Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Experimental and computational study on rhodium-catalyzed C4(5)$_{aryl}$–H activation/annulations of imidazoles with alkynes: Facile synthesis of six types of N-heterocycles

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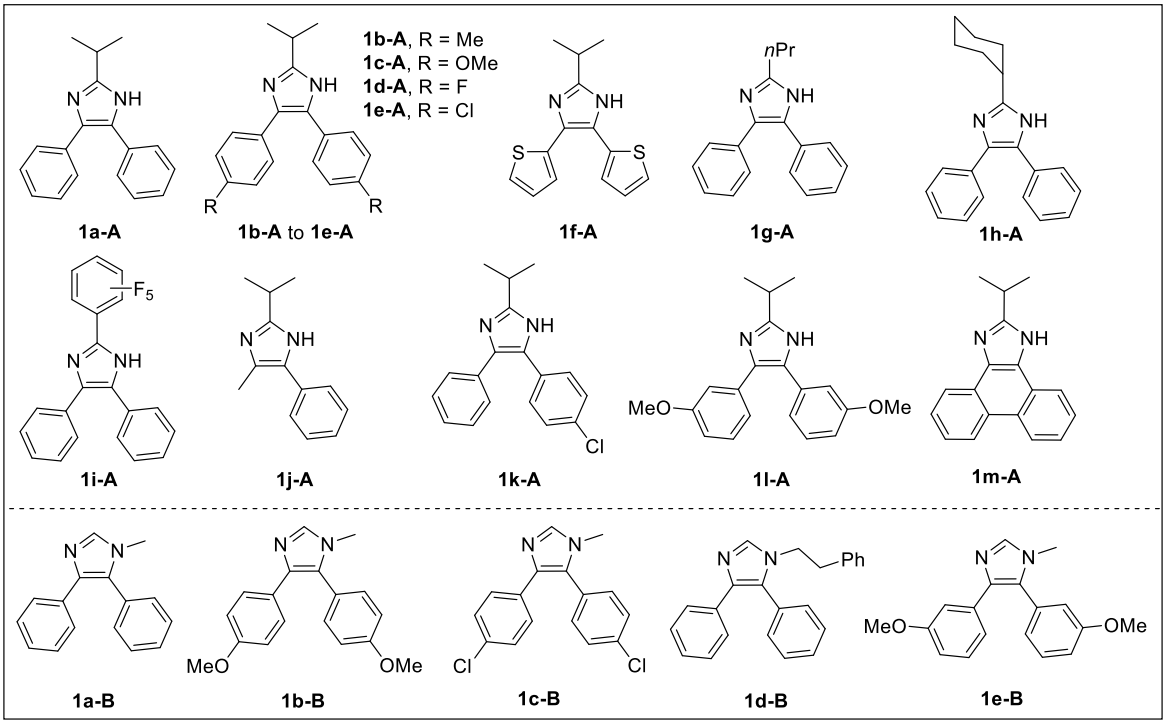
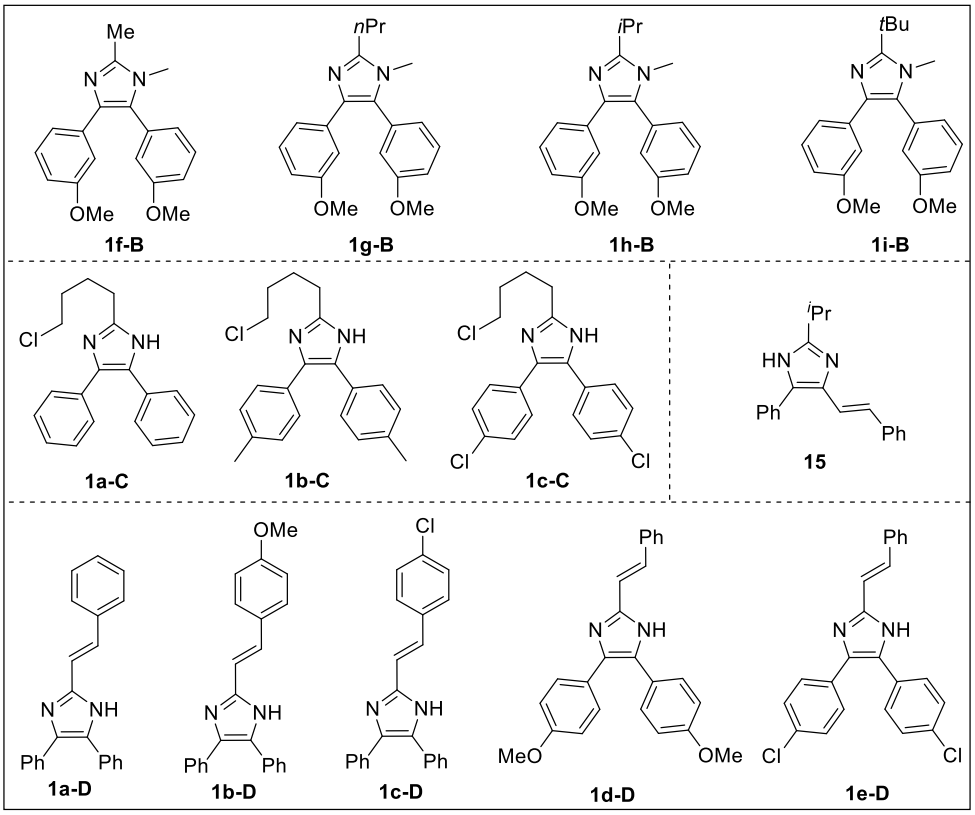
1. General remarks

NMR spectra were obtained on a BRUKER Ascend 400 and 500. The ^{1}H NMR (400 and 500 MHz) chemical shifts were measured relative to $CDCl_3$ or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26 ppm; DMSO-d_6: δ = 2.50 ppm). The ^{13}C NMR (100 and 125 MHz) chemical shifts were given using $CDCl_3$ or DMSO-d_6 the internal standard ($CDCl_3$: δ = 77.16 ppm; DMSO-d_6: δ = 39.52 ppm). High-resolution mass spectra (HR-MS) were obtained with a BRUKER solanX 70 FT-MS (ESI^+). Fluorescence emission spectra were obtained using a Hitachi F-7000 fluorescence spectrometer. Melting points were determined with SGW® X-4 and are uncorrected.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Benzils, diphenylacetylene, 4,5-diphenyl-1,3-dihydro-2*H*-imidazol-2-one, AgOAc, $Cu(OTf)_2$ and $Cu(OAc)_2{\cdot}H_2O$ were purchased from Beijing Innochem Chemical Engineering Reagent (China) Co., Ltd and Energy Chemical. $[(Cp^*RhCl_2)_2]$[1] and alkynes[2] were prepared according to the literature procedures.

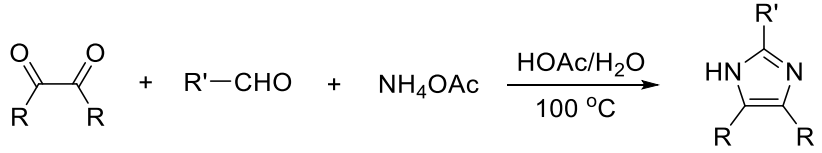




2. General procedures.

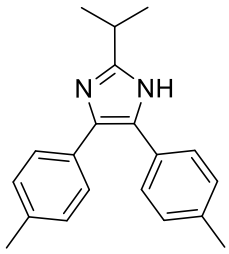
2.1 General procedure for the synthesis of N-H imidazoles (1-A, 1-C, 1-D and 15)

Compounds **1a-A**[3], **1d-A**[4], **1g-A**[5], **1h-A**[6], **1j-A**[7], **1a-D**[8], **1e-D**[8] and **12**[5] were prepared according to modified literature procedure.



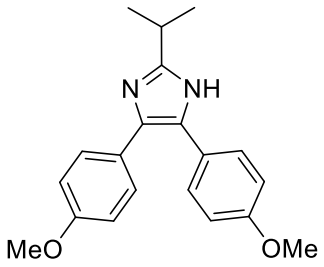
A solution of benzil (1 mmol), aldehyde (1 mmol, 1 equiv), NH_4OAc (11 mmol, 902 mg, 11 equiv), glacial acetic acid (3.6 mL) and H_2O (0.4 mL) was reacted at 100 °C for 7 h. The reaction mixture was cooled to room temperature. Afterwards, it was diluted with H_2O (10 mL) and then aq. $NaHCO_3$ solution was added, and the mixture was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phase was dried with Na_2SO_4. The volatiles were evaporated under reduced pressure, and the residue was passed through silica gel column.

2-isopropyl-4,5-di-*p*-tolyl-1*H*-imidazole (1b-A)



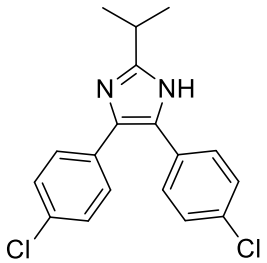
White solid (225 mg, 77% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 1/1, v/v). M.p.: 187.2–189.2 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.37 (d, J = 7.5 Hz, 4H), 7.10 (d, J = 7.5 Hz, 4H), 3.15–3.10 (m, 1H), 2.34 (s, 6H), 1.36 (d, J = 7.5 Hz, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 152.86, 136.84, 129.32, 127.69, 28.46, 21.85, 21.37 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{20}H_{23}N_2$ ($[M+H]^+$) 291.1861, found 291.1859.

2-isopropyl-4,5-bis(4-methoxyphenyl)-1*H*-imidazole (1c-A)



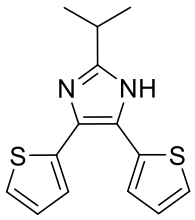
White solid (214 mg, 73% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 1/1, v/v). M.p.: 191.8–193.8 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.37 (d, J = 9.0 Hz, 4H), 6.82 (d, J = 9.0 Hz, 4H), 3.79 (s, 6H), 3.15–3.10 (m, 1H), 1.33–1.31 (m, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 158.91, 152.68, 129.77, 129.19, 125.20, 114.06, 55.36, 28.20, 21.72 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{20}H_{23}N_2O_2$ ($[M+H]^+$) 323.1760, found 323.1762.

4,5-bis(4-chlorophenyl)-2-isopropyl-1*H*-imidazole (1e-A)



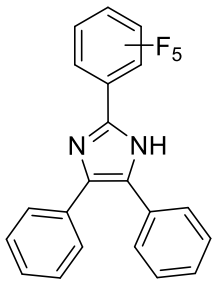
Yellow solid (222 mg, 67% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 10/1→2/1, v/v). M.p.: 201.3–203.3 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.36 (d, J = 8.0 Hz, 4H), 7.27–7.26 (m, 4H, cover the solvent), 3.16–3.10 (m, 1H), 1.37 (d, J = 7.0 Hz, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 153.75, 133.47, 130.92, 129.19, 129.02, 28.38, 21.75 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{18}H_{17}Cl_2N_2$ ($[M+H]^+$) 331.0769, found 331.0766.

2-isopropyl-4,5-di(thiophen-2-yl)-1*H*-imidazole (1f-A)



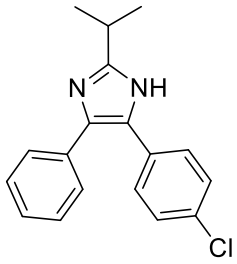
Yellow solid (233 mg, 93% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 5/1→3/2, v/v). M.p.: 211.1–213.1 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.26–7.25 (m, 2H, cover the solvent), 7.21 (s, 2H), 7.01 (s, 2H), 3.10–3.05 (m, 1H), 1.33 (d, *J* = 7.0 Hz, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 153.62, 153.59, 127.43, 125.88, 125.39, 28.42, 21.70 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{14}H_{15}N_2S_2$ ($[M+H]^+$) 275.0677, found 275.0679.

2-(perfluorophenyl)-4,5-diphenyl-1*H*-imidazole (1i-A)



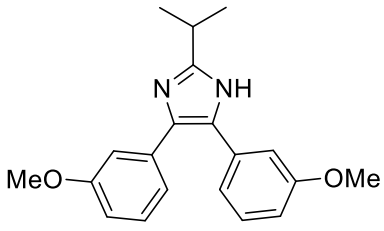
White solid (197 mg, 51% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 3/1, v/v). M.p.: 186.4–188.4 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 10.93 (br s, 1H), 7.46–7.45 (m, 4H), 7.27–7.26 (m, 6H, cover the solvent) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 133.45, 129.00, 128.81, 128.73, 128.62, 128.03, 127.90 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{21}H_{12}F_5N_2$ ($[M+H]^+$) 387.0921, found 387.0915.

5-(4-chlorophenyl)-2-isopropyl-4-phenyl-1*H*-imidazole (1k-A)



White solid (262 mg, 88% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 4/1, v/v). M.p.: 198.7–200.7 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 9.17 (br s, 1H), 7.42–7.41 (m, 4H), 7.32 (t, *J* = 6.8 Hz, 2H), 7.29–7.23 (m, 3H, cover the solvent), 3.12–3.07 (m, 1H), 1.36 (d, *J* = 7.0 Hz, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 153.51, 132.72, 129.04, 128.86, 128.72, 127.94, 127.92, 127.62, 28.49, 21.81 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{18}H_{18}ClN_2$ ($[M+H]^+$) 297.1159, found 297.1163.

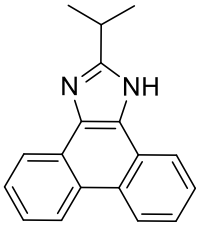
2-isopropyl-4,5-bis(3-methoxyphenyl)-1*H*-imidazole (1l-A)



White solid (300 mg, 93% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 2/1, v/v). M.p.: 117.7–119.7 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.18 (t, *J* = 7.3 Hz, 2H), 7.07–7.05 (m, 4H), 6.77 (d, *J* = 7.5 Hz, 2H), 3.67 (s, 3H),

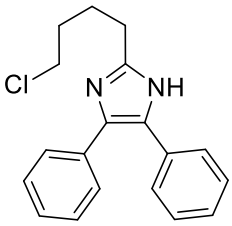
3.08–3.02(m, 1H), 1.30 (d, *J* = 6.5 Hz, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 159.67, 153.37, 134.51, 129.53, 120.46, 113.33, 113.05, 55.24, 28.41, 21.77 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{20}H_{23}N_2O_2$ ($[M+H]^+$) 323.1760, found 323.1762.

2-isopropyl-1*H*-phenanthro[9,10-*d*]imidazole (1m-A)



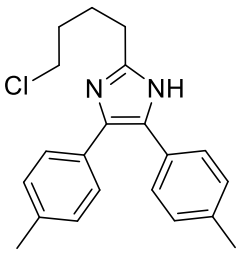
Yellow solid (80 mg, 31% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 5/1, v/v). M.p.: 228.0–230.0 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 8.73–8.71 (m, 2H), 8.54–8.52 (m, 2H), 7.57–7.54 (m, 4H), 3.46–3.40 (m, 1H), 1.42 (d, *J* = 7.0 Hz, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 157.35, 130.53, 128.45, 127.27, 125.54, 124.32, 123.81, 122.15, 29.17, 21.96 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{18}H_{17}N_2$ ($[M+H]^+$) 261.1392, found 261.1390.

2-(4-chlorobutyl)-4,5-diphenyl-1*H*-imidazole (1a-C)



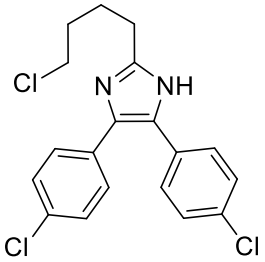
White solid (124 mg, 40% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 1/1, v/v). M.p.: 135.7–137.7 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.47 (d, *J* = 8.5 Hz, 2H), 7.43–7.38 (m, 3H), 7.34 (d, *J* = 7.0 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 2H), 7.12 (t, *J* = 7.3 Hz, 1H), 3.69 (s, 2H), 3.01 (s, 2H), 1.96 (s, 4H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 144.63, 136.75, 134.94, 131.27, 130.83, 128.98, 128.35, 128.17, 127.48, 126.90, 126.20, 44.01, 25.02, 23.18, 20.95 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{19}H_{20}ClN_2$ ($[M+H]^+$) 311.1315, found 311.1317.

2-(4-chlorobutyl)-4,5-di-*p*-tolyl-1*H*-imidazole (1b-C)



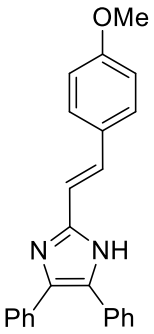
Yellow solid (117 mg, 36% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 1/1, v/v). M.p.: 138.0–140.0 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.37 (d, *J* = 8.0 Hz, 2H), 7.22 (s, 4H), 7.00 (d, *J* = 7.5 Hz, 2H), 3.67 (s, 2H), 2.99 (s, 2H), 2.41 (s, 3H), 2.27 (s, 3H), 1.94 (s, 4H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 144.35, 138.12, 135.69, 132.13, 130.70, 129.70, 128.90, 128.29, 127.65, 127.07, 126.76, 43.94, 25.00, 23.20, 21.49, 21.27, 20.97 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{21}H_{24}ClN_2$ ($[M+H]^+$) 339.1628, found339.1631.

2-(4-chlorobutyl)-4,5-bis(4-chlorophenyl)-1*H*-imidazole (1c-C)



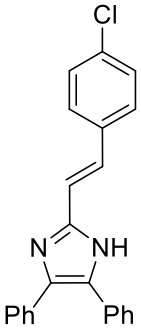
Yellow solid (99 mg, 26% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 1/1, v/v). M.p.: 152.9–154.9 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.41–7.39 (m, 2H), 7.36–7.34 (m, 2H), 7.25–7.22 (m, 2H), 7.17–7.15 (m, 2H), 3.67 (s, 2H), 2.97 (s, 2H), 195–1.94 (m, 4H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 145.22, 136.01, 134.70, 132.95, 132.20, 131.98, 129.47, 128.49, 128.21, 126.41, 44.06, 24.77, 23.03, 20.70 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{19}H_{18}Cl_3N_2$ ($[M+H]^+$) 379.0536, found 379.0530.

(*E*)-2-(4-methoxystyryl)-4,5-diphenyl-1*H*-imidazole (1b-D)



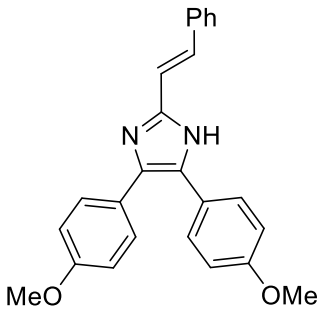
Yellow solid (345 mg, 95% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 5/1, v/v). M.p.: 170.9–172.9 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.52 (d, J = 7.0 Hz, 4H), 7.33–7.26 (m, 8H, cover the solvent), 7.23 (d, J = 16.5 Hz, 1H), 6.85–6.80 (m, 3H), 3.80–3.79 (m, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 159.91, 145.95, 132.70, 131.29, 129.09, 128.69, 128.15, 127.96, 127.55, 114.29, 114.00, 55.44 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{24}H_{20}N_2O$ ($[M+H]^+$) 352.1576, found 352.1576.

(*E*)-2-(4-chlorostyryl)-4,5-diphenyl-1*H*-imidazole (1c-D)



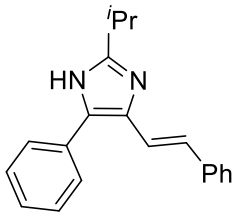
Yellow solid (354 mg, 99% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 5/1→3/1, v/v). M.p.: 216.0–218.0 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.53 (d, J = 7.0 Hz, 4H), 7.35–7.27 (m, 10H), 7.24 (d, J = 16.5 Hz, 1H), 6.89 (dd, J = 16.5 Hz, 5.5, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 145.12, 134.83, 134.09, 130.10, 129.11, 128.81, 127.94, 127.78, 116.70 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{23}H_{18}ClN_2$ ($[M+H]^+$) 357.1159, found 357.1161.

(*E*)-4,5-bis(4-methoxyphenyl)-2-styryl-1*H*-imidazole (1d-D)



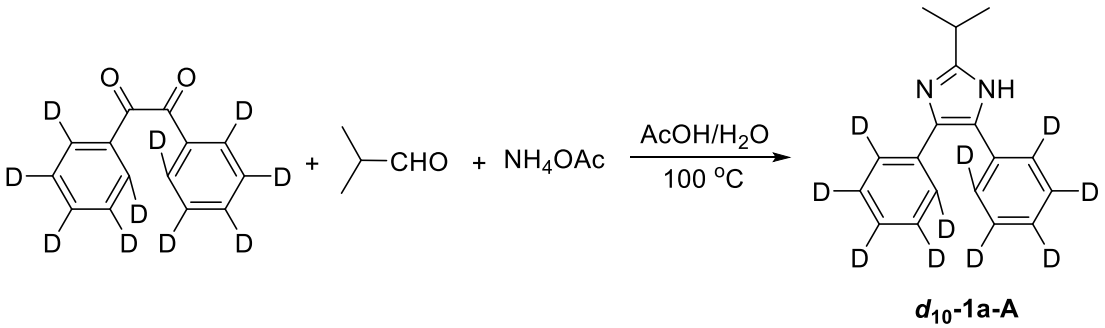
Yellow solid (357 mg, 93% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 5/1→3/1, v/v). M.p.: 167.1–169.1 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.44–7.42 (m, 4H), 7.32–7.21 (m, 6H, cover the solvent), 6.89 (d, J = 16.5 Hz, 1H), 6.83 (t, J = 8.5 Hz, 4H), 3.79 (s, 3H), 3.77 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 159.10, 144.90, 136.39, 131.29, 129.23, 128.81, 128.30, 128.27, 126.78, 125.11, 116.05, 114.13, 55.36 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{25}H_{22}N_2O_2$ ([M+H]$^+$) 382.1681, found 382.1683.

(*E*)-2-isopropyl-5-phenyl-4-styryl-1*H*-imidazole (15)



Yellow solid (135 mg, 47% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 1/1, v/v). M.p.: 169.4–171.4 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.78 (d, J = 5.0 Hz, 2H), 7.42–7.41 (m, 5H), 7.32–7.20 (m, 3H), 7.20–7.15 (m, 2H), 7.10–7.07 (m, 1H), 3.13–3.10 (m, 1H), 1.35 (d, J = 6.0 Hz, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 154.43, 137.72, 132.92, 128.84, 128.73, 128.55, 128.09, 127.39, 127.26, 127.00, 126.28, 117.80, 28.64, 21.78 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{20}H_{21}N_2$ ([M+H]$^+$) 289.1705, found 289.1707.

Synthesis of d_{10}-1a-A:

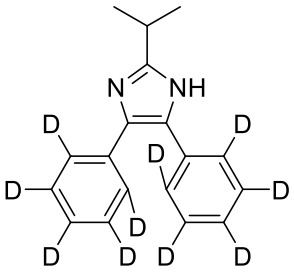


***d*$_{10}$-1a-A**

A solution of d_{10}-benzil[9] (0.5 mmol), isobutyraldehyde (0.5 mmol, 1 equiv), NH_4OAc (5 mmol, 451 mg), glacial acetic acid (1.5 mL) and H_2O (0.2 mL) was reacted at 100 °C for 7 h. The reaction mixture was cooled to room temperature. Afterwards, it was diluted with H_2O (5 mL) and then aq. $NaHCO_3$ solution was added, and the mixture was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phase was dried with Na_2SO_4. The volatiles were evaporated under reduced

pressure and the crude product was purified by silica gel column chromatography (petroleum ether/EtOAc = 2/1, v/v) to give ***d*₁₀-1a-A** as white solid (135 mg, 99% yield).

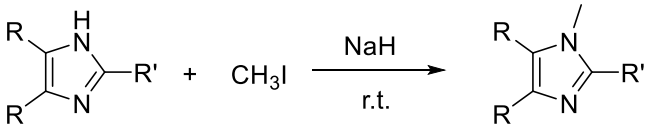
2-isopropyl-4,5-bis(phenyl-*d*₅)-1*H*-imidazole (*d*₁₀-1a-A)



M.p.: 196.1–198.1 ºC. **^{1}H NMR (500MHz, DMSO-*d*₆):** δ = 11.96 (s, 1H), 3.04–2.99 (m, 1H), 1.31 (d, J = 6.5 Hz, 6H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*₆):** δ = 153.10, 135.59, 134.89, 131.47, 128.09 (t, J = 24.7 Hz), 127.66 (t, J = 11.9 Hz), 127.38 (t, J = 11.8 Hz), 126.57 (t, J = 22.9 Hz), 125.91, 27.79, 21.72 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{18}H_9D_{10}N_2$ ($[M+H]^+$) 273.2113, found 273.2156.

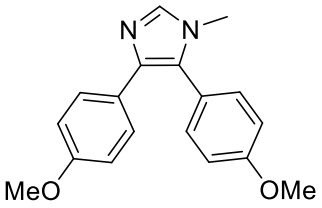
2.2 General procedure for the synthesis of *N*-methyl imidazoles 1-B

Compounds **1a-B**[10], **1c-B**[11] **and 1d-B**[12] were prepared according to modified literature procedure.



The mixture of NaH (60% weight dispersion in mineral oil, 1.4 mmol, 61.3 mg), imidazole (1.12 mmol) and dry THF (2 mL) was stirred below 30 °C for 1 h at room temperature, before CH_3I (1.18 mmol, 73.5 μL) was added dropwise to react overnight. After the reaction was completed, the mixture was worked-up with H_2O (20 mL) and CH_2Cl_2 (3 × 20 mL). The combined organic phase was dried with Na_2SO_4, evaporated *in vacuo*, and purified by flash column chromatography on silica gel.

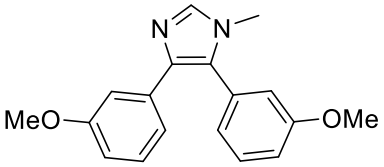
4,5-bis(4-methoxyphenyl)-1-methyl-1*H*-imidazole (1b-B)



Yellow oil (168mg, 57% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 1/1, v/v). **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.54 (s, 1H), 7.41 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 8.5 Hz, 2H), 6.97 (d, J = 8.5 Hz, 2H), 6.76 (d, J = 8.5 Hz, 2H), 3.85(s, 3H), 3.75 (s, 3H), 3.44 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 159.72, 158.14, 137.82, 137.02,

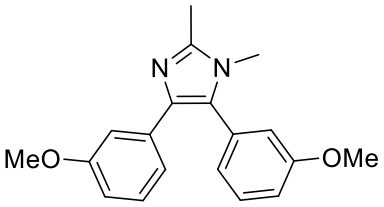
131.97, 127.75, 127.70, 127.53, 122.73, 114.45, 113.58, 55.30, 55.16, 32.11 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{21}H_{25}N_2O_2$ ($[M+H]^+$) 295.1447, found 295.1448.

4,5-bis(3-methoxyphenyl)-1-methyl-1*H*-imidazole (1e-B)



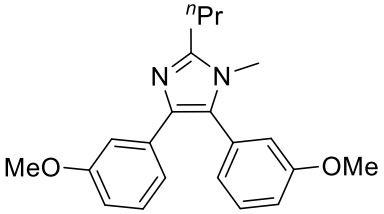
Yellow oil (141 mg, 48% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc/CH_3Cl = 3/2/1→1/1/1, v/v). **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.57–7.56 (m, 1H), 7.37 (td, J = 8.0 Hz, 2.7 Hz, 1H), 7.14 (s, 1H), 7.12–7.05 (m, 2H), 6.97 (d, J = 8.5 Hz, 1H), 6.94–6.93 (m, 1H), 6.87(s, 1H), 6.70 (d, J = 8.0 Hz, 1H), 3.78 (d, J = 3.0 Hz, 3H), 3.67 (d, J = 3.0 Hz, 3H), 3.48 (d, J = 4.0 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 160.05, 159.57, 138.10, 137.41, 136.02, 132.03, 130.19, 129.20, 129.05, 123.20, 119.12, 116.23, 114.46, 113.17, 111.16, 55.45, 55.13, 32.30 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{18}H_{19}N_2O_2$ ($[M+H]^+$) 295.1447, found 295.1444.

4,5-bis(3-methoxyphenyl)-1,2-dimethyl-1*H*-imidazole (1f-B)



Yellow oil (237 mg, 77% yield), purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 1/1, v/v). **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.37 (t, J = 8.0 Hz, 1H), 7.10 (t, J = 8.3 Hz, 1H), 7.04–7.03 (m, 2H), 6.97–6.95 (m, 1H), 6.92 (d, J = 7.5 Hz, 1H), 6.86 (d, J = 1.5 Hz, 1H), 6.70–6.68 (m, 1H), 3.78 (s, 3H), 3.64 (s, 3H), 3.38 (s, 3H), 2.49 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 160.04, 159.49, 144.68, 135.59, 132.44, 130.20, 129.22, 129.03, 123.38, 119.31, 116.34, 114.42, 113.03, 111.38, 55.48, 55.14, 31.31, 13.59 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{19}H_{21}N_2O_2$ ($[M+H]^+$) 309.1603, found 309.1600.

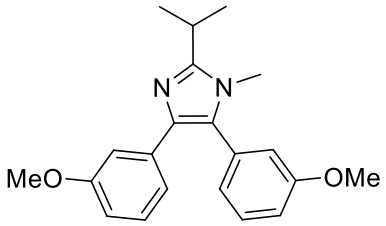
4,5-bis(3-methoxyphenyl)-1-methyl-2-propyl-1*H*-imidazole (1g-B)



Yellow oil (164 mg, 49% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc/CH_2Cl_2= 5/2/2, v/v). **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.35 (t, J = 8.0 Hz, 1H), 7.11–7.05 (m, 3H), 6.96–6.91 (m, 2H), 6.86 (s, 1H), 6.67 (d, J = 7.5 Hz, 1H), 3.78 (s, 3H), 3.64 (s, 3H), 3.38 (s, 3H), 2.76 (t, J = 7.8 Hz, 2H), 1.88–1.81(m, 2H), 1.07 (t, J

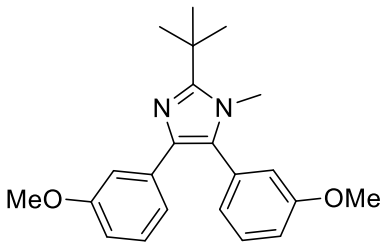
= 7.3 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 155.01, 154.46, 143.44, 131.28, 131.18, 127.92, 125.09, 124.12, 123.80, 118.45, 114.45, 111.38, 109.23, 107.72, 106.55, 50.45, 50.11, 26.08, 24.67, 16.80, 9.26 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{21}H_{25}N_2O_2$ ($[M+H]^+$) 337.1916, found 337.1919.

2-isopropyl-4,5-bis(3-methoxyphenyl)-1-methyl-1*H*-imidazole (1h-B)



Yellow oil (279 mg, 83% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 5/1, v/v). **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.35 (t, J = 7.8 Hz, 1H), 7.10–7.06 (m, 3H), 6.95–6.91 (m, 2H), 6.87–6.86 (m, 1H), 6.67–6.65 (m, 1H), 3.77 (s, 3H), 3.64 (s, 3H), 3.39 (s, 3H), 3.11–3.06 (m, 1H), 1.43 (d, J = 7.0 Hz, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 159.94, 159.40, 152.74, 136.40, 136.01, 132.86, 130.00, 129.06, 128.67, 123.44, 119.55, 116.36, 114.18, 112.49, 111, 55.39, 55.03, 30.80, 26.75, 21.41 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{21}H_{25}N_2O_2$ ($[M+H]^+$) 337.1916, found 337.1917.

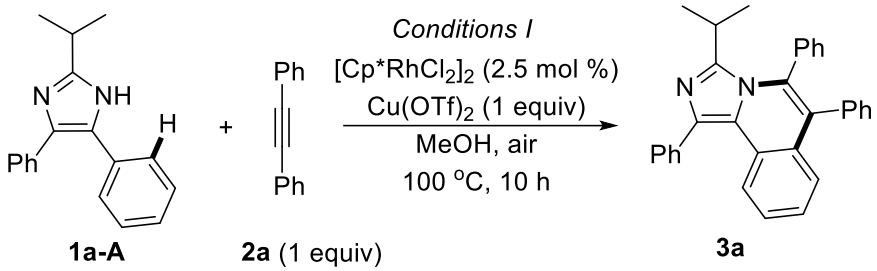
2-(tert-butyl)-4,5-bis(3-methoxyphenyl)-1-methyl-1*H*-imidazole (1i-B)



Yellow oil (183 mg, 52% yield), purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 20/1, v/v). **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.37 (t, J = 7.8 Hz, 1H), 7.07 (d, J = 7.5 Hz, 3H), 6.96 (d, J = 8.0 Hz, 1H), 6.92 (d, J = 7.5 Hz, 1H),6.86 (s, 1H), 6.65–6.64 (m, 1H), 3.79 (s, 3H), 3.64 (s, 3H), 3.51 (s, 3H), 1.53 (s, 9H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 160.01, 159.41, 153.89, 136.47, 134.81, 133.13, 130.27, 130.10, 129.10, 123.70, 119.29, 116.53, 114.35, 112.36, 111.51, 55.46, 55.04, 33.67, 33.30, 29.53 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{22}H_{27}N_2O_2$ ($[M+H]^+$) 351.2073, found 351.2073.

2.3 Optimization data of the C4(5)-H activation/annulation of 1a-A and 2a

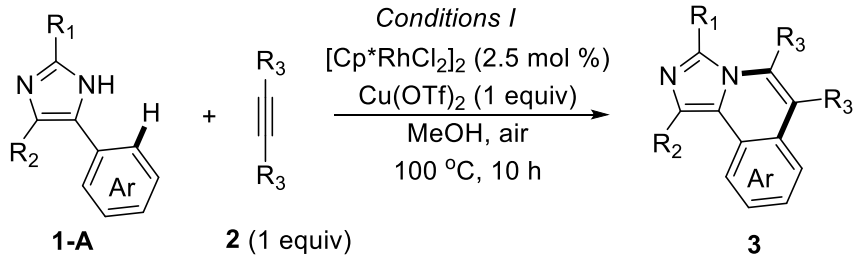
Table S1 Optimization of the reaction conditions [a]



Entry	Oxidant (x equiv)	Solvent (mL)	Yield (%)[b]
1	AgOAc (1)	DCE	27
2	AgOAc (1)	MeOH	64(67[c])
3	$Cu(OAc)_2·H_2O$ (1)	MeOH	61
4	$Cu(OAc)_2·H_2O$ (2)	*t*-BuOH	ND
5	$Cu(OAc)_2·H_2O$ (2)	Toluene	25
6	$Cu(OAc)_2·H_2O$ (2.2)	acetone	27[d]
7	AgOAc (1)/$Cu(OAc)_2·H_2O$ (0.2)	MeOH	41
8	AgOAc (0.1)/$Cu(OAc)_2·H_2O$ (1)	MeOH	42
9	AgOAc (1)/$Cu(OAc)_2·H_2O$ (1)	MeOH	39
10	Ag_2O (1)	MeOH	30
11	$AgNO_3$ (1)	MeOH	70
12	**$Cu(OTf)_2$** (1)	**MeOH**	**93**(89[e])
13	$Cu(OAc)_2·H_2O$ (2.2)	MeOH	90[f]
14	--	MeOH	68[g]

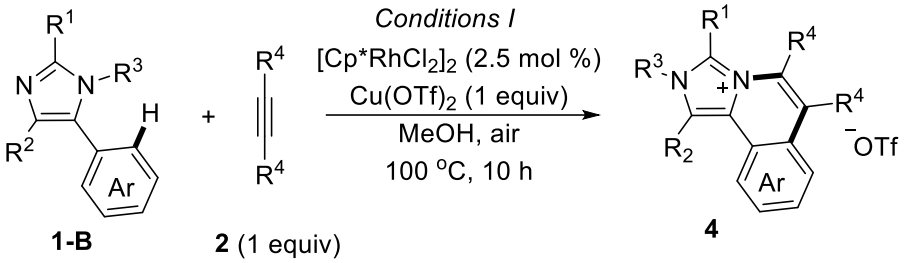
[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), oxidant (x equiv) in MeOH (1 mL) at 100 °C for 10 h under air. [b] Isolated yield. [c] Under a N_2 atmosphere. [d] At 120 °C under a N_2 atmosphere. [e] **2a** (2 equiv). [f] With $AgSbF_6$ (20 mol%) at 60 °C. [g] Under the O_2 atmosphere.

2.4 General procedure for the synthesis of products 3



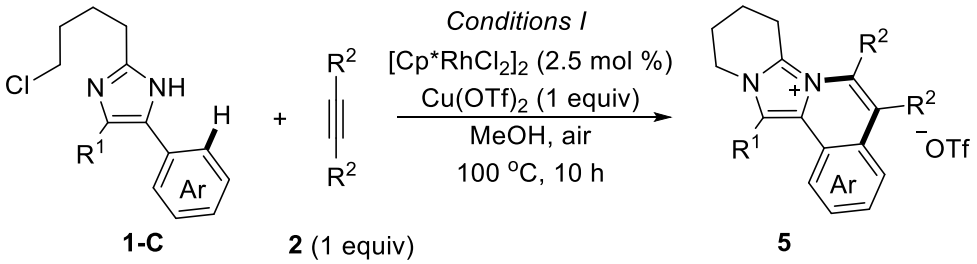
Conditions I: To a dry Schlenk tube (25 mL) with a magnetic stir bar was added imidazole **1-A** (0.1 mmol, 1.0 equiv), alkyne **2** (0.1 mmol, 1.0 equiv), $[RhCp^*Cl_2]_2$ (1.5 mg, 2.5 mol %), $Cu(OTf)_2$ (36.2 mg, 0.1 mmol, 1.0 equiv) and MeOH (1 mL). The mixture was stirred at 100 °C for 10 h under air. After the reaction was completed, the solvent was removed under reduced pressure, and the residue was purified by a silica gel column, eluting with petroleum ether/EtOAc (80/1→20/1, v/v) to afford product **3**.

2.5 General procedure for the synthesis of products 4



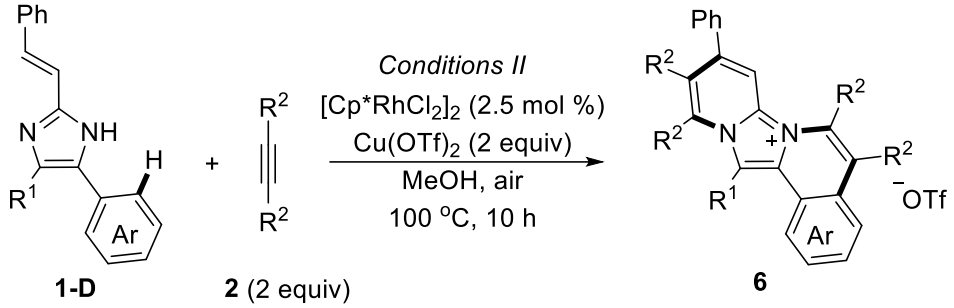
Conditions I: To a dry Schlenk tube (25 mL) with a magnetic stir bar was added imidazole **1-B** (0.1 mmol, 1.0 equiv), alkyne **2** (0.1 mmol, 1.0 equiv), $[RhCp^*Cl_2]_2$ (1.5 mg, 2.5 mol %), $Cu(OTf)_2$ (36.2 mg, 0.1 mmol, 1.0 equiv) and MeOH (1mL). The mixture was stirred at 100 °C for 10 h under air. After the reaction was completed, the solvent was removed under reduced pressure, and the residue was purified by a silica gel column, eluting with CH_2Cl_2/MeOH (100/1→40/1, v/v) to afford product **4**.

2.6 General procedure for the synthesis of products 5



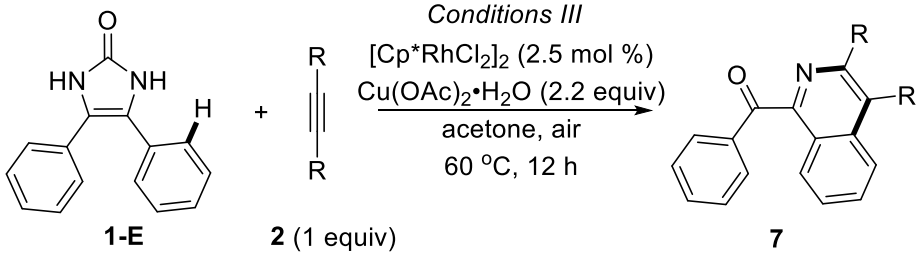
Conditions I: To a dry Schlenk tube (25 mL) with a magnetic stir bar was added imidazole **1-C** (0.1 mmol, 1.0 equiv), alkyne **2** (0.1 mmol, 1.0 equiv), $[RhCp^*Cl_2]_2$ (1.5 mg, 2.5 mol %), $Cu(OTf)_2$ (36.2 mg, 0.1 mmol, 1.0 equiv) and MeOH (1 mL). The mixture was stirred at 100 °C for 10 h under air. After the reaction was completed, the solvent was removed under reduced pressure, and the residue was purified by a silica gel column, eluting with CH_2Cl_2/MeOH (100/1→80/1, v/v) to afford product **5**.

2.7 General procedure for the synthesis of products 6



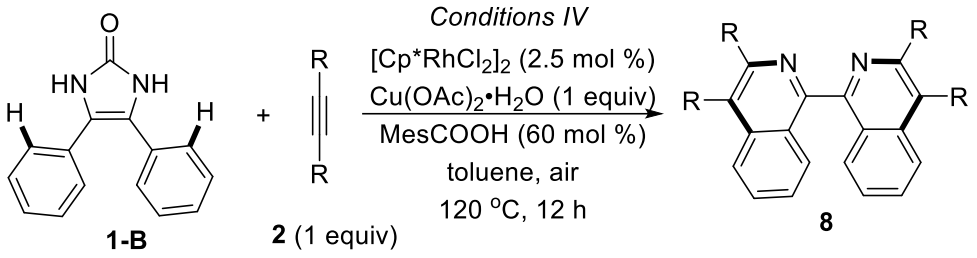
Conditions II: To a dry Schlenk tube (25 mL) with a magnetic stir bar was added imidazole **1-D** (0.1 mmol, 1.0 equiv), alkyne **2a** (0.2 mmol, 2.0 equiv), $[RhCp^*Cl_2]_2$ (1.5 mg, 2.5 mol %), $Cu(OTf)_2$ (72.4 mg, 0.2 mmol, 2.0 equiv) and MeOH (1 mL). The mixture was stirred at 100 °C for 10 h under air. After the reaction was completed, the solvent was removed under reduced pressure, and the residue was purified by a silica gel column, eluting with petroleum ether/EtOAc (2/1→1/1) or CH_2Cl_2/MeOH (100/1→60/1, v/v) to afford product **6**.

2.8 General procedure for the synthesis of products 7



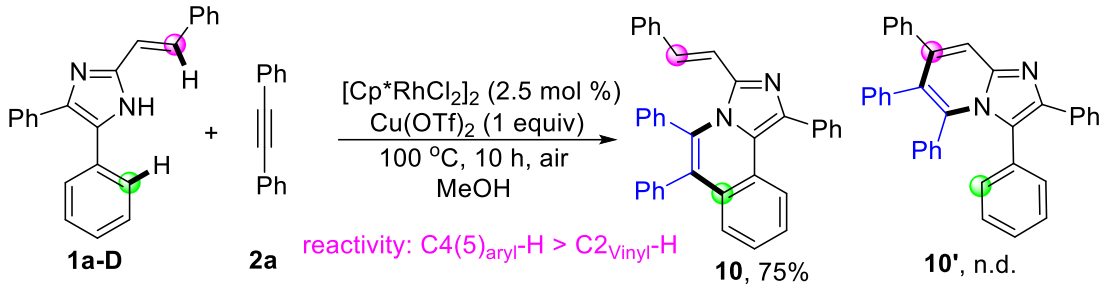
Conditions III: To a dry Schlenk tube (25 mL) with a magnetic stir bar was added imidazole **1-D** (23.6 mg, 0.1 mmol, 1.0 equiv), alkyne **2a** (0.1 mmol, 2.0 equiv), $[RhCp^*Cl_2]_2$ (1.5 mg, 2.5 mol %), $Cu(OAc)_2 \cdot H_2O$ (44 mg, 0.22 mmol, 2.2 equiv) and acetone (0.5 mL). The mixture was stirred at 60 °C for 12 h under air. After the reaction was completed, the solvent was removed under reduced pressure, and the residue was purified by a silica gel column, eluting with petroleum ether/EtOAc (60/1→40/1, v/v) to afford product **7**.

2.9 General procedure for the synthesis of products 8



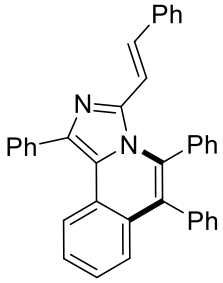
Conditions IV: To a dry Schlenk tube (25 mL) with a magnetic stir bar was added imidazole **1-B** (0.1 mmol, 1.0 equiv), alkyne **2a** (0.2 mmol, 2.0 equiv), $[RhCp^*Cl_2]_2$ (1.5 mg, 2.5 mol %), $Cu(OAc)_2 \cdot H_2O$ (20 mg, 0.1 mmol, 1 equiv), MesCOOH (9.8 mg, 60 mol %) and toluene (0.5 mL). The mixture was stirred at 120 °C for 12 h under air. After the reaction was completed, the solvent was removed under reduced pressure, and the residue was purified by a silica gel column, eluting with petroleum ether/EtOAc (60/1→40/1, v/v) to afford products **8**.

3 Chemo-selectivity experiments



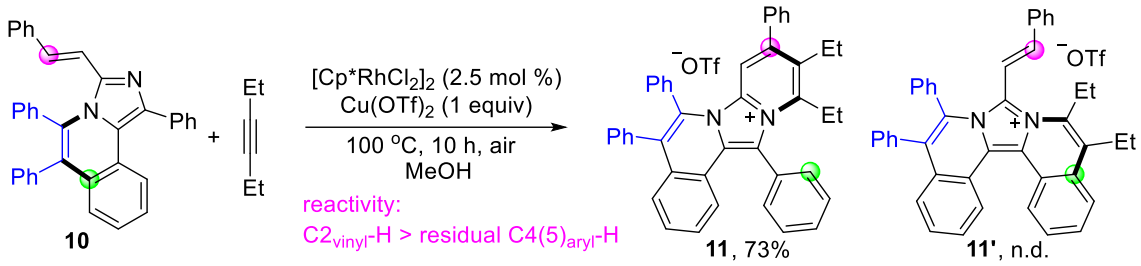
To a dry Schlenk tube with a magnetic stir bar was added **1a-D** (32.2 mg, 0.1 mmol, 1 equiv), **2a** (17.8 mg, 0.1 mmol, 1 equiv), $[RhCp^*Cl_2]_2$ (1.5 mg, 2.5 mol %), $Cu(OTf)_2$ (36.2 mg, 0.1 mmol, 1.0 equiv) and MeOH (1 mL). The mixture was stirred at 100 °C for 10 h under air. After the reaction was completed, the mixture was passed through a silica gel column (100-200 mesh), eluting with petroleum ether/EtOAc (50/1, v/v) to afford product **10** as a yellow solid.

(*E*)-1,5,6-triphenyl-3-styrylimidazo[5,1-*a*]isoquinoline (10)



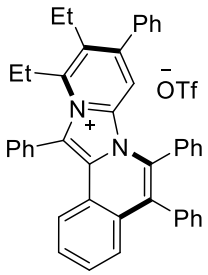
Yellow solid (38 mg, 76% yield). M.p.: 263.9–265.9 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 8.03 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 2H), 7.52–7.47 (m, 2H), 7.40–7.36 (m, 5H), 7.28–7.21 (m, 5H), 7.17–7.10 (m, 6H), 6.92 (d, *J* = 7.0 Hz, 2H), 5.85 (d, *J* = 15.5 Hz, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 140.44, 137.19, 136.62, 136.35, 136.03, 134.83, 132.84, 131.35, 131.19, 130.17, 129.24, 129.04, 128.94, 128.40, 128.26,

128.17, 127.84, 127.63, 127.28, 126.83, 126.62, 125.44, 125.28, 122.49, 116.97 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{37}H_{27}N_2$ ($[M+H]^+$) 499.2174, found 499.2177.

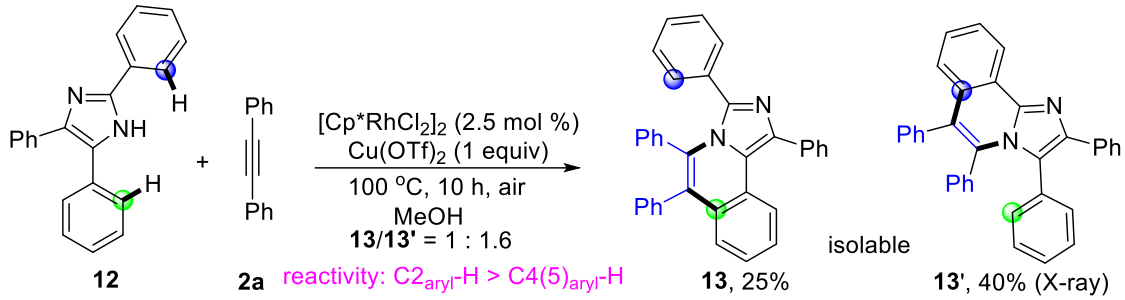


To a dry Schlenk tube with a magnetic stir bar was added **10** (49.8 mg, 0.1 mmol, 1 equiv), hex-3-yne (8.2 mg, 0.1 mmol, 1 equiv), $[RhCp^*Cl_2]_2$ (1.5 mg, 2.5 mol %), $Cu(OTf)_2$ (36.2 mg, 0.1 mmol, 1.0 equiv) and MeOH (1 mL). The mixture was stirred at 100 °C for 10 h under air. After the reaction was completed, the mixture was passed through a silica gel column (100-200 mesh), eluting with CH_2Cl_2/CH_3OH (80/1→70/1, v/v) to afford product **11**.

10,11-diethyl-5,6,9,13-tetraphenylpyrido[2',1':2,3]imidazo[5,1-*a*]isoquinolin-12-ium trifluoromethanesulfonate (11)

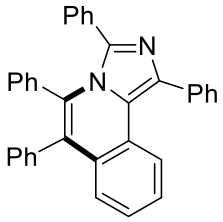


Yellow solid (53 mg, 73% yield). M.p.: 253.3–255.3 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.96 (d, J = 8.0 Hz, 2H), 7.81–7.74 (m, 3H), 7.47 (d, J = 7.5 Hz, 2H), 7.42 (t, J = 7.5 Hz, 1H), 7.36–7.30 (m, 5H), 7.29–7.23 (m, 6H, cover the solvent), 7.22–7.19 (m, 2H), 7.03 (d, J = 8.0 Hz, 3H), 6.13 (s, 1H), 2.92 (q, J = 7.3 Hz, 2H), 2.67 (q, J = 7.5 Hz, 2H), 1.00 (t, J = 7.3 Hz, 3H), 0.94 (t, J = 7.5 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 146.53, 143.55, 138.32, 134.64, 134.58, 132.87, 132.72, 132.63, 131.87, 131.82, 131.49, 131.11, 131.04, 130.40, 130.32, 129.97, 129.86, 129.46, 129.40, 128.94, 128.68, 128.44, 128.42, 128.37, 127.94, 127.71, 124.77, 121.93, 119.98, 113.08, 22.03, 21.93, 14.67, 13.80 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{43}H_{35}N_2^+$ ($[M-OTf^-]^+$) 579.2795, found 579.2796.



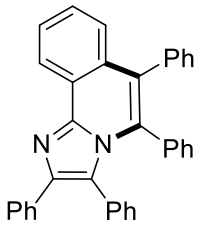
To a dry Schlenk tube with a magnetic stir bar was added **12** (29.6 mg, 0.1 mmol, 1 equiv), **2a** (17.8 mg, 0.1 mmol, 1 equiv), $[RhCp^*Cl_2]_2$ (1.5 mg, 2.5 mol %), $Cu(OTf)_2$ (36.2 mg, 0.1 mmol, 1.0 equiv) and MeOH (1 mL). The mixture was stirred at 100 °C for 10 h under air. After the reaction was completed, the mixture was passed through a silica gel column (100-200 mesh), eluting with petroleum ether/EtOAc (50/1→30/1, v/v) to afford products **13** as a yellow solid (12 mg, 25% yield) and **13'** as a white solid (19 mg, 40% yield).

1,3,5,6-tetraphenylimidazo[5,1-*a*]isoquinoline (13)

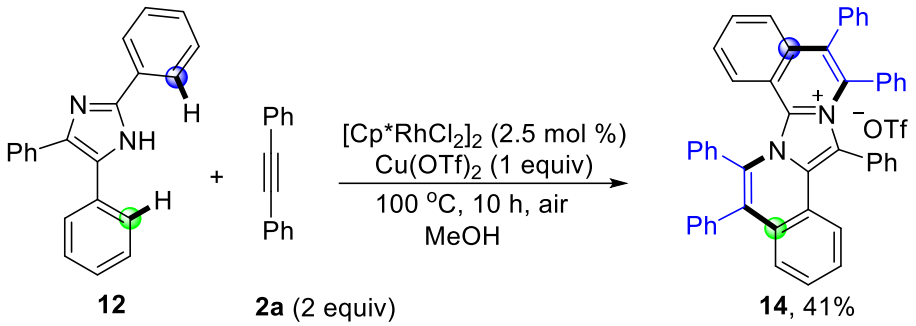


Yellow solid (12 mg, 25% yield). M.p.: 267.0–269.0 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 8.18 (d, J = 7.5 Hz, 1H), 7.85 (d, J = 7.0 Hz, 2H), 7.53 (t, J = 7.5 Hz, 2H), 7.45 (t, J = 7.3 Hz, 1H), 7.30–7.27 (m, 1H), 7.24–7.18 (m, 5H), 7.11–7.08 (m, 4H), 6.97 (t, J = 7.0 Hz, 1H), 6.93–6.88 (m, 4H), 6.81–6.73 (m, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 142.35, 136.78, 136.72, 135.22, 133.22, 132.92, 131.54, 131.47, 130.18, 129.91, 129.33, 128.81, 128.04, 127.98, 127.87, 127.64, 127.29, 127.16, 127.10, 126.98, 126.85, 126.54, 125.36, 125.20, 122.40 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{35}H_{25}N_2^+$ ($[M+H]^+$) 473.2018, found 473.2020.

2,3,5,6-tetraphenylimidazo[2,1-*a*]isoquinoline (13')

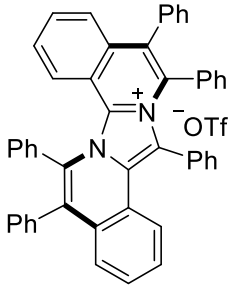


White solid (19 mg, 40% yield). M.p.: 266.8–268.8 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 8.97 (d, J = 7.5 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.48–7.45 (m, 3H), 7.28 (s, 1H), 7.21–7.16(m, 6H), 7.07 (d, J = 6.5 Hz, 2H), 6.98 (t, J = 6.8 Hz, 1H), 6.92–6.87 (m, 4H), 6.83–6.78 (m, 3H), 6.72 (t, J = 7.3 Hz, 2H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 143.31, 142.10, 136.58, 134.92, 134.83, 132.80, 132.08, 131.97, 131.56, 130.44, 128.40, 128.13, 127.89, 127.83, 127.76, 127.24, 127.14, 126.99, 126.93, 126.39, 126.24, 125.15, 123.79, 123.50 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{35}H_{25}N_2^+$ ($[M+H]^+$) 473.2018, found 473.2019.

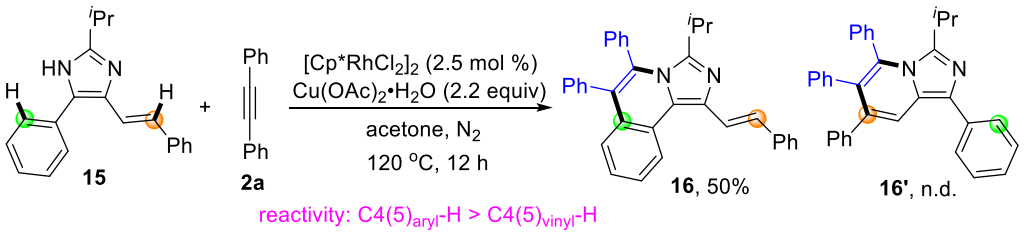


To a dry Schlenk tube with a magnetic stir bar was added **12** (29.6 mg, 0.1 mmol, 1 equiv), **2a** (35.6 mg, 0.2 mmol, 2 equiv), [RhCp*Cl_2]$_2$ (1.5 mg, 2.5 mol %), Cu(OTf)$_2$ (36.2 mg, 0.1 mmol, 1.0 equiv) and MeOH (1 mL). The mixture was stirred at 100 °C for 10 h under air. After the reaction was completed, the mixture was passed through a silica gel column (200-300 mesh), eluting with CH_2Cl_2/MeOH (40/1→20/1, v/v) to afford products **14** as a yellow solid (28 mg, 35% yield).

5,6,12,13,15-pentaphenylimidazo[2,1-*a*:4,3-*a*']diisoquinolin-14-ium trifluoromethanesulfonate (14)



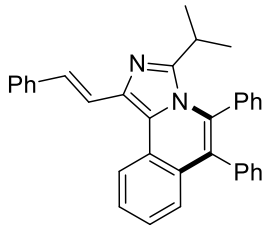
Yellow solid (28 mg, 35% yield). M.p.: 135.3–137.3 °C. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.87 (d, J = 8.5 Hz, 1H), 7.45-7.39 (m, 8H), 7.30–7.26 (m, 6H, cover the solvent), 7.22–7.17 (m, 8H), 7.11 (t, J = 7.8 Hz, 2H), 7.00–6.99 (m, 3H), 6.94 (m, J = 8.5 Hz, 1H), 6.91–6.84 (m, 3H), 6.79–6.76 (m, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 135.51, 135.06, 134.15, 133.50, 132.91, 132.68, 132.17, 131.74, 131.21, 131.08, 131.04, 130.94, 130.71, 130.56, 130.24, 130.11, 129.90, 129.48, 129.25, 129.05, 128.96, 128.63, 128.55, 128.30, 128.19, 128.09, 127.94, 127.70, 127.61, 127.45, 126.52, 126.24, 126.15, 124.16, 122.82, 116.97 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{49}H_{33}N_2$ ([M−OTf$^-$]$^+$) 649.2638, found 649.2635.



The mixture of **15** (0.1 mmol, 1 equiv), **2a** (0.1 mmol, 1 equiv), [RhCp*Cl_2]$_2$ (1.5 mg, 2.5 mol %), Cu(OAc)$_2$·H_2O (44 mg, 0.22 mmol, 2.2 equiv) and acetone (1 mL) was stirred at 120 °C

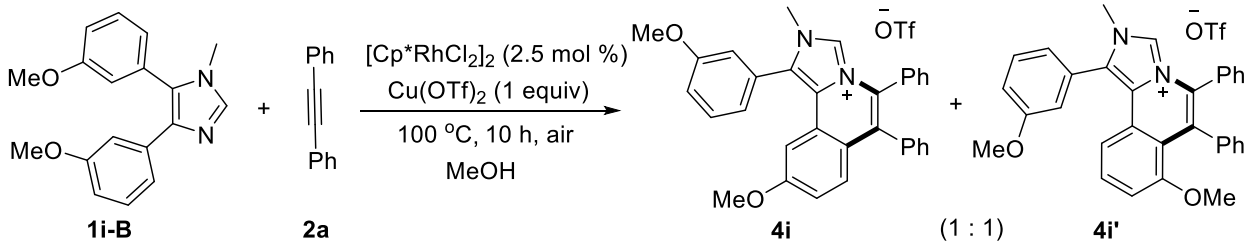
for 10 h under an N_2 atmosphere. After the reaction was completed, the mixture was passed through a silica gel column (200-300 mesh), eluting with petroleum ether/EtOAc (100/1→80/1, v/v) to afford product **16**.

(*E*)-3-isopropyl-5,6-diphenyl-1-styrylimidazo[5,1-*a*]isoquinoline (16)

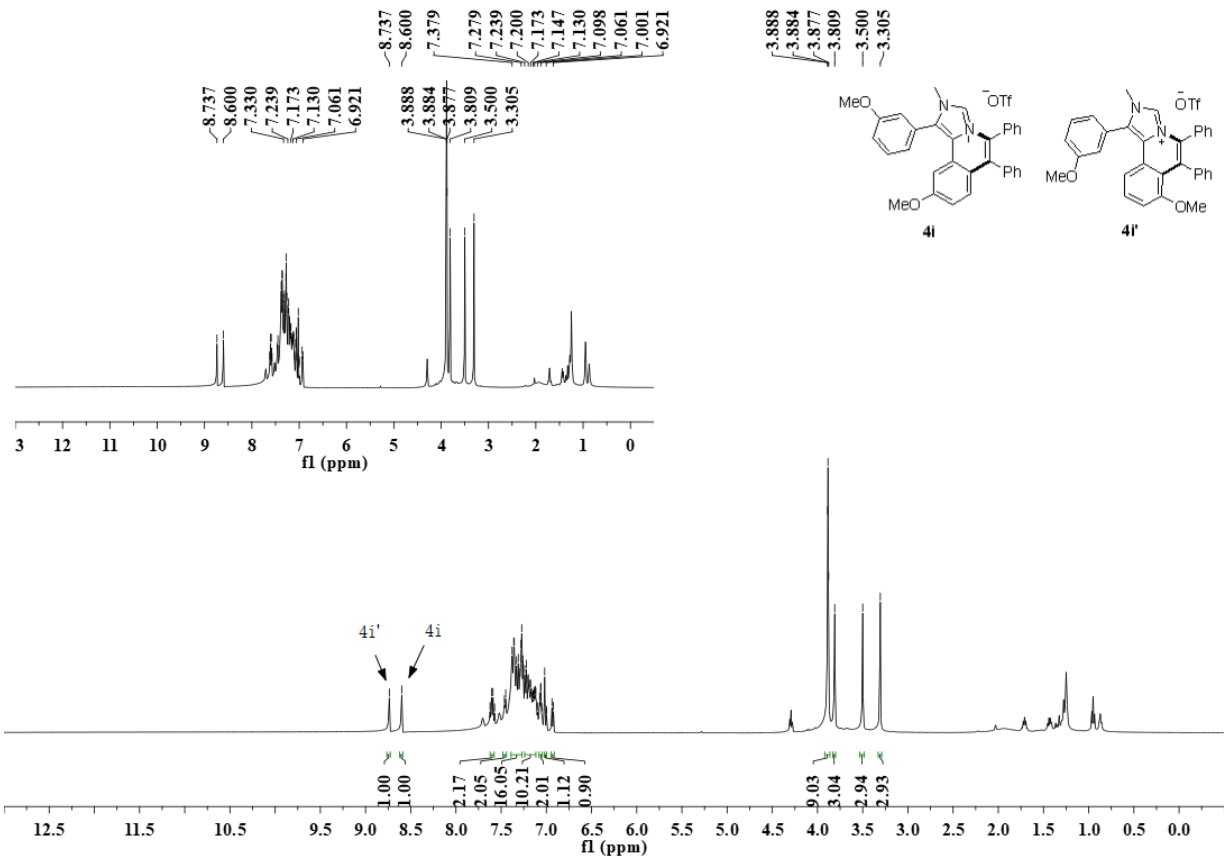


Yellow solid (23 mg, 50% yield). M.p.: 133.3–135.3 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 8.38 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 15.5 Hz, 1H), 7.67–7.64 (m, 3H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.27–7.18 (m, 10H, cover the solvent), 7.09–7.08 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 2.07–2.02 (m, 1H), 1.08 (d, *J* = 6.5 Hz, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 149.86, 138.50, 136.66, 134.88, 132.89, 131.42, 130.74, 129.98, 129.77, 128.76, 128.73, 128.18, 128.14, 128.07, 127.15, 127.07, 126.82, 126.70, 126.32, 126.13, 125.27, 123.12, 121.34, 27.66, 22.66 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{34}H_{29}N_2$ ($[M+H]^+$) 465.2331, found 465.2230.

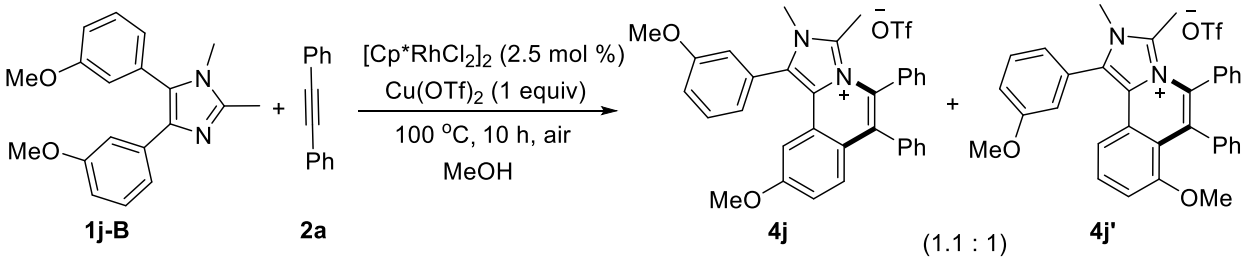
4 Regio-selectivity experiments



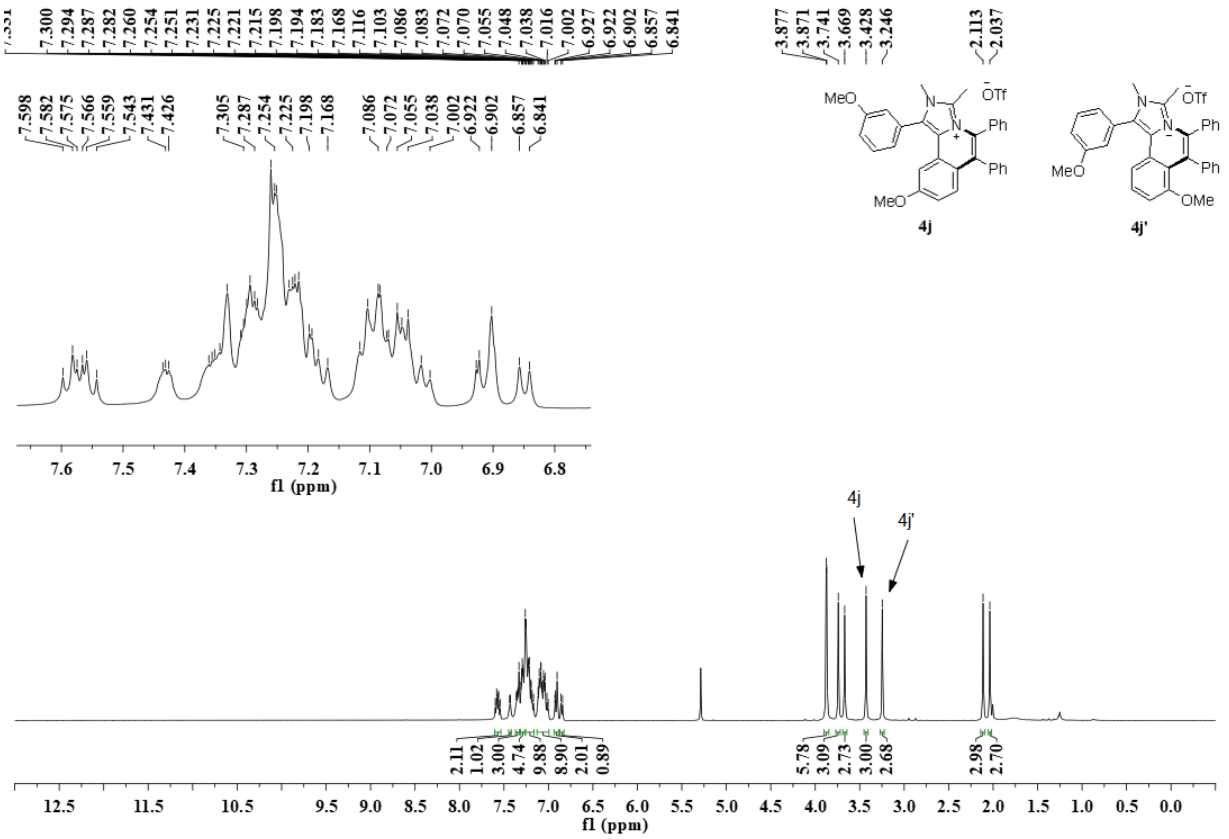
To a dry Schlenk tube with a magnetic stir bar was added **1i-B** (29.4 mg, 0.1 mmol, 1 equiv), **2a** (17.8 mg, 0.1 mmol, 1 equiv), $[RhCp^*Cl_2]_2$ (1.5 mg, 2.5 mol %), $Cu(OTf)_2$ (36.2 mg, 0.1 mmol, 1 equiv) and MeOH (1 mL). The mixture was stirred at 100 °C for 10 h under air. After the reaction was completed, the mixture was passed through a silica gel column (200-300 mesh), eluting with CH_2Cl_2/MeOH (80/1→60/1, v/v) to afford a mixture of **4i** and **4i'**. The ratio of **4i/4i'** was determined to be 1.0/1 by ^{1}H NMR (see below).



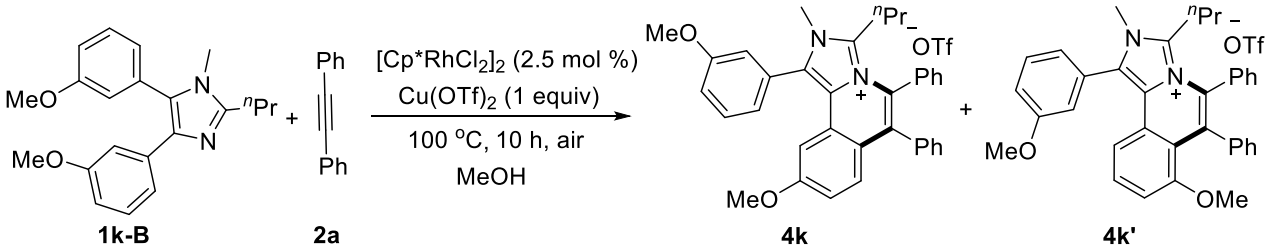
^{1}H NMR (500 MHz, $CDCl_3$) of **4i** and **4i'**



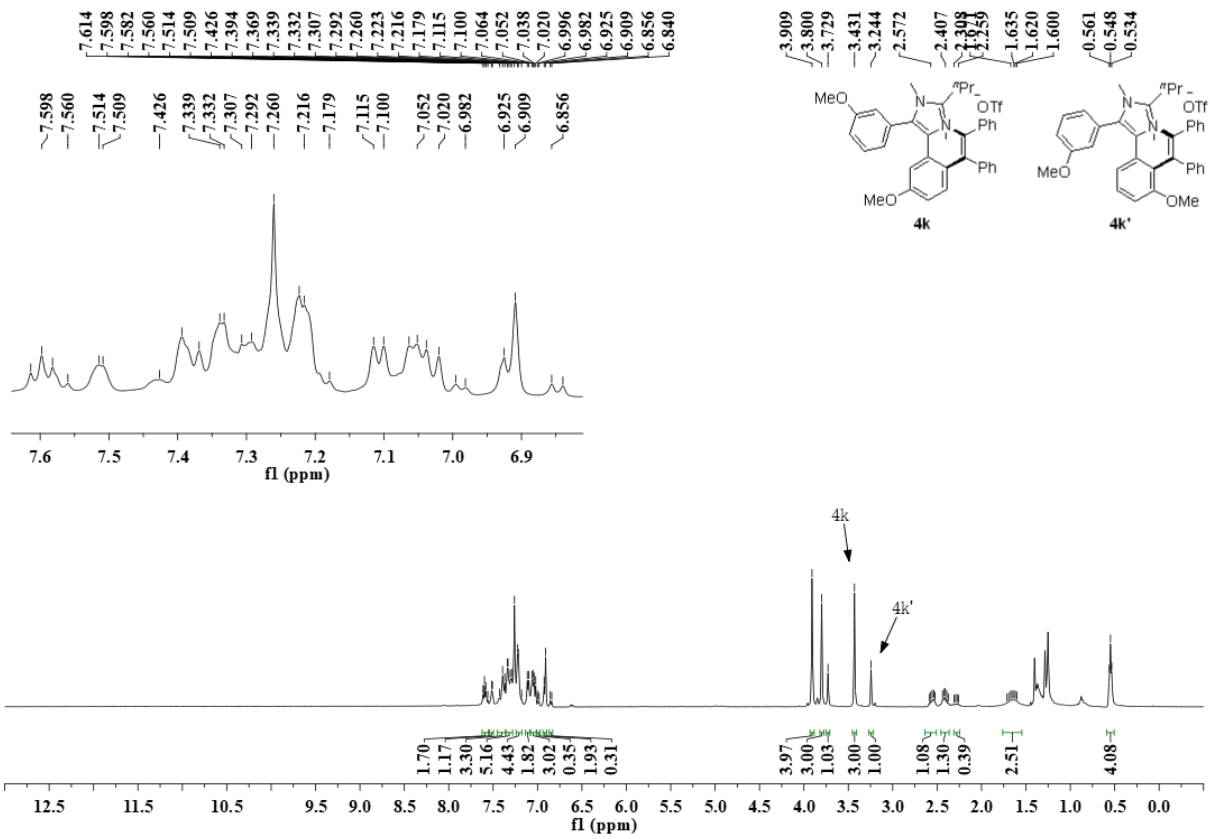
To a dry Schlenk tube with a magnetic stir bar was added **1j-B** (30.8 mg, 0.1 mmol, 1 equiv), **2a** (17.8 mg, 0.1 mmol, 1 equiv), $[RhCp^*Cl_2]_2$ (1.5 mg, 2.5 mol %), $Cu(OTf)_2$ (36.2 mg, 0.1 mmol, 1 equiv) and MeOH (1 mL). The mixture was stirred at 100 °C for 10 h under air. After the reaction was completed, the mixture was passed through a silica gel column (200-300 mesh), eluting with CH_2Cl_2/MeOH (80/1→60/1, v/v) to afford a mixture of **4j** and **4j'**. The ratio of **4j**/**4j'** was determined to be 3.00/2.68 = 1.1/1 by ^{1}H NMR (see below).



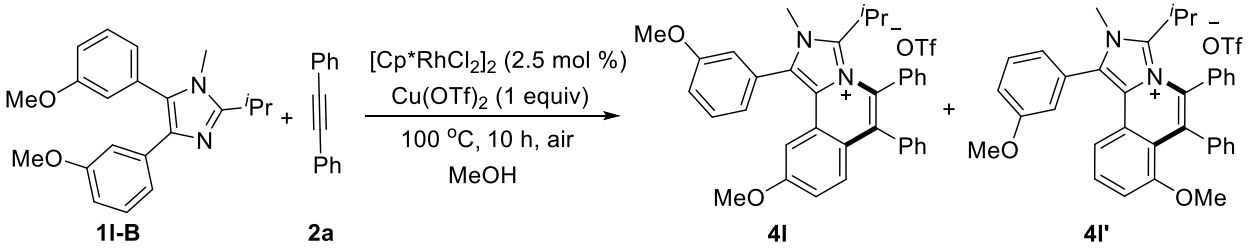
^{1}H NMR (500 MHz, $CDCl_3$) of **4j** and **4j'**



To a dry Schlenk tube with a magnetic stir bar was added **1k-B** (33.6 mg, 0.1 mmol, 1 equiv), **2a** (17.8 mg, 0.1 mmol, 1 equiv), $[RhCp^*Cl_2]_2$ (1.5 mg, 2.5 mol %), $Cu(OTf)_2$ (36.2 mg, 0.1 mmol, 1 equiv) and MeOH (1 mL). The mixture was stirred at 100 °C for 10 h under air. After the reaction was compeleted, the mixture was passed through a silica gel column (200-300 mesh), eluting with CH_2Cl_2/MeOH (80/1→60/1, v/v) to afford a mixture of **4k** and **4k'**. The ratio of **4k**/**4k'** was determined to be 3.00/1.00 = 3.0/1 by ^{1}H NMR (see below).

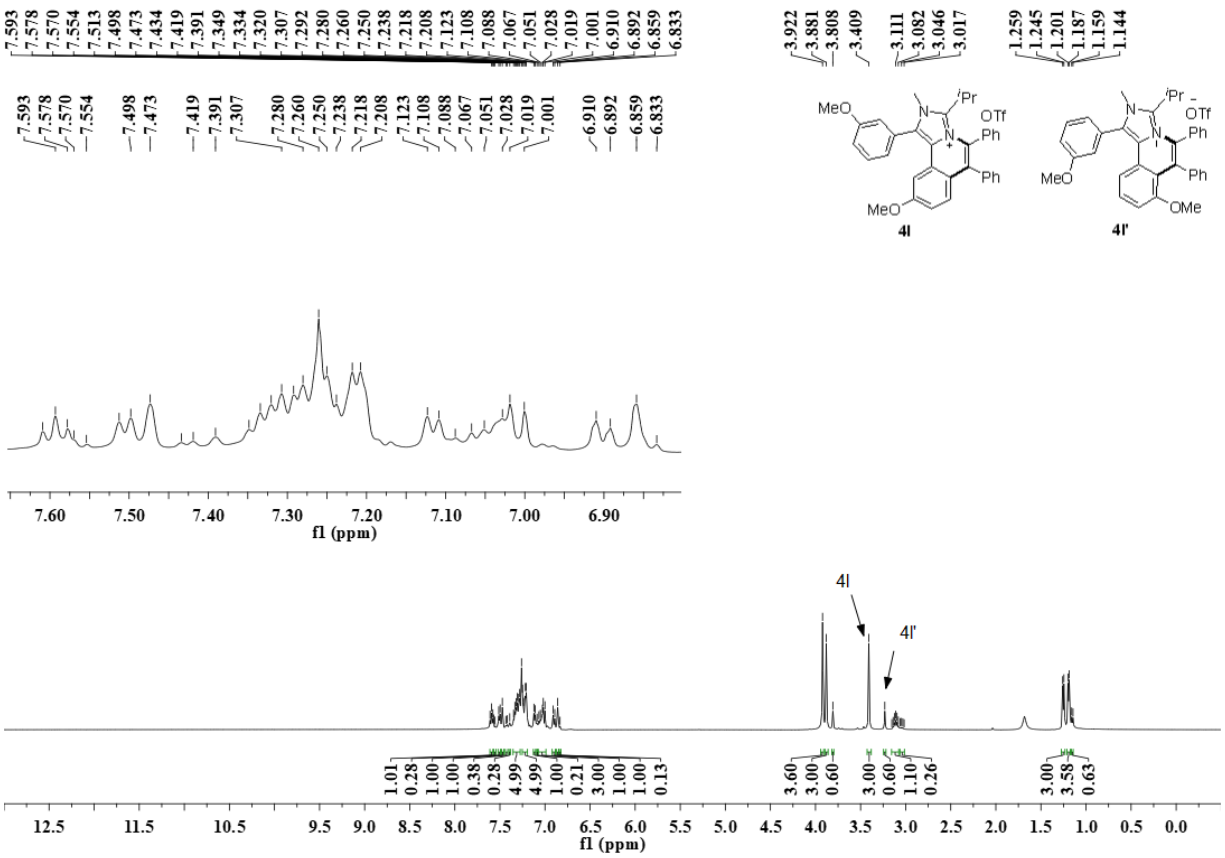


^{1}H NMR (500 MHz, $CDCl_3$) of **4k** and **4k'**



1l-B **2a** **4l** **4l'**

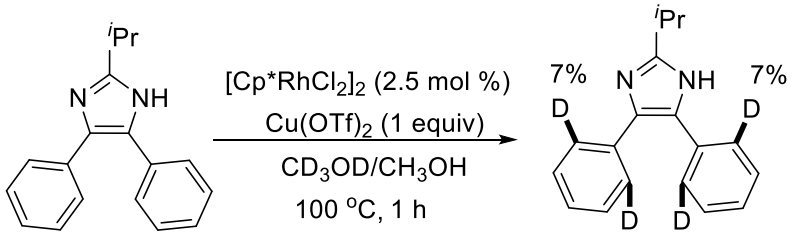
The mixture of **1l-B** (33.6 mg, 0.1 mmol, 1 equiv), **2a** (17.8 mg, 0.1 mmol, 1 equiv), $[RhCp^*Cl_2]_2$ (1.5 mg, 2.5 mol %), $Cu(OTf)_2$ (36.2 mg, 0.1 mmol, 1 equiv) and MeOH (1 mL) was stirred at 100 °C for 10 h under air. After the reaction was completed, the mixture was passed through a silica gel column (200-300 mesh), eluting with CH_2Cl_2/MeOH (70/1, v/v) to afford a mixture of **4l** and **4l'**. (**4l**/**4l'** ≈ 5/1). The ratio of **4l**/**4l'** was determined to be 3.00/0.60 = 5.0/1 by ^{1}H NMR (see below).



^{1}H NMR (500 MHz, $CDCl_3$) of **4l** and **4l'**

5 Isotope labeling experiments

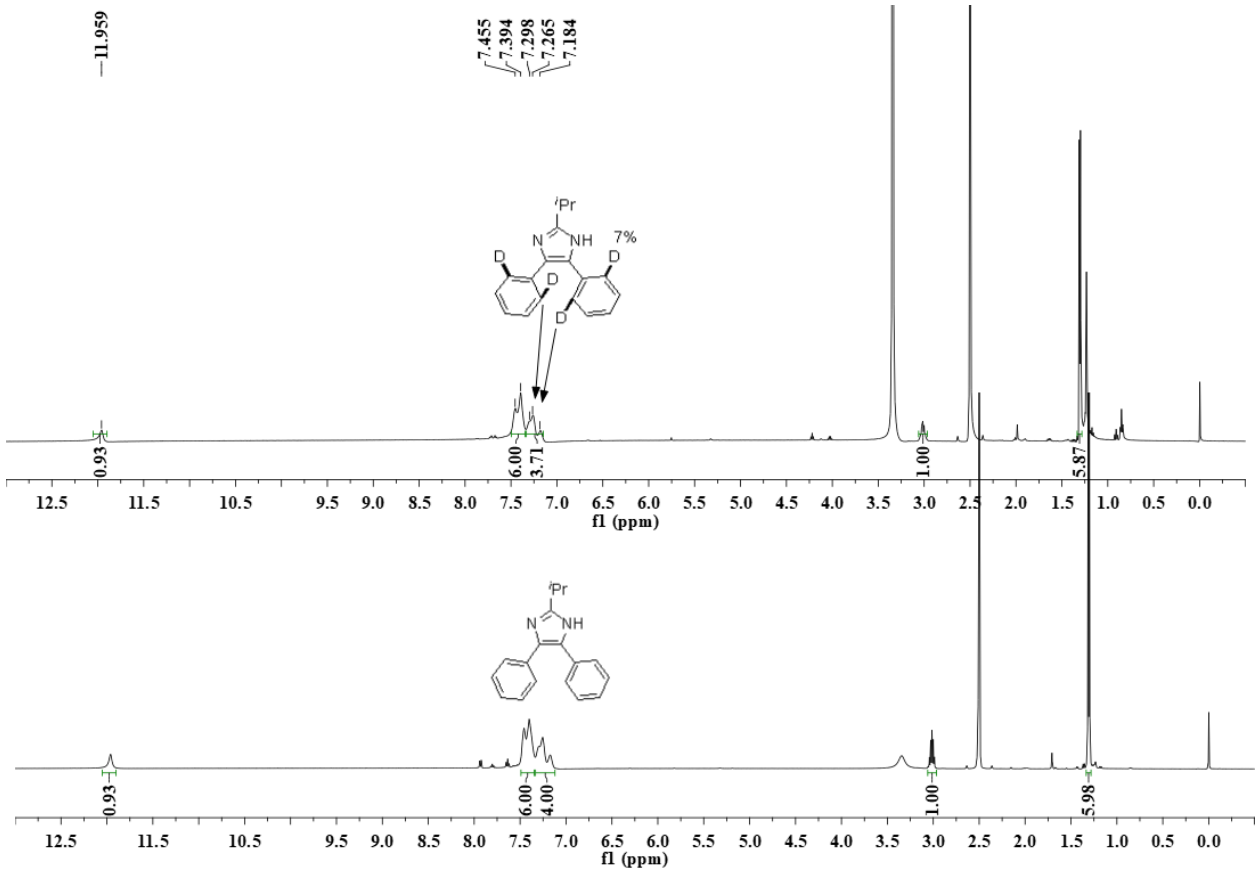
H-D exchange experiments:



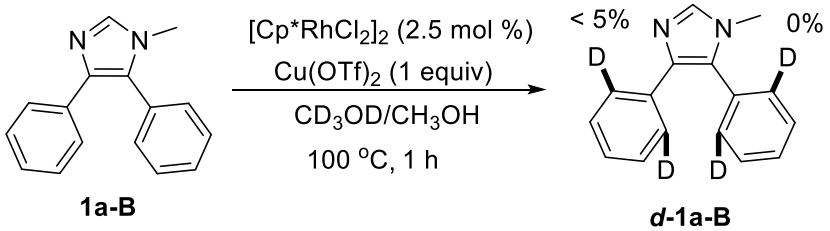
1a-A ***d*-1a-A**

The mixture of imidazole **1a-A** (13.1 mg, 0.05 mmol), [($Cp^*RhCl_2)_2$] (0.8 mg, 2.5 mol %), $Cu(OTf)_2$ (18.1 mg, 0.05 mmol, 1.0 equiv), CH_3OH (O.25 mL) and CD_3OD (0.25 mL) was reacted at 100 °C for 1 h under air. After the reaction was cooled down, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel,

eluting with petroleum ether/EtOAc (5/1, v/v) to afford corresponding deuterium ***d*-1a-A**. ^{1}H NMR analysis showed that 7% [(4.00-3.71)/4=0.07] hydrogen at the *ortho* positions of the phenyl ring was deuterated.



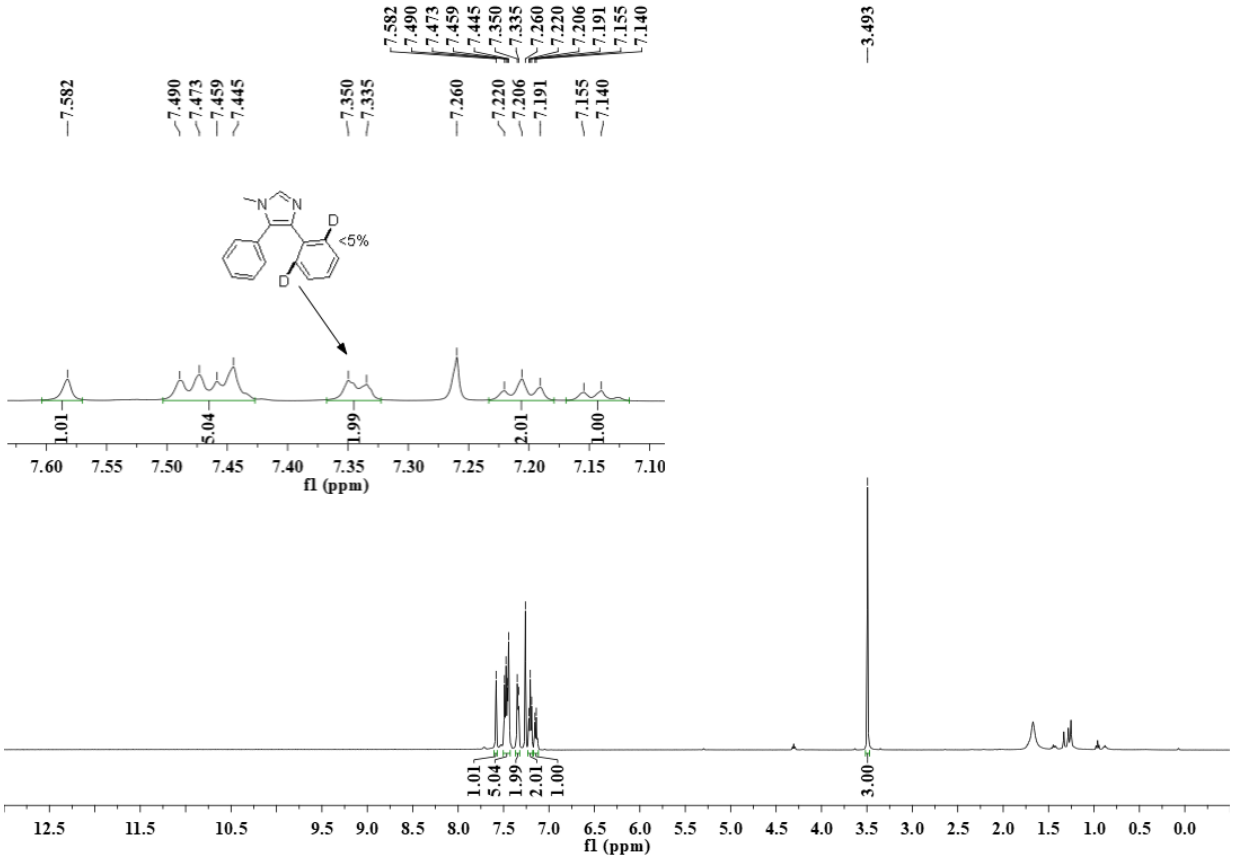
^{1}H NMR (500 MHz, DMSO-d_6) of ***d*-1a-A**



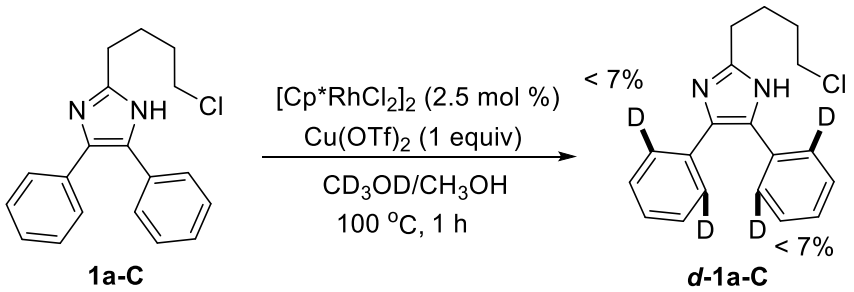
1a-B ***d*-1a-B**

The mixture of imidazole **1a-B** (11.7 mg, 0.05 mmol), [(Cp*$RhCl_2)_2$] (0.8 mg, 2.5 mol %), $Cu(OTf)_2$ (18.1 mg, 0.05 mmol, 1.0 equiv), CH_3OH (O.25 mL) and CD_3OD (0.25 mL) was reacted at 100 °C for 1 h under air. After the reaction was cooled down, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel,

eluting with CH_2Cl_2/CH_3OH (20/1, v/v) to afford corresponding deuterium ***d*-1a-B**. ^1H NMR analysis showed that <5% hydrogen at the *ortho* positions of the phenyl ring was deuterated.

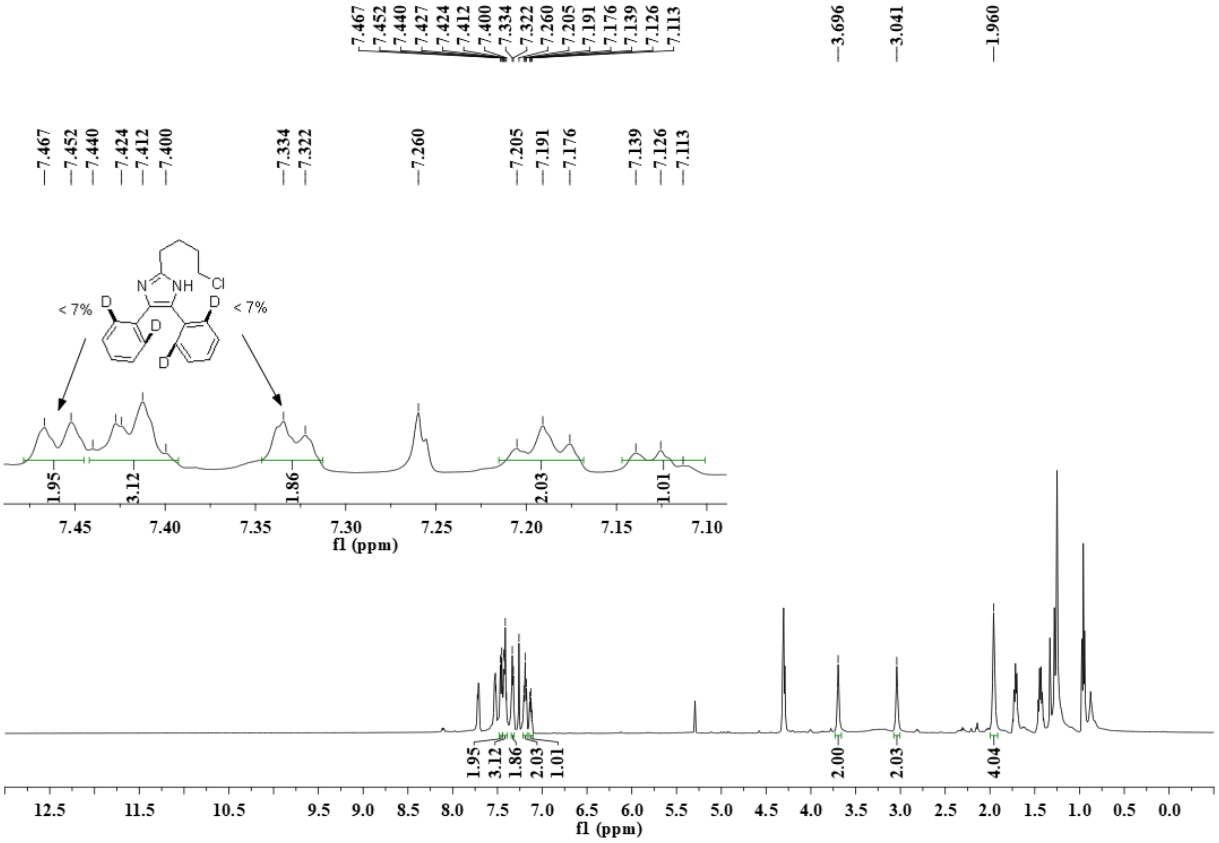


^1H NMR (500 MHz, $CDCl_3$) of ***d*-1a-B**

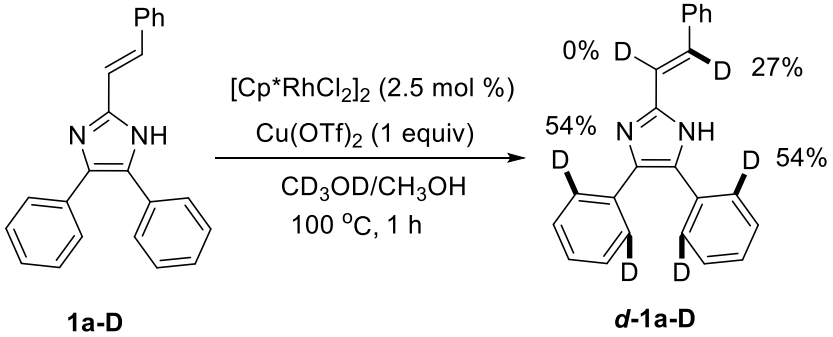


The mixture of imidazole **1a-C** (15.5 mg, 0.05 mmol), $[(Cp^*RhCl_2)_2]$ (0.8 mg, 2.5 mol %), $Cu(OTf)_2$ (18.1 mg, 0.05 mmol, 1.0 equiv), CH_3OH (O.25 mL) and CD_3OD (0.25 mL) was reacted at 100 °C for 1 h under air. After the reaction was cooled down the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel,

eluting with petroleum ether/EtOAc (5/1, v/v) to afford corresponding deuterium ***d*-1a-C**. ^{1}H NMR analysis showed that <7% hydrogen at the *ortho* positions of the phenyl ring was deuterated.

