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Three-component synthesis of atropisomeric *N*-naphthyl pyrazoles via Rh(III)-catalyzed cascade pyrazole annulation and Satoh-Miura benzannulation

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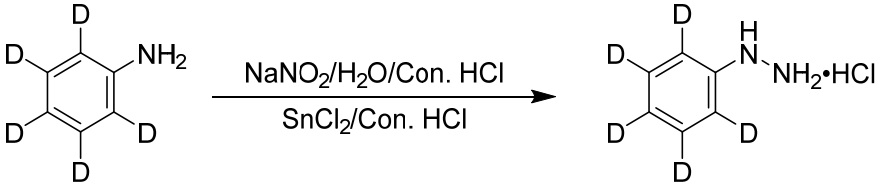
Contents

General experimental information

Enaminones **1**[1] and enaminal **5**[2] were synthesized following literature processes. All other chemicals and solvents used in the experiments were obtained from commercial sources and used directly without further treatment. ^{1}H and ^{13}C NMR spectra were recorded in 400 MHz apparatus and the frequencies for ^{1}H NMR and ^{13}C NMR test are 400 MHz and 100 MHz, respectively. The chemical shifts were reported in ppm with TMS as internal standard. The HMRS data for new compounds were acquired under ESI mode in a mass spectrometer equipped with TOF analyzer. Melting points were rested in an X-4A apparatus without correcting temperature.

The procedures for KIE experiment

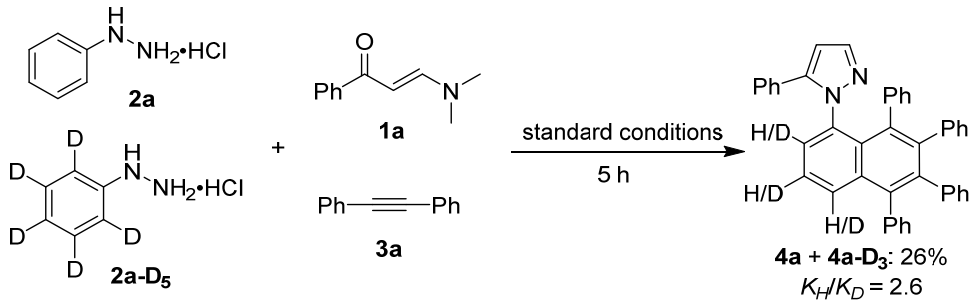
Synthesis of phenylhydrazine hydrochloride-[D5][3]



[D_5]-2a

To a solution of aniline-D_5 (1.0 mmol, 1 equiv) in 10 mL of 20% hydrochloric acid was added the solution of $NaNO_2$ (1.2 mmol, 1.2 equiv) in 2 mL H_2O dropwise with the cooling of ice-water bath. The reaction mixture was stirred at 0 to 5 °C for 1 h and resulted in clear solution. Subsequently, the solution of $SnCl_2$ (2.0 mmol, 2 equiv) in 5 mL of 35% hydrochloric acid was added dropwise at 0 to 5 °C. The mixture was further stirred at room temperature for 2 h. The solid product was filtered, washed with 35% hydrochloric acid for 3 times and dried in vacuum in the presence of anhydrous $CaCl_2$ to provide **[D_5]-2a** for the next reaction.

Intermolecular deuterium kinetic isotope effect measurement



A 1:1 mixture of phenylhydrazine hydrochlorides **2a** (0.22 mmol, 2.2 equiv) and **2a-D$_5$** (0.22 mmol, 2.2 equiv), enaminone **1a** (0.22 mmol, 2.2 equiv), diphenylacetylene **3a** (0.2 mmol, 1.0 × 2 equiv), [Cp*RhCl$_2$]$_2$ (10 mol%), Cu(OAc)$_2$·H$_2$O (0.44 mmol, 4.4 equiv), NaOAc (0.8 mmol, 8 equiv) in DMF (1.0 mL, 0.1 M) under argon. The mixture was then stirred at 110 ℃ with oil bath heating for 5 h. The solvent was removed under vacuo and the crude reaction mixture was poured into water and extracted with ethyl acetate (10 mL × 3). The organic layers were combined and washed with brine. After drying with anhydrous Na$_2$SO$_4$, the solvent was removed under vacuo. The residue was

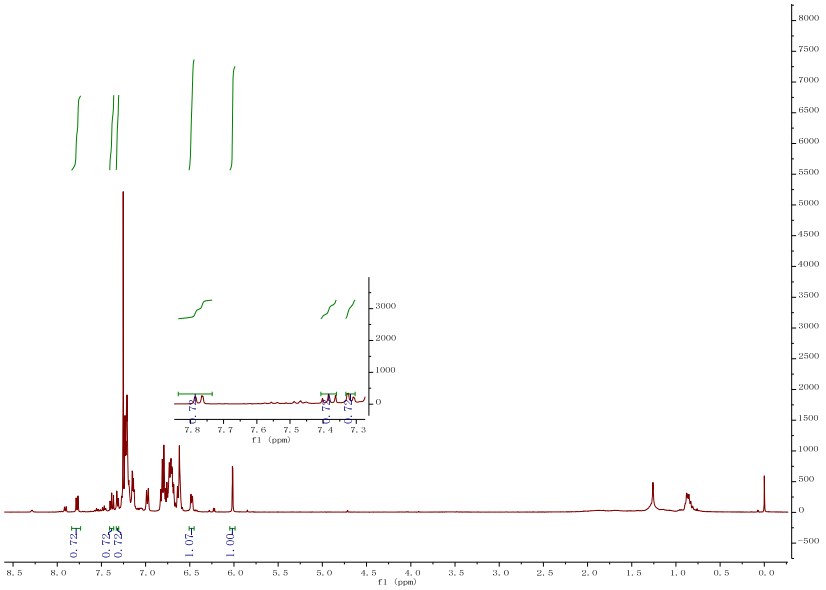


Figure S1 The ^{1}H NMR spectrum of mixed **4a** and **4a-D$_3$**

purified by silica gel column chromatography by using mixed petroleum ether/ethyl acetate (20:1) as the eluant to provide a mixture of **4a** and **4a-D$_4$**. The ratio of **4a** and **4a-D$_4$** was determined to be 2.6 : 1 by ^{1}H NMR analysis (k_H/k_D = 2.6, Figure S1).

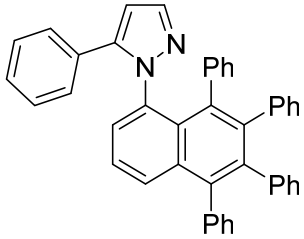
General procedure for the synthesis of 4 and 6

To a 10 mL sealed tube were added enaminone **1** or enaminal **5** (0.22 mmol, 2.2 equiv), hydrazine hydrochloride **2** (0.44 mmol, 4.4 equiv), diphenylacetylene **3** (0.2 mmol, 1.0 × 2 equiv), $[Cp^*RhCl_2]_2$ (0.01 mmol, 10 mol%), $Cu(OAc)_2 \cdot H_2O$ (0.44 mmol, 4.4 equiv), NaOAc (0.8 mmol, 8.0 equiv) and DMF (1.0 mL, 0. 1M) under argon. The mixture was then stirred at 110 ℃ with oil bath heating for 18 h. Upon completion, the reaction mixture was allowed to cool down to room temperature. After adding 10 mL of water, the resulting mixture was extracted with ethyl acetate (10 mL × 3). Then the organic layers were combined, washed by 5 mL brine, and dried over anhydrous Na_2SO_4. After filtration, the solvent in the acquired solution was removed under reduced pressure. The residue was subjected to flash silica gel column chromatography to provide pure products with the elution of mixed petroleum ether/ethyl acetate (v /v = 20:1-3:1).

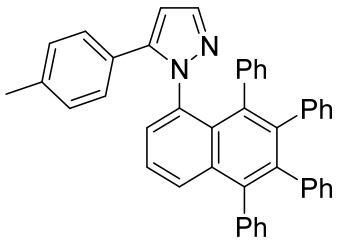
Procedure for the 1 mmol-scale synthesis of 4a

To a 100 mL sealed tube were added enaminone **1a** (2.2 mmol. 2.2 equiv), hyrazine **2a** (4.4 mmol, 4.4 equiv), diphenylacetylene **3a** (2.0 mmol, 1.0 equiv × 2), $[Cp^*RhCl_2]_2$ (10 mol%), $Cu(OAc)_2 \cdot H_2O$ (4.4 mmol, 4.4 equiv), NaOAc (8.0 mmol, 8 equiv) and DMF (10 mL, 0.1 M) under argon. The mixture was then stirred at 110 ℃ with oil bath heating for 18 h. After being cooled down to room temperature, 30 mL of water was added, and the resulting mixture was extracted with ethyl acetate (30 mL × 3). The organic layers were combined, washed by 15 mL brine, and dried over Na_2SO_4. After filtration, the solvent in the acquired solution was removed under reduced pressure. The residue was subjected to flash silica gel column chromatography to provide pure product **4a** (241.0 mg, 42%) with the elution of mixed petroleum ether/ethyl acetate (v /v = 20:1).

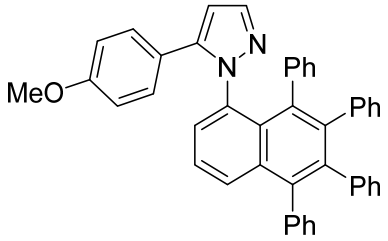
Characterization data of products 4 and 6



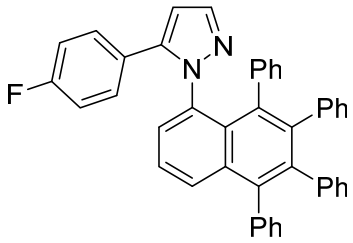
5-Phenyl-1-(5,6,7,8-tetraphenylnaphthalen-1-yl)-1*H*-pyrazole (**4a**). Eluent: V_{PET}/V_{EA} = 20:1; yellow solid (41.5 mg, 72% yield); mp 181-183 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 5.4 Hz, 4H), 7.14 (d, *J* = 5.4 Hz, 2H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.85 – 6.67 (m, 10H), 6.61 (q, *J* = 8.5, 7.3 Hz, 3H), 6.48 (d, *J* = 6.6 Hz, 1H), 6.01 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 139.8, 139.7, 139.7, 138.8, 138.6, 137.5, 136.3, 134.4, 131.7, 131.4, 131.1, 131.1, 131.0, 130.9, 130.1, 129.2, 128.9, 128.2, 128.0, 127.8, 127.7, 127.6, 127.4, 126.6, 126.6, 126.4, 126.2, 126.1, 125.4, 125.4, 125.2, 125.0, 124.9, 106.1; ESI-HRMS Calcd for $C_{43}H_{31}N_2$ $[M + H]^+$ 575.2482, found 575.2466.



1-(5,6,7,8-Tetraphenylnaphthalen-1-yl)-5-(p-tolyl)-1*H*-pyrazole (**4b**). Eluent: V_{PET}/V_{EA} = 20:1; white solid (43.6 mg, 74% yield); mp 226-228 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.6 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 14.8 Hz, 3H), 7.20 (d, *J* = 11.3 Hz, 3H), 7.04 (q, *J* = 8.0 Hz, 4H), 6.97 (d, *J* = 7.8 Hz, 1H), 6.79 (d, *J* = 6.4 Hz, 4H), 6.74 (dd, *J* = 11.4, 5.9 Hz, 4H), 6.70 – 6.58 (m, 6H), 6.49 (d, *J* = 6.7 Hz, 1H), 5.97 (s, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 142.5, 140.4, 140.3, 139.7, 139.7, 139.6, 138.7, 138.7, 137.3, 136.4, 134.4, 131.7, 131.5, 131.1, 131.1, 131.0, 131.0, 130.9, 130.1, 129.2, 128.9, 128.8, 128.2, 127.7, 127.6, 127.6, 127.3, 126.6, 126.6, 126.4, 126.2, 126.0, 126.0, 125.4, 125.3, 125.1, 125.0, 124.9, 105.7, 21.2; ESI-HRMS Calcd for $C_{44}H_{33}N_2$ $[M + H]^+$ 589.2638, found 589.2642.

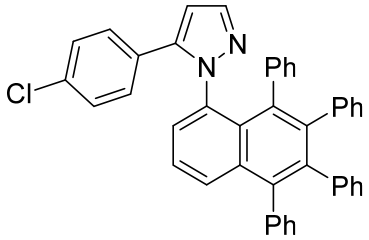


5-(4-Methoxyphenyl)-1-(5,6,7,8-tetraphenylnaphthalen-1-yl)-1*H*-pyrazole (**4c**). Eluent: V_{PET}/V_{EA} = 10:1; yellow solid (48.2 mg, 80% yield); mp 222-224 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.37 (dd, *J* = 8.5, 7.2 Hz, 1H), 7.30 (dd, *J* = 7.2, 1.5 Hz, 1H), 7.23 (q, *J* = 1.4 Hz, 2H), 7.21 – 7.20 (m, 1H), 7.18 (dd, *J* = 4.8, 1.9 Hz, 2H), 7.09 (d, *J* = 2.1 Hz, 1H), 7.07 (d, *J* = 2.2 Hz, 1H), 6.96 (dq, *J* = 7.7, 1.3 Hz, 1H), 6.80 (ddd, *J* = 6.0, 2.7, 1.6 Hz, 3H), 6.78 – 6.73 (m, 5H), 6.72 – 6.67 (m, 4H), 6.63 (dddd, *J* = 7.0, 5.7, 3.6, 1.6 Hz, 3H), 6.49 (dt, *J* = 7.3, 2.0 Hz, 1H), 5.91 (d, *J* = 1.9 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 143.3, 142.5, 140.3, 140.3, 139.7, 139.7, 138.7, 138.6, 137.6, 136.3, 134.4, 131.7, 131.4, 131.1, 131.1, 131.0, 130.9, 130.1, 129.2, 128.9, 128.2, 127.6, 127.5, 126.6, 126.6, 126.4, 126.2, 126.0, 125.4, 125.3, 125.1, 124.9, 124.9, 113.5, 105.3, 55.2; ESI-HRMS Calcd for $C_{44}H_{33}N_2O$ $[M + H]^+$ 605.2587, found 605.2595.

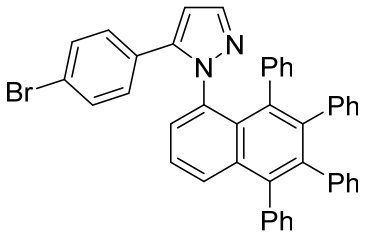


5-(4-Fluorophenyl)-1-(5,6,7,8-tetraphenylnaphthalen-1-yl)-1*H*-pyrazole (**4d**). Eluent: V_{PET}/V_{EA} = 20:1; yellow solid (44.8 mg, 76% yield); mp 196-198 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 7.1 Hz, 1H), 7.25 – 7.22 (m, 3H), 7.22 – 7.15 (m, 3H), 7.09 (dd, *J* = 8.5, 5.3 Hz, 2H), 6.97 (d, *J* = 7.8 Hz, 1H), 6.90 (t, *J* = 8.5 Hz, 2H), 6.84 – 6.76 (m, 5H), 6.74 – 6.67 (m, 5H), 6.61 (t, *J* = 7.4 Hz, 2H), 6.55 (d, *J* = 7.6 Hz, 1H), 6.51 – 6.44 (m, 1H), 5.95 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (d, *J* = 248.1 Hz), 142.6 (d, *J* = 10.0 Hz), 140.2, 140.2, 139.9, 139.7, 139.6, 138.8, 138.5, 137.2, 136.1, 134.4, 131.6, 131.4, 131.1, 131.0, 131.0, 130.9, 130.9, 130.0, 129.6, 129.5, 129.4, 128.9, 128.1, 127.7, 127.6, 126.7,

126.6, 126.5, 126.3 (d, J = 3.5 Hz), 126.3, 126.2, 126.1, 125.4, 125.2, 125.0, 124.9, 115.0 (d, J = 21.6 Hz), 106.0; ESI-HRMS Calcd for $C_{43}H_{30}FN_2$ $[M + H]^+$ 593.2388, found 593.2397.

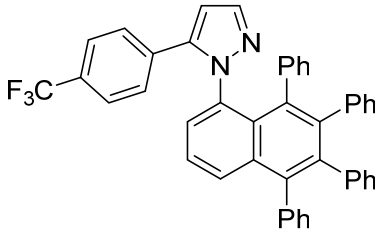


5-(4-Chlorophenyl)-1-(5,6,7,8-tetraphenylnaphthalen-1-yl)-1*H*-pyrazole (**4e**). Eluent: V_{PET}/V_{EA} = 20:1; yellow solid (50.0 mg, 82% yield); mp 248-250 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, J = 8.5, 1.4 Hz, 1H), 7.39 (dd, J = 8.5, 7.2 Hz, 1H), 7.30 (dd, J = 7.3, 1.4 Hz, 1H), 7.25 – 7.15 (m, 8H), 7.05 (d, J = 8.6 Hz, 2H), 6.96 (d, J = 7.6 Hz, 1H), 6.80 (tt, J = 7.1, 3.0 Hz, 5H), 6.70 (dtd, J = 6.3, 4.6, 3.7, 2.0 Hz, 5H), 6.64 – 6.57 (m, 2H), 6.55 (d, J = 7.6 Hz, 1H), 6.50 (tt, J = 4.7, 2.4 Hz, 1H), 5.97 (d, J = 1.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 142.3, 140.2, 140.2, 140.0, 139.8, 139.5, 138.9, 138.5, 137.2, 136.1, 134.4, 133.4, 131.6, 131.4, 131.1, 131.0, 131.0, 130.9, 130.0, 129.5, 129.0, 128.9, 128.6, 128.3, 128.0, 127.7, 127.6, 126.7, 126.6, 126.5, 126.2, 126.2, 126.1, 125.4, 125.2, 125.0, 124.9, 106.2; ESI-HRMS Calcd for $C_{43}H_{30}ClN_2$ $[M + H]^+$609.2092, found 609.2098.

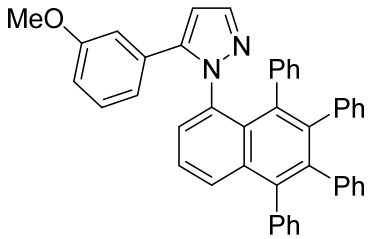


5-(4-Bromophenyl)-1-(5,6,7,8-tetraphenylnaphthalen-1-yl)-1*H*-pyrazole (**4f**). Eluent: V_{PET}/V_{EA} = 20:1; yellow solid (43.8 mg, 67% yield); mp 252-254 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, J = 8.5, 1.4 Hz, 1H), 7.40 (d, J = 7.6 Hz, 1H), 7.35 – 7.29 (m, 3H), 7.23 – 7.15 (m, 5H), 6.97 (t, J = 8.3 Hz, 3H), 6.83 – 6.77 (m, 5H), 6.70 (ddt, J = 7.7, 4.9, 2.4 Hz, 6H), 6.64 – 6.59 (m, 2H), 6.56 – 6.49 (m, 2H), 5.98 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 142.3, 140.2, 140.1, 140.0, 139.8, 139.5, 138.9, 138.5, 137.2, 136.1, 134.4, 131.6, 131.4, 131.2, 131.1, 131.0, 131.0, 130.9,

130.0, 129.5, 129.2, 129.1, 129.0, 128.9, 128.3, 128.0, 127.8, 127.7, 127.6, 126.7, 126.6, 126.5, 126.2, 126.2, 126.1, 125.4, 125.4, 125.2, 125.0, 124.9, 121.6, 106.2; ESI-HRMS Calcd for $C_{43}H_{30}BrN_2$ $[M + H]^+$ 653.1587, found 653.1600.

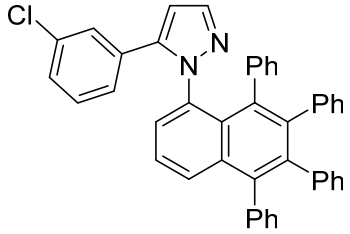


1-(5,6,7,8-Tetraphenylnaphthalen-1-yl)-5-(4-(trifluoromethyl)phenyl)-1*H*-pyrazole (**4g**). Eluent: V_{PET}/V_{EA} = 20:1; yellow solid (35.3 mg, 55% yield); mp 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.40 (dd, *J* = 8.5, 7.2 Hz, 1H), 7.31 (dd, *J* = 7.2, 1.4 Hz, 1H), 7.27 (s, 1H), 7.25 – 7.21 (m, 5H), 7.18 (td, *J* = 4.9, 2.4 Hz, 2H), 6.96 (d, *J* = 7.9 Hz, 1H), 6.84 – 6.80 (m, 2H), 6.80 – 6.75 (m, 3H), 6.70 (qd, *J* = 6.1, 2.2 Hz, 5H), 6.64 – 6.56 (m, 2H), 6.55 – 6.51 (m, 1H), 6.48 (dq, *J* = 6.8, 2.6, 2.0 Hz, 1H), 6.07 (d, *J* = 1.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 141.9, 140.2, 140.1, 140.0, 139.9, 139.5, 138.9, 138.5, 137.2, 136.0, 134.4, 133.5, 131.6, 131.3, 131.1, 131.0 (d, *J* = 1.7 Hz), 130.9, 129.9, 129.6, 129.2 (d, *J* = 32.5 Hz), 128.9, 128.0, 127.8, 127.7, 127.6, 126.7, 126.6, 126.5, 126.3, 126.1, 125.4 (d, *J* = 1.7 Hz), 125.3, 125.1, 125.0, 125.0, 124.9, 122.7, 106.9; ESI-HRMS Calcd for $C_{44}H_{30}F_3N_2$ $[M + H]^+$ 643.2356, found 643.2361.

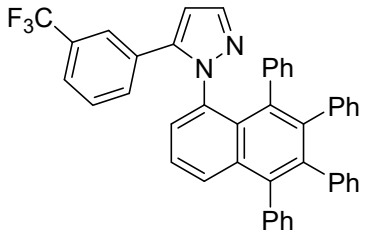


5-(3-Methoxyphenyl)-1-(5,6,7,8-tetraphenylnaphthalen-1-yl)-1*H*-pyrazole (**4h**). Eluent: V_{PET}/V_{EA} = 10:1; yellow liquid (38.7 mg, 64% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dt, *J* = 8.2, 1.5 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.36 (dt, *J* = 7.3, 1.5 Hz, 1H), 7.25 – 7.16 (m, 6H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.98 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.83 – 6.76 (m, 5H), 6.75 – 6.66 (m, 6H), 6.63 – 6.55 (m, 4H), 6.52 – 6.47 (m, 1H), 6.00 (t, *J* = 1.5 Hz, 1H), 3.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)

δ 159.1, 143.4, 142.5, 140.3, 140.2, 139.8, 139.7, 139.6, 138.7, 138.4, 137.6, 136.3, 134.3, 131.7, 131.4, 131.4, 131.1, 131.0, 131.0, 130.9, 130.1, 129.2, 129.1, 129.0, 128.3, 127.7, 127.5, 126.6, 126.6, 126.4, 126.2, 126.1, 125.5, 125.4, 125.2, 125.0, 125.0, 120.6, 113.5, 112.7, 106.2, 55.0; ESI-HRMS Calcd for $C_{44}H_{33}N_2O$ $[M + H]^+$ 605.2587, found 605.2589.

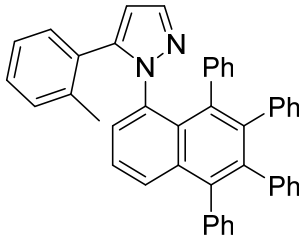


5-(3-Chlorophenyl)-1-(5,6,7,8-tetraphenylnaphthalen-1-yl)-1*H*-pyrazole (**4i**). Eluent: V_{PET}/V_{EA} = 20:1; yellow liquid (40.9 mg, 67% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.42 (dd, *J* = 8.5, 7.2 Hz, 1H), 7.36 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.27 (t, *J* = 1.4 Hz, 1H), 7.21 (dq, *J* = 8.2, 2.1 Hz, 3H), 7.19 – 7.11 (m, 3H), 6.98 (ddt, *J* = 8.8, 5.7, 1.6 Hz, 3H), 6.90 – 6.74 (m, 6H), 6.74 – 6.66 (m, 5H), 6.63 – 6.56 (m, 2H), 6.49 (tt, *J* = 6.1, 1.9 Hz, 2H), 6.00 (d, *J* = 1.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 142.1, 140.2, 140.1, 139.9, 139.8, 139.5, 138.8, 138.4, 137.1, 135.9, 134.3, 133.9, 131.8, 131.6, 131.3, 131.3, 131.1, 130.9, 130.0, 129.4, 129.2, 128.8, 128.1, 127.8, 127.7, 127.5, 127.4, 126.7, 126.5, 126.5, 126.3, 126.3, 126.1, 125.9, 125.4, 125.4, 125.3, 125.0, 124.9, 106.5; ESI-HRMS Calcd for $C_{43}H_{30}ClN_2$ $[M + H]^+$ 609.2092, found 609.2102.

