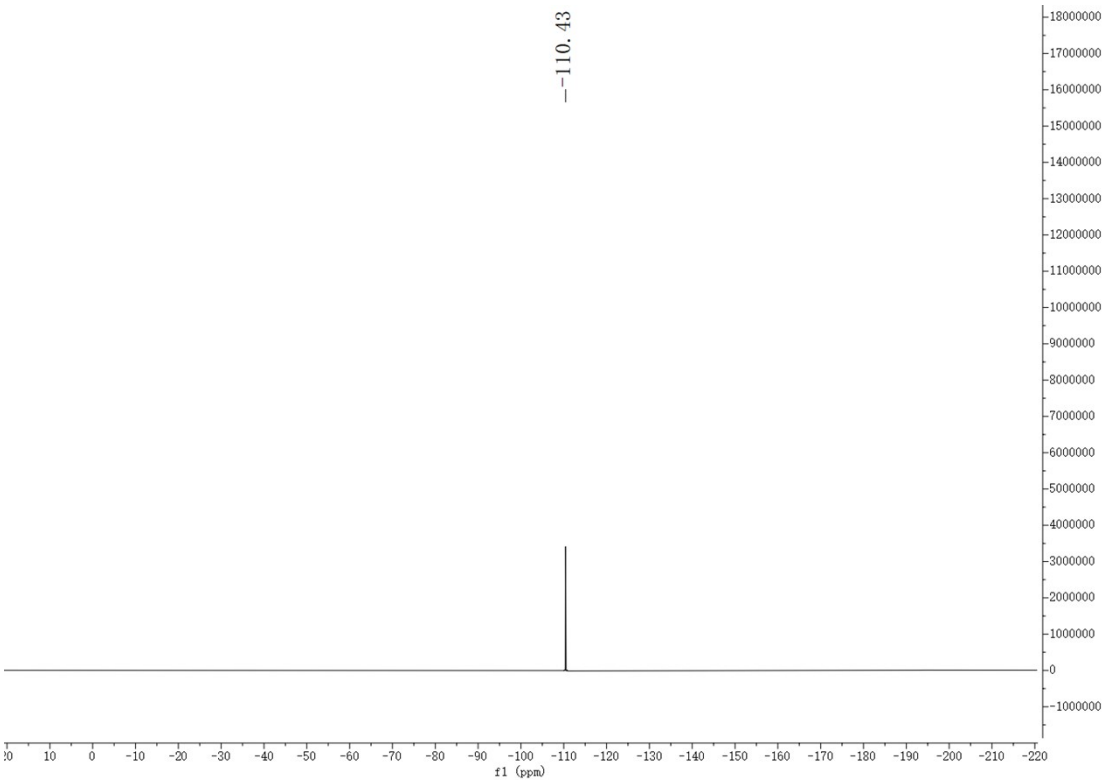

Figure S66. ^{19}F NMR Spectrum of 4i (376 MHz, $CDCl_3$)

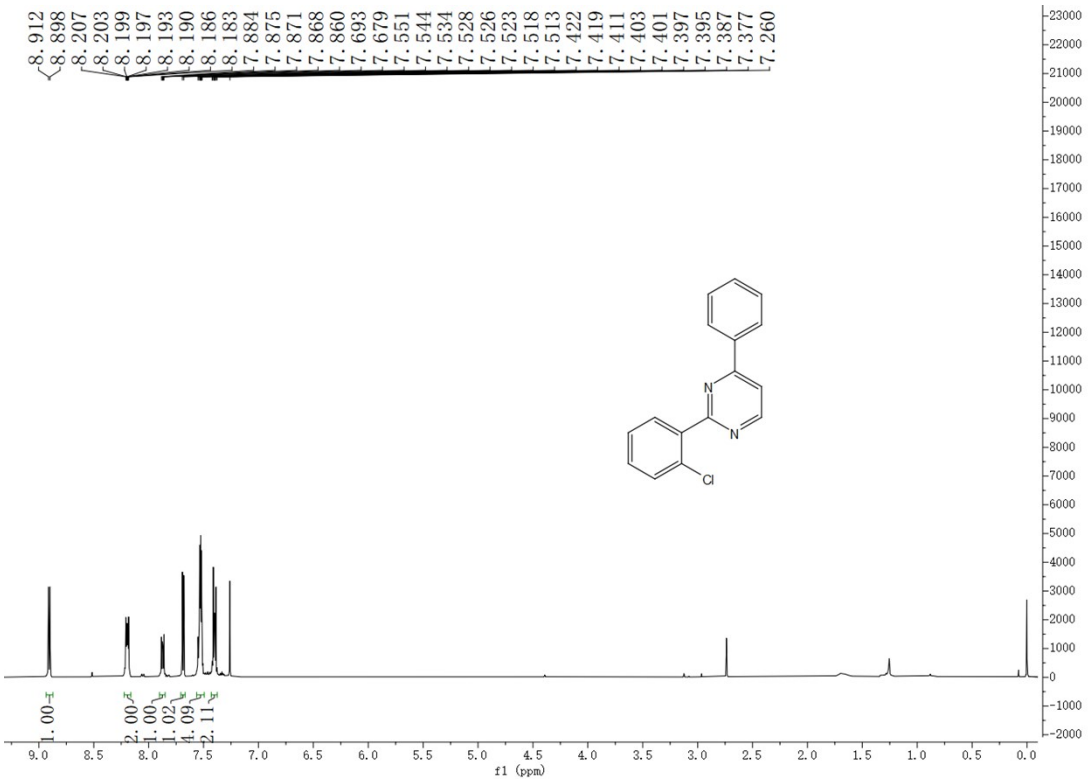

Figure S67. ^{1}H NMR Spectrum of 4j (400 MHz, $CDCl_3$)

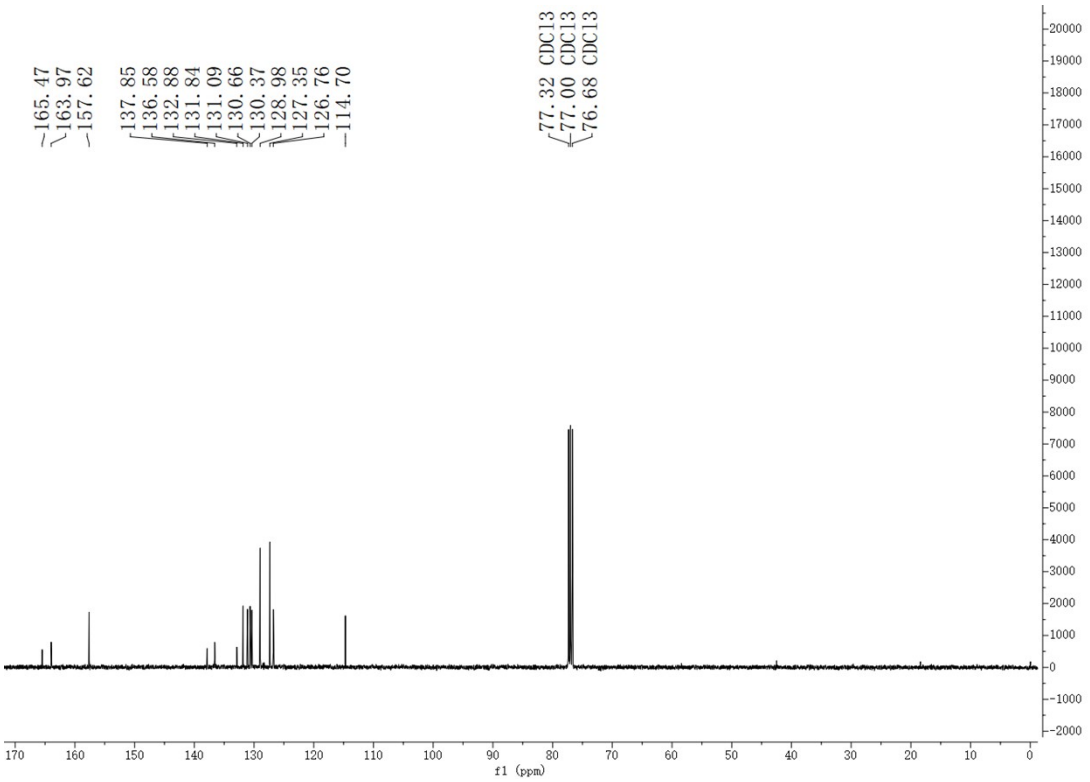

Figure S68. ^{13}C NMR Spectrum of 4j (100 MHz, $CDCl_3$)

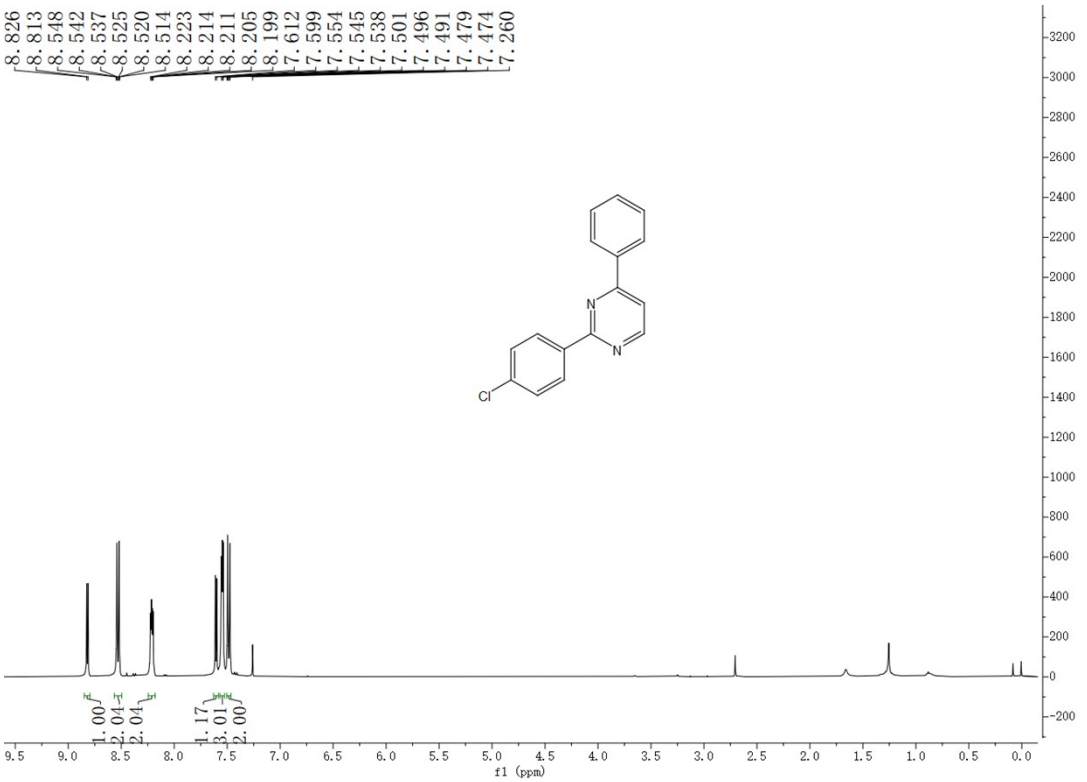

Figure S69. ^{1}H NMR Spectrum of 4k (400 MHz, $CDCl_3$)

