Electronic Supplementary Information

A Bifunctional Strategy to *N*-Heterocyclic Carbene Stabilized Iridium Complex Catalyzed *N*-Alkylation of Amines with Alcohols in Aqueous

Ming Huang,[a] Yinwu Li,[a] Jiahao Liu,[a] Xiao-Bing Lan,[a] Yan Liu,[b] Cunyuan Zhao[a] and Zhuofeng Ke*[,a]

[a]School of Materials Science and Engineering, PCFM Lab, School of Chemistry, Sun Yat-sen University, Guangzhou 510275, China. E-mail: kezhf3@mail.sysu.edu.cn
[b]School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, P. R. China.

Table of Contents

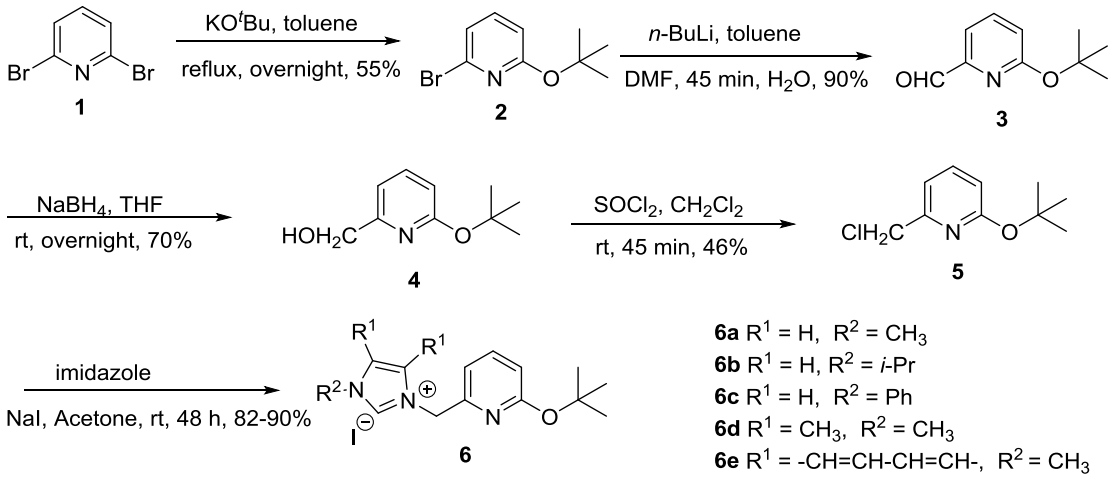
I. General Information

Unless otherwise stated, all manipulations were carried out under dry argon using conventional Schlenk and glove box techniques. Non-halogenated solvents were dried over sodium benzophenone ketyl and halogenated solvents over CaH_2. 1-phenylimidazole,[1] 1, 4, 5-trimethyl-1*H*-imidazole,[2] and 2-(bromomethyl)-6-methoxypyridine[3] were prepared according to the literature procedure. All other reagents were purchased from commercial sources and used without further purification.

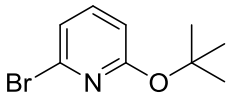
NMR spectra were recorded using a Bruker 400 MHz spectrometer, and chemical shifts are reported relative to TMS for ^{1}H and ^{13}C. ESI-MS spectra were taken on a Shimadzu LCMS-2010 instrument. GC analyses were recorded in a Shimadzu GC-2014C device equipped with a Wondacap 1 column. High resolution mass spectrometric (HRMS) data were obtained using an LTQ Orbitrap Elite instrument, using a sample concentration of approximately 1 ppm. Elemental analyses were provided by an Elemental Analyzer (Vario EL).

II. Preparation of the ligands and the Ir complexes

Scheme S1. Synthesis of the Imidazolium Salts 6



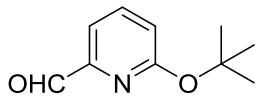
Synthesis of 2-bromo-6-(*tert*-butoxy)pyridine （2）[4]



2

To a solution of 2, 6-dibromopyridine (**1**) (9.48 g, 40.0 mmol, 1.00 equiv.) in toluene (150 mL) was added potassium *tert*-butoxide (4.48 g, 40.0 mmol, 1.00 equiv.), and the suspension was stirred for 12 h at 110 ^{o}C. The reaction mixture was filtered over celite and the solvent removed under reduced pressure. The residue was purified by column chromatography over silica gel (PE), yielding 5.04 g (22.0 mmol, 55%) of the desired product as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.57 (d, *J* = 8.1 Hz, 1H), 1.58 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.09, 140.12, 137.74, 119.58, 111.56, 81.00, 28.54; MS (ESI) $[M+H]^+$ 229.55.

Synthesis of 6-(*tert*-butoxy)picolinaldehyde （3）[5]

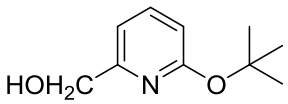


3

A solution of 2-bromo-6-(*tert*-butoxy)pyridine (**2**) (5 g, 22.0 mmol, 1.00 equiv.) in toluene (70 mL) was cooled to -78 ℃. To this stirring mixture, a solution of *n*-BuLi (8.8 ml, 2.5 mol/l in *n*-hexane, 1.00 equiv.) was added dropwise, maintaining a temperature at/or below -78 ℃ (~0.5 hours). Then, excess anhydrous DMF (3.4 mL, 44.0 mmol) was added and the reaction was stirred for 45 min at 0 ^{o}C. The reaction was then quenched with saturation NH_4Cl solution (30 ml), and extracted with EtOAc (30 mL x 3). The organic fractions were combined and the solvent was removed

under reduced pressure. The crude aldehyde was obtained as yellow oil 3.54 g (19.8 mmol, 90%), which used for next reaction directly.

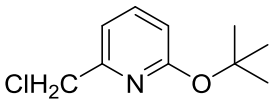
Synthesis of (6-(*tert*-butoxy)pyridin-2-yl)methanol (4)[5]



4

To a solution of $NaBH_4$ (1.52 g, 40.0 mmol, 2 equiv.) in THF (50 mL) was added 6-(*tert*-butoxy)picolinaldehyde （**3**） (3.5 g, 20.0 mmol, 1.00 equiv.), and the suspension was stirred for 2 h at rt. The reaction was then quenched with H_2O (20 mL), and extracted with EtOAc (40 mL x 3). The organic fractions were combined and the solvent was removed under reduced pressure. The residue was purified by column chromatography over silica gel (PE: EtOAc = 40: 1), yielding 2.5 g (14.0 mmol, 70 %) of the desired product as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (t, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 7.3 Hz, 1H), 6.55 (d, *J* = 8.2 Hz, 1H), 4.64 (d, *J* = 5.0 Hz, 2H), 3.42 (t, *J* = 5.1 Hz, 1H), 1.59 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.50, 156.39, 139.16, 112.35, 111.91, 79.90, 64.02, 29.09; MS (ESI) $[M+H]^+$ 181.65.

Synthesis of 2-(*tert*-butoxy)-6-(chloromethyl)pyridine (5)[6]



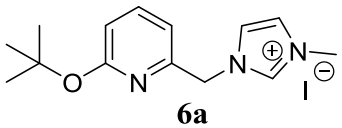
5

A solution of (6-(*tert*-butoxy)pyridin-2-yl)methanol (**4**) (2.5 g, 14.0 mmol, 1.00 equiv) in CH_2Cl_2 (70 mL) was cooled to 0 ℃. To this stirring mixture, $SOCl_2$ (1.53 ml, 1.50 equiv) was added dropwise, and the suspension was stirred for 45 min at rt. The reaction was then quenched with saturation $NaHCO_3$ solution (PH = 8), and extracted with CH_2Cl_2 (30 mL x 3). The organic fractions were combined and the solvent was removed under reduced pressure. The residue was purified by column chromatography over silica gel (PE), yielding 1.28 g (6.5 mmol, 46 %) of the desired product as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 8.2, 7.3 Hz, 1H), 6.92 (d, *J* = 7.2 Hz, 1H), 6.57 (d, *J* = 8.3 Hz, 1H), 4.53 (s, 2H), 1.60 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.58, 153.52, 139.03, 114.67, 112.75, 80.11, 47.09, 28.75; MS (ESI) $[M+H]^+$ 199.60.

General Method for the Preparation of imidazolium Salts 6a−e.[7]

To a solution of 2-(*tert*-butoxy)-6-(chloromethyl)pyridine (**5**) (1.02 mmol) in acetone (6 mL) was slowly added the imidazoles (1 mmol) and NaI (1 mmol). After it was stirred at rt for 48 h, the solution was filtered through Celite and the solvent was removed under vacuum to afford a yellow solid. Then, the product was recrystallized from dichloromethane/ diethyl ether.

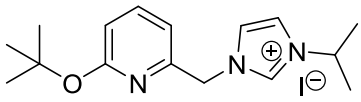
Synthesis of 1-((6-(*tert*-butoxy)pyridin-2-yl)methyl)-3-methyl-1*H*-imidazol-3-ium iodide (6a)



6a

Following the general method using 2-(*tert*-butoxy)-6-(chloromethyl)pyridine (**5**) (0.2 g, 1.02 mmol), 1-methylimidazole (0.082 g, 1 mmol) and NaI (0.15 g, 1mmol) in 6 mL of acetone, gave **6a** as a white solid. Yield: 0.33 g (90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 14.6 Hz, 2H), 7.16 (d, *J* = 7.2 Hz, 1H), 6.61 (d, *J* = 8.3 Hz, 1H), 5.56 (s, 2H), 4.09 (s, 3H), 1.47 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.87, 148.87, 139.65, 137.11, 123.48, 122.87, 115.53, 114.12, 80.00, 54.14, 37.11, 28.58; MS (ESI) $[M-I]^+$ 245.55.

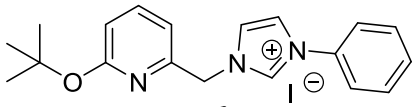
Synthesis of 1-((6-(*tert*-butoxy)pyridin-2-yl)methyl)-3-isopropyl-1*H*-imidazol-3-ium iodide (6b)



6b

Following the general method using 2-(*tert*-butoxy)-6-(chloromethyl)pyridine (**5**) (0.2 g, 1.02 mmol), 1-isopropylimidazole (0.110 g, 1 mmol) and NaI (0.15 g, 1mmol) in 6 mL of acetone, gave **6b** as a white solid. Yield: 0.34 g (83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (s, 1H), 7.55 (t, *J* = 1.8 Hz, 1H), 7.52-7.50 (m, 1H), 7.49 – 7.46 (m, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 6.56 (d, *J* = 8.3 Hz, 1H), 5.60 (s, 2H), 4.82 (hept, *J* = 6.7 Hz, 1H), 1.60 (d, *J* = 6.7 Hz, 6H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.86, 149.04, 139.60, 135.60, 123.02, 120.16, 115.55, 113.98, 79.86, 54.03, 53.56, 28.62, 23.22; MS (ESI) $[M-I]^+$ 273.55.

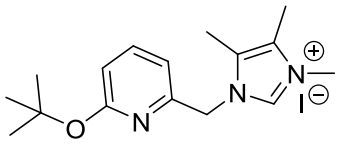
Synthesis of 1-((6-(*tert*-butoxy)pyridin-2-yl)methyl)-3-phenyl-1*H*-imidazol-3-ium iodide (6c)



6c

Following the general method using 2-(*tert*-butoxy)-6-(chloromethyl)pyridine (**5**) (0.2 g, 1.02 mmol), 1- phenylimidazole (0.144 g, 1 mmol) and NaI (0.15 g, 1mmol) in 6 mL of acetone, gave **6c** as a white solid. Yield: 0.35 g (80 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.78 (s, 1H), 7.75 (d, *J* = 7.4 Hz, 2H), 7.64 (s, 1H), 7.61 – 7.52 (m, 5H), 7.31 (d, *J* = 7.2 Hz, 1H), 6.63 (d, *J* = 8.3 Hz, 1H), 5.85 (s, 2H), 1.47 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.88, 148.86, 139.68, 135.64, 134.34, 130.67, 130.45, 124.06, 121.99, 120.65, 115.83, 114.10, 79.93, 54.35, 28.59; MS (ESI) $[M-I]^+$ 307.55.

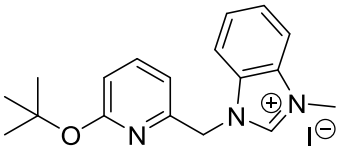
Synthesis of 1-((6-(*tert*-butoxy)pyridin-2-yl)methyl)-3-methyl-1*H*-4,5-di-methyl-imidazol-3-ium iodide (6d)



6d

Following the general method using 2-(*tert*-butoxy)-6-(chloromethyl)pyridine (**5**) (0.2 g, 1.02 mmol), 1,4,5-trimethyl-1*H*-imidazole (0.110 g, 1 mmol) and NaI (0.15 g, 1mmol) in 6 mL of acetone, gave **6d** as a white solid. Yield: 0.34 g (82 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.51 (dd, *J* = 8.3, 7.3 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 1H), 6.54 (d, *J* = 8.3 Hz, 1H), 5.45 (s, 2H), 3.90 (s, 3H), 2.23 (s, 3H), 2.16 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.87, 149.23, 139.66, 136.19, 127.26, 127.11, 114.71, 113.58, 79.85, 51.66, 34.39, 28.44, 8.94, 8.67; MS (ESI) $[M-I]^+$ 273.75.

Synthesis of 1-((6-(*tert*-butoxy)pyridin-2-yl)methyl)-3-methyl-1*H*-benzo[d]-imidazol-3-ium iodide (6e)



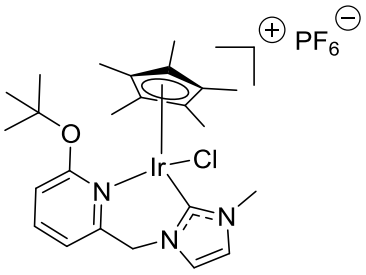
6e

Following the general method using 2-(*tert*-butoxy)-6-(chloromethyl)pyridine (**5**) (0.2 g, 1.02 mmol), 1-methylbenzimidazole (0.132 g, 1 mmol) and NaI (0.15 g, 1mmol) in 6 mL of acetone, gave **6e** as a white solid. Yield: 0.37 g (87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.97 (s, 1H), 7.79 – 7.70 (m, 2H), 7.66 – 7.48 (m, 3H), 7.20 (d, *J* = 7.6 Hz, 1H), 6.53 (d, *J* = 8.3 Hz, 1H), 5.86 (s, 2H), 4.26 (s, 3H), 1.24 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.85, 148.81, 142.70, 139.71, 131.91, 131.53, 127.40, 115.22, 114.04, 113.96, 112.87, 79.88, 51.95, 34.24, 28.36; MS (ESI) $[M-I]^+$ 290.50.

General Method for the Preparation of Iridium Complexes 7a−e.

A suspension of the appropriate imidazolium salts (**6a−e**, 0.5 mmol) and silver oxide (0.25 equiv) in CH_2Cl_2 (6 mL) was stirred at room temperature in the dark for 2h. Then the $[Cp^*IrCl_2]_2$ (0.25 equiv) and KPF_6 (0.5 equiv) were added to the mixture and stirred at room temperature for 3 h. After filtered through a pad of Celite, the filtrate was removed by evaporation and the product was recrystallized from dichloromethane/ diethyl ether.

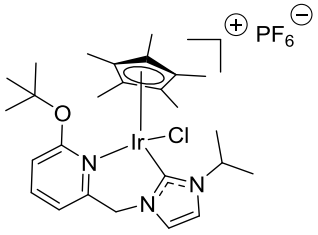
Synthesis of 7a



7a

Following the general method using imidazolium salt (**6a**) (0.19 g, 0.5 mmol), silver oxide (0.058 g, 0.25 mmol), $[Cp^*IrCl_2]_2$ (0.199 g, 0.25 mmol) and KPF_6 (0.092g, 0.5 equiv) in 6 mL of CH_2Cl_2, gave **7a** as a yellow solid. Yield: 0.32 g (85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 8.7, 7.3 Hz, 1H), 7.45 (d, J = 2.0 Hz, 1H), 7.37 (d, J = 6.9 Hz, 1H), 7.11 (d, J = 8.6 Hz, 1H), 6.99 (d, J = 2.0 Hz, 1H), 5.44 (d, J = 15.5 Hz, 1H), 4.59 (d, J = 15.5 Hz, 1H), 3.93 (s, 3H), 1.67 (s, 15H), 1.66 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.52, 153.98, 153.81, 141.76, 123.80, 122.64, 118.90, 113.34, 90.66, 84.61, 56.34, 37.10, 29.04, 10.01; ^{31}P NMR (162 MHz, $CDCl_3$) δ -144.26 (sept, ^2J(P, F) = 712 Hz, PF_6); HRMS (ESI, m/z): calcd for $C_{24}H_{34}ON_3ClIr$ $[M - PF_6]^+$ 608.20142, found 608.20189; Anal. Calcd for $C_{24}H_{34}ClF_6IrN_3OP$: C, 38.27; H, 4.55; N, 5.58; Found: C, 38.58; H, 4.65; N, 5.46.

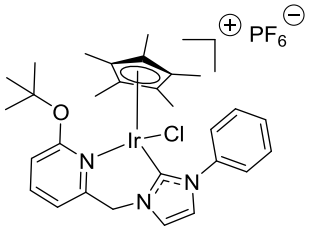
Synthesis of 7b



7b

Following the general method using imidazolium salt (**6b**) (0.205 g, 0.5 mmol), silver oxide (0.058 g, 0.25 mmol), $[Cp^*IrCl_2]_2$ (0.199 g, 0.25 mmol) and KPF_6 (0.092g, 0.5 equiv) in 6 mL of CH_2Cl_2, gave **7b** as a yellow solid. Yield: 0.21 g (53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 8.7, 7.3 Hz, 1H), 7.48 (d, *J* = 1.7 Hz, 1H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.11 (d, *J* = 8.7 Hz, 1H), 7.05 (d, *J* = 2.1 Hz, 1H), 5.42 (d, *J* = 15.4 Hz, 1H), 4.94 (hept, *J* = 6.2 Hz, 1H), 4.55 (d, *J* = 15.3 Hz, 1H), 1.66 (s, 15H), 1.64(s, 9H), 1.50 (d, *J* = 6.9 Hz, 3H), 1.46 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.43, 153.78, 152.94, 141.83, 122.96, 118.78, 118.69, 113.34, 90.63, 84.51, 56.24, 50.87, 28.97, 25.12, 24.62, 9.92; ^{31}P NMR (162 MHz, $CDCl_3$) δ -144.24 (sept, ^2J(P, F) = 712 Hz, PF_6); HRMS (ESI, m/z): calcd for $C_{26}H_{38}ON_3ClIr$ $[M - PF_6]^+$ 636.23272, found 636.23419; Anal. Calcd for $C_{26}H_{38}ClF_6IrN_3OP$: C, 39.97; H, 4.90; N, 5.38; Found: C, 40.19; H, 4.93; N, 5.19.

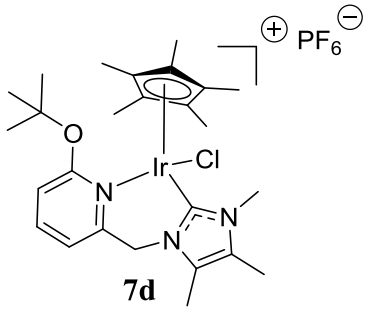
Synthesis of 7c



7c

Following the general method using imidazolium salt (**6c**) (0.222 g, 0.5 mmol), silver oxide (0.058 g, 0.25 mmol), $[Cp^*IrCl_2]_2$ (0.199 g, 0.25 mmol) and KPF_6 (0.092g, 0.5 equiv) in 6 mL of CH_2Cl_2, gave **7c** as a yellow solid. Yield: 0.20 g (47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.83 (m, 2H), 7.81 (dd, *J* = 8.7, 7.3 Hz, 1H), 7.60 (d, *J* = 2.0 Hz, 1H), 7.50 – 7.43 (m, 3H), 7.41 (d, *J* = 7.0 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 1H), 7.06 (d, *J* = 2.0 Hz, 1H), 5.51 (d, *J* = 15.3 Hz, 1H), 4.69 (d, *J* = 15.3 Hz, 1H), 1.67 (s, 9H), 1.40 (s, 15H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.52, 155.24, 153.50, 141.84, 139.07, 129.65, 128.98, 128.85, 126.19, 122.55, 118.59, 113.79, 91.01, 84.59, 56.87, 29.10, 9.63; ^{31}P NMR (162 MHz, $CDCl_3$) δ -144.22 (sept, ^2J(P, F) = 712 Hz, PF_6); HRMS (ESI, m/z): calcd for $C_{29}H_{36}ON_3ClIr$ $[M - PF_6]^+$ 670.21707, found 670.21766; Anal. Calcd for $C_{29}H_{36}ClF_6IrN_3OP$: C, 42.72; H, 4.45; N, 5.15; Found: C, 42.49; H, 4.53; N, 5.06.

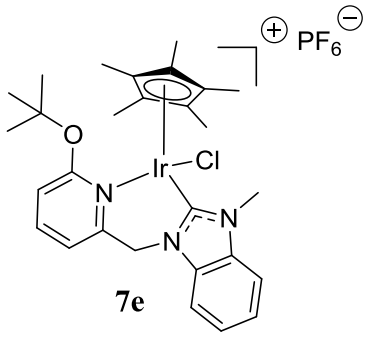
Synthesis of 7d



7d

Following the general method using imidazolium salt (**6d**) (0.205 g, 0.5 mmol), silver oxide (0.058 g, 0.25 mmol), $[Cp^*IrCl_2]_2$ (0.199 g, 0.25 mmol) and KPF_6 (0.092g, 0.5 equiv) in 6 mL of CH_2Cl_2, gave **7d** as a yellow solid. Yield: 0.24 g (58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 8.7, 7.3 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.10 (d, *J* = 8.6 Hz, 1H), 5.27 (d, *J* = 15.7 Hz, 1H), 4.46 (d, *J* = 15.7 Hz, 1H), 3.76 (s, 3H), 2.32 (s, 3H), 2.16 (s, 3H), 1.66 (s, 15H), 1.66 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.57, 154.24, 152.37, 141.66, 126.91, 125.51, 118.60, 113.27, 90.56, 84.49, 53.41, 34.48, 29.00, 9.96, 9.55, 8.82; ^{31}P NMR (162 MHz, $CDCl_3$) δ -144.35 (sept, ^2J(P, F) = 712 Hz, PF_6); HRMS (ESI, m/z): calcd for $C_{26}H_{38}ON_3ClIr$ $[M - PF_6]^+$ 636.23272, found 636.23328; Anal. Calcd for $C_{26}H_{38}ClF_6IrN_3OP$: C, 39.97; H, 4.90; N, 5.38; Found: C, 40.16; H, 4.96; N, 5.26.

Synthesis of 7e



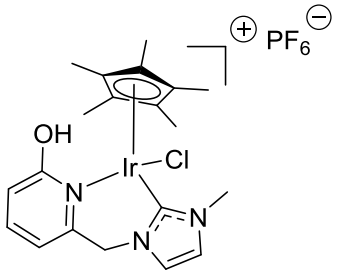
7e

Following the general method using imidazolium salt (**6e**) (0.214 g, 0.5 mmol), silver oxide (0.058 g, 0.25 mmol), $[Cp^*IrCl_2]_2$ (0.199 g, 0.25 mmol) and KPF_6 (0.092g, 0.5 equiv) in 6 mL of CH_2Cl_2, gave **7e** as a yellow solid. Yield: 0.278 g (65 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.78 (dd, *J* = 8.7, 7.3 Hz, 1H), 7.50 (d, *J* = 7.1 Hz, 1H), 7.45 – 7.27 (m, 3H), 7.14 (d, *J* = 8.5 Hz, 1H), 5.82 (d, *J* = 15.8 Hz, 1H), 4.70 (d, *J* = 15.8 Hz, 1H), 4.11 (s, 3H), 1.70 (s, 15H), 1.66 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.29, 164.52, 153.39, 141.98, 135.66, 133.38, 124.71, 124.14, 119.13, 113.62, 111.18, 110.64, 91.48, 84.80, 52.89, 34.25, 29.01, 10.03; ^{31}P NMR (162 MHz, $CDCl_3$) δ -144.24 (sept, ^2J(P, F) = 712 Hz, PF_6); HRMS (ESI, m/z): calcd for $C_{28}H_{36}ON_3ClIr$ $[M - PF_6]^+$ 658.21707, found 658.21759; Anal. Calcd for $C_{28}H_{36}ClF_6IrN_3OP$: C, 41.87; H, 4.52; N, 5.23; Found: C, 41.88; H, 4.54; N, 5.19.

General Method for the Preparation of Iridium Complexes 8a−e.

An oven-dried sealed tube with stir bar was charged with iridium complexes **7a**−**e** (0.2 mmol) and MeCN (8 mL). After refluxed at 100 ^{o}C for 24 h, the solution was cooled to rt and removed by evaporation. The desired products **8a**−**e** were obtained with quantitative yield.

Synthesis of 8a

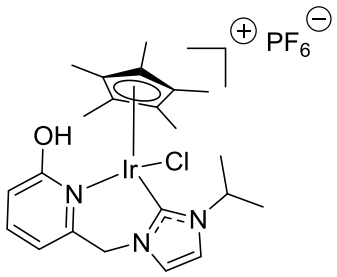


8a

Following the general method using **7a** (0.162 g, 0.2 mmol), in 8 mL of MeCN, gave **8a** as a yellow solid. Yield: 0.151 g (100 %). ^{1}H NMR (400 MHz, DMSO) δ 12.65 (s, 1H), 7.84 (dd, *J* = 8.3, 7.3 Hz, 1H), 7.59 (d, *J* = 1.9 Hz, 1H), 7.51 (d, *J* = 1.9 Hz, 1H), 7.20 (d, *J* = 7.1 Hz, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 5.45 (d, *J* = 15.1 Hz, 1H),

4.57 (d, *J* = 15.0 Hz, 1H), 3.78 (s, 3H), 1.67 (s, 15H); ^{13}C NMR (101 MHz, DMSO) δ 165.55, 154.46, 151.91, 142.24, 123.72, 121.69, 116.28, 112.33, 90.32, 53.97, 36.35, 9.05; ^{31}P NMR (162 MHz, DMSO) δ -144.19 (sept, ^{2}J(P, F) = 712 Hz, PF_6); HRMS (ESI, m/z): calcd for $C_{20}H_{26}ON_3ClIr$ $[M - PF_6]^+$ 552.13882, found 552.13958; Anal. Calcd for $C_{20}H_{26}ClF_6IrN_3OP$•0.15MeCN: C, 34.67; H 3.79; N 6.27. Found: C, 35.04; H, 3.73; N, 5.95.

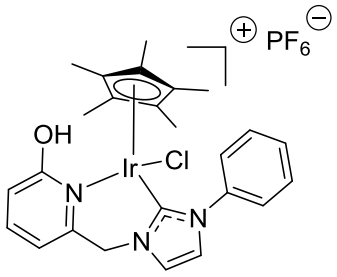
Synthesis of 8b



8b

Following the general method using **7b** (0.168 g, 0.2 mmol), in 8 mL of MeCN, gave **8b** as a yellow solid. Yield: 0.157g (100 %).^{1}H NMR (400 MHz, DMSO) δ 12.44 (s, 1H), 7.84 (t, *J* = 7.5 Hz, 1H), 7.70 (d, *J* = 2.0 Hz, 1H), 7.64 (d, *J* = 1.9 Hz, 1H), 7.22 (d, *J* = 7.0 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 5.45 (d, *J* = 15.2 Hz, 1H), 4.64-4.58 (m, 1H), 4.55 (d, *J* = 15.1 Hz, 1H), 1.65 (s, 15H), 1.52 (d, *J* = 6.8 Hz, 3H), 1.39 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, DMSO) δ 165.61, 153.32, 152.07, 142.32, 122.49, 119.19, 116.36, 112.50, 90.36, 54.10, 50.78, 24.86, 23.28, 9.19; ^{31}P NMR (162 MHz, DMSO) δ -144.19 (sept, ^{2}J(P, F) = 712 Hz, PF_6); HRMS (ESI, m/z): calcd for $C_{20}H_{26}ON_3ClIr$ $[M - HCl - PF_6]^+$ 544.19344, found 544.19403; Anal. Calcd for $C_{22}H_{30}ClF_6IrN_3OP$•0.15MeCN: C, 36.63; H, 4.20; N, 6.03; Found: C, 36.85; H, 4.20; N, 5.67.

Synthesis of 8c

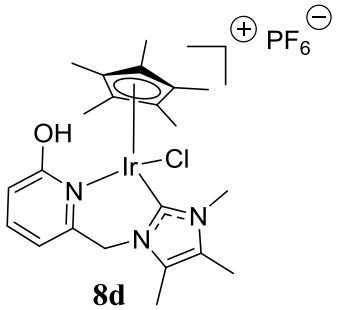


8c

Following the general method using **7c** (0.175 g, 0.2 mmol), in 8 mL of MeCN, gave **8c** as a yellow solid. Yield: 0.163g (100 %). ^{1}H NMR (400 MHz, DMSO) δ 12.55 (s, 1H), 7.94 (dd, *J* = 6.4, 3.0 Hz, 2H), 7.91 – 7.85 (m, 1H), 7.81 (d, *J* = 1.9 Hz, 1H), 7.66 (d, *J* = 1.9 Hz, 1H), 7.56 – 7.49 (m, 3H), 7.25 (d, *J* = 7.0 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 5.56 (d, *J* = 15.1 Hz, 1H), 4.66 (d, *J* = 14.9 Hz, 1H), 1.37 (s, 16H); ^{13}C

NMR (101 MHz, DMSO) δ 165.55, 154.63, 151.58, 142.36, 138.89, 129.06, 128.59, 128.24, 125.93, 122.38, 116.24, 112.85, 90.74, 54.64, 9.03; ^{31}P NMR (162 MHz, DMSO) δ -144.19 (sept, ^{2}J(P, F) = 712 Hz, PF_6); HRMS (ESI, m/z): calcd for $C_{25}H_{38}ON_3ClIr$ [M – PF_6]$^+$ 614.15447, found 614.15454; Anal. Calcd for $C_{25}H_{28}ClF_6IrN_3OP$•0.15MeCN: C, 39.71; H, 3.75; N, 5.77; Found: C, 39.88; H, 3.84; N, 5.39.

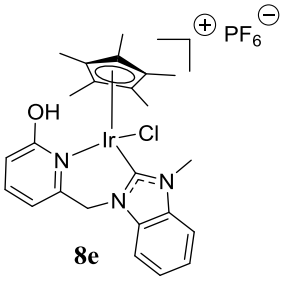
Synthesis of 8d



8d

Following the general method using **7d** (0.168 g, 0.2 mmol), in 8 mL of MeCN, gave **8d** as a yellow solid. Yield: 0.157g (100 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.55 (s, 1H), 7.82 (t, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 7.3 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 5.28 (d, *J* = 15.3 Hz, 1H), 4.40 (d, *J* = 15.2 Hz, 1H), 3.64 (s, 3H), 2.33 (s, 3H), 2.21 (s, 3H), 1.66 (s, 15H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.56, 152.72, 152.19, 142.16, 126.21, 124.36, 116.48, 112.33, 90.17, 50.99, 33.94, 9.07, 8.83, 8.57; ^{31}P NMR (162 MHz, DMSO) δ -144.20 (sept, ^{2}J(P, F) = 712 Hz, PF_6); HRMS (ESI, m/z): calcd for $C_{22}H_{29}ON_3Ir$ [M –HCl- PF_6]$^+$ 544.19344, found 544.19366; Anal. Calcd for $C_{22}H_{30}ClF_6IrN_3OP$•0.20MeCN: C, 36.69; H, 4.21; N, 6.11; Found: C, 37.06; H, 4.18; N, 5.73.

Synthesis of 8e



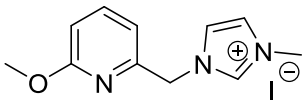
8e

Following the general method using **7e** (0.172 g, 0.2 mmol), in 8 mL of MeCN, gave **8e** as a yellow solid. Yield: 0.161g (100 %). ^{1}H NMR (400 MHz, DMSO) δ 12.92 (s, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.90 – 7.83 (m, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.37 (m, 3H), 6.97 (d, *J* = 8.3 Hz, 1H), 5.99 (d, *J* = 15.3 Hz, 1H), 4.67 (d, *J* = 15.2 Hz, 1H), 4.01 (s, 3H), 1.74 (s, 15H); ^{13}C NMR (101 MHz, DMSO) δ 168.28, 165.65, 151.75, 142.33, 134.97, 133.14, 123.66, 123.52, 116.26, 112.51, 111.32, 111.03, 91.29, 50.56, 33.82, 9.10; ^{31}P NMR (162 MHz, DMSO) δ -144.19 (sept, ^{2}J(P, F) = 712 Hz, PF_6); HRMS (ESI, m/z): calcd for $C_{24}H_{27}ON_3Ir$ [M –HCl- PF_6]$^+$

566.17779, found 566.17895; Anal. Calcd for $C_{24}H_{28}ClF_6IrN_3OP$•0.15MeCN: C, 38.75; H, 3.81; N, 5.86; Found: C, 39.16; H, 3.71; N, 5.54.

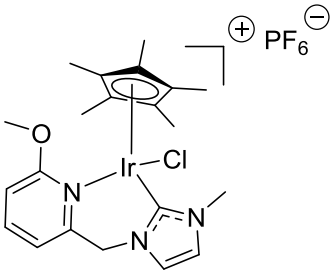
Synthesis of complex 9

Synthesis of 3-methyl-6-methoxyl-1-(2-picolyl)imidazolium iodide 6f



6f

Following the general method for the synthesis of **6** using 2-(bromomethyl)-6-methoxypyridine (0.201 g, 1.02 mmol), 1-methylimidazole (0.088 g, 1 mmol) and NaI (0.15 g, 1mmol) in 6 mL of acetone, gave **6f** as a white solid. Yield: 0.245 g (74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.63 (t, J = 1.7 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.20 (d, J = 7.1 Hz, 1H), 6.67 (d, J = 8.3 Hz, 1H), 5.54 (s, 2H), 4.07 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.13, 149.25, 139.94, 136.93, 123.37, 123.07, 116.28, 111.69 , 53.87, 53.81, 37.23; MS (ESI) $[M\text{-}I]^+$ 203.65.

