Supporting Information

Electrochemical synthesis of dipyrazolo/dipyrimidine-fused pyridines via oxidative domino cyclization of C(sp3)–H bonds

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General Information:

All products were characterized by ^{1}H NMR and ^{13}C NMR, using TMS as an internal reference (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz). HRMS (ESI) data were recorded on a Q-TOF Premier. Flash column chromatography was performed using silica gel (200-300 mesh). All the compounds **1**, **2**, **4** and **6** were purchased from commercial supplies and used without purification.

Experimental Section

Representative Procedures for the Synthesis of 3 (3aa as an Example): An undivided cell was equipped with a magnet stirrer, two platinum plates (1.0 x 1.0 cm^2) electrodes as the working electrode and counter electrode (as shown in Figure S1). In the electrolytic cell, a mixture of 2-methylquinoline **1a** (0.3 mmol, 43.0 mg, 1.0 equiv), 3-methyl-1-phenyl-1H-pyrazol-5-amine **2a** (0.60 mmol, 103.9 mg, 2.0 equiv), NH_4I (0.3 mmol, 43.5 mg, 1.0 equiv), DMF (3.0 mL) was allowed to stir and electrolyze at a constant current conditions (10 mA) at oil bath (120 ^{o}C) (the electrolysis setup is shown in Figure S2). After the reaction was completed (15 h), 30 mL water was added and extracted with EtOAc 3 times (3×30 mL). The extract was dried over anhydrous Na_2SO_4. Then the solvent was removed with a rotary evaporator and the residue was purified by column chromatography on silica gel to afford the desired product **3aa** (117.0 mg, 84%). The product was dried under high vacuum for at least 0.5 h before it was weighed and characterized by NMR spectroscopy.

Representative Procedures for the Synthesis of 5 (5aa as an Example): An undivided cell was equipped with a magnet stirrer, two platinum plates (1.0 x 1.0 cm^2) electrodes as the working electrode and counter electrode. In the electrolytic cell, a mixture of 2-methylquinoline **1a** (0.3 mmol, 43.0 mg, 1.0 equiv), 6-amino-1,3-dimethylpyrimidine-2,4(1H,3H)-dione **4a** (0.6 mmol, 93.1 mg, 2.0 equiv), NH_4I (0.3 mmol, 43.5 mg, 1.0 equiv), DMF (3.0 mL) was allowed to stir and electrolyze at a constant current conditions (10 mA) at oil bath (120 ^{o}C). After the reaction was completed (15 h), 30 mL water was added and extracted with EtOAc 3 times (3×30 mL). The extract was dried over anhydrous Na_2SO_4. Then the solvent was removed with a rotary evaporator and the residue was purified by column chromatography on silica gel to afford the desired product **5aa** (105.0 mg, 81%). The product was dried under high vacuum for at least 0.5 h before it was weighed and characterized by NMR spectroscopy.

Representative Procedures for the Synthesis of 7 (7aa as an Example): An undivided cell was equipped with a magnet stirrer, two platinum plates (1.0 x 1.0 cm^2) electrodes as the working electrode and counter electrode. In the electrolytic cell, a mixture of acetophenone **6a** (0.3 mmol, 3.0 mg, 1.0 equiv), 3-methyl-1-phenyl-1H-pyrazol-5-amine **2a** (0.60 mmol, 103.9 mg, 2.0 equiv.), NH_4I (0.3 mmol, 43.5 mg, 1.0 equiv), DMF (3.0 mL) was allowed to stir and electrolyze at a constant current conditions (10 mA) at oil bath (130 ^oC). After the reaction was completed (15 h), 30 mL water was added and extracted with EtOAc 3 times (3×30 mL). The extract was dried over anhydrous Na_2SO_4. Then the solvent was removed with a rotary evaporator and the residue was purified by column chromatography on silica gel to afford the desired product **7aa** (110.0 mg, 83%). The product was dried under high vacuum for at least 0.5 h before it was weighed and characterized by NMR spectroscopy.

Procedure for the Synthesis of 3aa: An undivided cell was equipped with a magnet stirrer, two platinum plates (1.5 x 1.5 cm^2) electrodes as the working electrode and counter electrode. In the electrolytic cell, a mixture of 2-methylquinoline **1a** (4 mmol, 573 mg, 1.0 equiv), 3-methyl-1-phenyl-1H-pyrazol-5-amine **2a** (8 mmol, 1386 mg, 2.0 equiv), NH_4I (4 mmol, 579.8 mg, 1.0 equiv), DMF (40.0 mL) was allowed to stir and electrolyze at a constant current conditions (I = 23 mA, J = 10 mA/cm^2) at oil bath (120 ^oC). After the reaction was completed (about 3.7 days), 30 mL water was added and extracted with EtOAc 3 times (3×200 mL). The extract was dried over anhydrous Na_2SO_4. Then the solvent was removed with a rotary evaporator and the residue was purified by column chromatography on silica gel to afford the desired product **3aa** (1350 mg, 76%).

Photographic Depiction of the Electrolysis Setup (3aa as an Example):

Figure S1 Electrodes and electrolysis Cell

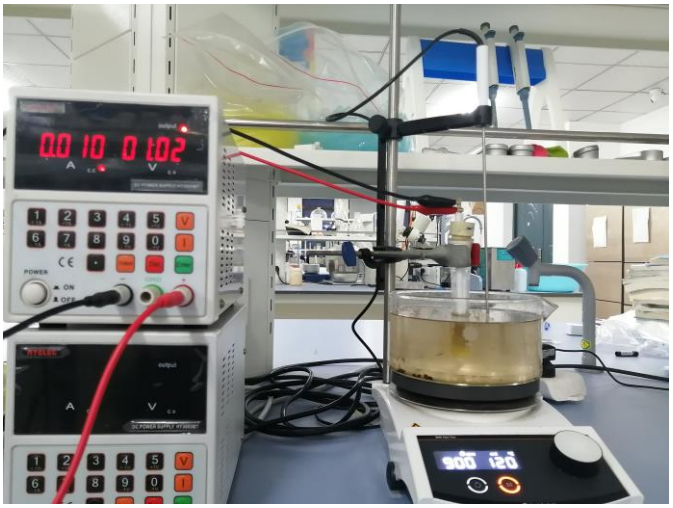


Figure S2 Electrolysis setup

Photoluminescence spectra of 3aa and 5aa

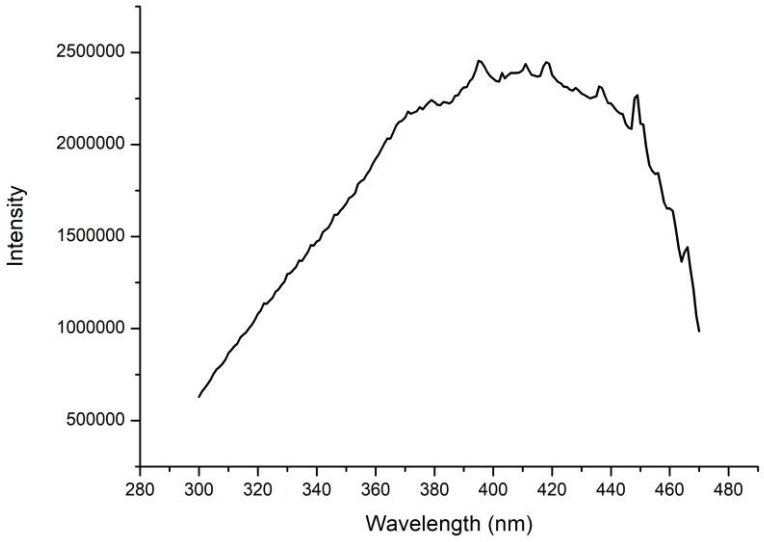


Figure S3 Photoluminescence absorption spectrum of **3aa** in solid powders

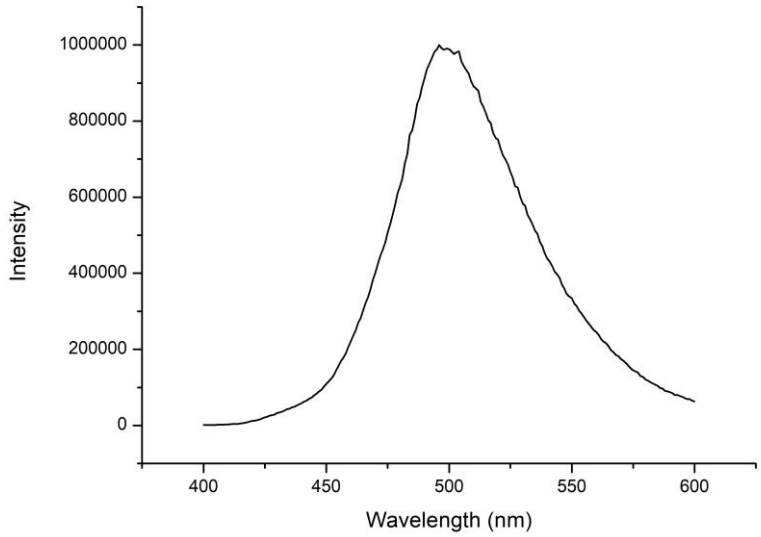


Figure S4 Photoluminescence emission spectrum of **3aa** in solid powders upon excitation at 418 nm

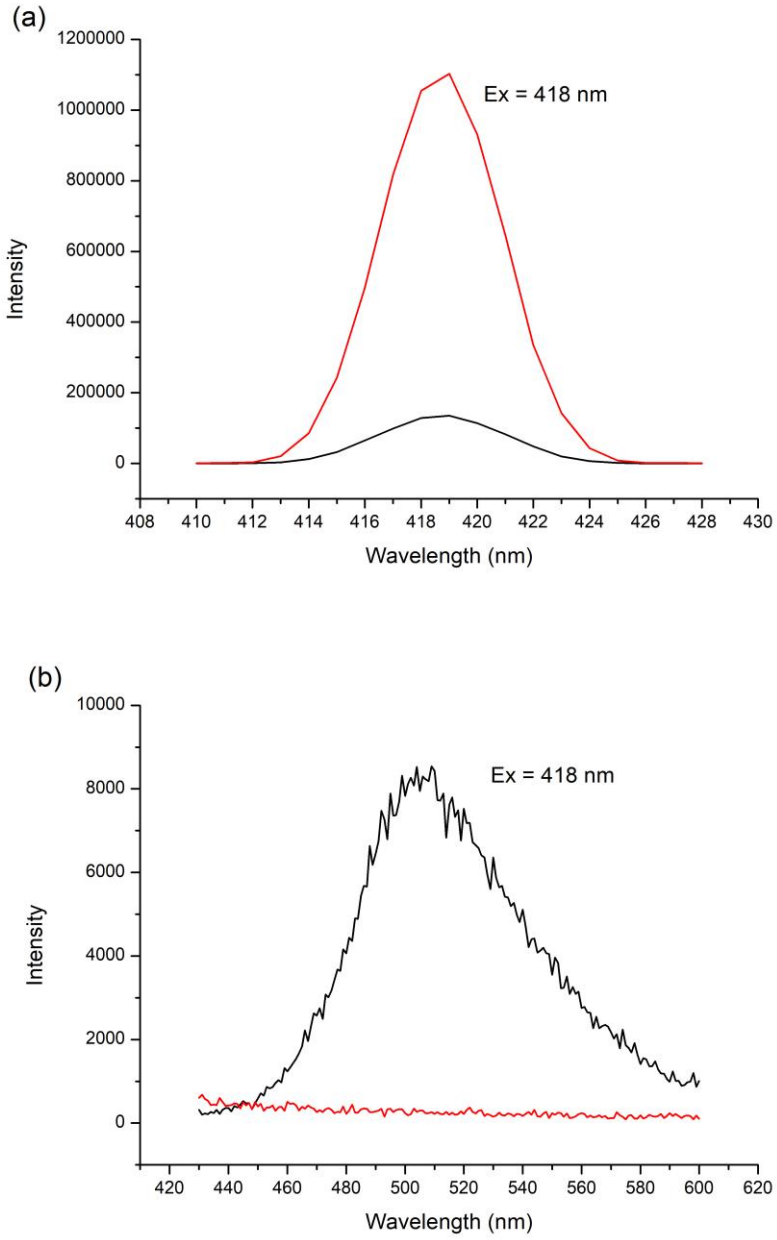


Figure S5 Photoluminescence (PL) quantum yield of **3aa**.

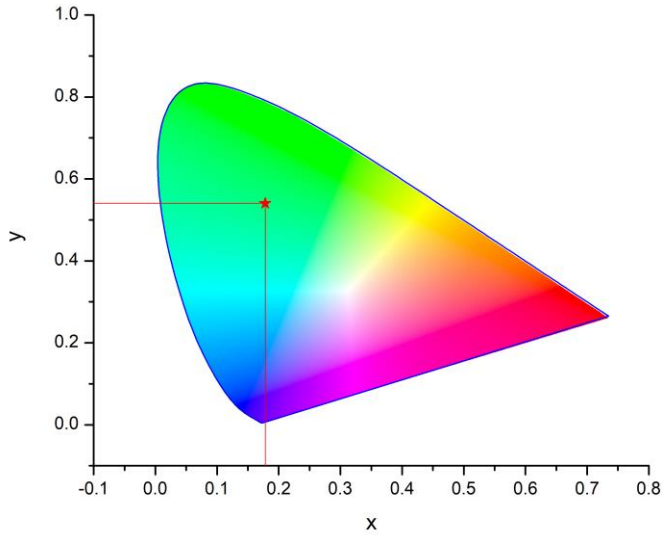


Figure S6 Chromaticity output (CIE 1931) of **3aa** (x = 0.17817, y = 0.54036).

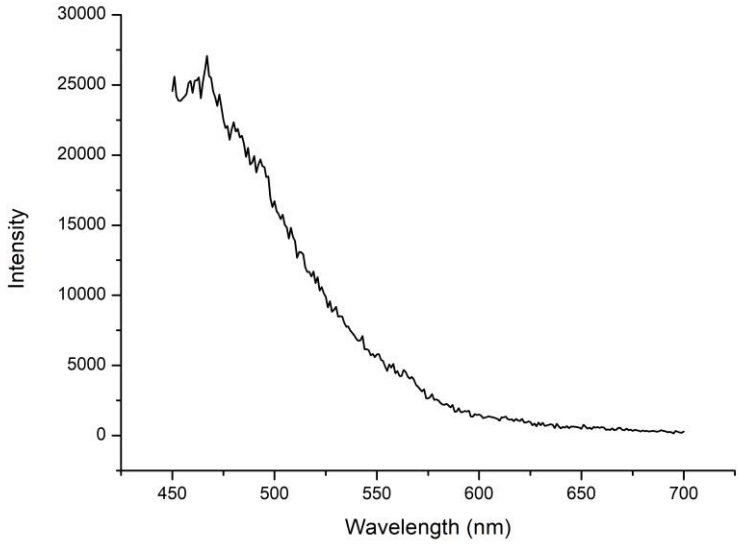


Figure S7 Photoluminescence emission spectrum of **5aa** in solid powders

Detail Descriptions for Products

3,5-Dimethyl-1,7-diphenyl-4-(quinolin-2-yl)-1,7-dihydrodipyrazolo[3,4-b:4',3'-e]pyridine (**3aa**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.23) to give the product

as a green solid: 84% yield, (117 mg); m.p. 227-230 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.44 – 8.42 (m, 5H), 8.25 (d, *J* = 7.2 Hz, 1H), 8.03 (d, *J* = 6.8 Hz, 1H), 7.91 – 7.87 (m, 1H), 7.76 – 7.71 (m, 2H), 7.58 – 7.54 (m, 4H), 7.33 – 7.29 (m, 2H), 2.07 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 153.5, 150.8, 147.5, 144.0, 139.6, 139.2, 136.3, 130.8, 129.8, 129.0, 127.9, 127.8, 127.5, 125.2, 122.1, 120.4, 113.1, 15.0. These data are in accordance with the literature. [1]

3,5-Dimethyl-4-(6-methylquinolin-2-yl)-1,7-diphenyl-1,7-dihydrodipyrazolo[3,4-b:4',3'-e]pyridine (**3ba**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.25) to give the product as a brown solid: 74% yield, (107 mg); m.p. 212-214 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.44 – 8.42 (m, 4H), 8.33 (d, *J* = 7.6 Hz, 1H), 8.13 (d, *J* = 8.8 Hz, 1H), 7.78 (s, 1H), 7.73 – 7.70 (m, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.58 – 7.54 (m, 4H), 7.33 – 7.31 (m, 2H), 2.65 (s, 3H), 2.07 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 152.5, 150.8, 146.1, 144.1, 139.6, 139.4, 137.9, 136.0, 133.1, 129.4, 129.0, 127.5, 126.7, 125.2, 122.0, 120.4, 113.2, 21.7, 14.9. These data are in accordance with the literature. [1]

4-(6-(tert-Butyl)quinolin-2-yl)-3,5-dimethyl-1,7-diphenyl-1,7-dihydrodipyrazolo[3,4-b:4',3'-e]pyridine (**3ca**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.30) to give the product as a yellow solid: 88% yield, (138 mg); m.p. 223-226 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.45 – 8.42 (m, 4H), 8.38 (d, *J* = 7.6 Hz, 1H), 8.18 (d, *J* = 8.8 Hz, 1H), 7.98 (dd, *J* = 9.2 Hz, *J* = 2.4 Hz, 1H), 7.92 – 7.91 (m, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.58 – 7.54 (m, 4H), 7.33 – 7.29 (m, 2H), 2.08 (s, 6H), 1.52 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 152.7, 150.8, 150.8, 146.0, 144.1, 139.6, 139.4, 136.3, 129.8, 129.2, 129.0, 127.3, 125.2, 122.8, 122.0, 120.4, 113.2, 35.1, 31.2, 15.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{31}N_6$ 523.2610; Found: 523.2608.

4-(6-Methoxyquinolin-2-yl)-3,5-dimethyl-1,7-diphenyl-1,7-dihydrodipyrazolo[3,4-b:4',3'-e]pyridine (**3da**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.15) to give the product as a white solid: 40% yield, (60 mg); m.p. 262-264℃; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.44 – 8.42 (m, 4H), 8.31 (d, *J* = 7.6 Hz, 1H), 8.13 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.58 – 7.52 (m, 5H), 7.33 – 7.29 (m, 2H), 7.27 – 7.26 (m, 1H), 4.03 (s, 3H), 2.08 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 158.7, 150.8, 150.7, 144.1, 143.6, 139.6, 139.4, 134.9, 131.2, 129.0, 128.7, 125.2, 123.7, 122.3, 120.4, 113.2, 105.1, 55.7, 14.9. These data are in accordance with the literature. [1]

4-(6-Fluoroquinolin-2-yl)-3,5-dimethyl-1,7-diphenyl-1,7-dihydrodipyrazolo[3,4-b:4',3'-e]pyridine (**3ea**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.24) to give the product as a green solid: 72% yield, (105 mg); m.p. 236-237℃; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.43 – 8.41 (m, 4H), 8.37 (d, *J* = 8.4 Hz, 1H), 8.27 – 8.23 (m, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.68 – 7.63 (m, 2H), 7.58 – 7.54 (m, 4H), 7.33 – 7.30 (m, 2H), 2.06 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 161.1 (d, *J* = 248.9 Hz), 152.8 (d, *J* = 2.8 Hz), 150.8, 144.6, 143.9, 139.6, 138.8, 135.7 (d, *J* = 5.5 Hz), 132.4 (d, *J* = 9.3 Hz), 129.0, 128.2 (d, *J* = 10.2 Hz), 125.3, 122.8, 121.2 (d, *J* = 25.6 Hz), 120.4, 113.0, 110.9 (d, *J* = 21.7 Hz), 14.9; ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ = -111.0. These data are in accordance with the literature. [1]

4-(6-Chloroquinolin-2-yl)-3,5-dimethyl-1,7-diphenyl-1,7-dihydrodipyrazolo[3,4-b:4',3'-e]pyridine (**3fa**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.27) to give the product as a yellow solid: 83% yield, (124 mg); m.p. 226-229℃; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.43 – 8.41 (m, 4H), 8.34 (d, *J* = 8.0 Hz, 1H), 8.18 (d, *J* = 8.8 Hz, 1H), 8.02 – 8.01 (m, 1H), 7.82 (dd, *J* = 9.2 Hz, *J* = 2.4 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.58 – 7.54 (m, 4H), 7.34 – 7.29 (m, 2H), 2.06 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 153.8, 150.8, 145.8, 143.8, 139.6, 138.6, 135.4, 133.7, 131.8, 131.4, 129.0, 128.0, 126.6, 125.3, 123.0, 120.4, 113.0, 14.9. These data are in accordance with the literature. [1]

4-(6-Bromoquinolin-2-yl)-3,5-dimethyl-1,7-diphenyl-1,7-dihydrodipyrazolo[3,4-b:4',3'-e]pyridine (**3ga**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.30) to give the product as a yellow solid: 71% yield, (116 mg); m.p. 213-216℃; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.43 – 8.40 (m, 4H), 8.32 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 2.4 Hz, 1H), 8.11 (d, *J* = 9.2 Hz, 1H), 7.95 (d, *J* = 8.8 Hz, *J* = 2.4 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.58 – 7.53 (m, 4H), 7.34 – 7.29 (m, 2H), 2.05 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 153.9, 150.7, 146.0, 143.8, 139.5, 138.6, 135.3, 134.3, 131.4, 129.9, 129.0, 128.5, 125.3, 123.0, 121.9, 120.4, 112.9, 14.9. These data are in accordance with the literature.[1]

4-(7-Chloroquinolin-2-yl)-3,5-dimethyl-1,7-diphenyl-1,7-dihydrodipyrazolo[3,4-b:4',3'-e]pyridine (**3ha**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.22) to give the product as a yellow solid: 63% yield, (94 mg); m.p. 227-229℃; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.43 – 8.40 (m, 5H), 8.24 (d, *J* = 2.0 Hz, 1H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.72 – 7.68 (m, 2H), 7.58 – 7.54 (m, 4H), 7.34 – 7.30 (m, 2H), 2.07 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 154.7, 150.8, 147.8, 143.8, 139.6, 138.6, 136.8, 136.2, 129.1, 129.0, 129.0, 128.8, 125.8, 125.3, 122.3, 120.5, 113.0, 14.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{22}ClN_6$ 501.1594; Found: 501.1586.

