Supporting Information

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SUPPORTING INFORMATIONS 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, $^{13}C\{^{1}H\}$, and ^{11}B NMR spectra were recorded on a Bruker Avance III HD 400 MHz spectrometer. EPR spectra of **2**$^{\bullet}$ and **3**$^{\bullet}$ were recorded using an ESP-300D spectrometer (Bruker, Billerica, MA) equipped with an ER-4102 rectangular cavity. X-ray intensity data for **2**$^{\bullet}$, **3**$^{\bullet}$, and **4** were collected 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**$^{\bullet}$: To a slurry of **1**$^{\bullet}$ (0.660 g, 1.04 mmol) in hexane (45 mL) at -78 °C was added a solution of BBr_3 (0.902 g, 3.60 mmol) in hexane (35 mL). The mixture was allowed to gradually warm to the room temperature over night, and stirred for a further 2 h. After the volatile materials were removed in vacuo, the residue was extracted using 100 mL of toluene. Removing toluene from the filtrate in vacuo gave raw material of **2**$^{\bullet}$ (0.565 g, 83.1% yield). X-ray quality dark blue crystals of **2**$^{\bullet}$ were obtained in the concentrated toluene solution at room temperature. Mp: melt at 215–216 °C. UV-vis (λ/nm): 431 (shoulder), 564 (shoulder), 606, 654. Crystal data for **2**$^{\bullet}$: $C_{27}H_{34}BBr_2N_2S_3$, fw = 653.37, orthorhombic, *P*nma, a = 11.5767(6) Å, b = 17.8070(9) Å, c = 15.3595(9) Å, β = 101.457(6)°, V = 3166.3(3) Å^3, Z = 4, R1 = 0.0560 for 2292 data ($I > 2\sigma(I)$), wR_2 = 0.1596 (all data).

Compound **3**$^{\bullet}$: 10 mL of hexane solution of $(C_6H_{11})_2BCl$ (0.330 g, 1.55 mmol) was added to a Schlenk flask containing **1**$^{\bullet}$ (0.983 g, 1.55 mmol) in 40 mL of hexane at 0 °C. The mixture was allowed to gradually warm to the room temperature and stirred for a further 8 h. After the volatile materials were removed in vacuo, the residue was extracted using 60 mL of toluene. Removing toluene from the filtrate in vacuo gave raw dark blue powder of **3**$^{\bullet}$ in a quantitative yield. X-ray quality dark blue crystals of **3**$^{\bullet}$ were obtained by keeping the concentrated toluene or hexane solution of **3**$^{\bullet}$ at -35 °C over 3 days. Mp: gradually decomposed (> 118°C). UV-vis (λ/nm): 596, 630. Crystal data for **3**$^{\bullet}$: $C_{39}H_{56}BN_2S_3$, fw = 659.84, monolinic, $P2_1/c$, a = 10.8184(14) Å, b = 22.527(3) Å, c = 16.534(2) Å, β = 103.111(3)°, V = 3924.2(9) Å^3, Z = 4, R1 = = 0.0739 for 4536 data ($I > 2\sigma(I)$), wR_2 = 0.2120 (all data).

Compound **4**: A Schlenk tube containing 0.538 g (0.72 mmol) of **3**$^{\bullet}$ in 10 mL of toluene was heated in an oil bath at a temperature of 50 °C for 6 h. After the volatile materials were removed from the greenish solution in vacuo, the residue was kept at 30 °C for two days, inducing crystallization of **4**. The mixture was then rinsed using cold hexane, giving

crystalline solid of **4** (0.147 g, 48.4% yield in terms of ^{1}H NMR data). X-ray quality yellow-green crystals of **4** were obtained by recrystallization in the toluene/hexane mixed solvent at room temperature. Mp: gradually decomposed (> 185°C) and melt (222-223°C). ^{1}H NMR (400.14 MHz, C_6D_6): δ 0.56-0.85 (m, 5H, C_6H_{11}), 0.99-1.21 (m, 7H, C_6H_{11}), 1.24 [d, 12H, $CH(CH_3)_2$], 1.45-1.67 (m, 10H, C_6H_{11}), 1.52 [d, 12H, $CH(CH_3)_2$], 1.93 (d, 2H, C_6H_{11}), 2.03 (d, 4H, C_6H_{11}), 2.31 (d, 4H, C_6H_{11}), 2.48 (tt, 1H, SC_6H_{11}), 2.77 [m, 4H, $CH(CH_3)_2$], 7.06 [d, 4H, Ar-*H*), 7.19 [t, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (100.63 MHz, C_6D_6): δ 23.7, 25.5 [$CH(CH_3)_2$], 29.9 [$CH(CH_3)_2$], 25.2, 26.0, 28.9, 29.7, 31.5, 34.8, 51.6 (C_6H_{11}), 34.7 (bs, *C*B), 129.7 (N*CC*N), 125.0, 131.6, 132.0, 146.6 (Ar-*C*), 143.8 [N*C*(=S)N]. ^{11}B NMR (128.38 MHz, C_6D_6): δ 18.85. Crystal data for **4**: $C_{45}H_{67}BN_2S_3$, fw = 742.99, monoclinic, *C*2/c, a = 34.0880(16) Å, b = 10.7509(5) Å, c = 26.1095(12) Å, β = 111.7780(10)°, V = 8885.6(7) Å^3, Z = 8, R1 = 0.0542 for 6992 data ($I > 2\sigma(I)$), wR_2 = 0.1473 (all data).

