Electronic Supplementary Information for

Spiro-Fused Bis-Hexa-*peri*-hexabenzocoronene

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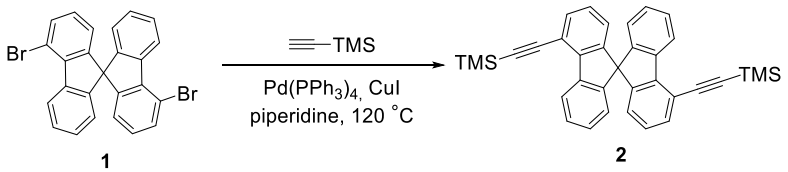
1. Experimental Section

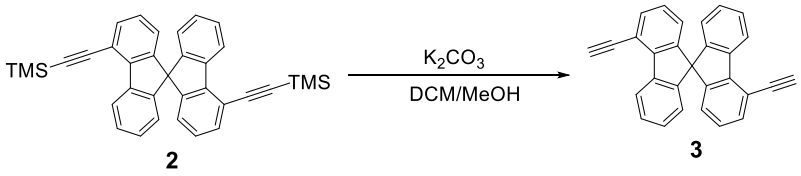
General Methods

Unless otherwise noted, the materials were purchased from Aldrich, Acros, and other commercial sources and used as received without further purification. Preparative column chromatography was performed on silica gel from Merck with a grain size of 0.063–0.200 mm (silica gel). NMR spectra were recorded in CD_2Cl_2 or $C_2D_2Cl_4$ on AVANCE 300 or 500 MHz Bruker spectrometers. Abbreviations: s = singlet, d = doublet, t = triplet. Mass spectrometry (MS) and High-resolution MS (HRMS) were performed on a SYNAPT G2 Si high resolution time-of-flight mass spectrometer (Waters Corp., Manchester, UK) by matrix-assisted laser desorption/ionization (MALDI) using 7,7,8,8-tetracyanoquinodimethane (TCNQ) as matrix. Absorption spectra were recorded on a Perkin-Elmer Lambda 900 spectrophotometer. Photoluminescence spectra were recorded on a J&MTIDAS spectrofluorometer. The quantum yield was measured using quinine sulfate (in 0.5 M H_2SO_4 solution under air, Φ_F: 0.546) as a reference.[1] Cyclic voltammetry (CV) was performed on a WaveDriver 20 Bipotentiostat/Galvanostat (Pine Instruments Company) and measurements were carried out in 1,1,2,2-tetrachloroethane containing 0.1 M *n*-Bu_4NPF_6 as supporting electrolyte (scan rate: 100 mV s^{-1}). A glassy carbon electrode was used as a working electrode, a platinum wire as a counter electrode, and a silver wire as a reference electrode.

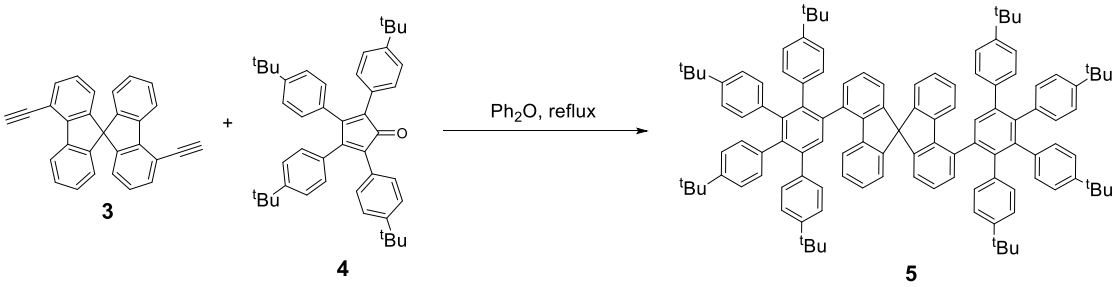
Synthesis



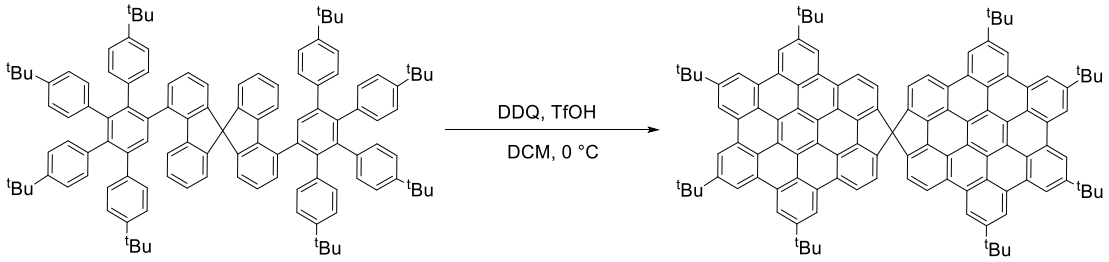
4,4'-bis[(trimethylsilyl)ethynyl]-9,9'-spirobifluorene (**2**): Under argon atmosphere, 4,4'-dibromo-9,9'-spirobifluorene[2] (**1**) (297 mg, 0.626 mmol), tetrakis(triphenylphosphine) palladium(0) ($Pd(PPh_3)_4$, 87.0 mg, 0.0752 mmol), copper (I) iodide (CuI, 14.3 mg, 0.0752 mmol), and trimethylsilylacetylene (0.740 mL, 5.24 mmol) were dissolved in 20 mL of degassed piperidine in a sealed tube. The resulting solution was heated to 120 °C and stirred overnight. Then, the solvent was evaporated under reduced pressure, and the crude product was purified by silica gel column chromatography using dichloromethane/hexane (1/5) as the eluent, affording the title compound as a white powder (273 mg, 86%). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K, ppm) δ 8.45 (dt, J = 7.7, 1.1 Hz, 2H), 7.27–7.18 (m, 4H), 6.96 (td, J = 7.5, 1.2 Hz, 2H), 6.86 (t, J = 7.6 Hz, 2H), 6.49–6.42 (m, 4H), 0.20 (s, 18H). ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K, ppm) δ 149.29, 148.99, 142.21, 141.73, 132.87, 128.78, 128.09, 127.71, 124.50, 123.88, 123.45, 117.01, 104.07, 100.08, 65.19, 0.00. HRMS (MALDI-TOF, positive) m/z: Calcd for $C_{35}H_{32}Si_2$: 508.2043; Found: 508.2036 (M^+)



4,4'-diethynyl-9,9'-spirobifluorene (**3**): Under arogon atmosphere, potassium carbonate (K_2CO_3, 109 mg, 0.786 mmol) was added to a solution of 4,4'-bis[(trimethylsilyl)ethynyl]-9,9'-spirobifluorene (**2**) (100 mg, 0.197 mmol) in 5.6 mL of dichloromethane/methanol (v/v = 1/1). The resulting suspension was stirred overnight at room temperature, and then filtered through a pad of silica gel. After evaporation of the solvents, the residue was subjected to silica gel column chromatography with dichloromethane/hexane (1/8) as the eluent, affording the title compound as a white powder (70.0 mg, 98%). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K, ppm) δ 8.55 (dt, J = 7.8, 1.0 Hz, 2H), 7.42 (dd, J = 7.7, 1.1 Hz, 2H), 7.33 (td, J = 7.6, 1.2 Hz, 2H), 7.09 (td, J = 7.5, 1.2 Hz, 2H), 7.00 (t, J = 7.7 Hz, 2H), 6.62–6.58 (m, 4H), 3.58 (s, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K, ppm) δ 149.32, 148.90, 142.47, 141.52, 133.40, 128.88, 128.27, 127.73, 124.81, 123.93, 123.39, 115.91, 82.60, 82.54, 65.21. HRMS (MALDI-TOF, positive) m/z: Calcd for $C_{29}H_{16}$: 364.1252; Found: 364.1218 (M^+).



4-{4,4''-di-*tert*-butyl-3',6'-bis(4-*tert*-butylphenyl)-[1,1':2',1''-terphenyl]-4'-yl}-4'-{4,4''-di-*tert*-butyl-5',6'-bis(4-*tert*-butylphenyl)-[1,1':2',1''-terphenyl]-3'-yl}-9,9'-spirobifluorene (**5**): Under arogon atmosphere, 4,4'-diethynyl-9,9'-spirobifluorene (**3**) (34.5 mg, 0.0946 mmol) and **4** (121 mg, 0.199 mmol) were dissolved in 2 mL of diphenyl ether (Ph_2O) and the resulting solution was refluxed for 20 h. After cooling to room temperature, methanol was added to the reaction mixture. The precipitate was collected by filtration and subjected to silica gel column chromatography with dichloromethane/hexane (1/4) as the eluent, affording the title compound as a white solid (118 mg, 82%). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K, ppm) δ 7.66–7.63 (m, 2H), 7.37–6.64 (m, 43H), 6.56 (dt, J = 7.6, 1.4 Hz, 1H), 6.13 (t, J = 7.2 Hz, 1H) 6.09–6.00 (m, 1H), 1.29–1.30 (m, 18H), 1.24 (s, 18H), 1.19–1.02 (m, 36H). ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K, ppm) δ 149.86, 149.82, 149.54, 149.45, 149.33, 149.25, 148.91, 148.62, 148.60, 148.41, 142.97, 142.95, 142.76, 142.73, 142.40, 142.39, 141.09, 141.07, 140.57, 140.57, 140.55, 140.52, 140.34, 140.33, 140.09, 139.77, 139.73, 139.60, 139.57, 139.57, 139.52, 139.44, 139.42, 138.04, 137.90, 137.67, 137.45, 131.72, 131.60, 131.56, 131.34, 130.59, 130.40, 129.97, 127.70, 127.68, 127.61, 127.55, 126.98, 126.96, 124.77, 124.00, 123.87, 123.58, 123.43, 122.44, 122.14, 122.07, 65.49, 34.61, 34.51, 34.37, 31.41, 31.38, 31.35, 31.32. HRMS (MALDI-TOF, positive) m/z: Calcd for $C_{117}H_{120}$: 1524.9390; Found: 1524.9332 (M^+).



