Electronic Supplementary Information

Strategic Molecular Design of *closo*-*ortho*-Carboranyl Luminophore to Manifest Thermally Activated Delayed Fluorescence

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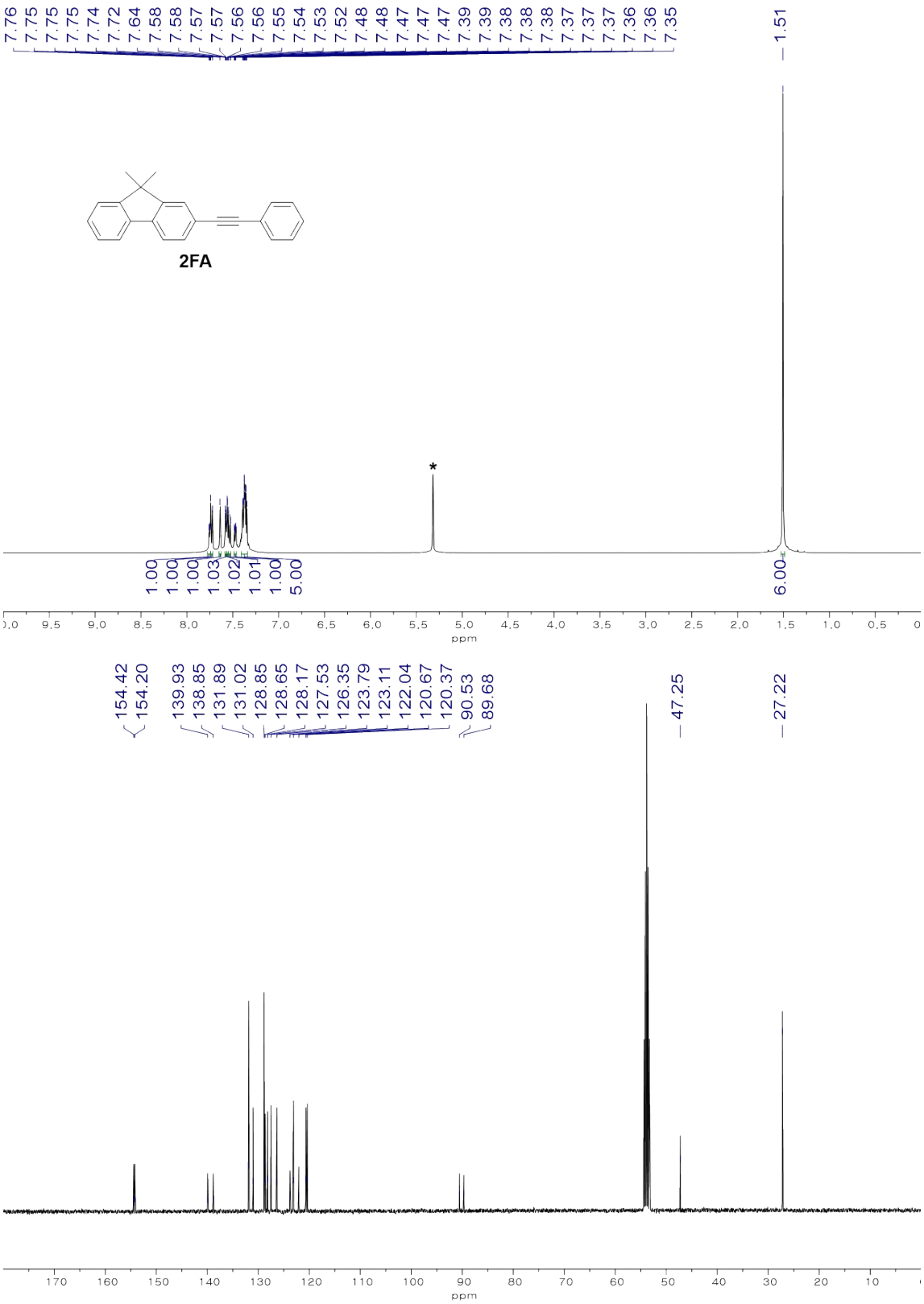

Fig. S1 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2FA** in CD_2Cl_2 (∗ from residual CH_2Cl_2 in CD_2Cl_2).

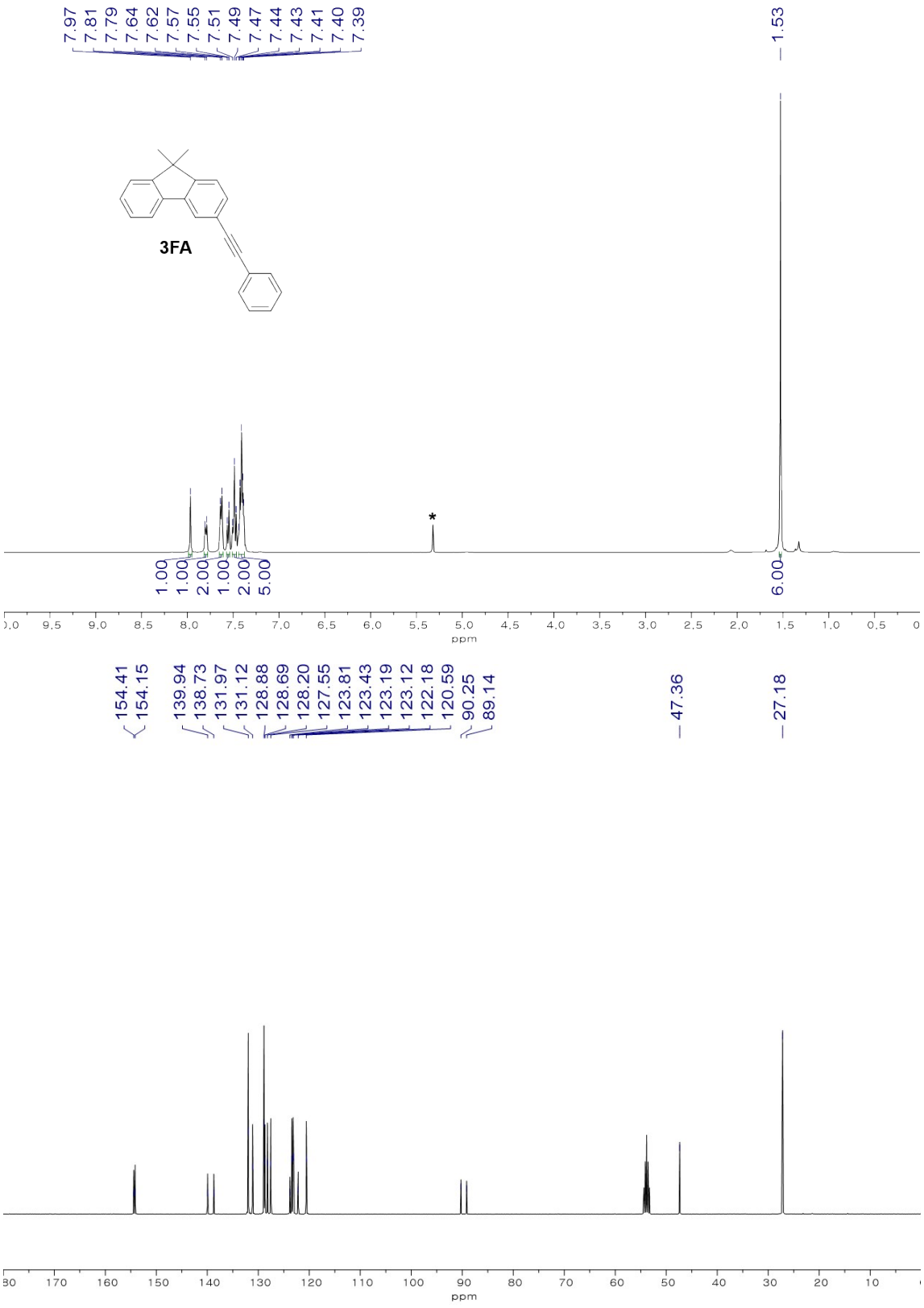

Fig. S2 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3FA** in CD_2Cl_2 (∗ from residual CH_2Cl_2 in CD_2Cl_2).

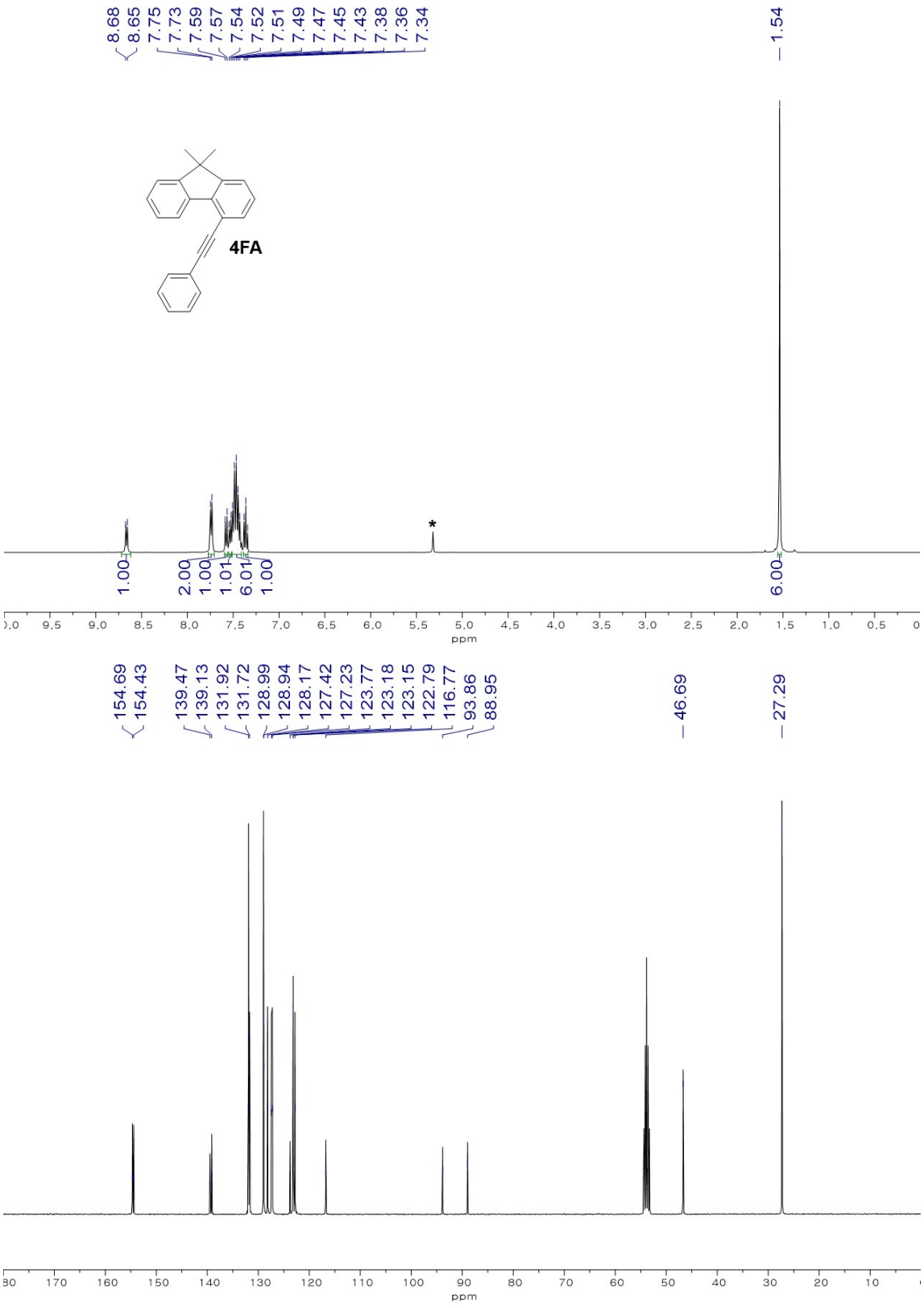

Fig. S3 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **4FA** in CD_2Cl_2 (∗ from residual CH_2Cl_2 in CD_2Cl_2).

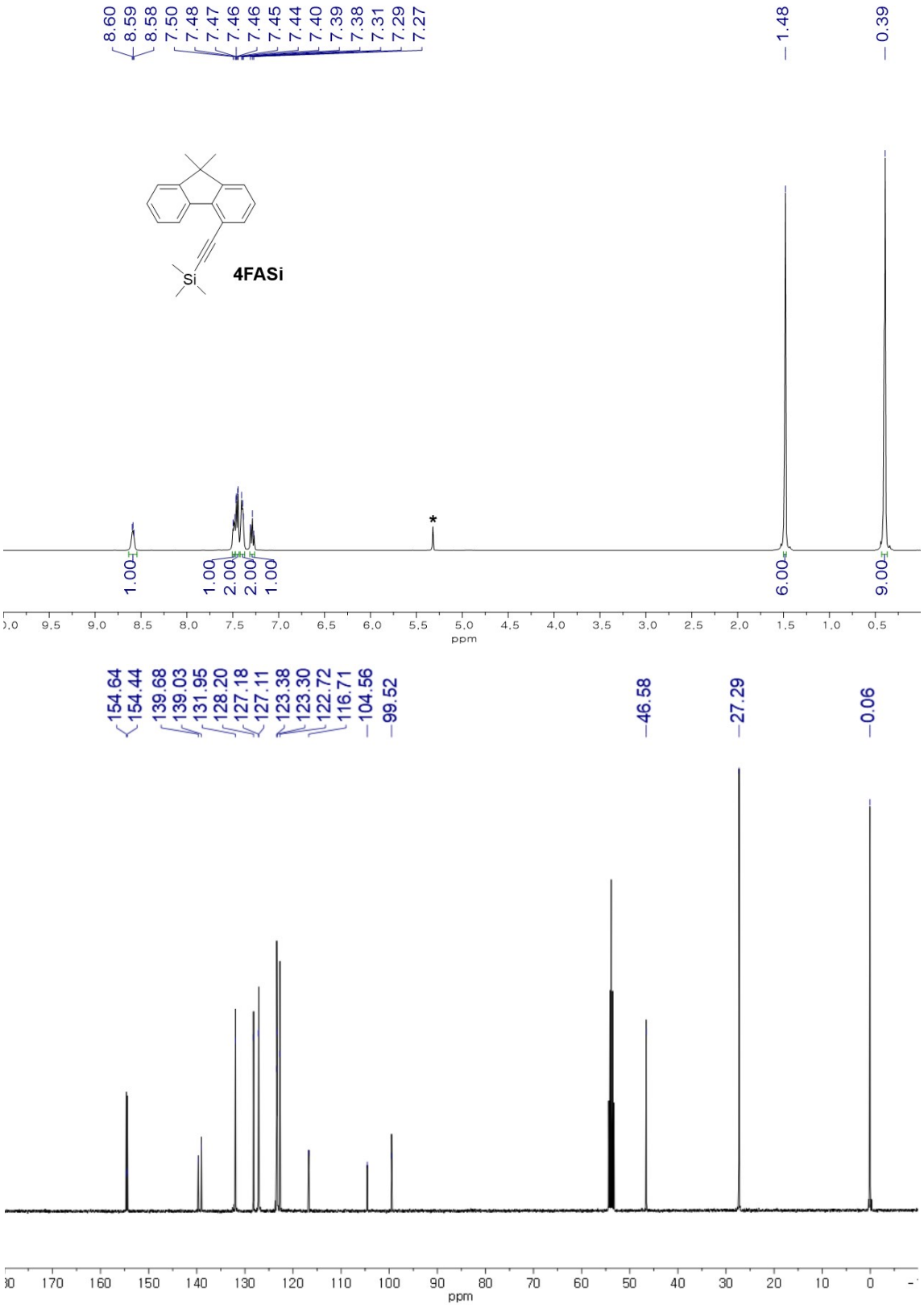

Fig. S4 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **4FASi** in CD_2Cl_2 (∗ from residual CH_2Cl_2 in CD_2Cl_2).

