Supporting Information

Tunable Aggregation-Induced Emission to Aggregation-Caused Quenching Transition in Benzimidazole–Acrylonitrile Luminogens: Experimental and Theoretical Insights

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1. ^{1}H & ^{13}C NMR and HRMS Spectra of the Compounds

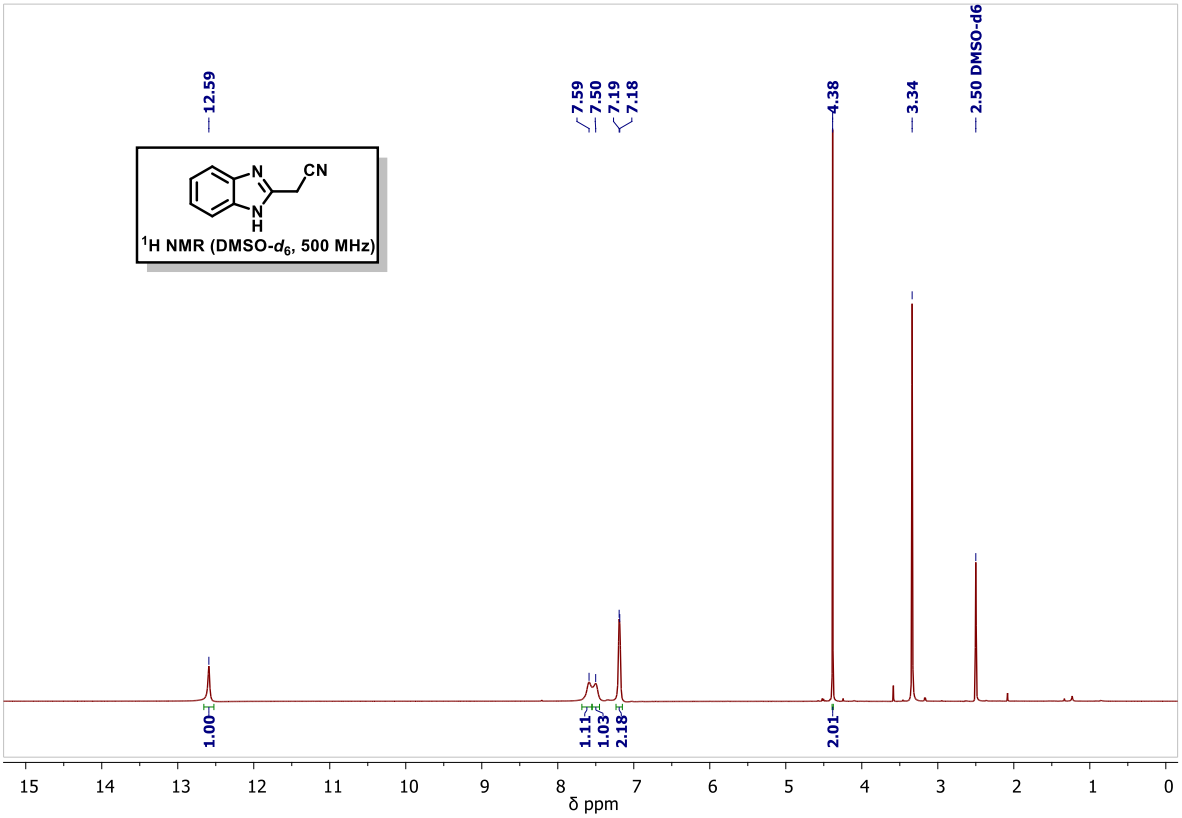

Figure S1. ^{1}H NMR spectra (500 MHz, RT) of compound **A** in DMSO-d_6.

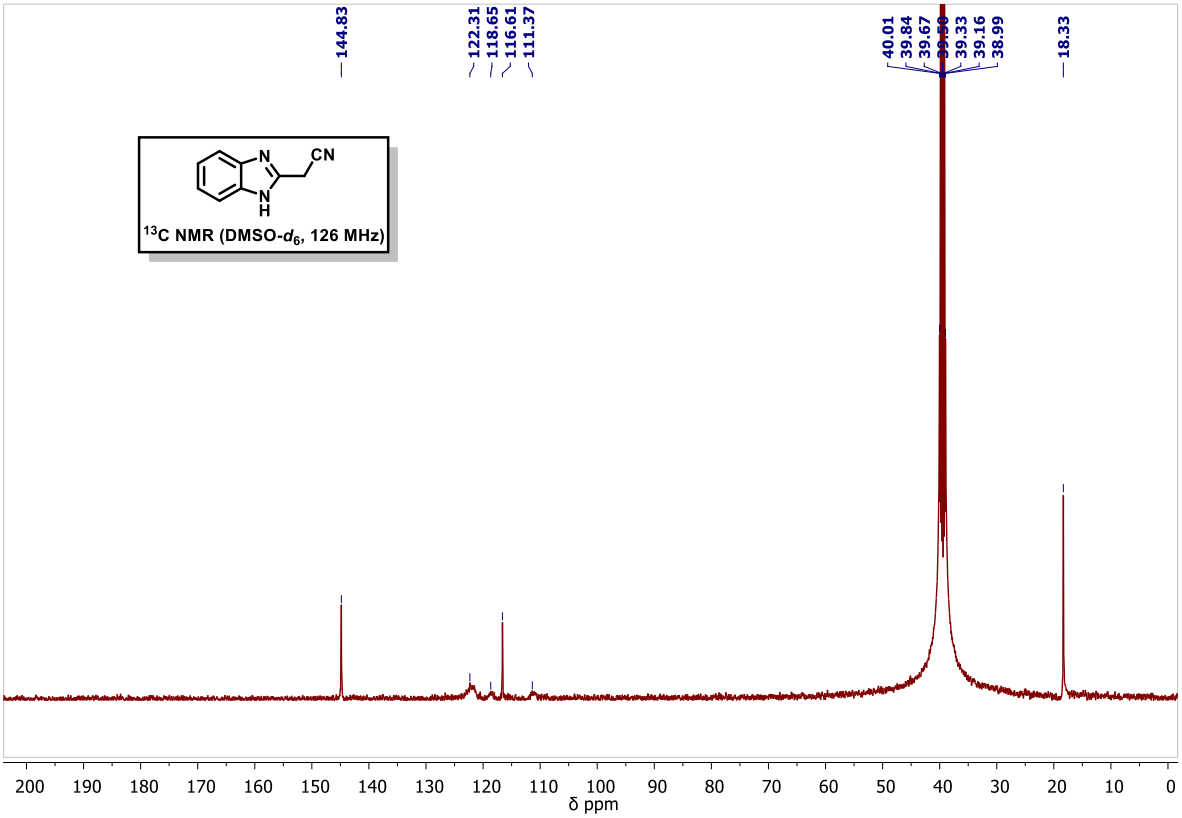

Figure S2. $^{13}C\{^{1}H\}$ NMR spectra (126 MHz, RT) of compound **A** in DMSO-d_6.

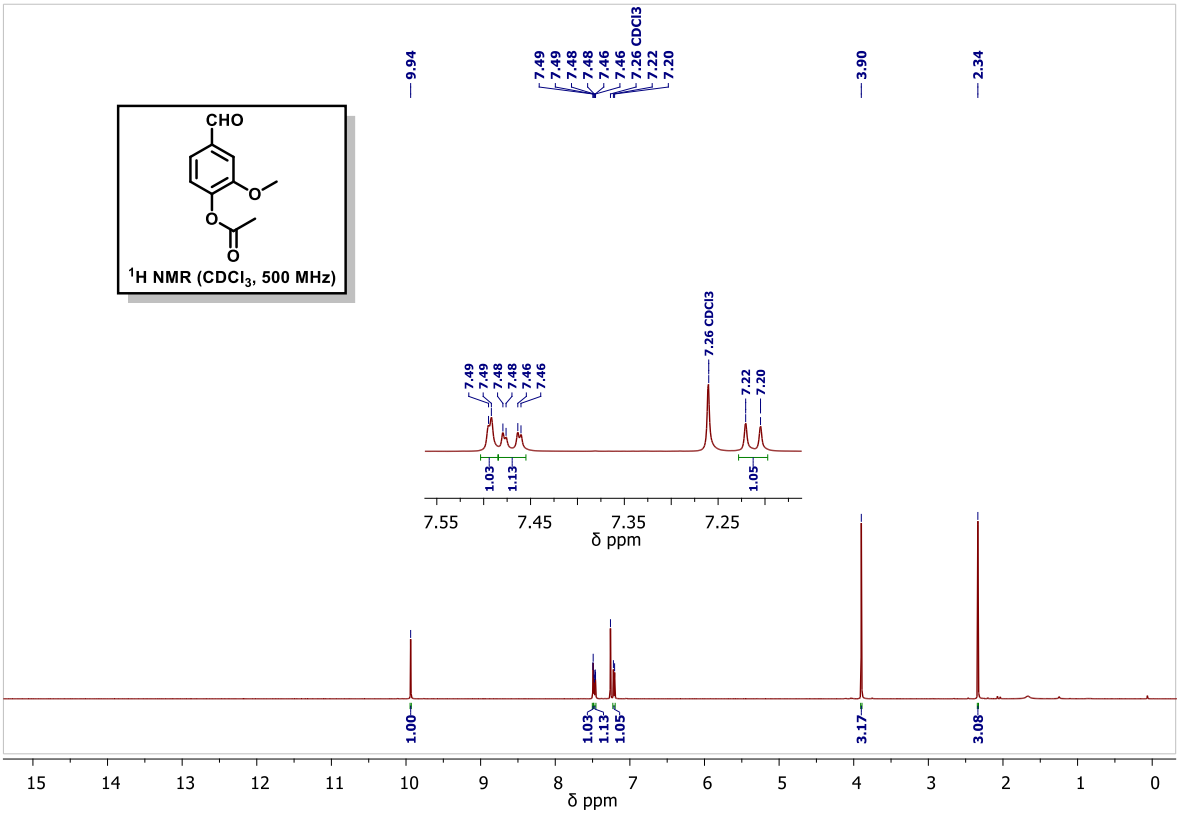

Figure S3. ^{1}H NMR spectra (500 MHz, RT) of compound **Ba** in $CDCl_3$.

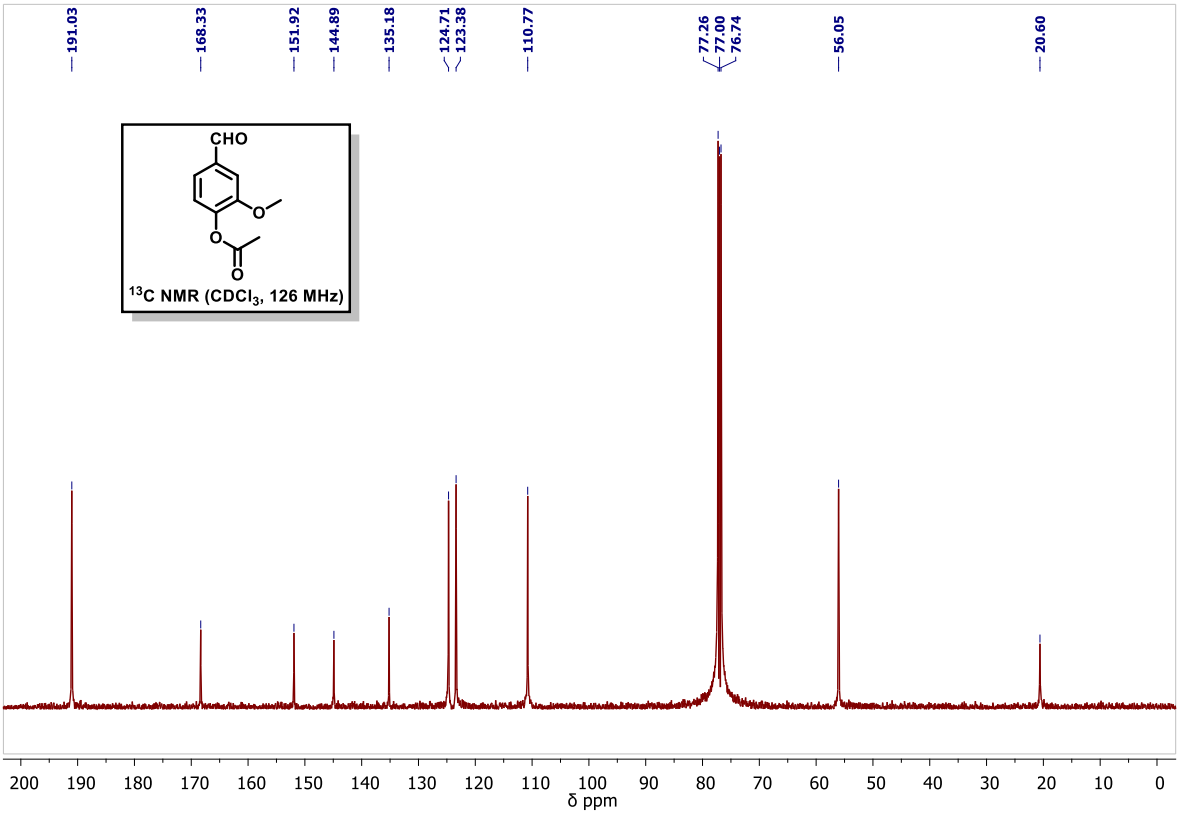

Figure S4. $^{13}C\{^1H\}$ NMR spectra (126 MHz, RT) of compound **Ba** in $CDCl_3$.

