SUPPORTING INFORMATION of SYNTHESES, STRUCTURES, AND COMPUTATIONS

Unusual nucleophilic reactivity of a dithiolene-based N-heterocyclic silane

Phuong M. Tran, Yuzhong Wang, Mitchell E. Lahm, Pingrong Wei,
Henry F. Schaefer III, and Gregory H. Robinson*

Department of Chemistry and the Center for Computational Chemistry, The University of Georgia, Athens, Georgia 30602-2556, United States.

To whom correspondence should be addressed. Email: robinson@uga.edu

Table of Contents

1) Synthesis and NMR spectra of **2**, **5**, **6**,**7**, **9**, **10**, and **12** S2-S15

2) Computational data of **5-Ph**, **6**, **7**, **8-Ph**, **9-Ph**, and **10-Ph** S16-S23

3) X-ray Data of **5**·**(toluene)$_2$**, **6**, **7**, **8**, **9**·**(toluene)$_2$**, and **10** S24-S53

4) References S54

SUPPORTING INFORMATION of SYNTHESES

Materials and Methods

General.

The syntheses of air-sensitive compounds were performed under purified argon using Schlenk techniques and an inert atmosphere drybox (M-Braun LabMaster SP). Chemicals were purchased from Aldrich and Strem and used as received. The solvents were dried and distilled under argon from Na/benzophenone prior to use. ^{1}H, ^{11}B, $^{11}B\{^{1}H\}$, $^{13}C\{^{1}H\}$ and $^{29}Si\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance III HD 400 MHz spectrometer and a Bruker Avance Neo 600MHz spectrometer equipped with a 5mm BBO probe. The chemical shifts were referenced to an external standard of $BF_3{\cdot}OEt_2$ for ^{11}B and $^{11}B\{^{1}H\}$ and TMS for $^{29}Si\{^{1}H\}$ NMR spectra. X-ray intensity data for **5·(toluene)$_2$**, **6**, **7**, **8**, **9·(toluene)$_2$**, and **10** were collected at 135K on a Bruker D8 Quest PHOTON 100 CMOS X-ray diffractometer system with Incoatec Microfocus Source (IμS) monochromated Mo Kα radiation (λ = 0.71073 Å, sealed tube) using phi and omega-scan technique.

Compound **2**: To a Schlenk tube charged with **1** (0.200 g, 0.494 mmol) in 10 mL of toluene was added a solution of 0.60 mL of BBr_3 (1.0 M in hexane, 0.600 mmol) in 5 mL of toluene. The reaction mixture was then stirred at room temperature overnight. After the solvent was removed in vacuum, the residue was extracted with 15 mL of hexane. Removing hexane from the filtrate in vacuum gave **2** as colorless crystalline powder (0.212 g, 65 % yield). The NMR data of **2** are consistent with the reported values.[1]

Compound **5**: To a Schlenk tube charged with **4** (0.200 g, 0.225 mmol) in 4 mL of toluene was slowly added a solution of 0.50 mL of BBr_3 (1.0 M in hexane, 0.500 mmol) in 4 mL of toluene. The reaction mixture was then stirred at room temperature for 2h. After filtration and subsequent rinsed with 15 mL of hexane, the residue was dried under vacuum, giving **5** as pale yellow solid (0.252 g, 81 % yield) (Note: the ^{11}B NMR spectrum of **5** indicates the presence of some impurity in this solid). X-ray quality yellow crystals of **5** were obtained via recrystallization in toluene. Mp: gradually decomposed (>143 °C) and melt at 250 °C. ^{1}H NMR (400.22 MHz, C_6D_6): δ 0.60 [d, 3H, CH(CH_3)$_2$], 0.77 [d, 3H, CH(CH_3)$_2$], 0.88 [m, 9H, CH(CH_3)$_2$], 0.93 [d, 3H, CH(CH_3)$_2$], 1.08 [m, 12H, CH(CH_3)$_2$], 1.25 [d, 3H, CH(CH_3)$_2$], 1.28 [d, 3H, CH(CH_3)$_2$], 1.37 [d, 3H, CH(CH_3)$_2$], 1.42 [d, 6H, CH(CH_3)$_2$], 1.51 [d, 3H, CH(CH_3)$_2$], 2.71 [m, 3H, CH(CH$_3$)$_2$], 2.94 [m, 1H, CH(CH$_3$)$_2$], 3.04 [m, 1H, CH(CH$_3$)$_2$], 3.15 [m, 2H, CH(CH$_3$)$_2$], 3.31 [m, 1H, CH(CH$_3$)$_2$], 5.61 [bs, 1H, NC−H], 6.05 [s, 1H, N=CH], 6.74 [d, 1H, Ar-H], 6.84 [d, 1H, Ar-H], 6.90-7.16 [m, 10H, Ar-H]. ^{11}B NMR (128.39 MHz, C_6D_6): δ -10.97 [d, $^{2}J_{BH}$ = 7.8 Hz, NCBBr$_3$], -6.37 [s, SBBr$_3$]. $^{11}B\{^{1}H\}$ NMR (128.42 MHz, C_6D_6): δ -10.97 [NCBBr$_3$], -6.36 [SBBr$_3$]. $^{29}Si\{^{1}H\}$ NMR (79.51 MHz, toluene-d$_8$): δ 8.12. Crystal data for **5·(toluene)$_2$**: $C_{67}H_{86}B_2Br_6N_4S_3Si$, fw = 1572.74, triclinic, P-1, a = 11.0692(8) Å, b = 16.5906(12) Å, c = 21.0529(15) Å, α = 81.044(2)°, β = 83.385(2)°, γ = 71.370(2)°, V = 3610.1(5) Å^3, Z = 2, R1 = 0.0441 for 18897 data ($I > 2\sigma(I)$), wR$_2$ = 0.1072 (all data).

Compound **6** and **7**: To a Schlenk tube charged with **5** (0.1 g, 0.064 mmol) in 15 mL of toluene was added 0.15 mL of BBr_3 (1.0 M in hexane, 0.150 mmol). The reaction mixture was then heated to 100 °C and stirred overnight. After the solvent was removed in vacuum, the residue was combined with 4 mL of toluene. The slurry was heated under reflux and kept stationary at room temperature over 5 days, giving a mixture of X-ray quality colorless crystals of **6** and **7** in ca. 1:1 ratio (in terms of the ^{1}H NMR data). Crystals of **6** and **7** were manually separated based on their different shape (**6**: square blocks, **7**: long rods) for the NMR analyses. For **6**: Mp: gradually decomposed (>150°C) and melt at 235 °C. ^{1}H NMR (400.22 MHz, C_6D_6): δ 1.18 [d, 12H, CH(C*H*$_3$)$_2$], 1.28 [d, 12H, CH(C*H*$_3$)$_2$], 2.91 [m, 4H, C*H*(CH$_3$)$_2$], 6.75 [s, 2H, NC*H*], 7.12 [d, 4H, Ar-*H*], 7.22 [t, 2H, Ar-*H*]. ^{11}B NMR (128.42 MHz, C_6D_6): δ28.60 (bs). ^{13}C{^{1}H} NMR (100.65 MHz, C_6D_6): δ 24.32, 25.54 [CH(*C*H$_3$)$_2$], 29.07 [*C*H(CH$_3$)$_2$], 125.52 [N*CC*N], 127.15, 129.95, 137.19, 145.01 [Ar-*C*]. Crystal data for **6**: $C_{26}H_{36}B_2Br_4N_2$, fw = 717.83, triclinic, P-1, a = 10.8955(14) Å, b = 12.618(2) Å, c = 12.7576(15) Å, α = 73.361(5)°, β = 89.927(4)°, γ = 64.433(4)°, V = 1500.7(4) Å^3, Z = 2, R1 = 0.0441 for 5372 data ($I > 2\sigma(I)$), wR_2 = 0.1206 (all data). For **7**: Mp: gradually decomposed (>137 °C) and melt at 217 °C. ^{1}H NMR (400.22 MHz, C_6D_6): δ 0.99 [d, 12H, CH(C*H*$_3$)$_2$], 1.42 [d, 12H, CH(C*H*$_3$)$_2$], 2.79 [m, 4H, C*H*(CH$_3$)$_2$], 7.06 [d, 4H, Ar-*H*], 7.19 [t, 2H, Ar-*H*]. ^{11}B NMR (128.42 MHz, C_6D_6): δ -6.36 [s, $SBBr_3$], 51.15 [bs, SBS]. ^{13}C{^{1}H} NMR (100.65 MHz, C_6D_6): δ 24.54, 25.53 [CH(*C*H$_3$)$_2$], 29.98 [*C*H(CH$_3$)$_2$], 126.07 [N*CC*N], 129.03, 131.52, 132.67, 146.63 [Ar-*C*]. Crystal data for **7**: $C_{27}H_{34}B_2Br_4N_2S_3$, fw = 824.00, monoclinic, P2$_1$/c, a = 18.3185(13) Å, b = 9.6977(7) Å, c = 18.5961(13) Å, α = 90°, β = 94.033(3)°, γ = 90°, V = 3295.4(4) Å^3, Z = 4, R1 = 0.0408 for 5784 data ($I > 2\sigma(I)$), wR_2 = 0.0877 (all data).

Compound **9**: To a Schlenk tube charged with **4** (0.200 g, 0.225 mmol) in 5 mL of toluene was slowly added a solution of BI_3 (0.176 g, 0.450 mmol) in 10 mL of toluene. The reaction mixture was then stirred at room temperature overnight. After filtration, the filtrate was concentrated under vacuum to approximately 2 mL. The resulting pale-yellow crystalized powder of **9** was subsequently isolated and dried under vacuum. Yield: 0.269 g (72%). X-ray quality pale-yellow crystals of **9** were obtained via recrystallization in toluene. Mp: gradually decomposed (>169 °C) and melt at 231 °C.^{1}H NMR (599.98 MHz, C_6D_6): δ 1.04 [d, 6H, CH(C*H*$_3$)$_2$], 1.11 [d, 6H, CH(C*H*$_3$)$_2$], 1.17 [d, 6H, CH(C*H*$_3$)$_2$], 1.20 [d, 12H, CH(C*H*$_3$)$_2$], 1.27 [d, 6H, CH(C*H*$_3$)$_2$], 1.51 [d, 6H, CH(C*H*$_3$)$_2$], 1.58 [d, 6H, CH(C*H*$_3$)$_2$], 2.68 [m, 2H, C*H*(CH$_3$)$_2$], 2.83 [m, 2H, C*H*(CH$_3$)$_2$], 2.87 [m, 2H, C*H*(CH$_3$)$_2$], 2.97 [m, 2H, C*H*(CH$_3$)$_2$], 6.25 [d, 1H, NC*H*], 6.76 [d, 1H, NC*H*], 7.01-7.19 [m, 12H, Ar-*H*].^{11}B NMR (192.50 MHz, C_6D_6): δ -82.85 [bs, SBI_3], 6.02 [bs, NBI_2]. ^{29}Si{^{1}H} NMR (119.20 MHz, C_6D_6): δ-18.80.^{13}C{^{1}H} NMR (150.88 MHz, C_6D_5Br): δ 24.25, 24.32, 24.87, 25.17, 25.81, 25.84, 26.11 [CH(*C*H$_3$)$_2$], 29.08, 29.66, 29.85, 30.03 [*C*H(CH$_3$)$_2$], 124.48,127.22 [N*CC*N], 125.54, 125.81, 126.03, 126.08, 126.36, 128.90, 129.67, 132.15, 133.02, 134.82, 139.63, 144.61, 146.54, 146.58, 147.25 [Ar-*C* and S*CC*S]. Crystal data for **9·(toluene)$_2$**: $C_{67}H_{86}B_2I_6N_4S_3Si$, fw = 1854.68, monoclinic, P2$_{1/c}$, a = 20.950(19) Å, b = 12.762(11) Å, c = 28.79(2) Å, α = 90°, β = 101.17(3)°, γ = 90°, V = 7552(11) Å^3, Z = 4, R1 = 0.0661 for 7518 data ($I > 2\sigma(I)$), wR_2 = 0.1052 (all data).

Compound **10**: To a Schlenk tube charged with **4** (0.200 g, 0.225 mmol) in 5 mL of toluene was slowly added a solution of 0.45 mL of BCl_3 (1.0 M in heptane, 0.450 mmol) in 5 mL

of toluene. The reaction mixture was then stirred at room temperature overnight. After the volatile materials were removed in vacuum, the residue was washed with hexane, giving **10** as white powder (0.043 g, 19% yield). X-ray quality colorless crystals of **10** were obtained by concentrating the parent solution at room temperature. Mp: gradually decomposed (>121 °C) and melt at 222 °C. ^{1}H NMR (599.98 MHz, C_6D_5Br): δ 0.28 [d, 3H, CH(C*H*$_3$)$_2$], 0.64 [d, 3H, CH(C*H*$_3$)$_2$], 1.03 [d, 3H, CH(C*H*$_3$)$_2$], 1.09 [d, 3H, CH(C*H*$_3$)$_2$], 1.12 [d, 9H, CH(C*H*$_3$)$_2$], 1.23 [m, 9H, CH(C*H*$_3$)$_2$], 1.27 [d, 3H, CH(C*H*$_3$)$_2$], 1.31 [d, 3H, CH(C*H*$_3$)$_2$], 1.34 [m, 6H, CH(C*H*$_3$)$_2$], 1.37 [d, 3H, CH(C*H*$_3$)$_2$], 1.40 [d, 3H, CH(C*H*$_3$)$_2$], 2.50 [m, 1H, C*H*(CH$_3$)$_2$], 2.67 [m, 1H, C*H*(CH$_3$)$_2$], 2.74 [m, 1H, C*H*(CH$_3$)$_2$], 2.84 [m, 1H, C*H*(CH$_3$)$_2$], 2.98 [m, 1H, C*H*(CH$_3$)$_2$], 3.08 [m, 1H, C*H*(CH$_3$)$_2$], 3.54 [m, 1H, C*H*(CH$_3$)$_2$], 3.78 [m, 1H, C*H*(CH$_3$)$_2$], 5.73 [m, 2H, NC*H*], 6.95-7.28 [m, 12H, Ar-*H*]. ^{11}B NMR (192.50 MHz, C_6D_5Br): δ 53.28 (bs). ^{29}Si{^{1}H} NMR (119.20 MHz, C_6D_5Br): δ -33.47. ^{13}C{^{1}H} NMR (150.88 MHz, C_6D_5Br): δ 22.10, 22.55, 22.75, 23.04, 23.48, 23.62, 23.78, 24.05, 24.14, 24.51, 24.75, 24.83, 25.80, 26.06, 26.21, 26.29, 26.83 [CH(*C*H$_3$)$_2$], 28.05, 28.36, 28.76, 28.81, 28.85, 28.92 [*C*H(CH$_3$)$_2$], 119.83, 120.16 [N*CC*N], 122.03, 122.31, 123.50, 123.89, 124.08, 124.22, 124.30, 124.88, 128.08, 128.16, 128.97, 130.16, 130.36, 131.96, 132.06, 135.37, 136.16, 146.09, 146.36, 147.24, 147.31, 147.48, 147.53, 147.58 [Ar-*C* and S*CC*S], 169.73 [*C*=S]. Crystal data for **10**: $C_{53}H_{70}BCl_3N_4S_3Si$, fw = 1004.56, monoclinic, $P2_{1/c}$, a = 14.4876(10) Å, b = 20.1276(13) Å, c = 18.9921(12) Å, α = 90°, β = 91.557(2)°, γ = 90°, V = 5536.1(6) Å^3, Z = 4, R1 = 0.0566 for 6835 data ($I > 2\sigma(I)$), wR_2 = 0.1141 (all data).

Compound **12**: To a Schlenk tube charged with **4** (0.200 g, 0.225 mmol) in 5 mL of toluene was slowly added a solution of 1.15 mL of BCl_3 (1.0 M in heptane, 1.150 mmol) in 5 mL of toluene. The reaction mixture was then stirred at room temperature for 2h. After the volatile materials were removed in vacuum, the residue was recrystallized in hot hexane, giving **12** as colorless crystallized solid (0.071 g, 58% yield). Mp: gradually decomposed (>154 °C) and melt at 262 °C.^{1}H NMR (599.98 MHz, C_6D_6): δ 1.16 [d, 12H, CH(C*H*$_3$)$_2$], 1.26 [d, 12H, CH(C*H*$_3$)$_2$], 2.93 [m, 4H, C*H*(CH$_3$)$_2$], 6.51 [s, 2H, NC*H*], 7.11 [d, 4H, Ar-*H*], 7.20 [t, 2H, Ar-*H*]. ^{11}B NMR (192.50 MHz, C_6D_6): δ 32.27 (s, $w_{1/2}$ = 230 Hz). ^{13}C{^{1}H} NMR (150.88 MHz, C_6D_6): δ 24.40, 25.24 [CH(*C*H$_3$)$_2$], 28.98 [*C*H(CH$_3$)$_2$], 124.63 [N*CC*N], 125.40, 129.86, 135.96, 145.33 [Ar-*C*].