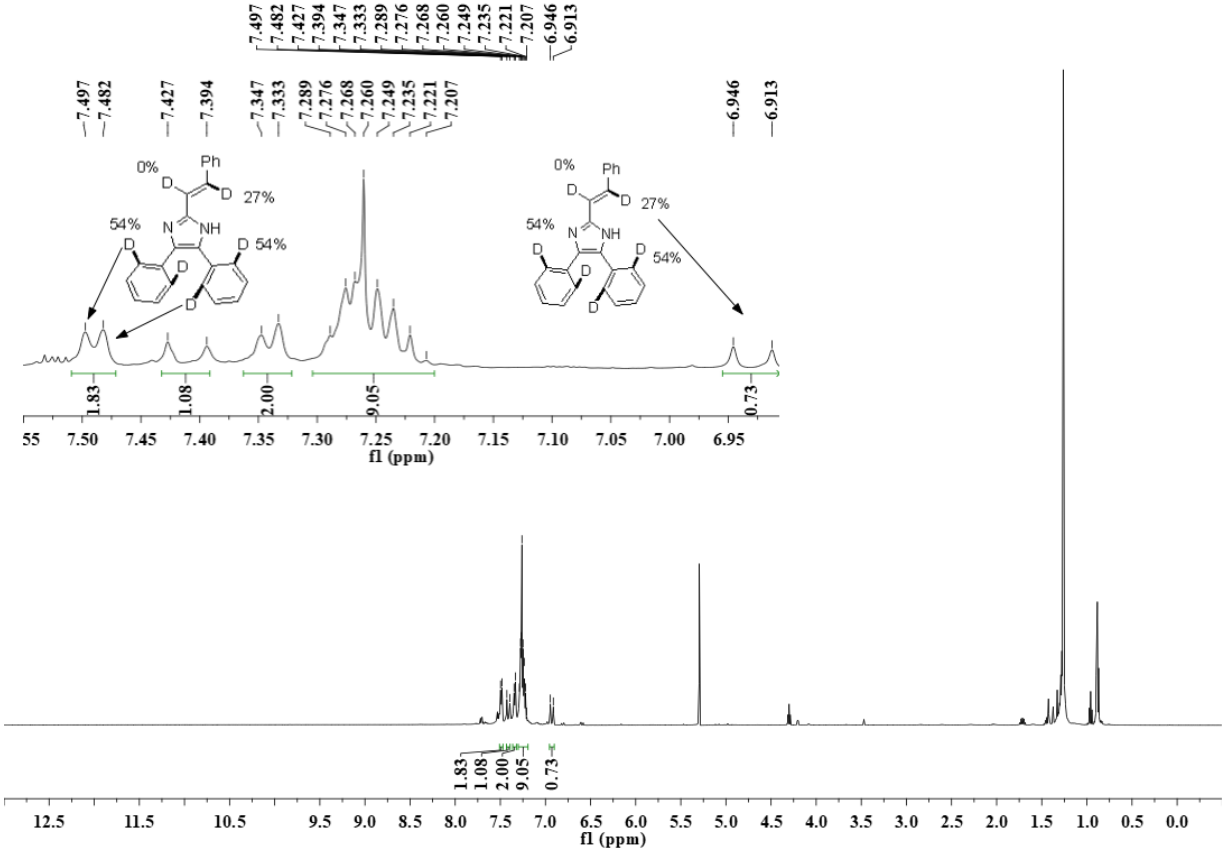


^{1}H NMR (500 MHz, $CDCl_3$) of ***d*-1a-C**

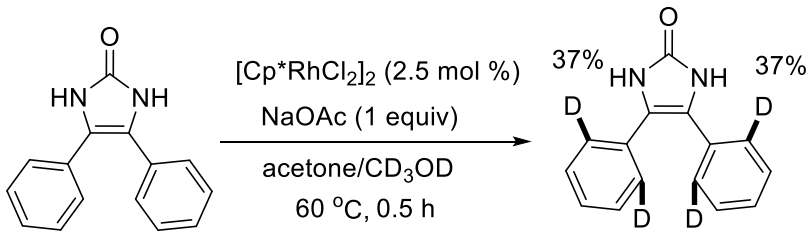


The mixture of imidazole **1a-D** (16.1 mg, 0.05 mmol), [($Cp^*RhCl_2)_2$] (0.8 mg, 2.5 mol %), $Cu(OTf)_2$ (18.1 mg, 0.05 mmol, 1.0 equiv), CH_3OH (O.25 mL) and CD_3OD (0.25 mL) was reacted at 100 °C for 1 h under air. After the reaction was cooled down, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel,

eluting with petroleum ether/EtOAc (10/1, v/v) to afford corresponding deuterium ***d*-1a-D**. ^{1}H NMR analysis showed that 54% [(4-1.83)/4=0.54] hydrogen at the *ortho* positions of the phenyl ring was deuterated and 27% [(1-0.73)/1=0.27] hydrogen at the alkene was deuterated.



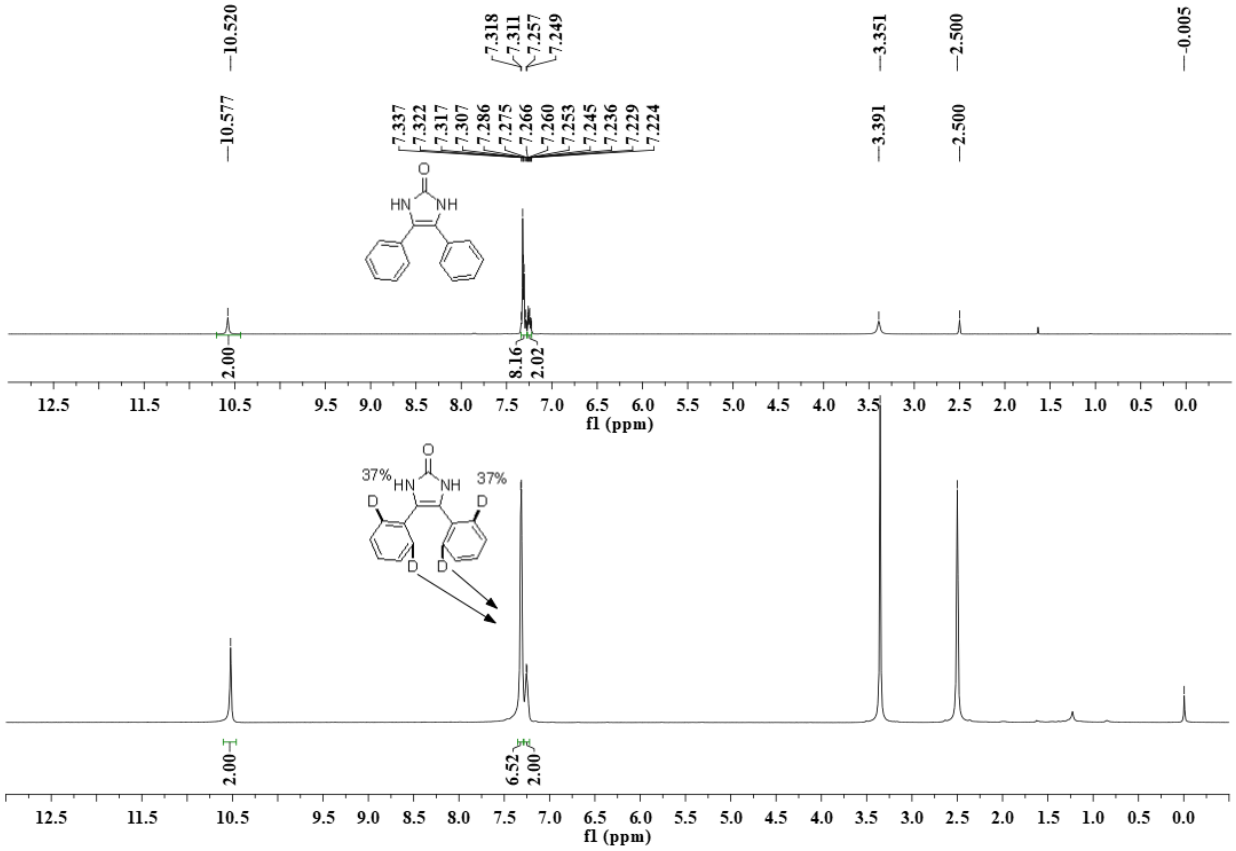
^{1}H NMR (500 MHz, $CDCl_3$) of ***d*-1a-D**



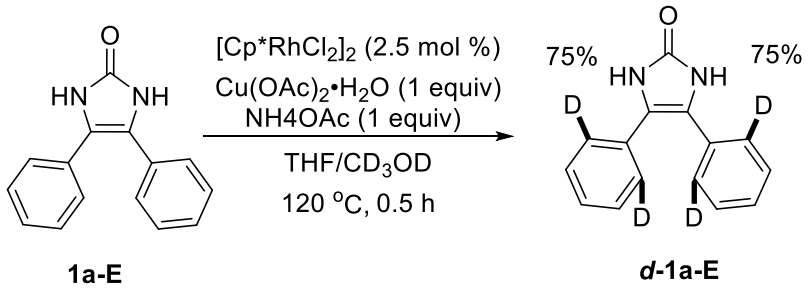
1a-E ***d*-1a-E**

The mixture of imidazole **1a-E** (11.8 mg, 0.05 mmol), [$(Cp^*RhCl_2)_2$] (0.8 mg, 2.5 mol %), NaOAc (6.8 mg, 1 equiv), acetone (0.25 mL) and CD_3OD (0.25 mL) was reacted at 60 °C for 0.5 h under air. After the reaction was cooled down, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel, eluting with

CH_2Cl_2/CH_3OH (40/1, v/v) to afford corresponding deuterium ***d*-1a-E**. ^1H NMR analysis showed that 37% [(8-6.52)/4=0.37] hydrogen at the *ortho* positions of the phenyl ring was deuterated.



^1H NMR (500 MHz, DMSO-d_6) of ***d*-1a-E**

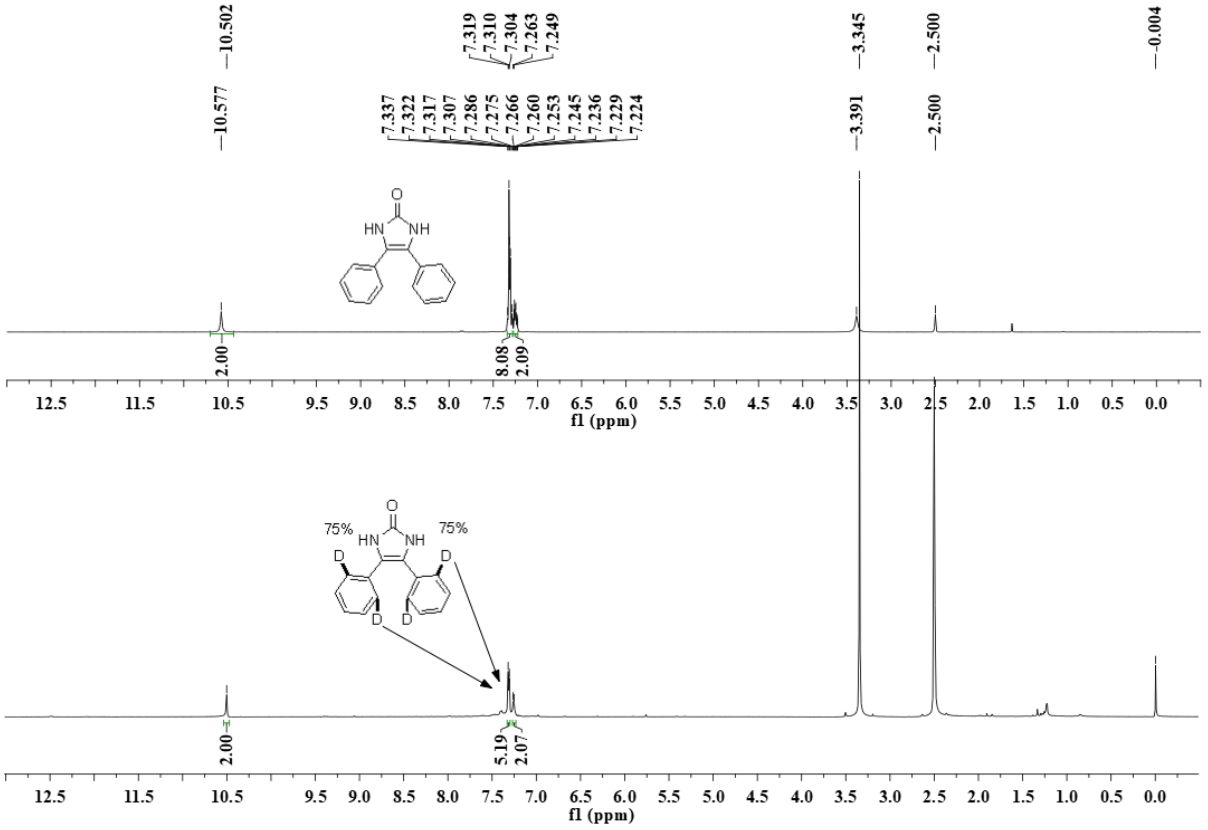


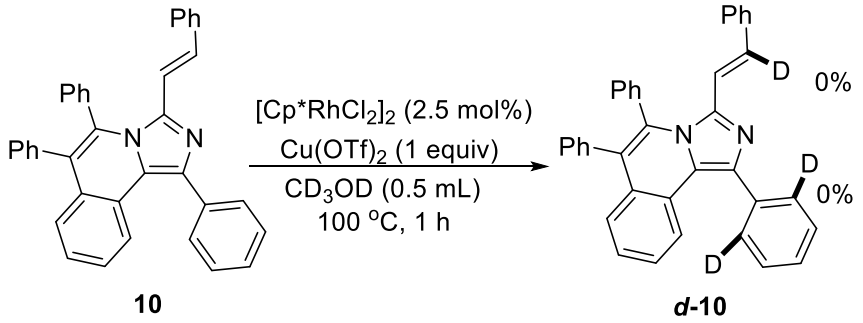
1a-E ***d*-1a-E**

The mixture of imidazole **1a-E** (11.8 mg, 0.05 mmol), [$(Cp^*RhCl_2)_2$] (0.8 mg, 2.5 mol %), $Cu(OAc)_2 \cdot H_2O$ (10mg, 1 equiv), NH_4OAc (7.7 mg, 2 equiv), THF (0.25 mL) and CD_3OD (0.25 mL) was reacted at 120 °C for 0.5 h under air. After the reaction was cooled down the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel, eluting with petroleum ether/EtOAc (1/1, v/v) to afford corresponding deuterium ***d*-**

1a-E. ^{1}H NMR analysis showed that 75% [(8-5.19)/4=0.75] hydrogen at the *ortho* positions of the phenyl ring was deuterated.

^{1}H NMR (500 MHz, DMSO-d_6) of ***d*-1a-E**

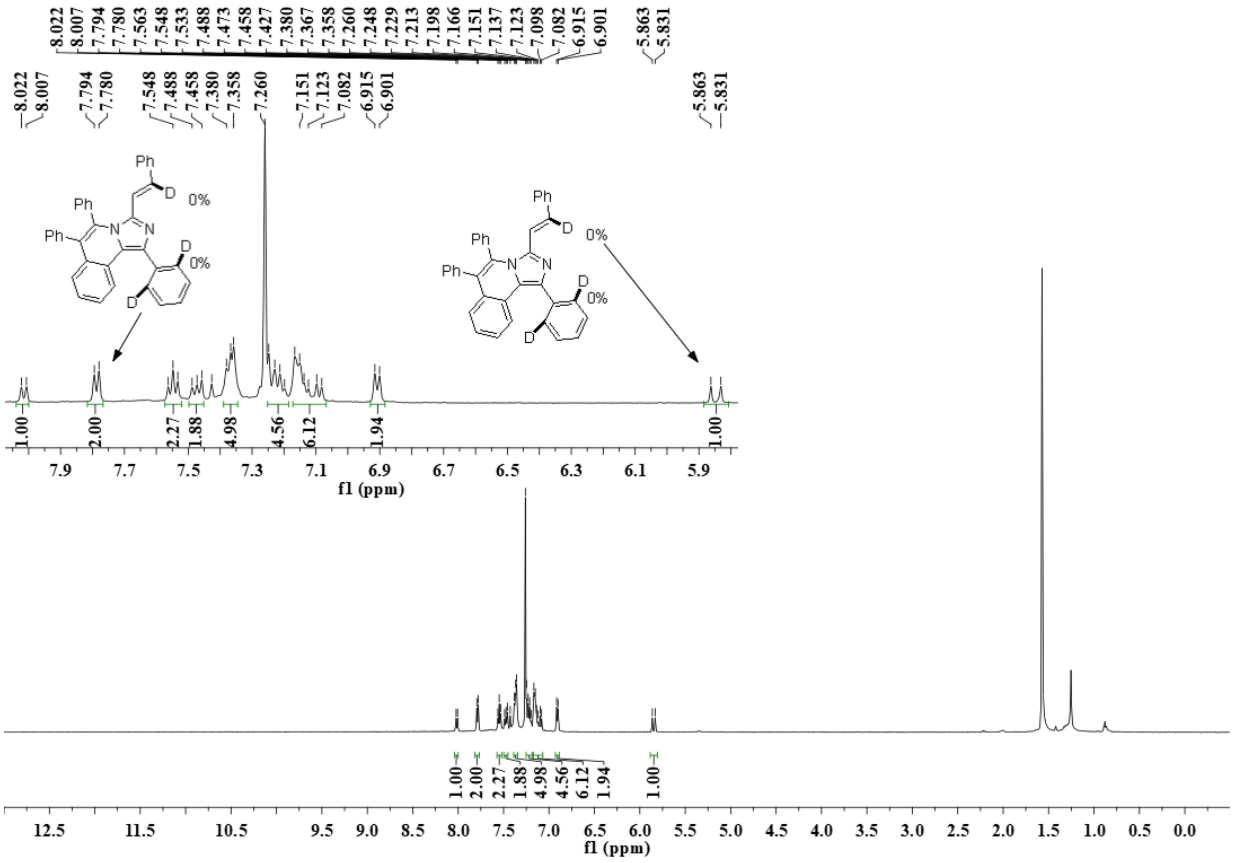




10 ***d*-10**

The mixture of imidazole **10** (24.9 mg, 0.05 mmol), [(Cp*$RhCl_2)_2$] (0.8 mg, 2.5 mol %), $Cu(OTf)_2$ (18.1 mg, 0.05 mmol, 1.0 equiv) and CD_3OD (0.5 mL) was reacted at 100 °C for 1 h under air. After the reaction was cooled down, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel, eluting with petroleum ether/EtOAc (50/1, v/v) to afford corresponding deuterium ***d*-10**. ^{1}H NMR analysis showed that 0%

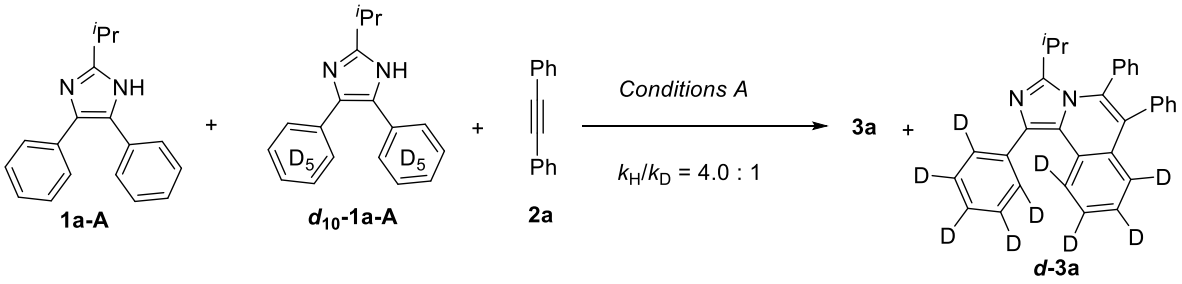
hydrogen at the alkene was deuterated, and 0% hydrogen at the *ortho* positions of the phenyl ring was deuterated.



^{1}H NMR (500 MHz, $CDCl_3$) of ***d*-10**

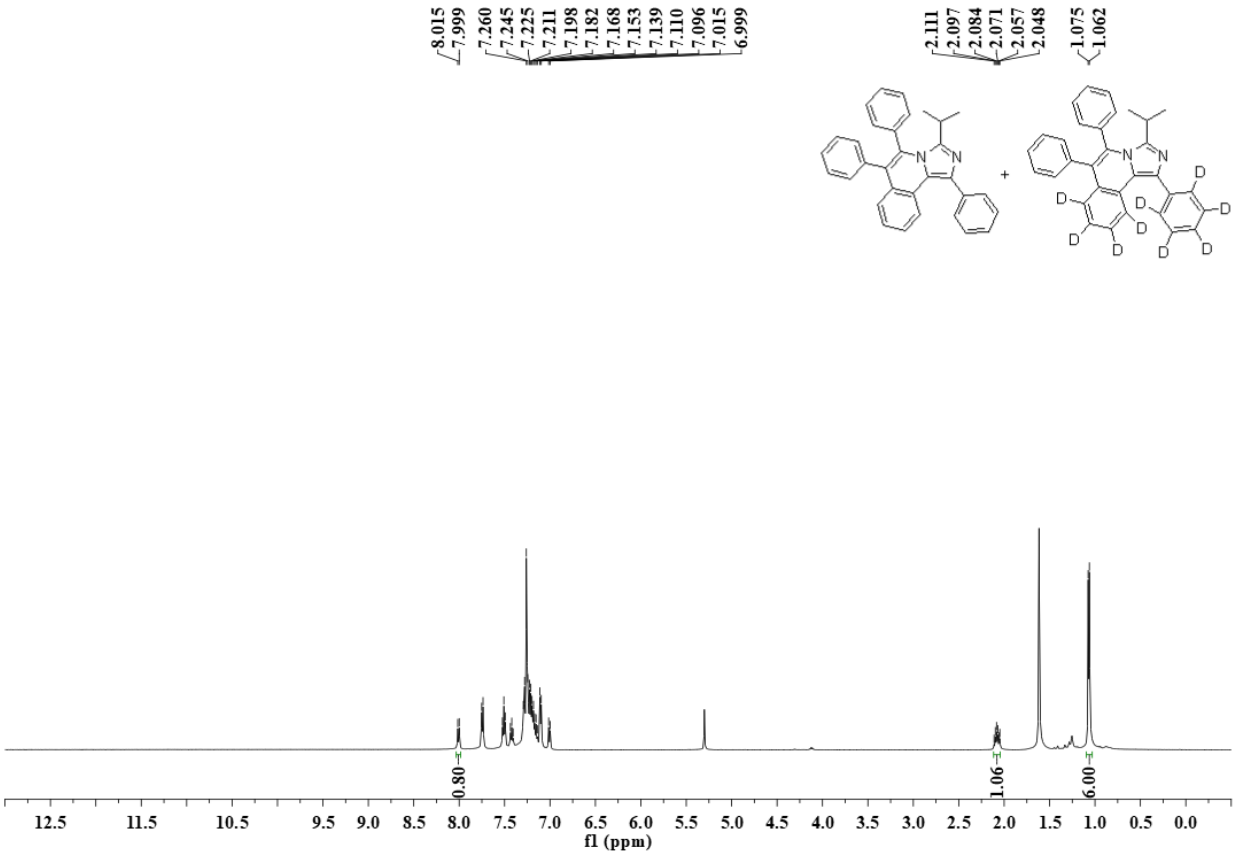
Kinetic isotope effect (KIE):

(1) Competition experiment:



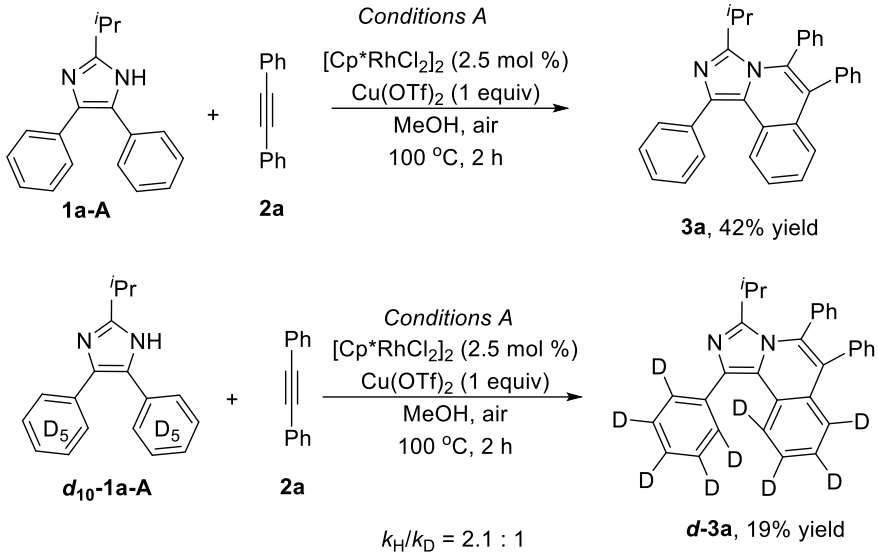
The mixture of imidazole **1a-A** (13.1 mg, 0.05 mmol), ***d*$_{10}$-1a-A** (13.6 mg, 0.05 mmol), **2a** (17.8 mg, 0.1 mmol, 2 equiv), [(Cp^*RhCl_2)$_2$] (1.5 mg, 2.5 mol %), $Cu(OTf)_2$ (36.2 mg, 0.1 mmol, 2

equiv) and MeOH (1 mL) was reacted at 100 °C for 2 h under air. After the reaction was cooled down the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel, eluting with petroleum ether/EtOAc (20/1, v/v) to afford corresponding deuterium **3a** and ***d*-3a** (15 mg, 34%) as a white solid. The ratio of **3a**/(***d*-3a**) in the crude mixture of products was determined to be 4.0 [k_H/k_D = 0.8/(1.0-0.8)] by ^{1}H NMR (see below).



^{1}H NMR spectrum of **3a**/(***d*-3a**) in the crude mixture

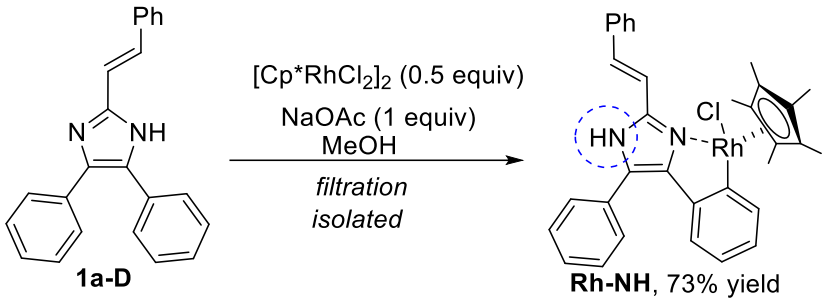
(2) Parallel experiment:



Two sets of reactions were carried out in a parallel manner follow the general procedure: the mixture of **1a** (26.2 mg, 0.1 mmol) or ***d*$_{10}$-1a-A** (27.1 mg, 0.1 mmol), **2a** (17.8 mg, 0.1 mmol, 1 equiv), [(Cp*RhCl$_2$)$_2$] (1.5 mg, 2.5 mol %), Cu(OTf)$_2$ (36.2 mg, 0.1 mmol, 1 equiv) and MeOH (1 mL) was stirred at 100 °C for 2 h under air. After the reaction was cooled down the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel, eluting with petroleum ether/EtOAc (40/1→20/1, v/v) to afford corresponding deuterium **3a** (18.5 mg, 42%) and (***d*-3a**) (8.7 mg, 19%) as a white solid. The k_H/k_D (2.1/1.0) ratio value was calculated according to the isolated yields of **3a**/(***d*-3a**) = 18.5/8.7 = 2.1.

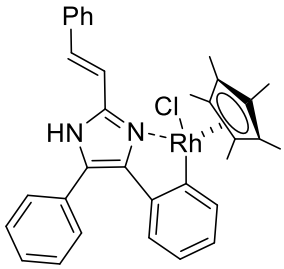
3-isopropyl-5,6-diphenyl-1-(phenyl-d5)imidazo[5,1-a]isoquinoline-7,8,9,10-d4 (*d*-3a). White (8.7 mg, 19% yield). M.p.: 239.7–241.7 ºC. **^{1}H NMR (500MHz, CDCl$_3$)**: δ = 7.20–7.18 (m, 8H, cover the solvent), 7.11–7.10 (m, 2H), 2.09 (s, 1H), 1.07 (d, J = 4.5 Hz, 6H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$)**: δ = 148.99, 137.17, 136.80, 135.06, 134.23, 132.57, 131.42, 130.80, 128.95, 128.73, 128.16, 128.02, 127.02, 126.53, 125.66, 123.98, 27.48, 22.75 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{32}H_{18}D_9N_2$ ([M+H]$^+$) 448.2739, found 448.2740.

6 Synthesis of complex Rh-NH



To a dry Schlenk tube with a magnetic stir bar was added **1a-D** (16.1 mg, 0.05 mmol, 1 equiv), [(Cp*$RhCl_2$)$_2$] (10 mg, 0.025 mmol, 0.5 equiv), NaOAc (24.6 mg, 6 equiv) and MeOH (1 mL). The mixture was stirred at 60 °C for 48 h under an N_2 atmosphere. After the reaction was cooled down the precipitate was collected by filtration and washed with MeOH (1 mL) to afford **Rh-NH** (11 mg, 73%) as a brown solid.

Cp*Rh((*E*)-4,5-diphenyl-2-styryl-1*H*-imidazole)Cl



Brown solid (11 mg, 73% yield). M.p.: 196.1–198.1 ºC. **^{1}H NMR (500MHz, DMSO-*d*$_6$):** δ = 13.93 (s, 1H), 7.91 (d, *J* = 16.5 Hz, 1H), 7.72 (d, *J* = 7.0 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 5H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.0 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.0 Hz, 1H), 7.01–6.94 (m, 2H), 1.66 (s, 15H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 165.73, 147.39, 142.89, 140.18, 136.94, 135.76, 129.88, 129.78, 129.39, 128.24, 127.26, 125.08, 121.41, 114.52, 101.67, 101.63, 9.51 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{33}H_{32}N_2Rh$ ([M-Cl]) 559.1621, found 559.1630.

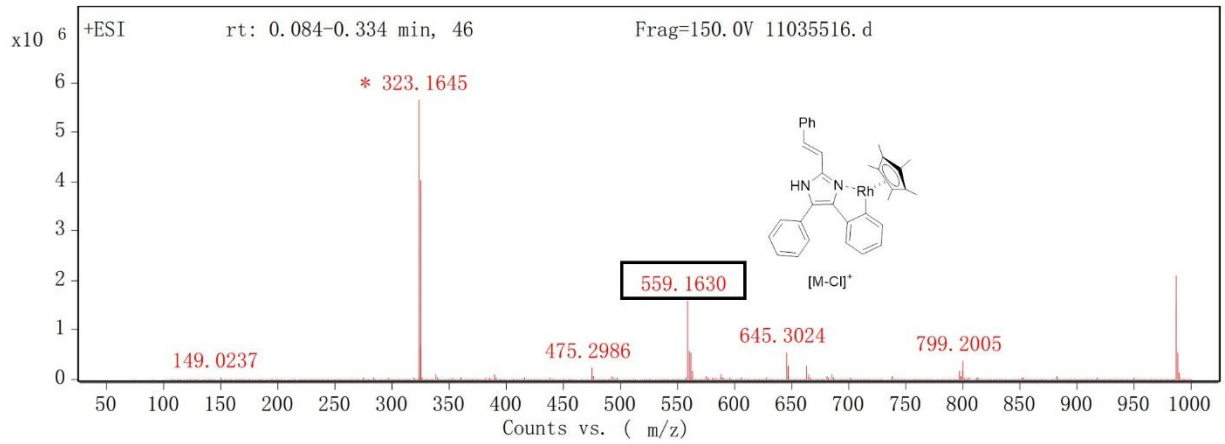
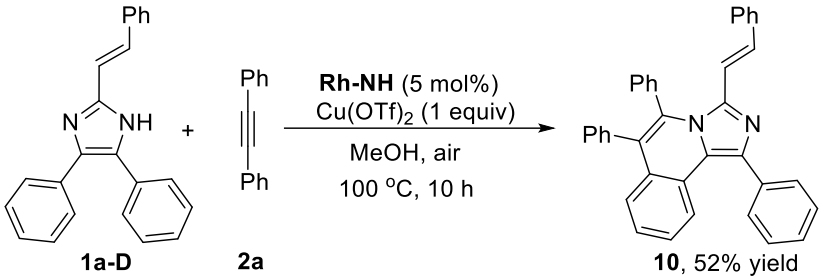


Figure S1 **ESI-HRMS spectrum of mechanistic study**



To a dry Schlenk tube with a magnetic stir bar was added **1a-D** (16.1 mg, 0.05 mmol, 1 equiv), **2a** (8.9 mg, 0.05 mmol, 1 equiv), **Rh-NH** (1.4 mg, 5 mol%), $Cu(OTf)_2$ (18.1 mg, 0.05 mmol, 1 equiv) and MeOH (0.5 mL) was stirred at 100 °C for 10 h under air. After the reaction was completed, the mixture was passed through a silica gel column (100-200 mesh), eluting with petroleum ether/EtOAc (40/1→20/1, v/v) to afford the product **10** (13 mg, 52%) as a yellow solid.

7 Proposed mechanism of the synthesis of products 6

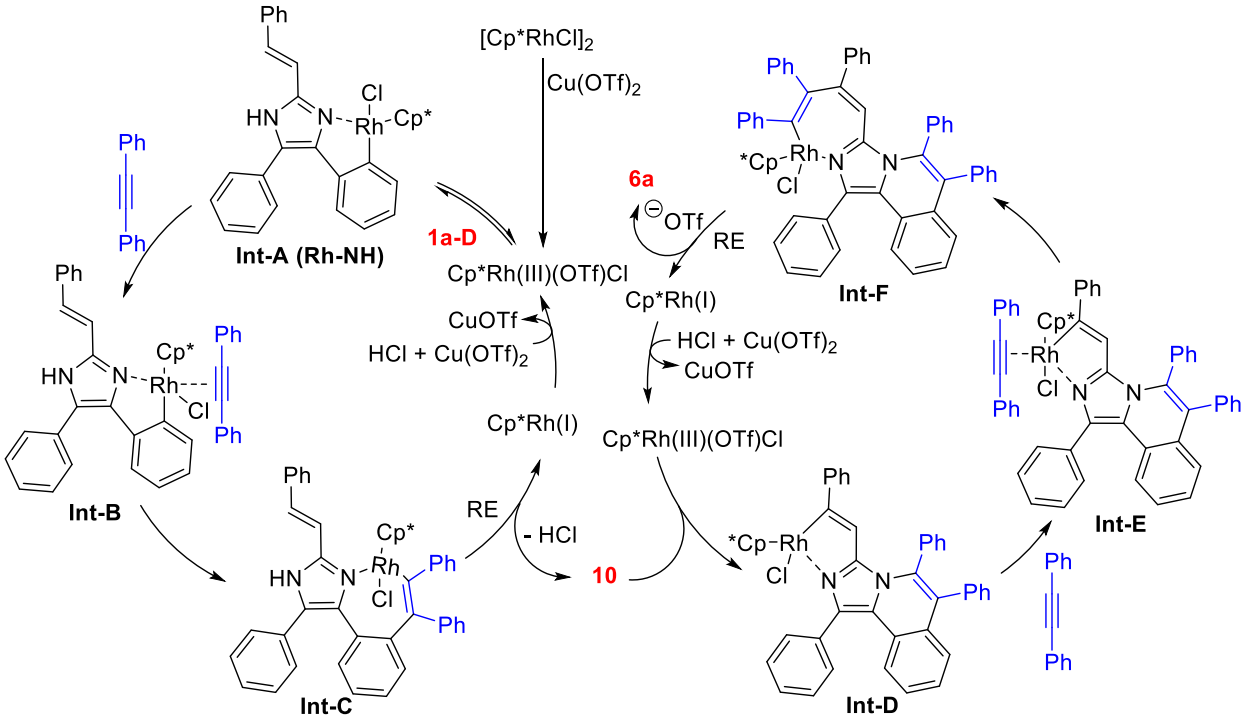


Figure S2 **Proposed mechanism**

8 Photophysical Properties

Fluorescence spectra of 13 and 13′

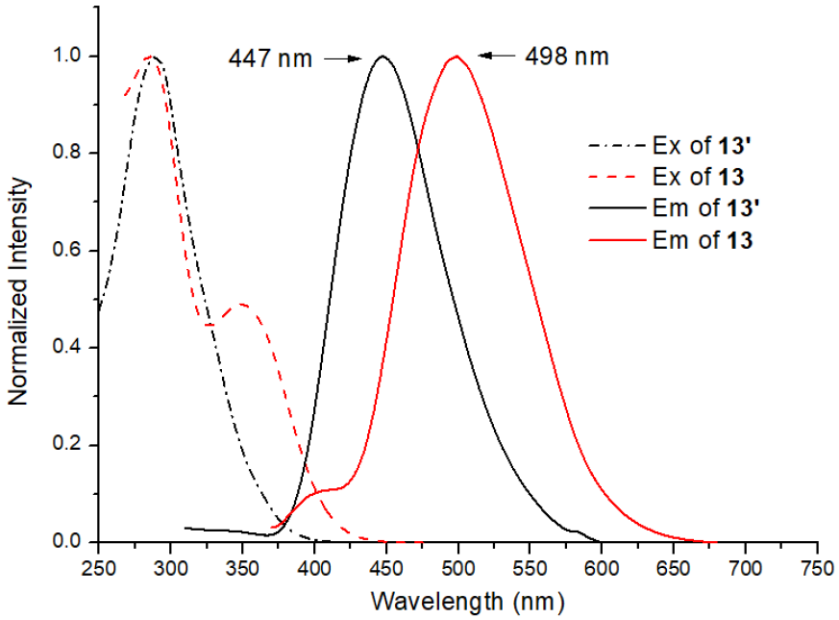


Figure S3 **(**Dashed line) excitation spectra and (full line) emission spectra of **13** and **13′.** (**13**: λ_{ex} = 290 nm; **13′**: λ_{ex} = 350 nm).

9 X-ray Crystallographic Analysis

General Crystal Growing Conditions of **3o**: X-ray quality single crystals of **3o** was grown from the co-solvent of DCM, EA and petroleum ether (5:1:1, v/v) at room temperature by slow evaporation for 3 days.

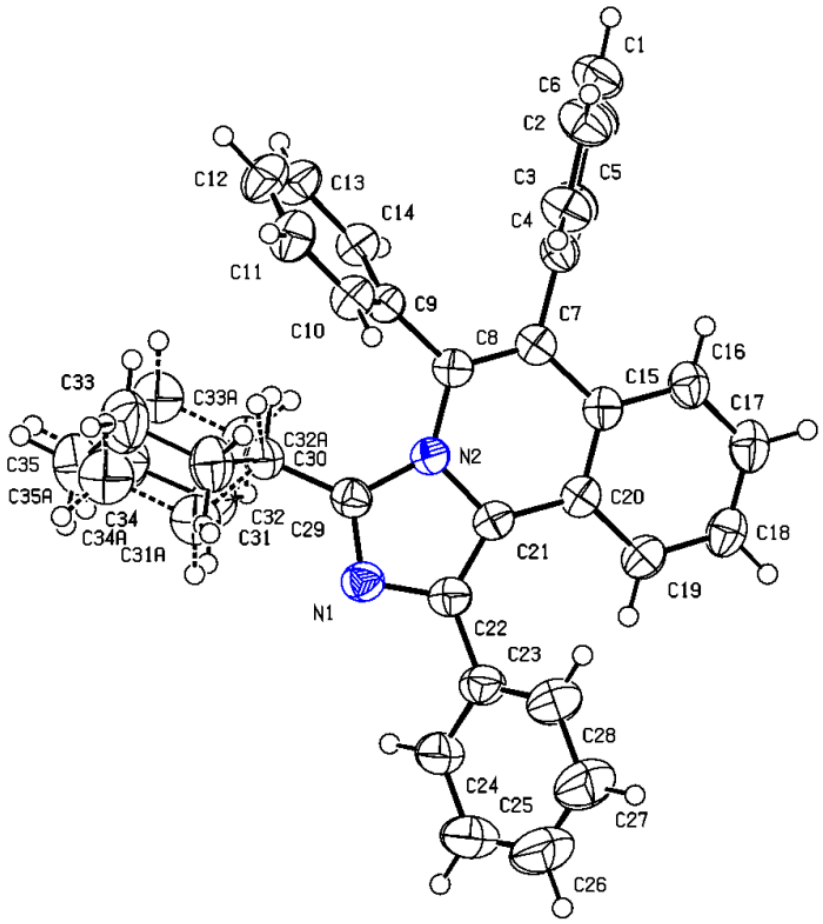


Figure S4 The molecular structure of **3o** (CCDC 2192426). Thermal ellipsoids are shown at the 50% probability level.

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

Identification code	tyn
Empirical formula	$C_{35}H_{30}N_2$
Formula weight	478.61
Temperature/K	193.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.8910(10)
b/Å	17.766(2)
c/Å	15.4481(16)
α/°	90
β/°	99.452(6)
γ/°	90
Volume/Å^3	2677.7(5)
Z	4
ρ_{calc}g/cm^3	1.187

μ/mm^{-1}	0.069
F(000)	1016.0
Crystal size/mm^3	0.13 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.572 to 55.13
Index ranges	$-12 \leq h \leq 12$, $-19 \leq k \leq 23$, $-17 \leq l \leq 20$
Reflections collected	25087
Independent reflections	6091 [R_{int} = 0.0786, R_{sigma} = 0.0695]
Data/restraints/parameters	6091/1179/358
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0601, wR_2 = 0.1450
Final R indexes [all data]	R_1 = 0.1075, wR_2 = 0.1719
Largest diff. peak/hole / e $Å^{-3}$	0.25/-0.24

Table S3 **Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for tyn. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.**

Atom	*x*	*y*	*z*	U(eq)
N2	2962.1(13)	4101.2(8)	5622.1(9)	35.2(3)
N1	3628.7(15)	3002.6(9)	6234.8(10)	43.2(4)
C20	2030.9(16)	3767.3(11)	4097.3(12)	38.1(4)
C9	3226.3(16)	5436.8(10)	6126.2(11)	36.7(4)
C8	2751.7(16)	4875.1(10)	5430.7(11)	36.1(4)
C7	2192.9(16)	5088.5(11)	4609.1(12)	37.1(4)
C15	1781.9(16)	4537.8(11)	3915.4(12)	38.9(4)
C30	3621.0(19)	4026.6(12)	7310.4(12)	44.5(4)
C21	2767.1(16)	3557.3(10)	4948.8(12)	37.4(4)
C4	1985.8(17)	5907.6(11)	4411.0(12)	39.0(4)
C10	4622.8(18)	5572.1(12)	6385.8(13)	44.1(4)
C14	2297.7(18)	5867.9(11)	6494.5(12)	42.5(4)
C19	1515.2(18)	3233.0(12)	3455.6(13)	45.6(5)
C22	3245.6(18)	2893.4(11)	5346.6(13)	41.7(4)
C29	3448.8(17)	3720.2(11)	6396.2(12)	39.8(4)
C16	1128.3(19)	4748.1(13)	3072.0(12)	47.8(5)
C3	3068.2(19)	6367.0(12)	4290.8(13)	49.3(5)
C23	3443(2)	2152.3(12)	4963.2(14)	49.2(5)
C13	2747(2)	6411.6(12)	7112.0(14)	52.9(5)
C18	842(2)	3452.8(13)	2645.4(13)	50.6(5)
C5	697.0(18)	6230.7(12)	4364.2(13)	49.8(5)
C11	5071(2)	6109.7(13)	7008.2(14)	54.1(5)
C17	680(2)	4210.7(14)	2446.9(13)	53.5(5)

Table S3 **Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for tyn. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.**

Atom	*x*	*y*	*z*	U(eq)
C6	504(2)	6992.6(13)	4215.2(15)	58.3(6)
C12	4136(2)	6530.9(13)	7371.7(14)	58.8(6)
C1	1592(2)	7440.9(13)	4102.1(14)	57.2(6)
C2	2873(2)	7127.0(13)	4138.0(15)	57.6(6)
C24	3188(3)	1504.4(13)	5400.2(16)	66.5(6)
C28	3958(2)	2090.0(14)	4179.9(17)	67.0(6)
C25	3411(3)	804.3(16)	5042(2)	93.7(9)
C27	4146(3)	1392.8(18)	3821(2)	92.3(9)
C26	3872(4)	762.0(19)	4260(3)	106.5(10)
C31	2776(4)	3554(3)	7868(2)	64.7(10)
C34	2856(5)	3853(3)	8814(3)	75.7(12)
C32	5083(4)	4054(3)	7761(2)	63.5(9)
C35	4345(6)	3913(3)	9211(3)	76.7(11)
C33	5188(5)	4382(3)	8679(3)	84.6(12)
C35A	3414(8)	3935(5)	9140(5)	71.7(15)
C33A	2410(6)	4408(4)	8508(4)	65.4(13)
C34A	4826(8)	3859(5)	8869(5)	76.0(15)
C31A	4604(6)	3518(4)	7940(4)	62.4(12)
C32A	2255(5)	4080(3)	7592(3)	53.9(11)

Table S4 **Anisotropic Displacement Parameters (Å^2×10^3) for tyn. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.**

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N2	31.1(7)	34.8(8)	38.9(8)	-2.0(7)	3.3(6)	0.7(6)
N1	40.5(8)	39.9(9)	47.8(9)	-2.0(8)	2.9(7)	2.3(7)
C20	29.8(8)	43.8(10)	40.7(9)	-3.4(8)	6.0(7)	-2.7(7)
C9	33.8(8)	37.2(9)	38.4(9)	0.5(8)	4.0(7)	-2.1(7)
C8	28.5(7)	36.6(10)	42.7(9)	0.0(8)	4.5(7)	-0.9(7)
C7	28.3(7)	40.6(10)	42.3(9)	1.2(8)	5.5(7)	-2.3(7)
C15	30.6(8)	46.3(11)	39.6(9)	0.0(8)	4.7(7)	-3.8(7)
C30	45.2(9)	43.9(10)	42.1(10)	0.4(8)	0.7(8)	0.9(8)
C21	31.8(8)	38.1(10)	42.5(9)	-3.7(8)	6.3(7)	-1.9(7)
C4	35.1(8)	42.1(10)	38.9(9)	2.6(8)	3.3(7)	-0.7(8)
C10	35.0(8)	49.0(11)	48.4(10)	-4.1(9)	6.8(8)	-5.2(8)
C14	35.5(8)	45.3(11)	46.3(10)	-3.1(8)	5.9(7)	-0.1(8)
C19	40.2(9)	47.7(11)	48.9(11)	-5.9(9)	7.1(8)	-5.9(8)
C22	36.8(9)	38.7(10)	48.8(11)	-2.0(8)	4.5(8)	-0.3(8)
C29	34.7(8)	40.1(10)	43.3(10)	1.7(8)	2.6(7)	1.3(7)

Table S4 **Anisotropic Displacement Parameters ($Å^2×10^3$) for tyn. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.**

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C16	44.5(10)	54.4(12)	42.7(10)	3.0(9)	2.5(8)	-4.3(9)
C3	34.9(9)	48.4(11)	64.4(12)	9.2(10)	7.7(8)	0.6(8)
C23	47.2(10)	41.0(11)	56.4(12)	-3.1(9)	-0.3(9)	4.5(9)
C13	52.3(11)	52.1(13)	54.7(12)	-12.8(10)	9.7(9)	3.4(10)
C18	47.1(10)	60.2(14)	43.1(11)	-8.5(10)	3.5(9)	-9.7(10)
C5	33.7(9)	51.8(12)	62.7(12)	9.1(10)	4.5(8)	1.7(8)
C11	41.4(10)	65.0(14)	54.4(12)	-7.5(11)	3.1(9)	-13.9(10)
C17	51.4(11)	67.8(15)	39.3(10)	0.8(10)	1.7(9)	-9.4(10)
C6	41.9(10)	57.6(13)	73.4(14)	11.4(11)	3.8(10)	14.0(10)
C12	60.5(12)	58.2(14)	55.9(13)	-16.3(11)	4.1(10)	-14.2(11)
C1	56.6(12)	45.6(12)	65.7(14)	10.8(10)	-1.5(10)	4.4(10)
C2	46.0(11)	52.0(13)	72.5(14)	14.4(11)	2.8(10)	-7.0(10)
C24	86.6(15)	43.1(13)	63.3(14)	-0.4(11)	-7.5(12)	0.5(11)
C28	70.9(13)	57.3(14)	75.1(15)	-11.2(12)	19.1(12)	10.5(11)
C25	131(2)	45.4(15)	94(2)	-0.3(14)	-12.4(17)	8.3(15)
C27	114(2)	73.8(19)	91.1(19)	-22.5(16)	21.9(16)	24.6(16)
C26	142(2)	66.0(19)	106(2)	-26.6(18)	4(2)	31.0(18)
C31	74(2)	69(2)	52.6(18)	0.6(17)	13.9(16)	-9.0(18)
C34	80(2)	83(2)	64(2)	0(2)	11.4(19)	-6(2)
C32	55.5(17)	79(2)	51.3(17)	1.3(17)	-4.2(15)	-2.1(17)
C35	79(2)	95(2)	56(2)	8(2)	6.5(19)	4(2)
C33	83(2)	100(3)	64(2)	-2(2)	-10.5(19)	-13(2)

Table S5 **Bond Lengths for tyn.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N2	C8	1.415(2)	C19	C18	1.374(3)
N2	C21	1.410(2)	C22	C23	1.470(3)
N2	C29	1.390(2)	C16	C17	1.379(3)
N1	C22	1.376(2)	C3	C2	1.379(3)
N1	C29	1.317(2)	C23	C24	1.379(3)
C20	C15	1.411(3)	C23	C28	1.392(3)
C20	C21	1.444(3)	C13	C12	1.382(3)
C20	C19	1.406(3)	C18	C17	1.384(3)
C9	C8	1.485(2)	C5	C6	1.381(3)
C9	C10	1.395(2)	C11	C12	1.379(3)
C9	C14	1.388(2)	C6	C1	1.372(3)
C8	C7	1.353(2)	C1	C2	1.377(3)
C7	C15	1.459(3)	C24	C25	1.393(4)

Table S5 **Bond Lengths for tyn.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C7	C4	1.494(3)	C28	C27	1.382(3)
C15	C16	1.407(3)	C25	C26	1.363(5)
C30	C29	1.497(3)	C27	C26	1.360(5)
C30	C31	1.543(4)	C31	C34	1.546(6)
C30	C32	1.499(4)	C34	C35	1.503(6)
C30	C31A	1.548(6)	C32	C33	1.520(6)
C30	C32A	1.489(5)	C35	C33	1.513(7)
C21	C22	1.377(3)	C35A	C33A	1.526(9)
C4	C3	1.383(3)	C35A	C34A	1.528(9)
C4	C5	1.389(2)	C33A	C32A	1.515(7)
C10	C11	1.376(3)	C34A	C31A	1.540(8)
C14	C13	1.379(3)			

Table S6 **Bond Angles for tyn.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C21	N2	C8	120.97(14)	N1	C22	C23	119.67(17)
C29	N2	C8	132.19(15)	C21	C22	C23	130.24(18)
C29	N2	C21	106.69(15)	N2	C29	C30	127.19(17)
C29	N1	C22	107.56(16)	N1	C29	N2	110.31(16)
C15	C20	C21	118.52(16)	N1	C29	C30	122.19(17)
C19	C20	C15	118.90(17)	C17	C16	C15	120.7(2)
C19	C20	C21	122.55(18)	C2	C3	C4	120.76(18)
C10	C9	C8	120.30(16)	C24	C23	C22	120.2(2)
C14	C9	C8	121.04(15)	C24	C23	C28	118.8(2)
C14	C9	C10	118.55(17)	C28	C23	C22	120.9(2)
N2	C8	C9	118.94(15)	C14	C13	C12	120.01(19)
C7	C8	N2	119.47(16)	C19	C18	C17	119.96(19)
C7	C8	C9	121.50(17)	C6	C5	C4	120.93(18)
C8	C7	C15	121.53(18)	C10	C11	C12	120.03(18)
C8	C7	C4	119.09(16)	C16	C17	C18	120.41(19)
C15	C7	C4	119.38(15)	C1	C6	C5	120.04(19)
C20	C15	C7	119.08(16)	C11	C12	C13	119.98(19)
C16	C15	C20	118.73(18)	C6	C1	C2	119.7(2)
C16	C15	C7	122.18(18)	C1	C2	C3	120.4(2)
C29	C30	C31	109.9(2)	C23	C24	C25	119.8(3)
C29	C30	C32	113.7(2)	C27	C28	C23	120.8(3)
C29	C30	C31A	110.0(3)	C26	C25	C24	119.9(3)
C32	C30	C31	109.2(3)	C26	C27	C28	119.2(3)
C32A	C30	C29	109.3(2)	C27	C26	C25	121.3(3)

Table S6 **Bond Angles for tyn.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C32A	C30	C31A	111.1(3)	C30	C31	C34	113.1(3)
N2	C21	C20	118.85(16)	C35	C34	C31	107.7(4)
C22	C21	N2	105.22(15)	C30	C32	C33	111.0(3)
C22	C21	C20	135.45(18)	C34	C35	C33	114.1(4)
C3	C4	C7	121.28(16)	C35	C33	C32	109.7(4)
C3	C4	C5	118.24(19)	C33A	C35A	C34A	113.7(6)
C5	C4	C7	120.46(16)	C32A	C33A	C35A	110.0(5)
C11	C10	C9	120.73(18)	C35A	C34A	C31A	107.1(6)
C13	C14	C9	120.69(17)	C34A	C31A	C30	109.5(5)
C18	C19	C20	121.0(2)	C30	C32A	C33A	109.9(4)
N1	C22	C21	110.02(17)				

Table S7 **Torsion Angles for tyn.**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N2	C8	C7	C15	0.9(2)	C14	C9	C8	N2	-112.40(19)
N2	C8	C7	C4	-179.47(14)	C14	C9	C8	C7	71.2(2)
N2	C21	C22	N1	4.14(19)	C14	C9	C10	C11	1.4(3)
N2	C21	C22	C23	-172.74(18)	C14	C13	C12	C11	0.5(3)
N1	C22	C23	C24	39.7(3)	C19	C20	C15	C7	173.86(15)
N1	C22	C23	C28	-136.8(2)	C19	C20	C15	C16	-5.3(2)
C20	C15	C16	C17	3.1(3)	C19	C20	C21	N2	-164.97(15)
C20	C21	C22	N1	-167.33(18)	C19	C20	C21	C22	5.6(3)
C20	C21	C22	C23	15.8(3)	C19	C18	C17	C16	-3.3(3)
C20	C19	C18	C17	0.9(3)	C22	N1	C29	N2	-0.74(19)
C9	C8	C7	C15	177.26(15)	C22	N1	C29	C30	173.35(16)
C9	C8	C7	C4	-3.1(2)	C22	C23	C24	C25	-178.4(2)
C9	C10	C11	C12	-1.1(3)	C22	C23	C28	C27	179.8(2)
C9	C14	C13	C12	-0.1(3)	C29	N2	C8	C9	6.7(3)
C8	N2	C21	C20	-15.2(2)	C29	N2	C8	C7	-176.82(16)
C8	N2	C21	C22	171.57(14)	C29	N2	C21	C20	168.74(15)
C8	N2	C29	N1	-172.08(15)	C29	N2	C21	C22	-4.44(17)
C8	N2	C29	C30	14.2(3)	C29	N1	C22	C21	-2.2(2)
C8	C9	C10	C11	177.76(19)	C29	N1	C22	C23	175.05(16)
C8	C9	C14	C13	-177.10(18)	C29	C30	C31	C34	-177.8(3)
C8	C7	C15	C20	-2.9(2)	C29	C30	C32	C33	179.1(3)
C8	C7	C15	C16	176.28(16)	C29	C30	C31A	C34A	177.4(4)
C8	C7	C4	C3	77.1(2)	C29	C30	C32A	C33A	-178.6(4)
C8	C7	C4	C5	-101.4(2)	C3	C4	C5	C6	-1.0(3)
C7	C15	C16	C17	-176.11(17)	C23	C24	C25	C26	-0.4(4)

Table S7 **Torsion Angles for tyn.**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C7	C4	C3	C2	-177.77(19)	C23	C28	C27	C26	-2.5(4)
C7	C4	C5	C6	177.48(19)	C5	C4	C3	C2	0.7(3)
C15	C20	C21	N2	12.9(2)	C5	C6	C1	C2	0.0(3)
C15	C20	C21	C22	-176.54(19)	C6	C1	C2	C3	-0.3(3)
C15	C20	C19	C18	3.5(3)	C24	C23	C28	C27	3.2(3)
C15	C7	C4	C3	-103.3(2)	C24	C25	C26	C27	1.2(5)
C15	C7	C4	C5	78.3(2)	C28	C23	C24	C25	-1.8(3)
C15	C16	C17	C18	1.3(3)	C28	C27	C26	C25	0.3(5)
C30	C31	C34	C35	-54.1(5)	C31	C30	C29	N2	122.0(3)
C30	C32	C33	C35	58.3(5)	C31	C30	C29	N1	-51.1(3)
C21	N2	C8	C9	-168.12(14)	C31	C30	C32	C33	-57.8(4)
C21	N2	C8	C7	8.3(2)	C31	C34	C35	C33	54.8(6)
C21	N2	C29	N1	3.30(18)	C34	C35	C33	C32	-57.9(6)
C21	N2	C29	C30	-170.42(16)	C32	C30	C29	N2	-115.3(3)
C21	C20	C15	C7	-4.1(2)	C32	C30	C29	N1	71.6(3)
C21	C20	C15	C16	176.74(15)	C32	C30	C31	C34	56.9(4)
C21	C20	C19	C18	-178.72(17)	C35A	C33A	C32A	C30	-56.2(7)
C21	C22	C23	C24	-143.6(2)	C35A	C34A	C31A	C30	57.4(7)
C21	C22	C23	C28	39.8(3)	C33A	C35A	C34A	C31A	-57.1(9)
C4	C7	C15	C20	177.47(15)	C34A	C35A	C33A	C32A	56.8(8)
C4	C7	C15	C16	-3.4(2)	C31A	C30	C29	N2	-161.7(3)
C4	C3	C2	C1	0.0(3)	C31A	C30	C29	N1	25.2(3)
C4	C5	C6	C1	0.7(3)	C31A	C30	C32A	C33A	59.7(5)
C10	C9	C8	N2	71.4(2)	C32A	C30	C29	N2	75.9(3)
C10	C9	C8	C7	-105.0(2)	C32A	C30	C29	N1	-97.1(3)
C10	C9	C14	C13	-0.8(3)	C32A	C30	C31A	C34A	-61.4(6)
C10	C11	C12	C13	0.1(3)					

Table S8 **Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for tyn.**

Atom	*x*	*y*	*z*	U(eq)
H30	3251.88	4551.67	7278.53	53
H30A	4180(50)	4540(30)	7370(30)	53
H10	5271.86	5290.07	6130.12	53
H14	1342.34	5787.52	6319.43	51
H19	1633.98	2711.98	3584.18	55
H16	994.47	5266.25	2931.62	57
H3	3956.33	6156.61	4313.7	59
H13	2102.57	6704.31	7359.02	64

Table S8 **Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for tyn.**

Atom	*x*	*y*	*z*	U(eq)
H18	488.67	3084.94	2221.76	61
H5	-62.68	5923.24	4435.76	60
H11	6025.3	6190.84	7187.59	65
H17	256.53	4361.36	1876.32	64
H6	-381.21	7206.57	4191	70
H12	4445.53	6902.8	7800.36	71
H1	1461.53	7965.17	3999.55	69
H2	3626.64	7435.76	4057.06	69
H24	2860.93	1535.23	5943.98	80
H28	4182.36	2532.29	3888.34	80
H25	3240.91	356.84	5343.8	112
H27	4463.62	1354.82	3274.78	111
H26	4005.02	282.12	4015.43	128
H31A	3112.16	3027.88	7891.44	78
H31B	1805.83	3549.85	7578	78
H34A	2411.8	4353.06	8807.07	91
H34B	2379.08	3504.7	9163.16	91
H32A	5624.9	4367.07	7412.69	76
H32B	5472.52	3539.88	7798.49	76
H35A	4739.84	3400	9278.64	92
H35B	4416.1	4135.53	9804.05	92
H33A	6157.53	4385.95	8968.86	102
H33B	4848.38	4906.82	8642.7	102
H35C	3021.58	3426.26	9181.41	86
H35D	3524.16	4165.96	9730.78	86
H33C	1507.41	4416.61	8706.18	78
H33D	2749.37	4931.88	8503.48	78
H34C	5419.41	3526.4	9283.49	91
H34D	5270.69	4357.91	8868.56	91
H31C	4208.39	3006.92	7952.35	75
H31D	5493.74	3475.68	7728.77	75
H32C	1836	3573.97	7585.36	65
H32D	1642.88	4404.95	7178.4	65

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
H30	0.592(3)	H30A	0.408(3)	C31	0.592(3)
H31A	0.592(3)	H31B	0.592(3)	C34	0.592(3)
H34A	0.592(3)	H34B	0.592(3)	C32	0.592(3)

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
H32A	0.592(3)	H32B	0.592(3)	C35	0.592(3)
H35A	0.592(3)	H35B	0.592(3)	C33	0.592(3)
H33A	0.592(3)	H33B	0.592(3)	C35A	0.408(3)
H35C	0.408(3)	H35D	0.408(3)	C33A	0.408(3)
H33C	0.408(3)	H33D	0.408(3)	C34A	0.408(3)
H34C	0.408(3)	H34D	0.408(3)	C31A	0.408(3)
H31C	0.408(3)	H31D	0.408(3)	C32A	0.408(3)
H32C	0.408(3)	H32D	0.408(3)		

General Crystal Growing Conditions of **3s**: X-ray quality single crystals of **3s** was grown from the co-solvent of DCM, MeOH, EA and petroleum ether (5:1:1:1, v/v) at room temperature by slow evaporation for one week.

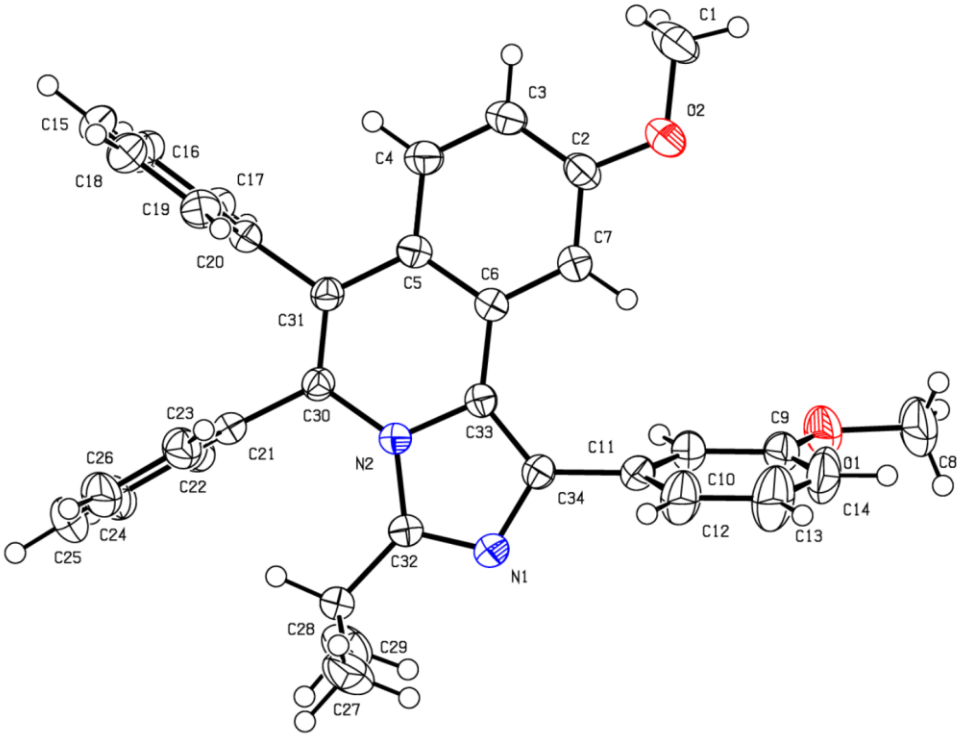


Figure S5 The molecular structure of **3s** (CCDC 2176133). Thermal ellipsoids are shown at the 50% probability level.

Table S9 **Crystal data and structure refinement for TYN-116.**

Identification code	TYN-116
Empirical formula	$C_{34}H_{30}N_2O_2$
Formula weight	498.60

Temperature/K	193.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.3102(5)
b/Å	13.4519(8)
c/Å	23.6430(13)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2643.0(3)
Z	4
ρ_{calc}g/cm^3	1.253
μ/mm^{-1}	0.078
F(000)	1056.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.484 to 54.998
Index ranges	$-10 \leq h \leq 8$, $-15 \leq k \leq 17$, $-30 \leq l \leq 30$
Reflections collected	23771
Independent reflections	5985 [R_{int} = 0.0517, R_{sigma} = 0.0428]
Data/restraints/parameters	5985/0/347
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0436, wR_2 = 0.1080
Final R indexes [all data]	R_1 = 0.0509, wR_2 = 0.1129
Largest diff. peak/hole / e Å^{-3}	0.36/-0.25
Flack parameter	-0.5(8)

Table S10 **Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for TYN-116. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.**

Atom	*x*	*y*	*z*	U(eq)
N2	6079(2)	5339.1(13)	2611.0(8)	24.8(4)
O2	7057(2)	6857.3(15)	5001.6(7)	47.2(5)
O1	4291(3)	3138.1(15)	5066.4(8)	54.8(6)
N1	3875(2)	4457.8(14)	2783.0(8)	30.9(4)
C20	9763(3)	6942.1(17)	2426.3(9)	27.3(5)
C33	5772(3)	5411.8(16)	3194.2(9)	25.3(4)
C32	4882(3)	4743.2(17)	2381.3(10)	28.4(5)
C6	6798(3)	6008.1(16)	3549.2(9)	25.1(4)
C30	7396(3)	5843.8(16)	2362.0(9)	25.6(4)
C34	4406(3)	4851.3(16)	3284.9(9)	27.2(4)
C11	3546(3)	4626.2(17)	3820.6(10)	31.1(5)
C17	11282(3)	6521.5(19)	2412.3(11)	34.0(5)
C31	8386(3)	6395.0(16)	2691.6(9)	26.1(4)
C28	4701(3)	4364.9(18)	1786.0(10)	33.5(5)
C7	6496(3)	6144.1(17)	4125.4(9)	30.6(5)
C5	8130(3)	6487.5(16)	3296.8(9)	26.9(4)
C21	7647(3)	5743.8(16)	1742.5(10)	28.5(5)
C2	7489(3)	6739.0(18)	4450.6(10)	33.5(5)
C19	9549(3)	7896.0(18)	2211.6(11)	35.0(5)
C10	4250(3)	4008.4(18)	4216.9(10)	35.6(5)
C4	9135(3)	7072.6(18)	3639.1(10)	33.6(5)
C22	8605(3)	4981(2)	1533.7(11)	38.1(6)
C15	12357(3)	7980(2)	1972.7(12)	42.5(6)
C9	3476(4)	3773(2)	4721.9(11)	42.4(6)
C3	8828(3)	7201.6(19)	4207.7(11)	37.2(6)

Table S10 **Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for TYN-116. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.**

Atom	*x*	*y*	*z*	U(eq)
C18	10851(3)	8409(2)	1984.8(12)	41.6(6)
C16	12562(3)	7036(2)	2183.7(12)	43.1(6)
C23	6911(3)	6394.4(19)	1366.9(10)	38.9(6)
C24	8770(4)	4851(2)	958.8(12)	51.0(7)
C26	7083(4)	6251(2)	787.7(12)	51.4(8)
C25	7987(4)	5478(3)	589.4(12)	55.6(8)
C29	5176(4)	3277(2)	1767.3(13)	54.9(8)
C12	2026(4)	5009(2)	3926.8(14)	51.0(7)
C27	2973(4)	4488(3)	1582.6(13)	56.0(8)
C14	1972(4)	4170(3)	4827.9(14)	59.5(9)
C1	8082(4)	7448(4)	5351.9(14)	73.0(12)
C13	1258(4)	4776(3)	4429.0(16)	69.8(10)
C8	3597(6)	2901(3)	5603.0(14)	75.4(11)

Table S11 **Anisotropic Displacement Parameters (Å^2×10^3) for TYN-116. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.**

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N2	24.0(9)	26.4(9)	23.9(9)	-1.4(7)	-0.2(7)	-2.3(7)
O2	47.5(11)	64.5(12)	29.5(9)	-10.4(9)	-0.6(8)	-10.9(10)
O1	74.3(15)	57.7(12)	32.3(10)	12.4(9)	1.6(10)	-9.9(11)
N1	27.5(10)	34.7(10)	30.5(10)	-1.8(8)	1.6(8)	-6.0(8)
C20	27.5(11)	30.4(11)	24.1(10)	-3.4(9)	1.1(9)	-4.1(9)
C33	25.8(10)	25.7(10)	24.3(10)	-0.3(8)	0.9(9)	0.6(8)
C32	27.5(11)	30.1(11)	27.4(11)	-0.6(9)	-1.5(9)	-4.6(9)
C6	25.3(10)	24.7(10)	25.2(10)	-0.5(8)	-1.0(8)	1.3(8)

Table S11 **Anisotropic Displacement Parameters ($Å^2×10^3$) for TYN-116. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.**

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C30	24.0(10)	26.1(10)	26.6(10)	-0.2(8)	1.5(9)	-0.5(8)
C34	24.8(11)	29.3(10)	27.5(11)	-0.3(9)	1.6(9)	-0.4(8)
C11	29.9(12)	33.0(11)	30.4(11)	-2.5(9)	3.2(10)	-4.8(9)
C17	30.2(12)	34.0(12)	37.8(13)	-0.4(10)	2.1(10)	-1.7(10)
C31	23.7(10)	27.1(10)	27.4(11)	-1.7(8)	2.1(8)	0.0(8)
C28	36.7(12)	37.5(12)	26.4(11)	-2.4(9)	0.3(10)	-11.0(10)
C7	31.1(12)	33.6(11)	27.2(11)	-0.4(9)	1.0(9)	-1.5(9)
C5	26.1(10)	27.3(10)	27.4(11)	-2.2(9)	-1.6(9)	0.6(8)
C21	26.3(11)	31.5(11)	27.7(11)	-0.9(9)	0.7(9)	-6.5(9)
C2	34.7(12)	41.0(13)	24.8(11)	-4.8(10)	-2.5(10)	0.8(10)
C19	35.7(12)	32.2(12)	37.1(13)	-0.7(10)	-0.5(11)	0.3(10)
C10	39.3(13)	37.4(12)	30.0(12)	1.4(10)	5.1(10)	-3.6(10)
C4	30.9(12)	36.3(12)	33.7(12)	-4.5(10)	-1.7(10)	-4.4(10)
C22	34.5(13)	44.3(14)	35.6(13)	-8.1(11)	1.1(11)	2.8(11)
C15	40.1(14)	47.0(15)	40.3(14)	-4.6(12)	9.0(12)	-18.0(12)
C9	56.3(17)	40.1(13)	31.0(13)	0.9(11)	4.6(12)	-13.3(13)
C3	36.8(13)	41.4(13)	33.4(12)	-7.6(11)	-4.8(11)	-5.6(11)
C18	50.4(16)	34.5(12)	39.7(13)	3.1(11)	1.4(12)	-10.6(11)
C16	28.4(12)	47.5(14)	53.2(16)	-4.5(13)	6.6(12)	-3.9(11)
C23	47.8(15)	36.2(13)	32.7(13)	2.6(10)	-1.0(11)	-2.5(11)
C24	49.4(17)	62.4(18)	41.2(15)	-17.1(14)	8.7(13)	-1.7(15)
C26	73(2)	49.6(16)	31.9(13)	10.7(12)	-6.5(14)	-14.1(15)
C25	72(2)	67(2)	27.7(13)	-8.3(13)	7.9(14)	-15.5(17)
C29	74(2)	47.5(16)	43.7(16)	-15.1(13)	-4.6(15)	2.1(15)
C12	39.6(15)	63.0(18)	50.4(16)	8.7(14)	12.1(13)	7.2(14)
C27	51.6(17)	75(2)	41.7(16)	-12.3(15)	-14.6(14)	1.2(16)

Table S11 **Anisotropic Displacement Parameters ($Å^2×10^3$) for TYN-116. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.**

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C14	61(2)	72(2)	46.4(17)	5.3(15)	26.1(15)	-7.2(17)
C1	61(2)	122(3)	36.0(15)	-28.0(19)	0.8(15)	-28(2)
C13	49.2(19)	92(3)	68(2)	8(2)	29.8(17)	11.9(19)
C8	112(3)	78(2)	36.6(16)	16.7(16)	10.9(19)	-21(2)

Table S12 **Bond Lengths for TYN-116.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N2	C33	1.406(3)	C17	C16	1.380(3)
N2	C32	1.388(3)	C31	C5	1.452(3)
N2	C30	1.416(3)	C28	C29	1.517(4)
O2	C2	1.361(3)	C28	C27	1.523(4)
O2	C1	1.429(4)	C7	C2	1.383(3)
O1	C9	1.361(3)	C5	C4	1.404(3)
O1	C8	1.430(4)	C21	C22	1.389(3)
N1	C32	1.323(3)	C21	C23	1.389(3)
N1	C34	1.372(3)	C2	C3	1.398(4)
C20	C17	1.384(3)	C19	C18	1.391(4)
C20	C31	1.498(3)	C10	C9	1.393(3)
C20	C19	1.391(3)	C4	C3	1.379(3)
C33	C6	1.440(3)	C22	C24	1.377(4)
C33	C34	1.380(3)	C15	C18	1.379(4)
C32	C28	1.504(3)	C15	C16	1.375(4)
C6	C7	1.397(3)	C9	C14	1.382(5)
C6	C5	1.413(3)	C23	C26	1.390(4)
C30	C31	1.354(3)	C24	C25	1.377(5)

Table S12 **Bond Lengths for TYN-116.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C30	C21	1.486(3)	C26	C25	1.366(5)
C34	C11	1.485(3)	C12	C13	1.384(4)
C11	C10	1.382(3)	C14	C13	1.381(5)
C11	C12	1.387(4)			

Table S13 **Bond Angles for TYN-116.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C33	N2	C30	120.96(18)	C32	C28	C29	109.1(2)
C32	N2	C33	107.11(18)	C32	C28	C27	110.7(2)
C32	N2	C30	131.92(19)	C29	C28	C27	110.0(2)
C2	O2	C1	117.6(2)	C2	C7	C6	120.7(2)
C9	O1	C8	118.1(3)	C6	C5	C31	119.48(19)
C32	N1	C34	107.79(19)	C4	C5	C6	118.6(2)
C17	C20	C31	120.4(2)	C4	C5	C31	121.9(2)
C17	C20	C19	119.0(2)	C22	C21	C30	119.9(2)
C19	C20	C31	120.5(2)	C23	C21	C30	120.8(2)
N2	C33	C6	120.20(19)	C23	C21	C22	119.4(2)
C34	C33	N2	105.28(18)	O2	C2	C7	116.3(2)
C34	C33	C6	134.5(2)	O2	C2	C3	123.4(2)
N2	C32	C28	129.3(2)	C7	C2	C3	120.3(2)
N1	C32	N2	109.88(19)	C18	C19	C20	119.9(2)
N1	C32	C28	120.7(2)	C11	C10	C9	121.5(3)
C7	C6	C33	122.3(2)	C3	C4	C5	121.5(2)
C7	C6	C5	119.5(2)	C24	C22	C21	120.1(3)
C5	C6	C33	118.14(19)	C16	C15	C18	119.4(2)
N2	C30	C21	118.36(18)	O1	C9	C10	115.2(3)

Table S13 **Bond Angles for TYN-116.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C31	C30	N2	119.54(19)	O1	C9	C14	125.7(3)
C31	C30	C21	122.1(2)	C14	C9	C10	119.1(3)
N1	C34	C33	109.93(19)	C4	C3	C2	119.4(2)
N1	C34	C11	120.3(2)	C15	C18	C19	120.4(2)
C33	C34	C11	129.8(2)	C15	C16	C17	120.7(3)
C10	C11	C34	119.8(2)	C21	C23	C26	119.8(3)
C10	C11	C12	119.1(2)	C25	C24	C22	120.1(3)
C12	C11	C34	121.1(2)	C25	C26	C23	120.0(3)
C16	C17	C20	120.5(2)	C26	C25	C24	120.5(3)
C30	C31	C20	119.48(19)	C13	C12	C11	119.4(3)
C30	C31	C5	121.64(19)	C13	C14	C9	119.5(3)
C5	C31	C20	118.86(19)	C14	C13	C12	121.5(3)

Table S14 **Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for TYN-116.**

Atom	*x*	*y*	*z*	U(eq)
H17	11444.11	5873.34	2561.28	41
H28	5431.32	4751.33	1531.8	40
H7	5598.51	5824.66	4295.53	37
H19	8514.55	8196.46	2219.98	42
H10	5285.15	3738.34	4143.15	43
H4	10046.26	7386.79	3475.32	40
H22	9147.42	4548.98	1787.8	46
H15	13246.07	8333.43	1819.82	51
H3	9520.45	7601.41	4432.32	45
H18	10701.11	9059.5	1837.19	50

Table S14 **Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for TYN-116.**

Atom	*x*	*y*	*z*	U(eq)
H16	13595.63	6735.16	2172.01	52
H23	6292.52	6936.05	1505.26	47
H24	9424.53	4328.81	816.98	61
H26	6571.17	6690.38	529.84	62
H25	8077.39	5371.97	193.36	67
H29A	6315.63	3210.04	1867.46	82
H29B	5001.58	3016.49	1385.07	82
H29C	4519.58	2901.31	2037.11	82
H12	1516.3	5427.37	3657.2	61
H27A	2244.2	4139.79	1841.13	84
H27B	2866.44	4208.41	1201.75	84
H27C	2696.72	5196.51	1573.96	84
H14	1432.62	4026.18	5172.62	71
H1A	8181.56	8115.99	5189.79	109
H1B	9148.28	7139.24	5373.82	109
H1C	7619.38	7494.83	5732.21	109
H13	217.68	5039.69	4501	84
H8A	2555.06	2575.2	5545.72	113
H8B	3443.89	3512.48	5821.73	113
H8C	4317.34	2452.43	5809.54	113

General Crystal Growing Conditions of **13'**: X-ray quality single crystals of **13'** was grown from the co-solvent of DCM, MeOH, EA and petroleum ether (5:1:1:1, v/v) at room temperature by slow evaporation for 2 days.

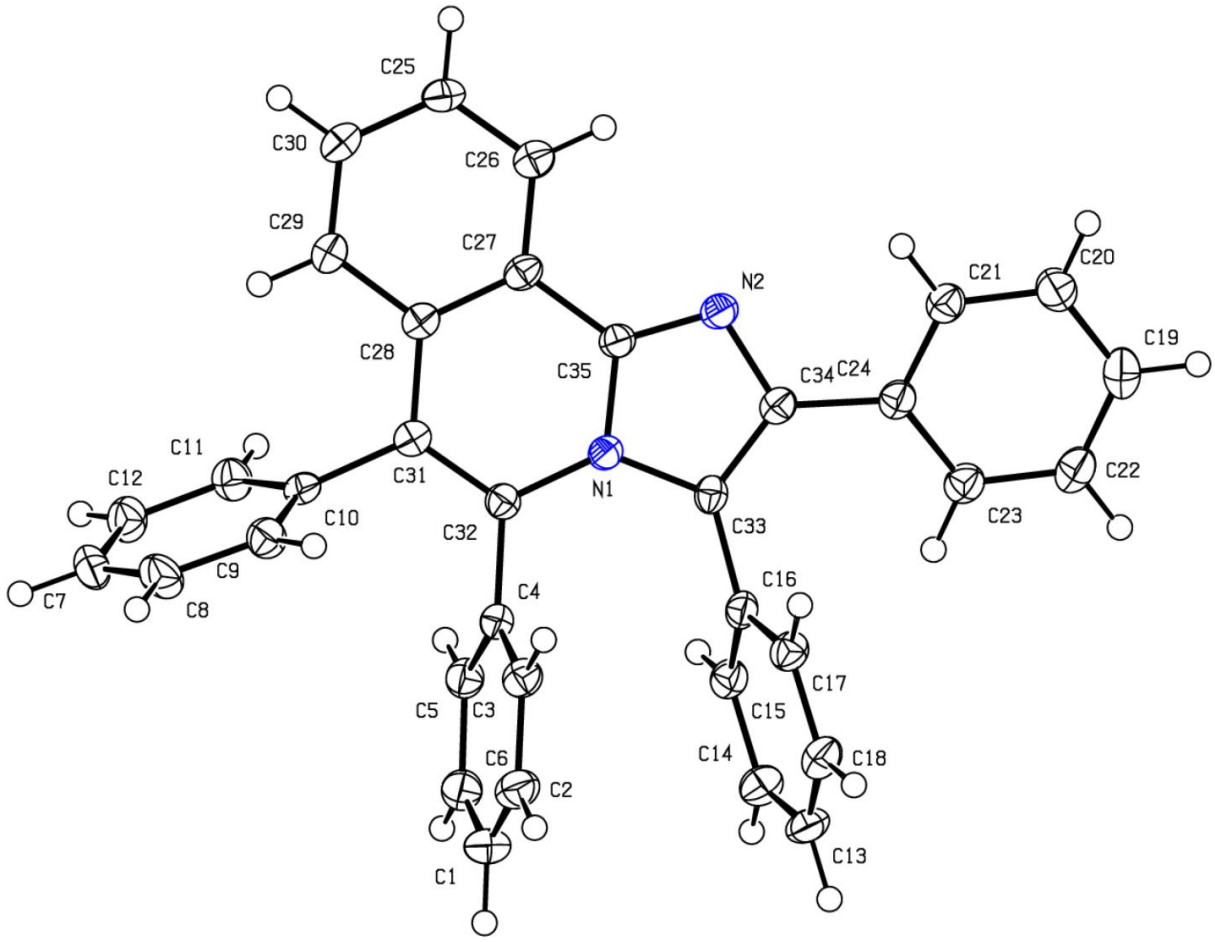


Figure S6 The molecular structure of **13'** (CCDC 2176134). Thermal ellipsoids are shown at the 50% probability level.

Table S15 **Crystal data and structure refinement for TYN-84.**

Identification code	TYN-84
Empirical formula	$C_{35}H_{24}N_2$
Formula weight	472.56
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	9.9002(17)
b/Å	10.9305(19)
c/Å	12.260(2)

α/°	109.205(7)
β/°	92.503(8)
γ/°	101.866(8)
Volume/Å^3	1217.2(4)
Z	2
ρ_{calc}g/cm^3	1.289
μ/mm^{-1}	0.075
F(000)	496.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.234 to 50.816
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -14 ≤ l ≤ 14
Reflections collected	13958
Independent reflections	4390 [R_{int} = 0.0806, R_{sigma} = 0.0805]
Data/restraints/parameters	4390/0/335
Goodness-of-fit on F^2	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.0748, wR_2 = 0.2064
Final R indexes [all data]	R_1 = 0.0897, wR_2 = 0.2274
Largest diff. peak/hole / e Å^{-3}	0.30/-0.37

Table S16 **Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for TYN-84. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.**

Atom	*x*	*y*	*z*	U(eq)
N1	7460.4(18)	5179.6(16)	4968.4(14)	20.6(5)
N2	7909.5(18)	7172.0(17)	4730.3(15)	22.0(5)
C10	6426(2)	3932.1(19)	7422.8(18)	21.6(5)
C24	8572(2)	6620(2)	2741.8(18)	22.6(5)
C27	7198(2)	7091(2)	6622.6(17)	21.1(5)
C7	5785(3)	2439(2)	8868(2)	30.0(6)

Table S16 **Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for TYN-84. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.**

Atom	*x*	*y*	*z*	U(eq)
C28	6838(2)	6235(2)	7259.1(18)	20.4(5)
C35	7517(2)	6537(2)	5449.7(18)	20.2(5)
C21	9187(2)	7962(2)	2959.9(19)	24.7(5)
C25	7047(2)	8986(2)	8269.4(19)	25.3(5)
C34	8120(2)	6217(2)	3733.0(18)	21.6(5)
C32	7090(2)	4319.7(19)	5603.4(18)	20.1(5)
C33	7857(2)	4978(2)	3845.9(17)	20.1(5)
C11	5087(2)	3669(2)	7731.8(19)	26.4(5)
C23	8360(2)	5742(2)	1587.2(18)	25.8(5)
C30	6728(2)	8154(2)	8927.4(19)	25.6(5)
C4	7074(2)	2884(2)	5037.1(17)	21.2(5)
C16	8005(2)	3702(2)	2995.2(17)	21.4(5)
C31	6780(2)	4820(2)	6715.7(18)	21.3(5)
C5	5812(2)	1943(2)	4658.3(18)	24.8(5)
C9	7436(2)	3428(2)	7834.3(19)	26.0(5)
C3	8310(2)	2471(2)	4883.8(18)	24.2(5)
C26	7281(2)	8462(2)	7127.4(19)	24.3(5)
C22	8755(2)	6207(2)	697(2)	30.7(6)
C20	9562(2)	8425(2)	2067(2)	29.6(6)
C8	7108(3)	2694(2)	8561(2)	32.0(6)
C6	5792(2)	610(2)	4103.6(19)	28.7(6)
C29	6610(2)	6802(2)	8431.8(18)	23.2(5)
C15	6853(2)	2677(2)	2401.3(18)	23.7(5)
C2	8283(2)	1138(2)	4348.9(19)	29.6(6)
C17	9324(2)	3531(2)	2732.6(18)	24.3(5)

Table S16 **Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for TYN-84. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.**

Atom	*x*	*y*	*z*	U(eq)
C19	9344(2)	7545(2)	926(2)	31.8(6)
C12	4763(2)	2918(2)	8448(2)	29.9(6)
C13	8337(3)	1350(2)	1342.1(19)	28.9(6)
C1	7022(3)	199(2)	3951(2)	30.9(6)
C18	9492(2)	2367(2)	1917.1(19)	27.5(5)
C14	7021(2)	1512(2)	1586.5(19)	28.0(6)

Table S17 **Anisotropic Displacement Parameters (Å^2×10^3) for TYN-84. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.**

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N1	24.9(10)	20.4(9)	17.6(9)	6.1(7)	3.6(7)	8.1(8)
N2	25.0(10)	21.4(9)	19.5(9)	5.4(7)	2.4(7)	7.5(7)
C10	25.8(12)	17.5(10)	18.0(10)	2.2(8)	3.2(8)	4.2(9)
C24	23.2(11)	26.2(11)	20.7(11)	8.6(9)	3.6(9)	9.6(9)
C27	20.0(11)	23.1(11)	19.3(11)	4.6(9)	1.5(9)	7.7(9)
C7	35.0(14)	29.2(12)	31.9(12)	17.8(10)	9.9(10)	7.2(10)
C28	18.6(11)	22.4(11)	19.7(10)	5.6(9)	1.3(8)	6.2(9)
C35	22.4(11)	19.1(10)	18.8(10)	5.3(8)	1.9(8)	6.0(8)
C21	25.1(12)	26.7(11)	23.0(11)	7.9(9)	4.2(9)	8.5(9)
C25	28.5(12)	18.5(10)	25.1(11)	2.3(9)	3.0(9)	5.8(9)
C34	22.0(11)	23.3(10)	19.6(10)	6.1(8)	3.4(8)	7.2(9)
C32	18.9(11)	20.6(11)	21.3(11)	7.7(9)	3.5(8)	4.9(9)
C33	20.2(11)	23.3(11)	16.5(10)	7.2(8)	1.2(8)	3.9(9)
C11	25.8(12)	28.8(11)	26.9(11)	11.9(9)	1.7(9)	8.0(9)
C23	27.3(12)	27.8(11)	23.0(11)	7.9(9)	2.7(9)	9.7(9)

Table S17 **Anisotropic Displacement Parameters ($Å^2×10^3$) for TYN-84. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.**

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C30	26.1(12)	27.7(11)	19.6(10)	2.7(9)	3.9(9)	7.5(9)
C4	26.1(12)	20.7(10)	17.5(10)	6.9(8)	3.8(8)	6.5(9)
C16	24.7(12)	24.5(10)	17.1(10)	8.6(8)	4.6(9)	7.6(9)
C31	20.9(11)	21.4(11)	20.5(10)	5.7(9)	2.2(8)	5.3(9)
C5	24.8(12)	25.7(11)	23.4(11)	8.5(9)	3.9(9)	5.0(9)
C9	24.3(12)	26.8(11)	28.6(11)	10.8(9)	6.3(9)	7.2(9)
C3	24.0(12)	25.5(11)	22.0(11)	6.6(9)	0.9(9)	6.5(9)
C26	23.7(12)	24.5(11)	23.4(11)	5.8(9)	1.8(9)	7.3(9)
C22	33.5(13)	38.0(13)	22.1(11)	9.1(10)	5.3(10)	13.2(11)
C20	30.3(13)	29.4(12)	32.6(12)	14.3(10)	6.9(10)	8.1(10)
C8	34.3(14)	31.4(12)	39.8(13)	19.9(11)	6.3(11)	14.8(10)
C6	31.5(13)	25.0(11)	26.0(11)	6.9(9)	4.2(10)	1.7(10)
C29	22.9(11)	26.8(11)	20.0(11)	7.4(9)	4.5(9)	6.5(9)
C15	24.6(12)	26.3(11)	20.9(10)	8.1(9)	2.8(9)	7.5(9)
C2	34.4(14)	28.3(11)	26.2(12)	6.2(9)	4.1(10)	13.1(10)
C17	23.3(12)	25.0(11)	21.2(10)	5.5(9)	2.2(9)	2.9(9)
C19	30.5(13)	42.2(14)	29.7(12)	19.5(11)	8.5(10)	10.8(11)
C12	27.5(13)	33.4(12)	31.8(12)	14.4(10)	9.4(10)	7.4(10)
C13	39.0(14)	23.9(11)	20.8(11)	1.2(9)	3.5(10)	11.7(10)
C1	37.9(14)	21.4(11)	31.7(12)	5.0(9)	5.3(10)	9.7(10)
C18	27.5(12)	32.8(12)	23.0(11)	7.8(9)	5.6(9)	11.3(10)
C14	27.8(13)	27.8(12)	24.4(11)	4.4(9)	1.2(9)	5.6(10)

Table S18 **Bond Lengths for TYN-84.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C35	1.393(3)	C32	C4	1.489(3)
N1	C32	1.410(3)	C32	C31	1.367(3)
N1	C33	1.407(3)	C33	C16	1.481(3)
N2	C35	1.316(3)	C11	C12	1.392(3)
N2	C34	1.379(3)	C23	C22	1.387(3)
C10	C11	1.394(3)	C30	C29	1.379(3)
C10	C31	1.502(3)	C4	C5	1.393(3)
C10	C9	1.386(3)	C4	C3	1.389(3)
C24	C21	1.397(3)	C16	C15	1.397(3)
C24	C34	1.480(3)	C16	C17	1.394(3)
C24	C23	1.402(3)	C5	C6	1.386(3)
C27	C28	1.406(3)	C9	C8	1.390(3)
C27	C35	1.442(3)	C3	C2	1.382(3)
C27	C26	1.404(3)	C22	C19	1.387(3)
C7	C8	1.378(3)	C20	C19	1.389(3)
C7	C12	1.384(3)	C6	C1	1.382(3)
C28	C31	1.456(3)	C15	C14	1.383(3)
C28	C29	1.415(3)	C2	C1	1.393(3)
C21	C20	1.384(3)	C17	C18	1.383(3)
C25	C30	1.402(3)	C13	C18	1.390(3)
C25	C26	1.377(3)	C13	C14	1.383(3)
C34	C33	1.379(3)			

Table S19 **Bond Angles for TYN-84.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C35	N1	C32	121.41(17)	C12	C11	C10	120.8(2)

Table S19 **Bond Angles for TYN-84.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C35	N1	C33	105.58(17)	C22	C23	C24	120.2(2)
C33	N1	C32	133.00(17)	C29	C30	C25	120.46(19)
C35	N2	C34	105.78(17)	C5	C4	C32	120.05(19)
C11	C10	C31	119.95(19)	C3	C4	C32	120.47(19)
C9	C10	C11	119.0(2)	C3	C4	C5	119.48(19)
C9	C10	C31	120.89(19)	C15	C16	C33	121.98(19)
C21	C24	C34	118.25(19)	C17	C16	C33	119.53(18)
C21	C24	C23	118.1(2)	C17	C16	C15	118.43(19)
C23	C24	C34	123.58(19)	C28	C31	C10	118.41(18)
C28	C27	C35	118.65(19)	C32	C31	C10	120.71(18)
C26	C27	C28	120.78(19)	C32	C31	C28	120.8(2)
C26	C27	C35	120.5(2)	C6	C5	C4	120.2(2)
C8	C7	C12	119.6(2)	C10	C9	C8	119.8(2)
C27	C28	C31	119.43(19)	C2	C3	C4	120.0(2)
C27	C28	C29	118.13(19)	C25	C26	C27	119.9(2)
C29	C28	C31	122.4(2)	C19	C22	C23	120.9(2)
N1	C35	C27	119.95(19)	C21	C20	C19	119.9(2)
N2	C35	N1	112.20(17)	C7	C8	C9	121.1(2)
N2	C35	C27	127.83(19)	C1	C6	C5	120.3(2)
C20	C21	C24	121.4(2)	C30	C29	C28	120.6(2)
C26	C25	C30	120.14(19)	C14	C15	C16	120.7(2)
N2	C34	C24	119.03(18)	C3	C2	C1	120.5(2)
N2	C34	C33	110.95(19)	C18	C17	C16	120.82(19)
C33	C34	C24	130.02(19)	C22	C19	C20	119.3(2)
N1	C32	C4	118.32(17)	C7	C12	C11	119.7(2)
C31	C32	N1	119.71(18)	C14	C13	C18	119.66(19)

Table S19 **Bond Angles for TYN-84.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C31	C32	C4	122.0(2)	C6	C1	C2	119.5(2)
N1	C33	C16	126.48(18)	C17	C18	C13	120.1(2)
C34	C33	N1	105.49(17)	C15	C14	C13	120.3(2)
C34	C33	C16	128.0(2)				

Table S20 **Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for TYN-84.**

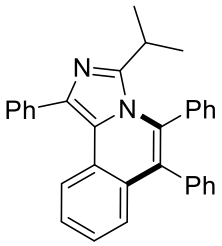
Atom	*x*	*y*	*z*	U(eq)
H7	5575.04	1936.27	9366.64	36
H21	9351.5	8569.02	3737.96	30
H25	7103	9914.02	8611.72	30
H11	4387.15	4006.65	7450.67	32
H23	7943.78	4824.57	1414.22	31
H30	6591.44	8525.18	9720.45	31
H5	4963.33	2215.54	4780.62	30
H9	8349.24	3584.62	7620.25	31
H3	9174.6	3105.96	5146.85	29
H26	7498.15	9026.42	6682.28	29
H22	8619.91	5600.98	-80.3	37
H20	9968.73	9342.85	2233.34	35
H8	7807.68	2362.88	8849.89	38
H6	4928.32	-24.12	3826.86	34
H29	6372.81	6245.19	8881.6	28
H15	5944.33	2781.52	2558.86	28
H2	9131.53	858.67	4251.57	35
H17	10118.69	4224.05	3118.73	29

Table S20 **Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for TYN-84.**

Atom	*x*	*y*	*z*	U(eq)
H19	9595.6	7857.59	308.76	38
H12	3844.21	2735.05	8646.21	36
H13	8450.59	547.65	783.88	35
H1	7007.45	-715.72	3578.44	37
H18	10397.49	2261.54	1749.64	33
H14	6229.28	819.6	1193.19	34

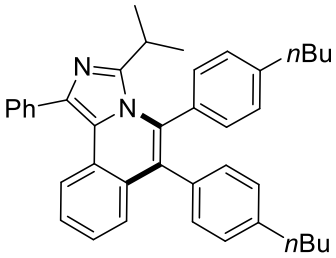
10 Experimental data for the described substances

3-isopropyl-1,5,6-triphenylimidazo[5,1-*a*]isoquinoline (3a)



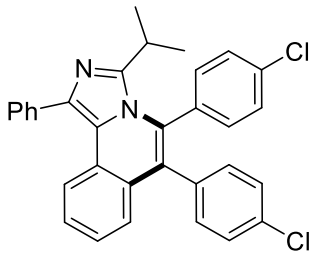
White solid (41 mg, 93% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 50/1, v/v). M.p.: 242.5–244.5 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 8.01 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 2H), 7.51 (t, J = 7.5 Hz, 2H), 7.43 (t, J = 7.5 Hz, 1H), 7.30–7.28 (m, 3H), 7.26–7.15 (m, 7H, cover the solvent), 7.15–7.20 (m, 3H), 7.11 (d, J = 7.0 Hz, 2H), 7.01 (d, J = 8.0 Hz, 1H), 2.13–2.07 (m, 1H), 1.08 (d, J = 6.5 Hz, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 148.94, 137.18, 136.74, 135.00, 134.15, 132.54, 131.40, 130.77, 130.23, 129.01, 128.81, 128.74, 128.16, 128.01, 127.82, 127.49, 127.03, 126.66, 126.08, 125.70, 123.99, 122.08, 27.47, 22.73 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{32}H_{27}N_2$ ($[M+H]^+$) 439.2174, found 439.2168.