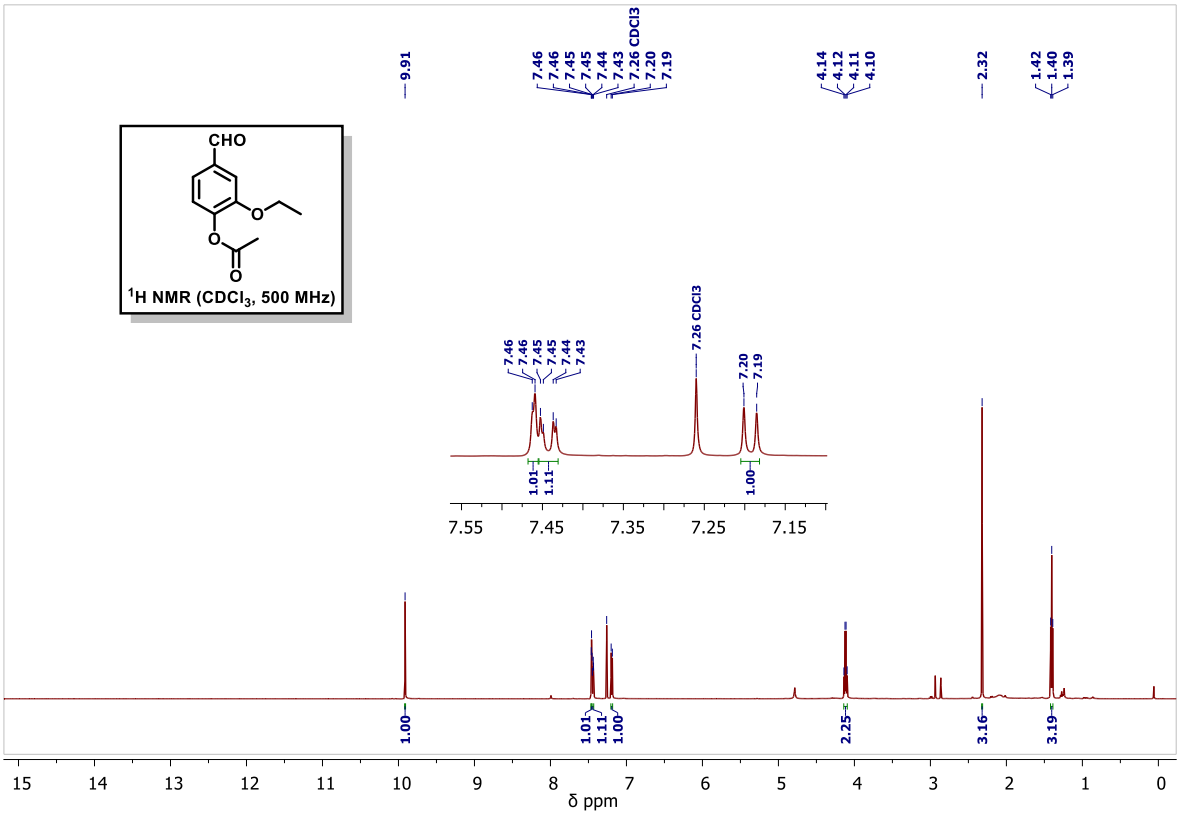

Figure S5. ^{1}H NMR spectra (500 MHz, RT) of compound **Bb** in $CDCl_3$.

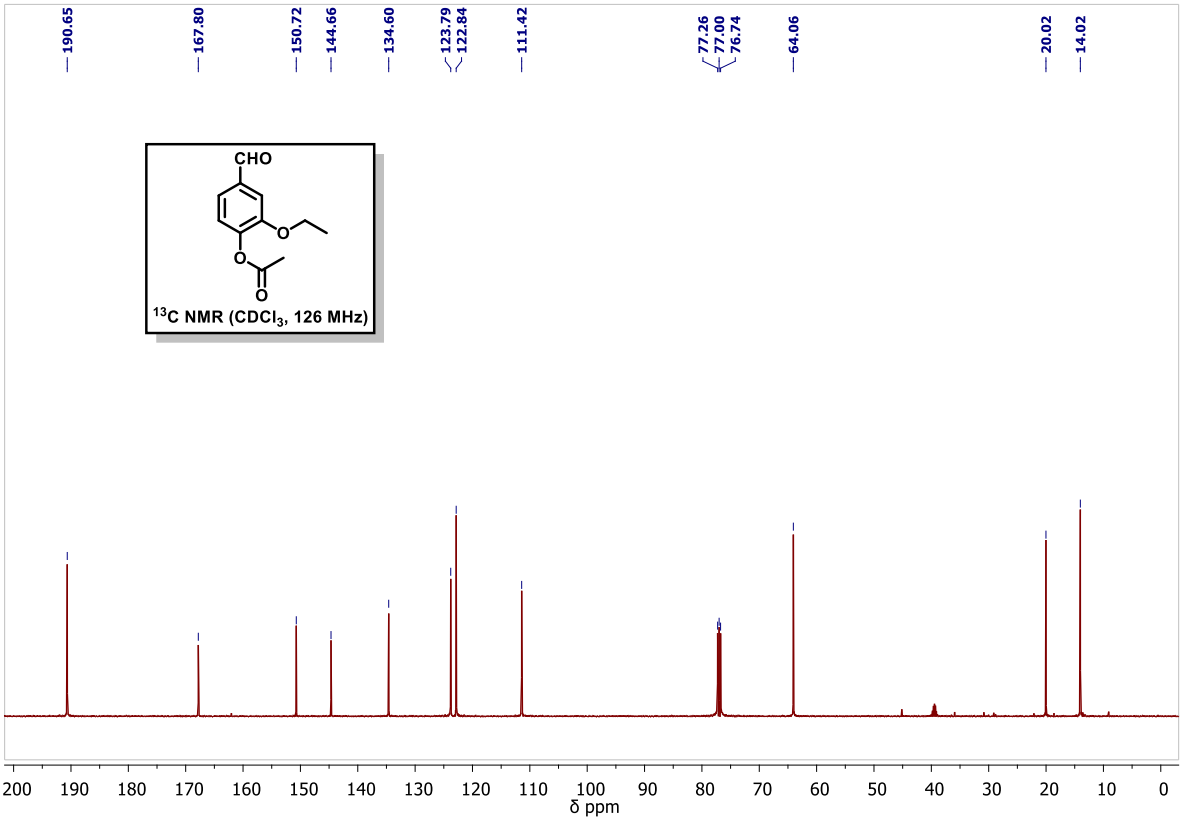

Figure S6. $^{13}C\{^1H\}$ NMR spectra (126 MHz, RT) of compound **Bb** in $CDCl_3$.

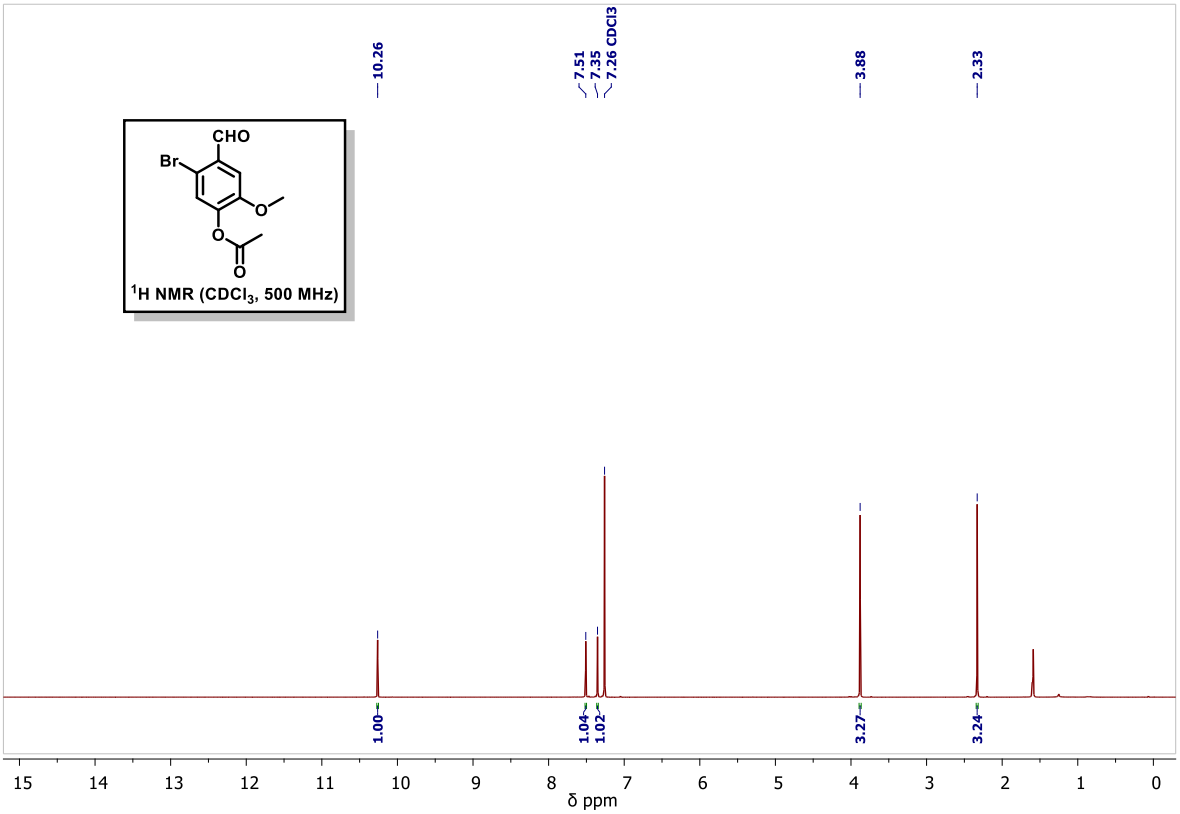

Figure S7. ^{1}H NMR spectra (500 MHz, RT) of compound **Ca** in $CDCl_3$.

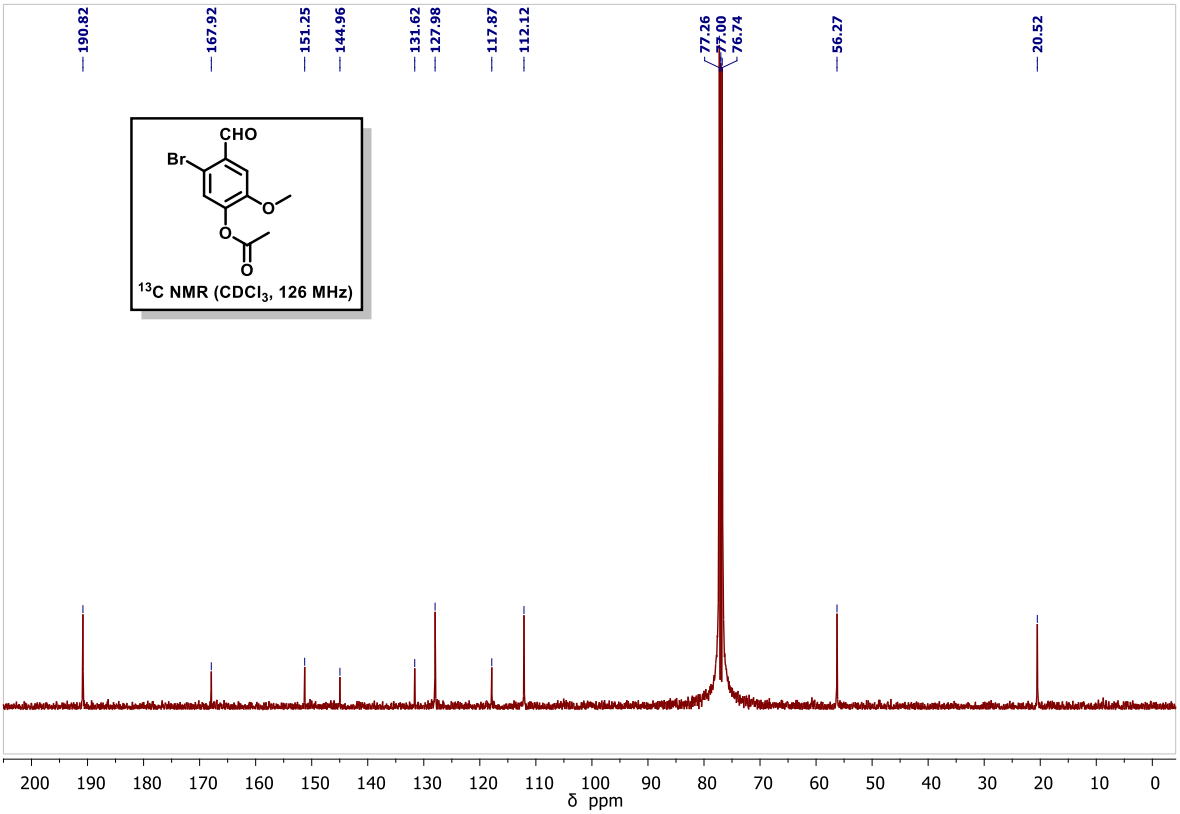

Figure S8. $^{13}C\{^{1}H\}$ NMR spectra (126 MHz, RT) of compound **Ca** in $CDCl_3$.

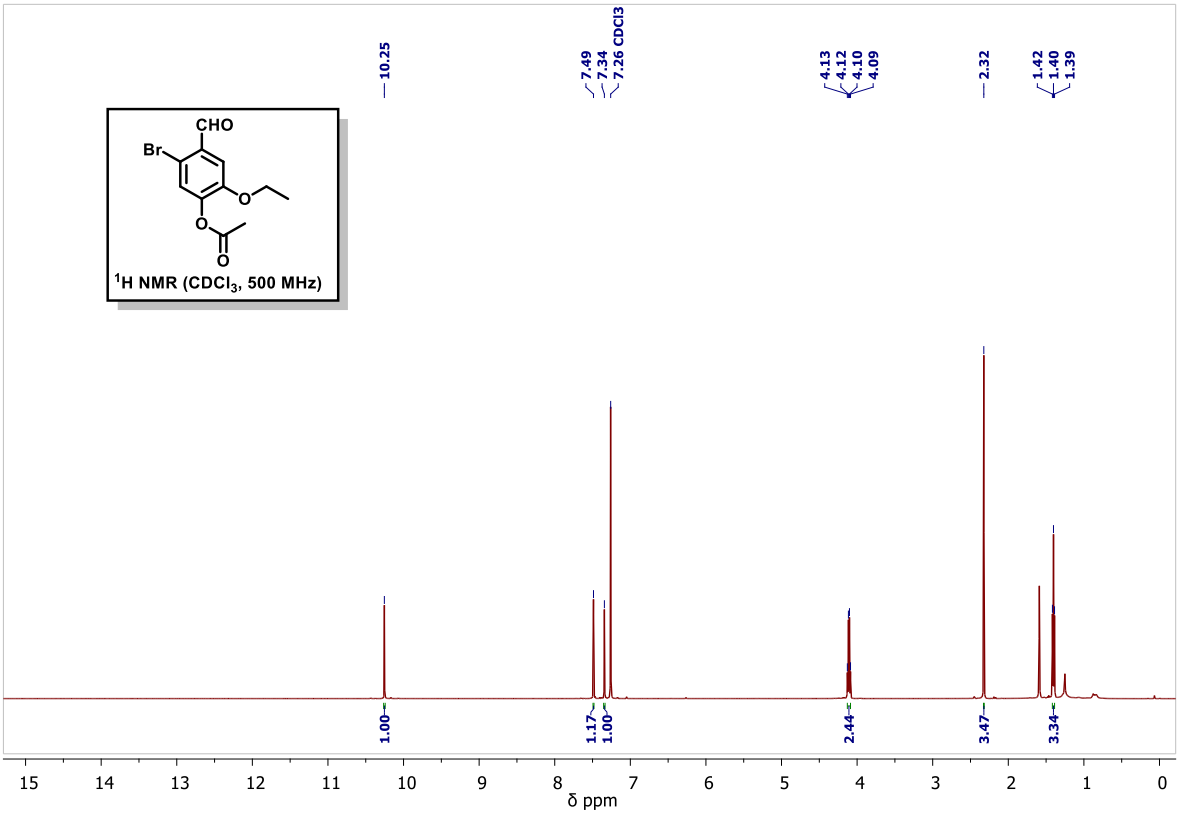

Figure S9. ^{1}H NMR spectra (500 MHz, RT) of compound **Cb** in $CDCl_3$.

