Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Push-Pull Isomers of Indolizino[6,5,4,3-def]phenanthridine Decorated by a Triarylboron Moiety

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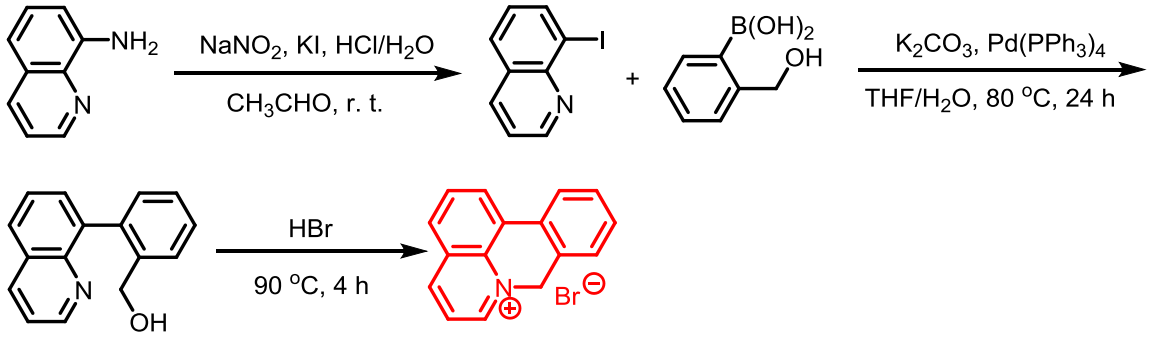
Supporting Information

Table of contents

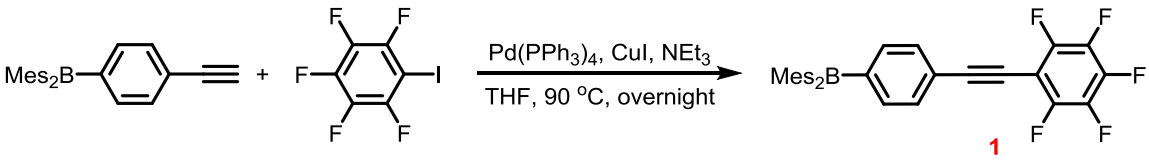
I. Synthetic Procedure



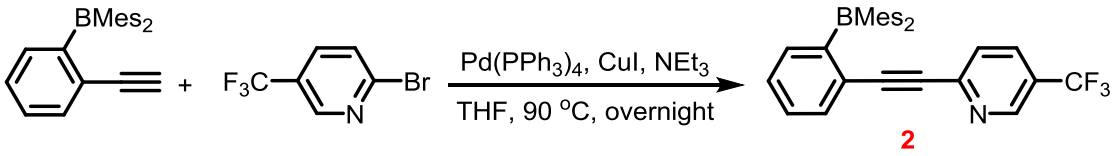
8-iodoquinoline: Quinolin-8-amine (3.34 g, 23 mmol) was added to a mixture of HCl/H_2O (15:15 mL) and was cooled to 5 °C in an ice bath. $NaNO_2$ (1.74 g, 25 mmol) was then added dropwise, followed by the addition of KI (1.74 g, 25 mmol) in 15 mL of H_2O. After stirring overnight, the mixture was neutralized with NaOH and the solvent was removed in *vacuo* and the product was isolated by column chromatography on silica gel using hexane/ethyl acetate (5:1) as an eluent. 8-iodoquinoline was isolated as a yellow solid (2.90 g, 49% yield).

(2-(quinolin-8-yl)phenyl)methanol: 8-iodoquinoline (1.70 g, 6.6 mmol), (2-(hydroxymethyl)phenyl)boronic acid (1.32 g, 8.7 mmol), $Pd(PPh_3)_4$ (0.418 g, 0.36 mmol), and K_2CO_3 (13.8 g, 100 mmol) were reacted in a mixture of THF/H_2O (60:20 ml) for 24 hr at 85 °C. After the mixture was cooled to room temperature, the solvent was removed in *vacuo* and the product was isolated by column chromatography on silica gel using hexane/ethyl acetate (2:1 → 1:1) as an eluent. (2-(quinolin-8-yl)phenyl)methanol was isolated as a yellow solid (1.181 g, 70% yield).

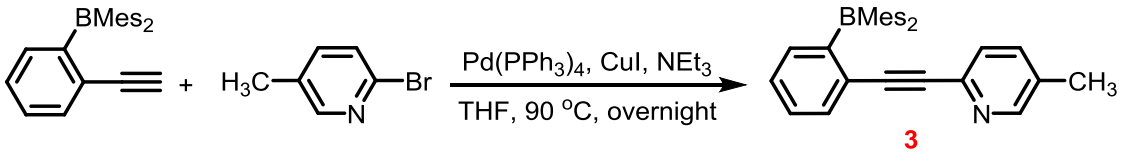
8*H*-pyrido[3,2,1-*de*]phenanthridin-7-ium bromide: (2-(quinolin-8-yl)phenyl)methanol (943 mg, 4 mmol) and hydrobromic acid (0.544 mL, 4.8 mmol) were reacted for 4 hr at 90 °C. After cooled to room temperature, ether (3 x 30 mL) and dichloromethane (10 ml) were added and the supernatant was removed. The mixture was then air-dried overnight and the remaining solvent was removed in *vacuo* to yield a yellow solid (2.036 g, 84% yield). ^{1}H NMR (700 MHz, DMSO-d_6): δ 9.49 (d, J = 7.3 Hz, 1H), 9.28 (d, J = 8.2 Hz, 1H), 8.85 (d, J = 7.4 Hz, 1H), 8.38 (d, J = 8.1 Hz, 1H), 8.31 (d, J = 8.3 Hz, 1H), 8.26 (t, J = 7.6 Hz, 1H), 8.07 (t, J = 7.8 Hz, 1H), 7.60 – 7.51 (m, 3H), 6.31 (s, 2H). ^{13}C NMR (176 MHz, DMSO): δ 149.01, 147.14, 135.12, 130.70, 130.60, 130.37, 129.78, 129.62, 128.89, 128.28, 126.89, 126.67, 125.82, 124.14, 123.17, 56.97. HR-ESIMS (*m/z*): $[M + H]^+$ calcd. for $C_{16}H_{12}N$: 218.0964; found: 218.0970.



Alkyne 1: (4-ethynylphenyl)dimesitylborane (485 mg, 1.38 mmol), 1,2,3,4,5-pentafluoro-6-iodobenzene (490 mg, 1.67 mmol), $Pd(PPh_3)_4$ (80 mg, 0.07 mmol), CuI (26 mg, 0.14 mmol) and Et_3N (3 ml) were reacted in THF (25 mL) overnight at 90 °C. After the mixture was cooled to room temperature, the solvent was removed in *vacuo* and the product was isolated by column chromatography on silica gel using hexane/ethyl acetate (50:1) as an eluent. The product **1** was isolated as a white solid (500 mg, 70% yield). ^{1}H NMR (700 MHz, CD_2Cl_2): δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 6.7 Hz, 2H), 6.88 (s, 4H), 2.34 (s, 6H), 2.03 (s, 12H). ^{13}C NMR (176 MHz, CD_2Cl_2): δ 141.34, 140.76, 140.67, 139.14, 136.18, 135.90, 131.89, 131.23, 128.22, 128.08, 127.94, 124.35, 101.53, 74.46, 23.13, 20.92. HR-EIMS (m/z): [M]+ calcd. for $C_{32}H_{26}BF_5$: 516.2048; found: 516.2039



Alkyne 2: (2-ethynylphenyl)dimesitylborane (700 mg, 2 mmol), 2-bromo-5-(trifluoromethyl)pyridine (565 mg, 2.5 mmol), $Pd(PPh_3)_4$ (115 mg, 0.10 mmol), CuI (57 mg, 0.30 mmol) and Et_3N (3 ml) were reacted in THF (25 mL) overnight at 90 °C. After the mixture was cooled to room temperature, the solvent was removed in *vacuo* and the product was isolated by column chromatography on silica gel using hexane/ethyl acetate (30:1) as an eluent. The product **2** was isolated as a yellow solid (900 mg, 91% yield). ^{1}H NMR (700 MHz, CD_2Cl_2): δ 8.78 (s, 1H), 7.78 (d, *J* = 8.3, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.50 (t, 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 8.3 Hz, 1H), 6.80 (s, 4H), 2.27 (s, 6H), 2.04 (s, 12H). ^{13}C NMR (176 MHz, CD_2Cl_2): δ 150.67, 146.87, 146.38, 140.83, 139.29, 134.61, 133.34, 132.50, 130.48, 129.07, 128.29, 126.74, 125.35, 124.50, 124.31, 122.79, 92.16, 90.43, 22.89, 20.88. HR-EIMS (*m/z*): $[M]^+$ calcd. for $C_{32}H_{29}BNF_3$: 495.2345; found: 495.2340.



Alkyne 3: (2-ethynylphenyl)dimesitylborane (350 mg, 1 mmol), 2-bromo-5-methylpyridine (260 mg, 1.5 mmol), $Pd(PPh_3)_4$ (60 mg, 0.05 mmol), CuI (28 mg, 0.15 mmol) and Et_3N (3 ml) were reacted in THF (25 mL) overnight at 90 °C. After the mixture was cooled to room temperature, the solvent was removed in *vacuo* and the product was isolated by column chromatography on silica gel using hexane/ethyl acetate (30:1) as an eluent. The product **3** was isolated as an orange solid (300 mg, 68% yield). ^{1}H NMR (700 MHz, CD_2Cl_2): δ 8.35 (d, J = 5.1 Hz, 1H), 7.65 (d, J = 7.7 Hz, 1H), 7.47 (t, J = 7.6, 1H), 7.37 (t, J = 7.5, 1H), 7.30 (d, J = 7.6 Hz, 1H), 7.00 (d, J = 5.1 Hz, 1H), 6.82 (s, 4H), 6.53 (s, 1H), 2.31 (s, 3H), 2.29 (s, 6H), 2.04 (s, 12H). ^{13}C NMR (176 MHz, CD2Cl2): δ 149.30, 146.72, 143.06, 140.82, 139.11, 134.31, 133.11, 131.93, 131.88, 131.82, 130.33, 128.43, 128.28, 128.05, 126.07, 123.41, 104.21, 91.67, 22.88, 20.95, 20.44. HR-ESIMS (m/z): $[M+H]^+$ calcd. for $C_{32}H_{33}BN$: 442.2701; found: 442.2711.

II. NMR Spectra

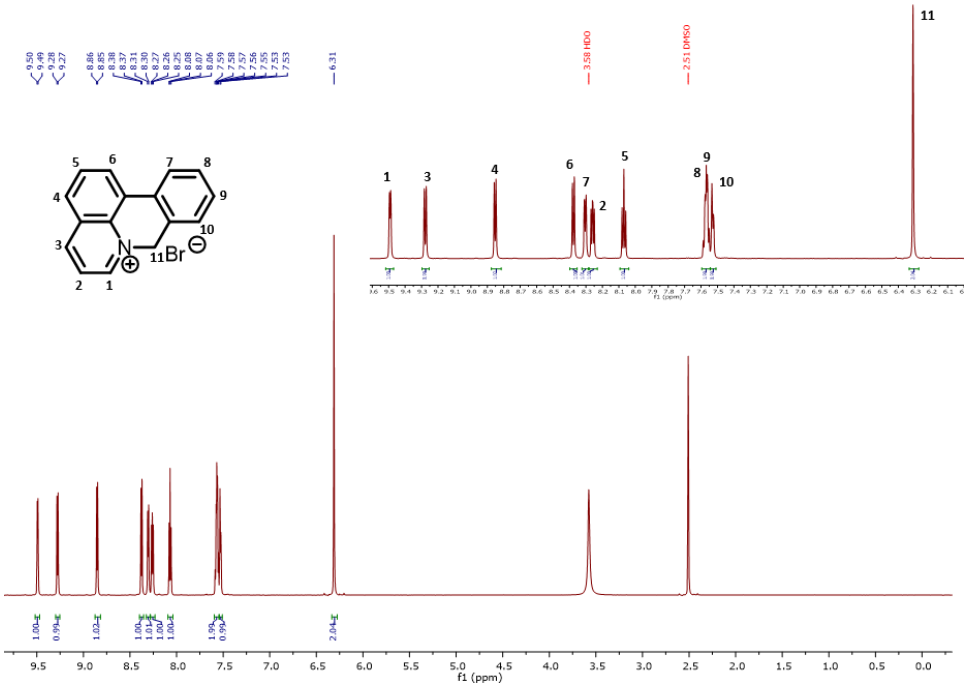


Figure S1. ^{1}H NMR spectrum of 8*H*-pyrido[3,2,1-*de*]phenanthridin-7-ium bromide in DMSO-d_6

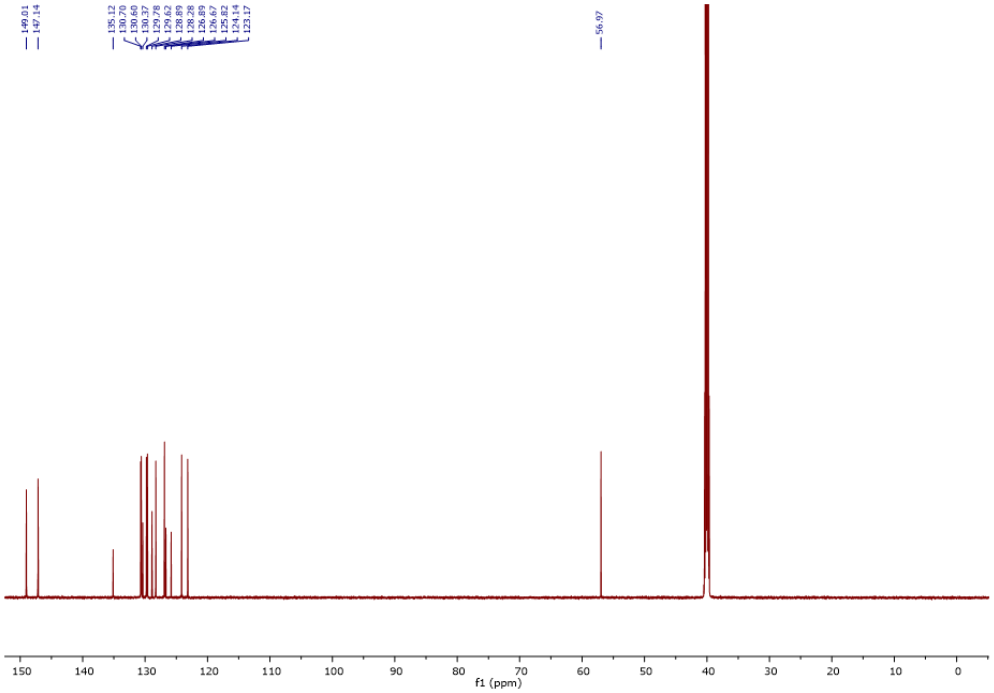


Figure S2. ^{13}C NMR spectrum of 8*H*-pyrido[3,2,1-*de*]phenanthridin-7-ium bromide in DMSO-d_6