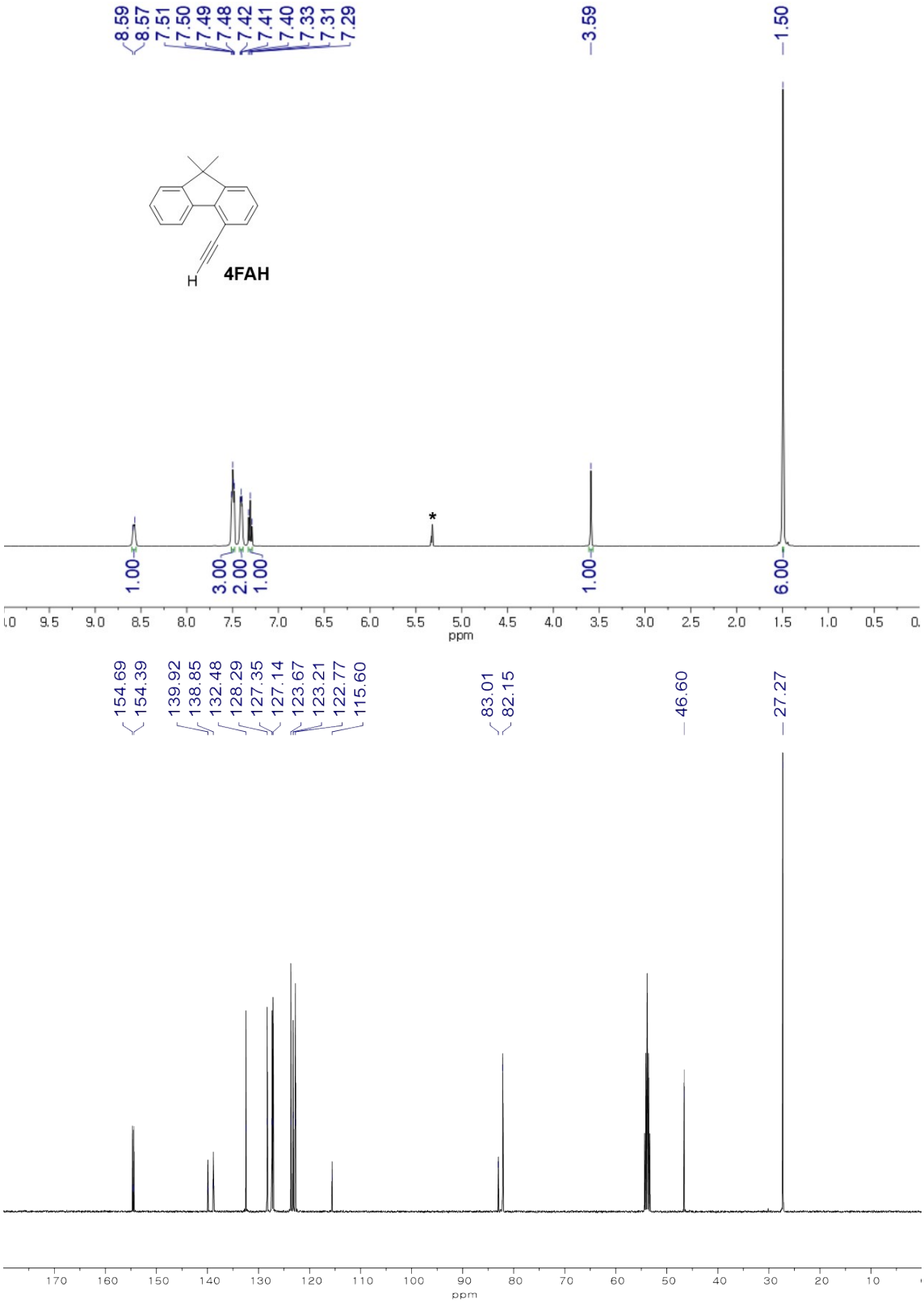

Fig. S5 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **4FAH** in CD_2Cl_2 (∗ from residual CH_2Cl_2 in CD_2Cl_2).

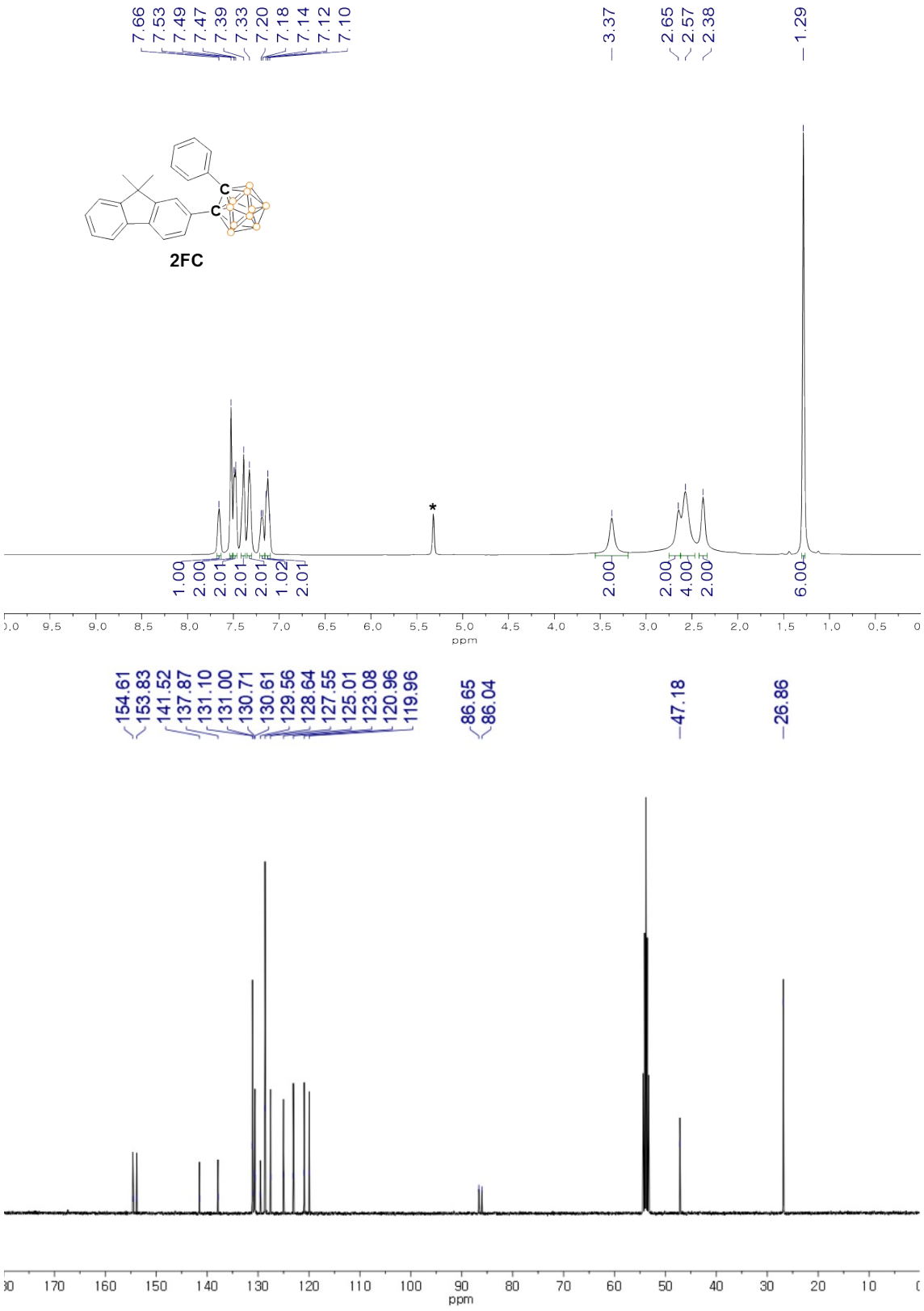

Fig. S6 $^{1}H\{^{11}B\}$ (top) and ^{13}C (bottom) NMR spectra of **2FC** in CD_2Cl_2 (∗ from residual CH_2Cl_2 in CD_2Cl_2).

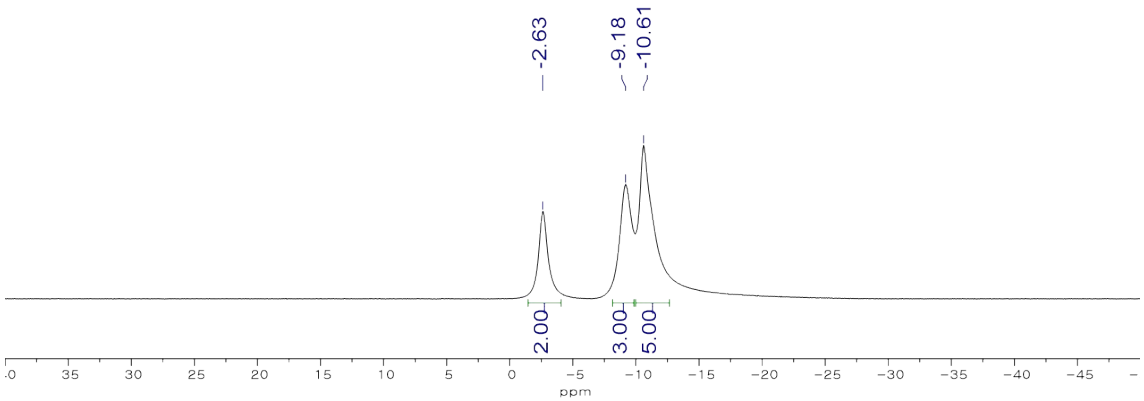

Fig. S7 $^{11}B\{^{1}H\}$ NMR spectra of **2FC** in CD_2Cl_2.

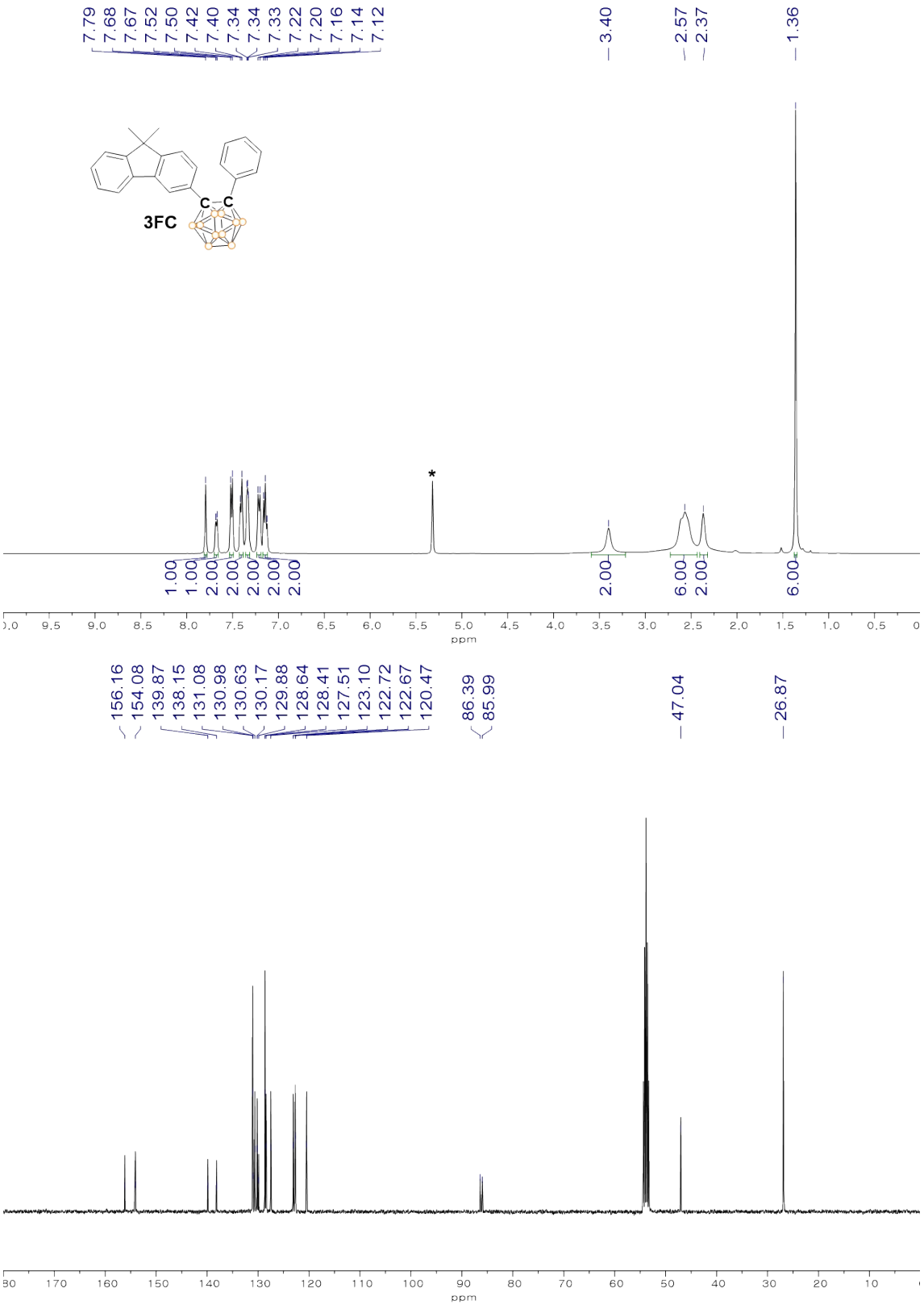

Fig. S8 $^{1}H\{^{11}B\}$ (top) and ^{13}C (bottom) NMR spectra of **3FC** in CD_2Cl_2 (∗ from residual CH_2Cl_2 in CD_2Cl_2).