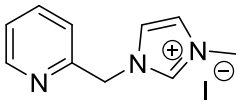


9a

Following the general method for the synthesis of **7** using imidazolium salt (**9a**) (0.166 g, 0.5 mmol), silver oxide (0.058 g, 0.25 mmol), $[Cp^*IrCl_2]_2$ (0.199 g, 0.25 mmol) and KPF_6 (0.092g, 0.5 equiv) in 6 mL of CH_2Cl_2, gave **9** as a yellow solid. Yield: 0.30 g (80 %). ^{1}H NMR (400 MHz, DMSO) δ 8.06 (dd, *J* = 8.5, 7.4 Hz, 1H), 7.59 (d, *J* = 1.9 Hz, 1H), 7.51 (d, *J* = 1.9 Hz, 1H), 7.38 (d, *J* = 7.3 Hz, 1H), 7.27 (d, *J* = 8.5 Hz, 1H), 5.52 (d, *J* = 15.0 Hz, 1H), 4.57 (d, *J* = 14.9 Hz, 1H), 3.99 (s, 3H), 3.78 (s, 3H), 1.66 (s, 16H); ^{13}C NMR (101 MHz, DMSO) δ 165.74, 154.34, 152.93, 143.34, 123.77, 121.70, 117.96, 109.08, 90.38, 58.28, 53.97, 36.38, 9.07; ^{31}P NMR (162 MHz, DMSO) δ -144.19 (sept, ^2J(P, F) = 712 Hz, PF_6); HRMS (ESI, m/z): calcd for $C_{21}H_{28}ON_3ClIr$ $[M - PF_6]^+$ 566.15447, found 566.15493; Anal. Calcd for $C_{21}H_{28}ClF_6IrN_3OP$: C, 35.47; H, 3.97; N, 5.91; Found: C, 35.79; H, 3.96; N, 5.89.

Synthesis of complex 9b

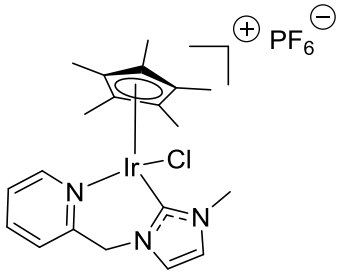
Synthesis of 3-methyl-1-(pyridin-2-ylmethyl)-1*H*-imidazol-3-ium iodide (6g)



6g

Following the general method for the synthesis of **6** using picolyl chloride (0.130 g, 1.02 mmol, prepared by basifying of picolyl chloride hydrochloride),

1-methylimidazole (0.088 g, 1 mmol) and NaI (0.15 g, 1mmol) in 6 mL of acetone, gave **6g** as a white solid. Yield: 0.192 g (64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (s, 1H), 8.31 (d, *J* = 4.7 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.47 (t, *J* = 1.6 Hz, 1H), 7.34 (s, 1H), 7.13 – 7.06 (m, 1H), 5.51 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.11, 149.88, 137.73, 136.82, 124.10, 123.82, 123.49, 123.01, 54.00, 37.25; MS (ESI) $[M\text{-}I]^+$ 173.65.



9b

Following the general method for the synthesis of **7** using imidazolium salt (**9b**) (0.151 g, 0.5 mmol), silver oxide (0.058 g, 0.25 mmol), $[Cp^*IrCl_2]_2$ (0.199 g, 0.25 mmol) and KPF_6 (0.092g, 0.5 equiv) in 6 mL of CH_2Cl_2, gave **9b** as a yellow solid. Yield: 0.24 g (64 %). ^{1}H NMR (400 MHz, DMSO) δ 8.78 (d, *J* = 5.3 Hz, 1H), 8.10 (t, *J* = 7.1 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.65 – 7.51 (m, 3H), 5.61 (d, *J* = 15.8 Hz, 1H), 4.74 (d, *J* = 15.7 Hz, 1H), 3.81 (s, 3H), 1.64 (s, 15H); ^{13}C NMR (101 MHz, DMSO) δ 157.13, 154.83, 154.18, 140.47, 126.62, 125.30, 123.50, 122.12, 90.46, 53.52, 36.46, 8.74; ^{31}P NMR (162 MHz, DMSO) δ -144.20 (sept, ^{2}J(P, F) = 712 Hz, PF_6); HRMS (ESI, m/z): calcd for $C_{20}H_{26}N_3ClIr$ $[M - PF_6]^+$ 536.1439, found 536.14447; Anal. Calcd for $C_{20}H_{26}ClF_6IrN_3P$: C, 35.27; H, 3.85; N, 6.17; Found: C, 35.51; H, 3.76; N, 6.11.

III. Single Crystal X-Ray Diffraction of 8a

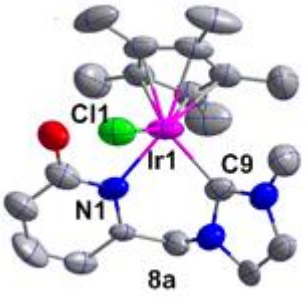


Figure S1. Molecular structure of complex **8a** with thermal ellipsoids shown at 50% probability level. Hydrogen atoms and PF_6 group were omitted for clarity. Selected bond lengths [Å] and bond angles [deg] for complex 1: Ir1−N1 2.050 (10), Ir1−C9 2.116 (10), Ir1−Cl1 2.474(3); Cl1−Ir1−N1 91.0(5), Cl1−Ir1−C9 84.3(5).

Table S1. Crystal data and structure refinement for 8a

Identification code	CCDC 1828919
Empirical formula	C_{20} H_{26} Cl F_6 Ir N_3 O P
Formula weight	697.06
Temperature	293 K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pnma
Unit cell dimensions	a = 13.5409(7) Å
	b = 12.9814(8) Å
	c = 13.6168(8) Å
Volume	2393.6(2) $Å^3$
Z	4
Density (calculated)	1.934 Mg/m^3
Absorption coefficient	5.821 mm^{-1}
F(000)	1352
Crystal size	0.15 x 0.2 x 0.4 mm^3
Theta range for data collection	2.992 to 25.677 °.

Index ranges	-16<=h<=16, -15<=k<=15, -16<=l<=16
Reflections collected	30879
Independent reflections	2380 [R(int) = 0.0898]
Completeness to theta =	99.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2380 / 83 / 210
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	R1 = 0.0406, wR2 = 0.1057
R indices (all data)	R1 = 0.0475, wR2 = 0.1115
Extinction coefficient	n/a

IV. Synthesis of *N*-alkylated amines via alkylation of amines with alcohols

1, GC analysis method for the condition optimization.

GC analysis method:

Injector: Mode: Split; temp.: 330 ^{o}C; Gas: N_2 Pressure: 1.34 bar; Split ratio: 39:1; Split flow: 67.6 mL/min.

Column: Wondacap 1 column Capillary column (30 m x 0.25 mm); Nominal film thickness: 0.250 μm; Temperature program: Initial temperature 100 ℃, heat to 120 ℃ with 5 ℃/min, then heat to 200 ℃ with 50 ℃/min, hold for 5 min.

Initial Flow: 1.62 mL/min; Average velocity: 39.4 cm/sec, Pressure: 1.34 bar. Detector (FID): Temp.: 330 ^{o}C; Hydrogen flow: 40.0 mL/min; Air flow: 400.0 mL/min.

Preparation of GC sample:

Dilute the crude reaction mixture with 5 mL of EtOAc, filtered through syringe filter and collected in GC vials for analysis.

Retention times: Benzaldehyde: 2.79 min; Aniline: 2.87 min; Benzyl alcohol: 3.33 min; *N*-1-diphenylmethanimine: 8.66 min; *N*, *N*-benzylphenylamine: 9.05 min.

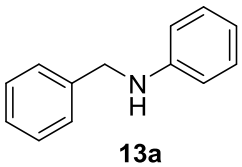
2, General procedure of *N*-alkylation of amines with alcohols

A mixture of aniline (0.5 mmol), benzylalcohol (0.5 mmol), and Ir complex (0.01 mmol), was heated in water (1 mL) to 110 ℃ in a closed vessel under N_2 for 24 h. After cooled to rt, the crude reaction mixture was diluted with 5 mL of EtOAc, filtered through a syringe filter and collected in GC vials for analysis.

3, Substrate Screening

A mixture of amine (0.5 mmol), alcohol (0.5 mmol), and Ir complex (0.01 mmol), was heated in water (1 mL) to 110 ℃ in a closed vessel under N_2 for 24 h. After cooled to rt, the crude reaction mixture was extracted with dichloromethane. The solvent was evaporated to dryness and the corresponding amine was purified by column chromatography with silica gel (ethyl acetate/ petroleum ether). The yields were calculated based on isolated products.

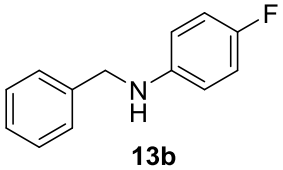
N-benzylaniline (**13a**).



13a

The compound was prepared as described in the general method (Colorless oil, 90% isolated yield, 82 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.35 (m, 4H), 7.34 – 7.27 (m, 1H), 7.20 (t, *J* = 7.5 Hz, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 2H), 4.35 (s, 2H), 4.04 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.27, 139.56, 129.37, 128.73, 127.61, 127.32, 117.67, 112.96, 48.42; MS (ESI) $[M+H]^+$ 183.65.

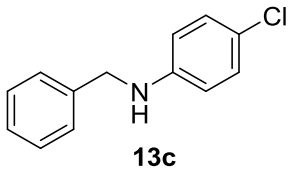
N-benzyl-4-fluoroaniline (**13b**).



13b

The compound was prepared as described in the general method (Colorless oil, 82% isolated yield, 82 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 4H), 7.34 – 7.28 (m, 1H), 6.90 (t, *J* = 8.8 Hz, 2H), 6.62 – 6.54 (m, 2H), 4.31 (s, 2H), 3.94 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.00 (d, J_{C-F} = 236.3 Hz), 144.61, 139.36, 128.79, 127.60, 127.43, 115.78 (d, J_{C-F}= 22.2 Hz), 113.76 (d, J_{C-F}= 7.4 Hz), 49.05; MS (ESI) $[M+H]^+$ 201.60.

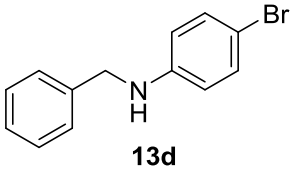
N-benzyl-4-chloroaniline (**13c**).



13c

The compound was prepared as described in the general method (Colorless oil, 85% isolated yield, 92 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 4.5 Hz, 4H), 7.32 - 7.28 (m, 1H), 7.15 – 7.08 (m, 2H), 6.59 – 6.53 (m, 2H), 4.31 (s, 2H), 4.07 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.77, 139.05, 129.18, 128.82, 127.53, 127.49, 122.21, 114.03 , 48.46; MS (ESI) $[M+H]^+$ 217.60.

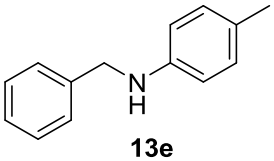
N-benzyl-4-bromoaniline (**13d**).



13d

The compound was prepared as described in the general method (Colorless oil, 87% isolated yield, 114 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.34 (m, 4H), 7.31 – 7.28 (m, 1H), 7.27 – 7.22 (m, 2H), 6.54 – 6.48 (m, 2H), 4.31 (s, 2H), 4.09 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 138.9, 132.0, 128.8, 127.5, 127.4, 114.5, 109.2, 48.3; MS (ESI) $[M+H]^+$ 263.40.

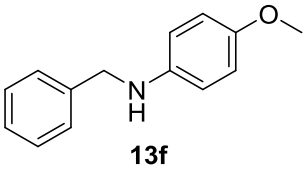
N-benzyl-4-bromoaniline (**13e**).



13e

The compound was prepared as described in the general method (Colorless oil, 70% isolated yield, 69 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 - 7.35 (m, 4H), 7.32 – 7.27 (m, 1H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.64 – 6.52 (m, 2H), 4.34 (s, 2H), 3.92 (s, 1H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.05, 139.79, 129.86, 128.71, 127.61, 127.26, 126.85, 113.11, 48.76, 20.52; MS (ESI) $[M+H]^+$ 197.65.

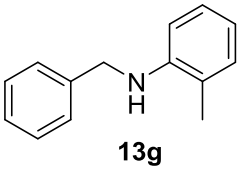
N-benzyl-4-methoxyaniline (**13f**).



13f

The compound was prepared as described in the general method (Colorless oil, 75% isolated yield, 80 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.35 (m, 4H), 7.33 – 7.30 (m, 1H), 6.87 – 6.78 (m, 2H), 6.67 – 6.61 (m, 2H), 4.32 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.25, 142.55, 139.79, 128.67, 127.62, 127.24, 114.99, 114.18, 55.8, 49.30; MS (ESI) $[M+H]^+$ 213.60.

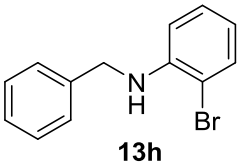
N-benzyl-2-methylaniline (**13g**).



13g

The compound was prepared as described in the general method (yellow oil, 76% isolated yield, 75 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dt, *J* = 14.9, 7.5 Hz, 4H), 7.30 (t, *J* = 6.9 Hz, 1H), 7.10 (dd, *J* = 12.8, 7.2 Hz, 2H), 6.69 (t, *J* = 7.4 Hz, 1H), 6.63 (d, *J* = 8.1 Hz, 1H), 4.39 (s, 2H), 3.88 (s, 1H), 2.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.21, 139.64, 130.20, 128.80, 127.68, 127.39, 127.30, 122.06, 117.32, 110.11, 48.46, 17.70; MS (ESI) $[M+H]^+$ 197.85.

N-benzyl-2-bromoaniline (**13h**).

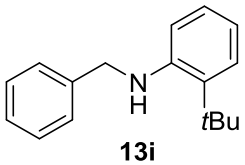


13h

The compound was prepared as described in the general method (yellow oil, 78% isolated yield, 102 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.8 Hz, 1H), 7.43 – 7.33 (m, 4H), 7.32 – 7.28 (m, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.67 – 6.51 (m, 2H), 4.78 (s, 1H), 4.42 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.92, 138.82, 132.51,

128.86, 128.62, 127.48, 127.36, 118.10, 111.75, 109.80, 48.13; MS (ESI) $[M+H]^+$ 261.75.

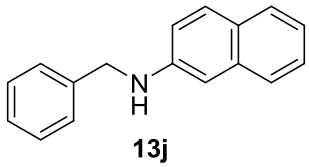
N-benzyl-2-(tert-butyl)aniline (**13i**).



13i

The compound was prepared as described in the general method (yellow oil, 65% isolated yield, 78 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.34 (m, 4H), 7.34 – 7.27 (m, 2H), 7.16 – 7.07 (m, 1H), 6.76 – 6.70 (m, 1H), 6.68 (d, *J* = 8.1 Hz, 1H), 4.42 (s, 2H), 4.30 (s, 1H), 1.45 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.25, 139.74, 133.35, 128.84, 127.60, 127.32, 126.32, 117.34, 112.04, 48.96, 34.33, 30.07; MS (ESI) $[M+H]^+$ 240.00.

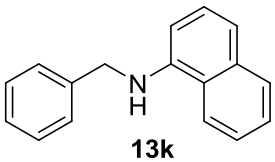
N-benzylnaphthalen-2-amine (**13j**).



13j

The compound was prepared as described in the general method (yellow oil, 92% isolated yield, 108 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.57 (m, 3H), 7.48 – 7.41 (m, 2H), 7.41 – 7.36 (m, 3H), 7.34 – 7.29 (m, 1H), 7.24 – 7.20 (m, 1H), 6.93 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.86 (d, *J* = 2.3 Hz, 1H), 4.45 (s, 2H), 4.20 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.89, 139.29, 135.30, 129.09, 128.82, 127.76, 127.74, 127.46, 126.45 , 126.12, 122.18, 117.98, 104.77, 48.49; MS (ESI) $[M+H]^+$ 233.60.

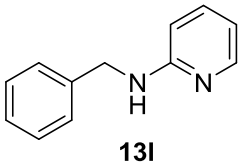
N-benzylnaphthalen-1-amine (**13k**).



13k

The compound was prepared as described in the general method (yellow oil, 85% isolated yield, 99 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (t, *J* = 7.0 Hz, 2H), 7.51 – 7.43 (m, 4H), 7.43 – 7.32 (m, 4H), 7.28 (d, *J* = 8.2 Hz, 1H), 6.65 (d, *J* = 7.4 Hz, 1H), 4.71 (s, 1H), 4.52 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.34, 139.22, 134.42, 128.86, 128.83, 127.87, 127.53, 126.74, 125.88, 124.88, 123.50, 120.02, 117.77, 104.88, 48.75; MS (ESI) $[M+H]^+$ 233.60.

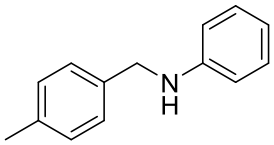
N-benzylpyridin-2-amine (**13l**).



13l

The compound was prepared as described in the general method (yellow oil, 80% isolated yield, 74 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 4.6 Hz, 1H), 7.44 – 7.30 (m, 5H), 7.29 (s, 1H), 6.63 – 6.56 (m, 1H), 6.38 (d, *J* = 8.4 Hz, 1H), 4.85 (s, 1H), 4.51 (d, *J* = 5.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.76, 148.30, 139.28, 137.61, 128.75, 127.50, 127.35, 113.26, 106.89, 46.44; MS (ESI) $[M+H]^+$ 184.60.

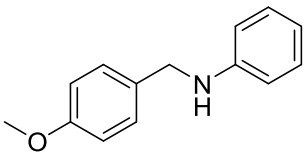
N-(4-methylbenzyl)aniline (**13m**).



13m

The compound was prepared as described in the general method (yellow oil, 79 % isolated yield, 78 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.1 Hz, 2H), 7.17 (dd, *J* = 11.3, 8.0 Hz, 4H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 2H), 4.28 (s, 2H), 3.98 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.35, 137.00, 136.48, 129.43, 129.37, 127.65, 117.61, 112.96, 48.21, 21.24; MS (ESI) $[M+H]^+$ 197.65.

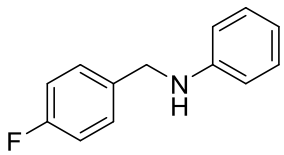
N-(4-methoxybenzyl)aniline (**13n**).



13n

The compound was prepared as described in the general method (yellow oil, 75 % isolated yield, 80 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.7 Hz, 2H), 7.21 (dd, *J* = 8.5, 7.4 Hz, 2H), 6.95 – 6.86 (m, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.66 (dd, *J* = 8.6, 1.0 Hz, 2H), 4.28 (s, 2H), 3.97 (s, 1H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.96, 148.32, 131.53, 129.36, 128.91, 117.60, 114.13, 112.95, 55.41, 47.90; MS (ESI) $[M+H]^+$ 213.60.

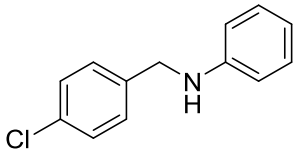
N-(4-fluorobenzyl)aniline (**13o**).



13o

The compound was prepared as described in the general method (yellow oil, 80 % isolated yield, 80 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 8.3, 5.5 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 2H), 7.06 (t, *J* = 8.6 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 8.2 Hz, 2H), 4.32 (s, 2H), 4.04 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.15 (d, J_{C-F} = 246.4Hz), 148.06, 135.23 (d, J_{C-F} = 2.9 Hz), 129.40, 129.10 (d, J_{C-F} = 8.0 Hz), 117.84, 115.54 (d, J_{C-F} = 21.2Hz), 112.99, 47.71; MS (ESI) $[M+H]^+$ 201.60.

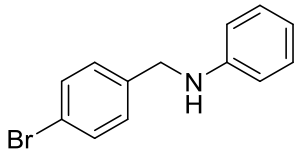
N-(4-chlorobenzyl)aniline (**13p**).



13p

The compound was prepared as described in the general method (yellow oil, 85 % isolated yield, 92 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 4H), 7.18 (dd, *J* = 8.5, 7.4 Hz, 2H), 6.76 – 7.62 (m, 1H), 6.64 – 6.60 (m, 2H), 4.32 (s, 2H), 4.07 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.95, 138.13, 132.99, 129.42, 128.87, 128.82, 117.93, 113.01, 47.74 ; MS (ESI) $[M+H]^+$ 217.50.

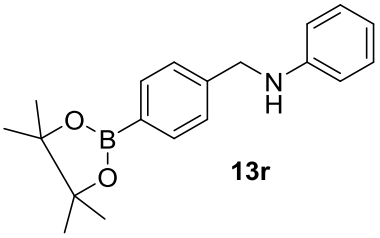
N-(4-bromobenzyl)aniline (**13q**).



13q

The compound was prepared as described in the general method (yellow oil, 82 % isolated yield, 107 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.22 (m, 2H), 7.18 (dd, *J* = 8.4, 7.5 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.7 Hz, 2H), 4.30 (s, 2H), 4.08 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.92, 138.67, 131.82, 129.42, 129.16, 121.04, 117.94, 113.01, 47.78; MS (ESI) $[M+H]^+$ 263.30.

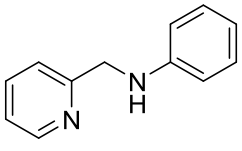
N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)aniline (**13r**).



13r

The compound was prepared as described in the general method (yellow oil, 46 % isolated yield, 71 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.18 (dd, *J* = 8.5, 7.4 Hz, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.66 – 6.55 (m, 2H), 4.36 (s, 2H), 4.08 (s, 1H), 1.36 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.18, 142.85, 135.26, 129.36, 126.85, 117.70, 112.99, 83.90, 48.49, 24.99; MS (ESI) $[M+H]^+$ 310.05.

N-(pyridin-2-ylmethyl)aniline (**13s**).

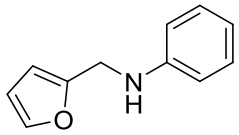


13s

The compound was prepared as described in the general method (yellow oil, 55 % isolated yield, 51 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.8 Hz, 1H), 7.64 (td, *J* = 7.7, 1.8 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.22 – 7.14 (m, 3H), 6.73 (t, *J* = 7.8 Hz, 1H), 6.70 – 6.65 (m, 2H), 4.47 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.64,

149.31, 148.00, 136.74, 129.35, 122.20, 121.67, 117.70, 113.16, 49.42; MS (ESI) $[M+H]^+$ 184.65.

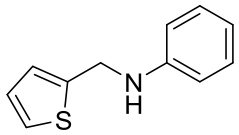
N-(furan-2-ylmethyl)aniline (**13t**).



13t

The compound was prepared as described in the general method (yellow oil, 50 % isolated yield, 43 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 1.6 Hz, 1H), 7.21 (dd, *J* = 8.4, 7.5 Hz, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 7.7 Hz, 2H), 6.34 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.25 (d, *J* = 3.1 Hz, 1H), 4.33 (s, 2H), 4.04 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.87, 147.75, 142.04, 129.36, 118.16, 113.29, 110.46, 107.10, 41.58; MS (ESI) $[M+H]^+$173.70.

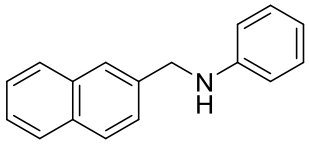
N-(thiophen-2-ylmethyl)aniline (**13u**).



13u

The compound was prepared as described in the general method (yellow oil, 70 % isolated yield, 66 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 3H), 7.05 (d, *J* = 3.3 Hz, 1H), 7.00 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.79 (t, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 7.7 Hz, 2H), 4.54 (s, 2H), 4.05 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.70, 143.05, 129.37, 126.95, 125.11, 124.67, 118.18, 113.27, 43.50; MS (ESI) $[M+H]^+$ 189.60.

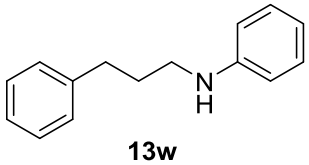
N-(naphthalen-2-ylmethyl)aniline (**13v**).



13v

The compound was prepared as described in the general method (yellow oil, 86 % isolated yield, 100 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 - 7.81 (m, 4H), 7.55 – 7.42 (m, 3H), 7.25 – 7.15 (m, 2H), 6.79 – 6.65 (m, 3H), 4.51 (s, 2H), 4.15 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.30, 137.08, 133.62, 132.86, 129.42, 128.50, 127.88, 127.82, 126.28, 126.04, 125.85, 117.77, 113.06, 48.64; MS (ESI) $[M+H]^+$ 233.65.

N-(3-phenylpropyl)aniline (**13w**).

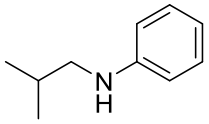


13w

The compound was prepared as described in the general method (yellow oil, 60 % isolated yield, 63 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.31 (m, 2H), 7.26 – 7.17

(m, 5H), 6.76 – 6.70 (m, 1H), 6.62 (d, *J* = 1.0 Hz, 1H), 6.60 (d, *J* = 0.9 Hz, 1H), 3.64 (d, *J* = 11.8 Hz, 1H), 3.17 (t, *J* = 7.0 Hz, 2H), 2.82 – 2.71 (t, *J* = 7.0 Hz, 2H), 2.02 – 1.94 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.47, 141.79, 129.35, 128.55, 128.52, 126.07, 117.34, 112.87, 43.54, 33.53, 31.19; MS (ESI) $[M+H]^+$ 211.60.

N-isobutylaniline (**13x**).



13x

The compound was prepared as described in the general method (yellow oil, 25 % isolated yield,13 mg). 1H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.16 (m, 2H), 6.73 - 6.69 (m, 1H), 6.66 – 6.60 (m, 2H), 3.72 (s, 1H), 2.96 (d, J = 6.8 Hz, 2H), 1.92 (hept, *J* = 6.7 Hz, 1H), 1.03 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.35, 150.17, 137.99, 129.00, 127.82, 127.49, 107.87, 47.12; MS (ESI) $[M+H]^+$ 149.70.

3, General procedure of *N*-alkylation of *p*-methylbenzenesulfonamide with alcohols

A mixture of *p*-methylbenzenesulfonamide (0.5 mmol), benzylalcohol (0.5 mmol), Na_2CO_3(0.01/0.25/0.5 mmol) and **8a** (0.01 mmol), was heated in water (1 mL) to 110 ℃ in a closed vessel under N_2 for 24 h. After cooled to rt, the crude reaction mixture was diluted with 5 mL of EtOAc, filtered through a syringe filter and collected in GC vials for analysis.

Table S2. Optimization of *N*-alkylation of *p*-Methylbenzenesulfonamide with Alcohols

entry	Na_2CO_3 (mmol)	Conversion(%)	Imine(%)	Amine(%)
1	0	0	0	0
2	0.01	44.7	1.3	43.4
3	0.25	71.6	1.6	70.0
4	0.5	94.2	0.3	93.9

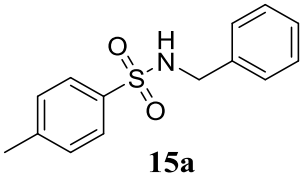
[a]*N*-alkylation reaction conditions: 0.5 mmol *p*-methylbenzenesulfonamide, 0.5 mmol benzyl alcohol, 2 mol% **8a**, Na_2CO_3, 1 mL water, 110 °C, 24 h; [b]Values given are yields with respect to unreacted *p*-methylbenzenesulfonamide, as determined by analysis of the GC.

Substrate Screening

Under a nitrogen atmosphere, to a 15-mL closed vessel were added *p*-methylbenzenesulfonamide (0.5 mmol), alcohol (0.5 mmol), Na_2CO_3(0.5 mmol)

and **8a** (0.01 mmol), and water (1 mL). The mixture was heated at 110 ^{o}C for 24 h and allowed to cool to ambient temperature. In the case of **15i** and **15k**, the mixture was concentrated under vacuum and purified by flash column chromatography with petroleum ether /ethyl acetate to afford the corresponding product. In the other cases, the reaction mixture became clear and a large amount of precipitation appeared after about 1 hour. The precipitation was isolated by simple filtration, washed with water three times and dried under vacuum to afford the desired *N*-alkylated product.

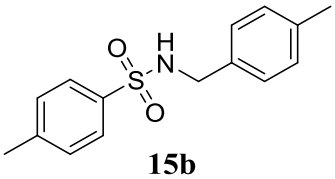
N-benzyl-4-methylbenzenesulfonamide (**15a**).



15a

The compound was prepared as described in the general method (white solid, 89% isolated yield, 116 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.29 - 7.26 (m, 3H), 7.24 – 7.17 (m, 2H), 4.85 (s, 1H), 4.13 (d, *J* = 6.2 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.64, 136.94, 136.40, 129.86, 128.79, 127.99, 127.30, 47.37, 21.67; MS (ESI) $[M+Na]^+$ 283.95.

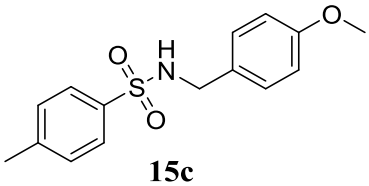
4-methyl-N-(4-methylbenzyl)benzenesulfonamide (**15b**).



15b

The compound was prepared as described in the general method (white solid, 83% isolated yield, 114 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.08 (s, 4H), 4.68 (s, 1H), 4.07 (s, 2H), 2.44 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.62, 137.83, 136.95, 133.31, 129.86, 129.48, 127.99, 127.33, 47.18, 21.68, 21.22; MS (ESI) $[M+Na]^+$ 297.90.

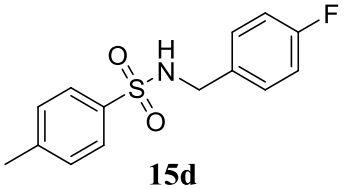
N-(4-methoxybenzyl)-4-methylbenzenesulfonamide (**15c**).



15c

The compound was prepared as described in the general method (white solid, 85% isolated yield, 124 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.12 - 7.08 (m, 2H), 6.81 – 6.77 (m, 2H), 4.69 (s, 1H), 4.04 (d, *J* = 3.7 Hz, 2H), 3.77 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.41, 143.59, 136.99, 129.85, 129.39, 128.39, 127.31, 114.17, 55.41, 46.91, 21.68; MS (ESI) $[M+Na]^+$ 313.95.

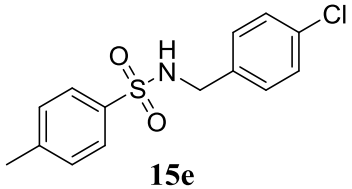
N-(4-fluorobenzyl)-4-methylbenzenesulfonamide (**15d**).



15d

The compound was prepared as described in the general method (white solid, 82% isolated yield, 114 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.7 Hz, 2H), 7.22 – 7.11 (m, 2H), 6.94 (t, *J* = 8.3 Hz, 2H), 4.97 (s, 1H), 4.08 (d, *J* = 5.0 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.46 ($J_{C, F}$ = 247.5 Hz), 143.74, 136.91, 132.26 ($J_{C, F}$ =3.0 Hz), 129.87, 129.74 ($J_{C, F}$ = 9.1 Hz), 127.26, 115.63 ($J_{C, F}$ = 21.2 Hz), 46.64, 21.66; MS (ESI) $[M+Na]^+$ 301.95.

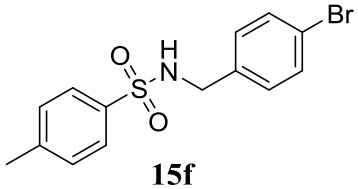
N-(4-chlorobenzyl)-4-methylbenzenesulfonamide (**15e**).



15e

The compound was prepared as described in the general method (white solid, 90% isolated yield, 132 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.70 (m, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.25 – 7.20 (m, 2H), 7.15 – 7.10 (m, 2H), 4.99 (s, 1H), 4.08 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.80, 136.88, 135.01, 133.82, 129.89, 129.34, 128.89, 127.25, 46.66, 21.68; MS (ESI) $[M+Na]^+$ 317.95.

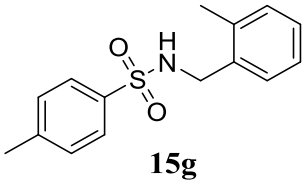
N-(4-bromobenzyl)-4-methylbenzenesulfonamide (**15f**).



15f

The compound was prepared as described in the general method (white solid, 90% isolated yield, 152 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.70 (m, 2H), 7.40 – 7.35 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 2H), 4.99 (s, 1H), 4.06 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.81, 136.88, 135.53, 131.85, 129.90, 129.67, 127.25, 121.92, 46.72, 21.69; MS (ESI) $[M+Na]^+$ 360.95.

4-methyl-N-(2-methylbenzyl)benzenesulfonamide (**15g**).

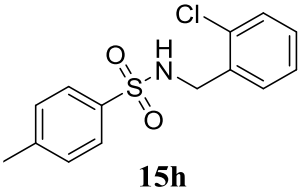


15g

The compound was prepared as described in the general method (white solid, 43% isolated yield, 59 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.21 – 7.15 (m, 1H), 7.14 – 7.09 (m, 3H), 4.49 (t, *J* = 5.6 Hz, 1H), 4.09 (d, *J* = 5.9 Hz, 2H), 2.44 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ

143.69, 136.87, 136.72, 134.00, 130.75, 129.87, 129.00, 128.40, 127.34, 126.33, 45.55, 21.70, 18.94; MS (ESI) $[M+Na]^+$ 299.57

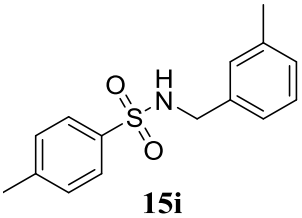
N-(2-chlorobenzyl)-4-methylbenzenesulfonamide (**15h**).



15h

The compound was prepared as described in the general method (white solid, 51% isolated yield, 75 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 7.32 – 7.26 (m, 2H), 7.26 (s, 1H), 7.24 (s, 1H), 7.22 – 7.13 (m, 2H), 4.92 (t, *J* = 6.3 Hz, 1H), 4.24 (d, *J* = 6.5 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.61, 137.05, 134.01, 133.52, 130.46, 129.77, 129.63, 129.44, 127.22, 45.35, 21.67; MS (ESI) $[M+Na]^+$ 319.30

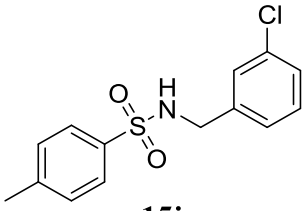
4-methyl-N-(3-methylbenzyl)benzenesulfonamide (**15i**).



