## Orbitally Matched Edge-Doping in Graphene Nanoribbons

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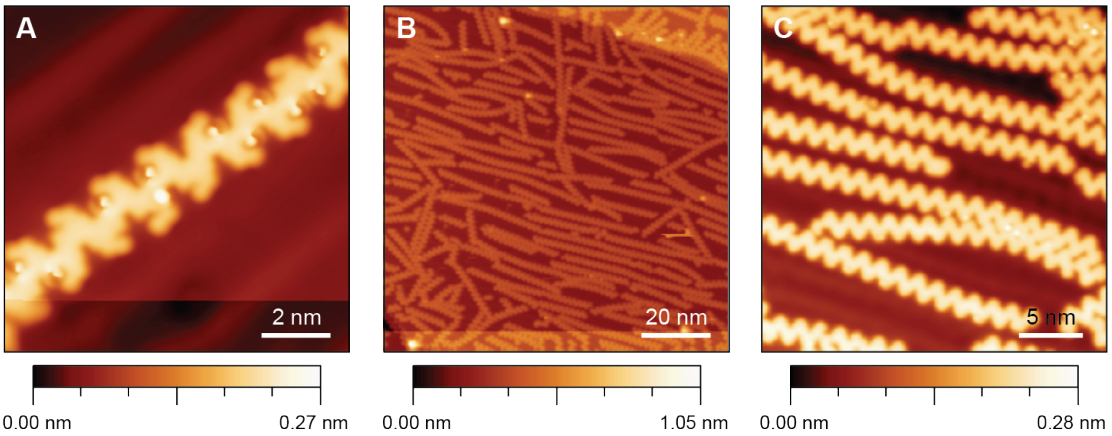


**Figure S1**. A) STM topographical image of O-doped cGNR polymer intermediate. Uncyclized wings protruding from polymer backbone appear as brighter protrusions. This polymer intermediate is representative of the intermediate structures also observed for the S-doped and N-doped precursor polymers; other examples of precursor polymer intermediates from this series of GNRs can be found in the literature.[4] B) Representative large area STM topographical image of O-doped cGNR and C) magnified image of O-doped cGNR illustrating the virtually quantitative yield of fully cyclodehydrogenated GNRs. ($V_{bias}$ = 50mV, $I_t$ = 20 pA)

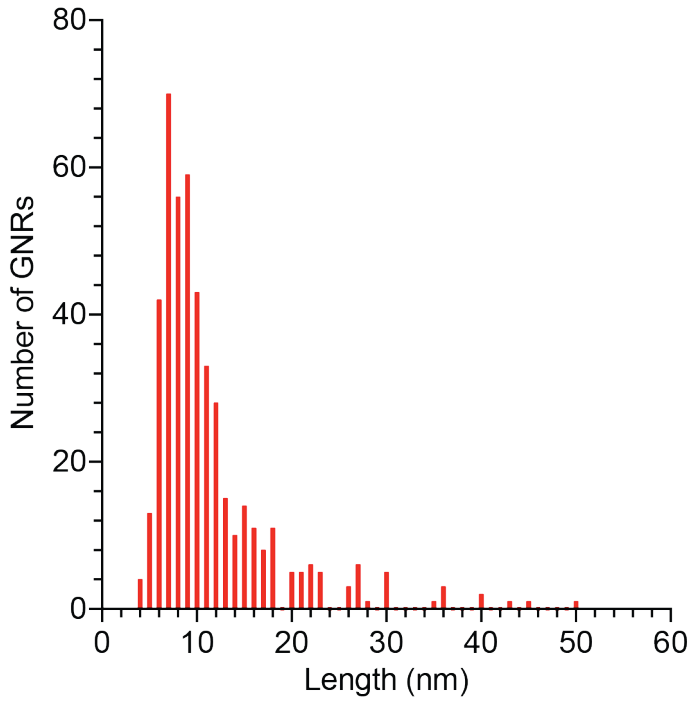


**Figure S2**. Statistical analysis on GNR length distribution. Data set combined from samples of O-, S-, and N-doped cGNRs; distribution is representative of all samples.

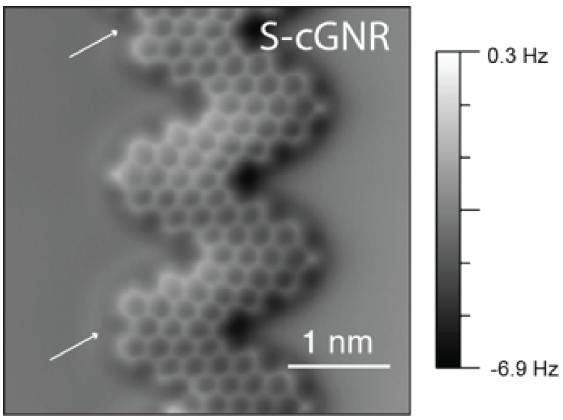


**Figure S3**. nc-AFM frequency shift image of S-cGNR; areas that have lost S-dopant atom indicated with white arrow.

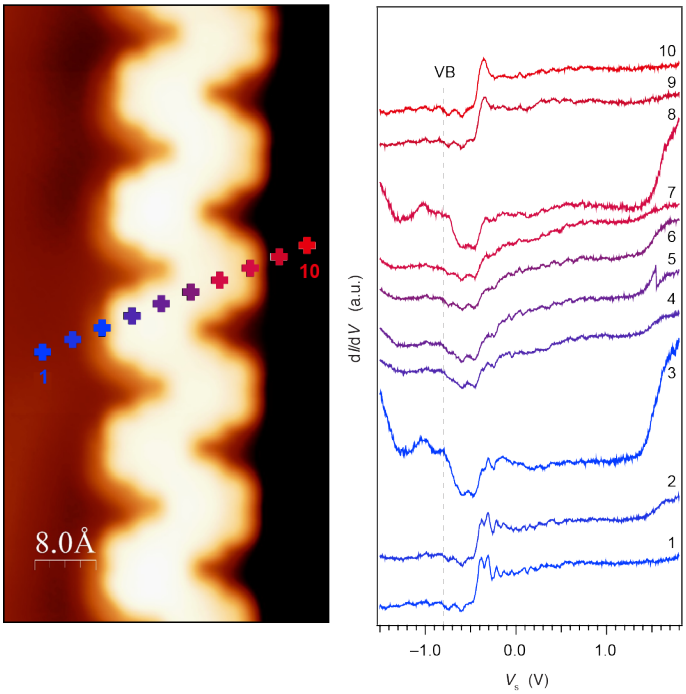


**Figure S4**. STM topographic image (left) and corresponding d*I*/d*V* point spectra (right) of O-doped cGNR recorded at various positions above the GNR. Spectra recorded at positions marked on the GNR (left), with the first spectrum shown in blue, moving across the ribbon to the tenth spectrum shown in red. Spectra are offset vertically (set point: $V_{bias}$ = 0.05 V, $I_t$ = 20 pA).

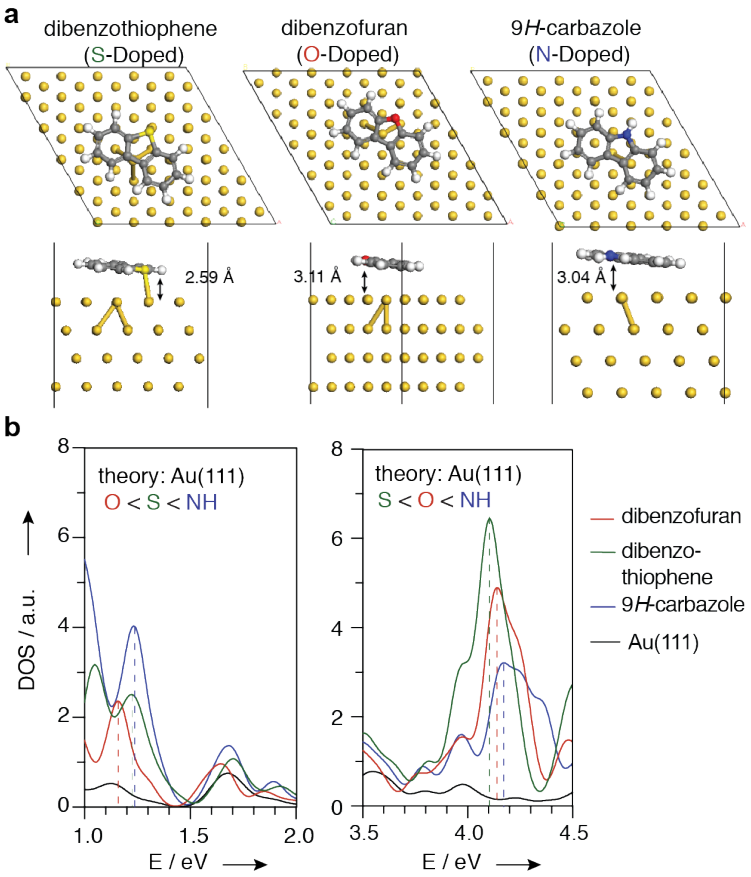


**Figure S5**. a) Schematic of structure of dibenzothiophene (left), dibenzofuran (middle), and 9*H*-carbazole (right) molecules on four-layer Au(111) substrate (upper panels; Color coding: C (gray), N (blue), O (red), S (green), H (white)); calculated heteroatom dopant height above the Au(111) surface (lower panels). b) Total density of states (DOS) from DFT-LDA calculations of dibenzofuran (red), dibenzothiophene (green), 9*H*-carbazole (red), on Au(111) surface (with the DOS of Au(111) surface only shown in black).

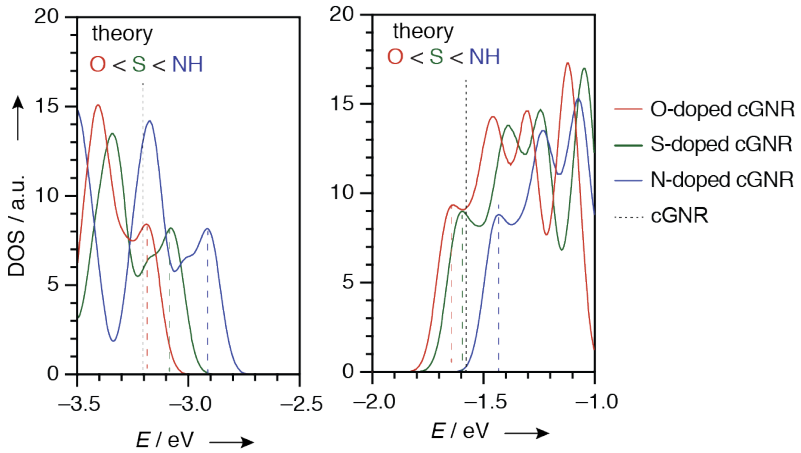


**Figure S6**. Density of states from DFT-LDA calculations of free-standing O-doped cGNR (red), S-doped cGNR (green), and N-doped cGNR (blue); dashed lines indicate valence and conduction band positions. Origin of energy scale is set at the vacuum level.

**Materials and General Methods.** Unless otherwise stated, all manipulations of air- and/or moisture-sensitive compounds were carried out in oven-dried glassware under and atmosphere of $N_2$. All solvents and reagents were purchased from Alfa Aesar, Spectrum Chemicals, Acros Organics, TCI America, Matrix Scientific, and Sigma-Aldrich and were used as received unless otherwise noted. Organic solvents were dried by passing through a column of alumina. Flash column chromatography was performed on SiliCycle silica gel (particle size 40–63 μm). Thin layer chromatography was performed using SiliCycle silica gel 60 Å F-254 precoated plates (0.25 mm thick) and visualized by UV absorption. All $^{1}$H and {$^{1}$H}$^{13}$C NMR spectra were recorded on Bruker AV-600, AV-500, and AVQ-400 spectrometers and are referenced to residual solvent peaks ($CDCl_3$ $^{1}$H NMR $\delta$ = 7.26 ppm, $^{13}$C NMR $\delta$ = 77.16 ppm). High resolution mass spectrometry (EI) was performed on an Autospec Permier (Waters) sector spectrometer in positive ionization mode. ESI mass spectrometry was performed on a Finnigan LTQFT (Thermo) spectrometer. X-ray crystallography was performed on a MicroSTAR-H APEX II, using a microfocus rotating anode (Cu-$K_\alpha$ radiation), Kappa Geometry with DX (Enraf-Nonoius build) goniostat, a Bruker APEX II detector, Helios multilayer mirrors as the radiation monochromator, and Oxford Cryostream 700 held at 100 K (**1a**) or on an APEX II QUAZAR, using a Microfocus Sealed Source (Incoatec; Cu-$K_\alpha$ radiation), Kappa Geometry with DX (Bruker-AXS build) goniostat, a Bruker APEX II detector, QUAZAR multilayer mirrors as the radiation monochromator, and Oxford Cryostream 700 held at 100 K (**1b**,**c**). Crystallographic data were resolved with SHELXT, refined with SHELXL-2014, and visualized with ORTEP-32. 1-iododibenzofuran[1,2], 4-bromo-9*H*-carbazole[1,3], and 1-bromodibenzothiophene[1] were synthesized following literature procedures.

Synthetic Procedures

*tert-butyl 4-bromo-9H-carbazole-9-carboxylate* (**4**): A 150 mL Schlenk flask was charged with 4-bromo-9*H*-carbazole (3.15 g, 12.8 mmol), di-*tert*-butyl dicarbonate (5.59 g, 25.6 mmol) and 4-dimethylaminopyridine (1.56 g, 12.8 mmol) in acetonitrile (51 mL), and the reaction mixture was stirred at 25 °C for 2 h. The reaction mixture was extracted with $CH_2Cl_2$ (100 mL). The combined organic layers were dried over $MgSO_4$ and concentrated on a rotary evaporator. Column chromatography (hexane/EtOAc 1:0–50:1) yielded **4** (3.49 g, 77%) as a colorless solid. $^1$H NMR (600 MHz, 25 °C, $CDCl_3$) $\delta$ = 8.82 (ddd, $J$ = 7.9, 1.4, 0.7 Hz, 1H), 8.38–8.32 (m, 2H), 7.55–7.51 (m, 2H), 7.41 (ddd, $J$ = 8.1, 7.3, 1.1 Hz, 1H), 7.30 (t, $J$ = 8.1 Hz, 1H), 1.77 (s, 10H) ppm; $^{13}$C NMR (151 MHz, 25 °C, $CDCl_3$) $\delta$ = 150.7, 139.9, 138.7, 127.6, 127.5, 127.3, 125.1, 124.2, 122.8, 122.4, 116.0, 115.8, 115.1, 84.5, 28.3 ppm; HRMS (EI) m/z: $[C_{17}H_{16}BrNO]^+$, calcd. For $[C_{17}H_{16}BrNO]$ 345.0364; found 345.0368.

*tert-butyl 4-ethynyl-9H-carbazole-9-carboxylate* (**3a**): A 100 mL sealable Schlenk flask was charged with **4** (1.00 g, 2.9 mmol) in toluene (20 mL) and $NEt_3$ (20 mL). The reaction mixture was degassed and $Pd(PPh_3)_4$ (0.67 g, 0.58 mmol) and CuI (55 mg, 0.29 mmol) were added. TMSA (4 mL) was added, and the flask was sealed and stirred at 90 °C for 18 h. The reaction mixture was cooled to 25 °C, and extracted with $Et_2O$ (100 mL). The combined organic layers were dried over $MgSO_4$, and concentrated on a rotary evaporator. Column chromatography (hexane/$CH_2Cl_2$ 1:0–20:1) yielded an inseparable mixture of partially deprotected **3a**. A 250 mL round bottom flask was charged with the crude intermediate in MeOH (77 mL) and THF (77 mL). $K_2CO_3$ (3 g) was added and the reaction mixture was stirred for 2 h at 25 °C. The reaction was extracted with $Et_2O$ (100 mL), the combined organic layers were dried over $MgSO_4$ and concentrated on a rotary evaporator. Column chromatography (hexane/$C_6H_6$ 1:0–10:1) yielded **3a** (28 mg, 20%) as a colorless oil. $^1$H NMR (600 MHz, 25 °C, $CDCl_3$) $\delta$ = 8.80–8.75 (m, 1H), 8.39 (d, $J$ = 8.4 Hz, 1H), 8.33 (d, $J$ = 8.4 Hz, 1H), 7.55–7.49 (m, 2H), 7.45–7.35 (m, 2H), 3.58 (s, 1H), 1.77 (s, 10H) ppm; $^{13}$C NMR (151 MHz, 25 °C, $CDCl_3$) $\delta$ = 150.7, 138.5, 138.4, 128.1, 127.4, 126.1, 125.6, 125.0, 122.8, 121.7, 116.7, 115.6, 114.6, 84.0, 82.3, 82.0, 28.2 ppm; HRMS (EI) m/z: $[C_{19}H_{17}NO_2]^+$, calcd. For $C_{19}H_{17}NO_2$] 291.1259; found 291.1255.

