Supplementary Information

Donor Position Driven Excited State Modulation in Benzoylthiophene-Carbazole Emitters: Divergent TTA/RTP Pathway for High Efficiency Blue-Cyan OLEDs

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Supplementary Information

Experimental section

General Methods

All chemicals were obtained from commercial suppliers and used without further purification unless otherwise noted. Solvents were dried by standard distillation methods prior to use. Organic products were purified by column chromatography on silica gel (100–200 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a JEOL 400 MHz spectrometer at 298 K in $CDCl_3$, with tetramethylsilane (TMS) as an internal standard. High-resolution mass spectra (HRMS) were acquired using a high-resolution mass spectrometer. UV–Vis absorption spectra were measured on a Cary 100 UV–Vis spectrophotometer, while fluorescence emission spectra were recorded using a Shimadzu spectrofluorometer. Fluorescence quantum yields were determined with a calibrated integrating sphere attached to the same instrument. Thermal properties were evaluated using a PerkinElmer Pyris Diamond thermogravimetric analyzer (TGA) and a Shimadzu DSC-60 Plus differential scanning calorimeter (DSC) under a nitrogen atmosphere at a heating rate of 10 °C·min^{-1}. FTIR spectra were collected on a PerkinElmer Spectrum 2 spectrophotometer in the range of 400–4000 cm^{-1}. Morphological analyses were performed using a Carl Zeiss Ultra Plus field-emission scanning electron microscope (FE-SEM)

Theoretical Computations

All computational calculations for dyes **4a**, **4b**, and **4c** were performed using the ORCA 5.0.4 package. Ground-state geometries of the compounds were optimized at the B3LYP/def2-svp level of theory under vacuum. Frequency calculations were performed and found no negative frequencies. Time-dependent DFT (TD-DFT) calculations were carried out at the same functional with def2-tzvp basis set to determine vertical excitation energies and oscillator strengths. The charge transfer indices and related parameters were estimated using Multiwfn software.

OLED Device Fabrication

OLEDs were constructed on patterned ITO/glass substrates (100 nm, 20 Ω/sq) following established procedures.1 The device stack comprised HAT CN (hole injection), NPB (hole transport), CBP:10 wt% emitter (emissive layer), TmPyPB (electron transport), and LiF/Al cathodes. Organic layers and Al were deposited at 1 Å s^{-1}, while LiF was deposited at 0.1 Å s^{-1}, using a Kurt J. Lesker Spectros thermal evaporator under 10^{-7} mbar without breaking vacuum. All

materials (Sigma Aldrich, Lumtec) were purified by gradient sublimation. Pixel areas of 4, 8 and 16 mm² were fabricated. Device performance was measured with a Labsphere integrating sphere coupled to a source meter and Ocean Optics USB4000 spectrometer inside a glovebox.

Synthesis

(5-bromothiophen-2-yl)(phenyl) methanone (2a)[1]

A mixture of benzoyl chloride (2.81 g, 20.0 mmol) and 2-bromothiophene (3.42 g, 21.0 mmol) in DCM (50 mL) was cooled in an ice bath, and $AlCl_3$ (5.34 g, 40.0 mmol) was added portionwise over 10 min under vigorous stirring. The reaction mixture was then stirred at room temperature for 2-4 h and quenched with 1 M HCl (aq., 100 mL). The resulting mixture was filtered under reduced pressure, and the layers were separated. The aqueous phase was extracted with DCM (3 × 50 mL). The combined organic extracts were washed with water (3 × 100 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by silica gel column chromatography using 10-12% DCM/hexane as the eluent to afford the product as a light yellow solid (9.6 g, 87%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.82 (dt, J = 8.4, 1.7 Hz, 2H), 7.60 (m, 1H), 7.50 (m, 2H), 7.38 (d, J = 4.0 Hz, 1H), 7.13 (d, J = 4.0 Hz, 1H).

(4-bromothiophen-2-yl)(phenyl)methanone (2b) / (3-bromothiophen-2-yl)(phenyl) methanone (2c)

A mixture of benzoyl chloride (5.62 g, 40 mmol) and 3-bromothiophene (7.68 g, 42 mmol) in DCM (80 mL) was cooled in an ice bath, and $AlCl_3$ (10.68 g, 80 mmol) was added portionwise over 10 min under vigorous stirring. The reaction mixture was then stirred at room temperature for 2-4 h and quenched with 1 M HCl (aq., 100 mL). The mixture was filtered under reduced pressure, and the layers were separated. The aqueous layer was extracted with DCM (3×50 mL). The combined organic extracts were washed with water (3×100 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by silica gel column chromatography using 1-3% ethyl acetate/hexane as the eluent to afford the desired product.

(4-bromothiophen-2-yl)(phenyl)methanone (**2b**). White solid. Yield 1.9g (18%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.85 (d, J = 8.0 Hz, 2H), 7.62 (m, 2H), 7.53 (dd, J = 12.9, 4.4 Hz, 3H). ^{13}C NMR (500 MHz, $CDCl_3$, δ): 187.09 (s), 144.08 (s), 137.30 (s), 136.57 (s), 132.85 (s), 131.47 (s),

129.25 (s), 128.71 (s), 110.87 (s). HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{11}H_7OS$, 266.9479; found, 266.9475.

(3-bromothiophen-2-yl)(phenyl)methanone **(2c)**. Yellow liquid. Yield 8.58g (80%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.84 (d, J = 7.6 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.56 (d, J = 5.2 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H), 7.14 (d, J = 5.2 Hz, 1H). ^{13}C NMR (500 MHz, $CDCl_3$, δ): 188.19 (s), 137.83 (s), 135.82 (s), 133.10 (s), 132.86 (s), 131.22 (s), 129.82 (s), 128.47 (s), 115.33 (s). HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{11}H_7OS$, 266.9479; found, 266.9482.

(5-(4-(9H-carbazol-9-yl)phenyl)thiophen-2-yl)(phenyl)methanone (4a)

A mixture of **2a** (0.50 g, 1.87 mmol), (4-(9H-carbazol-9-yl)phenyl)boronic acid (0.59 g, 2.05 mmol), $Pd(PPh_3)_4$ (3 mol%), and K_2CO_3 (0.64 g, 4.68 mmol) was dissolved in a THF/water mixture (3:1 v/v) under an inert atmosphere. The reaction mixture was refluxed at 80 °C for 8 h. After completion (monitored by TLC), the mixture was cooled to room temperature and extracted with DCM. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using 25–30% DCM/hexane as the eluent to give a light yellow solid (0.70 g, 87%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.16 (d, *J* = 7.7 Hz, 2H), 7.92 (t, *J* = 7.4 Hz, 4H), 7.65 (dt, *J* = 14.8, 5.9 Hz, 4H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.46 (dt, *J* = 15.0, 8.1 Hz, 5H), 7.32 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (500 MHz, $CDCl_3$, δ):187.97 (s), 152.00 (s), 142.73 (s), 140.54 (s), 138.43 (s), 138.02 (s), 135.99 (s), 132.29 (s), 132.24 (s), 129.13 (s), 128.48 (s), 127.75 (s), 127.49 (s), 126.09 (s), 124.24 (s), 123.60 (s), 120.40 (s), 120.29 (s), 109.74 (s). HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{29}H_{19}NOS$, 430.1265; found, 430.1257.

(4-(4-(9H-carbazol-9-yl)phenyl)thiophen-2-yl)(phenyl)methanone (4b)

A mixture of **2b** (0.3 g, 1.12 mmol), (4-(9*H*-carbazol-9-yl)phenyl)boronic acid **(3)** (0.38 g, 1.34 mmol) and tetrakis(triphenylphosphine)palladium(0) (3 mol%) and potassium carbonate (0.37 g, 2.69 mmol) were taken in a mixture of THF:water (3:1 volume ratio) under inert atmosphere. Same procedure was followed as per given in synthesis of **4a**. The obtained residue was purified by column chromatography (20-25% DCM/Hexane). White solid. Yield 0.41 g (85%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.16 (dt, J = 7.8, 1.0 Hz, 2H), 7.99 (d, J = 1.5 Hz, 1H), 7.95 (m, 3H), 7.81 (m), 7.64 (m), 7.56 (m), 7.44 (m), 7.31 (ddd, J = 8.0, 6.5, 1.7 Hz). ^{13}C NMR (500 MHz, $CDCl_3$, δ): 188.33 (s), 144.51 (s), 142.40 (s), 140.77 (s), 138.01 (s), 137.32 (s), 133.94 (s), 133.39 (s),

132.64 (s), 129.34 (s), 129.26 (s), 128.70 (s), 127.90 (s), 127.62 (s), 126.11 (s), 123.54 (s), 120.49 (s), 120.20 (s), 109.80 (s). HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{29}H_{19}NOS$, 430.1265; found, 430.1254.

(3-(4-(9H-carbazol-9-yl)phenyl)thiophen-2-yl)(phenyl)methanone (4c)

A mixture of **2c** (0.3 g, 1.12 mmol), (4-(9*H*-carbazol-9-yl)phenyl)boronic acid **(3)** (0.38 g, 1.34 mmol) and tetrakis(triphenylphosphine)palladium(0) (3 mol%) and potassium carbonate (0.37 g, 2.69 mmol) were taken in a mixture of THF:water (3:1 volume ratio) under inert atmosphere. Same procedure was followed as per given in synthesis of **4a**. The obtained residue was purified by column chromatography (20-25% DCM/Hexane). Light yellow solid. Yield 0.39 g (81%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.13 (ddd, J = 7.8, 1.3, 0.8 Hz), 7.74 (t, J = 4.9 Hz), 7.67 (m), 7.41 (m), 7.34 (m), 7.29 (m), 7.27 (m), 7.25 (dd, J = 1.3, 0.9 Hz), 7.22 (m). ^{13}C NMR (500 MHz, $CDCl_3$, δ): 190.32 (s), 145.89 (s), 140.76 (s), 138.05 (s), 137.79 (s), 137.20 (s), 134.87 (s), 132.53 (s), 131.26 (s), 130.87 (s), 130.47 (s), 129.93 (s), 128.03 (s), 126.73 (s), 125.94 (s), 123.45 (s), 120.40 (s), 120.11 (s), 109.78 (s). HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{29}H_{19}NOS$, 430.1265; found, 430.1263.

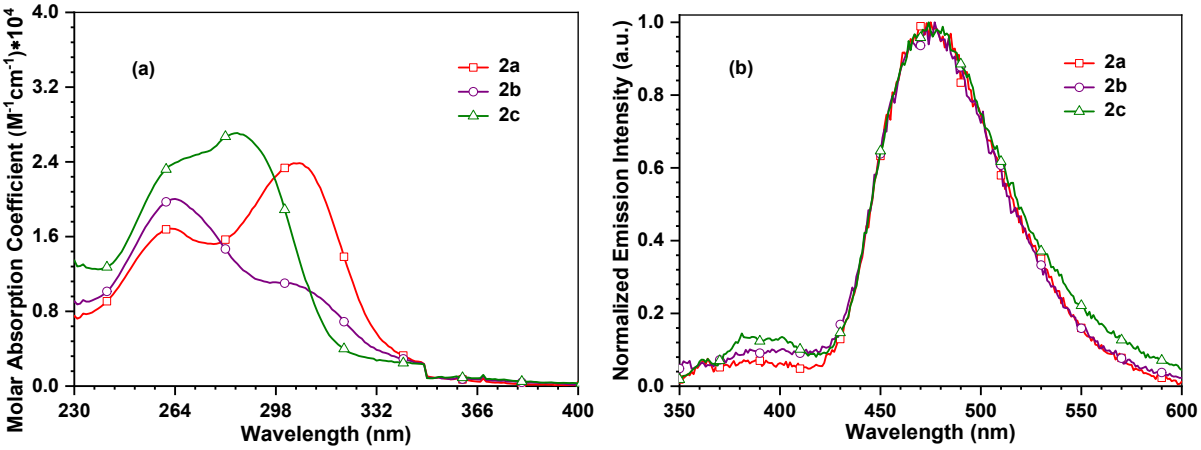


Figure S1. (a) Absorption, (b) emission spectra of the bromo derivatives, **2a**, **2b** and **2c** recorded in DCM.