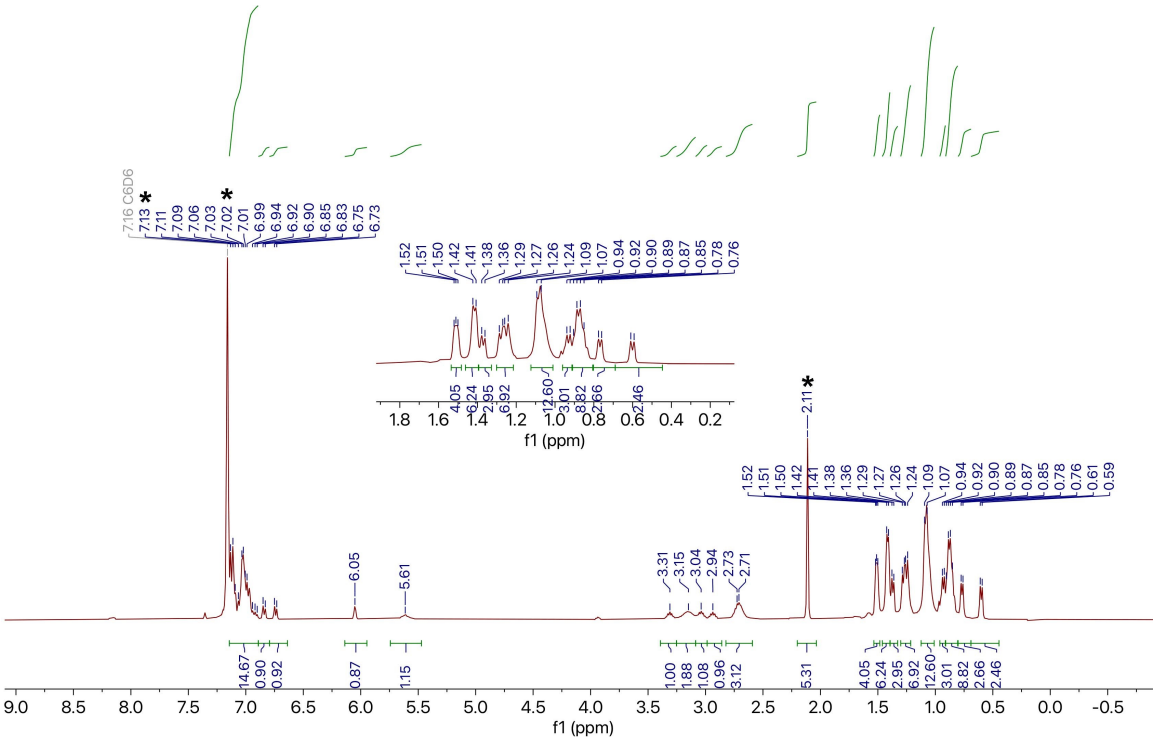

Figure S1. ^{1}H NMR spectrum of **5** in C_6D_6 (* resonances of toluene).

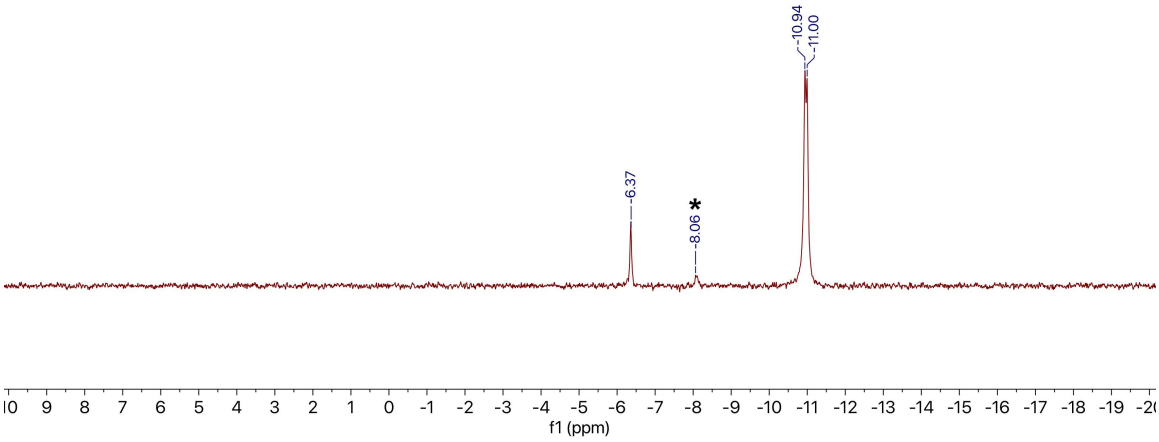

Figure S2. ^{11}B NMR spectrum of **5** in C_6D_6 (* resonance of impurity).

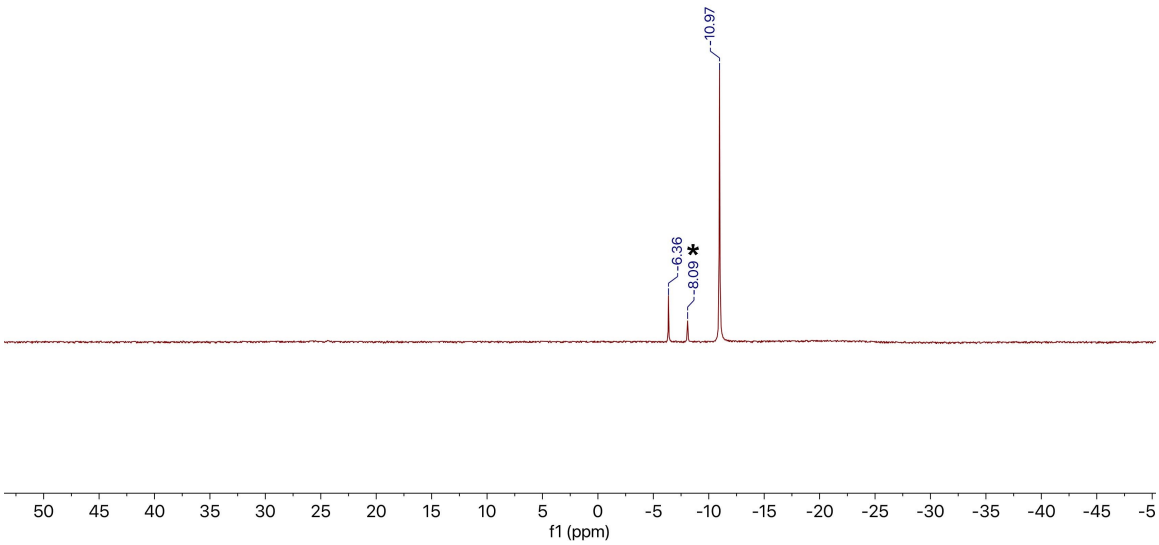

Figure S3. $^{11}B\{^{1}H\}$ NMR spectrum of **5** in C_6D_6 (* resonance of impurity).

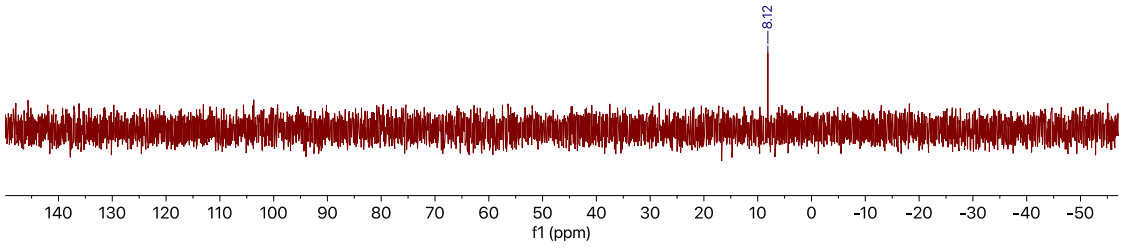

Figure S4. $^{29}Si\{^{1}H\}$ NMR spectrum of **5** in Toluene-d_8.

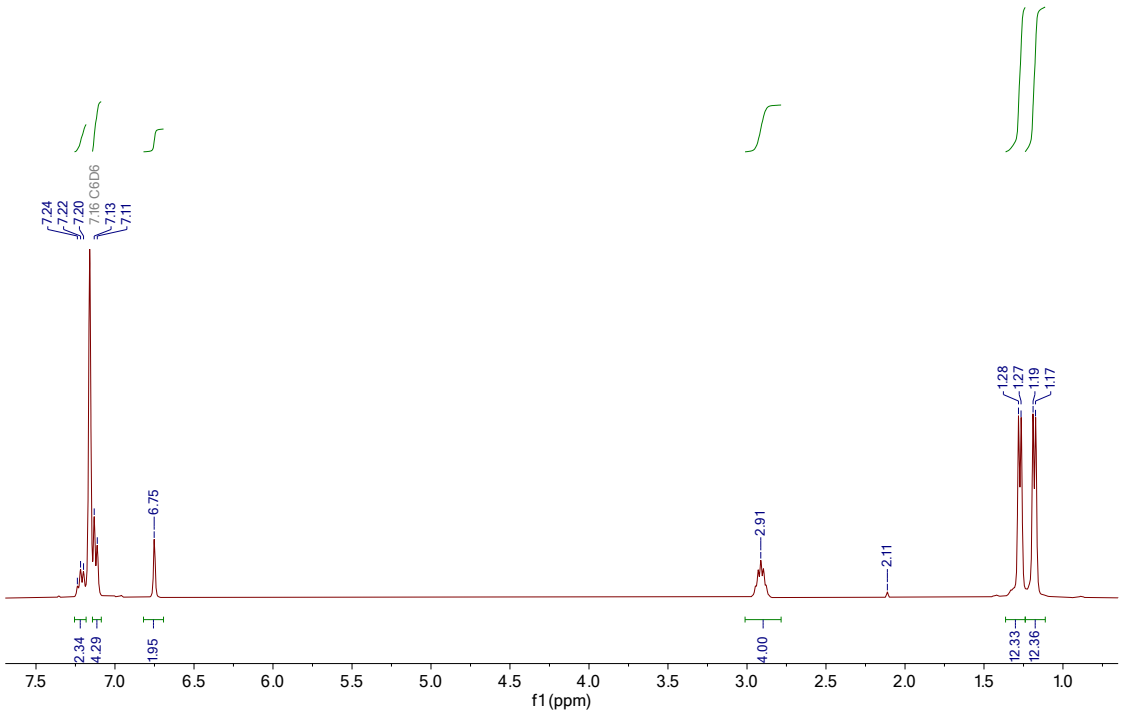

Figure S5. ^{1}H NMR spectrum of **6** in C_6D_6.

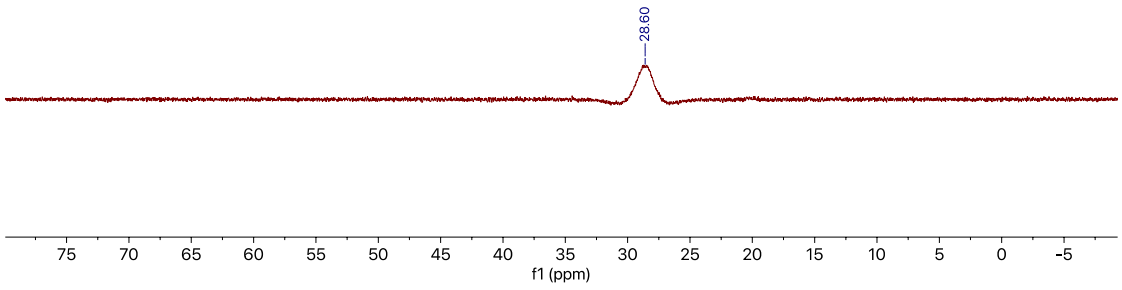

Figure S6. ^{11}B NMR spectrum of **6** in C_6D_6.

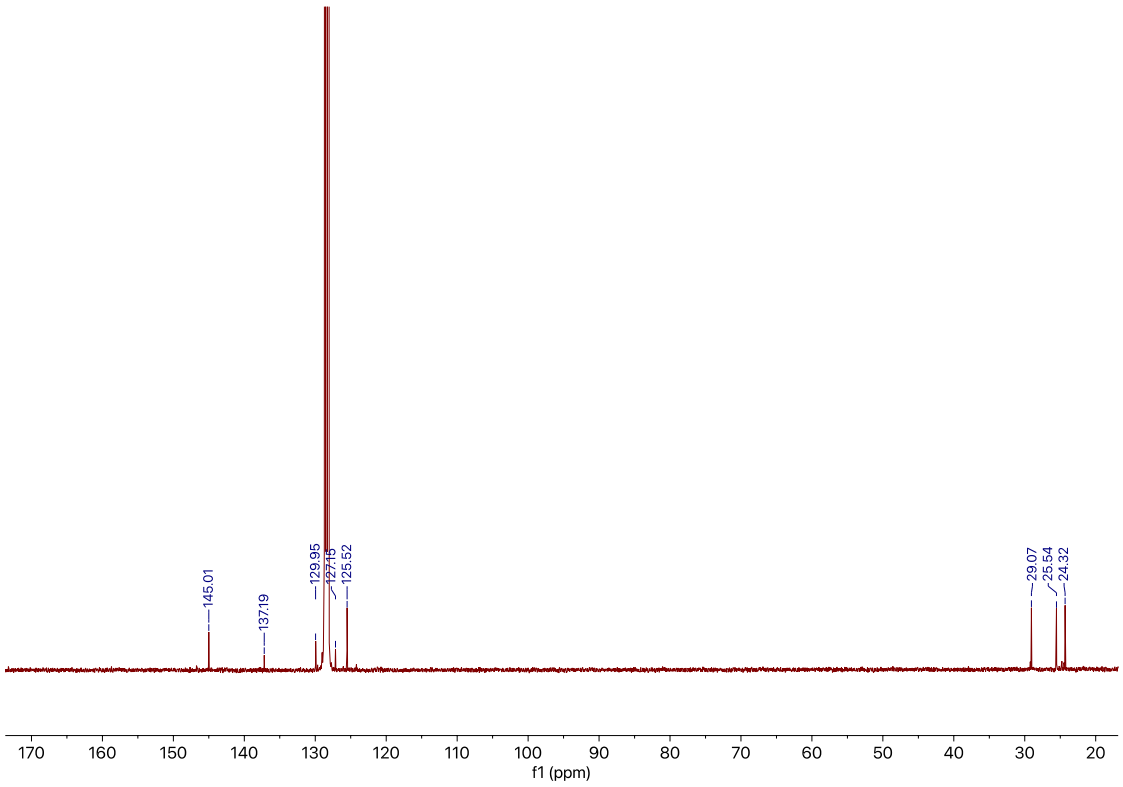

Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of **6** in C_6D_6.

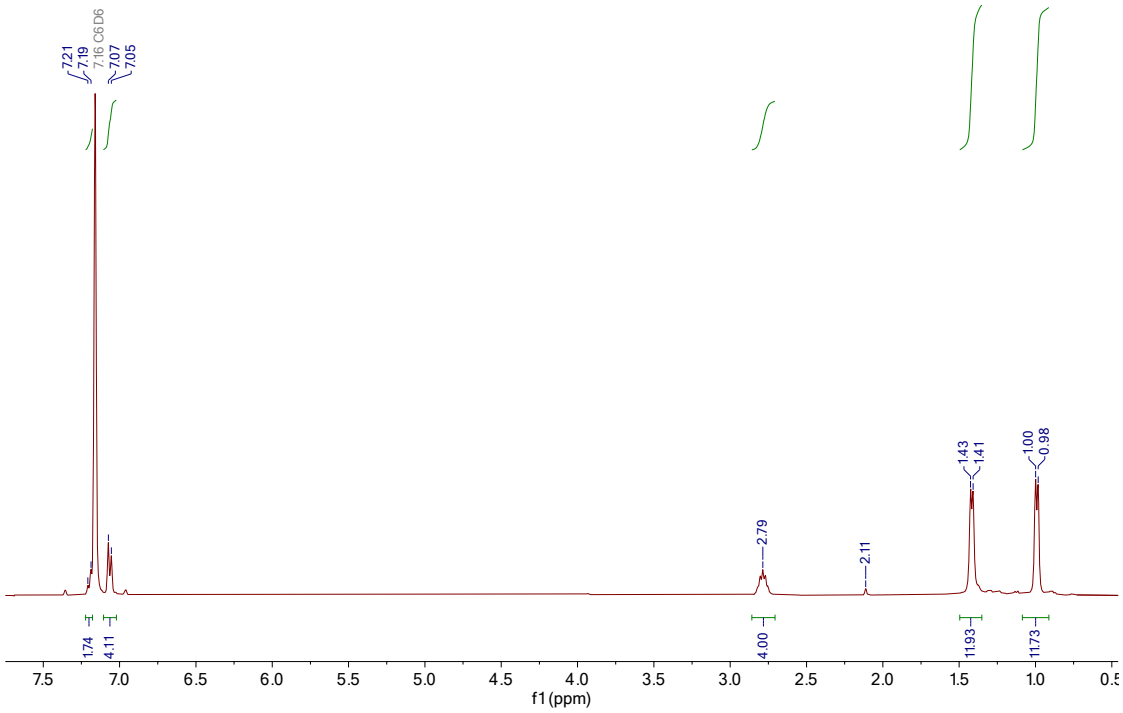

Figure S8. ^{1}H NMR spectrum of **7** in C_6D_6.

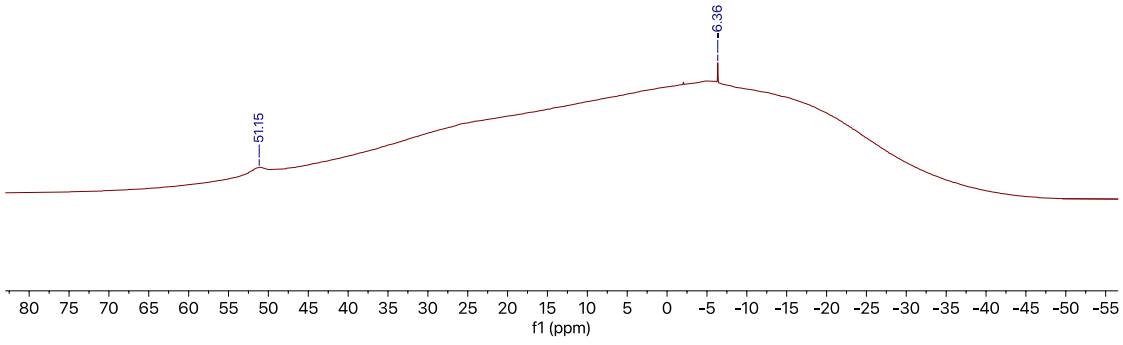

Figure S9. ^{11}B NMR spectrum of **7** in C_6D_6.