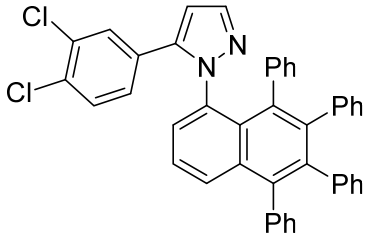


1-(5,6,7,8-Tetraphenylnaphthalen-1-yl)-5-(3-(trifluoromethyl)phenyl)-1*H*-pyrazole (**4j**). Eluent: V_{PET}/V_{EA} = 20:1; yellow liquid (48.7 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.48 – 7.39 (m, 3H), 7.36 – 7.30 (m, 2H), 7.27 (dd, *J* = 6.8, 5.0 Hz, 3H), 7.20 (td, *J* = 5.6, 5.2, 2.9 Hz, 2H), 7.13 (d, *J* = 9.6 Hz, 2H), 7.00 (dt, *J* = 7.5, 1.6 Hz, 1H), 6.89 (td, *J* = 7.6, 1.4 Hz, 1H), 6.86 – 6.80

(m, 1H), 6.77 (td, *J* = 7.1, 6.0, 3.3 Hz, 4H), 6.68 (dt, *J* = 14.9, 4.2 Hz, 4H), 6.60 – 6.51 (m, 2H), 6.45 (dt, *J* = 5.9, 2.3 Hz, 1H), 6.36 (dt, *J* = 7.7, 1.6 Hz, 1H), 6.05 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 142.0, 140.2, 140.1, 140.0, 140.0, 139.5, 139.0, 138.3, 137.0, 135.7, 134.3, 131.6, 131.3, 131.2, 131.1, 130.9, 130.9, 130.8, 130.4 (d, *J* = 32.3 Hz), 129.9, 129.6, 129.0, 128.5, 128.0, 127.7, 127.5, 126.7, 126.5, 126.5, 126.3, 126.3, 126.1, 125.4, 125.4, 125.1, 125.0, 124.2 (q, *J* = 3.9 Hz), 123.9 (q, *J* = 4.0, 3.5 Hz), 123.9 (d, *J* = 272.4 Hz), 106.6; ESI-HRMS Calcd for $C_{44}H_{30}F_3N_2$ $[M + H]^+$ 643.2356, found 643.2370.

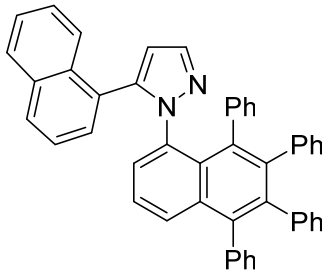


1-(5,6,7,8-Tetraphenylnaphthalen-1-yl)-5-(o-tolyl)-1*H*-pyrazole (**4k**). Eluent: V_{PET}/V_{EA} = 20:1; yellow solid (39.8 mg, 68% yield); mp 253-255 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.24 – 7.19 (m, 4H), 7.18 (s, 3H), 7.16 (d, *J* = 2.2 Hz, 2H), 7.13 (q, *J* = 1.7 Hz, 1H), 7.11 (s, 1H), 7.02 – 6.97 (m, 1H), 6.94 (dt, *J* = 7.2, 2.1 Hz, 2H), 6.86 – 6.78 (m, 5H), 6.77 (d, *J* = 6.8 Hz, 3H), 6.75 – 6.70 (m, 4H), 6.58 – 6.52 (m, 1H), 5.99 (d, *J* = 1.9 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 141.6, 140.4, 139.7, 139.6, 139.3, 138.9, 138.6, 137.0, 136.8, 136.3, 134.5, 133.0, 131.5, 131.2, 131.1, 131.0, 130.9, 130.7, 130.0, 129.8, 128.4, 128.4, 128.0, 127.9, 127.6, 127.5, 126.6, 126.4, 126.3, 126.1, 125.9, 125.5, 125.3, 125.1, 125.0, 124.6, 108.5, 21.2; ESI-HRMS Calcd for $C_{44}H_{33}N_2$ $[M + H]^+$ 589.2638, found 589.2650.

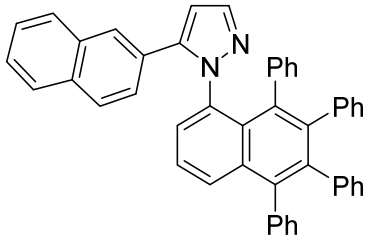


5-(3,4-Dichlorophenyl)-1-(5,6,7,8-tetraphenylnaphthalen-1-yl)-1*H*-pyrazole (**4l**). Eluent: V_{PET}/V_{EA} = 20:1; yellow liquid (40.3 mg, 63% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 7.1 Hz, 1H),

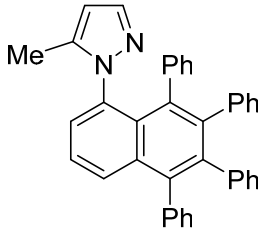
7.22 (ddd, J = 13.9, 7.0, 2.0 Hz, 6H), 7.15 (d, J = 8.6 Hz, 1H), 7.08 (d, J = 2.1 Hz, 1H), 6.97 (d, J = 7.7 Hz, 1H), 6.92 (dd, J = 8.5, 2.1 Hz, 1H), 6.87 – 6.76 (m, 5H), 6.76 – 6.67 (m, 5H), 6.60 (dt, J = 9.2, 5.6 Hz, 2H), 6.53 – 6.44 (m, 2H), 5.98 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 141.1, 140.1, 140.0, 139.9, 139.4, 138.9, 138.3, 136.8, 135.8, 134.3, 132.2, 131.6, 131.5, 131.3, 131.2, 131.1, 130.9, 130.9, 130.9, 130.1, 130.0, 129.9, 129.7, 129.5, 128.9, 128.0, 127.9, 127.7, 127.6, 126.9, 126.7, 126.6, 126.5, 126.4, 126.3, 126.2, 125.4, 125.4, 125.1, 125.0, 106.6; ESI-HRMS Calcd for $C_{43}H_{29}Cl_2N_2$ $[M + H]^+$ 643.1702, found 643.1708.



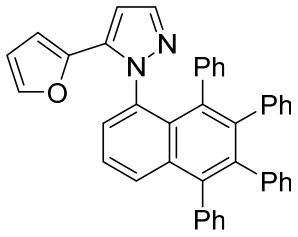
5-(Naphthalen-1-yl)-1-(5,6,7,8-tetraphenylnaphthalen-1-yl)-1*H*-pyrazole (**4m**). Eluent: V_{PET}/V_{EA} = 20:1; yellow solid (38.3 mg, 61% yield); mp 261-263 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 1H), 7.84 (dd, J = 8.1, 1.5 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.53 (dd, J = 8.4, 1.5 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.42 (ddd, J = 8.3, 6.8, 1.5 Hz, 1H), 7.37 (dd, J = 7.2, 1.3 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.22 – 7.11 (m, 5H), 7.06 (ddd, J = 8.4, 5.7, 3.2 Hz, 2H), 6.99 (dd, J = 7.3, 1.5 Hz, 1H), 6.96 – 6.92 (m, 1H), 6.87 (dd, J = 8.8, 6.9 Hz, 2H), 6.84 – 6.73 (m, 7H), 6.73 – 6.66 (m, 3H), 6.47 (dt, J = 5.9, 2.1 Hz, 1H), 6.17 (d, J = 1.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 140.8, 140.4, 140.3, 139.6, 139.5, 139.3, 139.3, 138.5, 136.8, 136.2, 134.4, 133.8, 133.0, 132.1, 131.4, 131.1, 131.1, 131.0, 130.9, 130.1, 128.6, 128.4, 128.3, 128.3, 128.1, 127.9, 127.8, 127.5, 127.5, 126.5, 126.4, 126.4, 126.3, 126.1, 126.0, 125.9, 125.5, 125.5, 125.3, 125.0, 124.7, 124.6, 109.5; ESI-HRMS Calcd for $C_{47}H_{33}N_2$ $[M + H]^+$ 625.2638, found 625.2645.



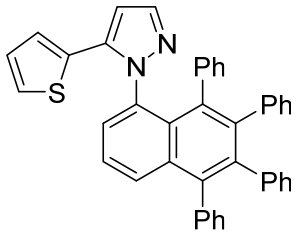
5-(Naphthalen-2-yl)-1-(5,6,7,8-tetraphenylnaphthalen-1-yl)-1*H*-pyrazole (**4n**). Eluent: V_{PET}/V_{EA} = 20:1; yellow liquid (43.8 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (td, *J* = 7.7, 2.8 Hz, 2H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.48 – 7.43 (m, 3H), 7.43 – 7.40 (m, 2H), 7.28 (d, *J* = 1.8 Hz, 1H), 7.26 (d, *J* = 2.0 Hz, 2H), 7.22 – 7.15 (m, 3H), 7.00 (dt, *J* = 7.8, 1.6 Hz, 1H), 6.84 (td, *J* = 7.6, 1.3 Hz, 1H), 6.79 – 6.70 (m, 5H), 6.70 – 6.64 (m, 3H), 6.64 – 6.60 (m, 2H), 6.60 – 6.54 (m, 3H), 6.35 (dt, *J* = 7.3, 1.7 Hz, 1H), 6.11 (d, *J* = 1.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 142.4, 140.3, 140.2, 139.8, 139.8, 139.6, 138.7, 138.5, 137.5, 136.1, 134.4, 132.9, 132.4, 131.7, 131.4, 131.2, 131.0, 131.0, 130.9, 130.9, 130.2, 129.3, 129.0, 128.3, 128.2, 127.7, 127.5, 127.5, 127.5, 126.9, 126.6, 126.5, 126.4, 126.4, 126.2, 126.2, 126.2, 126.0, 126.0, 125.5, 125.3, 125.2, 125.0, 106.4; ESI-HRMS Calcd for $C_{47}H_{33}N_2$ $[M + H]^+$ 625.2638, found 625.2647.



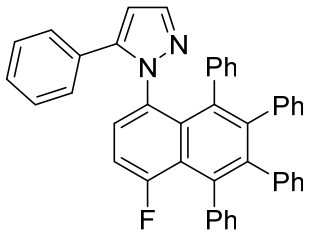
5-Methyl-1-(5,6,7,8-tetraphenylnaphthalen-1-yl)-1*H*-pyrazole (**4o**). Eluent: V_{PET}/V_{EA} = 20:1; yellow solid (34.7 mg, 68% yield); mp 209-211 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.41 (dd, *J* = 8.6, 7.1 Hz, 1H), 7.27 (d, *J* = 1.4 Hz, 1H), 7.23 (d, *J* = 4.5 Hz, 3H), 7.21 – 7.16 (m, 2H), 7.11 (d, *J* = 1.8 Hz, 1H), 6.90 – 6.86 (m, 1H), 6.80 (h, *J* = 5.0, 4.4 Hz, 6H), 6.77 – 6.65 (m, 7H), 6.56 (dq, *J* = 6.6, 2.6, 1.9 Hz, 1H), 5.44 (d, *J* = 1.8 Hz, 1H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 140.3, 140.2, 139.7, 139.6, 139.6, 139.5, 138.9, 138.7, 136.5, 136.3, 134.3, 131.5, 131.3, 131.2, 131.1, 131.0, 131.0, 130.9, 129.4, 129.2, 128.7, 128.4, 127.7, 127.5, 126.6, 126.4, 126.3, 126.3, 126.1, 125.4, 125.2, 125.2, 125.0, 124.8, 105.3, 12.2; ESI-HRMS Calcd for $C_{38}H_{29}N_2$ $[M + H]^+$ 513.2325, found 513.2344.



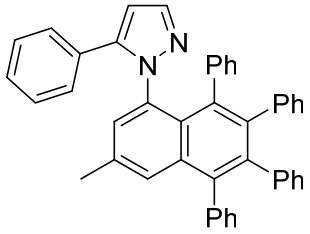
5-(Furan-2-yl)-1-(5,6,7,8-tetraphenylnaphthalen-1-yl)-1*H*-pyrazole (**4p**). Eluent: V_{PET}/V_{EA} = 20:1; brown liquid (27.2 mg, 48% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.44 (dd, *J* = 8.5, 7.1 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.26 (d, *J* = 3.9 Hz, 3H), 7.21 (tt, *J* = 4.2, 2.4 Hz, 3H), 6.88 – 6.62 (m, 12H), 6.59 – 6.44 (m, 3H), 6.28 (dd, *J* = 3.5, 1.8 Hz, 1H), 5.99 (d, *J* = 1.9 Hz, 1H), 5.74 (d, *J* = 3.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 142.6, 141.8, 140.3, 140.2, 139.9, 139.7, 139.6, 138.8, 138.6, 137.1, 136.3, 136.0, 134.3, 131.5, 131.2, 131.1, 131.0, 131.0, 130.9, 130.8, 130.1, 129.9, 129.1, 128.2, 127.7, 127.6, 126.7, 126.6, 126.4, 126.2, 126.2, 126.0, 125.4, 125.4, 125.1, 125.0, 124.9, 111.1, 107.4, 104.3; ESI-HRMS Calcd for $C_{41}H_{29}N_2O$ $[M + H]^+$ 565.2274, found 565.2286.



1-(5,6,7,8-Tetraphenylnaphthalen-1-yl)-5-(thiophen-2-yl)-1*H*-pyrazole (**4q**). Eluent: V_{PET}/V_{EA} = 20:1; brown liquid (30.9 mg, 53% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.9, 2.1 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.29 – 7.25 (m, 2H), 7.22 – 7.18 (m, 2H), 7.17 – 7.13 (m, 2H), 6.94 – 6.63 (m, 15H), 6.59 (td, *J* = 7.4, 1.5 Hz, 1H), 6.51 (ddt, *J* = 13.0, 7.8, 1.9 Hz, 2H), 5.94 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 140.3, 140.2, 139.9, 139.7, 139.6, 138.9, 138.6, 138.5, 136.6, 136.3, 134.3, 132.7, 131.5, 131.1, 131.0, 130.9, 130.9, 130.1, 130.0, 129.8, 128.4, 127.7, 127.6, 127.0, 126.6, 126.6, 126.4, 126.2, 126.1, 126.0, 125.7, 125.5, 125.4, 125.2, 125.0, 125.0, 124.8, 105.3; ESI-HRMS Calcd for $C_{41}H_{29}N_2S$ $[M + H]^+$ 581.2046, found 581.2058.

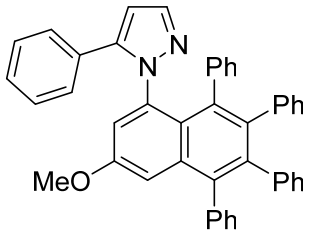


1-(4-Fluoro-5,6,7,8-tetraphenylnaphthalen-1-yl)-5-phenyl-1*H*-pyrazole (**4aa**). Eluent: V_{PET}/V_{EA} = 20:1; yellow solid (43.8 mg, 74% yield); mp 182-184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 8.2, 4.8 Hz, 1H), 7.22 (d, *J* = 3.7 Hz, 3H), 7.19 (s, 1H), 7.15 (d, *J* = 3.2 Hz, 3H), 7.14 – 7.09 (m, 4H), 7.09 – 7.04 (m, 1H), 6.93 (d, *J* = 7.3 Hz, 1H), 6.81 (d, *J* = 7.5 Hz, 1H), 6.76 (q, *J* = 6.4, 5.5 Hz, 3H), 6.67 (dt, *J* = 17.6, 7.3 Hz, 6H), 6.59 (d, *J* = 6.8 Hz, 2H), 6.56 (dd, *J* = 6.1, 2.7 Hz, 1H), 6.42 (dd, *J* = 6.0, 2.5 Hz, 1H), 6.01 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9 (d, *J* = 259.8 Hz), 143.4, 141.6, 141.4 (d, *J* = 4.8 Hz), 139.9, 139.8, 139.5, 138.0, 136.4, 135.2 (d, *J* = 1.9 Hz), 133.8 (d, *J* = 3.9 Hz), 131.6, 131.0, 130.9, 130.8, 130.7, 130.3, 130.0, 129.9, 129.8, 129.7, 128.9, 128.8, 128.1, 127.8, 127.6, 126.9, 126.8, 126.5, 126.3 (d, *J* = 2.2 Hz), 126.2, 126.1 (d, *J* = 2.1 Hz), 125.5, 125.4, 125.4, 125.1, 124.2 (d, *J* = 50.2 Hz), 123.8 (d, *J* = 8.8 Hz), 111.0 (d, *J* = 24.5 Hz), 106.2; ESI-HRMS Calcd for $C_{43}H_{30}FN_2$ $[M + H]^+$ 593.2388, found 593.2405.

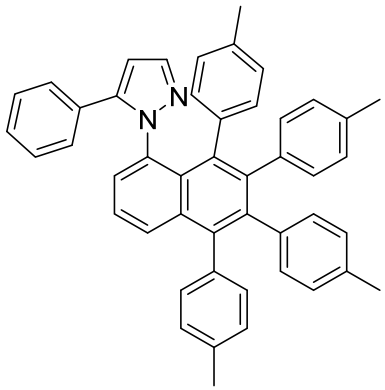


1-(3-Methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)-5-phenyl-1*H*-pyrazole (**4ab**). Eluent: V_{PET}/V_{EA} = 20:1; brown liquid (41.2 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.25 – 7.13 (m, 10H), 7.09 (dd, *J* = 6.5, 3.0 Hz, 2H), 6.95 (d, *J* = 7.7 Hz, 1H), 6.86 – 6.64 (m, 10H), 6.62 – 6.50 (m, 3H), 6.47 (dd, *J* = 6.9, 2.7 Hz, 1H), 5.99 (d, *J* = 2.0 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 141.5, 140.5, 140.4, 139.8, 139.8, 139.7, 138.5, 138.1, 137.4, 136.0, 134.8, 134.5, 131.6, 131.4, 131.2, 131.2, 131.1, 131.0, 130.9, 130.8, 130.2, 130.1, 128.2, 127.9, 127.7, 127.6, 127.5, 127.3, 126.5, 126.5, 126.4, 126.4, 126.2, 126.1, 126.0, 125.4, 125.2, 125.1, 124.9, 105.9,

21.2; ESI-HRMS Calcd for $C_{44}H_{33}N_2$ $[M + H]^+$ 589.2638, found 589.2652.

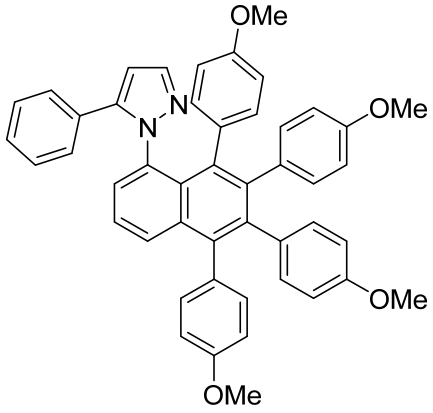


1-(3-Methoxy-5,6,7,8-tetraphenylnaphthalen-1-yl)-5-phenyl-1*H*-pyrazole (**4ac**). Eluent: V_{PET}/V_{EA} = 10:1; yellow solid (45.1 mg, 75% yield); mp 189-191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.16 (m, 8H), 7.15 – 7.10 (m, 3H), 7.04 (dd, *J* = 10.0, 3.0 Hz, 2H), 7.00 – 6.93 (m, 2H), 6.83 – 6.75 (m, 4H), 6.73 – 6.66 (m, 5H), 6.62 – 6.57 (m, 3H), 6.47 (dt, *J* = 7.1, 2.0 Hz, 1H), 5.99 (d, *J* = 2.0 Hz, 1H), 3.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 143.5, 140.5, 140.3, 140.2, 140.2, 139.8, 139.7, 138.6, 137.6, 136.2, 135.4, 131.7, 131.3, 131.2, 131.1, 130.9, 130.9, 130.1, 129.9, 129.7, 129.3, 128.5, 128.3, 128.1, 127.8, 127.7, 127.6, 127.5, 126.6, 126.5, 126.4, 126.2, 126.1, 126.0, 125.4, 125.3, 125.1, 124.8, 123.7, 120.3, 108.9, 106.1, 55.4; ESI-HRMS Calcd for $C_{44}H_{33}N_2O$ $[M + H]^+$ 605.2587, found 605.2598.

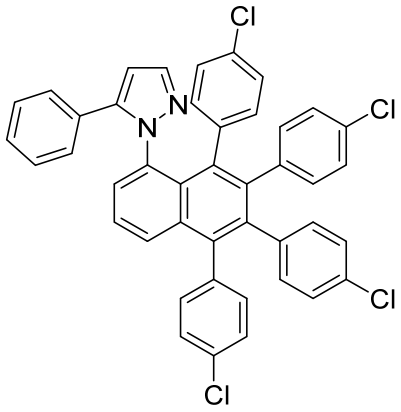


5-Phenyl-1-(5,6,7,8-tetra-p-tolylnaphthalen-1-yl)-1*H*-pyrazole (**4ad**). Eluent: V_{PET}/V_{EA} = 20:1; brown liquid (44.2 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.36 – 7.26 (m, 2H), 7.18 (dt, *J* = 8.3, 2.6 Hz, 4H), 7.13 – 7.01 (m, 6H), 6.81 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.59 (d, *J* = 7.9 Hz, 5H), 6.55 – 6.43 (m, 4H), 6.39 – 6.28 (m, 2H), 6.01 (d, *J* = 1.8 Hz, 1H), 2.31 (s, 3H), 2.05 (d, *J* = 3.3 Hz, 6H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 142.6, 140.0, 139.5, 138.6, 137.6, 137.5, 137.4, 136.9, 136.2, 135.8, 134.6, 134.3, 134.0, 133.9, 131.5, 131.3, 131.0,

130.9, 130.8, 130.8, 130.7, 130.3, 129.8, 129.6, 129.3, 129.1, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.3, 127.2, 127.1, 126.9, 126.8, 126.7, 126.0, 124.5, 105.8, 21.2, 21.0, 21.0; ESI-HRMS Calcd for $C_{47}H_{39}N_2$ $[M + H]^+$ 631.3108, found 631.3118.

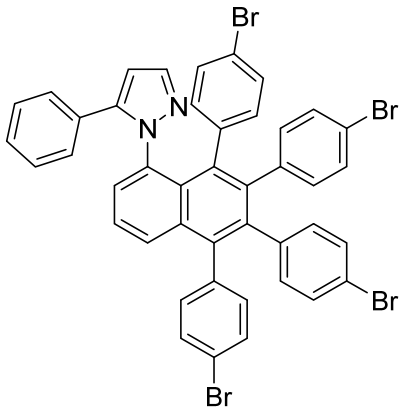


5-Phenyl-1-(5,6,7,8-tetrakis(4-methoxyphenyl)naphthalen-1-yl)-1*H*-pyrazole (**4ae**). Eluent: V_{PET}/V_{EA} = 3:1; brown liquid (49.1 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.29 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.22 (d, *J* = 1.9 Hz, 1H), 7.18 (dd, *J* = 5.1, 2.0 Hz, 3H), 7.12 – 7.04 (m, 4H), 6.84 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.81 – 6.77 (m, 2H), 6.60 (td, *J* = 10.6, 2.8 Hz, 2H), 6.47 (ddd, *J* = 8.5, 6.3, 2.2 Hz, 2H), 6.32 (dddd, *J* = 30.3, 14.2, 8.4, 2.6 Hz, 6H), 6.14 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.06 (d, *J* = 2.0 Hz, 1H), 3.78 (s, 3H), 3.65 – 3.50 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 156.9, 156.7, 143.3, 142.7, 140.0, 139.7, 138.5, 137.5, 136.0, 134.8, 133.2, 133.0, 132.6, 132.4, 132.2, 132.2, 132.0, 131.9, 131.9, 131.6, 131.0, 130.2, 129.1, 128.6, 128.4, 127.9, 127.7, 127.3, 124.6, 113.2, 113.1, 112.1, 111.9, 111.3, 106.0, 55.2, 55.1, 54.9; ESI-HRMS Calcd for $C_{47}H_{39}N_2O_4$ $[M + H]^+$ 695.2904, found 695.2916.

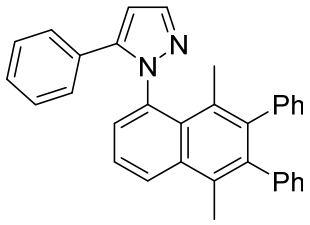


5-Phenyl-1-(5,6,7,8-tetrakis(4-chlorophenyl)naphthalen-1-yl)-1*H*-pyrazole (**4af**).

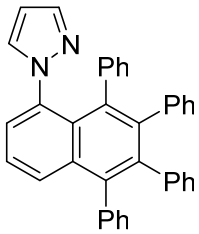
Eluent: V_{PET}/V_{EA} = 20:1; brown liquid (51.8 mg, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.36 (dd, *J* = 7.2, 1.5 Hz, 1H), 7.29 – 7.25 (m, 3H), 7.23 – 7.16 (m, 3H), 7.10 (tdd, *J* = 9.6, 7.1, 2.6 Hz, 4H), 6.91 – 6.83 (m, 3H), 6.83 – 6.76 (m, 2H), 6.74 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.68 – 6.57 (m, 3H), 6.52 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.46 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.38 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.12 (d, *J* = 1.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 141.0, 140.1, 138.4, 138.2, 138.1, 138.0, 137.5, 137.5, 136.5, 135.7, 134.3, 133.2, 132.6, 132.5, 132.2, 132.0, 132.0, 132.0, 131.9, 131.7, 131.5, 131.0, 129.8, 129.6, 129.0, 128.3, 128.2, 127.7, 127.6, 127.4, 127.3, 127.1, 126.9, 126.5, 125.8, 125.7, 106.2; ESI-HRMS Calcd for $C_{43}H_{27}Cl_4N_2$ $[M + H]^+$ 711.0923, found 711.0933.