3,5-Dimethyl-1,7-diphenyl-4-(6-(trifluoromethyl)quinolin-2-yl)-1,7-dihydrodipyrazolo[3,4-b:4',3'-e] pyridine (**3ia**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.32) to give the product as a yellow solid: 74% yield, (119 mg); m.p. 269-271℃; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.51 (d, *J* = 8.4 Hz, 1H), 8.43 – 8.35 (m, 6H), 8.06 (d, *J* = 6.8 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.58 – 7.54 (m, 4H), 7.34 – 7.30 (m, 2H), 2.04 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 155.9, 150.7, 148.3, 143.6, 139.5, 138.2, 137.1, 131.0, 129.7 (q, *J* = 32.6 Hz), 129.0, 126.5, 126.4, 125.9 (q, *J* = 4.4 Hz),

125.3, 123.8 (q, *J* = 270.8 Hz), 123.4, 120.4, 112.9, 14.9; ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ = -62.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{22}F_3N_6$ 535.1858; Found: 535.1858.

3,5-Dimethyl-4-(8-methylquinolin-2-yl)-1,7-diphenyl-1,7-dihydrodipyrazolo[3,4-b:4',3'-e]pyridine (**3ja**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.50) to give the product as a yellow solid: 69% yield, (100 mg); m.p. 236-238℃; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.45 (d, *J* = 7.6 Hz, 4H), 8.35 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 6.4 Hz, 1H), 7.72 (d, *J* = 6.8 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.62 – 7.55 (m, 5H), 7.34 – 7.30 (m, 2H), 2.85 (s, 3H), 2.09 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 152.1, 150.8, 146.6, 144.2, 140.0, 139.6, 137.9, 136.3, 130.6, 128.9, 127.5, 127.4, 125.8, 125.1, 122.1, 120.3, 113.1, 18.1, 15.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{25}N_6$ 481.2141; Found: 481.2136.

3,5-Dimethyl-4-(1,8-naphthyridin-2-yl)-1,7-diphenyl-1,7-dihydrodipyrazolo[3,4-b:4',3'-e]pyridine (**3ka**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 1:1, R_f = 0.16) to give the product as a brown solid: 77% yield, (108 mg); m.p. 269-272℃; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 9.29 (s, 1H), 8.44 – 8.41 (m, 6H), 7.80 (d, *J* = 6.8 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.57 – 7.53 (m, 4H), 7.32 – 7.26 (m, 2H), 2.07 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 157.0, 155.3, 155.0, 150.7, 143.9, 139.6, 138.4, 137.4, 137.2, 129.0, 125.2, 123.4, 123.2, 122.1, 120.4, 112.8, 15.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{22}N_7$ 468.1931; Found: 468.1922.

4-(Isoquinolin-1-yl)-3,5-dimethyl-1,7-diphenyl-1,7-dihydrodipyrazolo[3,4-b:4',3'-e]pyridine (**3la**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.15) to give the product as a yellow solid: 75% yield, (105 mg); m.p. 185-190℃; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.80 (d, *J* = 5.6 Hz, 1H), 8.47 – 8.44 (m, 4H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 5.6 Hz, 1H), 7.81 – 7.77 (m,

1H), 7.60 – 7.53 (m, 6H), 7.35 – 7.30 (m, 2H), 1.80 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 154.3, 150.8, 144.1, 142.1, 139.6, 137.3, 135.8, 131.0, 129.0, 128.4, 128.0, 127.2, 126.4, 125.3, 121.6, 120.4, 113.8, 14.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{23}N_6$ 467.1979; Found: 467.1981.

2-(3,5-Dimethyl-1,7-diphenyl-1,7-dihydrodipyrazolo[3,4-b:4',3'-e]pyridin-4-yl)benzo[d]thiazole (**3ma**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 10:1, R_f = 0.48) to give the product as a green solid: 32% yield, (45 mg); m.p. 213-216℃; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.43 – 8.40 (m, 4H), 8.28 (d, *J* = 7.6 Hz, 1H), 8.08 (d, *J* = 9.2 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.62 – 7.54 (m, 5H), 7.34 – 7.30 (m, 2H), 2.26 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 159.6, 152.9, 150.3, 143.6, 139.4, 135.8, 131.1, 129.0, 127.0, 126.4, 125.4, 124.2, 121.7, 120.4, 113.3, 14.6. These data are in accordance with the literature. [1]

1,3,5,7-Tetramethyl-4-(quinolin-2-yl)-1,7-dihydrodipyrazolo[3,4-b:4',3'-e]pyridine (**3ab**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 3:1, R_f = 0.26) to give the product as a yellow oil: 54% yield, (55 mg); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.37 (d, *J* = 7.6 Hz, 1H), 8.21 (d, *J* = 7.6 Hz, 1H), 7.99 (d, *J* = 6.8 Hz, 1H), 7.87 – 7.83 (m, 1H), 7.71 – 7.67 (m, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 4.10 (s, 6H), 1.99 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 154.0, 152.2, 147.4, 141.7, 138.7, 136.1, 130.6, 129.7, 127.8, 127.5, 127.4, 122.1, 111.1, 33.5, 14.8. These data are in accordance with the literature. [1]

1,3,7,9-Tetramethyl-5-(quinolin-2-yl)pyrido[2,3-d:6,5-d']dipyrimidine-2,4,6,8(1H,3H,7H,9H)-tetraone (**5aa**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 1:1, R_f = 0.15) to give the product as a white solid: 81% yield, (105 mg); m.p. >300℃; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.29 (d, *J* =

8.0 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 6.8 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.60 – 7.56 (m, 1H), 7.43 (d, *J* = 8.8 Hz, 1H), 3.81 (s, 6H), 3.27 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 159.0, 157.0, 156.7, 153.5, 150.7, 147.5, 135.1, 129.5, 129.0, 128.1, 127.1, 126.4, 120.1, 105.1, 30.4, 28.4. These data are in accordance with the literature.[1]

1,3,7,9-Tetramethyl-5-(6-methylquinolin-2-yl)pyrido[2,3-d:6,5-d']dipyrimidine-2,4,6,8(1H,3H,7H,9H)-tetraone (**5ba**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 1:1, R_f = 0.16) to give the product as a brown solid: 83% yield, (110 mg); m.p. >300℃; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.20 (d, *J* = 7.6 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.69 – 7.68 (m, 1H), 7.54 (d, *J* = 8.4 Hz, *J* = 2.0 Hz, 1H)，7.39 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 6H), 3.26 (s, 6H), 2.56 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 159.1, 157.2, 155.8, 153.6, 150.9, 146.2, 136.4, 134.6, 131.8, 128.7, 127.3, 127.1, 120.2, 105.2, 30.4, 28.5, 21.6. These data are in accordance with the literature.[1]

5-(6-Methoxyquinolin-2-yl)-1,3,7,9-tetramethylpyrido[2,3-d:6,5-d']dipyrimidine-2,4,6,8(1H,3H,7H,9H)-tetraone (**5da**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 1:1, R_f = 0.16) to give the product as a white solid: 76% yield, (105 mg); m.p. >300℃; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.18 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 9.2 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.20 – 7.19 (m, 1H), 3.95 (s, 3H), 3.79 (s, 6H), 3.26 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 159.1, 157.8, 157.3, 154.1, 153.6, 150.9, 143.6, 134.1, 130.4, 128.2, 122.1, 120.4, 106.0, 105.2, 55.6, 30.4, 28.5. These data are in accordance with the literature.[1]

5-(6-Bromoquinolin-2-yl)-1,3,7,9-tetramethylpyrido[2,3-d:6,5-d']dipyrimidine-2,4,6,8(1H,3H,7H,9H)-tetraone (**5ga**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 1:1, R_f = 0.17) to give the product as

a white solid: 60% yield, (92 mg); m.p. >300℃; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.19 (d, *J* = 8.0 Hz, 1H), 8.09 – 8.08 (m, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.79 – 7.76 (m, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 6H), 3.26 (s, 6H);^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 159.2, 157.4, 156.5, 153.7, 150.8, 146.1, 134.2, 133.1, 130.8, 130.2, 128.4, 121.2, 120.4, 105.1, 30.5, 28.6. These data are in accordance with the literature. [1]

(3,5-Dimethyl-1,7-diphenyl-1,7-dihydrodipyrazolo[3,4-b:4',3'-e]pyridin-4-yl)(phenyl)methanone (**7aa**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 20:1, R_f = 0.25) to give the product as a yellow solid: 83% yield, (110 mg); m.p. 212-213℃; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.42 – 8.39 (m, 5H), 7.74 – 7.69 (m, 1H), 7.59 – 7.54 (m, 7H), 7.35 – 7.31 (m, 2H), 2.32 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 193.9, 150.6, 143.3, 139.4, 136.9, 136.5, 135.1, 129.3, 129.0, 125.5, 120.4, 111.4, 14.3. These data are in accordance with the literature. [2]

(3,5-Dimethyl-1,7-diphenyl-1,7-dihydrodipyrazolo[3,4-b:4',3'-e]pyridin-4-yl)(p-tolyl)methanone (**7ba**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 20:1, R_f = 0.28) to give the product as a yellow solid: 62% yield, (85 mg); m.p. 230-232℃; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.42 – 8.40 (m, 5H), 7.58 – 7.54 (m, 5H), 7.35 – 7.30 (m, 4H), 2.48 (s, 3H), 2.32 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 193.4, 150.6, 146.5, 143.4, 139.4, 137.2, 134.2, 130.0, 129.0, 125.4, 120.4, 111.4, 21.9, 14.3. These data are in accordance with the literature. [2]

(3,5-Dimethyl-1,7-diphenyl-1,7-dihydrodipyrazolo[3,4-b:4',3'-e]pyridin-4-yl)(4-methoxyphenyl)methanone (**7ca**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 30:1, R_f = 0.22) to give the product as a yellow solid: 74% yield, (105 mg); m.p. 203-205℃; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.42 –

8.40 (m, 5H), 7.58 – 7.54 (m, 6H), 7.34 – 7.30 (m, 3H), 3.90 (s, 3H), 2.34 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 192.0, 165.0, 150.6, 143.4, 139.4, 137.3, 129.7, 129.0, 125.4, 120.3, 111.3, 55.7, 14.2. These data are in accordance with the literature.[2]

(3,5-Dimethyl-1,7-diphenyl-1,7-dihydrodipyrazolo[3,4-b:4',3'-e]pyridin-4-yl)(o-tolyl)methanone (**7da**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 30:1, R_f = 0.25) to give the product as a yellow solid: 55% yield, (75 mg); m.p. 221-224℃; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.41 – 8.39 (m, 4H), 7.58 – 7.54 (m, 5H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.22 – 7.18 (m, 1H), 2.91 (s, 3H), 2.32 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 195.3, 150.7, 143.4, 141.2, 139.4, 138.5, 134.9, 134.2, 134.1, 132.9, 129.0, 126.3, 125.4, 120.4, 111.3, 22.5, 14.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{24}N_5O$ 458.1981; Found: 458.1968.

(4-Chlorophenyl)(3,5-dimethyl-1,7-diphenyl-1,7-dihydrodipyrazolo[3,4-b:4',3'-e]pyridin-4-yl)methanone (**7ea**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 30:1, R_f = 0.21) to give the product as a yellow solid: 50% yield, (72 mg); m.p. 219-222℃; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.41 – 8.38 (m, 5H), 7.58 – 7.54 (m, 6H), 7.35 – 7.31 (m, 3H), 2.32 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 192.6, 150.5, 143.0, 141.9, 139.3, 136.0, 134.8, 129.8, 129.0, 125.5, 120.4, 111.2, 14.3. These data are in accordance with the literature.[2]

(3-Methyl-1,7-diphenyl-1,7-dihydrodipyrazolo[3,4-b:4',3'-e]pyridin-4-yl)(thiophen-2-yl)methanone (**7fa**)

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 30:1, R_f = 0.23) to give the product as a yellow solid: 59% yield, (80 mg); m.p. 207-209℃; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.41 – 8.38 (m, 4H), 7.95 – 7.93 (m, 1H), 7.59 – 7.55 (m, 4H), 7.35 – 7.31 (m, 3H), 7.18 – 7.16 (m, 1H),

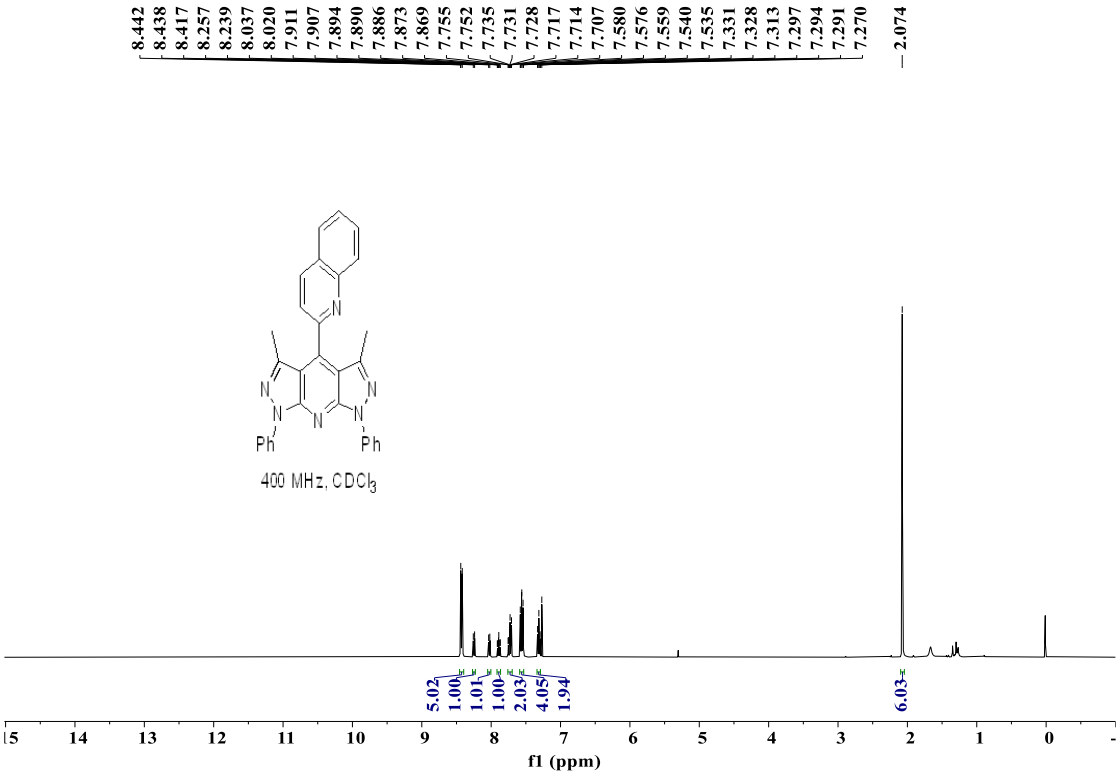
2.41 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 185.4, 150.6, 143.8, 143.2, 139.4, 137.3, 135.9, 129.0, 125.5, 120.4, 111.2, 14.2. These data are in accordance with the literature. [2]

Reference:

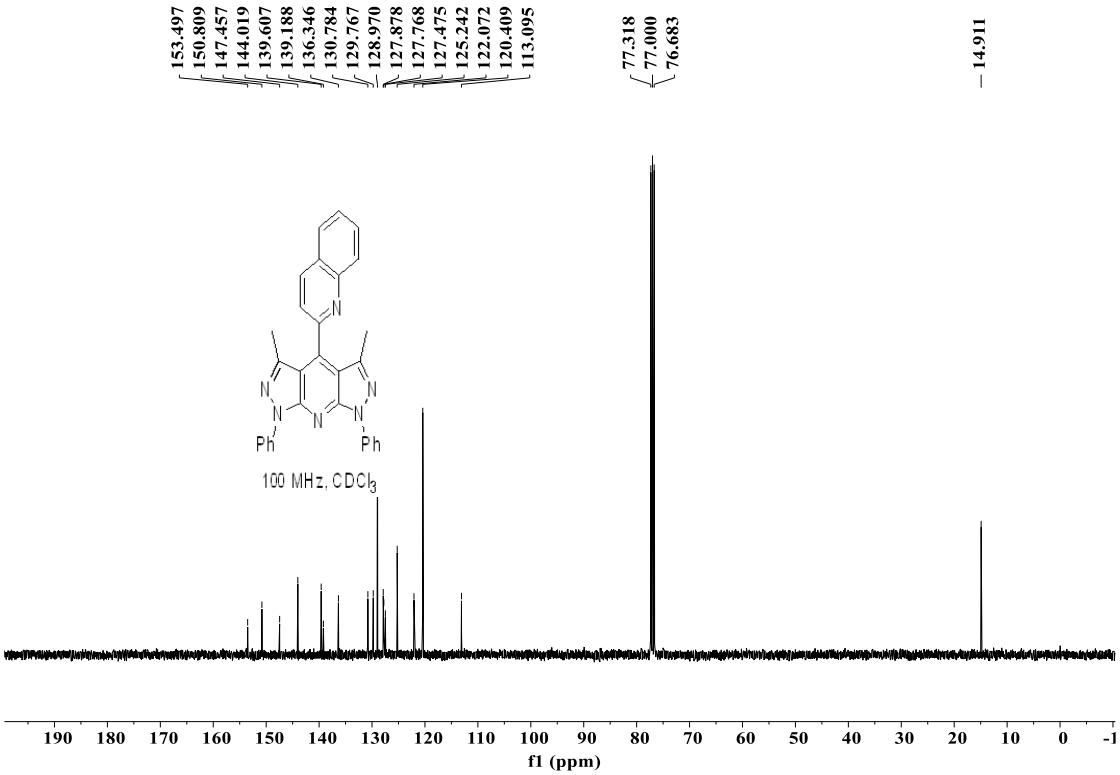
1. R.-J. Xie, J.-H. Liu, Q.-Y. Zhang, Y.-J. Yang, L.-Q. Song, T.-Q. Shao, K.-X. Liu, Y. P. Zhu, *Org. Chem. Front*., 2021, **8**, 2274.
2. Q. H. Gao, S. He, X. Wu, J. J. Zhang, S. P. Bai, Y. D. Wu, A. X. Wu, *Org. Chem. Front*., 2018, **5**, 765.