5,6-bis(4-butylphenyl)-3-isopropyl-1-phenylimidazo[5,1-*a*]isoquinoline (3b)



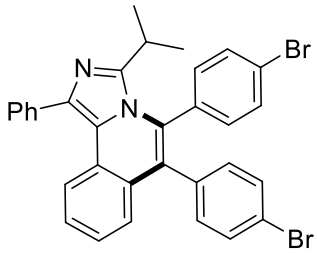
White solid (52 mg, 95% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc/CH_2Cl_2 = 40/2/1, v/v). M.p.: 115.8–117.8 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 8.00 (d, J = 7.5 Hz, 1H), 7.75 (d, J = 7.0 Hz, 2H), 7.51 (t, J = 7.5 Hz, 2H), 7.42 (t, J = 7.3 Hz, 1H), 7.21–7.14 (m, 4H), 7.08 (d, J = 7.5 Hz, 1H), 7.04–6.97 (m, 6H), 2.59–2.53 (m, 4H), 2.12–2.21 (m, 1H), 1.57–1.50 (m, 4H), 1.30–1.21 (m, 4H), 1.09 (d, J = 6.0 Hz, 6H), 0.90 (q, J = 7.2 Hz, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 148.78, 143.41, 141.44, 133.76, 132.68, 132.17, 131.13, 130.54, 130.30, 129.19, 128.83, 128.21, 127.97, 127.42, 126.77, 126.20, 125.47, 123.95, 122.07, 35.38, 33.56, 33.44, 29.84, 27.38, 22.67, 22.29, 21.92, 14.12, 14.06 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{40}H_{43}N_2$ ($[M+H]^+$) 551.3426, found 551.3428.

5,6-bis(4-chlorophenyl)-3-isopropyl-1-phenylimidazo[5,1-*a*]isoquinoline (3c)



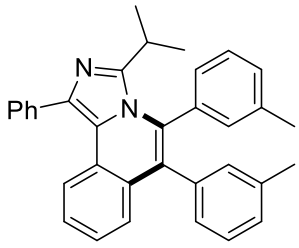
Grey solid (37 mg, 73% yield) via filtration. M.p.: 272.2–274.2 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 8.00 (d, J = 8.0 Hz, 1H), 7.74–7.72 (m, 2H), 7.51 (t, J = 7.5 Hz, 2H), 7.43 (t, J = 7.3 Hz, 1H), 7.29–7.27 (m, 2H), 7.25–7.20 (m, 5H), 7.19–7.15 (m, 1H), 7.02 (d, J = 8.5 Hz, 2H), 6.95 (d, J = 8.0 Hz, 1H), 2.15–2.10 (m, 1H), 1.11 (q, J = 6.5 Hz, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 148.69, 135.17, 134.88, 133.44, 133.16, 132.57, 131.95, 131.35, 130.21, 128.90, 128.82, 128.63, 128.53, 128.11, 128.02, 126.50, 126.40, 125.70, 123.99, 122.24, 27.68, 22.61 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{32}H_{25}Cl_2N_2$ ($[M+H]^+$) 507.1395, found 507.1397.

5,6-bis(4-bromophenyl)-3-isopropyl-1-phenylimidazo[5,1-*a*]isoquinoline (3d)



Yellow solid (55 mg, 92% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 60/1→40/1, v/v). M.p.: 285.0–287.0 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 8.00 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 7.0 Hz, 2H), 7.51 (t, J = 7.5 Hz, 2H), 7.45–7.39 (m, 5H), 7.24–7.15 (m, 4H), 6.97–6.94 (m, 3H), 2.17–2.09 (m, 1H), 1.12 (d, J = 7.0 Hz, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 148.63, 135.27, 133.52, 132.85, 132.17, 131.82, 131.61, 131.21, 130.23, 128.91, 128.45, 128.23, 128.11, 126.54, 125.62, 124.00, 123.47, 122.27, 121.71, 27.68, 22.56 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{32}H_{25}Br_2N_2$ ($[M+H]^+$) 597.0364, found 597.0365.

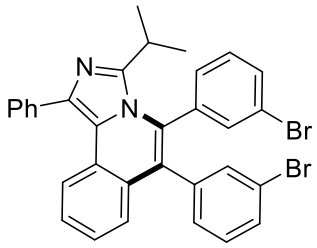
3-isopropyl-1-phenyl-5,6-di-m-tolylimidazo[5,1-*a*]isoquinoline (3e)



Yellow solid (34 mg, 72% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 80/1→60/1, v/v). M.p.: 171.5–173.5 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 8.01 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 2H), 7.51 (t, J = 7.5 Hz, 2H), 7.43 (t, J = 7.5 Hz, 1H), 7.21–7.10 (m, 5H), 7.08–7.04 (m, 3H), 7.00 (d, J = 7.5 Hz, 1H), 6.95–6.88 (m, 2H), 2.26 (t, J = 6.3 Hz, 6H), 2.16–2.09 (m, 1H), 1.12–1.09 (m, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 148.87, 137.74, 137.44, 136.49, 132.47, 132.05, 131.35, 131.27, 130.31, 129.44, 129.11, 128.83, 128.43, 128.36, 128.07, 127.99, 127.81, 127.48, 126.79, 126.22, 125.49,

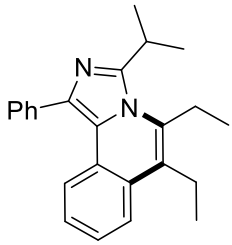
123.97, 122.09, 27.38, 22.72, 21.47, 21.43, 21.33, 21.32 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{34}H_{31}N_2$ ($[M+H]^+$) 467.2487, found 467.2490.

5,6-bis(3-bromophenyl)-3-isopropyl-1-phenylimidazo[5,1-*a*]isoquinoline (3f)



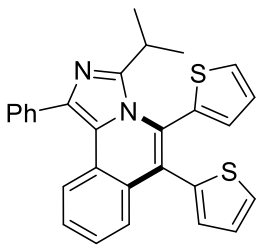
White solid (45 mg, 75% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 30/1, v/v). M.p.: 158.4–160.4 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 8.00–7.98 (m, 1H), 7.74 (d, J = 7.0 Hz, 2H), 7.54–7.51 (m, 3H), 7.47–7.45 (m, 2H), 7.38 (d, J = 9.5 Hz, 1H), 7.30–7.29 (m, 1H), 7.25–7.12 (m, 5H), 7.06–7.00 (m, 2H), 2.16–2.11 (m, 1H), 1.17–1.16 (m, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 148.54, 134.17, 134.04, 133.62, 133.42, 132.44, 132.41, 130.77, 130.32, 130.09, 129.97, 129.94, 129.86, 129.81, 129.75, 129.33, 129.17, 128.97, 128.24, 126.69, 123.89, 122.39, 122.35, 122.22, 27.62, 22.47 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{32}H_{25}Br_2N_2$ ($[M+H]^+$) 597.0364, found 597.0363.

5,6-diethyl-3-isopropyl-1-phenylimidazo[5,1-*a*]isoquinoline (3g)



Brown oil (31 mg, 91% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 80/1, v/v). **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.94 (d, J = 8.0 Hz, 1H), 7.69–7.67 (m, 3H), 7.47 (t, J = 7.5 Hz, 2H), 7.39 (t, J = 7.5 Hz, 1H), 7.34–7.31 (m, 1H), 7.15 (t, J = 7.0 Hz, 1H), 3.62–3.54 (m, 1H), 3.18 (q, J = 7.5 Hz, 2H), 2.93 (q, J = 7.5 Hz, 2H), 1.54 (d, J = 7.0 Hz, 6H), 1.36 (t, J = 7.3 Hz, 3H), 1.32 (t, J = 7.5 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 146.76, 131.11, 131.06, 130.36, 129.14, 128.98, 128.86, 128.40, 127.72, 127.39, 126.88, 124.34, 123.69, 122.77, 29.43, 23.43, 22.14, 21.04, 14.63, 14.17 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{24}H_{27}N_2$ ($[M+H]^+$) 343.2174, found 343.2176.

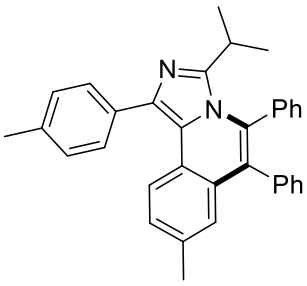
3-isopropyl-1-phenyl-5,6-di(thiophen-2-yl)imidazo[5,1-*a*]isoquinoline (3h)



Yellow solid (16 mg, 35% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 30/1→20/1, v/v). M.p.: 198.0–200.0 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.97–7.95 (m, 1H), 7.72 (d, J = 7.0 Hz, 2H), 7.50 (t, J = 7.5 Hz, 2H), 7.44–7.39 (m, 2H), 7.31 (d, J = 5.5 Hz, 1H), 7.22–7.20 (m, 3H), 7.09 (d, J = 3.0 Hz, 1H), 6.97 (t, J = 4.3 Hz, 2H),

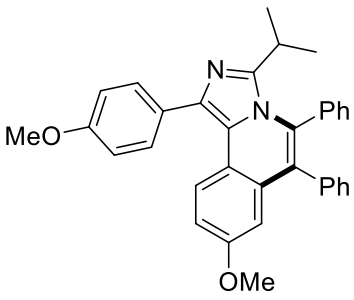
6.89 (d, *J* = 3.0 Hz, 1H), 2.22–2.14 (m, 1H), 1.24 (s, 3H) , 1.12 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 149.37, 137.05, 136.94, 135.12, 134.49, 130.93, 130.19, 130.04, 128.96, 128.85, 128.24, 127.92, 127.53, 126.81, 126.79, 126.70, 126.60, 126.28, 125.89, 123.96, 122.56, 122.02, 27.47, 23.48, 22.72 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{28}H_{23}N_2S_2$ ($[M+H]^+$) 451.1303, found 451.1302.

3-isopropyl-8-methyl-5,6-diphenyl-1-(*p*-tolyl)imidazo[5,1-*a*]isoquinoline (3i)



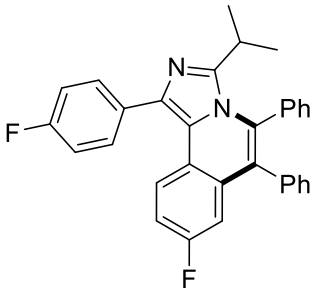
Yellow solid (41 mg, 88% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 40/1→20/1, v/v). M.p.: 235.7–237.7 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.61 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.28–7.26 (m, 3H), 7.24–7.22 (m, 5H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 6.5 Hz, 2H), 6.82 (s, 1H), 2.45 (s, 3H), 2.24 (s, 3H), 2.20–2.14 (m, 1H), 0.81 (d, *J* = 6.5 Hz, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 149.02, 140.26, 138.18, 135.41, 133.69, 132.00, 131.66, 131.46, 130.81, 130.44, 130.38, 130.14, 129.62, 129.01, 128.80, 128.27, 127.60, 127.20, 124.77, 122.37, 121.52, 26.02, 23.07, 21.69, 21.63 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{34}H_{31}N_2$ ($[M+H]^+$) 467.2487, found 467.2486.

3-isopropyl-8-methoxy-1-(4-methoxyphenyl)-5,6-diphenylimidazo[5,1-*a*]isoquinoline (3j)



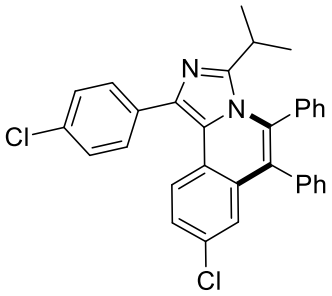
White solid (29 mg, 59% yield) via filtration. M.p.: 259.1–261.1 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.95 (d, *J* = 9.0 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.29–7.27 (m, 2H), 7.25–7.20 (m, 5H), 7.18–7.15 (m, 1H), 7.10–7.08 (m, 2H), 7.06–7.04 (m, 2H), 6.84 (dd, *J* = 9.0 Hz, 3.0 Hz, 1H), 6.48 (d, *J* = 2.5 Hz, 1H), 3.90 (s, 3H), 3.62 (s, 3H), 2.11–2.03 (m, 1H), 1.07 (d, *J* = 6.5 Hz, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 159.39, 157.80, 148.10, 136.68, 135.03, 133.08, 131.43, 131.33, 130.72, 130.67, 128.74, 128.15, 128.07, 127.09, 123.88, 123.60, 119.64, 115.10, 114.32, 110.15, 55.51, 55.27, 27.40, 22.74 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{34}H_{31}N_2O_2$ ($[M+H]^+$) 499.2386, found 499.2389.

8-fluoro-1-(4-fluorophenyl)-3-isopropyl-5,6-diphenylimidazo[5,1-*a*]isoquinoline (3k)



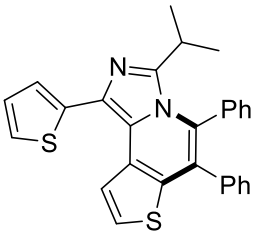
Yellow solid (38 mg, 80% yield), purification via a neutral alumina (200-300 mesh) gel column (petroleum ether/EtOAc = 20/1, v/v). M.p.: 195.0–197.0 ºC. **^{1}H NMR (500MHz, CDCl$_3$):** δ = 7.92–7.89 (m, 1H), 7.71–7.69 (m, 2H), 7.29–7.28 (m, 5H), 7.24–7.19 (m, 5H), 7.09–7.07 (m, 2H), 6.96 (td, J = 8.5 Hz, 2.3 Hz, 1H), 6.70 (dd, J = 10 Hz, 2.5 Hz, 1H), 2.12–2.05 (m, 1H), 1.10 (d, J = 5.5 Hz, 6H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$):** δ = 162.96(d, $J_{C\text{-}F}$ = 246.5 Hz), 161.20(d, $J_{C\text{-}F}$ = 244.1 Hz), 148.77, 135.87, 134.38, 133.57, 132.08(d, $J_{C\text{-}F}$ = 8.0 Hz), 131.23, 131.15, 130.55, 129.15, 128.37, 128.32, 127.50, 124.05(d, $J_{C\text{-}F}$ = 7.6 Hz), 123.71, 121.84, 116.04(d, $J_{C\text{-}F}$ = 21.5 Hz), 115.72, 112.48(d, $J_{C\text{-}F}$ = 23.3 Hz), 27.46, 22.63 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{32}H_{25}F_2N_2$ ([M+H]$^+$) 475.1986, found 475.1988.

8-chloro-1-(4-chlorophenyl)-3-isopropyl-5,6-diphenylimidazo[5,1-*a*]isoquinoline (3l)



White solid (38 mg, 76% yield) via filtration. M.p.: 225.4–227.4 ºC. **^{1}H NMR (500MHz, DMSO-*d*$_6$):** δ = 7.90 (d, J = 8.5 Hz, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 7.5 Hz, 2H), 7.47–7.45 (m, 3H), 7.32–7.18 (m, 8H), 6.78 (s, 1H), 1.98–1.96 (m, 1H), 0.97 (d, J = 6.5 Hz, 6H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 148.77, 135.20, 134.93, 133.55, 132.10, 131.22, 130.96, 130.82, 130.45, 130.31, 129.11, 128.90, 128.07, 128.00, 127.77, 127.39, 125.00, 123.11, 122.94, 122.63, 26.61, 22.54 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{32}H_{25}Cl_2N_2$ ([M+H]$^+$) 507.1395, found 507.1397.

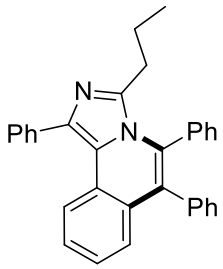
3-isopropyl-5,6-diphenyl-1-(thiophen-2-yl)imidazo[1,5-*a*]thieno[3,2-*c*]pyridine (3m)



Yellow solid (37 mg, 82% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 40/1, v/v). M.p.: 177.3–179.3 ºC. **^{1}H NMR (500MHz, CDCl$_3$):** δ = 7.56 (dd, J = 3.5 Hz, 1.0 Hz, 1H), 7.43 (dd, J = 5.0 Hz, 1.0 Hz, 1H), 7.29–7.27 (m, 5H), 7.23–7.17 (m, 4H), 7.12–7.10 (m, 3H), 6.73 (d, J = 5.5 Hz, 1H), 2.17–2.12 (m, 1H), 1.08 (d, J = 6.5 Hz, 6H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$):** δ = 148.56, 137.43, 137.11, 134.41, 134.31, 131.05, 130.92, 130.62, 128.92, 128.19, 128.02, 127.32, 127.14, 126.36, 126.20, 124.69, 124.31, 124.26,

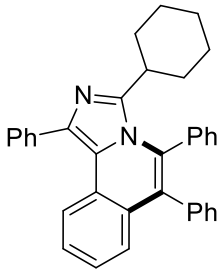
124.13, 122.92, 27.65, 22.65 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{28}H_{23}N_2S_2$ ($[M+H]^+$) 451.1303, found 451.1305.

1,5,6-triphenyl-3-propylimidazo[5,1-*a*]isoquinoline (3n)



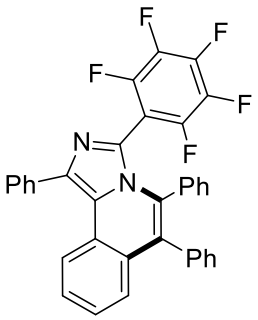
White solid (36 mg, 82% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc/CH_2Cl_2 = 40/1/1→20/1/1, v/v). M.p.: 162.8–164.8 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 8.09–8.07 (m, 1H), 7.74 (d, J = 7.5 Hz, 2H), 7.56 (t, J = 7.3 Hz, 2H), 7.51–7.48 (m, 1H), 7.29–7.22 (m, 10H, cover the solvent), 7.13–7.08 (m, 3H), 2.08–2.03 (m, 2H), 1.55–1.46 (m, 2H), 0.59 (t, J = 7.25 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 148.54, 134.17, 134.04, 133.62, 133.42, 132.44, 132.41, 130.77, 130.32, 130.09, 129.97, 129.94, 129.86, 129.81, 129.75, 129.33, 129.17, 128.97, 128.24, 126.69, 123.89, 122.39, 122.35, 122.22, 27.62, 22.47 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{32}H_{27}N_2$ ($[M+H]^+$) 439.2174, found 439.2175.

3-cyclohexyl-1,5,6-triphenylimidazo[5,1-*a*]isoquinoline (3o)



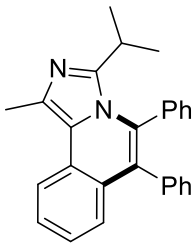
Yellow solid (31 mg, 64% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 50/1, v/v). M.p.: 253.3–255.3 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.99 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 2H), 7.50 (t, J = 7.5 Hz, 2H), 7.43–7.40 (m, 1H), 7.32–7.27 (m, 5H), 7.24–7.11 (m, 7H), 7.00 (d, J = 7.5 Hz, 1H), 1.61–1.53(m, 7H), 1.43–1.41 (m, 1H), 1.15–1.07 (m, 1H), 0.59–0.57 (m, 2H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 148.23, 137.42, 136.78, 135.17, 134.30, 132.68, 131.45, 130.81, 130.25, 129.03, 128.80, 128.65, 128.25, 128.03, 127.75, 127.46, 127.04, 126.63, 126.37, 126.01, 125.78, 123.76, 122.11, 37.45, 32.64, 26.40, 25.68 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{35}H_{31}N_2$ ($[M+H]^+$) 479.2487, found 479.2486.

3-(perfluorophenyl)-1,5,6-triphenylimidazo[5,1-*a*]isoquinoline (3p)



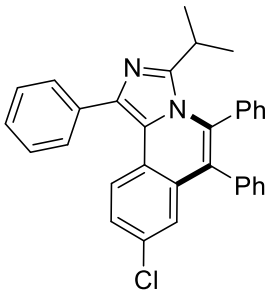
White solid (55 mg, 99% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 50/1, v/v). M.p.: 112.2–114.2 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 8.24 (dd, J = 8.0 Hz, 1.0 Hz, 1H), 7.83–7.81 (m, 2H), 7.55 (t, J = 7.5 Hz, 2H), 7.48 (t, J = 7.5 Hz, 1H), 7.37–7.30 (m, 2H), 7.25–7.19 (m, 4H), 7.15–7.11 (m, 4H), 7.02–7.01 (m, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 135.70, 132.19, 131.63, 131.13, 130.66, 130.06, 129.46, 129.11, 129.11, 128.95, 128.50, 128.20, 128.18, 127.69, 127.52, 127.49, 127.18, 126.29, 125.60, 124.76, 122.71 ppm. **^{19}F NMR (471 MHz, CDCl3):** δ = -135.35, -152.50, -162.91 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{35}H_{20}F_5N_2$ ($[M+H]^+$) 563.1547, found 563.1545.

3-isopropyl-1-methyl-5,6-diphenylimidazo[5,1-*a*]isoquinoline (3q)



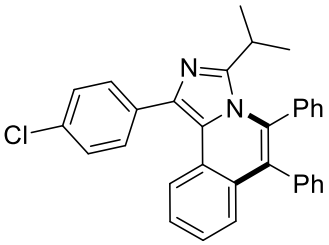
Yellow solid (19 mg, 51% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 30/1, v/v). M.p.: 191.9–193.9 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 8.16 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 7.8 Hz, 1H), 7.22–7.15 (m, 9H), 7.08–7.07 (m, 2H), 7.02 (d, J = 8.0 Hz, 1H), 2.86 (s, 3H), 2.06–2.00 (m, 1H), 1.03 (d, J = 7.0 Hz, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 147.61, 136.88, 135.14, 132.65, 131.43, 130.71, 129.89, 128.87, 128.66, 128.14, 128.02, 127.90, 126.98, 126.76, 126.62, 126.33, 125.20, 123.74, 122.17, 27.17, 22.74, 17.30 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{27}H_{25}N_2$ ($[M+H]^+$) 377.2018, found 377.2019.

8-chloro-3-isopropyl-1,5,6-triphenylimidazo[5,1-*a*]isoquinoline (3r)



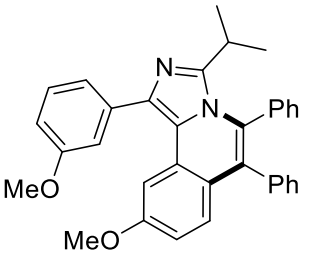
Yellow solid (19 mg, 40% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 60/1, v/v). M.p.: 229.9–231.9 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.93 (d, J = 8.5 Hz, 1H), 7.73 (d, J = 7.5 Hz, 2H), 7.53 (t, J = 7.5 Hz, 2H), 7.46 (t, J = 7.3 Hz, 1H), 7.27 (s, 5H), 7.25–7.17 (m, 4H), 7.09–7.07 (m, 2H), 6.98 (s, 1H), 2.13–2.08 (m, 1H), 1.13 (d, J = 5.5 Hz, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 148.98, 135.68, 134.32, 133.50, 132.26, 131.18, 130.56, 130.24, 129.17, 129.03, 128.50, 128.39, 128.32, 128.07, 127.53, 126.15, 123.83, 123.63, 123.44, 27.47, 22.58 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{32}H_{26}ClN_2$ ($[M+H]^+$) 473.1785, found 437.1786.

1-(4-chlorophenyl)-3-isopropyl-5,6-diphenylimidazo[5,1-*a*]isoquinoline (3r')

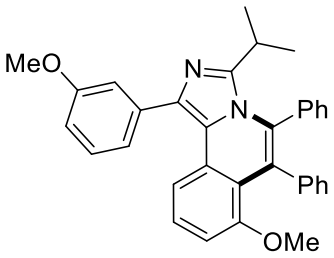


Yellow solid (23 mg, 48% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 80/1, v/v). M.p.: 230.7–232.7 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.98 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 7.0 Hz, 2H), 7.27–7.26 (m, 6H, cover the solvent), 7.24–7.18 (m, 4H), 7.11–7.09 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 1H), 2.13–2.09 (m, 1H), 1.12 (d, *J* = 6.0 Hz, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 148.94, 134.57, 132.37, 131.73, 131.70, 131.25, 131.22, 130.69, 129.16, 129.13, 129.07, 129.02, 128.37, 128.33, 128.12, 127.84, 127.24, 126.96, 124.25, 122.08, 27.46, 22.57 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{32}H_{26}ClN_2$ ($[M+H]^+$) 473.1785, found 437.1787.

3-isopropyl-9-methoxy-1-(3-methoxyphenyl)-5,6-diphenylimidazo[5,1-*a*]isoquinoline (3s) and 3-isopropyl-7-methoxy-1-(3-methoxyphenyl)-5,6-diphenylimidazo[5,1-*a*]isoquinoline (3s')



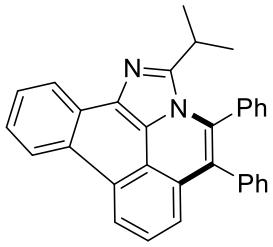
3s



3s'

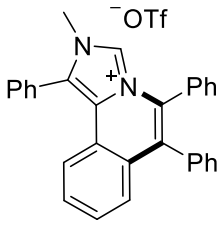
Yellow solid (47 mg, 95% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 20/1, v/v). **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.51 (s, 1H), 7.44 (t, *J* = 7.5 Hz, 1.24H), 7.37 (d, *J* = 7.0 Hz, 1H), 7.37–7.18 (m, 10.39H), 7.11–7.06 (m, 2.4H), 6.99–6.94 (m, 2H), 6.77 (d, *J* = 8.5 Hz, 0.94H), 3.89 (s, 3.3H), 3.55 (s, 3H), 3.24 (s, 0.3H), 2.14–2.12 (m, 1H), 2.06 (s, 0.09H), 1.11–1.06 (m, 6.6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 159.94, 158.92, 148.67, 136.80, 134.96, 131.26, 131.19, 130.94, 130.41, 130.23, 129.75, 129.62, 128.70, 128.49, 128.25, 128.15, 127.98, 127.01, 126.71, 126.61, 125.50, 123.99, 122.99, 122.77, 115.65, 115.51, 114.32, 104.40, 55.92, 55.51, 55.17, 27.40, 27.34, 22.78, 22.64 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{34}H_{31}N_2O_2$ ($[M+H]^+$) 499.2386, found 499.2387.

2-isopropyl-4,5-diphenyldibenzo[*de*,*g*]imidazo[4,5,1-*ij*]quinoline (3t)



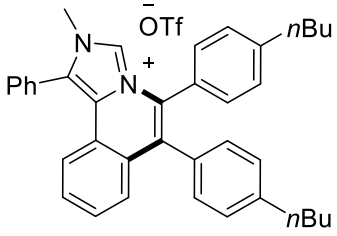
Yellow solid (40 mg, 90% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 50/1, v/v). M.p.: 250.2–252.2 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 8.85 (d, J = 7.5 Hz, 1H), 8.80 (d, J = 8.5 Hz, 1H), 8.69 (d, J = 8.0 Hz, 1H), 7.78 (t, J = 7.3 Hz, 1H), 7.72–7.65 (m, 2H), 7.41–7.39 (m, 2H), 7.34–7.28 (m, 5H), 7.25–7.22 (m, 4H), 2.48–2.39 (m, 1H), 1.26 (d, J = 6.5 Hz, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 152.18, 136.09, 133.86, 133.47, 131.15, 130.99, 129.30, 128.60, 128.41, 128.32, 127.87, 127.73, 127.38, 127.32, 125.96, 125.48, 125.07, 124.12, 123.20, 121.73, 121.39, 119.72, 27.69, 22.84 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{32}H_{25}N_2$ ([M+H]$^+$) 437.2018, found 437.2016.

2-methyl-1,5,6-triphenyl-2*H*-imidazo[5,1-*a*]isoquinolin-4-ium trifluoromethanesulfonate (4a)



White solid (41 mg, 73% yield), purification via a silica (100-200 mesh) gel column (CH_2Cl_2/CH_3OH = 90/1→80/1, v/v). M.p.: 263.7–265.7 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 8.85 (s, 1H), 7.75–7.66 (m, 5H), 7.54 (d, J = 8.0 Hz, 1H), 7.46–7.36 (m, 8H), 7.32–7.29 (m, 3H), 7.20–7.18 (m, 2H), 3.87 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 134.11, 131.71, 131.25, 130.77, 130.67, 130.62, 130.50, 130.44, 129.89, 129.79, 129.73, 129.37, 128.58, 128.35, 128.33, 128.06, 127.67, 126.00, 125.69, 123.17, 122.07, 119.50, 35.65 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{30}H_{23}N_2^+$ ([M−OTf$^-$]$^+$) 411.1856, found 411.1852.

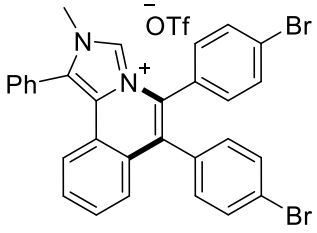
2,6-dimethyl-1,5-diphenyl-2*H*-imidazo[5,1-*a*]isoquinolin-4-ium trifluoromethanesulfonate (4b)



Yellow solid (66 mg, 99% yield), purification via a silica (100-200 mesh) gel column (CH_2Cl_2/CH_3OH = 40/1, v/v). M.p.: 214.2–216.2 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 8.87 (s, 1H), 7.73–7.66 (m, 5H), 7.53 (d, J = 8.0 Hz, 1H), 7.45–7.42 (m, 2H), 7.36–7.34 (m, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.11–7.09 (m, 2H), 7.06–7.05 (m, 2H), 3.88 (s, 3H), 2.60–2.57 (m, 4H), 1.60–1.53 (m, 4H), 1.34–1.26 (m, 4H), 0.91 (td, J = 7.3 Hz, 1.7 Hz, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 145.41, 142.95, 131.66, 131.34,

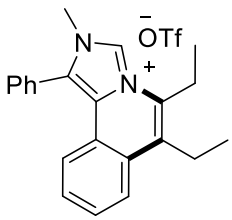
131.25, 130.67, 130.60, 130.48, 130.42, 130.12, 129.65, 129.60, 129.16, 128.51, 128.11, 127.56, 127.09, 126.09, 125.68, 123.11, 122.09, 121.98, 119.54, 35.64, 35.54, 35.41, 33.45, 33.16, 22.39, 22.28, 14.07, 14.04 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{38}H_{39}N_2^+$ ([M−OTf$^-$]$^+$) 523.3108, found 523.3110.

5,6-bis(4-bromophenyl)-2-methyl-1-phenyl-2*H*-imidazo[5,1-*a*]isoquinolin-4-ium trifluoromethanesulfonate (4c)



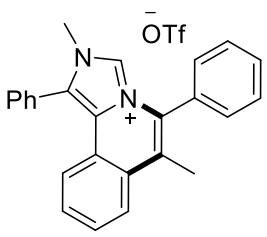
Yellow solid (46 mg, 64% yield), purification via a silica (100-200 mesh) gel column (CH_2Cl_2/CH_3OH = 60/1→50/1, v/v). M.p.: > 290.0 ºC. **^{1}H NMR (500MHz, DMSO-*d*$_6$):** δ = 9.41 (s, 1H), 7.81–7.80 (m, 3H), 7.76–7.72 (m, 4H), 7.32–7.29 (m, 3H), 7.63–7.58 (m, 3H), 7.54 (td, *J* = 7.5 Hz, 1.2 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 3H), 7.27–7.25 (m, 2H), 7.23 (dd, *J* = 8.5 Hz, 0.8 Hz, 1H), 3.77 (s, 3H) ppm. **^{13}C NMR (125 MHz, DMSO-*d*$_6$):** δ = 133.19, 132.78, 132.66, 132.45, 131.58, 131.48, 130.93, 130.21, 129.90, 129.60, 129.41, 129.29, 129.00, 128.92, 128.19, 127.27, 127.08, 125.82, 124.42, 124.01, 122.21, 121.84, 121.75, 34.77 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{30}H_{23}N_2^+$ ([M−OTf$^-$]$^+$) 569.0046, found 569.0044.

5,6-diethyl-2-methyl-1-phenyl-2*H*-imidazo[5,1-*a*]isoquinolin-4-ium trifluoromethanesulfonate (4d)



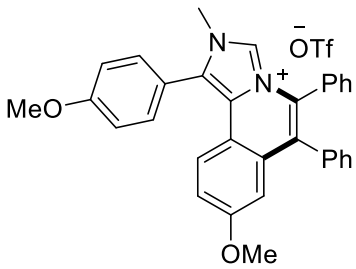
Yellow solid (41 mg, 89% yield), purification via a silica (100-200 mesh) gel column (CH_2Cl_2/CH_3OH = 80/1→60/1, v/v). M.p.: 206.5–208.5 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 10.09 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.73–7.69 (m, 3H), 7.63–7.59 (m, 1H), 7.54–7.52 (m, 2H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.34–7.30 (m, 1H), 4.01 (s, 3H), 3.27 (q, *J* = 7.5 Hz, 2H), 3.01 (q, *J* = 7.5 Hz, 2H), 1.47 (t, *J* = 7.5 Hz, 3H), 1.33 (t, *J* = 7.5 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 131.59, 131.49, 130.88, 130.38, 129.86, 128.38, 127.53, 127.29, 126.92, 126.08, 125.19, 124.79, 123.37, 121.62, 119.46, 35.19, 21.68, 20.91, 14.33, 11.60 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{22}H_{23}N_2^+$ ([M−OTf$^-$]$^+$) 315.1856, found 315.1858.

2,6-dimethyl-1,5-diphenyl-2*H*-imidazo[5,1-*a*]isoquinolin-4-ium trifluoromethanesulfonate (4e)



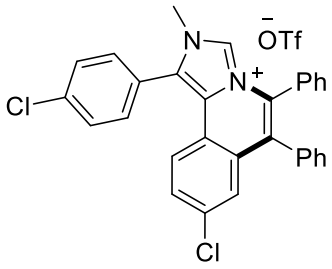
White solid (42 mg, 84% yield), purification via a silica (100-200 mesh) gel column (CH_2Cl_2/CH_3OH/ EtOAc = 80/1/2→60/1/2, v/v). M.p.: 229.1–231.1 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 8.67 (s, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.72–7.68 (m, 5H), 7.66–7.59 (m, 6H), 7.51 (d, J = 8.0 Hz, 1H), 7.40–7.37 (m, 1H), 3.83 (s, 3H), 2.35 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 131.65, 131.20, 131.14, 130.48, 130.41, 130.37, 130.21, 129.95, 129.68, 129.60, 129.25, 127.82, 127.49, 126.08, 125.47, 125.42, 123.76, 123.41, 121.98, 35.47, 15.55 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{25}H_{21}N_2^+$ ([M−OTf$^-$]$^+$) 349.1699, found 349.1697.

8-methoxy-1-(4-methoxyphenyl)-2-methyl-5,6-diphenyl-2*H*-imidazo[5,1-*a*]isoquinolin-4-ium trifluoromethanesulfonate (4f)



White solid (50 mg, 81% yield), purification via a silica (100-200 mesh) gel column (CH_2Cl_2/CH_3OH = 100/1, v/v). M.p.: 237.4–239.4 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 8.77 (s, 1H), 7.57–7.53 (m, 3H), 7.43–7.42 (m, 4H), 7.40–7.38 (m, 1H), 7.31–7.29 (m, 3H), 7.21–7.17 (m, 4H), 6.97 (dd, J = 9.0 Hz, 2.5 Hz, 1H), 6.77 (d, J = 2.5 Hz, 1H), 3.96 (s, 3H), 3.85 (s, 3H), 3.67 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 161.95, 160.38, 134.18, 132.77, 131.82, 130.87, 130.70, 130.59, 130.47, 130.24, 129.89, 129.71, 128.62, 128.39, 127.50, 125.99, 124.84, 117.66, 117.26, 115.84, 115.71, 111.17, 55.71, 55.48, 35.41 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{32}H_{27}N_2O_2^+$ ([M−OTf$^-$]$^+$) 471.2067, found 471.2066.

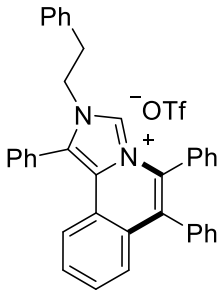
8-chloro-1-(4-chlorophenyl)-2-methyl-5,6-diphenyl-2*H*-imidazo[5,1-*a*]isoquinolin-4-ium trifluoromethanesulfonate (4g)



Yellow solid (52 mg, 82% yield), purification via a silica (100-200 mesh) gel column (CH_2Cl_2/CH_3OH = 80/1→60/1, v/v). M.p.: > 290.0 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 8.72 (s, 1H), 7.68 (q, J = 8.0 Hz, 4H), 7.46–7.42 (m, 3H), 7.39–7.31 (m, 8H), 7.17–7.15 (m, 2H), 3.80 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 138.35, 136.13, 133.36, 132.76, 131.54, 131.49, 130.89, 130.66, 130.56, 129.82,

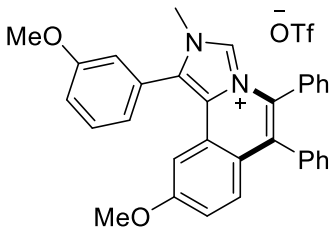
129.68, 129.65, 129.53, 128.78, 128.66, 128.64, 127.57, 126.58, 125.40, 124.41, 124.15, 120.33, 35.64 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{30}H_{21}Cl_2N_2^+$ ([M−OTf$^-$]$^+$) 479.1076, found 479.1074.

2-phenethyl-1,5,6-triphenyl-2*H*-imidazo[5,1-*a*]isoquinolin-4-ium trifluoromethanesulfonate (4h)

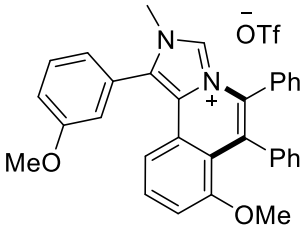


White solid (63 mg, 97% yield), purification via a silica (100-200 mesh) gel column (CH_2Cl_2/CH_3OH = 100/1, v/v). M.p.: 214.9–216.9 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 8.29 (s, 1H), 7.78–7.71 (m, 3H), 7.64–7.62 (m, 2H), 7.48–7.43 (m, 2H), 7.38–7.33 (m, 5H), 7.32–7.28 (m, 3H), 7.25–7.16 (m, 7H), 6.91–6.90 (m, 2H), 4.55 (t, *J* = 7.0 Hz, 2H), 2.91 (t, *J* = 7.0 Hz, 2H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 135.93, 134.05, 131.75, 131.42, 130.72, 130.56, 130.50, 130.40, 130.33, 129.90, 129.70, 129.61, 129.37, 129.13, 128.87, 128.56, 128.34, 128.06, 127.60, 127.48, 127.02, 125.99, 125.57, 123.21, 122.14, 122.07, 119.52, 49.74, 36.24 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{37}H_{29}N_2^+$ ([M−OTf$^-$]$^+$) 501.2325, found 501.2323.

9-methoxy-1-(3-methoxyphenyl)-2-methyl-5,6-diphenyl-2*H*-imidazo[5,1-*a*]isoquinolin-4-ium trifluoromethanesulfonate (4i) and 7-methoxy-1-(3-methoxyphenyl)-2-methyl-5,6-diphenyl-2*H*-imidazo[5,1-*a*]isoquinolin-4-ium trifluoromethanesulfonate (4i')



4i

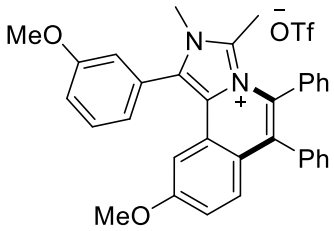


4i'

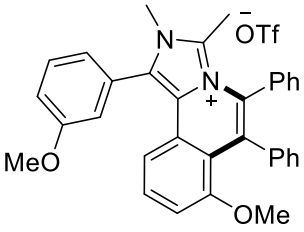
Yellow solid (48 mg, 77% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/MeOH = 80/1→60/1, v/v). **^{1}H NMR (500MHz, $CDCl_3$):** δ = 8.74 (s, 1H), 8.60 (s, 1H), 7.62–7.57 (m, 1H + 1H), 7.46–7.45 (m, 1H + 1H), 7.38–7.27 (m, 8H + 8H), 7.24–7.10 (m, 5H + 5H), 7.07–7.05 (m, 1H + 1H), 7.02–7.00 (m, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 3.89–3.88 (m, 6H + 3H), 3.81 (s, 3H), 3.50 (s, 3H), 3.31 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 160.82, 159.90, 157.49, 138.32, 134.22, 131.35, 131.23, 130.81, 130.78, 130.63, 130.59, 130.20, 130.00, 129.98, 129.63, 129.50, 129.44, 129.29, 128.79, 128.46, 128.35, 128.15, 127.55, 127.42, 127.32, 127.22, 127.11, 127.05, 127.02, 126.52, 125.38, 125.31, 123.69, 123.39, 123.30, 123.10, 122.93,

121.93, 119.00, 118.57, 117.77, 117.68, 116.07, 115.94, 115.87, 112.45, 105.35, 55.81, 55.73, 55.10, 35.45 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{32}H_{27}N_2O_2$ ([M−OTf$^-$]$^+$) 471.2067, found 471.2069.

9-methoxy-1-(3-methoxyphenyl)-2,3-dimethyl-5,6-diphenyl-2*H*-imidazo[5,1-*a*]isoquinolin-4-ium trifluoromethanesulfonate (4j) and 7-methoxy-1-(3-methoxyphenyl)-2,3-dimethyl-5,6-diphenyl-2*H*-imidazo[5,1-*a*]isoquinolin-4-ium trifluoromethanesulfonate (4j')



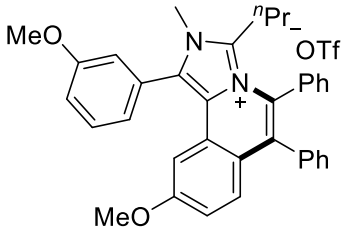
4j



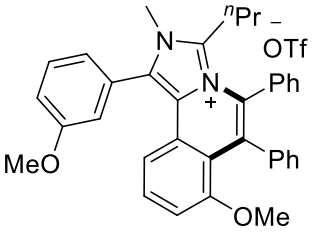
4j'

White solid (62 mg, 99% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/MeOH = 80/1→60/1, v/v). **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.60–7.54 (m, 2H), 7.44–7.43 (m, 1H), 7.36–7.33 (m, 3H), 7.30–7.28 (m, 4.7H), 7.25–7.17 (m, 9.88H), 7.12–7.00 (m, 8.9H), 6.93–6.90 (m, 2H), 6.85 (d, *J* = 8.0 Hz, 1H), 3.87 (d, *J* = 3.0 Hz, 6H), 3.74 (s, 3H), 3.67 (s, 2.75H), 3.43 (s, 3H), 3.25 (s, 2.68H), 2.11 (s, 3H), 2.04 (s, 2.7H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 161.04, 161.01, 159.89, 157.24, 138.86, 137.72, 137.62, 134.91, 132.32, 132.20, 132.09, 132.02, 131.75, 131.60, 131.35, 131.23, 130.65, 130.59, 130.52, 129.75, 129.66, 129.57, 129.24, 129.00, 128.67, 128.46, 128.37, 128.32, 128.23, 128.19, 127.80, 126.98, 126.85, 126.60, 126.39, 126.26, 125.15, 124.41, 123.98, 123.46, 123.22, 122.98, 118.32, 118.05, 117.95, 116.17, 116.05, 116.00, 112.24, 105.30, 55.92, 55.83, 55.04, 33.81, 33.75, 13.87, 13.67 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{33}H_{29}N_2O_2$ ([M−OTf$^-$]$^+$) 485.2224, found 485.2225.

7-methoxy-1-(3-methoxyphenyl)-2-methyl-5,6-diphenyl-3-propyl-2*H*-imidazo[5,1-*a*]isoquinolin-4-ium trifluoromethanesulfonate (4k) and 9-methoxy-1-(3-methoxyphenyl)-2-methyl-5,6-diphenyl-3-propyl-2*H*-imidazo[5,1-*a*]isoquinolin-4-ium trifluoromethanesulfonate (4k')



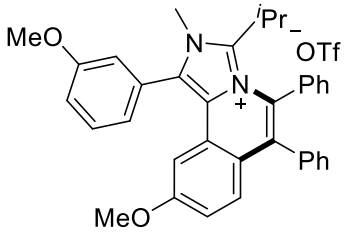
4k



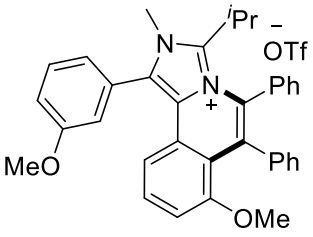
4k'

Yellow solid (47 mg, 71% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/MeOH = 80/1→60/1, v/v). **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.61–7.56 (m, 1.7H), 7.51 (d, J = 2.5 Hz, 1.17H), 7.43–7.37 (m, 3.3H), 7.34–7.29 (m, 5.16H), 7.22–7.18 (m, 4.43H), 7.11 (d, J = 7.5 Hz, 1.82H), 7.06–7.02 (m, 3H), 6.99 (d, J = 7.0 Hz, 0.35H), 6.93–6.91 (m, 1.93H), 6.85 (d, J = 8.0 Hz, 0.31H), 3.91 (s, 3.97H), 3.80 (s, 3H), 3.73 (s, 1H), 3.43 (s, 3H), 3.24 (s, 0.96H), 2.59–2.52 (m, 1.08H), 2.44–2.37 (m, 1.3H), 2.31–2.26 (m, 0.39H), 1.71–1.60 (m, 2.51H), 0.55 (t, J = 6.8 Hz, 4.08H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 161.17, 159.97, 141.12, 135.04, 132.19, 132.11, 132.02, 131.99, 131.56, 131.35, 131.24, 130.67, 130.58, 130.51, 129.80, 129.76, 129.64, 129.60, 129.28, 128.88, 128.82, 128.66, 128.58, 128.51, 128.43, 128.37, 128.29, 128.16, 127.79, 127.07, 126.86, 126.75, 126.51, 125.46, 124.13, 123.31, 123.07, 123.04, 118.44, 118.27, 116.19, 116.14, 112.26, 105.33, 56.04, 56.00, 55.95, 55.07, 33.69, 33.63, 27.76, 27.70, 21.32, 21.30, 13.67, 13.63 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{35}H_{33}N_2O_2$ ([M−OTf$^-$]$^+$) 513.2537, found 513.2539.

3-isopropyl-9-methoxy-1-(3-methoxyphenyl)-2-methyl-5,6-diphenyl-2*H*-imidazo[5,1-*a*]isoquinolin-4-ium trifluoromethanesulfonate (4l) and 3-isopropyl-7-methoxy-1-(3-methoxyphenyl)-2-methyl-5,6-diphenyl-2*H*-imidazo[5,1-*a*]isoquinolin-4-ium trifluoromethanesulfonate (4l')



4l

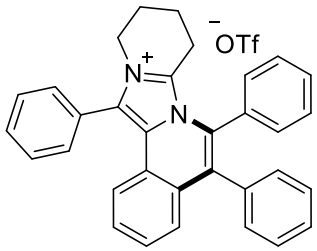


4l'

White solid (61 mg, 91% yield), purification via a silica (200-300 mesh) gel column (CH_2Cl_2/MeOH = 70/1, v/v). **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.60 (t, J = 8.0 Hz, 1H), 7.57–7.55 (m, 0.28H), 7.51 (d, J = 7.5 Hz, 1H), 7.47 (s, 1H), 7.43 (d, J = 7.5 Hz, 0.38H), 7.39 (s, 0.28H),

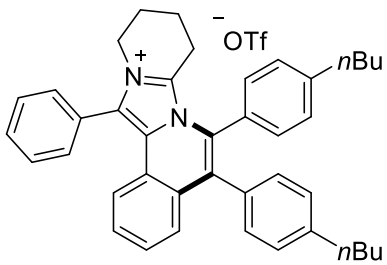
7.35–7.28 (m, 5H), 7.25–7.21 (m, 5H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.09 (m, 0.21H), 7.07–7.00 (m, 3H), 6.90 (d, *J* = 9.0 Hz, 1H), 6.86 (s, 1H), 6.83 (s, 0.13H), 3.92 (s, 3.6H), 3.88 (s, 3H), 3.81 (s, 0.6H), 3.41 (s, 3H), 3.23 (s, 0.6H), 3.15–3.08 (m, 1.1H), 3.06–3.02 (m, 0.26H), 1.25 (d, *J* = 7.0 Hz, 3H), 1.19 (d, *J* = 7.0 Hz, 3.58H), 1.15 (d, *J* = 7.5 Hz, 0.63H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 161.31, 160.02, 157.25, 143.75, 138.96, 135.18, 133.44, 133.38, 132.70, 131.35, 131.26, 131.00, 130.96, 130.69, 130.62, 130.57, 130.51, 130.05, 129.64, 129.43, 129.21, 129.04, 128.81, 128.53, 128.43, 128.32, 128.26, 128.13, 127.75, 127.10, 126.79, 126.30, 125.71, 124.16, 123.33, 123.08, 122.94, 122.19, 119.64, 118.82, 118.55, 118.51, 118.47, 116.18, 116.07, 115.89, 112.41, 105.32, 56.17, 56.08, 55.98, 55.03, 35.16, 25.60, 25.45, 18.91, 18.43, 18.39 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{35}H_{33}N_2O_2$ ([M−OTf$^-$]$^+$) 513.2537, found 513.2537.

5,6,13-triphenyl-8,9,10,11-tetrahydropyrido[2',1':2,3]imidazo[5,1-*a*]isoquinolin-12-ium trifluoromethanesulfonate (5a)



Yellow solid (38 mg, 63% yield), purification via a silica (100-200 mesh) gel column (CH_2Cl_2/CH_3OH = 80/1, v/v). M.p.: 256.9–258.9 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.74–7.69 (m, 5H), 7.47–7.43 (m, 3H), 7.37–7.28 (m, 5H), 7.25–7.22 (m, 3H), 7.13 (d, *J* = 6.5 Hz, 3H), 4.01–3.99 (m, 2H), 2.36–2.33 (m, 2H), 2.01–2.00 (m, 2H), 1.83–1.82 (m, 2H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 138.35, 136.13, 133.36, 132.76, 131.54, 131.49, 130.89, 130.66, 130.56, 129.82, 129.68, 129.65, 129.53, 128.78, 128.66, 128.64, 127.57, 126.58, 125.40, 124.41, 124.15, 120.33, 35.64 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{33}H_{27}N_2^+$ ([M−OTf$^-$]$^+$) 451.2169, found 451.2173.

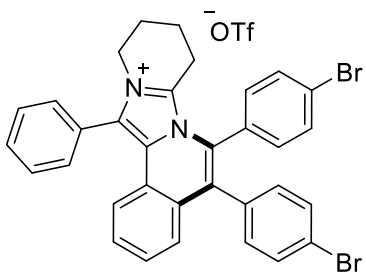
5,6-bis(4-butylphenyl)-13-phenyl-8,9,10,11-tetrahydropyrido[2',1':2,3]imidazo[5,1-*a*]isoquinolin-12-ium trifluoromethanesulfonate (5b)



Brown solid (55 mg, 77% yield), purification via a silica (100-200 mesh) gel column (CH_2Cl_2/CH_3OH = 100/1, v/v). M.p.: 154.4–156.4 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.73–7.67 (m, 5H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 2H), 7.24–7.19 (m, 2H), 7.08 (d, *J* = 7.5 Hz, 2H), 7.04–6.99 (m, 4H), 3.99 (t, *J* = 5.8 Hz, 2H), 2.58–2.53 (m, 4H), 2.37 (t, *J* = 6.3 Hz, 2H), 2.02–2.00 (m, 2H),

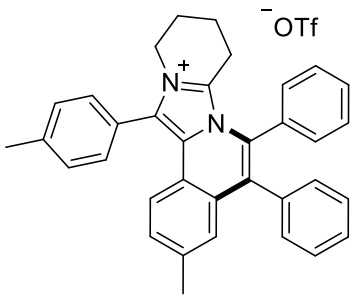
1.82–1.80 (m, 2H), 1.56–1.50 (m, 4H), 1.27–1.23 (m, 4H), 0.91–0.88 (m, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 144.66, 142.30, 138.32, 131.96, 131.83, 131.53, 131.48, 131.19, 130.63, 130.32, 129.73, 129.47, 129.06, 128.87, 128.27, 128.18, 127.69, 127.00, 125.69, 125.35, 123.29, 122.60, 46.28, 35.42, 35.36, 33.47, 33.27, 25.18, 22.25, 22.10, 20.73, 18.90, 14.05, 14.01 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{41}H_{43}N_2^+$ ([M−OTf$^-$]$^+$) 563.3421, found 563.3423.

5,6-bis(4-bromophenyl)-13-phenyl-8,9,10,11-tetrahydropyrido[2',1':2,3]imidazo[5,1-*a*]isoquinolin-12-ium trifluoromethanesulfonate (5c)



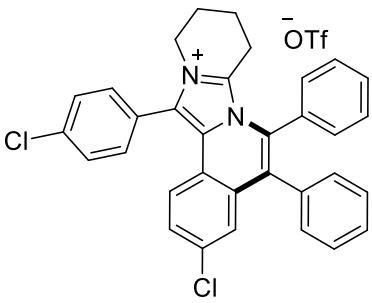
Yellow solid (51 mg, 67% yield), purification via a silica (100-200 mesh) gel column (CH_2Cl_2/CH_3OH = 80/1, v/v). M.p.: 186.0–188.0 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.71–7.67 (m, 5H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.43–7.34 (m, 6H), 7.29–7.26 (m, 1H, cover the solvent), 7.07 (d, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 2H), 3.96 (t, *J* = 5.8 Hz, 2H), 2.37 (t, *J* = 6.3 Hz, 2H), 2.04–1.99 (m, 2H), 1.87–1.84 (m, 2H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 138.48, 133.60, 132.38, 131.85, 131.80, 131.45, 131.34, 130.94, 130.63, 130.39, 130.33, 129.42, 129.28, 129.00, 127.37, 126.80, 125.96, 125.39, 124.69, 123.45, 122.78, 122.45, 46.34, 25.44, 20.60, 18.92 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{33}H_{25}Br_2N_2^+$ ([M−OTf$^-$]$^+$) 609.0359, found 609.0360.

3-methyl-5,6-diphenyl-13-(*p*-tolyl)-8,9,10,11-tetrahydropyrido[2',1':2,3]imidazo[5,1-*a*]isoquinolin-12-ium trifluoromethanesulfonate (5d)



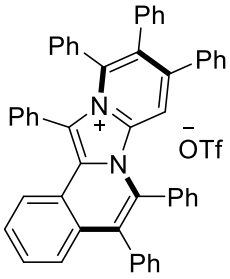
Yellow solid (45 mg, 72% yield), purification via a silica (100-200 mesh) gel column (CH_2Cl_2/CH_3OH = 100/1→80/1, v/v). M.p.: 120.3–122.3 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.58 (d, *J* = 8.0 Hz, 2H), 7.47–7.42 (m, 4H), 7.38 (d, *J* = 8.5 Hz, 1H), 7.29–7.28 (m, 3H), 7.25–7.20 (m, 3H), 7.13–7.10 (m, 3H), 6.90 (s, 1H), 3.98 (t, *J* = 5.8 Hz, 2H), 2.52 (s, 3H), 2.31 (t, *J* = 6.5 Hz, 2H), 2.26 (s, 3H), 2.00–1.97 (m, 2H), 1.81–1.79 (m, 2H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 141.44, 139.43, 137.93, 134.89, 132.29, 132.04, 131.33, 131.31, 131.00, 130.82, 130.44, 129.78, 129.51, 128.97, 128.31, 128.24, 127.76, 127.47, 125.50, 125.19, 123.87, 123.30, 120.35, 46.19, 25.08, 21.77, 20.73, 18.97 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{35}H_{31}N_2^+$ ([M−OTf$^-$]$^+$) 479.2482, found 479.2483.

3-chloro-13-(4-chlorophenyl)-5,6-diphenyl-8,9,10,11-tetrahydropyrido[2',1':2,3]imidazo[5,1-*a*]isoquinolin-12-ium trifluoromethanesulfonate (5e)



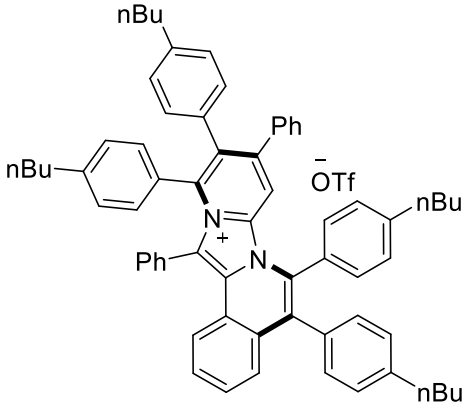
Pink solid (22 mg, 33% yield), purification via a silica (100-200 mesh) gel column (CH_2Cl_2/CH_3OH = 100/1→80/1, v/v). M.p.: > 290.0 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.72–7.71 (m, 2H), 7.67–7.65 (m, 2H), 7.45 (d, *J* = 6.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.33–7.27 (m, 5H), 7.25–7.24 (m, 2H), 7.12–7.10 (m, 3H), 3.97 (t, *J* = 5.8 Hz, 2H), 2.32 (t, *J* = 6.3 Hz, 2H), 2.03–1.98 (m, 2H), 1.82–1.77 (m, 2H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 139.18, 137.94, 135.54, 133.98, 133.02, 132.59, 131.89, 131.81, 131.15, 130.86, 130.70, 130.49, 130.06, 129.54, 128.51, 128.40, 128.19, 127.19, 125.13, 125.10, 124.66, 124.60, 120.91, 46.41, 25.16, 20.60, 18.82 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{33}H_{25}Cl_2N_2^+$ ([M−OTf^-]$^+$) 519.1389, found 519.1390.

5,6,9,10,11,13-hexaphenylpyrido[2',1':2,3]imidazo[5,1-*a*]isoquinolin-12-ium trifluoromethanesulfonate (6a)



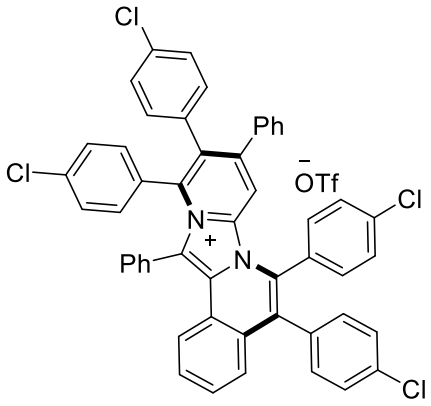
Yellow solid (69 mg, 84% yield), purification via a silica (100-200 mesh) gel column (CH_2Cl_2/CH_3OH = 100/1→80/1, v/v). M.p.: > 290.0 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.65–7.63 (m, 2H), 7.45–7.30 (m, 11H), 7.22–7.03 (m, 10H), 6.88–6.79 (m, 11H), 6.45 (s, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.33–7.27 (m, 5H), 7.25–7.24 (m, 2H), 7.12–7.10 (m, 3H), 3.97 (t, *J* = 5.8 Hz, 2H), 2.32 (t, *J* = 6.3 Hz, 2H), 2.03–1.98 (m, 2H), 1.82–1.77 (m, 2H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 145.01, 140.32, 137.74, 134.95, 134.75, 134.68, 134.53, 132.92, 132.70, 132.10, 132.02, 131.41, 131.32, 131.17, 131.04, 130.80, 130.25, 130.14, 129.90, 129.65, 129.48, 129.40, 128.92, 128.82, 128.63, 128.42, 128.24, 127.95, 127.86, 127.58, 127.43, 127.15, 124.95, 122.03, 121.21, 113.59 ppm. **^{19}F NMR(471 MHz, $CDCl_3$):** δ = -78.18 (s) ppm.**HRMS (ESI) *m/z*:** calcd for $C_{51}H_{35}N_2^+$ ([M−OTf^-]$^+$) 675.2795, found 675.2794.

5,6,10,11-tetrakis(4-butylphenyl)-9,13-diphenylpyrido[2',1':2,3]imidazo[5,1-*a*]isoquinolin-12-ium trifluoromethanesulfonate (6b)



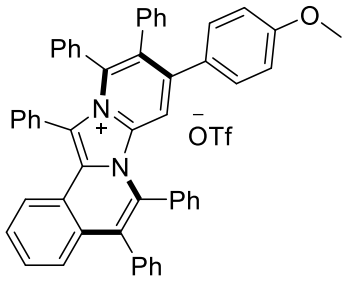
Yellow solid (48 mg, 46% yield), purification via a silica (100-200 mesh) gel column (CH_2Cl_2/CH_3OH = 100/1→80/1, v/v). M.p.: 85.2–87.2 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.48 (d, J = 8.0 Hz, 2H), 7.40 (t, J = 7.8 Hz, 1H), 7.31–7.27 (m, 4H), 7.22–7.18 (m, 4H), 7.16–7.09 (m, 6H), 7.02 (t, J = 7.8 Hz, 2H), 6.88–6.87 (m, 3H), 6.79 (d, J = 7.5 Hz, 2H), 6.64 (q, J = 10.8 Hz, 4H), 6.58–6.56 (m, 3H), 2.58 (t, J = 7.5 Hz, 2H), 2.51 (t, J = 8.0 Hz, 2H), 2.34–2.31 (m, 4H), 1.59–1.53 (m, 2H), 1.40–1.23 (m, 12H), 1.09–1.04 (m, 2H), 0.93–0.87 (m, 9H), 0.78 (t, J = 7.5 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 145.33, 145.08, 143.31, 142.48, 141.59, 140.59, 138.13, 134.78, 134.75, 133.08, 132.32, 132.26, 132.07, 131.96, 131.73, 131.17, 131.03, 130.95, 130.15, 130.02, 129.67, 129.65, 129.45, 129.44, 129.33, 128.90, 128.62, 128.39, 128.24, 128.05, 127.85, 127.66, 127.49, 127.40, 124.95, 122.06, 121.11, 113.52, 35 .55, 35.43, 35.38, 35.08, 33.48, 33.47, 33.24, 22.51, 22.33, 22.31, 21.85, 14.09, 14.07, 14.05, 13.97 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{67}H_{67}N_2^+$ ([M−OTf$^-$]$^+$) 899.5299, found 899.5301.

5,6,10,11-tetrakis(4-chlorophenyl)-9,13-diphenylpyrido[2',1':2,3]imidazo[5,1-*a*]isoquinolin-12-ium trifluoromethanesulfonate (6c)



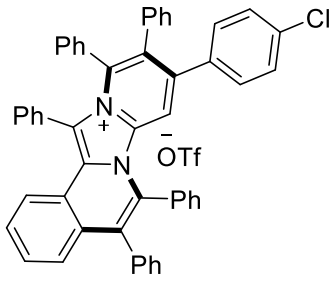
Yellow solid (50 mg, 53% yield), purification via a silica (100-200 mesh) gel column (CH_2Cl_2/CH_3OH = 80/1, v/v). M.p.: > 290.0 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.72–7.28 (m, 13H), 7.20–7.15 (m, 8H), 6.92–6.79 (m, 10H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 145.53, 139.68, 137.32, 137.04, 135.67, 135.17, 134.55, 133.90, 133.87, 133.72, 133.41, 133.21, 132.83, 132.80, 131.36, 131.23, 130.84, 130.53, 130.49, 130.04, 129.90, 129.73, 129.31, 129.24, 129.06, 128.71, 128.43, 128.36, 128.09, 127.98, 127.41, 125.19, 122.42, 122.09, 121.70 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{51}H_{31}Cl_2N_2^+$ ([M−OTf$^-$]$^+$) 813.1206, found 813.1204.

9-(4-methoxyphenyl)-5,6,10,11,13-pentaphenylpyrido[2',1':2,3]imidazo[5,1-*a*]isoquinolin-12-ium trifluoromethanesulfonate (6d)



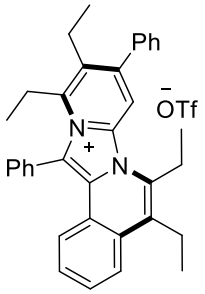
Yellow solid (49 mg, 57% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 2/1, v/v). M.p.: >290.0 ºC. **^{1}H NMR (500MHz, CDCl$_3$):** δ = 7.64 (d, J = 7.0 Hz, 2H), 7.45 (t, J = 7.5 Hz, 2H), 7.41–7.37 (m, 2H), 7.30–7.27 (m, 5H), 7.26–7.18 (m, 6H), 7.16–7.13 (m, 1H), 7.03–7.01 (m, 2H), 6.91–6.85 (m, 5H), 6.81–6.77 (m, 4H), 6.69 (d, J = 8.5 Hz, 2H), 6.56–6.53 (m, 3H), 3.69 (s, 3H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$):** δ = 159.65, 144.82, 140.31, 135.20, 134.96, 134.78, 134.52, 132.99, 132.82, 132.15, 132.09, 131.46, 131.39, 131.23, 131.10, 130.95, 130.93, 130.19, 130.15, 130.04, 129.87, 129.66, 129.54, 129.53, 129.47, 128.89, 128.78, 128.75, 128.43, 127.95, 127.58, 127.54, 127.45, 127.16, 124.95, 122.12, 121.09, 113.40, 113.12, 55.26 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{52}H_{37}N_2O^+$ ([M−OTf$^-$]$^+$) 705.2900, found 705.2902.

9-(4-chlorophenyl)-5,6,10,11,13-pentaphenylpyrido[2',1':2,3]imidazo[5,1-*a*]isoquinolin-12-ium trifluoromethanesulfonate (6e)



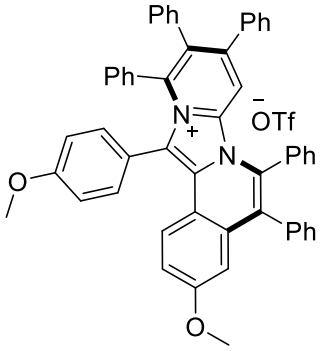
Yellow solid (48 mg, 55% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 1/1, v/v). M.p.: 273.8–275.8 ºC. **^{1}H NMR (500MHz, CDCl$_3$):** δ = 7.65 (d, J = 7.5 Hz, 2H), 7.45–7.35 (m, 5H), 7.32–7.27 (m, 5H), 7.24 (s, 2H), 7.21–7.14 (m, 4H), 7.05–7.00 (m, 4H), 6.90–6.85 (m, 5H), 6.82–6.73 (m, 6H), 6.50 (s, 1H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$):** δ = 143.65, 140.46, 136.39, 134.80, 134.77, 134.69, 134.49, 134.32, 132.98, 132.74, 132.13, 132.05, 131.45, 131.43, 131.16, 131.06, 130.74, 130.27, 130.18, 129.91, 129.72, 129.64, 129.46, 128.95, 128.82, 128.64, 128.44, 128.15, 127.99, 127.59, 127.45, 127.31, 124.99, 122.07, 121.35, 113.60 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{51}H_{34}ClN_2^+$ ([M−OTf$^-$]$^+$) 709.2405, found 709.2407.

5,6,10,11-tetraethyl-9,13-diphenylpyrido[2',1':2,3]imidazo[5,1-*a*]isoquinolin-12-ium trifluoromethanesulfonate (6f)



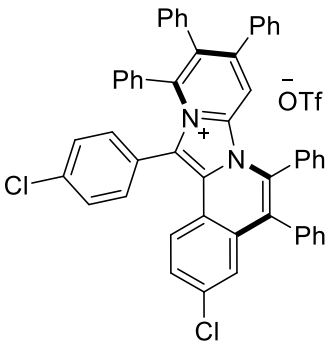
Yellow solid (35 mg, 55% yield), purification via a silica (100-200 mesh) gel column (CH_2Cl_2/CH_3OH = 80/1→60/1, v/v). M.p.: 177.0–179.0 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 8.21 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.82–7.77 (m, 3H), 7.74–7.71 (m, 2H), 7.61–7.58 (m, 1H), 7.56–7.48 (m, 5H), 7.18 (t, *J* = 7.8 Hz, 1H), 6.95 (d, *J* = 8.5 Hz, 1H), 3.46 (q, *J* = 7.5 Hz, 2H), 3.03 (q, *J* = 7.5 Hz, 2H), 2.91 (q, *J* = 7.3 Hz, 2H), 2.74 (q, *J* = 7.5 Hz, 2H), 1.54 (t, *J* = 7.5 Hz, 3H), 1.32 (t, *J* = 7.5 Hz, 3H), 1.03–0.97 (m, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 147.48, 143.62, 138.73, 133.79, 133.22, 133.17, 132.56, 131.84, 130.64, 130.44, 130.02, 129.77, 129.44, 129.00, 128.96, 128.69, 128.16, 126.68, 125.15, 124.44, 121.69, 119.70, 113.23, 22.89, 22.24, 21.95, 21.15, 14.80, 14.34, 13.86, 13.31 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{35}H_{35}N_2^+$ ([M−OTf$^-$]$^+$) 483.2795, found 483.2799.

3-methoxy-13-(4-methoxyphenyl)-5,6,9,10,11-pentaphenylpyrido[2',1':2,3]imidazo[5,1-*a*]isoquinolin-12-ium trifluoromethanesulfonate (6g)



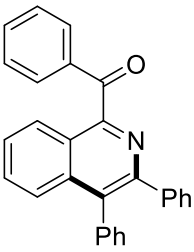
Yellow solid (57 mg, 64% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 1/1, v/v). M.p.: > 290.0 ºC. **^{1}H NMR (500MHz, $CDCl_3$):** δ = 7.63 (d, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.31–7.28 (m, 2H), 7.25–7.23 (m, 3H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.11–7.09 (m, 1H), 7.04–7.01 (m, 5H), 6.92–6.83 (m, 6H), 6.82–6.77 (m, 5H), 6.71 (d, *J* = 8.5 Hz, 2H), 6.66 (d, *J* = 3.0 Hz, 1H), 6.51 (s, 1H), 3.82 (s, 3H), 3.64 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 160.86, 160.47, 144.50, 140.23, 137.87, 135.07, 134.72, 134.61, 134.52, 134.49, 133.55, 132.83, 132.49, 132.18, 132.15, 131.37, 131.35, 131.21, 131.08, 131.07, 130.14, 129.67, 129.47, 128.59, 128.48, 128.17, 128.02, 127.86, 127.44, 127.43, 127.14, 126.87, 120.49, 119.69, 116.44, 115.60, 115.13, 113.57, 111.12, 55.55, 55.43 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{53}H_{39}N_2O_2^+$ ([M−OTf$^-$]$^+$) 735.3006, found 735.3005.

3-chloro-13-(4-chlorophenyl)-5,6,9,10,11-pentaphenylpyrido[2',1':2,3]imidazo[5,1-a]isoquinolin-12-ium trifluoromethanesulfonate (6h)



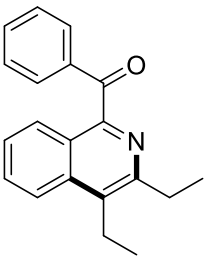
Yellow solid (70 mg, 77% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 3/2, v/v). M.p.: 156.4–158.4 ºC. **^{1}H NMR (500MHz, CDCl$_3$):** δ = 7.64 (d, J = 7.0 Hz, 2H), 7.42 (t, J = 7.5 Hz, 2H), 7.36–7.28 (m, 6H), 7.24–7.15 (m, 6H), 7.11 (t, J = 7.3 Hz, 1H), 7.05–6.98 (m, 5H), 6.94 (d, J = 9.0 Hz, 1H), 6.90–6.83 (m, 5H), 6.80–6.77 (m, 4H), 6.52 (s, 1H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$):** δ = 145.54, 140.32, 137.67, 136.83, 136.43, 135.18, 134.84, 134.78, 134.42, 134.01, 133.40, 133.16, 132.44, 132.25, 131.25, 131.17, 131.03, 130.94, 130.28, 129.78, 129.66, 129.41, 129.26, 128.87, 128.65, 128.58, 128.34, 128.28, 127.89, 127.62, 127.49, 127.27, 127.12, 127.00, 126.19, 120.39, 119.97, 113.69 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{51}H_{33}Cl_2N_2^+$ ([M−OTf$^-$]$^+$) 743.2015, found 743.2017.

(3,4-diphenylisoquinolin-1-yl)(phenyl)methanone (7a)



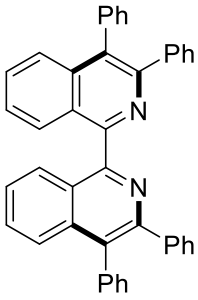
Yellow solid (20 mg, 55% yield), purification via a silica (200-300 mesh) gel column (petroleum ether/EtOAc = 60/1, v/v). **^{1}H NMR (500MHz, CDCl$_3$):** δ = 8.25 (d, J = 8.5 Hz, 1H), 8.13–8.11 (m, 2H), 7.76 (d, J = 8.5 Hz, 1H), 7.66–7.58 (m, 3H), 7.52 (t, J = 7.8 Hz, 2H), 7.43–7.38 (m, 5H), 7.32–7.31 (m, 2H), 7.18–7.17 (m, 3H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$):** δ = 194.87, 155.87, 148.97, 140.17, 137.15, 137.08, 136.78, 133.79, 132.53, 131.27, 131.13, 130.79, 130.51, 128.60, 128.56, 127.79, 127.44, 126.34, 126.14, 125.17 ppm. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in reference 13.

(3,4-diethylisoquinolin-1-yl)(phenyl)methanone (7b)



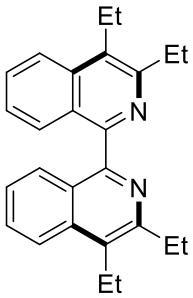
White oil (15 mg, 52% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 60/1, v/v). **^{1}H NMR (500MHz, CDCl$_3$):** δ = 8.15 (d, J = 8.0 Hz, 1H), 8.09 (d, J = 8.5 Hz, 1H), 7.99 (d, J = 7.5 Hz, 2H), 7.71 (t, J = 7.5 Hz, 1H), 7.59 (t, J = 13.5 Hz, 1H), 7.52–7.45 (m, 3H), 3.16 (q, J = 7.5 Hz, 2H), 3.03 (q, J = 7.5 Hz, 2H), 1.38–1.32 (m, 6H) ppm. **^{13}C NMR (125 MHz, CDCl$_3$):** δ = 195.25, 154.17, 152.59, 136.95, 135.88, 133.58, 131.53, 131.12, 130.31, 128.41, 126.75, 126.63, 124.99, 123.37, 28.31, 21.24, 15.20, 14.71 ppm. **HRMS (ESI) *m/z*:** calcd for $C_{20}H_{20}NO^+$ ([M+H]$^+$) 290.1545, found 290.1544.

3,3',4,4'-tetraphenyl-1,1'-biisoquinoline (8a)



Yellow solid (30 mg, 53% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 60/1→40/1, v/v). **^{1}H NMR (400MHz, $CDCl_3$):** δ = 8.09 (d, J = 6.8 Hz, 2H), 7.78 (d, J = 6.8 Hz, 2H), 7.63 (t, J = 5.8 Hz, 2H), 7.54 (t, J = 5.8 Hz, 2H), 7.44–7.39 (m, 10H), 7.35 (d, J = 5.2 Hz, 4H), 7.20–7.14 (m, 6H) ppm. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in reference 9.

3,3',4,4'-tetraethyl-1,1'-biisoquinoline (8b)



Yellow solid (15 mg, 41% yield), purification via a silica (100-200 mesh) gel column (petroleum ether/EtOAc = 60/1→40/1, v/v). **^{1}H NMR (400MHz, $CDCl_3$):** δ = 8.08 (d, J = 6.4 Hz, 2H), 7.67–7.63 (m, 4H), 7.35–7.32 (m, 2H), 3.20 (d, J = 6.0 Hz, 4H), 3.10–3.07 (m, 4H), 1.39 (t, J = 5.4 Hz, 12H) ppm. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in reference 9.

11 References

[1] Du, Y.; Hyster, T. K.; Rovis, T. Rhodium(III)-Catalyzed Oxidative Carbonylation of Benzamides with Carbon Monoxide. *Chem. Commun*. **2011**, *47*, 12074–12076.

[2] Villar, J. M.; Suárez, J.; Varela, J. A.; Saá, C. N-Doped Cationic PAHs by Rh(III)-Catalyzed Double C–H Activation and Annulation of 2-Arylbenzimidazoles with Alkynes. *Org. Lett*. **2017**, *19*, 1702–1705.

[3] Parthiban, D.; Karunakaran, R. J. Benzethonium Chloride Catalyzed one Pot Synthesis of 2,4,5-Trisubstituted Imidazoles and 1,2,4,5-Tetrasubstituted Imidazoles in Aqueous Ethanol As A Green Solvent. *Orient. J. Chem.* **2018**, *34*, 3004–3015.

[4] Reddy, M. V.; Jeong, Y. T. Indium Trifluoride: A Highly Efficient Catalyst for the Synthesis of Fluorine-Containing 2,4,5-Trisubstituted Imidazoles under Solvent-Free Conditions. *J. Fluo. Chem.* **2012**, *142*, 45–51.

[5] Fekri, L. Z.; Nateghi-Sabet, M. 1, 4-Diazabicyclo[2.2.2]octanium Diacetate: An Effective, Mild and Reusable Catalyst for the Synthesis of 2,4,5–Trisubstituted Imidazoles. *Chem Rev Lett.* **2021**, *4*, 37–42.

[6] Kumar, D.; Kommi, D. N.; Patela, A. R.; Chakraborti, A. K. Catalytic Procedures for Multicomponent Synthesis of Imidazoles: Selectivity Control during the Competitive Formation of Tri- and Tetrasubstituted Imidazoles. *Green Chem*. **2012**, *14*, 2038–2049.

[7] Gelens, E.; Kanter, F. J. J. D.; Schmitz, R. F.; Sliedregt, L. A. J. M.; Steen, B. J. V.; Kruse, C. G.; Leurs, R.; Groen, M. B.; Orru, R.V.A. Efficient Library Synthesis of Imidazoles Using a Multicomponent Reaction and Microwave Irradiation. *Mol. Divers.* **2006**, *10*, 17–22.

[8] Li, B.; Gu, Q.; Zhao, T.; He, Y.; Tong, Y.; Zhang, Y. Microwave-Assisted Synthesis of 2-Substituted-4,5-diarylimidazoles from Benzoin Carboxylate Derivatives under Solvent-Free Conditions. *Chin. J. Org. Chem.* **2012**, *32*, 1459–1467.

[9] Li, S.; Lv, H.; Xie, R.; Yu, Y.; Ye, X.; Kong, X. The C–H Activation/Bidirecting Group Strategy for Selective Direct Synthesis of Diverse 1,1′-Biisoquinolines. *Org. Lett.* **2020**, *22*, 4207−4212.

[10] Folkertsma, E.; Benthem, S. H.; Witteman, L.; van Slagmaat, C. A. M. R.; Lutz, M.; Klein Gebbink, R. J. M.; Moret, M.-E. Formation of Exceptionally Weak C–C Bonds by Metal-Templated Pinacol Coupling. *Dalton Trans.* **2017**, *46*, 6177–6182.

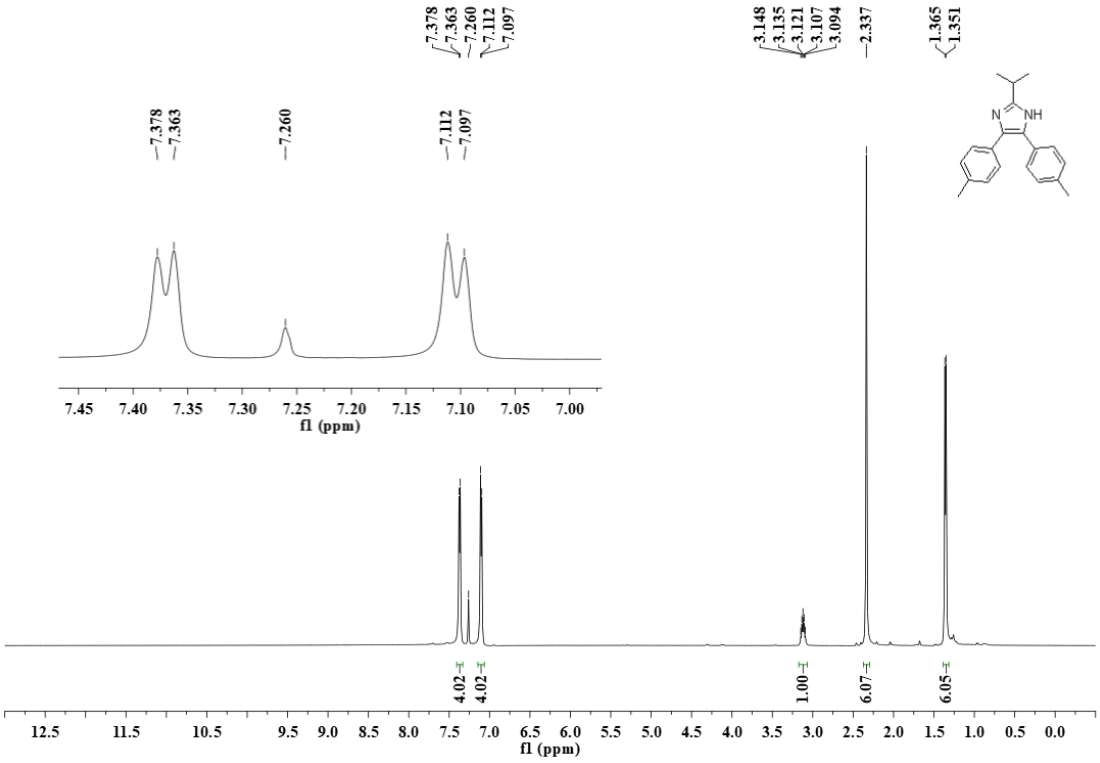
[11] Plummer, C. W.; Finke, P. E.; Mills, S. G.; Wang, J.; Tong, X.; Doss, G. A.; Fong, T. M.; Lao, J. Z.; Schaeffer, M.-T.; Chen, J.; Shen, C.-P.; Stribling, D. S.; Shearman, L. P.; Strackd, A. M.; Ploegc, L. H. T. V. Synthesis and Activity of 4,5-Diarylimidazoles as Human CB1 Receptor Inverse Agonists. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 1441–1446.

[12] Sharma, S. D.; Hazarika, P.; Konwar, D. An Efficient and One-Pot Synthesis of 2,4,5-Trisubstituted and 1,2,4,5-Tetrasubstituted Tmidazoles Catalyzed by $InCl_3 \cdot 3H_2O$. *Tetrahedron Letters* **2008**, *49*, 2216–2220.

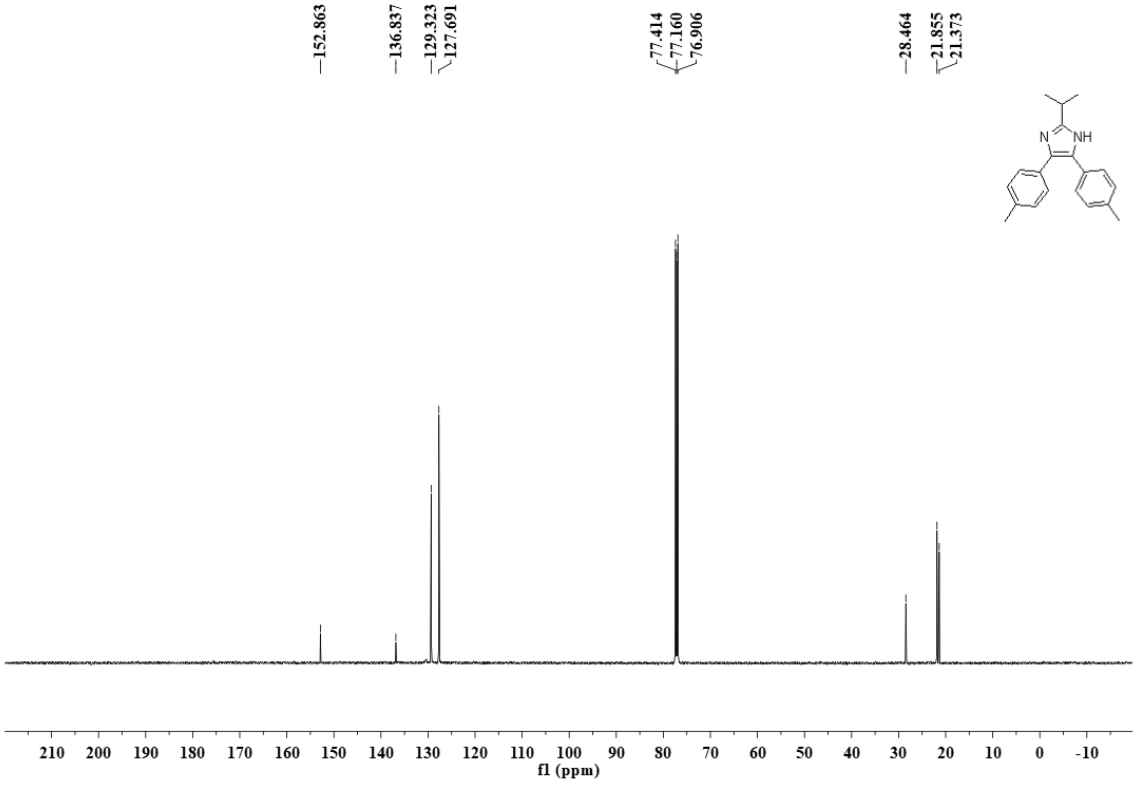
[13] Zhang, J.; Qian, H.; Liu, Z.; Xiong, C.; Zhang, Y. Rhodium(III)-Catalyzed One-Pot Access to Isoquinolines and Heterocycle-Fused Pyridines in Aqueous Medium through C–H Cleavage. *Eur. J. Org. Chem.* **2014**, 8110–8118.