Table S1. (a) Absorption and emission spectral data of the **2a**, **2b** and **2c** recorded in 1×10^{-4} M and 1×10^{-5} M DCM solution, respectively.

Compounds	λ_{abs} (nm) (ε_{max} $\times10^4$ (M^{-1} cm^{-1}))[a]	λ_{em} (nm)[a]
2a	262(1.67), 305(2.37)	475
2b	262(1.99), 303(1.09)	475
2c	262(2.36), 285(2.69)	474

[a] Measured in DCM solution.

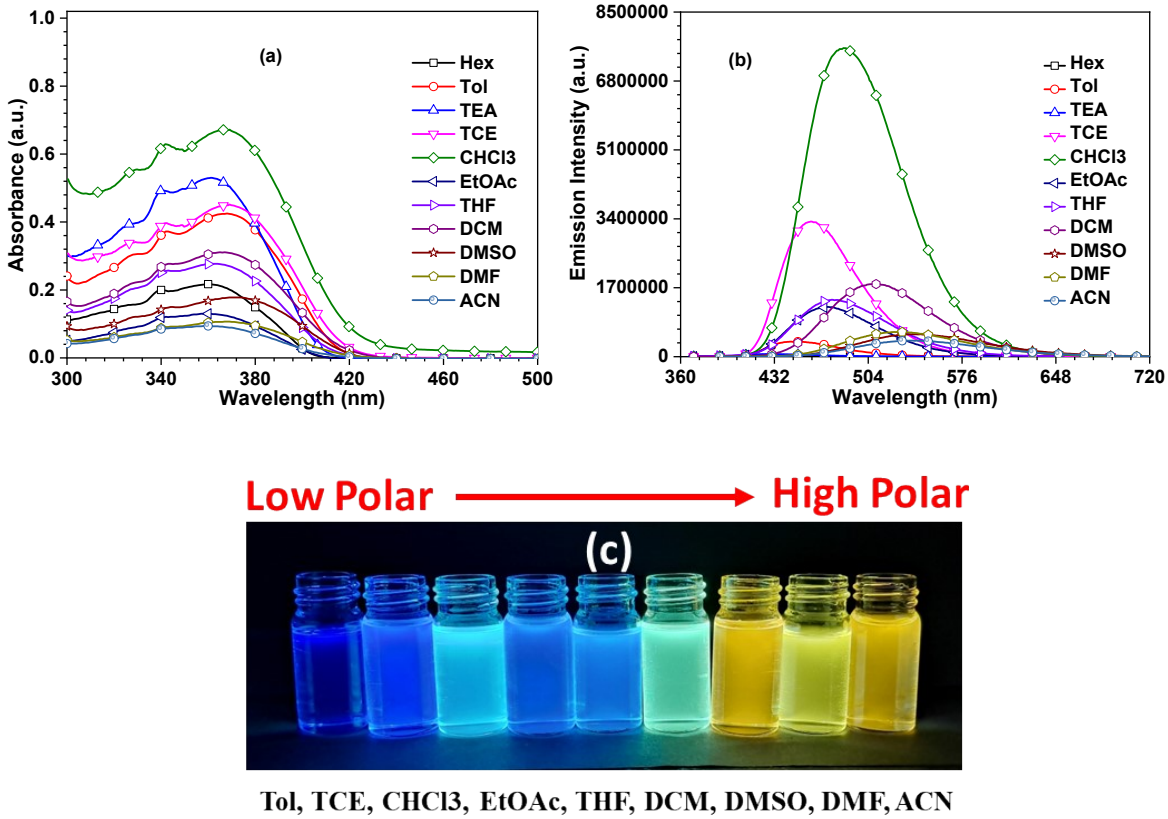


Figure S2. (a) Absorption, (b) emission spectra of **4a** recorded in different solvents and (c) visual image of the excited (365 nm) **4a** in different solvents.

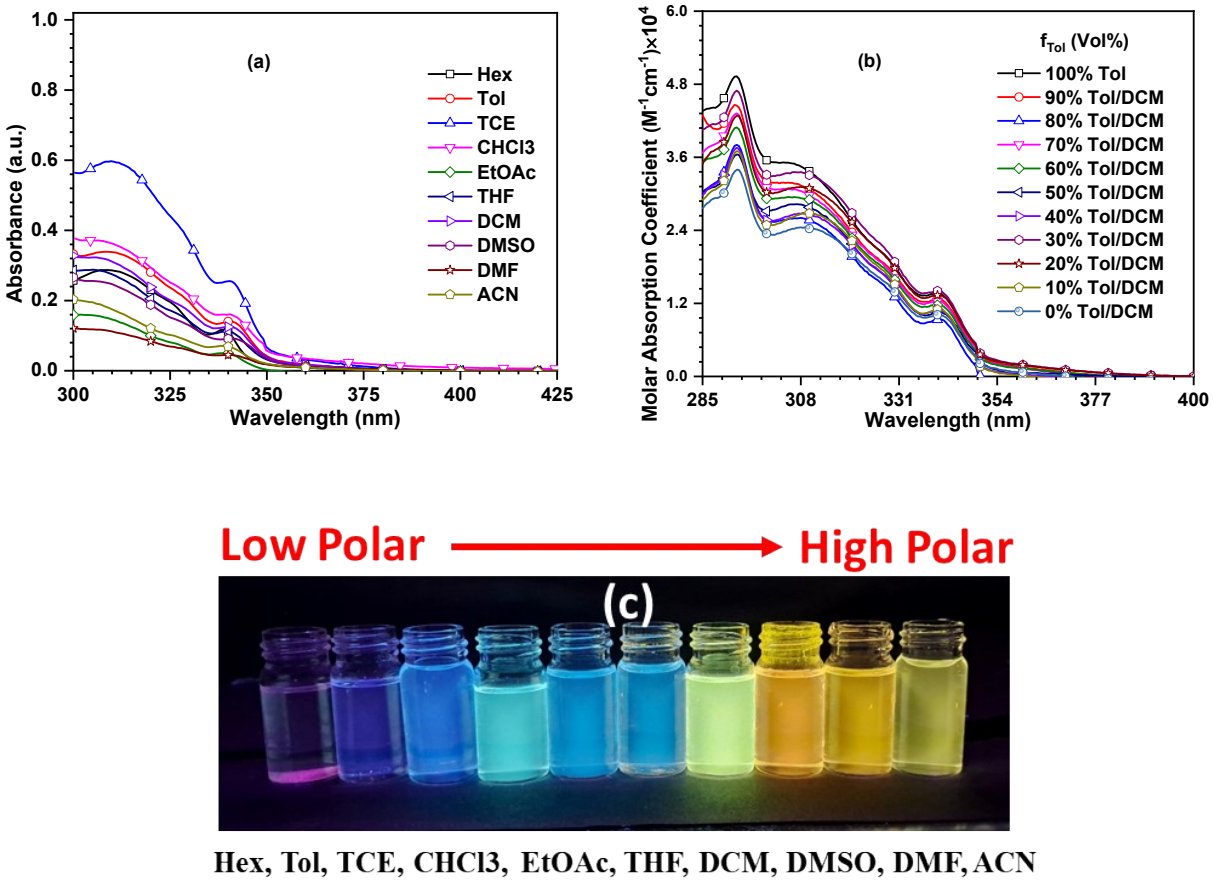
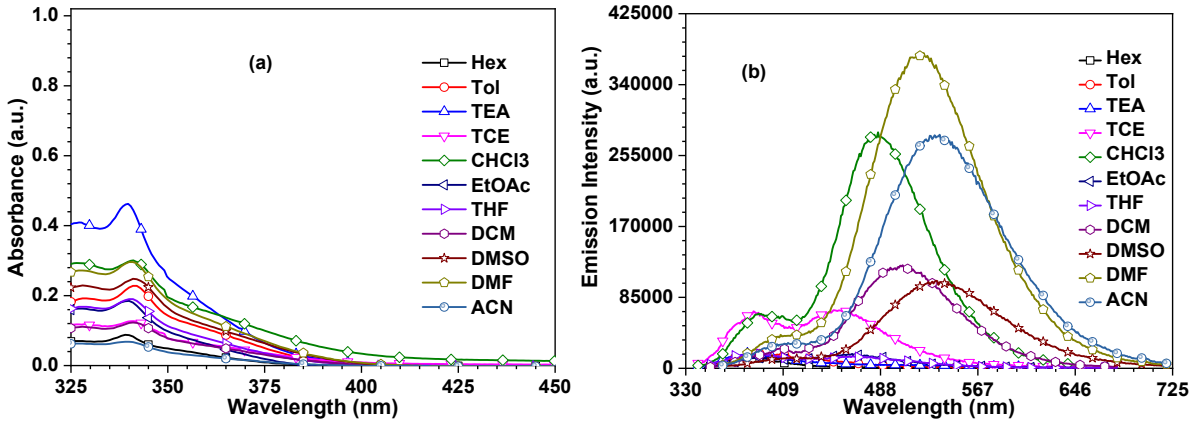


Figure S3. (a) Absorption spectra of **4b** recorded in different solvents, (b) absorption spectra of the dye **4b** recorded in toluene/DCM solvents and (c) visual image of the excited (365 nm) **4b** in different solvents.



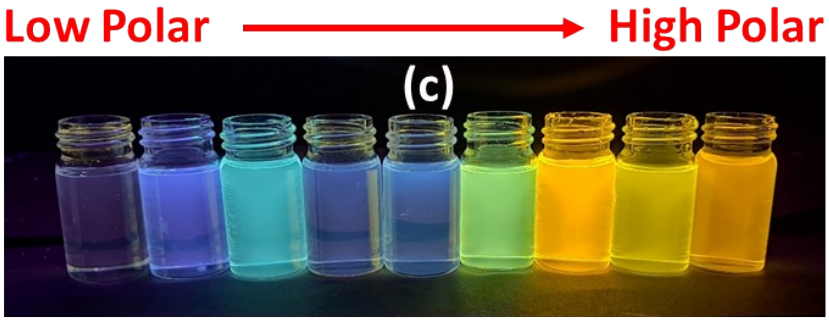


Figure S4. (a) Absorption, (b) emission spectra of **4c** recorded in different solvents and (c) visual image of the excited (365 nm) **4c** in different solvents.

Table S2. Solvatochromic data of **4a** in various solvents.

Solvent	E^N_T	Orientation Polarizability (Δf)	λ_{abs} (nm)	λem (nm)	Stokes Shift (nm)	Δν (cm^{-1})	FWHM (nm)
Hex	0.009	0.0012	359	425	66	4325.7	61
TOL	0.099	0.014	367	448	81	4926.5	62
TEA	0.043	0.045	360	430	70	4521.9	63
TCE	0.160	0.085	369	460	91	5361.1	67
CHCl3	0.259	0.149	367	485	118	6629.4	84
EtOAc	0.228	0.199	360	472	112	6591.3	76
THF	0.207	0.210	363	478	115	6627.7	80
DCM	0.309	0.217	367	510	143	7714.5	91
DMSO	0.444	0.263	372	542	170	8431.5	107
DMF	0.386	0.276	368	529	161	8270.3	102
ACN	0.460	0.305	361	539	178	9147.9	111

Table S3. Solvatochromic data of **4b** in various solvents.

Solvent	E^N_T	Orientation Polarizability (Δf)	λ_{abs} (nm)	λem (nm)	Stokes Shift (nm)	Δν (cm^{-1})	FWHM (nm)
Hex	0.009	0.0012	309	360	51	4738.1	48
TOL	0.099	0.014	309	367	58	5624.4	121
TCE	0.160	0.085	310	456	146	10328.2	75
CHCl3	0.259	0.149	306	488	182	11932.8	88
EtOAc	0.228	0.199	304	470	166	11618.1	78
THF	0.207	0.210	305	369	64	11645.2	156
DCM	0.309	0.217	305	510	205	13369.4	99
DMSO	0.444	0.263	305	547	242	14505.3	235
DMF	0.386	0.276	305	531	226	13954.4	111
ACN	0.460	0.305	305	542	237	14336.7	115

Table S4. Solvatochromic data of **4c** in various solvents.