5,5',8,8',11,11',14,14'-octa-*tert*-butyl-1,1'-spirobi(tetrabenzo[*ef,hi,kl,no*]fluoreno[3,4,5,6-*qrabc*]coronene) (**SB-HBC**): Under arogon atmosphere, precursor **5** (80.0 mg, 0.0524 mmol) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ, 157 mg, 0.692 mmol) were dissolved in 16 mL of dry dichloromethane. After cooled to 0 °C, to the solution was added dropwise triflic acid (TfOH, 0.16 mL) and stirred for 1 hour. Then, trimethylamine was added to quench the reaction, followed by the addition of methanol. The resulting precipitate was collected by filtration and subjected to silica gel column chromatography with chloroform as the eluent, affording the title compound as a yellow solid (56.0 mg, 71%). ^{1}H NMR (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 393 K, ppm) δ 9.46 (s, 8H), 9.44 (s, 4H), 9.28 (s, 4H), 8.98 (d, J = 8.1 Hz, 4H), 7.76 (d, J = 7.9 Hz, 4H), 1.93 (s, 36H), 1.85 (s, 36H). ^{13}C NMR (125 MHz, 1,1,2,2-tetrachloroethane-d_2, 393 K, ppm) δ 150.20, 149.83, 144.38, 138.21, 131.82, 131.40, 131.02, 130.86, 129.96, 125.40, 124.46, 122.82, 122.52, 121.89, 121.20, 120.71, 120.48, 119.78, 119.60, 119.45, 119.36, 75.59, 35.89, 35.82, 32.13, 32.05. HR-MS (MALDI-TOF, positive) m/z: Calcd for $C_{117}H_{96}$: 1500.7512; Found: 1500.7416 (M^+).

2. X-ray Crystallography

The single crystal suitable for X-ray analysis were obtained by diffusing pentane vapor into a solution of **SB-HBC** in tetrahydrofuran. The structures were deposited at The Cambridge Crystallographic Data Centre and the data can be obtained free of charge via www.ccdc.cam.ac.uk/structures.

Crystal data for **SB-HBC** (CCDC number: 1848515)

formula	$C_{117}H_{96}$, x(C_5H_{12})		
molecular weight	1715.34 gmol^{-1}		
absorption	μ = 0.058 mm^{-1}		
crystal size	0.02 x 0.02 x 0.23 mm^3 brown needle		
space group	I 2/a (monoclinic)		
lattice parameters	a = 20.9930(13)Å		
(calculate from	b = 17.0469(8)Å	ß = 90.228(5)°	
9461 reflections with	c = 30.788(2)Å		
2.8° < θ < 61.7°)	V = 11017.9(11)Å^3	z = 4	F(000) = 3686
temperature	-80°C		
density	d_{xray} = 1.034 gcm^{-3}		

data collection

diffractometer	STOE IPDS 2T
radiation	Cu-K_α IμS mirror system
Scan – type	ω scans
Scan – width	1°
scan range	2° ≤ θ < 68°
	-14 ≤ h ≤ 25 -20 ≤ k ≤ 14 -35 ≤ l ≤ 36
number of reflections:	
measured	36069
unique	9886 (R_{int} = 0.2039)
observed	3083 (|F|/σ(F) > 4.0)

data correction, structure solution and refinement

corrections	Lorentz and polarisation correction.
Structure solution	Program: SHELXT-2014
refinement	Program: SHELXL-2016 (full matrix). 604 refined parameters, weighting scheme: $w=1/[\sigma^2(F_o^2) + (0.2*P)^2]$ with $(Max(F_o^2,0)+2*F_c^2)/3$. H-atoms at calculated positions and refined with isotropic displacement parameters, non H- atoms refined anisotropically. Solvent molecules isotropic refined.
R-values	wR2 = 0.6109 (R1 = 0.2358 for observed reflections, 0.3471 for all reflections)
goodness of fit	S = 1.508
maximum deviation	
of parameters	0.001 * e.s.d
maximum peak height in diff. Fourier synthesis	1.09, -0.50 eÅ^{-3}
remark	crystal containes big amount of pentane, which is located in at least two channels, main molecule exhibit C_2 symmetry

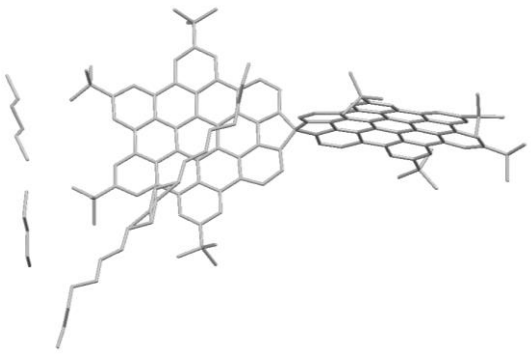


Figure S1. Crystal structure of **SB-HBC** with hydrogen atoms removed for clarity (crystal structure contains several highly disordered pentane molecules which are spread over different positions in the unit cell).

3. DFT Calculations

DFT calculations were performed using the Gaussian 09 software package.[3] The geometry and frontier molecular orbitals were calculated at the B3LYP/6-31G level. The UV-vis absorption spectra were simulated by time-dependent DFT (TD-DFT) calculations at the same level of theory.

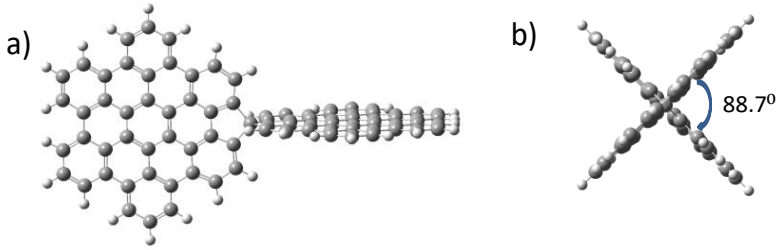


Figure S2. Topview (a) and sideview (b) of the optimized structure of **SB-HBC** model compound without *tert*-butyl groups.

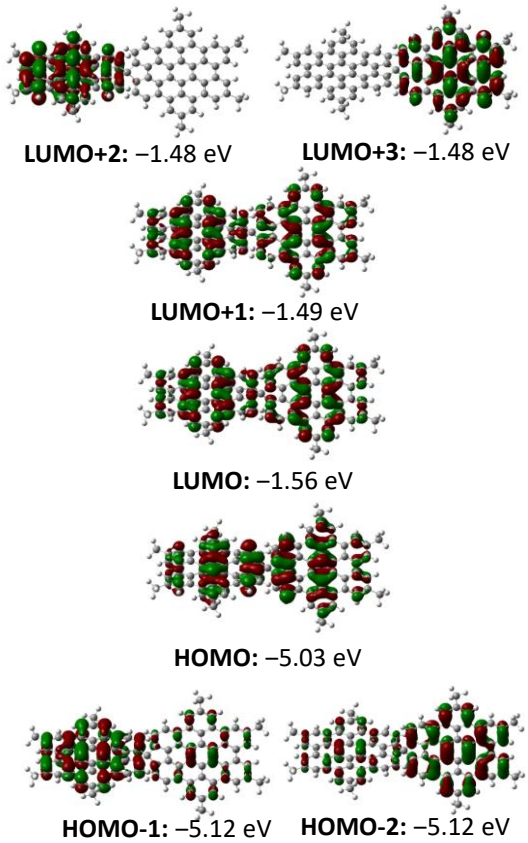


Figure S3. Energies and shapes of frontier molecular orbitals of **SB-HBC** model compound.

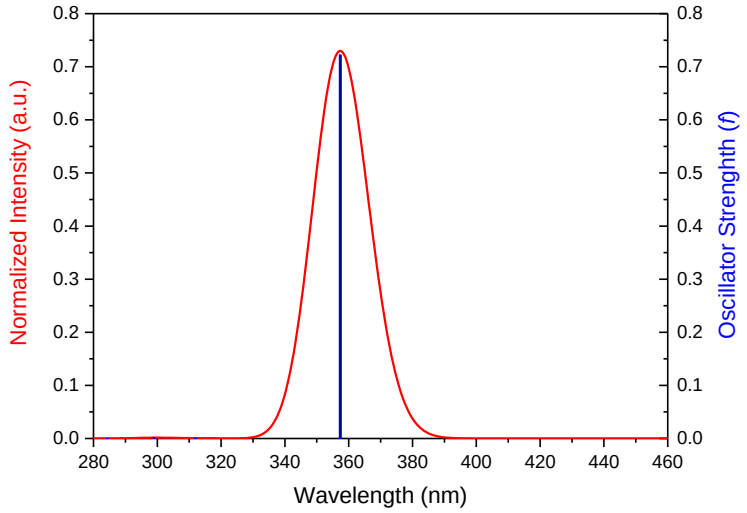


Figure S4. Simulated UV-Vis spectrum of unsubsituted HBC.