12 Copies of ^{1}H and ^{13}C spectra

^{1}H NMR (500 MHz, $CDCl_3$) of **1b-A**



^{13}C NMR (125 MHz, $CDCl_3$) of **1b-A**



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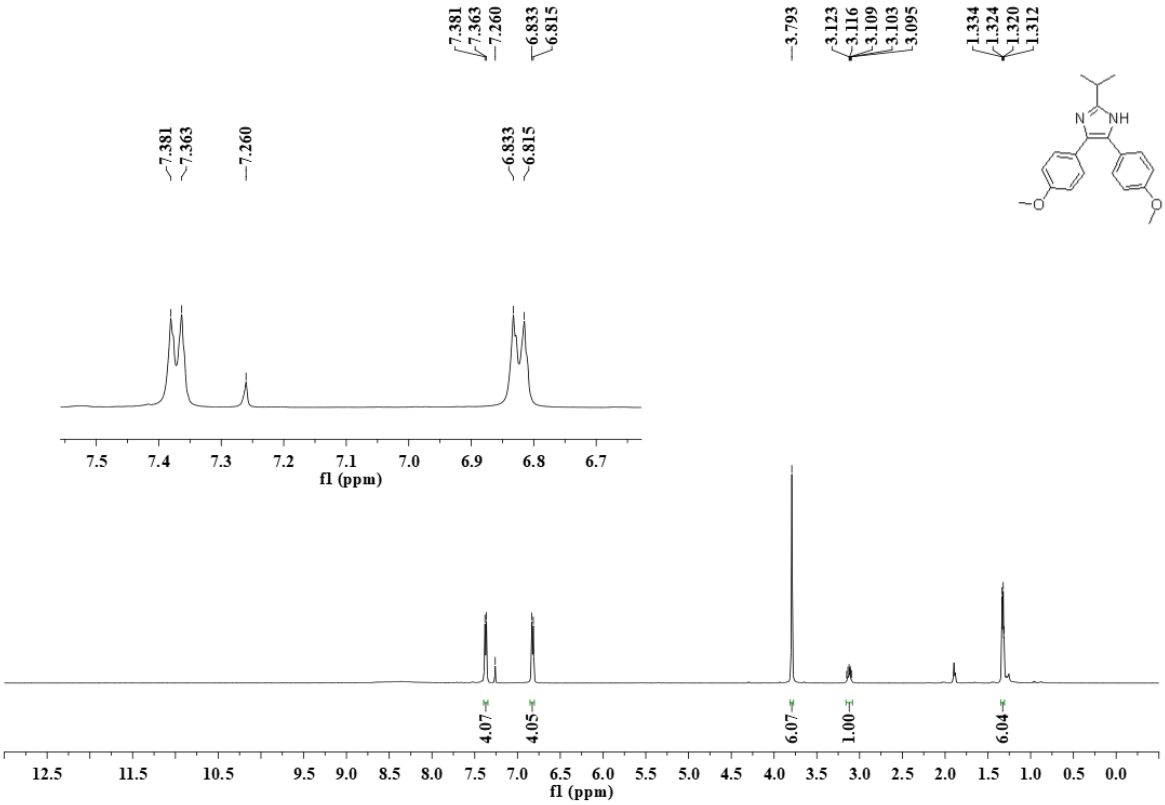
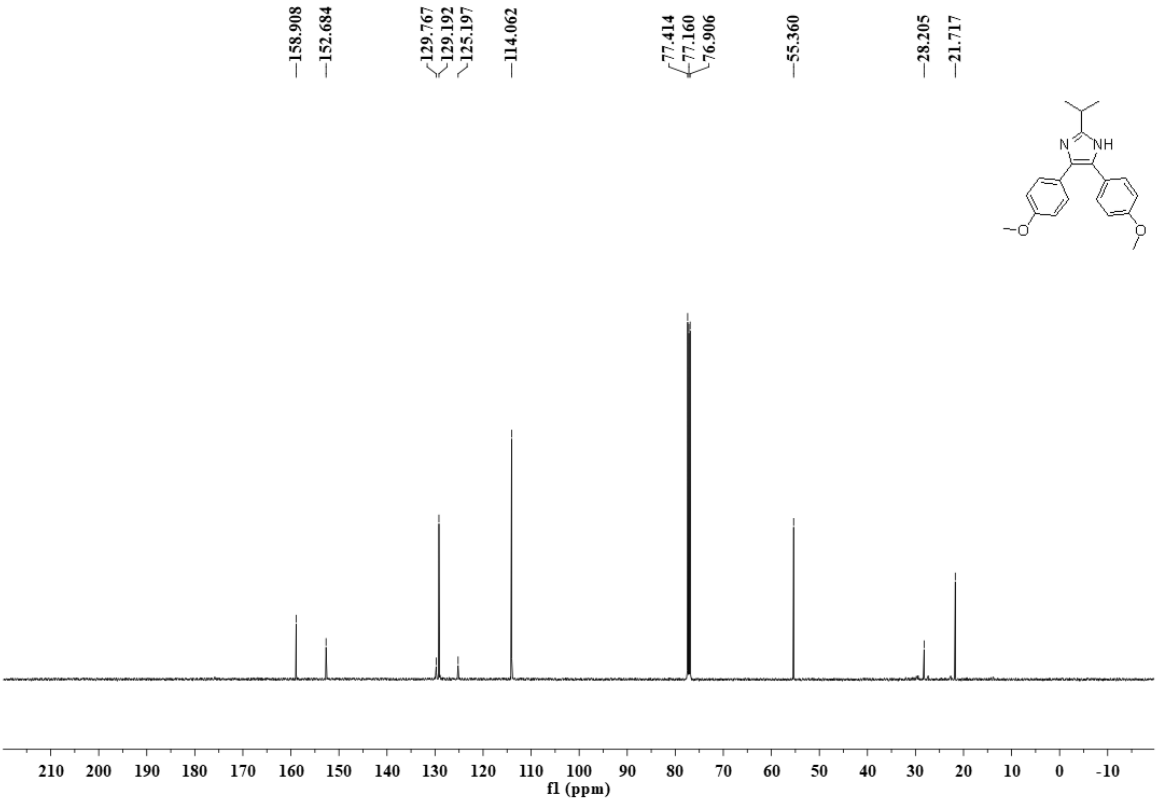
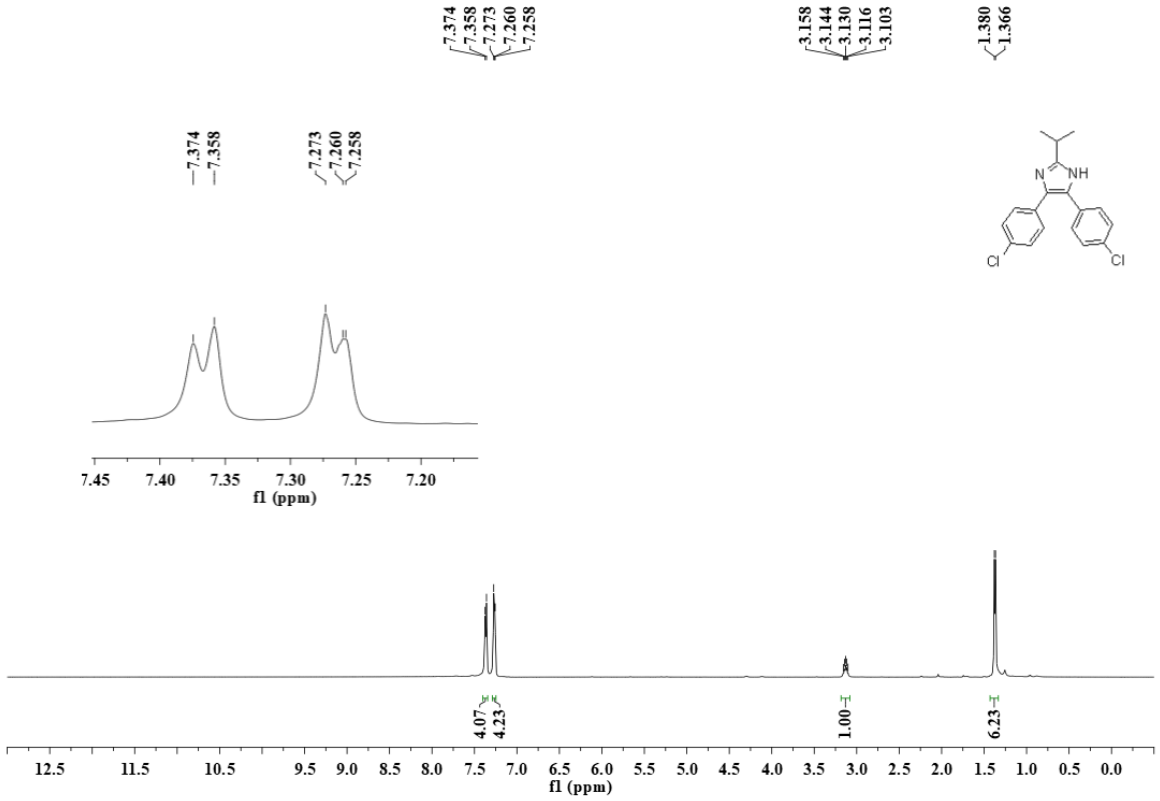


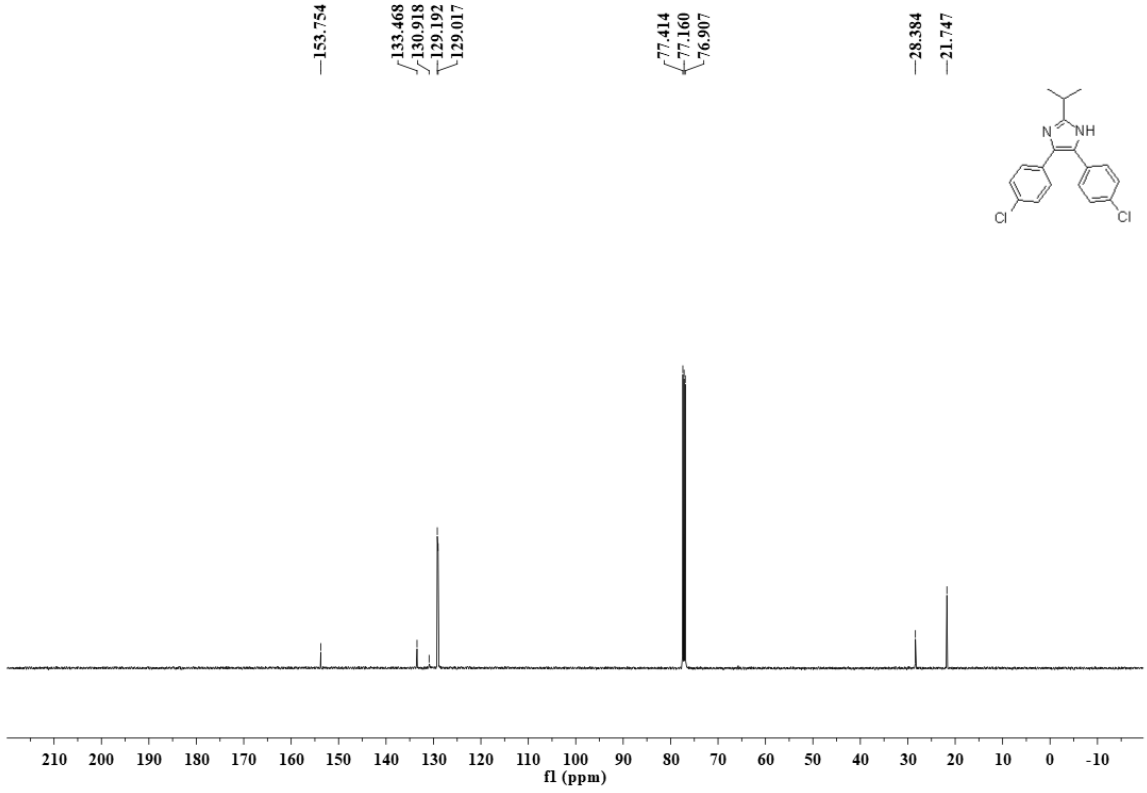
^{13}C NMR (125 MHz, $CDCl_3$) of **1c-A**



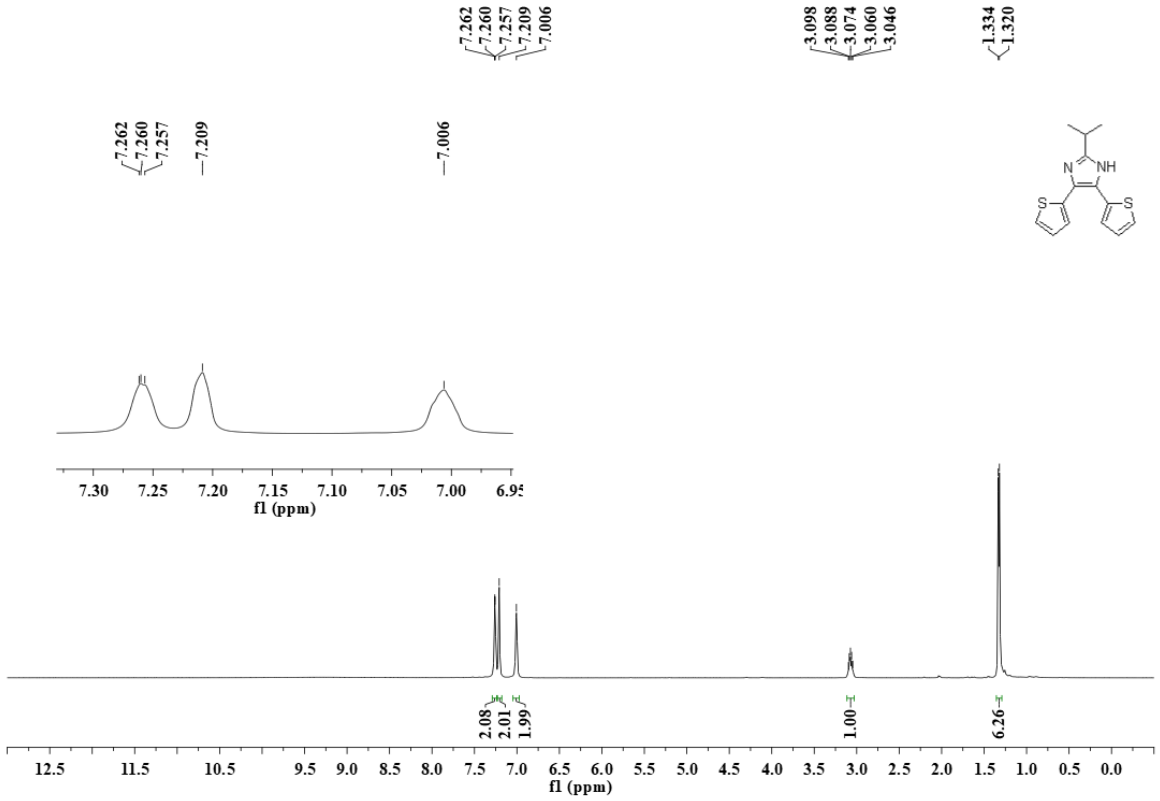
^{1}H NMR (500 MHz, $CDCl_3$) of **1e-A**



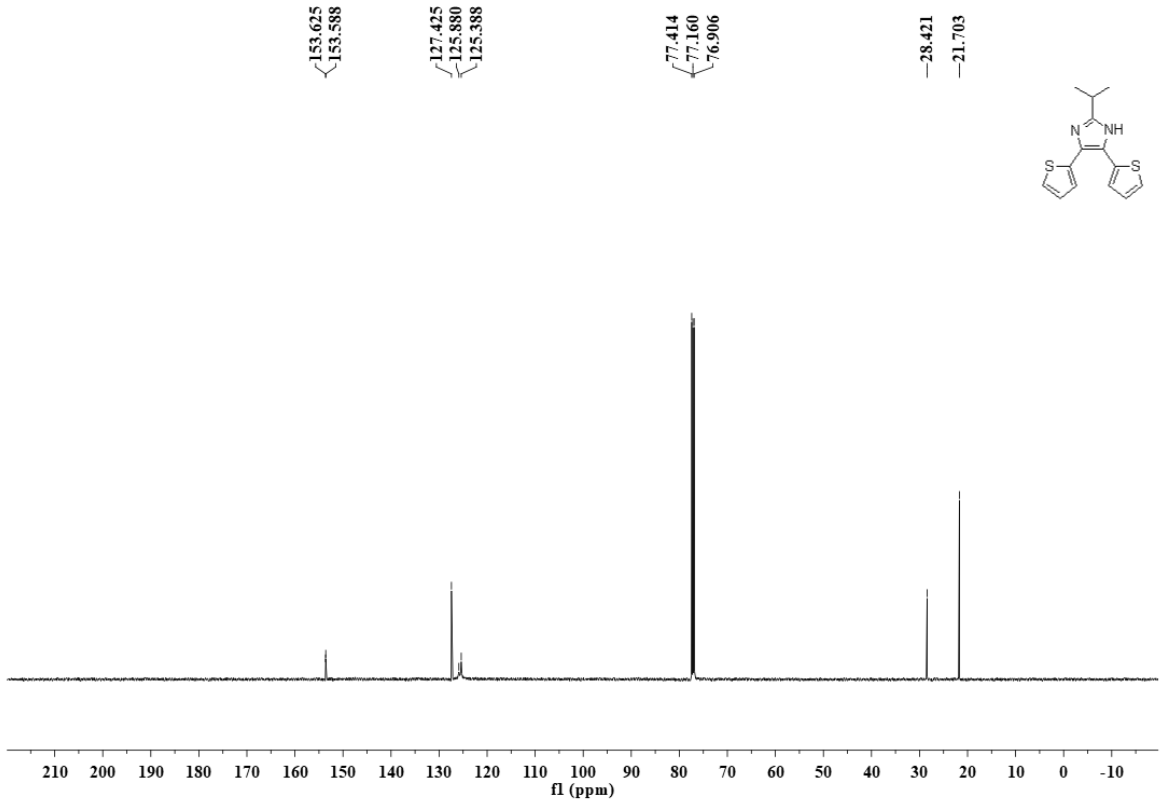
^{13}C NMR (125 MHz, $CDCl_3$) of **1e-A**



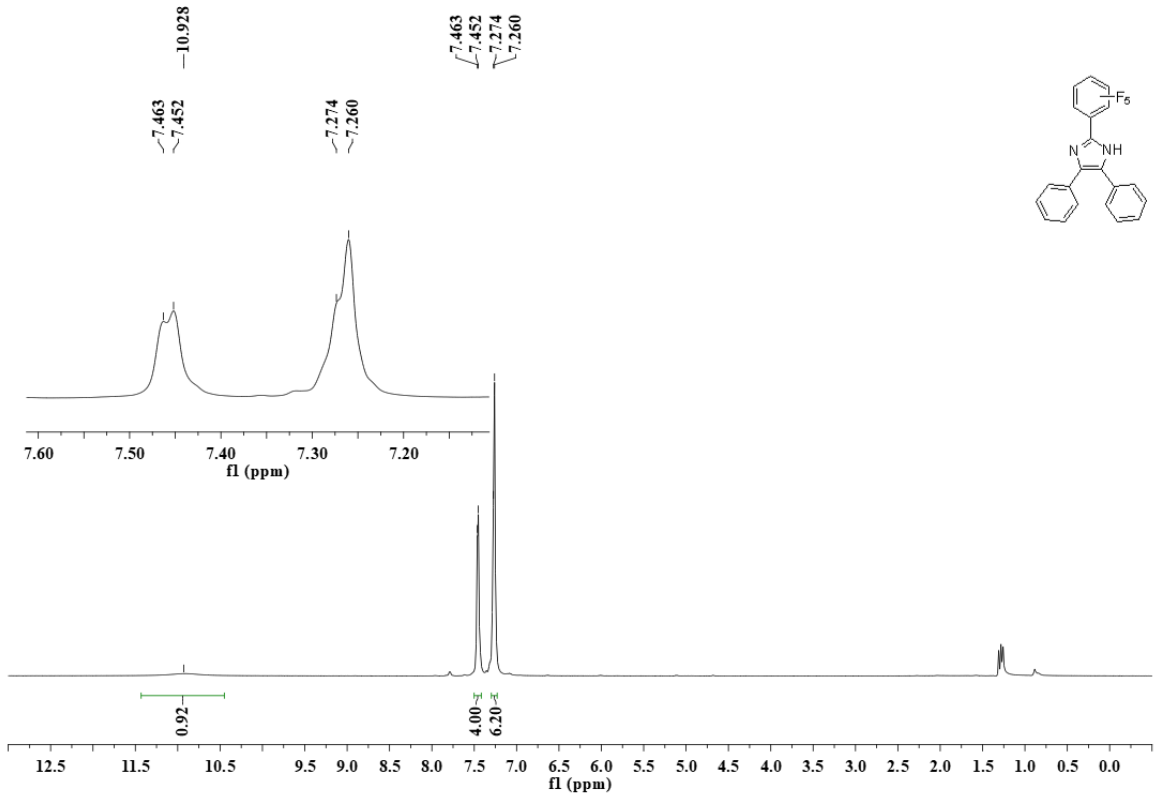
^{1}H NMR (500 MHz, $CDCl_3$) of **1f-A**



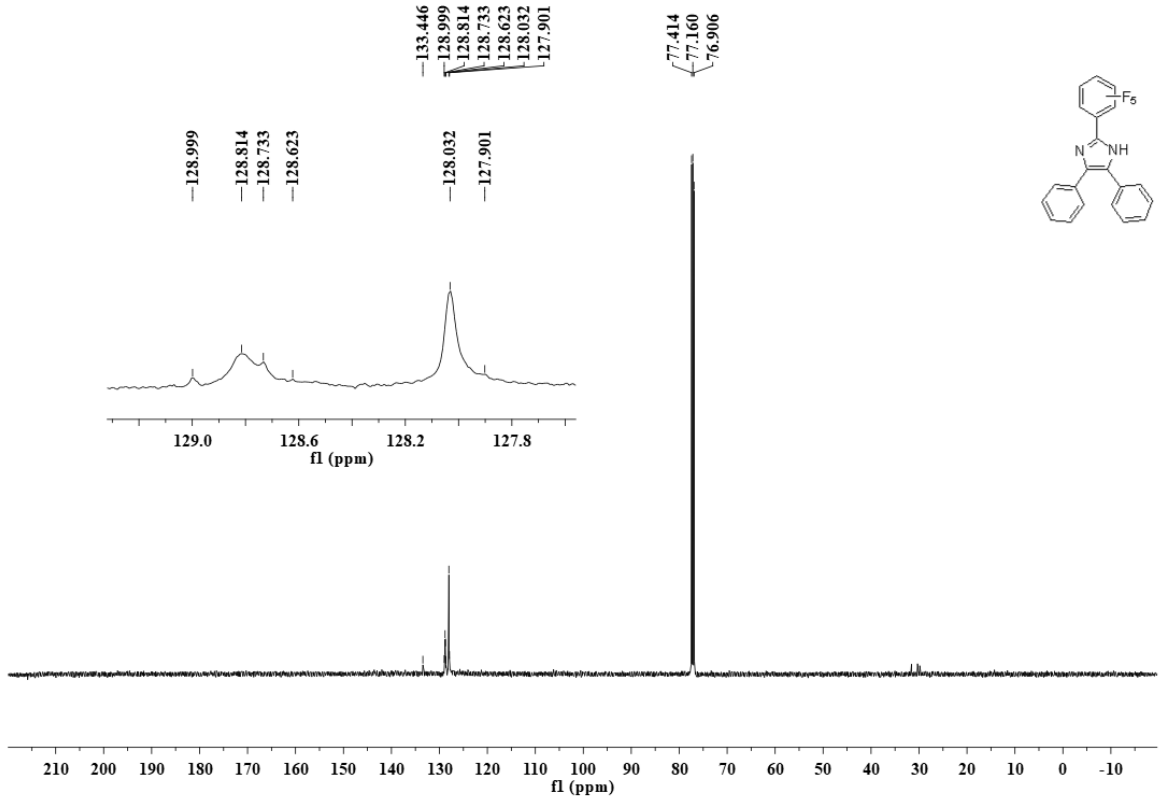
^{13}C NMR (125 MHz, $CDCl_3$) of **1f-A**



^{1}H NMR (500 MHz, $CDCl_3$) of **1i-A**



^{13}C NMR (125 MHz, $CDCl_3$) of **1i-A**



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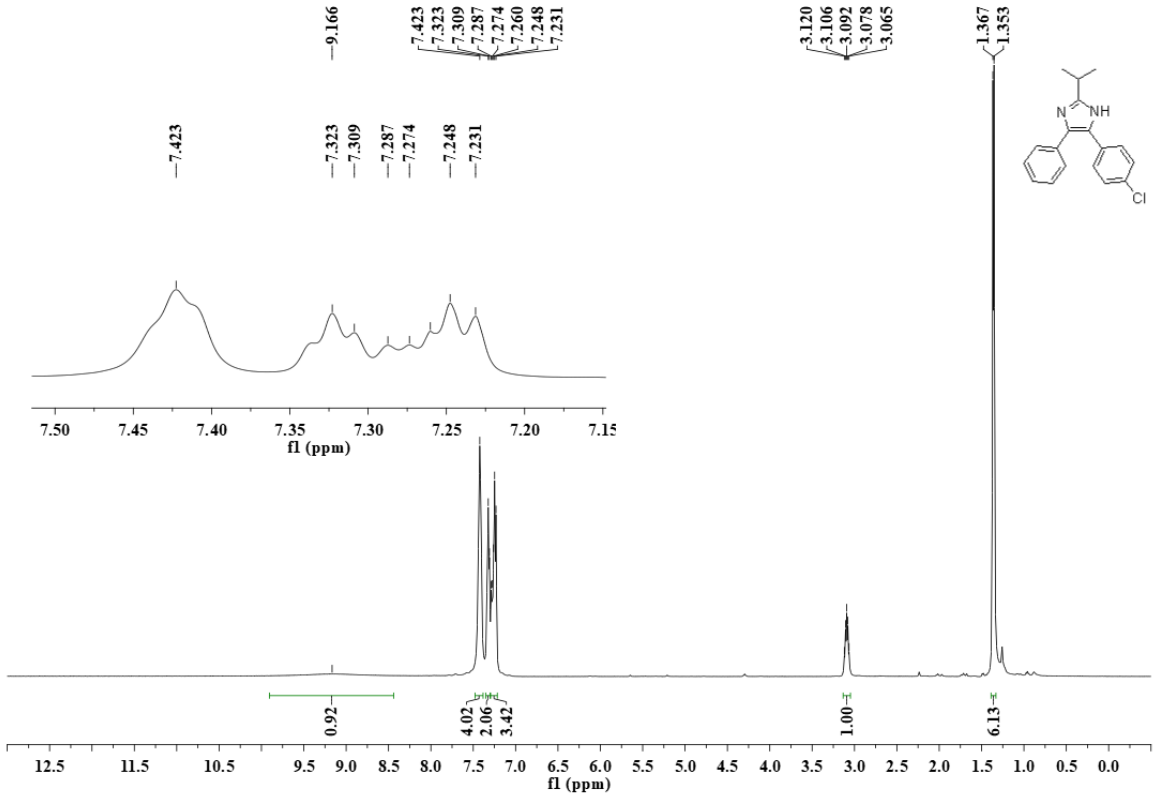

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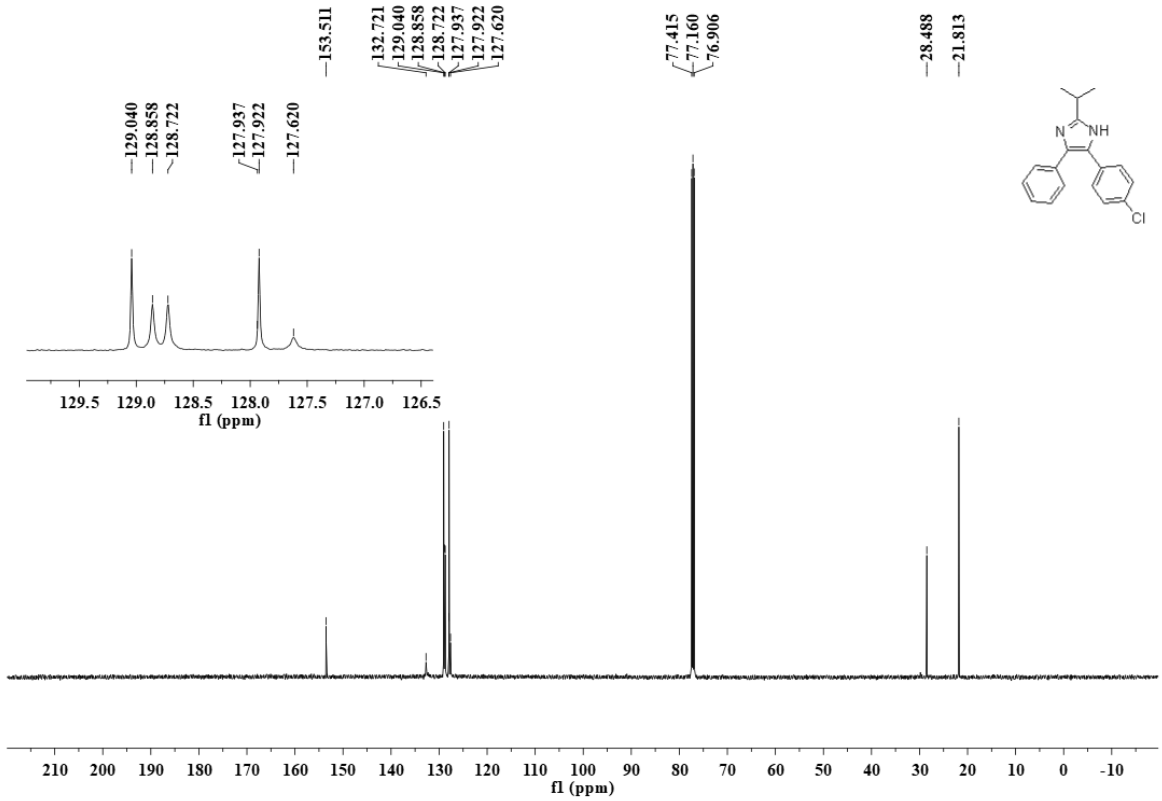
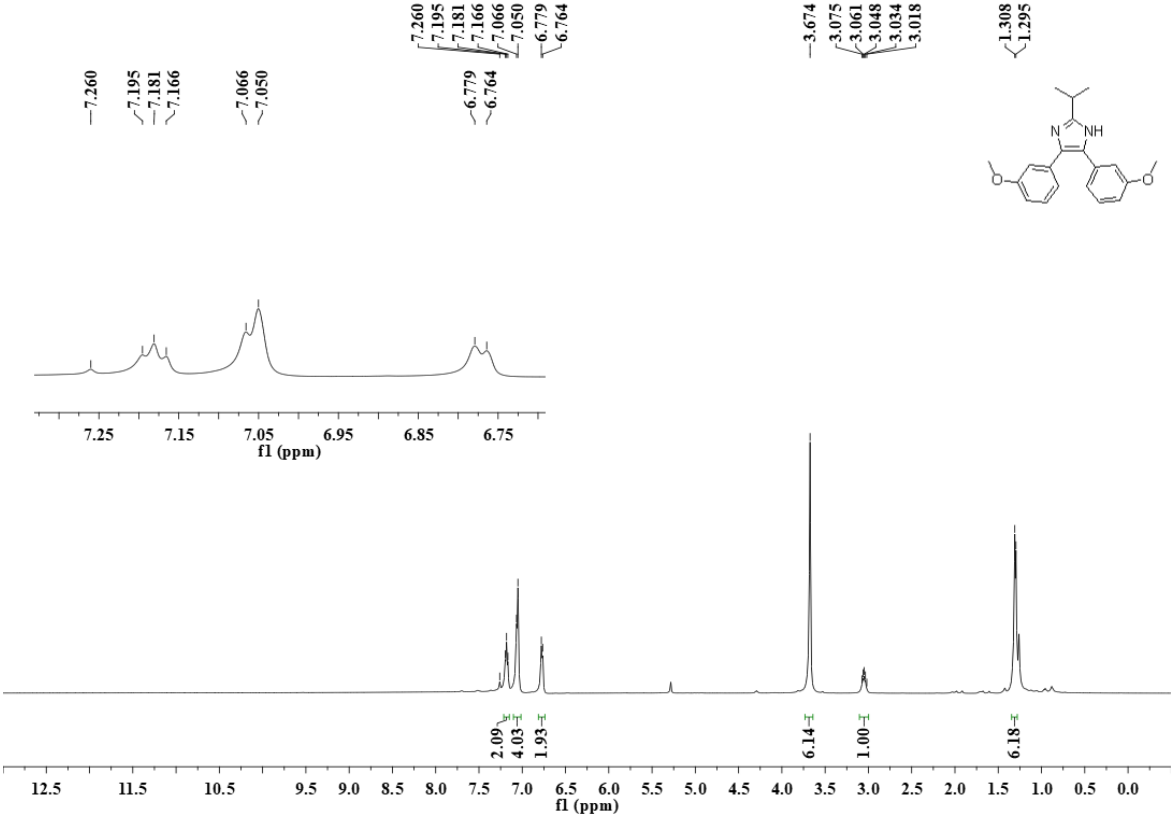
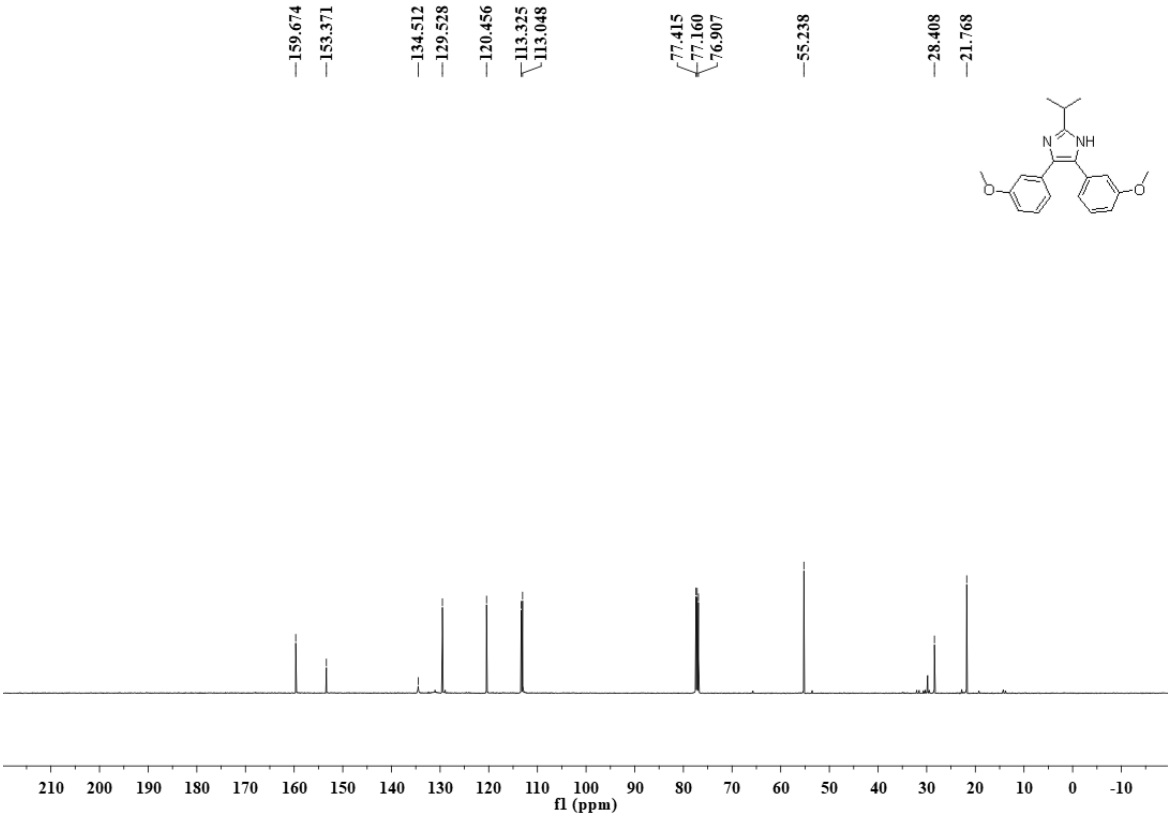


^{1}H NMR (500 MHz, $CDCl_3$) of **1l-A**



^{13}C NMR (125 MHz, $CDCl_3$) of **1l-A**



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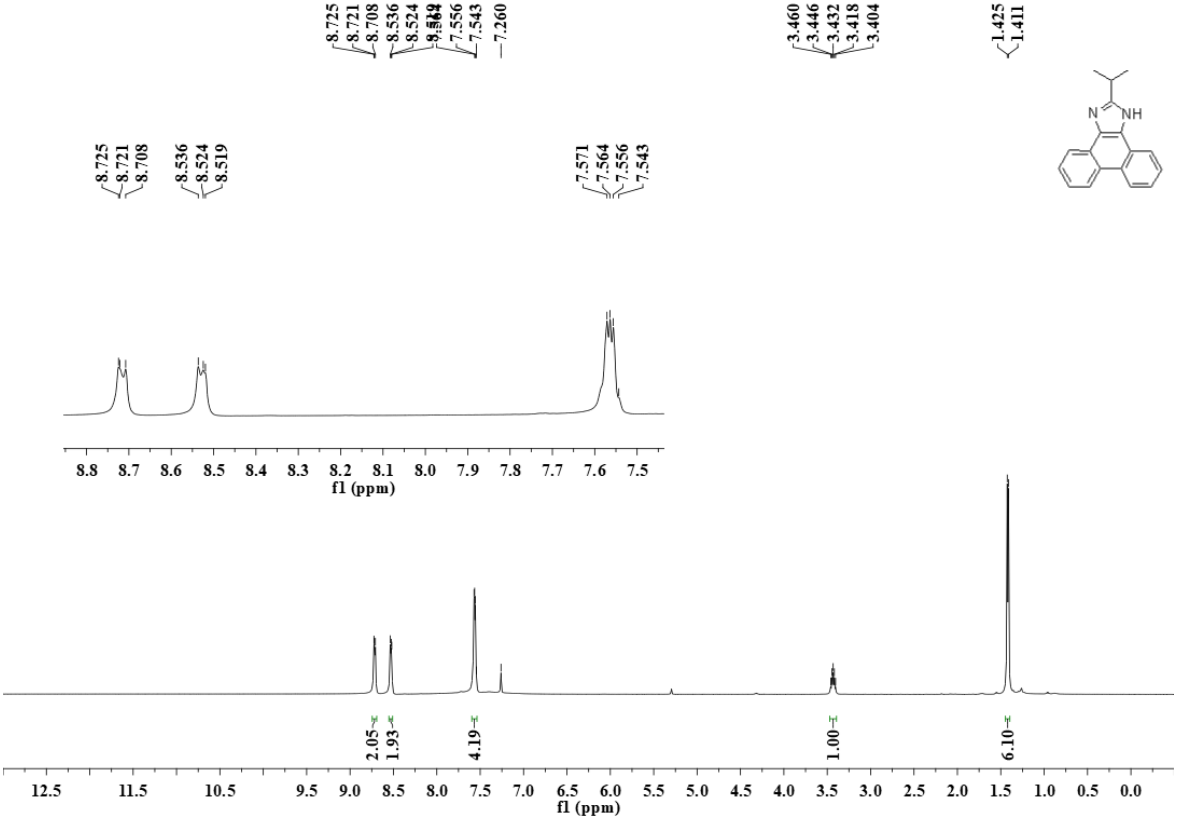
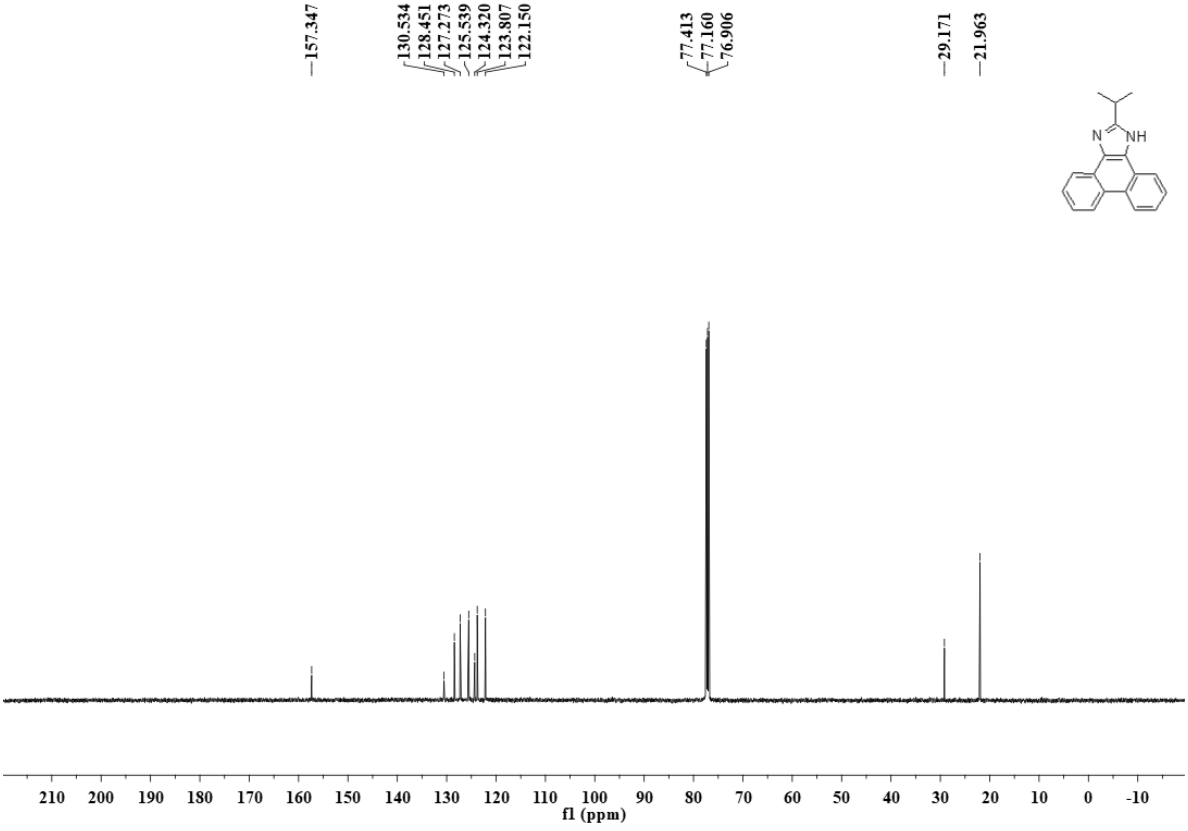
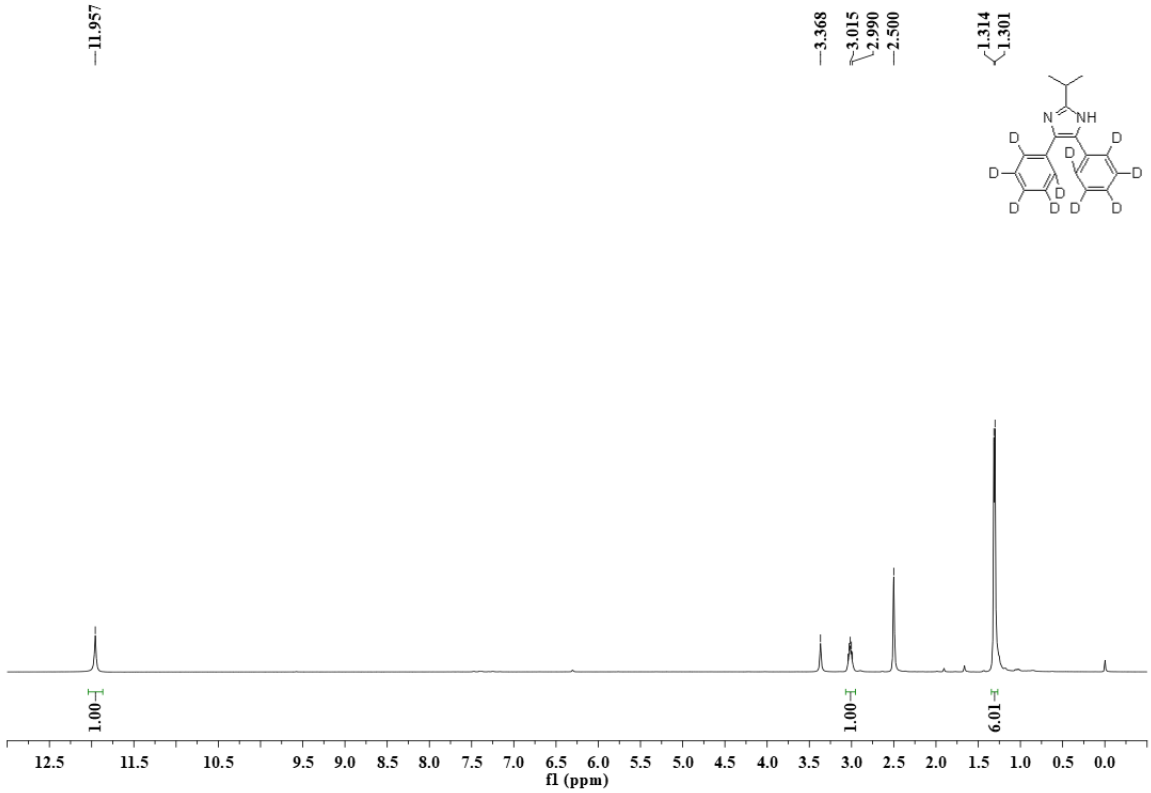


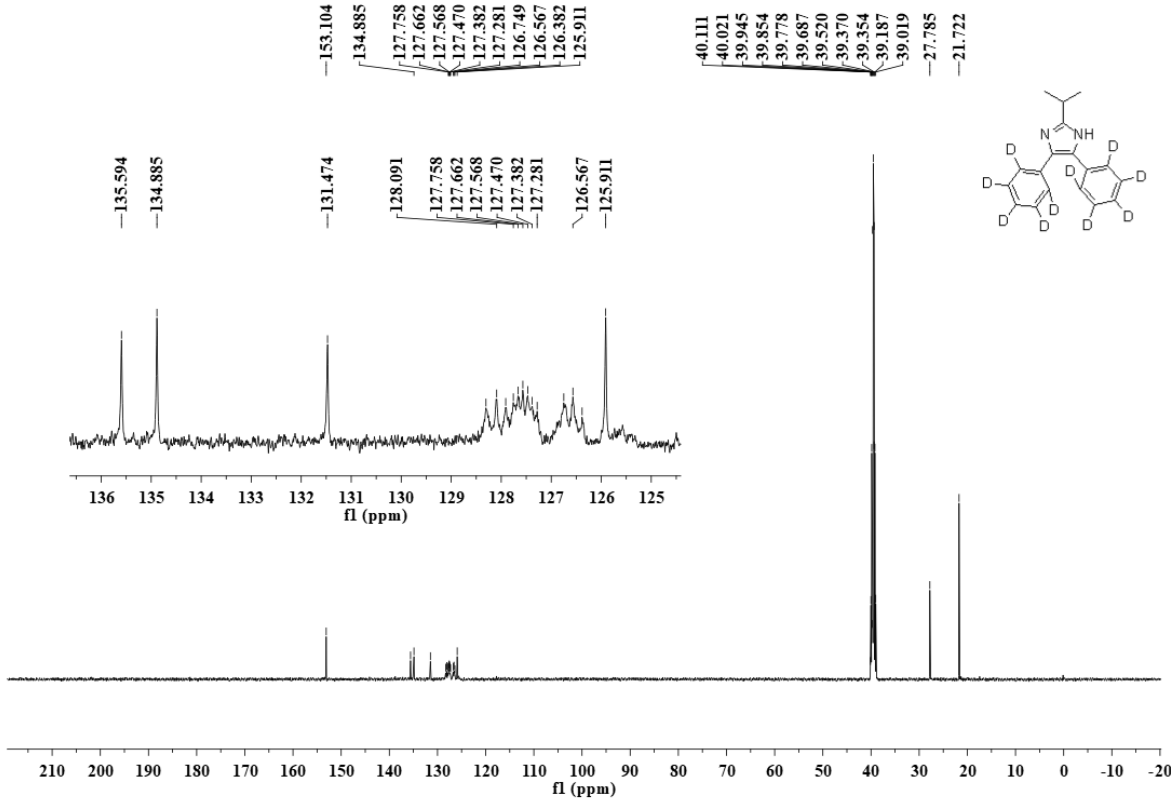
^{13}C NMR (125 MHz, $CDCl_3$) of **1m-A**



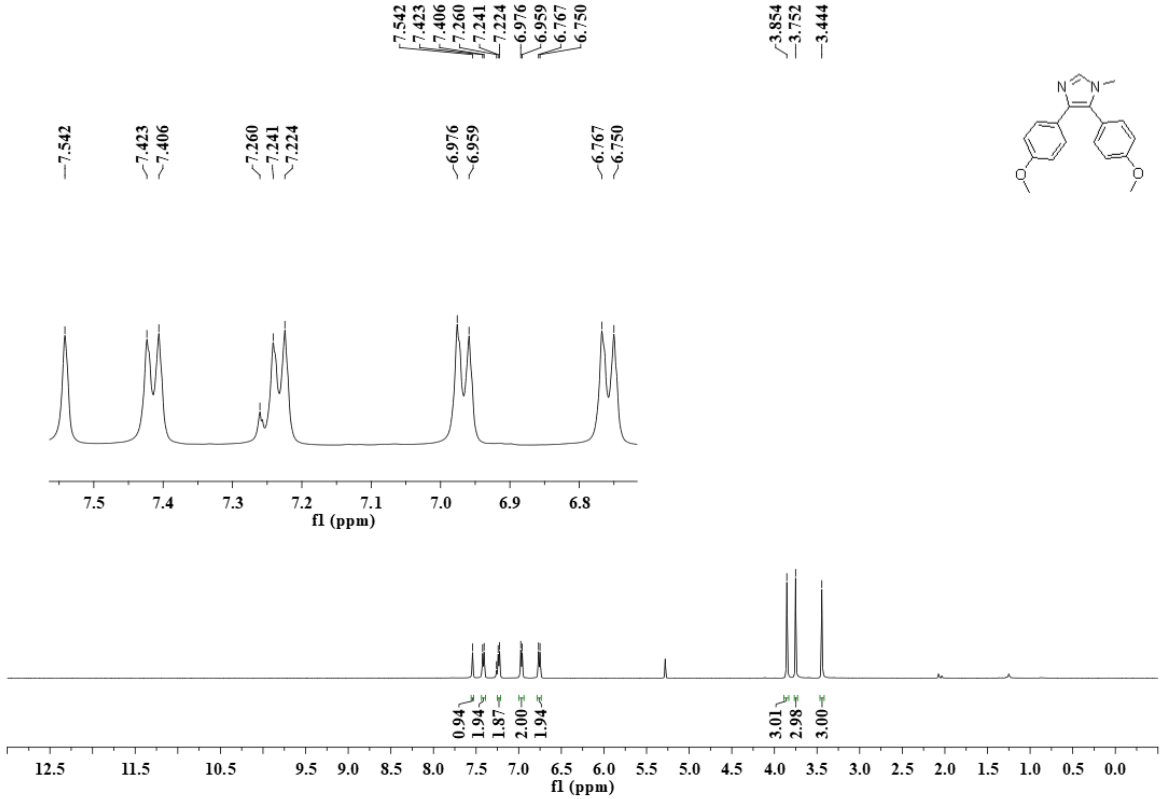
^{1}H NMR (500 MHz, DMSO-d_6) of ***d*$_{10}$-1a-A**



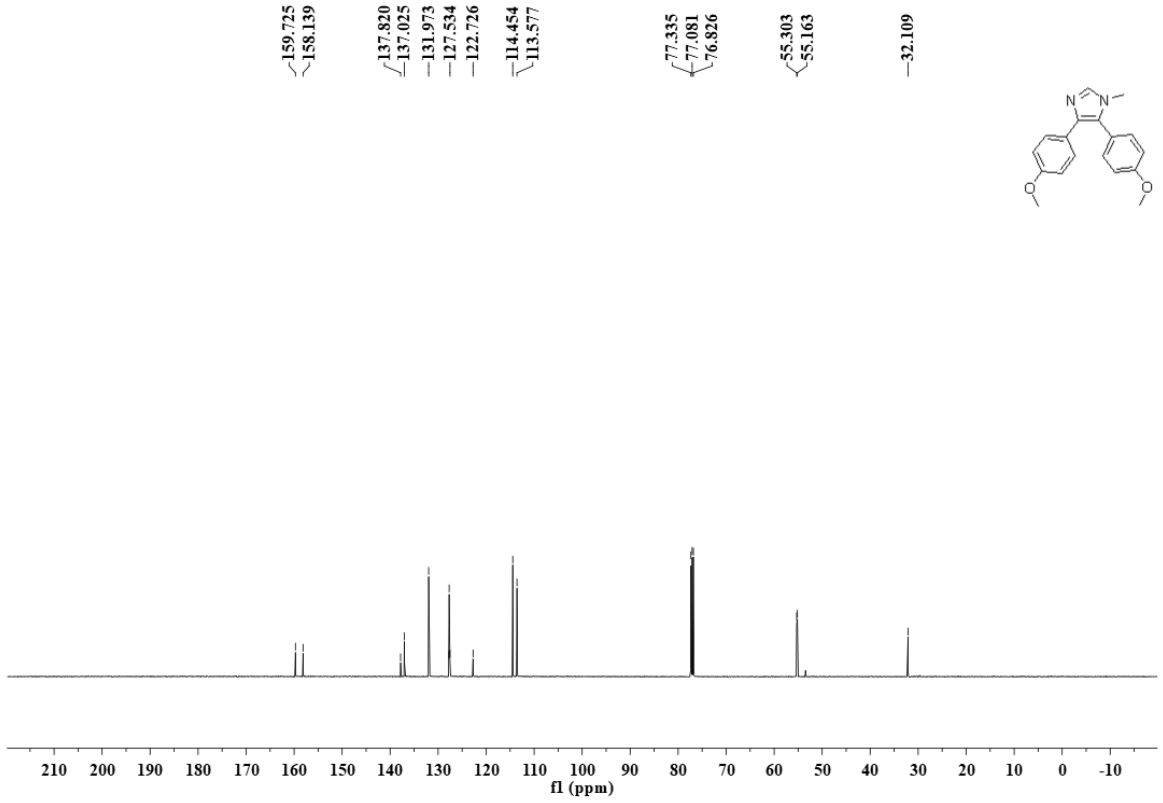
^{13}C NMR (125 MHz, DMSO-d_6) of ***d*$_{10}$-1a-A**



^{1}H NMR (500 MHz, $CDCl_3$) of **1b-B**



^{13}C NMR (125 MHz, $CDCl_3$) of **1b-B**



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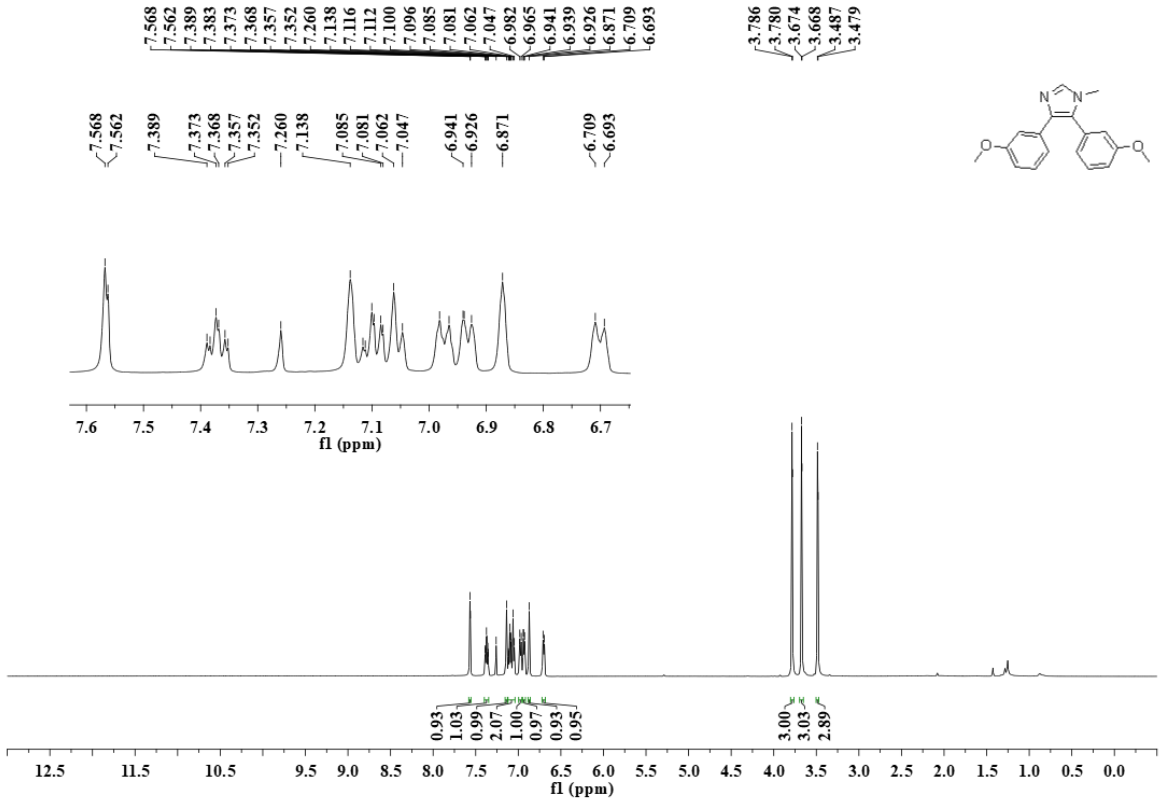
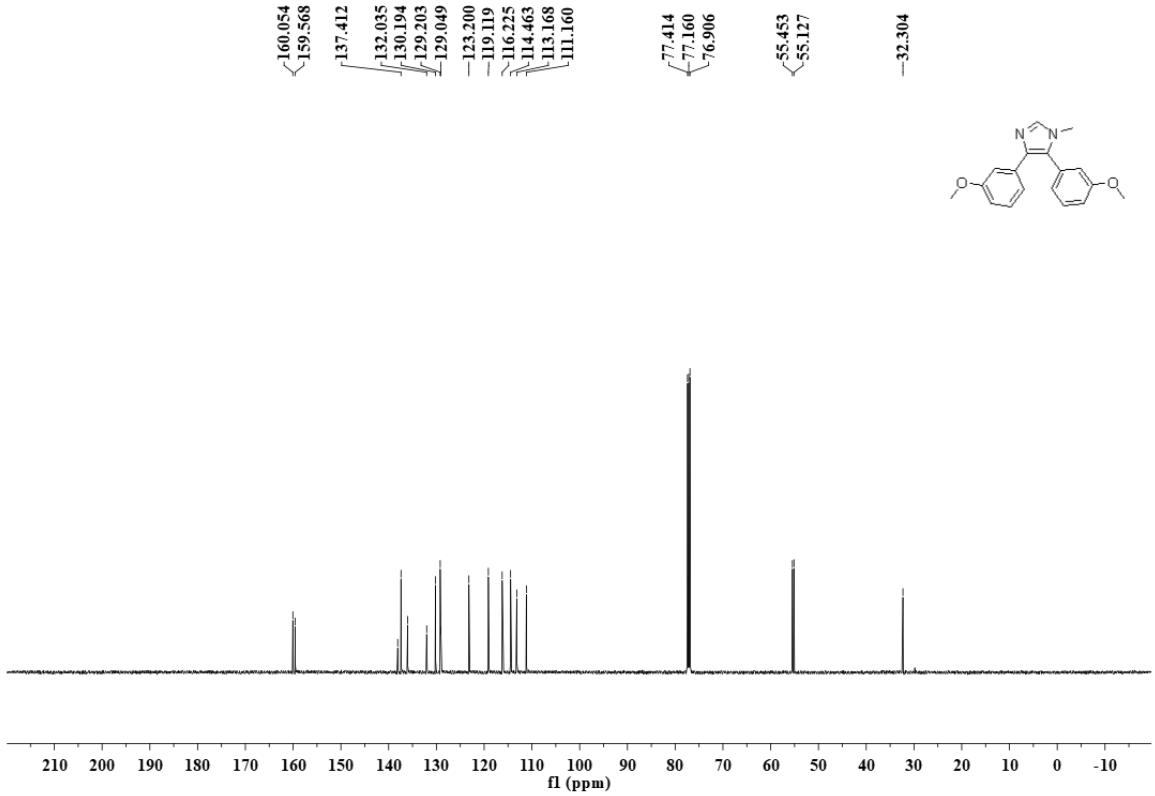


^{13}C NMR (125 MHz, $CDCl_3$) of **1e-B**



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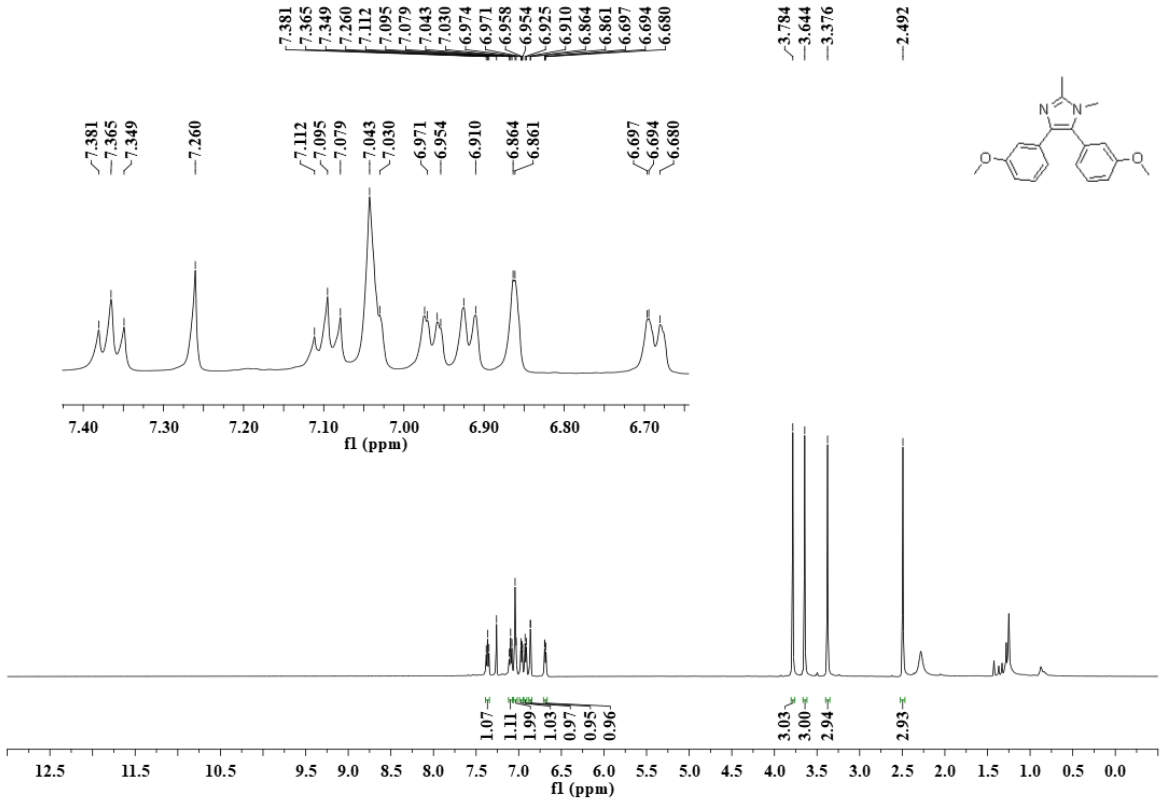
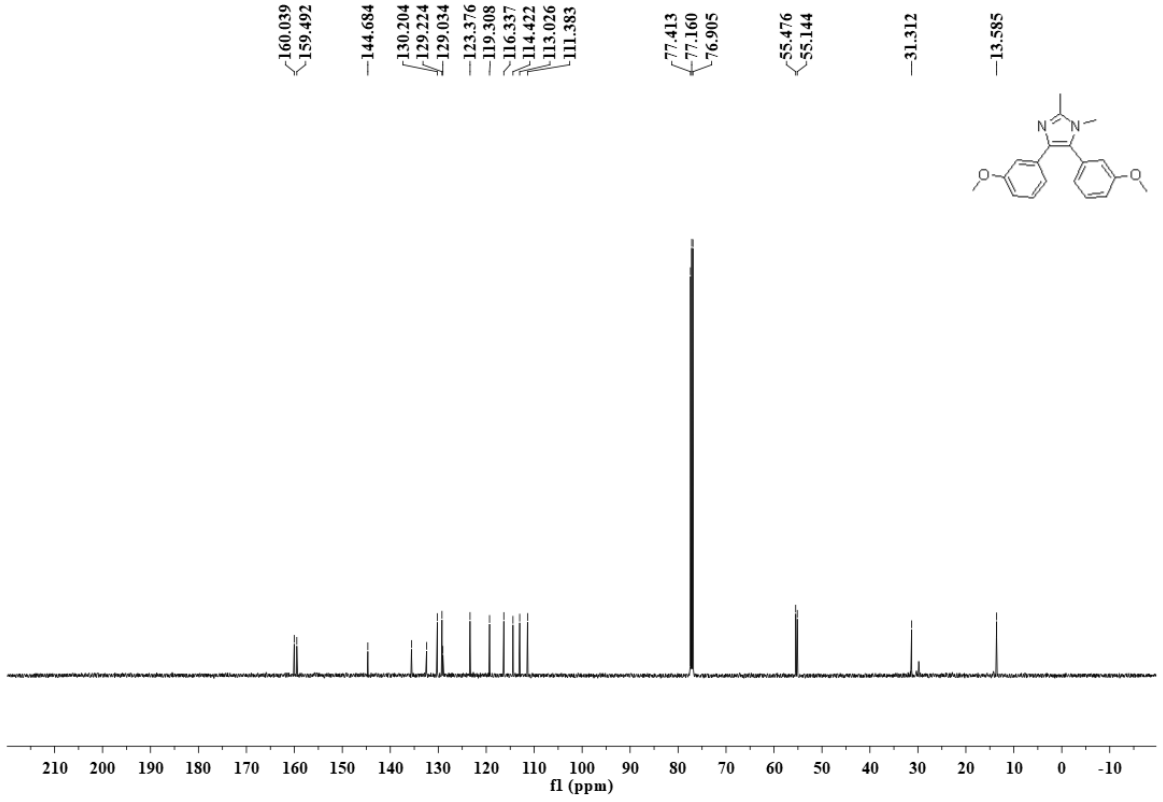
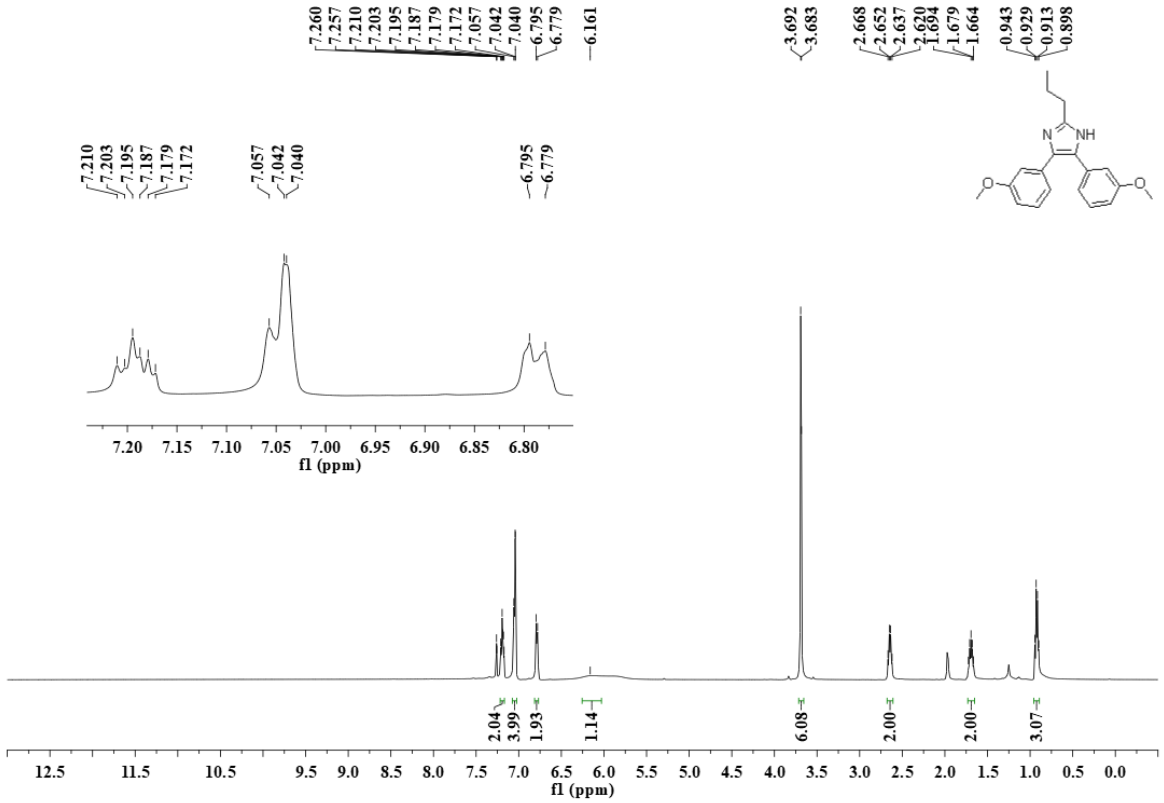


^{13}C NMR (125 MHz, $CDCl_3$) of **1f-B**



^{1}H NMR (500 MHz, $CDCl_3$) of **1g-B**



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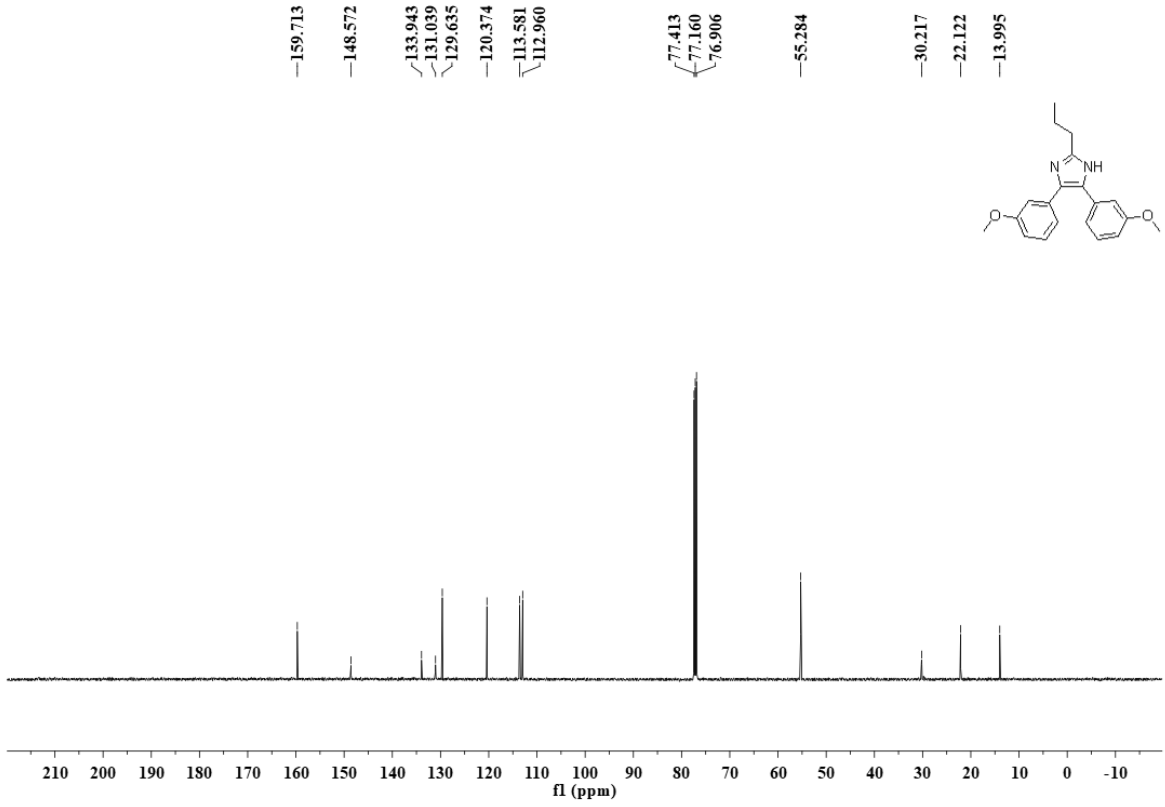
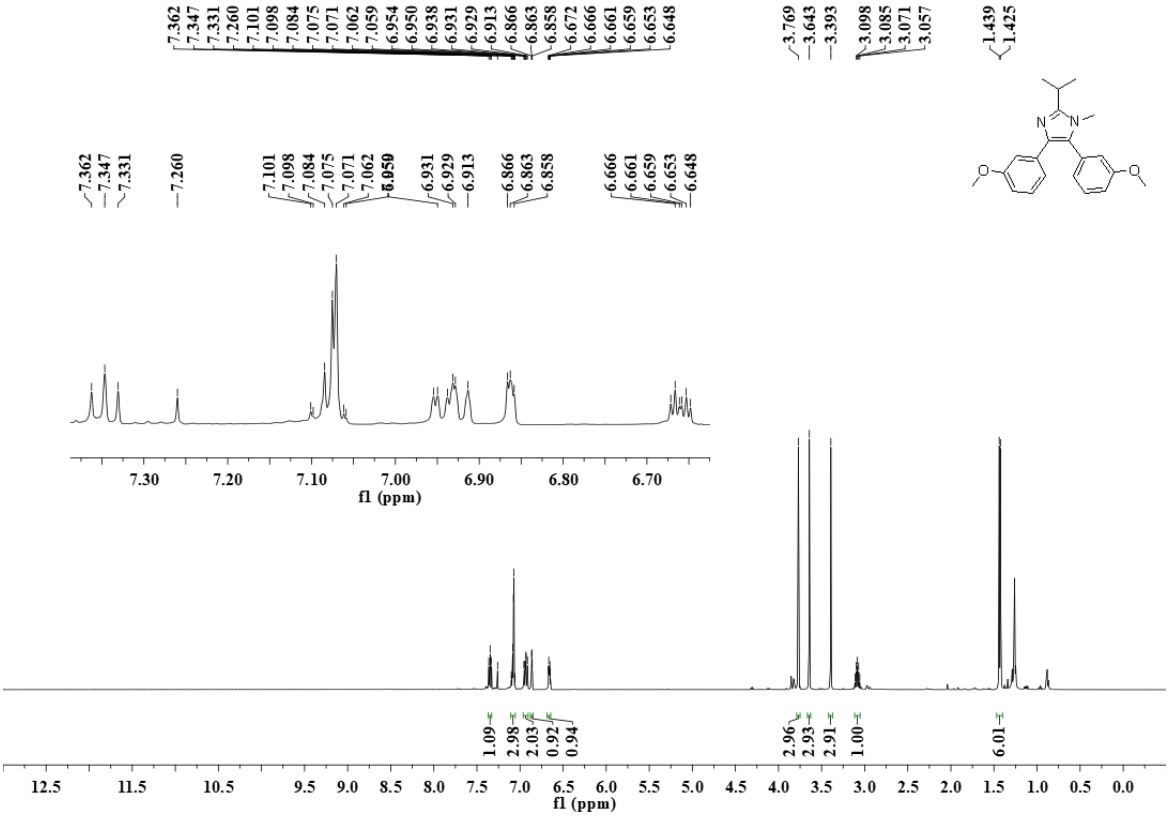


^{1}H NMR (500 MHz, $CDCl_3$) of **1h-B**



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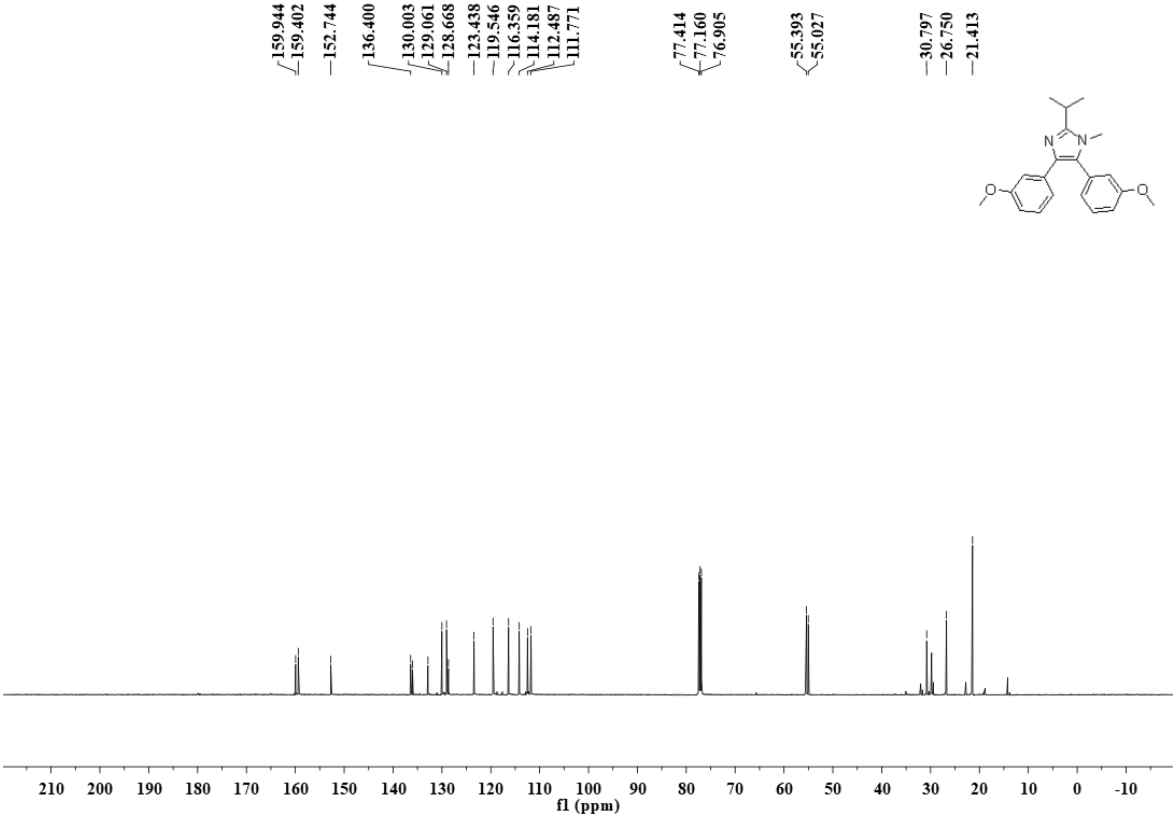

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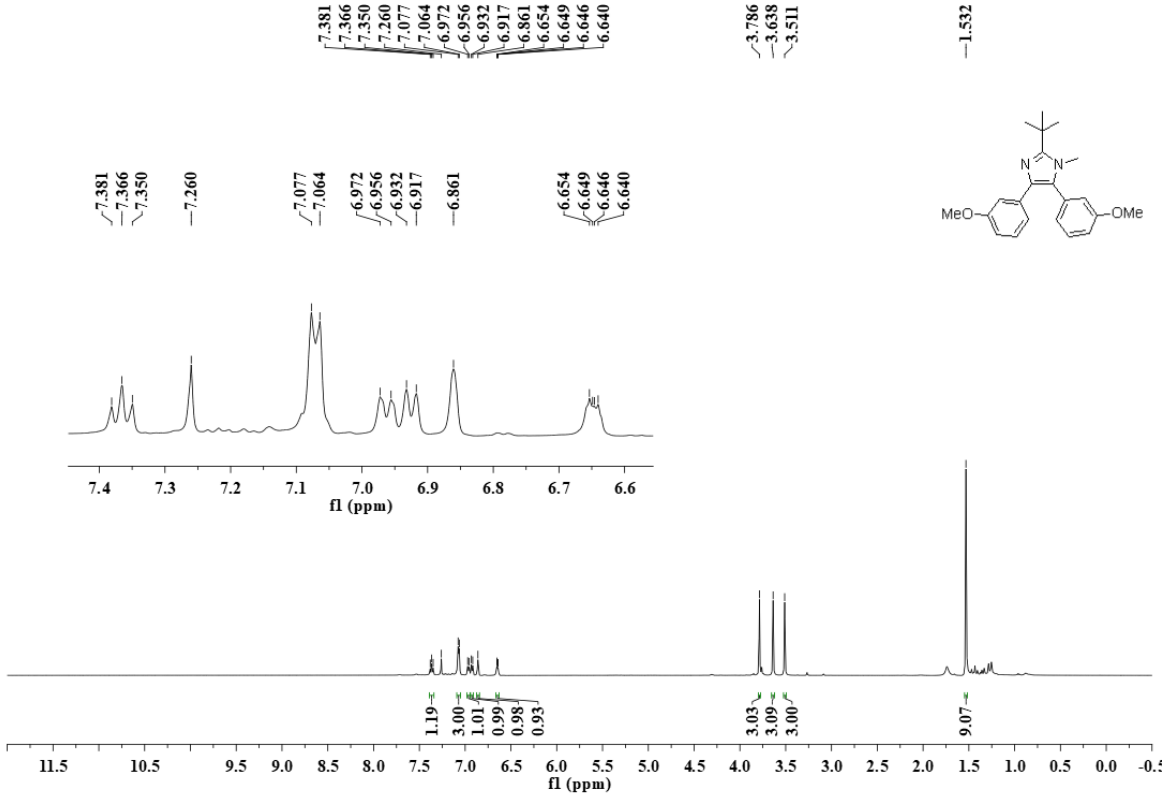
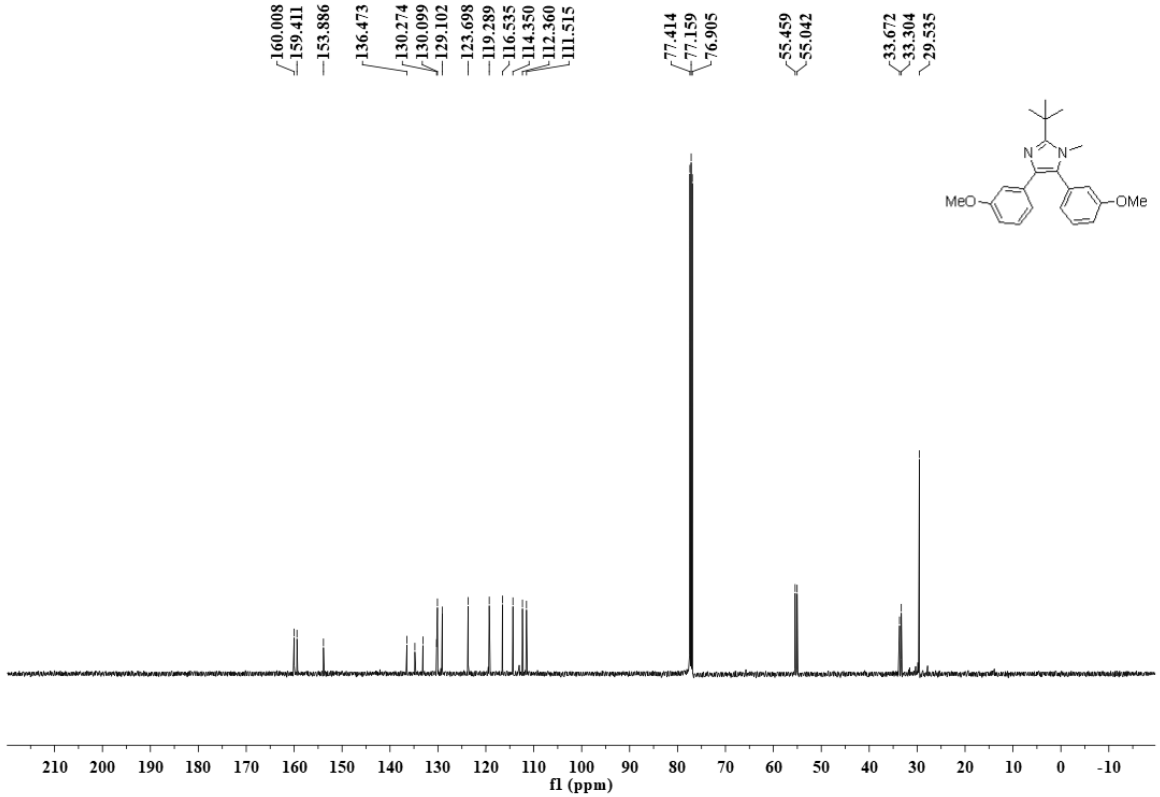
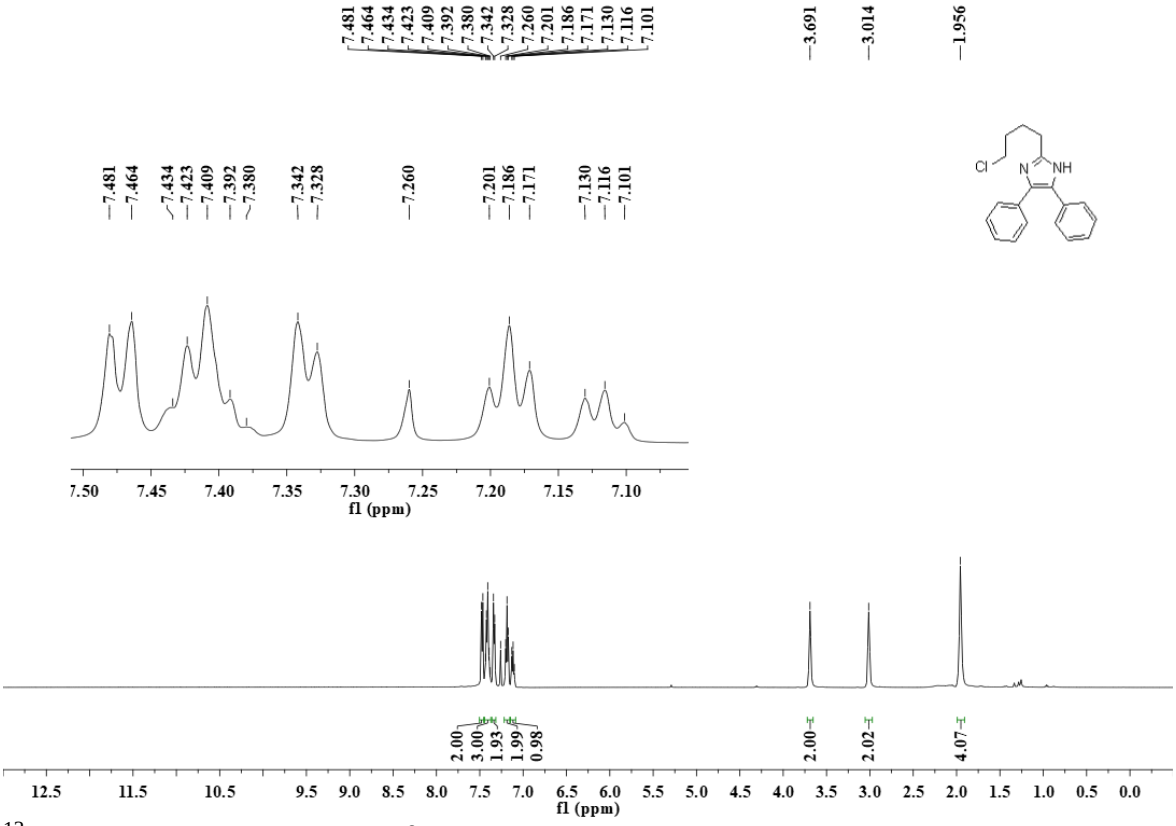


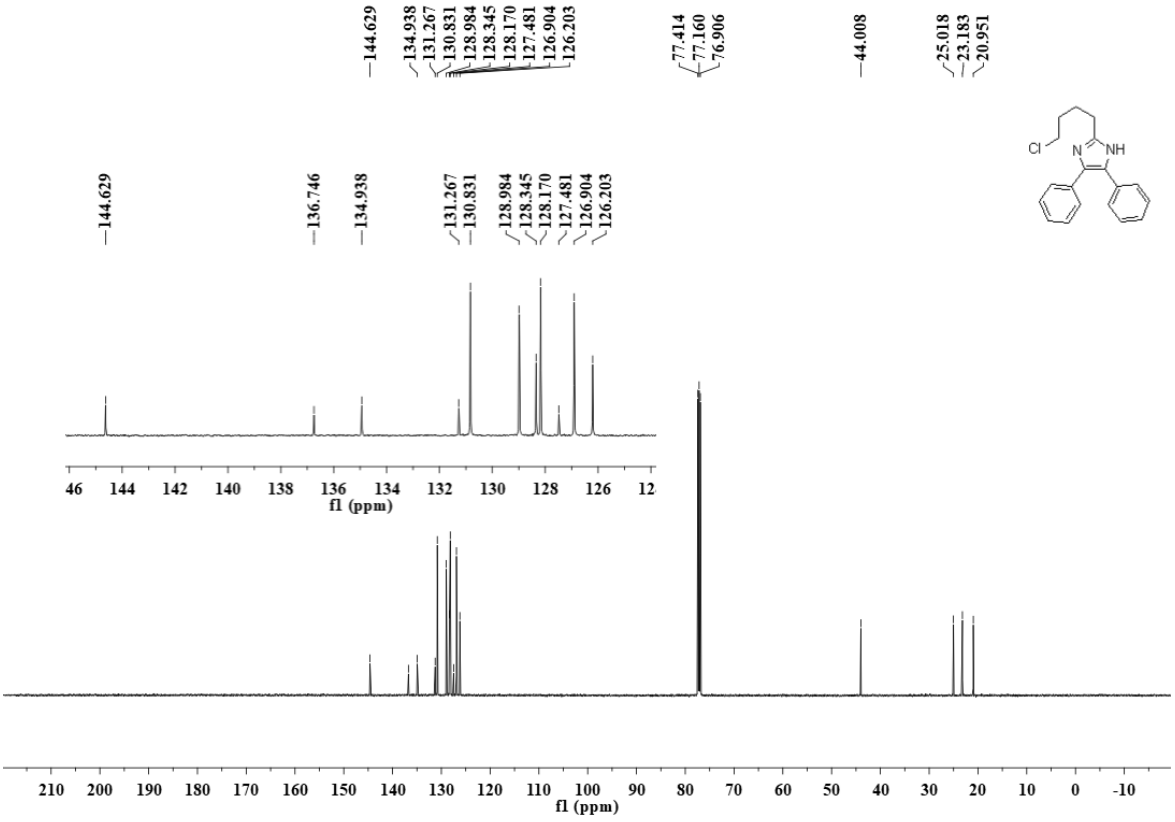
^{13}C NMR (125 MHz, $CDCl_3$) of **1i-B**



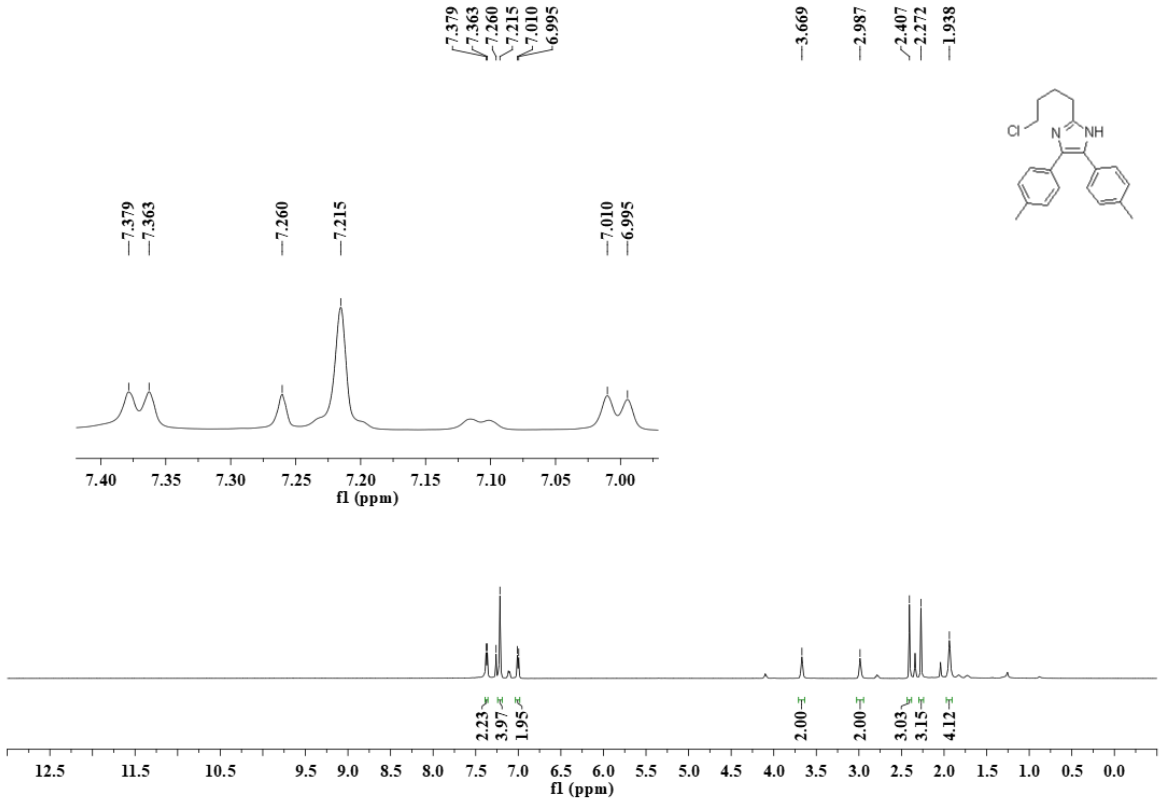
^{1}H NMR (500 MHz, $CDCl_3$) of **1a-C**



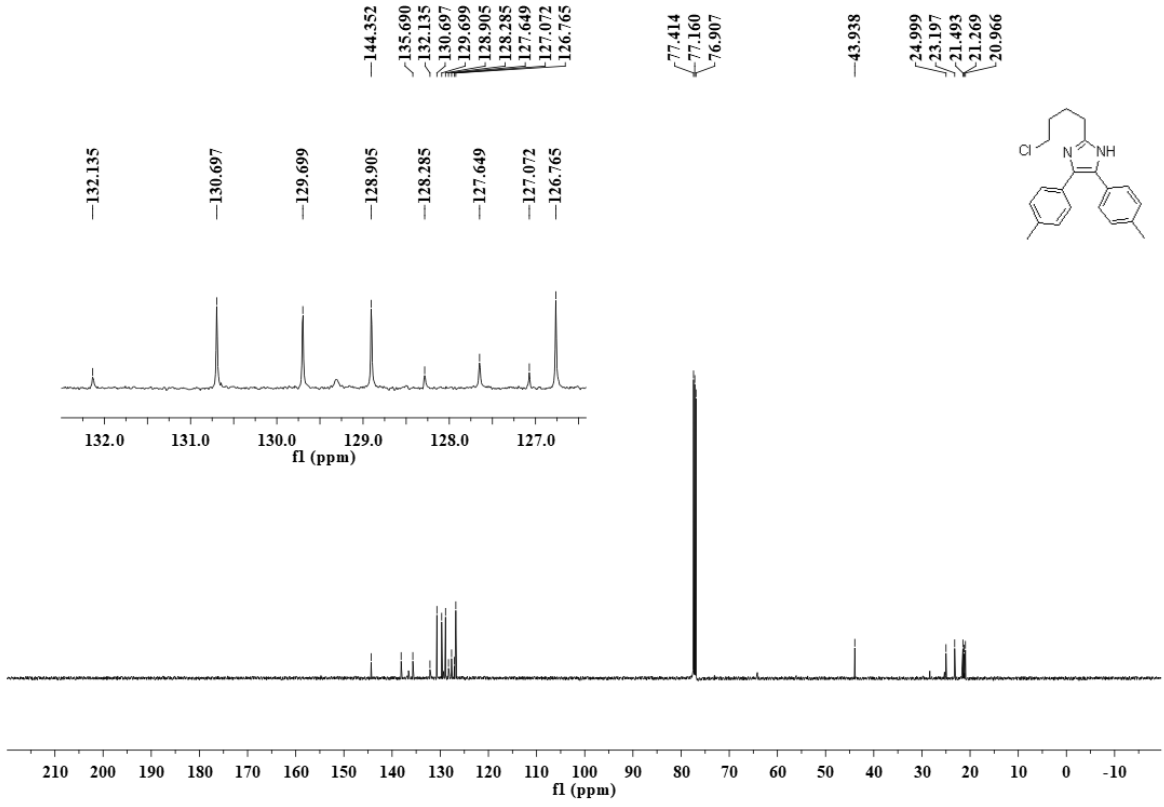
^{13}C NMR (125 MHz, $CDCl_3$) of **1a-C**



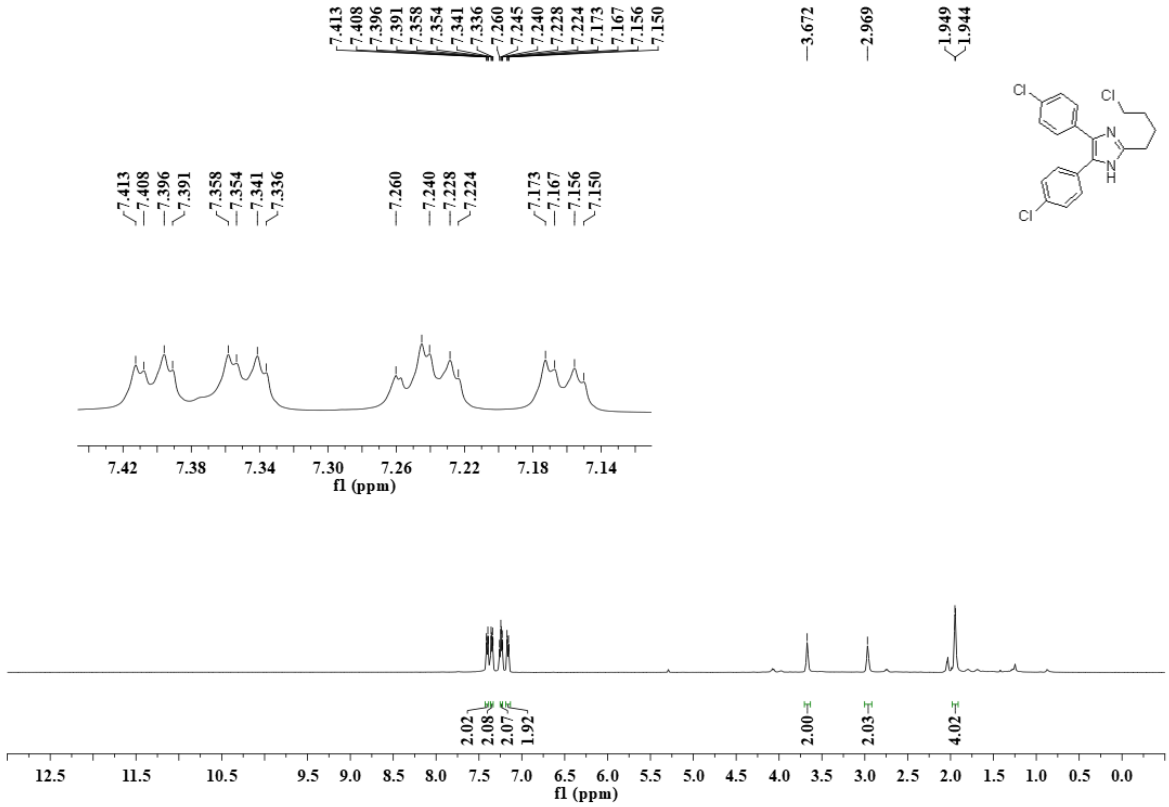
^{1}H NMR (500 MHz, $CDCl_3$) of **1b-C**



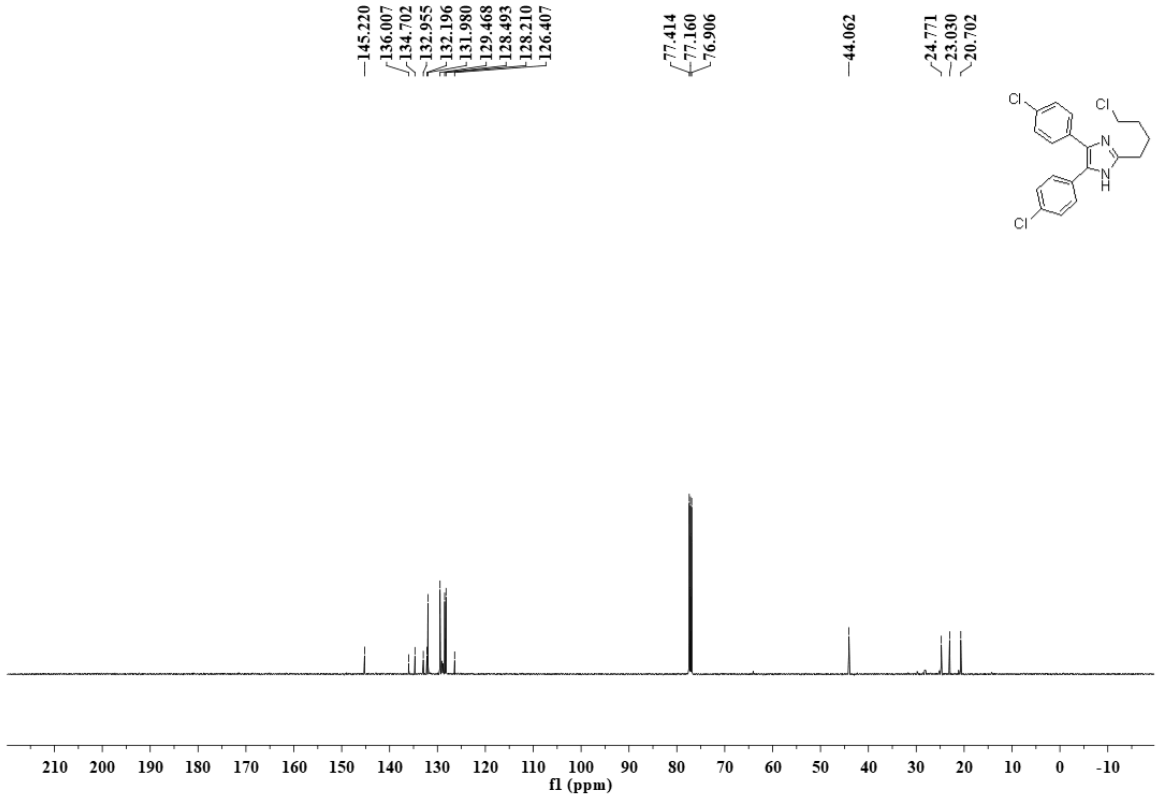
^{13}C NMR (125 MHz, $CDCl_3$) of **1b-C**



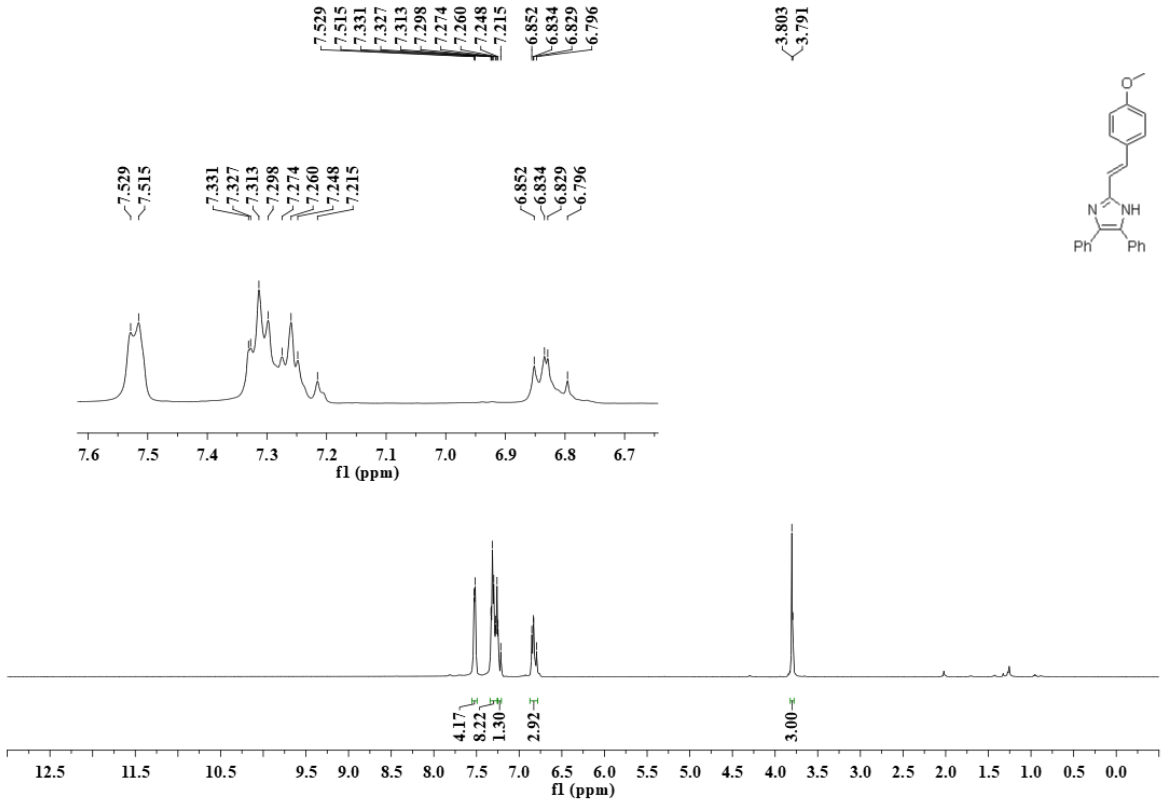
^{1}H NMR (500 MHz, $CDCl_3$) of **1c-C**



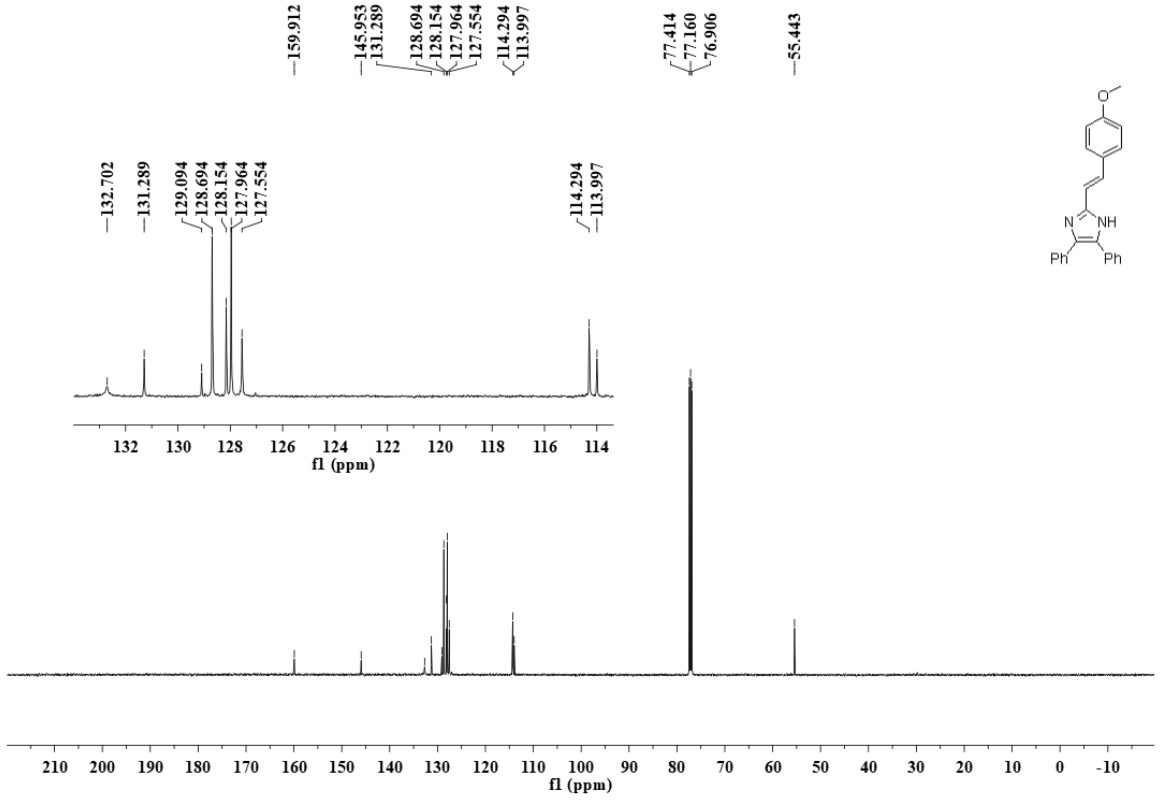
^{13}C NMR (125 MHz, $CDCl_3$) of **1c-C**



