Electronic Supplementary Information (ESI)

Modular synthesis of substituted-9,14-diaryl-9,14-dihydrodibenzo[a,c]phenazine *via* subsequent Buchwald-Hartwig amination and C-H amination strategy

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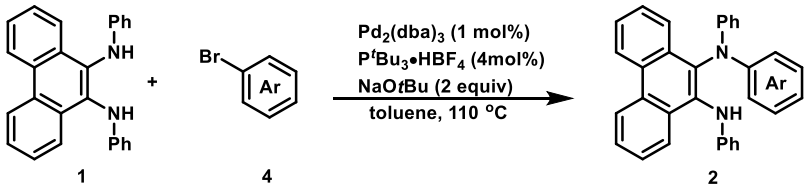
Contents

1. General Experimental Protocols

All reactions were carried out under nitrogen atmosphere and anhydrous conditions unless otherwise indicated. Toluene was distilled from sodium/benzophenone. Dimethyl sulfone was purchased from Adamas [99.8%, SafeDry, with molecular sieves, Water ≤ 50 ppm (by K.F.), SafeSeal]. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.20 mm Huanghai silica gel plates (HSGF 254) using UV light as the visualizing agent. Chromatographic purification of products was accomplished using forced-flow chromatography on silica gel (Huanghai, 300-400 mesh). All new compounds were characterized by means of ^{1}H-NMR, ^{13}C-NMR, ^{19}F-NMR, and HR-MS. NMR spectra were recorded using a Bruker AVANCE III 400 MHz NMR spectrometer and can be found at the end of the paper. High-resolution mass spectra (HRMS) were recorded on a Waters GCT Premier mass spectrometer using EI-TOF, or JEOC AccuTOF LC-plus 4G using ESI, or Agilent Technologies 7250 GCQTOF using EI. The UV/Vis spectra were recorded on a Nicolet CARY 100 spectrophotometer. The fluorescence spectra were recorded on Horiba Fluoromax 4. Single crystal X-ray diffraction data was collected at 193(2) K for **3f** on a Bruker D8 Venture diffractometer. All ^{1}H-NMR data are reported in δ units, parts per million (ppm), and were calibrated relative to the signals for residual chloroform (7.26 ppm) in deuterochloroform ($CDCl_3$). All ^{13}C-NMR data are reported in ppm relative to $CDCl_3$ (77.16 ppm) and were obtained with ^{1}H decoupling. The following abbreviations or combinations thereof were used to explain the multiplicities: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet. N^9,N^{10}-diphenylphenanthrene-9,10-diamine **1** was prepared followed by the reported procedure.[1]

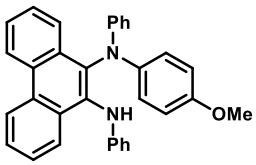
2. General procedure A for the Buchwald-Hartwig Amination



1 4 2

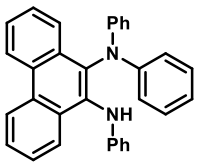
To an oven-dried 10 mL Schlenk tube was added **1** (1.0 equiv), **4** (1.0 equiv), Pd_2dba_3 (1 mol%), P^tBu_3•HBF_4 (4 mol%), and NaO^tBu (2.0 equiv). The sealed tube was backfilled with N_2 (this process was repeated for three times) before toluene (4 mL) was added. The mixture was subsequently heated to 110 ºC until **1** was consumed completely. After cooling to RT, the mixture was quenched with saturated NH_4Cl solution, diluted and extracted with EtOAc, washed with brine and the organic extracts were then combined and concentrated *in vacuo*. Purification by column chromatography to afford the desired product.

N^9-(4-methoxyphenyl)-N^9,N^{10}-diphenylphenanthrene-9,10-diamine (2a)



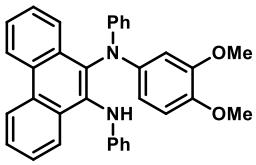
General procedure A was followed on 15 mmol scale with a reaction time of 17 hours and purification by flash column chromatography on silica gel (PE/DCM = 10/1–4/1) to afford **2a** as a yellow-green solid (6.92 g, 99%). M.P. = 45–46 ºC; $\mathbf{R_f}$ = 0.43 (PE/DCM = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.88 (t, *J* = 7.2 Hz, 2H), 8.28 (ddd, *J* = 8.4, 2.4, 1.2 Hz, 2H), 7.77 (td, *J* = 7.6, 0.8 Hz, 1H), 7.70 (td, *J* = 7.6, 1.2 Hz, 1H), 7.66–7.61 (m, 2H), 7.34–7.28 (m, 4H), 7.23–7.19 (m, 4H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.94–6.88 (m, 3H), 6.69 (d, *J* = 7.6, 2H), 6.00 (bs, 1H), 3.80 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.2, 147.2, 146.1, 139.3, 135.4, 133.5, 131.4, 130.6, 130.4, 129.9, 129.4, 128.8, 127.4, 127.0, 126.7, 126.1, 126.1, 125.1, 123.4, 123.0, 122.9, 120.6, 119.4, 118.6 115.8, 114.8, 55.3; **HRMS ESI:** (m/z) $[M+H]^+$: calcd. for $C_{33}H_{27}N_2O$: 467.2118; found: 467.2124.

N^9,N^9,N^{10}-triphenylphenanthrene-9,10-diamine (2b)



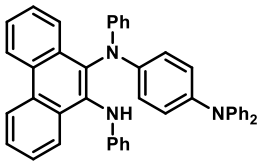
General procedure A was followed on 0.5 mmol scale with a reaction time of 10 hours and purification by flash column chromatography on silica gel (PE to PE/DCM = 10/1) to afford **2b** as a white solid (200.0 mg, 92%). M.P. = 211–212 ºC; $\mathbf{R_f}$ = 0.54 (PE/EtOAc = 50/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.78 (t, *J* = 8.4 Hz, 2H), 8.06 (dd, *J* = 8.0, 0.8 Hz, 1H), 8.02 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.70 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.62 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.52 (qd, *J* = 8.4, 1.2 Hz, 2H), 7.19–7.12 (m, 8H), 7.05 (t, *J* = 7.6 Hz, 2H), 6.90 (ddd, *J* = 8.4, 6.8, 1.6 Hz, 2H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.50 (d, *J* = 8.0, Hz, 2H), 5.86 (bs, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.5, 146.0, 135.7, 133.3, 131.4, 130.8, 130.4, 129.9, 129.5, 128.8, 127.5, 127.1, 126.8, 126.3, 126.2, 125.1, 123.0, 123.0, 121.9, 120.5, 119.6, 115.9; **HRMS ESI:** (m/z) $[M+H]^+$: calcd. for $C_{32}H_{25}N_2$: 437.2012; found: 437.2014.

N^9-(3,4-dimethoxyphenyl)-N^9,N^{10}-diphenylphenanthrene-9,10-diamine (2c)



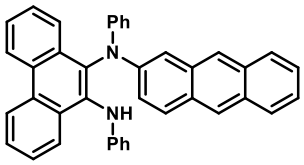
General procedure A was followed on 5 mmol scale with a reaction time of 11 hours and purification by flash column chromatography on silica gel (PE/DCM = 1/1) to afford **2c** as a yellow solid (2.43 g, 98%). M.P. = 105–106 ºC; $\mathbf{R_f}$ = 0.46 (PE/DCM = 1/1). **^{1}H NMR** (400 MHz, CDCl3): δ 8.76 (t, J = 8.0 Hz, 2H), 8.05 (d, J = 8.0 Hz, 2H), 7.68 (t, J = 8.0 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.50 (q, J = 7.6 Hz, 2H), 7.16 (t, J = 8.0 Hz, 2H), 7.06–6.99 (m, 4H), 6.87 (t, J = 7.6 Hz, 1H), 6.77–6.65 (m, 4H), 6.49 (d, J = 8.0 Hz, 2H), 5.84 (bs, 1H), 3.79 (s, 3H), 3.57 (s, 3H); **^{13}C NMR** (100 MHz, CDCl3): δ 149.6, 147.4, 146.3, 145.0, 139.8, 135.4, 133.7, 131.5, 130.7, 130.5, 130.1, 129.6, 128.9, 127.4, 127.1, 126.8, 126.2, 126.2, 125.2, 123.0, 120.8, 119.5, 118.9, 115.6, 114.5, 112.1, 106.8, 56.2, 56.0; **HRMS ESI**: (m/z) $[M+H]^+$: calcd. for $C_{34}H_{29}N_2O_2$: 497.2224; found: 497.2216.

N^9-(4-(diphenylamino)phenyl)-N^9,N^{10}-diphenylphenanthrene-9,10-diamine (2d)



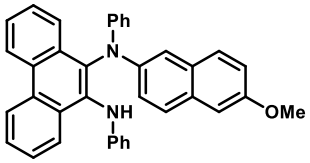
General procedure A was followed on 1 mmol scale with a reaction time of 22 hours and purification by flash column chromatography on silica gel (PE/DCM = 10/1–3/1) to afford **2d** as a yellow solid (412.8 mg, 68%). M.P. = 168–170 ºC; $\mathbf{R_f}$ = 0.61 (PE/DCM = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.81 (t, *J* = 7.2 Hz, 2H), 8.08 (d, *J* = 7.6 Hz, 2H), 7.72 (t, *J* = 7.2 Hz, 1H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.28–7.21 (m, 6H), 7.15–7.10 (m, 6H), 7.03–7.01 (m, 6H), 6.93–6.86 (m, 4H), 6.56 (d, *J* = 8.0 Hz, 2H), 6.09 (bs, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.8, 146.6, 145.9, 142.3, 141.6, 135.8, 132.8, 131.3, 130.8, 130.3, 129.6, 129.5, 129.2, 128.8, 127.5, 127.1, 126.7, 126.2, 126.1, 126.0, 125.0, 123.5, 123.0, 123.0, 122.6, 122.3, 121.0, 119.7, 118.9, 116.2; **HRMS ESI** (m/z) $[M]^+$: calcd. for $C_{44}H_{33}N_3$: 603.2669; found: 603.2661.

N^9-(anthracen-2-yl)-*N*^{9},*N*^{10}-diphenylphenanthrene-9,10-diamine (2e)



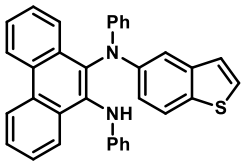
General procedure A was followed on 0.5 mmol scale with a reaction time of 3 hours and purification by flash column chromatography on Al_2O_3 (PE/DCM = 5/1) to afford **2e** as a yellow solid (208.9 mg, 78%). M.P. = 276–277 ºC; $\mathbf{R_f}$ = 0.50 (PE/EtOAc = 50/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.79 (t, *J* = 9.2 Hz, 2H), 8.25 (s, 1H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.94 (s, 1H), 7.91–7.89 (m, 1H), 7.83 (d, *J* = 9.2 Hz, 1H), 7.80–7.78 (m, 1H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.48–7.41 (m, 2H), 7.38–7.34 (m, 3H), 7.20–7.14 (m, 4H), 6.98–6.91 (m, 3H), 6.63 (t, *J* = 7.2 Hz, 1H), 6.46 (d, *J* = 8.0 Hz 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.3, 146.1, 143.4, 135.8, 133.6, 132.8, 132.3, 131.3, 131.0, 130.8, 130.5, 130.1, 129.7, 129.6, 128.8, 128.7, 128.3, 127.8, 127.7, 127.3, 126.9, 126.4, 126.3, 126.1, 125.6, 125.1, 124.7, 124.4, 123.1, 123.1, 122.4, 122.2, 121.1, 119.6, 115.8, 115.1; **HRMS ESI**: (m/z) $[M+H]^+$: calcd. for $C_{40}H_{29}N_2$: 537.2325; found: 537.2340.

N^9-(6-methoxynaphthalen-2-yl)-*N*^{9},*N*^{10}-diphenylphenanthrene-9,10-diamine (2f)



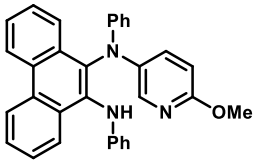
General procedure A was followed on 1 mmol scale with a reaction time of 23 hours and purification by flash column chromatography on silica gel (PE/DCM = 5/1–2/1) to afford **2f** as a yellow solid (425.3 mg, 82%). M.P. = 87–88 ºC; $\mathbf{R_f}$ = 0.39 (PE/DCM = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.82 (t, *J* = 8.4 Hz, 2H), 8.14 (ddd, *J* = 8.0, 4.4, 0.4 Hz, 2H), 7.73 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.66–7.62 (m, 2H), 7.59–7.46 (m, 3H), 7.42–7.39 (m, 2H), 7.24–7.16 (m, 4H), 7.11–7.04 (m, 4H), 6.94 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.55 (d, *J* = 7.8 Hz, 2H), 5.90 (bs, 1H), 3.91 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.8, 146.9, 146.1, 142.1, 135.7, 133.7, 131.4, 130.8, 130.7, 130.5, 130.1, 129.9, 129.5, 128.8, 128.4, 128.1, 127.5, 127.1, 126.8, 126.3, 126.2, 125.2, 123.0, 123.0, 122.3, 121.6, 120.1, 119.5, 119.1, 117.6, 115.7; 105.9, 55.4; **HRMS ESI:** (m/z) $[M+H]^+$: calcd. for $C_{37}H_{29}N_2O$: 517.2274; found: 517.2281.

N^9-(benzo[b]thiophen-5-yl)-*N*^{9},*N*^{10}-diphenylphenanthrene-9,10-diamine (2g)



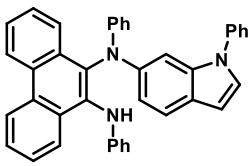
General procedure A was followed on 0.5 mmol scale with a reaction time of 17 hours and purification by flash column chromatography on silica gel (PE/DCM = 10/1–8/1) to afford **2g** as a yellow-green solid (217.2 mg, 88%). M.P. = 98–99 ºC; $\mathbf{R_f}$ = 0.57 (PE/DCM = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.83 (t, *J* = 8.0 Hz, 2H), 8.16 (ddd, *J* = 8.0, 5.6, 0.8 Hz, 2H), 7.76–7.64 (m, 3H), 7.60–7.53 (m, 3H), 7.38–7.33 (m, 2H), 7.25–7.19 (m, 4H), 7.09-7.05 (m, 3H), 6.98-6.94 (m, 1H), 6.78 (t, *J* = 7.8 Hz, 1H), 6.56 (d, *J* = 7.6 Hz, 2H), 5.95 (bs, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.0, 146.1, 143.6, 140.9 135.7, 133.8, 133.7, 131.4, 130.8, 130.5, 130.1, 129.5, 128.8, 127.6, 127.4, 127.1, 126.8, 126.2, 125.2, 123.6, 123.3, 123.0, 123.0, 121.6, 120.0, 119.5, 119.3, 115.7, 115.5; **HRMS ESI:** (m/z) $[M+H]^+$: calcd. for $C_{34}H_{25}N_2S$: 493.1733; found: 493.1720.

N^9-(6-methoxypyridin-3-yl)-*N*^{9},*N*^{10}-diphenylphenanthrene-9,10-diamine (2h)



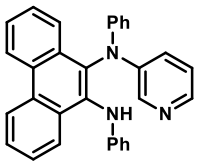
General procedure A was followed on 7 mmol scale with a reaction time of 4 hours and purification by flash column chromatography on silica gel (PE/DCM = 3/1–DCM) to afford **2h** as a yellow solid (3.44 g, 99%). M.P. = 74–75 ºC; $\mathbf{R_f}$ = 0.69 (PE/acetone = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.76 (dd, *J* = 8.4, 4.4 Hz, 2H), 8.03 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.98–7.96 (m, 2H), 7.68 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.62 (ddd, *J* = 8.0, 6.8, 0.8 Hz, 1H), 7.53–7.48 (m, 2H), 7.40 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.20-7.16 (m, 2H), 7.05–6.97 (m, 4H), 6.89 (t, *J* = 7.6 Hz, 1H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.49 (d, *J* = 8.8 Hz, 1H), 6.45 (d, *J* = 7.6 Hz, 2H), 5.81 (s, 1H), 3.81 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.8, 146.8, 145.9, 140.7, 136.8, 135.6, 133.5, 133.0, 131.0, 130.9, 130.5, 129.9, 129.8, 129.0, 127.6, 127.3, 126.9, 126.4, 126.2, 124.9, 123.2, 123.0, 121.2, 119.6, 118.2, 115.7, 111.1, 53.6; **HRMS ESI:** (m/z) $[M+H]^+$: calcd. for $C_{32}H_{26}N_3O$: 468.2070; found: 468.2067.

N^9,*N*^{10}-diphenyl-*N*^{9}-(1-phenyl-1H-indol-6-yl)phenanthrene-9,10-diamine (2i)



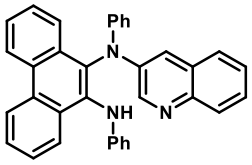
General procedure A was followed on 0.5 mmol scale with a reaction time of 24 hours and purification by flash column chromatography on silica gel (PE/DCM = 10/1) to afford **2i** as a yellow-green solid (221.4 mg, 80%). M.P. = 120–121 ºC; $\mathbf{R_f}$ = 0.38 (PE/EtOAc = 60/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.76 (t, *J* = 8.8 Hz, 2H), 8.07 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.67 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.59 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H) 7.52–7.44 (m, 3H), 7.38–7.32 (m, 3H), 7.27–7.24 (m, 3H), 7.21 (d, *J* = 3.2 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 2H), 7.07 (td, *J* = 8.4, 1.6, 3H), 6.95 (t, *J* = 7.2 Hz, 2H), 6.86 (t, *J* = 7.2 Hz, 1H), 6.68 (t, *J* = 7.2 Hz, 1H), 6.58 (d, *J* = 3.2 Hz, 1H), 6.43 (d, *J* = 8.4 Hz, 2H), 5.85 (bs, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.7, 146.3, 142.1, 139.7, 136.5, 135.4, 134.0, 131.6, 130.8, 130.5, 130.2, 129.7, 129.5, 128.8, 127.9, 127.4, 126.9, 126.7, 126.3, 126.2, 126.1, 125.4, 125.3, 124.0, 123.0, 123.0, 121.9, 121.0, 119.5, 119.3, 116.5, 115.7, 104.1, 103.6; **HRMS ESI:** (m/z) $[M+H]^+$: calcd. for $C_{40}H_{30}N_3$: 552.2434; found: 552.2420.

***N*⁹,*N*¹⁰-diphenyl-*N*⁹-(pyridin-3-yl)phenanthrene-9,10-diamine (2j)**



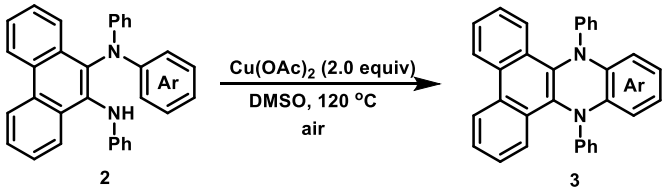
General procedure A was followed on 0.2 mmol scale with a reaction time of 2 hours and purification by flash column chromatography on silica gel (PE/EtOAc = 5/1) with 2% Et_3N to afford **2j** as a brown-yellow solid (76 mg, 87%). M.P. = 179–181 ºC; $\mathbf{R_f}$ = 0.36 (PE/EtOAc = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.77 (dd, *J* = 8.4, 4.4 Hz, 2H), 8.45 (d, *J* = 2.0 Hz, 1H), 8.07–8.03 (m, 2H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.70 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.63 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.54–7.48 (m, 2H), 7.29–7.26 (m, 1H), 7.24–7.13 (m, 4H), 7.04–6.95 (m, 4H), 6.73 (t, *J* = 7.6 Hz, 1H), 6.46 (d, *J* = 8.4 Hz, 2H), 5.80 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.7, 145.5, 143.0, 142.5, 142.1, 136.0, 132.4, 131.0, 130.7, 130.5, 129.9, 129.8, 129.0, 127.7, 127.5, 127.0, 126.7, 126.5, 126.3, 124.7, 123.8, 123.2, 123.1, 122.9, 120.5, 119.8, 115.7; **HRMS ESI:** (m/z) $[M+H]^+$: calcd. for $C_{31}H_{24}N_3$: 438.1965; found: 438.1966.

***N*⁹,*N*¹⁰-diphenyl-*N*⁹-(quinolin-3-yl)phenanthrene-9,10-diamine (2k)**



General procedure A was followed on 0.5 mmol scale with a reaction time of 6 hours and purification by flash column chromatography on silica gel (PE/EtOAc = 10/1) to afford **2k** as a brown-red solid (212.2 mg, 87%). M.P. = 113–115 ºC; $\mathbf{R_f}$ = 0.47 (PE/EtOAc = 5/2). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.93 (d, *J* = 2.0 Hz, 1H), 8.80 (t, *J* = 7.6 Hz, 2H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.52–7.47 (m, 3H), 7.36 (d, *J* = 4.0 Hz, 2H), 7.25–7.16 (m, 4H), 7.03–6.95 (m, 3H), 6.65 (t, *J* = 7.2 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 2H), 5.80 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.9, 145.8, 145.7, 143.6, 140.1, 136.0, 132.8, 131.0, 130.7, 130.6, 130.0, 130.0, 128.9, 128.8, 127.8, 127.6, 127.4, 127.1, 127.1, 126.7, 126.6, 126.3, 124.7, 123.2, 123.1, 120.4, 119.7, 115.5; **HRMS ESI**: (m/z) $[M+H]^+$: calcd. for $C_{35}H_{26}N_3$: 488.2121; found: 488.2129.

3. General procedure B for the C-H Amination

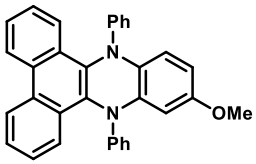


2 3

To an 8 mL vial equipped with a stir bar was added **2** (1.0 equiv) and $Cu(OAc)_2$ (2.0 equiv) dissolved in DMSO (using $CaCl_2$ drying tube as a desiccator) under air. The mixture was subsequently heated to 120 ºC and monitored by TLC until **2** was completely consumed. After cooling to RT, the mixture was quenched with water and filtered. The filtrate was diluted and extracted with EtOAc, washed with brine and the organic extracts were then combined and concentrated *in vacuo*. Purification by column chromatography yielded the desired product.

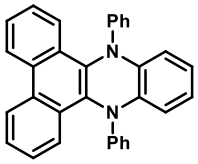
Characterization Data for products

11-methoxy-9,14-diphenyl-9,14-dihydrodibenzo[a,c]phenazine (3a)



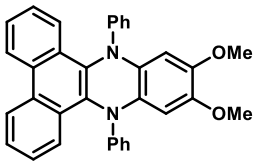
General procedure B was followed on 0.2 mmol scale with a reaction time of 12 hours and purification by flash column chromatography on silica gel (PE/DCM = 5/1–4/1) to afford **3a** as a chartreuse solid (53.7 mg, 58%). M.P. = 219–220 ºC; $\mathbf{R_f}$ = 0.53 (PE/DCM = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.76 (d, *J* = 8.4 Hz, 2H), 8.19 (dd, *J* = 14.4, 7.6 Hz, 2H), 7.69–7.64 (m, 3H), 7.61–7.55 (m, 2H), 7.37 (bs, 1H), 7.10–7.03 (m, 6H), 6.98–6.92 (m, 3H), 6.84–6.78 (m, 2H), 3.92 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.5, 148.4, 147.5, 146.1, 138.7, 138.4, 137.9, 129.9, 129.9, 129.7, 129.5, 128.8, 128.7, 128.1, 127.1, 127.0, 126.6, 126.6, 124.7, 124.7, 123.1, 123.1, 121.3, 120.7, 117.2, 116.3, 113.1, 110.6, 55.9; **HRMS EI:** calcd. for $C_{33}H_{24}N_2O$: 464.1883; found: 464.1886.

9,14-diphenyl-9,14-dihydrodibenzo[a,c]phenazine (3b)



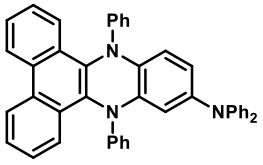
General procedure B was followed on 0.1 mmol scale with a reaction time of 13 hours and purification by flash column chromatography on silica gel (PE/DCM = 10/1) to afford **3b** as a white solid (16.7 mg, 38%). $\mathbf{R_f}$ = 0.61 (PE/EtOAc = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.74 (d, *J* = 8.4 Hz, 2H), 8.14 (d, *J* = 8.0 Hz, 2H), 7.76 (dd, *J* = 5.6, 3.6 Hz, 2H), 7.65 (t, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.35 (dd, *J* = 5.2, 3.6 Hz, 2H), 7.05–6.95 (m, 8H), 6.78 (t, *J* = 6.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.8, 145.0, 138.3, 130.0, 129.6, 128.9, 127.5, 127.1, 126.6, 125.5, 124.7, 123.1, 121.1, 116.9. This product is matched with reported data.[2]

11,12-dimethoxy-9,14-diphenyl-9,14-dihydrodibenzo[a,c]phenazine (3c)



General procedure B was followed on 1.165 mmol scale with a reaction time of 12 hours and purification by flash column chromatography on silica gel (PE/DCM = 5/1–2/1) to afford **3c** as a yellow solid (479.1 mg, 83%). M.P. = 174–175 ºC; $\mathbf{R_f}$ = 0.46 (PE/EtOAc = 10/3). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.76 (d, *J* = 8.0 Hz, 2H), 8.21 (d, *J* = 8.0 Hz, 2H), 7.67 (t, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 2H), 7.32 (s, 2H), 7.05–6.95 (m, 8H), 6.78 (t, *J* = 7.2 Hz, 2H), 4.02 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.2, 146.8, 139.1, 138.0, 129.8, 129.7, 128.7, 127.1, 126.6, 124.7, 123.1, 120.8, 116.3, 111.0, 56.5; **HRMS EI:** calcd. for $C_{34}H_{26}N_2O_2$: 494.1989; found: 494.1997.

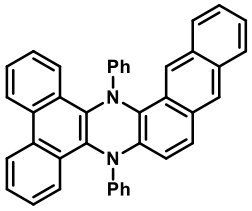
N,N,9,14-tetraphenyl-9,14-dihydrodibenzo[a,c]phenazin-11-amine (3d)



General procedure B was followed on 0.5 mmol scale with a reaction time of 6 hours and purification by flash column chromatography on silica gel (PE/DCM = 20/1–2/1) to afford **3d** as a yellow solid (93.3 mg, 31%). M.P. = 277–278 ºC; $\mathbf{R_f}$ = 0.51 (PE/EtOAc = 35/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.75 (d, *J* = 8.4 Hz, 2H), 8.13 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.68–7.48 (m, 6H),

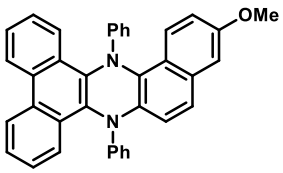
7.34–7.30 (m, 4H), 7.23–7.21 (m, 4H), 7.10–7.00 (m, 9H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.84–6.78 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.0, 147.8, 147.5, 145.7, 145.5, 139.7, 138.4, 137.9, 130.0, 130.0, 129.5, 129.5, 128.9, 128.8, 127.6, 127.1, 127.0, 126.6, 126.6, 124.7, 124.4, 123.1, 123.1, 123.0, 121.1, 121.0, 120.8, 117.0, 116.6; **HRMS ESI**: (m/z) [M]+: calcd. for $C_{44}H_{31}N_3$: 601.2513; found: 603.2501.