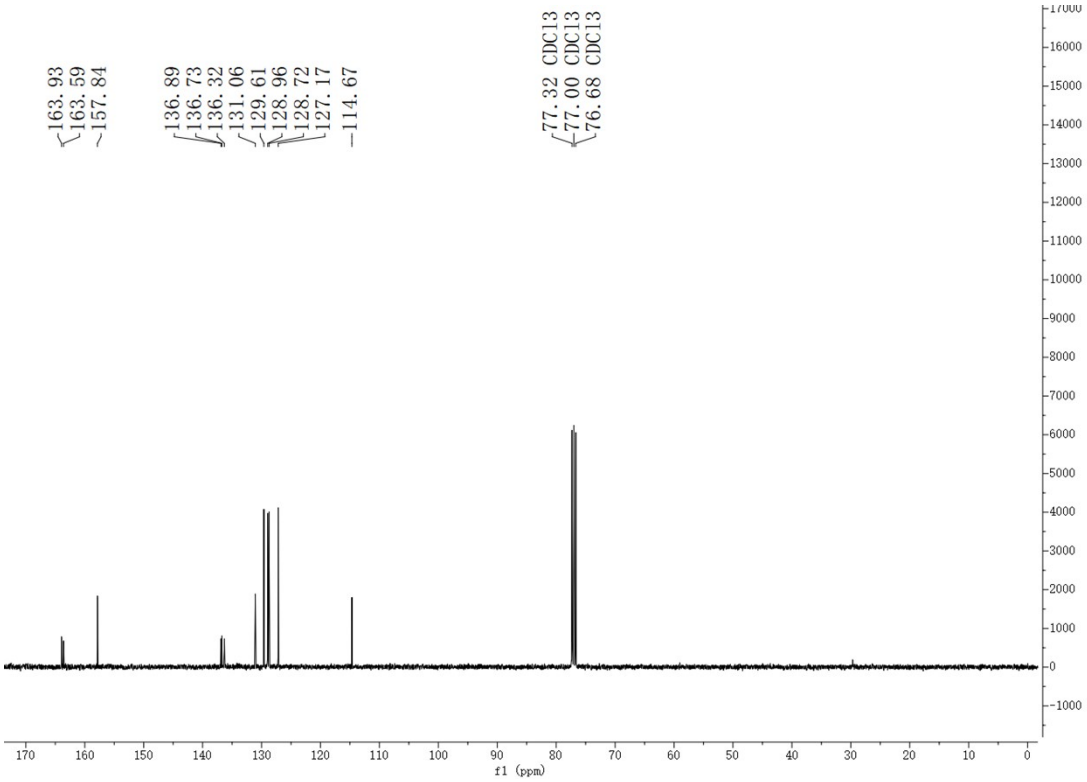

Figure S70. ^{13}C NMR Spectrum of 4k (100 MHz, $CDCl_3$)

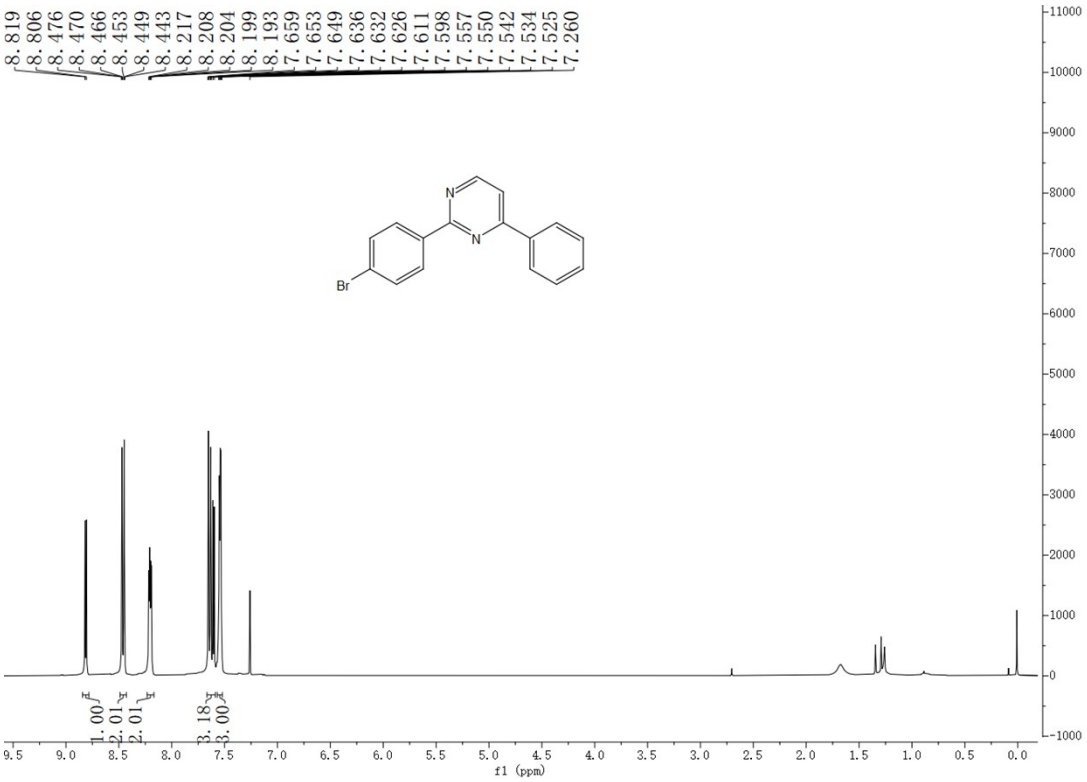

Figure S71. ^{1}H NMR Spectrum of 4l (400 MHz, $CDCl_3$)

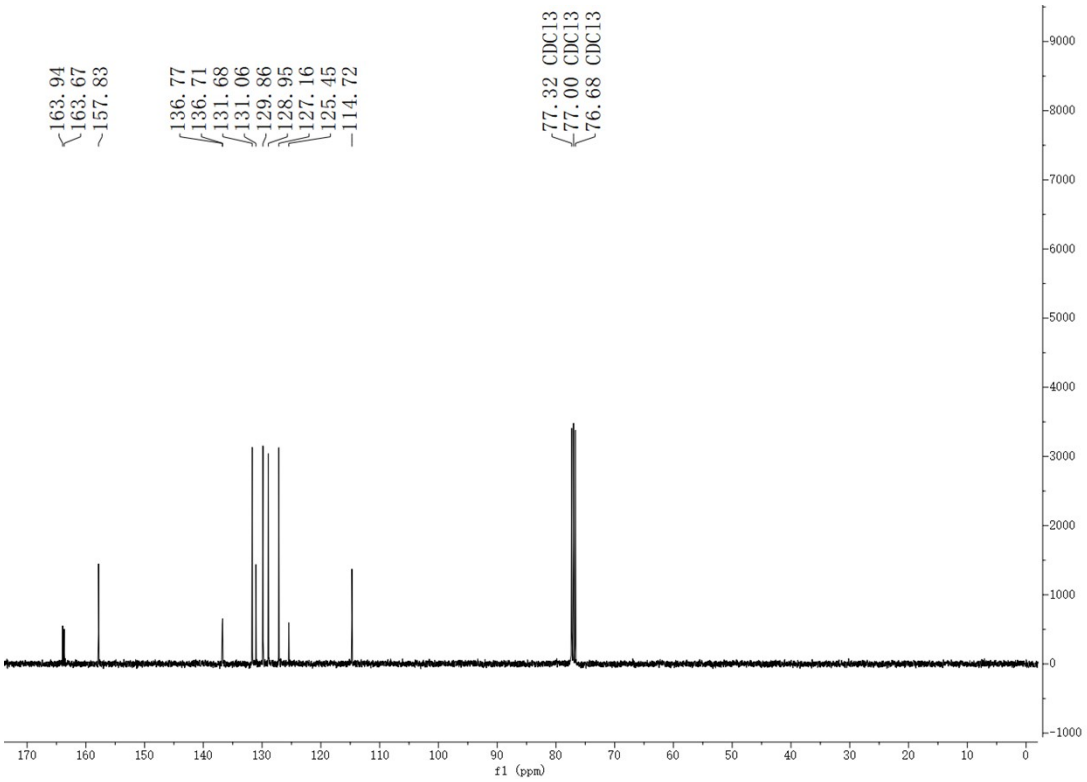

Figure S72. ^{13}C NMR Spectrum of 4l (100 MHz, $CDCl_3$)

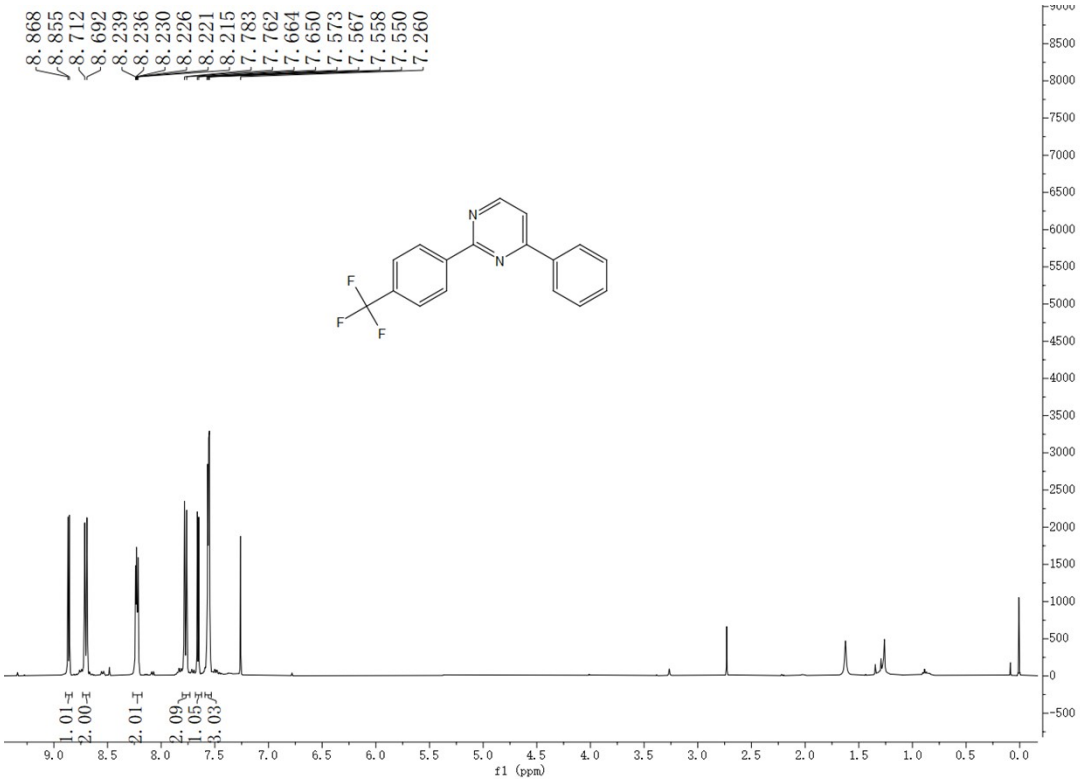

Figure S73. ^{1}H NMR Spectrum of 4m (400 MHz, $CDCl_3$)