NMR Spectra of products

3aa-^{1}H NMR



3aa-^{13}C NMR



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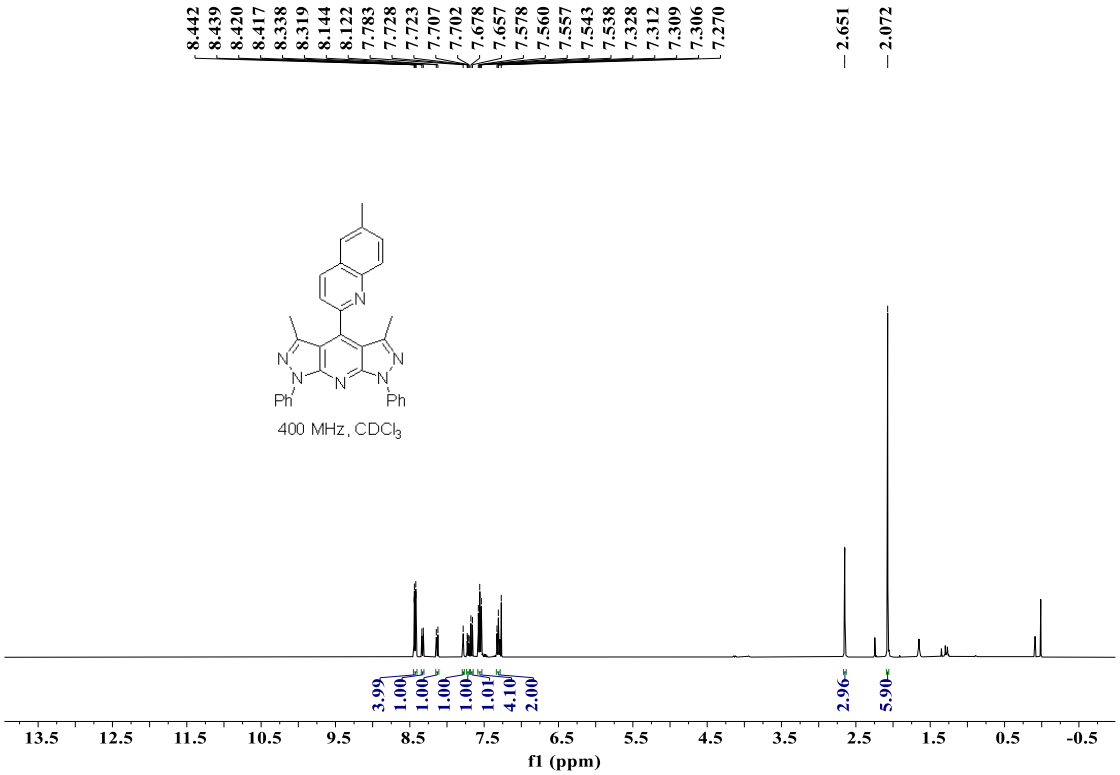

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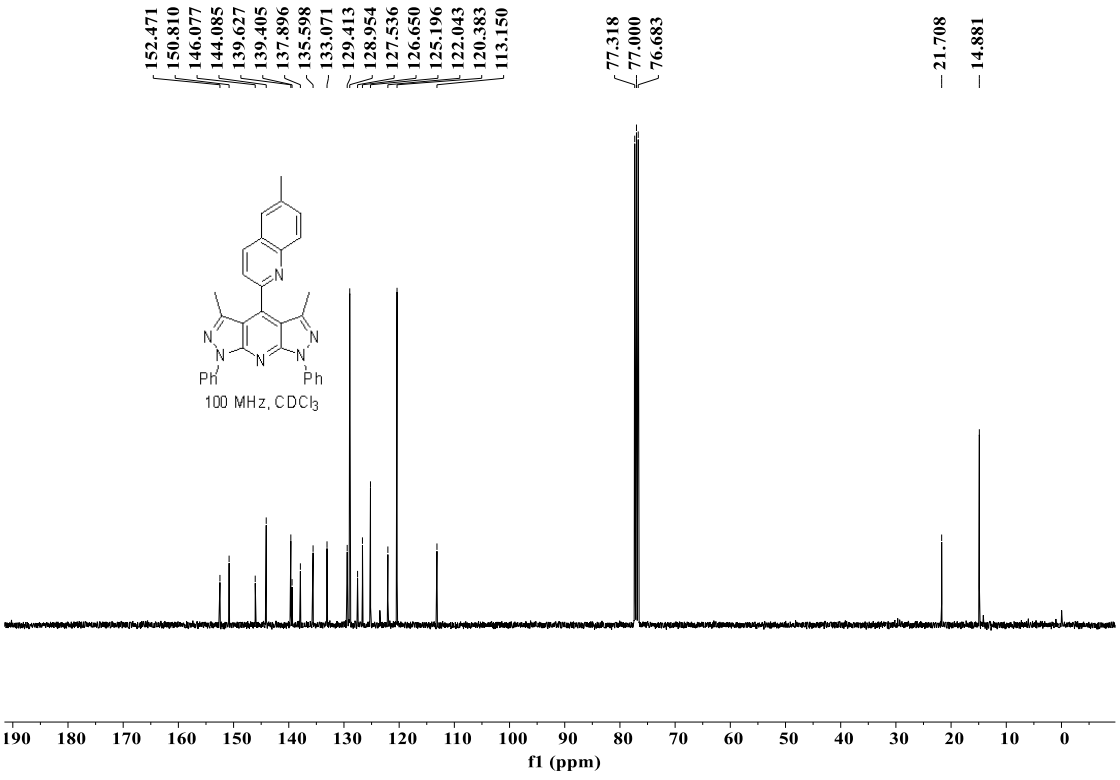

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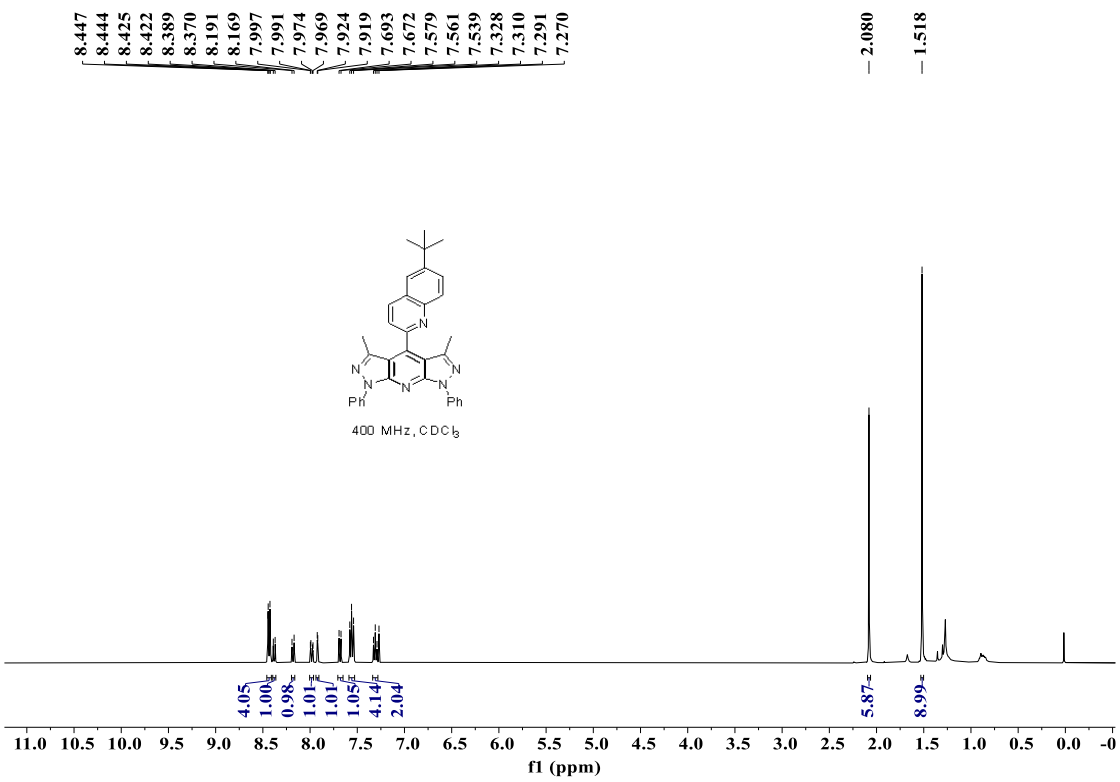

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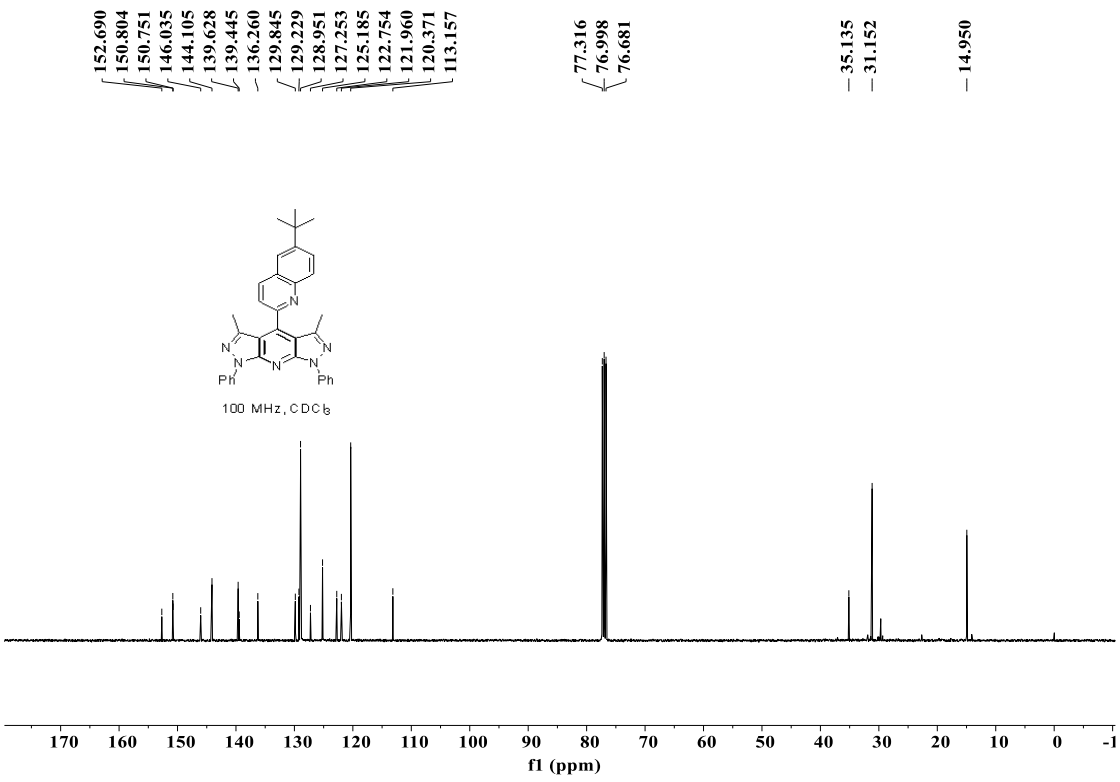

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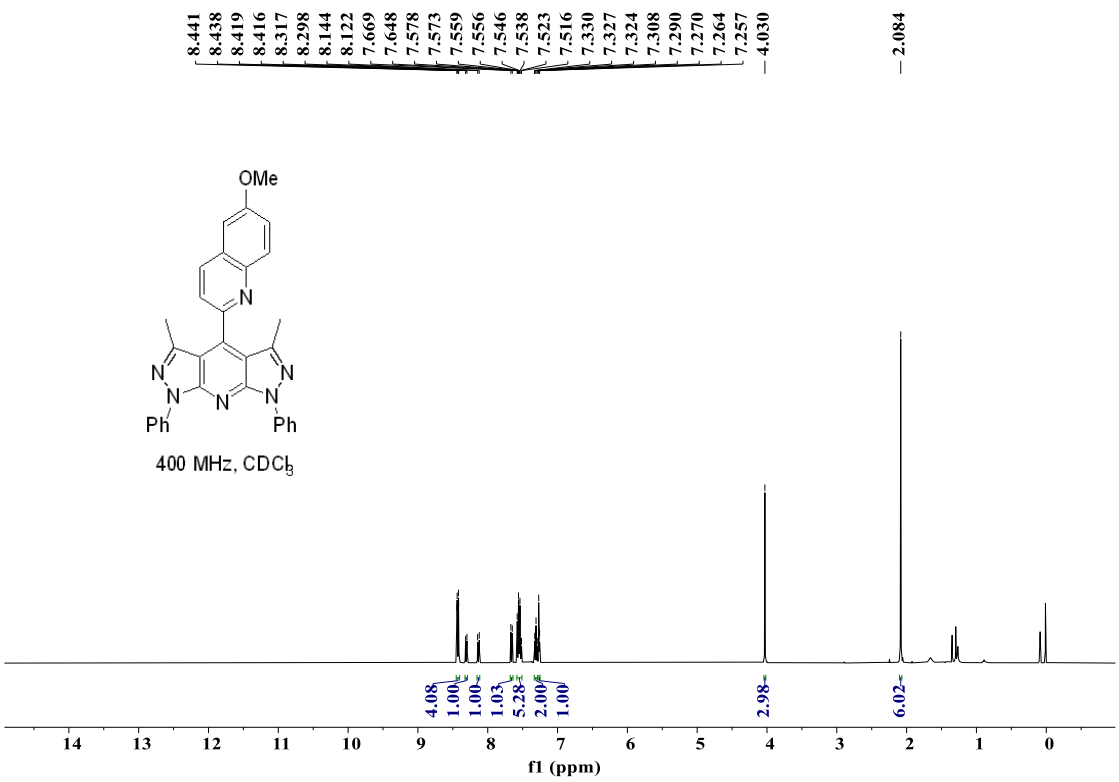

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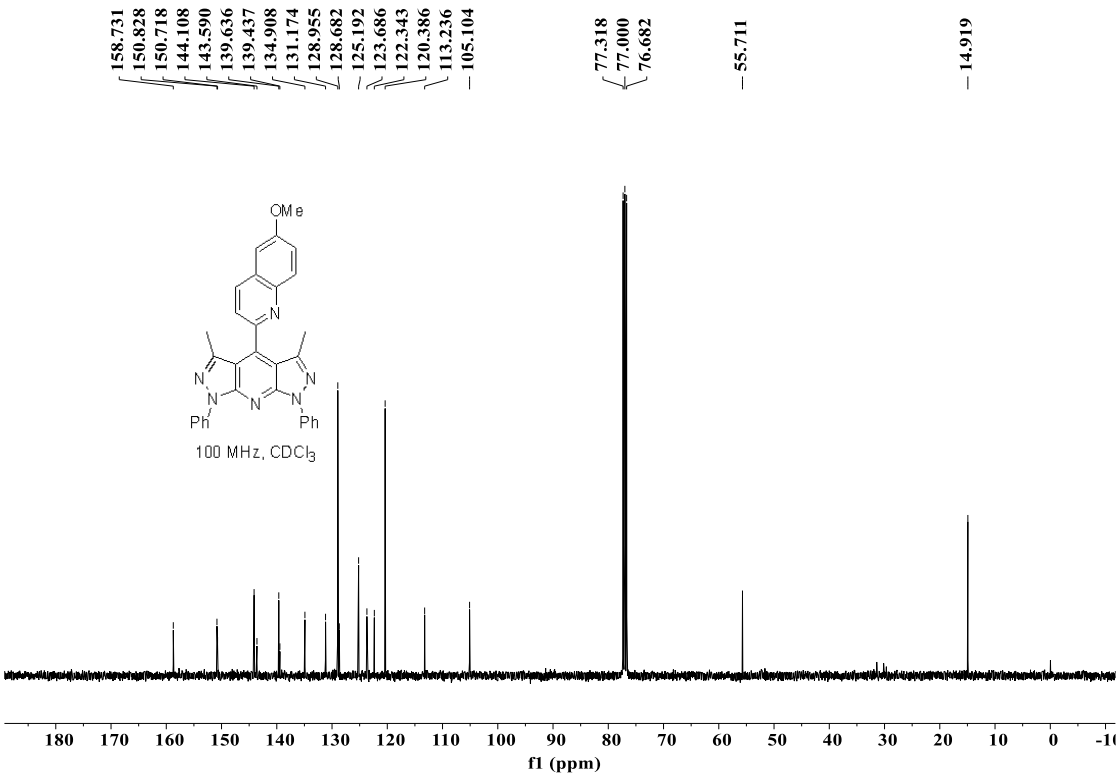

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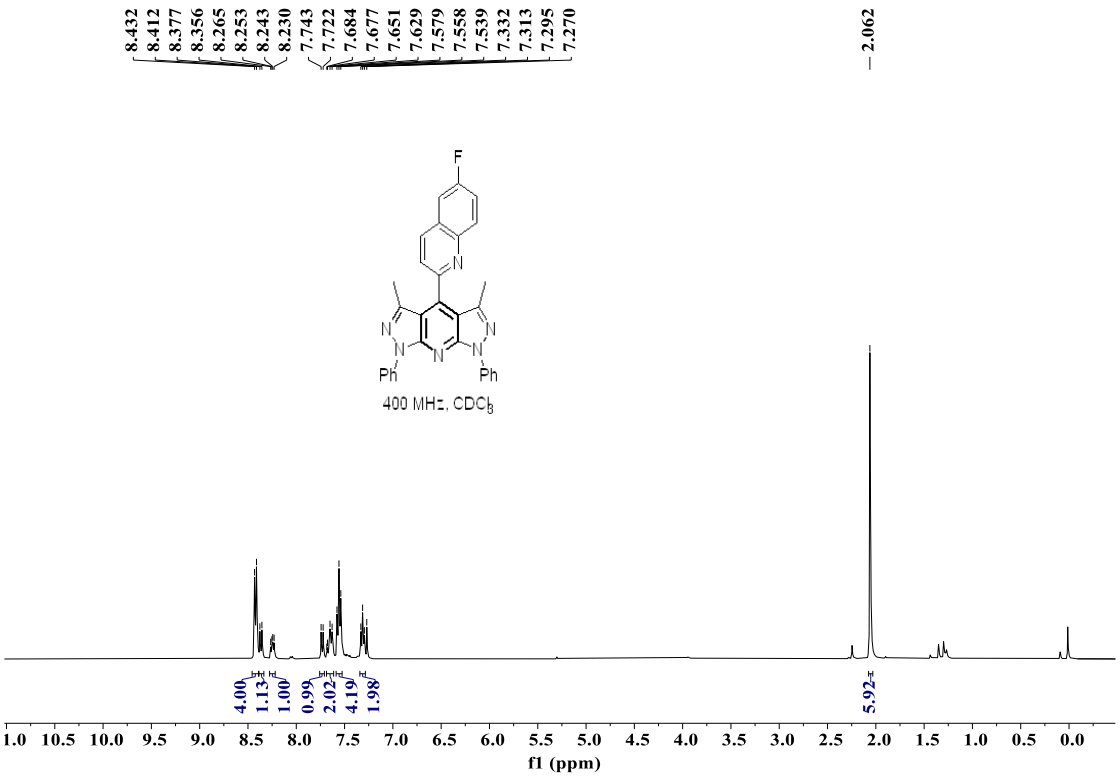

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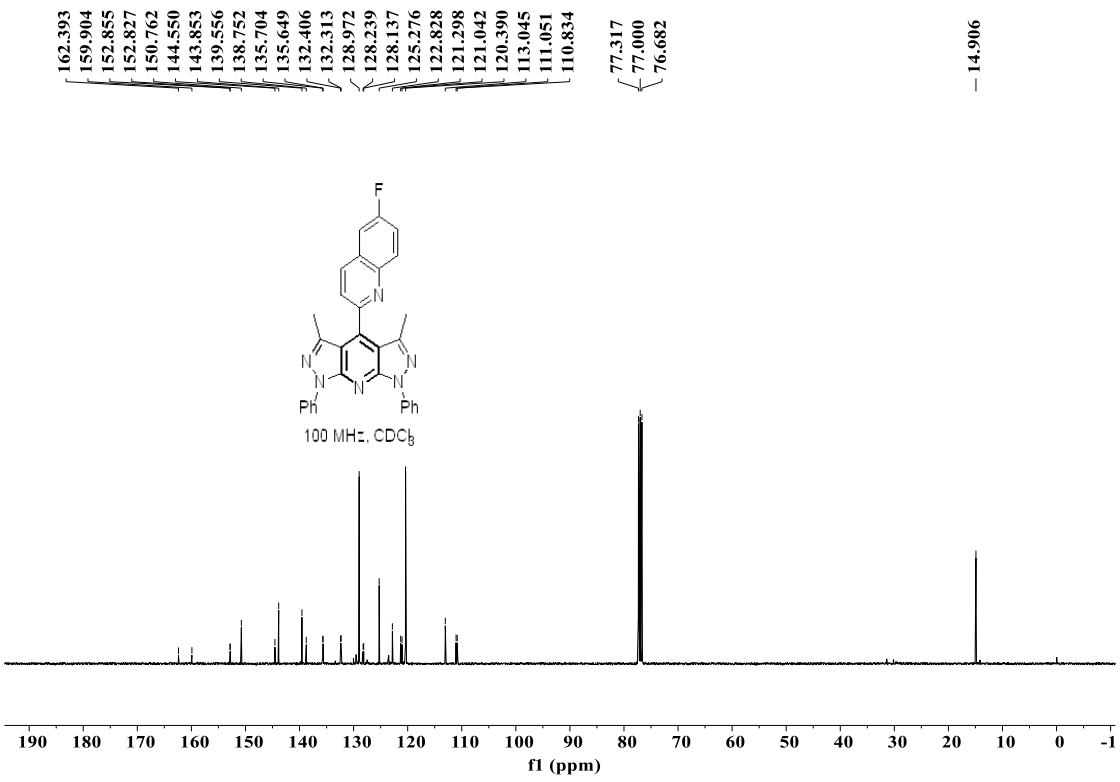
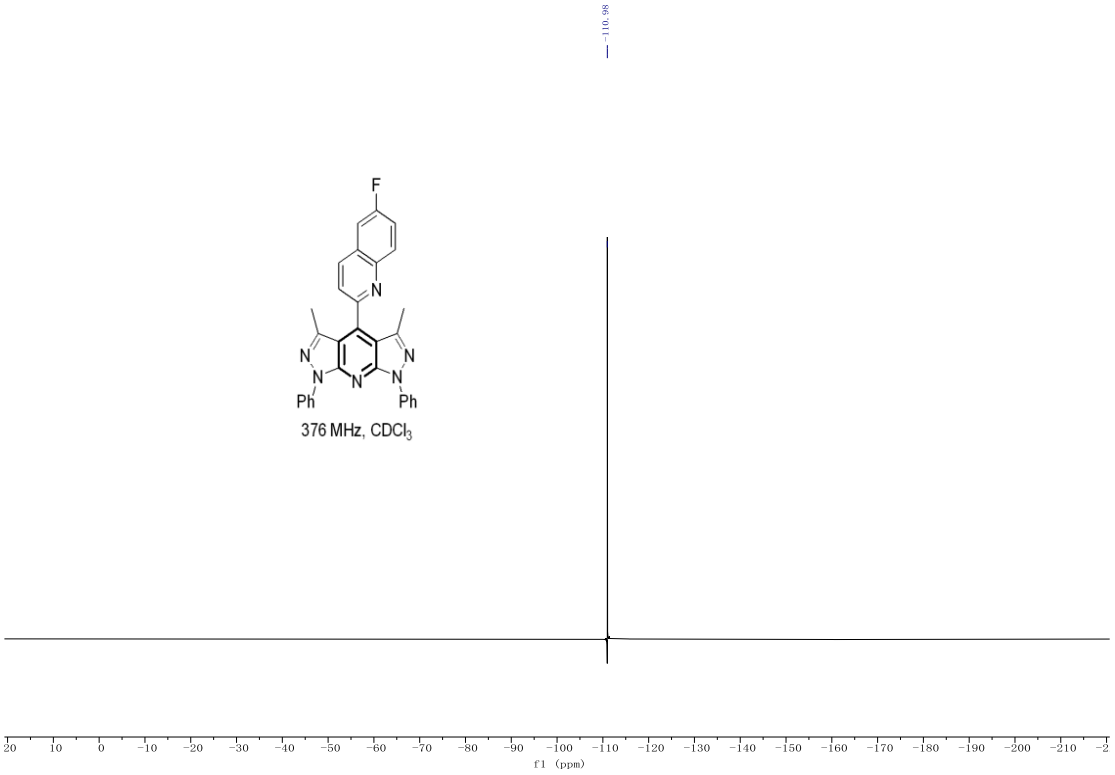