*(dibenzofuran-1-ylethynyl)trimethylsilane* (**3b-TMS**): A 5 mL sealable Schlenk flask was charged with 1-iododibenzofuran (13 mg, 0.04 mmol) in THF (1 mL) and $NEt_3$ (1 mL). The reaction mixture degassed, and $Pd(PPh_3)_4$ (7.6 mg, 0.01 mmol) and CuI (0.5 mg, 0.01 mmol) were added. TMSA (0.1 mL) was added, and the flask was sealed and stirred at 80 °C for 16 h. The reaction mixture was cooled to 25 °C, and concentrated on a rotary evaporator. The reaction mixture was extracted with $CH_2Cl_2$ (50 mL), and the combined organic layers were washed with $H_2O$, dried over $MgSO_4$, and concentrated on a rotatory evaporator. Column chromatography (hexane) yielded **3b-TMS** (8.4 mg, 79%) as a colorless oil. $^1$H NMR (600 MHz, 25 °C, $CDCl_3$) $\delta$ = 8.43 (d, $J$ = 7.7 Hz, 1H), 7.56 (dd, $J$ = 20.8, 8.2, 2H), 7.52–7.47 (m, 1H), 7.45 (d, $J$ = 7.3 Hz, 1H), 7.38, (t, $J$ = 7.9 Hz, 2H), 0.38 (s, 9H) ppm; $^{13}$C NMR (151 MHz, 25 °C, $CDCl_3$) $\delta$ = 156.3,

155.7, 127.5, 126.9, 126.6, 124.8, 123.8, 122.7, 122.2, 166.7, 112.0, 111.3, 102.8, 99.5, –0.06 ppm; HRMS (ESI-TOF) m/z: $[C_{17}H_{16}OSi]^+$, calcd. for $[C_{17}H_{16}OSi]$ 264.0975; found 264.0970.

*1-ethynyldibenzothiophene* (**3c**): A 10 mL sealable Schlenk flask was charged with 1-bromodibenzothiophene (70.0 mg, 0.27 mmol) in toluene (2.6 mL) and $NEt_3$ (2.6 mL). The reaction mixture was degassed, and $Pd(PPh_3)_4$ (62.4 mg, 0.05 mmol) and CuI (5.1 mg, 0.03 mmol) were added. TMSA (1 mL) was added, and the flask was sealed and stirred at 90 °C for 18 h. The reaction mixture was cooled to 25 °C, and extracted with $Et_2O$ (100 mL). The combined organic layers were dried over $MgSO_4$, and the reaction mixture was concentrated on a rotary evaporator. Column chromatography (hexane) yielded an inseparable mixture of partially deprotected **3c**. A 25 mL round bottom flask was charged with the crude intermediate in THF (8 mL) and MeOH (8 mL). $K_2CO_3$ (1 g) was added, and the reaction mixture was stirred at 25 °C for 2 h. The reaction mixture was extracted with $CH_2Cl_2$, and the combined organic layers were washed with $H_2O$, dried over $MgSO_4$, and concentrated on a rotatory evaporator. Column chromatography (hexane) yielded **3c** (41.8 mg, 75%) as a colorless oil. $^1$H NMR (600 MHz, 25 °C, $CDCl_3$) $\delta$ = 9.21–9.15 (m, 1 H), 7.90–7.84 (m, 2H), 7.65 (dd, $J$ = 7.4, 0.8 Hz, 1H), 7.50(m, 2H), 7.41 (t, $J$ = 7.7 Hz, 1H), 3.65 (s, 1H) ppm; $^{13}$C NMR (151 MHz, 25 °C, $CDCl_3$) $\delta$ = 140.2, 139.82, 135.4, 134.7, 131.1, 127.2, 125.8, 124.9, 124.4, 123.7, 122.6, 117.3, 83.4, 82.9 ppm; HRMS (EI) m/z: $[C_{14}H_8S]^+$, calcd. for $[C_{14}H_8S]$ 208.0349; found 208.0347.

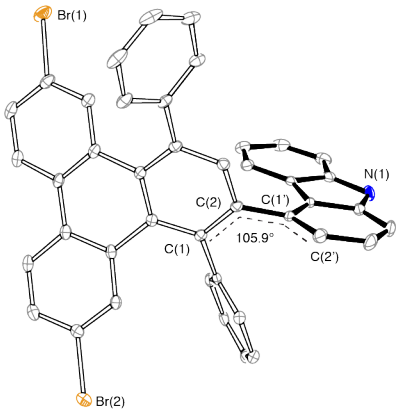


**Figure S7**. ORTEP representation of the molecular structures of the **1a**. Thermal ellipsoids are drawn at the 50% probability level. Color coding: C (gray), Br (orange), N (blue). Hydrogen atoms and solvent molecules are omitted for clarity.

**Table S1**. Crystal data and structure refinement for **1a**.

| | | |
|---|---|---|
| CCDC no. | 1567587 | |
| Empirical formula | $C_{43}H_{26}Br_2Cl_3N$ | |
| Formula weight | 822.82 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | $a$ = 9.1436(6) Å | $\alpha$ = 93.985(2)° |
| | $b$ = 13.3703(8) Å | $\beta$ = 92.921(3)° |
| | $c$ = 14.1905(8) Å | $\gamma$ = 94.285(3)° |
| Volume | 1723.04(18) Å$^3$ | |
| Z | 2 | |
| Density (calculated) | 1.586 Mg/ m$^3$ | |
| Absorption coefficient | 2.619 mm$^{-1}$ | |
| F(000) | 824 | |
| Crystal size | 0.050 x 0.050 x 0.030 mm$^3$ | |
| Theta range for data collection | 1.441° to 25.422° | |
| Index ranges | $-11 \le h \le 11$, $-16 \le k \le 16$, $-17 \le l \le 17$ | |
| Reflections collected | 46988 | |
| Independent reflections | 6333 [R(int) = 0.0345] | |
| Completeness to theta = 25.000° | 100.0 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.928 and 0.850 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 6333 / 0 / 468 | |
| Goodness-of-fit on F$^2$ | 1.038 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0272, wR2 = 0.0658 | |
| R indices (all data) | R1 = 0.0329, wR2 = 0.0683 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.598 and –0.490 eÅ$^{-3}$ | |

**Table S2**. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **1a**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 6041(2) | 7114(2) | 2019(1) | 16(1) |
| C(2) | 5589(2) | 6125(2) | 1672(1) | 16(1) |
| C(3) | 4255(2) | 5480(2) | 1728(1) | 17(1) |
| C(4) | 2916(2) | 5585(2) | 2146(2) | 20(1) |
| C(5) | 1839(3) | 4790(2) | 2043(2) | 24(1) |
| C(6) | 2091(3) | 3888(2) | 1536(2) | 27(1) |
| C(7) | 3409(3) | 3755(2) | 1136(2) | 26(1) |
| C(8) | 4485(3) | 4551(2) | 1238(1) | 21(1) |
| C(9) | 6574(2) | 5552(2) | 1168(1) | 21(1) |
| C(10) | 7989(3) | 5938(2) | 1015(2) | 28(1) |
| C(11) | 8409(2) | 6908(2) | 1368(2) | 28(1) |
| C(12) | 7456(2) | 7495(2) | 1866(2) | 22(1) |
| C(13) | 5023(2) | 7696(1) | 2591(1) | 14(1) |
| C(14) | 3838(2) | 8141(1) | 2183(1) | 14(1) |
| C(15) | 2794(2) | 8556(1) | 2775(1) | 14(1) |
| C(16) | 1678(2) | 9214(2) | 2437(1) | 15(1) |
| C(17) | 1894(2) | 9757(2) | 1633(1) | 16(1) |
| C(18) | 907(2) | 10419(2) | 1363(1) | 17(1) |
| C(19) | -345(2) | 10567(2) | 1852(2) | 22(1) |
| C(20) | -539(2) | 10070(2) | 2657(2) | 21(1) |
| C(21) | 468(2) | 9406(2) | 2984(2) | 17(1) |
| C(22) | 314(2) | 8944(2) | 3877(2) | 17(1) |
| C(23) | -986(2) | 8960(2) | 4367(2) | 21(1) |
| C(24) | -1143(2) | 8512(2) | 5200(2) | 24(1) |
| C(25) | 19(2) | 8004(2) | 5548(2) | 21(1) |
| C(26) | 1318(2) | 7978(2) | 5109(2) | 19(1) |
| C(27) | 1511(2) | 8471(2) | 4272(1) | 16(1) |
| C(28) | 2858(2) | 8386(1) | 3752(1) | 15(1) |
| C(29) | 4181(2) | 8073(2) | 4167(1) | 16(1) |
| C(30) | 5230(2) | 7741(2) | 3576(1) | 16(1) |
| C(31) | 3663(2) | 8080(2) | 1123(1) | 15(1) |

| | | | | |
|---|---|---|---|---|
| C(32) | 4694(2) | 8565(2) | 584(2) | 18(1) |
| C(33) | 4508(2) | 8505(2) | -395(2) | 21(1) |
| C(34) | 3310(2) | 7944(2) | -855(2) | 23(1) |
| C(35) | 2283(2) | 7450(2) | -327(2) | 21(1) |
| C(36) | 2461(2) | 7516(2) | 654(2) | 17(1) |
| C(37) | 4588(2) | 8140(2) | 5204(1) | 18(1) |
| C(38) | 4471(2) | 9029(2) | 5764(2) | 22(1) |
| C(39) | 4993(3) | 9118(2) | 6706(2) | 30(1) |
| C(40) | 5627(3) | 8317(2) | 7097(2) | 32(1) |
| C(41) | 5719(3) | 7429(2) | 6559(2) | 27(1) |
| C(42) | 5214(2) | 7342(2) | 5615(2) | 21(1) |
| C(43) | 8278(5) | 4930(3) | 4091(3) | 29(1) |
| C(43A) | 7747(9) | 4876(5) | 4278(5) | 29(1) |
| N(1) | 5888(2) | 4610(1) | 914(1) | 24(1) |
| Cl(1) | 8876(3) | 6144(2) | 3813(2) | 46(1) |
| Cl(2) | 7064(2) | 4358(1) | 3179(1) | 51(1) |
| Cl(3) | 7440(6) | 4957(3) | 5207(3) | 62(1) |
| Cl(1A) | 9030(5) | 5897(3) | 4100(3) | 47(1) |
| Cl(2A) | 6102(3) | 5007(2) | 3615(2) | 54(1) |
| Cl(3A) | 7438(9) | 4799(5) | 5424(5) | 45(1) |
| Br(1) | 1302(1) | 11194(1) | 316(1) | 21(1) |
| Br(2) | -246(1) | 7252(1) | 6626(1) | 31(1) |

**Table S3**. Bond lengths [Å] and angles [°] for **1a**.

| | |
|---|---|
| C(1)-C(12) | 1.387(3) |
| C(1)-C(2) | 1.403(3) |
| C(1)-C(13) | 1.493(3) |
| C(2)-C(9) | 1.415(3) |
| C(2)-C(3) | 1.449(3) |
| C(3)-C(4) | 1.399(3) |
| C(3)-C(8) | 1.416(3) |
| C(4)-C(5) | 1.388(3) |
| C(4)-H(4) | 0.9500 |
| C(5)-C(6) | 1.401(3) |
| C(5)-H(5) | 0.9500 |
| C(6)-C(7) | 1.376(4) |
| C(6)-H(6) | 0.9500 |
| C(7)-C(8) | 1.388(3) |
| C(7)-H(7) | 0.9500 |
| C(8)-N(1) | 1.383(3) |
| C(9)-N(1) | 1.379(3) |
| C(9)-C(10) | 1.390(3) |
| C(10)-C(11) | 1.377(4) |
| C(10)-H(10) | 0.9500 |
| C(11)-C(12) | 1.401(3) |
| C(11)-H(11) | 0.9500 |
| C(12)-H(12) | 0.9500 |
| C(13)-C(14) | 1.394(3) |
| C(13)-C(30) | 1.397(3) |
| C(14)-C(15) | 1.420(3) |
| C(14)-C(31) | 1.501(3) |
| C(15)-C(28) | 1.420(3) |
| C(15)-C(16) | 1.480(3) |
| C(16)-C(17) | 1.408(3) |
| C(16)-C(21) | 1.412(3) |
| C(17)-C(18) | 1.371(3) |
| C(17)-H(17) | 0.9500 |
| C(18)-C(19) | 1.388(3) |

| | |
|---|---|
| C(18)-Br(1) | 1.904(2) |
| C(19)-C(20) | 1.372(3) |
| C(19)-H(19) | 0.9500 |
| C(20)-C(21) | 1.410(3) |
| C(20)-H(20) | 0.9500 |
| C(21)-C(22) | 1.457(3) |
| C(22)-C(23) | 1.408(3) |
| C(22)-C(27) | 1.414(3) |
| C(23)-C(24) | 1.372(3) |
| C(23)-H(23) | 0.9500 |
| C(24)-C(25) | 1.391(3) |
| C(24)-H(24) | 0.9500 |
| C(25)-C(26) | 1.371(3) |
| C(25)-Br(2) | 1.904(2) |
| C(26)-C(27) | 1.411(3) |
| C(26)-H(26) | 0.9500 |
| C(27)-C(28) | 1.475(3) |
| C(28)-C(29) | 1.422(3) |
| C(29)-C(30) | 1.384(3) |
| C(29)-C(37) | 1.495(3) |
| C(30)-H(30) | 0.9500 |
| C(31)-C(32) | 1.394(3) |
| C(31)-C(36) | 1.397(3) |
| C(32)-C(33) | 1.388(3) |
| C(32)-H(32) | 0.9500 |
| C(33)-C(34) | 1.387(3) |
| C(33)-H(33) | 0.9500 |
| C(34)-C(35) | 1.389(3) |
| C(34)-H(34) | 0.9500 |
| C(35)-C(36) | 1.389(3) |
| C(35)-H(35) | 0.9500 |
| C(36)-H(36) | 0.9500 |
| C(37)-C(42) | 1.396(3) |
| C(37)-C(38) | 1.396(3) |
| C(38)-C(39) | 1.391(3) |
| C(38)-H(38) | 0.9500 |

| | |
|---|---|
| C(39)-C(40) | 1.390(4) |
| C(39)-H(39) | 0.9500 |
| C(40)-C(41) | 1.378(4) |
| C(40)-H(40) | 0.9500 |
| C(41)-C(42) | 1.389(3) |
| C(41)-H(41) | 0.9500 |
| C(42)-H(42) | 0.9500 |
| C(43)-Cl(1) | 1.751(4) |
| C(43)-Cl(2) | 1.756(4) |
| C(43)-Cl(3) | 1.793(6) |
| C(43)-H(43) | 1.0000 |
| C(43A)-Cl(3A) | 1.673(10) |
| C(43A)-Cl(2A) | 1.760(7) |
| C(43A)-Cl(1A) | 1.773(8) |
| C(43A)-H(43A) | 1.0000 |
| N(1)-H(1) | 0.8800 |
| C(12)-C(1)-C(2) | 118.58(19) |
| C(12)-C(1)-C(13) | 122.27(19) |
| C(2)-C(1)-C(13) | 119.04(18) |
| C(1)-C(2)-C(9) | 119.4(2) |
| C(1)-C(2)-C(3) | 133.78(19) |
| C(9)-C(2)-C(3) | 106.79(18) |
| C(4)-C(3)-C(8) | 118.7(2) |
| C(4)-C(3)-C(2) | 134.83(19) |
| C(8)-C(3)-C(2) | 106.45(18) |
| C(5)-C(4)-C(3) | 119.2(2) |
| C(5)-C(4)-H(4) | 120.4 |
| C(3)-C(4)-H(4) | 120.4 |
| C(4)-C(5)-C(6) | 120.6(2) |
| C(4)-C(5)-H(5) | 119.7 |
| C(6)-C(5)-H(5) | 119.7 |
| C(7)-C(6)-C(5) | 121.5(2) |
| C(7)-C(6)-H(6) | 119.3 |
| C(5)-C(6)-H(6) | 119.3 |
| C(6)-C(7)-C(8) | 117.9(2) |
| C(6)-C(7)-H(7) | 121.0 |

| | |
|---|---|
| C(8)-C(7)-H(7) | 121.0 |
| N(1)-C(8)-C(7) | 129.4(2) |
| N(1)-C(8)-C(3) | 108.52(19) |
| C(7)-C(8)-C(3) | 122.1(2) |
| N(1)-C(9)-C(10) | 129.8(2) |
| N(1)-C(9)-C(2) | 108.47(19) |
| C(10)-C(9)-C(2) | 121.7(2) |
| C(11)-C(10)-C(9) | 117.8(2) |
| C(11)-C(10)-H(10) | 121.1 |
| C(9)-C(10)-H(10) | 121.1 |
| C(10)-C(11)-C(12) | 121.8(2) |
| C(10)-C(11)-H(11) | 119.1 |
| C(12)-C(11)-H(11) | 119.1 |
| C(1)-C(12)-C(11) | 120.8(2) |
| C(1)-C(12)-H(12) | 119.6 |
| C(11)-C(12)-H(12) | 119.6 |
| C(14)-C(13)-C(30) | 119.35(19) |
| C(14)-C(13)-C(1) | 122.65(18) |
| C(30)-C(13)-C(1) | 117.90(18) |
| C(13)-C(14)-C(15) | 119.36(18) |
| C(13)-C(14)-C(31) | 117.51(17) |
| C(15)-C(14)-C(31) | 122.92(18) |
| C(28)-C(15)-C(14) | 119.38(18) |
| C(28)-C(15)-C(16) | 117.31(18) |
| C(14)-C(15)-C(16) | 123.21(18) |
| C(17)-C(16)-C(21) | 118.66(19) |
| C(17)-C(16)-C(15) | 120.73(18) |
| C(21)-C(16)-C(15) | 120.15(19) |
| C(18)-C(17)-C(16) | 120.42(19) |
| C(18)-C(17)-H(17) | 119.8 |
| C(16)-C(17)-H(17) | 119.8 |
| C(17)-C(18)-C(19) | 121.8(2) |
| C(17)-C(18)-Br(1) | 118.97(16) |
| C(19)-C(18)-Br(1) | 119.16(16) |
| C(20)-C(19)-C(18) | 118.2(2) |
| C(20)-C(19)-H(19) | 120.9 |