5,14-diphenyl-5,14-dihydrodibenzo[a,c]naphtho[2,3-h]phenazine (3e)



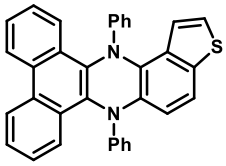
General procedure B was followed on 0.056 mmol scale with a reaction time of 10 hours and purification by flash column chromatography on Al_2O_3 (PE–PE/EtOAc = 50/1) to afford **3e** as a yellow-green solid (27.1 mg, 91%). M.P. = 199–201 °C; **R_f** = 0.37 (PE/EtOAc = 50/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.97 (s, 1H), 8.75 (d, *J* = 8.0 Hz, 2H), 8.70 (d, *J* = 8.0 Hz, 1H), 8.51 (s, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 7.6 Hz, 1H), 8.05–7.96 (m, 3H), 7.79–7.70 (m, 2H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.51–7.47 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 7.2 Hz, 2H), 6.91 (t, *J* = 7.6 Hz, 2H), 6.85 (t, *J* = 7.2 Hz, 1H), 6.71 (t, *J* = 7.2 Hz, 1H), 6.66 (d, *J* = 8.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.6, 147.1, 143.6, 139.9, 139.1, 138.8, 132.4, 131.6, 130.7, 130.3, 130.2, 130.0, 129.7, 129.5, 129.0, 128.7, 128.6, 128.3, 127.5, 127.2, 127.1, 126.9, 126.7, 126.1, 125.6, 125.6, 125.0, 124.6, 123.2, 123.1, 122.1, 122.1, 120.0, 118.8, 115.6; **HRMS ESI:** (m/z) $[M+H]^+$: calcd. for $C_{40}H_{27}N_2$: 535.2169; found: 535.2167.

3-methoxy-7,16-diphenyl-7,16-dihydrotribenzo[a,c,h]phenazine (3f)



General procedure B was followed on 0.5 mmol scale with a reaction time of 14 hours and purification by flash column chromatography on silica gel (PE/DCM = 5/1–3/1) to afford **3f** as a white solid (182.0 mg, 71%). M.P. = 273–274 °C; **R_f** = 0.55 (PE/DCM = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.73 (d, *J* = 8.4 Hz, 2H), 8.56 (dd, *J* = 6.4, 2.0 Hz, 2H), 8.41 (d, *J* = 8.8 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.73–7.69 (m, 2H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.35 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.27 (d, *J* = 2.4 Hz, 1H), 7.11–7.03 (m, 4H), 6.96 (t, *J* = 7.6 Hz, 2H), 6.83 (t, *J* = 6.8 Hz, 1H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 2H), 3.98 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.8, 149.0, 147.4, 142.0, 140.1, 139.9, 139.3, 133.0, 130.6, 130.0, 129.6, 129.5, 128.8, 128.5, 127.4, 127.0, 126.9, 126.7, 126.6, 126.4, 125.4, 125.2, 124.9, 124.5, 123.1, 123.1, 121.5, 119.9, 119.8, 117.7, 115.3, 106.2, 55.5; **HRMS ESI:** (m/z) $[M+H]^+$: calcd. for $C_{37}H_{27}N_2O$: 515.2118; found: 515.2108.

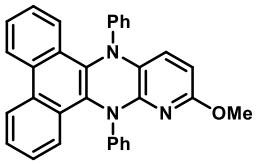
6,15-diphenyl-6,15-dihydrodibenzo[a,c]thieno[3,2-h]phenazine (3g)



General procedure B was followed on 0.2 mmol scale with a reaction time of 14 hours and purification by flash column chromatography on silica gel (PE/ EtOAc = 50/1) to afford **3g** as a white solid (43.3 mg, 44%). M.P. = 131–132°C; **R_f** = 0.43 (PE/EtOAc = 50/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.75 (d, *J* =

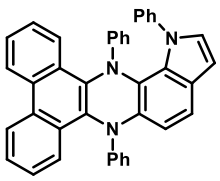
8.0 Hz, 2H), 8.37 (dd, *J* = 7.6, 1.2 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.71–7.63 (m, 4H), 7.58–7.54(m, 2H), 7.01–7.00 (m, 4H), 6.95 (t, *J* = 8.0 Hz, 2H), 6.79–6.75 (m, 1H), 6.72–6.68 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.1, 147.7, 142.8, 139.9, 139.6, 139.1, 138.7, 137.6, 130.3, 130.1, 129.8, 129.7, 128.8, 128.7, 128.2, 127.3, 127.1, 126.8, 126.8, 124.9, 124.7, 124.3, 123.2, 123.2, 122.3, 121.2, 120.1, 120.0, 117.1, 115.0; **HRMS ESI:** (m/z) $[M+H]^+$: calcd. for $C_{34}H_{23}N_2S$: 491.1577; found: 491.1583.

11-methoxy-9,14-diphenyl-9,14-dihydrodibenzo[f,h]pyrido[2,3-b]quinoxaline(3h)



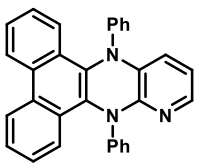
General procedure B was followed on 1.3 mmol scale with a reaction time of 8 hours and purification by flash column chromatography on silica gel (PE/ DCM = 5/1) to afford **3h** as a white solid (545.1 mg, 90%). M.P. = 234–236 ºC; **R_f** = 0.66 (PE/acetone = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.71 (d, *J* = 8.0 Hz, 2H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.81 (t, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.2, Hz, 2H), 7.10–7.02 (m, 3H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.84 (t, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 4.08 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.7, 154.6, 149.6, 145.7, 138.0, 136.0, 134.8, 130.8, 129.8, 129.3, 129.2, 129.0, 128.9, 128.1, 127.8, 127.3, 126.6, 126.4 125.2, 124.5, 124.0, 123.2, 123.1, 123.0, 121.3, 116.5, 150.2, 54.2; **HRMS ESI**: (m/z) $[M+H]^+$: calcd. for $C_{32}H_{24}N_3O$: 466.1914; found: 466.1907.

1,6,15-triphenyl-6,15-dihydro-1H-dibenzo[a,c]pyrrolo[2,3-h]phenazine (3i)



General procedure B was followed on 0.2 mmol scale with a reaction time of 20 hours and purification by flash column chromatography on silica gel (PE/EtOAc = 100/1–50/1) to afford **3i** as a yellow-green solid (77.2 mg, 70%). M.P. = 115–117 ºC; **R_f** = 0.51 (PE/EtOAc = 50/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.70 (t, *J* = 9.2 Hz, 2H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.71–7.60(m, 4H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.49–7.43 (m, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.29–7.26 (m, 4H), 7.15 (d, *J* = 3.2 Hz, 1H), 6.90–6.85 (m, 5H), 6.79 (t, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 3.2 Hz, 1H), 6.71–6.66 (m, 1H), 6.58 (t, *J* = 7.2 Hz, 1H), 6.42 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.4, 148.0, 142.3, 140.8, 140.8, 140.6, 133.6, 132.3, 130.7, 130.4, 129.9, 129.8, 129.4, 128.9, 128.8, 128.5, 128.0, 127.8, 127.7, 127.0, 126.7, 126.6, 126.4, 125.9, 125.0, 123.1, 122.6, 120.7, 120.4, 119.9, 118.6, 117.0, 115.8, 103.6; **HRMS ESI:** (m/z) $[M+H]^+$: calcd. for $C_{40}H_{28}N_3$: 550.2278; found: 550.2267.

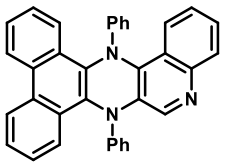
9,14-diphenyl-9,14-dihydrodibenzo[f,h]pyrido[2,3-b]quinoxaline (3j)



General procedure B was followed on 0.2 mmol scale with a reaction time of 10 hours and purification by flash column chromatography on Al_2O_3 gel (PE–PE/EtOAc = 50/1) to afford **3j** as a brown solid (25.9 mg, 30%). M.P. = 270–271 ºC; **R_f** = 0.46 (PE/EtOAc = 50/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.71 (dd, *J* = 8.4, 4.0 Hz, 2H), 8.37 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.10 (d, *J* = 8.0, 1H), 7.94 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.88 (d, *J* =

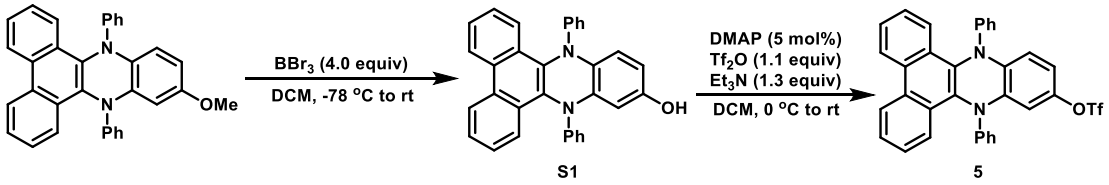
8.4, 1H), 7.73 (d, *J* = 8.0, 2H), 7.63 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.60–7.53 (m, 2H), 7.39 (ddd, *J* = 8.0, 6.8, 0.8 Hz, 1H), 7.23–7.18 (m, 3H), 7.14–7.10 (m, 2H), 7.06–7.00 (m, 3H), 6.90 (t, *J* = 7.2, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.2, 148.3, 145.7, 144.4, 135.9, 135.7, 134.5, 134.5, 130.6, 130.0, 129.2, 129.0, 128.9, 128.2, 127.2, 126.8, 126.6, 126.5, 125.3, 124.4, 123.7, 123.1, 123.1, 122.0, 122.0, 119.5, 117.2; **HRMS ESI:** (m/z) $[M+H]^+$: calcd. for $C_{31}H_{22}N_3$: 436.1808; found: 436.1805.

7,16-diphenyl-7,16-dihydrodibenzo[f,h]quinolino[3,4-b]quinoxaline (3k)



General procedure B was followed on 0.2 mmol scale with a reaction time of 4 hours and purification by flash column chromatography on silica gel (PE/EtOAc = 50/1–10/1) to afford **3k** as a brown solid (81.5 mg, 84%). M.P. = 160–161 ºC; **R_f** = 0.44 (PE/EtOAc = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.49 (s, 1H), 8.76–8.73 (m, 2H), 8.49–8.46 (m, 1H), 8.41 (d, *J* = 8.4 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.75 (ddd, *J* = 8.0, 6.4, 0.8 Hz, 1H), 7.72–7.63 (m, 4H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.13–7.05 (m, 4H), 6.96 (t, *J* = 8.0 Hz, 2H), 6.89 (t, *J* = 6.8 Hz, 1H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.4, 147.9, 147.4, 146.9, 146.5, 140.4, 139.3, 137.7, 130.3, 130.2, 129.9, 129.7, 129.3, 129.3, 129.1, 128.8, 127.6, 127.6, 127.2, 127.1, 127.0, 126.7, 124.8, 124.4, 123.7, 123.2, 123.2, 123.0, 120.8, 119.2, 115.4; **HRMS ESI:** (m/z) $[M+H]^+$: calcd. for $C_{35}H_{24}N_3$: 486.1965; found: 486.1964.

11-methoxy-9,14-diphenyl-9,14-dihydrodibenzo[a,c]phenazine (5)

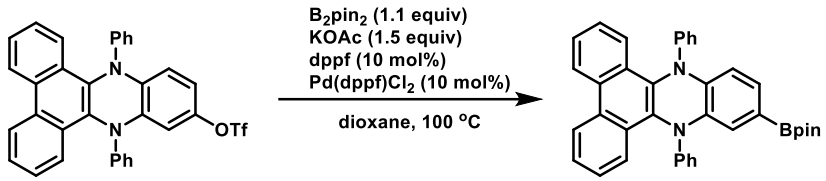


To a round-bottomed flask with 11-methoxy-9,14-diphenyl-9,14-dihydrodibenzo[a,c] Phenazine **3a** (3.81 mmol, 1.77 g) in DCM (30 mL) was added BBr_3 (15.2 mmol, 1.45 mL) at -78 ºC, the reaction mixture was allowed to slowly warm to 25 ºC and then stirred for 3 h. The reaction mixture was quenched with water, the aqueous layer was extracted three times with DCM and separated organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, PE/DCM = 2/1 to 100% DCM) to afford the product **S1** as a white solid (1.66 g, 97%).

To a round-bottomed flask with **S1** (5.8 mmol, 2.55 g), DMAP (0.29 mmol, 35.4 mg) in DCM (25 mL) was added Et_3N (7.54 mmol, 1.10 mL) and Tf_2O (6.38 mmol, 1.073 mL) at 0 ºC, the reaction mixture was stirred at room temperature for 3 h. The reaction mixture was quenched with water, the aqueous layer was extracted three times with DCM and separated organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, PE/DCM = 10/1) to afford the product **5** as a white solid (3.05 g, 90%). M.P. = 169–171 ºC. **R_f** = 0.62 (PE/EA = 50/1). **^{1}H NMR** (400 MHz,

$CDCl_3$): δ 8.75 (d, *J* = 8.0 Hz, 2H), 8.15 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.75 (d, *J* = 2.8 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 2H), 7.58 (tdd, *J* = 10.0, 3.2, 1.2 Hz. 2H), 7.29 (dd, *J* = 8.8, 2.8 Hz. 1H), 7.17–7.05 (m, 8H), 6.95–6.91 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.4, 147.2, 146.3, 146.1, 145.0, 137.4, 137.2, 130.2, 130.1, 129.2, 129.2, 129.1, 129.1, 127.6, 127.2, 127.2, 126.8, 124.5, 123.2, 122.4, 122.3, 118.9 (q, *J* = 319.1 Hz), 118.2, 117.9. 117.7; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -72.5; **HRMS (EI):** calcd. for $C_{33}H_{21}F_3N_2O_3S$: 582.1225; found: 582.1224.

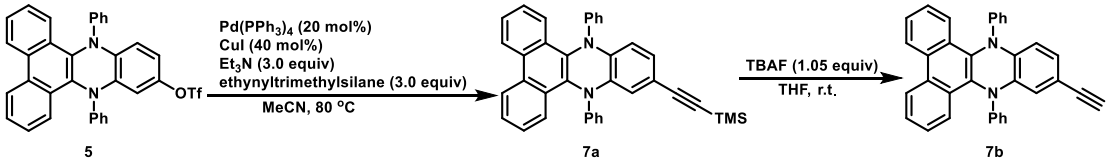
9,14-diphenyl-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,14-dihydrodibenzo[a,c]phenazine (6)



5 6

An oven-dried Schlenk tube containing a stirring bar was charged with **5** (0.2 mmol, 116.5 mg), B_2pin_2 (0.22 mmol, 55.9 mg), KOAc (0.3 mmol, 29.4 mg), $Pd(dppf)Cl_2$ (0.02 mmol 14.6 mg), dppf (0.02 mmol, 11.1 mg). Then the Schlenk tube was evacuated and backfilled with N_2 (This process was repeated for three times). 4 mL1,4-dioxane was then added and the tube was equipped with a balloon filled with N_2 at 100 °C for 12 h. The reaction mixture was quenched with water, the aqueous layer was extracted three times with EtOAc and separated organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, PE/DCM = 20/1–5/1) to afford the product **6** as a white solid (63.9 mg, 57%). M.P. = 165–166 °C; **R_f** = 0.50 (PE/EA = 20/1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.73 (d, *J* = 7.6 Hz, 2H), 8.21 (s, 1H), 8.12 (dd, *J* = 14.4, 8.0 Hz, 2H), 7.80 (q, *J* = 7.2 Hz, 2H), 7.66–7.51 (m, 4H), 7.05–6.98 (m, 8H), 6.82–6.77 (m, 2H), 1.40 (s, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.0, 147.9, 144.2, 138.2, 138.0, 133.8, 132.2, 130.0, 130.0, 129.6, 129.5, 128.9, 128.8, 127.1, 127.0, 126.0, 126.0, 124.7, 123.1, 123.1, 121.4, 121.0, 117.2, 116.7, 84.1, 25.0; **HRMS ESI**: (m/z) $[M+H]^+$: calcd. for $C_{38}H_{34}BN_2O_2$: 561.2708.; found: 561.2711.

9,14-diphenyl-11-((trimethylsilyl)ethynyl)-9,14-dihydrodibenzo[a,c]phenazine (7a) and 11-ethynyl-9,14-diphenyl-9,14-dihydrodibenzo[a,c]phenazine (7b)



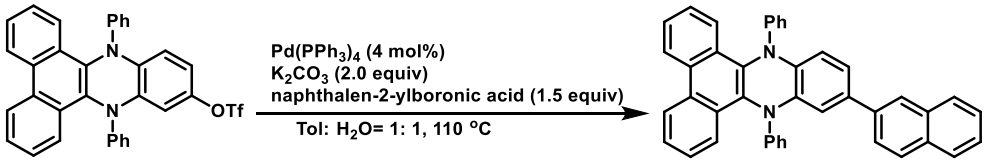
5 7a 7b

An oven-dried Schlenk tube containing a stirring bar was charged with **5** (0.687 mmol, 400 mg), CuI (0.275 mmol, 53 mg), $Pd(PPh_3)_4$ (0.137 mmol, 159 mg). Then the sealed tube was evacuated and backfilled with N_2 (This process was repeated for three times). 10 mL MeCN and ethynyltrimethylsilane (2.061 mmol, 286 μL) were then added at room temperature and the reaction mixture was stirred at 110 °C for 12 h. The reaction

mixture was quenched with water, the aqueous layer was extracted three times with EtOAc and separated organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, PE/DCM = 10/1) to afford the product **7a** as a yellow solid (287.1 mg, 79%). M.P. = 108–109 ºC; $\mathbf{R_f}$ = 0.58 (PE/EA = 30/1).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.73 (d, *J* = 8.4 Hz, 2H), 8.10 (ddd, *J* = 9.6, 8.4, 1.2 Hz, 2H), 7.86 (d, *J* = 1.6 Hz, 1H), 7.68–7.62 (m, 3H), 7.57–7.51 (m, 2H),7.46 (dd, *J* = 8.4, 2.0 Hz. 1H), 7.07–7.03 (m, 4H), 6.99–6.97 (m, 4H), 6.85–6.80 (m, 2H), 0.30 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.7, 147.5, 145.5, 144.5, 137.8, 137.7, 130.7, 130.1, 130.0, 129.5, 129.4, 129.3, 129.0, 129.0, 127.2, 127.1, 126.8, 126.7, 126.7, 124.7, 124.6, 123.2, 123.1, 121.7, 121.5, 120.3, 117.5. 117.1, 104.6, 94.8, 0.1; **HRMS ESI:** (m/z) $[M+H]^+$: calcd. for $C_{37}H_{31}N_2Si$: 531.2251; found: 531.2245.

To a round-bottomed flask with **7a** (6 mmol, 3.18 g) in THF (70 ml) was added TBAF (6.3 mmol, 1 M in THF, 6.3 mL) at room temperature for 5 min. The reaction mixture was quenched with water, the aqueous layer was extracted three times with EtOAc and separated organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, PE/DCM = 10/1 to 8/1) to afford the product **7b** as a white solid (2.31 g, 84%). M.P. = 202–203 ºC; $\mathbf{R_f}$ = 0.58 (PE/EA = 30/1).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.75 (d, *J* = 8.4 Hz, 2H), 8.16 (ddd, *J* = 8.8, 8.4, 1.2 Hz, 2H), 7.96 (d, *J* = 1.6 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.66 (ddt, *J* = 8.4, 7.6, 1.6 Hz, 2H), 7.60–7.55 (m, 2H), 7.53 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.12–7.05 (m, 8H), 6.90–6.85 (m, 2H) 3.19 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.6, 147.4, 145.7, 144.6, 137.7, 137.6, 130.8, 130.1, 130.0, 129.5, 129.4, 129.3, 129.0, 129.0, 127.2, 127.1, 126.9, 126.7, 126.7, 124.6, 124.6, 123.2, 123.1, 121.8, 121.6, 119.2, 117.6. 117.3, 83.2, 77.8; **HRMS ESI:** (m/z) $[M+H]^+$: calcd. for $C_{34}H_{23}N_2$: 459.1856; found: 459.1850.

11-(naphthalen-2-yl)-9,14-diphenyl-9,14-dihydrodibenzo[a,c]phenazine (8a)

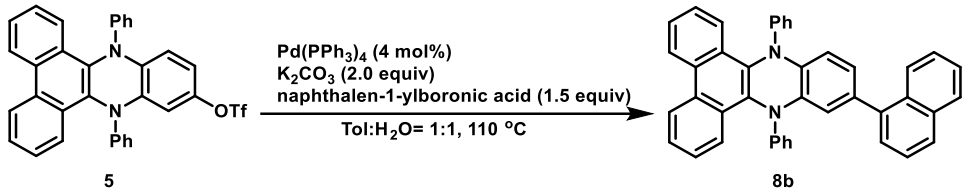


5 **8a**

An oven-dried Schlenk tube containing a stirring bar was charged with **5** (0.5 mmol, 291.3 mg), K_2CO_3 (1.0 mmol, 138.2 mg), naphthalen-1-ylboronic acid (0.75 mmol, 129.0 mg), $Pd(PPh_3)_4$ (0.002 mmol, 23.1 mg). Then the sealed tube was evacuated and backfilled with N_2 (This process was repeated for three times). 2.5 mL toluene and 2.5 ml H_2O were then added at room temperature and the reaction mixture was stirred at 110 ºC for 12 h. The reaction mixture was quenched with sat. aq. NH_4Cl, the aqueous layer was extracted three times with EtOAc and separated organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, PE/DCM = 5/1) to afford the product **8a** as a pale-yellow solid (250.0 mg, 89%). M.P. = 274–275 ºC; $\mathbf{R_f}$ = 0.50 (PE/DCM = 3/1); **^{1}H NMR** (400 MHz, $CDCl_3$): 8.76 (d, J = 8.4 Hz, 2H), 8.19 (d, J =

7.6 Hz, 1H), 8.15 (d, J = 7.6 Hz, 1H), 8.11 (dd, J = 10.8, 2.0 Hz, 2H), 7.95 (t, J = 8.8 Hz, 2H), 7.92–7.79 (m, 3H), 7.75–7.62 (m, 3H), 7.62–7.47 (m, 4H), 7.13–6.98 (m, 8H), 6.88–6.75 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.9, 147.8, 145.2, 144.4, 138.7, 138.3, 138.2, 137.8, 133.8, 132.8, 130.1, 130.1, 129.7, 129.5, 129.0, 128.8, 128.4, 127.8, 127.5, 127.2, 127.1, 126.7, 126.6, 126.4, 126.2, 125.9, 125.6, 124.8, 124.7, 124.6, 123.2, 121.4, 121.3, 117.2, 116.9. **HRMS ESI:** (m/z) $[M+H]^+$: calcd. for $C_{42}H_{29}N_2$: 561.2325; found: 561.2310.

11-(naphthalen-1-yl)-9,14-diphenyl-9,14-dihydrodibenzo[a,c]phenazine (8b)



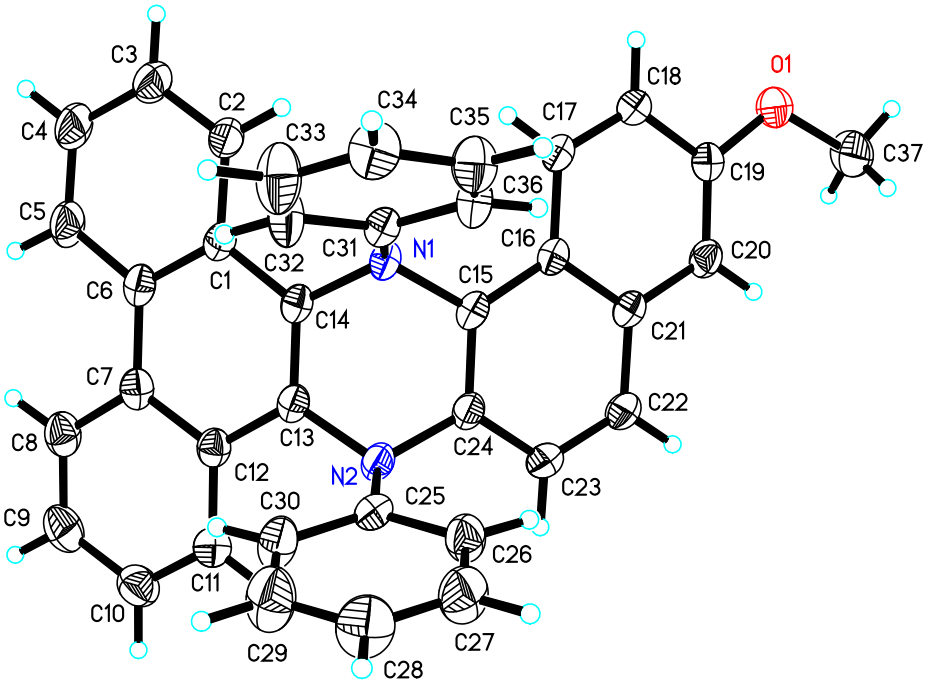
5 8b

An oven-dried Schlenk tube containing a stirring bar was charged with **5** (0.5 mmol, 291.3 mg), K_2CO_3 (1.0 mmol, 138.2 mg), naphthalen-1-ylboronic acid (0.75 mmol, 129.0 mg), $Pd(PPh_3)_4$ (0.02 mmol, 23.1 mg). Then the sealed tube was evacuated and backfilled with N_2 (This process was repeated for three times). 2.5 mL toluene and 2.5 ml H_2O were then added at room temperature and the reaction mixture was stirred at 110 °C for 23 h. The reaction mixture was quenched with sat. aq. NH_4Cl, the aqueous layer was extracted three times with EtOAc and separated organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, PE/DCM = 5/1) to afford the product **8b** as a pale-yellow solid (240.8 mg, 86%). M.P. = 297–298 °C; **R_f** = 0.50 (PE/DCM = 3/1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.76 (d, *J* = 8.4 Hz, 2H), 8.16 (dd, *J* = 8.0, 0.8 Hz, 1H), 8.10 (dd, *J* = 8.0, 0.8 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.96-7.85 (m, 4H), 7.66 (dtd, *J* = 8.0, 6.8, 1.2 Hz, 2H), 7.59–7.44 (m, 7H), 7.12–7.02 (m, 8H), 6.88–6.78 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.9, 147.9, 144.8, 144.0, 139.5, 138.2, 138.1, 138.1, 134.0, 131.8, 130.1, 129.6, 129.5, 129.0, 129.0, 128.8, 128.5, 128.1, 127.2, 127.2, 127.2, 127.1, 126.9, 126.7, 126.4, 126.1, 126.1, 125.6, 124.7, 123.2, 123.2, 121.4, 121.4, 117.3, 117.3. **HRMS ESI:** (m/z) $[M+H]^+$: calcd. for $C_{42}H_{29}N_2$: 561.2325; found: 561.2309.

