Supplementary Information

Facile synthesis, aggregation-induced emission, mechano- and thermochromism of *o*-carborane-tetraphenylethene dyads with a short CH(OH) linker

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Table of contents

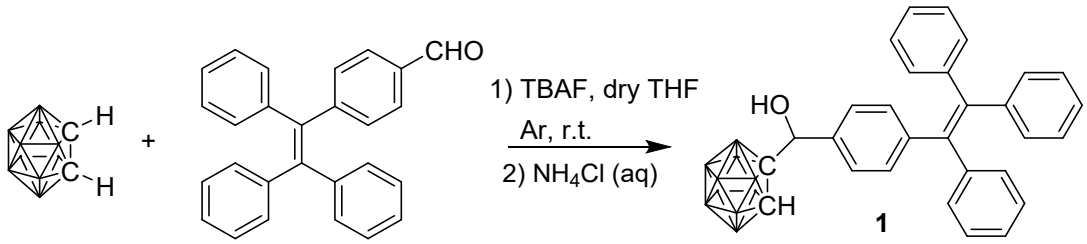
Experimental section
Table S1. Photophysical data for the parent TPE
Scheme S1 Molecular structures of reported *o*-carborane-TPE compounds
Table S2. Synthesis and photophysical data for reported *o*-carborane-TPE compounds
Table S3 Crystal data and structure refinement for **1** and **2**
Table S4 Selected bond lengths and angles, and torsion angles for **1** and **2**
Fig. S1 CIE 1931 chromaticity coordinates of **1** (a), **2** (b), **3** (c), **4** (d)
Fig. S2 PXRD patterns of **1** (a), **2** (b), **3** (c), **4** (d)
Fig S3. FT-IR spectrum of **1** (KBr pellet)
Fig S4. ^{1}H-NMR spectrum of **1** in $CDCl_3$
Fig S5. ^{13}C-NMR spectrum of **1** in $CDCl_3$
Fig S6. ^{11}B{^{1}H}-NMR spectrum of **1** in CH_2Cl_2
FigS7. FT-IR spectrum of **2** (KBr pellet)
Fig S8. ^{1}H-NMR spectrum of **2** in $CDCl_3$
Fig S9. ^{13}C-NMR spectrum of **2** in $CDCl_3$
Fig S10. ^{11}B{^{1}H}-NMR spectrum of **2** in CH_2Cl_2
Fig S11. ^{19}F-NMR spectrum of **2** in CH_2Cl_2
Fig S12. FT-IR spectrum of **3** (KBr pellet)
Fig S13. ^{1}H-NMR spectrum of **3** in $CDCl_3$
Fig S14. ^{13}C-NMR spectrum of **3** in $CDCl_3$
Fig S15. ^{11}B{^{1}H}-NMR spectrum of **3** in CH_2Cl_2
FigS16. FT-IR spectrum of **4** (KBr pellet)
Fig S17. ^{1}H-NMR spectrum of **4** in $CDCl_3$
Fig S18. ^{13}C-NMR spectrum of **4** in $CDCl_3$
Fig S19. ^{11}B{^{1}H}-NMR spectrum of **4** in CH_2Cl_2
Fig S20. ^{19}F-NMR spectrum of **4** in CH_2Cl_2

Experimental section

General

Standard Schlenk techniques were used for the synthetic reactions under Ar. Tetrahydrofuran (THF) was dried with sodium-benzophenone, and other solvents were commercially available and used without further purification. IR spectra were recorded in the range 400-4000 cm^{-1} on a Perkin Elmer Spectrum RX I spectrometer using KBr pellets. ^{1}H-NMR analyses were performed on a Bruker Avance III 600 MHz and 400 MHz spectrometer. ^{19}F-NMR and ^{11}B{^{1}H}-NMR spectra were recorded in dichloromethane solutions (D_2O was added for locking) on a Bruker AVANCE III 500 spectrometer. As internal references for ^{1}H- and ^{13}C-NMR spectroscopy the signals of $CDCl_3$ were used and calculated relative to tetramethylsilane (TMS). Melting points were measured with a SGW X-4 apparatus and were not corrected. The high resolution mass spectra were measured on a Thermo Fisher Scientific LTQ FTICR-MS instrument (DART positive ion mode) and Waters Micromass GCT Premier (EI (70eV)). UV-Vis spectra were recorded on a UV3600 Plus spectrometer. Emission spectra were measured on an Edinburgh FLS920 fluorimeter, using a front-face sample configuration for solid samples. Absolute fluorescence quantum yields were obtained using an integrating sphere. For the variable temperature emission spectra of the powder samples, a temperature controller (TCB1402C) made by Techcomp company was applied, and for the silica gel composites on TLC plates, a hot plate was used to heat up the TLC plates and the emission spectra were then measured as soon as possible.

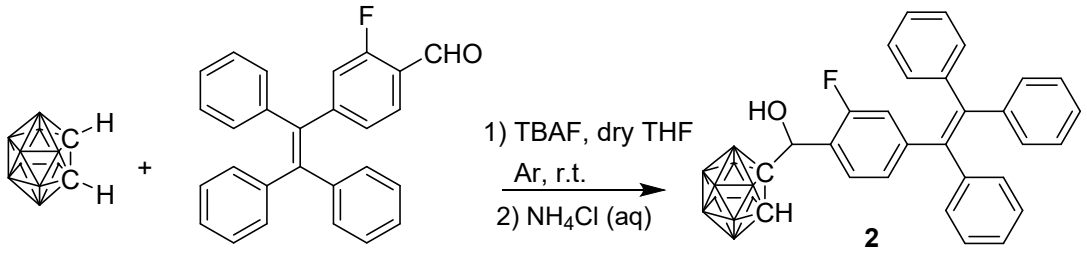
Synthesis of compound 1



Under argon, *o*-carborane (77.1 mg, 0.54 mmol), 1-(4-formylphenyl)-1,2,2-triphenylethene (217.4 mg, 0.60 mmol) and 20 mL of dry THF were added into a Schlenk tube. To the mixture a THF solution of tetrabutylammonium fluoride (1 $mol \cdot L^{-1}$, 1.6 mL, 1.6 mmol) was added dropwise via syringe under stirring and reacted for 1 h at room temperature. Then the reaction mixture was quenched by 15 mL of an aqueous solution of saturated ammonium chloride and stirred for additional 10 min before it was transferred to a separation funnel. The organic phase was separated, and the water phase was extracted with CH_2Cl_2 (15 mL × 3). The organic phases were combined and dried with anhydrous Na_2SO_4, concentrated and separated using preparative thin

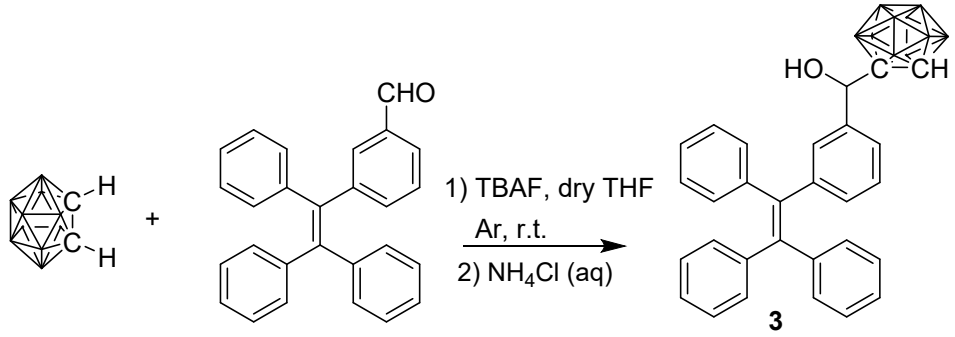
layer chromatography (eluent CH_2Cl_2/*n*-hexane = 1/2, *V*/*V*) to give a yellowish solid (compound **1**, 134.2 mg, yield 50.3%), *m.p*. 176.8-177.3 °C; R_f = 0.1 (CH_2Cl_2/*n*-hexane = 1/2, *V*/*V*); FT-IR (KBr, ν/cm^{-1}): 3065, 2924, 2583 (B-H), 1604, 1490, 1078, 702; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 - 6.93 (m, 19H, Ar-*H*), 5.16 (s, 1H, C*H*OH), 3.63 (s, 1H, C_{cage}-*H*), 2.58 (s, 1H, O*H*); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.67, 143.39, 143.10, 142.94, 142.17, 140.02, 136.25, 131.60, 131.36, 131.26, 131.22, 127.89, 127.76 (d, *J* = 3.17 Hz), 127.75, 126.81, 126.77 (d, *J* = 1.87 Hz), 125.88, 78.69, 74.84, 59.36; ^{11}B{^{1}H} NMR (128 MHz, CH_2Cl_2) δ -3.73 (2B), -4.65 (1B), -9.05 (1B), -9.52 (1B), -11.28 (1B), -12.63 (2B), -13.27 (1B), -14.20 (1B); DART-HRMS *m/z* (%): calcd. for $C_{29}H_{31}B_{10}O$, 505.3305, found 505.3350 $[M+H]^+$.