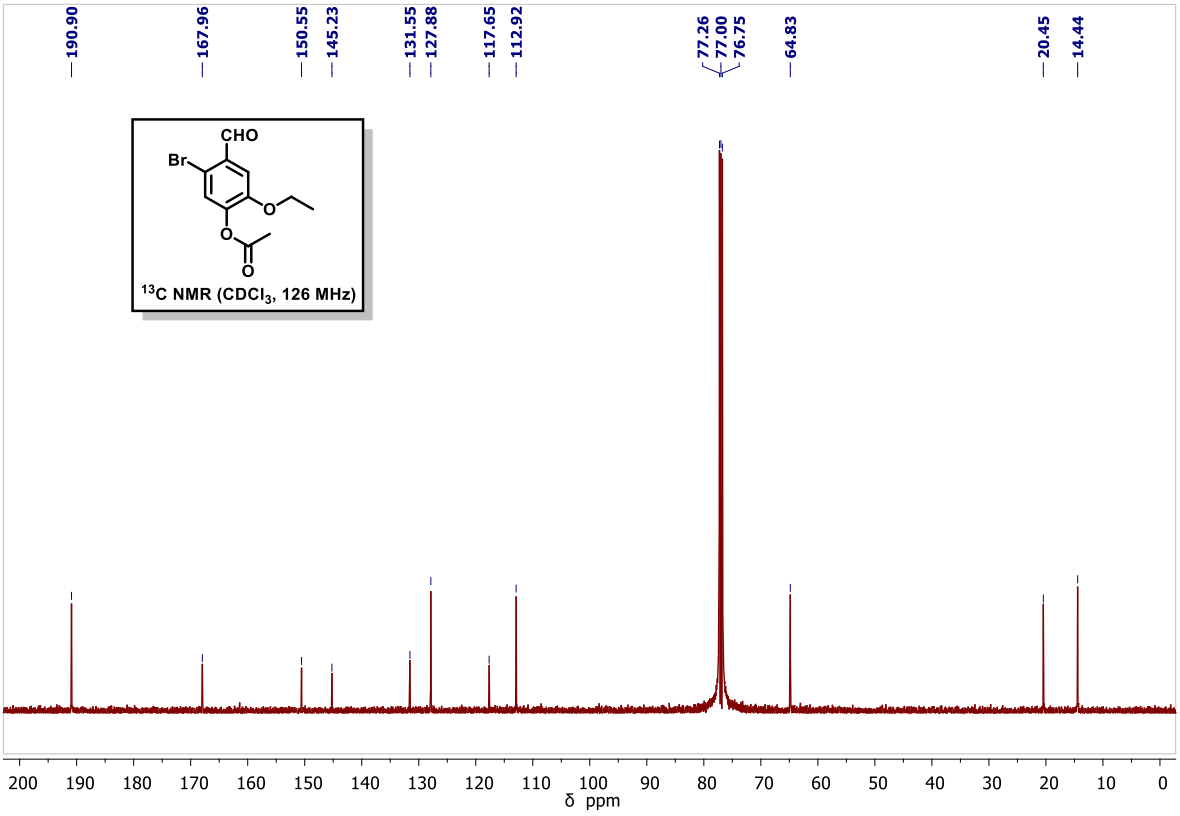

Figure S10. $^{13}C\{^{1}H\}$ NMR spectra (126 MHz, RT) of compound **Cb** in $CDCl_3$.

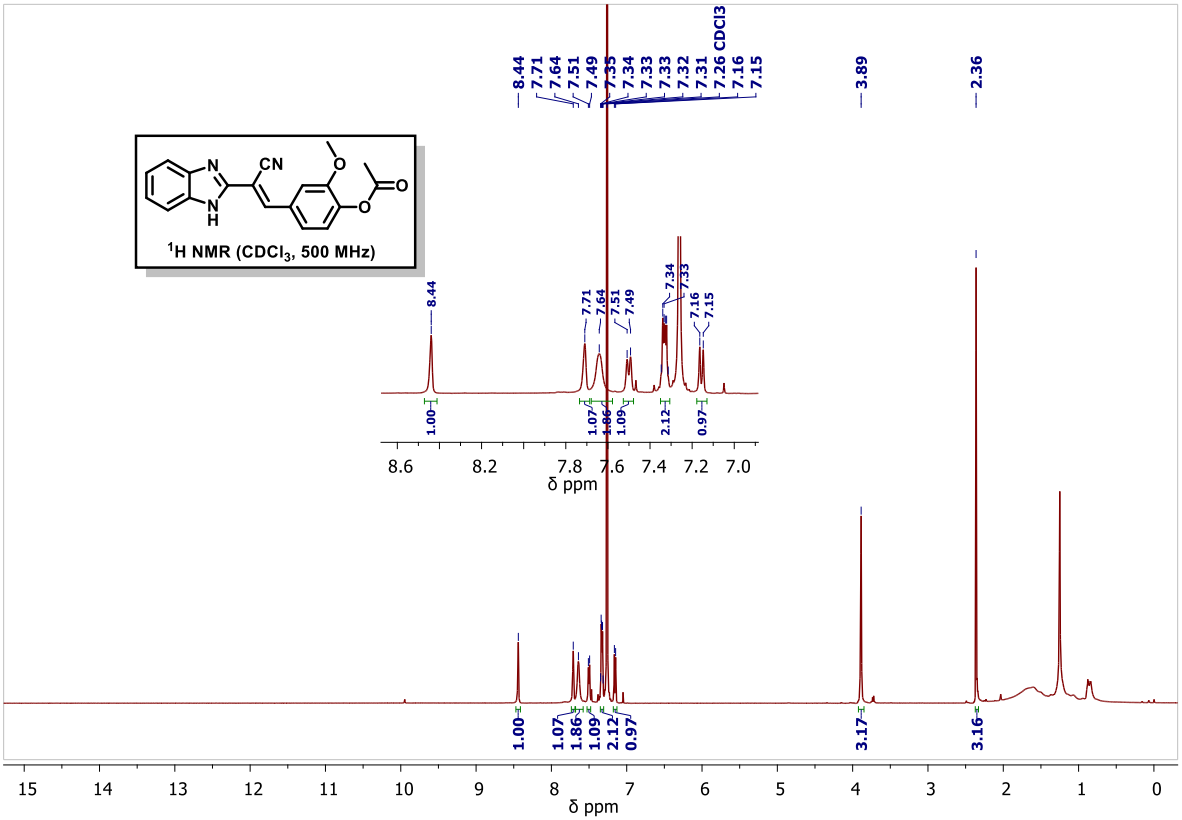

Figure S11. ^{1}H NMR spectra (500 MHz, RT) of compound **1** in $CDCl_3$.

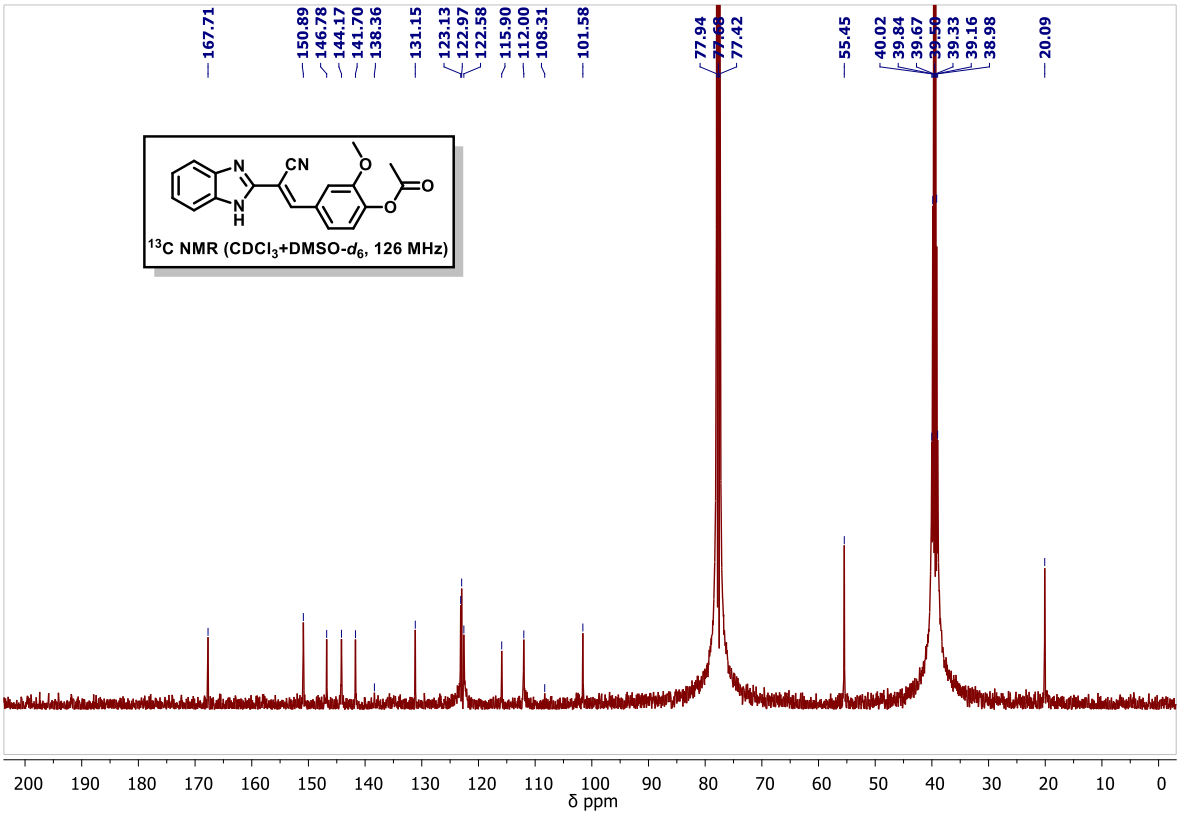

Figure S12. $^{13}C\{^{1}H\}$ NMR spectra (126 MHz, RT) of compound **1** in $CDCl_3$ + DMSO-d_6.

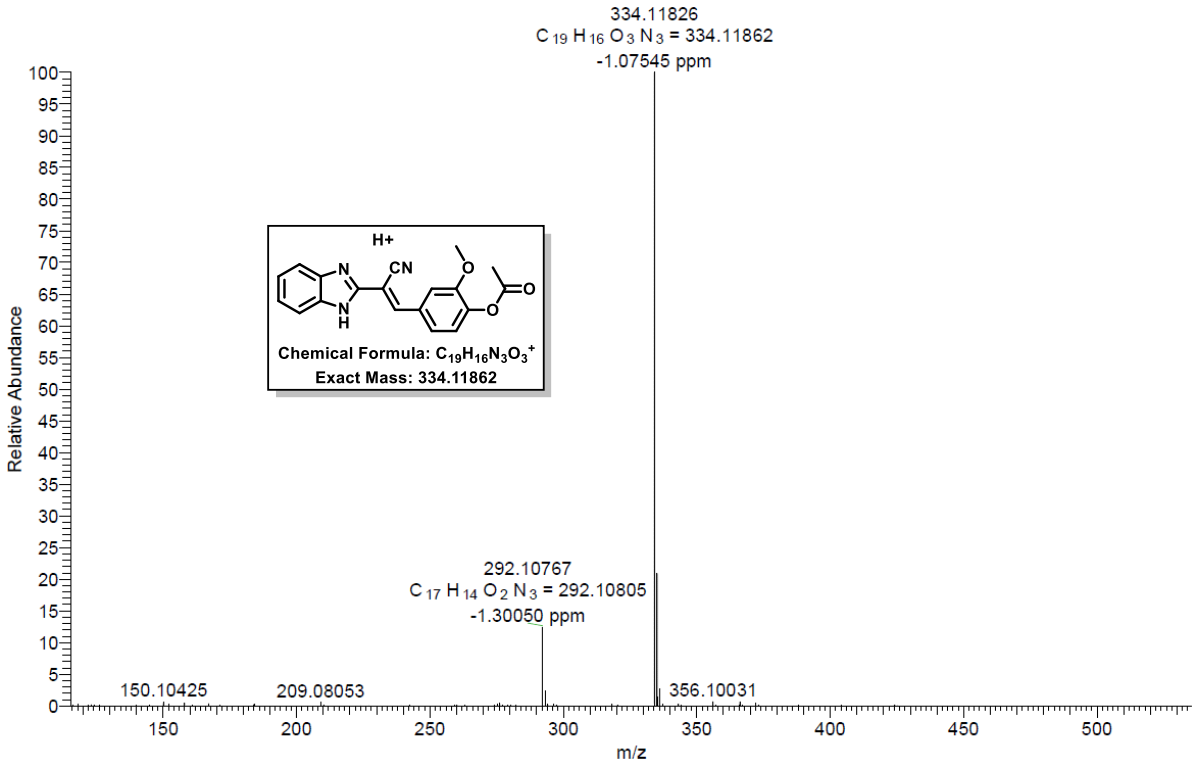

Figure S13. HRMS (ESI-TOF) spectrum of compound **1**.