4. X-ray Crystallography

Single crystals suitable for X-ray crystal analysis were obtained from EtOAc and DCM provided good quality crystals. Details of crystal data and structural refinements are given.

X-ray crystallographic data of compound (3f). (CCDC 1973195)



ORTEP of **3f** showing thermal ellipsoids at the 30% probability level.

Single crystal X-ray diffraction data was collected at 193(2) K for **3f** on a Bruker D8 Venture diffractometer.

Table 1. Crystal data and structure refinement of **3f**.

Identification code	mo_d8v181051_0m	
Empirical formula	C37 H26 N2 O	
Formula weight	514.60	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P n	
Unit cell dimensions	a = 7.9242(3) Å	α= 90 °.
	b = 9.1825(4) Å	β= 93.0000(10) °.
	c = 18.6310(8) Å	γ = 90 °.
Volume	1353.81(10) $Å^3$	
Z	2	
Density (calculated)	1.262 Mg/m^3	
Absorption coefficient	0.076 mm^{-1}	
F(000)	540	
Crystal size	0.200 x 0.170 x 0.130 mm^3	

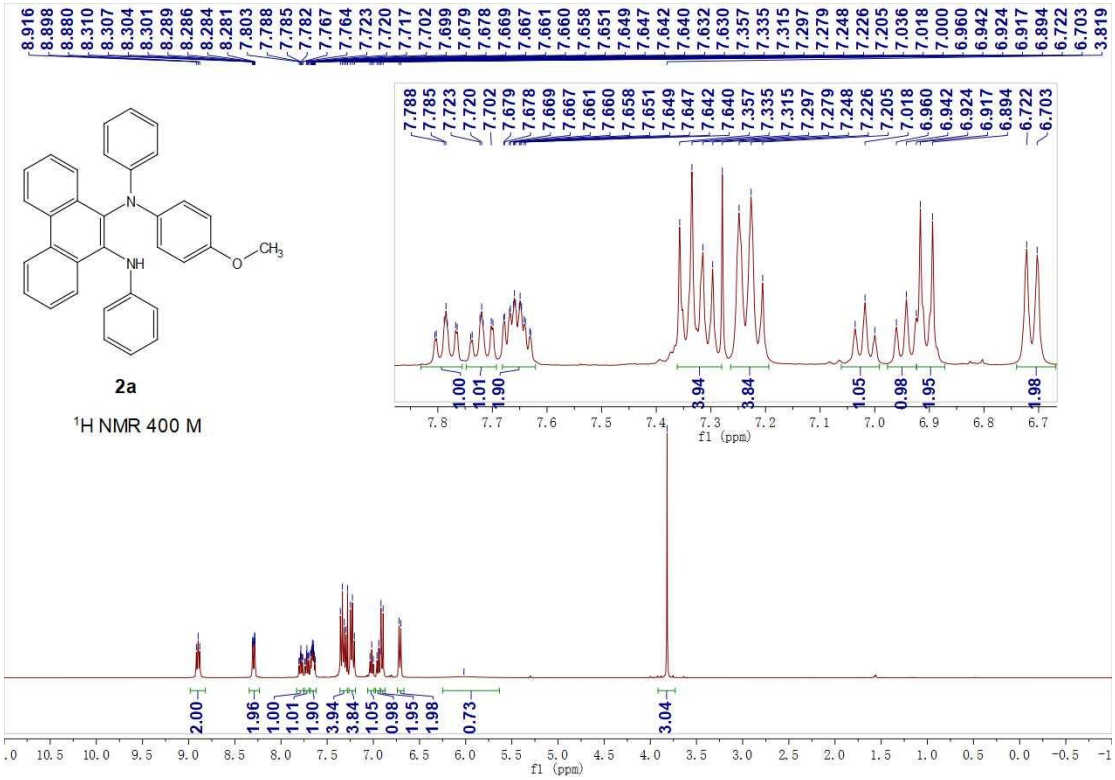
Theta range for data collection	3.117 to 25.998 °.
Index ranges	-9<=h<=9, -11<=k<=11, -22<=l<=22
Reflections collected	13446
Independent reflections	4726 [R(int) = 0.0350]
Completeness to theta = 25.242 °	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6222
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4726 / 2 / 363
Goodness-of-fit on F^2	1.086
Final R indices [I>2sigma(I)]	R1 = 0.0355, wR2 = 0.0827
R indices (all data)	R1 = 0.0422, wR2 = 0.0877
Absolute structure parameter	-0.6(9)
Extinction coefficient	0.073(8)
Largest diff. peak and hole	0.117 and -0.103 e.$Å^{-3}$

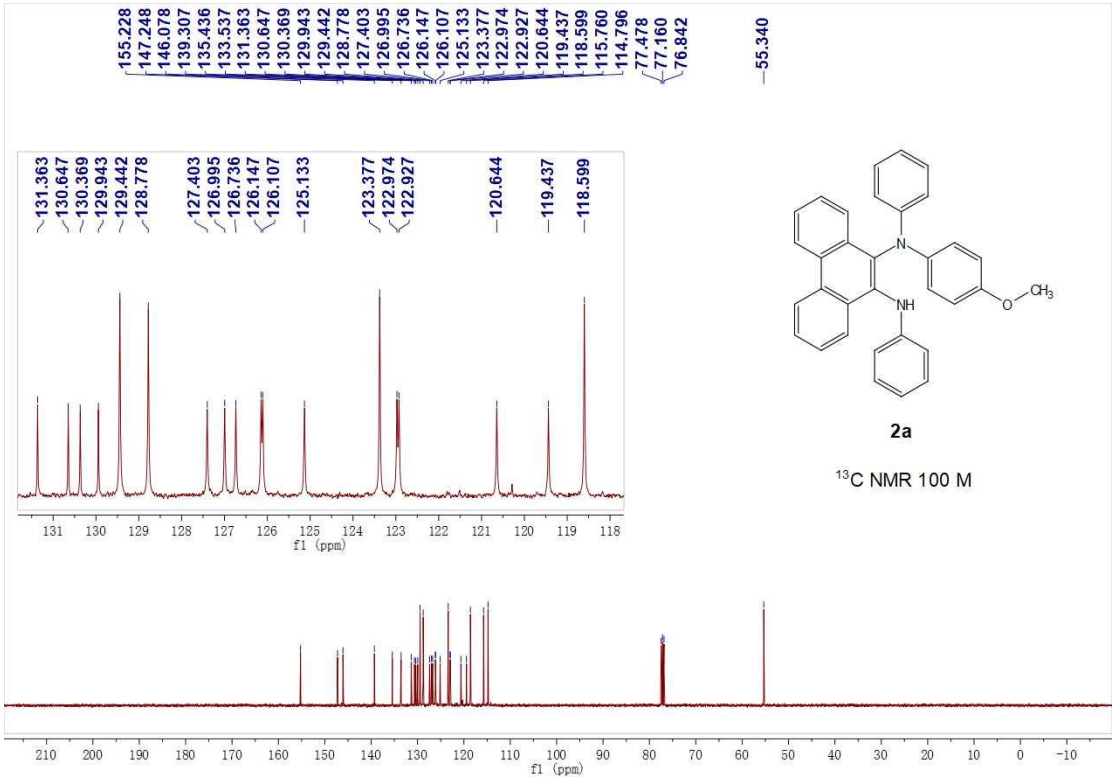
5. Reference

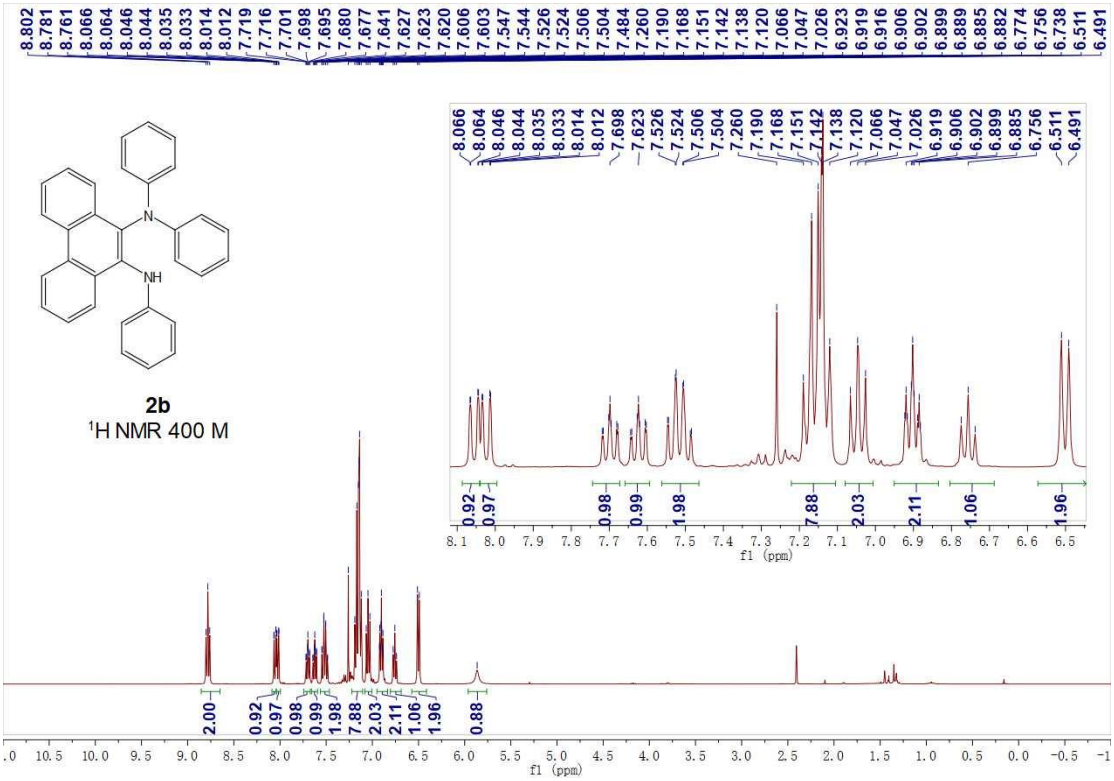
1 H. Zhou, L. Sun, W. Chen, G. Tian, Y. Chen, Y. Li and J. Su, *Tetrahedron*, 2016, **72**, 2300-2305.

2 Z. Zhang, Y. S. Wu, K. C. Tang, C. L. Chen, J. W. Ho, J. Su, H. Tian and P. T. Chou, *J. Am. Chem. Soc.*, 2015, **137**, 8509-8520.

6. NMR Data



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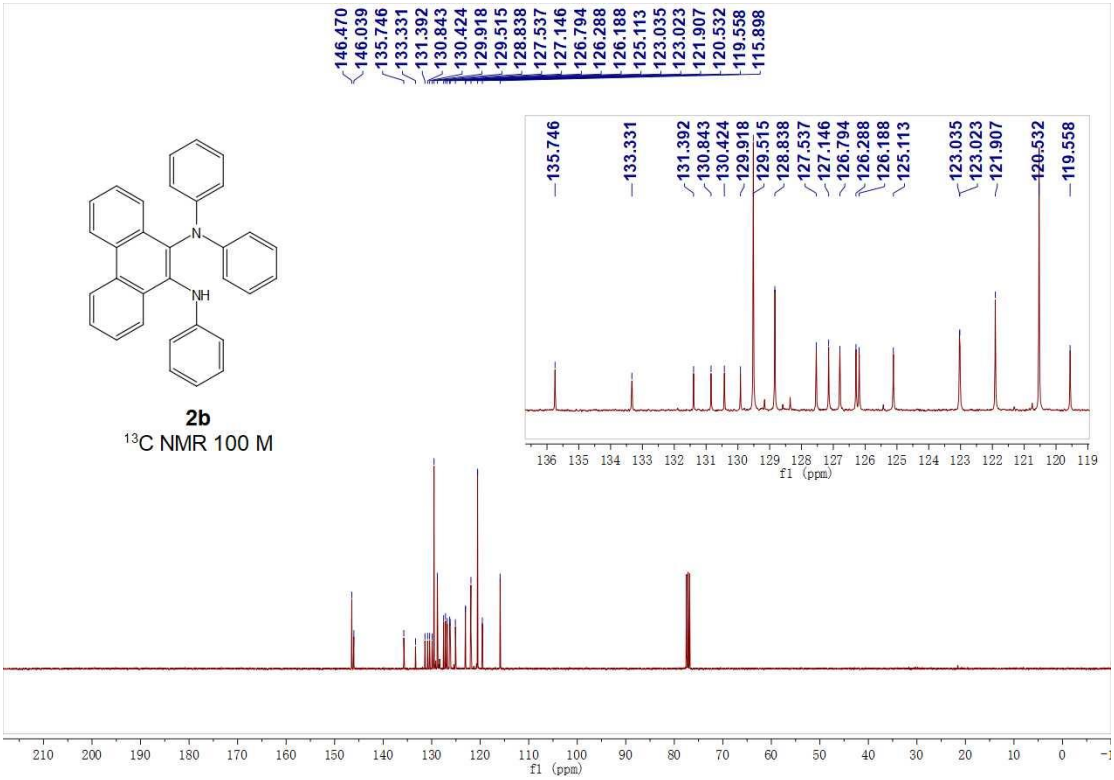
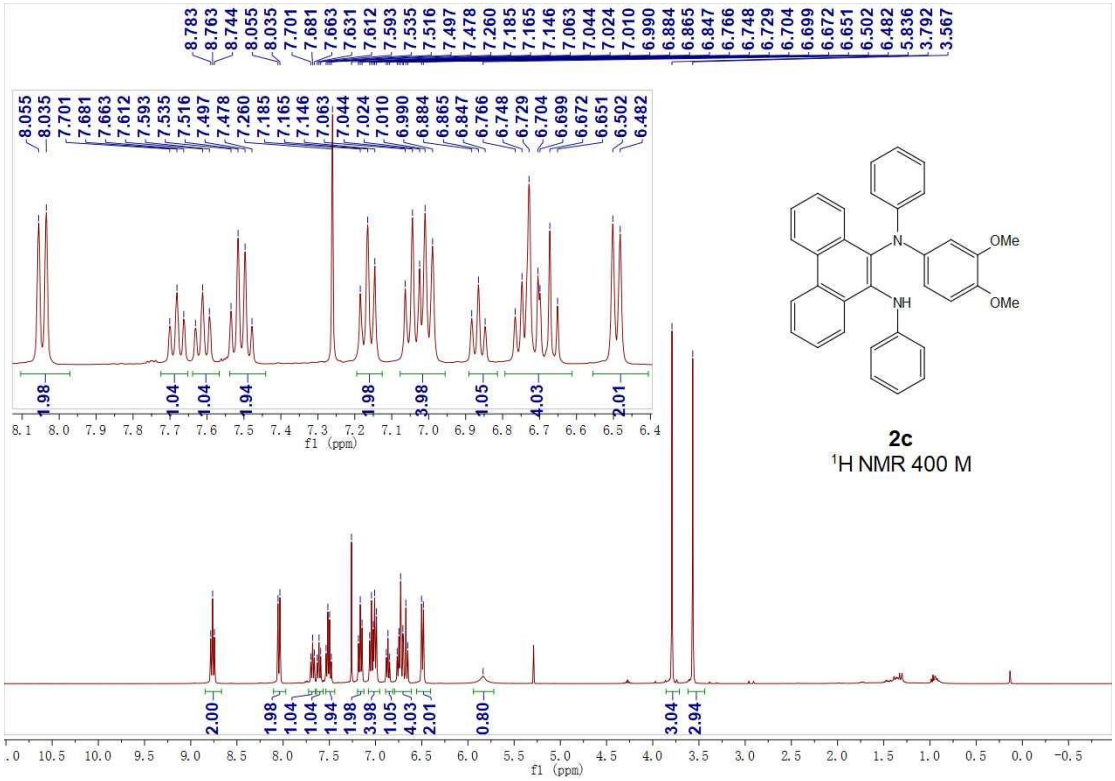
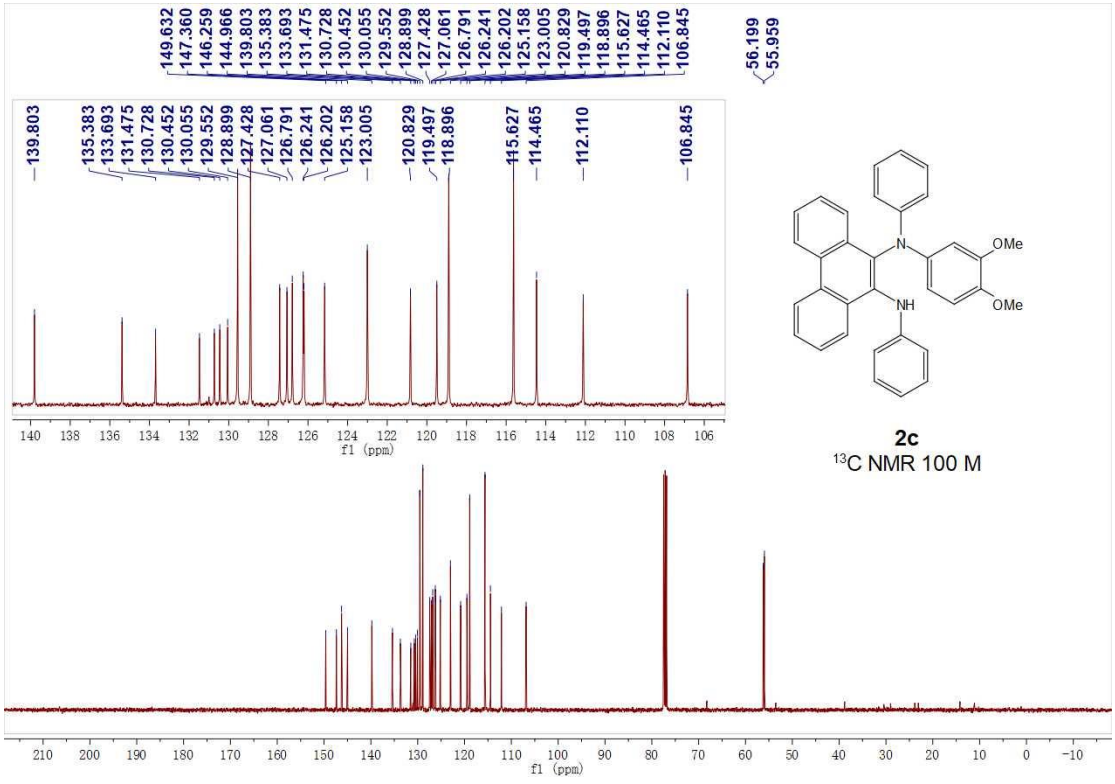
N
NH
2b
1H NMR 400 M
2.00 0.92 0.97 0.98 0.99 1.98 7.88 2.03 2.11 1.06 1.96 0.88
f1 (ppm)


146.470 146.039 135.746 133.331 131.392 130.843 130.424 129.918 129.515 128.838 127.537 127.146 126.794 126.288 126.188 125.113 123.035 123.023 121.907 120.532 119.558 115.898
N
NH
2b
13C NMR 100 M
f1 (ppm)



