Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Luminescent solvent-free liquids based on Schiff-base boron difluoride complexes with polyethylene glycol chains

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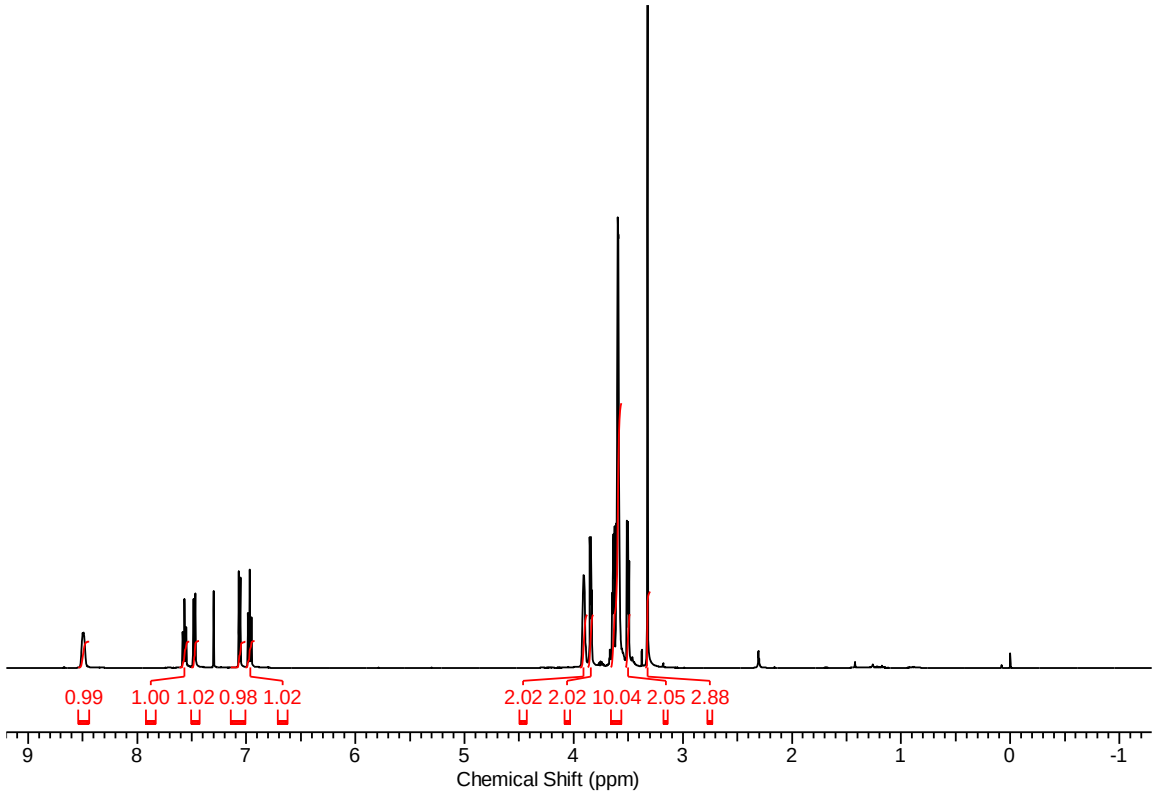
1. NMR Chart

(a)



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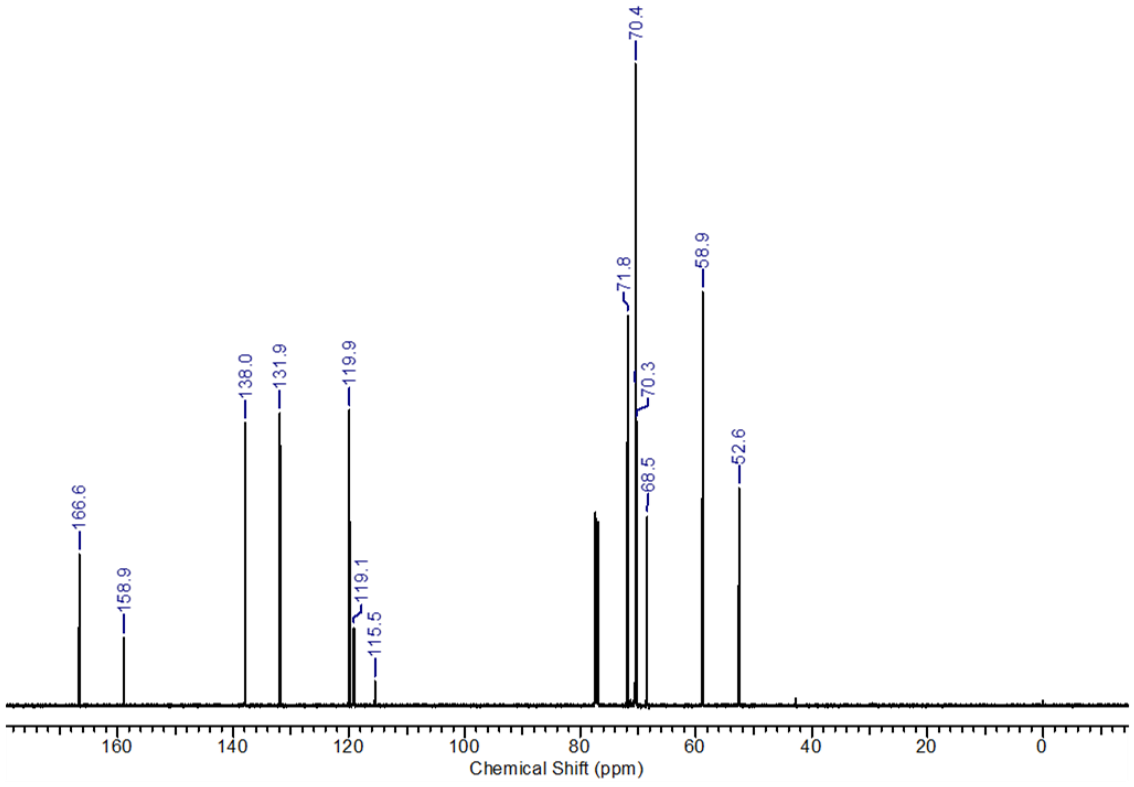
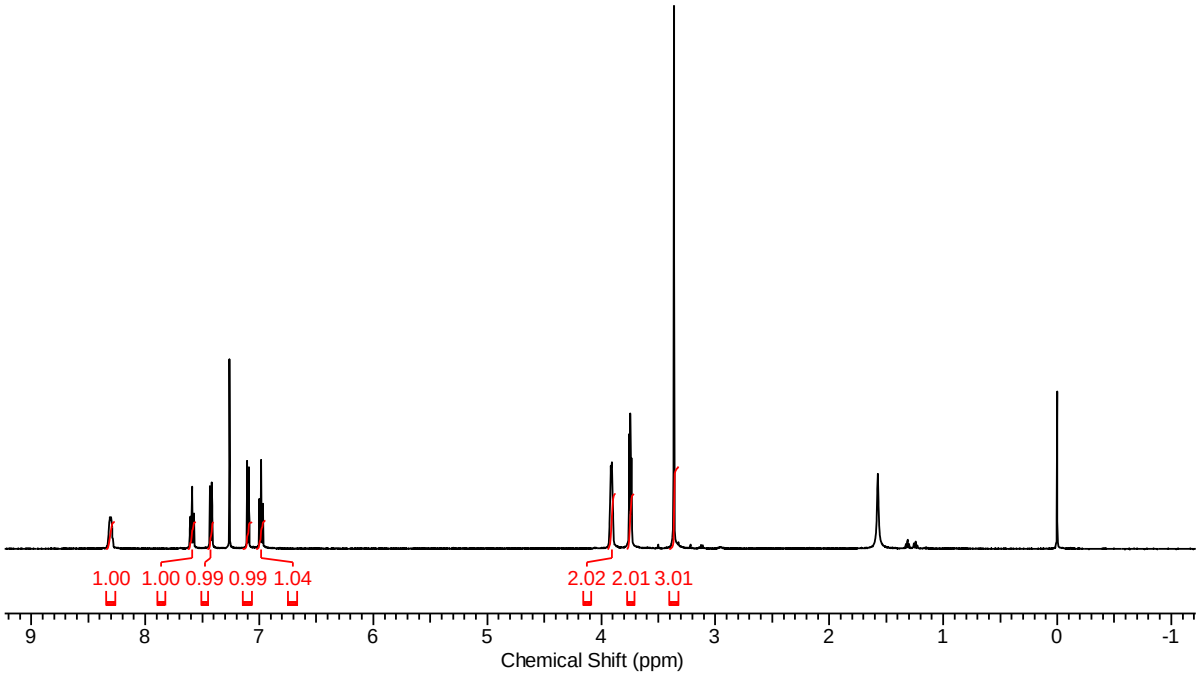


Fig. S1 (a) ^{1}H and (b) ^{13}C NMR spectra of **1a** in $CDCl_3$.

(a)