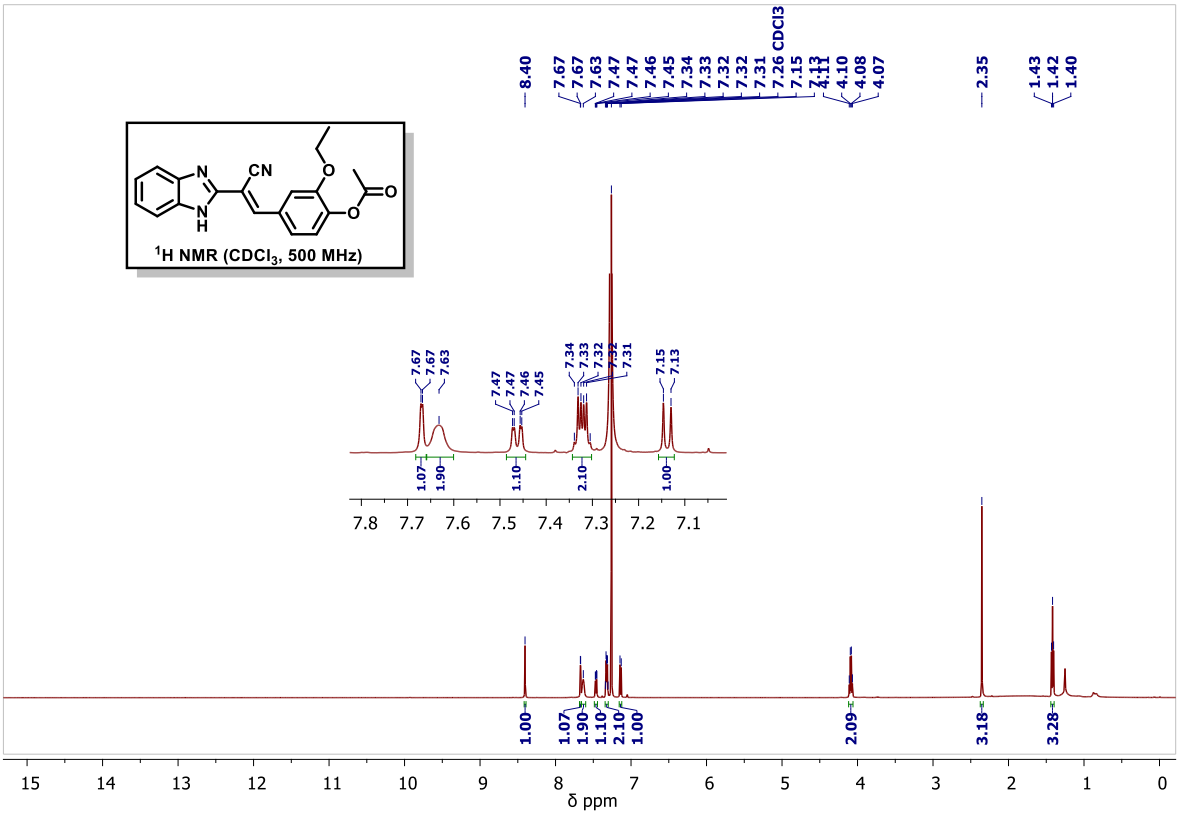

Figure S14. ^{1}H NMR spectra (500 MHz, RT) of compound **2** in $CDCl_3$.

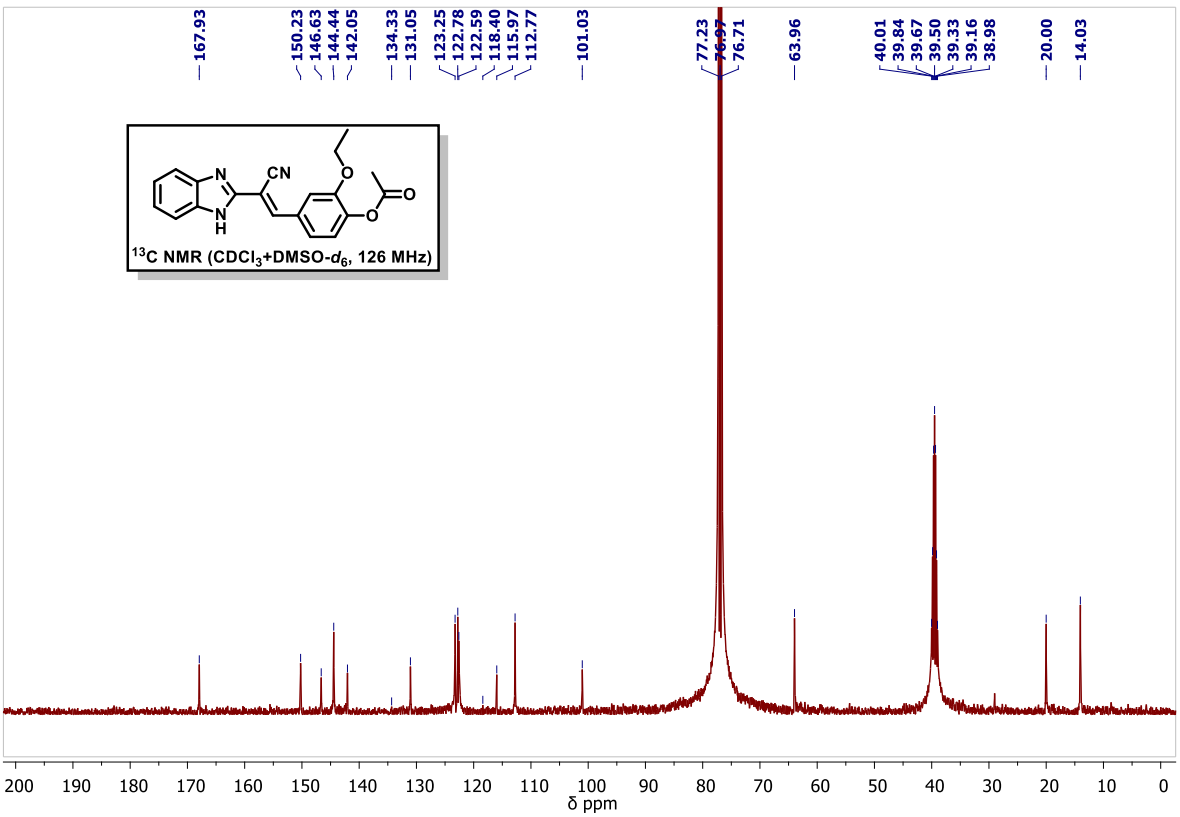

Figure S15. $^{13}C\{^{1}H\}$ NMR spectra (126 MHz, RT) of compound **2** in $CDCl_3$ + DMSO-d_6.

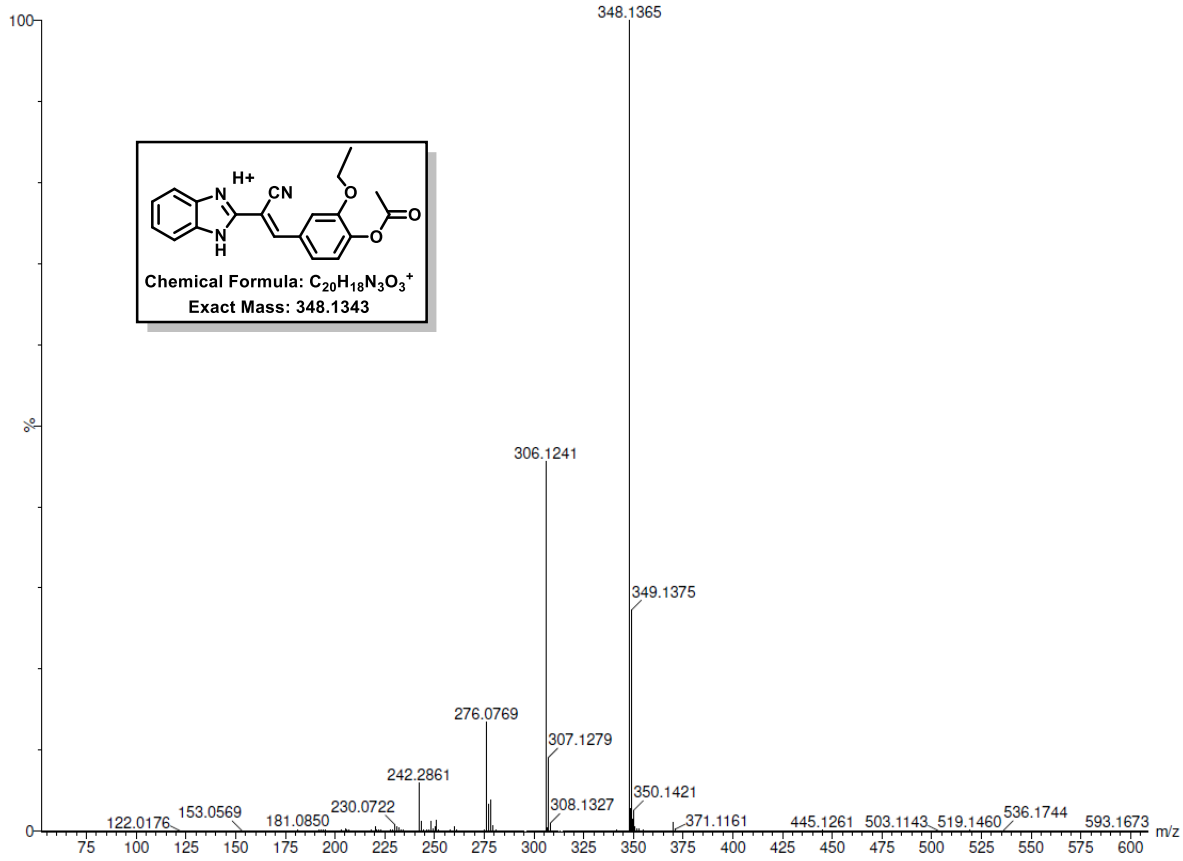

Figure S16. HRMS (ESI-TOF) spectrum of compound **2**.

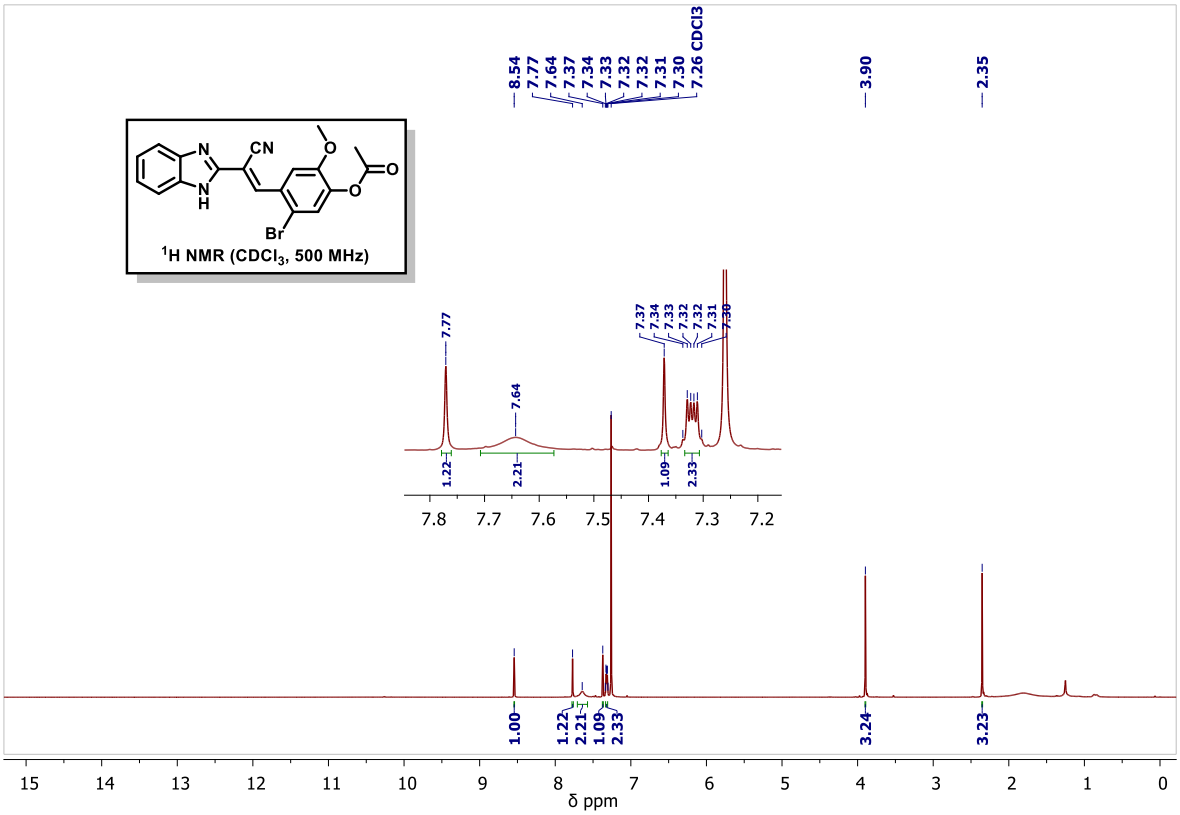

Figure S17. ^{1}H NMR spectra (500 MHz, RT) of compound **3** in $CDCl_3$.

