

Electronic Supplementary Information (ESI) for

Novel multifunctional organic semiconductor materials based on 4,8-substituted 1,5-naphthyridine : synthesis, single crystal structures , opto-electrical properties and quantum chemistry calculation

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I. General Methods

All reactions were performed under a nitrogen atmosphere. Solvents were carefully dried and distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored by thin-layer chromatography (TLC) with Merck pre-coated glass plates. Flash column chromatography and preparative TLC were carried out using silica gel from Merck (300–400 mesh).

Melting points were measured on an X-4 microscope electrothermal apparatus (Taike China) and were uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AV spectrometer (500 MHz or 400 MHz for ^1H and 125 MHz for ^{13}C). Mass spectra were recorded on a Agilent 1100 mass spectrometer. Fourier transformation infrared (FTIR) spectra were recorded in KBr pellets using an AVATAR 370 FTIR spectrometer (Thermo Nicolet). The elemental analyses were performed with a Vario El III elemental analyzer.

The diffraction data of single crystals **1b**, **1e** and **1f** were collected on a Nonius CAD4 single crystal diffractometer equipped with a graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) by using an $\omega/2\theta$ scan mode at 293 K. The crystal structures were solved by the direct method and refined by the full-matrix leastsquares procedure on F2 using SHELXL-97 program.^[1] All nonhydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced at calculated positions. For compounds **1b**, **1e** and **1f** full crystallographic data were submitted as CIF files with the Cambridge Crystallographic Data Center, CCDC Nos. 881205 for **1b**, 866640 for **1e**, 881204 for **1f**, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: www:http://www.ccdc.cam.ac.uk).

Physical measurements

Thermogravimetric analysis (TGA) of the molecules and differential scanning calorimetry (DSC) were conducted on NETZSCH STA 409 PC/PG ((heating rate of $10^\circ\text{C min}^{-1}$). Optical absorption spectra were obtained by using a HP-8453 UV/vis/near-IR Spectrophotometer (Agilent). Photoluminescence spectra were carried out on a LS-55 spectrofluorometer (Perkine-Elmer). The electrochemical experiments were carried out using a CHI 660C electrochemistry workstation (CHI USA). A standard one-compartment three-electrode cell was used with a Pt electrode as the working electrode, a Pt wire as the counter electrode and a Ag/Ag $^+$ electrode (Ag in 0.1M AgNO $_3$ solution, from CHI, Inc.) as the reference electrode. TBAP (0.1 M) was used as the supporting electrolyte. The

scan rate was 100 mV s⁻¹.

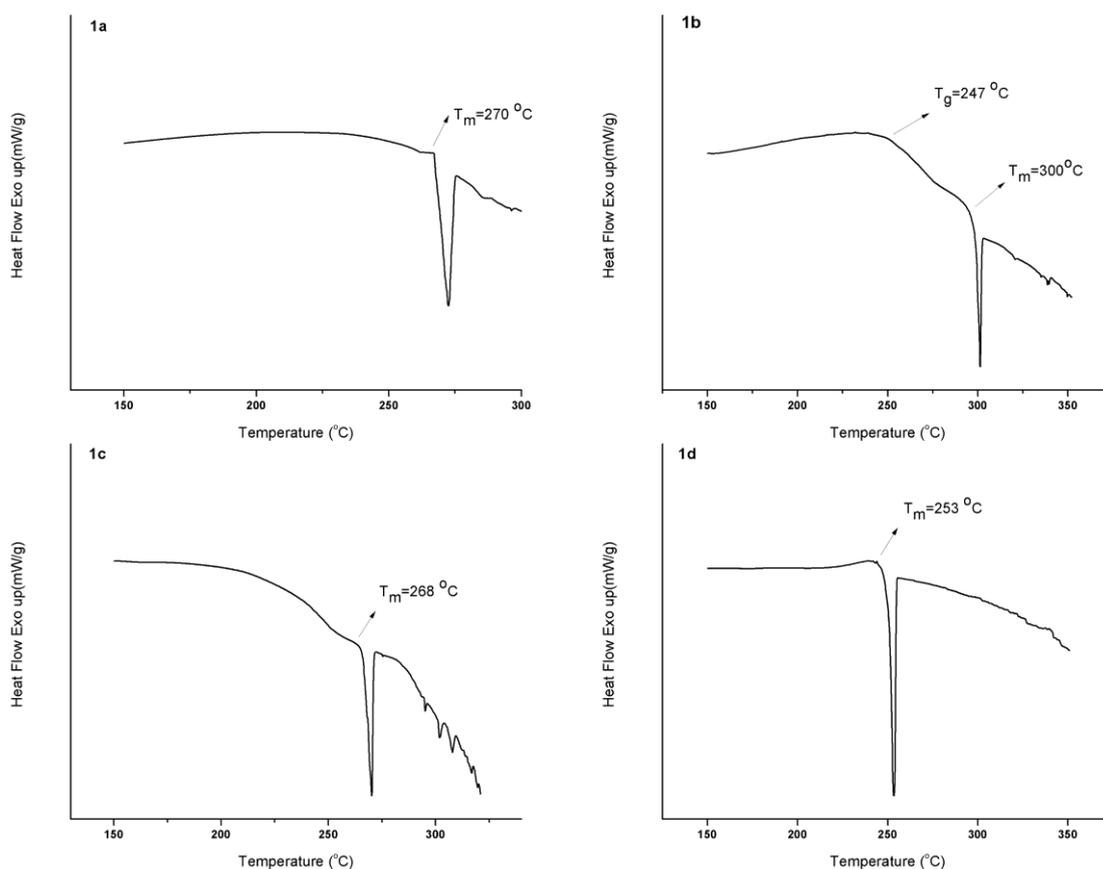
Measurements of fluorescence quantum yields

The fluorescence quantum yields (Φ_u) of compounds **1a-1h** were determined in chromatographic grade solvents. The optical density of the dilute solution of all compounds (the reference and compounds **1a-1h**) was less than 0.06 at the excitation wavelength, using 9,10-diphenylanthracene ($\Phi_s = 0.9 \pm 0.02$ in cyclohexane) as a reference at excitation wavelengths of 320/365 nm. The quantum yield is calculated using equation. ¹

$$\Phi_u = \Phi_s \left(\frac{A_s F_u / A_u F_s}{\eta_u / \eta_s} \right)^2 \quad (1)$$

Where: the u subscript refers to the unknown and s to the standard and other symbols have the following meanings: Φ is quantum yield, A is absorbance at the excitation wavelength, F the integrated emission area across the band η is the refractive index of the solvent.

Calculation methods and results. To understand electronic structures of 4,8-substituted 1,5-naphthyridine compounds **1a-1h**, the ground-state geometry of the molecules were first optimized at AM1 level and then their frontier molecular orbitals were calculated at the B3LYP/6-31G* level of theory with Gaussian 09.



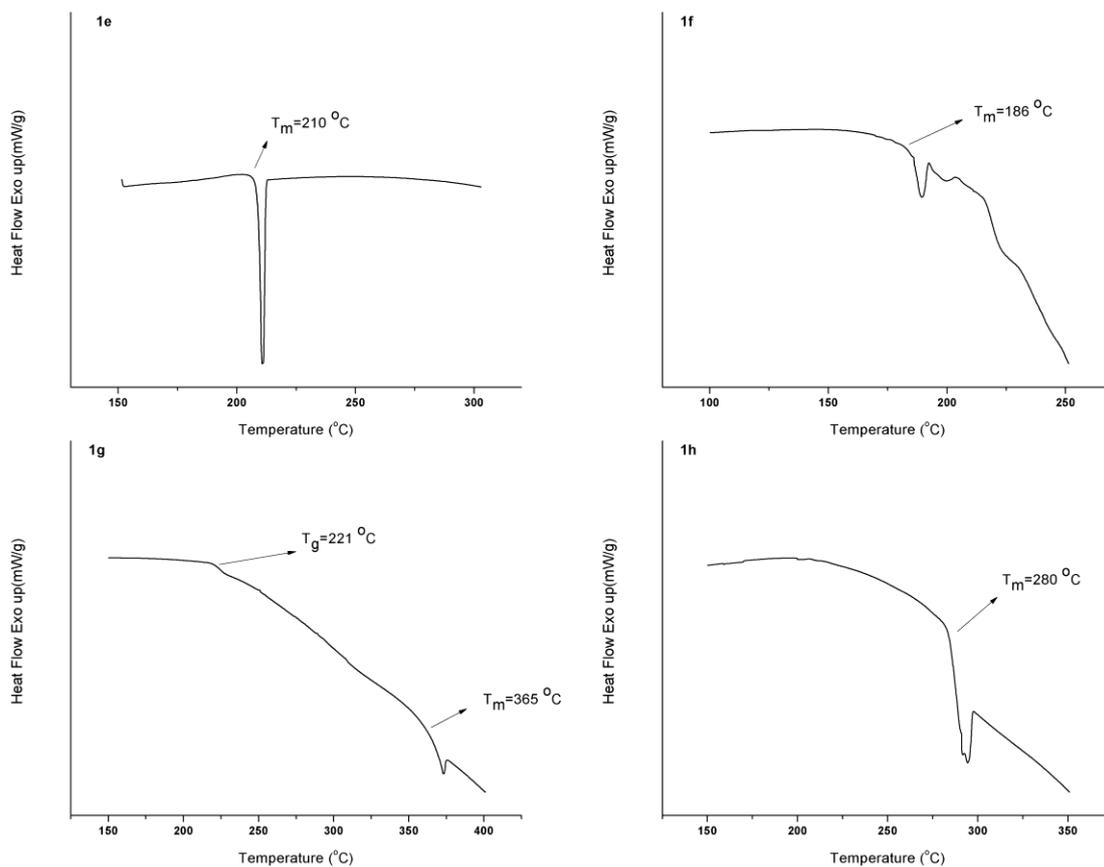
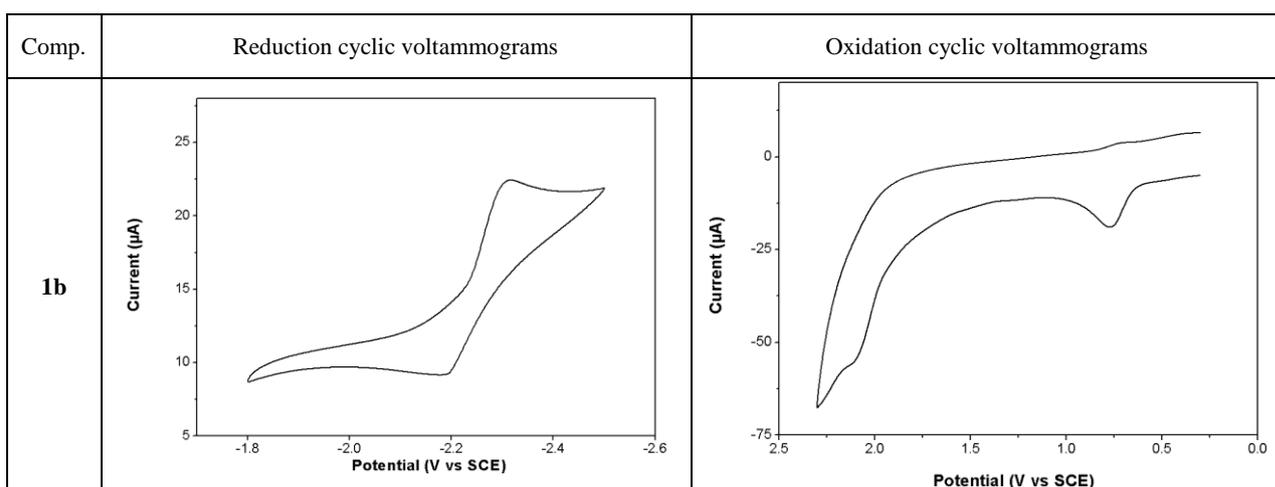
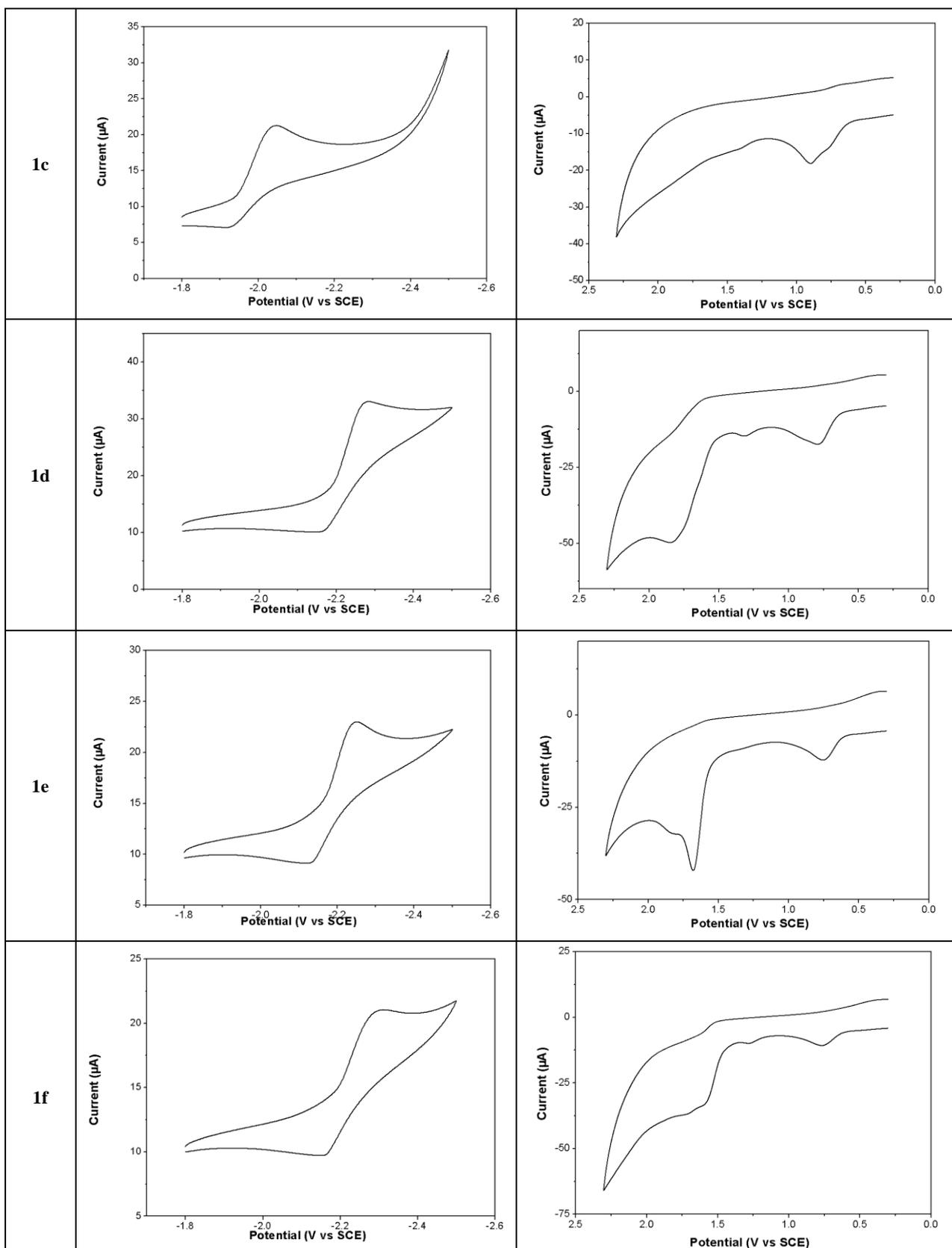


Figure S1. DSC thermograms of **1a-1h** under a nitrogen atmosphere at a heating rate of 10 °C min⁻¹.

Table S1. Reduction cyclic voltammograms and Oxidation cyclic voltammograms of compounds **1b-1g** (10⁻⁴ mol·L⁻¹) in CH₂Cl₂/acetonitrile (7:3 v/v), TBAP (0.1 M), Scan rate= 100 mV/s.





