Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Tuning Excited-State Intramolecular Proton Transfer (ESIPT) process of indole-pyrrole systems by π-conjugation and substitution effects: Experimental and Computational studies

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1 Tables and figures

Table S1 Experimental ^{1}H NMR chemical shifts of the N-H hydrogen in $CDCl_3$

Compounds	N1−H Chemical Shift (ppm)
NDAB-H[a]	15.78
NDAB-6[a]	16.30
BNDAB-1	16.33
BNDAB-2	16.93
BNDAB-3	15.89
BNDAB-4	16.40

[a]*Data obtained from Ref: Res Chem Intermed (2017) 43, 5337-5344 and Journal of Molecular Liquids 286 (2019) 110887.*

Table S2 Photophysical properties of AIE 1-4 in different solvents at room temperature.

Comp.	Solvent	λ_{abs} ($\varepsilon/10^5$ M^{-1} cm^{-1})(nm)	λ_{ex} (nm)	λ_{em} (nm)	□□$\Delta\nu$		Φ_f a (%)	τ_{exp}/ns (pre-exp. factor)[c]
					(nm)	(cm^{-1})		
NDAB-H[b]	Toluene	305 (2.28), 415 (1.40)	415	580	165	6855	6.0	580 nm: 0.49 (700.3), 5.58 (15.3)
	DCM	303 (3.07), 411 (1.71)	411	578	167	7030	5.1	
	MeOH	300 (3.42), 410 (1.83)	410	580	170	7149	2.8	
	DMSO	307 (3.98), 416 (2.07)	416	584	168	6915	11.2	
NDAB-6[b]	Toluene	404 (4.23)	404	580	176	7511	22	570 nm: 0.78 (4010.9), 4.99 (22.7)
	DCM	299 (1.46), 400 (2.89)	400	575	175	7609	27	
	MeOH	307 (0.74), 397 (2.14)	397	573	176	7737	14	
	DMSO	309 (2.34), 400 (4.43)	400	579	179	7729	28	
BNDAB-1	Toluene	339 (0.39), 437 (0.28)	420	510, 596	73, 159	3275, 6105	20	500 nm: 1.28 (285.2); 590 nm: 1.20 (884.5)
	DCM	331 (0.43), 433 (0.31)		520, 595	97, 162	3864, 6288	15	
	MeOH	329 (0.38), 431 (0.26)		526, 592	95, 161	4190, 6310	8	
	DMSO	330 (0.42), 438 (0.27)		536, 596	98, 158	4174, 6053	32	
BNDAB-2	Toluene	416 (0.13)	410	590	174	7089	60	580 nm: 2.16 (504.1)
	DCM	411 (0.18)		584	173	7208	62	

	MeOH	407 (0.15)		580	173	7329	27	
	DMSO	409 (0.15)		589	180	7472	40	
BNDAB-3	Toluene	336 (0.25), 430 (0.25)	410	530, 596	100, 166	4388, 6477	10	530 nm: 0.65 (178.5); 590 nm: 0.57 (545.7)
	DCM	327 (0.23), 473 (0.30)		510, 593	37, 120	1534, 4278	11	
	MeOH	326 (0.29), 423 (0.27)		520, 590	97, 167	4410, 6692	4	
	DMSO	328 (0.31), 429 (0.26)		528, 593	99, 164	4371, 6447	11	
BNDAB-4	Toluene	400 (0.50)	400	502, 546	102,146	5080, 6685	9	500 nm: 1.56 (202.1); 540 nm: 1.23 (372.4)
	DCM	402 (0.49)		546	144	6561	2	
	MeOH	396 (0.62)		543	147	6836	1	
	DMSO	401 (0.54)		547	146	6656	6	

Footnote: [a]Fluorescence quantum yields were calculated using Rhodamine B (Φ_f □= 0.49 in ethanol) or fluorescein (Φ_f = 0.90 in 0.1 N NaOH aqueous solution) as the reference.[b]The data are from Ref: Res Chem Intermed (2017) 43, 5337–5344 and Journal of Molecular Liquids 286 (2019) 110887. [c] Measured in Toluene at room temperature.

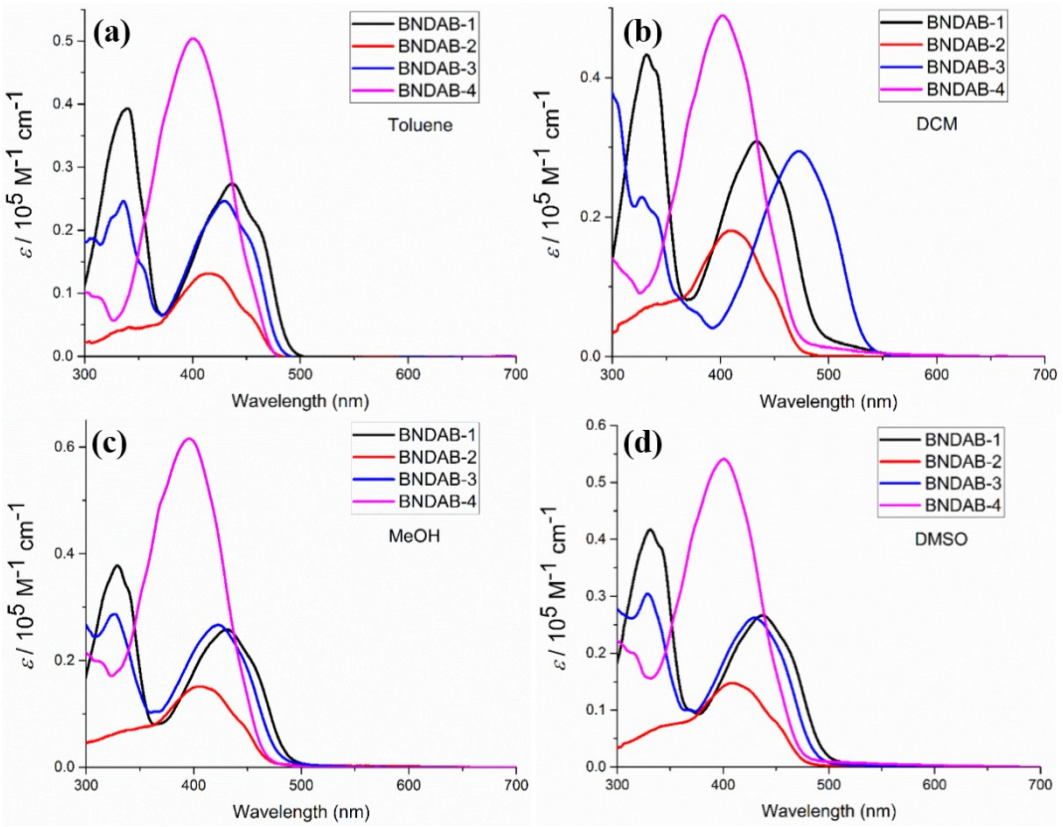

Fig. S1 UV-Vis spectra of **BNDAB-1-4** in toluene (a), DCM (b), MeOH (c), DMSO (d)

