Electronic supplementary information

Modulating Radiative Efficiency in *ortho*-Carboranyl Luminophores through Electron-Donating Substituents : Insights from Intramolecular-Charge-Transfer-Based Emissions

Soyeon Kim,[a‡] Dong Kyun You,[a‡] Namkyun Kim,[a] Ilsup Shin,[a] Dongwook Kim,[b] and Kang Mun Lee*[a]

[a] Department of Chemistry, Institute for Molecular Science and Fusion Technology, Kangwon National University, Chuncheon 24341, Republic of Korea.

[b] Department of Chemistry, Korea Advanced Institute of Science and Technology, (KAIST), Daejeon 34141, Republic of Korea

‡ The first and second authors contributed equally to this work.

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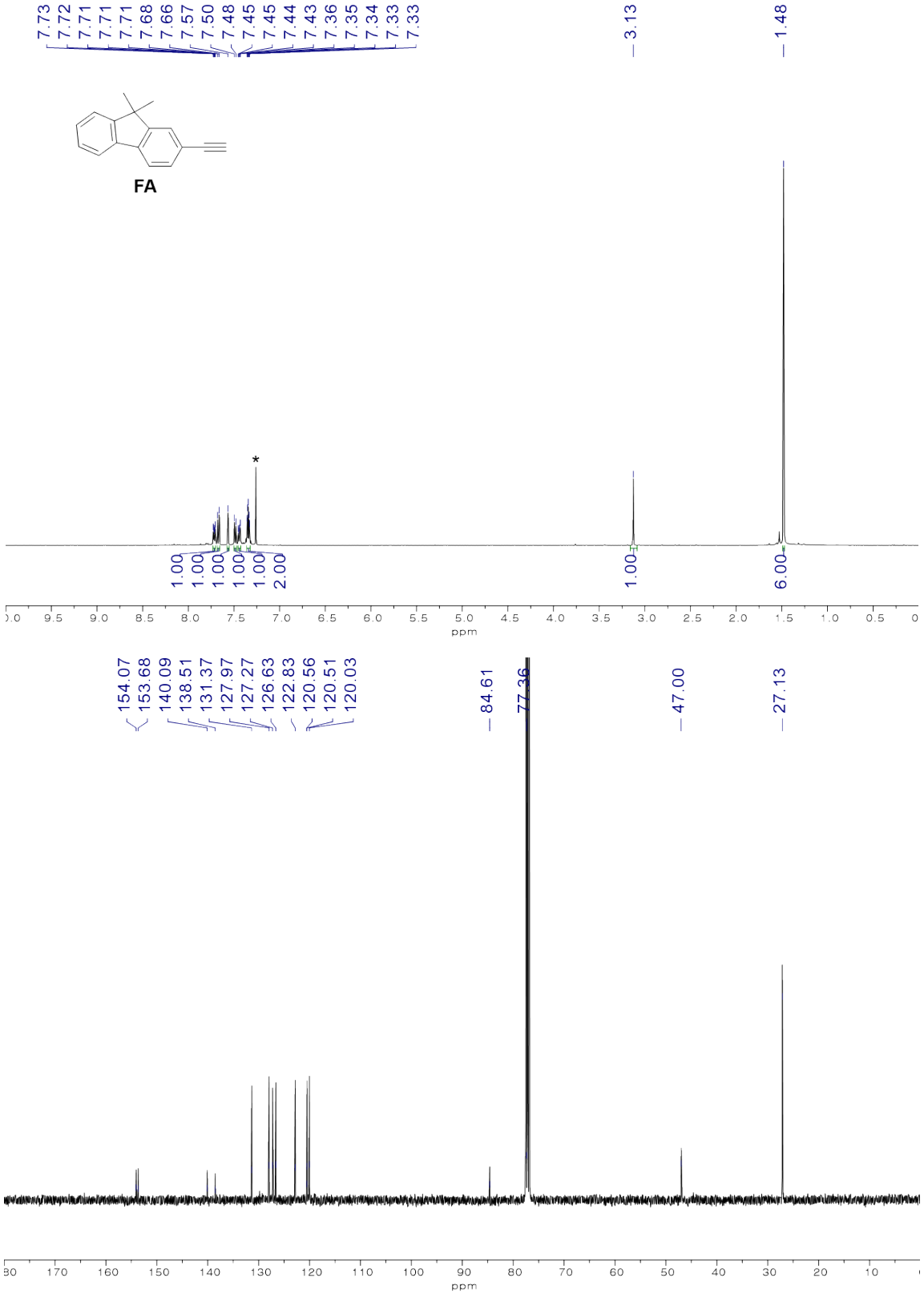

Fig. S1 ^{1}H (top) and ^{13}C (bottom) nuclear magnetic resonance (NMR) spectra of **FA** in $CDCl_3$ (*from residual $CHCl_3$ in $CDCl_3$).

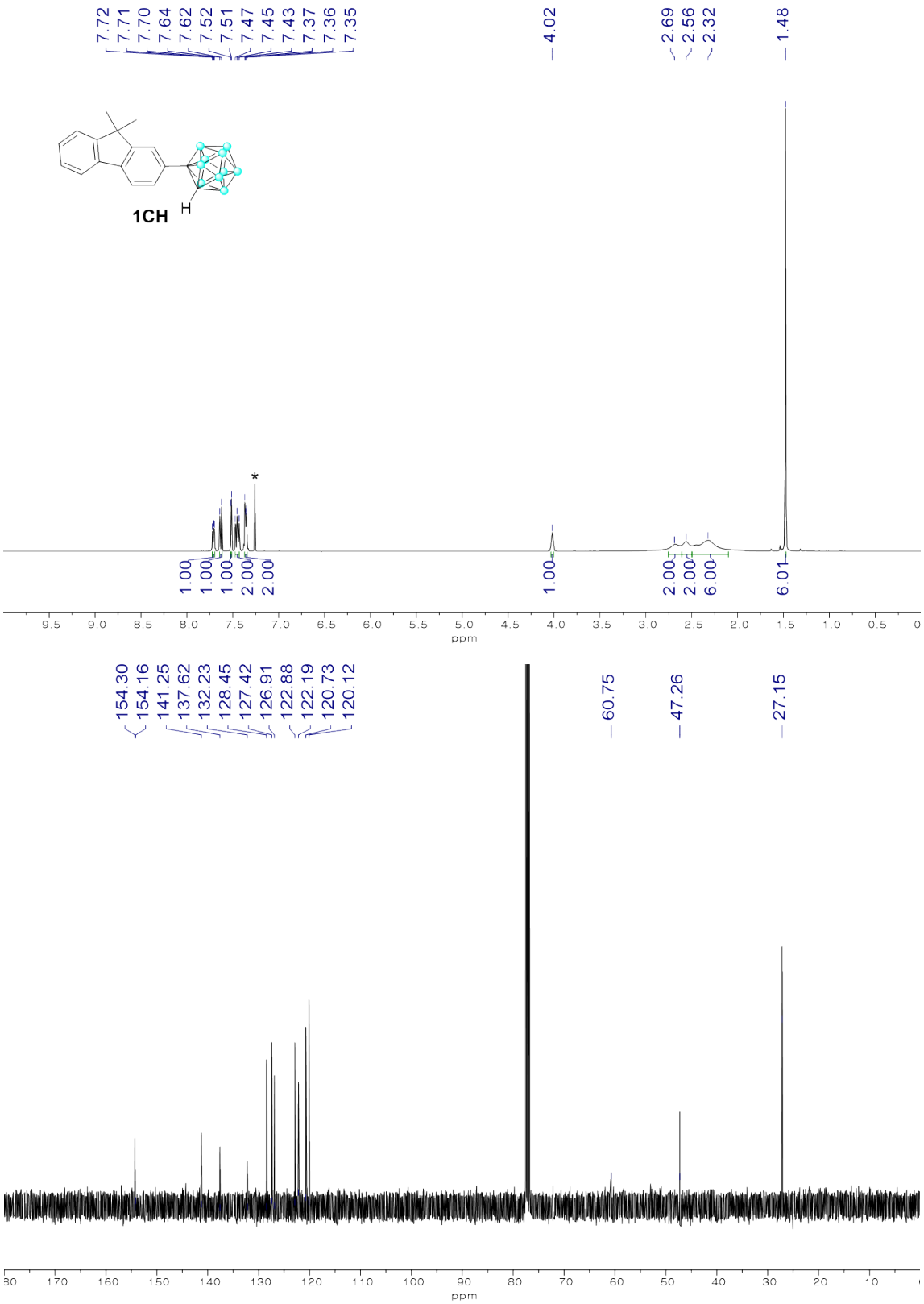

Fig. S2 $^{1}H\{^{11}B\}$ (top) and ^{13}C (bottom) nuclear magnetic resonance (NMR) spectra of **1CH** in $CDCl_3$ (*from residual $CHCl_3$ in $CDCl_3$).

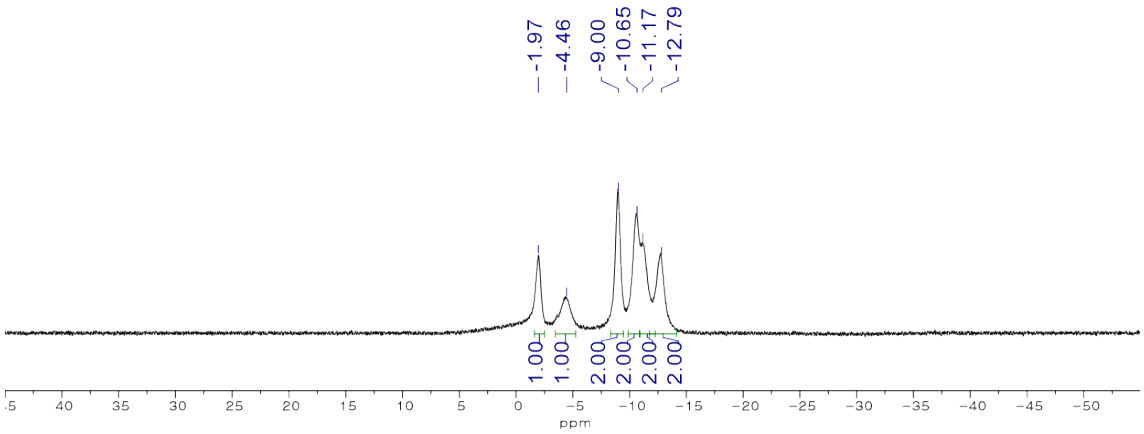

Fig. S3 $^{11}B\{^{1}H\}$ NMR spectra of **1CH** in $CDCl_3$.

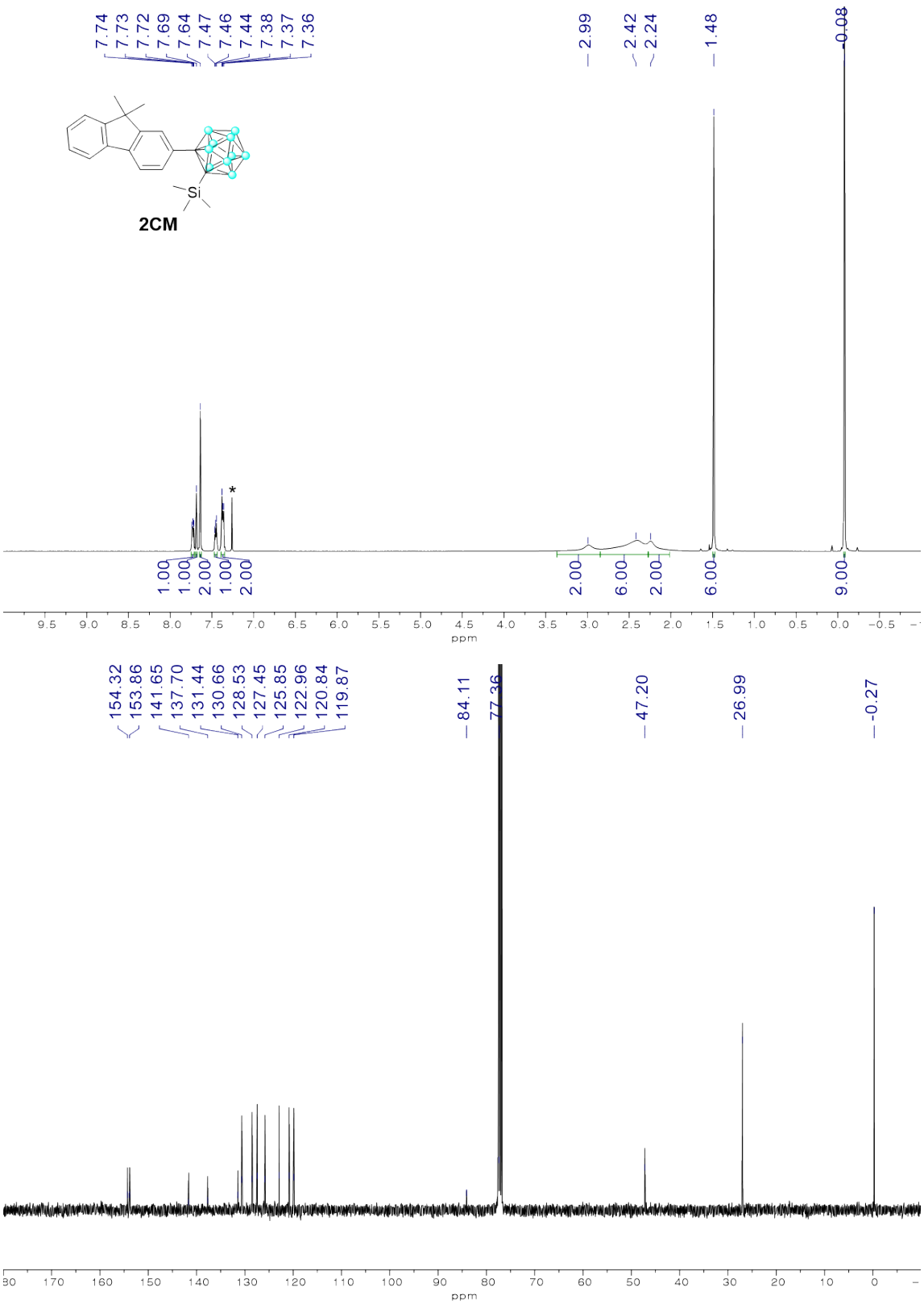

Fig. S4 $^{1}H\{^{11}B\}$ (top) and ^{13}C (bottom) nuclear magnetic resonance (NMR) spectra of **2CM** in $CDCl_3$ (*from residual $CHCl_3$ in $CDCl_3$).

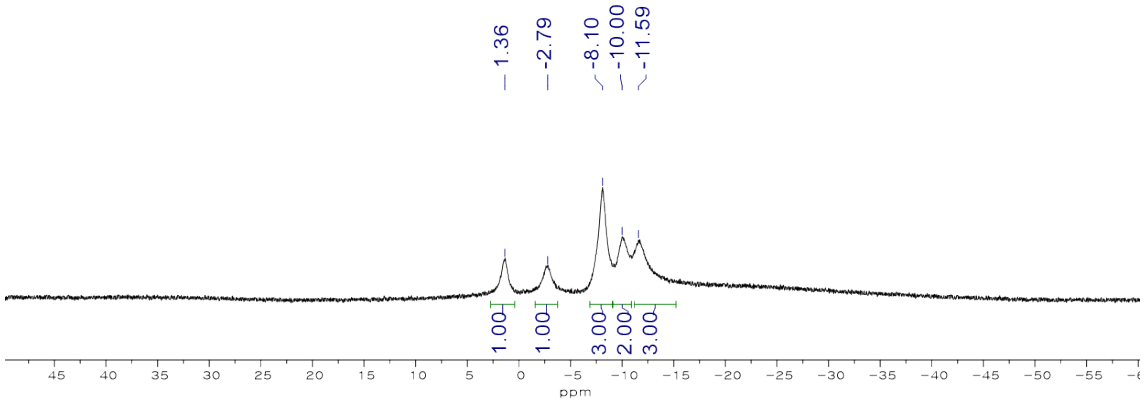

Fig. S5 $^{11}B\{^{1}H\}$ NMR spectra of **2CM** in $CDCl_3$.