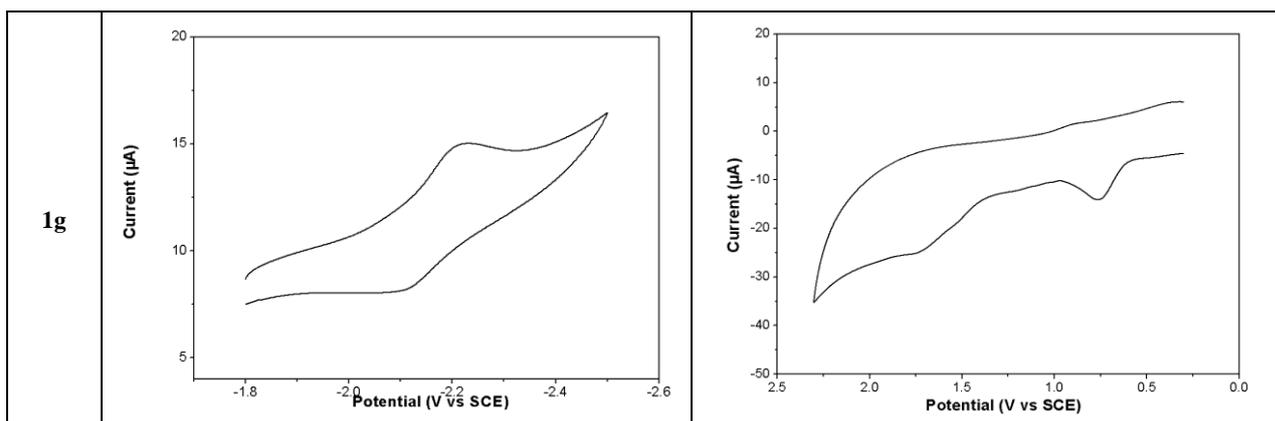
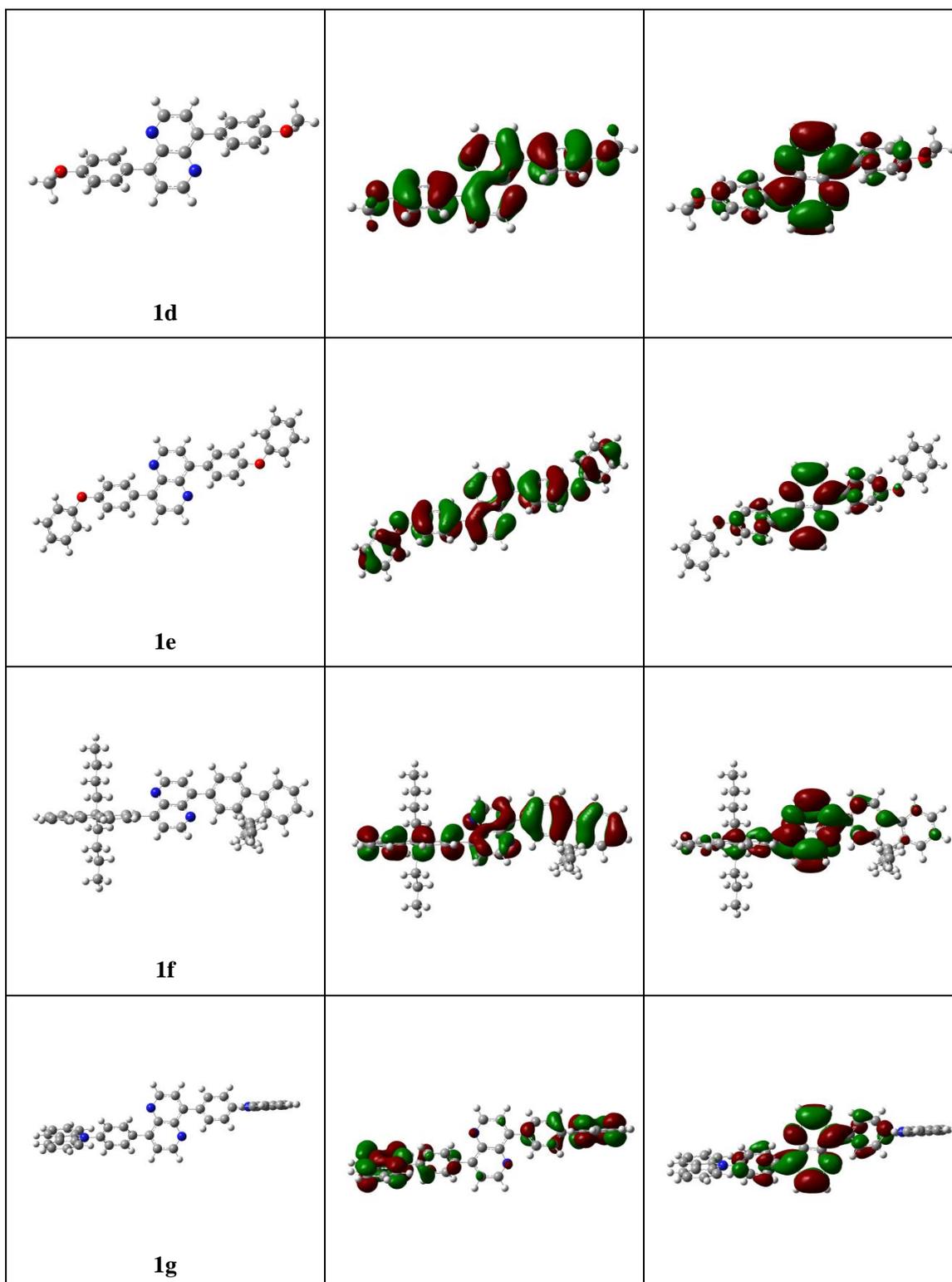
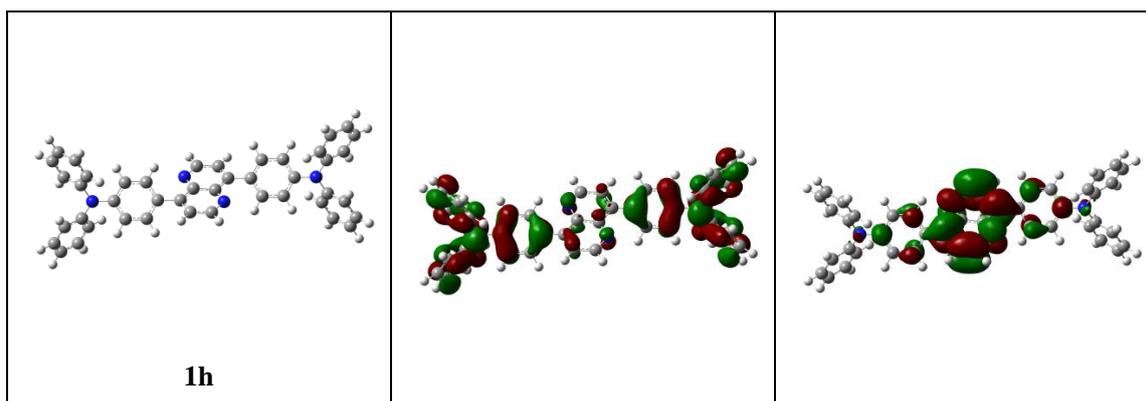


Table S2. Frontier molecular orbital plots of optimized structures of compounds **1a-1h**.

Optimised Structure	HOMO	LUMO
 1a		
 1b		
 1c		





II. Absorption spectra and emission spectra of 4,8-substituted 1,5-naphthyridines 1a-1h recorded in different solvents

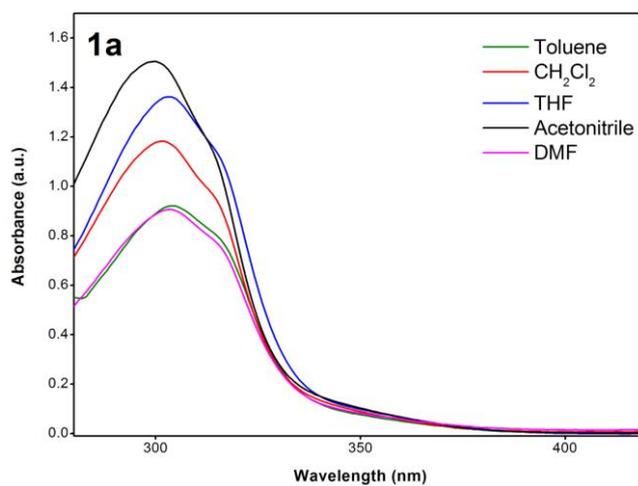


Figure S2. Absorption spectra of **1a** recorded in different solvents.

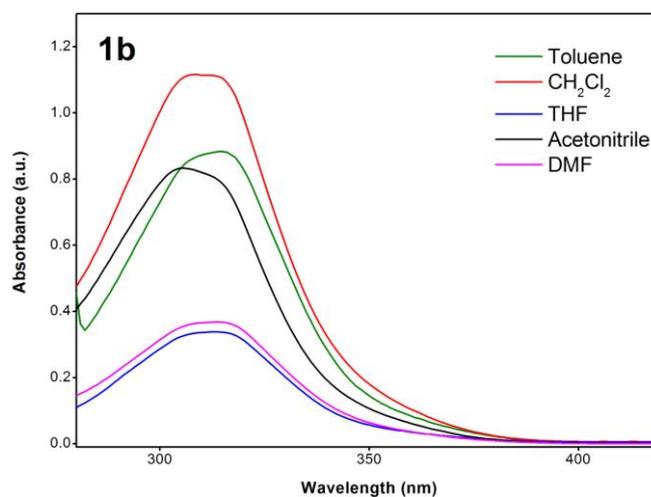


Figure S3. Absorption spectra of **1b** recorded in different solvents.

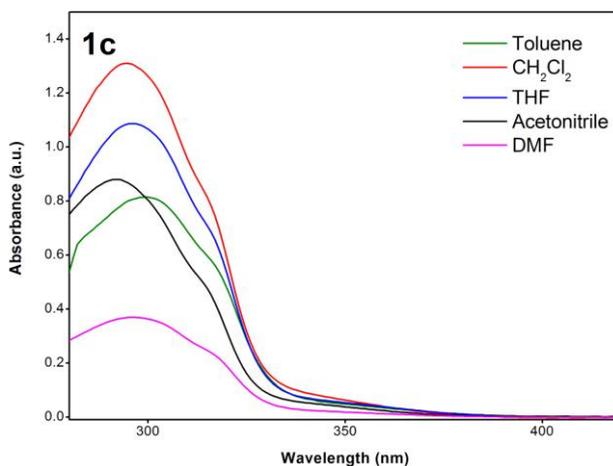


Figure S4. Absorption spectra of **1c** recorded in different solvents.

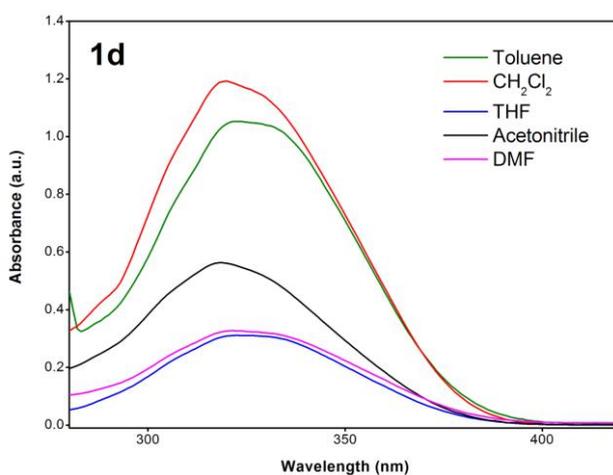


Figure S5. Absorption spectra of **1d** recorded in different solvents.

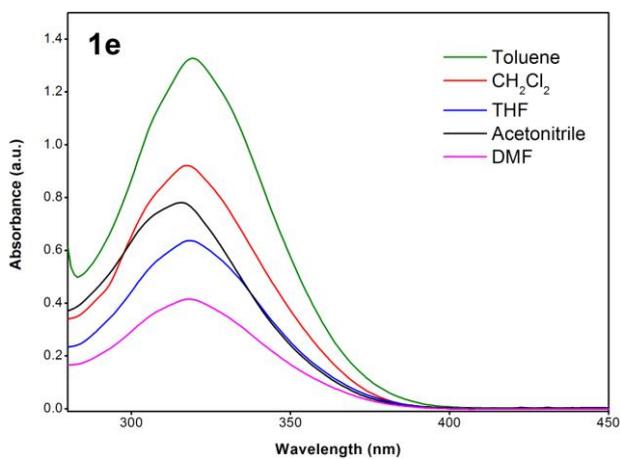


Figure S6. Absorption spectra of **1e** recorded in different solvents.

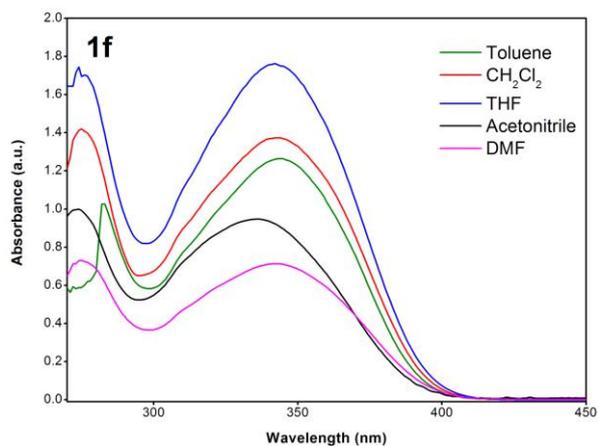


Figure S7. Absorption spectra of **1f** recorded in different solvents.

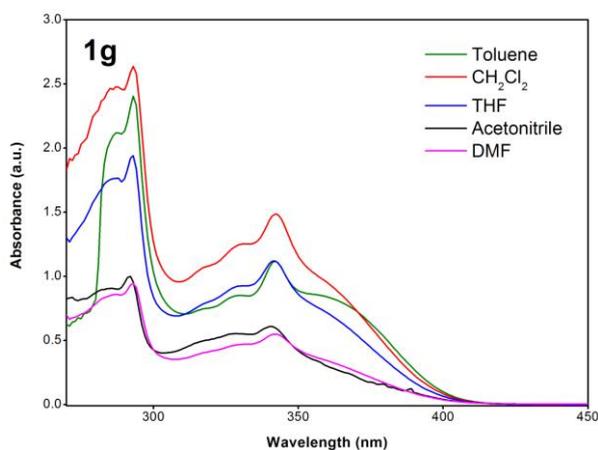


Figure S8. Absorption spectra of **1g** recorded in different solvents.

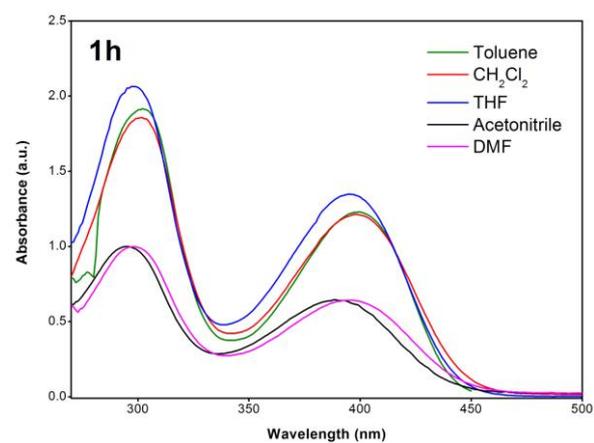


Figure S9. Absorption spectra of **1h** recorded in different solvents.

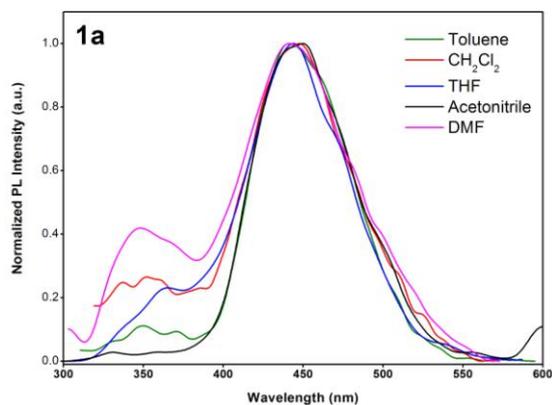


Figure S10. Emission spectra of **1a** recorded in different solvents.

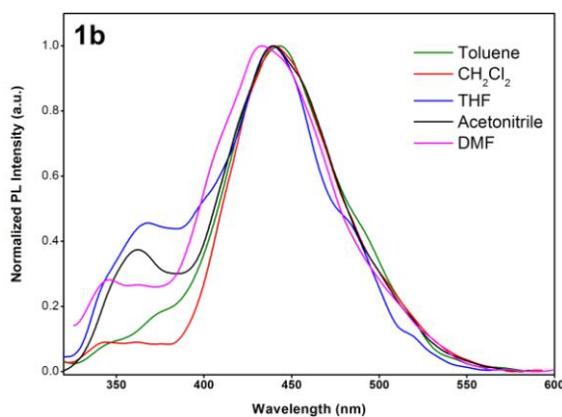


Figure S11. Emission spectra of **1b** recorded in different solvents.