Solvent	E^N_T	Orientation Polarizability (Δf)	λ_{abs} (nm)	λem (nm)	Stokes Shift (nm)	Δν (cm^{-1})	FWHM (nm)
Hex	0.009	0.0012	339	383	44	3388.8	53
TOL	0.099	0.014	341	387	46	3485.7	55
TEA	0.043	0.045	339	389	50	3791.5	59
TCE	0.160	0.085	341	447	106	6954.1	135
CHCl3	0.259	0.149	341	481	140	8535.4	83
EtOAc	0.228	0.199	339	464	125	7946.8	132
THF	0.207	0.210	340	461	121	7719.7	121
DCM	0.309	0.217	341	505	164	9523.5	94
DMSO	0.444	0.263	341	535	194	10633	108
DMF	0.386	0.276	341	526	185	10314	104
ACN	0.460	0.305	340	532	192	10614	108

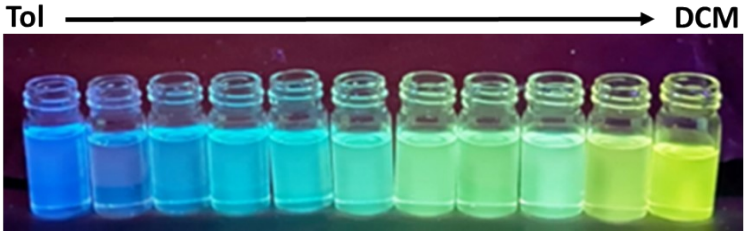


Figure S5. visual image of the excited (365 nm) **4c** in toluene/DCM binary solvent.

Figure S6. Photoexcited at 365nm image of the dyes **4a**, **4b** and **4c** drop-cast thin films.

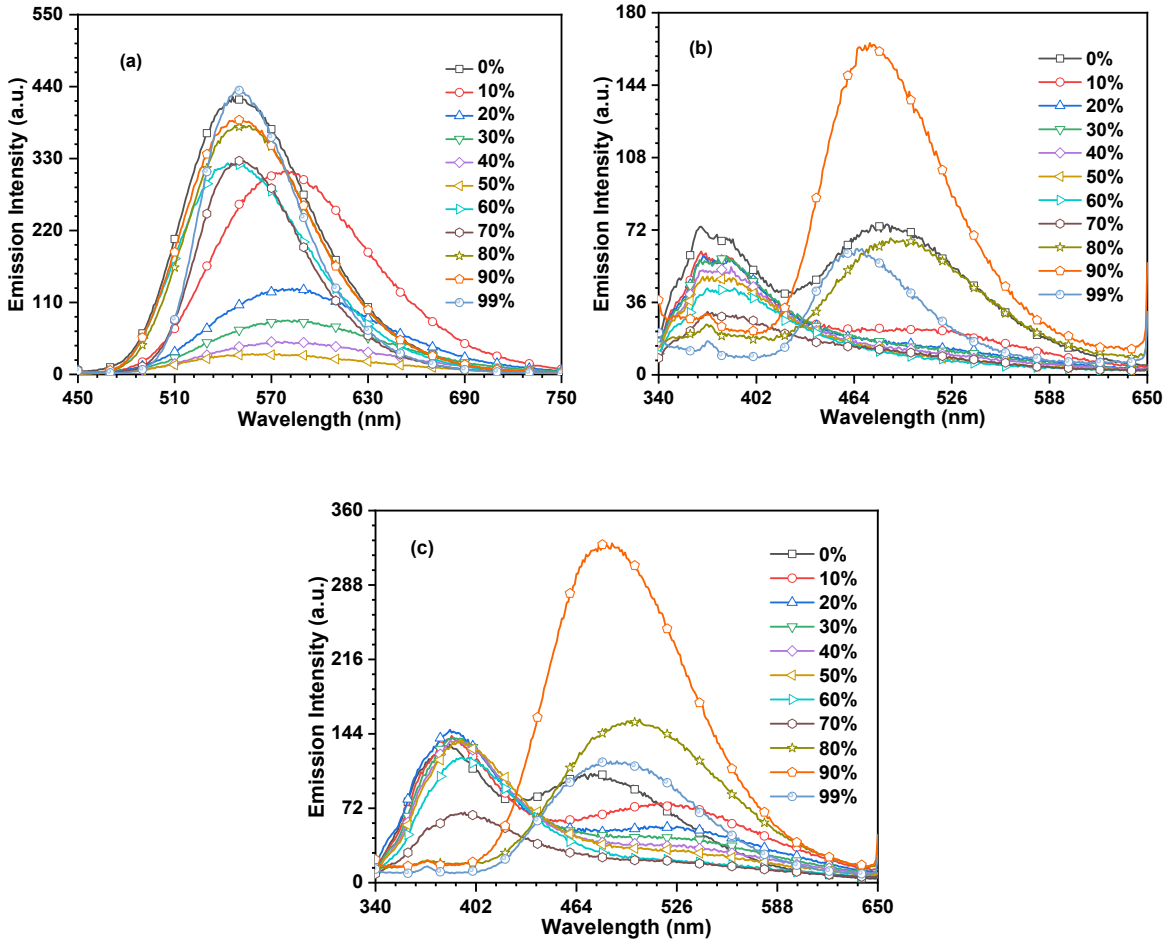


Figure S7. Changes in the emission observed on changing the water ratio in THF for the dyes (a) **4a**, (b) **4b**, and (c) **4c**.

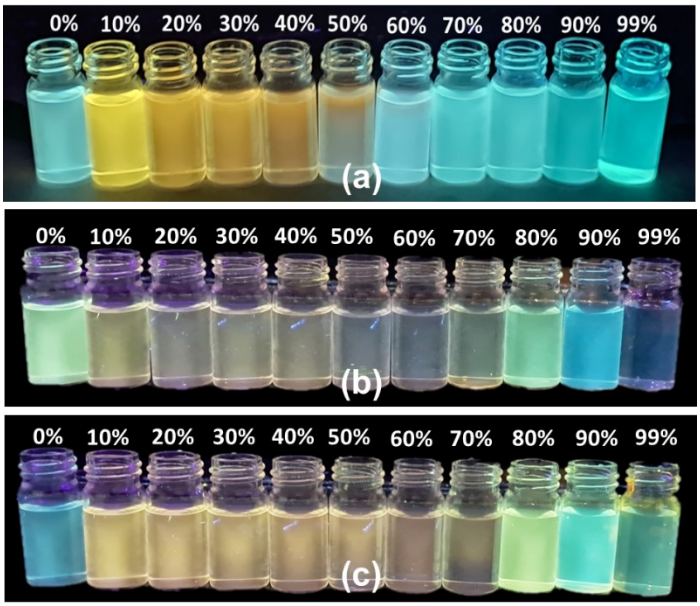


Figure S8. Visual images of the photoexcited (365 nm) dyes (a) **4a**, (b) **4b**, (c) **4c** in different water ratios in THF.

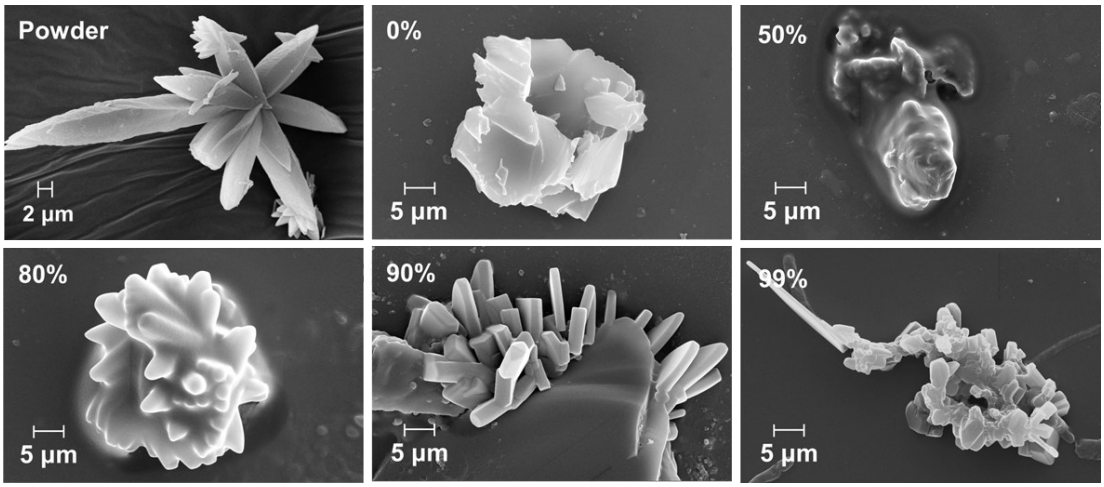


Figure S9. SEM images of **4a** in powder and aggregated forms obtained from different water ratio.

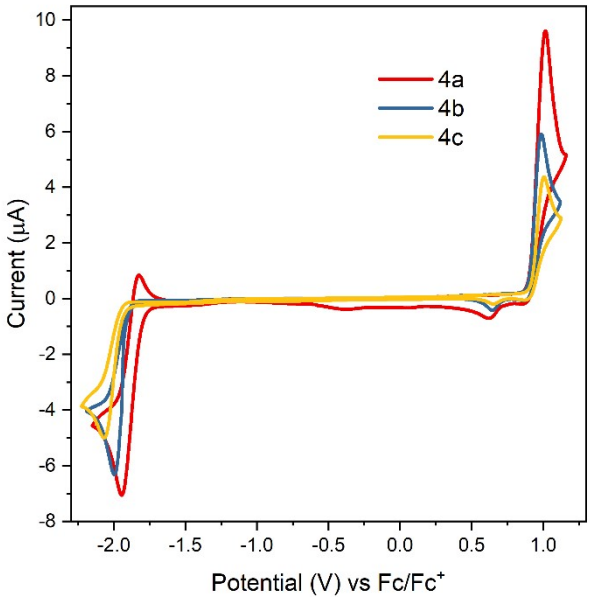


Figure S10. Cyclic voltammograms of 1 mM of emitter (**4a**-**4c**) in 0.1 M Bu_4NBF_4 in DCM electrolyte at a scan rate of 50 mV/s.

Table S5. Electrochemical parameters extracted from cyclic voltammograms.

Emitters	LUMO (eV)	HOMO (eV)	Band gap (eV)
4a	-3.31	-6.00	-2.69
4b	-3.20	-6.01	-2.81
4c	-3.18	-6.02	-2.84

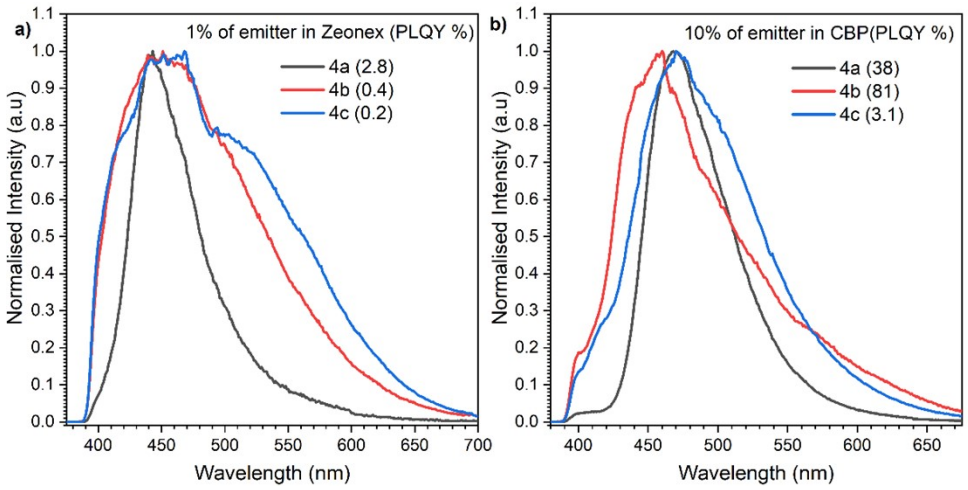


Figure S11. Steady-state PL emission of **4a-4c** in ambient condition: 1 wt% of emitter in Zeonex (a); 10 wt% of emitters in CBP; PLQY was measured at ambient condition. Spectra were recorded at 300K using λ_{ex} = 355 nm.