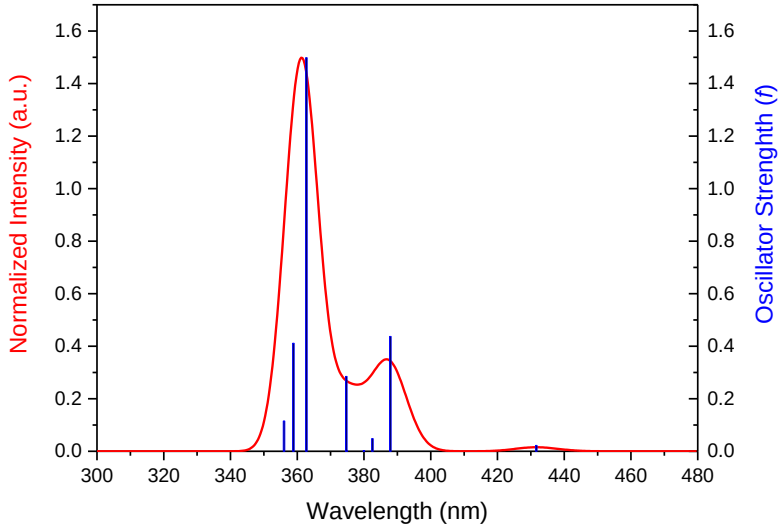


Figure S5. Simulated UV-Vis spectrum of unsubsituted **SB-HBC**.

Table S1. Major transitions of HBC calculated by TDDFT.

excited state	energy (eV)	wavelength (nm)	oscillator strength (*f*)	Description (H:HOMO, L:LUMO)
1	2.8889	429.17	0	H-1→L (0.49705) H→L+1 (0.49702)
2	3.0241	409.99	0	H-1→L+1 (-0.49737) H→L (0.49899)
3	3.2808	377.91	0	H-2→L (0.29354) H→L+2 (0.63491)

4	3.2815	377.82	0	H-2→L+1 (-0.29349) H-1→L+2 (0.63492)
5	3.4697	357.34	0.7219	H-1→L (-0.36775) H-1→L+1 (-0.32324) H→L (-0.32217) H→L+1 (0.36777)
6	3.4697	357.33	0.7223	H-1→L (-0.32271) H-1→L+1 (0.36838) H→L (0.36716) H→L+1 (0.32273)
7	3.6145	343.02	0	H-2→L (0.63018) H→L+2 (-0.29122)
8	3.6152	342.95	0	H-2→L+1 (0.63018) H-1→L+2 (0.29118)
9	3.8147	325.02	0	H-2→L+2 (0.69516)
10	3.9745	311.95	0.0005	H-3→L (0.13422) H→L+3 (0.67581)

Table S2. Major transitions of **SB-HBC** calculated by TDDFT.

excited state	energy (eV)	wavelength (nm)	oscillator strength (*f*)	Description (H:HOMO, L:LUMO)
1	2.8725	431.63	0.0225	H-3→L+1 (0.28120) H-2→L+3 (0.31170) H-1→L+2 (0.31172) H→L (0.46530)
2	2.8847	429.81	0	H-3→L (0.34494) H-2→L+2 (0.33235) H-1→L+3 (0.33233) H→L+1 (0.38658)
3	3.0047	412.63	0	H-3→L+3 (0.26971) H-2→L+1 (-0.28282) H-1→L (-0.36868) H→L+2 (0.43525)
4	3.0048	412.63	0	H-3→L+2 (0.26973) H-2→L (-0.36867) H-1→L+1 (-0.28283) H→L+3 (0.43523)
5	3.1962	387.91	0.4374	H-4→L (0.20165) H-3→L+1 (-0.30186) H-2→L+3 (-0.22073) H-2→L+5 (0.11446) H-1→L+2 (-0.22075) H-1→L+4 (-0.11447) H→L (0.48703)

6	3.2314	383.68	0	H-4→L+1 (0.17356) H-3→L (-0.39417) H-2→L+4 (-0.17633) H-1→L+5 (0.17633) H→L+1 (0.48332)
7	3.2413	382.51	0.0482	H-4→L+3 (0.18417) H-3→L+2 (-0.31361) H-3→L+4 (0.24171) H-2→L (0.23662) H-1→L+1 (0.10245) H→L+3 (0.46473)
8	3.2413	382.51	0.0482	H-4→L+2 (0.18417) H-3→L+3 (-0.31360) H-3→L+5 (-0.24168) H-2→L+1 (0.10243) H-1→L (0.23665) H→L+2 (0.46477)
9	3.2633	379.94	0.0027	H-5→L+3 (-0.13003) H-3→L+3 (0.13287) H-3→L+5 (-0.20557) H→L+4 (0.62446)
10	3.2633	379.94	0.0027	H-5→L+2 (0.13004) H-3→L+2 (-0.13292) H-3→L+4 (-0.20555) H→L+5 (0.62445)

The cartesian coordinates of all the optimized structures are listed as follows:

HBC

	X	Y	Z		X	Y	Z
C	2.1068742	4.6837226	0.0036168	C	3.0030004	-4.1664648	-0.0010357
C	1.8750303	3.3002449	0.0014782	C	1.9207723	-3.2739068	0.0001899
C	0.5329647	2.8210113	0.0009950	C	-2.9827839	-2.3475317	-0.0004081
C	-0.5417495	3.7567775	0.0017203	C	-4.3160636	-2.7837500	-0.0022750
C	-0.2528631	5.1294634	0.0036970	C	-5.3675305	-1.8798464	-0.0038520
C	1.0557484	5.5880280	0.0047952	C	-5.1100132	-0.5174192	-0.0035008
C	0.2643610	1.3990267	0.0001749	C	-3.7958831	-0.0263887	-0.0019387
C	1.3438575	0.4705809	-0.0001109	C	-3.5245330	1.4092547	-0.0014733
C	1.0795219	-0.9284210	-0.0000604	C	-4.5688658	2.3458502	-0.0019862
C	-0.2643615	-1.3990245	0.0001672	C	-4.3117430	3.7083571	-0.0014541
C	-1.3438557	-0.4705803	-0.0001095	C	-3.0030022	4.1664646	-0.0002755
C	-1.0795209	0.9284223	-0.0000737	C	-1.9207726	3.2739076	0.0003978
C	-0.5329636	-2.8210109	0.0011027	H	3.1178410	5.0696349	0.0046767
C	0.5417489	-3.7567761	0.0019297	H	-1.0531856	5.8578101	0.0046502
C	0.2528627	-5.1294624	0.0044504	H	1.2573673	6.6549681	0.0065972
C	-1.0557479	-5.5880255	0.0058471	H	1.0531860	-5.8578079	0.0057337
C	-2.1068752	-4.6837209	0.0043439	H	-1.2573671	-6.6549648	0.0081410
C	-1.8750301	-3.3002448	0.0016803	H	-3.1178425	-5.0696328	0.0056945
C	2.7098096	0.9489737	-0.0005997	H	4.5466570	3.8409924	-0.0018666
C	2.1767253	-1.8721277	-0.0004457	H	6.3923224	2.2387369	-0.0038449
C	-2.7098107	-0.9489744	-0.0007181	H	5.9499358	-0.1648681	-0.0035898
C	-2.1767254	1.8721287	-0.0003444	H	5.5996783	-2.0168277	-0.0038165
C	2.9827845	2.3475307	-0.0002034	H	5.1348548	-4.4165120	-0.0035252

C	4.3160653	2.7837472	-0.0015558	H	2.8320845	-5.2350191	-0.0011092
C	5.3675328	1.8798433	-0.0028095	H	-4.5466529	-3.8409958	-0.0028590
C	5.1100133	0.5174165	-0.0027480	H	-6.3923193	-2.2387412	-0.0053712
C	3.7958829	0.0263860	-0.0017195	H	-5.9499361	0.1648644	-0.0046495
C	3.5245328	-1.4092535	-0.0016685	H	-5.5996792	2.0168263	-0.0027965
C	4.5688649	-2.3458507	-0.0027179	H	-5.1348575	4.4165118	-0.0019614
C	4.3117410	-3.7083568	-0.0025157	H	-2.8320879	5.2350190	-0.0000185