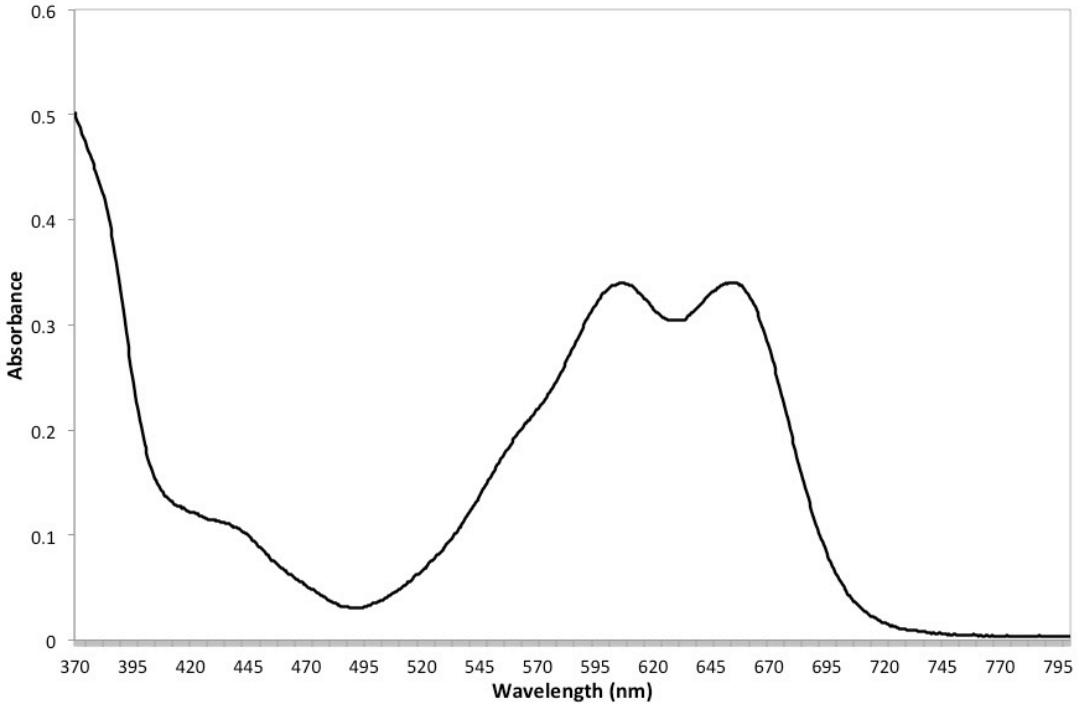

Figure S1. The UV-Vis absorption spectrum for **2**$^{\bullet}$.

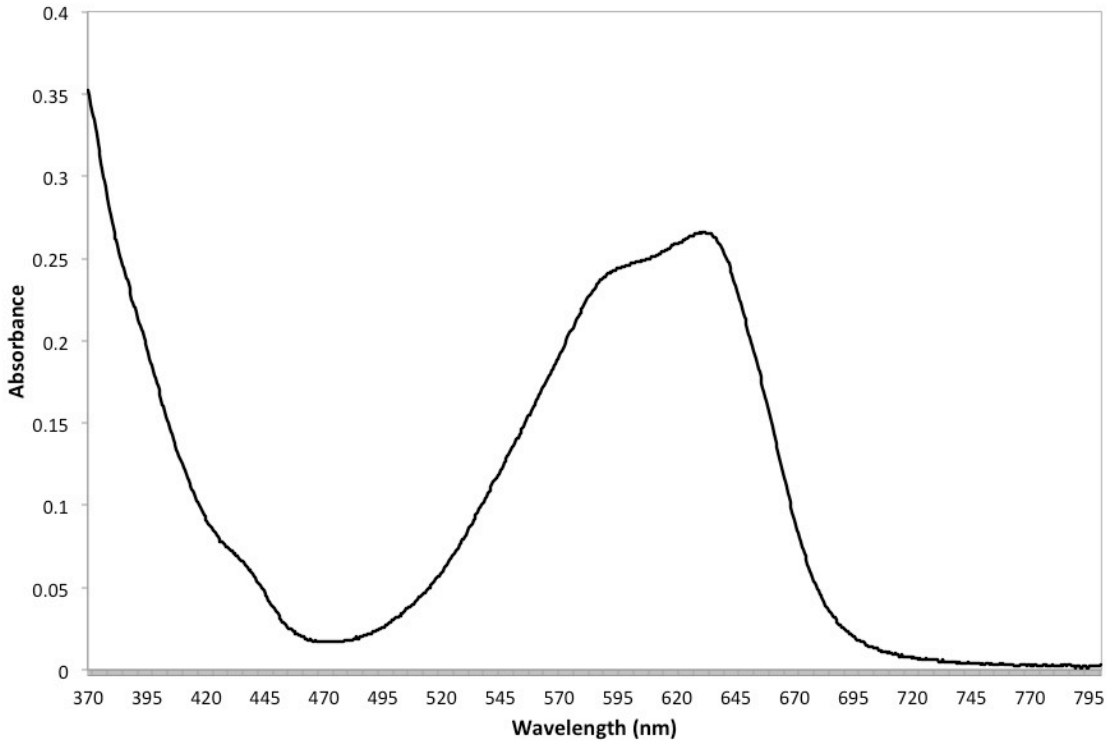

Figure S2. The UV-Vis absorption spectrum for **3**$^{\bullet}$.

