Electronic Supplementary Information

Highly red-emissive salen−indium complexes: Impact of 4-amino-substitution on the photophysical properties

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Contents

Experimental Section

X-ray crystallography

Single crystals suitable for X-ray diffraction study were grown from diethyl ether/EtOH solution of **2**. Single crystal of **2** was coated with Paratone oil and mounted onto a glass capillary. The crystallographic measurements were performed on a Bruker APEX II CCD detector diffractometer with a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by a full-matrix least-squares method on F^2 by using the SHELXTL/PC package, resulting in X-ray crystallographic data of **2** in CIF format (CCDC 2091666). Hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. The detailed crystallographic data are given in Table S1 and S2.

Cyclic Voltammetry

Cyclic voltammetry measurements were carried out in MeCN (1 mM) with a three-electrode cell configuration consisting of platinum working and counter electrodes and an $Ag/AgNO_3$ (0.01 M in MeCN) reference electrode at room temperature. The redox potentials were recorded at a scan rate of 100 mV/s and are reported with reference to the ferrocene/ferrocenium (Fc/Fc^+) redox couple.

^{1}H and ^{13}C NMR Spectra

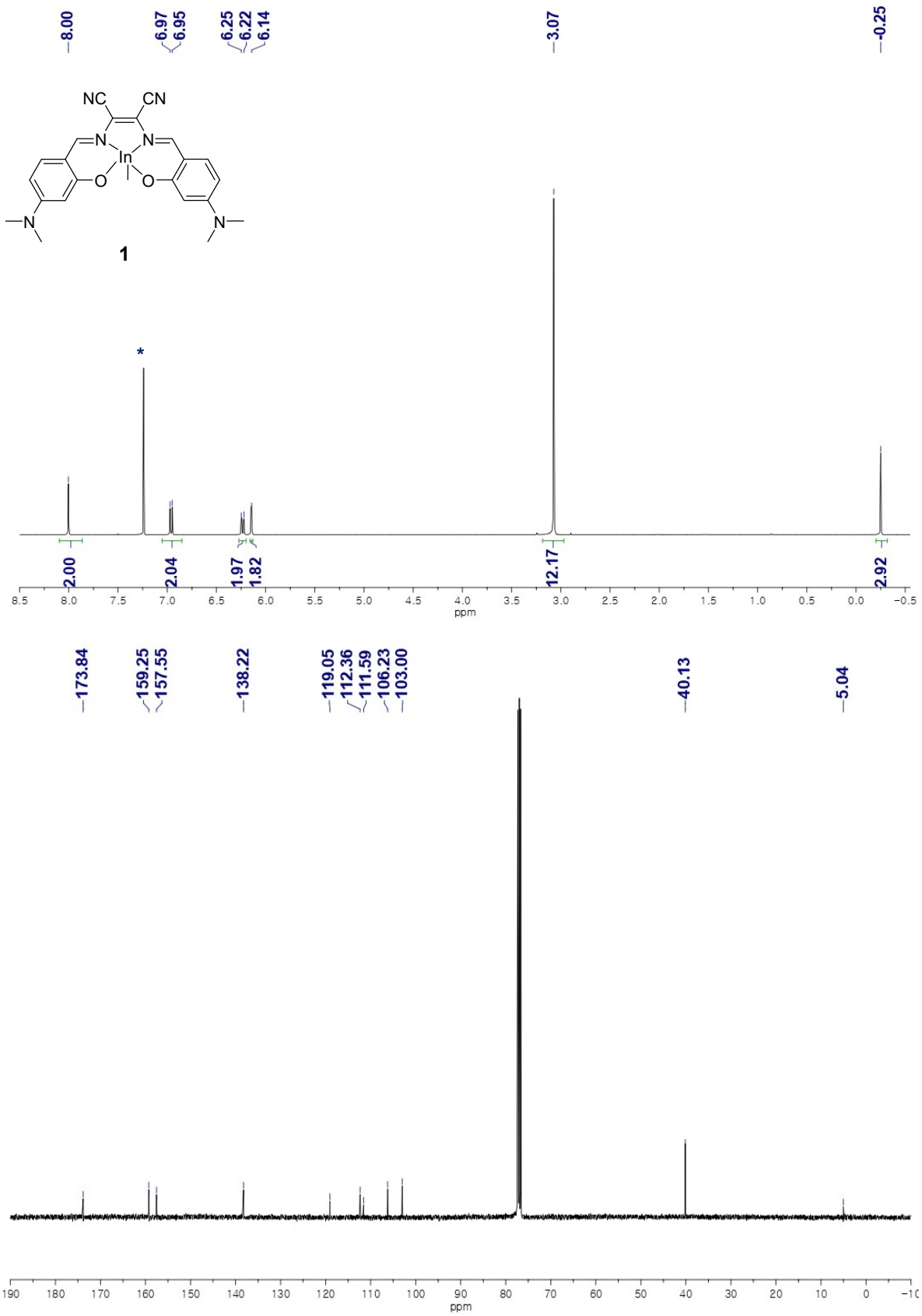

Fig. S1 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **1** (*from residual $CHCl_3$ in $CDCl_3$).

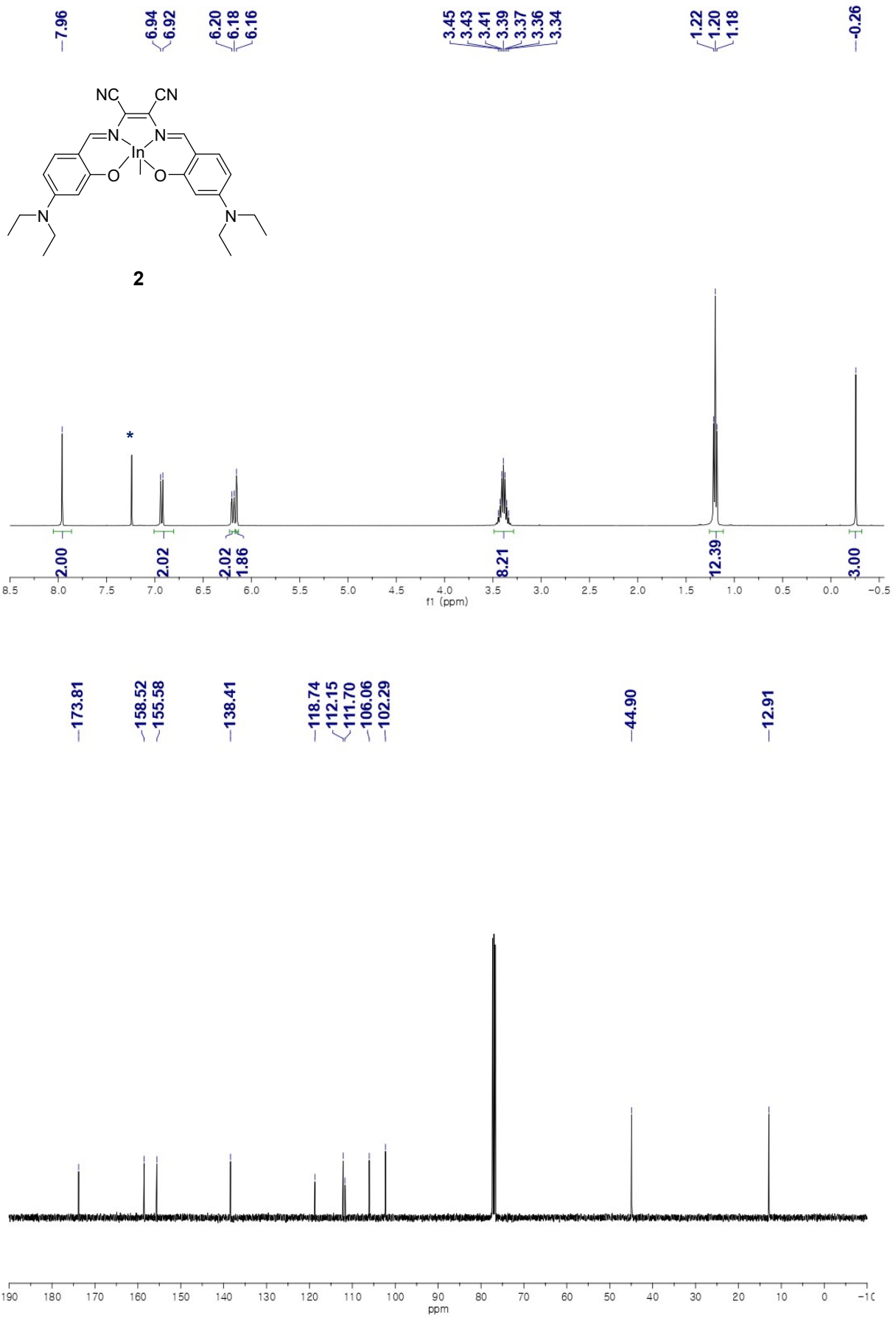

Fig. S2 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2** (*from residual $CHCl_3$ in $CDCl_3$).