Synthesis of compound 2



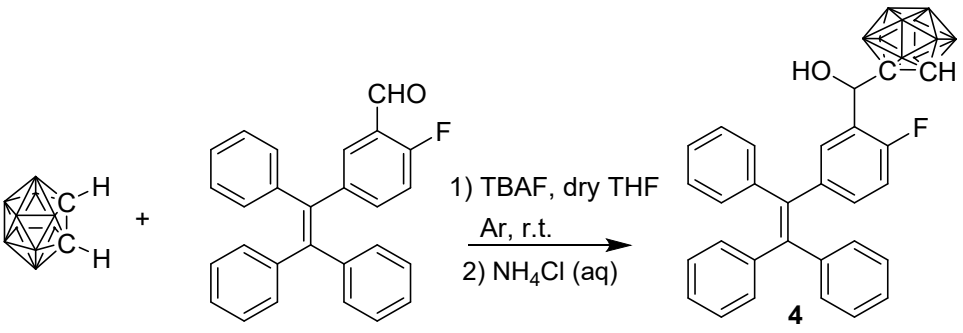
Under argon, *o*-carborane (77.1 mg, 0.54 mmol), 1-(3-fluoro-4-formylphenyl)-1,2,2-triphenyl-ethene (226.8 mg, 0.60 mmol) and 20 mL of dry THF were added into a Schlenk tube. To the mixture a THF solution of tetrabutylammonium fluoride (1 mol·L^{-1}, 1.6 mL,1.6 mmol) was added dropwise via syringe under stirring and reacted for 2 h at room temperature. Then reaction mixture was quenched by 15 mL of an aqueous solution of saturated ammonium chloride and stirred for additional 10 min before it was transferred to a separation funnel. The organic phase was separated, and the water phase was extracted with CH_2Cl_2 (15 mL × 3). The organic phases were combined and dried with anhydrous Na_2SO_4, concentrated and separated using preparative thin layer chromatography (eluent ethyl acetate/*n*-hexane = 1/5, *V*/*V*) to give a yellowish solid (compound **2**, 127.5 mg, yield 49%); *m.p*. 161.2-162.1 °C, R_f = 0.48 (ethyl acetate/*n*-hexane = 1/5, *V*/*V*); FT-IR (KBr, ν/cm^{-1}): 3072, 2960, 2577 (B-H), 1612, 1413, 702; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21-7.05 (m, 10H, ArH), 7.5-7.00 (m, 4H, ArH), 6.99 (dd, *J* = 8.0, 1.4 Hz, 2H, ArH), 6.87 (dd, *J* = 8.0, 1.5 Hz, 1H, ArH), 6.74 (dd, *J* = 11.5, 1.4 Hz, 1H, ArH), 5.47 (s, 1H, CHOH), 3.85 (s, 1H, cage-CH); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.32, 158.03, 147.67, 147.62, 142.97 (d, *J* = 4.14Hz), 142.79, 142.41, 138.88, 131.21, 131.16, 128.02, 127.94, 127.56 (d, *J* = 3.46Hz), 127.16, 126.97, 126.82, 123.96, 123.88, 118.35, 118.21, 78.19, 68.96, 58.92, 29.75; ^{11}B{^{1}H} NMR (128 MHz, CH_2Cl_2) δ -3.60 (2B), -4.71 (1B), -9.19 (1B), -9.55 (1B), -12.23 (2B), -13.36 (1B), -13.81 (2B); ^{19}F (377 MHz, CH_2Cl_2) δ -118.01; DART-HRMS *m/z* (%): calcd. for $C_{29}H_{31}B_{10}O_1F_1$, 522.3362, found 522.3357 $[M+H]^+$.

Synthesis of compound 3



Under argon, *o*-carborane (145.2 mg, 1.0 mmol), 1-(3-formylphenyl)-1,2,2-triphenylethene (433.7 mg, 1.2 mmol) and 25 mL of dry THF were added into a Schlenk tube. To the mixture a THF solution of tetrabutylammonium fluoride (1 mol·L^{-1}, 3 mL, 3 mmol) was added dropwise via syringe under stirring and reacted for 2 h at room temperature. Then reaction mixture was quenched by 15 mL of an aqueous solution of saturated ammonium chloride and stirred for additional 10 min before it was transferred to a separation funnel. The organic phase was separated, and the water phase was extracted with CH_2Cl_2 (15 mL × 3). The organic phases were combined and dried with anhydrous Na_2SO_4, concentrated and separated using column chromatography (eluent ethyl acetate/*n*-hexane = 1/5, *V*/*V*) to give colorless oily liquid, which solidified to give a white solid in two days (compound **3**, 280.5 mg, yield 55.6%); *m.p.* 180.4-181.0 °C; R_f = 0.31 (ethyl acetate/*n*-hexane = 1/5, *V*/*V*); FT-IR (KBr, ν/cm^{-1}): 3090, 3053, 3019, 2585 (B-H), 1491, 1441, 1072, 764, 700; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 -6.98 (m, 19 H), 5.07 (s, 1 H), 3.50 (s, 1 H), 2.38 (s, 1 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.89, 143.46, 143.34, 143.27, 142.02, 140.14, 138.11, 132.68, 131.50, 131.37, 131.31, 129.37, 128.41, 128.10, 127.97, 127.88, 127.13, 126.86 (d, *J* = 4.05Hz), 124.95, 78.55, 75.03, 59.15, 54.51; ^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ -2.32 (1B), -3.25 (1B), -4.33 (1B), -8.82 (1B), -9.26 (1B), -11.09 (1B), -12.89 (2B), -13.64 (1B), -14.78 (1B); DART-MS *m/z* (%): calcd. for $C_{29}H_{33}B_{10}O$, 505.3529, found 505.3416 $[M+H]^+$.

Synthesis of compound 4



Under argon, *o*-carborane (145.2 mg, 1.0 mmol), 1-(4-fluoro-3-formylphenyl)-1,2,2-triphenyl-ethene (433.7 mg, 1.2 mmol) and 25 mL of dry THF were added into a Schlenk tube. To the mixture a THF solution of tetrabutylammonium fluoride (1 mol·L^{-1}, 3 mL, 3 mmol) was added

dropwise via syringe under stirring and reacted for 2 h at room temperature. Then reaction mixture was quenched by 15 mL of an aqueous solution of saturated ammonium chloride and stirred for additional 10 min before it was transferred to a separation funnel. The organic phase was separated, and the water phase was extracted with CH_2Cl_2 (15 mL × 3). The organic phases were combined and dried with anhydrous Na_2SO_4, concentrated and separated using column chromatography (eluent ethyl acetate/*n*-hexane = 1/5, *V*/*V*) to give colorless oily liquid, which then solidified to afford a white solid in two days (compound **4**, 314 mg, yield 60.2%); *m.p*. 167.0-167.6 °C; R_f = 0.35 (ethyl acetate/*n*-hexane = 1/5, *V*/*V*); FT-IR (KBr, ν/cm^{-1}): 3082, 3055, 3019, 2583 (B-H), 1493, 1256, 1041, 764, 698; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 - 7.09 (m, 10 H), 7.04 - 6.99 (m, 7 H), 7.01 - 6.98 (m, 2 H), 6.85 (t, *J* = 9.26 Hz, 1H), 5.42 (s, 1 H), 3.58 (s, 1 H), 2.39 (s, 1 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.04, 157.40, 143.31, 143.05, 142.88, 142.01, 140.70 (d, *J* = 4.35 Hz), 140.69, 139.14, 133.93, 133.88, 131.37, 131.19, 131.15, 130.35, 128.09, 127.91, 127.77, 127.05, 126.85, 126.80, 125.53, 125.45, 115.38, 115.23, 77.77, 68.70, 58.68; ^{11}B{^{1}H} NMR (128 MHz, CH_2Cl_2) δ -2.94 (1B), -3.70 (2B), -4.88 (1B), -9.69 (2B), -12.51 (2B), -13.34 (1B), - 13.90 (2B); ^{19}F NMR (377 MHz, CH_2Cl_2) δ -119.21; DART-MS *m/z* (%): calcd. for $C_{29}H_{32}B_{10}OF$, 523.3435, found 523.3438 $[M+H]^+$.

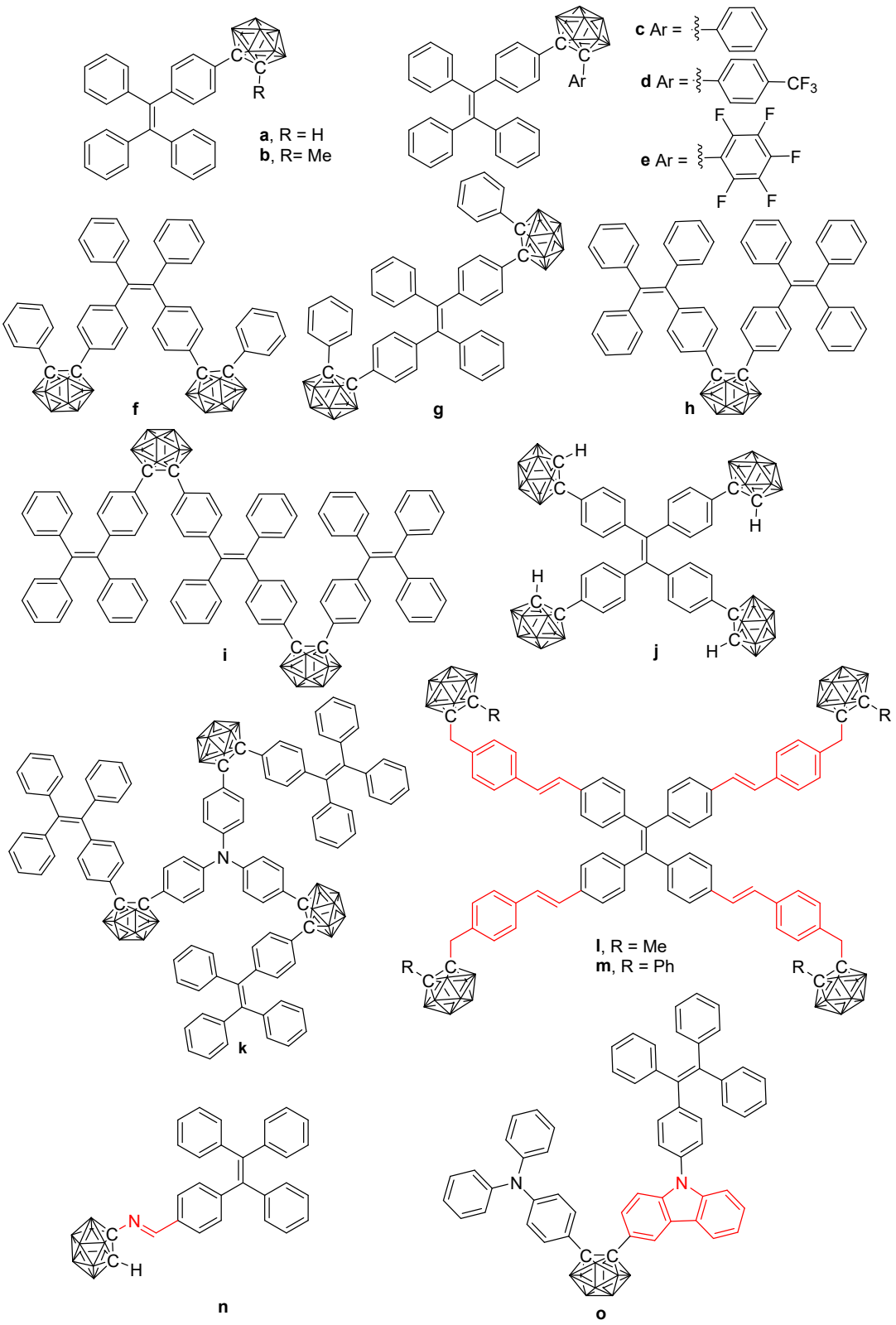
Preparation of the silica gel composites