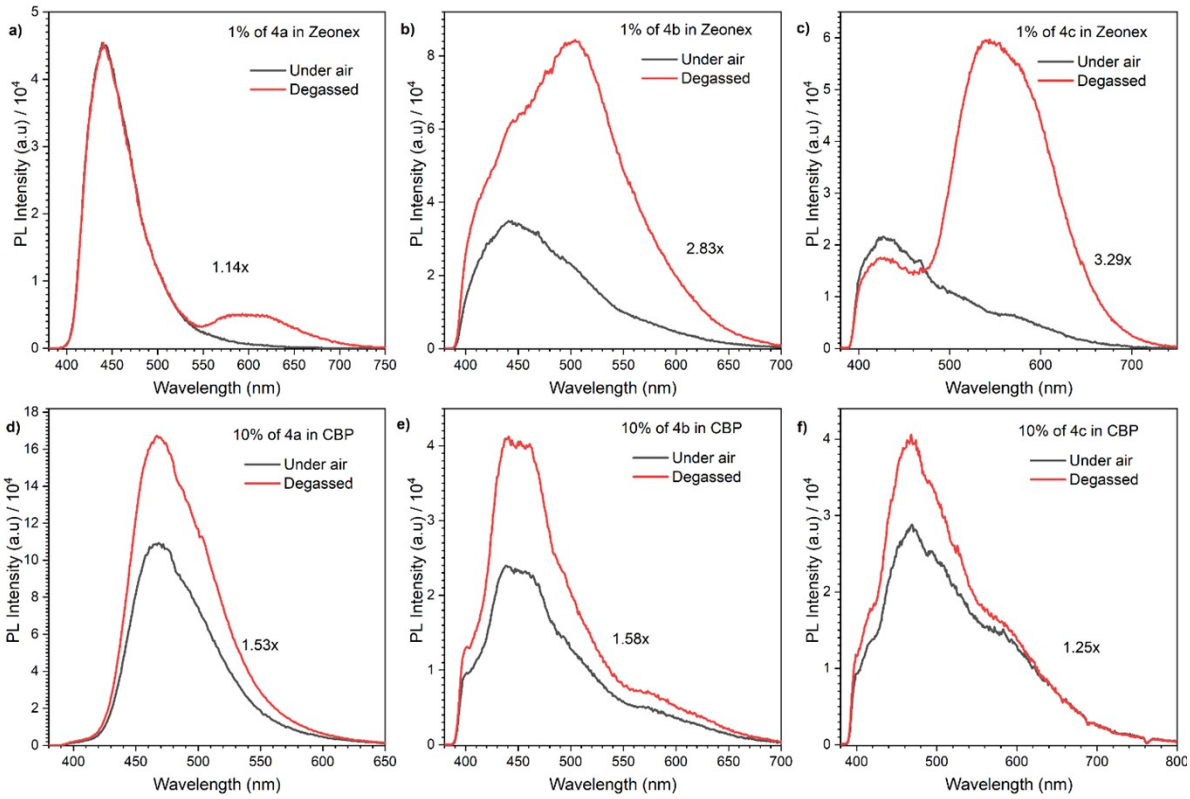


Figure S12. Steady-state photoluminescence (PL) spectra in Zeonex® in the presence of air (Under air) and in a vacuum (degassed) for the compounds **4a-4c**. Recorded at 300 K using λ_{ex}=355 nm.

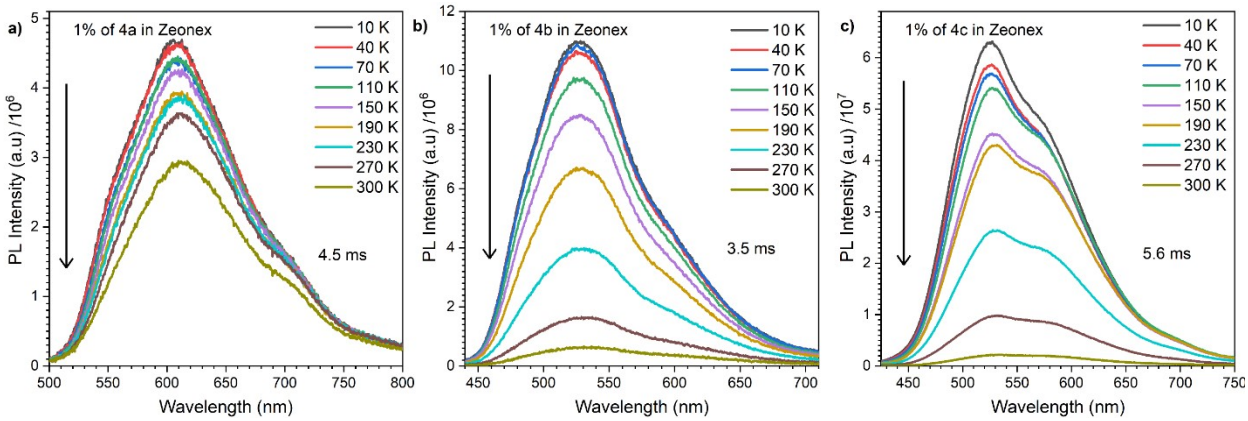


Figure S13. Temperature dependent time resolved PH spectra of the 1wt% of emitters (**4a**-**4c**) in Zeonex and λ_{ex}=355 nm.

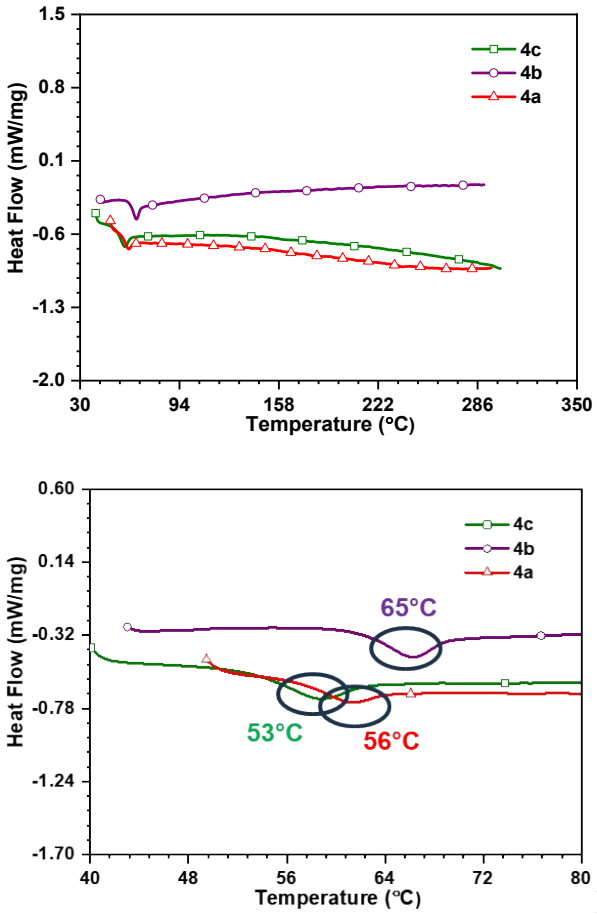


Figure S14. Differential scanning calorimetry (DSC) traces of **4a**, **4b** and **4c**.

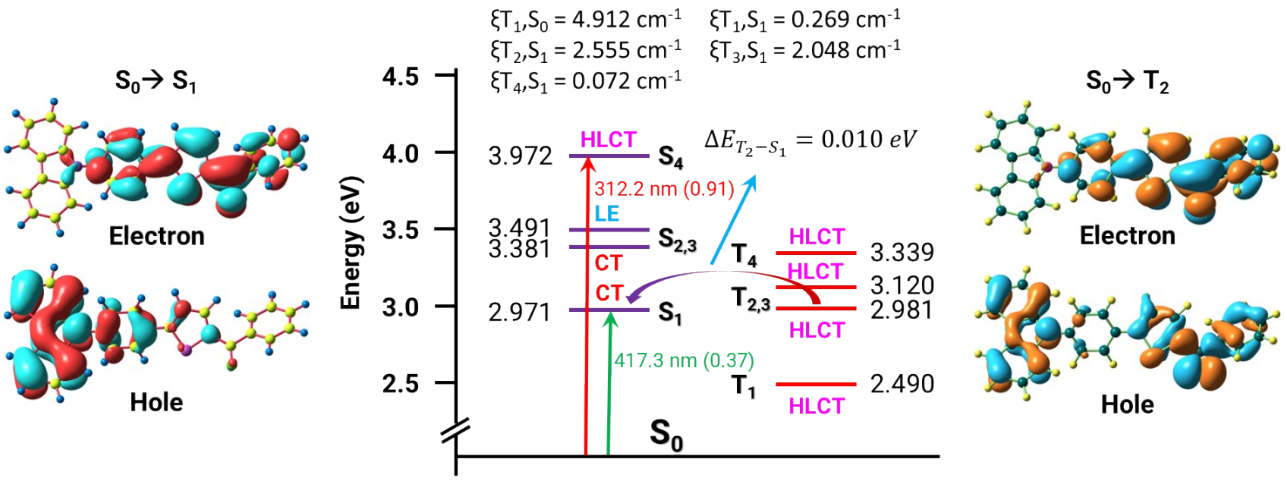


Figure S15. Energy level diagram of **4a**.

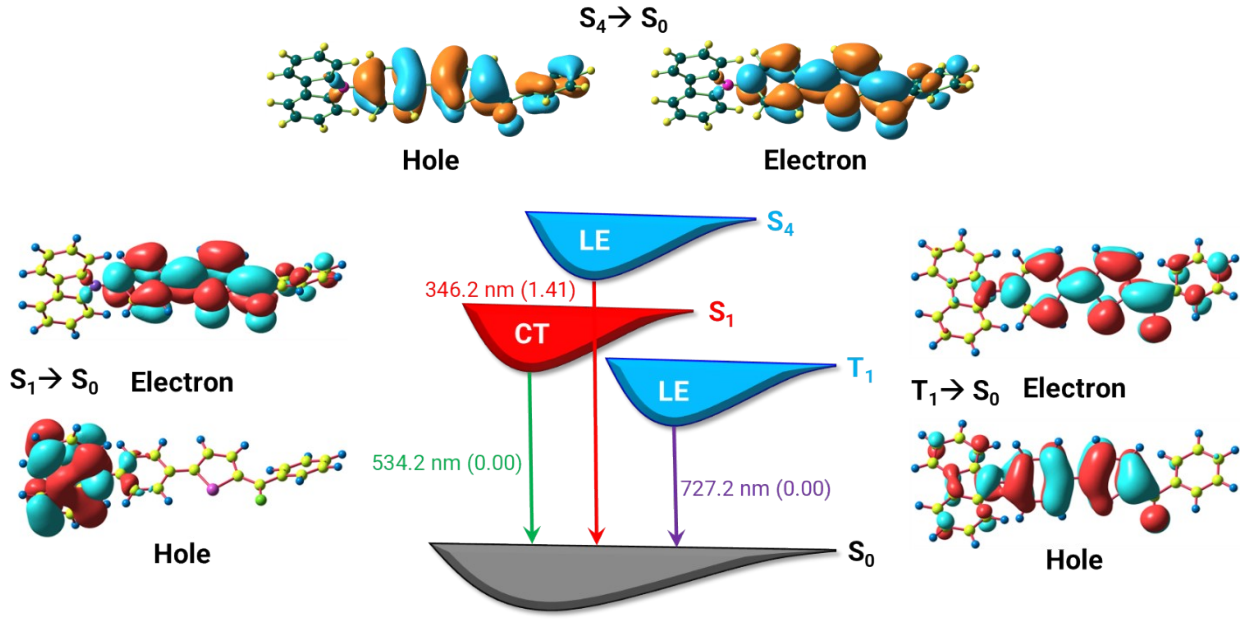


Figure S16. Emission NTO analysis of **4a**.