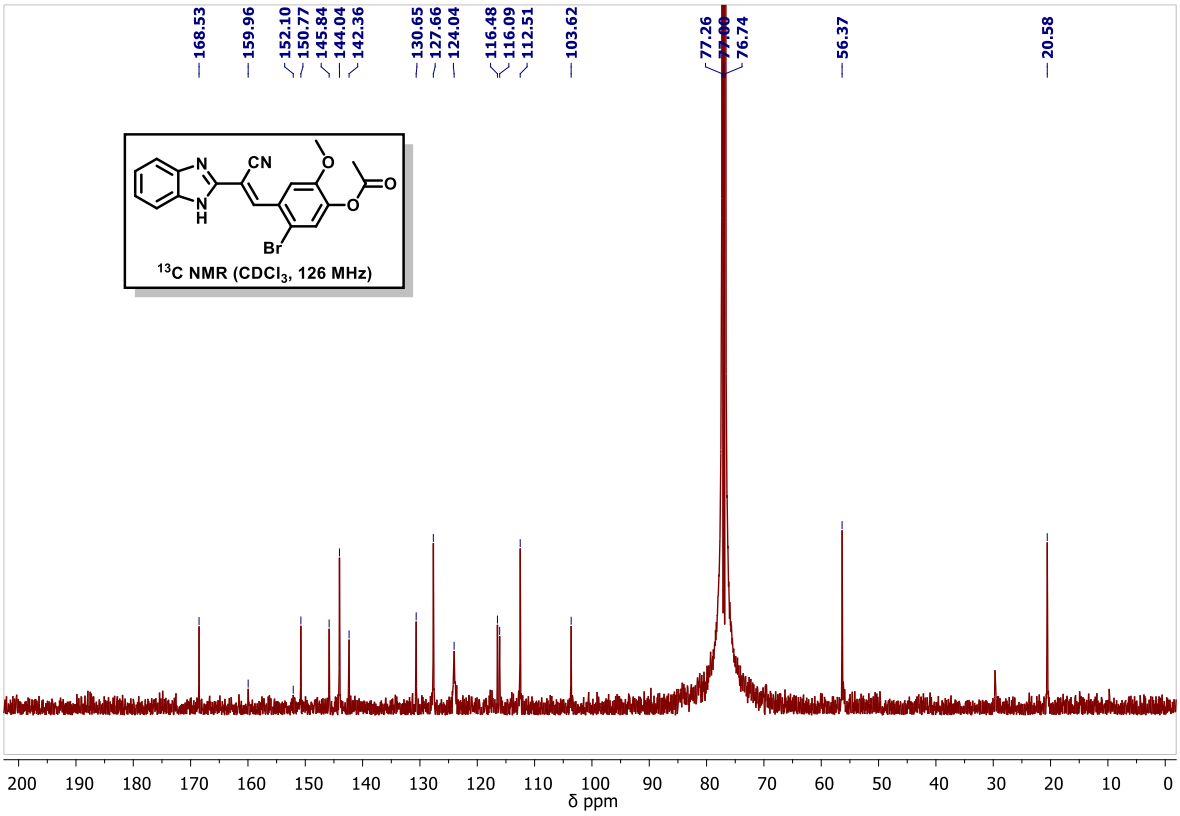

Figure S18. $^{13}C\{^{1}H\}$ NMR spectra (126 MHz, RT) of compound **3** in $CDCl_3$.

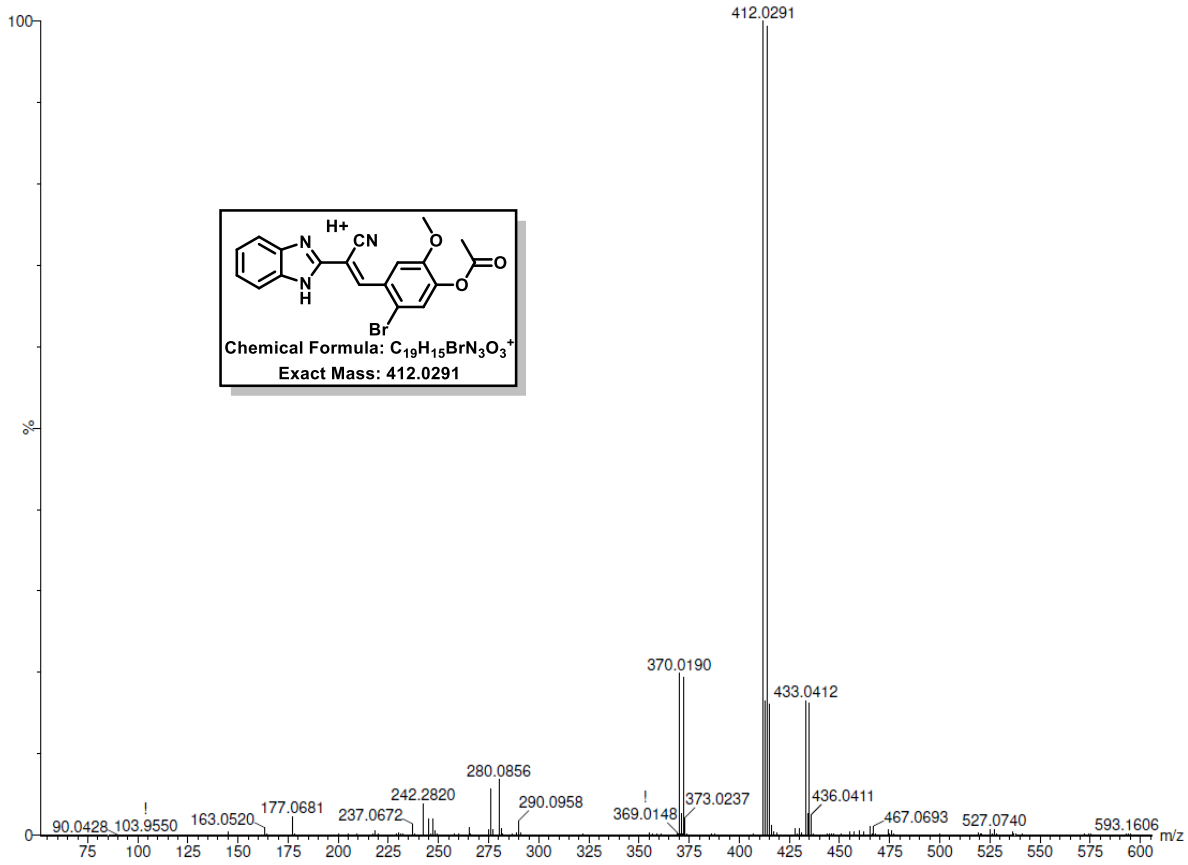

Figure S19. HRMS (ESI-TOF) spectrum of compound **3**.

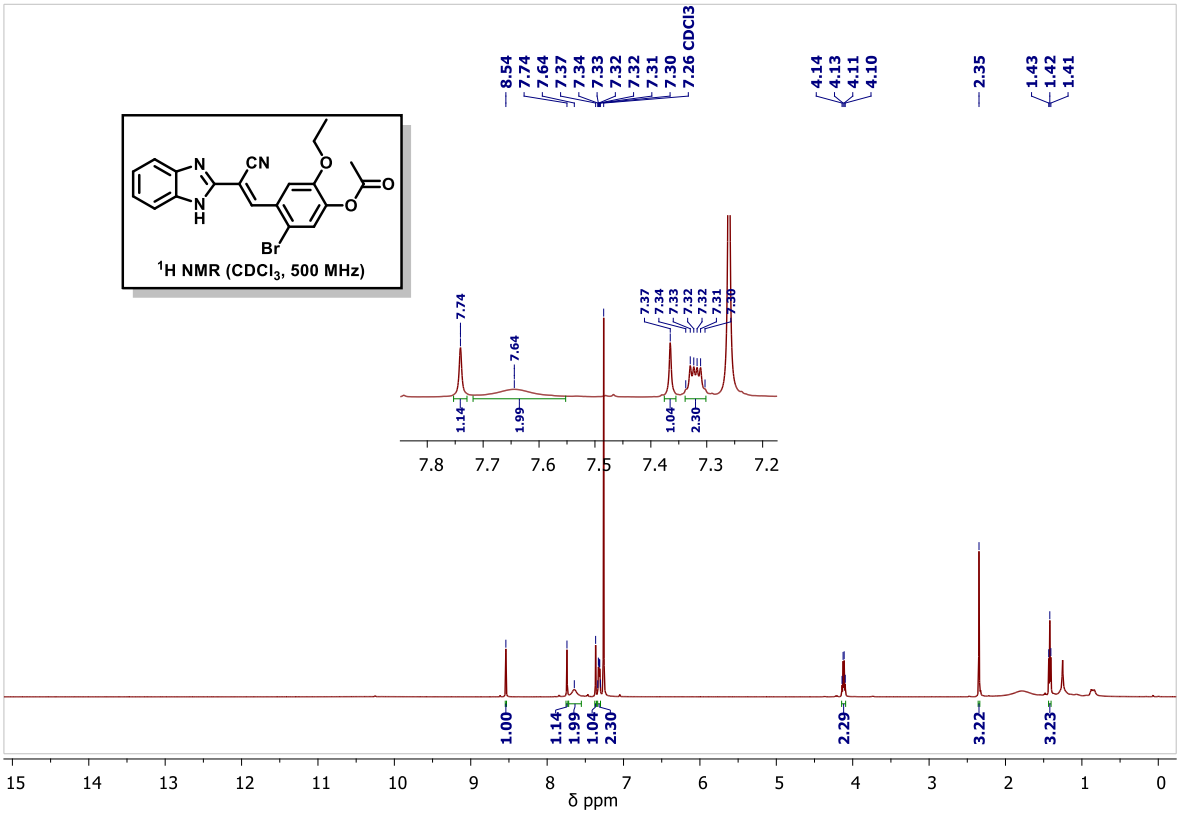

Figure S20. ^{1}H NMR spectra (500 MHz, RT) of compound **4** in $CDCl_3$.

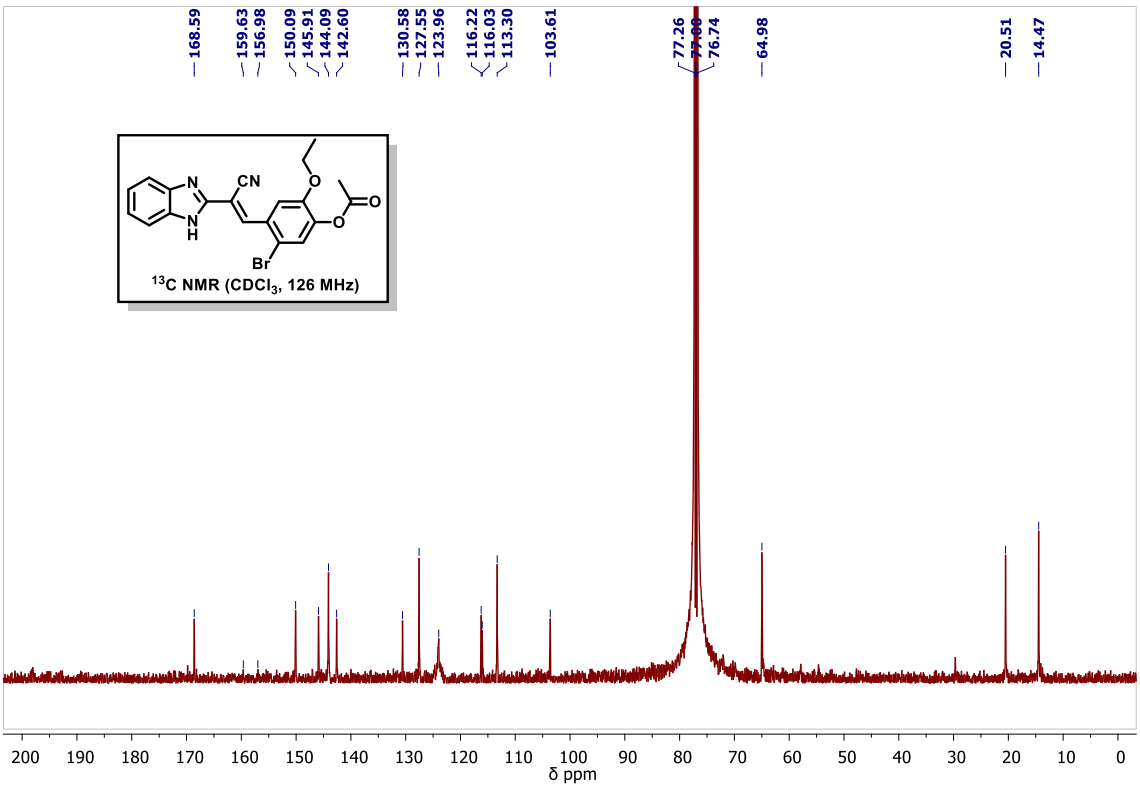

Figure S21. $^{13}C\{^{1}H\}$ NMR spectra (126 MHz, RT) of compound **4** in $CDCl_3$.

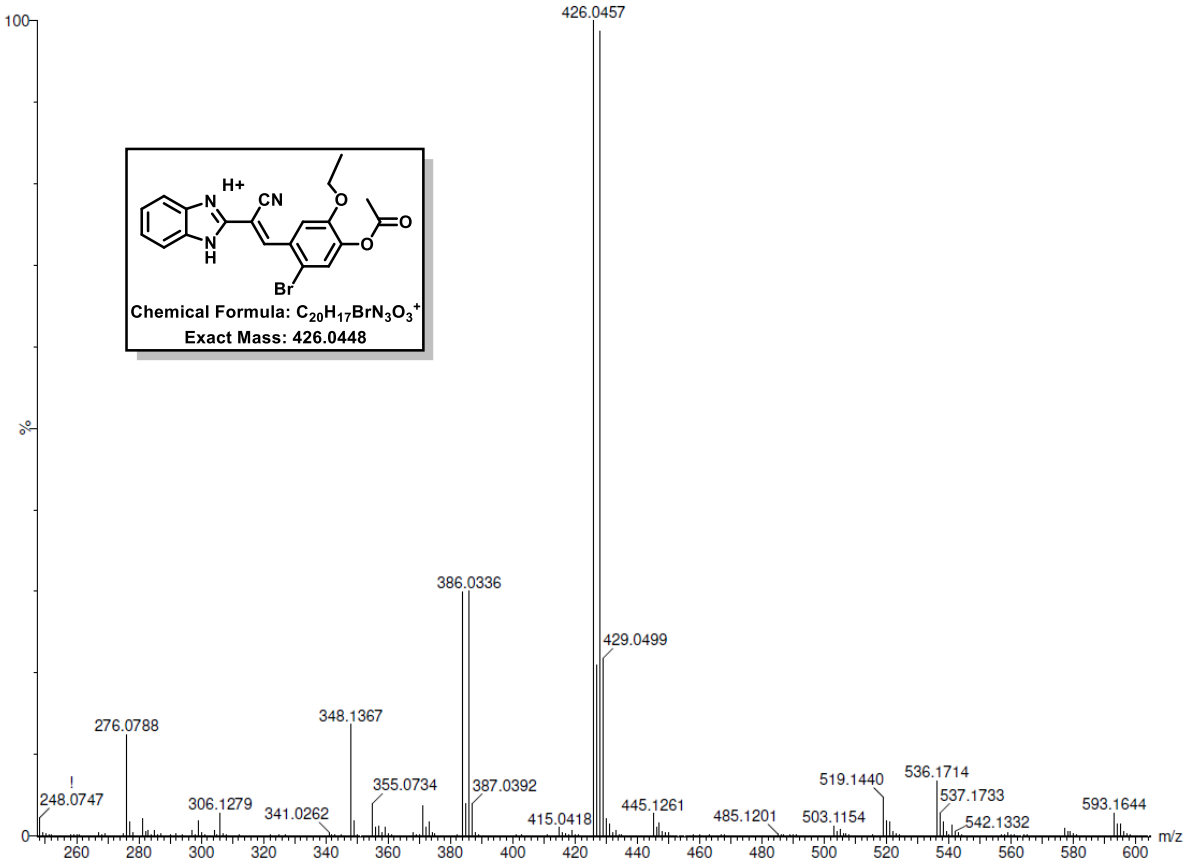

Figure S22. HRMS (ESI-TOF) spectrum of compound **4**.

