Electronic Supplementary Information

2-Phenylpyridine- and 2-(Benzo[b]thiophen-2-yl)pyridine-based *o*-Carboranyl Compounds: Impact of the Structural Formation of Aromatic Rings on Photophysical Properties

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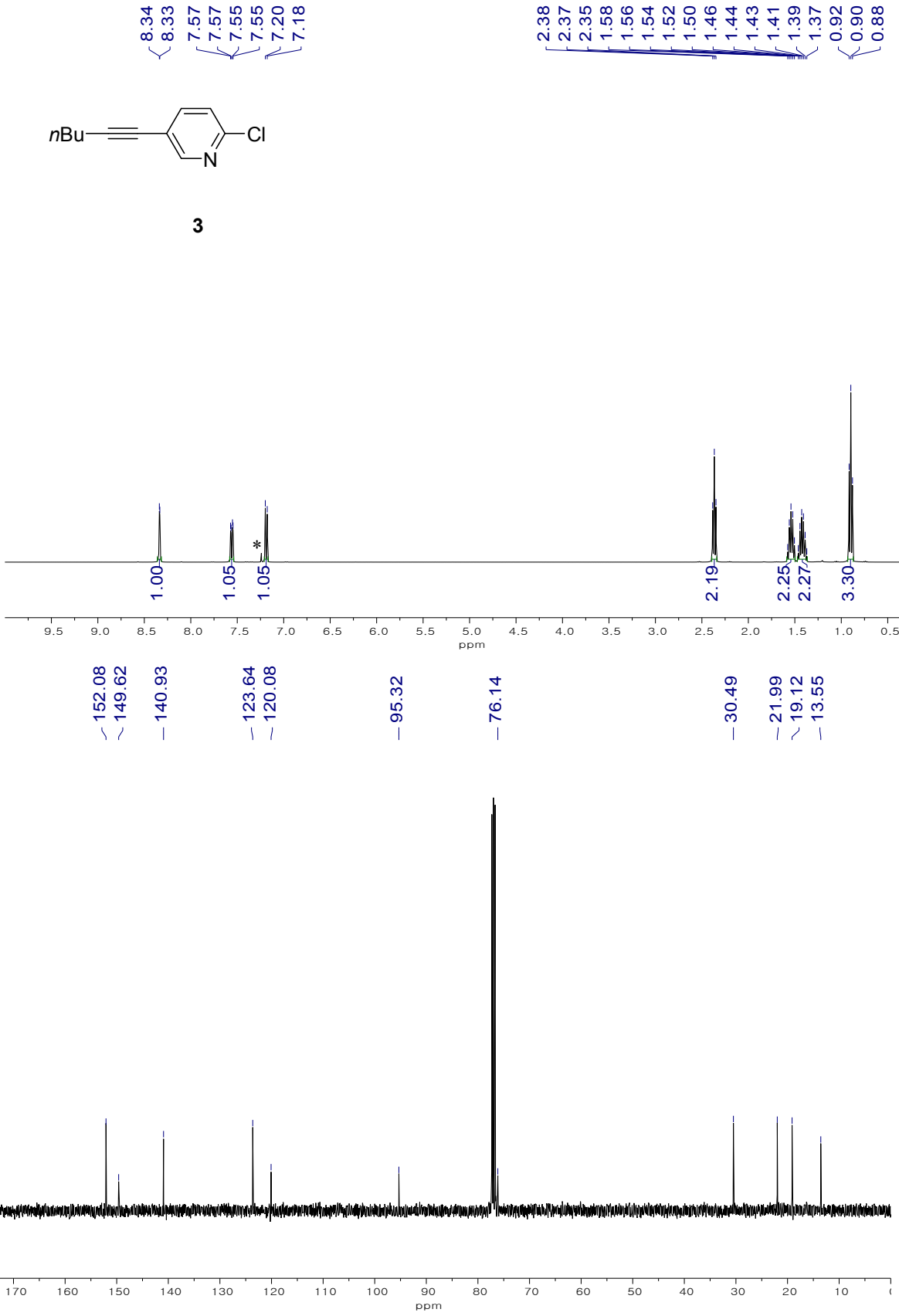


3

Fig. S1 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3** (∗ from residual $CHCl_3$ in $CDCl_3$).

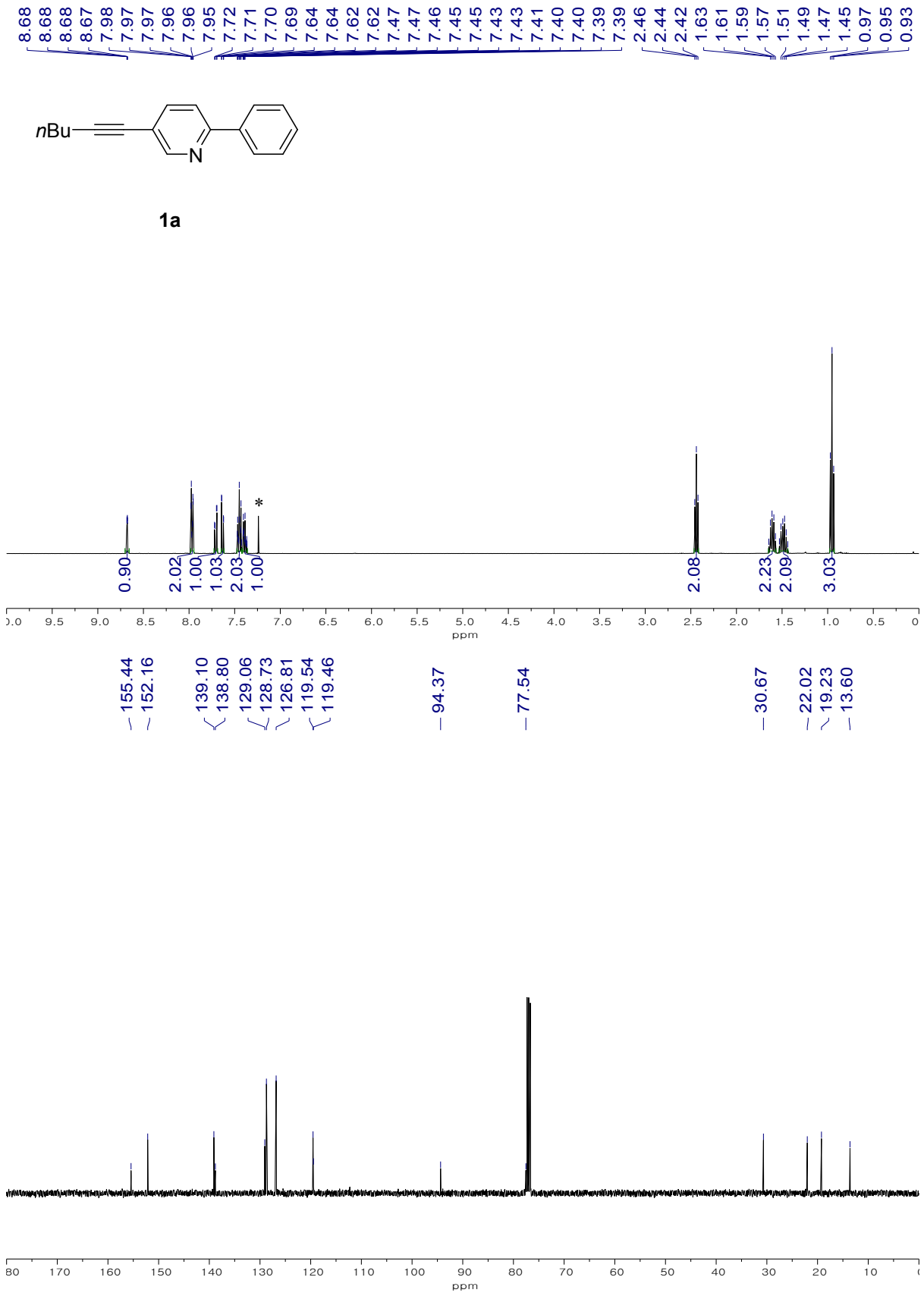


Fig. S2 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **1a** (* from residual $CHCl_3$ in $CDCl_3$).