SB-HBC

	X	Y	Z		X	Y	Z
C	7.1292660	-0.5046387	0.5047348	C	-7.1292488	-0.5048440	-0.5046801
C	7.1292500	0.5047184	-0.5048021	C	-5.9019887	-1.0122849	-1.0119207
C	5.9019912	1.0120097	-1.0121956	C	-5.8596913	-2.0370157	-2.0362614
C	4.6905268	0.5034755	-0.5036123	C	-5.8597695	2.0368110	2.0363600
C	4.6905426	-0.5034305	0.5035917	C	-8.3727748	1.0198450	1.0192775
C	5.9020237	-1.0119192	1.0121786	C	-8.3727367	-1.0198398	-1.0194837
C	5.8597644	-2.0362753	2.0368960	C	-4.6100405	2.5417321	2.5413298
C	8.3727721	-1.0196358	1.0194934	C	-4.6314968	3.5310549	3.5308801
C	8.3727392	1.0196251	-1.0196916	C	-5.8340334	4.0238391	4.0239603
C	5.8596964	2.0364776	-2.0367993	C	-7.0423993	3.5400360	3.5400030
C	3.4526340	1.0183381	-1.0186743	C	-7.0867434	2.5474075	2.5468967
C	3.4526662	-1.0183035	1.0186841	C	-8.3617039	2.0303296	2.0292705
C	8.3616985	-2.0299285	2.0296782	C	-9.5895385	2.5096947	2.5075007
C	9.5895318	-2.5092650	2.5079406	C	-10.7935008	2.0202224	2.0176092
C	10.7934954	-2.0199254	2.0179197	C	-10.8053880	1.0383956	1.0365658
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C	9.6099347	0.5186194	-0.5186978	C	-10.8053497	-1.0379711	-1.0372827
C	10.8053523	1.0378308	-1.0374100	C	-10.7934255	-2.0196857	-2.0184378
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C	8.3616319	2.0299227	-2.0298713	C	-7.0866463	-2.5477250	-2.5467327
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C	5.8338910	4.0237253	-4.0241797	C	-4.6313634	-3.5316611	-3.5303331
C	4.6313725	3.5306888	-3.5313083	C	-4.6099422	-2.5420351	-2.5410860
C	4.6099487	2.5412939	-2.5418301	H	9.6192706	-3.2747349	3.2728515
C	3.3496797	2.0121208	-2.0127125	H	11.7308879	-2.4079409	2.4049884
C	2.0412383	2.3957623	-2.3965404	H	11.7617168	-0.6797698	0.6775649
C	0.8701719	1.8400063	-1.8406437	H	11.7616959	0.6791992	-0.6784334
C	0.9835770	0.8556343	-0.8559577	H	11.7308106	2.4071340	-2.4060911
C	2.2750961	0.4983323	-0.4985630	H	9.6191662	3.2741709	-3.2736418
C	2.2751098	-0.4983642	0.4985467	H	7.9580699	3.9483759	-3.9484492
C	0.9836023	-0.8556118	0.8560343	H	5.8300623	4.7915291	-4.7920316
C	0.8702365	-1.8398969	1.8408138	H	3.6987544	3.9216682	-3.9224702
C	2.0413201	-2.3955946	2.3967293	H	1.9129567	3.1574730	-3.1585179
C	3.3497491	-2.0119716	2.0128395	H	-0.0961588	2.1905065	-2.1912698
C	4.6100341	-2.5409907	2.5420682	H	-0.0960815	-2.1903397	2.1915321
C	4.6314880	-3.5300864	3.5318454	H	1.9130619	-3.1572470	3.1587703
C	5.8340234	-4.0228626	4.0249366	H	3.6988812	-3.9209768	3.9231252
C	7.0423906	-3.5392556	3.5407865	H	5.8302198	-4.7903370	4.7931176
C	7.0867370	-2.5468385	2.5474689	H	7.9582022	-3.9473311	3.9493144
C	-0.0000005	0.0000072	0.0000610	H	-1.9129480	-3.1586800	-3.1573009
C	-0.9835748	-0.8559709	-0.8556084	H	0.0961644	-2.1914333	-2.1903281
C	-0.9836043	0.8559724	0.8556860	H	0.0960761	2.1913046	2.1905827
C	-2.2750951	-0.4985146	-0.4983725	H	-1.9130696	3.1584782	3.1575491
C	-3.4526315	-1.0186783	-1.0183286	H	-3.6988908	3.9221078	3.9219996

C	-3.3496746	-2.0127979	-2.0120295	H	-5.8302318	4.7914784	4.7919765
C	-2.0412320	-2.3966604	-2.3956327	H	-7.9582120	3.9481277	3.9485123
C	-0.8701670	-1.8407473	-1.8398900	H	-9.6192796	3.2752907	3.2722852
C	-0.8702409	1.8406653	1.8400581	H	-11.7308945	2.4082681	2.4046448
C	-2.0413260	2.3965115	2.3958221	H	-11.7617186	0.6797853	0.6775332
C	-3.3497541	2.0126542	2.0121633	H	-11.7616943	-0.6792249	-0.6784230
C	-3.4526686	1.0186422	1.0183515	H	-11.7308047	-2.4074716	-2.4057686
C	-2.2751109	0.4985503	0.4983694	H	-9.6191582	-3.2747354	-3.2730870
C	-4.6905256	-0.5036284	-0.5034566	H	-7.9580597	-3.9491843	-3.9476464
C	-4.6905438	0.5035785	0.5034465	H	-5.8300498	-4.7926824	-4.7908784
C	-5.9020263	1.0121908	1.0119067	H	-3.6987441	-3.9228042	-3.9213285
C	-7.1292674	0.5047600	0.5046100				

4. Excitation Spectra

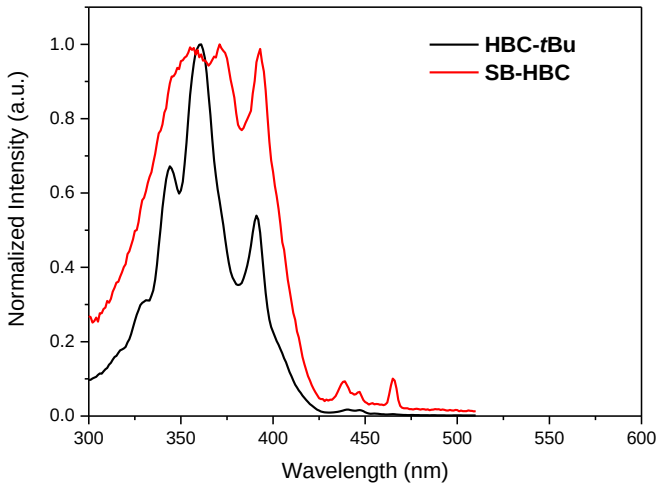

Figure S6. Excitation spectra of the diluted solution of **HBC-*t*Bu** and **SB-HBC** in dichloromethane.

5. Absorption Spectral Changes Upon Oxidation.

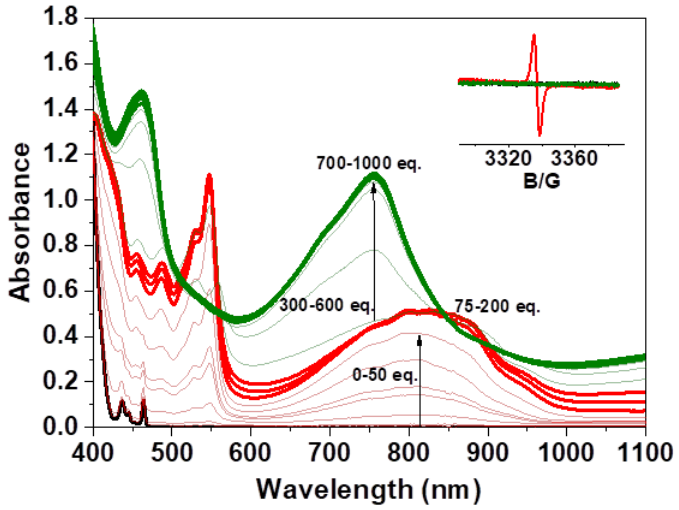

Figure S7. Spectral changes upon the oxidation of **SB-HBC** (2.0×10^{-5} mol L^{-1} in dichloromethane) by incremental addition of $SbCl_5$ (1.0 mol L^{-1} in dichloromethane). Inset: EPR curves of **SB-HBC** in dichloromethane before (black line) and after the addition of 50 (red line) and 1000 eq. (green line) of $SbCl_5$.

6. EPR Measurements

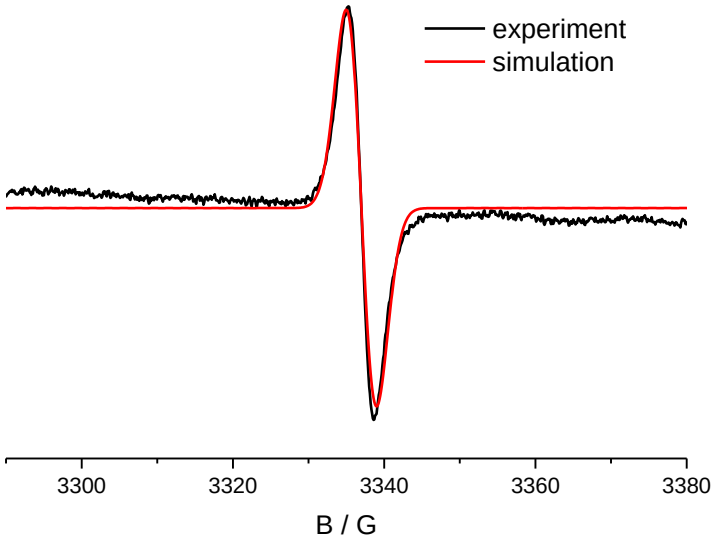

Figure S8. Experimental and simulated EPR spectra of **SB-HBC** radical cation.

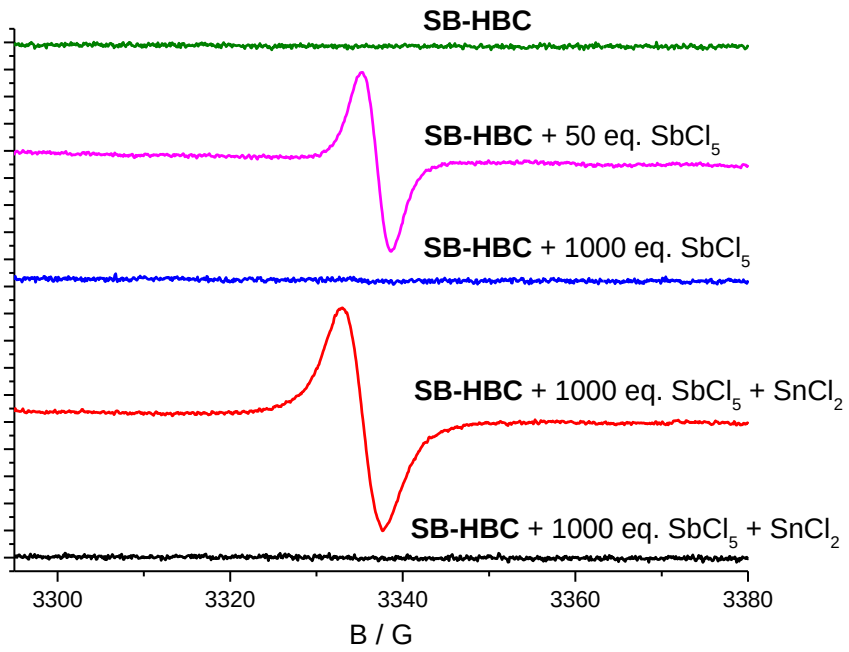

Figure S9. EPR spectra of **SB-HBC** in dichloromethane upon oxidation with $SbCl_5$ and then reduction with a large excess of $SnCl_2$ at room temperature.