The corresponding sample (5 mg) was dissolved in 5 mL of dichloromethane, the resulting solution was dropped (3 drops) on an analytical silica gel plate (1 × 1 cm), and the silica gel composites were obtained after being dried in air (1 min) and measured.

Table S1. Photophysical data for the parent TPE

[a] λ_{em} (nm)	[a] Φ	[a] τ (ns)	ref. in the text
439	0.23	1.44	[28]
475 (amorphous)	0.49 (film)	-	[29]
440 (crystalline)			
453 (crystals)	0.25	3.99	[30]
[b]472 (aggregates)	0.25	1.42	[31]
445	0.24	-	[32]

[a] solid, [b] in THF/water with 90% water fraction, - not reported.



Scheme S1 Molecular structures of reported *o*-carborane-TPE compounds

Table S2. Synthesis and photophysical data for reported *o*-carborane-TPE compounds

Comp.	linker	synthesis	[a] λ_{em} (nm)	[a] τ (ns)	[a] Φ	[c]ref.
a	-	alkynyl-TPE + $B_{10}H_{12}(SEt_2)_2$	452	7.21	0.18	28
b	-	alkynyl-TPE + $B_{10}H_{12}(SEt_2)_2$	533	4.81	0.58	28
c	-	alkynyl-TPE + $B_{10}H_{12}(SEt_2)_2$	553 (powder)[28], 522 (crystal)[37]	7.30 (powder)[28], 4.85 (crystal)[37]	0.63 (powder)[28], 0.95 (crystal)[37]	28, 37
d	-	alkynyl-TPE + $B_{10}H_{12}(NCCH_3)_2$	597	9.02	0.91	38
e	-	alkynyl-TPE + $B_{10}H_{12}(NCCH_3)_2$	678	7.04	0.59	38
f	-	alkynyl-TPE + $B_{10}H_{12}(NCCH_3)_2$	528	6.23	0.99	39
g	-	alkynyl-TPE + $B_{10}H_{12}(NCCH_3)_2$	534[37], 533[39]	5.56[37], 5.95[39]	0.90[37], 0.90[39]	37, 39
h	-	alkynyl-TPE + $B_{10}H_{12}(SEt_2)_2$	560 (powder)	11.9 (powder)	0.55 (powder)	40
i	-	alkynyl-TPE + $B_{10}H_{12}(NCCH_3)_2$	565	5.48	0.68	41
j	-	alkynyl-TPE + $B_{10}H_{12}(SEt_2)_2$	452	2.96	0.34	28
k	-	alkynyl-TPE + $B_{10}H_{12}(NCCH_3)_2$	563	-	0.62	42
l		(Pd-cat.) styryl-C_2B_{10} + Br-TPE	559	1.34[b]	0.51[b]	43
m		(Pd-cat.) styryl-C_2B_{10} + Br-TPE	561	1.05[b]	0.56[b]	43
n	C=N	C_2B_{10}-NH_2 + TPE-CHO	480 (crystal), 483 (powder)	-	0.99 (crystal)	44
o		1) alkynyl-9H-carbazole + $B_{10}H_{12}(SEt_2)_2$ 2) (Pd-cat.) Br-TPE + carbazole (C-N coupling)	608	9.1	0.99	45

[a] solid, [b] THF/H_2O, 1:1000, [c] ref. in the text, - no linker or not reported.

Table S3. Crystal data and structure refinement for **1** and **2**

compounds	**1**	**2**
Empirical formula	$C_{29}H_{32}B_{10}O_{0.97}$	$C_{29}H_{32}B_{10}OF$
Formula weight	504.25	522.64
Temperature/K	293(2)	293(2)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	9.9704(8)	9.8582(6)
b/Å	11.7142(7)	11.8389(6)
c/Å	13.6657(10)	13.8893(8)
α/°	78.019(6)	77.753(4)
β/°	88.318(6)	88.625(5)
γ/°	69.186(7)	70.879(5)
Volume/Å^3	1457.70(18)	1494.92(15)
Z	2	2
ρ_{calc}g/cm^3	1.149	1.161
μ/mm^{-1}	0.062	0.067
F(000)	528	544
Crystal size/mm^3	0.4 × 0.4 × 0.4	0.4 × 0.4 × 0.3
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.74 to 52.74	6.01 to 50.7
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -17 ≤ l ≤ 17	-11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -16 ≤ l ≤ 16
Reflections collected	17889	16950
Independent reflections	5943 [R_{int} = 0.0265, R_{sigma} = 0.0308]	5470 [R_{int} = 0.0287, R_{sigma} = 0.0311]
Data/restraints/parameters	5943/5/373	5470/0/370
Goodness-of-fit on F^2	1.056	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0560, wR_2 = 0.1448	R_1 = 0.0657, wR_2 = 0.1809
Final R indexes [all data]	R_1 = 0.0823, wR_2 = 0.1636	R_1 = 0.0917, wR_2 = 0.2021
Largest diff. peak/hole / e Å^{-3}	0.26/-0.36	0.76/-0.25
CCDC number	1901606	2216881

Table S4. Selected bond lengths and angles, and torsion angles for **1** and **2**

Compounds	bond lengths (Å)		angles [°]		torsion angles [°]	
1	C1-C2	1.673	C1-C2-C3	120.60	C1-C2-C3-C4	8.59
	C2-C3	1.550	C2-C3-C4	112.86	C1-C2-C3-O1	-115.37
	C3-C4	1.505	C2-C3-O1	119.14	C1-C2-C3-O1’	135.66
	C3-O1	1.211	C2-C3-O1’	110.47	C2-C3-C4-C5	90.74
	C3-O1’	1.406	O1-C3-O1’	95.49	C10-C11-C18-C21	-47.06
	C10-C11	1.350	C10-C11-C18	123.57	C10-C11-C24-C25	-52.64
	C10-C9	1.497	C10-C11-C24	121.42	C11-C10-C9-C6	-62.67
	C10-C12	1.492	C11-C10-C12	124.25	C11-C10-C12-C15	-49.62
	C11-C18	1.492				
	C11-C24	1.495				
2	C28-C29	1.659	C27-C28-C29	120.10	C29-C28-C27-C24	-89.43
	C27-C28	1.555	C28-C27-C24	112.73	C29-C28-C27-O1	30.74
	C24-C27	1.511	C28-C27-O1	109.30	C28-C27-C24-C25	-89.96
	C27-O1	1.429	C8-C7-C6	122.50	C8-C7-C6-C5	48.82
	C7-C8	1.354	C8-C7-C15	122.30	C8-C7-C15-C20	49.62
	C8-C21	1.500	C7-C8-C9	123.60	C7-C8-C21-C26	56.16
	C8-C9	1.488			C7-C8-C9-C10	49.83
	C7-C6	1.492				
	C7-C15	1.488				
	C18-F1	1.346				

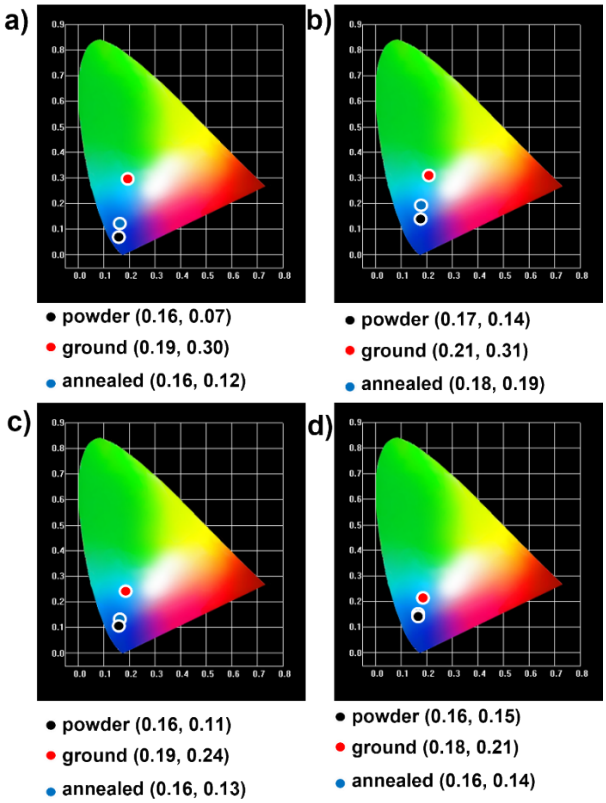


Fig. S1 CIE 1931 chromaticity coordinates of **1** (a), **2** (b), **3** (c), **4** (d)