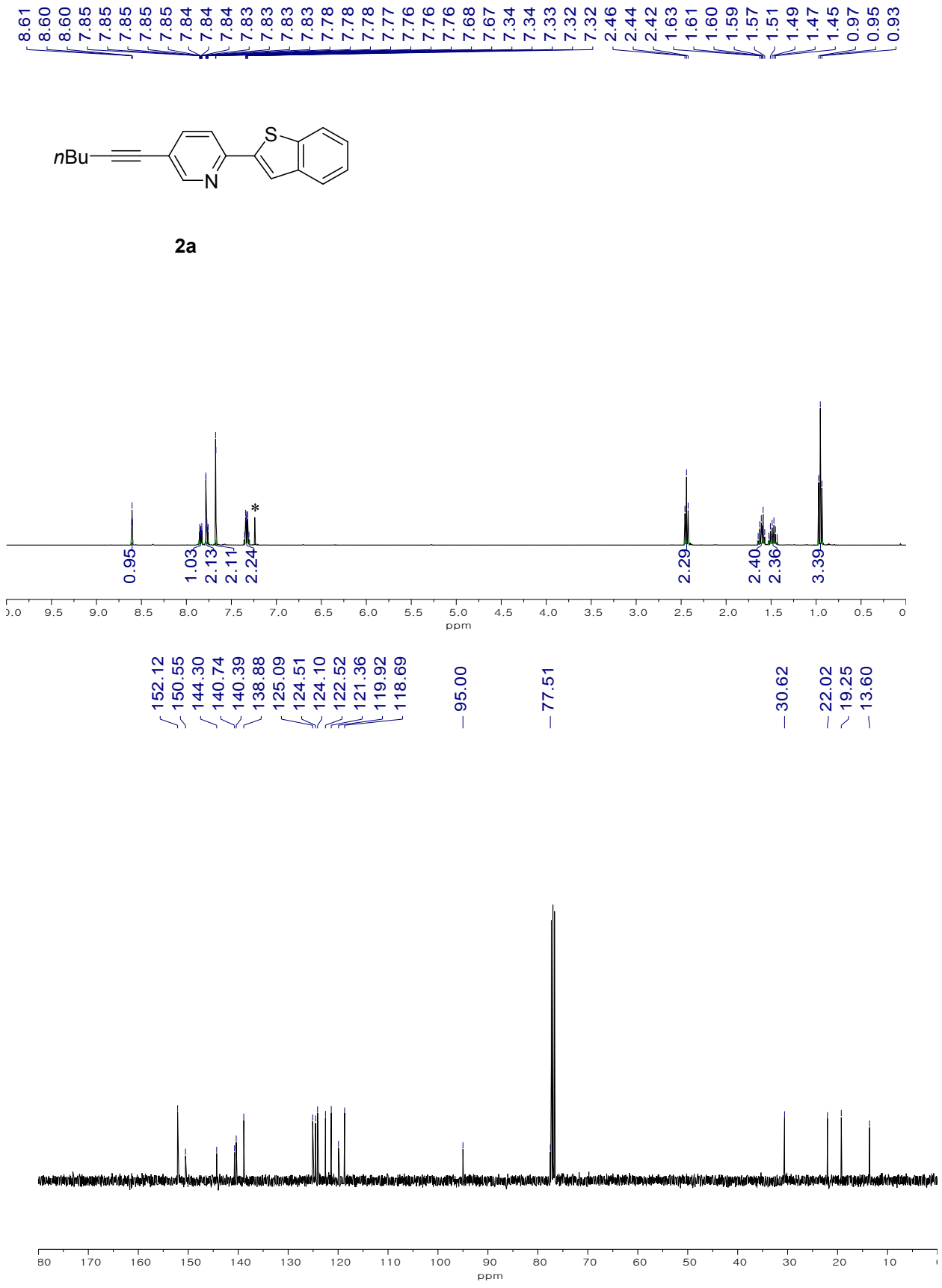
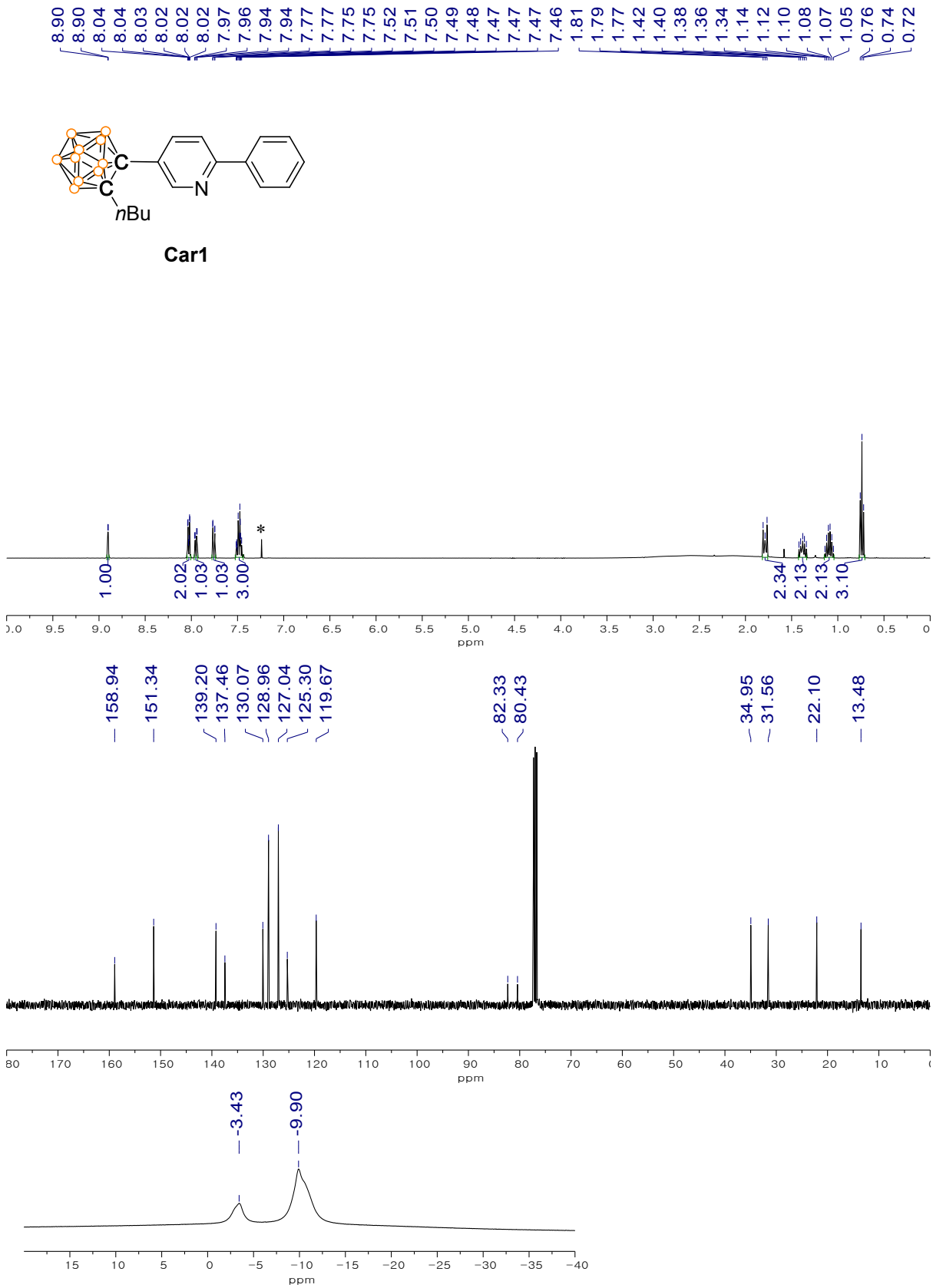


Fig. S3 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2a** (∗ from residual $CHCl_3$ in $CDCl_3$).



Car1

Fig. S4 ^{1}H (top), ^{13}C (middle) and ^{11}B (bottom) NMR spectra of **Car1** (∗ from residual $CHCl_3$ in $CDCl_3$).

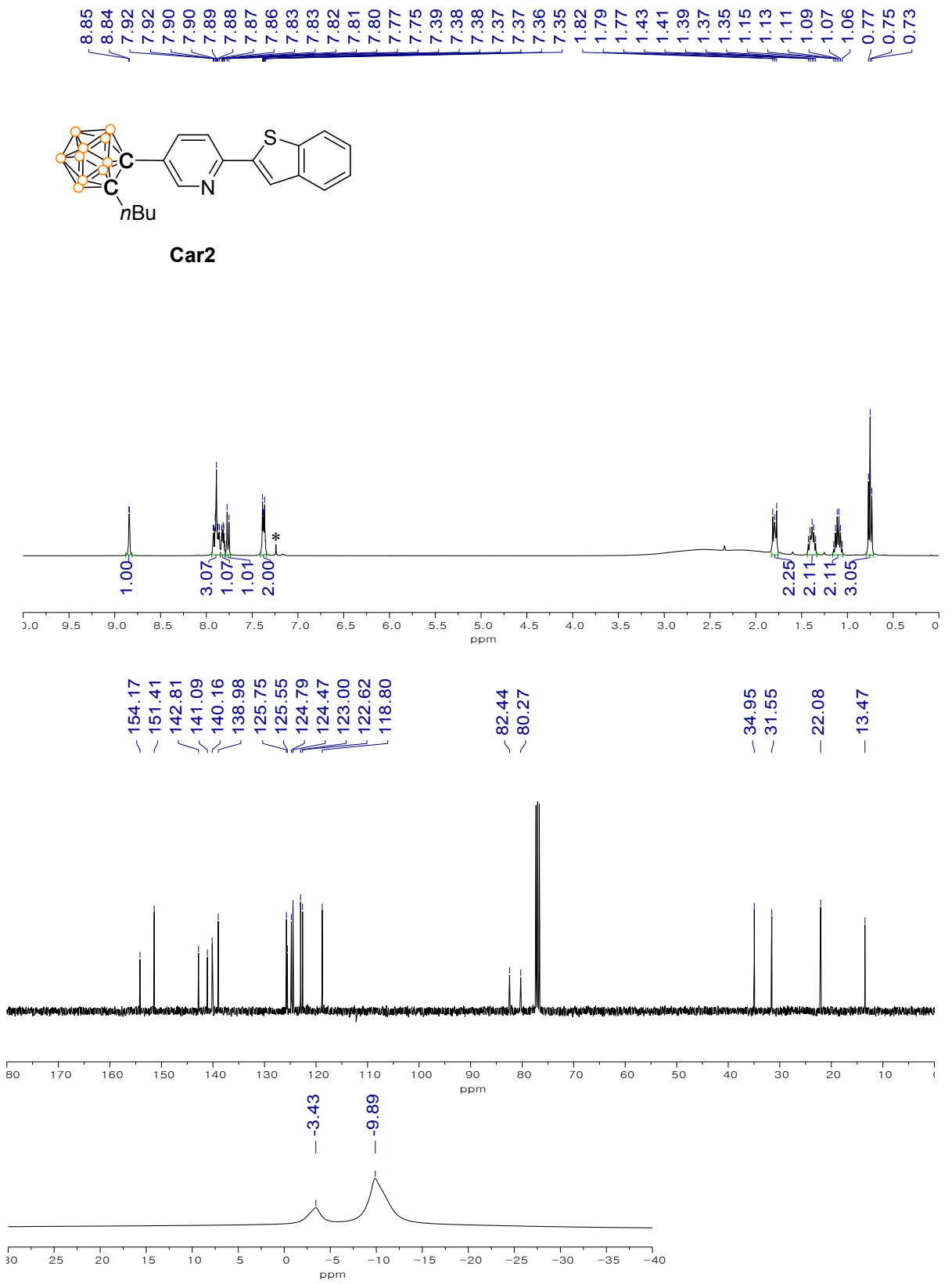


Fig. S5 ^{1}H (top), ^{13}C (middle) and ^{11}B (bottom) NMR spectra of **Car2** (∗ from residual $CHCl_3$ in $CDCl_3$).