15i

The compound was prepared as described in the general method (white solid, 76% isolated yield, 104 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 5.0 Hz, 2H), 4.84 (s, 1H), 4.07 (d, *J* = 6.2 Hz, 2H), 2.43 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.56, 138.48, 136.99, 136.28, 129.81, 128.72, 128.68, 128.65, 127.30, 124.98, 47.34, 21.64, 21.36; MS (ESI) $[M+Na]^+$ 299.66

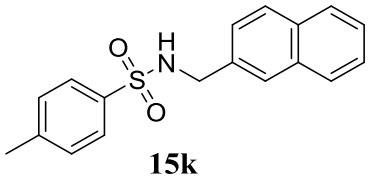
N-(3-chlorobenzyl)-4-methylbenzenesulfonamide (**15j**).



15j

The compound was prepared as described in the general method (white solid, 86% isolated yield, 127 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.21 – 7.18 (m, 2H), 7.12 (s, 1H), 7.11 – 7.05 (m, 1H), 5.05 (s, 1H), 4.09 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.84, 138.52, 136.86, 134.57, 130.02, 129.90, 128.07, 128.04, 127.24, 126.05, 46.73, 21.67; MS (ESI) $[M+Na]^+$ 319.24

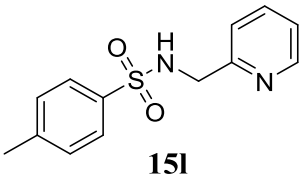
4-methyl-N-(naphthalen-2-ylmethyl)benzenesulfonamide (**15k**).



15k

The compound was prepared as described in the general method (white solid, 91% isolated yield, 142 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.67 (m, 5H), 7.59 (s, 1H), 7.46 (dt, *J* = 6.2, 3.4 Hz, 2H), 7.30 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.26 (s, 1H), 7.24 (s, 1H), 4.97 (t, *J* = 5.2 Hz, 1H), 4.27 (d, *J* = 5.8 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.66, 137.01, 133.75, 133.27, 132.96, 129.83, 128.65, 127.87, 127.77, 127.30, 126.81, 126.44, 126.27, 125.79, 47.57, 21.63; MS (ESI) $[M+Na]^+$ 333.95.

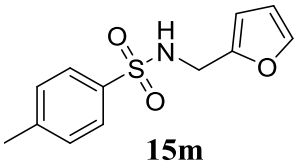
4-methyl-N-(pyridin-2-ylmethyl)benzenesulfonamide (**15l**).



15l

The compound was prepared as described in the general method (white solid, 66% isolated yield, 86 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 4.5 Hz, 1H), 7.71 (s, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.15 (dd, *J* = 15.4, 7.5 Hz, 2H), 6.12 (s, 1H), 4.22 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.05, 149.05, 143.43, 136.89, 136.71, 129.70, 127.29, 122.69, 122.09, 47.57, 21.59; MS (ESI) $[M+H]^+$ 263.05.

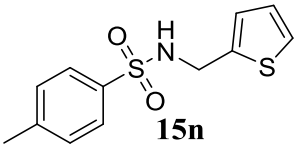
N-(furan-2-ylmethyl)-4-methylbenzenesulfonamide (**15m**).



15m

The compound was prepared as described in the general method (white solid, 43% isolated yield, 54 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.23 (m, 1H), 6.23-6.22 (m, 1H), 6.09 (d, *J* = 3.2 Hz, 1H), 4.71 (t, *J* = 5.5 Hz, 1H), 4.17 (d, *J* = 6.0 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.61, 143.65, 142.66, 136.96, 129.80, 127.28, 110.54, 108.35, 40.31, 21.68; MS (ESI) $[M+Na]^+$ 273.95.

4-methyl-N-(thiophen-2-ylmethyl)benzenesulfonamide (**15n**).

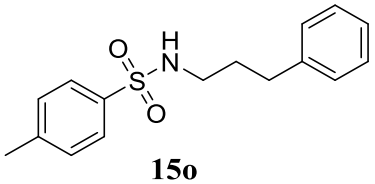


15n

The compound was prepared as described in the general method (white solid, 48% isolated yield, 64 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 5.0 Hz, 1H), 6.89-6.86 (m, 2H), 4.73 (t, *J* = 5.5 Hz, 1H),

4.33 (d, *J* = 6.1 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.81, 139.02, 136.87, 129.91, 127.35, 127.02, 126.66, 125.99, 42.26, 21.71; MS (ESI) $[M+Na]^+$ 289.90.

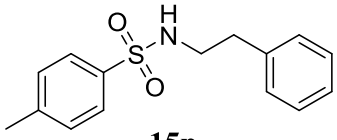
4-methyl-N-(3-phenylpropyl)benzenesulfonamide (**15o**).



15o

The compound was prepared as described in the general method (white solid, 60% isolated yield, 86 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.71 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.24 (m, 2H), 7.23 – 7.17 (m, 1H), 7.12 -7.18 (m, 2H), 4.63 (t, *J* = 6.1 Hz, 1H), 2.99 (q, *J* = 6.8 Hz, 2H), 2.62 (t, *J* = 7.4 Hz, 2H), 2.45 (s, 3H), 1.84-1.77 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.53, 140.99, 137.03, 129.84, 128.59, 128.47, 127.23, 126.20, 42.76, 32.85, 31.28, 21.66; MS (ESI) $[M+Na]^+$ 321.95.

4-methyl-N-phenethylbenzenesulfonamide (**15p**).



15p

The compound was prepared as described in the general method (white solid, 52% isolated yield, 71 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.26 (m, 3H), 7.26 – 7.19 (m, 2H), 7.11 – 7.05 (m, 2H), 4.43 (s, 1H), 3.21 (q, *J* = 6.8 Hz, 2H), 2.76 (t, *J* = 7.0 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.57, 137.77, 137.00, 129.85, 128.89, 128.86, 127.22, 126.95, 44.32, 35.92, 21.66; MS (ESI) $[M+Na]^+$ 299.44.

V. Mechanism Details

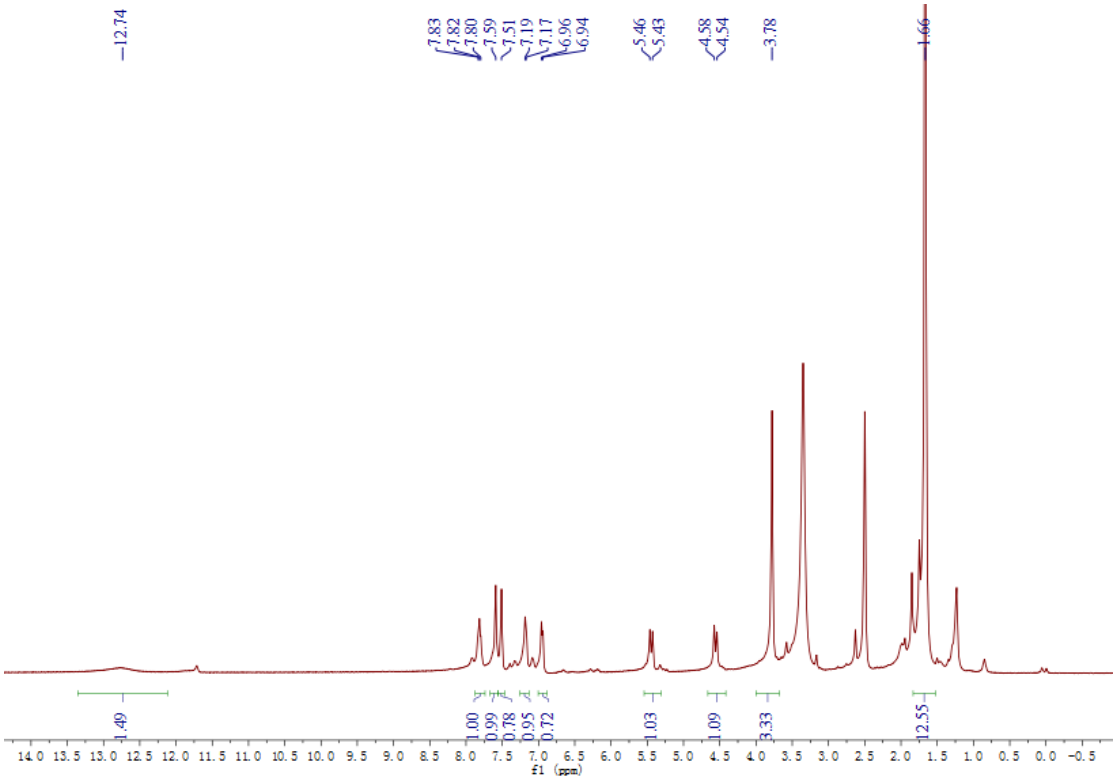


Figure S2. The ^{1}H NMR spectra of the crude product of **7a** in DMSO-d_6, which heated in water at 110 ^{o}C for 24 h.

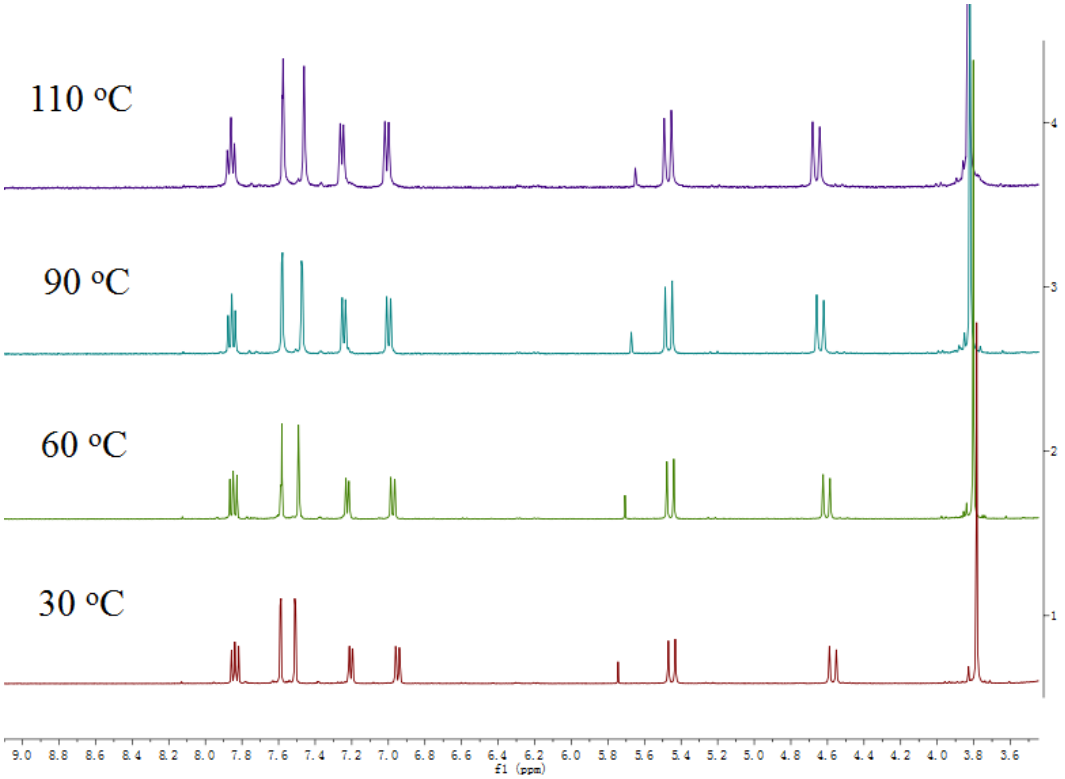


Figure S3. The variable-temperature ^{1}H NMR spectra of **8a** in DMSO-d_6

.

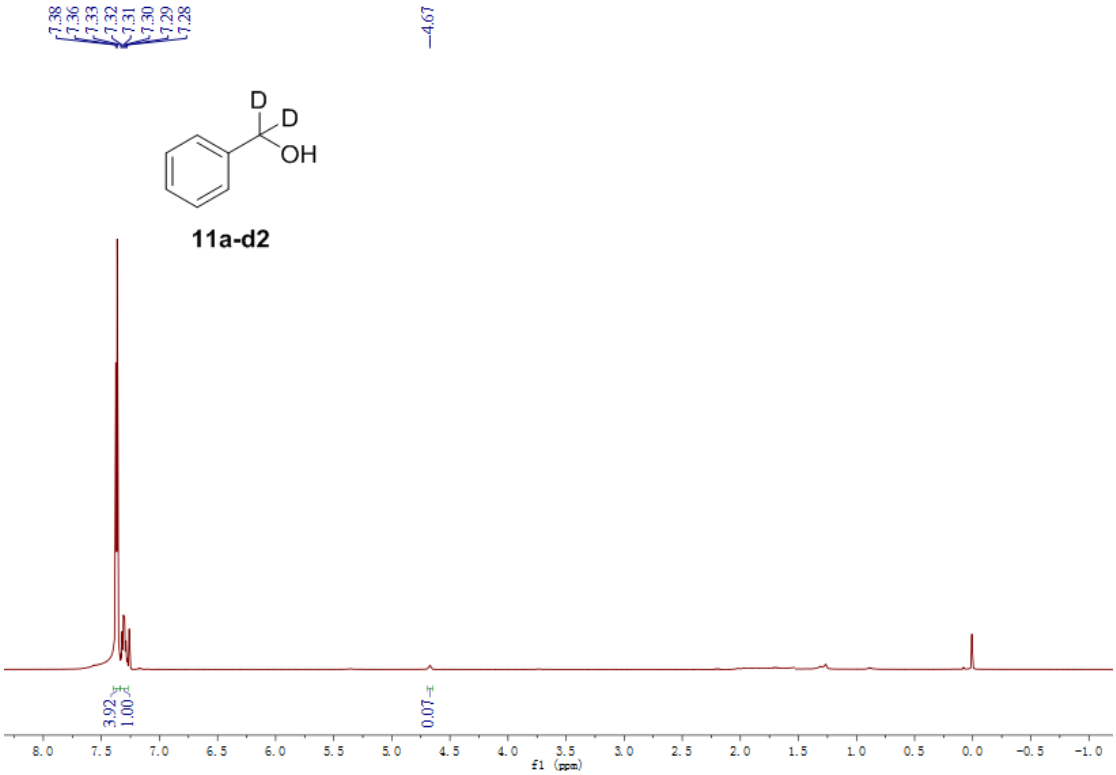


Figure S4. The ^{1}H NMR spectra of **11a-d2** in $CDCl_3$.

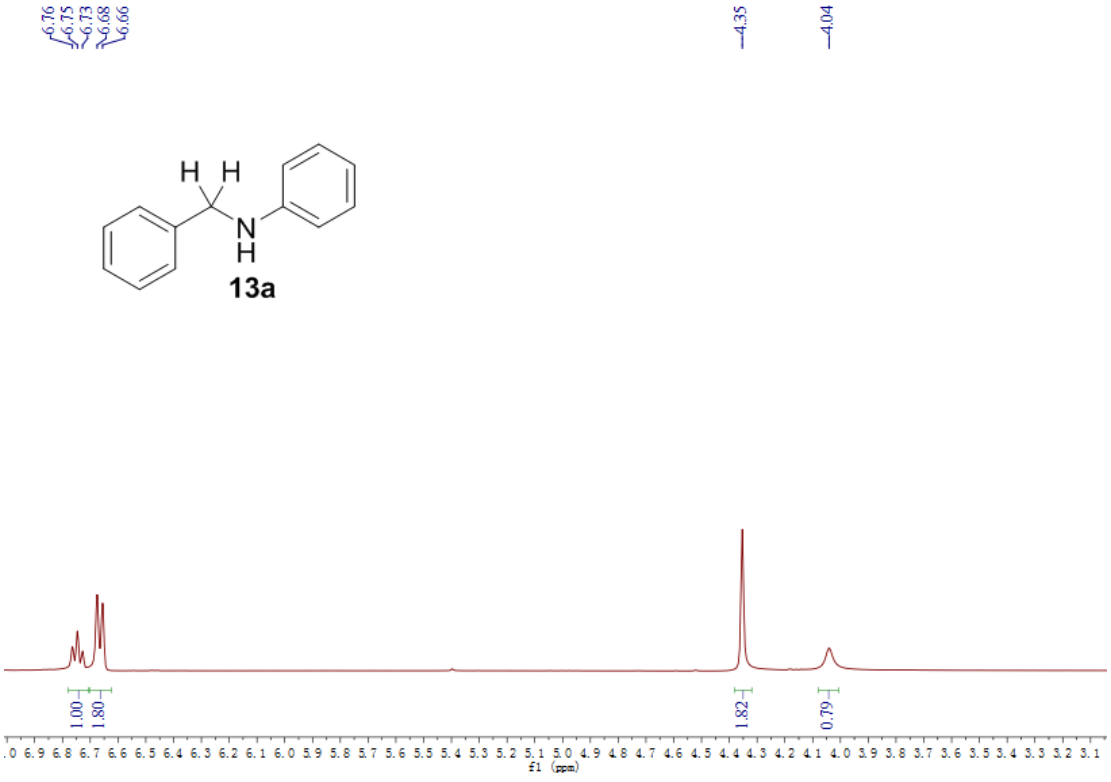


Figure S5. The ^{1}H NMR ($CDCl_3$) spectra of **13a** in the range of 3-7 ppm.

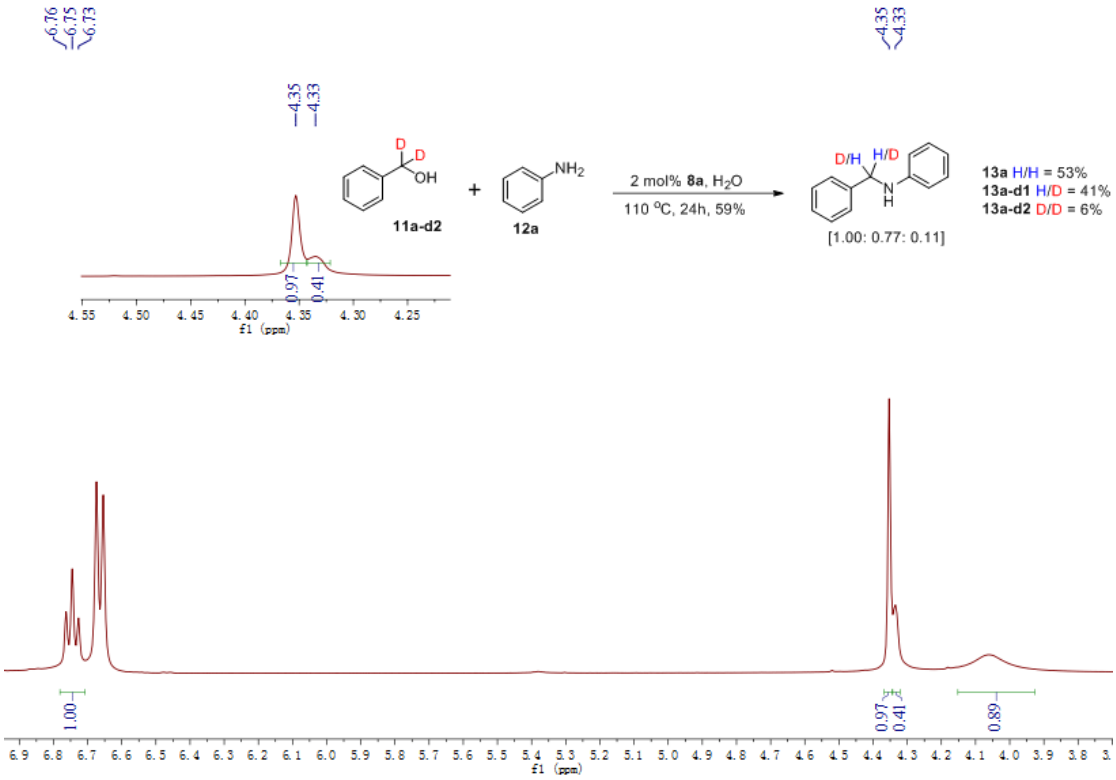


Figure S6. The ^{1}H NMR ($CDCl_3$) spectra of the products of the reaction of **11a-d2** with **12a** in the range of 3-7 ppm.

Conversion was calculated by ^{1}H NMR integration ratio.

	11a+11a-d1	11a	11a-d1	11a-d2
Signal δ	6.75[*para*-H, (1H)]	4.35[benzyl-H, (2H)]	4.33[benzyl-H, (2H)]	
Integral Value	1.00	0.97/1.82 = 0.53	0.41	
Calculated ratio		53%	41%	6%

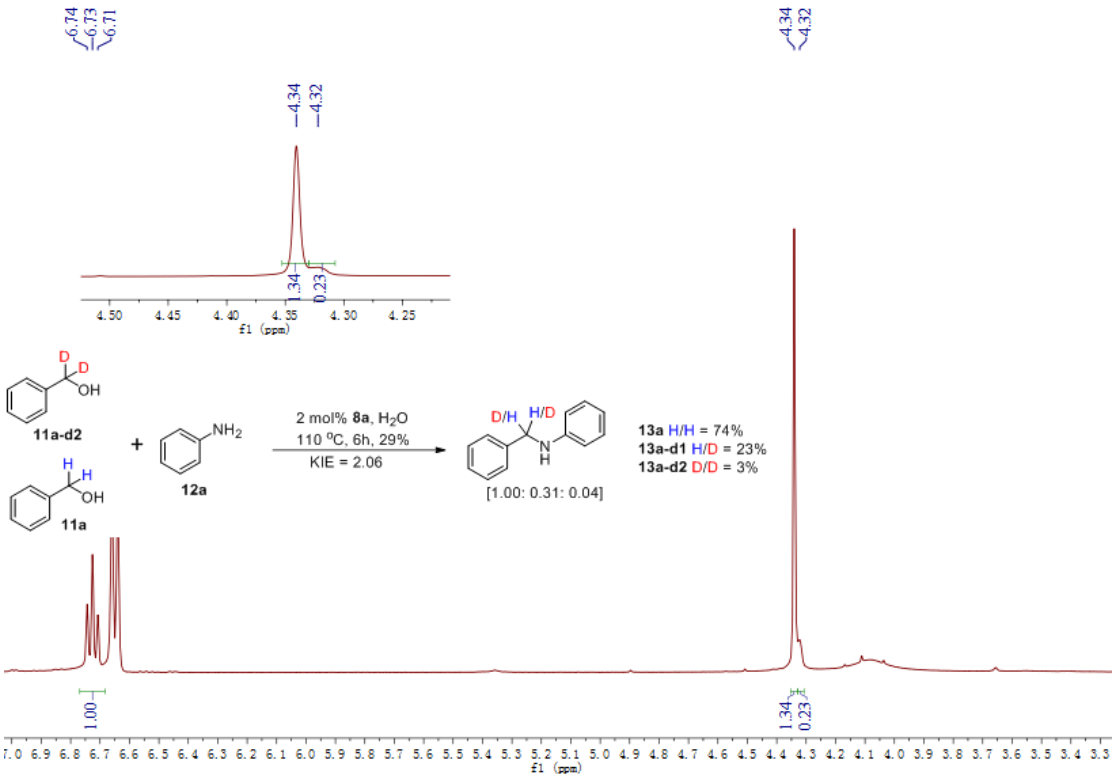


Figure S7. The ^{1}H NMR ($CDCl_3$) spectra of the products of intermolecular competition reactions in the range of 3-7 ppm.

Conversion was calculated by ^{1}H NMR integration ratio.

	11a+11a-d1	**11a**	**11a-d1**	**11a-d2**
Signal δ	6.75[*para*-H, (1H)]	4.35[benzyl-H, (2H)]	4.33[benzyl-H, (2H)]	
Integral Value	1.00	1.34/1.82 = 0.53	0.23	
Calculated ratio		74%	23%	3%
KIE		KIE = 2.09	29% 11a	23% 11a

Due the influnce of the H/D exchange, we calculated the **11a-d1**(23%) or **11a-d2** (3%) would provide the 29% **11a** or 23% **11a**, respectively. And the average value is 26%, which the KIE = (74% - 26%)/23% = 2.09.

The parallel reactions

Due to the product is insoluble in water, we can't analysis the reaction process in one vessel by the time interval. Therefore, we have conducted 5 separated reactions for the **11a** or **11a-d2**. A mixture of **12a**(0.5 mmol), **11a** or **11a-d2** (0.5 mmol), and **8a** (0.01 mmol), was heated in water (1 mL) to 110 ℃ in a closed vessel under N_2 for

certain time(2h, 3h, 4h, 5h, 6h). After cooled to rt, the crude reaction mixture was diluted with 5 mL of EtOAc, filtered through a syringe filter and collected in GC vials for analysis.

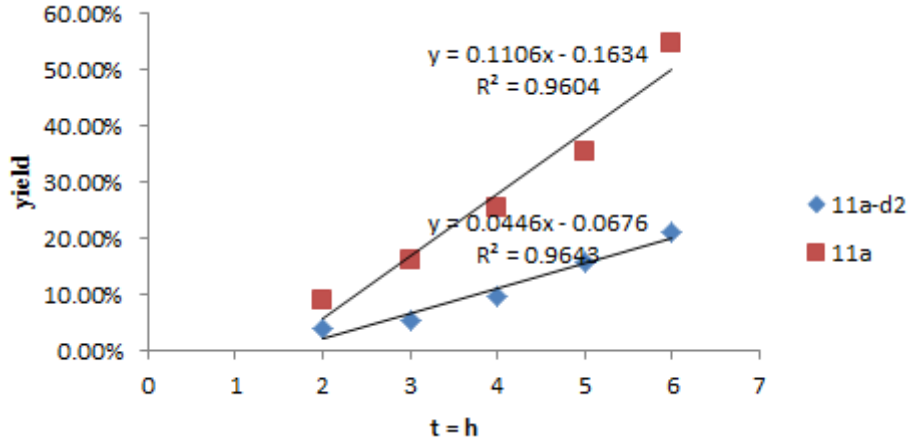


Figure S8. The plot of initial rates for KIE measurements.

Computational Section

Computational Details

All the structures were optimized by the density functional theory (DFT)[8] at the M06-L[9] functional with basis sets I (BSI, lanl2dz[10] for Ir and 6-31G** for the other atoms) in the gas phase. Frequency analysis calculations for optimized structures were performed to characterize the structures to be minima (no imaginary frequency). Based on M06-L/BSI optimized geometries, the energy results were further refined by calculating the single point energy at the M06-L/BSII (SMD[11], water) level of theory (BSII designates SDD[12] for Ir and 6-311++G**[13] for the other atoms). All the calculations were performed with the Gaussian 09 program.[14] The 3D optimized structures were displayed by CYLview visualization program.[15]

Firstly, we have studied the possible form of the starting species by DFT calculations (**Figure S9**). The initial step of the reaction involved the formation of cation iridium species by the elimination of HCl of **8a,** followed by the coordinated with the H_2O. The deprotonation of the reactive 2-HP or methylene

spacer in the ligand backbone, would give the active intermediate **Cat-1** or **Cat-2**, respectively. The **Cat-3** could be formed by the deprotonation of the two active sites, simultaneously. And, the **Cat-1** has the lowest energy (30.5 kcal/mol and 27.8 kcal/mol lower than that of **Cat-2** and **Cat-3**, respectively). These results indicated that the deprotonation of **8a** is more favored via the 2-HP in accord with the studies of the stepwise deprotonation of **8a**, and the **Cat-1** would be the starting species for the catalytic cycle.

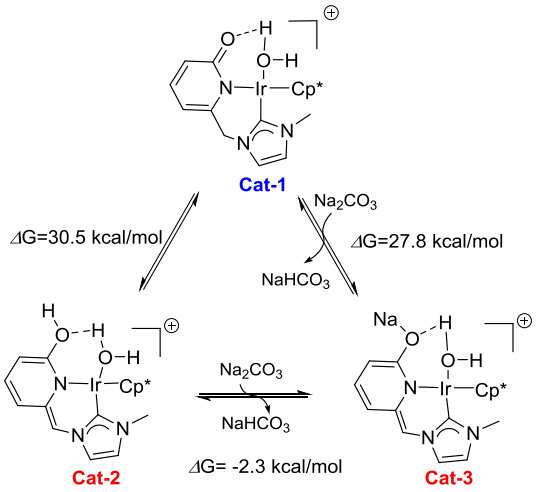


Figure S9. The Comparison of the Deprotonation of **8a** (free energies are given in kcal/mol)

Herein, we have also calculated the details of the catalytic cycle for the *N*-alkylation reactions by DFT studies. Firstly, the catalytic cycle (**Figure S10**) begins with the coordination of the benzyl alcohol **11a** to the **Cat-1**, forming **IM-1** (4.7 kcal/mol). From **IM-1**, the dehydrogenation of the alcohol would occur via either an inner-sphere or an outer-sphere mechanism. The outer-sphere pathway initiates from **IM-2** (9.9 kcal/mol), which is formed by the dissociation of the benzyl alcohol from **IM-1**. From **IM-2**, the dehydrogenation of **11a** undergoes via transition state **TS-1** (25.3 kcal/mol), leading to an iridium hydride intermediate **IM-3** (15.9 kcal/mol). The **TS-1** involves a bifunctional step, in which the α-hydrogen and the proton of the

alcohol would transfer synchronously to the metal center and pyridone oxygen, respectively. Then the dissociation of the benzaldehyde, resulting in the iridium hydride **IM-4** (8.9 kcal/mol). The overall barrier for the outer-sphere dehydrogenation is 25.3 kcal/mol relative to **Cat-1**. In the inner-sphere steps, the proton of the alcohol in the **IM-1** transfers to the pyridone oxygen to give **IM-5** (11.7 kcal/mol), via **TS-2** (10.4 kcal/mol). Then the dissociation of the pyridine ligand and the β-H agostic interaction lead to the **IM-6** (23.7 kcal/mol) and **IM-7** (25.3 kcal/mol), respectively. From **INT-7**, the β-hydride elimination (**TS-3**, 30.9 kcal/mol) takes place, to provide **IM-8** (26.6 kcal/mol). The overall barrier for the inner-sphere dehydrogenation is 30.9 kcal/mol relative to **Cat-1**, which is 5.6 kcal/mol higher than that of the outer-sphere pathway.

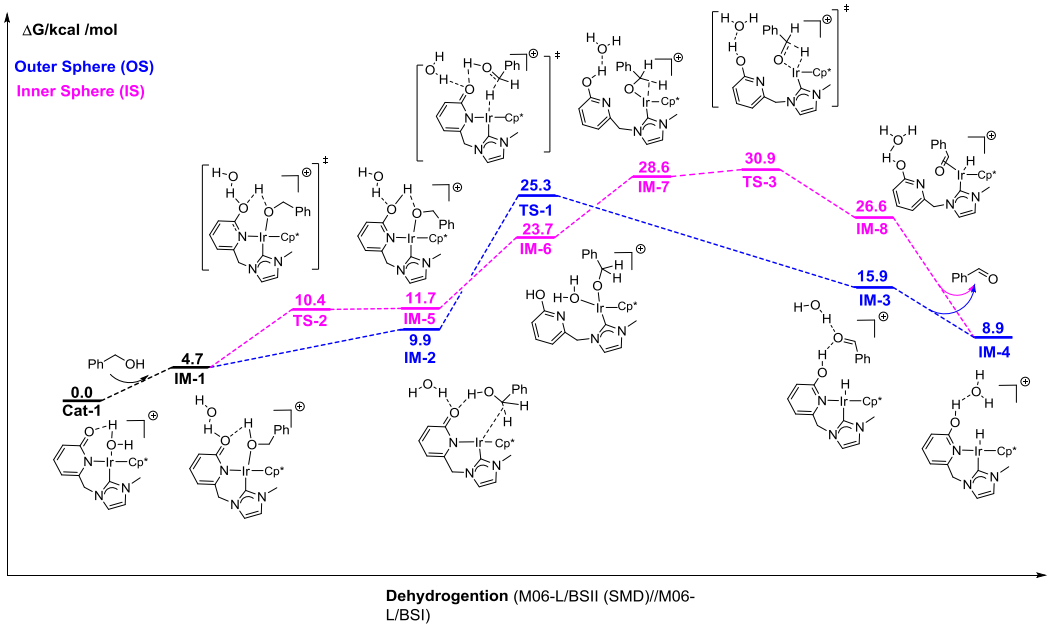


Figure S10. Calculated free-energy profile for the dehydrogenation of benzyl alcohol with **8a**. Free energies are given in kcal/mol.

The hydrogenation of imine would take place similar to the reverse of the alcohol oxidation (**Figure S11**). The outer-sphere steps begin with the formation of a hydrogen bond between imine and **IM-4**, forming **IM-9** (14.3 kcal/mol). From **IM-9**, the proton and hydride are transferred asynchronously, though **TS-4** (15.2 kcal/mol) and **TS-5** (15.1 kcal/mol), leading to **IM-10** (13.1

kcal/mol) and **IM-11** (-0.2 kcal/mol), respectively. The overall barrier for the hydrogenation of imines is 6.3 kcal/mol (from **IM-3** to **TS-4**). Finally, the *N*-alkylated product will be released and the catalytic species **Cat-1** is regenerated. The inner-sphere routes start from the dissociation of the pyridine ligand and the dissociation of the H_2O with **IM-4**, forming **IM-12** (16.3 kcal/mol). Then the dissociation of the imine with **IM-12**, leading to **IM-13** (28.8 kcal/mol). From **IM-13**, the hydrogenation of imine undergoes via transition state **TS-6** (33.7 kcal/mol), leading to **IM-14** (28.9 kcal/mol). Then the dissociation of the pyridine ligand to give **IM-15** (24.6 kcal/mol), followed by a proton transfer to form the **IM-16** (-0.1 kcal/mol). The overall energy barrier is 24.8 kcal/mol (from **IM-3** to **TS-5**), which is 18.5 kcal/mol higher than that of the outer-sphere pathway. Therefore, both the dehydrogenation and hydrogenation steps are favored via the outer-sphere mechanism, and the RDS is involved in the dehydrogenation step, which is consistent with the experimental KIE results.