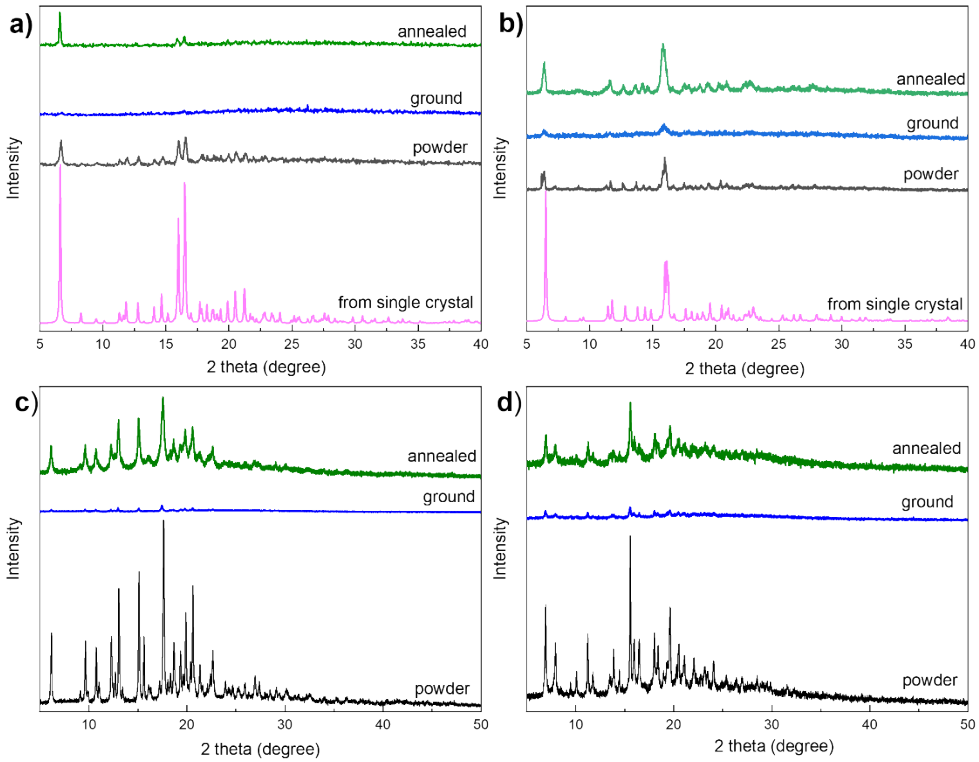


Fig. S2 PXRD patterns of **1** (a), **2** (b), **3** (c), **4** (d)

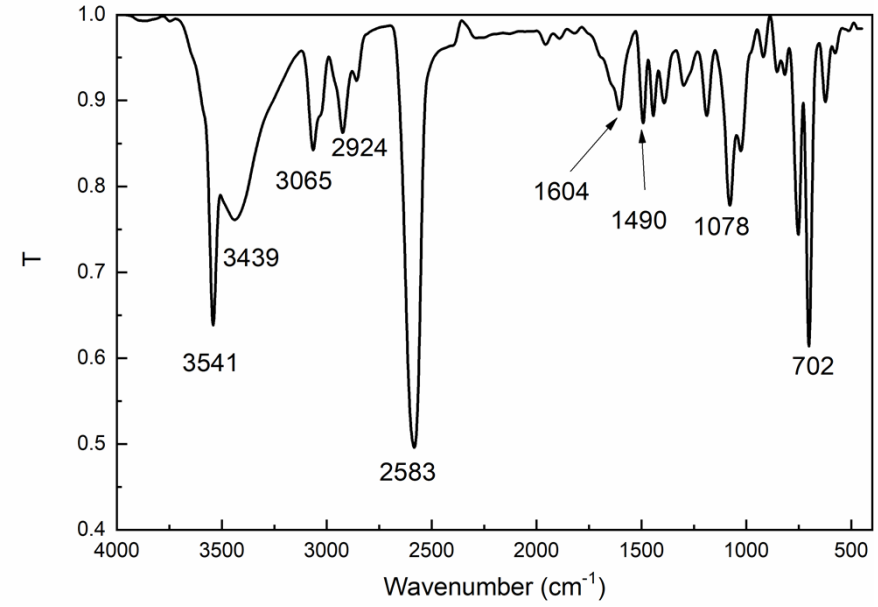


Fig. S3. FT-IR spectrum of **1** (KBr pellet)