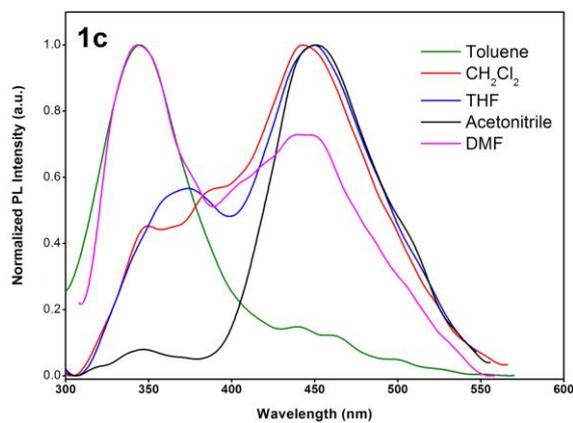


Figure S12. Emission spectra of **1c** recorded in different solvents.

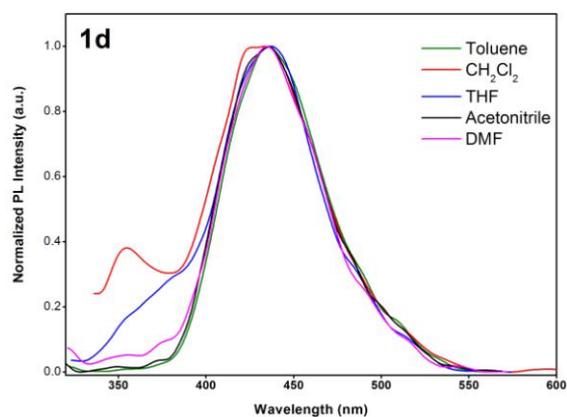


Figure S13. Emission spectra of **1d** recorded in different solvents.

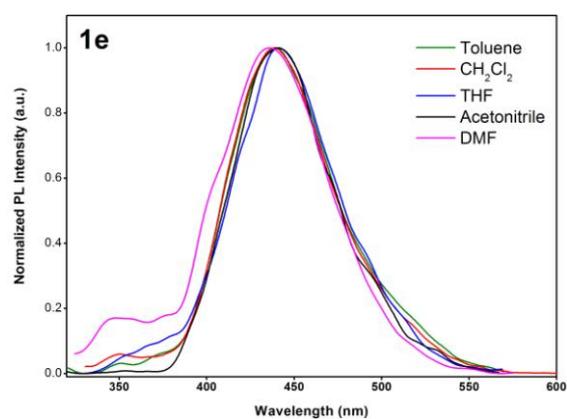


Figure S14. Emission spectra of **1e** recorded in different solvents.

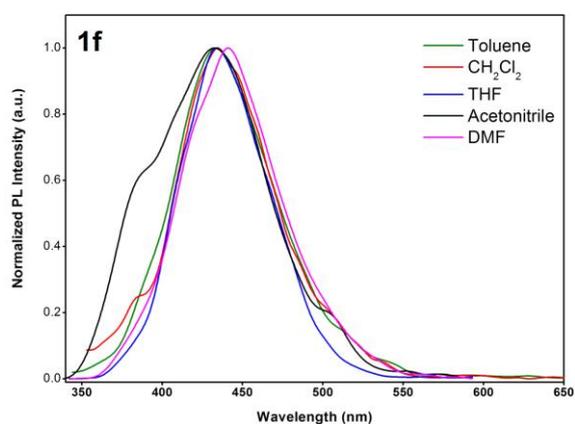


Figure S15. Emission spectra of **1f** recorded in different solvents.

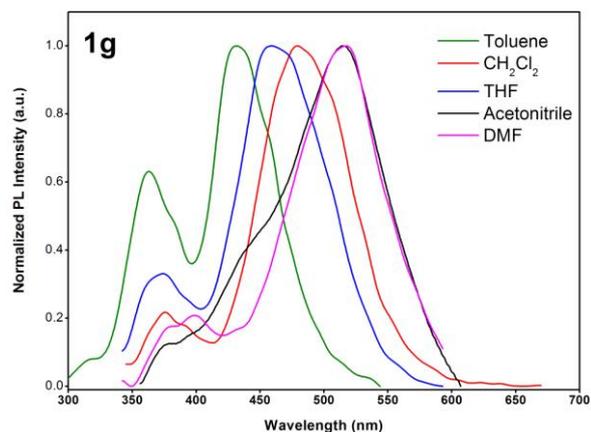


Figure S16. Emission spectra of **1g** recorded in different solvents.

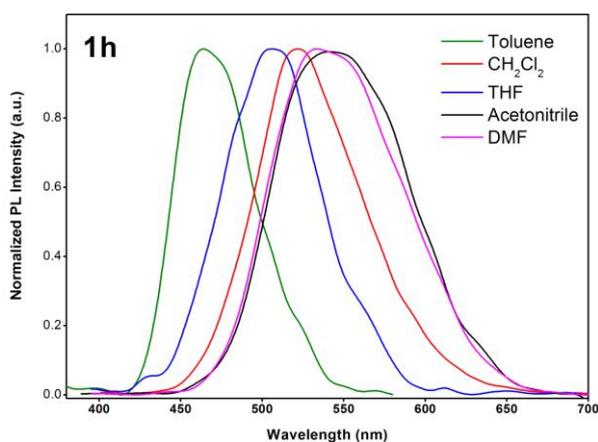


Figure S17. Emission spectra of **1h** recorded in different solvents.

III. Experimental details for synthesis of intermediates

Synthesis of 1,5-naphthyridine-4,8(1H,5H)-dione (5). Compound **5** was synthesized according to the method described in the literature.^[2] Yield was 92.3% as gray solid; m.p.>300°C. ¹H-NMR(CDCl₃+TFA, 300MHz): δ (ppm) =9.17 (s 1H), 8.46 (d 1H *J*=5.31Hz), 7.38 (d 1H *J*=5.29Hz).

General procedure for synthesis of compound 2a-2e

The slution of aryl magnesium bromide (0.3 mole) in THF (200 ml) was added into the solution of trimethylborate (46.8g, 0.45 mole) in THF (200 mL) slowly at -20~-30 °C. After addition the mixture was stired at -20~-30 °C for 3h and stired at 0 °C overnight. added 10% H₂SO₄ (190 mL) at 0 °C and stired at 10 °C for 10h. The ending mixture was extracted with diethyl ether (350 mL*3). Evaporation of the dried (Na₂SO₄) diethyl ether extract gave

gray solid which could be filtered and dried in vacuo. The solid washed with hot hexane, got white solid aryl boronic acid.

Phenylboronic acid (2a). Yield was 82.4% as white solid; m.p. 214-218 °C (lit.^[3]: 216-219 °C). ¹H-NMR(CDCl₃, 400MHz): δ (ppm)=8.24 (d 2H *J*=6.80 Hz), 7.59 (dd 1H *J*_{ab}=7.32 Hz and *J*_{bc}=7.36 Hz), 7.51 (dd 2H *J*_{ab}=7.48 Hz and *J*_{bc}=7.48 Hz).

(4-(tert-butyl)phenyl)boronic acid (2b). Yield was 72.8% as white solid; m.p. 158-160 °C (lit.^[3]: 160 °C). ¹H-NMR(CDCl₃, 500MHz): δ (ppm)=8.17 (d 2H *J*=6.65 Hz), 7.54 (d 2H *J*=6.65 Hz), 1.38 (s, 9H).

(4-(trifluoromethyl)phenyl)boronic acid (2c). Yield was 83.5% as white solid. ¹H-NMR (DMSO-*d*₆, 400 MHz): δ (ppm)= 8.31 (s, 2H), 8.00 (d 2H *J* = 8.1 Hz), 7.68 (d 2H *J* = 8.1 Hz).

(4-methoxyphenyl)boronic acid (2d) Yield was 59.5% as white solid; m.p. 158-163 °C (lit.^[4]: 159-164 °C). ¹H-NMR(CDCl₃, 400MHz): δ (ppm)= 8.17 (d 2H *J*=8.40 Hz), 7.02 (d 2H *J*=8.40 Hz), 3.89 (s, 3H).

(4-phenoxyphenyl)boronic acid (2e). Yield was 93.3% as white solid. ¹H-NMR(DMSO-*d*₆, 500MHz): δ (ppm)= 7.94 (s, 2H), 7.79 (d 2H *J*=8.60 Hz), 7.40 (dd 2H *J*_{ab}=7.40 Hz and *J*_{bc}=7.45 Hz), 7.16 (dd 1H *J*_{ab}=6.35 Hz and *J*_{bc}=7.40 Hz), 7.03 (d 2H *J*=7.40 Hz), 6.93 (d 2H *J*=8.60 Hz).

General procedure for synthesis of compound 2f-2h

n-BuLi(55mmol) was added slowly into a three-necked flask, protected by Ar and cooled by dry-ice (-78 °C), containing 50 mmol of Ar-Br (**3f-3h**) and 50 ml of tetrahydrofuran (THF). The reaction was kept at -78°C for 3 h. 100 mmol of B(OCH₃)₃ were added rapidly to the flask and the reaction continued for 2 h. As the temperature was raised to 0 °C, 50 ml of 2 N HCl was added to the flask and the reaction continued for another 3 h. Ether was used to extract the product and was rotated to dryness after dried with anhydrous sodium sulphate. Then the crude product was purified by column chromatography (silica gel, hexane/ethyl acetate) to give the desired product.

(9,9-dibutyl-9H-fluoren-2-yl)boronic acid (2f). Yield was 90.7% as white solid. ¹H-NMR (500 MHz, DMSO-*d*₆): δ (ppm)= 7.79 (s 2H), 7.83 (s 1H), 7.74-7.80 (m, 3H), 7.42-7.44 (m 1H), 7.31-7.33 (m 2H), 1.95-1.98 (m 4H CH₂), 0.98-1.04 (m 4H CH₂), 0.61 (t 6H CH₃), 0.46-0.50 ppm (m, 4H; CH₂).

(4-(9H-carbazol-9-yl)phenyl)boronic acid (2g). Yield was 88.4% as white solid. ¹H-NMR (500 MHz, DMSO-*d*₆): δ (ppm)= 8.25 (d 2H *J*=7.75 Hz), 8.20 (s 1H), 8.09 (d 2H *J*=7.75 Hz), 7.59 (d 2H *J*=7.80 Hz), 7.41–7.46 (m 2H), 7.30 (m 1H).

(4-(diphenylamino)phenyl)boronic acid (2h). Yield was 72.8% as white solid; m.p. 226-228°C (lit. ^[5] 228-229°C). ¹H-NMR (300 MHz, DMSO-*d*₆): δ (ppm)= 7.85(s 1H), 7.68(d 1H *J*=8.52 Hz), 7.31 (dd 2H *J*_{ab}=7.50 Hz and *J*_{bc}=8.22 Hz), 7.00–7.08 (m 3H), 6.89 (d 1H *J*=8.49 Hz).

IV. Characterization Data of New Compounds

Synthesis of 4,8-dibromo-1,5-naphthyridine (4). POBr₃ (14.3 g) was dissolved into Acetonitrile (50 mL) and heated to 80 °C for 1 h. The compound **5** (1.62 g) was ground to a powder and added into flask in many portion. After addition react for 5 h at 170 °C and cool it to r.t. The orange mixture was carefully decomposed with ice (100 g) and then neutralized with concentrated ammonia to pH= 8. The resulting gray mixture was extracted with DCM (100 mL* 3) and the extract was evaporated on vacuum and then recrystallized with benzene (80 mL) at -5 °C. Yield was 79.3% as white little crystal. ¹H NMR (CDCl₃, 500 MHz): δ (ppm)=8.84(d 1H *J*=4.60Hz), 8.05(d 1H *J*=4.60Hz); ¹³C NMR (CDCl₃, 125 MHz): δ (ppm)=151.12, 142.64, 136.67, 129.19; TOF-MS (ES+) calcd for C₈H₄Br₂N₂ ([M+1]⁺): 286.87, found 286.8; Elemental analysis calcd (%) for C₈H₄Br₂N₂: C 33.37, H 1.40, N 9.73; found C 33.32, H 1.44, N 9.71; IR (KBr): ν(tilde) (cm⁻¹) =3853.2, 3750.6, 3648.9, 3060.1, 3018.0, 1489.1, 1465.3, 1375.2, 1263.9, 1178.7, 1022.7, 865.4, 710.4, 595.9, 499.3

General procedure for synthesis of **1a-1h**

Pd(OAc)₂ (33 mg, 0.15 mmol) and K₂CO₃ (1.66 g, 12.0 mmol) were added to a three-necked flask containing compound **4** (0.864 g, 3.0 mmol), compound **2a-2h** (12.0 mmol), H₂O (17.5 ml) and DMF (15 ml). The mixture was heated to 80 °C for 50 h and then cool to room temperature. The cooled mixture was extracted with dichloromethane (50 ml* 3). The extract was washed with brine, dried with anhydrous Na₂SO₄. The solvent was removed on vacuum. Products **1a-1h** was obtained by recrystallization with methanol and THF twice.

4,8-diphenyl-1,5-naphthyridine (1a). Yield was 60.2% as white solid. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) = 9.03(d 1H $J=4.35$ Hz), 7.78(d 2H $J=7.15$ Hz), 7.63(d 1H $J=4.35$ Hz), 7.54(dd 2H $J_{ab}=7.15$ Hz and $J_{bc}=8.05$ Hz), 7.49 (dd 1H $J_{ab}=7.30$ Hz and $J_{bc}=7.30$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) = 150.47, 148.70, 142.50, 137.20, 130.50, 128.64, 128.23, 124.01; TOF-MS (ES+) calcd for $\text{C}_{20}\text{H}_{14}\text{N}_2$ ([M]): 282.12, found ($[\text{M}+1]^+$) 283.1; Elemental analysis calcd (%) for $\text{C}_{20}\text{H}_{14}\text{N}_2$: C 85.08, H 5.00, N 9.92; found C 88.45, H 5.04, N 6.51; IR (KBr): $\nu(\text{tilde})$ (cm^{-1}) = 3647.9, 3061.5, 3019.6, 2359.8, 2338.6, 1579.7, 1508.0, 1484.6, 1442.61495.4, 863.0, 764.8, 610.0, 576.5.

4,8-bis(4-(tert-butyl)phenyl)-1,5-naphthyridine(1b). Yield was 72.5% as white solid. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) = 9.03(d 1H $J=4.36$ Hz), 7.76(d 2H $J=8.40$ Hz), 7.63(d 1H $J=4.36$ Hz), 7.57(d 2H $J=8.40$ Hz), 1.40 (s 9H); ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) = 151.56, 150.39, 148.50, 142.61, 134.25, 130.24, 125.33, 123.90, 34.72, 31.34; TOF-MS (ES+) calcd for $\text{C}_{28}\text{H}_{30}\text{N}_2$ ($[\text{M}+1]^+$): 395.24, found 395.2; ($[\text{M}+\text{Na}]^+$): 417.24, found 417.2; Elemental analysis calcd (%) for $\text{C}_{28}\text{H}_{30}\text{N}_2$: C 85.24, H 7.66, N 7.10; found C 85.18, H 7.71, N 7.11; IR (KBr): $\nu(\text{tilde})$ (cm^{-1}) = 3853.5, 3735.3, 3649.2, 2959.5, 2360.6, 1491.5, 1388.7, 1362.5, 1268.6, 834.6, 680.8, 586.5.

4,8-bis(4-(trifluoromethyl)phenyl)-1,5-naphthyridine (1c). Yield was 55.2% as pale solid. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm) = 9.07(1H d $J=4.30$ Hz), 7.90(d 2H $J=8.05$ Hz), 7.82(d 2H $J=8.20$ Hz), 7.67(d 1H $J=4.25$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) = 150.81, 147.41, 142.16, 140.51, 130.86, 130.64, 125.24, 125.21, 124.34; TOF-MS (ES+) calcd for $\text{C}_{22}\text{H}_{12}\text{F}_6\text{N}_2$ ($[\text{M}+1]^+$): 419.09, found 419.1; Elemental analysis calcd (%) for $\text{C}_{22}\text{H}_{12}\text{F}_6\text{N}_2$: C 63.16, H 2.89, F 27.25, N 6.70; found C 63.13, H 2.93, N 6.75; IR (KBr): $\nu(\text{tilde})$ (cm^{-1}) = 3473.6, 2361.1, 1618.8, 1568.3, 1494.2, 1410.0, 1332.9, 1304.3, 1247.3, 1198.7, 1169.2, 1106.9, 1068.9, 840.6, 831.6, 744.7, 605.9, 558.0.