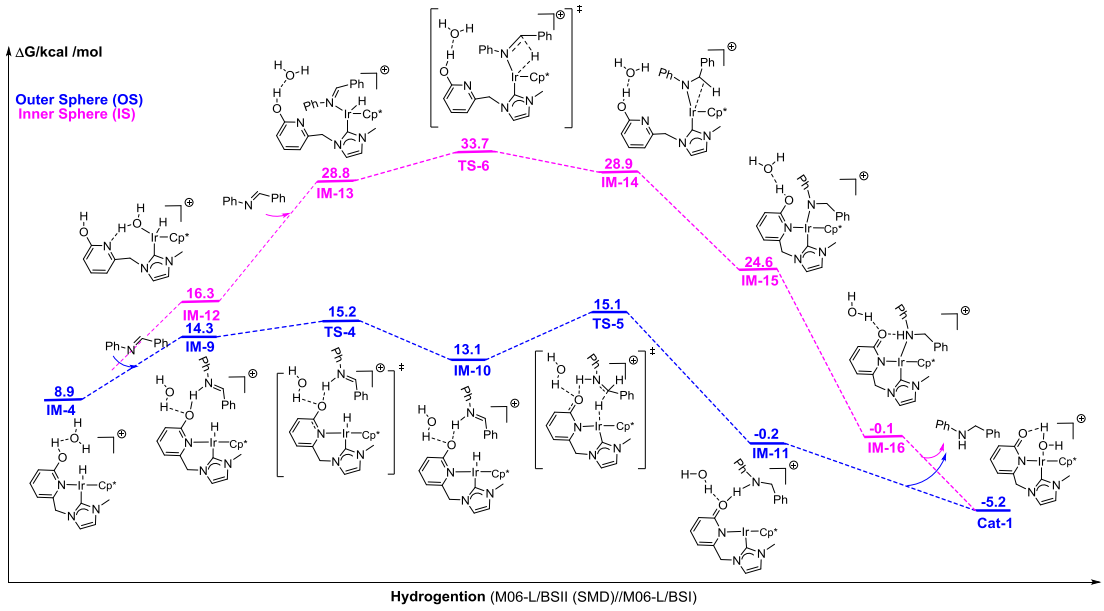
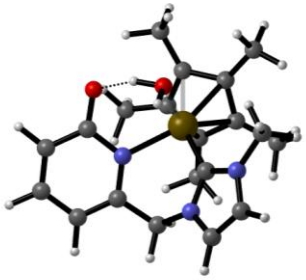


Figure S11. Calculated free-energy profile for the hydrogenation of imine with **8a**.

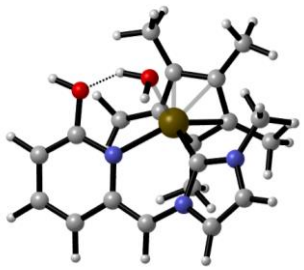
Free energies are given in kcal/mol.

Cat-1



77 0.365629 -0.191235 -0.104607
7 0.990934 2.778812 -0.789840
7 -0.736987 2.528016 0.466560
7 -1.776988 -0.075749 -0.218718
6 0.239904 1.832453 -0.168166
6 0.489922 4.044826 -0.536663
1 0.946108 4.933358 -0.942915
6 -0.600584 3.886170 0.254639
1 -1.279503 4.608369 0.678636
6 -2.515895 0.814876 0.491000
6 -3.889443 0.743051 0.552678
1 -4.448018 1.476893 1.123042
6 -4.535034 -0.304441 -0.130296
1 -5.616504 -0.393947 -0.082169
6 -3.804512 -1.196655 -0.870725
1 -4.269879 -2.003234 -1.425740
6 -2.385093 -1.082019 -0.965168
6 2.149561 2.499395 -1.618731
1 2.230898 1.418016 -1.738730
1 3.058556 2.888432 -1.152927
1 2.030854 2.961113 -2.600926
6 2.302983 -1.173455 0.007058
6 2.081817 -0.402114 1.192281
6 0.870489 -0.901020 1.829916
6 0.431167 -2.074880 1.073482
6 1.284906 -2.228129 -0.044469
6 3.422173 -1.037186 -0.961398
1 4.151873 -1.842198 -0.821524
1 3.953883 -0.090570 -0.838145
1 3.065533 -1.097347 -1.993940
6 2.921023 0.715046 1.698987
1 3.645351 0.343828 2.431661
1 2.318141 1.481509 2.193714
1 3.484663 1.196844 0.896609
6 0.347241 -0.495216 3.160869
1 0.826305 -1.076254 3.957132
1 -0.729743 -0.669739 3.238347
1 0.540244 0.560755 3.369847
6 -0.761096 -2.899137 1.394907
1 -0.498667 -3.688344 2.107744
1 -1.169790 -3.369625 0.498674
1 -1.554045 -2.298729 1.849935
6 1.179624 -3.247010 -1.118670
1 1.843684 -4.092467 -0.906775
1 1.477348 -2.836135 -2.086960
1 0.160415 -3.622394 -1.218837
6 -1.765673 1.863031 1.262789
1 -1.269417 1.411789 2.131625
1 -2.452540 2.625426 1.633795
8 -1.668173 -1.841650 -1.677658
1 -0.522384 -0.949230 -2.317779
8 0.180927 -0.216731 -2.378785
1 -0.298407 0.552969 -2.709025

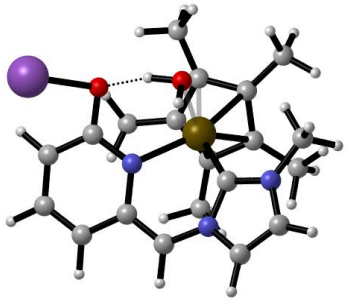
Cat-2



77 0.252168 -0.293963 -0.152196
7 2.247741 2.023557 -0.613809
7 0.330146 2.700523 0.149755
7 -1.649062 0.668382 -0.460010
6 0.988823 1.586135 -0.289602
6 2.371526 3.371404 -0.364408
1 3.279723 3.913012 -0.575590
6 1.177139 3.798740 0.118214
1 0.841836 4.778271 0.417759
6 -0.997413 2.762226 0.577739
1 -1.259038 3.658376 1.120694
6 -1.958262 1.835590 0.247019
6 -3.321443 2.064013 0.630092
1 -3.537711 2.930404 1.245925
6 -4.314381 1.240996 0.194730
1 -5.347150 1.436023 0.465056

6 -4.004524 0.139944 -0.642750
1 -4.777456 -0.483445 -1.078704
6 -2.679691 -0.092522 -0.904002
6 3.272627 1.218548 -1.244139
1 2.889981 0.204091 -1.361909
1 4.179545 1.198838 -0.633921
1 3.522080 1.620349 -2.229674
6 1.631138 -1.955452 0.215484
6 1.648132 -1.037818 1.314471
6 0.293493 -0.950234 1.844369
6 -0.512878 -1.943876 1.136311
6 0.288219 -2.530568 0.127901
6 2.787407 -2.404876 -0.604518
1 3.080824 -3.422754 -0.324353
1 3.662711 -1.767010 -0.462983
1 2.547063 -2.420399 -1.671908
6 2.822955 -0.308545 1.857888
1 3.199885 -0.821185 2.749452
1 2.567284 0.713018 2.151743
1 3.643174 -0.260997 1.138469
6 -0.135373 -0.171402 3.035548
1 0.030874 -0.740980 3.957045
1 -1.198031 0.078979 2.985234
1 0.417142 0.768169 3.117063
6 -1.941069 -2.224292 1.430322
1 -2.023289 -2.860807 2.317863
1 -2.432872 -2.740553 0.604108
1 -2.503083 -1.308033 1.636264
6 -0.112744 -3.564772 -0.859906
1 0.263332 -4.549622 -0.560488
1 0.299153 -3.353459 -1.851452
1 -1.197285 -3.638722 -0.952757
8 -2.264353 -1.156371 -1.669672
1 -3.047469 -1.625742 -1.981679
8 0.227998 -0.270582 -2.526197
1 0.105526 0.660762 -2.753853
1 -0.656684 -0.662477 -2.637508

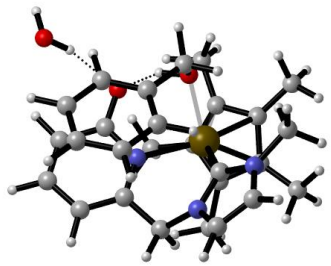
Cat-3



77 0.365808 -0.326148 -0.104873
7 2.492192 1.705405 -1.066687
7 0.871786 2.634316 0.041659
7 -1.409972 0.890296 -0.139267
6 1.286824 1.438989 -0.471476
6 2.829605 3.030871 -0.907070
1 3.736786 3.445830 -1.316121
6 1.819519 3.614887 -0.212199
1 1.673141 4.634858 0.104360
6 -0.326162 2.867652 0.728627
1 -0.351259 3.783775 1.300503
6 -1.438593 2.065114 0.614198
6 -2.657958 2.436053 1.272263
1 -2.650264 3.310752 1.913629
6 -3.791037 1.704263 1.075968
1 -4.708454 1.974622 1.592473
6 -3.788098 0.604289 0.183945
1 -4.633963 -0.083638 0.158304
6 -2.574337 0.200931 -0.401693
6 3.269434 0.748498 -1.824343
1 2.717244 -0.192293 -1.857176
1 4.245461 0.581405 -1.359480
1 3.426246 1.106784 -2.845047
6 1.574374 -2.124568 0.161863
6 1.868769 -1.169269 1.188868
6 0.634525 -0.887130 1.908324
6 -0.387472 -1.793254 1.384775
6 0.171794 -2.520068 0.306431
6 2.529229 -2.740954 -0.797229
1 2.769183 -3.767707 -0.498885
1 3.470878 -2.188764 -0.844978
1 2.111522 -2.785047 -1.807964
6 3.190772 -0.560596 1.491438
1 3.671376 -1.092392 2.319532
1 3.095212 0.488438 1.785402

1 3.866728 -0.609973 0.634509
6 0.488922 -0.005073 3.095699
1 0.709057 -0.550531 4.020629
1 -0.527493 0.390010 3.173587
1 1.165860 0.851429 3.040606
6 -1.786335 -1.868680 1.876963
1 -1.848168 -2.540048 2.740630
1 -2.462393 -2.244278 1.105475
1 -2.155577 -0.889164 2.194611
6 -0.530305 -3.498222 -0.563730
1 -0.418878 -4.517546 -0.176837
1 -0.123289 -3.489370 -1.578813
1 -1.596324 -3.269725 -0.629316
8 -2.512805 -0.805516 -1.234838
8 -0.167356 -0.434520 -2.362592
1 -0.187219 0.496748 -2.617317
1 -1.115819 -0.642415 -2.099880
11 -4.416765 -0.276414 -2.192497

IM-1



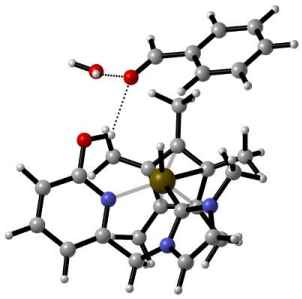
77 0.983164 -0.149672 -0.043112
7 0.690896 2.904694 -0.524833
7 -0.259879 2.221664 1.278444
7 -0.886099 -0.610325 0.912818
6 0.428200 1.781194 0.195743
6 0.162665 4.022227 0.099277
1 0.252347 5.009931 -0.323644
6 -0.436234 3.589635 1.236813
1 -0.964114 4.126351 2.008790
6 -0.653899 1.342789 2.373915
1 -1.275708 1.923821 3.057342
1 0.258591 1.063937 2.918312
6 -1.391750 0.107016 1.946877
6 -2.494285 -0.310221 2.660168
1 -2.871940 0.295894 3.476466
6 -3.099532 -1.526972 2.306435
1 -3.961381 -1.885648 2.862167
6 -2.624181 -2.243122 1.238195
1 -3.105700 -3.149164 0.885770
6 -1.517360 -1.765181 0.479932
6 1.393863 2.940187 -1.791433
1 1.631400 1.915466 -2.082492
1 2.317365 3.518616 -1.702184
1 0.766259 3.397271 -2.560994
6 2.933717 -0.555889 -0.920020
6 3.094399 0.108040 0.339419
6 2.467503 -0.715167 1.363489
6 2.035698 -1.958400 0.721335
6 2.294265 -1.850598 -0.664817
6 3.444128 -0.122611 -2.247430
1 4.303765 -0.732098 -2.546553
1 3.773149 0.919144 -2.238953
1 2.681752 -0.234868 -3.024349
6 3.765120 1.411960 0.584955
1 4.786715 1.251956 0.945532
1 3.237680 2.001210 1.341108
1 3.830021 2.013474 -0.324913
6 2.520669 -0.482012 2.830882
1 3.408618 -0.956936 3.264100
1 1.648874 -0.905916 3.337708
1 2.574028 0.583511 3.071794
6 1.378300 -3.091649 1.420558
1 2.131126 -3.771064 1.834604
1 0.735275 -3.658219 0.744762
1 0.759088 -2.743322 2.252435
6 1.944887 -2.834516 -1.718779
1 2.817413 -3.443331 -1.980502
1 1.612540 -2.329925 -2.629919
1 1.142415 -3.498525 -1.393566
8 -1.082223 -2.349547 -0.565792
6 -2.368245 0.833068 -1.714849
6 -3.317996 -0.168996 -1.489593
6 -4.399573 0.068211 -0.649654
6 -4.562917 1.316602 -0.050560
6 -3.641498 2.331043 -0.298436
6 -2.549772 2.086758 -1.126809
1 -3.215923 -1.151139 -1.948831
1 -5.116338 -0.729152 -0.473482
1 -5.414188 1.501535 0.598743
1 -3.776079 3.314170 0.145658

1 -1.833732 2.882329 -1.328385
6 -1.176007 0.554956 -2.572010
1 -1.468848 0.104360 -3.528034
1 -0.625001 1.474029 -2.793039
8 -0.208525 -0.350988 -1.983668
1 -0.665204 -1.180226 -1.652206
8 -3.525360 -3.396108 -1.514361
1 -2.585363 -3.272561 -1.302164
1 -3.559082 -4.179357 -2.067491

IM-2

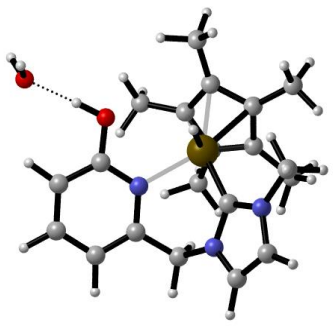
77 -0.933644 -0.054579 0.001087
7 -0.407346 -3.076322 -0.533341
7 0.171837 -2.427936 1.433360
7 0.784350 0.396771 1.163118
6 -0.370604 -1.980011 0.272548
6 0.113198 -4.180844 0.118118
1 0.182886 -5.145764 -0.357902
6 0.474726 -3.771862 1.360244
1 0.907047 -4.312353 2.187149
6 0.385020 -1.547977 2.579469
1 0.881723 -2.125314 3.360553
1 -0.600612 -1.251233 2.962484
6 1.196715 -0.336724 2.229987
6 2.273010 0.033385 3.002371
1 2.574910 -0.580597 3.843422
6 2.948132 1.226139 2.683287
1 3.792512 1.547527 3.286112
6 2.541684 1.977428 1.612699
1 3.035375 2.904221 1.340986
6 1.449715 1.558665 0.794578
6 -0.825338 -3.080285 -1.921534
1 -1.198519 -2.085649 -2.170369
1 -1.615195 -3.818037 -2.078525
1 0.021439 -3.316284 -2.571260
6 -2.551629 0.523689 -1.365368
6 -3.058715 -0.331809 -0.343601
6 -2.787452 0.327526 0.931143
6 -2.236789 1.655978 0.645344
6 -2.088551 1.774021 -0.751982
6 -2.556257 0.293346 -2.832046
1 -3.322304 0.916192 -3.307664
1 -2.777138 -0.745350 -3.089617
1 -1.595571 0.574930 -3.276825
6 -3.766637 -1.628257 -0.510756
1 -4.846003 -1.488652 -0.388664
1 -3.447680 -2.367096 0.230032
1 -3.606472 -2.052793 -1.504456
6 -3.235927 -0.147860 2.263253
1 -4.269572 0.167980 2.449091
1 -2.623222 0.270050 3.066291
1 -3.211733 -1.238871 2.334553
6 -1.871330 2.657418 1.676591
1 -2.775765 3.145923 2.056691
1 -1.205126 3.431318 1.286338
1 -1.379996 2.183618 2.532029
6 -1.596874 2.940031 -1.519696
1 -2.447878 3.445989 -1.992019
1 -0.924275 2.625592 -2.322458
1 -1.075749 3.658842 -0.883355
8 1.053342 2.185854 -0.227455
1 0.482947 -0.270314 -1.511505
6 1.252551 0.002422 -2.313993
1 1.038169 -0.710405 -3.123203
6 2.615106 -0.221235 -1.721844
6 3.630565 0.717119 -1.910800
6 2.883817 -1.376564 -0.982065
6 4.893420 0.504027 -1.365400
1 3.423684 1.609519 -2.494029
6 4.144816 -1.589894 -0.437390
1 2.097897 -2.116975 -0.833850
6 5.153494 -0.645726 -0.625738
1 5.677688 1.238754 -1.522011
1 4.343108 -2.492417 0.134725
1 6.138767 -0.809599 -0.199897
8 0.405796 4.752604 0.580605
1 0.836389 3.988892 0.160342
1 0.668439 5.515758 0.061650
8 1.001820 1.272338 -2.799485
1 1.121685 1.858322 -2.024354

IM-3



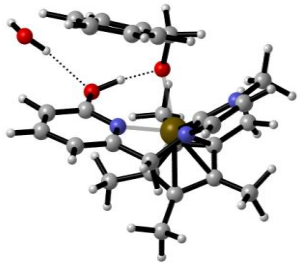
77 0.527182 -0.111007 0.379683
7 0.201539 -2.911408 -0.954704
7 2.222485 -2.189013 -0.884593
7 1.986541 0.683404 -1.057942
6 0.946129 -1.848446 -0.550870
6 1.000321 -3.887825 -1.527049
1 0.592224 -4.810351 -1.907125
6 2.275716 -3.431490 -1.489362
1 3.199300 -3.873330 -1.827392
6 3.337803 -1.294101 -0.620478
1 4.254918 -1.772683 -0.967794
1 3.416469 -1.157837 0.467143
6 3.160264 0.038677 -1.290759
6 4.153612 0.578212 -2.084077
1 5.074627 0.028239 -2.243859
6 3.947307 1.833397 -2.666156
1 4.716270 2.285269 -3.284488
6 2.749223 2.481846 -2.466335
1 2.521238 3.441962 -2.913101
6 1.771040 1.868036 -1.669879
6 -1.241151 -2.996432 -0.852557
1 -1.611714 -2.042774 -0.475714
1 -1.534908 -3.801762 -0.174152
1 -1.671510 -3.185527 -1.838650
6 -0.514686 -0.562107 2.204388
6 0.896837 -0.808399 2.492917
6 1.598855 0.411948 2.334718
6 0.631662 1.452248 1.989994
6 -0.666232 0.867719 1.994908
6 -1.626467 -1.527018 2.431984
1 -1.962518 -1.503803 3.475366
1 -1.318252 -2.553603 2.213763
1 -2.493912 -1.299404 1.803604
6 1.466124 -2.131760 2.865697
1 1.328209 -2.324567 3.935324
1 2.538377 -2.191897 2.660177
1 0.977304 -2.948317 2.325466
6 3.052527 0.659160 2.533434
1 3.226067 1.222199 3.457506
1 3.478553 1.255081 1.718970
1 3.623137 -0.270230 2.611829
6 0.953238 2.897667 1.835328
1 1.008464 3.382127 2.817527
1 0.198919 3.423288 1.241719
1 1.926454 3.041700 1.355898
6 -1.959947 1.587235 1.887841
1 -2.332594 1.809831 2.895085
1 -2.721061 0.974745 1.396131
1 -1.866691 2.538099 1.356069
8 0.614272 2.484531 -1.512358
6 -4.066121 0.669863 -0.991902
6 -5.205360 0.629472 -0.178447
6 -5.966059 -0.530364 -0.099674
6 -5.593915 -1.649028 -0.843757
6 -4.460380 -1.613141 -1.660316
6 -3.692612 -0.459926 -1.733010
1 -5.482794 1.514615 0.391368
1 -6.849422 -0.563896 0.529963
1 -6.194341 -2.552855 -0.794596
1 -4.192452 -2.487284 -2.247523
1 -2.805308 -0.399270 -2.359082
6 -3.266880 1.893502 -1.035182
1 -3.664382 2.744748 -0.438420
1 -0.598715 0.060328 -0.771140
8 -2.214290 2.015847 -1.649960
1 -0.014961 1.880995 -1.054559
1 -1.573049 3.737631 -0.906266
8 -1.570369 4.242585 -0.079724
1 -1.380865 5.147785 -0.336029

IM-4



77 0.367295 -0.309792 -0.165278
7 2.146545 1.919264 -1.377168
7 0.911142 2.576775 0.252021
7 -1.448149 0.869229 0.161446
6 1.218216 1.474007 -0.487216
6 2.405454 3.267403 -1.191358
1 3.119000 3.801200 -1.798307
6 1.621996 3.687013 -0.168279
1 1.514248 4.654990 0.293908
6 -0.075246 2.509823 1.316999
1 -0.154502 3.495643 1.778246
1 0.288701 1.803576 2.076026
6 -1.416050 2.060055 0.811952
6 -2.549540 2.824529 1.021794
1 -2.471906 3.771411 1.544729
6 -3.776052 2.352131 0.553178
1 -4.683584 2.927422 0.707435
6 -3.824312 1.145027 -0.112425
1 -4.752395 0.738577 -0.499668
6 -2.635905 0.422106 -0.301636
6 2.764544 1.100313 -2.399689
1 2.229715 0.150771 -2.434575
1 3.818578 0.921068 -2.169052
1 2.691355 1.595466 -3.369718
6 1.784960 -1.931698 -0.143629
6 1.944477 -1.236600 1.127266
6 0.726858 -1.333111 1.851779
6 -0.194699 -2.131969 1.051241
6 0.463177 -2.544864 -0.136201
6 2.881889 -2.261956 -1.095753
1 3.360240 -3.210833 -0.825530
1 3.662615 -1.496699 -1.096286
1 2.513173 -2.363238 -2.120321
6 3.181746 -0.538944 1.569889
1 3.863574 -1.237063 2.067920
1 2.962928 0.266817 2.276222
1 3.724817 -0.102748 0.726761
6 0.439860 -0.825405 3.221061
1 0.485090 -1.632394 3.962426
1 -0.561949 -0.387980 3.291711
1 1.162185 -0.065753 3.532962
6 -1.561693 -2.514640 1.495499
1 -1.508737 -3.280438 2.277846
1 -2.156004 -2.915089 0.672849
1 -2.102768 -1.661166 1.916658
6 -0.081617 -3.443790 -1.188294
1 0.164326 -4.489954 -0.972868
1 0.329005 -3.203989 -2.171728
1 -1.168607 -3.362074 -1.257589
8 -2.603171 -0.743027 -0.932820
1 -0.016447 -0.209062 -1.726923
1 -3.503930 -0.974067 -1.264482
8 -5.084274 -1.302839 -1.858688
1 -5.546966 -2.099026 -1.581990
1 -5.219059 -1.247921 -2.809316

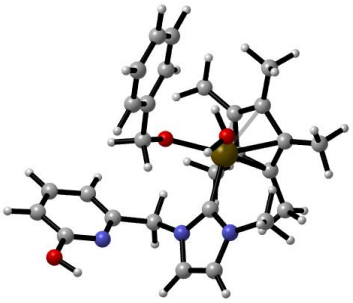
IM-5



77 0.981543 -0.188755 -0.077153
7 0.847459 2.888897 -0.518922
7 -0.104640 2.223320 1.288939
7 -0.941091 -0.545268 0.914156
6 0.539747 1.765993 0.182475
6 0.385381 4.020292 0.133489
1 0.516946 5.009278 -0.275008
6 -0.215591 3.599881 1.273676
1 -0.704778 4.148502 2.062553
6 -0.485925 1.350620 2.389674
1 -1.016887 1.954250 3.127923
1 0.436819 0.987418 2.864249
6 -1.338309 0.182502 1.986331
6 -2.441817 -0.168630 2.739082
1 -2.731315 0.439731 3.588991
6 -3.163950 -1.312142 2.384755
1 -4.031070 -1.612515 2.964481
6 -2.798341 -2.031259 1.267744
1 -3.373928 -2.870438 0.891515
6 -1.693786 -1.600390 0.517105
6 1.539461 2.916390 -1.792176
1 1.694349 1.888093 -2.120000
1 2.504526 3.421288 -1.692521
1 0.938259 3.443586 -2.536923
6 2.945095 -0.560822 -0.872844

6 3.065734 -0.048522 0.475099
6 2.402852 -0.966173 1.366958
6 1.949489 -2.104063 0.567455
6 2.289420 -1.864403 -0.786285
6 3.582005 -0.022218 -2.104281
1 4.485916 -0.590399 -2.351142
1 3.881566 1.021880 -1.985635
1 2.908945 -0.090559 -2.964542
6 3.760592 1.202656 0.877165
1 4.802924 0.992205 1.138115
1 3.289595 1.666675 1.748342
1 3.767723 1.939775 0.070355
6 2.381823 -0.912706 2.853363
1 3.164224 -1.554813 3.274209
1 1.428242 -1.264334 3.260259
1 2.561586 0.098712 3.227376
6 1.248479 -3.290521 1.124363
1 1.971539 -3.997752 1.545047
1 0.663256 -3.811621 0.365509
1 0.566341 -3.008679 1.932462
6 1.951782 -2.697327 -1.966355
1 2.859298 -3.008236 -2.493650
1 1.334680 -2.122828 -2.666706
1 1.398943 -3.595485 -1.685835
8 -1.353201 -2.232861 -0.592913
6 -2.272465 0.894406 -1.698447
6 -3.306818 -0.040937 -1.585298
6 -4.431516 0.231361 -0.814355
6 -4.554491 1.459505 -0.165528
6 -3.553938 2.417622 -0.307879
6 -2.424539 2.133088 -1.071276
1 -3.237425 -1.003644 -2.086789
1 -5.207695 -0.523744 -0.727040
1 -5.437012 1.676599 0.429879
1 -3.656561 3.390631 0.167035
1 -1.653920 2.892099 -1.195252
6 -1.023176 0.562130 -2.467852
1 -1.295302 0.168665 -3.458926
1 -0.454150 1.486757 -2.647684
8 -0.189158 -0.419908 -1.874301
1 -0.882810 -1.543133 -1.228152
8 -4.007166 -3.223025 -1.307866
1 -3.044183 -3.193903 -1.361594
1 -4.266536 -3.960238 -1.865586

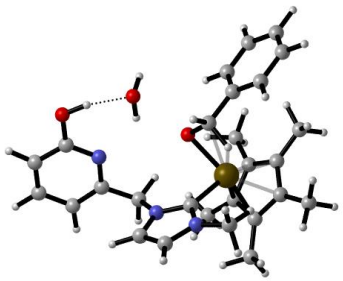
IM-6



77 -1.130059 -0.269042 0.070312
7 0.111534 -1.819691 -2.284634
7 1.314237 -2.056297 -0.515805
7 3.919822 -1.158359 -0.129992
6 0.210169 -1.410578 -0.986108
6 1.131585 -2.697229 -2.608992
1 1.224757 -3.125428 -3.594058
6 1.888319 -2.841865 -1.496014
1 2.786308 -3.407111 -1.310818
6 1.836806 -1.961364 0.839535
1 1.979144 -2.985396 1.209142
1 1.072748 -1.473851 1.445307
6 3.126931 -1.186361 0.949302
6 3.449474 -0.566762 2.149843
1 2.760859 -0.598233 2.988854
6 4.663373 0.118415 2.229793
1 4.950581 0.619071 3.149727
6 5.493956 0.172220 1.125149
1 6.442112 0.696890 1.130689
6 5.067458 -0.487352 -0.033210
6 -0.949741 -1.466992 -3.208926
1 -0.536576 -0.979172 -4.095454
1 -1.638235 -0.783108 -2.714735
1 -1.487620 -2.365034 -3.524396
6 -2.584592 -1.826368 0.403515
6 -1.953783 -1.374590 1.644817
6 -2.383701 0.004257 1.882876
6 -3.130353 0.425399 0.756272
6 -3.255434 -0.702463 -0.171622
6 -2.521974 -3.208396 -0.139175
1 -3.284989 -3.840428 0.327653
1 -1.549653 -3.672389 0.051616
1 -2.693796 -3.228003 -1.218249
6 -1.256880 -2.230051 2.639961

1 -1.972416 -2.641076 3.361483
1 -0.513341 -1.659459 3.204371
1 -0.750821 -3.074278 2.164289
6 -1.916960 0.828779 3.024775
1 -2.118740 0.330144 3.977380
1 -2.405787 1.804787 3.049111
1 -0.833316 0.992673 2.944760
6 -3.710450 1.771576 0.508566
1 -4.791376 1.763867 0.687364
1 -3.561740 2.085687 -0.529314
1 -3.270875 2.532647 1.156519
6 -4.061908 -0.676426 -1.420401
1 -5.132756 -0.672285 -1.188661
1 -3.868420 -1.550086 -2.047087
1 -3.854868 0.219170 -2.014106
8 5.857645 -0.445886 -1.118403
1 5.412930 -0.959249 -1.806053
6 1.383313 1.451295 0.241112
1 2.302133 1.554161 0.845688
6 0.920547 2.837658 -0.156208
6 -0.215635 3.403921 0.432428
6 1.599361 3.562505 -1.140982
6 -0.670238 4.661410 0.033085
1 -0.731199 2.835490 1.204795
6 1.152943 4.821162 -1.532287
1 2.487771 3.133405 -1.603488
6 0.011427 5.371981 -0.951760
1 -1.555201 5.089964 0.497482
1 1.690562 5.371349 -2.299241
1 -0.341881 6.350101 -1.263502
8 0.459689 0.725093 0.977931
1 1.716281 0.910534 -0.673103
8 -0.969692 1.284792 -1.743702
1 -0.980465 2.156067 -1.307408
1 -0.081946 1.250593 -2.126215

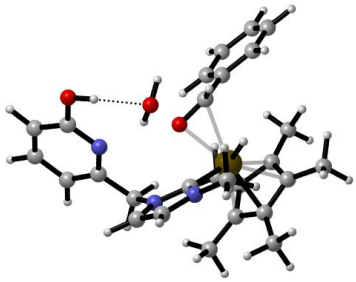
IM-7



77 0.856825 -0.613678 -0.028102
7 -0.899180 -1.833619 2.194618
7 -2.082174 -1.311689 0.474919
7 -3.693574 1.126403 -0.170932
6 -0.813136 -1.274185 0.955412
6 -2.200293 -2.204424 2.478461
1 -2.476153 -2.650034 3.420884
6 -2.943383 -1.878196 1.393711
1 -3.999061 -1.979000 1.195208
6 -2.511300 -0.854410 -0.853363
1 -2.640448 -1.732414 -1.496175
1 -1.698681 -0.237982 -1.244879
6 -3.790063 -0.068726 -0.777224
6 -4.974344 -0.577514 -1.286126
1 -4.998460 -1.549599 -1.769793
6 -6.131200 0.204633 -1.162244
1 -7.079676 -0.154555 -1.550087
6 -6.057812 1.432403 -0.542112
1 -6.921045 2.076429 -0.419965
6 -4.805498 1.861821 -0.057433
6 0.195432 -1.970542 3.135425
1 0.242303 -2.995645 3.509806
1 0.063701 -1.288956 3.979425
1 1.127573 -1.728538 2.622705
6 2.709544 -1.788365 -0.004517
6 1.637111 -2.548479 -0.570172
6 1.157148 -1.827583 -1.742766
6 2.020250 -0.667264 -1.929247
6 2.955429 -0.633612 -0.861674
6 3.527443 -2.151528 1.183197
1 4.489279 -2.571439 0.868623
1 3.033380 -2.903472 1.803229
1 3.744971 -1.281036 1.809107
6 1.113442 -3.853276 -0.087343
1 1.592962 -4.679320 -0.622915

1 0.035171 -3.937640 -0.248261
1 1.302774 -3.998396 0.979138
6 0.140482 -2.314645 -2.710052
1 0.612724 -2.931340 -3.483675
1 -0.367512 -1.489092 -3.214984
1 -0.617946 -2.930992 -2.220254
6 1.873782 0.331698 -3.017984
1 2.280831 -0.058894 -3.956846
1 2.398486 1.260145 -2.782458
1 0.821849 0.577977 -3.190870
6 4.027156 0.368533 -0.635505
1 4.182839 0.559552 0.429734
1 3.803406 1.328281 -1.106768
1 4.976291 0.003276 -1.043701
8 -4.735140 3.048131 0.531639
1 -3.793233 3.222020 0.785244
6 0.501357 1.563403 0.892419
1 -0.132725 1.919231 1.727260
6 1.664876 2.476913 0.626557
6 1.769127 3.117003 -0.609123
6 2.628910 2.716850 1.608742
6 2.832654 3.980498 -0.863117
1 1.007785 2.920349 -1.359164
6 3.693828 3.574356 1.353380
1 2.546322 2.226827 2.578888
6 3.799070 4.205952 0.114623
1 2.904984 4.482176 -1.824339
1 4.441692 3.753233 2.120275
1 4.628109 4.878718 -0.083210
8 -0.230637 1.193680 -0.200153
1 0.951391 0.592515 1.452497
8 -2.053958 3.166349 0.924551
1 -1.610740 3.774914 0.325255
1 -2.066335 2.315103 0.444805