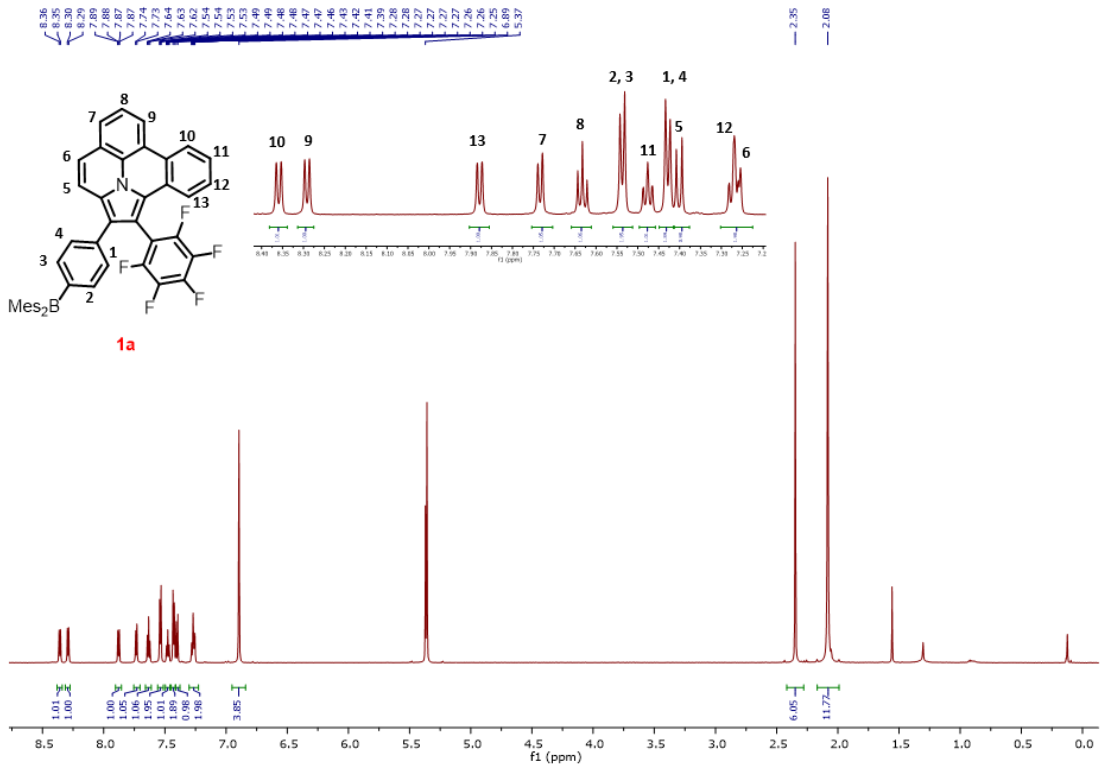


Figure S3. ^{1}H NMR spectrum of compound **1a** in CD_2Cl_2

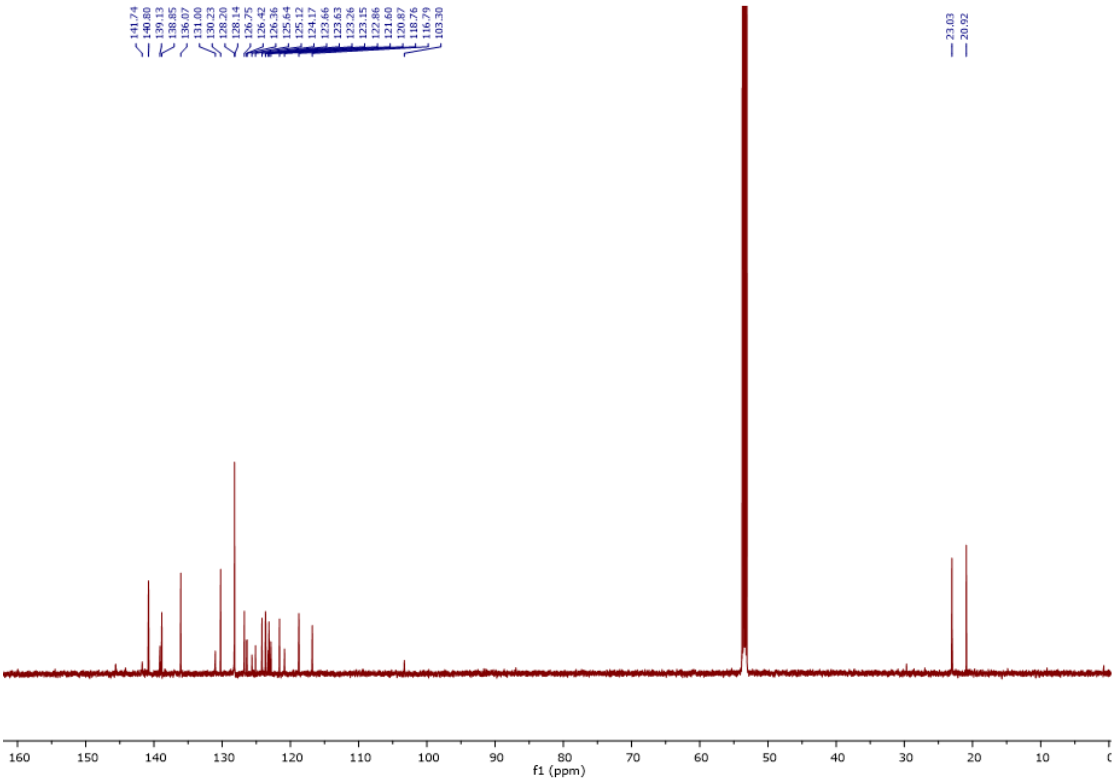


Figure S4. ^{13}C NMR spectrum of compound **1a** in CD_2Cl_2

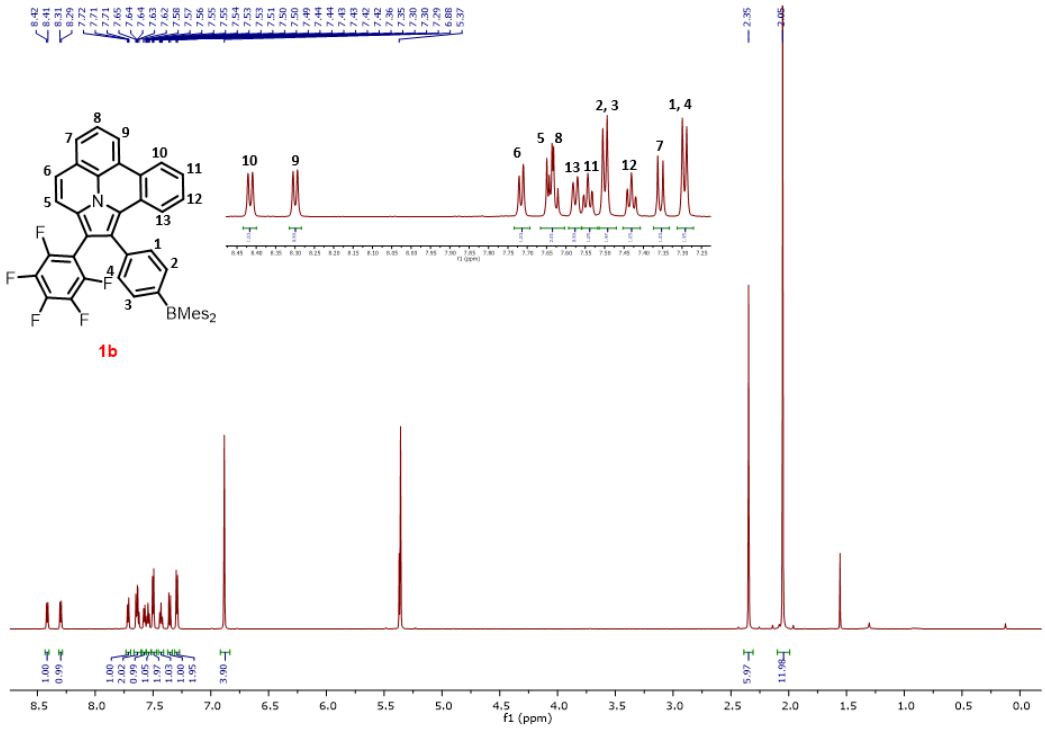


Figure S5. ^{1}H NMR spectrum of compound **1b** in CD_2Cl_2

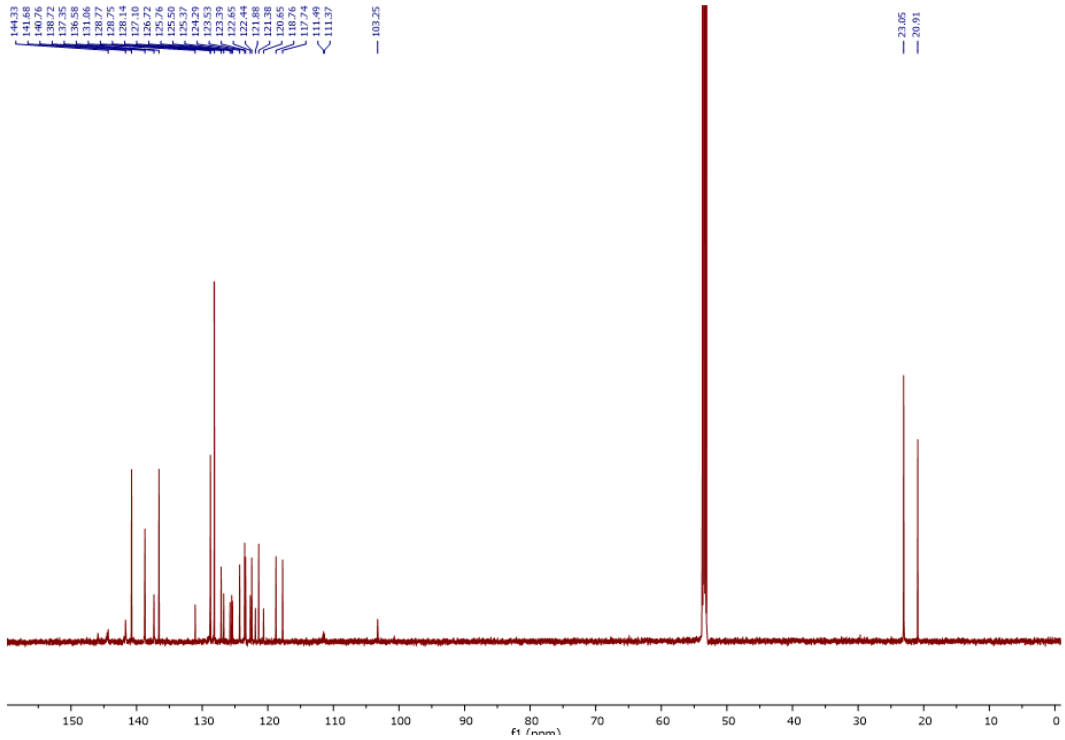


Figure S6. ^{13}C NMR spectrum of compound **1b** in CD_2Cl_2

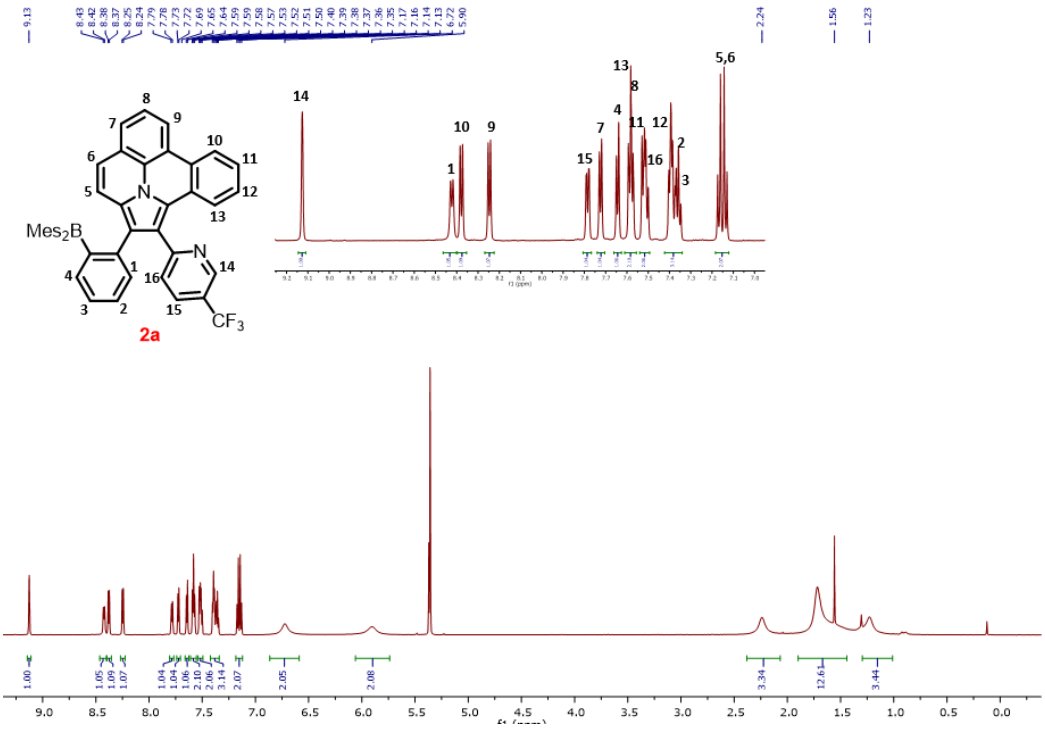


Figure S7. ^{1}H NMR spectrum of compound **2a** in CD_2Cl_2

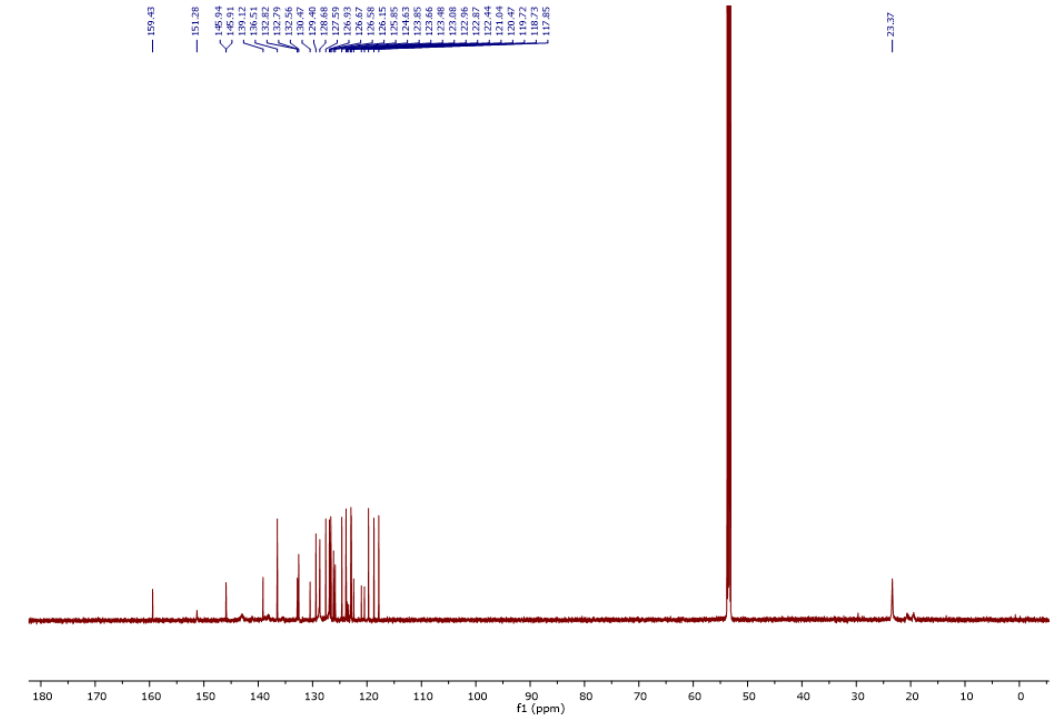


Figure S8. ^{13}C NMR spectrum of compound **2a** in CD_2Cl_2

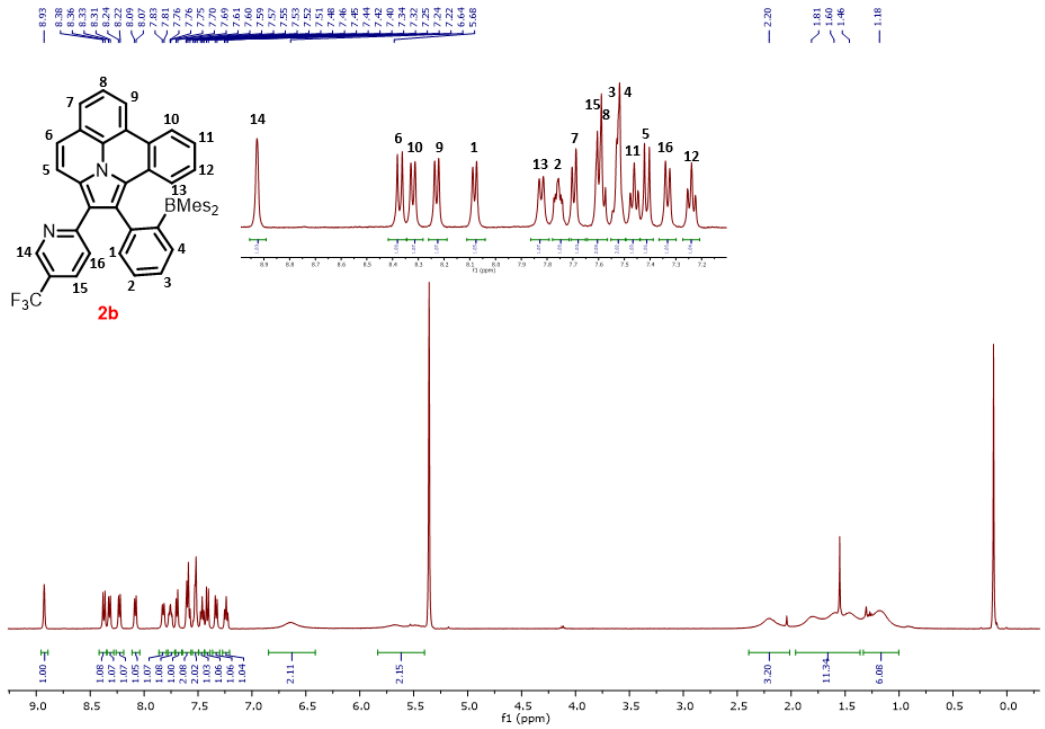


Figure S9. ^{1}H NMR spectrum of compound **2b** in CD_2Cl_2

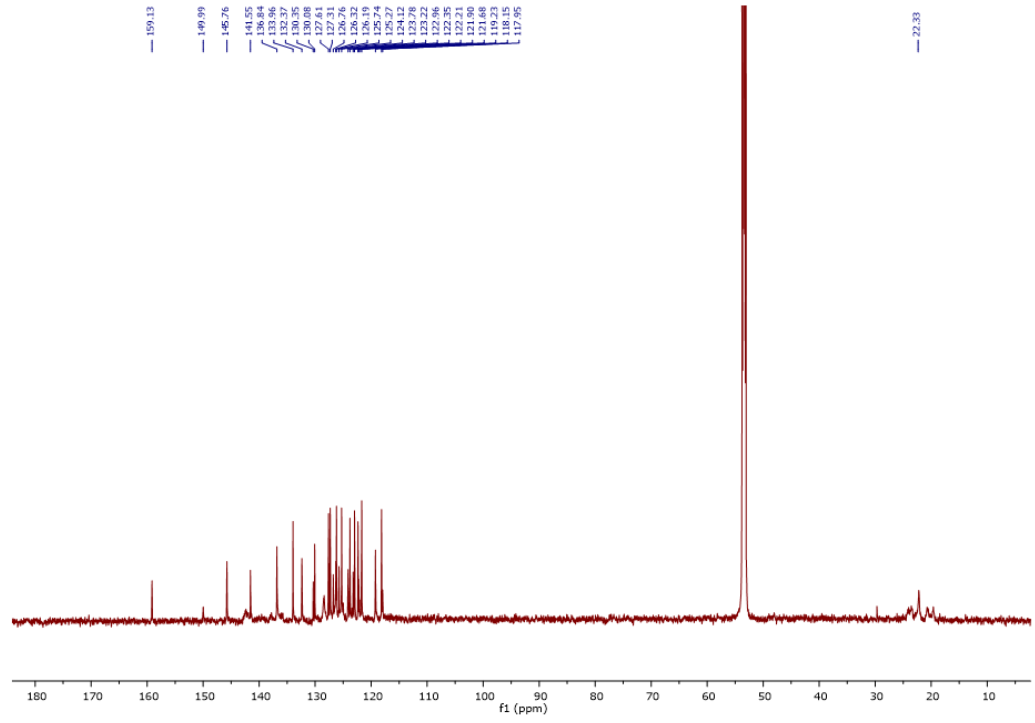


Figure S10. ^{13}C NMR spectrum of compound **2b** in CD_2Cl_2

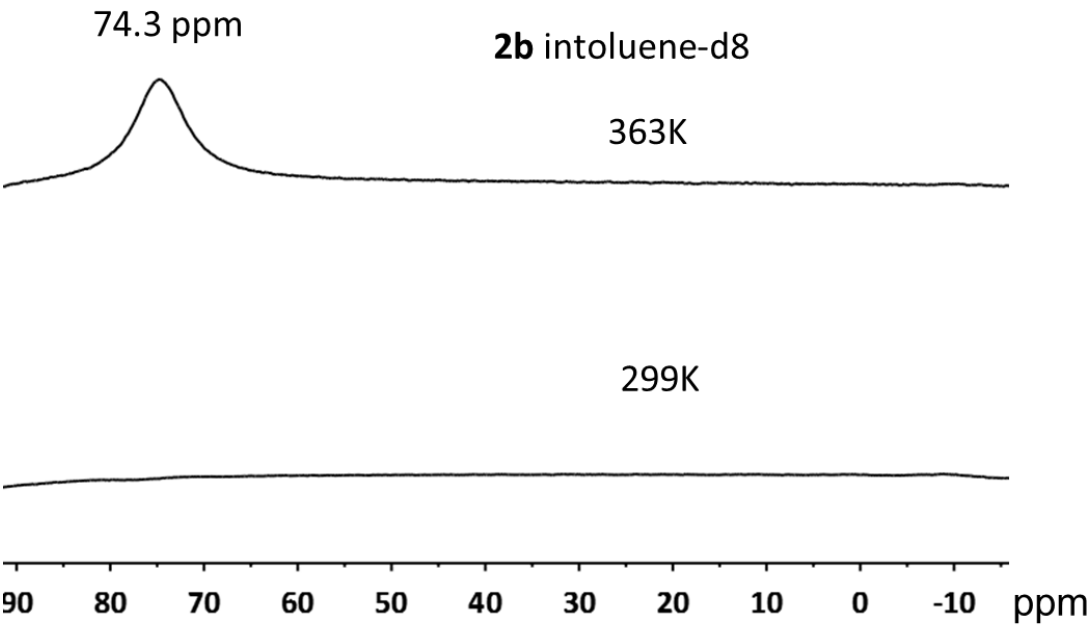


Figure S11. ^{11}B NMR spectrum of compound **2b** in d_8-toluene.