4,8-bis(4-methoxyphenyl)-1,5-naphthyridine (1d). Yield was 72.7% as white crystals. ^1H NMR ($\text{DMSO}-d_6$, 500 MHz): δ (ppm) = 8.99(d 1H $J=4.35$ Hz), 7.79(d 2H $J=8.75$ Hz), 7.65(d 1H $J=4.35$ Hz), 7.10(d 2H $J=8.75$ Hz), 3.86 (s 3H O- CH_3); ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm) = 160.15, 151.21, 148.10, 142.08, 137.33, 131.09, 128.88, 128.46, 124.62; TOF-MS (ES+) calcd for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_2$ ($[\text{M}+1]^+$): 343.14, found 343.2; ($[\text{M}+\text{Na}]^+$): 465.14, found 465.1; Elemental analysis calcd (%) for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_2$: C 77.17, H 5.30, N 8.18, O 9.35; found C 77.18, H 5.28, N 8.21, O 9.33; IR (KBr): $\nu(\text{tilde})$ (cm^{-1}) = 3857.6, 3742.4, 3627.2, 2998.4, 2956.6, 2831.0, 2360.0,

2341.8, 1604.3, 1498.9, 1466.4, 1275.6, 1243.4, 1180.3, 1048.1, 1026.0, 837.7, 824.1, 559.3.

4,8-bis(4-phenoxyphenyl)-1,5-naphthyridine (1e). Yield was 75.8% as yellow crystals. m.p.209- 211 °C. ¹H NMR (CDCl₃, 500 MHz): δ (ppm)=9.04(1H d *J*=4.30 Hz), 7.79(d 2H *J*=8.60 Hz), 7.65(d 2H *J*=4.20 Hz), 7.39(dd 2H *J*_{ab}=7.65 Hz and *J*_{bc}=8.25 Hz), 7.13-7.18(m 5H); ¹³C NMR (CDCl₃, 125 MHz): δ (ppm)=158.36, 156.50,150.34, 148.06, 142.46, 132.10, 131.53, 129.86, 123.86, 123.80, 119.78, 117.97; TOF-MS (ES+) calcd for C₃₂H₂₂N₂O₂ ([M+1]⁺): 467.17, found 467.1; ([M+Na]⁺): 489.17, found 489.1;Elemental analysis calcd (%) for C₃₂H₂₂N₂O₂: C 82.38, H 4.75, N 6.00, O 6.86; found C 82.36, H 4.75, N 6.00, O 6.89; IR (KBr): nu(tilde) (cm⁻¹) =3752.7, 3647.9, 3040.3, 3009.2, 2360.6, 1586.5, 1498.5, 1228.0, 1199.2, 1161.3, 872.7, 839.6, 774.9, 697.4, 504.5, 491.3.

4,8-bis(9,9-dibutyl-9H-fluoren-2-yl)-1,5-naphthyridine (1f). Yield was 67.8% as light yellow crystals. m.p.212- 214 °C.¹H NMR (CDCl₃, 500 MHz): δ (ppm)=9.06(d 1H *J*=4.30 Hz), 7.87(m 2H), 7.78(m 2H), 7.72(d 1H *J*=4.30 Hz), 7.40-7.34(m 3H), 2.03(t 4H CH₃-CH₂- CH₂-CH₂-), 1.13 (m 4H CH₃-CH₂-), 0.83(m 4H CH₃-CH₂-CH₂-), 0.74 2.03(t 4H CH₃-); ¹³C NMR (CDCl₃, 125 MHz): δ (ppm)=151.41, 150.56, 150.35, 149.02, 142.77, 141.60, 140.61, 135.81, 129.65, 127.32, 126.85, 125.42, 123.88, 122.97, 120.02, 119.37, 55.09, 39.99, 26.16, 23.11, 13.83; TOF-MS (ES+) calcd for C₅₀H₅₄N₂ ([M+1]⁺): 683.43, found 683.4; Elemental analysis calcd (%) for C₅₀H₅₄N₂: C 87.93, H 7.97, N 4.10; found C 87.89, H 8.02, N 4.09; IR (KBr): nu(tilde) (cm⁻¹) =3853.4, 3735.3, 2957.7, 2921.1, 2856.3, 2360.3, 1740.6, 1559.1, 1506.6, 1463.9, 1398.6, 1266.0, 1098.2, 860.9,833.0, 740.9, 721.4.

4,8-bis(4-(9H-carbazol-9-yl)phenyl)-1,5-naphthyridine (1g). Yield was 69.5% as light yellow solid. ¹H NMR (CDCl₃, 500 MHz): δ (ppm)=9.18 (d 1H *J*= 4.25 Hz), 8.18 (d 2H *J*= 7.75 Hz), 8.11 (d 2H *J*= 8.25 Hz), 7.83 (d 1H *J*=4.25 Hz), 7.80 (d 2H *J*= 8.30 Hz), 7.62 (d 2H *J*= 8.20 Hz), 7.46 (q 2H *J*= 7.25 Hz), 7.33 (q 2H *J*_{ab}= 7.25 Hz and *J*_{bc}= 7.65 Hz); ¹³C NMR (CDCl₃, 125 MHz): δ (ppm)=152.47, 149.52, 140.38, 131.92, 130.13, 128.07, 127.69, 126.54, 124.33, 121.18, 120.71, 117.75, 110.97, 109.81; TOF-MS (ES+) calcd for C₄₄H₂₈N₄ ([M+1]⁺): 613.26, found 613.3; Elemental analysis calcd (%) for C₄₄H₂₈N₄: C 86.25, H 4.61, N 9.14; found C 86.28, H 4.57, N 9.15; IR (KBr): nu(tilde) (cm⁻¹) =3047.5, 1602.9, 1497.5, 1477.8, 1450.1, 1359.8, 1335.3, 1316.9, 1227.7, 1170.9, 1119.3, 828.7, 750.3, 724.5, 625.0, 563.7.

4,8-bis(4-(Diphenylamino) phenyl)-1,5-naphthyridine (1h). Yield was 41.4% as yellow solid. ^1H NMR (CDCl_3 , 500 MHz): δ (ppm)=9.02(d 1H $J=4.15$ Hz), 7.73(d 2H $J=8.35$ Hz), 7.65(d 1H $J=4.15$ Hz), 7.31(dd 4H $J_{ab}=7.60$ Hz and $J_{bc}=8.00$ Hz), 7.22-7.18(m 6H), 7.07(d 2H $J=7.30$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz): δ (ppm)=150.18, 148.37, 147.97, 147.41, 142.66, 131.54, 130.31, 129.36, 125.17, 123.46, 122.01; TOF-MS (ES+) calcd for $\text{C}_{44}\text{H}_{32}\text{N}_4$ ($[\text{M}+1]^+$): 617.26, found 617.1; Elemental analysis calcd (%) for $\text{C}_{44}\text{H}_{32}\text{N}_4$: C 85.69, H 5.23, N 9.08; found C 85.67, H 5.28, N 9.05; IR (KBr): $\nu(\text{tilde})$ (cm^{-1})=3060.1, 3035.8, 2918.2, 2849.7, 2362.9, 1589.9, 1490.9, 1393.6, 1325.5, 1282.7, 755.6, 697.2.

