**Supporting information**

# Nickel Complexes Supported by a New Class of Fused Imidazonaphthyridine Tridentate N,N,N-Ligands for Ethylene Oligomerization and Isolation of a Key Ni-Al Intermediate

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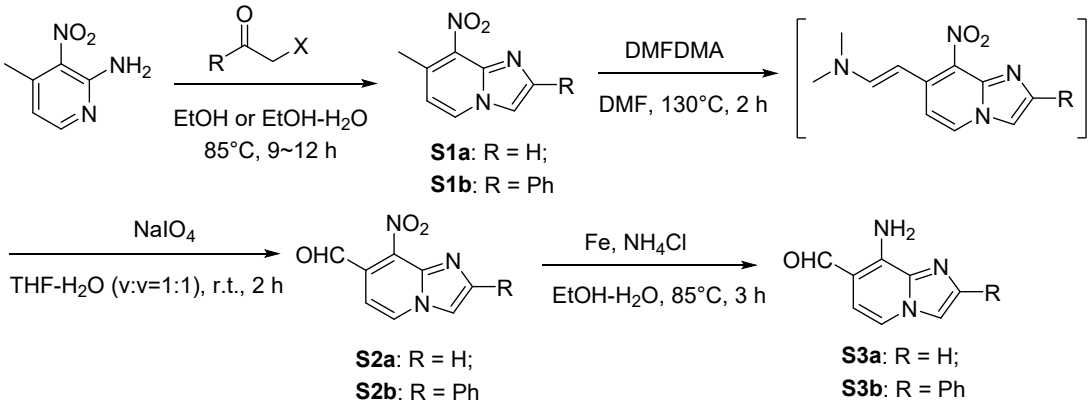
## 1. Synthesis of Ligands L1-L5

### 1.1 Synthesis of 8-aminoimidazo[1,2-a]pyridine-7-carbaldehydes S3




1.1.1 Synthesis of nitro compound **S1**[1]

To a solution of 2-amino-4-methyl-3-nitropyridine (7.63 g, 49.6 mmol) in ethanol (80 mL) was added chloroacetaldehyde (40% in water) (35 mL, 178.6 mmol) slowly and the resulting mixture was refluxed at 85 °C for 9 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was alkalinized with $NaHCO_3$ (100 mL). After filtration and drying in vacuo, 7-methyl-8-nitroimidazo[1,2-a]pyridine (**S1a**)[1] was obtained as yellow solid; yield: 8.42 g (96%); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.16 (d, $J$ = 6.8 Hz, 1H), 7.68 (d, $J$ = 1.2 Hz, 1H), 7.64 (d, $J$ = 1.2 Hz, 1H), 6.73 (d, $J$ = 6.8 Hz, 1H), 2.49 (s, 3H).

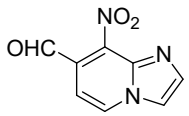
To a solution of 2-amino-4-methyl-3-nitropyridine (10.12 g, 65.3 mmol) in EtOH-$H_2O$ (1:1 v/v, 150 mL) was added α-bromoacetophenone (13.08 g, 65.3 mmol) slowly and the resulting mixture was refluxed at 85 °C for 9 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was recrystallized at 0 °C. After filtration and drying in vacuo, 7-methyl-8-nitro-2-phenylimidazo[1,2-a]pyridine (**S1b**) was obtained as yellow solid; yield: 8.75 g (53%); m.p. 194.7~195.9 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.10 (d, $J$ = 6.8 Hz, 1H), 9.74 (d, $J$ = 7.2 Hz, 2H), 7.86 (s, 1H), 7.42 (t, $J$ = 7.6 Hz, 2H), 7.36-7.32 (m, 1H), 6.66 (d, $J$ = 7.2 Hz, 1H), 2.46 (s, 3H); $^{13}$C NMR (151 MHz, DMSO) $\delta$ 145.3, 137.5, 137.2, 132.8, 128.95, 128.93, 128.8, 128.3, 125.8, 114.4, 110.6, 16.8; HRMS (TOF-EI): m/z $[M]^+$ calcd. for $C_{14}H_{11}N_3O_2^+$: 253.0851; Found: 253.0853.

1.1.2 General Procedure for the synthesis of nitroaldehyde compound **S2**

To a solution of the nitro compound **S1** (45.5 mmol) dissolved in super dry DMF (65 mL), was added DMF-DMA (7.9 mL, 68.2 mmol) under $N_2$. The reaction mixture was heated to 130 °C for 2h. After cooling to 90 °C, the solvent and excess reactant were evaporated under reduced pressure to afford crude product as red solid that was used in the next step without further purification.

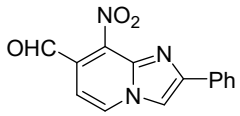
To a solution of the above-mentioned crude product in THF/$H_2O$ (1/1, v/v) (270 mL), sodium periodate (10.76 g, 50.0 mmol) was added and the reaction mixture was stirred at room temperature for 2 h. After completion, the THF was removed by evaporation and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 40 mL). The combined organic layers were dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash silica gel chromatography (100~200 mesh silica gel, petroleum ether/ethyl acetate = 4:3 as eluent) to afford nitroaldehyde compound **S2**.

8-Nitroimidazo[1,2-a]pyridine-7-carbaldehyde (**S2a**)[1]




General procedure was followed on **S1a** (8.12 g, 45.5 mmol) to afford **S2a**. Yellow solid; yield: 2.71 g (32%); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.19 (s, 1H), 8.39 (d, $J$ = 6.8 Hz, 1H), 7.99 (d, $J$ = 1.2 Hz, 1H), 7.91 (d, $J$ = 1.2 Hz, 1H), 7.41 (d, $J$ = 7.2 Hz, 1H).

8-Nitro-2-phenylimidazo[1,2-a]pyridine-7-carbaldehyde (**S2b**)

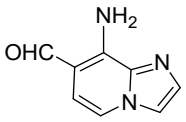



General procedure was followed on **S1b** (11.52 g, 45.5 mmol) to afford **S2b**. Orange solid; yield: 4.33 g (36%); m.p. 148.9~150.1°C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.16 (s, 1H), 8.33 (d, $J$ = 7.2 Hz, 1H), 8.14 (s, 1H), 7.99 (dd, $J$ = 8.0, 2.0 Hz, 2H), 7.49-7.36 (m, 4H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 184.8, 151.0, 136.6, 131.7, 129.5, 128.9, 127.5, 126.6, 122.5, 111.7, 108.5; HRMS (TOF-EI): m/z $[M]^+$ calcd. for $C_{14}H_9N_3O_3^+$: 267.0644; Found: 267.0642.

1.1.3 General Procedure for the synthesis of amino aldehyde compound **S3**

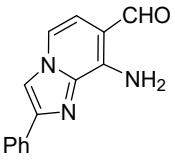
To a solution of compound **S2** (15.0 mmol) dissolved in a mixture of ethanol/water (82.5 mL, 10:1, v/v), powder of iron (4.23 g, 75.2 mmol) and $NH_4Cl$ (0.48 g, 9.1 mmol) were added. The reaction mixture was stirred at 90 °C for 3 h. After cooling at room temperature, the reaction mixture was filtered on Celite and washed by ethyl acetate, then the lower boiling point organic solvent in the filtrate was removed by evaporation under reduced pressure. The aqueous phase was extracted with $CH_2Cl_2$ (3 × 40 mL). The combined organic layers were dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash silica gel chromatography (100~200 mesh silica gel, petroleum ether/ethyl acetate = 3:2 as eluent) to afford amino aldehyde compound **S3**.

8-Aminoimidazo[1,2-a]pyridine-7-carbaldehyde (**S3a**)[1]




General procedure was followed on **S2a** (2.94 g, 15.0 mmol) to afford **S3a**. Yellow solid; yield: 1.43 g (62%); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.81 (s, 1H), 8.57 (br s, NH), 7.59 (d, $J$ = 1.2 Hz, 1H), 7.54 (d, $J$ = 1.2 Hz, 1H), 7.45 (d, $J$ = 6.8 Hz, 1H), 6.84 (d, $J$ = 6.8 Hz, 1H), 6.57 (br s, NH).

8-Amino-2-phenylimidazo[1,2-a]pyridine-7-carbaldehyde (**S3b**)

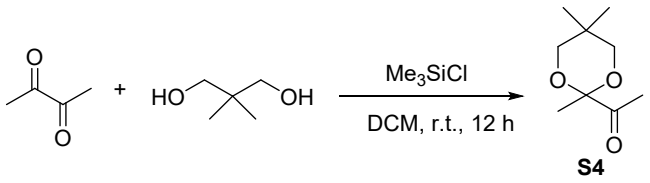



General procedure was followed on **S2b** (4.02 g, 15.0 mmol) to afford **S3b**. Yellow solid; yield: 2.52 g (70%); m.p. 158.2~159.6 ℃; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.80 (s, 1H), 8.52 (br s, 1H), 7.92 (dt, $J$ = 7.2, 1.6 Hz, 2H), 7.78 (s, 1H), 7.46-7.42 (m, 3H), 7.37-7.33 (m, 1H), 6.82 (d, $J$ = 7.2 Hz, 1H), 6.52 (br s, 1H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 191.0, 145.8, 141.3, 137.5,

133.2, 128.8, 128.1, 125.8, 114.9, 113.4, 111.4, 107.3; HRMS (TOF-EI): m/z $[M]^+$ calcd. for $C_{14}H_{11}N_3O^+$: 237.0902; Found: 237.0899.

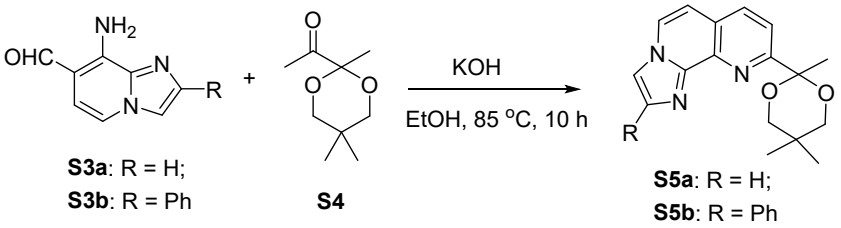
### 1.2 Synthesis of 2-acetyl-imidazo[1,2-h][1,7]naphthyridines

1.2.1 Synthesis of 1-(2,5,5-trimethyl-1,3-dioxan-2-yl)ethan-1-one **(S4)**[2]




To a solution of 2,2-dimethylpropane-1,3-diol (2.92 g, 27.5 mmol) and TMSCl (2.72 g, 25.0 mmol) in 10 mL of $CH_2Cl_2$ was added the solution of 2,3-butanedione (2.24 g, 25 mmol) in 30 mL of $CH_2Cl_2$ dropwise with stirring. The resulting mixture was stirred at room temperature overnight (monitored by TLC). After completion, the reaction was quenched by addition of 20 mL of saturated $NaHCO_3$ solution and extracted by $CH_2Cl_2$ (3×10 mL). Combined the organic phase and dried over anhydrous $Na_2SO_4$. Filtered, concentrated, the residue was purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate = 30:1) to give compound **S4** as colorless oil; yield: 4.03 g (94%); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 3.49 (dt, $J$ = 11.6, 1.2 Hz, 2H), 3.40 (d, $J$ = 11.2 Hz, 2H), 2.23 (s, 3H), 1.42 (s, 3H), 1.56 (s, 3H), 0.72 (s, 3H).

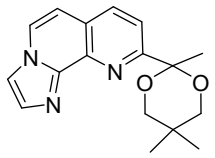
1.2.2 General procedure for the synthesis of 9-(2,5,5-trimethyl-1,3-dioxan-2-yl)imidazo[1,2-h][1,7]naphthyridines **S5**




A solution of aminoaldehye **S3** (8.2 mmol), **S4** (1.73 g, 9.8 mmol) and KOH (23.0 mg, 0.41 mmol, 0.05 eq.) in 25 mL of EtOH was stirred at 85°C for 10 h. After completion, the EtOH was evaporated under reduced pressure and the residue was purified by flash silica gel

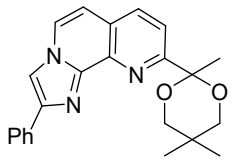
chromatograph (100~200 mesh silica gel) to give **S5**.

9-(2,5,5-Trimethyl-1,3-dioxan-2-yl)imidazo[1,2-h][1,7]naphthyridine (**S5a**)



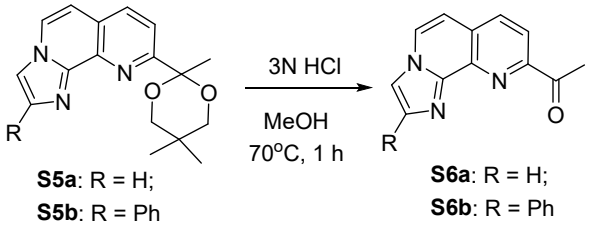
General procedure was followed on **S3a** (1.32 g, 8.2 mmol) and purified by chromatograph (using DCM:EtOH = 30:1 as eluent) to afford **S5a**. Yellow solid; yield: 2.43 g (97%); m.p. 91.3~92.5 ℃; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.07 (d, $J$ = 8.4 Hz, 1H), 8.02 (d, $J$ = 6.8 Hz, 1H), 7.77 (d, $J$ = 8.4 Hz, 1H), 7.73 (d, $J$ = 1.2 Hz, 1H), 7.65 (d, $J$ = 1.2 Hz, 1H), 7.04 (d, $J$ = 6.8 Hz, 1H), 3.60 (d, $J$ = 10.8 Hz, 2H), 3.55 (d, $J$ = 11.2 Hz, 2H),1.72 (s, 3H), 1.26 (s, 3H), 0.64 (s, 3H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 161.6, 142.8, 140.1, 135.7, 132.6, 124.2, 124.0, 121.2, 114.9, 111.5, 100.2, 72.3, 29.9, 29.0, 22.9, 22.0; HRMS (TOF-EI): m/z $[M]^+$ calcd. for $C_{17}H_{19}N_3O_2^+$: 297.1477; Found: 297.1475.

2-Phenyl-9-(2,5,5-trimethyl-1,3-dioxan-2-yl)imidazo[1,2-h][1,7]naphthyridine (**S5b**)



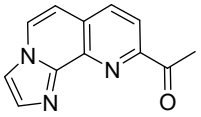
General procedure was followed on **S3b** (1.91 g, 8.2 mmol) and purified by chromatograph (using petroleum ether: ethyl acetate = 2:1 as eluent) to afford **S5b**. Orange solid; yield: 2.71 g (90%); m.p. 100.5~102.1 ℃; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.09-8.03 (m, 4H), 7.92 (s, 1H), 7.75 (d, $J$ = 8.0 Hz, 1H), 7.45 (t, $J$ = 7.2 Hz, 2H), 7.32 (t, $J$ = 7.2 Hz, 1H), 7.05 (d, $J$ = 7.2 Hz, 1H), 3.61 (d, $J$ = 11.2 Hz, 2H), 3.55 (d, $J$ = 11.2 Hz, 2H), 1.72 (s, 3H), 1.30 (s, 3H), 0.63 (s, 3H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 161.3, 144.9, 142.8, 139.8, 136.0, 133.0, 128.8, 128.0, 126.0, 124.2, 124.1, 121.1, 111.6, 110.6, 72.4, 30.0, 29.7, 22.8, 21.9; HRMS (TOF-EI): m/z $[M]^+$ calcd. for $C_{23}H_{23}N_3O_2^+$: 373.1790; Found: 373.1787.

1.2.3 General procedure for the synthesis of 2-acetyl-imidazo[1,2-h][1,7]naphthyridines **S6**



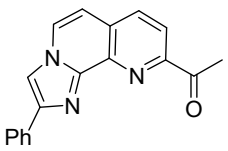

A solution of **S5**, 3M HCl solution (4 mL) in 15 mL of MeOH was stirred at 70 °C for 1h. After completion, the excess of MeOH was removed by evaporation, and the residue was nenutralized by addition of saturated $NaHCO_3$ solution, extracted by $CH_2Cl_2$ (3×30 mL). Combined the organic phase and dried over $Na_2SO_4$. Filtered, concentrated under reduced pressure, the residue was purified by flash silica gel chromatography (100~200 mesh silica gel) to give **S6**.

1-(Imidazo[1,2-h][1,7]naphthyridin-9-yl)ethan-1-one (**S6a**)



General procedure was followed on **S5a** (2.42 g, 8.1 mmol) and purified by chromatograph (using DCM:EtOH = 30:1 as eluent) to afford **S6a**. Yellow solid; yield: 1.63 g (92%); m.p. 150.2-153.8 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.24 (d, $J$ = 8.4 Hz, 1H), 8.16 (d, $J$ = 8.4 Hz, 1H), 8.10 (d, $J$ = 7.2 Hz, 1H), 7.78 (d, $J$ = 1.2 Hz, 1H), 7.69 (d, $J$ = 1.2 Hz, 1H), 7.08 (d, $J$ = 7.2 Hz, 1H), 2.98 (s, 3H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 200.0, 153.4, 142.4, 139.6, 135.6, 133.0, 127.2, 125.7, 120.2, 115.4, 111.3, 26.0; HRMS (TOF-EI): m/z $[M]^+$ calcd. for $C_{12}H_9N_3O^+$: 211.0476; Found: 211.0478.