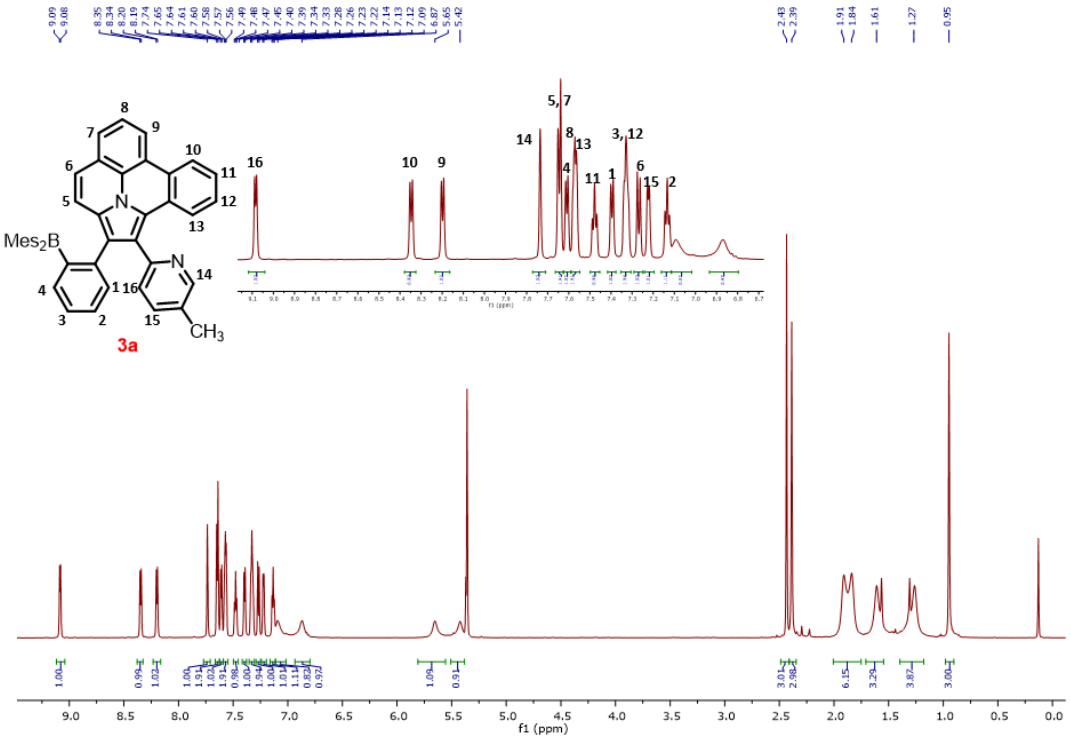


Figure S12. ^{1}H NMR spectrum of compound **3a** in CD_2Cl_2

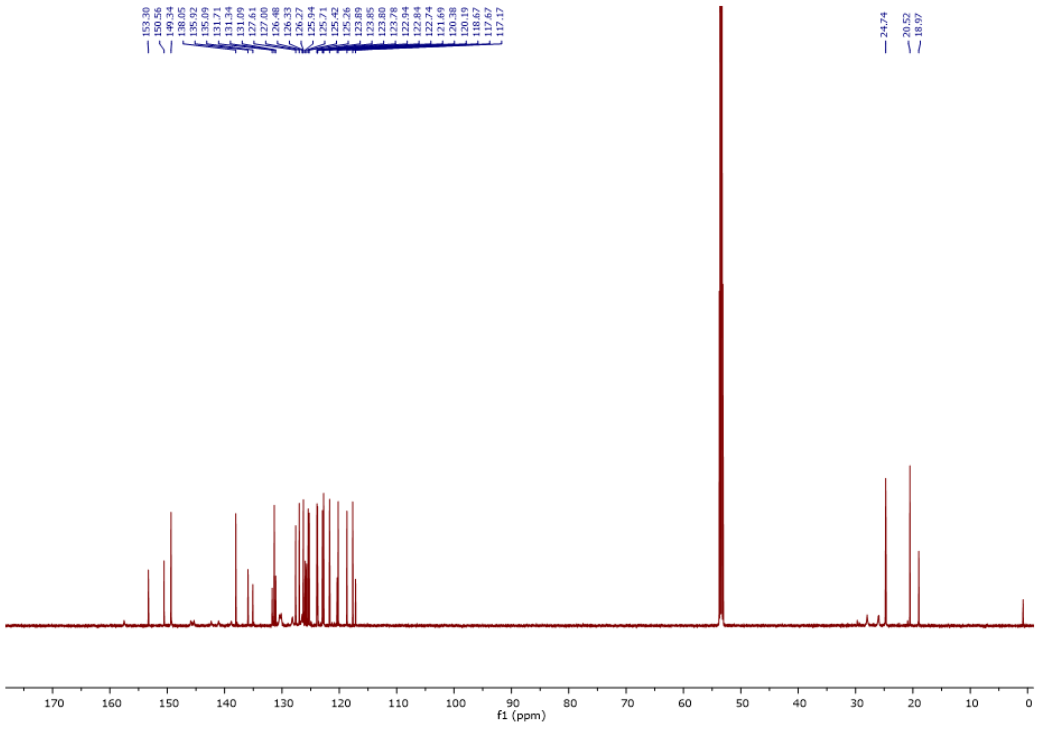


Figure S13. ^{13}C NMR spectrum of compound **3a** in CD_2Cl_2

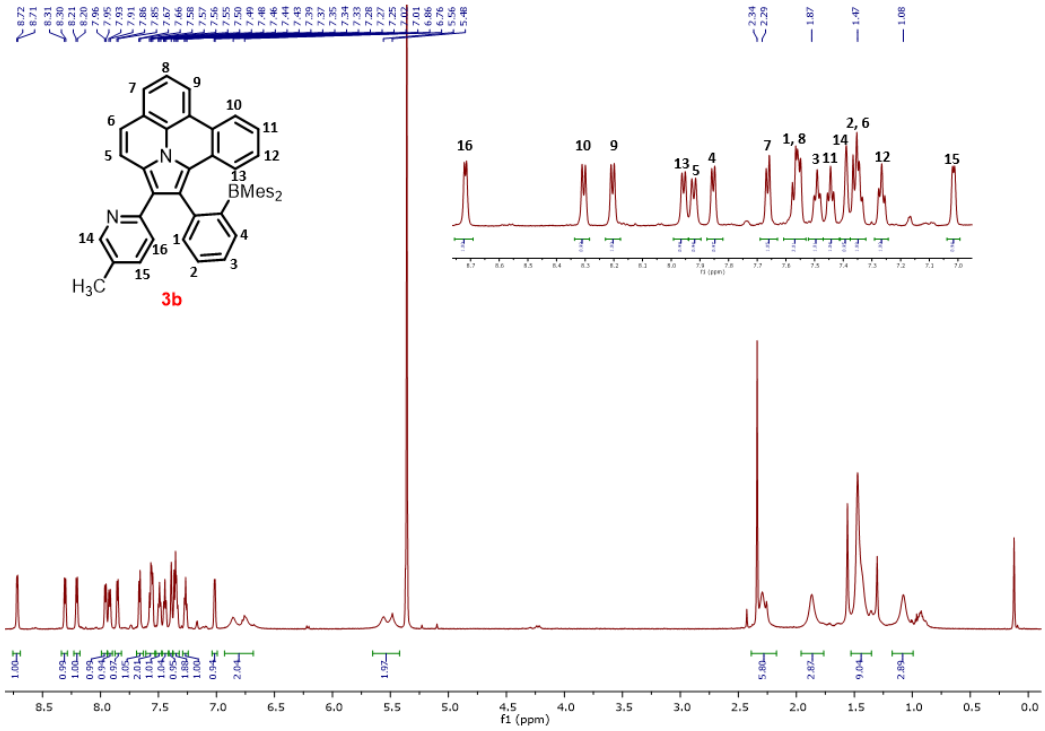


Figure S14. ^{1}H NMR spectrum of compound **3b** in CD_2Cl_2

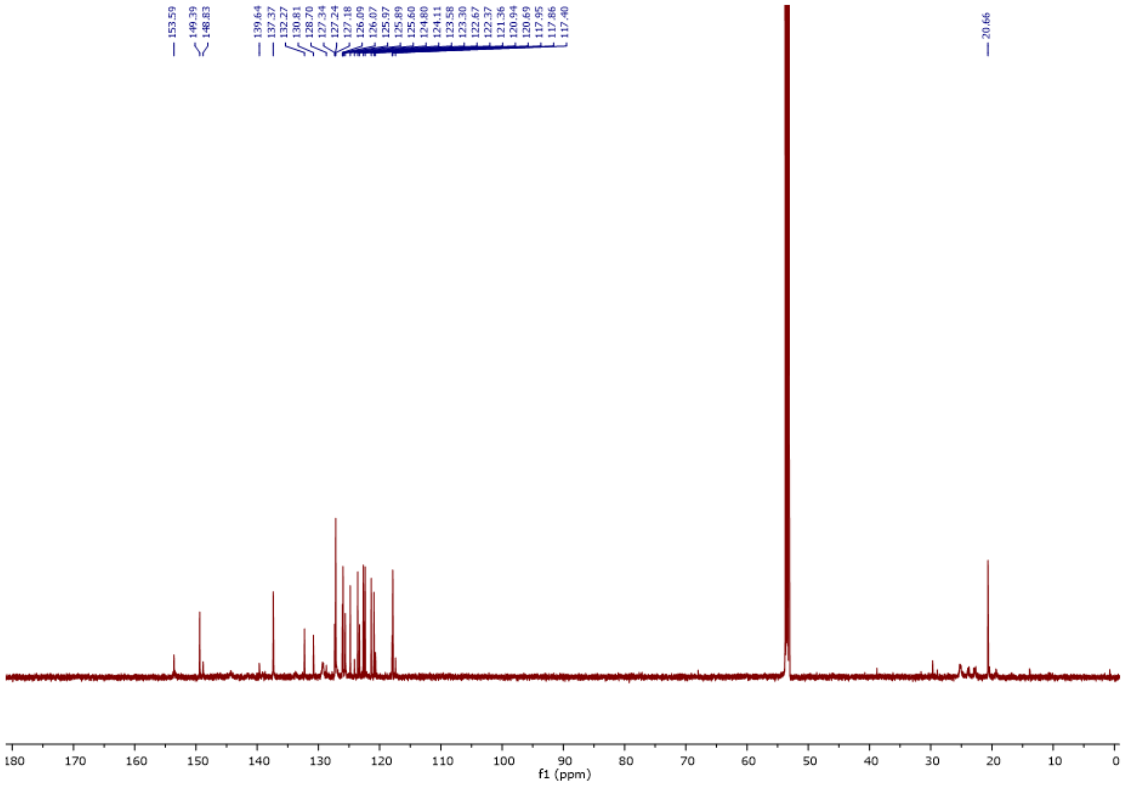


Figure S15. ^{13}C NMR spectrum of compound **3b** in CD_2Cl_2.

III. UV-Vis and fluorescence data

UV-vis and Fluorescent Spectra

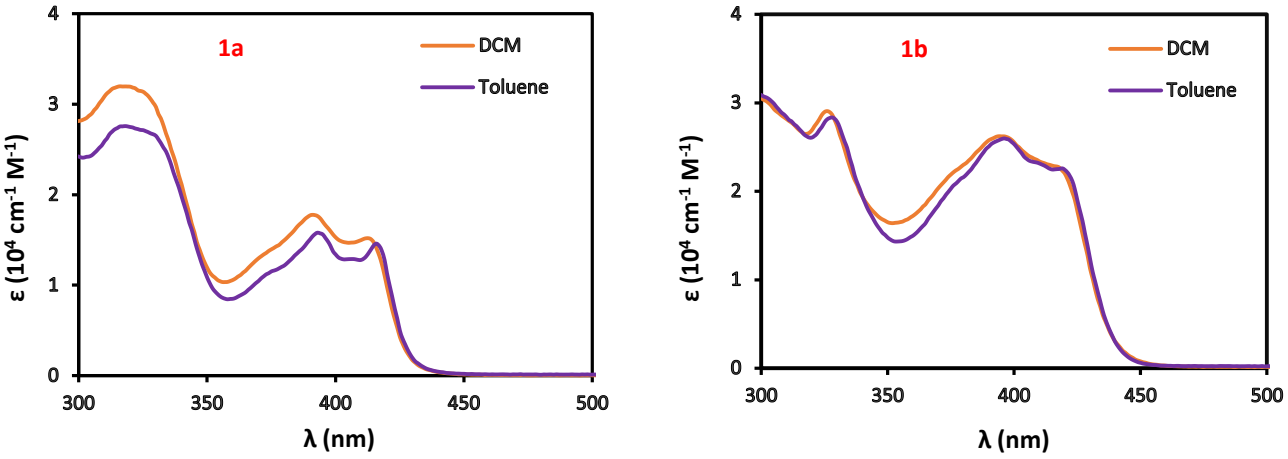


Figure S16. UV-vis spectra of compounds **1a** and **1b** in CH_2Cl_2 and toluene (c= 2×10^{-5} mol/L)

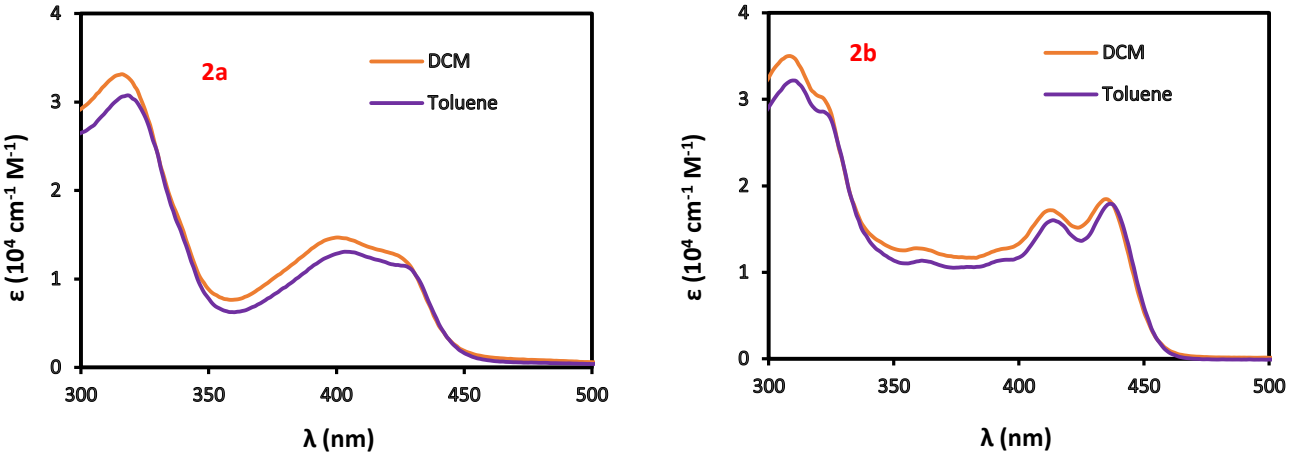


Figure S17. UV-vis spectra of compounds **2a** and **2b** in CH_2Cl_2 and toluene (c= 2×10^{-5} mol/L)

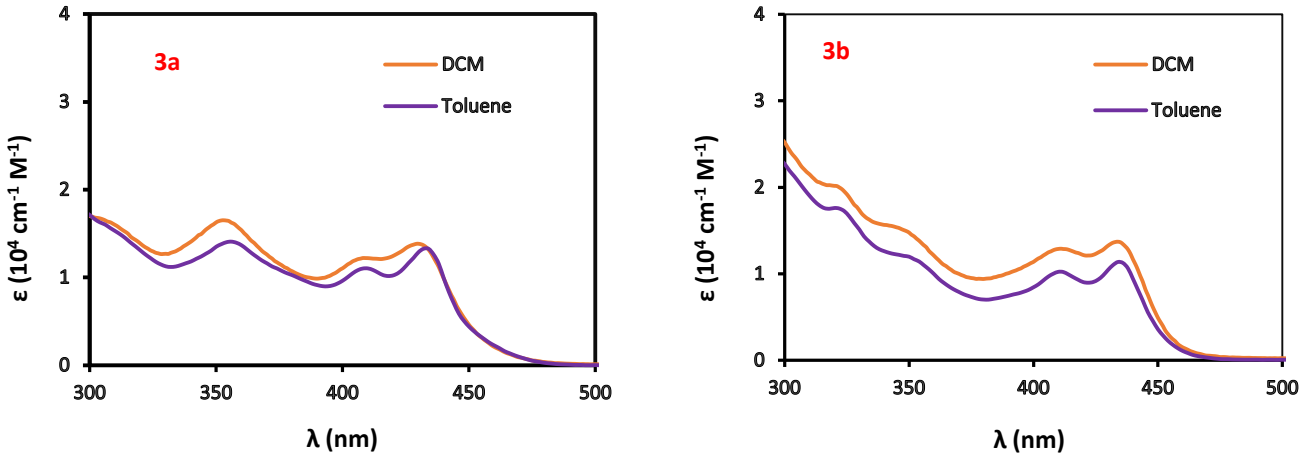


Figure S18. UV-vis spectra of compounds **3a** and **3b** in CH_2Cl_2 and toluene (c= 2×10^{-5} mol/L)

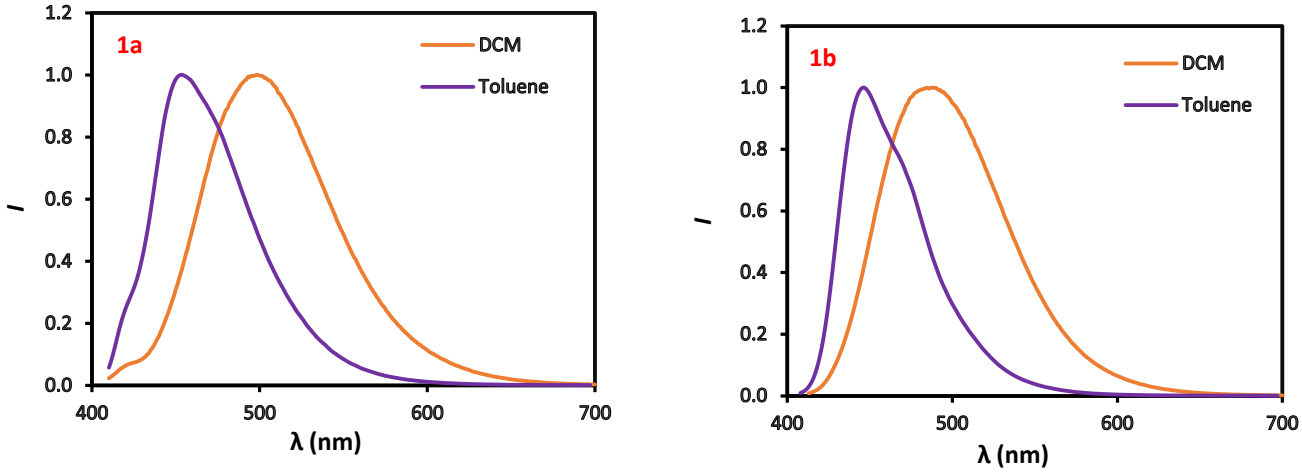


Figure S19. Fluorescence spectra of compounds **1a** and **1b** in CH_2Cl_2 and toluene (c= 2×10^{-5} mol/L)

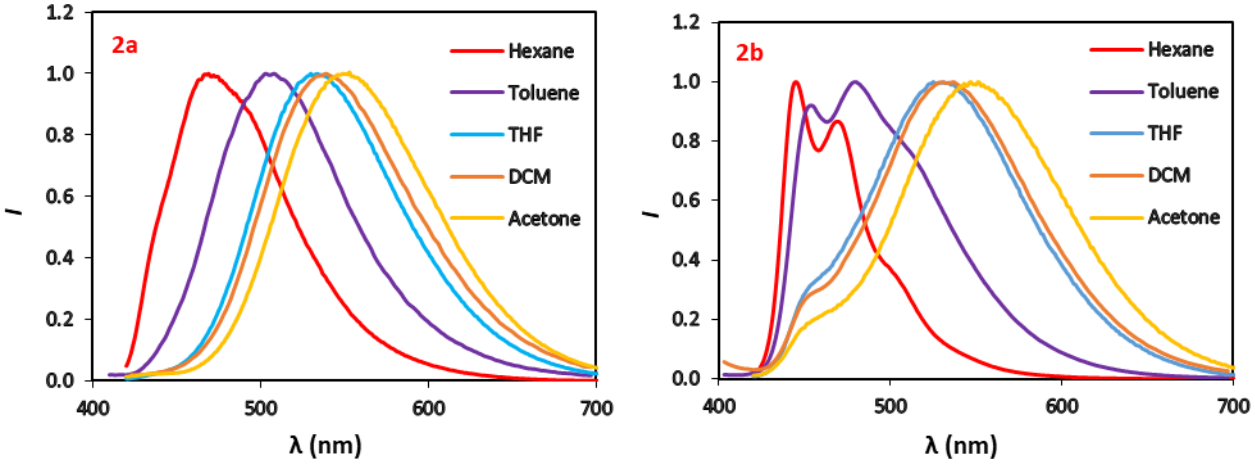


Figure S20. Fluorescence spectra of compounds **2a** and **2b** in hexane, toluene, THF, CH_2Cl_2 and acetone (c= 2×10^{-5} mol/L, λ_{ex}= 390 nm was used for the emission spectra of **2a** and **2b** in hexane, THF and acetone)

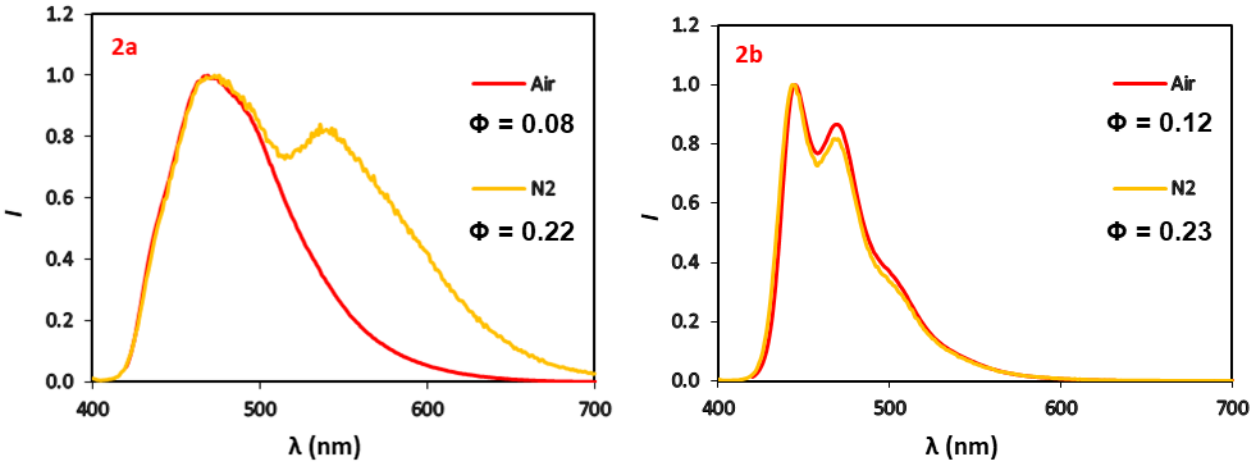


Figure S21. Fluorescence spectra of compounds **2a** and **2b** in hexane under air and N_2 (c= 2×10^{-5} mol/L, λ_{ex}= 390 nm)