V. Copies of ^1H and ^{13}C NMR Spectra of New Compounds

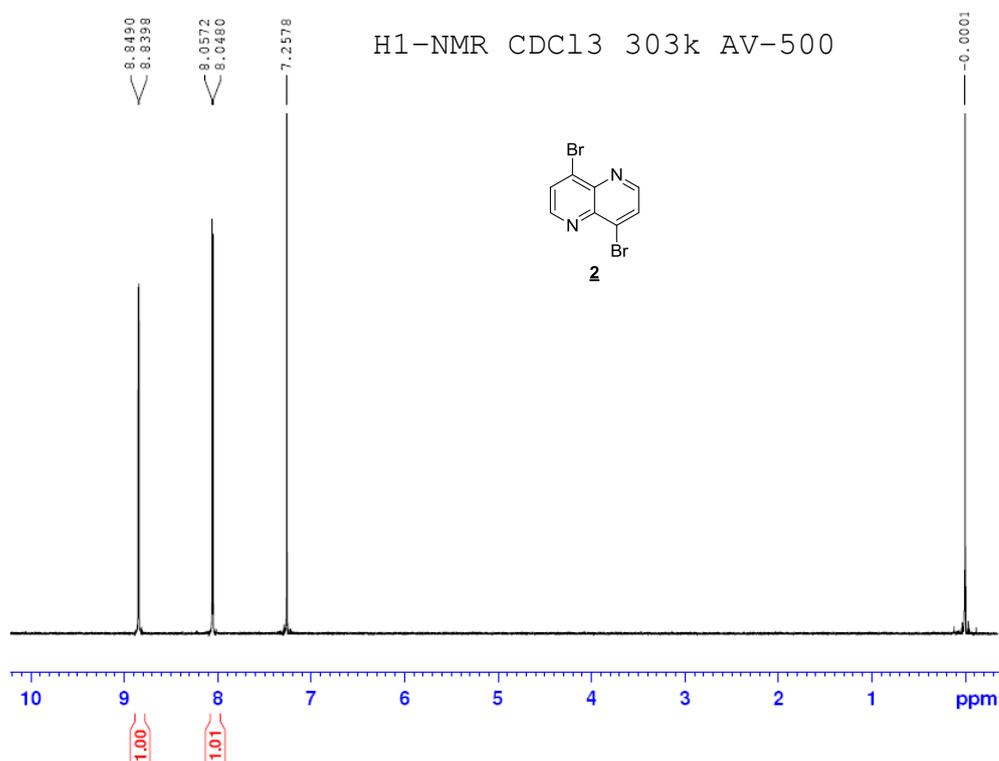


Figure S18. ^1H NMR spectrum of compound **4** in CDCl_3

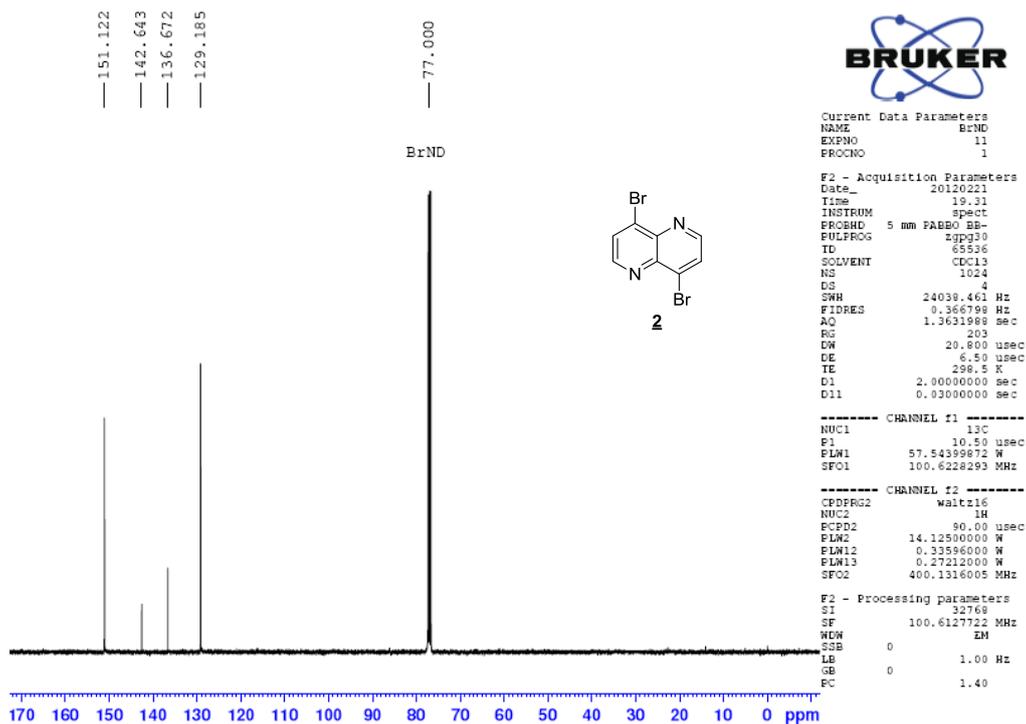


Figure S19. ^{13}C NMR spectrum of compound **4** in CDCl_3

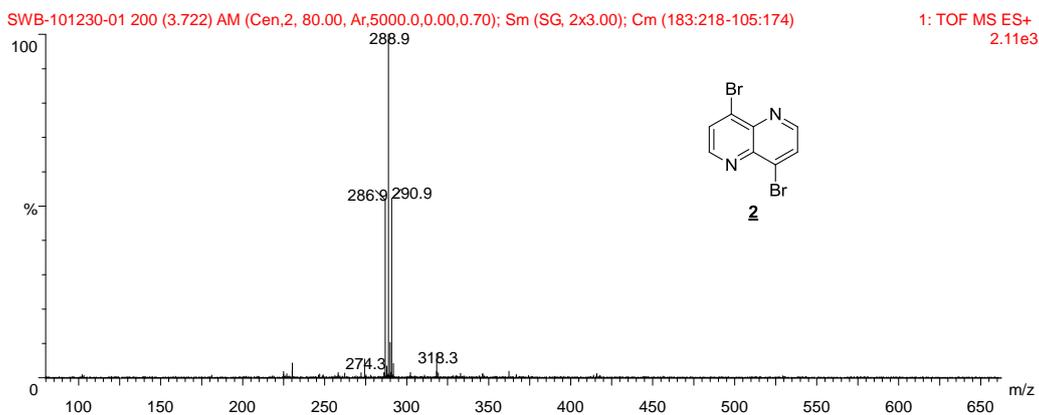


Figure S20. Mass spectrum of compound **4**

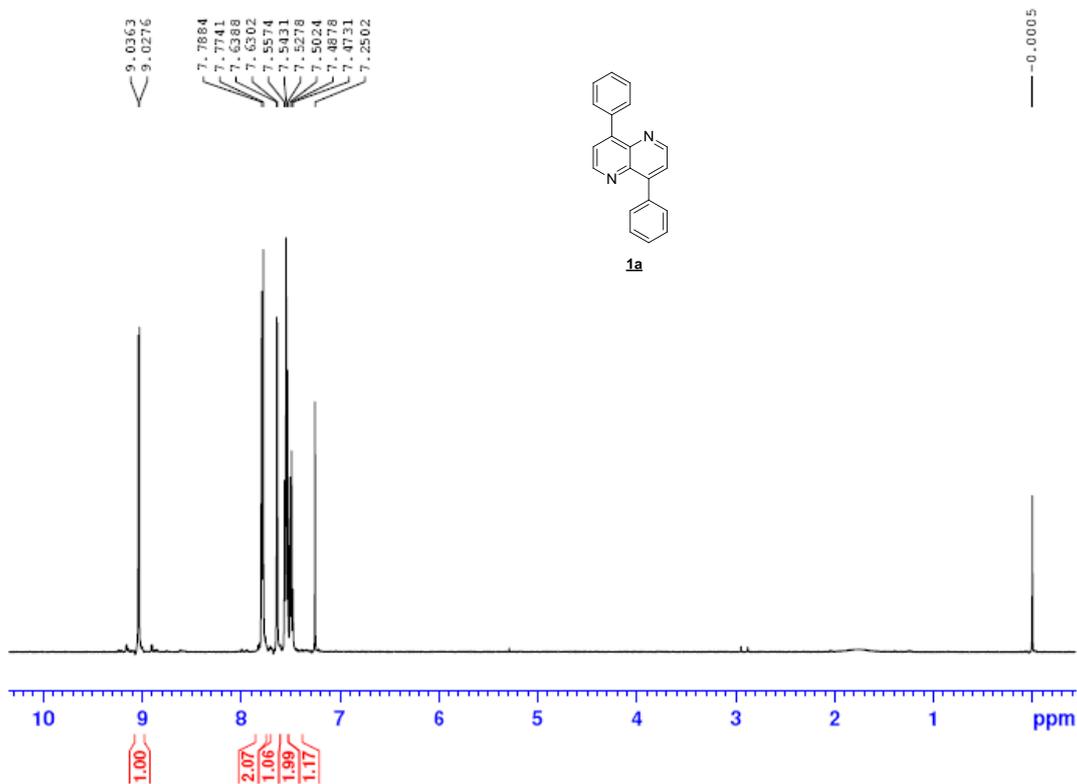


Figure S21. ¹H NMR spectrum of **1a** in CDCl₃

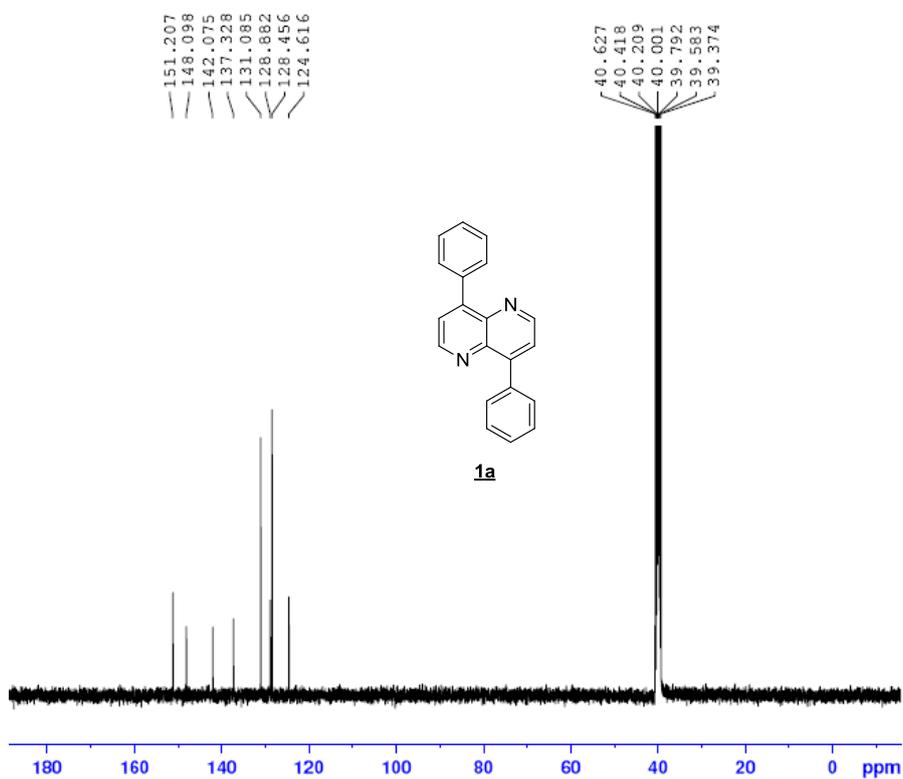


Figure S22. ¹³C NMR spectrum of **1a** in CDCl₃

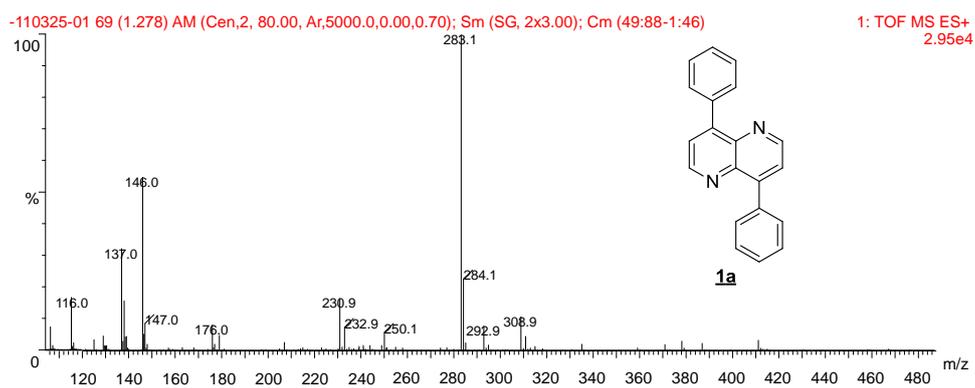


Figure S23. Mass spectrum of **1a**

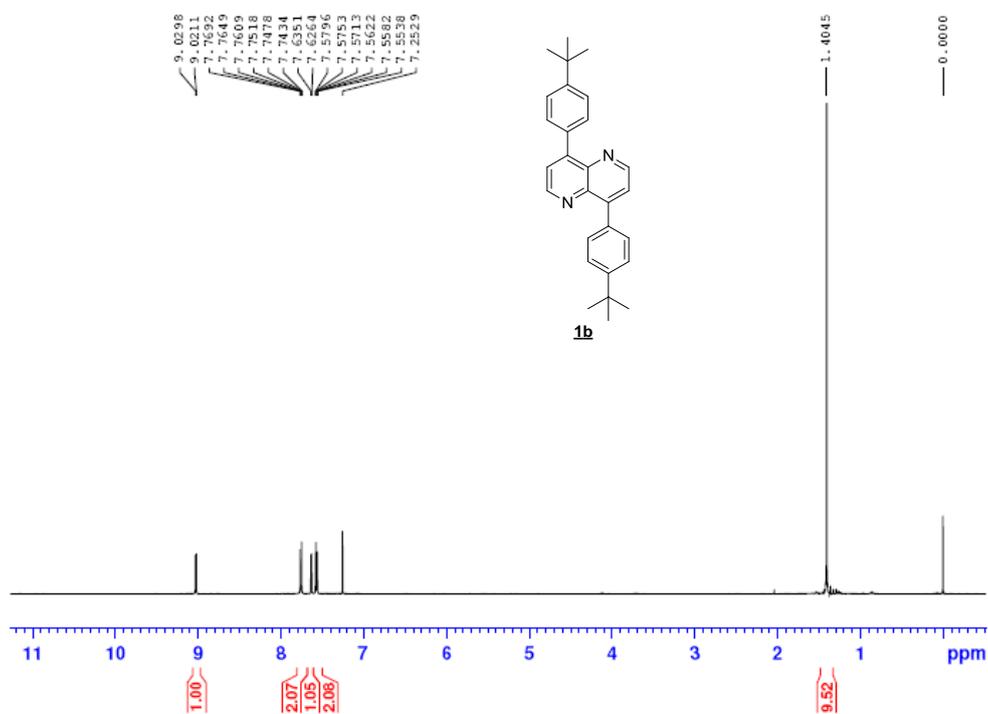


Figure S24. ^1H NMR spectrum of **1b** in CDCl_3

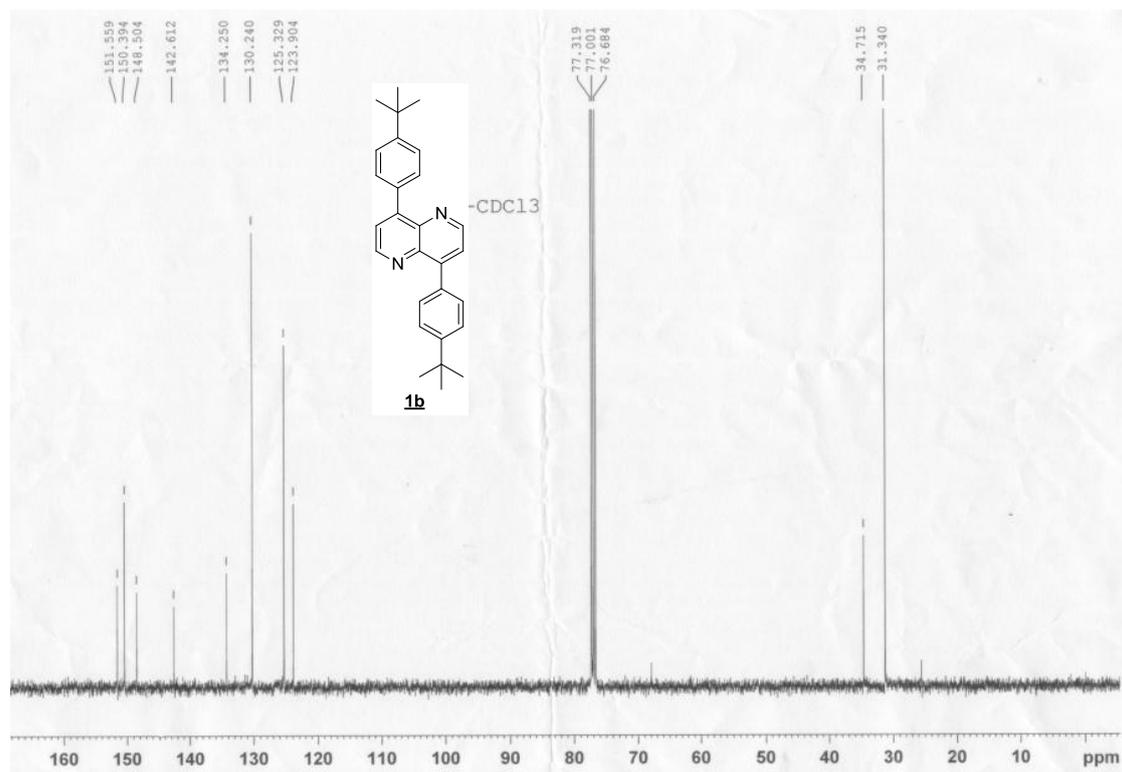


Figure S25. ¹³C NMR spectrum of **1b** in CDCl₃

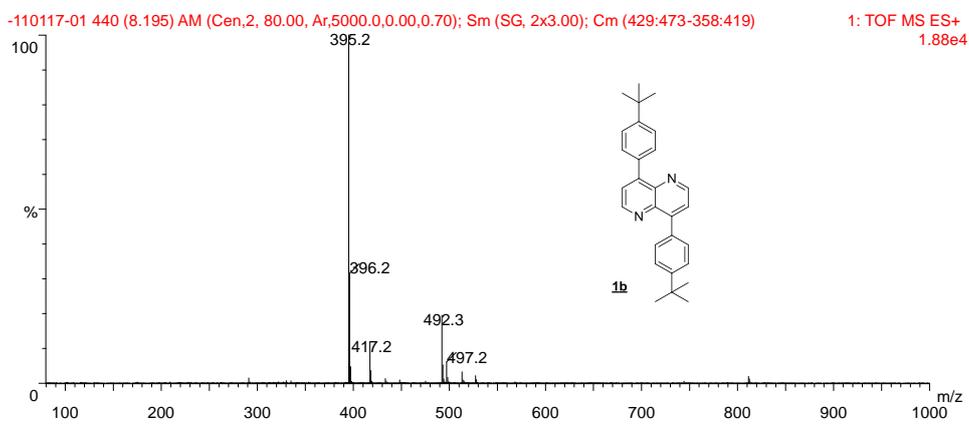


Figure S26. Mass spectrum of **1b**

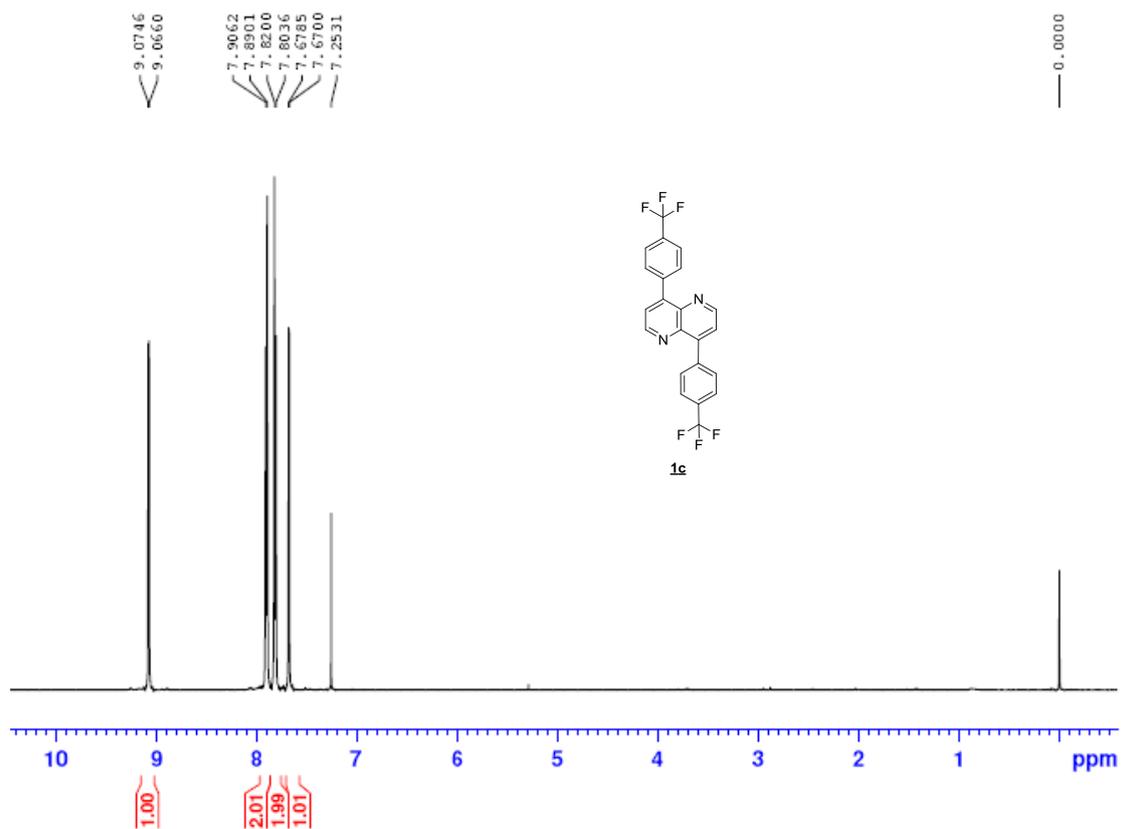
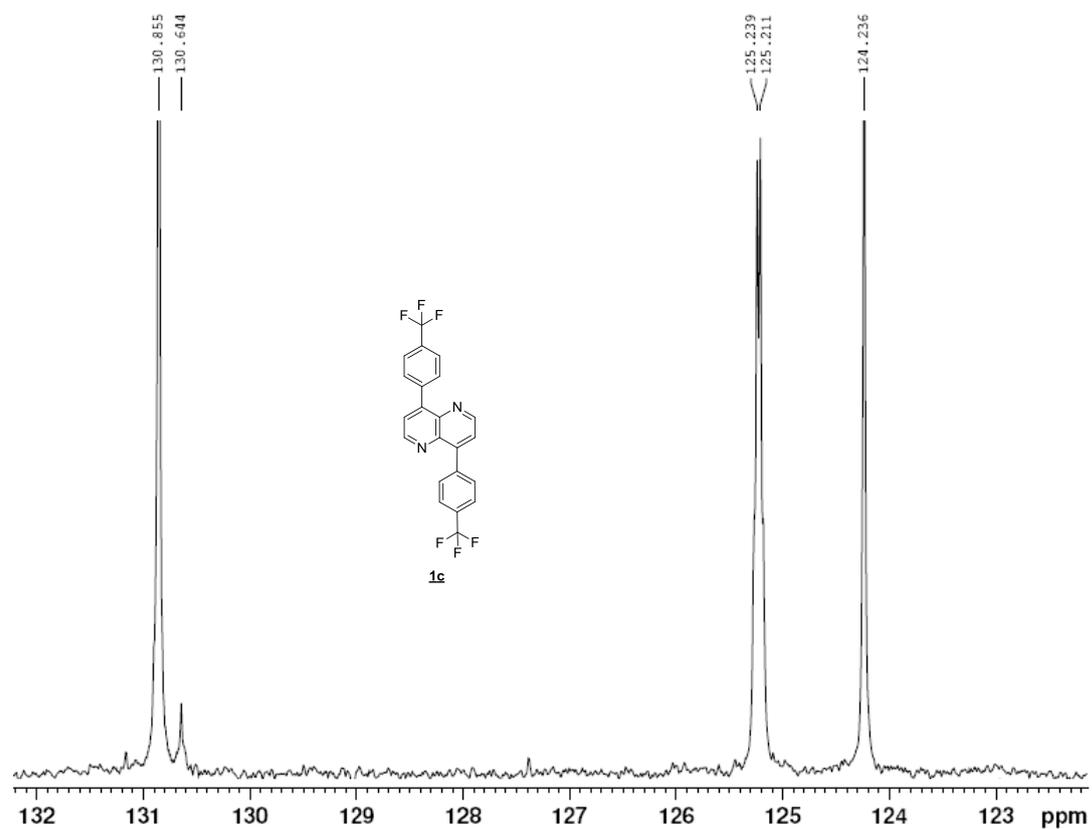