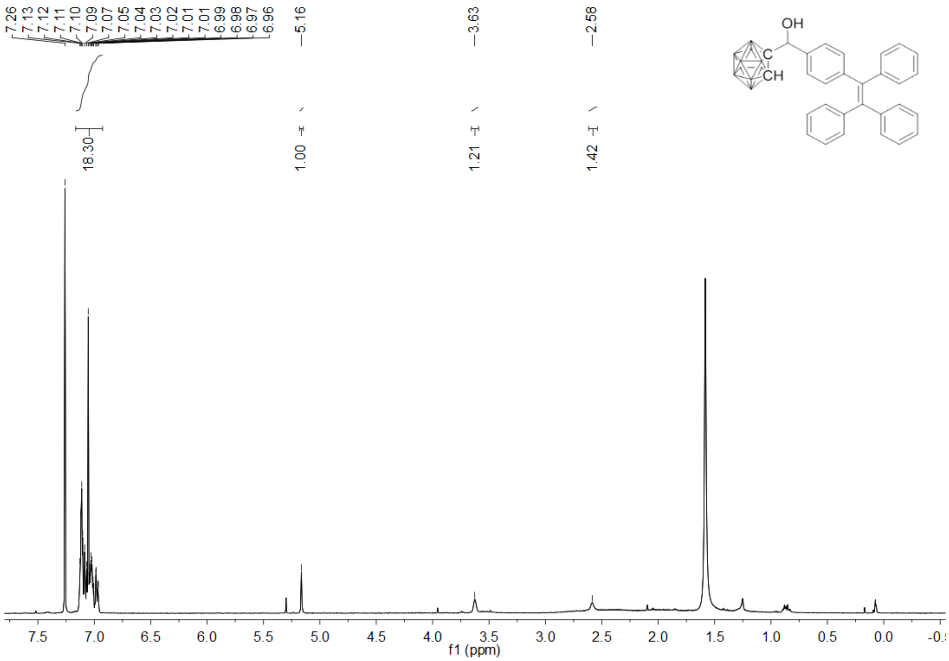


Fig. S4. ^{1}H-NMR spectrum of **1** in $CDCl_3$

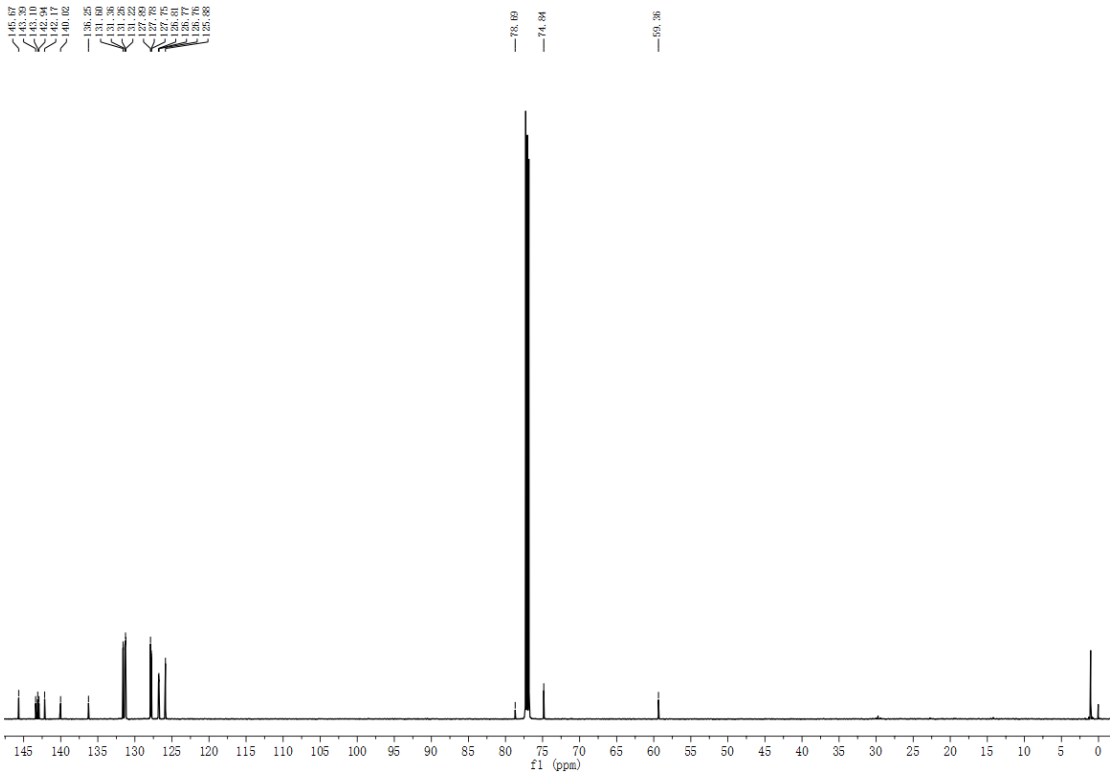


Fig. S5. ^{13}C-NMR spectrum of **1** in $CDCl_3$

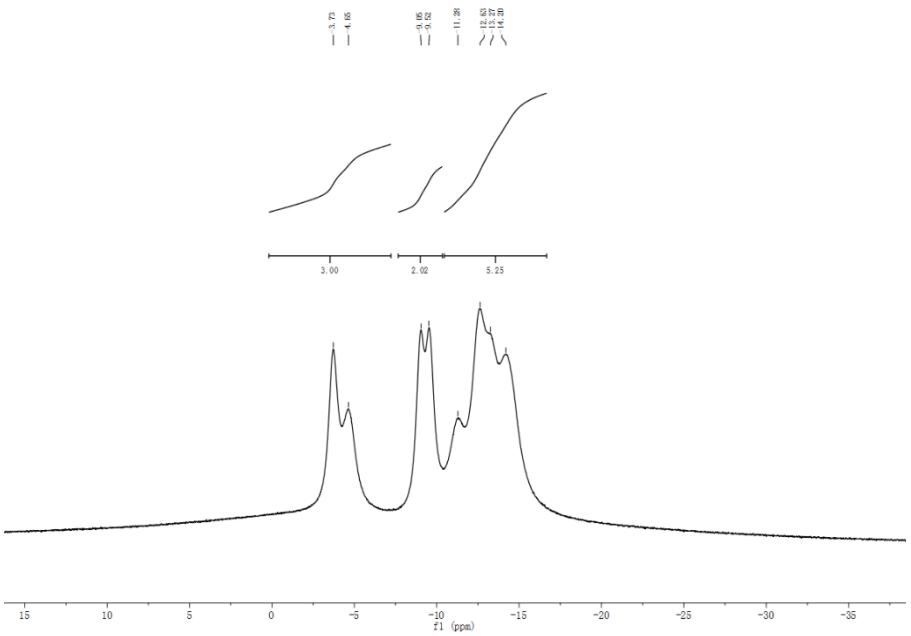


Fig. S6. $^{11}B\{^{1}H\}$-NMR spectrum of **1** in CH_2Cl_2

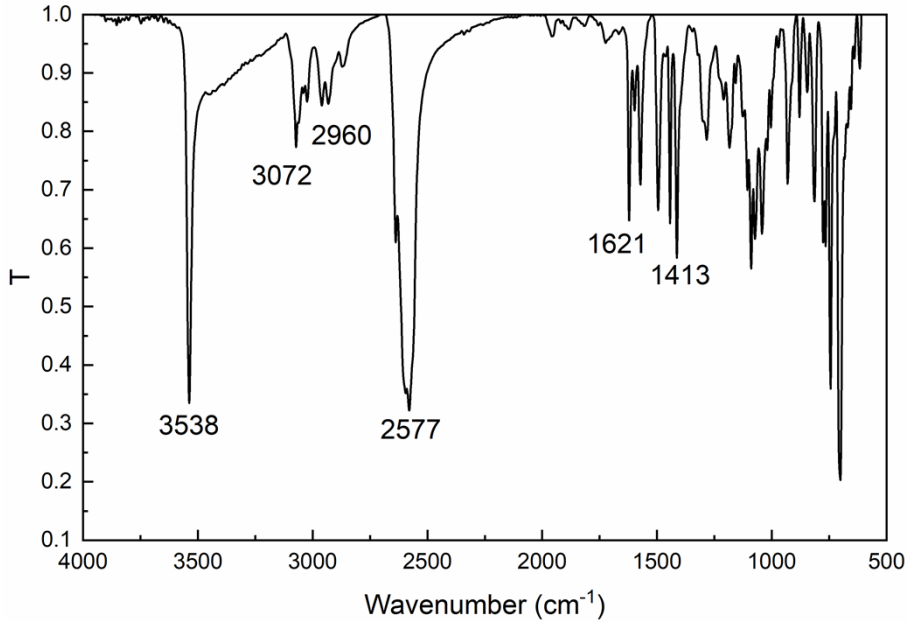
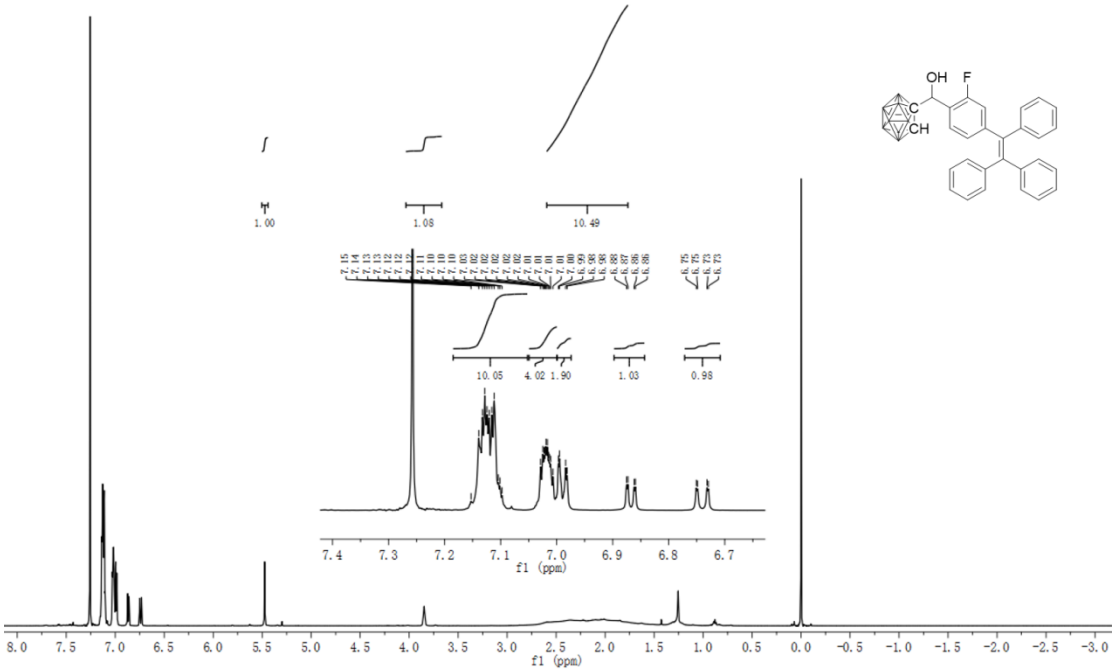


Fig. S7. FT-IR spectrum of **2** (KBr pellet)