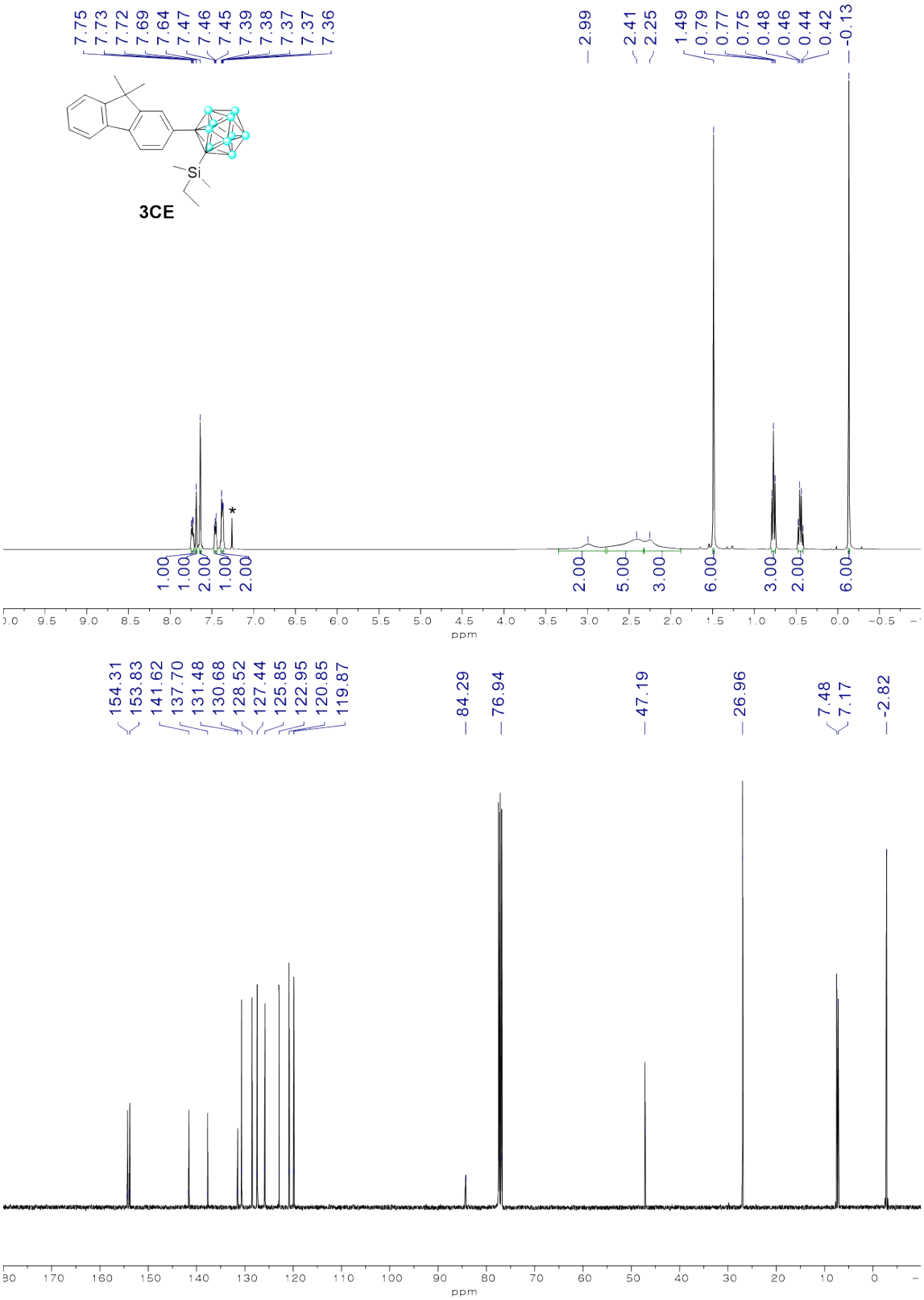

Fig. S6 $^{1}H\{^{11}B\}$ (top) and ^{13}C (bottom) nuclear magnetic resonance (NMR) spectra of **3CE** in $CDCl_3$ (*from residual $CHCl_3$ in $CDCl_3$).

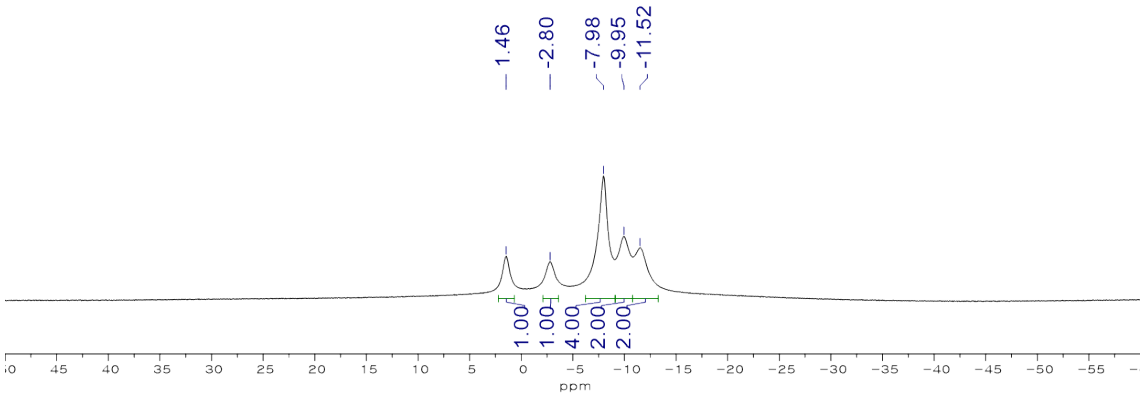

Fig. S7 $^{11}B\{^{1}H\}$ NMR spectra of **3CE** in $CDCl_3$.

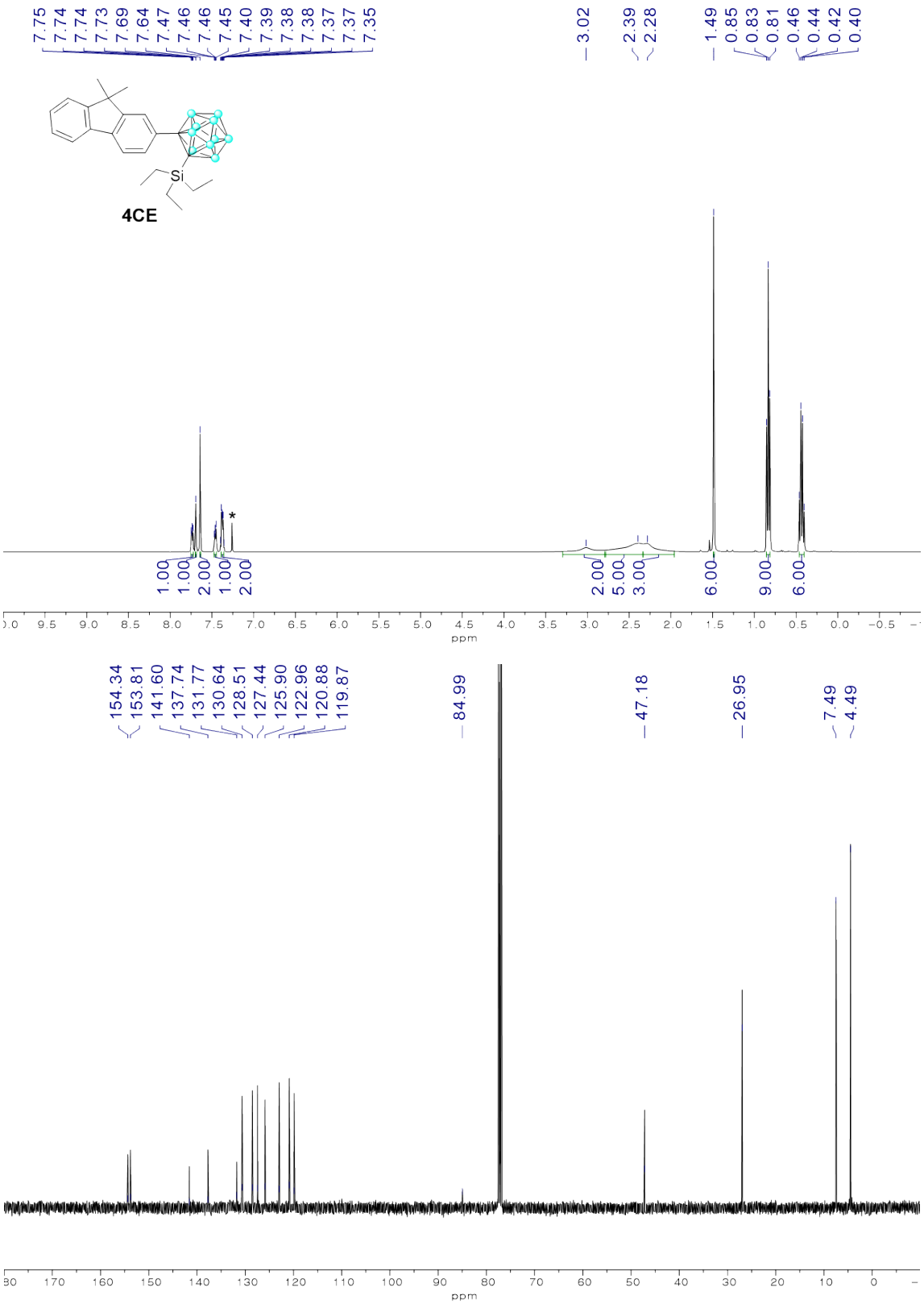

Fig. S8 $^{1}H\{^{11}B\}$ (top) and ^{13}C (bottom) nuclear magnetic resonance (NMR) spectra of **4CE** in $CDCl_3$ (*from residual $CHCl_3$ in $CDCl_3$).

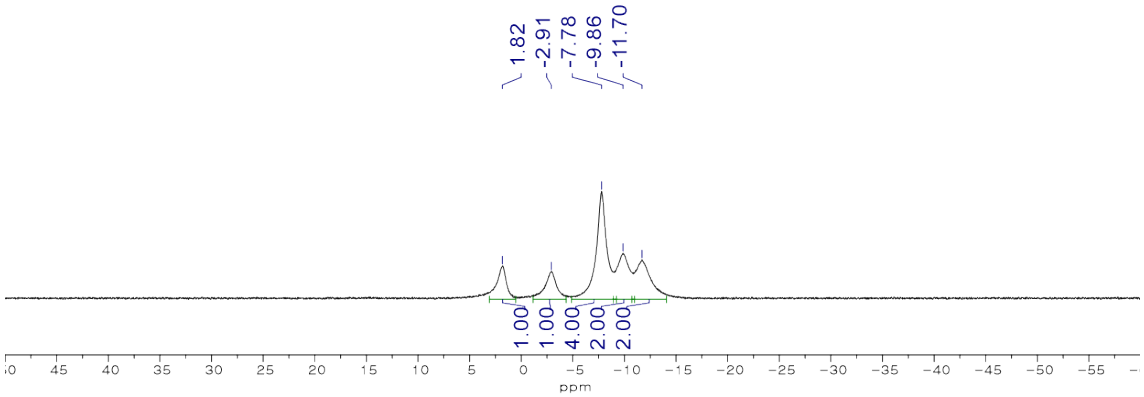

Fig. S9 $^{11}B\{^{1}H\}$ NMR spectra of **4CE** in $CDCl_3$.

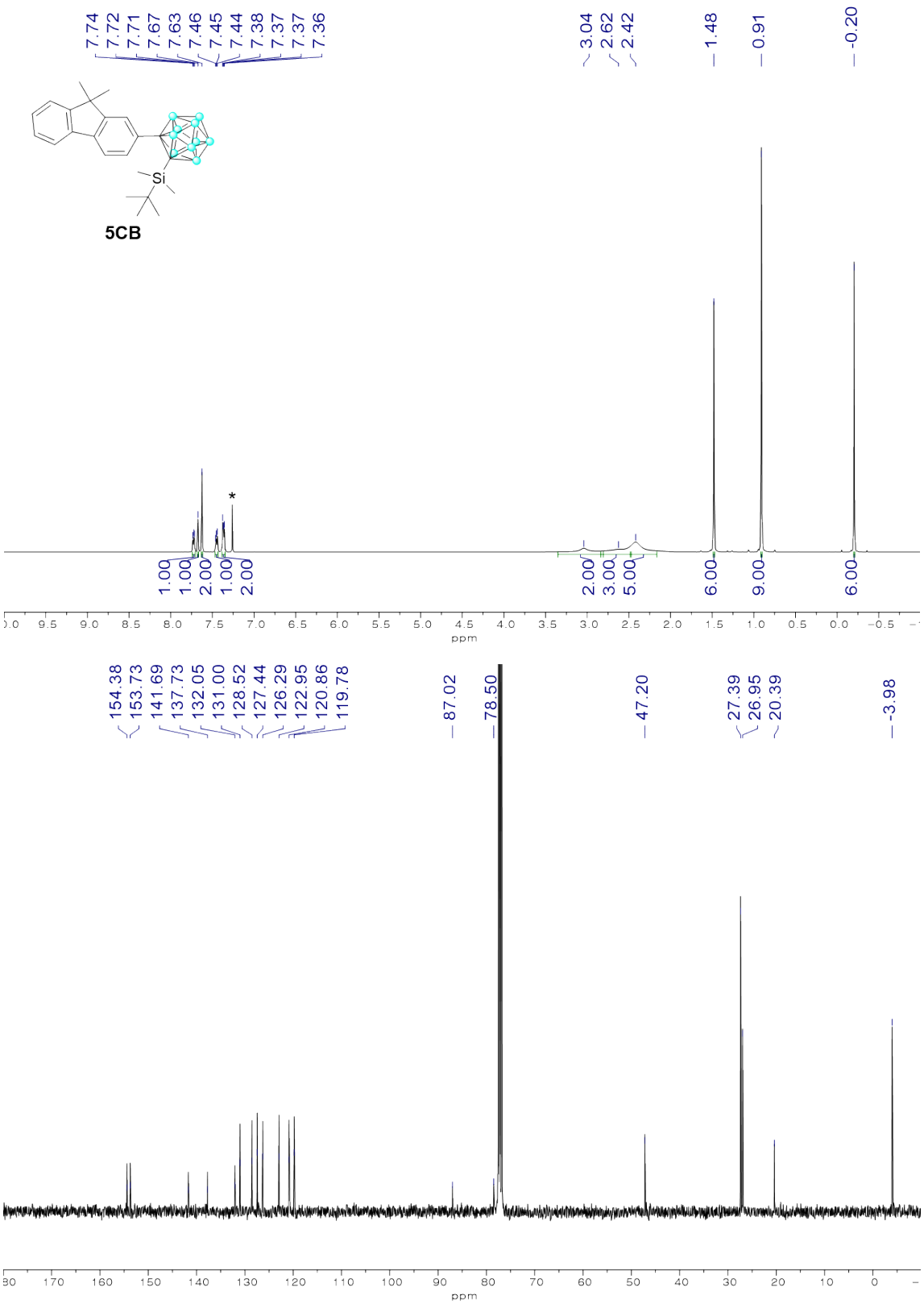

Fig. S10 $^{1}H\{^{11}B\}$ (top) and ^{13}C (bottom) nuclear magnetic resonance (NMR) spectra of **5CB** in $CDCl_3$ (*from residual $CHCl_3$ in $CDCl_3$).

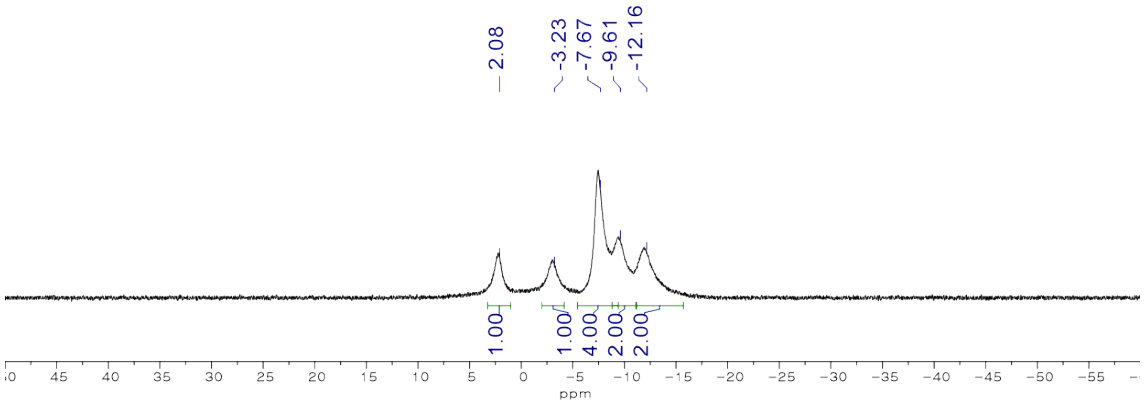

Fig. S11 $^{11}B\{^{1}H\}$ NMR spectra of **5CB** in $CDCl_3$.