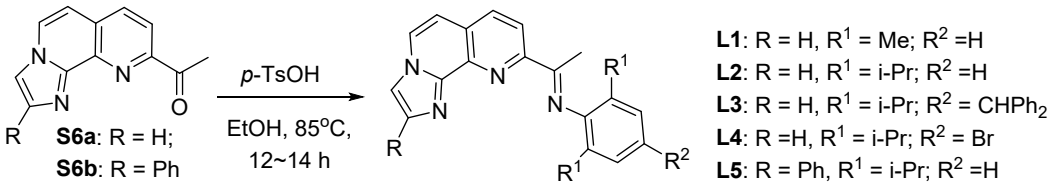
1-(2-Phenylimidazo[1,2-h][1,7]naphthyridin-9-yl)ethan-1-one (**S6b**)



General procedure was followed on **S5b** (2.71 g, 7.3 mmol) and purified by chromatograph (using petroleum ether: ethyl acetate = 2:1 as eluent) to afford **S6b**. Orange solid; yield: 2.03 g

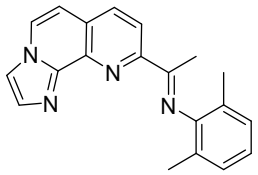
(94%); m.p. 177.8~180.1 ℃; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.24 (d, $J$ = 8.0 Hz, 1H), 7.16 (d, $J$ = 8.4 Hz, 1H), 8.11-8.09 (m, 3H), 7.97 (s, 1H), 7.49 (t, $J$ = 7.6 Hz, 2H), 7.36 (t, $J$ = 7.6 Hz, 1H), 7.09 (d, $J$ = 7.2 Hz, 1H), 3.03 (s, 3H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 200.2, 153.5, 145.4, 142.4, 139.3, 135.8, 133.1, 128.6, 128.1, 127.3, 126.1, 125.5, 120.3, 111.3, 110.9, 26.0; HRMS (TOF-EI): m/z $[M]^+$ calcd. for $C_{18}H_{13}N_3O^+$: 287.1059; Found: 287.1061.

### 1.3 Synthesis of 2-imino-imidazo[1,2-h][1,7]naphthyridine ligands L1-L5




General procedure: 2-Acetyl-imidazo[1,2-h][1,7]naphthyridine (**S6**, 1.0 equiv.), TsOH (0.15 equiv.) and anilines (1.2 equiv.) were added together in a Schlenk tube that was purged three times with argon and then stirred at 85 °C for 72 hours in anhydrous EtOH under argon. After completion, the solvent was removed by rotary evaporation under argon, and the residue was recrystallized by MeOH and washed with icy MeOH for three times (3 × 1 mL). After drying in vacuo, the corresponding ligands **L1~L5** were obtained.

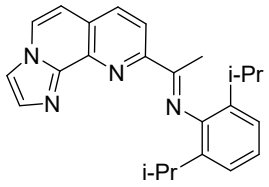
(E)-*N*-(2,6-Dimethylphenyl)-1-(imidazo[1,2-h][1,7]naphthyridin-9-yl)ethan-1-imine (**L1**)



General procedure was followed on **S6a** (500.0 mg, 2.4 mmol), TsOH (68.5 mg, 0.36 mmol), 2,6-dimethylaniline (0.36 ml, 2.9 mmol) and anhydrous EtOH (15 mL), affording **L1** as yellow solid (470.0 mg, 64%); m.p. 153.5~155.6 ℃; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.62 (d, $J$ = 8.4 Hz, 1H), 8.13 (d, $J$ = 8.4 Hz, 1H), 8.06 (d, $J$ = 7.2 Hz, 1H), 7.77 (d, $J$ = 0.8 Hz, 1H), 7.68 (d, $J$ = 1.2 Hz, 1H), 7.10 (d, $J$ = 7.2 Hz, 1H), 7.08 (d, $J$ = 7.6 Hz, 2H), 6.95 (t, $J$ = 7.6 Hz, 1H), 2.44 (s, 3H), 2.05 (s, 6H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 167.7, 156.7, 148.7, 142.9,

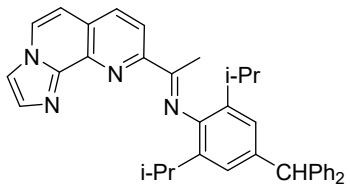
139.5, 135.1, 132.8, 127.9, 125.7, 125.3, 124.6, 123.1, 120.6, 115.1, 111.6, 17.9, 16.9; HRMS (TOF-EI): m/z $[M]^+$ calcd. for $C_{20}H_{18}N_4^+$: 314.1531; Found: 314.1526.

(E)-*N*-(2,6-Diisopropylphenyl)-1-(imidazo[1,2-h][1,7]naphthyridin-9-yl)ethan-1-imine (**L2**)




General procedure was followed on **S6a** (500.0 mg, 2.4 mmol), TsOH (68.5 mg, 0.36 mmol), 2,6-diisopropylaniline (0.55 ml, 2.9 mmol) and anhydrous EtOH (15 mL), affording **L2** as yellow solid (531.0 mg, 61%); m.p. 183.2~185.1 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.62 (d, $J$ = 8.4 Hz, 1H), 8.14 (d, $J$ = 8.4 Hz, 1H), 8.07 (d, $J$ = 7.2 Hz, 1H), 7.77 (s, 1H), 7.69 (s, 1H), 7.18 (d, $J$ = 6.8 Hz, 2H), 7.13-7.09 (m, 2H), 2.78 (hept, $J$ = 6.8 Hz, 2H), 2.48 (s, 3H), 1.15 (d, $J$ = 6.8 Hz, 12H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 167.5, 156.8, 146.4, 142.9, 139.6, 135.7, 135.1, 132.9, 125.7, 124.6, 123.7, 123.0, 120.7, 115.1, 111.6, 28.3, 23.2, 22.8, 17.6; HRMS (TOF-EI): m/z $[M]^+$ calcd. for $C_{24}H_{26}N_4^+$: 370.2157; Found: 370.2160.

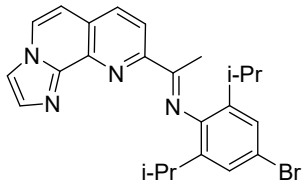
(E)-N-(4-benzhydryl-2,6-diisopropylphenyl)-1-(imidazo[1,2-h][1,7]naphthyridin-9-yl)ethan-1-imine (**L3**)




General procedure was followed on **S6a** (500.0 mg, 2.4 mmol), TsOH (68.5 mg, 0.36 mmol), 4-benzhydryl-2,6-diisopropylaniline (996.0 mg, 2.9 mmol) and anhydrous EtOH (15 mL), affording **L3** as yellow solid (620.0 mg, 49%). m.p. 195.9~197.4 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.61 (d, $J$ = 8.4 Hz, 1H), 8.13 (d, $J$ = 8.4 Hz, 1H), 8.07 (d, $J$ = 7.2 Hz, 1H), 7.77 (d, $J$ = 1.2 Hz, 1H), 7.69 (d, $J$ = 1.2 Hz, 1H), 7.32-7.28 (m, 4H), 7.24-7.20 (m, 2H), 7.18-7.16 (m, 4H), 7.10 (d, $J$ = 7.2 Hz, 1H), 6.91 (s, 2H), 5.54 (s, 1H), 2.73 (hept, $J$ = 6.8 Hz, 2H), 2.49 (s,

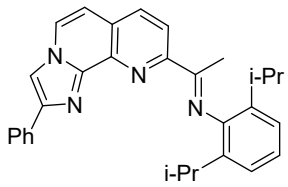
3H), 1.06 (d, $J$ = 6.8 Hz, 6H), 1.03 (d, $J$ = 6.8 Hz, 6H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 167.6, 156.8, 144.7, 144.5, 143.0, 139.6, 138.6, 135.4, 135.1, 133.0, 129.5, 128.1, 126.0, 125.7, 124.6, 124.3, 120.7, 115.1, 111.6, 56.9, 28.3, 23.2, 22.9, 17.7; HRMS (TOF-EI): m/z $[M]^+$ calcd. for $C_{37}H_{36}N_4^+$: 536.2940; Found: 536.2939.

(E)-N-(4-bromo-2,6-diisopropylphenyl)-1-(imidazo[1,2-h][1,7]naphthyridin-9-yl)ethan-1-imine (**L4**)




General procedure was followed on **S6a** (500.0 mg, 2.4 mmol), TsOH (68.5 mg, 0.36 mmol), 4-bromo-2,6-diisopropylaniline (0.6 mL, 2.9 mmol) and anhydrous EtOH (15 mL), affording **L4** as yellow solid (511.0 mg, 49%). m.p. 207.2~208.7 ℃; 1H NMR (400 MHz, $CDCl_3$) $\delta$ 8.57 (d, $J$ = 8.8 Hz, 1H), 8.14 (d, $J$ = 8.8 Hz, 1H), 8.07 (d, $J$ = 6.4 Hz, 1H), 7.77 (s, 1H), 7.69 (s, 1H), 7.26 (s, 2H), 7.11 (d, $J$ = 6.8 Hz, 1H), 2.76-2.70 (m, 2H), 2.47 (s, 3H), 1.13 (d, $J$ = 6.4 Hz, 12H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 168.2, 156.5, 145.5, 142.9, 139.6, 133.0, 126.3, 125.8, 124.8, 120.6, 117.0, 115.1, 111.6, 28.4, 23.0, 22.6, 17.7; HRMS (TOF-EI): m/z $[M]^+$ calcd. for $C_{24}H_{25}BrN_4^+$:448.1263; Found: 448.1259.

(*E*)-*N*-(2,6-Diisopropylphenyl)-1-(2-phenylimidazo[1,2-h][1,7]naphthyridin-9-yl)ethan-1-imine (**L5**)

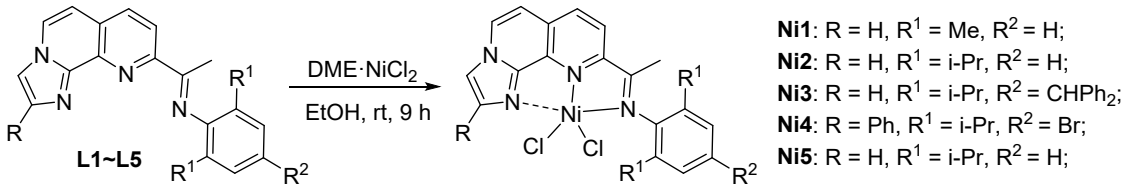



General procedure was followed on **S6b** (500.0 mg, 1.7 mmol), TsOH (49.5 mg, 0.26 mmol), 2,6-diisopropylaniline (0.38 ml, 2.04 mmol) and anhydrous EtOH (15 mL), affording **L5** as yellow solid (500.0 mg, 65%). m.p. 257.1~258.7 ℃; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.65

(d, *J* = 8.4 Hz, 1H), 8.16-8.07 (m, 4H), 7.98 (s, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.12 (d, *J* = 7.2 Hz, 2H), 2.84-2.74 (m, 2H), 2.53 (s, 3H), 1.17 (d, *J* = 2.8 Hz, 6H), 1.15 (d, *J* = 2.8 Hz, 6H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 167.4, 156.7, 146.4, 145.3, 142.9, 139.3, 135.7, 135.2, 133.3, 128.6, 127.9, 126.2, 125.9, 124.5, 123.7, 123.0, 120.8, 111.7, 110.7, 28.3, 23.2, 22.9, 17.5; HRMS (TOF-EI): m/z $[M]^+$ calcd. for $C_{30}H_{30}N_4^+$: 446.2470; Found: 446.2466.

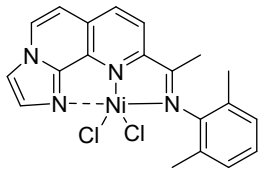
## 2. Synthesis of Nickel Complexes Ni1-Ni5 and Ni3-Al

### 2.1 Synthesis of Nickel Complexes Ni1-Ni5



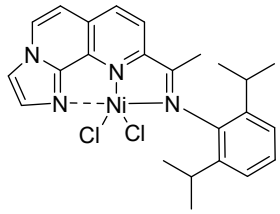

General procedure: DME·$NiCl_2$ and ligand **L1-L5** were added together in a Schlenk tube that was purged three times with argon and then stirred at room temperature for 9 hours in super dry EtOH under argon. After completion, the solvent was removed by filtration under argon, and the residue was washed with $Et_2O$ for three times (3 × 5 mL). After drying in vacuo, the corresponding nickel complexes **Ni1-Ni5** were obtained.

Nickle complex **Ni1**:



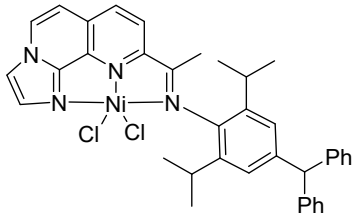
General procedure was followed on **L1** (200.0 mg, 0.62 mmol), DME·$NiCl_2$ (123.0 mg, 0.56 mmol) and super dry EtOH (6 mL), affording **Ni1** as yellow solid (161.0 mg, 57%). Anal. Calcd. for $C_{20}H_{18}Cl_2N_4Ni$·0.5 EtOH (%): C, 54.01; H, 4.53; N, 12.00; Found: C, 53.70; H, 4.13; N,12.18.

Nickle complex **Ni2**:



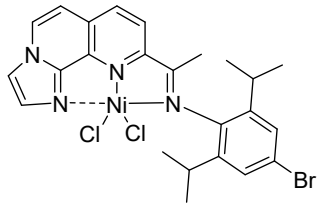
General procedure was followed on **L2** (100.0 mg, 0.27 mmol), DME·$NiCl_2$ (54.9 mg, 0.25 mmol) and super dry EtOH (5 mL), affording **Ni2** as yellow solid (69.2 mg, 51%). Anal. Calcd. for $C_{24}H_{26}Cl_2N_4Ni$·0.5 EtOH (%): C, 57.40; H, 5.59; N, 10.71; Found: C, 57.24; H, 5.16; N, 10.98.

Nickle complex **Ni3**:



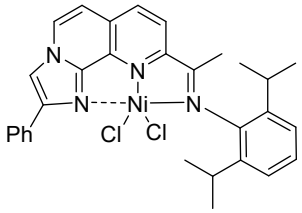
General procedure was followed on **L3** (200.0 mg, 0.37 mmol), DME·$NiCl_2$ (90.1 mg, 0.41 mmol) and super dry EtOH (6 mL), affording **Ni3** as yellow solid (104.7 mg, 42%). Anal. Calcd. for $C_{37}H_{36}Cl_2N_4Ni·H_2O$ (%): C, 64.94; H, 5.60; N, 8.19; Found: C, 64.95; H, 5.58; N,7.90.

Nickle complex **Ni4**:



General procedure was followed on **L4** (200.0 mg, 0.45 mmol), DME·$NiCl_2$ (110.0 mg, 0.50 mmol) and super dry EtOH (6 mL), affording **Ni4** as yellow solid (153.2 mg, 59%). Anal. Calcd. for $C_{24}H_{25}BrCl_2N_4Ni$·0.5 $H_2O$ (%): C, 49.02; H, 4.46; N, 9.53; Found: C, 49.36; H, 4.14; N, 9.15.

Nickle complex **Ni5**:




General procedure was followed on **L5** (100.0 mg, 0.22 mmol), DME·$NiCl_2$ (39.5 mg, 0.18 mmol) and super dry EtOH (5 mL), affording **Ni5** as yellow solid (77.1 mg, 60%). Anal. Calcd. for $C_{30}H_{30}Cl_2N_4Ni·0.5$ EtOH (%): C, 62.14; H, 5.55; N, 9.35; Found: C, 62.11; H,5.2; N, 9.45.

**2.2 Synthesis of Nickel Complexes Ni3-Al**

Inside a glovebox, complex **Ni3** (60 mg, 0.09 mmol), $PPh_3$ (236 mg, 0.9 mmol), 18 mL of THF, and 12 mL of diethyl ether were charged into a 50 mL Schlenk tube. The mixture was stirred at room temperature for 30 min, followed by the dropwise addition of $Et_2AlCl$ (0.9 mL, 0.9 mmol, 1 M in toluene). After stirring for an additional 10 min, the resulting mixture was filtered to afford a pale-yellow solution. n-Hexane (10 mL) was slowly added along the wall, and the solution was maintained at −40 °C for recrystallization over 72 h. The crystalline solid was collected by filtration and washed with cold n-hexane, affording yellow crystals of the **Ni3**–**Al** complex ([**L3**·$NiCl(THF)_2$]$^{+}$·$EtAlCl_3^{-}$) (23 mg, 27%). Anal. Calc for $C_{47}H_{57}AlCl_4N_4NiO_2·H_2O$: C, 59.08; H, 6.22; N, 5.86. Found: C, 59.00; H, 6.25; N, 5.48.

**3. Oligomerization of ethylene: General procedure**

Before the reaction, a 250 mL stainless-steel reactor was dried at 120 °C under vacuum for 3 h, cooled down to the desired reaction temperature and then recharged with ethylene three times. The nickel complex catalyst was first weighed into a Schlenk vessel under nitrogen; then, toluene and cocatalyst were added into the Schlenk vessel in turn. The resulting mixture was stirred for 1 min and immediately added to the stainless-steel reactor. Then, the reactor was immediately pressurized. After the specified reaction time, the reaction was stopped by shutting in the ethylene feed. The reaction system was cooled to around -20 °C, depressurized, and

quenched by the addition of 30 mL of 10% aq. HCl solution. A small sample of the upper-layer solution was filtered through a layer of Celite and analyzed by GC using nonane as the internal standard. The individual oligomerization products were identified by GC-MS.