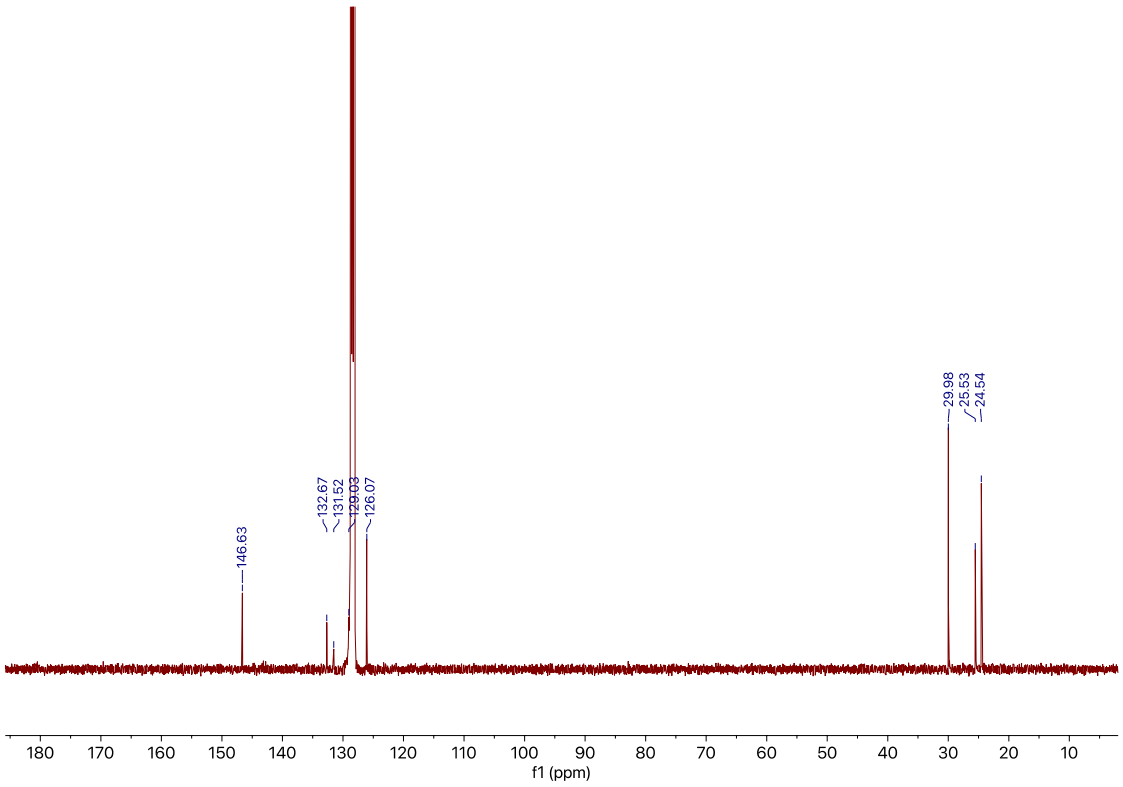

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of **7** in C_6D_6.

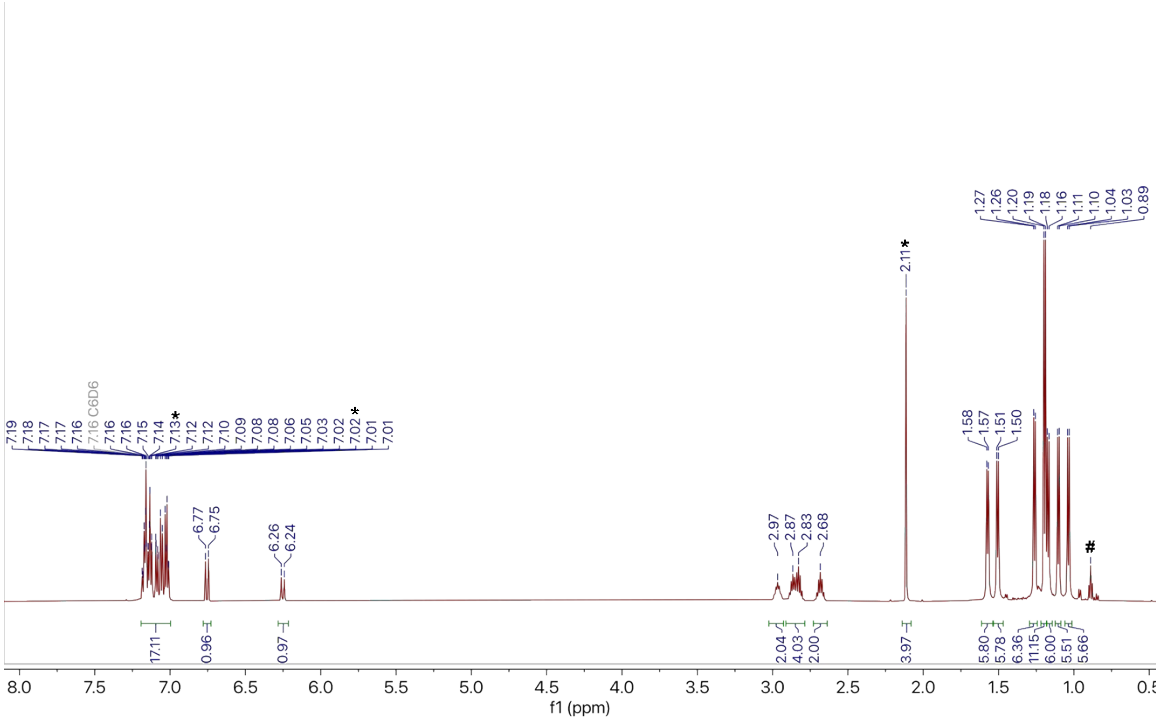

Figure S11. ^{1}H NMR spectrum of **9** in C_6D_6 (* resonances of toluene, # resonance of hexane).

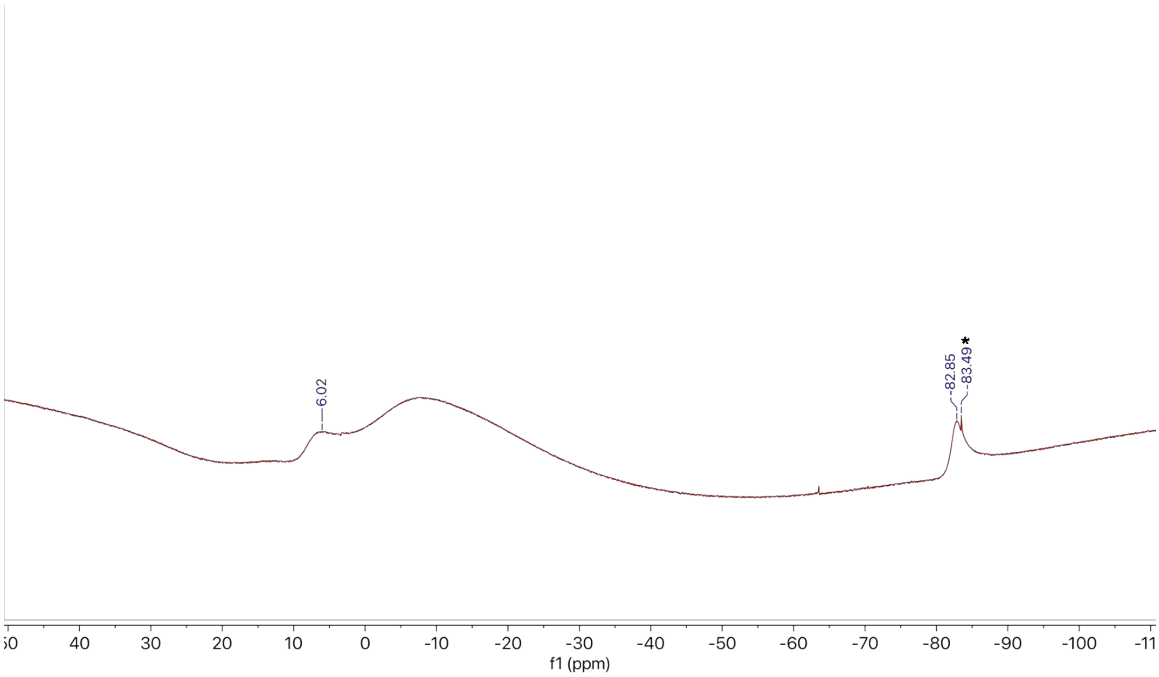

Figure S12. ^{11}B NMR spectrum of **9** in C_6D_6 (* resonance of impurity).

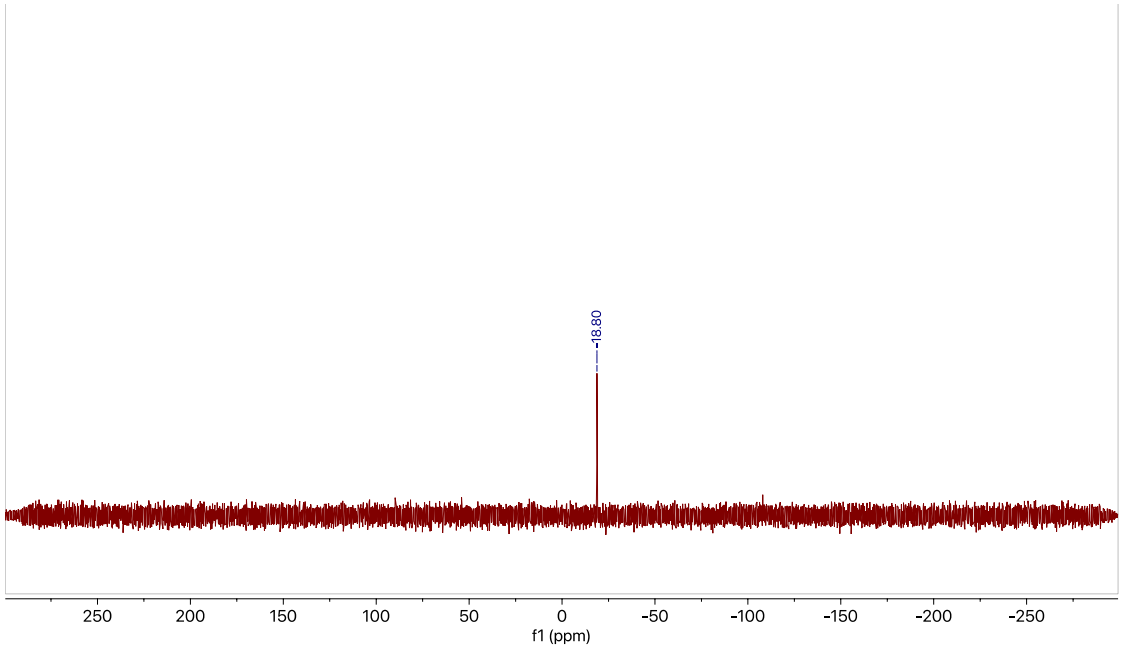

Figure S13. $^{29}Si\{^1H\}$ NMR spectrum of **9** in C_6D_6.

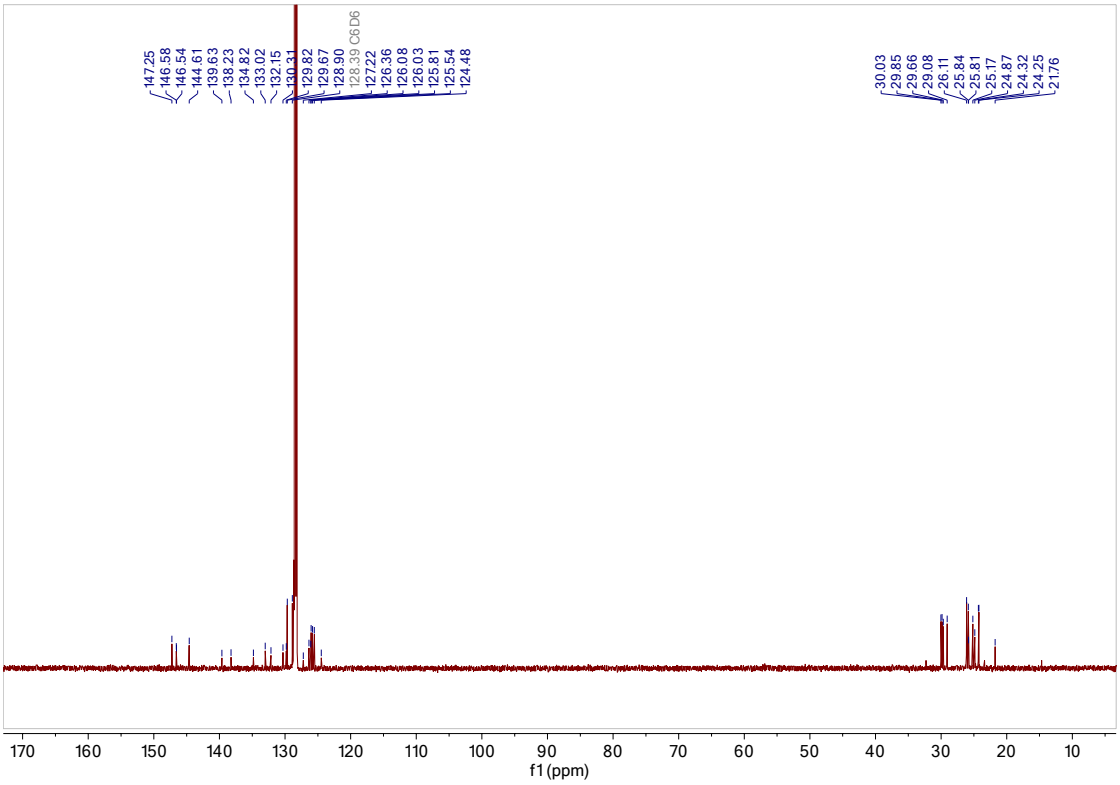

Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of **9** in C_6D_6.

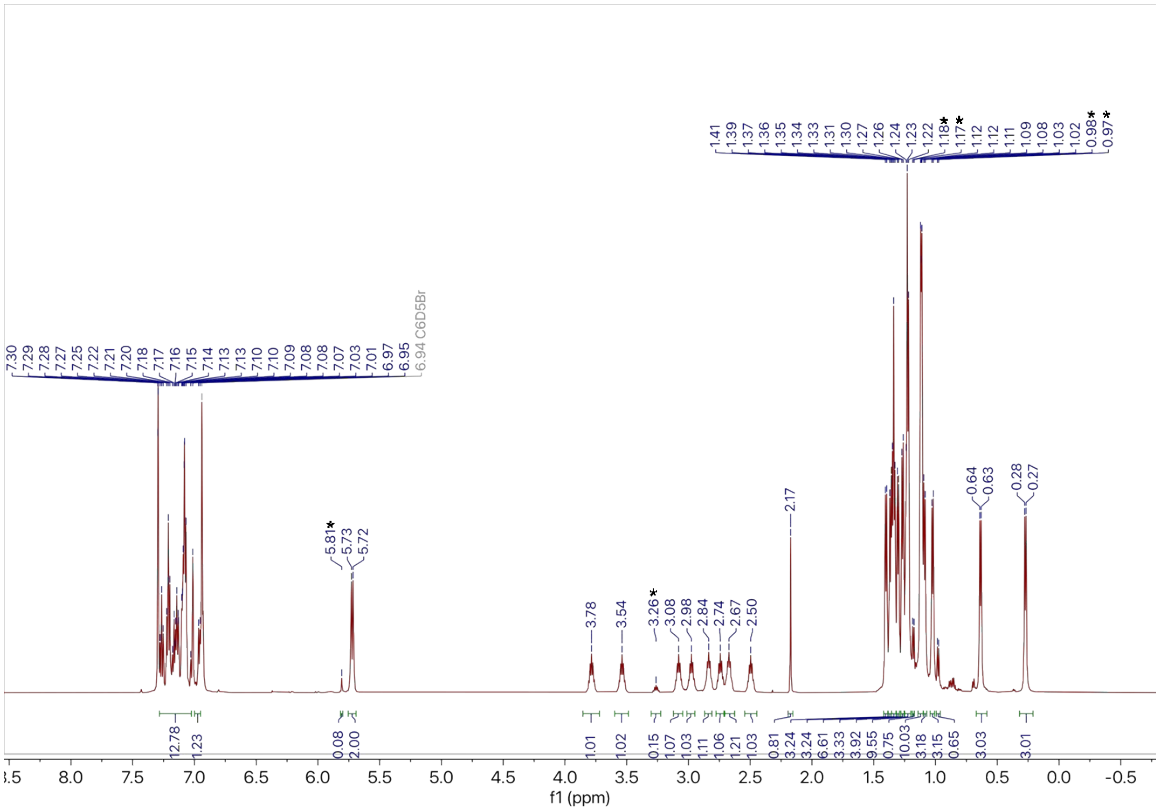

Figure S15. ^{1}H NMR spectrum of **10** in C_6D_5Br, * resonances of the impurity (4%).