| | |
|---|---|
| C(18)-C(19)-H(19) | 120.9 |
| C(19)-C(20)-C(21) | 122.2(2) |
| C(19)-C(20)-H(20) | 118.9 |
| C(21)-C(20)-H(20) | 118.9 |
| C(20)-C(21)-C(16) | 118.4(2) |
| C(20)-C(21)-C(22) | 121.80(19) |
| C(16)-C(21)-C(22) | 119.75(19) |
| C(23)-C(22)-C(27) | 118.80(19) |
| C(23)-C(22)-C(21) | 122.07(19) |
| C(27)-C(22)-C(21) | 119.12(18) |
| C(24)-C(23)-C(22) | 122.2(2) |
| C(24)-C(23)-H(23) | 118.9 |
| C(22)-C(23)-H(23) | 118.9 |
| C(23)-C(24)-C(25) | 117.9(2) |
| C(23)-C(24)-H(24) | 121.0 |
| C(25)-C(24)-H(24) | 121.0 |
| C(26)-C(25)-C(24) | 122.2(2) |
| C(26)-C(25)-Br(2) | 118.79(17) |
| C(24)-C(25)-Br(2) | 118.85(16) |
| C(25)-C(26)-C(27) | 120.2(2) |
| C(25)-C(26)-H(26) | 119.9 |
| C(27)-C(26)-H(26) | 119.9 |
| C(26)-C(27)-C(22) | 118.47(19) |
| C(26)-C(27)-C(28) | 120.75(19) |
| C(22)-C(27)-C(28) | 120.32(18) |
| C(15)-C(28)-C(29) | 118.59(18) |
| C(15)-C(28)-C(27) | 118.14(18) |
| C(29)-C(28)-C(27) | 123.10(18) |
| C(30)-C(29)-C(28) | 118.54(18) |
| C(30)-C(29)-C(37) | 116.33(18) |
| C(28)-C(29)-C(37) | 124.99(18) |
| C(29)-C(30)-C(13) | 122.13(19) |
| C(29)-C(30)-H(30) | 118.9 |
| C(13)-C(30)-H(30) | 118.9 |
| C(32)-C(31)-C(36) | 118.55(19) |
| C(32)-C(31)-C(14) | 121.37(18) |

| | |
|---|---|
| C(36)-C(31)-C(14) | 120.07(18) |
| C(33)-C(32)-C(31) | 120.5(2) |
| C(33)-C(32)-H(32) | 119.7 |
| C(31)-C(32)-H(32) | 119.7 |
| C(34)-C(33)-C(32) | 120.5(2) |
| C(34)-C(33)-H(33) | 119.8 |
| C(32)-C(33)-H(33) | 119.8 |
| C(33)-C(34)-C(35) | 119.5(2) |
| C(33)-C(34)-H(34) | 120.2 |
| C(35)-C(34)-H(34) | 120.2 |
| C(34)-C(35)-C(36) | 120.1(2) |
| C(34)-C(35)-H(35) | 120.0 |
| C(36)-C(35)-H(35) | 120.0 |
| C(35)-C(36)-C(31) | 120.8(2) |
| C(35)-C(36)-H(36) | 119.6 |
| C(31)-C(36)-H(36) | 119.6 |
| C(42)-C(37)-C(38) | 118.7(2) |
| C(42)-C(37)-C(29) | 120.25(19) |
| C(38)-C(37)-C(29) | 120.80(19) |
| C(39)-C(38)-C(37) | 120.3(2) |
| C(39)-C(38)-H(38) | 119.8 |
| C(37)-C(38)-H(38) | 119.8 |
| C(40)-C(39)-C(38) | 120.0(2) |
| C(40)-C(39)-H(39) | 120.0 |
| C(38)-C(39)-H(39) | 120.0 |
| C(41)-C(40)-C(39) | 120.2(2) |
| C(41)-C(40)-H(40) | 119.9 |
| C(39)-C(40)-H(40) | 119.9 |
| C(40)-C(41)-C(42) | 119.9(2) |
| C(40)-C(41)-H(41) | 120.0 |
| C(42)-C(41)-H(41) | 120.0 |
| C(41)-C(42)-C(37) | 120.8(2) |
| C(41)-C(42)-H(42) | 119.6 |
| C(37)-C(42)-H(42) | 119.6 |
| Cl(1)-C(43)-Cl(2) | 109.6(2) |
| Cl(1)-C(43)-Cl(3) | 111.1(3) |

| | |
|---|---|
| Cl(2)-C(43)-Cl(3) | 111.2(3) |
| Cl(1)-C(43)-H(43) | 108.3 |
| Cl(2)-C(43)-H(43) | 108.3 |
| Cl(3)-C(43)-H(43) | 108.3 |
| Cl(3A)-C(43A)-Cl(2A) | 110.8(5) |
| Cl(3A)-C(43A)-Cl(1A) | 111.8(5) |
| Cl(2A)-C(43A)-Cl(1A) | 109.1(4) |
| Cl(3A)-C(43A)-H(43A) | 108.3 |
| Cl(2A)-C(43A)-H(43A) | 108.3 |
| Cl(1A)-C(43A)-H(43A) | 108.3 |
| C(9)-N(1)-C(8) | 109.75(17) |
| C(9)-N(1)-H(1) | 125.1 |
| C(8)-N(1)-H(1) | 125.1 |

**Table S4**. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1a**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 15(1) | 23(1) | 11(1) | 5(1) | 2(1) | 6(1) |
| C(2) | 18(1) | 22(1) | 10(1) | 5(1) | 3(1) | 10(1) |
| C(3) | 24(1) | 16(1) | 10(1) | 3(1) | 1(1) | 7(1) |
| C(4) | 26(1) | 18(1) | 15(1) | 2(1) | 3(1) | 4(1) |
| C(5) | 28(1) | 24(1) | 20(1) | 5(1) | 4(1) | -1(1) |
| C(6) | 40(1) | 21(1) | 19(1) | 4(1) | -3(1) | -6(1) |
| C(7) | 44(2) | 17(1) | 16(1) | 0(1) | -3(1) | 6(1) |
| C(8) | 31(1) | 21(1) | 13(1) | 4(1) | 1(1) | 10(1) |
| C(9) | 25(1) | 29(1) | 12(1) | 3(1) | 2(1) | 13(1) |
| C(10) | 24(1) | 44(2) | 20(1) | 3(1) | 8(1) | 20(1) |
| C(11) | 14(1) | 48(2) | 25(1) | 7(1) | 7(1) | 6(1) |
| C(12) | 18(1) | 30(1) | 20(1) | 5(1) | 1(1) | 3(1) |
| C(13) | 15(1) | 13(1) | 16(1) | 3(1) | 3(1) | -2(1) |
| C(14) | 14(1) | 12(1) | 15(1) | 1(1) | 3(1) | -3(1) |
| C(15) | 14(1) | 10(1) | 17(1) | -1(1) | 2(1) | -2(1) |
| C(16) | 15(1) | 12(1) | 18(1) | -5(1) | 0(1) | 1(1) |
| C(17) | 15(1) | 15(1) | 17(1) | -3(1) | 1(1) | 1(1) |
| C(18) | 20(1) | 13(1) | 17(1) | -2(1) | -2(1) | 0(1) |
| C(19) | 20(1) | 21(1) | 25(1) | -2(1) | -3(1) | 7(1) |
| C(20) | 16(1) | 21(1) | 26(1) | -4(1) | 4(1) | 5(1) |
| C(21) | 15(1) | 15(1) | 20(1) | -5(1) | 1(1) | 1(1) |
| C(22) | 16(1) | 14(1) | 19(1) | -4(1) | 4(1) | -1(1) |
| C(23) | 18(1) | 20(1) | 26(1) | -4(1) | 5(1) | 3(1) |
| C(24) | 20(1) | 24(1) | 26(1) | -5(1) | 12(1) | -2(1) |
| C(25) | 27(1) | 18(1) | 19(1) | -2(1) | 9(1) | -6(1) |
| C(26) | 20(1) | 16(1) | 19(1) | -1(1) | 5(1) | -2(1) |
| C(27) | 17(1) | 13(1) | 17(1) | -5(1) | 4(1) | -3(1) |
| C(28) | 18(1) | 10(1) | 17(1) | -1(1) | 4(1) | -1(1) |
| C(29) | 17(1) | 14(1) | 15(1) | 1(1) | 2(1) | -2(1) |
| C(30) | 15(1) | 15(1) | 18(1) | 3(1) | 1(1) | 1(1) |
| C(31) | 15(1) | 14(1) | 16(1) | 1(1) | 2(1) | 7(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(32) | 17(1) | 18(1) | 19(1) | 2(1) | 3(1) | 4(1) |
| C(33) | 21(1) | 25(1) | 20(1) | 5(1) | 7(1) | 7(1) |
| C(34) | 28(1) | 30(1) | 12(1) | 0(1) | 2(1) | 18(1) |
| C(35) | 18(1) | 24(1) | 22(1) | -4(1) | -4(1) | 13(1) |
| C(36) | 14(1) | 17(1) | 21(1) | 1(1) | 3(1) | 6(1) |
| C(37) | 14(1) | 23(1) | 16(1) | 1(1) | 5(1) | -5(1) |
| C(38) | 22(1) | 22(1) | 21(1) | 0(1) | 8(1) | -6(1) |
| C(39) | 33(1) | 35(1) | 19(1) | -10(1) | 10(1) | -14(1) |
| C(40) | 27(1) | 51(2) | 14(1) | 4(1) | 3(1) | -14(1) |
| C(41) | 23(1) | 39(1) | 19(1) | 11(1) | 2(1) | -5(1) |
| C(42) | 19(1) | 26(1) | 17(1) | 4(1) | 3(1) | -3(1) |
| N(1) | 32(1) | 24(1) | 20(1) | -2(1) | 4(1) | 17(1) |
| Cl(1) | 49(1) | 23(1) | 64(2) | -3(1) | -4(1) | -3(1) |
| Cl(2) | 59(1) | 42(1) | 47(1) | 17(1) | -31(1) | -22(1) |
| Cl(3) | 68(1) | 47(2) | 72(3) | -2(2) | 9(2) | 13(1) |
| Cl(1A) | 43(2) | 56(2) | 41(2) | 15(1) | -1(1) | -10(2) |
| Cl(2A) | 61(2) | 55(1) | 43(1) | 28(1) | -30(1) | -23(1) |
| Cl(3A) | 54(2) | 32(2) | 48(2) | 10(2) | -18(2) | -6(1) |
| Br(1) | 24(1) | 17(1) | 22(1) | 3(1) | -3(1) | 2(1) |
| Br(2) | 38(1) | 28(1) | 28(1) | 5(1) | 16(1) | -4(1) |

**Table S5**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for **1a**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(4) | 2745 | 6193 | 2495 | 24 |
| H(5) | 924 | 4858 | 2319 | 29 |
| H(6) | 1336 | 3356 | 1467 | 32 |
| H(7) | 3578 | 3138 | 801 | 31 |
| H(10) | 8644 | 5545 | 680 | 34 |
| H(11) | 9372 | 7186 | 1271 | 34 |
| H(12) | 7781 | 8161 | 2101 | 27 |
| H(17) | 2731 | 9663 | 1276 | 19 |
| H(19) | -1048 | 10999 | 1636 | 26 |
| H(20) | -1380 | 10177 | 3005 | 25 |
| H(23) | -1781 | 9293 | 4111 | 25 |
| H(24) | -2019 | 8548 | 5530 | 28 |
| H(26) | 2090 | 7626 | 5369 | 22 |
| H(30) | 6120 | 7536 | 3848 | 19 |
| H(32) | 5530 | 8940 | 890 | 21 |
| H(33) | 5207 | 8850 | -754 | 26 |
| H(34) | 3193 | 7899 | -1526 | 27 |
| H(35) | 1458 | 7066 | -636 | 25 |
| H(36) | 1756 | 7174 | 1011 | 20 |
| H(38) | 4032 | 9576 | 5499 | 26 |
| H(39) | 4917 | 9726 | 7082 | 36 |
| H(40) | 5997 | 8383 | 7738 | 38 |
| H(41) | 6129 | 6877 | 6832 | 32 |
| H(42) | 5295 | 6731 | 5243 | 25 |
| H(43) | 9153 | 4526 | 4139 | 35 |
| H(43A) | 8157 | 4240 | 4039 | 35 |
| H(1) | 6283 | 4121 | 595 | 29 |

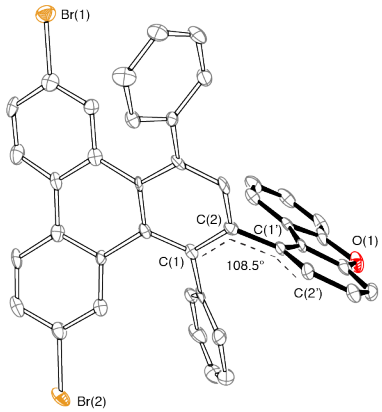


**Figure S8**. ORTEP representation of the molecular structures of the **1b**. Thermal ellipsoids are drawn at the 50% probability level. Color coding: C (gray), Br (orange), O (red). Hydrogen atoms and solvent molecules are omitted for clarity.

**Table S6**. Crystal data and structure refinement for **1b**.

| | | |
|---|---|---|
| CCDC no. | 1567589 | |
| Empirical formula | $C_{42}H_{24}Br_2O$ | |
| Formula weight | 704.43 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | P b c a | |
| Unit cell dimensions | $a$ = 7.8289(5) Å | $\alpha$ = 90° |
| | $b$ = 24.8954(18) Å | $\beta$ = 90° |
| | $c$ = 31.810(2) Å | $\gamma$ = 90° |
| Volume | 6200.0(7) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.509 $Mg/m^3$ | |
| Absorption coefficient | 2.649 $mm^{-1}$ | |
| F(000) | 2832 | |
| Crystal size | 0.100 x 0.010 x 0.005 $mm^3$ | |
| Theta range for data collection | 1.280° to 25.393° | |
| Index ranges | $-9 \le h \le 9$, $-29 \le k \le 30$, $-38 \le l \le 38$ | |
| Reflections collected | 59809 | |
| Independent reflections | 5706 [R(int) = 0.1869] | |
| Completeness to theta = 25.000° | 100.0 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7896 and 0.7196 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 5706 / 0 / 406 | |
| Goodness-of-fit on $F^2$ | 1.007 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0655, wR2 = 0.1404 | |
| R indices (all data) | R1 = 0.1384, wR2 = 0.1738 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 1.323 and –0.986 $eÅ^{-3}$ | |