7. NMR and MS spectra

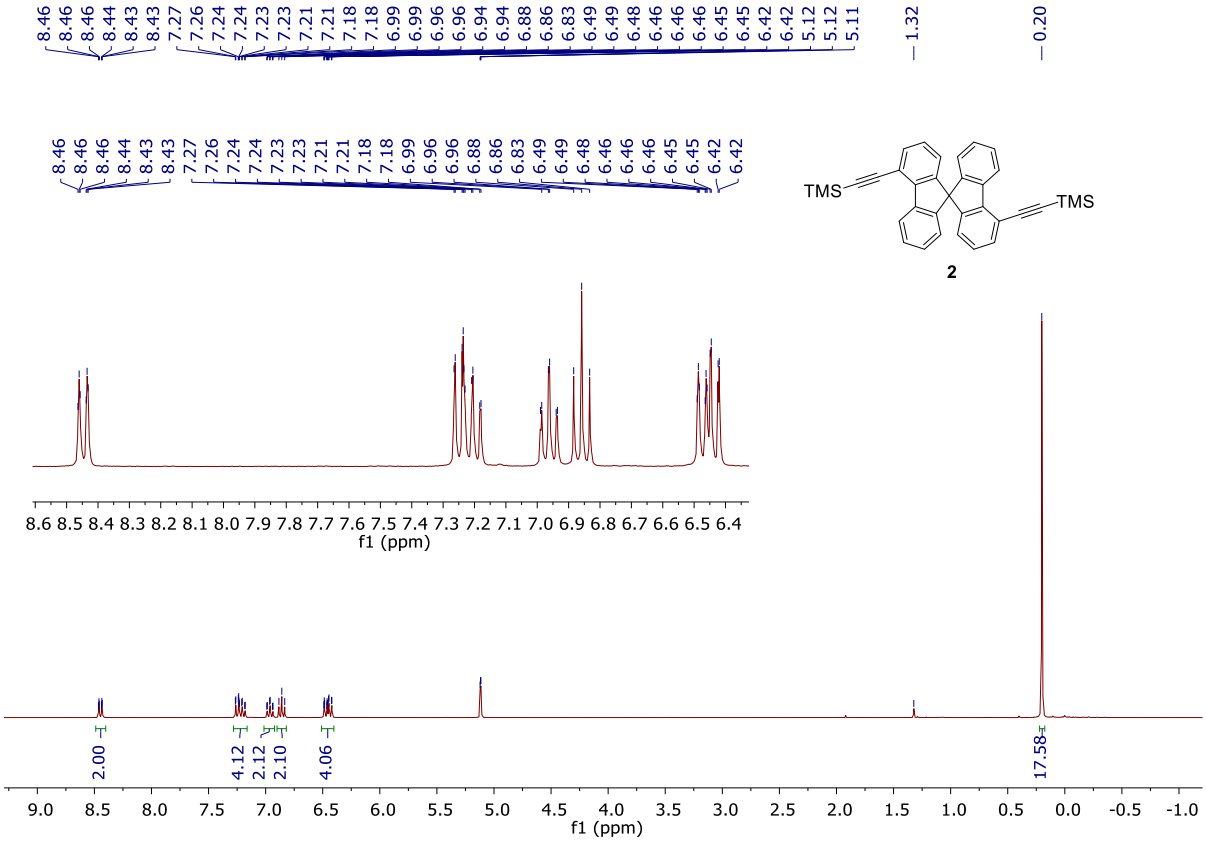

Figure S10. ^{1}H NMR spectrum of **2** (300 MHz, 298 K, CD_2Cl_2).

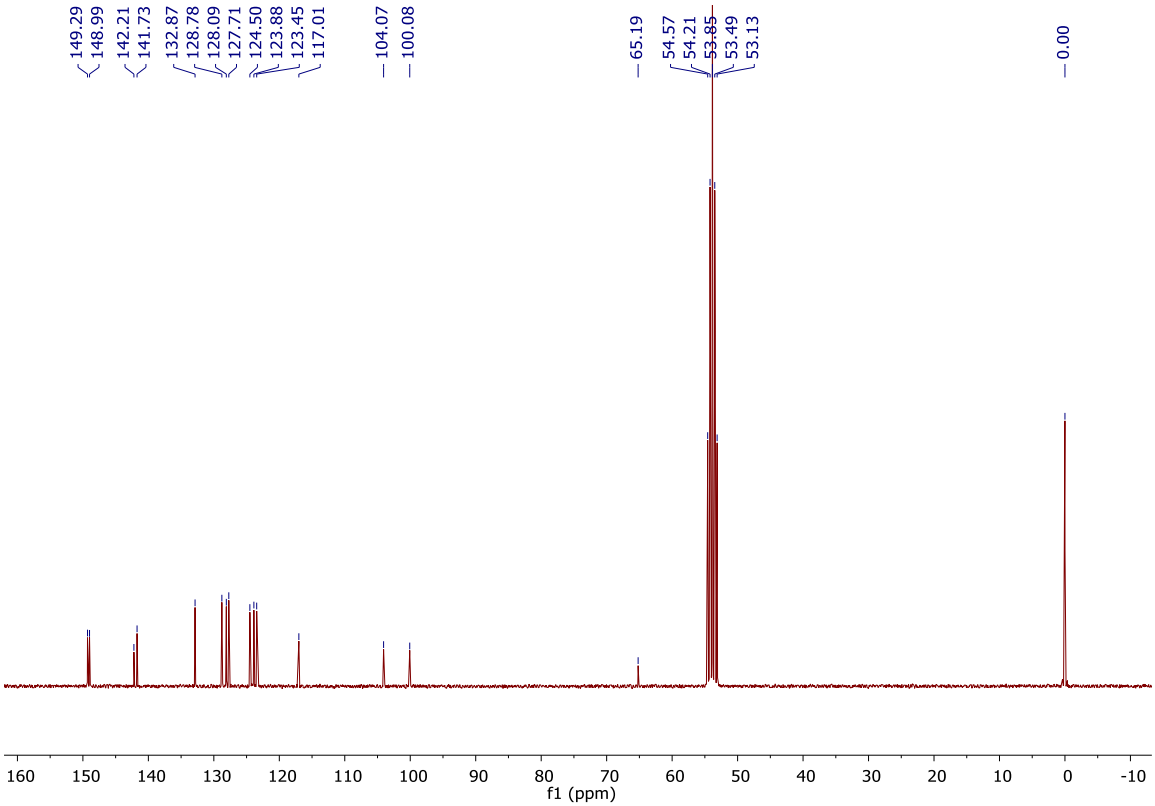

Figure S11. ^{13}C NMR spectrum of **2** (75 MHz, 298 K, CD_2Cl_2).

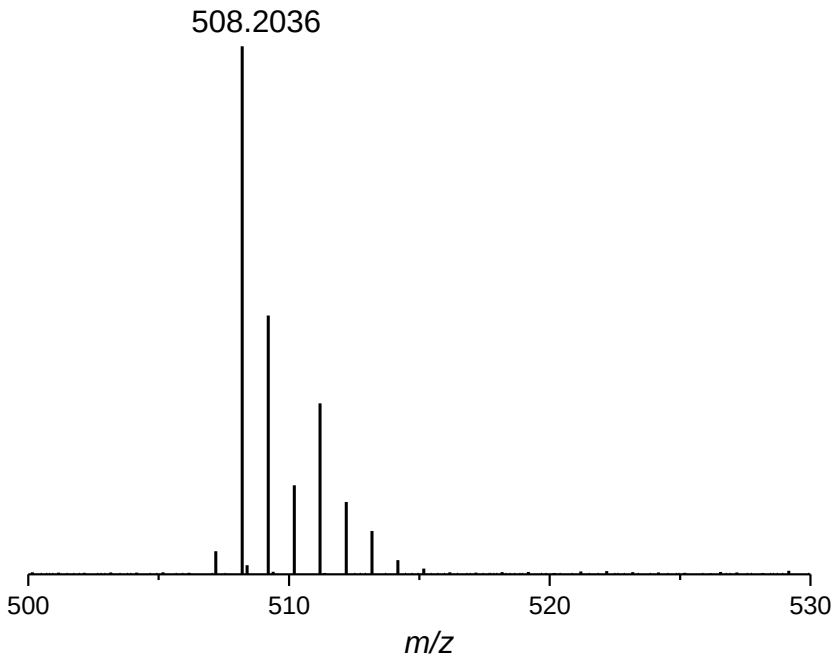

Figure S12. HRMS (MALDI-TOF) spectrum of **2** (matrix:TCNQ).