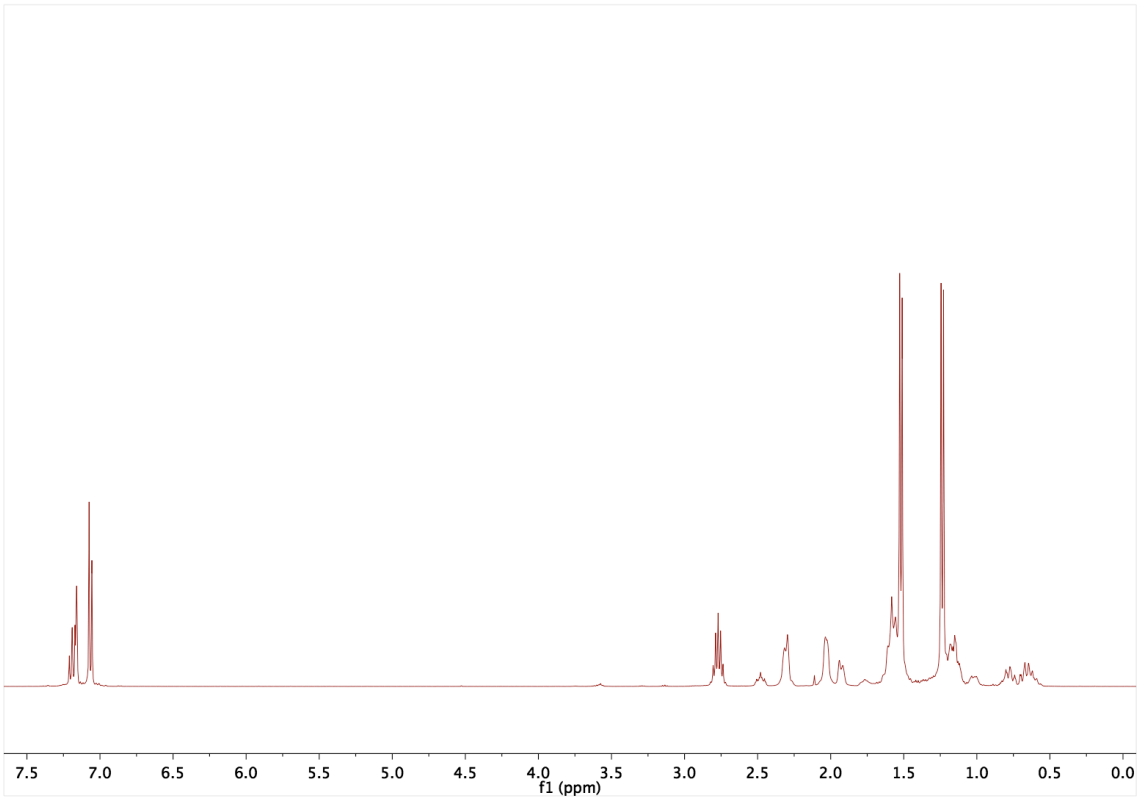

Figure S3. ^{1}H NMR spectrum of **4** in C_6D_6.

SUPPORTING INFORMATIONS of COMPUTATIONS

All computations employed the Gaussian09 programs:
For Gaussian 09: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09*, revision D.01; Gaussian, Inc., Wallingford CT, 2013.

Table S1. Coordinates of the B3LYP/6-311G** optimized geometry of **2**$^{\bullet}$ (in C_{2v} symmetry).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	0.000000	0.000000	-2.981062
2	35	0	1.674042	0.000000	-4.105978
3	35	0	-1.674042	0.000000	-4.105978
4	16	0	0.000000	0.000000	3.458848
5	16	0	0.000000	1.594834	-1.799948
6	7	0	0.000000	1.110422	0.958129
7	6	0	0.000000	0.000000	1.805597
8	6	0	0.000000	0.701399	-0.349184
9	6	0	0.000000	2.491977	1.389458
10	6	0	1.235701	3.136161	1.574029
11	6	0	1.204227	4.480583	1.952858
12	1	0	2.136586	5.011391	2.104481
13	6	0	0.000000	5.146696	2.138973
14	1	0	0.000000	6.190633	2.431909
15	6	0	-1.204227	4.480583	1.952858
16	1	0	-2.136586	5.011391	2.104481
17	6	0	-1.235701	3.136161	1.574029
18	6	0	-2.575788	2.434781	1.386228
19	1	0	-2.381074	1.397727	1.104517
20	6	0	-3.394305	3.069763	0.246211
21	1	0	-4.325506	2.516329	0.096866
22	1	0	-3.656956	4.106568	0.474036
23	1	0	-2.841444	3.060904	-0.695585
24	6	0	-3.379086	2.402059	2.700166
25	1	0	-2.805312	1.931742	3.501320
26	1	0	-3.653110	3.409631	3.025171
27	1	0	-4.304425	1.835753	2.561838
28	6	0	2.575788	2.434781	1.386228
29	1	0	2.381074	1.397727	1.104517
30	6	0	3.394305	3.069763	0.246211
31	1	0	4.325506	2.516329	0.096866
32	1	0	2.841444	3.060904	-0.695585
33	1	0	3.656956	4.106568	0.474036
34	6	0	3.379086	2.402059	2.700166
35	1	0	4.304425	1.835753	2.561838
36	1	0	3.653110	3.409631	3.025171
37	1	0	2.805312	1.931742	3.501320
38	16	0	0.000000	-1.594834	-1.799948
39	7	0	0.000000	-1.110422	0.958129
40	6	0	0.000000	-0.701399	-0.349184
41	6	0	0.000000	-2.491977	1.389458
42	6	0	1.235701	-3.136161	1.574029
43	6	0	1.204227	-4.480583	1.952858
44	1	0	2.136586	-5.011391	2.104481
45	6	0	0.000000	-5.146696	2.138973
46	1	0	0.000000	-6.190633	2.431909
47	6	0	-1.204227	-4.480583	1.952858
48	1	0	-2.136586	-5.011391	2.104481
49	6	0	-1.235701	-3.136161	1.574029
50	6	0	-2.575788	-2.434781	1.386228
51	1	0	-2.381074	-1.397727	1.104517
52	6	0	-3.394305	-3.069763	0.246211
53	1	0	-4.325506	-2.516329	0.096866
54	1	0	-3.656956	-4.106568	0.474036
55	1	0	-2.841444	-3.060904	-0.695585
56	6	0	-3.379086	-2.402059	2.700166
57	1	0	-2.805312	-1.931742	3.501320