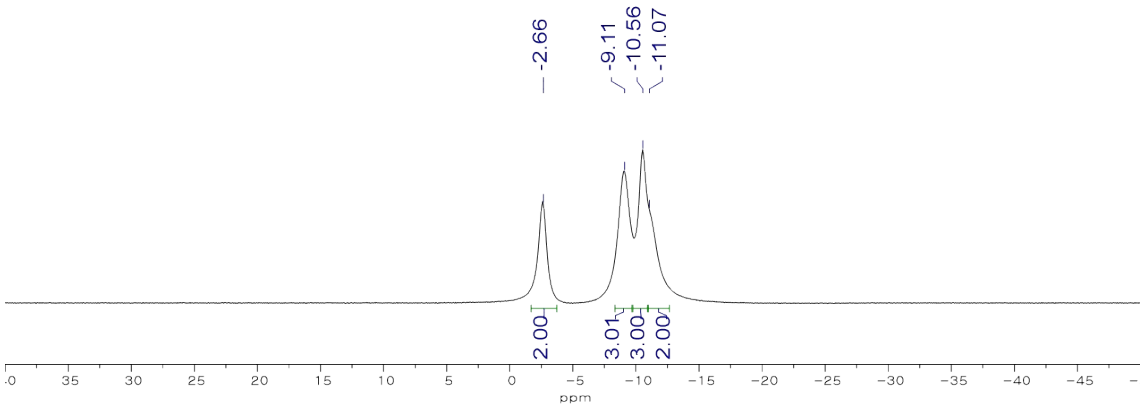

Fig. S9 $^{11}B\{^{1}H\}$ NMR spectra of **3FC** in CD_2Cl_2.

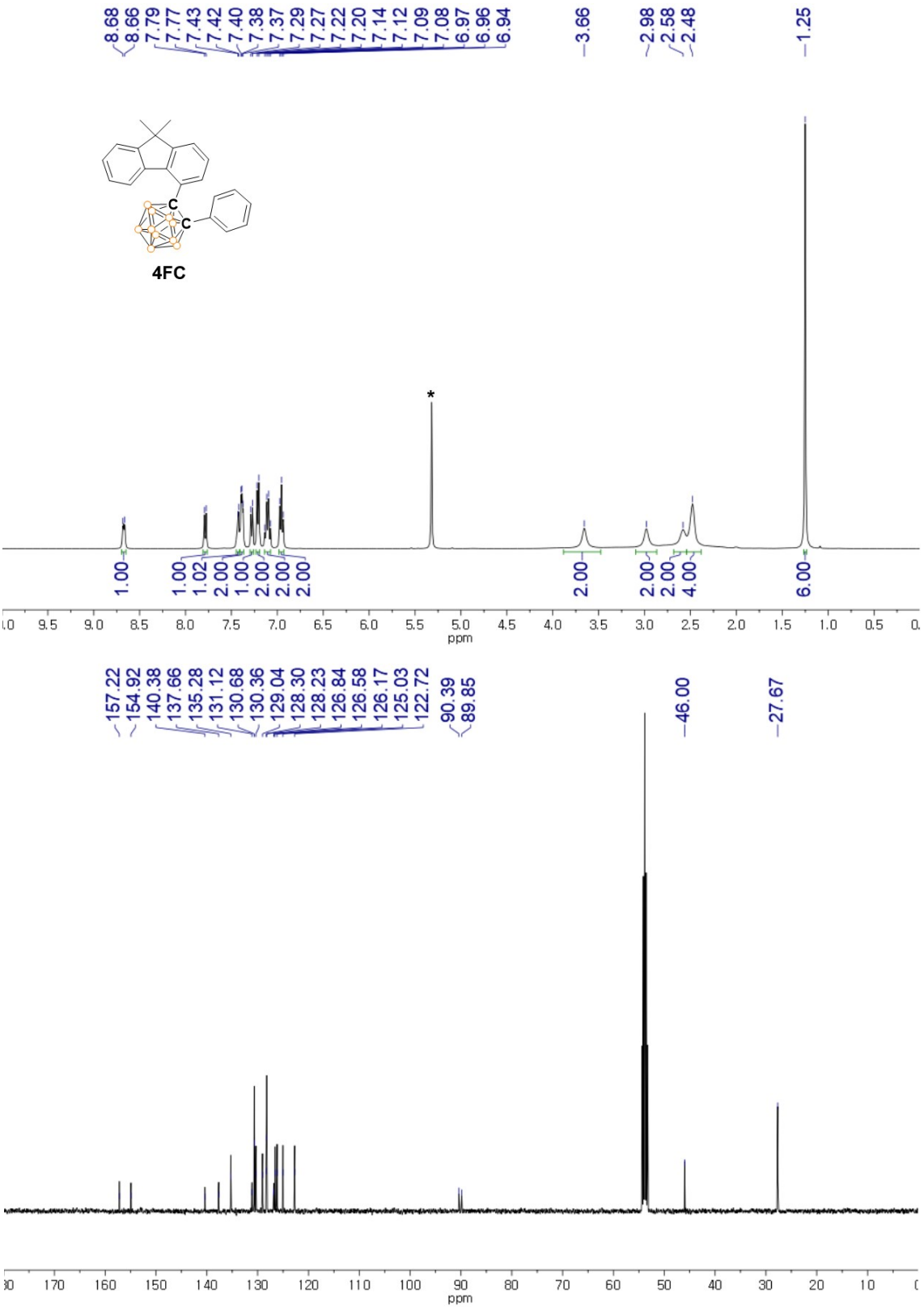

Fig. S10 $^{1}H\{^{11}B\}$ (top) and ^{13}C (bottom) NMR spectra of **4FC** in CD_2Cl_2 (∗ from residual CH_2Cl_2 in CD_2Cl_2).

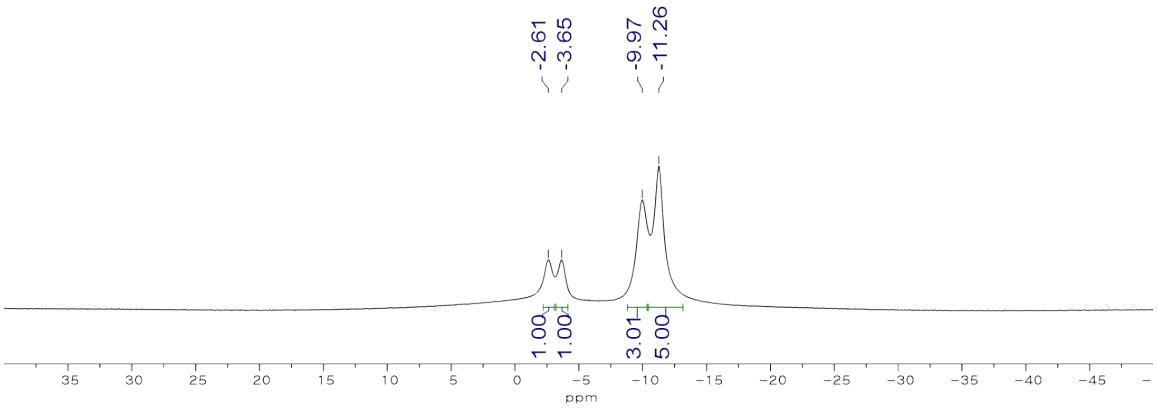

Fig. S11 $^{11}B\{^{1}H\}$ NMR spectra of **4FC** in CD_2Cl_2.

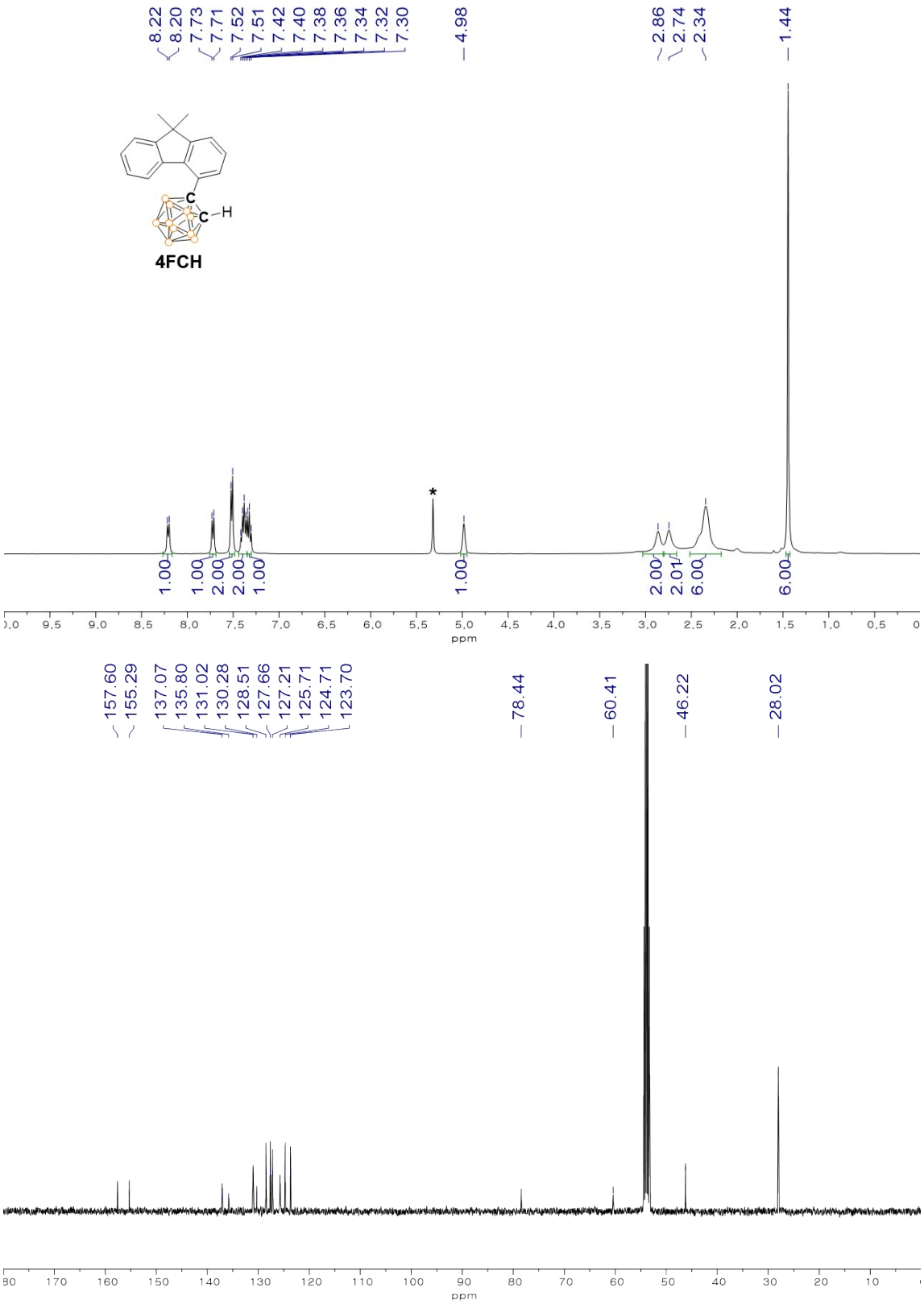

Fig. S12 $^{1}H\{^{11}B\}$ (top) and ^{13}C (bottom) NMR spectra of **4FCH** in CD_2Cl_2 (∗ from residual CH_2Cl_2 in CD_2Cl_2).

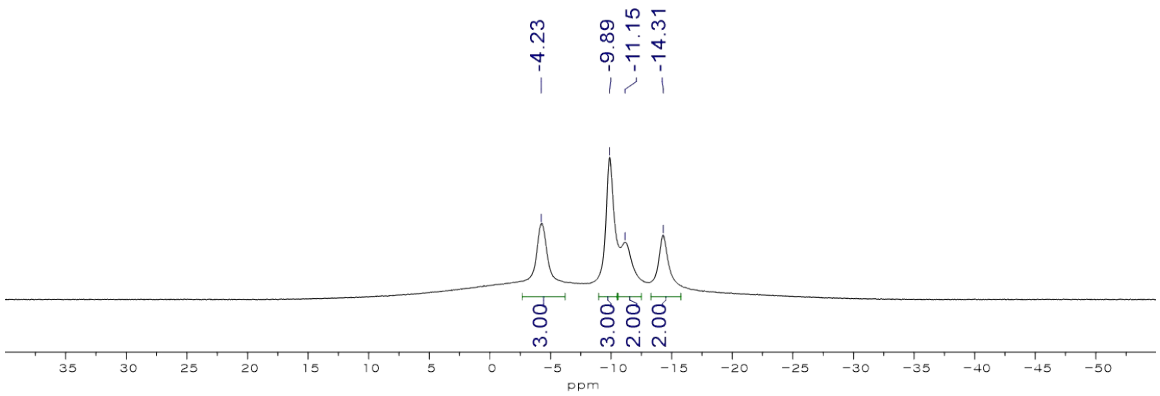

Fig. S13 $^{11}B\{^{1}H\}$ NMR spectra of **4FCH** in CD_2Cl_2.