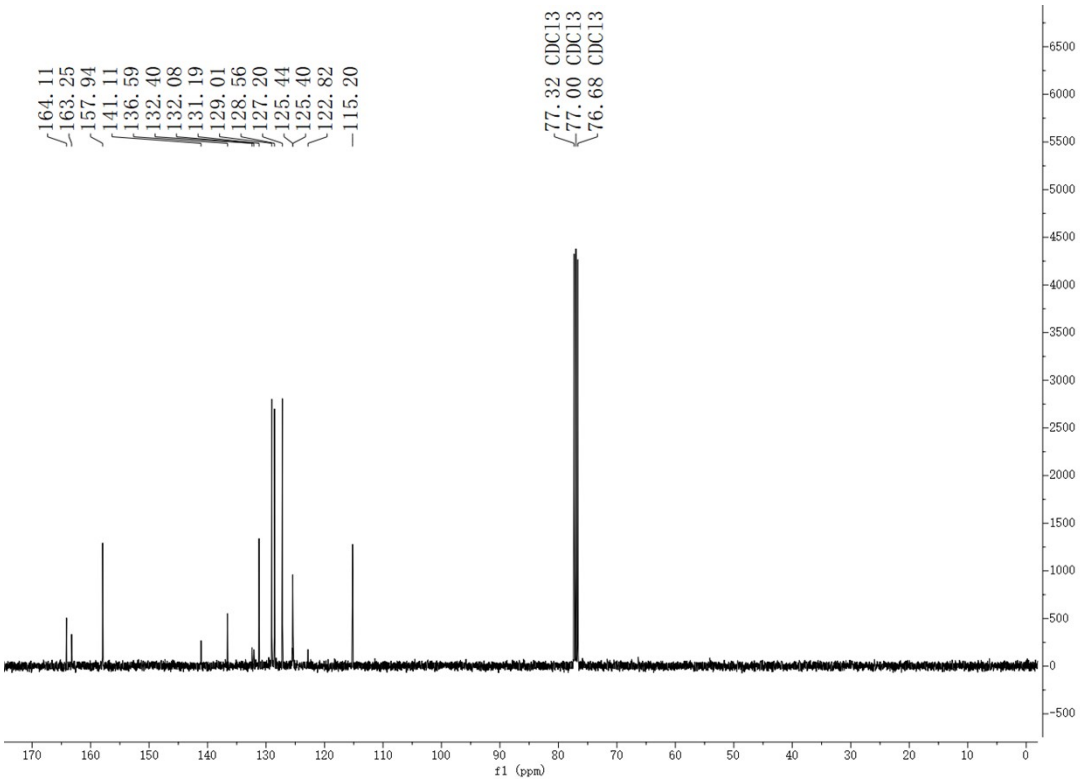

Figure S74. ^{13}C NMR Spectrum of 4m (100 MHz, $CDCl_3$)

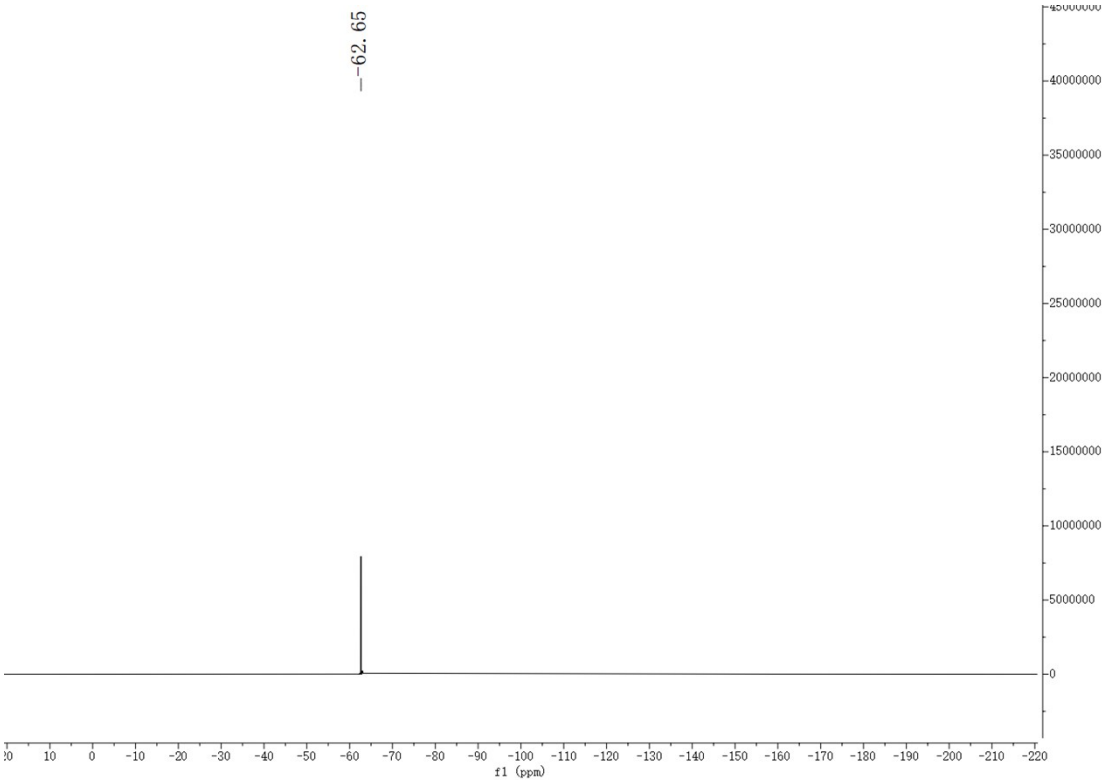

Figure S75. ^{19}F NMR Spectrum of 4m (376 MHz, $CDCl_3$)

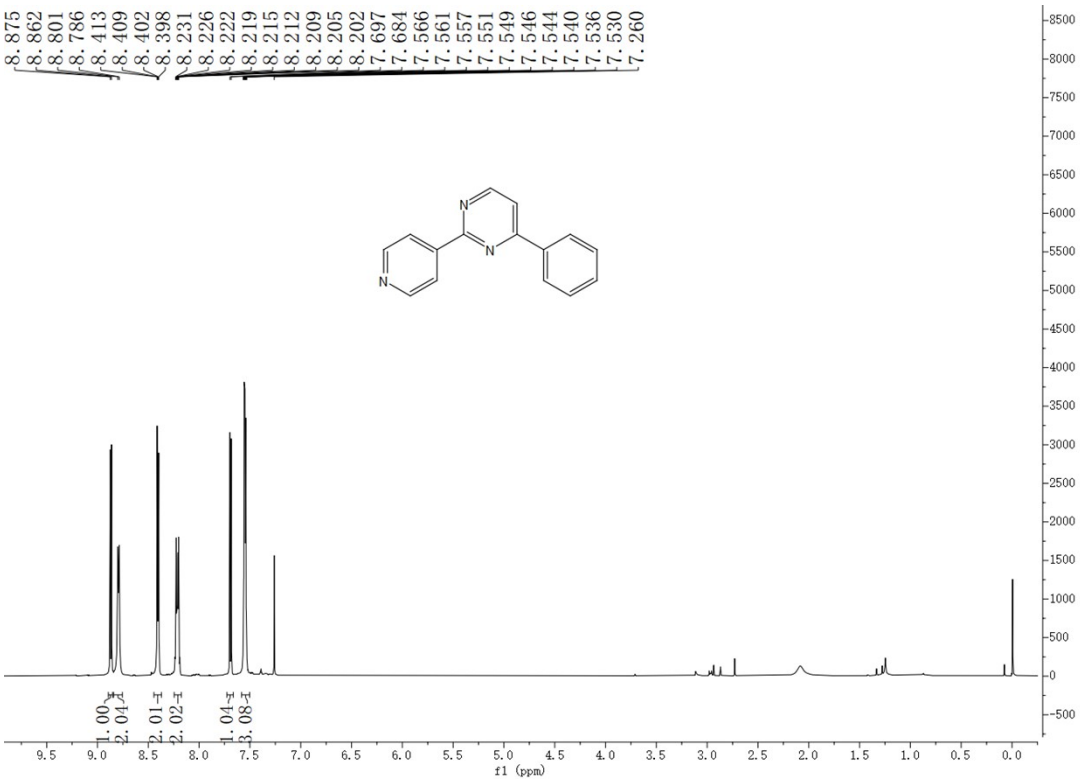

Figure S76. ^{1}H NMR Spectrum of 4n (400 MHz, $CDCl_3$)

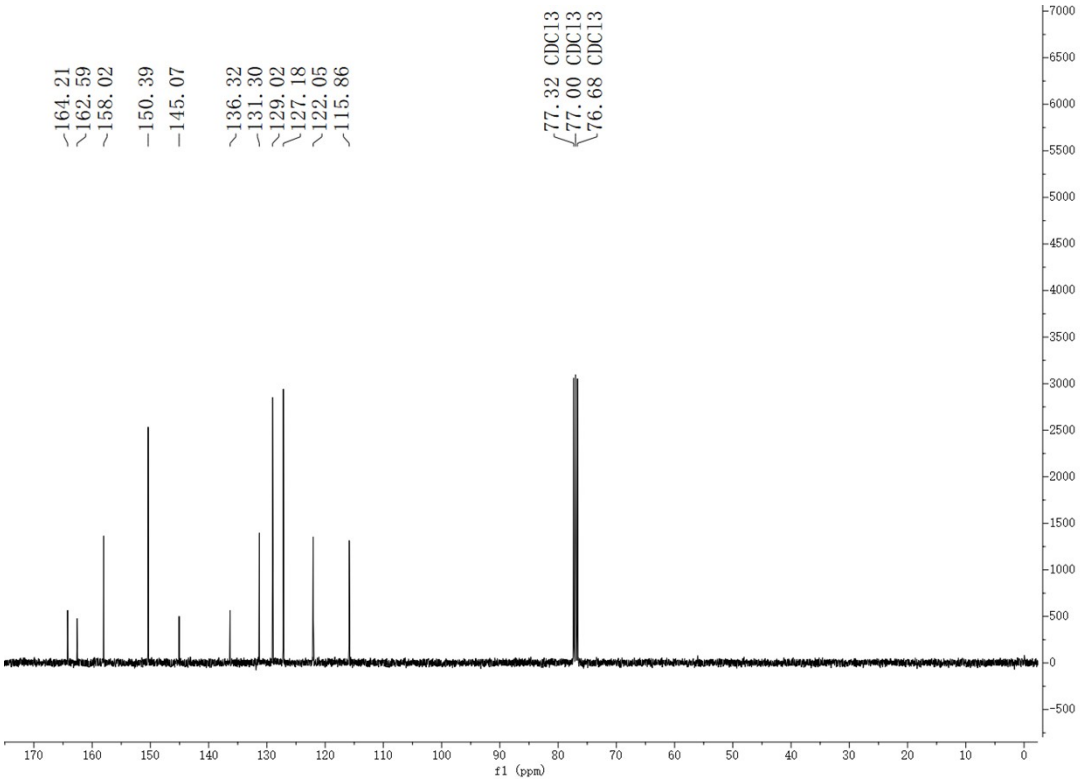

Figure S77. ^{13}C NMR Spectrum of 4n (100 MHz, $CDCl_3$)