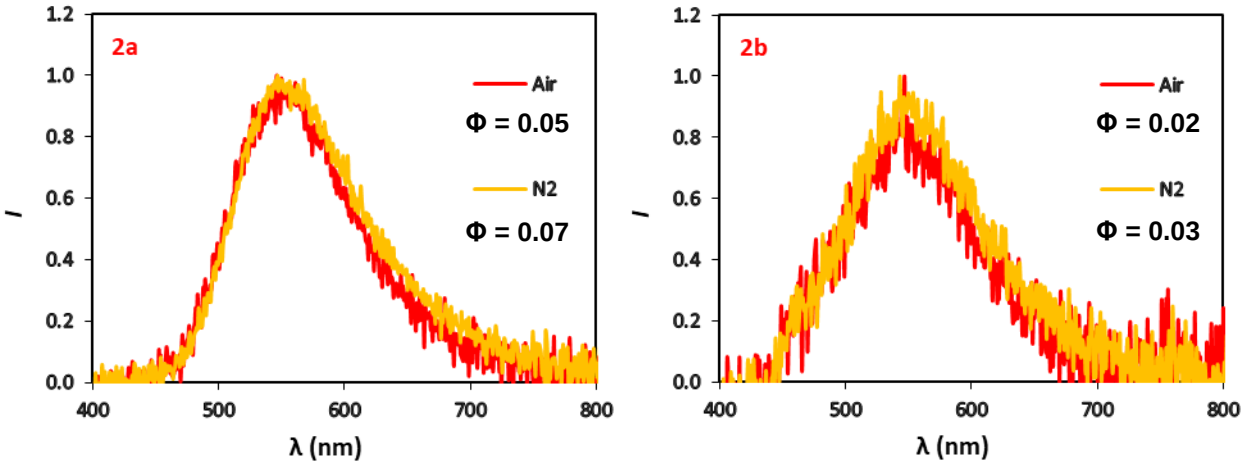


Figure S22. Fluorescence spectra of compounds **2a** and **2b** in THF under air and N_2 (c= 2×10^{-5} mol/L, λ_{ex}= 390 nm)

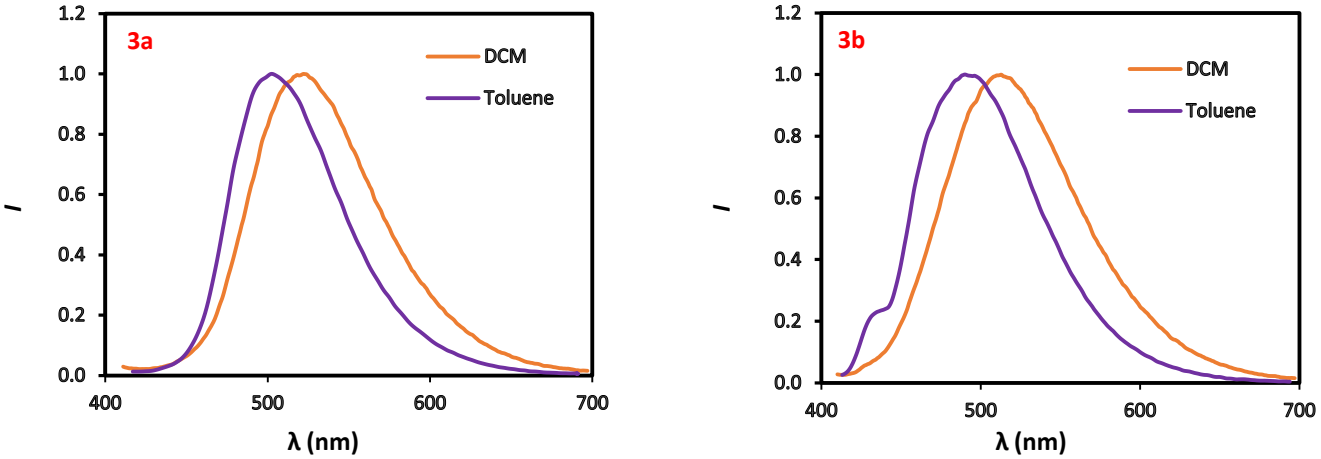


Figure S23. Fluorescence spectra of compounds **3a** and **3b** in CH_2Cl_2 and toluene (c= 2×10^{-5} mol/L)

Fluorescence Spectra at Different Concentrations in CH_2Cl_2

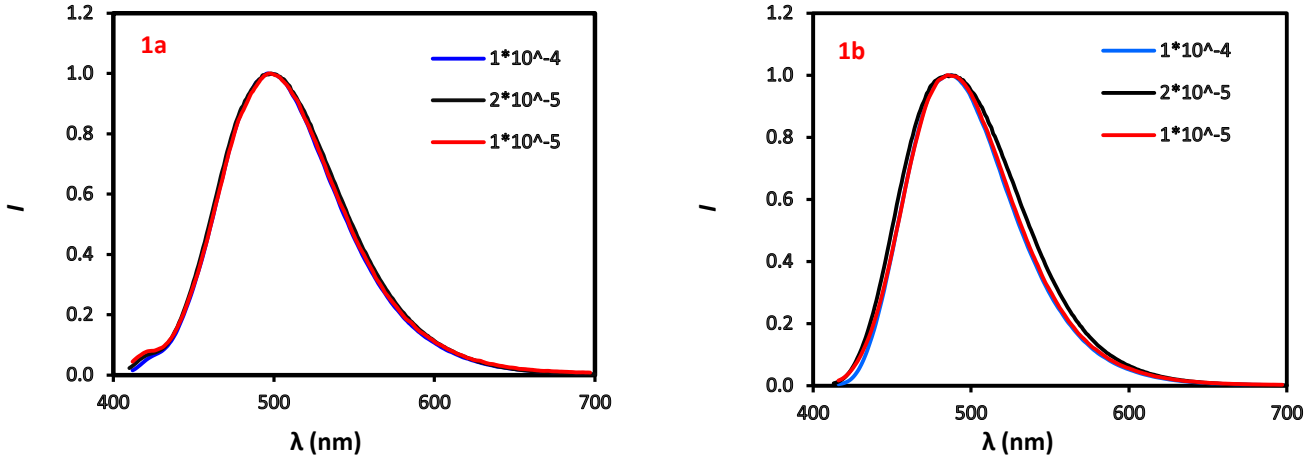


Figure S24. Fluorescence spectra of compounds **1a** and **1b** at different concentrations of CH_2Cl_2 solution.

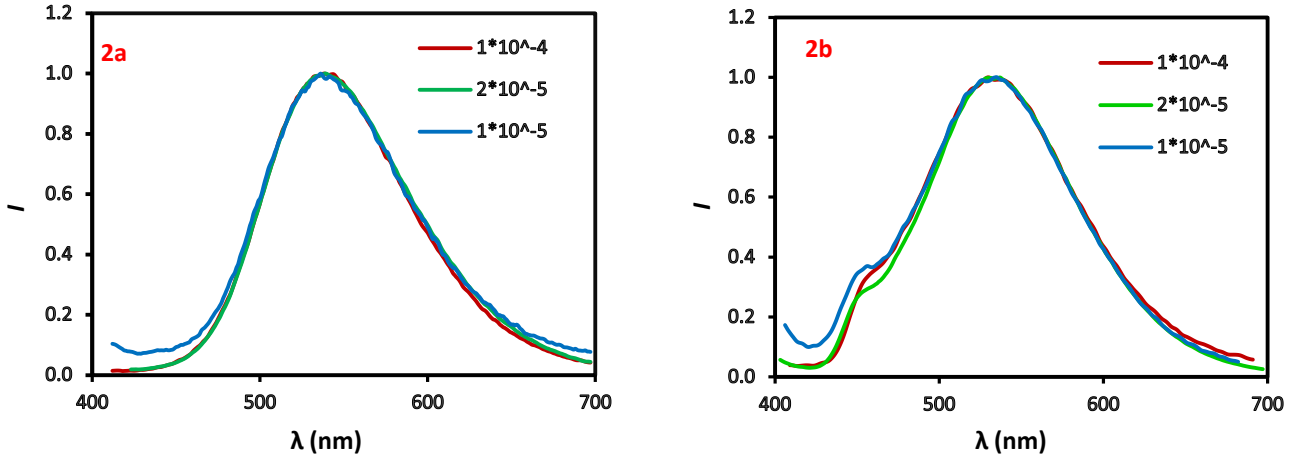


Figure S25. Fluorescence spectra of compounds **2a** and **2b** at different concentrations of CH_2Cl_2 solution.

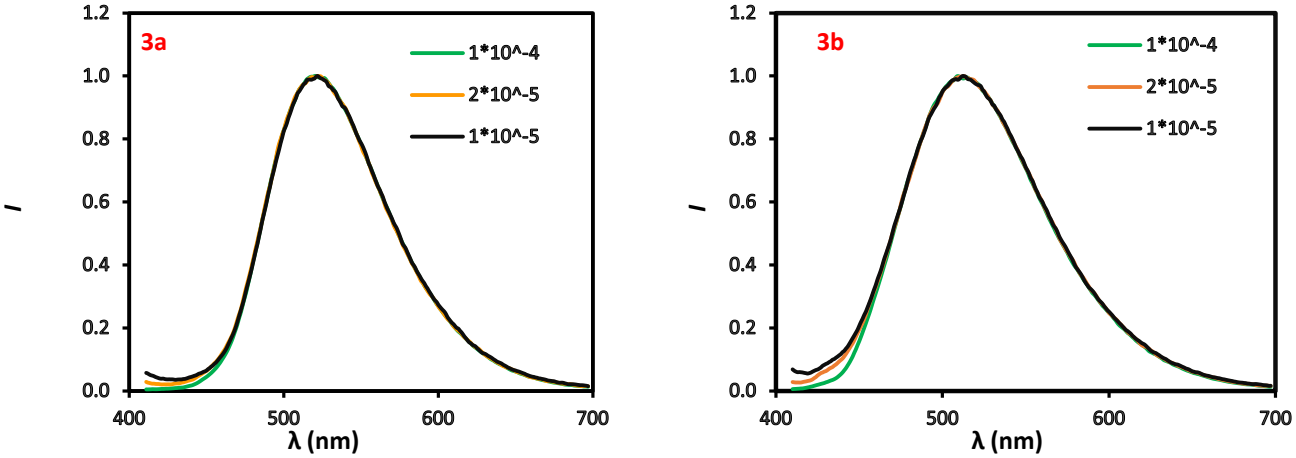


Figure S26. Fluorescence spectra of compounds **3a** and **3b** at different concentrations of CH_2Cl_2 solution

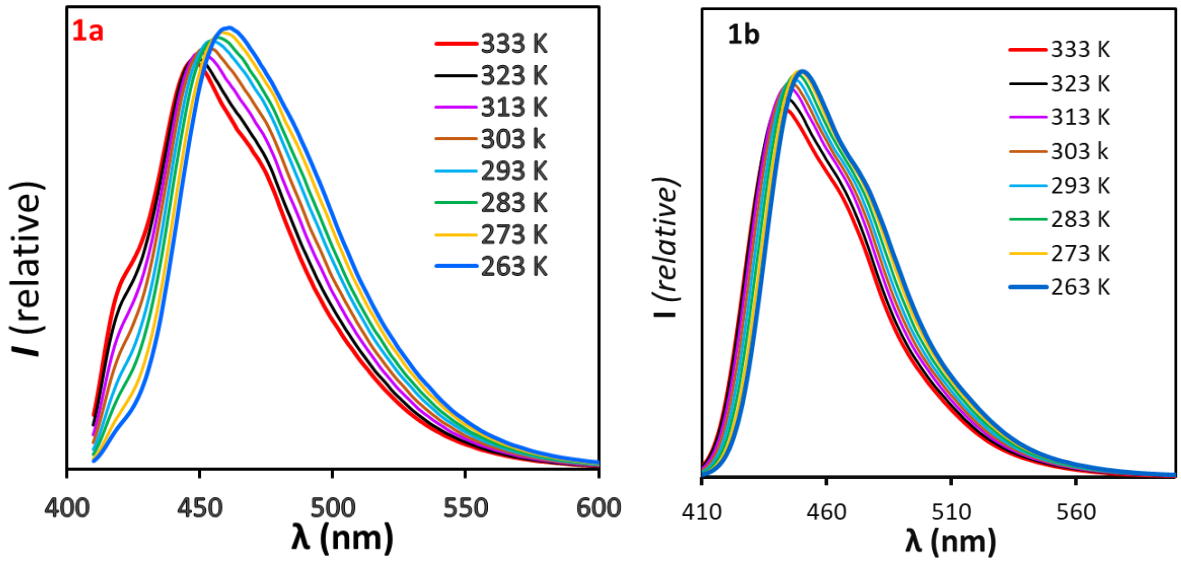


Figure S27. Emission spectra of compounds **1a** and **1b** in toluene (c= 2×10^{-5} mol/L) recorded between 263 K and 333 K

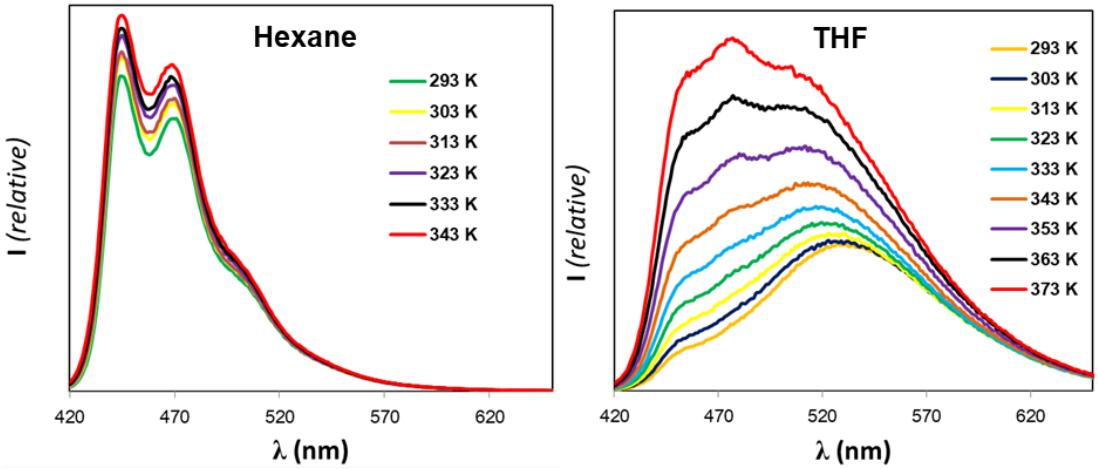


Figure S28. Emission spectra of compounds **2b** in hexane and THF (c= 2×10^{-5} mol/L, λ_{ex}= 390 nm)

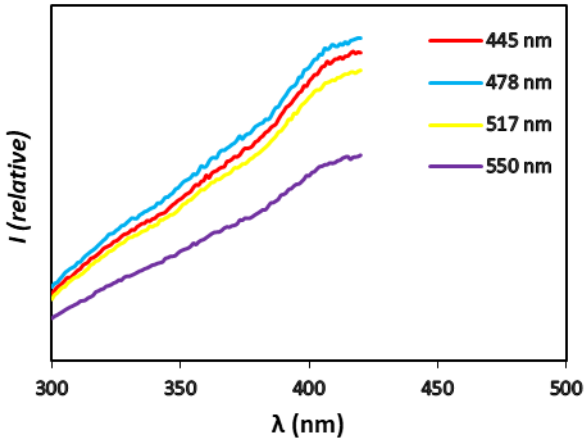


Figure S29. Excitation spectra of compounds **2b** in THF (c= 2×10^{-5} mol/L) at 373 K

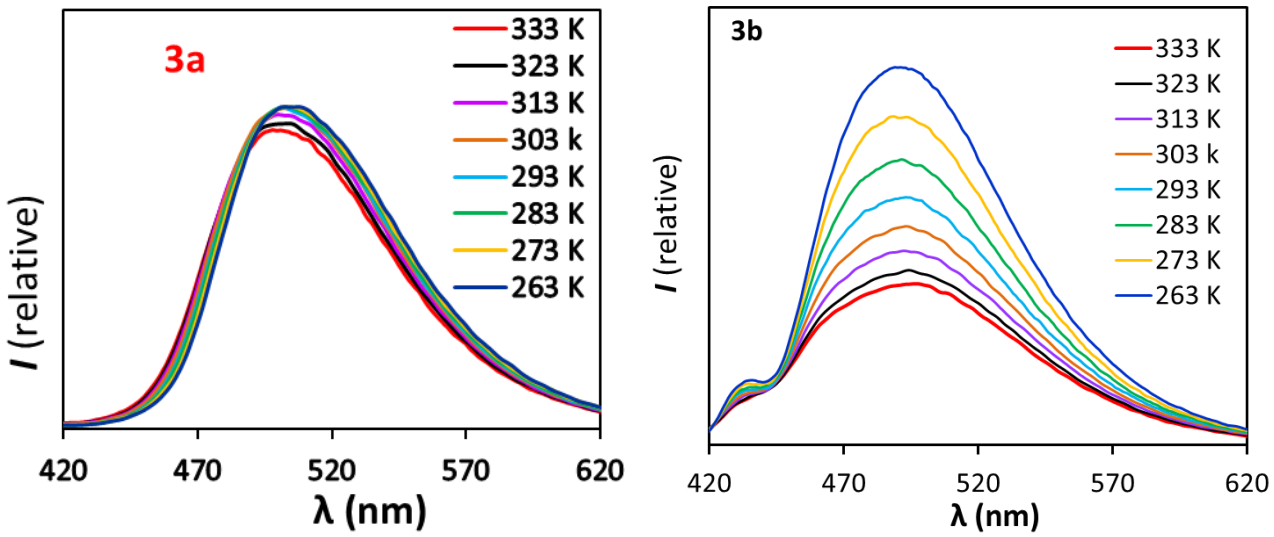


Figure S30. Emission spectra of compounds **3a** and **3b** in toluene (c= 2×10^{-5} mol/L) recorded between 263 K and 333 K.

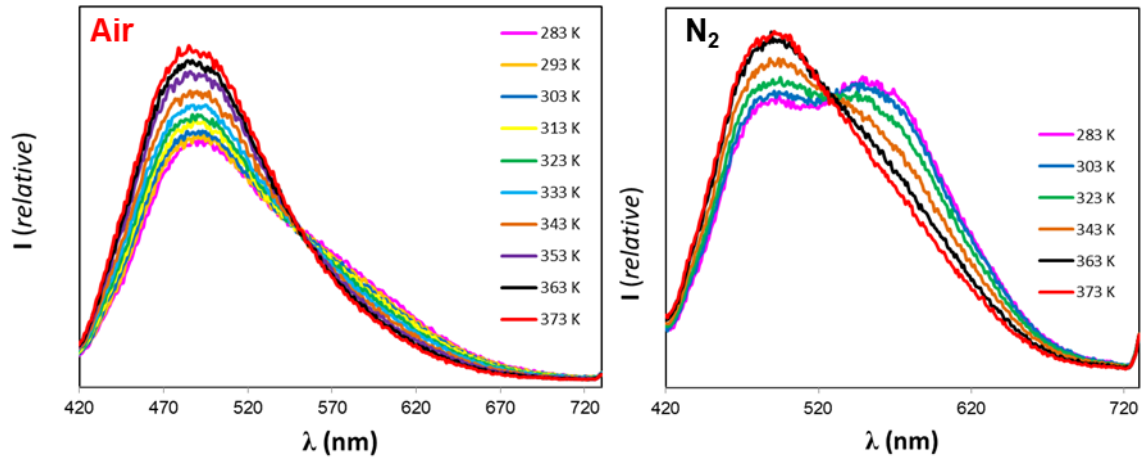


Figure S31. Emission spectra of compounds **2a** in PMMA films (5 wt%) recorded under air and N_2 between 283 K and 373 K (λ_{ex}= 380 nm).

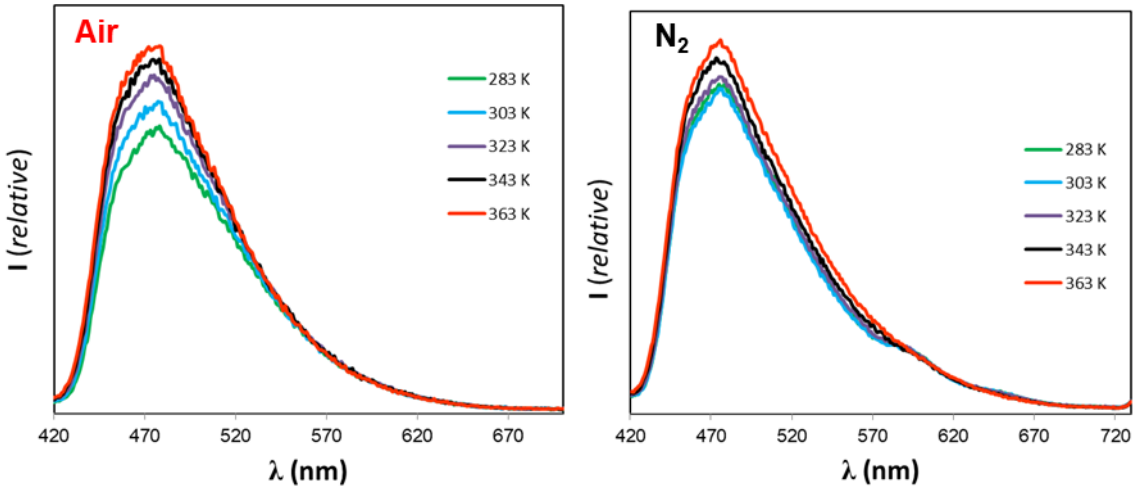


Figure S32. Emission spectra of compounds **2b** in PMMA films (5 wt%) recorded under air and N_2 between 283 K and 363 K (λ_{ex}= 380 nm).