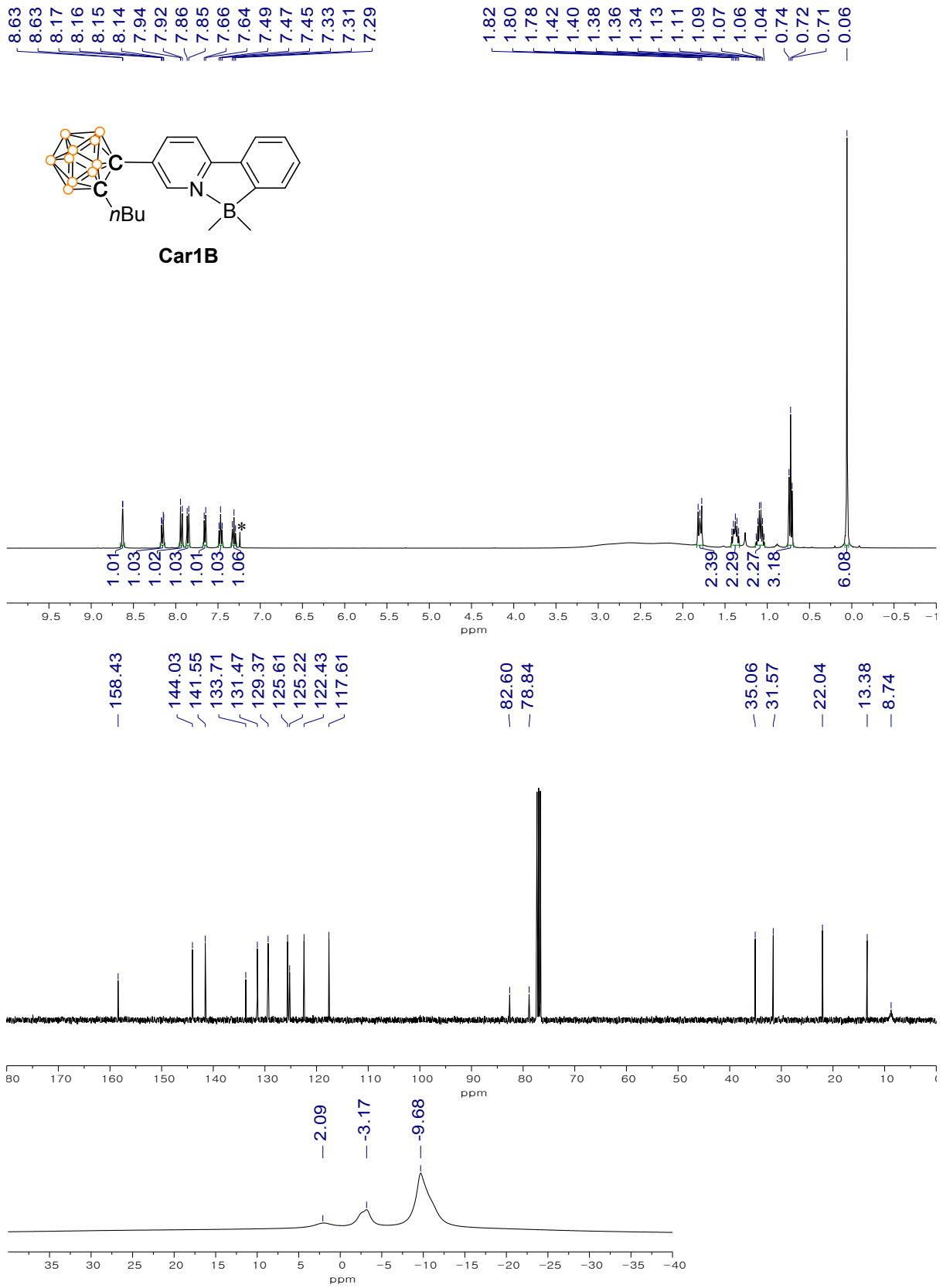


Fig. S6 ^{1}H (top), ^{13}C (middle) and ^{11}B (bottom) NMR spectra of **Car1B** (∗ from residual $CHCl_3$ in $CDCl_3$).

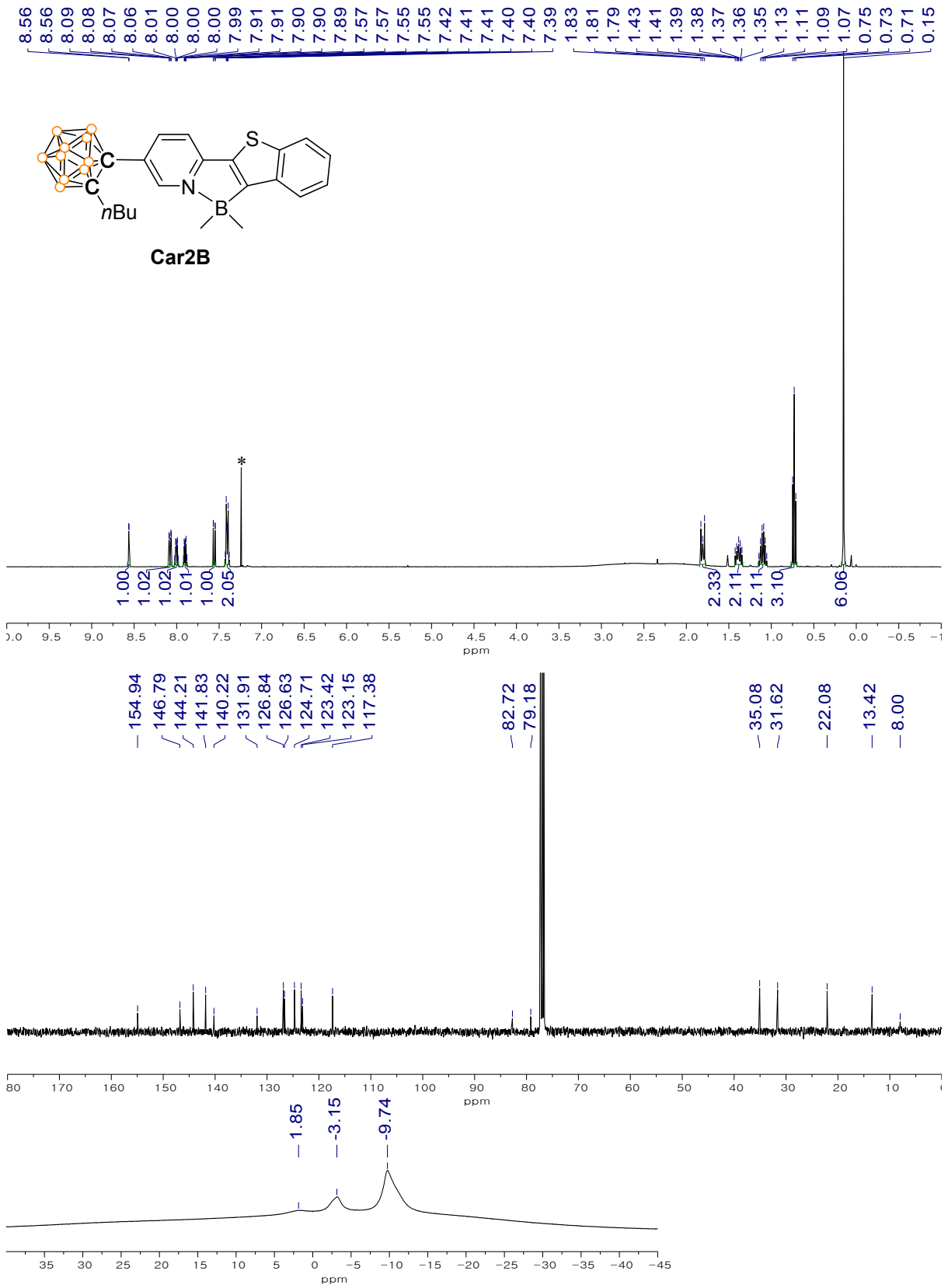


Fig. S7 ^{1}H (top), ^{13}C (middle) and ^{11}B (bottom) NMR spectra of **Car2B** (∗ from residual $CHCl_3$ in $CDCl_3$).

Table S1 Crystallographic data and parameters for **Car2B**

Compound	**Car2B**
Formula	$C_{21}H_{32}B_{11}NS$
Formula weight	449.44
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	7.1573(10)
b (Å)	10.8234(16)
c (Å)	34.496(5)
V (Å^3)	2672.3(7)
Z	4
ρ_{calc}(g cm^{-3})	1.117
μ (mm^{-1})	0.133
F(000)	944
T (K)	296(2)
Scan mode	*multi-scan*
hkl range	$-7 < h < 9$, $-13 < k < 13$, $-44 < l < 43$
Measd reflns	39730
Unique reflns [R_{int}]	5837 [0.1258]
Reflns used for refinement	5837
Refined parameters	310
R_1[a] (I > 2σ(I))	0.0689
wR_2[b] all data	0.1756
GOF on F^2	1.048
ρ_{fin} (max/min) (e Å^{-3})	0.373, −0.377

[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 **Car2B**

Compound	**Car2B**
	lengths
B1–N	1.649(7)
B1–C9	1.612(7)
B1–C16	1.623(7)
B1–C17	1.617(8)
C1–C2	1.714(7)
	angles
N–B1–C9	95.0(3)
C16–B1–C17	114.8(4)
C2–C1–C4	119.3(4)
C1–C2–C18	117.5(4)

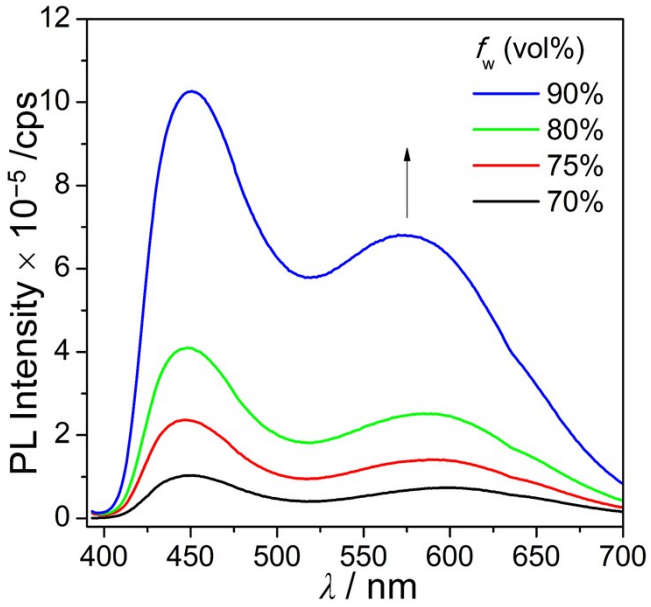


Fig. S8 PL spectra of **Car2B** in THF/water mixtures (volume fraction of water, f_w = 70% to 90%, 5.0 × 10^{-4} M, λ_{ex} = 383 nm).

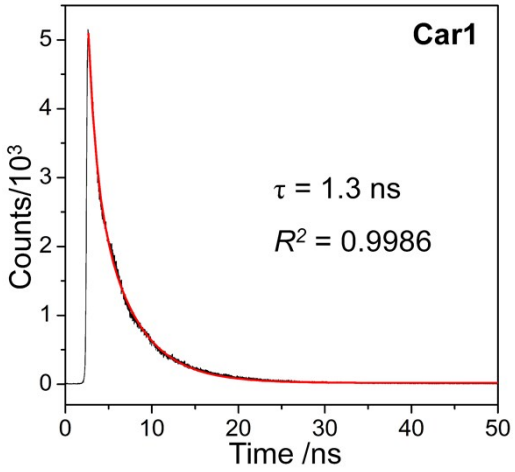


Fig. S9 Emission decay curves for **Car1** in film (5 wt% doped on PMMA) detected at 465 nm, and these exponential fitting curves (red-line, single exponential curve fitting).