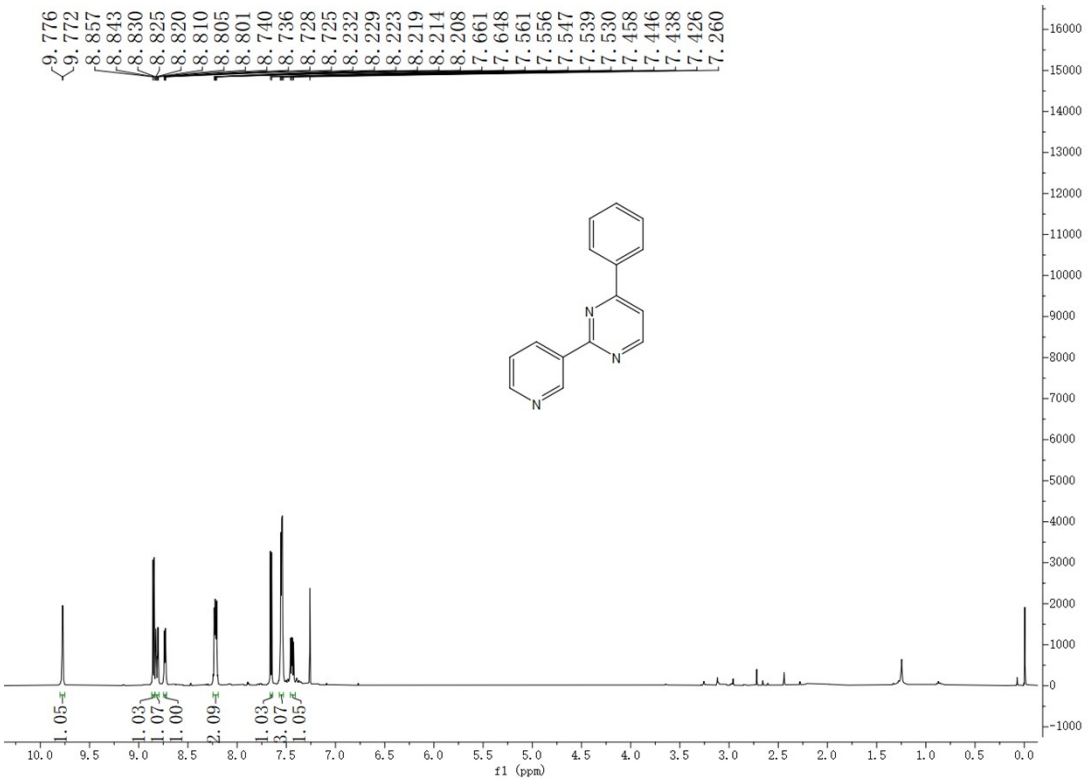

Figure S78. ^{1}H NMR Spectrum of 4o (400 MHz, $CDCl_3$)

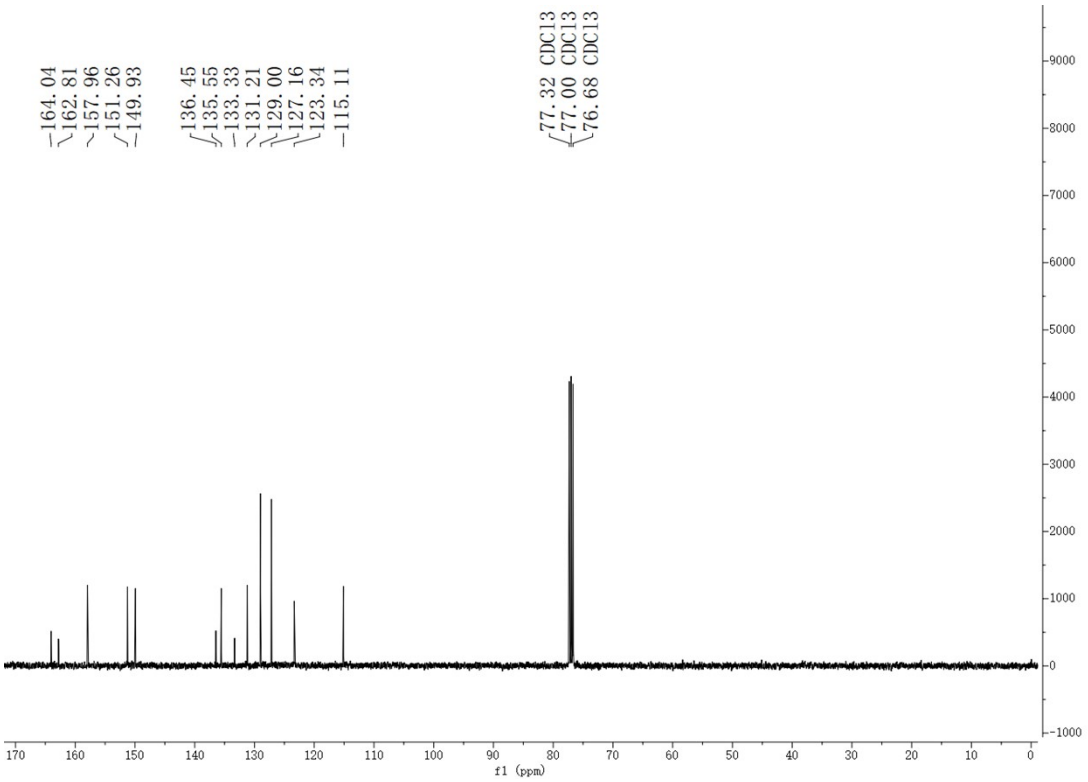

Figure S79. ^{13}C NMR Spectrum of 4o (100 MHz, $CDCl_3$)

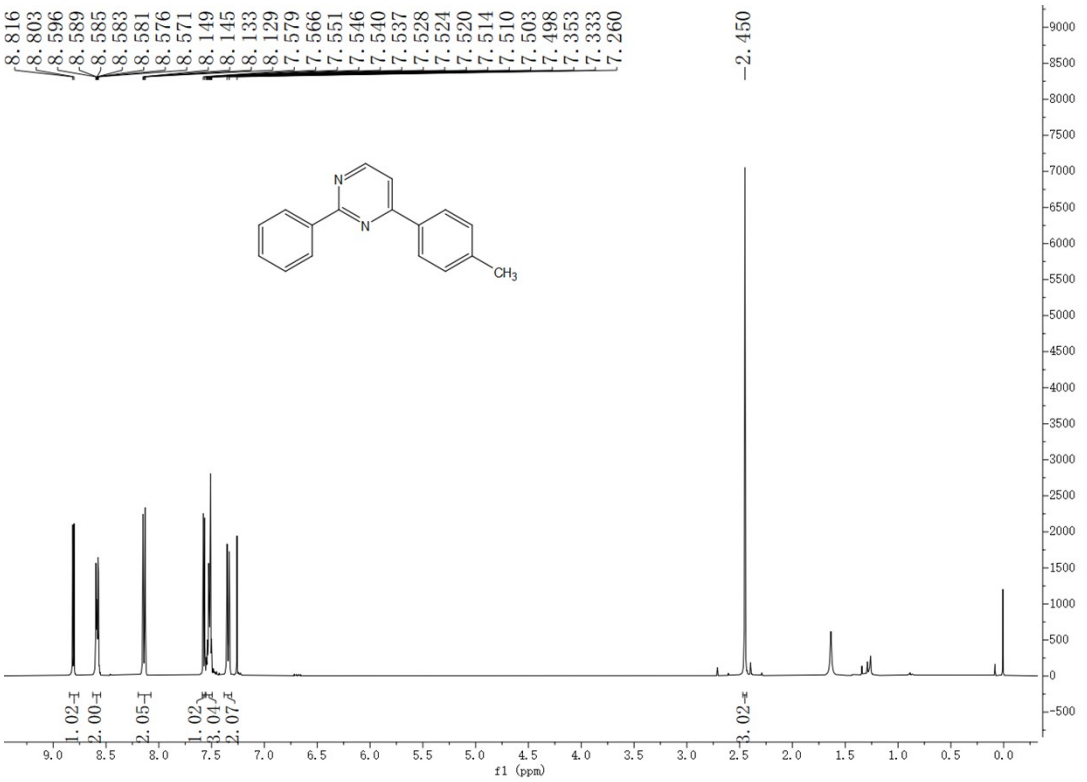

Figure S80. ^{1}H NMR Spectrum of 4p (400 MHz, $CDCl_3$)