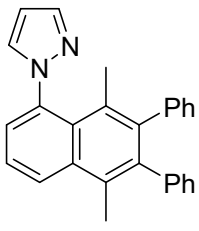
5-Phenyl-1-(5,6,7,8-tetrakis(4-bromophenyl)naphthalen-1-yl)-1*H*-pyrazole (**4ag**). Eluent: V_{PET}/V_{EA} = 20:1; brown liquid (45.0 mg, 51% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.45 – 7.39 (m, 3H), 7.37 (dd, *J* = 7.2, 1.5 Hz, 1H), 7.26 (d, *J* = 1.9 Hz, 1H), 7.20 (dd, *J* = 5.2, 2.1 Hz, 3H), 7.11 – 7.04 (m, 3H), 7.01 (dt, *J* = 8.8, 2.5 Hz, 3H), 6.95 (td, *J* = 8.5, 2.1 Hz, 2H), 6.90 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.76 (ddd, *J* = 17.2, 8.2, 2.2 Hz, 2H), 6.57 (ddd, *J* = 12.7, 8.8, 2.1 Hz, 2H), 6.46 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.39 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.32 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.13 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 140.8, 140.1, 138.5, 138.4, 138.2, 138.1, 137.9, 137.6, 137.0, 135.6, 134.2, 132.9, 132.8, 132.5, 132.4, 132.3, 132.3, 132.2, 131.3, 131.2, 130.4, 130.2, 130.0, 129.9, 129.8, 129.7, 129.5, 129.0, 128.8, 128.3, 128.2, 127.7, 127.6, 125.8, 121.4, 120.4, 120.0, 119.8, 106.2; ESI-HRMS Calcd for $C_{43}H_{27}Br_4N_2$ $[M + H]^+$ 886.8902, found 886.8918.



1-(5,8-Dimethyl-6,7-diphenylnaphthalen-1-yl)-5-phenyl-1*H*-pyrazole (**4ah**). Eluent: V_{PET}/V_{EA} = 20:1; yellow liquid (30.0 mg, 67% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.73 (d, *J* = 1.9 Hz, 1H), 7.49 (dd, *J* = 8.5, 7.2 Hz, 1H), 7.35 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.20 (d, *J* = 1.3 Hz, 4H), 7.10 (ddd, *J* = 8.2, 5.1, 1.9 Hz, 2H), 7.08 – 6.98 (m, 5H), 6.97 – 6.92 (m, 2H), 6.91 – 6.86 (m, 1H), 6.74 (dt, *J* = 7.3, 1.8 Hz, 1H), 6.61 (d, *J* = 2.0 Hz, 1H), 2.46 (s, 3H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 142.5, 141.7, 141.5, 140.2, 140.0, 139.8, 137.4, 134.3, 130.4, 130.4, 130.2, 130.2, 130.1, 129.9, 129.6, 129.2, 129.0, 128.8, 128.4, 128.3, 128.1, 127.9, 127.9, 127.4, 127.3, 127.2, 127.2, 126.8, 126.4, 126.0, 125.9, 124.7, 106.5, 17.6, 17.3; ESI-HRMS Calcd for $C_{33}H_{27}N_2$ $[M + H]^+$ 451.2169, found 451.2184.



1-(5,6,7,8-Tetraphenylnaphthalen-1-yl)-1*H*-pyrazole (**6a**).[4] Eluent: V_{PET}/V_{EA} = 20:1; yellow solid (36.0 mg, 72% yield); mp 183-185 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.69 (m, 1H), 7.43 – 7.35 (m, 2H), 7.24 – 7.16 (m, 6H), 7.14 (d, *J* = 2.4 Hz, 1H), 6.84 – 6.71 (m, 13H), 6.67 – 6.57 (m, 2H), 5.71 (t, *J* = 2.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 140.3, 140.2, 139.9, 139.8, 139.6, 139.5, 138.8, 138.0, 136.2, 134.3, 132.3, 131.3, 131.2, 131.0, 129.0, 127.7, 127.6, 127.6, 126.6, 126.6, 126.3, 125.4, 125.1, 125.1, 124.8, 106.0.



1-(5,8-Dimethyl-6,7-diphenylnaphthalen-1-yl)-1*H*-pyrazole (**6b**).[4] Eluent: V_{PET}/V_{EA} = 20:1; yellow liquid (8.7 mg, 23% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.73 (d, *J* = 1.9 Hz, 1H), 7.65 (d, *J* = 2.3 Hz, 1H), 7.58 (t, *J* = 7.9 Hz, 1H), 7.50 (dd, *J* = 7.2, 1.4 Hz, 1H), 7.13 (t, *J* = 7.7 Hz, 2H), 7.10 – 7.04 (m, 3H), 7.04 – 7.00 (m, 1H), 6.98 – 6.94 (m, 2H), 6.91 (s, 2H), 6.45 (t, *J* = 2.0 Hz, 1H), 2.48 (s, 3H), 1.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 141.7, 141.4, 140.3, 140.1, 138.1, 134.1, 132.6, 130.3, 129.7, 129.1, 129.1, 127.3, 127.3, 127.0, 126.0, 125.9, 124.5, 106.6, 17.7, 16.7.

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1. (a) J. Ying, T. Liu, Y. Liu and J.-P. Wan, *Org. Lett.,* 2022**, 24**, 2404-2408. (b) H. Guo, L. Tian, Y. Liu and J.-P. Wan, *Org. Lett.,* 2022**, 24**, 228-233. (c) K. Chen, B. Zhao, Y. Liu and J.-P. Wan, *J. Org. Chem.,* 2022, **87**, 14957-14964.

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3. (a) K. Muralirajan and C.-H. Cheng, *Adv. Synth. Catal.,* 2014**, 356**, 1571-1576. (b) S. Baruah, P. Saikia, G. Duarah and S. Gogoi, *Org. Lett.,* 2018, **20**, 3753-3757. (c) S. Borthakur, B. Sarma and S. Gogoi, *Org. Lett.,* 2019, **21**, 7878-7882.

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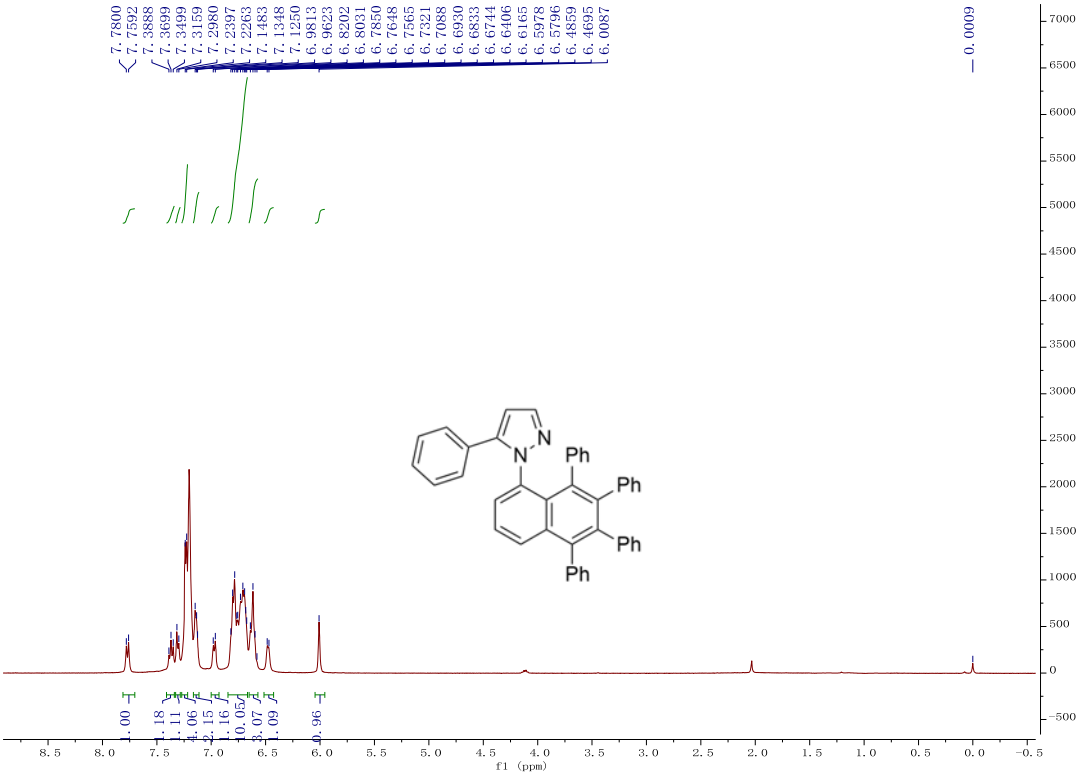
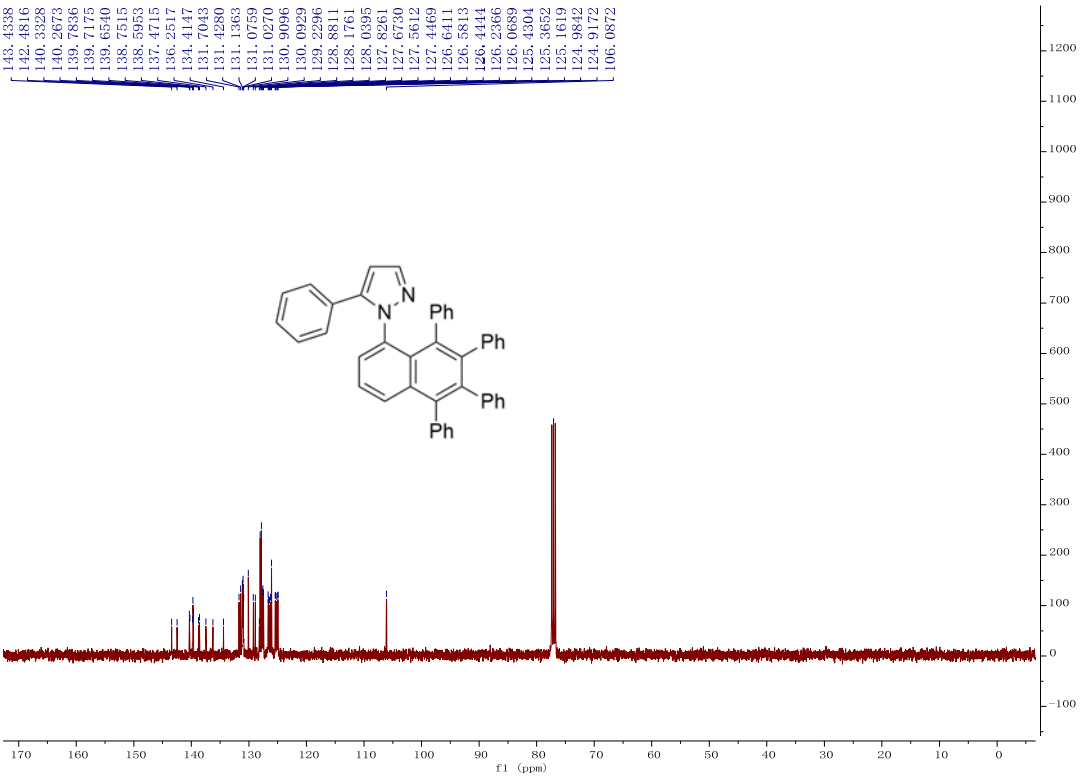
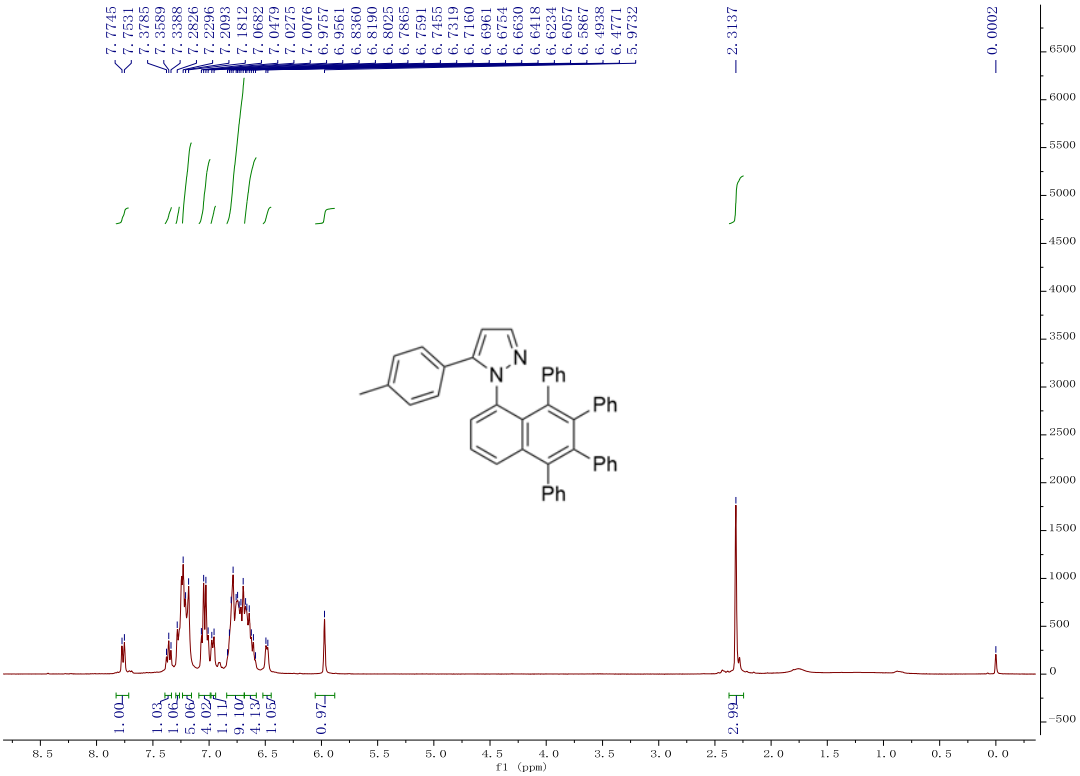
The ^{1}H and ^{13}C NMR spectra



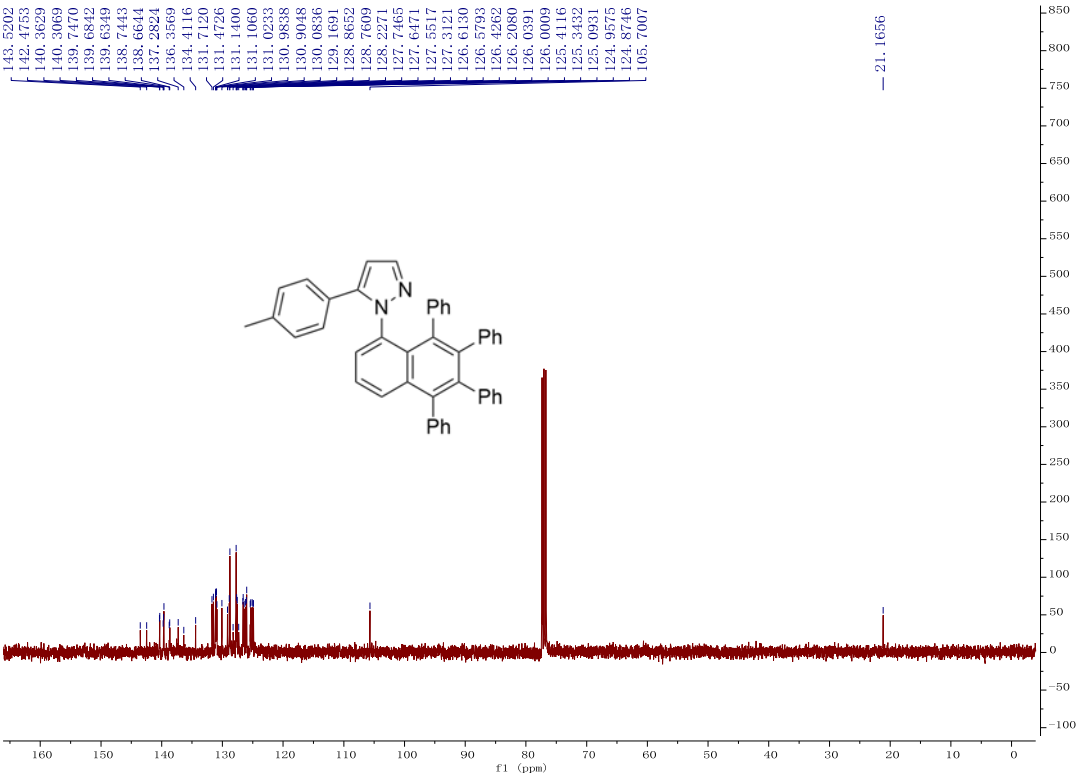
^{1}H NMR spectrum of **4a** (400 MHz, $CDCl_3$)



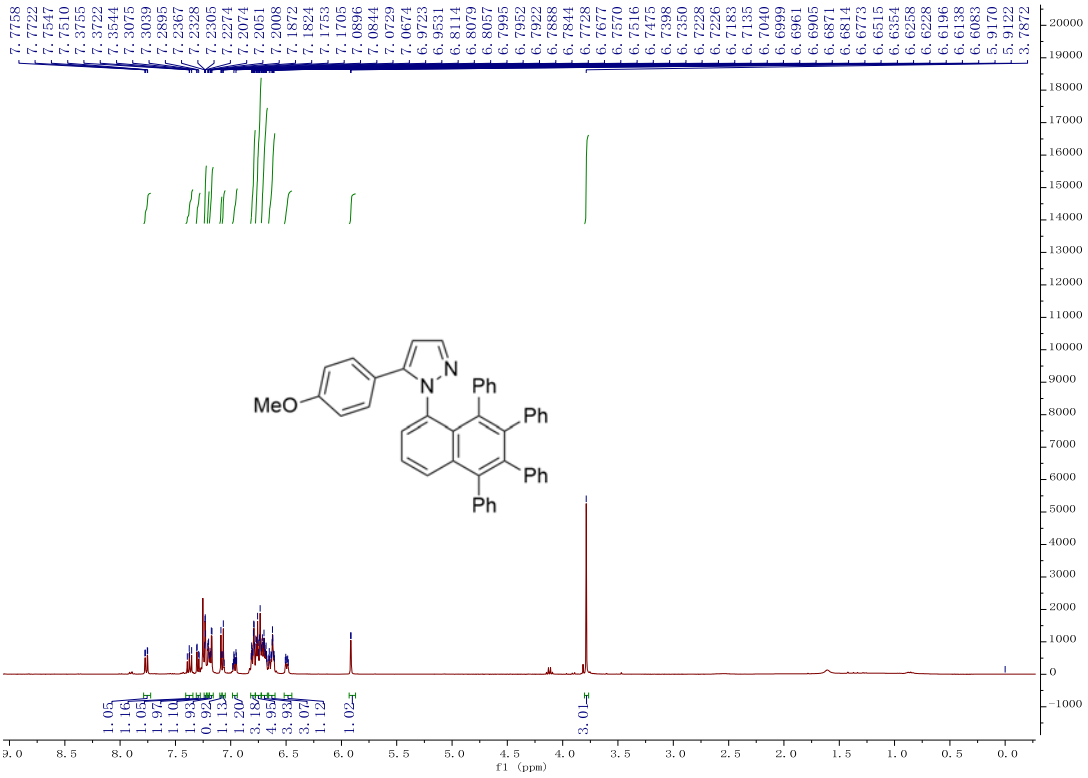
^{13}C NMR spectrum of **4a** (100 MHz, $CDCl_3$)



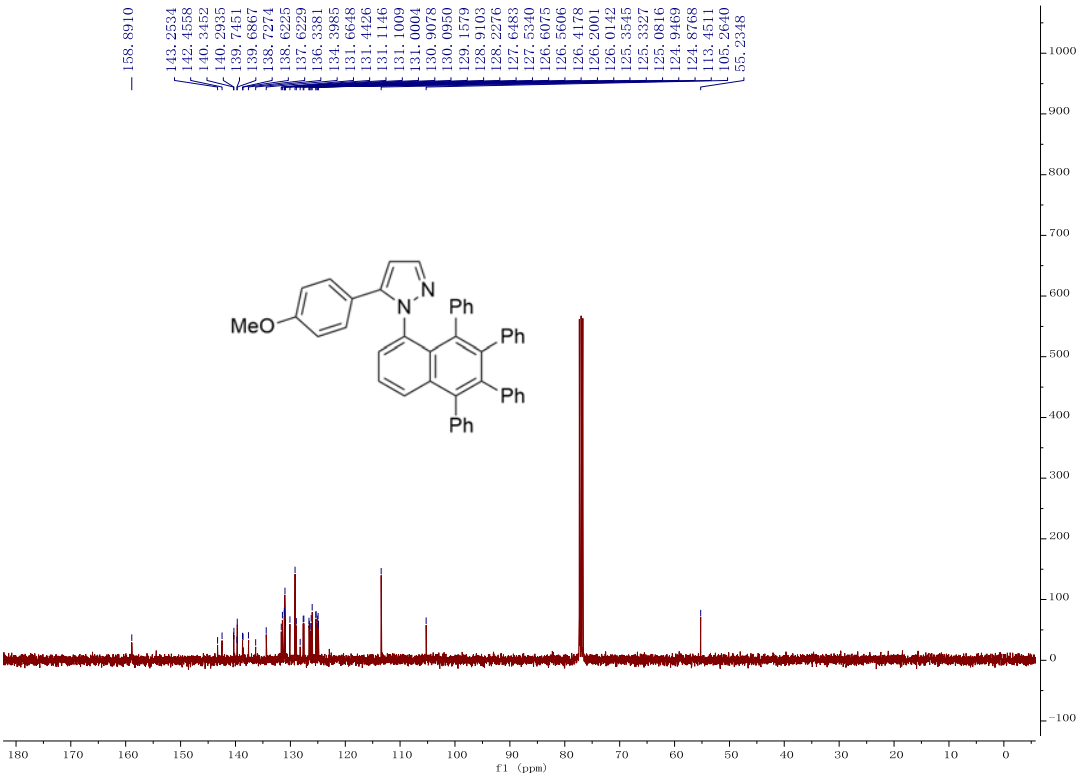
^{1}H NMR spectrum of **4b** (400 MHz, $CDCl_3$)



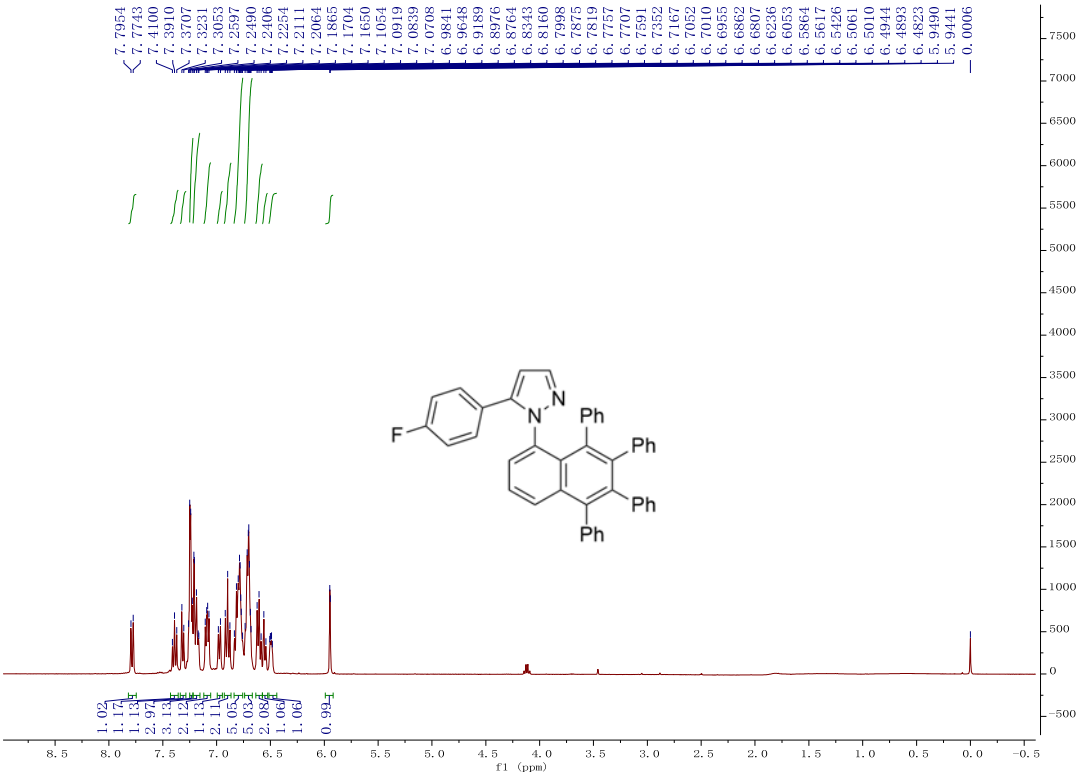
^{13}C NMR spectrum of **4b** (100 MHz, $CDCl_3$)