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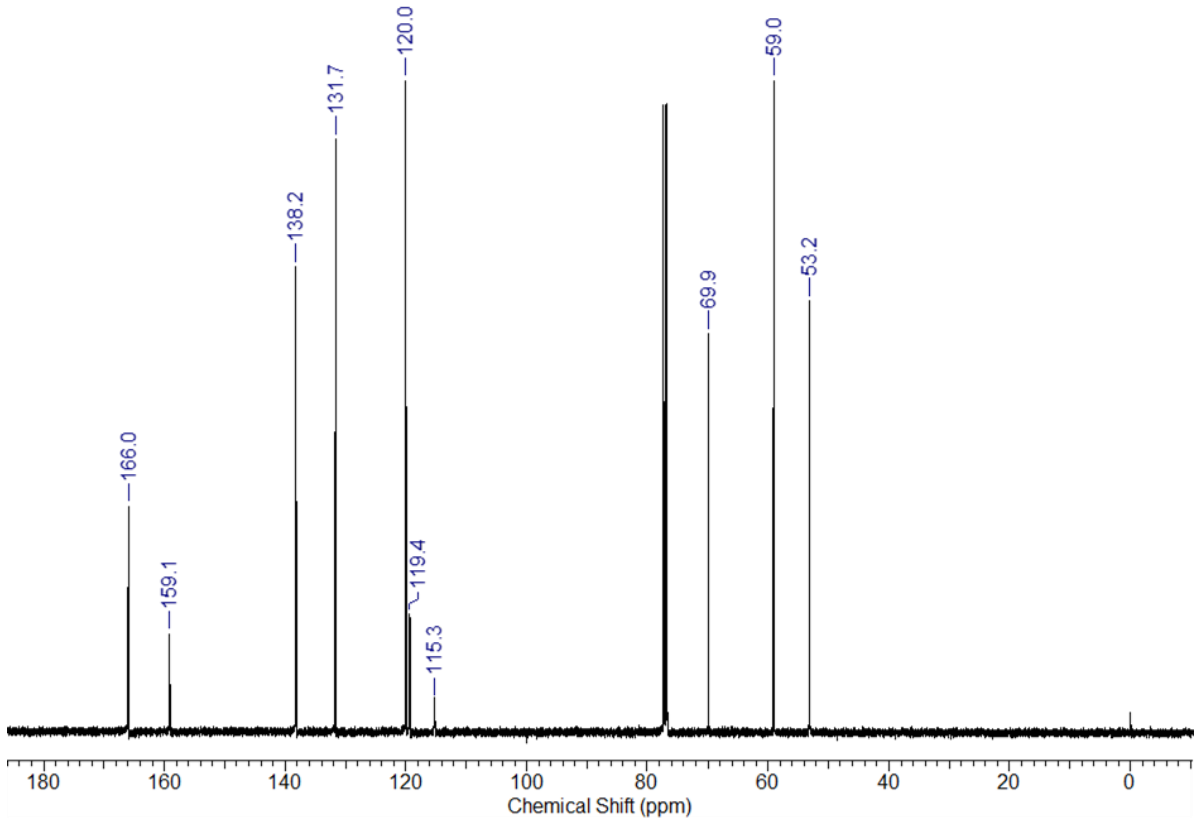
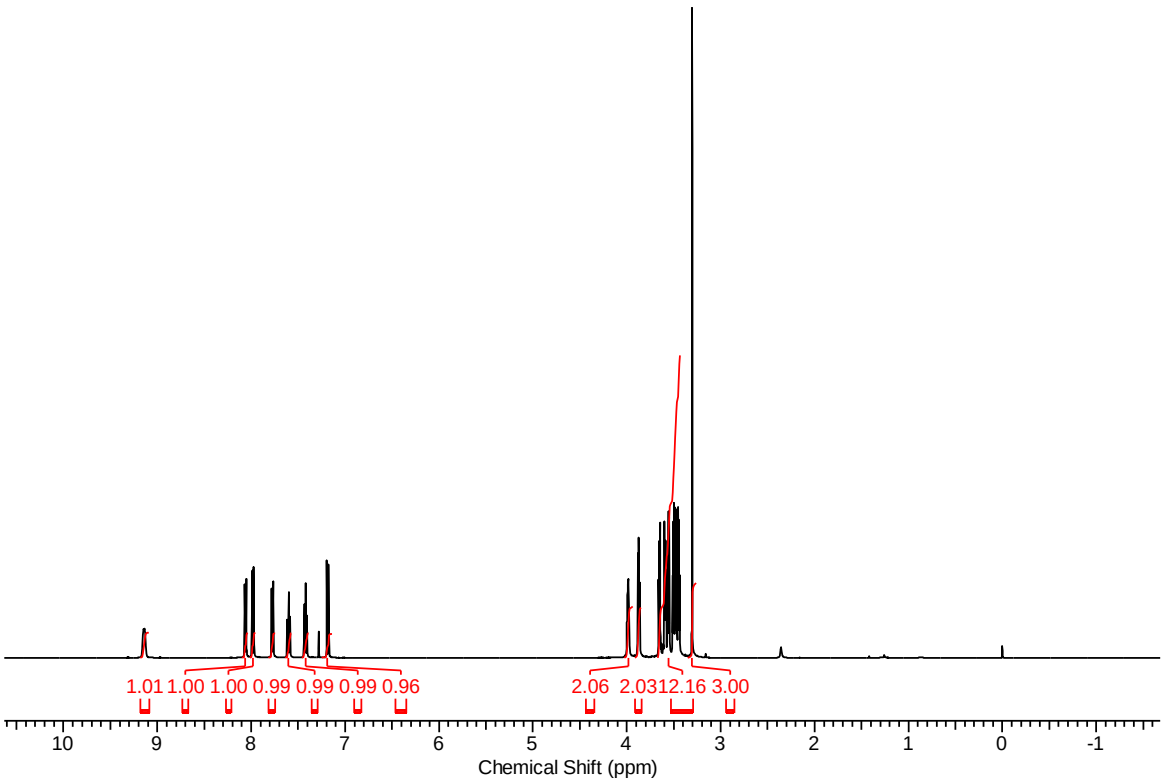


Fig. S2 (a) ^{1}H and (b) ^{13}C NMR spectra of **1b** in $CDCl_3$.

(a)



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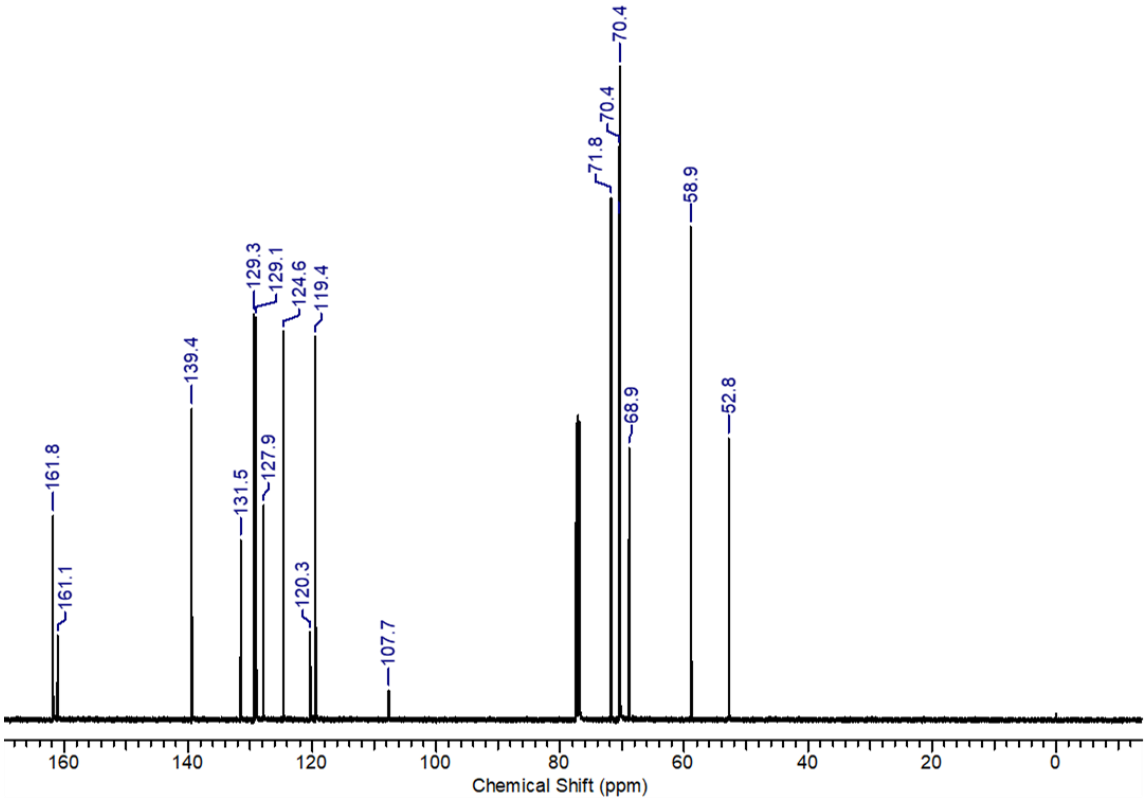
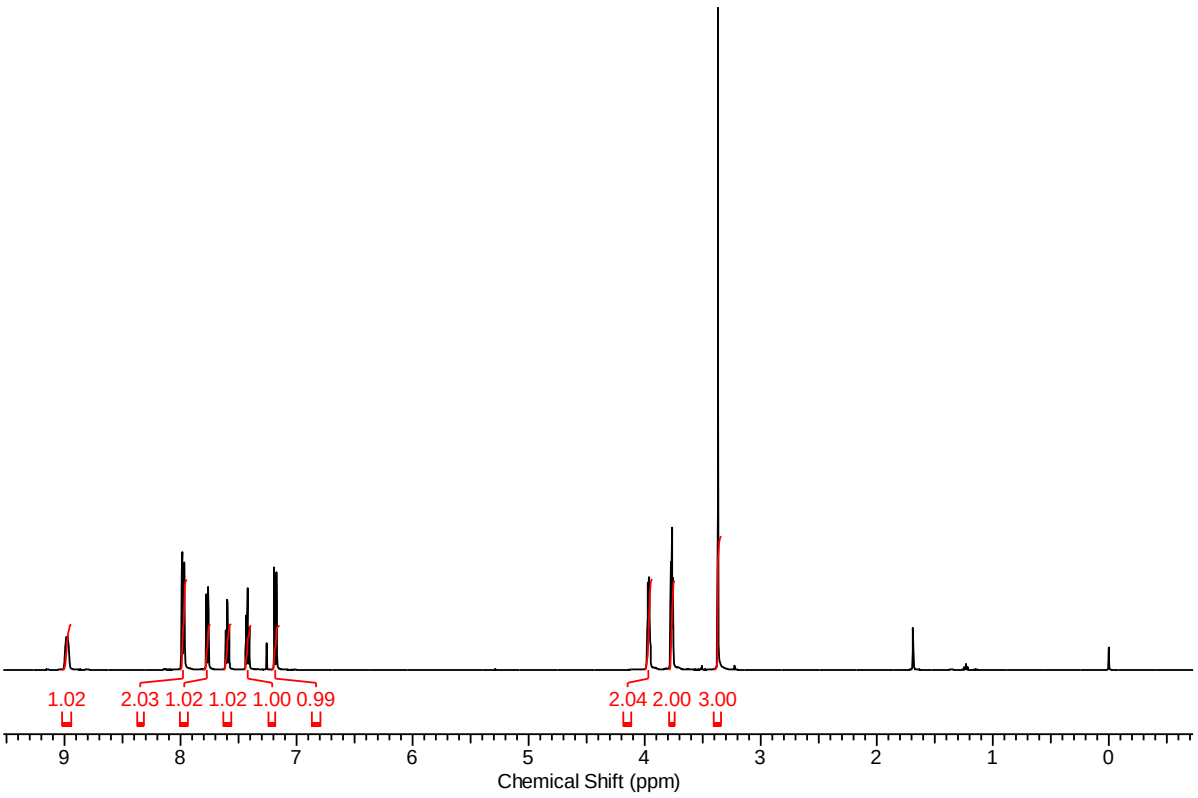


Fig. S3 (a) ^{1}H and (b) ^{13}C NMR spectra of **2a** in $CDCl_3$.