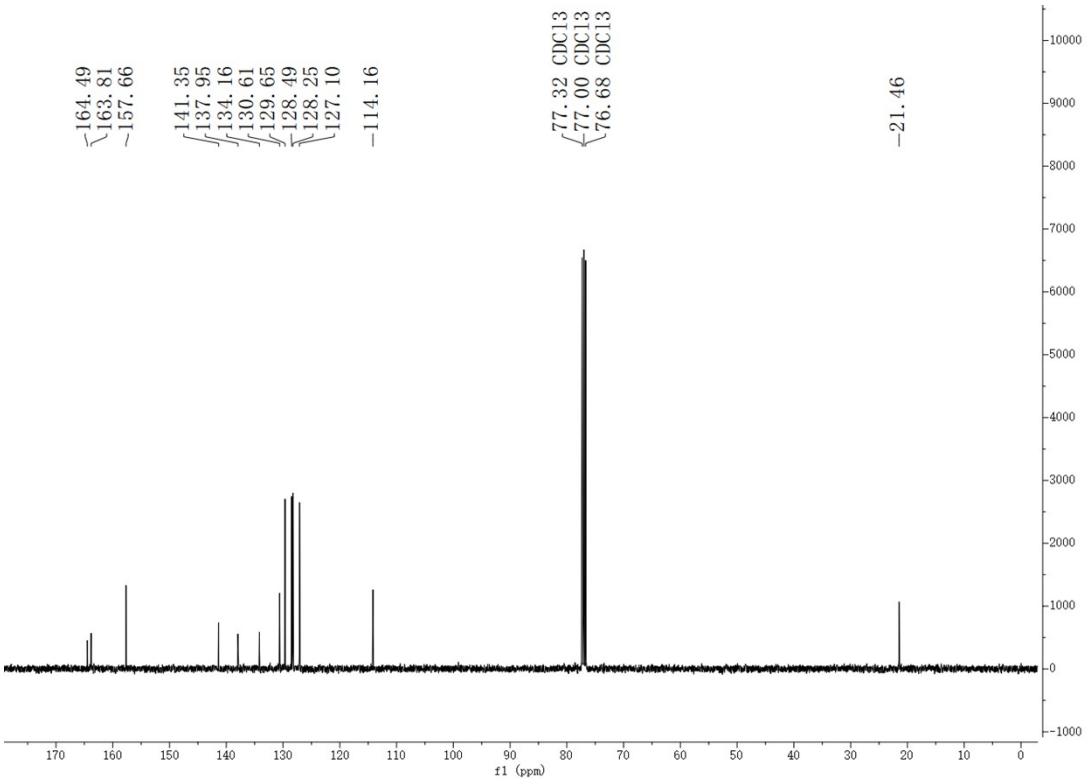

Figure S81. ^{13}C NMR Spectrum of 4p (100 MHz, $CDCl_3$)

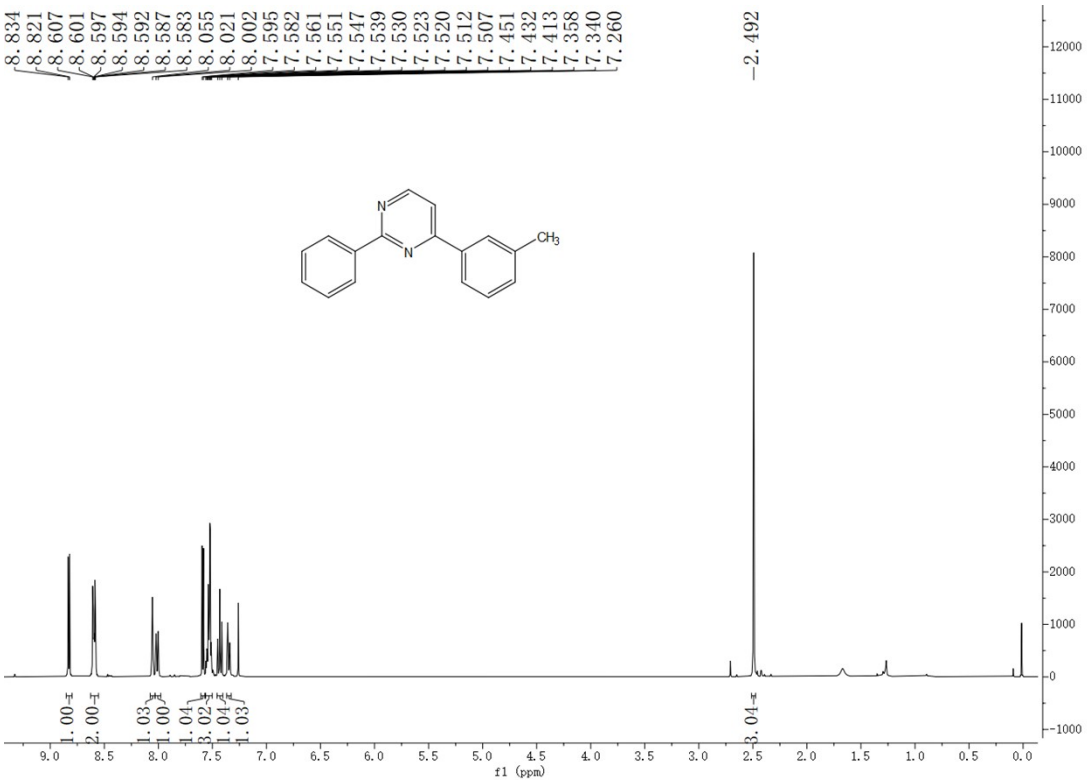

Figure S82. ^{1}H NMR Spectrum of 4q (400 MHz, $CDCl_3$)

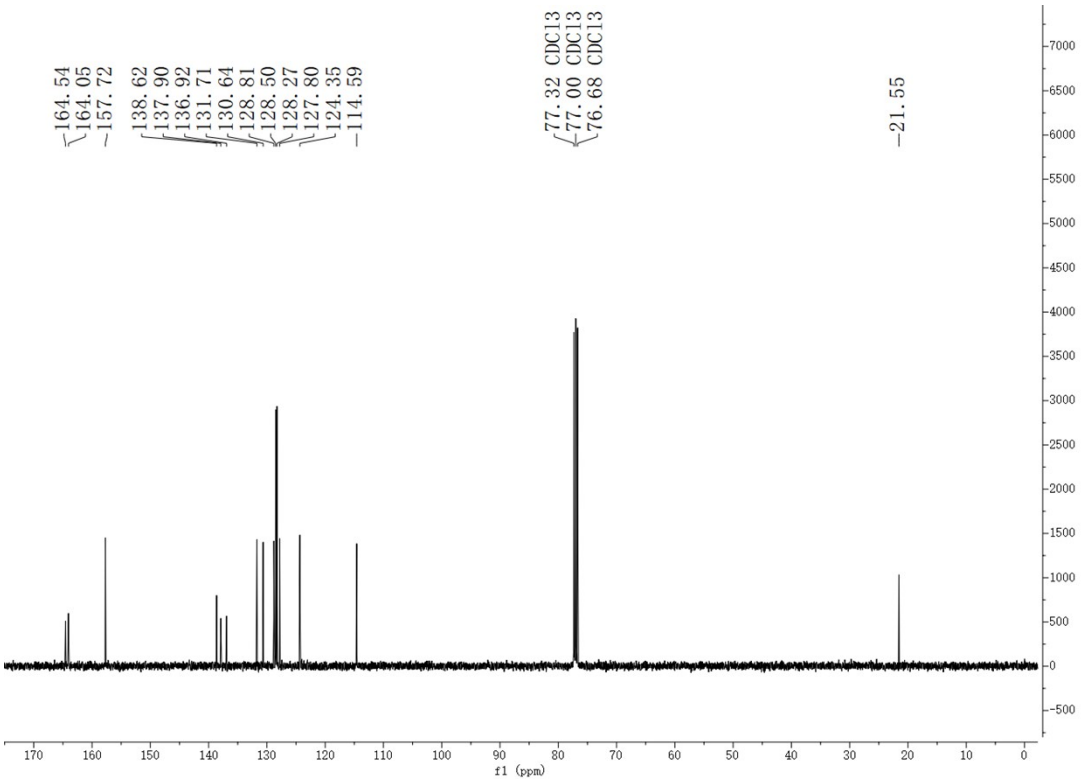

Figure S83. ^{13}C NMR Spectrum of 4q (100 MHz, $CDCl_3$)

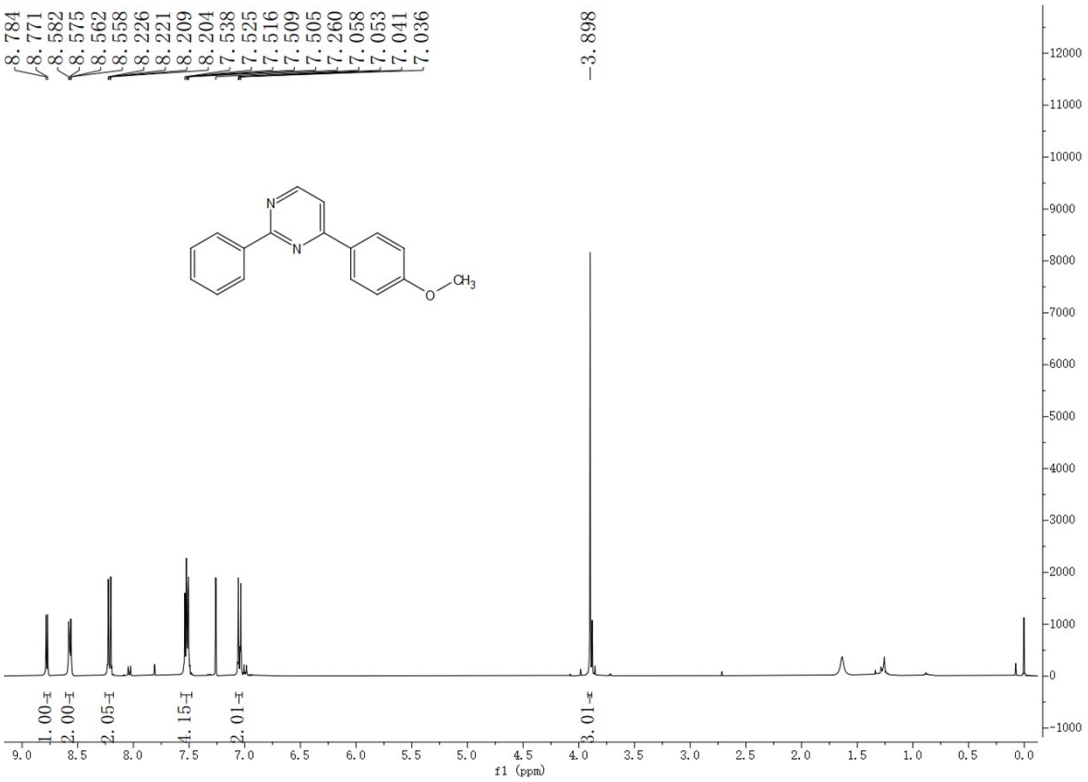

Figure S84. ^{1}H NMR Spectrum of 4r (400 MHz, $CDCl_3$)