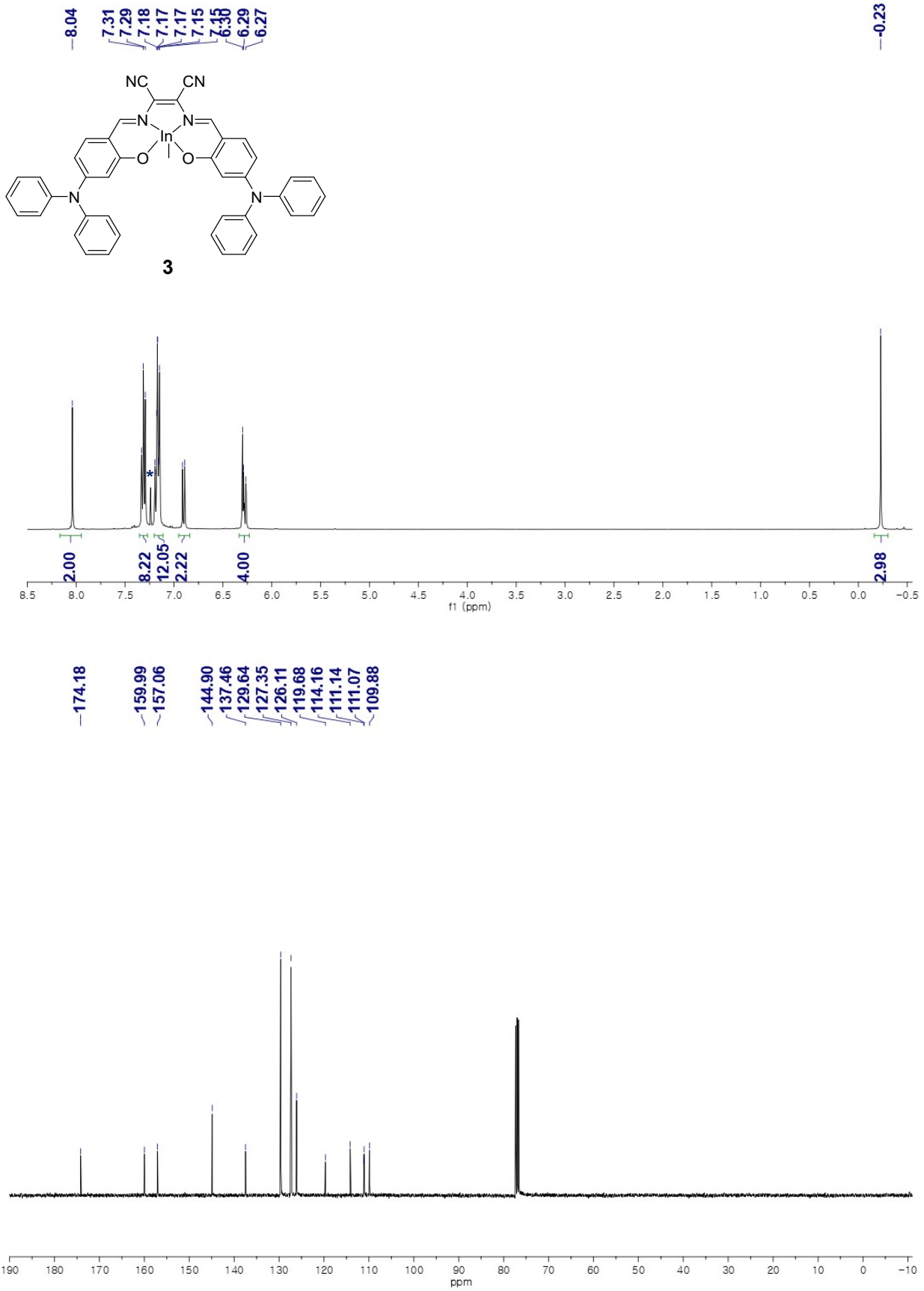

Fig. S3 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3** (∗ from residual $CHCl_3$ in $CDCl_3$).

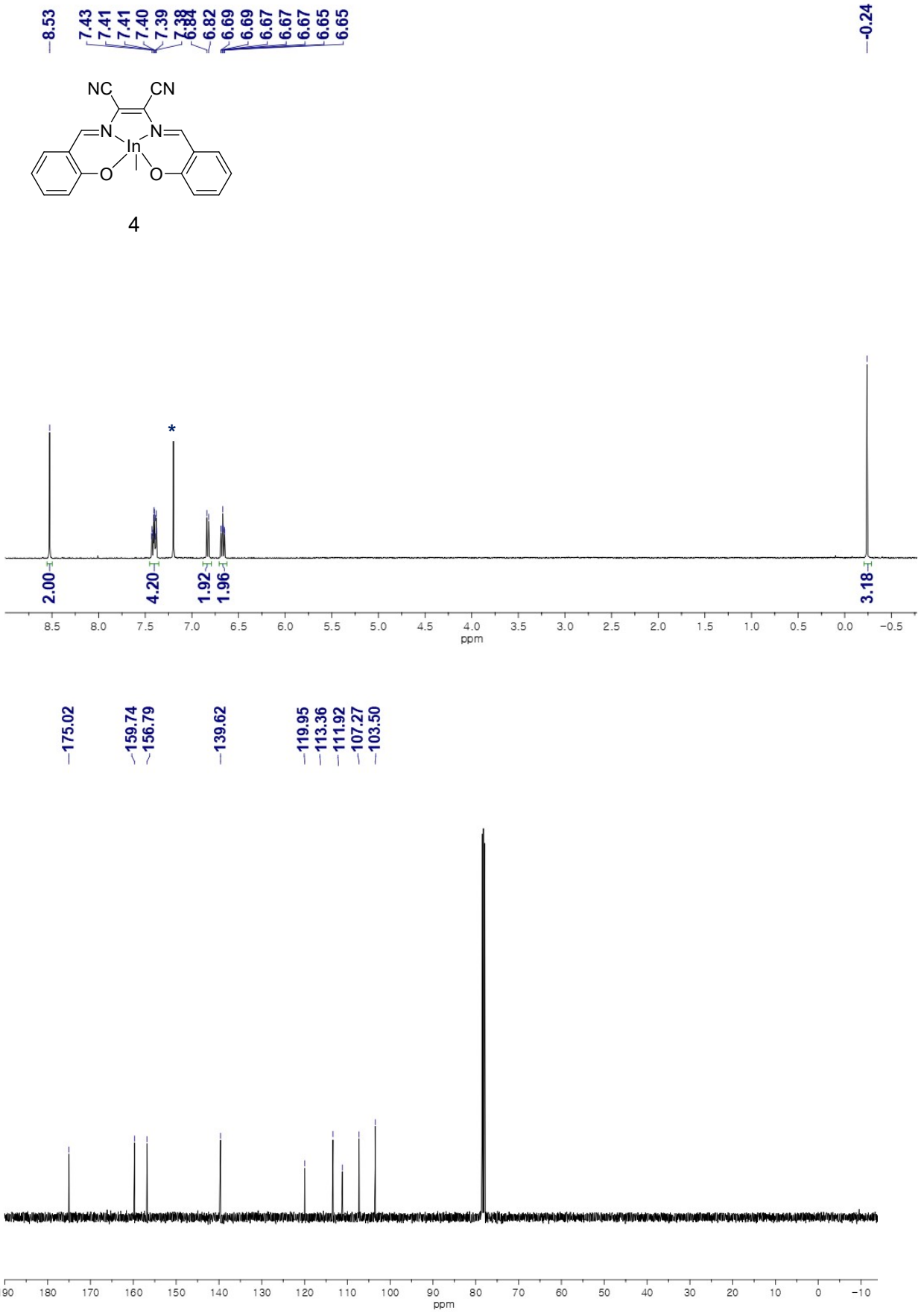

Fig. S4 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **4** (* from residual $CHCl_3$ in $CDCl_3$).

Table S1 Crystallographic data and parameters for **2**

Compound	**2**
Formula	$C_{27}H_{31}InN_6O_2$
Formula weight	586.40
Crystal system	Monoclinic
Space group	P21/n
a (Å)	10.744(2)
b (Å)	20.929(4)
c (Å)	12.803(2)
α (°)	90
β (°)	90.00(3)
γ (°)	90
V (Å^3)	2878.9(10)
Z	4
ρ_{calc}(g cm^{-3})	1.353
μ (mm^{-1})	0.853
F(000)	1200
T (K)	293(2)
Scan mode	*multi-scan*
hkl range	$-13 < h < 13$, $-26 < k < 26$, $-16 < l < 13$
Measurement reflns	27424
Unique reflns [R_{int}]	6409 [0.0544]
Reflns used for refinement	6409
Refined parameters	330
R_1[a] (I > 2σ(I))	0.0487
wR_2[b] all data	0.1557
GOF on F^2	1.000
ρ_{fin} (max/min) (e Å^{-3})	0.520, −0.730

[a] $R_1 = \sum||Fo| - |Fc||/\sum|Fo|$. [b] $wR_2 = \{[\sum w(Fo^2 - Fc^2)^2]/[\sum w(Fo^2)^2]\}^{1/2}$.

Table S2 Selected bond lengths (Å) and angles (°) for **2**

Compound	**2**
	lengths
In–O1	2.145(3)
In–O2	2.131(3)
In–N1	2.297(3)
In–N2	2.282(3)
In-C1	2.174(7)
	Angles
O1-In-O2	91.66(10)
O1-In-N1	81.15(11)
O1-In-N2	134.29(13)
O2-In-N1	134.61(12)
O2-In-N2	81.91(11)
O1-In-C1	115.50(2)
O2-In-C1	112.34(19)
N1-In-N2	72.43(11)
N1-In-C1	111.10(2)
N2-In-C1	108.60(2)

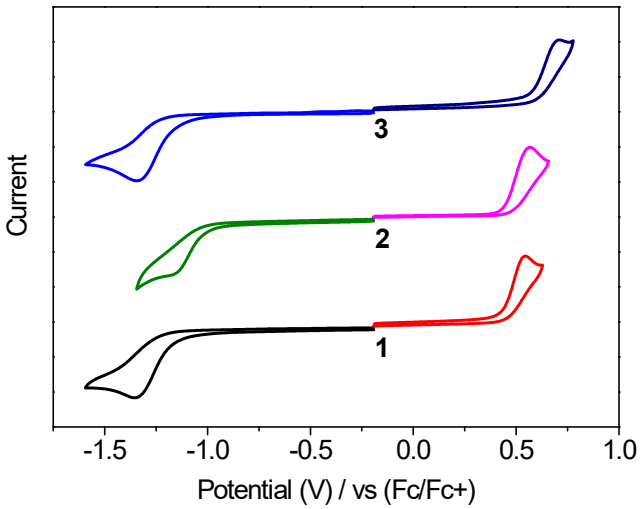

Fig. S5 Cyclic voltammograms (CV) for **1**−**3** (1 mM in MeCN, scan rate = 100 mV/s).