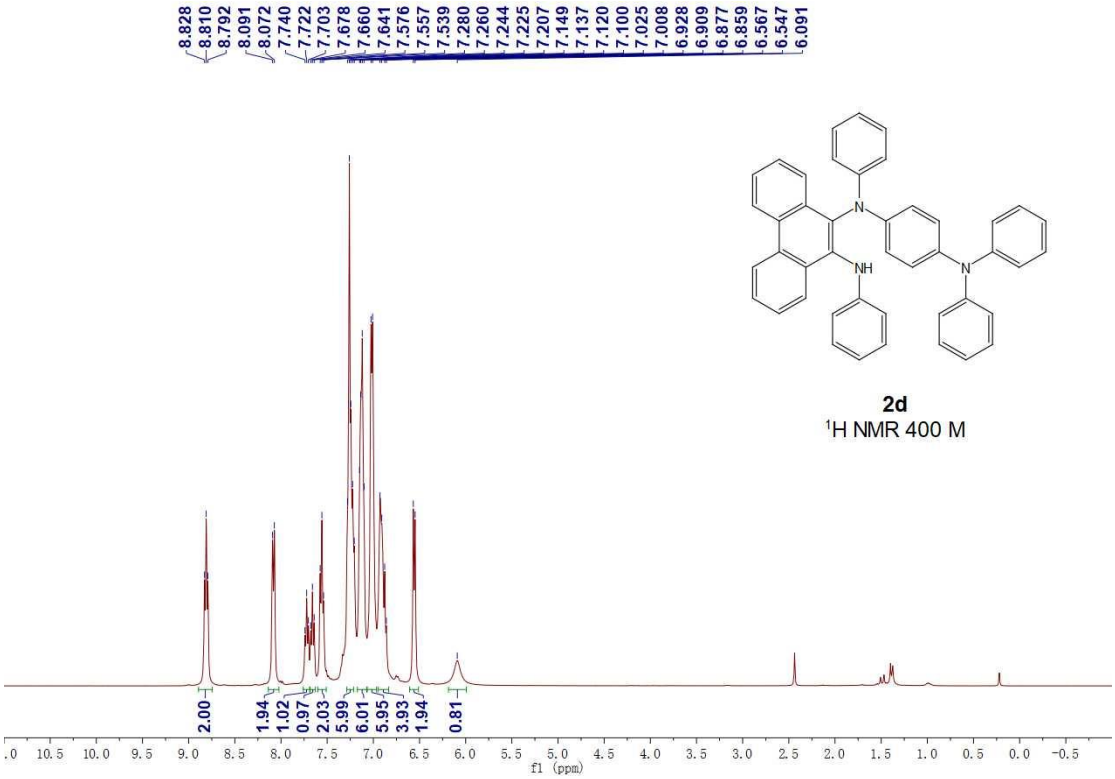
2c

^{1}H NMR 400 M



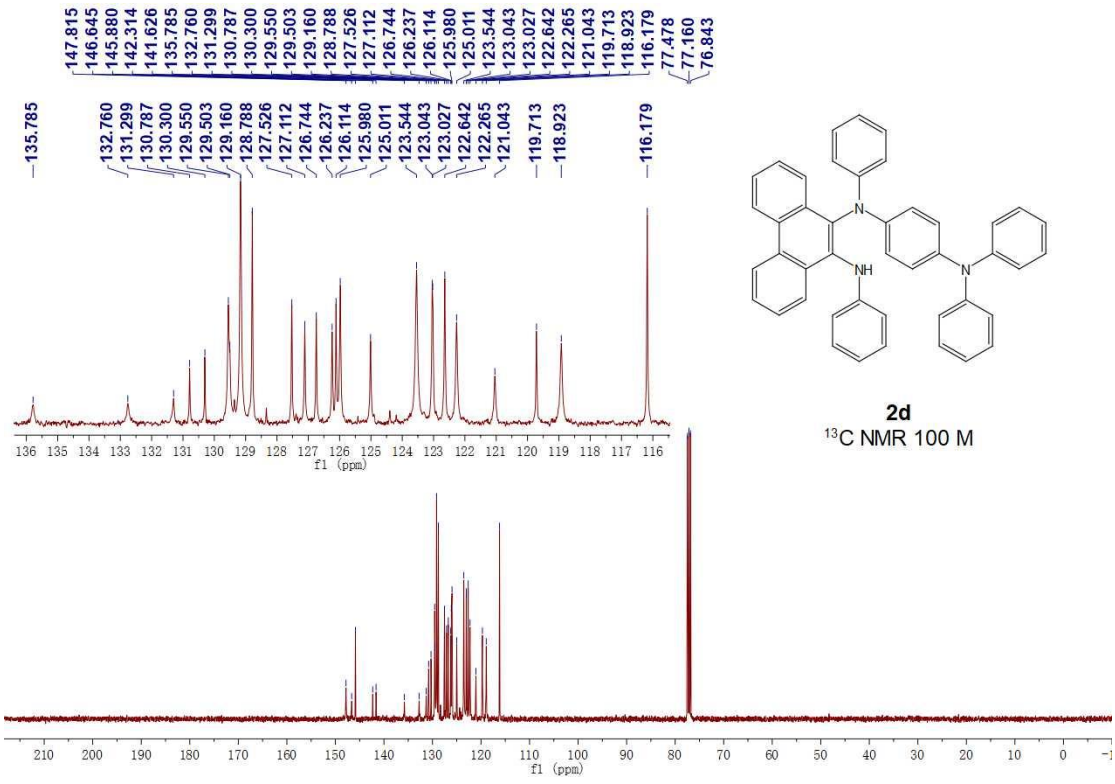
2c

^{13}C NMR 100 M



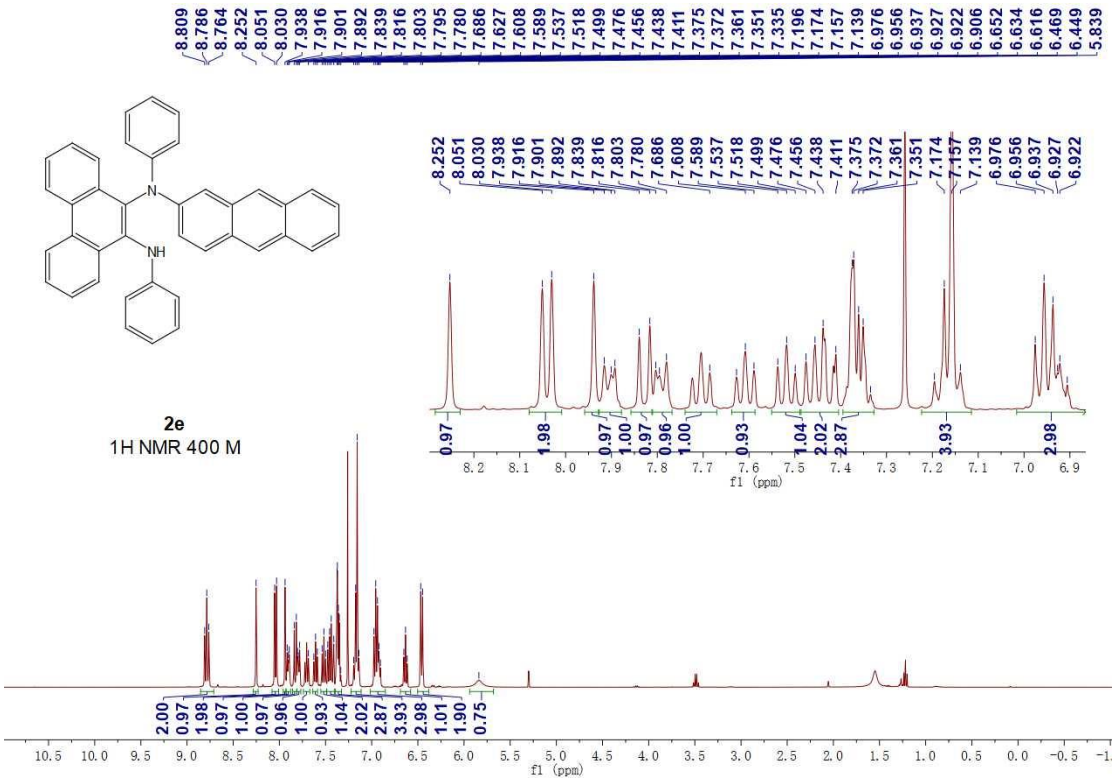
2d

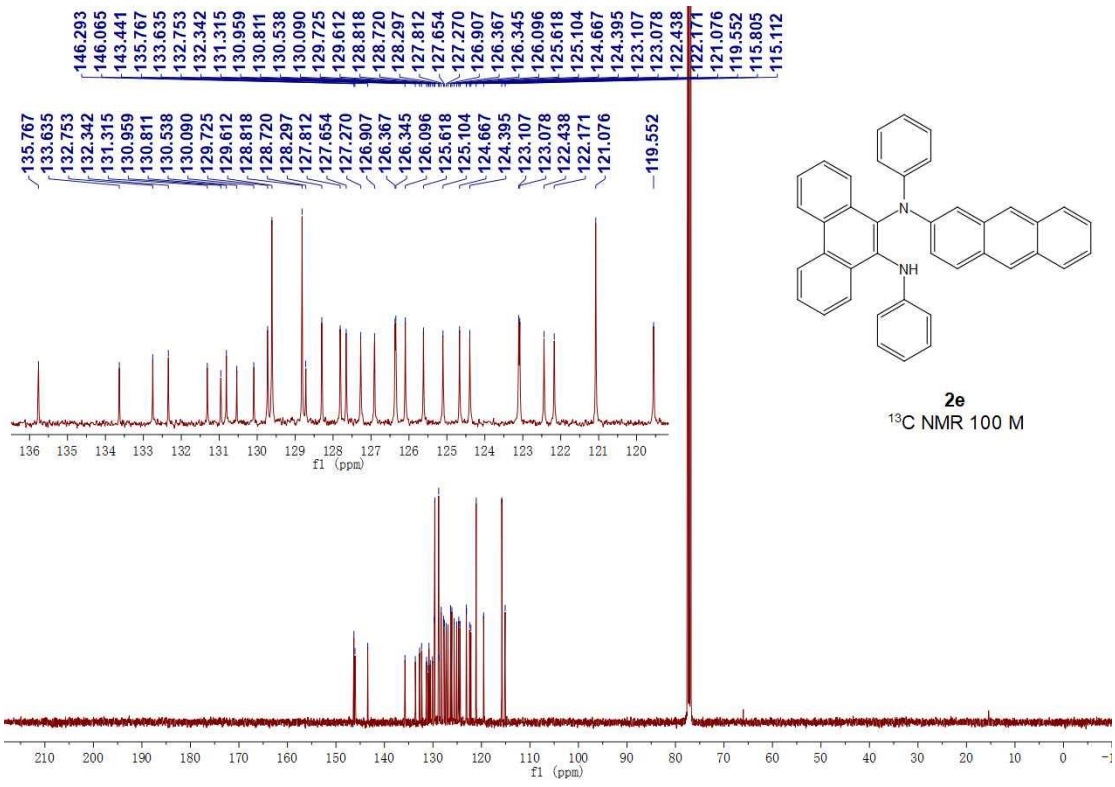
^{1}H NMR 400 M

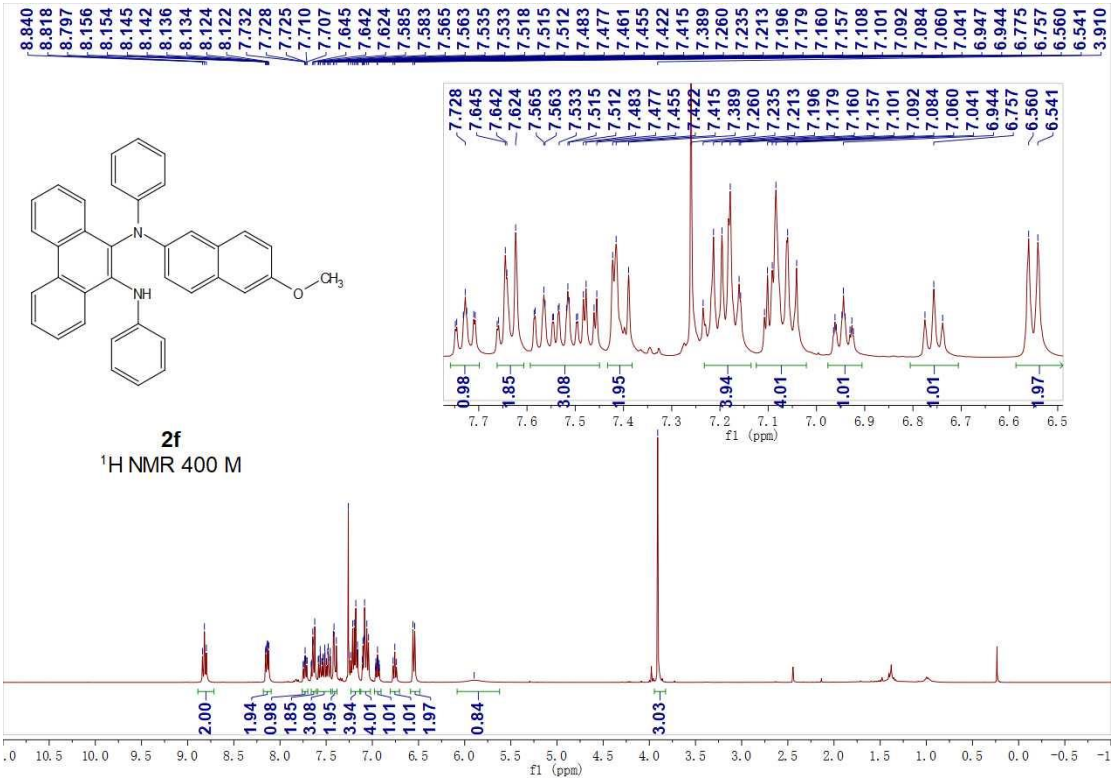


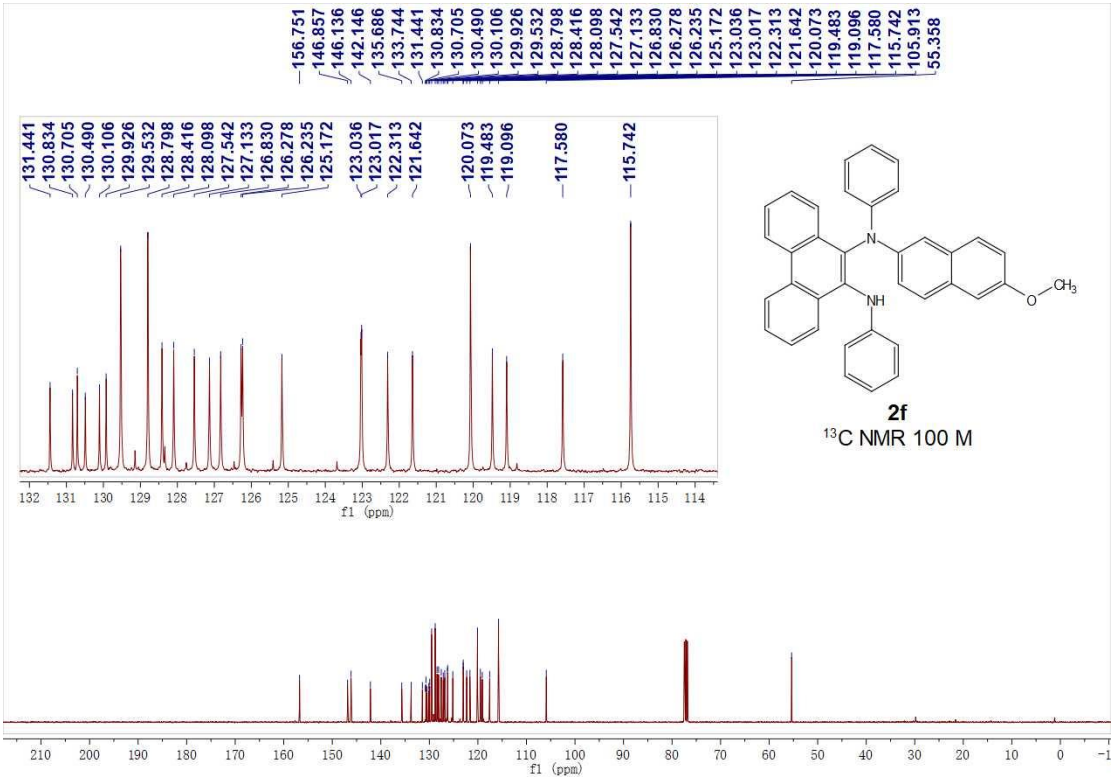
2d

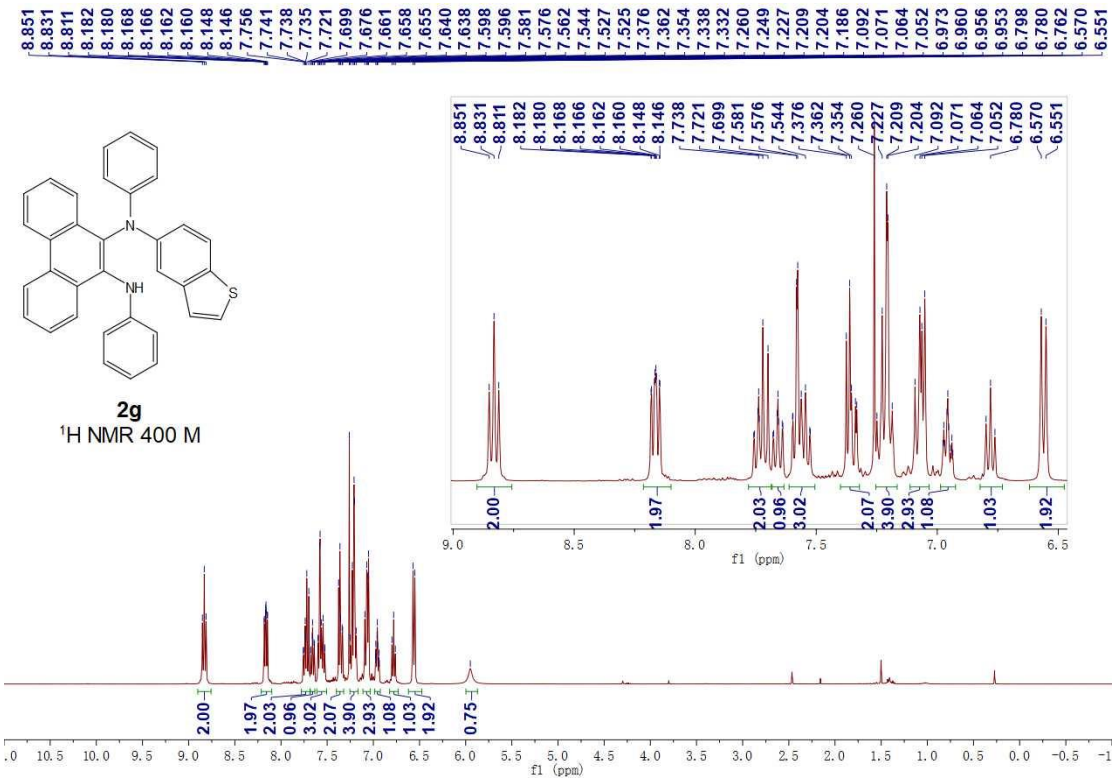
^{13}C NMR 100 M

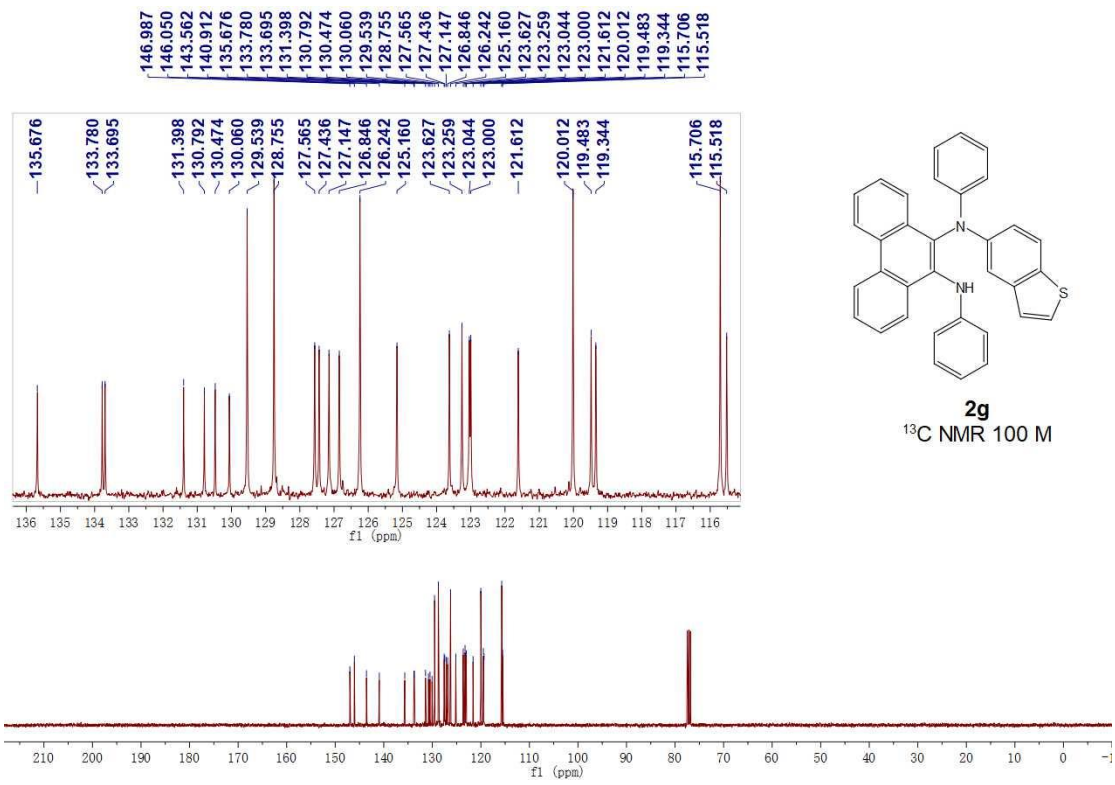

2e
1H NMR 400 M

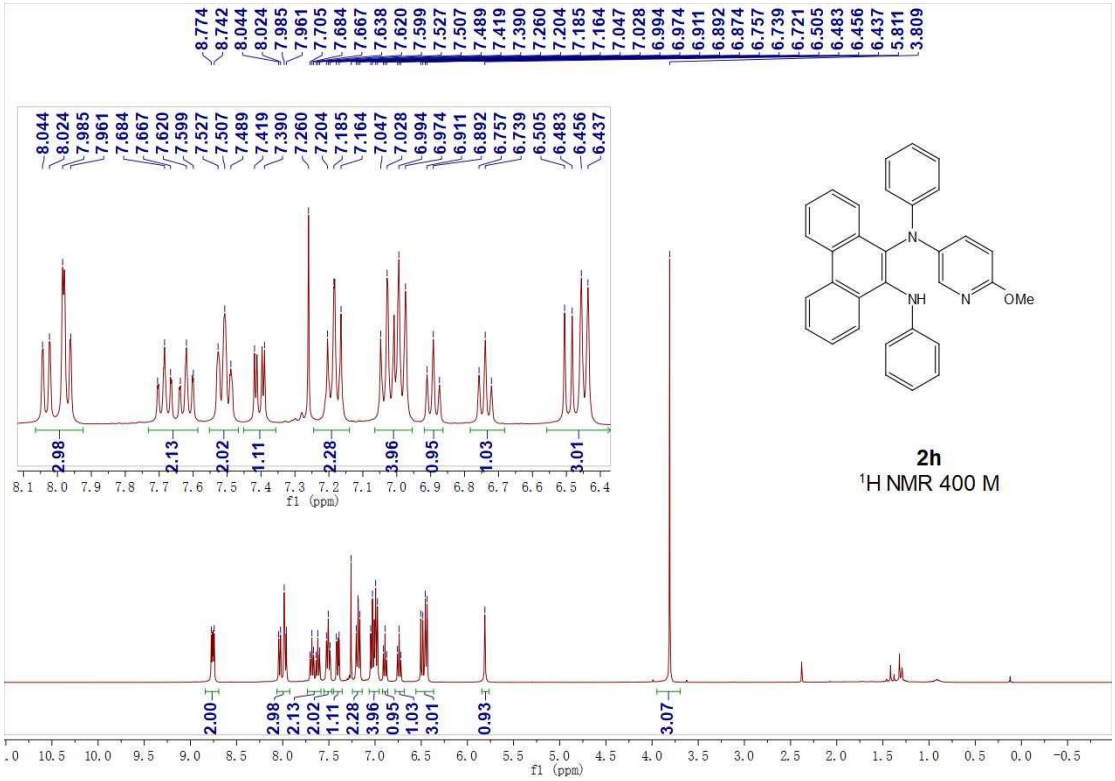

2e
13C NMR 100 M

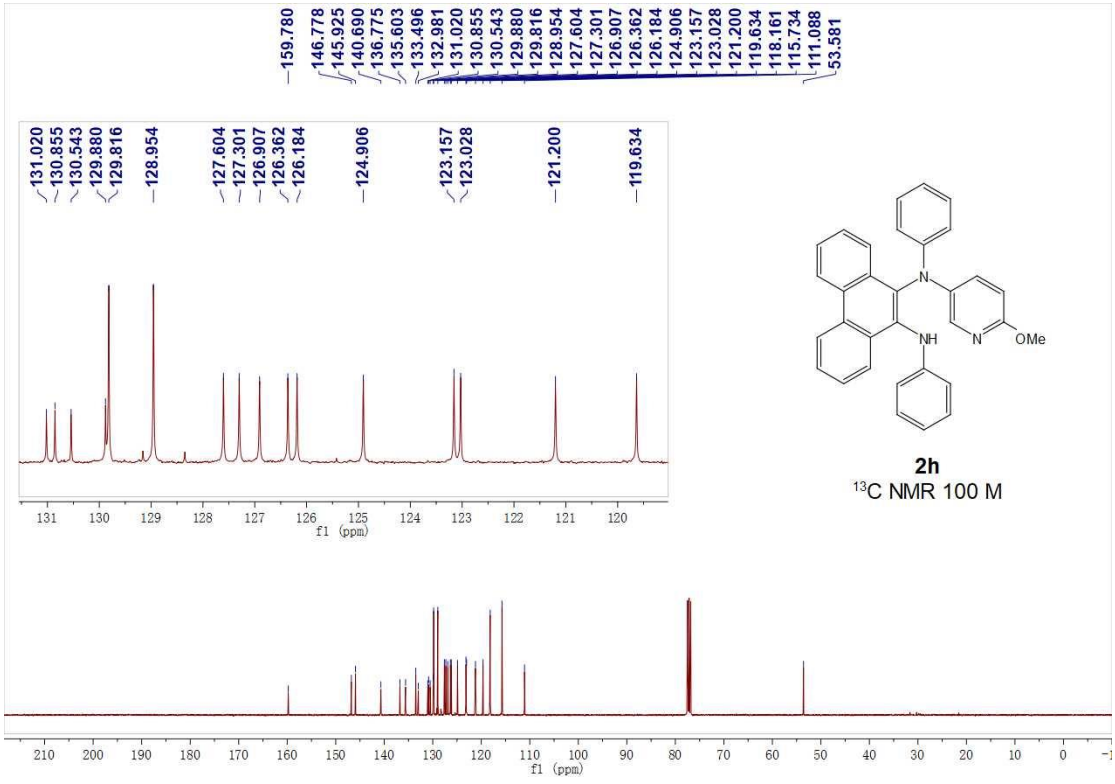

2f
1H NMR 400 M

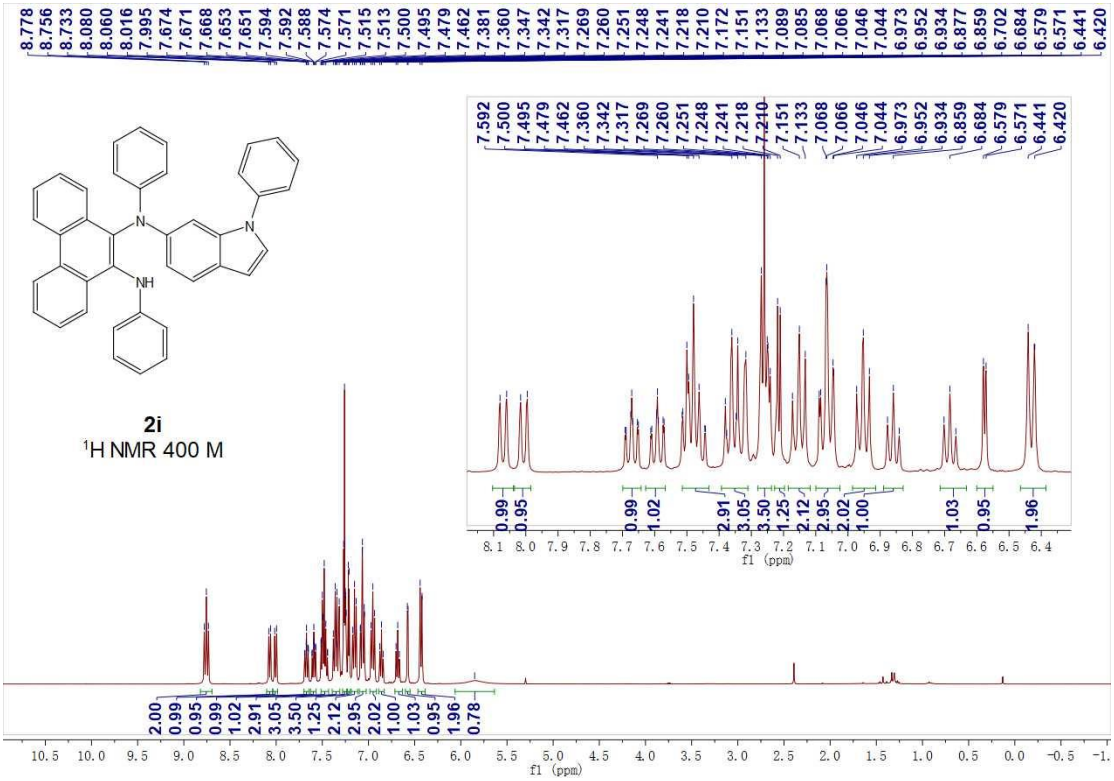

2f
13C NMR 100 M

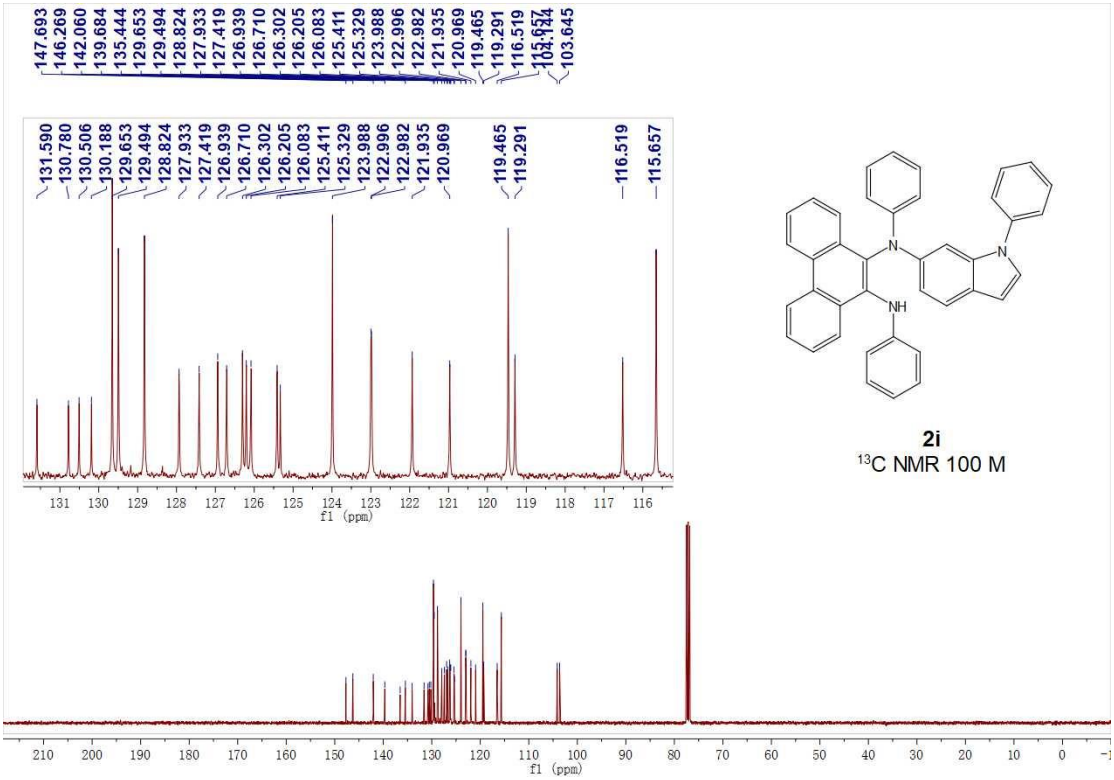

8.851 8.831 8.811 8.182 8.180 8.168 8.166 8.162 8.160 8.148 8.146 7.756 7.741 7.738 7.735 7.721 7.699 7.676 7.661 7.658 7.655 7.640 7.638 7.598 7.596 7.581 7.576 7.562 7.544 7.527 7.525 7.376 7.362 7.354 7.338 7.332 7.260 7.249 7.227 7.209 7.204 7.186 7.092 7.071 7.064 7.052 6.973 6.960 6.956 6.953 6.798 6.780 6.762 6.570 6.551
N
NH
S
2g
1H NMR 400 M
2.00 1.97 2.03 0.96 3.02 2.07 3.90 2.93 1.08 1.03 0.75 1.92
f1 (ppm)