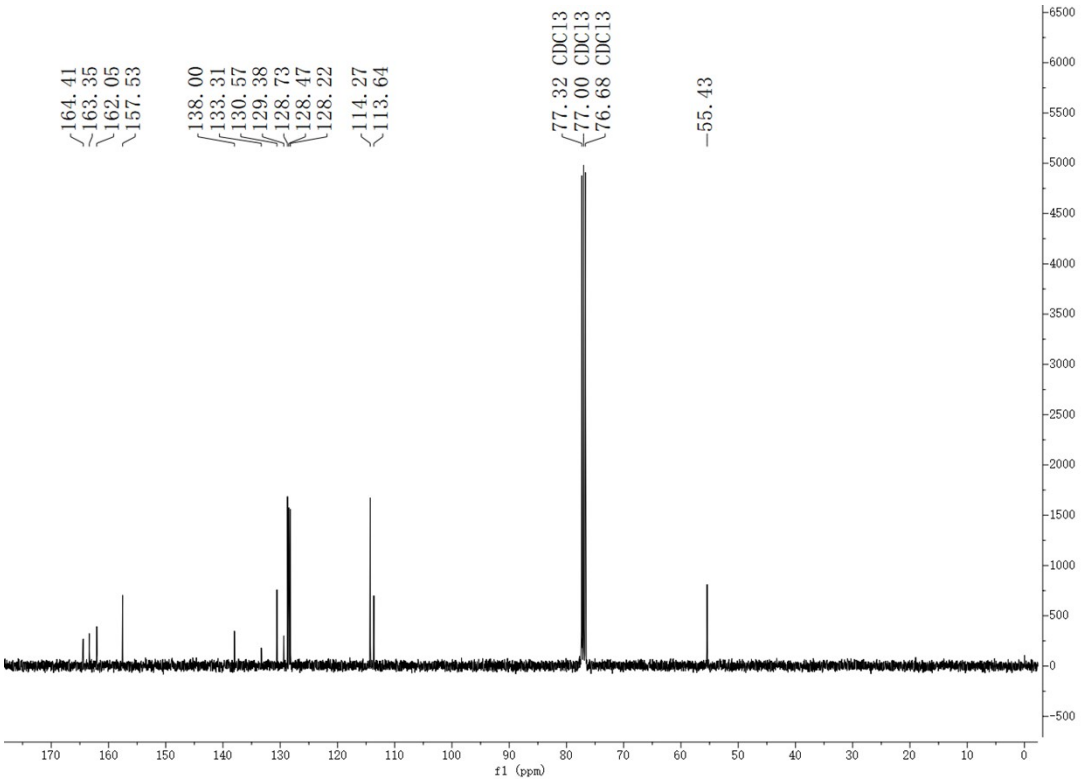

Figure S85. ^{13}C NMR Spectrum of 4r (100 MHz, $CDCl_3$)

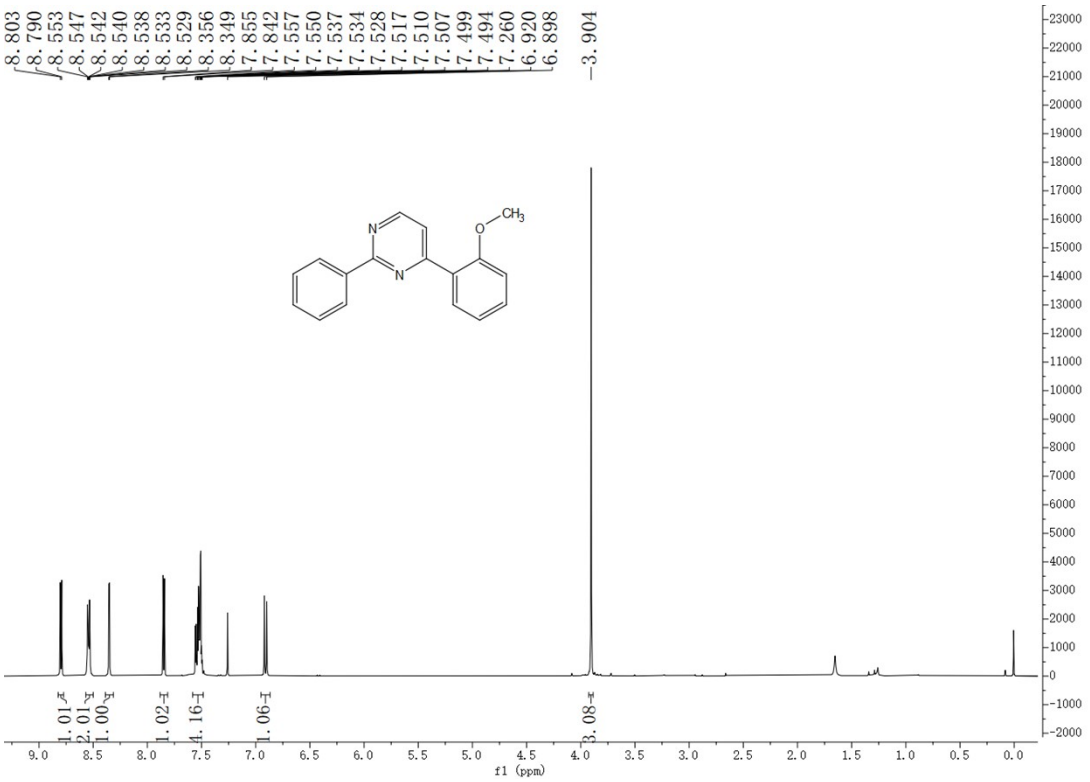

Figure S86. ^{1}H NMR Spectrum of 4s (400 MHz, $CDCl_3$)

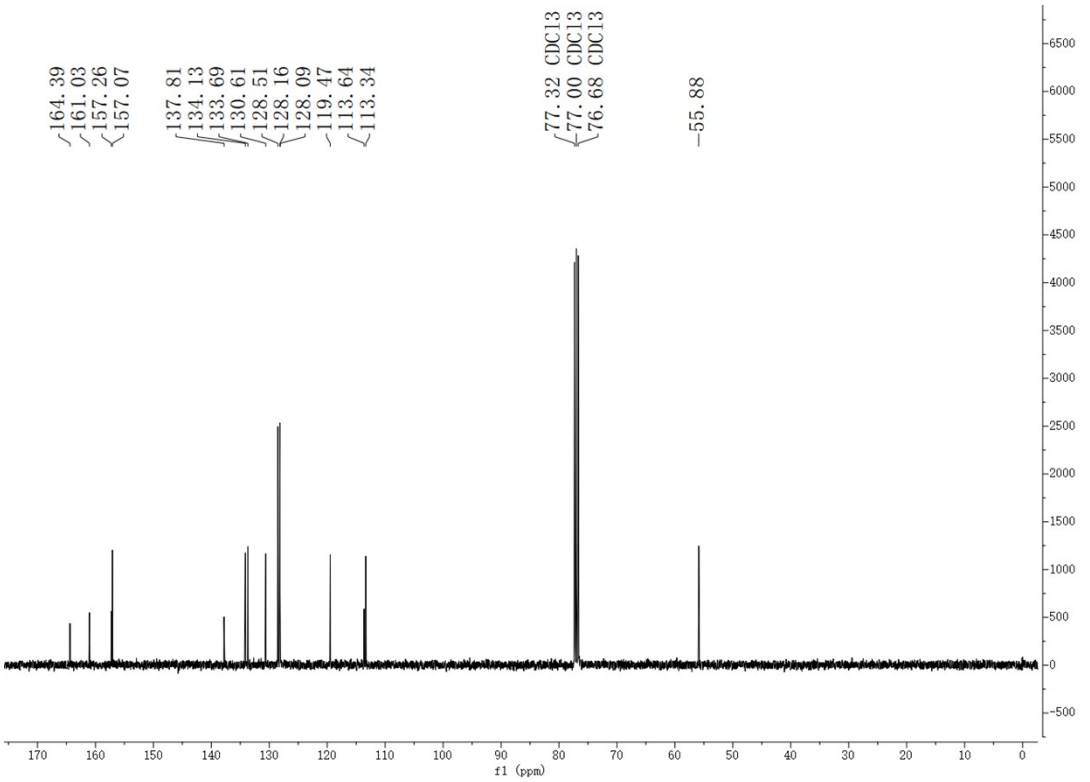

Figure S87. ^{13}C NMR Spectrum of 4s (100 MHz, $CDCl_3$)

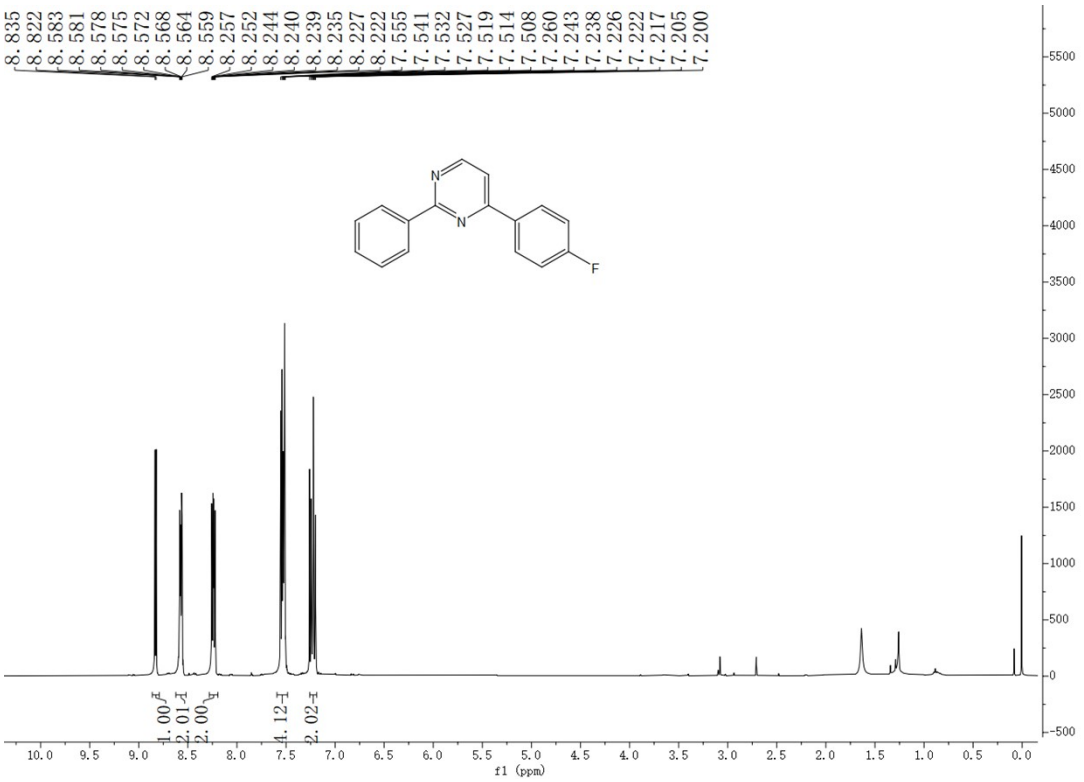

Figure S88. ^{1}H NMR Spectrum of 4t (400 MHz, $CDCl_3$)