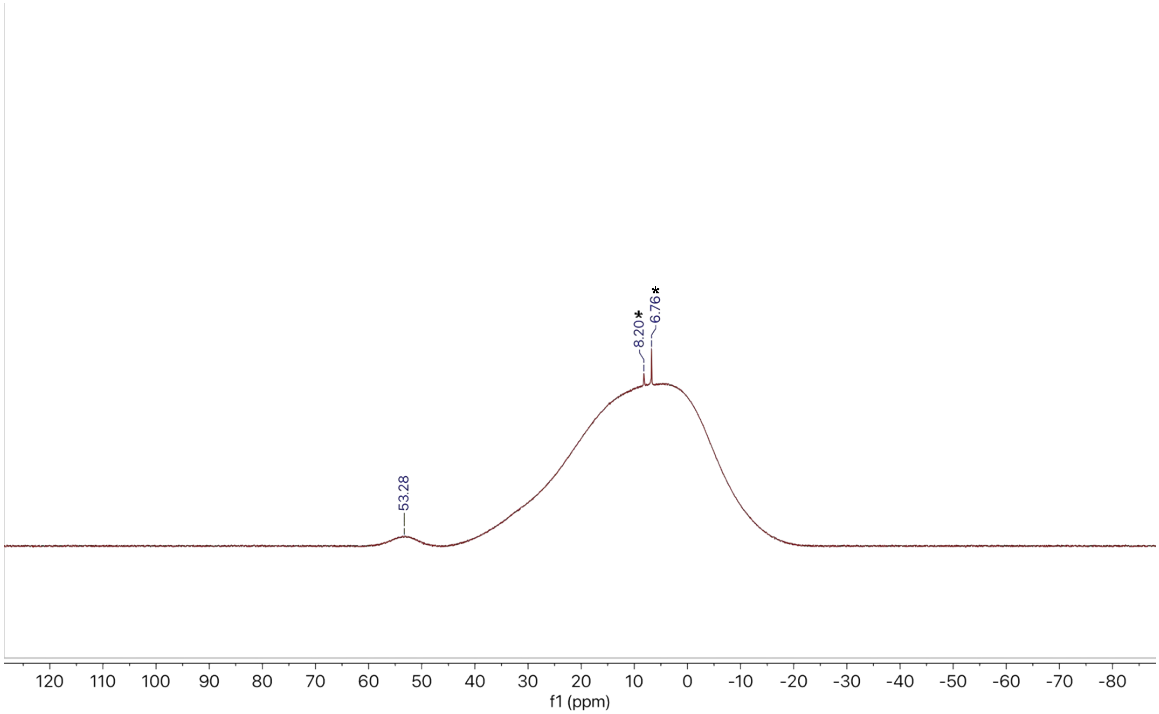

Figure S16. ^{11}B NMR spectrum of **10** in C_6D_5Br (* resonances of impurities).

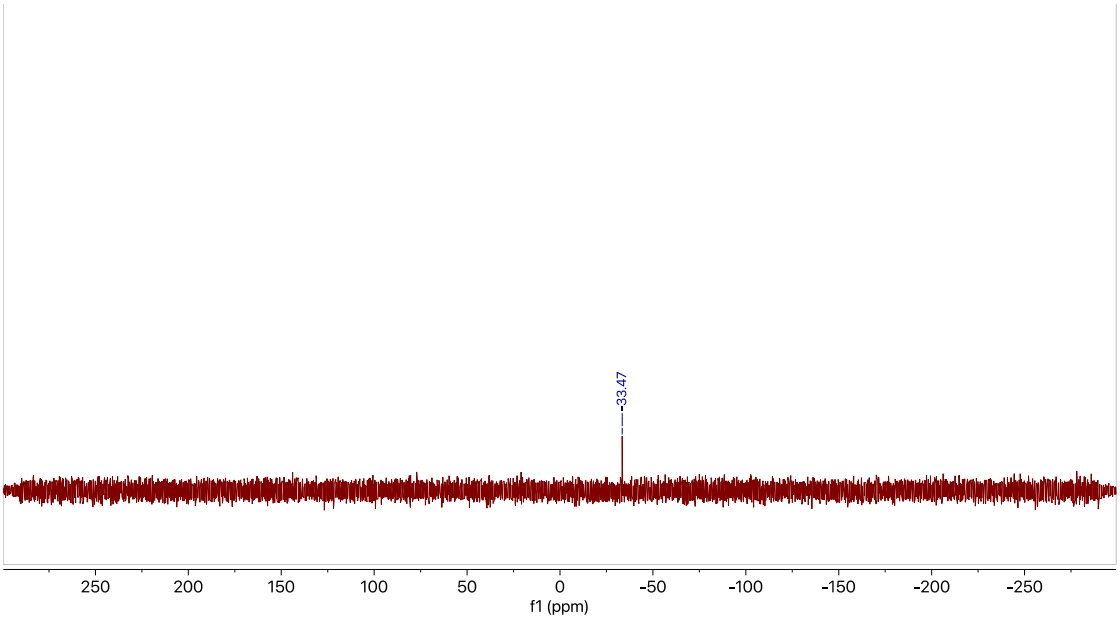

Figure S17. $^{29}Si\{^1H\}$ NMR spectrum of **10** in C_6D_5Br.

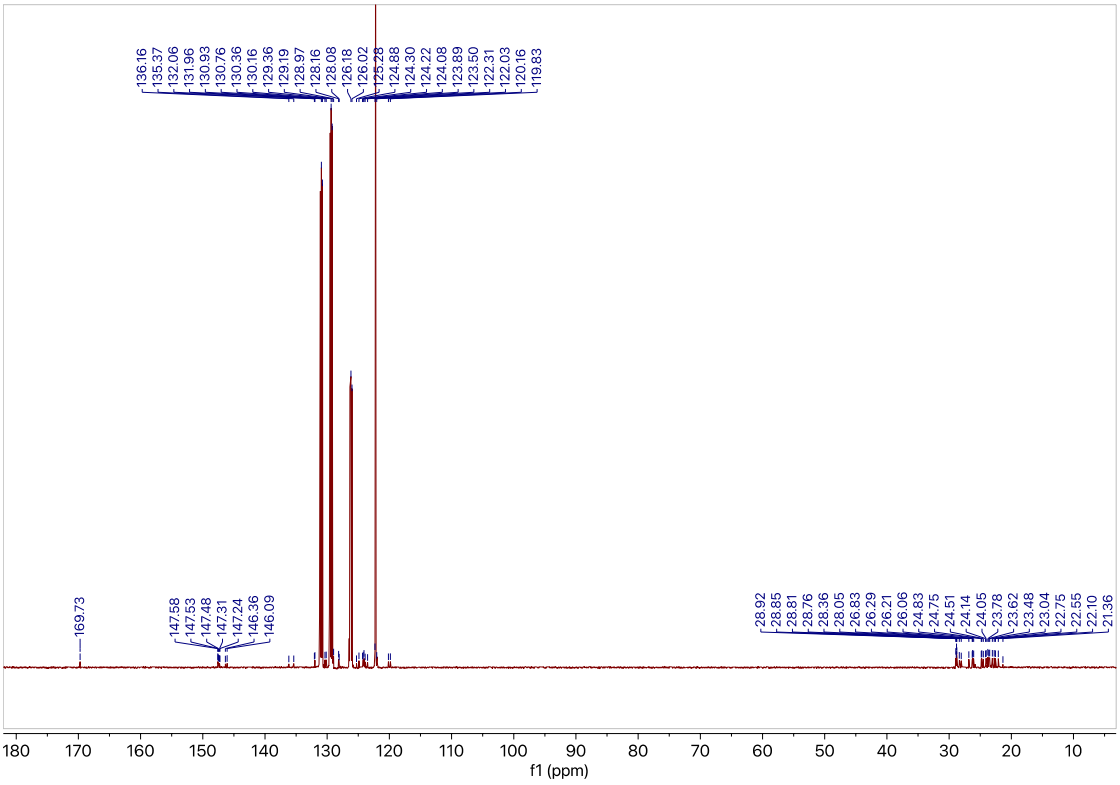

Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of **10** in C_6D_5Br.

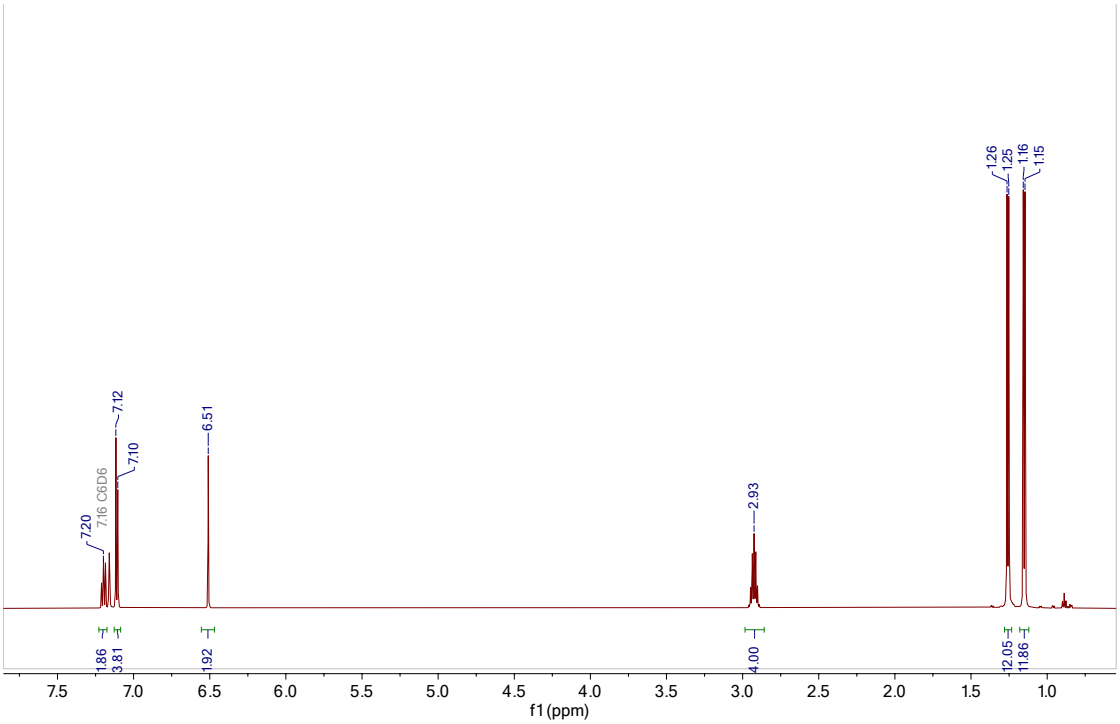

Figure S19. ^{1}H NMR spectrum of **12** in C_6D_6.

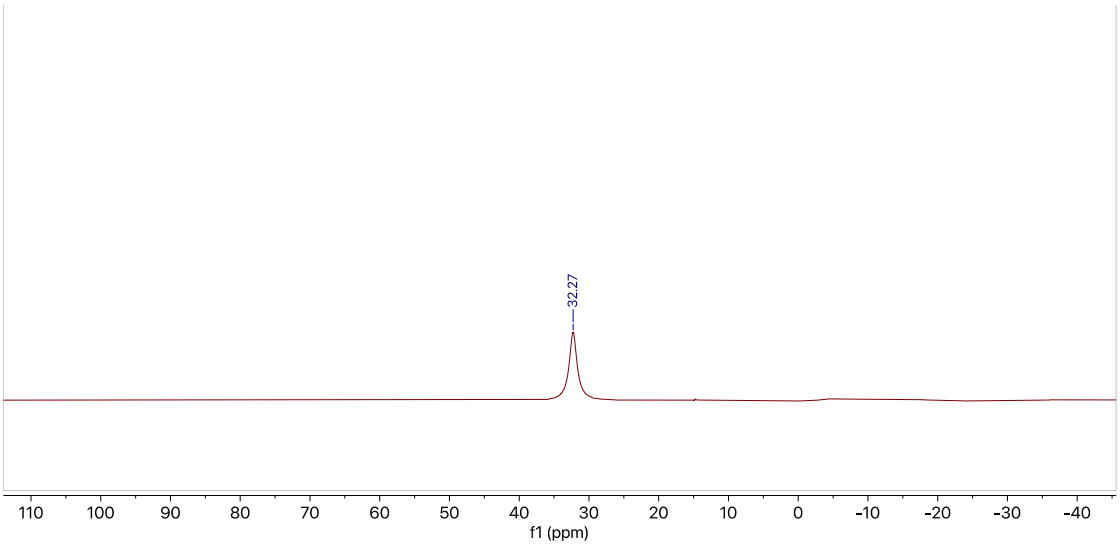

Figure S20. ^{11}B NMR spectrum of **12** in C_6D_6.

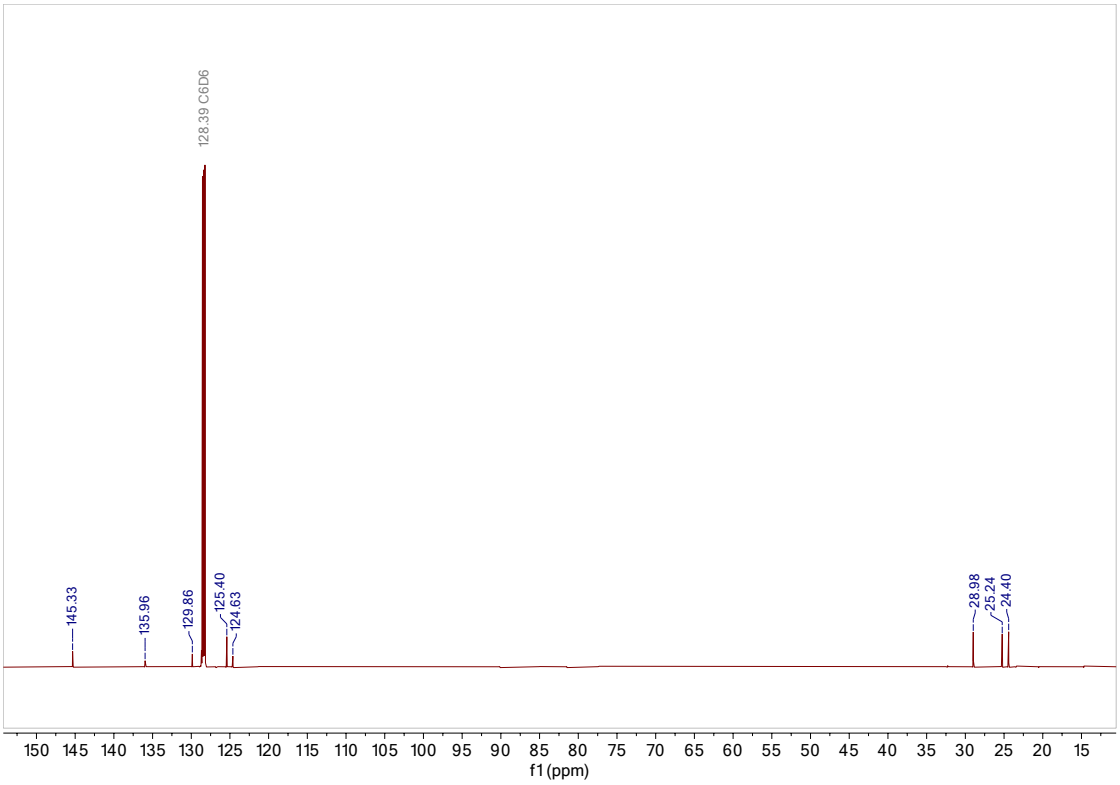

Figure S21. $^{13}C\{^1H\}$ NMR spectrum of **12** in C_6D_6.

SUPPORTING INFORMATION of COMPUTATIONS

All computations employed the Gaussian 16 (Revision C.01) program:

Gaussian 16, Revision C.01,
M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria,
M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone,
G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich,
J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian,
J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young,
F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone,
T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega,
G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda,
J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai,
T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta,
F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin,
V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand,
K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar,
J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi,
J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas,
J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.

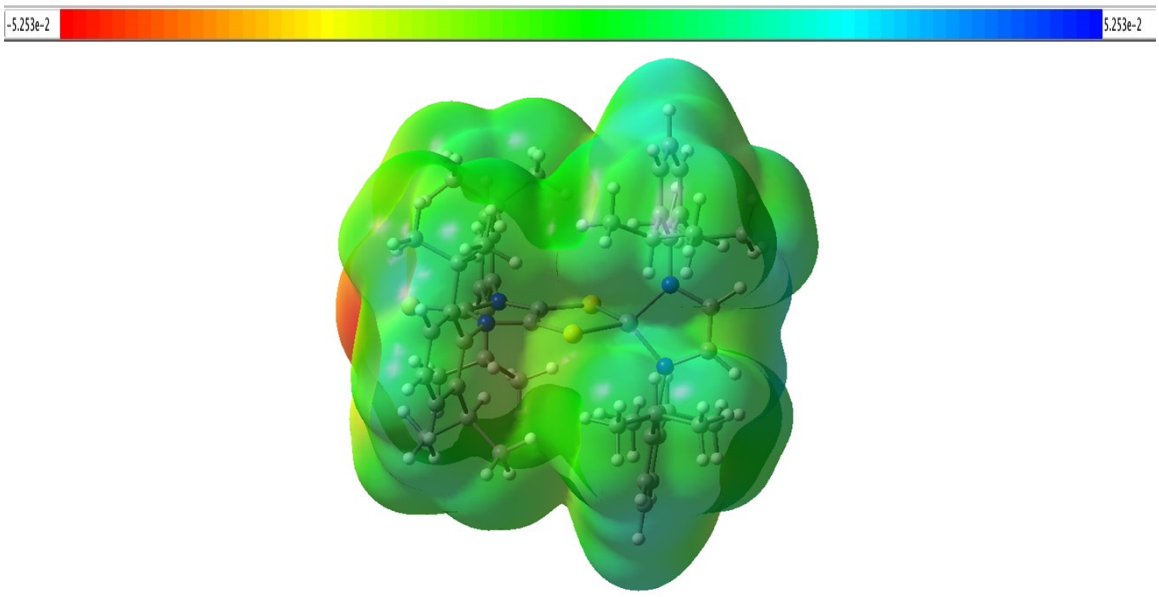

Figure S22. The electrostatic potential map of **4** at B3LYP/6-311G** level of theory.