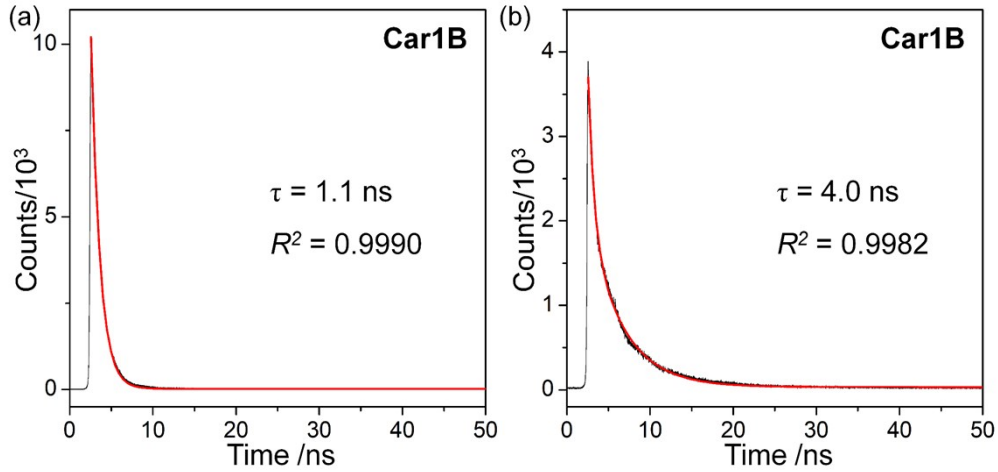


Fig. S10 Emission decay curves for **Car1B** in (a) toluene (5.0×10^{-5} M) and (b) film (5 wt% doped on PMMA) detected at 390 nm, and these exponential fitting curves (red-line, single exponential curve fitting).

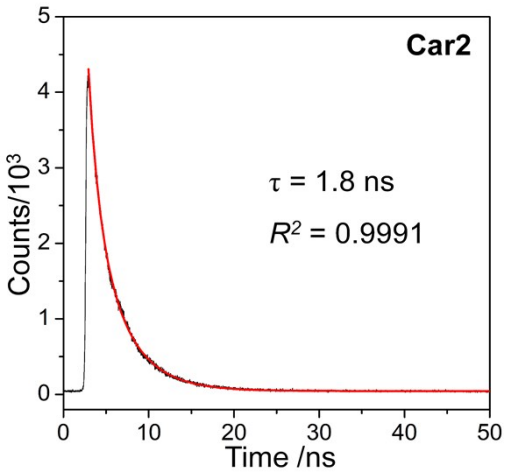


Fig. S11 Emission decay curve for **Car2** in film (5 wt% doped on PMMA) detected at 502 nm and its exponential fitting curve (red-line, single exponential curve fitting).

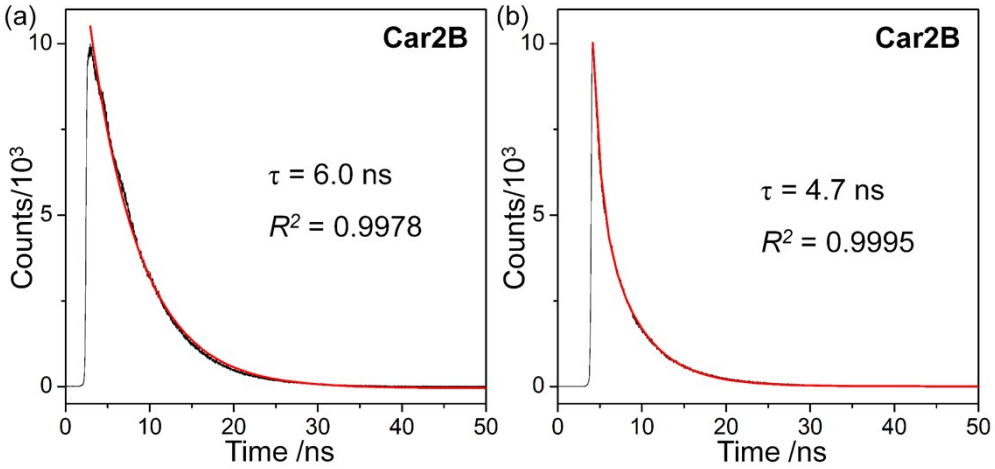


Fig. S12 Emission decay curve for **Car2B** in (a) toluene (5.0×10^{-5} M) and (b) film (5 wt% doped on PMMA) detected at 445 nm and its exponential fitting curve (red-line, single exponential curve fitting).

Computational details

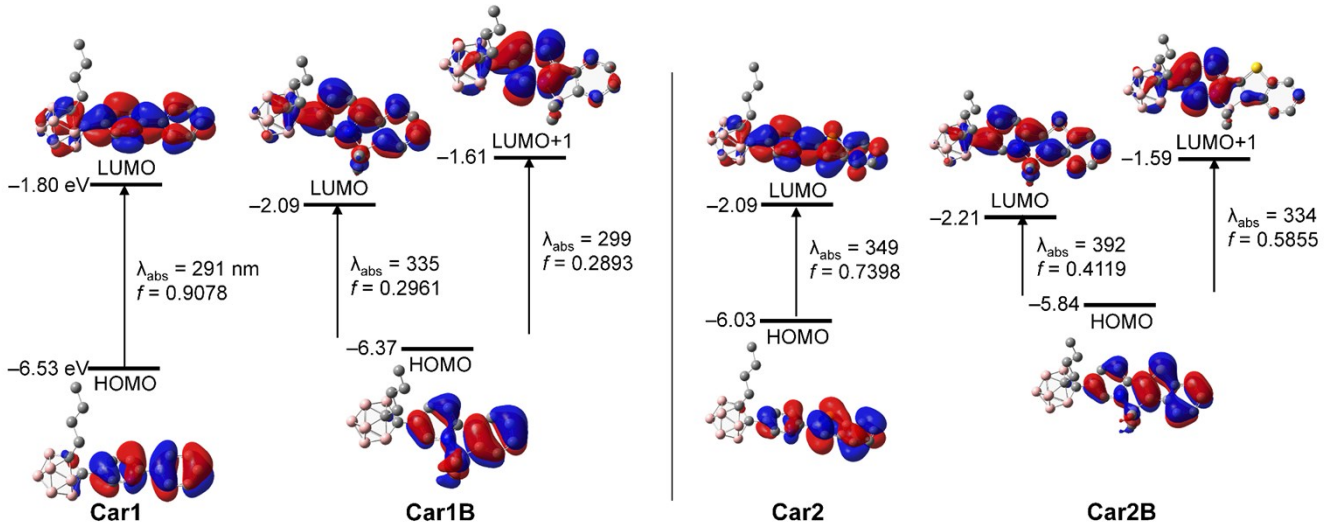


Fig. S13 Frontier molecular orbitals for *o*-carboranyl complexes at their ground state (S_0) with their relative energies from DFT calculation (isovalue 0.04). The transition energy (in nm) was calculated using the TD-B3LYP method with 6-31G(d) basis sets.

Table S3 The major low-energy electronic transition for *o*-carborane compounds at their ground state (S_0) calculated using the TD-B3LYP method with 6-31G(d) basis sets.

	λ_{calc}/ nm	f_{calc}	Assignment
Car1	291.00	0.9078	HOMO → LUMO (94.8%)
Car1B	335.01	0.2961	HOMO → LUMO (94.0%)
	299.28	0.2893	HOMO → LUMO+1 (87.2%)
Car2	349.38	0.7398	HOMO → LUMO (97.8%)
Car2B	392.36	0.4119	HOMO → LUMO (95.0%)
	334.02	0.5855	HOMO → LUMO+1 (89.2%)

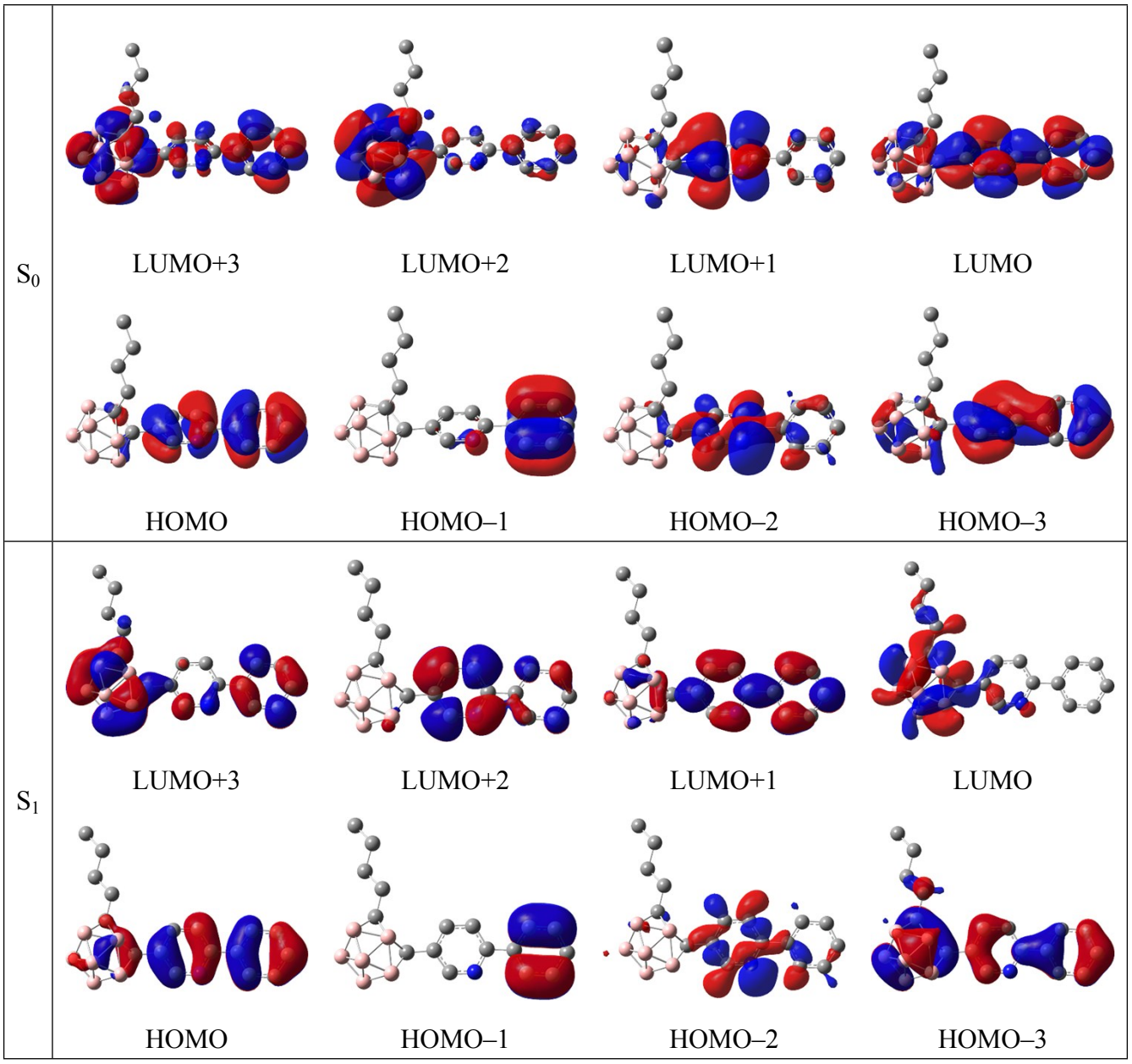


Fig. S14 The selected frontier orbitals of **Car1** from B3LYP calculations (Isovalue = 0.04 a.u.) at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in toluene.