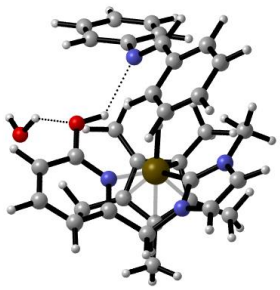
IM-8



77 -0.811768 -0.656499 -0.165686
7 1.396019 -2.297837 -1.541344
7 2.100282 -1.429137 0.298903
7 3.496983 0.853497 -0.087505
6 1.015401 -1.478054 -0.526384
6 2.696021 -2.730166 -1.365064
1 3.181952 -3.376338 -2.078019
6 3.140598 -2.180606 -0.211578
1 4.097839 -2.237433 0.281374
6 2.274340 -0.550740 1.448030
1 2.534592 -1.157173 2.322710
1 1.306256 -0.078424 1.641937
6 3.343950 0.485790 1.190724
6 4.111536 1.001687 2.223171
1 3.971275 0.664496 3.245648
6 5.077699 1.962025 1.900261
1 5.699093 2.392594 2.679939
6 5.258306 2.345964 0.585832
1 6.007166 3.069957 0.286812
6 4.439279 1.750423 -0.386723
6 0.622045 -2.579584 -2.736358
1 1.094844 -3.402471 -3.271621
1 0.599267 -1.694807 -3.376741
1 -0.397234 -2.860509 -2.470013
6 -2.817484 -1.546285 0.036010
6 -1.774069 -2.407946 0.565414
6 -1.246730 -1.769923 1.772034
6 -1.889558 -0.514404 1.907255
6 -2.863716 -0.368097 0.840305
6 -3.725065 -1.867262 -1.097198
1 -4.627894 -2.366742 -0.728554
1 -3.252011 -2.534263 -1.821264
1 -4.039213 -0.966358 -1.629184
6 -1.503235 -3.814197 0.157921
1 -2.058375 -4.509442 0.797499
1 -0.442312 -4.067030 0.243910
1 -1.813749 -4.004164 -0.872119
6 -0.274142 -2.397665 2.704513
1 -0.776386 -3.140967 3.334105
1 0.185188 -1.665178 3.372627
1 0.523862 -2.920707 2.168903
6 -1.640014 0.497006 2.967236
1 -2.320977 0.345729 3.812388
1 -1.805845 1.511327 2.595710

1 -0.619552 0.440955 3.354934
6 -3.864121 0.722047 0.720742
1 -4.156520 0.897041 -0.317218
1 -3.495629 1.667592 1.124462
1 -4.770783 0.458463 1.277656
8 4.603226 2.084503 -1.667451
1 3.957128 1.570233 -2.199889
6 -0.487073 1.573756 -0.954525
1 -0.275547 1.360078 -2.014845
6 -1.539678 2.553013 -0.690624
6 -1.539571 3.303152 0.494281
6 -2.521892 2.789643 -1.661131
6 -2.516164 4.269286 0.703278
1 -0.749646 3.132717 1.221143
6 -3.507493 3.743206 -1.440369
1 -2.510022 2.210171 -2.583239
6 -3.505208 4.483430 -0.258146
1 -2.504701 4.865007 1.611185
1 -4.272399 3.918928 -2.190359
1 -4.267422 5.238304 -0.090897
8 0.370380 1.219818 -0.071827
1 -0.903820 -0.734218 -1.757965
8 2.254840 0.779875 -2.611728
1 1.775252 1.593687 -2.794287
1 2.268148 0.717154 -1.634678

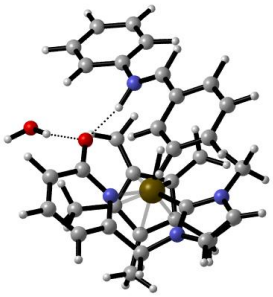
IM-9



77 0.336583 -0.816781 -0.526021
7 2.350560 1.319325 -1.544601
7 3.182580 -0.075188 -0.136943
7 0.992123 -0.789362 1.557281
6 2.030565 0.231929 -0.795604
6 3.673513 1.678176 -1.354581
1 4.114378 2.522531 -1.859973
6 4.201951 0.803002 -0.464411
1 5.193401 0.722837 -0.048319
6 3.258848 -1.212020 0.765829
1 4.272598 -1.266901 1.167045
1 3.078741 -2.124426 0.182798
6 2.263623 -1.130174 1.890717
6 2.622642 -1.428687 3.191748
1 3.648047 -1.698418 3.420009
6 1.644292 -1.389121 4.190243
1 1.894135 -1.649159 5.213619
6 0.366415 -0.981312 3.871643
1 -0.422864 -0.896032 4.608661
6 0.083189 -0.642373 2.543736
6 1.421364 2.044400 -2.388534
1 0.410592 1.710395 -2.143924
1 1.627864 1.854746 -3.445676
1 1.505688 3.114766 -2.187956
6 -0.941677 -1.380406 -2.176389
6 0.339826 -2.029784 -2.359159
6 0.543970 -2.957846 -1.280085
6 -0.618301 -2.872878 -0.426964
6 -1.549017 -1.938428 -0.978421
6 -1.622870 -0.479915 -3.145235
1 -2.215360 -1.061396 -3.861153
1 -0.909335 0.115556 -3.721055
1 -2.304485 0.205567 -2.633089
6 1.263264 -1.815747 -3.505836
1 1.050339 -2.529283 -4.309391
1 2.309457 -1.951443 -3.215922
1 1.158514 -0.811756 -3.924578
6 1.655036 -3.940287 -1.151301
1 1.398492 -4.895854 -1.624787
1 1.885498 -4.161868 -0.104194
1 2.571677 -3.585060 -1.632913
6 -0.807634 -3.658296 0.821861
1 -1.125140 -4.678184 0.576233
1 -1.566576 -3.227004 1.481470
1 0.127069 -3.747715 1.386180
6 -2.930183 -1.674618 -0.490915
1 -3.639419 -2.364602 -0.964091
1 -3.258467 -0.658974 -0.727941
1 -3.011055 -1.817893 0.591094
8 -1.121962 -0.159889 2.257785
1 -0.298611 0.648456 -0.277268
1 -1.121037 0.273043 1.370354
6 -4.057465 1.319459 1.243268

6 -3.206695 1.915253 0.300911
6 -3.646558 2.058191 -1.024099
6 -4.913665 1.618838 -1.393251
6 -5.760962 1.045014 -0.447358
6 -5.329977 0.904443 0.871640
1 -3.707763 1.221174 2.267991
1 -2.969072 2.480719 -1.763943
1 -5.238820 1.719803 -2.425078
1 -6.749661 0.703696 -0.737832
1 -5.991406 0.464867 1.613149
6 -1.356970 3.317955 0.221268
1 -1.918136 4.018453 -0.419613
6 0.037177 3.652672 0.468271
6 0.863543 2.825967 1.247048
6 0.581964 4.806134 -0.113165
6 2.200587 3.142674 1.427185
1 0.426855 1.944115 1.705704
6 1.925308 5.120507 0.065052
1 -0.057967 5.453774 -0.709235
6 2.737162 4.287166 0.832226
1 2.832525 2.501157 2.036961
1 2.336764 6.019611 -0.384119
1 3.785527 4.533571 0.977045
7 -1.911030 2.261317 0.698120
8 -2.945012 -2.227869 3.029193
1 -2.736360 -1.303638 2.854887
1 -3.900963 -2.256995 3.115649

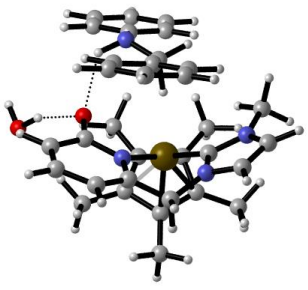
IM-10



77 0.620281 -0.763966 -0.479365
7 2.547991 1.478343 -1.417079
7 3.266076 0.346186 0.262634
7 0.890495 -0.477544 1.656900
6 2.214156 0.439772 -0.598639
6 3.775287 2.013470 -1.064582
1 4.215843 2.838281 -1.602057
6 4.229078 1.302626 -0.002043
1 5.140211 1.381274 0.569646
6 3.293247 -0.673855 1.301917
1 4.227037 -0.572949 1.858704
1 3.297332 -1.653280 0.806216
6 2.115310 -0.575696 2.231403
6 2.300952 -0.615477 3.599505
1 3.301992 -0.692338 4.009912
6 1.169787 -0.572091 4.426333
1 1.279509 -0.625756 5.505881
6 -0.074857 -0.436125 3.861831
1 -0.972151 -0.364038 4.468136
6 -0.235634 -0.343580 2.449753
6 1.713369 1.985934 -2.484776
1 0.724514 1.534899 -2.379924
1 2.131801 1.732501 -3.463150
1 1.629957 3.072661 -2.403025
6 -0.259438 -1.629856 -2.257024
6 1.074890 -2.172338 -2.108945
6 1.126680 -2.943129 -0.897537
6 -0.188085 -2.873732 -0.297970
6 -1.053058 -2.109172 -1.134431
6 -0.794264 -0.915376 -3.448740
1 -1.253110 -1.616521 -4.155637
1 -0.006430 -0.380857 -3.986579
1 -1.560853 -0.186680 -3.166557
6 2.194738 -2.009358 -3.075929
1 2.212331 -2.839735 -3.790403
1 3.164925 -1.991286 -2.570127
1 2.101955 -1.085190 -3.652499
6 2.252095 -3.794764 -0.424163
1 2.148608 -4.827985 -0.778738
1 2.294336 -3.841125 0.669190
1 3.219327 -3.431698 -0.785403
6 -0.563901 -3.526454 0.984571
1 -0.742359 -4.596155 0.825350
1 -1.475680 -3.098649 1.411635
1 0.237982 -3.443028 1.726219
6 -2.513600 -1.909666 -0.938513
1 -3.080952 -2.724437 -1.404705
1 -2.857530 -0.976255 -1.393136
1 -2.782830 -1.889343 0.121313
8 -1.373255 -0.145485 1.911860
1 -0.212475 0.615844 -0.486804

1 -1.851121 1.132265 0.901533
6 -4.295706 0.429820 0.895565
6 -3.708367 1.313106 -0.010758
6 -4.352060 1.658059 -1.203691
6 -5.600829 1.114401 -1.473421
6 -6.195370 0.228742 -0.572667
6 -5.539540 -0.113703 0.607077
1 -3.777221 0.162974 1.808829
1 -3.866820 2.301976 -1.932485
1 -6.102987 1.364933 -2.402603
1 -7.164635 -0.202728 -0.802420
1 -5.978866 -0.816987 1.306606
6 -1.926019 2.936120 -0.094064
1 -2.583732 3.554548 -0.704643
6 -0.611539 3.433699 0.181979
6 0.282333 2.788337 1.059262
6 -0.210119 4.617056 -0.467282
6 1.549707 3.307602 1.258852
1 -0.026236 1.890576 1.581065
6 1.065251 5.125278 -0.269895
1 -0.905223 5.124088 -1.132518
6 1.947136 4.466664 0.588432
1 2.233685 2.805660 1.937519
1 1.371161 6.036102 -0.774641
1 2.944565 4.866513 0.748321
7 -2.419247 1.800514 0.313064
8 -3.339971 -2.046251 2.491077
1 -2.606255 -1.407278 2.435943
1 -3.212399 -2.501885 3.326571

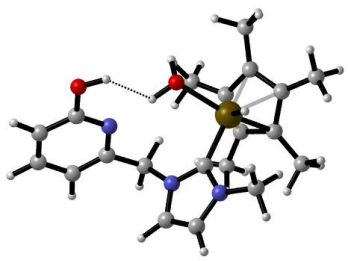
IM-11



77 0.020912 -1.014421 0.128079
7 1.681009 -1.208614 -2.483482
7 2.882366 -0.949817 -0.717303
7 1.197808 0.329592 1.262704
6 1.592425 -1.044145 -1.134820
6 3.003469 -1.213200 -2.892130
1 3.282209 -1.313336 -3.929073
6 3.759213 -1.054752 -1.777342
1 4.828499 -1.004989 -1.647128
6 3.262847 -0.851251 0.688996
1 4.337178 -0.660934 0.727056
1 3.092588 -1.832227 1.154994
6 2.533819 0.217311 1.452894
6 3.205388 0.993258 2.372410
1 4.277705 0.887513 2.493527
6 2.461840 1.891321 3.160133
1 2.962660 2.480275 3.923675
6 1.114077 2.037417 2.953919
1 0.511586 2.725705 3.537902
6 0.452270 1.296841 1.929089
6 0.550786 -1.269010 -3.388370
1 -0.362361 -1.151070 -2.801960
1 0.528236 -2.226079 -3.915938
1 0.610600 -0.461609 -4.123435
6 -1.755143 -2.235065 -0.344149
6 -0.631332 -3.070503 -0.070828
6 -0.188883 -2.770826 1.287198
6 -1.145159 -1.835165 1.875718
6 -2.086804 -1.497546 0.881035
6 -2.606792 -2.265875 -1.561510
1 -3.473565 -2.915654 -1.392762
1 -2.071700 -2.662717 -2.428273
1 -2.992278 -1.273177 -1.809474
6 -0.033851 -4.095200 -0.965542
1 -0.449863 -5.082454 -0.737030
1 1.050758 -4.163018 -0.844064
1 -0.244968 -3.889874 -2.017537
6 0.899776 -3.456064 2.027363
1 0.507371 -4.328403 2.563672
1 1.348766 -2.794383 2.773497
1 1.684804 -3.812414 1.354454
6 -1.082115 -1.330127 3.270230
1 -1.402102 -2.115563 3.964362
1 -1.721921 -0.457868 3.425854
1 -0.058825 -1.056358 3.548704
6 -3.249422 -0.592731 1.029652
1 -4.135156 -1.188714 1.283572
1 -3.470911 -0.063981 0.099460

1 -3.096536 0.139207 1.827093
8 -0.750743 1.454040 1.586216
1 -0.264504 0.815189 -1.013396
1 -1.163000 2.860352 0.032252
6 -3.622854 2.713314 -0.291997
6 -2.627267 2.233914 -1.160542
6 -3.003340 1.386399 -2.212998
6 -4.340619 1.032287 -2.381583
6 -5.319554 1.501518 -1.511570
6 -4.948217 2.349882 -0.466482
1 -3.333597 3.370441 0.525697
1 -2.260872 1.006407 -2.909539
1 -4.615150 0.381218 -3.207810
1 -6.358624 1.221124 -1.650101
1 -5.700602 2.730597 0.218075
6 -0.234883 1.878696 -1.464715
1 -0.378531 1.699947 -2.536854
6 1.124967 2.468690 -1.235035
6 1.394784 3.368004 -0.200187
6 2.175500 2.086664 -2.074575
6 2.682342 3.857779 -0.004491
1 0.600607 3.702353 0.461477
6 3.464472 2.571096 -1.880391
1 1.973970 1.414092 -2.906997
6 3.723130 3.457704 -0.837769
1 2.869802 4.557948 0.804652
1 4.261693 2.268892 -2.554629
1 4.725131 3.847927 -0.686337
7 -1.313174 2.638559 -0.945807
8 -2.561083 1.586551 3.649902
1 -1.969244 1.758925 2.895167
1 -3.330760 2.140554 3.503741

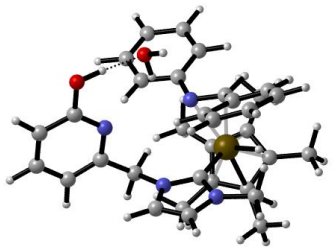
IM-12



77 1.035258 -0.123113 -0.411474
7 -0.210218 2.653953 -0.798564
7 -1.357762 1.504652 0.609218
7 -3.109261 -0.691060 -0.356045
6 -0.277498 1.415363 -0.229753
6 -1.219903 3.477079 -0.338647
1 -1.323762 4.496288 -0.675179
6 -1.948709 2.753989 0.543540
1 -2.821199 3.009298 1.123586
6 -1.896133 0.415633 1.413861
1 -2.036445 0.771477 2.439293
1 -1.128959 -0.368396 1.425512
6 -3.194414 -0.099199 0.853574
6 -4.395207 0.054247 1.522278
1 -4.425445 0.534825 2.494990
6 -5.562415 -0.425842 0.913535
1 -6.521232 -0.323601 1.412114
6 -5.492695 -1.018033 -0.330213
1 -6.365384 -1.393351 -0.851093
6 -4.230226 -1.124194 -0.932716
6 0.777688 3.063885 -1.781619
1 0.540956 2.646366 -2.762415
1 1.762269 2.704707 -1.481227
1 0.783897 4.152233 -1.840368
6 2.735354 0.481203 0.685940
6 1.869304 -0.111143 1.710318
6 1.658564 -1.461630 1.372822
6 2.437912 -1.761680 0.166360
6 3.167106 -0.597250 -0.196730
6 3.350290 1.834125 0.775287
1 4.189411 1.835810 1.480848
1 2.630778 2.582083 1.122167
1 3.738866 2.165017 -0.191367
6 1.329250 0.631269 2.880105
1 2.108243 0.769124 3.638368
1 0.502189 0.101920 3.360256
1 0.976920 1.630297 2.602795
6 0.825946 -2.458216 2.098870
1 1.454242 -3.184530 2.626630
1 0.189673 -3.035300 1.418566
1 0.177246 -1.989134 2.842909
6 2.555817 -3.111224 -0.450612
1 3.314351 -3.712131 0.064386
1 2.841268 -3.053571 -1.503117
1 1.618927 -3.673711 -0.387614

6 4.183790 -0.479338 -1.274417
1 5.187291 -0.651822 -0.869453
1 4.177137 0.514798 -1.727630
1 4.016703 -1.207457 -2.070575
8 -4.152826 -1.692221 -2.141551
1 1.182271 0.382827 -1.924248
1 -3.243374 -1.625559 -2.462974
8 -0.658365 -1.354740 -1.372415
1 -1.537284 -1.094638 -0.974746
1 -0.517104 -2.275564 -1.128153

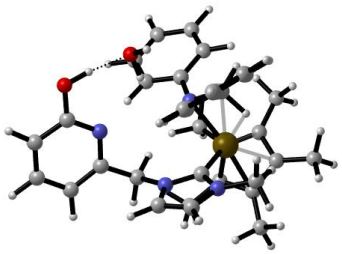
IM-13



77 1.383339 -0.166347 -0.200100
7 -0.007170 -2.717350 -1.198327
7 -1.159494 -0.978955 -1.727564
7 -3.467755 0.372338 -0.376624
6 -0.024630 -1.357045 -1.077106
6 -1.119373 -3.165911 -1.882140
1 -1.292024 -4.215085 -2.060339
6 -1.844172 -2.073262 -2.217801
1 -2.778328 -1.965440 -2.746528
6 -1.627758 0.391331 -1.942726
1 -1.422675 0.664725 -2.983363
1 -1.025399 1.029189 -1.289008
6 -3.099611 0.526000 -1.661619
6 -3.989562 0.768519 -2.696672
1 -3.634785 0.885785 -3.716465
6 -5.353307 0.857782 -2.382989
1 -6.085415 1.043451 -3.163259
6 -5.756235 0.709480 -1.075560
1 -6.795509 0.774757 -0.775061
6 -4.772535 0.478417 -0.090544
6 0.958808 -3.625320 -0.605433
1 0.888002 -3.603203 0.485827
1 1.972970 -3.359936 -0.908703
1 0.738945 -4.634307 -0.953890
6 2.907806 -0.158532 -1.716522
6 2.077790 0.988526 -2.064135
6 2.177846 1.939901 -1.017688
6 3.068616 1.409934 -0.001465
6 3.564430 0.152153 -0.458080
6 3.244310 -1.277524 -2.639324
1 3.965814 -0.950038 -3.396193
1 2.360653 -1.646939 -3.167707
1 3.694656 -2.118943 -2.107248
6 1.369154 1.154119 -3.360718
1 2.075037 1.466301 -4.139063
1 0.589465 1.917130 -3.306207
1 0.915364 0.218388 -3.700927
6 1.531033 3.273931 -0.975486
1 2.185130 4.020368 -1.441357
1 1.336327 3.605225 0.048114
1 0.581108 3.290513 -1.516956
6 3.602417 2.152525 1.173239
1 4.594411 2.556306 0.939103
1 3.718839 1.509405 2.050260
1 2.964010 2.991520 1.452355
6 4.627788 -0.652892 0.201163
1 5.615714 -0.302413 -0.118541
1 4.557081 -1.712705 -0.054068
1 4.586989 -0.566674 1.289537
8 -5.172639 0.365746 1.165358
1 1.810863 -1.557737 0.411101
1 -4.377784 0.309341 1.761425
6 0.575465 2.519737 2.412558
6 -0.266665 1.931433 1.456891
6 -1.226752 2.737199 0.825326
6 -1.319143 4.093572 1.110730
6 -0.457726 4.675470 2.037771
6 0.480913 3.879087 2.691904
1 1.301724 1.924135 2.956356
1 -1.932878 2.263332 0.149148
1 -2.079613 4.693919 0.620239
1 -0.532304 5.733303 2.269349
1 1.136766 4.315605 3.440270
6 0.471710 -0.326687 1.830836
1 1.209942 0.031689 2.558319
6 -0.051356 -1.676206 2.135710
6 0.684200 -2.504214 2.993946
6 -1.260868 -2.151635 1.607211

6 0.234858 -3.781134 3.309204
1 1.618805 -2.136062 3.414260
6 -1.705833 -3.432712 1.921041
1 -1.843209 -1.514197 0.942699
6 -0.961519 -4.252148 2.769147
1 0.813784 -4.408092 3.980668
1 -2.643825 -3.790013 1.504160
1 -1.316819 -5.247992 3.016553
7 -0.313649 0.547342 1.147380
8 -2.920955 0.340275 2.607455
1 -2.719435 -0.483028 3.063522
1 -2.324841 0.341989 1.838783

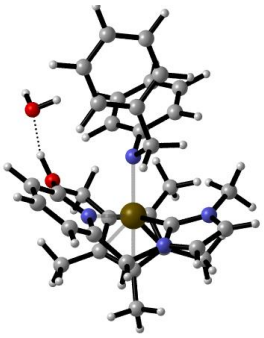
IM-14



77 1.410550 -0.201291 -0.223299
7 -0.193736 -2.736677 -0.958119
7 -1.159301 -0.970070 -1.715558
7 -3.359538 0.824872 -0.616118
6 -0.079632 -1.379711 -0.998066
6 -1.333197 -3.156603 -1.616800
1 -1.609647 -4.197357 -1.673039
6 -1.937576 -2.044270 -2.099952
1 -2.843280 -1.913418 -2.671933
6 -1.472804 0.419906 -2.066358
1 -1.177876 0.587867 -3.107813
1 -0.850022 1.041973 -1.416779
6 -2.930017 0.737315 -1.888441
6 -3.746982 0.916207 -2.993766
1 -3.342402 0.840496 -3.998785
6 -5.100118 1.206214 -2.771570
1 -5.775230 1.357582 -3.608759
6 -5.565433 1.304504 -1.479675
1 -6.598499 1.535664 -1.247487
6 -4.653689 1.112685 -0.419623
6 0.654375 -3.627552 -0.190620
1 0.140535 -3.947820 0.721269
1 1.567669 -3.094214 0.080801
1 0.912551 -4.503589 -0.788993
6 2.930976 -0.638371 -1.736672
6 2.302194 0.659360 -1.963608
6 2.685420 1.537695 -0.871600
6 3.426068 0.771482 0.070940
6 3.580133 -0.575186 -0.469711
6 2.915480 -1.785267 -2.682754
1 3.732120 -1.699055 -3.408078
1 1.981323 -1.829179 -3.249558
1 3.036927 -2.741685 -2.167134
6 1.653529 1.087575 -3.229764
1 2.411333 1.417887 -3.949722
1 0.966686 1.922597 -3.072199
1 1.098477 0.269449 -3.696036
6 2.321326 2.969322 -0.766676
1 3.056131 3.580157 -1.303580
1 2.288533 3.313008 0.270183
1 1.342117 3.169312 -1.209891
6 4.057217 1.268076 1.322665
1 5.109738 1.518943 1.148526
1 4.034592 0.516405 2.117545
1 3.556412 2.164931 1.694921
6 4.361595 -1.663380 0.174463
1 5.430555 -1.529658 -0.026771
1 4.082449 -2.648876 -0.206172
1 4.238891 -1.669241 1.260587
8 -5.110800 1.230364 0.816202
1 1.165839 -1.114657 1.401596
1 -4.350506 1.156659 1.455382
6 0.964793 2.317653 2.444580
6 0.070330 1.905527 1.444016
6 -0.679836 2.892777 0.783134
6 -0.525593 4.237637 1.091414
6 0.373636 4.636273 2.079083
6 1.107892 3.667167 2.757884
1 1.561810 1.594299 2.993707
1 -1.418986 2.570457 0.051278
1 -1.126901 4.978425 0.572022
1 0.485858 5.685960 2.331111
1 1.798344 3.959642 3.544948
6 0.289776 -0.479425 1.901171
1 0.817375 -0.143206 2.802525
6 -0.692974 -1.569186 2.245021

6 -0.367318 -2.428752 3.299541
6 -1.878763 -1.776857 1.534202
6 -1.206902 -3.482295 3.642352
1 0.550578 -2.262692 3.861947
6 -2.717040 -2.836967 1.876942
1 -2.146706 -1.098837 0.725652
6 -2.383623 -3.692320 2.925264
1 -0.948420 -4.133992 4.471516
1 -3.639309 -2.988005 1.321909
1 -3.043315 -4.513199 3.190077
7 -0.168671 0.569194 1.034353
8 -2.923441 1.059561 2.339928
1 -2.869578 0.248502 2.855415
1 -2.335368 0.899811 1.580802

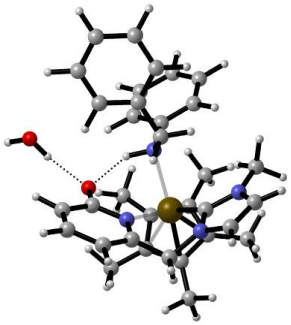
IM-15



77 1.138269 0.151126 -0.098224
7 1.102477 -0.351899 2.953670
7 1.525976 -2.126326 1.822389
7 0.402086 -1.812762 -0.924986
6 1.234974 -0.804475 1.677123
6 1.296737 -1.373777 3.866991
1 1.226533 -1.211211 4.930500
6 1.564257 -2.495144 3.154934
1 1.782235 -3.503048 3.469945
6 1.779352 -2.999728 0.686495
1 1.937373 -4.009551 1.068655
1 2.709244 -2.673304 0.203238
6 0.671200 -2.996542 -0.326512
6 0.007279 -4.164144 -0.660110
1 0.245491 -5.088671 -0.145364
6 -0.957686 -4.123105 -1.669364
1 -1.498802 -5.021264 -1.949986
6 -1.197754 -2.933559 -2.325156
1 -1.917267 -2.855425 -3.133288
6 -0.485292 -1.785766 -1.938009
6 0.721902 0.997049 3.323091
1 0.526408 1.560698 2.407285
1 1.518763 1.477044 3.896492
1 -0.188612 0.975249 3.927724
6 1.835349 2.220816 -0.381972
6 2.836784 1.434198 0.299707
6 3.267974 0.376939 -0.587032
6 2.535292 0.538158 -1.816537
6 1.673199 1.676383 -1.715192
6 1.233123 3.479243 0.127671
1 1.894050 4.325782 -0.092651
1 1.084131 3.453498 1.210999
1 0.262927 3.684060 -0.329762
6 3.460673 1.745438 1.613427
1 4.451086 2.185900 1.453955
1 3.600866 0.851809 2.229579
1 2.875307 2.470407 2.182038
6 4.393568 -0.562944 -0.331863
1 5.357293 -0.087608 -0.550834
1 4.331176 -1.454797 -0.961722
1 4.428485 -0.886528 0.713675
6 2.678894 -0.327084 -3.015587
1 3.485159 0.048989 -3.655876
1 1.762870 -0.346582 -3.608646
1 2.932904 -1.355993 -2.744931
6 0.950396 2.299535 -2.855332
1 1.667480 2.779370 -3.532166
1 0.250524 3.067192 -2.522101
1 0.393943 1.560029 -3.437397
8 -0.608051 -0.632964 -2.577946
1 -1.546282 -0.532583 -2.894791
6 -1.920918 2.394363 1.264503
6 -1.537575 1.610543 0.158936
6 -1.733945 2.168783 -1.117023
6 -2.250868 3.447931 -1.282406
6 -2.605780 4.216815 -0.172959
6 -2.443156 3.674314 1.098832
1 -1.816403 1.992748 2.269614
1 -1.458527 1.563684 -1.974425
1 -2.388903 3.847036 -2.285412
1 -3.017495 5.213069 -0.299656
1 -2.727471 4.252630 1.974239
6 -3.094823 -0.657498 1.126053

6 -4.028240 -0.032649 1.953023
6 -3.566345 -1.442986 0.068767
6 -5.395794 -0.175515 1.725074
1 -3.678812 0.575382 2.785228
6 -4.930937 -1.587184 -0.168458
1 -2.846115 -1.965986 -0.559396
6 -5.851387 -0.946226 0.660379
1 -6.106746 0.320210 2.379886
1 -5.274457 -2.207875 -0.992585
1 -6.916843 -1.056433 0.481705
7 -1.018064 0.306651 0.247046
6 -1.609202 -0.484357 1.326342
1 -1.441363 -0.097945 2.351032
1 -1.137118 -1.476610 1.300068
8 -3.215785 -0.424495 -2.912102
1 -3.465315 -0.287786 -1.984601
1 -3.628585 0.300767 -3.390452

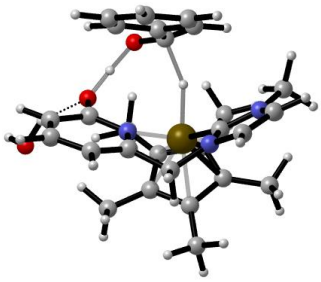
IM-16



77 -1.153095 -0.179463 -0.152229
7 -1.243014 -0.479031 2.946334
7 -1.761999 1.488556 2.263378
7 -0.560238 1.903184 -0.390147
6 -1.360397 0.270647 1.814193
6 -1.556393 0.265938 4.070564
1 -1.509587 -0.150432 5.064038
6 -1.887375 1.506867 3.638273
1 -2.195395 2.387985 4.177963
6 -2.119415 2.580043 1.364275
1 -2.353393 3.452434 1.976242
1 -3.036747 2.288806 0.836749
6 -1.048195 2.917683 0.373451
6 -0.646862 4.225584 0.218195
1 -1.065720 4.997603 0.854371
6 0.304835 4.524943 -0.772201
1 0.655075 5.545424 -0.899382
6 0.794790 3.523241 -1.565738
1 1.563692 3.689895 -2.313187
6 0.355568 2.173846 -1.402027
6 -0.842640 -1.868708 2.990765
1 -0.671336 -2.206437 1.966462
1 -1.626243 -2.474988 3.451952
1 0.077712 -1.982235 3.570673
6 -1.677307 -2.161197 -0.987864
6 -2.779806 -1.623633 -0.246330
6 -3.169297 -0.369186 -0.866571
6 -2.340411 -0.201896 -2.049089
6 -1.426823 -1.285068 -2.126910
6 -1.021260 -3.474961 -0.763528
1 -1.541754 -4.252566 -1.334633
1 -1.042299 -3.774511 0.288015
1 0.022450 -3.471742 -1.087776
6 -3.478742 -2.264610 0.899679
1 -4.425550 -2.700401 0.562423
1 -3.716479 -1.547088 1.691201
1 -2.887683 -3.074010 1.333734
6 -4.380367 0.424004 -0.522695
1 -5.273987 -0.018093 -0.978843
1 -4.310004 1.451696 -0.889567
1 -4.552210 0.455352 0.557839
6 -2.416140 0.934887 -3.000659
1 -3.134863 0.711680 -3.797301
1 -1.444903 1.127421 -3.461058
1 -2.748808 1.853109 -2.508872
6 -0.478784 -1.534699 -3.243028
1 -1.030425 -1.842460 -4.138627
1 0.226158 -2.332672 -3.002772
1 0.089235 -0.633400 -3.486305
8 0.786831 1.216548 -2.111252
1 1.312855 0.232296 -0.667605
6 1.887909 -2.594401 0.878242
6 1.746993 -1.617385 -0.106628
6 2.243272 -1.850475 -1.390087
6 2.820761 -3.077842 -1.700376
6 2.929201 -4.069503 -0.727743
6 2.475824 -3.816140 0.564458
1 1.566220 -2.395501 1.895262
1 2.185428 -1.057156 -2.132541
1 3.206912 -3.249354 -2.700915

1 3.388173 -5.023338 -0.967809
1 2.588402 -4.570013 1.337845
6 3.158199 0.580457 1.242001
6 4.036069 0.018392 2.169735
6 3.674689 1.321927 0.174759
6 5.409679 0.207820 2.045396
1 3.638883 -0.571705 2.994769
6 5.046336 1.498584 0.040056
1 3.014975 1.758164 -0.573400
6 5.915658 0.946508 0.979441
1 6.084652 -0.228510 2.775791
1 5.424838 2.064703 -0.805288
1 6.987715 1.087245 0.877568
7 1.123145 -0.347062 0.161160
6 1.677818 0.364699 1.353234
1 1.426974 -0.211689 2.251018
1 1.131142 1.312549 1.414005
8 3.323301 2.087704 -2.959300
1 3.457432 2.221023 -3.899769
1 2.436140 1.697808 -2.882713