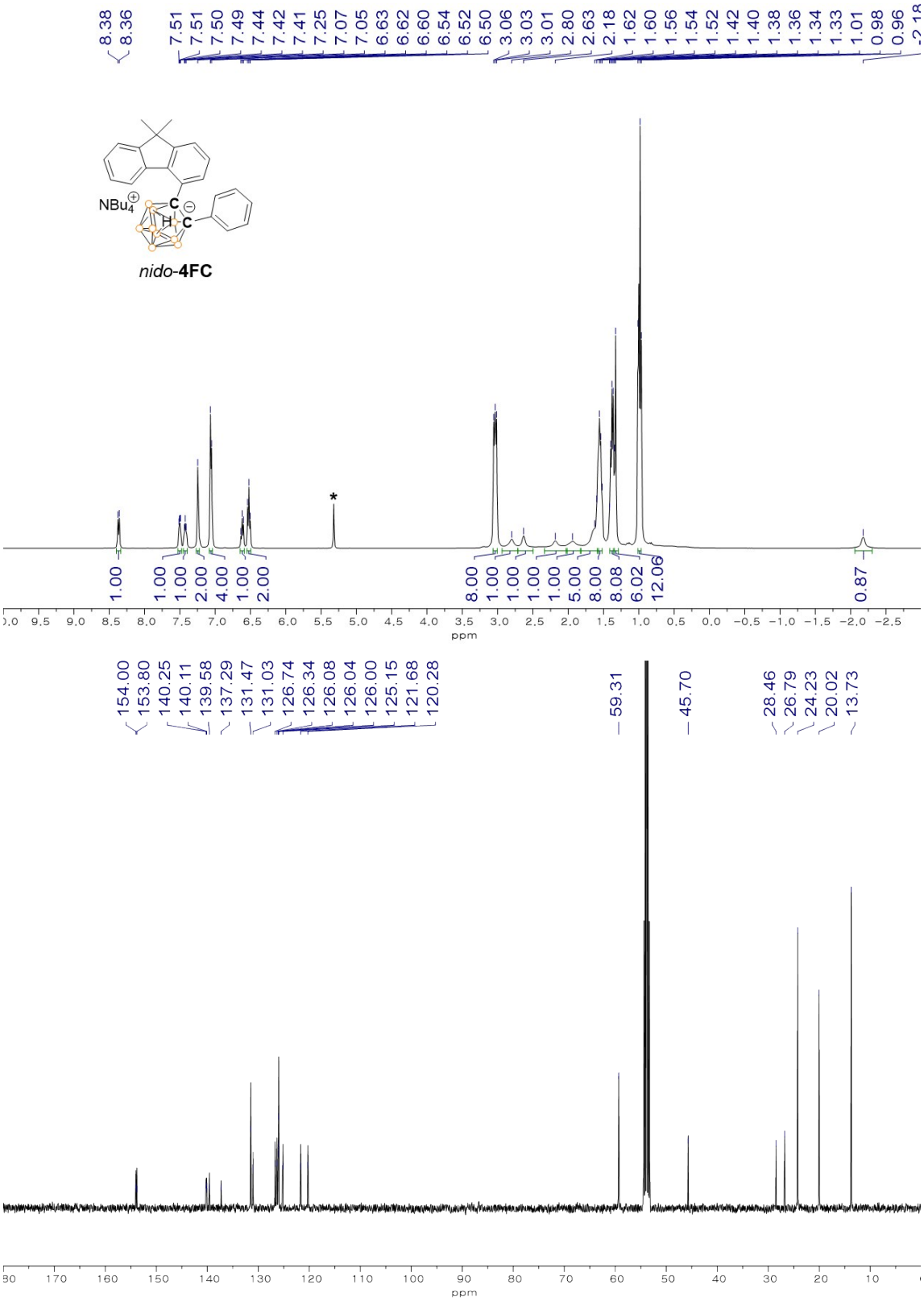

Fig. S14 $^{1}H\{^{11}B\}$ (top) and ^{13}C (bottom) NMR spectra of *nido*-**4FC** in CD_2Cl_2 (∗ from residual CH_2Cl_2 in CD_2Cl_2).

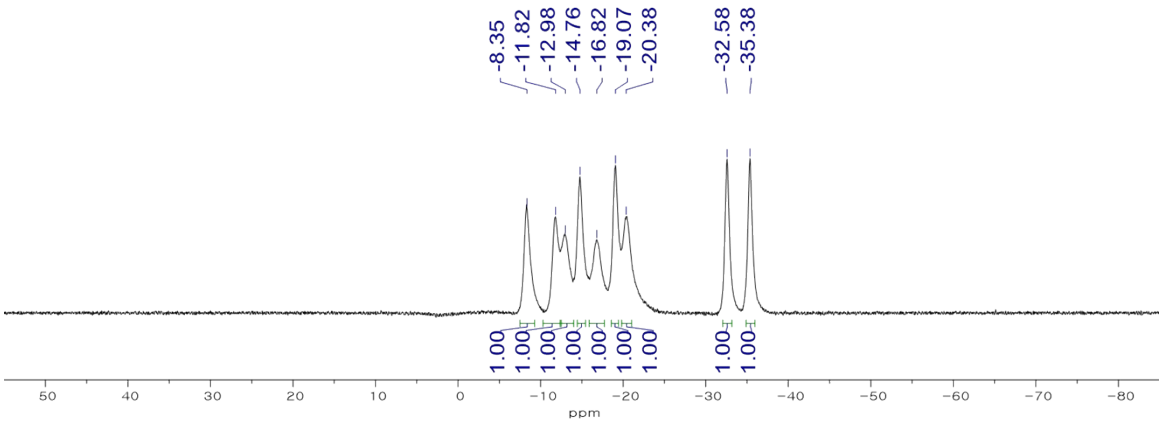

Fig. S15 $^{11}B\{^{1}H\}$ NMR spectra of *nido*-**4FC** in CD_2Cl_2.

Table S1 Crystallographic data and parameters for **2FC**, **3FC**, **4FC**, and **4FCH**

Compound	**2FC**	**3FC**	**4FC**·($^1/_2C_6H_{14}$)	**4FCH**
Formula	$C_{23}H_{28}B_{10}$	$C_{23}H_{28}B_{10}$	$C_{23}H_{28}B_{10}$·($^1/_2C_6H_{14}$)	$C_{17}H_{24}B_{10}$
Fomula weight	412.55	412.55	455.64	336.46
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	P_{-1}	P_{-1}	$P2_1/n$	$P2_1/n$
a (Å)	10.315(2)	11.777(2)	12.3205(4)	12.297(2)
b (Å)	10.817(2)	13.127(3)	10.0468(4)	10.173(2)
c (Å)	11.741(2)	15.795(3)	22.4474(8)	15.922(3)
α (°)	89.82(3)	90.00(3)	90	90
β (°)	77.69(3)	87.43(3)	99.6900(11)	98.61(3)
γ (°)	69.51(3)	90.00(3)	90	90
V (Å^3)	1195.3(5)	2439.4(8)	2738.93(17)	1969.4(7)
Z	2	4	4	4
ρ_{calc}(g cm^{-3})	1.146	1.123	1.105	1.135
μ (mm^{-1})	0.058	0.057	0.057	0.056
F(000)	432	864	964	704
T (K)	293(2)	293(2)	173(2)	293(2)
Scan mode	*multi*	*multi*	*multi*	*multi*
hkl range	–13 → +13, –12 → +14, –15 → +14	–14 → +15, –16 → +16, –20 → +20	–15 → +15, –12 → +12, –28 → +28	–15 → +15, –13 → +13, –20 → +20
Measd reflns	12089	24177	57059	19385
Unique reflns [R_{int}]	5455 [0.0410]	11002 [0.0785]	5977 [0.0768]	4526 [0.0573]
Reflns used for refinement	5455	11002	5977	4526
Refined parameters	300	599	388	250
R_1[a] (I>2σ(I))	0.0516	0.0751	0.0535	0.0722
wR_2[b] all data	0.1296	0.2190	0.1448	0.2709
GOF on F^2	1.004	1.006	1.052	1.029
ρ_{fin} (max/min) (e Å^{-3})	0.290, –0.368	0.282, –0.423	0.412, –0.241	0.528, –0.392

[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 **2FC**, **3FC**, **4FC**, and **4FCH**.

	2FC	**3FC**	**4FC**	**4FCH**
lengths				
C2–C14	1.4992(19)	–	–	–
C3–C14	–	1.506(3)	–	–
C4–C14	–	–	1.5096(16)	1.521(3)
C14–C15	1.746(2)	1.734(3)	1.7576(16)	1.745(3)
C15–C16	1.501(2)	1.501(3)	1.519(4)	–
angles				
C1–C2–C14	120.79(12)	–	–	–
C3–C2–C14	120.18(12)	–	–	–
C2–C3–C14	–	121.8(2)	–	–
C4–C3–C14	–	118.8(2)	–	–
C3–C4–C14	–	–	115.04(10)	113.6(2)
C11–C4–C14	–	–	127.43(10)	127.57(19)
C2–C14–C15	119.25(11)	–	–	–
C3–C14–C15	–	120.35(18)	–	–
C4–C14–C15	–	–	117.03(9)	116.86(18)
C14–C15–C16	118.92(11)	119.31(19)	117.08(18)	–

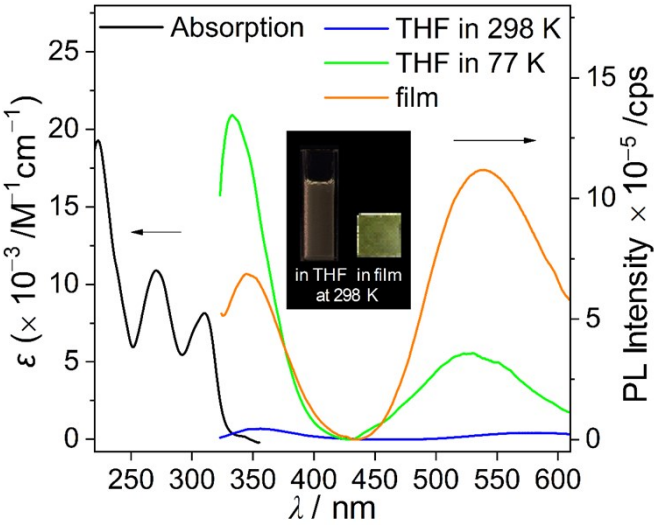

Fig. S16 UV-vis absorption (left side) and PL spectra (right side) for **4FCH** (λ_{ex} = 309 nm). Black line: absorption spectra in THF (3.0×10^{-5} M), blue line: PL spectra in THF (3.0×10^{-5} M) at 298 K, green line: PL spectra in THF (3.0×10^{-5} M) at 77 K, and orange line: PL spectra in film (5 wt% doped with PMMA) at 298 K. Inset figures show the emission color in each state under irradiation by a hand-held UV lamp (λ_{ex} = 265 nm).

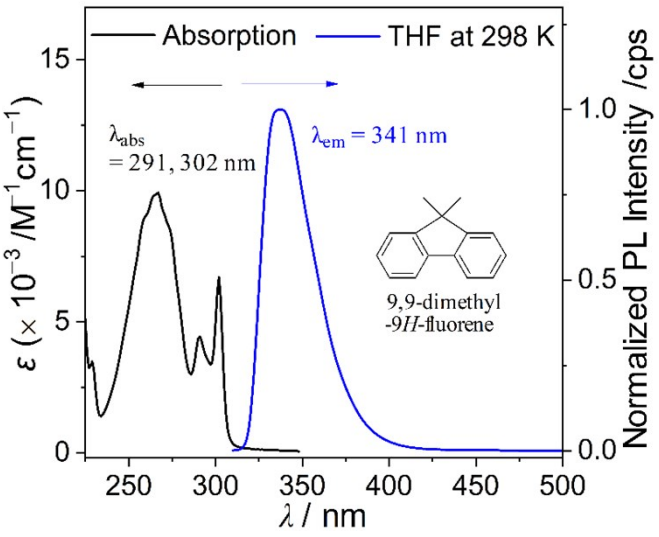

Fig. S17 UV-vis absorption and PL spectra for 9,9-dimethyl-9*H*-fluorene (λ_{ex} = 302 nm) in THF (3.0×10^{-5} M) at 298 K.

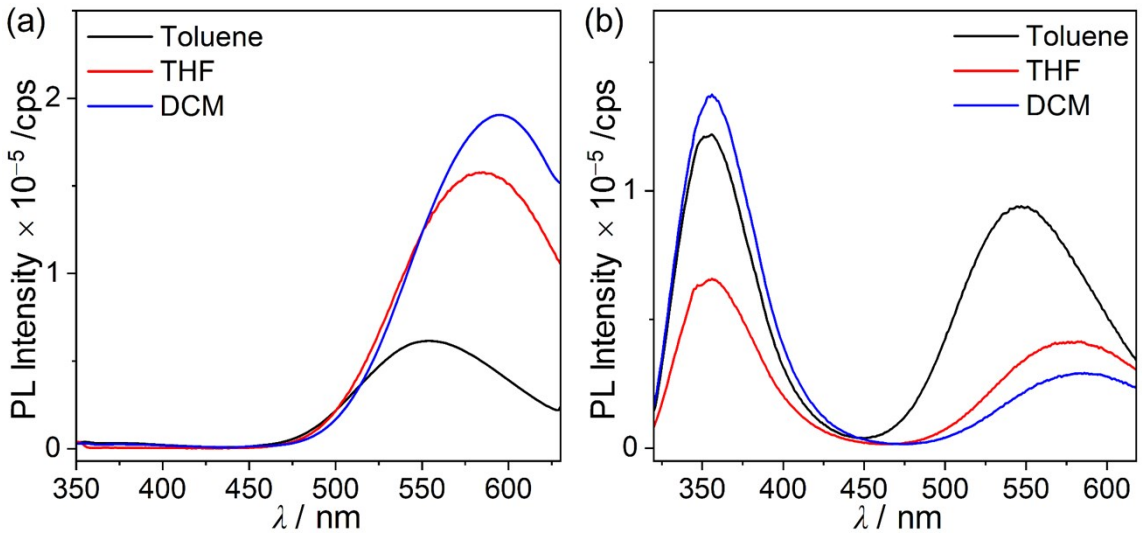

Fig. S18 PL spectra of (a) **4FC** (λ_{ex} = 318 nm) and (b) **4FCH** (λ_{ex} = 309 nm) in various organic solvents (3.0×10^{-5} M) at 298 K.