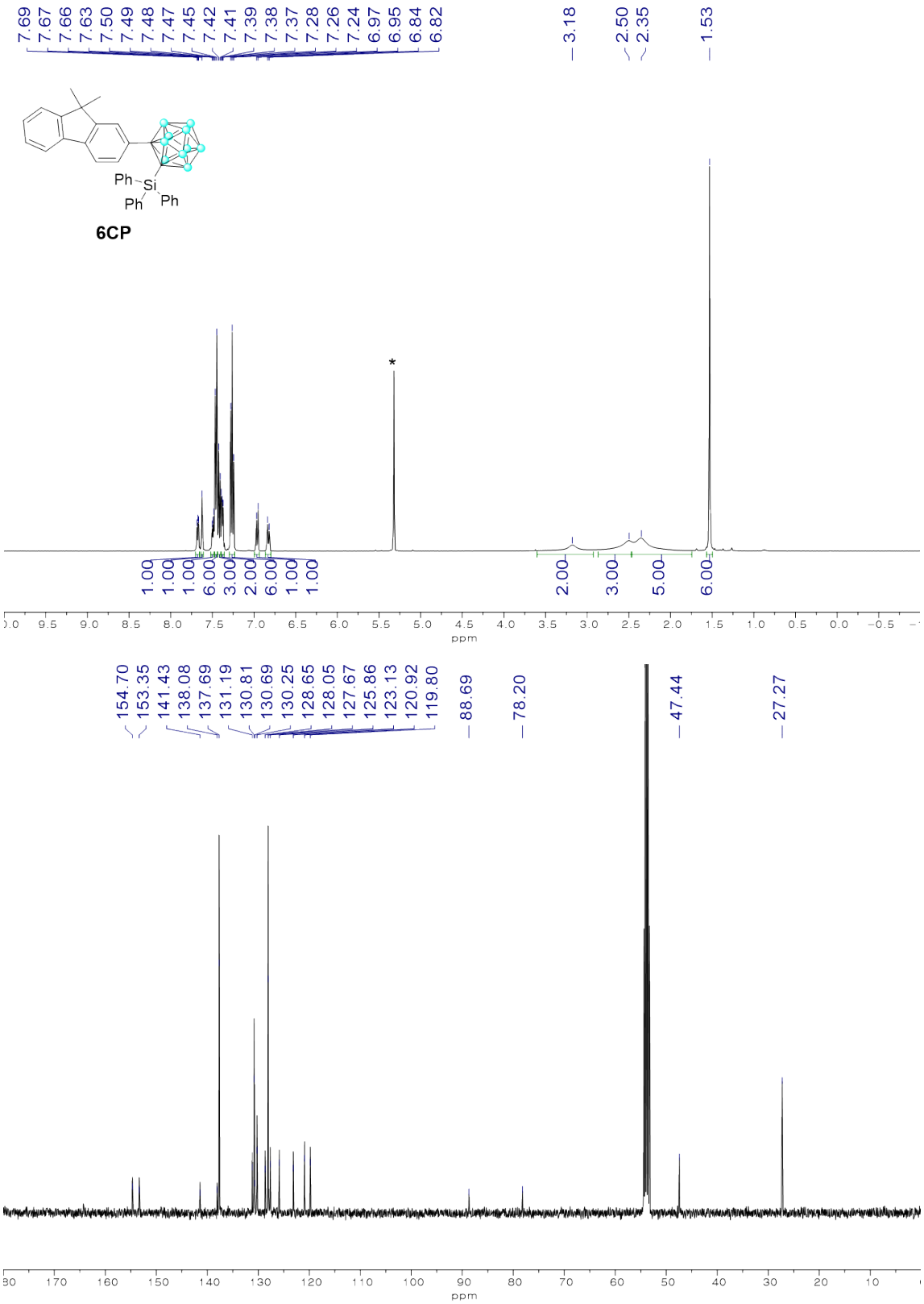

Fig. S12 $^{1}H\{^{11}B\}$ (top) and ^{13}C (bottom) nuclear magnetic resonance (NMR) spectra of **6CP** in CD_2Cl_2 (*from residual CH_2Cl_2 in CD_2Cl_2).

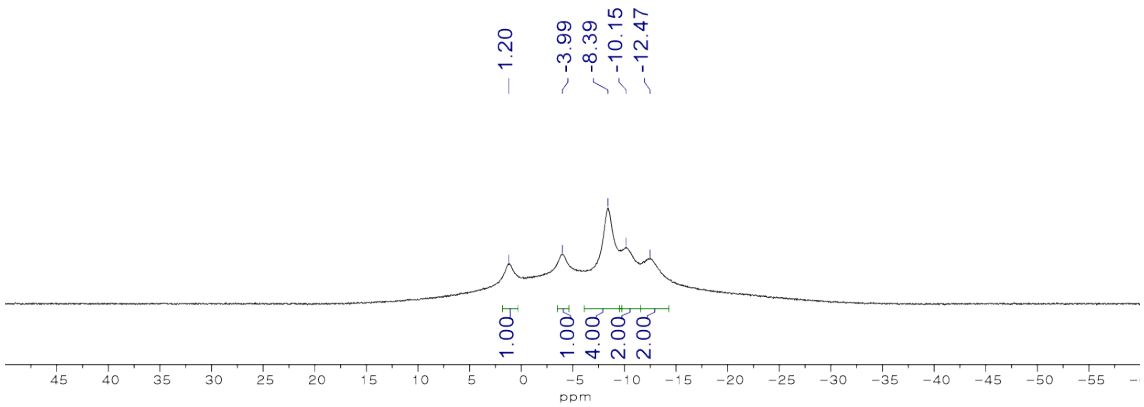

Fig. S13 $^{11}B\{^{1}H\}$ NMR spectra of **6CP** in CD_2Cl_2.

Table S1 Crystallographic data and parameters for **1CH–6CP**

Compound CCDC#	**1CH** 2389101	**2CM** 2389102	**3CE** 2389103	**4CE** 2389106	**5CB** 2389104	**6CP** 2389105
Formula	$C_{17}H_{24}B_{10}$	$C_{20}H_{32}B_{10}Si$	$C_{21}H_{34}B_{10}Si$	$C_{23}H_{38}B_{10}Si$	$C_{23}H_{38}B_{10}Si$	$C_{35}H_{38}B_{10}Si$
Formula weight	336.46	408.64	422.67	450.72	450.72	594.84
Crystal system	Orthorhombic	Triclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_12_12_1$	P_{-1}	P_{-1}	P_{-1}	$P2_1/c$	P_{-1}
a (Å)	6.9920(2)	9.3569(6)	9.0417(4)	11.0532(6)	11.2901(6)	11.5149(7)
b (Å)	10.1133(3)	10.8812(6)	11.2430(5)	13.0146(6)	9.1352(4)	14.8401(10)
c (Å)	27.3441(9)	12.1208(7)	12.4505(6)	19.2255(9)	25.9770(12)	21.6004(15)
α (°)	90	98.2648(19)	98.9030(15)	95.7529(18)	90	103.837(2)
β (°)	90	94.752(2)	93.8354(17)	90.2216(19)	93.4738(18)	95.280(2)
γ (°)	90	92.699(2)	91.7182(18)	105.5694(16)	90	99.771(2)
V (Å^3)	1933.56(10)	1214.88(12)	1246.57(10)	2649.4(2)	2674.3(2)	3497.9(4)
Z	4	2	2	4	4	4
ρ_{calc}(g cm^{-3})	1.156	1.117	1.126	1.130	1.119	1.130
μ (mm^{-1})	0.057	0.103	0.102	0.100	0.099	0.092
F(000)	704	432	448	960	960	1248
T (K)	203(2)	203(2)	203(2)	203(2)	203(2)	203(2)
Scan mode	*φ and ω-scan*	*φ and ω-scan*	*φ and ω-scan*	*φ and ω-scan*	*φ and ω-scan*	*φ and ω-scan*
hkl range	$-8 < h < 9$, $-13 < k < 13$, $-32 < l < 36$	$-11 < h < 11$, $-13 < k < 13$, $-14 < l < 14$	$-11 < h < 11$, $-14 < k < 14$, $-15 < l < 15$	$-13 < h < 13$, $-15 < k < 15$, $-23 < l < 23$	$-14 < h < 12$, $-11 < k < 9$, $-33 < l < 33$	$-14 < h < 14$, $-18 < k < 18$, $-26 < l < 26$
Measd reflns	21842	33576	27362	49407	29952	101254
Unique reflns [R_{int}]	4675 [0.0686]	4780 [0.0597]	5432 [0.0870]	9913 [0.1150]	5825 [0.0911]	13635 [0.1092]
Reflns used for refinement	4675	4780	5432	9913	5825	13635
Refined parameters	246	316	314	663	314	978
R_1[a] (I > 2σ(I))	0.0430	0.0450	0.0517	0.0649	0.0605	0.0680
wR_2[b] all data	0.1122	0.1229	0.1424	0.1526	0.1373	0.1368
GOF on F^2	1.052	1.021	1.030	1.047	1.070	1.084
ρ_{fin} (max/min) (e Å^{-3})	0.165, −0.232	0.219, −0.390	0.587, −0.356	0.216, −0.329	0.263, −0.261	0.275, −0.290

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

Table S2 Selected bond lengths (Å) and angles (°) for **1CH–6CP**

Compound	**1CH**	**2CM**	**3CE**	**4CE**	**5CB**	**6CP**
			length (Å)			
C2–C14	1.502(3)	1.501(2)	1.507(2)	1.505(4)	1.503(3)	1.506(3)
C9–C10	1.524(3)	1.520(2)	1.524(2)	1.525(4)	1.519(3)	1.523(4)
C9–C13	1.521(3)	1.519(2)	1.524(3)	1.524(4)	1.523(3)	1.520(4)
C14–C15	1.645(3)	1.708(2)	1.710(2)	1.727(4)	1.739(3)	1.758(3)
C15–Si	–	1.9340(16)	1.9368(18)	1.944(3)	1.949(2)	1.945(3)
			angles (°)			
C1–C2–C14	117.64(18)	119.39(14)	119.42(16)	120.9(2)	118.91(19)	120.4(2)
C2–C14–C15	120.07(16)	120.08(12)	119.83(14)	121.3(2)	120.04(17)	121.2(2)
C9–C10–C11	111.21(17)	111.11(14)	110.99(15)	110.8(2)	111.15(18)	111.0(2)
C9–C13–C12	111.37(17)	111.34(14)	111.60(15)	111.6(2)	111.23(19)	111.4(2)
C10–C9–C13	100.94(16)	101.00(13)	100.84(15)	100.7(2)	100.96(17)	101.0(2)
C10–C11–C12	108.22(17)	108.21(14)	108.40(16)	108.4(2)	108.35(19)	108.5(2)
C11–C12–C13	108.23(18)	108.32(14)	108.11(16)	108.4(2)	108.3(2)	108.0(2)
C14–C15–Si	–	122.37(10)	121.74(11)	124.08(17)	120.66(14)	123.10(16)

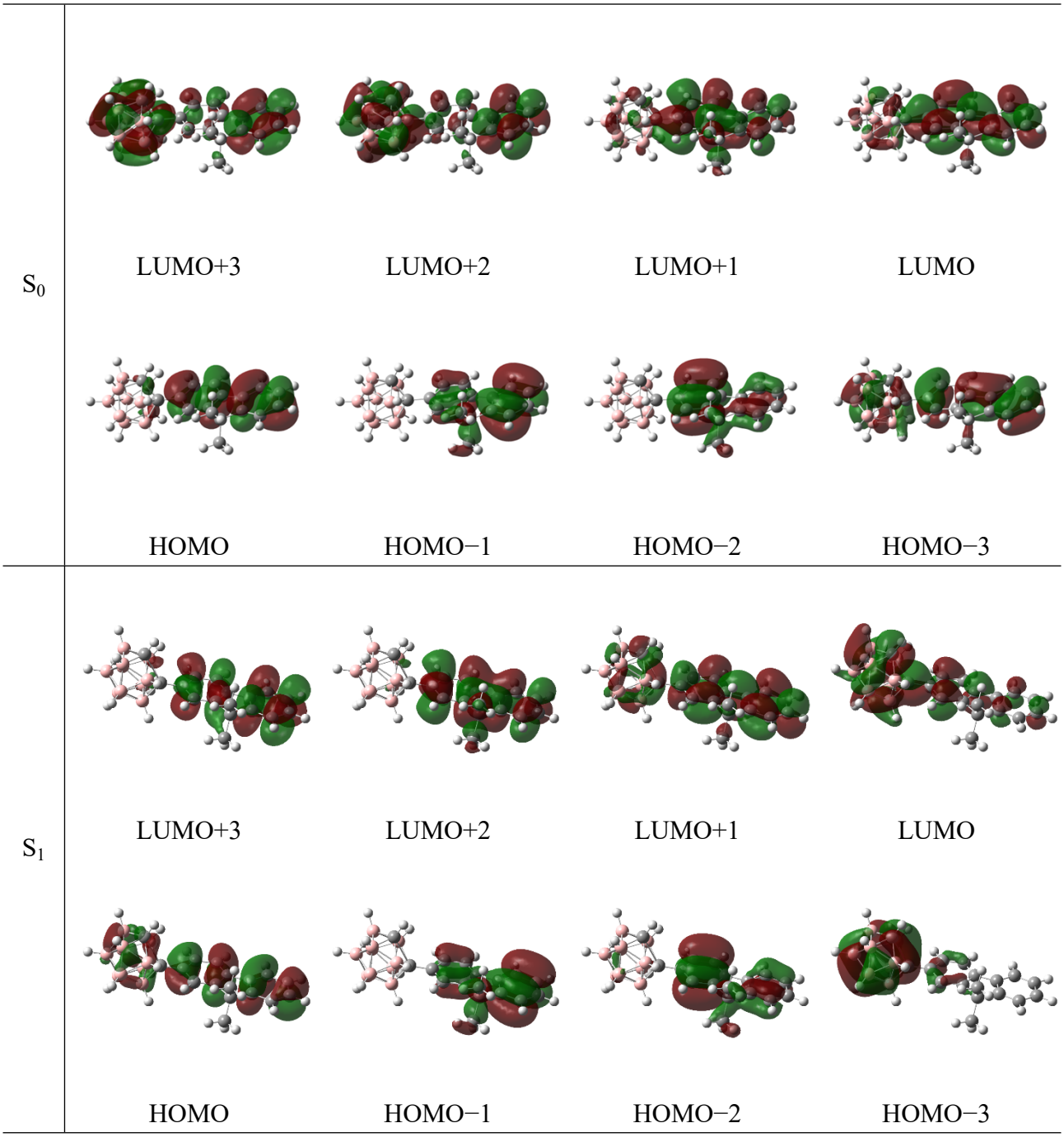

Fig. S14 Selected frontier orbitals of **1CH** from CAM-B3LYP calculations (Isovalue = 0.02 a.u.) at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