References:

[1] Andaloussi, M.; Moreau, E.; Masurier, N.; Lacroix, J.; Gaudreault, R. C.; Chezal, J.-M.; El Laghdach, A.; Canitrot, D.; Debiton, E.; Teulade, J.-C.; Chavignon, O. Novel imidazo[1,2-a]naphthyridinic systems (part 1): Synthesis, antiproliferative and DNA-intercalating activities. *Eur. J. Med. Chem.* **2008**, *43*, 2505-2517.

[2] Levine, S. G.; Mauney, C. U. Facile preparation of a butane-2,3-dione monoketal. *Synth. Commun.* **1988**, *18*, 689-691.

## 4. X-Ray Crystallography for Nickel Complexes

Crystallization procedures of Nickel complexes **Ni1**–**Ni3** and **Ni5**: Single crystals of **Ni1**–**Ni3** and **Ni5** suitable for single-crystal X-ray diffraction were grown by slow diffusion of diethyl ether (4.0 mL) into a DMF solution (0.5 mL) of nickel complexes **Ni1**–**Ni3** or **Ni5** (20 mg) in a dried Schlenk tube under an argon atmosphere.

Crystallization procedure of Nickel complex **Ni3-Al**: In a glovebox, $PPh_3$ (78 mg, 300 μmol) was added to a solution of complex **Ni3** (20 mg, 30 μmol) in 10 mL of THF/$Et_2O$ (3:2 v/v). After stirring at room temperature for 30 min, $Et_2AlCl$ (0.3 mL, 300 μmol, 1 M in toluene) was added. The resulting mixture was stirred for another 10 min, and then filtered to obtain a pale-yellow solution. Single crystal of **Ni3–Al** suitable for single-crystal X-ray diffraction was grown by slowly diffusing n-hexane (5 mL) into the above solution at -40 °C in a dried Schlenk tube under an argon atmosphere.

All of these crystals were mounted on a glass fiber. Crystallographic measurements were made on a Bruker APEX-II CCD area detector using graphite monochromated Cu-Kα radiation ($\lambda_{Cu\text{-}K\alpha}$ = 1.54178 Å). Refinements and reductions of the collected data were achieved using the Bruker SAINT program and applied to all complexes with absorption correction (multi-scan). The structures were solved by directed methods and refined on $F^2$ by the full-matrix least-squares techniques with the SHELXTL-2016 program.

Key details of the crystals and structure refinement data are summarized in Table S1-S5. Further crystallographic details may be found in the respective CIF files, which were deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK.

**Table S1 Crystal data and structure refinement for Ni1**.

| | |
|---|---|
| CCDC No. | 2542431 |
| Empirical formula | $C_{23}H_{25}Cl_2N_5NiO$ |
| Formula weight | 517.09 |
| Temperature/K | 290.0 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 10.4692(2) |
| b/Å | 11.8245(2) |
| c/Å | 13.6613(2) |
| α/° | 65.2764(9) |
| β/° | 82.8550(9) |
| γ/° | 65.3355(9) |
| Volume/Å$^3$ | 1393.43(4) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.232 |
| μ/mm$^{-1}$ | 2.941 |
| F(000) | 536.0 |
| Crystal size/mm$^3$ | 0.1 × 0.1 × 0.1 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 7.136 to 149.396 |
| Index ranges | $-13 \leq h \leq 12$, $-14 \leq k \leq 14$, $-17 \leq l \leq 16$ |
| Reflections collected | 19502 |
| Independent reflections | 5581 [$R_{int}$ = 0.0322, $R_{sigma}$ = 0.0321] |
| Data/restraints/parameters | 5581/1/313 |
| Goodness-of-fit on F$^2$ | 1.078 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0419, $wR_2$ = 0.1209 |
| Final R indexes [all data] | $R_1$ = 0.0443, $wR_2$ = 0.1228 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.34/-0.40 |

**Table S2 Crystal data and structure refinement for Ni2.**

| | |
|---|---|
| CCDC No. | 2542445 |
| Empirical formula | $C_{24}H_{26}Cl_2N_4Ni$ |
| Formula weight | 500.10 |
| Temperature/K | 200.00 |
| Crystal system | orthorhombic |
| Space group | Pbca |
| a/Å | 14.6615(2) |
| b/Å | 15.7274(3) |
| c/Å | 19.5070(3) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 4498.07(13) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.477 |
| μ/mm$^{-1}$ | 3.576 |
| F(000) | 2080.0 |
| Crystal size/mm$^3$ | 0.04 × 0.03 × 0.015 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 9.41 to 149.074 |
| Index ranges | $-18 \leq h \leq 17$, $-19 \leq k \leq 14$, $-23 \leq l \leq 23$ |
| Reflections collected | 39760 |
| Independent reflections | 4590 [$R_{int}$ = 0.0580, $R_{sigma}$ = 0.0281] |
| Data/restraints/parameters | 4590/0/285 |
| Goodness-of-fit on F$^2$ | 1.030 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0367, $wR_2$ = 0.0935 |
| Final R indexes [all data] | $R_1$ = 0.0446, $wR_2$ = 0.0981 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.91/-0.31 |

**Table S3 Crystal data and structure refinement for Ni3.**

| | |
|---|---|
| CCDC No. | 2542441 |
| Empirical formula | $C_{40}H_{43}Cl_2N_5NiO$ |
| Formula weight | 739.40 |
| Temperature/K | 200.0 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 9.8014(2) |
| b/Å | 15.5910(3) |
| c/Å | 16.5325(3) |
| α/° | 116.0100(10) |
| β/° | 92.7180(10) |
| γ/° | 105.9430(10) |
| Volume/Å$^3$ | 2141.58(7) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.147 |
| μ/mm$^{-1}$ | 2.058 |
| F(000) | 776.0 |
| Crystal size/mm$^3$ | 0.05 × 0.01 × 0.01 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 6.68 to 149.766 |
| Index ranges | -12 ≤ h ≤ 12, -17 ≤ k ≤ 19, -20 ≤ l ≤ 20 |
| Reflections collected | 44850 |
| Independent reflections | 8765 [$R_{int}$ = 0.0489, $R_{sigma}$ = 0.0327] |
| Data/restraints/parameters | 8765/7/485 |
| Goodness-of-fit on F$^2$ | 1.069 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0335, w$R_2$ = 0.0912 |
| Final R indexes [all data] | $R_1$ = 0.0410, w$R_2$ = 0.0951 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.27/-0.33 |

**Table S4 Crystal data and structure refinement for Ni5.**

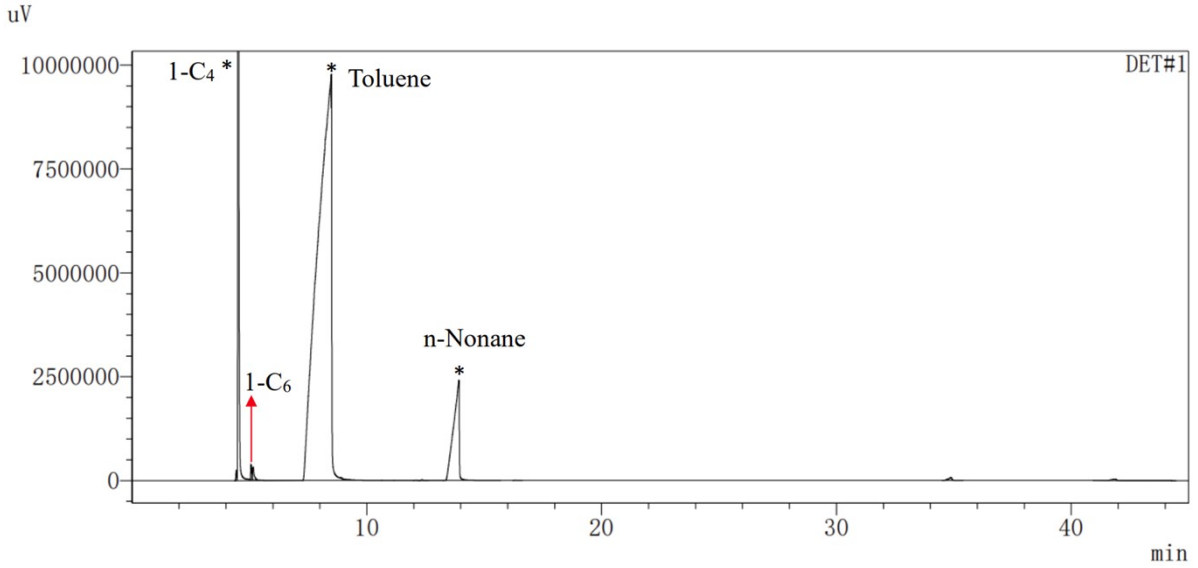
| | |
|---|---|
| CCDC No. | 2542434 |
| Empirical formula | $C_{33}H_{37}Cl_2N_5NiO$ |
| Formula weight | 649.28 |
| Temperature/K | 200.0 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 12.9309(2) |
| b/Å | 13.2937(2) |
| c/Å | 19.3267(4) |
| α/° | 90 |
| β/° | 100.2736(9) |
| γ/° | 90 |
| Volume/Å$^3$ | 3268.99(10) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.319 |
| μ/mm$^{-1}$ | 2.619 |
| F(000) | 1360.0 |
| Crystal size/mm$^3$ | 0.1 × 0.1 × 0.1 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 6.948 to 149.406 |
| Index ranges | -15 ≤ h ≤ 15, -15 ≤ k ≤ 16, -24 ≤ l ≤ 23 |
| Reflections collected | 41821 |
| Independent reflections | 6654 [$R_{int}$ = 0.0373, $R_{sigma}$ = 0.0254] |
| Data/restraints/parameters | 6654/0/386 |
| Goodness-of-fit on $F^2$ | 1.082 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0420, $wR_2$ = 0.1209 |
| Final R indexes [all data] | $R_1$ = 0.0453, $wR_2$ = 0.1233 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.53/-0.52 |

**Table S5 Crystal data and structure refinement for Ni3-Al**.

| | |
|---|---|
| CCDC No. | 2542443 |
| Empirical formula | $C_{51}H_{64}AlCl_4N_4NiO_3$ |
| Formula weight | 1008.55 |
| Temperature/K | 150.00 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 13.6838(5) |
| b/Å | 14.2840(5) |
| c/Å | 16.1028(6) |
| α/° | 101.275(2) |
| β/° | 90.059(2) |
| γ/° | 108.916(2) |
| Volume/Å$^3$ | 2912.95(19) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.150 |
| μ/mm$^{-1}$ | 2.621 |
| F(000) | 1062.0 |
| Crystal size/mm$^3$ | 0.07 × 0.04 × 0.03 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 5.61 to 150.334 |
| Index ranges | -17 ≤ h ≤ 17, -15 ≤ k ≤ 17, -20 ≤ l ≤ 20 |
| Reflections collected | 50560 |
| Independent reflections | 11858 [$R_{int}$ = 0.0569, $R_{sigma}$ = 0.0520] |
| Data/restraints/parameters | 11858/12/605 |
| Goodness-of-fit on F$^2$ | 1.085 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0508, w$R_2$ = 0.1484 |
| Final R indexes [all data] | $R_1$ = 0.0614, w$R_2$ = 0.1570 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.44/-0.72 |

## 5. Gas chromatograms (GC) of the oligomers

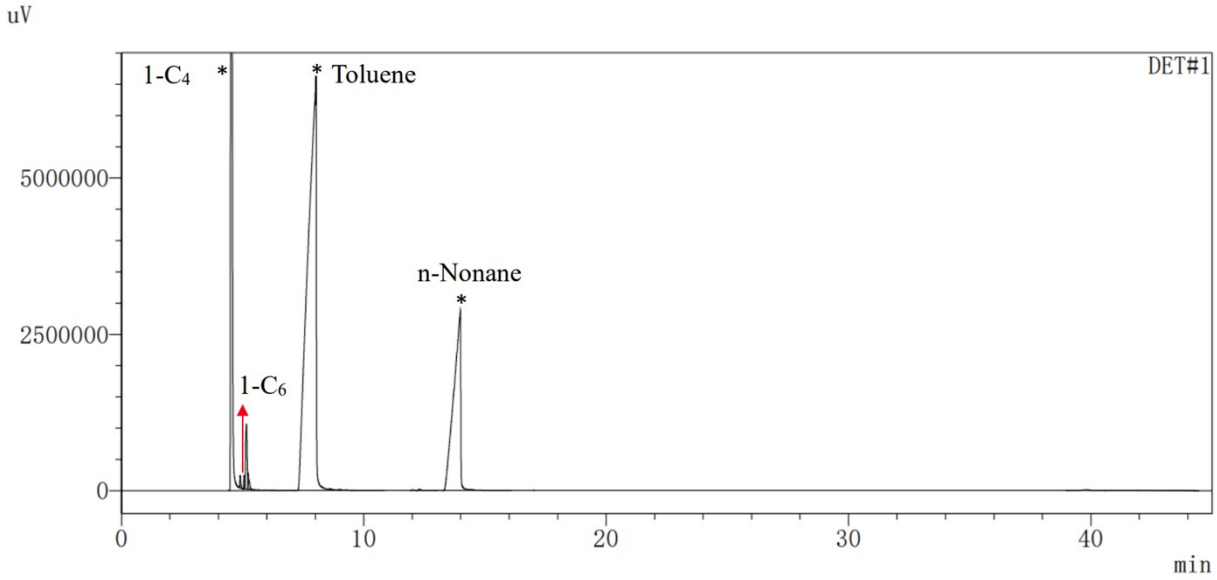
Quantitative gas chromatographic analysis of the products of oligomerization was performed on a Shimadzu GC 2014 Series GC instrument with a J&W DB-1 column working at 30 °C for 10 min and then heating at 10 °C $min^{-1}$ until 280 °C. n-Nonane was used as an internal standard.




DET#1

| Peak No | Ret. Time(min) | Peak height | Area(counts) | Area(%) | SepCode |
|---|---|---|---|---|---|
| 1 | 4.439 | 245807 | 569926 | 0.1129 | |
| 2 | 4.515 | 22158910 | 65803324 | 12.9659 | SV |
| 3 | 5.069 | 363796 | 1124589 | 0.2229 | T |
| 4 | 5.161 | 313041 | 1492983 | 0.2949 | TV |
| 5 | 8.493 | 9787744 | 396355228 | 78.0919 | SV |
| 6 | 8.903 | 22857 | 64177 | 0.0139 | T |
| 7 | 12.087 | 9261 | 51052 | 0.0109 | T |
| 8 | 12.343 | 16344 | 82994 | 0.0169 | TV |
| 9 | 13.923 | 2420827 | 40484420 | 7.9769 | |
| 10 | 16.321 | 6945 | 41329 | 0.0089 | |
| 11 | 34.876 | 72644 | 777321 | 0.1539 | |
| 12 | 41.861 | 33228 | 531472 | 0.1059 | |
| 13 | 42.927 | 1801 | 58797 | 0.0129 | V |
| 14 | 44.218 | 1976 | 114859 | 0.0239 | V |
| Total | | 35455182 | 507552471 | 100.0009 | |

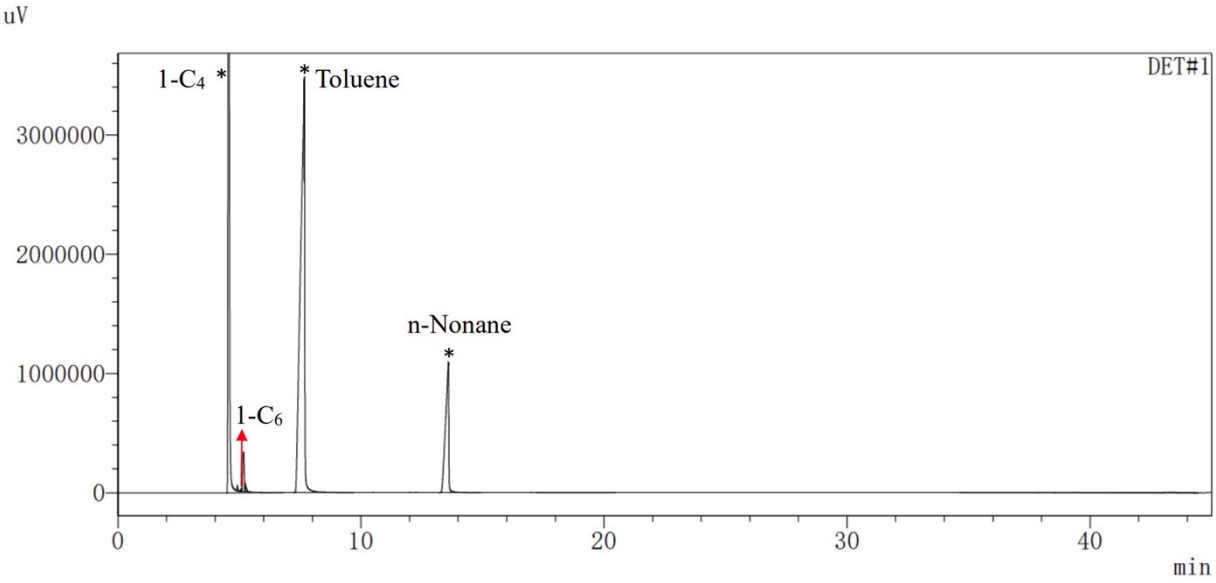
**Figure S1** GC trace and data for oligomers produced with complex **Ni3**/$Et_2AlCl$ at 20 °C and 3.0 MPa of ethylene pressure (Table 3, entry 12)