2. Photophysical Properties of the Compounds

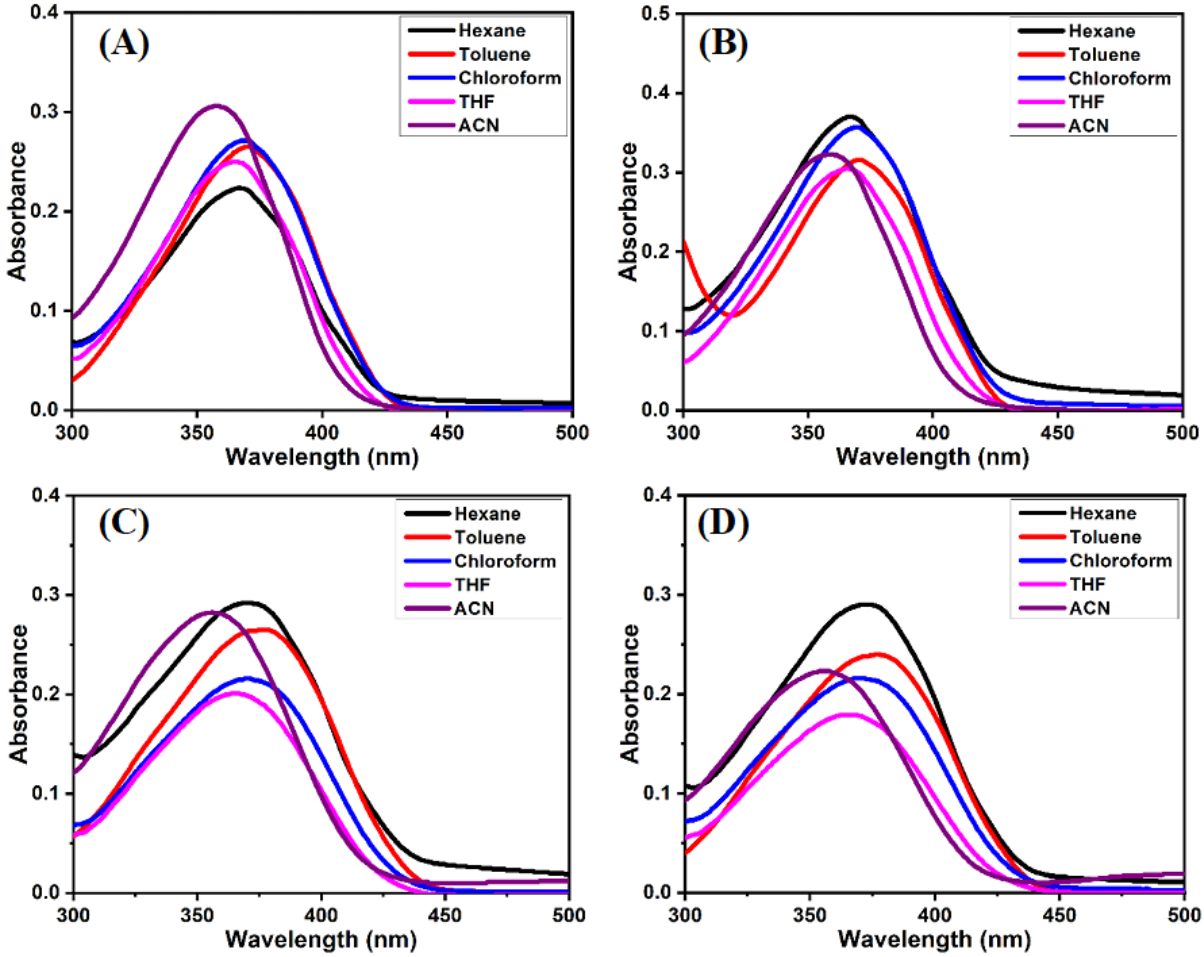

Figure S23. Absorption spectra of compound **1 (A)**, compound **2 (B)**, compound **3 (C)**, and compound **4 (D)** in different polarities of solvents.

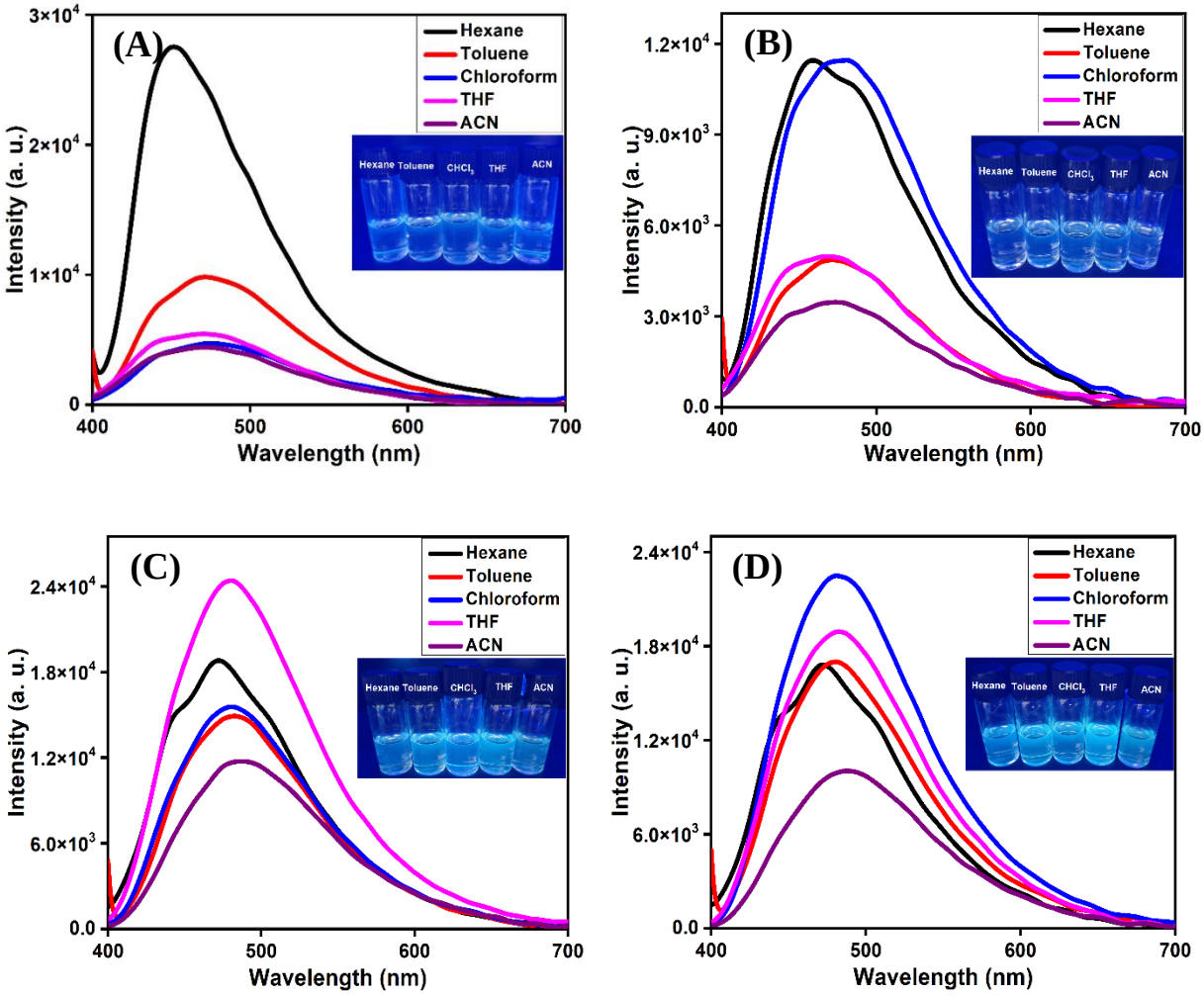

Figure S24. Emission spectra of compound **1 (A)**, compound **2 (B)**, compound **3 (C)**, and compound **4 (D)** in different polarities of solvents. (Con. 1×10^{-5} M, λ_{ex} = 375 nm). Digital photos taken under a UV 365 nm lamp are incorporated alongside the spectral profiles.

Table S1. Optical data of compounds **1-4** in different polarities of solvents (λ_{ex} = 375 nm for compounds).

S. No.	Compound	Solvents (dielectric constant, ε)	λ_{abs} (nm)	λ_{em} (nm)	$\Delta\nu$ [a]	ε = A/C. l (mol^{-1}. ltr. cm^{-1})
1	**1**	Hexane (1.88)	367	452	5124	2.2×10^4
		Toluene (2.38)	370	472	5841	2.6×10^4
		$CHCl_3$ (4.81)	368	472	5987	2.7×10^4
		THF (7.58)	365	471	6166	2.5×10^4

		ACN (37.5)	358	472	6747	3.0×10^4
2	**2**	Hexane (1.88)	367	476	6240	3.7×10^4
		Toluene (2.38)	371	474	5857	3.1×10^4
		$CHCl_3$ (4.81)	370	482	6280	3.5×10^4
		THF (7.58)	366	471	6091	3.0×10^4
		ACN (37.5)	359	475	6803	3.2×10^4
3	**3**	Hexane (1.88)	371	473	5813	2.9×10^4
		Toluene (2.38)	377	483	5821	2.6×10^4
		$CHCl_3$ (4.81)	370	482	6280	2.1×10^4
		THF (7.58)	366	480	6489	2.0×10^4
		ACN (37.5)	356	487	7556	2.8×10^4
4	**4**	Hexane (1.88)	373	472	5623	2.9×10^4
		Toluene (2.38)	378	481	5665	2.4×10^4
		$CHCl_3$ (4.81)	371	483	6250	2.1×10^4
		THF (7.58)	367	483	6544	1.7×10^4
		ACN (37.5)	356	488	7598	2.2×10^4