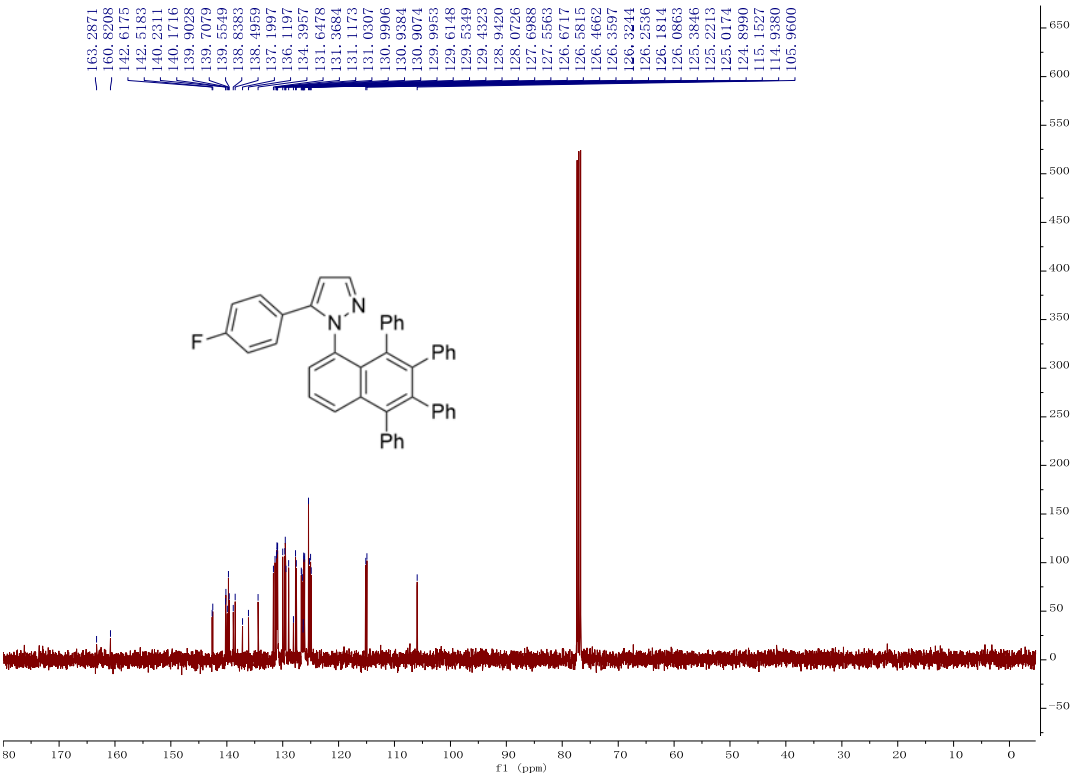
^{1}H NMR spectrum of **4c** (400 MHz, $CDCl_3$)



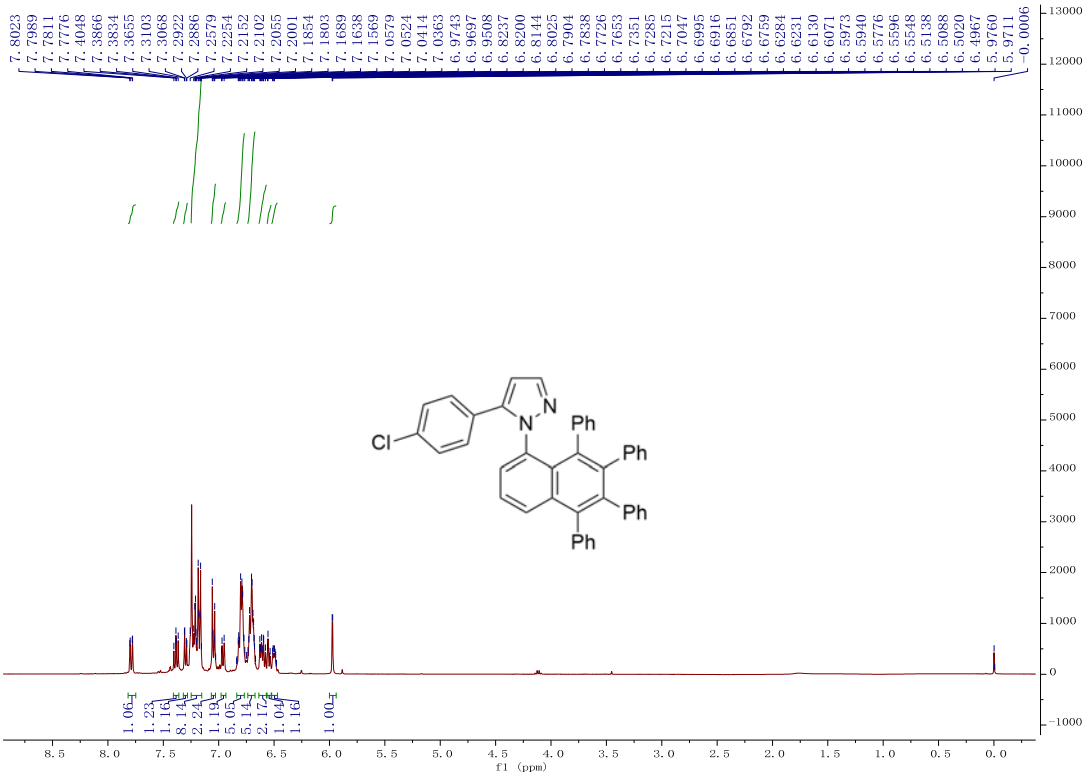
^{13}C NMR spectrum of **4c** (100 MHz, $CDCl_3$)



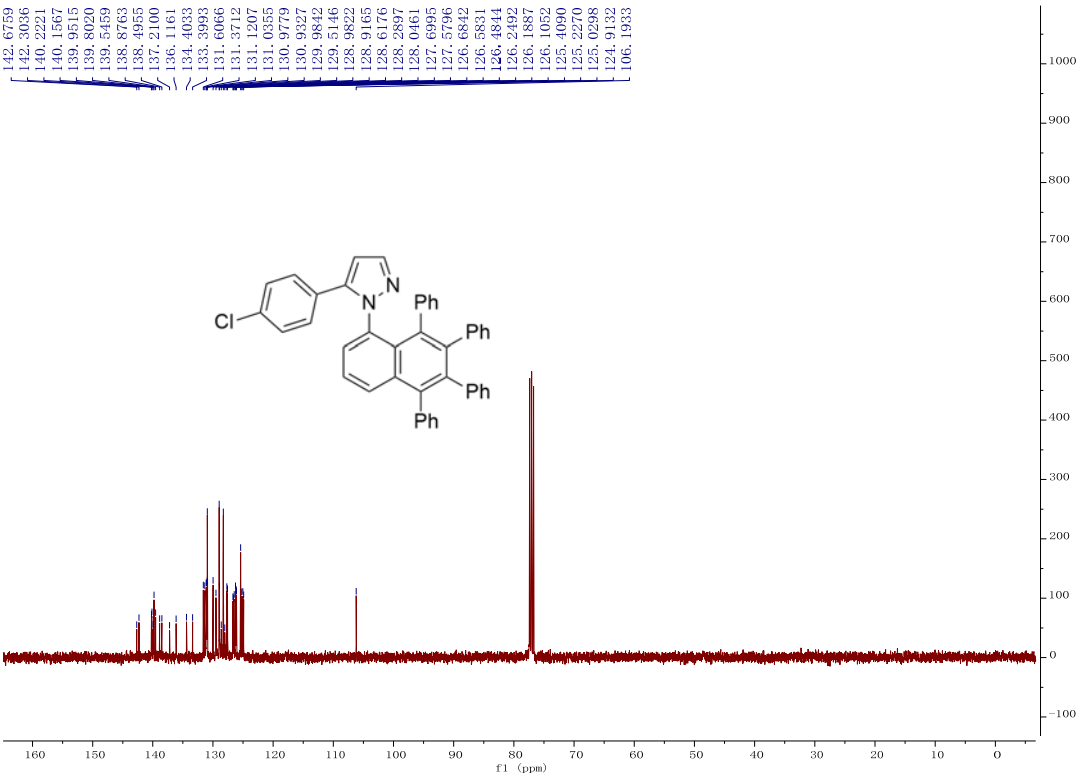
^{1}H NMR spectrum of **4d** (400 MHz, $CDCl_3$)



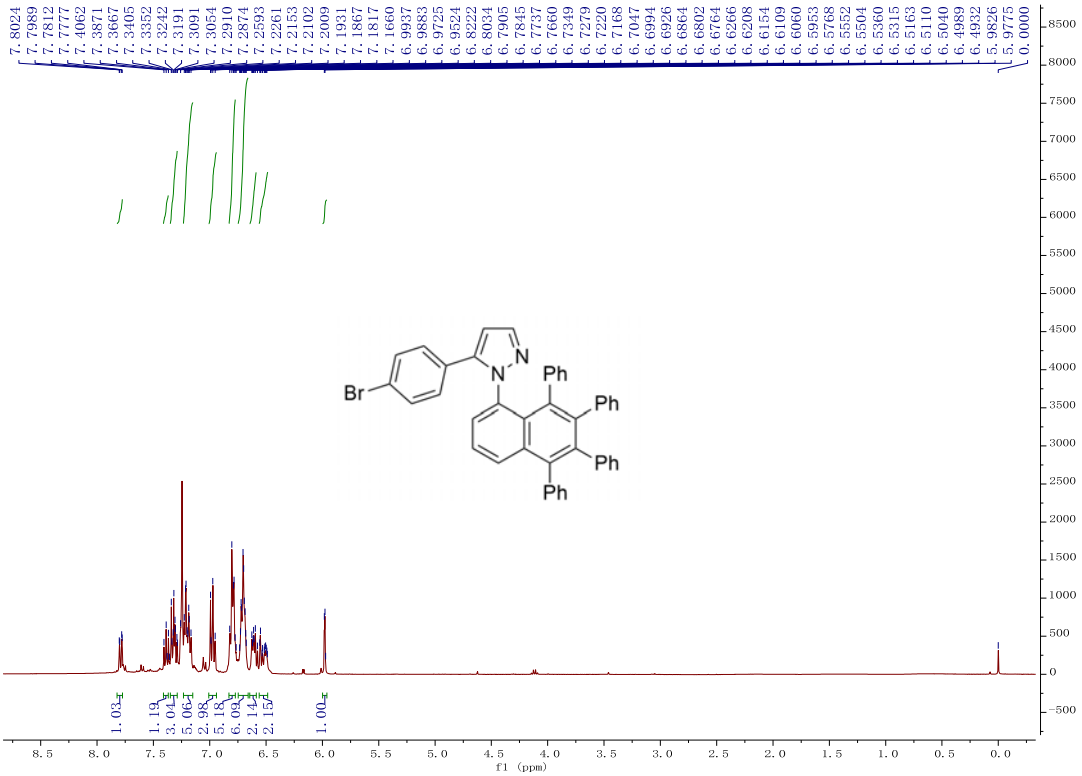
^{13}C NMR spectrum of **4d** (100 MHz, $CDCl_3$)



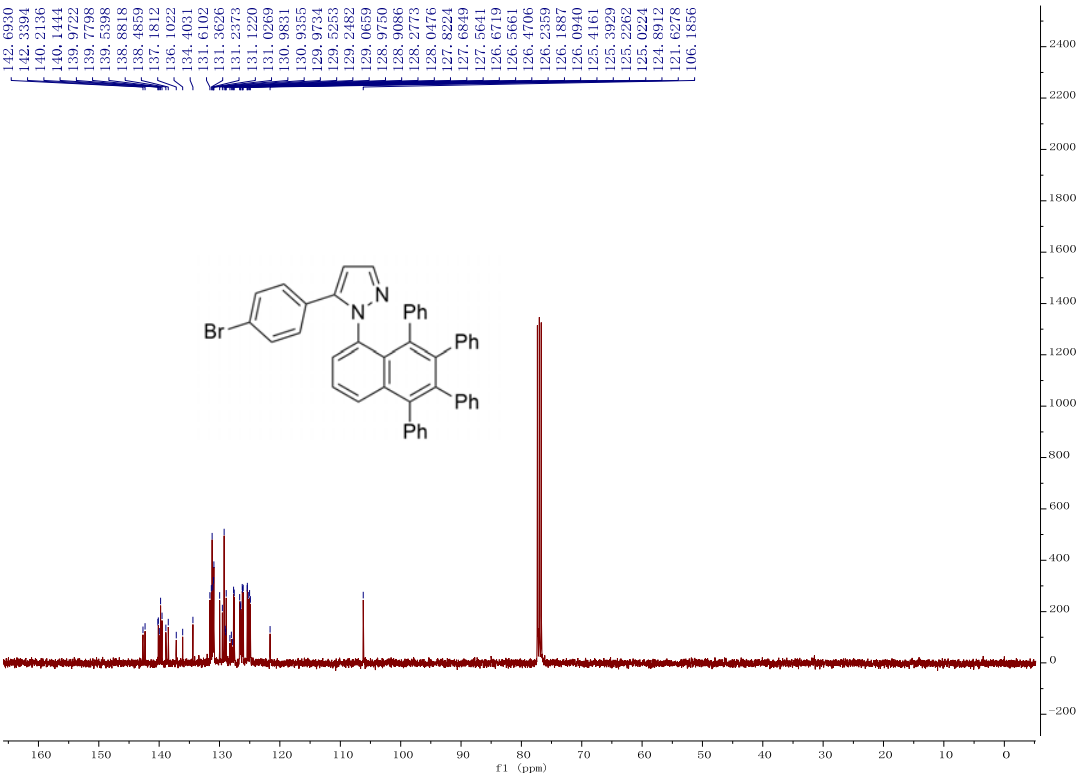
^{1}H NMR spectrum of **4e** (400 MHz, $CDCl_3$)



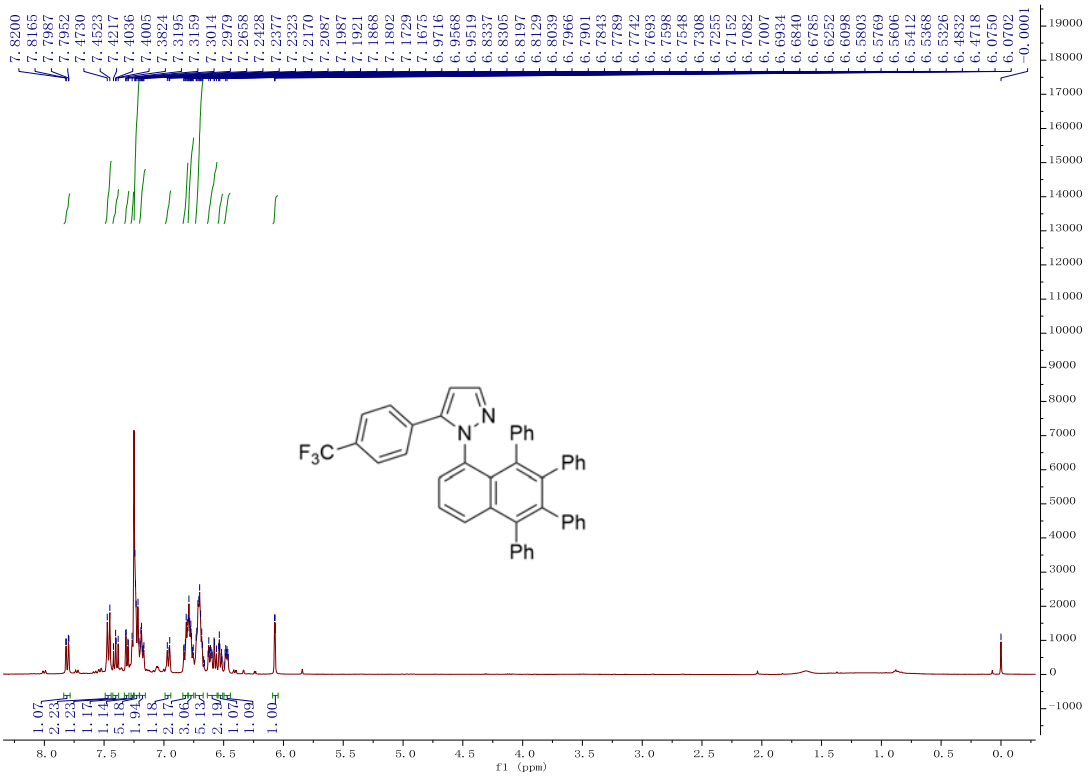
^{13}C NMR spectrum of **4e** (100 MHz, $CDCl_3$)



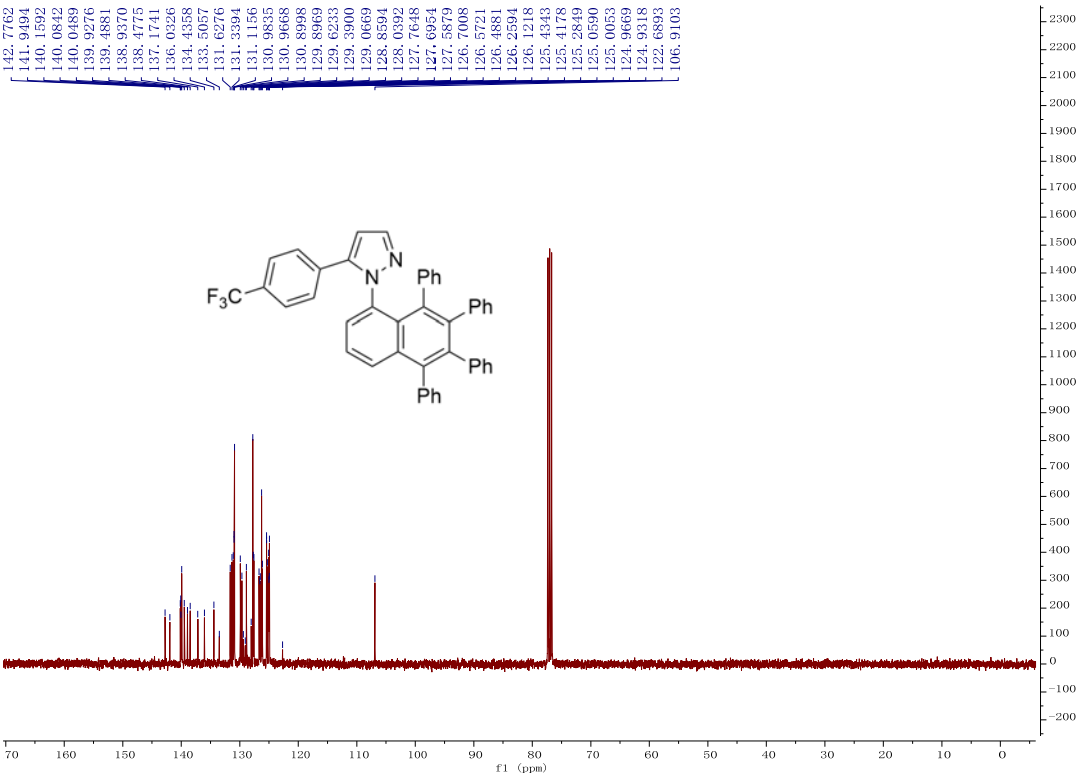
^{1}H NMR spectrum of **4f** (400 MHz, $CDCl_3$)



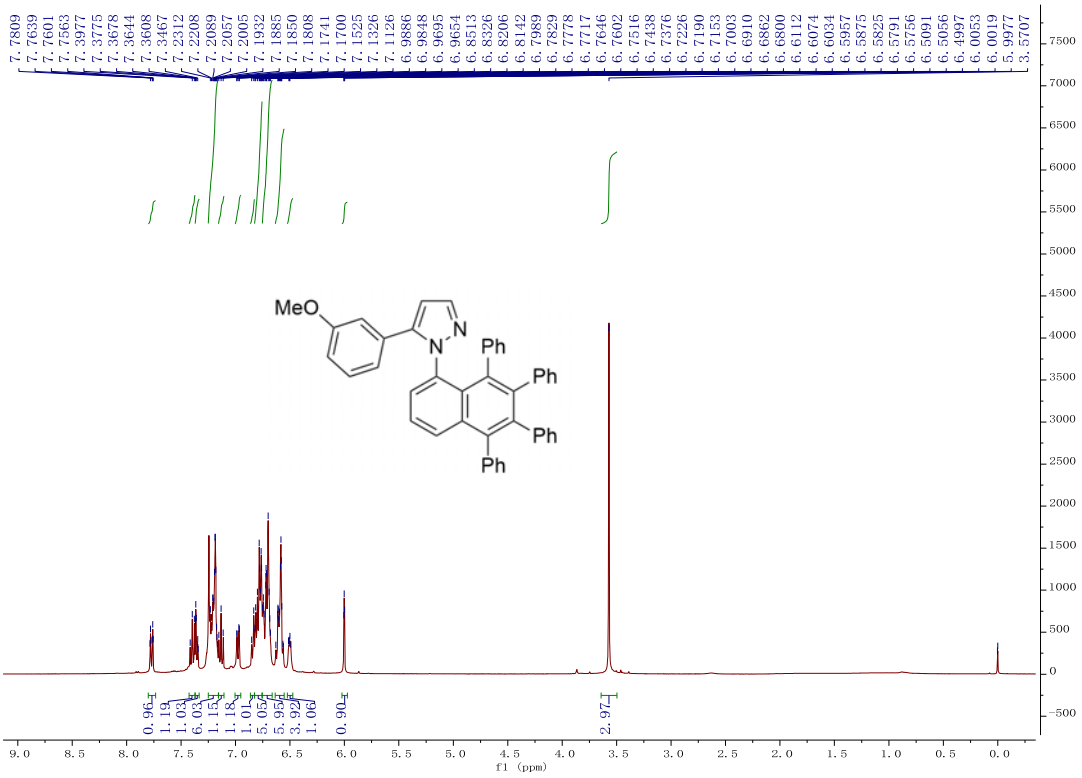
^{13}C NMR spectrum of **4f** (100 MHz, $CDCl_3$)



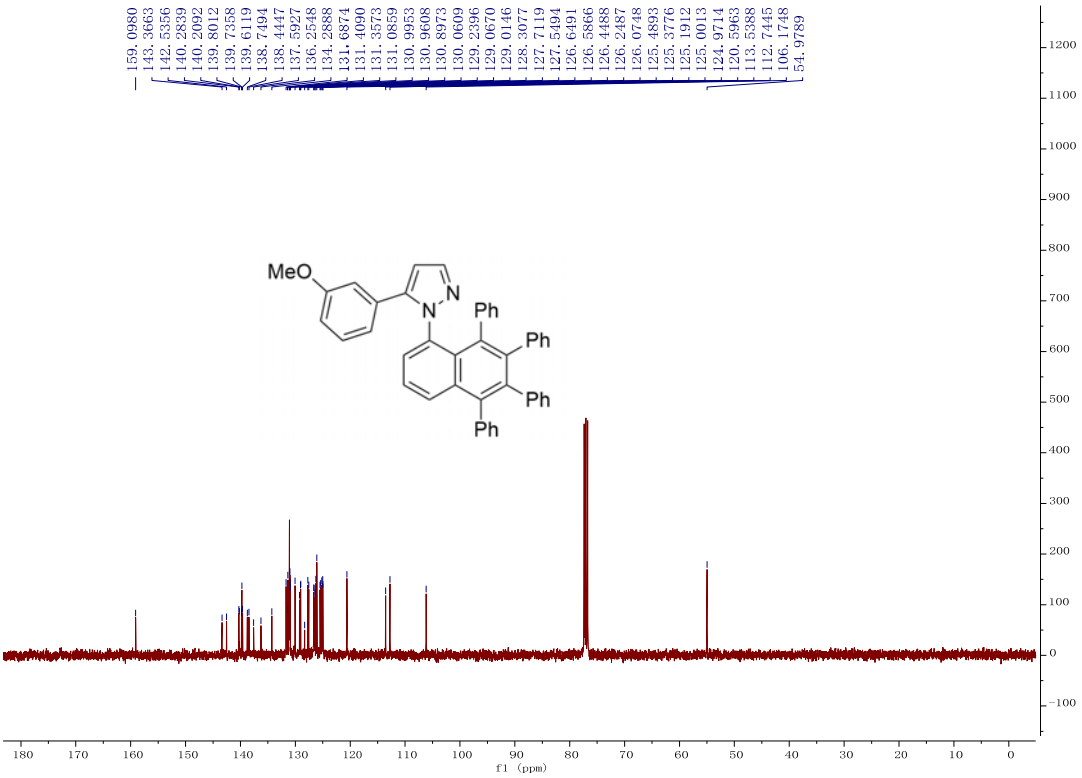
^{1}H NMR spectrum of **4g** (400 MHz, $CDCl_3$)



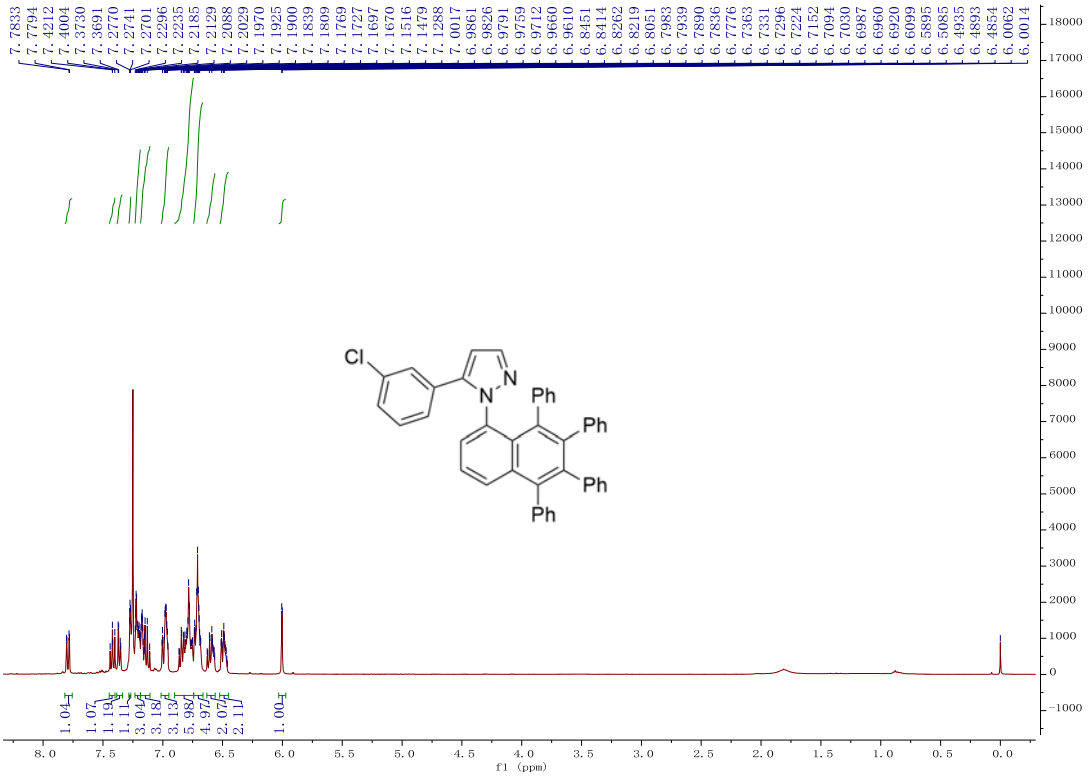
^{13}C NMR spectrum of **4g** (100 MHz, $CDCl_3$)