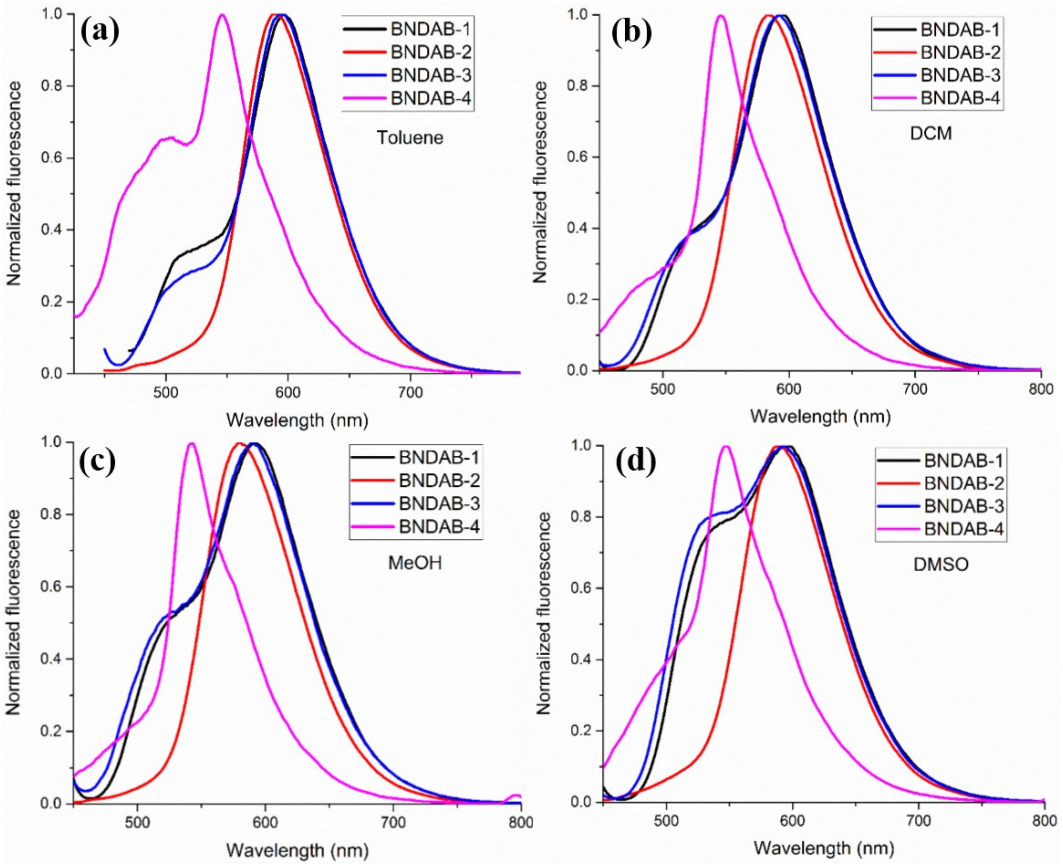

Fig. S2 Emission spectra of **BNDAB-1-4** in toluene (a), DCM (b), MeOH (c), DMSO (d)

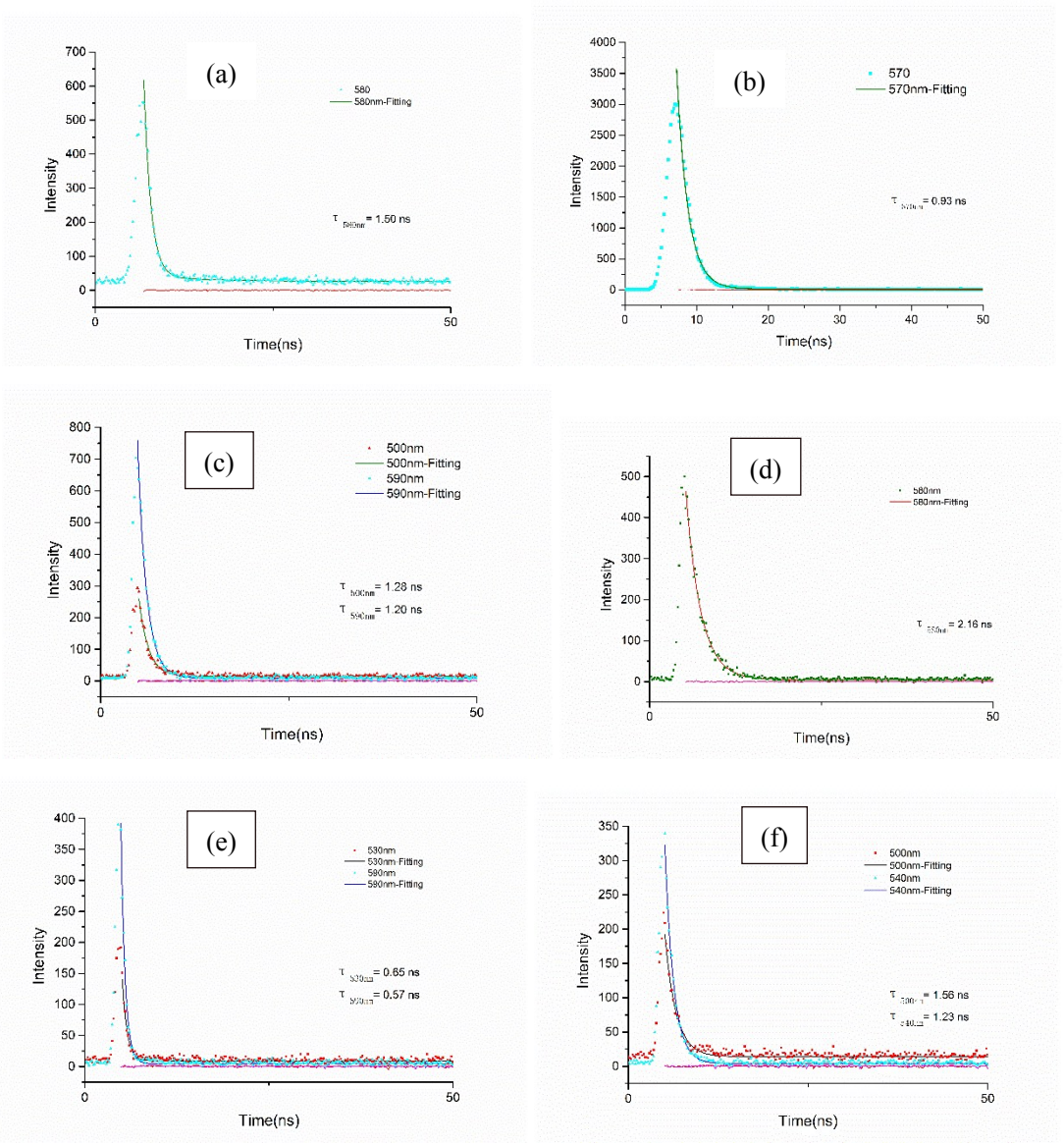

Fig. 3 The fluorescence decay dynamics in toluene of (a) NDAB-H, (b) NDAB-6, (c) BNDAB-1, (d) BNDAB-2, (e) BNDAB-3, (f) BNDAB-4. Squares (red or cyan) denote data points obtained for normal and/or tautomer emissions, respectively, with monitored wavelengths as depicted, while solid lines correspond to nonlinear fitting curves.

Table S3 The experiment absorption data and calculation data of **BNDABs** in toluene based on TDDFT calculations

Comp.	Observed λ_{abs} (nm) ($\varepsilon/10^4$ M^{-1} cm^{-1})	Computed λ_{abs} (nm)(f)
BNDAB-1	339 (0.39), 437 (0.28)	343.78 (0.49), 455.65 (0.42)
BNDAB-2	416 (0.13)	347.83 (0.24), 416.84 (0.23), 446.33 (0.75)
BNDAB-3	336 (0.25), 430 (0.25)	338.62 (0.36), 446.32 (0.48)
BNDAB-4	400 (0.50)	309.37 (0.17), 410.61 (0.34), 437.03 (0.78)

Table S4 Bond distance and angle of **NDAB**s in toluene in N-S_0, N-S_1, T-S_1 states based on DFT and TDDFT calculations