Table S3 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **1CH** from TD-CAM-B3LYP calculations using the CAM-B3LYP geometries at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF

state	λ_{calc} (/nm)	f_{calc}	Major contribution
			S_0
1	264.85	0.7989	HOMO → LUMO (91.21%)
2	245.53	0.0325	HOMO−2 → LUMO (35.09%)
			HOMO → LUMO+1 (52.03%)
3	239.60	0.0277	HOMO−1 → LUMO (54.01%)
			HOMO → LUMO+3 (24.65%)
4	207.27	0.1670	HOMO−2 → LUMO (51.36%)
			HOMO → LUMO+1 (35.66%)
5	198.78	0.0251	HOMO−3 → LUMO (18.22%)
			HOMO−2 → LUMO+1 (10.06%)
			HOMO−1 → LUMO+1 (27.81%)
			HOMO−1 → LUMO+3 (11.04%)
			HOMO → LUMO+4 (11.17%)
			S_1
1	435.63	0.2138	HOMO → LUMO (93.20%)
2	320.68	0.0007	HOMO–1 → LUMO (85.81%)
3	443.77	0.4609	HOMO–2 → LUMO (71.21%)
			HOMO–1 → LUMO (13.77%)
4	352.46	0.0001	HOMO–3 → LUMO (8.40%)
			HOMO–2 → LUMO (58.39%)
			HOMO–1 → LUMO+1 (9.93%)
5	349.93	0.0613	HOMO–6 → LUMO (20.84%)
			HOMO–5 → LUMO (14.13%)
			HOMO–3 → LUMO (23.84%)
			HOMO → LUMO+1 (21.72%)

Table S4 Molecular orbital energies (in eV) and molecular orbital distributions (in %) of **1CH** at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

	E (eV)	fluorene	carborane	terminal-H
		S_0		
LUMO+3	1.19	45.07	54.84	0.08
LUMO+2	1.18	52.99	46.94	0.06
LUMO+1	0.59	91.07	8.83	0.10
LUMO	–0.27	88.25	11.66	0.09
HOMO	–7.55	96.59	3.36	0.05
HOMO–1	–8.39	99.90	0.10	0.00
HOMO–2	–8.67	98.72	1.28	0.00
HOMO–3	–9.46	81.63	18.34	0.03
		S_1		
LUMO+3	1.18	95.14	4.86	0.00
LUMO+2	0.64	95.61	4.39	0.00
LUMO+1	–0.05	83.32	16.58	0.11
LUMO	–2.18	25.35	74.24	0.41
HOMO	–7.32	90.08	9.90	0.03
HOMO–1	–8.58	99.71	0.29	0.00
HOMO–2	–8.86	96.83	3.17	0.00
HOMO–3	–9.31	4.46	95.52	0.02

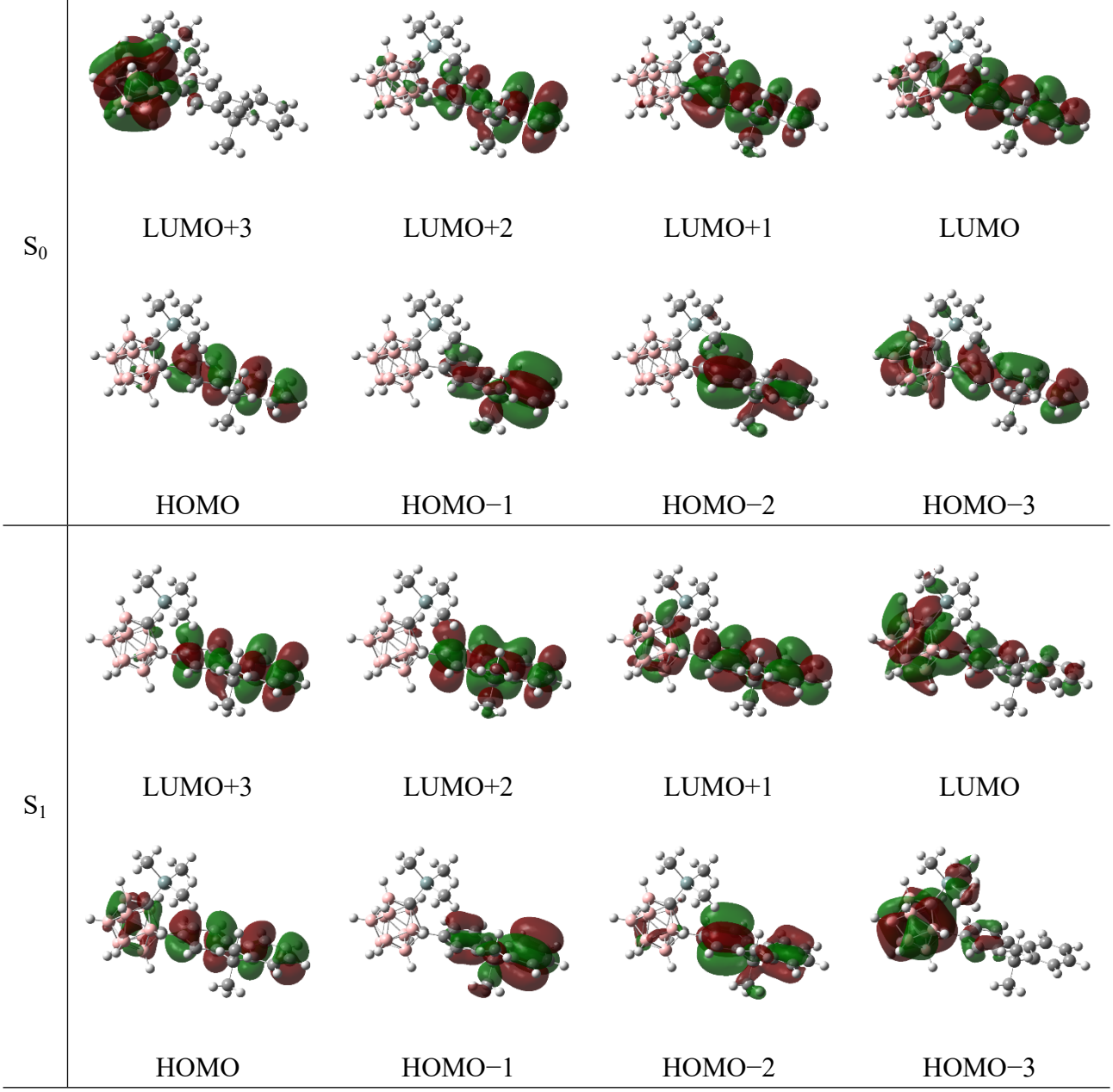

Fig. S15 Selected frontier orbitals of **2CM** from CAM-B3LYP calculations (Isovalue = 0.02 a.u.) at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

Table S5 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **2CM** from TD-CAM-B3LYP calculations using the CAM-B3LYP geometries at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

state	λ_{calc} (/nm)	f_{calc}	Major contribution
			S_0
1	267.09	0.0858	HOMO → LUMO (91.52%)
2	246.49	0.0302	HOMO–2 → LUMO (36.41%)
			HOMO → LUMO+1 (50.95%)
3	240.19	0.0260	HOMO–1 → LUMO (53.73%)
			HOMO → LUMO+3 (14.77%)
			HOMO → LUMO+4 (12.09%)
4	208.34	0.1664	HOMO–2 → LUMO (51.71%)
			HOMO → LUMO+1 (36.89%)
5	199.67	0.0159	HOMO–3 → LUMO (20.32%)
			HOMO–2 → LUMO+1 (8.45%)
			HOMO–1 → LUMO+1 (26.56%)
			HOMO → LUMO+3 (13.39%)
			S_1
1	434.57	1.0396	HOMO → LUMO (92.95%)
2	325.77	0.0030	HOMO–1 → LUMO (82.90%)
3	302.80	0.0240	HOMO–2 → LUMO (72.91%)
			HOMO–1 → LUMO (13.96%)
4	289.19	0.0215	HOMO–3 → LUMO (93.97%)
5	274.84	0.0469	HOMO–3 → LUMO (7.86%)
			HOMO–1 → LUMO (51.89%)
			HOMO–1 → LUMO+1 (9.45%)
			HOMO → LUMO+1 (12.26%)

Table S6 Molecular orbital energies (in eV) and molecular orbital distributions (in %) of **2CM** at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

	E (eV)	fluorene	carborane	silyl
		S_0		
LUMO+3	1.28	3.35	92.89	3.76
LUMO+2	1.20	93.75	5.70	0.55
LUMO+1	0.61	93.41	5.66	0.93
LUMO	–0.28	87.74	11.77	0.39
HOMO	–7.52	95.78	3.92	0.30
HOMO–1	–8.39	99.70	0.17	0.13
HOMO–2	–8.64	97.60	1.34	1.06
HOMO–3	–9.38	73.62	24.84	1.54
		S_1		
LUMO+3	1.21	95.26	4.36	0.38
LUMO+2	0.67	95.21	4.35	0.43
LUMO+1	–0.05	83.38	15.19	1.43
LUMO	–2.11	23.16	74.26	2.58
HOMO	–7.26	90.28	9.48	0.24
HOMO–1	–8.54	99.61	0.35	0.04
HOMO–2	–8.81	95.51	4.13	0.36
HOMO–3	–9.15	6.01	86.99	7.00

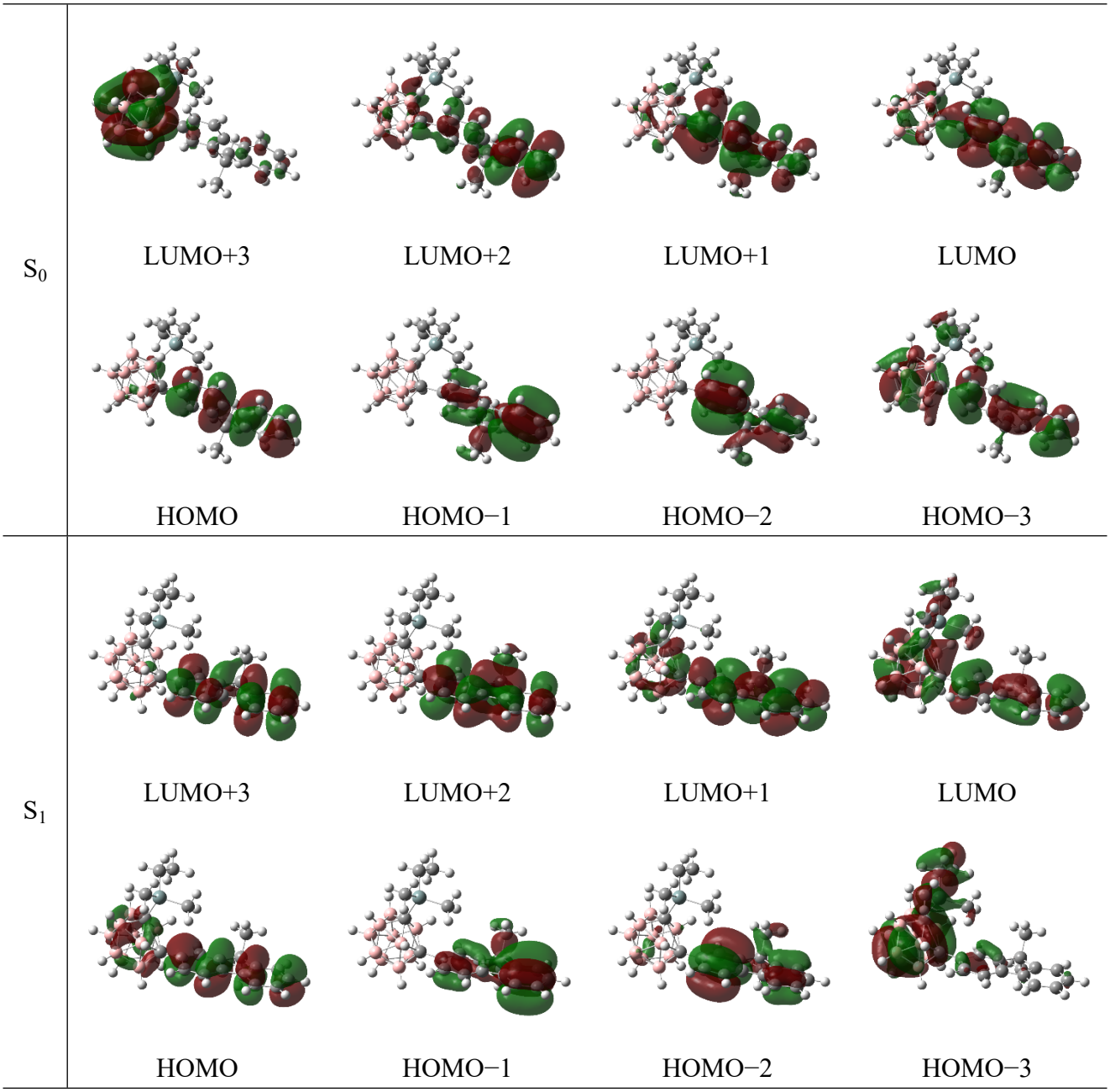

Fig. S16 Selected frontier orbitals of **3CE** from CAM-B3LYP calculations (Isovalue = 0.02 a.u.) at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

Table S7 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **3CE** from TD-CAM-B3LYP calculations using the CAM-B3LYP geometries at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

state	λ_{calc} (/nm)	f_{calc}	Major contribution
			S_0
1	266.08	0.8047	HOMO → LUMO (91.40%)
2	246.56	0.0270	HOMO–2 → LUMO (35.20%)
			HOMO → LUMO+1 (51.50%)
3	239.86	0.0256	HOMO → LUMO (53.58%)
			HOMO → LUMO+3 (18.82%)
			HOMO → LUMO+4 (9.29%)
4	208.10	0.1791	HOMO–2 → LUMO (52.51%)
			HOMO → LUMO+1 (35.61%)
5	199.76	0.0285	HOMO–3 → LUMO (18.05%)
			HOMO–2 → LUMO+1 (9.31%)
			HOMO–1 → LUMO+1 (24.58%)
			HOMO–1 → LUMO+3 (8.88%)
			HOMO → LUMO+3 (13.61%)
			S_1
1	438.38	1.0283	HOMO → LUMO (93.03%)
2	327.40	0.0019	HOMO–2 → LUMO (32.68%)
			HOMO–1 → LUMO (50.54%)
3	304.74	0.0213	HOMO–2 → LUMO (73.55%)
			HOMO–1 → LUMO (14.16%)
4	293.35	0.0304	HOMO–3 → LUMO (57.58%)
			HOMO–2 → LUMO (29.77%)
5	275.87	0.0534	HOMO–2 → LUMO (6.16%)
			HOMO–1 → LUMO (51.14%)
			HOMO–1 → LUMO+1 (8.79%)
			HOMO → LUMO+1(11.10%)

Table S8 Molecular orbital energies (in eV) and molecular orbital distributions (in %) of **3CE** at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

	E (eV)	fluorene	carborane	silyl
		S_0		
LUMO+3	1.26	5.44	89.68	4.88
LUMO+2	1.19	90.17	8.60	1.23
LUMO+1	0.59	90.47	7.82	1.71
LUMO	–0.26	87.49	11.82	0.68
HOMO	–7.52	95.83	3.85	0.32
HOMO–1	–8.38	99.78	0.14	0.08
HOMO–2	–8.64	97.89	1.51	0.60
HOMO–3	–9.37	72.23	22.65	5.12
		S_1		
LUMO+3	1.22	95.09	4.52	0.39
LUMO+2	0.68	95.15	4.37	0.48
LUMO+1	–0.04	84.02	14.80	1.18
LUMO	–2.13	22.81	74.63	2.56
HOMO	–7.25	90.19	9.49	0.31
HOMO–1	–8.53	99.61	0.31	0.07
HOMO–2	–8.80	95.61	3.63	0.76
HOMO–3	–9.12	6.38	67.25	26.36