58	1	0	-3.653110	-3.409631	3.025171
59	1	0	-4.304425	-1.835753	2.561838
60	6	0	2.575788	-2.434781	1.386228
61	1	0	2.381074	-1.397727	1.104517
62	6	0	3.394305	-3.069763	0.246211
63	1	0	4.325506	-2.516329	0.096866
64	1	0	2.841444	-3.060904	-0.695585
65	1	0	3.656956	-4.106568	0.474036
66	6	0	3.379086	-2.402059	2.700166
67	1	0	4.304425	-1.835753	2.561838
68	1	0	3.653110	-3.409631	3.025171
69	1	0	2.805312	-1.931742	3.501320

Table S2. Coordinates of the B3LYP/6-311G** optimized geometry of [**3-Ph**]$^{\bullet}$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	2.039405	-0.010684	0.014698
2	16	0	-4.494622	0.030183	-0.057499
3	16	0	0.766311	1.568350	0.363319
4	16	0	0.755375	-1.567659	-0.387273
5	7	0	-1.985926	1.091333	0.221131
6	7	0	-1.993661	-1.062266	-0.284412
7	6	0	-2.839782	0.019117	-0.037648
8	6	0	-0.670244	0.691950	0.134090
9	6	0	-0.675135	-0.674198	-0.188224
10	6	0	-2.440282	-2.393699	-0.594675
11	6	0	-2.799191	-3.252639	0.439579
12	6	0	-3.211698	-4.546457	0.135891
13	1	0	-3.495506	-5.220750	0.935162
14	6	0	-3.259801	-4.971798	-1.190313
15	1	0	-3.581272	-5.980329	-1.423235
16	6	0	-2.896464	-4.103475	-2.217472
17	1	0	-2.935226	-4.432638	-3.249064
18	6	0	-2.485233	-2.806656	-1.922589
19	6	0	-2.423076	2.425816	0.532815
20	6	0	-2.731438	2.753982	1.849392
21	6	0	-3.133581	4.051997	2.149615
22	1	0	-3.378391	4.315159	3.171808
23	6	0	-3.221593	5.007813	1.139430
24	1	0	-3.534858	6.017888	1.376828
25	6	0	-2.908991	4.667967	-0.175078
26	1	0	-2.979166	5.410043	-0.961482
27	6	0	-2.508308	3.371232	-0.484424
28	6	0	2.119696	0.606297	-2.605225
29	1	0	1.517008	1.510441	-2.450292
30	1	0	1.414609	-0.204126	-2.813799
31	6	0	3.029109	0.823352	-3.824375
32	1	0	3.554660	-0.112779	-4.055196
33	1	0	2.424197	1.064720	-4.705676
34	6	0	4.059620	1.930381	-3.570202
35	1	0	4.726896	2.037877	-4.432110
36	1	0	3.537352	2.889896	-3.458387
37	6	0	4.870087	1.647343	-2.299599
38	1	0	5.562086	2.472660	-2.098314
39	1	0	5.488727	0.754382	-2.459378
40	6	0	3.962460	1.414743	-1.081046
41	1	0	3.441741	2.353497	-0.844283
42	1	0	4.582126	1.181195	-0.210497
43	6	0	2.915202	0.298652	-1.317145
44	1	0	3.480422	-0.626950	-1.515655
45	6	0	2.849058	-0.336987	1.384911
46	1	0	3.431534	0.573112	1.603540
47	6	0	3.873441	-1.483267	1.198823
48	1	0	4.535627	-1.270672	0.354677
49	1	0	3.337622	-2.408480	0.943601
50	6	0	4.720406	-1.734424	2.456781
51	1	0	5.397101	-2.579801	2.289645
52	1	0	5.355979	-0.858018	2.640058
53	6	0	3.847213	-1.987508	3.691995
54	1	0	4.473345	-2.109306	4.582438
55	1	0	3.303135	-2.932433	3.561745

56	6	0	2.838925	-0.850506	3.896687
57	1	0	2.190100	-1.070005	4.752038
58	1	0	3.380394	0.071677	4.146159
59	6	0	1.989651	-0.614239	2.638544
60	1	0	1.300847	0.217677	2.813232
61	1	0	1.368271	-1.501439	2.461243
62	1	0	-2.759111	-2.905434	1.464493
63	1	0	-2.204825	-2.117820	-2.709901
64	1	0	-2.661092	1.998638	2.622160
65	1	0	-2.267569	3.089358	-1.502044

Table S3. Coordinates of the B3LYP/6-311G** optimized geometry of **4**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-3.014322	0.560264	1.012358
2	16	0	2.097715	-1.548525	0.590061
3	16	0	2.137782	1.353762	-0.878376
4	7	0	-0.622806	-0.832385	0.762385
5	7	0	-0.594665	1.130884	-0.223905
6	6	0	-1.425467	0.222110	0.390818
7	6	0	0.679878	-0.588041	0.386096
8	6	0	0.697574	0.653368	-0.238118
9	6	0	-1.007062	2.401967	-0.783490
10	6	0	-1.037958	3.529480	0.056320
11	6	0	-1.437328	4.741776	-0.512058
12	1	0	-1.473876	5.630784	0.106170
13	6	0	-1.778496	4.829373	-1.855139
14	1	0	-2.084109	5.781355	-2.274876
15	6	0	-1.713576	3.703834	-2.665593
16	1	0	-1.960668	3.789571	-3.717141
17	6	0	-1.320153	2.463739	-2.154002
18	6	0	-1.205462	1.268057	-3.094843
19	1	0	-0.940347	0.391053	-2.500692
20	6	0	-0.076534	1.482362	-4.122379
21	1	0	0.036383	0.592982	-4.748749
22	1	0	-0.298167	2.328558	-4.779403
23	1	0	0.876035	1.673068	-3.626345
24	6	0	-2.533049	0.957140	-3.809445
25	1	0	-2.426119	0.060329	-4.426080
26	1	0	-3.344688	0.786413	-3.099465
27	1	0	-2.835503	1.774738	-4.469508
28	6	0	-0.623042	3.486093	1.522438
29	1	0	-0.437512	2.444587	1.792573
30	6	0	0.696916	4.252018	1.739295
31	1	0	1.492079	3.855639	1.105165
32	1	0	0.577290	5.315419	1.511911
33	1	0	1.016159	4.166166	2.781811
34	6	0	-1.728604	4.011879	2.455837
35	1	0	-2.664765	3.469576	2.308998
36	1	0	-1.424513	3.893417	3.499639
37	1	0	-1.922321	5.075381	2.290557
38	6	0	-1.072282	-2.032884	1.437322
39	6	0	-1.129028	-2.035096	2.842453
40	6	0	-1.566604	-3.207053	3.464841
41	1	0	-1.623884	-3.243658	4.546157
42	6	0	-1.919322	-4.327092	2.723882
43	1	0	-2.254925	-5.226213	3.228664
44	6	0	-1.826925	-4.303879	1.338649
45	1	0	-2.082495	-5.191962	0.772819
46	6	0	-1.394777	-3.160734	0.659789
47	6	0	-1.249165	-3.202272	-0.858570
48	1	0	-0.952870	-2.208343	-1.200080
49	6	0	-0.133637	-4.180301	-1.277273
50	1	0	0.002669	-4.153504	-2.362051
51	1	0	0.815474	-3.918149	-0.808081
52	1	0	-0.385114	-5.207347	-0.996650
53	6	0	-2.570291	-3.558156	-1.563964
54	1	0	-2.437876	-3.521101	-2.648868
55	1	0	-2.903257	-4.567865	-1.308553
56	1	0	-3.371526	-2.866757	-1.296038
57	6	0	-0.700462	-0.845603	3.693872