**Table S7**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **1b**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 144(9) | 2431(3) | 7040(2) | 26(2) |
| C(2) | -1398(9) | 2619(3) | 7185(2) | 31(2) |
| C(3) | -1678(9) | 3155(3) | 7147(2) | 33(2) |
| C(4) | -500(8) | 3497(3) | 6950(2) | 26(2) |
| C(5) | 1009(8) | 3294(2) | 6783(2) | 21(2) |
| C(6) | 1369(8) | 2750(3) | 6843(2) | 22(2) |
| C(7) | 2789(8) | 2409(3) | 6744(2) | 24(2) |
| C(8) | 4431(8) | 2475(3) | 6581(2) | 27(2) |
| C(9) | 5482(10) | 2031(3) | 6543(2) | 35(2) |
| C(10) | 4923(11) | 1521(3) | 6666(2) | 40(2) |
| C(11) | 3297(11) | 1447(3) | 6830(2) | 40(2) |
| C(12) | 2288(9) | 1894(3) | 6874(2) | 28(2) |
| C(13) | 2235(8) | 3642(2) | 6545(2) | 20(1) |
| C(14) | 2398(8) | 3580(2) | 6107(2) | 19(1) |
| C(15) | 3617(7) | 3900(2) | 5889(2) | 19(2) |
| C(16) | 3634(7) | 3944(2) | 5421(2) | 17(1) |
| C(17) | 2216(8) | 3806(2) | 5173(2) | 23(2) |
| C(18) | 2224(9) | 3885(3) | 4744(2) | 26(2) |
| C(19) | 3619(9) | 4115(3) | 4544(2) | 33(2) |
| C(20) | 4993(9) | 4263(3) | 4781(2) | 29(2) |
| C(21) | 5044(8) | 4188(3) | 5219(2) | 24(2) |
| C(22) | 6501(8) | 4371(2) | 5466(2) | 23(2) |
| C(23) | 8061(9) | 4514(3) | 5281(2) | 34(2) |
| C(24) | 9389(9) | 4719(3) | 5496(2) | 31(2) |
| C(25) | 9205(9) | 4774(3) | 5934(2) | 30(2) |
| C(26) | 7734(8) | 4605(2) | 6132(2) | 22(2) |
| C(27) | 6331(8) | 4414(2) | 5911(2) | 22(2) |
| C(28) | 4785(8) | 4222(2) | 6117(2) | 16(1) |
| C(29) | 4448(8) | 4320(3) | 6550(2) | 21(2) |
| C(30) | 3203(8) | 4024(3) | 6750(2) | 23(2) |
| C(31) | 1323(8) | 3162(3) | 5893(2) | 22(2) |
| C(32) | -452(9) | 3200(3) | 5893(2) | 31(2) |
| C(33) | -1438(10) | 2816(3) | 5678(2) | 38(2) |
| C(34) | -644(11) | 2404(3) | 5469(2) | 45(2) |
| C(35) | 1118(11) | 2352(3) | 5477(2) | 38(2) |
| C(36) | 2085(9) | 2736(3) | 5688(2) | 26(2) |
| C(37) | 5213(7) | 4782(3) | 6785(2) | 20(2) |
| C(38) | 5941(8) | 4715(3) | 7184(2) | 28(2) |
| C(39) | 6642(9) | 5149(3) | 7388(2) | 34(2) |
| C(40) | 6637(9) | 5653(3) | 7215(2) | 36(2) |
| C(41) | 5875(9) | 5728(3) | 6818(2) | 33(2) |
| C(42) | 5174(8) | 5295(2) | 6611(2) | 23(2) |
| O(1) | 680(6) | 1901(2) | 7054(2) | 35(1) |
| Br(1) | 296(1) | 3678(1) | 4427(1) | 37(1) |
| Br(2) | 10993(1) | 5077(1) | 6253(1) | 36(1) |

**Table S8.** Bond lengths [Å] and angles [°] for **1b**.

| | |
|---|---|
| C(1)-C(2) | 1.375(9) |
| C(1)-O(1) | 1.387(8) |
| C(1)-C(6) | 1.394(9) |
| C(2)-C(3) | 1.359(9) |
| C(2)-H(2) | 0.9500 |
| C(3)-C(4) | 1.402(9) |
| C(3)-H(3) | 0.9500 |
| C(4)-C(5) | 1.391(9) |
| C(4)-H(4) | 0.9500 |
| C(5)-C(6) | 1.396(9) |
| C(5)-C(13) | 1.497(9) |
| C(6)-C(7) | 1.434(9) |
| C(7)-C(8) | 1.396(9) |
| C(7)-C(12) | 1.404(9) |
| C(8)-C(9) | 1.384(9) |
| C(8)-H(8) | 0.9500 |
| C(9)-C(10) | 1.400(10) |
| C(9)-H(9) | 0.9500 |
| C(10)-C(11) | 1.388(11) |
| C(10)-H(10) | 0.9500 |
| C(11)-C(12) | 1.370(9) |
| C(11)-H(11) | 0.9500 |
| C(12)-O(1) | 1.382(8) |
| C(13)-C(30) | 1.379(9) |
| C(13)-C(14) | 1.408(8) |
| C(14)-C(15) | 1.424(8) |
| C(14)-C(31) | 1.502(9) |
| C(15)-C(28) | 1.417(8) |
| C(15)-C(16) | 1.490(8) |
| C(16)-C(17) | 1.405(8) |
| C(16)-C(21) | 1.415(8) |
| C(17)-C(18) | 1.379(9) |
| C(17)-H(17) | 0.9500 |
| C(18)-C(19) | 1.387(9) |
| C(18)-Br(1) | 1.887(7) |
| C(19)-C(20) | 1.363(10) |
| C(19)-H(19) | 0.9500 |
| C(20)-C(21) | 1.406(9) |
| C(20)-H(20) | 0.9500 |
| C(21)-C(22) | 1.460(9) |
| C(22)-C(23) | 1.402(9) |
| C(22)-C(27) | 1.425(9) |
| C(23)-C(24) | 1.344(10) |
| C(23)-H(23) | 0.9500 |
| C(24)-C(25) | 1.406(10) |
| C(24)-H(24) | 0.9500 |
| C(25)-C(26) | 1.379(9) |
| C(25)-Br(2) | 1.886(7) |
| C(26)-C(27) | 1.388(9) |
| C(26)-H(26) | 0.9500 |
| C(27)-C(28) | 1.456(8) |
| C(28)-C(29) | 1.423(8) |
| C(29)-C(30) | 1.378(9) |
| C(29)-C(37) | 1.497(9) |

| | |
|---|---|
| C(30)-H(30) | 0.9500 |
| C(31)-C(36) | 1.380(9) |
| C(31)-C(32) | 1.393(9) |
| C(32)-C(33) | 1.407(10) |
| C(32)-H(32) | 0.9500 |
| C(33)-C(34) | 1.372(10) |
| C(33)-H(33) | 0.9500 |
| C(34)-C(35) | 1.386(11) |
| C(34)-H(34) | 0.9500 |
| C(35)-C(36) | 1.392(9) |
| C(35)-H(35) | 0.9500 |
| C(36)-H(36) | 0.9500 |
| C(37)-C(42) | 1.394(9) |
| C(37)-C(38) | 1.402(9) |
| C(38)-C(39) | 1.374(9) |
| C(38)-H(38) | 0.9500 |
| C(39)-C(40) | 1.371(10) |
| C(39)-H(39) | 0.9500 |
| C(40)-C(41) | 1.407(10) |
| C(40)-H(40) | 0.9500 |
| C(41)-C(42) | 1.379(9) |
| C(41)-H(41) | 0.9500 |
| C(42)-H(42) | 0.9500 |

| | |
|---|---|
| C(2)-C(1)-O(1) | 125.3(6) |
| C(2)-C(1)-C(6) | 124.2(6) |
| O(1)-C(1)-C(6) | 110.4(6) |
| C(3)-C(2)-C(1) | 116.4(6) |
| C(3)-C(2)-H(2) | 121.8 |
| C(1)-C(2)-H(2) | 121.8 |
| C(2)-C(3)-C(4) | 122.1(7) |
| C(2)-C(3)-H(3) | 119.0 |
| C(4)-C(3)-H(3) | 119.0 |
| C(5)-C(4)-C(3) | 120.6(7) |
| C(5)-C(4)-H(4) | 119.7 |
| C(3)-C(4)-H(4) | 119.7 |
| C(4)-C(5)-C(6) | 118.2(6) |
| C(4)-C(5)-C(13) | 121.9(6) |
| C(6)-C(5)-C(13) | 120.0(6) |
| C(1)-C(6)-C(5) | 118.3(6) |
| C(1)-C(6)-C(7) | 107.1(6) |
| C(5)-C(6)-C(7) | 134.6(6) |
| C(8)-C(7)-C(12) | 118.4(6) |
| C(8)-C(7)-C(6) | 136.4(6) |
| C(12)-C(7)-C(6) | 105.1(6) |
| C(9)-C(8)-C(7) | 119.1(7) |
| C(9)-C(8)-H(8) | 120.5 |
| C(7)-C(8)-H(8) | 120.5 |
| C(8)-C(9)-C(10) | 121.0(7) |
| C(8)-C(9)-H(9) | 119.5 |
| C(10)-C(9)-H(9) | 119.5 |
| C(11)-C(10)-C(9) | 120.8(7) |
| C(11)-C(10)-H(10) | 119.6 |
| C(9)-C(10)-H(10) | 119.6 |
| C(12)-C(11)-C(10) | 117.4(7) |
| C(12)-C(11)-H(11) | 121.3 |

| | |
|---|---|
| C(10)-C(11)-H(11) | 121.3 |
| C(11)-C(12)-O(1) | 125.3(7) |
| C(11)-C(12)-C(7) | 123.3(7) |
| O(1)-C(12)-C(7) | 111.4(6) |
| C(30)-C(13)-C(14) | 119.5(6) |
| C(30)-C(13)-C(5) | 120.8(6) |
| C(14)-C(13)-C(5) | 119.7(5) |
| C(13)-C(14)-C(15) | 118.9(6) |
| C(13)-C(14)-C(31) | 118.3(5) |
| C(15)-C(14)-C(31) | 122.8(6) |
| C(28)-C(15)-C(14) | 119.9(6) |
| C(28)-C(15)-C(16) | 117.6(5) |
| C(14)-C(15)-C(16) | 122.3(5) |
| C(17)-C(16)-C(21) | 117.7(6) |
| C(17)-C(16)-C(15) | 122.4(5) |
| C(21)-C(16)-C(15) | 119.5(5) |
| C(18)-C(17)-C(16) | 121.2(6) |
| C(18)-C(17)-H(17) | 119.4 |
| C(16)-C(17)-H(17) | 119.4 |
| C(17)-C(18)-C(19) | 121.1(6) |
| C(17)-C(18)-Br(1) | 119.1(5) |
| C(19)-C(18)-Br(1) | 119.8(5) |
| C(20)-C(19)-C(18) | 118.7(7) |
| C(20)-C(19)-H(19) | 120.7 |
| C(18)-C(19)-H(19) | 120.7 |
| C(19)-C(20)-C(21) | 122.2(6) |
| C(19)-C(20)-H(20) | 118.9 |
| C(21)-C(20)-H(20) | 118.9 |
| C(20)-C(21)-C(16) | 119.1(6) |
| C(20)-C(21)-C(22) | 121.1(6) |
| C(16)-C(21)-C(22) | 119.8(6) |
| C(23)-C(22)-C(27) | 118.6(6) |
| C(23)-C(22)-C(21) | 122.2(6) |
| C(27)-C(22)-C(21) | 119.1(6) |
| C(24)-C(23)-C(22) | 123.8(7) |
| C(24)-C(23)-H(23) | 118.1 |
| C(22)-C(23)-H(23) | 118.1 |
| C(23)-C(24)-C(25) | 117.4(6) |
| C(23)-C(24)-H(24) | 121.3 |
| C(25)-C(24)-H(24) | 121.3 |
| C(26)-C(25)-C(24) | 120.6(6) |
| C(26)-C(25)-Br(2) | 119.7(5) |
| C(24)-C(25)-Br(2) | 119.7(5) |
| C(25)-C(26)-C(27) | 122.2(7) |
| C(25)-C(26)-H(26) | 118.9 |
| C(27)-C(26)-H(26) | 118.9 |
| C(26)-C(27)-C(22) | 117.0(6) |
| C(26)-C(27)-C(28) | 122.9(6) |
| C(22)-C(27)-C(28) | 119.9(6) |
| C(15)-C(28)-C(29) | 118.3(5) |
| C(15)-C(28)-C(27) | 119.5(6) |
| C(29)-C(28)-C(27) | 122.2(6) |
| C(30)-C(29)-C(28) | 119.1(6) |
| C(30)-C(29)-C(37) | 117.6(6) |
| C(28)-C(29)-C(37) | 122.8(6) |
| C(29)-C(30)-C(13) | 122.7(6) |

| | |
|---|---|
| C(29)-C(30)-H(30) | 118.7 |
| C(13)-C(30)-H(30) | 118.7 |
| C(36)-C(31)-C(32) | 119.0(6) |
| C(36)-C(31)-C(14) | 120.3(6) |
| C(32)-C(31)-C(14) | 120.7(6) |
| C(31)-C(32)-C(33) | 120.0(7) |
| C(31)-C(32)-H(32) | 120.0 |
| C(33)-C(32)-H(32) | 120.0 |
| C(34)-C(33)-C(32) | 119.7(7) |
| C(34)-C(33)-H(33) | 120.2 |
| C(32)-C(33)-H(33) | 120.2 |
| C(33)-C(34)-C(35) | 120.8(7) |
| C(33)-C(34)-H(34) | 119.6 |
| C(35)-C(34)-H(34) | 119.6 |
| C(34)-C(35)-C(36) | 119.1(7) |
| C(34)-C(35)-H(35) | 120.5 |
| C(36)-C(35)-H(35) | 120.5 |
| C(31)-C(36)-C(35) | 121.3(7) |
| C(31)-C(36)-H(36) | 119.3 |
| C(35)-C(36)-H(36) | 119.3 |
| C(42)-C(37)-C(38) | 118.6(6) |
| C(42)-C(37)-C(29) | 119.8(6) |
| C(38)-C(37)-C(29) | 121.6(6) |
| C(39)-C(38)-C(37) | 119.7(7) |
| C(39)-C(38)-H(38) | 120.2 |
| C(37)-C(38)-H(38) | 120.2 |
| C(40)-C(39)-C(38) | 122.1(7) |
| C(40)-C(39)-H(39) | 119.0 |
| C(38)-C(39)-H(39) | 119.0 |
| C(39)-C(40)-C(41) | 118.8(7) |
| C(39)-C(40)-H(40) | 120.6 |
| C(41)-C(40)-H(40) | 120.6 |
| C(42)-C(41)-C(40) | 119.7(7) |
| C(42)-C(41)-H(41) | 120.2 |
| C(40)-C(41)-H(41) | 120.2 |
| C(41)-C(42)-C(37) | 121.2(7) |
| C(41)-C(42)-H(42) | 119.4 |
| C(37)-C(42)-H(42) | 119.4 |
| C(12)-O(1)-C(1) | 105.9(5) |

**Table S9.** Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1b**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 42(4) | 24(4) | 12(4) | -5(3) | -3(3) | -8(3) |
| C(2) | 36(4) | 39(5) | 18(4) | -4(3) | 7(3) | -14(3) |
| C(3) | 38(4) | 48(5) | 14(4) | -2(3) | 3(3) | -2(4) |
| C(4) | 29(4) | 34(4) | 15(4) | 0(3) | 4(3) | -4(3) |
| C(5) | 27(4) | 25(4) | 11(3) | 2(3) | -3(3) | -6(3) |
| C(6) | 30(4) | 29(4) | 8(3) | 1(3) | -1(3) | -9(3) |
| C(7) | 34(4) | 31(4) | 7(3) | -4(3) | -3(3) | 0(3) |
| C(8) | 38(4) | 28(4) | 15(4) | -2(3) | -2(3) | 6(3) |
| C(9) | 43(4) | 44(5) | 19(4) | -6(3) | -1(3) | 9(4) |
| C(10) | 63(6) | 39(5) | 18(4) | -6(3) | -8(4) | 13(4) |
| C(11) | 75(6) | 29(5) | 16(4) | 2(3) | -2(4) | 7(4) |
| C(12) | 48(5) | 28(4) | 10(4) | -2(3) | 3(3) | -3(3) |
| C(13) | 22(3) | 24(4) | 15(4) | -3(3) | -1(3) | 3(3) |
| C(14) | 27(4) | 14(3) | 15(4) | 0(3) | -1(3) | 2(3) |
| C(15) | 23(4) | 18(3) | 14(4) | 4(3) | 1(3) | 7(3) |
| C(16) | 20(3) | 20(4) | 12(3) | -2(3) | 7(3) | -1(3) |
| C(17) | 32(4) | 17(4) | 21(4) | -1(3) | 3(3) | 1(3) |
| C(18) | 38(4) | 25(4) | 17(4) | -3(3) | 1(3) | -2(3) |
| C(19) | 53(5) | 28(4) | 17(4) | 5(3) | 3(4) | 4(4) |
| C(20) | 41(5) | 34(4) | 12(4) | 4(3) | 11(3) | -1(3) |
| C(21) | 31(4) | 22(4) | 19(4) | -4(3) | 9(3) | 1(3) |
| C(22) | 35(4) | 19(4) | 15(4) | 2(3) | 5(3) | 1(3) |
| C(23) | 42(5) | 33(4) | 26(5) | -1(3) | 13(4) | -5(4) |
| C(24) | 29(4) | 35(4) | 30(5) | 6(3) | 16(3) | -7(3) |
| C(25) | 34(4) | 21(4) | 33(5) | -3(3) | 2(4) | 0(3) |
| C(26) | 20(3) | 23(4) | 23(4) | -1(3) | 2(3) | 2(3) |
| C(27) | 29(4) | 16(4) | 22(4) | 0(3) | 4(3) | 5(3) |
| C(28) | 20(3) | 21(3) | 8(3) | 5(3) | 5(3) | 1(3) |
| C(29) | 26(4) | 27(4) | 9(3) | 0(3) | -3(3) | 7(3) |
| C(30) | 32(4) | 33(4) | 4(3) | -3(3) | 5(3) | 3(3) |
| C(31) | 39(4) | 25(4) | 3(3) | 0(3) | 3(3) | -2(3) |
| C(32) | 33(4) | 43(5) | 16(4) | -4(3) | 4(3) | -10(3) |
| C(33) | 39(5) | 48(5) | 28(5) | 2(4) | -5(4) | -17(4) |
| C(34) | 71(7) | 33(5) | 32(5) | 1(4) | -18(4) | -24(4) |
| C(35) | 66(6) | 28(4) | 21(4) | -4(3) | -12(4) | -1(4) |
| C(36) | 34(4) | 29(4) | 15(4) | 3(3) | -3(3) | -7(3) |
| C(37) | 15(3) | 30(4) | 14(3) | 1(3) | 5(3) | -1(3) |
| C(38) | 30(4) | 32(4) | 20(4) | 4(3) | 1(3) | 0(3) |
| C(39) | 41(4) | 47(5) | 14(4) | -5(4) | -4(3) | -3(4) |
| C(40) | 45(5) | 40(5) | 23(4) | -14(4) | -3(4) | -13(4) |
| C(41) | 39(4) | 25(4) | 36(5) | -15(3) | -3(4) | 4(3) |
| C(42) | 28(4) | 22(4) | 17(4) | 0(3) | 3(3) | 4(3) |
| O(1) | 58(4) | 27(3) | 19(3) | -4(2) | 7(2) | -8(2) |
| Br(1) | 52(1) | 44(1) | 14(1) | -3(1) | -9(1) | 1(1) |
| Br(2) | 24(1) | 39(1) | 43(1) | 3(1) | -4(1) | -1(1) |