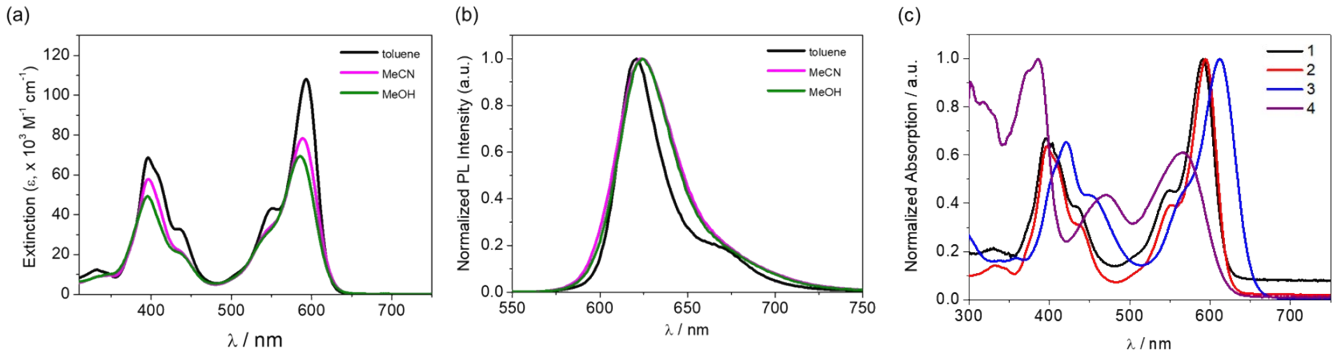

Fig. S6 (a) UV−vis absorption and (b) PL spectra of **2** in various organic solvents (20 μM) at 298 K. (c) Normalized absorption spectra of **1**−**4** in toluene at 298 K.

Table S3 UV−vis absorption and PL spectra of **2** in various organic solvents (20 μM) at 298 K

Solvent	λ_{abs} /nm (ε)	λ_{ex} /nm	λ_{em} /nm	Φ_{PL} /%
toluene	397 (47.46), 437 (23.14), 551 (29.19), 594 (74.65)	400	617	74.3
DCM	397 (50.95), 597 (73.15)	398	629	54.4
acetone	396 (58.17), 592 (81.84)	397	620	52.0
MeCN	396 (58.17), 589 (78.34)	396	624	67.5
MeOH	395 (49.22), 586 (69.33)	392	624	43.8

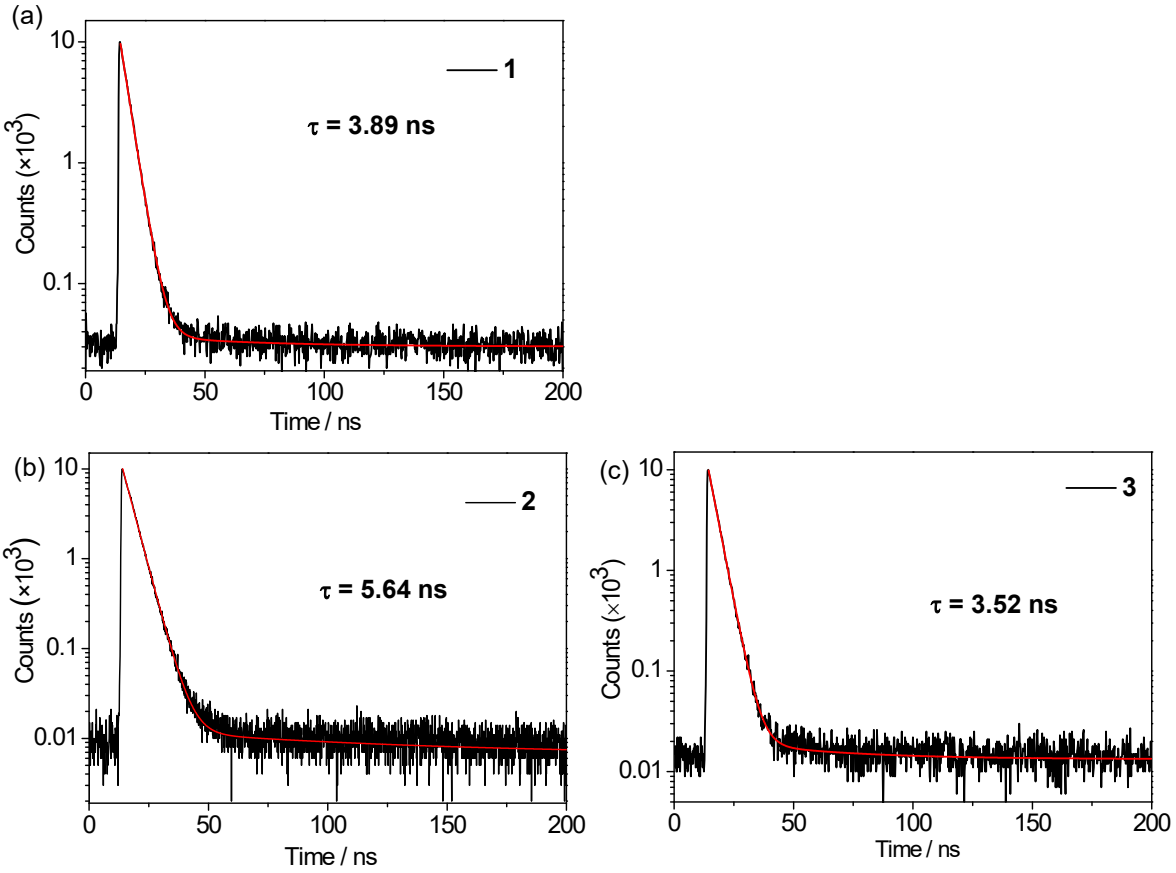

Fig. S7 Emission decay curves of toluene (20 μM) solutions of (a) **1**, (b) **2**, and (c) **3** at 298 K (black line). The red-line corresponds to the single-exponential fitting curves.

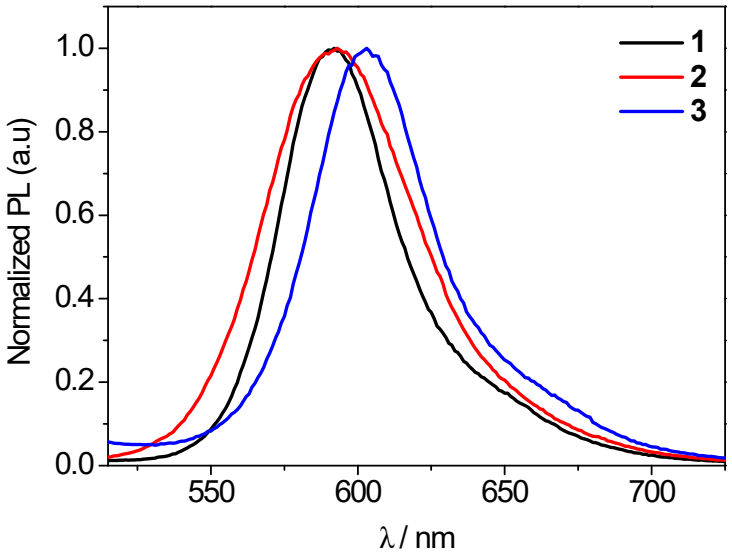

Fig. S8 PL spectra of **1**−**3** in film state (1 wt% doped on PMMA) at 298 K.

Computational Results

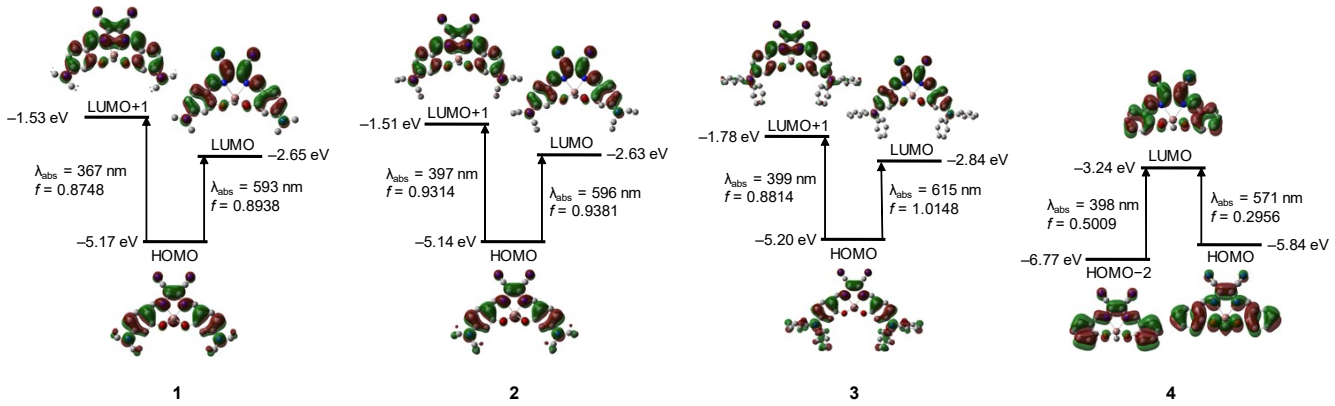

Fig. S9 Frontier molecular orbitals for **1**−**4** at their ground state (S_0) with their relative energies from DFT calculation (isovalue 0.04). The transition energy (in nm) was calculated using the TD-B3LYP method with 6-31G(d, p) basis sets.

