Supporting Information for

Protoisomerization of indigo di- and mono-imines

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General Experimental Considerations

All reactions and manipulations were carried out under an argon atmosphere using standard Schlenk or glovebox techniques unless stated otherwise. CH_2Cl_2 was dried and distilled over CaH_2 under argon prior to use. THF was dried and distilled over sodium and benzophenone under argon. All reagents were purchased from Sigma-Aldrich and used as received with the exception of DABCO which was sublimed prior to use. NMR spectra were recorded at room temperature on a 300 MHz or 500 MHz Bruker instrument. Electronic spectra were recorded at room temperature on a Perkin-Elmer 1050 instrument in CH_2Cl_2. Mass spectra were recorded on a Q-TOF II instruments using an electrospray ionization source and an Orbitrap mass analyzer in both positive and negative modes.

Indigo bis(2,6-dimethylphenyliminium) trifluoroacetate (2a)

Excess trifluoroacetic acid was added to a solution of **1** (77 mg; 164.4 mmol; 1eq). The resulting solution was stirred at room temperature for 1 hour. The teal solution was washed with 1M HCl solution (2 x 100 mL), dried over magnesium sulfate, filtered, and evaporated in vacuo to yield 88 mg of a dark black-green powder (92.0 %). X-Ray quality crystals were grown from slow evaporation of a saturated dichloromethane solution. ^{1}H NMR (CD_2Cl_2, 300 MHz, 298 K): 16.02 (s, 1*H*), 13.07 (s, 2*H*), 7.41 (m, 4*H*), 7.16 (s, 6*H*), 6.68 (t, 2*H*, $^3J_{HH}$ = 7.6 Hz), 6.31 (d, 2*H*, $^3J_{HH}$ = 8.1 Hz). ^{13}C NMR (CD_2Cl_2, 75.5 MHz, 298K): 158.5, 148.7, 140.9, 135.9, 130.9, 129.5, 127.9, 125.8, 122.1, 117.3, 113.7, 18.2. IR (thin film, cm^{-1}): 3269, 2913, 2851, 1613. UV-Vis (CH_2Cl_2; λ_{max} (nm) (ε ($M^{-1}cm^{-1}$))): 650 (22, 000). HRMS: Calcd for $C_{32}H_{29}N_4$ *m/z* = 469.23922, found *m/z* = 469.23830.

indigo bis(2,6-deimthylphenyliminium)tetrafluoroborate (2b)

Excess tetrafluoroboric acid was added to a solution of DmPNindigo (93 mg; 0.198 mmol; 1 eq) in 20 mL dichloromethane with an immediate colour change from purple to teal. The resulting solution was stirred at room temperature for 30 minutes. The teal solution was washed with 1M HCl solution (2x 100 mL), dried over magnesium sulfate, filtered and evaporated in vacuo to yield 87 mg of a dark black-green powder (79.2%). X-Ray quality crystals were grown from slow evaporation of a saturated solution in dichloromethane. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): 16.47 (s, 1*H*), 9.71 (s, 2*H*), 7.49 (t, 2*H*, $^3J_{HH}$ = 7.8 Hz), 7.38 (d, 2*H*, $^3J_{HH}$ = 8.3 Hz), 7.18 (m, 6*H*), 6.74 (t, 2*H*, $^3J_{HH}$ =7.8 Hz), 6.35 (d, 2*H*, $^3J_{HH}$ = 8.3 Hz). ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): 159.3, 148.6, 140.5, 136.6, 130.6, 130.0, 129.6, 128.2, 125.9, 122.9, 117.4, 113.9, 18.2.

indigo mono(2,6-dimethylphenylimine (6)