IV. TD-DFT Computational Calculation Data

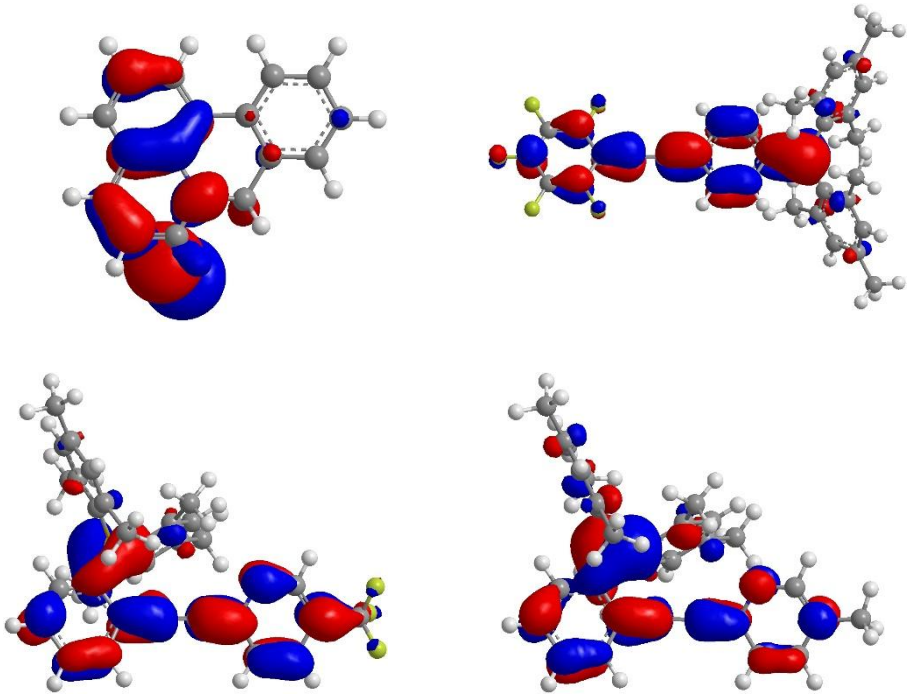


Figure S33. HOMO of 8*H*-pyrido[3,2,1-*de*]phenanthridine-7-ium-8-ide (top left) and LUMO of the internal alkynes used for the synthesis of **1a**/**b** (top right), **2a/b** (bottom left) and **3a/b** (bottom right).

Table S1. TD-DFT calculated electronic transition configurations for **1a** along with their corresponding excitation energies and oscillator strengths

Spin State	Transition Configuration	Excitation Energy	Oscillator Strength
S_1	HOMO → LUMO (98%)	419 nm (2.96 eV)	0.3002
S_2	HOMO → LUMO+1 (71%) HOMO → LUMO+2 (21%)	377 nm (3.29 eV)	0.0816
S_3	HOMO → LUMO+1 (22%) HOMO → LUMO+2 (63%)	366 n (3.39 eV)	0.0367
S_4	HOMO-2 → LUMO (87%)	351 nm (3.54 eV)	0.0749
S_5	HOMO-3 → LUMO (35%) HOMO-1 → LUMO (48%)	340 nm (3.64 eV)	0.1465
S_6	HOMO-3 → LUMO (18%) HOMO → LUMO+3 (53%) HOMO → LUMO+4 (10%)	336 nm (3.69 eV)	0.0153

Table S2. Primary orbitals which contribute to the calculated transitions of **1a** (iso = 0.03)

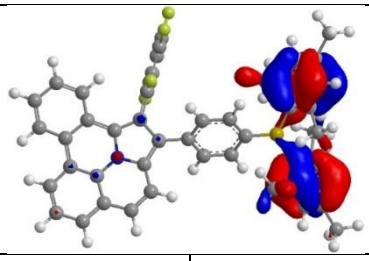
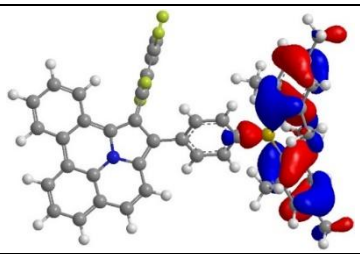
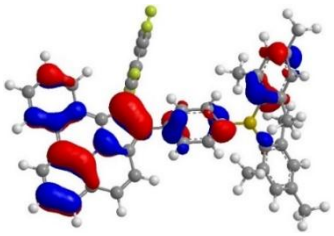
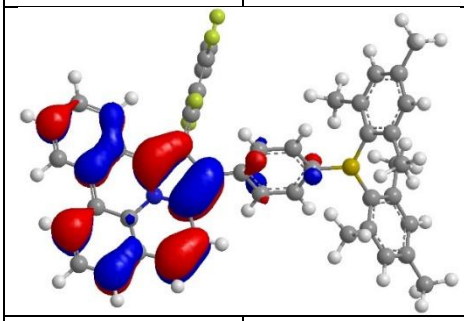
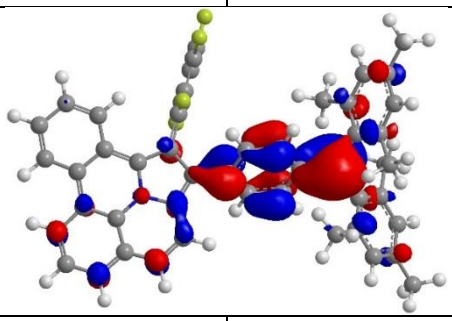
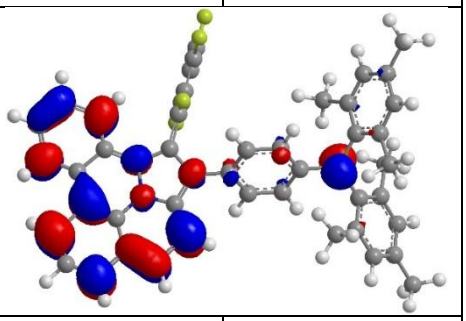
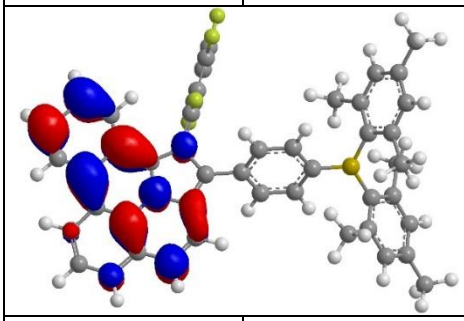
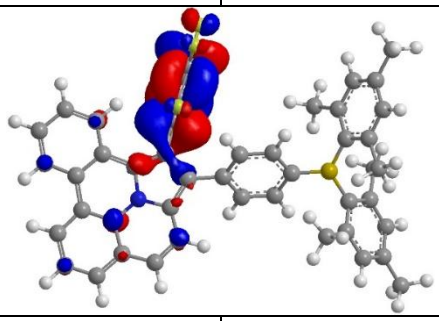
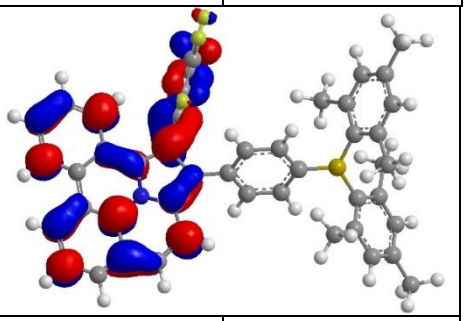
					
HOMO-3	-6.07 eV	HOMO-2	-5.99 eV	HOMO-1	-5.95 eV
					
HOMO	-5.07 eV	LUMO	-1.72 eV	LUMO+1	-1.33 eV
					
LUMO+2	-1.02 eV	LUMO+3	-0.77 eV	LUMO+4	-0.74 eV

Table S3. TD-DFT calculated electronic transition configurations for **1b** along with their corresponding excitation energies and oscillator strengths

Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
S_1	HOMO → LUMO (98%)	423 nm (2.93 eV)	0.0935
S_2	HOMO → LUMO+1 (89%)	382 nm (3.25 eV)	0.1827
S_3	HOMO → LUMO+2 (82%)	366 nm (3.39 eV)	0.0342
S_4	HOMO-2 → LUMO (94%)	356 nm (3.49 eV)	0.0798
S_5	HOMO-3 → LUMO (42%) HOMO-1 → LUMO (50%)	343 nm (3.62 eV)	0.2322
S_6	HOMO-4 → LUMO (37%) HOMO-3 → LUMO (34%) HOMO-1 → LUMO (12%)	335 nm (3.70 eV)	0.0438

Table S4. Primary orbitals which contribute to the calculated transitions of **1b** (iso = 0.03)

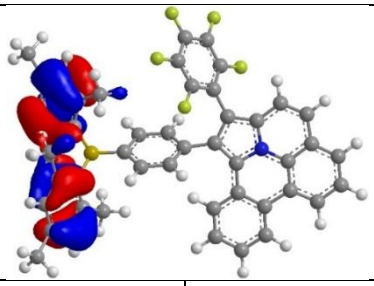
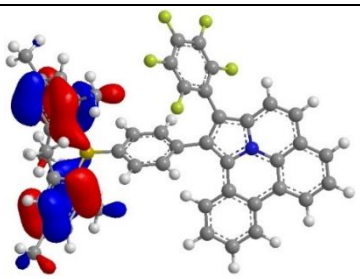
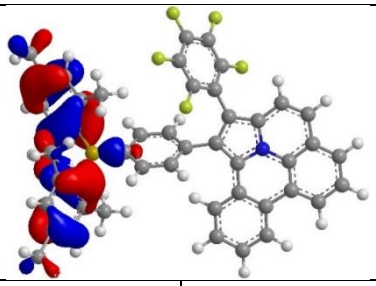
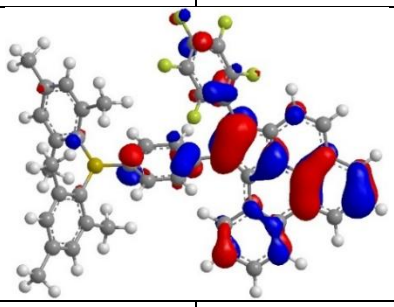
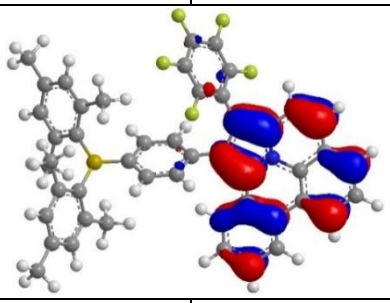
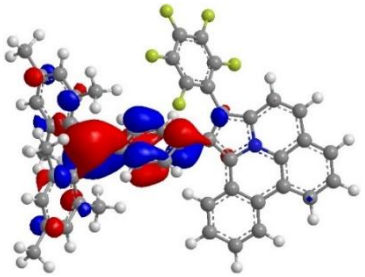
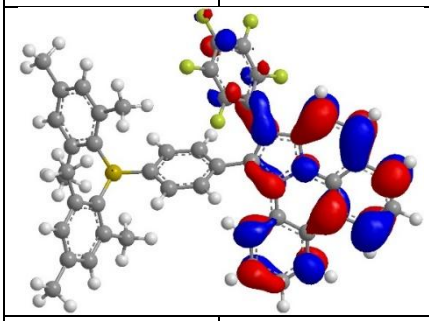
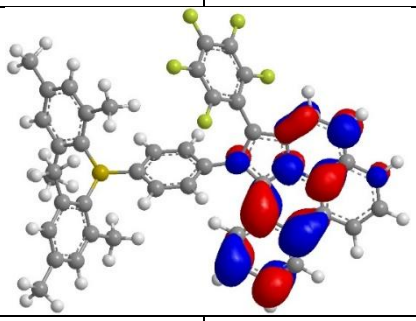
					
HOMO-4	-6.13 eV	HOMO-3	-6.10 eV	HOMO-2	-5.97 eV
					
HOMO-1	-5.91 eV	HOMO	-5.09 eV	LUMO	-1.73 eV
					
LUMO+1	-1.46 eV	LUMO+2	-0.99 eV		

Table S5. TD-DFT calculated electronic transition configurations for **2a** along with their corresponding excitation energies and oscillator strengths

Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
S_1	HOMO → LUMO (98%)	454 nm (2.73 eV)	0.0050
S_2	HOMO → LUMO+1 (95%)	421 nm (2.95 eV)	0.0985
S_3	HOMO → LUMO+2 (40%) HOMO → LUMO+4 (10%)	380 nm (3.27 eV)	0.0763
S_4	HOMO → LUMO+3 (10%) HOMO → LUMO+4 (73%)	368 nm (3.37 eV)	0.0346
S_5	HOMO-1 → LUMO (83%)	366 nm (3.39 eV)	0.0175
S_6	HOMO → LUMO+3 (85%) HOMO → LUMO+4 (11%)	359 nm (3.45 eV)	0.0049

Table S6. Primary orbitals which contribute to the calculated transitions of **2a** (iso = 0.03)

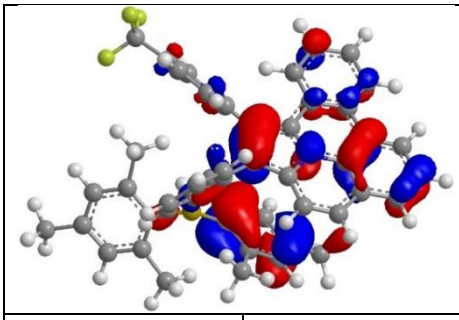
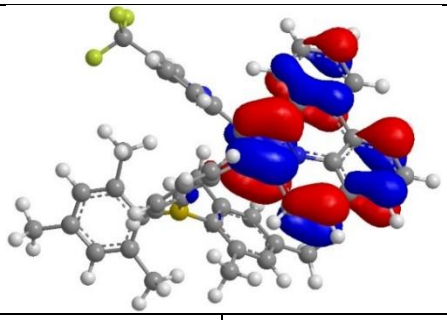
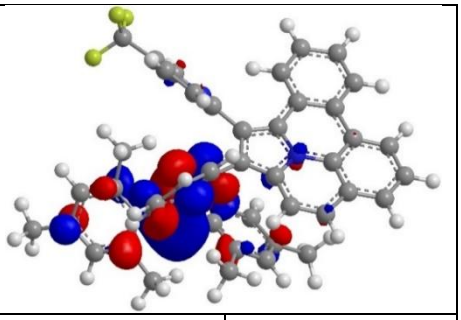
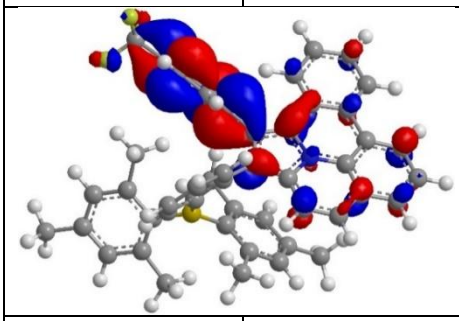
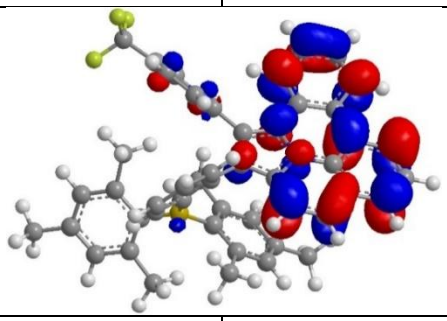
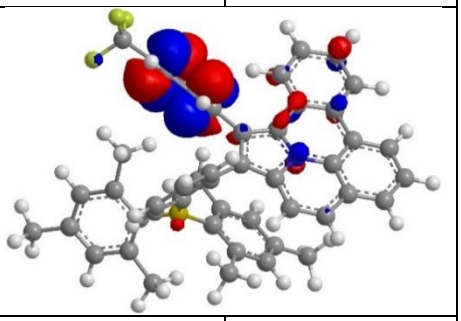
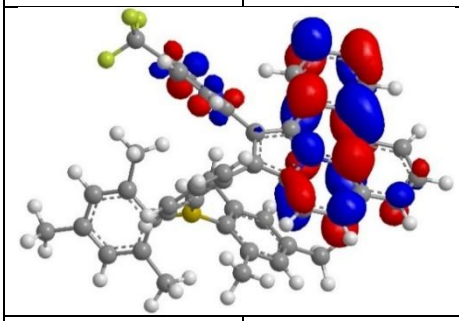
					
HOMO-1	-5.70 eV	HOMO	-4.89 eV	LUMO	-1.61 eV
					
LUMO+1	-1.43 eV	LUMO+2	-1.16 eV	LUMO+3	-0.91 eV
					
LUMO+4	-0.80 eV				

Table S7. TD-DFT calculated electronic transition configurations for **2b** along with their corresponding excitation energies and oscillator strengths

Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
S_1	HOMO → LUMO (43%) HOMO → LUMO+1 (55%)	438 nm (2.83 eV)	0.0079
S_2	HOMO → LUMO (53%) HOMO → LUMO+1 (42%)	410 nm (3.03 eV)	0.2106
S_3	HOMO → LUMO+2 (50%) HOMO → LUMO+3 (37%)	375 nm (3.31 eV)	0.0243
S_4	HOMO-1 → LUMO (37%) HOMO-1 → LUMO+1 (54%)	368 nm (3.38 eV)	0.0309
S_5	HOMO → LUMO+2 (40%) HOMO → LUMO+3 (50%)	355 nm (3.49 eV)	0.0151
S_6	HOMO-1 → LUMO (45%) HOMO-1 → LUMO+1 (28%)	351 nm (3.54 eV)	0.1166

Table S8. Primary orbitals which contribute to the calculated transitions of **2b** (iso = 0.03)

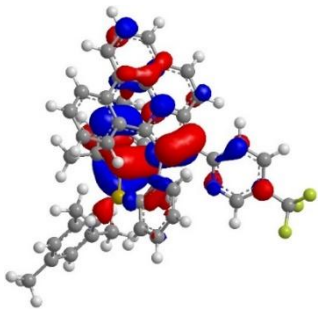
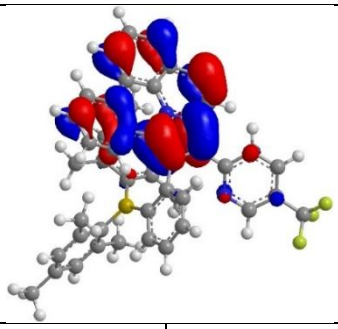
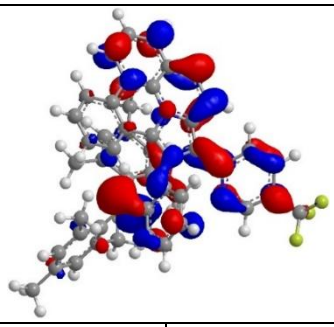
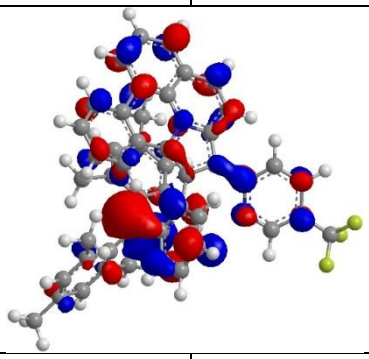
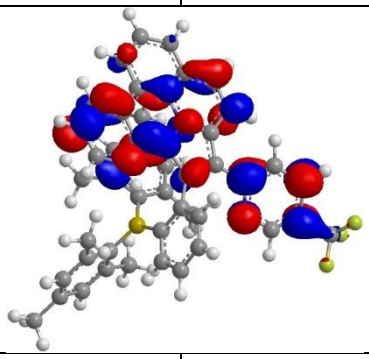
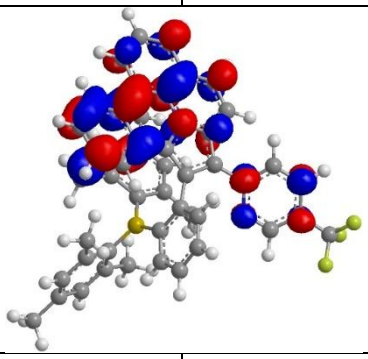
					
HOMO-1	-5.67 eV	HOMO	-5.00 eV	LUMO	-1.60 eV
					
LUMO+1	-1.57 eV	LUMO+2	-1.03 eV	LUMO+3	-0.94 eV

Table S9. TD-DFT calculated electronic transition configurations for **3a** along with their corresponding excitation energies and oscillator strengths

Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
S_1	HOMO → LUMO (98%)	465 nm (2.67 eV)	0.0070
S_2	HOMO → LUMO+1 (82%)	385 nm (3.22 eV)	0.1676
S_3	HOMO → LUMO+2 (85%)	379 nm (3.27 eV)	0.0422
S_4	HOMO → LUMO+3 (79%)	370 nm (3.35 eV)	0.0150
S_5	HOMO-1 → LUMO (84%)	369 nm (3.36 eV)	0.0142
S_6	HOMO-3 → LUMO (27%) HOMO-2 → LUMO (71%)	344 nm (3.60 eV)	0.0032