Table S4 The major electronic transition for **1**−**4** at ground state (S_0) calculated using the TD-B3LYP method with 6-31G(d, p) basis sets[a]

	λ_{calc}/ nm	f_{calc}	Assignment
1	593.15	0.8938	HOMO → LUMO (98.3%)
	366.61	0.8748	HOMO → LUMO+1 (75.5%)
2	595.91	0.9381	HOMO → LUMO (98.5%)
	397.38	0.9314	HOMO → LUMO+1 (75.7%)
3	614.83	1.0148	HOMO → LUMO (98.9%)
	398.95	0.8814	HOMO → LUMO+1 (87.8%)
4	570.52	0.2956	HOMO → LUMO (98.6%)
	397.93	0.5009	HOMO−2 → LUMO (96.0%)

[a] Singlet energies for the vertical transition calculated at the optimized S_0 geometries.

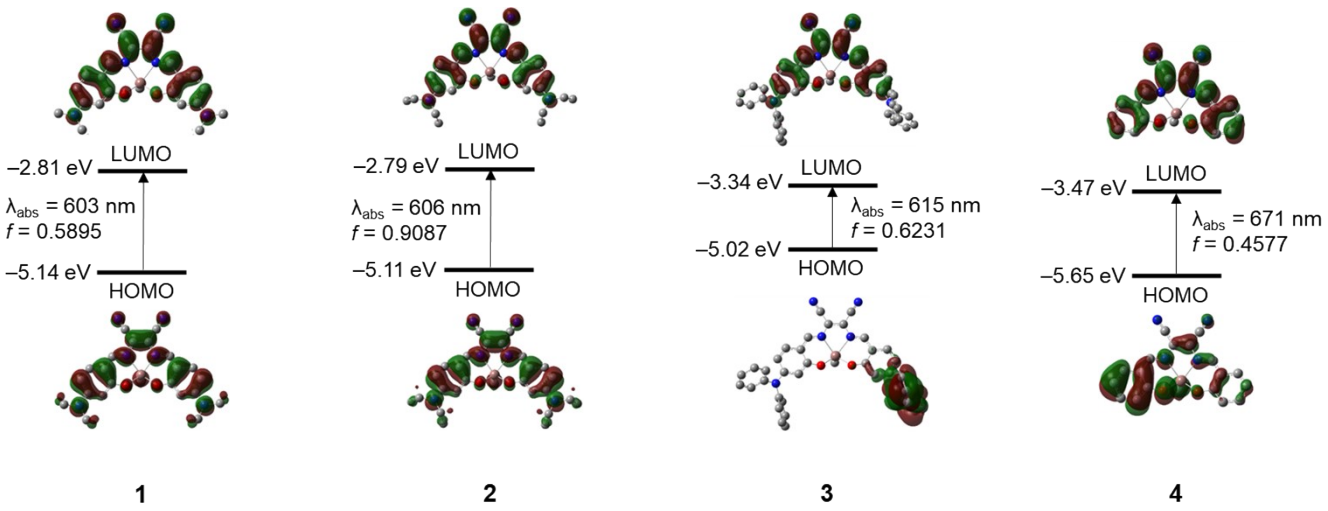

Fig. S10 Frontier molecular orbitals for **1**−**4** at their first singlet excited state (S_1) with their relative energies from DFT calculation (isovalue 0.04). The transition energy (in nm) was calculated using the TD-B3LYP method with 6-31G(d, p) basis sets.

Table S5 The major electronic transition for **1**−**4** at first singlet excited state (S_1) calculated using the TD-B3LYP method with 6-31G(d, p) basis sets[a]

	λ_{calc}/ nm	f_{calc}	Assignment
1	603.30	0.8595	HOMO → LUMO (98.0%)
2	605.58	0.9087	HOMO → LUMO (98.4%)
3	615.42	0.6231	HOMO → LUMO (99.1%)
4	670.58	0.4577	HOMO → LUMO (99.4%)

[a] Singlet energies for the vertical transition calculated at the optimized S_0 geometries.

Table S6 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **1** from TD-B3LYP calculations using the B3LYP geometries at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in toluene

state	λ_{calc} (nm)	f_{calc}	major contribution
		S_0	
1	593.15	0.8938	HOMO → LUMO (98.3%)
2	466.12	0.0930	HOMO−2 → LUMO (97.8%)
3	462.66	0.0110	HOMO−1 → LUMO (76.5%)
4	430.93	0.1196	HOMO−3 → LUMO (65.1%)
5	366.61	0.8748	HOMO → LUMO+1 (75.5%)
		S_1	
1	603.30	0.8595	HOMO → LUMO (98.0%)
2	493.93	0.1225	HOMO−2 → LUMO (97.5%)
3	488.74	0.0050	HOMO−1 → LUMO (75.0%)
4	449.54	0.1515	HOMO−3 → LUMO (64.2%)
5	373.69	0.1389	HOMO → LUMO+1 (77.9%)

Table S7 Molecular orbital energies (in eV) and molecular orbital distributions (in %) of **1** at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in toluene

	E (eV)	$EtCN_2$ imine	In−Me	Substituent	Phenoxy
			S_0		
LUMO+3	−0.20	94.4	3.4	0.0	2.2
LUMO+2	−0.84	61.0	0.1	3.8	35.1
LUMO+1	−1.53	28.0	1.3	6.6	64.1
LUMO	−2.65	45.3	0.2	5.7	48.8
HOMO	−5.17	31.4	2.6	19.5	46.5
HOMO−1	−5.76	3.8	0.1	39.3	56.7
HOMO−2	−5.80	0.6	5.7	17.1	76.6
HOMO−3	−5.93	10.6	0.2	4.7	84.5
			S_1		
LUMO+3	−0.18	94.3	3.5	0.0	2.3
LUMO+2	−0.90	59.8	0.1	3.8	36.3
LUMO+1	−1.55	29.6	1.3	6.3	62.8
LUMO	−2.81	45.9	0.2	5.7	48.2
HOMO	−5.14	31.4	2.9	18.6	47.1
HOMO−1	−5.79	3.0	0.2	38.3	58.5
HOMO−2	−5.80	0.5	6.5	18.3	74.7
HOMO−3	−5.93	10.9	0.2	6.6	82.3

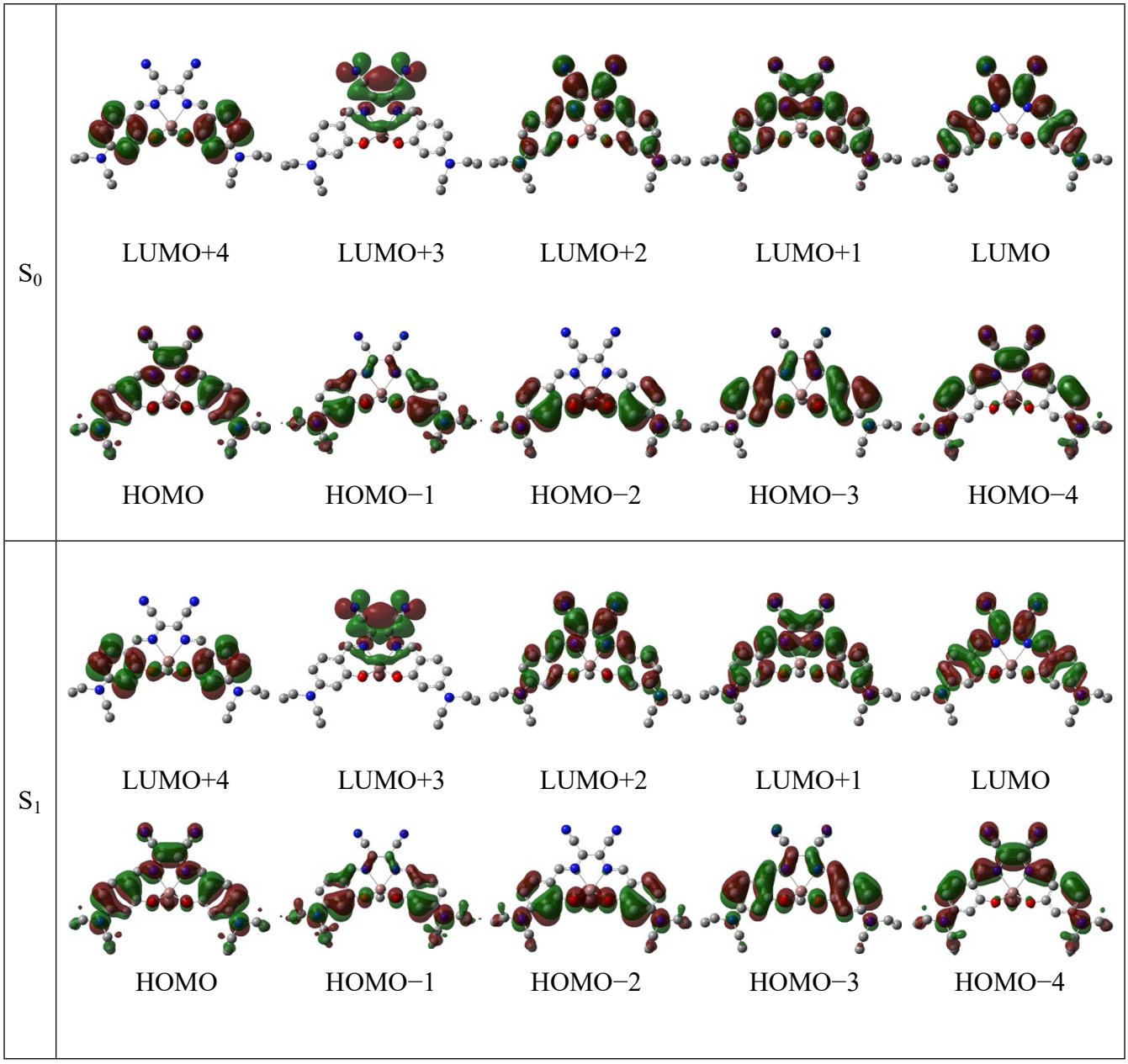

Fig. S11 The selected frontier orbitals of **2** from TD-B3LYP calculations (Isovalue = 0.04 a.u.) at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in toluene.