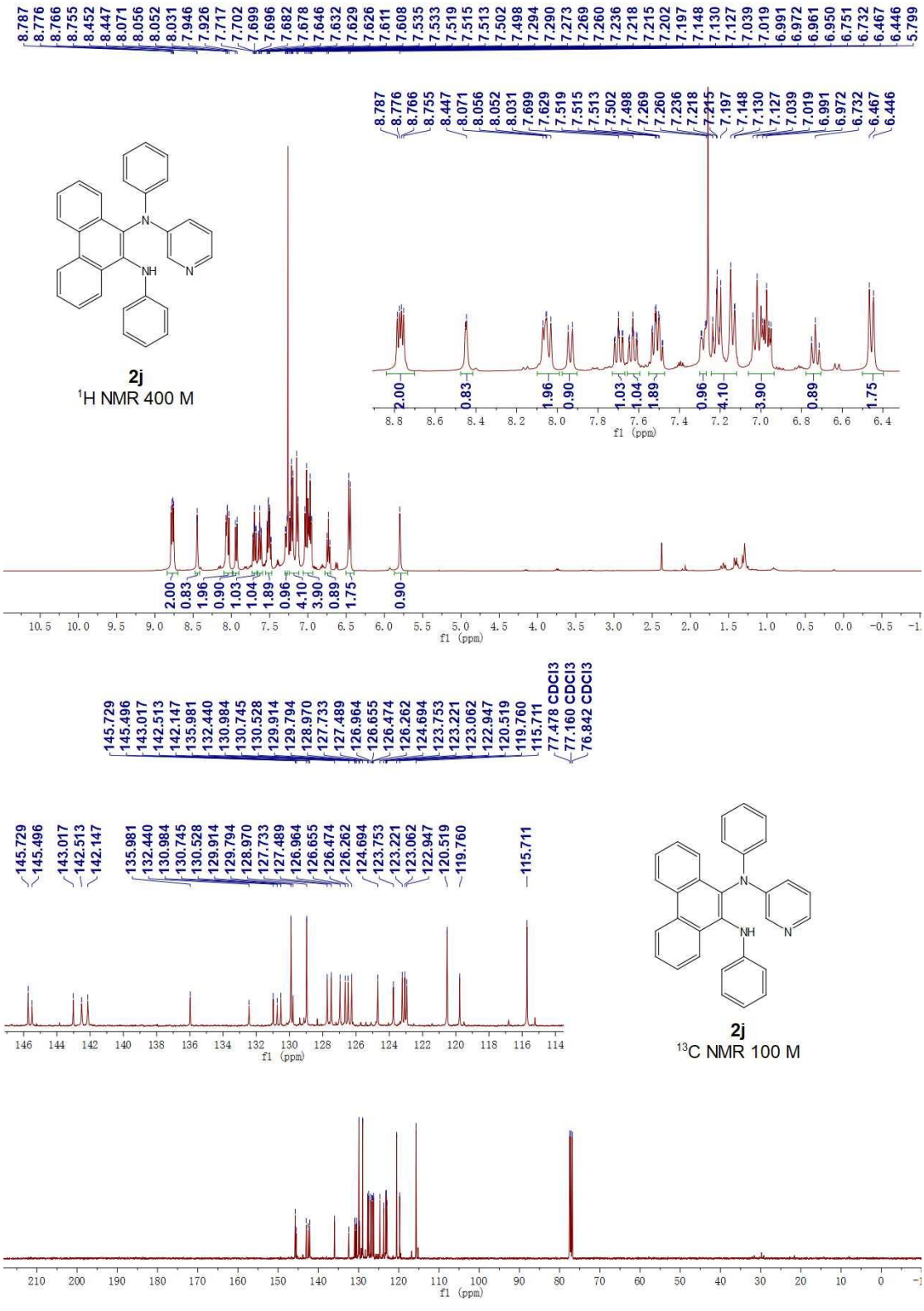

146.987 146.050 143.562 140.912 135.676 133.780 133.695 131.398 130.792 130.474 130.060 129.539 128.755 127.565 127.436 127.147 126.846 126.242 125.160 123.627 123.259 123.044 123.000 121.612 120.012 119.483 119.344 115.706 115.518
N
NH
S
2g
13C NMR 100 M
f1 (ppm)

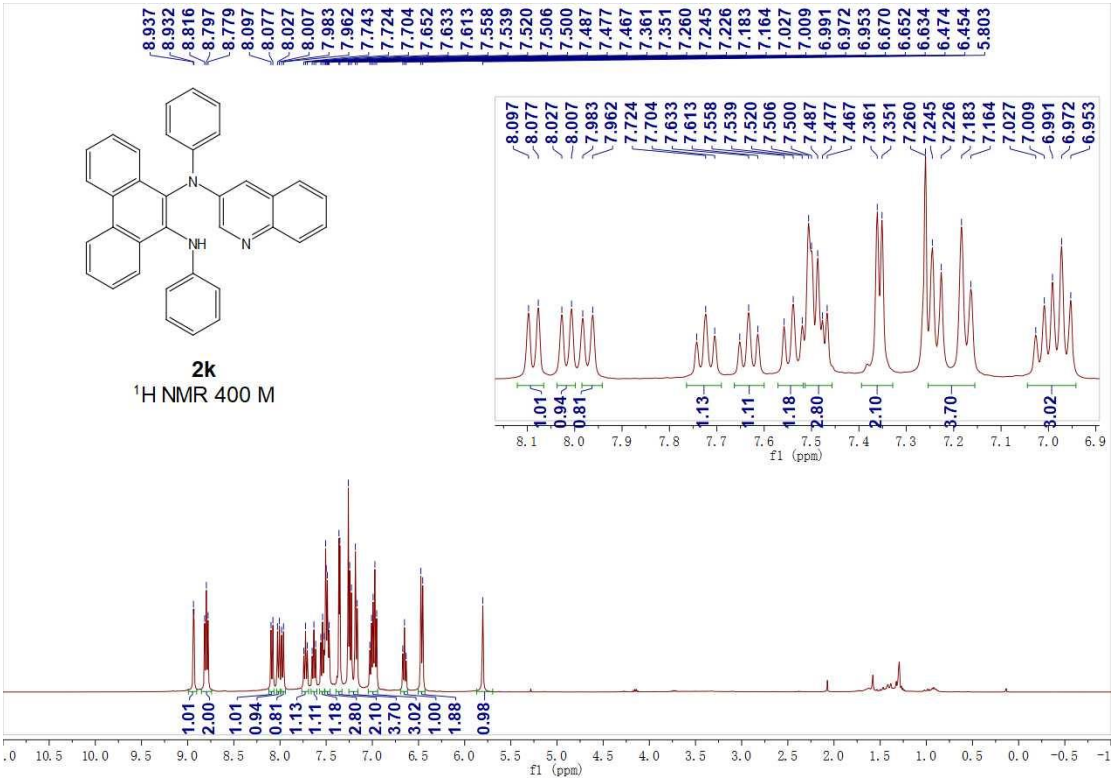

8.774
8.742
8.044
8.024
7.985
7.961
7.705
7.684
7.667
7.638
7.620
7.599
7.527
7.507
7.489
7.419
7.390
7.260
7.204
7.185
7.164
7.047
7.028
6.994
6.974
6.911
6.892
6.874
6.757
6.739
6.721
6.505
6.483
6.456
6.437
5.811
3.809
2.98
2.13
2.02
1.11
2.28
3.96
0.95
1.03
3.01
2.00
0.93
3.07
f1 (ppm)
N
NH
N
OMe
2h
1H NMR 400 M


159.780
146.778
145.925
140.690
136.775
135.603
133.496
132.981
131.020
130.855
130.543
129.880
129.816
128.954
127.604
127.301
126.907
126.362
126.184
124.906
123.157
123.028
121.200
119.634
118.161
115.734
111.088
53.581
f1 (ppm)
N
NH
N
OMe
2h
13C NMR 100 M


2i
1H NMR 400 M
f1 (ppm)

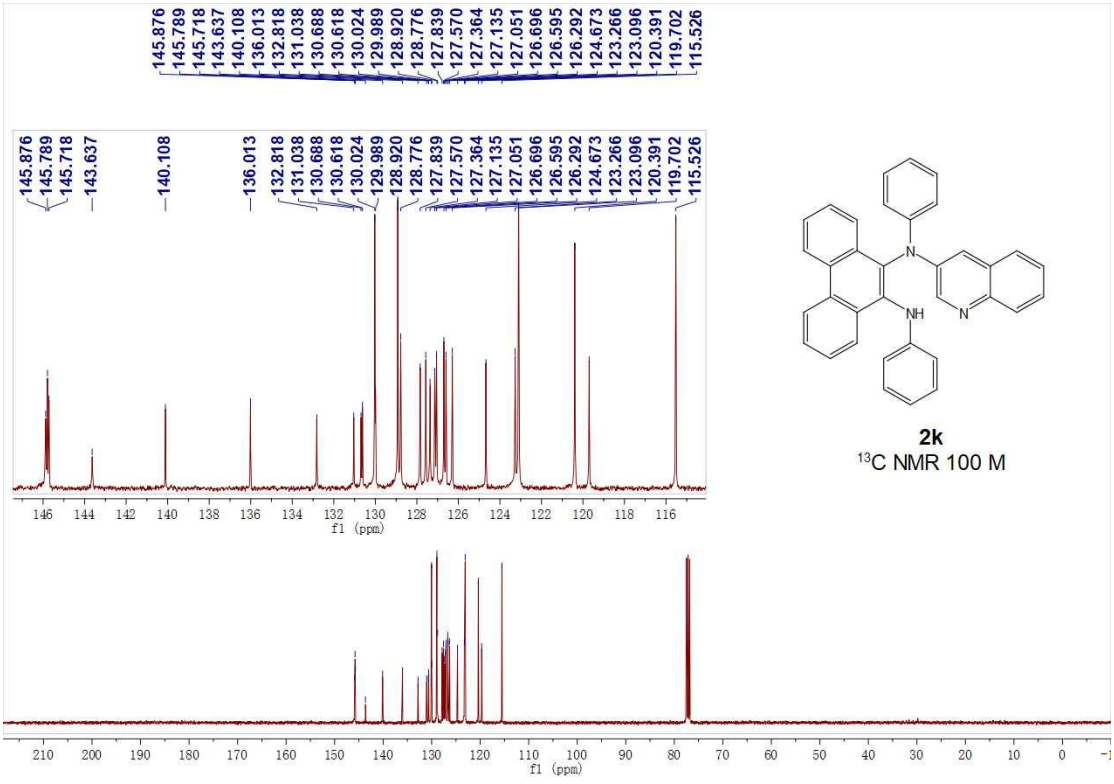

2i
13C NMR 100 M
f1 (ppm)


8.787
8.776
8.766
8.755
8.452
8.447
8.071
8.056
8.052
8.031
7.946
7.926
7.717
7.702
7.699
7.696
7.682
7.678
7.646
7.632
7.629
7.626
7.611
7.608
7.535
7.533
7.519
7.515
7.513
7.502
7.498
7.294
7.290
7.273
7.269
7.260
7.236
7.218
7.215
7.202
7.197
7.148
7.130
7.127
7.039
7.019
6.991
6.972
6.961
6.950
6.751
6.732
6.467
6.446
5.799
2j
1H NMR 400 M
2.00
0.83
1.96
0.90
1.03
1.04
1.89
0.96
4.10
3.90
0.89
1.75
0.90
f1 (ppm)
145.729
145.496
143.017
142.513
142.147
135.981
132.440
130.984
130.745
130.528
129.914
129.794
128.970
127.733
127.489
126.964
126.655
126.474
126.262
124.694
123.753
123.221
123.062
122.947
120.519
119.760
115.711
77.478 CDCl3
77.160 CDCl3
76.842 CDCl3
2j
13C NMR 100 M
f1 (ppm)



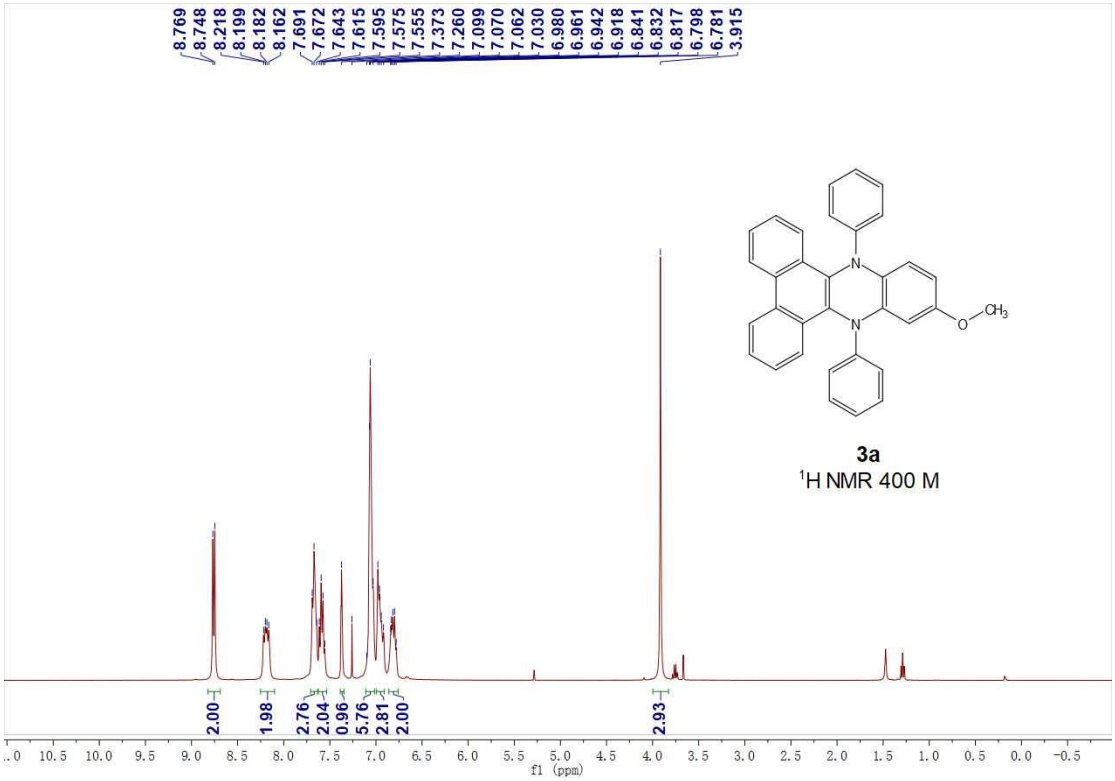
2k

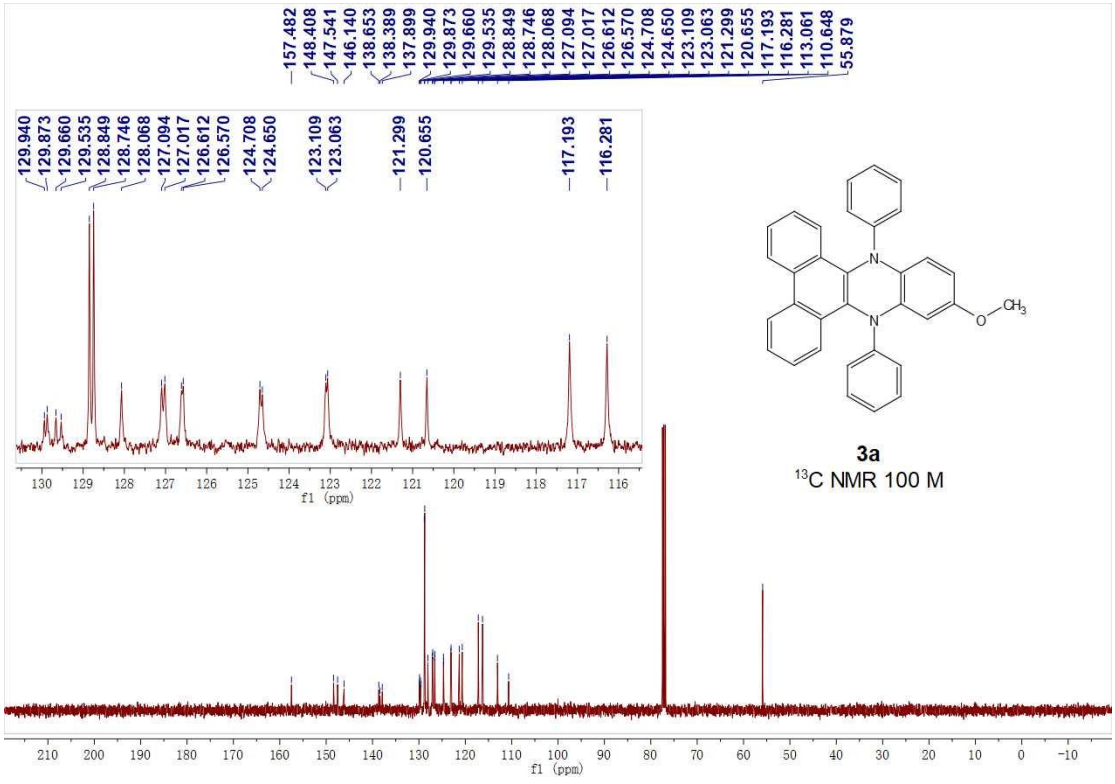
^{1}H NMR 400 M

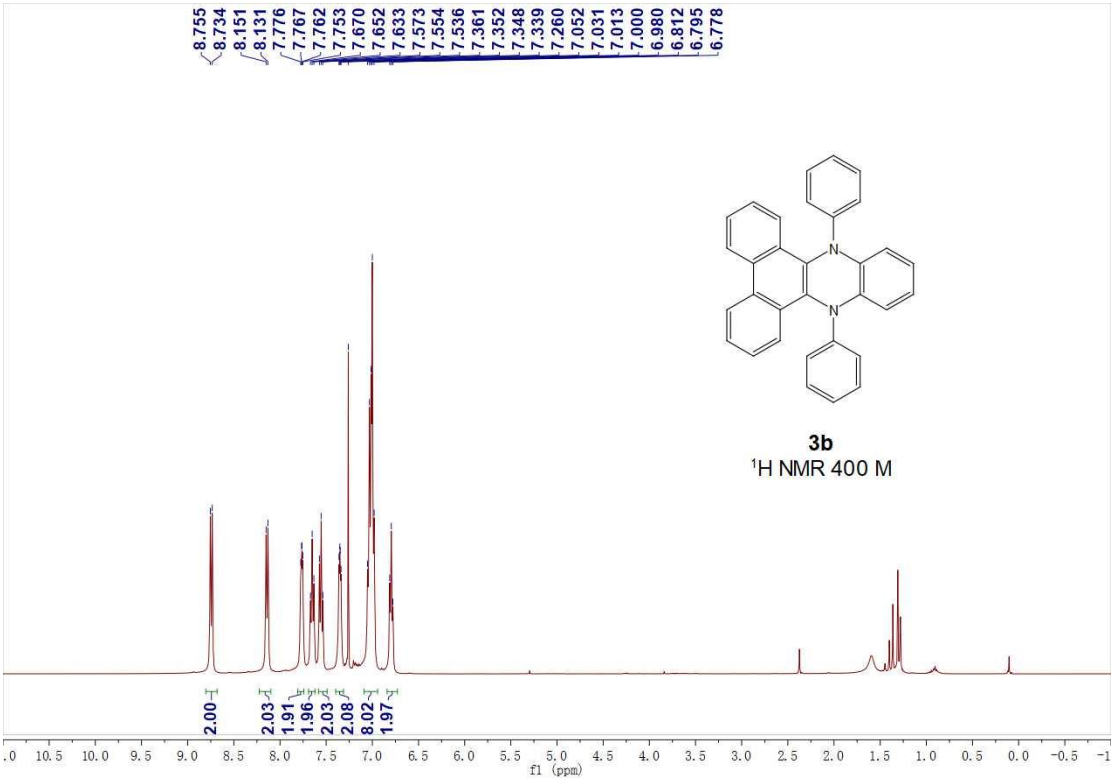


2k

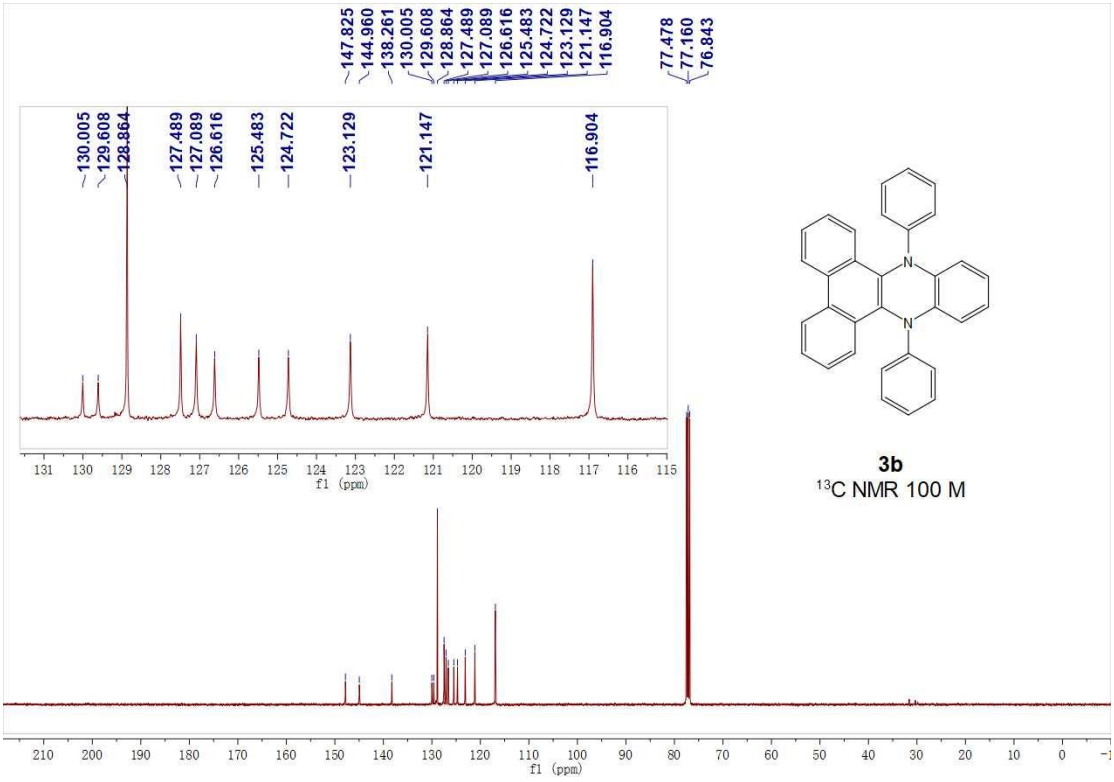
^{13}C NMR 100 M


8.769
8.748
8.218
8.199
8.182
8.162
7.691
7.672
7.643
7.615
7.595
7.575
7.555
7.373
7.260
7.099
7.070
7.062
7.030
6.980
6.961
6.942
6.918
6.841
6.832
6.817
6.798
6.781
3.915
2.00
1.98
2.76
2.04
0.96
5.76
2.81
2.00
2.93
f1 (ppm)
N
N
O
CH3
3a
1H NMR 400 M

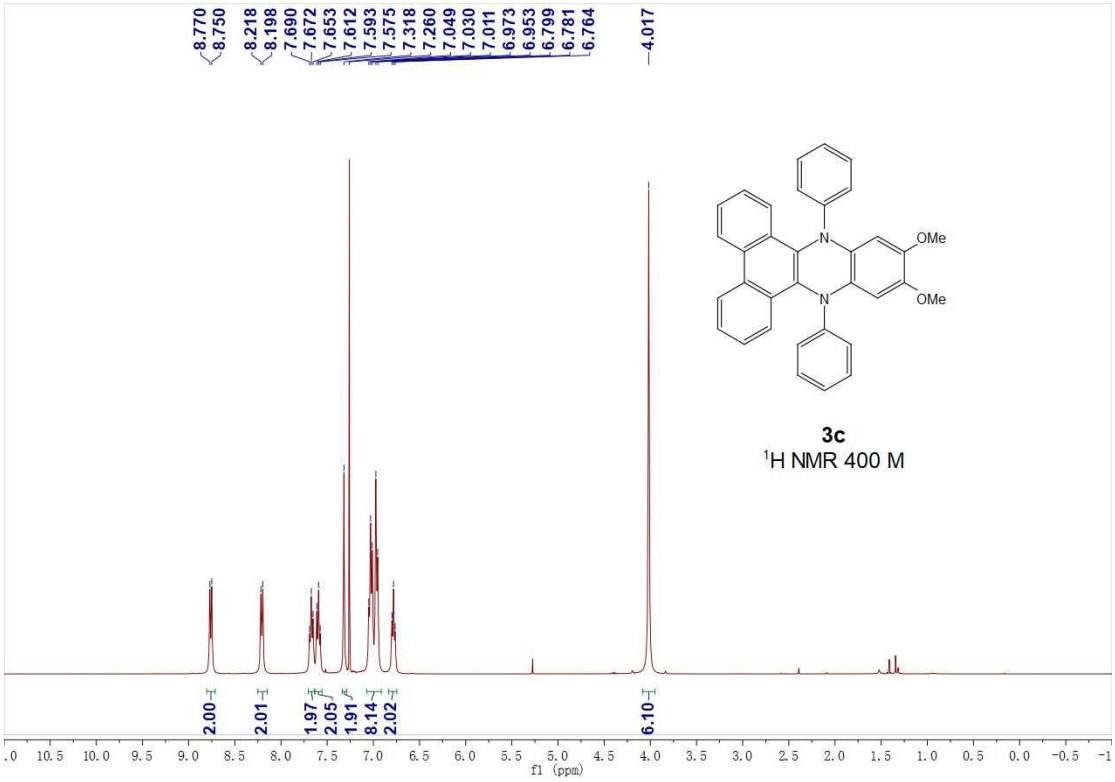

157.482
148.408
147.541
146.140
138.653
138.389
137.899
129.940
129.873
129.660
129.535
128.849
128.746
128.068
127.094
127.017
126.612
126.570
124.708
124.650
123.109
123.063
121.299
120.655
117.193
116.281
113.061
110.648
55.879
f1 (ppm)
N
N
O
CH3
3a
13C NMR 100 M