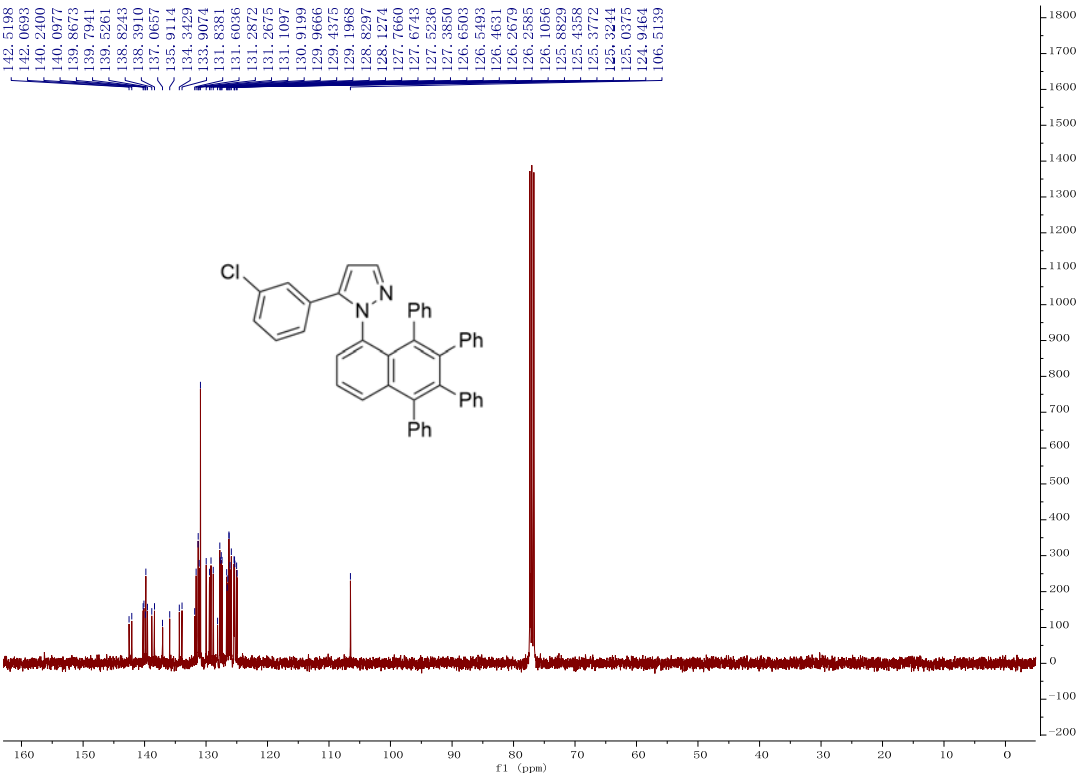
^{1}H NMR spectrum of **4h** (400 MHz, $CDCl_3$)



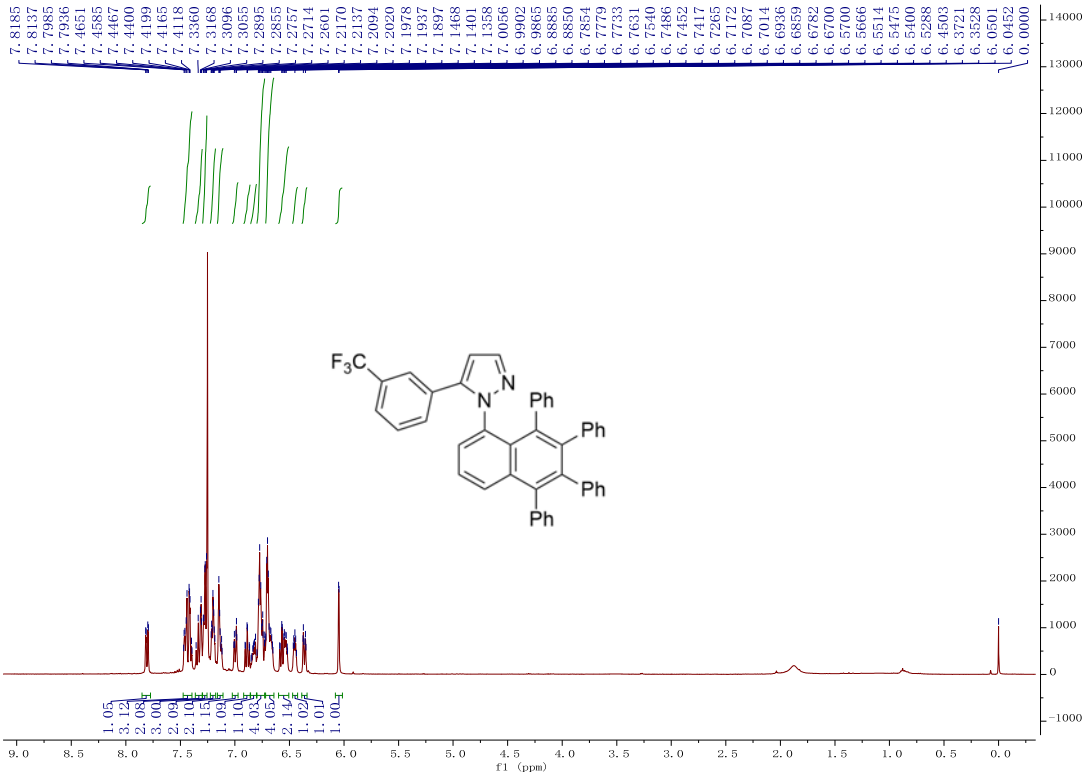
^{13}C NMR spectrum of **4h** (100 MHz, $CDCl_3$)



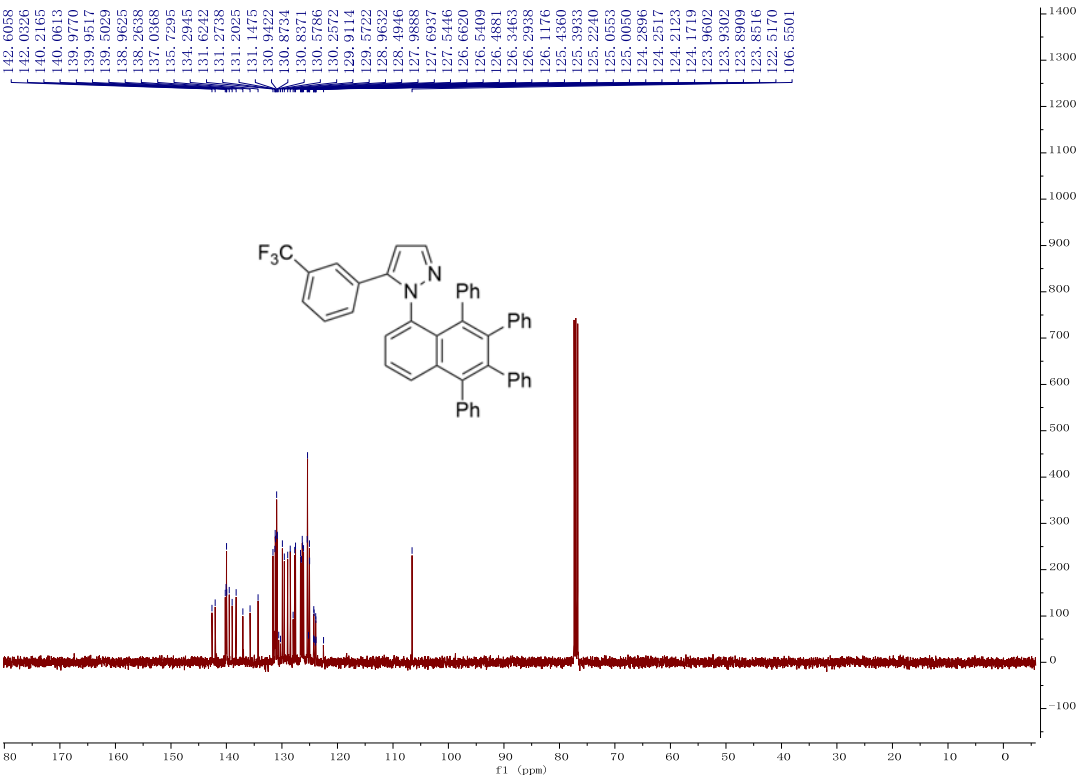
^{1}H NMR spectrum of **4i** (400 MHz, $CDCl_3$)



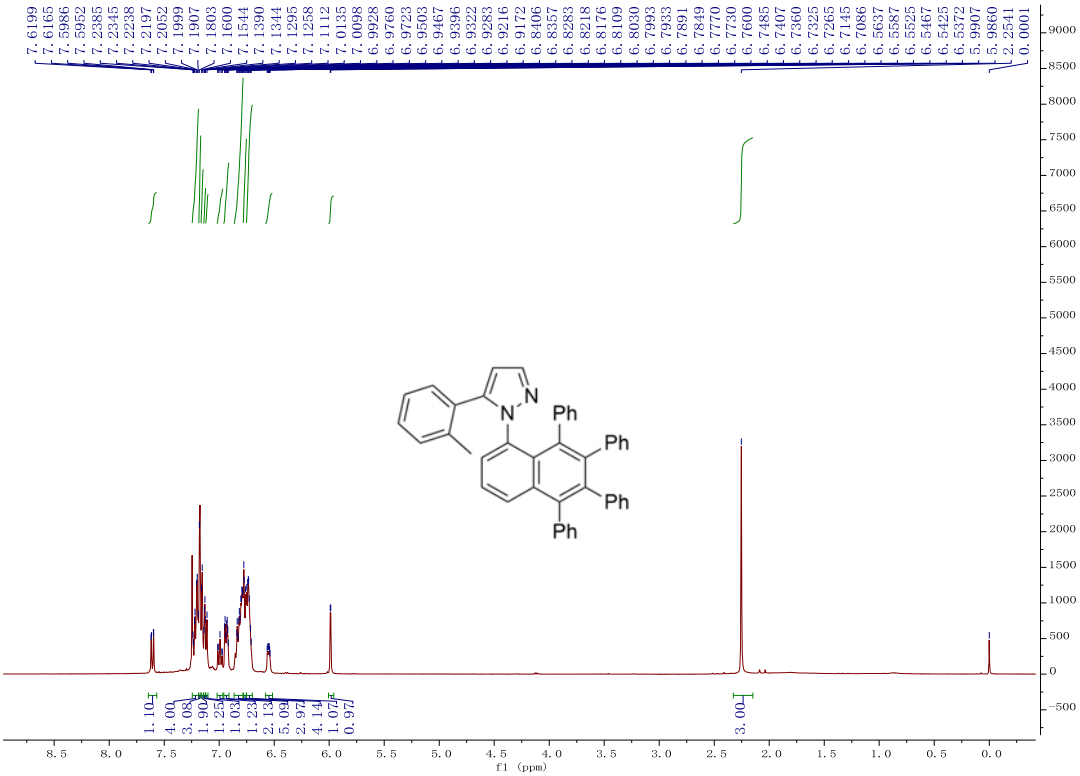
^{13}C NMR spectrum of **4i** (100 MHz, $CDCl_3$)



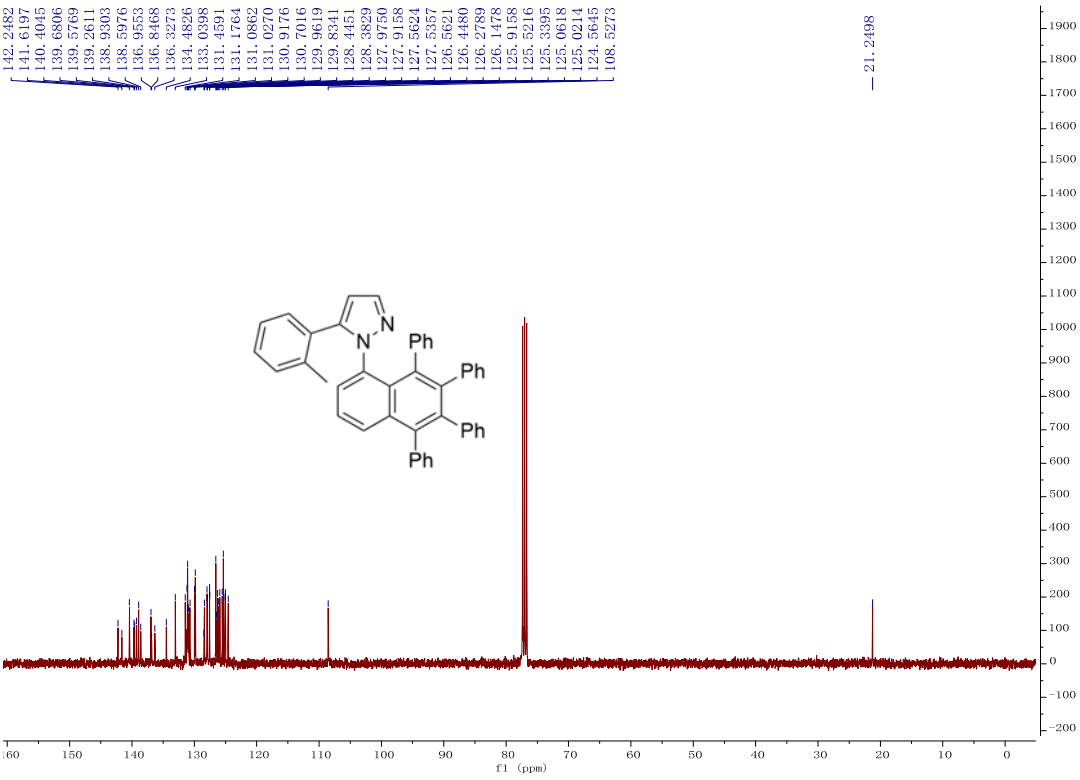
^{1}H NMR spectrum of **4j** (400 MHz, $CDCl_3$)



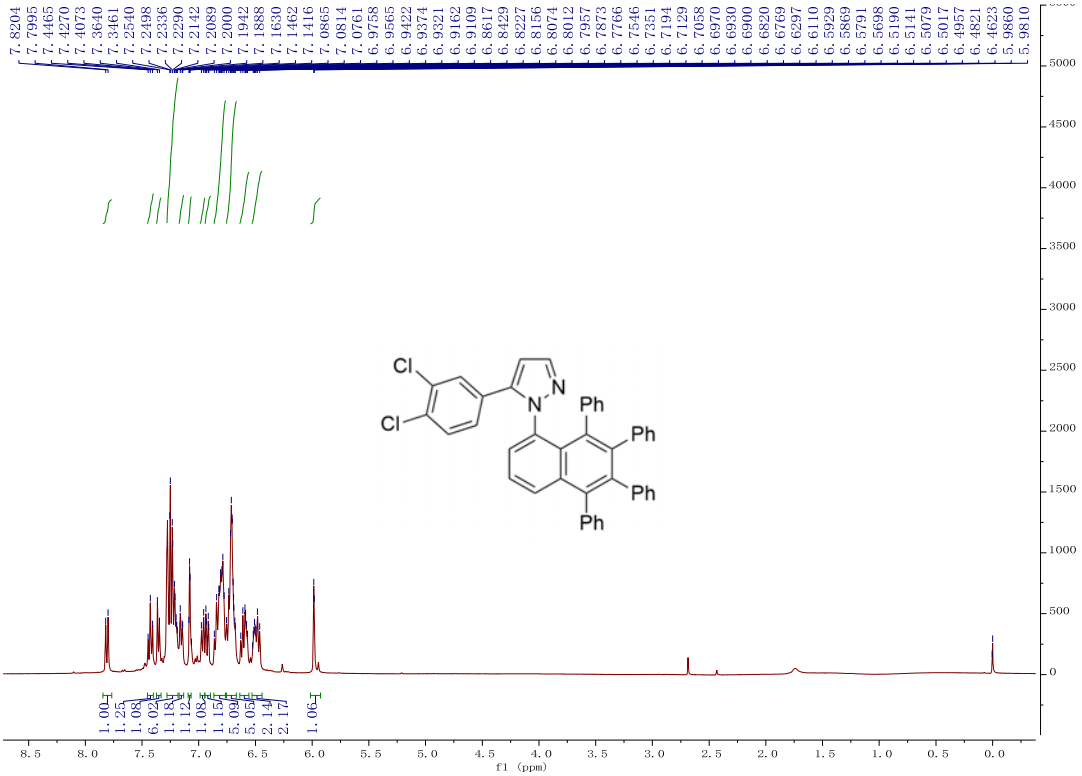
^{13}C NMR spectrum of **4j** (100 MHz, $CDCl_3$)



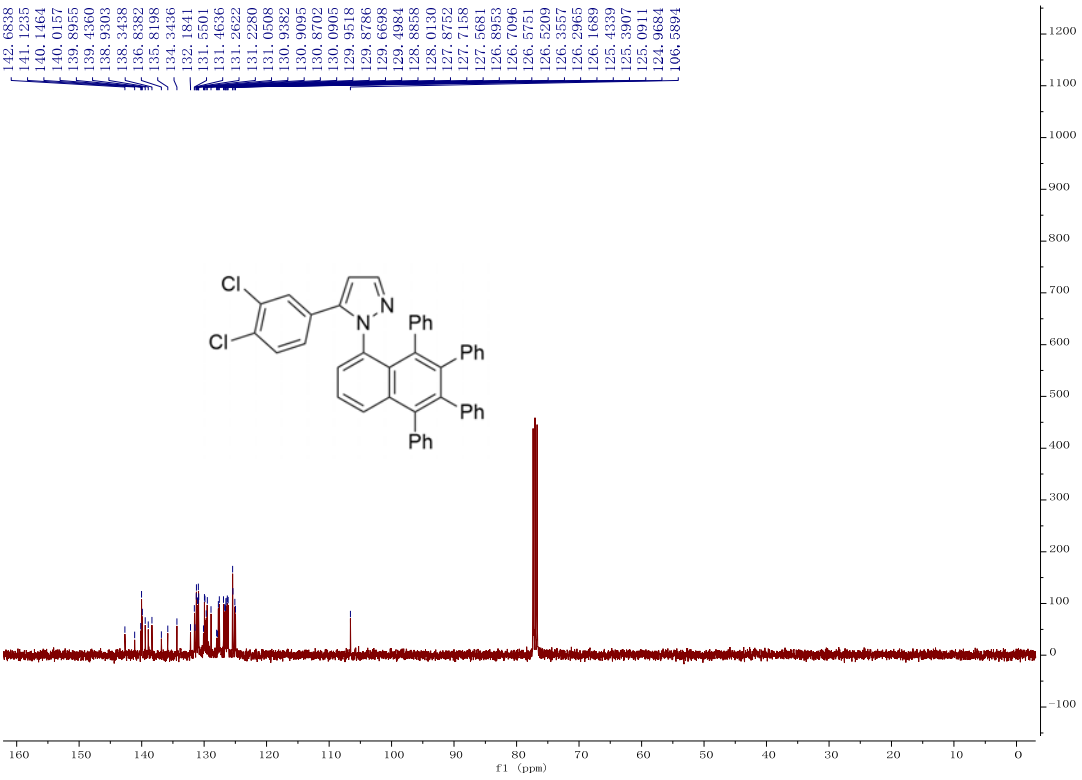
^{1}H NMR spectrum of **4k** (400 MHz, $CDCl_3$)



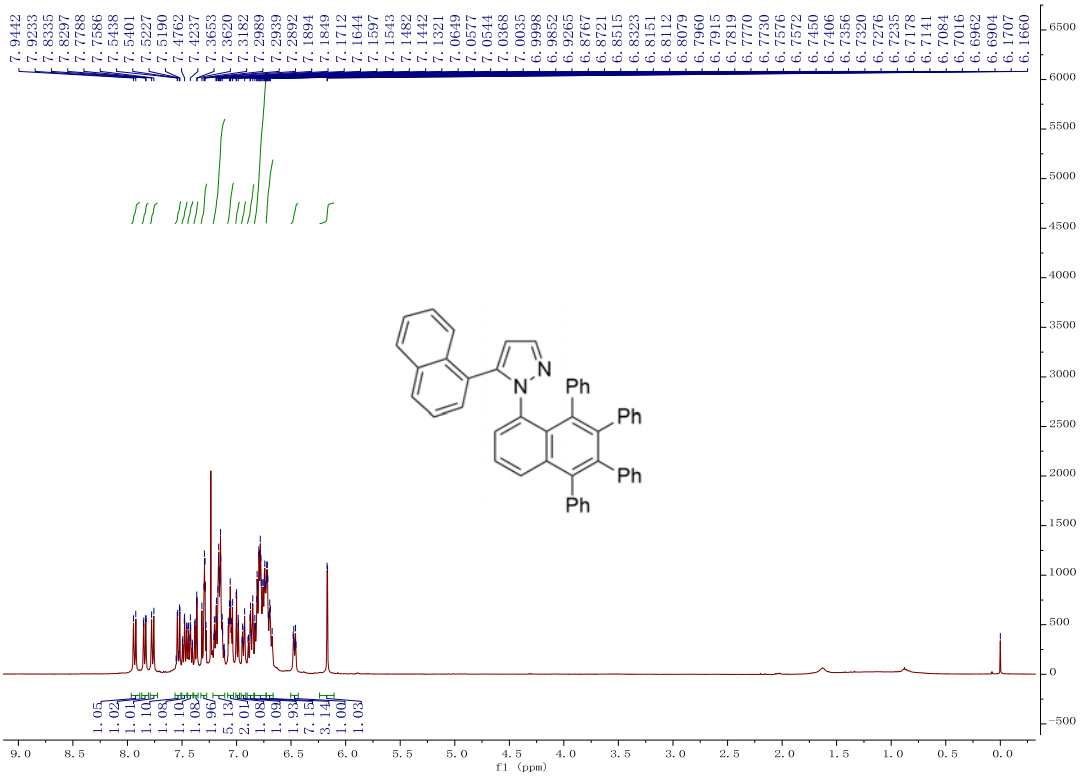
^{13}C NMR spectrum of **4k** (100 MHz, $CDCl_3$)



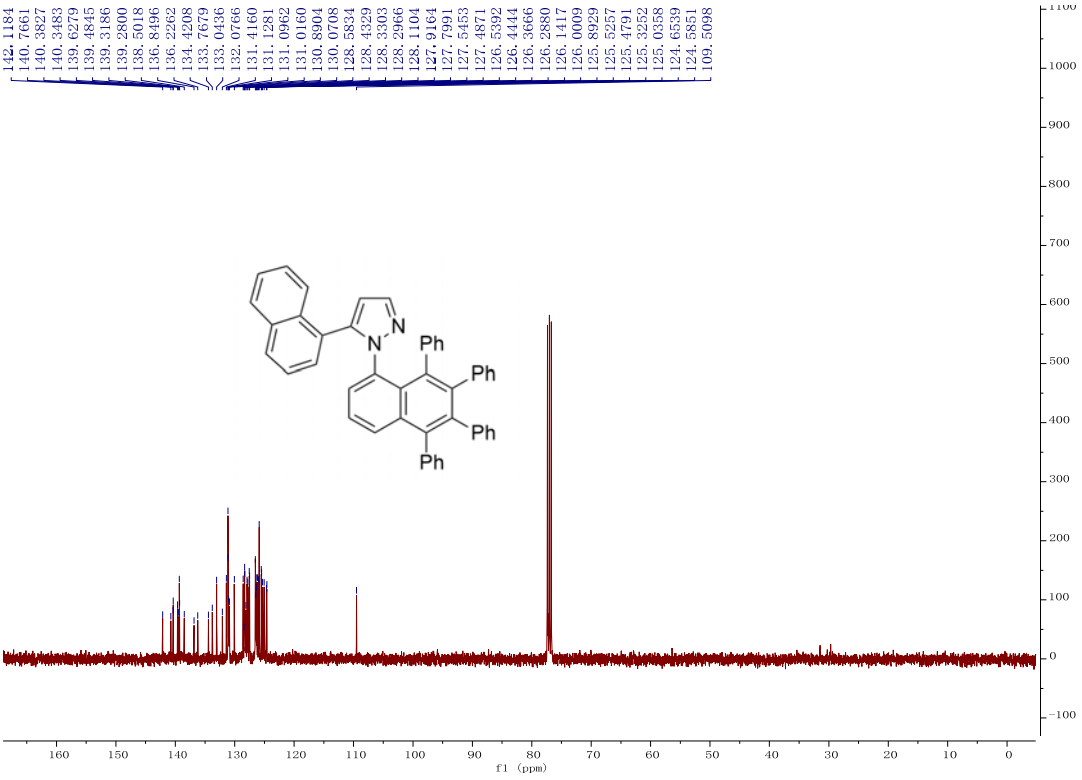
^{1}H NMR spectrum of **4l** (400 MHz, $CDCl_3$)