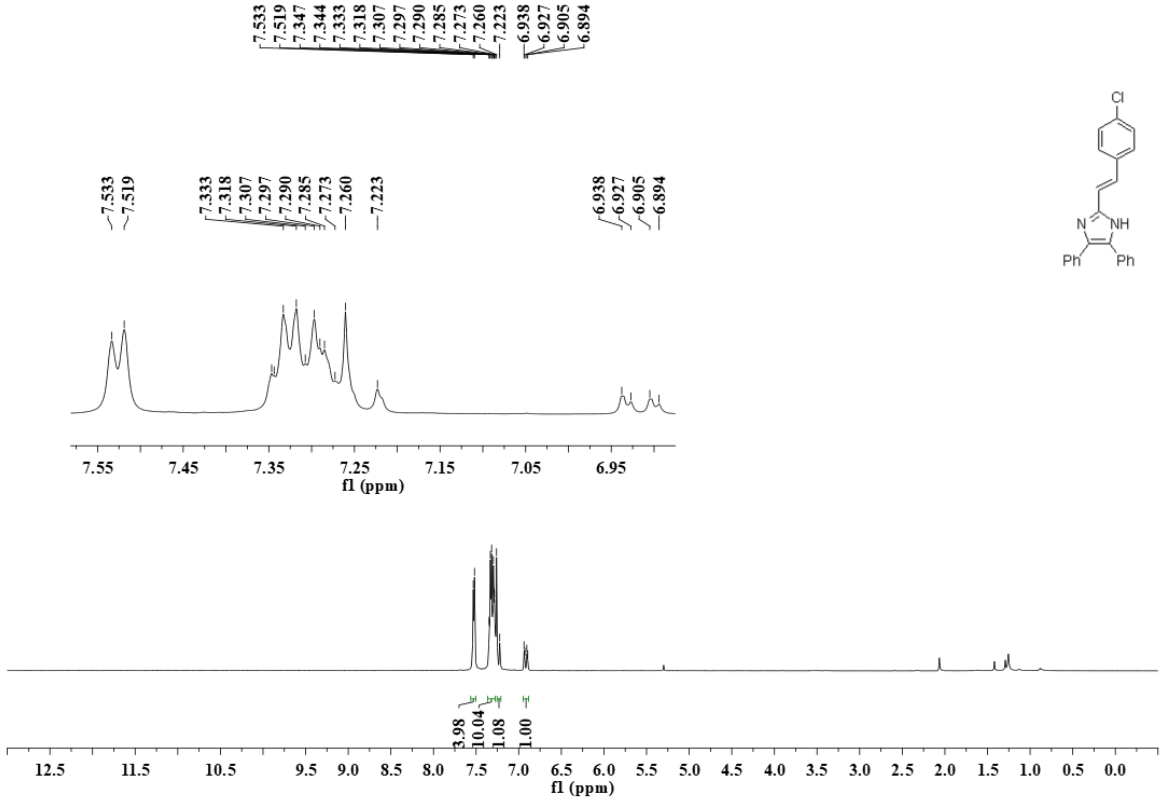
^{1}H NMR (500 MHz, $CDCl_3$) of **1b-D**



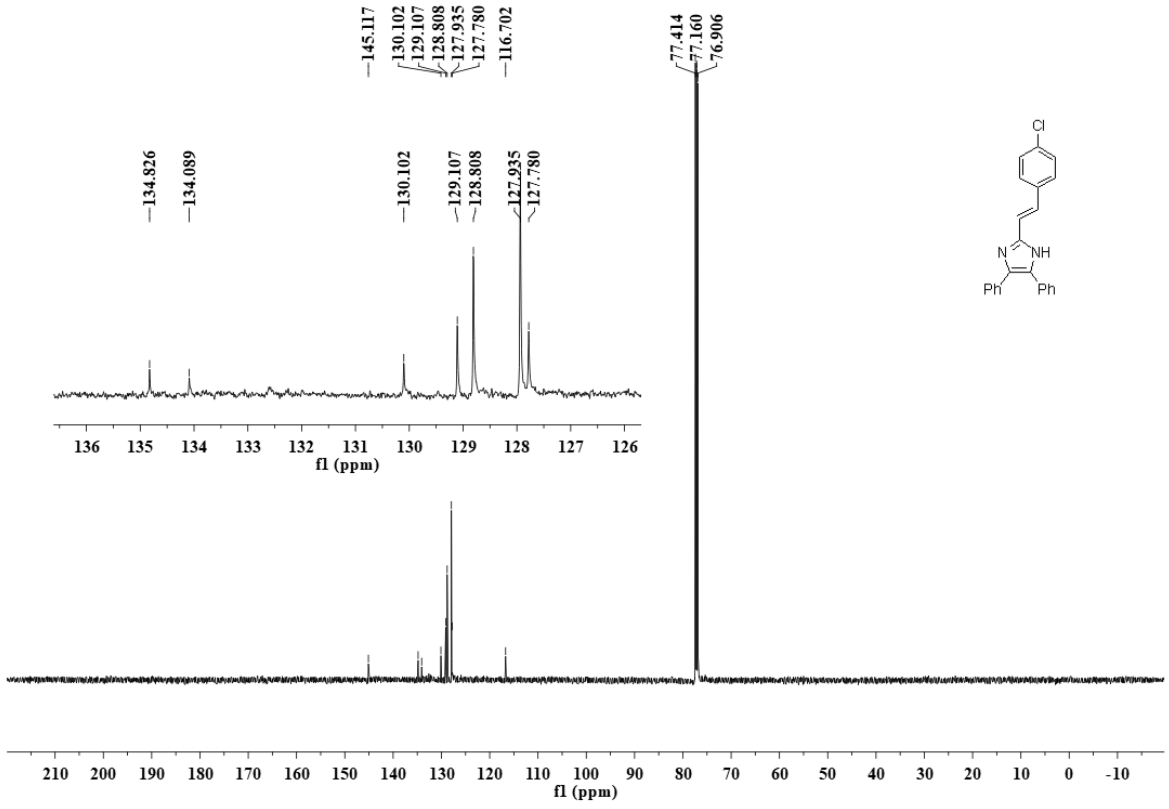
^{13}C NMR (125 MHz, $CDCl_3$) of **1b-D**



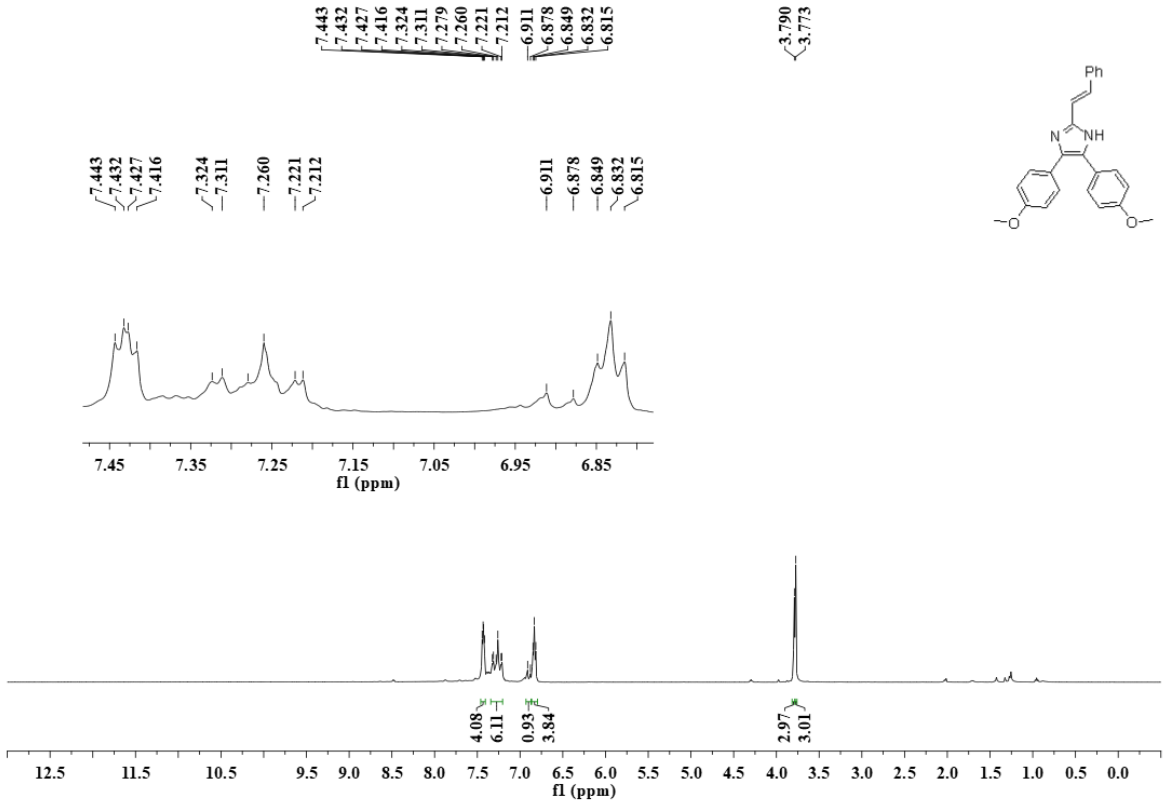
^{1}H NMR (500 MHz, $CDCl_3$) of **1c-D**



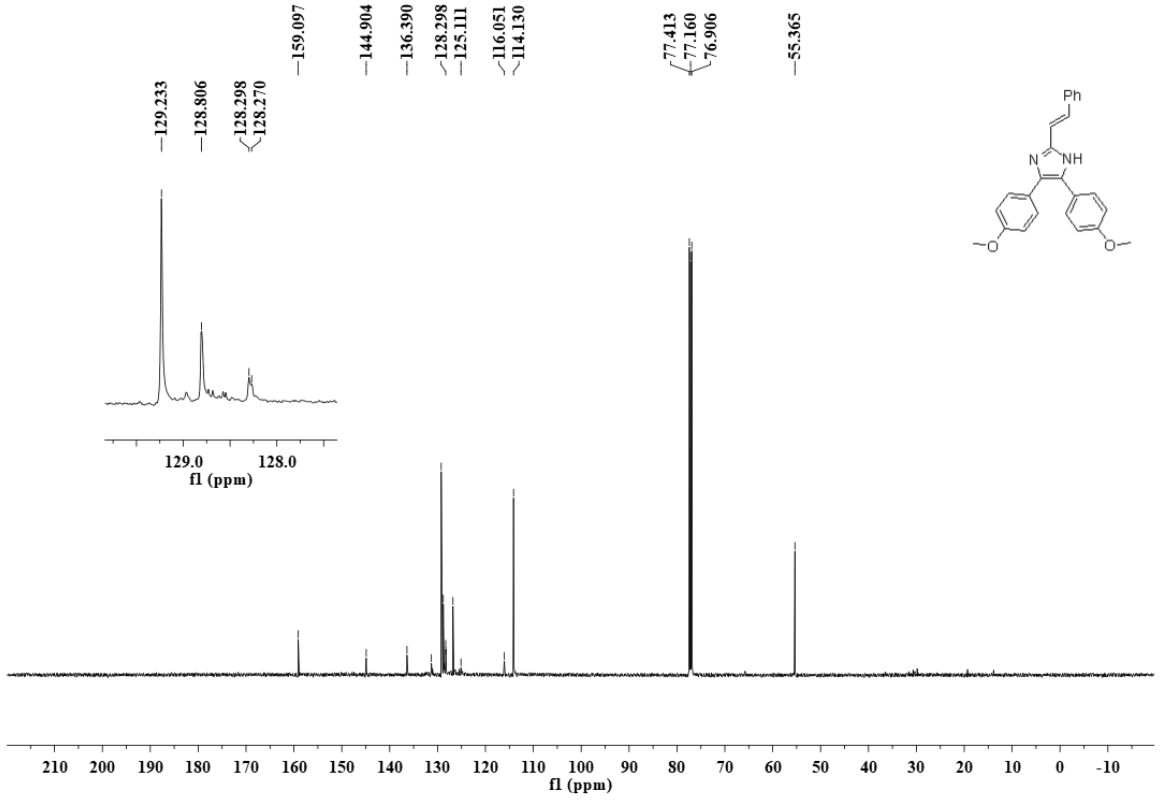
^{13}C NMR (125 MHz, $CDCl_3$) of **1c-D**



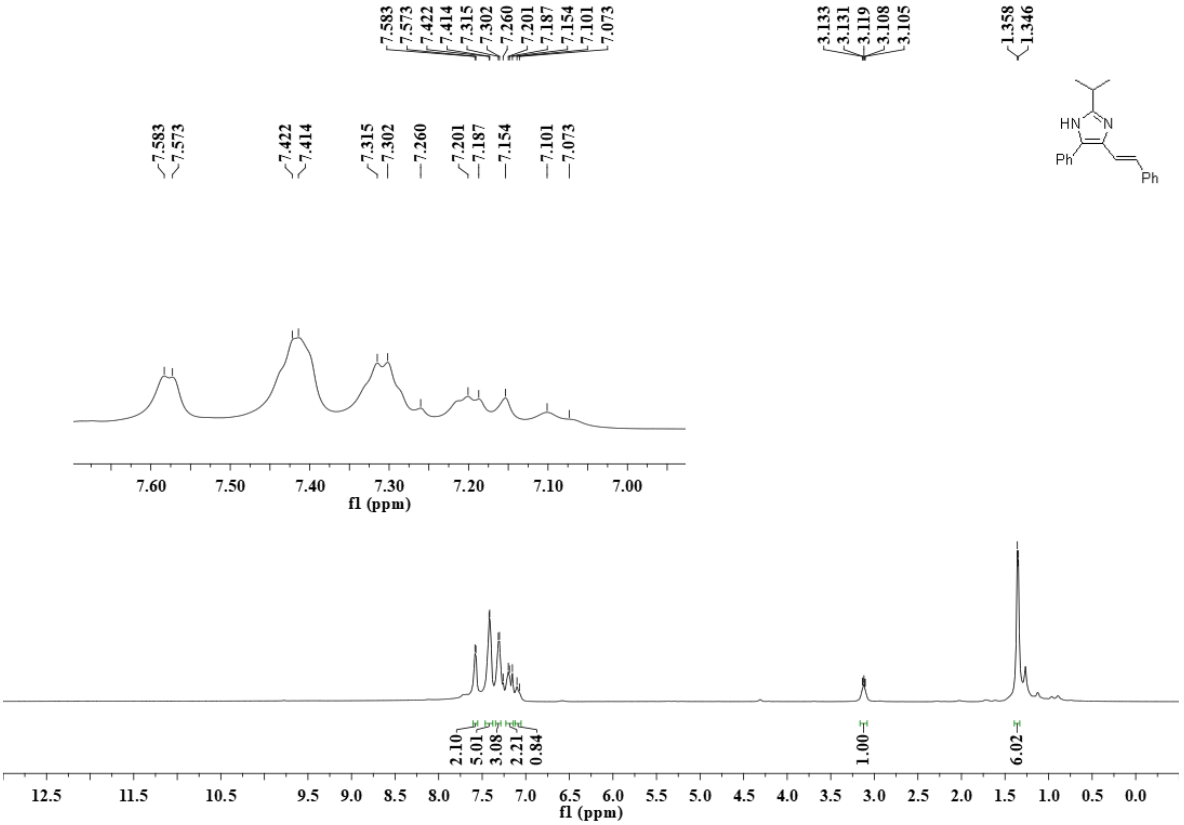
^{1}H NMR (500 MHz, $CDCl_3$) of **1d-D**



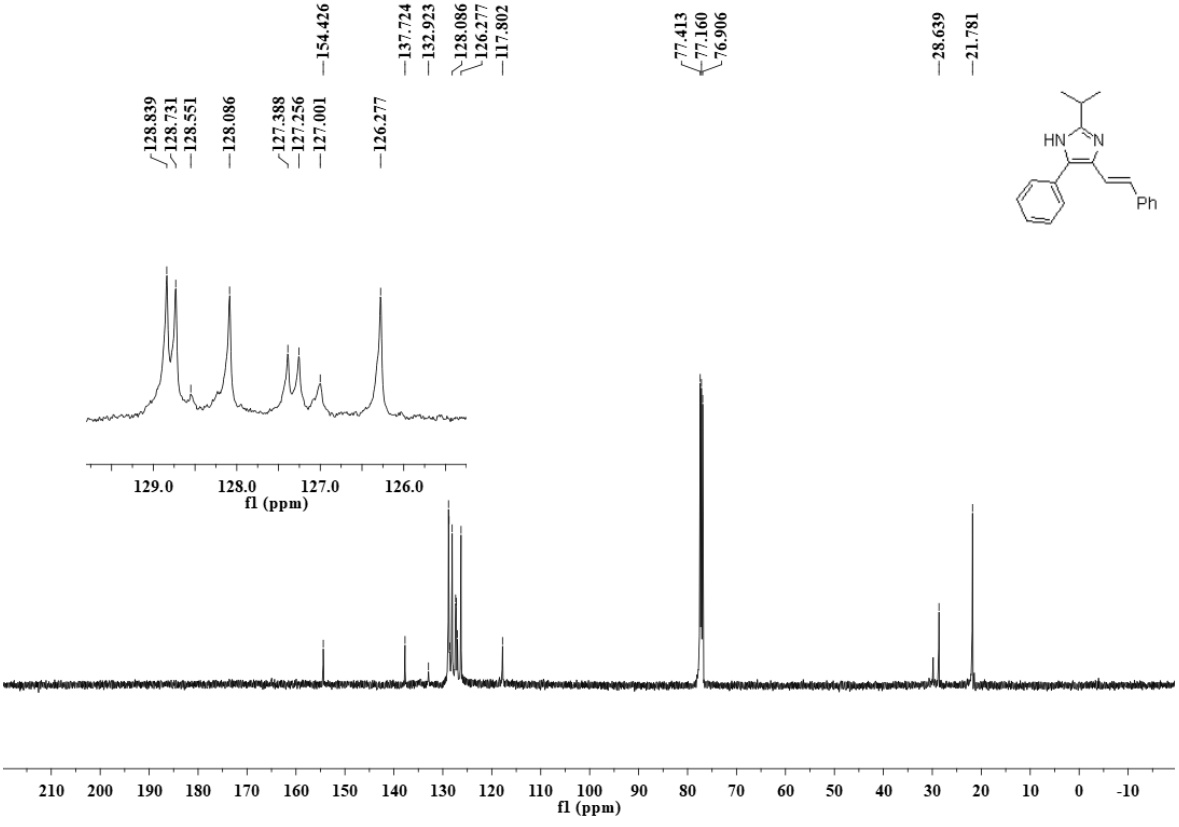
^{13}C NMR (125 MHz, $CDCl_3$) of **1d-D**



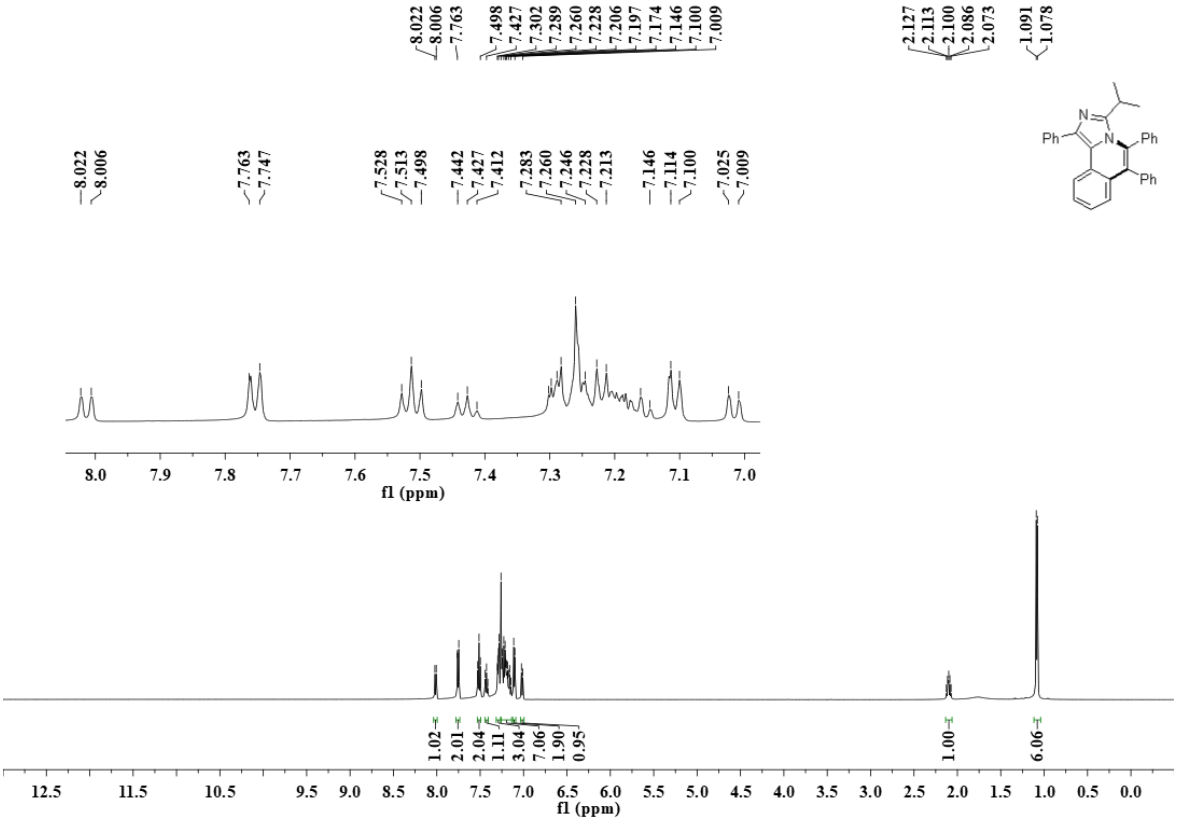
^{1}H NMR (500 MHz, $CDCl_3$) of **15**



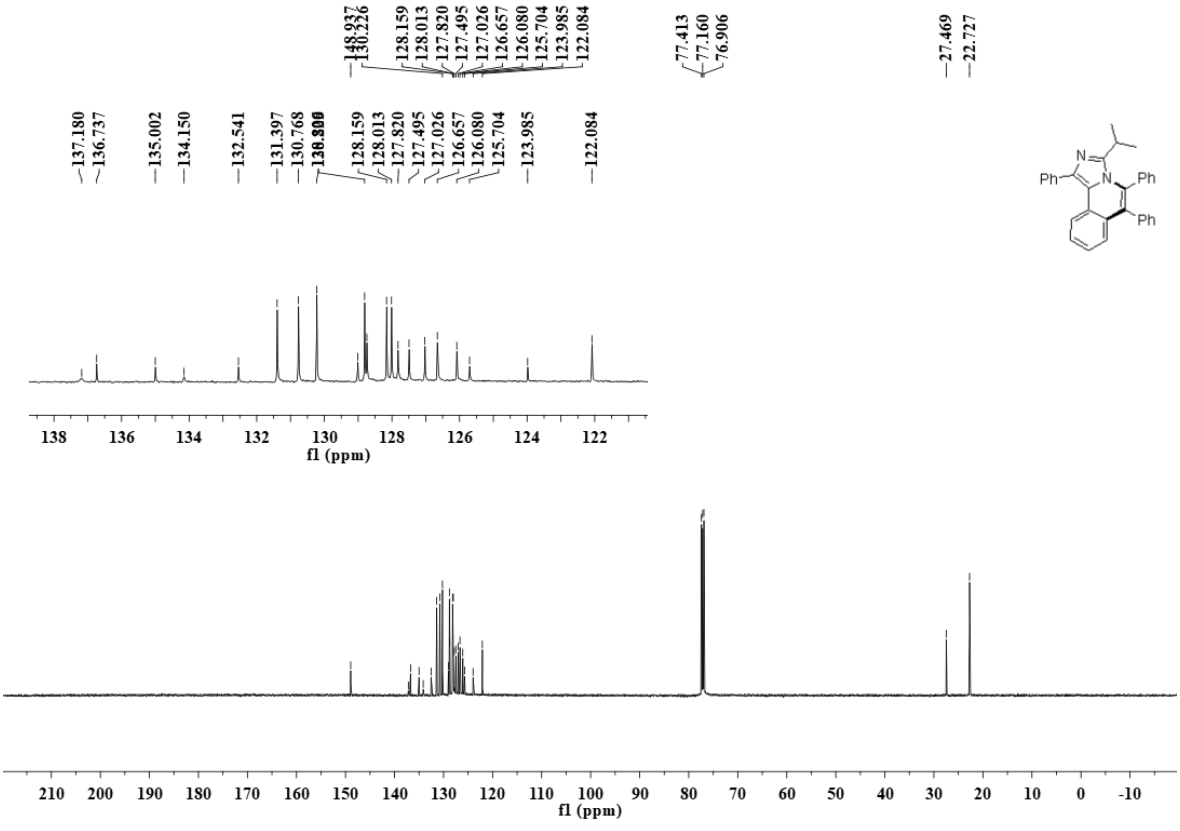
^{13}C NMR (125 MHz, $CDCl_3$) of **15**



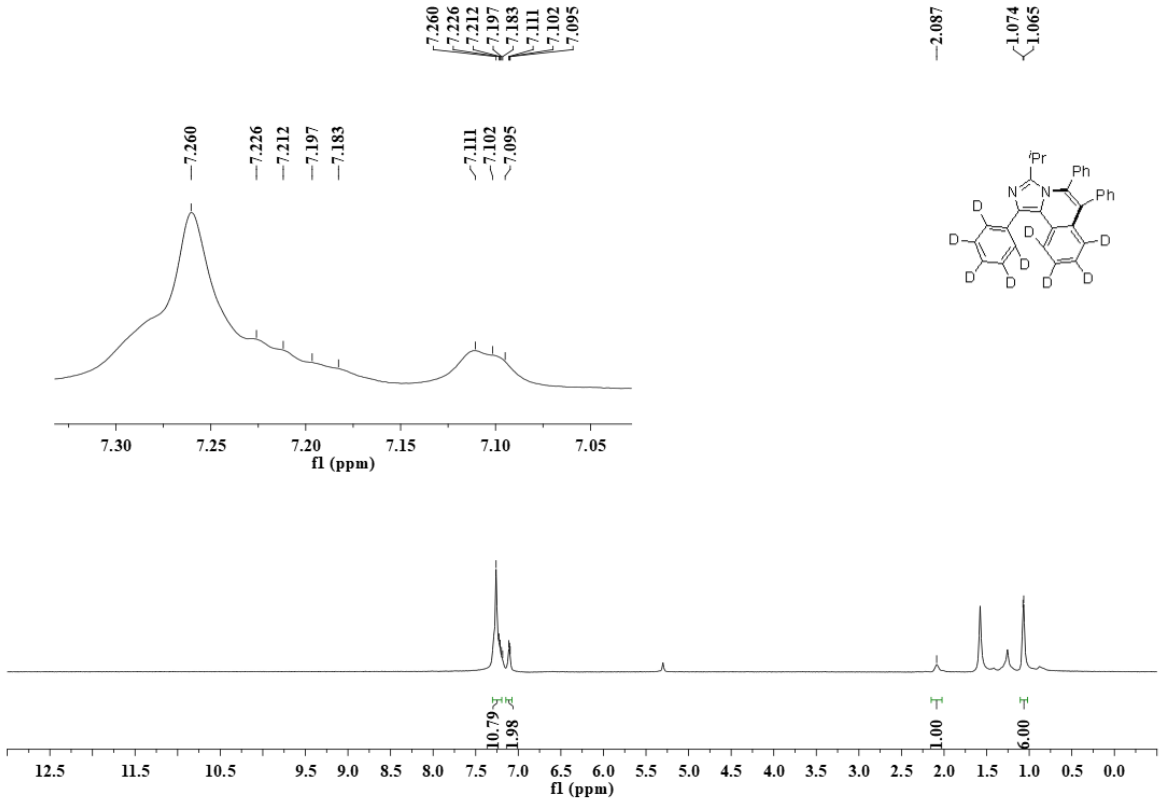
^{1}H NMR (500 MHz, $CDCl_3$) of **3a**



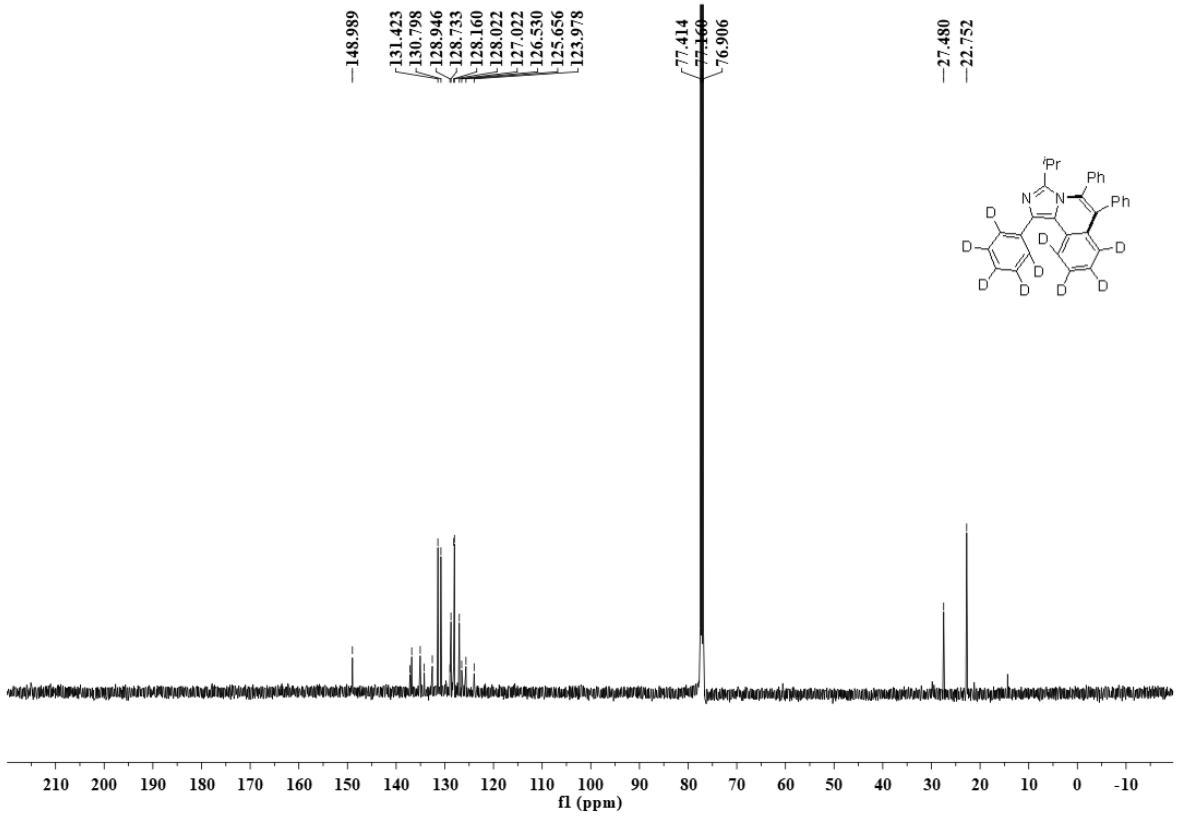
^{13}C NMR (125 MHz, $CDCl_3$) of **3a**



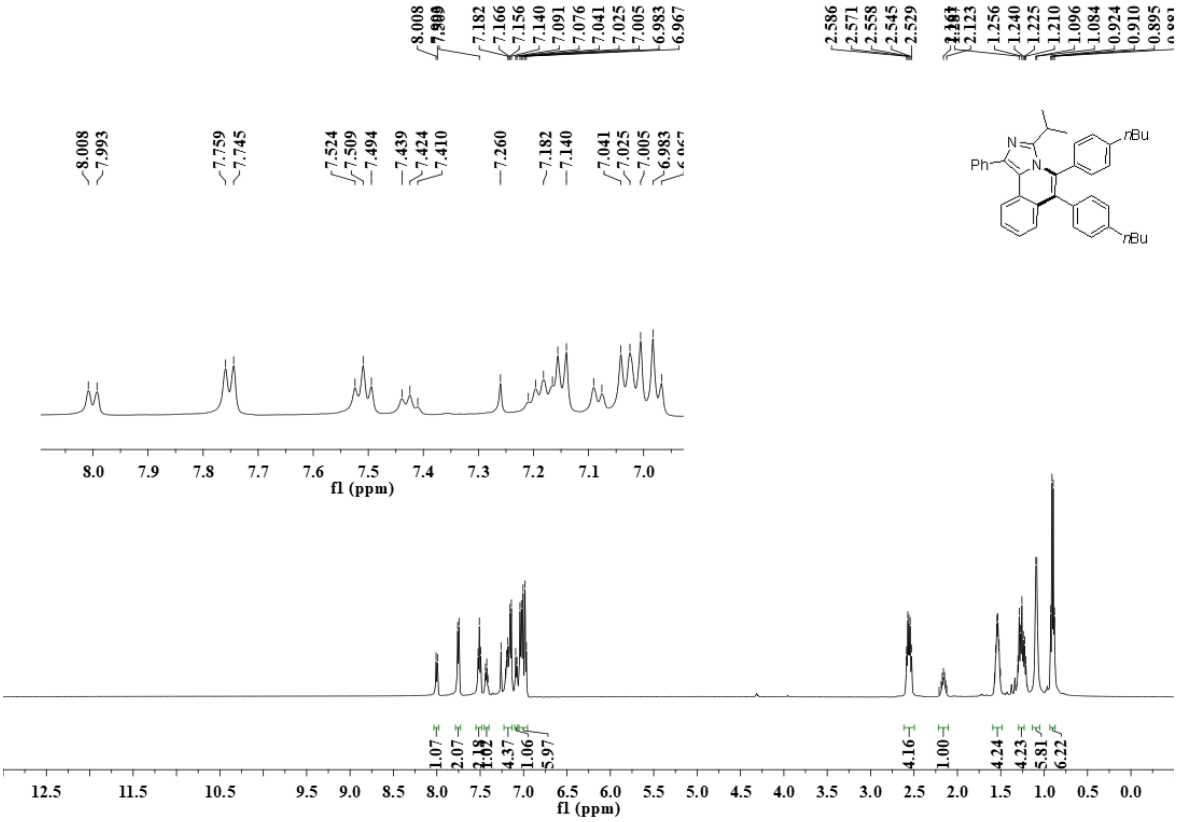
^{1}H NMR (500 MHz, $CDCl_3$) of ***d*-3a**



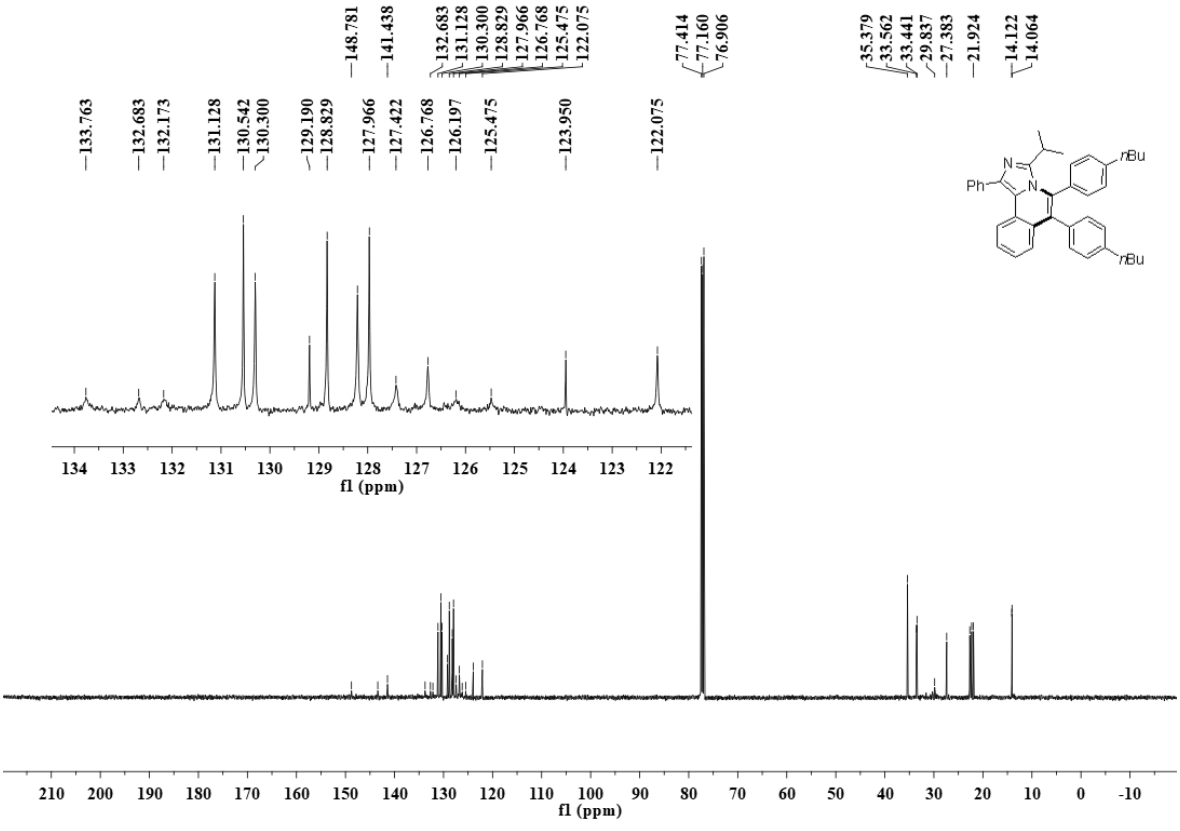
^{13}C NMR (125 MHz, $CDCl_3$) of ***d*-3a**



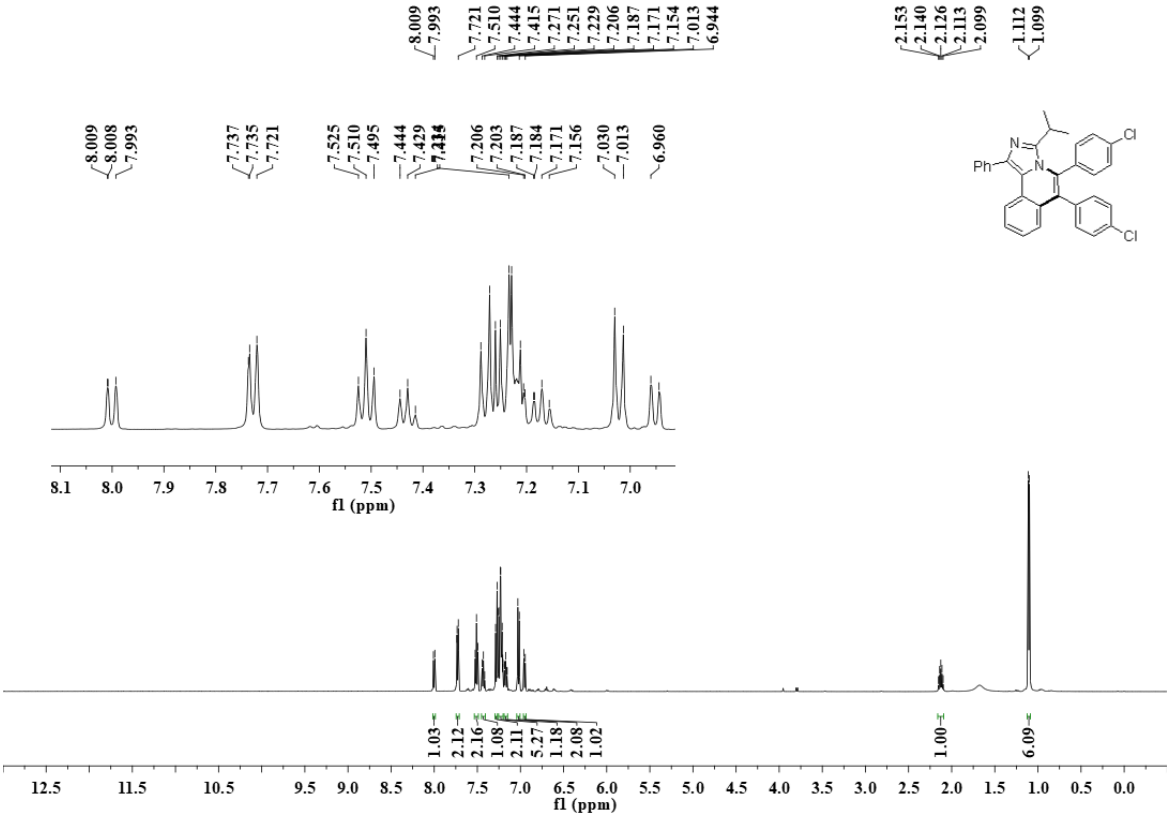
^{1}H NMR (500 MHz, $CDCl_3$) of **3b**



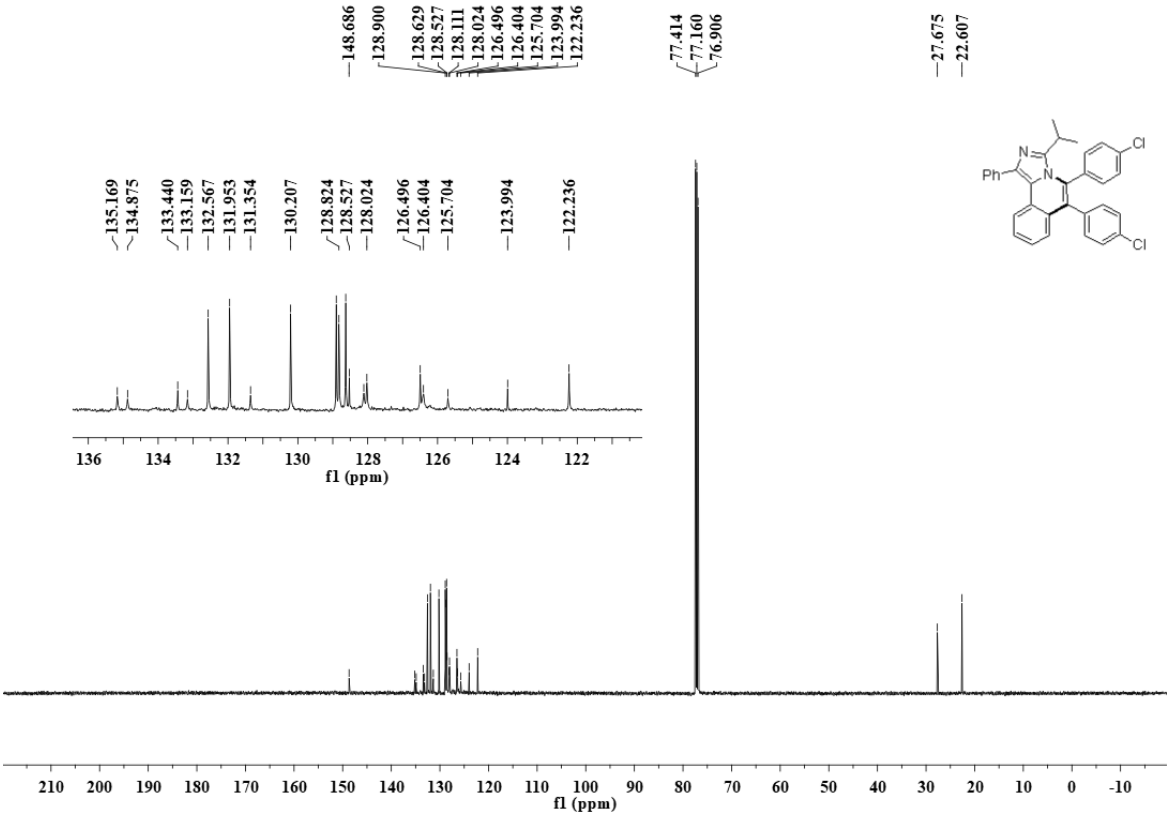
^{13}C NMR (125 MHz, $CDCl_3$) of **3b**



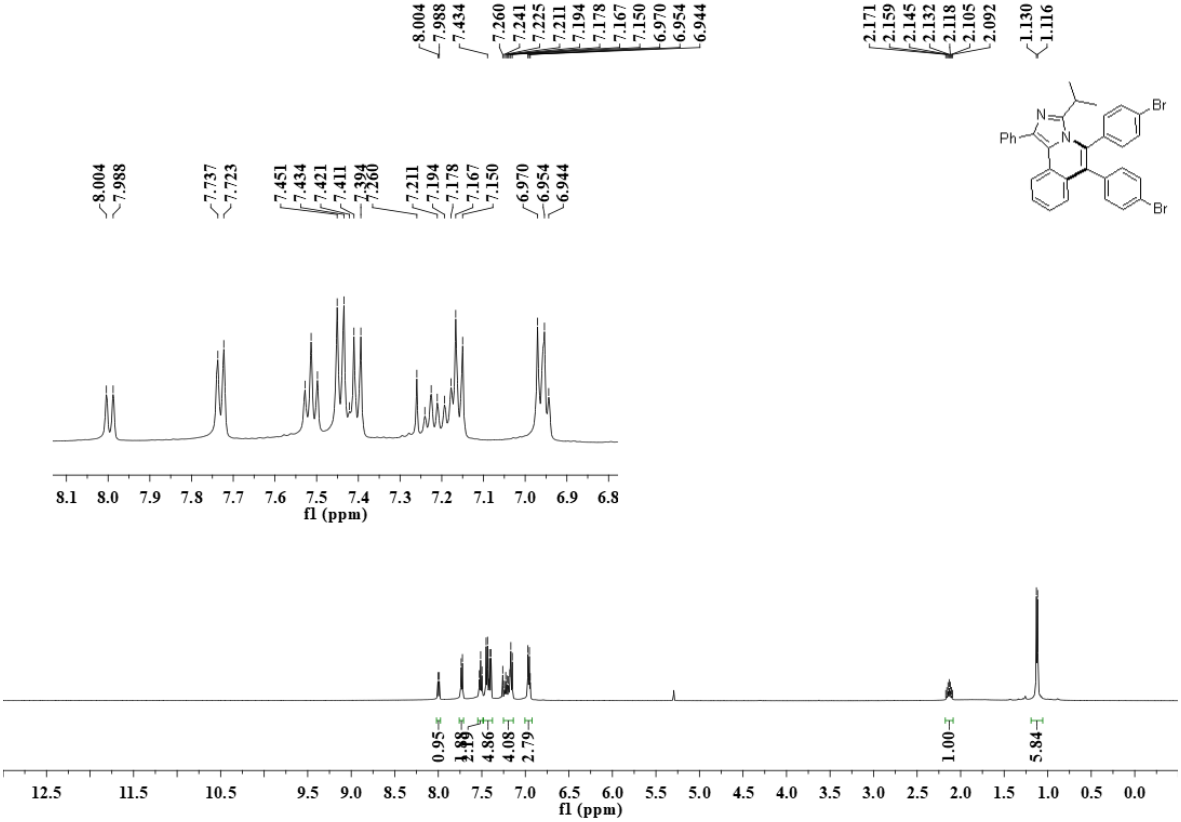
^{1}H NMR (500 MHz, $CDCl_3$) of **3c**



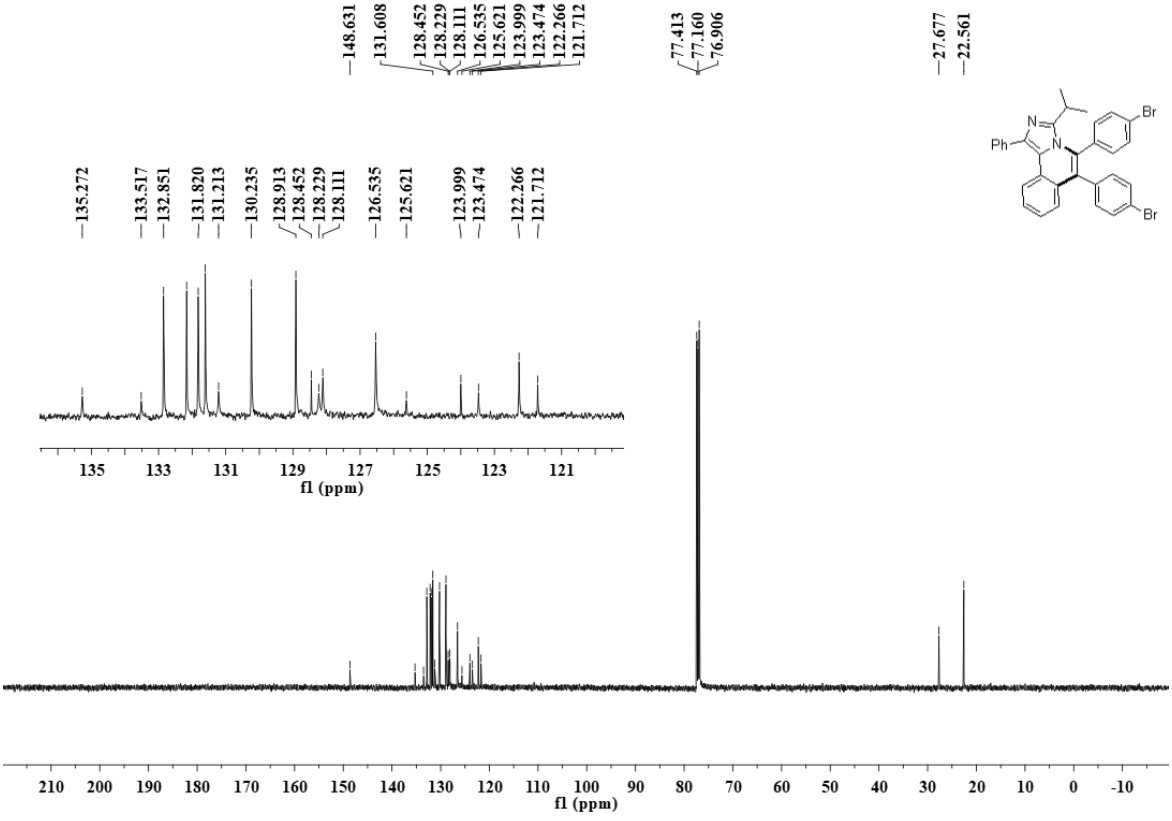
^{13}C NMR (125 MHz, $CDCl_3$) of **3c**



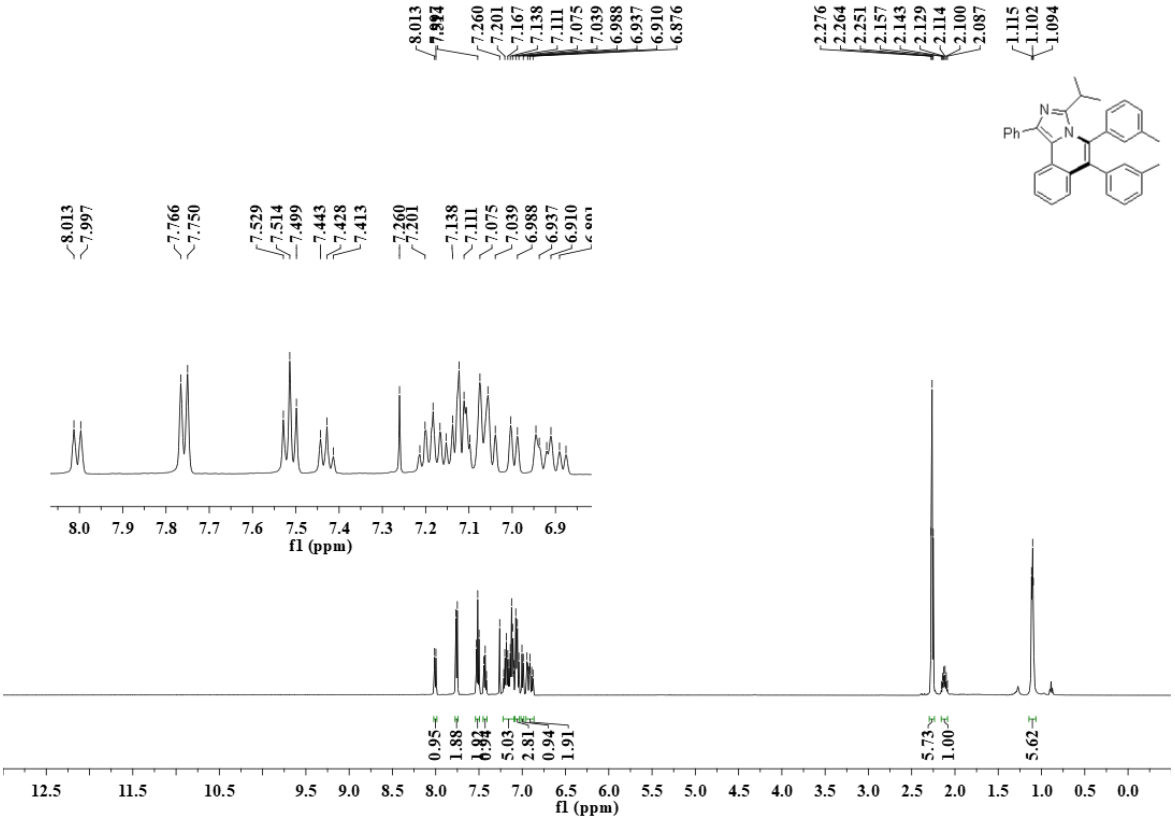
^{1}H NMR (500 MHz, $CDCl_3$) of **3d**



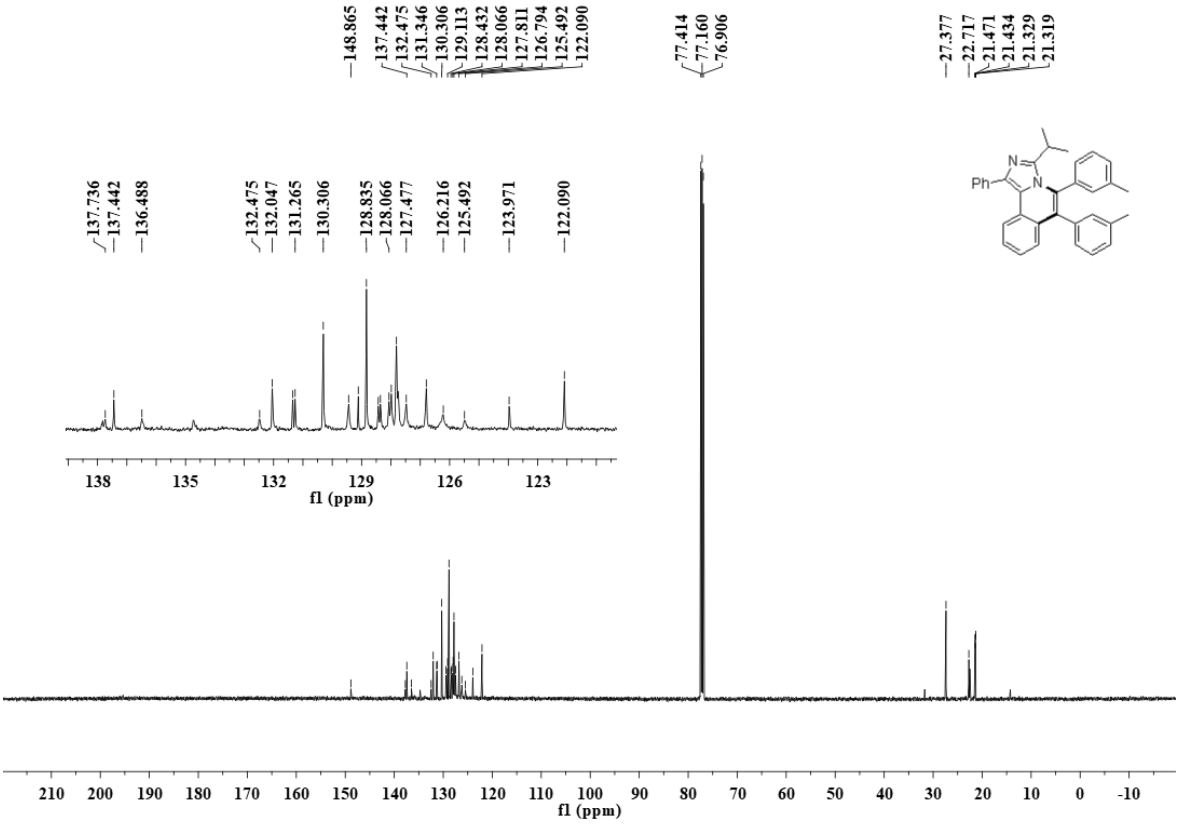
^{13}C NMR (125 MHz, $CDCl_3$) of **3d**



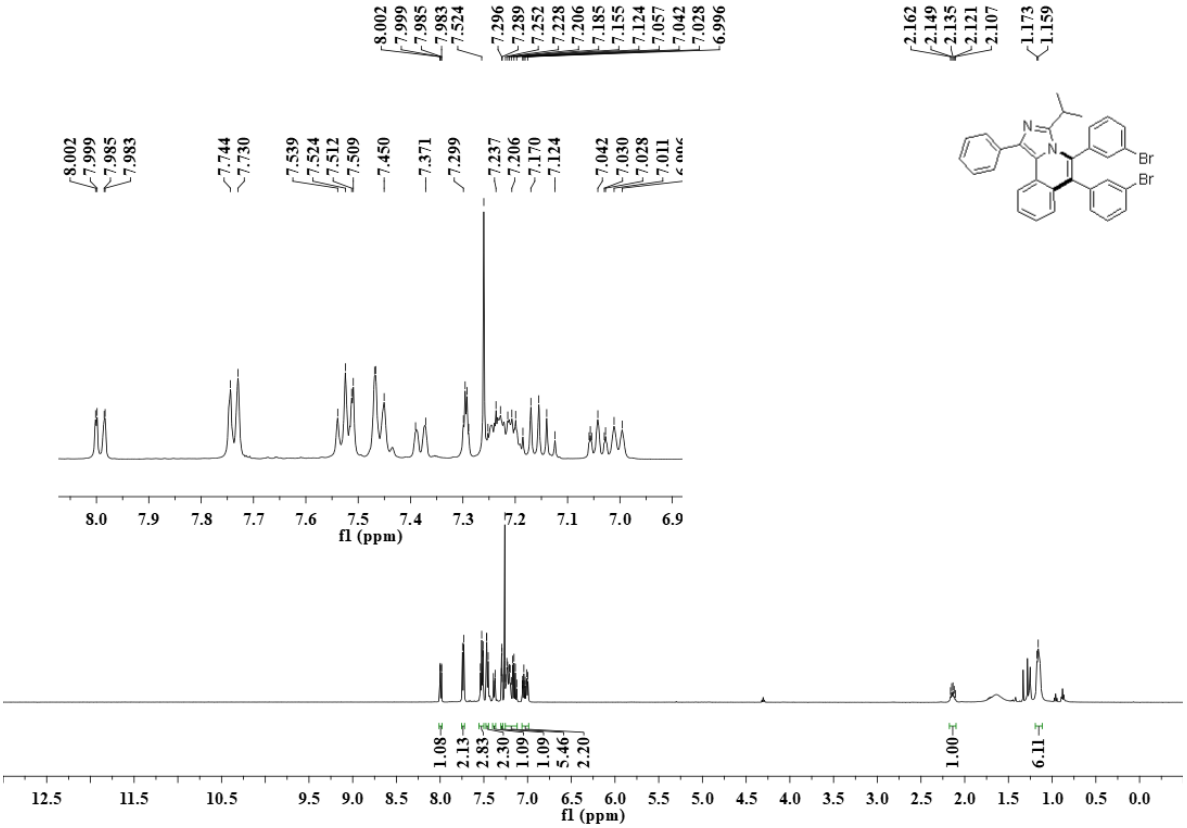
^{1}H NMR (500 MHz, $CDCl_3$) of **3e**



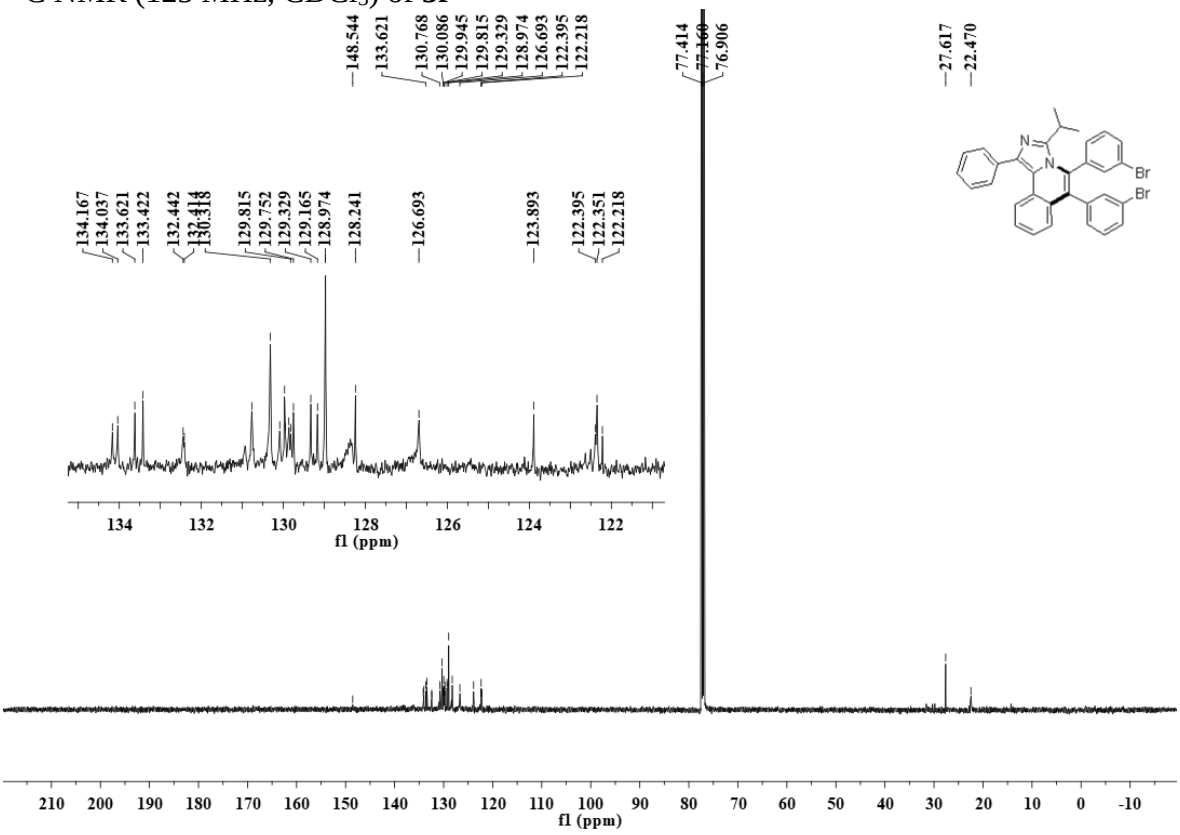
^{13}C NMR (125 MHz, $CDCl_3$) of **3e**



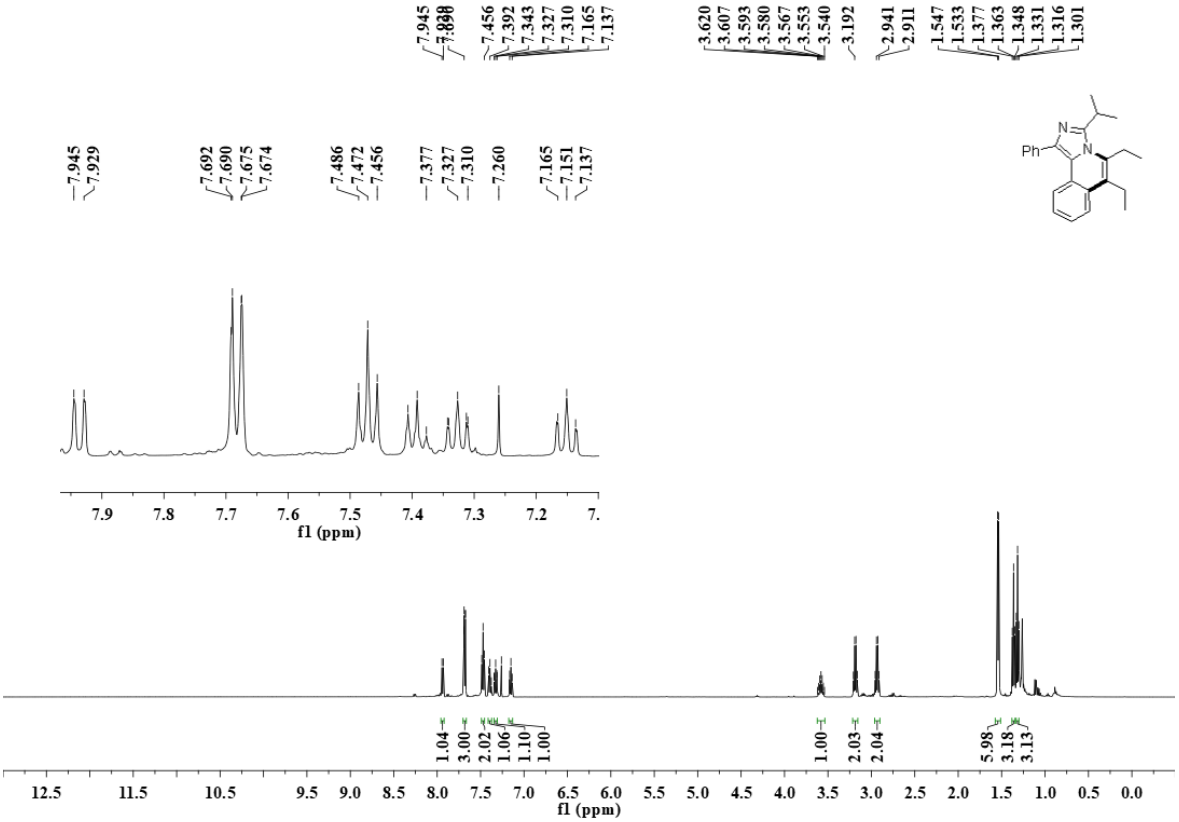
^{1}H NMR (500 MHz, $CDCl_3$) of **3f**



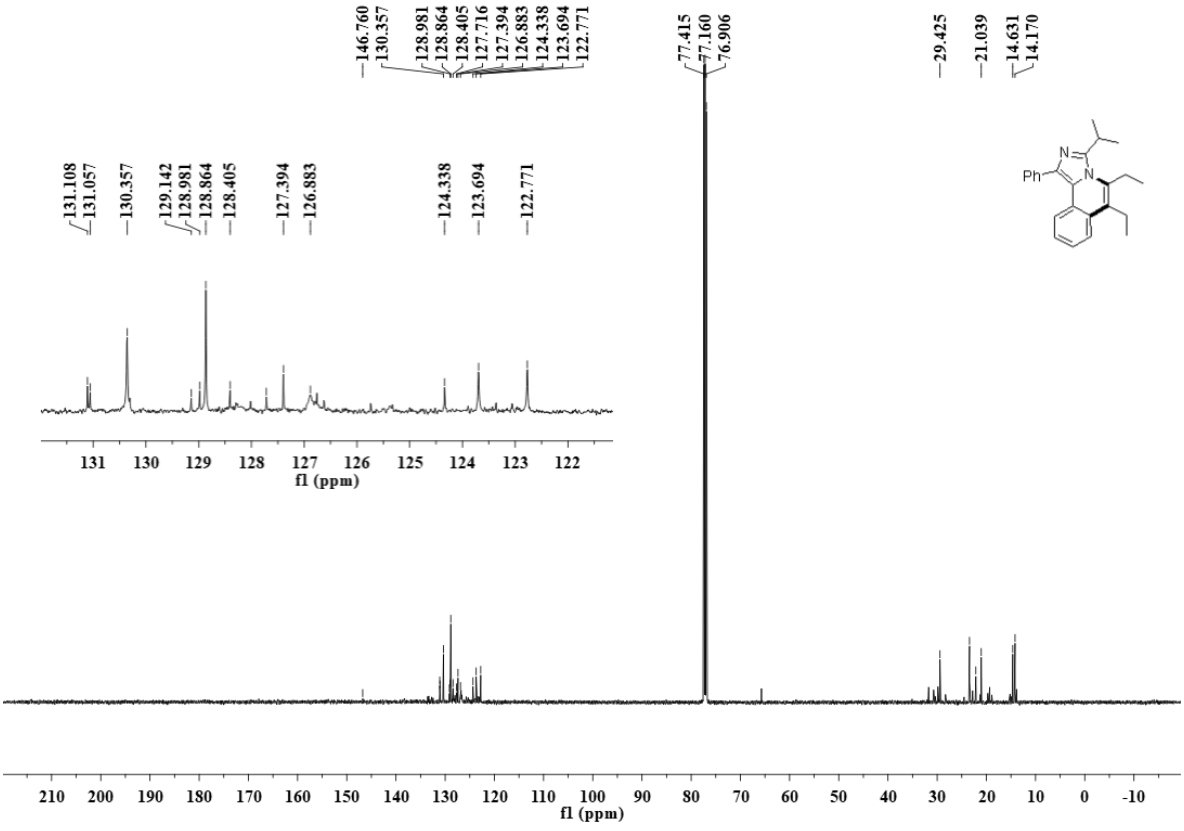
^{13}C NMR (125 MHz, $CDCl_3$) of **3f**



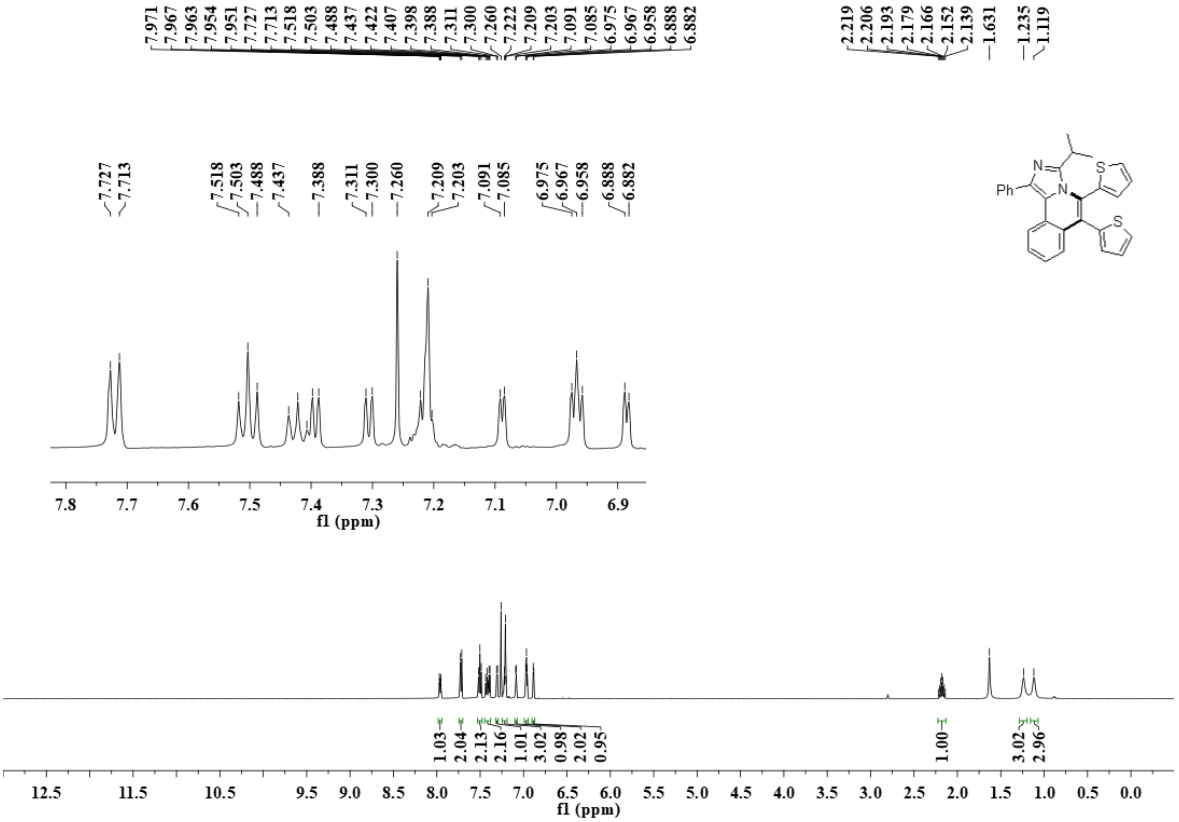
^{1}H NMR (500 MHz, $CDCl_3$) of **3g**



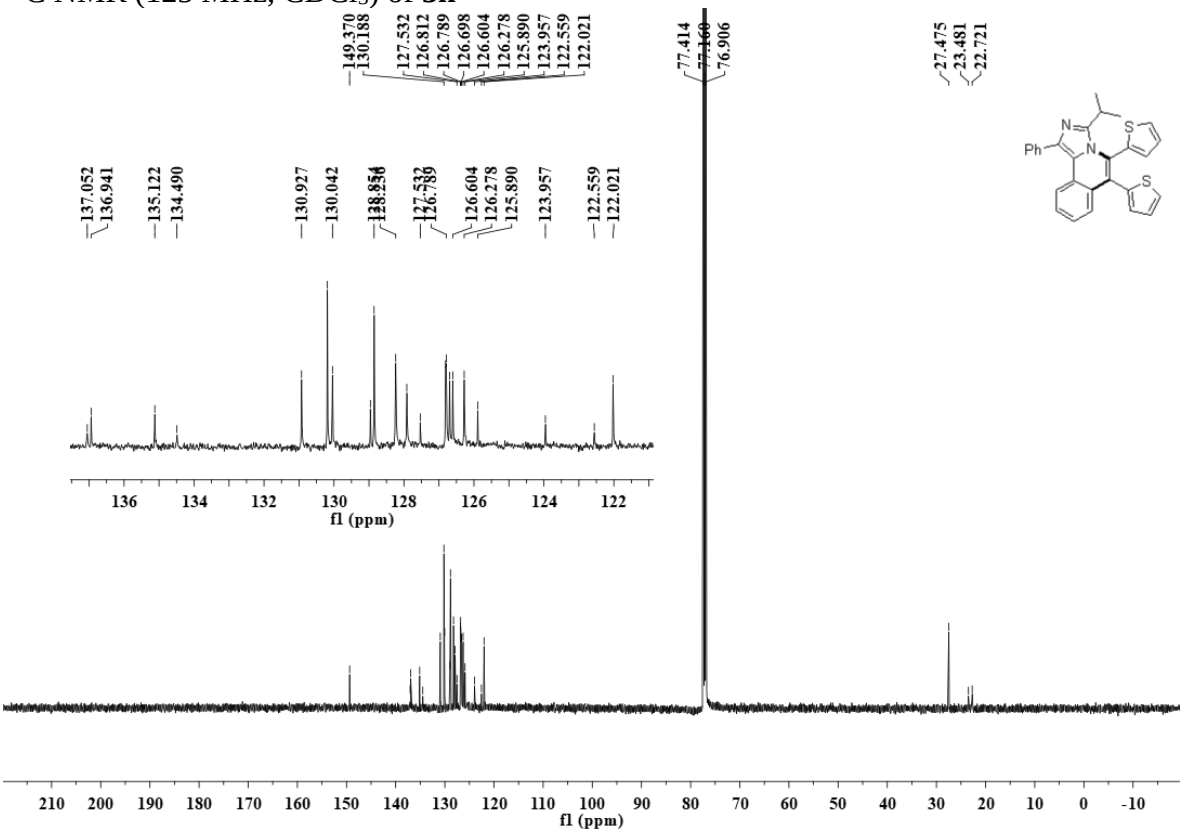
^{13}C NMR (125 MHz, $CDCl_3$) of **3g**



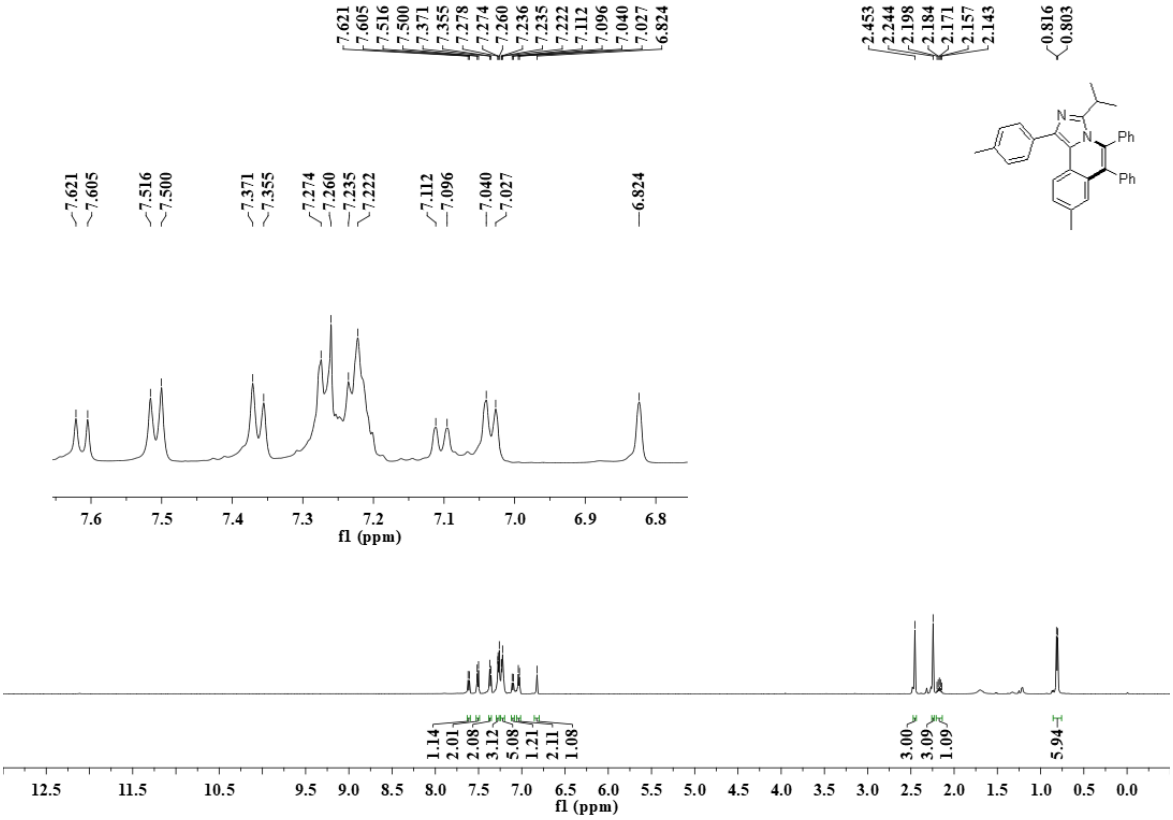
^{1}H NMR (500 MHz, $CDCl_3$) of **3h**



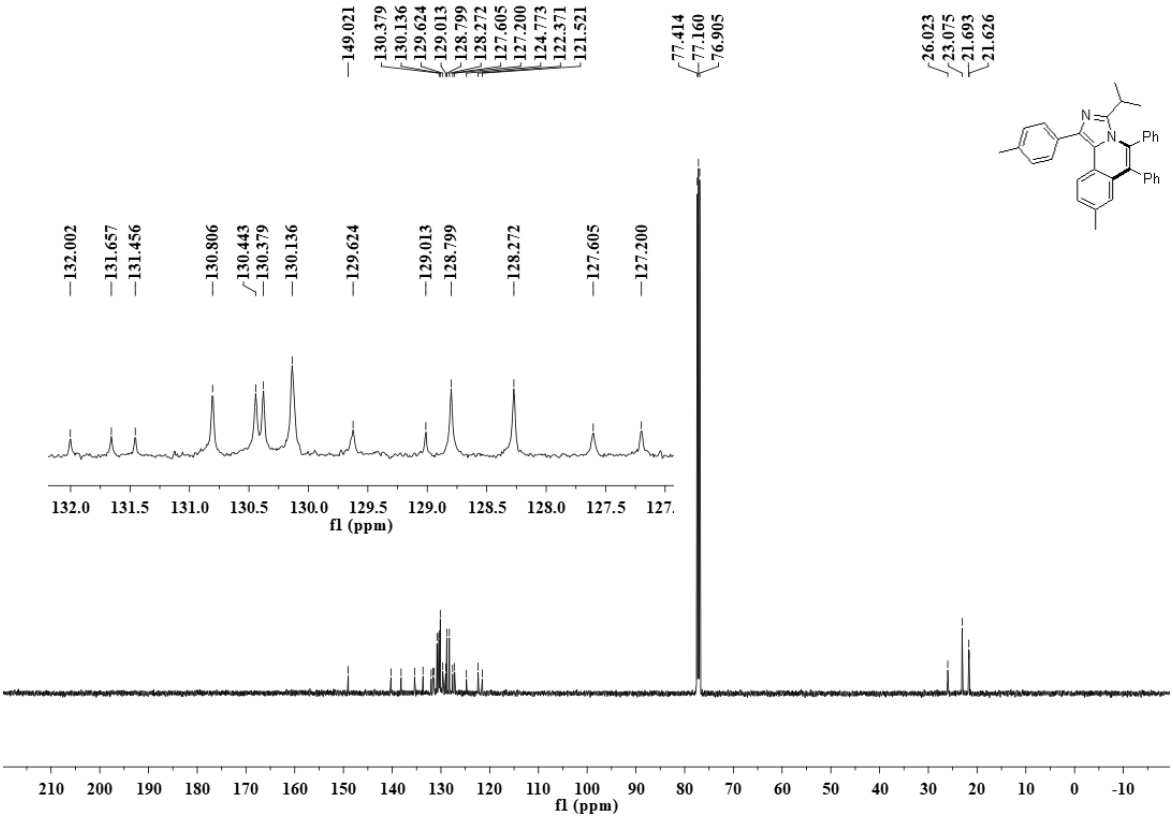
^{13}C NMR (125 MHz, $CDCl_3$) of **3h**



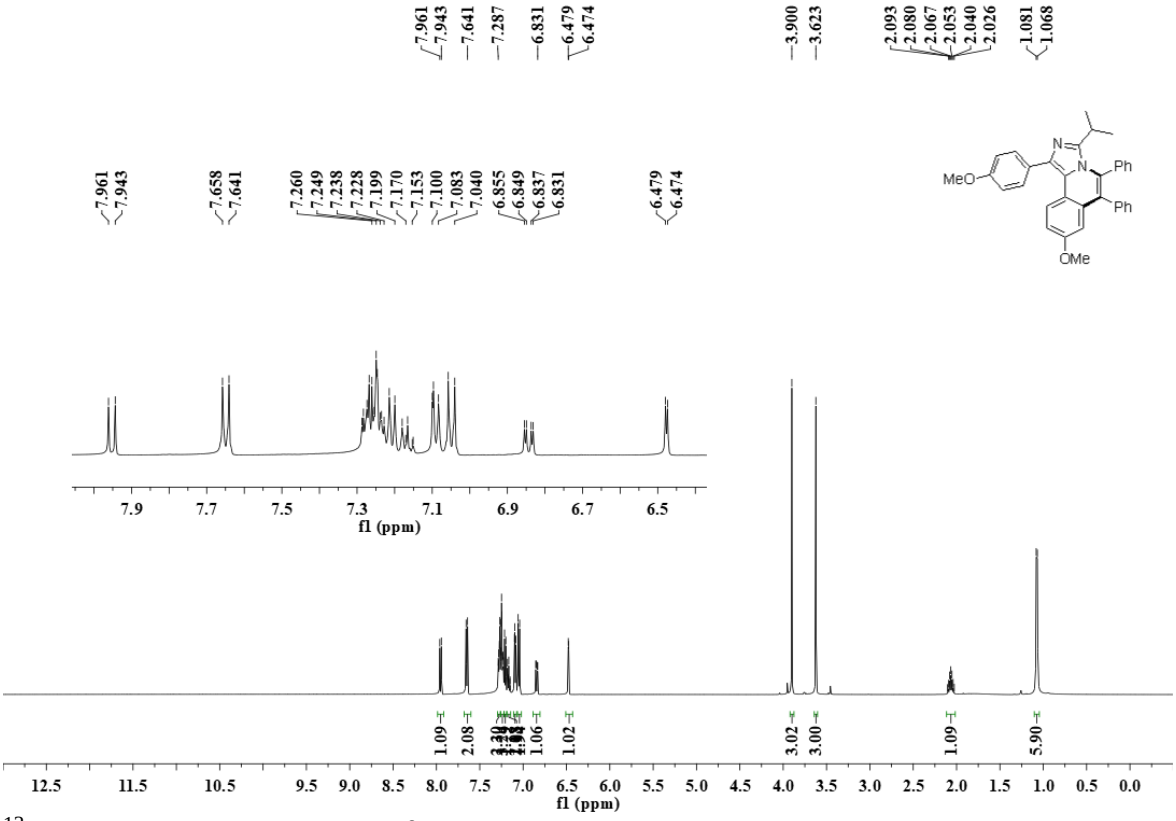
^{1}H NMR (500 MHz, $CDCl_3$) of **3i**



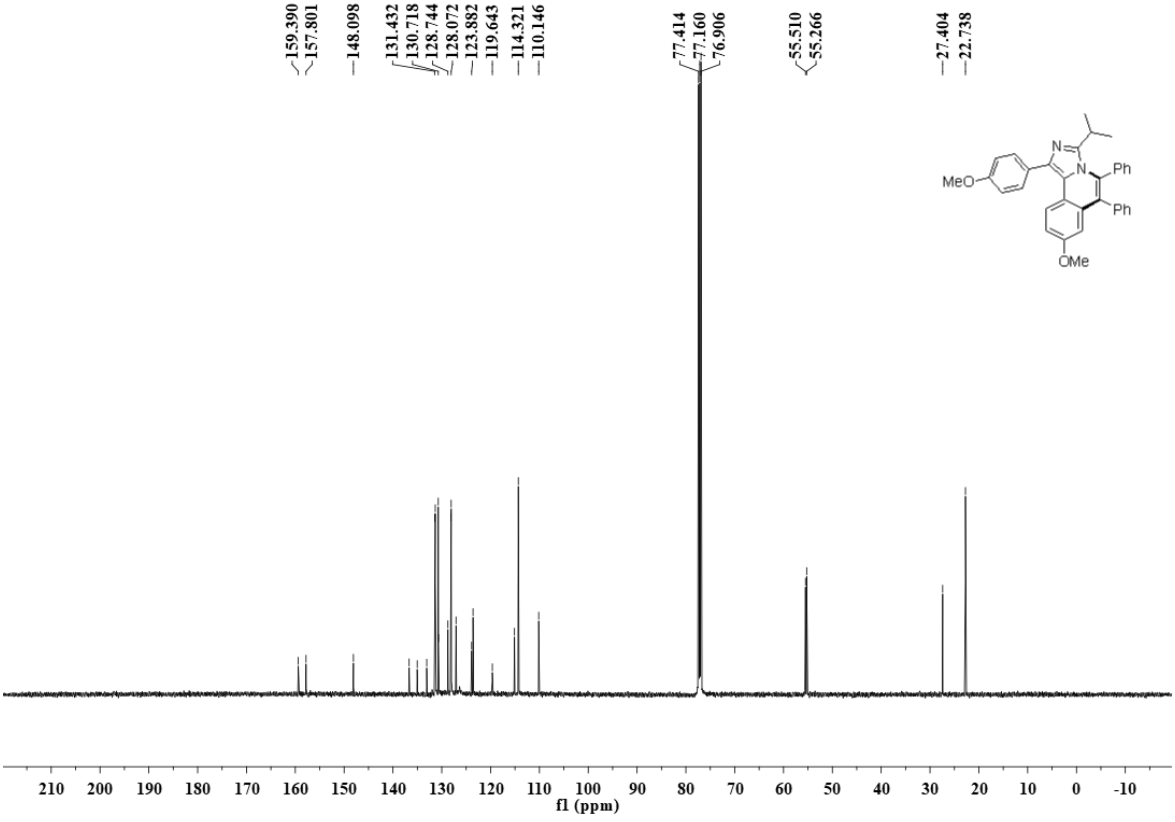
^{13}C NMR (125 MHz, $CDCl_3$) of **3i**



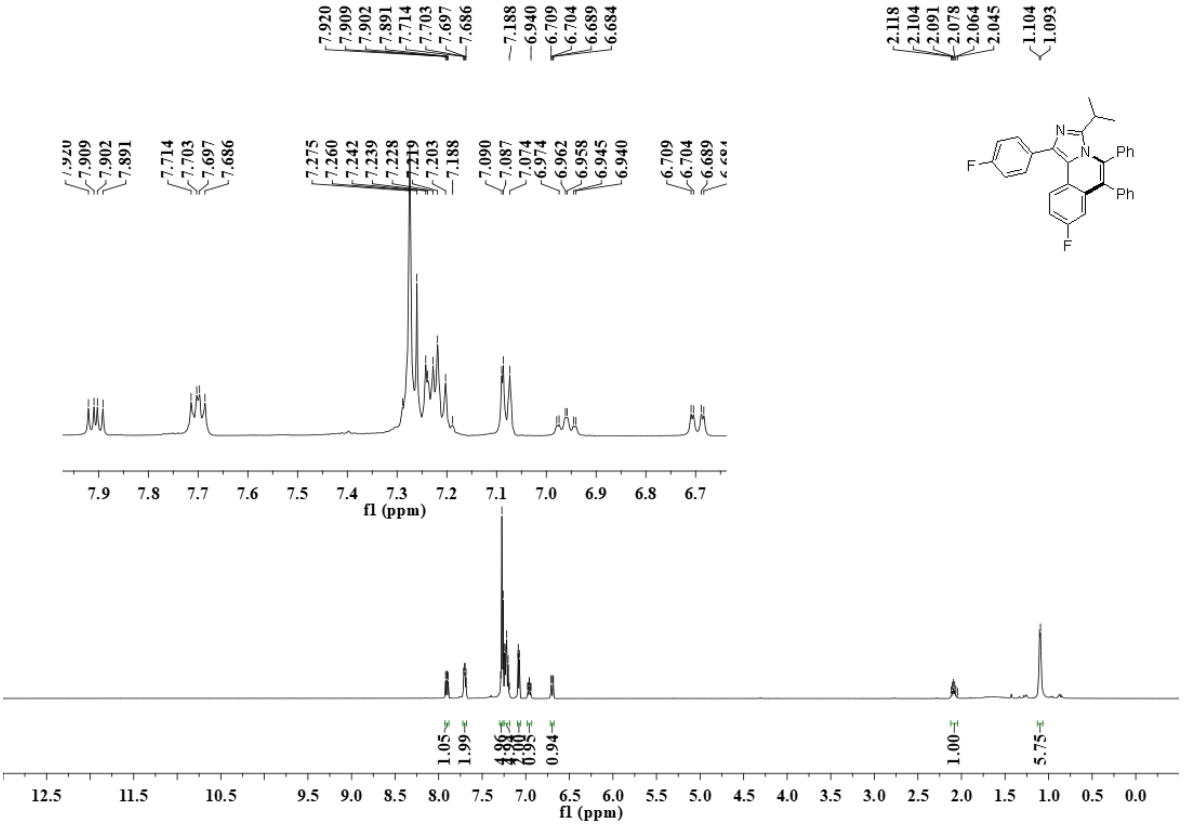
^{1}H NMR (500 MHz, $CDCl_3$) of **3j**



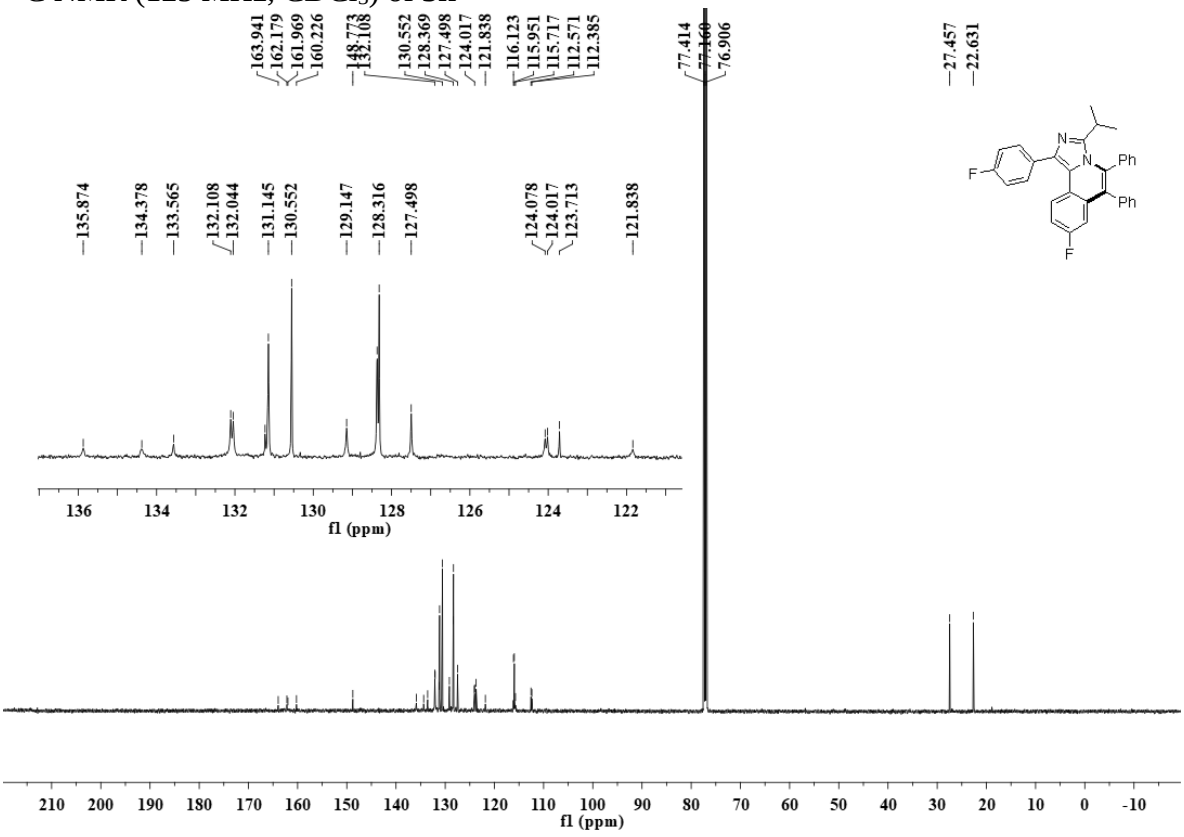
^{13}C NMR (125 MHz, $CDCl_3$) of **3j**