Table S4 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **Car1** from TD-B3LYP calculations using the B3LYP geometries at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in toluene

state	λ_{calc} (/nm)	f_{calc}	Major contribution
		S_0	
1	291.00	0.9078	HOMO → LUMO (94.8%)
2	280.77	0.0393	HOMO−2 → LUMO (76.4%)
			HOMO−1 → LUMO (18.7%)
3	271.66	0.0146	HOMO−2 → LUMO (19.1%)
			HOMO−1 → LUMO (65.7%)
4	258.89	0.0383	HOMO → LUMO+1 (78.9%)
		S_1	
1	461.67	0.1295	HOMO → LUMO (96.0%)
2	441.67	0.0002	HOMO−1 → LUMO (86.6%)
3	421.39	0.0004	HOMO−2 → LUMO (99.7%)
4	414.33	0.0084	HOMO−3 → LUMO (98.9%)

Table S5 Molecular orbital energies (in eV) and molecular orbital distributions (in %) of **Car1** at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in toluene

	E (eV)	*n*Bu+Carborane	ppy
		S_0	
LUMO+2	−0.28	90.8	9.2
LUMO+1	−1.07	7.6	92.4
LUMO	−1.80	12.8	87.2
HOMO	−6.53	2.6	97.4
HOMO−1	−7.01	0.1	99.9
HOMO−2	−7.38	3.1	96.9
		S_1	
LUMO+2	−0.90	5.2	94.8
LUMO+1	−1.71	8.0	92.0
LUMO	−3.87	96.6	3.4
HOMO	−6.09	9.4	90.6
HOMO−1	−7.03	0.0	100.0
HOMO−2	−7.31	4.3	95.7

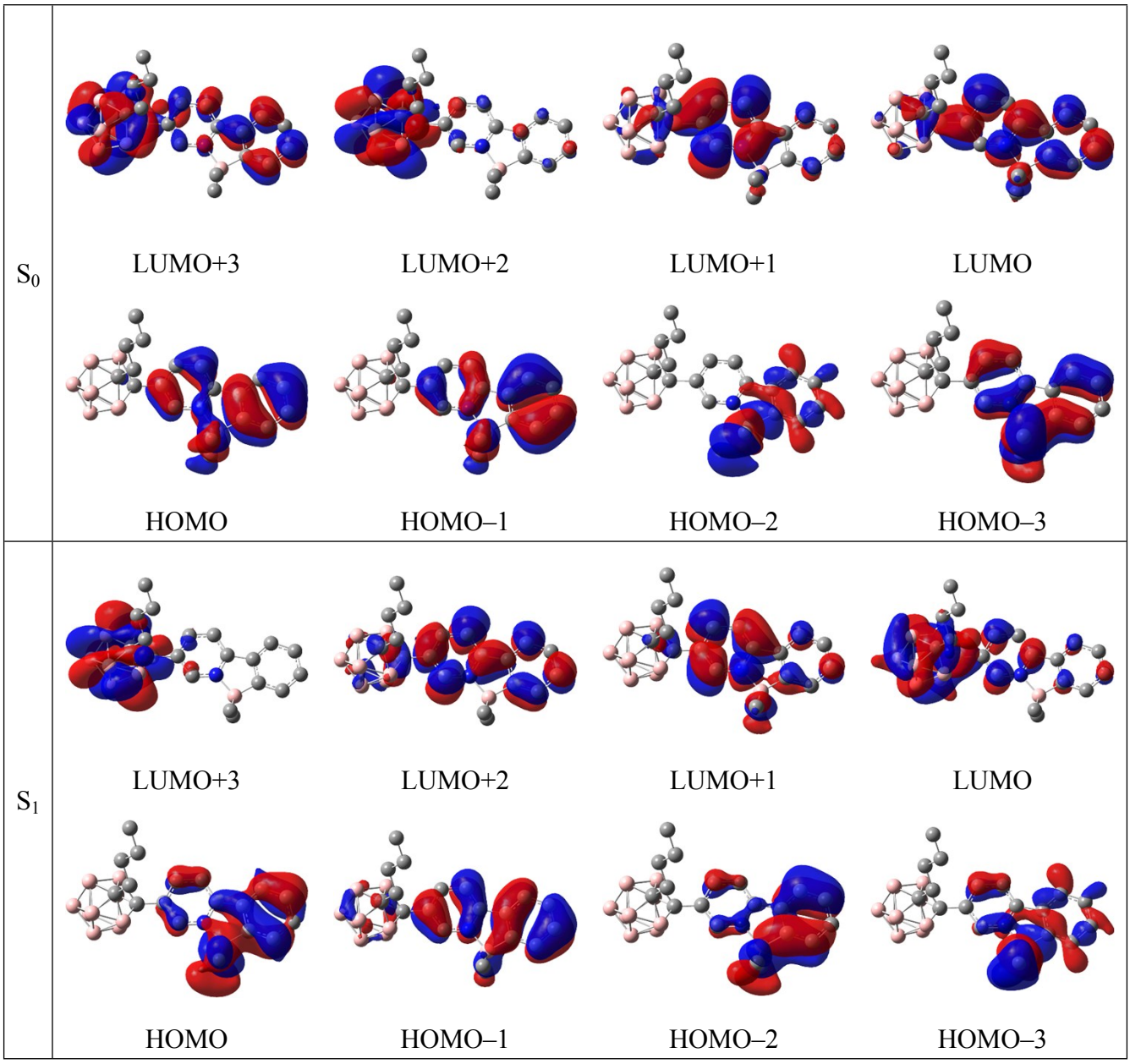


Fig. S15 The selected frontier orbitals of **Car1B** from B3LYP calculations (Isovalue = 0.04 a.u.) at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in toluene.

Table S6 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **Car1B** from TD-B3LYP calculations using the B3LYP geometries at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in toluene

state	λ_{calc} (/nm)	f_{calc}	Major contribution
		S_0	
1	335.01	0.2961	HOMO → LUMO (94.0%)
2	308.64	0.1688	HOMO−1 → LUMO (85.8%)
3	299.28	0.2893	HOMO → LUMO+1 (87.2%)
4	280.22	0.1589	HOMO−1 → LUMO+1 (88.6%)
		S_1	
1	461.36	0.5313	HOMO → LUMO (99.5%)
2	426.37	0.0065	HOMO−1 → LUMO (99.4%)
3	402.36	0.0451	HOMO−2 → LUMO (98.9%)
4	375.70	0.1315	HOMO → LUMO+1 (96.7%)

Table S7 Molecular orbital energies (in eV) and molecular orbital distributions (in %) of **Car1B** at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in toluene

	E (eV)	*n*Bu+Carborane	ppy+BMe_2
		S_0	
LUMO+2	−0.38	94.8	5.2
LUMO+1	−1.61	7.7	92.3
LUMO	−2.09	26.6	73.4
HOMO	−6.37	1.3	98.7
HOMO−1	−6.64	1.4	98.6
HOMO−2	−7.42	0.0	100
		S_1	
LUMO+2	−1.33	10.5	89.5
LUMO+1	−1.86	4.9	95.1
LUMO	−3.57	81.6	18.4
HOMO	−5.72	0.5	99.5
HOMO−1	−6.63	5.6	94.5
HOMO−2	−7.71	0.1	99.9

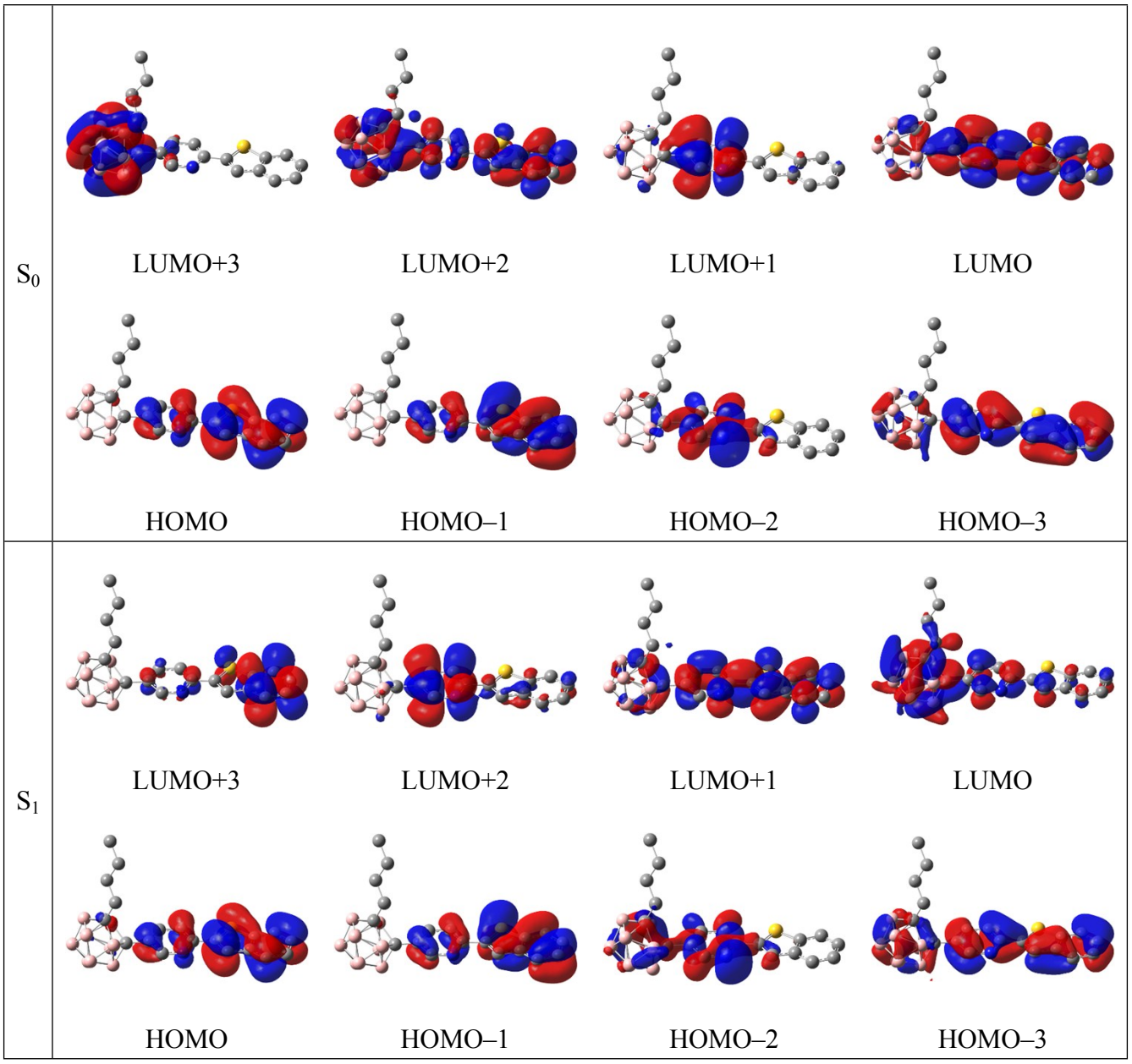


Fig. S16 The selected frontier orbitals of **Car2** from B3LYP calculations (Isovalue = 0.04 a.u.) at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in toluene.