3ea -^{19}F NMR



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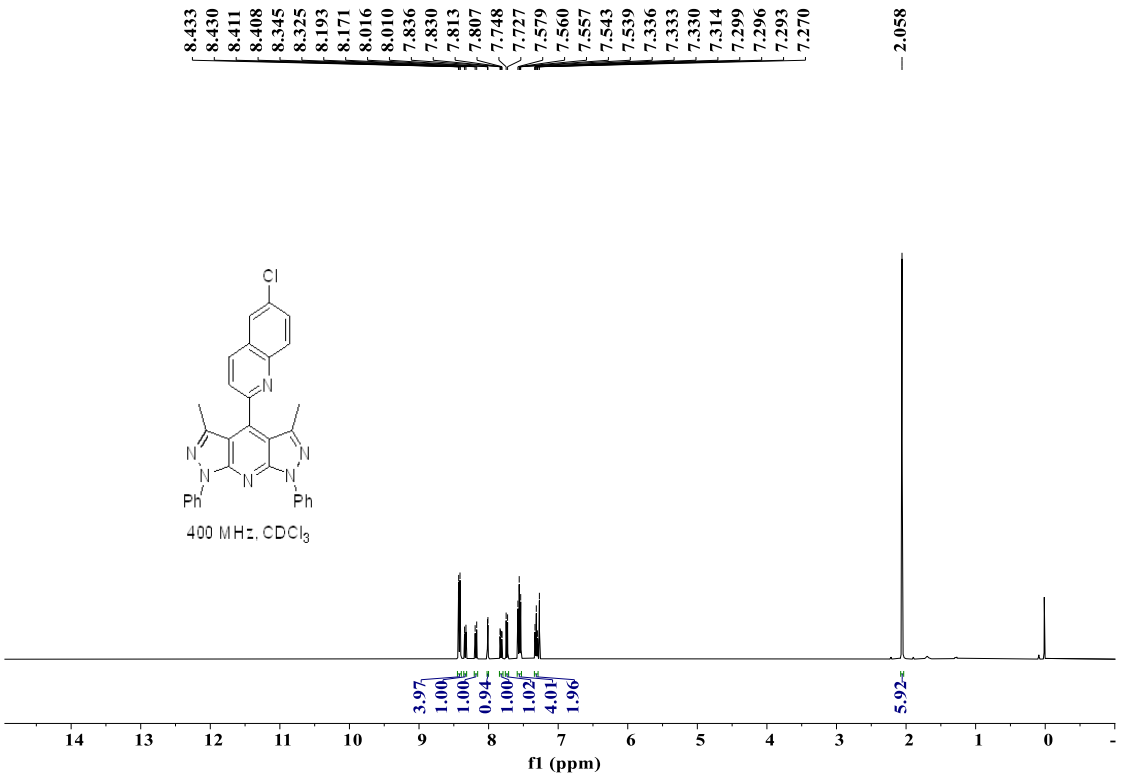
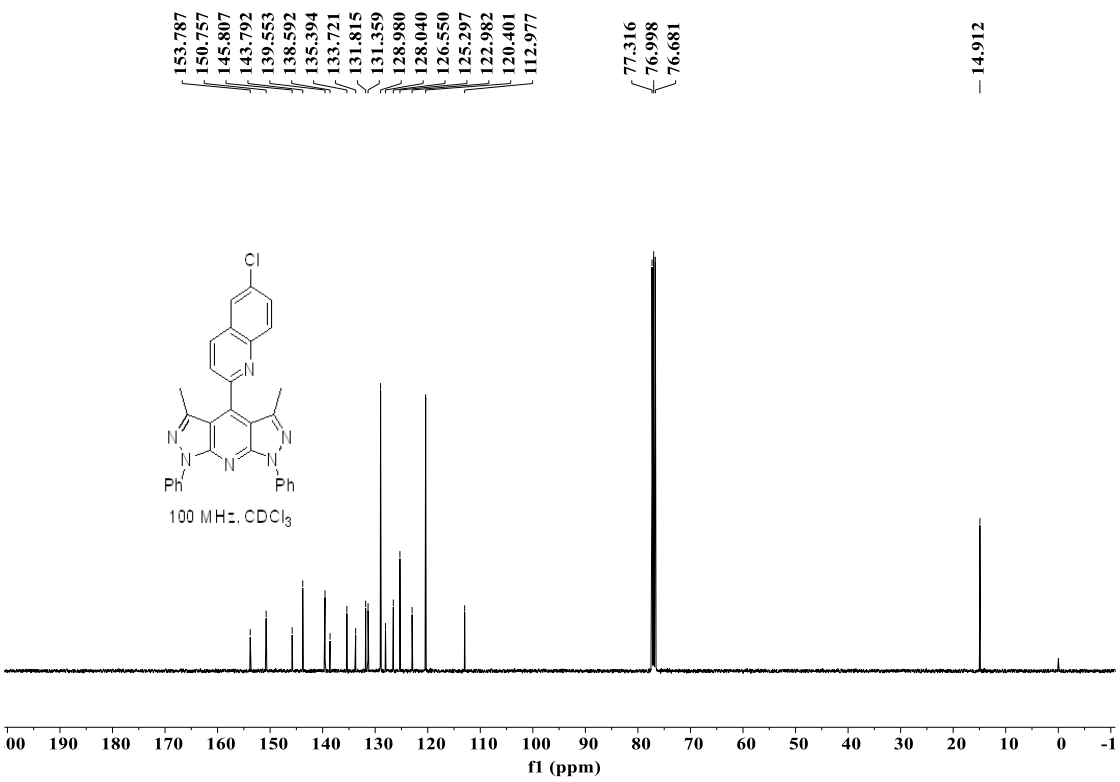
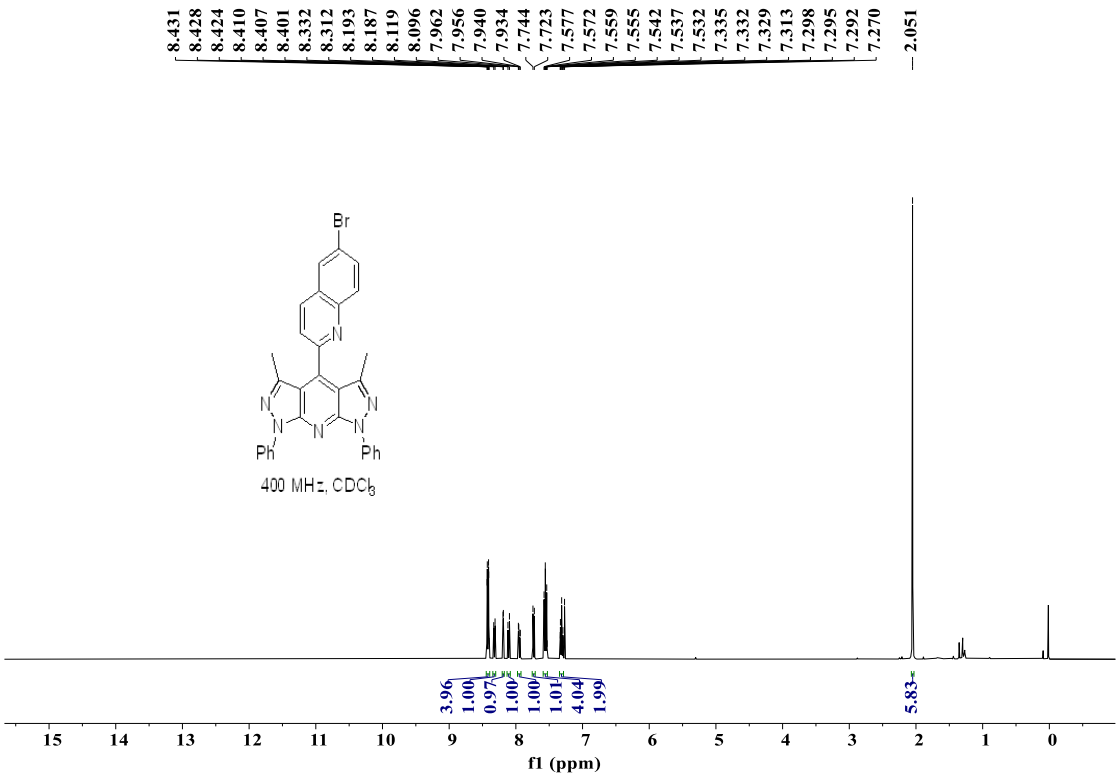