A 1.0 M toluene solution of $TiCl_4$ (9.8 mL; 9.80 mmol; 1.8 eq) was added dropwise to a 1,4-dioxane solution containing DABCO (1.00 g; 8.92 mmol; 1.7 eq) and 2,6-dimethylaniline (1.63 g; 13.4 mmol; 2.5 eq), immediately generating a white vapour and a green precipitate. After fuming subsided, indigo (1.40 g; 5.33 mmol; 1 eq) was added. The dark blue mixture was refluxed overnight (19 hours). The resulting solution was filtered while warm and the solid was washed with diethyl ether until the washing were colourless. The filtrate was concentrated to dryness to yield 1.12 g of a purple powder (57 %).^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): 9.59 (broad singlet, 1*H*), 9.28 (singlet, 1*H*), 7.67 (d, 1*H*, $^3J_{HH}$ = 7.9 Hz), 7.38 (tofd, 1*H*, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 1.2 Hz), 7.24 (tofd, 1*H*, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 1.2 Hz), 7.09 (d, 2*H*, $^3J_{HH}$ = 7.7 Hz), 7.00 (m, 3*H*), 6.88 (tofd, 1*H*, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 0.9 Hz), 6.57 (tofd, 1*H*, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 0.9 Hz), 6.38 (d, 1*H*, $^3J_{HH}$ = 7.8 Hz), 2.02 (s, 6*H*). ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K): 186.1, 161.7, 151.0, 149.1, 148.6, 134.6, 133.2, 128.3, 127.1, 125.6, 125.1, 124.0, 123.8, 120.8, 120.7, 119.9, 119.6, 118.2, 112.1, 111.4, 17.7. IR (thin film, cm^{-1}): 2960, 1682, 1667, 1554, 1190, 792, 746, 721, 582. UV-Vis (CH_2Cl_2, λ (ε)): 592 (21350). HRMS: Calcd for $C_{24}H_{19}N_3O + H^+$ *m/z* = 366.16011, found *m/z* = 366.16005.

Indigo mono(2,6-dimethylphenyliminium) chloride (7):

An excess of concentrated hydrochloric acid was added to a solution of monoDmPNindigo (38 mg; 0.104 mmol) in 20 mL dichloromethane with an immediate colour change from purple to teal. The resulting solution was stirred at room temperature for 30 minutes. The teal solution was washed with 1M HCl solution (2 x 100 mL), dried over magnesium sulfate, filtered, and evaporated in vacuo to yield 33 mg of a dark black-green powder (86.8%). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): 14.64 (s, 1*H*), 13.05 (s, 1*H*), 12.79 (s, 1*H*), 7.77 (d, 1*H*, $^3J_{HH}$ = 8.1 Hz), 7.58 (t of d, 1*H*, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.1 Hz) 7.45 (t of d, 1*H*, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.1 Hz), 7.28 (m, 5*H*), 7.11 (m, 1*H*), 6.65 (t, 1H, $^3J_{HH}$ = 7.4 Hz), 6.31 (d, 1*H*, $^3J_{HH}$ = 8.1 Hz), 2.17 (s, 6*H*). ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): 184.3, 159.1, 156.0, 149.5, 149.0, 136.4, 136.2, 132.8, 132.1, 130.9, 127.8, 127.5, 123.9, 123.0, 121.0, 120.0, 117.9, 113.3, 112.1, 15.7. IR (thin film, cm^{-1}): 3100 (broad), 2339, 1680, 1658, 1608, 1557, 1196, 792, 746, 721, 582. UV-Vis (CH_2Cl_2; λ_{max} (nm) (ε ($M^{-1}cm^{-1}$))): 659 (13,800). Calcd for $C_{24}H_{19}N_3OH^+$ *m/z* = 366.16011, found *m/z* = 366.16005.

Figure S1. ^{1}H NMR spectrum of **2a** in CD_2Cl_2.