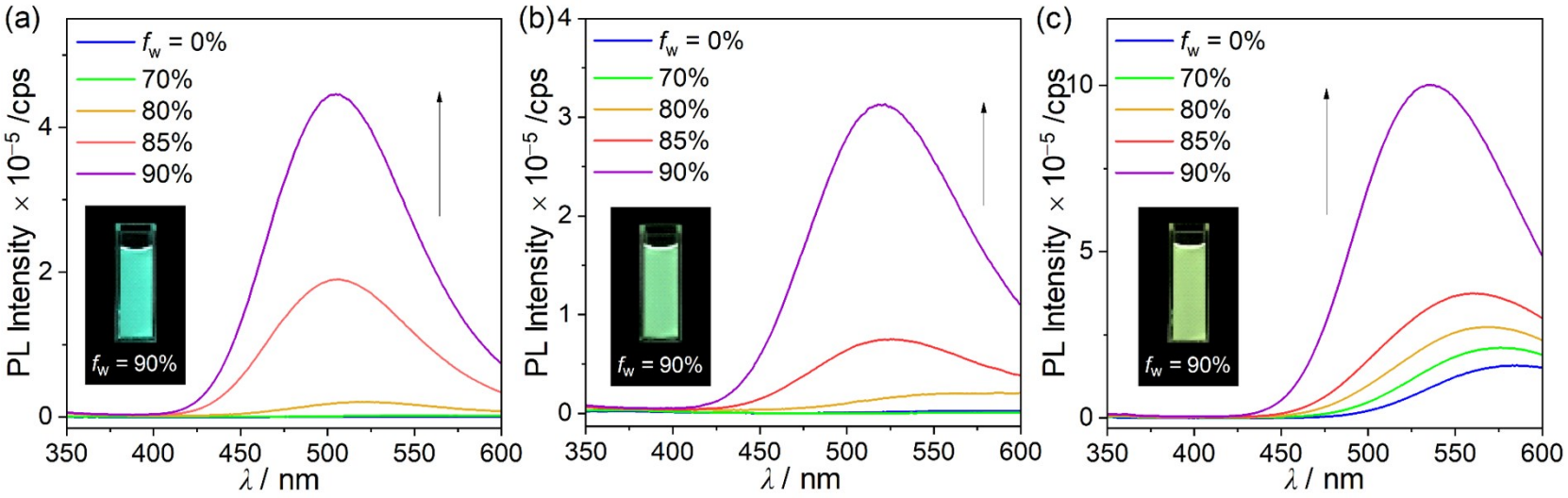

Fig. S19 PL spectra of (a) **2FC**, (b) **3FC**, and (c) **4FC** in THF/distilled water mixtures (3.0×10^{-5} M, λ_{ex} = 307 nm for **2FC**, 302 nm for **3FC**, and 318 nm for **4FC**). Inset figures show the emission color in each state under irradiation by a hand-held UV lamp (λ_{ex} = 265 nm).

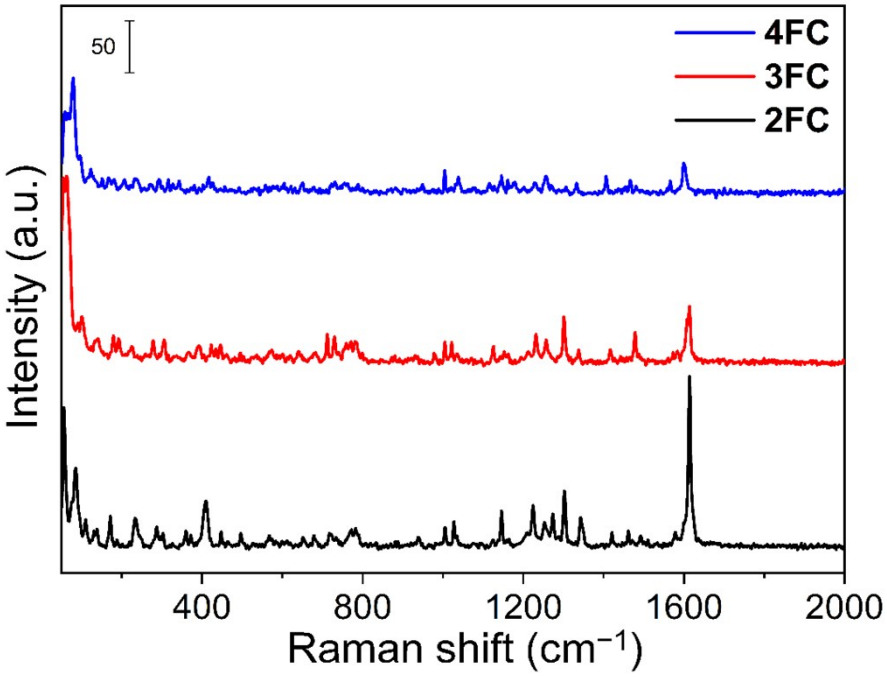

Fig. S20 Raman spectra of **2FC**, **3FC**, and **4FC** in THF (3.0×10^{-5} M) (Laser: 633 nm (He-Ne laser), Exposure time: 3 s, Object: ×100 vis, Power: 0.3 mW).

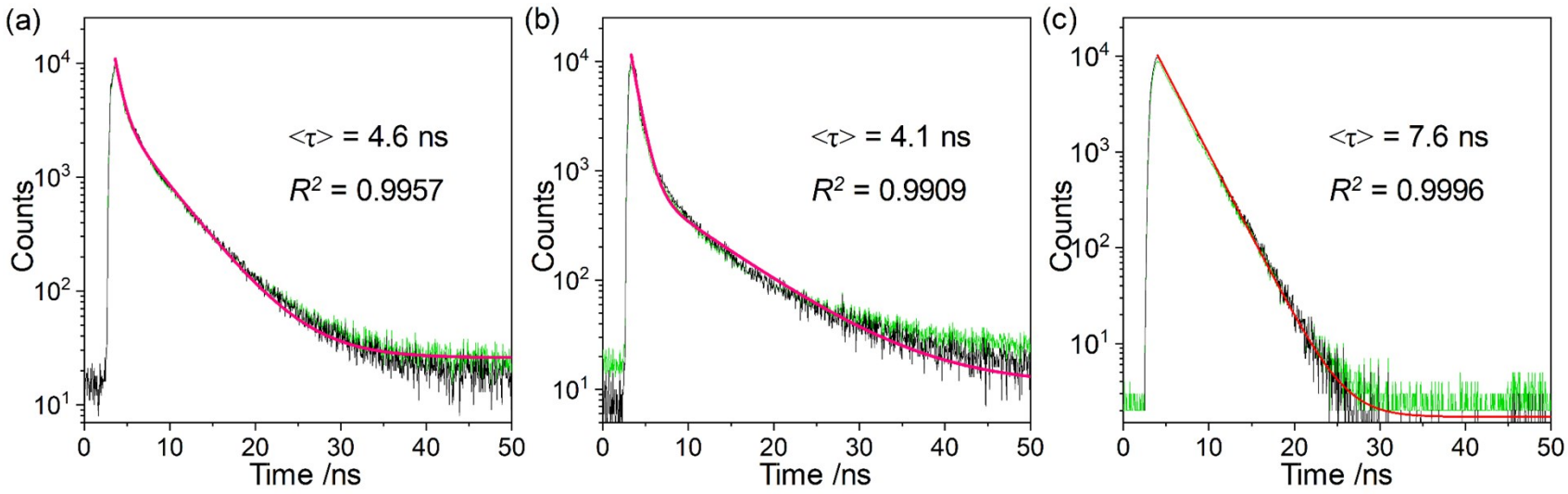

Fig. S21 Emission decay curves for (a) **2FC**, (b) **3FC**, and (c) **4FCH** in the film state (5 wt% doped in PMMA) detected at each ICT based emission maxima at both 298 K (black-line) and 77 K (green-line). Each red-line is its single exponential fitting curve for the decay curves at 298 K.

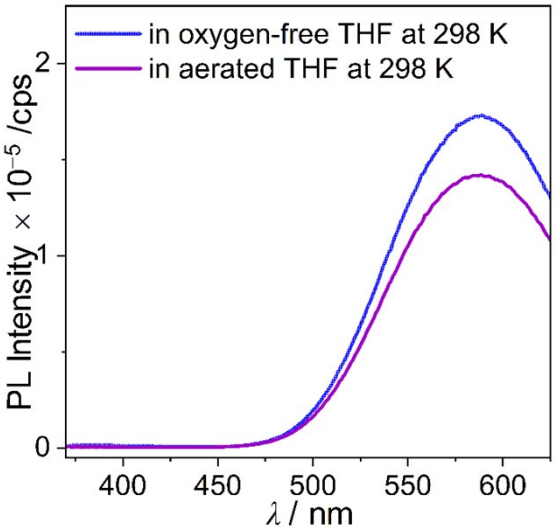

Fig. S22 PL spectra of **4FC** (λ_{ex} = 318 nm) in oxygen-free and aerated THF (3.0×10^{-5} M) at 298 K.

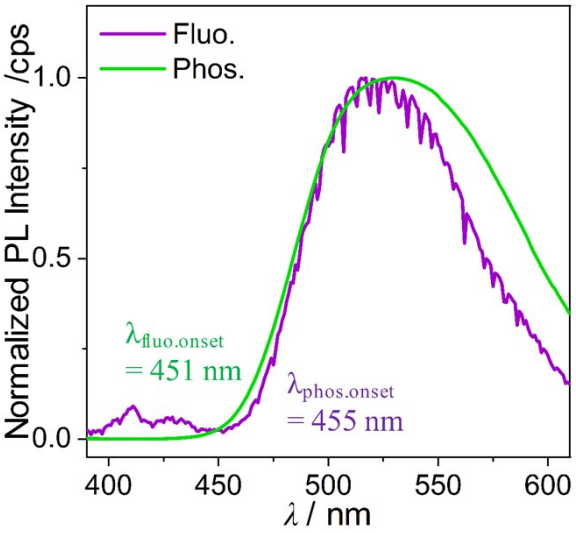

Fig. S23 Fluorescent (green solid line, prompt PL) and phosphorescent (purple solid line, 100 ns delayed PL) spectra of **4FC** in THF at 77 K (3.0×10^{-5} M, λ_{ex} = 318 nm).

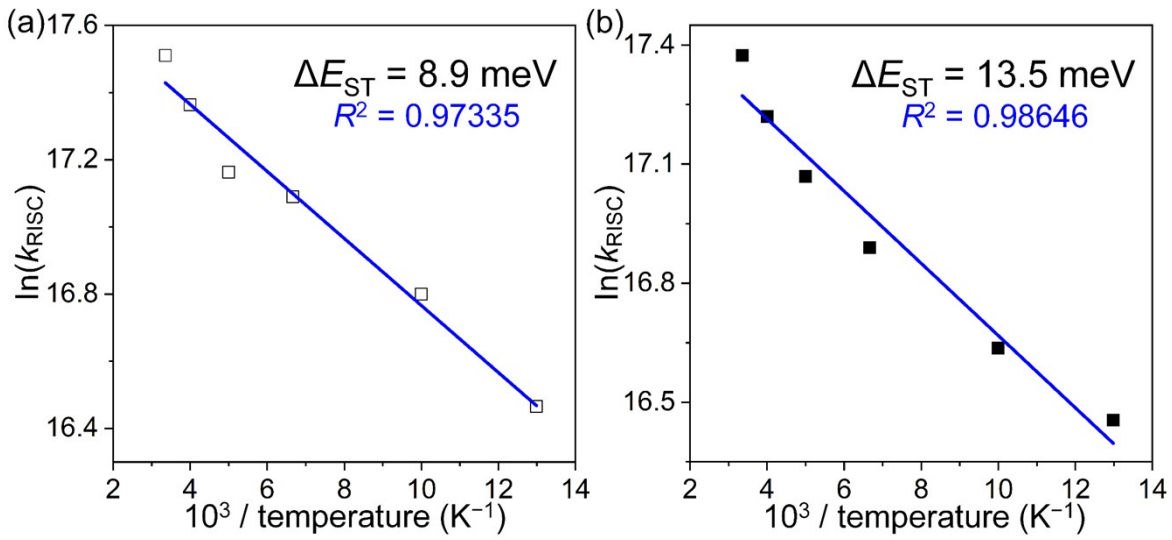

Fig. S24 Arrhenius plots of the RISC rate constant (k_{RISC}) of **4FC** (a) in THF and (b) film state. ΔE_{ST} of each state was determined from least-squares fitting

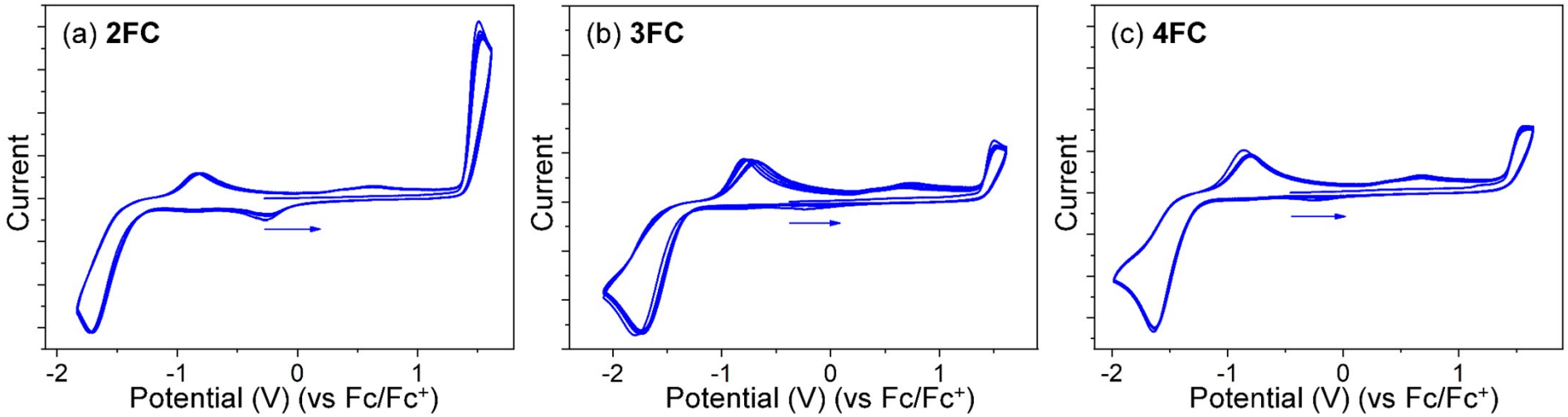

Fig. S25 Cyclic voltammograms of (a) **2FC**, (b) **3FC**, and (c) **4FC** showing oxidation and reduction on consecutive five-time cycles (5×10^{-4} M in DCM, scan rate = 100 mV/s).