Table S8 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **2** from TD-B3LYP calculations using the B3LYP geometries at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in toluene

state	λ_{calc} (nm)	f_{calc}	major contribution
		S_0	
1	595.91	0.9381	HOMO → LUMO (98.5%)
2	467.38	0.0816	HOMO−2 → LUMO (97.9%)
3	464.04	0.0175	HOMO−1 → LUMO (77.3%)
4	431.80	0.1194	HOMO−3 → LUMO (66.5%)
5	397.38	0.9314	HOMO → LUMO+1 (75.7%)
		S_1	
1	605.58	0.9087	HOMO → LUMO (98.4%)
2	494.92	0.1055	HOMO−2 → LUMO (97.8%)
3	489.69	0.0101	HOMO−1 → LUMO (74.4%)
4	450.55	0.1552	HOMO−3 → LUMO (64.4%)
5	374.09	0.1997	HOMO → LUMO+1 (78.4%)

Table S9 Molecular orbital energies (in eV) and molecular orbital distributions (in %) of **2** at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in toluene

	E (eV)	$EtCN_2$ imine	In−Me	Substituent	Phenoxy
		S_0			
LUMO+3	−0.19	94.3	3.5	0.0	2.2
LUMO+2	−0.83	60.9	0.1	3.8	35.2
LUMO+1	−1.51	27.9	1.3	6.6	64.2
LUMO	−2.63	45.2	0.2	5.8	48.8
HOMO	−5.14	31.2	2.4	20.2	46.1
HOMO−1	−5.72	4.3	0.1	40.0	55.5
HOMO−2	−5.78	0.7	5.8	16.7	76.7
HOMO−3	−5.91	10.2	0.2	4.0	85.6
		S_1			
LUMO+3	−0.17	94.2	3.5	0.0	2.3
LUMO+2	−0.89	59.7	0.1	3.8	36.4
LUMO+1	−1.53	29.5	1.3	6.3	62.9
LUMO	−2.79	45.9	0.2	5.9	48.1
HOMO	−5.11	31.3	2.7	19.4	46.5
HOMO−1	−5.75	3.7	0.2	39.7	56.4
HOMO−2	−5.79	0.6	6.5	17.8	75.1
HOMO−3	−5.91	10.3	0.2	5.2	84.3

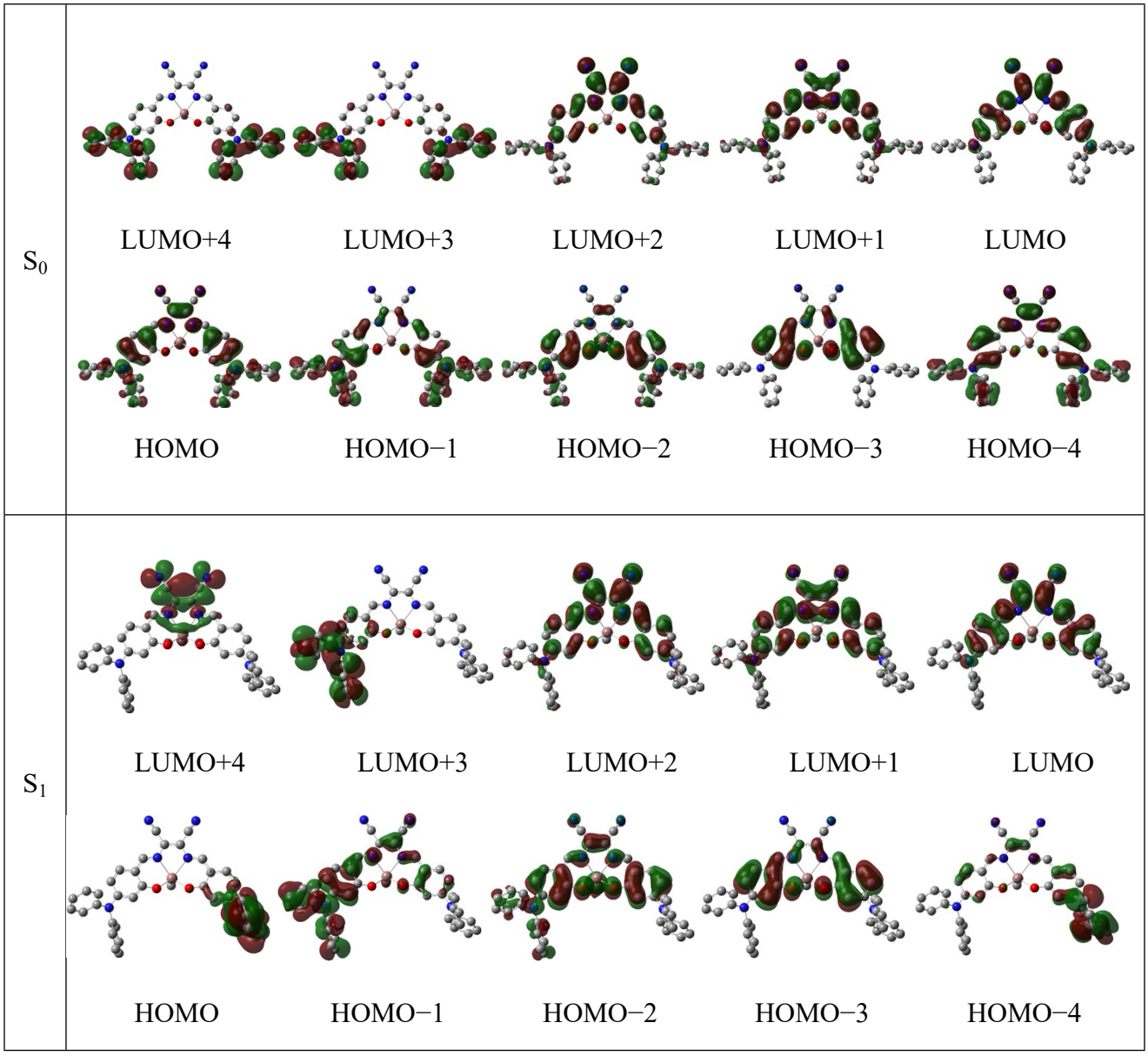

Fig. S12 The selected frontier orbitals of **3** from TD-B3LYP calculations (Isovalue = 0.04 a.u.) at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in toluene.

Table S10 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **3** from TD-B3LYP calculations using the B3LYP geometries at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in toluene

state	λ_{calc} (nm)	f_{calc}	major contribution
		S_0	
1	614.83	1.0148	HOMO → LUMO (98.9%)
2	514.71	0.1905	HOMO−1 → LUMO (94.4%)
3	498.66	0.0015	HOMO−2 → LUMO (98.1%)
4	456.02	0.0731	HOMO−3 → LUMO (89.3%)
5	398.95	0.8814	HOMO → LUMO+1 (87.8%)
		S_1	
1	615.42	0.6231	HOMO → LUMO (99.1%)
2	585.43	0.0944	HOMO−1 → LUMO (98.6%)
3	514.81	0.1011	HOMO−2 → LUMO (96.9%)
4	493.35	0.0346	HOMO−3 → LUMO (95.9%)
5	421.27	0.4082	HOMO → LUMO+1 (95.4%)

Table S11 Molecular orbital energies (in eV) and molecular orbital distributions (in %) of **3** at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in toluene

	E (eV)	$EtCN_2$ imine	In−Me	Substituent	Phenoxy
			S_0		
LUMO+3	−0.61	0.1	0.1	93.9	5.9
LUMO+2	−1.08	58.0	0.1	9.7	32.2
LUMO+1	−1.78	26.7	1.1	9.6	62.6
LUMO	−2.84	42.7	0.2	6.8	50.3
HOMO	−5.20	22.8	1.5	40.1	35.7
HOMO−1	−5.55	4.4	0.1	67.3	28.2
HOMO−2	−5.78	5.4	6.3	23.4	64.9
HOMO−3	−6.01	6.2	0.3	1.7	91.9
			S_1		
LUMO+3	−0.60	0.1	0.2	91.9	7.8
LUMO+2	−1.40	58.9	0.1	4.4	36.6
LUMO+1	−2.09	29.4	1.2	5.3	64.1
LUMO	−3.34	45.2	0.2	4.3	50.3
HOMO	−5.02	0.6	0.0	95.4	4.0
HOMO−1	−5.44	11.1	0.7	61.7	26.5
HOMO−2	−5.90	12.2	7.1	13.2	67.5
HOMO−3	−6.18	4.8	0.3	3.5	91.4