FigS8. ^{1}H-NMR spectrum of **2** in $CDCl_3$

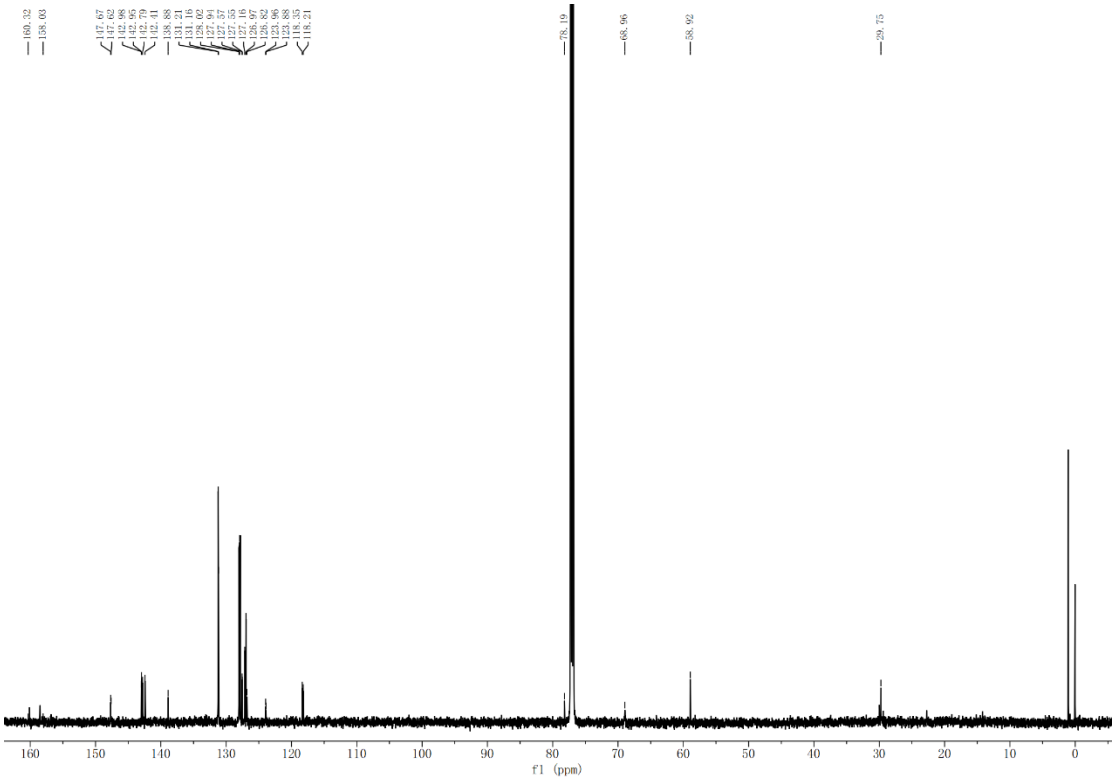


Fig. S9. ^{13}C-NMR spectrum of **2** in $CDCl_3$

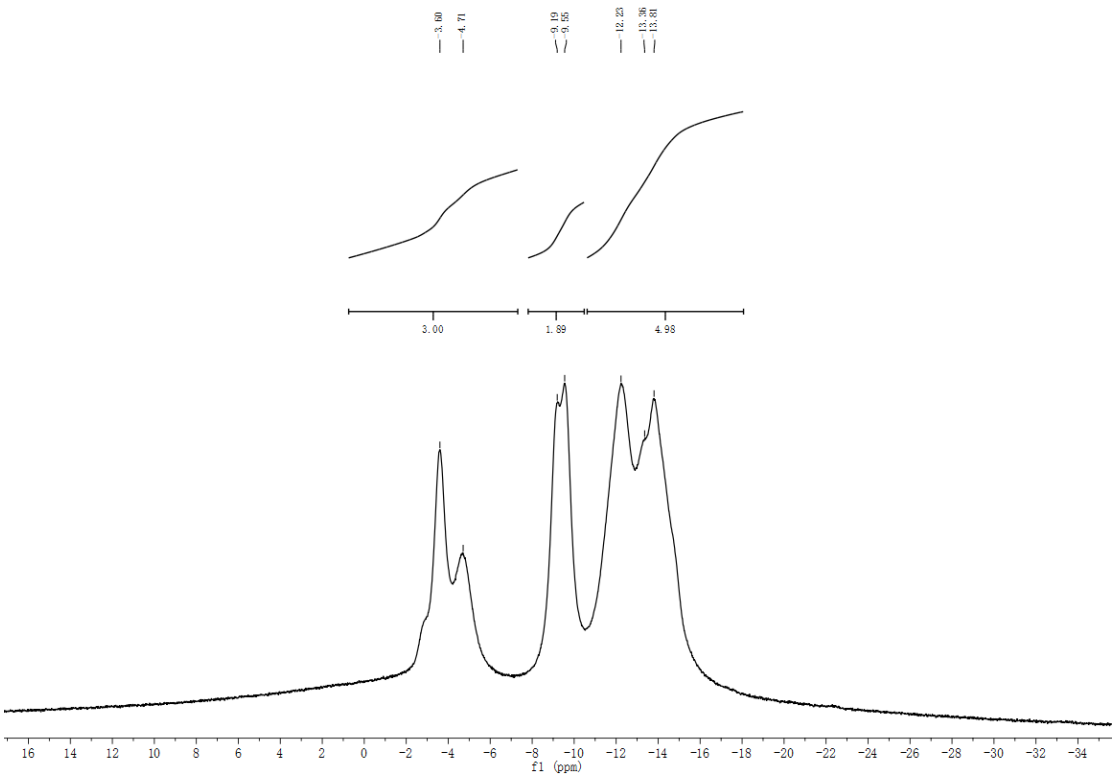


Fig. S10. $^{11}B\{^{1}H\}$-NMR spectrum of **2** in CH_2Cl_2

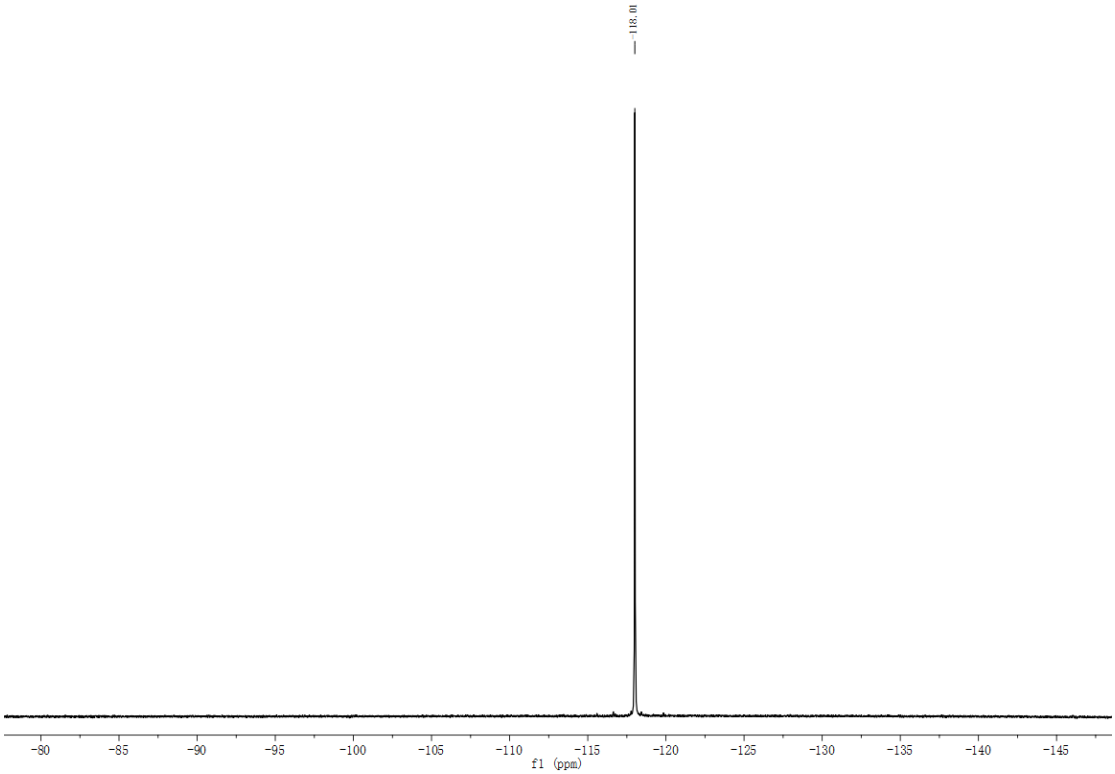


Fig. S11. ^{19}F-NMR spectrum of **2** in CH_2Cl_2

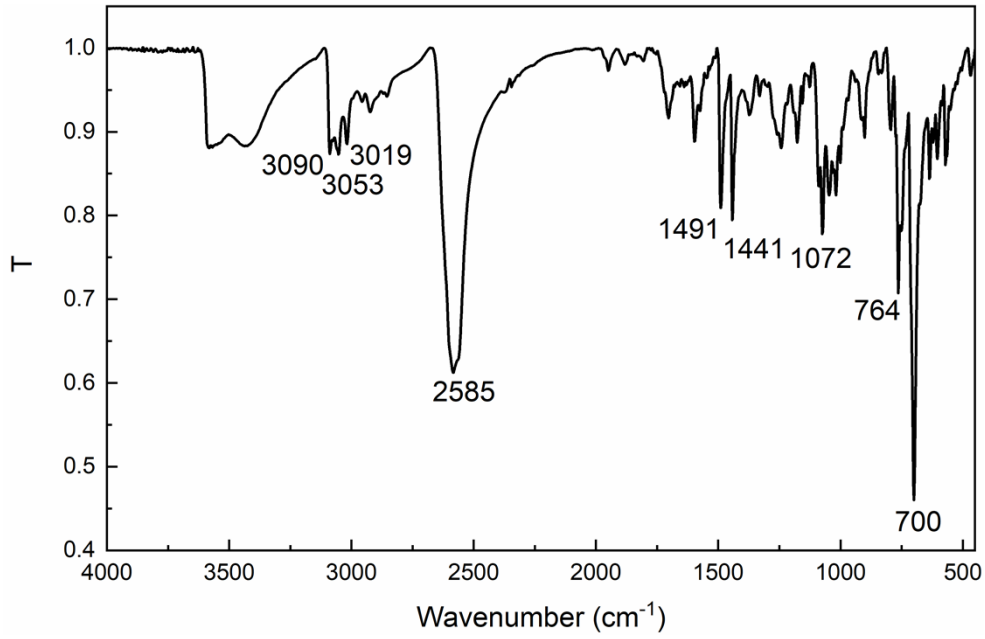


Fig. S12. FT-IR spectrum of **3** (KBr pellet)