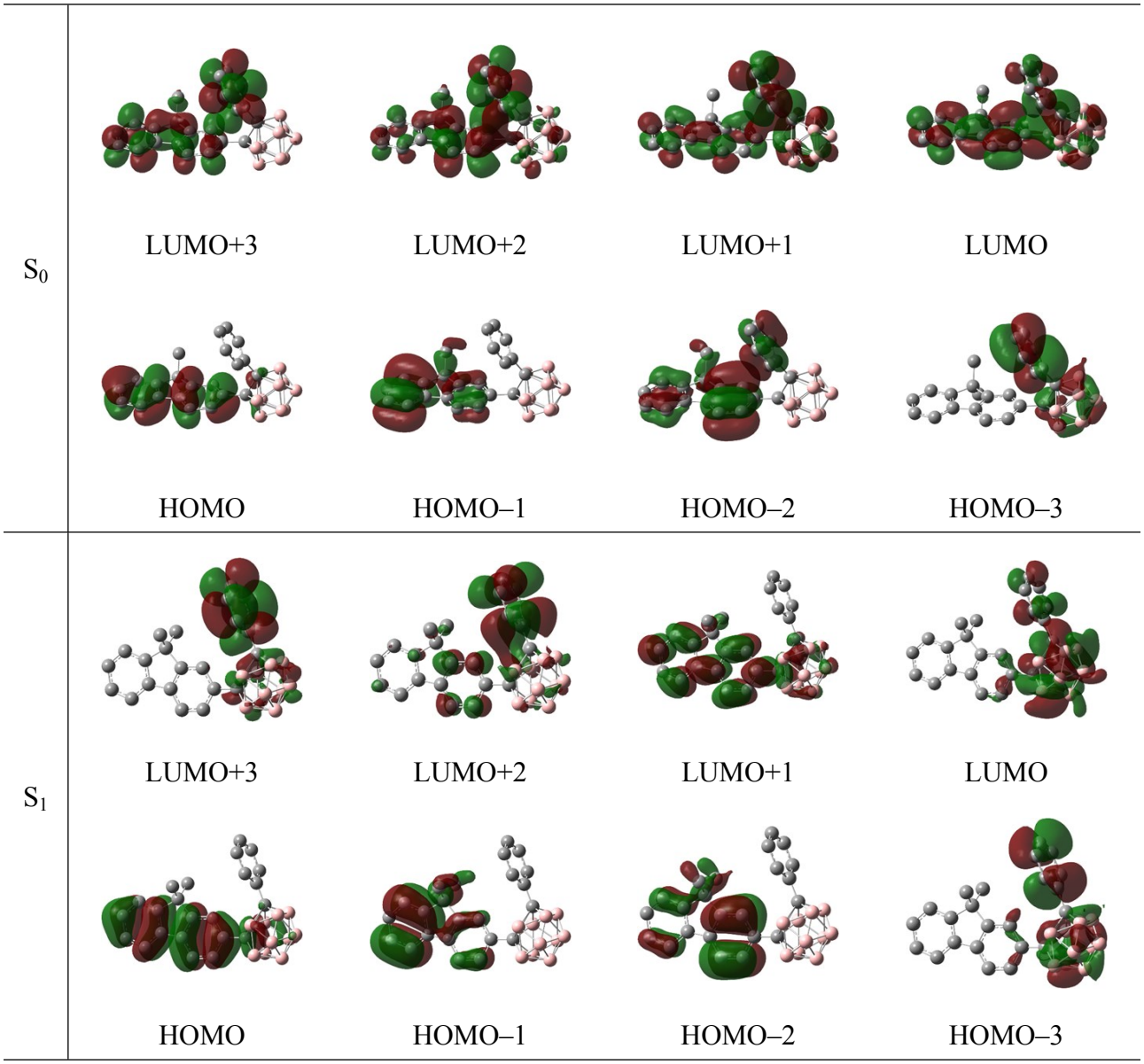

Fig. S26 The selected frontier orbitals of **2FC** from PBE0 calculations (Isovalue = 0.04 a.u.) at their ground state (S_0) and the first excited state (S_1) fully optimized geometries in THF.

Table S3 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **2FC** from TD-PBE0 calculations using the PBE0 geometries at their ground state (S_0) and the first excited state (S_1) fully optimized geometries in THF

state	λ_{calc} (nm)	f_{calc}	Major contribution
		S_0	
1	305.99	0.6475	HOMO → LUMO (97.7%)
2	273.36	0.0334	HOMO−2 → LUMO (25.7%)
			HOMO → LUMO+1 (37.2%)
			HOMO → LUMO+2 (25.1%)
3	269.03	0.0289	HOMO−2 → LUMO (8.7%)
			HOMO−1 → LUMO (60.7%)
			HOMO → LUMO+1 (9.7%)
			HOMO → LUMO+2 (7.6%)
			HOMO → LUMO+5 (8.0%)
4	266.69	0.1457	HOMO−1 → LUMO (19.1%)
			HOMO → LUMO+1 (50.4%)
			HOMO → LUMO+2 (15.1%)
5	250.39	0.0103	HOMO−4 → LUMO (60.3%)
			HOMO−2 → LUMO (19.3%)
		S_1	
1	488.25	0.2301	HOMO → LUMO (98.3%)
2	474.38	0.0010	HOMO−1 → LUMO (65.6%)
			HOMO−2 → LUMO (33.1%)
3	449.49	0.0002	HOMO−5 → LUMO (8.6%)
			HOMO−2 → LUMO (87.3%)
4	410.33	0.0038	HOMO−4 → LUMO (21.8%)
			HOMO−3 → LUMO (76.8%)
5	388.05	0.0488	HOMO−4 → LUMO (98.2%)

Table S4 Molecular orbital distributions (in %) and energies (in eV) of **2FC** at their ground state (S_0) and the first excited state (S_1) fully optimized geometries in THF

	E (eV)	carborane	phenyl	fluorene
		S_0		
LUMO+3	−0.37	3.2	53.0	43.8
LUMO+2	−0.71	10.4	34.2	55.4
LUMO+1	−1.04	19.3	51.3	29.4
LUMO	−1.60	30.2	11.2	58.6
HOMO	−6.12	3.9	0.2	96.0
HOMO−1	−6.82	0.1	0.3	99.7
HOMO−2	−7.04	0.7	13.5	85.8
HOMO−3	−7.16	11.4	88.0	0.6
		S_1		
LUMO+3	−0.52	12.3	87.0	0.7
LUMO+2	−0.65	8.3	79.5	12.2
LUMO+1	−1.31	10.2	0.3	89.5
LUMO	−3.72	83.6	14.2	2.2
HOMO	−5.69	6.7	0.0	93.3
HOMO−1	−6.82	0.2	0.1	99.7
HOMO−2	−7.03	1.7	0.1	98.2
HOMO−3	−7.28	18.5	79.9	1.5

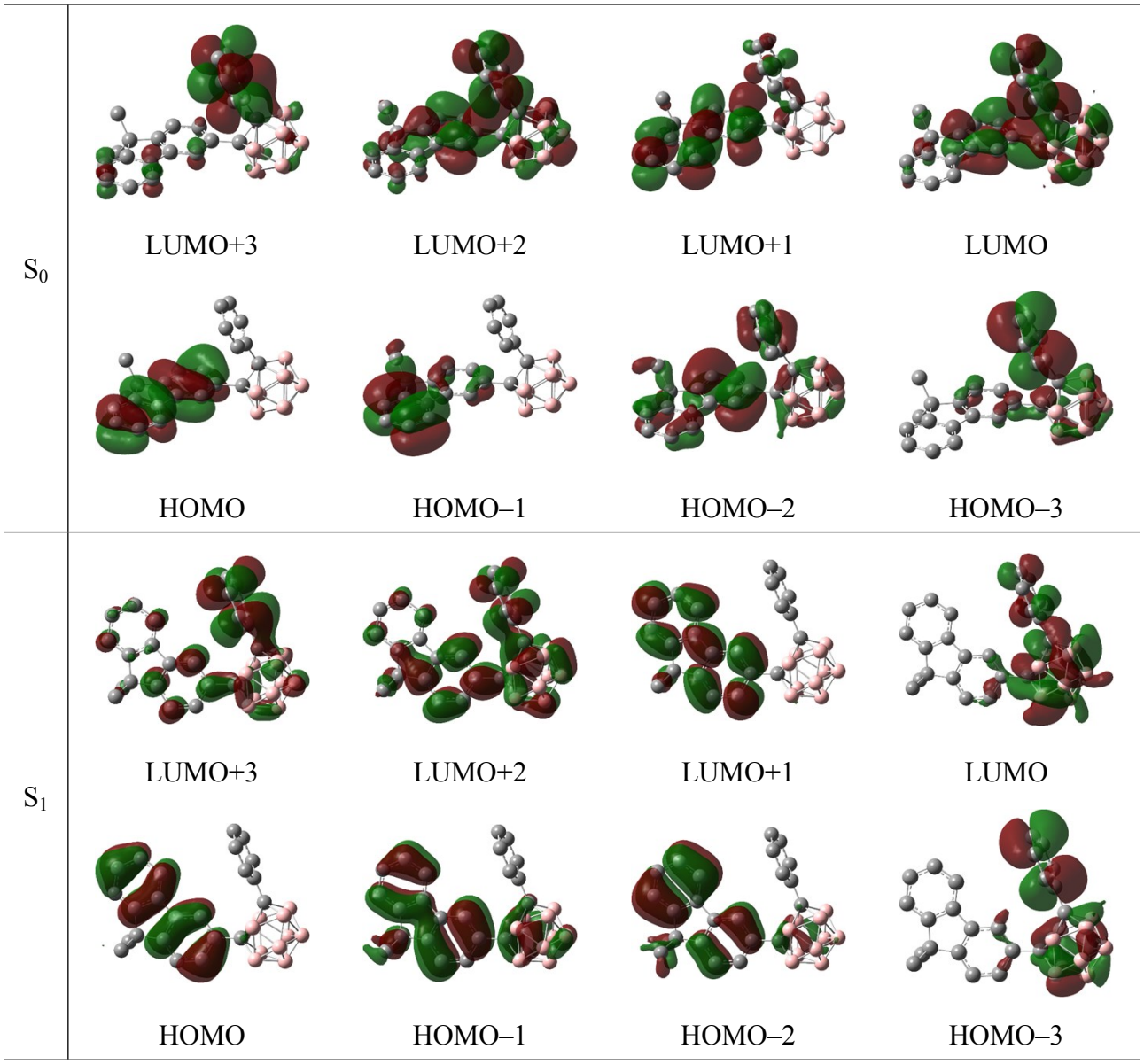

Fig. S27 The selected frontier orbitals of **3FC** from PBE0 calculations (Isovalue = 0.04 a.u.) at their ground state (S_0) and the first excited state (S_1) fully optimized geometries in THF.

Table S5 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **3FC** from TD-PBE0 calculations using the PBE0 geometries at their ground state (S_0) and the first excited state (S_1) fully optimized geometries in THF

state	λ_{calc} (nm)	f_{calc}	Major contribution
		S_0	
1	302.58	0.4473	HOMO–2 → LUMO+1 (2.9%)
			HOMO → LUMO (90.5%)
2	276.96	0.1264	HOMO → LUMO (5.8%)
			HOMO → LUMO+1 (81.9%)
3	265.99	0.0462	HOMO–2 → LUMO+1 (5.5%)
			HOMO → LUMO+1 (8.7%)
			HOMO → LUMO+2 (78.9%)
4	257.38	0.0250	HOMO–1 → LUMO (29.1%)
			HOMO–1 → LUMO+1 (39.4%)
			HOMO → LUMO+5 (22.3%)
5	250.26	0.0321	HOMO–1 → LUMO (61.8%)
			HOMO–1 → LUMO+1 (25.2%)
			HOMO → LUMO+5 (6.1%)
		S_1	
1	494.52	0.1894	HOMO → LUMO (98.9%)
2	442.93	0.0001	HOMO–2 → LUMO (13.9%)
			HOMO–1 → LUMO (83.4%)
3	406.45	0.0003	HOMO–2 → LUMO (85.1%)
			HOMO–1 → LUMO (14.6%)
4	382.14	0.0038	HOMO–3 → LUMO (98.7%)
5	372.47	0.0351	HOMO–4 → LUMO (98.4%)

Table S6 Molecular orbital distributions (in %) and energies (in eV) of **3FC** at their ground state (S_0) and the first excited state (S_1) fully optimized geometries in THF

	E (eV)	carborane	phenyl	fluorene
		S_0		
LUMO+3	–0.46	7.2	85.9	6.9
LUMO+2	–0.81	15.0	38.6	46.4
LUMO+1	–1.16	5.2	6.4	88.4
LUMO	–1.40	41.4	27.6	31.1
HOMO	–6.10	1.2	0.2	98.6
HOMO−1	–6.81	0.6	0.1	99.3
HOMO−2	–7.03	7.5	9.8	82.7
HOMO−3	–7.17	10.1	86.5	3.4
		S_1		
LUMO+3	–0.57	11.7	69.6	18.6
LUMO+2	–0.71	21.8	23.6	54.5
LUMO+1	–1.20	3.0	0.5	96.5
LUMO	–3.66	83.1	14.4	2.5
HOMO	–5.76	5.9	0.0	94.1
HOMO−1	–6.74	13.5	0.2	86.3
HOMO−2	–6.89	4.5	0.1	95.4
HOMO−3	–7.27	18.7	80.1	1.3