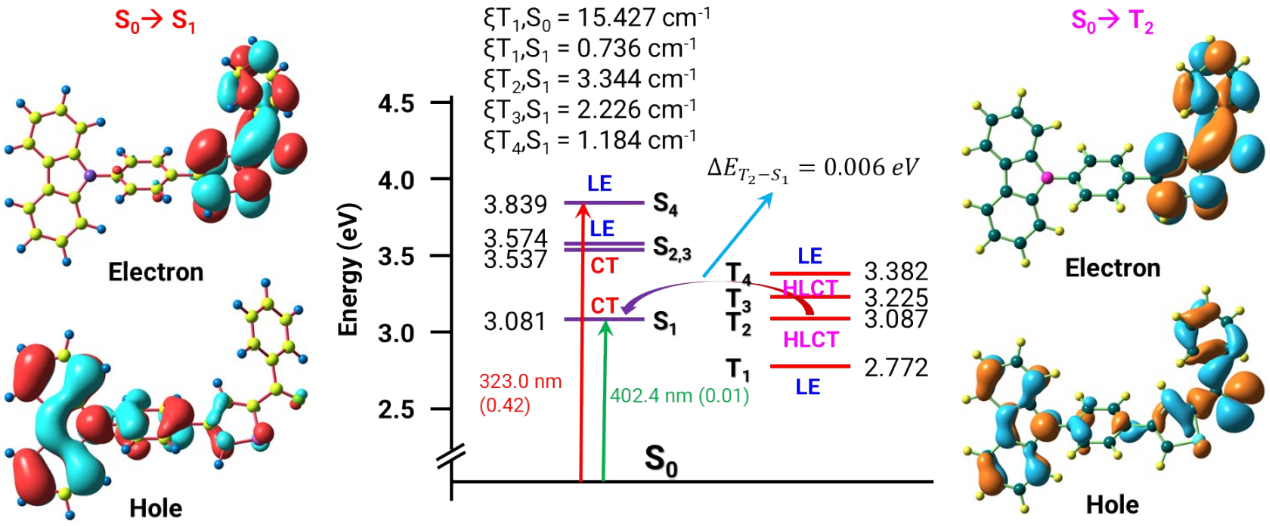


Figure S17. Energy level diagram of **4b**.

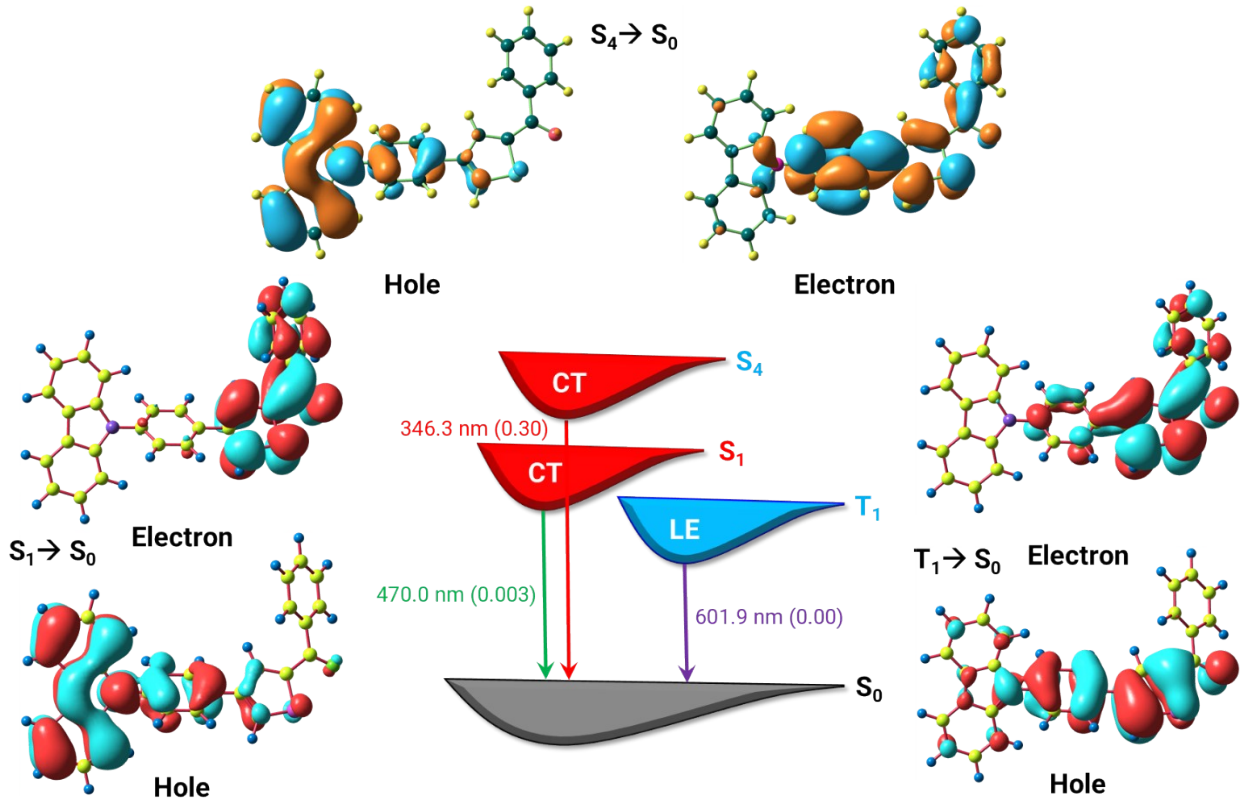


Figure S18. Emission NTO analysis of **4b**.

Single Crystal Analysis

Table S6. Crystal data and structure refinement data for 4a	
Identification code	**4a**
CCDC	2516523
Empirical formula	$C_{29}H_{19}NOS$
Formula weight	429.51
Temperature/K	100.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	25.2496(12)
b/Å	13.1469(6)
c/Å	25.8557(13)
α/°	90
β/°	95.084(2)
γ/°	90
Volume/Å^3	8549.1(7)
Z	16
ρ_{calc}g/cm^3	1.335
μ/mm^{-1}	0.174
F(000)	3584.0
Crystal size/mm^3	0.41 × 0.24 × 0.069
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.162 to 54.976
Index ranges	$-32 \le h \le 32$, $-17 \le k \le 17$, $-33 \le l \le 33$
Reflections collected	224007
Independent reflections	19513 [R_{int} = 0.0870, R_{sigma} = 0.0455]
Data/restraints/parameters	19513/0/1153
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0428, wR_2 = 0.0953
Final R indexes [all data]	R_1 = 0.0633, wR_2 = 0.1095
Largest diff. peak/hole / e Å^{-3}	0.29/-0.30

Table S7. Crystal data and structure refinement data for 4b	
Identification code	**4b**
CCDC	2516522
Empirical formula	$C_{29}H_{19}NOS$
Formula weight	429.51
Temperature/K	273.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	15.597(5)
b/Å	7.801(2)
c/Å	17.993(6)
α/°	90
β/°	96.173(10)
γ/°	90
Volume/Å^3	2176.7(11)
Z	4
ρ_{calc}g/cm^3	1.311
μ/mm^{-1}	0.171
F(000)	896.0
Crystal size/mm^3	0.256 × 0.136 × 0.086
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.698 to 56.63
Index ranges	$-20 \leq h \leq 20$, $-10 \leq k \leq 10$, $-23 \leq l \leq 23$
Reflections collected	32640
Independent reflections	5390 [R_{int} = 0.0939, R_{sigma} = 0.0589]
Data/restraints/parameters	5390/0/289
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0474, wR_2 = 0.1107
Final R indexes [all data]	R_1 = 0.0679, wR_2 = 0.1253
Largest diff. peak/hole / e Å^{-3}	0.28/-0.33

Table S8. Crystal data and structure refinement data for **4c**	
Identification code	**4c**
CCDC	2516524
Empirical formula	$C_{30}H_{23}NO_2S$
Formula weight	461.55
Temperature/K	296.15
Crystal system	monoclinic
Space group	C2/c
a/Å	41.689(5)
b/Å	7.5671(9)
c/Å	34.585(4)
α/°	90
β/°	121.555(3)
γ/°	90
Volume/Å^3	9297.1(19)
Z	16
ρ_{calc}g/cm^3	1.319
μ/mm^{-1}	0.168
F(000)	3872.0
Crystal size/mm^3	0.216 × 0.119 × 0.109
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.924 to 53.382
Index ranges	$-52 \leq h \leq 52$, $-9 \leq k \leq 9$, $-43 \leq l \leq 39$
Reflections collected	57410
Independent reflections	9762 [R_{int} = 0.1049, R_{sigma} = 0.0798]
Data/restraints/parameters	9762/0/578
Goodness-of-fit on F^2	1.197
Final R indexes [I>=2σ (I)]	R_1 = 0.1174, wR_2 = 0.2105
Final R indexes [all data]	R_1 = 0.1430, wR_2 = 0.2218
Largest diff. peak/hole / e Å^{-3}	0.55/-0.40

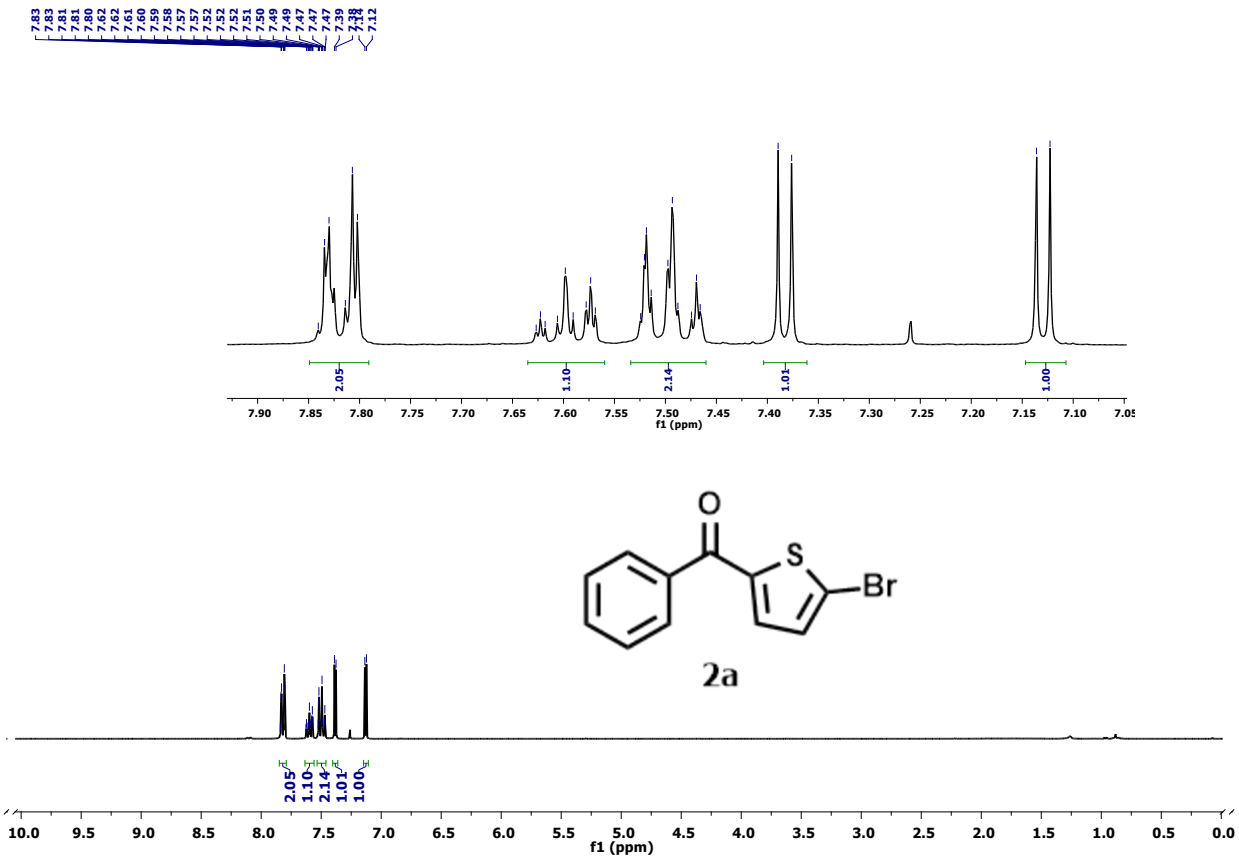


Figure S19. ^{1}H NMR spectrum of **2a** recorded in $CDCl_3$.