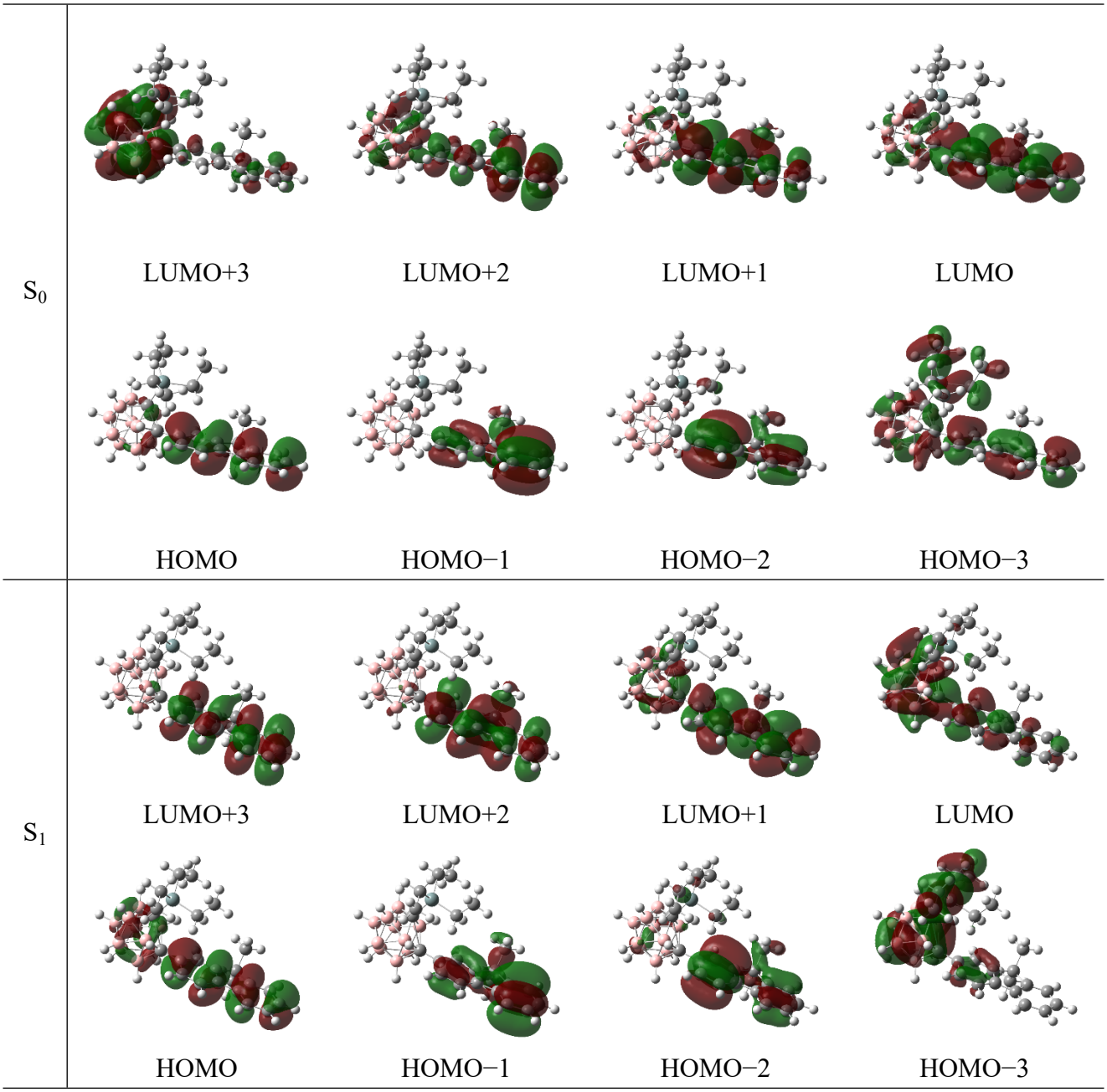

Fig. S17 Selected frontier orbitals of **4CE** from CAM-B3LYP calculations (Isovalue = 0.02 a.u.) at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

Table S9 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **4CE** from TD-CAM-B3LYP calculations using the CAM-B3LYP geometries at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

state	λ_{calc} (/nm)	f_{calc}	Major contribution
			S_0
1	267.06	0.7977	HOMO → LUMO (91.24%)
2	247.02	0.0270	HOMO–2 → LUMO (35.60%)
			HOMO → LUMO+1 (49.96%)
3	240.12	0.0247	HOMO–1 → LUMO (52.99%)
			HOMO → LUMO+3 (9.37%)
			HOMO → LUMO+4 (18.37%)
4	208.72	0.1755	HOMO–2 → LUMO (52.91%)
			HOMO → LUMO+1 (36.16%)
5	200.52	0.0251	HOMO–5 → LUMO (10.54%)
			HOMO–3 → LUMO (9.69%)
			HOMO–1 → LUMO+1 (22.58%)
			HOMO → LUMO+3 (20.45%)
			S_1
1	441.78	0.9949	HOMO → LUMO (92.97%)
2	331.83	0.0016	HOMO–2 → LUMO (44.76%)
			HOMO–1 → LUMO (40.24%)
3	306.46	0.0199	HOMO–2 → LUMO (73.16%)
			HOMO–1 → LUMO (14.38%)
4	297.77	0.0273	HOMO–3 → LUMO (86.14%)
5	278.56	0.1269	HOMO–3 → LUMO (19.33%)
			HOMO–1 → LUMO (24.12%)
			HOMO → LUMO+1 (8.47%)

Table S10 Molecular orbital energies (in eV) and molecular orbital distributions (in %) of **4CE** at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

	E (eV)	fluorene	carborane	silyl
		S_0		
LUMO+3	1.24	8.14	85.88	5.98
LUMO+2	1.18	85.97	11.75	2.28
LUMO+1	0.60	89.99	7.73	2.28
LUMO	–0.27	86.05	12.94	1.01
HOMO	–7.51	95.68	3.99	0.33
HOMO–1	–8.38	99.60	0.18	0.22
HOMO–2	–8.61	96.38	1.55	2.07
HOMO–3	–9.31	48.53	18.85	32.61
		S_1		
LUMO+3	1.22	94.96	4.52	0.52
LUMO+2	0.68	94.99	4.37	0.64
LUMO+1	–0.04	84.58	14.26	1.16
LUMO	–2.16	22.04	75.30	2.66
HOMO	–7.25	90.08	9.43	0.49
HOMO–1	–8.53	99.55	0.31	0.14
HOMO–2	–8.78	93.61	3.95	2.44
HOMO–3	–9.04	5.69	47.60	46.72

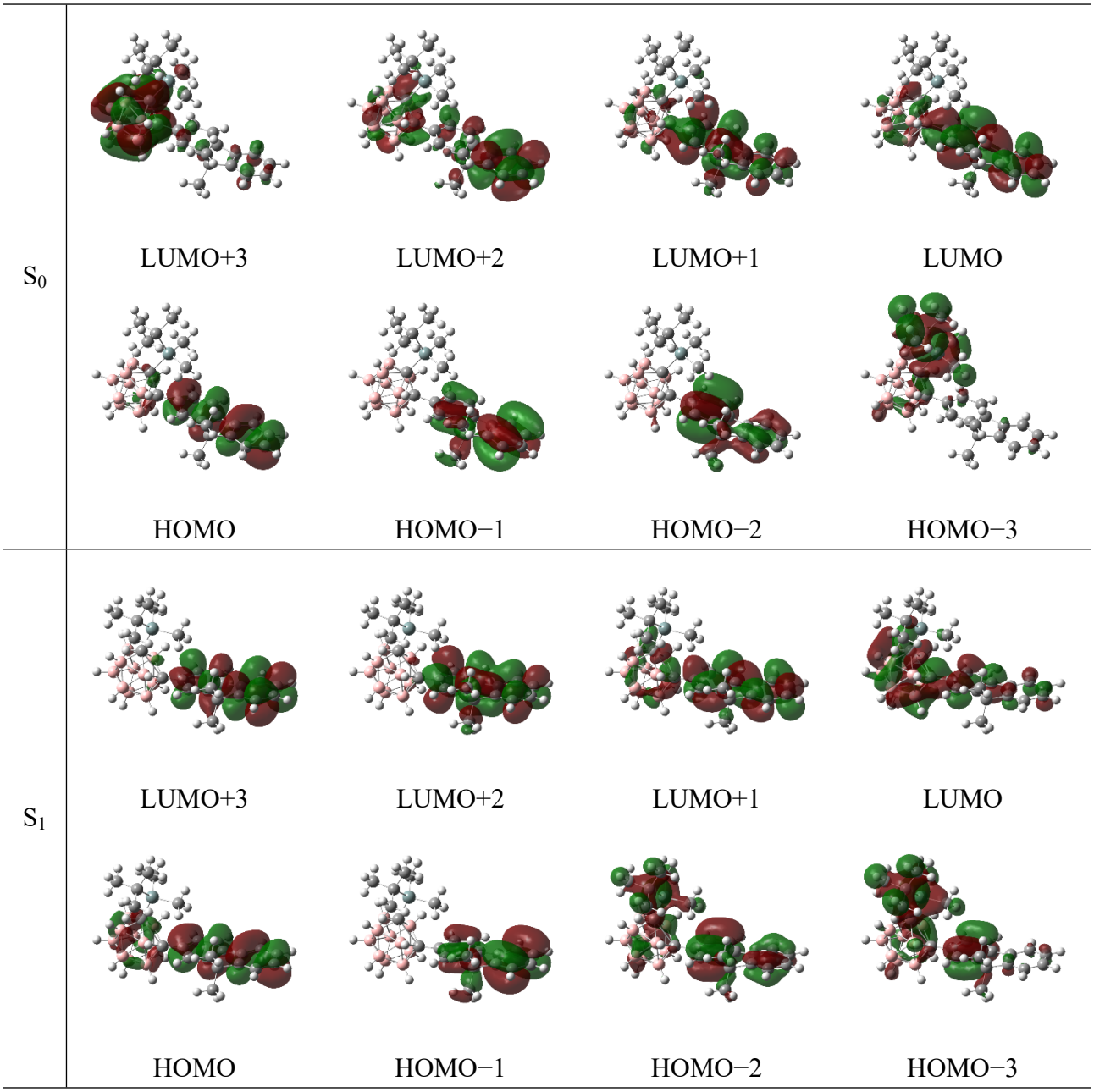

Figure S18 Selected frontier orbitals of **5CB** from CAM-B3LYP calculations (Isovalue = 0.02 a.u.) at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

Table S11 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **5CB** from TD-CAM-B3LYP calculations using the CAM-B3LYP geometries at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

state	λ_{calc} (/nm)	f_{calc}	Major contribution
			S_0
1	267.10	0.8198	HOMO → LUMO (91.38%)
2	247.04	0.0249	HOMO–2 → LUMO (36.02%)
			HOMO → LUMO+1 (49.72%)
3	240.09	0.0251	HOMO → LUMO (52.99%)
			HOMO → LUMO+3 (9.61%)
			HOMO → LUMO+4 (18.27%)
4	208.56	0.1802	HOMO–2 → LUMO (52.23%)
			HOMO → LUMO+1 (35.81%)
5	200.64	0.0341	HOMO–4 → LUMO (19.01%)
			HOMO–1 → LUMO+1 (20.70%)
			HOMO → LUMO+3 (22.68%)
			S_1
1	443.99	0.9966	HOMO → LUMO (93.00%)
2	333.61	0.0047	HOMO–2 → LUMO (61.51%)
			HOMO–1 → LUMO (15.66%)
3	307.13	0.0200	HOMO–3 → LUMO (11.54%)
			HOMO–2 → LUMO (65.49%)
			HOMO–1 → LUMO (14.14%)
4	299.74	0.0539	HOMO–6 → LUMO (48.20%)
			HOMO–5 → LUMO (19.15%)
			HOMO–3 → LUMO (22.08%)
5	280.17	0.0793	HOMO–6 → LUMO (22.48%)
			HOMO–4 → LUMO (9.42%)
			HOMO–3 → LUMO (29.83%)
			HOMO–1 → LUMO (12.66%)

Table S12 Molecular orbital energies (in eV) and molecular orbital distributions (in %) of **5CB** at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

	E (eV)	fluorene	carborane	silyl
		S_0		
LUMO+3	1.25	6.96	88.38	4.67
LUMO+2	1.17	81.19	16.28	2.53
LUMO+1	0.59	89.45	8.50	2.05
LUMO	–0.28	85.71	13.39	0.90
HOMO	–7.51	95.63	3.99	0.38
HOMO–1	–8.38	99.76	0.14	0.10
HOMO–2	–8.63	97.60	1.52	0.88
HOMO–3	–9.08	2.95	8.00	89.05
		S_1		
LUMO+3	1.22	95.11	4.44	0.45
LUMO+2	0.68	95.04	4.38	0.58
LUMO+1	–0.04	84.87	13.88	1.25
LUMO	–2.18	21.64	75.49	2.87
HOMO	–7.24	90.12	9.40	0.49
HOMO–1	–8.52	99.39	0.34	0.27
HOMO–2	–8.78	65.19	9.48	25.33
HOMO–3	–8.83	33.98	11.60	54.42

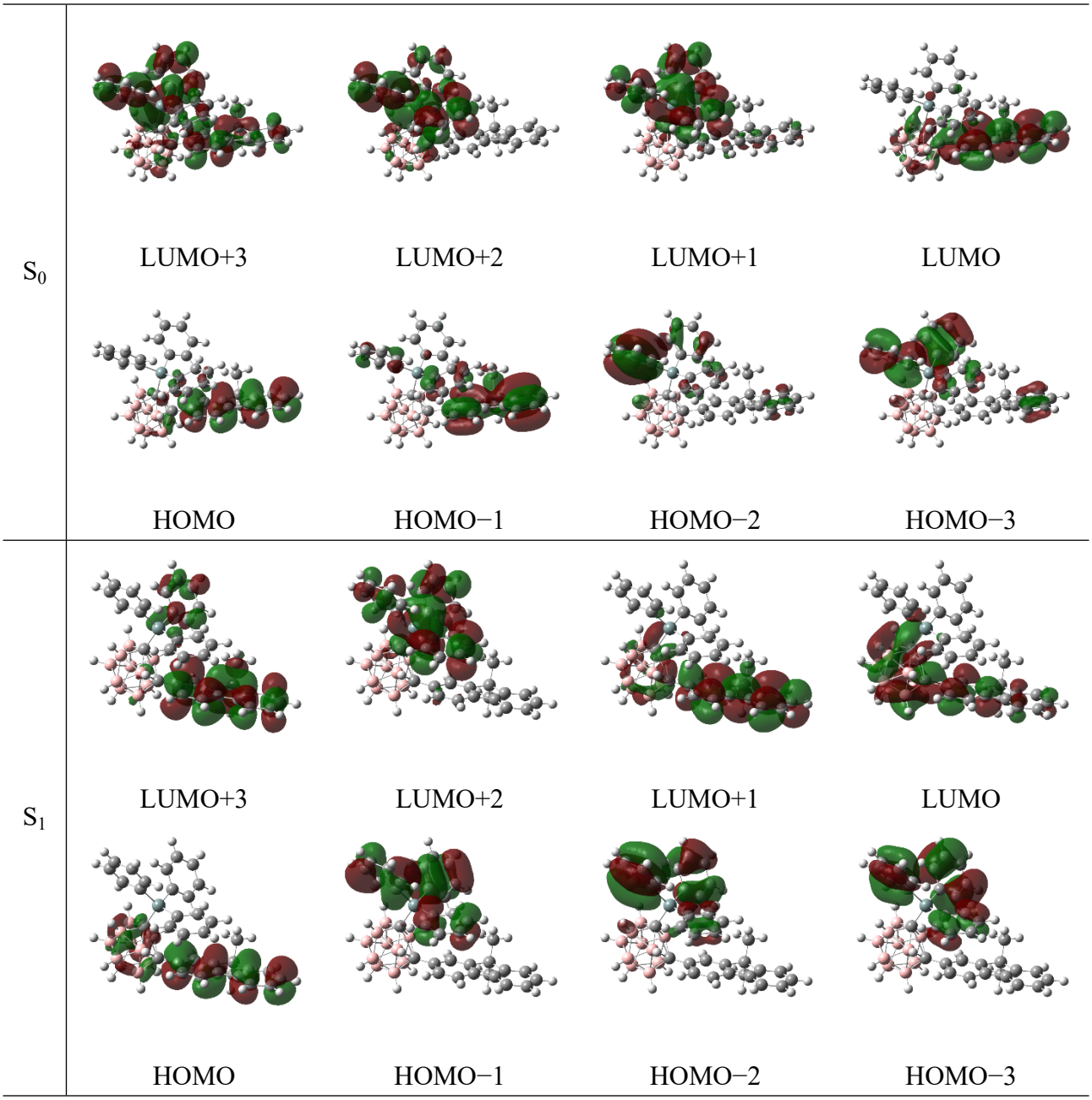

Fig. S19 Selected frontier orbitals of **6CP** from CAM-B3LYP calculations (Isovalue = 0.02 a.u.) at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

Table S13 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **6CP** from TD-CAM-B3LYP calculations using the CAM-B3LYP geometries at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

state	λ_{calc} (/nm)	f_{calc}	Major contribution
			S_0
1	269.51	0.7704	HOMO → LUMO (89.88%)
2	247.67	0.0261	HOMO–2 → LUMO (13.63%)
			HOMO–1 → LUMO (25.19%)
			HOMO → LUMO+1 (44.31%)
3	240.50	0.0171	HOMO–1 → LUMO (48.06%)
			HOMO → LUMO+2 (36.88%)
4	229.36	0.0065	HOMO–3 → LUMO (24.12%)
			HOMO–2 → LUMO+1 (46.66%)
			HOMO–1 → LUMO+1 (17.35%)
			S_1
1	445.76	0.9705	HOMO → LUMO (93.08%)
2	331.66	0.0010	HOMO–1 → LUMO (72.72%)
3	310.29	0.0166	HOMO–3 → LUMO (10.17%)
			HOMO–2 → LUMO (32.35%)
			HOMO–1 → LUMO (10.52%)
			HOMO–1 → LUMO+1 (19.50%)
4	308.19	0.0190	HOMO–4 → LUMO (11.73%)
			HOMO–3 → LUMO (28.25%)
			HOMO–1 → LUMO (7.11%)
			HOMO–1 → LUMO (17.34%)
			HOMO–1 → LUMO+1 (19.05%)
5	296.74	0.0122	HOMO–5 → LUMO (9.66%)
			HOMO–4 → LUMO (19.68%)
			HOMO–3 → LUMO (9.40%)
			HOMO–1 → LUMO (38.85%)

Table S14 Molecular orbital energies (in eV) and molecular orbital distributions (in %) of **6CP** at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in THF.