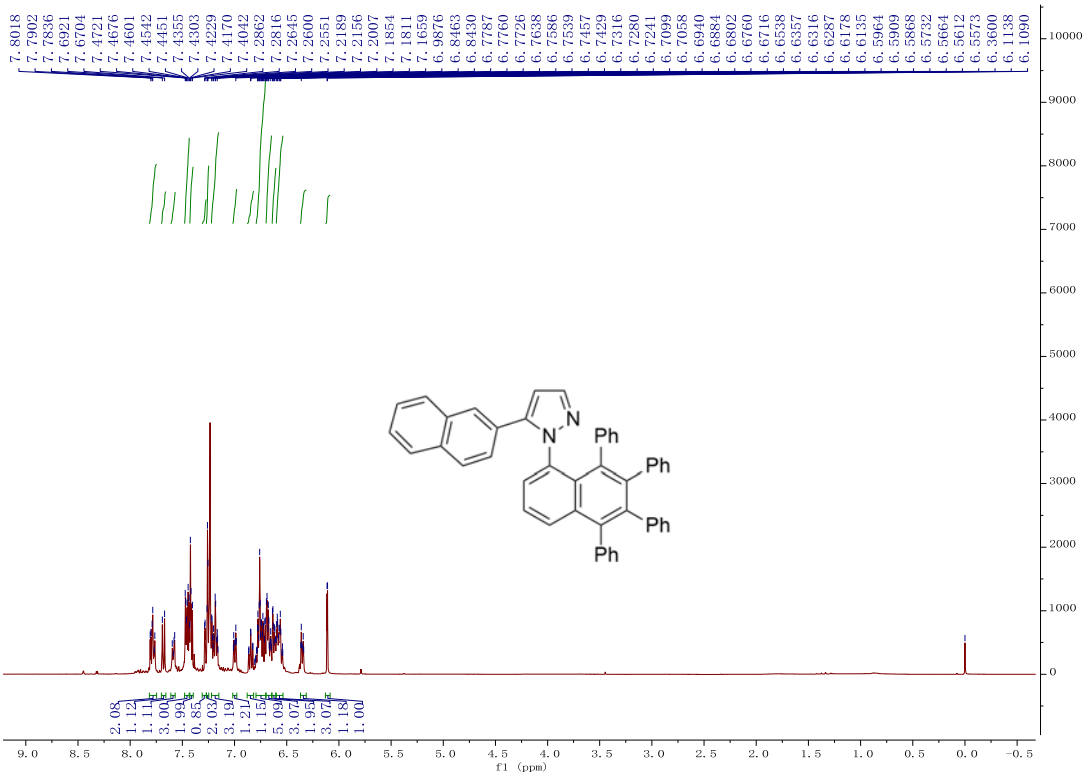
^{13}C NMR spectrum of **4l** (100 MHz, $CDCl_3$)



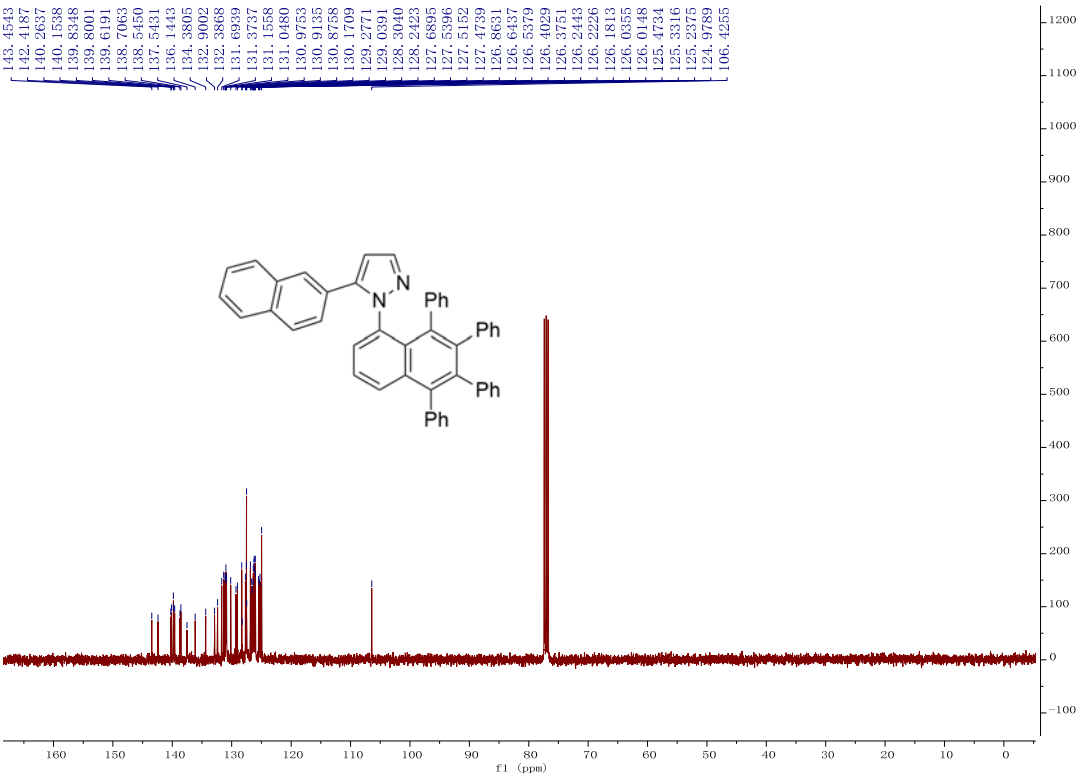
^{1}H NMR spectrum of **4m** (400 MHz, $CDCl_3$)



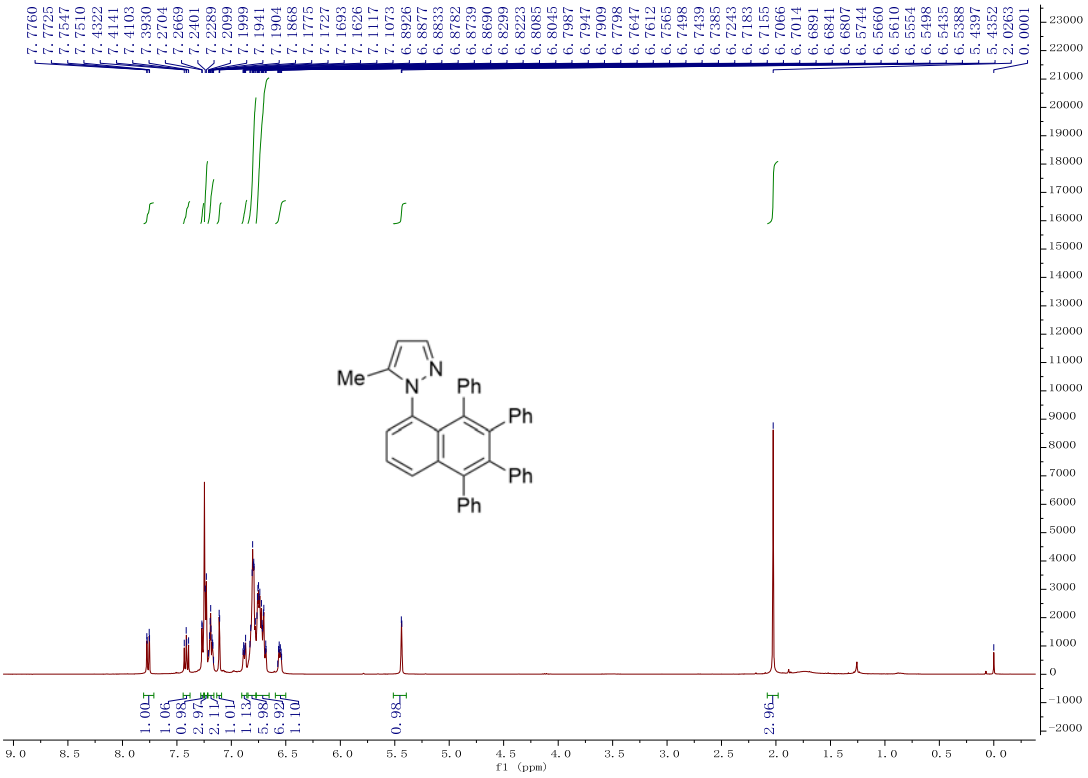
^{13}C NMR spectrum of **4m** (100 MHz, $CDCl_3$)



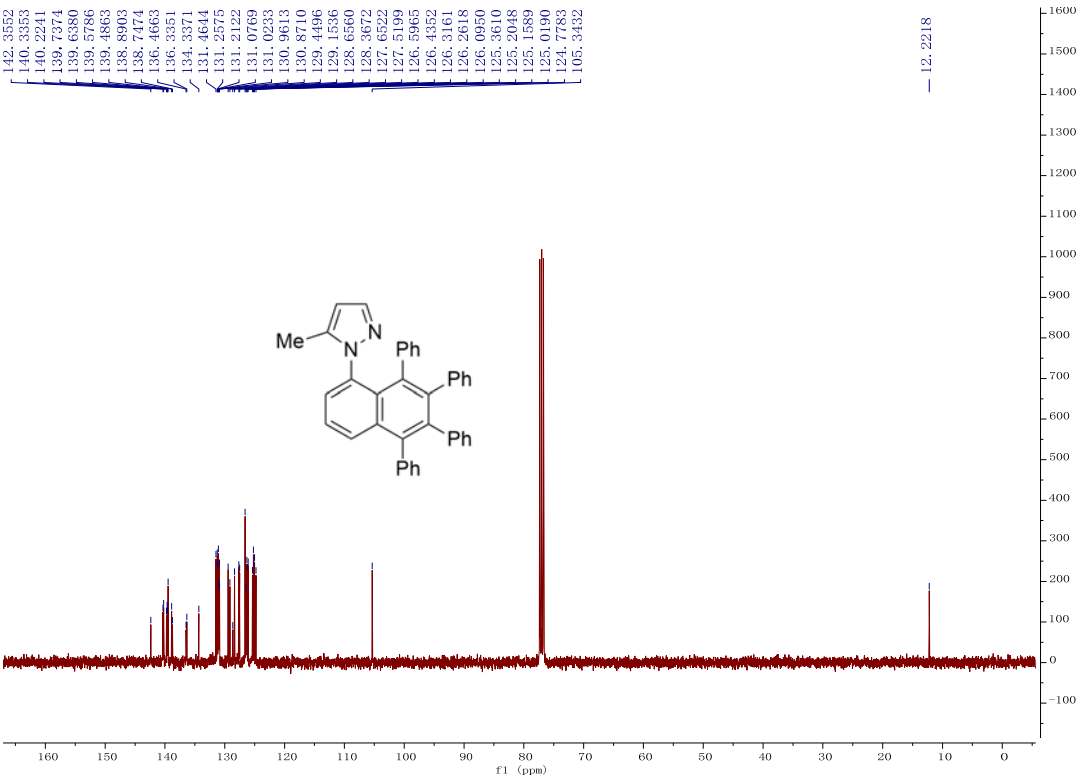
^{1}H NMR spectrum of **4n** (400 MHz, $CDCl_3$)



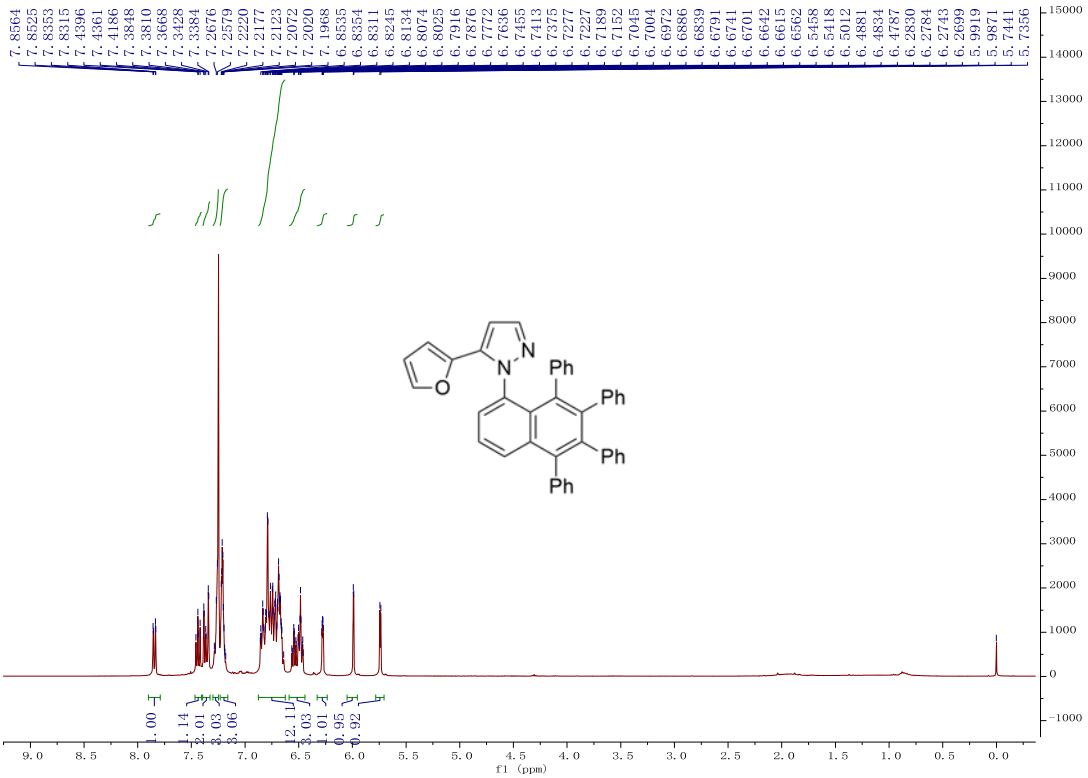
^{13}C NMR spectrum of **4n** (100 MHz, $CDCl_3$)



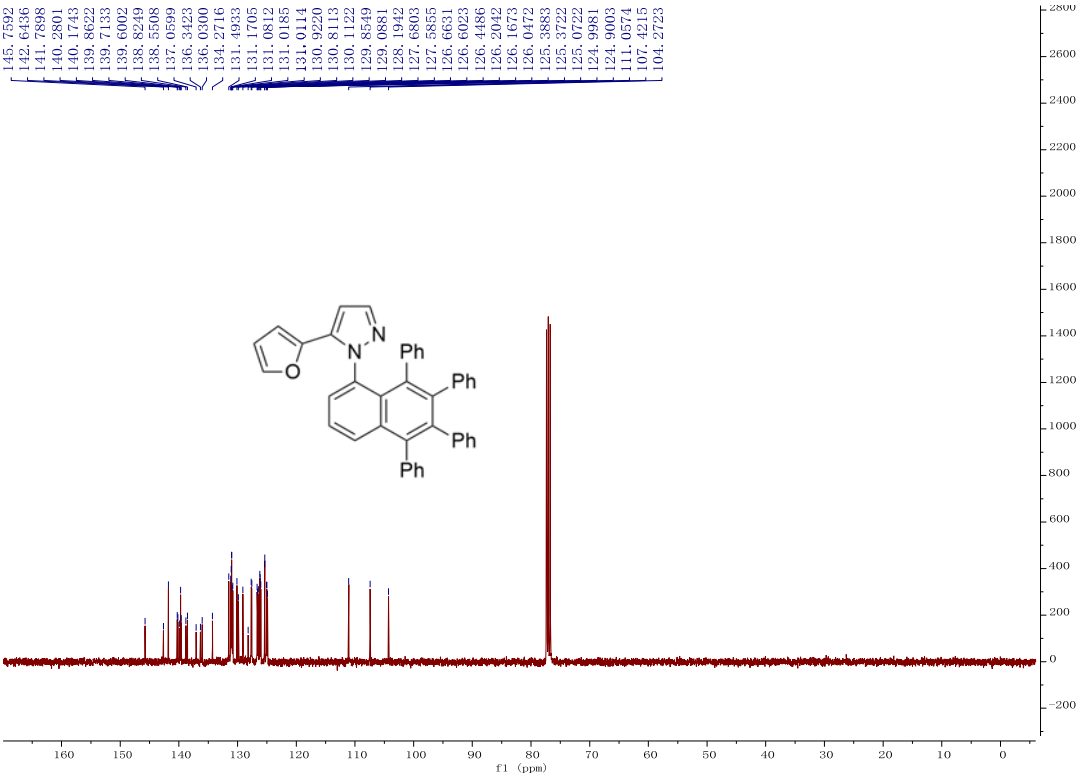
^{1}H NMR spectrum of **4o** (400 MHz, $CDCl_3$)



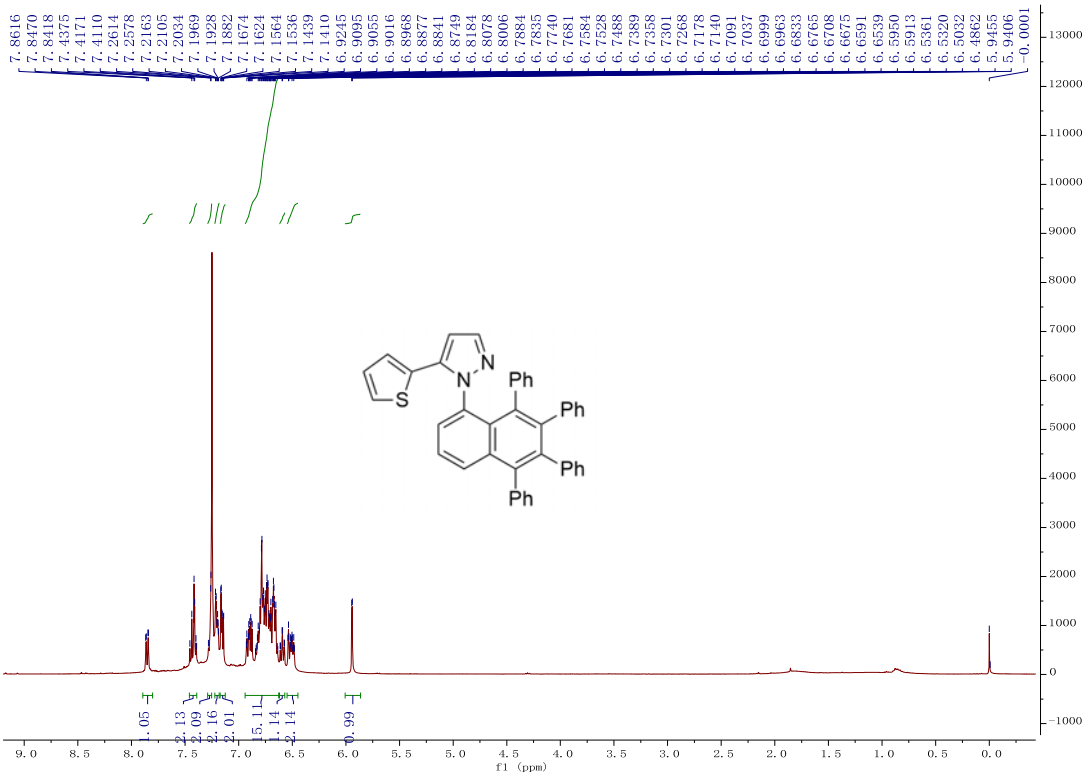
^{13}C NMR spectrum of **4o** (100 MHz, $CDCl_3$)



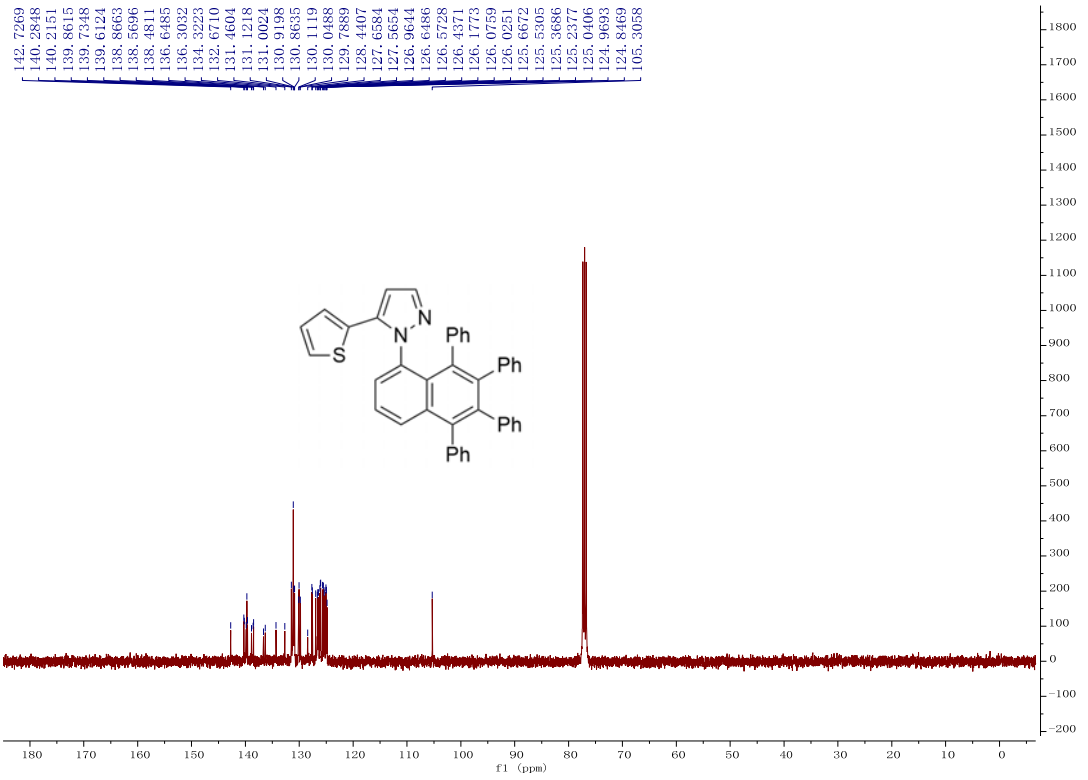
^{1}H NMR spectrum of **4p** (400 MHz, $CDCl_3$)



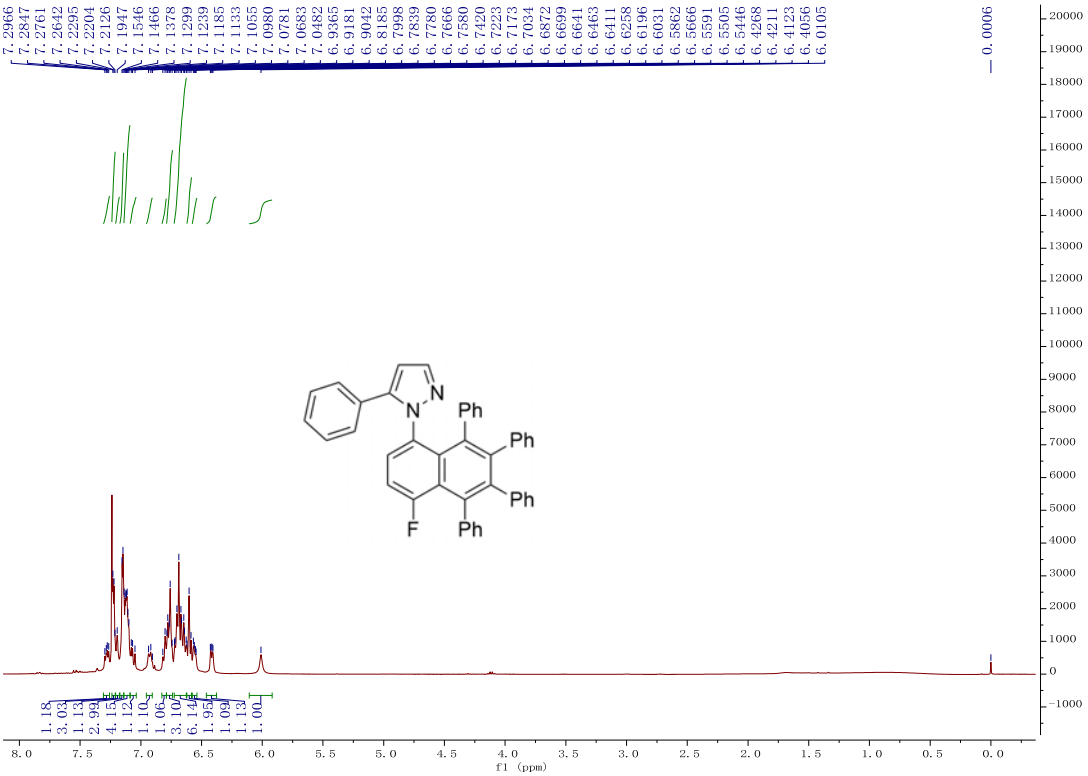
^{13}C NMR spectrum of **4p** (100 MHz, $CDCl_3$)