Table S10. Primary orbitals which contribute to the calculated transitions of **3a** (iso = 0.03)

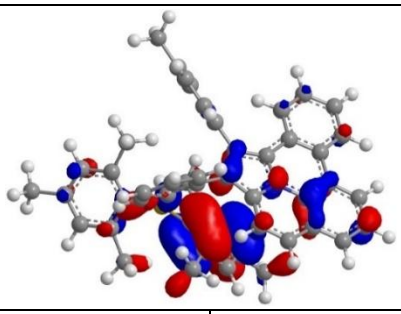
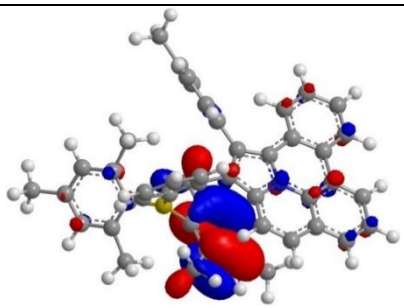
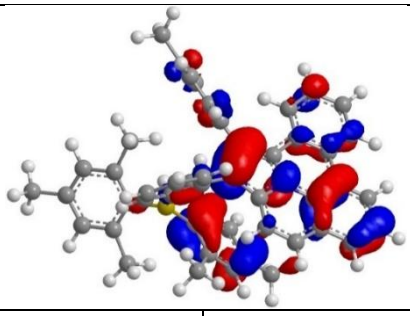
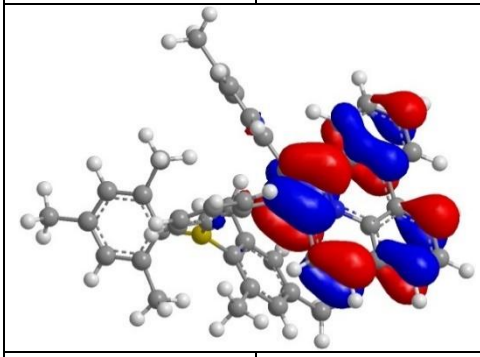
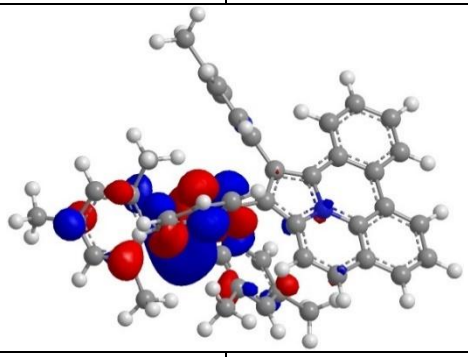
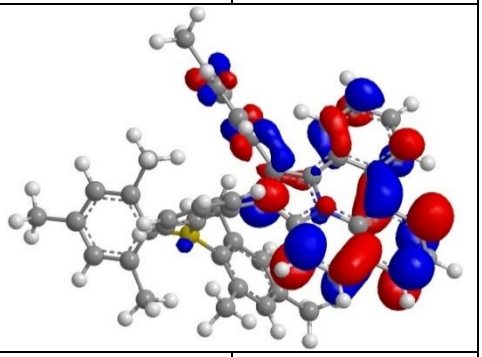
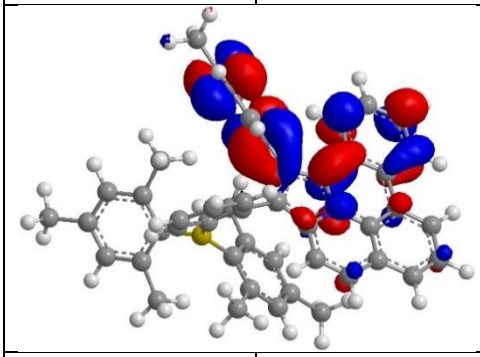
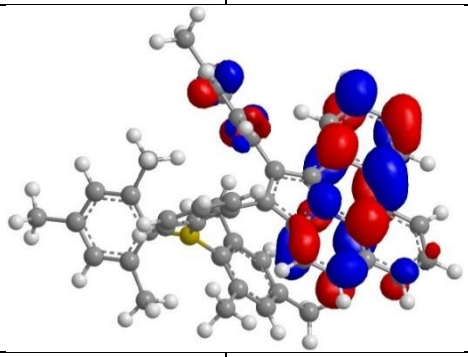
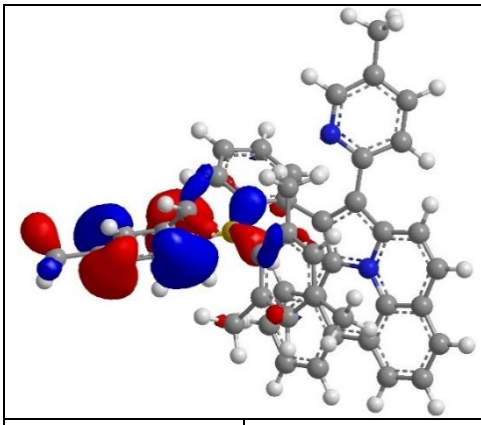
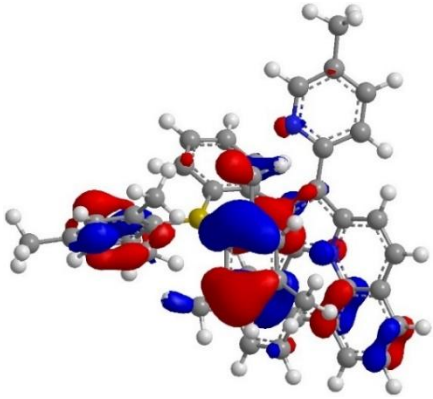
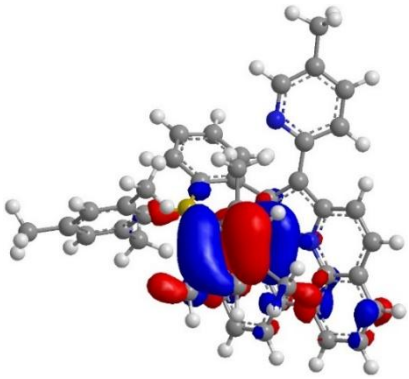
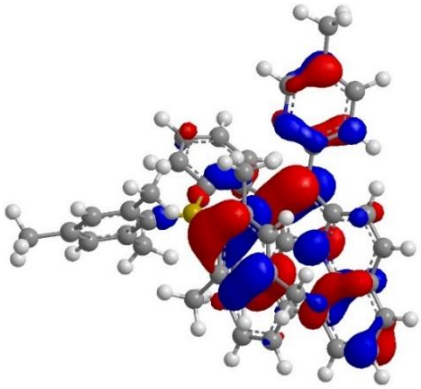
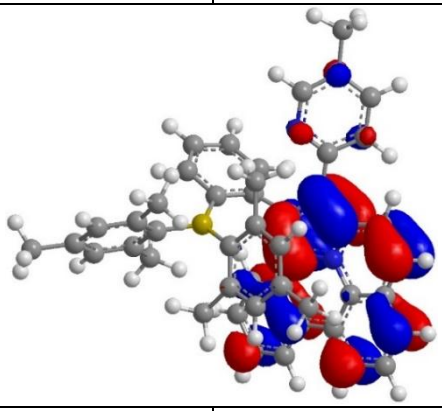
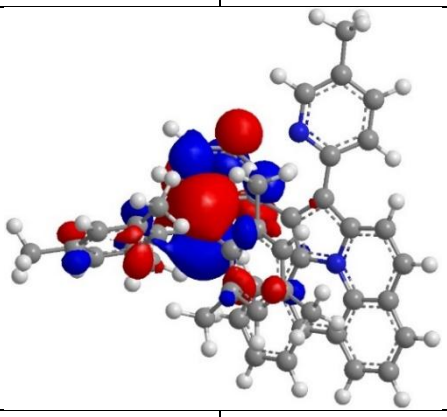
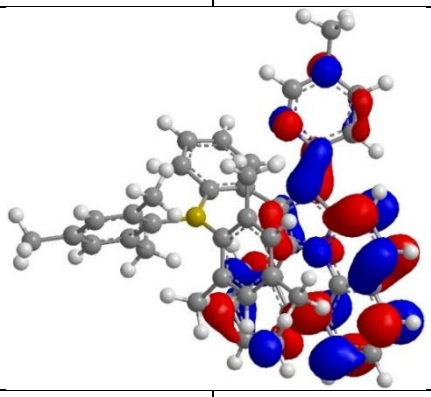
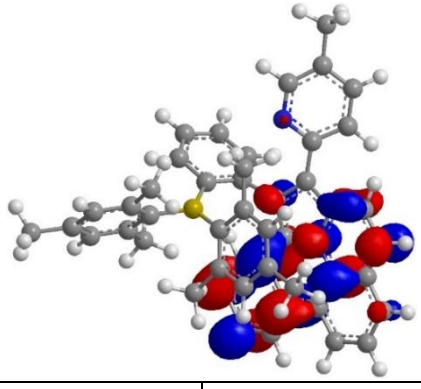
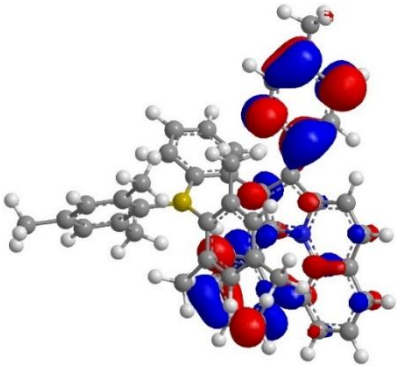
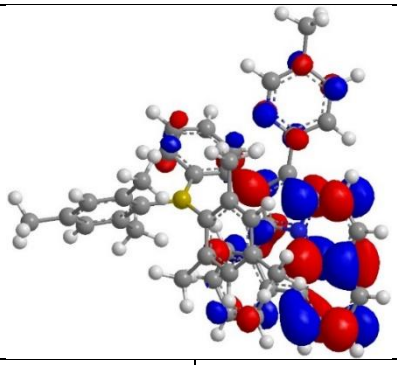
					
HOMO-3	-5.81 eV	HOMO-2	-5.79 eV	HOMO-1	-5.53 eV
					
HOMO	-4.71 eV	LUMO	-1.50 eV	LUMO+1	-1.04 eV
					
LUMO+2	-0.91 eV	LUMO+3	-0.64 eV		

Table S11. TD-DFT calculated electronic transition configurations for **3b** along with their corresponding excitation energies and oscillator strengths

Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
S_1	HOMO → LUMO (98%)	452 nm (2.74 eV)	0.0056
S_2	HOMO → LUMO+1 (93%)	401 nm (3.09 eV)	0.1877
S_3	HOMO → LUMO+2 (84%)	378 nm (3.28 eV)	0.0248
S_4	HOMO-1 → LUMO (92%)	375 nm (3.31 eV)	0.0223
S_5	HOMO-1 → LUMO+1 (47%)	349 nm (3.55 eV)	0.0154
	HOMO → LUMO+3 (18%)		
	HOMO → LUMO+4 (18%)		
S_6	HOMO-4 → LUMO (24%)	347 nm (3.57 eV)	0.0320
	HOMO-3 → LUMO (13%)		
	HOMO-2 → LUMO (46%)		

Table S12. TD-DFT calculated electronic transition configurations for **3b** along with their corresponding excitation energies and oscillator strengths

					
HOMO-4	-5.83 eV	HOMO-3	-5.76 eV	HOMO-2	-5.74 eV
					
HOMO-1	-5.48 eV	HOMO	-4.77 eV	LUMO	-1.46 eV
					
LUMO+1	-1.29 eV	LUMO+2	-0.80 eV	LUMO+3	-0.60 eV

	
LUMO+4	-0.41 eV

V. X-ray Crystallographic Data

Table S13. Crystal data and structure refinement for 1b.

Identification code	1b	
Empirical formula	C49 H36 B Cl3 F5 N	
Formula weight	850.95	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.2594(11) Å	□ = 90°.
	b = 24.311(2) Å	□ = 97.933(5)°.
	c = 20.696(2) Å	□ = 90°.
Volume	4115.9(8) $Å^3$	
Z	4	
Density (calculated)	1.373 Mg/m^3	
Absorption coefficient	0.282 mm^{-1}	
F(000)	1752	
Crystal size	0.240 x 0.060 x 0.060 mm^3	
Theta range for data collection	2.490 to 27.139°.	
Index ranges	-10<=h<=10, -31<=k<=31, -26<=l<=26	
Reflections collected	64838	
Independent reflections	9101 [R(int) = 0.1110]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.985 and 0.935	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9101 / 0 / 539	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0675, wR2 = 0.1587	
R indices (all data)	R1 = 0.1391, wR2 = 0.2030	
Extinction coefficient	0.0023(5)	
Largest diff. peak and hole	0.681 and -0.692 $e.Å^{-3}$	

Table S13a. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 1b. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	2249(5)	2795(2)	2322(2)	39(1)
N(1)	7863(3)	4401(1)	5186(1)	31(1)
C(1)	7506(4)	3504(1)	5029(1)	36(1)
C(2)	6558(4)	3785(1)	4507(1)	33(1)
C(3)	6769(4)	4346(1)	4617(1)	31(1)
C(4)	8319(4)	3889(1)	5449(1)	34(1)
C(5)	6089(4)	4848(1)	4316(1)	31(1)
C(6)	4822(4)	4839(1)	3788(2)	36(1)
C(7)	4188(4)	5318(1)	3504(2)	42(1)
C(8)	4785(4)	5821(1)	3740(2)	44(1)
C(9)	6002(4)	5843(1)	4266(2)	42(1)
C(10)	6671(4)	5362(1)	4568(1)	33(1)
C(11)	7913(4)	5386(1)	5147(2)	34(1)
C(12)	8565(4)	5873(1)	5437(2)	44(1)
C(13)	9675(5)	5864(2)	6002(2)	50(1)
C(14)	10180(4)	5376(2)	6296(2)	45(1)
C(15)	9596(4)	4873(1)	6028(2)	37(1)
C(16)	10066(4)	4347(2)	6308(2)	44(1)
C(17)	9450(4)	3875(1)	6034(2)	40(1)
C(18)	8458(4)	4894(1)	5454(1)	32(1)
C(19)	5531(4)	3512(1)	3953(1)	33(1)
C(20)	5780(4)	3614(1)	3310(2)	37(1)
C(21)	4766(4)	3380(1)	2797(2)	37(1)
C(22)	3494(4)	3027(1)	2900(2)	35(1)
C(23)	3319(4)	2907(1)	3546(2)	39(1)
C(24)	4313(4)	3149(1)	4065(2)	38(1)
C(25)	1929(4)	3138(1)	1673(2)	42(1)
C(26)	1560(5)	3706(2)	1684(2)	48(1)
C(27)	1417(5)	4016(2)	1110(2)	59(1)

C(28)	1641(6)	3785(2)	518(2)	68(1)
C(29)	1965(5)	3230(2)	505(2)	63(1)
C(30)	2099(4)	2902(2)	1059(2)	48(1)
C(31)	2463(5)	2299(2)	989(2)	60(1)
C(32)	1206(6)	3999(2)	2294(2)	60(1)
C(33)	1508(8)	4133(2)	-97(2)	107(2)
C(34)	1380(4)	2240(1)	2466(2)	38(1)
C(35)	-324(4)	2222(1)	2472(2)	42(1)
C(36)	-1055(4)	1741(2)	2652(2)	46(1)
C(37)	-172(5)	1274(2)	2838(2)	46(1)
C(38)	1497(5)	1291(1)	2834(2)	47(1)
C(39)	2282(4)	1758(1)	2654(2)	42(1)
C(40)	4112(5)	1736(2)	2664(2)	54(1)
C(41)	-986(5)	757(2)	3039(2)	63(1)
C(42)	-1351(5)	2731(2)	2333(2)	58(1)
C(43)	7604(4)	2898(1)	5088(2)	41(1)
C(44)	8130(6)	2577(2)	4609(2)	65(1)
C(45)	8013(8)	2012(2)	4607(2)	86(2)
C(46)	7392(7)	1749(2)	5097(2)	73(1)
C(47)	6886(5)	2045(1)	5591(2)	52(1)
C(48)	7014(4)	2613(1)	5581(2)	41(1)
C(49)	5444(6)	272(2)	6339(2)	67(1)
Cl(1)	5324(2)	154(1)	7160(1)	94(1)
Cl(2)	4463(2)	-265(1)	5872(1)	106(1)
Cl(3)	7468(2)	318(1)	6204(1)	110(1)
F(1)	6488(3)	2894(1)	6072(1)	57(1)
F(2)	6251(3)	1789(1)	6074(1)	73(1)
F(3)	7252(5)	1199(1)	5091(1)	113(1)
F(4)	8533(7)	1720(1)	4129(1)	157(2)
F(5)	8762(4)	2817(1)	4116(1)	102(1)

Table S13b. Bond lengths [Å] and angles [°] for 1b.

B(1)-C(22)	1.570(5)	C(22)-C(23)	1.396(4)
B(1)-C(25)	1.570(5)	C(23)-C(24)	1.390(4)
B(1)-C(34)	1.577(5)	C(25)-C(26)	1.415(5)
N(1)-C(18)	1.382(4)	C(25)-C(30)	1.419(5)
N(1)-C(3)	1.388(4)	C(26)-C(27)	1.398(5)
N(1)-C(4)	1.389(4)	C(26)-C(32)	1.512(5)
C(1)-C(4)	1.385(4)	C(27)-C(28)	1.385(6)
C(1)-C(2)	1.418(4)	C(28)-C(29)	1.376(6)
C(1)-C(43)	1.481(4)	C(28)-C(33)	1.520(6)
C(2)-C(3)	1.390(4)	C(29)-C(30)	1.389(5)
C(2)-C(19)	1.485(4)	C(30)-C(31)	1.509(5)
C(3)-C(5)	1.446(4)	C(34)-C(35)	1.409(5)
C(4)-C(17)	1.424(4)	C(34)-C(39)	1.415(5)
C(5)-C(6)	1.405(4)	C(35)-C(36)	1.391(5)
C(5)-C(10)	1.413(4)	C(35)-C(42)	1.505(5)
C(6)-C(7)	1.374(4)	C(36)-C(37)	1.375(5)
C(7)-C(8)	1.381(5)	C(37)-C(38)	1.380(5)
C(8)-C(9)	1.377(5)	C(37)-C(41)	1.511(5)
C(9)-C(10)	1.404(4)	C(38)-C(39)	1.384(5)
C(10)-C(11)	1.466(4)	C(39)-C(40)	1.510(5)
C(11)-C(18)	1.399(4)	C(43)-C(48)	1.376(5)
C(11)-C(12)	1.402(4)	C(43)-C(44)	1.377(5)
C(12)-C(13)	1.383(5)	C(44)-F(5)	1.342(5)
C(13)-C(14)	1.370(5)	C(44)-C(45)	1.377(6)
C(14)-C(15)	1.401(5)	C(45)-F(4)	1.336(5)
C(15)-C(18)	1.411(4)	C(45)-C(46)	1.357(7)
C(15)-C(16)	1.436(5)	C(46)-F(3)	1.342(4)
C(16)-C(17)	1.348(5)	C(46)-C(47)	1.364(6)
C(19)-C(24)	1.382(4)	C(47)-F(2)	1.344(4)
C(19)-C(20)	1.397(4)	C(47)-C(48)	1.384(5)
C(20)-C(21)	1.379(4)	C(48)-F(1)	1.346(4)
C(21)-C(22)	1.396(5)	C(49)-Cl(3)	1.736(5)