58	1	0	-0.485584	-0.009313	3.025635
59	6	0	-1.810709	-0.389080	4.657522
60	1	0	-1.493802	0.509318	5.194613
61	1	0	-2.733211	-0.158828	4.120915
62	1	0	-2.034264	-1.155101	5.405260
63	6	0	0.601039	-1.162126	4.456772
64	1	0	1.399740	-1.452630	3.771758
65	1	0	0.933536	-0.283649	5.016985
66	1	0	0.450767	-1.977571	5.170398
67	5	0	3.387124	-0.204130	-0.320825
68	6	0	2.989629	-1.381096	-2.704342
69	1	0	2.369660	-2.164209	-2.249793
70	1	0	2.311273	-0.567672	-2.977921
71	6	0	3.657935	-1.946164	-3.967086
72	1	0	4.192142	-1.138983	-4.486131
73	1	0	2.897301	-2.313881	-4.666198
74	6	0	4.649164	-3.066912	-3.628064
75	1	0	4.096879	-3.923636	-3.219022
76	1	0	5.151023	-3.423832	-4.534475
77	6	0	5.680862	-2.595465	-2.596096
78	1	0	6.315193	-1.822833	-3.050857
79	1	0	6.346771	-3.421682	-2.321320
80	6	0	5.011415	-2.016050	-1.339421
81	1	0	5.784882	-1.662827	-0.651230
82	1	0	4.481043	-2.824647	-0.816497
83	6	0	4.009094	-0.879869	-1.659429
84	1	0	4.587580	-0.080302	-2.152438
85	6	0	4.442635	0.332634	0.790196
86	1	0	4.994490	-0.560893	1.127962
87	6	0	5.493278	1.300344	0.192137
88	1	0	4.980344	2.195929	-0.186358
89	1	0	5.988752	0.844239	-0.670053
90	6	0	6.557069	1.733953	1.213698
91	1	0	7.155977	0.858511	1.498491
92	1	0	7.250402	2.448599	0.755227
93	6	0	5.926856	2.340235	2.473570
94	1	0	6.702465	2.589558	3.206452
95	1	0	5.431751	3.284346	2.209393
96	6	0	4.893821	1.385818	3.086005
97	1	0	4.415742	1.854011	3.954634
98	1	0	5.408927	0.490780	3.460117
99	6	0	3.831879	0.966524	2.058115
100	1	0	3.128458	0.266790	2.518736
101	1	0	3.248547	1.850016	1.769234
102	6	0	-4.271392	-0.072601	-0.239575
103	1	0	-3.683741	-0.483242	-1.063275
104	6	0	-5.125818	-1.168377	0.410099
105	1	0	-5.570506	-0.769792	1.330379
106	1	0	-4.494570	-2.008420	0.708964
107	6	0	-6.249034	-1.637277	-0.530974
108	1	0	-6.863914	-2.383915	-0.019028
109	1	0	-5.808896	-2.141770	-1.400400
110	6	0	-7.113873	-0.465120	-1.011576
111	1	0	-7.653081	-0.037545	-0.156717
112	1	0	-7.874119	-0.818915	-1.714703
113	6	0	-6.253349	0.624038	-1.664364
114	1	0	-5.812663	0.230790	-2.589205
115	1	0	-6.871347	1.478961	-1.955605
116	6	0	-5.130569	1.101107	-0.726891
117	1	0	-4.502157	1.845269	-1.221707
118	1	0	-5.575925	1.598393	0.143762

SUPPORTING INFORMATIONS of X-RAY

Compound **2•**

Table S4. Sample and crystal data for **2•**.

Identification code	**2•**	
Chemical formula	$C_{27}H_{34}BBr_2N_2S_3$	
Formula weight	653.37 g/mol	
Temperature	297(2) K	
Wavelength	0.71073 Å	
Crystal size	0.100 x 0.240 x 0.300 mm	
Crystal system	orthorhombic	
Space group	Pnma (No. 62)	
Unit cell dimensions	a = 11.5767(6) Å	α = 90°
	b = 17.8070(9) Å	β = 90°
	c = 15.3595(9) Å	γ = 90°
Volume	3166.3(3) $Å^3$	
Z	4	
Density (calculated)	1.371 g/cm^3	
Absorption coefficient	2.776 mm^{-1}	
F(000)	1332	

Table S5. Data collection and structure refinement for **2•**.