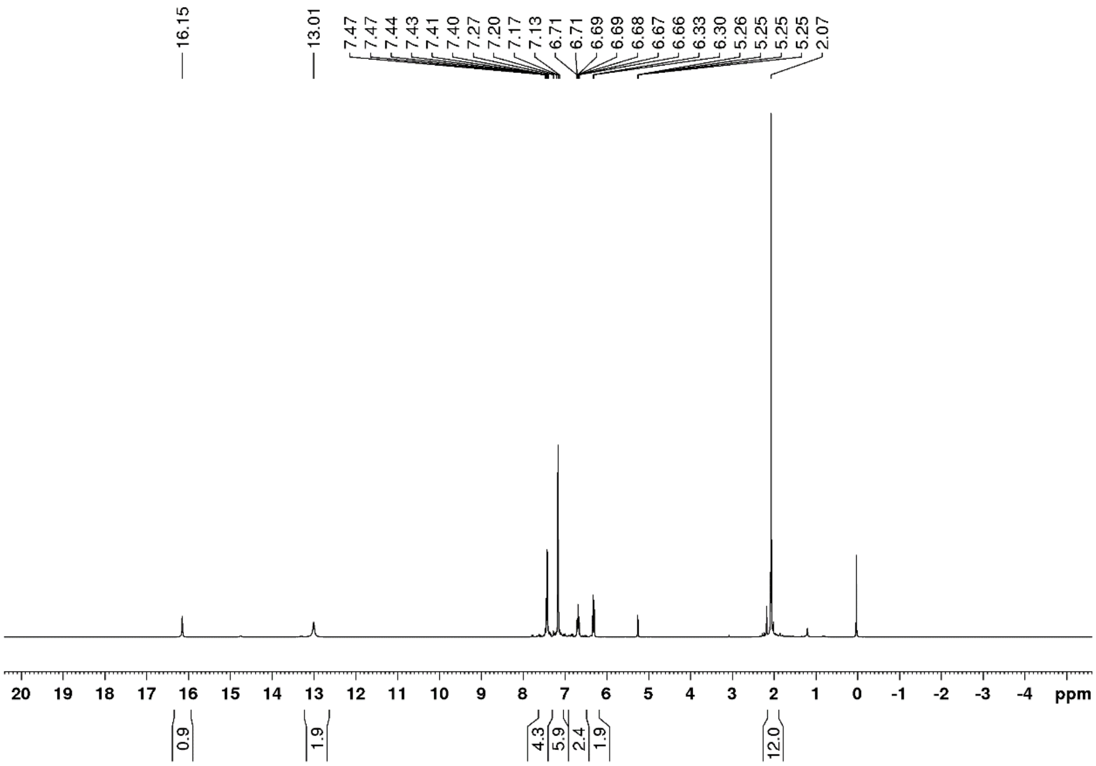

Figure S2. ^{13}C NMR spectrum of **2a** in CD_2Cl_2.

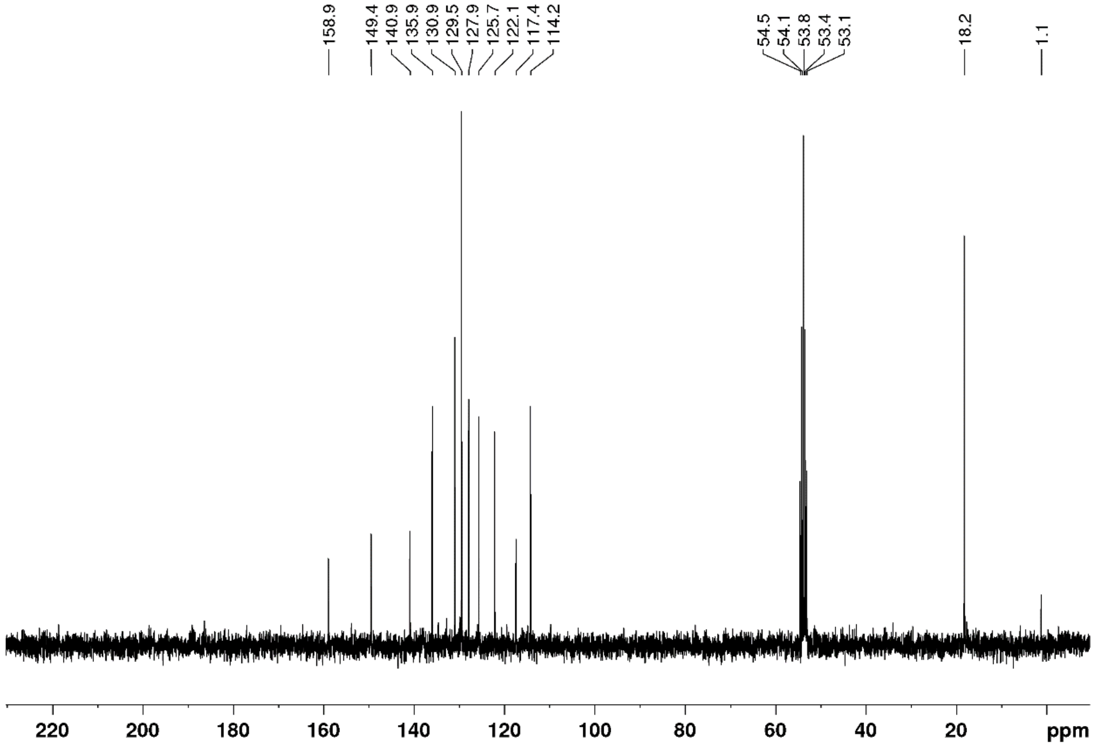

Figure S3. ^{1}H NMR spectrum of **2b** in CD_2Cl_2.