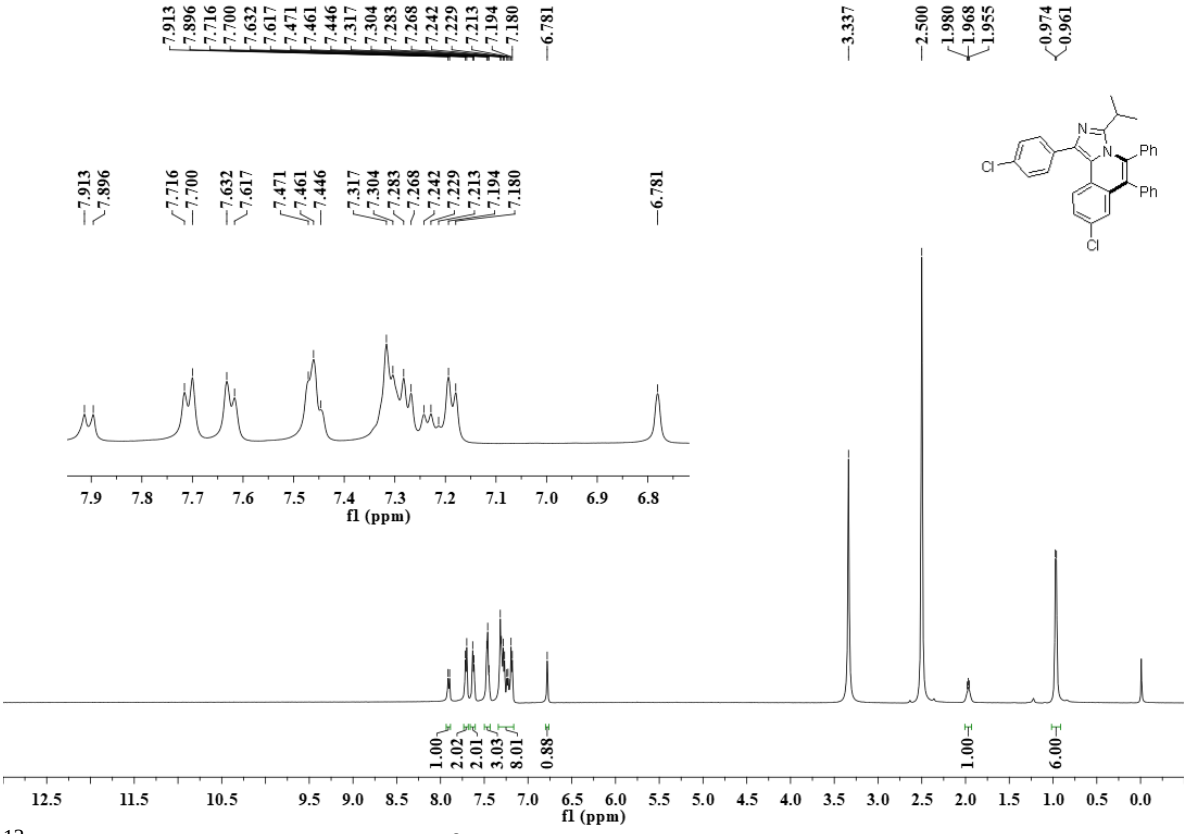
^{1}H NMR (500 MHz, $CDCl_3$) of **3k**



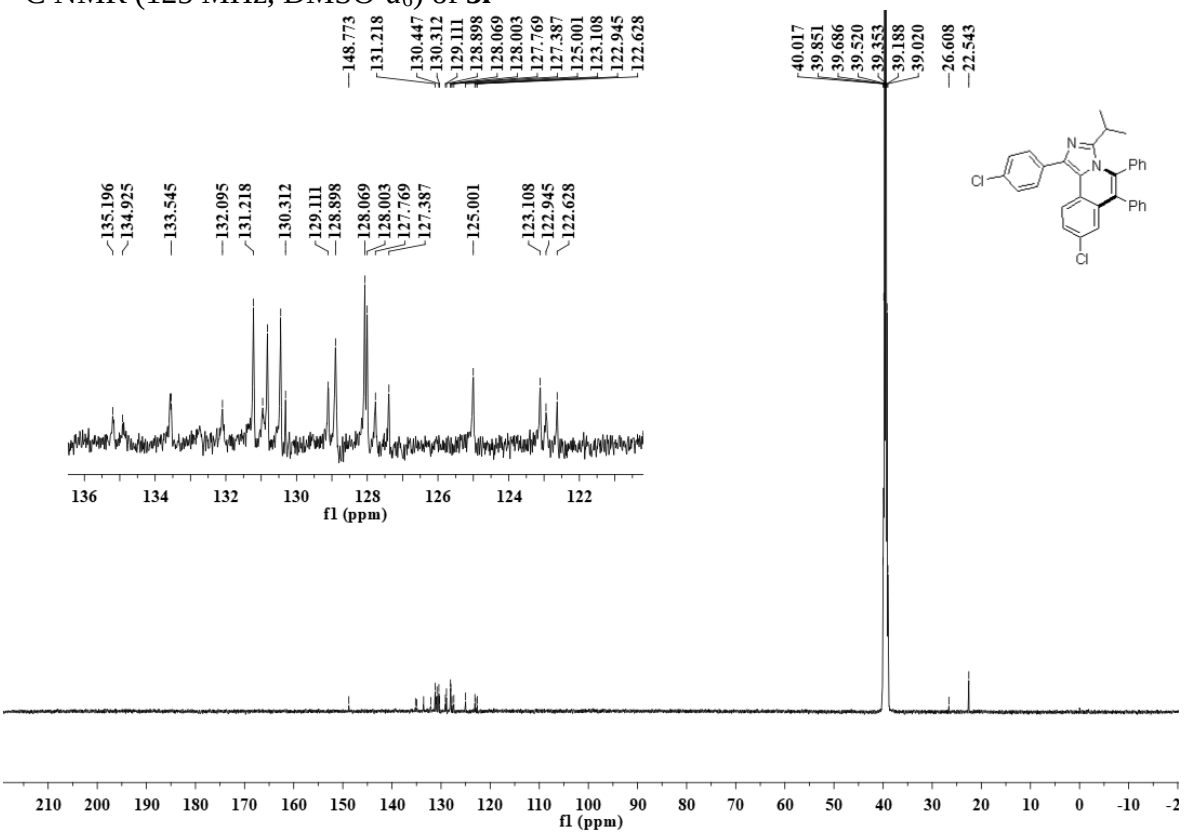
^{13}C NMR (125 MHz, $CDCl_3$) of **3k**



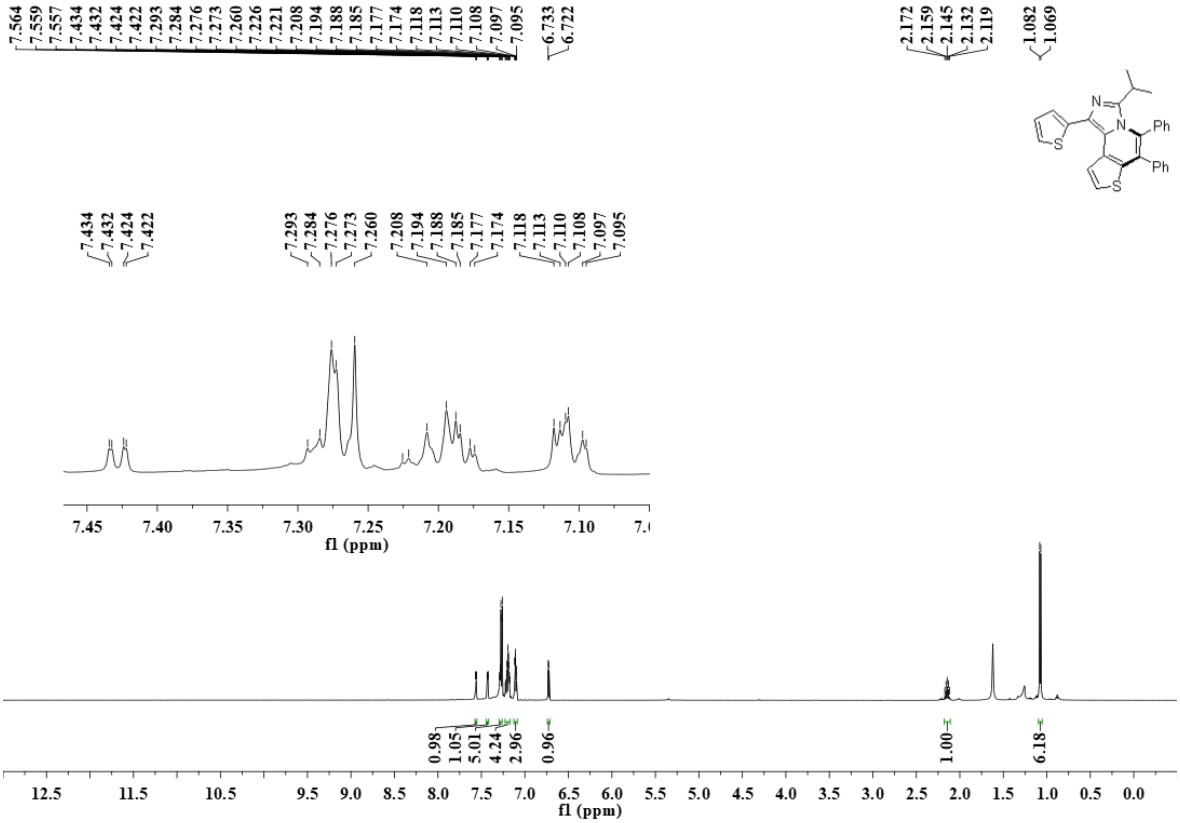
^{1}H NMR (500 MHz, DMSO-d_6) of **3l**



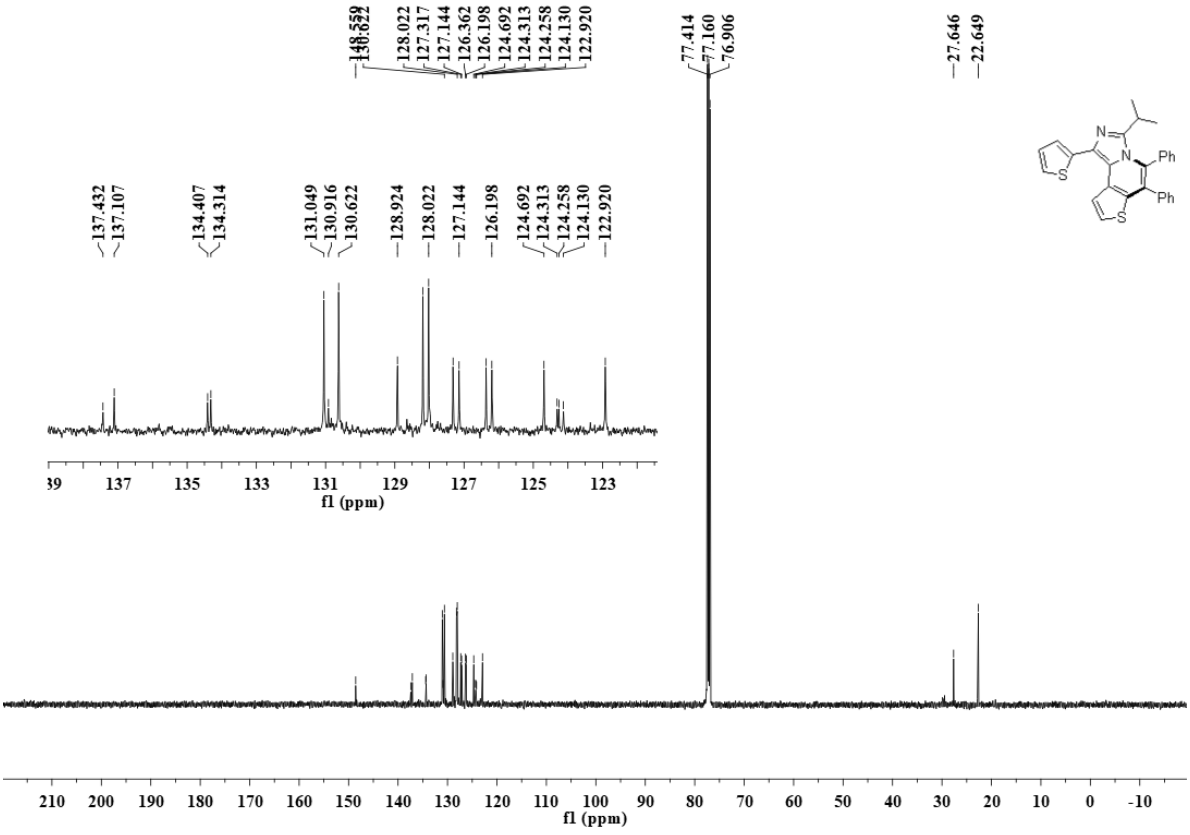
^{13}C NMR (125 MHz, DMSO-d_6) of **3l**



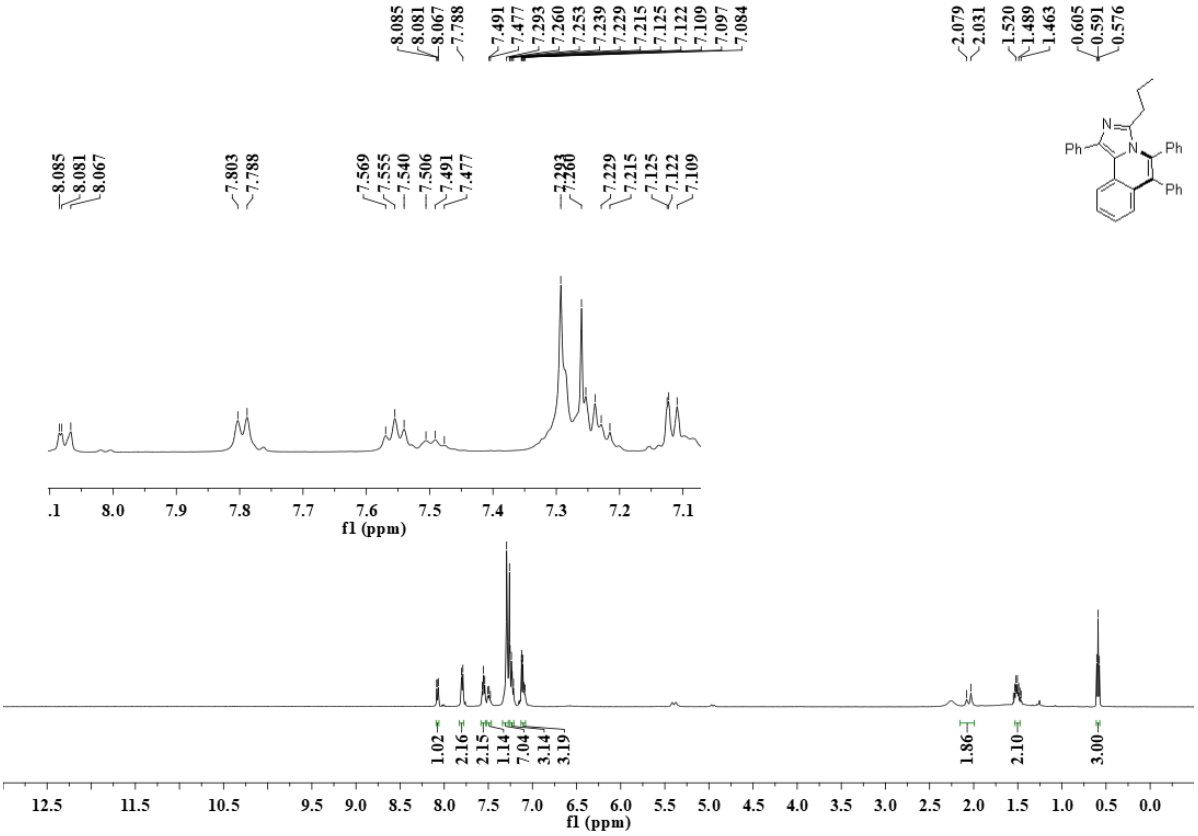
^{1}H NMR (500 MHz, $CDCl_3$) of **3m**



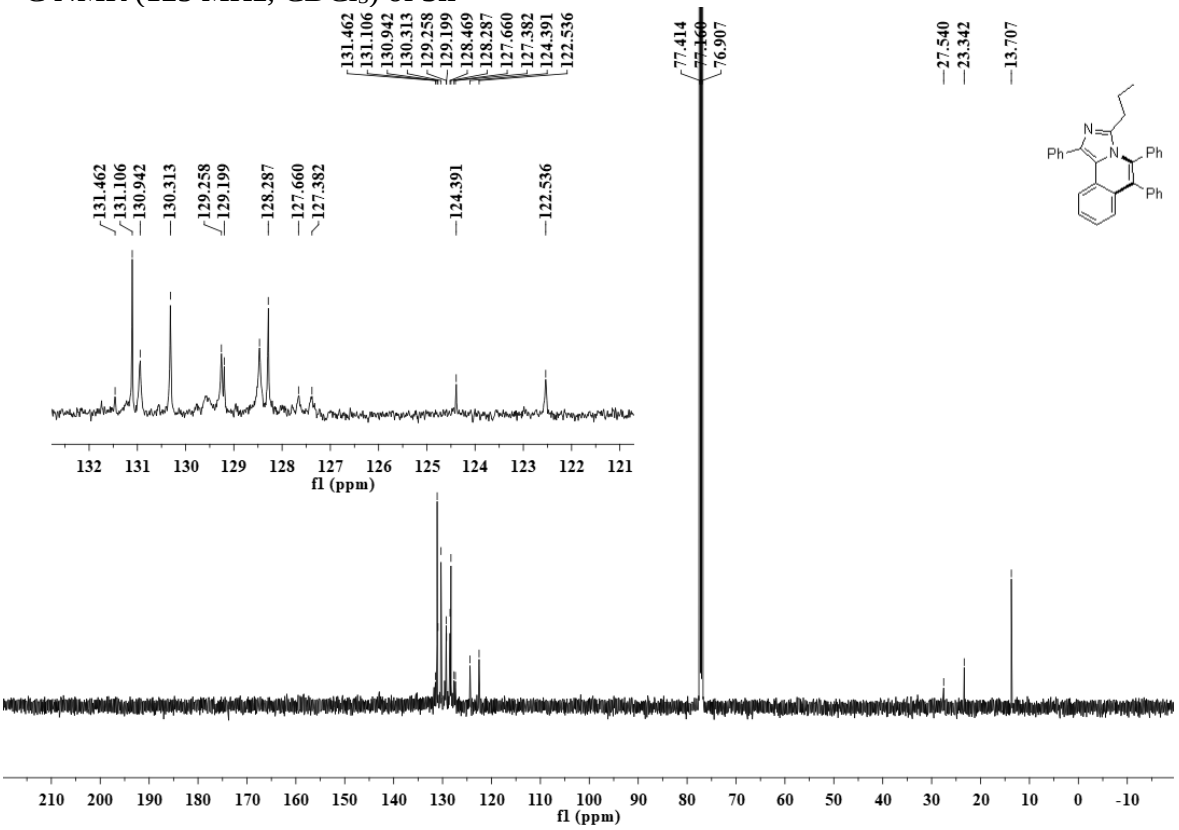
^{13}C NMR (125 MHz, $CDCl_3$) of **3m**



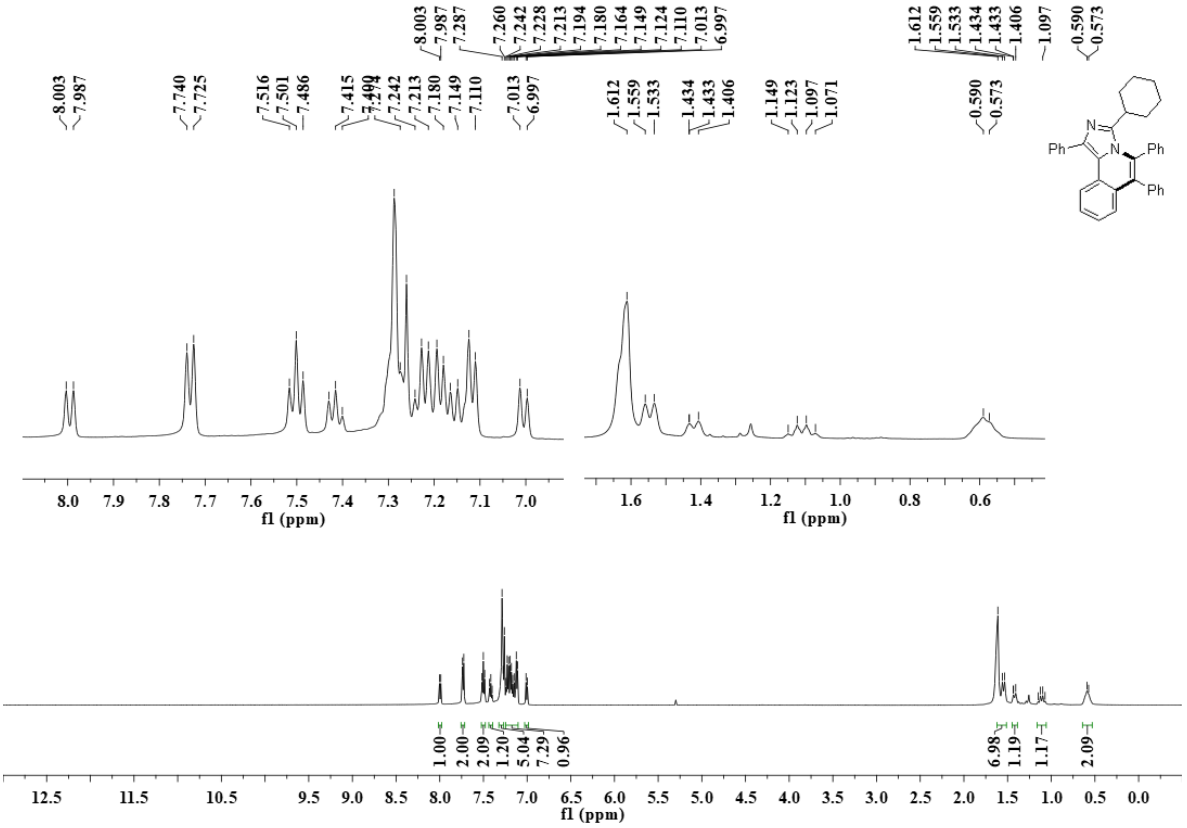
^{1}H NMR (500 MHz, $CDCl_3$) of **3n**



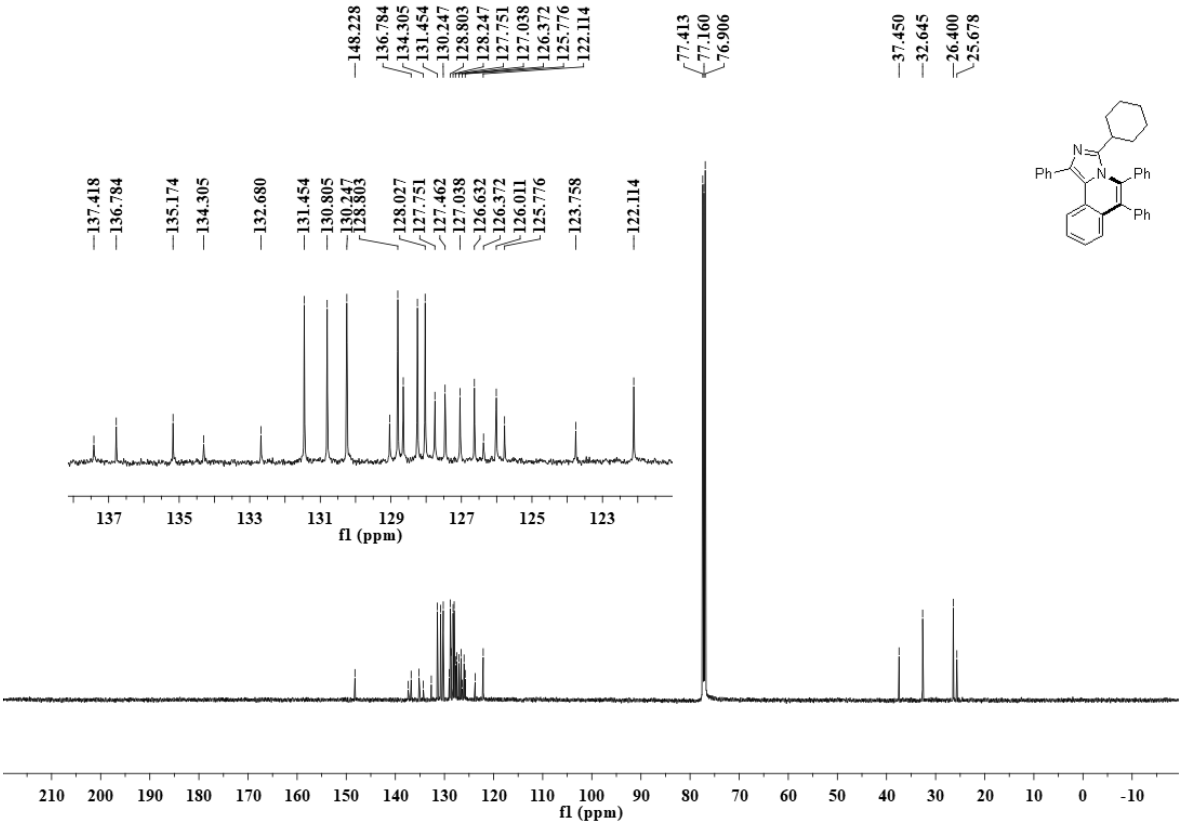
^{13}C NMR (125 MHz, $CDCl_3$) of **3n**



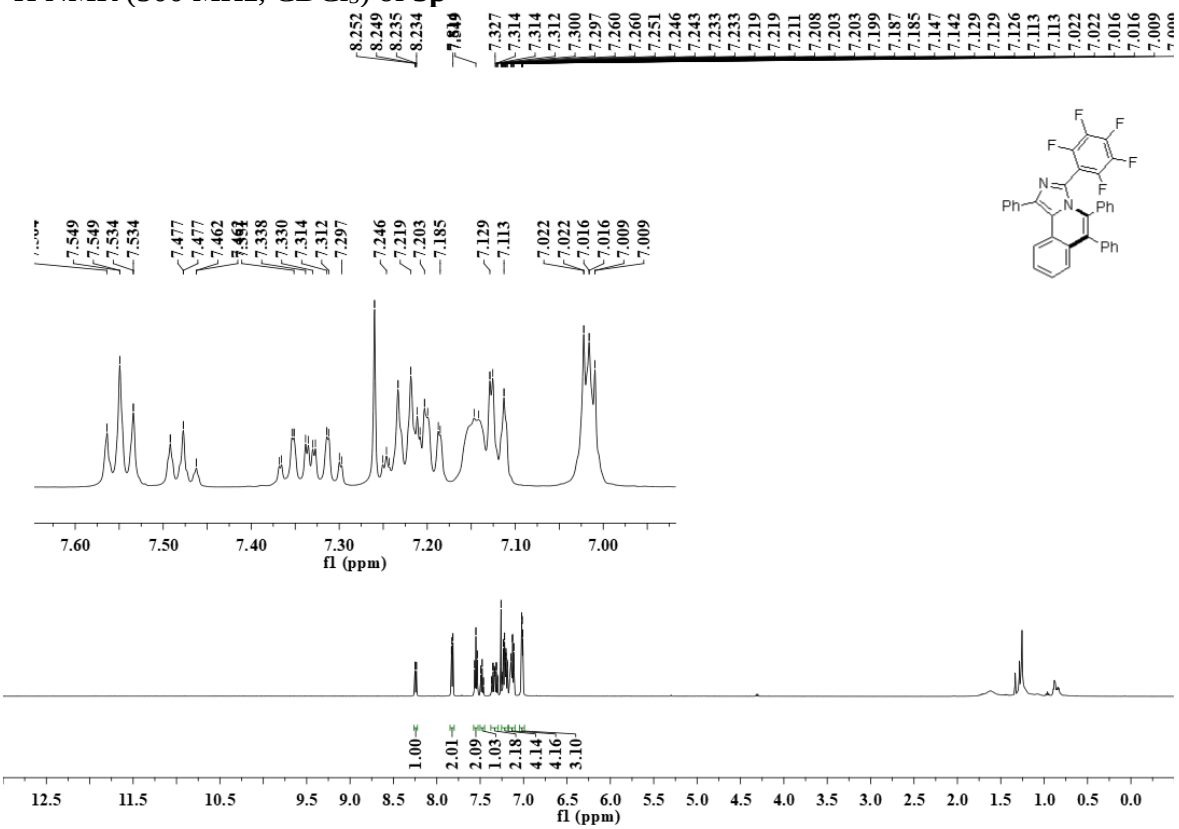
^{1}H NMR (500 MHz, $CDCl_3$) of **3o**



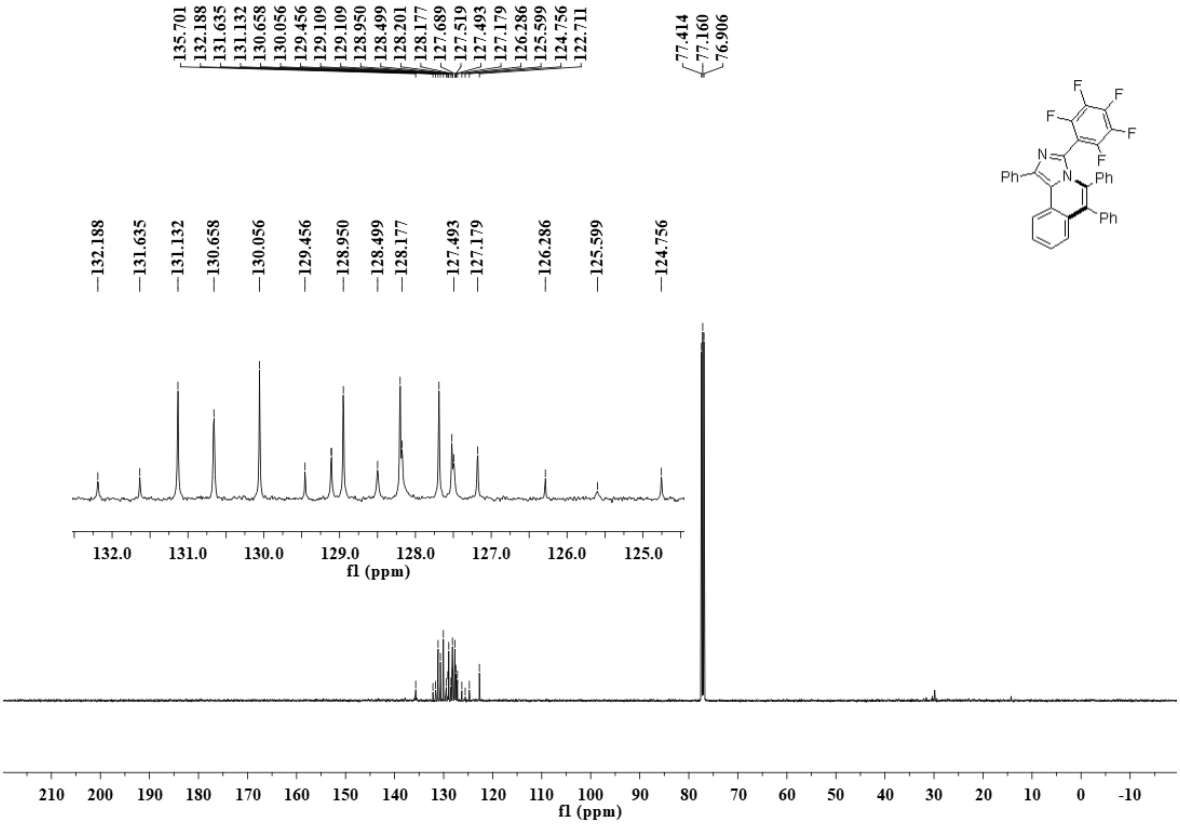
^{13}C NMR (125 MHz, $CDCl_3$) of **3o**



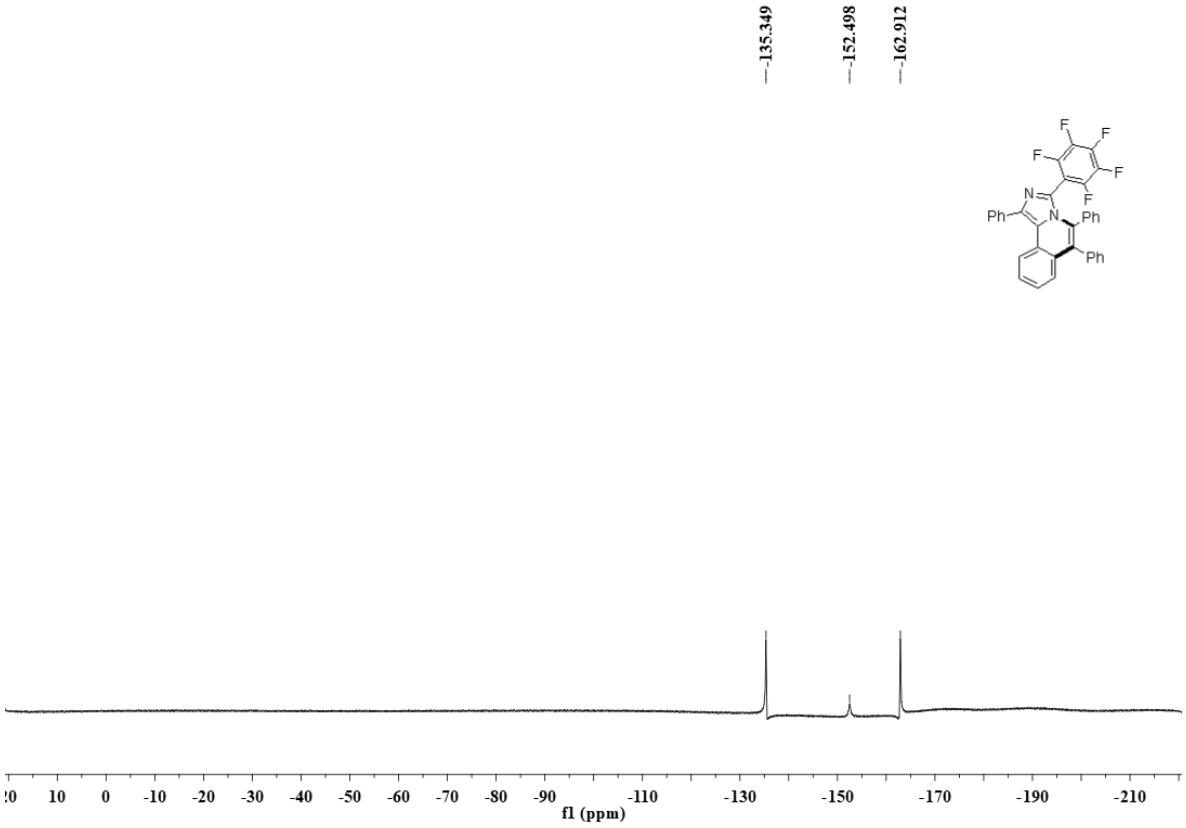
^{1}H NMR (500 MHz, $CDCl_3$) of **3p**



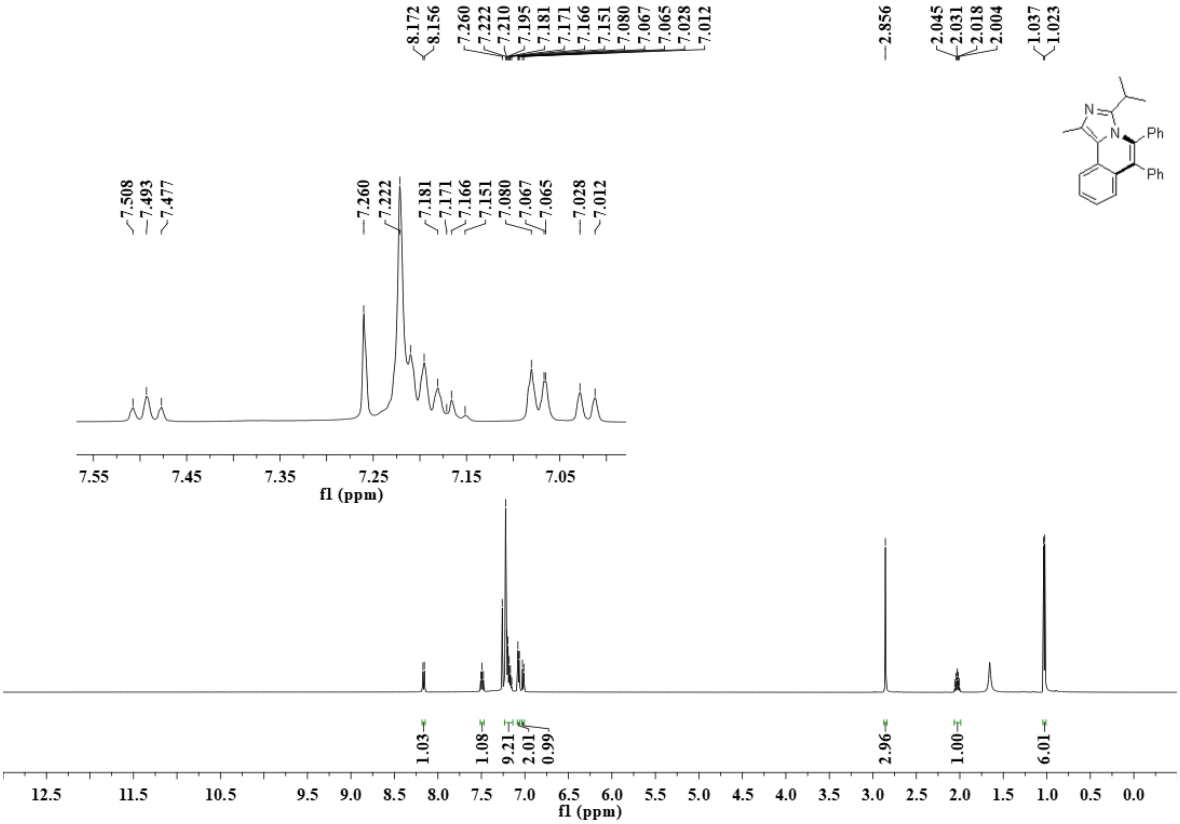
^{13}C NMR (125 MHz, $CDCl_3$) of **3p**



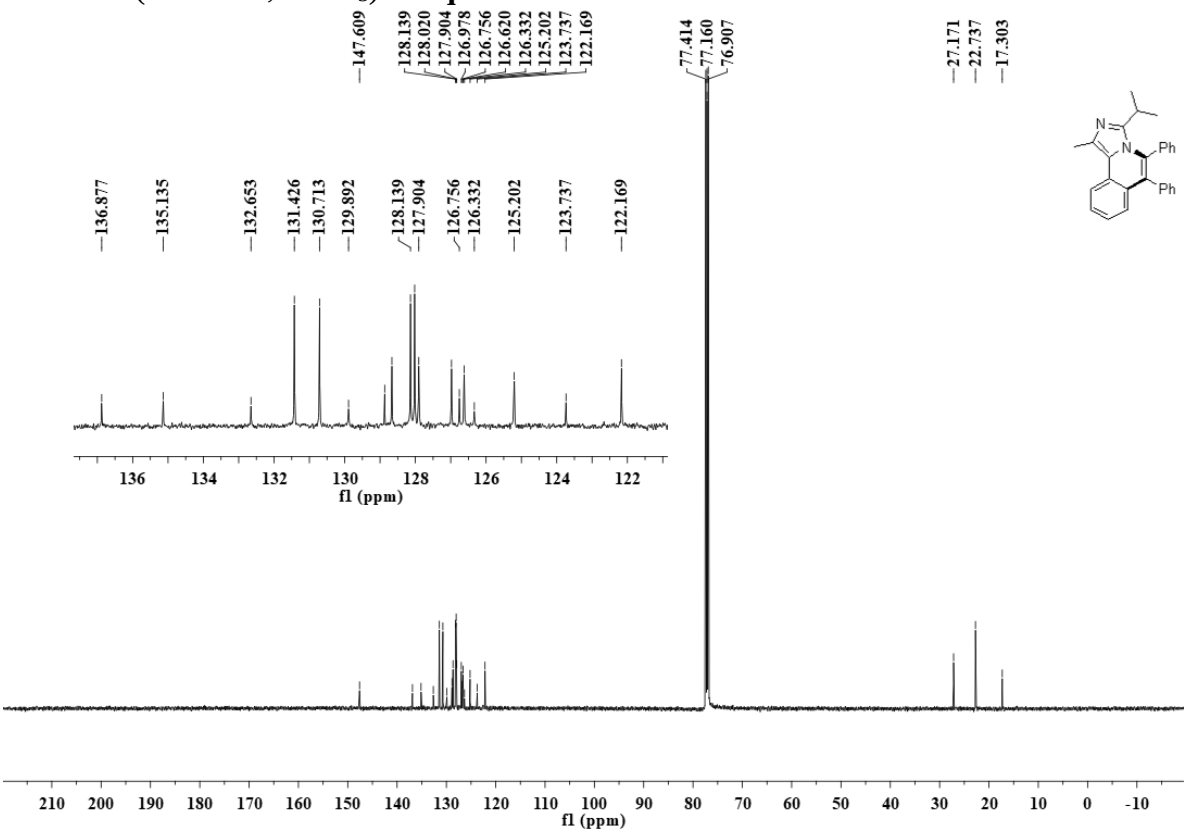
^{19}F NMR (471 MHz, $CDCl_3$) of **3p**



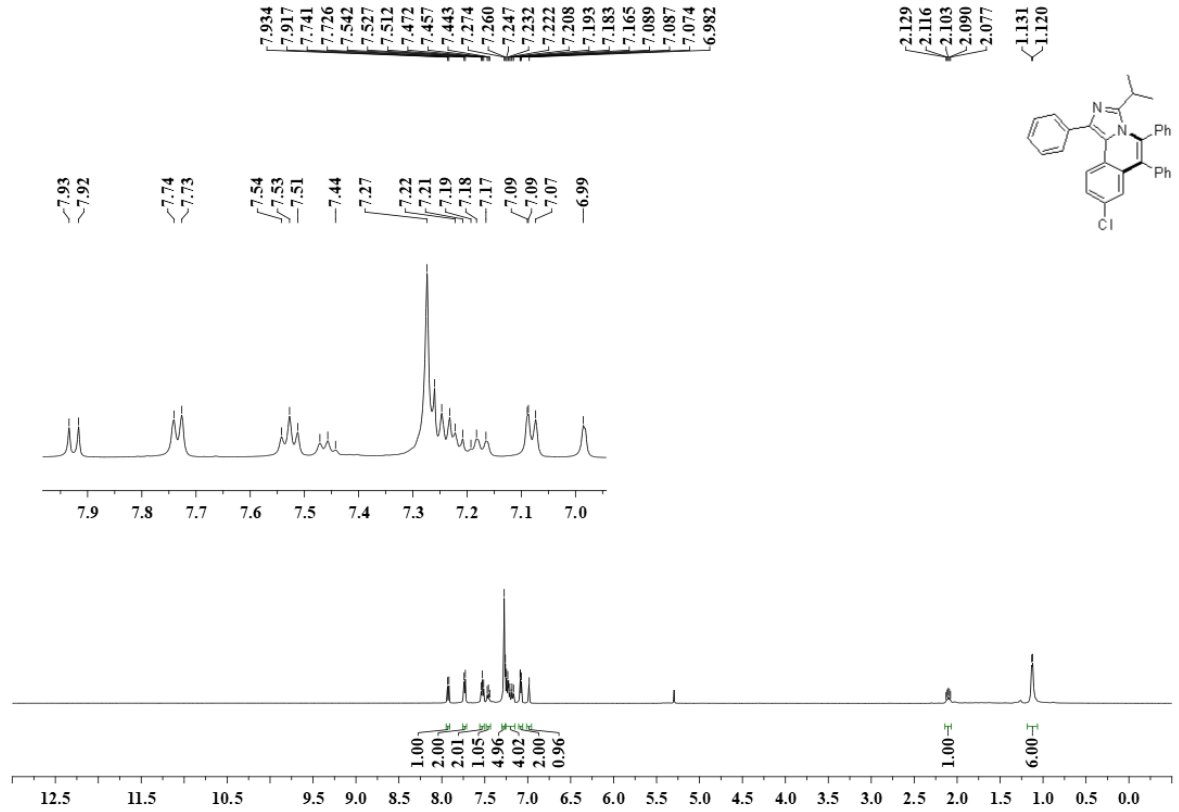
^{1}H NMR (500 MHz, $CDCl_3$) of **3q**



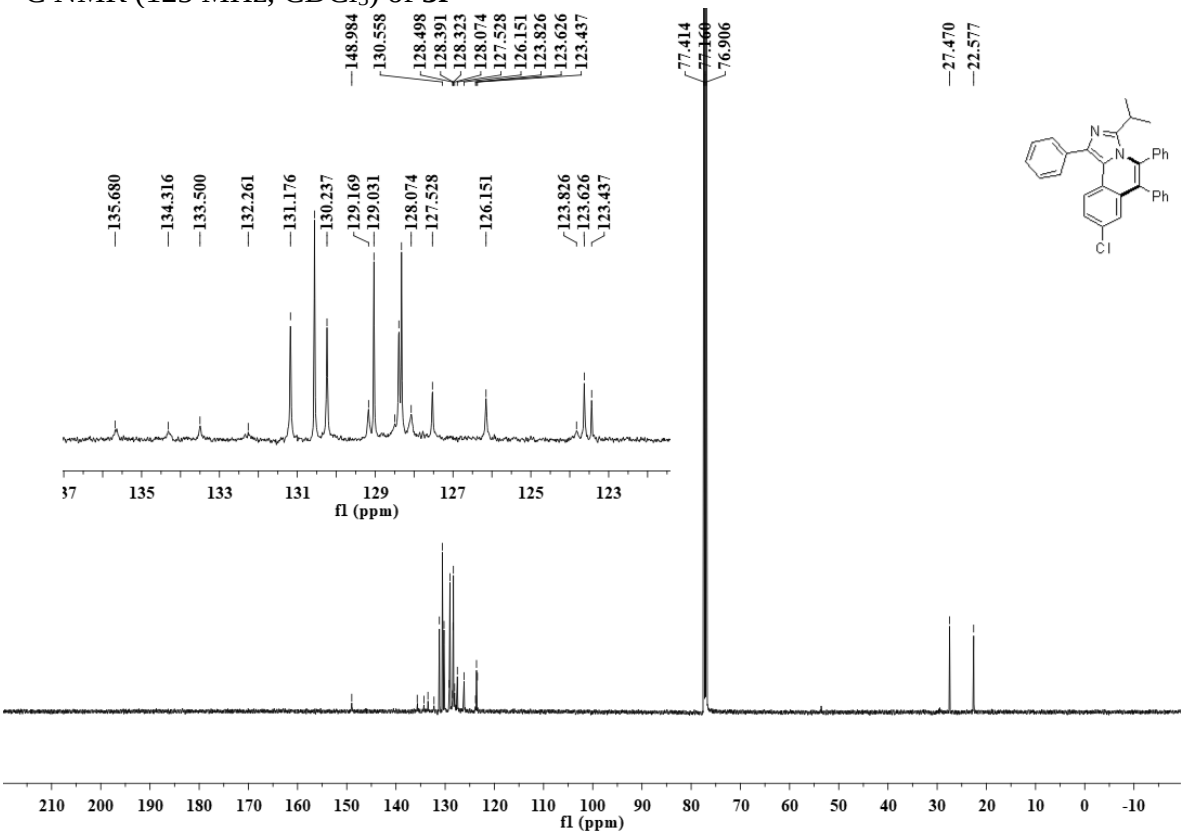
^{13}C NMR (125 MHz, $CDCl_3$) of **3q**



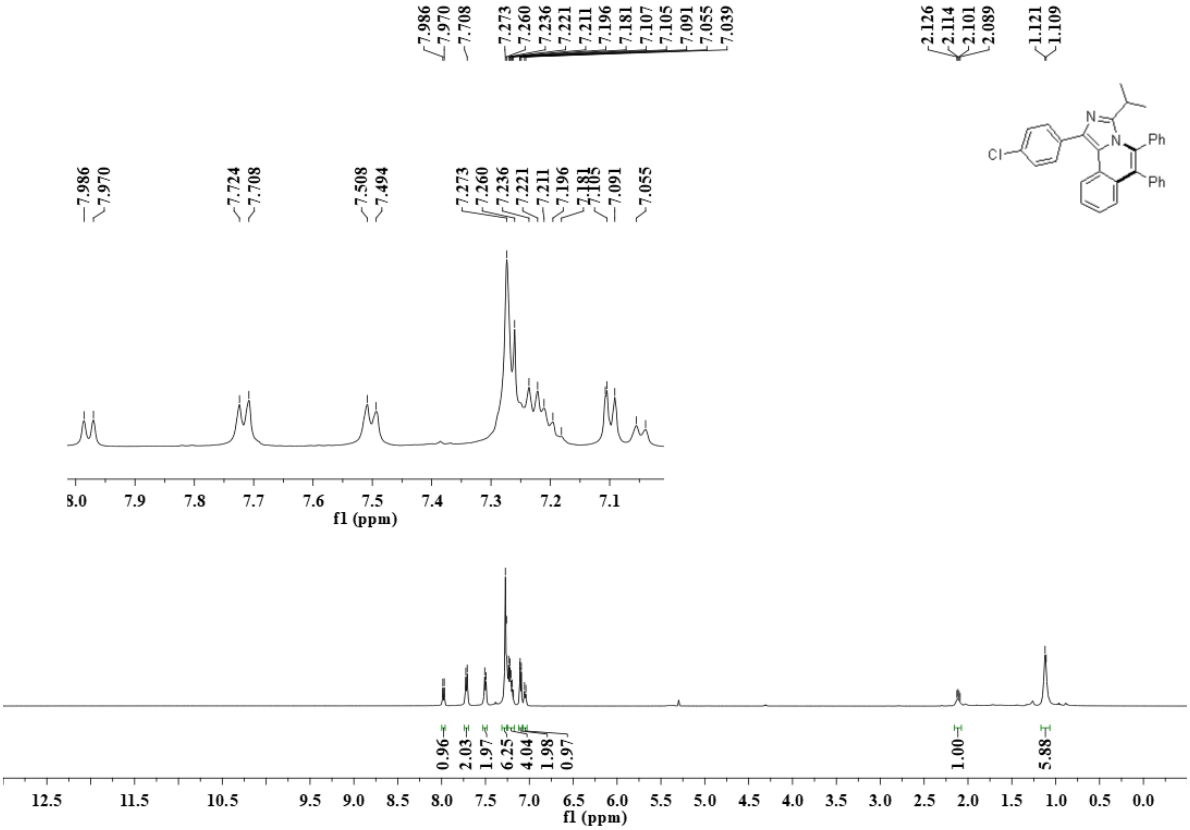
^{1}H NMR (500 MHz, $CDCl_3$) of **3r**



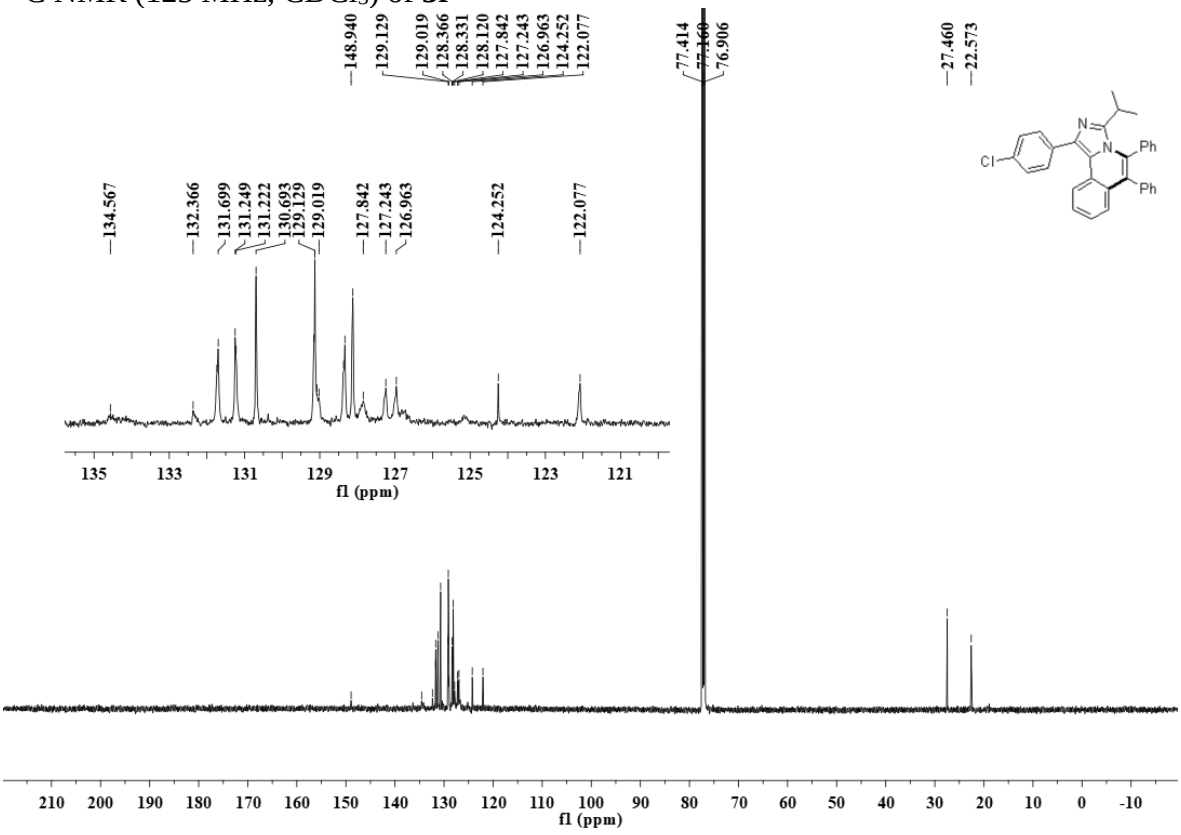
^{13}C NMR (125 MHz, $CDCl_3$) of **3r**



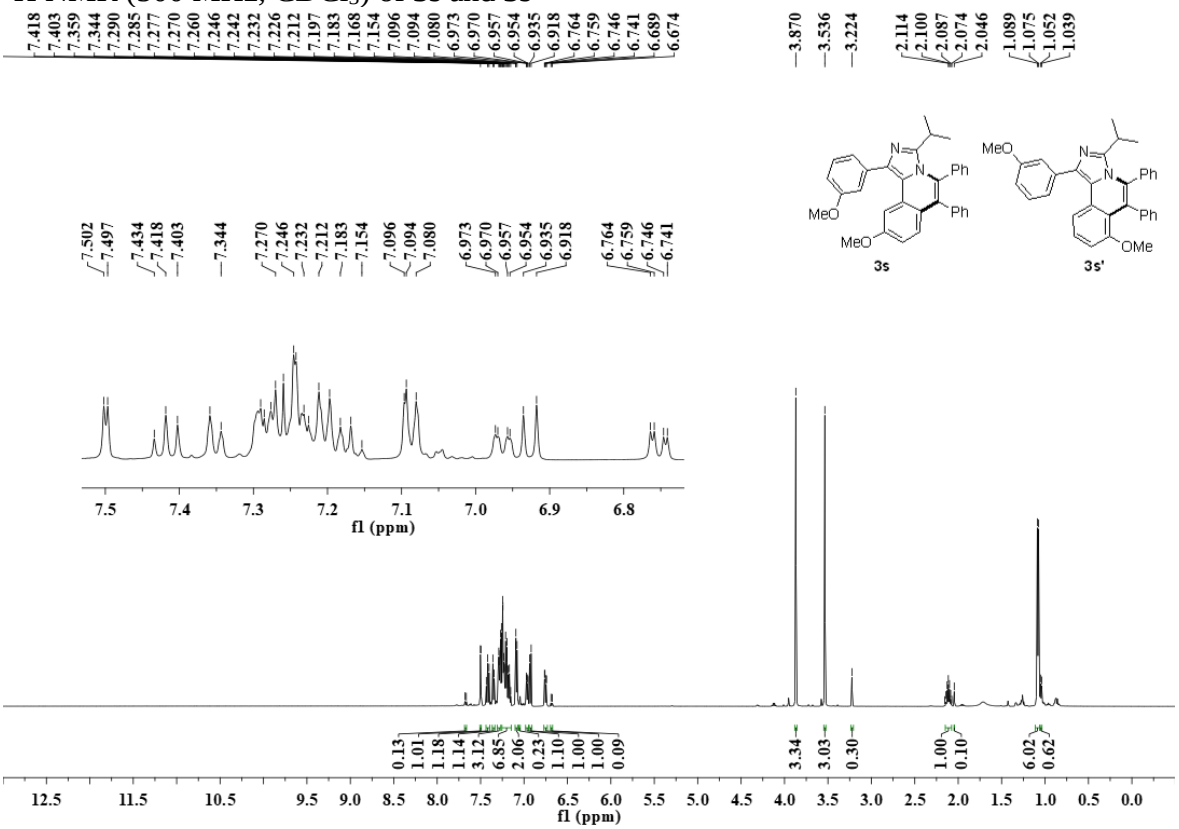
^{1}H NMR (500 MHz, $CDCl_3$) of **3r'**



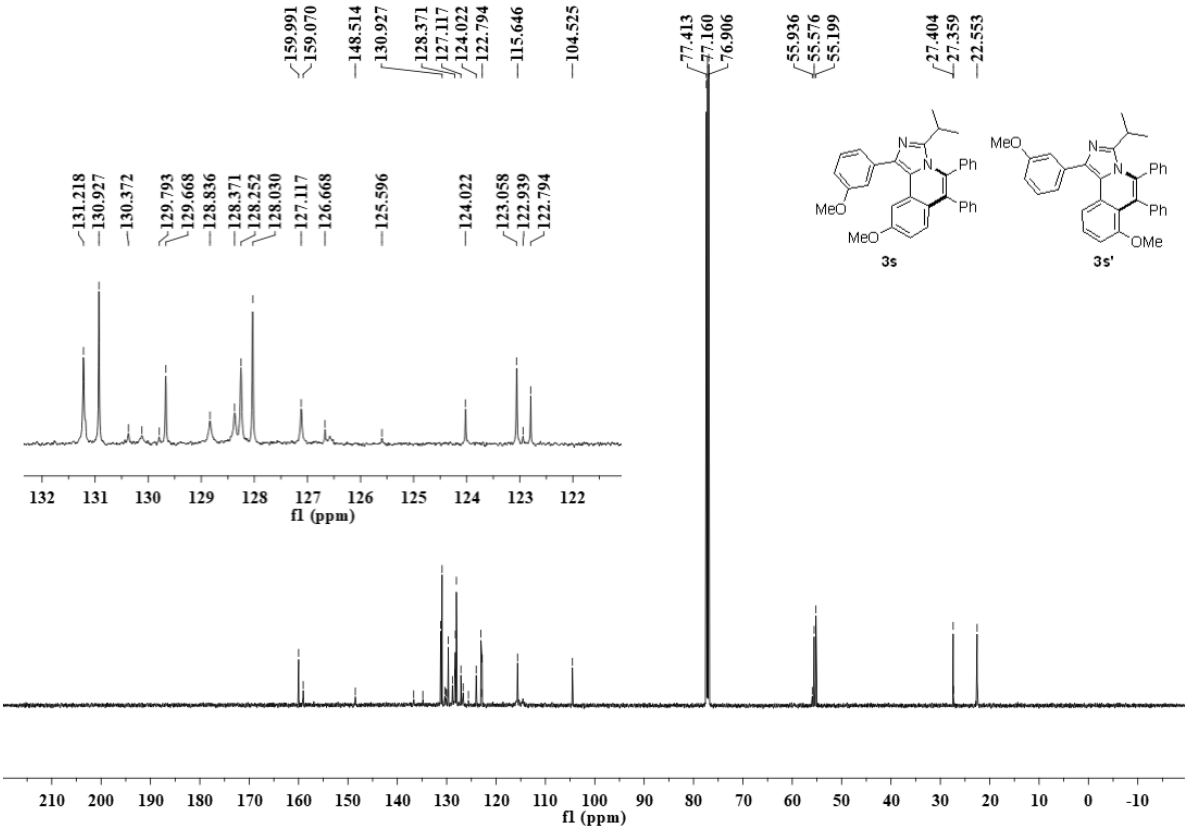
^{13}C NMR (125 MHz, $CDCl_3$) of **3r'**



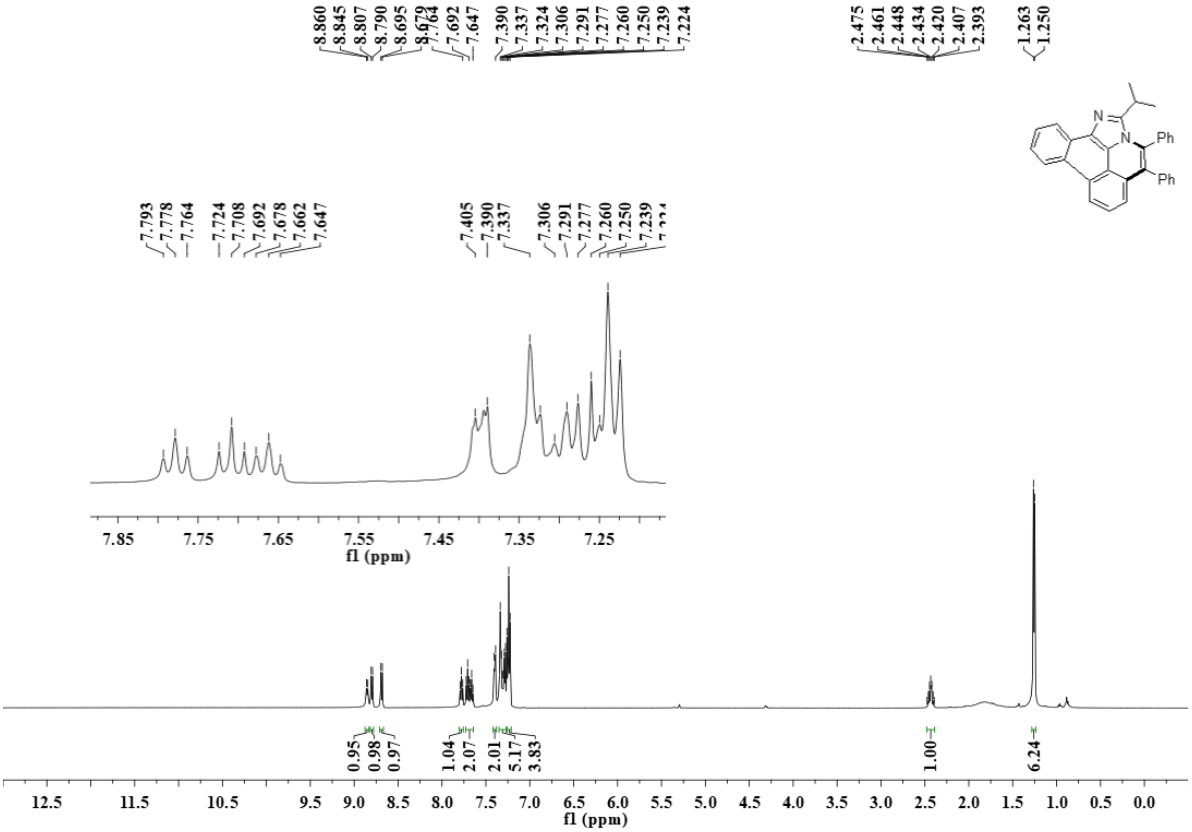
^{1}H NMR (500 MHz, $CDCl_3$) of **3s** and **3s′**



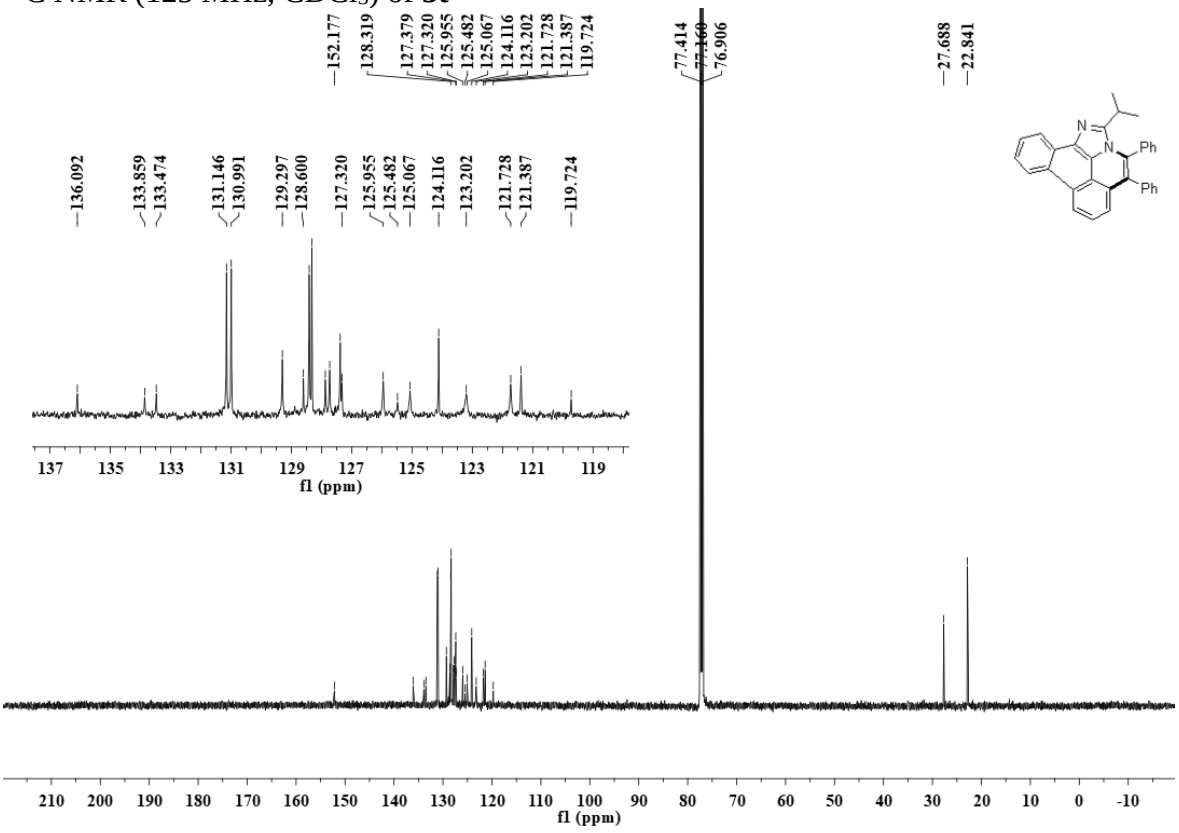
^{13}C NMR (125 MHz, $CDCl_3$) of **3s** and **3s′**



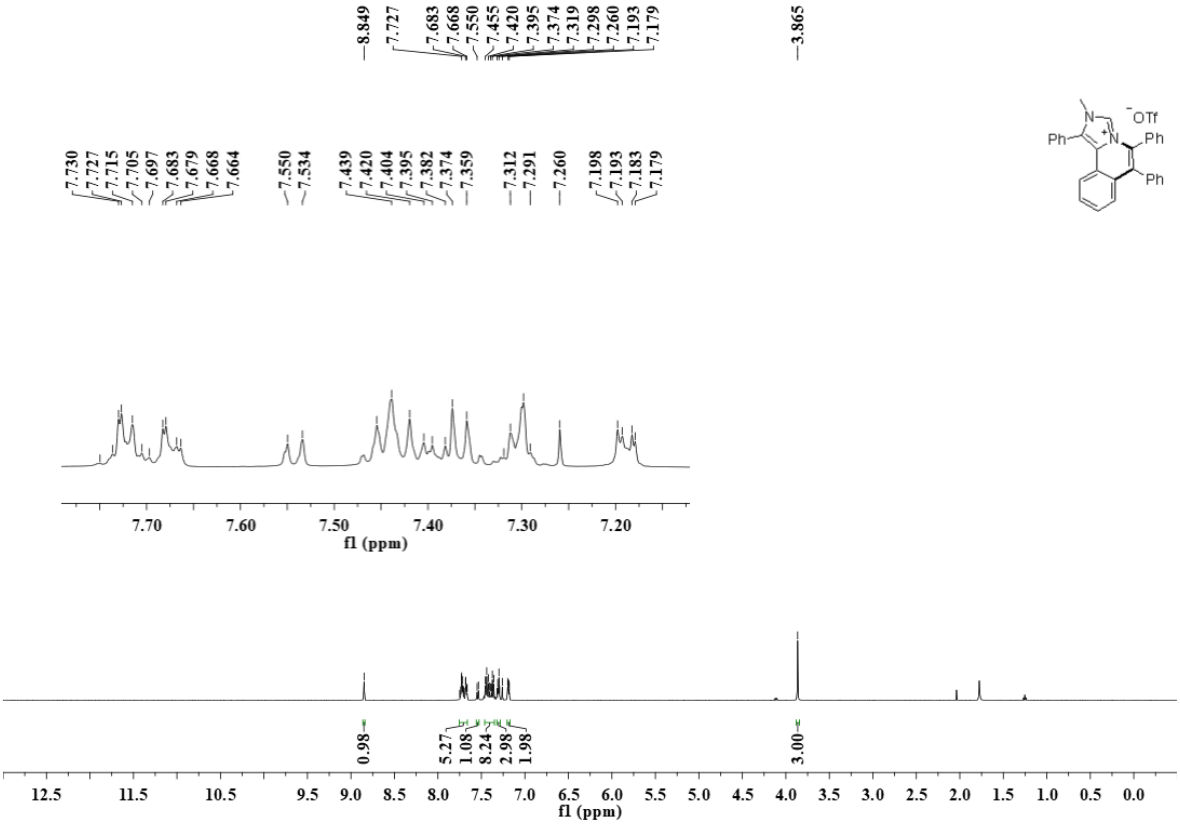
^{1}H NMR (500 MHz, $CDCl_3$) of **3t**



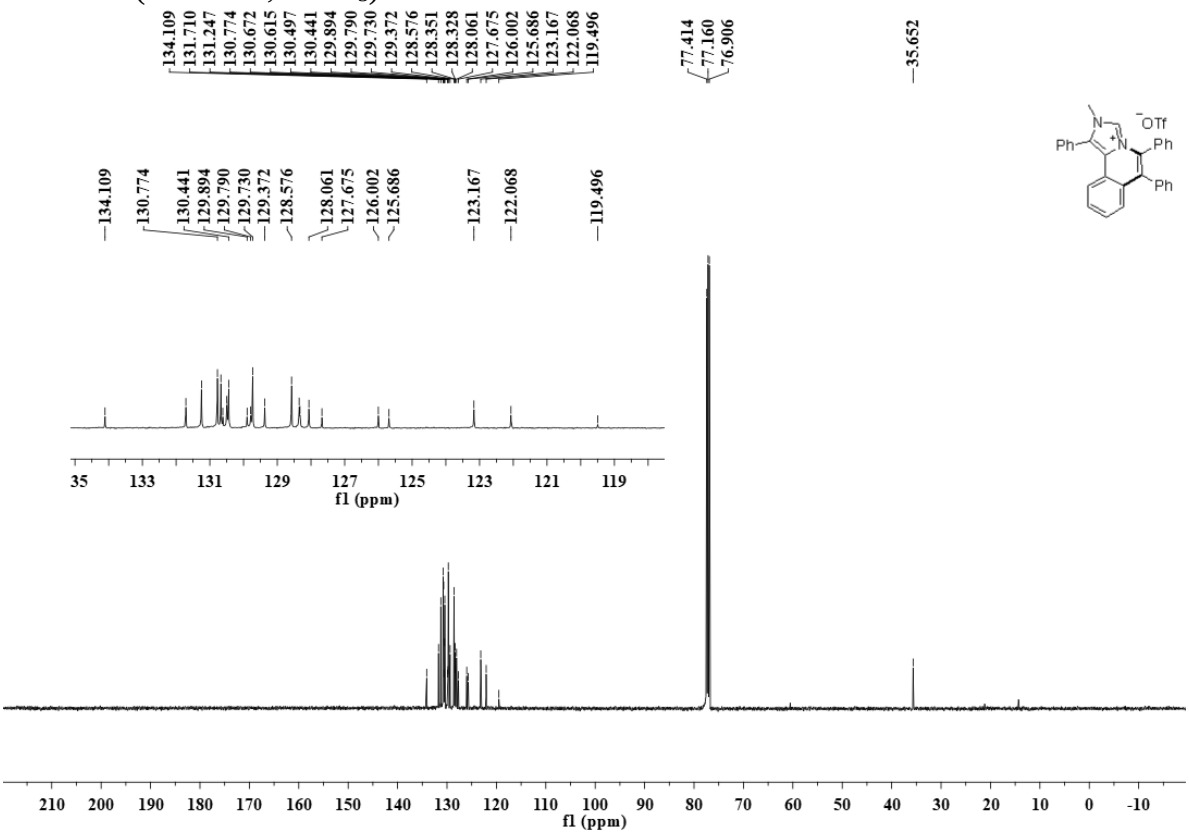
^{13}C NMR (125 MHz, $CDCl_3$) of **3t**



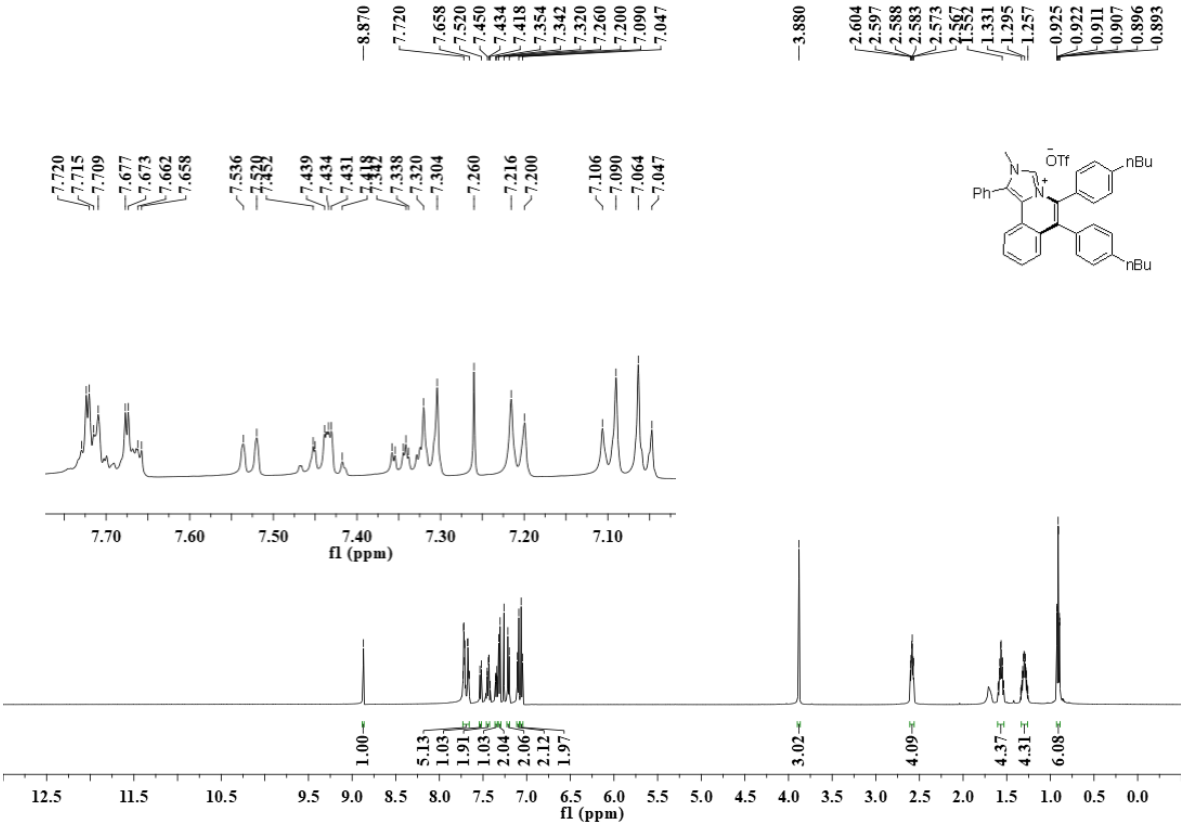
^{1}H NMR (500 MHz, $CDCl_3$) of **4a**



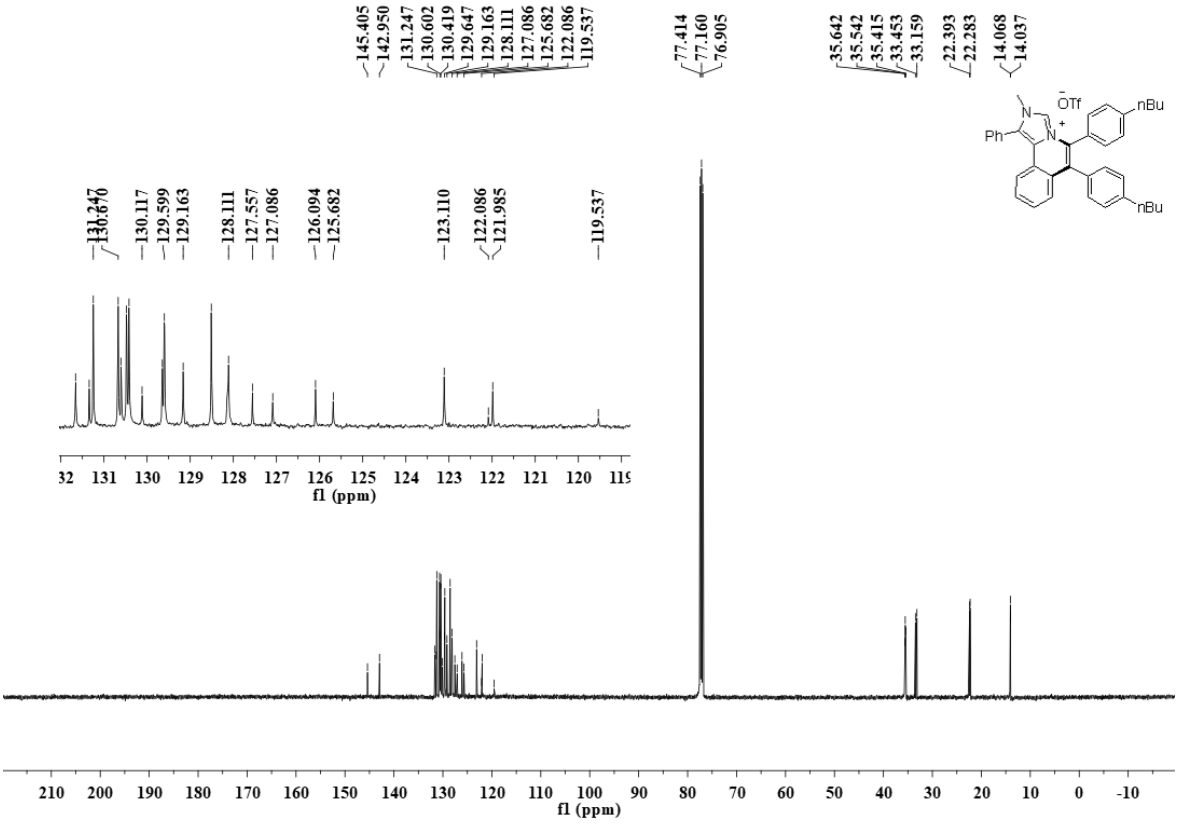
^{13}C NMR (125 MHz, $CDCl_3$) of **4a**



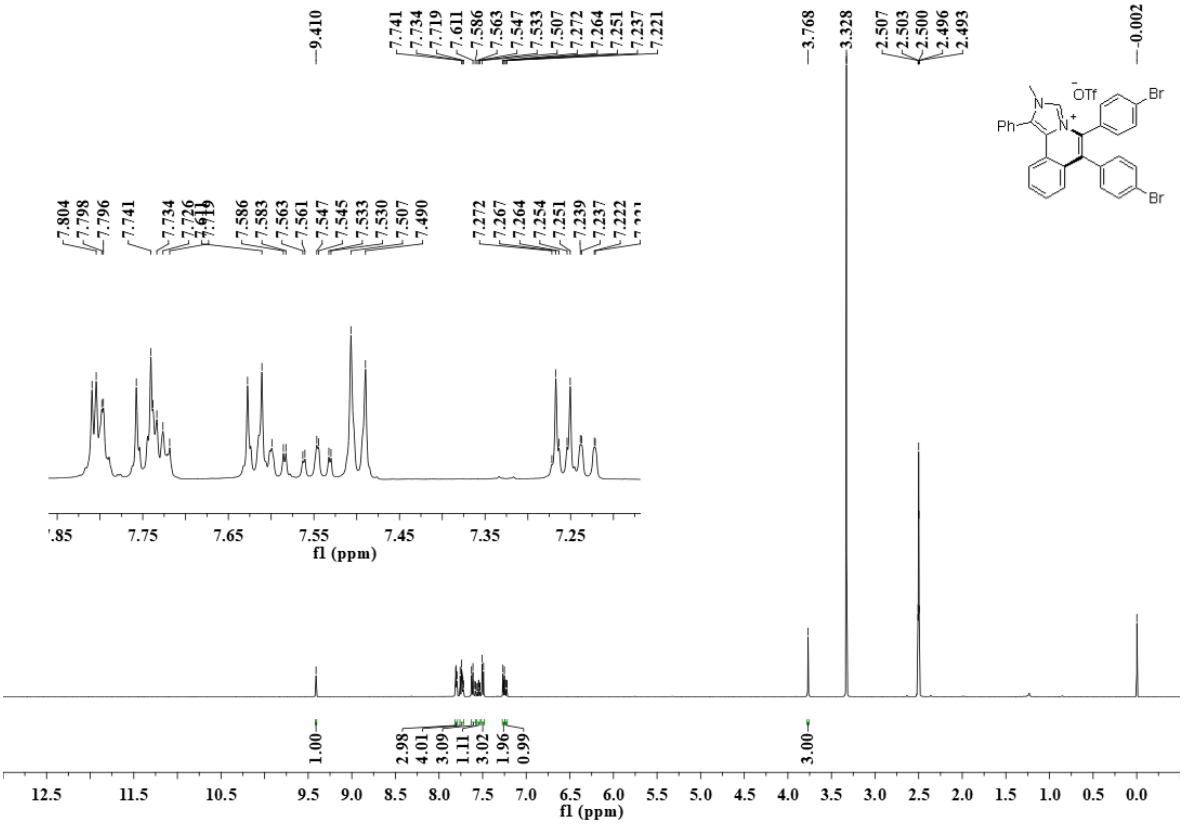
^{1}H NMR (500 MHz, $CDCl_3$) of **4b**



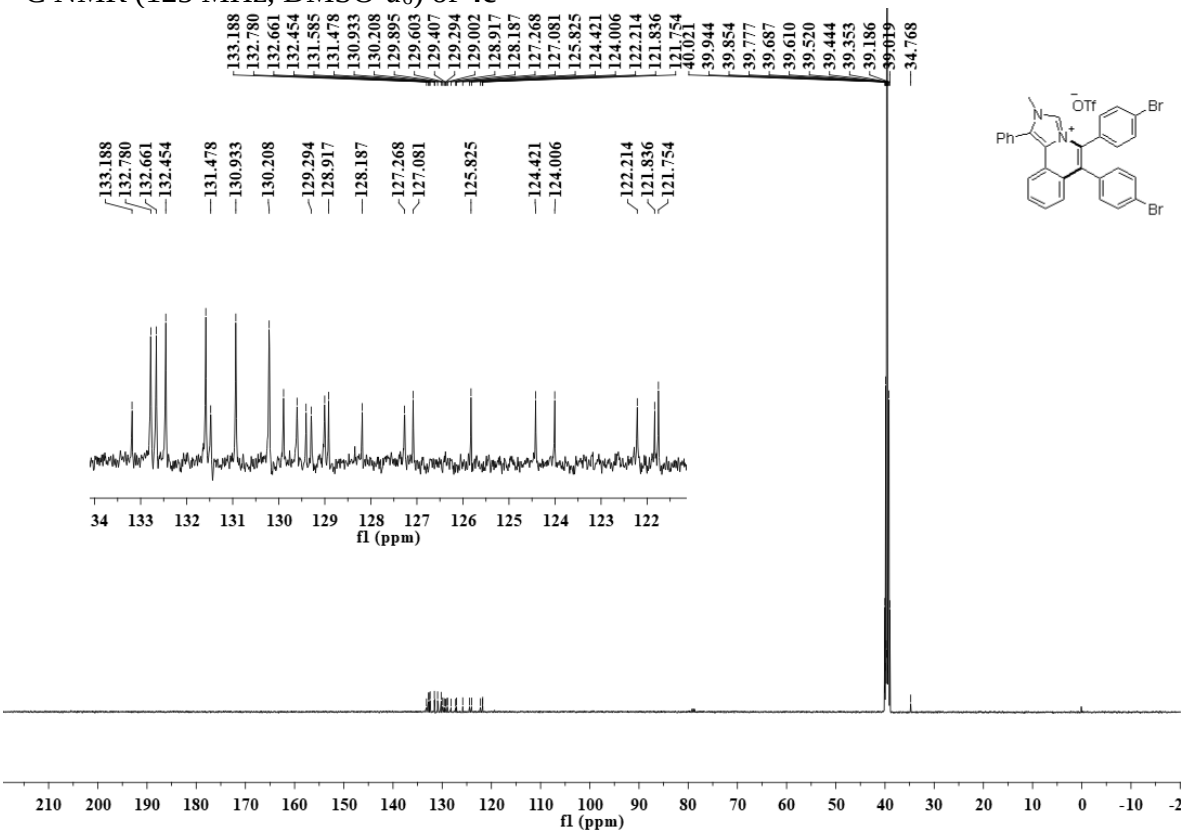
^{13}C NMR (125 MHz, $CDCl_3$) of **4b**



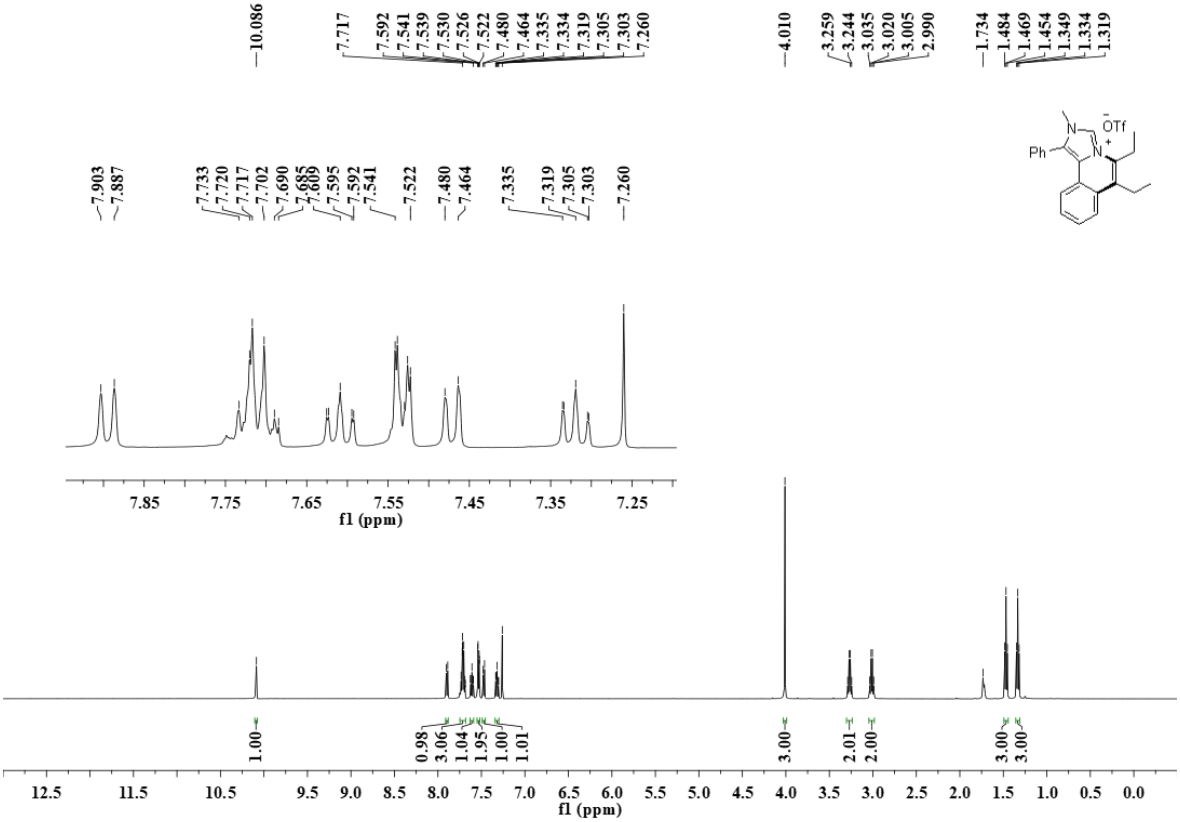
^{1}H NMR (500 MHz, DMSO-d_6) of **4c**



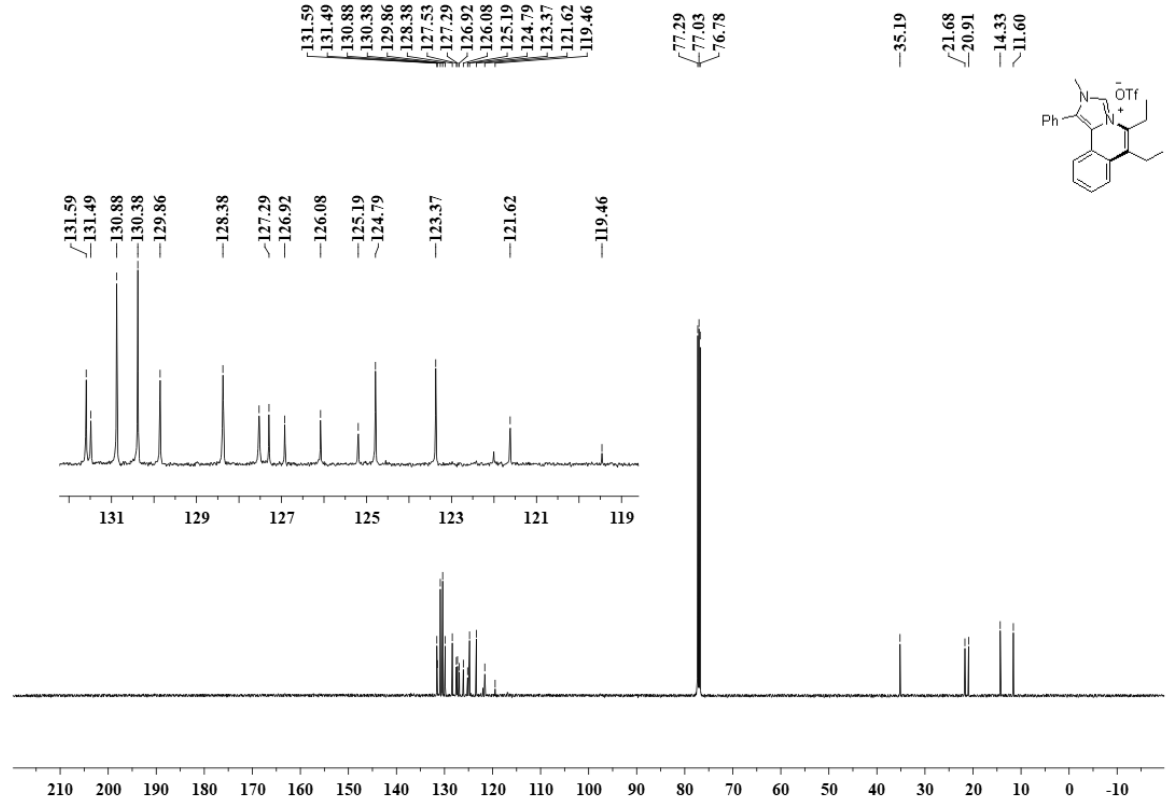
^{13}C NMR (125 MHz, DMSO-d_6) of **4c**



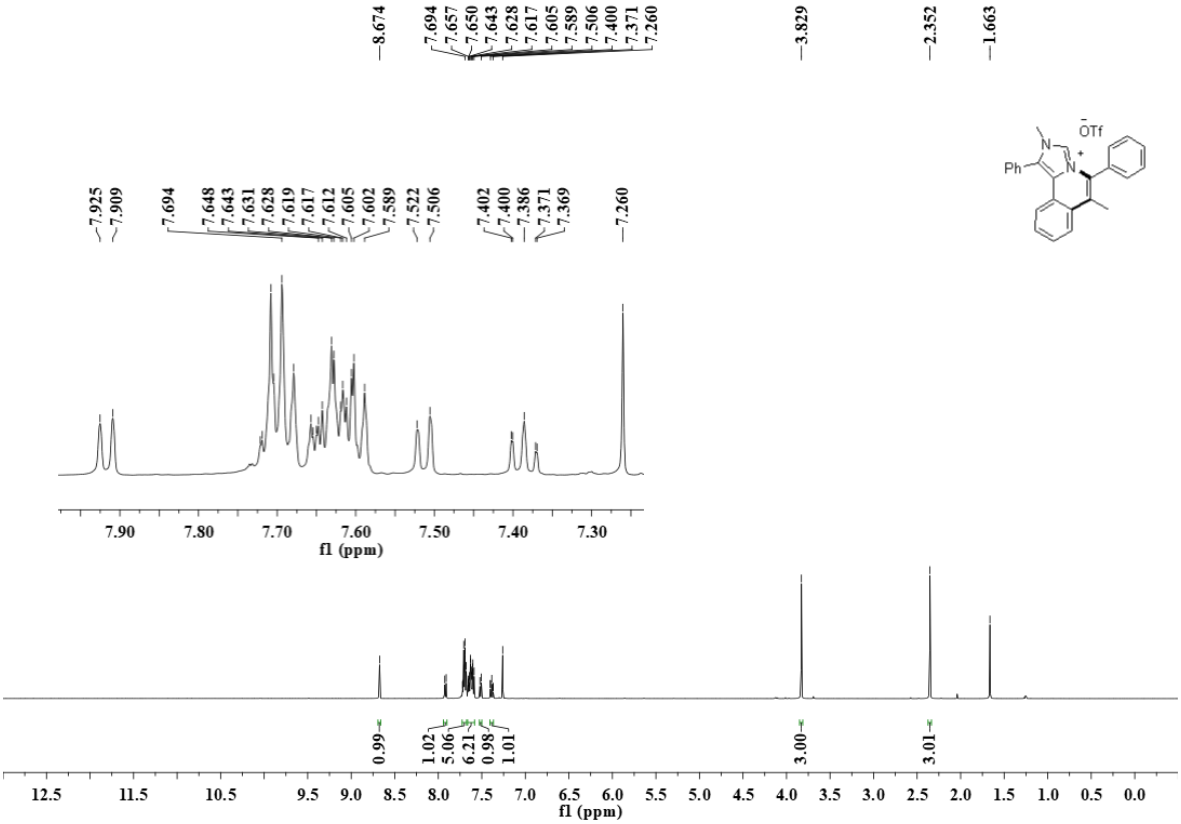
^{1}H NMR (500 MHz, $CDCl_3$) of **4d**



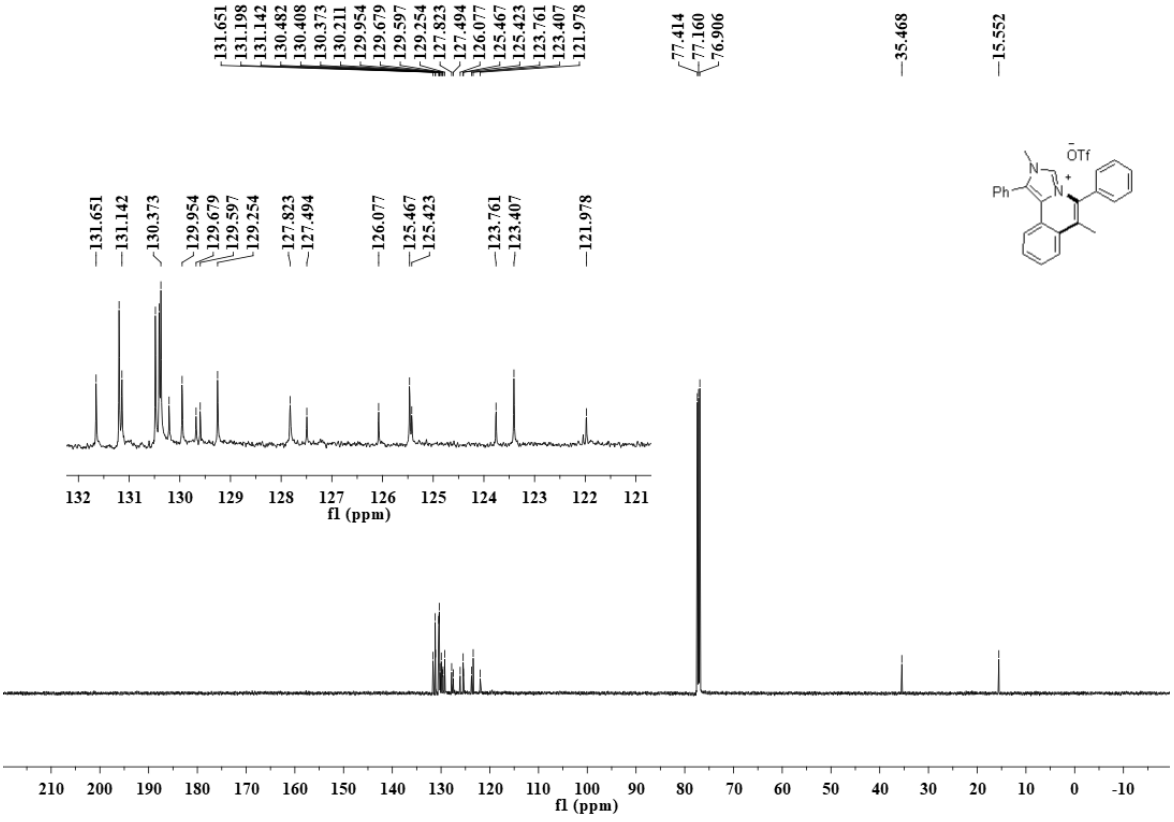
^{13}C NMR (125 MHz, $CDCl_3$) of **4d**