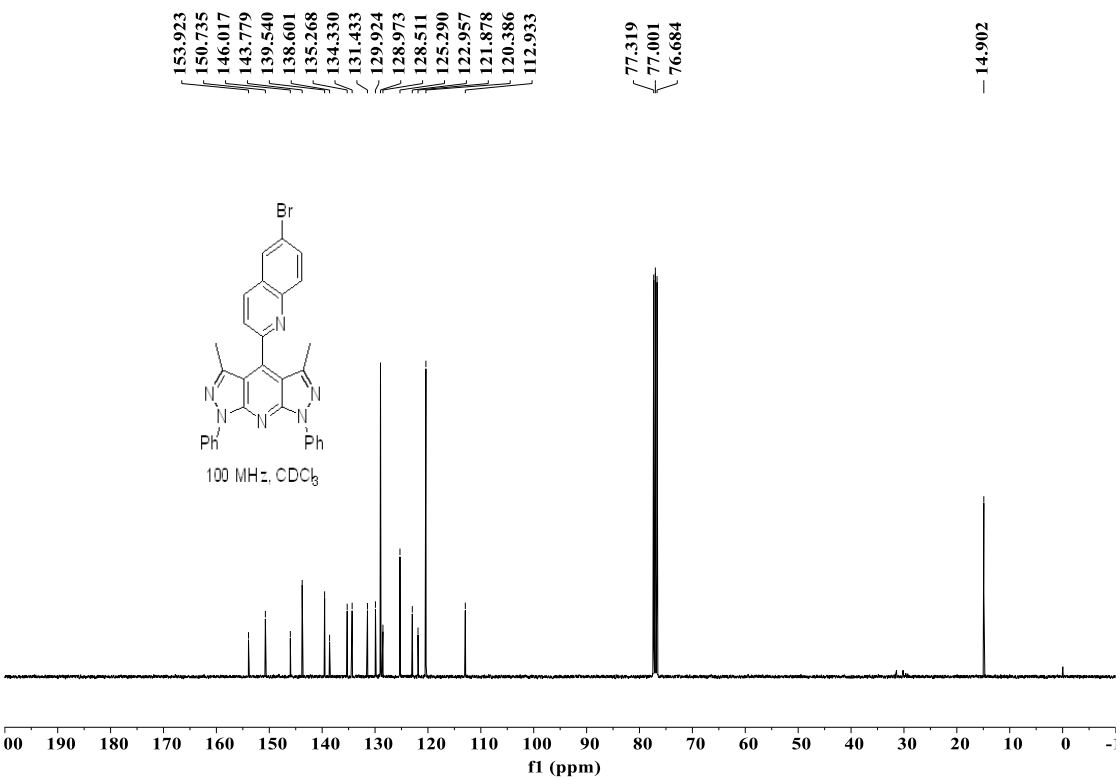
3fa -^{13}C NMR



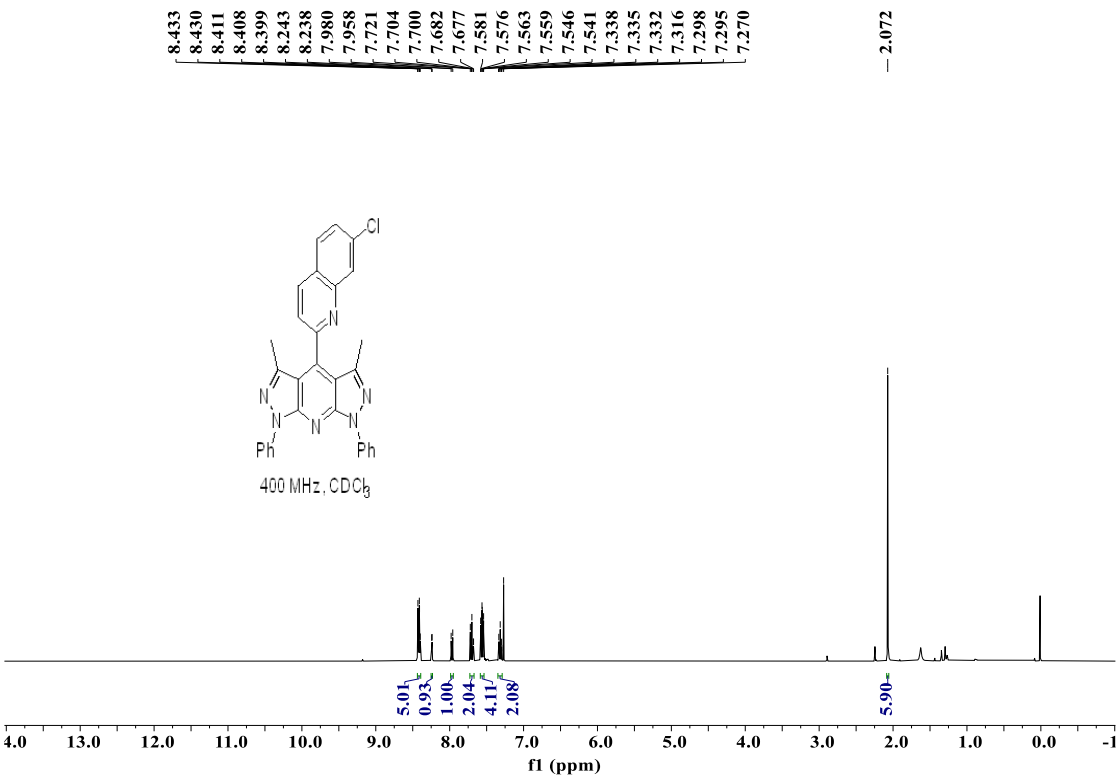
3ga-^{1}H NMR



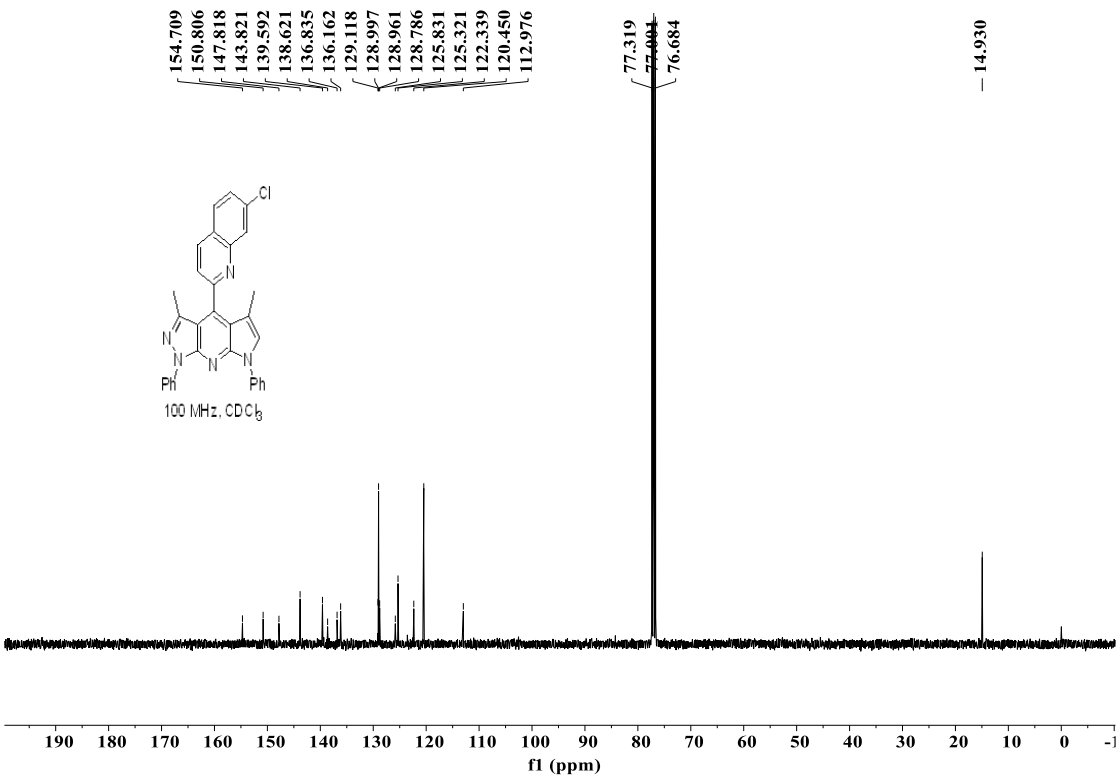
3ga -^{13}C NMR



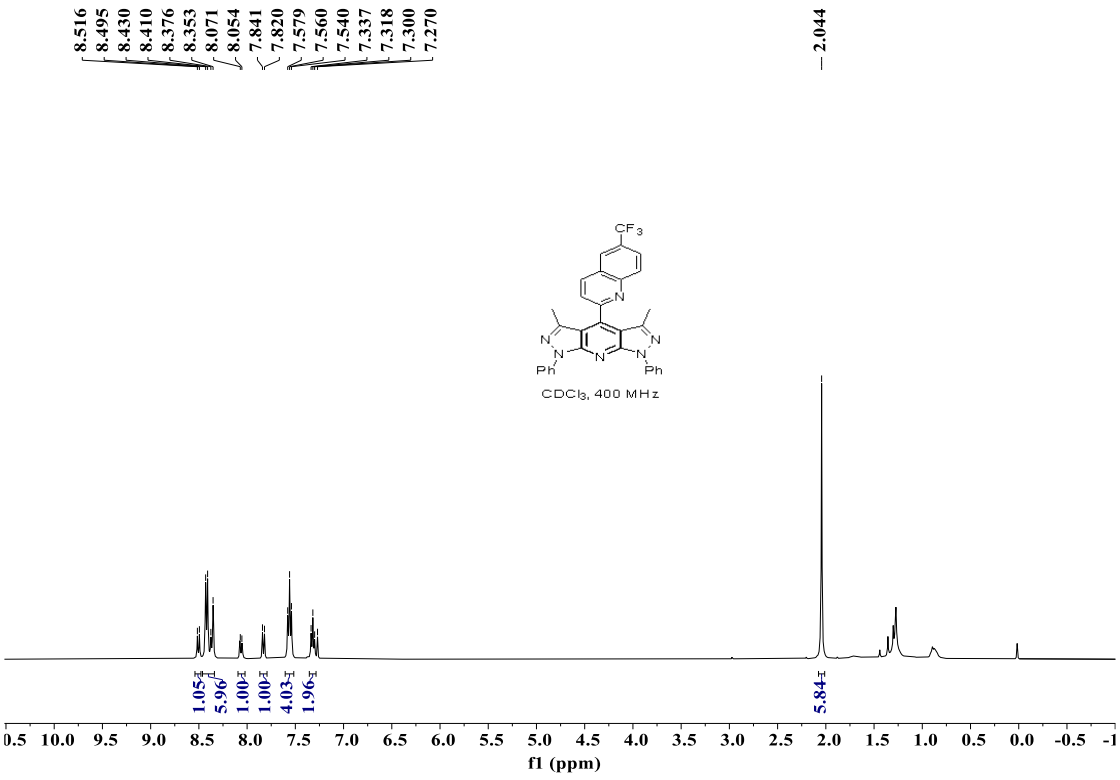
3ha-^{1}H NMR



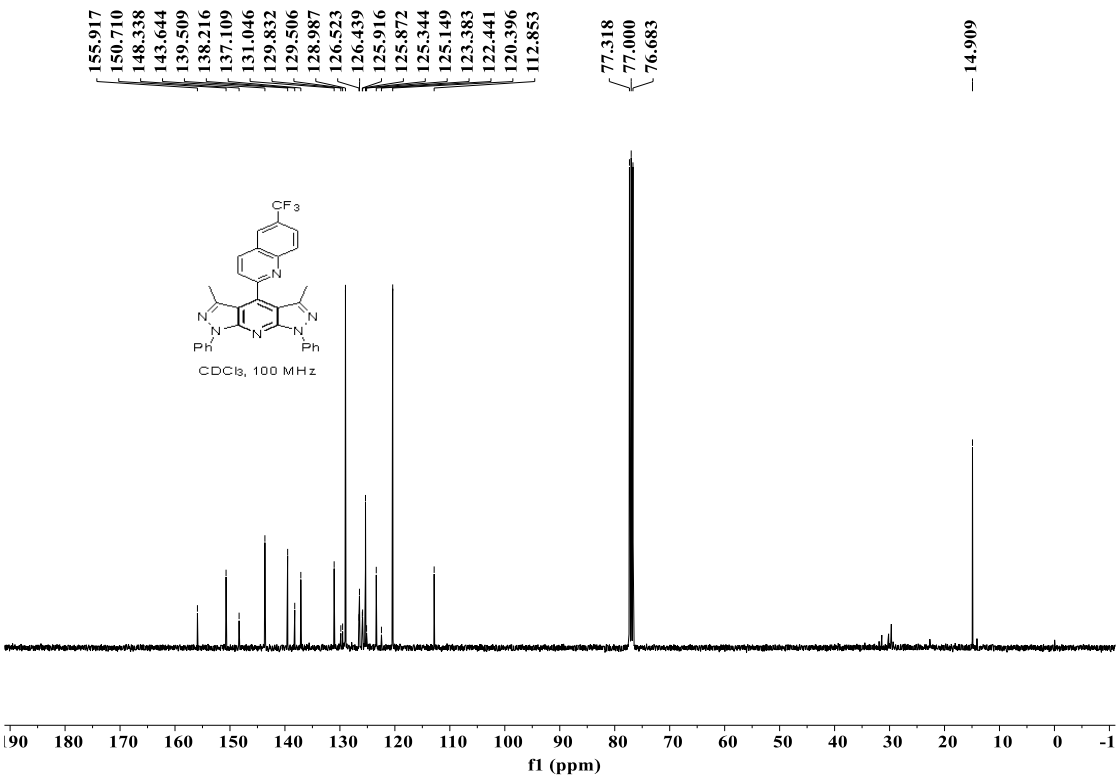
3ha -^{13}C NMR



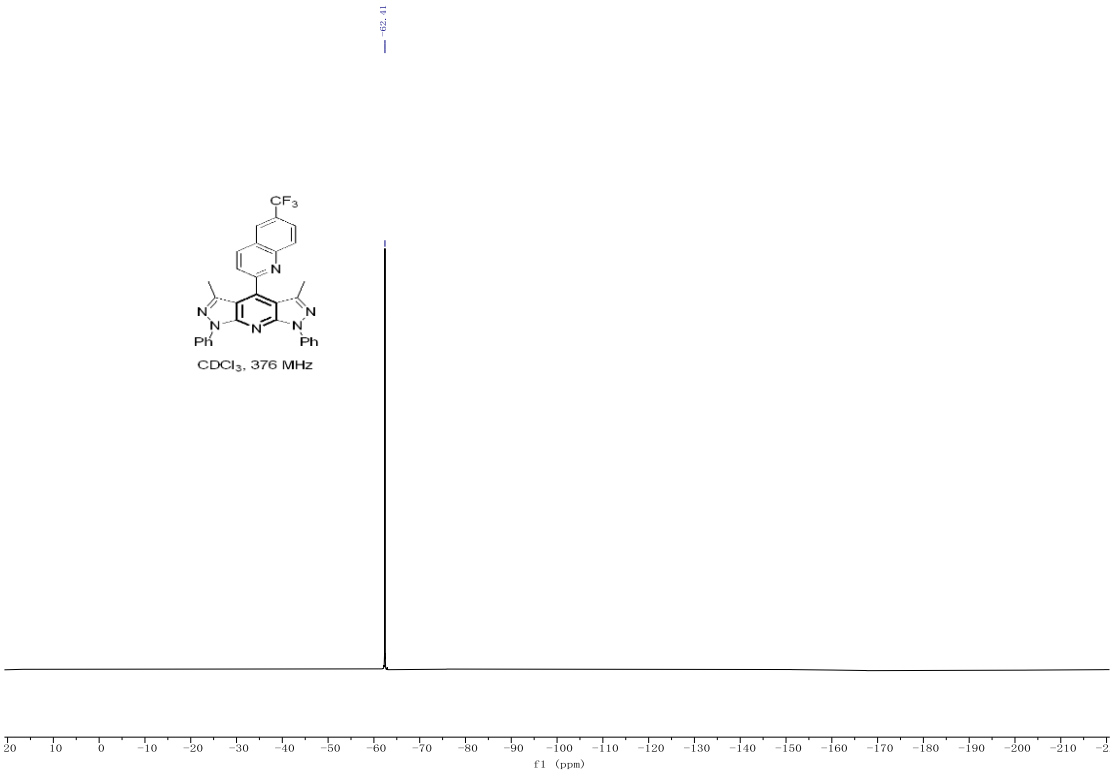
3ia-^{1}H NMR



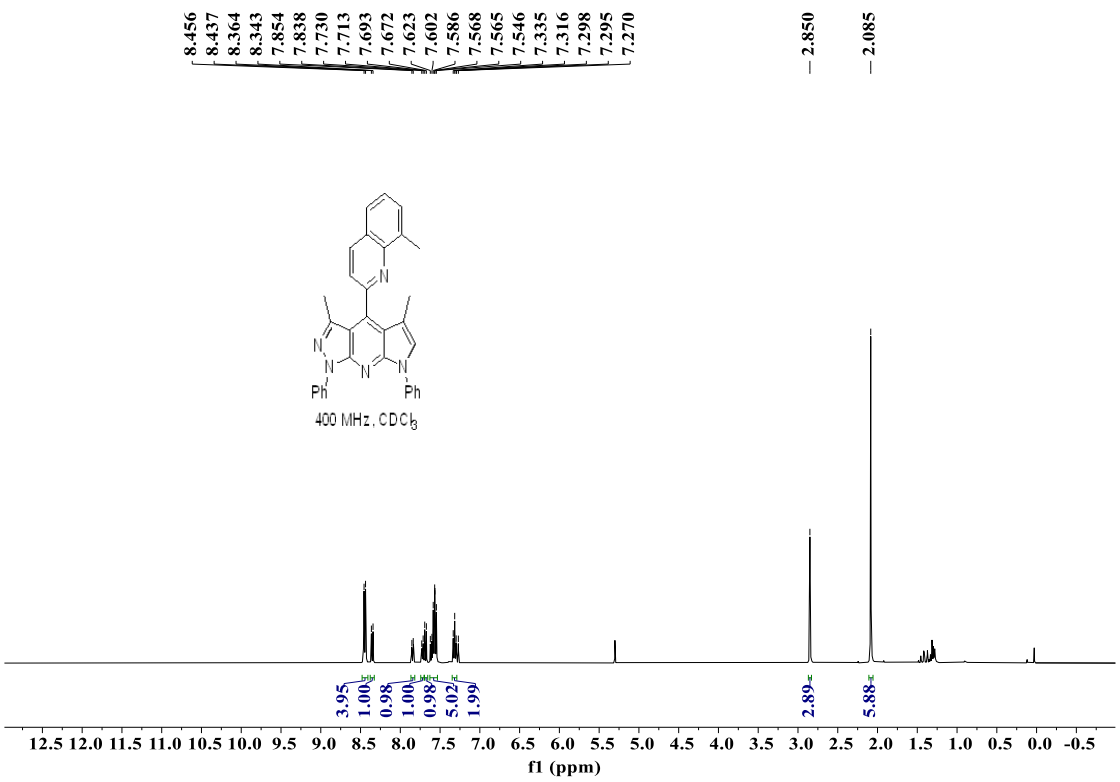
3ia -^{13}C NMR



3ia -^{19}F NMR



3ja-^{1}H NMR



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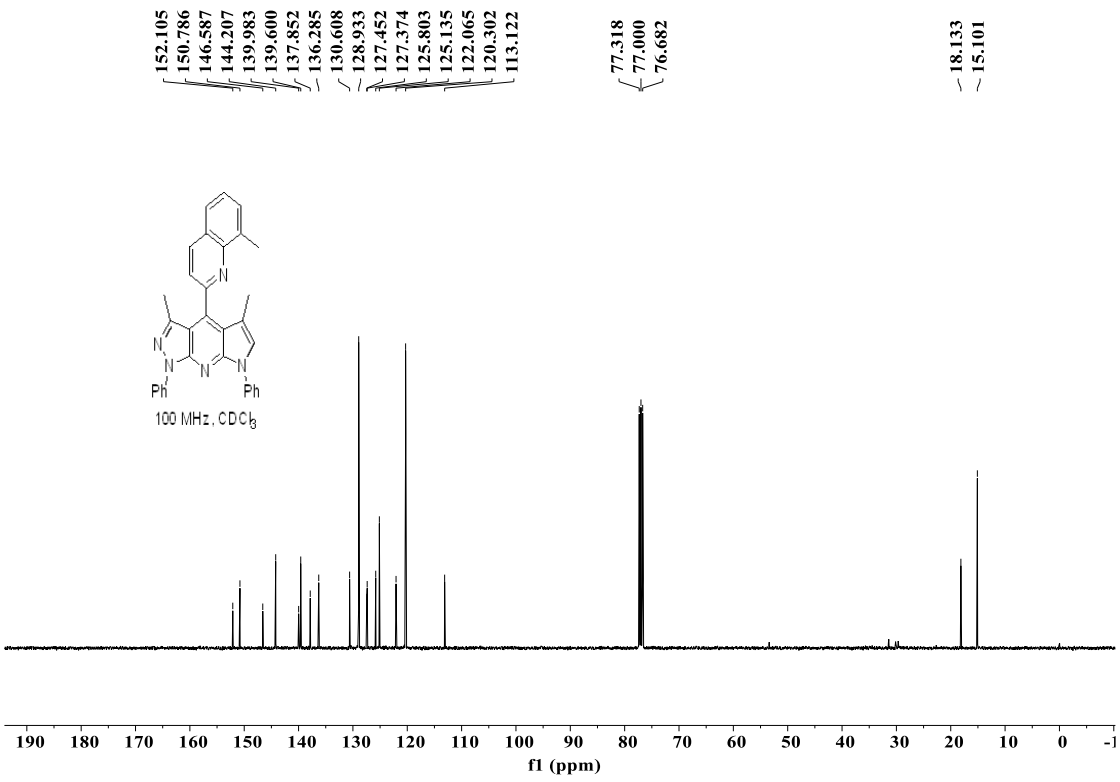
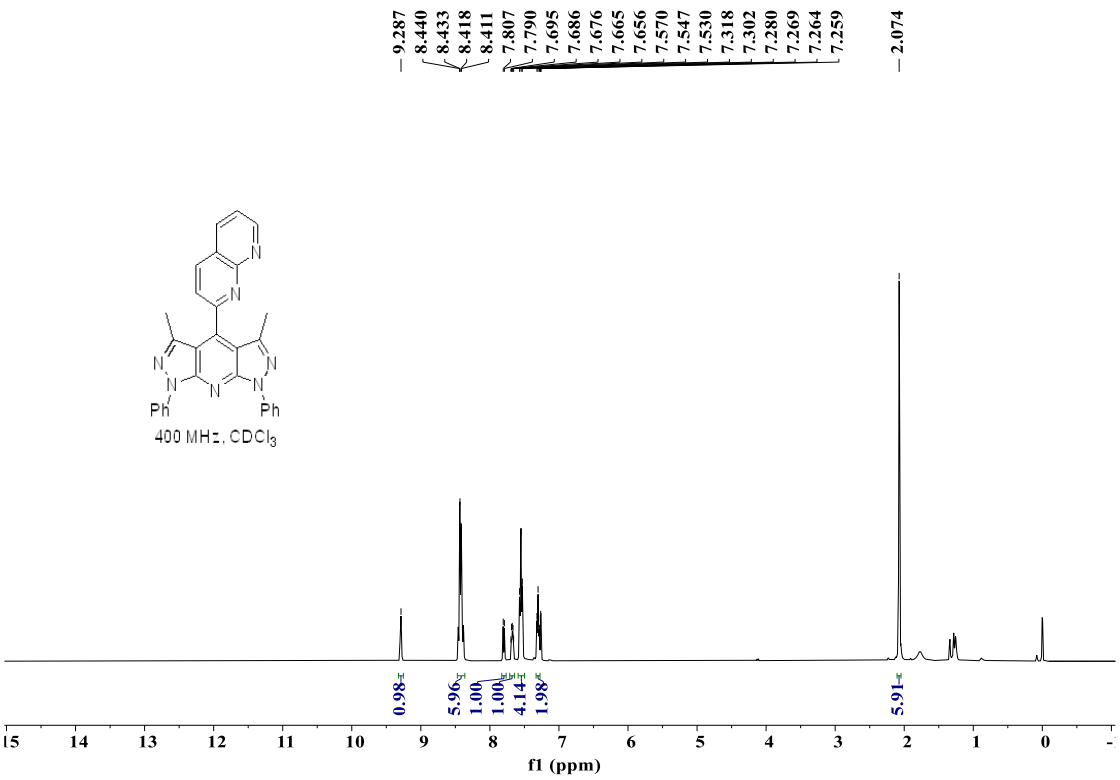


3ka-^{1}H NMR



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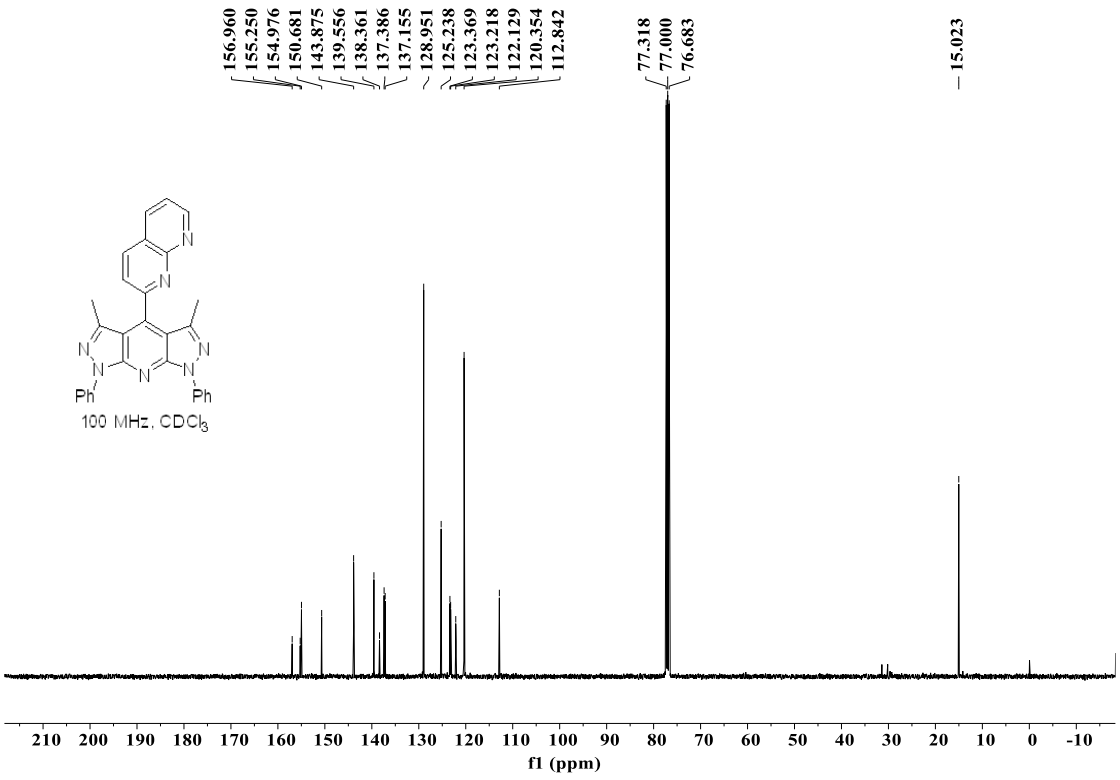

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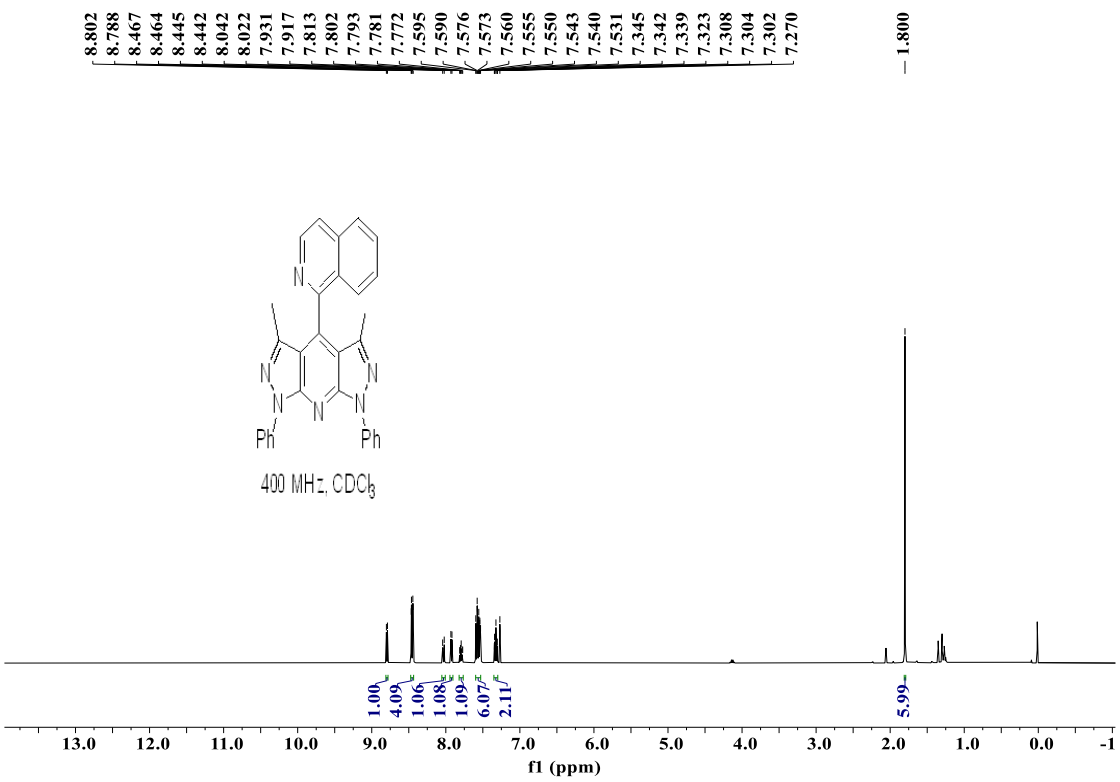