DET#1

| Peak No | Ret. Time(min) | Peak height | Area(counts) | Area(%) | SepCode |
|---|---|---|---|---|---|
| 1 | 4.533 | 21069905 | 81925479 | 26.8529 | S |
| 2 | 4.903 | 202158 | 528172 | 0.1739 | T |
| 3 | 5.066 | 217547 | 517591 | 0.1709 | T |
| 4 | 5.159 | 1048342 | 4637410 | 1.5209 | TV |
| 5 | 5.229 | 251661 | 946723 | 0.3109 | TV |
| 6 | 8.030 | 6633177 | 158569630 | 51.9729 | SV |
| 7 | 8.606 | 12981 | 56006 | 0.0189 | T |
| 8 | 9.014 | 8287 | 41005 | 0.0139 | T |
| 9 | 12.028 | 10786 | 68013 | 0.0229 | |
| 10 | 12.289 | 18347 | 124884 | 0.0419 | V |
| 11 | 13.986 | 2893324 | 57116111 | 18.7209 | |
| 12 | 39.844 | 11684 | 275588 | 0.0909 | |
| 13 | 41.600 | 1417 | 79605 | 0.0269 | V |
| 14 | 44.202 | 1976 | 217947 | 0.0719 | V |
| Total | | 32381593 | 305104163 | 100.0009 | |

**Figure S2** GC trace and data for oligomers produced with complex **Ni3**/$Et_2AlCl$/$PPh_3$ (10 equiv.) at 20 °C and 3.0 MPa of ethylene pressure (Table 4, entry 6)



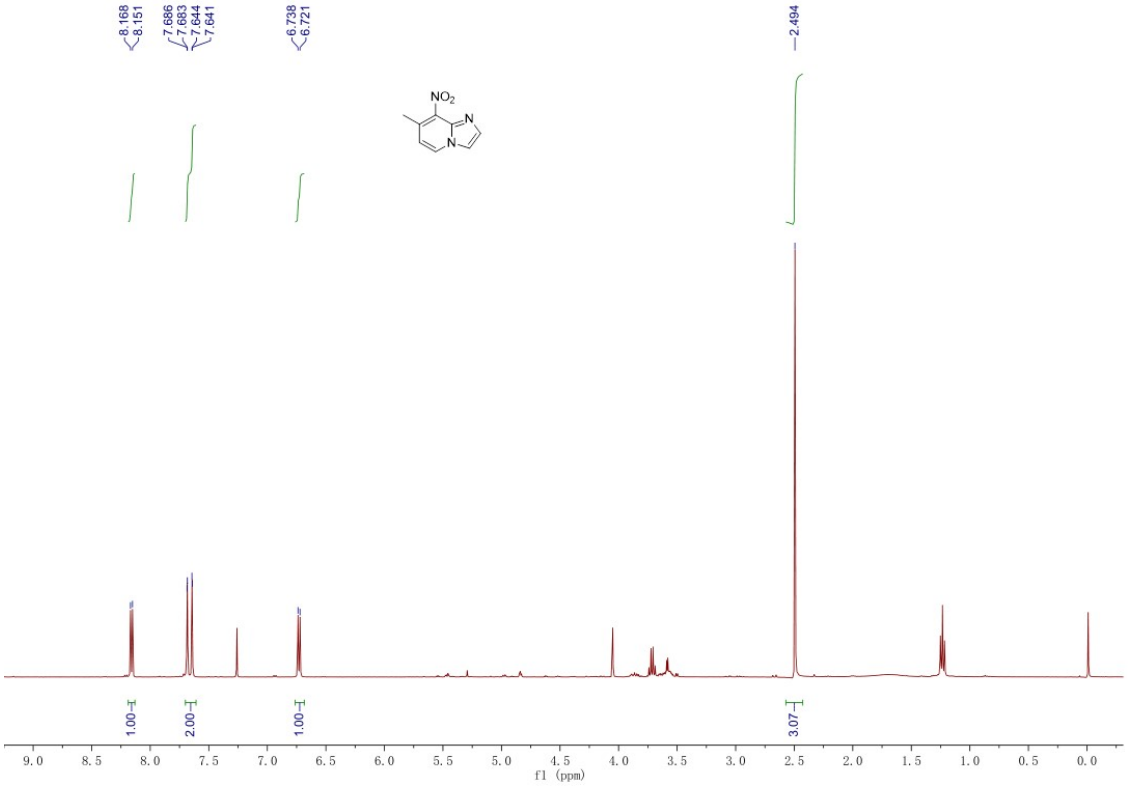

DET#1

| Peak No | Ret. Time(min) | Peak height | Area(counts) | Area(%) | SepCode |
|---|---|---|---|---|---|
| 1 | 4.555 | 8727511 | 29321301 | 35.0869 | S |
| 2 | 4.915 | 46893 | 120407 | 0.1449 | T |
| 3 | 5.079 | 13399 | 29565 | 0.0359 | T |
| 4 | 5.169 | 200873 | 875934 | 1.0489 | TV |
| 5 | 5.241 | 71544 | 247669 | 0.2969 | TV |
| 6 | 7.674 | 3637323 | 41924884 | 50.4689 | |
| 7 | 13.597 | 1097102 | 10097168 | 12.0829 | |
| 8 | 17.938 | 474 | 41979 | 0.0509 | |
| 9 | 37.761 | 1387 | 159713 | 0.1919 | |
| 10 | 37.991 | 1483 | 61035 | 0.0739 | V |
| 11 | 43.266 | 4732 | 610018 | 0.7309 | V |
| 12 | 43.817 | 2540 | 80500 | 0.0969 | V |
| Total | | 13805261 | 83570173 | 100.0009 | |

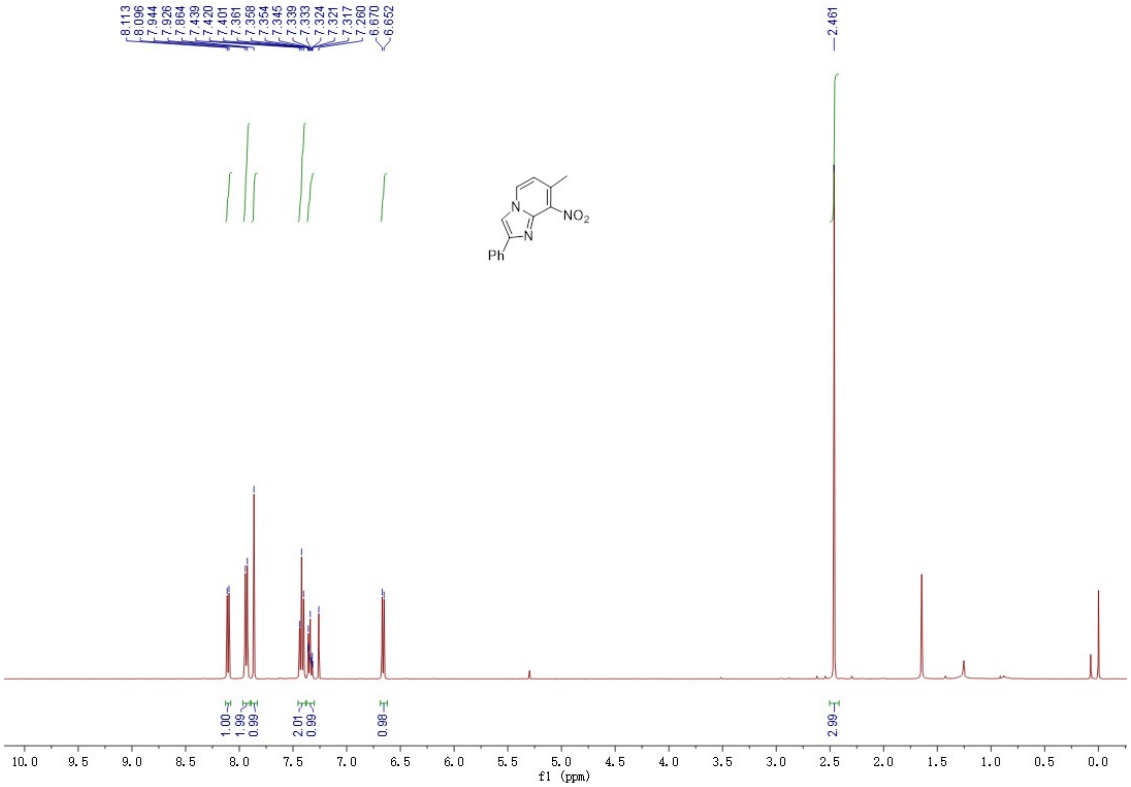
**Figure S3** GC trace and data for oligomers produced with complex **Ni3-Al**/$Et_2AlCl/PPh_3$ (10 equiv.) at 20 °C and 3.0 MPa of ethylene pressure (Table 4, entry 9)

## 6. NMR spectrum of Compounds S1-S6 and L1-L5

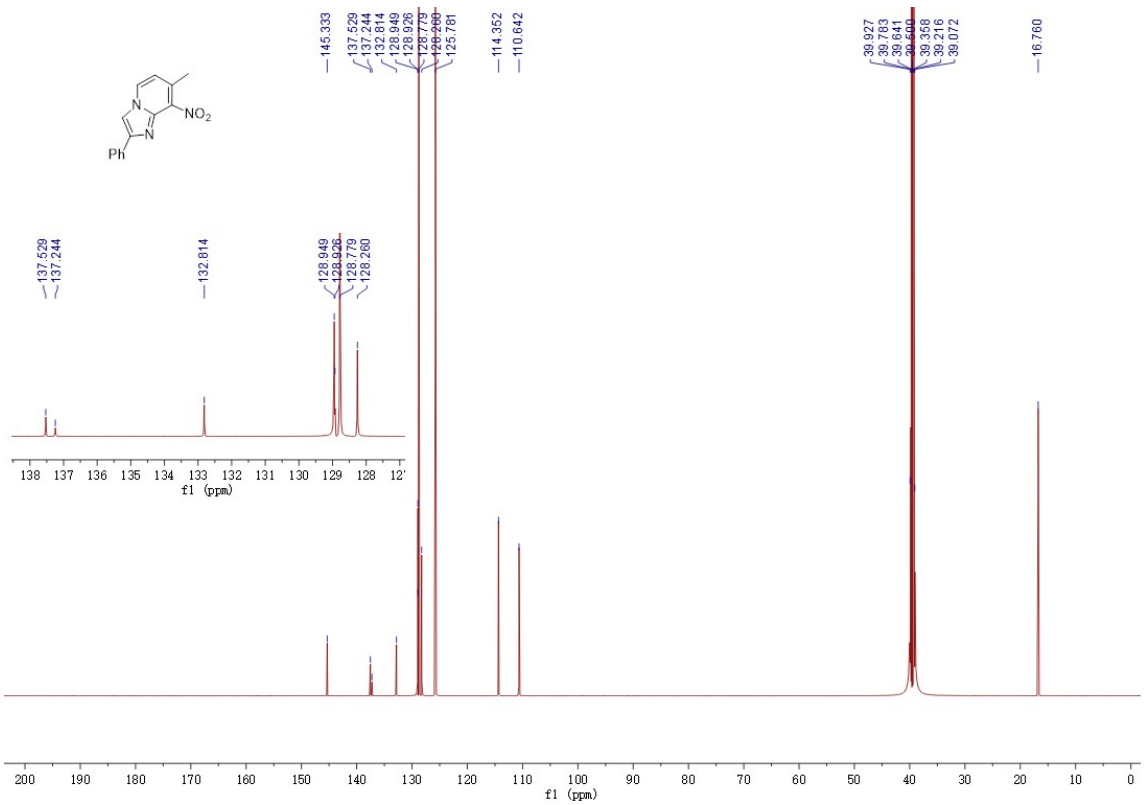
$^1$H NMR of **S1a** (400 M, $CDCl_3$)



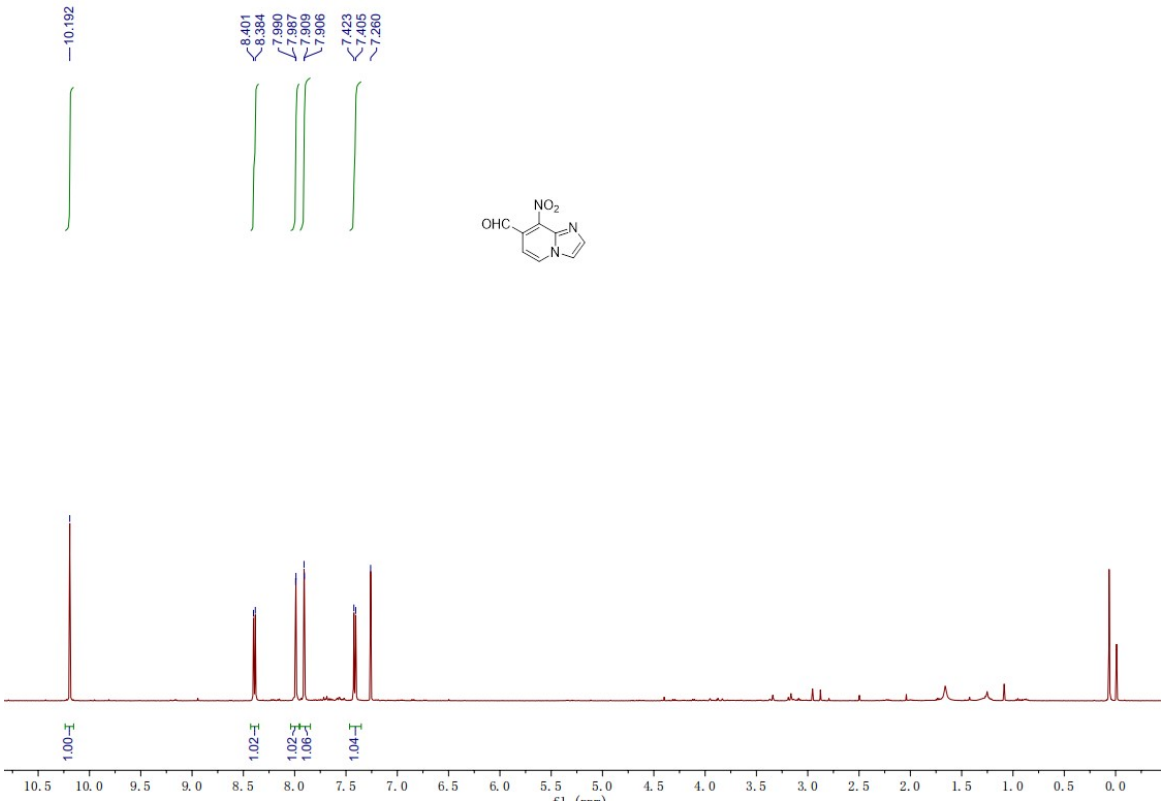

$^1$H NMR of **S1b** (400 M, $CDCl_3$)



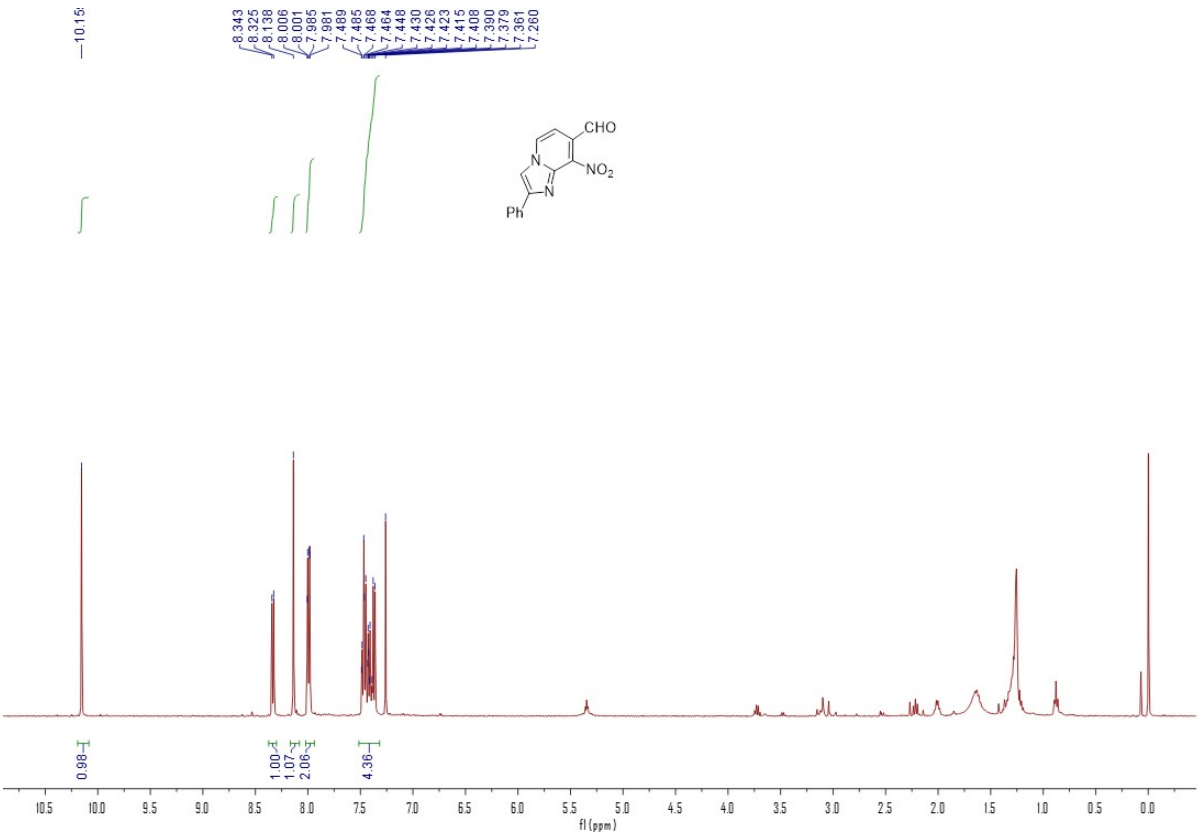
$^{13}$C NMR of **S1b** (151 M, DMSO)