Table S8 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **Car2** from TD-B3LYP calculations using the B3LYP geometries at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in toluene

state	λ_{calc} (/nm)	f_{calc}	Major contribution
			S_0
1	349.38	0.7398	HOMO → LUMO (97.8%)
2	325.54	0.4230	HOMO−1 → LUMO (95.4%)
3	287.41	0.0179	HOMO−2 → LUMO (79.7%)
			HOMO → LUMO+1 (17.9%)
4	286.61	0.0782	HOMO−2 → LUMO (18.4%)
			HOMO → LUMO+1 (75.9%)
			S_1
1	469.16	0.5465	HOMO → LUMO (99.9%)
2	441.30	0.2459	HOMO−1 → LUMO (99.1%)
3	380.61	0.0059	HOMO−2 → LUMO (91.6%)
4	346.31	0.0056	HOMO−5 → LUMO (13.1%)
			HOMO−4 → LUMO (77.1%)

Table S9 Molecular orbital energies (in eV) and molecular orbital distributions (in %) of **Car2** at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in toluene

	E (eV)	*n*Bu+Carborane	btp
		S_0	
LUMO+2	−0.53	41.9	58.1
LUMO+1	−1.10	7.0	93.0
LUMO	−2.09	12.7	88.3
HOMO	−6.03	1.5	98.5
HOMO−1	−6.46	0.9	99.1
HOMO−2	−7.50	3.6	96.4
		S_1	
LUMO+2	−1.07	4.7	95.3
LUMO+1	−1.79	12.1	87.9
LUMO	−3.40	85.3	14.7
HOMO	−5.88	3.7	96.3
HOMO−1	−6.60	2.1	97.9
HOMO−2	−7.49	13.2	86.8

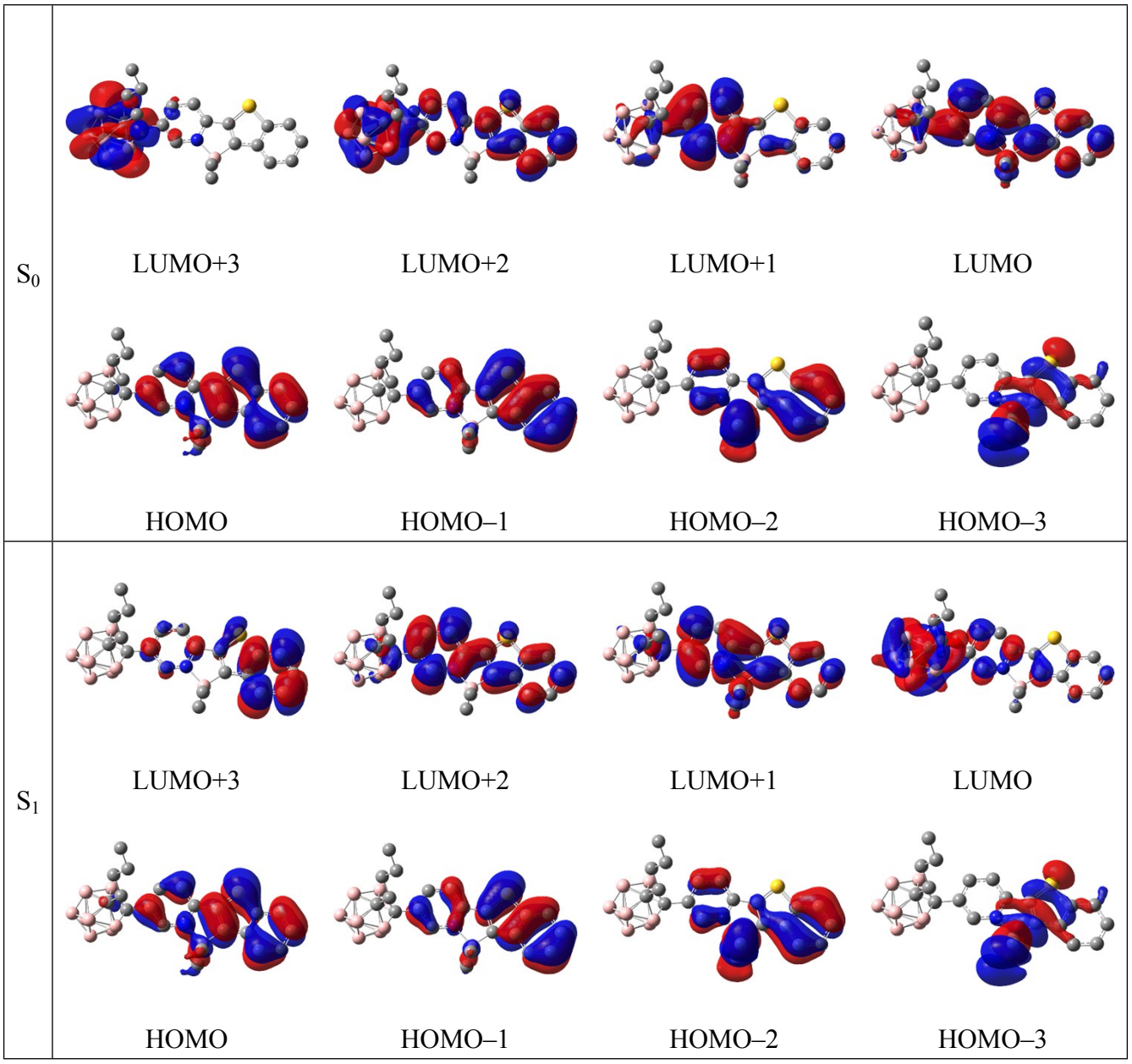


Fig. S17 The selected frontier orbitals of **Car2B** from B3LYP calculations (Isovalue = 0.04 a.u.) at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in toluene.

Table S10 Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **Car2B** from TD-B3LYP calculations using the B3LYP geometries at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in toluene

state	λ_{calc} (/nm)	f_{calc}	Major contribution
		S_0	
1	392.36	0.4119	HOMO → LUMO (95.0%)
2	342.24	0.0580	HOMO−1 → LUMO (51.7%)
			HOMO → LUMO+1 (45.3%)
3	334.02	0.5855	HOMO → LUMO+1 (89.2%)
4	288.76	0.0484	HOMO−1 → LUMO+1 (91.6%)
		S_1	
1	466.82	0.4331	HOMO → LUMO (99.8%)
2	410.20	0.0089	HOMO−1 → LUMO (99.1%)
3	408.11	0.0914	HOMO → LUMO+1 (92.0%)
4	369.55	0.0105	HOMO−2 → LUMO (95.5%)

Table S11 Molecular orbital energies (in eV) and molecular orbital distributions (in %) of **Car2B** at the ground state (S_0) and first singlet excited state (S_1) optimized geometries in toluene

	E (eV)	*n*Bu+Carborane	btp+BMe_2
		S_0	
LUMO+2	−0.54	44.0	56.0
LUMO+1	−1.59	8.1	91.9
LUMO	−2.21	24.6	75.4
HOMO	−5.84	1.4	98.6
HOMO−1	−6.43	0.9	99.1
HOMO−2	−7.29	0.2	99.8
		S_1	
LUMO+2	−1.45	6.8	93.2
LUMO+1	−1.96	7.7	92.3
LUMO	−3.47	79.9	20.1
HOMO	−5.72	3.5	96.4
HOMO−1	−6.56	1.8	98.1
HOMO−2	−7.28	0.2	99.8

Table S12 Cartesian coordinates of the ground state (S_0) fully optimized geometry in toluene of **Car1** from B3LYP calculations (in Å)

Atom	x	y	z
C	-2.537815	0.173383	0.330428
H	-3.914115	-2.942379	2.103123
H	-1.595266	-0.896585	2.375950
H	-4.341371	0.119471	2.020933
H	-5.833338	-1.758125	0.009850
H	-1.184727	-3.386090	0.722081
H	-4.588839	0.952956	-0.849159
H	-3.844119	-3.953928	-0.805305
H	-1.937042	0.434684	-2.077410
H	-1.406204	-2.529830	-2.130009
H	-4.281384	-1.523159	-2.639577
B	-2.213696	-1.138535	1.399822
B	-3.548988	-2.275102	1.189824
B	-3.856957	-0.524058	1.150522
B	-1.995911	-2.587181	0.393927
B	-4.657511	-1.584277	-0.028834
B	-3.993616	-0.021920	-0.542048
B	-3.507853	-2.854663	-0.500803
B	-2.423886	-0.319642	-1.310862
B	-2.127557	-2.076820	-1.306149
B	-3.762617	-1.447532	-1.572917
C	-1.954585	1.530869	0.736453
H	-1.988858	1.596035	1.828815
H	-0.894906	1.544073	0.458720
C	-2.646868	2.760767	0.131280
H	-3.697155	2.789098	0.446114
H	-2.648054	2.687927	-0.963712
C	-1.952478	4.062392	0.555352
H	-1.942100	4.128578	1.652106
H	-0.900502	4.031987	0.239209
C	-2.626861	5.308659	-0.026666
H	-3.670469	5.384623	0.301958
H	-2.109882	6.221757	0.288871
H	-2.624397	5.284604	-1.123200
C	0.060131	-0.781158	-0.161278
C	2.076178	-0.116339	-1.309789
C	0.881290	-1.038891	0.948418
C	2.807369	-0.364380	-0.136095
H	2.571823	0.212012	-2.215911
H	0.453580	-1.433173	1.865520
C	4.273848	-0.145727	-0.053767
C	4.941291	0.714701	-0.942618
C	6.402672	-0.618413	1.023858
C	6.319734	0.903450	-0.849802
H	4.384318	1.261828	-1.696831
C	7.056400	0.235307	0.130945
H	6.968063	-1.141912	1.789926
H	6.816735	1.578662	-1.540685
H	8.130656	0.381629	0.201267
C	-1.415117	-1.068356	-0.127789
N	2.197309	-0.837320	0.969983
C	0.703668	-0.323264	-1.319728
H	0.144146	-0.142495	-2.229996
C	5.024824	-0.804260	0.935526
H	4.513128	-1.464788	1.626690