	Category	N-S_0	T-S_0	N-S_1	T-S_1	N-S_1-N-S_0
NDAB-H	N-H(Å)	1.03514	1.50940	1.06097	1.63142	0.02583
	N...H(Å)	1.74973	1.10522	1.65512	1.06747	-0.09461
	Angle(º)	151.76075	159.35021	155.75502	157.47575	3.99427
NDAB-6	N-H(Å)	1.03819	1.50934	1.06721	1.67293	0.02902
	N...H(Å)	1.73839	1.10613	1.61522	1.05139	-0.12317
	Angle(º)	151.96211	159.42846	155.61430	155.40165	3.65219
BNDAB-1	N-H(Å)	1.03454	1.52039	1.05392	1.62218	0.01938
	N...H(Å)	1.75664	1.10021	1.68201	1.06984	-0.07463
	Angle(º)	152.40036	159.56897	155.35287	158.13365	2.95251
BNDAB-2	N-H(Å)	1.03767	1.52508	1.05895	1.66219	0.02128
	N...H(Å)	1.74555	1.09961	1.65368	1.05481	-0.09187
	Angle(º)	152.60301	159.56124	155.66623	156.48710	3.06322
BNDAB-3	N-H(Å)	1.03483	1.48077	1.05699	1.61305	0.02216
	N...H(Å)	1.74901	1.11745	1.66401	1.07160	-0.085
	Angle(º)	151.63230	159.71596	155.06347	157.96968	3.43117
BNDAB-4	N-H(Å)	1.03830	1.50015	1.06586	1.65541	0.02756
	N...H(Å)	1.73525	1.10956	1.62525	1.05654	-0.11
	Angle(º)	151.93534	159.49063	155.67335	156.21554	3.73801

Table S5 Nonconjugation coefficient (ξ) and their corresponding △ξ from tautomer to normal for **NDAB-H**, **BNDAB-1** and **BNDAB-3** in ground state and excited state

	nonconjugation coefficient (ξ)				△ξ	
	normal		tautomer			
	S_0	S_1	S_0	S_1	S_0	S_1
NDAB-H	0.08906	0.01454	0.06165	0.02403	0.02741	0.00949
BNDAB-1	0.08669	0.02303	0.06070	0.03788	0.02599	0.01485
BNDAB-3	0.08687	0.02647	0.06178	0.03915	0.02509	0.01268

Table S6 Nonconjugation coefficient (ξ) and their corresponding △ξ from tautomer to normal for **NDAB-6**, **BNDAB-2** and **BNDAB-4** in ground state and excited state

	nonconjugation coefficient (ξ)				△ξ	
	normal		tautomer			
	S_0	S_1	S_0	S_1	S_0	S_1
NDAB-6	0.09402	0.0361	0.07182	0.03174	0.0222	-0.00436
BNDAB-2	0.09194	0.00055	0.07116	0.02693	0.02078	0.02638
BNDAB-4	0.09158	0.00933	0.0708	0.02837	0.02078	0.01904

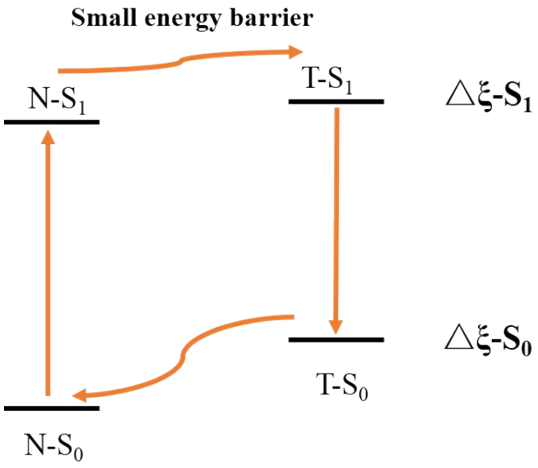

Fig. S4 Schematic graph of energy barrier

Table S7 The major transition configuration of excited states of **BNDAB-1-4** in toluene

name	Wavelength (nm)	Osc. Strength	Major contribs (>15%)
BNDAB-1	455.65	0.4179	HOMO->LUMO (99.6%)
	343.78	0.4926	H-1->LUMO (25.9%), HOMO->L+1 (72.9%)
BNDAB-2	446.33	0.7538	HOMO->LUMO (89.2%)
	416.84	0.2329	HOMO->L+1 (89.1%)
	347.83	0.2413	H-1->L+1 (95.8%)
BNDAB-3	446.32	0.4795	HOMO->LUMO (99.5%)
	338.62	0.3757	H-1->LUMO (57.6%), HOMO->L+2 (37.3%)
BNDAB-4	437.03	0.7837	HOMO->LUMO (90.3%)
	410.61	0.3381	HOMO->L+1 (90.2%)
	309.37	0.17	H-2->LUMO (52.2%), H-2->L+1 (19.4%), H-1->L+2 (17.0%)

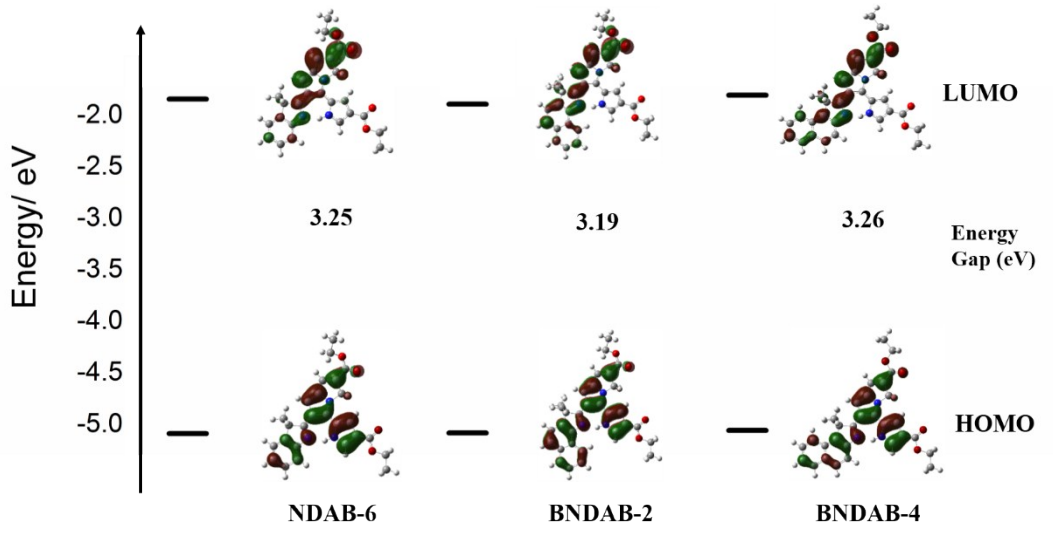

Fig. S5 Computed frontier orbitals for **NDAB-6**, **BNDAB-2**, **BNDAB-4** in their normal form

involved in the first singlet excitation in toluene.

Table S8 Orbits energy

compounds	Energy (eV)				
	HOMO-1	HOMO	LUMO	LUMO+1	Gap
NDAB-H	-0.60491	-1.29718	-4.68312	-5.82274	3.39
NDAB-6	-1.56195	-1.84304	-5.09102	-6.12071	3.25
BNDAB-1	-0.65743	-1.49065	-4.66026	-5.47987	3.17
BNDAB-2	-1.69936	-1.89257	-5.08449	-5.74382	3.19
BNDAB-3	-0.83023	-1.44602	-4.66842	-5.56232	3.22
BNDAB-4	-1.6248	-1.80495	-5.06	-5.77947	3.26

Table S9 Calculated N-S_0, T-S_0 states energy of **NDAB-H**, **NDAB-6** and **BNDAAB-1-4** and the energy difference between the ground-state normal and tautomer forms (ΔE_3) in toluene based on DFT calculations

S_0	normal	tautomer	ΔE_3
NDAB-H	-975.92215	-975.90860	8.5028
BNDAB-1	-1129.56598	-1129.55238	8.5341
BNDAB-3	-1129.56323	-1129.54938	8.6910
NDAB-6	-1510.31665	-1510.30446	7.6493
BNDAB-2	-1663.96034	-1663.94818	7.6305
BNDAB-4	-1663.97325	-1663.96108	7.6370

Note:ΔE_3: the energy difference between the ground-state normal and tautomer forms

ΔE (eV) = $E_{T\text{-}S0}$-$E_{N\text{-}S0}$

Table S10 Calculated potential energy of **NDABs** in toluene N-S_1, highest energy in S_1 (H-S_1) state, T-S_1 states based on DFT and TDDFT calculations