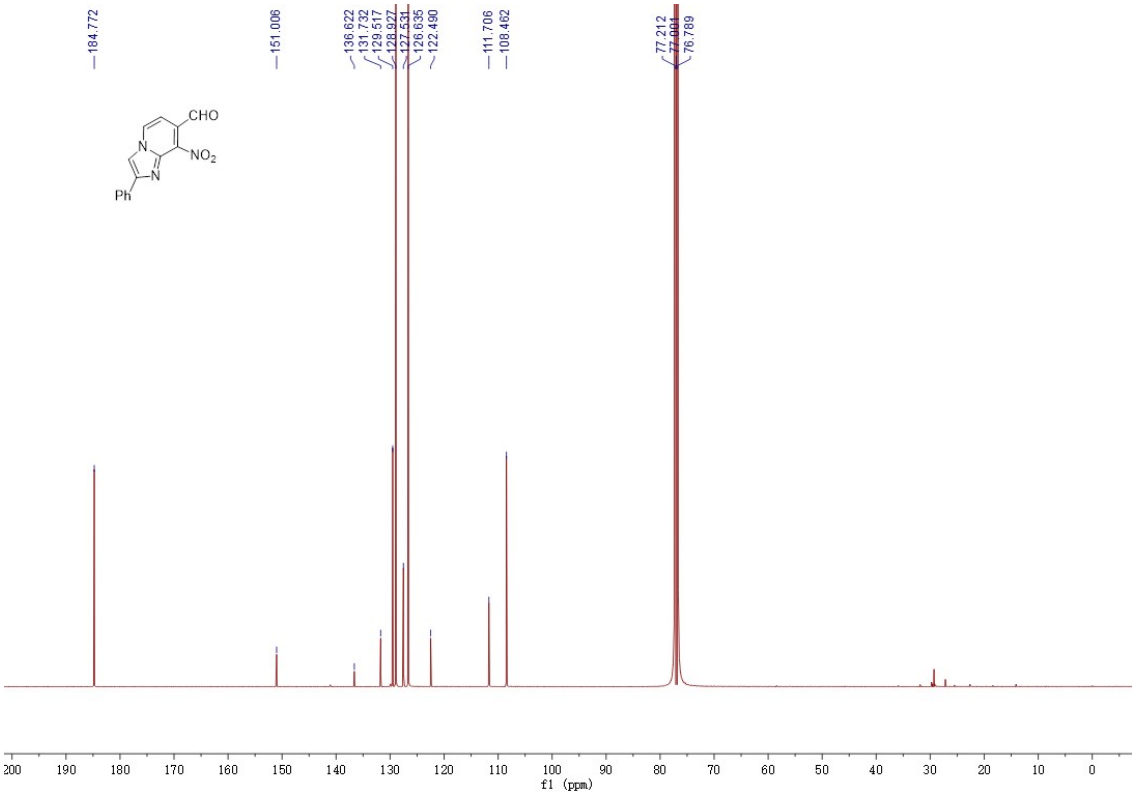

$^{1}$H NMR of **S2a** (400 M, $CDCl_3$)



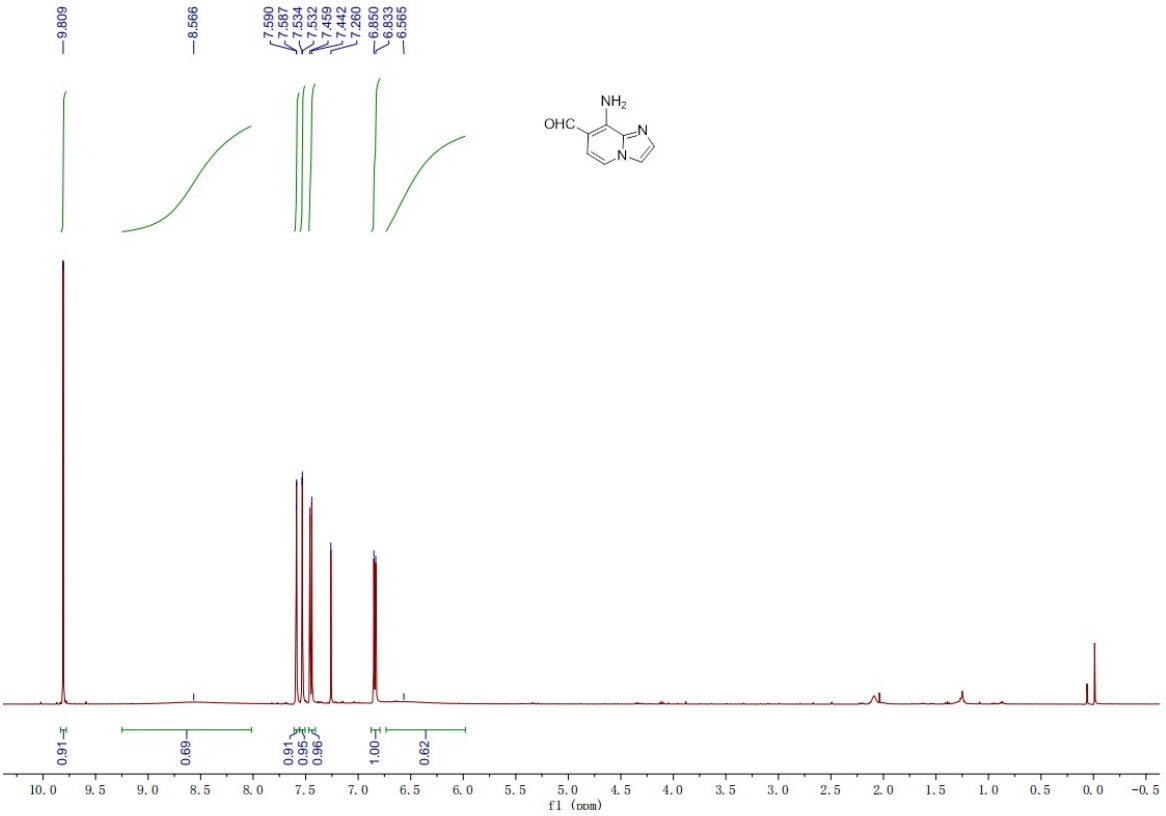
$^{1}$H NMR of **S2b** (400 M, $CDCl_3$)



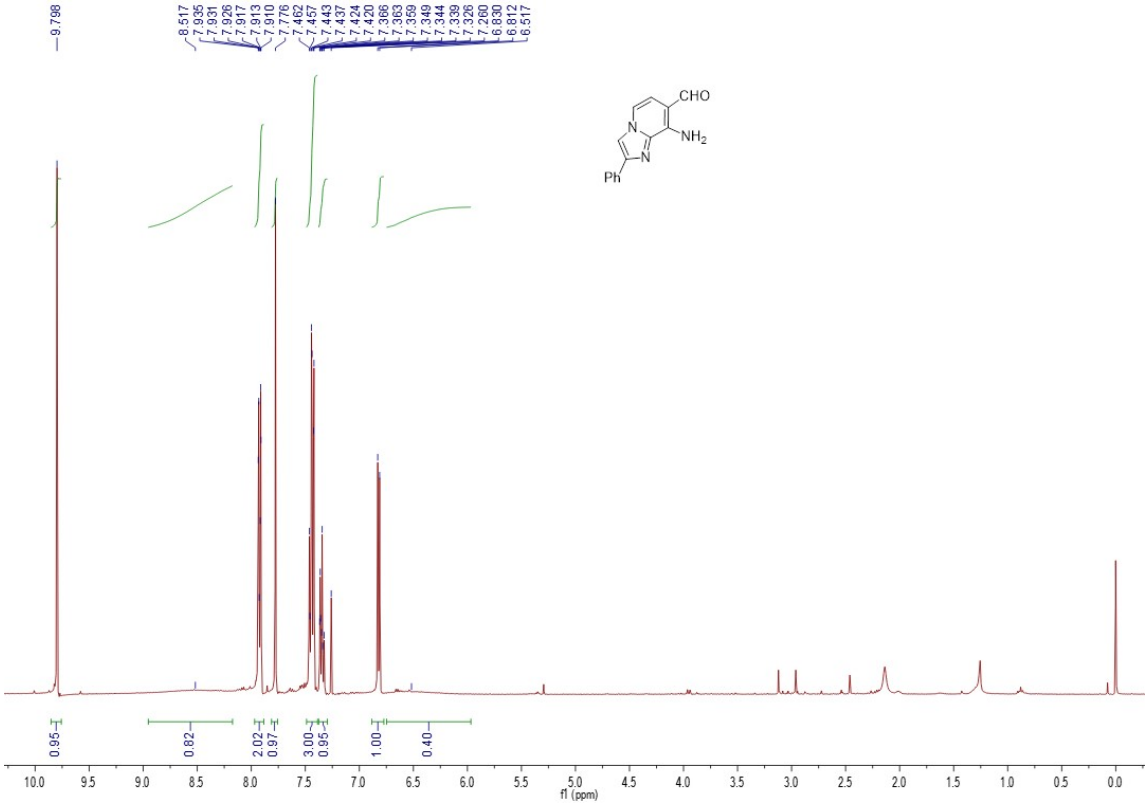

$^{13}$C NMR of **S2b** (151 M, $CDCl_3$)



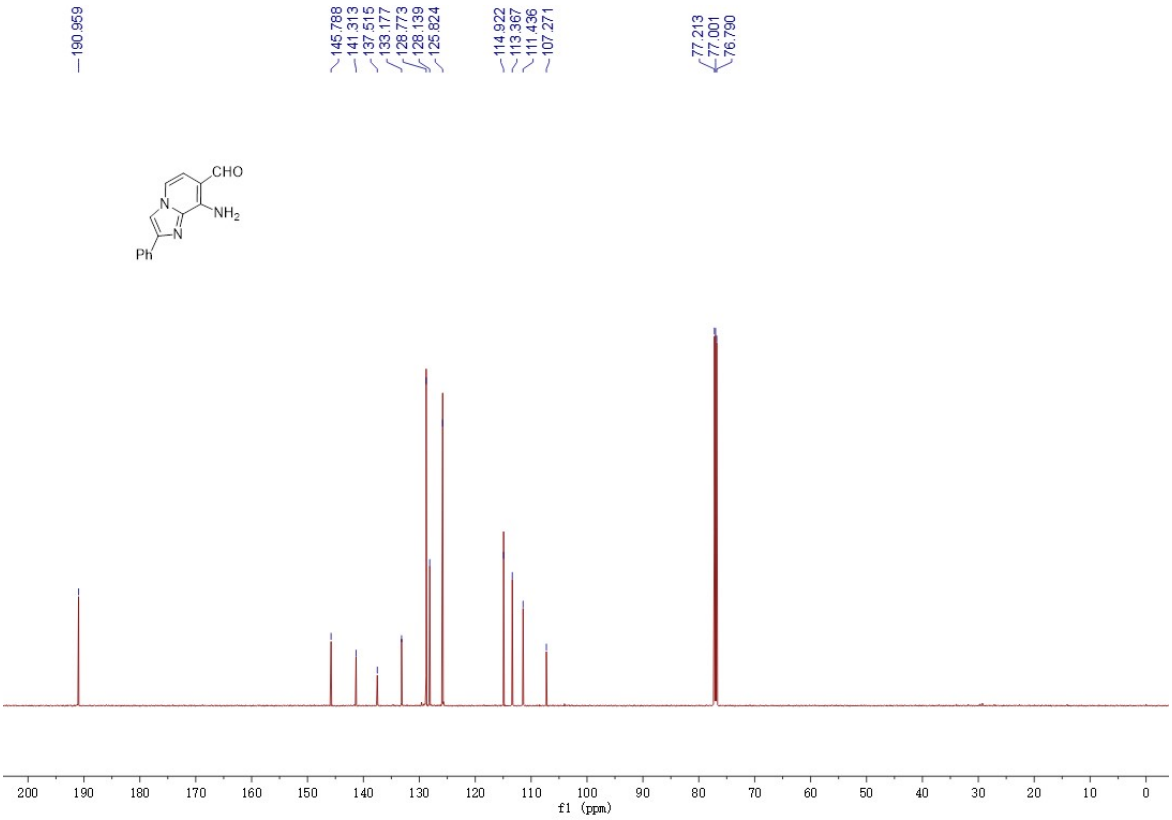
$^1$H NMR of **S3a** (400 M, $CDCl_3$)



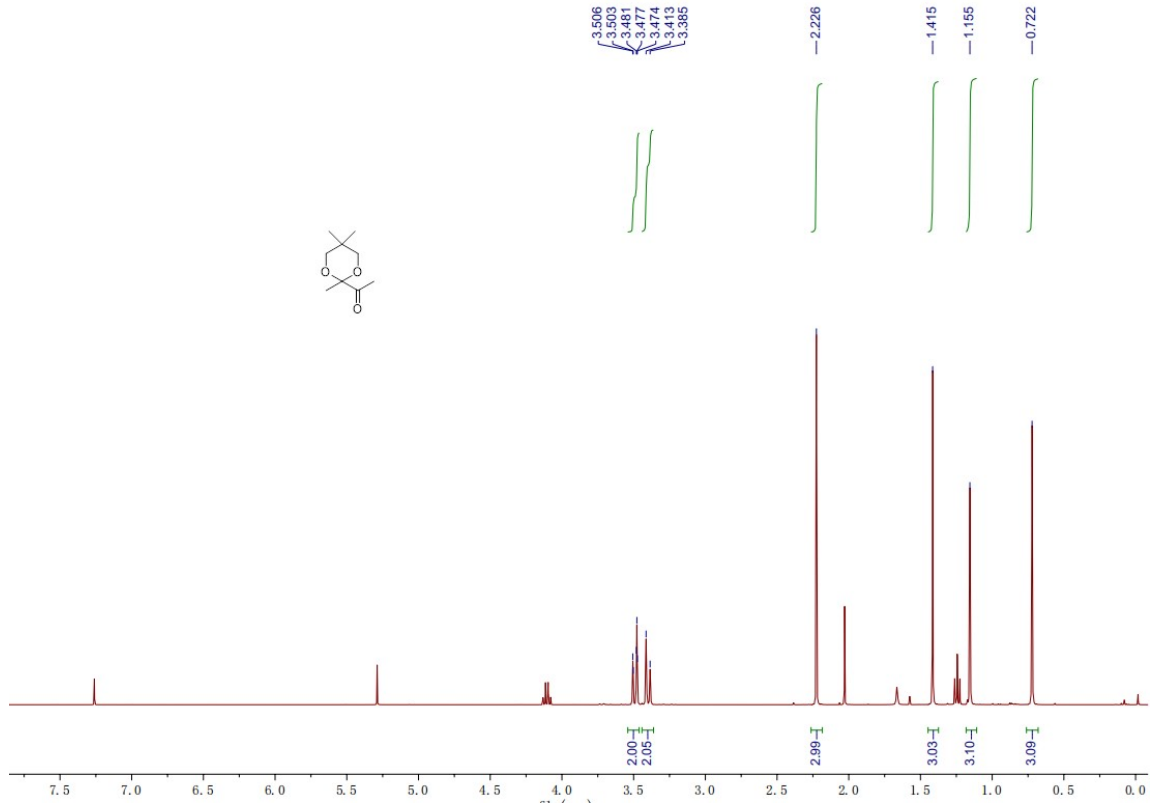

$^1$H NMR of **S3b** (400 M, $CDCl_3$)



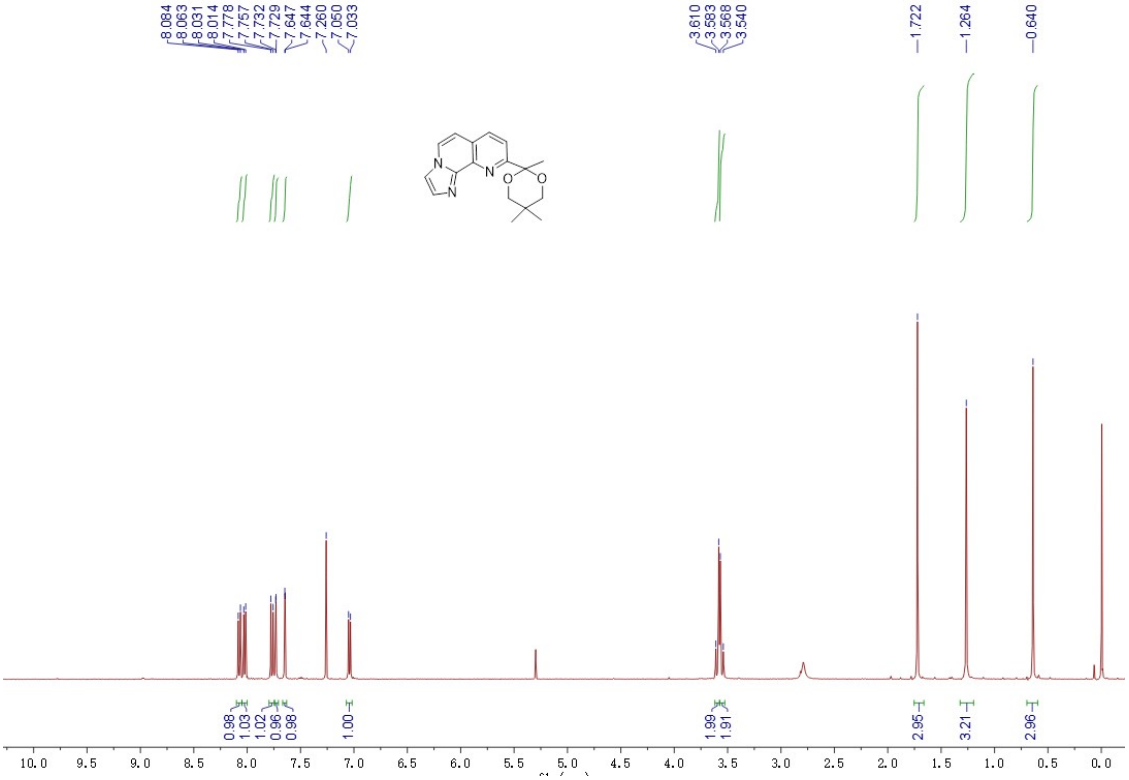
$^{13}$C NMR of **S3b** (151 M, $CDCl_3$)