3b
^{1}H NMR 400 M

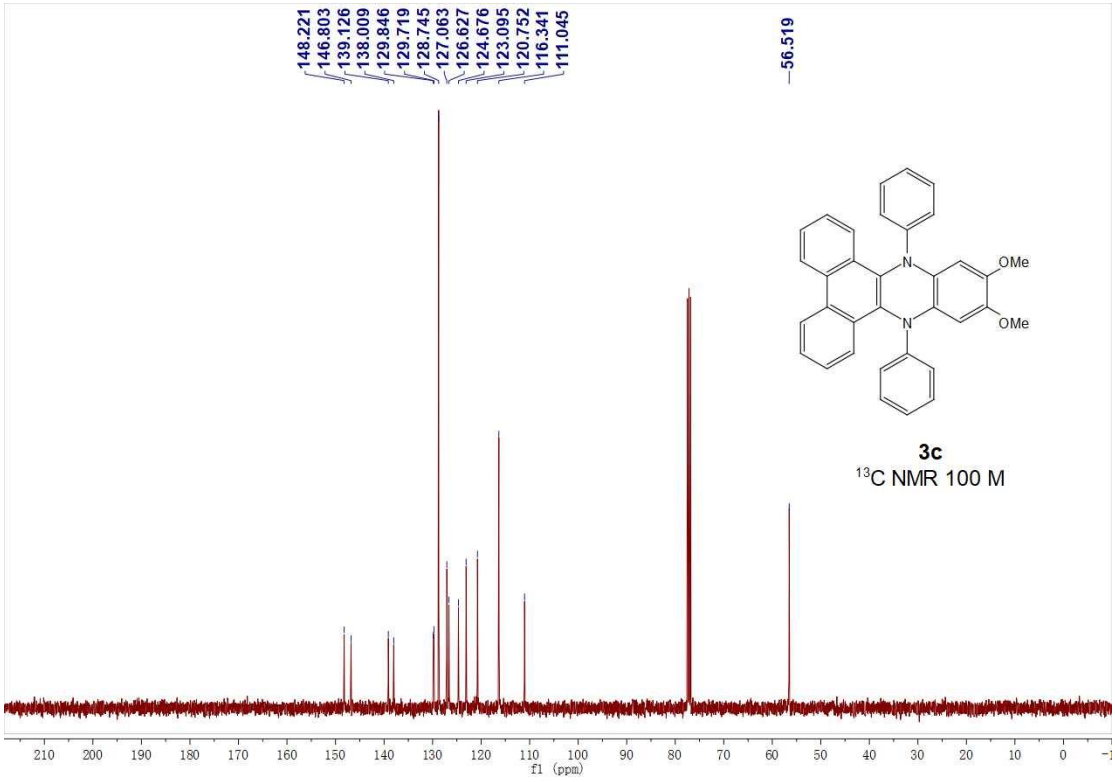


3b
^{13}C NMR 100 M



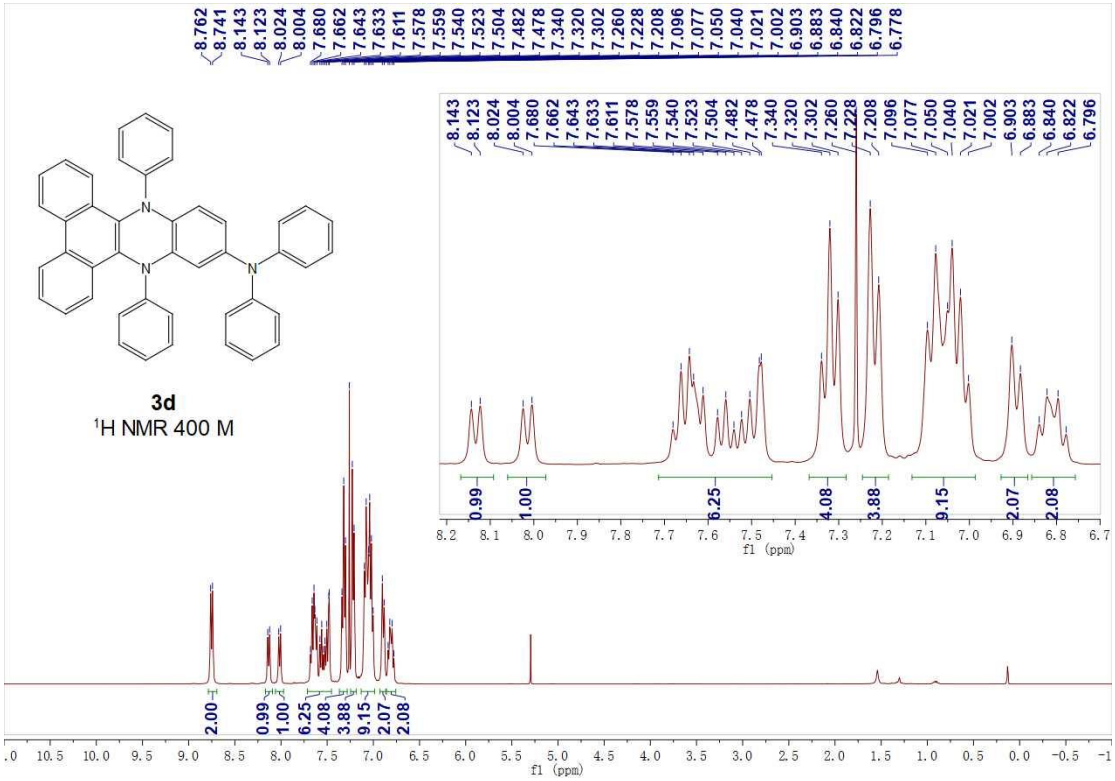
3c

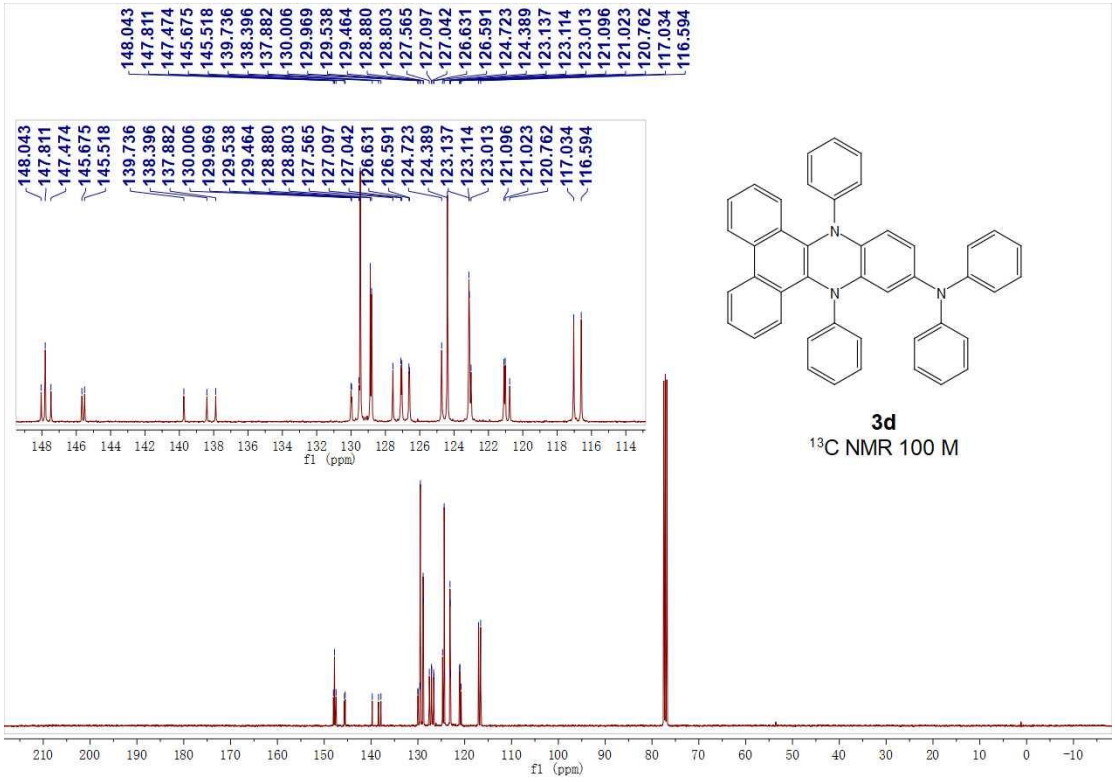
^{1}H NMR 400 M

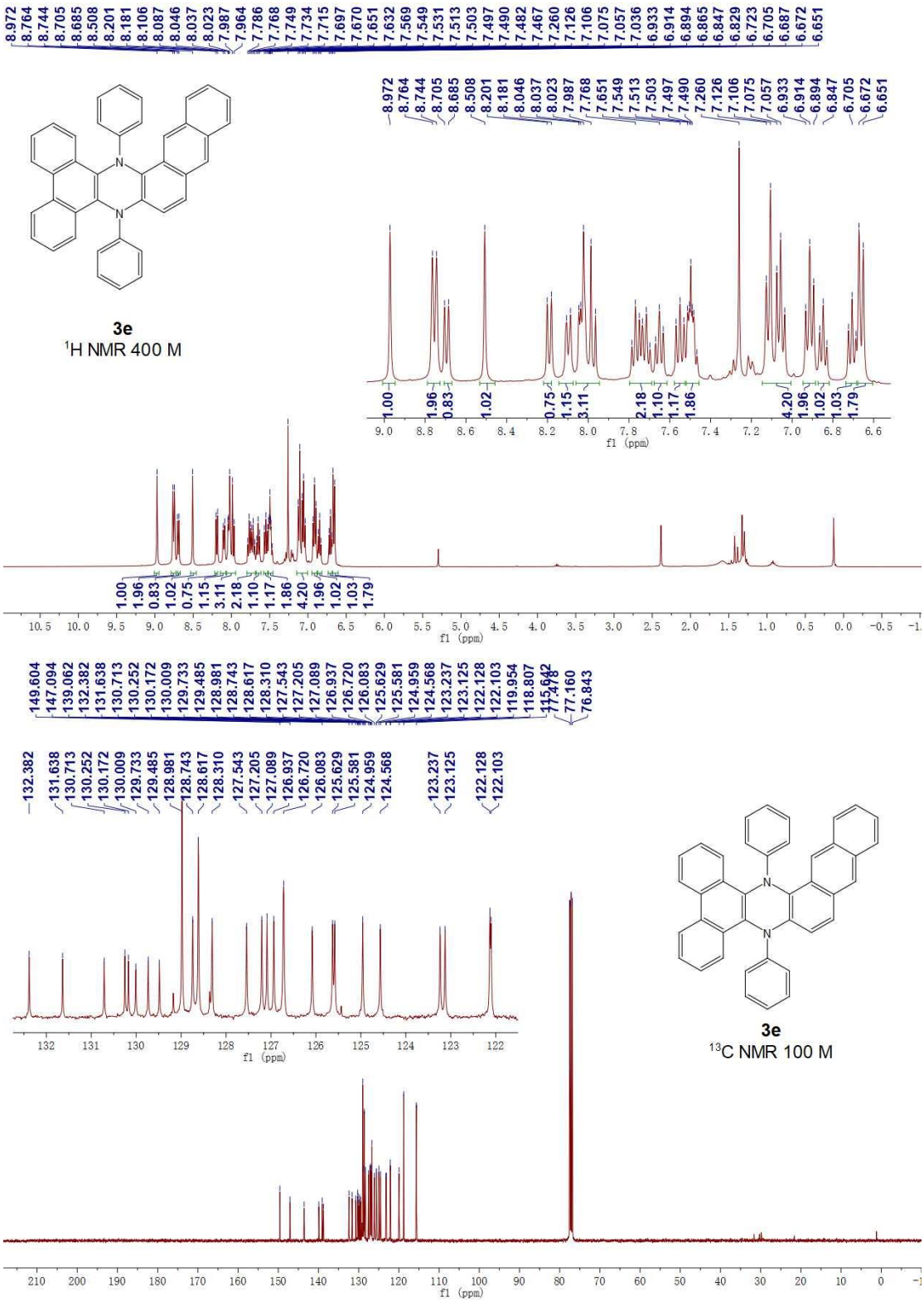


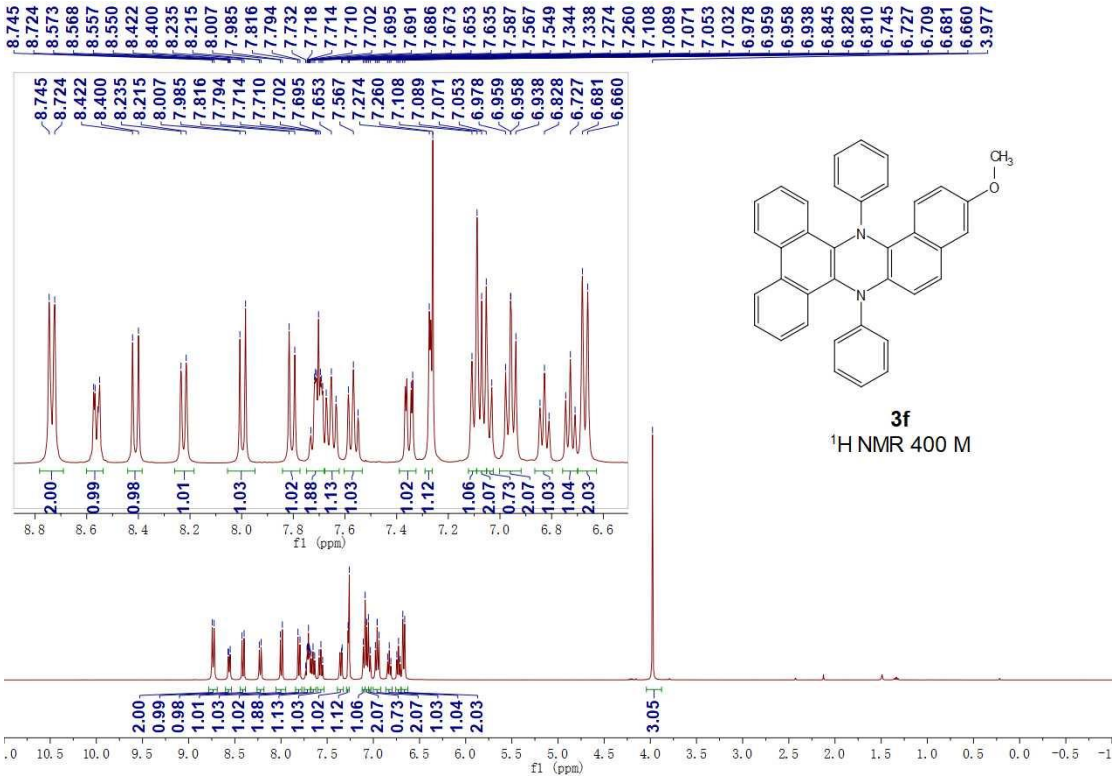
3c

^{13}C NMR 100 M


3d
1H NMR 400 M
f1 (ppm)

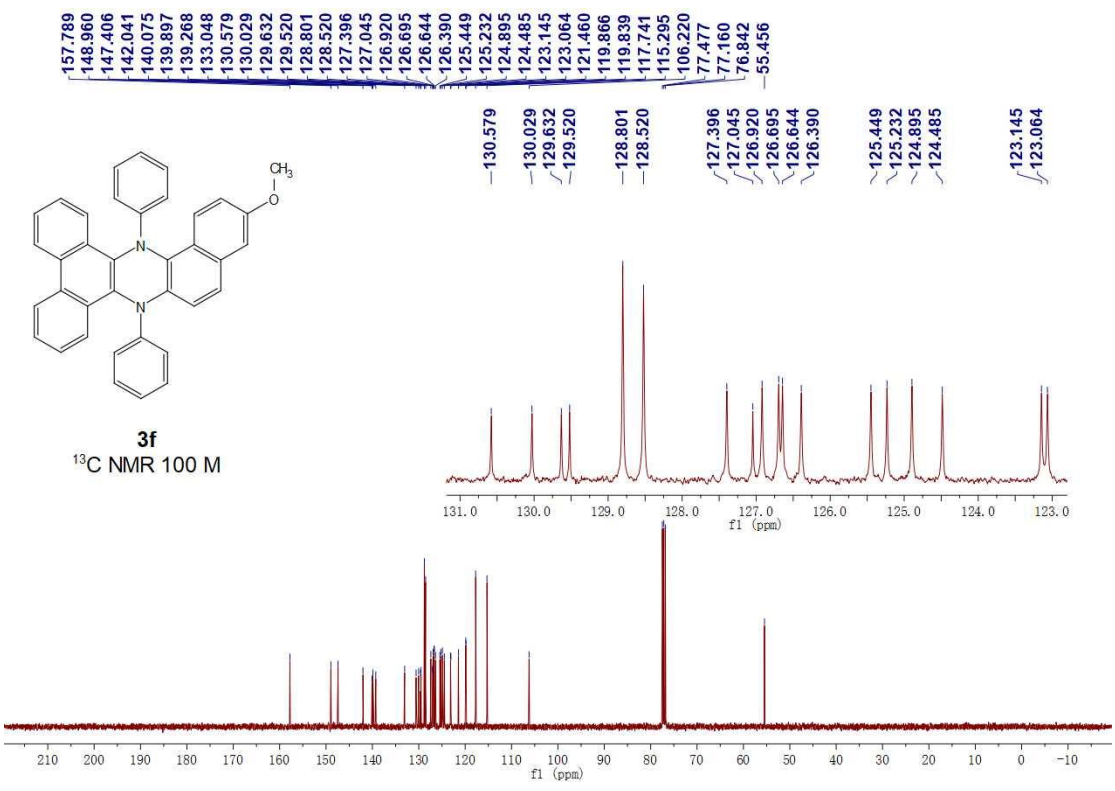

3d
13C NMR 100 M
f1 (ppm)


8.972
8.764
8.744
8.705
8.685
8.508
8.201
8.181
8.106
8.087
8.046
8.037
8.023
7.987
7.964
7.786
7.768
7.749
7.734
7.715
7.697
7.670
7.651
7.632
7.569
7.549
7.531
7.513
7.503
7.497
7.490
7.482
7.467
7.260
7.126
7.106
7.075
7.057
7.036
6.933
6.914
6.894
6.865
6.847
6.829
6.723
6.705
6.687
6.672
6.651
3e
1H NMR 400 M
1.00
1.96
0.83
1.02
0.75
1.15
3.11
2.18
1.10
1.17
1.86
4.20
1.96
1.02
1.03
1.79
f1 (ppm)
149.604
147.094
139.062
132.382
131.638
130.713
130.252
130.172
130.009
129.733
129.485
128.981
128.743
128.617
128.310
127.543
127.205
127.089
126.937
126.720
126.083
125.629
125.581
124.959
124.568
123.237
123.125
122.128
122.103
119.954
118.807
115.642
77.478
77.160
76.843
3e
13C NMR 100 M
f1 (ppm)