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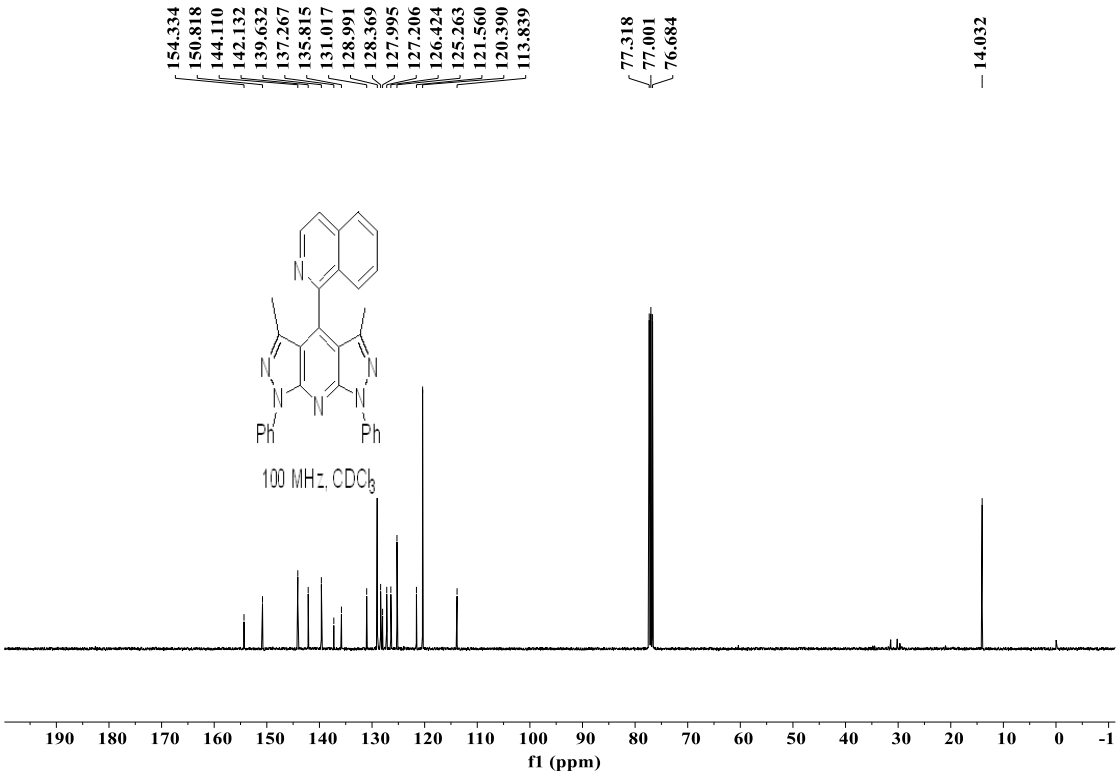
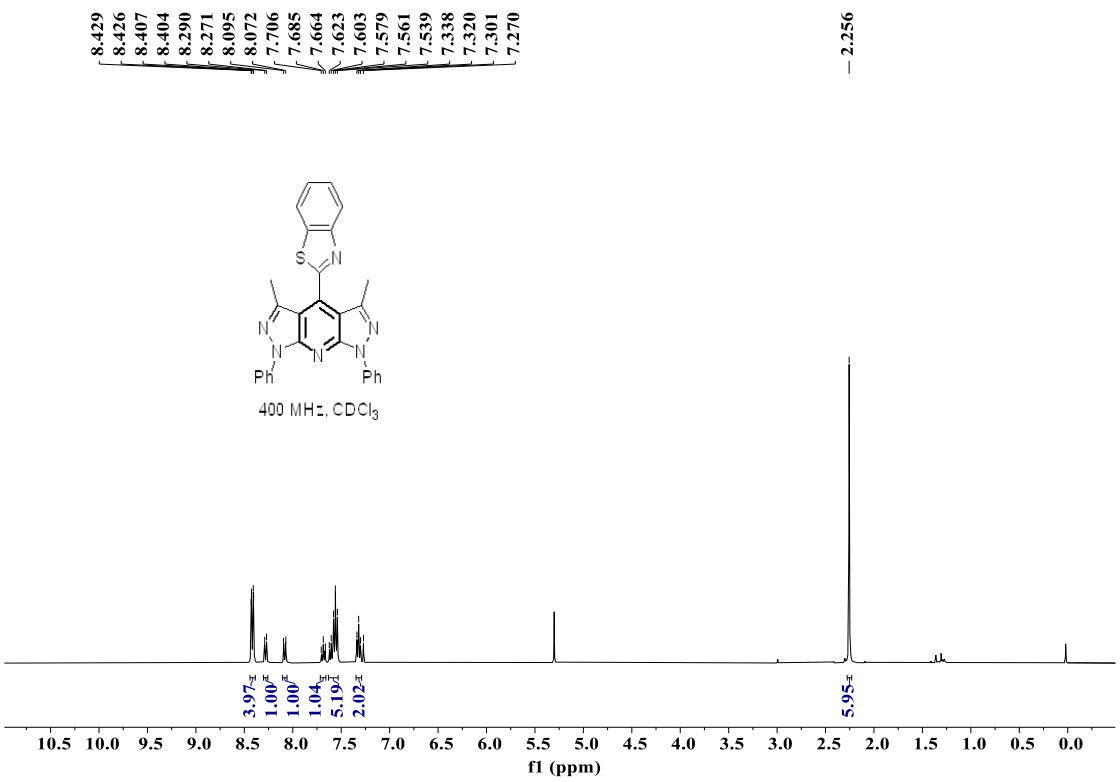


3ma-^{1}H NMR



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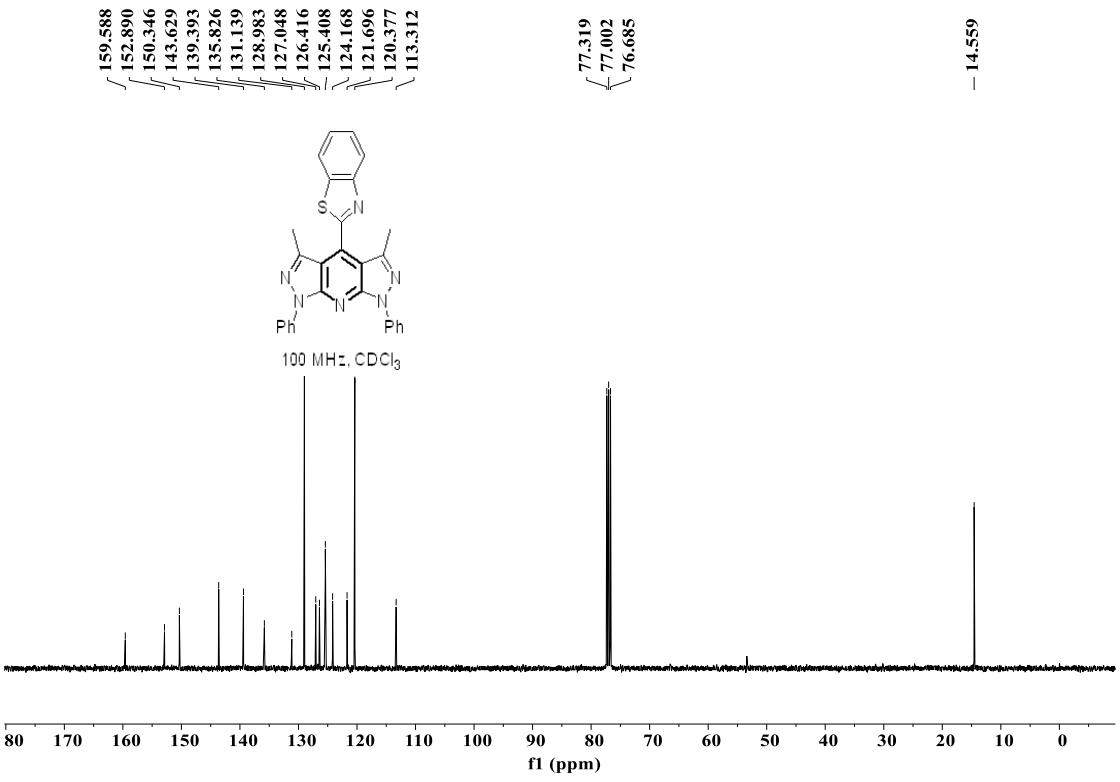
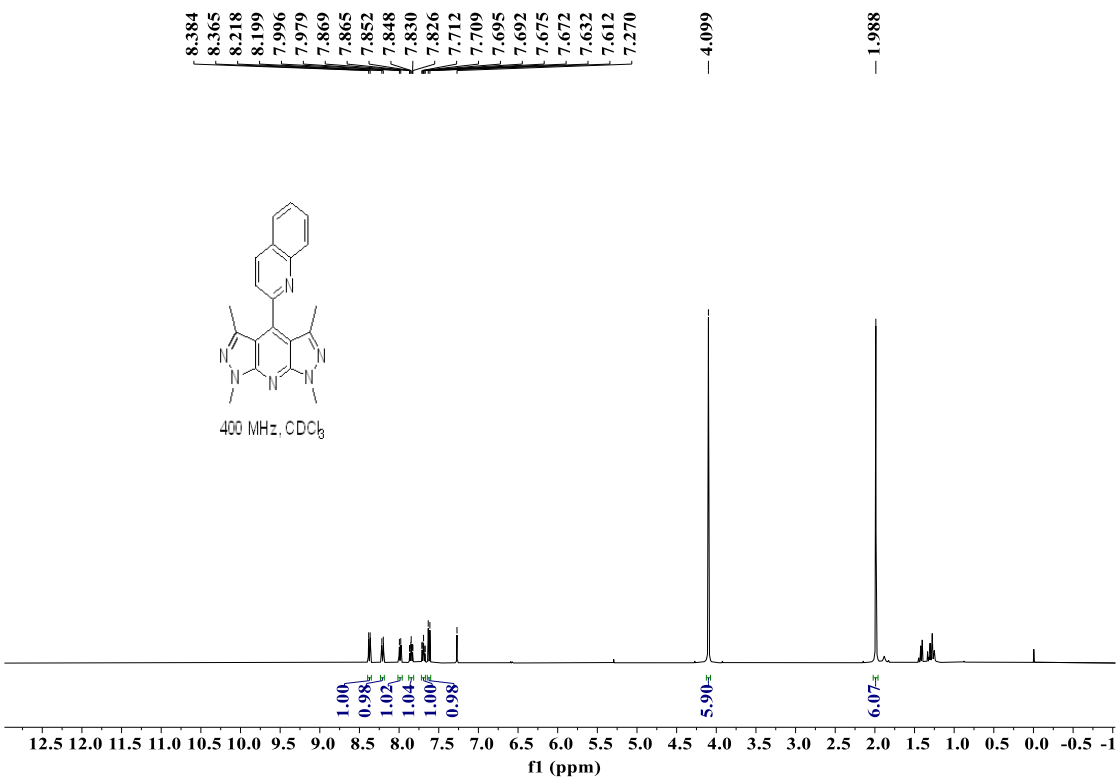


3ab-^{1}H NMR



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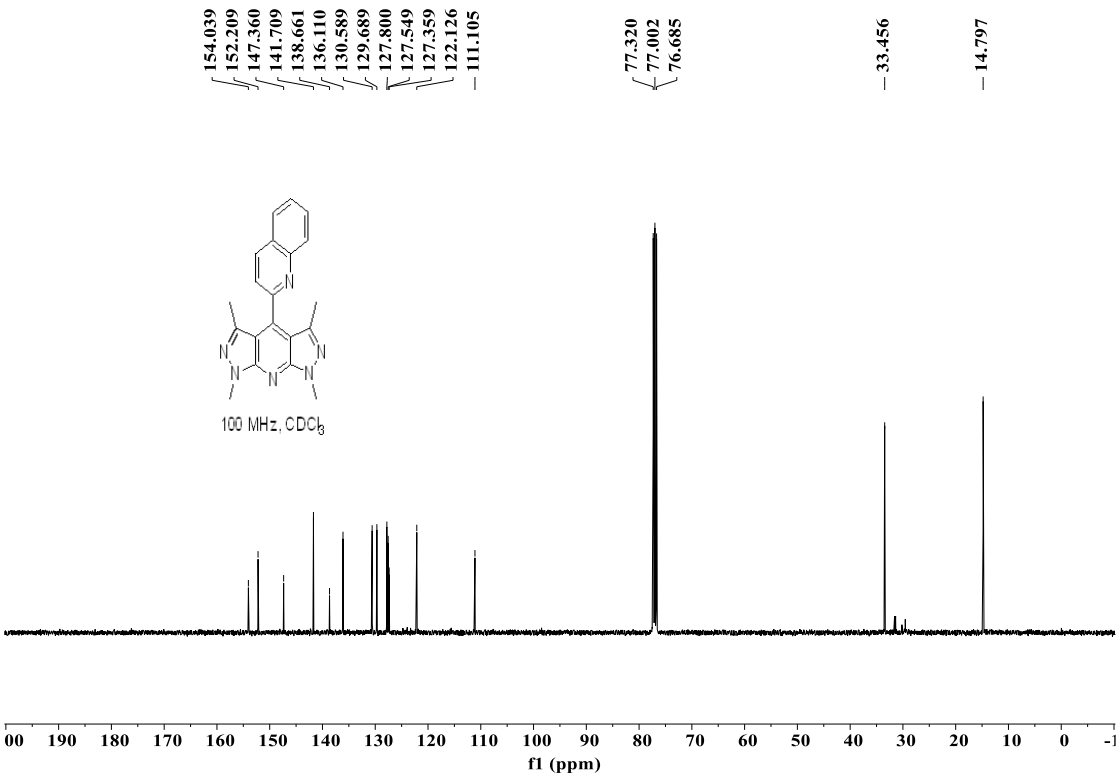
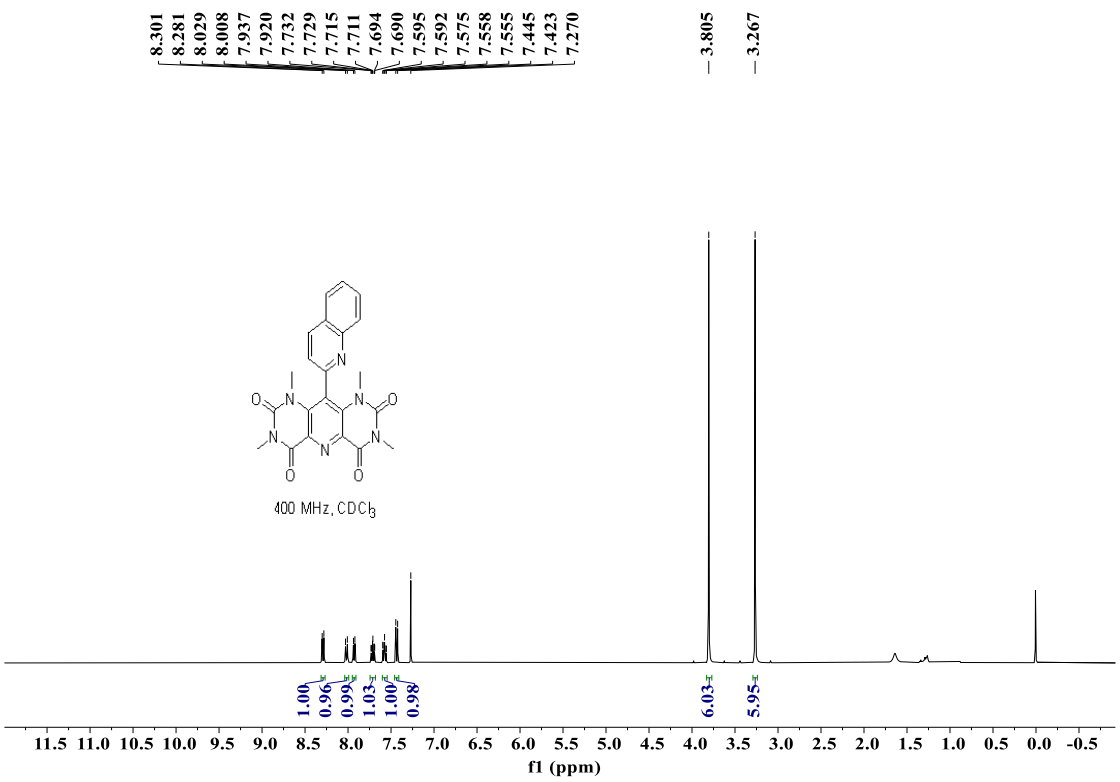
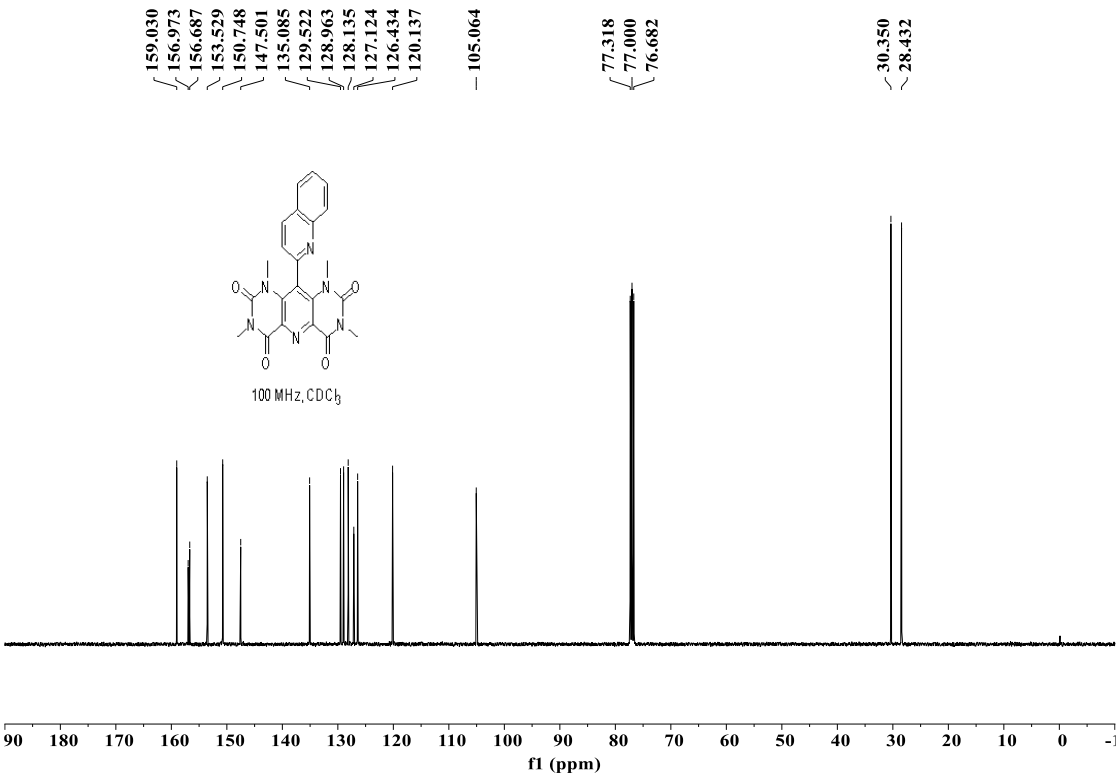


5aa-^{1}H NMR



5aa -^{13}C NMR



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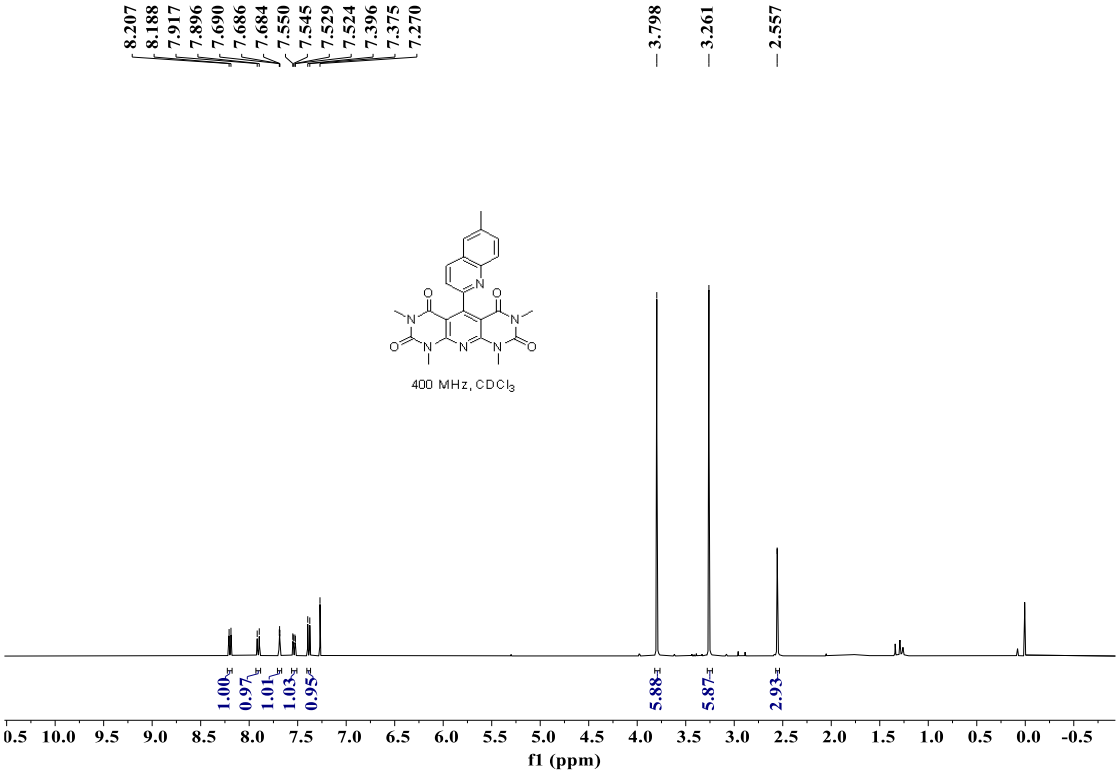
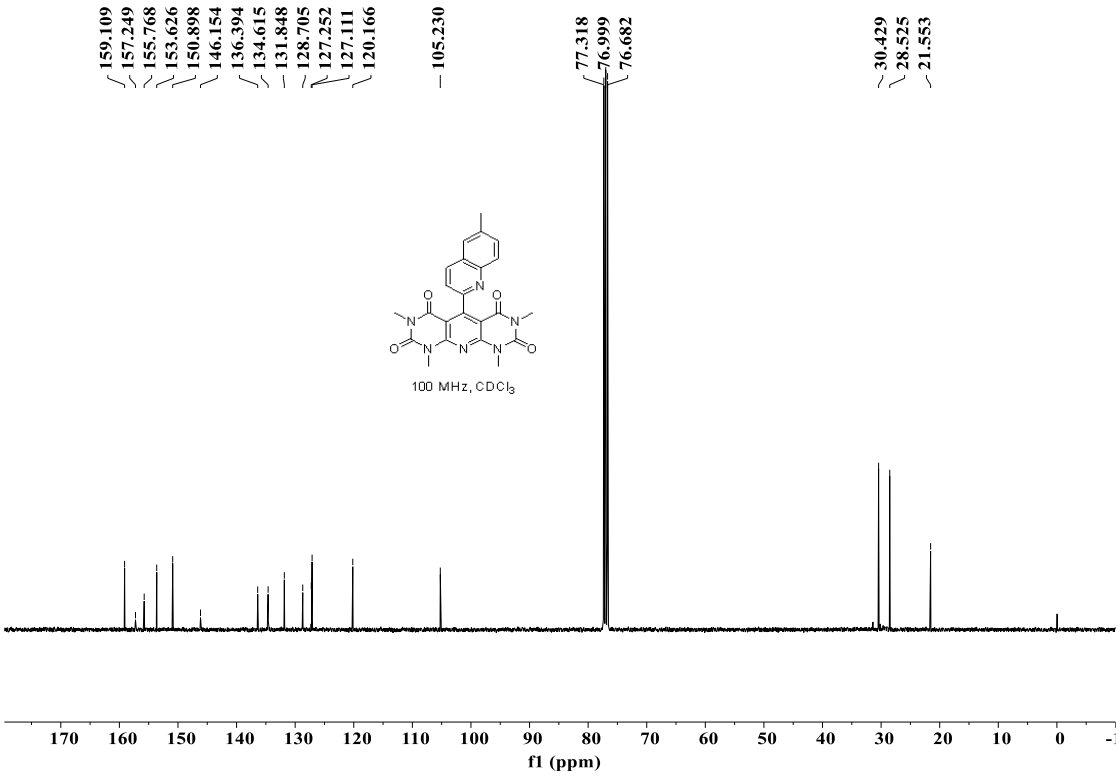
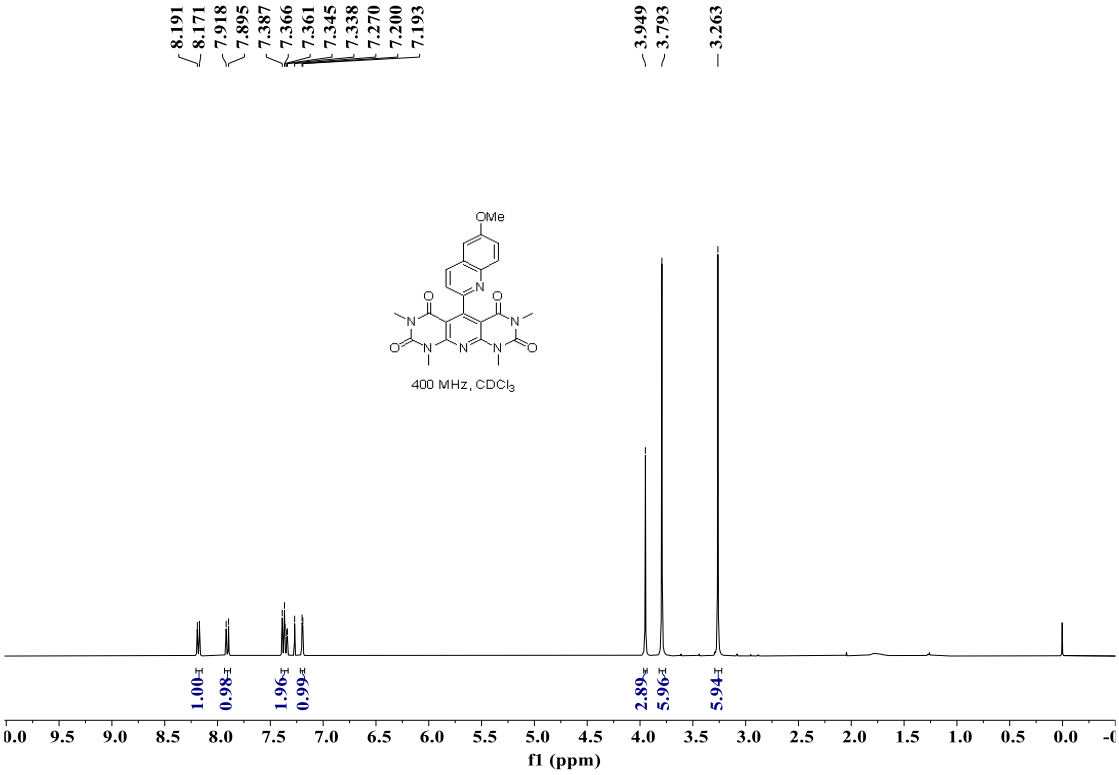