Table S1. Coordinates of the B3LYP/6-311G** geometry of **5-Ph**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	-1.898039	-0.066705	0.764901
2	16	0	4.578433	1.358503	0.176463
3	16	0	-0.254635	-0.735732	2.012058
4	16	0	-0.891079	1.093026	-0.764474
5	5	0	5.462266	-0.303617	-0.585968
6	5	0	-5.408021	-0.413229	-0.582601
7	35	0	4.043075	-1.593299	-1.316906
8	35	0	6.561300	-1.191365	0.855730
9	35	0	6.638412	0.398286	-2.071896
10	35	0	-5.679470	-2.040468	-1.725383
11	35	0	-7.205291	0.261574	0.141091
12	35	0	-4.443330	1.072733	-1.639734
13	7	0	2.320995	0.193416	1.313256
14	7	0	1.908401	1.368791	-0.487625
15	7	0	-3.070440	-1.267027	0.473862
16	7	0	-3.141289	0.963333	1.624772
17	6	0	2.908631	0.940434	0.336044
18	6	0	0.955817	0.138364	1.083341
19	6	0	0.696794	0.873095	-0.032767
20	6	0	2.061949	2.212632	-1.652046
21	6	0	2.652332	1.700488	-2.802484
22	6	0	2.770093	2.526479	-3.916772
23	1	0	3.239804	2.142445	-4.813932
24	6	0	2.294900	3.835508	-3.877155
25	1	0	2.390042	4.471642	-4.749324
26	6	0	1.702357	4.331745	-2.717642
27	1	0	1.337317	5.351183	-2.683496
28	6	0	1.585427	3.519897	-1.593269
29	6	0	2.981201	-0.428216	2.438309
30	6	0	3.130680	-1.810521	2.455820
31	6	0	3.725603	-2.406772	3.564234
32	1	0	3.860295	-3.481201	3.583392
33	6	0	4.168904	-1.624452	4.627126
34	1	0	4.642451	-2.092947	5.481878
35	6	0	4.019179	-0.239014	4.590008
36	1	0	4.375120	0.370487	5.411857
37	6	0	3.417282	0.368350	3.493151
38	6	0	-4.434241	-0.815719	0.774962
39	1	0	-5.026724	-1.571657	1.296813
40	6	0	-4.323476	0.404706	1.549616
41	1	0	-5.194175	0.895572	1.967097
42	6	0	-2.951879	2.288665	2.161521
43	6	0	-3.720572	3.341226	1.664756
44	6	0	-3.540800	4.617529	2.190754
45	1	0	-4.134458	5.438964	1.808109
46	6	0	-2.597599	4.839084	3.191920
47	1	0	-2.460392	5.834908	3.596284
48	6	0	-1.828203	3.780680	3.671797
49	1	0	-1.097748	3.949087	4.454070
50	6	0	-1.998941	2.498440	3.157572
51	6	0	-2.784988	-2.607389	0.053006
52	6	0	-3.221239	-3.691750	0.818316
53	6	0	-2.903659	-4.988471	0.429230
54	1	0	-3.253681	-5.825177	1.022645
55	6	0	-2.129003	-5.212485	-0.707825
56	1	0	-1.877794	-6.223810	-1.004704
57	6	0	-1.683101	-4.130430	-1.461388
58	1	0	-1.088286	-4.294454	-2.352194
59	6	0	-2.018283	-2.830541	-1.091245
60	1	0	-1.417613	1.669200	3.540279
61	1	0	-4.425376	3.162666	0.861353
62	1	0	-3.802847	-3.523199	1.717283
63	1	0	-1.716327	-1.992327	-1.707206
64	1	0	1.138757	3.895539	-0.680511
65	1	0	3.024311	0.684133	-2.814518
66	1	0	2.817057	-2.399291	1.603755
67	1	0	3.299125	1.443559	3.445736

Table S2. Coordinates of the B3LYP/6-311G** geometry of **6** (in C_{2h} symmetry).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	-4.724339	0.911088	-0.000017
2	35	0	-2.293473	3.148450	-0.000010
3	5	0	-2.816248	1.269985	-0.000006
4	7	0	-1.864929	0.232116	0.000000
5	6	0	-0.468045	0.479345	-0.000001
6	1	0	-0.201902	1.524664	-0.000014
7	6	0	-2.286547	-1.165326	0.000007
8	6	0	-2.472814	-1.821185	1.232034
9	6	0	-2.882502	-3.157324	1.201835
10	1	0	-3.042029	-3.684605	2.135267
11	6	0	-3.089810	-3.820628	0.000018
12	1	0	-3.409730	-4.856679	0.000023
13	6	0	-2.882494	-3.157337	-1.201805
14	1	0	-3.042014	-3.684627	-2.135232
15	6	0	-2.472805	-1.821199	-1.232014
16	6	0	-2.251572	-1.139707	-2.578958
17	1	0	-1.909514	-0.120845	-2.389872
18	6	0	-1.152609	-1.843952	-3.397287
19	1	0	-0.214992	-1.903109	-2.840140
20	1	0	-1.444904	-2.862257	-3.668640
21	1	0	-0.963334	-1.295950	-4.324753
22	6	0	-3.558360	-1.044328	-3.389734
23	1	0	-4.337826	-0.524898	-2.829242
24	1	0	-3.386095	-0.498036	-4.321656
25	1	0	-3.936868	-2.036569	-3.651677
26	6	0	-2.251593	-1.139679	2.578973
27	1	0	-1.909531	-0.120819	2.389879
28	6	0	-1.152637	-1.843917	3.397319
29	1	0	-0.215015	-1.903076	2.840182
30	1	0	-0.963373	-1.295908	4.324782
31	1	0	-1.444933	-2.862220	3.668676
32	6	0	-3.558388	-1.044291	3.389736
33	1	0	-3.386132	-0.497986	4.321651
34	1	0	-4.337850	-0.524869	2.829230
35	1	0	-3.936897	-2.036530	3.651689
36	35	0	4.724339	-0.911087	0.000009
37	35	0	2.293474	-3.148451	0.000013
38	5	0	2.816248	-1.269985	0.000011
39	7	0	1.864929	-0.232116	0.000007
40	6	0	0.468045	-0.479346	0.000011
41	1	0	0.201902	-1.524665	0.000023
42	6	0	2.286547	1.165326	-0.000004
43	6	0	2.472809	1.821181	-1.232033
44	6	0	2.882497	3.157320	-1.201841
45	1	0	3.042019	3.684597	-2.135276
46	6	0	3.089809	3.820628	-0.000027
47	1	0	3.409729	4.856679	-0.000036
48	6	0	2.882498	3.157340	1.201799
49	1	0	3.042022	3.684634	2.135224
50	6	0	2.472809	1.821202	1.232015
51	6	0	2.251582	1.139715	2.578962
52	1	0	1.909521	0.120853	2.389882
53	6	0	1.152624	1.843967	3.397294
54	1	0	0.215005	1.903123	2.840151
55	1	0	1.444923	2.862272	3.668641
56	1	0	0.963353	1.295969	4.324762
57	6	0	3.558374	1.044338	3.389732
58	1	0	4.337836	0.524904	2.829238
59	1	0	3.386113	0.498050	4.321657
60	1	0	3.936885	2.036580	3.651670
61	6	0	2.251581	1.139670	-2.578969
62	1	0	1.909522	0.120810	-2.389869
63	6	0	1.152621	1.843904	-3.397312
64	1	0	0.215001	1.903064	-2.840171
65	1	0	0.963353	1.295891	-4.324772
66	1	0	1.444915	2.862206	-3.668674
67	6	0	3.558373	1.044280	-3.389738
68	1	0	3.386113	0.497971	-4.321651
69	1	0	4.337838	0.524861	-2.829234
70	1	0	3.936880	2.036517	-3.651697

Table S3. Coordinates of the B3LYP/6-311G** geometry of **7**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	-4.361310	-0.649555	-0.503966
2	5	0	3.200403	0.179099	-0.146038
3	35	0	-6.218388	-1.031461	-0.774598
4	35	0	3.781714	-1.705331	0.294418
5	35	0	2.829729	0.413235	-2.127081
6	35	0	4.571890	1.515790	0.523344
7	16	0	1.619915	0.769405	0.943509
8	16	0	-3.124297	-1.969836	-0.317957
9	16	0	-3.729539	1.055900	-0.427546
10	7	0	-0.466891	-0.978713	0.136852
11	7	0	-0.910739	1.184906	0.077570
12	6	0	0.086691	0.266486	0.298303
13	6	0	-1.812787	-0.821238	-0.157638
14	6	0	-2.085209	0.509100	-0.191885
15	6	0	-0.835459	2.632770	0.219525
16	6	0	-1.101401	3.187794	1.485364
17	6	0	-1.104366	4.581296	1.583236
18	1	0	-1.297582	5.044855	2.543156
19	6	0	-0.862412	5.379813	0.474367
20	1	0	-0.870762	6.459416	0.573294
21	6	0	-0.603054	4.800535	-0.760126
22	1	0	-0.407950	5.436096	-1.614421
23	6	0	-0.578381	3.412628	-0.923104
24	6	0	-0.298200	2.817581	-2.298410
25	1	0	-0.038086	1.765562	-2.166653
26	6	0	0.904559	3.485662	-2.987272
27	1	0	1.147528	2.946161	-3.905691
28	1	0	0.690207	4.522065	-3.262913
29	1	0	1.789027	3.468389	-2.349816
30	6	0	-1.546480	2.892643	-3.201182
31	1	0	-1.336742	2.434764	-4.171772
32	1	0	-2.403254	2.375751	-2.763306
33	1	0	-1.839259	3.932033	-3.376763
34	6	0	-1.377233	2.354604	2.732758
35	1	0	-1.316701	1.298126	2.462724
36	6	0	-2.797564	2.602157	3.276851
37	1	0	-2.990570	1.954382	4.136506
38	1	0	-2.921575	3.636846	3.607362
39	1	0	-3.559879	2.399347	2.521075
40	6	0	-0.317686	2.604707	3.822857
41	1	0	-0.495973	1.946907	4.678149
42	1	0	0.689550	2.414599	3.448942
43	1	0	-0.356482	3.635492	4.185178
44	6	0	0.112732	-2.293074	0.394145
45	6	0	0.175050	-2.731276	1.730787
46	6	0	0.624559	-4.034243	1.954424
47	1	0	0.696691	-4.401844	2.970799
48	6	0	0.971922	-4.866252	0.900103
49	1	0	1.313181	-5.876167	1.097607
50	6	0	0.891136	-4.406512	-0.406045
51	1	0	1.178565	-5.062138	-1.217998
52	6	0	0.468805	-3.107156	-0.699286
53	6	0	0.425272	-2.653993	-2.157105
54	1	0	0.327129	-1.566224	-2.171721
55	6	0	1.727158	-2.997958	-2.905819
56	1	0	2.606007	-2.652766	-2.363669
57	1	0	1.818795	-4.075310	-3.071641
58	1	0	1.722980	-2.515245	-3.886213
59	6	0	-0.775948	-3.260270	-2.911298
60	1	0	-0.778777	-2.912213	-3.948042
61	1	0	-0.712998	-4.352312	-2.926887
62	1	0	-1.732968	-2.989317	-2.464022
63	6	0	-0.238280	-1.878672	2.925549
64	1	0	-0.490235	-0.879607	2.567040
65	6	0	0.914881	-1.713488	3.932444
66	1	0	0.618779	-1.029210	4.732542
67	1	0	1.180496	-2.667337	4.396017
68	1	0	1.805610	-1.310941	3.448249
69	6	0	-1.496734	-2.448761	3.609245
70	1	0	-1.807462	-1.799330	4.432715
71	1	0	-2.332293	-2.534366	2.909830
72	1	0	-1.306847	-3.442499	4.023688

Table S4. Coordinates of the mPW1PW91/LANL2DZ geometry of **8-Ph**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	-1.971962	0.110272	0.888956
2	16	0	4.666882	1.540215	0.349441
3	16	0	-0.253799	-0.546686	2.194257
4	16	0	-0.885018	1.334330	-0.647631
5	5	0	5.548426	-0.184280	-0.392153
6	5	0	-5.472679	-0.445538	-0.329589
7	53	0	3.946714	-1.640265	-1.136056
8	53	0	6.792924	-1.109783	1.234424
9	53	0	6.827055	0.542701	-2.107780
10	53	0	-7.475173	0.376369	0.431398
11	53	0	-4.388403	1.110891	-1.621066
12	53	0	-5.827169	-2.329746	-1.485866
13	7	0	2.347235	0.395015	1.483219
14	7	0	1.950987	1.578478	-0.331527
15	7	0	-3.103777	-1.175576	0.720206
16	7	0	-3.239548	1.119004	1.749898
17	6	0	2.949619	1.135107	0.498926
18	6	0	0.976970	0.349667	1.245879
19	6	0	0.728348	1.092144	0.123395
20	6	0	2.113310	2.431008	-1.486481
21	6	0	2.904890	2.010109	-2.559852
22	6	0	3.038448	2.854105	-3.669322
23	1	0	3.659304	2.541042	-4.500353
24	6	0	2.379012	4.091155	-3.703612
25	1	0	2.485660	4.737870	-4.567449
26	6	0	1.584506	4.495585	-2.620158
27	1	0	1.077353	5.453418	-2.642318
28	6	0	1.451963	3.666676	-1.500105
29	6	0	3.003345	-0.232794	2.605239
30	6	0	2.935101	-1.623985	2.740030
31	6	0	3.538136	-2.224288	3.851768
32	1	0	3.504977	-3.302052	3.960275
33	6	0	4.203698	-1.439095	4.803342
34	1	0	4.680901	-1.910546	5.655293
35	6	0	4.269397	-0.046399	4.647276
36	1	0	4.796858	0.559368	5.375085
37	6	0	3.662794	0.567246	3.545854
38	6	0	-4.480075	-0.769630	1.032712
39	1	0	-5.039903	-1.538370	1.573948
40	6	0	-4.401077	0.487762	1.772411
41	1	0	-5.267847	0.929548	2.248379
42	6	0	-3.066938	2.468949	2.218816
43	6	0	-4.039658	3.432825	1.910347
44	6	0	-3.870269	4.743380	2.371778
45	1	0	-4.615515	5.493544	2.133719
46	6	0	-2.735054	5.088804	3.119907
47	1	0	-2.606266	6.106103	3.471702
48	6	0	-1.763310	4.118590	3.407721
49	1	0	-0.886855	4.382899	3.988474
50	6	0	-1.921480	2.803091	2.955839
51	6	0	-2.751126	-2.499384	0.304884
52	6	0	-3.212738	-3.617734	1.019393
53	6	0	-2.809331	-4.900759	0.634405
54	1	0	-3.175259	-5.762786	1.181528
55	6	0	-1.928208	-5.075582	-0.443886
56	1	0	-1.614924	-6.071729	-0.735458
57	6	0	-1.460497	-3.956132	-1.145400
58	1	0	-0.787918	-4.081994	-1.986623
59	6	0	-1.875236	-2.669975	-0.778856
60	1	0	3.403882	1.049023	-2.532600
61	1	0	0.855720	3.979930	-0.649890
62	1	0	3.715987	1.640664	3.408635
63	1	0	2.452067	-2.224350	1.978494
64	1	0	-1.184924	2.046806	3.204612
65	1	0	-4.891732	3.172840	1.290757
66	1	0	-3.874930	-3.492259	1.869215
67	1	0	-1.563721	-1.809357	-1.363117

Table S5. Coordinates of the mPW1PW91/LANL2DZ geometry of **9-Ph**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	53	0	-7.228593	-1.104678	1.520224
2	53	0	-6.550760	-1.094208	-2.146540
3	53	0	-5.060904	1.558612	0.032249
4	53	0	0.853050	4.650568	0.182969
5	53	0	8.167792	-0.090787	-0.319559
6	53	0	7.160660	-3.639027	-0.090604
7	14	0	1.303380	2.200407	0.133511
8	16	0	-4.141541	-1.893856	0.274954
9	16	0	0.352829	1.104075	1.883848
10	16	0	0.238838	1.158417	-1.586080
11	5	0	-5.730768	-0.624030	-0.106136
12	5	0	6.577162	-1.555396	-0.111044
13	7	0	-1.982926	-0.432982	1.299841
14	7	0	-2.056825	-0.393430	-0.899904
15	7	0	3.015225	1.890738	0.083503
16	7	0	5.220892	-1.167713	0.005201
17	6	0	-2.706452	-0.856899	0.213841
18	6	0	-0.890154	0.310279	0.860332
19	6	0	-0.941913	0.342549	-0.509069
20	6	0	-2.434434	-0.639446	-2.271187
21	6	0	-2.402571	-1.949676	-2.762719
22	6	0	-2.742375	-2.177509	-4.100769
23	1	0	-2.736934	-3.188880	-4.490757
24	6	0	-3.097340	-1.103504	-4.930640
25	1	0	-3.365744	-1.285765	-5.965369
26	6	0	-3.122080	0.202375	-4.421591
27	1	0	-3.416137	1.030124	-5.056285
28	6	0	-2.793775	0.442502	-3.082040
29	6	0	-2.266349	-0.729969	2.683738
30	6	0	-1.299408	-1.421152	3.426598
31	6	0	-1.551493	-1.703282	4.774245
32	1	0	-0.811717	-2.238429	5.358930
33	6	0	-2.762176	-1.305199	5.361219
34	1	0	-2.958888	-1.531937	6.403288
35	6	0	-3.720445	-0.619959	4.600640
36	1	0	-4.660648	-0.318205	5.046879
37	6	0	-3.475838	-0.321313	3.254446
38	6	0	3.470527	0.545105	0.088938
39	1	0	2.692182	-0.203613	0.178939
40	6	0	4.768076	0.185244	-0.005767
41	1	0	5.549115	0.927413	-0.097045
42	6	0	4.179855	-2.174975	0.145005
43	6	0	3.806440	-2.609591	1.423227
44	6	0	2.800991	-3.577052	1.555994
45	1	0	2.521856	-3.931335	2.542467
46	6	0	2.168319	-4.096968	0.416080
47	1	0	1.396506	-4.851902	0.520646
48	6	0	2.541949	-3.646768	-0.859585
49	1	0	2.059227	-4.050644	-1.742718
50	6	0	3.548267	-2.681007	-0.998242
51	6	0	3.996240	2.950213	0.006478
52	6	0	4.552742	3.468773	1.185071
53	6	0	5.504004	4.494831	1.108854
54	1	0	5.932431	4.901221	2.018372
55	6	0	5.898105	4.997478	-0.140598
56	1	0	6.632849	5.793144	-0.197303
57	6	0	5.342952	4.470757	-1.316505
58	1	0	5.647271	4.857699	-2.282719
59	6	0	4.391686	3.444035	-1.245505
60	1	0	-4.208617	0.216198	2.664911
61	1	0	-0.375977	-1.743571	2.957469
62	1	0	-2.843490	1.441798	-2.667049
63	1	0	-2.134868	-2.771104	-2.108844
64	1	0	4.238699	3.070079	2.143648
65	1	0	3.957025	3.025054	-2.146823
66	1	0	4.310492	-2.204844	2.293912
67	1	0	3.853381	-2.330220	-1.977913