[a] $\Delta\nu$ is stokes shift, $\nu_{abs} - \nu_{em}$

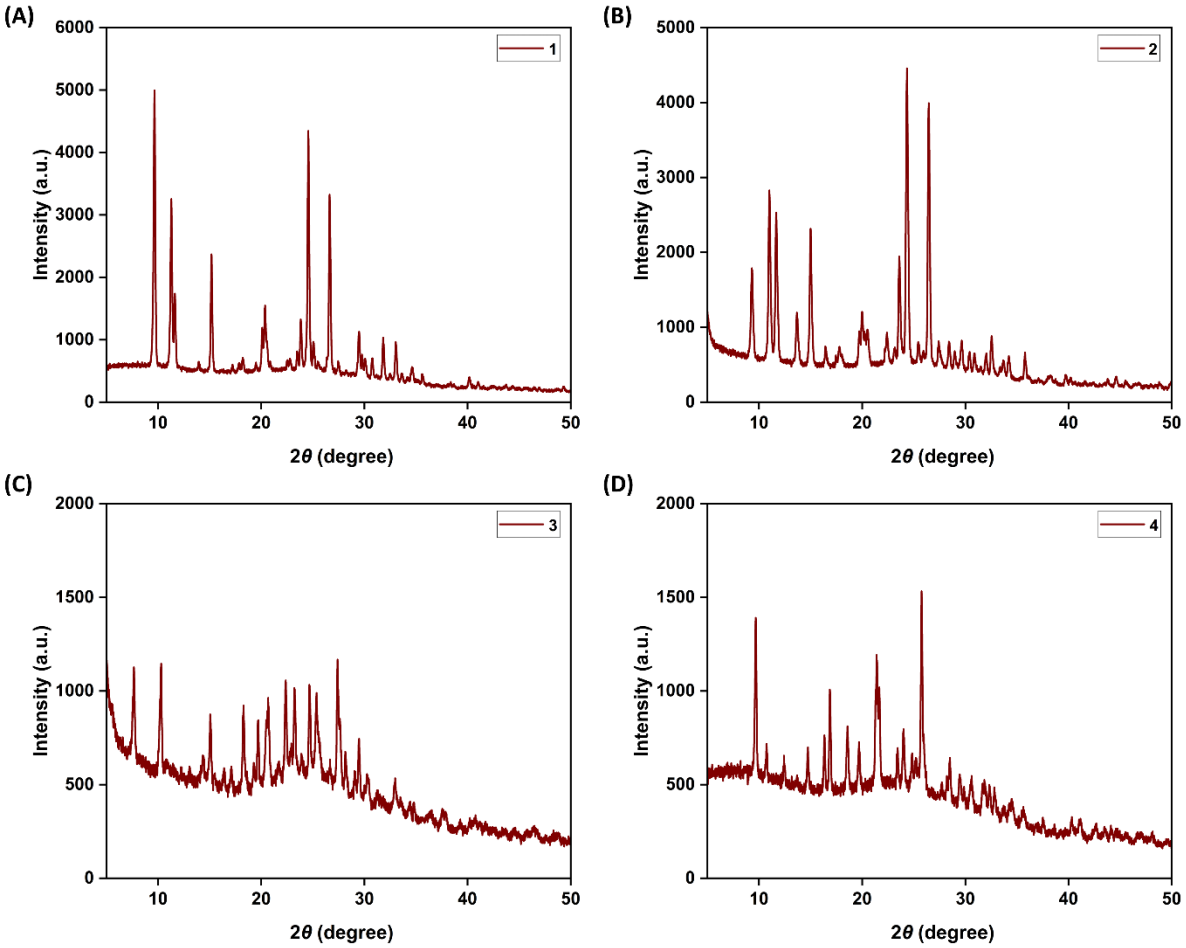

Figure S25. PXRD patterns of compounds **(A) 1, (B) 2, (C) 3,** and **(D) 4.**

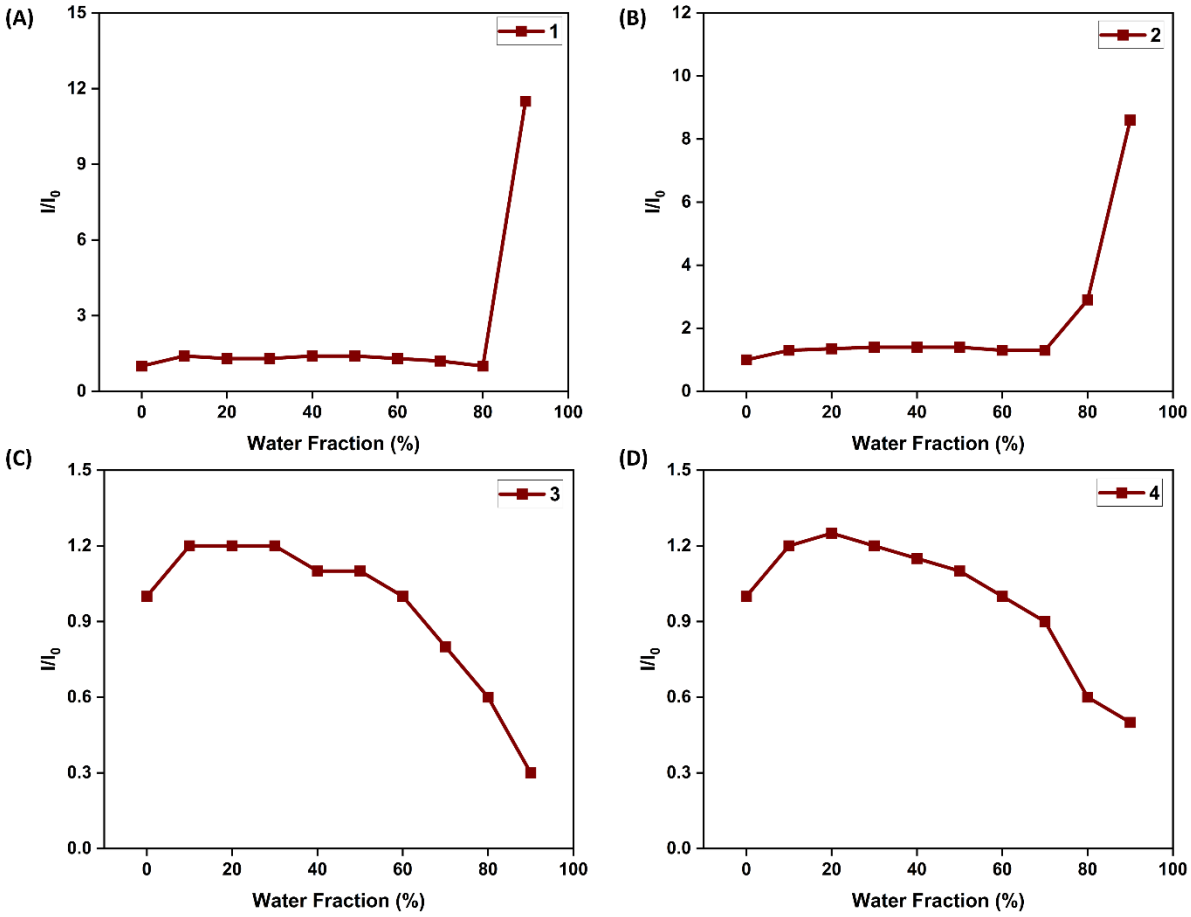

Figure S26. The plots of relative PL intensity (I/I_0) of obtained compounds **1 (A)**, **2 (B)**, **3 (C)**, and **4 (D),** respectively, versus different water fractions. I_0 and I are the values of PL intensity at the maximum peak in THF and THF/water mixtures, respectively.

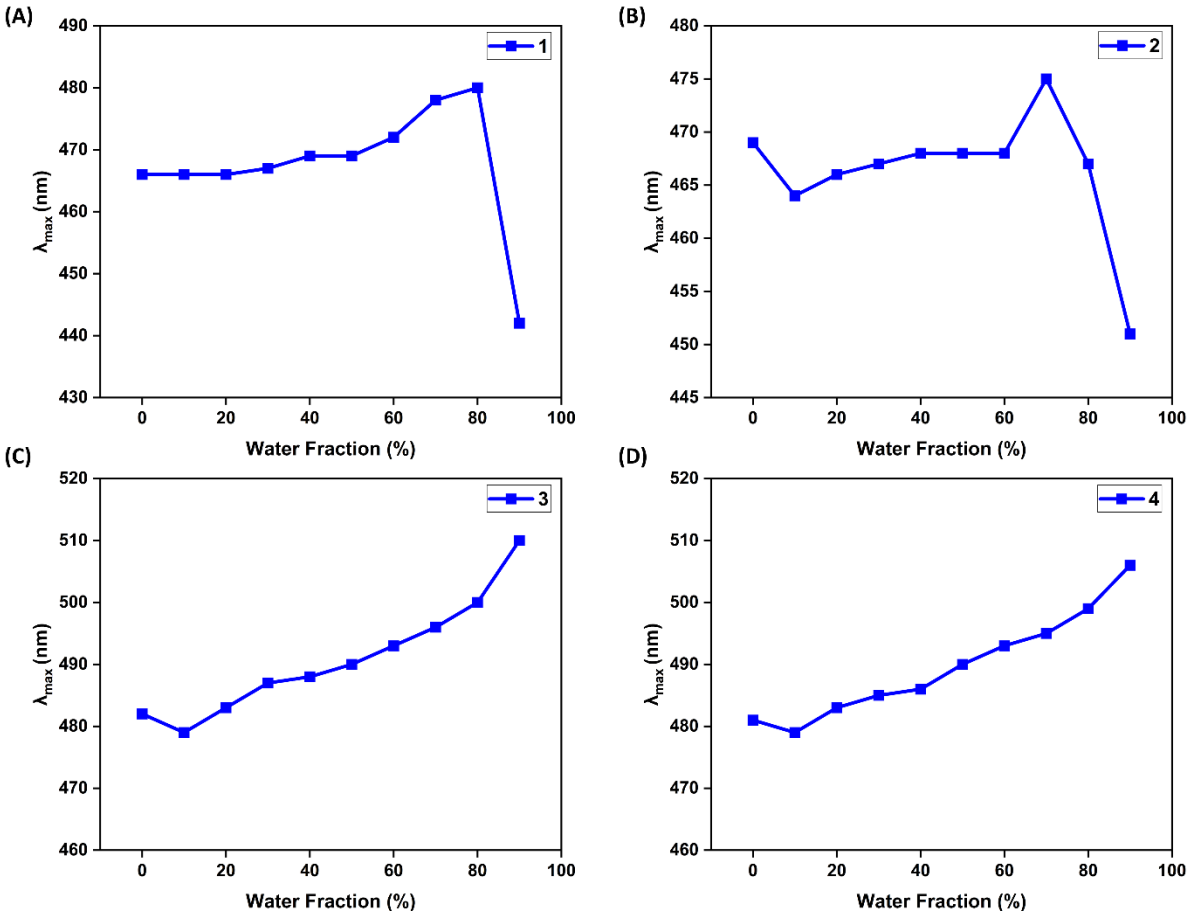

Figure S27. The plots of relative wavelength (λ_{max}) of the obtained compounds **1 (A)**, **2 (B)**, **3 (C)**, and **4 (D),** respectively, versus different water fractions in THF.

Table S2. Lifetime parameters of compounds **1-4** in solution (THF) and AIE ((f_w) of 90% in THF)

Compound	**In solution (THF)**				**In AIE ((fw) of 90% in THF)**			
	τ_{avr}	**Φ_f**	**K_r, 10^9 S^{-1}**	**K_{nr}, 10^9 S^{-1}**	**τ_{avr}**	**Φ_f**	**K_r, 10^9 S^{-1}**	**K_{nr}, 10^9 S^{-1}**
1	0.033	0.05	1.51	28.78	0.354	0.38	1.07	1.75
2	0.032	0.08	2.50	28.75	0.356	0.31	0.87	1.93
3	0.107	0.21	1.96	7.38	0.111	0.11	0.99	8.01
4	0.103	0.29	2.81	6.89	0.119	0.19	1.59	6.81

$K_r = \Phi_f/\tau_{avr}$; $K_{nr} = (1- \Phi_f)/\tau_{avr}$.

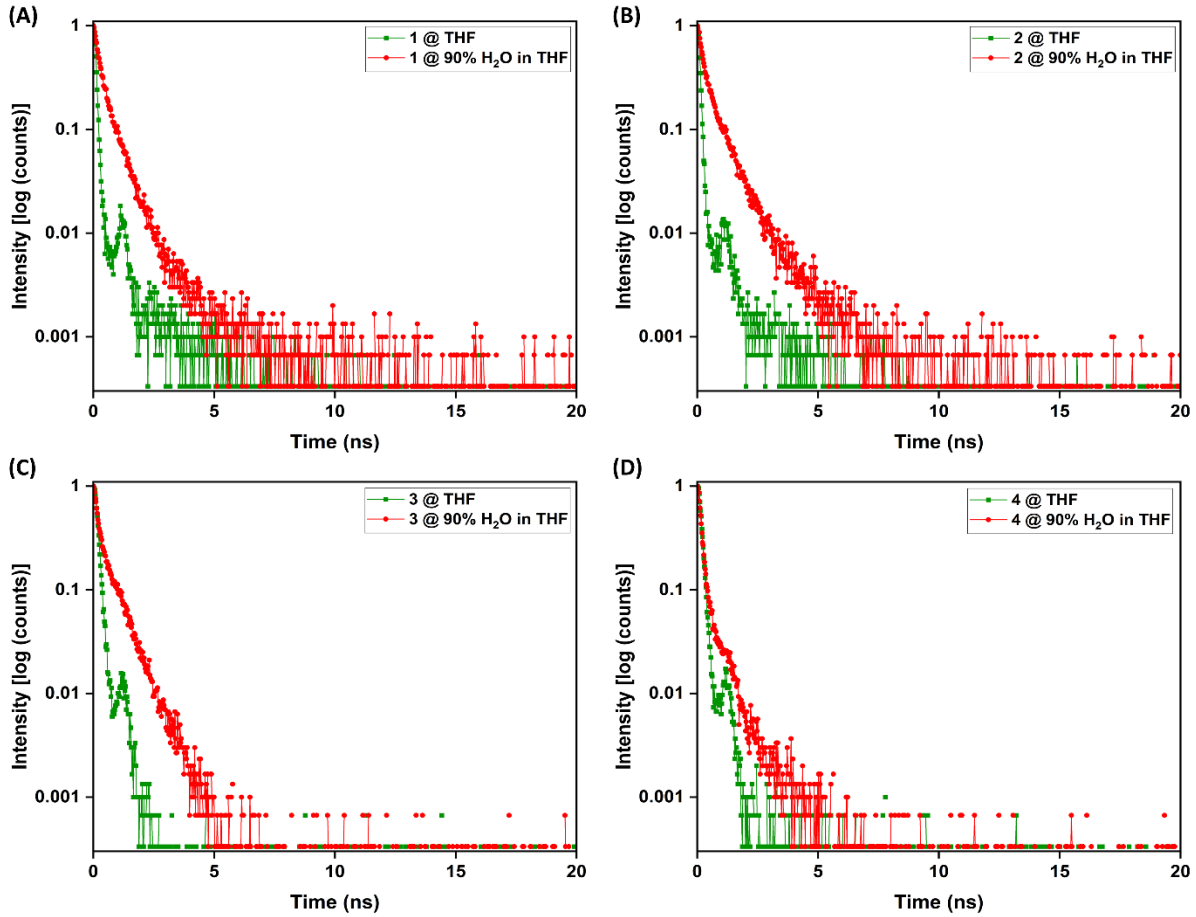

Figure S28. Lifetime profiles of compounds **(A) 1, (B) 2, (C) 3,** and **(D) 4** in THF and 90% water fraction in AIE.

3. Dynamic Light Scattering studies

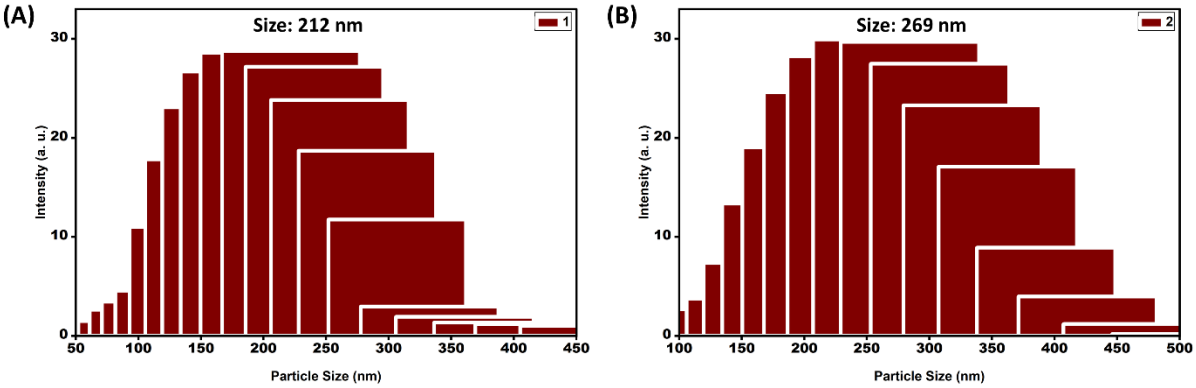

Figure S29. Size distributions of the aggregates of (A) **1**, (B) **2**, (C) **3**, and (D) **4**, THF-water mixtures with f_w = 90% (Con. 1×10^{-5} M).

4. DFT Calculations

Table S3. DFT data of molecule **1**.