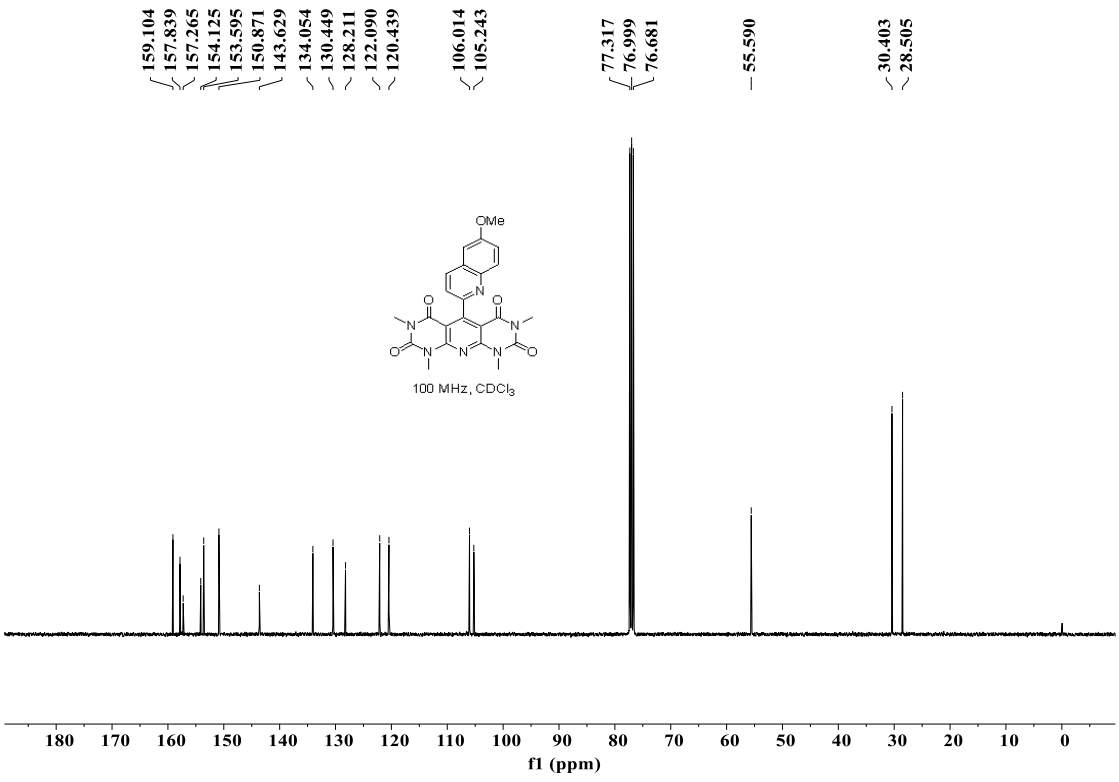
5ba -^{13}C NMR



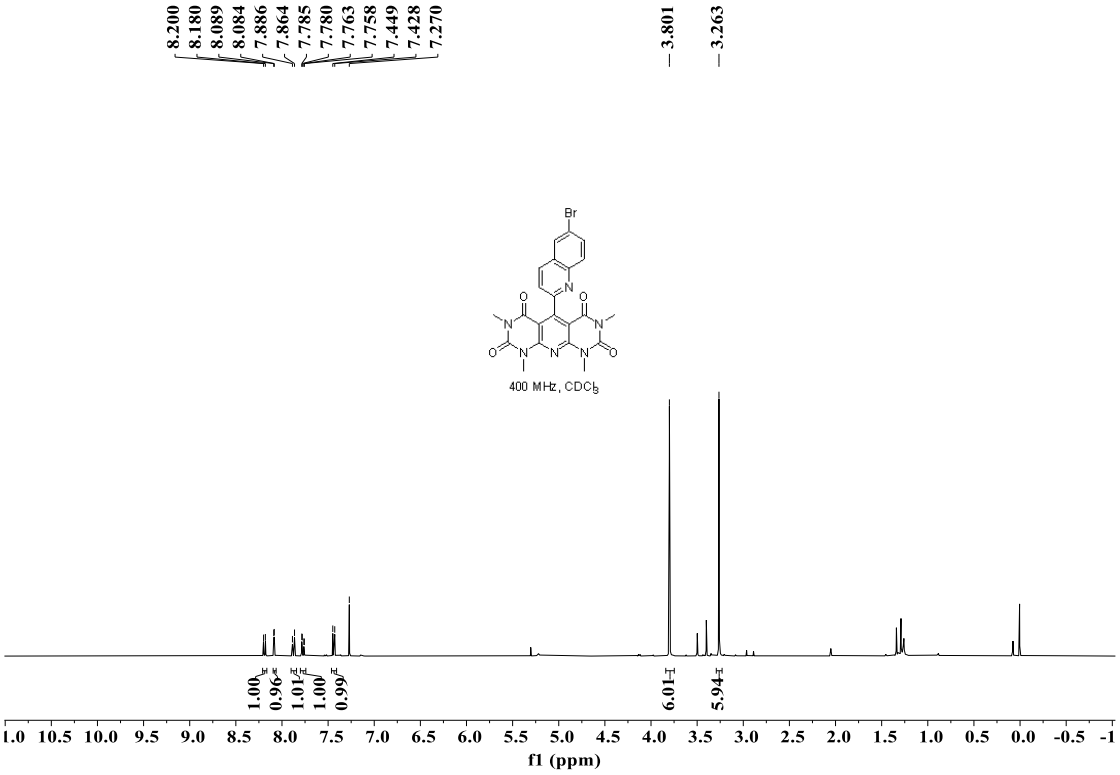
5da-^{1}H NMR



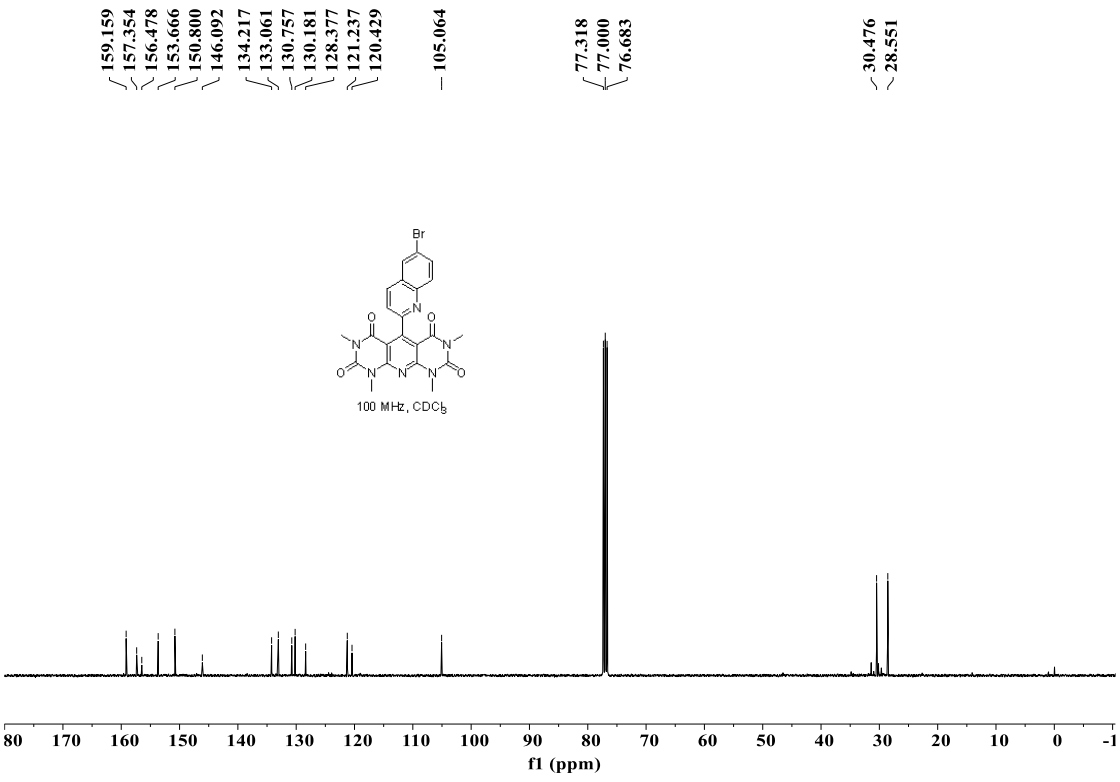
5da -^{13}C NMR



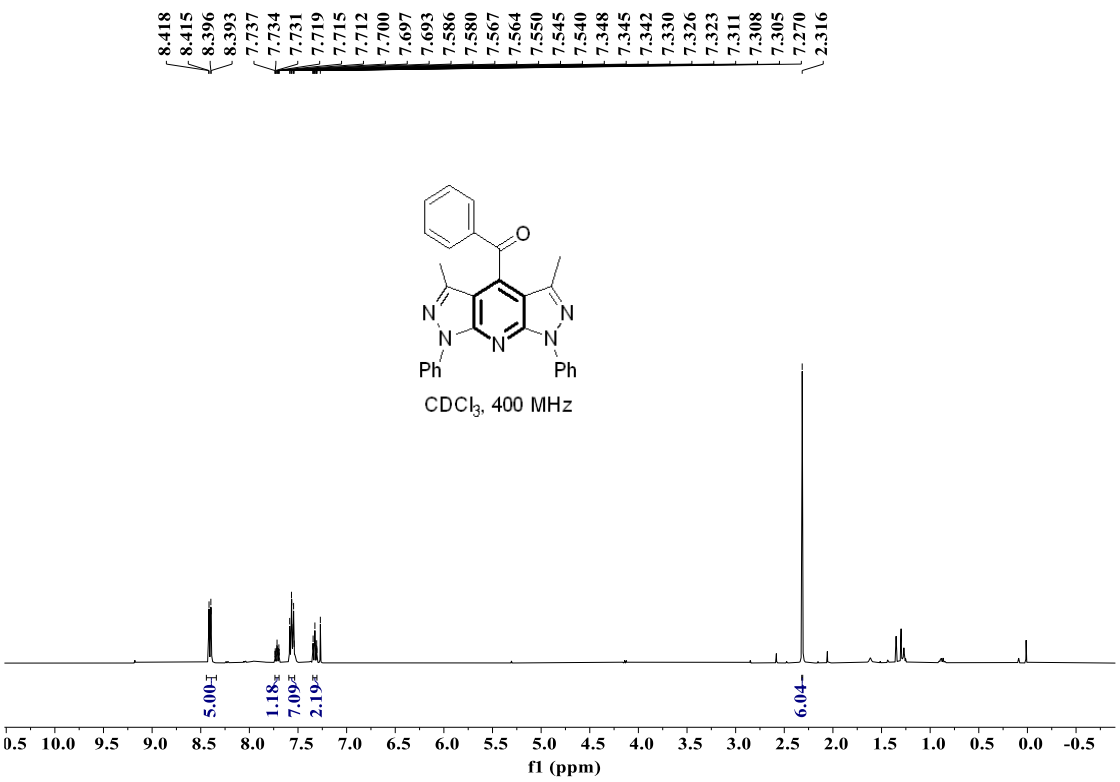
5ga-^{1}H NMR



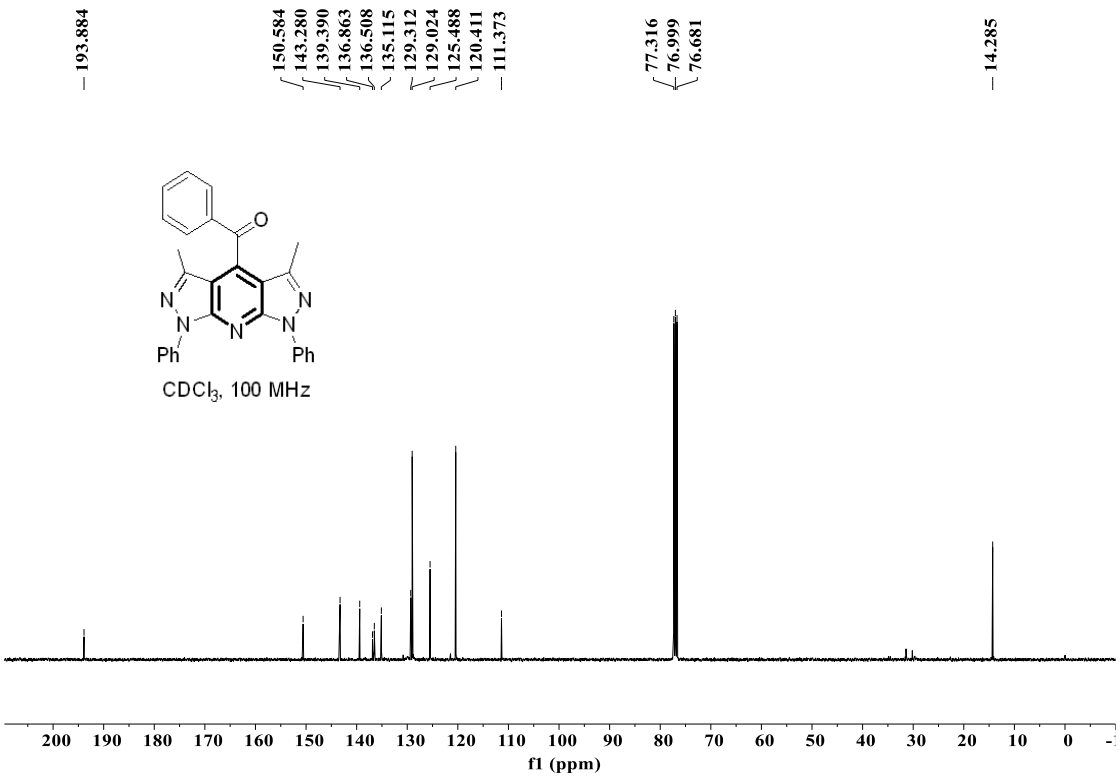
5ga -^{13}C NMR



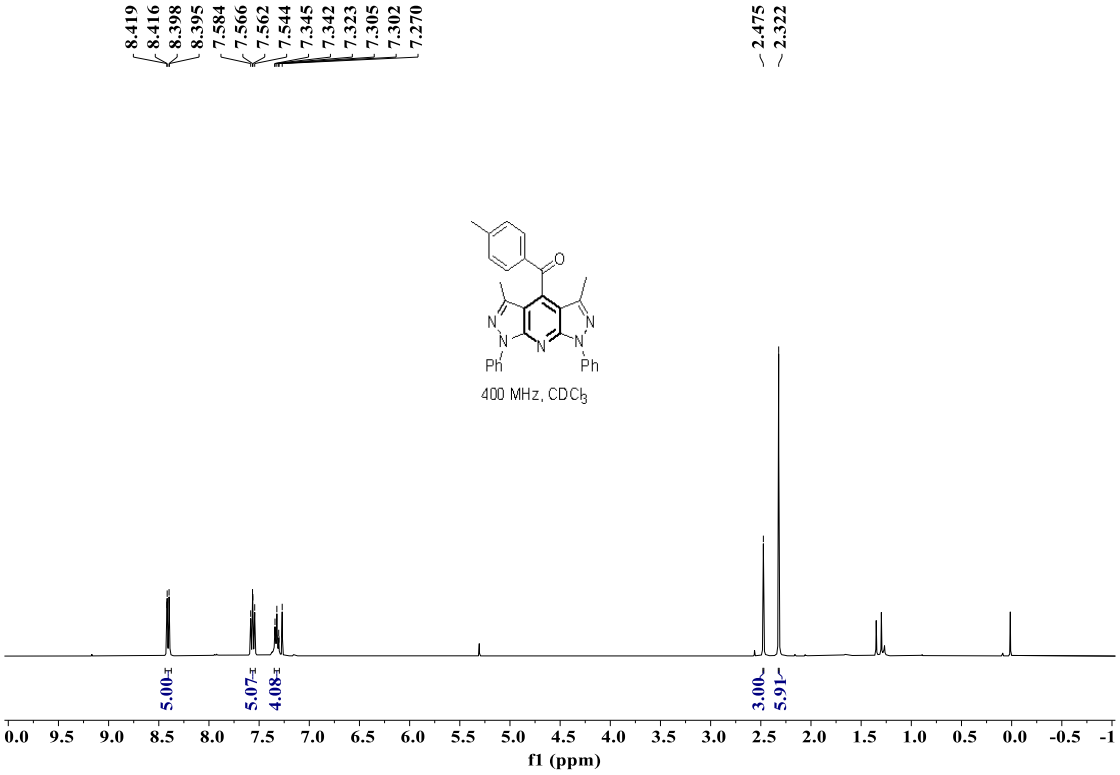
7aa-^{1}H NMR



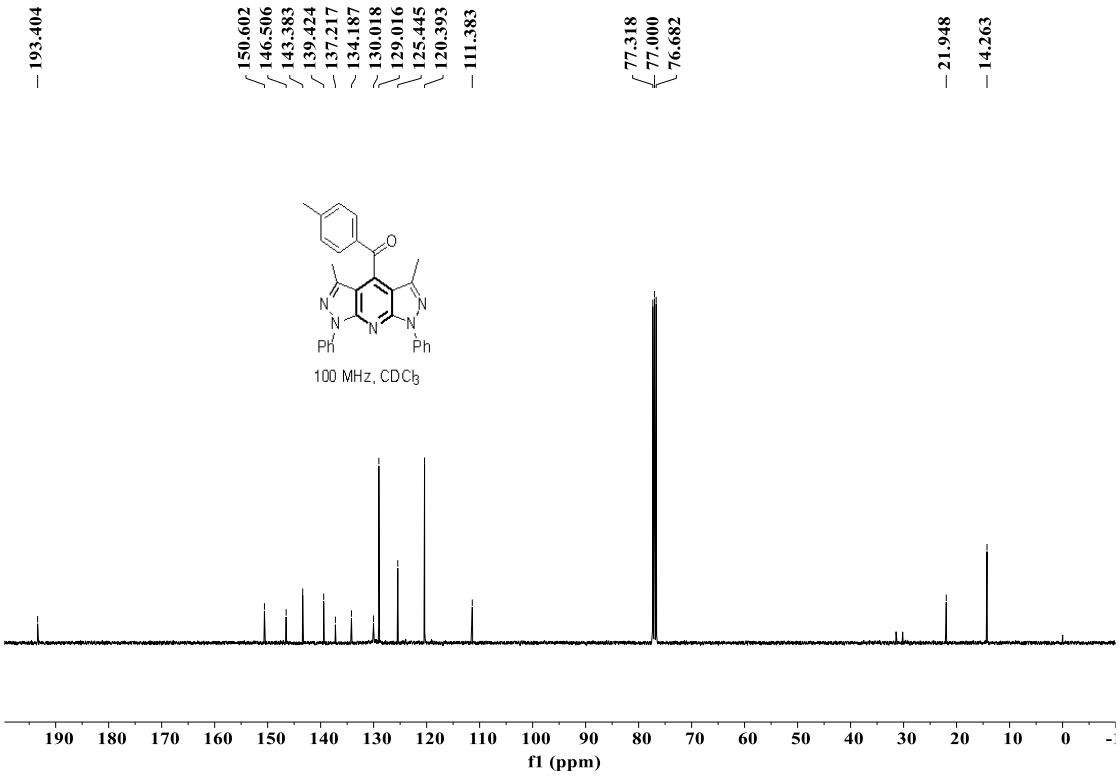
7aa -^{13}C NMR



7ba-^{1}H NMR



7ba -^{13}C NMR