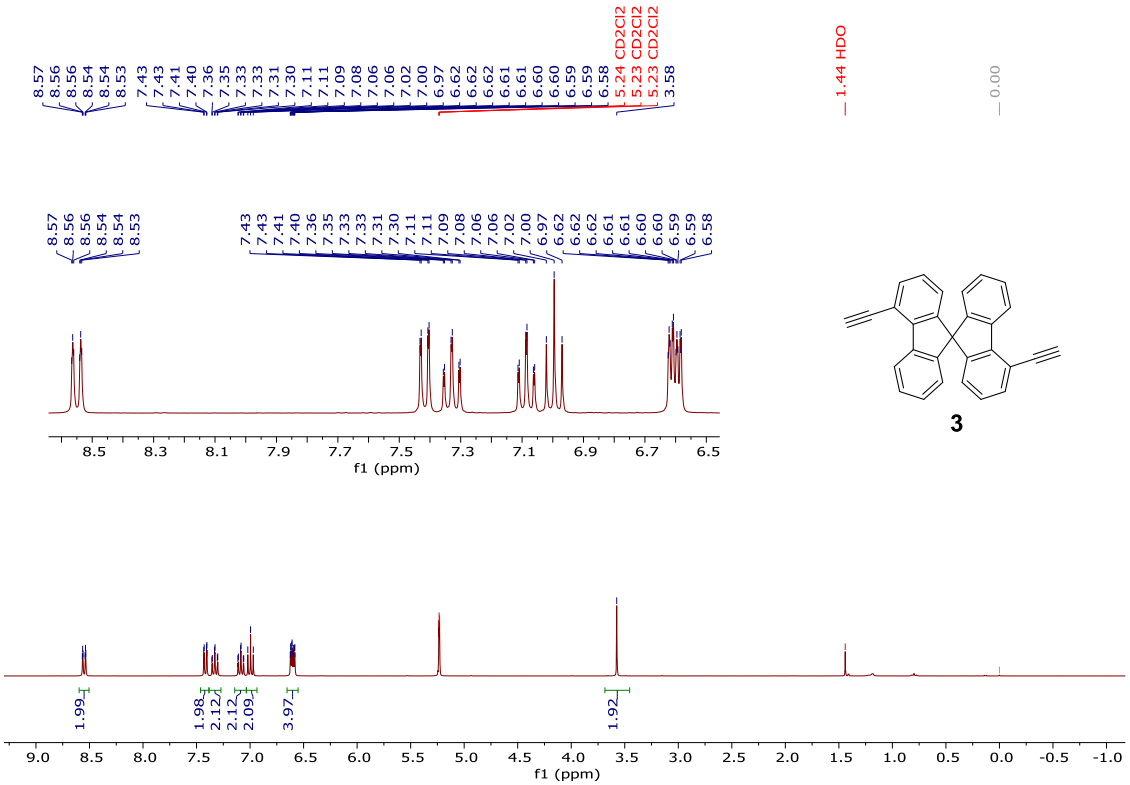

Figure S13.[1]H NMR spectrum of **3** (300 MHz, 298 K, CD_2Cl_2).

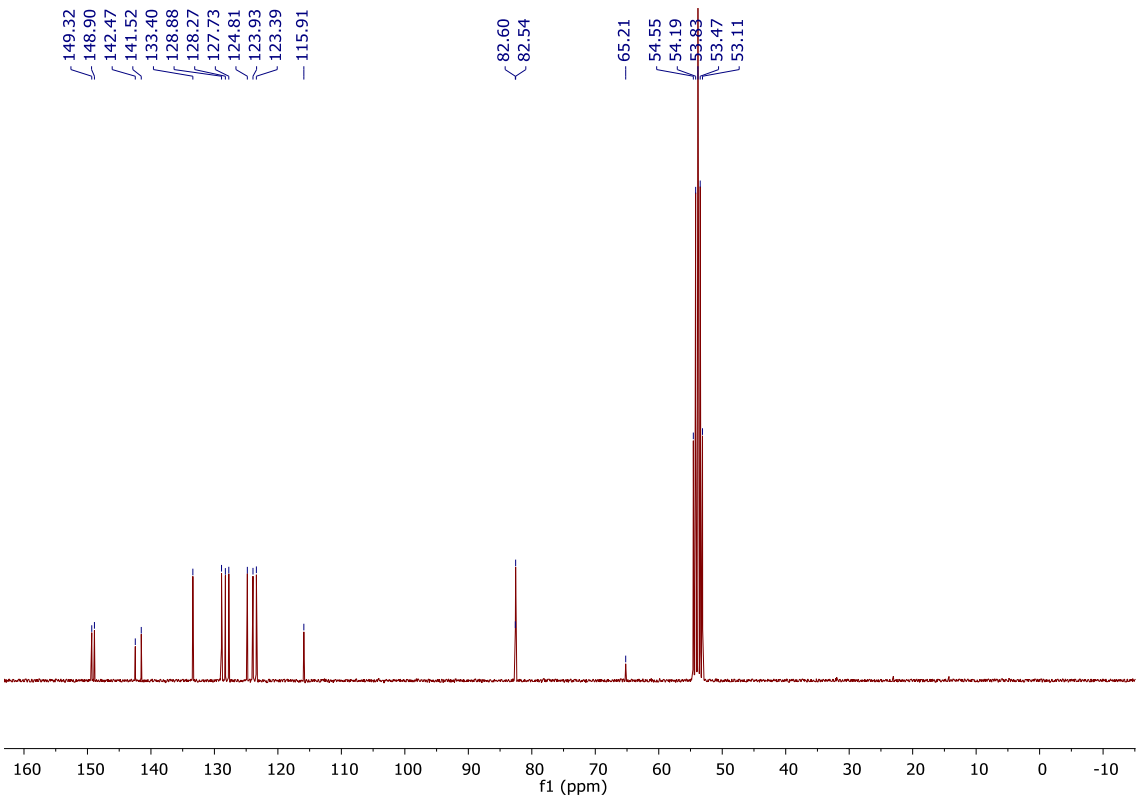

Figure S14. [13]C NMR spectrum of **3** (75 MHz, 298 K, CD_2Cl_2).

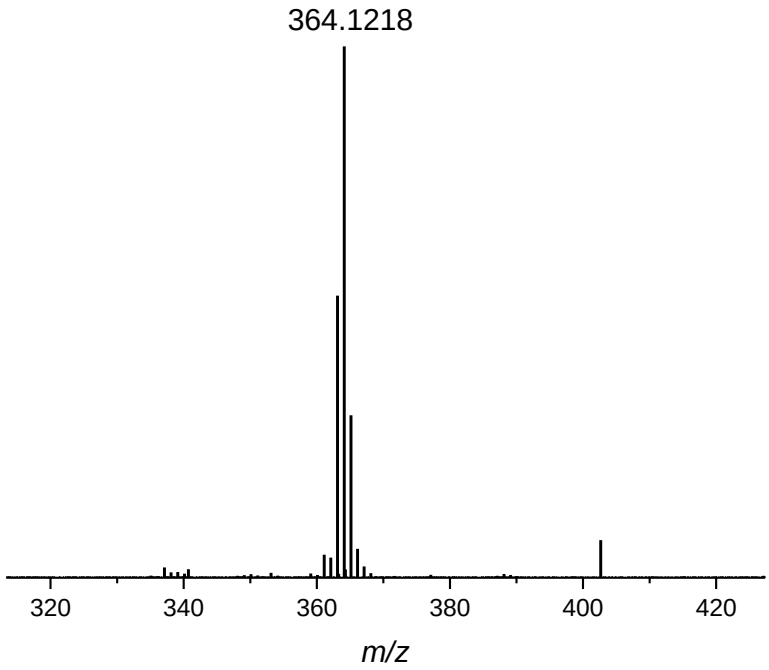

Figure S15. HRMS (MALDI-TOF) spectrum of **3** (matrix:TCNQ).

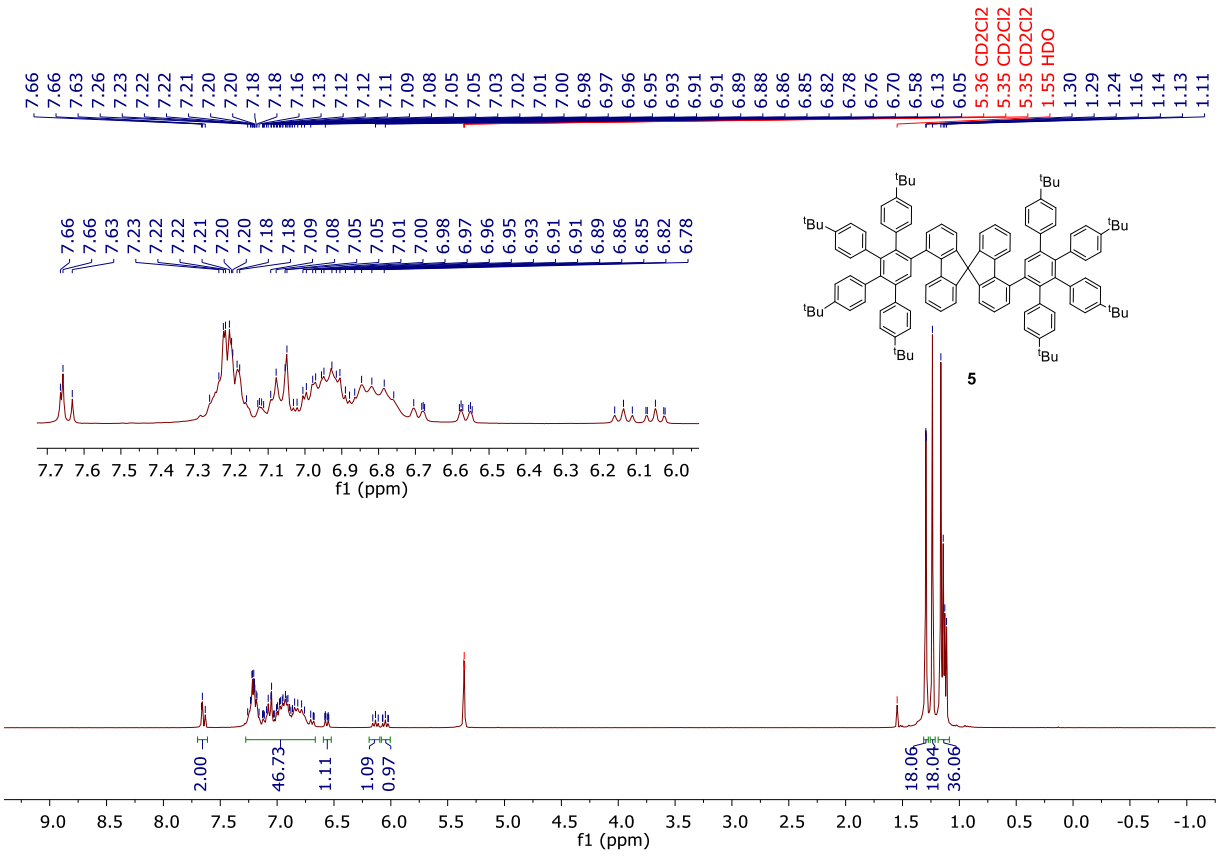

Figure S16.^{1}H NMR spectrum of **5** (300 MHz, 298 K, CD_2Cl_2).