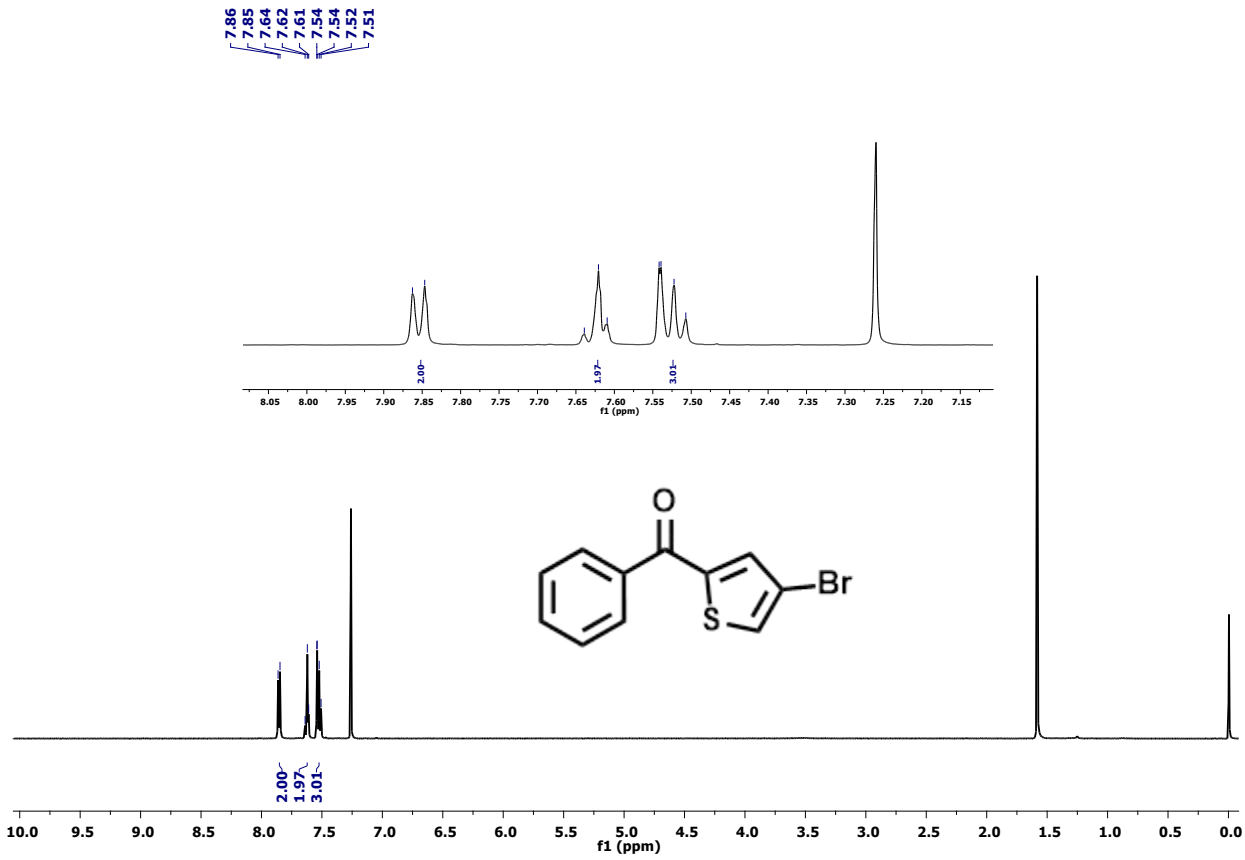


Figure S20. ^{1}H NMR spectrum of **2b** recorded in $CDCl_3$.

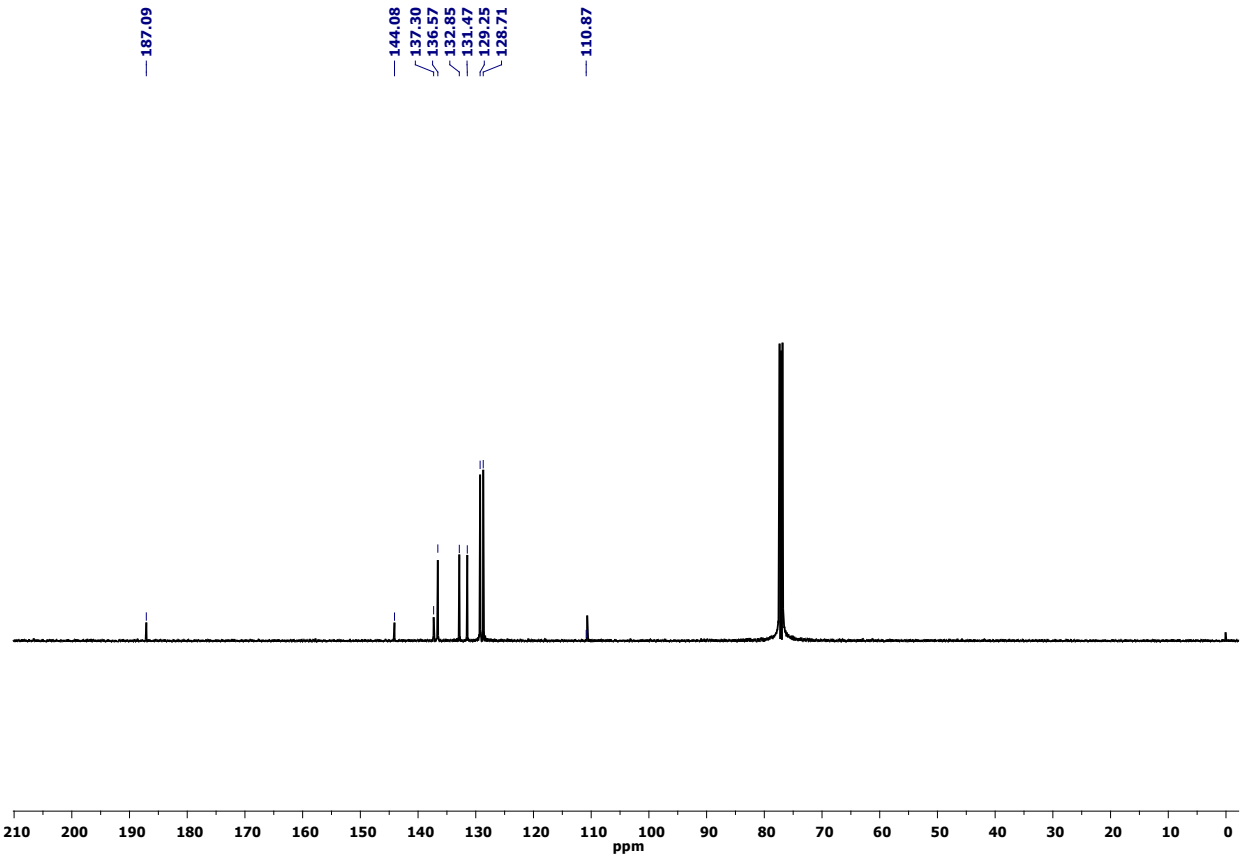


Figure S21. ^{13}C NMR spectrum of **2b** recorded in $CDCl_3$.

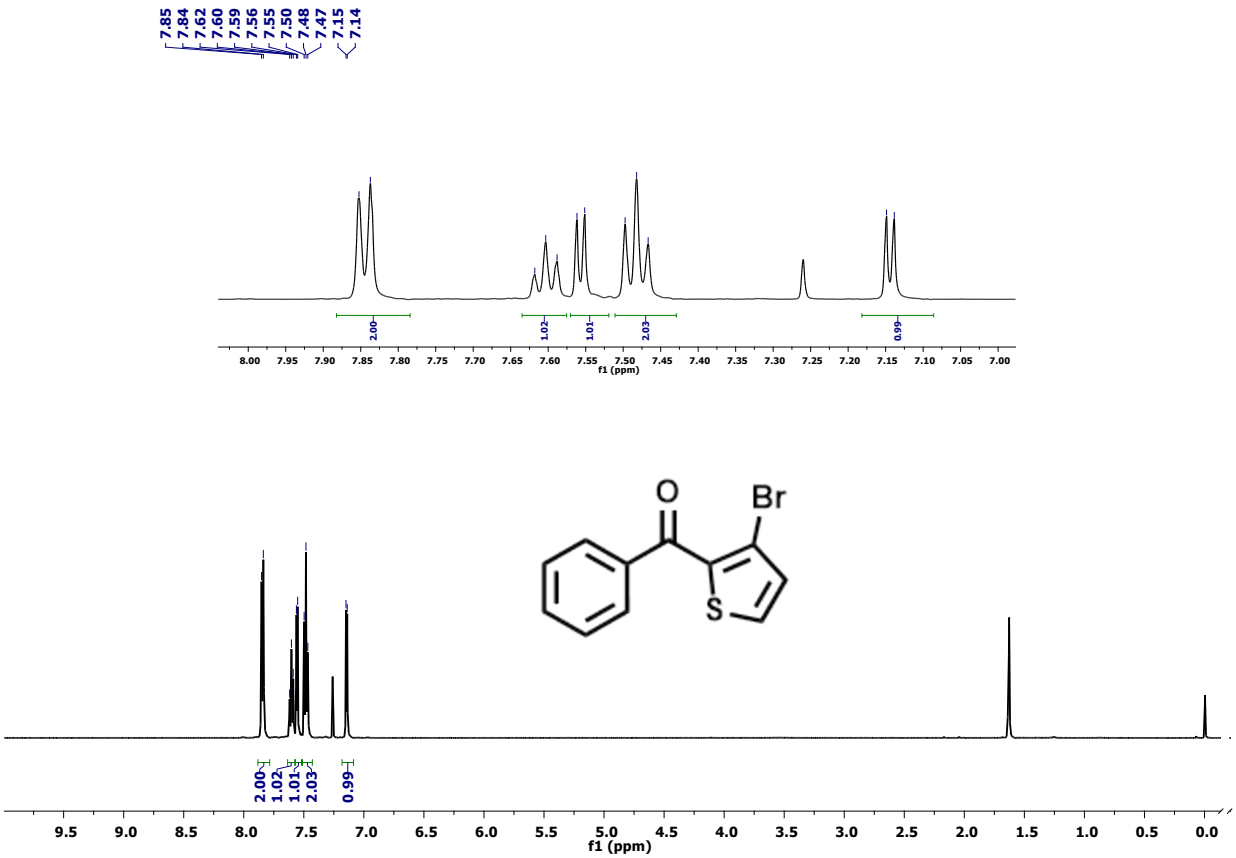


Figure S22. ^{1}H NMR spectrum of **2c** recorded in $CDCl_3$.