Figure S27. ¹H NMR spectrum of **1c** in CDCl₃



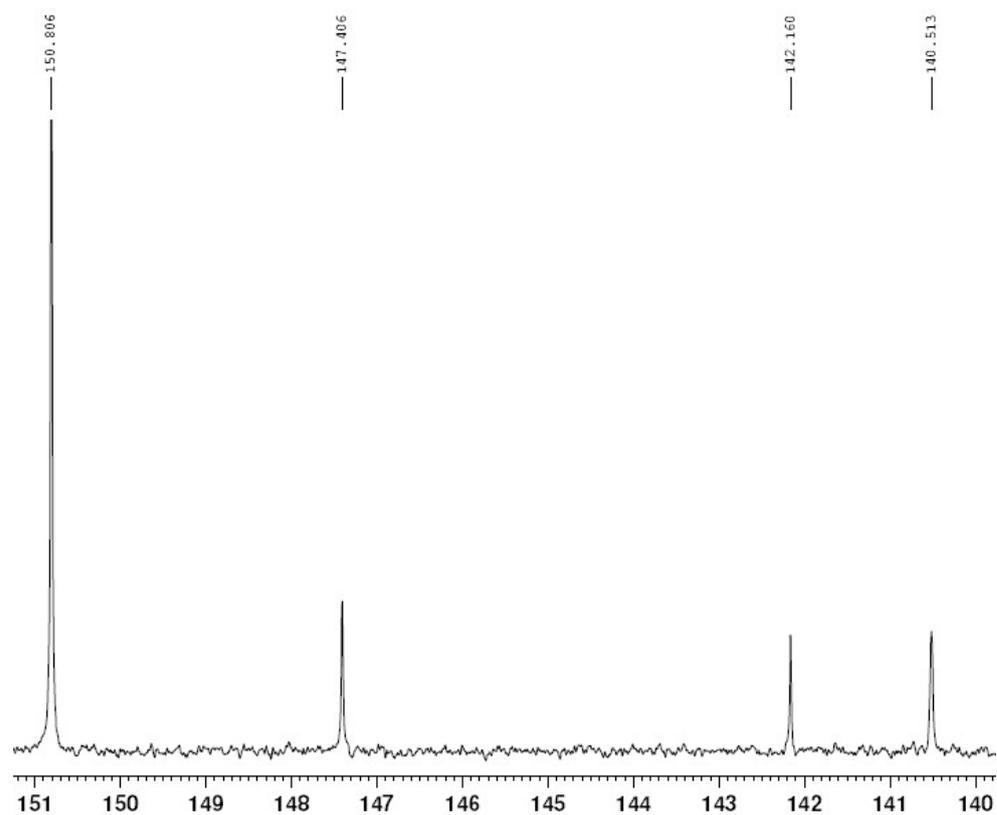


Figure S28. ^{13}C NMR spectrum of **1c** in CDCl_3

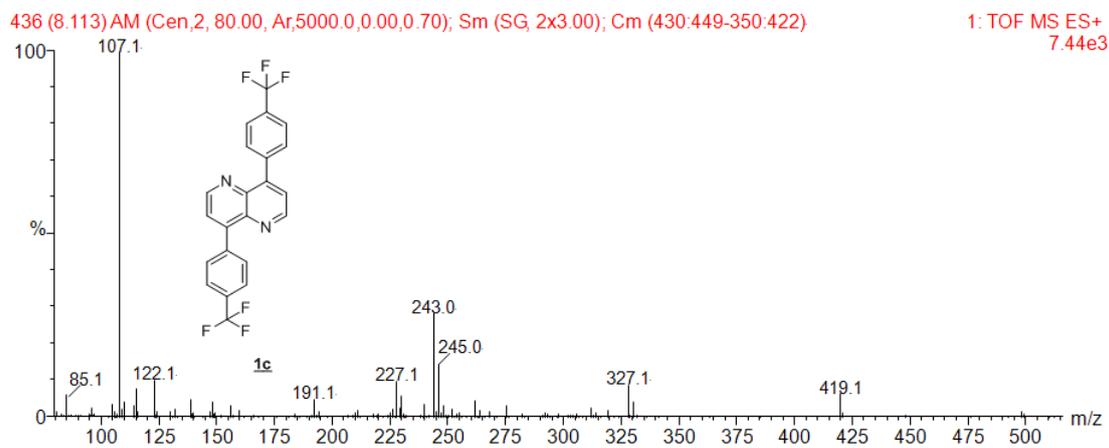


Figure S29. Mass spectrum of **1c**

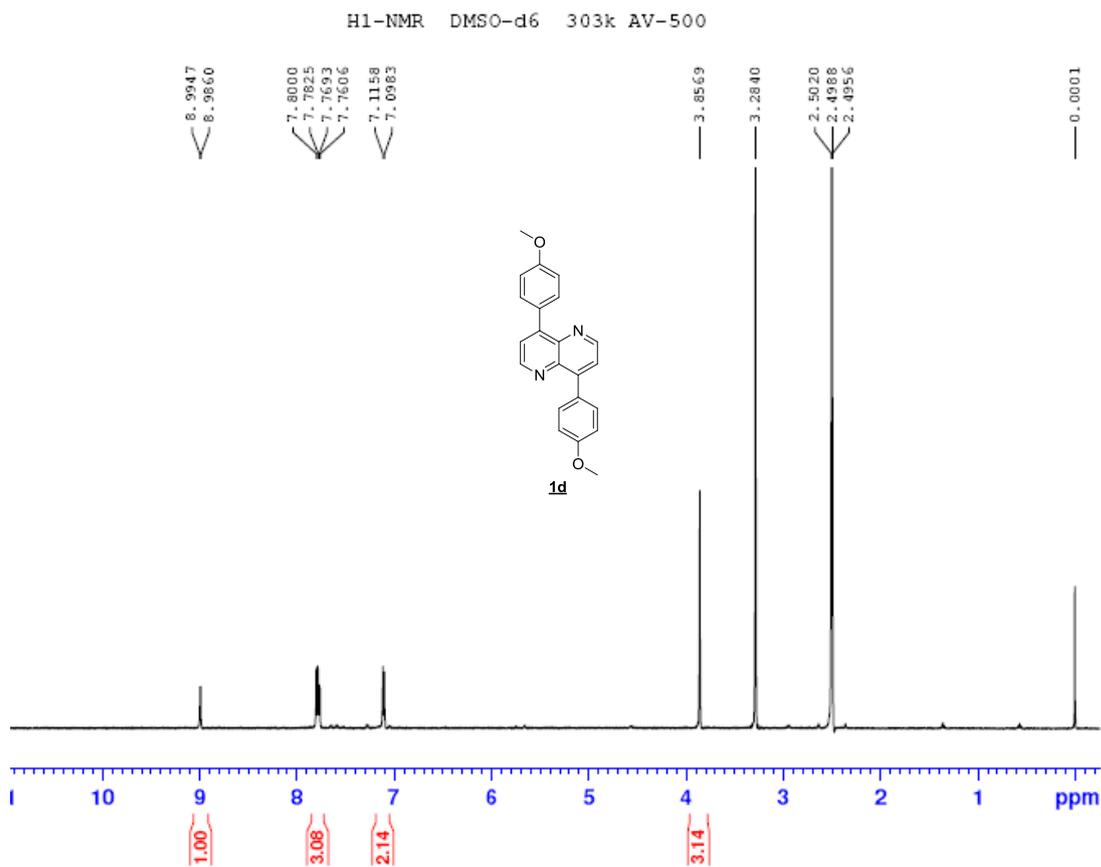


Figure S30. ^1H NMR spectrum of **1d** in CDCl_3

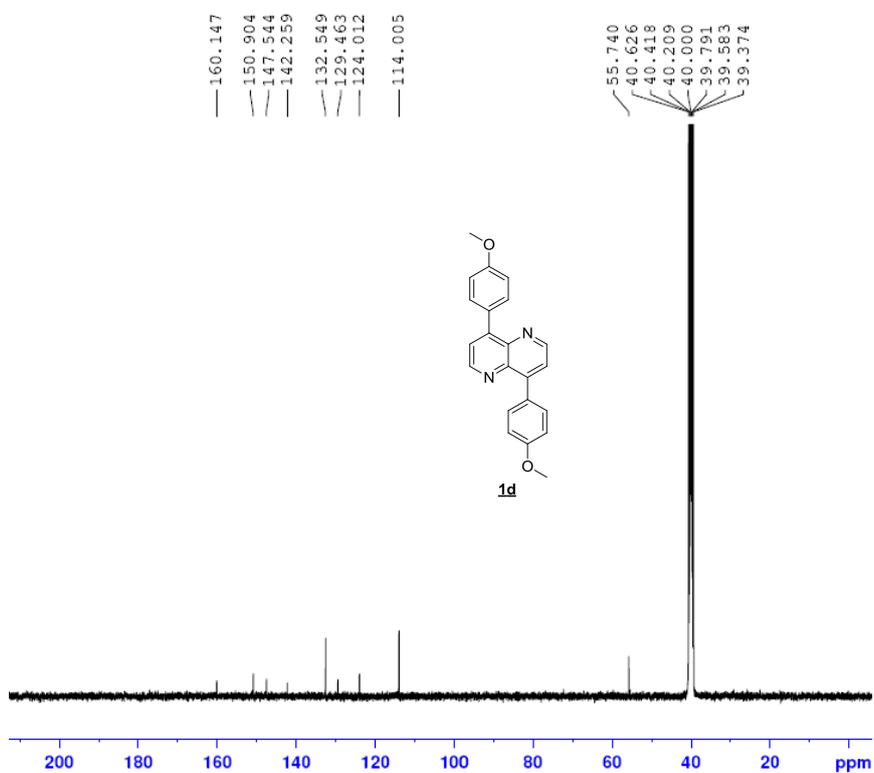


Figure S31. ^{13}C NMR spectrum of **1d** in CDCl_3

SWB-110409-03 2013 (37.469) AM (Cen,2, 80.00, Ar,5000.0,0.00,0.70); Sm (SG, 2x3.00); Cm (1976:2061-1847:1963); TOF MS ES+ 1.65e4