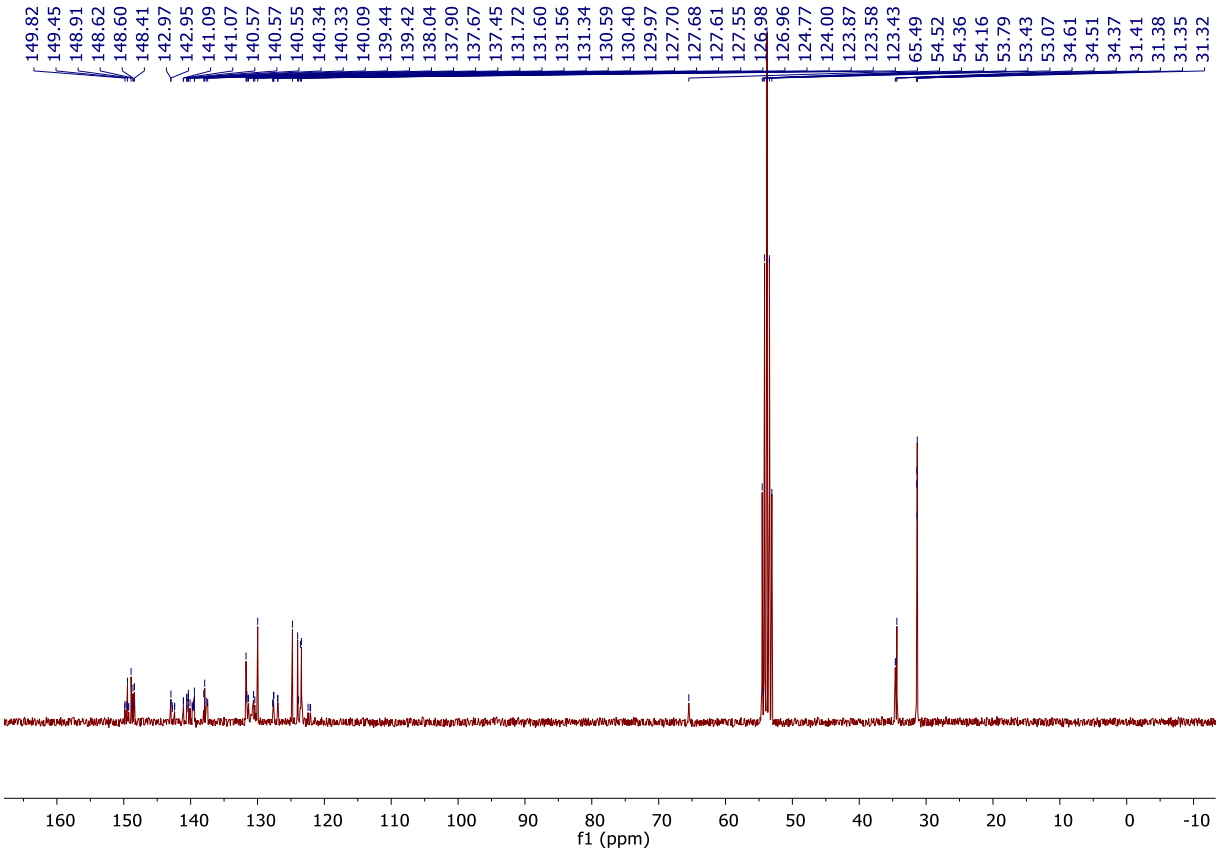

Figure S17.[13]C NMR spectrum of **5** (75 MHz, 298 K, CD_2Cl_2).

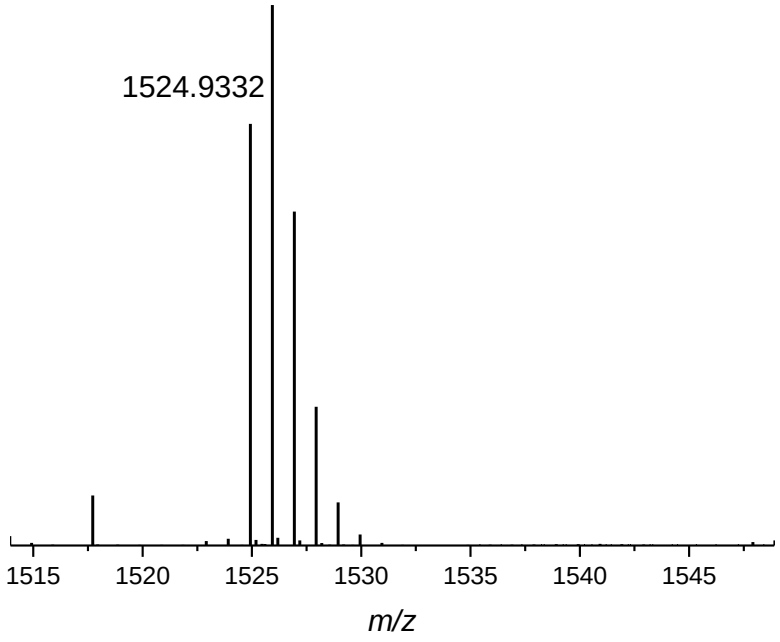

Figure S18. HRMS (MALDI-TOF) spectrum of **5** (matrix:TCNQ).

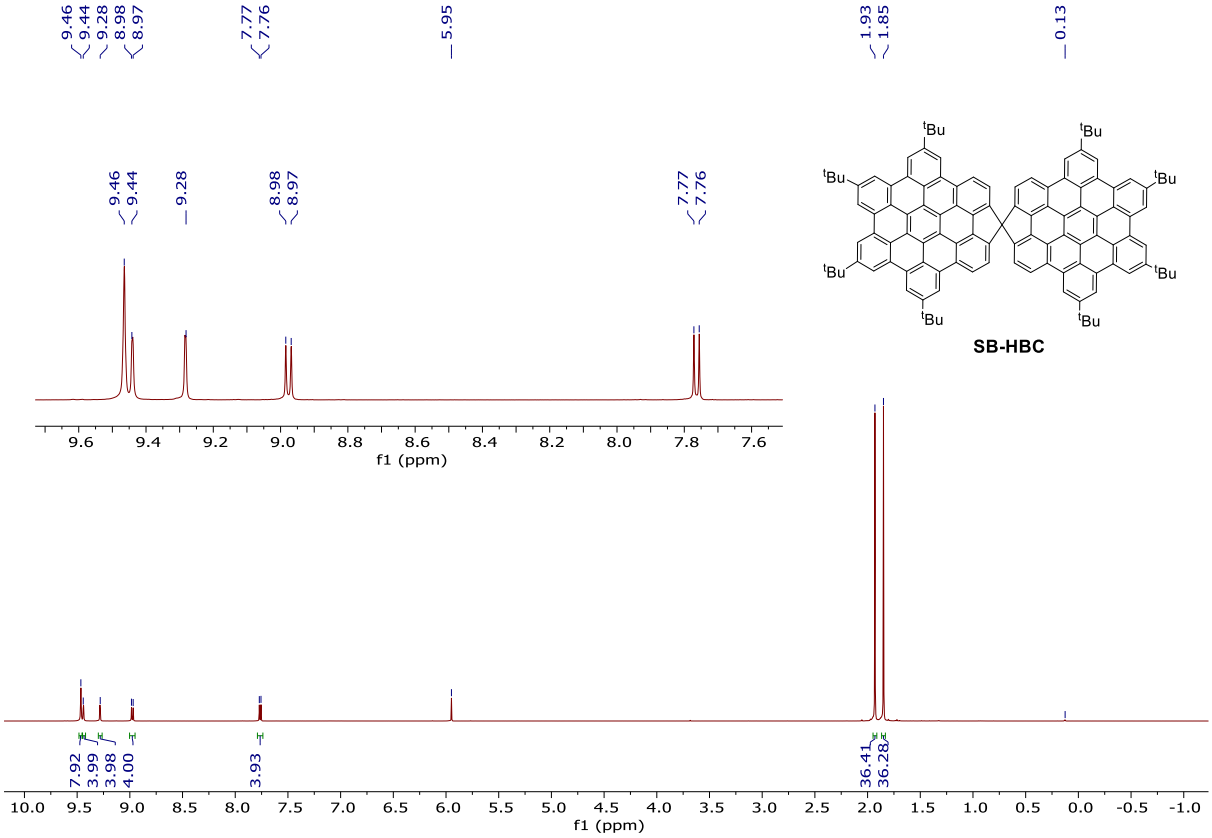

Figure S19. ^{1}H NMR spectrum of **SB-HBC** (500 MHz, 393 K, 1,1,2,2-tetrachloroethane-d_2).