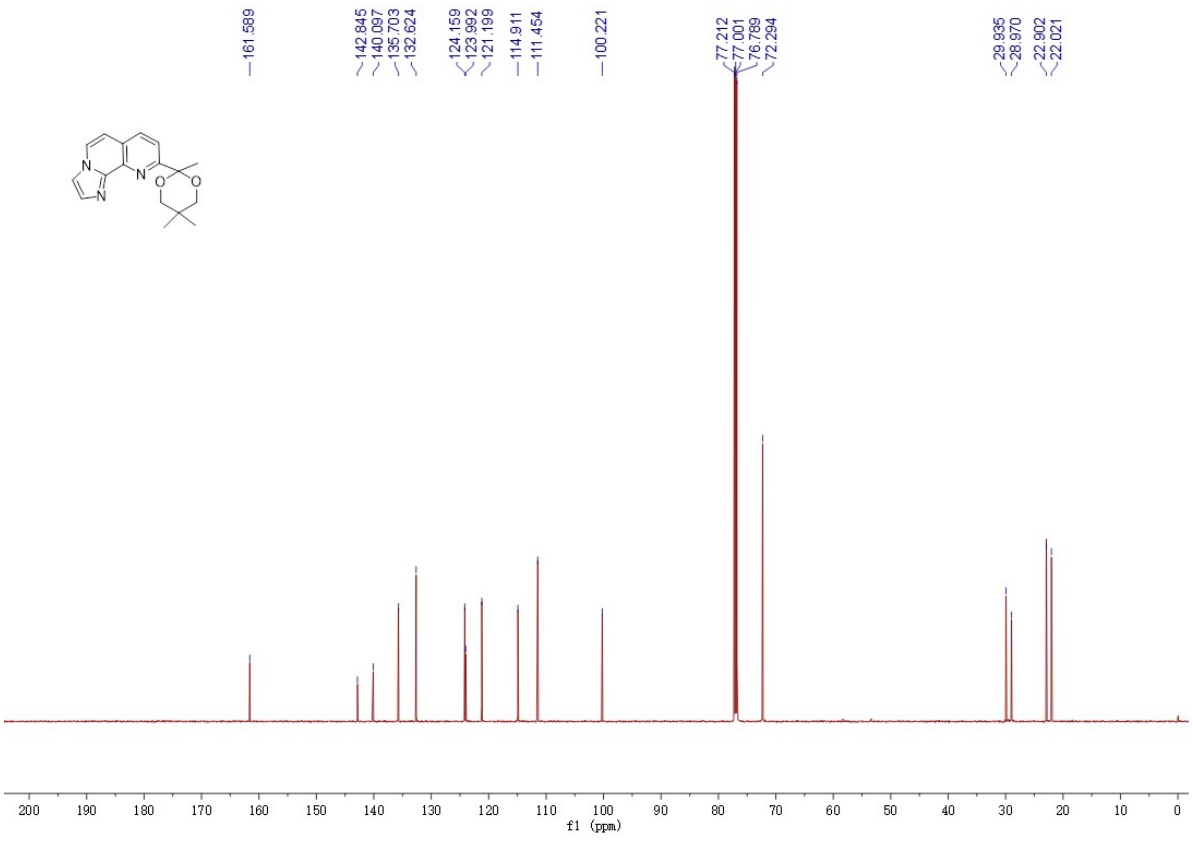

$^{1}$H NMR of **S4** (400 M, $CDCl_3$)



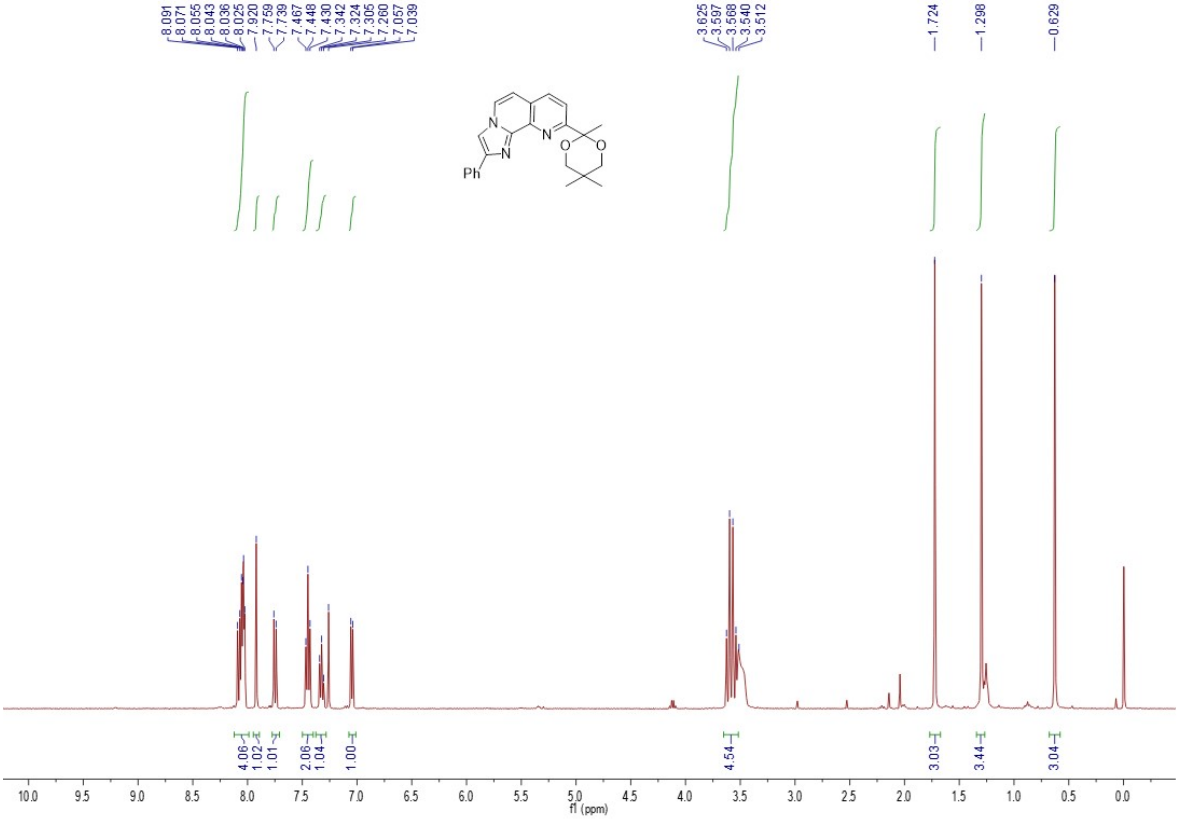
$^{1}$H NMR of **S5a** (400 M, $CDCl_3$)



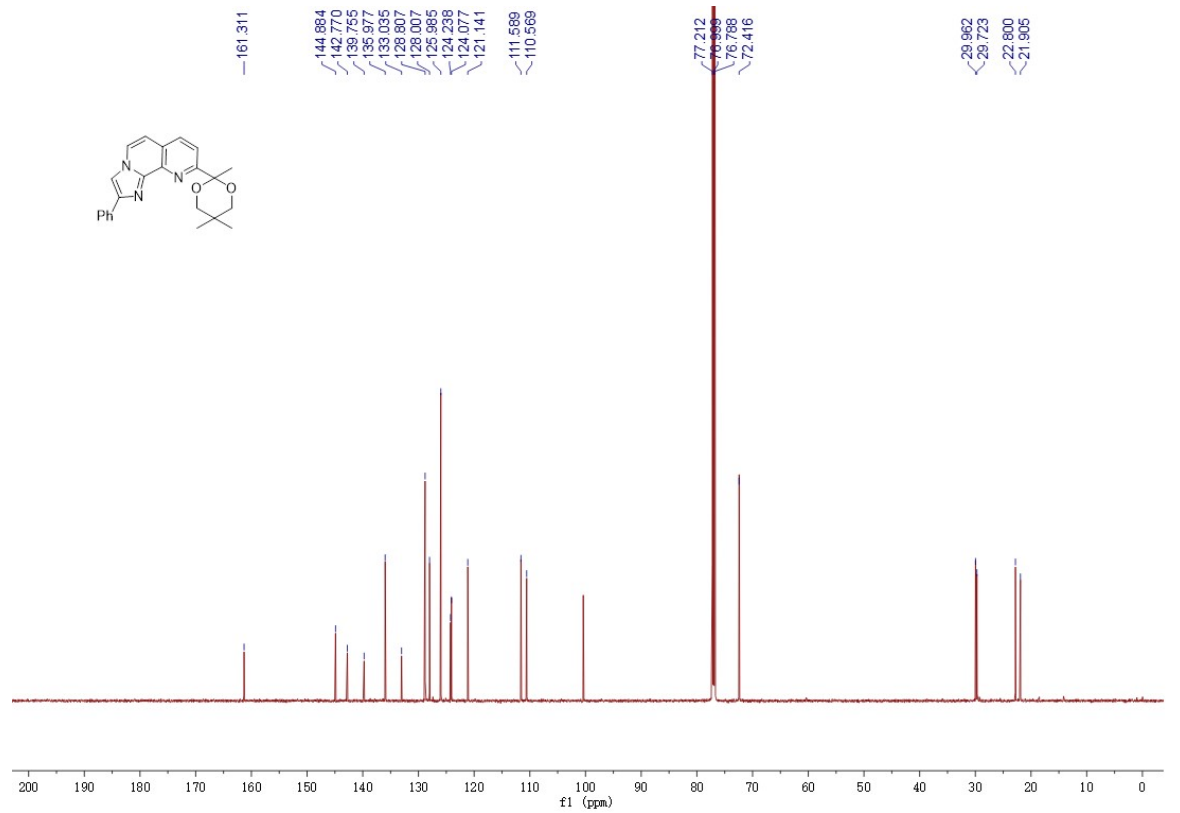

$^{13}$C NMR of **S5a** (151 M, $CDCl_3$)



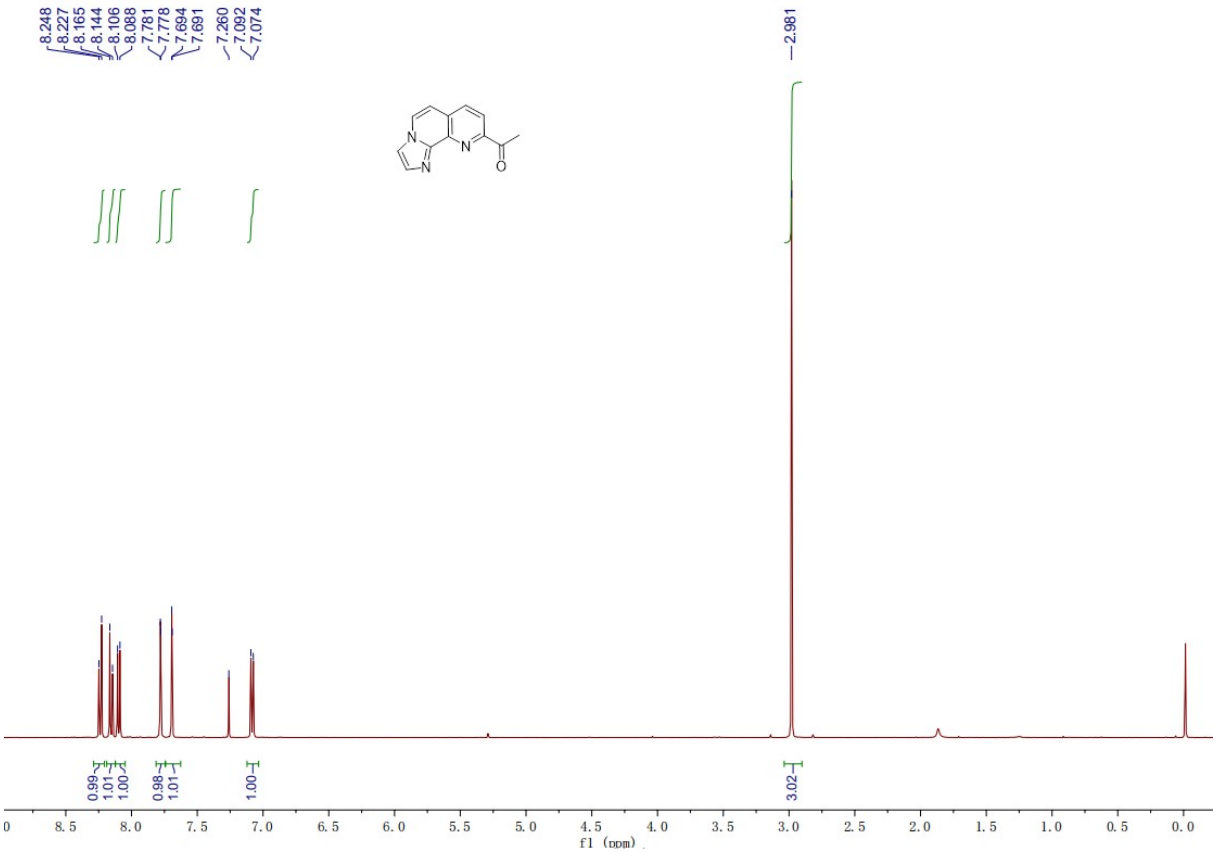
$^{1}$H NMR of **S5b** (400 M, $CDCl_3$)



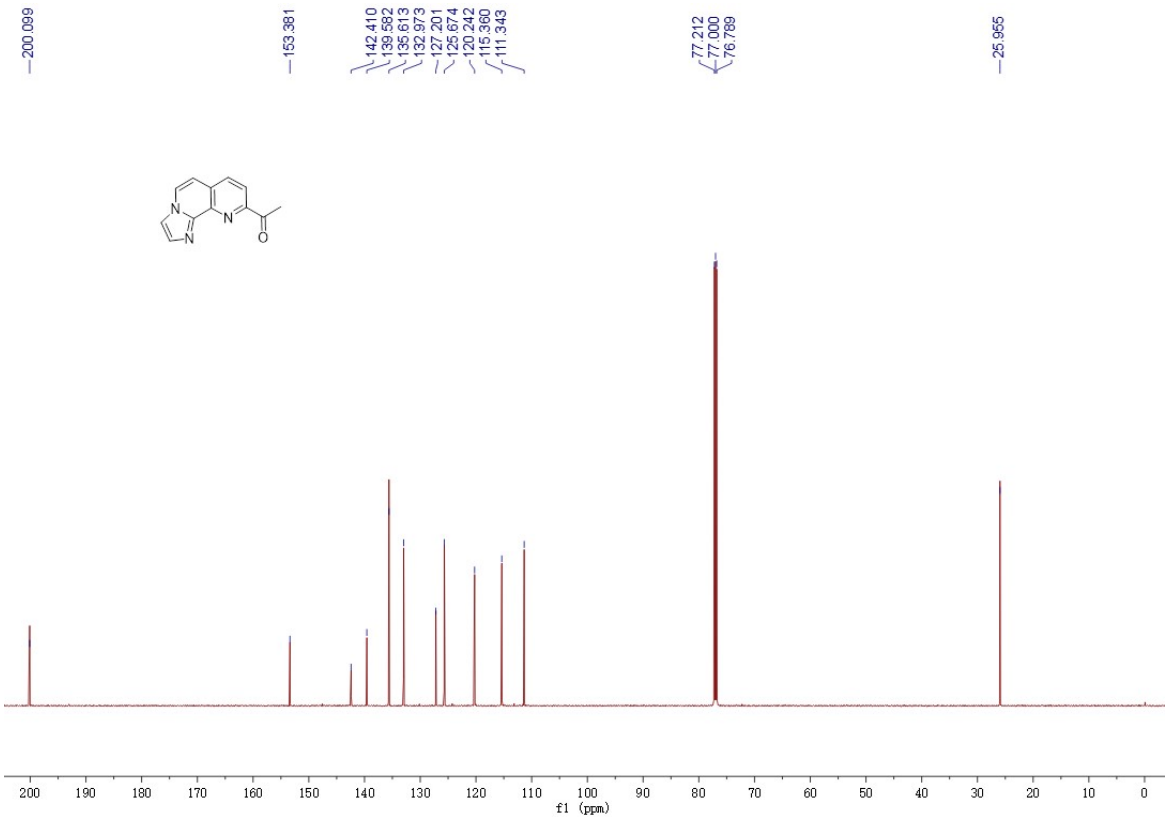

$^{13}$C NMR of **S5b** (151 M, $CDCl_3$)