Entry	Energy (hartree)			ΔE_1 (Kcal/ mol)	ΔE_2 (Kcal/ mol)
	N-S_1	H-S_1	T-S_1		
NDAB-H	-975.82197	-975.81826	-975.82181	0.0992	2.3153
BNDAB-1	-1129.47262	-1129.46738	-1129.47045	1.3617	3.2882
BNDAB-3	-1129.46788	-1129.46330	-1129.46614	1.0919	2.8740
NDAB-6	-1510.21546	-1510.21408	-1510.22160	-3.8529	0.8660
BNDAB-2	-1663.86469	-1663.86173	-1663.86796	-2.0520	1.8574
BNDAB-4	-1663.87539	-1663.87318	-1663.87916	-2.3657	1.3868

Note: ΔE (eV) = $E_{T\text{-}S1}$-$E_{N\text{-}S1}$; ΔE (eV) = $E_{H\text{-}S1}$-$E_{N\text{-}S1}$

2 Detailed Synthesis and Characterizations

All reagents and solvents were obtained from commercial sources and used without further purification, unless otherwise noted. All chromatographic separations were carried out on silica gel (300-400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400 MHz spectrometer at 298 K. $CDCl_3$ was used as solvent and TMS as internal reference. The chemical shifts were reported in parts per million (δ) relative to the appropriate reference signal: residual chloroform (δ_H 7.26). High resolution mass spectra were measured on Bruker APCI instrument or SYNAPT G2 analysis instrument. UV–Vis spectra in various solvents were detected on Shimadzu UV-2600 in 10 mm quartz cell spectrometer. Fluorescence spectra were obtained using a Shimadzu FL-4500 spectrometer, emission wavelengths λ are reported in nm.

3 Procedure for the Synthesis of BNDABs

To a mixture of substituted 2,3,3-trimethylbenzoindole (1 mmol), 4-acetyl-2-formylpyrrole or 2-formylpyrrole (2 mmol), AcOH (86 uL, 1.5 mmol) and piperidine (0.1mL, 1.4 mmol) in toluene (50 mL) was added and the mixture was refluxed for 4 h. The completion of reaction was confirmed by TLC. The brown dark reaction mixture was cooled, concentrated to viscous liquid and chromatographic separation. By column chromatography (silica gel, petroleum/dichloromethane 4:1 to 1:3) to give the corresponding product **BNDABs** as a solid.

BNDAB-1: Orange red solid, 130 mg, yield: 36%, 4 h.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 16.33 (s, 1H), 8.57 (d, *J*=8.3, 1H), 7.94 (d, *J*=8.3, 1H), 7.75 (d, *J*=8.2, 1H), 7.67 (t, *J*=7.2, 1H), 7.57 – 7.49 (m, 2H), 7.29 (d, *J*=1.1, 1H), 6.81 – 6.76 (m, 2H), 6.69 (d, *J*=1.6, 1H), 6.55 (dd, *J*=5.8, 2.5, 1H), 6.50 (dt, *J*=6.0, 1.9, 1H), 4.76 (s, 2H), 1.71 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 181.18, 147.61, 142.48, 139.82, 133.91, 129.01, 128.61, 128.44, 126.23, 125.93, 125.55, 125.43, 124.81, 122.99, 122.49, 119.37, 117.91, 115.63, 109.71, 106.72, 99.75, 55.20, 54.90, 25.24. HRMS (ESI) Calcd. for $C_{25}H_{21}N_3$ $[M+H]^+$: 364.1735, found 364.1800.