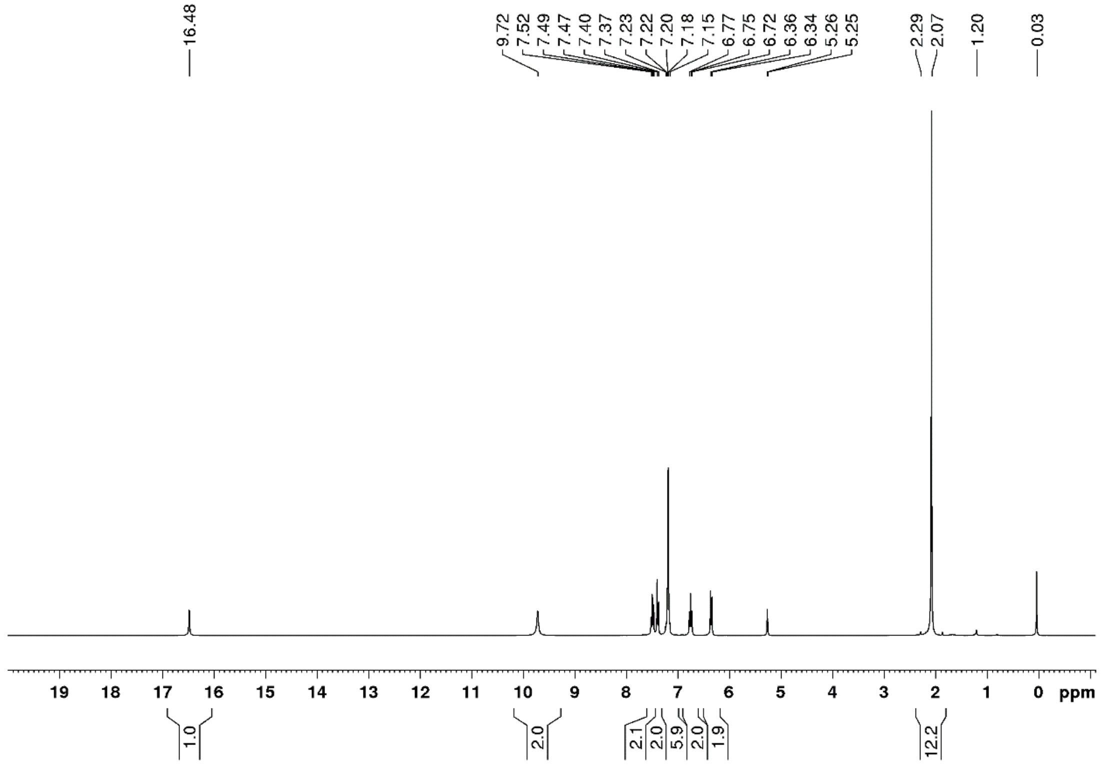

Figure S4. ^{13}C NMR spectrum of **2b** in CD_2Cl_2.