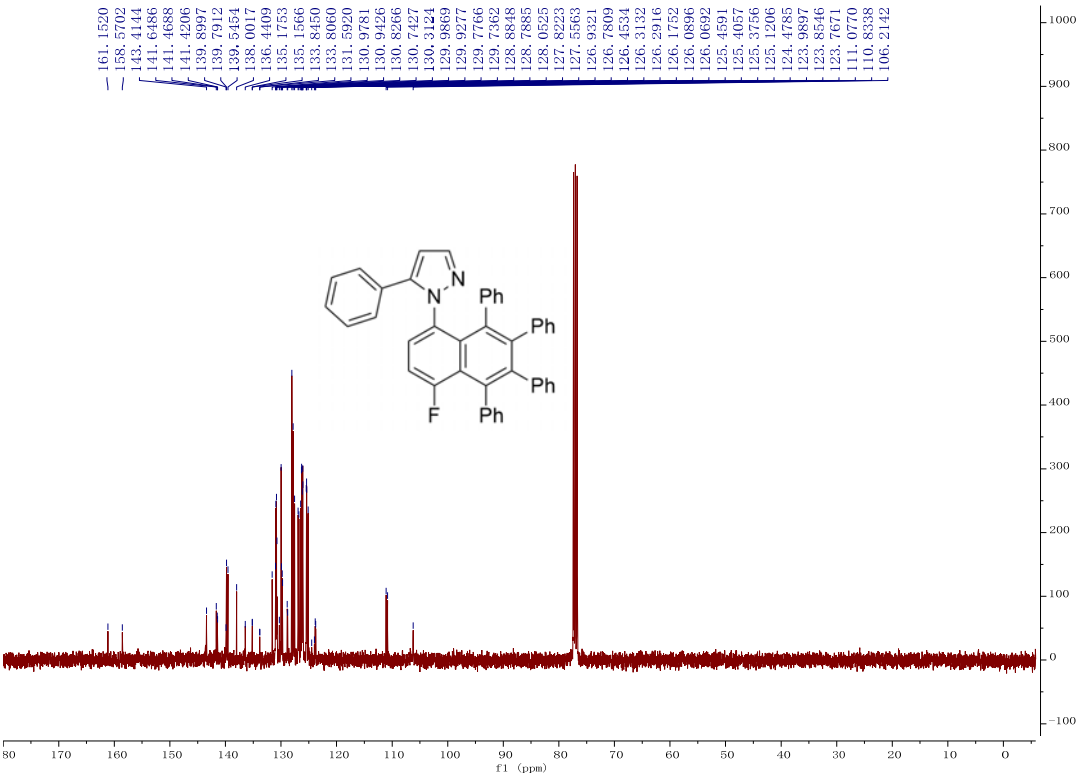
^{1}H NMR spectrum of **4q** (400 MHz, $CDCl_3$)



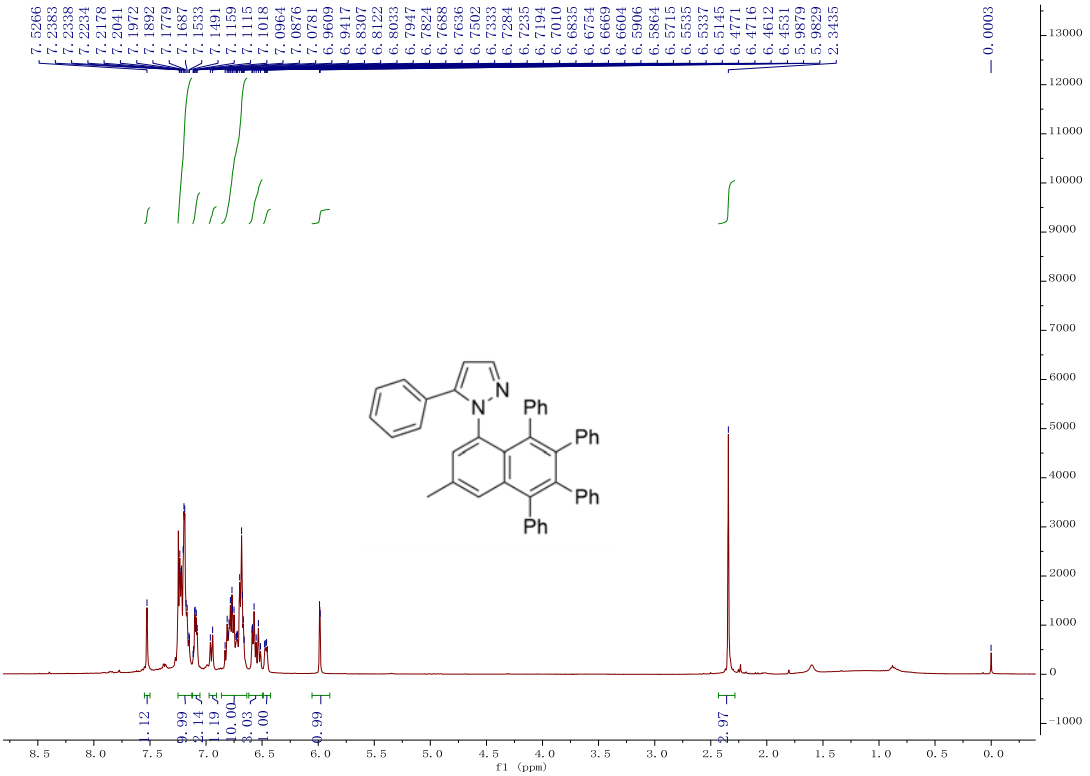
^{13}C NMR spectrum of **4q** (100 MHz, $CDCl_3$)



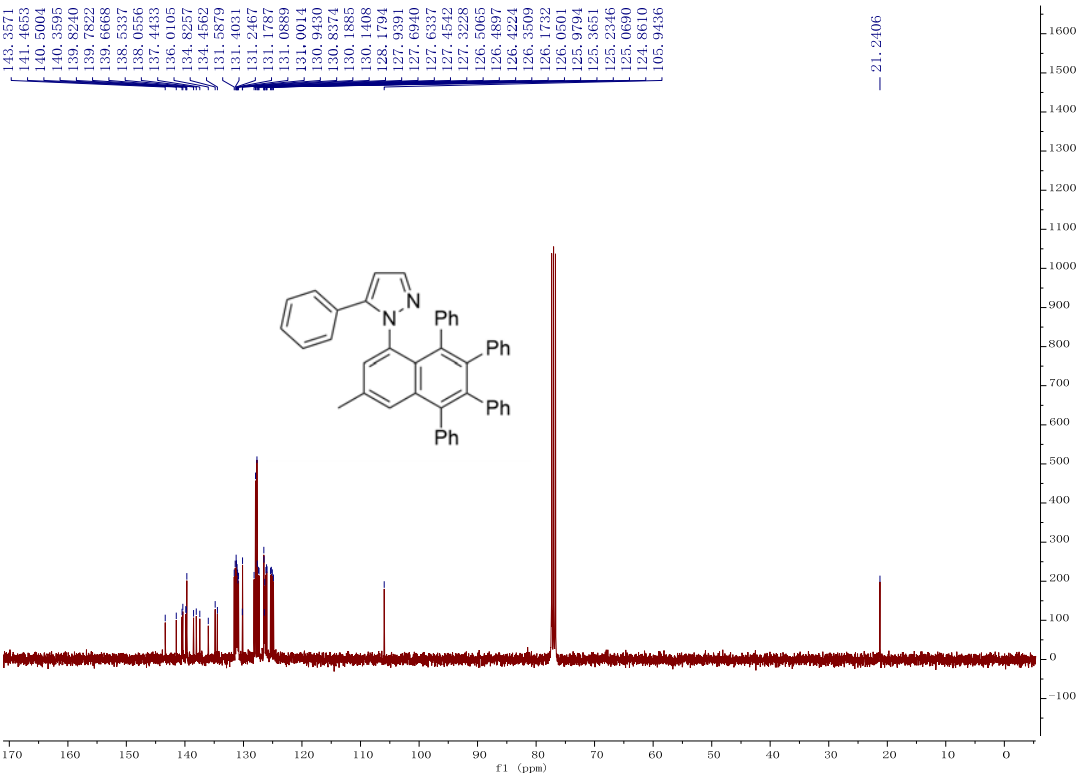
^{1}H NMR spectrum of **4aa** (400 MHz, $CDCl_3$)



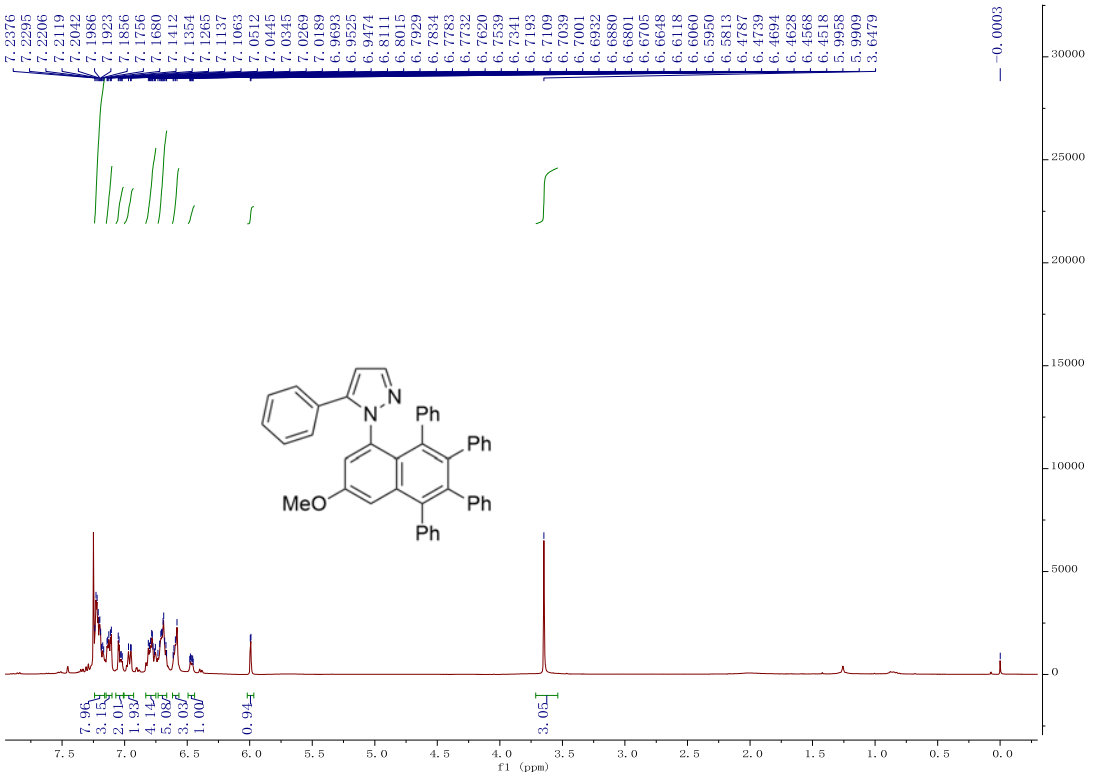
^{13}C NMR spectrum of **4aa** (100 MHz, $CDCl_3$)



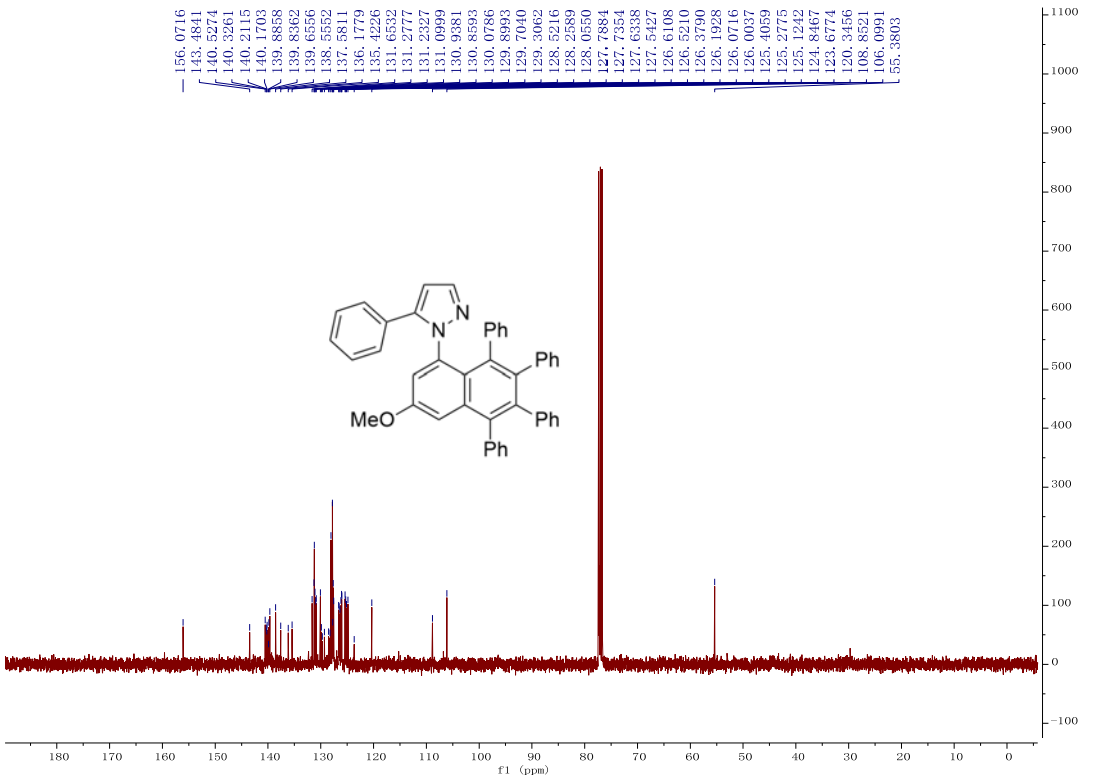
^{1}H NMR spectrum of **4ab** (400 MHz, $CDCl_3$)



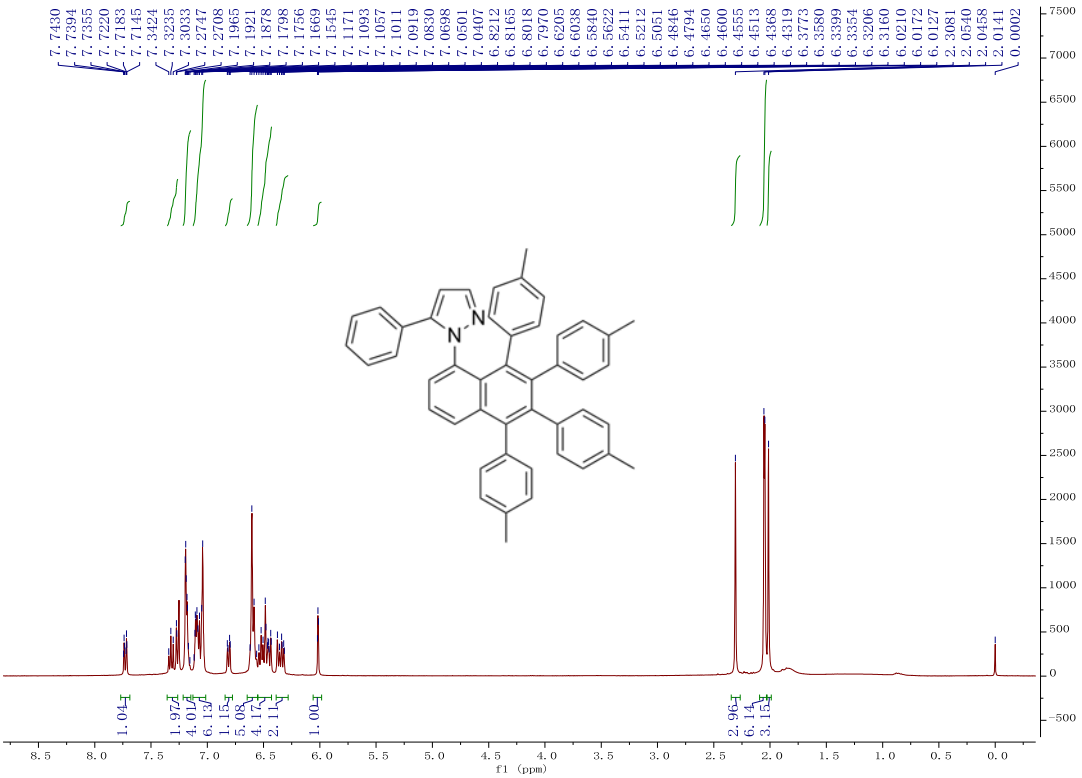
^{13}C NMR spectrum of **4ab** (100 MHz, $CDCl_3$)



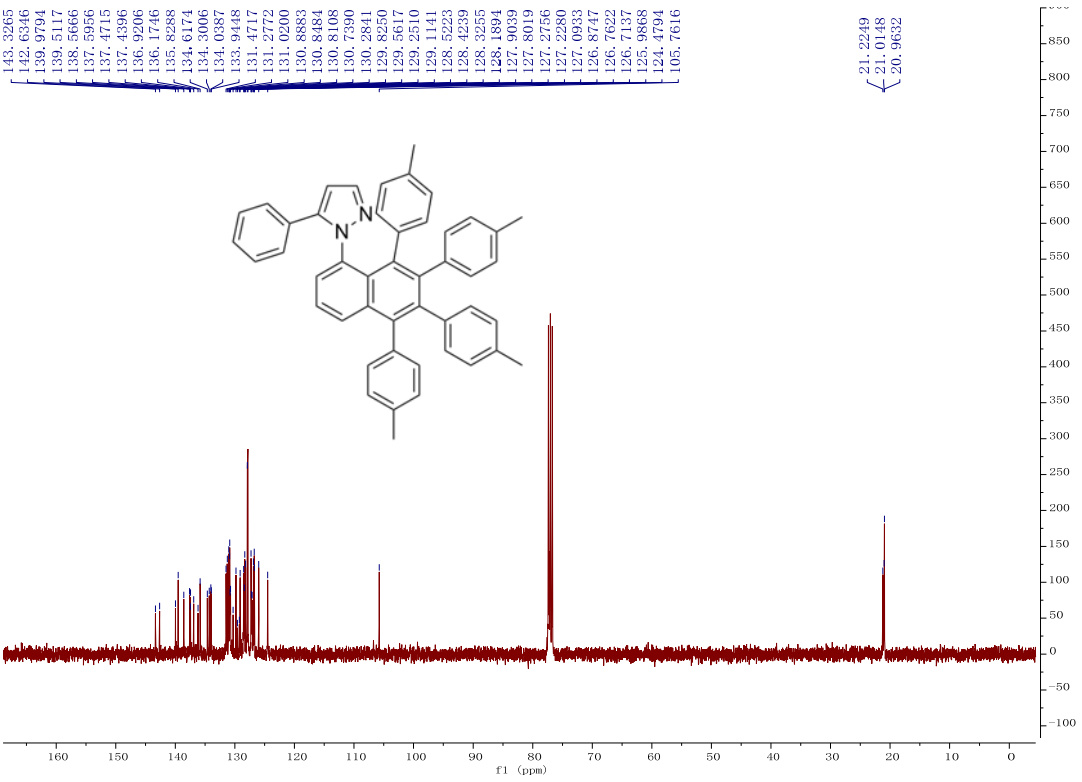
^{1}H NMR spectrum of **4ac** (400 MHz, $CDCl_3$)



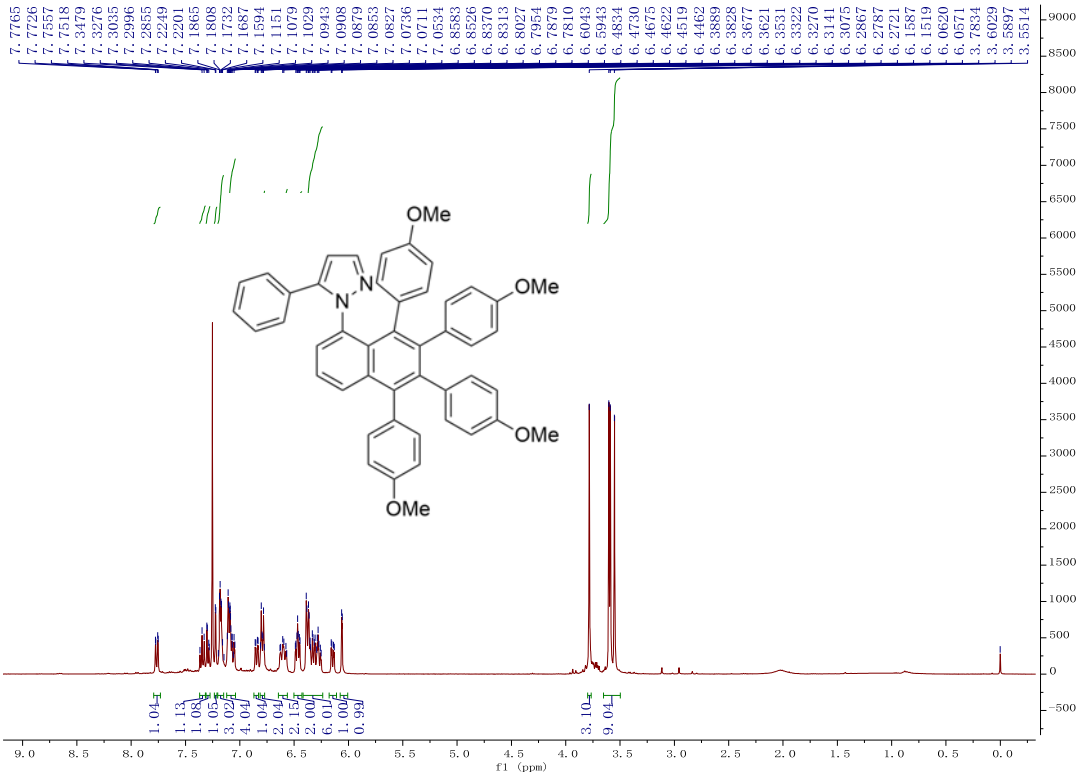
^{13}C NMR spectrum of **4ac** (100 MHz, $CDCl_3$)



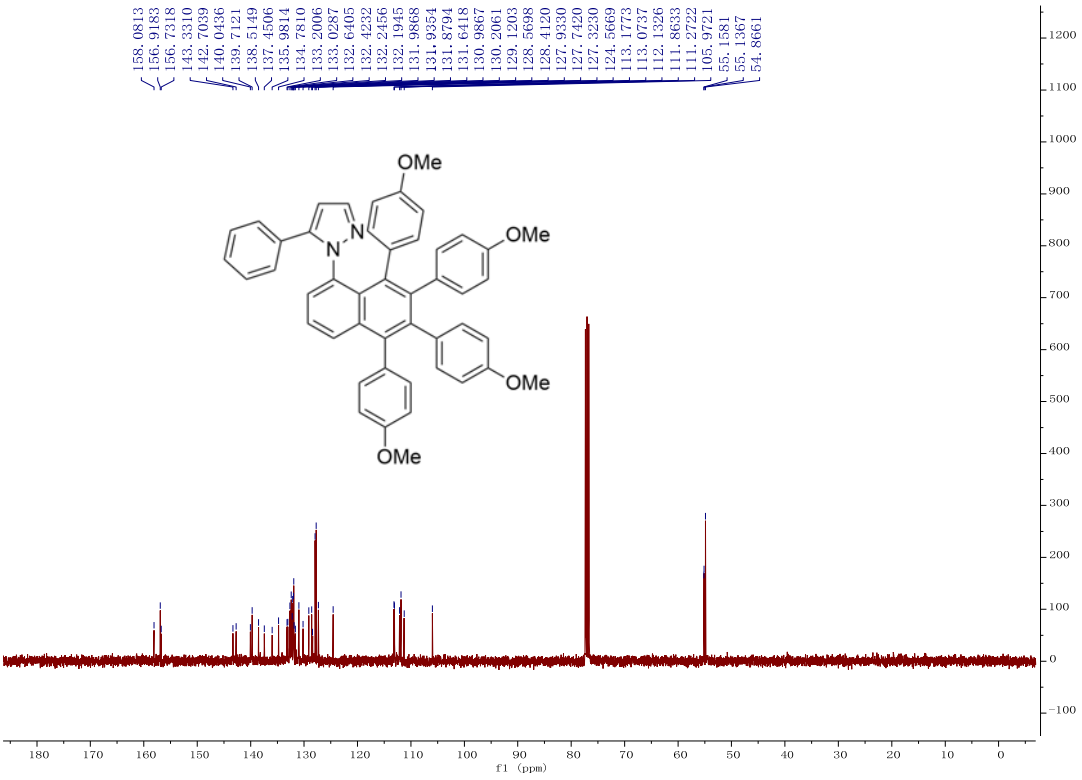
^{1}H NMR spectrum of **4ad** (400 MHz, $CDCl_3$)



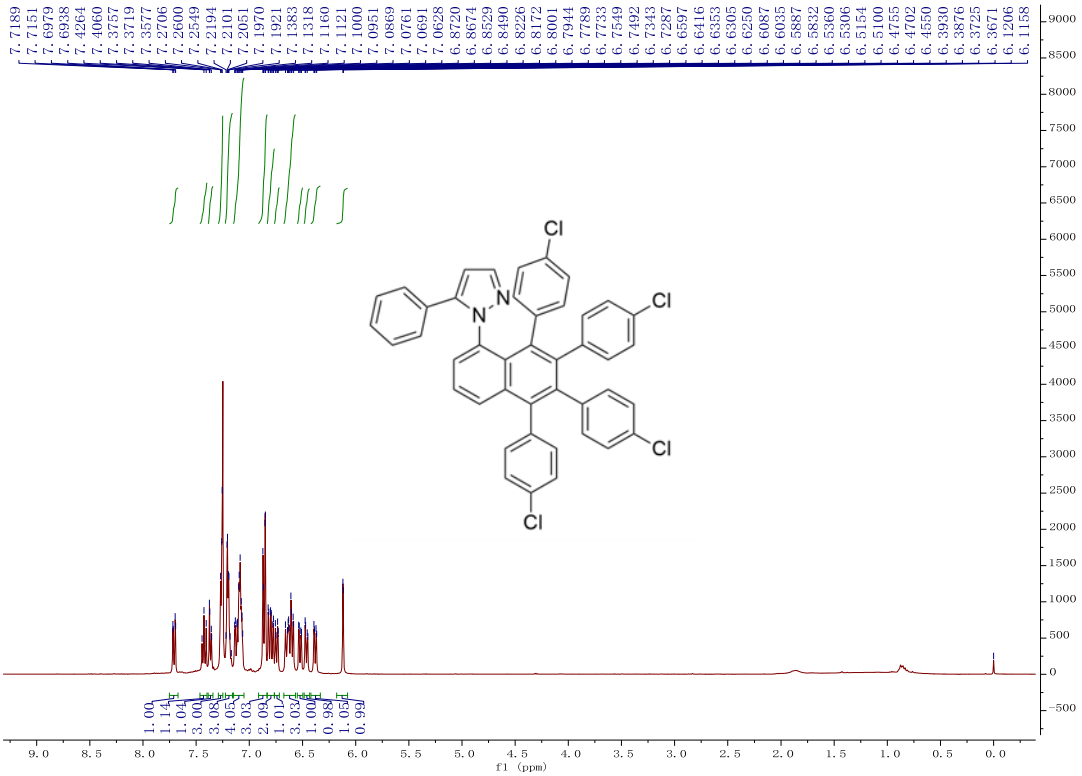
^{13}C NMR spectrum of **4ad** (100 MHz, $CDCl_3$)