Theta range for data collection	2.48 to 25.25°	
Index ranges	-13<=h<=13, -21<=k<=20, -18<=l<=18	
Reflections collected	50177	
Independent reflections	2968 [R(int) = 0.0829]	
Coverage of independent reflections	99.8%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.7456 and 0.1650	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2968 / 22 / 178	
Goodness-of-fit on F^2	1.094	
Δ/σ_{max}	0.002	
Final R indices	2292 data; I>2σ(I)	R1 = 0.0560, wR2 = 0.1366
	all data	R1 = 0.0800, wR2 = 0.1596
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0687P)^2+5.4186P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.938 and -0.790 eÅ^{-3}	
R.M.S. deviation from mean	0.077 eÅ^{-3}	

Table S6. Bond lengths (Å) for **2•**.

B1-S2	1.927(4)	B1-S2	1.927(4)
B1-Br2'	1.983(11)	B1-Br1	1.942(8)
B1-Br2	1.984(10)	B1-Br1'	2.022(8)
S1-C1	1.623(5)	S2-C2	1.682(3)
N1-C2	1.357(4)	N1-C1	1.396(4)
N1-C3	1.441(4)	C1-N1	1.396(4)
C2-C2	1.394(7)	C3-C8	1.390(5)
C3-C4	1.396(5)	C4-C5	1.393(5)
C4-C12	1.512(6)	C5-C6	1.371(6)
C6-C7	1.365(7)	C7-C8	1.377(6)
C8-C9	1.521(6)	C9-C10	1.527(8)
C9-C11	1.523(7)	C12-C14	1.514(7)
C12-C13	1.513(7)		

Table S7. Bond angles (°) for **2•**.

S2-B1-S2	110.3(3)	S2-B1-Br2'	112.5(3)
S2-B1-Br2'	112.5(3)	S2-B1-Br1	112.7(3)
S2-B1-Br1	112.7(3)	Br2'-B1-Br1	95.7(5)
S2-B1-Br2	106.3(3)	S2-B1-Br2	106.3(3)
Br1-B1-Br2	108.2(4)	S2-B1-Br1'	107.4(3)
S2-B1-Br1'	107.4(3)	Br2'-B1-Br1'	106.5(5)
Br2-B1-Br1'	119.0(4)	C2-S2-B1	92.4(2)
C2-N1-C1	110.3(3)	C2-N1-C3	124.9(3)
C1-N1-C3	124.7(3)	N1-C1-N1	104.5(4)
N1-C1-S1	127.73(19)	N1-C1-S1	127.73(19)
N1-C2-C2	107.45(18)	N1-C2-S2	130.8(3)
C2-C2-S2	121.69(12)	C8-C3-C4	124.1(3)
C8-C3-N1	118.0(3)	C4-C3-N1	117.9(3)
C5-C4-C3	116.0(4)	C5-C4-C12	121.4(4)
C3-C4-C12	122.6(3)	C6-C5-C4	121.4(4)
C5-C6-C7	120.1(4)	C8-C7-C6	122.2(4)
C7-C8-C3	116.2(4)	C7-C8-C9	122.1(4)
C3-C8-C9	121.7(3)	C10-C9-C8	110.0(4)
C10-C9-C11	110.7(4)	C8-C9-C11	112.2(4)
C4-C12-C14	110.8(4)	C4-C12-C13	112.4(4)
C14-C12-C13	110.9(5)		

Compound 3•

Table S8. Sample and crystal data for **3•.**

Identification code	uga1267	
Chemical formula	$C_{39}H_{56}BN_2S_3$	
Formula weight	659.84 g/mol	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.100 x 0.250 x 0.340 mm	
Crystal system	monoclinic	
Space group	$P2_1/c$ (No. 14)	
Unit cell dimensions	a = 10.8184(14) Å	α = 90°
	b = 22.527(3) Å	β = 103.111(3)°
	c = 16.534(2) Å	γ = 90°
Volume	3924.2(9) $Å^3$	
Z	4	
Density (calculated)	1.117 g/cm^3	
Absorption coefficient	0.217 mm^{-1}	
F(000)	1428	

Table S9. Data collection and structure refinement for **3•.**

Theta range for data collection	2.21 to 26.02°	
Index ranges	-13<=h<=13, -27<=k<=27, -20<=l<=20	
Reflections collected	70942	
Independent reflections	7746 [R(int) = 0.1088]	
Coverage of independent reflections	99.9%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.7454 and 0.6212	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	7746 / 0 / 406	
Goodness-of-fit on F^2	1.043	
Δ/σ_{max}	0.001	
Final R indices	4536 data; I>2σ(I)	R1 = 0.0739, wR2 = 0.1719
	all data	R1 = 0.1340, wR2 = 0.2120
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0899P)^2+3.4455P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.340 and -0.284 eÅ^{-3}	
R.M.S. deviation from mean	0.068 eÅ^{-3}	

Table S10. Bond lengths (Å) for **3•.**

B1-C33	1.607(6)	B1-C34	1.612(6)
B1-S3	2.028(4)	B1-S2	2.026(4)
S1-C1	1.633(4)	S2-C2	1.680(3)
S3-C3	1.694(3)	N1-C2	1.373(4)
N1-C1	1.394(4)	N1-C16	1.454(4)
N2-C3	1.361(4)	N2-C1	1.388(4)
N2-C4	1.453(4)	C2-C3	1.388(4)
C4-C5	1.388(5)	C4-C9	1.390(5)
C5-C6	1.387(5)	C5-C13	1.512(6)
C6-C7	1.364(6)	C7-C8	1.373(6)
C8-C9	1.392(5)	C9-C10	1.507(6)
C10-C11	1.514(6)	C10-C12	1.493(7)
C13-C14	1.521(7)	C13-C15	1.526(8)
C16-C17	1.377(5)	C16-C21	1.385(5)
C17-C18	1.401(6)	C17-C25	1.507(6)
C18-C19	1.366(7)	C19-C20	1.357(7)
C20-C21	1.392(5)	C21-C22	1.515(6)
C22-C24	1.523(6)	C22-C23	1.513(6)
C25-C26	1.501(7)	C25-C27	1.486(7)
C28-C33	1.531(5)	C28-C29	1.521(6)
C29-C30	1.504(7)	C30-C31	1.512(7)
C31-C32	1.528(6)	C32-C33	1.531(5)
C34-C39	1.531(5)	C34-C35	1.527(5)
C35-C36	1.529(6)	C36-C37	1.491(6)
C37-C38	1.520(6)	C38-C39	1.512(6)

Table S11. Bond angles (°) for **3•**.