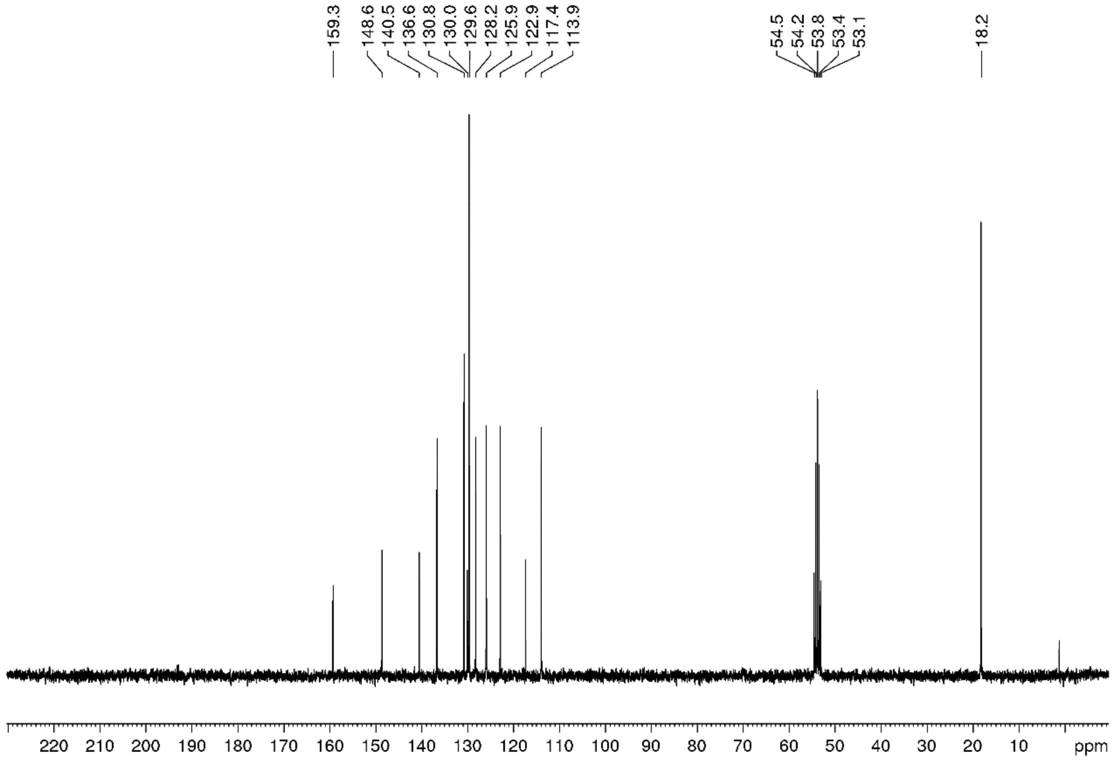

Figure S5. ^{1}H NMR spectrum of **6** in CD_2Cl_2.