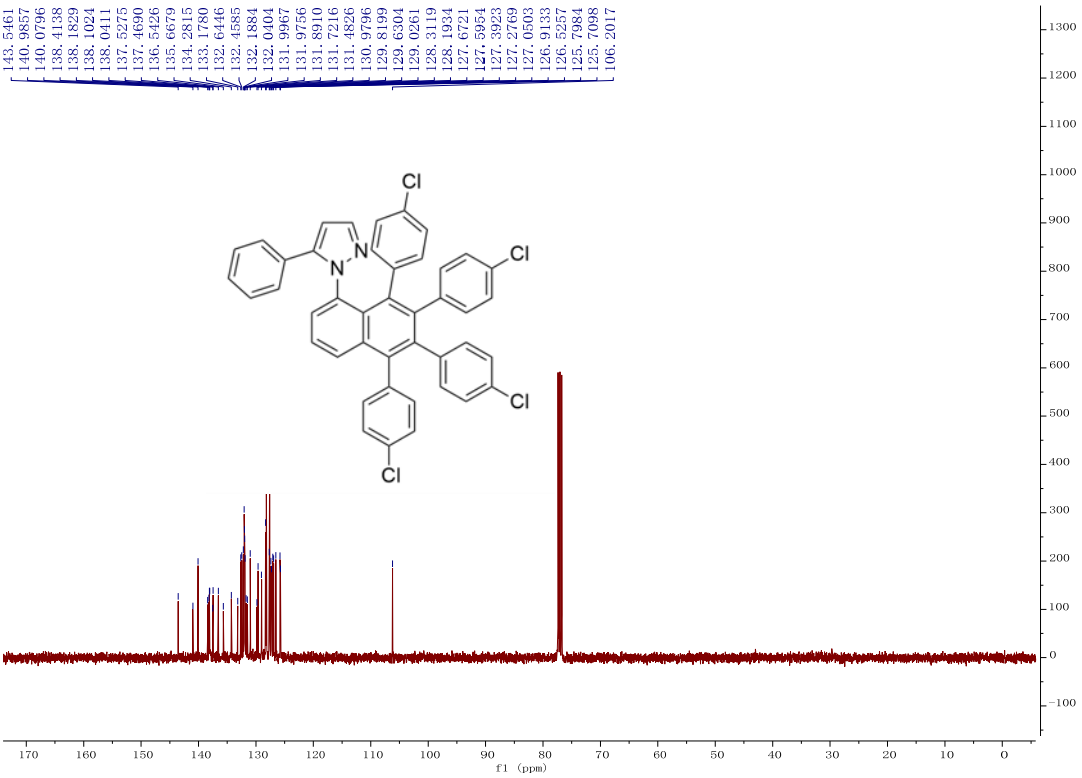
^{1}H NMR spectrum of **4ae** (400 MHz, $CDCl_3$)



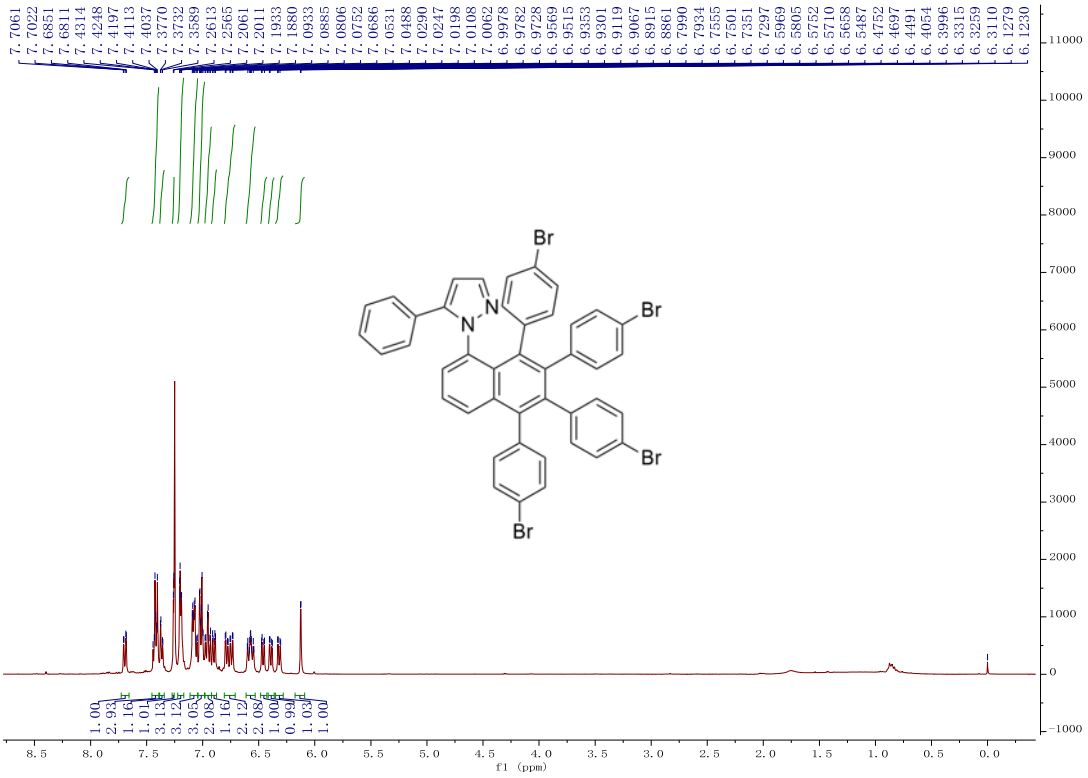
^{13}C NMR spectrum of **4ae** (100 MHz, $CDCl_3$)



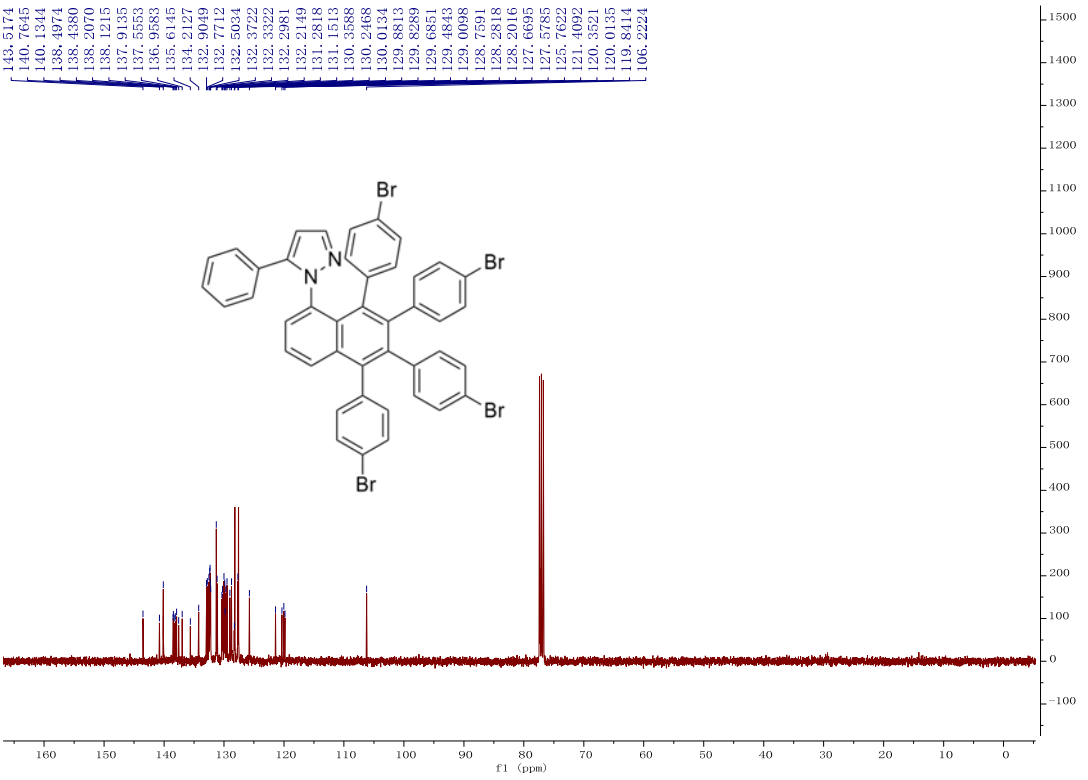
^{1}H NMR spectrum of **4af** (400 MHz, $CDCl_3$)



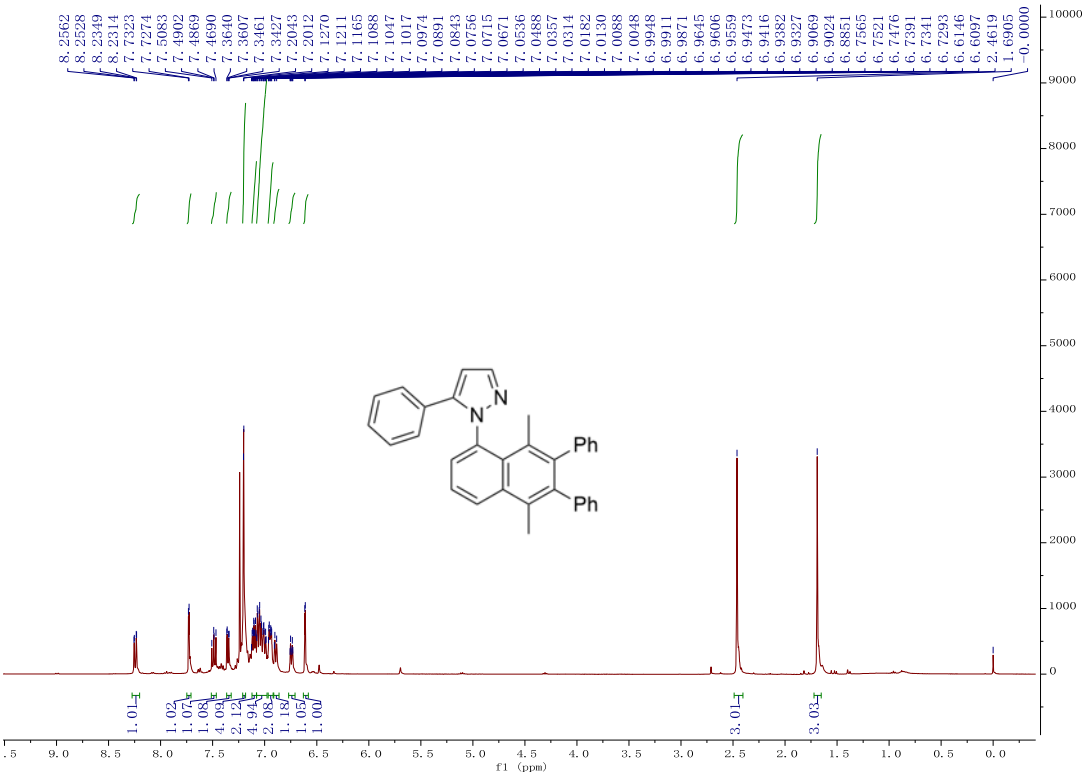
^{13}C NMR spectrum of **4af** (100 MHz, $CDCl_3$)



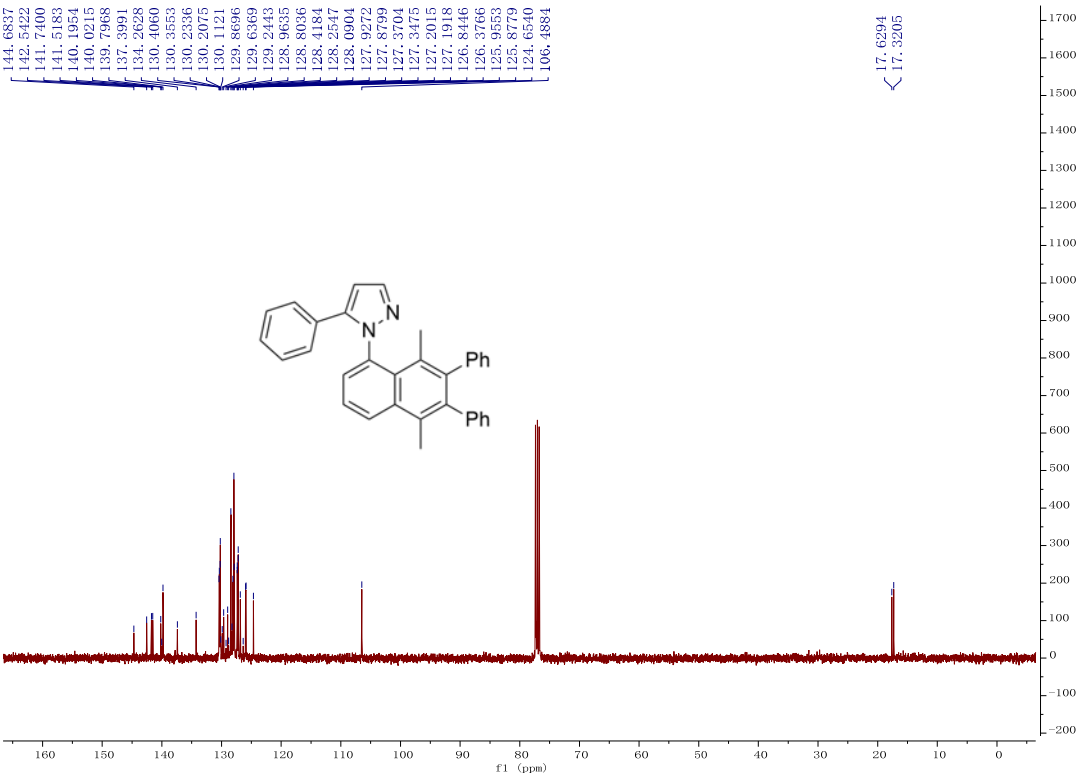
^{1}H NMR spectrum of **4ag** (400 MHz, $CDCl_3$)



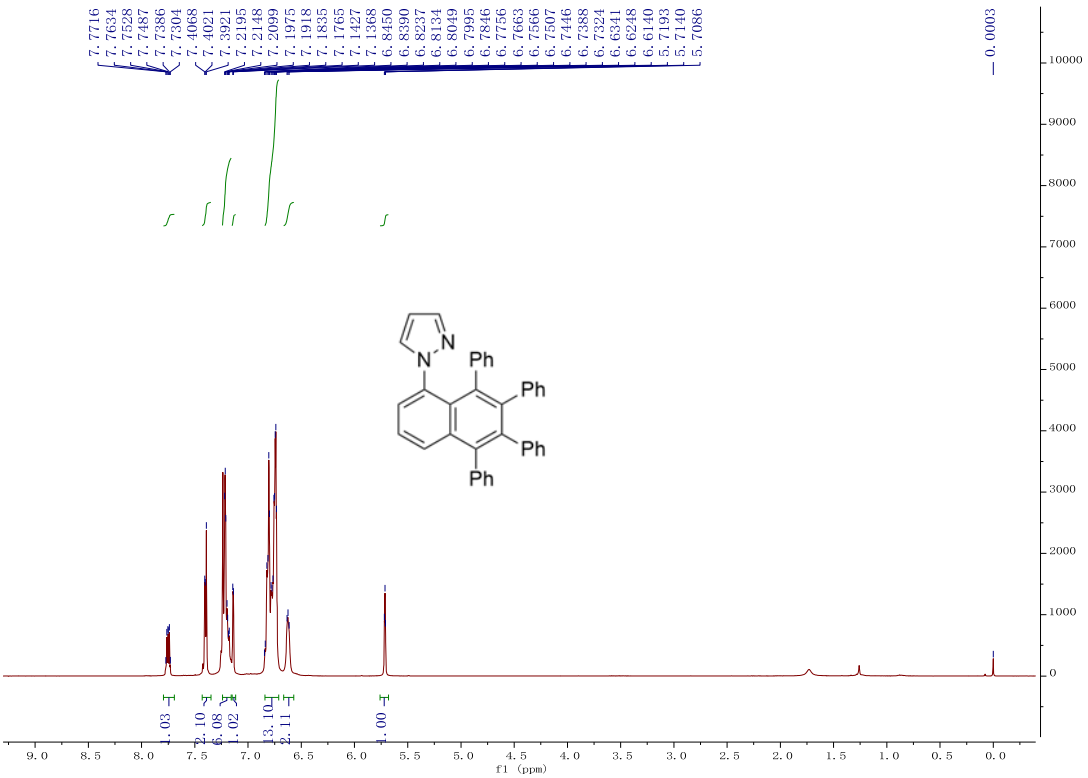
^{13}C NMR spectrum of **4ag** (100 MHz, $CDCl_3$)



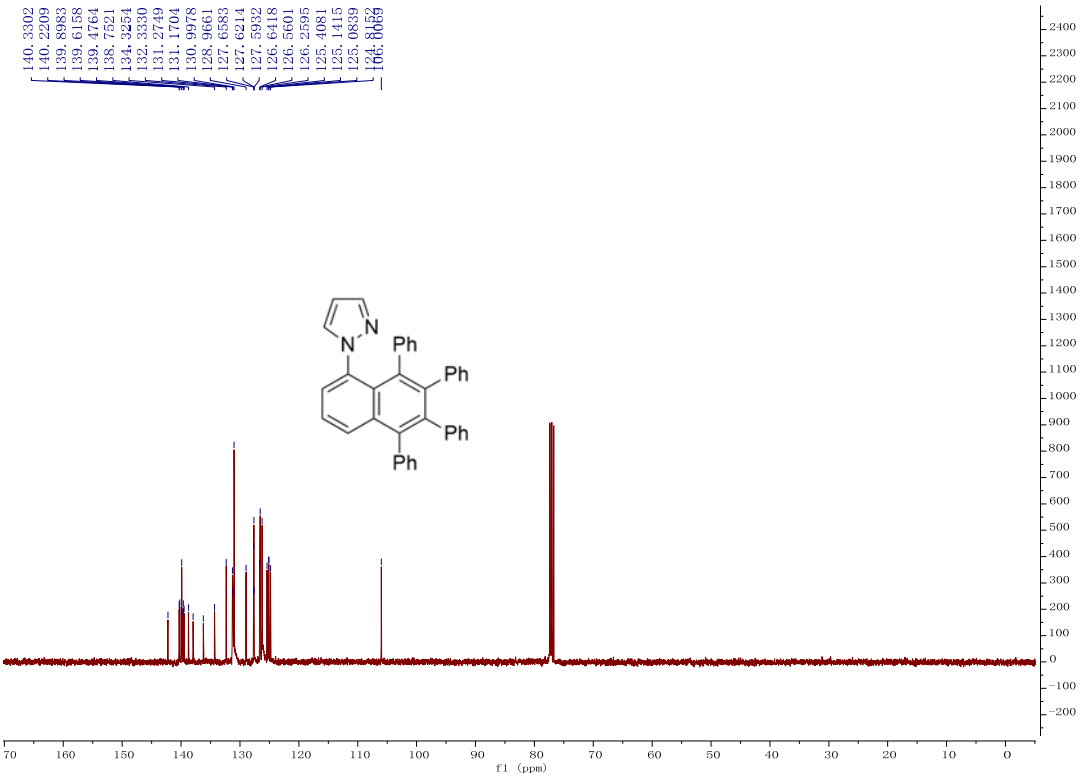
^{1}H NMR spectrum of **4ah** (400 MHz, $CDCl_3$)



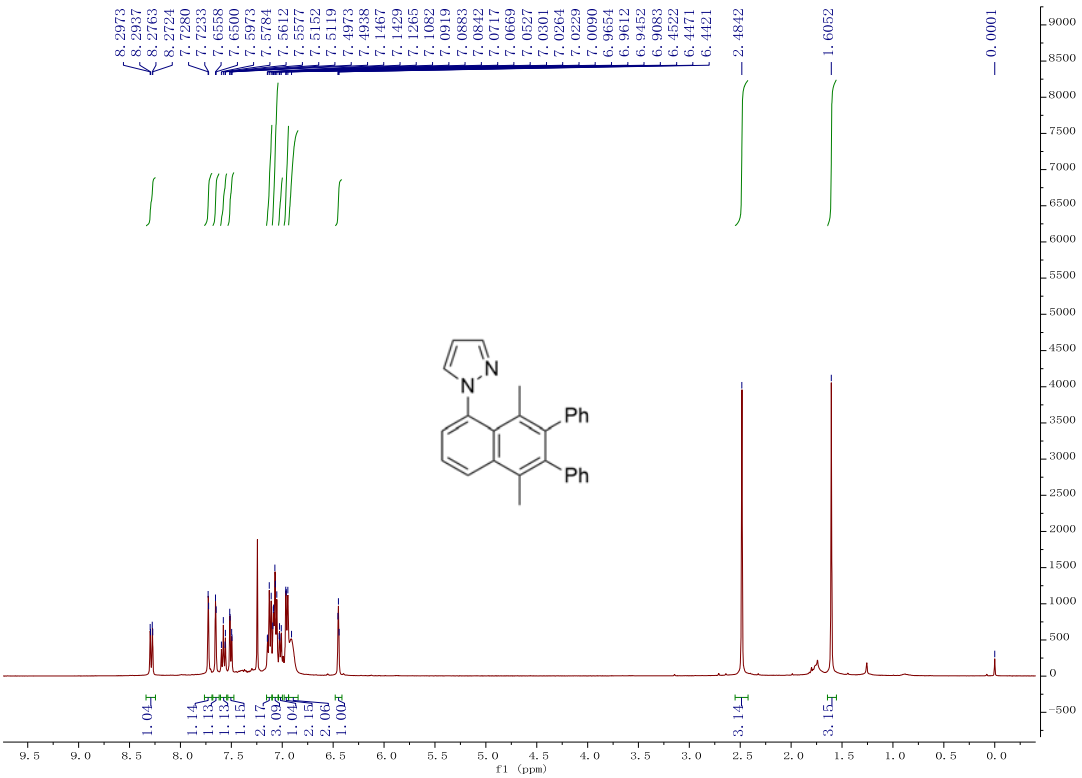
^{13}C NMR spectrum of **4ah** (100 MHz, $CDCl_3$)



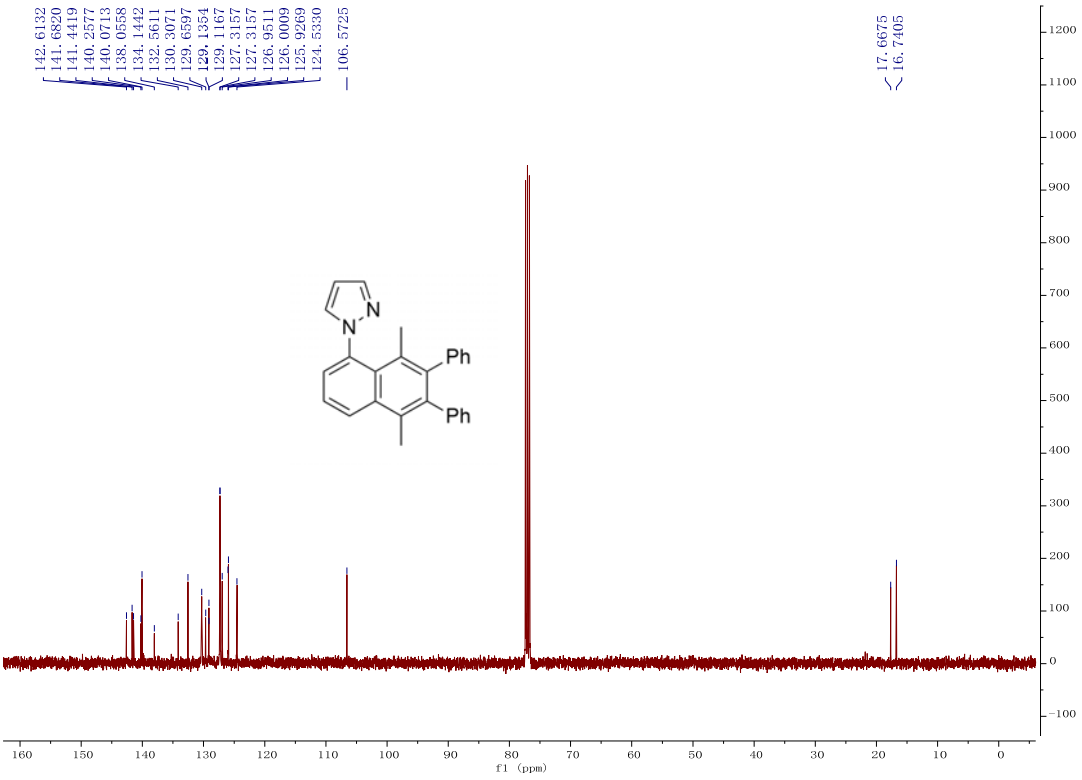
^{1}H NMR spectrum of **6a** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **6a** (100 MHz, $CDCl_3$)



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



^{13}C NMR spectrum of **6b** (100 MHz, $CDCl_3$)