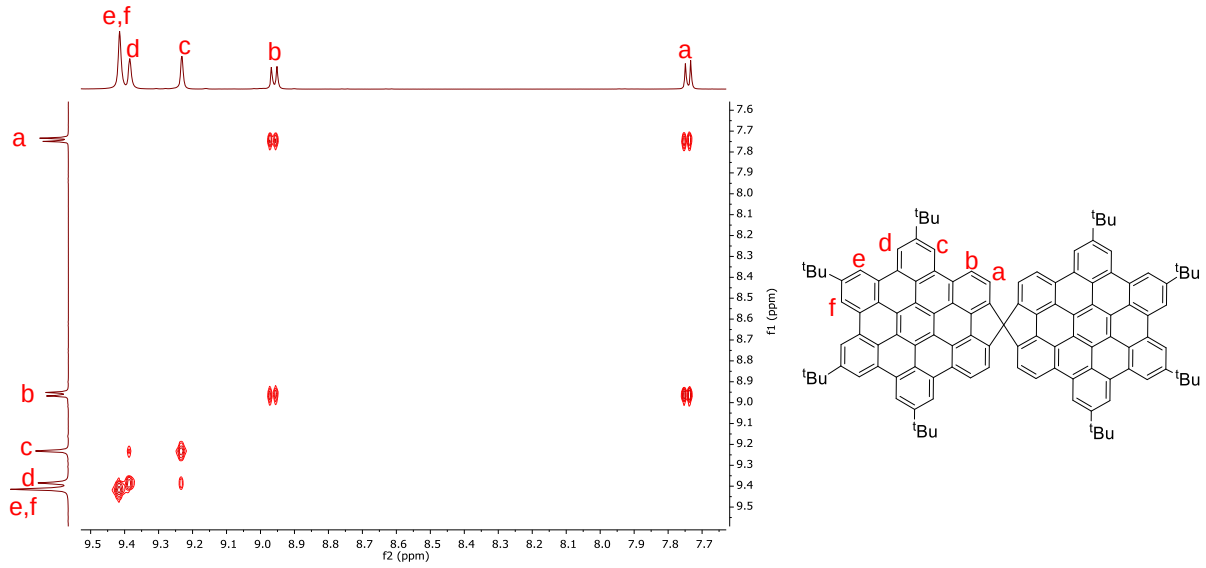

Figure S20. 2D ^{1}H-^{1}H COSY NMR spectrum of **SB-HBC** (500 MHz, 298 K, 1,1,2,2-tetrachloroethane-d_2).

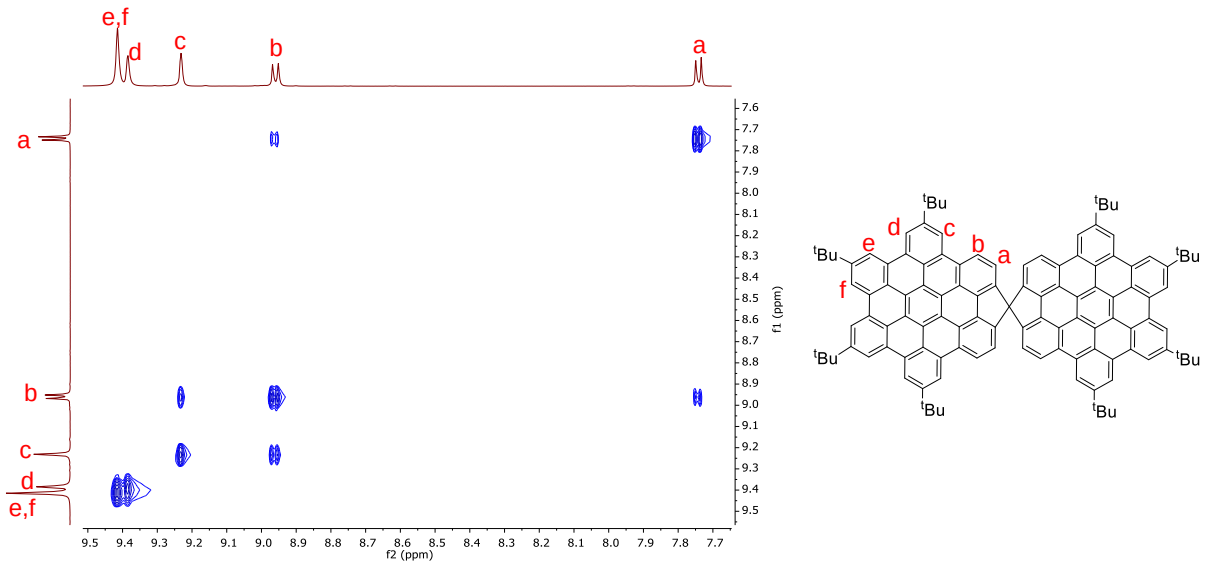

Figure S21. 2D ^{1}H-^{1}H NOESY NMR spectrum of **SB-HBC** (500 MHz, 298 K, 1,1,2,2-tetrachloroethane-d_2).

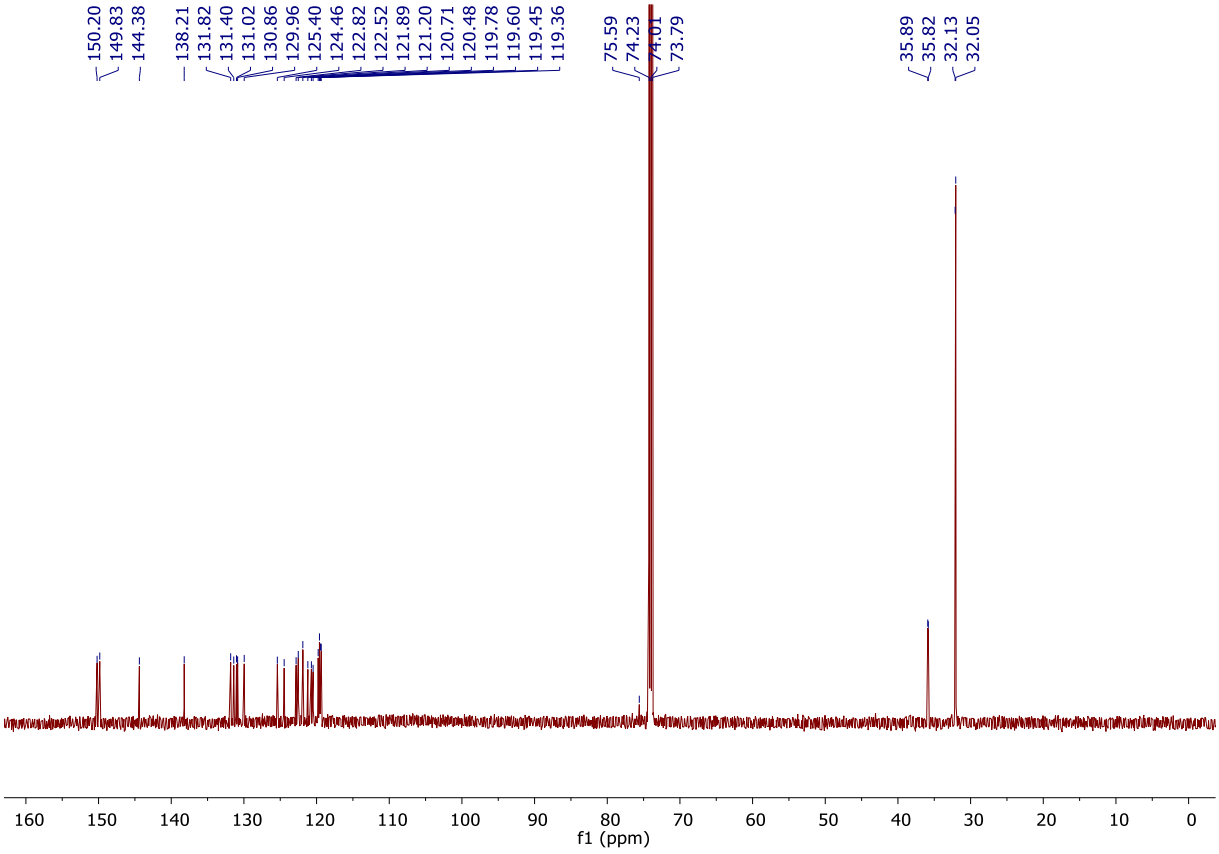

Figure S22. ^{13}C NMR spectrum of **SB-HBC** (125 MHz, 393 K, 1,1,2,2-tetrachloroethane-d_2).

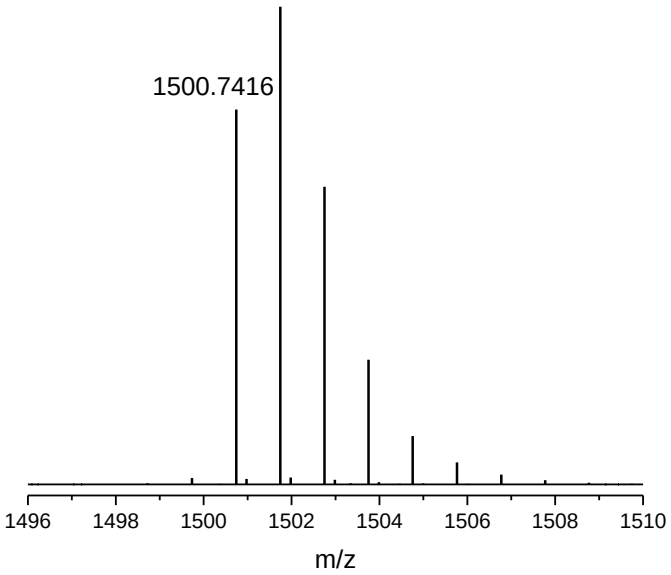

Figure S23. MALDI-TOF MS spectrum of **SB-HBC** (matrix:TCNQ).

1. Meech, S. R.; Phillips, D. *J. Photochem.* **1983**, *23*, 193-217.
2. Fan, C.; Chen, Y.; Gan, P.; Yang, C.; Zhong, C.; Qin, J.; Ma, D. *Org. Lett.* **2010**, *12*, 5648-5651.
3. Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.;Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2013.