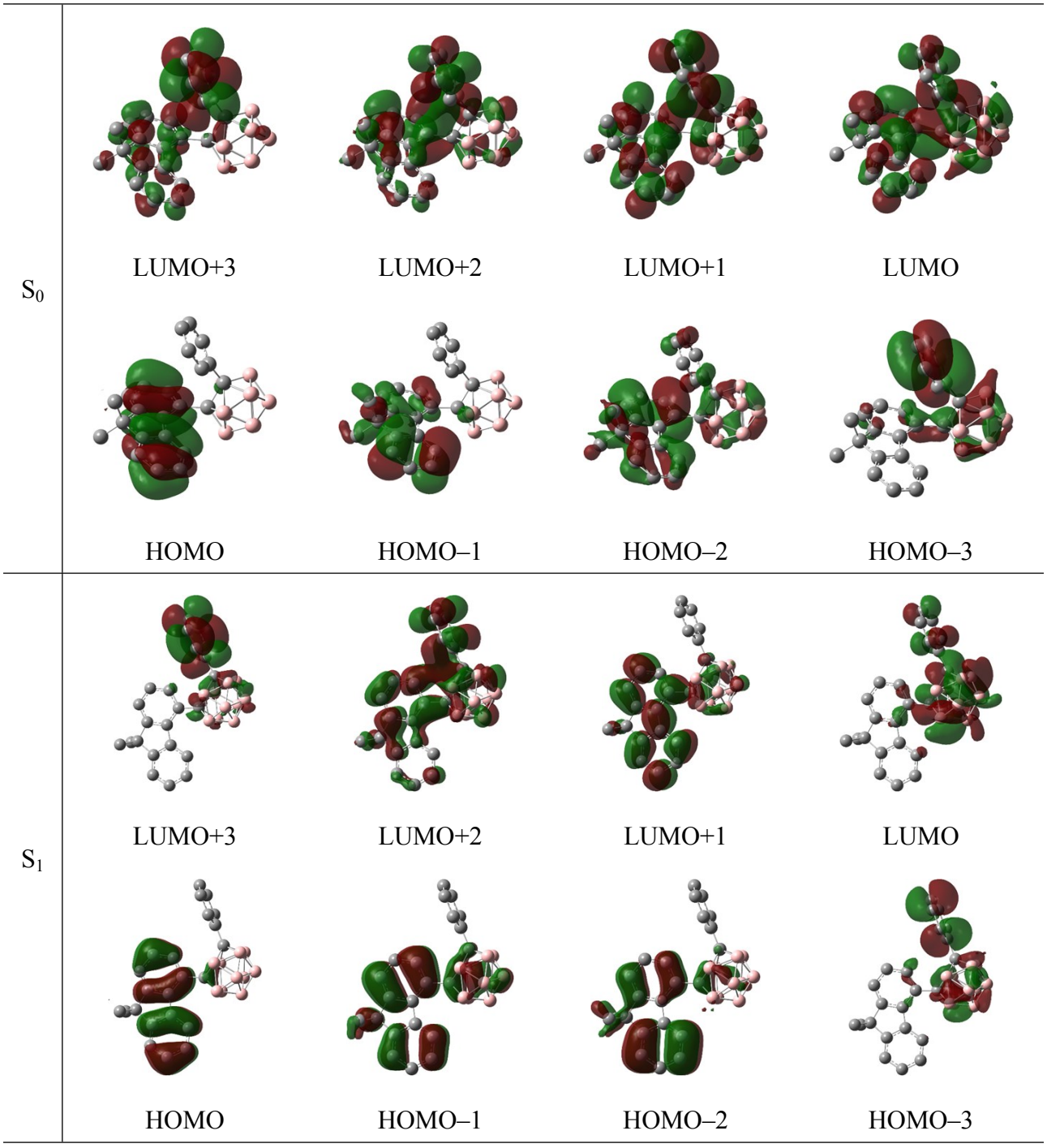

Fig. S28 The selected frontier orbitals of **4FC** from PBE0 calculations (Isovalue = 0.04 a.u.) at their ground state (S_0) and the first excited state (S_1) fully optimized geometries in THF.

Table S7 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **4FC** from TD-PBE0 calculations using the PBE0 geometries at their ground state (S_0) and the first excited state (S_1) fully optimized geometries in THF

state	λ_{calc} (nm)	f_{calc}	Major contribution
		S_0	
1	323.50	0.2787	HOMO → LUMO (96.9%)
2	285.75	0.0474	HOMO–1 → LUMO (89.8%)
3	275.73	0.1179	HOMO–2 → LUMO (33.3%)
			HOMO → LUMO+1 (58.2%)
4	273.58	0.0890	HOMO–2 → LUMO (42.1%)
			HOMO → LUMO+1 (33.6%)
			HOMO → LUMO+2 (17.3%)
5	261.39	0.0063	HOMO–4 → LUMO (77.9%)
			HOMO–3 → LUMO+1 (14.7%)
		S_1	
1	548.21	0.2214	HOMO → LUMO (98.8%)
2	478.38	0.0001	HOMO–2 → LUMO (14.4%)
			HOMO–1 → LUMO (83.0%)
3	418.76	0.0030	HOMO–2 → LUMO (84.2%)
			HOMO–1 → LUMO (15.3%)
4	407.02	0.0031	HOMO–3 → LUMO (99.2%)
5	373.38	0.0815	HOMO–4 → LUMO (98.9%)

Table S8 Molecular orbital distributions (in %) and energies (in eV) of **4FC** at their ground state (S_0) and the first excited state (S_1) fully optimized geometries in THF

	E (eV)	carborane	phenyl	fluorene
		S_0		
LUMO+3	−0.40	4.9	72.4	22.6
LUMO+2	−0.73	12.3	34.1	53.7
LUMO+1	−1.12	16.6	35.2	48.2
LUMO	−1.79	38.9	12.5	48.6
HOMO	−6.13	1.3	0.2	98.6
HOMO−1	−6.73	1.7	0.5	97.8
HOMO−2	−6.98	9.1	6.0	84.9
HOMO−3	−7.16	10.7	85.1	4.2
		S_1		
LUMO+3	−0.50	11.1	88.1	0.8
LUMO+2	−0.69	16.7	40.2	43.0
LUMO+1	−1.36	9.9	0.1	89.9
LUMO	−3.72	84.6	13.5	1.9
HOMO	−5.79	1.4	0.0	98.6
HOMO−1	−6.70	12.7	0.2	87.1
HOMO−2	−6.83	6.2	0.1	93.8
HOMO−3	−7.22	17.0	81.4	1.6

Table S9 Cartesian coordinates of the ground state (S_0) fully optimized geometry of **2FC** in THF from PBE0 calculations (in Å)

Atom	X	Y	Z
C	-2.825263	0.392881	-0.088949
C	-1.908726	-1.054788	-0.013381
B	-4.144284	0.297189	0.982725
B	-4.363337	0.076851	-0.756657
B	-4.048784	-1.301406	1.741842
B	-5.164113	-1.021831	0.383523
B	-4.219407	-2.520748	0.459633
B	-4.399415	-1.662498	-1.089527
B	-2.615188	-2.130456	1.110695
B	-2.832600	-2.348892	-0.627431
B	-2.922188	-0.744849	-1.365877
B	-2.575994	-0.393087	1.418193
H	-4.479461	1.303739	1.513493
H	-4.841540	0.934188	-1.422932
H	-6.344864	-0.986977	0.528356
H	-4.406027	-1.465344	2.864536
H	-1.864258	0.109179	2.214162
H	-2.409242	-0.498810	-2.400367
H	-5.006850	-2.096975	-2.015376
H	-4.705645	-3.589630	0.653203
H	-1.873116	-2.822756	1.725071
H	-2.251273	-3.204397	-1.207527
C	-2.115185	1.696950	-0.316011
C	-1.768708	2.119746	-1.602977
C	-1.828622	2.533019	0.769110
C	-1.130976	3.340671	-1.796309
H	-2.000361	1.501244	-2.461696
C	-1.192367	3.753561	0.572542
H	-2.111604	2.236529	1.772998
C	-0.836002	4.159546	-0.710448
H	-0.867855	3.651029	-2.802784
H	-0.979163	4.388601	1.426870
H	-0.337934	5.112091	-0.863685
C	-0.427754	-0.984583	-0.248038
C	0.442565	-0.475471	0.725869
C	0.097838	-1.455975	-1.459777
C	1.802487	-0.432898	0.471305
H	0.056230	-0.115830	1.672649
C	1.463862	-1.424234	-1.714088
H	-0.569167	-1.860166	-2.213031
C	2.910487	0.090222	1.369649
C	2.319232	-0.905551	-0.745311
H	1.845445	-1.799290	-2.659131
C	4.132223	-0.155428	0.499440
C	3.771712	-0.735735	-0.728482
C	5.464412	0.116395	0.778652
C	4.737743	-1.047943	-1.683441
C	6.433115	-0.195910	-0.176902
H	5.756575	0.564801	1.724908
C	6.072491	-0.772746	-1.396723
H	4.460392	-1.497256	-2.633071
H	7.479067	0.011488	0.030010
H	6.840461	-1.008883	-2.127485
C	2.989623	-0.701215	2.683276
H	3.833964	-0.354391	3.287525
H	2.076332	-0.564035	3.271298
H	3.119114	-1.770189	2.492316
C	2.724739	1.586624	1.663751
H	3.565268	1.967389	2.252635
H	2.661256	2.165362	0.737953
H	1.807250	1.755109	2.236976

Table S10 Cartesian coordinates of the first excited state (S_1) fully optimized geometry of **2FC** in THF from PBE0 calculations (in Å)

Atom	X	Y	Z
C	3.014062	0.464676	0.000159
C	1.632747	-1.546361	-0.000091
B	4.239065	-0.098928	-0.897459
B	4.239007	-0.098957	0.897793
B	3.992245	-1.769347	-1.422282
B	5.025313	-1.414153	0.000143
B	4.027272	-2.861543	0.000037
B	3.992086	-1.769441	1.422420
B	2.525122	-2.584830	-0.888174
B	2.525046	-2.584821	0.888083
B	2.513341	-0.701744	1.177575
B	2.513528	-0.701635	-1.177537
H	4.787520	0.681581	-1.611756
H	4.787425	0.681479	1.612197
H	6.216025	-1.505265	0.000233
H	4.442700	-2.076238	-2.484232
H	1.891103	-0.300762	-2.112516
H	1.890825	-0.301019	2.112559
H	4.442397	-2.076423	2.484406
H	4.539467	-3.940134	0.000041
H	1.943511	-3.351782	-1.591715
H	1.943304	-3.351795	1.591498
C	2.496446	1.835968	0.000083
C	2.229403	2.508090	1.205847
C	2.229960	2.508214	-1.205734
C	1.714781	3.799274	1.203635
H	2.433796	2.008151	2.147622
C	1.715336	3.799394	-1.203626
H	2.434791	2.008377	-2.147468
C	1.450581	4.452073	-0.000022
H	1.521927	4.300249	2.148150
H	1.522910	4.300456	-2.148181
H	1.047784	5.460424	-0.000060
C	0.175665	-1.491277	-0.000164
C	-0.478391	-0.233822	-0.000150
C	-0.597424	-2.691185	-0.000189
C	-1.846355	-0.186634	-0.000109
H	0.119560	0.671844	-0.000163
C	-1.968548	-2.655654	-0.000143
H	-0.072869	-3.640167	-0.000242
C	-2.756085	1.025808	-0.000083
C	-2.608587	-1.395248	-0.000084
H	-2.547981	-3.572706	-0.000155
C	-4.116477	0.357443	0.000025
C	-3.994049	-1.060163	0.000001
C	-5.369916	0.939915	0.000107
C	-5.130977	-1.892412	0.000060
C	-6.492395	0.107984	0.000172
H	-5.490590	2.018587	0.000118
C	-6.374734	-1.295132	0.000148
H	-5.030388	-2.972648	0.000041
H	-7.482720	0.552316	0.000243
H	-7.272111	-1.904142	0.000199
C	-2.549796	1.878494	-1.261809
H	-3.263320	2.707595	-1.276901
H	-1.540551	2.300662	-1.272253
H	-2.687713	1.285550	-2.169877
C	-2.549597	1.878632	1.261498
H	-3.263113	2.707740	1.276613
H	-2.687373	1.285800	2.169663
H	-1.540346	2.300800	1.271741

Table S11 Cartesian coordinates of the ground state (S_0) fully optimized geometry of **3FC** in THF from PBE0 calculations (in Å)

Atom	X	Y	Z
C	2.843042	0.272783	0.222702
C	1.804036	-1.008747	-0.259326
B	4.425626	-0.027514	-0.332443
B	3.980809	-0.299719	1.355204
B	4.361215	-1.580737	-1.182260
B	4.957251	-1.503478	0.493022
B	3.885771	-2.826355	-0.003831
B	3.636582	-2.025213	1.565192
B	2.690864	-2.169689	-1.137776
B	2.245445	-2.441935	0.549867
B	2.312446	-0.880204	1.373244
B	3.023184	-0.444154	-1.323819
H	5.069783	0.917830	-0.646851
H	4.315772	0.458559	2.203936
H	6.103962	-1.661585	0.769502
H	5.059283	-1.792592	-2.121803
H	2.707569	0.175410	-2.277399
H	1.529451	-0.556390	2.194177
H	3.808856	-2.559176	2.614047
H	4.244122	-3.957809	-0.091954
H	2.118705	-2.725590	-2.015874
H	1.366128	-3.185312	0.835633
C	2.304799	1.672988	0.296242
C	1.702065	2.149344	1.465092
C	2.452200	2.543050	-0.789497
C	1.236847	3.458004	1.536567
H	1.602574	1.503733	2.329673
C	1.987234	3.851315	-0.714541
H	2.941978	2.204671	-1.695377
C	1.372660	4.312109	0.446203
H	0.770402	3.808980	2.451867
H	2.110847	4.511435	-1.567491
H	1.008977	5.333553	0.503517
C	-0.007226	-0.427541	-1.908352
C	-1.338890	-0.187150	-2.241294
C	0.368678	-0.714978	-0.589330
C	-2.307123	-0.238724	-1.250711
H	-1.600767	0.032400	-3.272718
C	-0.613089	-0.785077	0.405613
H	0.743079	-0.402044	-2.689628
C	-3.804783	-0.017474	-1.363826
C	-1.940346	-0.543733	0.069818
H	-0.345705	-1.036329	1.425870
C	-4.244718	-0.241541	0.073789
C	-3.148571	-0.548329	0.896936
C	-5.523938	-0.177619	0.608663
C	-3.323199	-0.794179	2.257303
C	-5.700599	-0.423391	1.971552
H	-6.379903	0.059352	-0.018326
C	-4.609566	-0.729198	2.787756
H	-2.477029	-1.032893	2.895848
H	-6.696757	-0.376780	2.402014
H	-4.765983	-0.918204	3.845781
C	-4.449054	-1.038785	-2.313073
H	-5.535815	-0.909003	-2.330557
H	-4.077033	-0.903813	-3.333782
H	-4.229934	-2.062909	-1.998282
C	-4.122270	1.410934	-1.831190
H	-5.204420	1.575410	-1.842813
H	-3.668321	2.152833	-1.168263
H	-3.744893	1.576902	-2.845311