(a)



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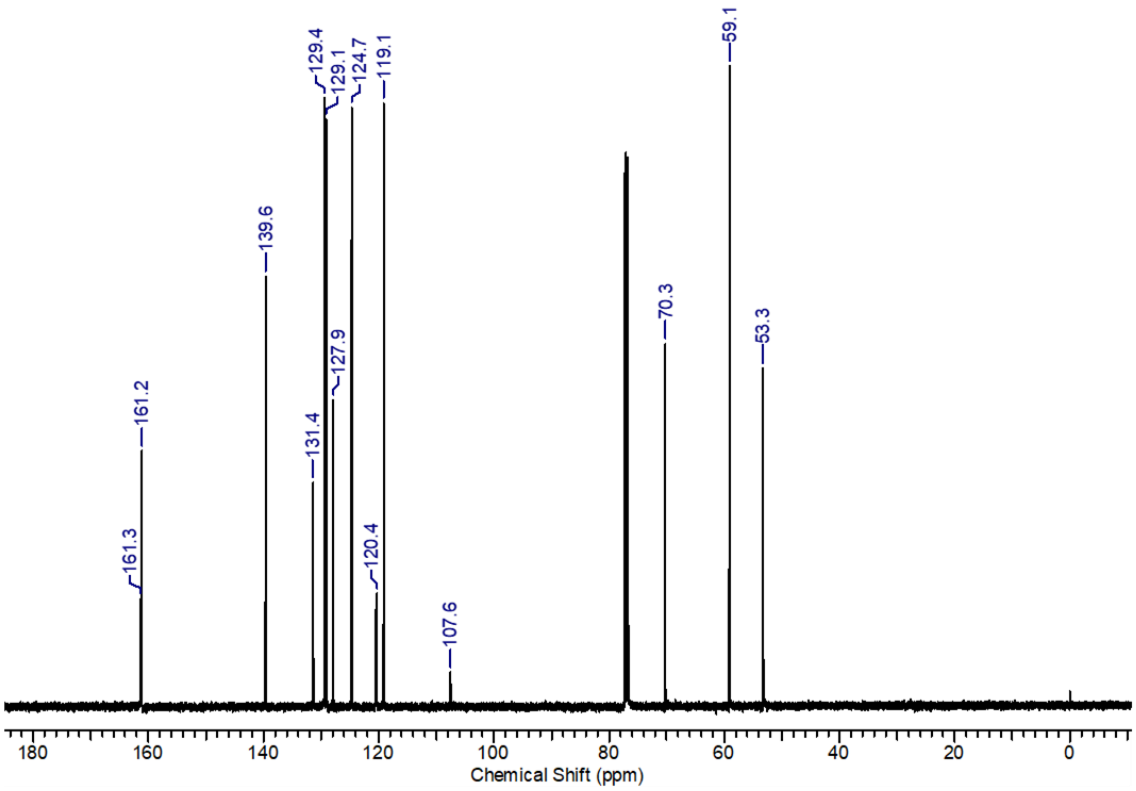
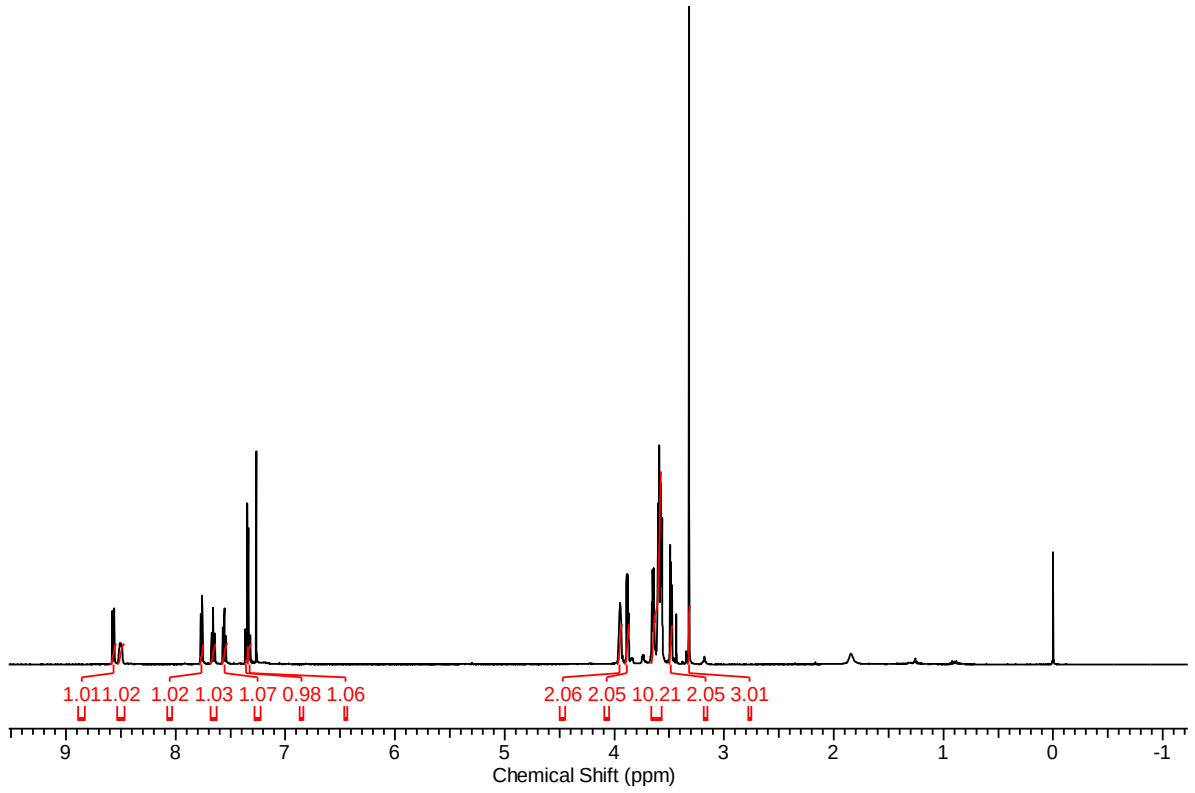


Fig. S4 (a) ^{1}H and (b) ^{13}C NMR spectra of **2b** in $CDCl_3$.

(a)



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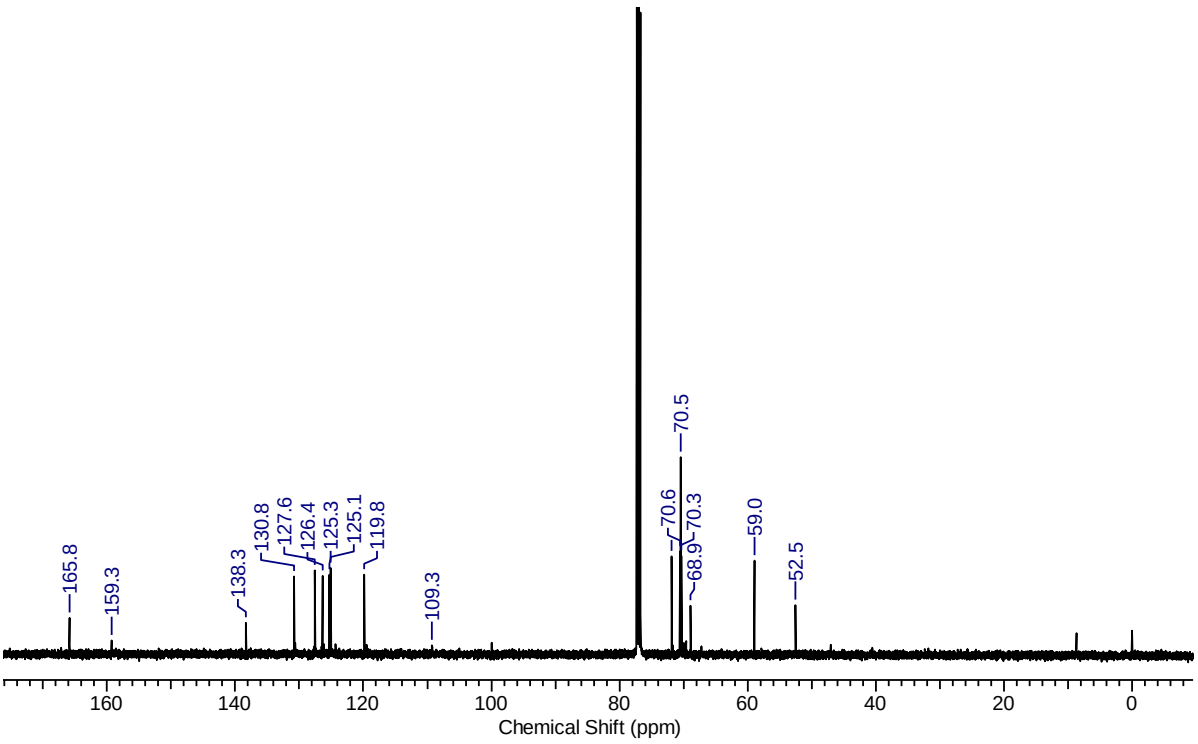
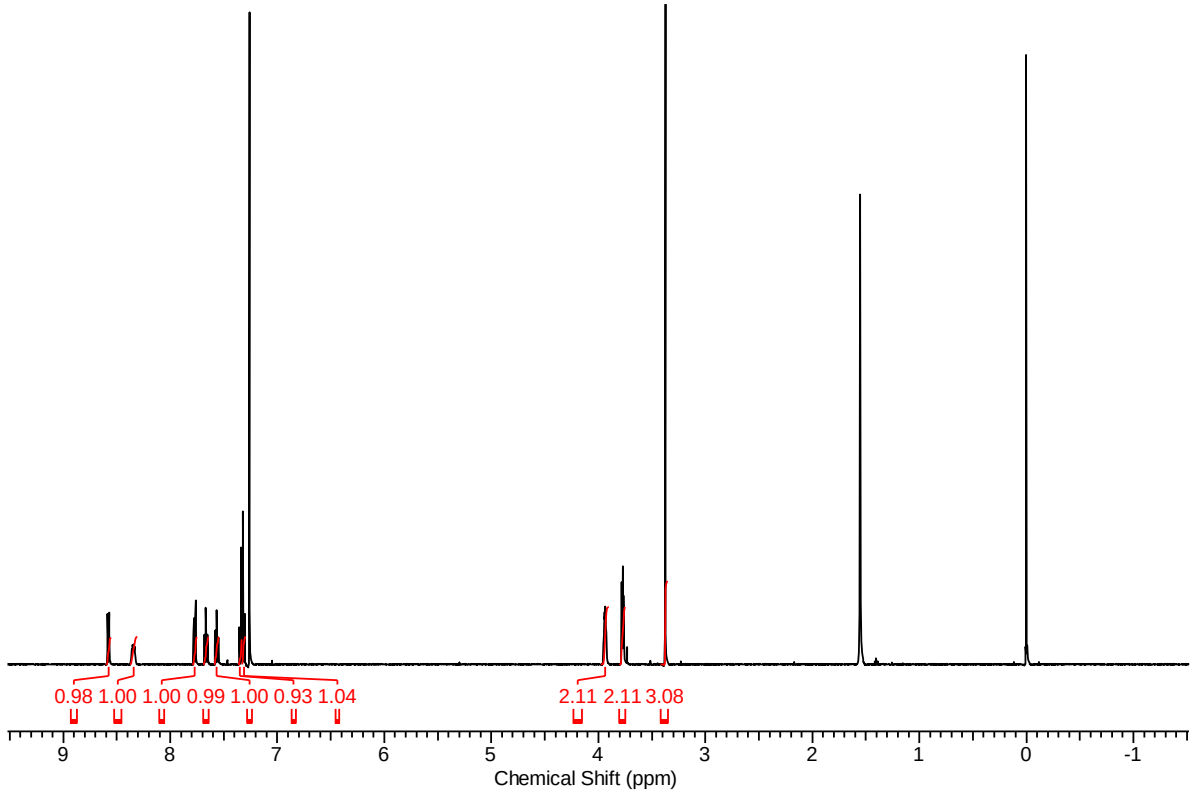


Fig. S5 (a) ^{1}H and (b) ^{13}C NMR spectra of **3a** in $CDCl_3$.