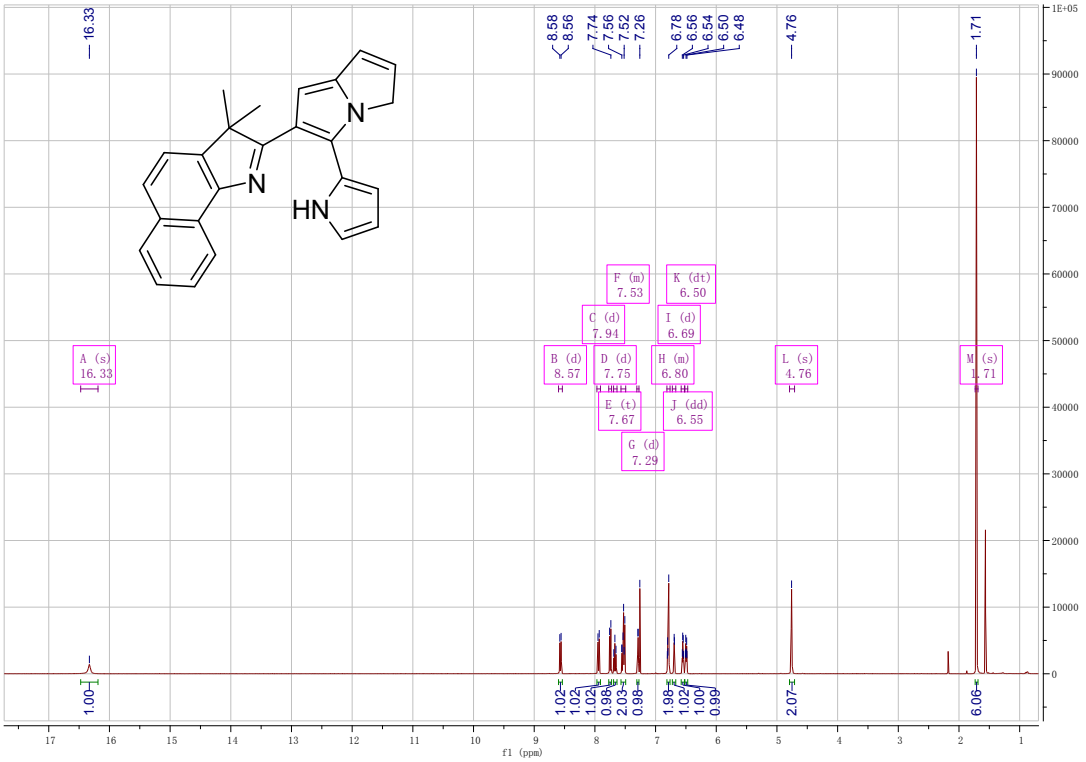

Fig. S6 ^{1}H NMR spectra of **BNDAB-1**

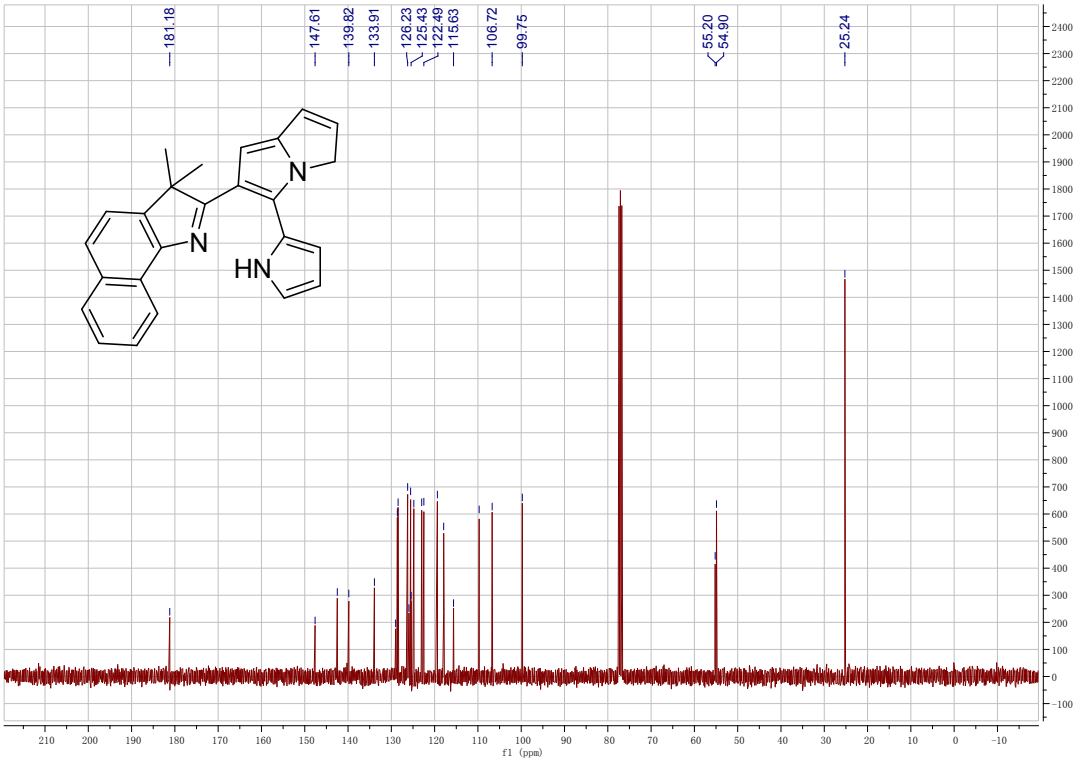

Fig. S7 ^{13}C NMR spectra of **BNDAB-1**

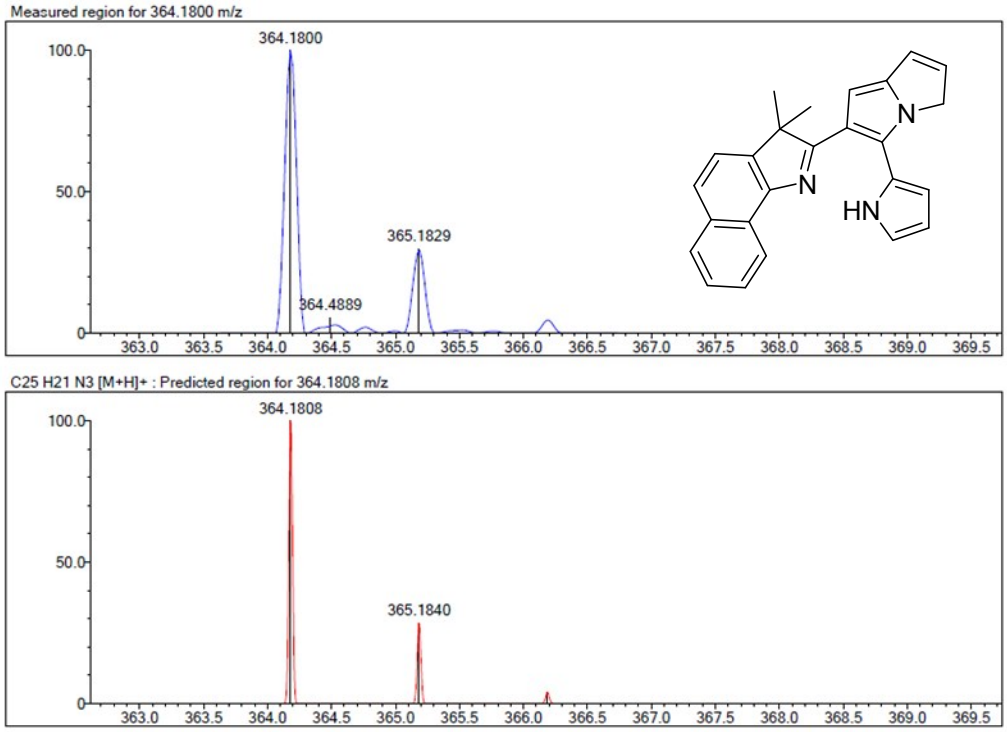

Fig. S8 HRMS (ESI) spectra of **BNDAB-1**

BNDAB-2: Orange solid, 142 mg, yield: 28%, 4 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 16.93 (s, 1H), 8.46 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.88 (dd, *J* = 2.7, 1.2 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.59 (t, *J* = 1.8 Hz, 1H), 7.58 – 7.55 (m, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.15 (s, 1H), 7.06 (s, 1H), 4.98 (s, 2H), 4.38 (dq, *J* = 11.8, 7.1 Hz, 5H), 1.70 (s, 6H), 1.42 (dd, *J* = 4.5, 2.6 Hz, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 180.41, 165.37, 163.25, 146.70, 142.73, 138.40, 133.89, 131.99, 130.22, 129.26, 128.57, 126.70, 125.86, 125.83, 125.78, 125.62, 123.70, 122.57, 119.27, 117.84, 117.78, 108.53, 105.51, 60.96, 60.08, 55.39, 54.05, 46.02, 25.12, 24.43, 24.42, 22.69, 14.66, 14.48, 8.53, 0.02. HRMS (ESI) Calcd. for $C_{31}H_{29}N_3O_4$ $[M+H]^+$: 508.2231, found 508.2218.