Table S6. Coordinates of the B3LYP/6-311G** geometry of **10-Ph**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	1.889172	1.280338	-0.694905
2	16	0	-1.666300	-4.296898	0.196174
3	16	0	-2.424241	1.103888	-0.594508
4	16	0	0.756390	0.590472	1.024859
5	17	0	0.812556	0.795442	-2.416781
6	17	0	-3.371056	0.792140	2.398000
7	17	0	-4.252223	3.145887	0.681654
8	5	0	-3.344151	1.646963	0.866215
9	7	0	-2.229590	-1.657861	-0.284276
10	7	0	-0.276246	-1.974197	0.659095
11	7	0	2.258638	2.959479	-0.433269
12	7	0	3.571018	0.841829	-0.812281
13	6	0	-1.389860	-2.653053	0.188484
14	6	0	-1.654752	-0.398626	-0.083405
15	6	0	-0.429250	-0.591444	0.478641
16	6	0	0.782326	-2.607001	1.397064
17	6	0	0.761640	-2.553654	2.788562
18	6	0	1.781029	-3.164814	3.512106
19	1	0	1.769094	-3.125929	4.595096
20	6	0	2.807045	-3.830404	2.844558
21	1	0	3.598541	-4.309657	3.409416
22	6	0	2.814929	-3.883712	1.452532
23	1	0	3.611732	-4.398033	0.929789
24	6	0	1.800402	-3.270995	0.722556
25	6	0	-3.505606	-1.904399	-0.896366
26	6	0	-3.607041	-1.914064	-2.284481
27	6	0	-4.847184	-2.133709	-2.877619
28	1	0	-4.931876	-2.142469	-3.957941
29	6	0	-5.972443	-2.347366	-2.084493
30	1	0	-6.936564	-2.521152	-2.548402
31	6	0	-5.859158	-2.343400	-0.695468
32	1	0	-6.732124	-2.516816	-0.077252
33	6	0	-4.622975	-2.121904	-0.095550
34	6	0	3.664745	3.139624	-0.478722
35	1	0	4.070241	4.137340	-0.428800
36	6	0	4.361223	2.012443	-0.676987
37	1	0	5.428172	1.940202	-0.816018
38	6	0	4.195493	-0.430122	-0.939330
39	6	0	5.259115	-0.776528	-0.097307
40	6	0	5.906018	-1.998351	-0.250506
41	1	0	6.730490	-2.250909	0.406758
42	6	0	5.490881	-2.899351	-1.229681
43	1	0	5.997300	-3.850192	-1.348366
44	6	0	4.422756	-2.563563	-2.058240
45	1	0	4.096389	-3.251066	-2.830541
46	6	0	3.781974	-1.334187	-1.923857
47	6	0	1.395461	4.023857	-0.057205
48	6	0	1.767742	4.916122	0.955701
49	6	0	0.922430	5.961845	1.313047
50	1	0	1.223802	6.644331	2.099815
51	6	0	-0.309601	6.122645	0.682499
52	1	0	-0.969172	6.933351	0.968519
53	6	0	-0.685078	5.230446	-0.319065
54	1	0	-1.638081	5.346985	-0.822208
55	6	0	0.163754	4.194219	-0.697968
56	1	0	-0.050452	-2.045206	3.294010
57	1	0	1.791696	-3.311581	-0.358416
58	1	0	5.565386	-0.089467	0.682596
59	1	0	2.982918	-1.062490	-2.601548
60	1	0	-2.720899	-1.757810	-2.887452
61	1	0	-4.516185	-2.128218	0.981715
62	1	0	-0.120411	3.528135	-1.503072
63	1	0	2.708211	4.774673	1.474769

SUPPORTING INFORMATION of X-RAY

Compound **5·(toluene)$_2$**

Table S7. Sample and crystal data for Compound **5·(toluene)$_2$**.

Identification code	**5·(toluene)$_2$**	
Chemical formula	$C_{67}H_{86}B_2Br_6N_4S_3Si$	
Formula weight	1572.74 g/mol	
Temperature	135(2) K	
Wavelength	0.71073 Å	
Crystal size	0.140 x 0.230 x 0.300 mm	
Crystal system	triclinic	
Space group	P-1 (No. 2)	
Unit cell dimensions	a = 11.0692(8) Å	α = 81.044(2)°
	b = 16.5906(12) Å	β = 83.385(2)°
	c = 21.0529(15) Å	γ = 71.370(2)°
Volume	3610.1(5) Å^3	
Z	2	
Density (calculated)	1.447 g/cm^3	
Absorption coefficient	3.480 mm^{-1}	
F(000)	1596	

Table S8. Data collection and structure refinement for **5·(toluene)$_2$**.

Theta range for data collection	1.95 to 34.34°	
Index ranges	-17<=h<=17, -26<=k<=26, -33<=l<=33	
Reflections collected	178861	
Independent reflections	30247 [R(int) = 0.0920]	
Max. and min. transmission	0.7470 and 0.3820	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	30247 / 514 / 863	
Goodness-of-fit on F^2	1.025	
Δ/σ_{max}	0.002	
Final R indices	18897data; I>2σ(I)	R1 = 0.0441, wR2 = 0.0909
	all data	R1 = 0.0984, wR2 = 0.1072
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0421P)^2+0.8911P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.998 and -1.256 eÅ^{-3}	
R.M.S. deviation from mean	0.112 eÅ^{-3}	

Table S9. Bond lengths (Å) for **5·(toluene)$_2$**.

Si1-N3	1.6797(18)	Si1-N4	1.8197(18)
Si1-S2	2.1312(7)	Si1-S3	2.1444(8)
S1-C1	1.725(2)	S1-B1	1.932(2)
S2-C2	1.737(2)	S3-C3	1.739(2)
B1-Br1	1.990(2)	B1-Br2	1.996(2)
B1-Br3	2.029(2)	B2-C28	1.656(3)
B2-Br4	1.983(3)	B2-Br6	2.024(3)
B2-Br5	2.045(3)	N1-C1	1.364(2)
N1-C2	1.387(3)	N1-C16	1.456(2)
N2-C1	1.358(2)	N2-C3	1.375(3)
N2-C4	1.462(2)	N3-C42	1.452(3)
N3-C28	1.479(3)	N4-C29	1.293(3)
N4-C30	1.459(3)	C2-C3	1.353(3)
C4-C5	1.399(3)	C4-C9	1.392(3)
C5-C6	1.395(3)	C5-C13	1.513(3)
C6-C7	1.380(3)	C7-C8	1.376(3)
C8-C9	1.407(3)	C9-C10	1.515(3)
C10-C12	1.525(3)	C10-C11	1.525(3)
C13-C14	1.531(3)	C13-C15	1.536(3)
C16-C21	1.408(3)	C16-C17	1.395(3)
C17-C18	1.394(3)	C17-C25	1.521(3)
C18-C19	1.377(3)	C19-C20	1.381(3)
C20-C21	1.391(3)	C21-C22	1.520(3)
C22-C24	1.528(3)	C22-C23	1.525(3)
C25-C26	1.535(3)	C25-C27	1.540(3)
C28-H28	0.95(3)	C28-C29	1.462(3)
C29-H29	0.94(3)	C30-C31	1.405(3)
C30-C35	1.399(3)	C31-C32	1.394(3)
C31-C39	1.518(3)	C32-C33	1.376(4)
C33-C34	1.382(4)	C34-C35	1.390(3)
C35-C36	1.525(3)	C36-C38	1.525(3)
C36-C37	1.528(4)	C39-C40	1.516(4)
C39-C41	1.530(4)	C42-C47	1.397(3)
C42-C43	1.409(3)	C43-C44	1.393(3)
C43-C51	1.518(3)	C44-C45	1.373(4)
C45-C46	1.377(4)	C46-C47	1.397(3)
C47-C48	1.519(3)	C48-C49	1.525(4)
C48-C50	1.536(4)	C51-C53	1.536(3)
C51-C52	1.529(3)	C54-C60	1.501(10)
C54-C55	1.39	C54-C59	1.39

C55-C56	1.39	C56-C57	1.39
C57-C58	1.39	C58-C59	1.39
C54'-C59'	1.381(13)	C54'-C60'	1.541(12)
C54'-C55'	1.414(13)	C55'-C56'	1.410(14)
C56'-C57'	1.373(15)	C57'-C58'	1.344(14)
C58'-C59'	1.372(14)	C61-C62	1.39
C61-C66	1.39	C61-C67	1.595(10)
C62-C63	1.39	C63-C64	1.39
C64-C65	1.39	C65-C66	1.39
C61'-C62'	1.418(14)	C61'-C67'	1.562(12)
C61'-C66'	1.415(14)	C62'-C63'	1.371(14)
C63'-C64'	1.380(14)	C64'-C65'	1.343(15)
C65'-C66'	1.395(16)		

Table S10. Bond angles (°) for **5·(toluene)$_2$**.

N3-Si1-N4	91.15(8)	N3-Si1-S2	113.49(6)
N4-Si1-S2	116.63(6)	N3-Si1-S3	125.15(7)
N4-Si1-S3	107.84(6)	S2-Si1-S3	102.98(3)
C1-S1-B1	107.44(10)	C2-S2-Si1	93.66(7)
C3-S3-Si1	93.26(7)	S1-B1-Br1	111.59(11)
S1-B1-Br2	112.55(12)	Br1-B1-Br2	111.33(11)
S1-B1-Br3	100.91(11)	Br1-B1-Br3	111.54(11)
Br2-B1-Br3	108.45(11)	C28-B2-Br4	109.81(16)
C28-B2-Br6	110.17(15)	Br4-B2-Br6	111.45(13)
C28-B2-Br5	108.60(15)	Br4-B2-Br5	109.16(12)
Br6-B2-Br5	107.59(12)	C1-N1-C2	108.02(15)
C1-N1-C16	129.32(17)	C2-N1-C16	122.03(16)
C1-N2-C3	109.22(16)	C1-N2-C4	126.36(17)
C3-N2-C4	122.08(16)	C42-N3-C28	121.86(17)
C42-N3-Si1	124.88(14)	C28-N3-Si1	111.75(13)
C29-N4-C30	124.46(18)	C29-N4-Si1	110.06(14)
C30-N4-Si1	125.49(14)	N2-C1-N1	107.36(17)
N2-C1-S1	121.35(15)	N1-C1-S1	130.61(14)
C3-C2-N1	108.05(17)	C3-C2-S2	124.80(16)
N1-C2-S2	127.09(14)	N2-C3-C2	107.34(17)
N2-C3-S3	127.55(14)	C2-C3-S3	125.11(16)
C5-C4-C9	124.04(18)	C5-C4-N2	119.43(17)
C9-C4-N2	116.43(17)	C6-C5-C4	116.25(19)
C6-C5-C13	119.58(19)	C4-C5-C13	124.17(18)
C7-C6-C5	121.5(2)	C8-C7-C6	120.64(19)
C7-C8-C9	120.7(2)	C4-C9-C8	116.83(19)
C4-C9-C10	123.86(18)	C8-C9-C10	119.27(19)
C9-C10-C12	112.39(19)	C9-C10-C11	110.63(19)
C12-C10-C11	110.86(19)	C5-C13-C14	110.60(19)
C5-C13-C15	110.86(18)	C14-C13-C15	110.25(19)
C21-C16-C17	123.72(18)	C21-C16-N1	116.74(17)
C17-C16-N1	119.26(18)	C16-C17-C18	116.5(2)
C16-C17-C25	125.56(18)	C18-C17-C25	117.96(19)
C19-C18-C17	121.7(2)	C18-C19-C20	120.2(2)
C19-C20-C21	121.3(2)	C16-C21-C20	116.51(19)
C16-C21-C22	124.02(18)	C20-C21-C22	119.43(19)
C21-C22-C24	110.01(19)	C21-C22-C23	112.87(19)
C24-C22-C23	111.5(2)	C17-C25-C26	112.7(2)
C17-C25-C27	110.21(18)	C26-C25-C27	108.55(18)
H28-C28-N3	110.5(16)	H28-C28-C29	107.7(16)
N3-C28-C29	106.47(17)	H28-C28-B2	106.7(16)
N3-C28-B2	115.42(17)	C29-C28-B2	109.90(18)
H29-C29-N4	117.6(15)	H29-C29-C28	125.2(15)
N4-C29-C28	117.20(19)	C31-C30-C35	123.6(2)
C31-C30-N4	119.38(19)	C35-C30-N4	116.95(18)
C30-C31-C32	116.4(2)	C30-C31-C39	123.0(2)
C32-C31-C39	120.5(2)	C33-C32-C31	121.4(2)

C34-C33-C32	120.5(2)	C33-C34-C35	121.2(2)
C34-C35-C30	116.6(2)	C34-C35-C36	121.3(2)
C30-C35-C36	121.6(2)	C35-C36-C38	114.8(2)
C35-C36-C37	108.5(2)	C38-C36-C37	110.5(2)
C40-C39-C31	113.7(2)	C40-C39-C41	110.0(2)
C31-C39-C41	109.6(2)	C47-C42-C43	121.33(19)
C47-C42-N3	119.90(19)	C43-C42-N3	118.62(18)
C44-C43-C42	118.3(2)	C44-C43-C51	117.7(2)
C42-C43-C51	123.96(19)	C45-C44-C43	120.9(2)
C46-C45-C44	120.1(2)	C45-C46-C47	121.6(2)
C42-C47-C46	117.7(2)	C42-C47-C48	123.52(19)
C46-C47-C48	118.5(2)	C47-C48-C49	109.0(2)
C47-C48-C50	113.0(2)	C49-C48-C50	110.2(2)
C43-C51-C53	111.5(2)	C43-C51-C52	111.0(2)
C53-C51-C52	111.0(2)	C60-C54-C55	119.3(9)
C60-C54-C59	120.7(9)	C55-C54-C59	120.0
C56-C55-C54	120.0	C55-C56-C57	120.0
C58-C57-C56	120.0	C57-C58-C59	120.0
C58-C59-C54	120.0	C59'-C54'-C60'	114.5(12)
C59'-C54'-C55'	119.5(12)	C60'-C54'-C55'	126.0(13)
C56'-C55'-C54'	114.4(13)	C57'-C56'-C55'	123.4(14)
C56'-C57'-C58'	121.0(15)	C59'-C58'-C57'	117.1(15)
C58'-C59'-C54'	123.8(13)	C62-C61-C66	120.0
C62-C61-C67	99.9(7)	C66-C61-C67	123.7(7)
C63-C62-C61	120.0	C62-C63-C64	120.0
C65-C64-C63	120.0	C64-C65-C66	120.0
C65-C66-C61	120.0	C62'-C61'-C67'	105.7(13)
C62'-C61'-C66'	115.5(12)	C67'-C61'-C66'	96.9(14)
C63'-C62'-C61'	120.5(13)	C64'-C63'-C62'	121.5(13)
C65'-C64'-C63'	114.2(14)	C66'-C65'-C64'	121.1(16)
C65'-C66'-C61'	113.9(15)		

Compound **6**

Table S11. Sample and crystal data for Compound **6**.

Identification code	**6**	
Chemical formula	$C_{26}H_{36}B_2Br_4N_2$	
Formula weight	717.83 g/mol	
Temperature	135(2) K	
Wavelength	0.71073 Å	
Crystal size	0.160 x 0.240 x 0.300 mm	
Crystal system	triclinic	
Space group	P-1 (No. 2)	
Unit cell dimensions	a = 10.8955(14) Å	α = 73.361(5)°
	b = 12.618(2) Å	β = 89.927(4)°
	c = 12.7576(15) Å	γ = 64.433(4)°
Volume	1500.7(4) $Å^3$	
Z	2	
Density (calculated)	1.589 g/cm^3	
Absorption coefficient	5.381 mm^{-1}	
F(000)	712	

Table S12. Data collection and structure refinement for **6**.

Theta range for data collection	1.89 to 27.10°
Index ranges	-13<=h<=13, -16<=k<=16, -16<=l<=16
Reflections collected	45339
Independent reflections	6613 [R(int) = 0.0741]
Coverage of independent reflections	99.9%
Absorption correction	Multi-Scan
Max. and min. transmission	0.7456 and 0.3306
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	6613 / 12 / 308
Goodness-of-fit on F^2	1.015
Final R indices	5372 data; I>2σ(I) R1 = 0.0441, wR2 = 0.1105
	all data R1 = 0.0627, wR2 = 0.1206
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0647P)^2+2.2327P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.714 and -1.173 eÅ^{-3}
R.M.S. deviation from mean	0.125 eÅ^{-3}

Table S13. Bond lengths (Å) for **6**.