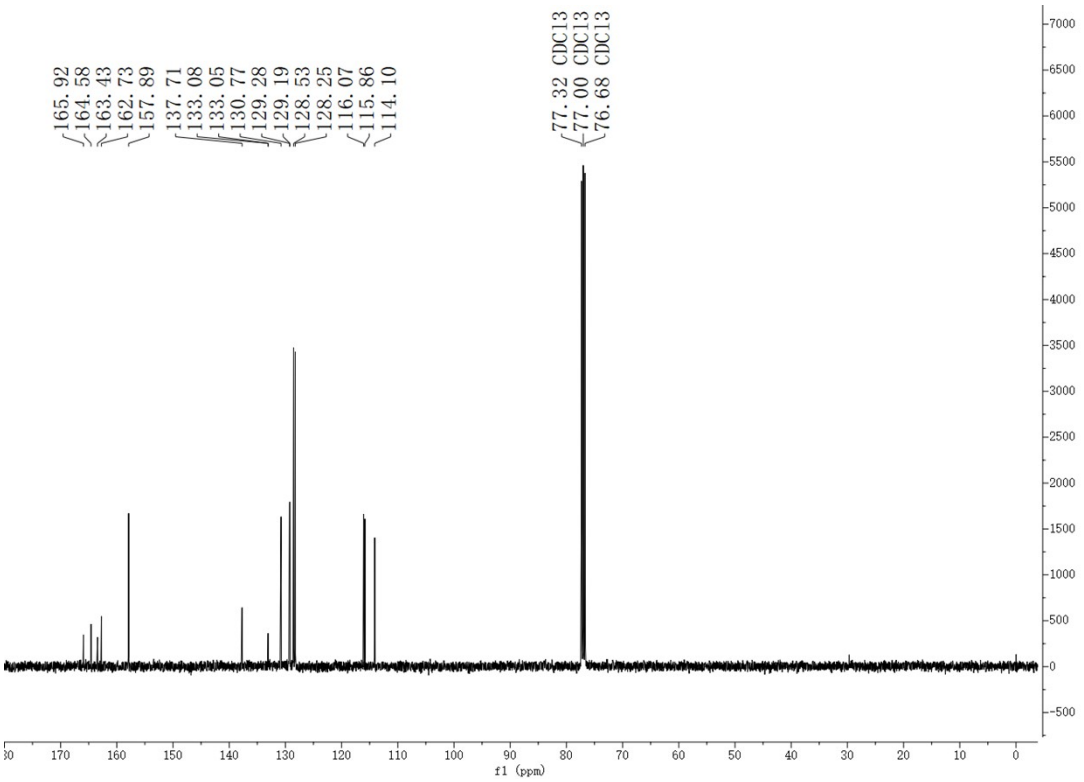

Figure S89. ^{13}C NMR Spectrum of 4t (100 MHz, $CDCl_3$)

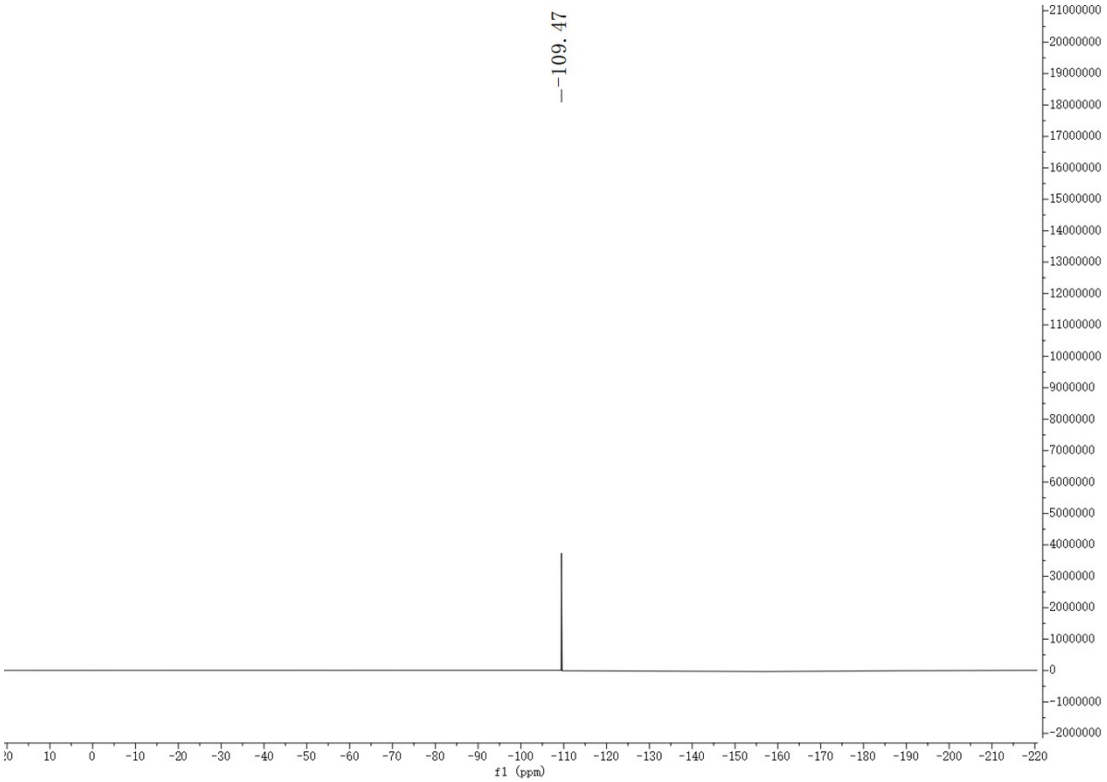

Figure S90. ^{19}F NMR Spectrum of 4t (376 MHz, $CDCl_3$)

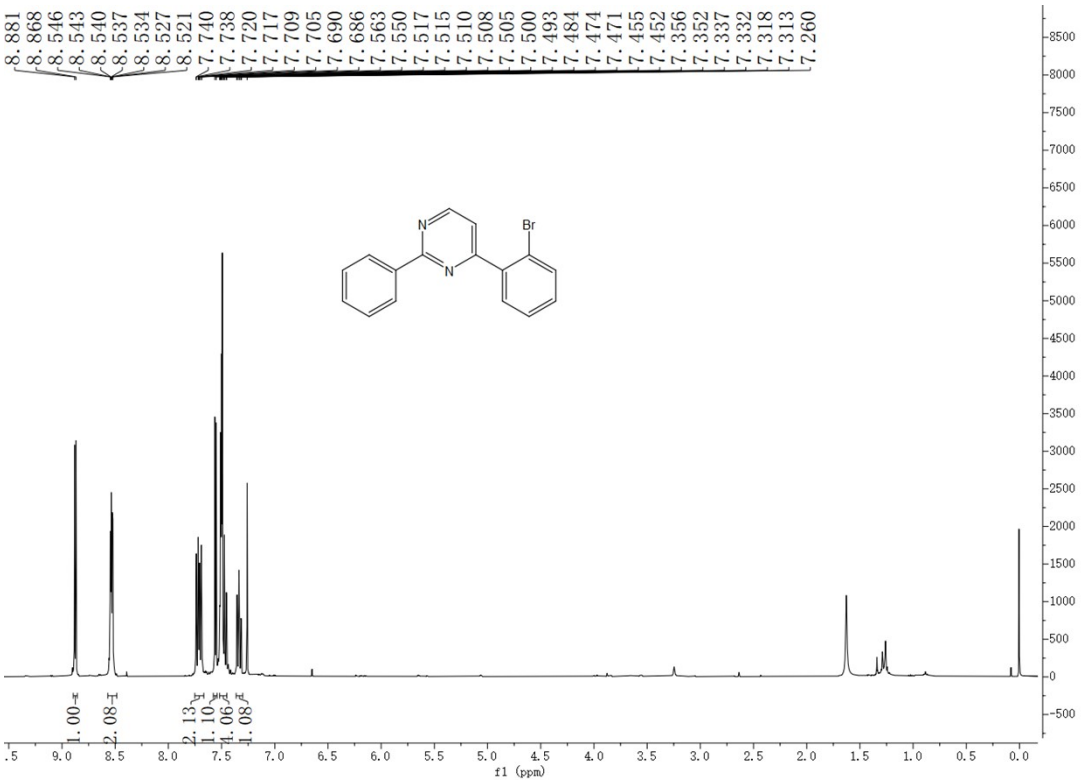

Figure S91. ^{1}H NMR Spectrum of 4u (400 MHz, $CDCl_3$)

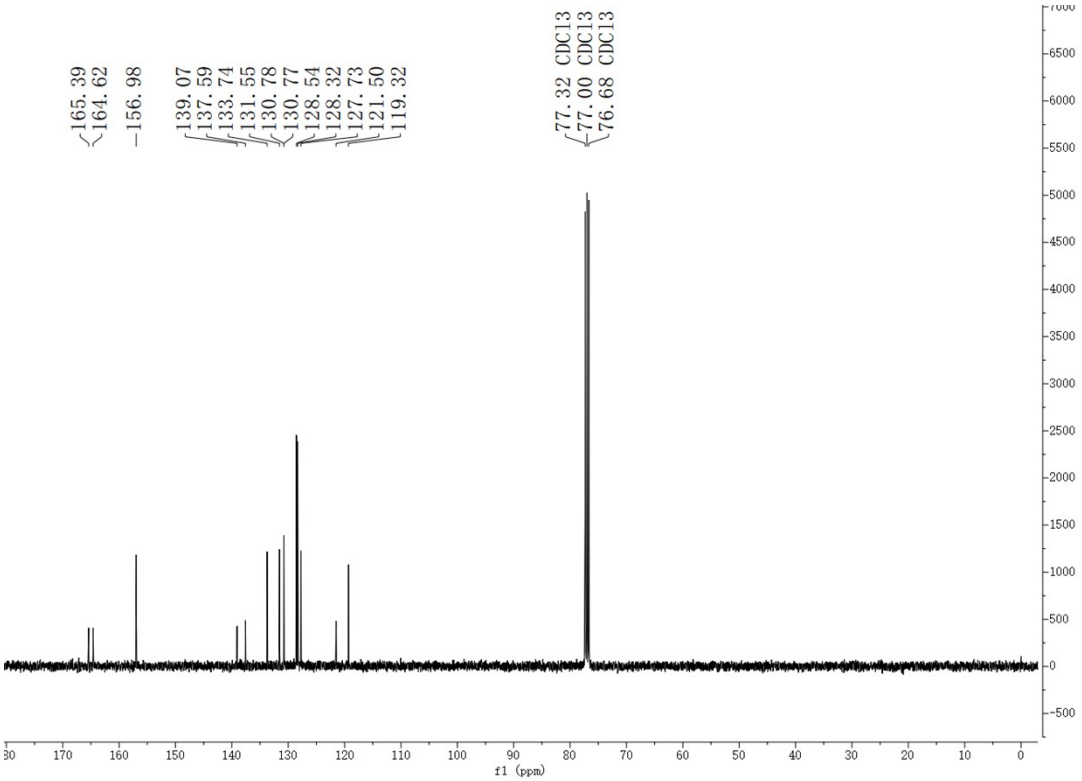

Figure S92. ^{13}C NMR Spectrum of 4u (100 MHz, $CDCl_3$)