Table S13 Cartesian coordinates of the first excited state (S_1) fully optimized geometry in toluene of **Car1** from B3LYP calculations (in Å)

Atom	x	y	z
C	-2.922062	0.067626	0.246152
H	-3.151748	-3.099916	2.368654
H	-1.482579	-0.406496	2.210949
H	-4.577175	-0.612837	1.856967
H	-5.122667	-2.968975	-0.051362
H	-0.423821	-3.235886	1.355244
H	-4.703908	-0.232297	-1.366712
H	-2.653183	-4.551480	-0.346989
H	-1.645356	0.106931	-1.893871
H	-0.549193	-2.848508	-1.837736
H	-3.348230	-2.482518	-2.571200
B	-1.943525	-0.917261	1.238142
B	-2.905716	-2.521491	1.354667
B	-3.808850	-1.024072	1.044459
B	-1.262368	-2.658768	0.738254
B	-4.061308	-2.423558	-0.022882
B	-3.874736	-0.802644	-0.734619
B	-2.587215	-3.368880	-0.199919
B	-2.032643	-0.630940	-1.042321
B	-1.330513	-2.441870	-1.037061
B	-3.014725	-2.167601	-1.469879
C	-2.982554	1.566440	0.489549
H	-3.017212	1.736187	1.573747
H	-2.049135	2.032180	0.142004
C	-4.159244	2.306685	-0.167630
H	-5.103832	1.849193	0.156016
H	-4.113087	2.180318	-1.257225
C	-4.171465	3.802512	0.172844
H	-4.219336	3.926022	1.264072
H	-3.221015	4.255154	-0.144327
C	-5.336990	4.554533	-0.478101
H	-6.301932	4.147438	-0.151744
H	-5.319194	5.619476	-0.219179
H	-5.297160	4.475576	-1.571552
C	0.541809	-0.761618	0.004365
C	2.161194	1.017433	0.176775
C	1.663602	-1.644093	-0.149377
C	3.204749	0.061916	0.008840
H	2.386344	2.067465	0.310740
H	1.477859	-2.706814	-0.277307
C	4.608806	0.427450	-0.005246
C	5.042073	1.778557	0.100695
C	6.939627	-0.276029	-0.144845
C	6.390473	2.086221	0.083050
H	4.323495	2.583421	0.190577
C	7.345356	1.063203	-0.038176
H	7.681843	-1.061782	-0.238251
H	6.710589	3.119632	0.162430
H	8.402022	1.311236	-0.049885
C	-0.821389	-1.273887	-0.012857
N	2.921546	-1.264530	-0.147284
C	0.846468	0.604808	0.174660
H	0.048813	1.326325	0.306051
C	5.593645	-0.593682	-0.130856
H	5.261399	-1.620374	-0.212376

Table S14 Cartesian coordinates of the ground state (S_0) fully optimized geometry in toluene of **Car1B** from B3LYP calculations (in Å)

Atom	x	y	z
C	-2.834080	0.126205	0.283202
H	-3.747052	-3.216469	1.941392
H	-1.571756	-1.008561	2.110336
H	-4.405362	-0.203228	2.162855
H	-5.990706	-2.046129	0.191182
H	-1.178999	-3.326307	0.218365
H	-5.066333	0.814660	-0.581212
H	-3.959828	-4.002346	-1.030206
H	-2.553683	0.611718	-2.149187
H	-1.814464	-2.285417	-2.506409
H	-4.797369	-1.490230	-2.592688
B	-2.285119	-1.231215	1.196444
B	-3.547300	-2.456963	1.049651
B	-3.985612	-0.737714	1.191307
B	-2.084802	-2.580427	0.054960
B	-4.844767	-1.772914	0.030572
B	-4.367593	-0.126924	-0.426551
B	-3.671098	-2.904785	-0.675923
B	-2.887183	-0.234442	-1.396034
B	-2.461882	-1.957073	-1.569876
B	-4.159303	-1.449028	-1.591056
C	-2.306830	1.493745	0.730834
H	-2.217232	1.475471	1.821729
H	-1.290944	1.615116	0.339292
C	-3.153784	2.703345	0.309379
H	-4.161745	2.616716	0.732809
H	-3.269984	2.716117	-0.781785
C	-2.520118	4.023089	0.770723
H	-2.394322	4.004093	1.862079
H	-1.510347	4.109912	0.346149
C	-3.350741	5.246940	0.371879
H	-4.355131	5.203891	0.810321
H	-2.876726	6.174286	0.712215
H	-3.465438	5.309876	-0.717104
C	-0.253565	-0.574568	-0.581389
C	1.558880	0.319390	-1.924764
C	0.689013	-0.828659	0.415348
C	2.446984	0.056225	-0.875615
H	1.919685	0.764102	-2.845005
H	0.425596	-1.294254	1.356014
C	3.879829	0.297886	-0.778596
C	4.364698	-0.139274	0.476505
C	4.705511	0.877723	-1.753095
C	5.731420	0.026859	0.729352
C	6.059390	1.027902	-1.468659
H	4.306899	1.205760	-2.709880
C	6.567762	0.603110	-0.230691
H	6.154074	-0.292311	1.680126
H	6.723171	1.474014	-2.203790
H	7.627476	0.726298	-0.020125
C	-1.690233	-0.981600	-0.402050
N	1.981029	-0.519962	0.268534
C	2.817051	0.106112	2.710718
H	1.915730	-0.266459	3.219956
H	3.638568	0.030413	3.436978
H	2.663134	1.176218	2.513587
C	3.304417	-2.358822	1.656796
H	4.154402	-2.552459	2.326191
H	2.414313	-2.769075	2.156717
H	3.472261	-2.952945	0.747776
C	0.217849	0.002151	-1.777540
H	-0.465494	0.197498	-2.595022
B	3.176595	-0.757871	1.375023

Table S15 Cartesian coordinates of the first excited state (S_1) fully optimized geometry in toluene of **Car1B** from B3LYP calculations (in Å)

Atom	x	y	z
C	-3.201818	0.117077	0.407549
H	-3.434208	-3.378799	1.947242
H	-1.569847	-0.850536	2.026074
H	-4.622505	-0.677291	2.194440
H	-5.775148	-2.620181	0.069001
H	-0.925367	-3.382759	0.395736
H	-5.325277	0.317163	-0.757681
H	-3.535077	-4.250248	-1.022195
H	-2.501055	0.519393	-1.957625
H	-1.620020	-2.378877	-2.551159
H	-4.512522	-1.798545	-2.635033
B	-2.226487	-1.124901	1.069952
B	-3.311121	-2.605406	1.046781
B	-4.075383	-1.011594	1.189761
B	-1.824754	-2.656943	0.104578
B	-4.679013	-2.156953	-0.027885
B	-4.462173	-0.444748	-0.459463
B	-3.356089	-3.122492	-0.673928
B	-2.752244	-0.346802	-1.178630
B	-2.214947	-2.085409	-1.561565
B	-3.931417	-1.692131	-1.598220
C	-2.955242	1.536428	0.886536
H	-3.043204	1.555808	1.980994
H	-1.910160	1.801768	0.666384
C	-3.870856	2.613718	0.285943
H	-4.914292	2.395802	0.548696
H	-3.814754	2.574812	-0.810369
C	-3.508146	4.025571	0.764485
H	-3.555044	4.060762	1.862246
H	-2.464027	4.242152	0.496784
C	-4.420484	5.108680	0.179556
H	-5.467052	4.938350	0.460734
H	-4.137106	6.105679	0.536258
H	-4.369880	5.118894	-0.916334
C	-0.035547	-0.713988	-0.630744
C	1.734814	0.312052	-1.963935
C	0.910707	-0.847118	0.396685
C	2.614265	0.148071	-0.899785
H	2.071276	0.768925	-2.887500
H	0.657148	-1.292388	1.350048
C	4.033511	0.519973	-0.766907
C	4.522616	0.142601	0.512690
C	4.826873	1.219885	-1.658579
C	5.862860	0.403210	0.839914
C	6.163414	1.501774	-1.297190
H	4.441664	1.568914	-2.611888
C	6.673230	1.104873	-0.058972
H	6.269694	0.066925	1.789392
H	6.800249	2.030380	-1.999344
H	7.704174	1.327062	0.197052
C	-1.416940	-1.182287	-0.463479
N	2.176439	-0.427520	0.252012
C	2.942218	-0.180983	2.828960
H	2.169658	-0.844082	3.236478
H	3.806832	-0.236893	3.499823
H	2.550464	0.844841	2.877117
C	3.943525	-2.218412	1.269790
H	4.778759	-2.306637	1.962446
H	3.051639	-2.740169	1.630244
H	4.216060	-2.522404	0.261137
C	0.418424	-0.119256	-1.824429
H	-0.273170	0.005018	-2.650390
B	3.352123	-0.536902	1.328338

Table S16 Cartesian coordinates of the ground state (S_0) fully optimized geometry in toluene of **Car2** from B3LYP calculations (in Å)