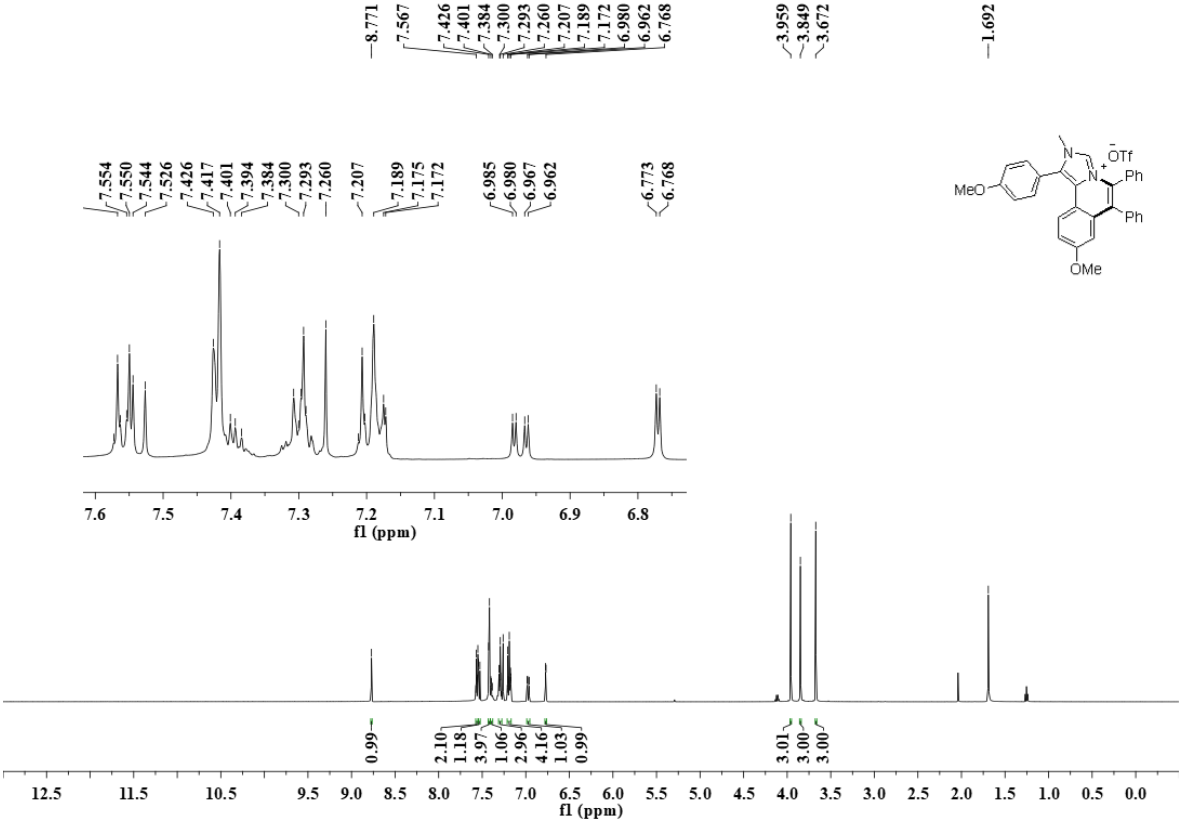
^{1}H NMR (500 MHz, $CDCl_3$) of **4e**



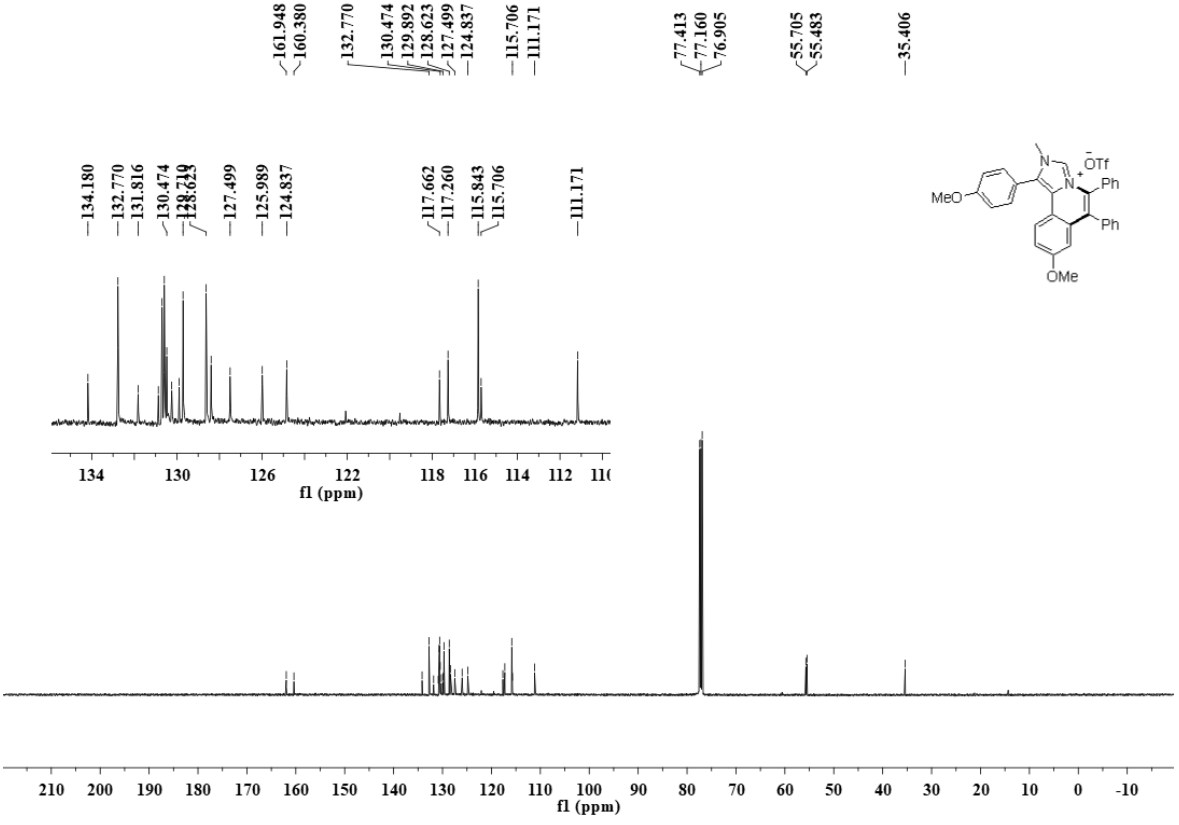
^{13}C NMR (125 MHz, $CDCl_3$) of **4e**



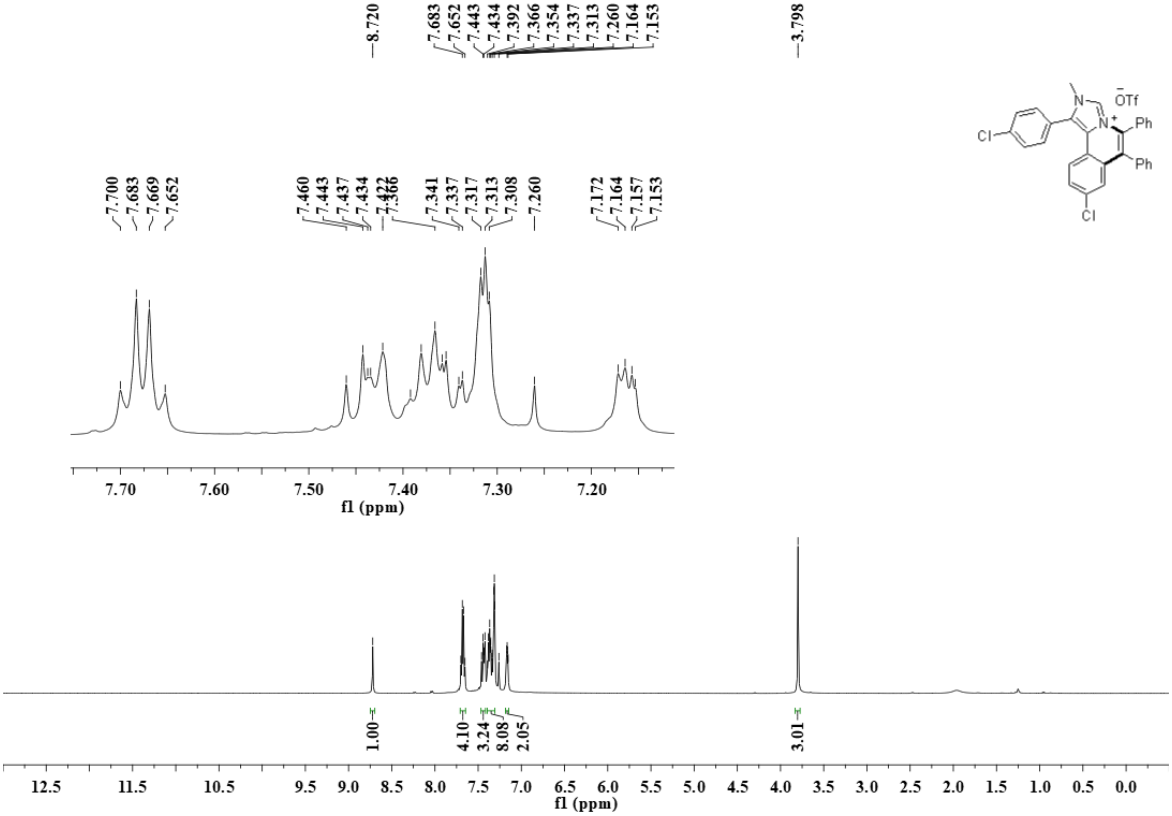
^{1}H NMR (500 MHz, $CDCl_3$) of **4f**



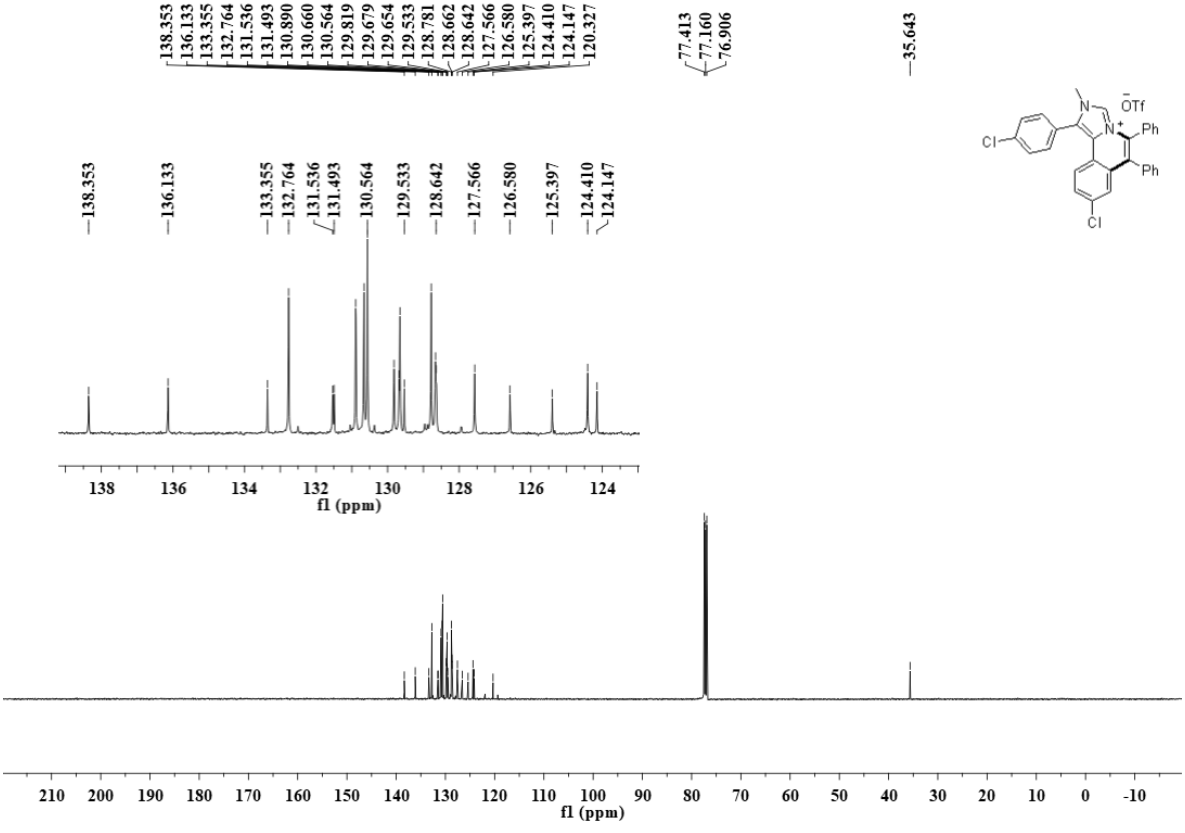
^{13}C NMR (125 MHz, $CDCl_3$) of **4f**



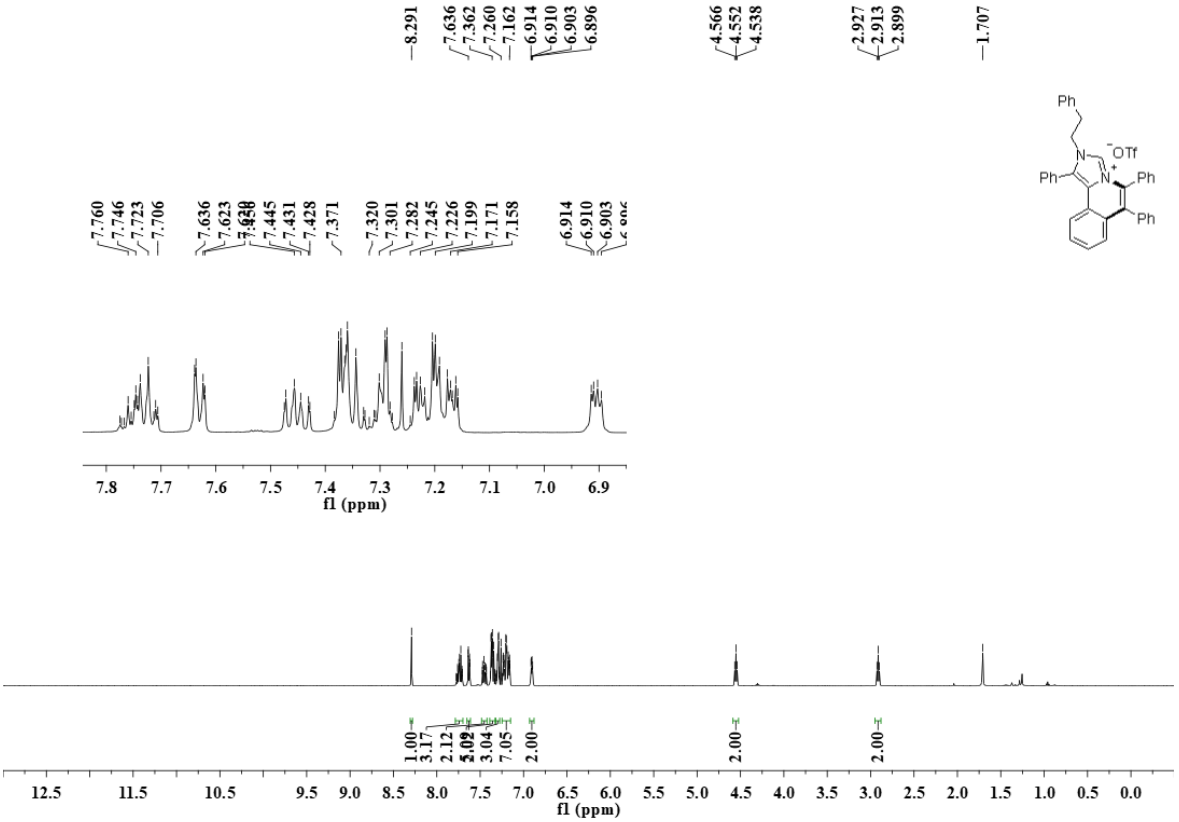
^{1}H NMR (500 MHz, $CDCl_3$) of **4g**



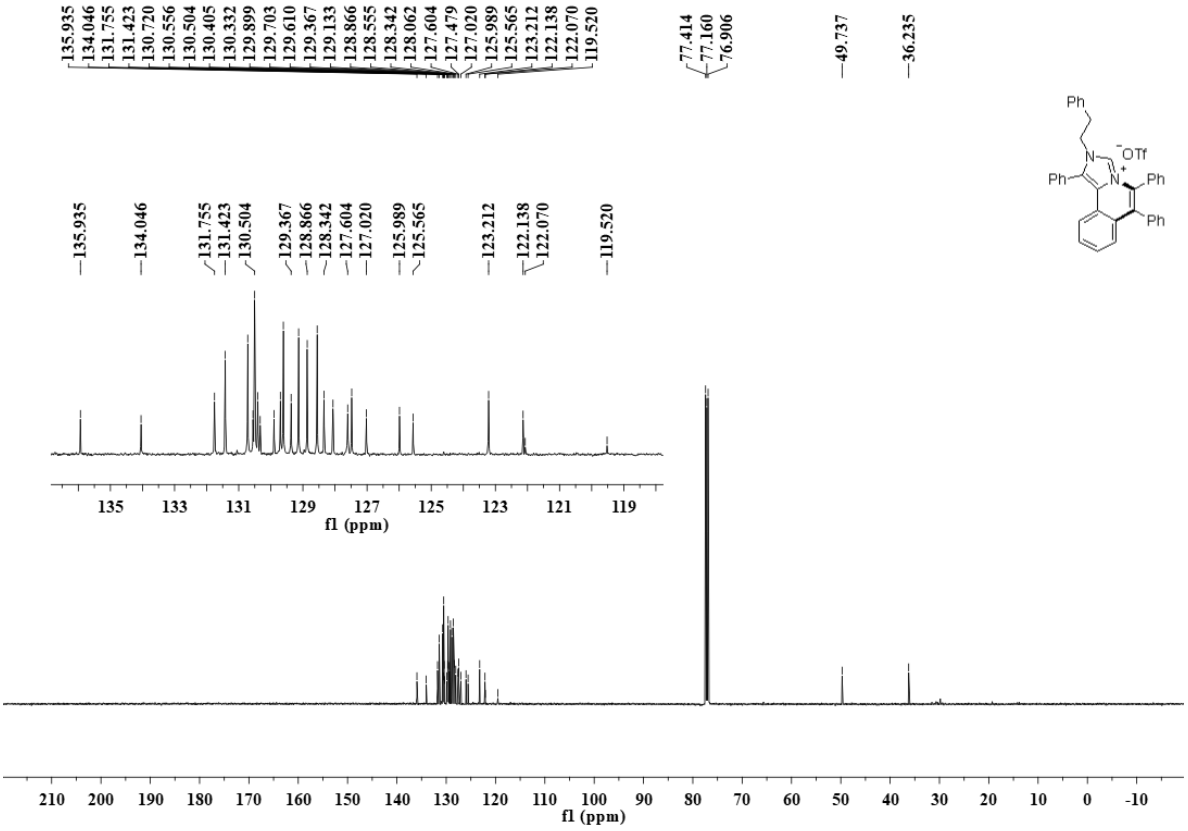
^{13}C NMR (125 MHz, $CDCl_3$) of **4g**



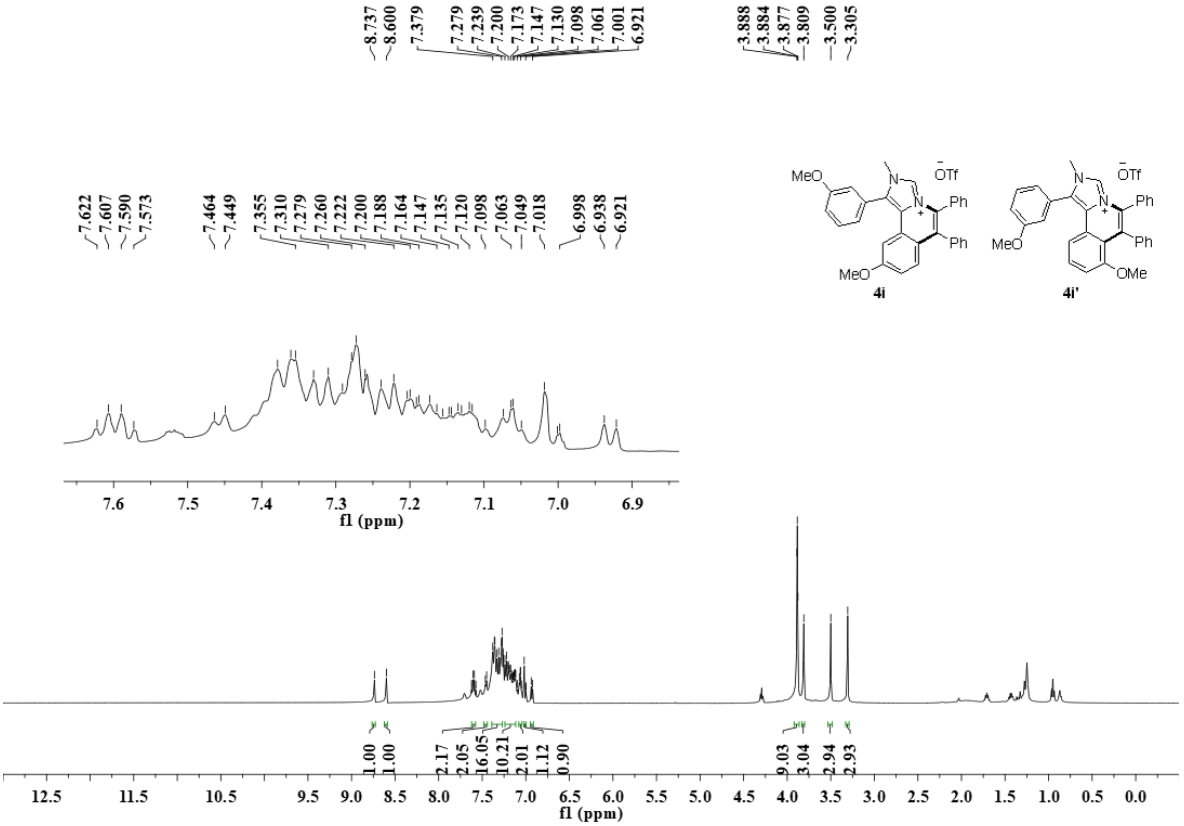
^{1}H NMR (500 MHz, $CDCl_3$) of **4h**



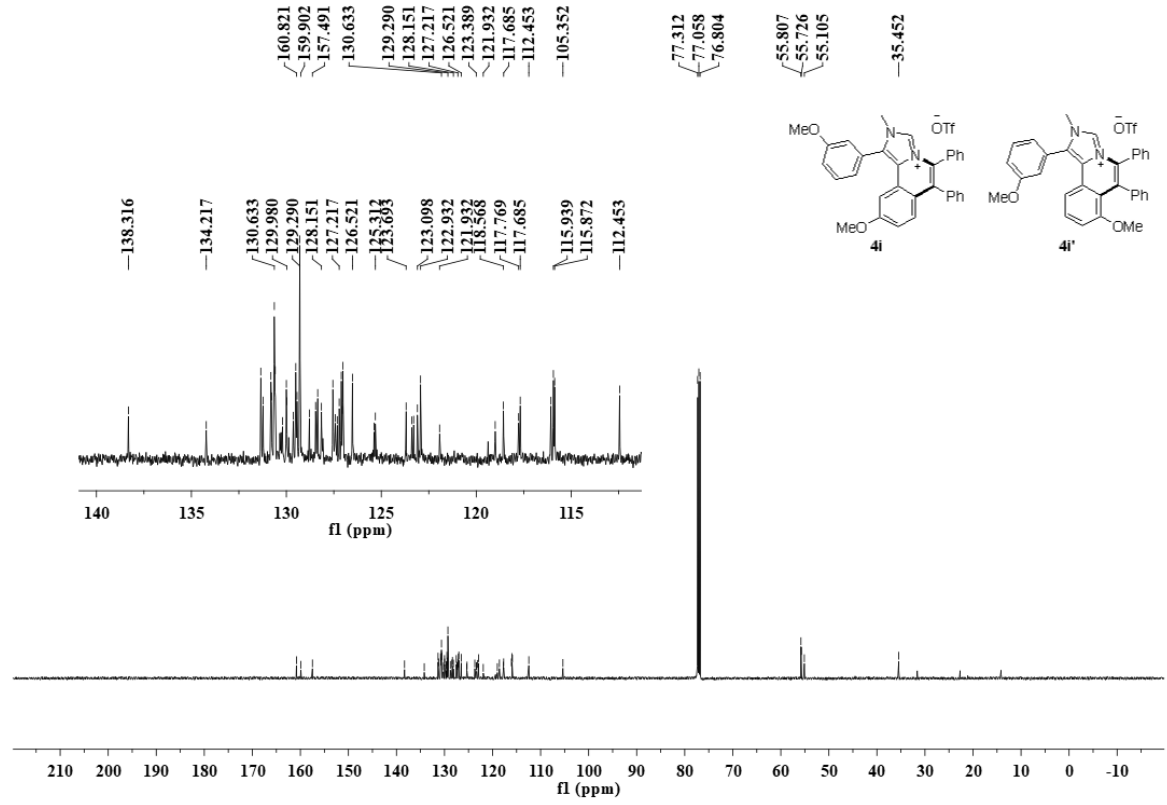
^{13}C NMR (125 MHz, $CDCl_3$) of **4h**



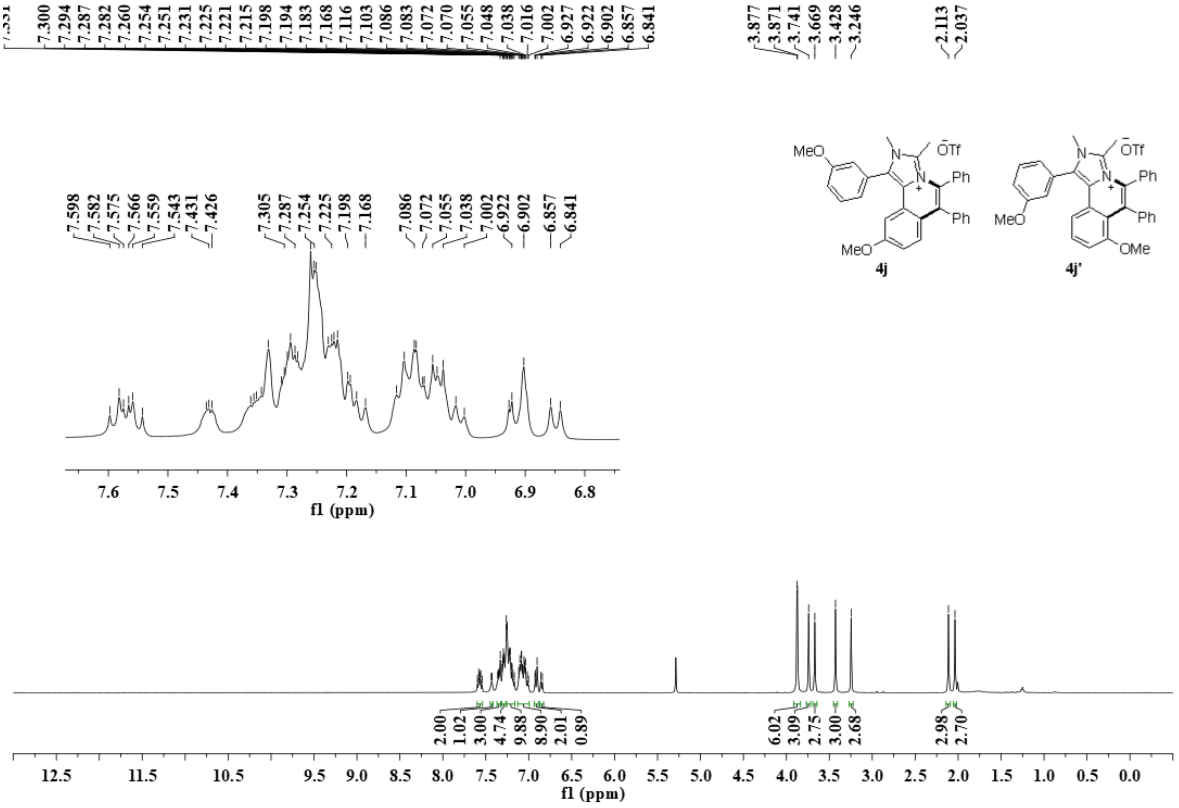
^{1}H NMR (500 MHz, $CDCl_3$) of **4i** and **4i′**



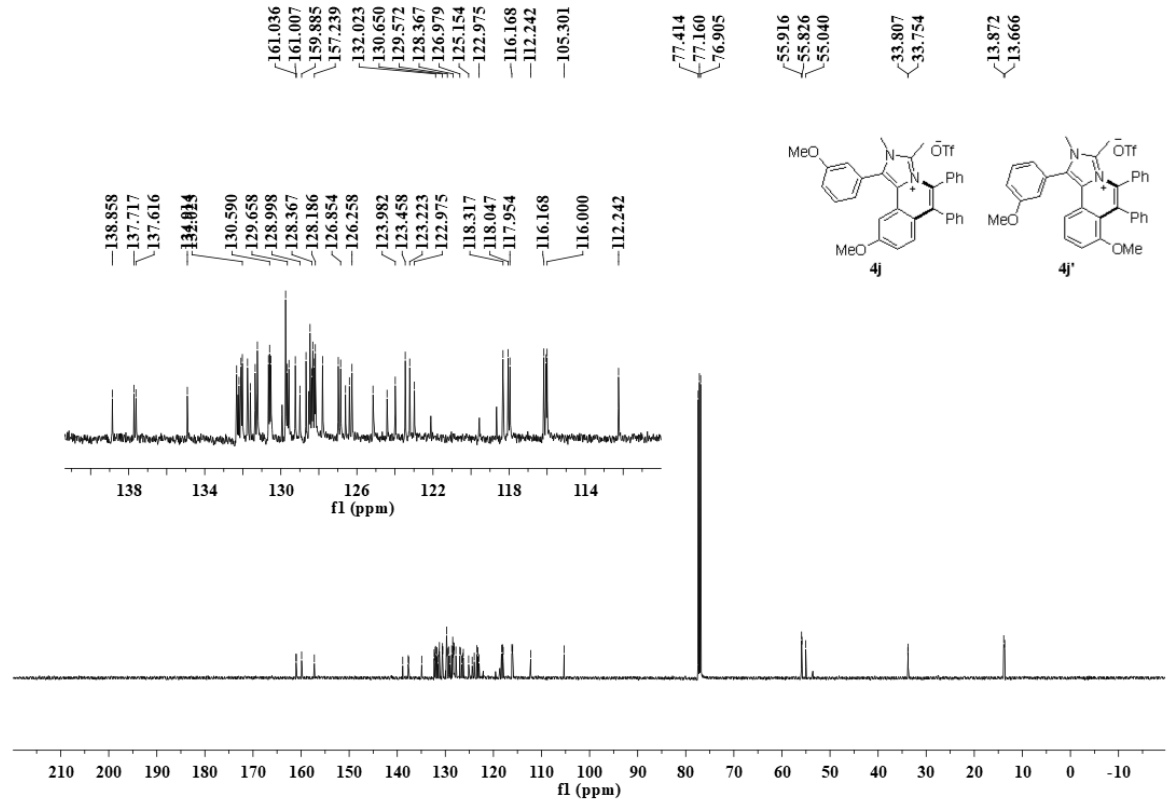
^{13}C NMR (125 MHz, $CDCl_3$) of **4i** and **4i′**



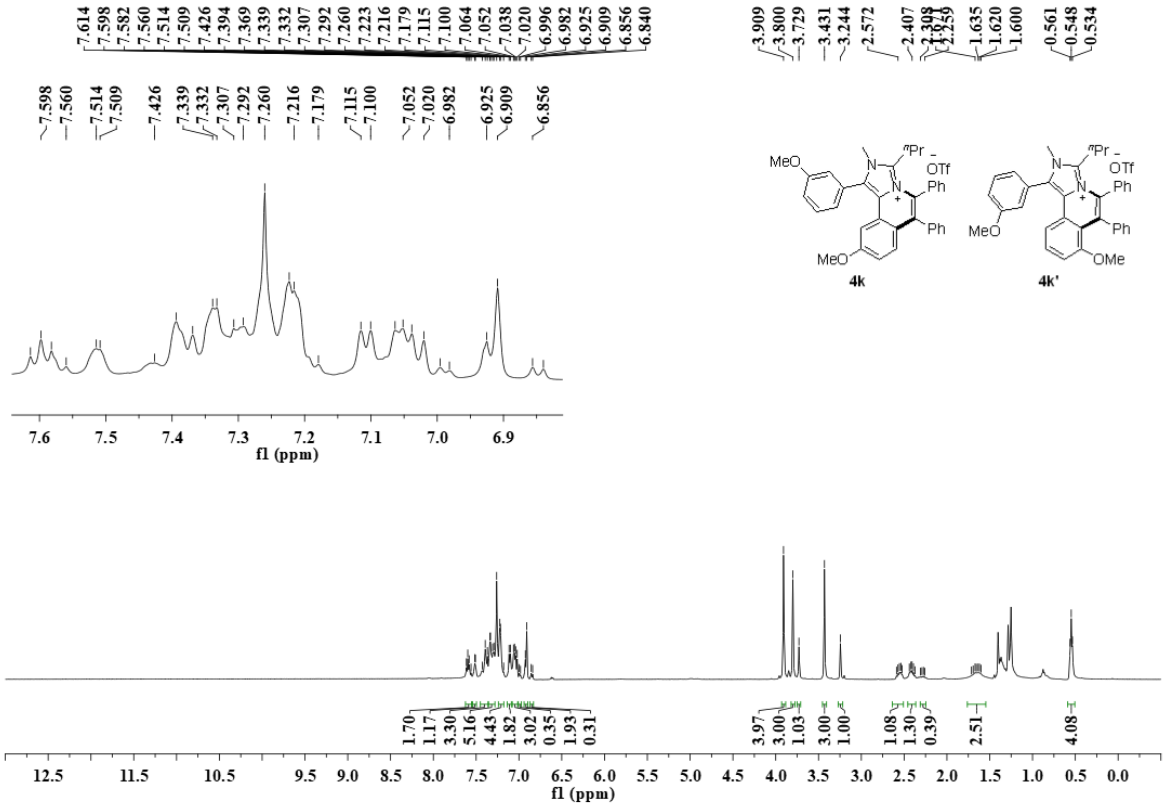
^{1}H NMR (500 MHz, $CDCl_3$) of **4j** and **4j′**



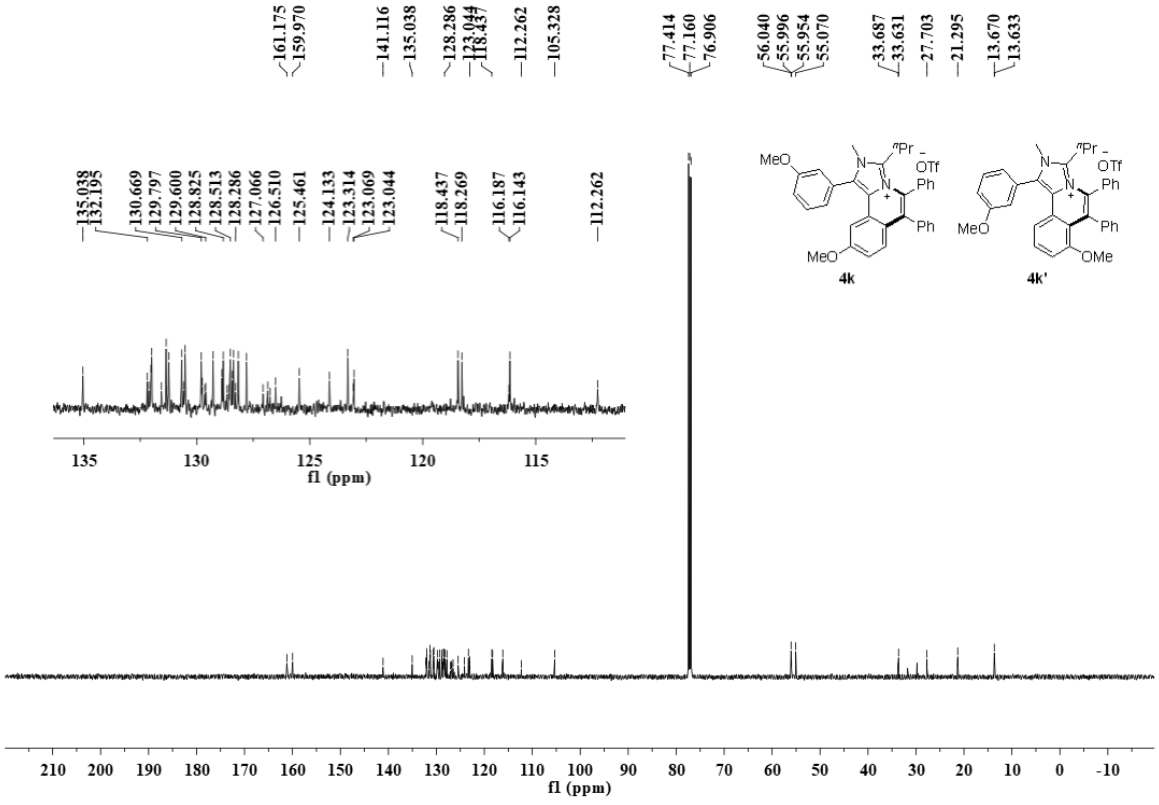
^{13}C NMR (125 MHz, $CDCl_3$) of **4j** and **4j′**



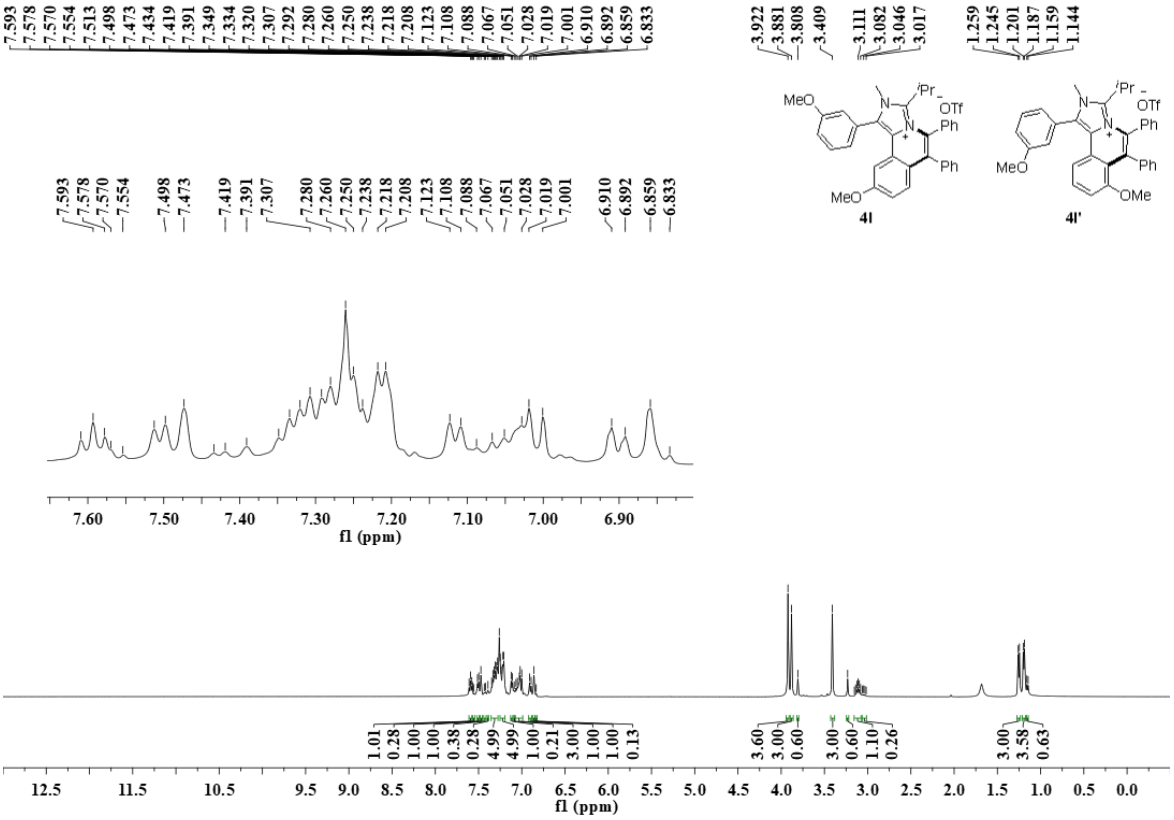
^{1}H NMR (500 MHz, $CDCl_3$) of **4k** and **4k′**



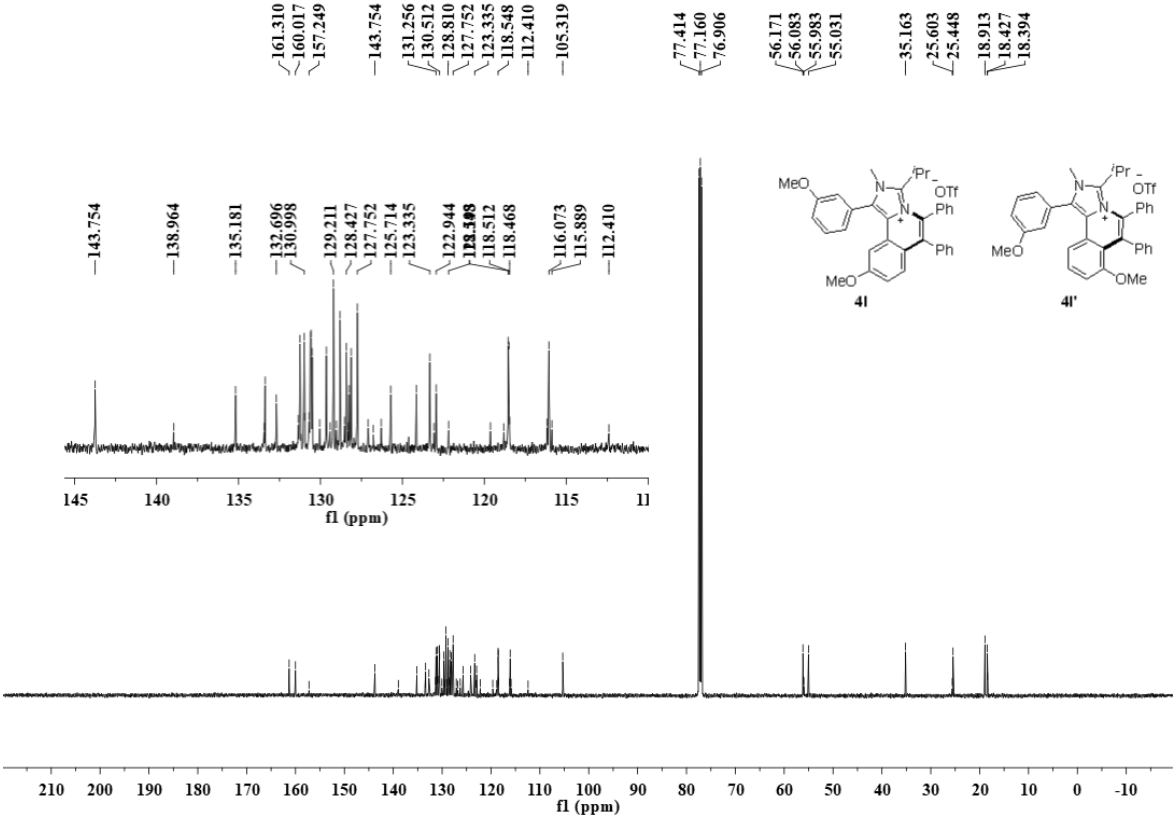
^{13}C NMR (125 MHz, $CDCl_3$) of **4k** and **4k′**



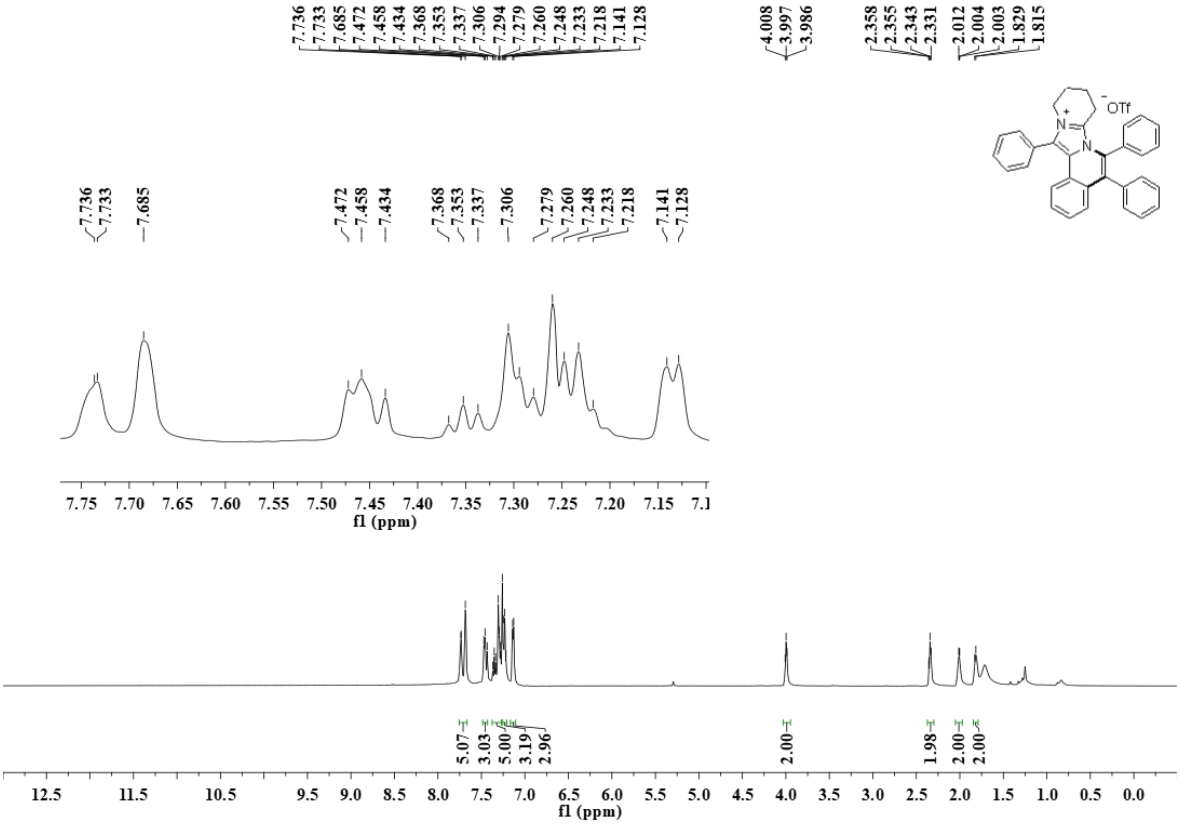
^{1}H NMR (500 MHz, $CDCl_3$) of **4l** and **4l′**



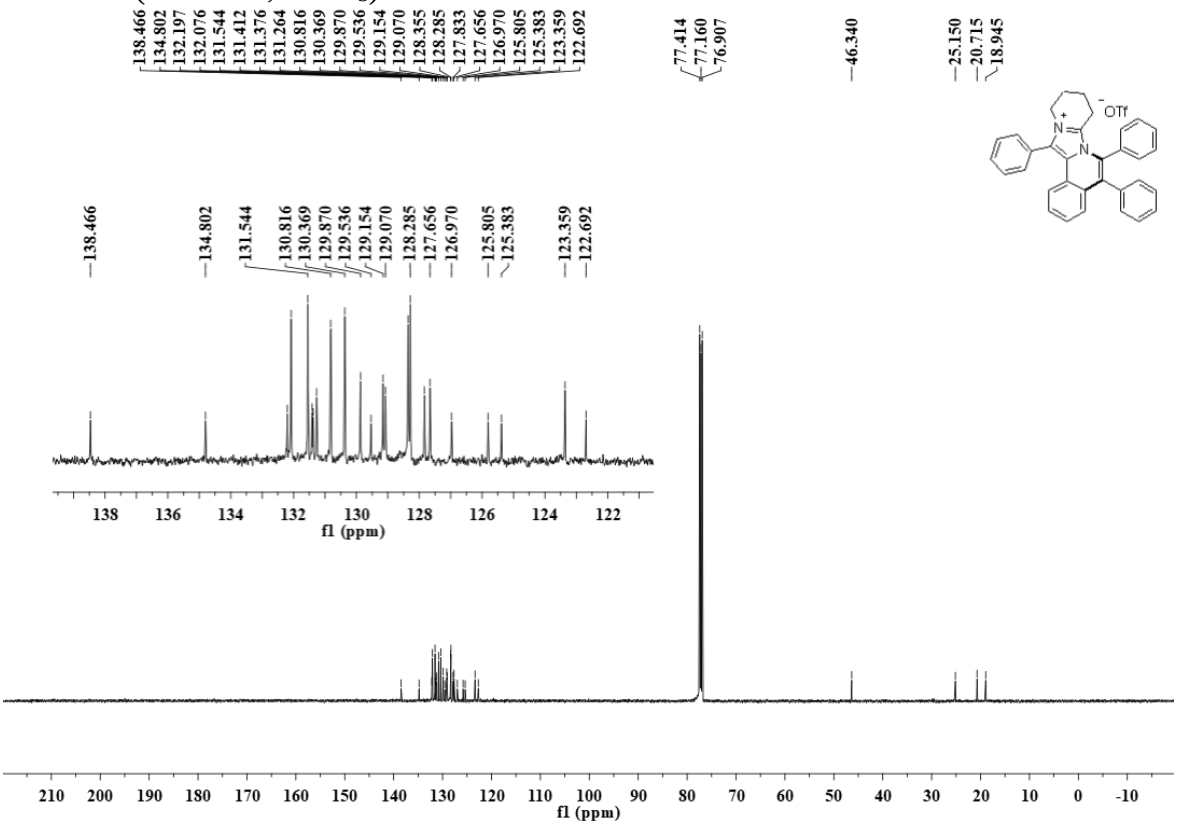
^{13}C NMR (125 MHz, $CDCl_3$) of **4l** and **4l′**



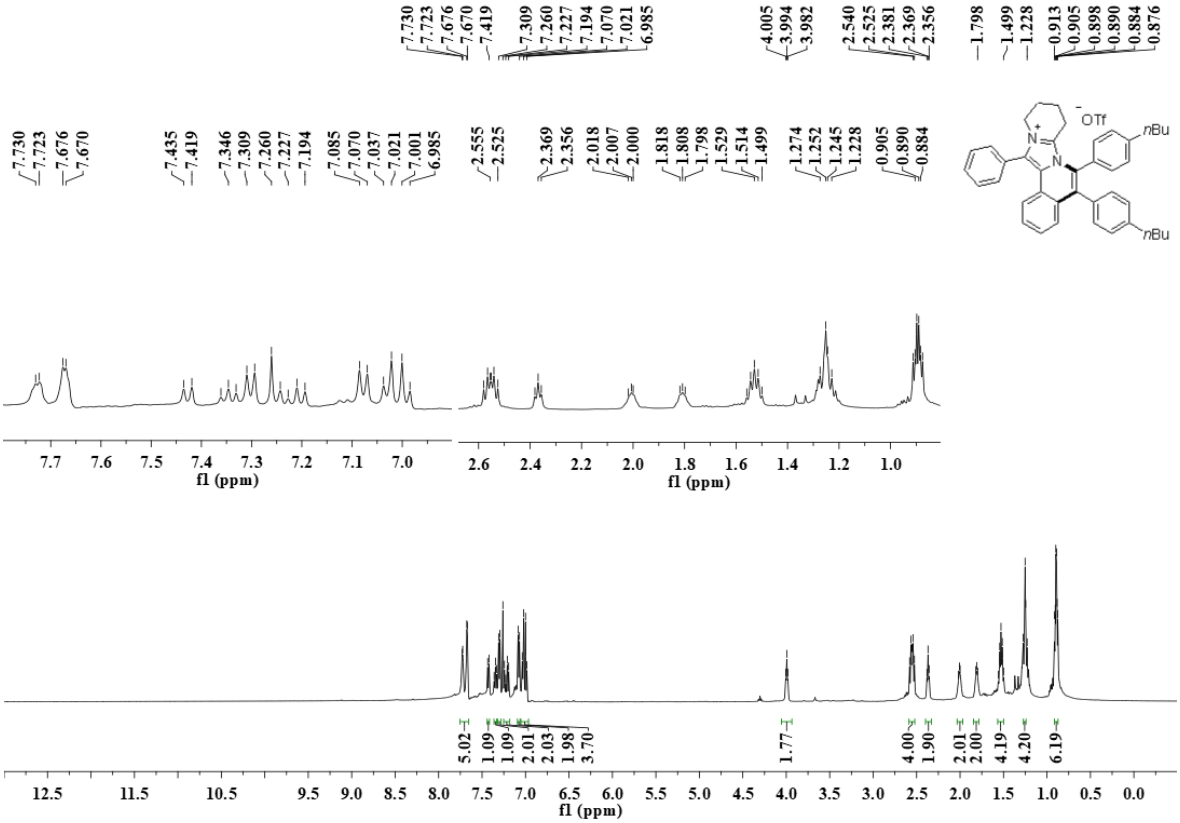
^{1}H NMR (500 MHz, $CDCl_3$) of **5a**



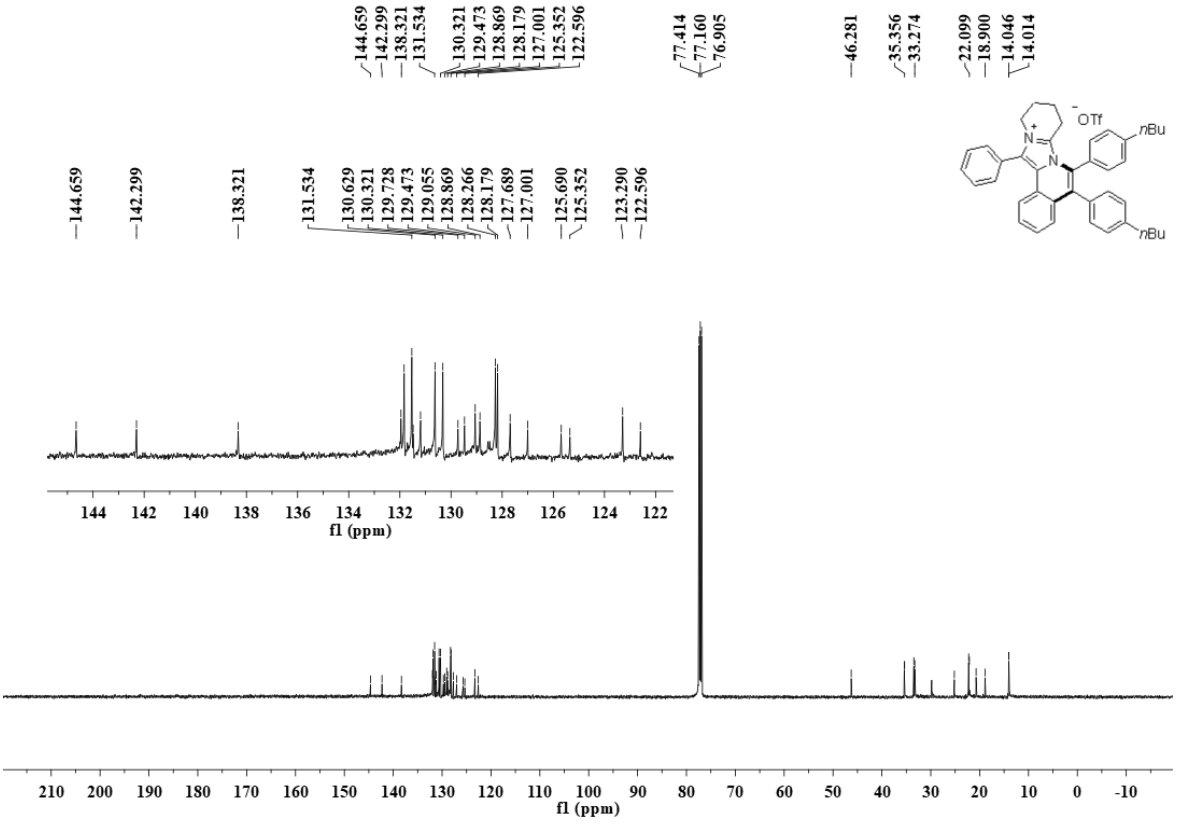
^{13}C NMR (125 MHz, $CDCl_3$) of **5a**



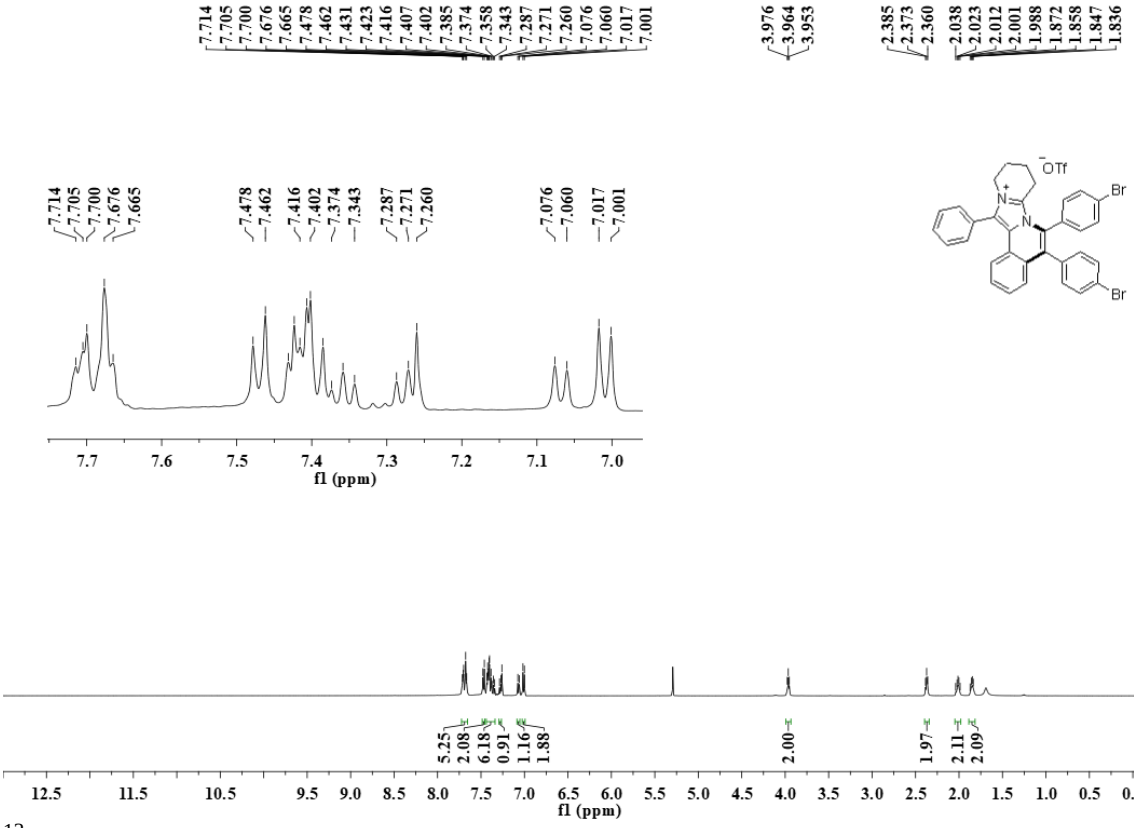
^{1}H NMR (500 MHz, $CDCl_3$) of **5b**



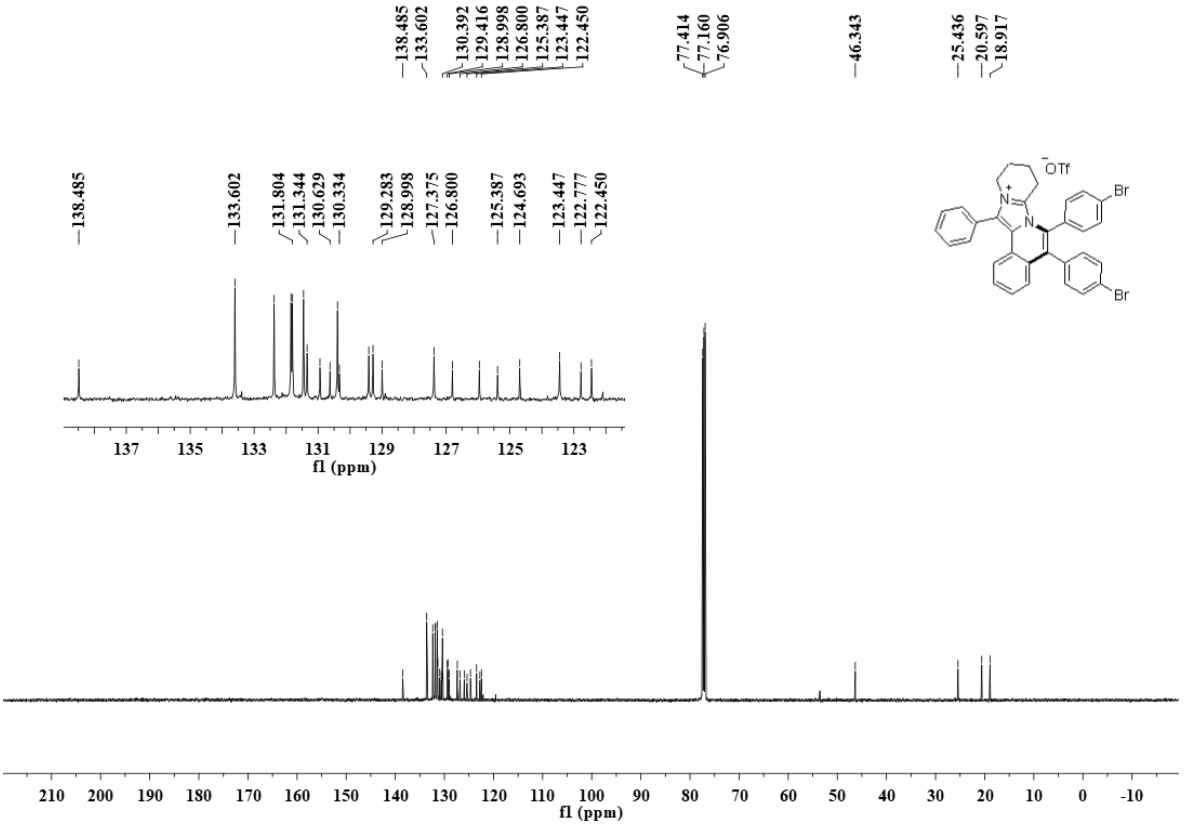
^{13}C NMR (125 MHz, $CDCl_3$) of **5b**



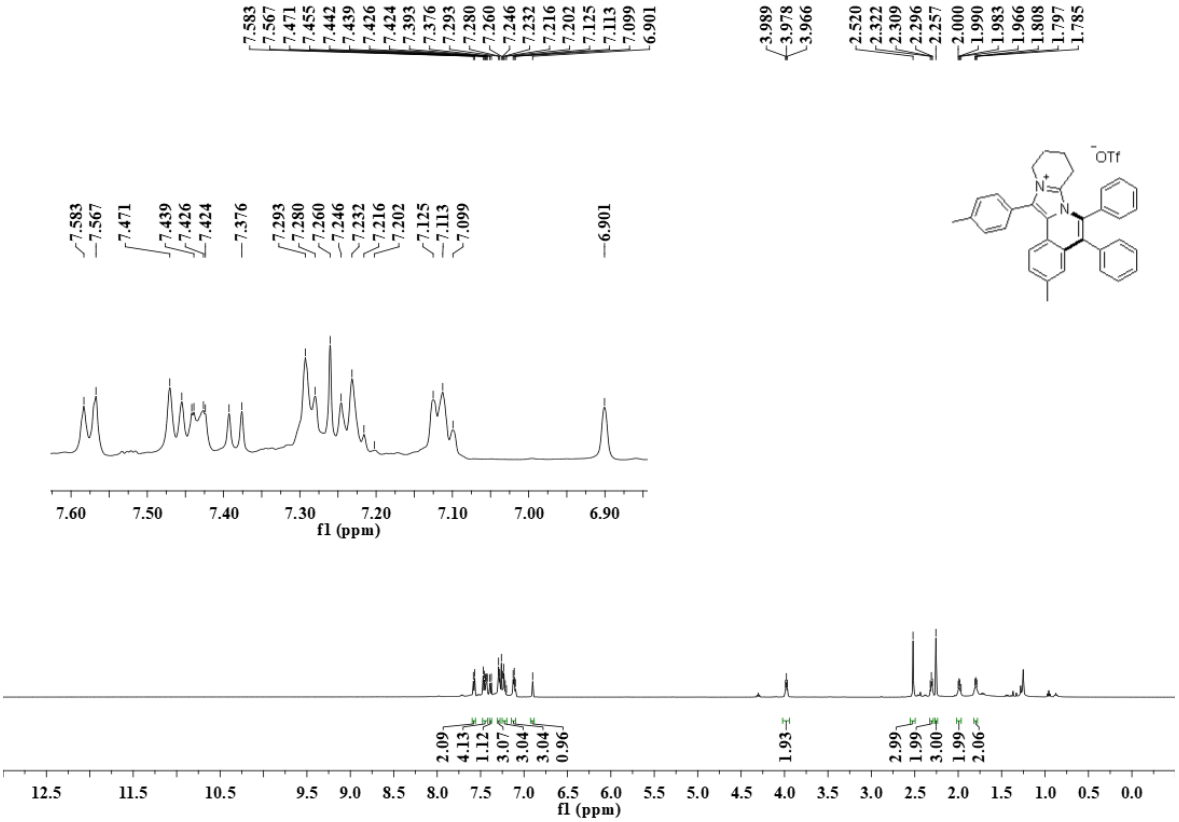
^{1}H NMR (500 MHz, $CDCl_3$) of **5c**



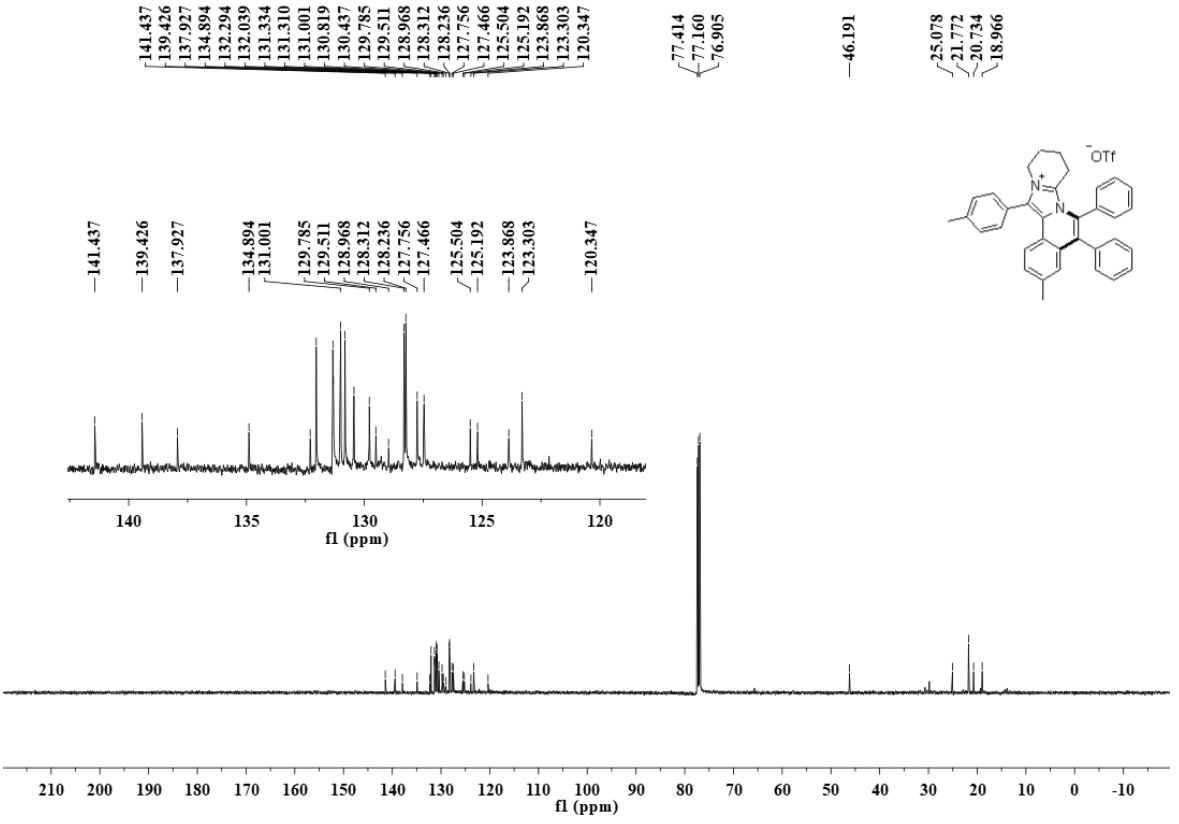
^{13}C NMR (125 MHz, $CDCl_3$) of **5c**



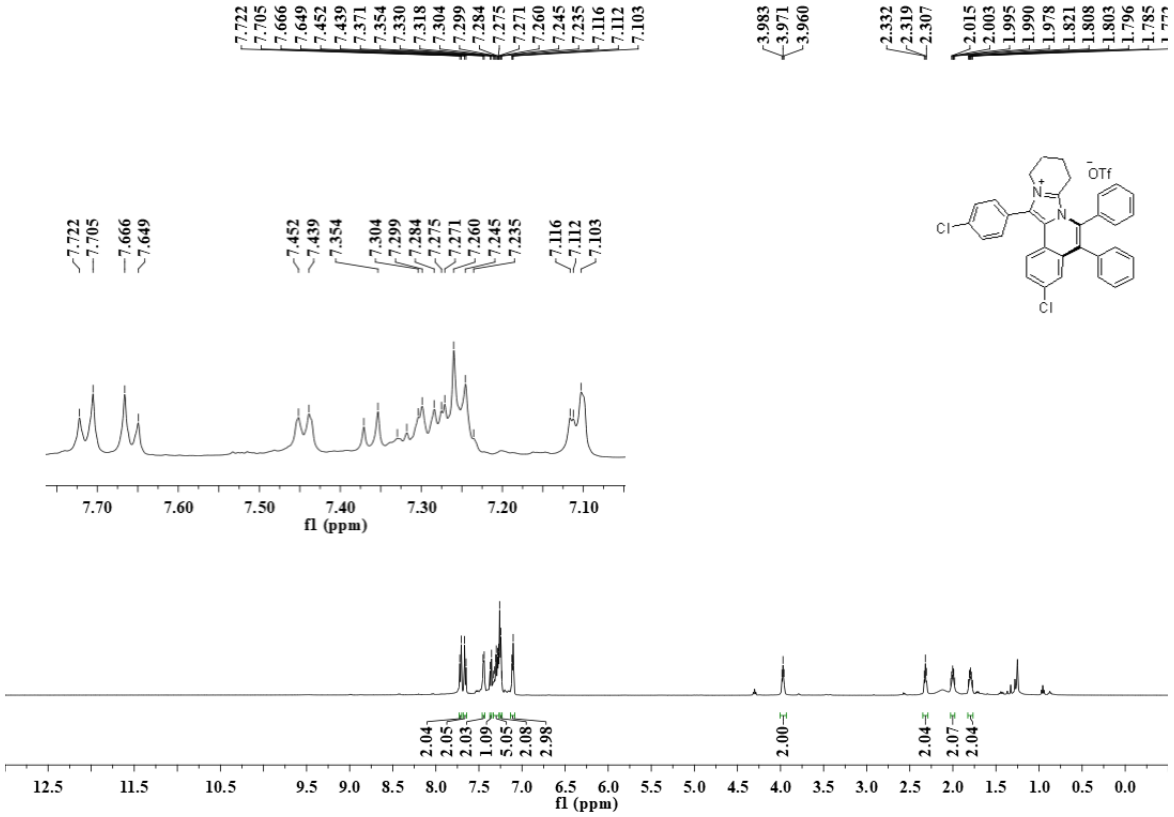
^{1}H NMR (500 MHz, $CDCl_3$) of **5d**



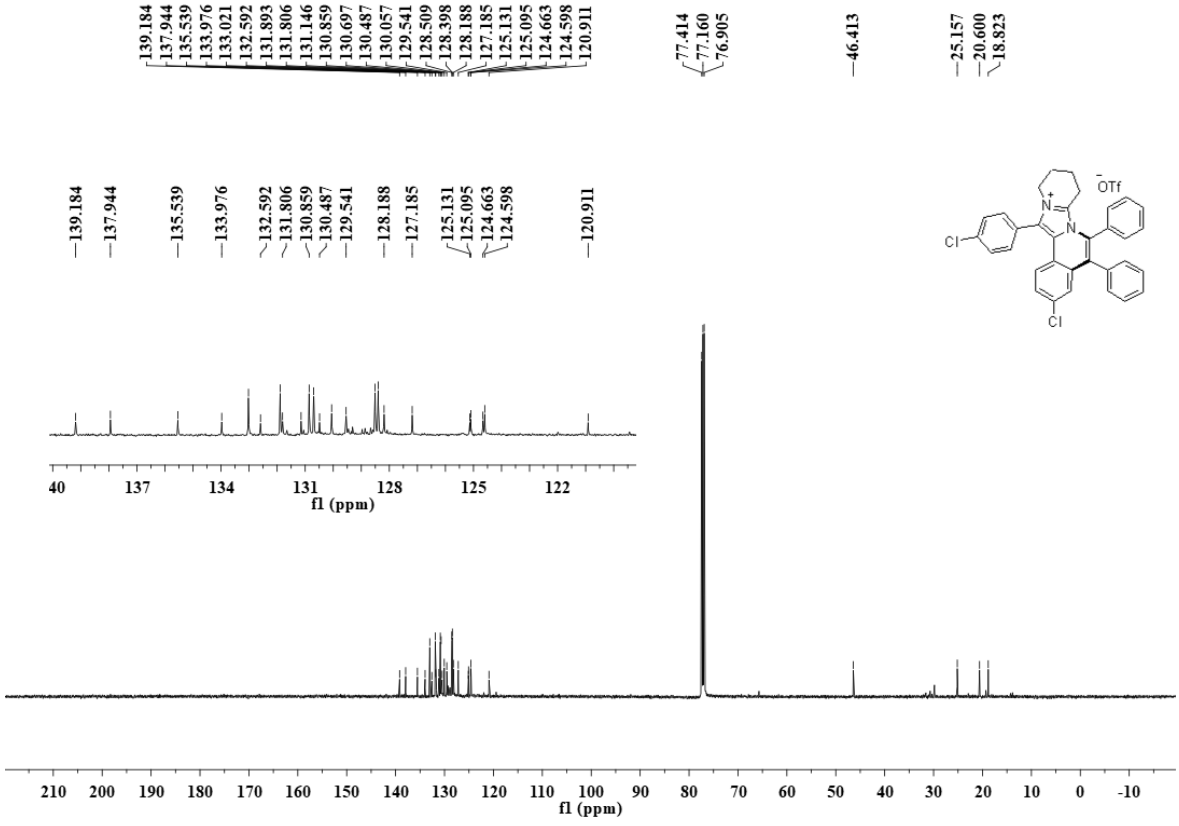
^{13}C NMR (125 MHz, $CDCl_3$) of **5d**



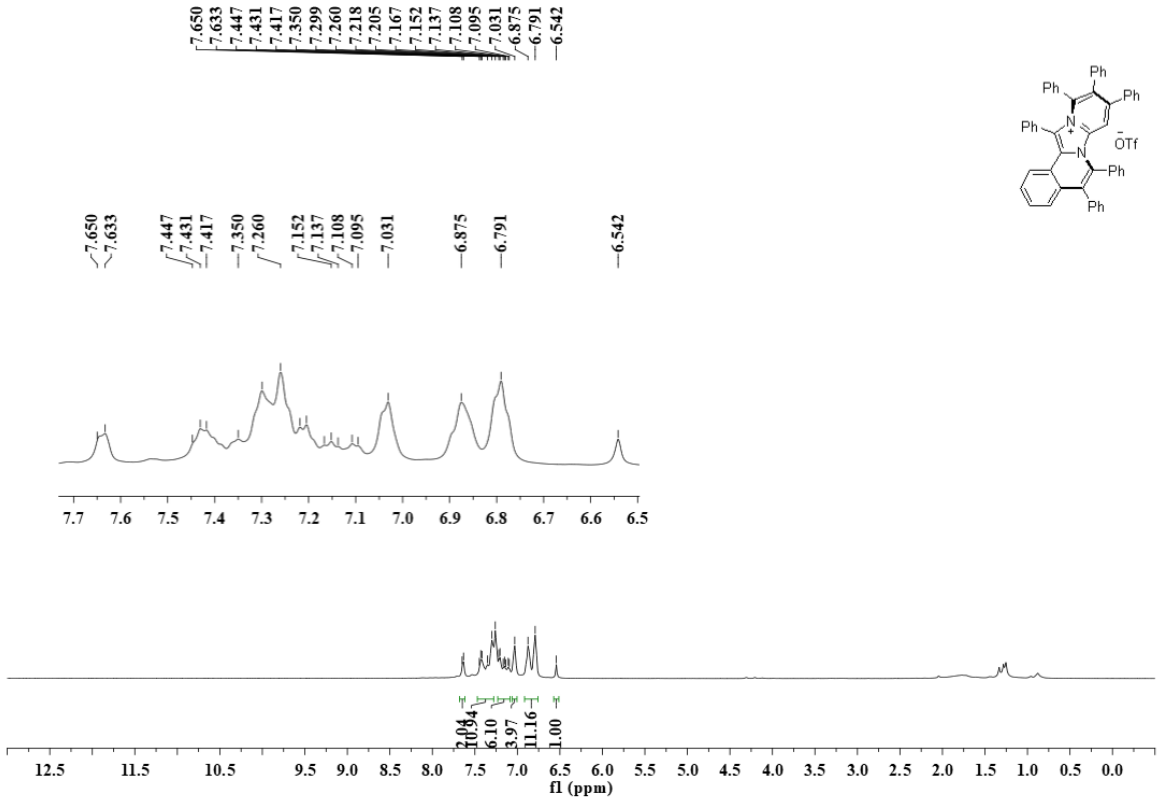
^{1}H NMR (500 MHz, $CDCl_3$) of **5e**



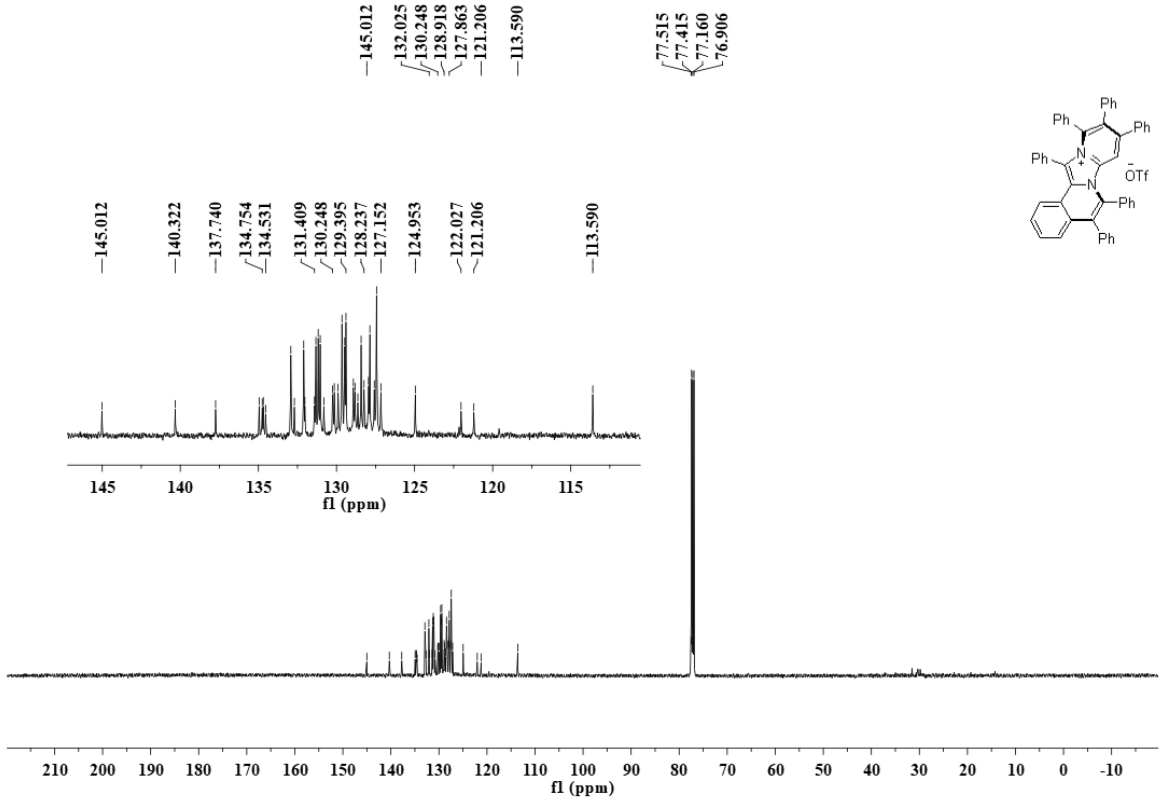
^{13}C NMR (125 MHz, $CDCl_3$) of **5e**



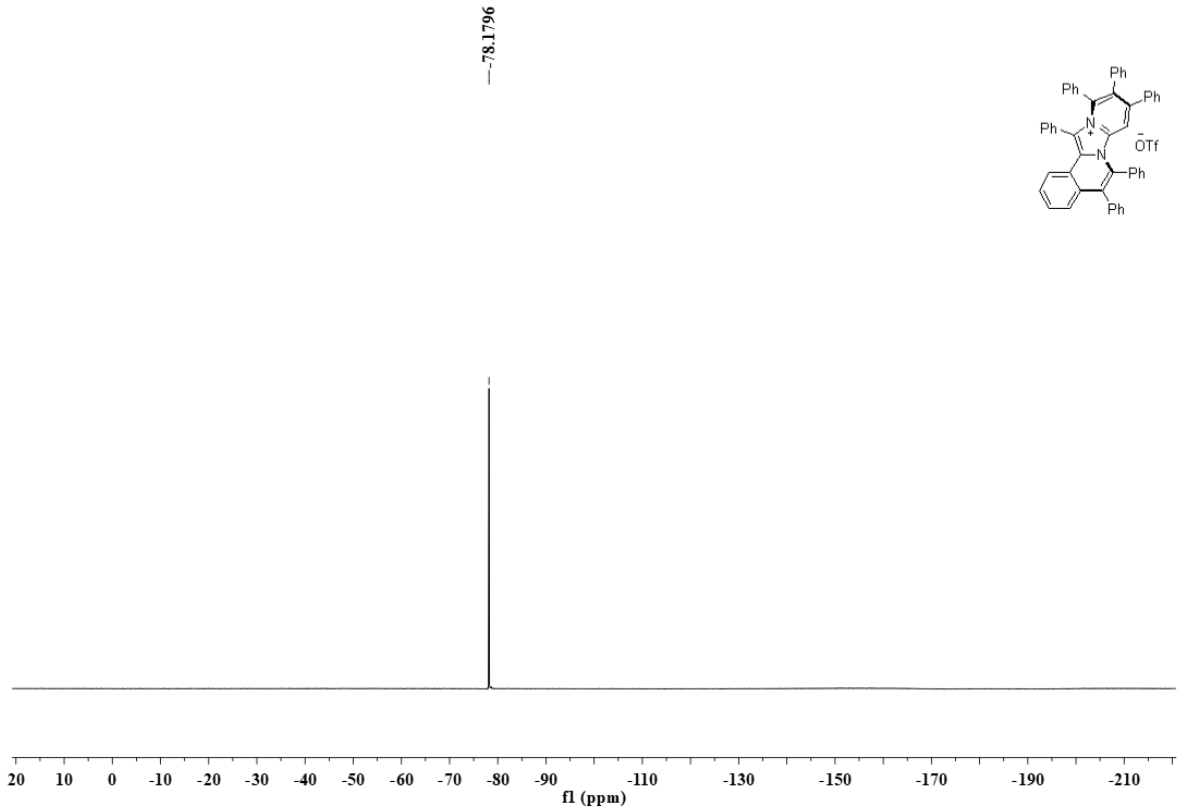
^{1}H NMR (500 MHz, $CDCl_3$) of **6a**



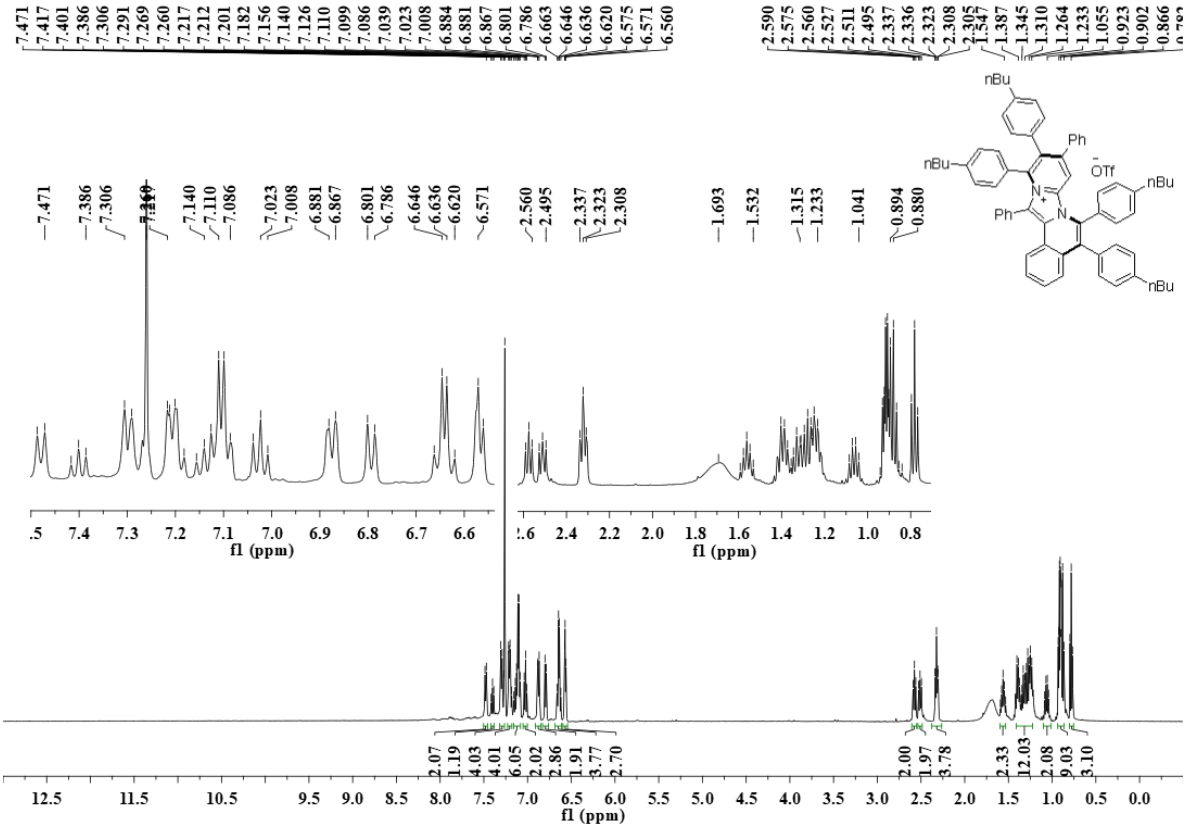
^{13}C NMR (125 MHz, $CDCl_3$) of **6a**



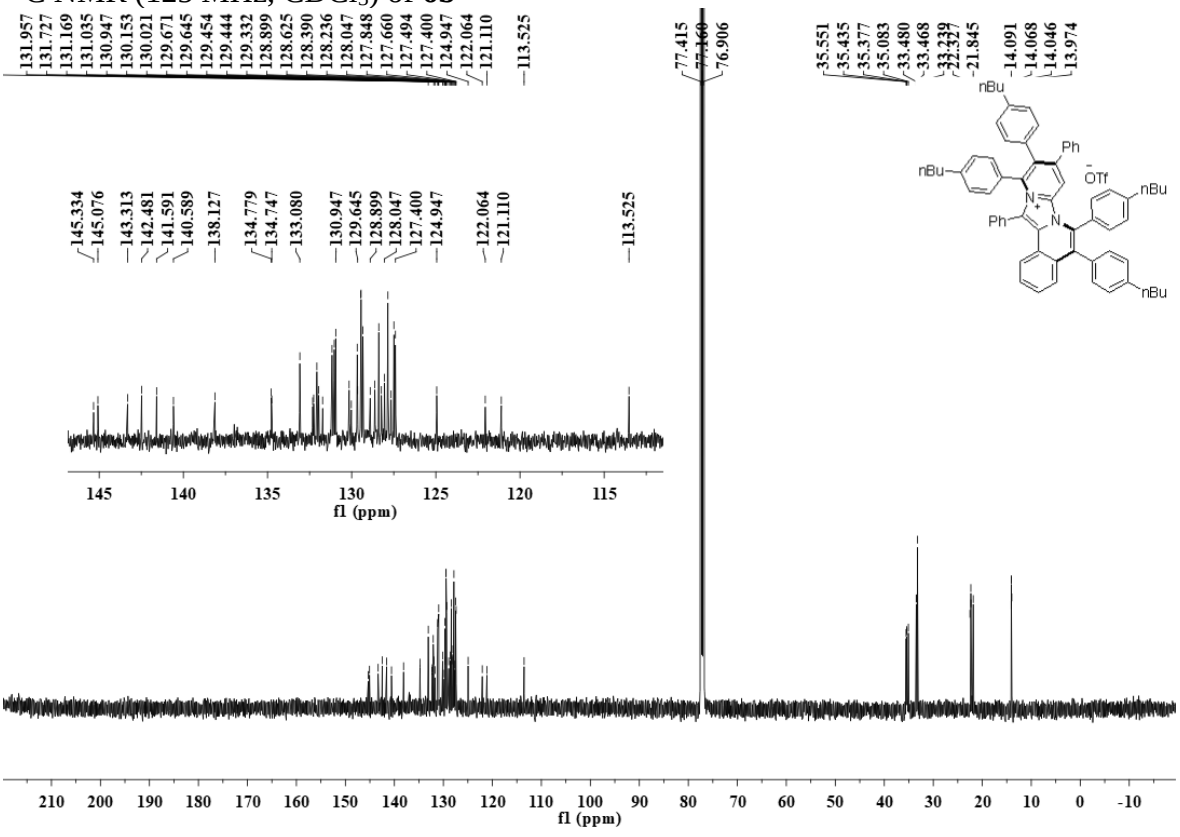
^{19}F NMR (471 MHz, $CDCl_3$) of **6a**



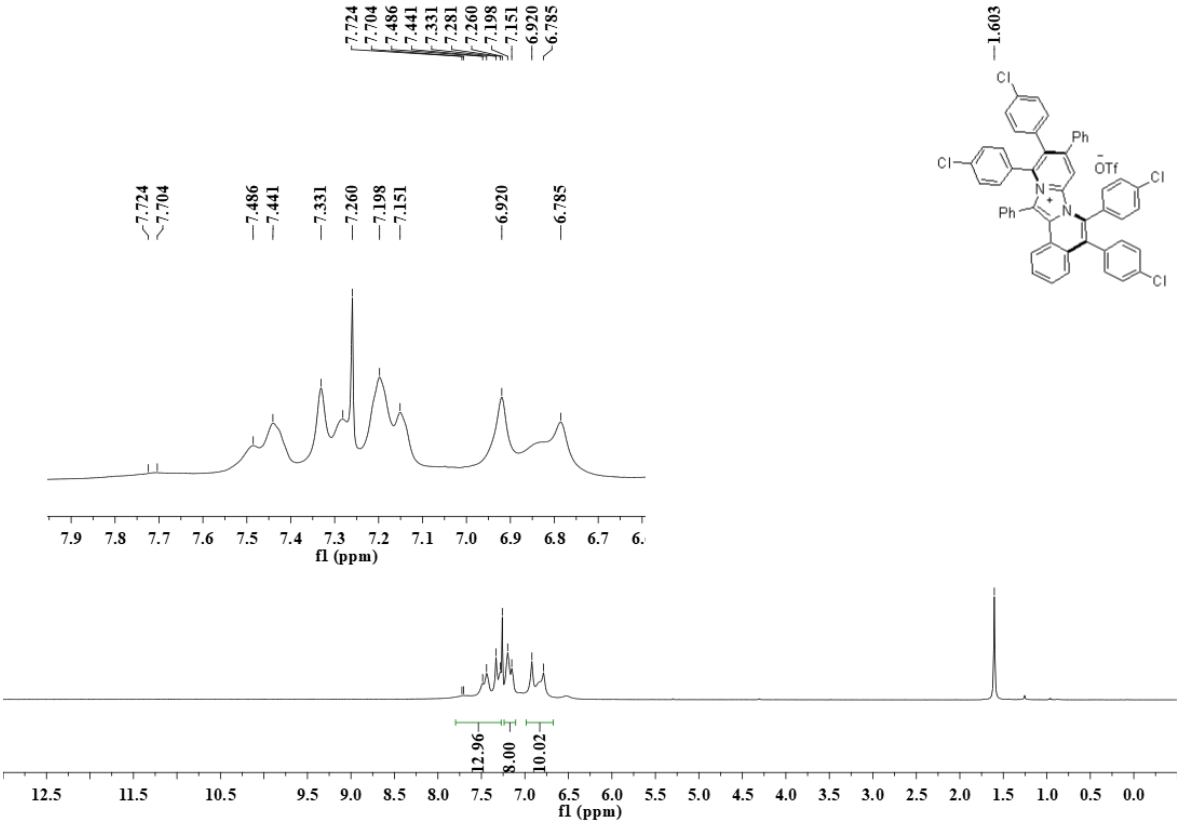
^{1}H NMR (500 MHz, $CDCl_3$) of **6b**



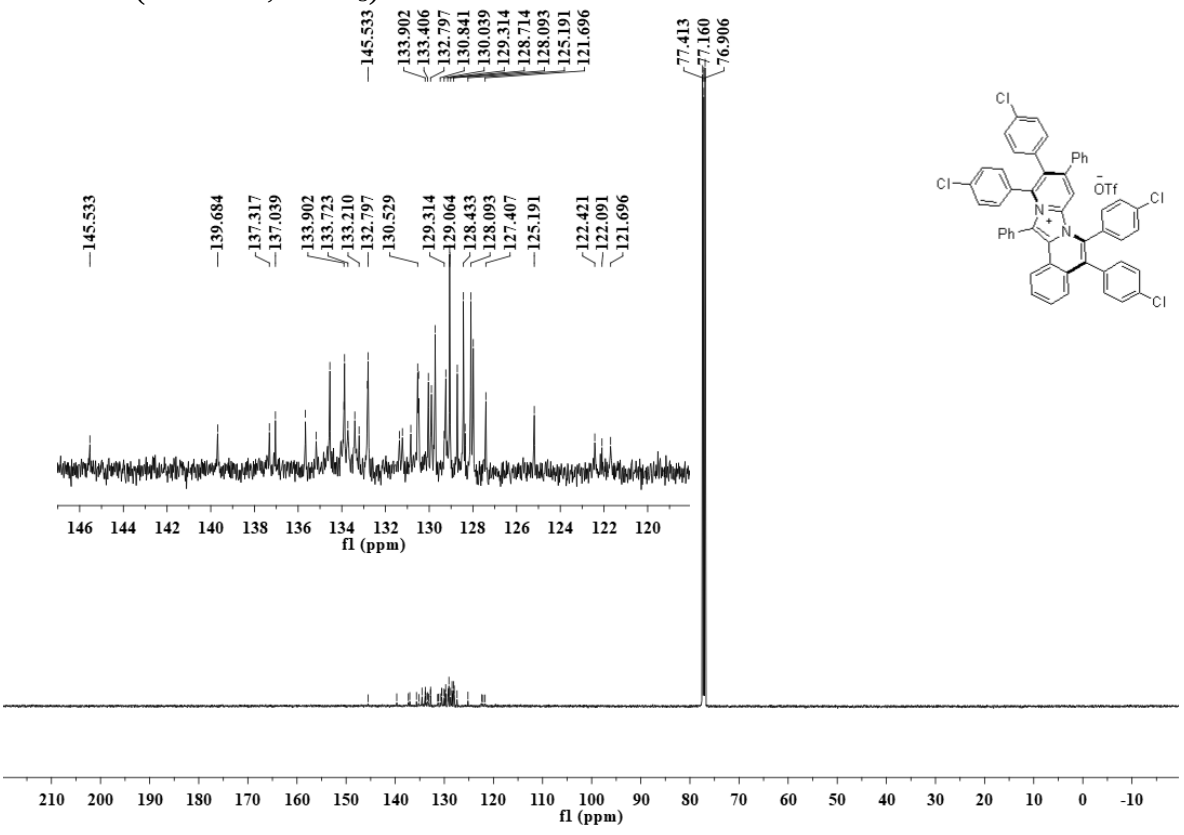
^{13}C NMR (125 MHz, $CDCl_3$) of **6b**