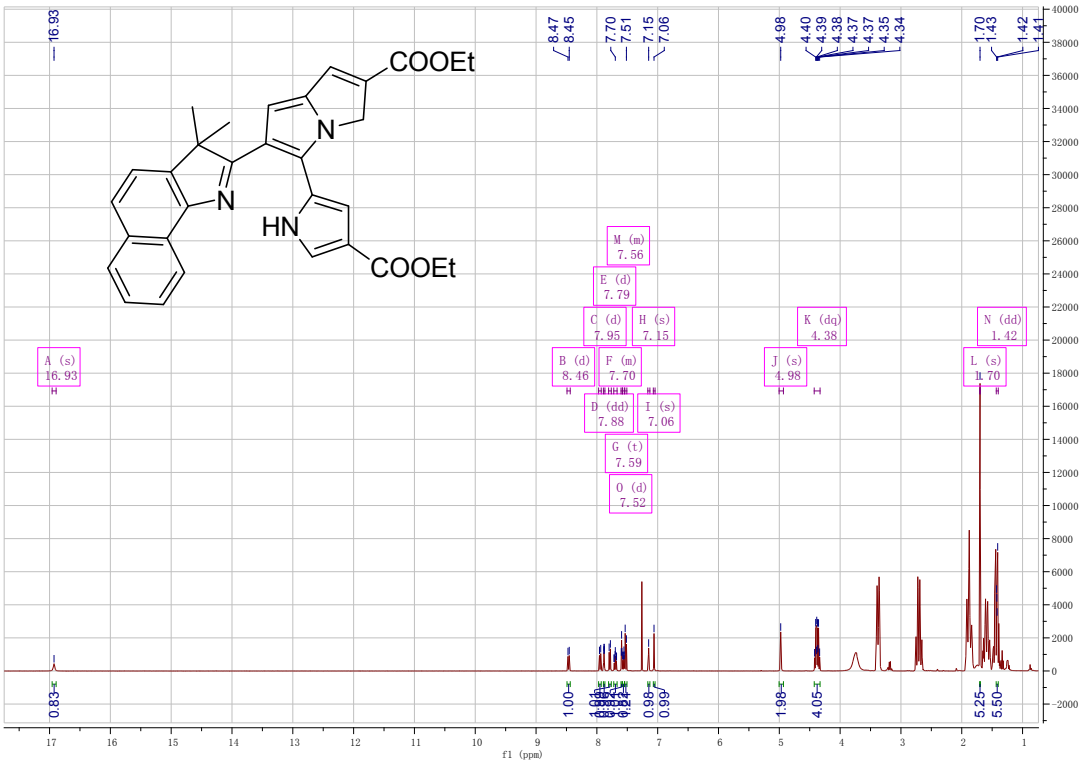

Fig. S9 ^{1}H NMR spectra of **BNDAB-2**

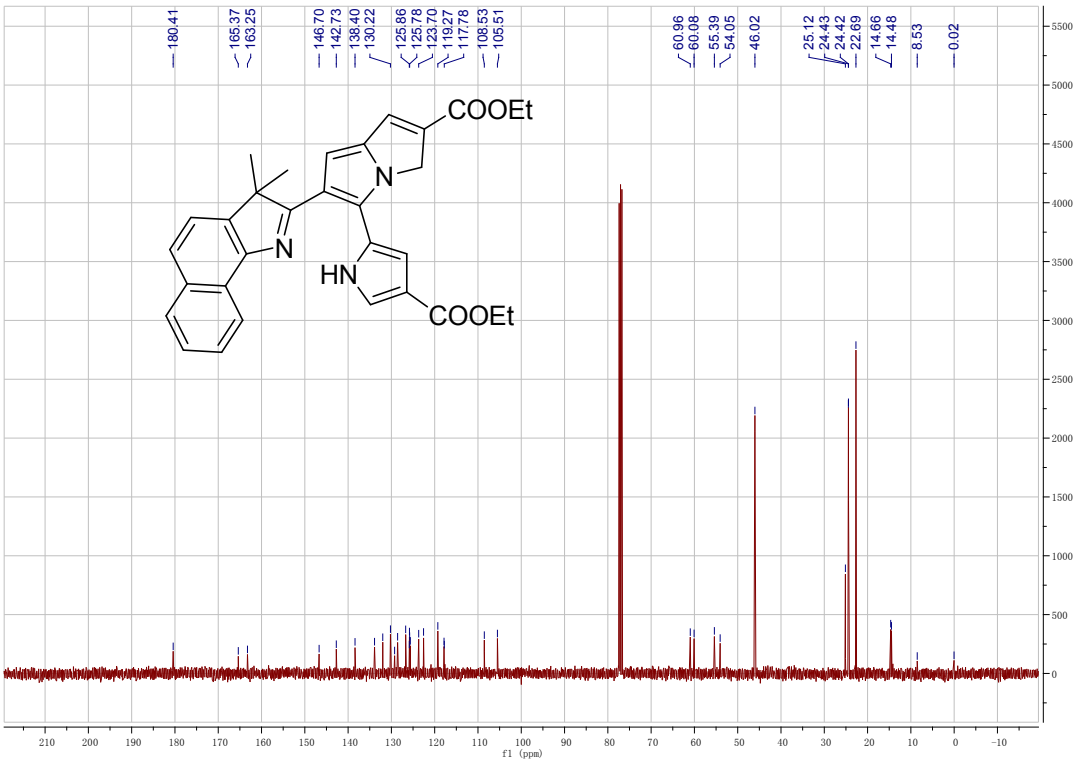

Fig. S10 ^{13}C NMR spectra of **BNDAB-2**

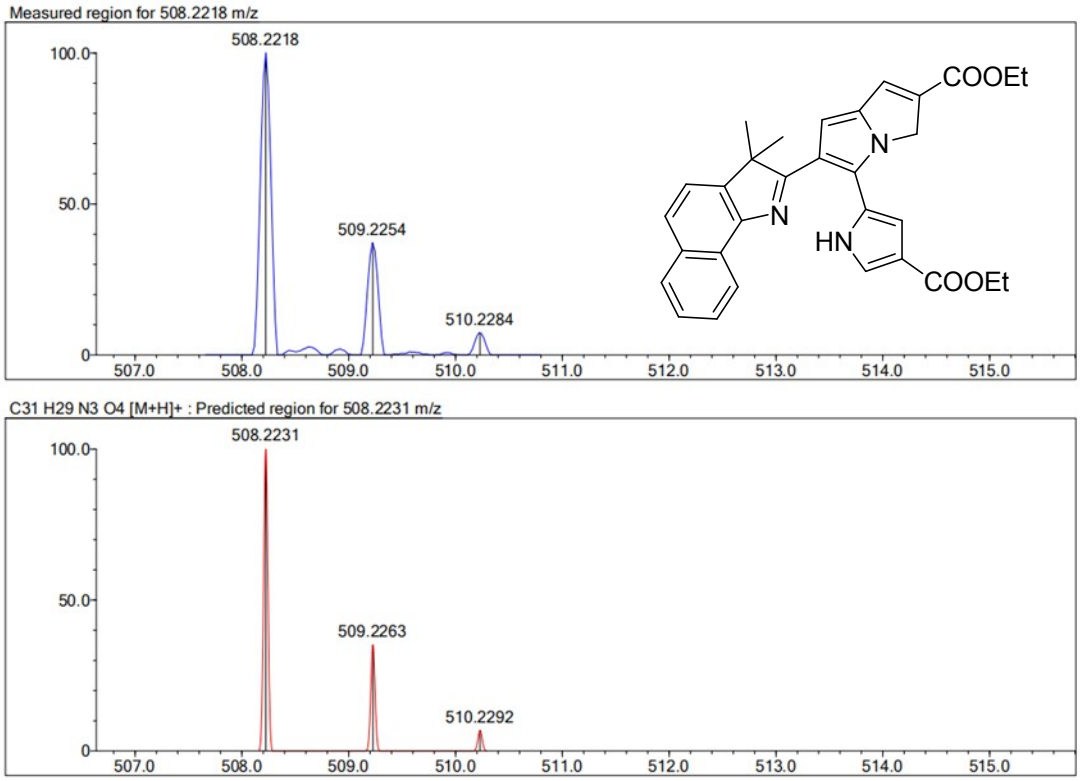

Fig. S11 HRMS (ESI) spectra of **BNDAB-2**

BNDAB-3: Orange red solid, 143 mg, yield: 39%, 4 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 15.89 (s, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.89 (q, *J* = 8.5 Hz, 2H), 7.58 (ddd, *J* = 8.3, 6.9, 1.2 Hz, 1H), 7.48 – 7.41 (m, 1H), 7.16 (d, *J* = 1.2 Hz, 1H), 6.83 (s, 1H), 6.80 (dt, *J* = 6.0, 2.1 Hz, 1H), 6.72 – 6.64 (m, 1H), 6.50 (ddt, *J* = 8.0, 6.0, 2.2 Hz, 2H), 4.75 (s, 2H), 1.92 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.06, 149.48, 139.72, 139.08, 132.20, 129.88, 129.06, 129.02, 128.57, 128.25, 126.36, 125.29, 123.98, 122.50, 122.48, 119.24, 117.82, 115.10, 109.53, 106.78, 99.74, 55.90, 54.98, 25.04. HRMS (ESI) Calcd. for $C_{25}H_{21}N_3$ $[M+H]^+$: 364.1735, found 364.1805.