(a)



(b)

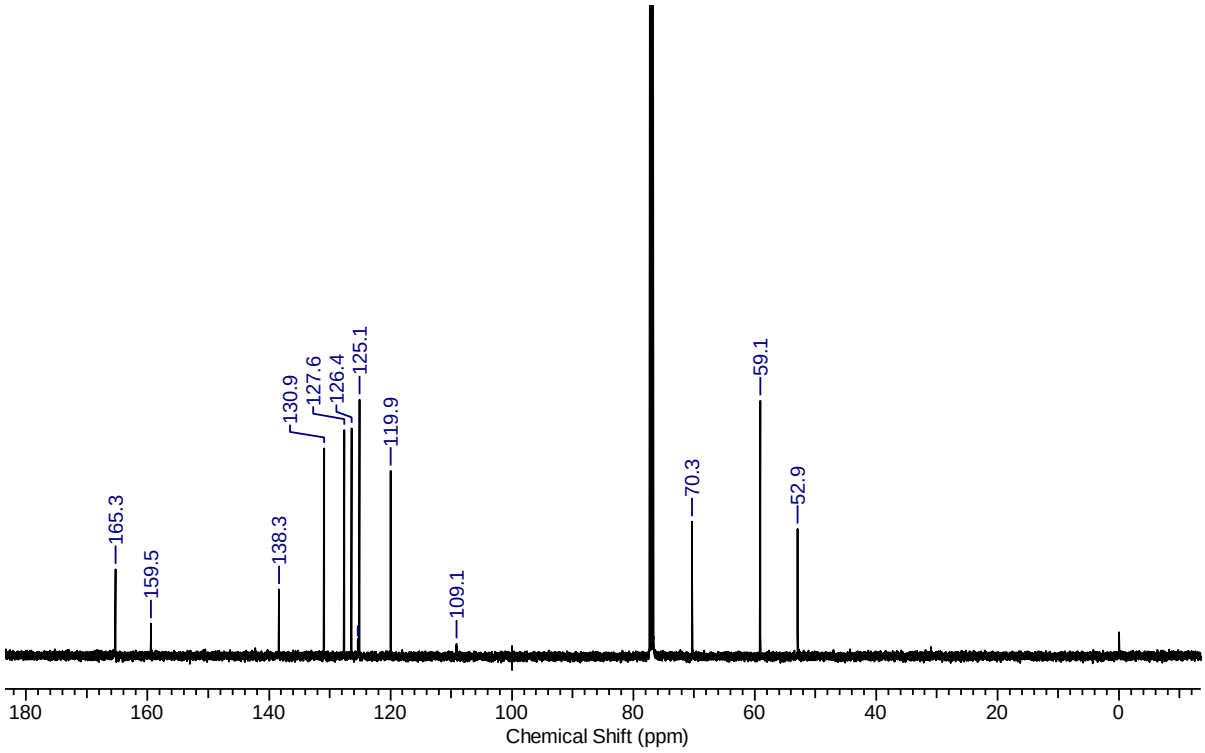
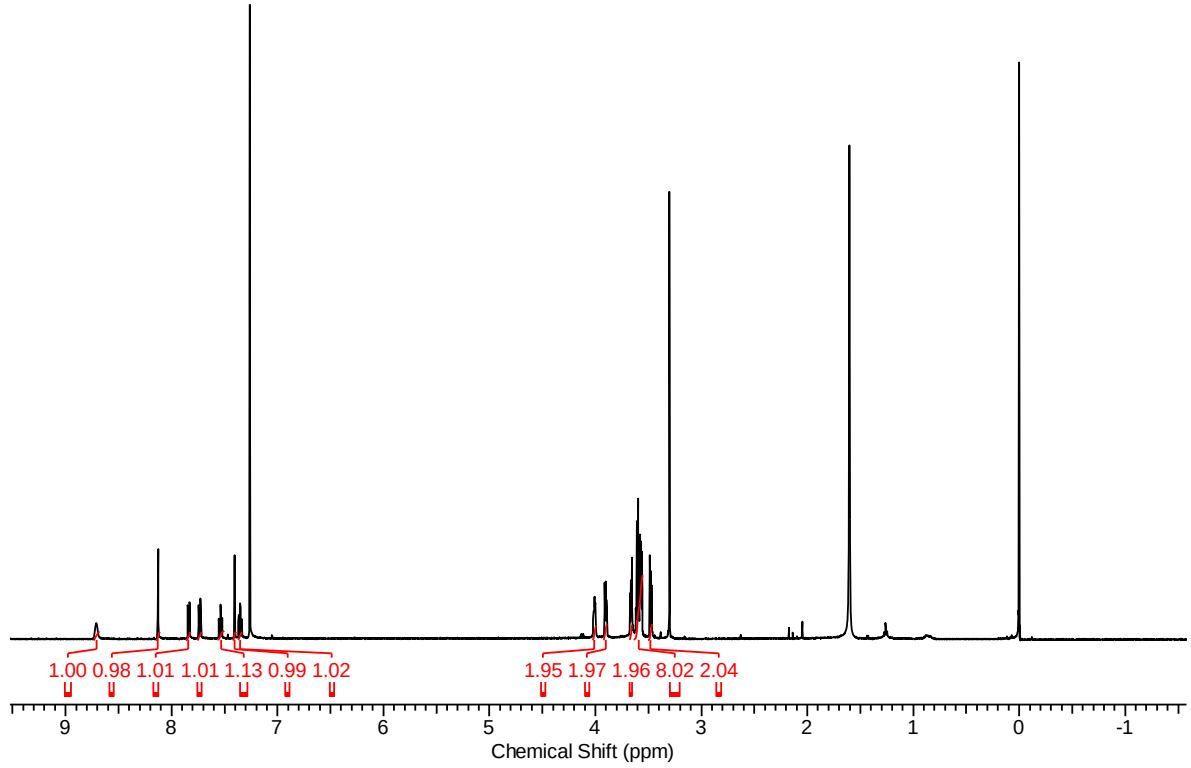


Fig. S6 (a) ^{1}H and (b) ^{13}C NMR spectra of **3b** in $CDCl_3$.

(a)



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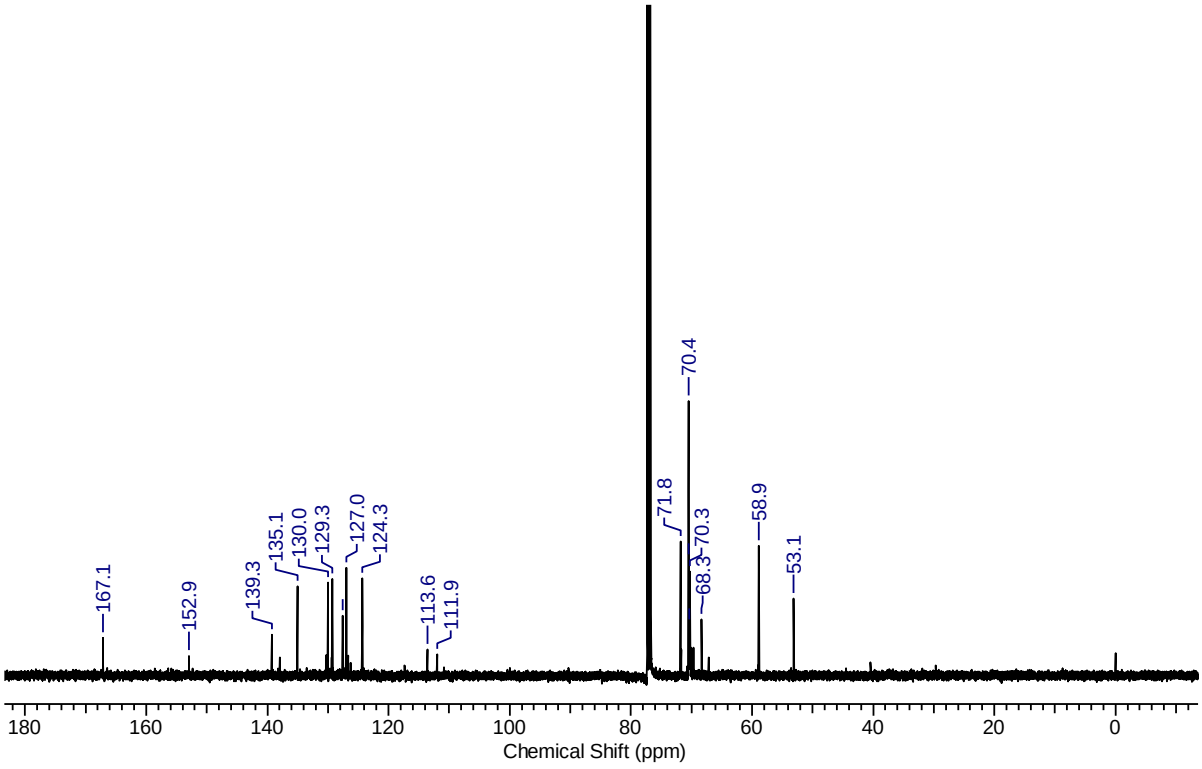
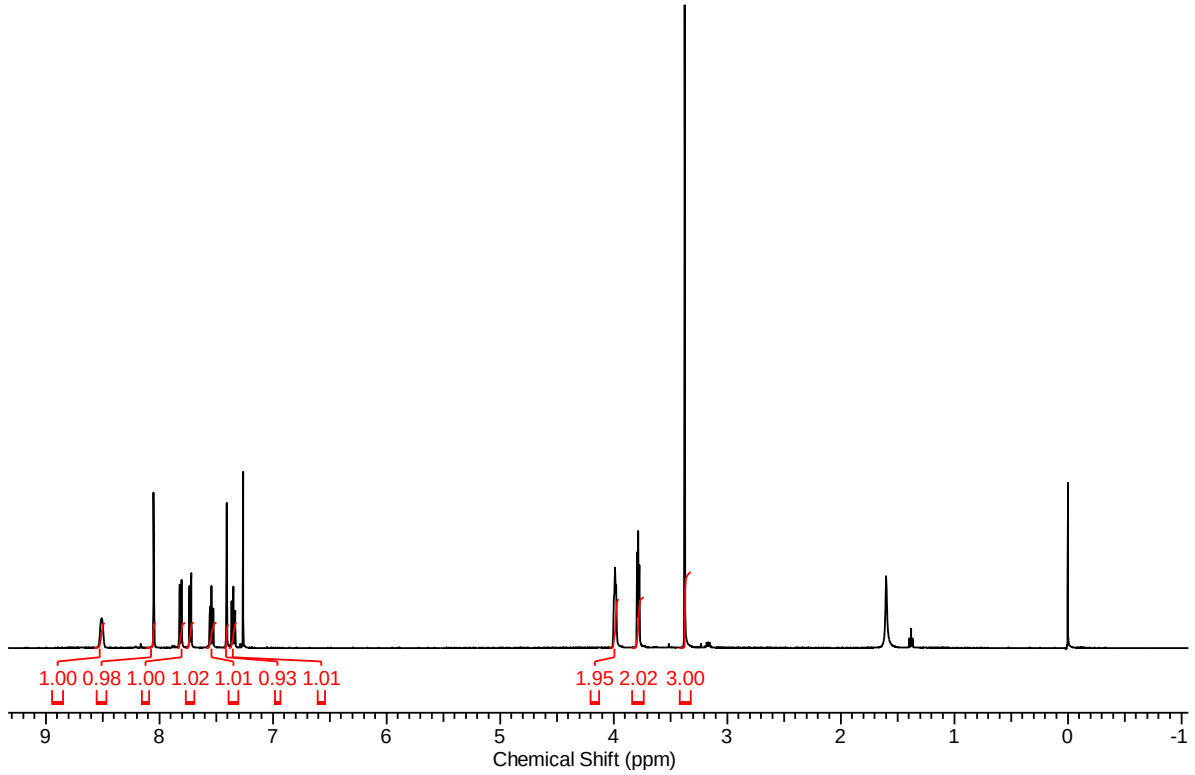


Fig. S7 (a) ^{1}H and (b) ^{13}C NMR spectra of **4a** in $CDCl_3$.