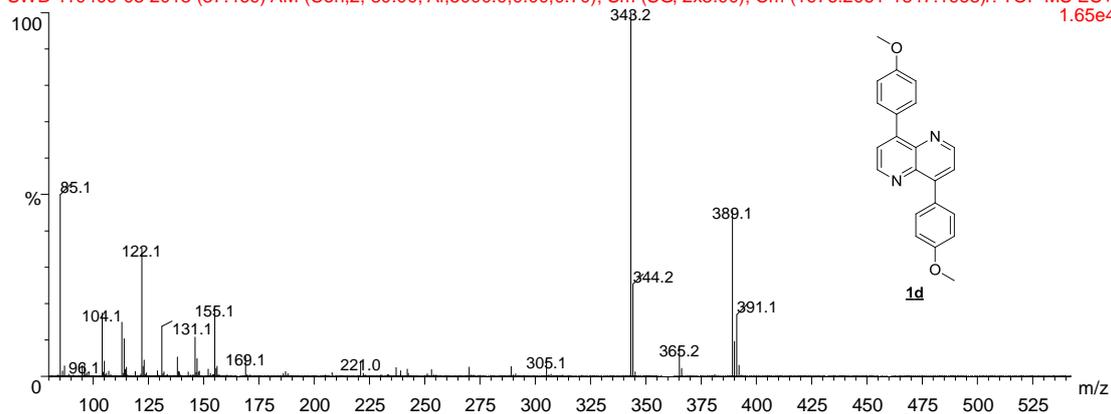


Figure S32. Mass spectrum of **1d**

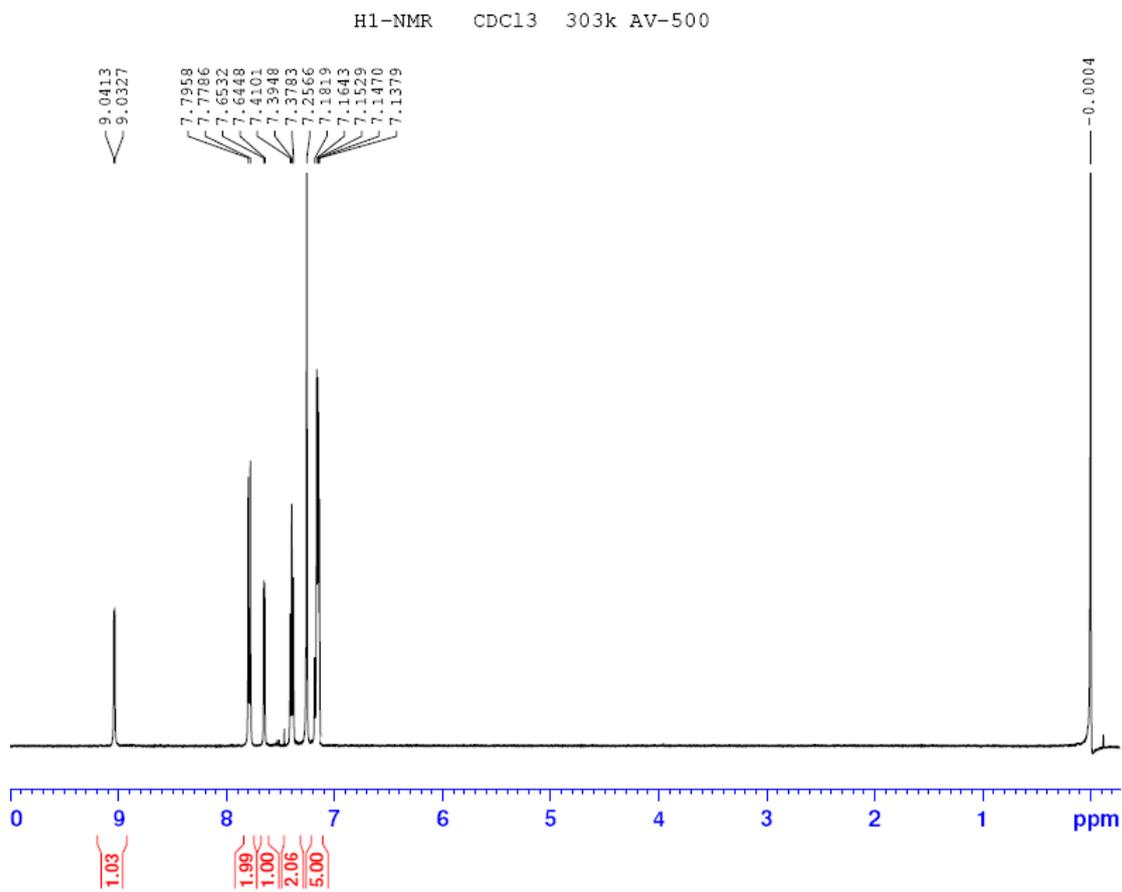


Figure S33. ¹H NMR spectrum of **1e** in CDCl₃

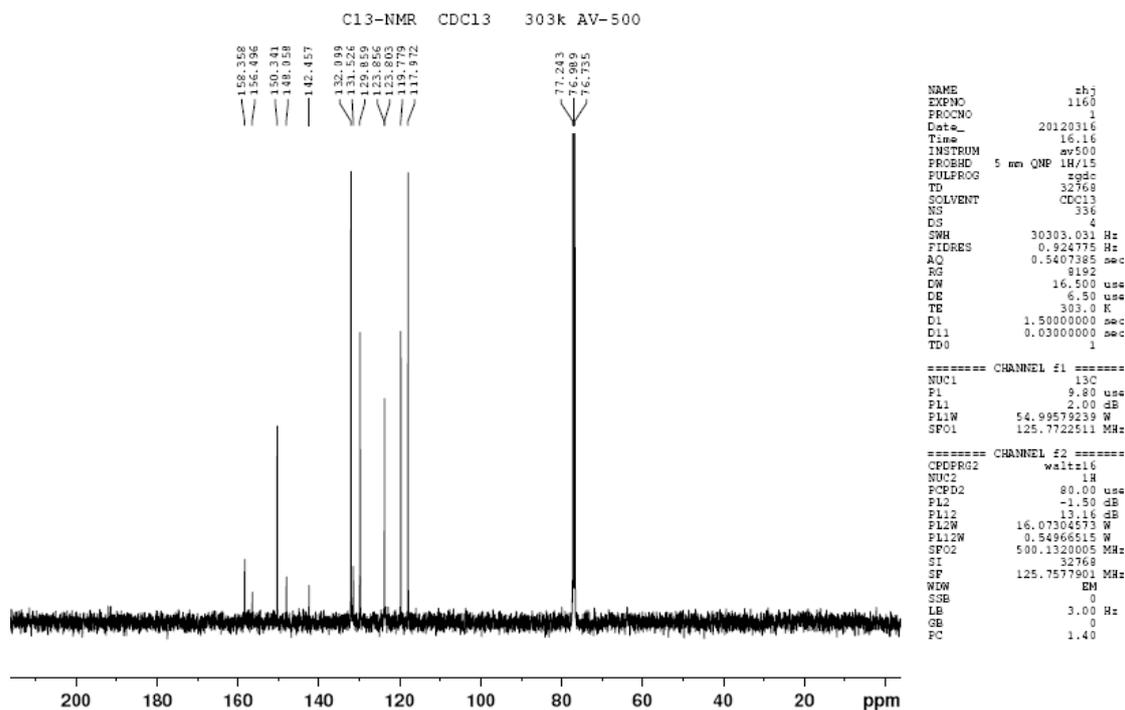


Figure S34. ¹³C NMR spectrum of **1e** in CDCl₃

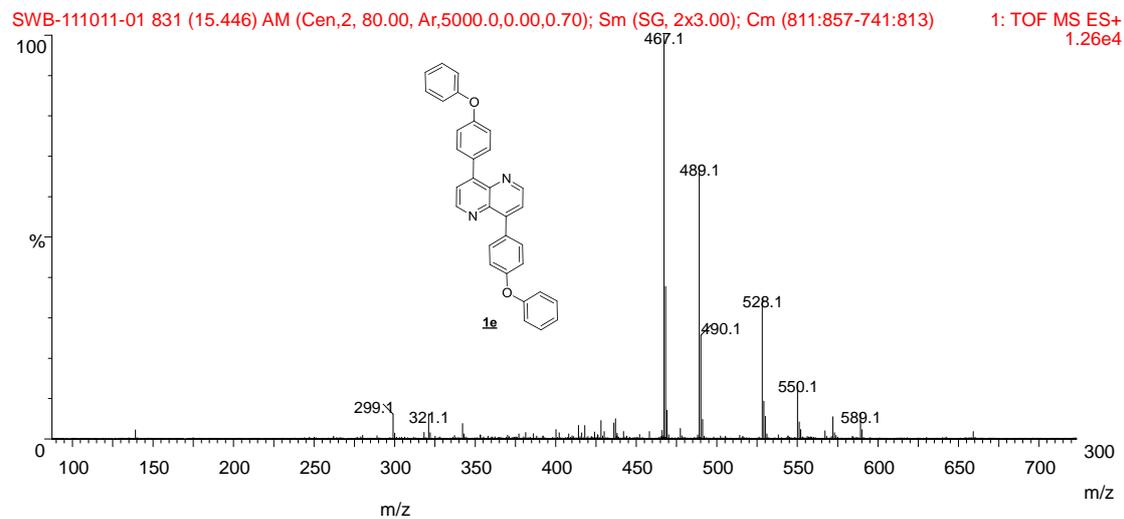


Figure S35. Mass spectrum of **1e**

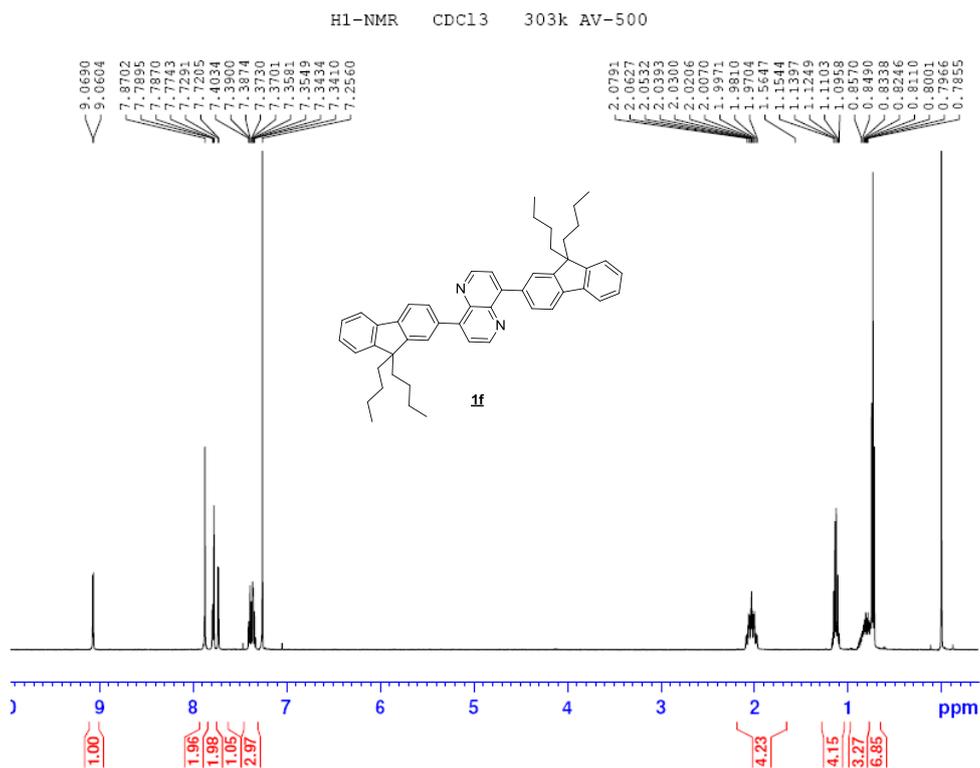


Figure S36. ^1H NMR spectrum of **1f** in CDCl_3

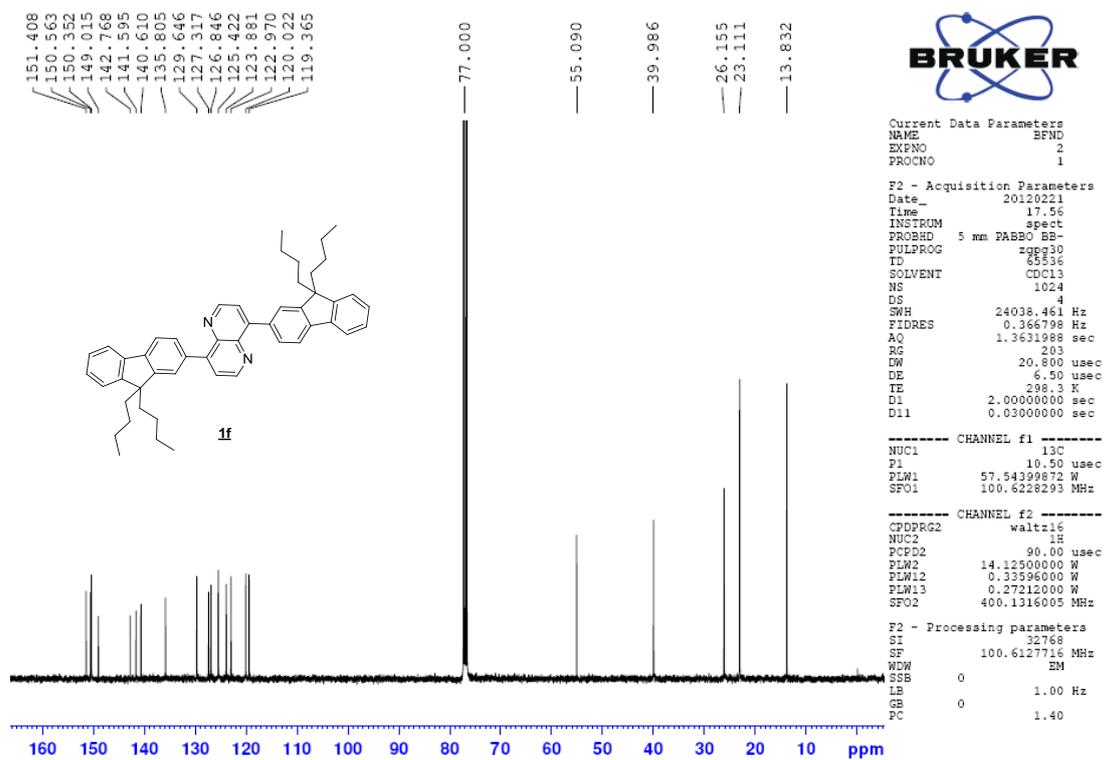


Figure S37. ^{13}C NMR spectrum of **1f** in CDCl_3

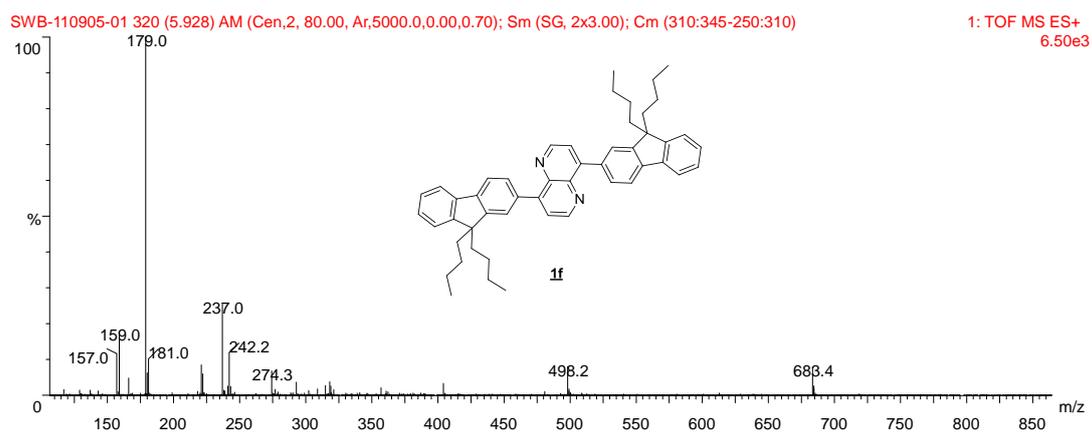


Figure S38. Mass spectrum of **1f**

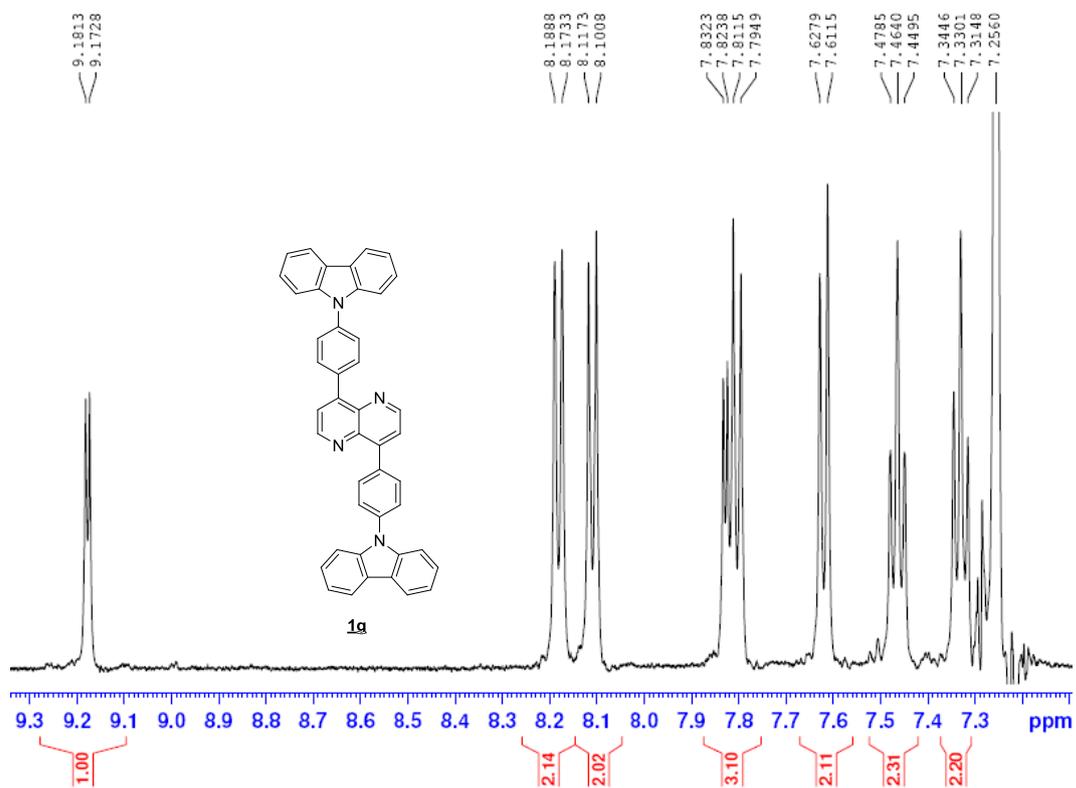


Figure S39. ^1H NMR spectrum of **1g** in CDCl_3

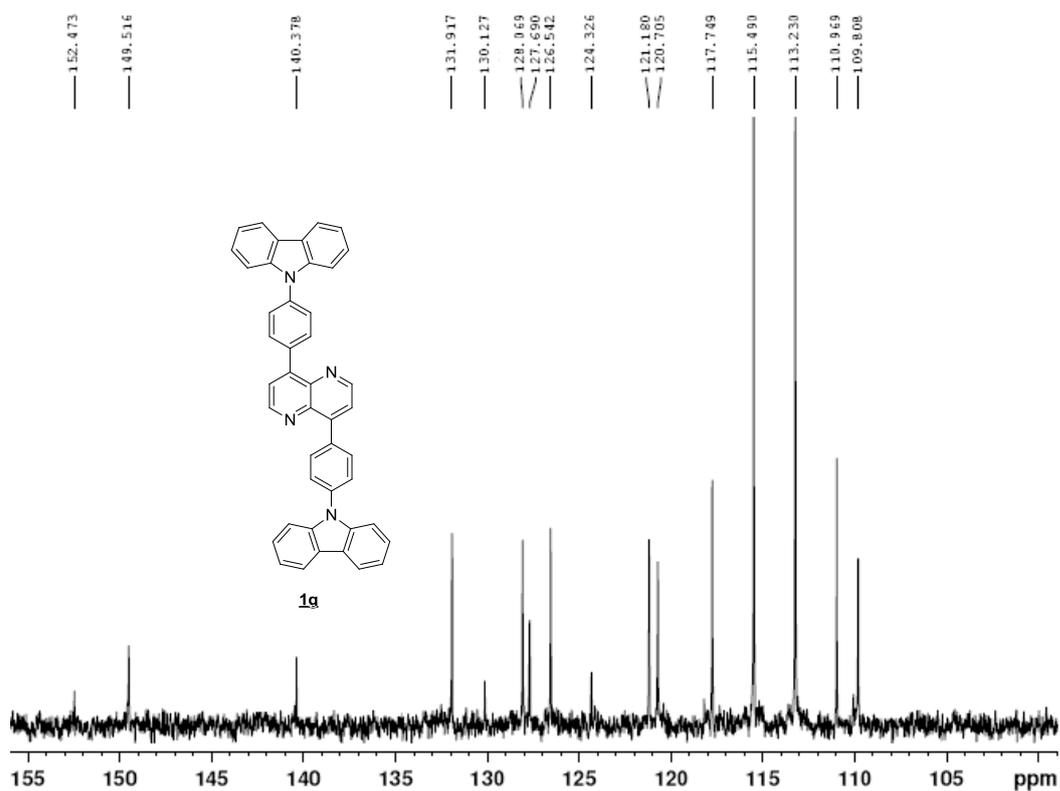


Figure S40. ¹³C NMR spectrum of **1g** in CDCl₃ + TFA

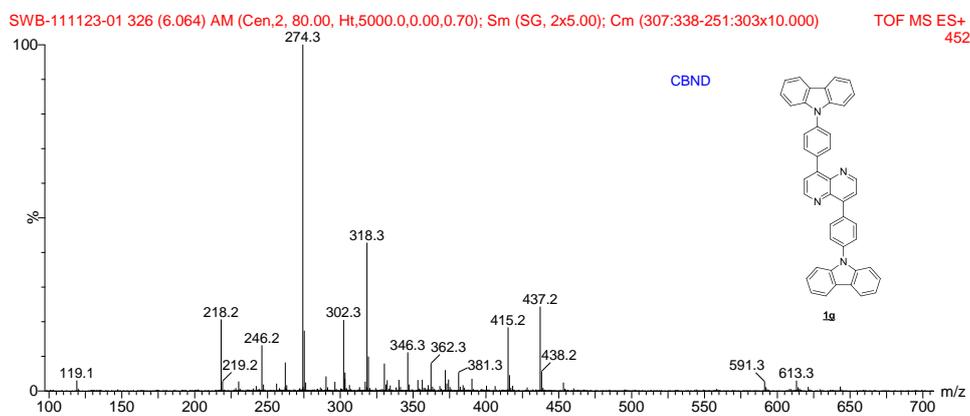


Figure S41. Mass spectrum of **1g**

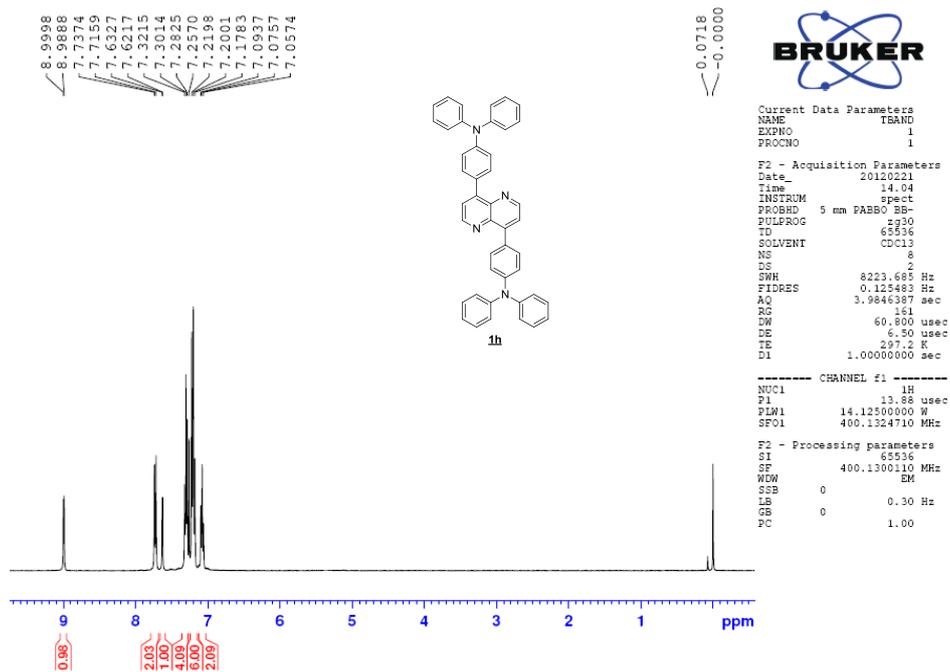


Figure S42. ¹H NMR spectrum of **1h** in CDCl₃

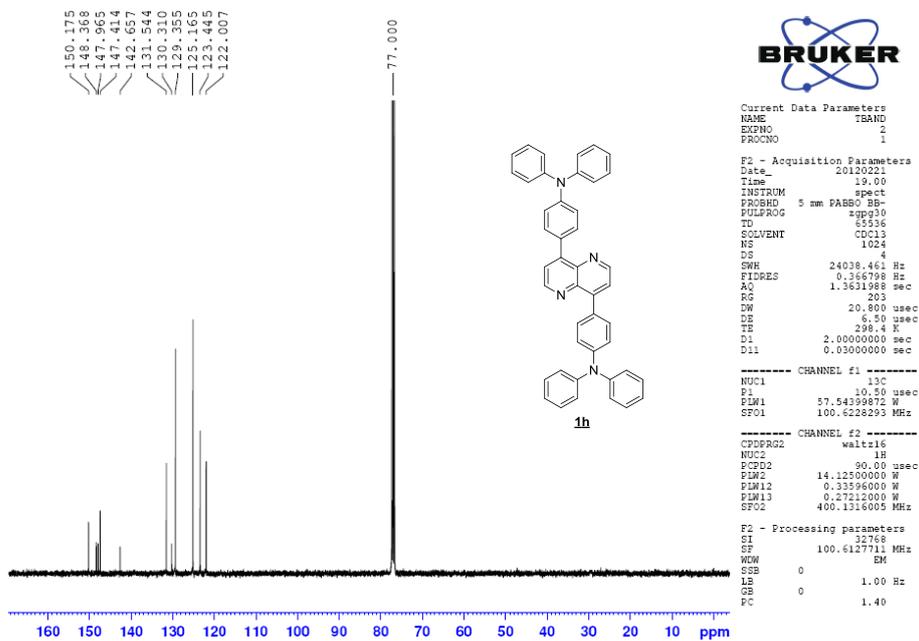


Figure S43. ¹³C NMR spectrum of **1h** in CDCl₃

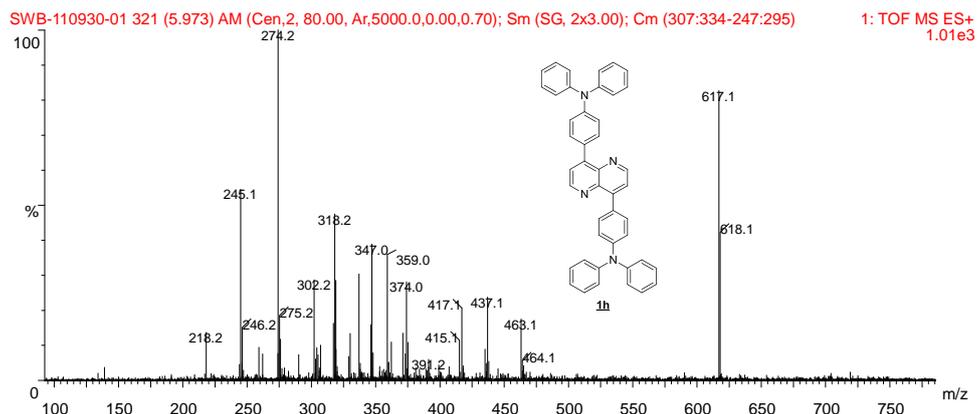


Figure S44. Mass spectrum of **1h**