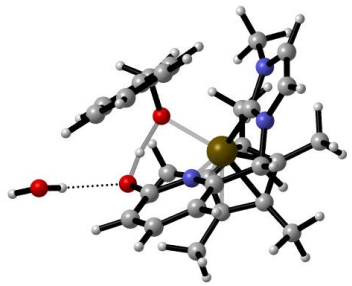
TS-1



77 -0.816144 -0.281514 -0.037192
7 0.542584 -3.074875 -0.020667
7 1.109807 -1.826262 1.632147
7 0.761903 0.972974 0.805095
6 0.328923 -1.843895 0.520726
6 1.440191 -3.801908 0.744301
1 1.738631 -4.803191 0.477651
6 1.796793 -3.014654 1.788888
1 2.464313 -3.193575 2.616639
6 1.091829 -0.708763 2.560447
1 1.798209 -0.924608 3.363703
1 0.089095 -0.660445 3.008651
6 1.414956 0.621601 1.943447
6 2.258262 1.484742 2.616166
1 2.761445 1.150579 3.517104
6 2.404657 2.792003 2.143473
1 3.031229 3.502402 2.674128
6 1.749732 3.162253 0.993477
1 1.821070 4.161857 0.580665
6 0.961715 2.225631 0.291960
6 -0.048901 -3.553391 -1.253468
1 -0.599111 -2.727046 -1.708526
1 -0.730620 -4.384870 -1.057953
1 0.729979 -3.891238 -1.942350
6 -2.709606 -0.404769 -1.114150
6 -2.790443 -1.185838 0.092095
6 -2.641215 -0.281867 1.217670
6 -2.488756 1.051479 0.681544
6 -2.536146 0.990811 -0.746647
6 -2.884015 -0.892307 -2.507738
1 -3.923818 -0.760151 -2.827746
1 -2.646491 -1.955096 -2.607655
1 -2.256956 -0.332687 -3.207162
6 -3.110093 -2.635457 0.191861
1 -4.168003 -2.773373 0.441057
1 -2.525818 -3.131611 0.972611
1 -2.931023 -3.156417 -0.751593
6 -2.805264 -0.643536 2.650429
1 -3.866090 -0.665853 2.928122
1 -2.320826 0.082885 3.308412
1 -2.396206 -1.634149 2.872533
6 -2.301148 2.273861 1.504803
1 -3.269921 2.608216 1.893036
1 -1.870907 3.106618 0.940983
1 -1.663473 2.076969 2.373178
6 -2.511128 2.128420 -1.702120
1 -3.510197 2.290917 -2.123011
1 -1.828785 1.934979 -2.535705
1 -2.194324 3.052657 -1.213910
8 0.394743 2.586937 -0.824247
1 0.141124 -0.367594 -1.429995
6 1.059518 0.162831 -2.567008
1 0.753370 -0.675193 -3.217366
6 2.359191 -0.015353 -1.888949
6 3.133484 1.088719 -1.513494
6 2.824125 -1.305858 -1.609025
6 4.327343 0.901854 -0.826947
1 2.797744 2.087587 -1.778034

6 4.013467 -1.492172 -0.920038
1 2.236528 -2.162717 -1.932665
6 4.761658 -0.385077 -0.515976
1 4.924436 1.762309 -0.539824
1 4.366737 -2.496816 -0.705079
1 5.695489 -0.528465 0.019787
8 -0.986299 4.894180 -0.084500
1 -0.449676 4.318592 -0.646996
1 -1.262314 5.619574 -0.649184
8 0.577594 1.312642 -2.843940
1 0.525146 1.976433 -1.798580

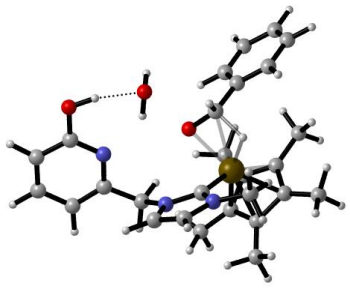
TS-2



77 0.983638 -0.187732 -0.071902
7 0.835837 2.884615 -0.546899
7 -0.101635 2.236512 1.275072
7 -0.926969 -0.532850 0.928629
6 0.536438 1.768990 0.169382
6 0.374574 4.021936 0.095634
1 0.500171 5.006676 -0.324744
6 -0.216849 3.612305 1.244811
1 -0.701742 4.168328 2.031196
6 -0.474663 1.374955 2.388413
1 -1.007104 1.984838 3.120392
1 0.451687 1.024172 2.864511
6 -1.322591 0.199539 1.998325
6 -2.423991 -0.148413 2.754512
1 -2.712524 0.463361 3.602277
6 -3.146845 -1.293781 2.404207
1 -4.012434 -1.592540 2.987244
6 -2.785396 -2.015085 1.288353
1 -3.362760 -2.855683 0.917923
6 -1.681509 -1.590166 0.528639
6 1.517238 2.898361 -1.825903
1 1.684362 1.866174 -2.135529
1 2.476044 3.417883 -1.742903
1 0.903720 3.403546 -2.575955
6 2.931818 -0.587713 -0.900599
6 3.079593 -0.029107 0.423445
6 2.431709 -0.914312 1.361990
6 1.962724 -2.079488 0.611983
6 2.273507 -1.885294 -0.756035
6 3.531334 -0.089719 -2.167394
1 4.421609 -0.672982 -2.427867
1 3.843053 0.954685 -2.090065
1 2.828935 -0.177321 -3.002245
6 3.779810 1.235388 0.771865
1 4.815391 1.029092 1.061480
1 3.297834 1.747050 1.609815
1 3.808633 1.929487 -0.071781
6 2.448207 -0.807609 2.845448
1 3.256293 -1.415987 3.267876
1 1.513357 -1.165040 3.288482
1 2.613641 0.220849 3.177432
6 1.262203 -3.242318 1.217613
1 1.986745 -3.960494 1.616488
1 0.632771 -3.759629 0.491711
1 0.621559 -2.933776 2.049344
6 1.919035 -2.761359 -1.899665
1 2.821310 -3.103910 -2.416671
1 1.306603 -2.210800 -2.622582
1 1.357898 -3.641048 -1.580637
8 -1.345009 -2.211593 -0.580220
6 -2.298968 0.860285 -1.702834
6 -3.337769 -0.068991 -1.581887
6 -4.456826 0.212879 -0.806330
6 -4.569478 1.444125 -0.161742
6 -3.563770 2.395754 -0.311686
6 -2.439405 2.102189 -1.079100
1 -3.275313 -1.035178 -2.077481
1 -5.235996 -0.538134 -0.711425
1 -5.447715 1.668647 0.437169
1 -3.658737 3.371003 0.160176
1 -1.665233 2.856514 -1.209442
6 -1.056134 0.514490 -2.474549
1 -1.331359 0.100986 -3.455912
1 -0.479662 1.429765 -2.671264
8 -0.215233 -0.456830 -1.861881
1 -0.868510 -1.484143 -1.244630
8 -3.968657 -3.247486 -1.291097

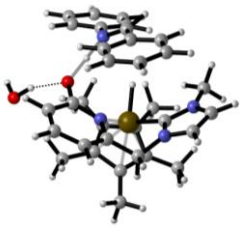
1 -3.004867 -3.186736 -1.307844
1 -4.181174 -4.011984 -1.831498

TS-3



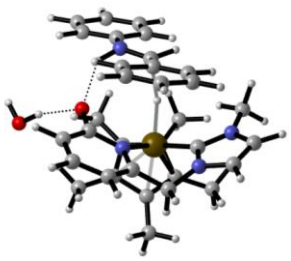
77 0.862492 -0.573768 0.017420
7 -0.956147 -1.646855 2.267920
7 -2.081774 -1.258960 0.476076
7 -3.727914 1.024892 -0.089327
6 -0.828865 -1.175699 0.996329
6 -2.263590 -2.011032 2.530927
1 -2.568401 -2.395761 3.490924
6 -2.971153 -1.766565 1.402863
1 -4.019518 -1.886082 1.178805
6 -2.475085 -0.875138 -0.880733
1 -2.611944 -1.782237 -1.479973
1 -1.637630 -0.307470 -1.296121
6 -3.738383 -0.059171 -0.882972
6 -4.826180 -0.426456 -1.657539
1 -4.792393 -1.318076 -2.275648
6 -5.965394 0.388710 -1.617062
1 -6.837588 0.139453 -2.213754
6 -5.978912 1.502926 -0.806022
1 -6.837443 2.160127 -0.732445
6 -4.827355 1.784705 -0.045663
6 0.104875 -1.730164 3.252991
1 0.164633 -2.744286 3.654871
1 -0.081516 -1.032117 4.072602
1 1.047965 -1.473243 2.770170
6 2.653433 -1.821053 0.039648
6 1.546626 -2.548856 -0.526571
6 1.122351 -1.860689 -1.728635
6 2.009827 -0.728926 -1.910852
6 2.948482 -0.701324 -0.837489
6 3.453897 -2.220130 1.228234
1 4.347216 -2.773517 0.918245
1 2.886727 -2.870404 1.898794
1 3.790690 -1.353049 1.802776
6 0.975702 -3.825209 -0.019596
1 1.429954 -4.674470 -0.540941
1 -0.104339 -3.878196 -0.182480
1 1.159750 -3.961425 1.048746
6 0.118840 -2.342639 -2.713587
1 0.598561 -2.964907 -3.478279
1 -0.373772 -1.515920 -3.232228
1 -0.654082 -2.953739 -2.240494
6 1.913601 0.244345 -3.029070
1 2.303881 -0.196653 -3.952729
1 2.484134 1.152449 -2.824444
1 0.875249 0.533902 -3.217264
6 4.062705 0.260998 -0.642734
1 4.235185 0.467634 0.417139
1 3.870244 1.218979 -1.131518
1 4.993648 -0.145696 -1.053063
8 -4.839044 2.851132 0.746496
1 -3.960198 2.921694 1.192436
6 0.536217 1.594401 0.762297
1 0.017640 1.819580 1.713368
6 1.725535 2.450881 0.487476
6 1.859373 3.054365 -0.765211
6 2.675484 2.701811 1.481526
6 2.943081 3.888441 -1.024996
1 1.096066 2.865709 -1.514886
6 3.761517 3.528673 1.218244
1 2.564668 2.240916 2.462546
6 3.898536 4.120825 -0.037198
1 3.038603 4.365463 -1.996339
1 4.500076 3.716571 1.991753
1 4.743677 4.771495 -0.240386
8 -0.254949 1.259352 -0.244696
1 1.069739 0.397646 1.408525
8 -2.199813 2.742294 1.513706
1 -1.774319 3.427310 0.987709
1 -2.276723 1.984545 0.897895

TS-4



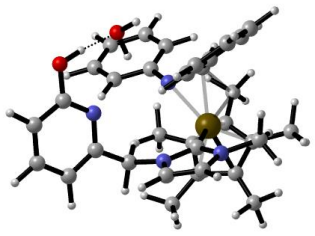
77 -0.010647 -1.043946 -0.124591
7 1.817907 -0.577485 -2.582426
7 2.875531 -0.737727 -0.718034
7 1.064585 0.195775 1.320332
6 1.621067 -0.772623 -1.247630
6 3.166841 -0.439312 -2.870703
1 3.525524 -0.285377 -3.876087
6 3.834608 -0.538443 -1.694607
1 4.888509 -0.490109 -1.470777
6 3.101962 -1.009386 0.691859
1 4.174916 -0.942911 0.884522
1 2.791772 -2.045365 0.886303
6 2.358764 -0.082714 1.615346
6 2.984875 0.391846 2.753410
1 4.023498 0.141708 2.942664
6 2.240717 1.155837 3.658817
1 2.689354 1.502007 4.585547
6 0.941525 1.486543 3.348542
1 0.326240 2.093826 4.003621
6 0.364382 1.051595 2.131941
6 0.755732 -0.511291 -3.562415
1 -0.193392 -0.528706 -3.022580
1 0.803143 -1.362044 -4.247890
1 0.830952 0.411448 -4.144641
6 -1.638934 -2.308031 -0.767114
6 -0.469782 -3.145640 -0.585522
6 -0.102157 -3.128750 0.803666
6 -1.054331 -2.277769 1.479862
6 -2.012950 -1.791113 0.540886
6 -2.454192 -2.182785 -2.006511
1 -3.256075 -2.930288 -2.023230
1 -1.853100 -2.334352 -2.907831
1 -2.923165 -1.196058 -2.074942
6 0.201265 -3.943403 -1.648197
1 -0.182357 -4.969616 -1.660021
1 1.282874 -3.999585 -1.491780
1 0.029346 -3.521104 -2.641591
6 0.951535 -3.950340 1.460616
1 0.544400 -4.893135 1.846606
1 1.399870 -3.429956 2.313820
1 1.755290 -4.213220 0.765569
6 -1.031871 -1.984277 2.937212
1 -1.443453 -2.835605 3.491871
1 -1.624600 -1.104255 3.202461
1 -0.010522 -1.836371 3.303860
6 -3.218670 -0.978420 0.855640
1 -4.069824 -1.625059 1.101539
1 -3.515466 -0.356618 0.005806
1 -3.041000 -0.324896 1.715442
8 -0.819471 1.454373 1.792195
1 -0.518272 0.290057 -0.856996
1 -0.976335 2.077576 0.668330
6 -3.590161 2.580325 0.239269
6 -2.614060 2.338874 -0.731326
6 -2.967575 1.805949 -1.974366
6 -4.304084 1.541446 -2.249132
6 -5.283906 1.803623 -1.292263
6 -4.924357 2.322847 -0.050065
1 -3.290152 2.981076 1.203680
1 -2.194728 1.557053 -2.698179
1 -4.580860 1.116555 -3.209507
1 -6.325491 1.592492 -1.512024
1 -5.685487 2.522691 0.697493
6 -0.362155 2.942047 -1.226916
1 -0.658051 3.108396 -2.267605
6 1.029980 3.110833 -0.884603
6 1.443479 3.367893 0.434444
6 1.993459 3.010172 -1.901573
6 2.792771 3.477305 0.730069
1 0.698309 3.511599 1.211092
6 3.344178 3.104496 -1.596592
1 1.673514 2.841214 -2.927664
6 3.744820 3.331142 -0.280579
1 3.104811 3.682817 1.749613
1 4.085284 3.009172 -2.384066
1 4.801353 3.419347 -0.044444
7 -1.269147 2.584441 -0.377061
8 -2.580289 0.845756 3.879885
1 -2.077357 1.230588 3.144287
1 -3.470157 1.191935 3.786138

TS-5



77 0.168250 -0.937755 0.140863
7 1.944650 -1.260655 -2.367525
7 3.033592 -0.663482 -0.612870
7 1.153493 0.674663 1.181049
6 1.778239 -0.951849 -1.048610
6 3.277671 -1.164700 -2.734416
1 3.611423 -1.370054 -3.739141
6 3.963712 -0.791198 -1.626174
1 5.015914 -0.614056 -1.469463
6 3.323682 -0.394857 0.789264
1 4.381929 -0.138720 0.867564
1 3.171534 -1.330382 1.344744
6 2.490559 0.694892 1.402057
6 3.096089 1.611765 2.238446
1 4.171645 1.589490 2.376896
6 2.284986 2.526233 2.928028
1 2.728706 3.228500 3.628466
6 0.932177 2.531447 2.704808
1 0.266737 3.219652 3.216314
6 0.336038 1.633003 1.769220
6 0.870770 -1.589696 -3.280083
1 -0.067761 -1.543281 -2.723401
1 1.005804 -2.594034 -3.689921
1 0.838438 -0.876060 -4.109411
6 -1.408526 -2.434145 -0.109081
6 -0.172103 -3.096169 0.215958
6 0.239336 -2.661528 1.531541
6 -0.786520 -1.763371 2.029281
6 -1.800060 -1.629770 1.044464
6 -2.274518 -2.715544 -1.285839
1 -2.990738 -3.511187 -1.049282
1 -1.697751 -3.052235 -2.152167
1 -2.852195 -1.834324 -1.577821
6 0.533811 -4.102981 -0.621864
1 0.263451 -5.117869 -0.310444
1 1.621207 -4.013557 -0.538863
1 0.267674 -4.006918 -1.677647
6 1.394921 -3.175567 2.312441
1 1.099294 -4.025137 2.940462
1 1.799965 -2.411805 2.983574
1 2.202357 -3.525246 1.661582
6 -0.754452 -1.116536 3.366169
1 -0.966467 -1.862131 4.141178
1 -1.488845 -0.313563 3.464826
1 0.236141 -0.704528 3.586498
6 -3.078038 -0.889774 1.204501
1 -3.825609 -1.537089 1.679532
1 -3.486128 -0.574317 0.241470
1 -2.953161 -0.009675 1.842420
8 -0.890899 1.681239 1.462656
1 -0.382579 0.232866 -0.953189
1 -1.572238 2.503326 -0.085749
6 -4.045722 2.149214 -0.355853
6 -3.054356 1.689700 -1.230306
6 -3.376722 0.765944 -2.229098
6 -4.683380 0.301608 -2.334234
6 -5.670360 0.750779 -1.459229
6 -5.345823 1.679785 -0.471963
1 -3.779785 2.865876 0.417668
1 -2.619258 0.390964 -2.911623
1 -4.929605 -0.420657 -3.107108
1 -6.686808 0.381850 -1.549316
1 -6.108381 2.039061 0.211757
6 -0.664354 1.774402 -1.686282
1 -0.826927 1.267644 -2.634912
6 0.621359 2.430419 -1.517813
6 0.841299 3.444430 -0.572406
6 1.682928 2.035717 -2.346733
6 2.096630 4.021530 -0.445254
1 0.032573 3.785486 0.067153
6 2.937209 2.613363 -2.217380
1 1.511684 1.269119 -3.098726
6 3.149144 3.602598 -1.257414
1 2.254481 4.800227 0.294243
1 3.746886 2.298490 -2.869044
1 4.128922 4.059021 -1.153641
7 -1.757163 2.186262 -1.042459
8 -2.568113 1.635444 3.648434
1 -2.030260 1.830131 2.859345
1 -3.411206 2.066442 3.495708

TS-6



77 1.385711 -0.216546 -0.189941
7 -0.193405 -2.754347 -0.965033
7 -1.176919 -0.985800 -1.695166
7 -3.380637 0.759455 -0.526971
6 -0.094814 -1.394469 -0.976664
6 -1.322265 -3.175177 -1.640597
1 -1.581944 -4.218665 -1.722421
6 -1.938848 -2.062346 -2.104892
1 -2.843351 -1.931680 -2.678736
6 -1.519823 0.401960 -2.025066
1 -1.255115 0.582680 -3.072244
1 -0.891280 1.030105 -1.387289
6 -2.979052 0.691416 -1.809412
6 -3.826521 0.861848 -2.893211
1 -3.445410 0.803391 -3.908601
6 -5.179930 1.120029 -2.635638
1 -5.878564 1.261904 -3.454971
6 -5.616129 1.199162 -1.332189
1 -6.648187 1.406029 -1.073945
6 -4.674516 1.019963 -0.296809
6 0.647373 -3.661749 -0.208410
1 0.128757 -3.984127 0.700588
1 1.567539 -3.146572 0.068862
1 0.888957 -4.534756 -0.817876
6 2.879318 -0.629342 -1.707137
6 2.226797 0.633978 -2.033234
6 2.560689 1.577822 -1.003372
6 3.354847 0.910989 -0.012393
6 3.570977 -0.447297 -0.463922
6 2.926089 -1.829067 -2.585888
1 3.723143 -1.729280 -3.331006
1 1.987753 -1.970758 -3.129319
1 3.123462 -2.741677 -2.017546
6 1.550619 0.937641 -3.322235
1 2.291113 1.185894 -4.091460
1 0.873436 1.790741 -3.236441
1 0.977392 0.082316 -3.691469
6 2.137987 2.998285 -0.973548
1 2.861006 3.611764 -1.523300
1 2.075497 3.390113 0.044783
1 1.161960 3.143595 -1.444305
6 4.010412 1.537154 1.167805
1 5.043152 1.816027 0.929373
1 4.051056 0.854474 2.021669
1 3.487550 2.441140 1.486757
6 4.431702 -1.452553 0.214490
1 5.476779 -1.315838 -0.085350
1 4.150862 -2.475629 -0.047326
1 4.392236 -1.358105 1.302146
8 -5.102198 1.121144 0.951392
1 1.308897 -1.190908 1.172412
1 -4.325900 1.055837 1.570864
6 0.968521 2.429003 2.342272
6 0.032625 1.979303 1.400104
6 -0.765450 2.928998 0.744463
6 -0.618733 4.285310 1.006190
6 0.322938 4.725108 1.934374
6 1.108051 3.789041 2.603989
1 1.599665 1.727264 2.880828
1 -1.532530 2.571263 0.060071
1 -1.256260 5.001370 0.495703
1 0.431659 5.783597 2.148326
1 1.832805 4.117324 3.344433
6 0.320203 -0.374792 1.865180
1 0.978651 -0.082743 2.692735
6 -0.537262 -1.548504 2.215909
6 -0.100364 -2.417193 3.222059
6 -1.748261 -1.807121 1.563070
6 -0.853911 -3.533207 3.569683
1 0.836208 -2.211228 3.738327
6 -2.496328 -2.929787 1.908218
1 -2.101238 -1.124241 0.791842
6 -2.051396 -3.796112 2.906175
1 -0.510411 -4.194304 4.359546
1 -3.436134 -3.122874 1.397694
1 -2.642467 -4.666117 3.175567
7 -0.231418 0.622945 1.070725
8 -2.892182 0.969910 2.455632
1 -2.836857 0.158838 2.970536
1 -2.285171 0.823874 1.708724

VI. References

1 A. K. Verma, J. Singh, V. K. Sankar, R. Chaudhary and R. Chandra, *Tetrahedron Lett.*, 2007, **48**, 4207.

2 Y. Zhou and Y. Gong, *Eur. J. Org. Chem.*, 2011, **2011**, 6092.

3 V. Bisai and R. Sarpong, *Org. Lett.*, 2010, **12**, 2551.

4 U. Gellrich, J. Huang, W. Seiche, M. Keller, M. Meuwly and B. Breit, *J. Am. Chem. Soc.*, 2011, **133**, 964.

5 X Wang, P. Rabbat, P. O'Shea, R. Tillyer, E. J. J. Grabowskib and P. J. Reiderb, *Tetrahedron Lett*., 2000, **41**, 4335.

6 M. A. H. Moelands, D. J. Schamhart, E. Folkertsma, M. Lutz, A. L. Spekb and R. J. M. K. Gebbink, *Dalton Trans.*, 2014, **43**,6769.

7 X. Wang, S. Liu, and G.-X. Jin, *Organometallics*, 2004, **23**, 6002.

8 P. Hohenberg and W. Kohn, *Phys. Rev.*, 1964, **136**, 864.

9 (a) S. H. Vosko, L.Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200, (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, **37**, 785, (c) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

10 P. J. Hay and W. R.Wadt, *J. Chem. Phys*., 1985, **82**, 299.

11 A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 4538.

12 D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß, *Theor. Chim. Acta* 1990, **77**, 123.

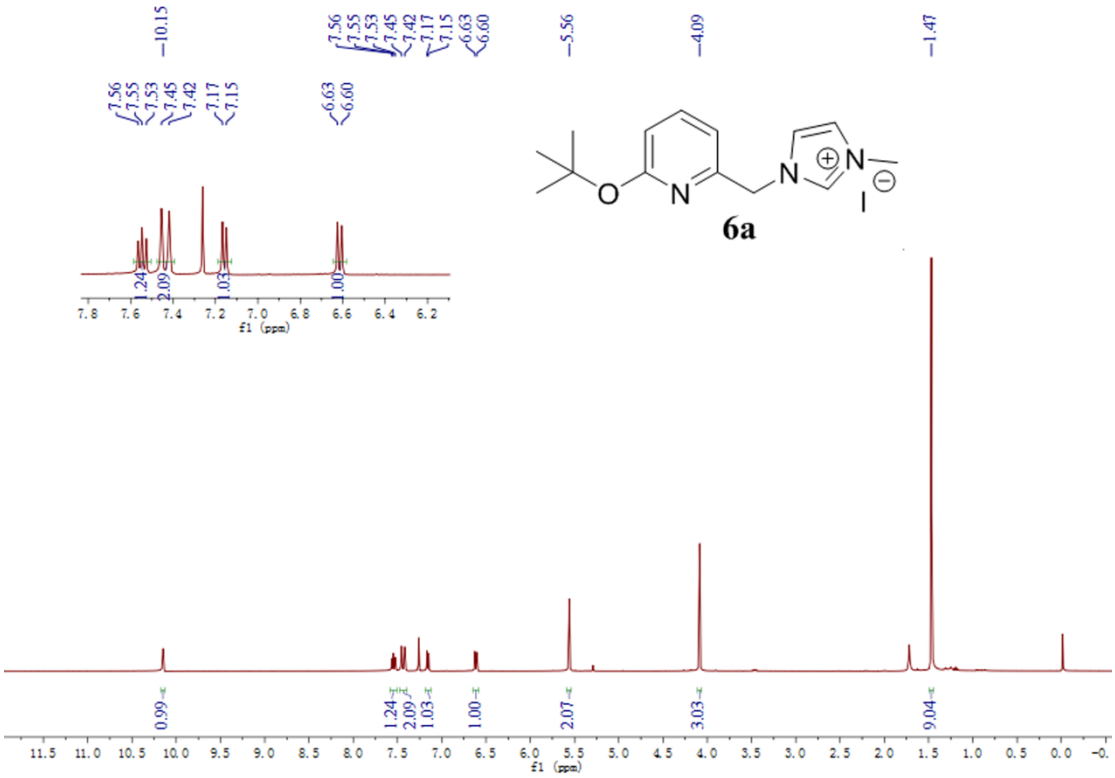
13 V. A. Rassolov, J. A. Pople, M. A. Ratner and T. L. Windus, *J. Chem. Phys.*, 1998, **109**, 1223.

14 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

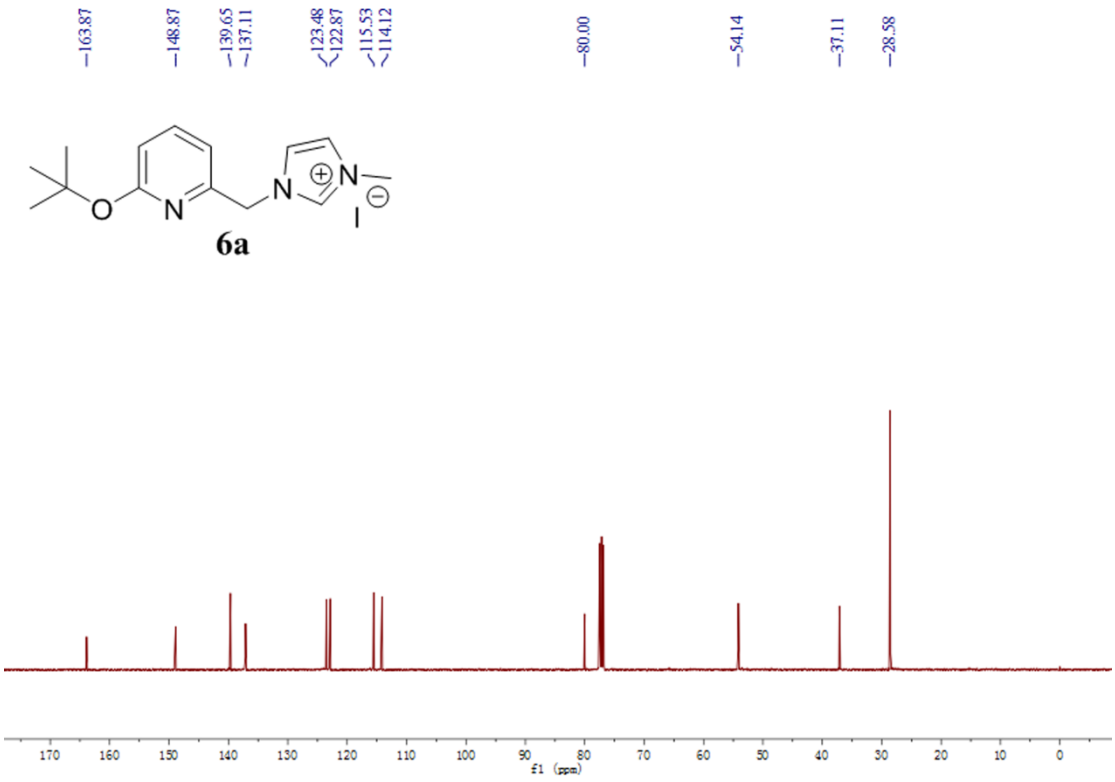
15 C. Y. Legault, CYLview, 1.0b; Université de Sherbrooke: Sherbrooke, Quebec, Canada, 2009, http://www.cylview.org.

VII. Spectroscopic Data (NMR Spectrum)

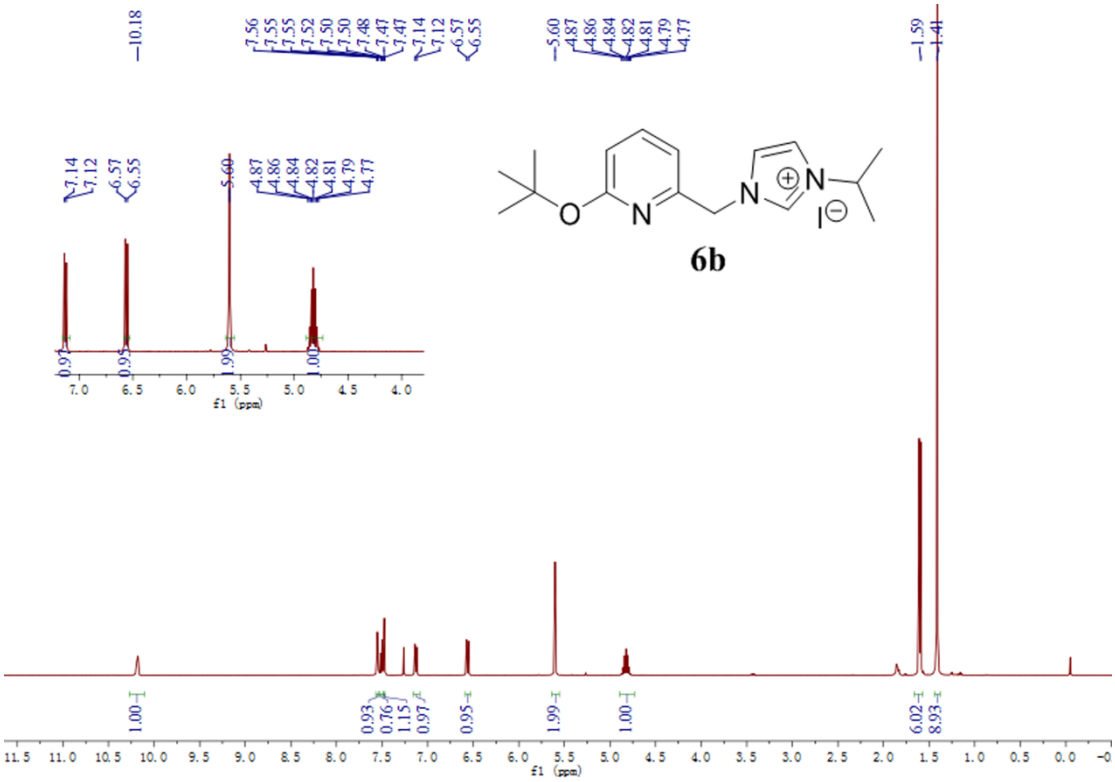
^{1}H NMR (**6a**) (400 MHz, $CDCl_3$)



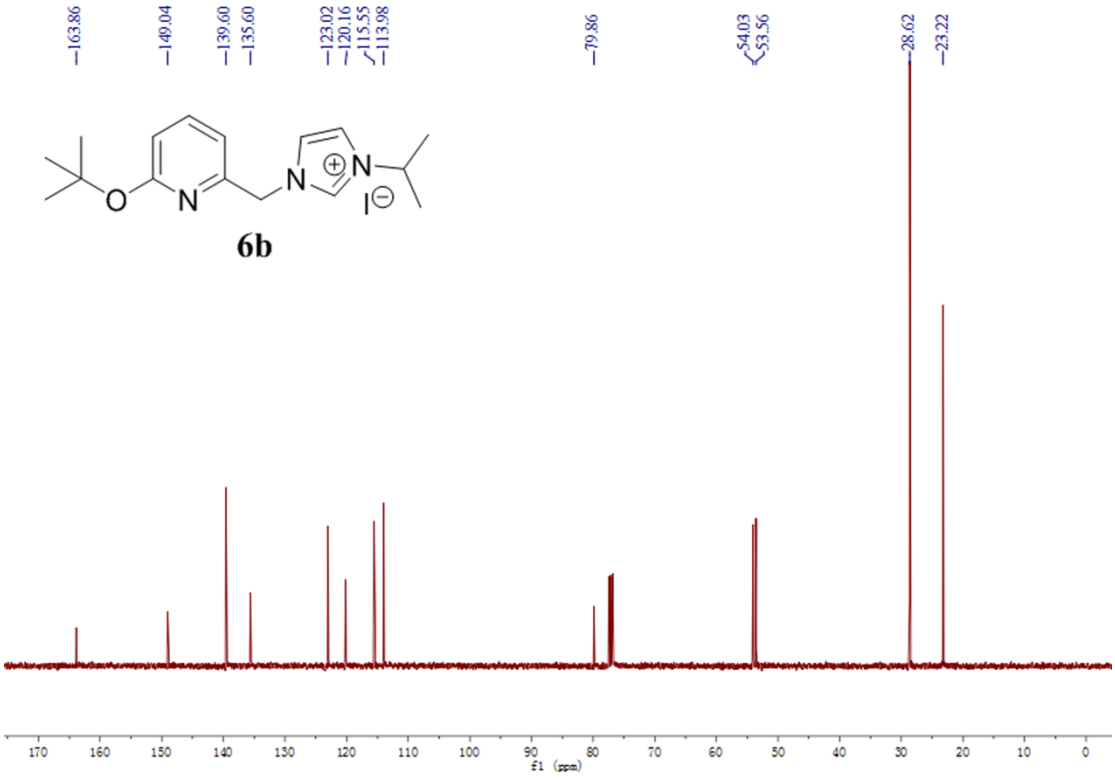
^{13}C NMR (**6a**) (101 MHz, $CDCl_3$)



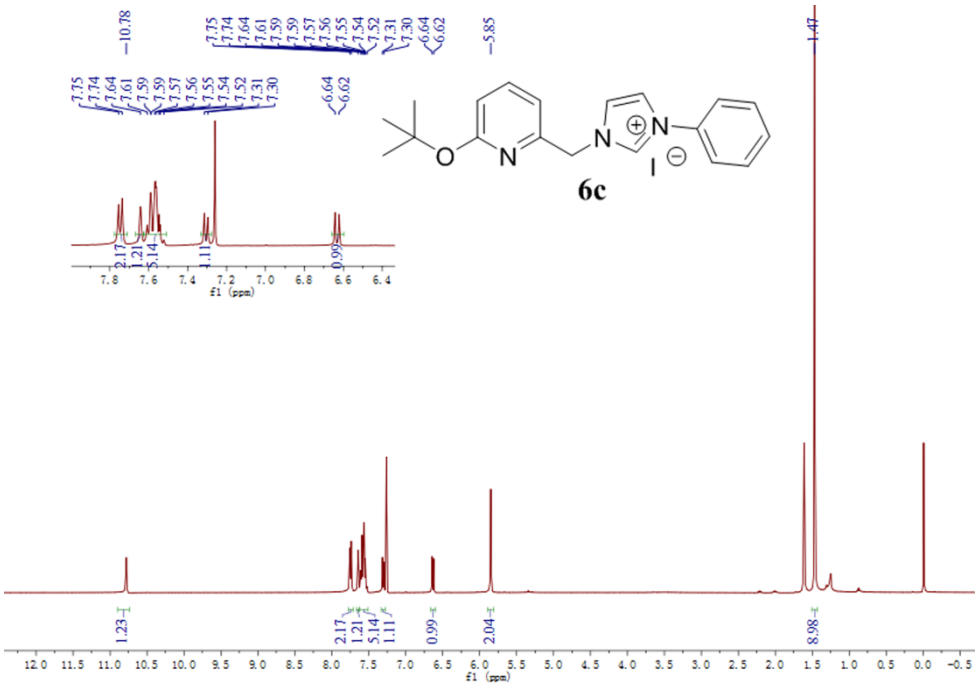
^{1}H NMR (**6b**) (400 MHz, $CDCl_3$)