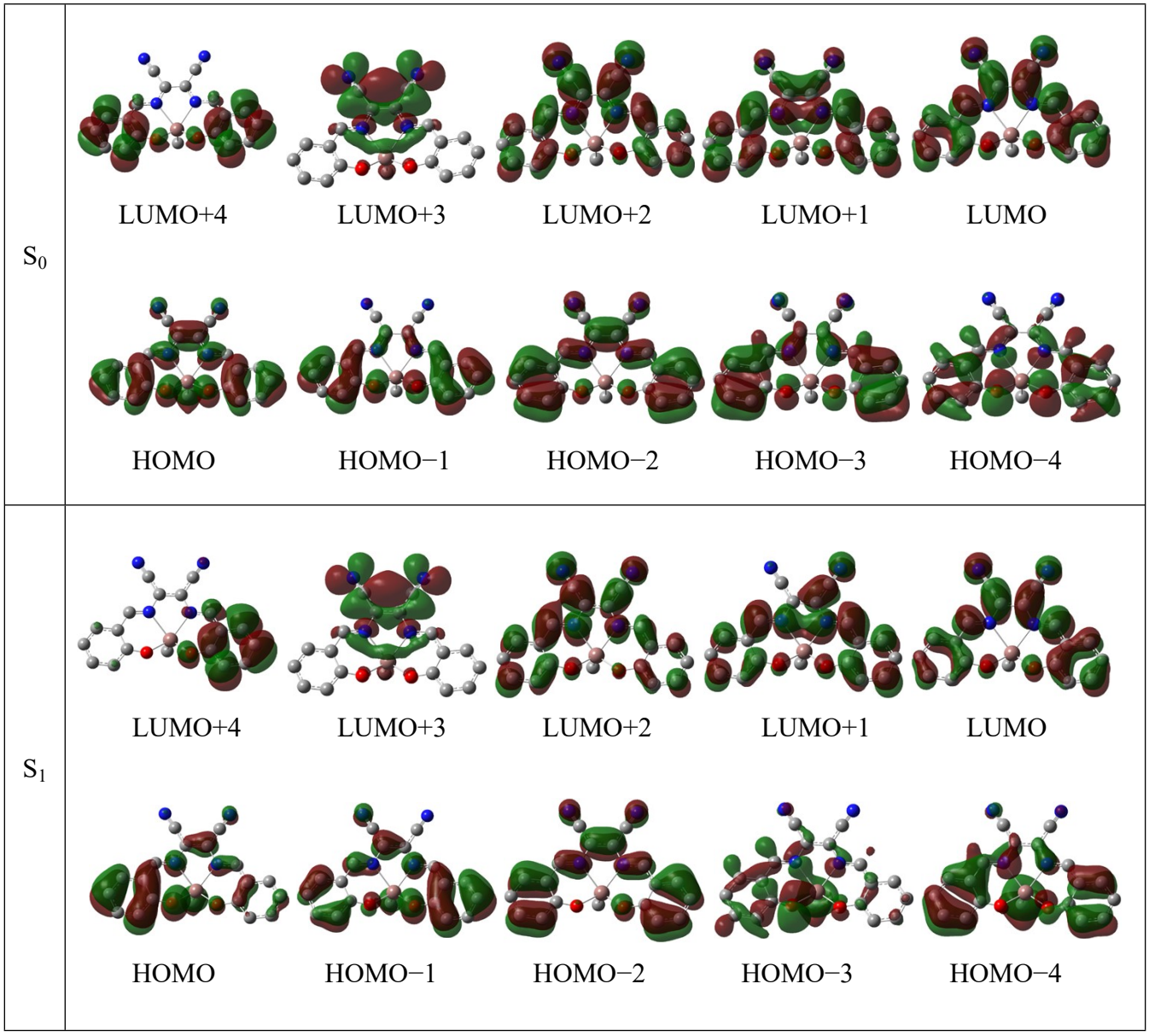

Fig. S13 The selected frontier orbitals of **4** from TD-B3LYP calculations (Isovalue = 0.04 a.u.) at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in toluene.

Table S12 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **4** from TD-

B3LYP calculations using the B3LYP geometries at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in toluene

state	λ_{calc} (nm)	f_{calc}	major contribution
		S_0	
1	570.52	0.2956	HOMO → LUMO (98.6%)
2	494.05	0.0760	HOMO−1 → LUMO (98.0%)
3	397.93	0.5009	HOMO−2 → LUMO (96.0%)
4	384.24	0.1461	HOMO → LUMO+1 (93.0%)
5	356.95	0.0066	HOMO−4 → LUMO (58.4%)
		S_1	
1	670.58	0.4577	HOMO → LUMO (99.4%)
2	541.23	0.1467	HOMO−1 → LUMO (97.3%)
3	423.30	0.1412	HOMO−2 → LUMO (93.2%)
4	414.32	0.0990	HOMO → LUMO+1 (94.6%)
5	394.11	0.0248	HOMO−3 → LUMO (90.1%)

Table S13 Molecular orbital energies (in eV) and molecular orbital distributions (in %) of **4** at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in toluene

	E (eV)	$EtCN_2$ imine	In−Me	Phenoxy
		S_0		
LUMO+3	−0.61	94.4	3.4	2.2
LUMO+2	−1.36	63.3	0.1	36.6
LUMO+1	−2.12	29.6	1.3	69.2
LUMO	−3.24	44.3	0.2	55.4
HOMO	−5.84	21.7	6.6	71.7
HOMO−1	−6.19	5.0	0.3	94.7
HOMO−2	−6.77	25.8	0.1	74.1
HOMO−3	−7.47	17.9	0.2	81.9
		S_1		
LUMO+3	−0.70	94.4	3.4	2.3
LUMO+2	−1.43	57.7	0.1	42.1
LUMO+1	−2.17	34.6	1.2	64.2
LUMO	−3.47	47.0	0.2	52.7
HOMO	−5.65	10.1	4.8	85.1
HOMO−1	−6.18	13.1	3.3	83.6
HOMO−2	−6.79	27.1	0.1	72.8
HOMO−3	−7.34	8.0	14.7	77.3

Table S14 Cartesian coordinates of the ground state (S_0) fully optimized geometry in toluene of **1** from B3LYP calculations (in Å)

Atom	x	y	z
In	0.000068	0.276966	0.790147
N	1.339326	1.894931	-0.104618
N	-1.339375	1.894917	-0.104360
O	1.474514	-0.952378	0.096258
O	-1.474638	-0.952377	0.096861
C	2.756573	-0.766609	-0.079199
C	3.592355	-1.894705	-0.147782
C	4.983511	-1.802411	-0.334419
C	5.569370	-0.498043	-0.470146
C	4.771941	0.611582	-0.423476
H	5.225268	1.593072	-0.540731
C	3.359748	0.546375	-0.230143
C	2.646130	1.759243	-0.277431
H	3.232024	2.655313	-0.501951
C	-2.646193	1.759224	-0.277082
H	-3.232086	2.655286	-0.501634
C	-3.359836	0.546376	-0.229683
C	-4.772009	0.611581	-0.423158
H	-5.225306	1.593058	-0.540630
C	-5.569448	-0.498040	-0.469802
C	-4.983634	-1.802399	-0.333782
C	-3.592473	-1.894699	-0.147201
C	-2.756689	-0.766606	-0.078614
C	0.000425	0.524970	2.919772
H	0.000175	-0.445366	3.425984
H	0.885471	1.076565	3.252409
H	-0.884174	1.077140	3.252638
H	3.101520	-2.852328	-0.038591
H	-3.101625	-2.852327	-0.038109
H	6.634592	-0.384398	-0.619201
H	-6.634629	-0.384396	-0.619140
C	0.693245	3.103282	-0.285400
C	-0.693329	3.103275	-0.285277
C	1.425611	4.312676	-0.502017
C	-1.425741	4.312662	-0.501756
N	2.075289	5.263942	-0.675050
N	-2.075452	5.263927	-0.674675
N	5.769659	-2.920768	-0.386301
N	-5.769821	-2.920744	-0.385285
C	-5.166517	-4.242355	-0.264204
H	-5.945000	-5.000685	-0.341637
H	-4.432058	-4.422075	-1.058654
H	-4.661138	-4.366533	0.701421
C	-7.213522	-2.812281	-0.566058
H	-7.470191	-2.338616	-1.521488
H	-7.647891	-3.811479	-0.559152
H	-7.680989	-2.235763	0.241017
C	7.213636	-2.812189	-0.564783
H	7.647747	-3.811510	-0.559971
H	7.471543	-2.336235	-1.518704
H	7.680296	-2.237762	0.244293
C	5.166561	-4.242324	-0.263672
H	4.430483	-4.421986	-1.056593
H	5.944817	-5.000711	-0.342824
H	4.663141	-4.366484	0.703015

Table S15 Cartesian coordinates of the first excited state (S_1) fully optimized geometry in toluene of **1** from B3LYP calculations (in Å)

Atom	x	y	z
In	-0.000031	0.287675	0.684940
N	1.351242	1.922927	-0.148295
N	-1.351246	1.922949	-0.148412
O	1.465665	-0.942362	-0.006064
O	-1.465571	-0.942339	-0.006486
C	2.758684	-0.771164	-0.123087
C	3.585711	-1.904909	-0.153820
C	4.982915	-1.822639	-0.290252
C	5.576084	-0.521805	-0.402997
C	4.782542	0.600358	-0.381107
H	5.249880	1.577313	-0.475036
C	3.370409	0.543998	-0.243409
C	2.663831	1.778278	-0.282493
H	3.263539	2.672198	-0.467364
C	-2.663815	1.778297	-0.282675
H	-3.263533	2.672203	-0.467589
C	-3.370378	0.543999	-0.243531
C	-4.782512	0.600335	-0.381135
H	-5.249869	1.577271	-0.475152
C	-5.576055	-0.521837	-0.402834
C	-4.982888	-1.822654	-0.289926
C	-3.585647	-1.904903	-0.153780
C	-2.758623	-0.771158	-0.123248
C	-0.000245	0.511747	2.825338
H	0.000235	-0.468683	3.309585
H	0.887163	1.061650	3.151036
H	-0.888228	1.060754	3.150982
H	3.082214	-2.858457	-0.067441
H	-3.082113	-2.858445	-0.067548
H	6.646947	-0.411065	-0.510698
H	-6.646917	-0.411107	-0.510545
C	0.714606	3.131795	-0.263814
C	-0.714585	3.131812	-0.263886
C	1.446066	4.335912	-0.421662
C	-1.446022	4.335930	-0.421798
N	2.098495	5.297950	-0.547626
N	-2.098457	5.297969	-0.547724
N	5.768879	-2.946698	-0.315614
N	-5.768904	-2.946685	-0.314820
C	-5.155076	-4.262875	-0.206769
H	-5.931363	-5.026395	-0.242696
H	-4.452209	-4.446329	-1.029325
H	-4.607352	-4.372551	0.737657
C	-7.216216	-2.845975	-0.461116
H	-7.496897	-2.366180	-1.406827
H	-7.644422	-3.847705	-0.452038
H	-7.668289	-2.277639	0.360844
C	7.216309	-2.845978	-0.460677
H	7.644347	-3.847793	-0.453010
H	7.497648	-2.364732	-1.405433
H	7.667982	-2.279017	0.362474
C	5.155081	-4.262822	-0.206717
H	4.451030	-4.446058	-1.028284
H	5.931217	-5.026433	-0.243937
H	4.608664	-4.372595	0.738486