**Table S10**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for **1b**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | -2224 | 2386 | 7307 | 37 |
| H(3) | -2704 | 3303 | 7256 | 40 |
| H(4) | -734 | 3871 | 6932 | 31 |
| H(8) | 4821 | 2820 | 6498 | 32 |
| H(9) | 6600 | 2073 | 6431 | 42 |
| H(10) | 5665 | 1221 | 6636 | 48 |
| H(11) | 2898 | 1101 | 6908 | 48 |
| H(17) | 1234 | 3655 | 5303 | 28 |
| H(19) | 3616 | 4168 | 4249 | 39 |
| H(20) | 5949 | 4421 | 4645 | 35 |
| H(23) | 8187 | 4463 | 4987 | 40 |
| H(24) | 10412 | 4823 | 5357 | 38 |
| H(26) | 7679 | 4620 | 6430 | 26 |
| H(30) | 3004 | 4085 | 7040 | 28 |
| H(32) | -997 | 3486 | 6038 | 37 |
| H(33) | -2649 | 2842 | 5677 | 46 |
| H(34) | -1309 | 2151 | 5317 | 54 |
| H(35) | 1659 | 2058 | 5341 | 46 |
| H(36) | 3295 | 2705 | 5690 | 31 |
| H(38) | 5950 | 4371 | 7314 | 33 |
| H(39) | 7146 | 5098 | 7656 | 41 |
| H(40) | 7140 | 5947 | 7360 | 43 |
| H(41) | 5843 | 6076 | 6695 | 40 |
| H(42) | 4656 | 5348 | 6344 | 27 |

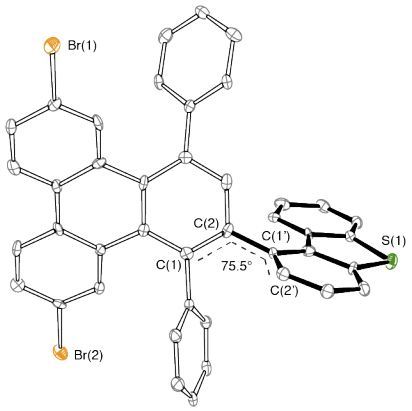


**Figure S9**. ORTEP representation of the molecular structures of the **1c**. Thermal ellipsoids are drawn at the 50% probability level. Color coding: C (gray), Br (orange), S (green). Hydrogen atoms are omitted for clarity.

**Table S11**. Crystal data and structure refinement for **1c**.

| | | |
|---|---|---|
| CCDC no. | 1567588 | |
| Empirical formula | $C_{49}H_{32}Br_2S$ | |
| Formula weight | 812.62 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P–1 | |
| Unit cell dimensions | $a$ = 7.0949(4) Å | $\alpha$ = 104.009(3)° |
| | $b$ = 16.1951(9) Å | $\beta$ = 92.325(3)° |
| | $c$ = 16.9526(9) Å | $\gamma$ = 93.650(3)° |
| Volume | 1882.97(18) Å$^3$ | |
| Z | 2 | |
| Density (calculated) | 1.433 Mg/ m$^3$ | |
| Absorption coefficient | 2.243 mm$^{-1}$ | |
| F(000) | 824 | |
| Crystal size | 0.050 x 0.040 x 0.020 m m$^3$ | |
| Theta range for data collection | 1.240° to 25.393° | |
| Index ranges | $-8 \le h \le 8$, $-19 \le k \le 19$, $-20 \le l \le 20$ | |
| Reflections collected | 11841 | |
| Independent reflections | 11841 [R(int) = 0.0503] | |
| Completeness to theta = 25.000° | 98.8 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.928 and 0.824 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 11841 / 0 / 436 | |
| Goodness-of-fit on F$^2$ | 1.027 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0520, wR2 = 0.1274 | |
| R indices (all data) | R1 = 0.0706, wR2 = 0.1360 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 1.103 and –0.480 eÅ$^{-3}$ | |

**Table S12**. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **1c**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 6384(8) | 6741(4) | 2586(4) | 21(1) |
| C(2) | 5713(7) | 7549(3) | 2734(3) | 16(1) |
| C(3) | 6559(8) | 8189(3) | 3396(3) | 16(1) |
| C(4) | 6439(8) | 9111(4) | 3464(3) | 17(1) |
| C(5) | 5972(7) | 9423(3) | 2782(4) | 19(1) |
| C(6) | 5929(8) | 10285(3) | 2845(4) | 17(1) |
| C(7) | 6375(8) | 10879(4) | 3583(3) | 18(1) |
| C(8) | 6888(7) | 10584(4) | 4242(4) | 19(1) |
| C(9) | 6975(8) | 9710(3) | 4198(3) | 14(1) |
| C(10) | 7634(7) | 9408(3) | 4900(3) | 16(1) |
| C(11) | 7878(8) | 9974(4) | 5696(4) | 19(1) |
| C(12) | 8413(8) | 9716(4) | 6365(4) | 20(1) |
| C(13) | 8742(8) | 8850(4) | 6260(3) | 17(1) |
| C(14) | 8535(7) | 8276(3) | 5509(3) | 16(1) |
| C(15) | 7993(7) | 8551(3) | 4801(3) | 14(1) |
| C(16) | 7710(8) | 7947(3) | 4001(3) | 15(1) |
| C(17) | 8428(7) | 7123(3) | 3796(3) | 16(1) |
| C(18) | 7863(8) | 6543(3) | 3072(3) | 15(1) |
| C(19) | 4043(8) | 7635(3) | 2209(3) | 15(1) |
| C(20) | 3845(9) | 7215(4) | 1395(3) | 23(1) |
| C(21) | 2158(9) | 7207(4) | 936(4) | 33(2) |
| C(22) | 662(9) | 7637(4) | 1292(4) | 30(2) |
| C(23) | 851(8) | 8074(4) | 2091(4) | 24(2) |
| C(24) | 2525(8) | 8078(3) | 2553(3) | 16(1) |
| C(25) | 9960(8) | 6878(3) | 4327(3) | 18(1) |
| C(26) | 11793(8) | 7249(4) | 4370(3) | 20(1) |
| C(27) | 13236(8) | 7032(4) | 4855(4) | 25(2) |
| C(28) | 12796(9) | 6444(3) | 5313(3) | 21(1) |
| C(29) | 10974(8) | 6061(3) | 5259(3) | 20(1) |
| C(30) | 9580(8) | 6258(3) | 4755(3) | 16(1) |
| C(31) | 8803(8) | 5751(3) | 2734(3) | 18(1) |
| C(32) | 10540(8) | 5852(4) | 2380(3) | 18(1) |
| C(33) | 11433(8) | 5179(4) | 1954(4) | 23(1) |
| C(34) | 10647(8) | 4344(4) | 1847(3) | 21(1) |
| C(35) | 8952(8) | 4233(3) | 2184(3) | 17(1) |
| C(36) | 5889(8) | 3718(4) | 2667(3) | 19(1) |
| C(37) | 4312(8) | 3288(4) | 2860(3) | 19(1) |
| C(38) | 3041(8) | 3743(4) | 3327(4) | 24(1) |
| C(39) | 3353(8) | 4630(4) | 3630(4) | 24(2) |
| C(40) | 4941(8) | 5060(4) | 3425(3) | 18(1) |
| C(41) | 6249(8) | 4610(3) | 2937(3) | 15(1) |
| C(42) | 7978(8) | 4926(4) | 2642(3) | 18(1) |
| C(43) | 9919(14) | 9017(6) | 250(6) | 67(3) |
| C(44) | 8237(11) | 9104(5) | 620(5) | 50(2) |
| C(45) | 6619(13) | 8691(6) | 299(6) | 68(3) |
| C(46) | 6484(13) | 8111(6) | -463(5) | 63(2) |
| C(47) | 8197(13) | 8025(6) | -850(6) | 68(3) |
| C(48) | 9851(12) | 8425(5) | -540(5) | 52(2) |
| C(49) | 11666(13) | 9444(6) | 621(6) | 80(3) |
| S(1) | 7724(2) | 3239(1) | 2096(1) | 23(1) |
| Br(1) | 5307(1) | 10699(1) | 1921(1) | 29(1) |
| Br(2) | 9478(1) | 8463(1) | 7189(1) | 26(1) |

**Table S13**. Bond lengths [Å] and angles [°] for **1c**.

| | |
|---|---|
| C(1)-C(2) | 1.389(7) |
| C(1)-C(18) | 1.407(8) |
| C(1)-H(1) | 0.9500 |
| C(2)-C(3) | 1.413(8) |
| C(2)-C(19) | 1.488(7) |
| C(3)-C(16) | 1.429(8) |
| C(3)-C(4) | 1.477(7) |
| C(4)-C(9) | 1.403(8) |
| C(4)-C(5) | 1.405(8) |
| C(5)-C(6) | 1.376(7) |
| C(5)-H(5) | 0.9500 |
| C(6)-C(7) | 1.392(8) |
| C(6)-Br(1) | 1.895(6) |
| C(7)-C(8) | 1.363(8) |
| C(7)-H(7) | 0.9500 |
| C(8)-C(9) | 1.405(8) |
| C(8)-H(8) | 0.9500 |
| C(9)-C(10) | 1.463(8) |
| C(10)-C(15) | 1.399(7) |
| C(10)-C(11) | 1.432(8) |
| C(11)-C(12) | 1.349(8) |
| C(11)-H(11) | 0.9500 |
| C(12)-C(13) | 1.406(8) |
| C(12)-H(12) | 0.9500 |
| C(13)-C(14) | 1.379(8) |
| C(13)-Br(2) | 1.898(6) |
| C(14)-C(15) | 1.424(8) |
| C(14)-H(14) | 0.9500 |
| C(15)-C(16) | 1.465(7) |
| C(16)-C(17) | 1.427(7) |
| C(17)-C(18) | 1.380(8) |
| C(17)-C(25) | 1.516(8) |
| C(18)-C(31) | 1.484(7) |
| C(19)-C(20) | 1.379(8) |
| C(19)-C(24) | 1.400(7) |
| C(20)-C(21) | 1.398(8) |
| C(20)-H(20) | 0.9500 |
| C(21)-C(22) | 1.385(9) |
| C(21)-H(21) | 0.9500 |
| C(22)-C(23) | 1.364(8) |
| C(22)-H(22) | 0.9500 |
| C(23)-C(24) | 1.395(8) |
| C(23)-H(23) | 0.9500 |
| C(24)-H(24) | 0.9500 |
| C(25)-C(26) | 1.389(8) |
| C(25)-C(30) | 1.394(8) |
| C(26)-C(27) | 1.402(8) |
| C(26)-H(26) | 0.9500 |
| C(27)-C(28) | 1.395(8) |
| C(27)-H(27) | 0.9500 |
| C(28)-C(29) | 1.387(8) |
| C(28)-H(28) | 0.9500 |
| C(29)-C(30) | 1.384(8) |
| C(29)-H(29) | 0.9500 |

| | |
|---|---|
| C(30)-H(30) | 0.9500 |
| C(31)-C(42) | 1.394(8) |
| C(31)-C(32) | 1.410(8) |
| C(32)-C(33) | 1.362(8) |
| C(32)-H(32) | 0.9500 |
| C(33)-C(34) | 1.397(8) |
| C(33)-H(33) | 0.9500 |
| C(34)-C(35) | 1.372(8) |
| C(34)-H(34) | 0.9500 |
| C(35)-C(42) | 1.436(7) |
| C(35)-S(1) | 1.751(6) |
| C(36)-C(37) | 1.373(8) |
| C(36)-C(41) | 1.409(7) |
| C(36)-S(1) | 1.761(6) |
| C(37)-C(38) | 1.357(8) |
| C(37)-H(37) | 0.9500 |
| C(38)-C(39) | 1.404(8) |
| C(38)-H(38) | 0.9500 |
| C(39)-C(40) | 1.387(8) |
| C(39)-H(39) | 0.9500 |
| C(40)-C(41) | 1.390(7) |
| C(40)-H(40) | 0.9500 |
| C(41)-C(42) | 1.454(8) |
| C(43)-C(44) | 1.370(11) |
| C(43)-C(49) | 1.424(12) |
| C(43)-C(48) | 1.443(11) |
| C(44)-C(45) | 1.318(11) |
| C(44)-H(44) | 0.9500 |
| C(45)-C(46) | 1.397(12) |
| C(45)-H(45) | 0.9500 |
| C(46)-C(47) | 1.403(11) |
| C(46)-H(46) | 0.9500 |
| C(47)-C(48) | 1.327(11) |
| C(47)-H(47) | 0.9500 |
| C(48)-H(48) | 0.9500 |
| C(49)-H(49A) | 0.9800 |
| C(49)-H(49B) | 0.9800 |
| C(49)-H(49C) | 0.9800 |
| C(2)-C(1)-C(18) | 122.3(5) |
| C(2)-C(1)-H(1) | 118.8 |
| C(18)-C(1)-H(1) | 118.8 |
| C(1)-C(2)-C(3) | 118.3(5) |
| C(1)-C(2)-C(19) | 115.7(5) |
| C(3)-C(2)-C(19) | 125.8(5) |
| C(2)-C(3)-C(16) | 119.1(5) |
| C(2)-C(3)-C(4) | 123.2(5) |
| C(16)-C(3)-C(4) | 117.6(5) |
| C(9)-C(4)-C(5) | 117.6(5) |
| C(9)-C(4)-C(3) | 120.6(5) |
| C(5)-C(4)-C(3) | 121.5(5) |
| C(6)-C(5)-C(4) | 121.1(5) |
| C(6)-C(5)-H(5) | 119.4 |
| C(4)-C(5)-H(5) | 119.4 |
| C(5)-C(6)-C(7) | 121.3(5) |
| C(5)-C(6)-Br(1) | 120.8(4) |
| C(7)-C(6)-Br(1) | 117.9(4) |

| | |
|---|---|
| C(8)-C(7)-C(6) | 118.0(5) |
| C(8)-C(7)-H(7) | 121.0 |
| C(6)-C(7)-H(7) | 121.0 |
| C(7)-C(8)-C(9) | 122.3(5) |
| C(7)-C(8)-H(8) | 118.8 |
| C(9)-C(8)-H(8) | 118.8 |
| C(4)-C(9)-C(8) | 119.5(5) |
| C(4)-C(9)-C(10) | 118.9(5) |
| C(8)-C(9)-C(10) | 121.6(5) |
| C(15)-C(10)-C(11) | 119.2(6) |
| C(15)-C(10)-C(9) | 119.9(5) |
| C(11)-C(10)-C(9) | 120.9(5) |
| C(12)-C(11)-C(10) | 122.9(5) |
| C(12)-C(11)-H(11) | 118.5 |
| C(10)-C(11)-H(11) | 118.5 |
| C(11)-C(12)-C(13) | 117.4(5) |
| C(11)-C(12)-H(12) | 121.3 |
| C(13)-C(12)-H(12) | 121.3 |
| C(14)-C(13)-C(12) | 122.2(5) |
| C(14)-C(13)-Br(2) | 119.3(4) |
| C(12)-C(13)-Br(2) | 118.5(4) |
| C(13)-C(14)-C(15) | 120.4(5) |
| C(13)-C(14)-H(14) | 119.8 |
| C(15)-C(14)-H(14) | 119.8 |
| C(10)-C(15)-C(14) | 117.9(5) |
| C(10)-C(15)-C(16) | 120.8(5) |
| C(14)-C(15)-C(16) | 121.2(5) |
| C(17)-C(16)-C(3) | 117.8(5) |
| C(17)-C(16)-C(15) | 124.8(5) |
| C(3)-C(16)-C(15) | 117.3(5) |
| C(18)-C(17)-C(16) | 121.1(5) |
| C(18)-C(17)-C(25) | 117.2(5) |
| C(16)-C(17)-C(25) | 121.5(5) |
| C(17)-C(18)-C(1) | 118.2(5) |
| C(17)-C(18)-C(31) | 124.5(5) |
| C(1)-C(18)-C(31) | 117.1(5) |
| C(20)-C(19)-C(24) | 117.9(5) |
| C(20)-C(19)-C(2) | 121.7(5) |
| C(24)-C(19)-C(2) | 120.1(5) |
| C(19)-C(20)-C(21) | 121.1(6) |
| C(19)-C(20)-H(20) | 119.5 |
| C(21)-C(20)-H(20) | 119.5 |
| C(22)-C(21)-C(20) | 120.1(6) |
| C(22)-C(21)-H(21) | 119.9 |
| C(20)-C(21)-H(21) | 119.9 |
| C(23)-C(22)-C(21) | 119.6(6) |
| C(23)-C(22)-H(22) | 120.2 |
| C(21)-C(22)-H(22) | 120.2 |
| C(22)-C(23)-C(24) | 120.5(6) |
| C(22)-C(23)-H(23) | 119.8 |
| C(24)-C(23)-H(23) | 119.8 |
| C(23)-C(24)-C(19) | 120.9(5) |
| C(23)-C(24)-H(24) | 119.6 |
| C(19)-C(24)-H(24) | 119.6 |
| C(26)-C(25)-C(30) | 118.8(5) |
| C(26)-C(25)-C(17) | 120.1(5) |