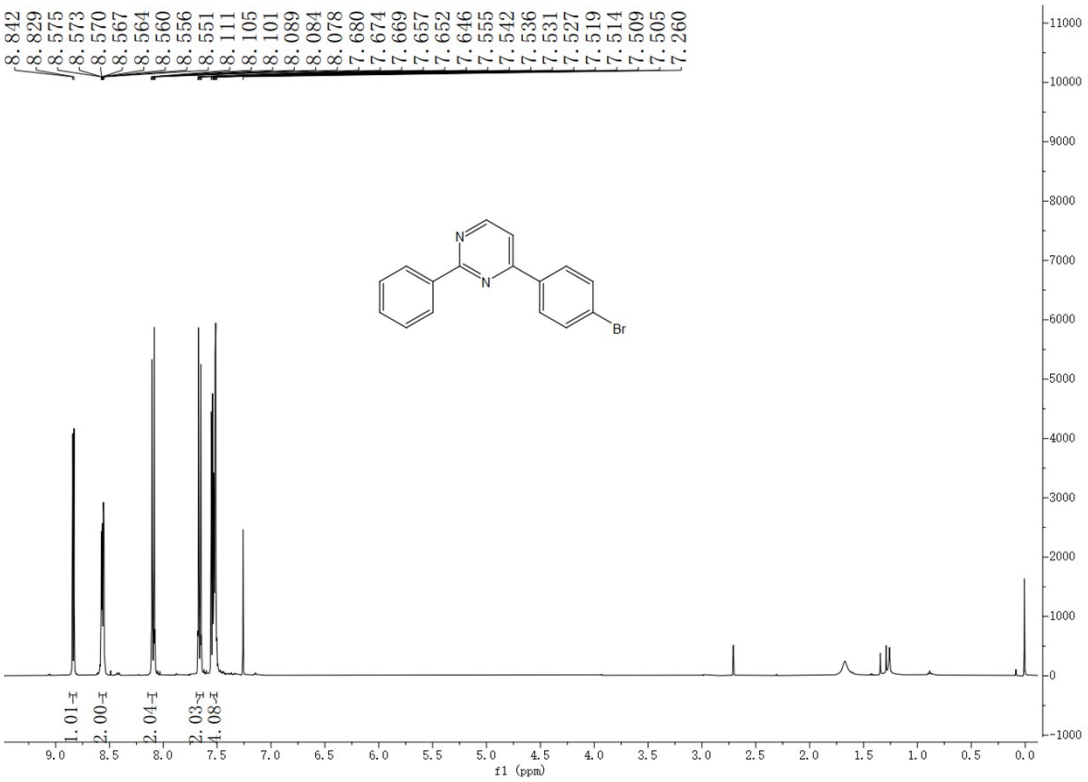

Figure S93. ^{1}H NMR Spectrum of 4v (400 MHz, $CDCl_3$)

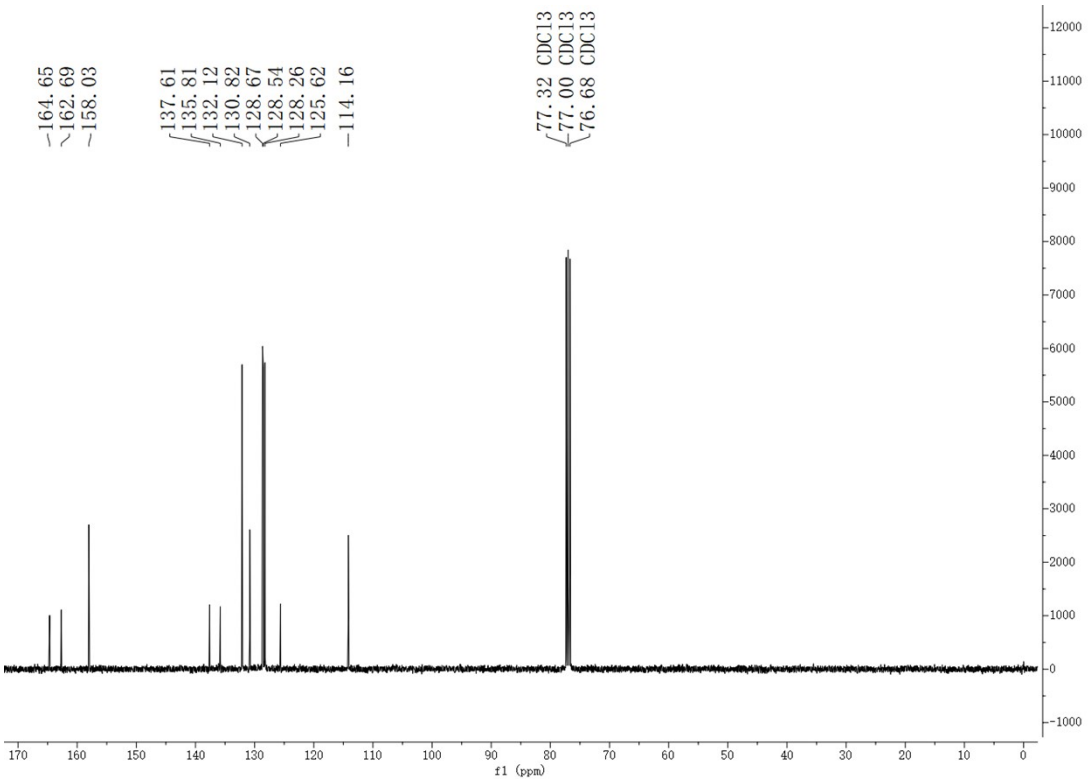

Figure S94. ^{13}C NMR Spectrum of 4v (100 MHz, $CDCl_3$)

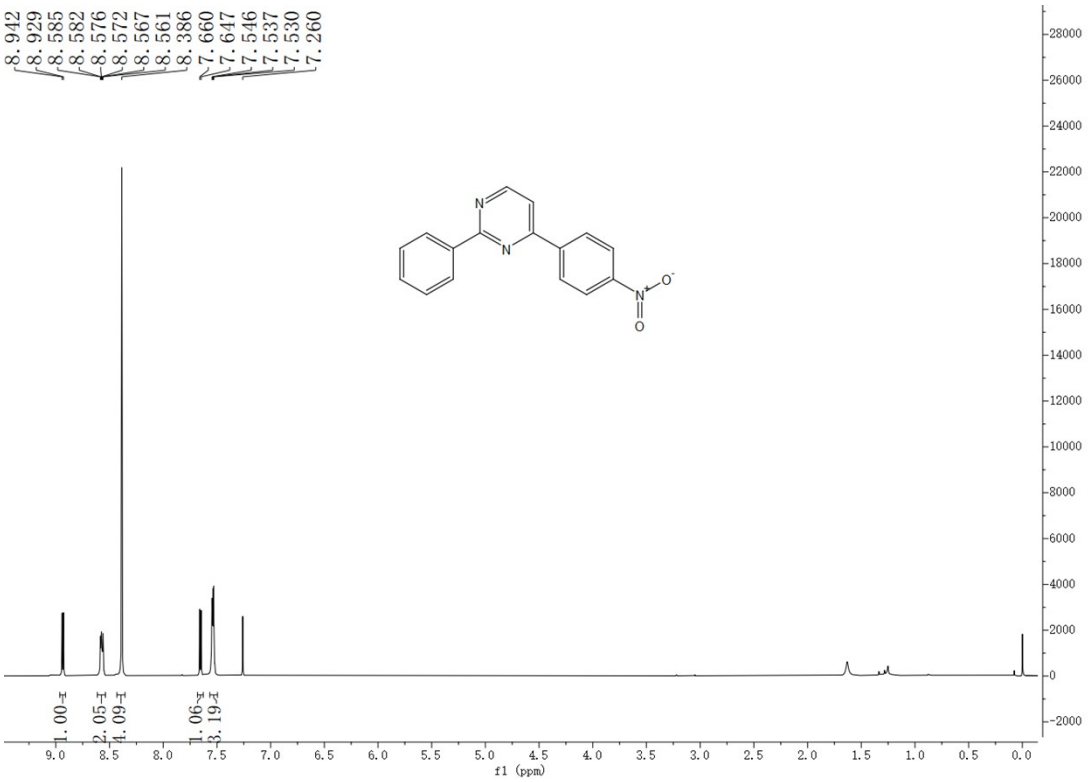

Figure S95. ^{1}H NMR Spectrum of 4w (400 MHz, $CDCl_3$)

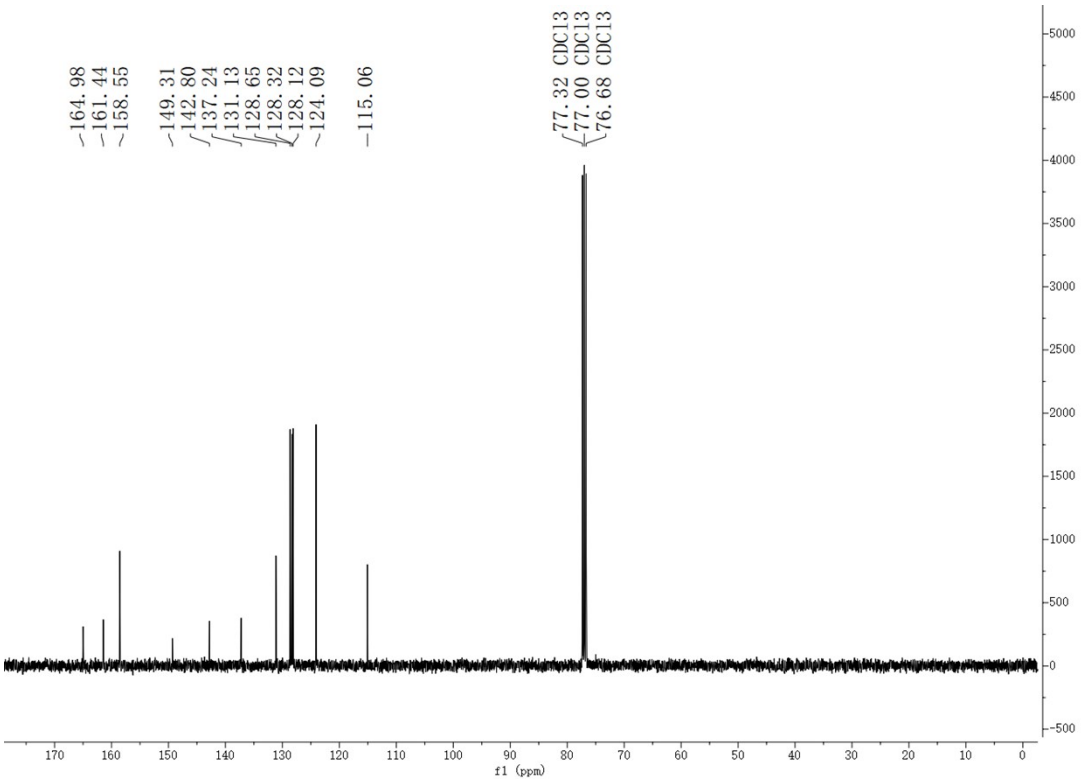

Figure S96. ^{13}C NMR Spectrum of 4w (100 MHz, $CDCl_3$)