	E (eV)	fluorene	carborane	silyl
		S_0		
LUMO+3	0.70	30.20	8.49	61.32
LUMO+2	0.64	1.49	9.75	88.76
LUMO+1	0.31	4.90	3.55	91.55
LUMO	–0.22	80.50	13.72	5.78
HOMO	–7.40	93.28	4.20	2.52
HOMO–1	–8.30	88.05	0.38	11.57
HOMO–2	–8.33	3.65	1.67	94.68
HOMO–3	–8.36	5.98	2.41	91.62
		S_1		
LUMO+3	0.73	82.00	5.13	12.86
LUMO+2	0.49	2.01	2.70	95.29
LUMO+1	0.00	83.26	13.14	3.60
LUMO	–2.11	21.49	75.91	2.60
HOMO	–7.18	89.49	9.57	0.94
HOMO–1	–8.24	0.39	1.40	98.21
HOMO–2	–8.29	0.45	2.66	96.89
HOMO–3	–8.32	0.12	1.66	98.22

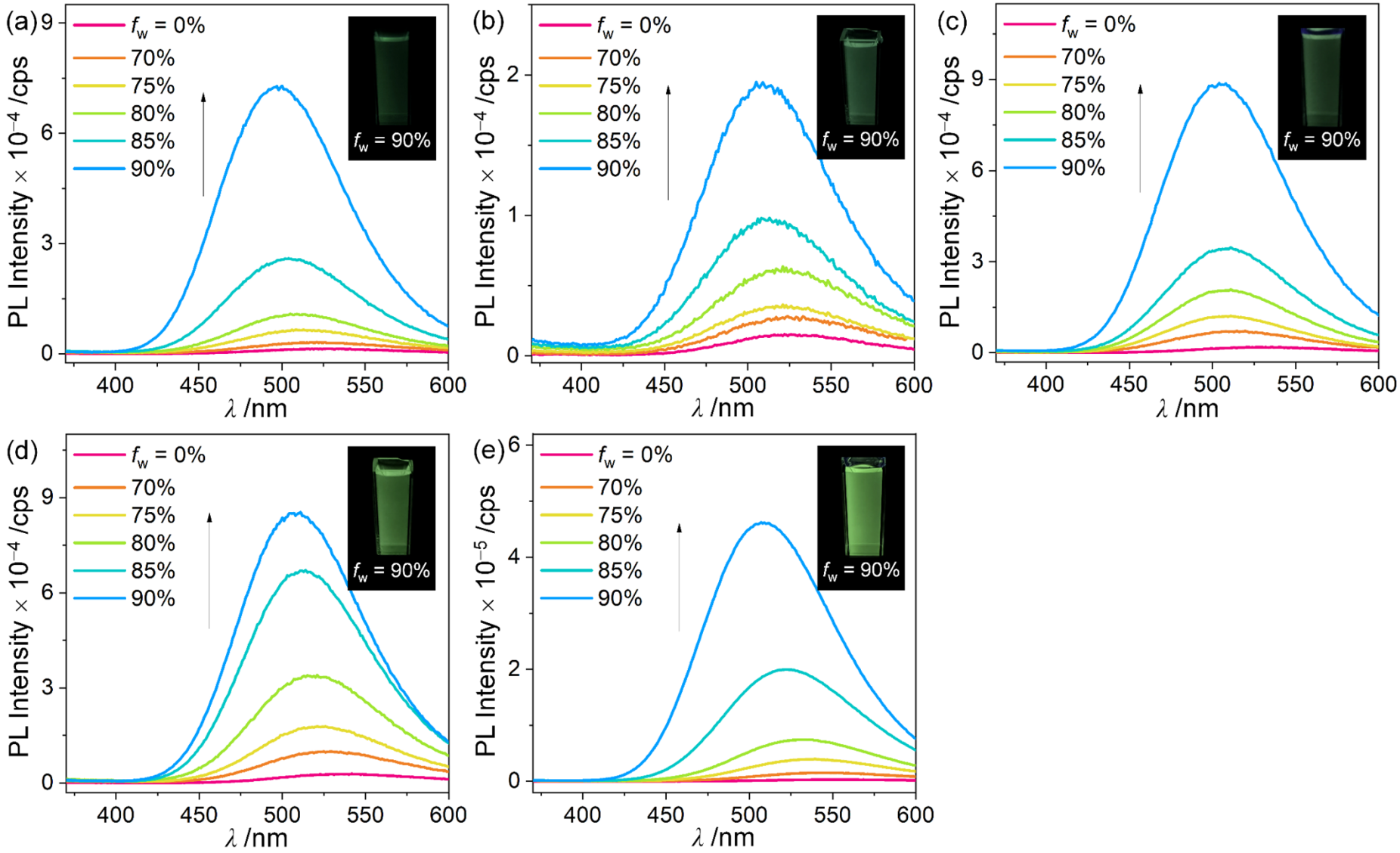

Fig. S20 PL spectra of (a) **2CM** (λ_{ex} = 308 nm). (b) **3CE** (λ_{ex} = 309 nm), (c) **4CE** (λ_{ex} = 310 nm), (d) **5CB** (λ_{ex} = 312 nm), and (e) **6CP** (λ_{ex} = 315 nm) in THF/distilled water mixtures (5.0 □ 10^{-5} M). Inset figures show the emission color in each state under irradiation by a hand-held UV lamp (λ_{ex} = 254 nm).

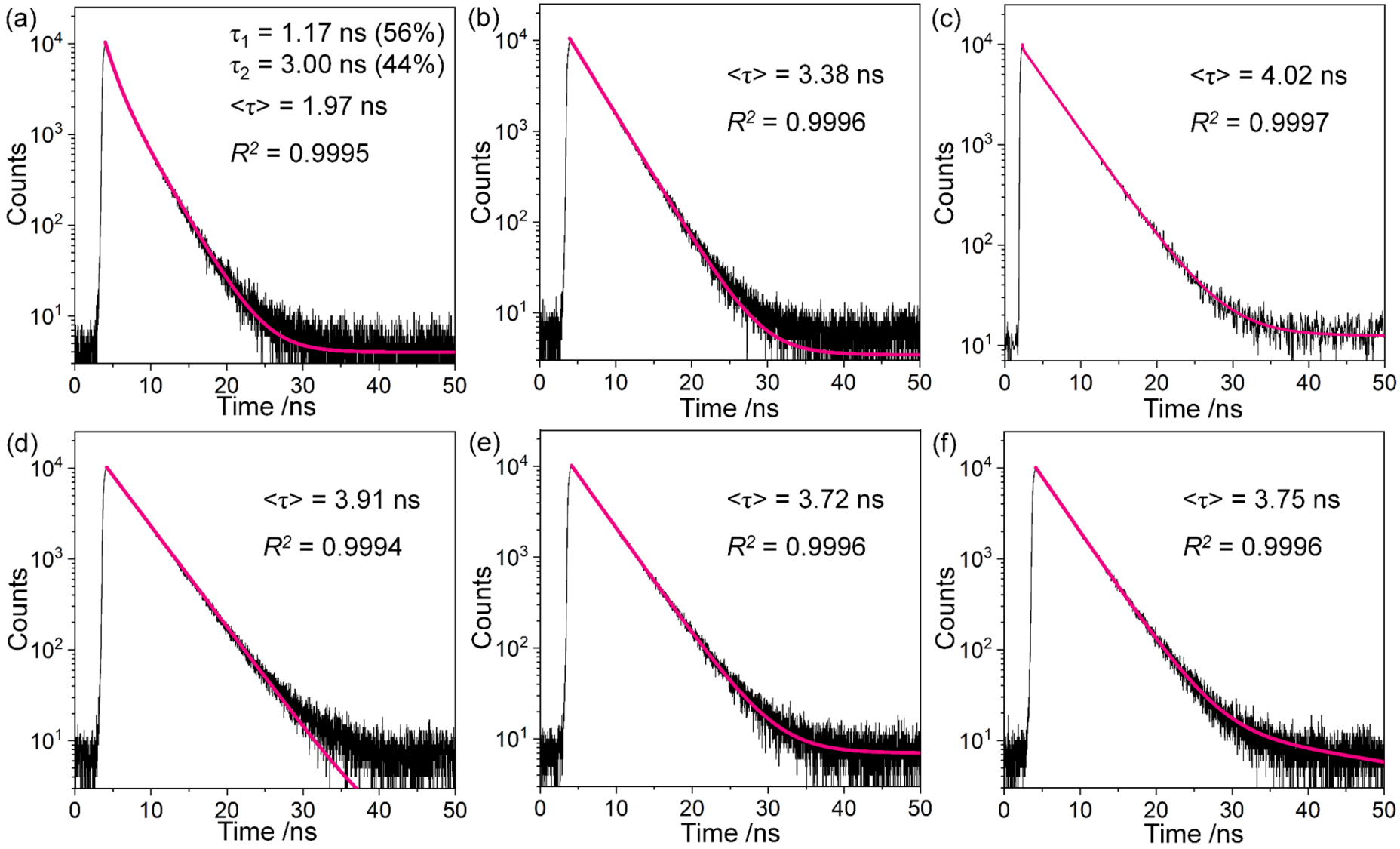

Fig. S21 Emission decay curves for fluorene-based silyl-*o*-carboranyl compounds **1CH–6CP** in crystalline states detected at each emission maximum at 298 K. Each pink line is its exponential fitting curve for the decay curves.

Table S15 Cartesian coordinates of the ground state (S_0) fully optimized geometry of **1CH** in THF from CAM-B3LYP calculations (in Å)

Atom	X	Y	Z
C	-3.16450	-0.48281	-1.28397
C	-2.26142	-0.25237	0.07667
B	-3.34821	-1.58768	-0.00765
H	-2.92158	-2.67540	-0.13630
B	-4.73045	-1.01705	-0.94545
H	-5.23291	-1.77940	-1.69571
B	-4.41392	0.64705	-1.44101
H	-4.70078	1.01144	-2.52803
B	-2.83001	1.11233	-0.81508
H	-2.04422	1.72256	-1.44456
B	-2.89719	1.06532	0.95061
H	-2.14055	1.73074	1.56674
B	-4.28161	1.64505	0.01394
H	-4.57829	2.79242	0.00564
B	-5.47026	0.32294	-0.06184
H	-6.63667	0.52518	-0.12894
B	-4.80294	-1.06899	0.82316
H	-5.47355	-1.86627	1.38802
B	-3.21397	-0.60176	1.44921
H	-2.66118	-1.05595	2.38963
B	-4.53099	0.58174	1.41703
H	-5.01104	0.97702	2.42686
C	1.47224	0.36127	0.01709
C	0.10834	0.58236	0.03000
H	-0.27759	1.59483	0.04072
C	-0.77317	-0.50686	0.03577
C	-0.25376	-1.80479	0.03874
H	-0.91928	-2.65669	0.06004
C	1.11780	-2.02999	0.02164
H	1.49500	-3.04734	0.02319
C	1.98157	-0.94351	0.00945
C	3.44730	-0.87050	-0.00524
C	4.40692	-1.87651	-0.01752
H	4.11853	-2.92299	-0.01760
C	5.75060	-1.51632	-0.02950
H	6.51470	-2.28662	-0.03898
C	6.12382	-0.17299	-0.02914
H	7.17627	0.09131	-0.03830
C	5.15957	0.83365	-0.01685
H	5.46175	1.87674	-0.01630
C	3.81931	0.48059	-0.00502
C	2.59650	1.38813	0.01005
C	2.53914	2.27318	-1.24535
H	3.39056	2.95886	-1.26919
H	1.62496	2.87342	-1.25253
H	2.56055	1.66891	-2.15547
C	2.56325	2.26309	1.27345
H	3.41527	2.94835	1.28636
H	2.60156	1.65141	2.17795
H	1.64953	2.86326	1.30310
H	-2.61436	-0.84429	-2.14245

Table S16 Cartesian coordinates of the first-excited state (S_1) fully optimized geometry of **1CH** in THF from CAM-B3LYP calculations (in Å)

Atom	X	Y	Z
C	7.10880	8.52530	17.48570
C	5.91172	8.40724	15.49606
B	7.55238	8.00571	15.94609
H	7.90369	6.88176	15.80184
B	8.54210	9.11629	17.03696
H	9.51683	8.72976	17.59245
B	7.24402	10.11052	17.75899
H	7.20529	10.50072	18.87895
B	5.76143	9.37758	16.94300
H	4.74929	9.29662	17.55656
B	5.72076	9.99292	15.21445
H	4.71204	10.31696	14.67880
B	6.46011	10.99630	16.45048
H	5.96134	12.04871	16.68813
B	8.22935	10.75886	16.42496
H	9.01070	11.63250	16.62678
B	8.53257	9.40994	15.29676
H	9.54923	9.30133	14.69075
B	7.03722	8.98476	14.48188
H	7.04158	8.53482	13.38315
B	7.33288	10.67998	14.92449
H	7.48253	11.49527	14.07160
C	2.68978	6.53982	15.23736
C	3.57245	7.54102	15.51460
H	3.25286	8.45618	15.99817
C	4.94880	7.38361	15.17343
C	5.36515	6.18171	14.50082
H	6.40618	6.08641	14.21975
C	4.48464	5.17796	14.22185
H	4.81591	4.27672	13.71868
C	3.12674	5.33710	14.59307
C	2.01447	4.47280	14.42682
C	1.93437	3.18746	13.85166
H	2.81804	2.70558	13.44831
C	0.70715	2.56183	13.81701
H	0.61322	1.57336	13.38204
C	-0.43273	3.19427	14.34324
H	-1.38688	2.67967	14.30427
C	-0.36361	4.46677	14.91401
H	-1.25833	4.93289	15.31278
C	0.85680	5.10791	14.95846
C	1.19631	6.47873	15.51846
C	0.90704	6.55492	17.02634
H	-0.16350	6.43999	17.21401
H	1.21681	7.52478	17.42387
H	1.43897	5.77272	17.57245
C	0.44014	7.59036	14.77281
H	-0.63659	7.49079	14.93235
H	0.63502	7.55128	13.69882
H	0.74627	8.57200	15.14316
H	6.98550	7.79295	18.27164

Table S17 Cartesian coordinates of the ground state (S_0) fully optimized geometry of **2CM** in THF from CAM-B3LYP calculations (in Å)