(a)



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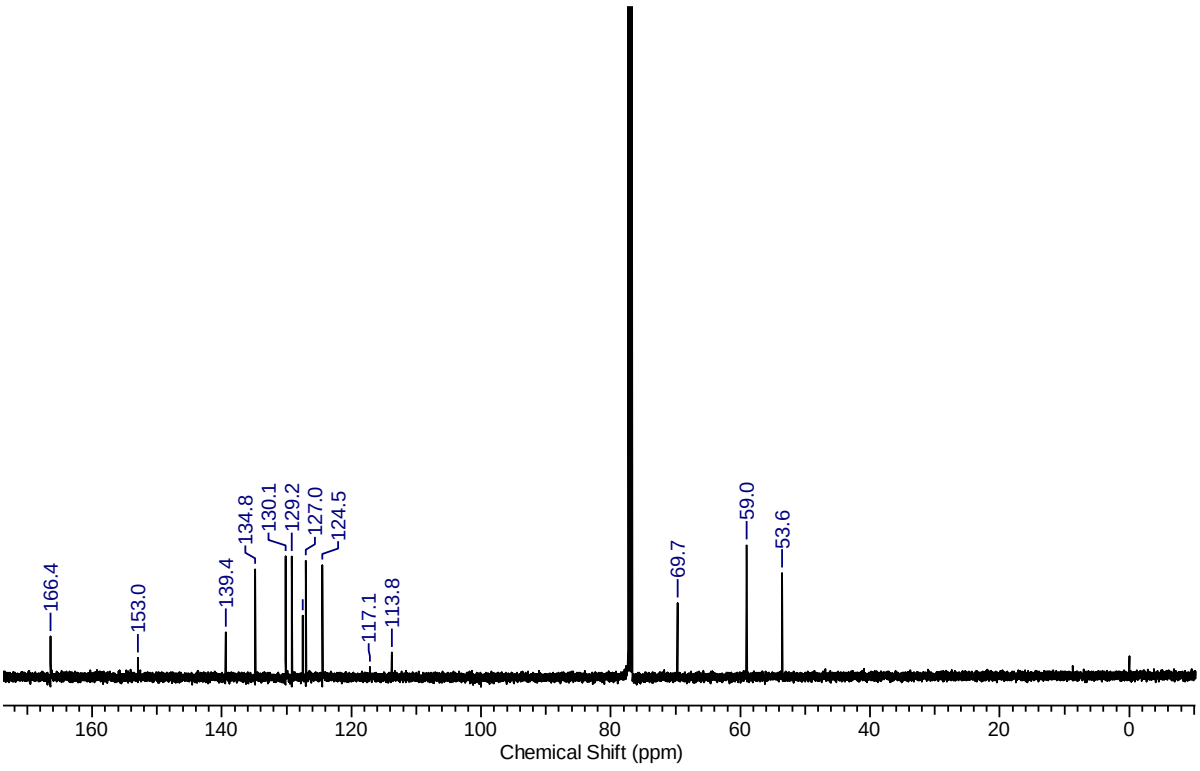

Fig. S8 (a) ^{1}H and (b) ^{13}C NMR spectra of **4b** in $CDCl_3$.

2. Single X-ray Structure Analysis

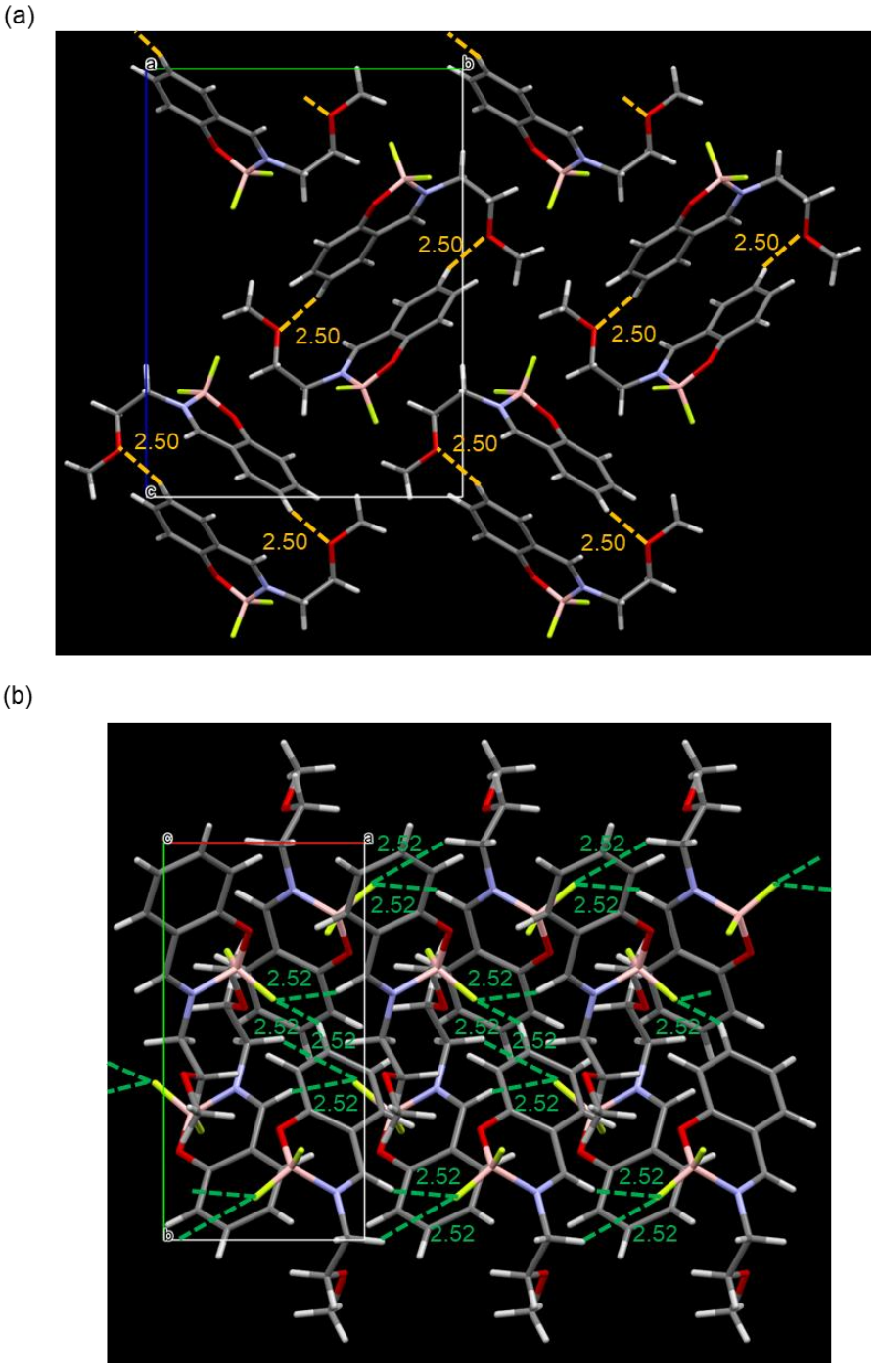

Fig. S9 Packing structure of **1b**. (a) The *a*-axis and (b) *b*-axis projections showing H··O (orange broken lines) and H··F (green broken lines) interactions.

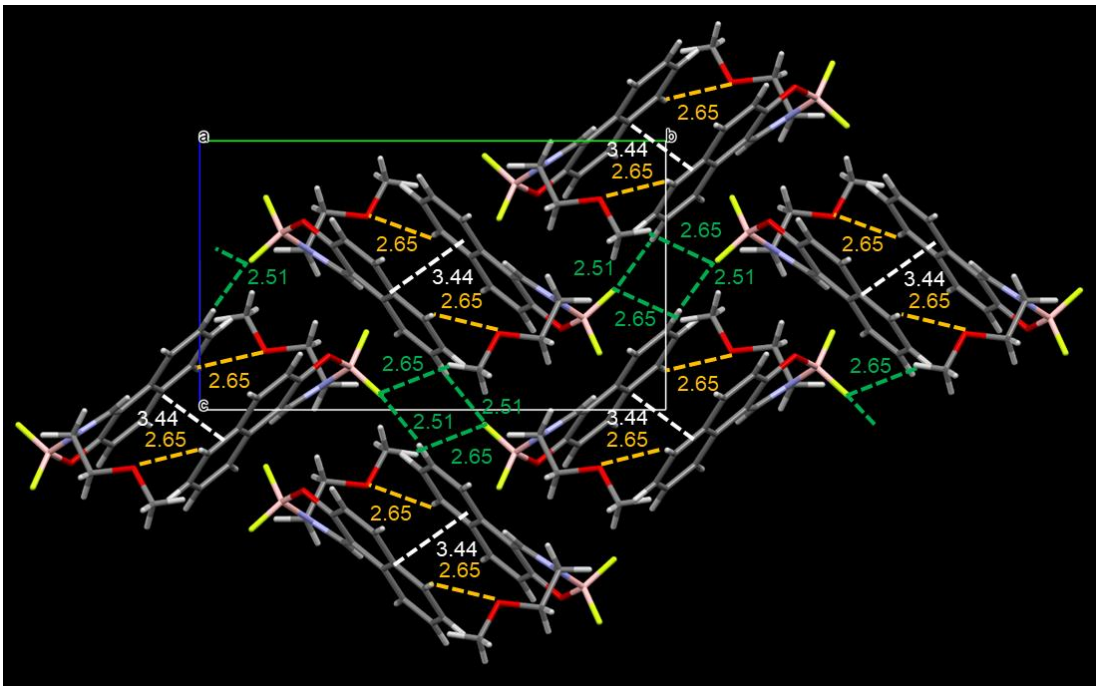

Fig. S10 Packing structure of **2b**. The *a*-axis projections showing π-π (white broken lines), H··O (orange broken lines) and H··F (green broken lines) interactions.