Table S16 Cartesian coordinates of the ground state (S_0) fully optimized geometry in toluene of **2** from B3LYP calculations (in Å)

Atom	x	y	z
In	0.000739	0.632848	0.720908
N	1.339483	2.303067	-0.071361
N	-1.33894	2.302846	-0.069926
O	1.473076	-0.552615	-0.0505
O	-1.474062	-0.553032	-0.044758
C	2.754925	-0.355986	-0.216472
C	3.589261	-1.478787	-0.35292
C	4.980874	-1.386433	-0.546346
C	5.563969	-0.072234	-0.590103
C	4.769276	1.034054	-0.473296
H	5.227756	2.018804	-0.524937
C	3.357343	0.963247	-0.285764
C	2.646242	2.177585	-0.253931
H	3.233074	3.085455	-0.421444
C	-2.645788	2.177449	-0.252275
H	-3.232372	3.085378	-0.420298
C	-3.357307	0.963384	-0.283621
C	-4.769066	1.034589	-0.472477
H	-5.227179	2.019467	-0.524945
C	-5.563988	-0.071469	-0.589796
C	-4.981359	-1.385861	-0.545108
C	-3.590069	-1.478629	-0.349694
C	-2.755509	-0.356036	-0.2128
C	0.003842	0.744916	2.862172
H	0.002491	-0.255753	3.305446
H	0.890128	1.272772	3.228349
H	-0.879487	1.27613	3.230641
H	3.089373	-2.435197	-0.288064
H	-3.090611	-2.435188	-0.283676
H	6.628995	0.05839	-0.720688
H	-6.628834	0.05948	-0.721558
C	0.693563	3.520468	-0.174133
C	-0.693193	3.520348	-0.17344
C	1.426034	4.741108	-0.312808
C	-1.425929	4.740895	-0.311459
N	2.075682	5.701541	-0.42469
N	-2.075702	5.701312	-0.422767
N	5.7633	-2.503465	-0.701314
N	-5.763884	-2.502659	-0.700998
C	-5.177555	-3.846996	-0.650656
H	-5.853475	-4.513615	-1.193519
H	-4.238647	-3.841925	-1.212887
C	-7.220721	-2.406115	-0.853388
H	-7.552045	-3.327061	-1.340897
H	-7.455896	-1.596992	-1.551705
C	7.220457	-2.407316	-0.850968
H	7.552441	-3.328437	-1.33769
H	7.457151	-1.598371	-1.54898
C	5.176606	-3.847676	-0.651887
H	5.853109	-4.514339	-1.193964
H	4.238459	-3.842324	-1.21537
C	4.941046	-4.393015	0.762915
H	4.468255	-5.379231	0.707402
H	5.882862	-4.499643	1.30873
H	4.286735	-3.733934	1.339556
C	7.989206	-2.215599	0.462867
H	7.836913	-3.062303	1.138019
H	9.062035	-2.132835	0.258865
H	7.670092	-1.307758	0.982388
C	-7.991897	-2.214416	0.459018
H	-9.064309	-2.131243	0.252973
H	-7.841186	-3.061311	1.13429
H	-7.673459	-1.30679	0.979328
C	-4.943959	-4.392181	0.764513
H	-5.886498	-4.498419	1.309159
H	-4.471421	-5.378562	0.709702
H	-4.290151	-3.733249	1.341897

Table S17 Cartesian coordinates of the first excited state (S_1) fully optimized geometry in toluene of **2** from B3LYP calculations (in Å)

Atom	x	y	z
In	-0.000510	0.654170	0.624164
N	1.350849	2.336700	-0.112377
N	-1.351429	2.336885	-0.113139
O	1.463467	-0.533847	-0.139392
O	-1.462943	-0.533353	-0.143327
C	2.755262	-0.354911	-0.259911
C	3.579832	-1.485616	-0.367185
C	4.976631	-1.406297	-0.522470
C	5.567575	-0.097578	-0.547091
C	4.777655	1.022516	-0.446428
H	5.249583	2.001275	-0.478084
C	3.366440	0.963921	-0.303729
C	2.662916	2.199459	-0.259971
H	3.263550	3.102439	-0.389953
C	-2.663452	2.199571	-0.260842
H	-3.264269	3.102486	-0.390460
C	-3.366658	0.963836	-0.304904
C	-4.777990	1.022047	-0.446464
H	-5.250262	2.000669	-0.477286
C	-5.567641	-0.098271	-0.546862
C	-4.976269	-1.406801	-0.523200
C	-3.579278	-1.485735	-0.369352
C	-2.754981	-0.354817	-0.262372
C	-0.002504	0.756564	2.773123
H	-0.002058	-0.249233	3.202449
H	0.884148	1.287357	3.131276
H	-0.890596	1.285961	3.129761
H	3.067093	-2.436625	-0.322802
H	-3.066201	-2.436603	-0.325862
H	6.637018	0.027256	-0.646434
H	-6.637215	0.026246	-0.645201
C	0.714486	3.550406	-0.150381
C	-0.714975	3.550503	-0.150692
C	1.445986	4.762012	-0.233186
C	-1.446320	4.762203	-0.233634
N	2.098397	5.730053	-0.299099
N	-2.098658	5.730279	-0.299713
N	5.758092	-2.531204	-0.659510
N	-5.757552	-2.531908	-0.659642
C	-5.160520	-3.870018	-0.607716
H	-5.848334	-4.550111	-1.117552
H	-4.238629	-3.866536	-1.198124
C	-7.216123	-2.445829	-0.790524
H	-7.547412	-3.364754	-1.281970
H	-7.466955	-1.631176	-1.476690
C	7.216498	-2.444763	-0.792031
H	7.547459	-3.363638	-1.283790
H	7.466351	-1.630092	-1.478527
C	5.161501	-3.869473	-0.606615
H	5.848943	-4.549471	-1.117076
H	4.238951	-3.866387	-1.195994
C	4.880438	-4.389883	0.810484
H	4.401266	-5.372976	0.754951
H	5.805337	-4.495304	1.384461
H	4.214868	-3.716731	1.356927
C	7.971423	-2.271672	0.533273
H	7.806672	-3.124514	1.197573
H	9.046724	-2.193803	0.341015
H	7.651770	-1.367060	1.058078
C	-7.969591	-2.273006	0.535647
H	-9.045128	-2.195356	0.344620
H	-7.803891	-3.125867	1.199687
H	-7.649539	-1.368374	1.060176
C	-4.877728	-4.390677	0.808954
H	-5.801965	-4.496509	1.383921
H	-4.398335	-5.373619	0.752653
H	-4.211747	-3.717466	1.354820

Table S18 Cartesian coordinates of the ground state (S_0) fully optimized geometry in toluene of **3** from B3LYP calculations (in Å)

Atom	x	y	z
In	0.000256	1.777476	0.738334
N	1.340036	3.285736	-0.337752
N	-1.340019	3.285762	-0.337172
O	1.474022	0.480260	0.177690
O	-1.474224	0.480395	0.179231
C	2.753118	0.645999	-0.023933
C	3.591103	-0.486062	0.032592
C	4.974011	-0.404900	-0.151269
C	5.569214	0.867670	-0.419339
C	4.774410	1.978361	-0.498537
H	5.227312	2.938915	-0.731796
C	3.360895	1.932318	-0.308637
C	2.646058	3.134294	-0.492337
H	3.232004	3.999720	-0.814948
C	-2.646076	3.134353	-0.491474
H	-3.232050	3.999783	-0.814022
C	-3.360958	1.932416	-0.307672
C	-4.774442	1.978463	-0.497777
H	-5.227305	2.939023	-0.731090
C	-5.569260	0.867763	-0.418772
C	-4.974080	-0.404805	-0.150678
C	-3.591224	-0.485965	0.033499
C	-2.753229	0.646116	-0.022805
C	0.000887	2.266110	2.823981
H	-0.007951	1.358683	3.435507
H	0.890284	2.844338	3.093368
H	-0.879497	2.859432	3.090149
H	3.115920	-1.434154	0.250222
H	-3.116077	-1.434055	0.251211
H	6.635429	0.941340	-0.589826
H	-6.635438	0.941441	-0.589473
C	0.693104	4.465790	-0.653557
C	-0.693168	4.465814	-0.653260
C	1.425587	5.643216	-1.004963
C	-1.425775	5.643256	-1.004320
N	2.075309	6.568840	-1.283559
N	-2.075602	6.568932	-1.282502
N	5.777280	-1.544552	-0.093659
N	-5.777334	-1.544510	-0.093361
C	7.159817	-1.458925	0.264988
C	8.123811	-2.117207	-0.511535
C	7.558540	-0.745327	1.404495
C	9.469286	-2.057740	-0.151582
H	7.812715	-2.670774	-1.391482
C	8.908530	-0.678277	1.748662
H	6.810187	-0.250088	2.014564
C	9.868621	-1.335244	0.975732
H	10.208264	-2.569965	-0.760725
H	9.206914	-0.122372	2.632679
H	10.917847	-1.287244	1.250668
C	5.234522	-2.849001	-0.331161
C	5.457058	-3.878663	0.592560
C	4.507506	-3.111562	-1.500836
C	4.957148	-5.157162	0.345933
H	6.020423	-3.672670	1.496810
C	3.999459	-4.388833	-1.732937
H	4.342448	-2.314633	-2.218366
C	4.224103	-5.417093	-0.813946
H	5.134020	-5.948485	1.068445
H	3.436486	-4.582315	-2.641246
H	3.831900	-6.412080	-1.001079
C	-5.234544	-2.848921	-0.330890
C	-4.506961	-3.111312	-1.500260
C	-5.457611	-3.878778	0.592496
C	-3.998899	-4.388570	-1.732375
H	-4.341483	-2.314250	-2.217545
C	-4.957681	-5.157263	0.345846
H	-6.021405	-3.672944	1.496514
C	-4.224077	-5.417013	-0.813719
H	-3.435491	-4.581895	-2.640449
H	-5.134977	-5.948723	1.068105
H	-3.831859	-6.411992	-1.000864
C	-7.160003	-1.458910	0.264822
C	-8.123743	-2.116976	-0.512189
C	-7.559086	-0.745542	1.404348
C	-9.469346	-2.057533	-0.152692
H	-7.812357	-2.670360	-1.392147