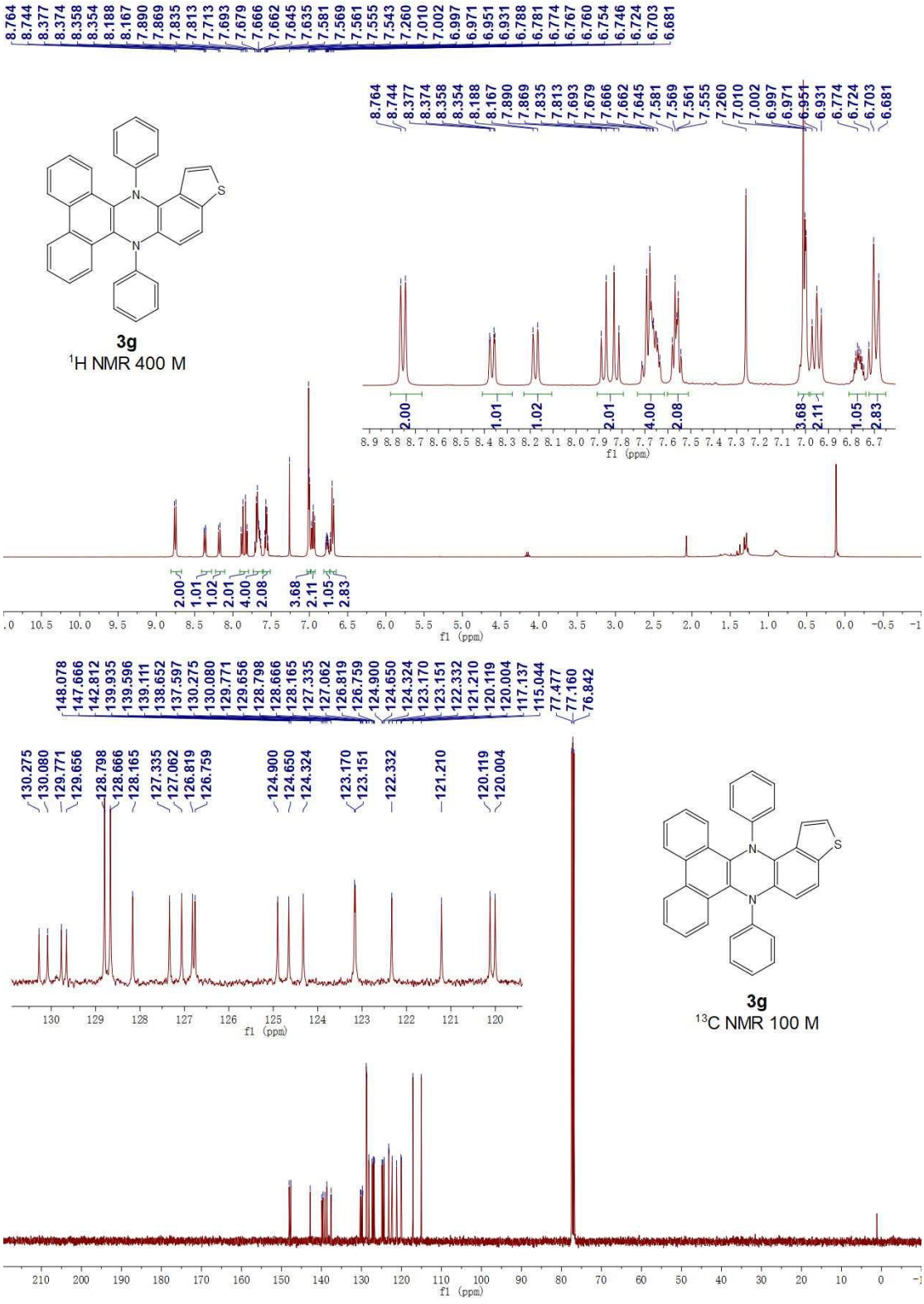
3f

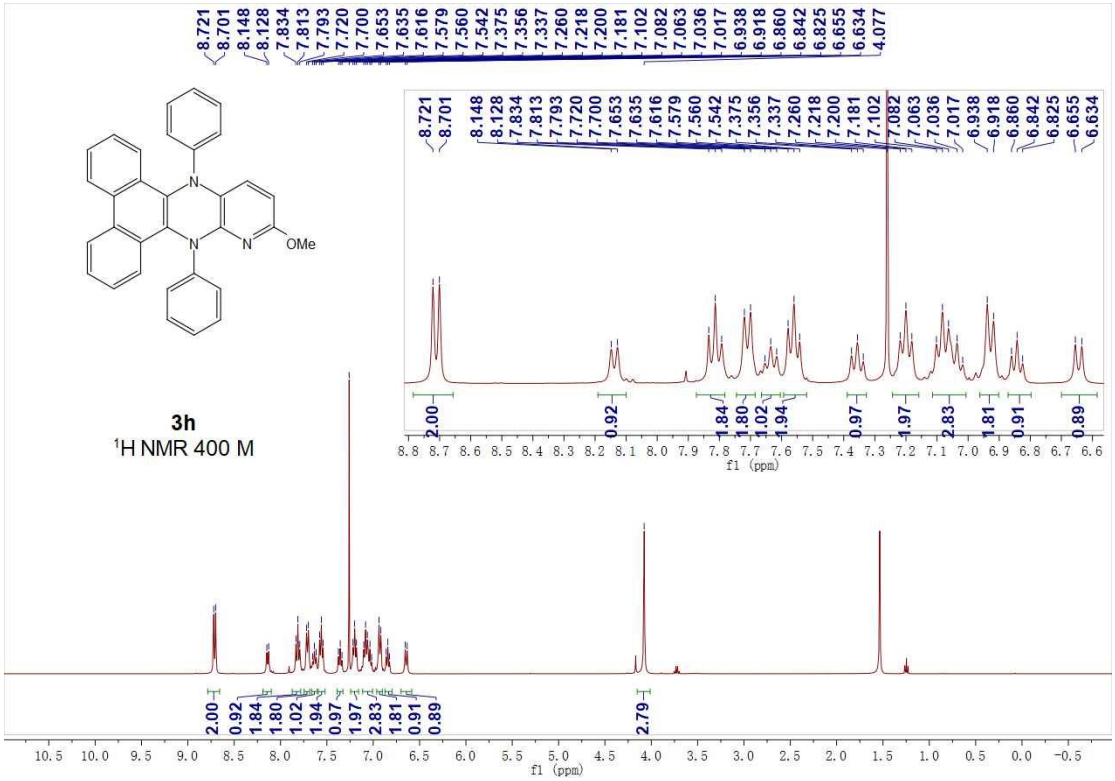
^{1}H NMR 400 M

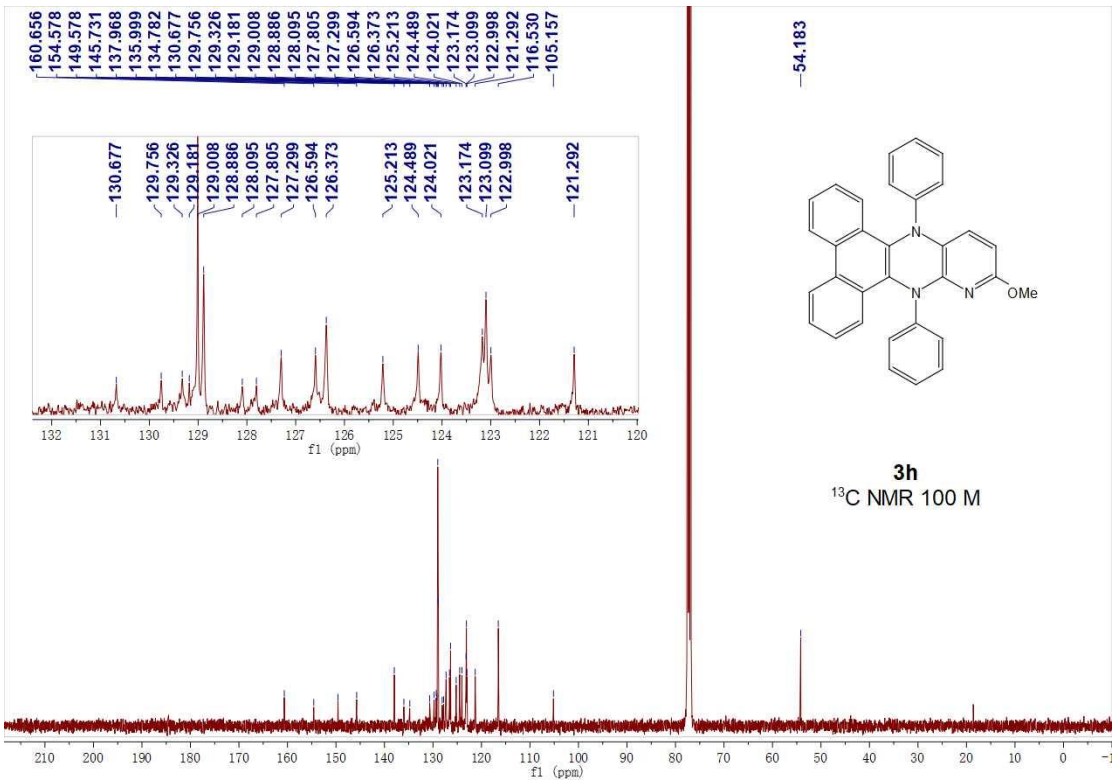


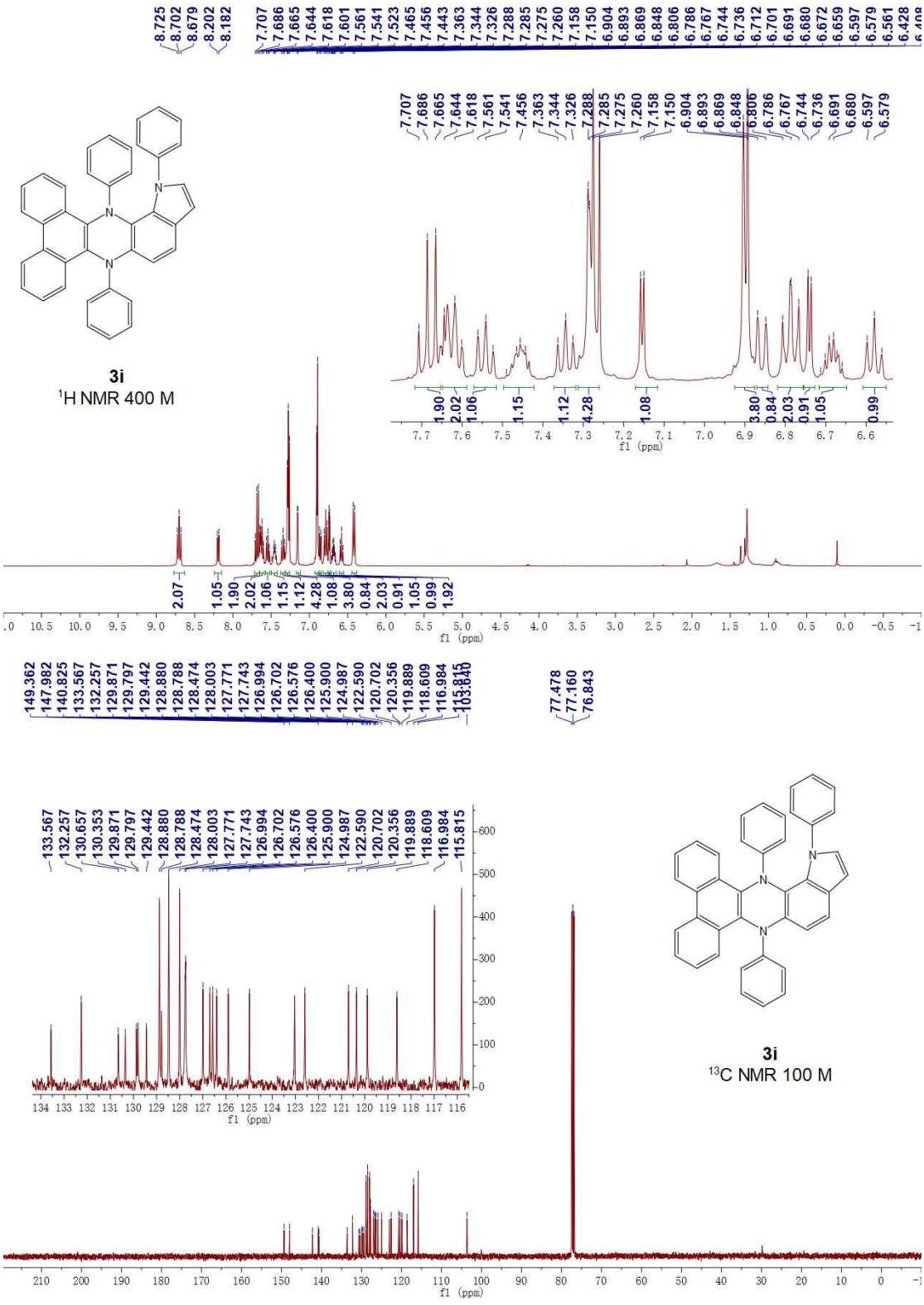
3f

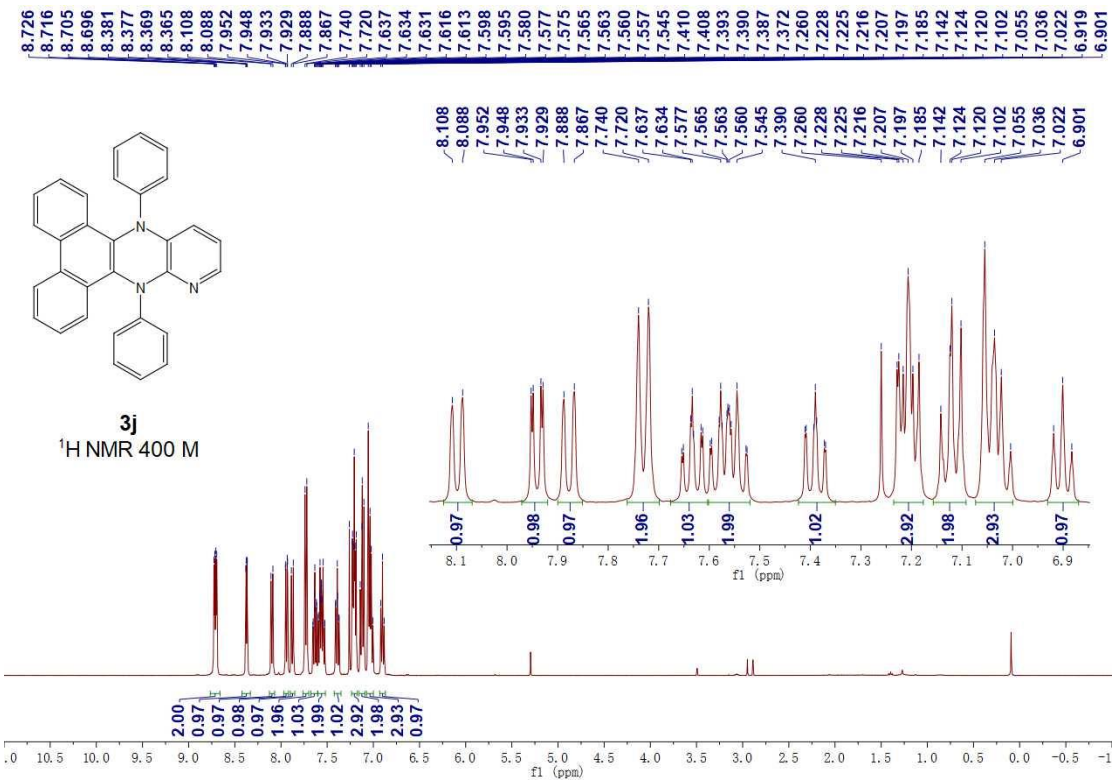
^{13}C NMR 100 M

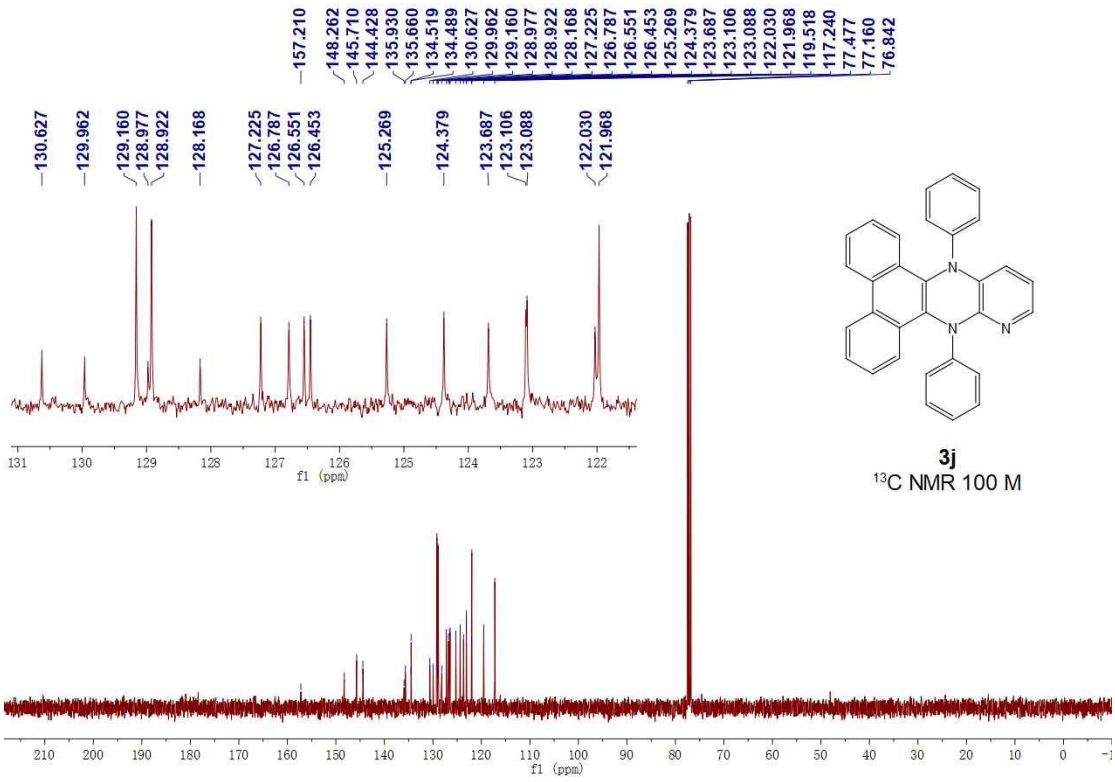

3g
1H NMR 400 M
3g
13C NMR 100 M

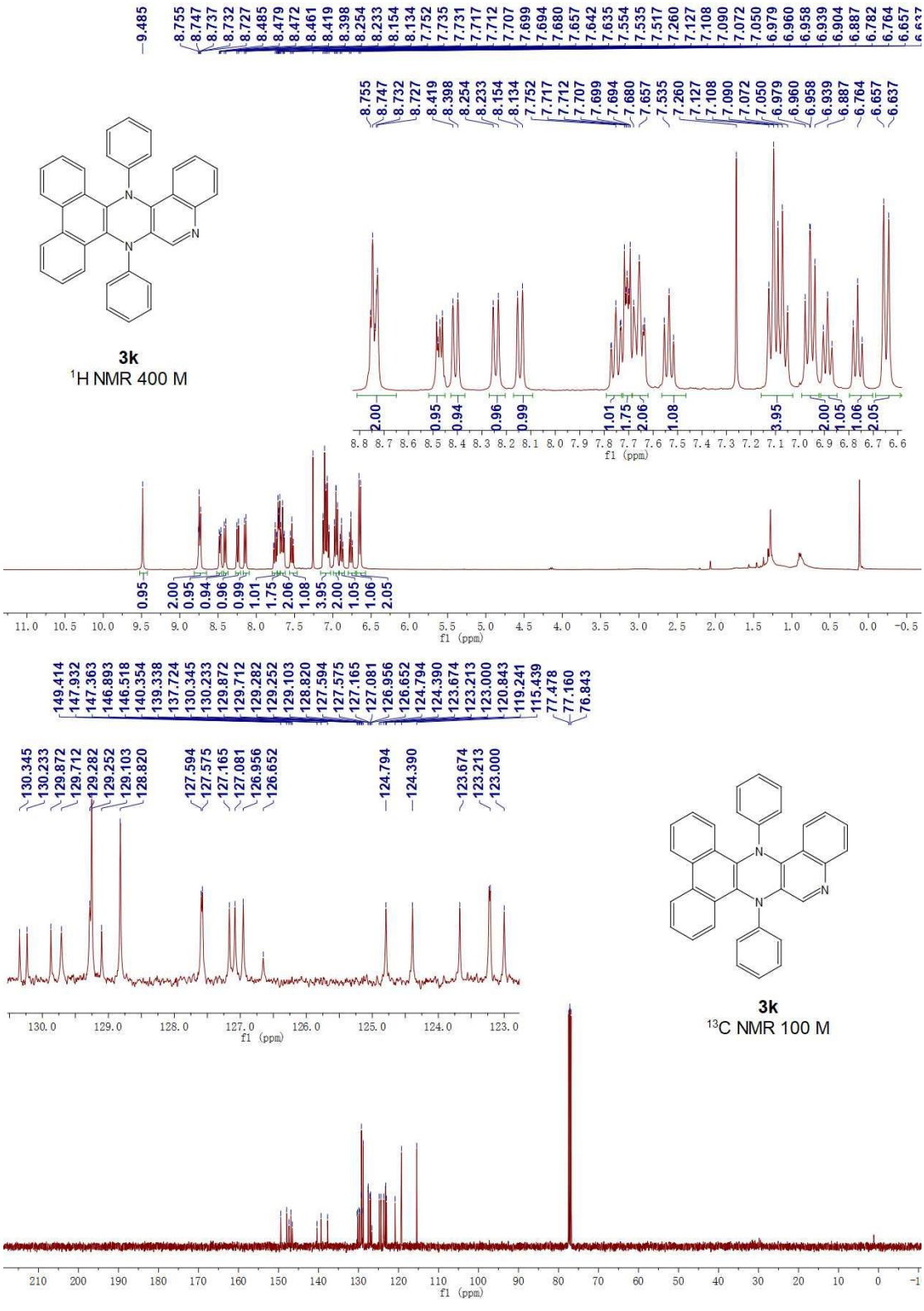

8.721
8.701
8.148
8.128
7.834
7.813
7.793
7.720
7.700
7.653
7.635
7.616
7.579
7.560
7.542
7.375
7.356
7.337
7.260
7.218
7.200
7.181
7.102
7.082
7.063
7.036
7.017
6.938
6.918
6.860
6.842
6.825
6.655
6.634
4.077
OMe
3h
1H NMR 400 M
2.00
0.92
1.84
1.80
1.02
1.94
0.97
1.97
2.83
1.81
0.91
0.89
2.79
f1 (ppm)

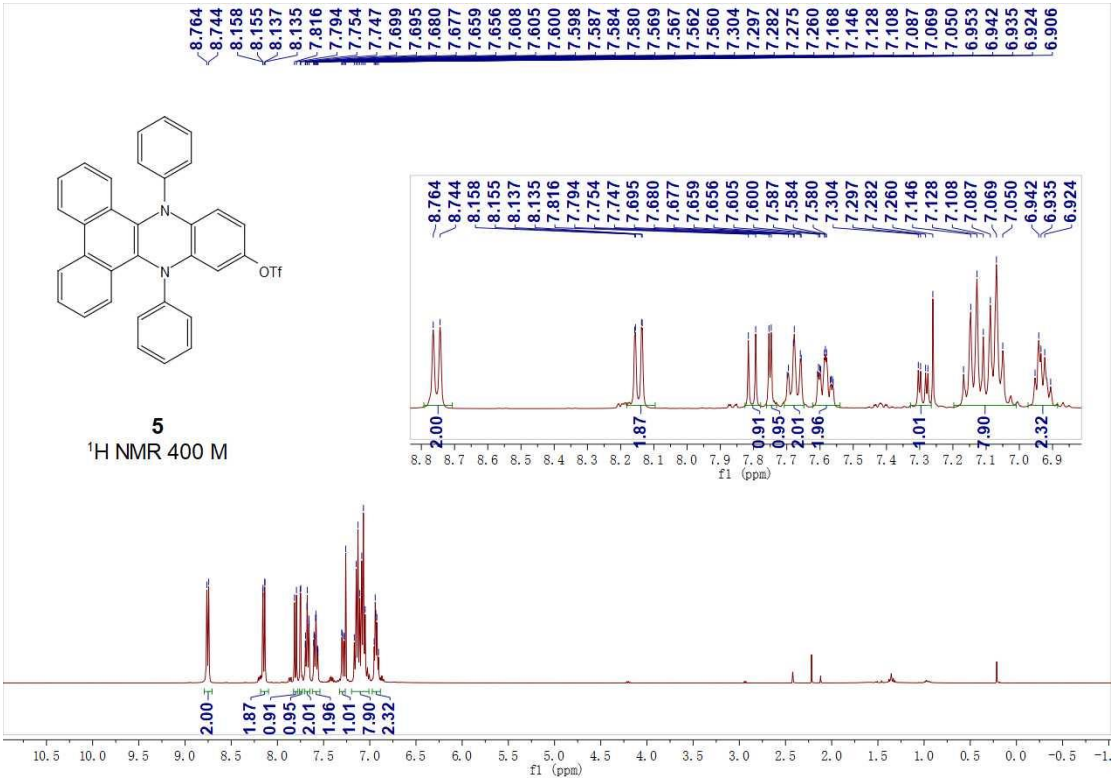

160.656
154.578
149.578
145.731
137.968
135.999
134.782
130.677
129.756
129.326
129.181
129.008
128.886
128.095
127.805
127.299
126.594
126.373
125.213
124.489
124.021
123.174
123.099
122.998
121.292
116.530
105.157
54.183
OMe
3h
13C NMR 100 M
f1 (ppm)

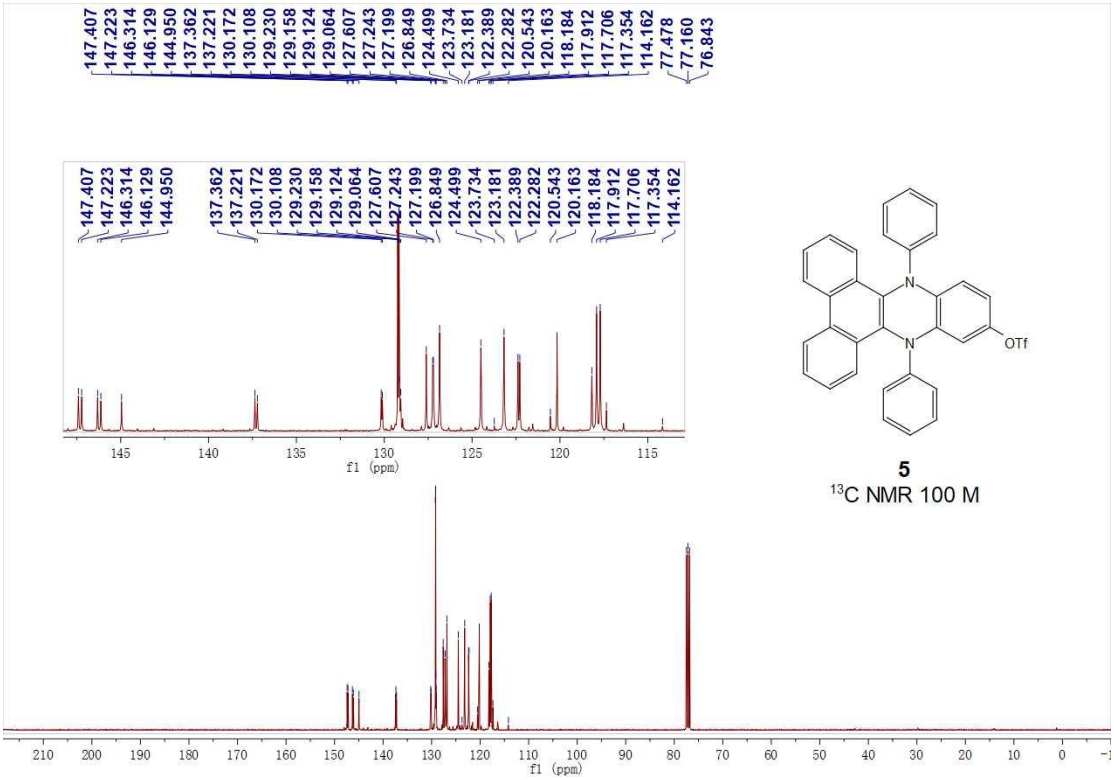

3i
1H NMR 400 M
3i
13C NMR 100 M
f1 (ppm)

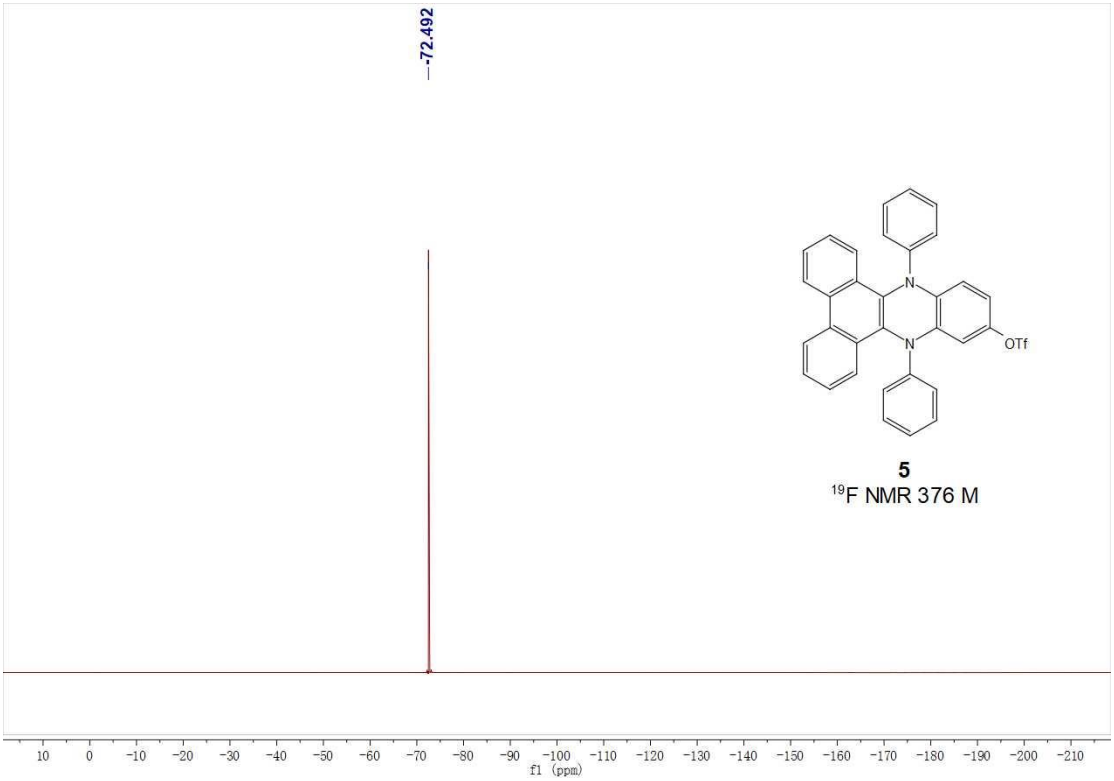

8.726 8.716 8.705 8.696 8.381 8.377 8.369 8.365 8.108 8.088 7.952 7.948 7.933 7.929 7.888 7.867 7.740 7.720 7.637 7.634 7.631 7.616 7.613 7.598 7.595 7.580 7.577 7.575 7.565 7.563 7.560 7.557 7.545 7.410 7.408 7.393 7.390 7.387 7.372 7.260 7.228 7.225 7.216 7.207 7.197 7.185 7.142 7.124 7.120 7.102 7.055 7.036 7.022 6.919 6.901
3j
1H NMR 400 M
2.00 0.97 0.97 0.98 0.97 1.96 1.03 1.99 1.02 2.92 1.98 2.93 0.97
f1 (ppm)


157.210 148.262 145.710 144.428 135.930 135.660 134.519 134.489 130.627 129.962 129.160 128.977 128.922 128.168 127.225 126.787 126.551 126.453 125.269 124.379 123.687 123.106 123.088 122.030 121.968 119.518 117.240 77.477 77.160 76.842
3j
13C NMR 100 M
f1 (ppm)


3k
1H NMR 400 M
3k
13C NMR 100 M

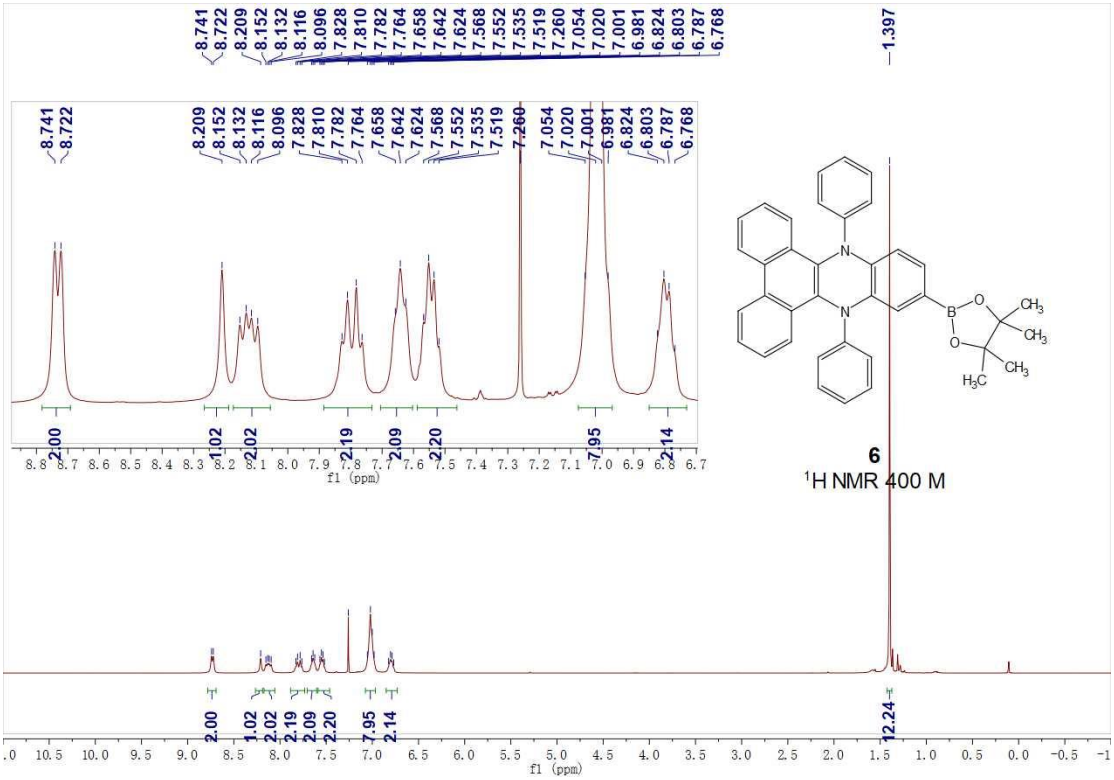

8.764 8.744 8.158 8.155 8.137 8.135 7.816 7.794 7.754 7.747 7.699 7.695 7.680 7.677 7.659 7.656 7.608 7.605 7.600 7.598 7.587 7.584 7.580 7.569 7.567 7.562 7.560 7.304 7.297 7.282 7.275 7.260 7.168 7.146 7.128 7.108 7.087 7.069 7.050 6.953 6.942 6.935 6.924 6.906
OTf
5
1H NMR 400 M
2.00 1.87 0.91 0.95 2.01 1.96 1.01 7.90 2.32
f1 (ppm)


147.407 147.223 146.314 146.129 144.950 137.362 137.221 130.172 130.108 129.230 129.158 129.124 129.064 127.607 127.243 127.199 126.849 124.499 123.734 123.181 122.389 122.282 120.543 120.163 118.184 117.912 117.706 117.354 114.162 77.478 77.160 76.843
OTf
5
13C NMR 100 M
f1 (ppm)