6	4.620462587	-0.951047554	0.153238202
6	5.125697031	0.371229104	0.054543762
6	6.492915996	0.658858293	0.086546552
6	7.356582163	-0.426401869	0.221790010
6	6.871409918	-1.749951728	0.321456083
6	5.508677852	-2.029008535	0.289001492
6	2.904156615	0.325069889	-0.036884329
1	6.869848527	1.675102655	0.010136978
1	8.428415387	-0.250461550	0.251054116
1	7.582434642	-2.565062146	0.425562488
1	5.131629003	-3.044560912	0.365244365
6	1.528143142	0.829711815	-0.143189163
6	0.474520429	-0.036686965	-0.108508487
1	0.775946909	-1.075919261	0.003862238
6	1.409380786	2.249062761	-0.278994643
7	1.402158422	3.409747534	-0.384985788
6	-0.961677154	0.181550673	-0.195387942
6	-1.590531965	1.435762976	-0.360704330
6	-1.781650837	-0.965990816	-0.113218889
6	-2.976870347	1.527592142	-0.425131659
6	-3.168654374	-0.881619769	-0.187209502
1	-1.336444927	-1.949225974	0.012617181
6	-3.769214676	0.382461549	-0.321970901
1	-3.464525889	2.489165439	-0.555587025
6	-4.523129264	-2.513994859	-1.265411332
1	-5.189476839	-1.769833045	-1.713489696
1	-3.738783571	-2.795434773	-1.978518734
8	-3.932334278	-2.014767449	-0.049535968
8	-5.140273595	0.496863182	-0.455748824
6	-6.015809259	0.266654077	0.598910057
8	-7.189183184	0.206493684	0.340109203
6	-5.420184388	0.145487655	1.980298997

1	-4.889413273	-0.807585877	2.075949388
1	-4.707883616	0.951261855	2.184342611
1	-6.234720468	0.176522686	2.705241067
7	4.000271958	1.165333775	-0.066041876
7	3.239007616	-0.942855266	0.093005417
1	3.973237948	2.172555151	-0.158159794
1	-5.094785333	-3.397473099	-0.976426789
1	-1.006561751	2.344218171	-0.439311858

Table S4. DFT data of molecule **2**.

6	-4.811254063	1.011264586	0.212576725
6	-5.384813704	-0.271153801	0.013284388
6	-6.765756346	-0.485491179	0.009790352
6	-7.572100922	0.632653992	0.214066817
6	-7.018462666	1.917277649	0.414679710
6	-5.642412109	2.123350848	0.416841395
6	-3.162778104	-0.339233905	-0.050872132
1	-7.195368367	-1.471641231	-0.143904735
1	-8.652114115	0.513466431	0.219190232
1	-7.686336108	2.760228023	0.570167673
1	-5.212652781	3.108775968	0.570440803
6	-1.814164504	-0.908708088	-0.178750607
6	-0.716921775	-0.103745354	-0.077367099
1	-0.965082309	0.940435847	0.100368951
6	-1.768775458	-2.320110681	-0.408340430
7	-1.821467446	-3.469880115	-0.592170980
6	0.706874207	-0.390773671	-0.165325063
6	1.272710422	-1.664280308	-0.397795759
6	1.583371440	0.706360937	-0.009130709
6	2.653219477	-1.824030019	-0.455972743
1	0.643831972	-2.535424696	-0.532569460
6	2.965144970	0.555339291	-0.076224974
1	1.186528567	1.701869212	0.170788298
6	3.501036753	-0.728409430	-0.281125900

1	3.092356678	-2.800538920	-0.637617193
6	4.361350767	2.218801670	-1.069507448
6	5.283448251	3.345389780	-0.644599501
1	4.905622548	1.444879377	-1.623306510
1	3.539033103	2.588293430	-1.696831990
1	5.712381777	3.824879625	-1.532093530
1	4.737012617	4.102267486	-0.071662601
1	6.105486176	2.965201793	-0.029370872
8	3.790731796	1.632113316	0.130263950
8	4.865501737	-0.903734573	-0.413059720
6	5.743712033	-0.744228009	0.651621244
8	6.919230925	-0.699276249	0.398138061
6	5.148936607	-0.683542084	2.037554076
1	4.652169761	0.280410755	2.189001181
1	4.408409103	-1.474464275	2.193435363
1	5.960143835	-0.785462442	2.759822885
7	-4.301661553	-1.114592392	-0.151965671
7	-3.431473176	0.932470988	0.166527434
1	-4.327115015	-2.112379098	-0.317746356

Table S5. DFT data of molecule **3**.

6	4.860354933	-0.998683985	-0.396587569
6	5.139302988	-0.134863945	0.694217176
6	6.432145704	0.056541813	1.190373622
6	7.453955857	-0.648489880	0.558331804
6	7.194470723	-1.512799394	-0.529832667
6	5.905803470	-1.698221133	-1.019150957
6	2.973331517	-0.171358263	0.200445268
1	6.636237622	0.720124536	2.026172172
1	8.475141527	-0.531064565	0.910468470
1	8.023960930	-2.041274388	-0.991756615
1	5.701478132	-2.360032844	-1.855507185
6	1.541174661	0.135797514	0.305829600
6	0.625624565	-0.487366753	-0.476382334

1	1.020216657	-1.251945126	-1.143239037
6	1.168357880	1.062974956	1.335746185
7	0.932787881	1.797289824	2.207610159
6	-0.835721760	-0.310301556	-0.456013796
6	-1.518123271	0.910333673	-0.616583990
6	-1.615741763	-1.470658877	-0.278484981
6	-2.910296188	0.971431123	-0.540993512
6	-3.003763738	-1.428475364	-0.198795214
1	-1.127288926	-2.435323268	-0.171884057
6	-3.647671457	-0.182303420	-0.297442149
1	-3.430510735	1.914316066	-0.668282713
6	-4.460190171	-3.108590788	-1.047797952
1	-5.202264688	-2.387248589	-1.404062978
1	-3.781469490	-3.386174783	-1.863313666
8	-3.708585167	-2.575365841	0.061121220
8	-5.027756007	-0.102722805	-0.268239369
6	-5.749281994	-0.252918341	0.911939181
8	-6.945644278	-0.334919522	0.819771787
6	-4.967767294	-0.272205404	2.202716354
1	-4.389095202	-1.198882231	2.278913147
1	-4.267718610	0.567260204	2.262073124
1	-5.676999398	-0.223005585	3.029956139
7	3.908328363	0.381252210	1.053062683
7	3.506236428	-0.996943346	-0.676219795
1	3.715937206	1.035204454	1.800902639
35	-0.606503179	2.532873416	-1.022509047
1	-4.961386892	-3.998700693	-0.664227596

Table S6. DFT data of molecule **4**.

6	-4.986298695	1.167657107	-0.356901939
6	-5.335793211	0.262518992	0.678643855
6	-6.645457900	0.126441935	1.148143526
6	-7.611023178	0.930470550	0.546465401
6	-7.280937863	1.837134839	-0.486650728

6	-5.975879767	1.967051701	-0.949801363
6	-3.164922712	0.186814288	0.211091910
1	-6.903745452	-0.569665230	1.941410296
1	-8.642798162	0.858634363	0.879478115
1	-8.068208614	2.443228541	-0.926624664
1	-5.717556707	2.660931093	-1.744188597
6	-1.757047477	-0.218558017	0.313466192
6	-0.793936507	0.386158239	-0.425203458
1	-1.132245729	1.210728563	-1.050277401
6	-1.459922426	-1.221999281	1.295174986
7	-1.288311514	-2.015732939	2.129098136
6	0.652571504	0.115692243	-0.409206925
6	1.258003390	-1.137178921	-0.622811549
6	1.503307335	1.215958183	-0.180163355
6	2.643531147	-1.288637906	-0.550519878
6	2.885986801	1.084373588	-0.101774060
1	1.075256483	2.203537886	-0.031733086
6	3.450320866	-0.194479914	-0.257211692
1	3.104304611	-2.255527434	-0.720276076
6	4.414415032	2.735149731	-0.906667401
6	5.230874127	3.896002793	-0.372817025
1	5.056812918	1.959579760	-1.338695591
1	3.698059043	3.066623085	-1.670266610
1	5.794501672	4.356542319	-1.192406155
1	4.582763995	4.657916075	0.073371537
1	5.944353715	3.555521145	0.384746832
8	3.664707689	2.169683909	0.202618350
8	4.822790106	-0.360883156	-0.237062102
6	5.557019199	-0.276839548	0.940815013
8	6.755696634	-0.246113451	0.843137941
6	4.785595491	-0.263723338	2.237902074
1	4.261789603	0.690950613	2.354052221
1	4.038823293	-1.063425138	2.270530175
1	5.495804451	-0.385023341	3.056876751

7	-4.145644875	-0.351840459	1.020170306
7	-3.631186617	1.094146063	-0.621730895
1	-4.006161907	-1.058940054	1.730435349
35	0.248750320	-2.679404655	-1.105445458

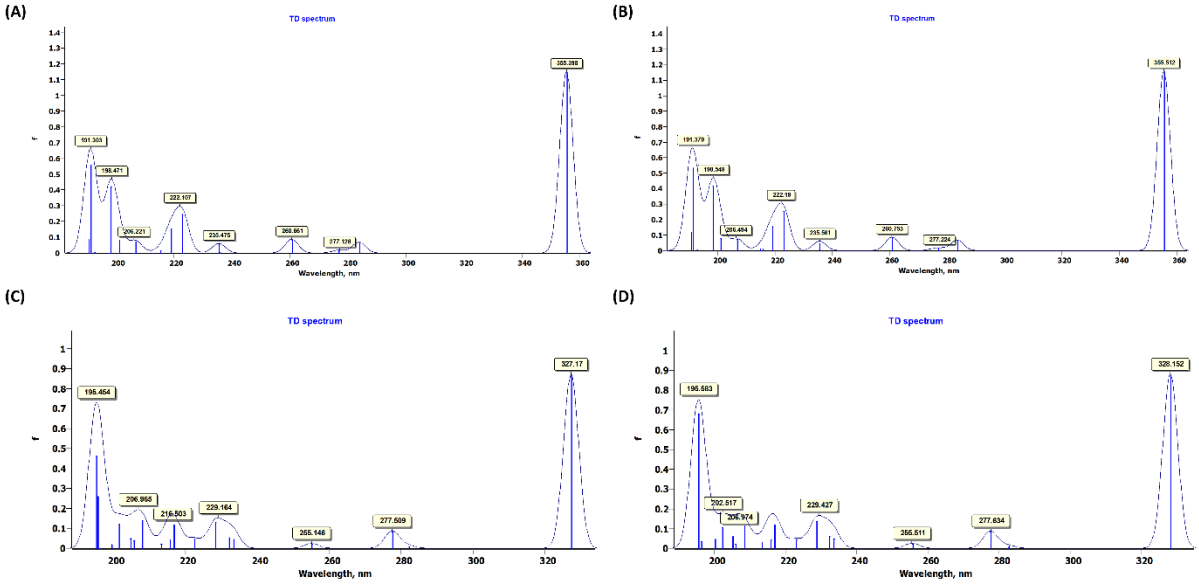

Figure S30. Simulated absorption spectra of compounds **1–4** (**A–D**), respectively, using CAM-B3LYP paired with 6-31+G(d) basis set in tetrahydrofuran solvent.

Table S7. Computed singlet vertical transitions involved in compound **1** from TD-DFT calculation using 6-31+G(d) basis set CAM-B3LYP functional in Gaussian09.

Excited States	**E (eV)**	**λ_{max} (nm)**	***f***	**Major transitions (%)[a]**
S_1	3.4888	355.37	1.1496	HOMO → LUMO (47.1 %)
S_2	4.3681	283.84	0.0679	HOMO-1 → LUMO (45.5 %)
S_3	4.4800	276.75	0.0173	HOMO-3 → LUMO (21.0 %) HOMO-2 → LUMO (19.9 %)
S_4	4.7571	260.63	0.0870	HOMO-3 → LUMO (17.3 %) HOMO-2 → LUMO (23.6 %)
S_5	5.2615	235.64	0.0047	HOMO-4 → LUMO (40.6 %)

[a] TD–DFT–predicted electronic transitions highlight only values greater than 10%, as mentioned in the table.

Table S8. Computed singlet vertical transitions involved in compound **2** from TD-DFT calculation using 6-31+G(d) basis set CAM-B3LYP functional in Gaussian09.

Excited States	**E (eV)**	**λ_{max} (nm)**	***f***	**Major transitions (%)[a]**
S_1	3.4878	355.48	1.1586	HOMO → LUMO (47.0 %)
S_2	4.3742	283.44	0.0680	HOMO-1 → LUMO (45.4 %)
S_3	4.4809	276.69	0.0182	HOMO-3 → LUMO (21.3 %) HOMO-2 → LUMO (19.6 %)
S_4	4.7548	260.76	0.0859	HOMO-3 → LUMO (17.0 %) HOMO-2 → LUMO (23.9 %)
S_5	5.2644	235.52	0.0507	HOMO → LUMO+2 (24.9 %)

[a] TD–DFT–predicted electronic transitions highlight only values greater than 10%, as mentioned in the table.

Table S9. Computed singlet vertical transitions involved in compound **3** from TD-DFT calculation using 6-31+G(d) basis set CAM-B3LYP functional in Gaussian09.

Excited States	**E (eV)**	**λ_{max} (nm)**	***f***	**Major transitions (%)[a]**
S_1	3.7886	327.25	0.8718	HOMO → LUMO (45.1 %)
S_2	4.3955	282.07	0.0129	HOMO-2 → LUMO (35.6 %)
S_3	4.4681	277.49	0.0865	HOMO-1 → LUMO (37.1 %)
S_4	4.8597	255.13	0.0247	HOMO-3 → LUMO (34.3 %)

[a] TD–DFT–predicted electronic transitions highlight only values greater than 10%, as mentioned in the table.

Table S10. Computed singlet vertical transitions involved in compound **4** from TD-DFT calculation using 6-31+G(d) basis set CAM-B3LYP functional in Gaussian09.

Excited States	**E (eV)**	**λ_{max} (nm)**	***f***	**Major transitions (%)[a]**
S_1	3.7785	328.13	0.8795	HOMO → LUMO (45.1 %)
S_2	4.3876	282.58	0.0150	HOMO-2 → LUMO (36.4 %)
S_3	4.4671	277.55	0.0874	HOMO-1 → LUMO (38.1 %)
S_4	4.8509	255.59	0.0255	HOMO-3 → LUMO (34.5 %)

[a] TD–DFT–predicted electronic transitions highlight only values greater than 10%, as mentioned in the table.