Br1-B1	1.905(5)	Br2-B1	1.919(5)
Br3-B2	1.919(5)	Br4-B2	1.918(5)
B1-N1	1.387(6)	B2-N2	1.378(6)
N1-C1	1.430(5)	N1-C2	1.449(5)
N2-C14	1.425(5)	N2-C15	1.466(5)
C1-C1#1	1.310(9)	C2-C3	1.404(8)
C2-C7	1.381(7)	C3-C4	1.395(8)
C3-C11	1.509(8)	C4-C5	1.383(8)
C5-C6	1.370(8)	C6-C7	1.412(7)
C7-C8	1.526(8)	C8-C10	1.509(8)
C8-C9	1.522(8)	C11-C13	1.529(8)
C11-C12	1.537(9)	C14-C14#2	1.319(9)
C15-C16	1.374(8)	C15-C20	1.394(7)
C16-C17	1.396(7)	C16-C24	1.516(8)
C17-C18	1.354(9)	C18-C19	1.405(9)
C19-C20	1.396(7)	C20-C21	1.535(8)
C21-C22	1.520(8)	C21-C23	1.537(9)
C24-C26	1.506(9)	C24-C25	1.524(9)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1, -y+1, -z+2
#2 -x+2, -y+1, -z+1

Table S14. Bond angles (°) for **6**.

N1-B1-Br1	121.5(4)	N1-B1-Br2	121.5(3)
Br1-B1-Br2	117.0(3)	N2-B2-Br4	121.8(4)
N2-B2-Br3	121.3(4)	Br4-B2-Br3	116.8(3)
C1-N1-B1	123.8(4)	C1-N1-C2	114.9(3)
B1-N1-C2	121.3(4)	B2-N2-C14	124.1(4)
B2-N2-C15	120.7(4)	C14-N2-C15	115.2(3)
N1-C1-C1#1	123.5(5)	C3-C2-C7	122.9(4)
C3-C2-N1	118.9(4)	C7-C2-N1	118.1(5)
C2-C3-C4	117.9(5)	C2-C3-C11	123.2(4)
C4-C3-C11	118.9(5)	C5-C4-C3	120.5(5)
C4-C5-C6	120.2(4)	C7-C6-C5	121.7(5)
C6-C7-C2	116.8(5)	C6-C7-C8	120.3(5)
C2-C7-C8	122.9(4)	C10-C8-C9	110.8(5)
C10-C8-C7	112.1(5)	C9-C8-C7	111.2(4)
C13-C11-C3	110.8(5)	C13-C11-C12	112.1(6)
C3-C11-C12	111.7(5)	N2-C14-C14#2	123.2(5)
C16-C15-C20	123.3(4)	C16-C15-N2	119.4(4)
C20-C15-N2	117.2(4)	C15-C16-C17	117.6(5)
C15-C16-C24	123.6(4)	C17-C16-C24	118.8(5)
C18-C17-C16	122.0(5)	C17-C18-C19	119.1(4)
C20-C19-C18	121.2(5)	C19-C20-C15	116.7(5)
C19-C20-C21	120.1(5)	C15-C20-C21	123.1(4)
C22-C21-C23	111.9(5)	C22-C21-C20	111.0(5)
C23-C21-C20	110.1(5)	C26-C24-C16	110.9(5)
C26-C24-C25	110.7(6)	C16-C24-C25	112.3(5)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1, -y+1, -z+2
#2 -x+2, -y+1, -z+1

Compound **7**

Table S15. Sample and crystal data for compound **7**.

Identification code	**7**
Chemical formula	$C_{27}H_{34}B_2Br_4N_2S_3$
Formula weight	824.00 g/mol
Temperature	135(2) K
Wavelength	0.71073 Å
Crystal size	0.140 x 0.230 x 0.290 mm
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
Unit cell dimensions	a = 18.3185(13) Å α = 90°
	b = 9.6977(7) Å β = 94.033(3)°
	c = 18.5961(13) Å γ = 90°
Volume	3295.4(4) $Å^3$
Z	4
Density (calculated)	1.661 g/cm^3
Absorption coefficient	5.096 mm^{-1}
F(000)	1632

Table S16. Data collection and structure refinement for **7**.

Theta range for data collection	2.65 to 27.88°
Index ranges	-24<=h<=24, -12<=k<=12, -24<=l<=24
Reflections collected	109263
Independent reflections	7863 [R(int) = 0.1375]
Max. and min. transmission	0.7457 and 0.4806
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	7863 / 0 / 343
Goodness-of-fit on F^2	1.000
Δ/σ_{max}	0.001
Final R indices	5784 data; I>2σ(I) R1 = 0.0408, wR2 = 0.0783
	all data R1 = 0.0702, wR2 = 0.0877
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0369P)^2+4.5247P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.596 and -0.555 eÅ^{-3}
R.M.S. deviation from mean	0.112 eÅ^{-3}

Table S17. Bond lengths (Å) for **7**.

B1-S3	1.808(4)	B1-S2	1.810(4)
B1-Br1	1.884(4)	B2-S1	1.935(4)
B2-Br2	1.991(4)	B2-Br3	1.997(4)
B2-Br4	2.027(4)	S1-C1	1.723(3)
S2-C2	1.741(3)	S3-C3	1.733(4)
N1-C1	1.366(4)	N1-C2	1.373(4)
N1-C16	1.458(4)	N2-C3	1.371(4)
N2-C1	1.362(4)	N2-C4	1.456(4)
C2-C3	1.347(5)	C4-C5	1.387(5)
C4-C9	1.405(5)	C5-C6	1.394(5)
C5-C13	1.515(5)	C6-C7	1.368(5)
C7-C8	1.382(5)	C8-C9	1.383(5)
C9-C10	1.516(5)	C10-C12	1.526(6)
C10-C11	1.535(5)	C13-C15	1.527(6)
C13-C14	1.535(5)	C16-C17	1.395(5)
C16-C21	1.398(5)	C17-C18	1.384(5)
C17-C25	1.512(5)	C18-C19	1.380(6)
C19-C20	1.375(6)	C20-C21	1.400(5)
C21-C22	1.512(6)	C22-C24	1.523(6)
C22-C23	1.532(6)	C25-C27	1.530(6)
C25-C26	1.518(6)		

Table S18. Bond angles (°) for **7**.

S3-B1-S2	116.0(2)	S3-B1-Br1	121.1(2)
S2-B1-Br1	122.8(2)	S1-B2-Br2	112.9(2)
S1-B2-Br3	111.9(2)	Br2-B2-Br3	112.2(2)
S1-B2-Br4	99.97(19)	Br2-B2-Br4	108.7(2)
Br3-B2-Br4	110.47(19)	C1-S1-B2	112.58(17)
C2-S2-B1	92.22(18)	C3-S3-B1	92.30(18)
C1-N1-C2	108.4(3)	C1-N1-C16	127.9(3)
C2-N1-C16	123.2(3)	C3-N2-C1	109.0(3)
C3-N2-C4	124.5(3)	C1-N2-C4	126.0(3)
N1-C1-N2	106.8(3)	N1-C1-S1	131.8(3)
N2-C1-S1	120.1(2)	C3-C2-N1	108.2(3)
C3-C2-S2	119.4(3)	N1-C2-S2	131.5(3)
C2-C3-N2	107.6(3)	C2-C3-S3	120.0(3)
N2-C3-S3	132.0(3)	C5-C4-C9	124.4(3)
C5-C4-N2	117.7(3)	C9-C4-N2	117.9(3)
C4-C5-C6	116.3(3)	C4-C5-C13	123.6(3)
C6-C5-C13	120.1(3)	C7-C6-C5	121.3(4)
C6-C7-C8	120.5(3)	C7-C8-C9	121.6(4)
C4-C9-C8	115.8(3)	C4-C9-C10	122.6(3)
C8-C9-C10	121.5(3)	C9-C10-C12	110.7(3)
C9-C10-C11	112.3(3)	C12-C10-C11	110.7(4)
C5-C13-C15	112.4(3)	C5-C13-C14	110.2(3)
C15-C13-C14	111.0(3)	C17-C16-C21	124.5(3)
C17-C16-N1	116.9(3)	C21-C16-N1	118.5(3)
C16-C17-C18	116.6(3)	C16-C17-C25	124.0(3)
C18-C17-C25	119.4(3)	C19-C18-C17	121.3(4)
C20-C19-C18	120.5(4)	C19-C20-C21	121.5(4)
C16-C21-C20	115.7(4)	C16-C21-C22	123.9(3)
C20-C21-C22	120.5(3)	C24-C22-C21	111.3(4)
C24-C22-C23	109.2(4)	C21-C22-C23	112.0(4)
C17-C25-C27	110.5(3)	C17-C25-C26	112.6(3)
C27-C25-C26	110.2(3)		

Compound **8**

Table S19. Sample and crystal data for compound **8**.

Identification code	**8**	
Chemical formula	$C_{53}H_{70}B_2I_6N_4S_3Si$	
Formula weight	1670.42 g/mol	
Temperature	135(2) K	
Wavelength	0.71073 Å	
Crystal size	0.140 x 0.230 x 0.300 mm	
Crystal system	monoclinic	
Space group	$P2_1/n$ (No. 14)	
Unit cell dimensions	a = 11.2064(9) Å	α = 90°
	b = 27.535(2) Å	β = 91.136(2)°
	c = 20.4784(15) Å	γ = 90°
Volume	6317.8(8) $Å^3$	
Z	4	
Density (calculated)	1.756 g/cm^3	
Absorption coefficient	3.104 mm^{-1}	
F(000)	3224	

Table S20. Data collection and structure refinement for **8**.

Theta range for data collection	2.09 to 27.48°
Index ranges	-14<=h<=14, -35<=k<=35, -26<=l<=26
Reflections collected	187491
Independent reflections	14489 [R(int) = 0.0966]
Max. and min. transmission	0.7456 and 0.5248
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	14489 / 2 / 629
Goodness-of-fit on F^2	1.040
Δ/σ_{max}	0.003
Final R indices	10190 data; I>2σ(I) R1 = 0.0718, wR2 = 0.1711
	all data R1 = 0.1088, wR2 = 0.2014
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0742P)^2+159.7453P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	2.384 and -1.390 eÅ^{-3}
R.M.S. deviation from mean	0.262 eÅ^{-3}

Table S21. Bond lengths (Å) for **8**.

Si1-N3	1.682(8)	Si1-N4	1.803(8)
Si1-S2	2.143(3)	Si1-S3	2.138(3)
S1-C1	1.741(10)	S1-B1	1.921(12)
S2-C2	1.745(9)	S3-C3	1.740(10)
B1-I1	2.210(11)	B1-I3	2.231(11)
B1-I2	2.250(11)	B2-C28	1.654(14)
B2-I4	2.237(12)	B2-I6	2.248(11)
B2-I5	2.247(13)	N1-C1	1.366(12)
N1-C2	1.392(11)	N1-C16	1.472(12)
N2-C3	1.343(12)	N2-C1	1.343(12)
N2-C4	1.444(12)	N3-C42	1.455(13)
N3-C28	1.472(12)	N4-C29	1.320(12)
N4-C30	1.455(12)	C2-C3	1.360(13)
C4-C5	1.378(14)	C4-C9	1.411(13)
C5-C6	1.423(14)	C5-C13	1.489(14)
C6-C7	1.371(15)	C7-C8	1.361(17)
C8-C9	1.402(15)	C9-C10	1.545(14)
C10-C11	1.519(16)	C10-C12	1.535(16)
C13-C14	1.542(15)	C13-C15	1.544(16)
C16-C21	1.394(14)	C16-C17	1.411(14)
C17-C18	1.428(14)	C17-C25	1.518(13)
C18-C19	1.381(16)	C19-C20	1.386(18)
C20-C21	1.382(15)	C21-C22	1.509(16)
C22-C23	1.525(16)	C22-C24	1.513(18)
C25-C26	1.510(16)	C25-C27	1.536(15)
C28-H28	1.00(2)	C28-C29	1.449(13)
C29-H29	0.96(2)	C30-C31	1.368(15)
C30-C35	1.415(14)	C31-C32	1.409(15)
C31-C39	1.518(16)	C32-C33	1.39(2)
C33-C34	1.36(2)	C34-C35	1.404(16)
C35-C36	1.487(17)	C36-C38	1.550(15)
C36-C37	1.526(15)	C39-C41	1.528(18)
C39-C40	1.509(17)	C42-C47	1.418(14)
C42-C43	1.406(14)	C43-C44	1.388(15)
C43-C51	1.523(14)	C44-C45	1.375(17)
C45-C46	1.367(17)	C46-C47	1.394(16)
C47-C48	1.514(15)	C48-C50	1.519(14)
C48-C49	1.532(15)	C51-C53	1.547(15)
C51-C52	1.541(16)		

Table S22. Bond angles (°) for **8**.

N3-Si1-N4	91.3(4)	N3-Si1-S2	112.8(3)
N4-Si1-S2	121.1(3)	N3-Si1-S3	126.2(3)
N4-Si1-S3	103.9(3)	S2-Si1-S3	102.70(14)
C1-S1-B1	109.4(5)	C2-S2-Si1	93.7(3)
C3-S3-Si1	93.8(3)	S1-B1-I1	113.2(5)
S1-B1-I3	101.3(5)	I1-B1-I3	111.1(5)
S1-B1-I2	110.1(5)	I1-B1-I2	111.9(5)
I3-B1-I2	108.7(5)	C28-B2-I4	109.5(6)
C28-B2-I6	108.0(7)	I4-B2-I6	108.7(5)
C28-B2-I5	110.9(7)	I4-B2-I5	108.3(5)
I6-B2-I5	111.4(5)	C1-N1-C2	107.3(7)
C1-N1-C16	129.1(8)	C2-N1-C16	123.3(8)
C3-N2-C1	110.0(8)	C3-N2-C4	121.0(8)
C1-N2-C4	127.5(8)	C42-N3-C28	120.7(7)
C42-N3-Si1	124.5(6)	C28-N3-Si1	112.7(6)
C29-N4-C30	122.6(8)	C29-N4-Si1	109.6(7)
C30-N4-Si1	127.8(6)	N1-C1-N2	107.6(8)
N1-C1-S1	130.1(8)	N2-C1-S1	121.2(7)
C3-C2-N1	107.1(8)	C3-C2-S2	124.2(7)
N1-C2-S2	128.6(7)	N2-C3-C2	108.0(8)
N2-C3-S3	127.0(7)	C2-C3-S3	125.0(7)
C5-C4-C9	124.2(9)	C5-C4-N2	120.0(9)
C9-C4-N2	115.7(8)	C4-C5-C6	115.5(9)
C4-C5-C13	124.7(9)	C6-C5-C13	119.7(9)
C7-C6-C5	121.4(10)	C8-C7-C6	121.4(10)
C7-C8-C9	120.5(10)	C8-C9-C4	116.9(9)
C8-C9-C10	119.9(9)	C4-C9-C10	123.1(9)
C11-C10-C12	112.4(9)	C11-C10-C9	110.3(10)
C12-C10-C9	110.9(9)	C5-C13-C14	111.9(9)
C5-C13-C15	111.2(9)	C14-C13-C15	111.2(9)
C21-C16-C17	124.7(9)	C21-C16-N1	117.7(9)
C17-C16-N1	117.5(8)	C16-C17-C18	115.8(9)
C16-C17-C25	126.9(9)	C18-C17-C25	117.1(9)
C19-C18-C17	120.4(11)	C18-C19-C20	120.5(11)
C21-C20-C19	122.5(11)	C16-C21-C20	116.1(11)
C16-C21-C22	123.6(10)	C20-C21-C22	120.2(10)
C23-C22-C21	112.6(10)	C23-C22-C24	109.4(13)
C21-C22-C24	112.3(11)	C26-C25-C27	108.8(9)
C26-C25-C17	113.0(9)	C27-C25-C17	111.8(9)
H28-C28-C29	115.(9)	H28-C28-N3	110.(9)

C29-C28-N3	106.4(7)	H28-C28-B2	95.(9)
C29-C28-B2	112.3(8)	N3-C28-B2	117.1(8)
H29-C29-N4	124.(8)	H29-C29-C28	118.(8)
N4-C29-C28	117.6(8)	C31-C30-C35	125.1(10)
C31-C30-N4	120.0(9)	C35-C30-N4	114.9(9)
C30-C31-C32	116.7(10)	C30-C31-C39	124.3(9)
C32-C31-C39	118.9(11)	C33-C32-C31	119.9(12)
C34-C33-C32	121.5(12)	C33-C34-C35	121.6(12)
C30-C35-C34	115.1(11)	C30-C35-C36	123.2(9)
C34-C35-C36	121.3(10)	C35-C36-C38	112.9(11)
C35-C36-C37	111.7(9)	C38-C36-C37	109.4(10)
C41-C39-C40	110.0(10)	C41-C39-C31	109.7(10)
C40-C39-C31	114.3(11)	C47-C42-C43	121.2(10)
C47-C42-N3	120.3(9)	C43-C42-N3	118.5(8)
C44-C43-C42	117.7(10)	C44-C43-C51	119.0(9)
C42-C43-C51	123.2(9)	C45-C44-C43	122.6(11)
C46-C45-C44	118.1(11)	C45-C46-C47	123.7(11)
C42-C47-C46	116.4(10)	C42-C47-C48	121.8(10)
C46-C47-C48	121.7(9)	C47-C48-C50	114.0(9)
C47-C48-C49	108.9(9)	C50-C48-C49	109.7(9)
C43-C51-C53	112.6(9)	C43-C51-C52	110.5(9)
C53-C51-C52	109.3(9)		

Compound **9·(toluene)$_2$**

Table S23. Sample and crystal data for compound **9·(toluene)$_2$**.