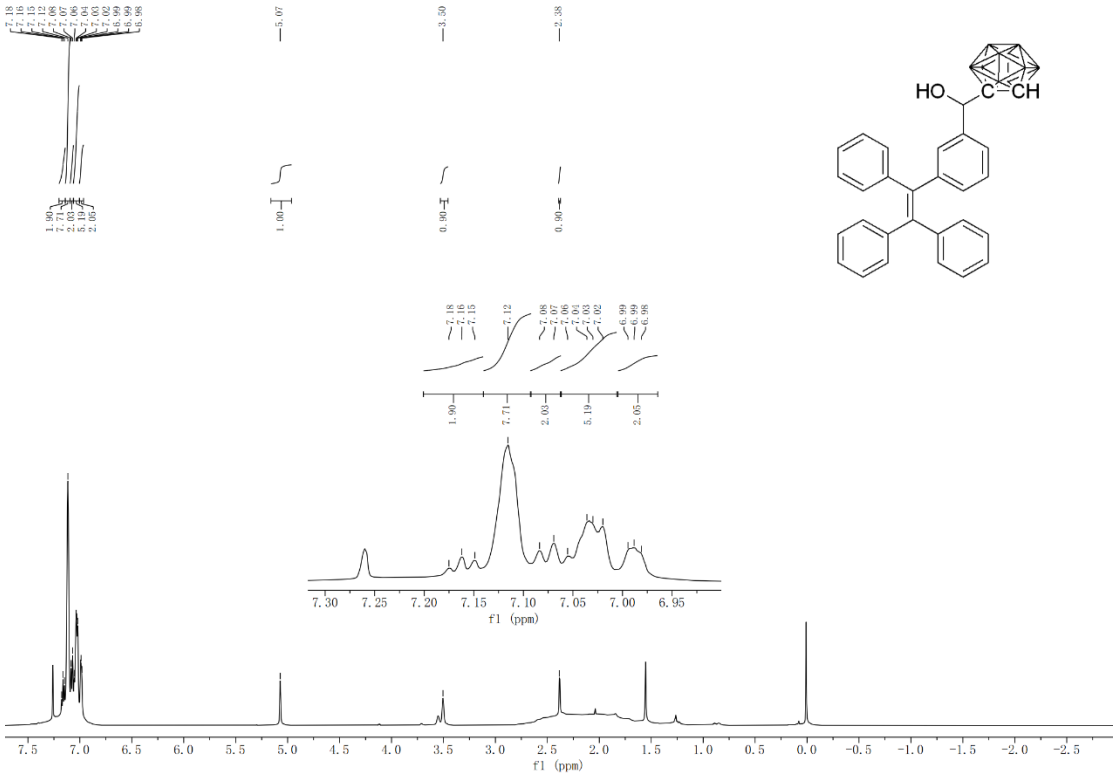


Fig. S13. ^{1}H-NMR spectrum of **3** in $CDCl_3$

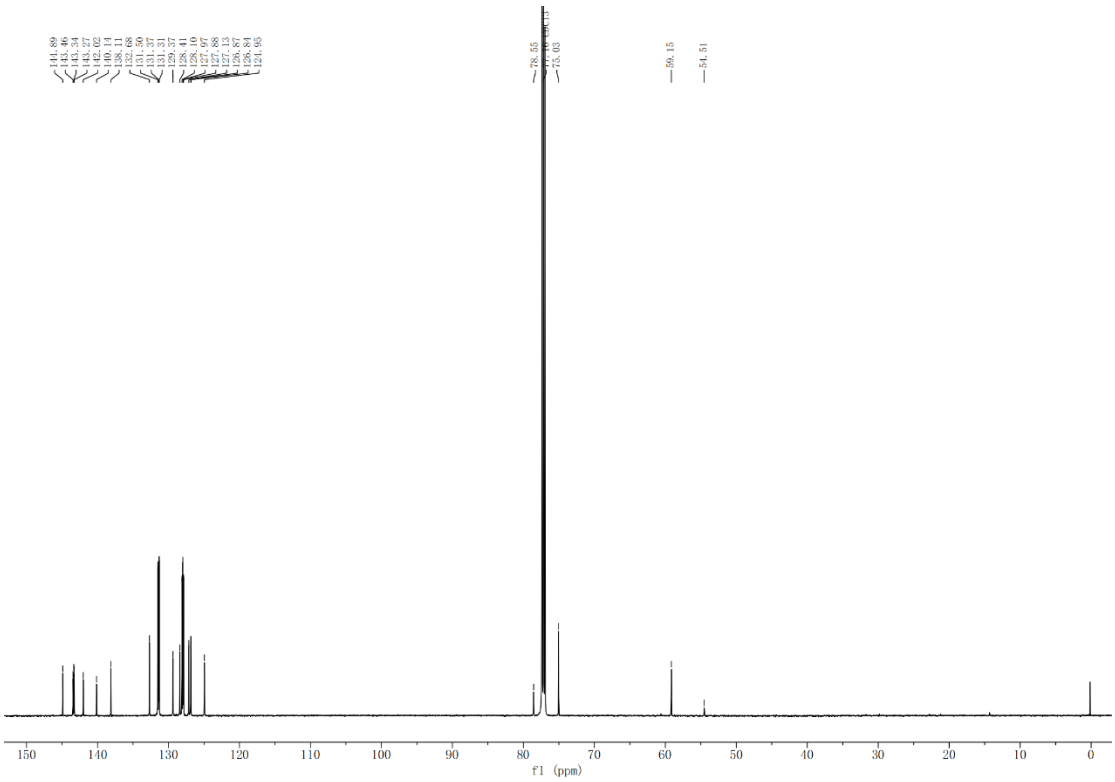


Fig. S14. ^{13}C-NMR spectrum of **3** in $CDCl_3$

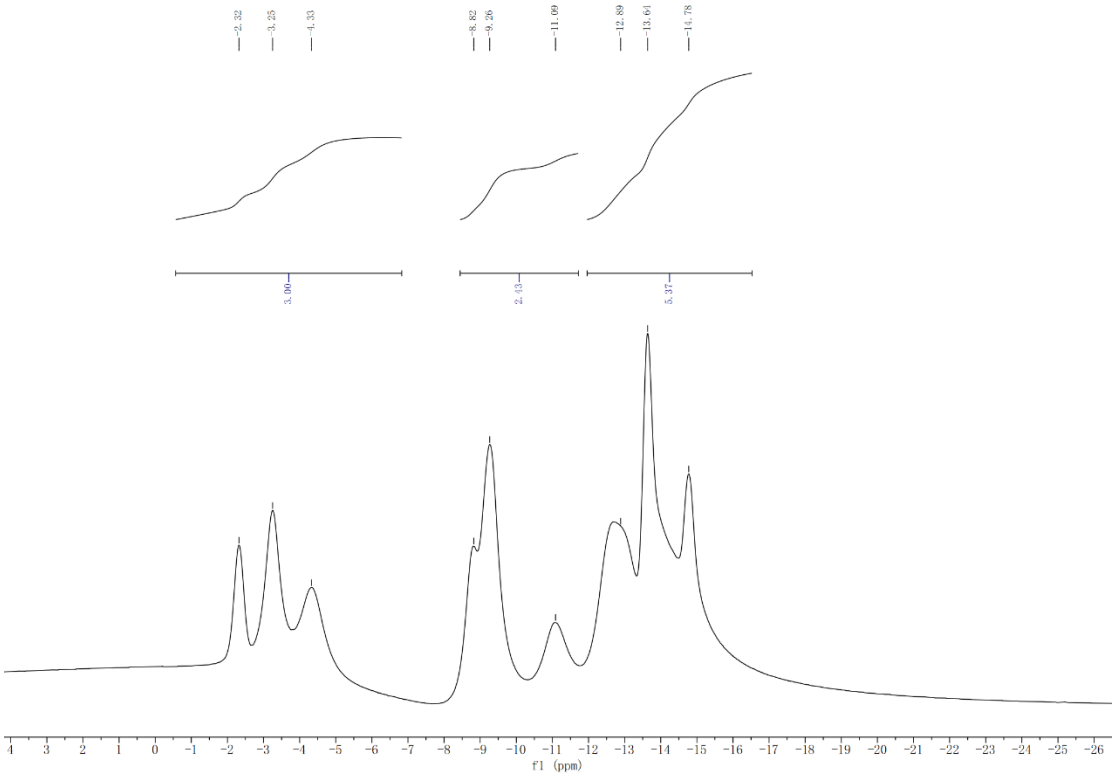


Fig. S15. ^{11}B{^{1}H}-NMR spectrum of **3** in $CDCl_3$

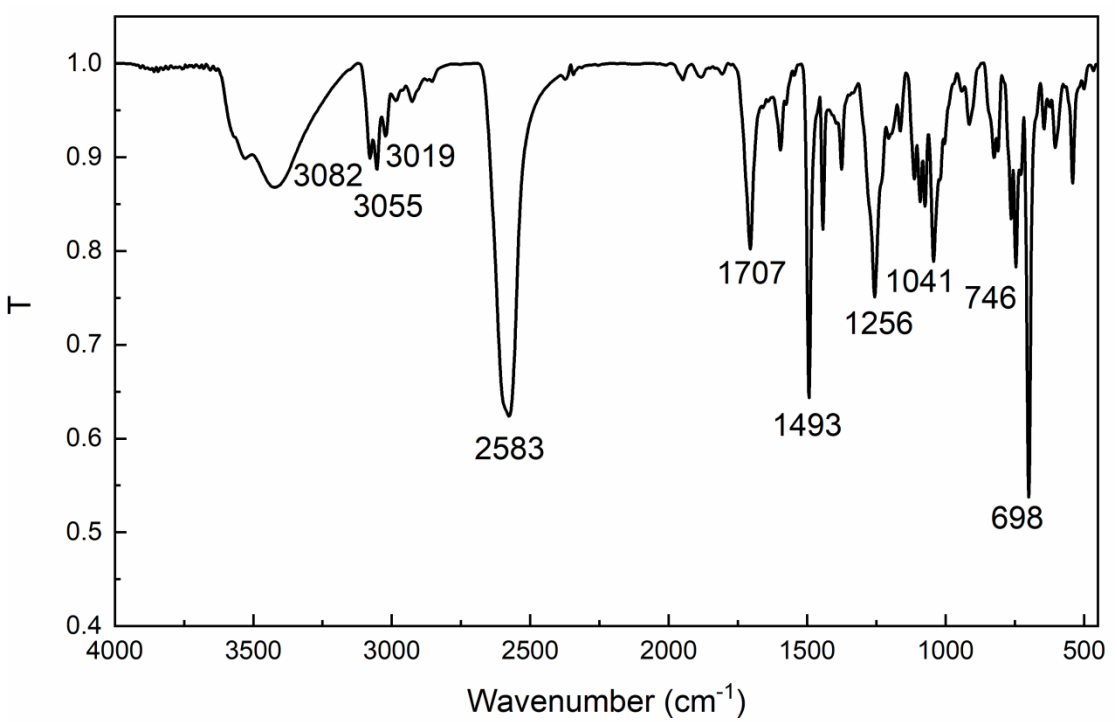


Fig. S16. FT-IR spectrum of **4** (KBr pellet)