C	-8.909190	-0.678513	1.748061
H	-6.810910	-0.250464	2.014766
C	-9.869036	-1.335274	0.974644
H	-10.208137	-2.569586	-0.762206
H	-9.207873	-0.122796	2.632094
H	-10.918356	-1.287288	1.249227

Table S19 Cartesian coordinates of the first excited state (S_1) fully optimized geometry in toluene of **3** from B3LYP calculations (in Å)

Atom	x	y	z
In	-0.018883	1.703653	0.795386
N	1.365995	3.293528	-0.021208
N	-1.346564	3.337468	-0.131100
O	1.440426	0.420549	0.201421
O	-1.467087	0.475012	0.019159
C	2.740645	0.592256	0.110313
C	3.565062	-0.552960	0.114701
C	4.954813	-0.474823	0.011716
C	5.570648	0.795359	-0.118783
C	4.783380	1.924815	-0.147564
H	5.258549	2.897807	-0.248168
C	3.368692	1.882312	-0.033369
C	2.671085	3.123933	-0.129444
H	3.286053	4.003427	-0.337320
C	-2.642893	3.208490	-0.303617
H	-3.233923	4.101549	-0.520520
C	-3.369956	1.958843	-0.279205
C	-4.766744	2.027790	-0.467873
H	-5.222491	3.008800	-0.574304
C	-5.577885	0.900611	-0.524601
C	-4.958886	-0.344690	-0.392187
C	-3.590351	-0.474876	-0.210725
C	-2.749394	0.667850	-0.140034
C	-0.192026	1.947763	2.921788
H	-0.055150	0.994097	3.441500
H	0.563858	2.644938	3.297203
H	-1.175546	2.343307	3.195674
H	3.071151	-1.513442	0.201654
H	-3.124319	-1.450384	-0.123068
H	6.649015	0.872760	-0.186004
H	-6.650687	0.981263	-0.658715
C	0.743990	4.512892	-0.196470
C	-0.676036	4.534859	-0.247052
C	1.499807	5.697528	-0.371630
C	-1.387783	5.740651	-0.469646
N	2.172925	6.644392	-0.509298
N	-2.038062	6.695737	-0.647877
N	5.749437	-1.644163	0.047340
N	-5.776519	-1.555108	-0.422722
C	6.933691	-1.732521	-0.738723
C	6.941323	-1.292272	-2.072023
C	8.109243	-2.270405	-0.190517
C	8.106335	-1.378246	-2.833140
H	6.033342	-0.884358	-2.503524
C	9.264344	-2.368903	-0.964535
H	8.110076	-2.607664	0.840804
C	9.272721	-1.919834	-2.287528
H	8.095931	-1.032082	-3.862845
H	10.165905	-2.786428	-0.525038
H	10.176267	-1.991327	-2.885416
C	5.362159	-2.763476	0.839135
C	4.925331	-2.584635	2.161581
C	5.429233	-4.062625	0.312055
C	4.555635	-3.684719	2.933224
H	4.875667	-1.583059	2.575362
C	5.074062	-5.158943	1.097151
H	5.761150	-4.206059	-0.710946
C	4.631590	-4.977986	2.409392
H	4.219743	-3.529197	3.954600
H	5.132279	-6.157959	0.674121
H	4.349881	-5.833101	3.016452
C	-5.888797	-2.262368	-1.607720
C	-5.601868	-1.621483	-2.843901
C	-6.230280	-3.644366	-1.607023
C	-5.712048	-2.328354	-4.027660
H	-5.321989	-0.576868	-2.850087
C	-6.321930	-4.334521	-2.803049
H	-6.364663	-4.164173	-0.667301
C	-6.075569	-3.683687	-4.019971
H	-5.510814	-1.826615	-4.967664
H	-6.561146	-5.392265	-2.791253
H	-6.145299	-4.232332	-4.952809
C	-6.438018	-1.935719	0.764340
C	-7.740253	-2.480014	0.711775
C	-5.824337	-1.708845	2.013581
C	-8.394622	-2.821583	1.889195
H	-8.243326	-2.583877	-0.242400

C	-6.487714	-2.067109	3.178509
H	-4.832668	-1.276255	2.053303
C	-7.771105	-2.626276	3.124854
H	-9.401847	-3.221925	1.842563
H	-6.002634	-1.910407	4.135981
H	-8.286063	-2.892919	4.041741

Table S20 Cartesian coordinates of the ground state (S_0) fully optimized geometry in toluene of **4** from B3LYP calculations (in Å)

Atom	x	y	z
In	-0.000027	-0.551261	0.682851
N	1.340724	1.153635	-0.072432
N	-1.340766	1.153662	-0.072412
O	1.473589	-1.690803	-0.146917
O	-1.473407	-1.690737	-0.147459
C	2.747151	-1.483556	-0.327017
C	3.595749	-2.606518	-0.527338
C	5.561447	-1.181377	-0.728136
C	4.770060	-0.069980	-0.561220
H	5.211318	0.923362	-0.584524
C	3.361810	-0.174481	-0.358379
C	2.638123	1.043811	-0.277767
H	3.218564	1.958113	-0.430924
C	-2.638174	1.043813	-0.277668
H	-3.218665	1.958107	-0.430690
C	-3.361786	-0.174515	-0.358365
C	-4.770071	-0.070087	-0.561003
H	-5.211406	0.923226	-0.584070
C	-5.561394	-1.181515	-0.728011
C	-3.595554	-2.606538	-0.527759
C	-2.747015	-1.483553	-0.327327
C	-0.000270	-0.482233	2.819915
H	-0.000143	-1.492840	3.238919
H	0.884824	0.038905	3.197263
H	-0.885624	0.038606	3.197069
H	3.129437	-3.585995	-0.516270
H	-3.129166	-3.585983	-0.516945
H	6.631198	-1.083203	-0.877220
H	-6.631174	-1.083397	-0.876925
C	0.691348	2.376664	-0.125918
C	-0.691396	2.376674	-0.125891
C	1.425018	3.602120	-0.217568
C	-1.425053	3.602155	-0.217484
N	2.074181	4.565609	-0.291288
N	-2.074195	4.565659	-0.291187
C	-4.954907	-2.459404	-0.713755
H	-5.570976	-3.343936	-0.851964
C	4.955064	-2.459311	-0.713555
H	5.571186	-3.343819	-0.851687

Table S21 Cartesian coordinates of the first excited state (S_1) fully optimized geometry in toluene of **4** from B3LYP calculations (in Å)

Atom	x	y	z
In	-0.000027	-0.551261	0.682851
N	1.340724	1.153635	-0.072432
N	-1.340766	1.153662	-0.072412
O	1.473589	-1.690803	-0.146917
O	-1.473407	-1.690737	-0.147459
C	2.747151	-1.483556	-0.327017
C	3.595749	-2.606518	-0.527338
C	5.561447	-1.181377	-0.728136
C	4.770060	-0.069980	-0.561220
H	5.211318	0.923362	-0.584524
C	3.361810	-0.174481	-0.358379
C	2.638123	1.043811	-0.277767
H	3.218564	1.958113	-0.430924
C	-2.638174	1.043813	-0.277668
H	-3.218665	1.958107	-0.430690
C	-3.361786	-0.174515	-0.358365
C	-4.770071	-0.070087	-0.561003
H	-5.211406	0.923226	-0.584070
C	-5.561394	-1.181515	-0.728011
C	-3.595554	-2.606538	-0.527759
C	-2.747015	-1.483553	-0.327327
C	-0.000270	-0.482233	2.819915
H	-0.000143	-1.492840	3.238919
H	0.884824	0.038905	3.197263
H	-0.885624	0.038606	3.197069
H	3.129437	-3.585995	-0.516270
H	-3.129166	-3.585983	-0.516945
H	6.631198	-1.083203	-0.877220
H	-6.631174	-1.083397	-0.876925
C	0.691348	2.376664	-0.125918
C	-0.691396	2.376674	-0.125891
C	1.425018	3.602120	-0.217568
C	-1.425053	3.602155	-0.217484
N	2.074181	4.565609	-0.291288
N	-2.074195	4.565659	-0.291187
C	-4.954907	-2.459404	-0.713755
H	-5.570976	-3.343936	-0.851964
C	4.955064	-2.459311	-0.713555
H	5.571186	-3.343819	-0.851687