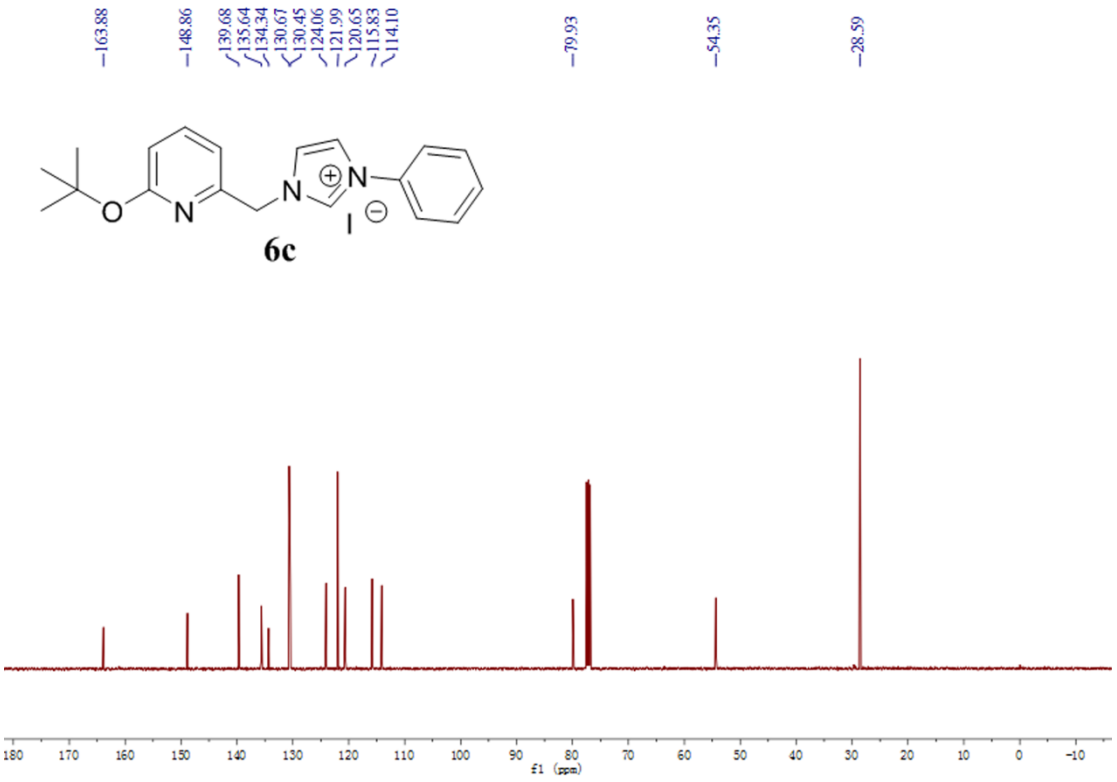
^{13}C NMR (**6b**) (101 MHz, $CDCl_3$)



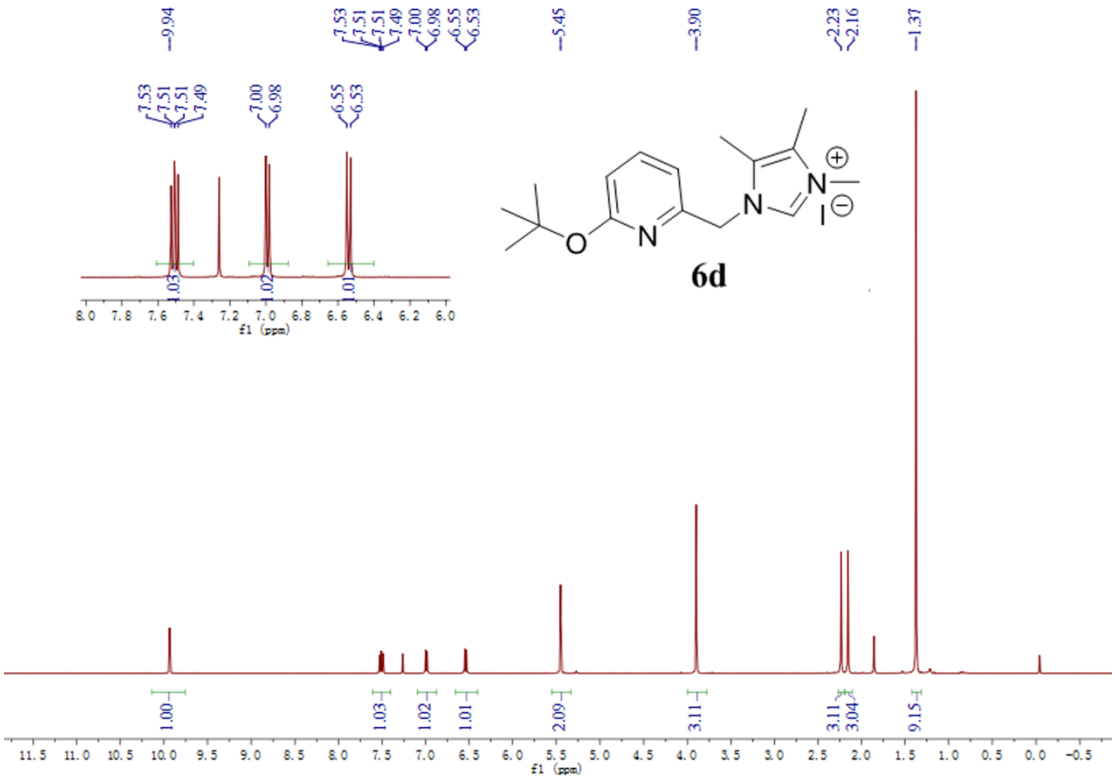
^{1}H NMR (**6c**) (400 MHz, $CDCl_3$)



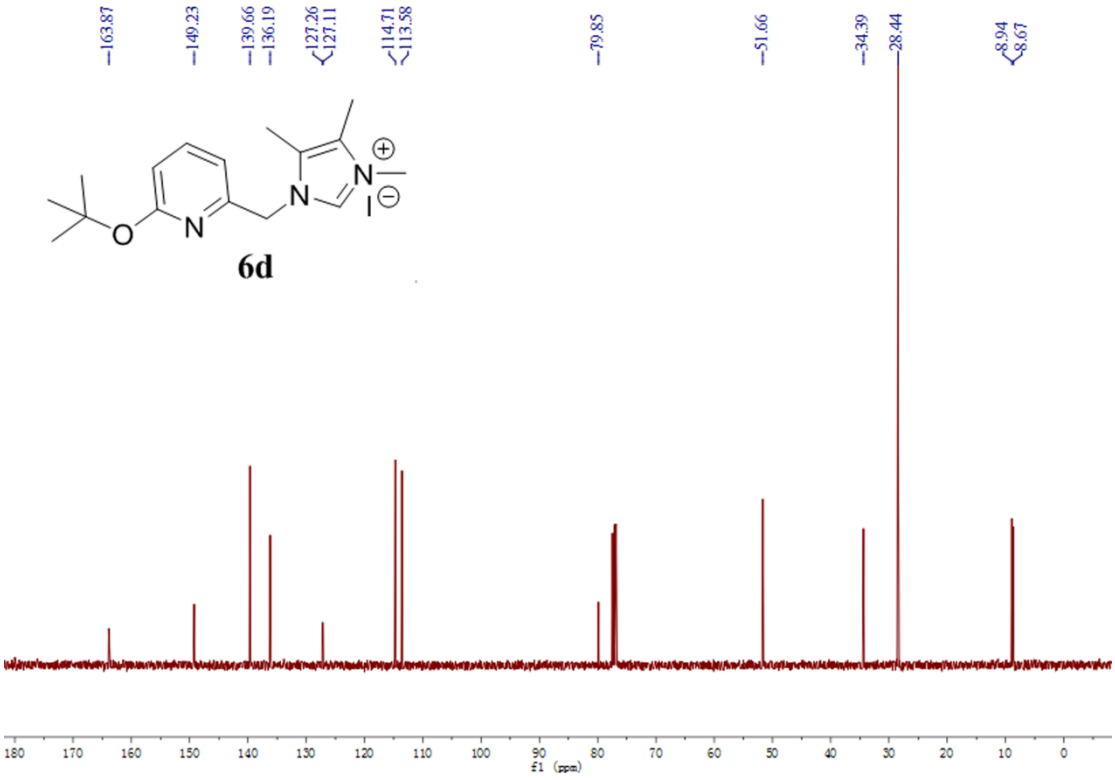
^{13}C NMR (**6c**) (101 MHz, $CDCl_3$)



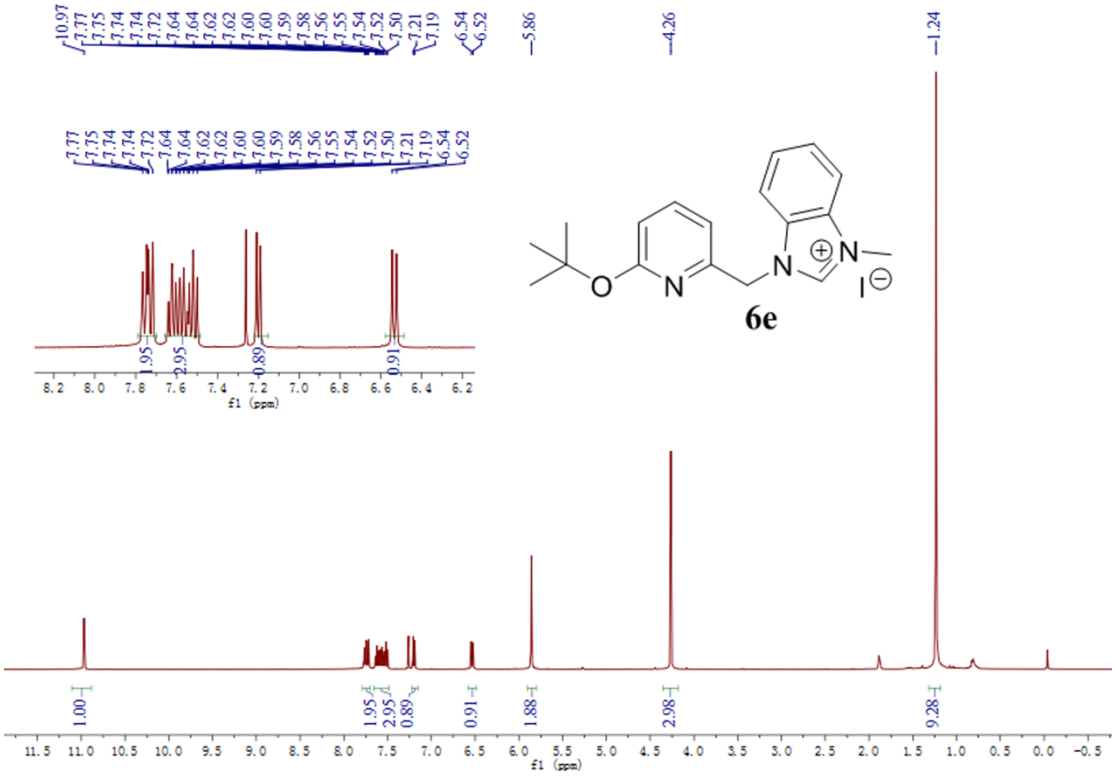
^{1}H NMR (**6d**) (400 MHz, $CDCl_3$)



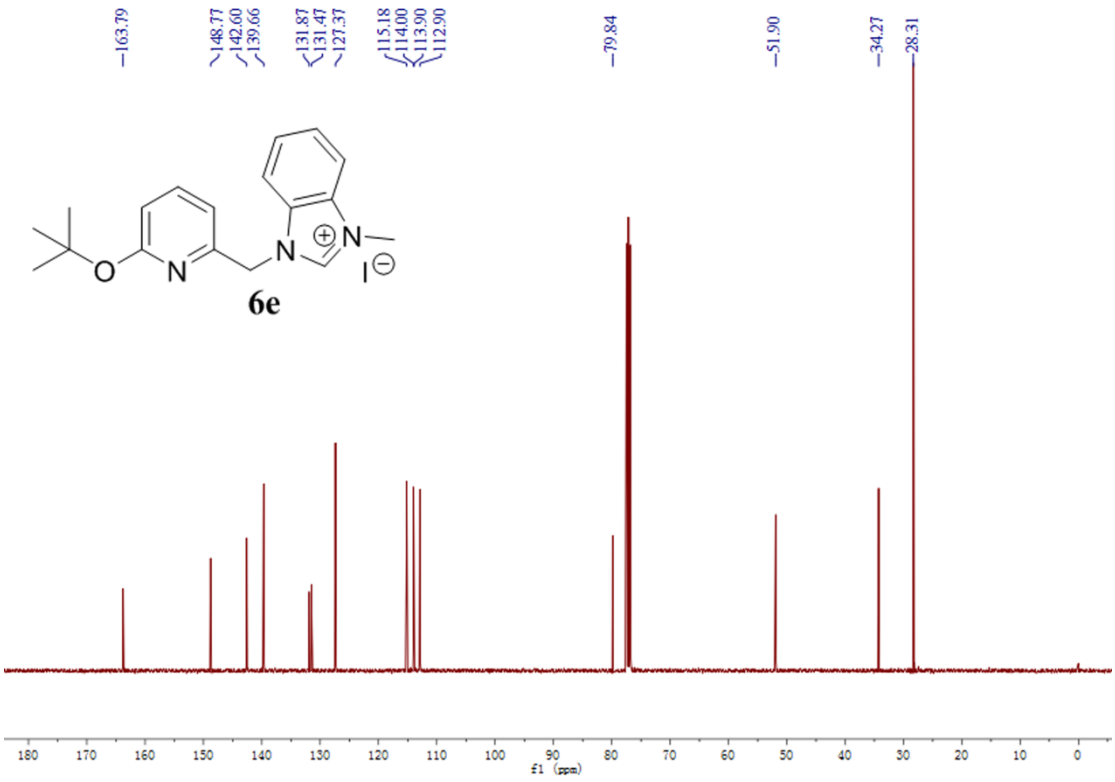
^{13}C NMR (**6d**) (101 MHz, $CDCl_3$)



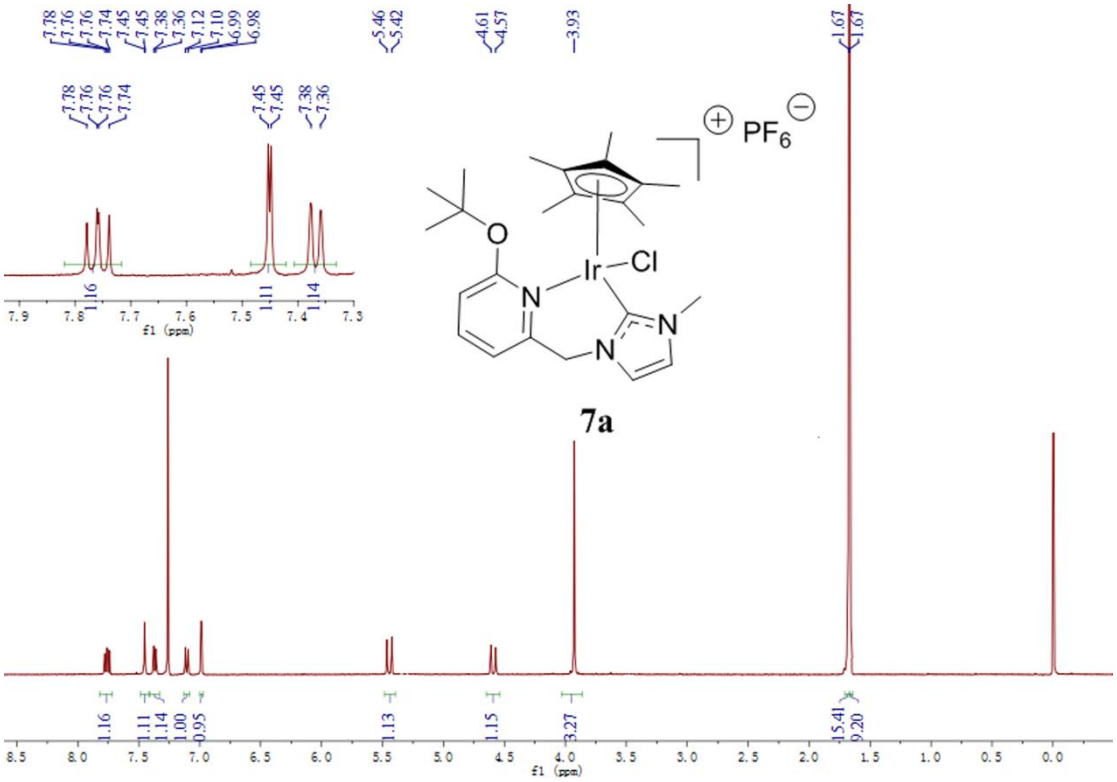
^{1}H NMR (**6e**) (400 MHz, $CDCl_3$)



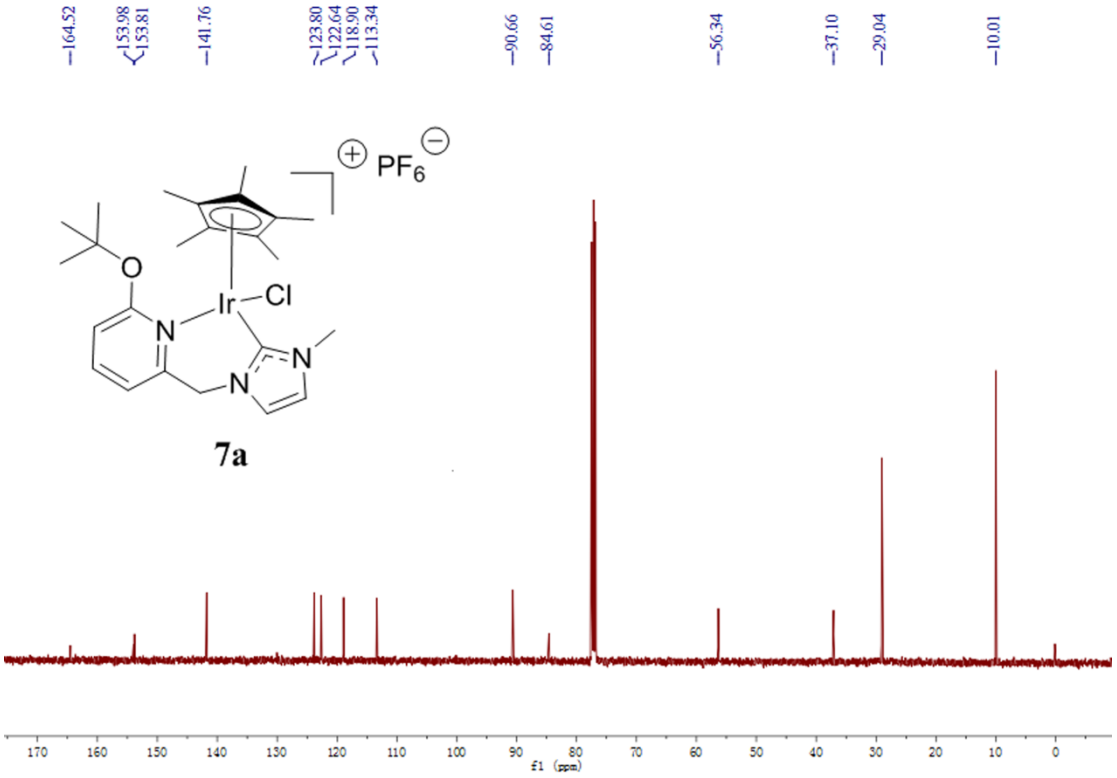
^{13}C NMR (**6e**) (101 MHz, $CDCl_3$)



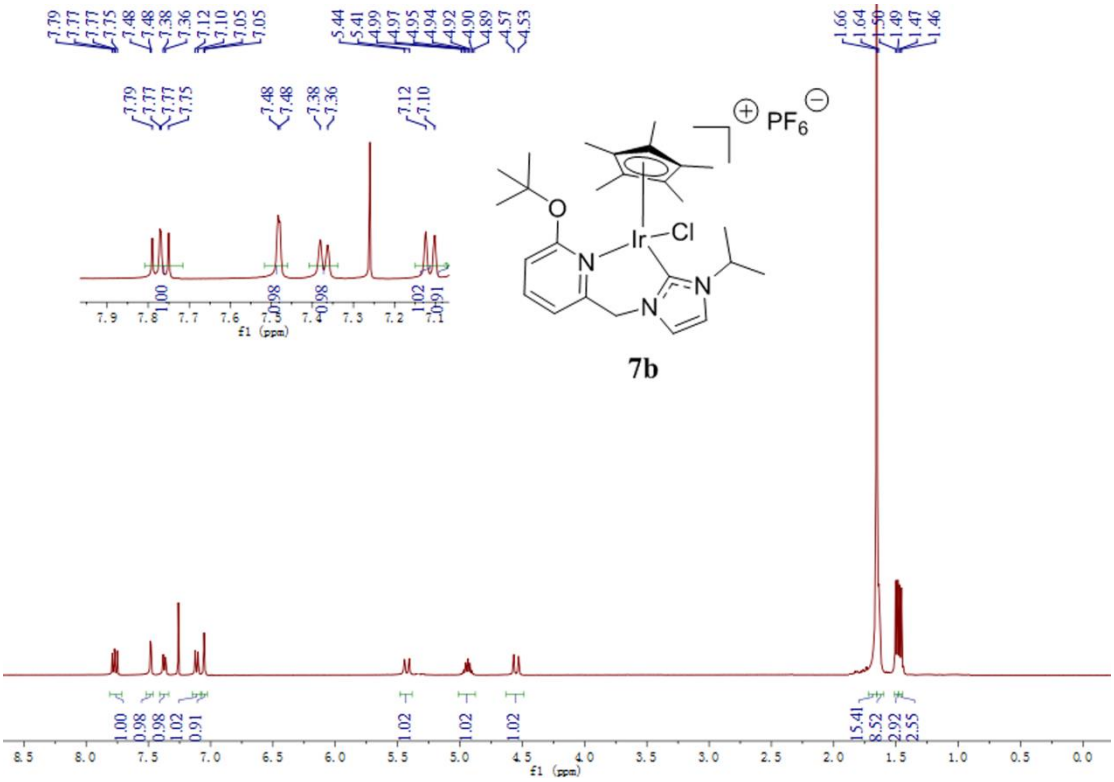
^{1}H NMR (**7a**) (400 MHz, $CDCl_3$)



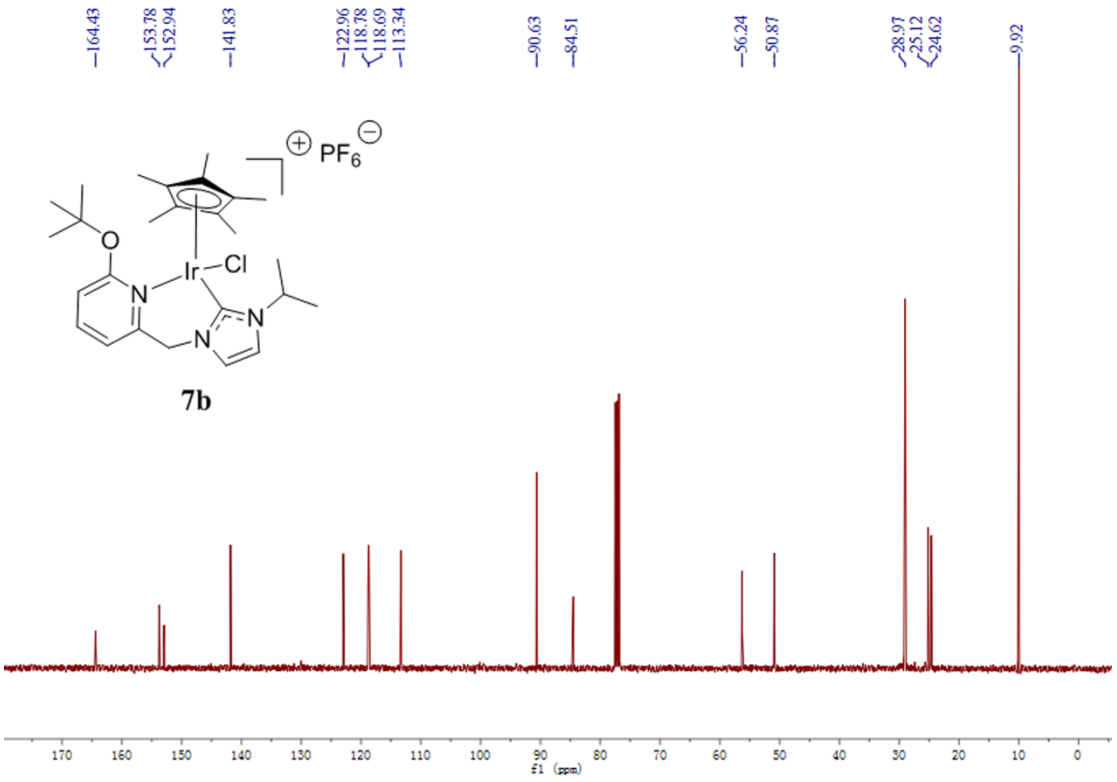
^{13}C NMR (**7a**) (101 MHz, $CDCl_3$)



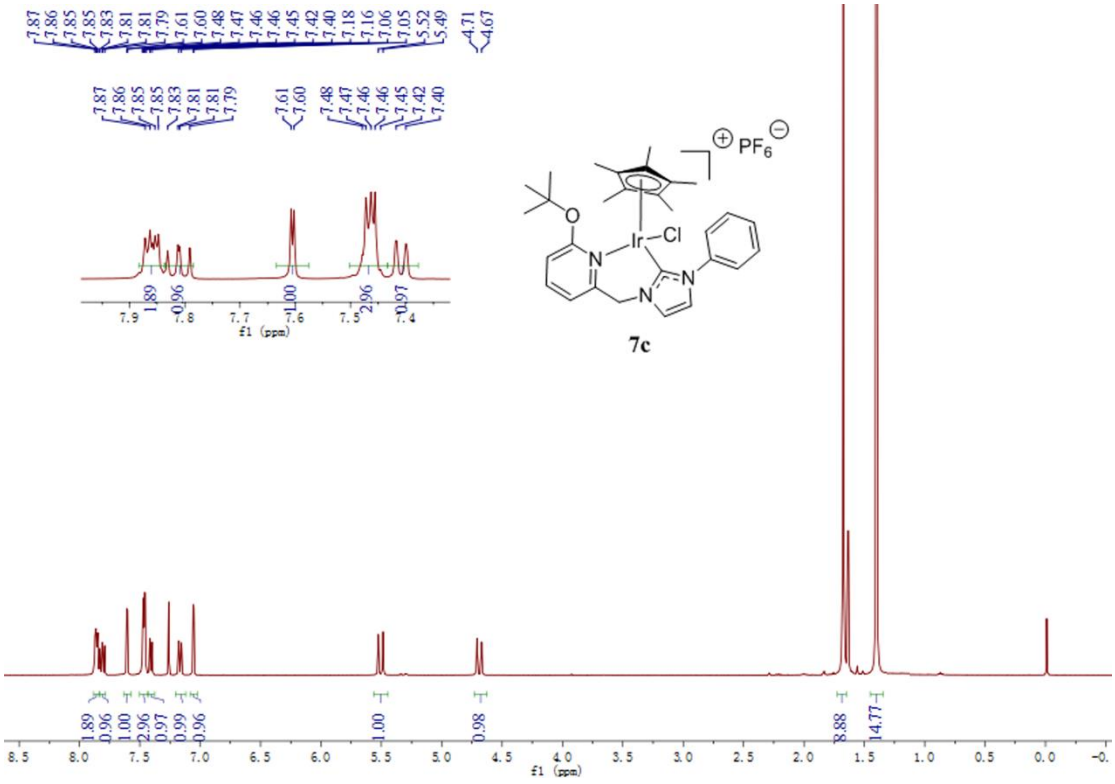
^{1}H NMR (**7b**) (400 MHz, $CDCl_3$)



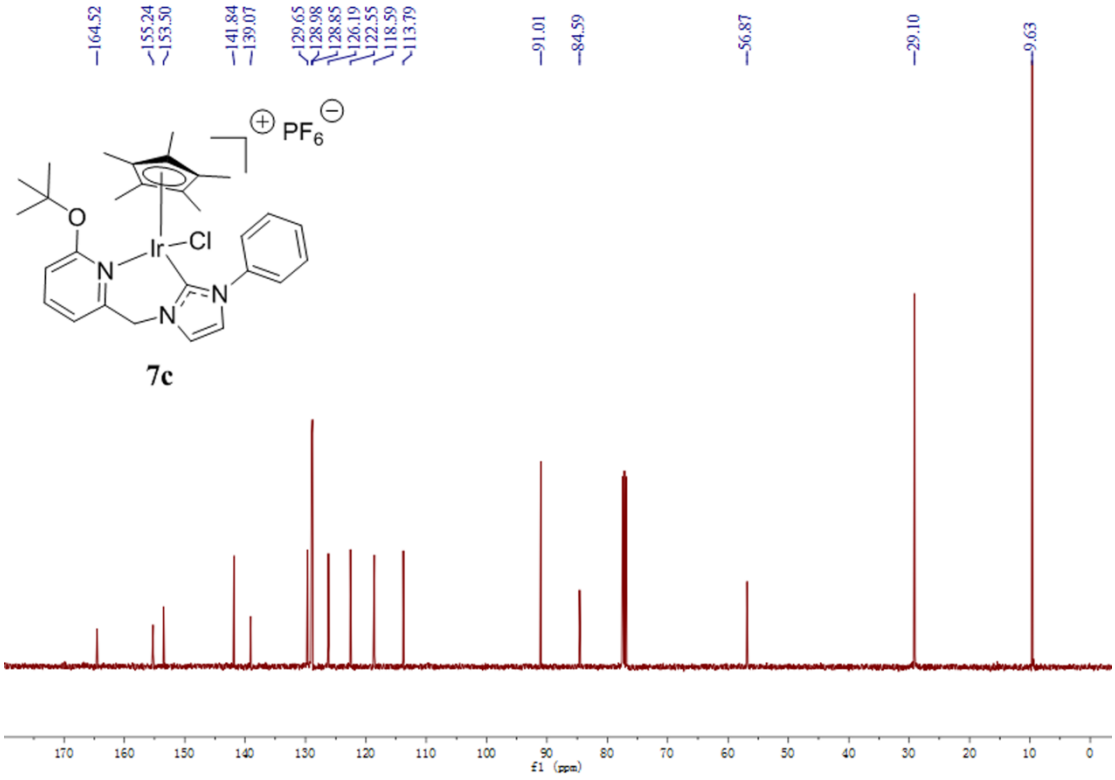
^{13}C NMR (**7b**) (101 MHz, $CDCl_3$)



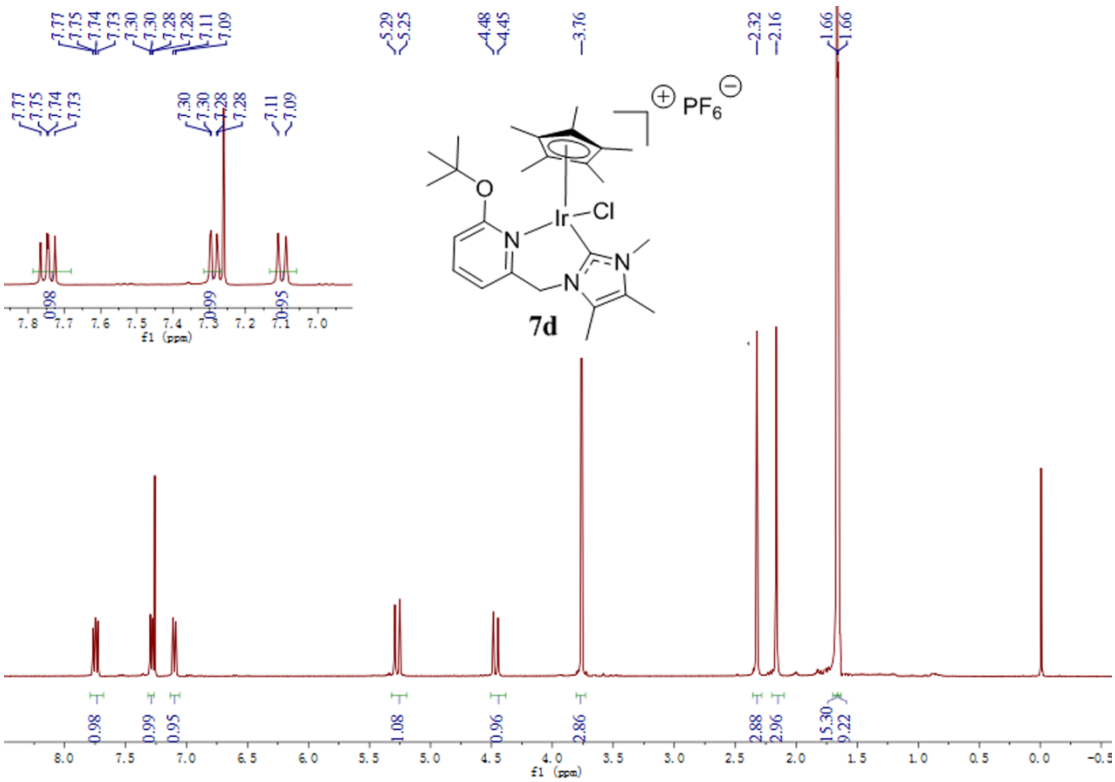
^{1}H NMR (**7c**) (400 MHz, $CDCl_3$)