| | |
|---|---|
| C(30)-C(25)-C(17) | 121.0(5) |
| C(25)-C(26)-C(27) | 121.2(6) |
| C(25)-C(26)-H(26) | 119.4 |
| C(27)-C(26)-H(26) | 119.4 |
| C(28)-C(27)-C(26) | 118.8(6) |
| C(28)-C(27)-H(27) | 120.6 |
| C(26)-C(27)-H(27) | 120.6 |
| C(29)-C(28)-C(27) | 120.0(6) |
| C(29)-C(28)-H(28) | 120.0 |
| C(27)-C(28)-H(28) | 120.0 |
| C(30)-C(29)-C(28) | 120.6(6) |
| C(30)-C(29)-H(29) | 119.7 |
| C(28)-C(29)-H(29) | 119.7 |
| C(29)-C(30)-C(25) | 120.4(6) |
| C(29)-C(30)-H(30) | 119.8 |
| C(25)-C(30)-H(30) | 119.8 |
| C(42)-C(31)-C(32) | 118.2(5) |
| C(42)-C(31)-C(18) | 124.7(5) |
| C(32)-C(31)-C(18) | 116.4(5) |
| C(33)-C(32)-C(31) | 122.7(6) |
| C(33)-C(32)-H(32) | 118.7 |
| C(31)-C(32)-H(32) | 118.7 |
| C(32)-C(33)-C(34) | 120.7(6) |
| C(32)-C(33)-H(33) | 119.6 |
| C(34)-C(33)-H(33) | 119.6 |
| C(35)-C(34)-C(33) | 117.5(5) |
| C(35)-C(34)-H(34) | 121.3 |
| C(33)-C(34)-H(34) | 121.3 |
| C(34)-C(35)-C(42) | 123.3(5) |
| C(34)-C(35)-S(1) | 124.1(4) |
| C(42)-C(35)-S(1) | 112.5(4) |
| C(37)-C(36)-C(41) | 122.8(5) |
| C(37)-C(36)-S(1) | 125.2(4) |
| C(41)-C(36)-S(1) | 112.0(4) |
| C(38)-C(37)-C(36) | 118.5(5) |
| C(38)-C(37)-H(37) | 120.8 |
| C(36)-C(37)-H(37) | 120.8 |
| C(37)-C(38)-C(39) | 121.1(6) |
| C(37)-C(38)-H(38) | 119.5 |
| C(39)-C(38)-H(38) | 119.5 |
| C(40)-C(39)-C(38) | 119.9(6) |
| C(40)-C(39)-H(39) | 120.0 |
| C(38)-C(39)-H(39) | 120.0 |
| C(39)-C(40)-C(41) | 120.1(5) |
| C(39)-C(40)-H(40) | 120.0 |
| C(41)-C(40)-H(40) | 120.0 |
| C(40)-C(41)-C(36) | 117.6(5) |
| C(40)-C(41)-C(42) | 129.4(5) |
| C(36)-C(41)-C(42) | 113.1(5) |
| C(31)-C(42)-C(35) | 117.6(5) |
| C(31)-C(42)-C(41) | 131.6(5) |
| C(35)-C(42)-C(41) | 110.8(5) |
| C(44)-C(43)-C(49) | 123.4(8) |
| C(44)-C(43)-C(48) | 115.9(8) |
| C(49)-C(43)-C(48) | 120.7(9) |
| C(45)-C(44)-C(43) | 124.3(9) |

| | |
|---|---|
| C(45)-C(44)-H(44) | 117.9 |
| C(43)-C(44)-H(44) | 117.9 |
| C(44)-C(45)-C(46) | 121.9(9) |
| C(44)-C(45)-H(45) | 119.0 |
| C(46)-C(45)-H(45) | 119.0 |
| C(45)-C(46)-C(47) | 114.2(9) |
| C(45)-C(46)-H(46) | 122.9 |
| C(47)-C(46)-H(46) | 122.9 |
| C(48)-C(47)-C(46) | 125.3(9) |
| C(48)-C(47)-H(47) | 117.3 |
| C(46)-C(47)-H(47) | 117.3 |
| C(47)-C(48)-C(43) | 118.4(8) |
| C(47)-C(48)-H(48) | 120.8 |
| C(43)-C(48)-H(48) | 120.8 |
| C(43)-C(49)-H(49A) | 109.5 |
| C(43)-C(49)-H(49B) | 109.5 |
| H(49A)-C(49)-H(49B) | 109.5 |
| C(43)-C(49)-H(49C) | 109.5 |
| H(49A)-C(49)-H(49C) | 109.5 |
| H(49B)-C(49)-H(49C) | 109.5 |
| C(35)-S(1)-C(36) | 91.6(3) |

**Table S14.** Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1c**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 20(3) | 14(3) | 25(4) | -1(3) | 7(3) | -1(3) |
| C(2) | 14(3) | 17(3) | 18(3) | 8(3) | 2(3) | -2(2) |
| C(3) | 15(3) | 8(3) | 23(3) | 0(2) | 7(2) | 0(2) |
| C(4) | 11(3) | 19(3) | 23(3) | 8(3) | 3(3) | 5(2) |
| C(5) | 13(3) | 17(3) | 20(3) | -7(3) | 1(3) | -5(2) |
| C(6) | 16(3) | 14(3) | 23(3) | 9(3) | 4(3) | 0(2) |
| C(7) | 19(3) | 13(3) | 19(3) | -1(3) | 6(3) | 1(3) |
| C(8) | 10(3) | 21(3) | 23(3) | -2(3) | 4(3) | -6(3) |
| C(9) | 13(3) | 15(3) | 12(3) | -2(2) | 6(2) | 1(2) |
| C(10) | 9(3) | 14(3) | 20(3) | -3(3) | 1(2) | -6(2) |
| C(11) | 19(3) | 11(3) | 24(3) | -2(2) | 9(3) | 2(3) |
| C(12) | 18(3) | 25(4) | 17(3) | 5(3) | 7(3) | 0(3) |
| C(13) | 9(3) | 25(3) | 15(3) | 4(3) | -3(2) | -2(3) |
| C(14) | 11(3) | 12(3) | 22(3) | 1(2) | 4(3) | -1(2) |
| C(15) | 10(3) | 12(3) | 20(3) | 3(2) | 0(2) | -3(2) |
| C(16) | 13(3) | 13(3) | 18(3) | 3(2) | 5(2) | 0(2) |
| C(17) | 11(3) | 18(3) | 19(3) | 6(3) | 4(2) | -3(2) |
| C(18) | 14(3) | 9(3) | 24(3) | 6(2) | 9(2) | -1(2) |
| C(19) | 19(3) | 8(3) | 19(3) | 7(2) | 1(2) | -2(2) |
| C(20) | 29(4) | 15(3) | 20(3) | -4(3) | -4(3) | 3(3) |
| C(21) | 42(4) | 37(4) | 18(3) | 1(3) | -10(3) | 7(3) |
| C(22) | 27(4) | 32(4) | 24(4) | -4(3) | -10(3) | 6(3) |
| C(23) | 21(3) | 17(3) | 37(4) | 10(3) | 6(3) | 1(3) |
| C(24) | 17(3) | 10(3) | 19(3) | 0(2) | 4(2) | -7(2) |
| C(25) | 23(3) | 12(3) | 16(3) | -1(2) | -3(3) | 4(3) |
| C(26) | 16(3) | 21(3) | 20(3) | -2(3) | 3(3) | 2(3) |
| C(27) | 19(3) | 19(3) | 32(4) | 1(3) | -2(3) | -2(3) |
| C(28) | 27(4) | 13(3) | 19(3) | -4(3) | -3(3) | 2(3) |
| C(29) | 34(4) | 10(3) | 15(3) | 1(2) | 3(3) | -2(3) |
| C(30) | 17(3) | 14(3) | 17(3) | 3(2) | 2(3) | -1(2) |
| C(31) | 22(3) | 14(3) | 14(3) | -3(2) | -4(3) | 5(3) |
| C(32) | 19(3) | 15(3) | 20(3) | 6(3) | 0(3) | -3(2) |
| C(33) | 21(3) | 26(4) | 20(3) | 2(3) | 3(3) | 6(3) |
| C(34) | 28(4) | 17(3) | 15(3) | 1(3) | 0(3) | 1(3) |
| C(35) | 20(3) | 10(3) | 21(3) | 0(2) | 1(3) | 5(2) |
| C(36) | 21(3) | 17(3) | 16(3) | 0(2) | -3(3) | 4(3) |
| C(37) | 26(3) | 13(3) | 17(3) | 4(3) | -2(3) | -2(3) |
| C(38) | 18(3) | 24(4) | 27(4) | 4(3) | -4(3) | -10(3) |
| C(39) | 18(3) | 36(4) | 20(3) | 8(3) | 1(3) | 1(3) |
| C(40) | 15(3) | 20(3) | 17(3) | 4(3) | -3(3) | 3(3) |
| C(41) | 18(3) | 8(3) | 15(3) | -2(2) | -1(2) | -4(2) |
| C(42) | 17(3) | 19(3) | 20(3) | 9(3) | -2(2) | 0(3) |
| S(1) | 24(1) | 13(1) | 30(1) | 2(1) | 5(1) | 1(1) |
| Br(1) | 37(1) | 21(1) | 30(1) | 10(1) | -2(1) | 3(1) |
| Br(2) | 29(1) | 26(1) | 20(1) | 6(1) | 0(1) | -6(1) |

**Table S15**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for **1c**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 5826 | 6308 | 2142 | 25 |
| H(5) | 5681 | 9032 | 2269 | 22 |
| H(7) | 6324 | 11473 | 3625 | 21 |
| H(8) | 7198 | 10984 | 4749 | 23 |
| H(11) | 7652 | 10557 | 5755 | 22 |
| H(12) | 8563 | 10104 | 6886 | 24 |
| H(14) | 8755 | 7694 | 5463 | 19 |
| H(20) | 4870 | 6926 | 1143 | 27 |
| H(21) | 2038 | 6906 | 379 | 40 |
| H(22) | -488 | 7628 | 982 | 36 |
| H(23) | -165 | 8378 | 2334 | 29 |
| H(24) | 2638 | 8385 | 3108 | 20 |
| H(26) | 12074 | 7659 | 4066 | 24 |
| H(27) | 14491 | 7280 | 4872 | 30 |
| H(28) | 13744 | 6306 | 5661 | 25 |
| H(29) | 10682 | 5660 | 5571 | 24 |
| H(30) | 8356 | 5969 | 4701 | 19 |
| H(32) | 11110 | 6413 | 2440 | 21 |
| H(33) | 12603 | 5279 | 1727 | 27 |
| H(34) | 11262 | 3871 | 1552 | 25 |
| H(37) | 4116 | 2685 | 2671 | 23 |
| H(38) | 1923 | 3456 | 3450 | 29 |
| H(39) | 2476 | 4936 | 3975 | 29 |
| H(40) | 5136 | 5662 | 3619 | 21 |
| H(44) | 8238 | 9486 | 1143 | 60 |
| H(45) | 5512 | 8791 | 594 | 81 |
| H(46) | 5332 | 7801 | -698 | 76 |
| H(47) | 8170 | 7651 | -1378 | 81 |
| H(48) | 10963 | 8324 | -831 | 63 |
| H(49A) | 11424 | 9984 | 998 | 120 |
| H(49B) | 12477 | 9559 | 200 | 120 |
| H(49C) | 12298 | 9083 | 921 | 120 |