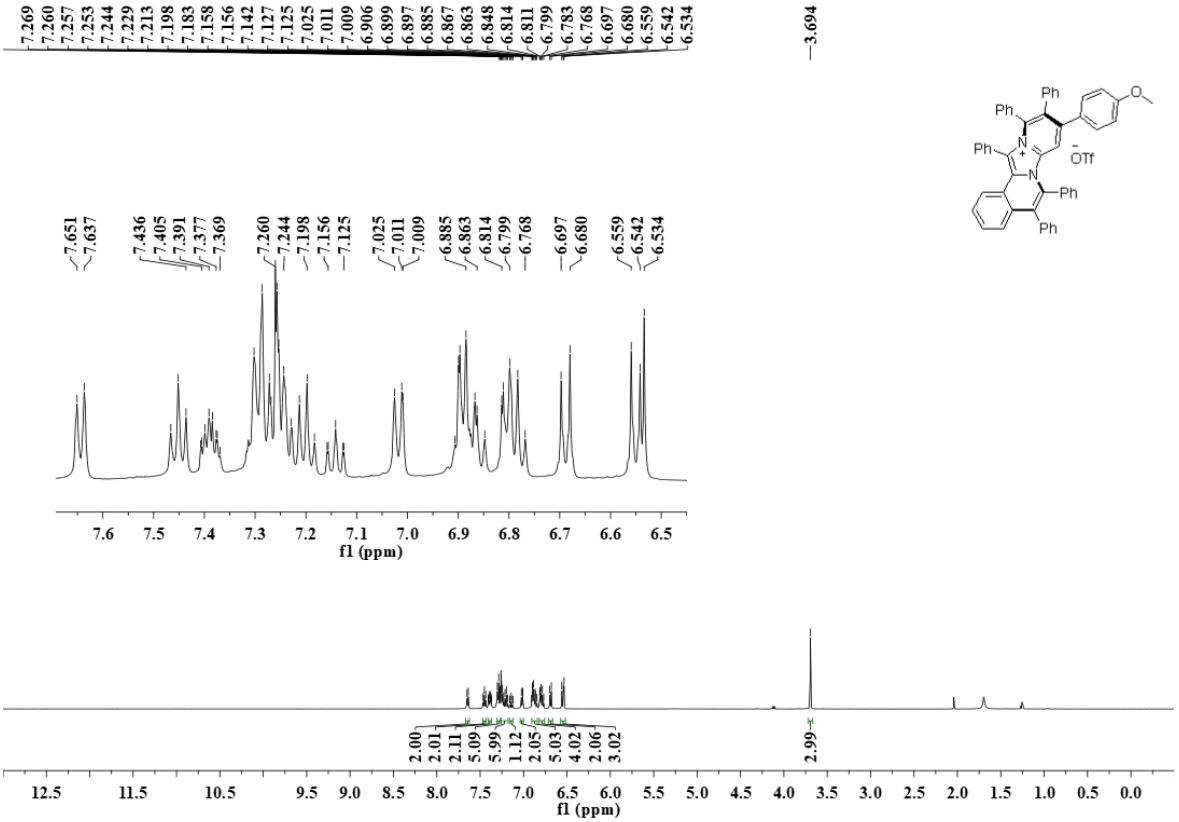
^{1}H NMR (500 MHz, $CDCl_3$) of **6c**



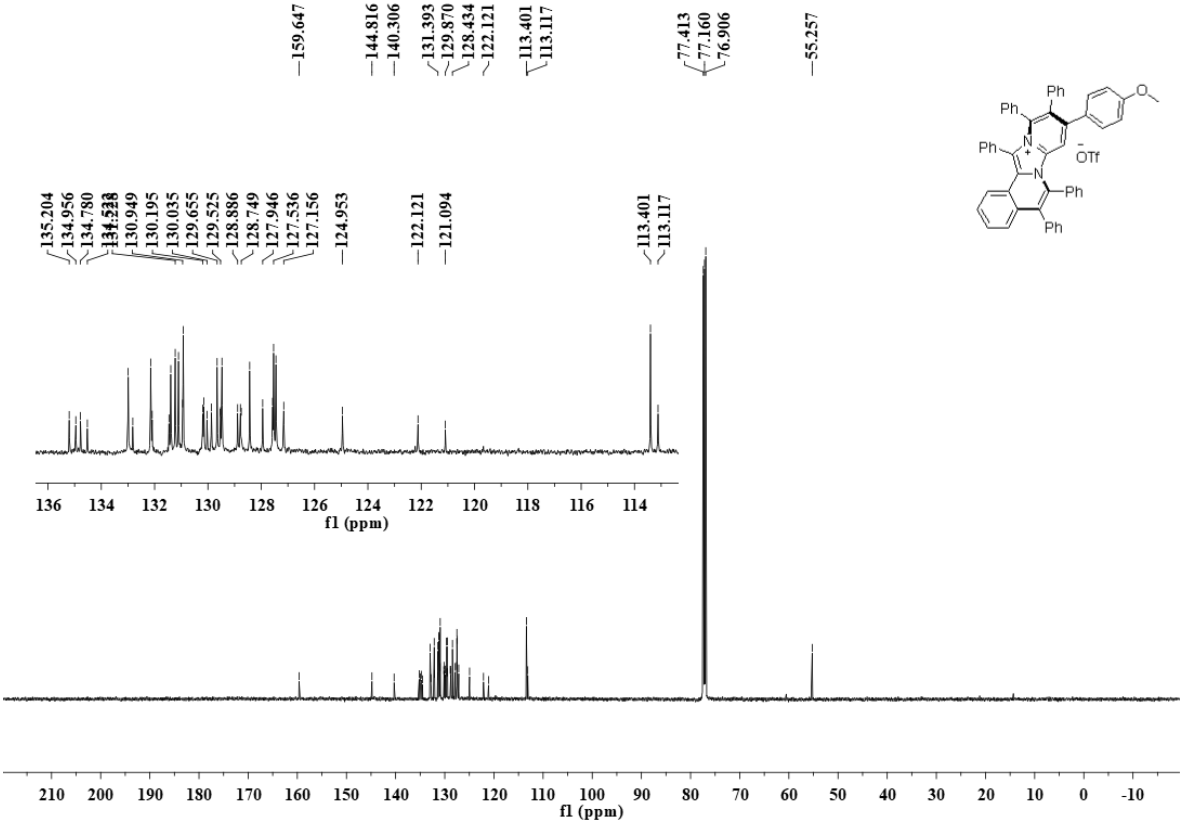
^{13}C NMR (125 MHz, $CDCl_3$) of **6c**



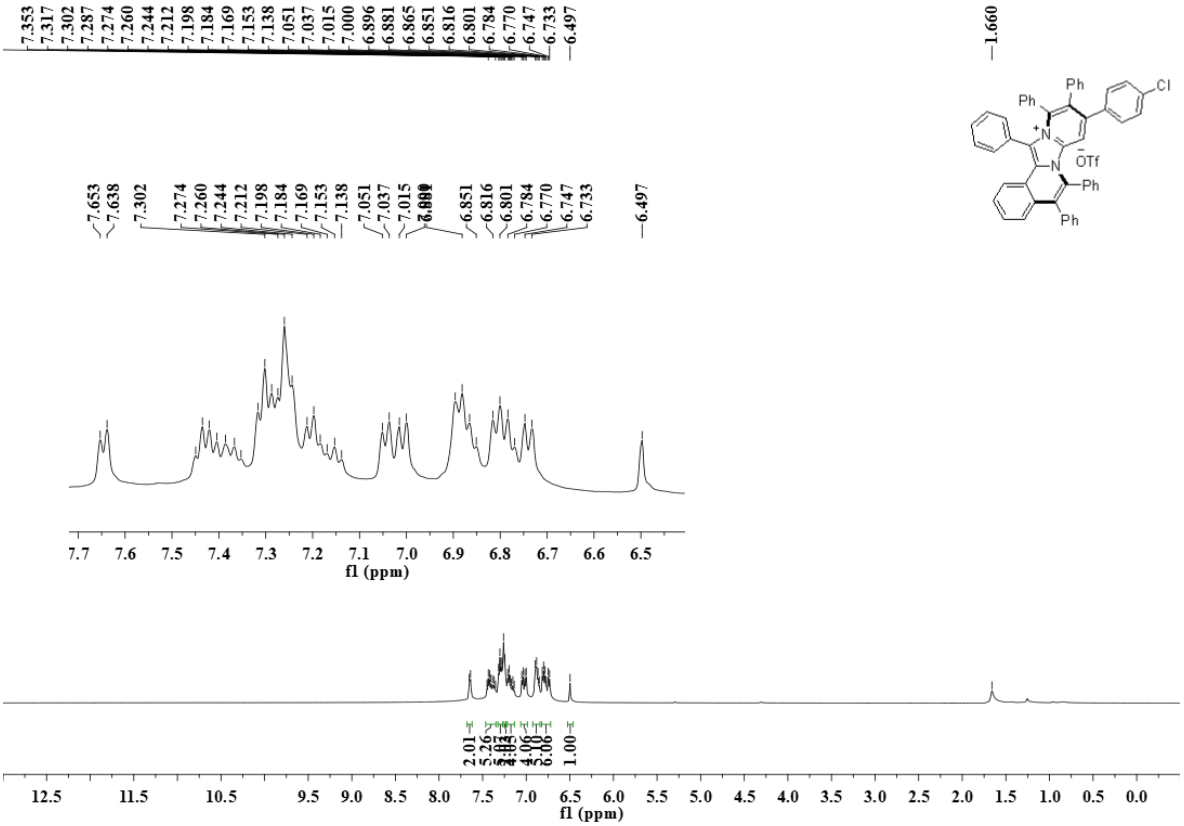
^{1}H NMR (500 MHz, $CDCl_3$) of **6d**



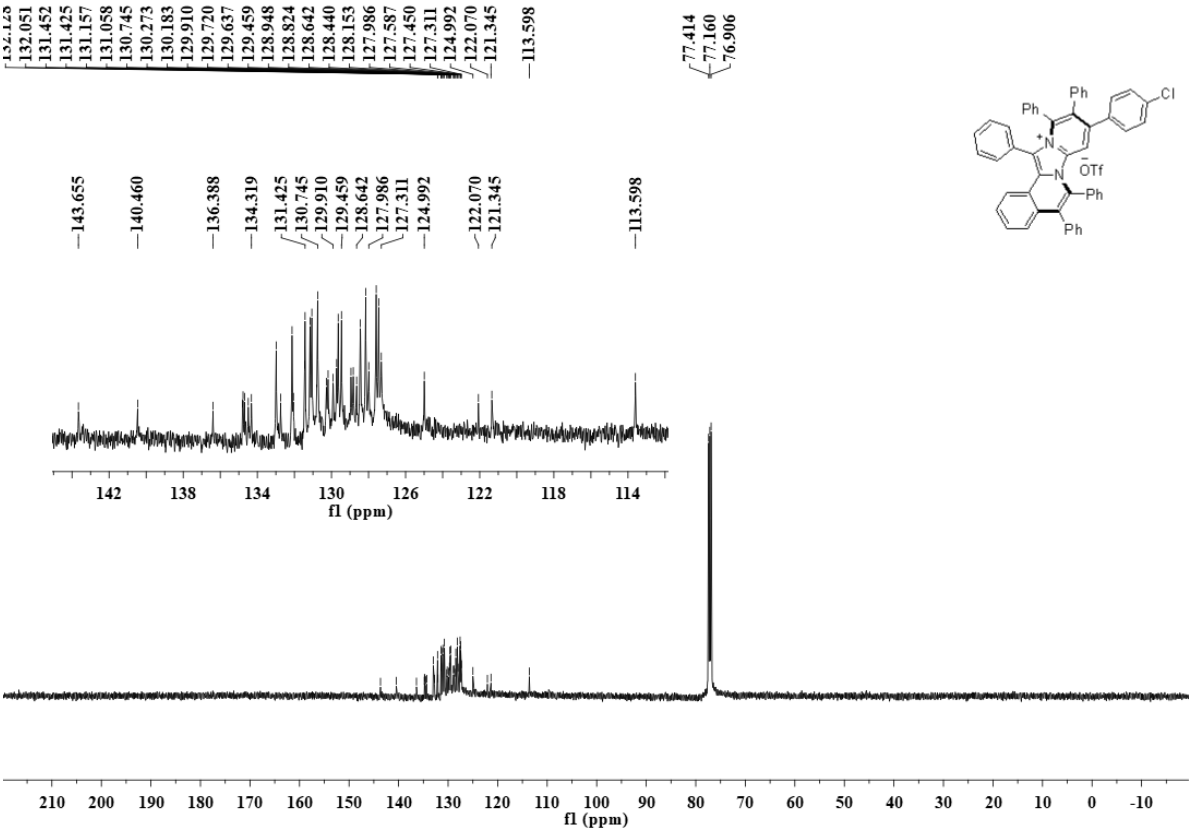
^{13}C NMR (125 MHz, $CDCl_3$) of **6d**



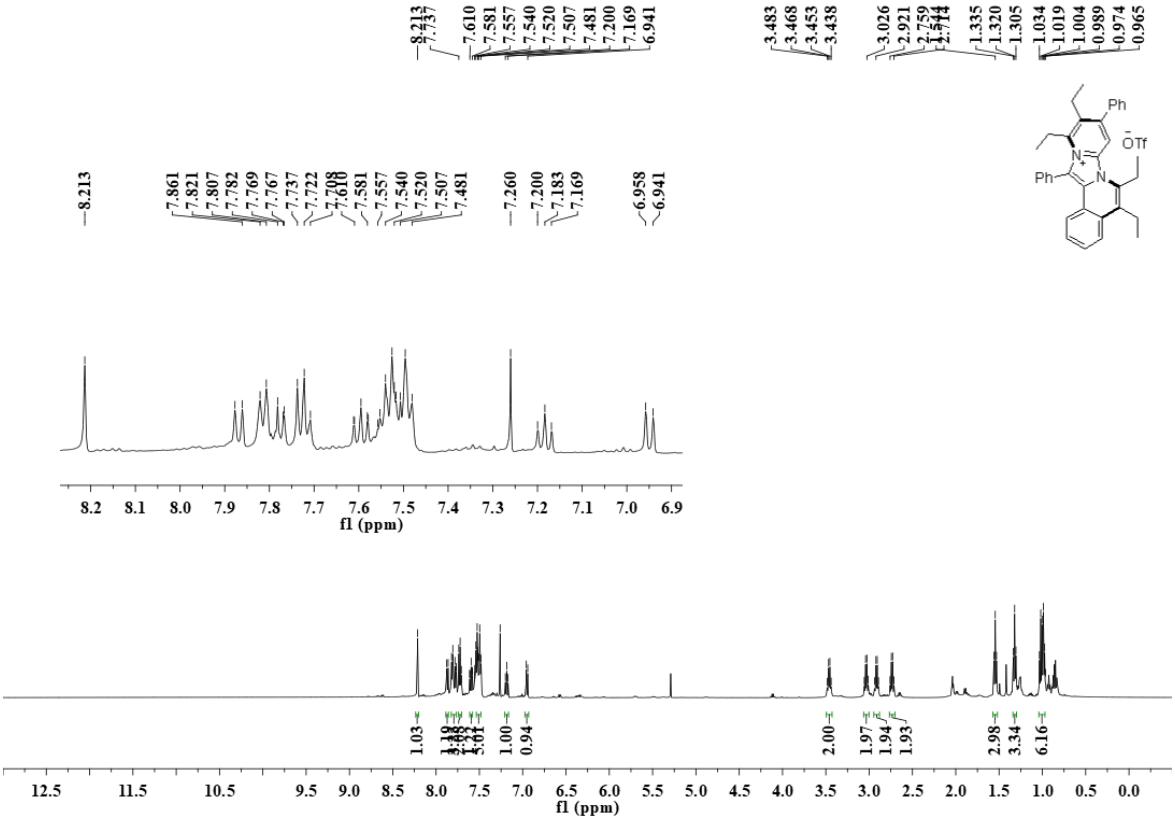
^{1}H NMR (500 MHz, $CDCl_3$) of **6e**



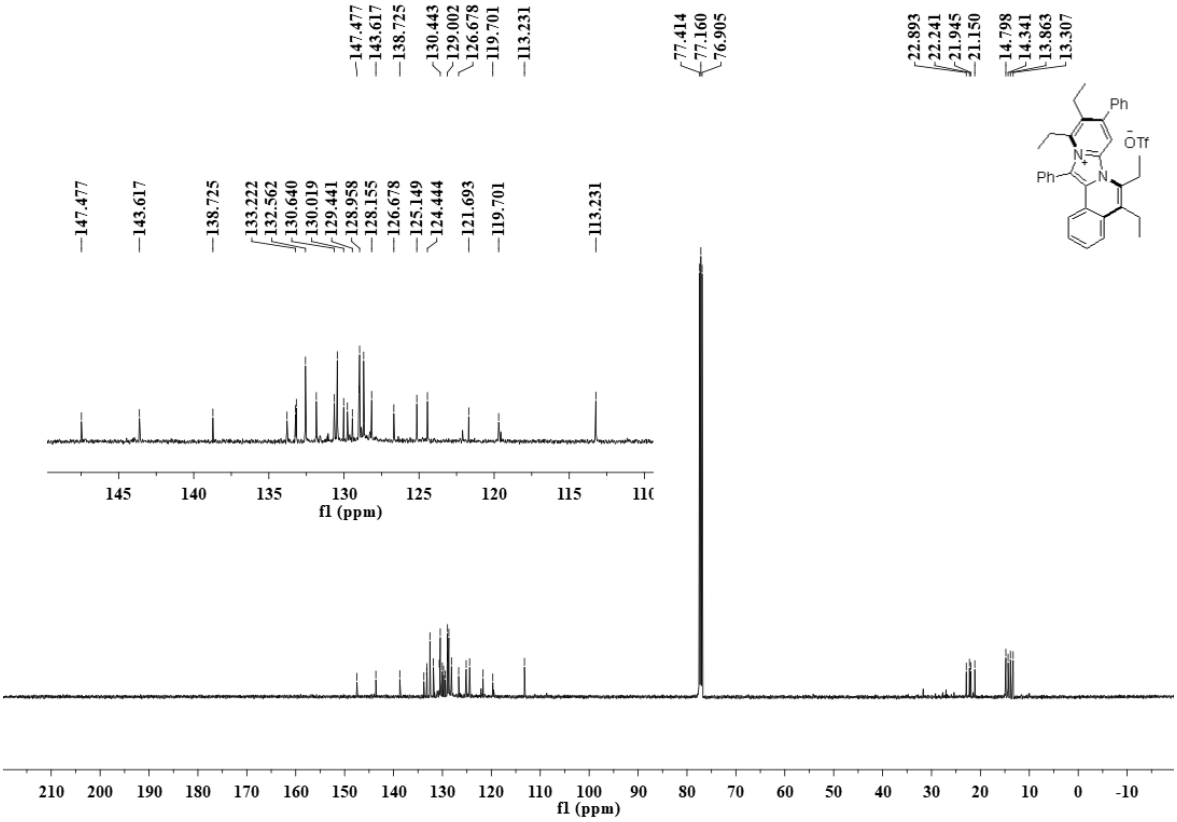
^{13}C NMR (125 MHz, $CDCl_3$) of **6e**



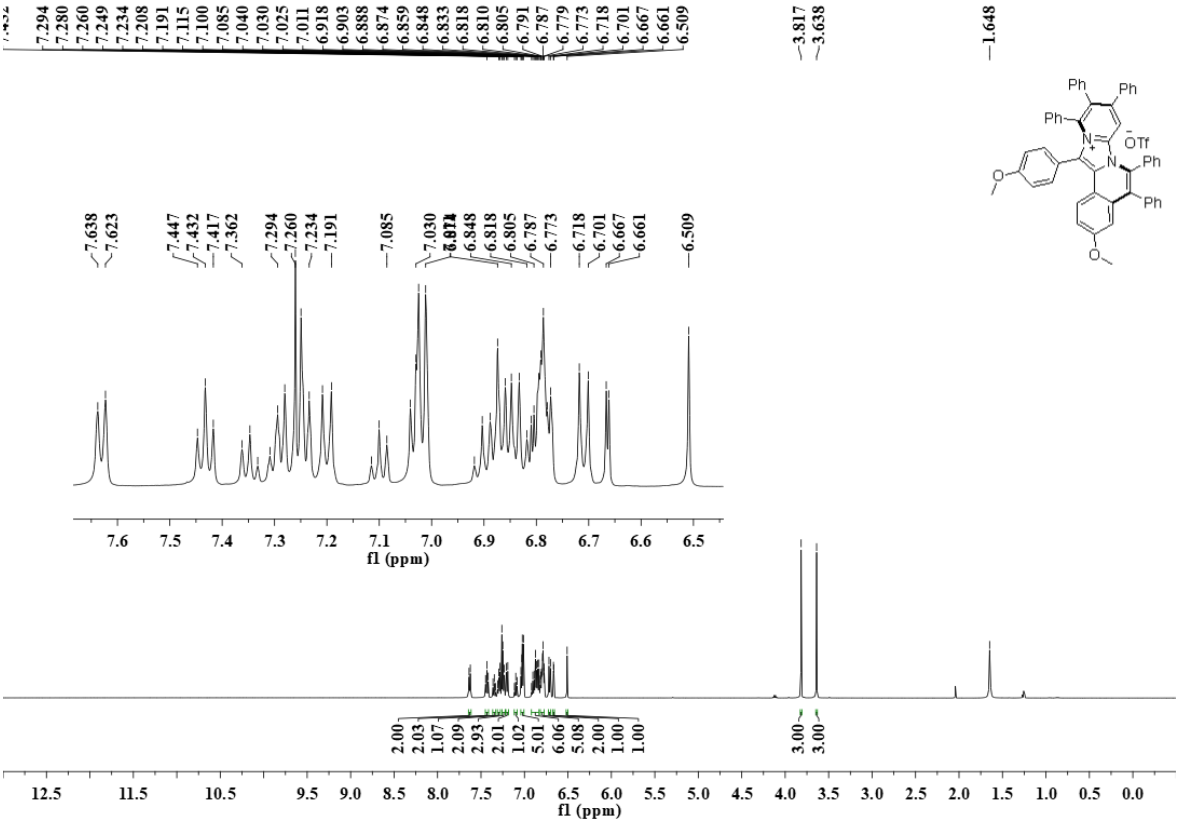
^{1}H NMR (500 MHz, $CDCl_3$) of **6f**



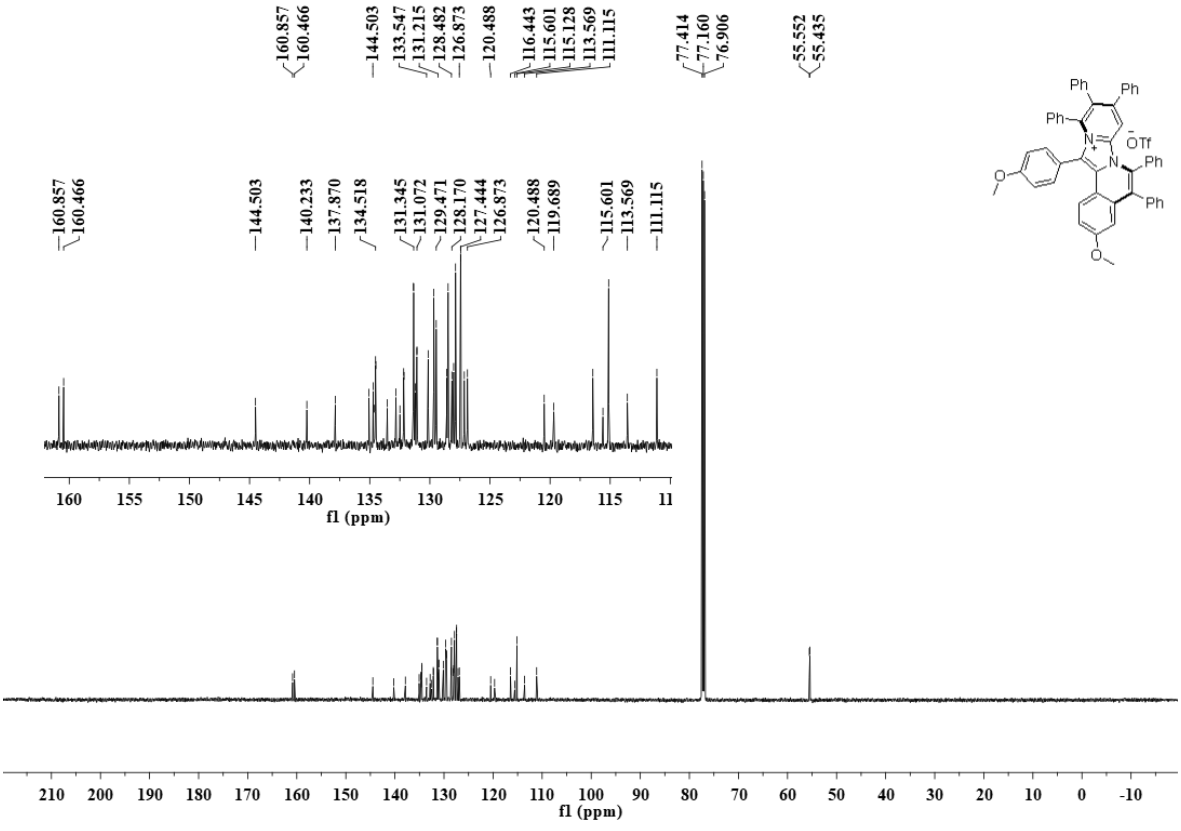
^{13}C NMR (125 MHz, $CDCl_3$) of **6f**



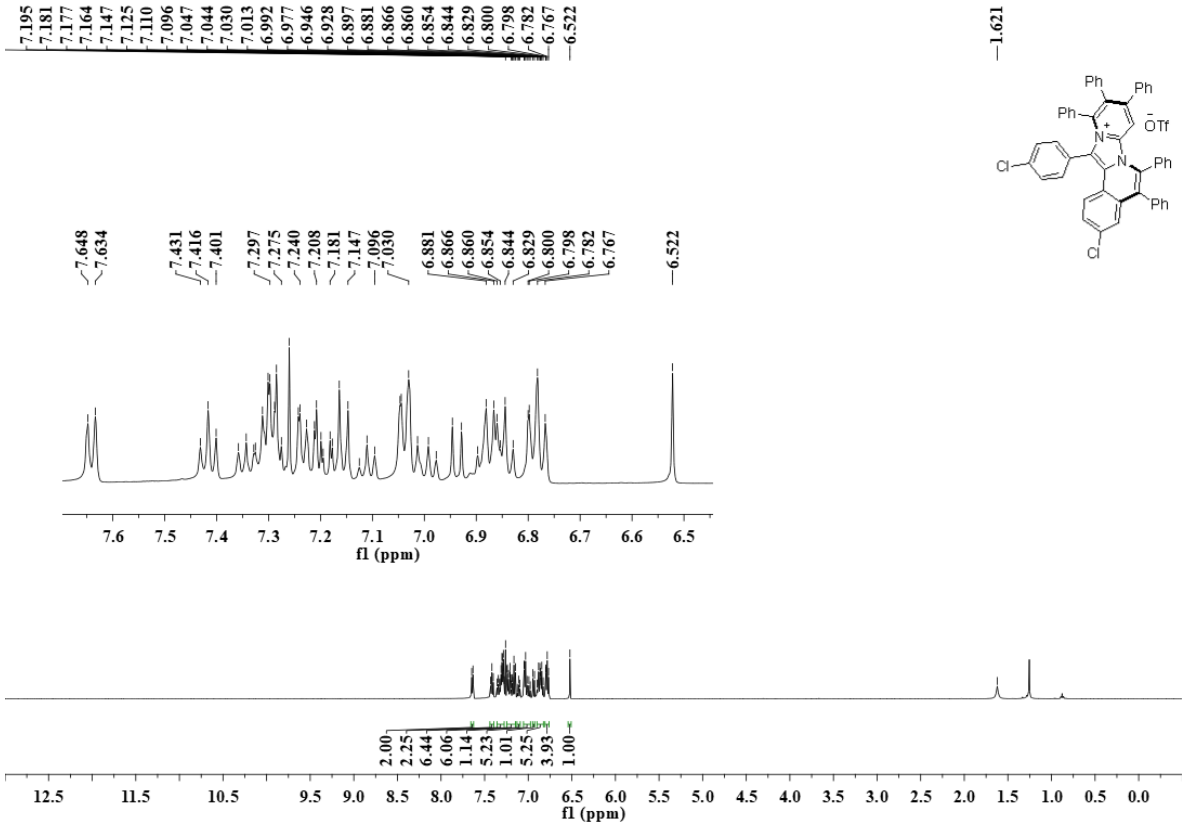
^{1}H NMR (500 MHz, $CDCl_3$) of **6g**



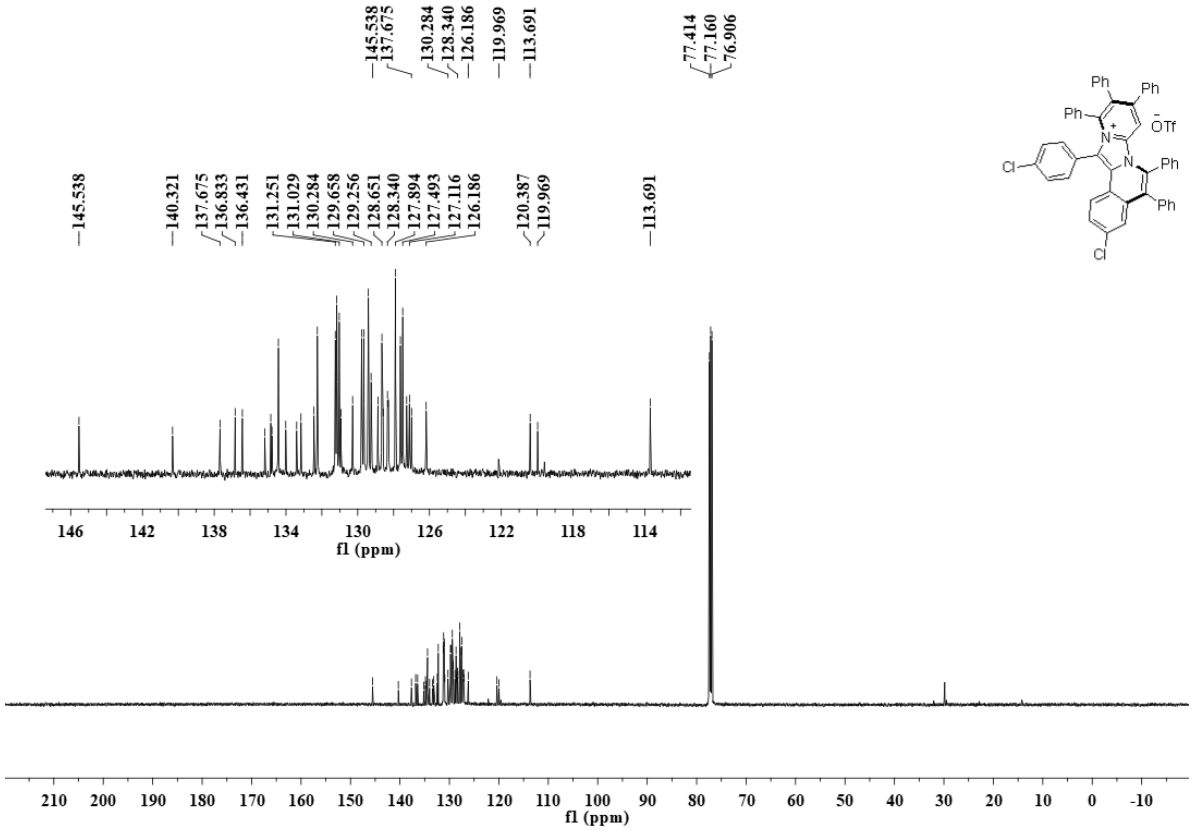
^{13}C NMR (125 MHz, $CDCl_3$) of **6g**



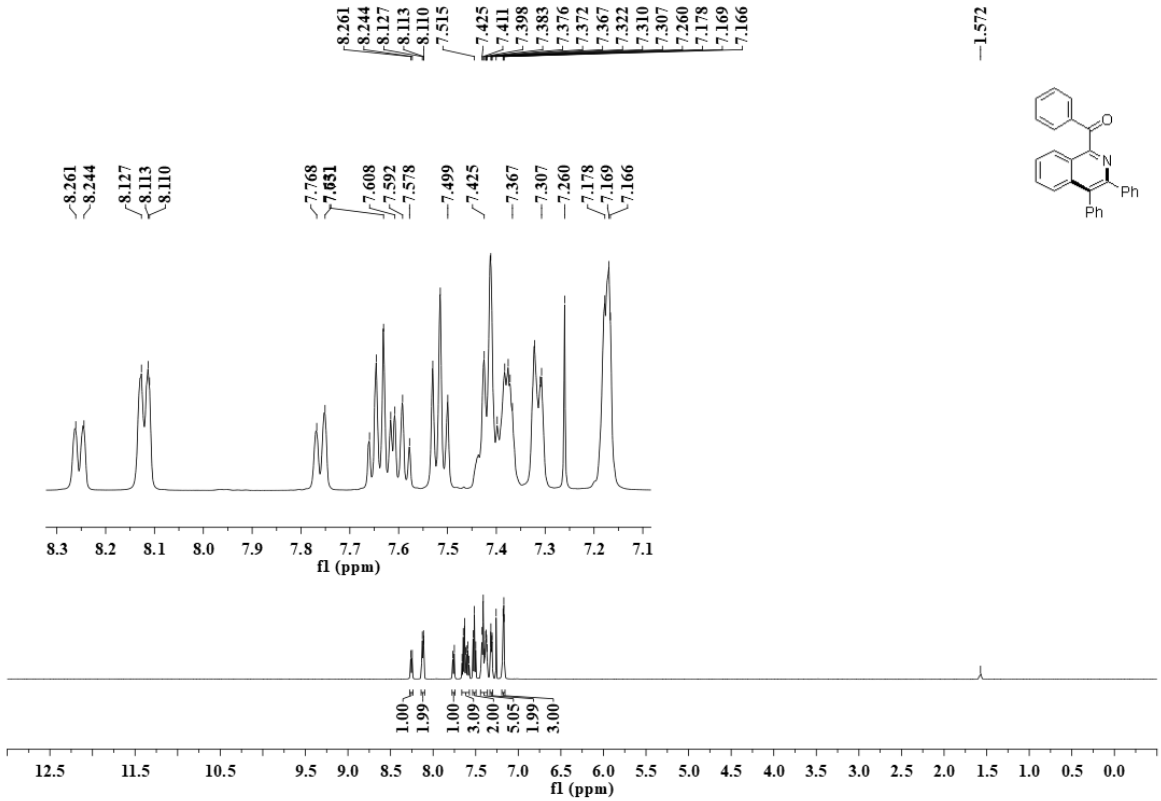
^{1}H NMR (500 MHz, $CDCl_3$) of **6h**



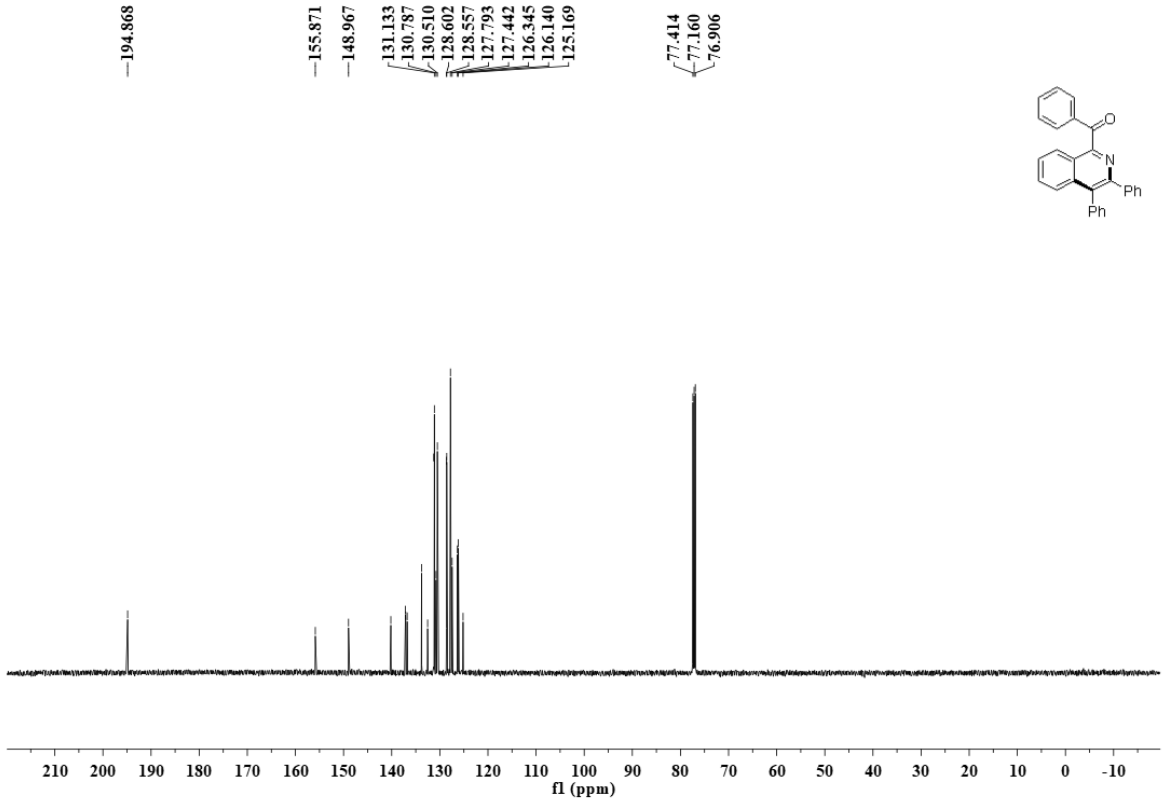
^{13}C NMR (125 MHz, $CDCl_3$) of **6h**



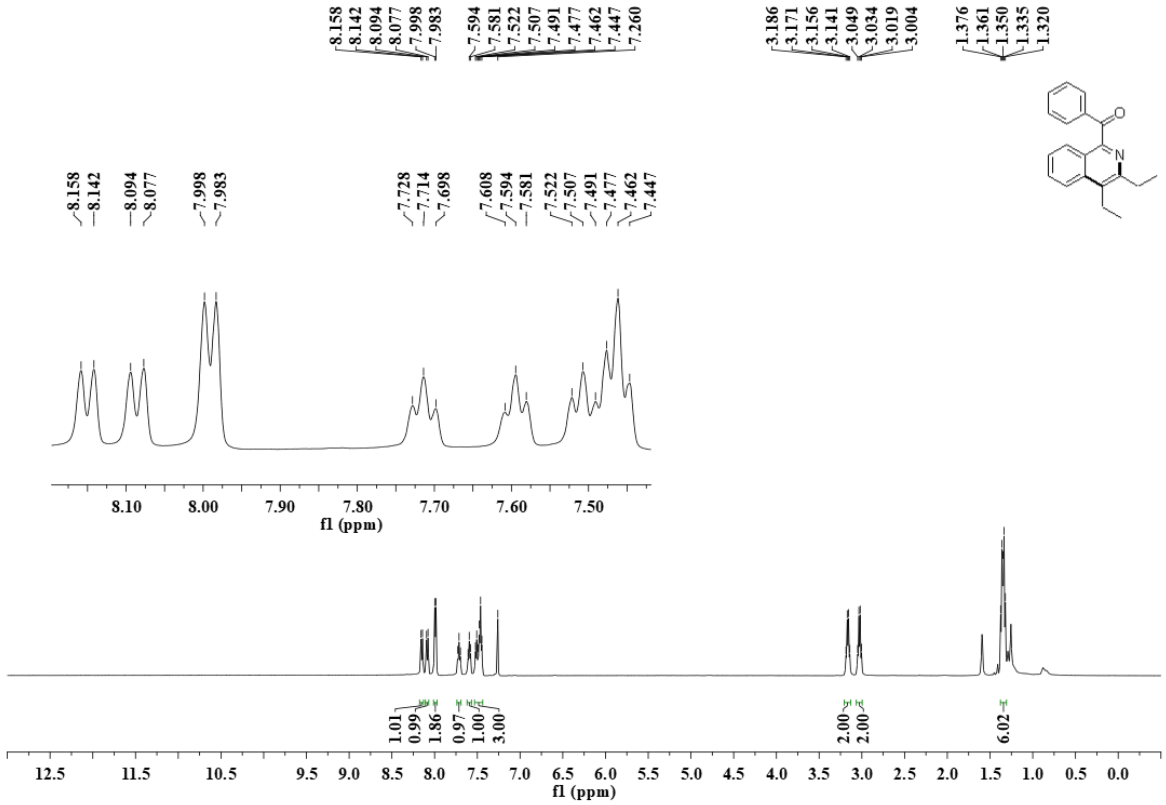
^{1}H NMR (500 MHz, $CDCl_3$) of **7a**



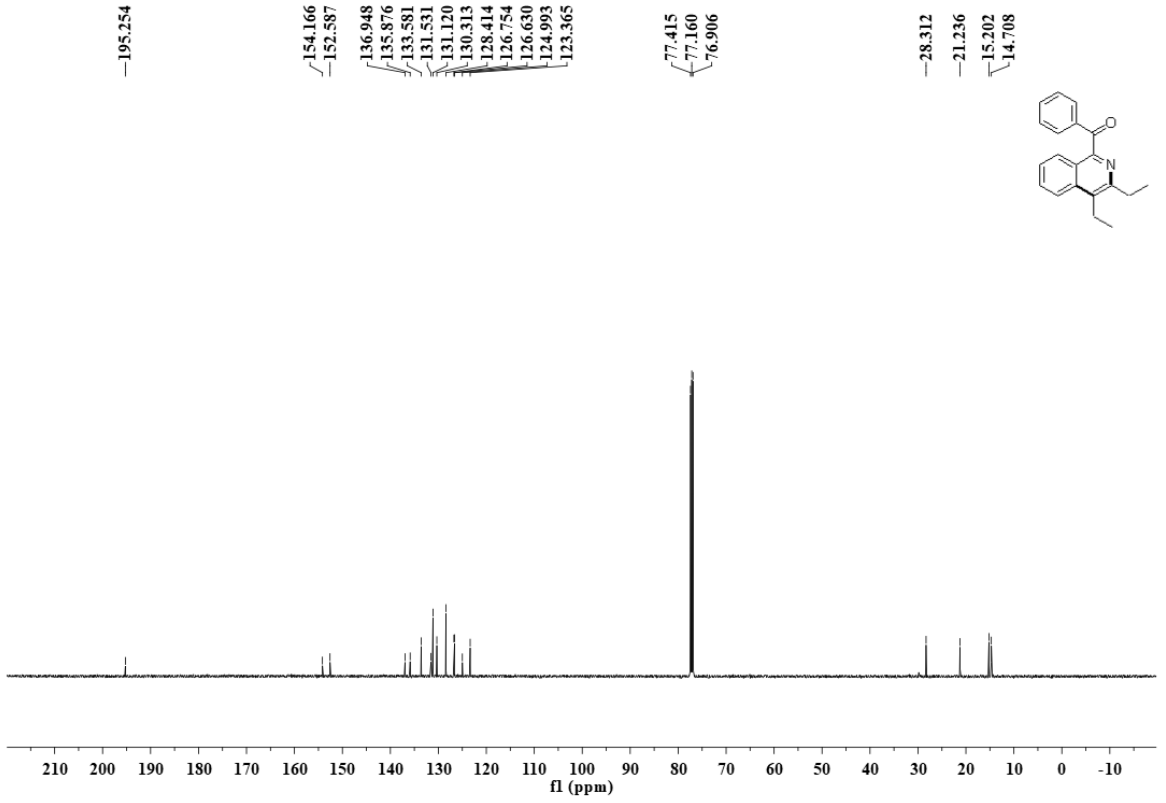
^{13}C NMR (125 MHz, $CDCl_3$) of **7a**



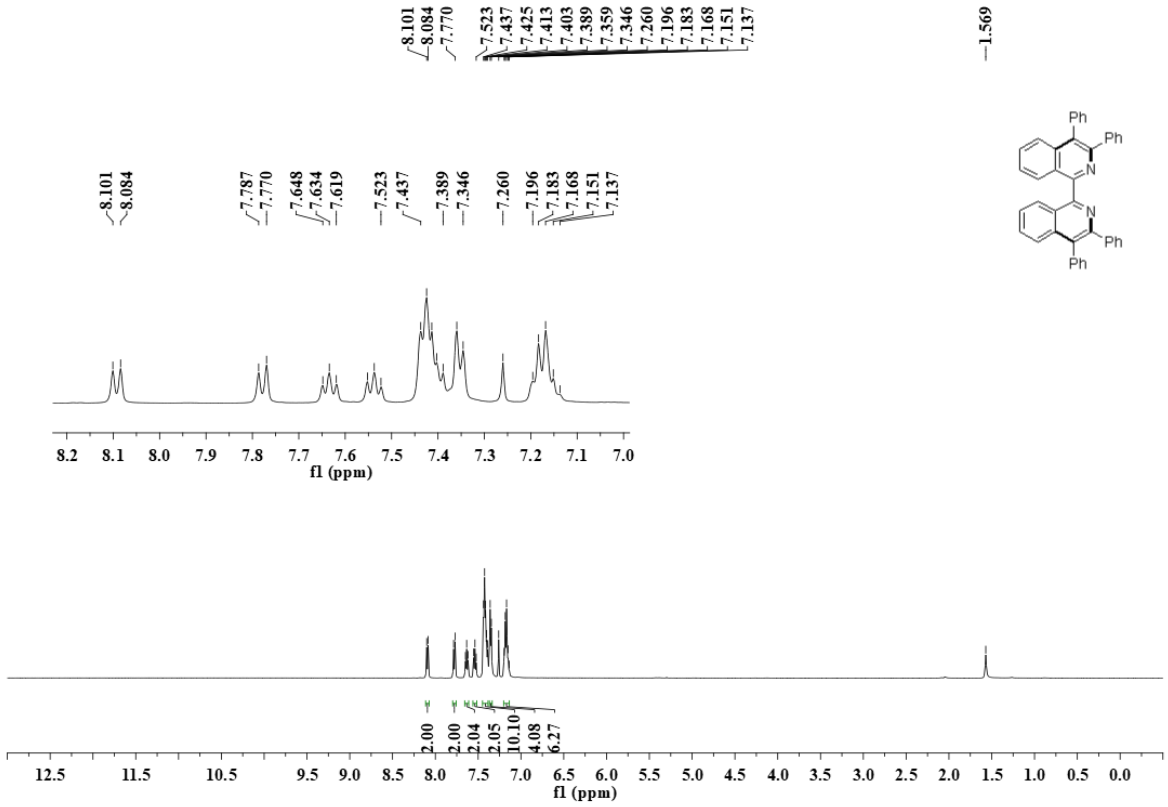
^{1}H NMR (500 MHz, $CDCl_3$) of **7b**



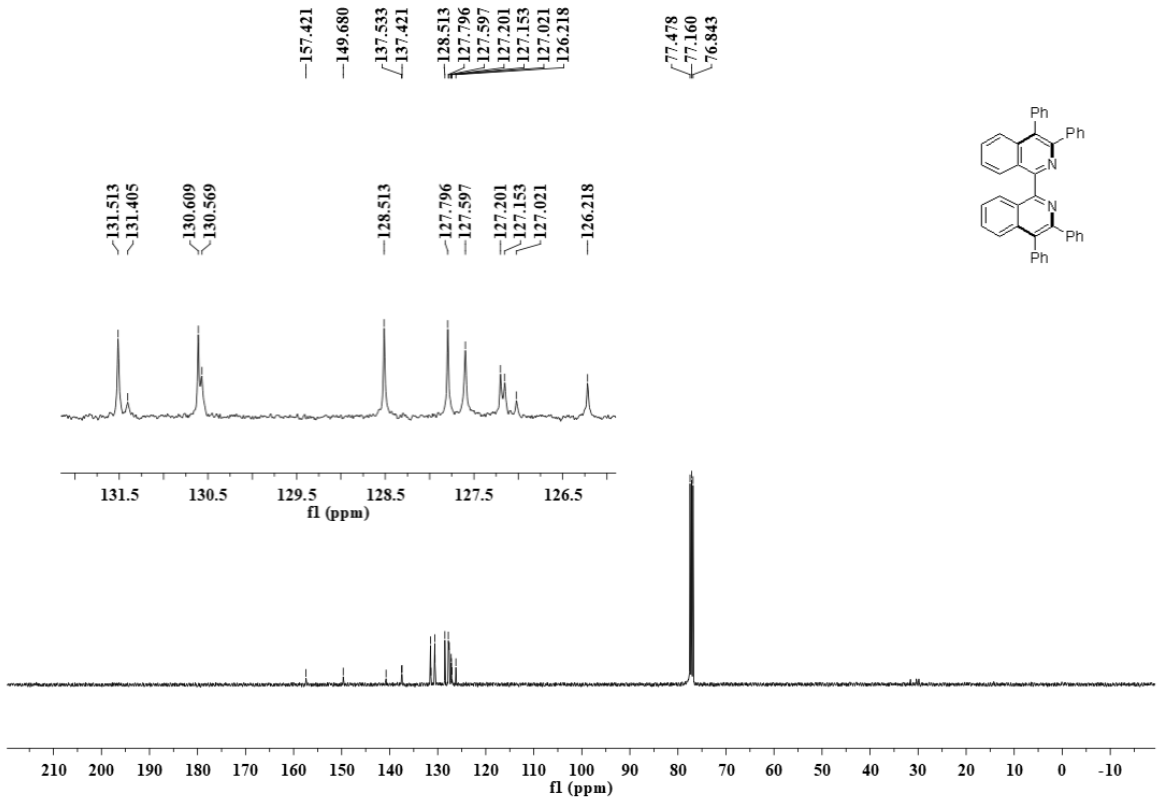
^{13}C NMR (125 MHz, $CDCl_3$) of **7b**



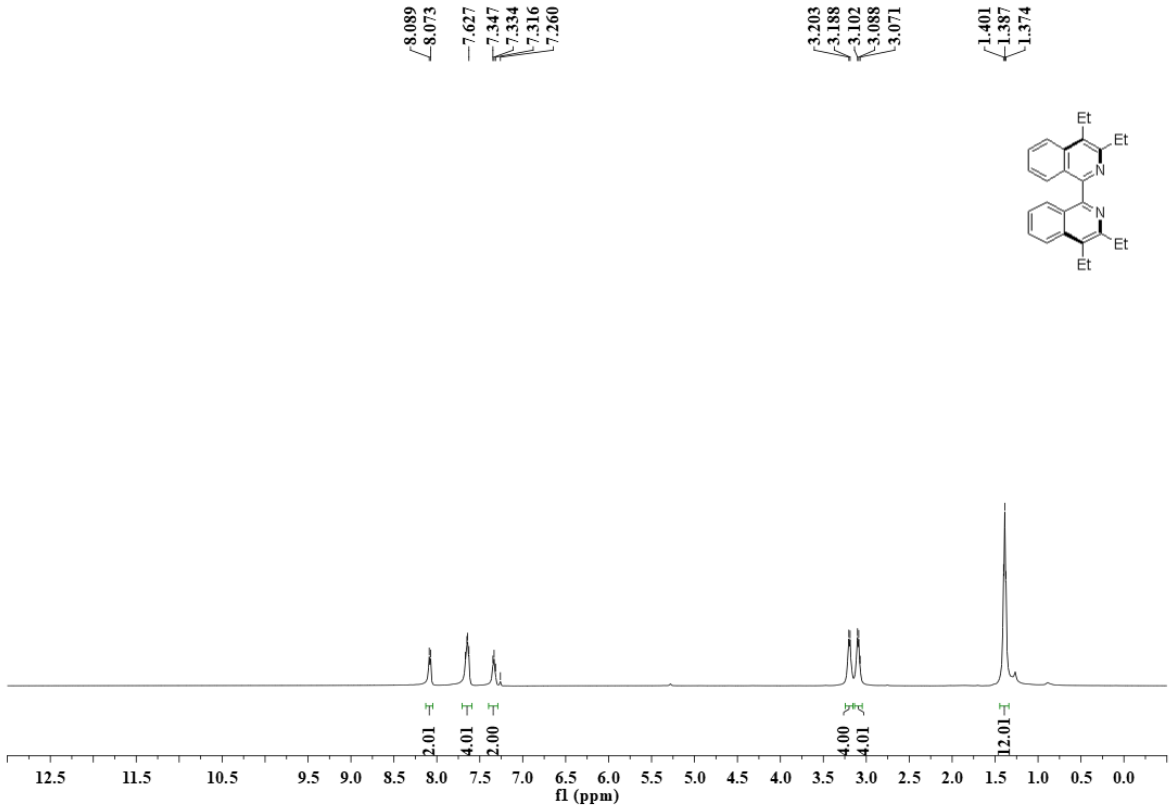
^{1}H NMR (400 MHz, $CDCl_3$) of **8a**



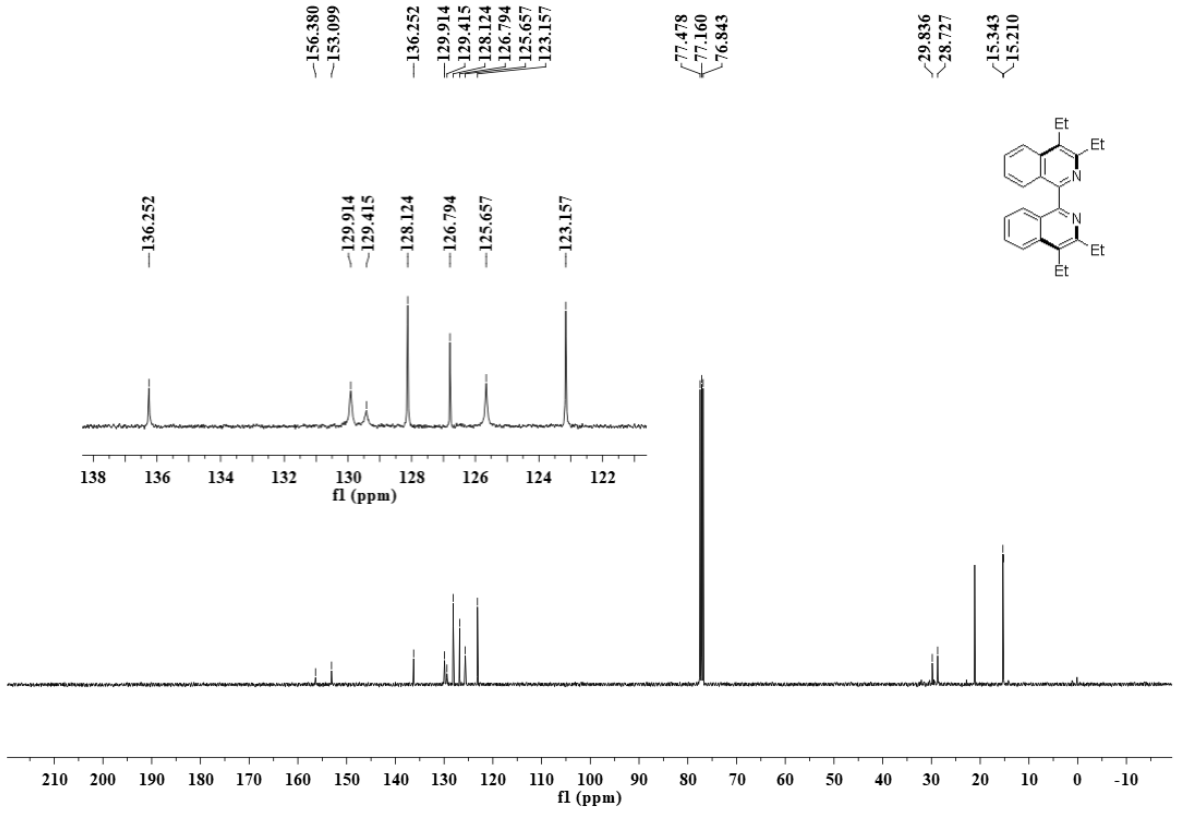
^{13}C NMR (100 MHz, $CDCl_3$) of **8a**



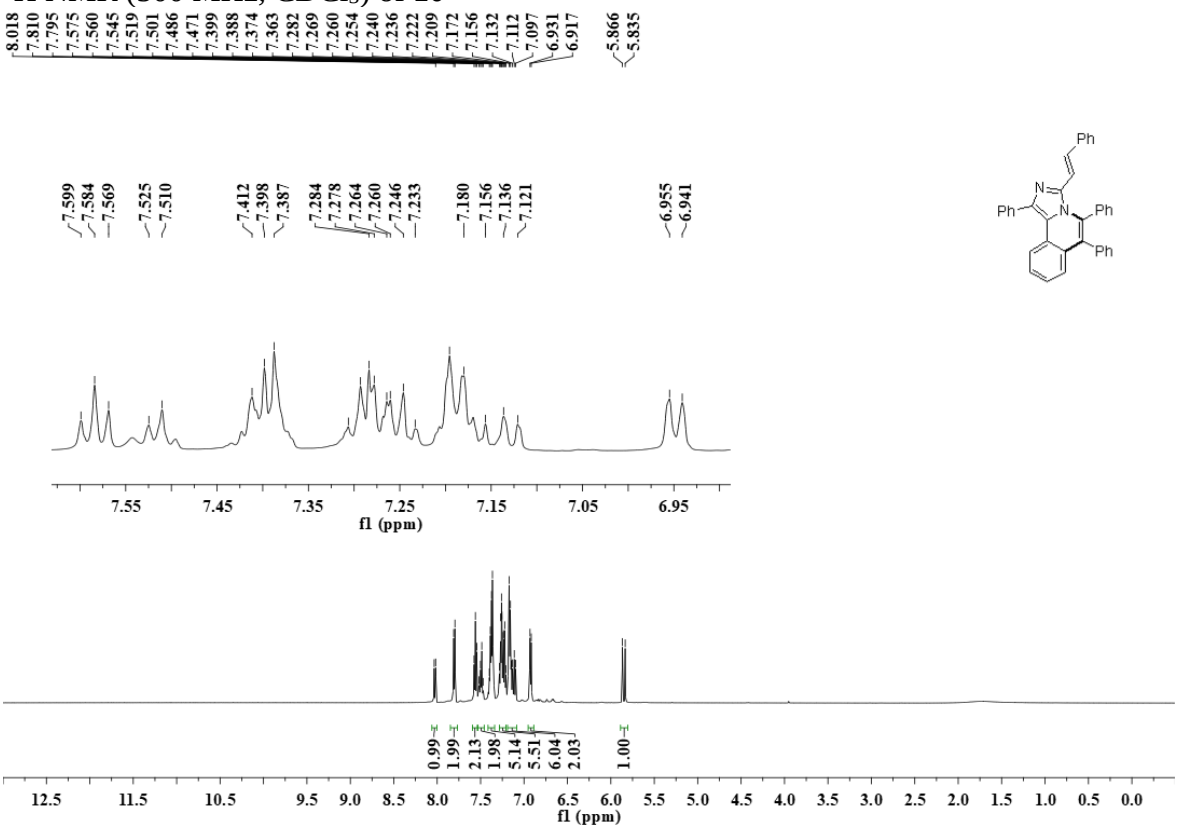
^{1}H NMR (400 MHz, $CDCl_3$) of **8b**



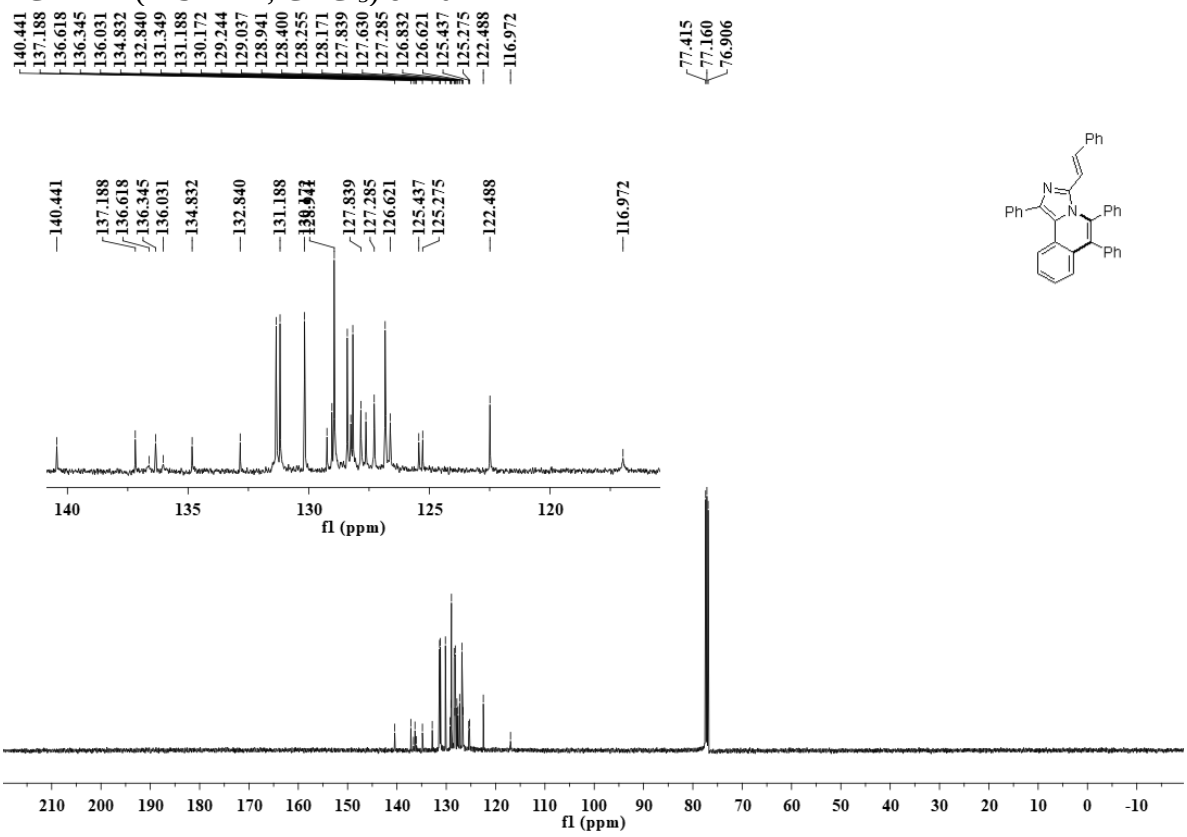
^{13}C NMR (100 MHz, $CDCl_3$) of **8b**



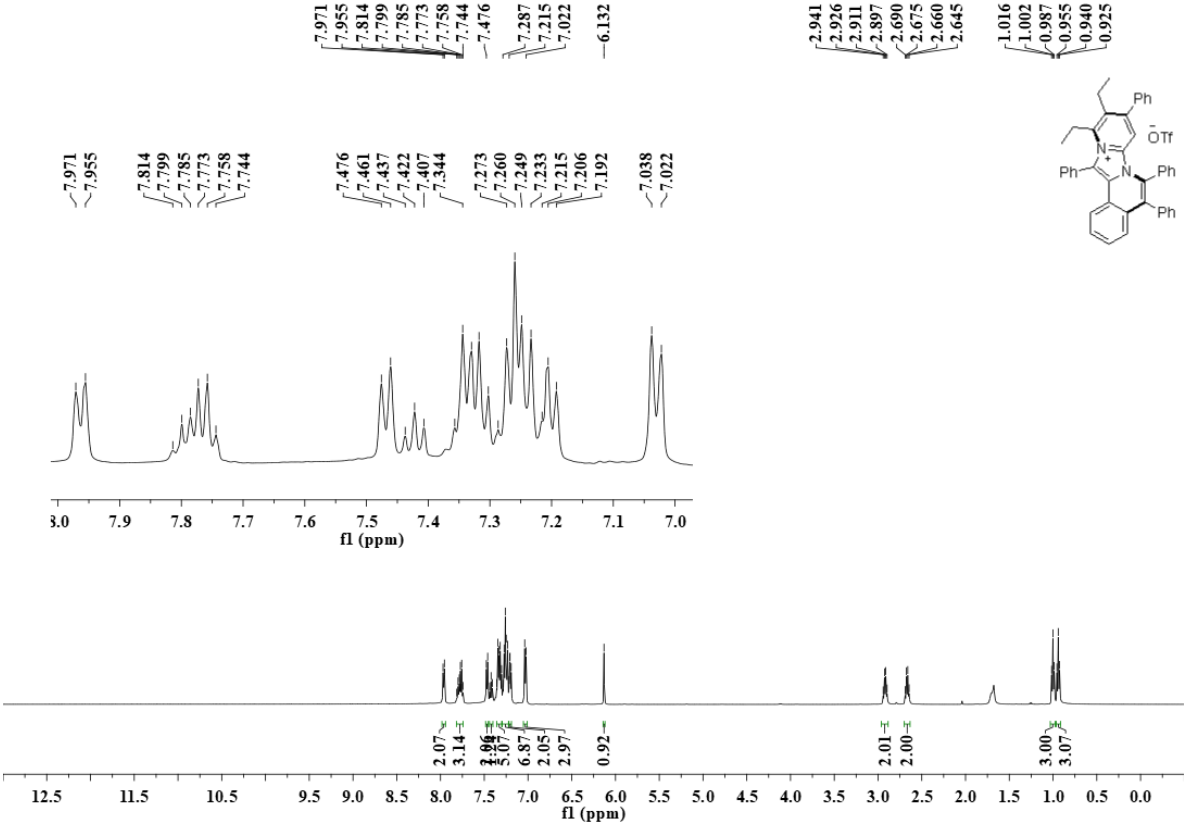
^{1}H NMR (500 MHz, $CDCl_3$) of **10**



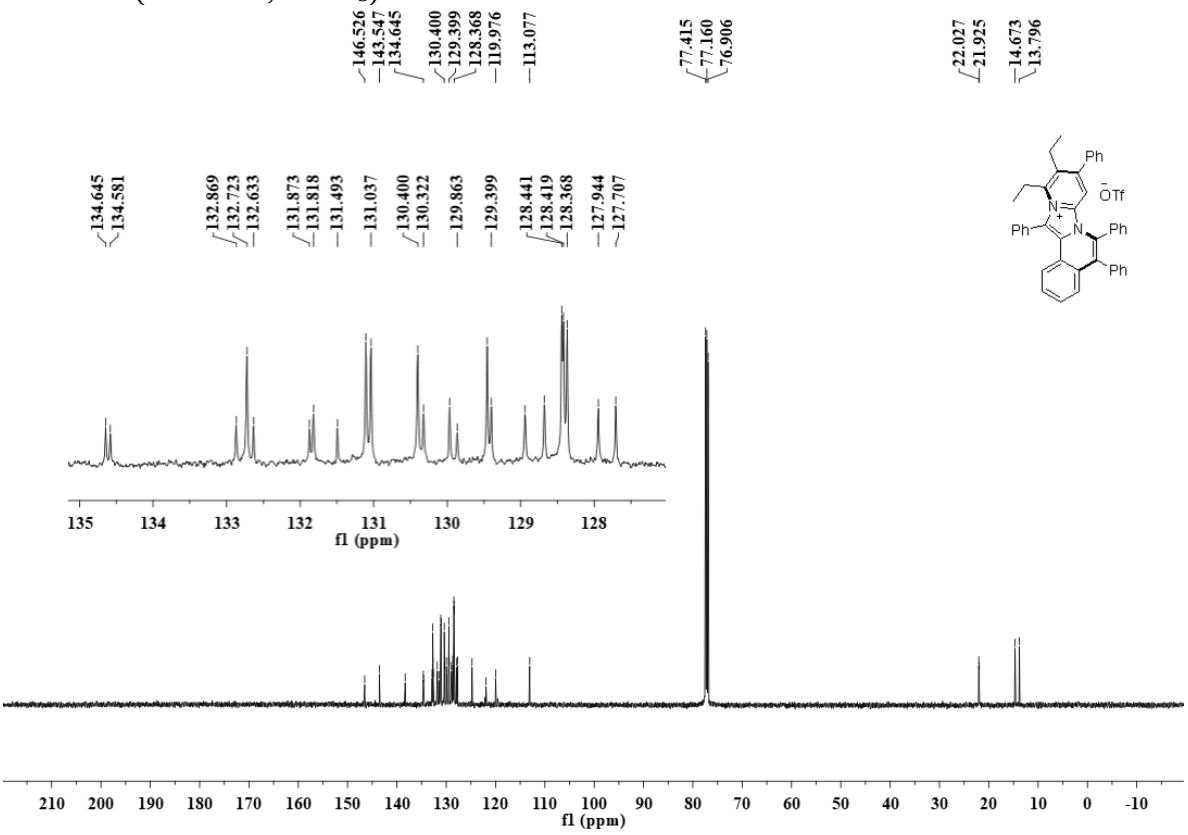
^{13}C NMR (125 MHz, $CDCl_3$) of **10**



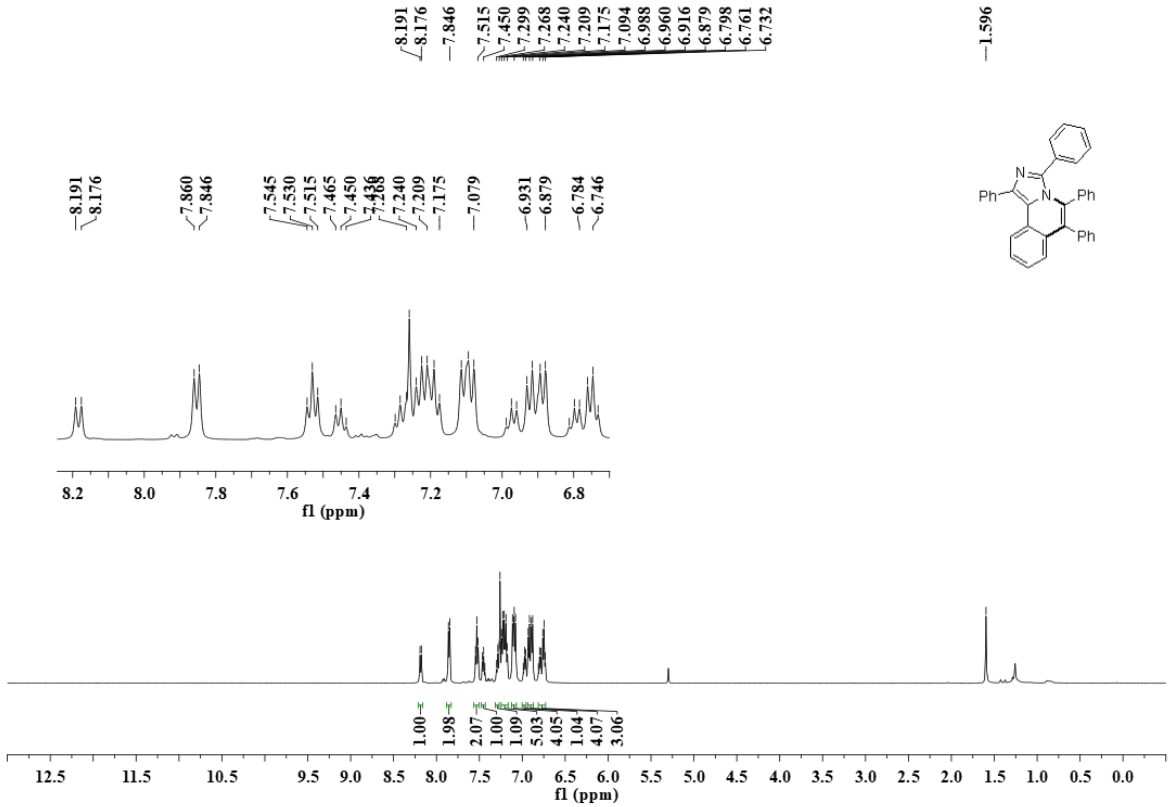
^{1}H NMR (500 MHz, $CDCl_3$) of **11**



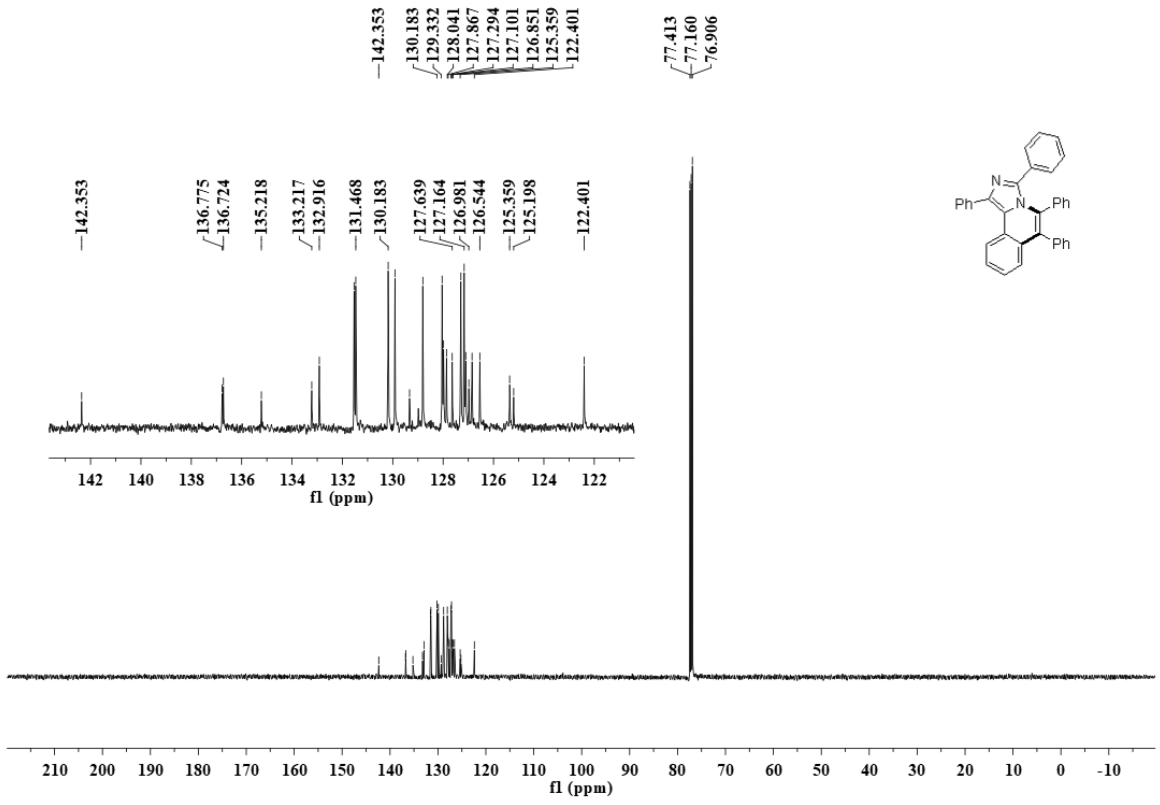
^{13}C NMR (125 MHz, $CDCl_3$) of **11**



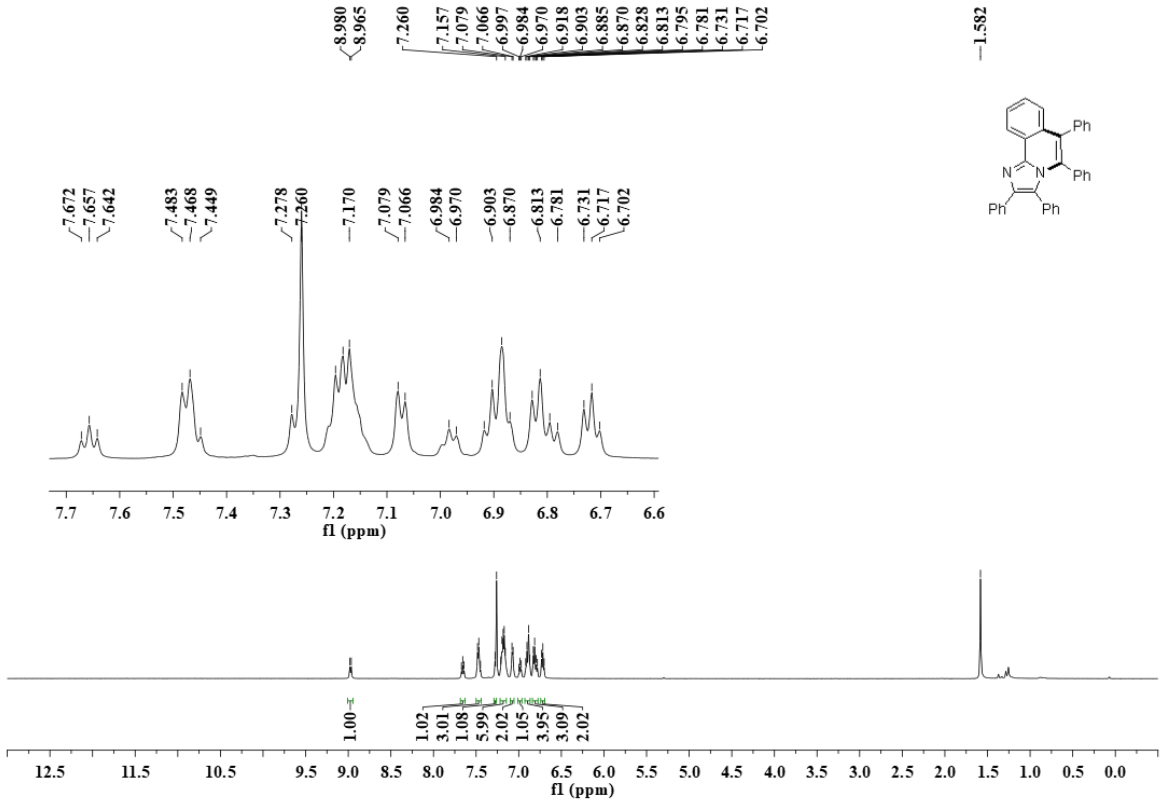
^{1}H NMR (500 MHz, $CDCl_3$) of **13**



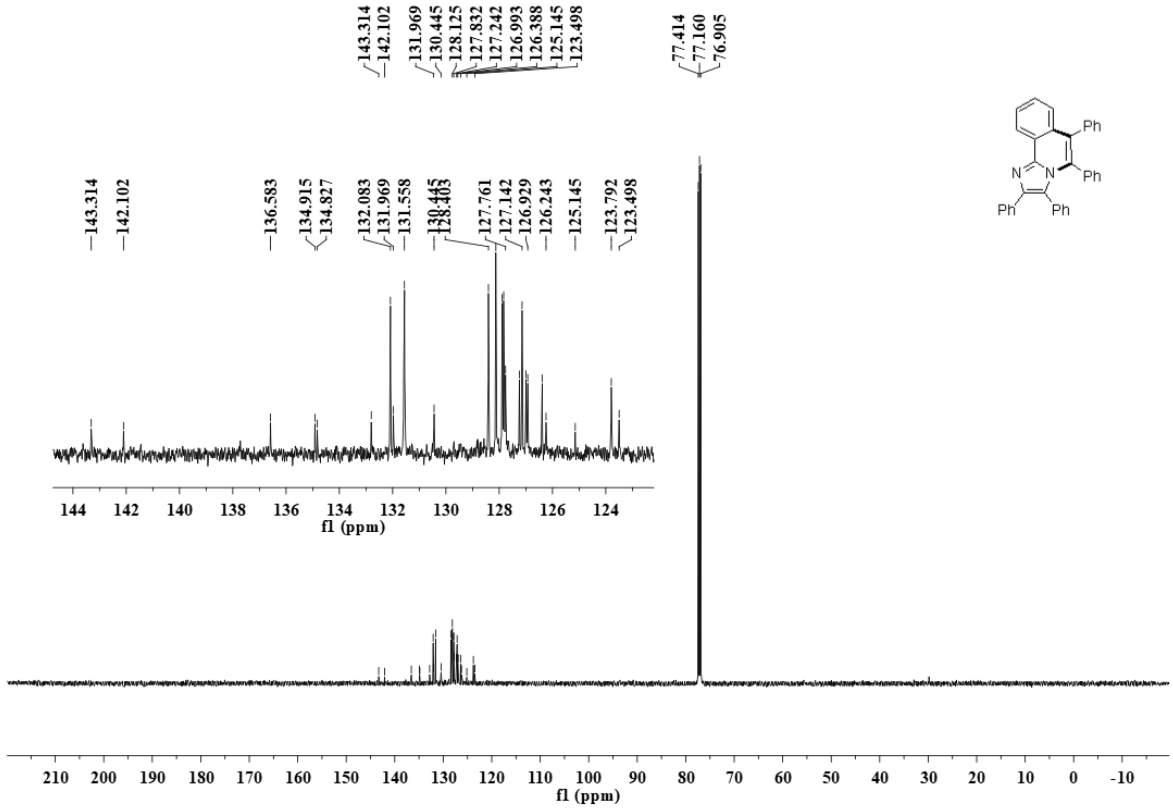
^{13}C NMR (125 MHz, $CDCl_3$) of **13**



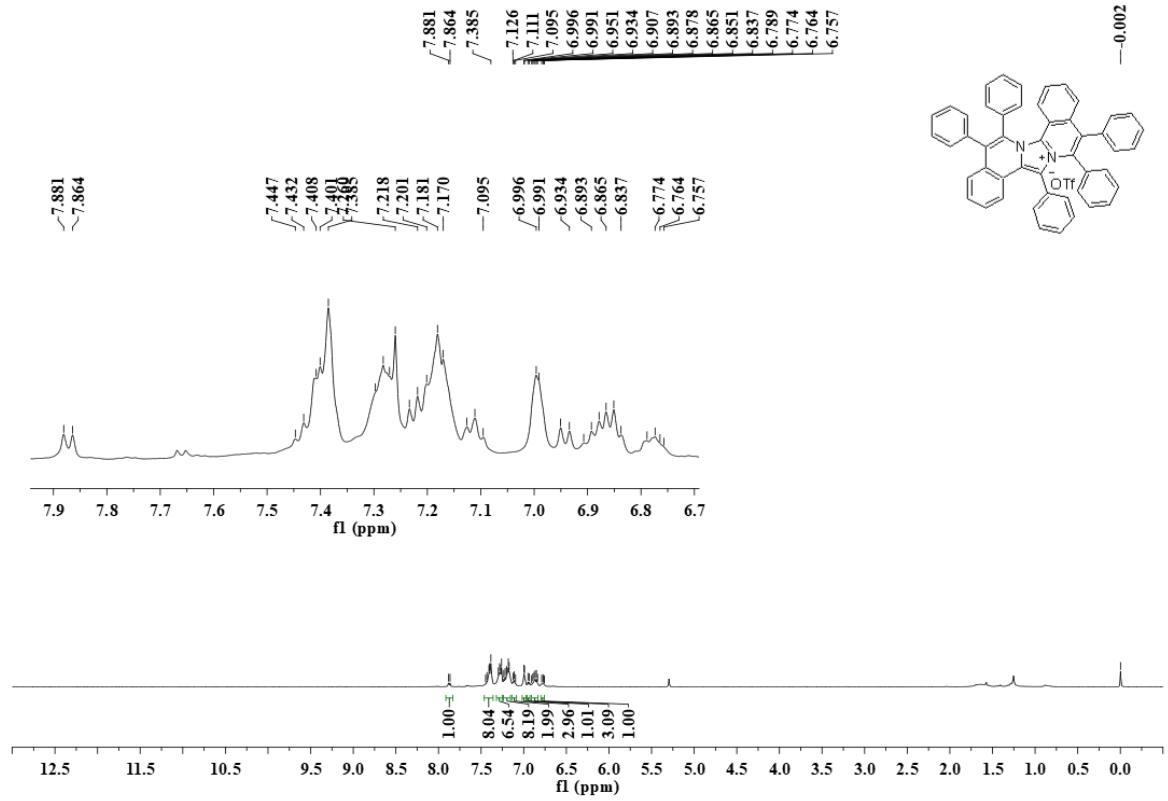
^{1}H NMR (500 MHz, $CDCl_3$) of **13'**



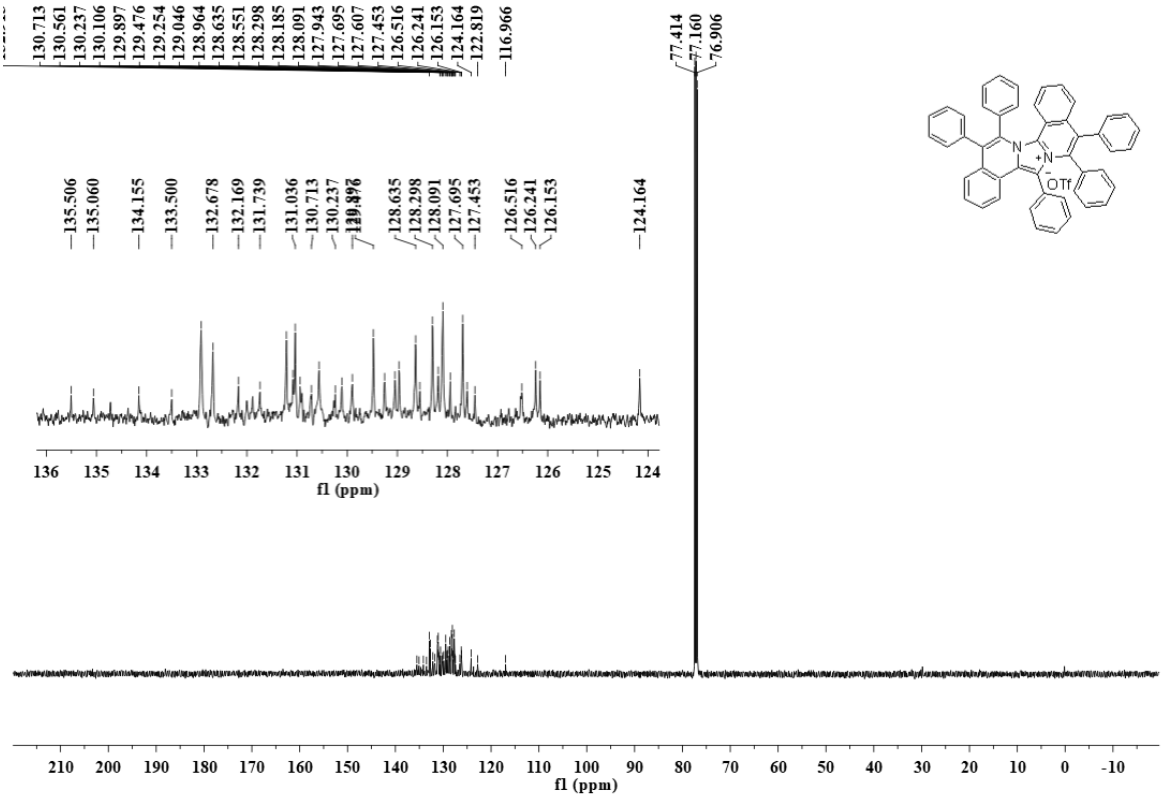
^{13}C NMR (125 MHz, $CDCl_3$) of **13'**



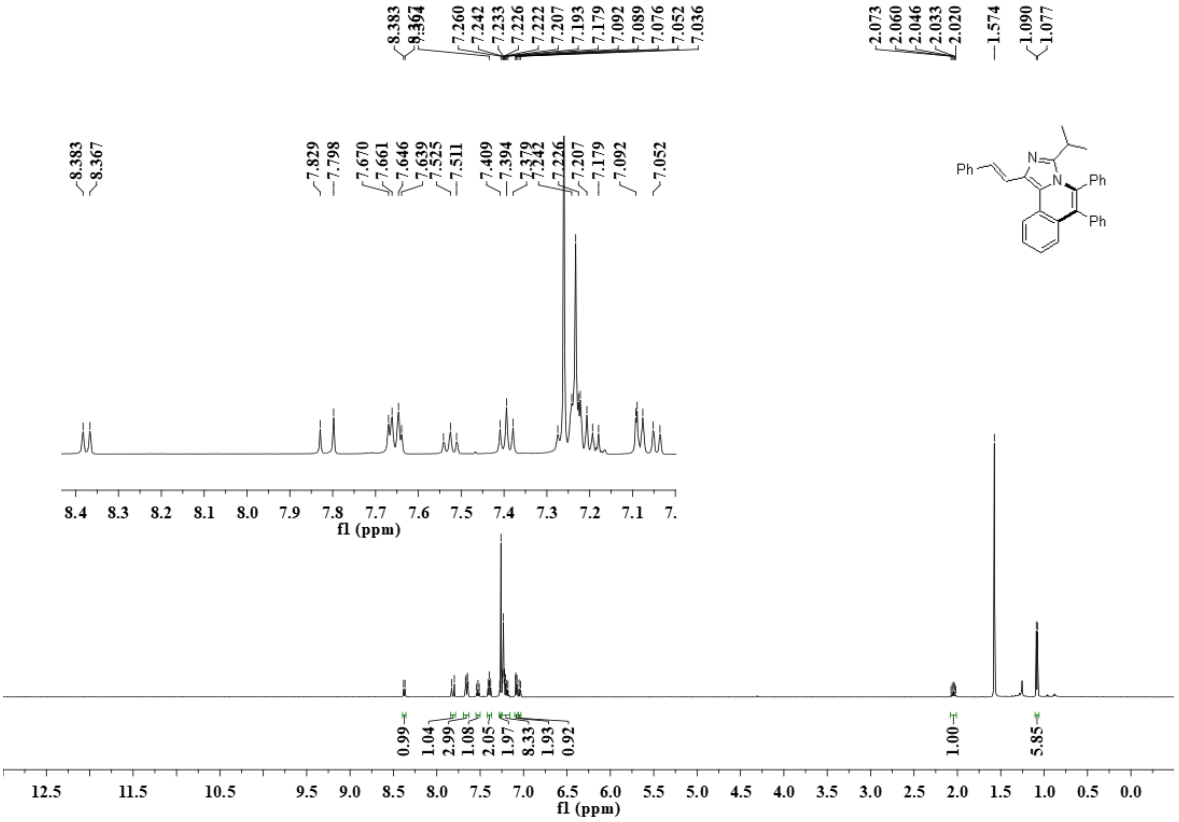
^{1}H NMR (500 MHz, $CDCl_3$) of **14**



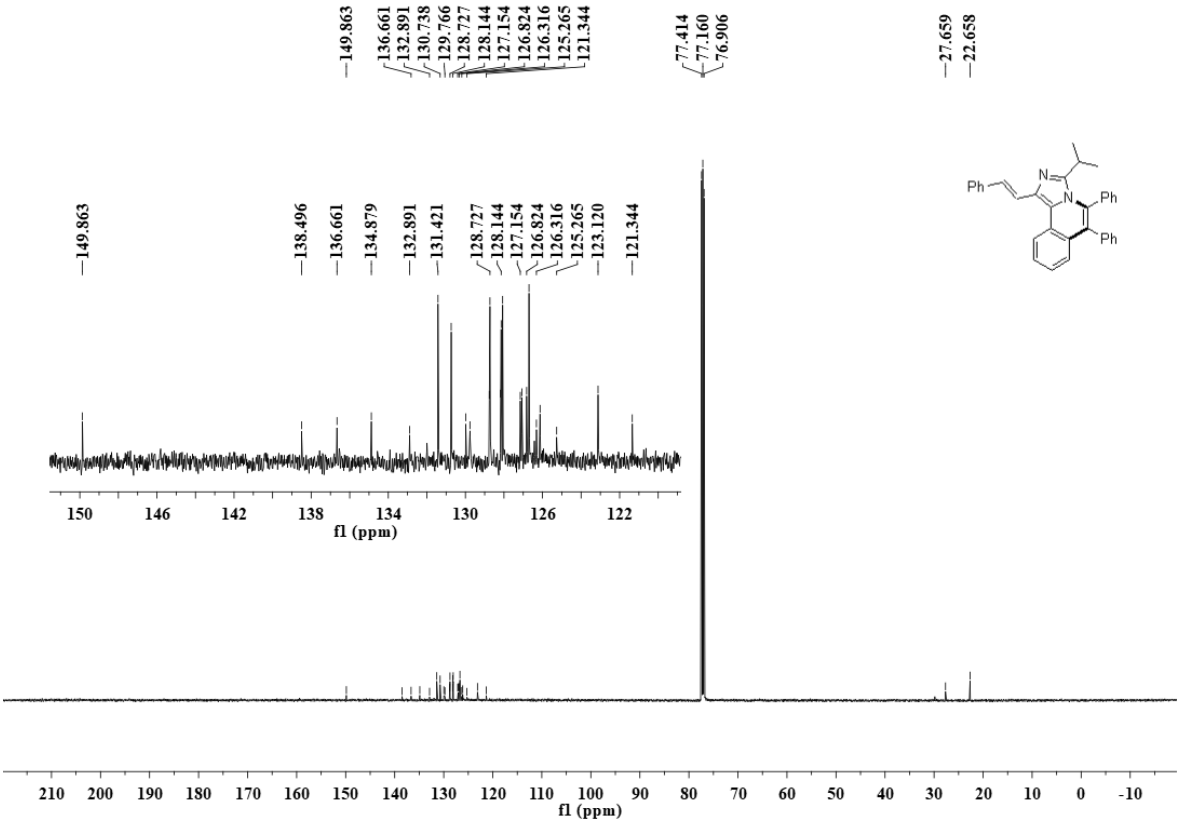
^{13}C NMR (125 MHz, $CDCl_3$) of **14**



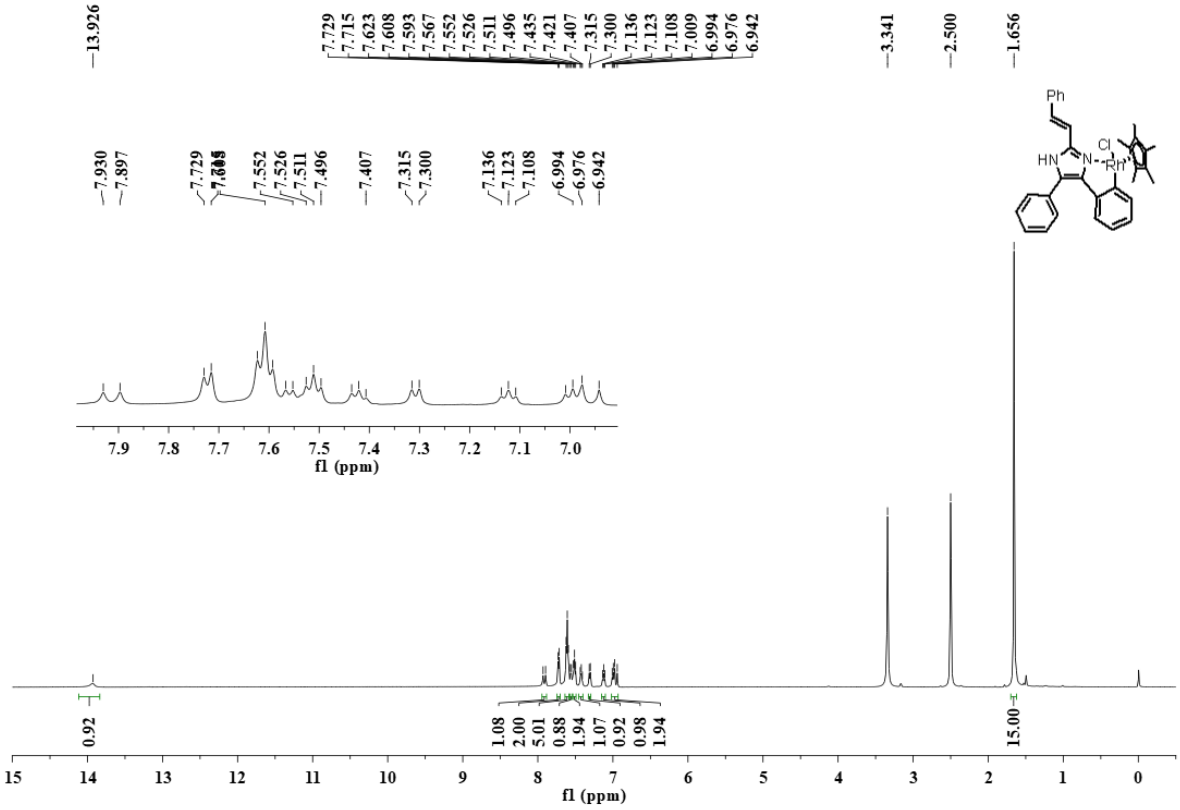
^{1}H NMR (500 MHz, $CDCl_3$) of **16**



^{13}C NMR (125 MHz, $CDCl_3$) of **16**



^{1}H NMR (500 MHz, DMSO-d_6) of **Rh-NH**



^{13}C NMR (125 MHz, DMSO-d_6) of **Rh-NH**