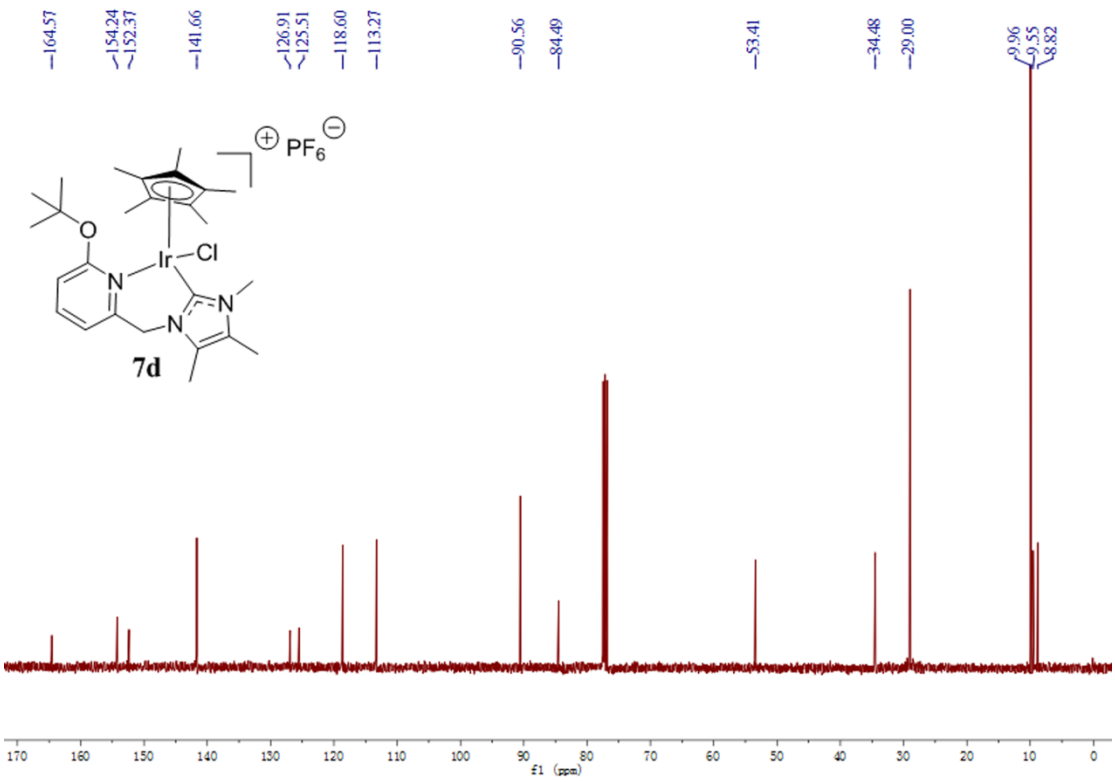
^{13}C NMR (**7c**) (101 MHz, $CDCl_3$)



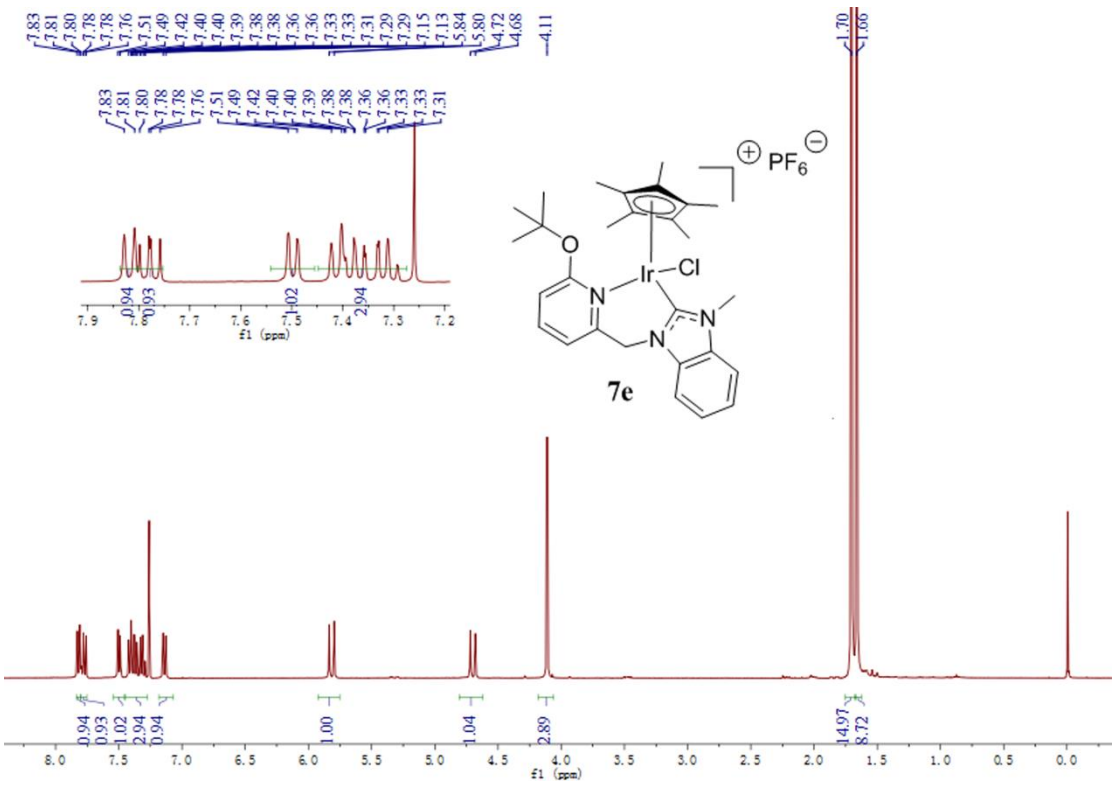
^{1}H NMR (**7d**) (400 MHz, $CDCl_3$)



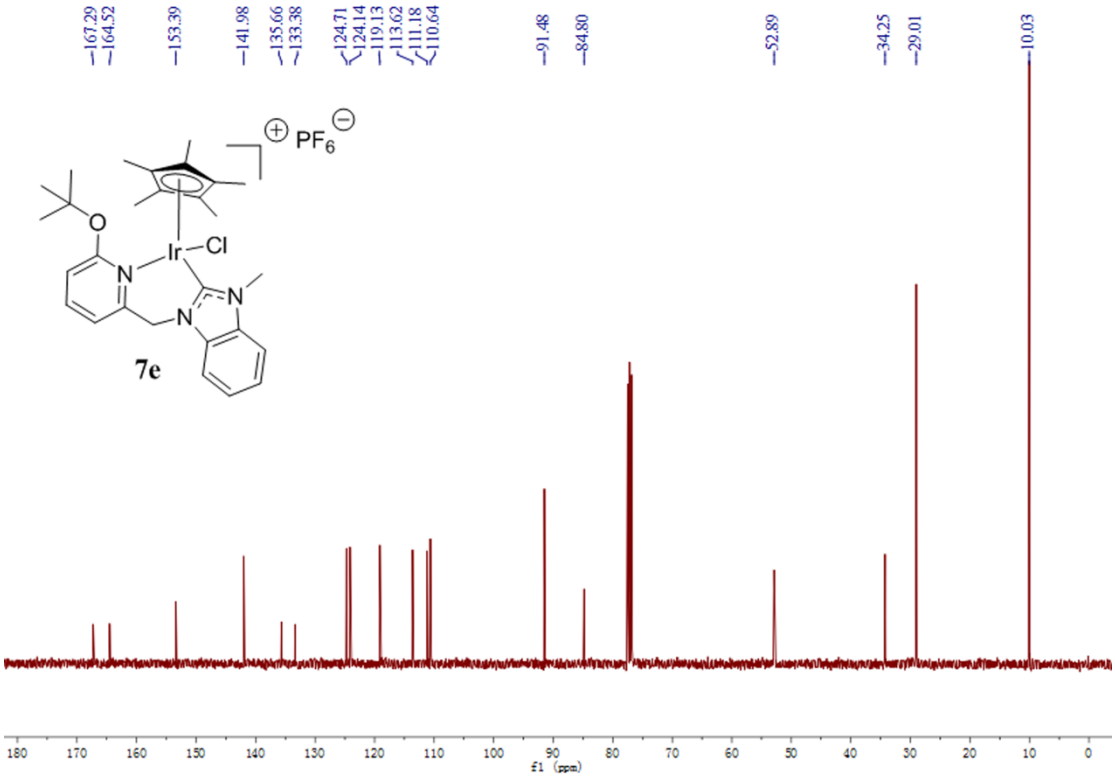
^{13}C NMR (**7d**) (101 MHz, $CDCl_3$)



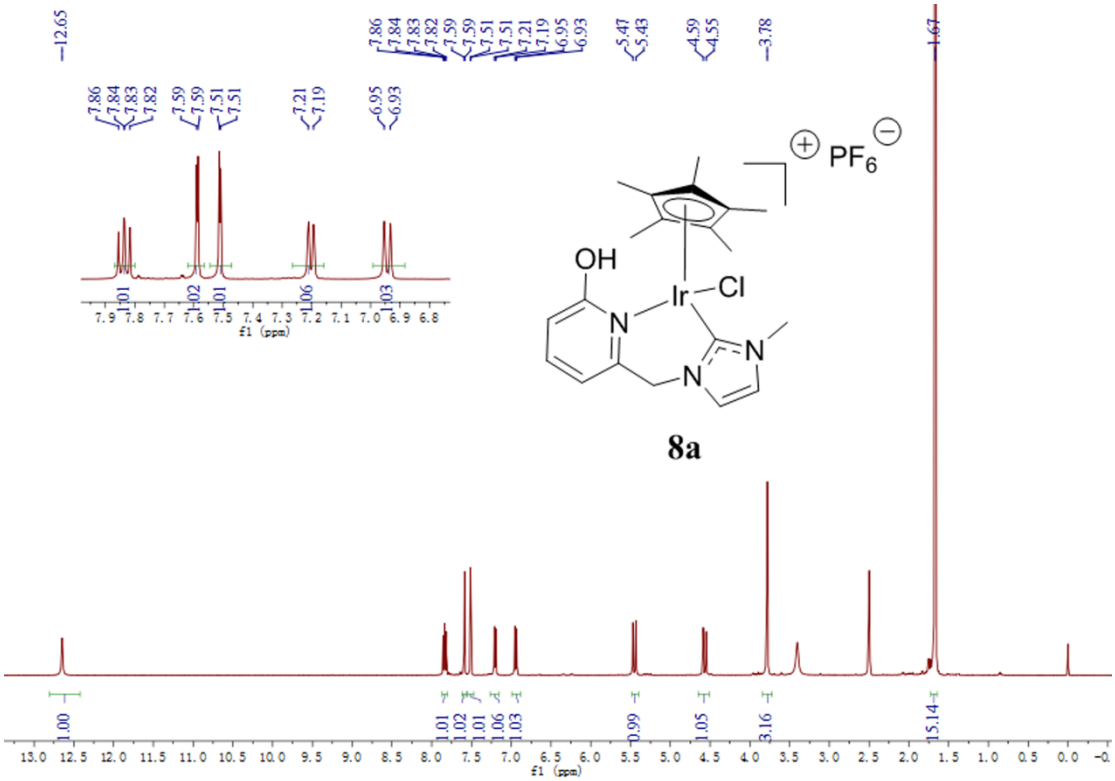
^{1}H NMR (**7e**) (400 MHz, $CDCl_3$)



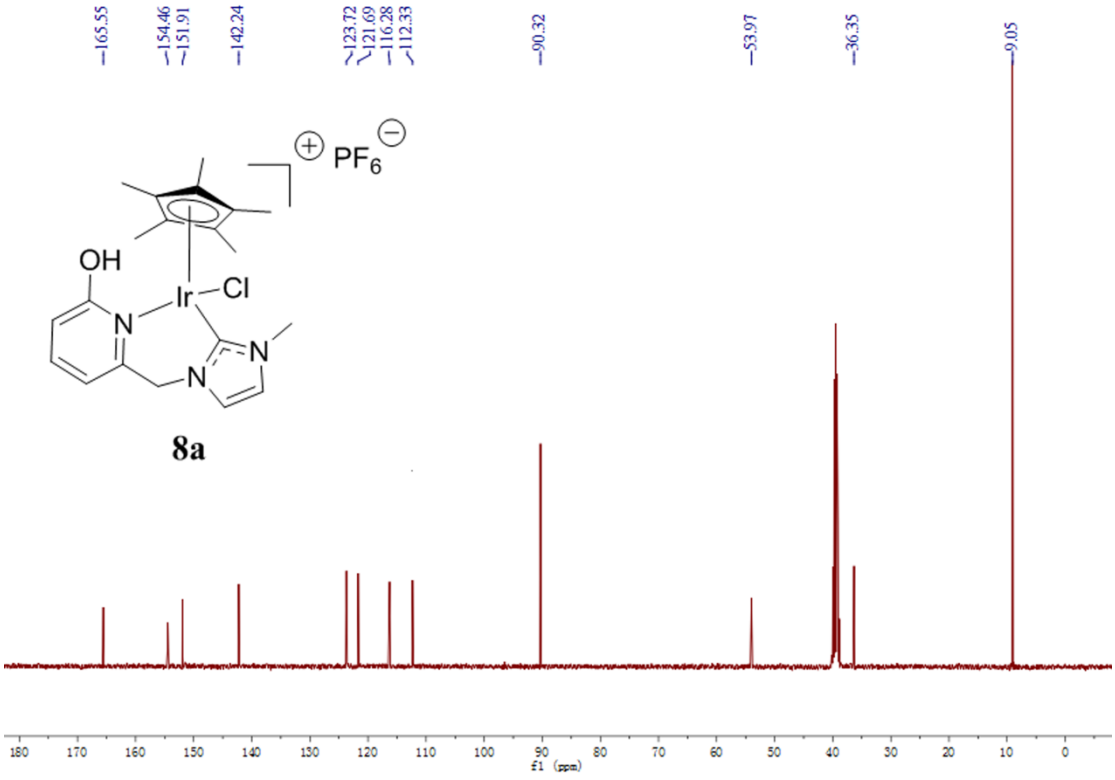
^{13}C NMR (**7e**) (101 MHz, $CDCl_3$)



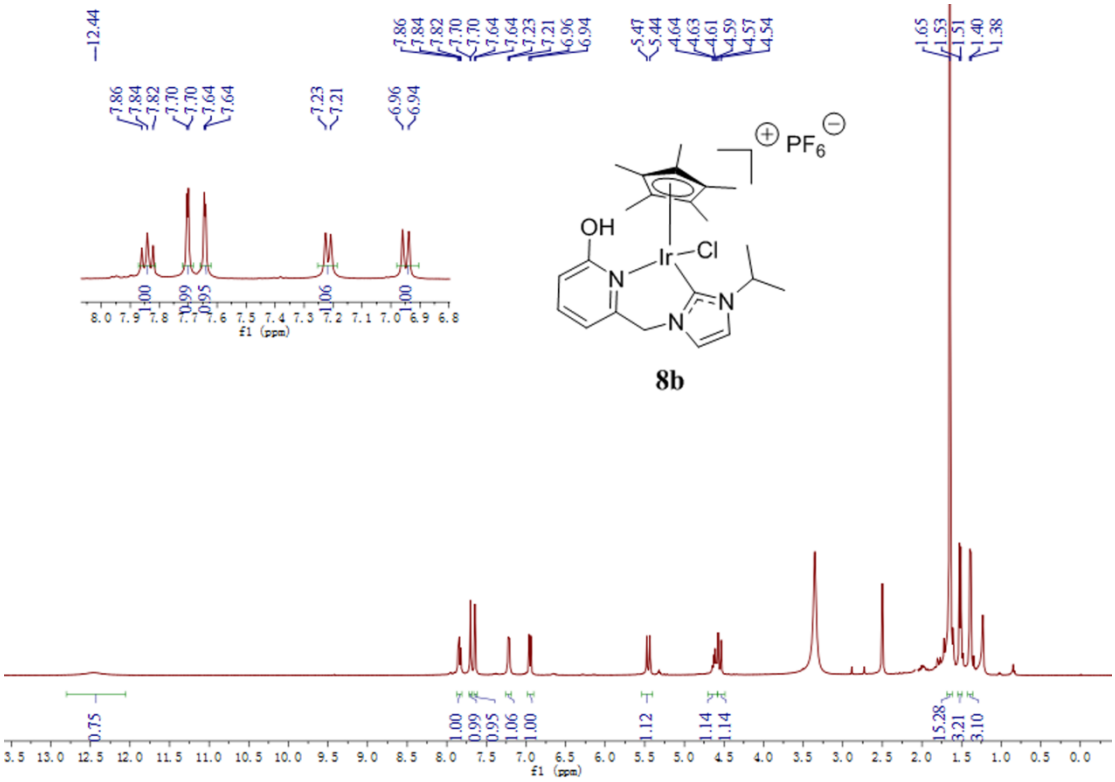
^{1}H NMR (**8a**) (400 MHz, DMSO-*d*6)



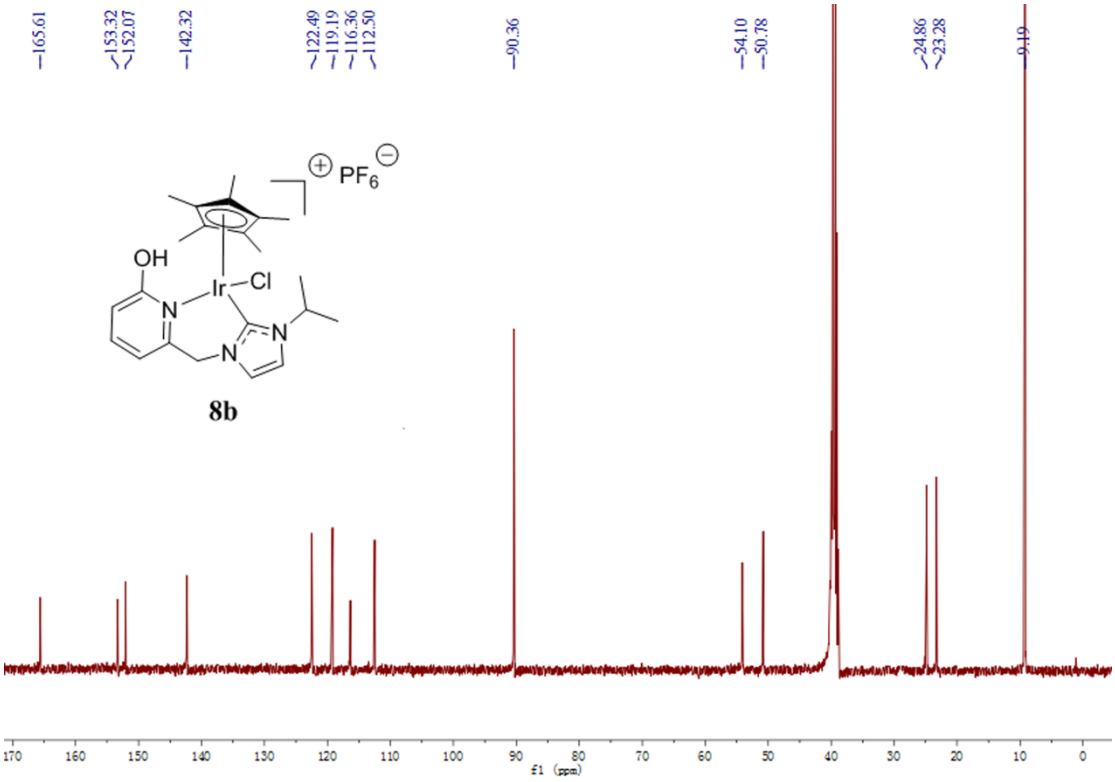
^{13}C NMR (**8a**) (101 MHz, DMSO-*d*6)



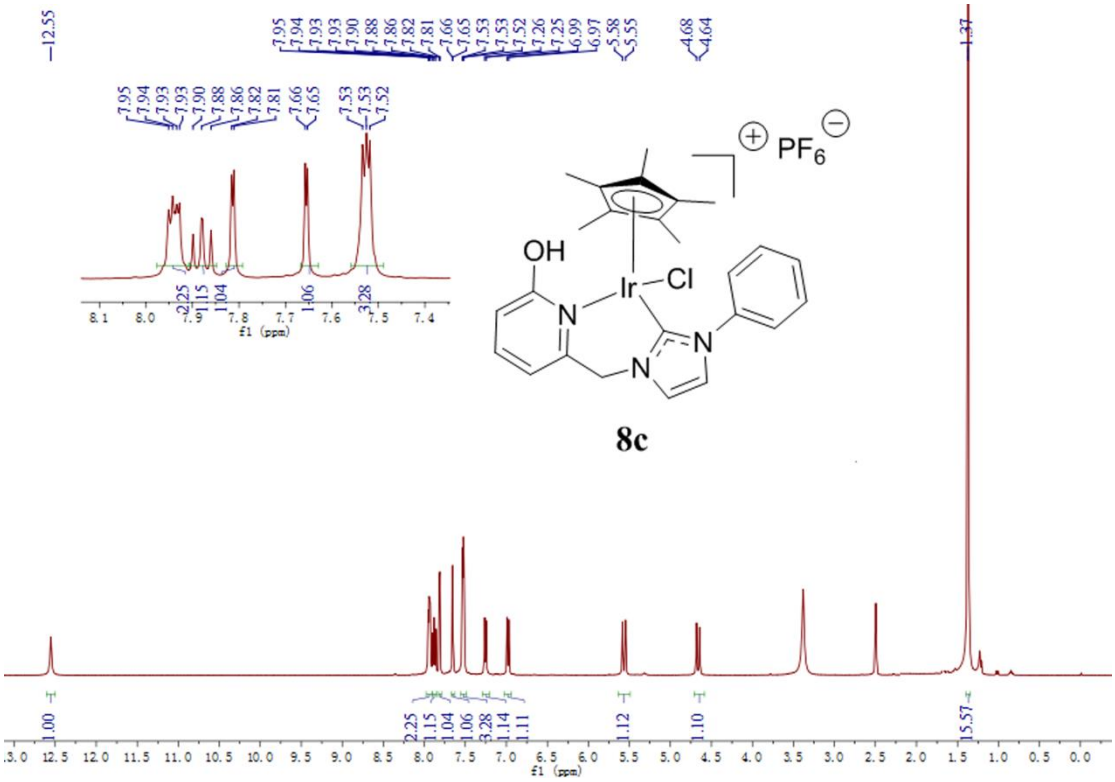
^{1}H NMR (**8b**) (400 MHz, DMSO-*d*6)



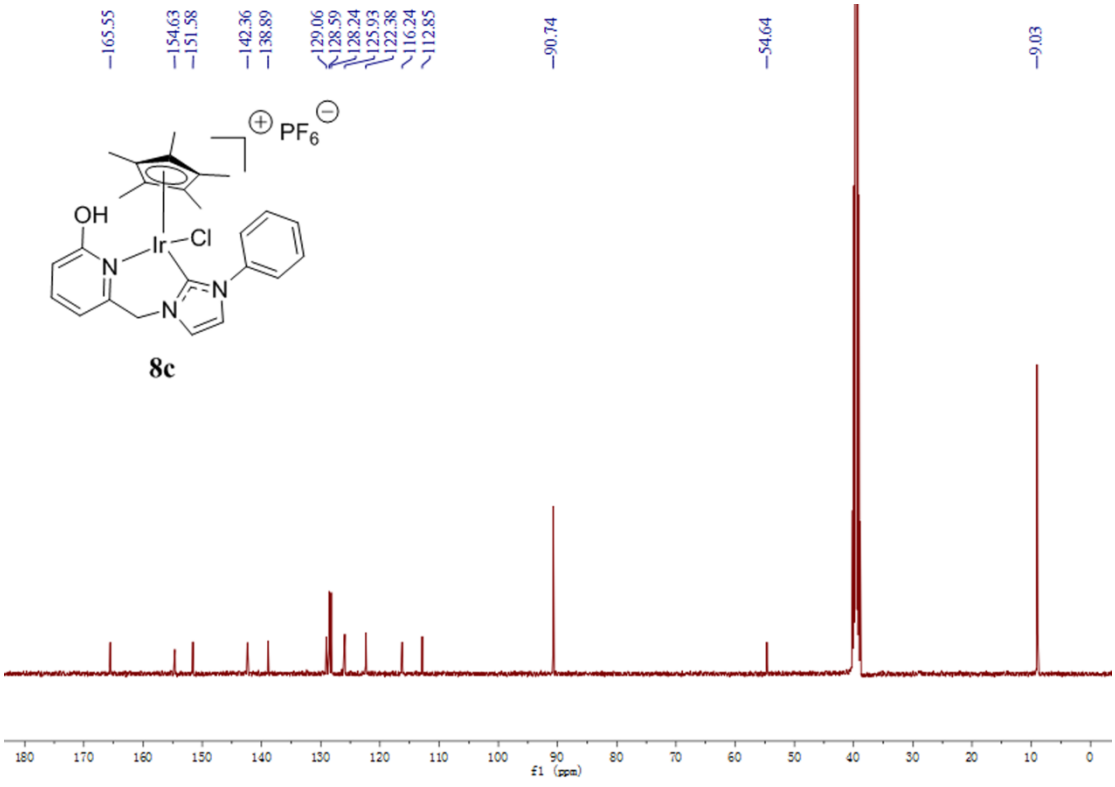
^{13}C NMR (**8b**) (101 MHz, DMSO-*d*6)



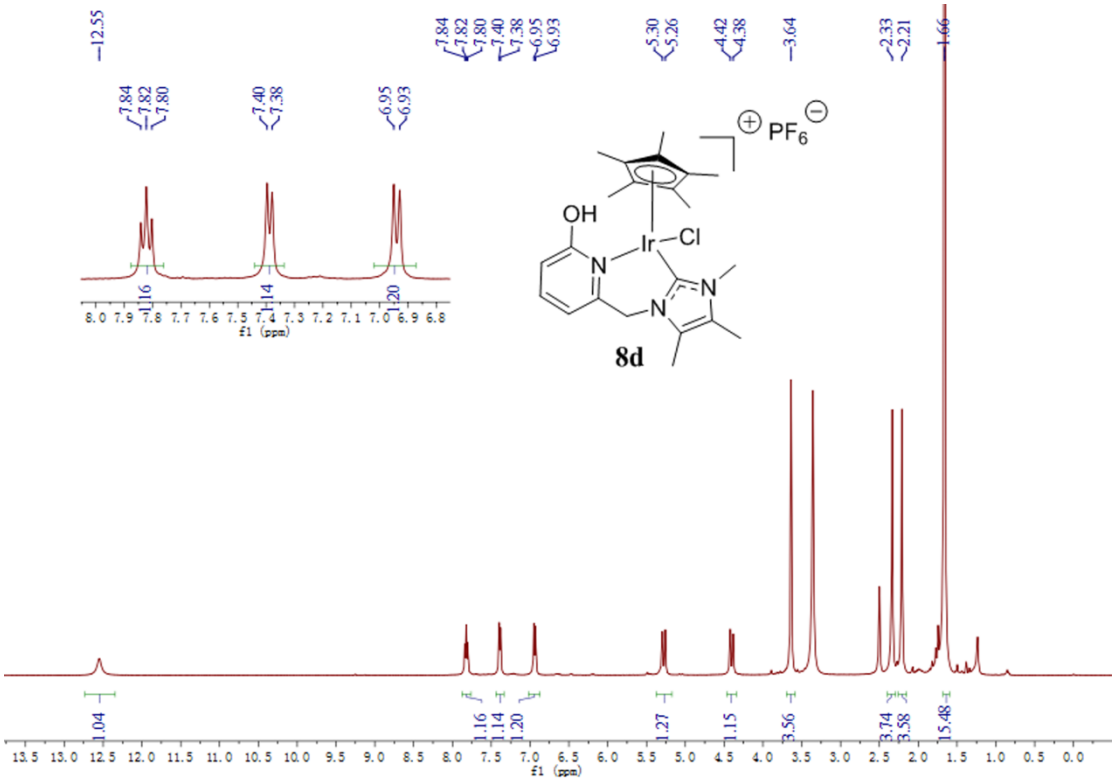
^{1}H NMR (**8c**) (400 MHz, DMSO-*d*6)



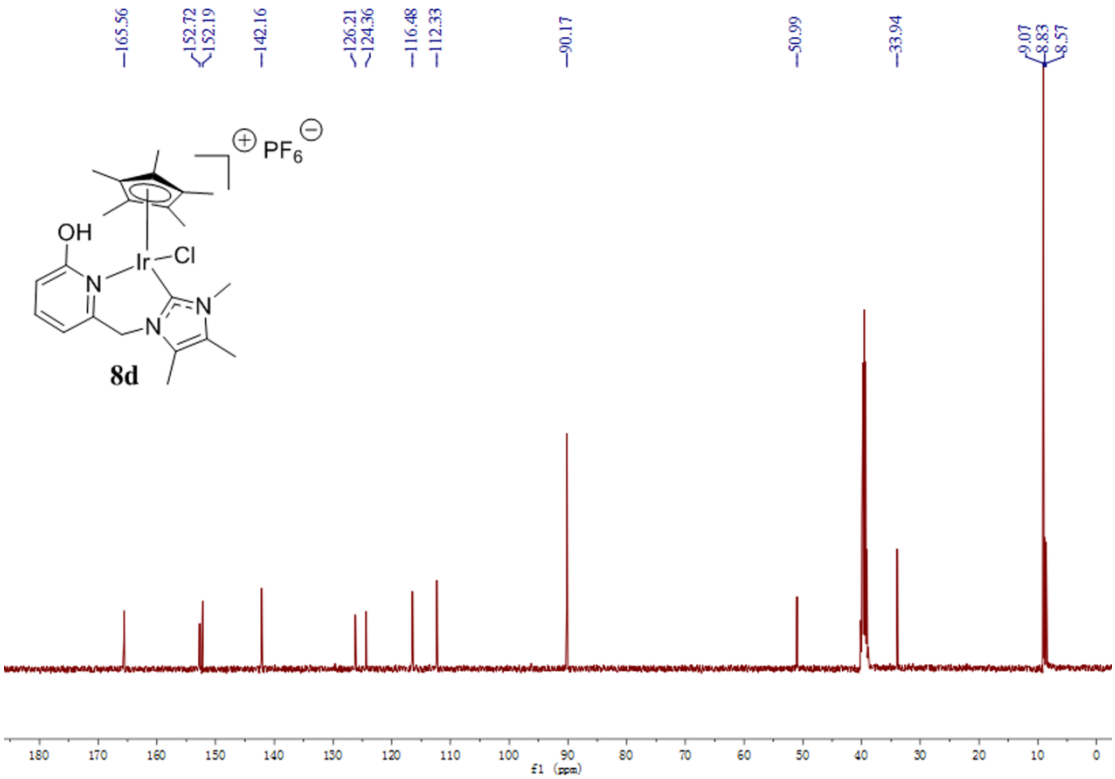
^{13}C NMR (**8c**) (101 MHz, DMSO-*d*6)



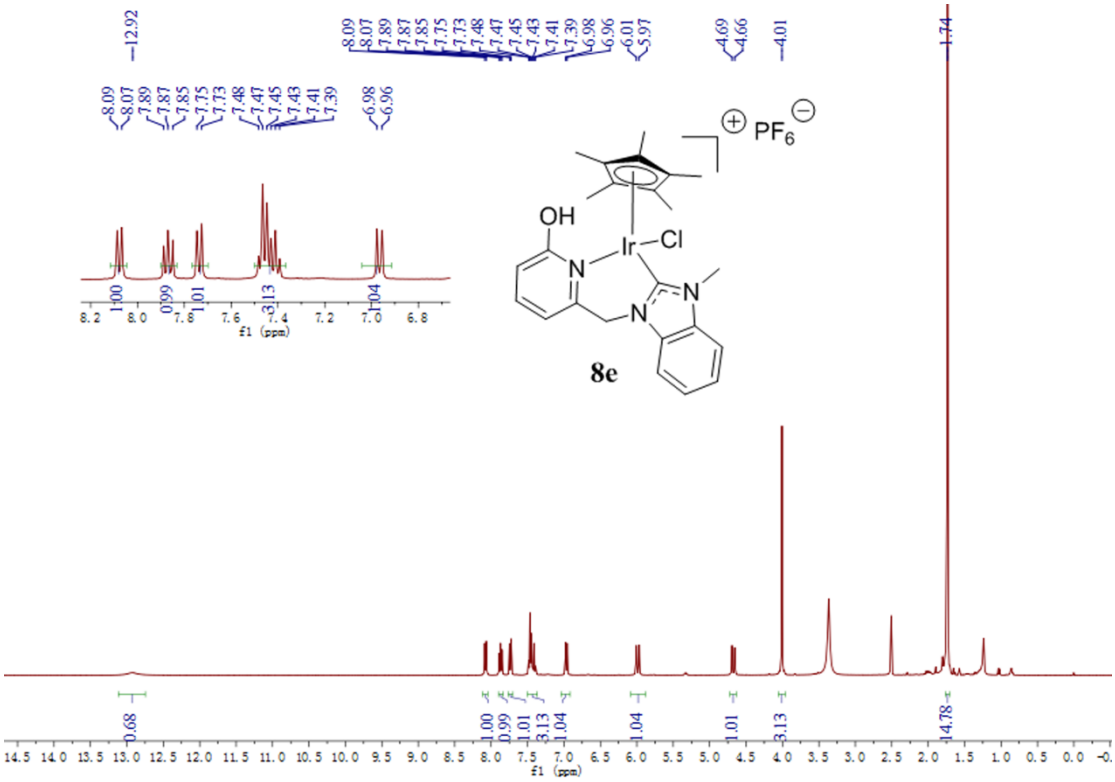
^{1}H NMR (**8d**) (400 MHz, DMSO-*d*6)



^{13}C NMR (**8d**) (101 MHz, DMSO-*d*6)



^{1}H NMR (**8e**) (400 MHz, DMSO-*d*6)



^{13}C NMR (**8e**) (101 MHz, DMSO-*d*6)