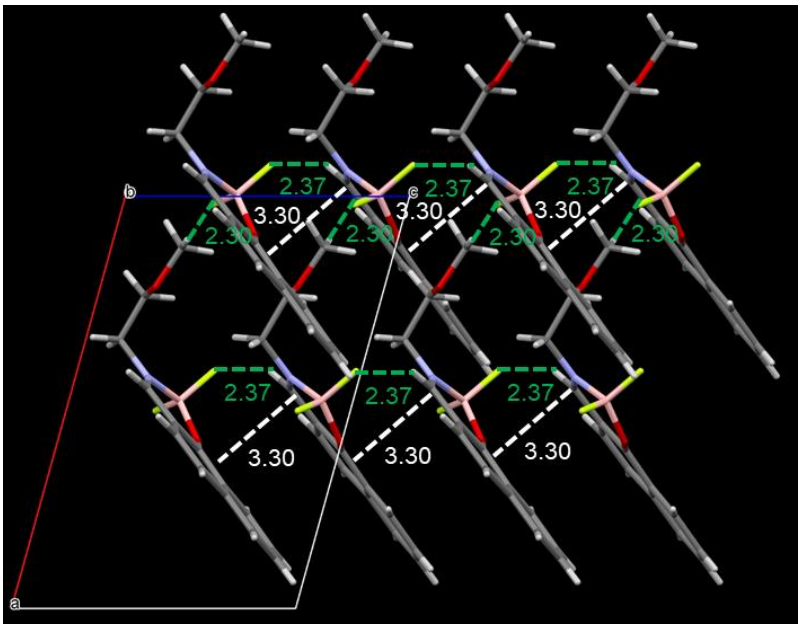

Fig. S11 Packing structure of **3b**. (a) The *b*-axis projections showing π-π (white broken lines) and H··F (green broken lines) interactions.

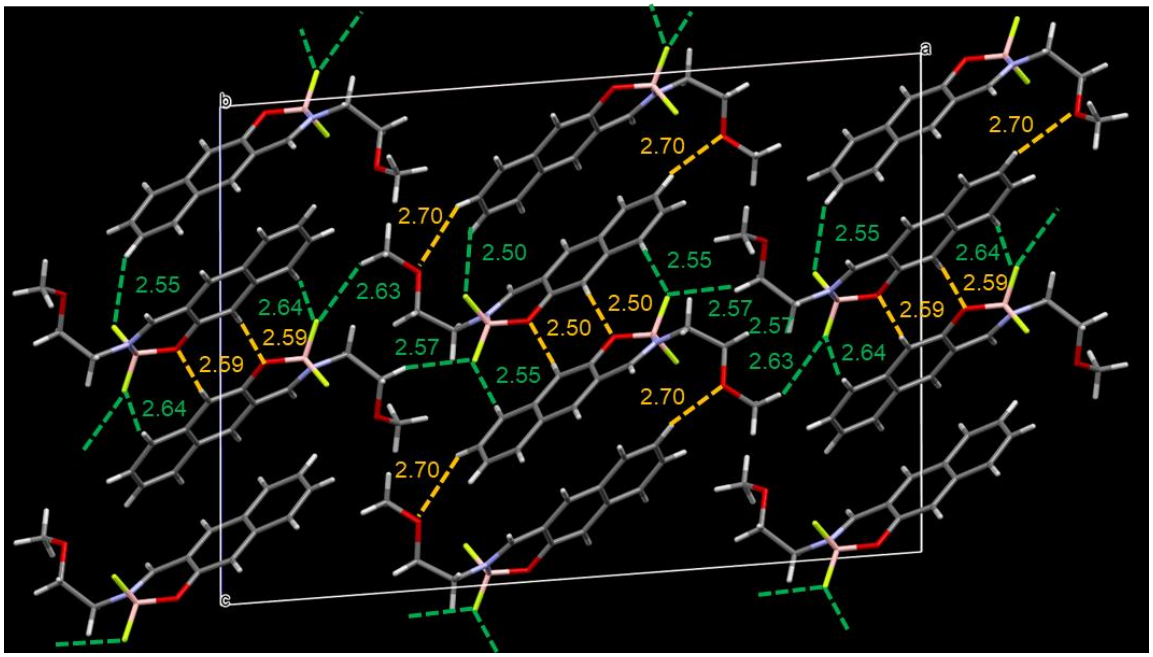

Fig. S12 Packing structure of **4b**. The *b*-axis projections showing H··O (orange broken lines) and H··F (green broken lines) interactions.

Table S1. Crystal data and structural refinement details for complexes **1b**–**4b**.

	1b	**2b**	**3b**	**4b**
Formula	$C_{10}H_{12}BF_2NO_2$	$C_{14}H_{14}BF_2NO_2$	$C_{14}H_{14}BF_2NO_2$	$C_{14}H_{14}BF_2NO_2$
M_F	227.02	277.07	277.07	277.07
T [K]	113.15	113.15	113.15	113.15
Crystal colour, habit	colourless, needle	colourless, brock	yellow, brock	yellow, plate
Crystal size [mm]	0.425×0.130×0.065	0.981×0.525×0.348	0.50×0.50×0.50	0.50×0.275×0.15
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$P2_12_12_1$ (#19)	$P2_1/n$ (#14)	Cc (#9)	$P2_1/c$ (#14)
a [Å]	5.8281(11)	9.7046(8)	12.7885(11)	24.5191(14)
b [Å]	11.540(2)	15.3874(9)	12.1016(11)	6.0356(3)
c [Å]	15.611(2)	9.7174(7)	8.5177(9)	17.3921(9)
α [°]	90	90	90	90
β [°]	90	113.886(8)	105.467(10)	94.286(5)
γ [°]	90	90	90	90
V [Å^3]	1049.9(3)	1326.80(18)	1269.6(2)	2566.6(2)
Z	4	4	4	8
D_{calcd} [g cm^{-3}]	1.436	1.387	1.450	1.434
Abs coeff (mm^{-1})	0.121	0.110	0.115	0.113
Abs correct	multi-scan	multi-scan	multi-scan	multi-scan
Transmiss max/min	1.000/0.966	0.963/0.900	1.000/0.633	1.000/0.827
F (000)	472	576	576	1152
θ range (°)	4.39–60.65	5.004–60.618	4.718–60.818	4.698–60.788
Rflns/unique	6264/2953	7336/3483	5208/2822	26908/7434
R_{int}	0.0512	0.0198	0.0257	0.0373
Data/params	2953/0/146	3483/0/182	2822/2/190	7434/0/363
Largest diff. peak and hole (e Å^{-3})	0.27/–0.29	0.31/–0.22	0.17/–0.36	0.38/–0.28
R_1 (I > 2σ(I))[a]	0.0655	0.0396	0.0386	0.0514
wR_2 (all reflections)[b]	0.1180	0.1063	0.0971	0.1197
Goodness of fit	0.980	1.084	1.018	1.015
CCDC No.	2298108	2298109	2298110	2298111

[a] $R_1 = \Sigma(||F_o|-|F_c||)/ \Sigma(|F_o|)$. [b] $wR_2 = [w(F_o^2-F_c^2)^2]/wF_o^2)^2]^{1/2}$.

3. Photophysical Properties

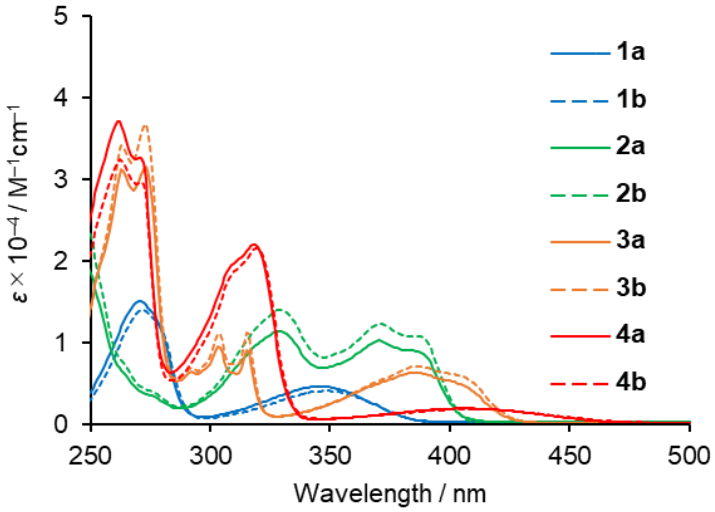

Fig. S13 UV-vis absorption spectra of 2.0×10^{-4} M solutions of **1a**–**4a** and **1b**–**4b** in CH_2Cl_2 at 298 K.

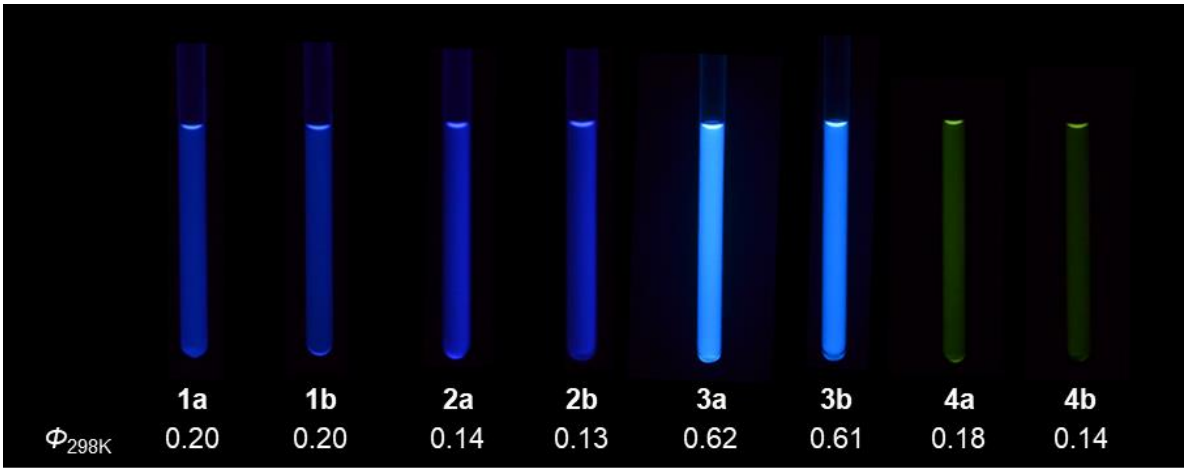

Fig. S14 Photographs of 2.0×10^{-4} M solutions of **1a**–**4a** and **1b**–**4b** in CH_2Cl_2 at 298 K under UV illumination at 365 nm.

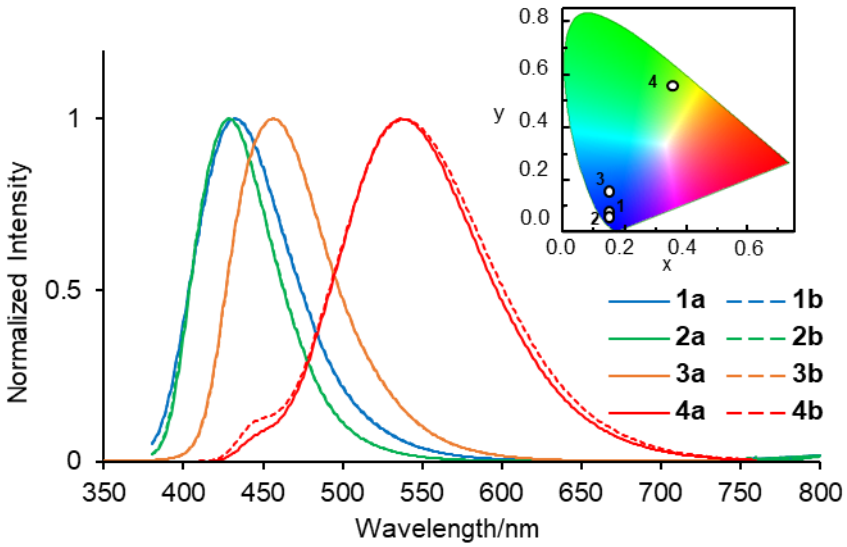

Fig. S15 Normalized emission spectra of 2.0×10^{-4} M solutions of **1a**–**4a** and **1b**–**4b** in CH_2Cl_2 (λ_{ex} = 350 (**1a**–**3a** and **1b**–**3b**), 400 nm (**4a** and **4b**)). The inset shows the CIE colour coordinates of the emissions.