C(49)-Cl(1)	1.740(4)	C(13)-C(12)-C(11)	121.3(3)
C(49)-Cl(2)	1.754(5)	C(14)-C(13)-C(12)	121.0(3)
		C(13)-C(14)-C(15)	120.8(3)
C(22)-B(1)-C(25)	118.4(3)	C(14)-C(15)-C(18)	117.1(3)
C(22)-B(1)-C(34)	115.5(3)	C(14)-C(15)-C(16)	124.0(3)
C(25)-B(1)-C(34)	126.1(3)	C(18)-C(15)-C(16)	118.9(3)
C(18)-N(1)-C(3)	125.2(2)	C(17)-C(16)-C(15)	121.6(3)
C(18)-N(1)-C(4)	124.0(2)	C(16)-C(17)-C(4)	120.2(3)
C(3)-N(1)-C(4)	110.9(2)	N(1)-C(18)-C(11)	119.1(3)
C(4)-C(1)-C(2)	108.7(3)	N(1)-C(18)-C(15)	117.8(3)
C(4)-C(1)-C(43)	127.1(3)	C(11)-C(18)-C(15)	123.2(3)
C(2)-C(1)-C(43)	124.1(3)	C(24)-C(19)-C(20)	118.5(3)
C(3)-C(2)-C(1)	107.8(3)	C(24)-C(19)-C(2)	120.5(3)
C(3)-C(2)-C(19)	127.5(3)	C(20)-C(19)-C(2)	121.0(3)
C(1)-C(2)-C(19)	124.7(3)	C(21)-C(20)-C(19)	120.5(3)
N(1)-C(3)-C(2)	106.5(2)	C(20)-C(21)-C(22)	121.8(3)
N(1)-C(3)-C(5)	117.0(3)	C(23)-C(22)-C(21)	117.0(3)
C(2)-C(3)-C(5)	136.4(3)	C(23)-C(22)-B(1)	120.7(3)
C(1)-C(4)-N(1)	106.1(2)	C(21)-C(22)-B(1)	122.2(3)
C(1)-C(4)-C(17)	136.3(3)	C(24)-C(23)-C(22)	121.6(3)
N(1)-C(4)-C(17)	117.6(3)	C(19)-C(24)-C(23)	120.5(3)
C(6)-C(5)-C(10)	118.6(3)	C(26)-C(25)-C(30)	117.1(3)
C(6)-C(5)-C(3)	121.7(3)	C(26)-C(25)-B(1)	121.0(3)
C(10)-C(5)-C(3)	119.7(3)	C(30)-C(25)-B(1)	121.7(3)
C(7)-C(6)-C(5)	121.3(3)	C(27)-C(26)-C(25)	120.4(3)
C(6)-C(7)-C(8)	120.1(3)	C(27)-C(26)-C(32)	116.8(3)
C(9)-C(8)-C(7)	120.0(3)	C(25)-C(26)-C(32)	122.7(3)
C(8)-C(9)-C(10)	121.3(3)	C(28)-C(27)-C(26)	121.8(4)
C(9)-C(10)-C(5)	118.7(3)	C(29)-C(28)-C(27)	117.8(4)
C(9)-C(10)-C(11)	121.3(3)	C(29)-C(28)-C(33)	121.4(4)
C(5)-C(10)-C(11)	120.0(3)	C(27)-C(28)-C(33)	120.8(5)
C(18)-C(11)-C(12)	116.6(3)	C(28)-C(29)-C(30)	122.7(4)
C(18)-C(11)-C(10)	118.8(3)	C(29)-C(30)-C(25)	120.2(4)
C(12)-C(11)-C(10)	124.6(3)	C(29)-C(30)-C(31)	118.2(3)

C(25)-C(30)-C(31)	121.6(3)	F(5)-C(44)-C(43)	119.8(3)
C(35)-C(34)-C(39)	117.4(3)	F(5)-C(44)-C(45)	117.7(4)
C(35)-C(34)-B(1)	120.6(3)	C(43)-C(44)-C(45)	122.5(4)
C(39)-C(34)-B(1)	121.7(3)	F(4)-C(45)-C(46)	119.7(4)
C(36)-C(35)-C(34)	119.9(3)	F(4)-C(45)-C(44)	120.3(4)
C(36)-C(35)-C(42)	119.2(3)	C(46)-C(45)-C(44)	120.1(4)
C(34)-C(35)-C(42)	120.6(3)	F(3)-C(46)-C(45)	120.2(4)
C(37)-C(36)-C(35)	122.4(3)	F(3)-C(46)-C(47)	119.9(4)
C(36)-C(37)-C(38)	117.8(3)	C(45)-C(46)-C(47)	119.9(3)
C(36)-C(37)-C(41)	121.7(4)	F(2)-C(47)-C(46)	120.4(3)
C(38)-C(37)-C(41)	120.6(4)	F(2)-C(47)-C(48)	120.8(3)
C(37)-C(38)-C(39)	122.1(3)	C(46)-C(47)-C(48)	118.8(4)
C(38)-C(39)-C(34)	120.3(3)	F(1)-C(48)-C(43)	119.2(3)
C(38)-C(39)-C(40)	118.3(3)	F(1)-C(48)-C(47)	117.4(3)
C(34)-C(39)-C(40)	121.4(3)	C(43)-C(48)-C(47)	123.3(3)
C(48)-C(43)-C(44)	115.3(3)	Cl(3)-C(49)-Cl(1)	110.7(3)
C(48)-C(43)-C(1)	122.8(3)	Cl(3)-C(49)-Cl(2)	109.9(3)
C(44)-C(43)-C(1)	121.5(3)	Cl(1)-C(49)-Cl(2)	109.3(2)

Table S13c. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 1b. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	34(2)	42(2)	42(2)	-8(2)	10(2)	8(2)
N(1)	33(2)	31(1)	28(1)	-1(1)	5(1)	1(1)
C(1)	42(2)	33(2)	32(2)	3(1)	6(1)	7(1)
C(2)	36(2)	33(2)	31(2)	0(1)	5(1)	2(1)
C(3)	32(2)	34(2)	27(1)	1(1)	7(1)	1(1)
C(4)	36(2)	35(2)	31(2)	2(1)	7(1)	7(1)
C(5)	33(2)	32(2)	30(2)	6(1)	12(1)	2(1)
C(6)	39(2)	38(2)	33(2)	2(1)	9(1)	3(1)
C(7)	42(2)	49(2)	35(2)	9(2)	7(2)	12(2)

C(8)	53(2)	39(2)	44(2)	16(2)	21(2)	15(2)
C(9)	51(2)	32(2)	48(2)	1(1)	18(2)	4(2)
C(10)	35(2)	32(2)	34(2)	4(1)	15(1)	3(1)
C(11)	32(2)	37(2)	37(2)	-3(1)	17(1)	-1(1)
C(12)	49(2)	37(2)	49(2)	-5(2)	17(2)	-3(2)
C(13)	50(2)	48(2)	53(2)	-18(2)	18(2)	-9(2)
C(14)	39(2)	60(2)	36(2)	-13(2)	11(2)	-9(2)
C(15)	32(2)	50(2)	32(2)	-5(1)	11(1)	-3(2)
C(16)	37(2)	63(2)	31(2)	0(2)	4(1)	2(2)
C(17)	40(2)	48(2)	32(2)	7(1)	6(1)	7(2)
C(18)	31(2)	37(2)	30(2)	-3(1)	13(1)	-2(1)
C(19)	39(2)	27(2)	32(2)	1(1)	4(1)	5(1)
C(20)	39(2)	35(2)	37(2)	0(1)	7(1)	-4(1)
C(21)	45(2)	36(2)	32(2)	0(1)	8(1)	3(2)
C(22)	37(2)	33(2)	36(2)	-1(1)	7(1)	2(1)
C(23)	41(2)	35(2)	43(2)	1(1)	10(2)	-5(2)
C(24)	45(2)	36(2)	34(2)	2(1)	10(2)	-1(2)
C(25)	38(2)	49(2)	38(2)	-3(1)	2(2)	-2(2)
C(26)	50(2)	50(2)	42(2)	4(2)	2(2)	0(2)
C(27)	64(3)	59(2)	52(2)	11(2)	-2(2)	0(2)
C(28)	79(3)	80(3)	43(2)	11(2)	-1(2)	-16(3)
C(29)	71(3)	84(3)	35(2)	-6(2)	8(2)	-17(2)
C(30)	39(2)	63(2)	40(2)	-9(2)	7(2)	-9(2)
C(31)	67(3)	65(3)	53(2)	-20(2)	22(2)	-10(2)
C(32)	79(3)	48(2)	55(2)	0(2)	11(2)	21(2)
C(33)	164(6)	103(4)	51(3)	26(3)	2(3)	-20(4)
C(34)	33(2)	43(2)	38(2)	-9(1)	4(1)	-3(2)
C(35)	37(2)	51(2)	40(2)	-10(2)	4(2)	0(2)
C(36)	36(2)	61(2)	43(2)	-10(2)	7(2)	-8(2)
C(37)	52(2)	49(2)	37(2)	-11(2)	6(2)	-18(2)
C(38)	52(2)	42(2)	46(2)	-11(2)	3(2)	-3(2)
C(39)	37(2)	42(2)	47(2)	-11(2)	2(2)	-4(2)
C(40)	45(2)	47(2)	71(3)	-6(2)	10(2)	6(2)
C(41)	69(3)	65(3)	56(2)	-7(2)	9(2)	-27(2)

C(42)	34(2)	72(3)	66(2)	-9(2)	5(2)	4(2)
C(43)	52(2)	34(2)	36(2)	0(1)	-1(2)	9(2)
C(44)	113(4)	46(2)	39(2)	7(2)	16(2)	29(2)
C(45)	169(6)	47(2)	42(2)	-5(2)	13(3)	39(3)
C(46)	124(4)	30(2)	55(2)	-3(2)	-19(3)	8(2)
C(47)	68(3)	35(2)	48(2)	7(2)	-6(2)	-2(2)
C(48)	47(2)	35(2)	39(2)	1(1)	-2(2)	-1(2)
C(49)	71(3)	69(3)	62(3)	9(2)	15(2)	4(2)
Cl(1)	125(1)	103(1)	58(1)	-11(1)	34(1)	1(1)
Cl(2)	115(1)	119(1)	82(1)	-30(1)	13(1)	-18(1)
Cl(3)	88(1)	131(1)	116(1)	28(1)	33(1)	-18(1)
F(1)	76(2)	43(1)	58(1)	5(1)	29(1)	5(1)
F(2)	92(2)	44(1)	82(2)	15(1)	9(1)	-14(1)
F(3)	222(4)	30(1)	75(2)	-6(1)	-15(2)	5(2)
F(4)	357(6)	63(2)	62(2)	0(1)	62(3)	83(3)
F(5)	188(3)	67(2)	64(2)	21(1)	68(2)	59(2)

Table S13d. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for 1b.

	x	y	z	U(eq)
H(6)	4395	4496	3625	44
H(7)	3338	5303	3145	50
H(8)	4356	6151	3539	53
H(9)	6395	6191	4428	51
H(12)	8239	6216	5242	53
H(13)	10093	6200	6190	59
H(14)	10936	5379	6686	53
H(16)	10829	4331	6695	52
H(17)	9773	3532	6231	48
H(20)	6653	3845	3224	44
H(21)	4938	3462	2363	45
H(23)	2500	2653	3633	47

H(24)	4155	3064	4500	45
H(27)	1158	4396	1128	71
H(29)	2104	3064	100	76
H(31A)	2169	2188	532	91
H(31B)	1827	2083	1265	91
H(31C)	3632	2233	1124	91
H(32A)	2151	4225	2467	90
H(32B)	995	3727	2622	90
H(32C)	245	4235	2188	90
H(33A)	1707	3902	-466	161
H(33B)	2322	4429	-36	161
H(33C)	410	4293	-184	161
H(36)	-2206	1735	2647	56
H(38)	2126	972	2960	57
H(40A)	4653	1878	3082	81
H(40B)	4420	1961	2307	81
H(40C)	4452	1355	2609	81
H(41A)	-536	661	3488	95
H(41B)	-783	455	2746	95
H(41C)	-2165	819	3012	95
H(42A)	-2509	2628	2259	86
H(42B)	-1059	2914	1943	86
H(42C)	-1154	2982	2706	86
H(49)	4877	626	6205	80

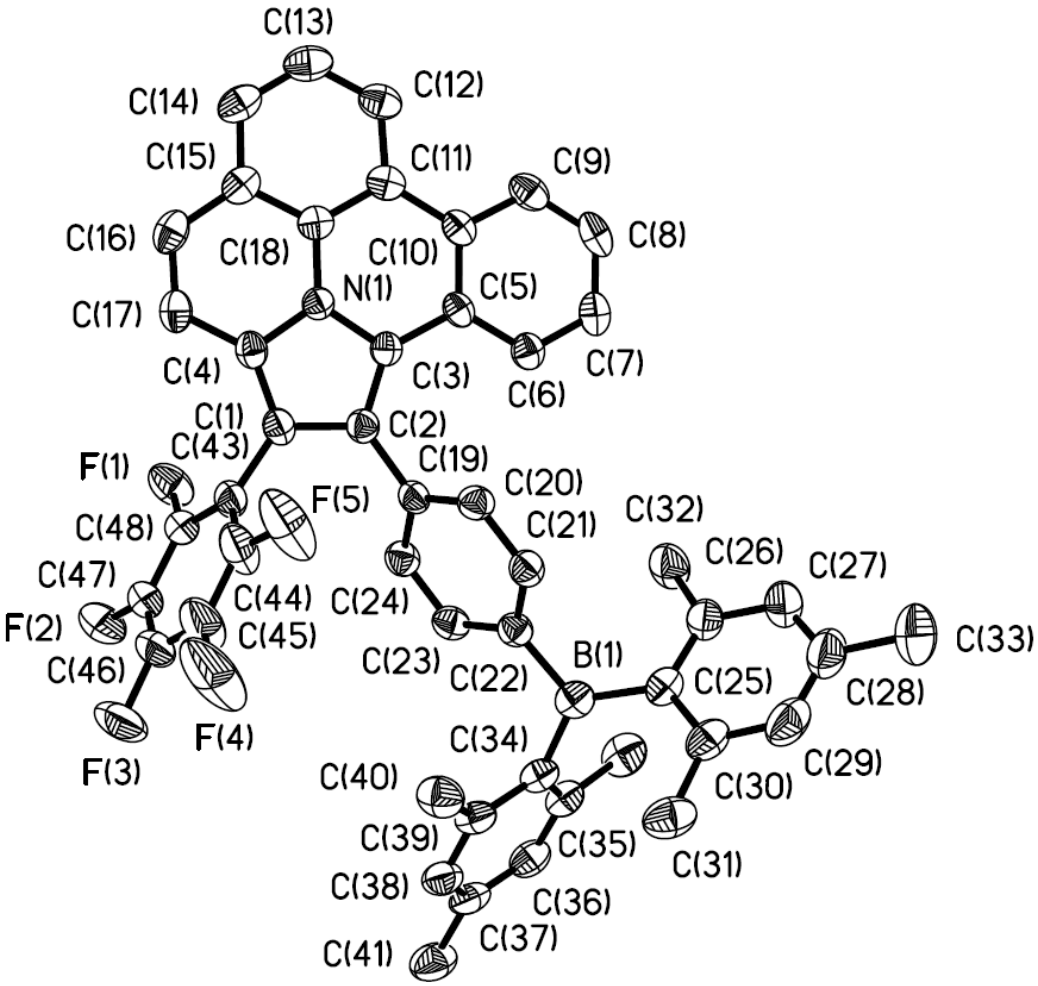


Figure S34. A diagram showing the structure of **1b** with labeling schemes.

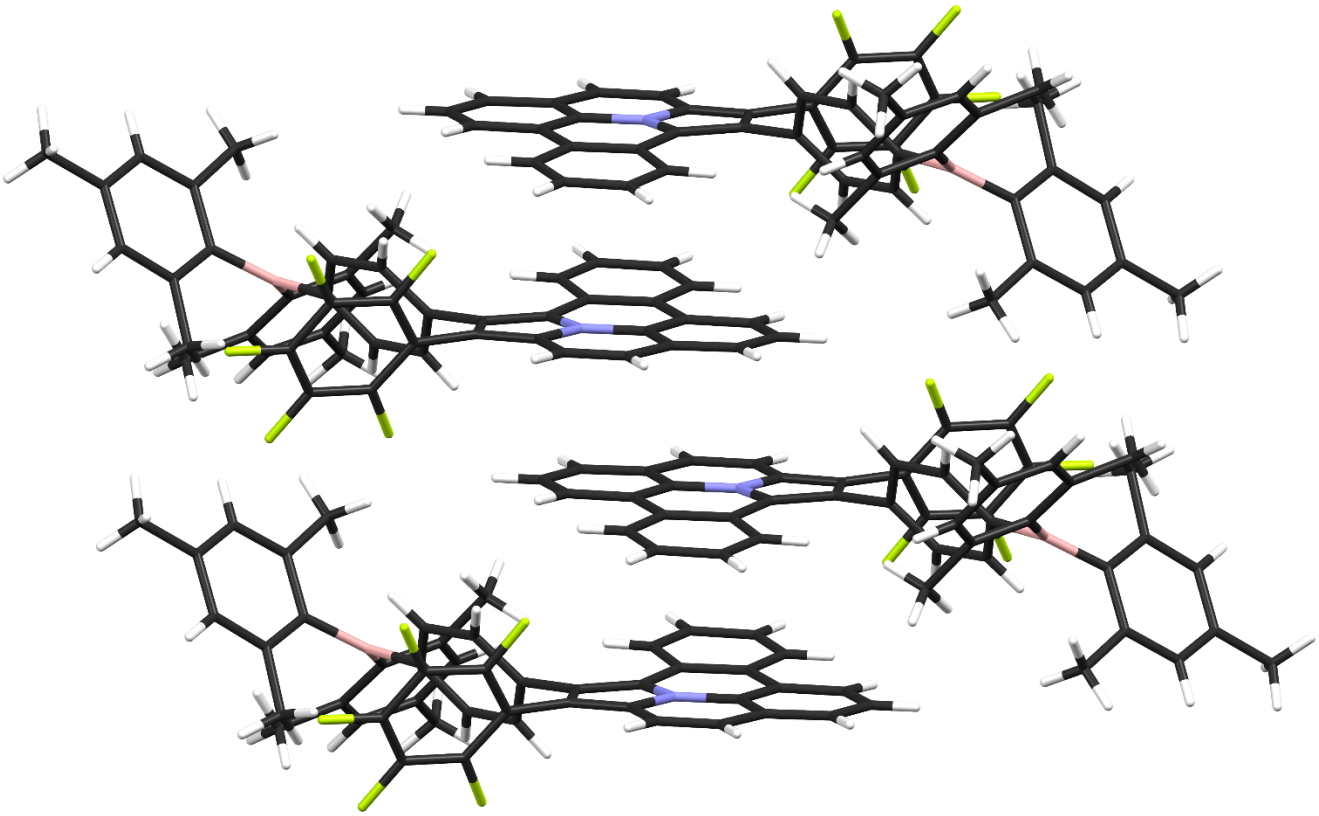


Figure S35. A diagram showing the intermolecular stacking of the IDP core of **1b**.

Table S14. Crystal data and structure refinement for 2a.

Identification code	2a	
Empirical formula	C49 H39 B Cl3 F3 N2	
Formula weight	829.98	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.5885(6) Å	□= 93.829(3)°.
	b = 14.6907(12) Å	□= 94.403(3)°.
	c = 16.3399(13) Å	□ = 98.387(3)°.
Volume	2027.2(3) $Å^3$	
Z	2	
Density (calculated)	1.360 Mg/m^3	
Absorption coefficient	0.278 mm^{-1}	
F(000)	860	
Crystal size	0.150 x 0.100 x 0.050 mm^3	
Theta range for data collection	2.406 to 28.373°.	
Index ranges	-11<=h<=11, -19<=k<=19, -21<=l<=21	
Reflections collected	67617	
Independent reflections	10119 [R(int) = 0.1615]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.986 and 0.959	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10119 / 0 / 556	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0806, wR2 = 0.1959	
R indices (all data)	R1 = 0.2054, wR2 = 0.2983	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.620 and -0.585 $e.Å^{-3}$	

Table S14a. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 2a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	7925(5)	5939(3)	8253(3)	35(1)
N(1)	6538(4)	8420(2)	6704(2)	35(1)
N(2)	4420(4)	5583(2)	5945(2)	38(1)
C(1)	5773(4)	7384(3)	7586(2)	36(1)
C(2)	5122(4)	7038(3)	6779(2)	35(1)
C(3)	5589(4)	7692(3)	6230(2)	35(1)
C(4)	6632(5)	8249(3)	7527(2)	36(1)
C(5)	5237(5)	7833(3)	5370(2)	39(1)
C(6)	4120(5)	7225(3)	4858(2)	45(1)
C(7)	3766(6)	7391(3)	4048(3)	55(1)
C(8)	4520(7)	8166(4)	3732(3)	64(1)
C(9)	5598(6)	8787(3)	4216(3)	58(1)
C(10)	6000(5)	8637(3)	5045(3)	45(1)
C(11)	7123(5)	9318(3)	5572(3)	45(1)
C(12)	8018(6)	10094(3)	5303(3)	63(1)
C(13)	8996(7)	10718(3)	5835(3)	67(2)
C(14)	9142(6)	10615(3)	6662(3)	54(1)
C(15)	8302(5)	9854(3)	6974(3)	43(1)
C(16)	8376(5)	9685(3)	7836(3)	45(1)
C(17)	7552(5)	8924(3)	8100(3)	42(1)
C(18)	7318(5)	9205(3)	6409(2)	38(1)
C(19)	5624(4)	6975(3)	8393(2)	34(1)
C(20)	4561(5)	7310(3)	8899(2)	40(1)
C(21)	4360(5)	7006(3)	9667(3)	44(1)
C(22)	5215(5)	6350(3)	9951(2)	43(1)
C(23)	6252(5)	5994(3)	9451(2)	40(1)

C(24)	6511(4)	6301(3)	8675(2)	35(1)
C(25)	4101(4)	6131(3)	6588(2)	35(1)
C(26)	2876(4)	5865(3)	7075(2)	37(1)
C(27)	1972(5)	5010(3)	6903(3)	41(1)
C(28)	2324(5)	4441(3)	6258(2)	40(1)
C(29)	3526(5)	4756(3)	5794(2)	40(1)
C(30)	1362(6)	3509(3)	6070(3)	56(1)
C(31)	8171(5)	4909(3)	8361(2)	36(1)
C(32)	6921(5)	4183(3)	8140(2)	40(1)
C(33)	7123(5)	3270(3)	8245(2)	43(1)
C(34)	8542(5)	3036(3)	8565(2)	43(1)
C(35)	9765(5)	3749(3)	8784(2)	42(1)
C(36)	9620(5)	4669(3)	8688(2)	37(1)
C(37)	11043(5)	5379(3)	8992(3)	43(1)
C(38)	5338(5)	4338(3)	7759(3)	49(1)
C(39)	8712(6)	2048(3)	8653(3)	59(1)
C(40)	9088(4)	6641(3)	7810(2)	38(1)
C(41)	9236(5)	6513(3)	6960(2)	41(1)
C(42)	10205(5)	7186(3)	6581(3)	49(1)
C(43)	11061(5)	7958(3)	7014(3)	51(1)
C(44)	10949(5)	8055(3)	7852(3)	47(1)
C(45)	9983(5)	7430(3)	8256(3)	41(1)
C(46)	9939(5)	7605(3)	9169(3)	48(1)
C(47)	8356(5)	5687(3)	6444(3)	50(1)
C(48)	12078(7)	8675(3)	6595(4)	72(2)
C(49)	3542(9)	962(6)	9102(6)	120(3)
Cl(1)	2943(3)	1593(2)	8271(2)	154(1)
Cl(2)	1943(2)	386(2)	9509(1)	110(1)
Cl(3)	4795(3)	223(2)	8722(2)	176(1)
F(1)	1850(20)	3002(13)	5607(13)	138(8)
F(2)	901(18)	3110(11)	6679(8)	89(5)

F(3)	5(17)	3618(13)	5632(9)	80(4)
F(1A)	1690(20)	2940(13)	6705(12)	122(7)
F(2A)	-150(20)	3469(13)	5955(13)	129(9)
F(3A)	1946(12)	2987(9)	5436(9)	51(2)

Table S14b. Bond lengths [Å] and angles [°] for 2a.