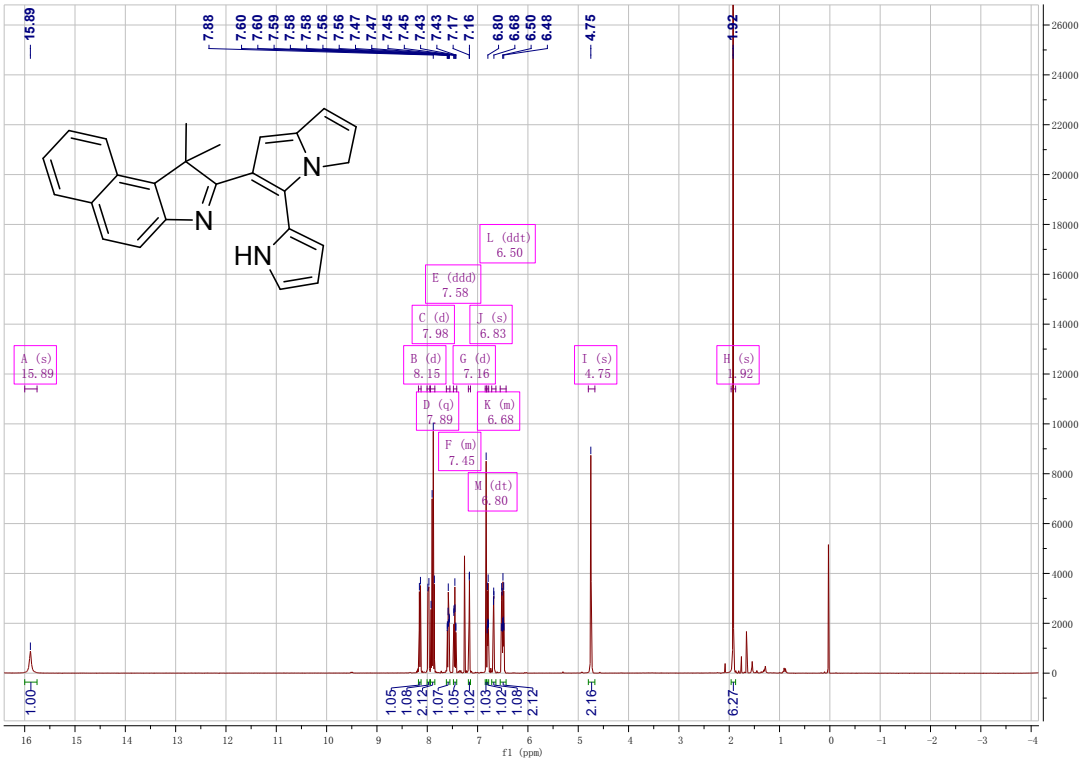

Fig. S12 ^{1}H NMR spectra of **BNDAB-3**

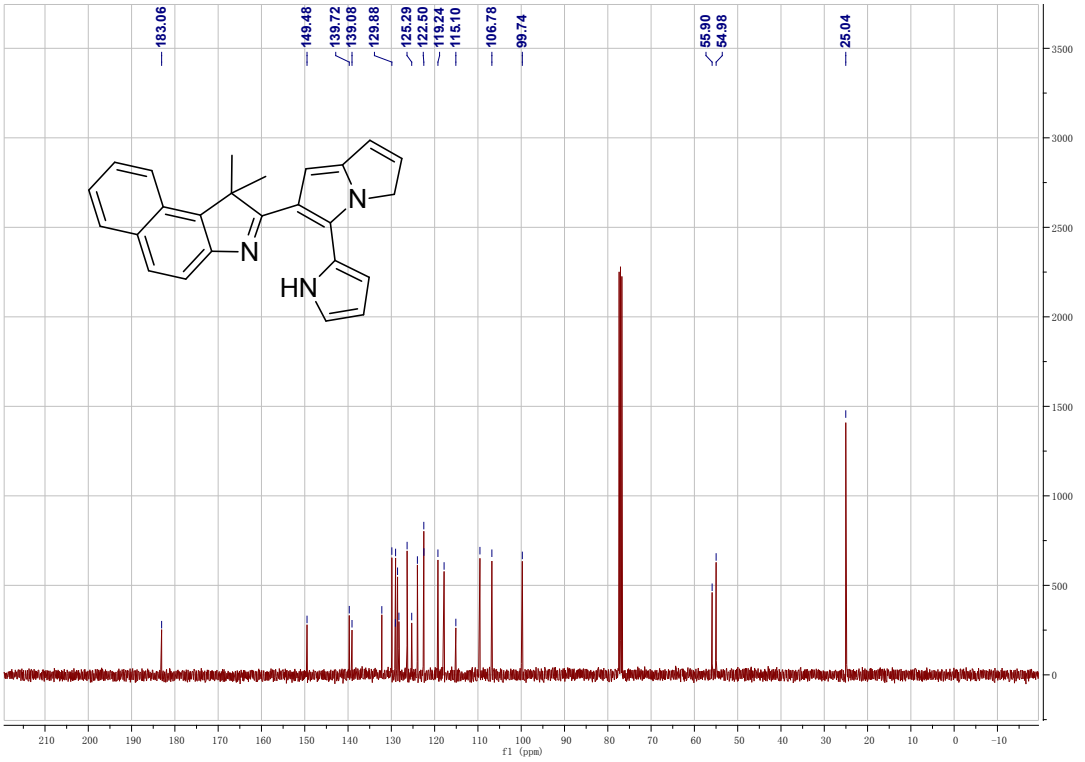

Fig. S13 ^{13}C NMR spectra of **BNDAB-3**

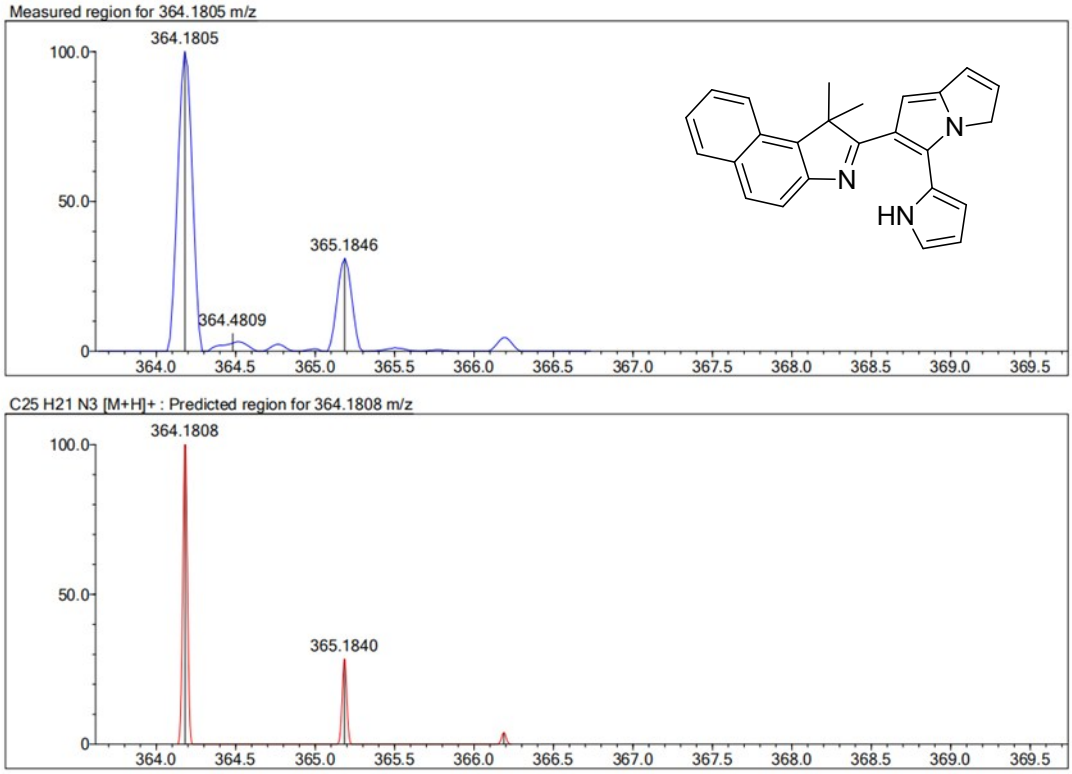

Fig. S14 HRMS (ESI) spectra of **BNDAB-3**

BNDAB-4: Orange solid, 113 mg, yield: 22%, 4 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 16.40 (s, 1H), 8.13 (d, *J*=8.4, 1H), 7.98 (d, *J*=8.1, 1H), 7.92 (d, *J*=8.5, 1H), 7.82 (d, *J*=8.5, 1H), 7.74 (s, 1H), 7.59 (t, *J*=1.8, 2H), 7.50 – 7.44 (m, 1H), 7.13 (s, 1H), 7.10 (s, 1H), 4.97 (s, 2H), 4.37 (dd, *J*=7.1, 2.9, 4H), 1.90 (s, 6H), 1.41 (td, *J*=7.1, 3.3, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.20, 165.19, 163.12, 148.56, 139.34, 138.26, 132.48, 131.99, 130.08, 129.93, 129.32, 128.11, 126.62, 125.40, 124.47, 123.58, 122.51, 119.00, 117.73, 117.23, 108.62, 105.40, 60.89, 59.93, 56.06, 54.15, 24.99, 14.63, 14.51. HRMS (ESI) Calcd. for $C_{31}H_{29}N_3O_4$ $[M+H]^+$: 508.22318, found 508.2213.