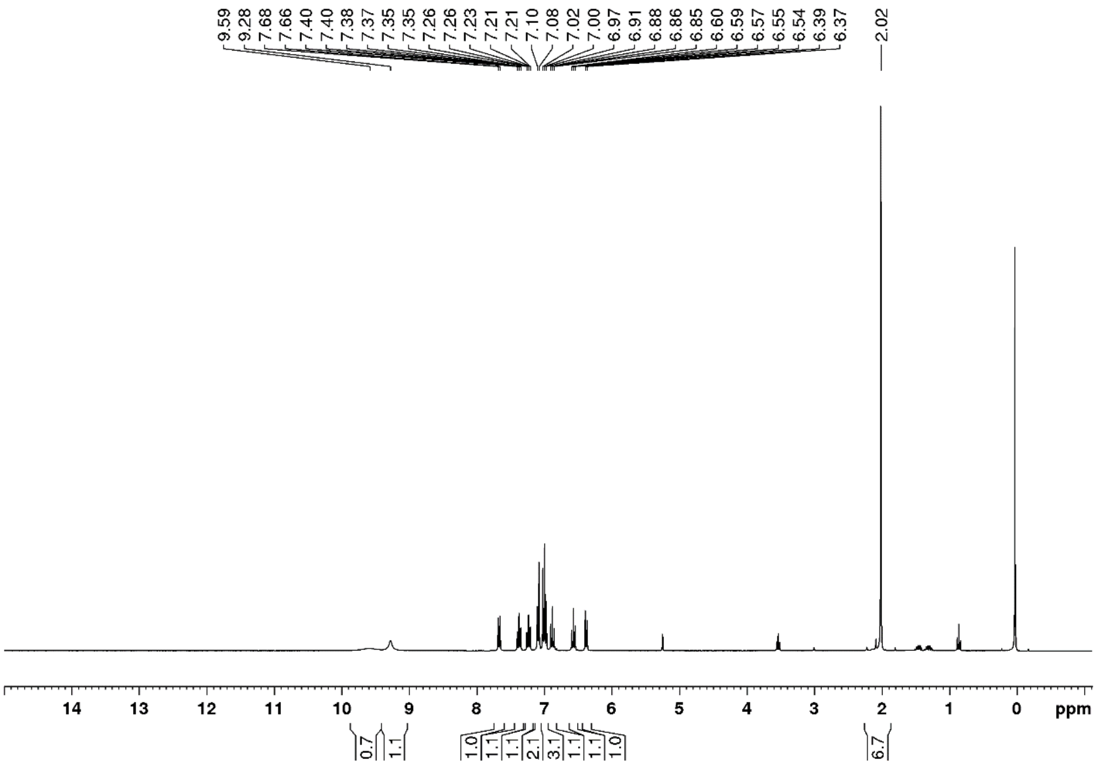

Figure S6. ^{13}C NMR spectrum of **6** in CD_2Cl_2.

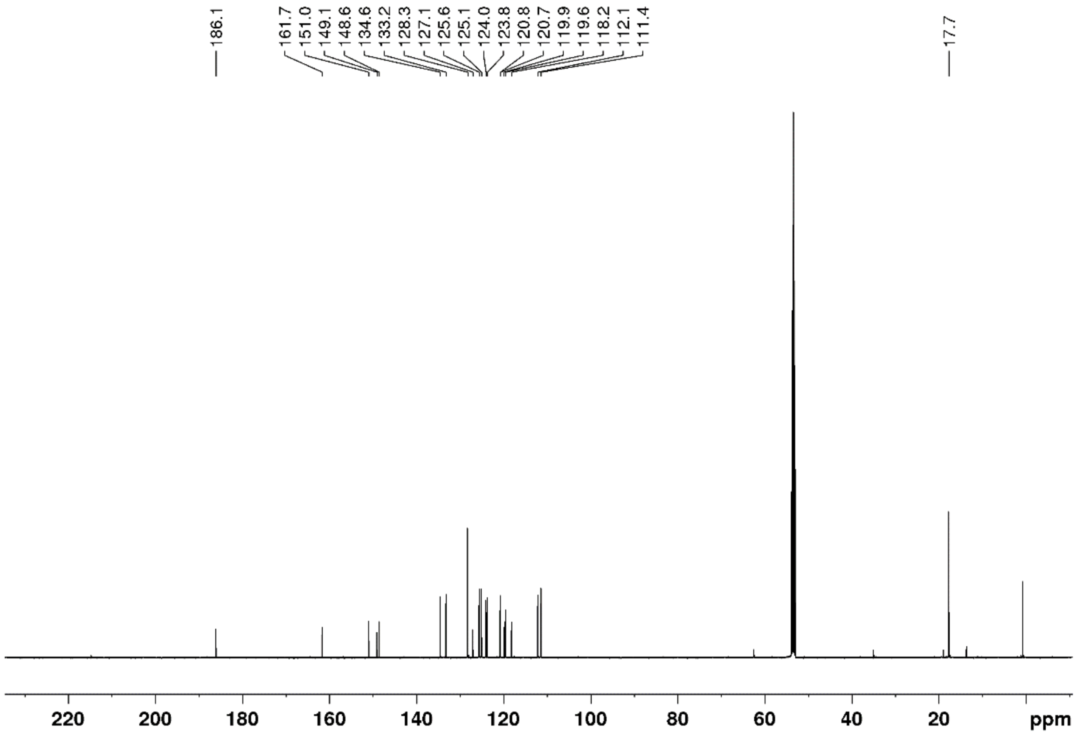

Figure S7. ^{1}H NMR spectrum of **7** in CD_2Cl_2.