B(1)-C(31)	1.577(6)	C(12)-C(13)	1.364(7)
B(1)-C(40)	1.580(6)	C(13)-C(14)	1.368(7)
B(1)-C(24)	1.581(6)	C(14)-C(15)	1.389(6)
N(1)-C(4)	1.383(5)	C(15)-C(18)	1.415(6)
N(1)-C(18)	1.382(5)	C(15)-C(16)	1.444(6)
N(1)-C(3)	1.395(5)	C(16)-C(17)	1.349(6)
N(2)-C(29)	1.336(5)	C(19)-C(20)	1.397(5)
N(2)-C(25)	1.351(5)	C(19)-C(24)	1.414(5)
C(1)-C(4)	1.386(5)	C(20)-C(21)	1.375(6)
C(1)-C(2)	1.422(5)	C(21)-C(22)	1.377(6)
C(1)-C(19)	1.492(5)	C(22)-C(23)	1.386(6)
C(2)-C(3)	1.395(5)	C(23)-C(24)	1.397(5)
C(2)-C(25)	1.485(5)	C(25)-C(26)	1.393(5)
C(3)-C(5)	1.450(5)	C(26)-C(27)	1.377(6)
C(4)-C(17)	1.421(5)	C(27)-C(28)	1.380(6)
C(5)-C(6)	1.395(6)	C(28)-C(29)	1.373(6)
C(5)-C(10)	1.420(6)	C(28)-C(30)	1.492(6)
C(6)-C(7)	1.381(6)	C(30)-F(1)	1.168(19)
C(7)-C(8)	1.377(7)	C(30)-F(2)	1.249(14)
C(8)-C(9)	1.363(7)	C(30)-F(2A)	1.288(17)
C(9)-C(10)	1.412(6)	C(30)-F(3)	1.355(17)
C(10)-C(11)	1.465(6)	C(30)-F(3A)	1.414(15)
C(11)-C(18)	1.389(6)	C(30)-F(1A)	1.412(17)
C(11)-C(12)	1.395(6)	C(31)-C(32)	1.405(6)

C(31)-C(36)	1.418(5)	C(3)-C(2)-C(1)	108.7(3)
C(32)-C(33)	1.398(6)	C(3)-C(2)-C(25)	127.5(3)
C(32)-C(38)	1.505(6)	C(1)-C(2)-C(25)	123.8(3)
C(33)-C(34)	1.387(6)	C(2)-C(3)-N(1)	105.8(3)
C(34)-C(35)	1.378(6)	C(2)-C(3)-C(5)	137.6(4)
C(34)-C(39)	1.495(6)	N(1)-C(3)-C(5)	116.2(3)
C(35)-C(36)	1.394(6)	N(1)-C(4)-C(1)	107.3(3)
C(36)-C(37)	1.515(6)	N(1)-C(4)-C(17)	118.2(4)
C(40)-C(41)	1.408(6)	C(1)-C(4)-C(17)	134.5(4)
C(40)-C(45)	1.416(6)	C(6)-C(5)-C(10)	118.7(4)
C(41)-C(42)	1.405(6)	C(6)-C(5)-C(3)	122.1(4)
C(41)-C(47)	1.501(6)	C(10)-C(5)-C(3)	119.1(4)
C(42)-C(43)	1.378(7)	C(7)-C(6)-C(5)	121.0(4)
C(43)-C(44)	1.379(6)	C(6)-C(7)-C(8)	120.1(5)
C(43)-C(48)	1.503(6)	C(9)-C(8)-C(7)	120.7(4)
C(44)-C(45)	1.382(6)	C(8)-C(9)-C(10)	120.8(5)
C(45)-C(46)	1.502(6)	C(9)-C(10)-C(5)	118.6(4)
C(49)-Cl(2)	1.709(9)	C(9)-C(10)-C(11)	120.8(4)
C(49)-Cl(3)	1.754(8)	C(5)-C(10)-C(11)	120.6(4)
C(49)-Cl(1)	1.780(10)	C(18)-C(11)-C(12)	116.2(4)
		C(18)-C(11)-C(10)	118.7(4)
C(31)-B(1)-C(40)	123.5(3)	C(12)-C(11)-C(10)	125.1(4)
C(31)-B(1)-C(24)	117.6(4)	C(13)-C(12)-C(11)	121.9(5)
C(40)-B(1)-C(24)	118.7(3)	C(12)-C(13)-C(14)	121.4(5)
C(4)-N(1)-C(18)	123.4(3)	C(13)-C(14)-C(15)	120.0(4)
C(4)-N(1)-C(3)	110.7(3)	C(14)-C(15)-C(18)	117.6(4)
C(18)-N(1)-C(3)	125.9(3)	C(14)-C(15)-C(16)	124.1(4)
C(29)-N(2)-C(25)	117.4(3)	C(18)-C(15)-C(16)	118.3(4)
C(4)-C(1)-C(2)	107.5(3)	C(17)-C(16)-C(15)	121.3(4)
C(4)-C(1)-C(19)	121.7(3)	C(16)-C(17)-C(4)	120.3(4)
C(2)-C(1)-C(19)	130.7(4)	N(1)-C(18)-C(11)	118.8(4)

N(1)-C(18)-C(15)	118.3(4)	F(3A)-C(30)-C(28)	112.2(6)
C(11)-C(18)-C(15)	122.9(4)	F(1A)-C(30)-C(28)	109.4(9)
C(20)-C(19)-C(24)	119.2(4)	C(32)-C(31)-C(36)	117.1(4)
C(20)-C(19)-C(1)	116.5(3)	C(32)-C(31)-B(1)	120.2(3)
C(24)-C(19)-C(1)	124.3(3)	C(36)-C(31)-B(1)	122.7(4)
C(21)-C(20)-C(19)	121.8(4)	C(33)-C(32)-C(31)	120.5(4)
C(20)-C(21)-C(22)	119.7(4)	C(33)-C(32)-C(38)	116.9(4)
C(21)-C(22)-C(23)	119.4(4)	C(31)-C(32)-C(38)	122.5(4)
C(22)-C(23)-C(24)	122.4(4)	C(34)-C(33)-C(32)	122.3(4)
C(23)-C(24)-C(19)	117.4(4)	C(35)-C(34)-C(33)	117.1(4)
C(23)-C(24)-B(1)	115.4(3)	C(35)-C(34)-C(39)	122.4(4)
C(19)-C(24)-B(1)	126.7(3)	C(33)-C(34)-C(39)	120.4(4)
N(2)-C(25)-C(26)	122.3(4)	C(34)-C(35)-C(36)	122.6(4)
N(2)-C(25)-C(2)	117.8(3)	C(35)-C(36)-C(31)	120.4(4)
C(26)-C(25)-C(2)	119.9(3)	C(35)-C(36)-C(37)	116.5(4)
C(27)-C(26)-C(25)	119.0(4)	C(31)-C(36)-C(37)	123.0(4)
C(26)-C(27)-C(28)	118.7(4)	C(41)-C(40)-C(45)	118.2(4)
C(29)-C(28)-C(27)	119.1(4)	C(41)-C(40)-B(1)	121.0(4)
C(29)-C(28)-C(30)	121.7(4)	C(45)-C(40)-B(1)	120.8(4)
C(27)-C(28)-C(30)	119.2(4)	C(42)-C(41)-C(40)	119.1(4)
N(2)-C(29)-C(28)	123.5(4)	C(42)-C(41)-C(47)	119.2(4)
F(1)-C(30)-F(2)	111.1(14)	C(40)-C(41)-C(47)	121.7(4)
F(1)-C(30)-F(3)	99.9(13)	C(43)-C(42)-C(41)	122.6(4)
F(2)-C(30)-F(3)	103.9(10)	C(44)-C(43)-C(42)	117.4(4)
F(2A)-C(30)-F(3A)	111.3(10)	C(44)-C(43)-C(48)	120.9(5)
F(2A)-C(30)-F(1A)	108.0(12)	C(42)-C(43)-C(48)	121.7(5)
F(3A)-C(30)-F(1A)	96.5(10)	C(43)-C(44)-C(45)	122.7(4)
F(1)-C(30)-C(28)	116.5(10)	C(44)-C(45)-C(40)	119.9(4)
F(2)-C(30)-C(28)	115.6(8)	C(44)-C(45)-C(46)	118.3(4)
F(2A)-C(30)-C(28)	117.3(9)	C(40)-C(45)-C(46)	121.8(4)
F(3)-C(30)-C(28)	107.7(9)	Cl(2)-C(49)-Cl(3)	112.9(5)

Cl(2)-C(49)-Cl(1)	111.1(4)	Cl(3)-C(49)-Cl(1)	107.0(5)

Table S14c. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 2a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	39(2)	40(3)	27(2)	1(2)	-3(2)	10(2)
N(1)	41(2)	31(2)	35(2)	3(1)	6(1)	11(1)
N(2)	42(2)	41(2)	31(2)	0(2)	1(1)	7(2)
C(1)	38(2)	33(2)	37(2)	5(2)	4(2)	10(2)
C(2)	40(2)	34(2)	32(2)	1(2)	4(2)	8(2)
C(3)	38(2)	33(2)	35(2)	3(2)	4(2)	5(2)
C(4)	46(2)	31(2)	32(2)	2(2)	2(2)	9(2)
C(5)	46(2)	42(2)	31(2)	3(2)	6(2)	9(2)
C(6)	53(3)	48(3)	34(2)	5(2)	2(2)	9(2)
C(7)	62(3)	64(3)	37(2)	8(2)	-2(2)	6(2)
C(8)	91(4)	68(3)	33(2)	10(2)	1(2)	11(3)
C(9)	85(4)	54(3)	38(3)	15(2)	10(2)	9(3)
C(10)	60(3)	40(2)	38(2)	7(2)	11(2)	12(2)
C(11)	57(3)	38(2)	41(2)	7(2)	12(2)	5(2)
C(12)	91(4)	48(3)	47(3)	8(2)	18(3)	-3(3)
C(13)	92(4)	44(3)	61(3)	5(2)	21(3)	-8(3)
C(14)	62(3)	36(3)	60(3)	1(2)	8(2)	-2(2)
C(15)	51(2)	29(2)	49(3)	2(2)	9(2)	5(2)
C(16)	53(3)	31(2)	49(3)	-2(2)	-1(2)	7(2)
C(17)	53(3)	34(2)	39(2)	-1(2)	-3(2)	10(2)
C(18)	46(2)	27(2)	43(2)	8(2)	10(2)	7(2)
C(19)	39(2)	31(2)	32(2)	2(2)	2(2)	4(2)
C(20)	45(2)	39(2)	38(2)	2(2)	6(2)	14(2)

C(21)	46(2)	49(3)	40(2)	-3(2)	10(2)	11(2)
C(22)	55(3)	45(3)	29(2)	4(2)	10(2)	2(2)
C(23)	45(2)	42(2)	35(2)	8(2)	5(2)	6(2)
C(24)	38(2)	34(2)	32(2)	3(2)	1(2)	3(2)
C(25)	38(2)	38(2)	30(2)	5(2)	0(2)	10(2)
C(26)	37(2)	41(2)	33(2)	2(2)	3(2)	5(2)
C(27)	35(2)	46(3)	41(2)	6(2)	5(2)	4(2)
C(28)	40(2)	41(2)	39(2)	2(2)	-1(2)	6(2)
C(29)	42(2)	41(2)	35(2)	-1(2)	2(2)	7(2)
C(30)	59(3)	50(3)	55(3)	-6(3)	7(3)	-2(2)
C(31)	42(2)	37(2)	30(2)	4(2)	4(2)	11(2)
C(32)	48(2)	38(2)	33(2)	6(2)	2(2)	10(2)
C(33)	57(3)	36(2)	37(2)	2(2)	5(2)	8(2)
C(34)	58(3)	39(2)	35(2)	5(2)	7(2)	14(2)
C(35)	51(2)	45(3)	35(2)	6(2)	5(2)	20(2)
C(36)	43(2)	40(2)	31(2)	3(2)	7(2)	10(2)
C(37)	46(2)	44(2)	40(2)	5(2)	2(2)	8(2)
C(38)	50(3)	42(3)	53(3)	5(2)	-3(2)	7(2)
C(39)	79(3)	42(3)	58(3)	3(2)	2(2)	21(2)
C(40)	38(2)	38(2)	40(2)	11(2)	5(2)	10(2)
C(41)	43(2)	50(3)	35(2)	12(2)	7(2)	18(2)
C(42)	53(3)	63(3)	40(2)	19(2)	14(2)	23(2)
C(43)	55(3)	47(3)	59(3)	23(2)	21(2)	18(2)
C(44)	45(2)	37(2)	61(3)	12(2)	12(2)	10(2)
C(45)	44(2)	38(2)	42(2)	10(2)	6(2)	9(2)
C(46)	59(3)	40(2)	45(3)	6(2)	4(2)	6(2)
C(47)	47(2)	70(3)	36(2)	0(2)	4(2)	13(2)
C(48)	85(4)	53(3)	94(4)	37(3)	41(3)	25(3)
C(49)	83(5)	115(6)	150(8)	-33(5)	-16(5)	11(4)
Cl(1)	83(1)	196(3)	183(3)	31(2)	15(2)	7(2)
Cl(2)	92(1)	130(2)	100(1)	-26(1)	-5(1)	19(1)

Cl(3)	90(2)	145(2)	295(4)	-36(2)	37(2)	39(1)
F(1)	176(13)	73(8)	152(15)	-58(8)	98(9)	-31(7)
F(2)	137(12)	66(8)	47(5)	12(4)	7(7)	-47(8)
F(3)	47(7)	91(8)	87(6)	-22(5)	-13(5)	-21(5)
F(1A)	182(17)	56(7)	106(9)	26(5)	-49(11)	-37(10)
F(2A)	41(5)	70(8)	270(30)	-37(13)	44(11)	-10(5)
F(3A)	48(4)	39(5)	59(5)	-17(3)	10(4)	-5(3)

Table S14d. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 2a.

	x	y	z	U(eq)
H(6)	3594	6688	5070	54
H(7)	3000	6970	3708	66
H(8)	4286	8269	3171	77
H(9)	6084	9326	3992	70
H(12)	7944	10189	4733	75
H(13)	9589	11237	5627	80
H(14)	9817	11064	7022	65
H(16)	9018	10119	8224	54
H(17)	7587	8839	8672	51
H(20)	3961	7759	8707	48
H(21)	3635	7248	10001	53
H(22)	5095	6142	10484	52
H(23)	6806	5525	9644	48
H(26)	2668	6268	7519	44
H(27)	1123	4815	7222	49
H(29)	3733	4365	5340	47
H(33)	6258	2792	8092	52
H(35)	10745	3607	9010	51

H(37A)	10943	5602	9562	65
H(37B)	11102	5897	8643	65
H(37C)	12005	5095	8969	65
H(38A)	4743	3748	7518	73
H(38B)	5492	4766	7327	73
H(38C)	4748	4600	8183	73
H(39A)	9831	1997	8771	88
H(39B)	8299	1679	8139	88
H(39C)	8118	1821	9105	88
H(42)	10272	7105	6004	59
H(44)	11560	8571	8164	56
H(46A)	10492	7163	9454	73
H(46B)	8838	7533	9305	73
H(46C)	10458	8235	9345	73
H(47A)	7300	5810	6258	76
H(47B)	8260	5150	6772	76
H(47C)	8933	5561	5964	76
H(48A)	11618	9247	6610	109
H(48B)	12138	8451	6022	109
H(48C)	13143	8793	6881	109
H(49)	4158	1406	9542	144

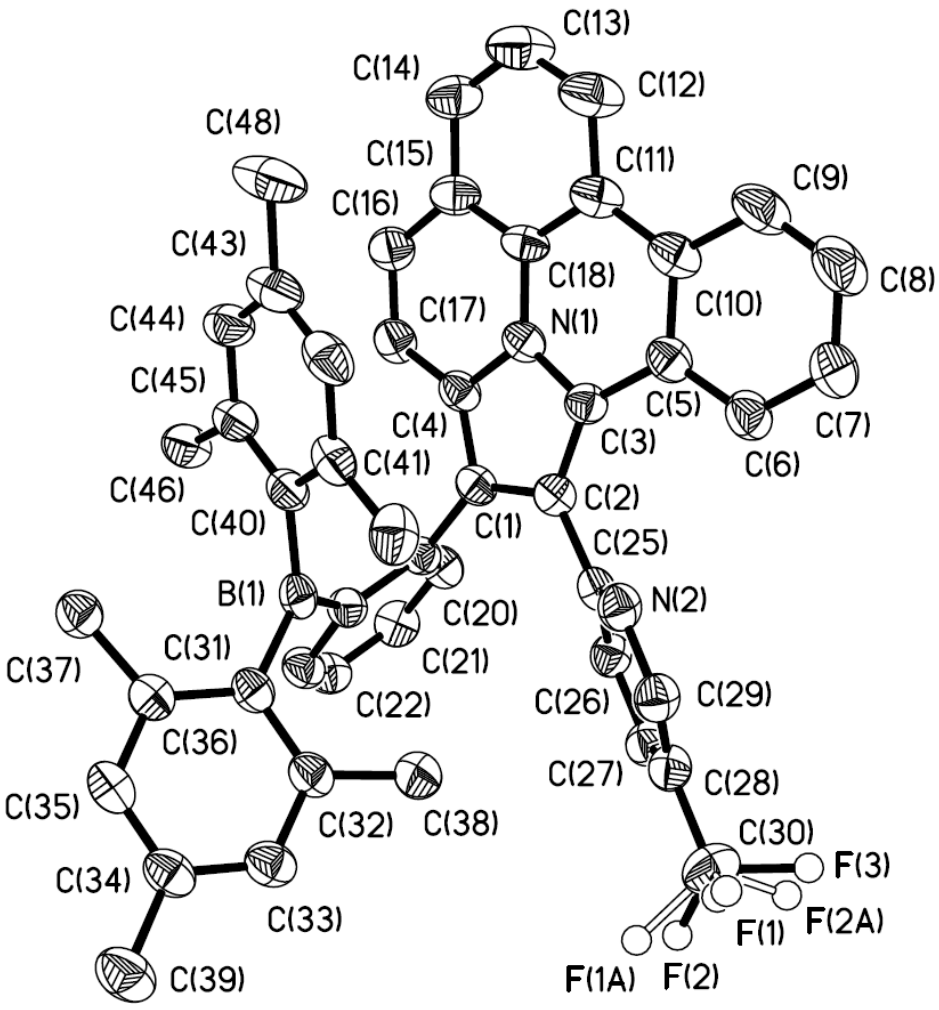


Figure S35. A diagram showing the structure of **2a** with labeling schemes.