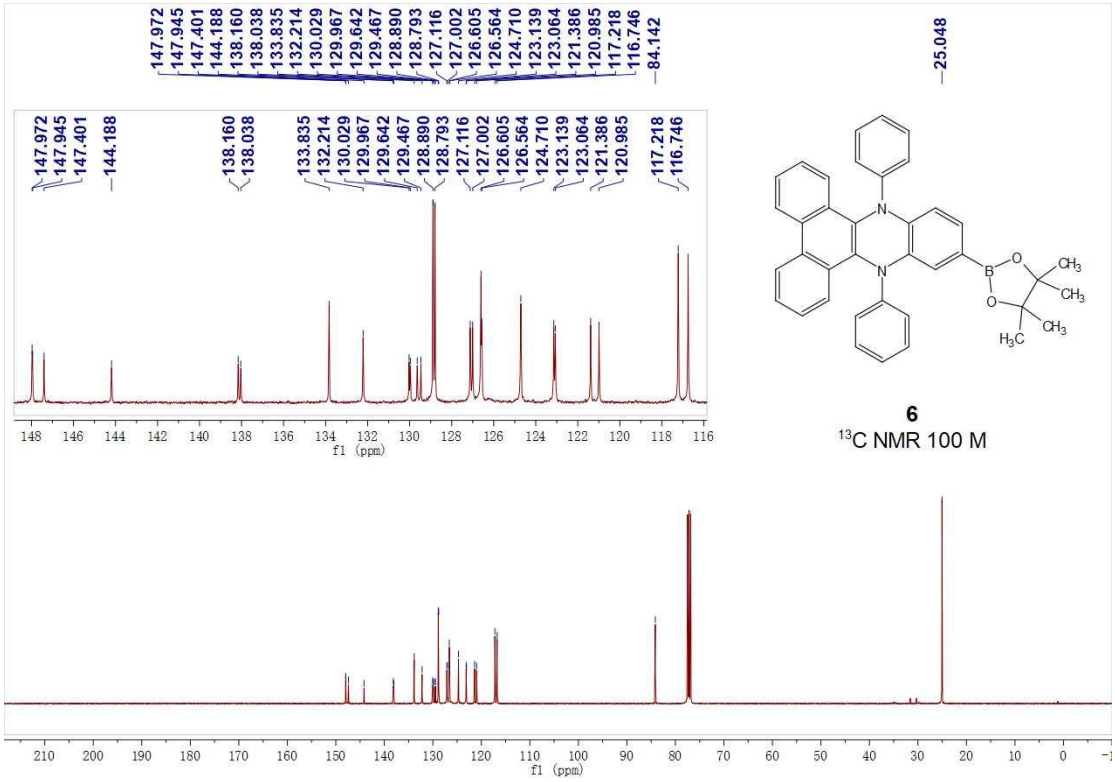
5

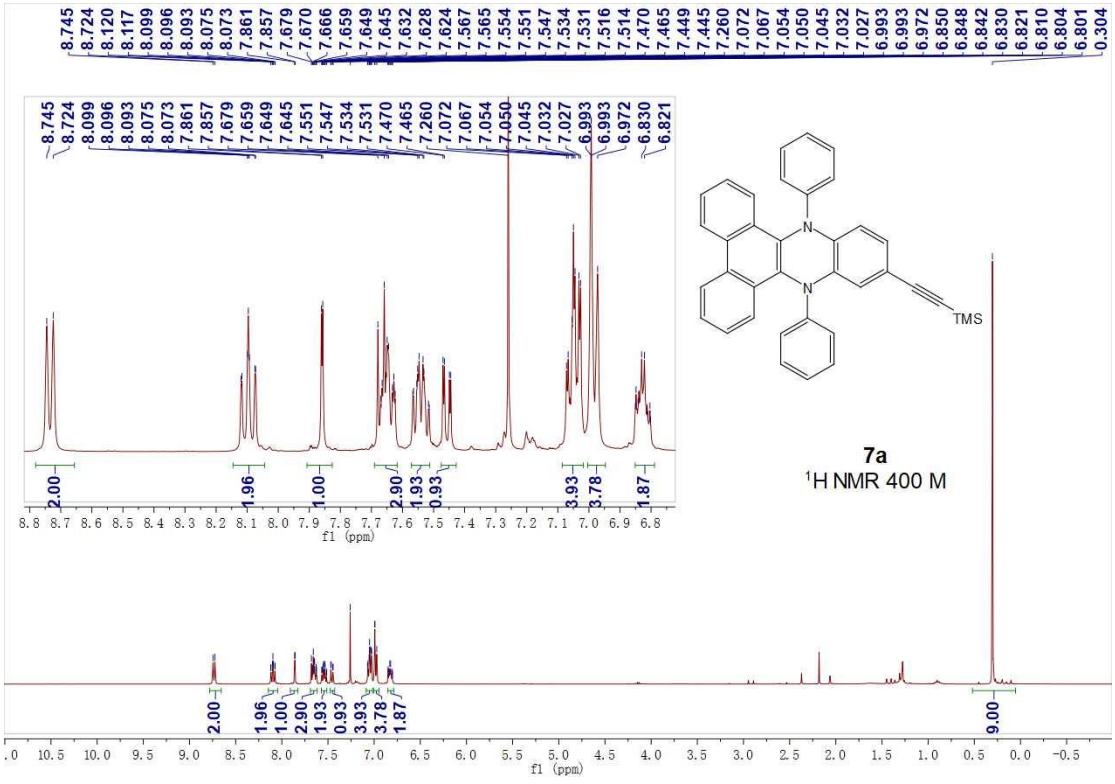
^{19}F NMR 376 M

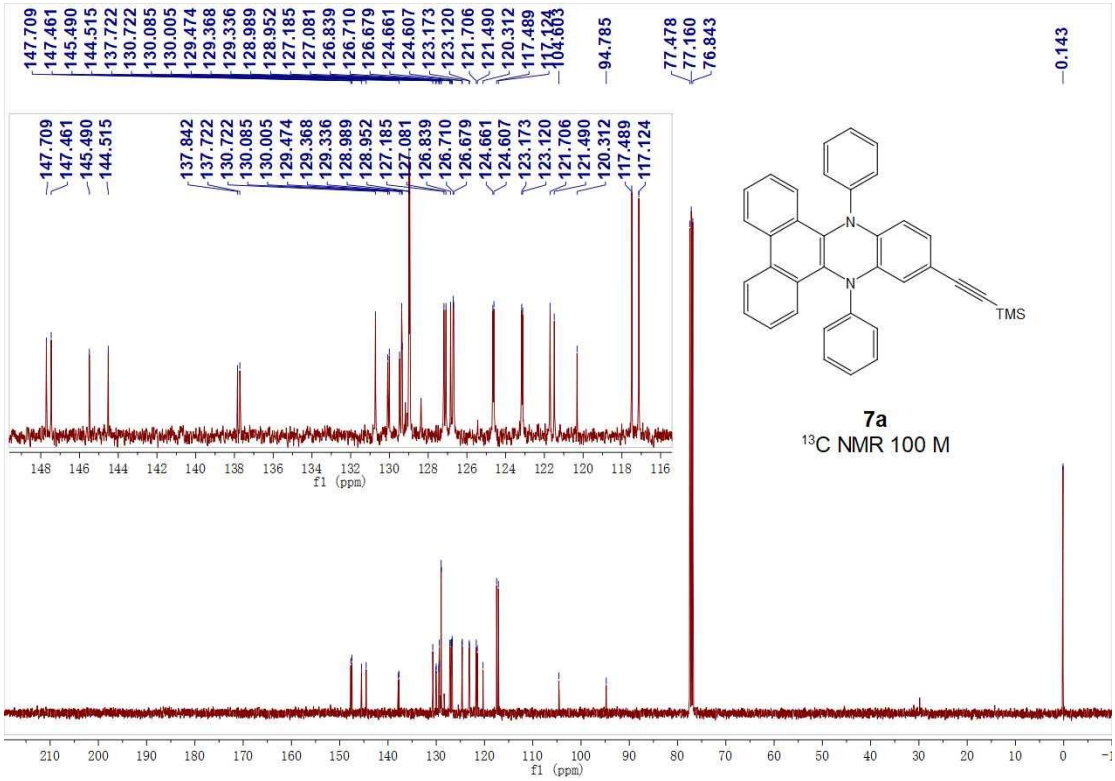


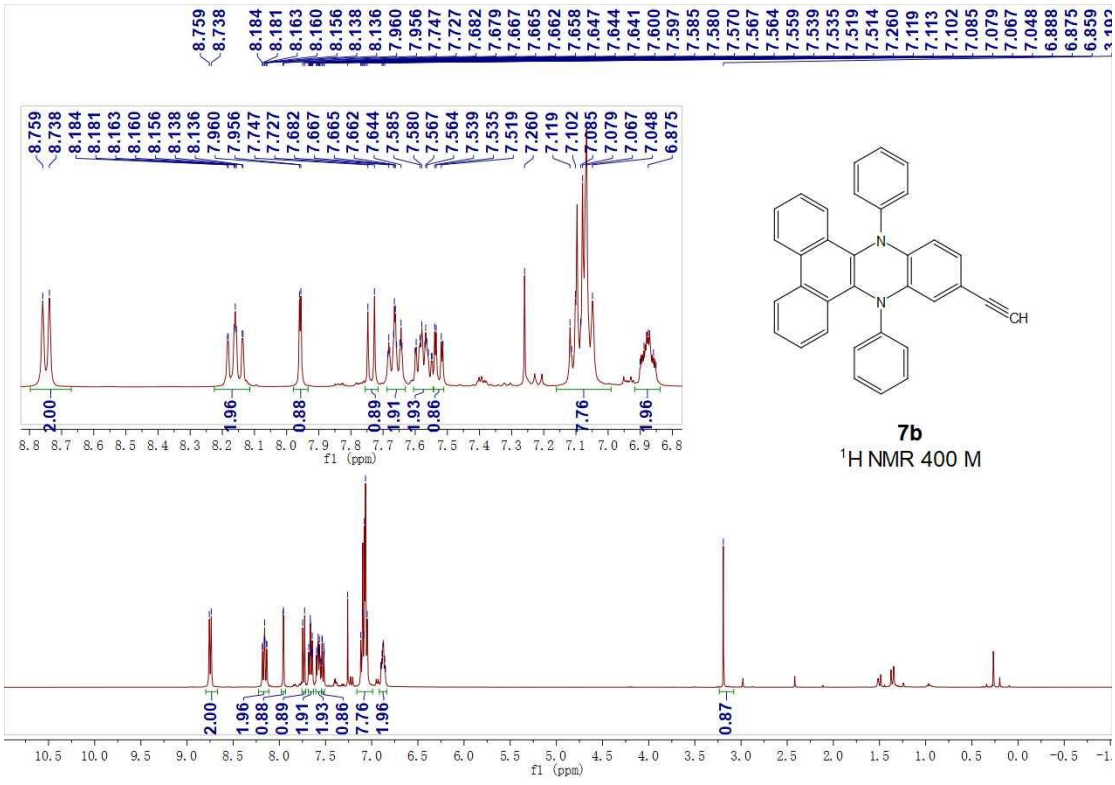
6

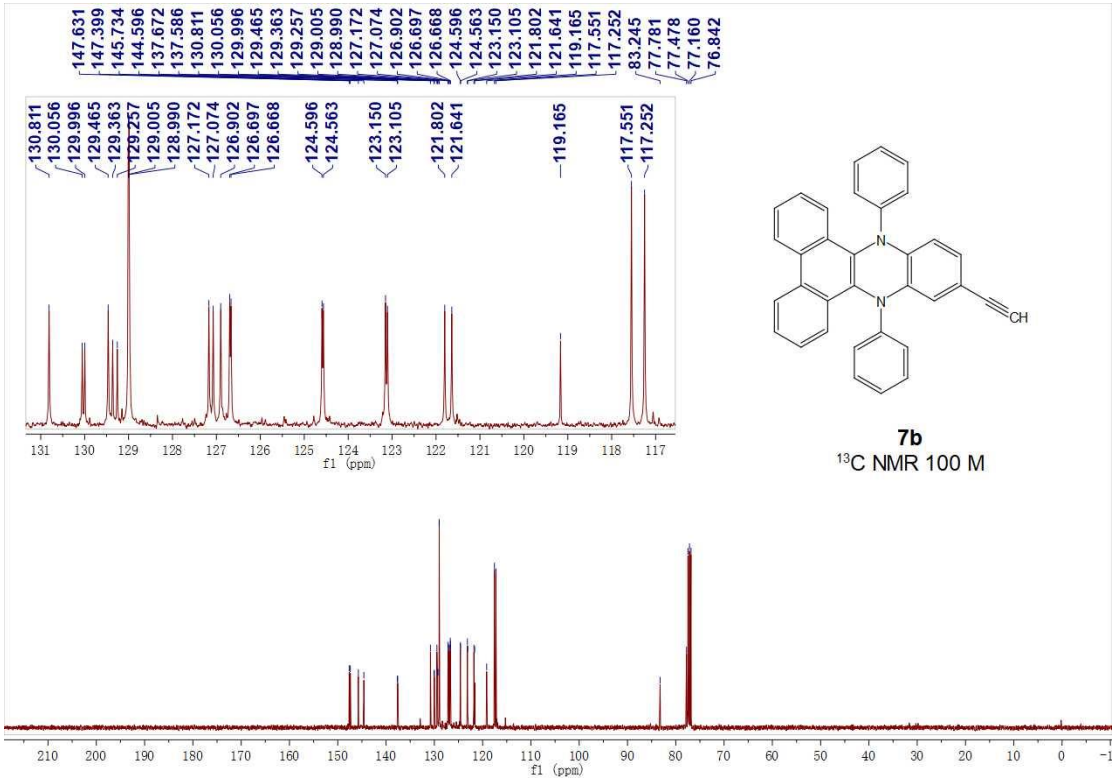
^{1}H NMR 400 M

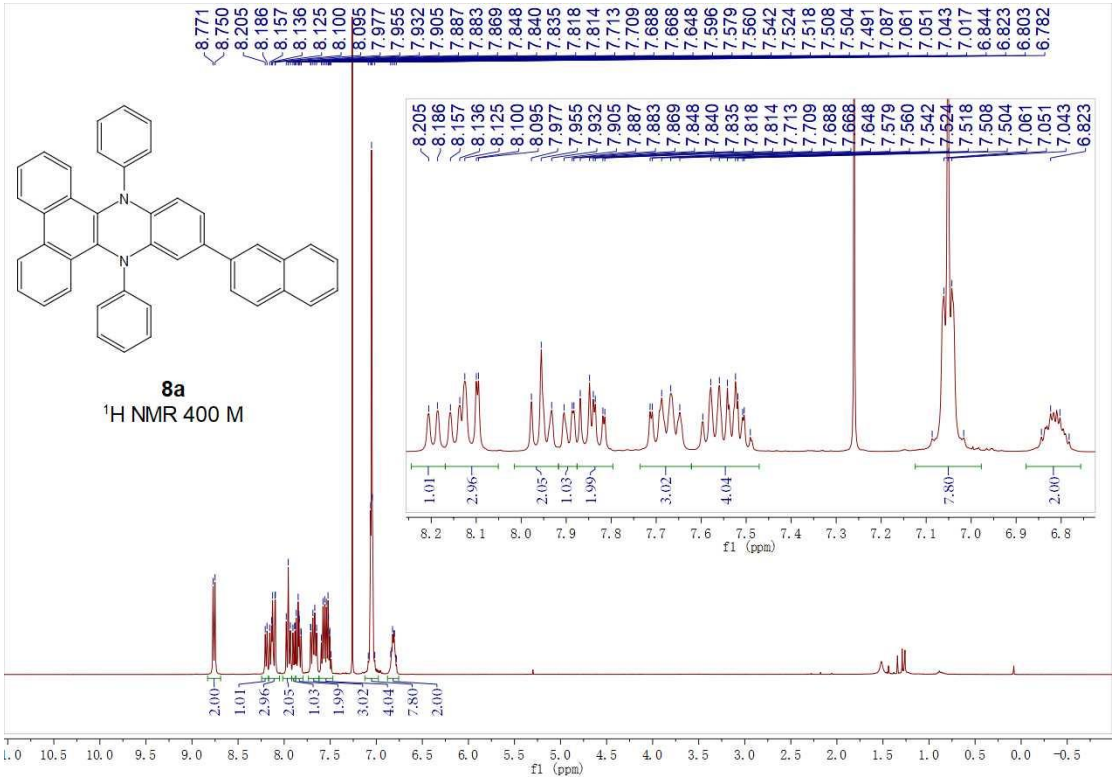

147.972
147.945
147.401
144.188
138.160
138.038
133.835
132.214
130.029
129.967
129.642
129.467
128.890
128.793
127.116
127.002
126.605
126.564
124.710
123.139
123.064
121.386
120.985
117.218
116.746
84.142
25.048
f1 (ppm)
6
13C NMR 100 M

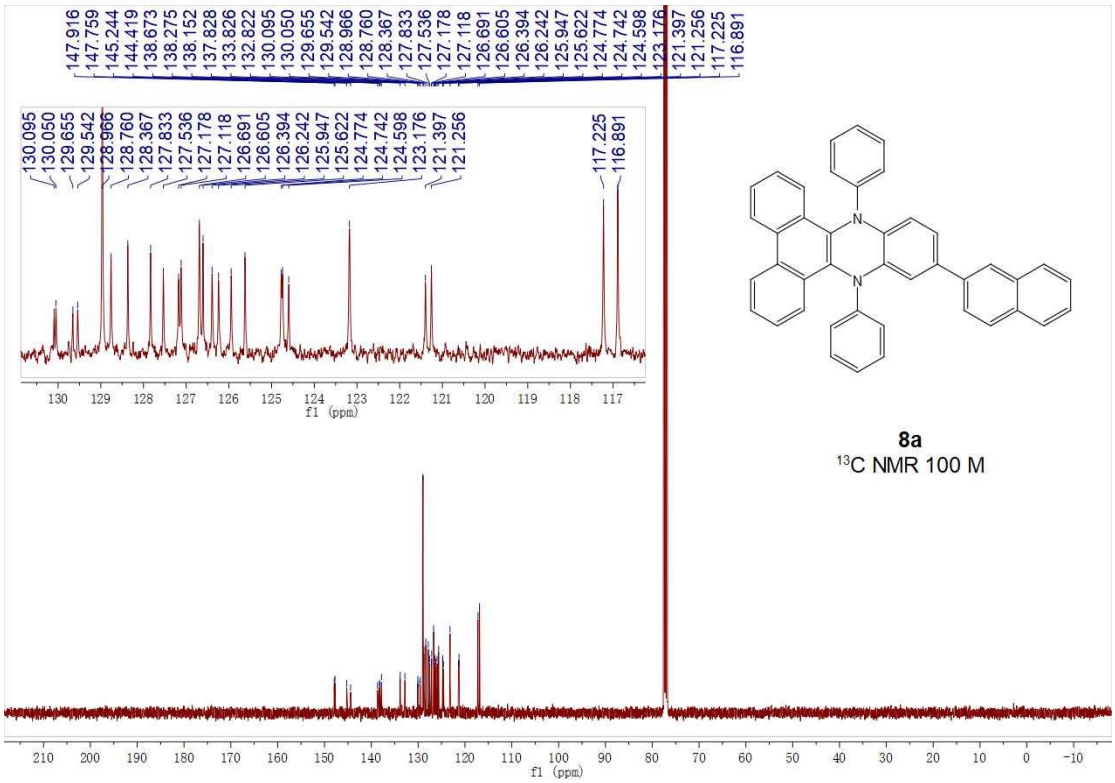

8.745
8.724
8.120
8.117
8.099
8.096
8.093
8.075
8.073
7.861
7.857
7.679
7.670
7.666
7.659
7.649
7.645
7.632
7.628
7.624
7.567
7.565
7.554
7.551
7.547
7.534
7.531
7.516
7.514
7.470
7.465
7.449
7.445
7.260
7.072
7.067
7.054
7.050
7.045
7.032
7.027
6.993
6.993
6.972
6.850
6.848
6.842
6.830
6.821
6.810
6.804
6.801
0.304
2.00
1.96
1.00
2.90
1.93
0.93
3.93
3.78
1.87
9.00
TMS
f1 (ppm)
7a
1H NMR 400 M


TMS
7a
13C NMR 100 M
f1 (ppm)

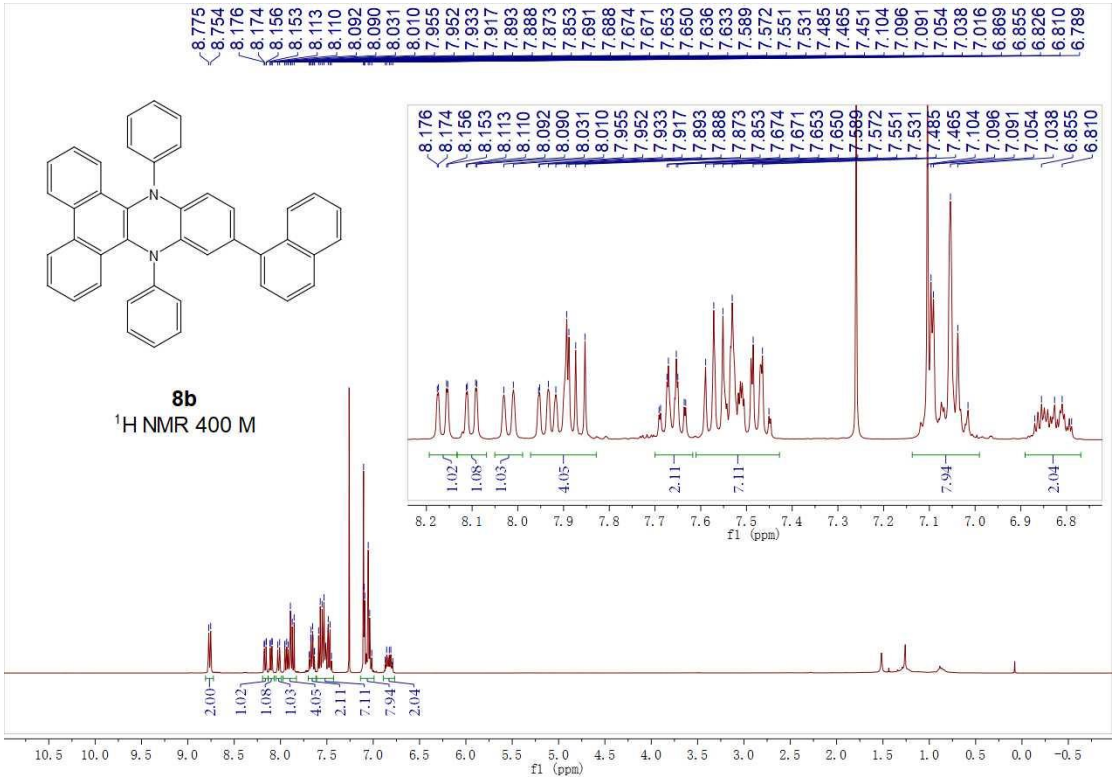

CH
7b
1H NMR 400 M
f1 (ppm)


147.631
147.399
145.734
144.596
137.672
137.586
130.811
130.056
129.996
129.465
129.363
129.257
129.005
128.990
127.172
127.074
126.902
126.697
126.668
124.596
124.563
123.150
123.105
121.802
121.641
119.165
117.551
117.252
83.245
77.781
77.478
77.160
76.842
f1 (ppm)
N
N
CH
7b
13C NMR 100 M

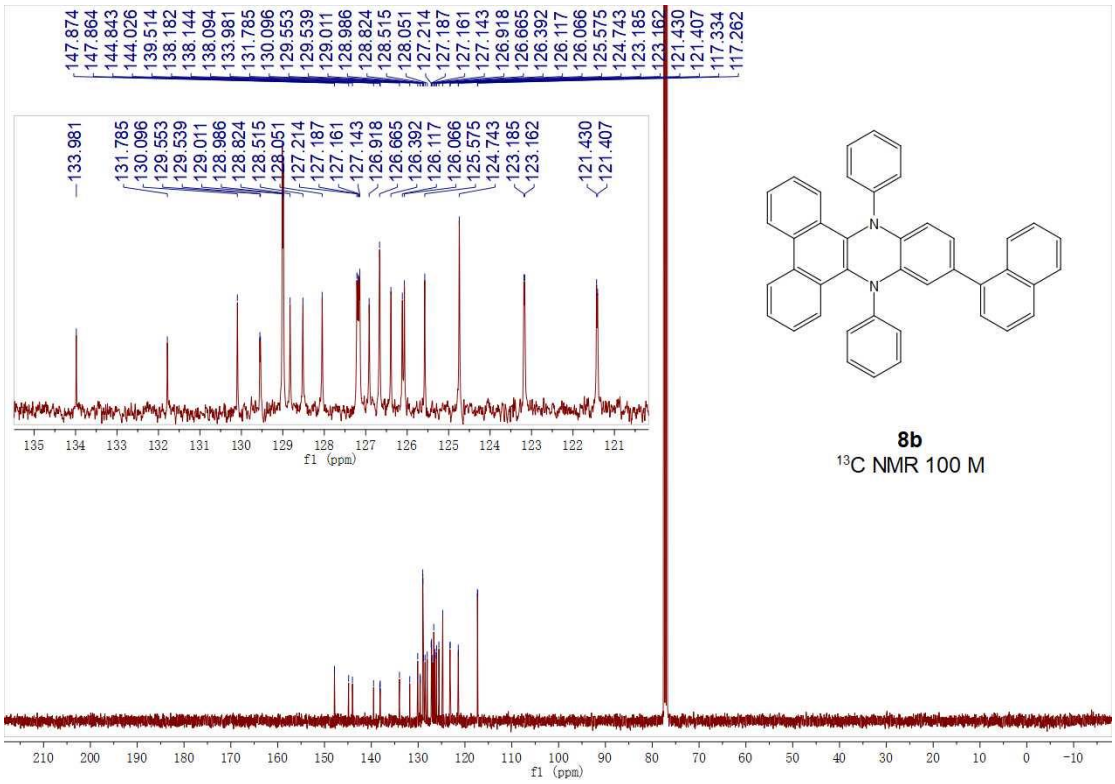

8.771
8.750
8.205
8.186
8.157
8.136
8.125
8.100
8.095
7.977
7.955
7.932
7.905
7.887
7.883
7.869
7.848
7.840
7.835
7.818
7.814
7.713
7.709
7.688
7.668
7.648
7.596
7.579
7.560
7.542
7.524
7.518
7.508
7.504
7.491
7.087
7.061
7.051
7.043
7.017
6.844
6.823
6.803
6.782
N
N
8a
1H NMR 400 M
f1 (ppm)



8a
^{13}C NMR 100 M



8b
^{1}H NMR 400 M


147.874
147.864
144.843
144.026
139.514
138.182
138.144
138.094
133.981
131.785
130.096
129.553
129.539
129.011
128.986
128.824
128.515
128.051
127.214
127.187
127.161
127.143
126.918
126.665
126.392
126.117
126.066
125.575
124.743
123.185
123.162
121.430
121.407
117.334
117.262
f1 (ppm)
N
N
8b
13C NMR 100 M