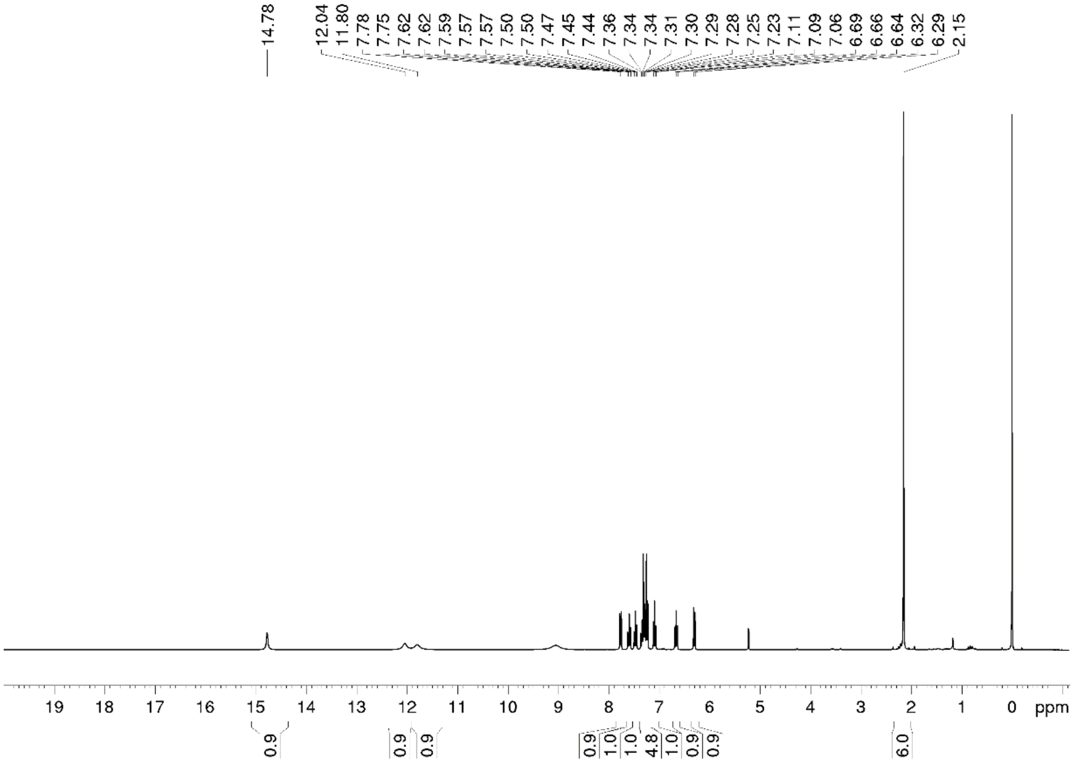

Figure S8. ^{13}C NMR spectrum of **7** in CD_2Cl_2.