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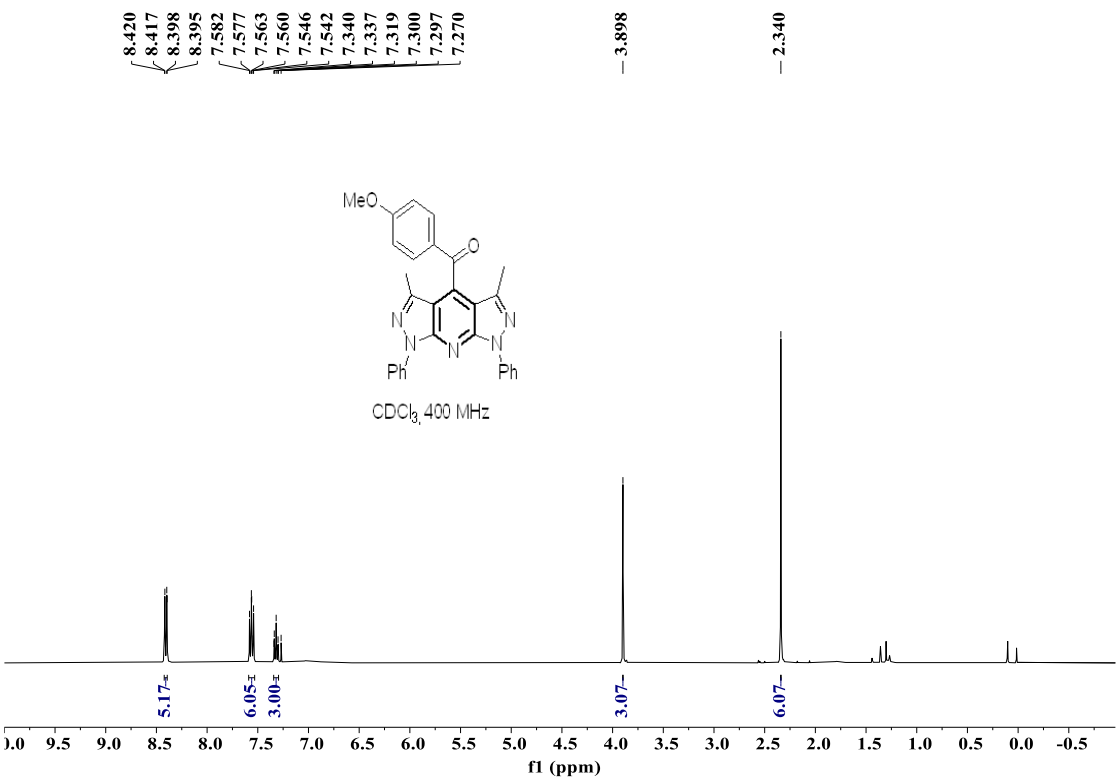

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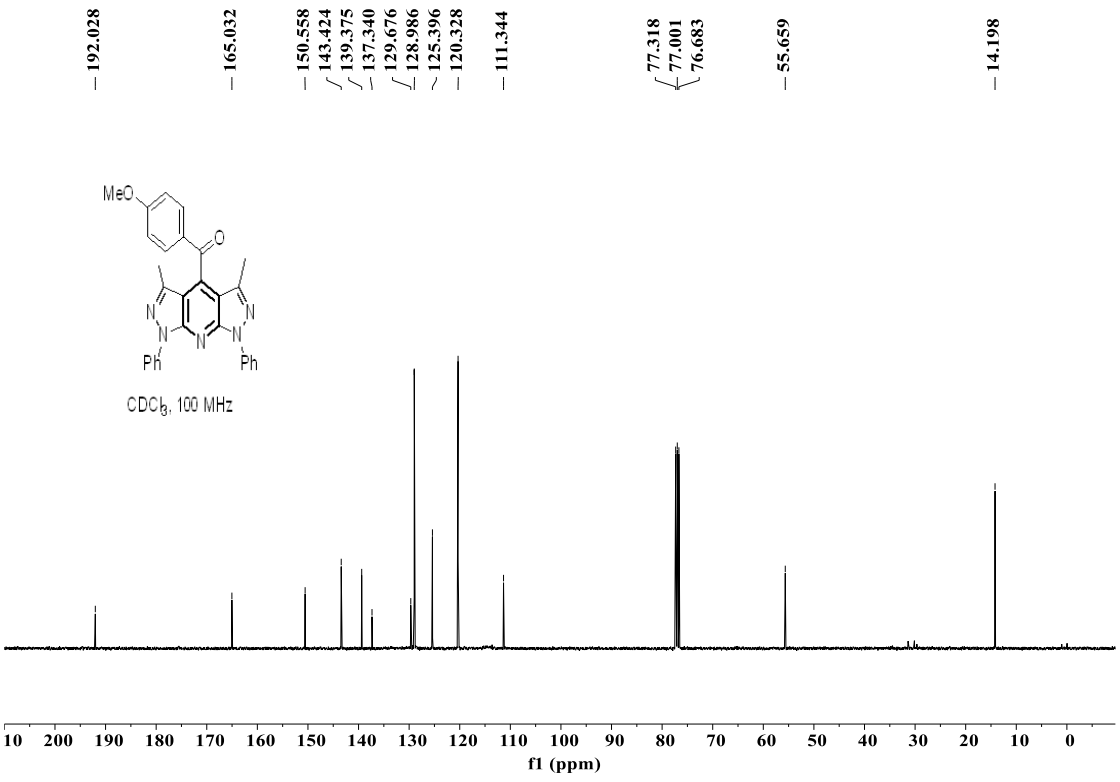
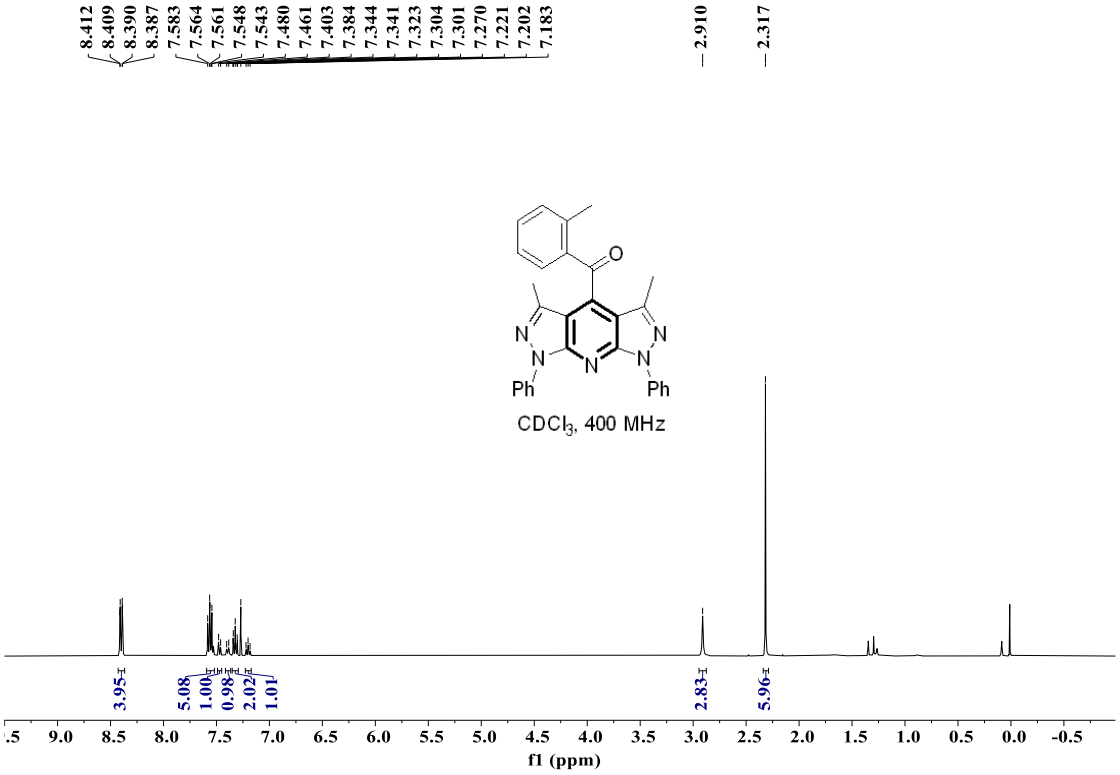
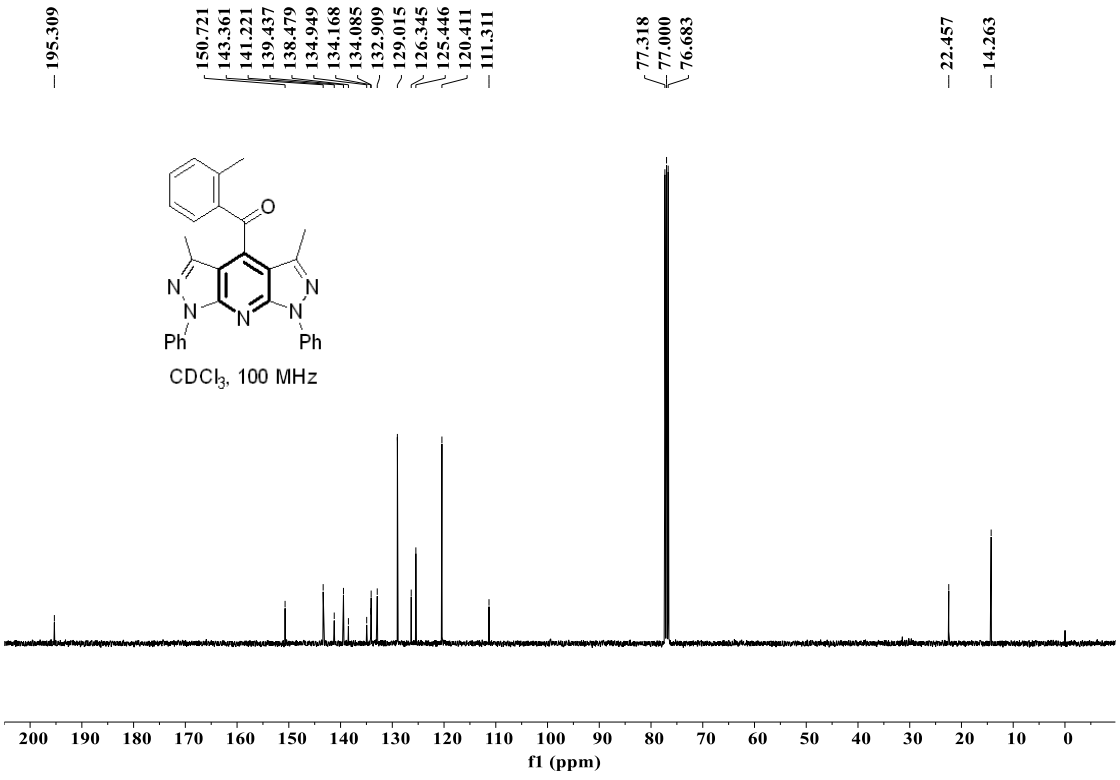


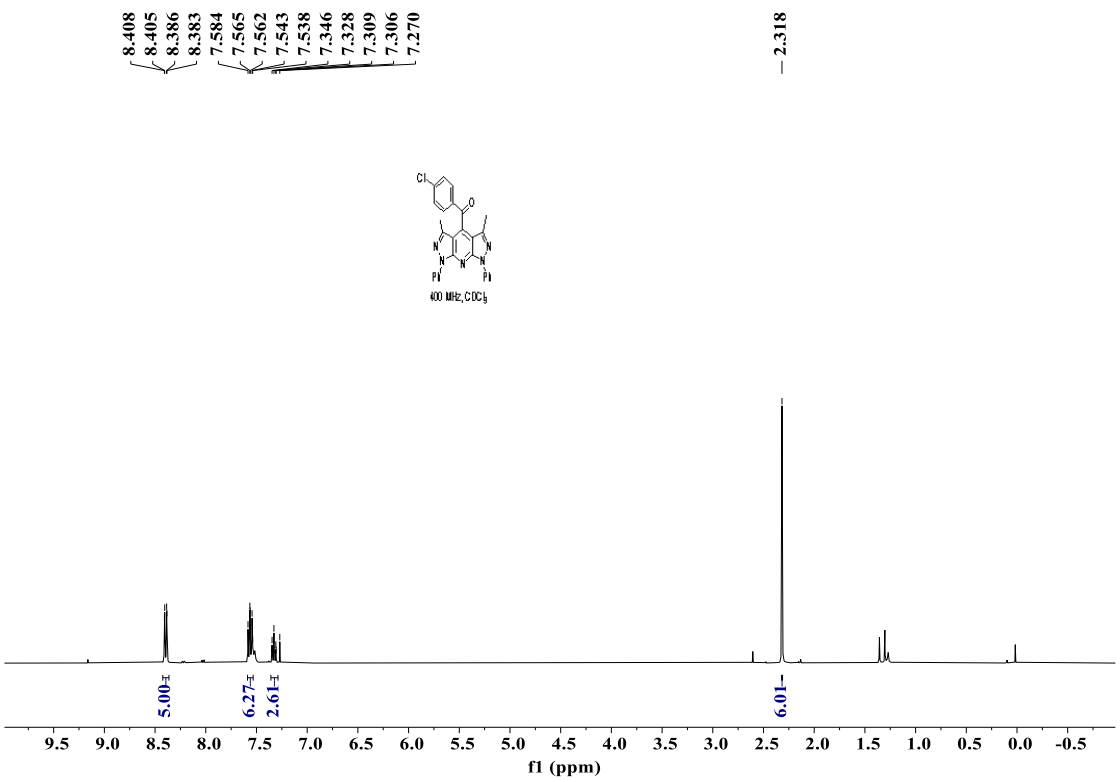
7da-^{1}H NMR



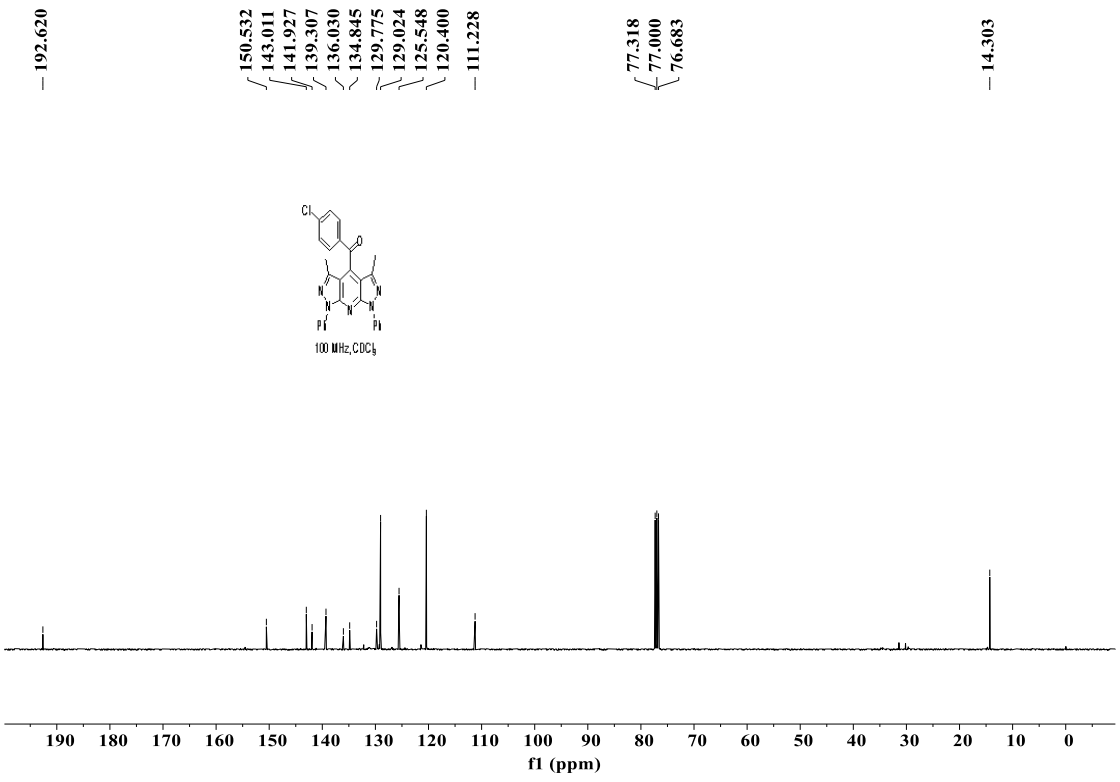
7da -^{13}C NMR



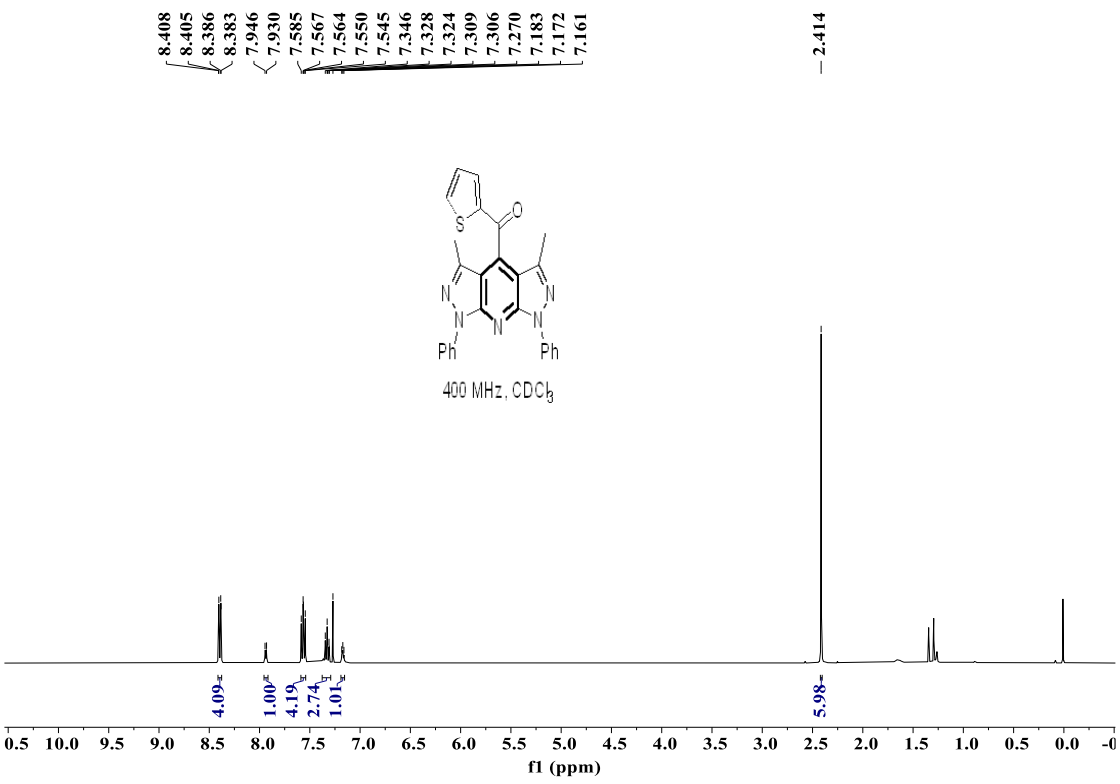
7ea-^{1}H NMR



7ea -^{13}C NMR



7fa-^{1}H NMR



7fa -^{13}C NMR