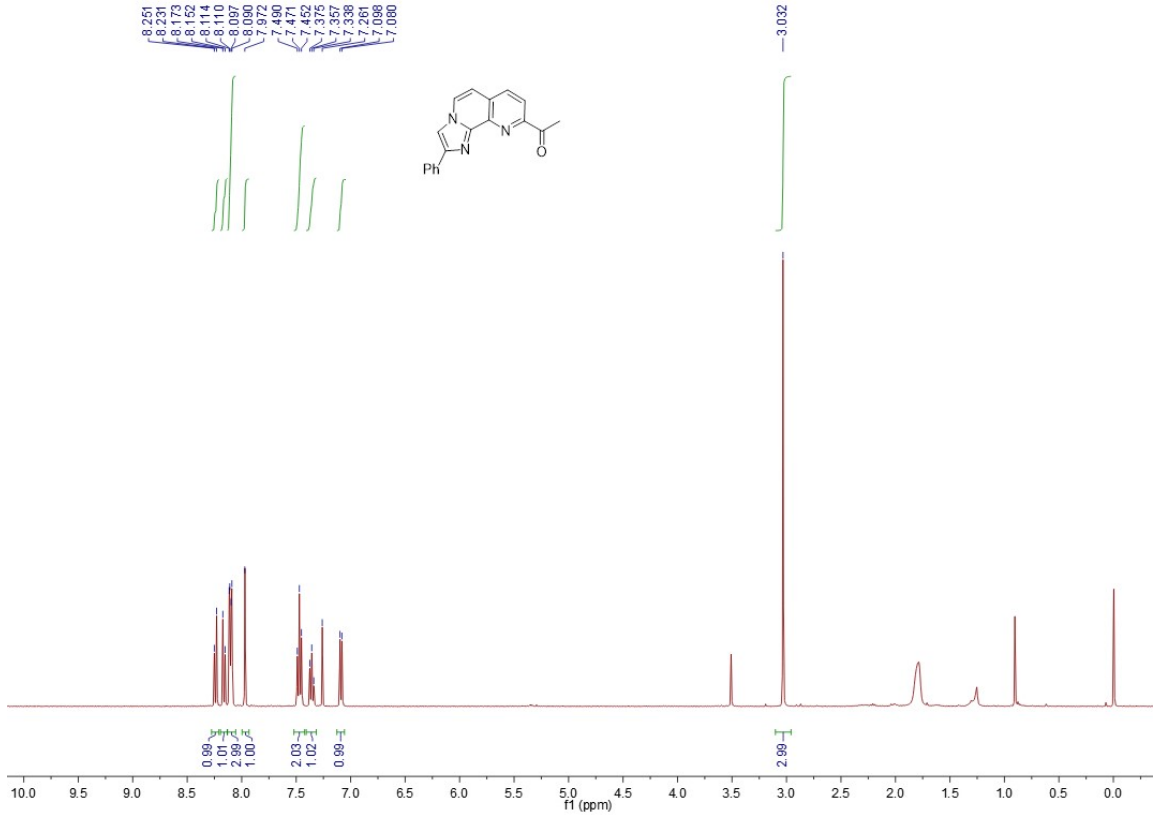
$^{1}$H NMR of **S6a** (400 M, $CDCl_3$)



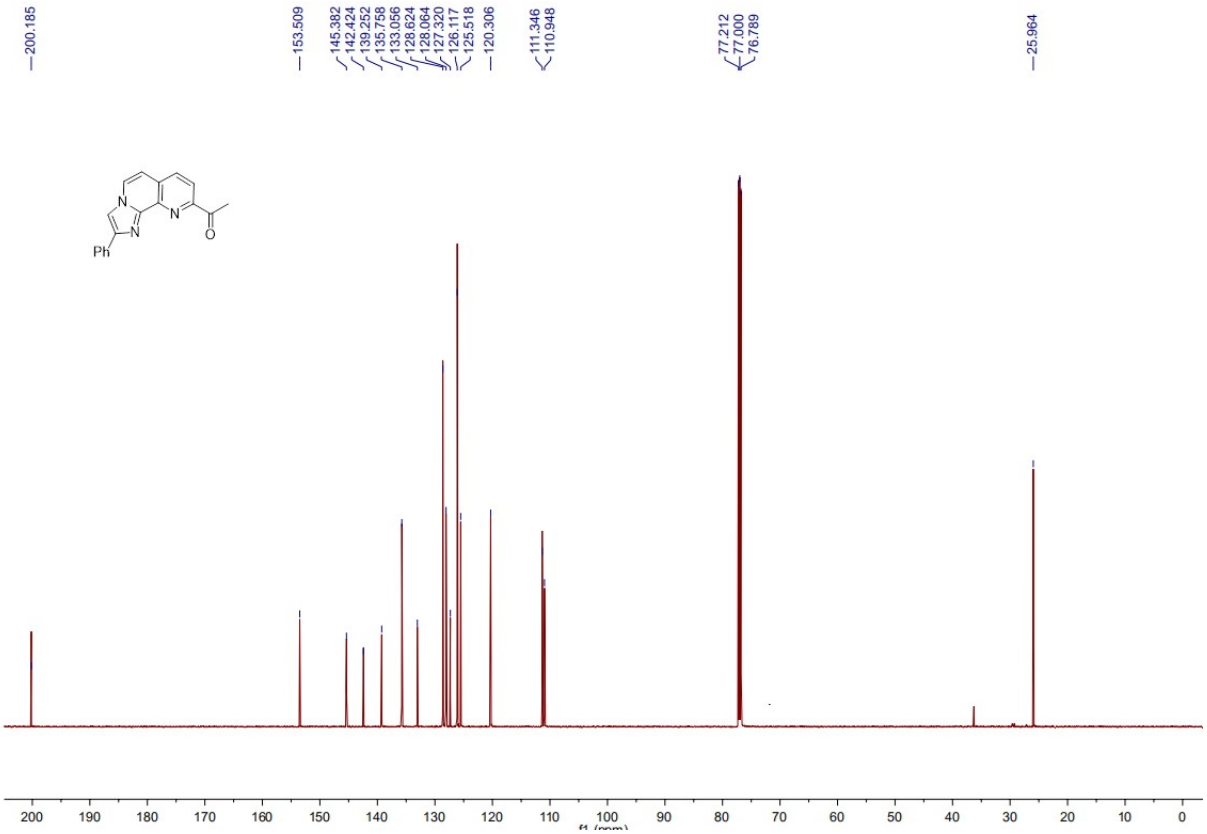

$^{13}$C NMR of **S6a** (151 M, $CDCl_3$)



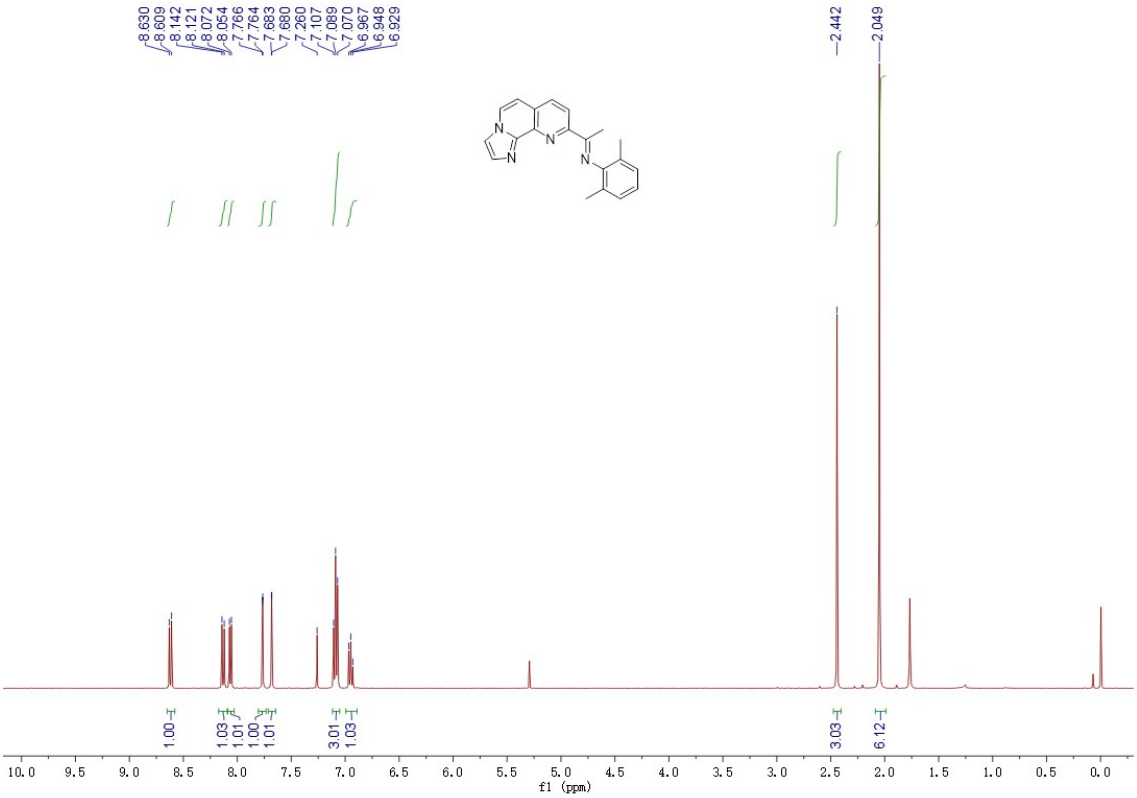
$^{1}$H NMR of **S6b** (400 M, $CDCl_3$)



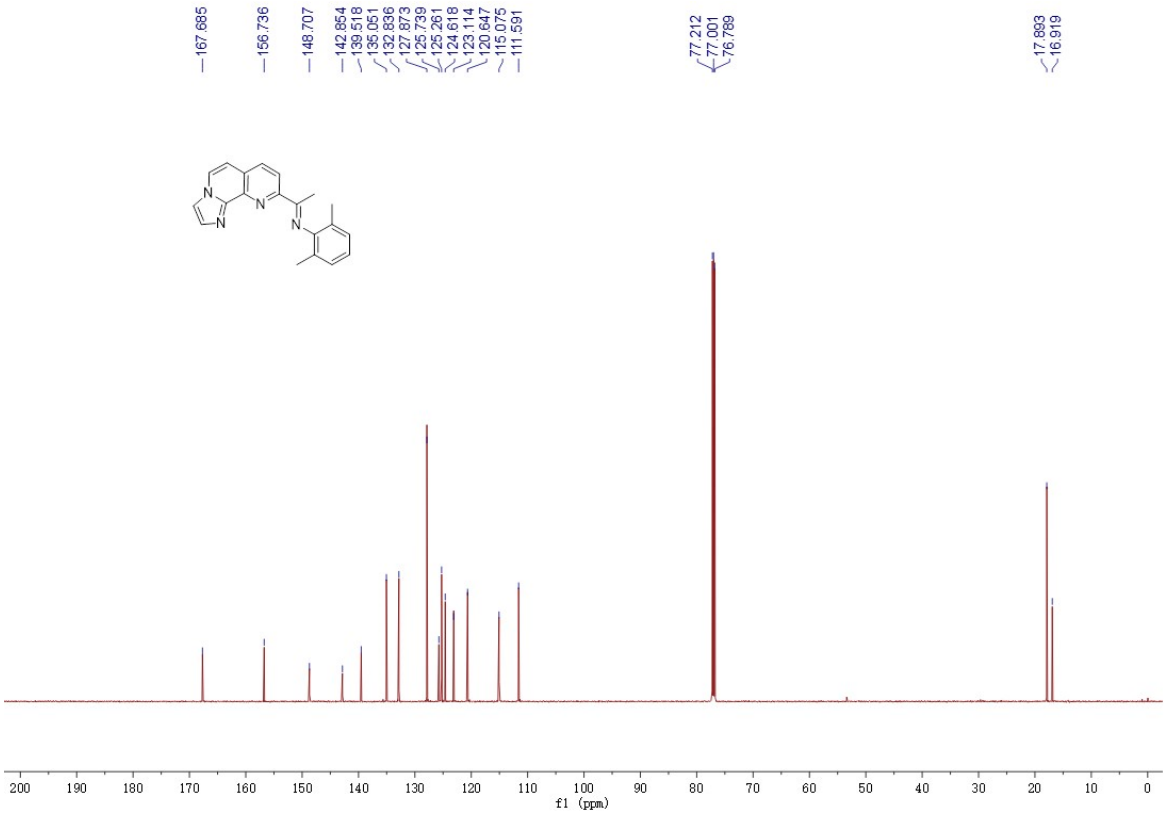

$^{13}$C NMR of **S6b** (151 M, $CDCl_3$)



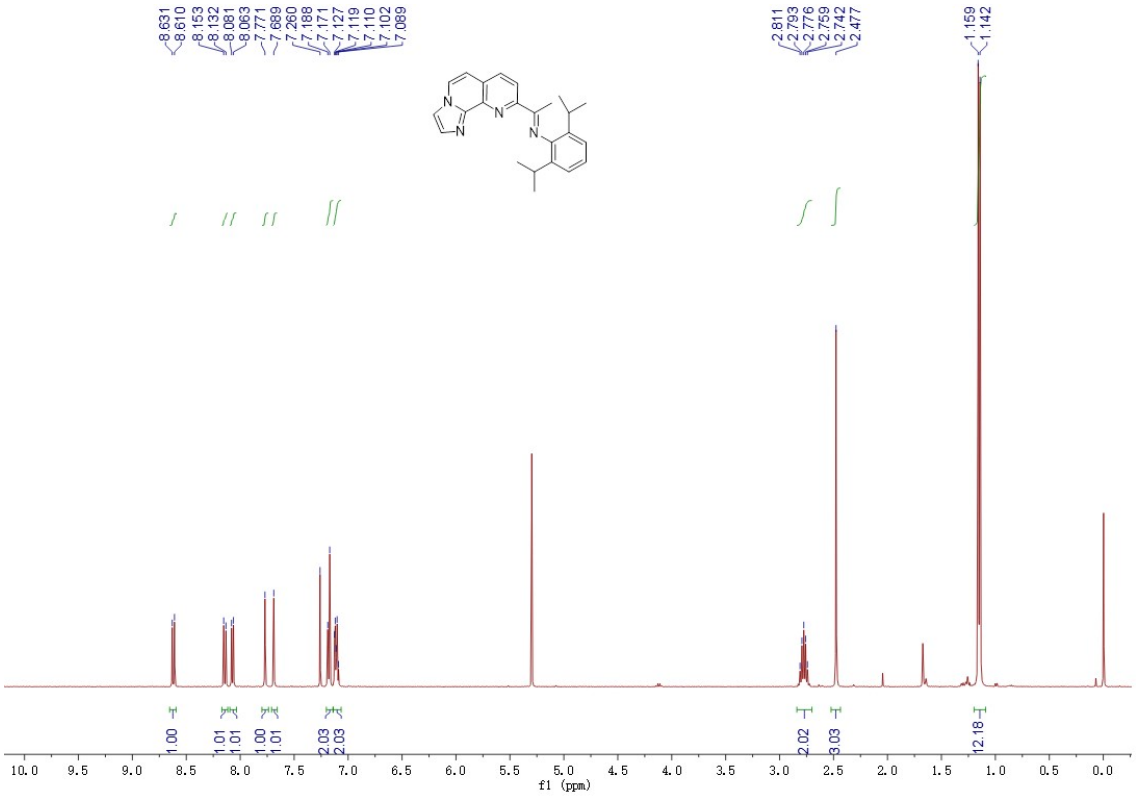
$^{1}$H NMR of **L1** (400 M, $CDCl_3$)



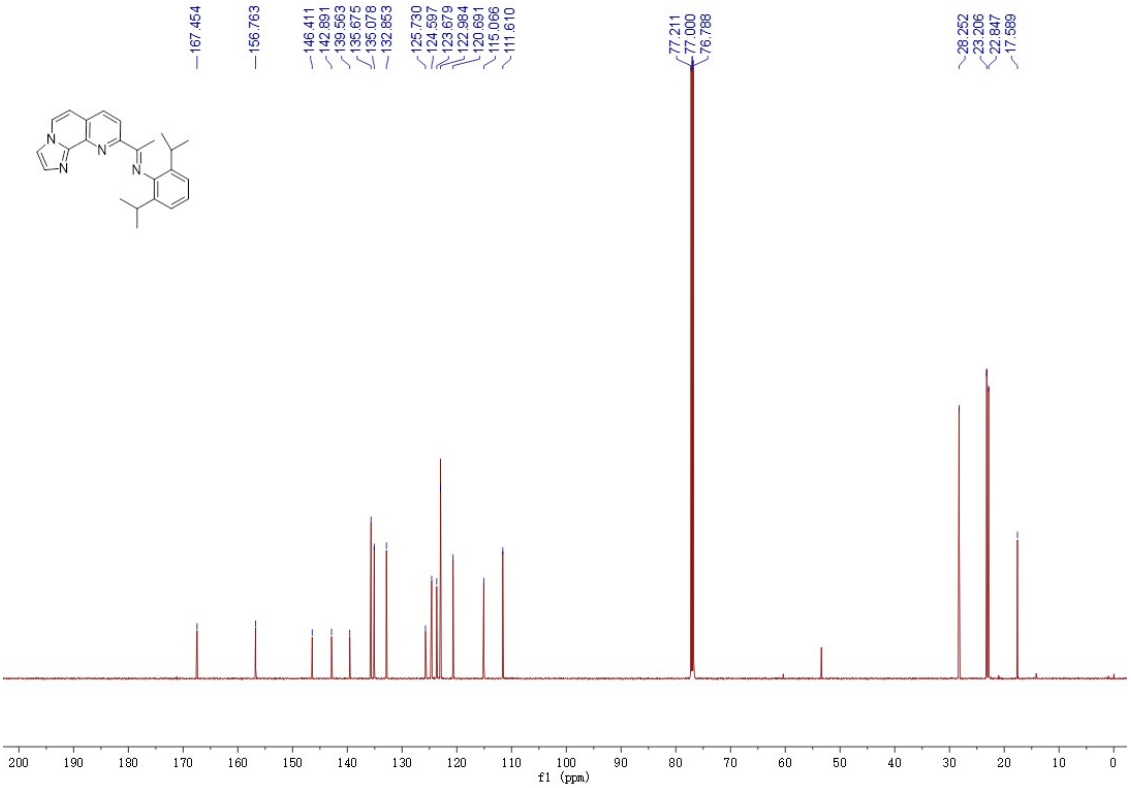

$^{13}$C NMR of **L1** (101 M, $CDCl_3$)