C33-B1-C34	118.8(3)	C33-B1-S3	107.5(3)
C34-B1-S3	110.1(3)	C33-B1-S2	108.4(3)
C34-B1-S2	107.7(3)	S3-B1-S2	103.27(18)
C2-S2-B1	94.94(16)	C3-S3-B1	95.26(17)
C2-N1-C1	110.1(3)	C2-N1-C16	126.6(3)
C1-N1-C16	123.3(3)	C3-N2-C1	110.1(3)
C3-N2-C4	125.8(3)	C1-N2-C4	124.1(3)
N2-C1-N1	105.0(3)	N2-C1-S1	127.7(3)
N1-C1-S1	127.3(3)	C3-C2-N1	106.8(3)
C3-C2-S2	122.9(3)	N1-C2-S2	130.3(2)
N2-C3-C2	108.1(3)	N2-C3-S3	130.7(3)
C2-C3-S3	121.2(3)	C5-C4-C9	124.1(3)
C5-C4-N2	118.2(3)	C9-C4-N2	117.6(3)
C4-C5-C6	116.1(4)	C4-C5-C13	123.1(3)
C6-C5-C13	120.8(4)	C7-C6-C5	122.2(4)
C6-C7-C8	119.9(4)	C7-C8-C9	121.5(4)
C4-C9-C8	116.3(4)	C4-C9-C10	123.7(3)
C8-C9-C10	120.0(4)	C9-C10-C11	110.9(4)
C9-C10-C12	113.2(4)	C11-C10-C12	111.9(5)
C14-C13-C5	110.9(4)	C14-C13-C15	112.5(5)
C5-C13-C15	111.9(4)	C17-C16-C21	124.8(3)
C17-C16-N1	117.9(3)	C21-C16-N1	117.2(3)
C16-C17-C18	115.9(4)	C16-C17-C25	122.7(3)
C18-C17-C25	121.4(4)	C19-C18-C17	120.9(4)
C20-C19-C18	121.0(4)	C19-C20-C21	121.3(4)
C16-C21-C20	116.0(4)	C16-C21-C22	124.0(3)
C20-C21-C22	120.1(4)	C21-C22-C24	111.2(4)
C21-C22-C23	112.2(4)	C24-C22-C23	112.0(4)
C17-C25-C26	111.9(4)	C17-C25-C27	113.5(4)
C26-C25-C27	110.6(5)	C33-C28-C29	114.2(4)
C30-C29-C28	111.7(4)	C31-C30-C29	110.6(5)
C30-C31-C32	111.4(4)	C31-C32-C33	112.6(4)
C28-C33-C32	109.1(3)	C28-C33-B1	115.6(3)
C32-C33-B1	112.6(3)	C39-C34-C35	108.5(3)
C39-C34-B1	116.3(3)	C35-C34-B1	113.8(3)

C34-C35-C36	111.7(4)	C37-C36-C35	111.9(4)
C36-C37-C38	111.7(4)	C39-C38-C37	111.4(4)
C38-C39-C34	112.5(3)		

Compound 4

Table S12. Sample and crystal data for **4**.

Identification code	uga1273
Chemical formula	$C_{45}H_{67}BN_2S_3$
Formula weight	742.99 g/mol
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal size	0.120 x 0.220 x 0.400 mm
Crystal system	monoclinic
Space group	C2/c (No. 15)
Unit cell dimensions	a = 34.0880(16) Å α = 90°
	b = 10.7509(5) Å β = 111.7780(10)°
	c = 26.1095(12) Å γ = 90°
Volume	8885.6(7) $Å^3$
Z	8
Density (calculated)	1.111 g/cm^3
Absorption coefficient	0.198 mm^{-1}
F(000)	3232

Table S13. Data collection and structure refinement for **4**.

Theta range for data collection	2.08 to 27.88°
Index ranges	-44<=h<=44, -14<=k<=14, -34<=l<=34
Reflections collected	143568
Independent reflections	10584 [R(int) = 0.0559]
Max. and min. transmission	0.7457 and 0.6045
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick 2008)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	10584 / 377 / 571
Goodness-of-fit on F^2	1.032
Δ/σ_{max}	0.001

Final R indices	6992 data; I>2σ(I)	R1 = 0.0542, wR2 = 0.1272
	all data	R1 = 0.0921, wR2 = 0.1473
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0648P)^2+5.2403P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.500 and -0.297 eÅ^{-3}	
R.M.S. deviation from mean	0.035 eÅ^{-3}	

Table S14. Bond lengths (Å) for **4**.