Atom	x	y	z
C	-3.572435	0.201270	0.372724
H	-4.983346	-2.896853	2.149212
H	-2.627007	-0.893616	2.403512
H	-5.358127	0.171481	2.082872
H	-6.904480	-1.671016	0.081224
H	-2.278288	-3.383999	0.737068
H	-5.621017	1.021244	-0.782125
H	-4.964343	-3.898412	-0.763742
H	-2.992814	0.459402	-2.041031
H	-2.515883	-2.513140	-2.110424
H	-5.377794	-1.453028	-2.584007
B	-3.259497	-1.120417	1.432763
B	-4.616896	-2.232865	1.234081
B	-4.894793	-0.476736	1.204534
B	-3.078835	-2.570069	0.419959
B	-5.726270	-1.517867	0.030325
B	-5.040366	0.034703	-0.484422
B	-4.604930	-2.806587	-0.459011
B	-3.484392	-0.288488	-1.271231
B	-3.219981	-2.050935	-1.276800
B	-4.846179	-1.390944	-1.522831
C	-2.960086	1.546064	0.777662
H	-2.996244	1.613822	1.869793
H	-1.899470	1.534386	0.503193
C	-3.622082	2.790450	0.168046
H	-4.670761	2.846760	0.484427
H	-3.626943	2.712889	-0.926590
C	-2.894418	4.076114	0.584995
H	-2.878911	4.146230	1.681435
H	-1.844560	4.018658	0.265587
C	-3.539823	5.336351	0.000205
H	-4.580000	5.439517	0.332257
H	-2.999166	6.237604	0.310059
H	-3.541942	5.307737	-1.096221
C	-0.996680	-0.800661	-0.153174
C	1.018174	-0.180188	-1.328278
C	-0.168320	-1.066837	0.951802
C	1.754997	-0.454923	-0.164656
H	1.508819	0.163493	-2.232942
H	-0.595662	-1.440711	1.877379
C	3.208550	-0.286006	-0.089756
C	-2.476197	-1.060107	-0.102940
N	1.151038	-0.901472	0.957756
C	5.639714	0.187910	-0.549515
C	5.392394	-0.272261	0.769527
C	6.929194	0.502961	-0.989168
C	6.479297	-0.413017	1.655901
C	7.983397	0.354444	-0.092684
H	7.105842	0.854093	-2.001314
C	7.759529	-0.100545	1.221529
H	6.306787	-0.763986	2.669554
H	8.993229	0.593655	-0.413387
H	8.600536	-0.207162	1.900503
S	4.150414	0.289538	-1.475639
C	-0.358515	-0.357327	-1.319822
H	-0.925946	-0.156415	-2.220725
C	4.001340	-0.532427	0.997257
H	3.596105	-0.891497	1.935583

Table S17 Cartesian coordinates of the first excited state (S_1) fully optimized geometry in toluene of **Car2** from B3LYP calculations (in Å)

Atom	x	y	z
C	-3.889067	0.277117	0.454582
H	-4.674550	-3.014181	2.250450
H	-2.522577	-0.724090	2.289233
H	-5.516192	-0.181808	2.176184
H	-6.748773	-2.155776	0.121098
H	-2.066747	-3.447246	0.929944
H	-5.863446	0.617181	-0.911426
H	-4.647408	-4.138323	-0.633501
H	-2.974460	0.373276	-1.875288
H	-2.400463	-2.636594	-2.139879
H	-5.194813	-1.750513	-2.521424
B	-3.127275	-1.010628	1.304576
B	-4.385752	-2.348717	1.303462
B	-4.943715	-0.666981	1.250461
B	-2.844583	-2.653262	0.502385
B	-5.597671	-1.842402	0.080008
B	-5.131261	-0.211279	-0.473407
B	-4.359206	-3.011620	-0.365043
B	-3.383333	-0.384339	-1.052847
B	-3.033678	-2.197321	-1.231803
B	-4.684616	-1.618232	-1.451213
C	-3.494992	1.690792	0.837783
H	-3.643762	1.810187	1.919116
H	-2.414224	1.809645	0.670147
C	-4.233715	2.815995	0.096998
H	-5.311561	2.734708	0.288955
H	-4.102607	2.692729	-0.986569
C	-3.745343	4.208963	0.515666
H	-3.867976	4.324924	1.601954
H	-2.666536	4.289749	0.319927
C	-4.482184	5.342947	-0.204523
H	-5.559406	5.306781	-0.000408
H	-4.114517	6.324593	0.116011
H	-4.348643	5.274585	-1.291257
C	-0.782999	-0.993844	-0.225761
C	1.187748	-0.255187	-1.416761
C	0.071684	-1.188498	0.888662
C	1.937025	-0.471435	-0.250182
H	1.654987	0.116180	-2.323966
H	-0.341913	-1.564863	1.820115
C	3.374892	-0.218308	-0.166605
C	-2.226649	-1.287496	-0.143444
N	1.373620	-0.937517	0.888273
C	5.796676	0.328470	-0.532597
C	5.511243	-0.053254	0.808986
C	7.069969	0.673692	-0.938027
C	6.568531	-0.080395	1.756216
C	8.103472	0.637836	0.026102
H	7.285488	0.965907	-1.960064
C	7.852966	0.265639	1.353228
H	6.363394	-0.370515	2.781485
H	9.110187	0.906250	-0.277073
H	8.667606	0.248160	2.068982
S	4.328481	0.288286	-1.523557
C	-0.176797	-0.521157	-1.401397
H	-0.770589	-0.360070	-2.293957
C	4.149440	-0.357004	0.999686
H	3.702506	-0.666162	1.935639

Table S18 Cartesian coordinates of the ground state (S_0) fully optimized geometry in toluene of **Car2B** from B3LYP calculations (in Å)

Atom	x	y	z
C	-3.707606	0.153213	0.332387
H	-4.656967	-3.236673	1.868407
H	-2.431035	-1.084384	2.081055
H	-5.245953	-0.223202	2.229450
H	-6.911196	-1.947696	0.217110
H	-2.130642	-3.329846	0.086930
H	-5.941101	0.922515	-0.456812
H	-4.949162	-3.893063	-1.127132
H	-3.466699	0.733420	-2.083759
H	-2.798214	-2.161324	-2.578084
H	-5.763031	-1.299938	-2.566676
B	-3.168472	-1.252452	1.174211
B	-4.459548	-2.444428	1.005002
B	-4.858004	-0.724555	1.227433
B	-3.021514	-2.556933	-0.025576
B	-5.763130	-1.691893	0.043256
B	-5.259457	-0.038580	-0.354929
B	-4.629474	-2.817389	-0.734266
B	-3.800758	-0.136817	-1.358875
B	-3.418229	-1.859082	-1.614545
B	-5.103880	-1.314986	-1.578094
C	-3.141673	1.489118	0.824653
H	-3.016606	1.419227	1.910039
H	-2.137236	1.612076	0.404883
C	-3.980024	2.730973	0.488324
H	-4.976388	2.640084	0.937721
H	-4.128238	2.798834	-0.596914
C	-3.309769	4.015943	0.993993
H	-3.152566	3.941062	2.078897
H	-2.311350	4.106696	0.544129
C	-4.129549	5.271490	0.680705
H	-5.120924	5.223802	1.147453
H	-3.628766	6.172984	1.050890
H	-4.275827	5.389627	-0.399875
C	-1.158669	-0.567961	-0.615830
C	0.645813	0.362060	-1.951071
C	-0.200810	-0.907907	0.341485
C	1.549125	0.009061	-0.940153
H	0.999658	0.853378	-2.850328
H	-0.457285	-1.423456	1.257908
C	2.969634	0.184289	-0.833020
C	3.491408	-0.318816	0.337242
C	-2.599253	-0.950275	-0.425494
N	1.094319	-0.627165	0.184852
C	2.025201	-0.168951	2.633899
H	1.126825	-0.547715	3.142854
H	2.862463	-0.309312	3.331497
H	1.896239	0.913851	2.501408
C	2.414865	-2.580660	1.417853
H	3.273545	-2.838176	2.053189
H	1.524179	-2.995995	1.911477
H	2.545189	-3.118026	0.468845
B	2.319381	-0.963628	1.241762
C	5.416351	0.550246	-0.767665
C	4.913653	-0.113467	0.389123
C	6.774210	0.846305	-0.913871
C	5.823525	-0.474981	1.403832
C	7.644504	0.475207	0.108298
H	7.145520	1.352707	-1.799782
C	7.172710	-0.181634	1.260217
H	5.459298	-0.982349	2.292552
H	8.703518	0.697473	0.012051
H	7.873206	-0.460310	2.042179
S	4.134203	0.923655	-1.926824
C	-0.698182	0.069556	-1.786620
H	-1.395309	0.332258	-2.572966

Table S19 Cartesian coordinates of the first excited state (S_1) fully optimized geometry in toluene of **Car2B** from B3LYP calculations (in Å)

Atom	x	y	z
C	-4.047563	0.230269	0.456627
H	-4.473138	-3.248478	2.006379
H	-2.435360	-0.856315	2.028916
H	-5.442891	-0.474931	2.291948
H	-6.808548	-2.321086	0.202769
H	-2.009148	-3.416920	0.379884
H	-6.172996	0.575229	-0.656416
H	-4.720297	-4.110120	-0.958305
H	-3.391916	0.577431	-1.938536
H	-2.723268	-2.357219	-2.546000
H	-5.580766	-1.595913	-2.541605
B	-3.134206	-1.086186	1.092464
B	-4.322507	-2.488296	1.099788
B	-4.958075	-0.841525	1.267262
B	-2.869262	-2.637578	0.112625
B	-5.684530	-1.943211	0.068025
B	-5.359123	-0.245101	-0.375939
B	-4.454426	-2.998060	-0.617045
B	-3.678323	-0.268742	-1.151097
B	-3.271965	-2.037150	-1.538798
B	-4.960248	-1.532824	-1.525036
C	-3.681683	1.625892	0.924078
H	-3.735871	1.649421	2.020556
H	-2.627187	1.813796	0.673291
C	-4.534190	2.766603	0.346909
H	-5.583320	2.622144	0.635865
H	-4.507666	2.727487	-0.750404
C	-4.060192	4.147372	0.819118
H	-4.076431	4.181105	1.917701
H	-3.010835	4.291101	0.524589
C	-4.909466	5.293678	0.260230
H	-5.957780	5.195876	0.568045
H	-4.547675	6.266719	0.612012
H	-4.886126	5.304950	-0.836531
C	-0.980375	-0.804337	-0.673665
C	0.812890	0.090851	-2.054116
C	-0.022247	-0.990483	0.338647
C	1.694875	-0.115409	-0.998271
H	1.163491	0.517294	-2.987550
H	-0.287752	-1.414351	1.299060
C	3.119323	0.148009	-0.875926
C	3.635928	-0.210024	0.381242
C	-2.394275	-1.184194	-0.460111
N	1.259830	-0.654476	0.177211
C	2.097106	0.126095	2.590867
H	1.196287	-0.245629	3.098205
H	2.912242	0.097735	3.325736
H	1.924272	1.178847	2.333588
C	2.651048	-2.382621	1.674465
H	3.493624	-2.513836	2.366065
H	1.758387	-2.774308	2.181430
H	2.842805	-3.017609	0.800175
B	2.466494	-0.805611	1.303586
C	5.541849	0.623841	-0.767794
C	5.035759	0.065870	0.439742
C	6.872179	0.968110	-0.927094
C	5.934349	-0.139716	1.507114
C	7.745274	0.749844	0.160005
H	7.244929	1.393385	-1.852985
C	7.280745	0.203968	1.357875
H	5.573575	-0.564435	2.438281
H	8.792602	1.013628	0.054161
H	7.970152	0.044933	2.180434
S	4.253489	0.801758	-1.985717
C	-0.526491	-0.257584	-1.886522
H	-1.226227	-0.101536	-2.699467