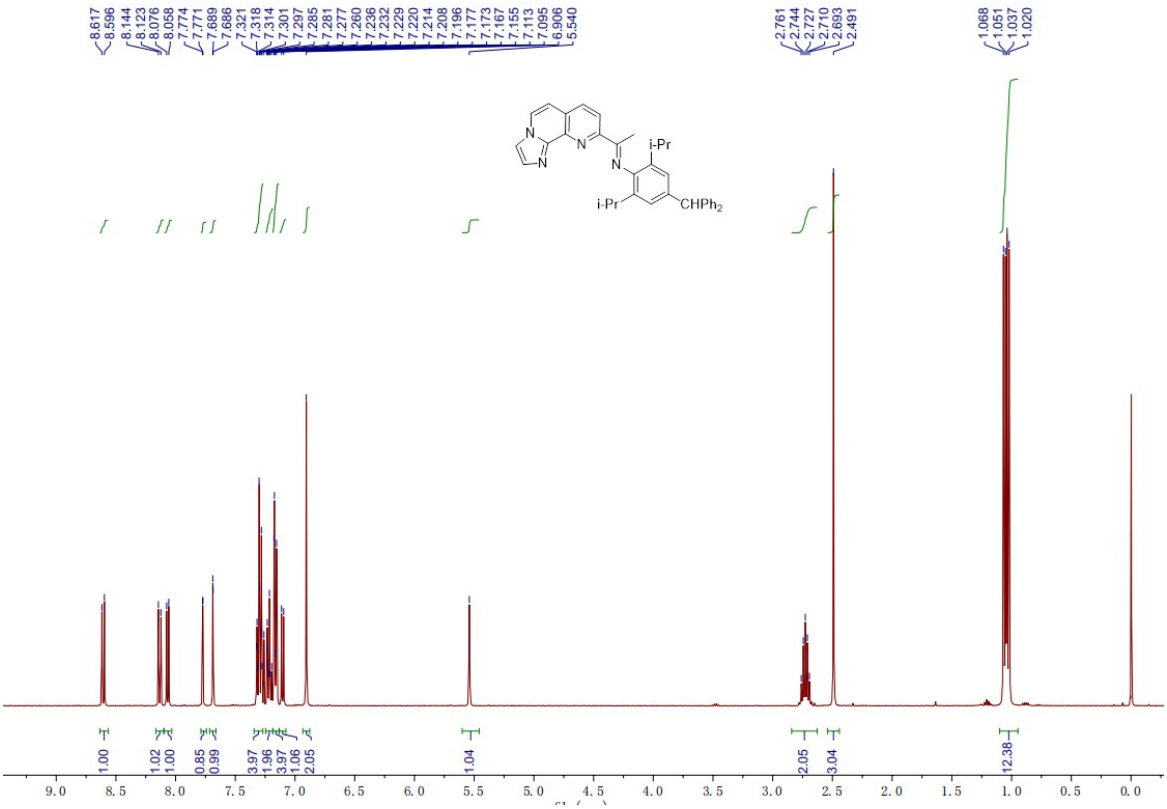
$^{1}$H NMR of **L2** (400 M, $CDCl_3$)



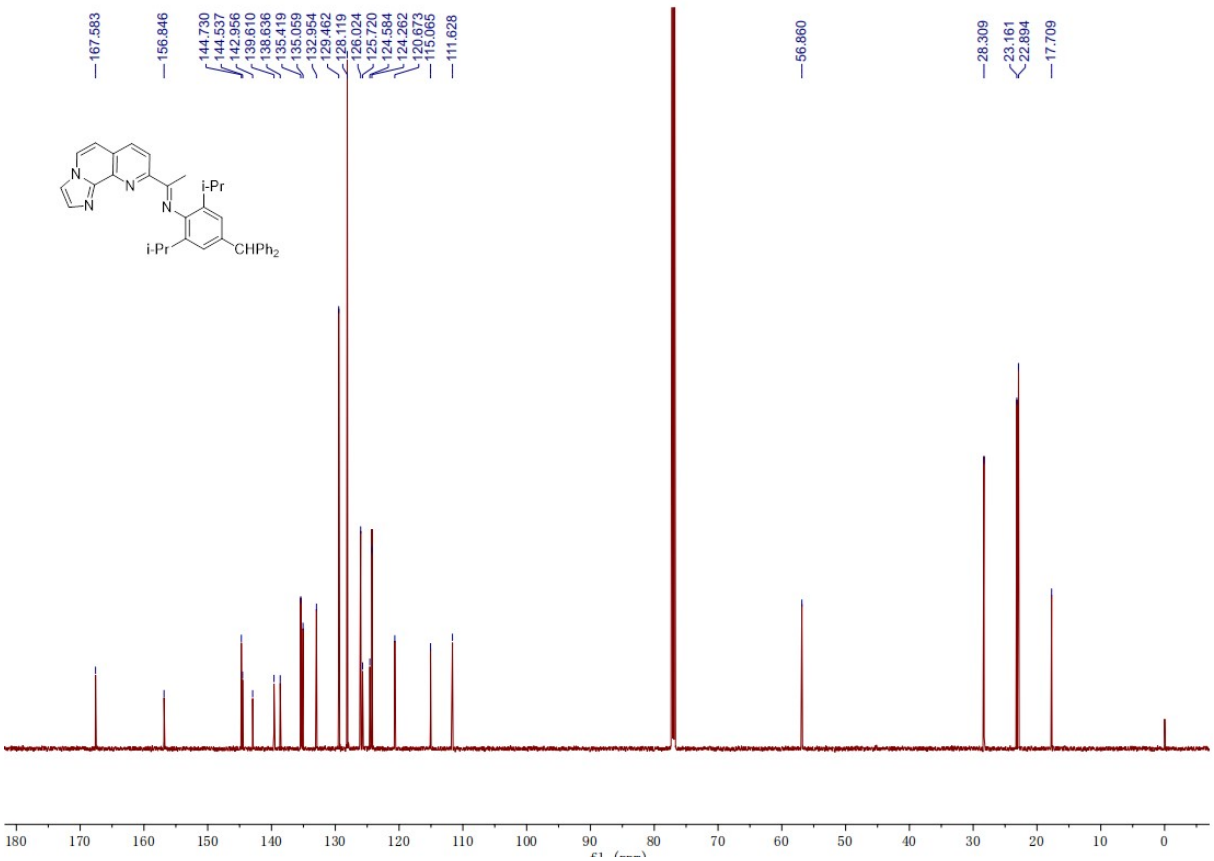

$^{13}$C NMR of **L2** (151 M, $CDCl_3$)



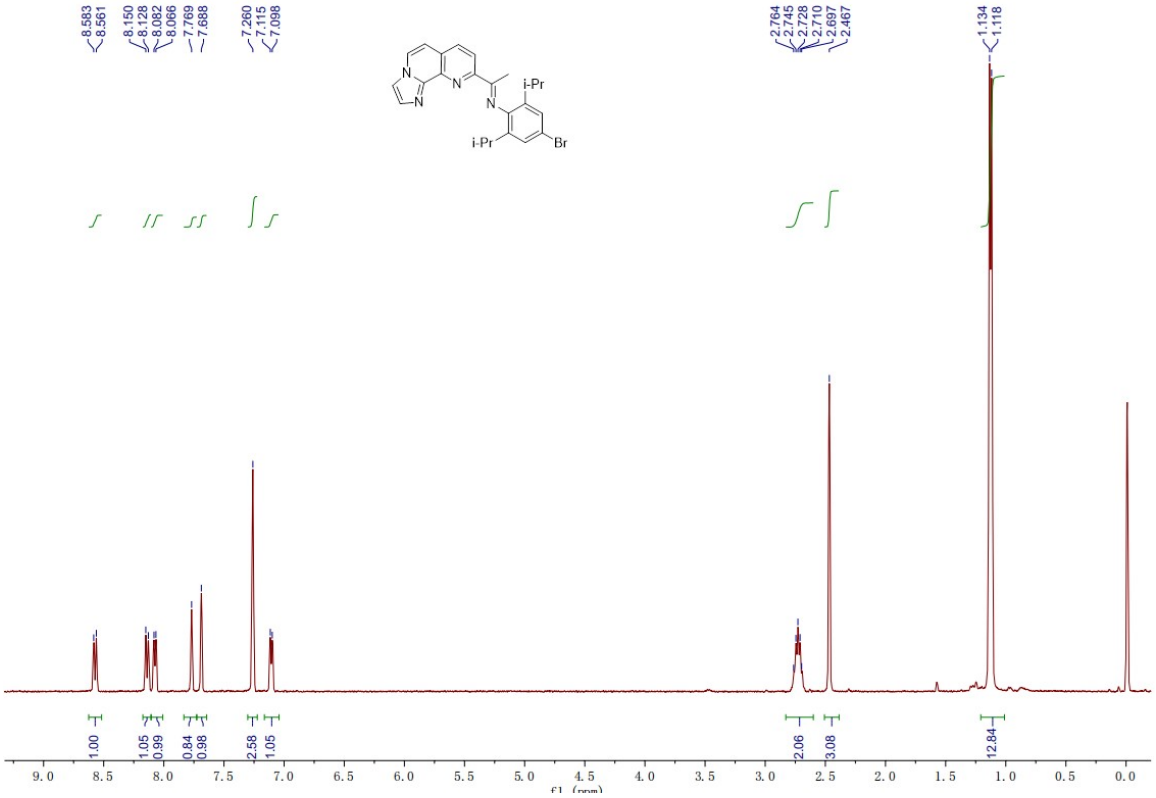
$^{1}$H NMR of **L3** (400 M, $CDCl_3$)



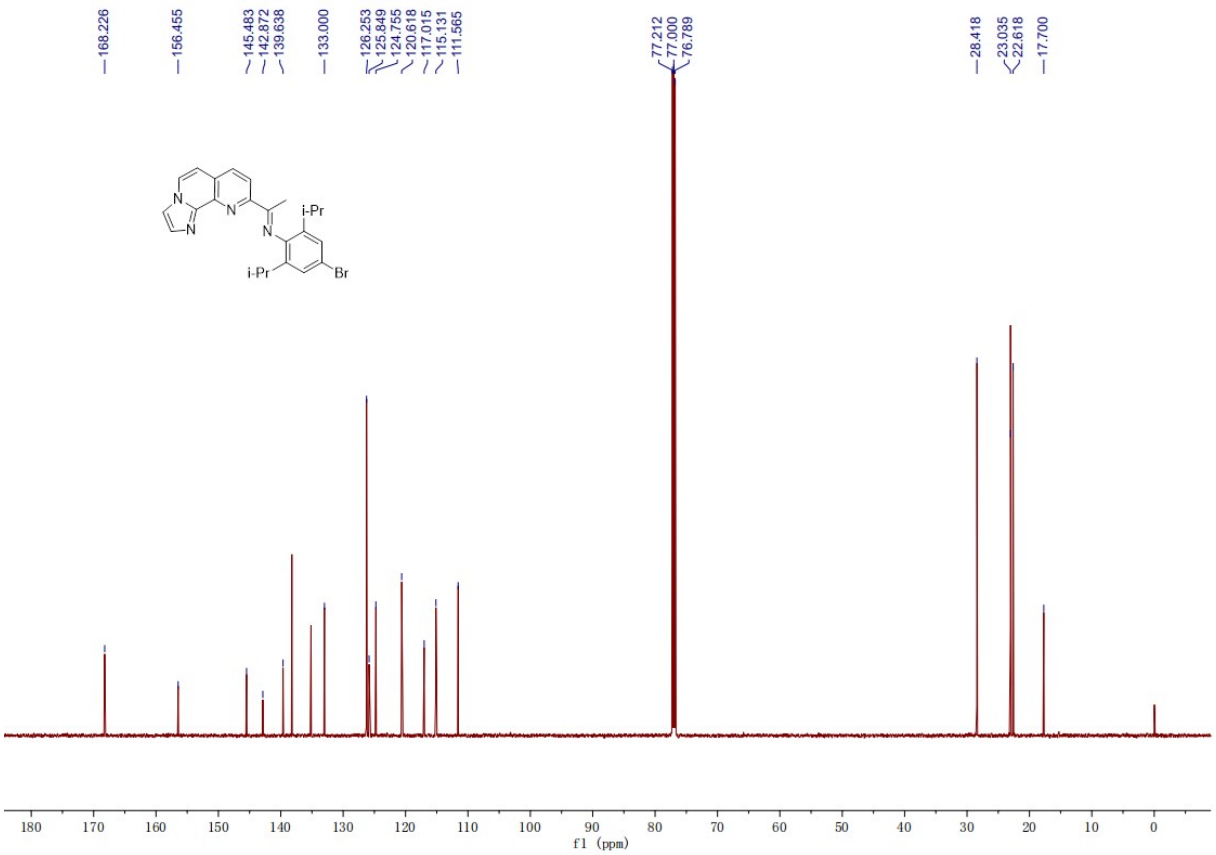

$^{13}$C NMR of **L3** (151 M, $CDCl_3$)



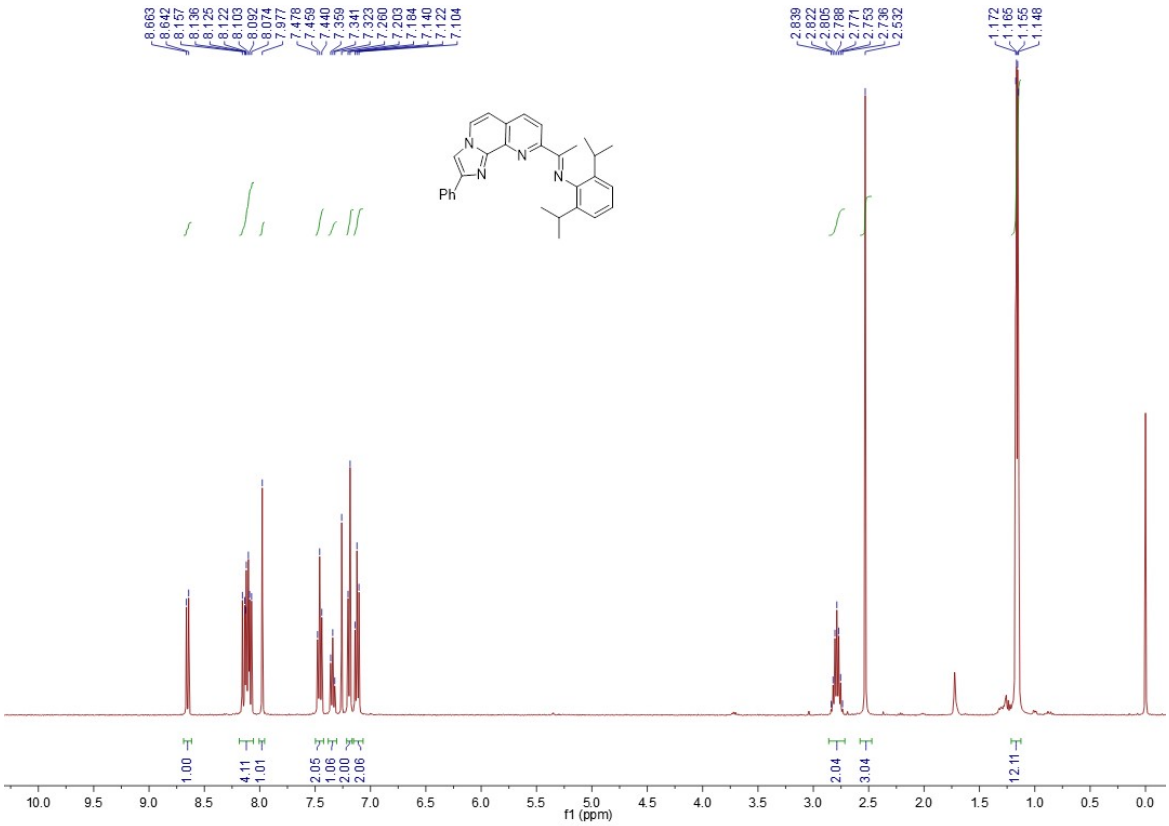
$^{1}$H NMR of **L4** (400 M, $CDCl_3$)




$^{13}$C NMR of **L4** (151 M, $CDCl_3$)



$^{1}$H NMR of **L5** (400 M, $CDCl_3$)




$^{13}$C NMR of **L5** (151 M, $CDCl_3$)