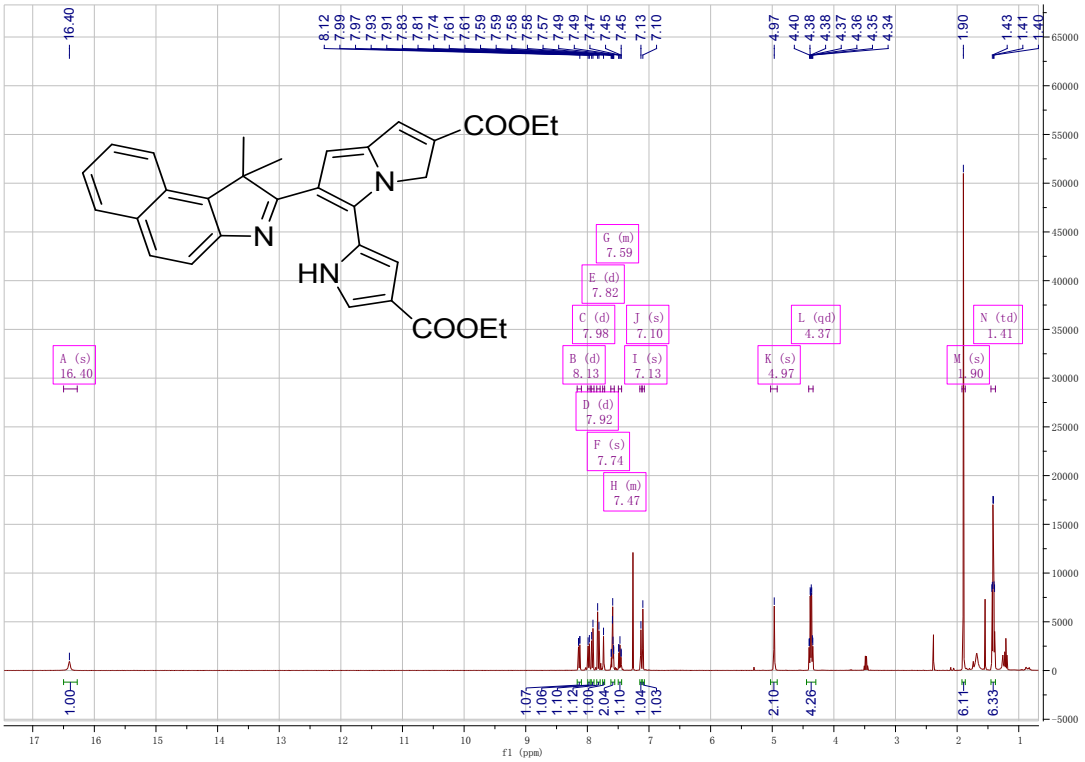

Fig. S15 ^{1}H NMR spectra of **BNDAB-4**

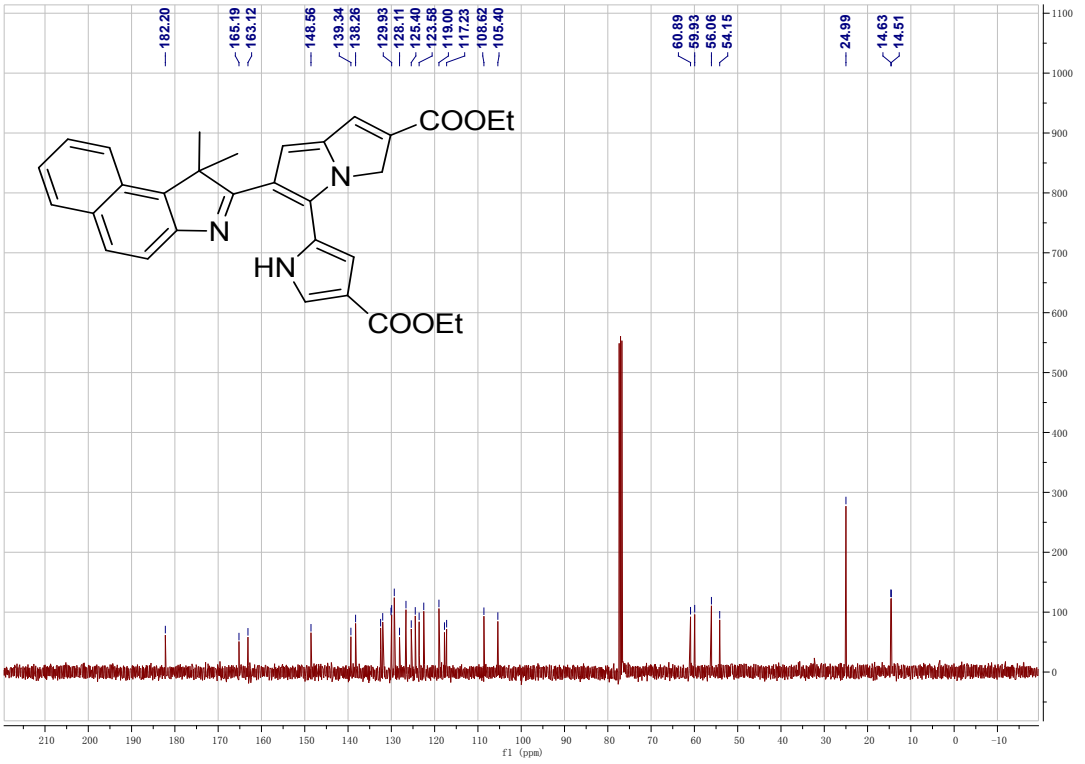

Fig. S16 ^{13}C NMR spectra of **BNDAB-4**

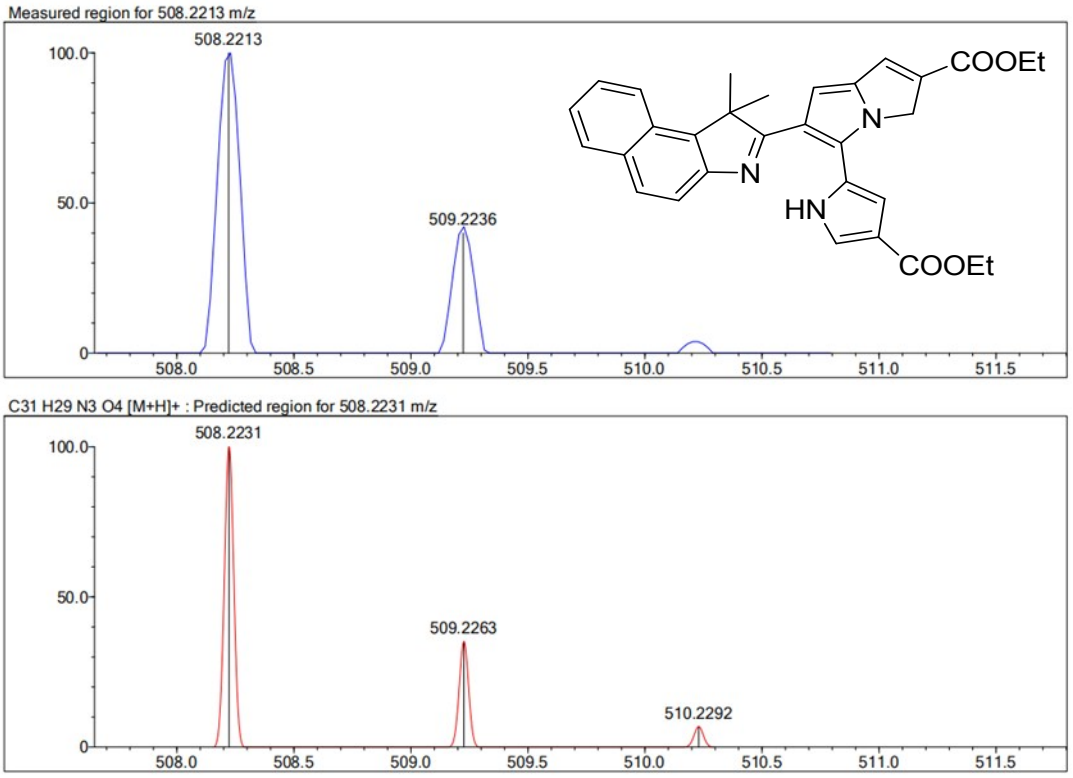

Fig. S17 HRMS (ESI) spectra of **BNDAB-4**