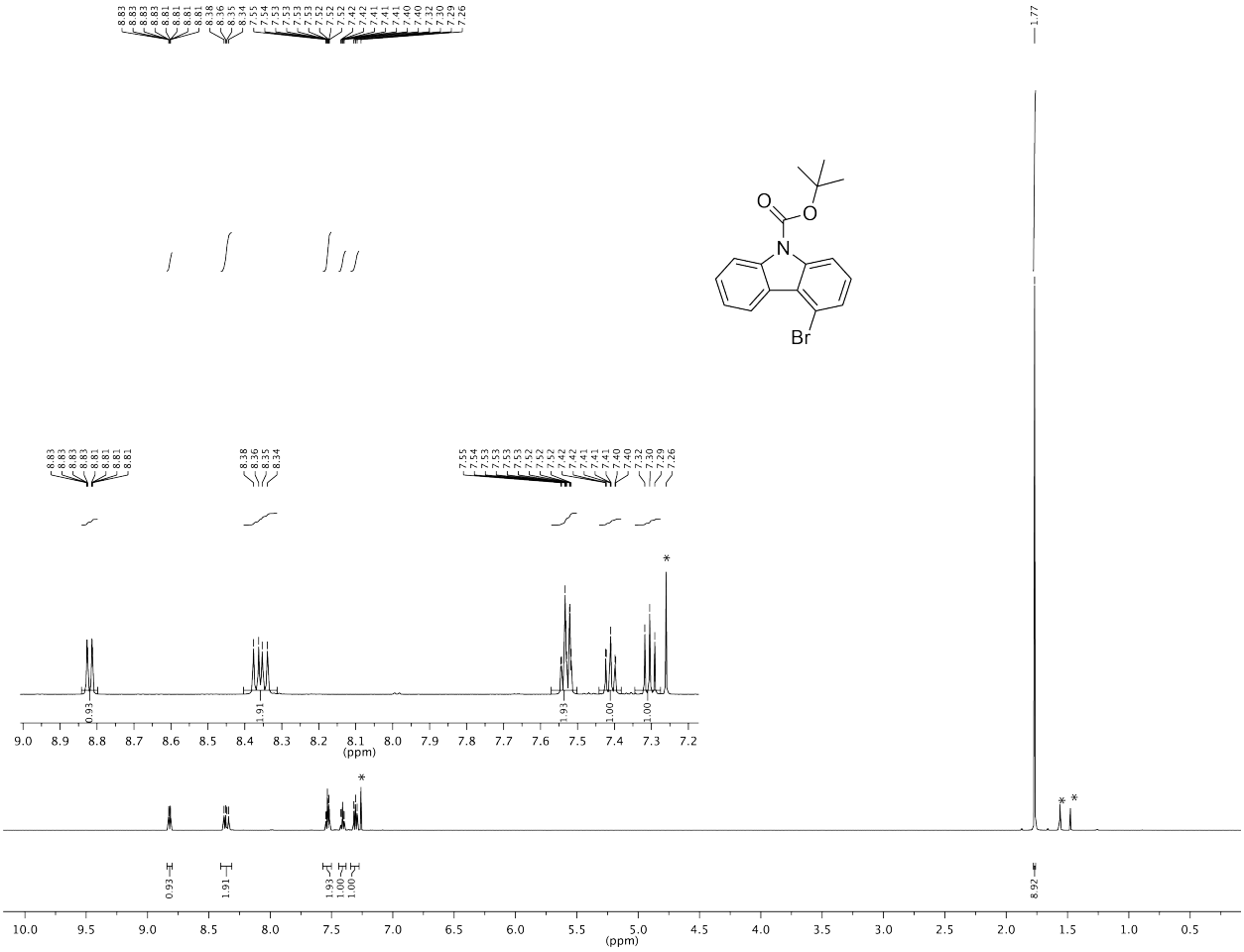


**Figure S10.** $^{1}$H NMR (600 MHz, 25 °C) spectrum of **4** (* solvent residual peak).

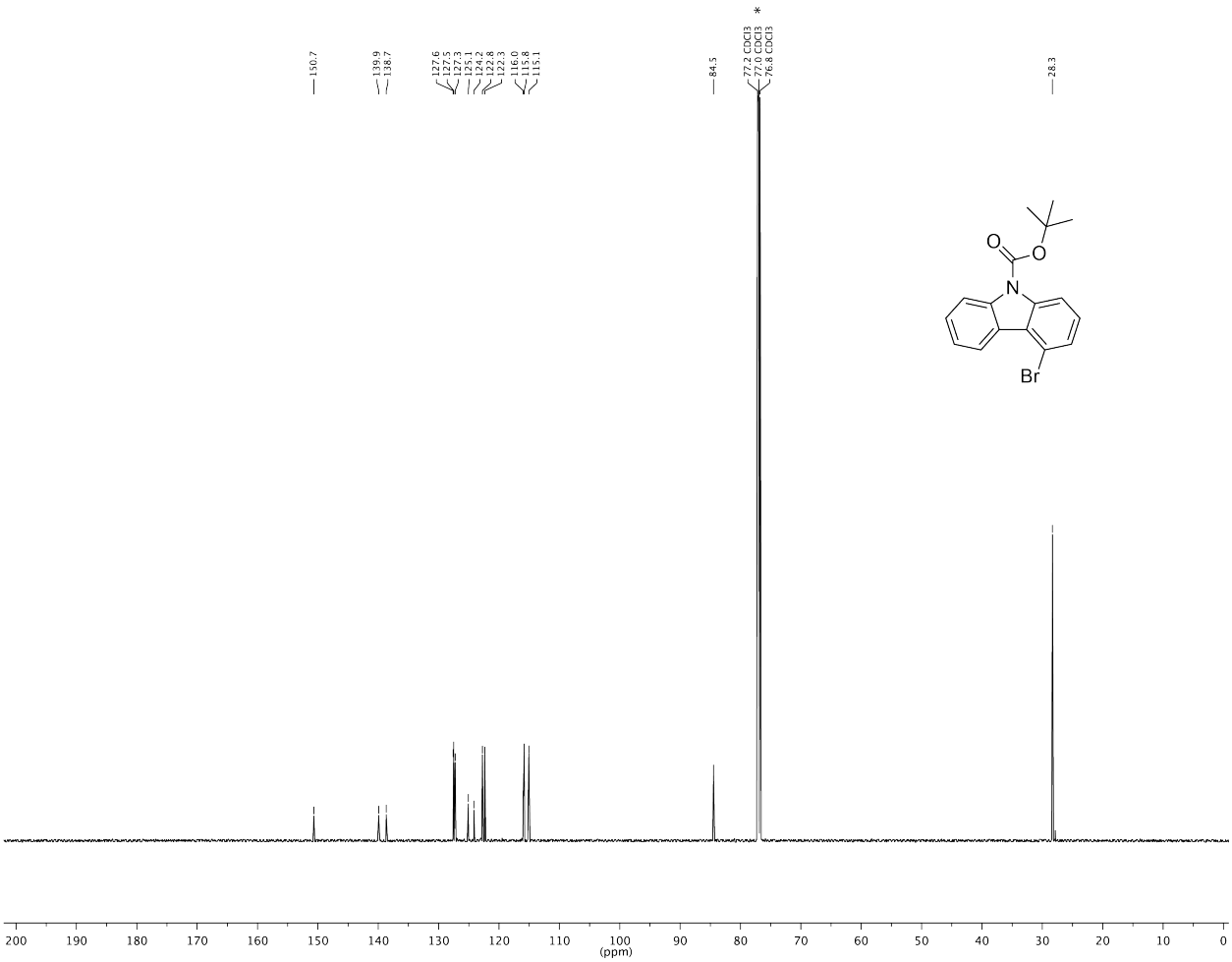


**Figure S11.** $^{13}$C NMR (151 MHz, 25 °C) spectrum of **4** (* solvent residual peak).

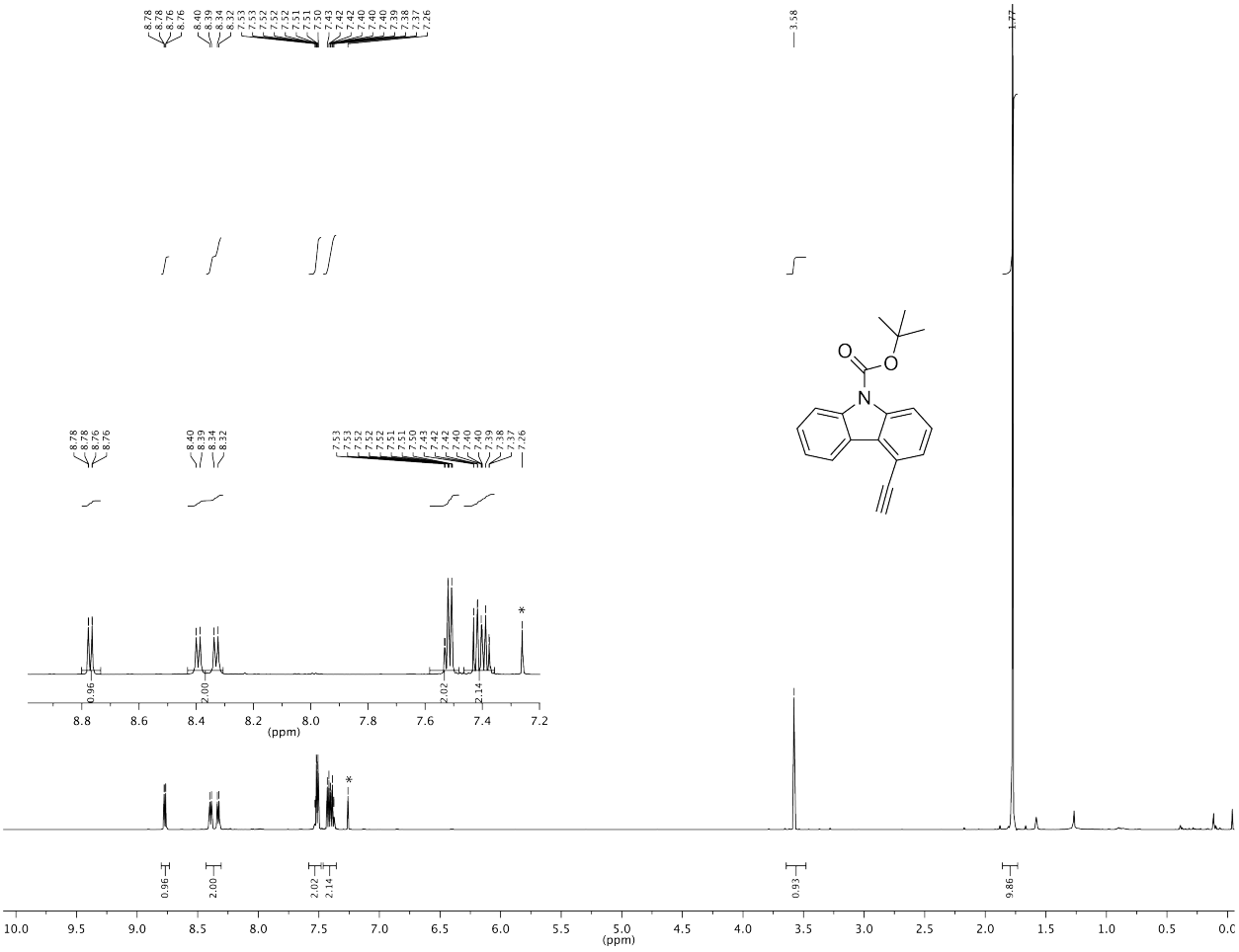


**Figure S12.** $^{1}$H NMR (600 MHz, 25 °C) spectrum of **3a** (* solvent residual peak).

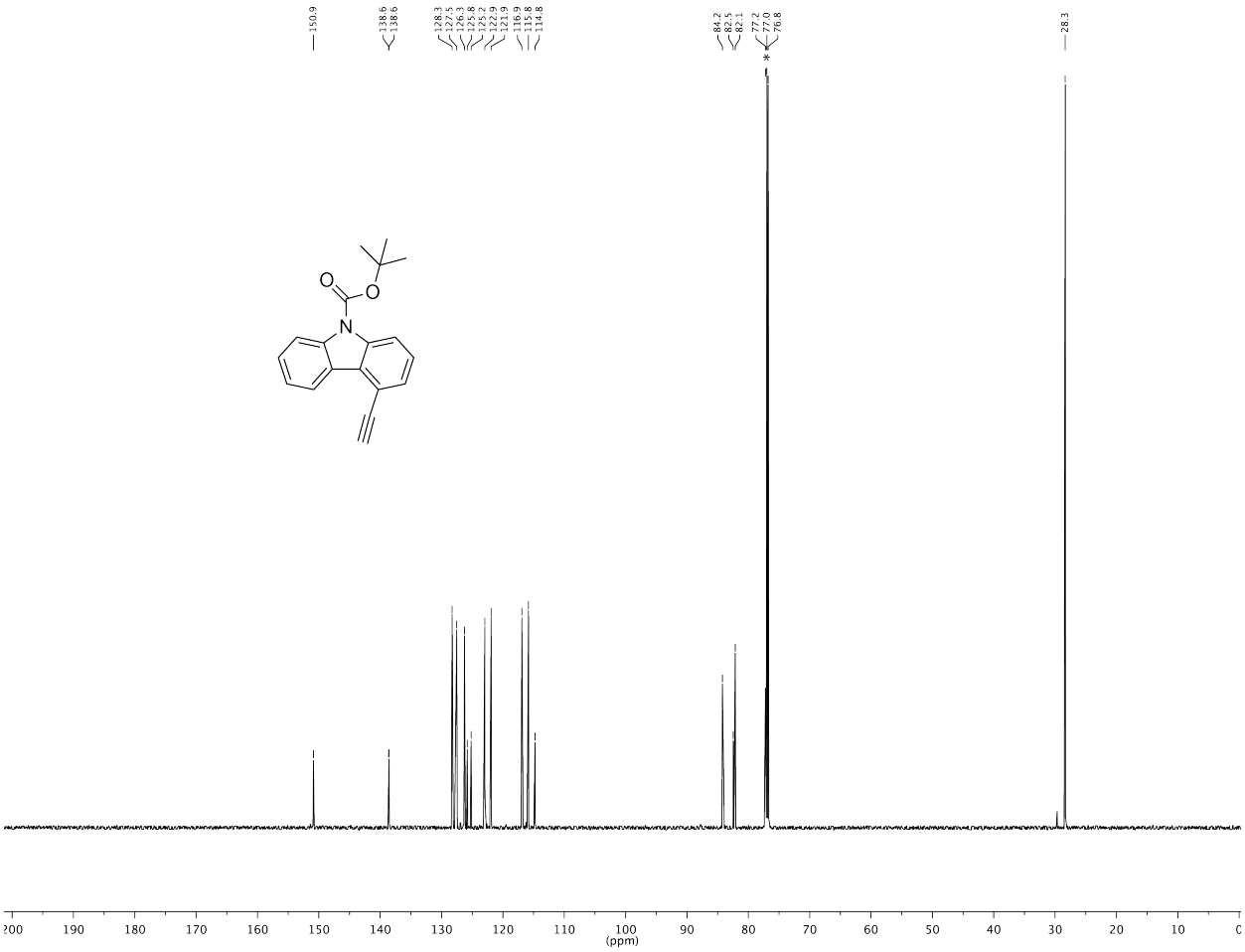


**Figure S13.** $^{13}$C NMR (151 MHz, 25 °C) spectrum of **3a** (* solvent residual peak).

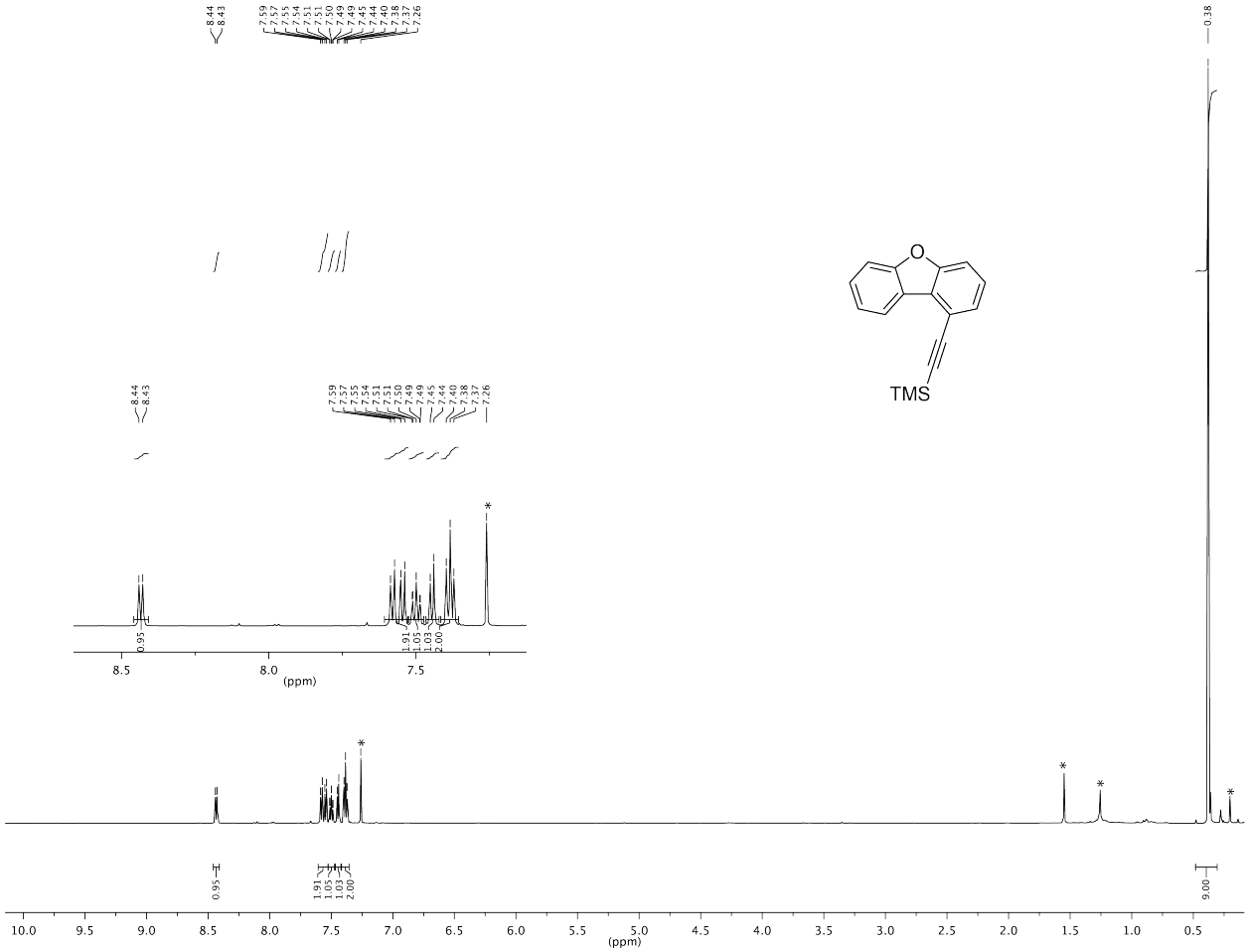


**Figure S14.** $^{1}$H NMR (500 MHz, 25 °C) spectrum of **3b-TMS** (* solvent residual peak).

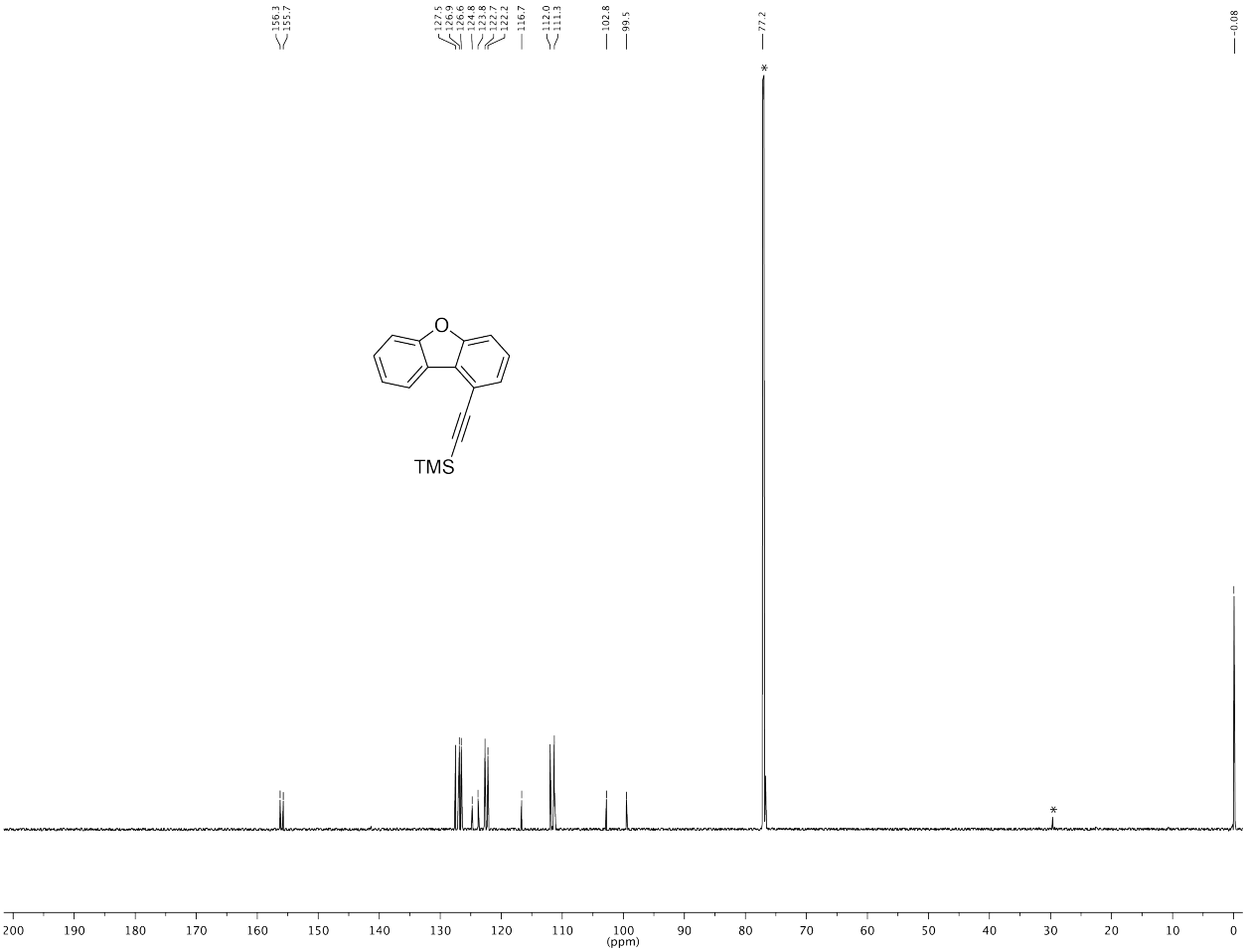