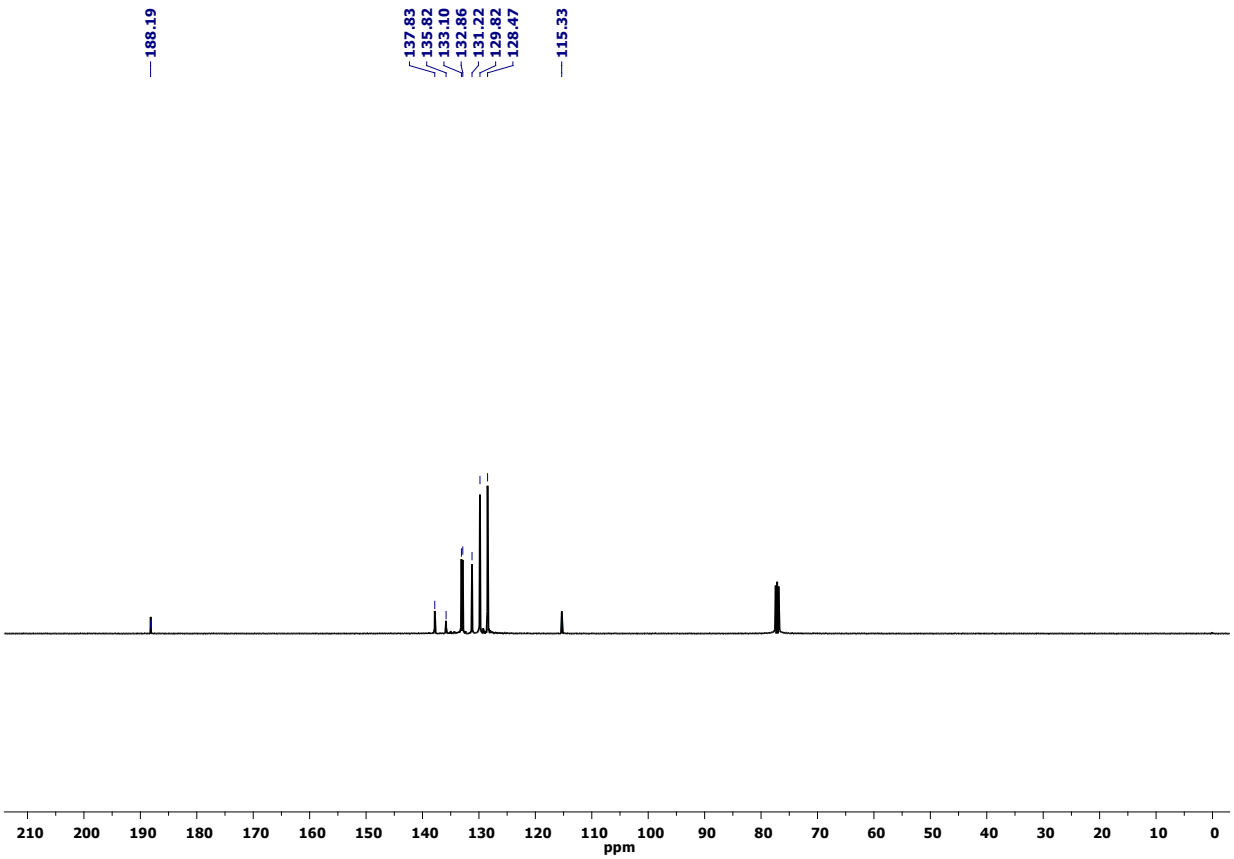


Figure S23. ^{13}C NMR spectrum of **2c** recorded in $CDCl_3$.

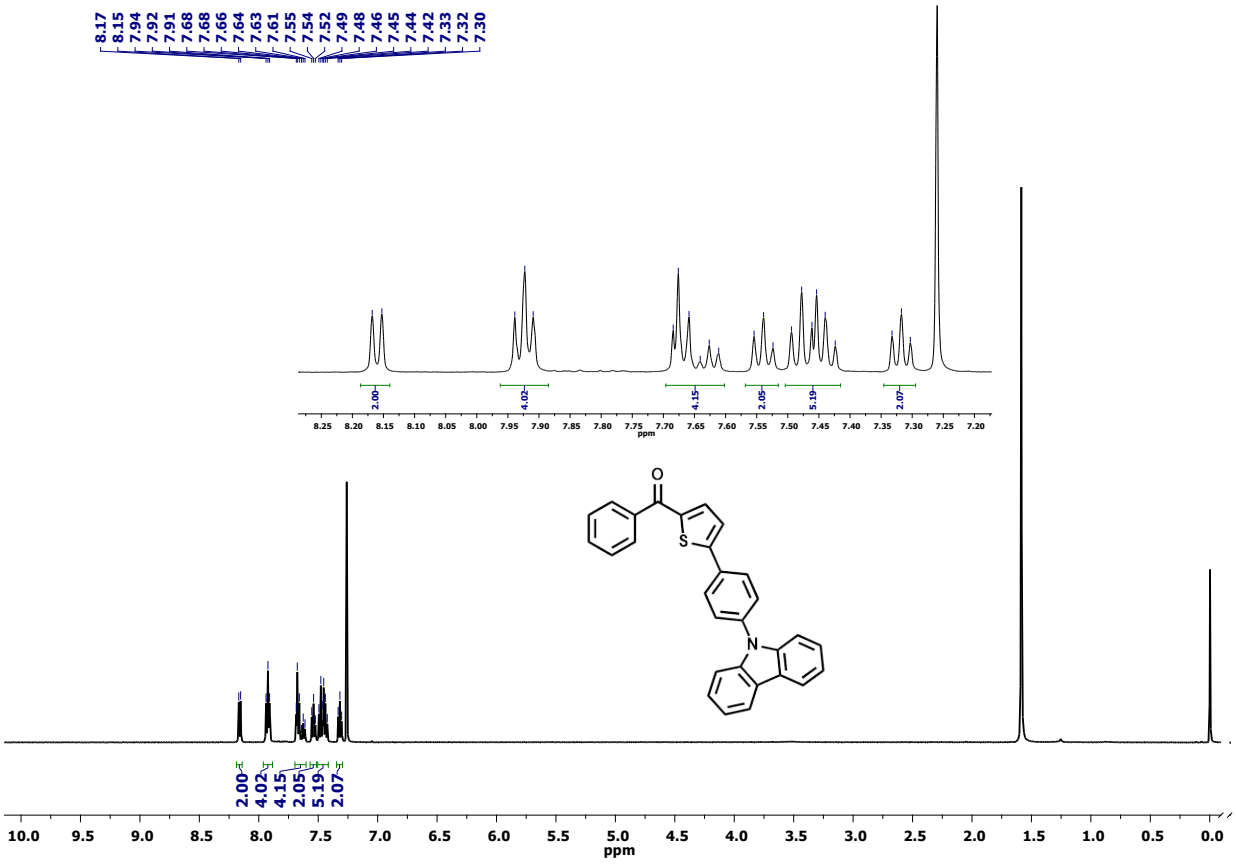


Figure S24. ^{1}H NMR spectrum of **4a** recorded in $CDCl_3$.

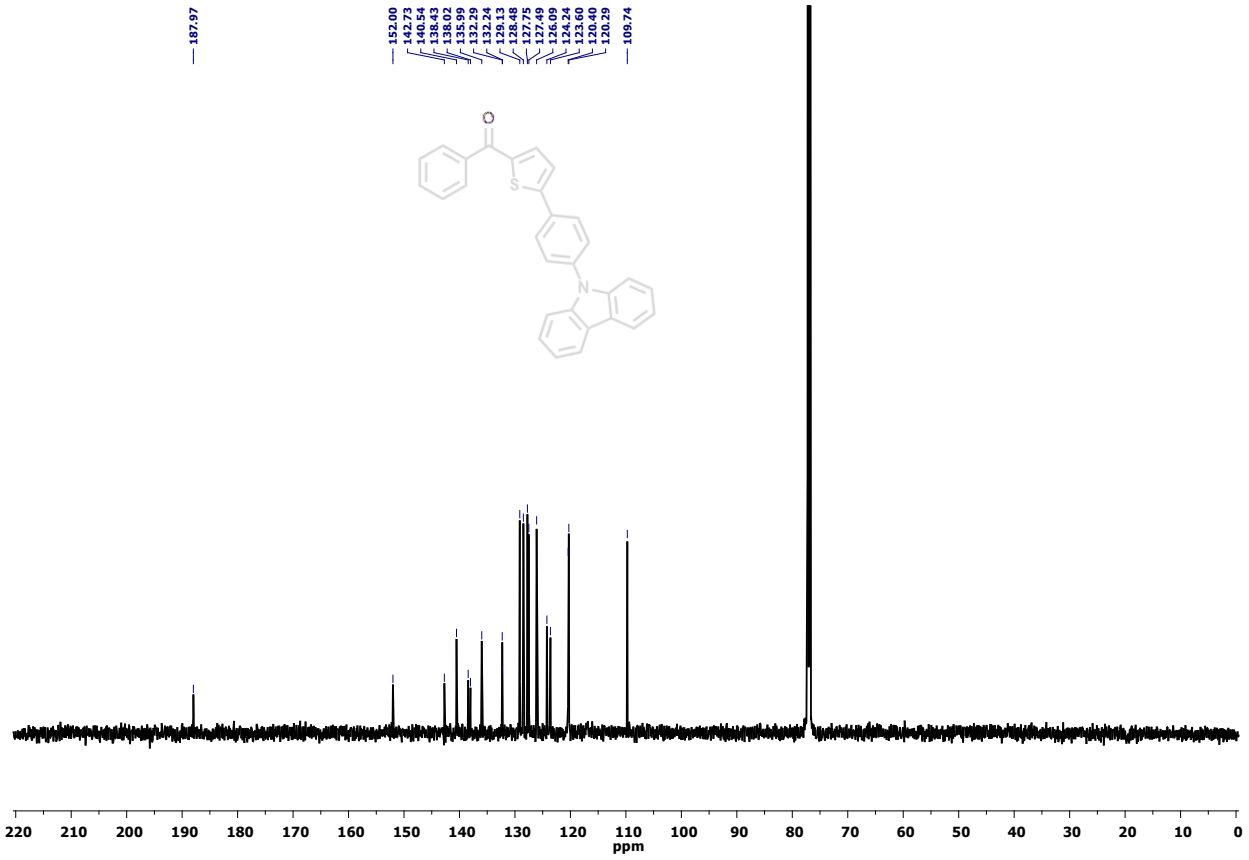


Figure S25. ^{13}C NMR spectrum of **4a** recorded in $CDCl_3$.

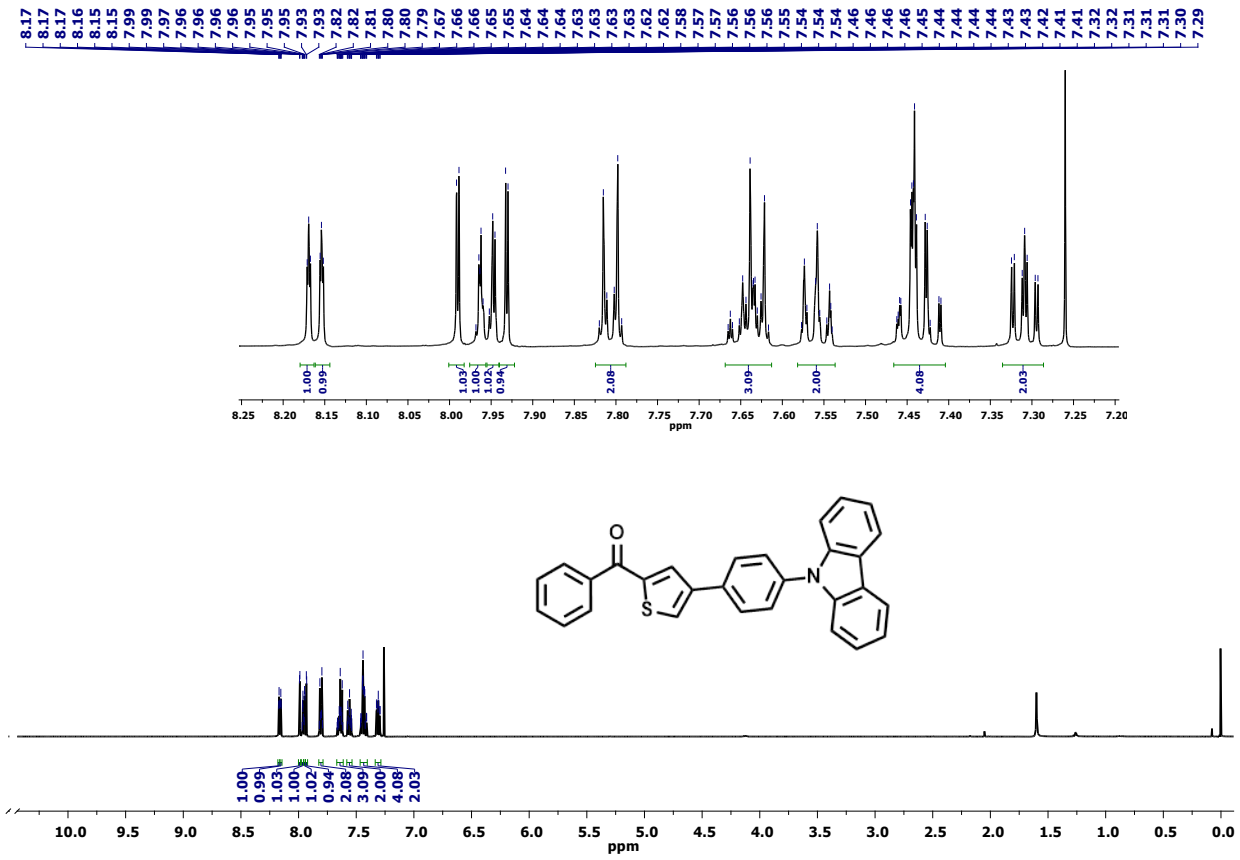


Figure S26. ^{1}H NMR spectrum of **4b** recorded in $CDCl_3$.