Identification code	**9·(toluene)$_2$**	
Chemical formula	$C_{67}H_{86}B_2I_6N_4S_3Si$	
Formula weight	1854.68 g/mol	
Temperature	135(2) K	
Wavelength	0.71073 Å	
Crystal size	0.040 x 0.140 x 0.200 mm	
Crystal system	monoclinic	
Space group	$P2_1/c$ (No. 14)	
Unit cell dimensions	a = 20.950(19) Å	α = 90°
	b = 12.762(11) Å	β = 101.17(3)°
	c = 28.79(2) Å	γ = 90°
Volume	7552(11) Å^3	
Z	4	
Density (calculated)	1.631 g/cm^3	
Absorption coefficient	2.606 mm^{-1}	
F(000)	3624	

Table S24. Data collection and structure refinement for **9·(toluene)$_2$**.

Theta range for data collection	1.75 to 25.35°
Index ranges	-25<=h<=25, -15<=k<=13, -34<=l<=30
Reflections collected	35959
Independent reflections	13805 [R(int) = 0.1128]
Max. and min. transmission	0.7454 and 0.5751
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	13805 / 24 / 738
Goodness-of-fit on F^2	1.003
Δ/σ_{max}	0.004
Final R indices	7518 data; I>2σ(I) R1 = 0.0661, wR2 = 0.0860
	all data R1 = 0.1552, wR2 = 0.1052
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0210P)^2]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.873 and -1.282 eÅ^{-3}
R.M.S. deviation from mean	0.188 eÅ^{-3}

Table S25. Bond lengths (Å) for **9·(toluene)$_2$**.

I1-B1	2.278(10)	I2-B1	2.200(10)
I3-B1	2.219(10)	I4-Si1	2.406(3)
I5-B2	2.119(11)	I6-B2	2.136(10)
Si1-N3	1.699(7)	Si1-S3	2.156(3)
Si1-S2	2.162(4)	S1-C1	1.731(8)
S1-B1	1.936(10)	S2-C2	1.750(8)
S3-C3	1.728(9)	B2-N4	1.393(11)
N1-C2	1.383(9)	N1-C1	1.371(9)
N1-C16	1.447(9)	N2-C3	1.409(9)
N2-C1	1.357(9)	N2-C4	1.455(9)
N3-C28	1.425(9)	N3-C42	1.454(10)
N4-C30	1.439(10)	N4-C29	1.442(9)
C2-C3	1.331(10)	C4-C9	1.401(10)
C4-C5	1.411(10)	C5-C6	1.375(10)
C5-C13	1.512(11)	C6-C7	1.371(11)
C7-C8	1.370(11)	C8-C9	1.394(10)
C9-C10	1.525(11)	C10-C11	1.506(12)
C10-C12	1.537(11)	C13-C14	1.519(11)
C13-C15	1.514(11)	C16-C17	1.403(10)
C16-C21	1.401(10)	C17-C18	1.385(11)
C17-C25	1.517(10)	C18-C19	1.371(11)
C19-C20	1.377(11)	C20-C21	1.393(10)
C21-C22	1.502(10)	C22-C24	1.514(12)
C22-C23	1.529(11)	C25-C27	1.499(12)
C25-C26	1.521(11)	C28-C29	1.326(10)
C30-C35	1.407(11)	C30-C31	1.410(11)
C31-C32	1.384(12)	C31-C39	1.509(12)
C32-C33	1.395(12)	C33-C34	1.375(12)
C34-C35	1.384(12)	C35-C36	1.492(11)
C36-C38	1.525(10)	C36-C37	1.533(11)
C39-C41	1.549(12)	C39-C40	1.541(11)
C42-C47	1.380(11)	C42-C43	1.410(11)
C43-C44	1.388(12)	C43-C51	1.498(11)
C44-C45	1.376(12)	C45-C46	1.383(12)
C46-C47	1.405(11)	C47-C48	1.510(11)
C48-C50	1.518(11)	C48-C49	1.546(12)
C51-C52	1.523(11)	C51-C53	1.527(11)
C54-C55	1.39	C54-C59	1.39
C54-C60	1.506(11)	C55-C56	1.39
C56-C57	1.39	C57-C58	1.39

C58-C59	1.39	C61-C62	1.358(14)
C61-C66	1.398(14)	C61-C67	1.501(14)
C62-C63	1.380(14)	C63-C64	1.370(14)
C64-C65	1.386(15)	C65-C66	1.362(14)

Table S26. Bond angles (°) for **9·(toluene)$_2$**.

N3-Si1-S3	110.4(3)	N3-Si1-S2	113.2(2)
S3-Si1-S2	100.27(13)	N3-Si1-I4	110.3(3)
S3-Si1-I4	111.82(12)	S2-Si1-I4	110.54(12)
C1-S1-B1	112.6(4)	C2-S2-Si1	90.4(3)
C3-S3-Si1	90.7(3)	S1-B1-I3	111.7(5)
S1-B1-I2	117.4(5)	I3-B1-I2	112.4(4)
S1-B1-I1	96.7(4)	I3-B1-I1	109.9(4)
I2-B1-I1	107.4(4)	N4-B2-I5	121.3(7)
N4-B2-I6	121.2(7)	I5-B2-I6	117.4(5)
C2-N1-C1	108.9(6)	C2-N1-C16	122.7(6)
C1-N1-C16	128.0(7)	C3-N2-C1	108.8(6)
C3-N2-C4	122.1(7)	C1-N2-C4	128.5(7)
C28-N3-C42	115.8(6)	C28-N3-Si1	119.1(6)
C42-N3-Si1	124.9(5)	B2-N4-C30	121.9(7)
B2-N4-C29	123.4(7)	C30-N4-C29	114.7(7)
N2-C1-N1	106.6(7)	N2-C1-S1	131.7(6)
N1-C1-S1	120.2(6)	C3-C2-N1	108.4(7)
C3-C2-S2	123.9(7)	N1-C2-S2	127.5(6)
N2-C3-C2	107.3(7)	N2-C3-S3	127.0(6)
C2-C3-S3	125.7(7)	C9-C4-C5	123.9(7)
C9-C4-N2	118.6(7)	C5-C4-N2	117.3(7)
C6-C5-C4	115.6(8)	C6-C5-C13	121.1(8)
C4-C5-C13	123.2(7)	C5-C6-C7	121.7(8)
C8-C7-C6	122.1(8)	C7-C8-C9	119.7(8)
C4-C9-C8	116.9(8)	C4-C9-C10	123.9(7)
C8-C9-C10	119.2(7)	C11-C10-C9	111.7(7)
C11-C10-C12	107.0(7)	C9-C10-C12	110.9(7)
C5-C13-C14	112.8(7)	C5-C13-C15	109.4(7)
C14-C13-C15	111.1(7)	C17-C16-C21	123.2(7)
C17-C16-N1	117.3(7)	C21-C16-N1	119.3(7)
C16-C17-C18	116.4(7)	C16-C17-C25	123.6(7)
C18-C17-C25	120.0(7)	C19-C18-C17	122.4(8)
C18-C19-C20	119.7(8)	C19-C20-C21	121.7(8)
C16-C21-C20	116.6(7)	C16-C21-C22	123.1(7)
C20-C21-C22	120.3(7)	C24-C22-C23	110.1(7)
C24-C22-C21	110.9(7)	C23-C22-C21	111.8(7)
C27-C25-C26	111.2(7)	C27-C25-C17	111.0(7)
C26-C25-C17	111.0(7)	C29-C28-N3	122.4(8)
C28-C29-N4	123.8(8)	C35-C30-C31	122.8(8)
C35-C30-N4	118.4(8)	C31-C30-N4	118.7(8)

C30-C31-C32	116.5(8)	C30-C31-C39	122.9(9)
C32-C31-C39	120.6(9)	C33-C32-C31	122.4(9)
C32-C33-C34	118.9(9)	C35-C34-C33	122.4(9)
C30-C35-C34	117.1(8)	C30-C35-C36	122.6(8)
C34-C35-C36	120.4(8)	C35-C36-C38	113.0(7)
C35-C36-C37	111.6(7)	C38-C36-C37	108.4(7)
C31-C39-C41	111.2(7)	C31-C39-C40	110.7(8)
C41-C39-C40	111.0(8)	C47-C42-C43	124.3(8)
C47-C42-N3	118.3(7)	C43-C42-N3	117.3(8)
C44-C43-C42	115.4(9)	C44-C43-C51	121.0(8)
C42-C43-C51	123.6(8)	C43-C44-C45	123.4(9)
C46-C45-C44	118.5(9)	C45-C46-C47	122.1(9)
C42-C47-C46	116.3(8)	C42-C47-C48	124.0(8)
C46-C47-C48	119.6(8)	C50-C48-C47	111.1(7)
C50-C48-C49	110.8(8)	C47-C48-C49	111.0(8)
C43-C51-C52	110.5(8)	C43-C51-C53	112.5(8)
C52-C51-C53	110.2(7)	C55-C54-C59	120.0
C55-C54-C60	123.0(8)	C59-C54-C60	117.0(8)
C54-C55-C56	120.0	C57-C56-C55	120.0
C56-C57-C58	120.0	C59-C58-C57	120.0
C58-C59-C54	120.0	C62-C61-C66	117.7(12)
C62-C61-C67	120.5(12)	C66-C61-C67	121.8(12)
C63-C62-C61	121.8(12)	C62-C63-C64	120.4(12)
C65-C64-C63	118.4(12)	C66-C65-C64	120.8(12)
C65-C66-C61	120.9(12)		

Compound **10**

Table S27. Sample and crystal data for compound **10**.

Identification code	**10**
Chemical formula	$C_{53}H_{70}BCl_3N_4S_3Si$
Formula weight	1004.56 g/mol
Temperature	135(2) K
Wavelength	0.71073 Å
Crystal size	0.140 x 0.220 x 0.320 mm
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
Unit cell dimensions	a = 14.4876(10) Å α = 90°
	b = 20.1276(13) Å β = 91.557(2)°
	c = 18.9921(12) Å γ = 90°
Volume	5536.1(6) $Å^3$
Z	4
Density (calculated)	1.205 g/cm^3
Absorption coefficient	0.338 mm^{-1}
F(000)	2136

Table S28. Data collection and structure refinement for **10**.

Theta range for data collection	2.37 to 25.46°	
Index ranges	-17<=h<=17, -24<=k<=24, -22<=l<=22	
Reflections collected	135304	
Independent reflections	10241 [R(int) = 0.1633]	
Max. and min. transmission	0.7452 and 0.5357	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	10241 / 0 / 586	
Goodness-of-fit on F^2	1.010	
Final R indices	6835 data; $I>2\sigma(I)$	R1 = 0.0566, wR2 = 0.0971
	all data	R1 = 0.1070, wR2 = 0.1141
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0260P)^2+8.4385P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.312 and -0.368 eÅ^{-3}	
R.M.S. deviation from mean	0.069 eÅ^{-3}	

Table S29. Bond lengths (Å) for **10**.

Si1-N4	1.710(2)	Si1-N3	1.710(2)
Si1-Cl1	2.0522(11)	Si1-S3	2.1417(11)
S1-C1	1.655(3)	S2-C2	1.746(3)
S2-B1	1.793(4)	S3-C3	1.747(3)
Cl2-B1	1.737(4)	Cl3-B1	1.743(4)
N1-C1	1.373(4)	N1-C2	1.397(4)
N1-C16	1.448(4)	N2-C1	1.373(4)
N2-C3	1.401(3)	N2-C4	1.445(4)
N3-C42	1.438(4)	N3-C28	1.416(4)
N4-C30	1.443(4)	N4-C29	1.414(4)
C2-C3	1.341(4)	C4-C9	1.395(4)
C4-C5	1.399(4)	C5-C6	1.395(4)
C5-C13	1.516(4)	C6-C7	1.376(5)
C7-C8	1.371(5)	C8-C9	1.394(4)
C9-C10	1.513(4)	C10-C11	1.517(5)
C10-C12	1.503(5)	C13-C14	1.530(5)
C13-C15	1.523(5)	C16-C21	1.392(4)
C16-C17	1.397(4)	C17-C18	1.392(4)
C17-C25	1.517(5)	C18-C19	1.367(5)
C19-C20	1.386(5)	C20-C21	1.394(4)
C21-C22	1.515(4)	C22-C24	1.529(5)
C22-C23	1.528(5)	C25-C27	1.522(5)
C25-C26	1.522(5)	C28-C29	1.328(4)
C30-C31	1.405(4)	C30-C35	1.409(4)
C31-C32	1.383(4)	C31-C39	1.517(4)
C32-C33	1.380(5)	C33-C34	1.374(5)
C34-C35	1.393(4)	C35-C36	1.509(4)
C36-C38	1.531(4)	C36-C37	1.531(5)
C39-C40	1.527(5)	C39-C41	1.528(5)
C42-C43	1.410(4)	C42-C47	1.402(4)
C43-C44	1.393(4)	C43-C51	1.518(4)
C44-C45	1.376(5)	C45-C46	1.383(5)
C46-C47	1.389(4)	C47-C48	1.520(5)
C48-C50	1.527(5)	C48-C49	1.529(5)
C51-C52	1.529(4)	C51-C53	1.523(4)

Table S30. Bond angles (°) for **10**.

N4-Si1-N3	92.86(12)	N4-Si1-Cl1	112.22(9)
N3-Si1-Cl1	116.28(9)	N4-Si1-S3	117.11(9)
N3-Si1-S3	111.26(9)	Cl1-Si1-S3	107.03(5)
C2-S2-B1	102.92(16)	C3-S3-Si1	108.44(10)
Cl2-B1-Cl3	119.7(2)	Cl2-B1-S2	124.2(2)
Cl3-B1-S2	116.1(2)	C1-N1-C2	110.3(2)
C1-N1-C16	122.2(2)	C2-N1-C16	126.4(2)
C1-N2-C3	110.3(2)	C1-N2-C4	122.7(2)
C3-N2-C4	126.3(2)	C42-N3-C28	119.9(2)
C42-N3-Si1	129.10(19)	C28-N3-Si1	109.45(19)
C30-N4-C29	119.2(2)	C30-N4-Si1	131.3(2)
C29-N4-Si1	109.35(19)	N1-C1-N2	104.8(2)
N1-C1-S1	127.6(2)	N2-C1-S1	127.7(2)
C3-C2-N1	107.6(2)	C3-C2-S2	131.9(2)
N1-C2-S2	120.6(2)	C2-C3-N2	107.1(2)
C2-C3-S3	131.1(2)	N2-C3-S3	121.5(2)
C9-C4-C5	123.6(3)	C9-C4-N2	118.7(3)
C5-C4-N2	117.6(3)	C6-C5-C4	116.8(3)
C6-C5-C13	120.3(3)	C4-C5-C13	122.8(3)
C7-C6-C5	120.7(3)	C6-C7-C8	121.2(3)
C7-C8-C9	121.0(3)	C4-C9-C8	116.7(3)
C4-C9-C10	122.7(3)	C8-C9-C10	120.6(3)
C9-C10-C11	111.7(3)	C9-C10-C12	111.3(3)
C11-C10-C12	110.2(3)	C5-C13-C14	110.5(3)
C5-C13-C15	112.6(3)	C14-C13-C15	111.2(3)
C21-C16-C17	123.9(3)	C21-C16-N1	118.8(3)
C17-C16-N1	117.3(3)	C18-C17-C16	116.2(3)
C18-C17-C25	121.0(3)	C16-C17-C25	122.8(3)
C17-C18-C19	122.0(3)	C18-C19-C20	120.1(3)
C21-C20-C19	120.9(3)	C16-C21-C20	116.8(3)
C16-C21-C22	122.6(3)	C20-C21-C22	120.6(3)
C21-C22-C24	111.3(3)	C21-C22-C23	110.9(3)
C24-C22-C23	111.6(3)	C17-C25-C27	112.5(3)
C17-C25-C26	111.6(3)	C27-C25-C26	111.3(3)
C29-C28-N3	113.8(3)	C28-C29-N4	114.1(3)
C31-C30-C35	121.6(3)	C31-C30-N4	118.9(3)
C35-C30-N4	119.4(3)	C32-C31-C30	118.1(3)
C32-C31-C39	120.1(3)	C30-C31-C39	121.9(3)
C33-C32-C31	121.3(3)	C34-C33-C32	120.1(3)
C33-C34-C35	121.5(3)	C34-C35-C30	117.4(3)

C34-C35-C36	120.4(3)	C30-C35-C36	122.1(3)
C35-C36-C38	110.1(3)	C35-C36-C37	111.9(3)
C38-C36-C37	110.7(3)	C31-C39-C40	111.7(3)
C31-C39-C41	111.1(3)	C40-C39-C41	110.9(3)
C43-C42-C47	122.0(3)	C43-C42-N3	118.9(3)
C47-C42-N3	119.1(3)	C42-C43-C44	117.4(3)
C42-C43-C51	122.1(3)	C44-C43-C51	120.4(3)
C45-C44-C43	121.4(3)	C44-C45-C46	120.2(3)
C47-C46-C45	121.2(3)	C46-C47-C42	117.8(3)
C46-C47-C48	120.3(3)	C42-C47-C48	121.7(3)
C47-C48-C50	113.7(3)	C47-C48-C49	109.6(3)
C50-C48-C49	110.6(3)	C52-C51-C43	110.8(3)
C52-C51-C53	110.1(3)	C43-C51-C53	113.5(3)

References:

1. Z. Liu, C. Cui, *J. Organomet. Chem.* **2020**, *906*, 121041.