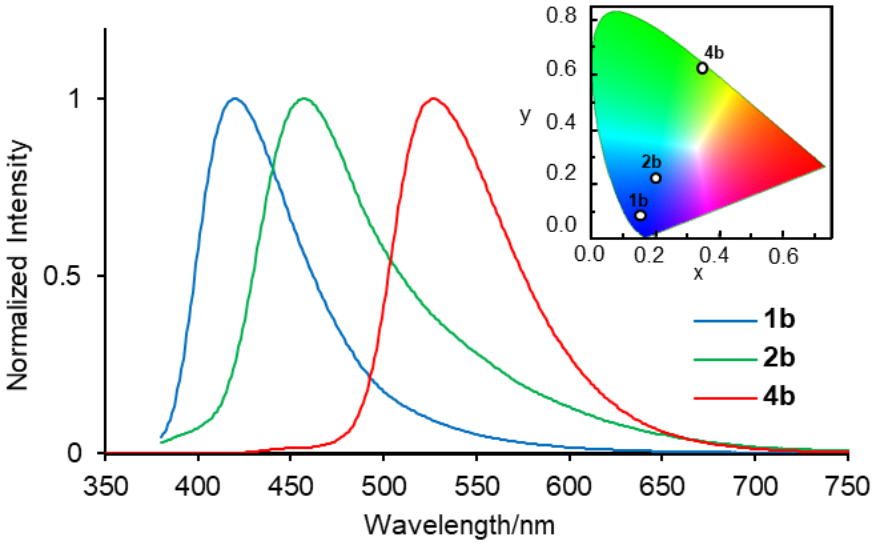

Fig. S16 Normalized emission spectra of crystals of **1b**, **2b** and **4b** (λ_{ex} = 350 (**1b** and **2b**), 400 nm (**4b**)). The inset shows the CIE colour coordinates of the emissions.

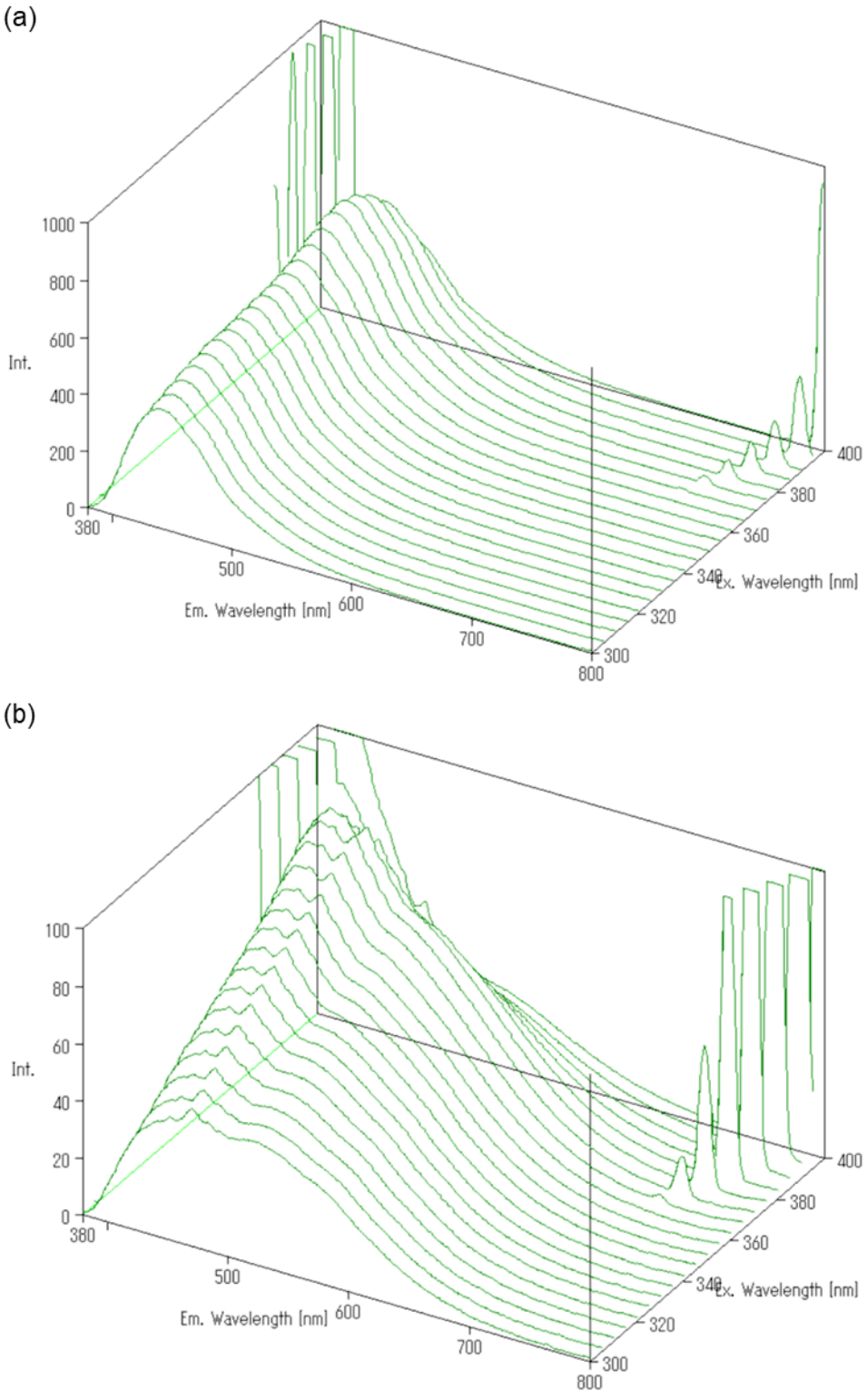

Fig. S17 Emission spectra of (a) **1a** in the solvent-free liquid state and (b) composite **V** by exciting at different wavelengths (300-400 nm).

4. Computational Methods

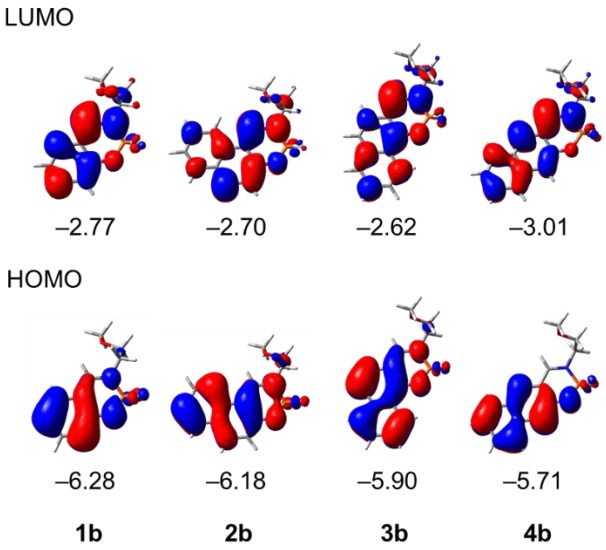

Fig. S18 Molecular orbitals (overhead views) and eigenvalues [eV] for the frontier orbitals of **1b**–**4b** estimated from DFT calculations (B3LYP/6-31+G(d,p)) on the basis of the optimized geometries in the S_1 excited states.

Table S2. Selected data for excitation energy, major configuration, coefficient, and oscillator strength for **1b–4b** (for the geometries optimized in the S_0 state).[a]

Compound	State	Excitation energy (eV)	Major configuration[b]	Coefficient	Oscillator strength
1b	S_1	3.60 (345 nm)	HOMO→LUMO	0.695	0.0839
2b	S_1	3.43 (361 nm)	HOMO→LUMO	0.697	0.1536
3b	S_1	3.24 (383 nm)	HOMO→LUMO	0.693	0.1171
4b	S_1	2.82 (439 nm)	HOMO→LUMO	0.699	0.0281

[a] Estimated by TD-DFT (B3LYP/6-31+G(d,p)) calculations based on the optimized geometries. [b] Molecular orbitals are shown in Fig. 6.

Table S3. Selected data for excitation energy, major configuration, coefficient, and oscillator strength for **1b–4b** (for the geometries optimized in the S_1 state).[a]

Compound	State	Excitation energy (eV)	Major configuration[b]	Coefficient	Oscillator strength
1b	S_1	2.98 (417 nm)	HOMO→LUMO	0.702	0.0593
2b	S_1	3.11 (399 nm)	HOMO→LUMO	0.700	0.1429
3b	S_1	2.85 (436 nm)	HOMO→LUMO	0.699	0.0974
4b	S_1	2.16 (574 nm)	HOMO→LUMO	0.705	0.0220

[a] Estimated by TD-DFT (B3LYP/6-31+G(d,p)) calculations based on the optimized geometries. [b] Molecular orbitals are shown in Fig. S18.

5. Cartesian Coordinates (in Å)

Table S4. Cartesian coordinates (in angstrom) of **1b** in S_0 state[a].

atom	x	y	z
F	1.100486	2.023845	1.154181
F	0.253734	2.768013	-0.85016
O	-1.113017	1.490993	0.583145
O	2.810681	-1.595824	0.034293
N	0.79614	0.435785	-0.638801
C	0.04841	-0.604319	-0.859774
H	0.483063	-1.451763	-1.388573
C	-1.843537	0.422976	0.307531
C	-1.311615	-0.672348	-0.426497
C	-2.117467	-1.802029	-0.695841
H	-1.691478	-2.630201	-1.256832
C	-3.175335	0.356953	0.761041
H	-3.571574	1.196174	1.322319
C	-3.945154	-0.762944	0.481197
H	-4.972157	-0.79934	0.833855
C	-3.425978	-1.852239	-0.249735
H	-4.046662	-2.717477	-0.45647
C	2.204829	0.435639	-1.059663
H	2.503177	1.473927	-1.216733
H	2.299155	-0.102241	-2.008713
C	3.11387	-0.209614	-0.018839
H	4.162323	-0.05643	-0.321649
H	2.959272	0.262625	0.960381
C	3.499102	-2.280055	1.070419
H	3.18859	-3.325886	1.024709
H	3.243667	-1.868417	2.05729
H	4.588813	-2.222144	0.931387
B	0.24576	1.742099	0.091183

[a] The geometry was optimized by DFT calculation (B3LYP/6-31+G (d,p)).