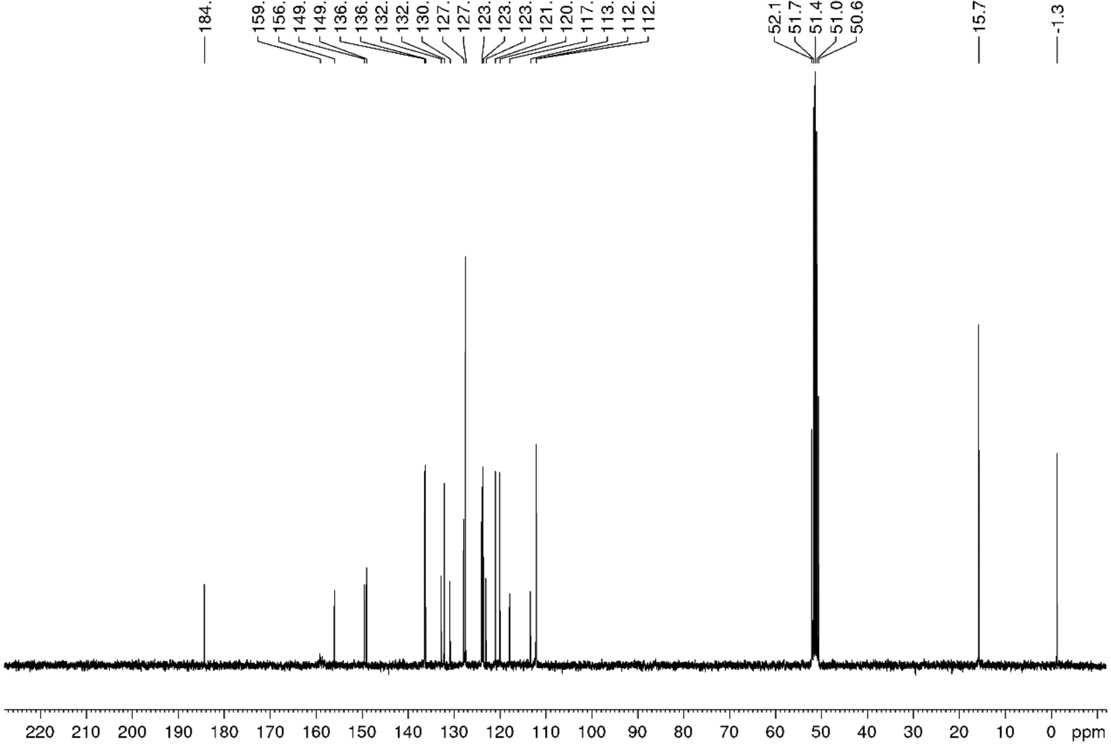

Figure S9. UV-Visible spectrum of **2a** in CH_2Cl_2, 50 µM, 298 K

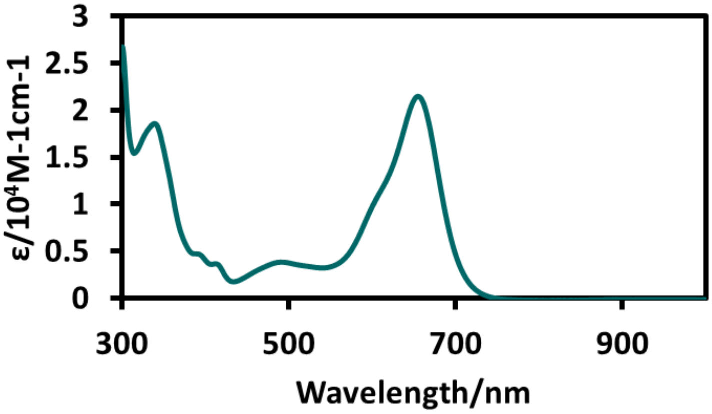

Figure S10. UV-Visible spectrum of **6** in CH_2Cl_2, 50 µM, 298 K

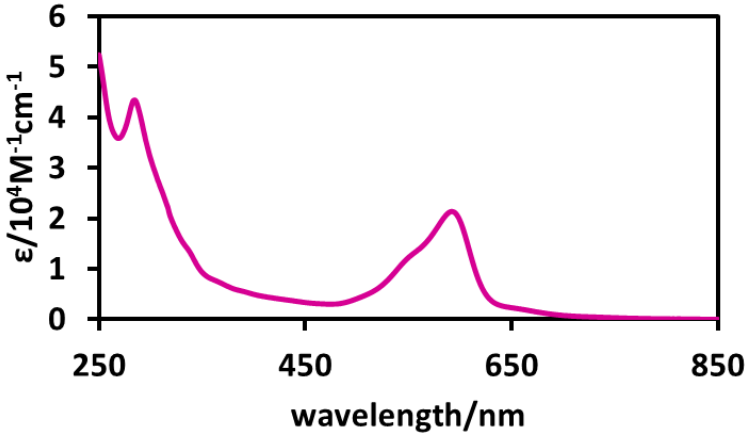

Figure S11. UV-Visible spectrum of **7** in CH_2Cl_2, 25 µM, 298 K

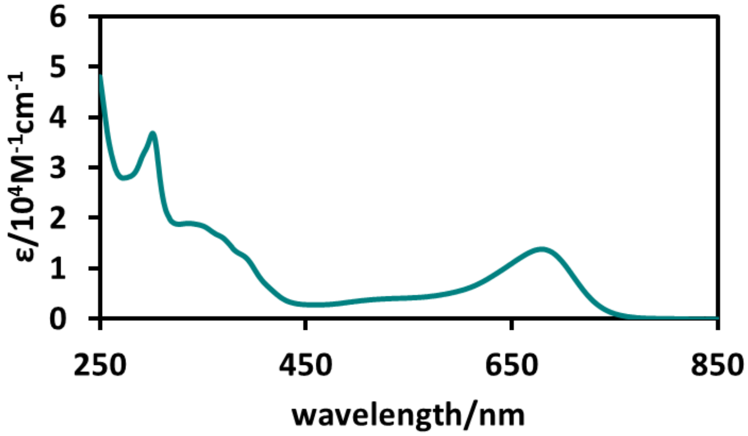

Figure S12. X-ray structure of **2b**. Hydrogen atoms except N-H hydrogens omitted for clarity. Thermal ellipsoids represented at 50%.