Atom	X	Y	Z
C	-2.84697	0.36629	0.04995
C	-1.74676	-0.86372	-0.32630
B	-2.87085	-0.34112	-1.50688
H	-2.49705	0.29612	-2.42253
B	-4.36370	0.01031	-0.64478
H	-5.02220	0.91542	-1.02521
B	-4.06984	-0.25023	1.06704
H	-4.52238	0.47235	1.88601
B	-2.39691	-0.76161	1.25391
H	-1.71269	-0.39880	2.13971
B	-2.20340	-2.31800	0.43621
H	-1.33172	-3.03342	0.79055
B	-3.68876	-1.95655	1.31525
H	-3.94342	-2.49935	2.33827
B	-4.91927	-1.48031	0.12467
H	-6.07632	-1.68168	0.29258
B	-4.16958	-1.53007	-1.48600
H	-4.77086	-1.76565	-2.48047
B	-2.49865	-2.05605	-1.28433
H	-1.82710	-2.59437	-2.09445
B	-3.76348	-2.75763	-0.26831
H	-4.07019	-3.89742	-0.38914
C	1.96752	-0.45357	0.32640
C	0.61824	-0.66770	0.53961
H	0.25884	-0.91596	1.53092
C	-0.27929	-0.57334	-0.53192
C	0.21565	-0.29765	-1.81120
H	-0.46180	-0.25836	-2.65416
C	1.57120	-0.08242	-2.02938
H	1.92803	0.13030	-3.03165
C	2.44767	-0.15513	-0.95491
C	3.90288	0.01726	-0.87815
C	4.83478	0.32168	-1.86406
H	4.52786	0.47545	-2.89393
C	6.17479	0.42643	-1.50522
H	6.91758	0.66338	-2.25980
C	6.57159	0.22924	-0.18325
H	7.62086	0.31431	0.08012
C	5.63507	-0.07622	0.80314
H	5.95539	-0.22838	1.82960
C	4.29859	-0.18141	0.45144
C	3.10349	-0.50197	1.33916
C	2.92037	0.55719	2.43785
H	3.77686	0.55561	3.11763
H	2.02341	0.34936	3.02824
H	2.82586	1.55805	2.00931
C	3.23202	-1.89805	1.96948
H	4.09335	-1.93571	2.64206
H	3.36142	-2.66619	1.20336
H	2.33970	-2.14161	2.55294
H	-2.30177	2.22929	0.24018
C	-3.84818	3.20596	0.64688
C	-1.07143	2.39062	1.64268
C	-1.57484	2.84809	-1.37060
H	-1.49373	2.05656	2.59363
H	-0.15032	1.83359	1.46062
H	-0.80792	3.44777	1.75004
H	-4.59754	3.14301	-0.14502
H	-4.31002	2.87990	1.58125
H	-3.57080	4.25883	0.76107
H	-1.31034	3.90308	-1.24572
H	-0.67097	2.30871	-1.66001
H	-2.29308	2.78184	-2.19156

Table S18 Cartesian coordinates of the first-excited state (S_1) fully optimized geometry of **2CM** in THF from CAM-B3LYP calculations (in Å)

Atom	X	Y	Z
C	7.17613	8.27856	17.33089
C	5.89169	8.37829	15.37608
B	7.53052	7.91065	15.69493
H	7.85326	6.80404	15.41746
B	8.58419	8.90211	16.81663
H	9.59124	8.46877	17.27486
B	7.34960	9.85694	17.67295
H	7.37358	10.18358	18.81530
B	5.82468	9.23101	16.88112
H	4.83223	9.14724	17.52395
B	5.71482	9.98582	15.20507
H	4.68707	10.36127	14.74394
B	6.53313	10.86819	16.48169
H	6.07212	11.90525	16.83634
B	8.29104	10.59682	16.35359
H	9.10363	11.43243	16.59175
B	8.50757	9.34124	15.10834
H	9.49662	9.25546	14.45406
B	6.96671	9.01610	14.33701
H	6.89914	8.65165	13.20878
B	7.32562	10.66176	14.89499
H	7.45636	11.54065	14.10396
C	2.65408	6.52227	15.20054
C	3.55642	7.49949	15.49992
H	3.27896	8.35798	16.09926
C	4.89834	7.39136	15.02720
C	5.25442	6.26685	14.20209
H	6.26694	6.21023	13.82374
C	4.35381	5.28743	13.90019
H	4.64094	4.44465	13.28179
C	3.03386	5.39556	14.40162
C	1.91113	4.54175	14.24547
C	1.78189	3.32204	13.55015
H	2.62717	2.89229	13.02427
C	0.55608	2.69230	13.55661
H	0.42477	1.75321	13.03132
C	-0.53381	3.25752	14.24077
H	-1.48821	2.74204	14.23017
C	-0.41516	4.46458	14.93228
H	-1.27204	4.87962	15.45197
C	0.80505	5.10818	14.93804
C	1.19264	6.41584	15.60736
C	1.04664	6.32709	17.13551
H	-0.00166	6.18569	17.41054
H	1.39666	7.25058	17.60373
H	1.62496	5.49399	17.54168
C	0.36886	7.59236	15.05966
H	-0.68840	7.46194	15.30436
H	0.46455	7.67318	13.97461
H	0.70447	8.53167	15.50632
H	7.02721	6.91719	18.63459
C	8.28219	7.24152	19.99849
C	5.29534	6.91879	19.36631
C	7.37155	5.24216	17.85353
H	5.05527	7.87983	19.82931
H	4.53461	6.71574	18.60718
H	5.21568	6.14600	20.13742
H	9.30365	7.23673	19.60894
H	8.11008	8.21025	20.47521
H	8.21200	6.46864	20.77038
H	7.29393	4.45453	18.60972
H	6.65998	5.01288	17.05531
H	8.37670	5.19762	17.42556

Table S19 Cartesian coordinates of the ground state (S_0) fully optimized geometry of **3CE** in THF from CAM-B3LYP calculations (in Å)

Atom	X	Y	Z
C	1.56269	-1.10505	-0.30263
C	2.72166	0.11514	-0.14557
B	2.24608	-0.76991	1.23367
H	1.58690	-0.23131	2.04809
B	1.96574	-2.43156	0.68687
H	1.07278	-3.04018	1.16507
B	2.23930	-2.47644	-1.05651
H	1.52642	-3.10644	-1.75819
B	2.68700	-0.84548	-1.56474
H	2.33695	-0.35536	-2.57406
B	4.20644	-0.42151	-0.78739
H	4.89475	0.38260	-1.31728
B	3.93022	-2.07188	-1.35963
H	4.50171	-2.49664	-2.30773
B	3.48952	-3.05900	0.04962
H	3.74050	-4.21658	0.11900
B	3.48114	-2.00334	1.47866
H	3.72864	-2.38217	2.57469
B	3.93877	-0.38601	0.94616
H	4.44828	0.43475	1.62463
B	4.71027	-1.79206	0.21112
H	5.85991	-2.01814	0.39739
C	-2.11777	-0.50830	0.35785
C	-0.78182	-0.79726	0.56024
H	-0.42424	-1.04547	1.55240
C	0.10832	-0.76650	-0.52098
C	-0.38104	-0.47547	-1.79823
H	0.28730	-0.48569	-2.64878
C	-1.72392	-0.18078	-2.00511
H	-2.07744	0.04439	-3.00587
C	-2.59217	-0.19154	-0.92182
C	-4.03328	0.07068	-0.83195
C	-4.95532	0.42296	-1.81115
H	-4.65071	0.54801	-2.84554
C	-6.28237	0.61361	-1.43969
H	-7.01728	0.88883	-2.18900
C	-6.67619	0.45379	-0.11181
H	-7.71530	0.60595	0.16148
C	-5.74953	0.10055	0.86788
H	-6.06736	-0.02156	1.89910
C	-4.42599	-0.09051	0.50359
C	-3.24340	-0.47531	1.38247
C	-3.45071	-1.85380	2.03011
H	-4.30383	-1.83065	2.71373
H	-2.56754	-2.14635	2.60494
H	-3.63775	-2.62039	1.27440
C	-2.98221	0.58264	2.46658
H	-3.83151	0.64572	3.15246
H	-2.82442	1.56958	2.02478
H	-2.09627	0.32294	3.05292
H	2.27291	2.01049	-0.29767
C	0.66616	2.40777	0.58124
H	0.55863	3.49742	0.60538
H	0.65223	2.05298	1.61427
H	-0.20330	1.99715	0.06573
C	2.14492	2.43477	-2.11855
H	1.97535	3.51182	-2.21479
H	1.31226	1.92311	-2.60605
H	3.06173	2.19218	-2.66204
C	3.68768	2.99281	0.47265
H	4.64253	2.51590	0.22879
H	3.69670	3.95162	-0.06134
C	3.59282	3.25885	1.97987
H	4.43846	3.85958	2.32676
H	3.59124	2.33287	2.56059
H	2.67935	3.80424	2.23222

Table S20 Cartesian coordinates of the first-excited state (S_1) fully optimized geometry of **3CE** in THF from CAM-B3LYP calculations (in Å)

Atom	X	Y	Z
C	7.39815	2.70190	9.80286
C	7.40839	1.37038	7.87429
B	8.28407	2.77373	8.31787
H	8.16805	3.74973	7.65232
B	8.99209	2.94942	10.01067
H	9.31123	4.00123	10.45972
B	8.05201	1.67582	10.88177
H	7.65360	1.75273	11.99775
B	7.00708	1.04139	9.50449
H	5.90367	0.67881	9.75293
B	8.07775	0.00249	8.43690
H	7.70193	-1.03221	7.99145
B	8.46137	0.13507	10.15453
H	8.40026	-0.84269	10.82817
B	9.72576	1.37721	10.37554
H	10.58752	1.30165	11.19218
B	9.94196	2.14507	8.77685
H	10.96823	2.64215	8.44015
B	9.00156	1.25716	7.57853
H	9.36192	1.21953	6.44770
B	9.74203	0.37968	8.93843
H	10.61803	-0.40090	8.74168
C	5.50017	5.91444	9.97956
C	6.49379	5.02679	9.69164
H	7.36820	5.32341	9.12512
C	6.38221	3.67389	10.13103
C	5.23656	3.29033	10.91224
H	5.17717	2.26934	11.26676
C	4.24116	4.17685	11.20425
H	3.38269	3.86990	11.79072
C	4.35372	5.50833	10.73572
C	3.48596	6.62077	10.89137
C	2.24585	6.72519	11.55359
H	1.80824	5.86532	12.04846
C	1.60629	7.94602	11.55555
H	0.65134	8.05844	12.05607
C	2.18185	9.05497	10.91198
H	1.65824	10.00485	10.92822
C	3.40927	8.96083	10.25350
H	3.83211	9.83198	9.76464
C	4.06282	7.74588	10.23990
C	5.39226	7.38323	9.60022
C	6.54525	8.20602	10.19707
H	6.41210	9.26672	9.96941
H	7.49989	7.88762	9.77075
H	6.59636	8.08976	11.28193
C	5.34439	7.56000	8.07346
H	5.19468	8.61172	7.81647
H	4.53219	6.97794	7.63188
H	6.28605	7.23373	7.62468
H	6.03080	1.44976	6.58789
C	4.87800	2.88177	6.99542
H	4.08759	2.95201	6.24131
H	5.40608	3.83881	7.01661
H	4.39749	2.74169	7.96802
C	5.05990	-0.16001	6.63566
H	4.19808	-0.10074	5.96350
H	4.68664	-0.37441	7.64071
H	5.67384	-1.00754	6.31977
C	6.74296	1.67434	4.85268
H	7.45803	0.86407	4.66796
H	5.91250	1.49808	4.15613
C	7.39386	3.02626	4.54203
H	7.72921	3.07873	3.50155
H	8.26562	3.20733	5.17588
H	6.69609	3.85404	4.70122

Table S21 Cartesian coordinates of the ground state (S_0) fully optimized geometry of **4CE** in THF from CAM-B3LYP calculations (in Å)

r	X	Y	Z
C	-1.49609	-1.31500	0.31349
C	-2.67825	-0.12327	0.04380
B	-2.62919	-0.94994	1.54137
H	-2.28544	-0.36074	2.49966
B	-2.15606	-2.61711	1.18929
H	-1.43615	-3.16795	1.94777
B	-1.87611	-2.72917	-0.55143
H	-0.96937	-3.36053	-0.97086
B	-2.18149	-1.12536	-1.24447
H	-1.53488	-0.65150	-2.10833
B	-3.88399	-0.75295	-0.99808
H	-4.41246	-0.01589	-1.75156
B	-3.39481	-2.40156	-1.37970
H	-3.63288	-2.88255	-2.43704
B	-3.39083	-3.32171	0.14049
H	-3.62147	-4.48492	0.17882
B	-3.85191	-2.21466	1.45268
H	-4.41822	-2.56039	2.43533
B	-4.15662	-0.63171	0.72832
H	-4.86565	0.20206	1.17819
B	-4.63134	-2.09772	-0.13853
H	-5.77670	-2.35781	-0.30575
C	2.17681	-0.68136	-0.36636
C	0.84119	-0.97268	-0.56810
H	0.48112	-1.20767	-1.56245
C	-0.04398	-0.96192	0.51707
C	0.45124	-0.69804	1.79802
H	-0.21326	-0.73292	2.65117
C	1.79379	-0.40367	2.00500
H	2.15202	-0.20015	3.00869
C	2.65616	-0.38781	0.91679
C	4.09600	-0.11942	0.82548
C	5.02154	0.21626	1.80722
H	4.72129	0.32020	2.84520
C	6.34638	0.41773	1.43361
H	7.08392	0.68031	2.18484
C	6.73464	0.28477	0.10114
H	7.77211	0.44489	-0.17374
C	5.80447	-0.05180	-0.88112
H	6.11803	-0.15315	-1.91588
C	4.48308	-0.25338	-0.51469
C	3.29729	-0.62358	-1.39555
C	3.50553	-1.98685	-2.07409
H	2.62028	-2.26988	-2.65049
H	3.69905	-2.76904	-1.33623
H	4.35481	-1.94619	-2.76167
C	3.02751	0.45714	-2.45498
H	2.86848	1.43356	-1.99055
H	2.13988	0.20731	-3.04316
H	3.87345	0.53869	-3.14306
H	-2.29773	1.80151	0.01736
C	-2.64742	2.50713	1.73653
H	-3.00841	3.52929	1.56847
H	-3.49594	1.97330	2.17704
C	-1.47945	2.54908	2.72944
H	-0.64414	3.14010	2.34428
H	-1.09179	1.55275	2.95333
H	-1.78794	2.99929	3.67733
C	-3.50144	2.58951	-1.20533
H	-4.51708	2.23835	-0.99454
H	-3.50756	3.65707	-0.95100
C	-3.18129	2.43172	-2.69680
H	-3.91250	2.96232	-3.31347
H	-3.19003	1.38545	-3.01049
H	-2.19517	2.83607	-2.94120
C	-0.52894	2.17196	-0.51610
H	0.17281	1.77157	0.22012
H	-0.30773	1.65332	-1.45466
C	-0.28674	3.68024	-0.68772
H	0.74847	3.87822	-0.97951
H	-0.47226	4.23051	0.23953
H	-0.93077	4.11452	-1.45716

Table S22 Cartesian coordinates of the first-excited state (S_1) fully optimized geometry of **4CE** in THF from CAM-B3LYP calculations (in Å)