Table S5. Cartesian coordinates (in angstrom) of **2b** in S_0 state[a].

atom	x	y	z
F	-2.510857	-1.54929	1.202906
F	-2.625806	-2.483134	-0.896567
O	-0.542569	-2.328225	0.163732
O	-2.571593	2.384219	0.204386
N	-1.664895	-0.279473	-0.663348
C	0.691248	-0.314102	-0.208942
C	-0.500245	0.311	-0.676204
H	-0.462766	1.31619	-1.085806
C	1.971289	0.363646	-0.185819
C	0.599497	-1.670496	0.173985
C	1.770135	-2.389177	0.54933
H	1.659192	-3.432597	0.822938
C	2.144129	1.731266	-0.516375
H	1.290617	2.340437	-0.793577
C	3.128585	-0.380472	0.203251
C	2.983936	-1.758007	0.559989
H	3.874351	-2.309524	0.851293
C	-2.852458	0.437858	-1.148393
H	-3.577718	-0.309942	-1.474918
H	-2.577391	1.055492	-2.009905
C	4.396075	0.251719	0.234336
H	5.262262	-0.33338	0.532425
C	3.394396	2.323743	-0.479157
H	3.494904	3.373889	-0.737644
C	4.53471	1.583359	-0.103688
H	5.509713	2.059754	-0.076891
C	-3.47263	1.321214	-0.07005
H	-4.430802	1.717073	-0.443899
H	-3.665063	0.731087	0.835933
B	-1.866828	-1.713068	-0.026293
C	-2.966843	3.181572	1.310648
H	-3.029604	2.582438	2.230087
H	-3.940521	3.660638	1.129685
H	-2.206458	3.955226	1.43571

[a] The geometry was optimized by DFT calculation (B3LYP/6-31+G(d,p)).

Table S6. Cartesian coordinates (in angstrom) of **3b** in S_0 state[a].

atom	x	y	z
F	-1.722131	2.092492	1.000438
F	-1.205973	2.65648	-1.167296
O	0.324535	1.386574	0.089554
O	-3.838611	-1.442802	0.437614
N	-1.815602	0.375648	-0.694286
C	0.228739	-0.870845	-0.661647
C	2.336137	0.138934	0.114013
C	0.92878	0.24231	-0.154385
C	2.99758	-1.101625	-0.146199
C	4.386458	-1.18918	0.121995
H	4.899301	-2.127289	-0.072432
C	0.918341	-2.098979	-0.912029
H	0.353513	-2.941626	-1.302352
C	5.082817	-0.104645	0.62188
H	6.147169	-0.191575	0.820903
C	-4.059086	-0.04741	0.29313
C	-1.167302	-0.737055	-0.903035
H	-1.727691	-1.594399	-1.273235
C	3.068064	1.238244	0.625398
H	2.543406	2.168382	0.812822
C	4.421136	1.118213	0.876046
H	4.978918	1.963198	1.267919
C	-3.267032	0.43702	-0.916828
H	-3.526214	-0.173111	-1.788487
H	-3.525031	1.475737	-1.13297
C	2.256859	-2.214246	-0.664431
H	2.777188	-3.147828	-0.855389
C	-4.416344	-1.981463	1.616952
H	-5.508987	-1.853076	1.620835
H	-3.99913	-1.507539	2.516989
H	-4.18238	-3.047971	1.629955
B	-1.095682	1.686096	-0.176084
H	-3.73929	0.49388	1.193578
H	-5.128493	0.156637	0.121493

[a] The geometry was optimized by DFT calculation (B3LYP/6-31+G(d,p)).

Table S7. Cartesian coordinates (in angstrom) of **4b** in S_0 state[a].

atom	x	y	z
F	2.309346	-1.587798	1.343972
F	2.374112	-2.72228	-0.657795
O	0.302875	-2.022475	0.174801
O	3.378565	2.083527	0.142171
N	1.945998	-0.343635	-0.683429
C	-0.66409	-1.116269	0.051442
C	-0.376642	0.187087	-0.481166
C	-2.724399	0.822379	-0.29144
C	-3.011101	-0.487461	0.238955
C	-1.396437	1.122419	-0.646061
H	-1.159981	2.103121	-1.053436
C	0.969918	0.490081	-0.86888
H	1.184627	1.44831	-1.340558
C	-1.969522	-1.430876	0.394292
H	-2.179692	-2.419722	0.788902
C	-3.784484	1.764573	-0.443074
H	-3.554807	2.748583	-0.84397
C	3.315716	0.028512	-1.067516
H	3.284645	0.624349	-1.985615
H	3.861995	-0.895274	-1.266368
C	-4.3591	-0.787927	0.59332
H	-4.586191	-1.771874	0.993967
C	-5.071832	1.437392	-0.089821
H	-5.873638	2.159647	-0.208058
C	4.020766	0.822247	0.028379
H	3.975724	0.274568	0.978774
H	5.077388	0.952467	-0.255912
C	-5.35721	0.146035	0.433687
H	-6.377777	-0.103079	0.709975
B	1.72942	-1.739397	0.080185
C	3.843116	2.850882	1.243159
H	3.281912	3.787542	1.239639
H	4.916026	3.074594	1.148946
H	3.669846	2.327055	2.193762

[a] The geometry was optimized by DFT calculation (B3LYP/6-31+G(d,p)).

Table S8. Cartesian coordinates (in angstrom) of **1b** in S_1 state[a].

atom	x	y	z
F	0.824796	1.842585	1.34022
F	0.386669	2.824762	-0.696744
O	-1.265199	1.529339	0.334318
O	2.996464	-1.519566	-0.008499
N	0.800599	0.449547	-0.635734
C	0.093382	-0.681196	-0.816313
H	0.580766	-1.547484	-1.244898
C	-1.926169	0.409468	0.17078
C	-1.298357	-0.744638	-0.402141
C	-2.078519	-1.873724	-0.533474
H	-1.642764	-2.772776	-0.961772
C	-3.289271	0.374636	0.569224
H	-3.705699	1.282906	0.992237
C	-4.066613	-0.796218	0.417131
H	-5.106109	-0.807067	0.724427
C	-3.46683	-1.913436	-0.128122
H	-4.021877	-2.835729	-0.264161
C	2.197322	0.491799	-1.050409
H	2.466289	1.538928	-1.21465
H	2.310682	-0.041385	-2.003505
C	3.166226	-0.109035	-0.031822
H	4.197597	0.14271	-0.332447
H	2.978827	0.319459	0.96271
C	3.764746	-2.153856	0.999176
H	3.563037	-3.225337	0.931919
H	3.485075	-1.795243	2.000851
H	4.841915	-1.982064	0.850378
B	0.223852	1.693828	0.089406

[a] The geometry was optimized by DFT calculation (B3LYP/6-31+G (d,p)).

Table S9. Cartesian coordinates (in angstrom) of **2b** in S_1 state[a].

atom	x	y	z
F	-2.437083	-1.608882	1.219281
F	-2.586703	-2.529358	-0.887661
O	-0.491042	-2.353454	0.133342
O	-2.625066	2.402641	0.180642
N	-1.676663	-0.308263	-0.66551
C	0.701381	-0.305417	-0.24441
C	-0.503092	0.32744	-0.689978
H	-0.500363	1.343081	-1.063417
C	1.959029	0.358345	-0.185642
C	0.651193	-1.69979	0.157663
C	1.813833	-2.389748	0.548982
H	1.705087	-3.433391	0.823422
C	2.103501	1.752149	-0.513438
H	1.226773	2.324548	-0.790812
C	3.14242	-0.374553	0.213937
C	3.044771	-1.754187	0.572553
H	3.941111	-2.288747	0.86881
C	-2.87836	0.390956	-1.103583
H	-3.615454	-0.362731	-1.392544
H	-2.647123	1.002395	-1.985662
C	4.366219	0.305208	0.233351
H	5.261366	-0.239717	0.52089
C	3.332877	2.394953	-0.477458
H	3.406015	3.447382	-0.729109
C	4.473584	1.66907	-0.106928
H	5.445252	2.152043	-0.075661
C	-3.485905	1.290511	-0.025657
H	-4.475815	1.635637	-0.368812
H	-3.614867	0.72317	0.906164
B	-1.832241	-1.73039	-0.038554
C	-3.01587	3.211131	1.27845
H	-3.010298	2.638744	2.217385
H	-4.020584	3.63398	1.126702
H	-2.293799	4.027651	1.350475

[a] The geometry was optimized by DFT calculation (B3LYP/6-31+G(d,p)).

Table S10. Cartesian coordinates (in angstrom) of **3b** in S_1 state[a].

atom	x	y	z
F	-1.661298	2.11024	1.014981
F	-1.163203	2.642645	-1.165572
O	0.362405	1.375535	0.088075
O	-3.997166	-1.412821	0.38797
N	-1.823029	0.377073	-0.659308
C	0.220245	-0.895095	-0.630022
C	2.366097	0.125163	0.110551
C	0.956312	0.225171	-0.14516
C	3.052129	-1.123707	-0.12476
C	4.449892	-1.21205	0.130995
H	4.952124	-2.158512	-0.050776
C	0.918265	-2.085909	-0.843337
H	0.373059	-2.952852	-1.208568
C	5.162154	-0.117315	0.601918
H	6.226925	-0.194152	0.793885
C	-4.110242	-0.000356	0.275343
C	-1.19318	-0.785876	-0.875562
H	-1.765301	-1.641674	-1.214247
C	3.110052	1.218762	0.586443
H	2.60041	2.159311	0.763197
C	4.484201	1.097307	0.827672
H	5.03387	1.958648	1.195511
C	-3.257496	0.472832	-0.900771
H	-3.521136	-0.115831	-1.789391
H	-3.49529	1.520103	-1.106858
C	2.307433	-2.214215	-0.601686
H	2.795112	-3.166179	-0.788049
C	-4.651574	-1.931658	1.532195
H	-5.731214	-1.717034	1.509496
H	-4.22876	-1.51523	2.458604
H	-4.504291	-3.014126	1.525199
B	-1.084898	1.662231	-0.175719
H	-3.775928	0.490051	1.200077
H	-5.161019	0.280812	0.089715

[a] The geometry was optimized by DFT calculation (B3LYP/6-31+G(d,p)).

Table S11. Cartesian coordinates (in angstrom) of **4b** in S_1 state[a].

atom	x	y	z
F	2.367483	-1.843186	1.246508
F	2.105285	-2.769191	-0.842908
O	0.232075	-1.936099	0.287799
O	3.564133	2.078777	0.129237
N	1.973844	-0.369075	-0.628206
C	-0.692582	-1.037694	0.097053
C	-0.363859	0.257148	-0.466106
C	-2.772349	0.849293	-0.281972
C	-3.08142	-0.435332	0.270128
C	-1.40284	1.146948	-0.63214
H	-1.192614	2.129122	-1.050833
C	0.999828	0.541384	-0.818244
H	1.265634	1.507935	-1.228717
C	-2.018731	-1.359704	0.448275
H	-2.201655	-2.34612	0.862575
C	-3.804225	1.769258	-0.462981
H	-3.581188	2.747281	-0.881101
C	3.345735	-0.03383	-0.991965
H	3.346452	0.541264	-1.926931
H	3.882741	-0.969013	-1.173365
C	-4.415327	-0.737117	0.614686
H	-4.643535	-1.713669	1.032646
C	-5.136277	1.450808	-0.111655
H	-5.91883	2.187419	-0.263924
C	4.094627	0.760999	0.076451
H	3.99425	0.264752	1.05183
H	5.164903	0.795867	-0.189501
C	-5.440367	0.202925	0.424823
H	-6.461256	-0.045428	0.695643
B	1.715605	-1.750381	0.017314
C	4.115244	2.856072	1.177354
H	3.644807	3.840922	1.130583
H	5.203817	2.973282	1.061061
H	3.912221	2.404848	2.159978

[a] The geometry was optimized by DFT calculation (B3LYP/6-31+G(d,p)).