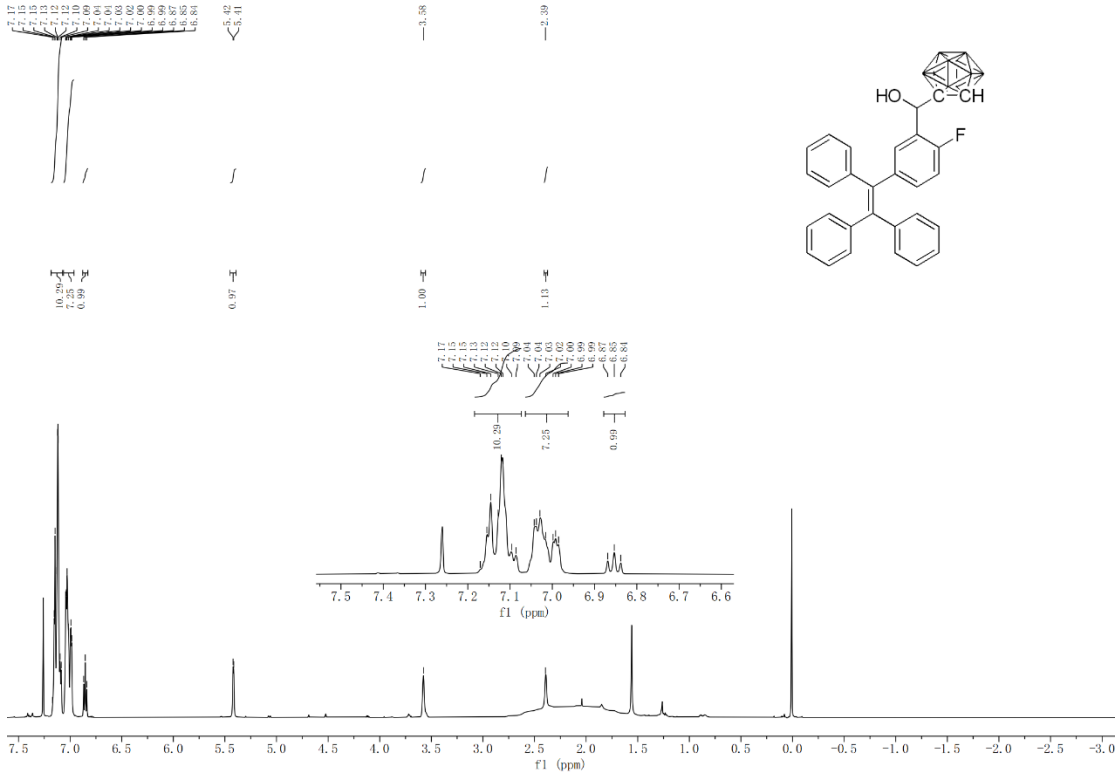


Fig. S17. ^{1}H-NMR spectrum of **4** in $CDCl_3$

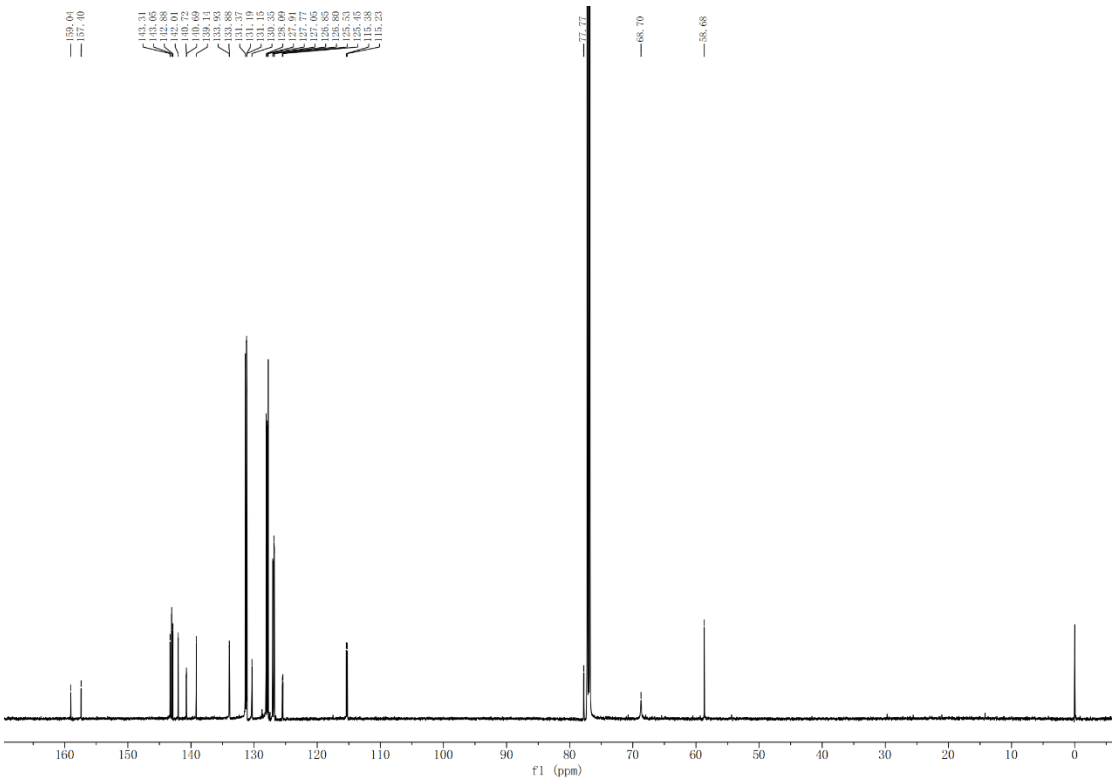


Fig. S18. ^{13}C-NMR spectrum of **4** in $CDCl_3$

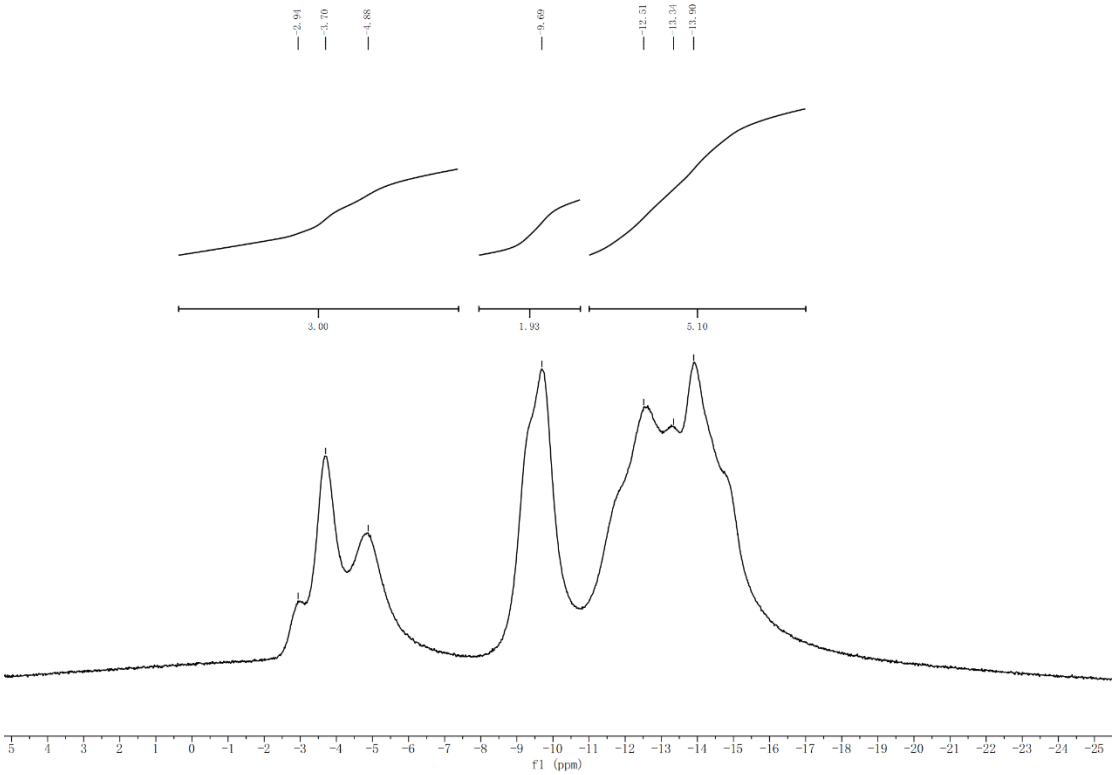


Fig. S19. ^{11}B{^{1}H}-NMR spectrum of **4** in CH_2Cl_2

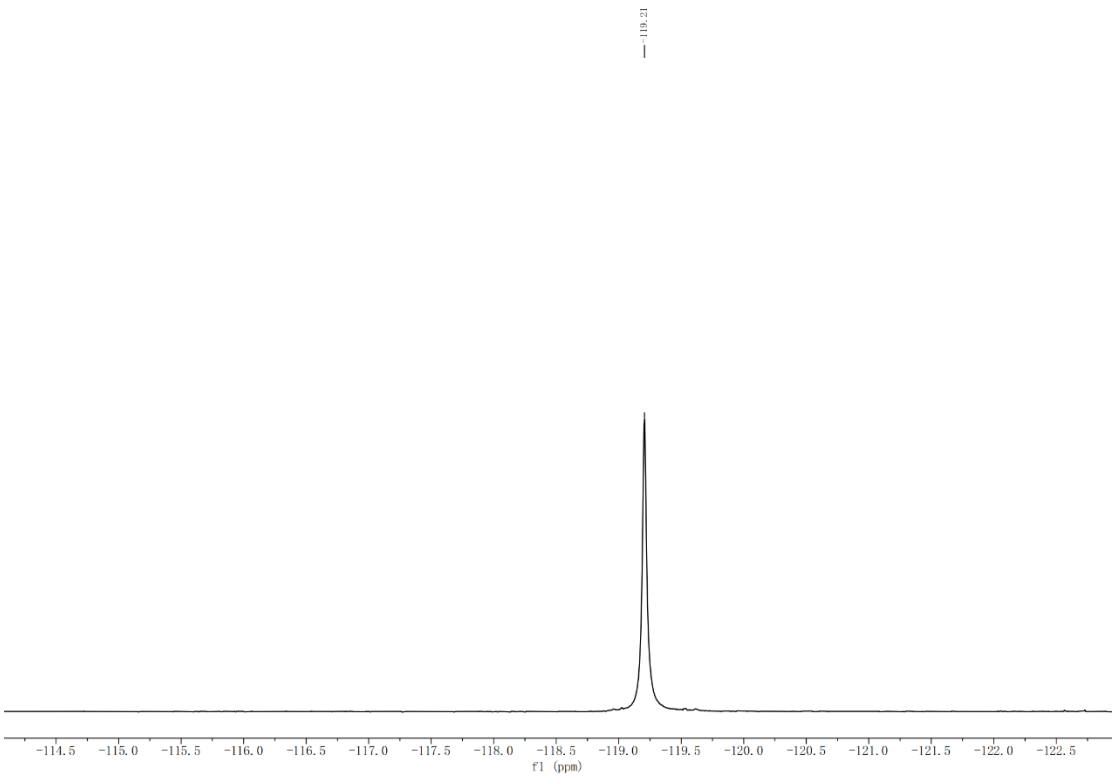


Fig. S20. ^{19}F-NMR spectrum of **4** in CH_2Cl_2