Atom	X	Y	Z
C	2.21252	6.78230	17.14389
C	3.60943	7.14817	15.28595
B	3.88628	6.47822	16.84123
H	4.26219	5.35573	16.91796
B	3.18431	7.26083	18.35613
H	3.08147	6.67506	19.38395
B	1.91885	8.31199	17.61111
H	0.84461	8.53087	18.06720
B	2.16929	7.90488	15.83010
H	1.21572	7.88536	15.12481
B	3.69009	8.77009	15.27909
H	3.75528	9.32390	14.23050
B	2.74026	9.47293	16.58746
H	2.23016	10.53246	16.41178
B	3.45975	9.00108	18.15318
H	3.48810	9.71147	19.10708
B	4.73764	7.81449	17.76388
H	5.69425	7.65529	18.45177
B	4.93786	7.73350	16.01325
H	5.99723	7.46106	15.55055
B	4.50333	9.28112	16.77759
H	5.26875	10.19182	16.76185
C	-0.96610	4.83540	16.89264
C	-0.08931	5.87558	16.80553
H	-0.38699	6.83046	16.38961
C	1.25265	5.70902	17.26013
C	1.63588	4.45151	17.84409
H	2.64761	4.34617	18.21417
C	0.76034	3.40847	17.93401
H	1.06752	2.46635	18.37353
C	-0.55941	3.58159	17.45182
C	-1.65914	2.68364	17.41845
C	-1.75737	1.34501	17.84842
H	-0.90457	0.84070	18.28899
C	-2.96281	0.69485	17.69330
H	-3.06987	-0.33516	18.01373
C	-4.06207	1.35597	17.11946
H	-4.99926	0.82148	17.00679
C	-3.97431	2.68192	16.69174
H	-4.83757	3.16889	16.25068
C	-2.77529	3.34841	16.84018
C	-2.42330	4.77706	16.46208
C	-3.27748	5.78936	17.24285
H	-2.96537	6.81010	17.00798
H	-3.18406	5.63998	18.32078
H	-4.33100	5.68795	16.97031
C	-2.57039	5.00936	14.94973
H	-1.96709	4.30004	14.37851
H	-2.25291	6.02199	14.68844
H	-3.61474	4.89562	14.64821
H	3.60019	6.05035	13.74957
C	5.30819	5.29513	13.44430
H	5.25512	4.82834	12.45191
H	6.02847	6.11510	13.34018
C	5.82822	4.27232	14.45921
H	5.12357	3.44609	14.59699
H	5.99284	4.72646	15.43887
H	6.77923	3.83799	14.13533
C	3.19033	7.05521	12.19928
H	3.93221	7.85733	12.10881
H	3.38238	6.38571	11.35048
C	1.77853	7.63703	12.07723
H	1.62923	8.11934	11.10611
H	1.58486	8.38646	12.84790
H	1.01225	6.86160	12.17622
C	2.31726	4.68256	13.99783
H	2.56763	4.13262	14.91288
H	1.34387	5.14937	14.18993
C	2.20307	3.70756	12.82005
H	1.45075	2.93497	13.00685
H	3.15141	3.19688	12.62662
H	1.91765	4.22230	11.89743

Table S23 Cartesian coordinates of the ground state (S_0) fully optimized geometry of **5CB** in THF from CAM-B3LYP calculations (in Å)

Atom	X	Y	Z
C	-2.45789	-0.38752	-0.13958
C	-1.14823	-1.47757	-0.29079
B	-2.29336	-1.35416	-1.55137
H	-2.00235	-0.83884	-2.56626
B	-3.85728	-1.11695	-0.78569
H	-4.63736	-0.41655	-1.33120
B	-3.59910	-1.04349	0.94935
H	-4.20731	-0.30473	1.63715
B	-1.87221	-1.21354	1.23782
H	-1.28550	-0.60063	2.05530
B	-1.39466	-2.83585	0.70413
H	-0.43691	-3.32853	1.19014
B	-2.95007	-2.58898	1.48967
H	-3.15369	-2.98722	2.58782
B	-4.19322	-2.53441	0.21912
H	-5.30800	-2.89513	0.40504
B	-3.38016	-2.72353	-1.34706
H	-3.89359	-3.21602	-2.29561
B	-1.65667	-2.92092	-1.03831
H	-0.87246	-3.46056	-1.73912
B	-2.82995	-3.64559	0.06716
H	-2.93958	-4.82466	0.14152
C	2.44938	-0.50027	0.36377
C	1.14853	-0.91722	0.56991
H	0.81444	-1.18309	1.56572
C	0.26204	-0.99128	-0.51201
C	0.72254	-0.67414	-1.79361
H	0.05985	-0.76490	-2.64394
C	2.02978	-0.25049	-2.00458
H	2.36138	-0.00704	-3.00855
C	2.89259	-0.15818	-0.92063
C	4.30049	0.24674	-0.83428
C	5.18569	0.67132	-1.81882
H	4.87284	0.74787	-2.85547
C	6.48667	0.99793	-1.44987
H	7.19271	1.33117	-2.20336
C	6.89127	0.90033	-0.11920
H	7.90976	1.15855	0.15205
C	6.00162	0.47436	0.86588
H	6.32770	0.40164	1.89920
C	4.70420	0.14759	0.50406
C	3.56344	-0.33759	1.38855
C	3.19449	0.70847	2.45270
H	4.03044	0.86762	3.13936
H	2.33621	0.37269	3.04164
H	2.94142	1.66679	1.99260
C	3.90564	-1.67644	2.06153
H	4.75143	-1.55600	2.74405
H	4.16883	-2.43455	1.32008
H	3.05534	-2.04461	2.64243
H	-2.18462	1.55474	-0.32009
C	-0.56168	2.04409	0.49073
H	-0.53230	3.13367	0.58300
H	0.29882	1.74060	-0.10676
H	-0.44396	1.62619	1.49258
C	-2.11110	1.91985	-2.15990
H	-1.96895	2.99313	-2.31073
H	-3.02485	1.62509	-2.68232
H	-1.27012	1.40986	-2.63383
C	-3.58764	2.58434	0.49383
C	-3.36904	4.04179	0.03136
H	-4.08443	4.69240	0.54758
H	-3.53619	4.16295	-1.04201
H	-2.36821	4.41783	0.26350
C	-3.48179	2.56178	2.02842
H	-4.25770	3.20499	2.46068
H	-2.51579	2.94136	2.37382
H	-3.61721	1.56206	2.44623
C	-5.00588	2.18045	0.06334
H	-5.72720	2.90385	0.46250
H	-5.29305	1.19561	0.43278
H	-5.11727	2.17775	-1.02537

Table S24 Cartesian coordinates of the first-excited state (S_1) fully optimized geometry of **5CB** in THF from CAM-B3LYP calculations (in Å)

Atom	X	Y	Z
C	7.35817	8.23400	17.25173
C	5.91812	8.33271	15.38702
B	7.57888	7.89654	15.57883
H	7.89958	6.79739	15.26455
B	8.70182	8.89898	16.62831
H	9.75382	8.48836	16.99542
B	7.51554	9.81583	17.58666
H	7.62107	10.15466	18.71749
B	5.94763	9.15153	16.90734
H	5.00617	9.03108	17.62015
B	5.69449	9.93784	15.25361
H	4.62710	10.29619	14.87677
B	6.58528	10.81763	16.47731
H	6.13158	11.83867	16.88383
B	8.33508	10.58929	16.21057
H	9.14452	11.44047	16.39961
B	8.48312	9.35427	14.93544
H	9.42249	9.29799	14.20881
B	6.89725	9.00920	14.27778
H	6.75070	8.65631	13.15348
B	7.26107	10.65325	14.83208
H	7.31200	11.54634	14.04784
C	2.64663	6.53167	15.27147
C	3.57695	7.48223	15.57006
H	3.33478	8.32994	16.19958
C	4.90199	7.35983	15.05672
C	5.21222	6.25154	14.19377
H	6.21241	6.18507	13.78522
C	4.28334	5.29789	13.89287
H	4.53576	4.46572	13.24561
C	2.98096	5.41965	14.43387
C	1.83660	4.59117	14.28891
C	1.66353	3.39311	13.56720
H	2.48441	2.96162	13.00536
C	0.42635	2.78611	13.59411
H	0.26164	1.86360	13.04923
C	-0.63152	3.35365	14.32456
H	-1.59559	2.85641	14.32991
C	-0.46927	4.54018	15.04182
H	-1.30235	4.95780	15.59694
C	0.76313	5.16056	15.02725
C	1.19502	6.44404	15.71584
C	1.08792	6.32349	17.24490
H	0.04506	6.19286	17.54480
H	1.46508	7.23075	17.72366
H	1.66306	5.47249	17.61697
C	0.38146	7.64895	15.21641
H	-0.67128	7.53504	15.48735
H	0.44938	7.75139	14.13108
H	0.74916	8.57114	15.67333
H	7.32353	6.74521	18.42167
C	5.83330	5.68229	17.96964
H	5.80697	4.77721	18.58291
H	5.88740	5.36778	16.92370
H	4.88786	6.21279	18.11125
C	8.88544	5.73628	18.12182
H	8.87216	4.81835	18.71680
H	9.78951	6.29235	18.38095
H	8.96382	5.44829	17.07024
C	7.21913	7.22766	20.27551
C	7.07373	5.93577	21.10082
H	7.05350	6.17950	22.17040
H	7.90816	5.24551	20.94190
H	6.14658	5.40228	20.87171
C	6.00259	8.12066	20.56299
H	5.93568	8.32733	21.63884
H	5.06501	7.63982	20.26571
H	6.06438	9.08124	20.04707
C	8.50059	7.94446	20.72957
H	8.42971	8.20073	21.79433
H	8.67405	8.87254	20.17965
H	9.38433	7.31108	20.60618

Table S25 Cartesian coordinates of the ground state (S_0) fully optimized geometry of **6CP** in THF from CAM-B3LYP calculations (in Å)

Atom	X	Y	Z
C	-0.41896	2.11105	-0.64174
C	-1.88898	1.31429	-0.24872
B	-0.41703	3.68861	-0.00016
H	0.62372	4.11456	0.36267
B	-1.12449	2.33904	0.89686
H	-0.62246	1.85591	1.84273
B	-2.86596	2.37818	0.65306
H	-3.53981	1.91504	1.50661
B	-1.96472	3.88677	0.81467
H	-2.06479	4.55588	1.78833
B	-1.72621	4.54711	-0.81641
H	-1.64288	5.71197	-1.02579
B	-2.46150	3.42166	-1.97431
H	-2.92074	3.75476	-3.01547
B	-3.17565	2.09918	-1.05510
H	-4.07851	1.43819	-1.42645
B	-3.24262	3.74061	-0.40991
H	-4.27870	4.31137	-0.32003
C	3.01550	0.77137	0.23085
C	1.77401	1.36831	0.35342
H	1.48734	1.83904	1.28657
C	0.89861	1.38358	-0.74089
C	1.31225	0.82130	-1.95229
H	0.65737	0.85222	-2.81221
C	2.55628	0.21761	-2.07785
H	2.84931	-0.21829	-3.02698
C	3.40682	0.18848	-0.98072
C	4.75722	-0.36189	-0.81751
C	5.57636	-1.03935	-1.71362
H	5.24655	-1.24089	-2.72799
C	6.83235	-1.45691	-1.28490
H	7.48633	-1.98731	-1.96925
C	7.25808	-1.19923	0.01744
H	8.24069	-1.53150	0.33630
C	6.43486	-0.51924	0.91385
H	6.77708	-0.32317	1.92571
C	5.18246	-0.10149	0.49217
C	4.11727	0.65386	1.27584
C	4.62240	2.04011	1.70890
H	5.45790	1.94191	2.40750
H	3.82850	2.60037	2.21086
H	4.96156	2.62194	0.84859
C	3.65060	-0.14183	2.50468
H	4.47664	-0.28325	3.20702
H	3.27278	-1.12663	2.21822
H	2.85550	0.39572	3.02976
H	-2.02583	-0.61916	0.11367
C	-0.87374	-1.59695	-1.00743
C	-1.08970	-1.64517	-2.39438
H	-1.91331	-1.09393	-2.83655
C	-0.28030	-2.40606	-3.22770
H	-0.47182	-2.42494	-4.29571
C	0.76774	-3.14778	-2.69147
H	1.40115	-3.74443	-3.34008
C	0.98919	-3.13155	-1.32055
H	1.79592	-3.71709	-0.89172
C	0.17427	-2.36833	-0.49032
H	0.36051	-2.38523	0.57728
C	-1.63528	-0.93008	1.92915
C	-0.34638	-0.76628	2.46151
H	0.46293	-0.41684	1.82898
C	-0.07131	-1.04577	3.79386
H	0.93594	-0.91453	4.17592
C	-1.08462	-1.49410	4.63534
H	-0.87208	-1.71134	5.67713
C	-2.36776	-1.66490	4.13286
H	-3.16454	-2.01680	4.78008
C	-2.63639	-1.38976	2.79528
H	-3.64410	-1.54120	2.42494
C	-3.79530	-1.18366	-0.22891
C	-4.00775	-2.35582	-0.96817
H	-3.16564	-2.88553	-1.39804
C	-5.28622	-2.86852	-1.16848
H	-5.41587	-3.77635	-1.74876
C	-6.38900	-2.22152	-0.62805
H	-7.38719	-2.61790	-0.78376
C	-6.20461	-1.06259	0.11930
H	-7.05836	-0.55058	0.55117
C	-4.92686	-0.55541	0.31595
H	-4.81856	0.34725	0.90545
B	-1.61547	1.87799	-1.84082
H	-1.43561	1.09853	-2.70131
B	-0.72069	3.40051	-1.71261
H	0.11199	3.62822	-2.51979

Table S26 Cartesian coordinates of the first-excited state (S_1) fully optimized geometry of **6CP** in THF from CAM-B3LYP calculations (in Å)

tom	X	Y	Z
C	5.83223	3.12221	12.15264
C	4.45141	1.33478	12.80859
B	6.21181	3.76781	13.59573
H	7.30190	4.22553	13.70520
B	5.92534	1.95786	13.42990
H	6.87324	1.25209	13.46892
B	4.44562	1.53129	14.42120
H	4.40819	0.56061	15.10536
B	5.43833	2.90688	14.91417
H	6.00155	2.84966	15.95947
B	4.71254	4.41277	14.29112
H	4.72621	5.44519	14.88181
B	3.37609	3.90049	13.22503
H	2.41605	4.57336	13.02783
B	3.15737	2.15875	13.36063
H	2.08133	1.69203	13.19187
B	3.67297	3.09406	14.78636
H	2.95262	3.19789	15.72736
C	8.88317	2.47342	10.09805
C	8.07458	2.60072	11.18839
H	8.42690	2.35610	12.18323
C	6.73012	3.04806	11.02210
C	6.27744	3.41271	9.70749
H	5.26574	3.78063	9.59811
C	7.08560	3.29266	8.61461
H	6.72512	3.56444	7.62910
C	8.40450	2.80995	8.79133
C	9.44377	2.58805	7.84911
C	9.46259	2.77331	6.45234
H	8.58480	3.13807	5.93091
C	10.62309	2.47980	5.76883
H	10.66908	2.61181	4.69388
C	11.75549	2.00867	6.45451
H	12.65673	1.78494	5.89379
C	11.74595	1.82237	7.83799
H	12.63411	1.45849	8.34341
C	10.59177	2.10931	8.53762
C	10.32435	1.99313	10.02870
C	11.26075	2.90384	10.83895
H	12.29838	2.58018	10.72411
H	11.00930	2.85904	11.90159
H	11.18528	3.94291	10.51088
C	10.44827	0.53694	10.50714
H	11.47275	0.17886	10.37798
H	9.77942	-0.12213	9.94853
H	10.19796	0.46464	11.56884
H	4.40401	-0.34787	11.93502
C	4.72292	-0.14957	10.08096
C	3.78709	0.51674	9.27265
H	2.88320	0.92322	9.71536
C	3.97816	0.66051	7.90410
H	3.23425	1.17754	7.30628
C	5.11844	0.13745	7.30210
H	5.27035	0.24682	6.23286
C	6.05312	-0.53852	8.07644
H	6.93863	-0.96348	7.61411
C	5.85154	-0.68359	9.44645
H	6.58631	-1.23400	10.02321
C	5.69081	-1.50931	12.68876
C	7.07222	-1.29565	12.55319
H	7.43753	-0.42714	12.01508
C	8.00207	-2.17493	13.09448
H	9.06319	-1.98232	12.97017
C	7.57352	-3.29773	13.79521
H	8.29762	-3.98507	14.22099
C	6.21278	-3.53304	13.94416
H	5.86722	-4.40659	14.48788
C	5.28716	-2.65091	13.39424
H	4.23006	-2.85991	13.51903
C	2.70284	-1.13940	12.15380
C	2.06115	-1.78617	11.08972
H	2.51919	-1.79027	10.10609
C	0.83765	-2.42696	11.26220
H	0.36203	-2.91774	10.41886
C	0.22719	-2.43746	12.51014
H	-0.72766	-2.93508	12.64720
C	0.84725	-1.80645	13.58412
H	0.37823	-1.81015	14.56291
C	2.06777	-1.16661	13.40478
H	2.53045	-0.68019	14.25782
B	4.14664	2.81374	11.97324
H	3.70354	2.77030	10.87742
B	4.90527	4.40331	12.52764
H	4.98648	5.35031	11.81598

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