VI. Crystal Structures and Packing Diagrams of Compounds **1b**, **1e** and **1f**

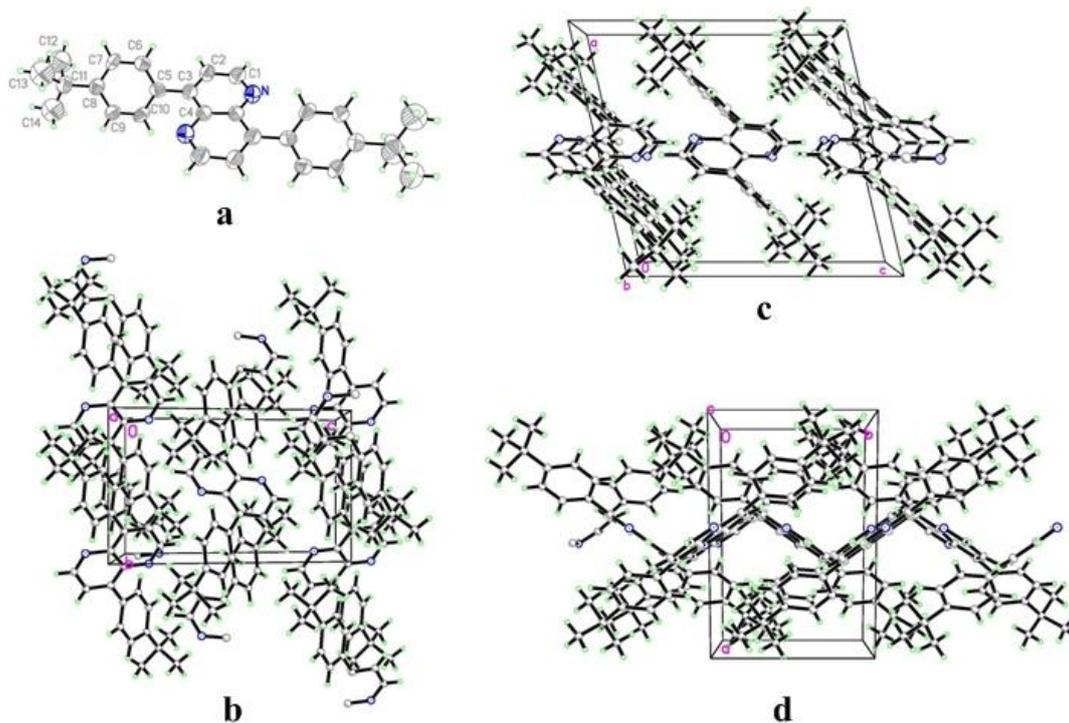


Figure S45. Single crystal structure of **1b** (a), view down the *a* axis (b), view down the *b* axis (c) and view down the *c* axis (d)

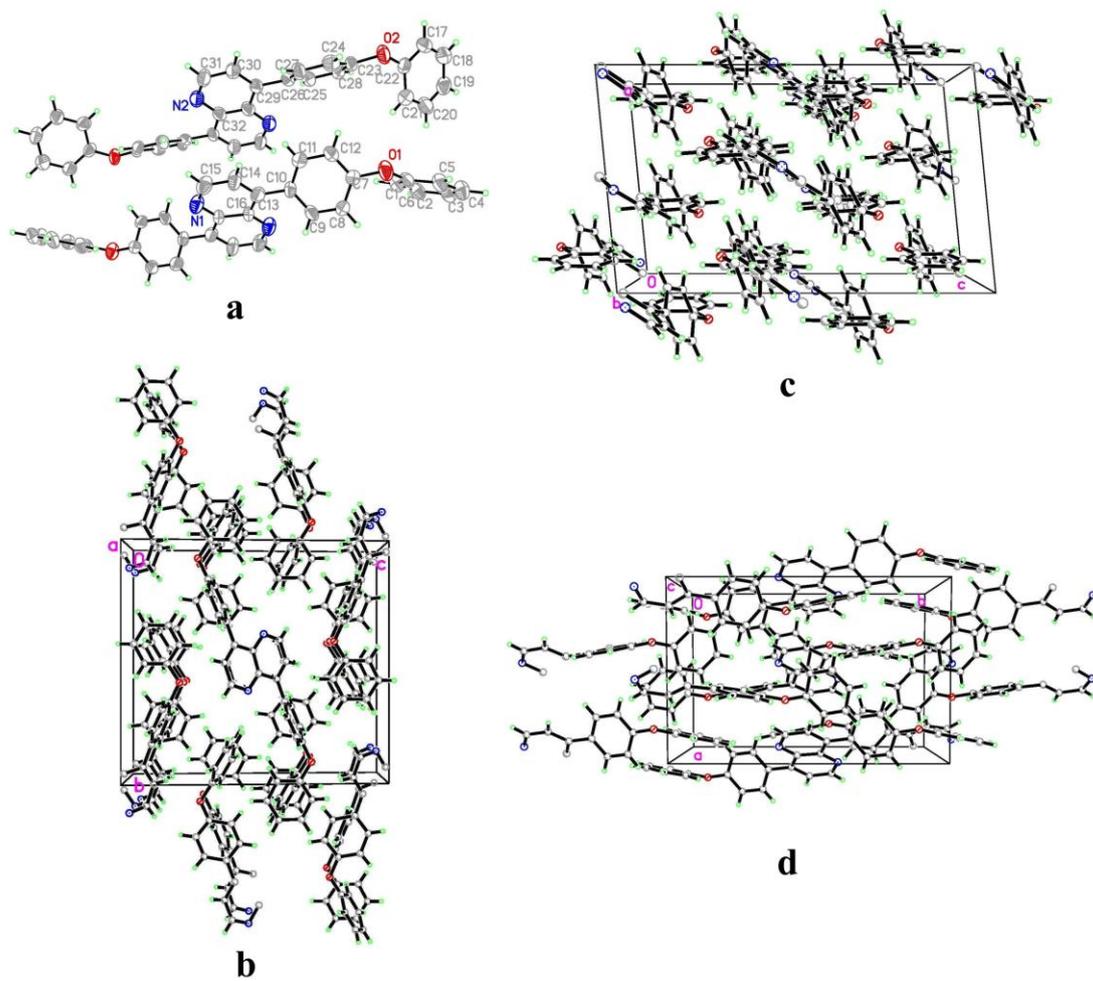


Figure S46. Single crystal structure of **1e** (a), view down the *a* axis (b), view down the *b* axis (c) and view down the *c* axis (d)

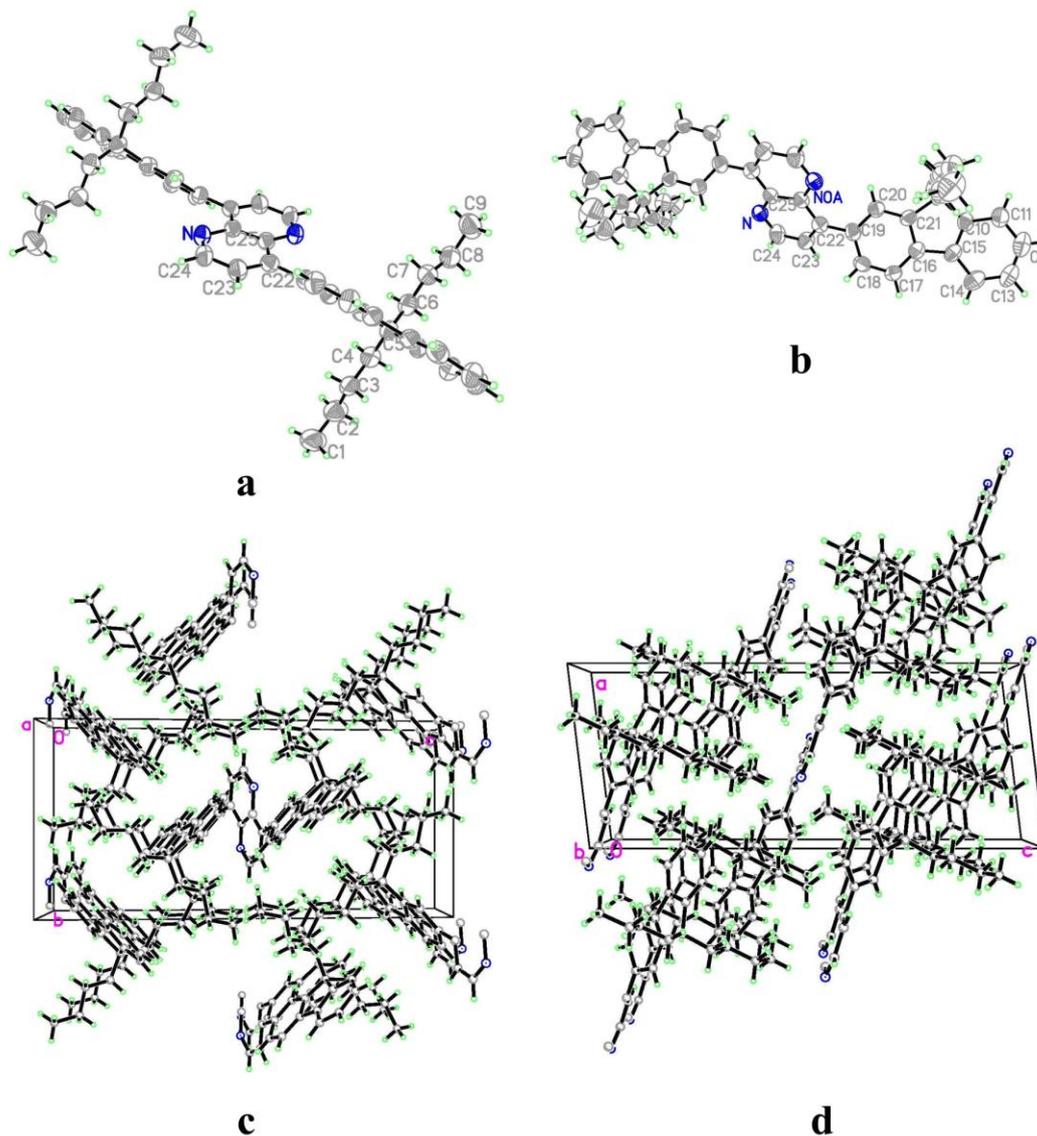


Figure S47. Single crystal structure of **1f** (a) (b), view down the *a* axis(c) and view down the *b* axis

- [1] G. M. Sheldrick, SHELXL-97. Program for the Refinement of Crystal Structures, Germany: University of Göttingen, 1997.
- [2] S. B. Brown, M. J. S. Dewar, *Journal of Organic Chemistry* 1978, 43, 1331.
- [3] W. Seaman, J. R. Johnson, *Journal of the American Chemical Society* 1931, 53, 711.
- [4] T. Leermann, F. d. r. R. Leroux, F. o. Colobert, *Organic Letters* 2011, 13, 4479.
- [5] M.-k. Leung, M.-Y. Chou, Y. O. Su, C. L. Chiang, H.-L. Chen, C. F. Yang, C.-C. Yang, C.-C. Lin, H.-T. Chen, *Organic Letters* 2003, 5, 839.