S1-C1	1.7256(18)	S1-C40'	1.833(12)
S1-C40	1.834(4)	S2-C2	1.7078(18)
S2-B1	2.027(2)	S3-C3	1.7120(18)
S3-B1	2.031(2)	N1-C1	1.356(2)
N1-C2	1.379(2)	N1-C16	1.449(2)
N2-C1	1.359(2)	N2-C3	1.378(2)
N2-C4	1.450(2)	C2-C3	1.365(2)
C4-C9	1.384(3)	C4-C5	1.389(3)
C5-C6	1.389(3)	C5-C13'	1.488(11)
C5-C13	1.560(8)	C6-C7	1.355(4)
C7-C8	1.358(4)	C8-C9	1.392(3)
C9-C10	1.504(7)	C9-C10'	1.531(13)
C10-C11	1.505(7)	C10-C12	1.553(9)
C10'-C11'	1.514(12)	C10'-C12'	1.558(12)
C13-C14	1.527(8)	C13-C15	1.509(8)
C13'-C15'	1.508(10)	C13'-C14'	1.496(11)
C16-C17	1.394(3)	C16-C21	1.396(3)
C17-C18	1.397(3)	C17-C25	1.512(3)
C18-C19	1.365(4)	C19-C20	1.361(4)
C20-C21	1.391(3)	C21-C22	1.516(3)
C22-C24	1.527(4)	C22-C23	1.524(3)
C25-C26	1.525(3)	C25-C27	1.515(4)
B1-C34	1.607(3)	B1-C33	1.611(3)
C28-C29	1.521(4)	C28-C33	1.527(3)
C29-C30	1.505(4)	C30-C31	1.512(4)
C31-C32	1.524(3)	C32-C33	1.531(3)
C34-C35	1.528(3)	C34-C39	1.530(3)
C35-C36	1.518(3)	C36-C37	1.511(4)

C37-C38	1.505(4)	C38-C39	1.528(4)
C40-C45	1.501(5)	C40-C41	1.488(5)
C41-C42	1.513(5)	C42-C43	1.587(6)
C43-C44	1.430(6)	C44-C45	1.596(6)
C40'-C45'	1.559(17)	C40'-C41'	1.522(13)
C41'-C42'	1.503(12)	C42'-C43'	1.525(13)
C43'-C44'	1.509(13)	C44'-C45'	1.559(13)

Table S15. Bond angles (°) for **4**.

C1-S1-C40'	111.4(7)	C1-S1-C40	104.81(16)
C2-S2-B1	94.96(8)	C3-S3-B1	95.03(8)
C1-N1-C2	109.33(14)	C1-N1-C16	125.75(14)
C2-N1-C16	124.91(14)	C1-N2-C3	109.44(14)
C1-N2-C4	124.54(14)	C3-N2-C4	125.61(15)
N2-C1-N1	106.82(14)	N2-C1-S1	124.40(13)
N1-C1-S1	127.79(14)	N1-C2-C3	107.29(15)
N1-C2-S2	129.69(13)	C3-C2-S2	123.01(14)
N2-C3-C2	107.12(15)	N2-C3-S3	130.53(13)
C2-C3-S3	122.35(14)	C9-C4-C5	123.29(18)
C9-C4-N2	118.87(18)	C5-C4-N2	117.85(18)
C6-C5-C4	116.8(2)	C6-C5-C13'	122.2(6)
C4-C5-C13'	118.5(6)	C6-C5-C13	119.2(3)
C4-C5-C13	123.0(3)	C5-C6-C7	121.2(2)
C8-C7-C6	120.7(2)	C7-C8-C9	121.6(2)
C4-C9-C8	116.4(2)	C4-C9-C10	120.9(5)
C8-C9-C10	122.7(5)	C4-C9-C10'	123.2(10)
C8-C9-C10'	119.7(10)	C9-C10-C11	106.1(5)
C9-C10-C12	109.1(7)	C11-C10-C12	108.9(7)
C9-C10'-C11'	124.0(14)	C9-C10'-C12'	115.4(10)
C11'-C10'-C12'	106.9(10)	C14-C13-C15	111.9(5)
C14-C13-C5	115.2(6)	C15-C13-C5	110.2(6)
C5-C13'-C15'	115.7(10)	C5-C13'-C14'	101.1(10)
C15'-C13'-C14'	110.5(9)	C17-C16-C21	124.17(18)
C17-C16-N1	117.92(18)	C21-C16-N1	117.91(17)
C16-C17-C18	115.9(2)	C16-C17-C25	122.76(19)
C18-C17-C25	121.3(2)	C19-C18-C17	121.3(2)
C18-C19-C20	121.1(2)	C19-C20-C21	121.3(2)
C20-C21-C16	116.2(2)	C20-C21-C22	119.6(2)

C16-C21-C22	124.27(18)	C21-C22-C24	112.5(2)
C21-C22-C23	110.7(2)	C24-C22-C23	109.0(2)
C26-C25-C17	112.4(2)	C26-C25-C27	111.3(3)
C17-C25-C27	111.2(2)	C34-B1-C33	117.05(16)
C34-B1-S2	108.86(14)	C33-B1-S2	107.78(15)
C34-B1-S3	108.18(15)	C33-B1-S3	109.62(14)
S2-B1-S3	104.64(9)	C29-C28-C33	113.3(2)
C28-C29-C30	111.5(2)	C31-C30-C29	111.0(2)
C30-C31-C32	111.3(2)	C31-C32-C33	113.9(2)
C28-C33-C32	109.00(19)	C28-C33-B1	116.59(18)
C32-C33-B1	111.96(17)	C35-C34-C39	109.14(18)
C35-C34-B1	112.28(17)	C39-C34-B1	115.79(17)
C34-C35-C36	113.8(2)	C37-C36-C35	111.4(2)
C38-C37-C36	110.5(2)	C37-C38-C39	111.5(2)
C34-C39-C38	113.4(2)	C45-C40-C41	110.9(3)
C45-C40-S1	104.8(3)	C41-C40-S1	114.7(3)
C40-C41-C42	113.6(3)	C41-C42-C43	107.7(4)
C42-C43-C44	112.0(4)	C45-C44-C43	109.6(4)
C40-C45-C44	112.1(4)	C45'-C40'-C41'	85.4(13)
C45'-C40'-S1	133.9(19)	C41'-C40'-S1	98.9(10)
C42'-C41'-C40'	110.5(11)	C43'-C42'-C41'	123.6(13)
C42'-C43'-C44'	111.8(13)	C43'-C44'-C45'	100.2(13)
C40'-C45'-C44'	100.8(12)		