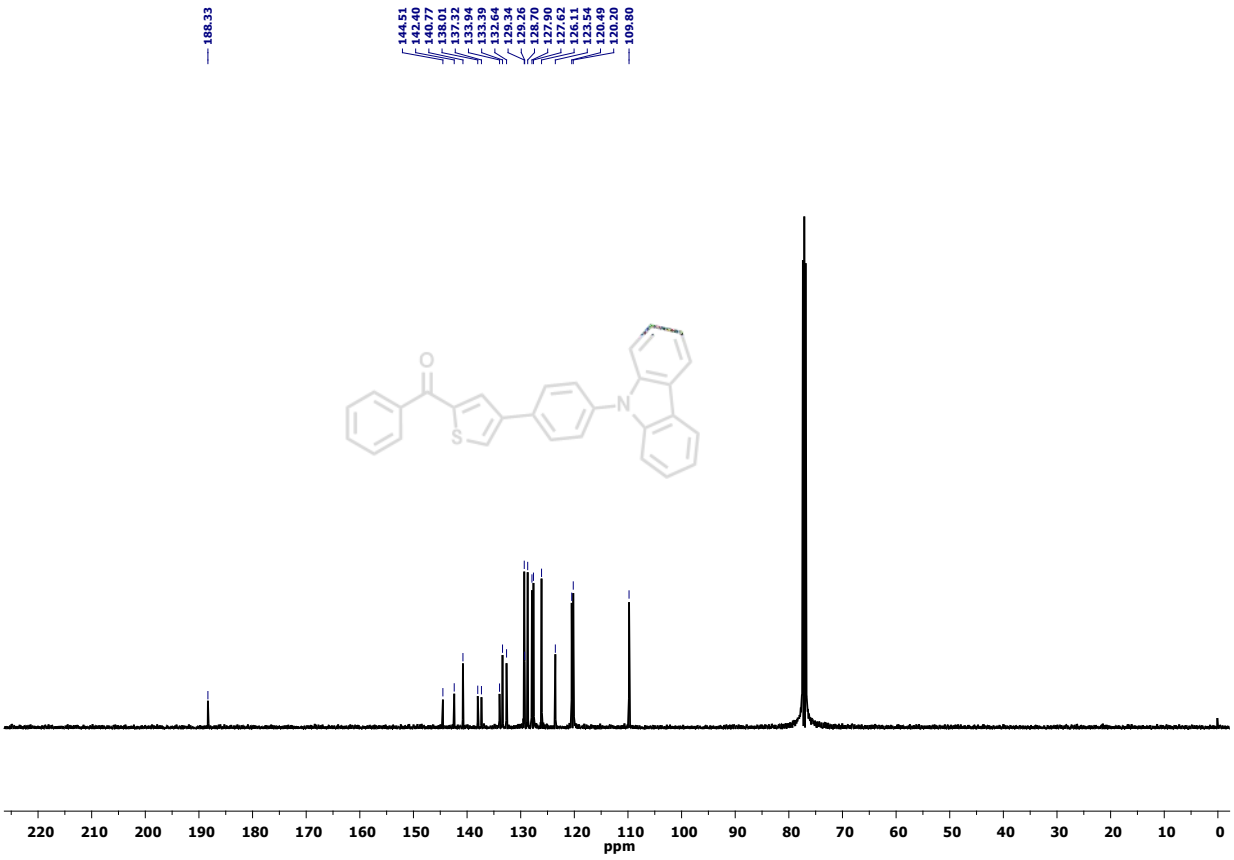


Figure S27. ^{13}C NMR spectrum of **4b** recorded in $CDCl_3$.

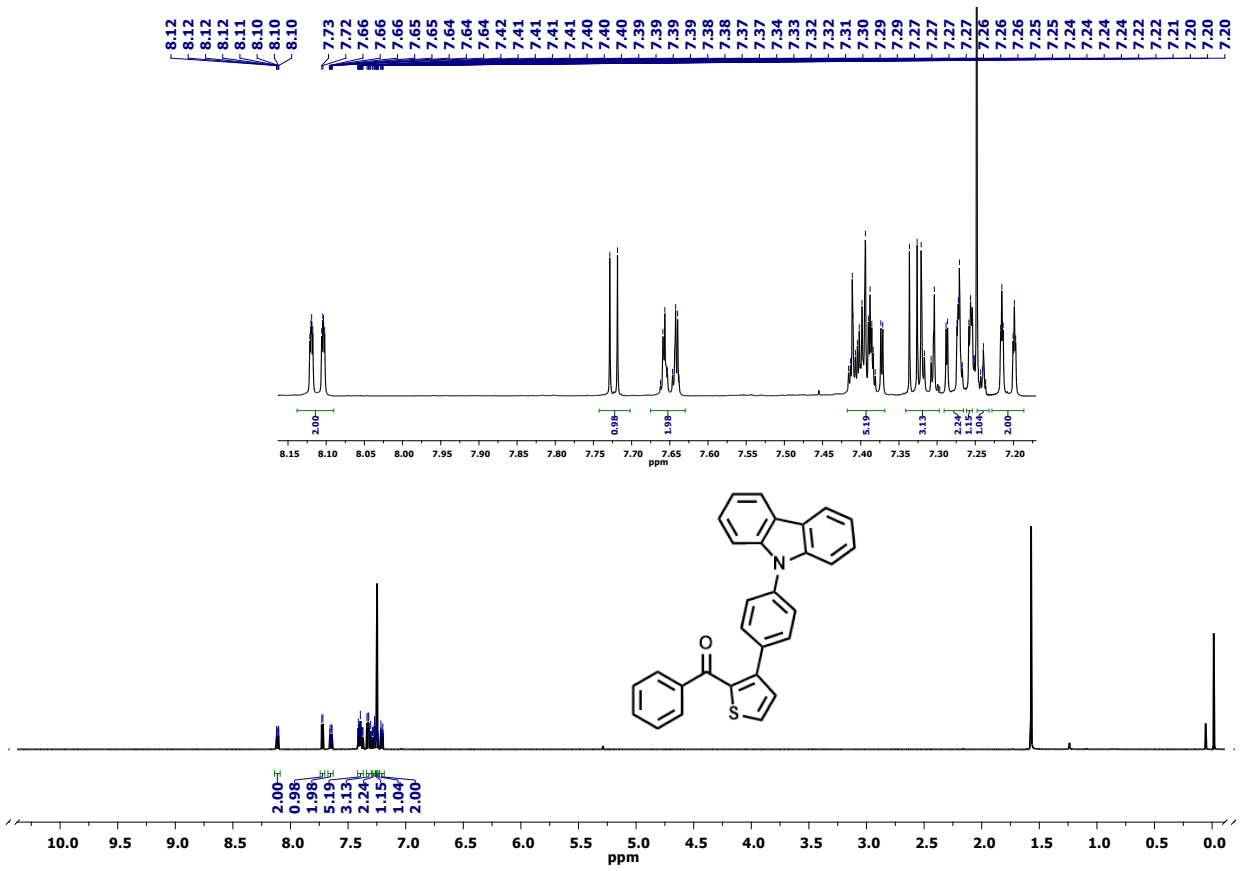


Figure S28. ^{1}H NMR spectrum of **4c** recorded in $CDCl_3$.

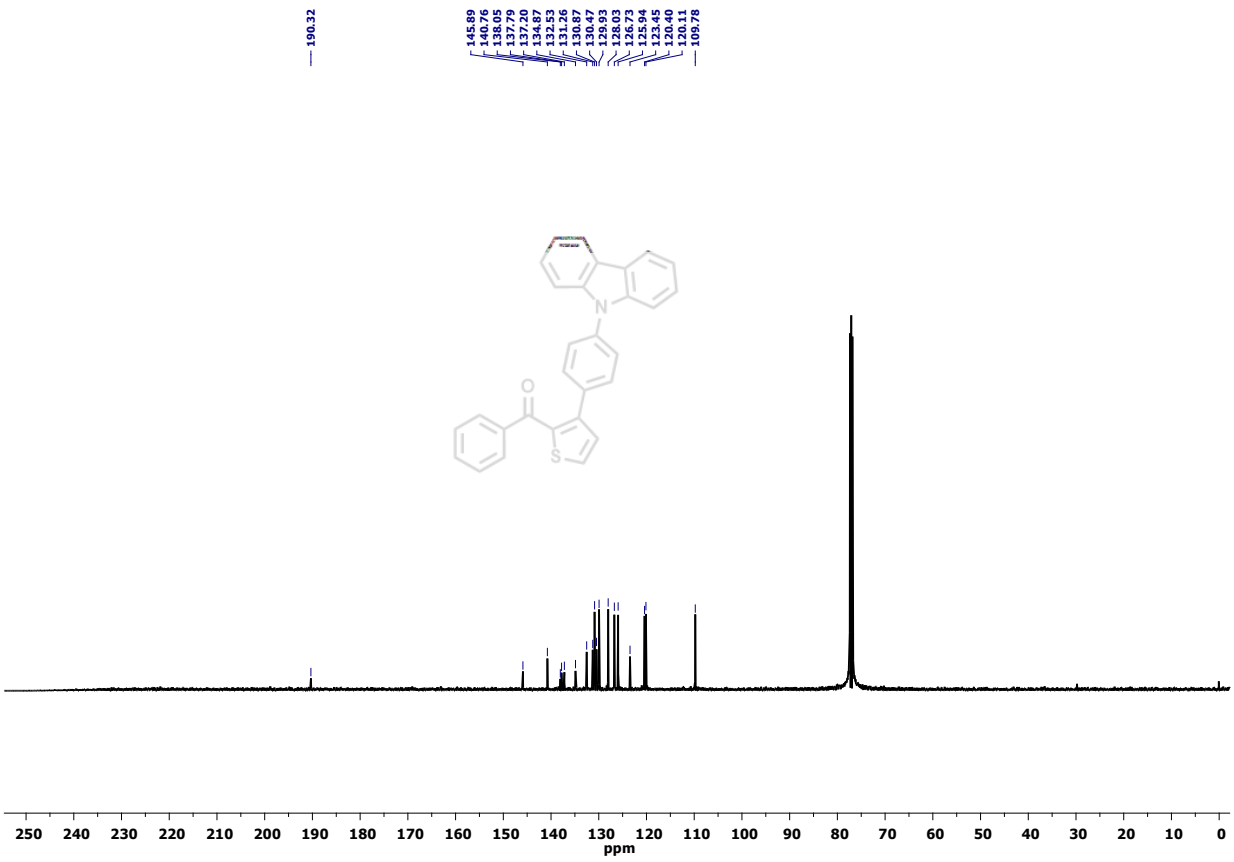


Figure S29. ^{13}C NMR spectrum of **4c** recorded in $CDCl_3$.

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