Table S12 Cartesian coordinates of the first excited state (S_1) fully optimized geometry of **3FC** in THF from PBE0 calculations (in Å)

Atom	X	Y	Z
C	2.952809	0.619540	-0.001835
C	1.719361	-1.456404	-0.003851
B	4.212002	0.148353	-0.908040
B	4.220157	0.141079	0.888348
B	4.083568	-1.529622	-1.439976
B	5.092722	-1.113132	-0.018868
B	4.189363	-2.621355	-0.020672
B	4.097257	-1.541196	1.408344
B	2.667381	-2.429828	-0.901222
B	2.676267	-2.437020	0.876587
B	2.548565	-0.582706	1.184633
B	2.537749	-0.572450	-1.193014
H	4.702929	0.972495	-1.616068
H	4.718180	0.959266	1.598310
H	6.287137	-1.123144	-0.024324
H	4.557140	-1.807705	-2.500270
H	1.886814	-0.208523	-2.124641
H	1.907148	-0.224561	2.125006
H	4.581644	-1.827335	2.461593
H	4.767112	-3.666778	-0.027650
H	2.131160	-3.234537	-1.600540
H	2.147821	-3.247852	1.574728
C	2.337600	1.948313	0.009217
C	2.038742	2.597452	1.220740
C	2.003512	2.602769	-1.190080
C	1.428748	3.845918	1.230490
H	2.293768	2.111853	2.157632
C	1.393085	3.851256	-1.176180
H	2.231091	2.121752	-2.136324
C	1.097385	4.480255	0.033173
H	1.212834	4.328573	2.179642
H	1.149601	4.338245	-2.116418
H	0.621664	5.456362	0.042401
C	-0.435458	-2.756511	0.014884
C	-1.827526	-2.861059	0.021610
C	0.246655	-1.501390	0.000857
C	-2.570362	-1.699328	0.012396
H	-2.298254	-3.838530	0.033527
C	-0.500274	-0.337405	-0.008762
H	0.165108	-3.660360	0.021185
C	-4.073266	-1.519767	0.017366
C	-1.898642	-0.430512	-0.004569
H	-0.008653	0.629363	-0.020280
C	-4.175281	-0.005773	-0.003896
C	-2.885050	0.597523	-0.016166
C	-5.304122	0.788073	-0.011748
C	-2.728921	1.999784	-0.037518
C	-5.141575	2.177631	-0.032142
H	-6.300027	0.357239	-0.002525
C	-3.866838	2.777975	-0.045109
H	-1.741790	2.450452	-0.048598
H	-6.021140	2.813435	-0.038486
H	-3.789225	3.859354	-0.061502
C	-4.698232	-2.105901	1.293103
H	-5.773970	-1.908414	1.308949
H	-4.553682	-3.189641	1.322408
H	-4.251908	-1.671275	2.191325
C	-4.713856	-2.143873	-1.232024
H	-5.789813	-1.946969	-1.240359
H	-4.278996	-1.736644	-2.148519
H	-4.569815	-3.228126	-1.230558

Table S13 Cartesian coordinates of the ground state (S_0) fully optimized geometry of **4FC** in THF from PBE0 calculations (in Å)

Atom	X	Y	Z
C	-2.244251	0.225676	-0.429534
C	-1.378336	-0.683951	0.792644
B	-3.926500	0.055540	-0.212815
B	-3.073340	-0.846783	-1.462401
B	-4.133732	-0.994526	1.194346
B	-4.278785	-1.664329	-0.449898
B	-3.421047	-2.573787	0.804231
B	-2.745096	-2.474071	-0.840876
B	-2.528871	-1.420089	1.818416
B	-1.684098	-2.334095	0.570313
B	-1.478951	-1.242819	-0.818379
B	-2.837649	0.192367	1.168730
H	-4.596135	0.996402	-0.484427
H	-3.143445	-0.538920	-2.605969
H	-5.320822	-2.009632	-0.909553
H	-5.053486	-0.850767	1.934963
H	-2.784292	1.183377	1.804470
H	-0.519640	-1.206299	-1.495263
H	-2.658762	-3.404391	-1.577198
H	-3.826741	-3.593766	1.264043
H	-2.231755	-1.527807	2.962028
H	-0.821075	-3.087157	0.872805
C	-1.657556	1.514786	-0.928124
C	-2.144970	2.733511	-0.442489
C	-0.659253	1.531283	-1.907955
C	-1.636176	3.938142	-0.914597
H	-2.933554	2.745084	0.301501
C	-0.149276	2.738179	-2.375374
H	-0.277481	0.603331	-2.316024
C	-0.632278	3.945339	-1.878687
H	-2.029169	4.872651	-0.526252
H	0.625399	2.730024	-3.136074
H	-0.233515	4.886181	-2.245804
C	-0.088731	-0.101230	1.323570
C	-0.229448	0.758540	2.426336
C	1.220025	-0.273158	0.792994
C	0.808023	1.530055	2.925964
H	-1.195064	0.835536	2.907405
C	2.234726	0.599716	1.257244
C	1.881361	-1.202940	-0.164563
C	2.044369	1.494448	2.295152
H	0.634878	2.175555	3.781001
C	3.526664	0.436358	0.488778
C	3.205773	-0.764368	-0.362045
C	1.493304	-2.408588	-0.761918
H	2.855610	2.137628	2.624653
C	4.080771	-1.437350	-1.203111
C	2.377321	-3.093153	-1.591370
H	0.523889	-2.845229	-0.576769
C	3.658998	-2.604066	-1.835095
H	5.093015	-1.069225	-1.349508
H	2.058065	-4.026139	-2.046409
H	4.334271	-3.145036	-2.491464
C	3.792780	1.684087	-0.371184
H	3.967036	2.558961	0.263277
H	4.680919	1.533617	-0.993198
H	2.942976	1.897742	-1.026102
C	4.723177	0.165309	1.410569
H	5.629772	-0.005019	0.821693
H	4.909333	1.021949	2.065938
H	4.548029	-0.715442	2.034676

Table S14 Cartesian coordinates of the first excited state (S_1) fully optimized geometry of **4FC** in THF from PBE0 calculations (in Å)

Atom	X	Y	Z
C	-2.910393	0.652373	-0.000472
C	-0.447620	0.841503	0.000995
B	-3.269813	1.956095	-0.896514
B	-3.270947	1.956877	0.894066
B	-1.825038	2.815250	-1.420494
B	-2.746419	3.396833	-0.001511
B	-0.993006	3.526614	-0.000454
B	-1.826846	2.816412	1.419115
B	-0.274047	2.178146	-0.900479
B	-0.275210	2.178889	0.901561
B	-1.703220	0.994816	1.170090
B	-1.701784	0.993834	-1.169874
H	-4.222607	1.878512	-1.608159
H	-4.224625	1.879709	1.604572
H	-3.424187	4.380200	-0.002250
H	-1.858180	3.361150	-2.481666
H	-1.620813	0.254183	-2.102396
H	-1.623468	0.256016	2.103405
H	-1.861217	3.363272	2.479752
H	-0.470482	4.601042	-0.000632
H	0.655440	2.236825	-1.642737
H	0.653198	2.238126	1.645130
C	-3.691312	-0.594179	-0.000477
C	-4.075769	-1.205289	1.204565
C	-4.074462	-1.206112	-1.205517
C	-4.816320	-2.381683	1.202758
H	-3.792345	-0.744781	2.146115
C	-4.815021	-2.382495	-1.203712
H	-3.790004	-0.746258	-2.147074
C	-5.188985	-2.978674	-0.000475
H	-5.106294	-2.833486	2.147280
H	-5.103973	-2.834940	-2.148239
H	-5.767141	-3.897896	-0.000472
C	0.375022	-0.386070	0.001834
C	-0.323240	-1.593750	0.002985
C	1.819578	-0.488424	0.001096
C	0.303231	-2.836677	0.002884
H	-1.405850	-1.565142	0.003772
C	2.437471	-1.789942	0.000560
C	2.880874	0.480848	0.000849
C	1.702001	-2.944563	0.001464
H	-0.306779	-3.734510	0.003743
C	3.944478	-1.703711	-0.000969
C	4.136936	-0.213215	-0.000494
C	2.885500	1.899189	0.001892
H	2.179893	-3.918613	0.001126
C	5.333213	0.471492	-0.001171
C	4.087933	2.569482	0.001250
H	1.964829	2.458188	0.003340
C	5.307779	1.867585	-0.000354
H	6.280148	-0.058438	-0.002300
H	4.096838	3.653751	0.002055
H	6.240996	2.421582	-0.000870
C	4.545308	-2.344747	1.260549
H	4.342413	-3.419397	1.271376
H	5.630290	-2.206958	1.275335
H	4.126657	-1.903123	2.168708
C	4.542284	-2.343474	-1.264593
H	5.627207	-2.205554	-1.281871
H	4.339402	-3.418121	-1.275960
H	4.121392	-1.900985	-2.171294

Table S15 Cartesian coordinates of the ground state (S_0) fully optimized geometry of **4FCH** in THF from PBE0 calculations (in Å)

Atom	X	Y	Z
C	-2.387596	-0.329877	1.332907
C	-1.643046	-0.423914	-0.163865
B	-4.073285	-0.486544	1.262837
B	-3.307693	1.080586	1.515830
B	-4.418337	-0.670580	-0.465051
B	-4.608932	0.917928	0.325330
B	-3.868410	0.807923	-1.281907
B	-3.168560	1.896239	-0.054583
B	-2.869808	-0.661934	-1.336429
B	-2.113383	0.917370	-1.090326
B	-1.769103	1.080880	0.649574
B	-3.010804	-1.450915	0.238128
H	-4.611002	-1.049770	2.157816
H	-3.323857	1.601271	2.581485
H	-5.676539	1.407286	0.516883
H	-5.329208	-1.332642	-0.848062
H	-2.848789	-2.596584	0.466265
H	-0.800881	1.526891	1.150020
H	-3.185214	3.082436	-0.140923
H	-4.388421	1.222482	-2.268999
H	-2.588197	-1.314838	-2.286019
H	-1.346526	1.314044	-1.900835
C	-0.292352	-1.108719	-0.270302
C	-0.341980	-2.499105	-0.465103
C	0.993593	-0.508834	-0.155043
C	0.777653	-3.315128	-0.419707
H	-1.299186	-2.966032	-0.651167
C	2.108182	-1.375790	-0.030354
C	1.547715	0.876366	-0.159738
C	2.015519	-2.751490	-0.145117
H	0.670710	-4.383944	-0.574250
C	3.395369	-0.627262	0.228661
C	2.931103	0.798559	0.097475
C	1.009415	2.134988	-0.456429
H	2.901233	-3.373334	-0.049154
C	3.731774	1.930763	0.152879
C	1.815914	3.268899	-0.416941
H	-0.023050	2.257397	-0.743163
C	3.167790	3.179230	-0.093061
H	4.793592	1.840484	0.367137
H	1.377376	4.234868	-0.649379
H	3.782190	4.074031	-0.057734
C	3.920260	-0.926726	1.642749
H	4.193383	-1.982492	1.737703
H	4.811932	-0.326833	1.850860
H	3.165766	-0.695763	2.400053
C	4.472605	-0.959240	-0.813899
H	5.370358	-0.357680	-0.641328
H	4.761096	-2.013198	-0.751041
H	4.114215	-0.759209	-1.827518
H	-1.810903	-0.739973	2.153660

Table S16 Cartesian coordinates of the first excited state (S_1) fully optimized geometry of **4FCH** in THF from PBE0 calculations (in Å)

Atom	X	Y	Z
C	-2.814676	-0.089101	1.719371
C	-1.530904	-0.454826	-0.260505
B	-4.326127	-0.410640	1.244298
B	-3.647302	1.239889	1.339120
B	-4.328410	-0.882860	-0.454314
B	-4.739159	0.797860	0.006569
B	-3.822072	0.504063	-1.458506
B	-3.256238	1.753326	-0.305874
B	-2.751441	-0.902729	-1.241579
B	-2.089558	0.758902	-1.177077
B	-1.938257	0.914311	0.687564
B	-2.849508	-1.295610	0.553722
H	-5.063865	-0.923572	2.027487
H	-3.847429	2.045399	2.194630
H	-5.842293	1.252016	-0.049378
H	-5.142426	-1.670438	-0.830777
H	-2.644866	-2.415627	0.905846
H	-1.056926	1.545493	1.178111
H	-3.292274	2.919415	-0.560156
H	-4.278823	0.748950	-2.534663
H	-2.498573	-1.718165	-2.073283
H	-1.354973	1.234192	-1.984736
C	-0.197548	-1.117403	-0.289600
C	-0.196914	-2.498110	-0.420035
C	1.096052	-0.512774	-0.150815
C	0.964693	-3.298188	-0.335689
H	-1.144254	-3.002959	-0.564770
C	2.257617	-1.346923	-0.004371
C	1.571030	0.851955	-0.163180
C	2.201852	-2.728747	-0.094016
H	0.863682	-4.374358	-0.435101
C	3.515193	-0.545381	0.226392
C	2.983068	0.855044	0.080710
C	0.922015	2.085728	-0.416085
H	3.093062	-3.337962	0.010557
C	3.698349	2.030798	0.133817
C	1.651355	3.255117	-0.373579
H	-0.128560	2.120499	-0.654378
C	3.027392	3.238455	-0.085629
H	4.765704	2.027258	0.331045
H	1.157314	4.201635	-0.564437
H	3.576846	4.173735	-0.046179
C	4.064644	-0.799576	1.640248
H	4.374683	-1.843539	1.744651
H	4.938524	-0.167379	1.823350
H	3.312840	-0.582546	2.403537
C	4.587771	-0.848794	-0.829622
H	5.463198	-0.211730	-0.673944
H	4.914699	-1.889856	-0.753370
H	4.209162	-0.677104	-1.840585
H	-2.440037	-0.299566	2.712457