**Figure S15.** $^{13}$C NMR (151 MHz, 25 °C) spectrum of **3b-TMS** (* solvent residual peak).

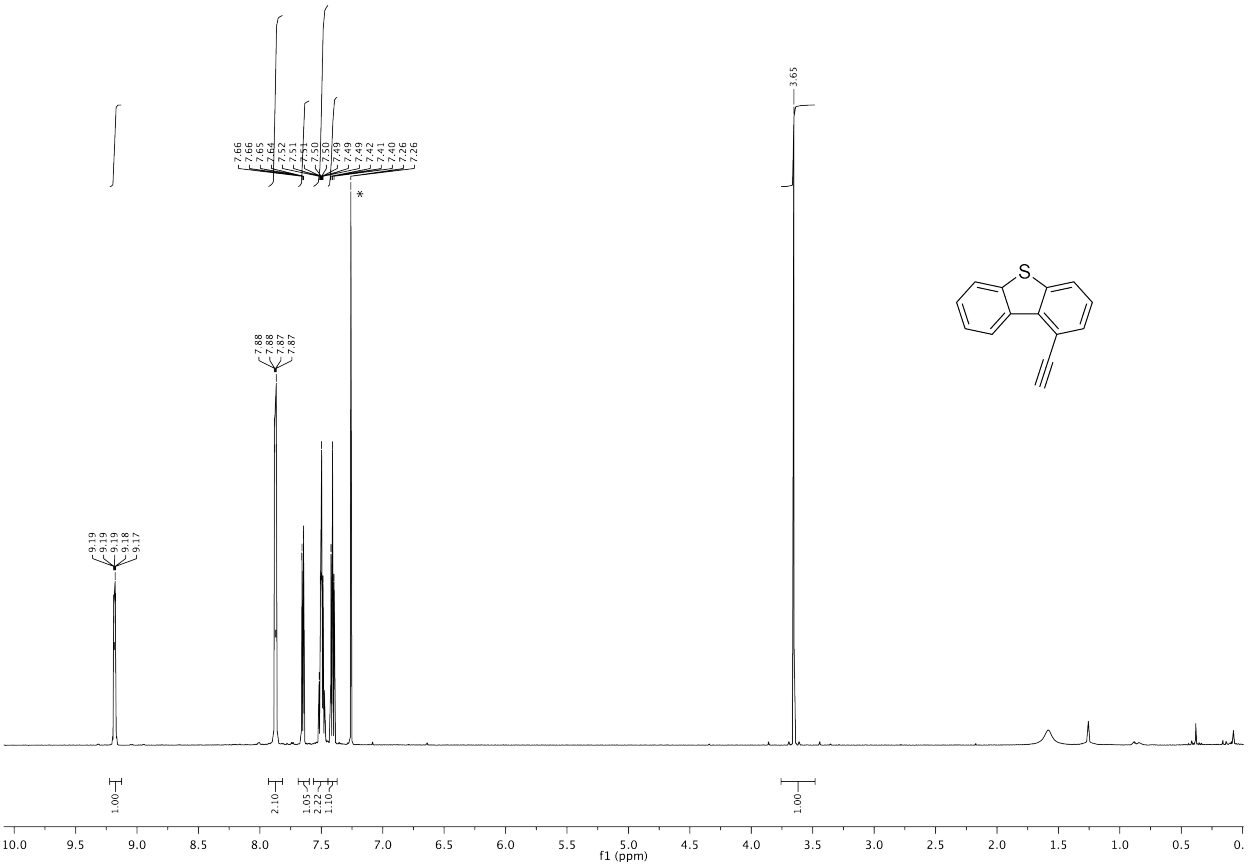


**Figure S16.** $^{1}$H NMR (500 MHz, 25 °C) spectrum of **3c** (* solvent residual peak).

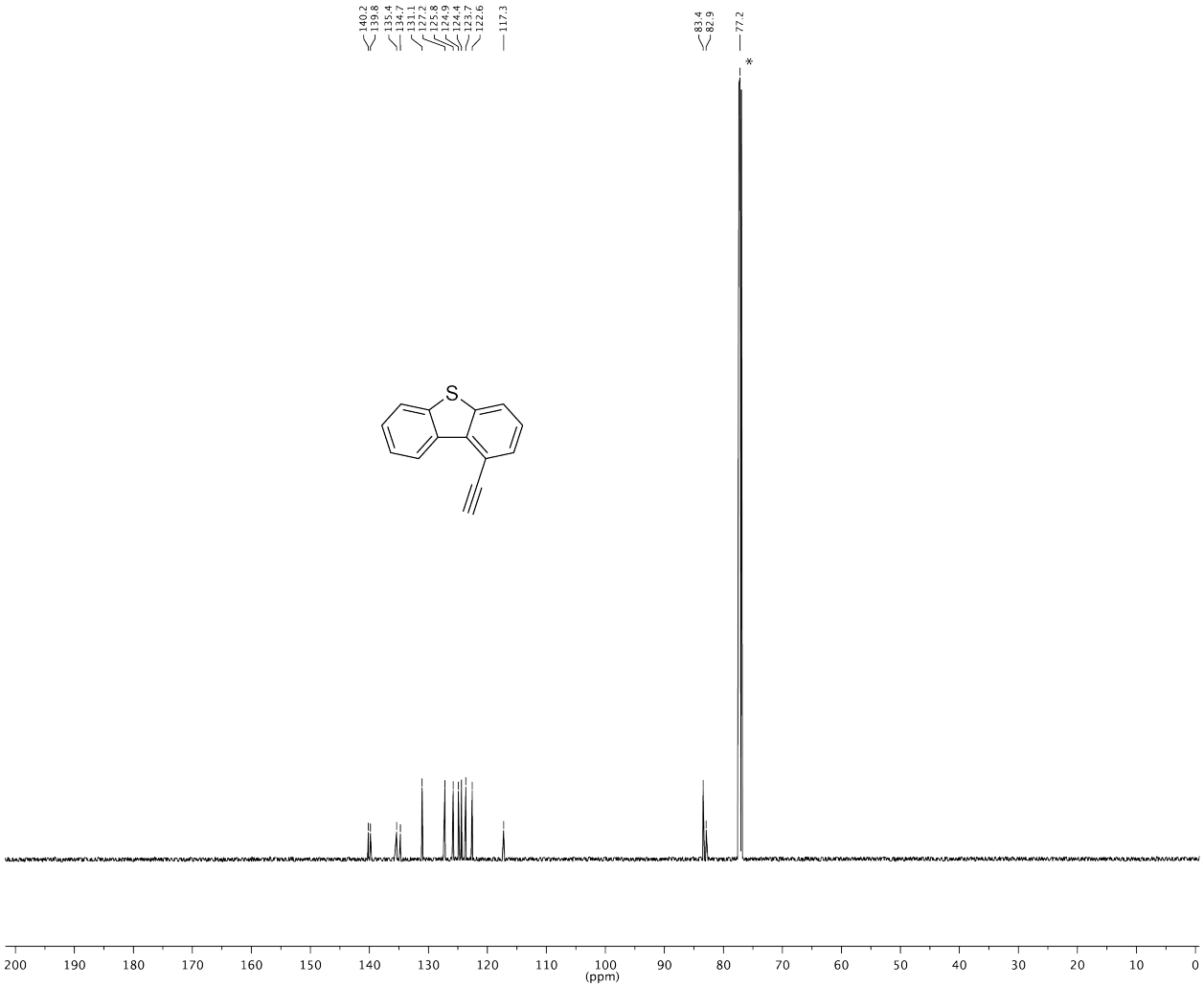


**Figure S17.** $^{13}$C NMR (151 MHz, 25 °C) spectrum of **3c** (* solvent residual peak).

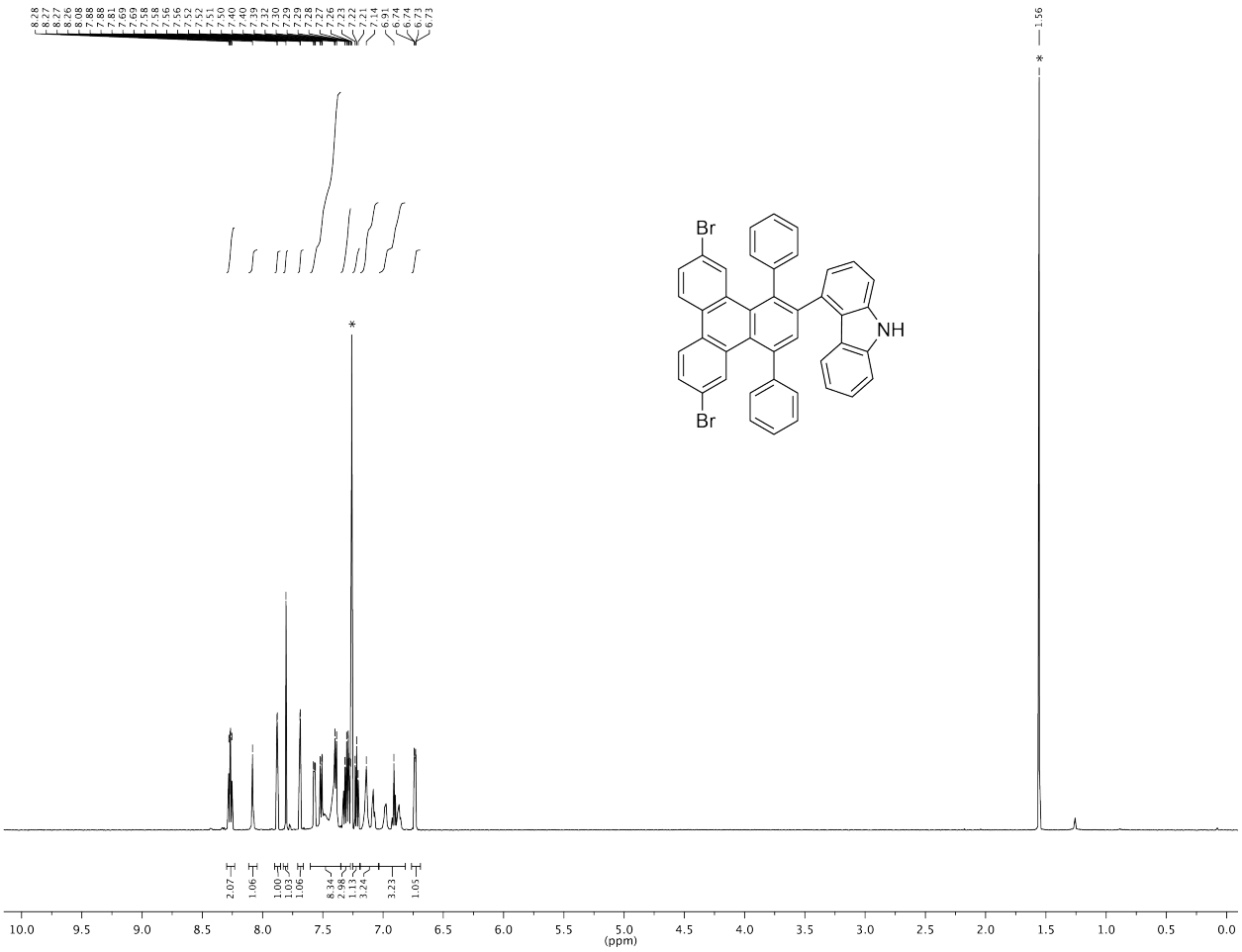


**Figure S18.** $^{1}$H NMR (600 MHz, 25 °C) spectrum of **1a** (* solvent residual peak).

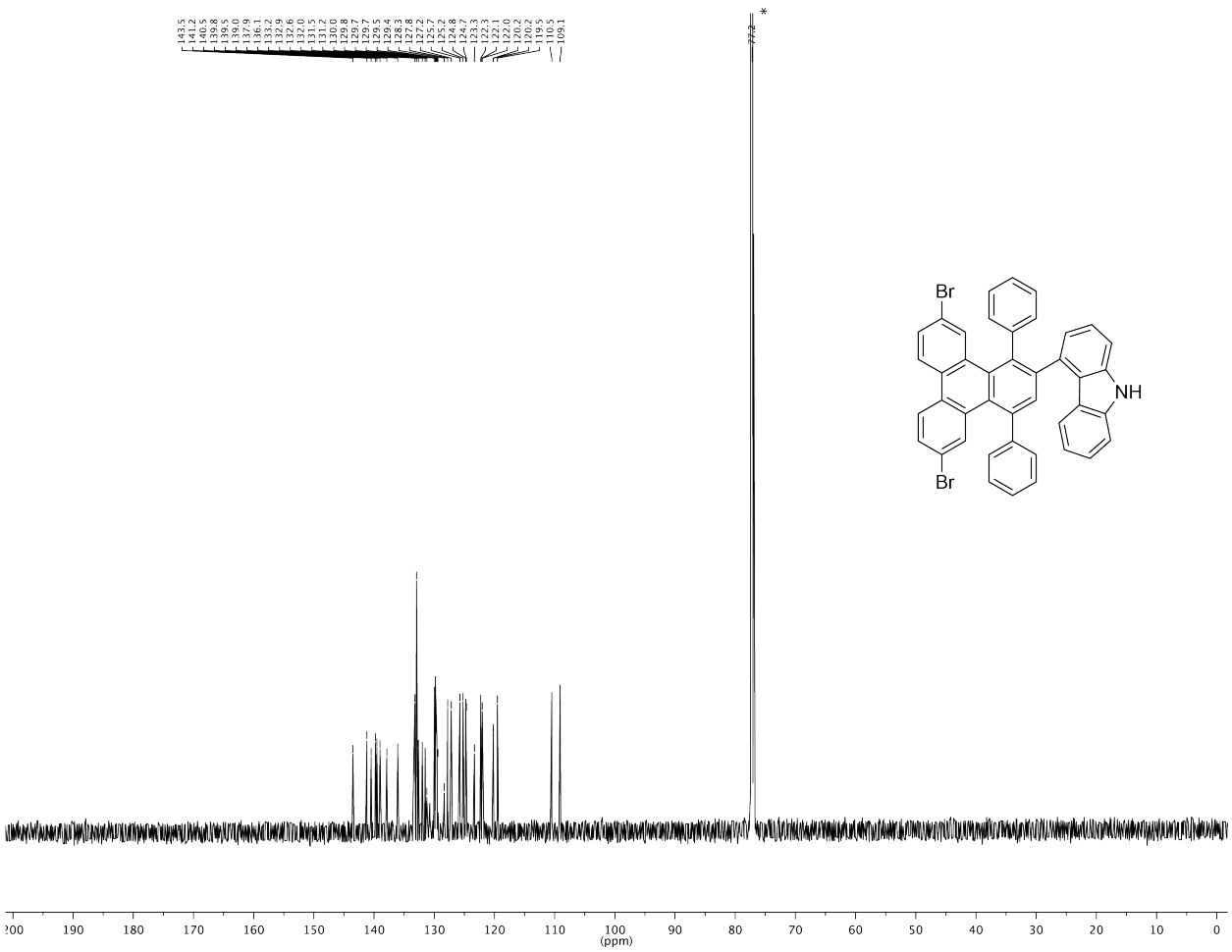


**Figure S19.** $^{13}$C NMR (151 MHz, 25 °C) spectrum of **1a** (* solvent residual peak).

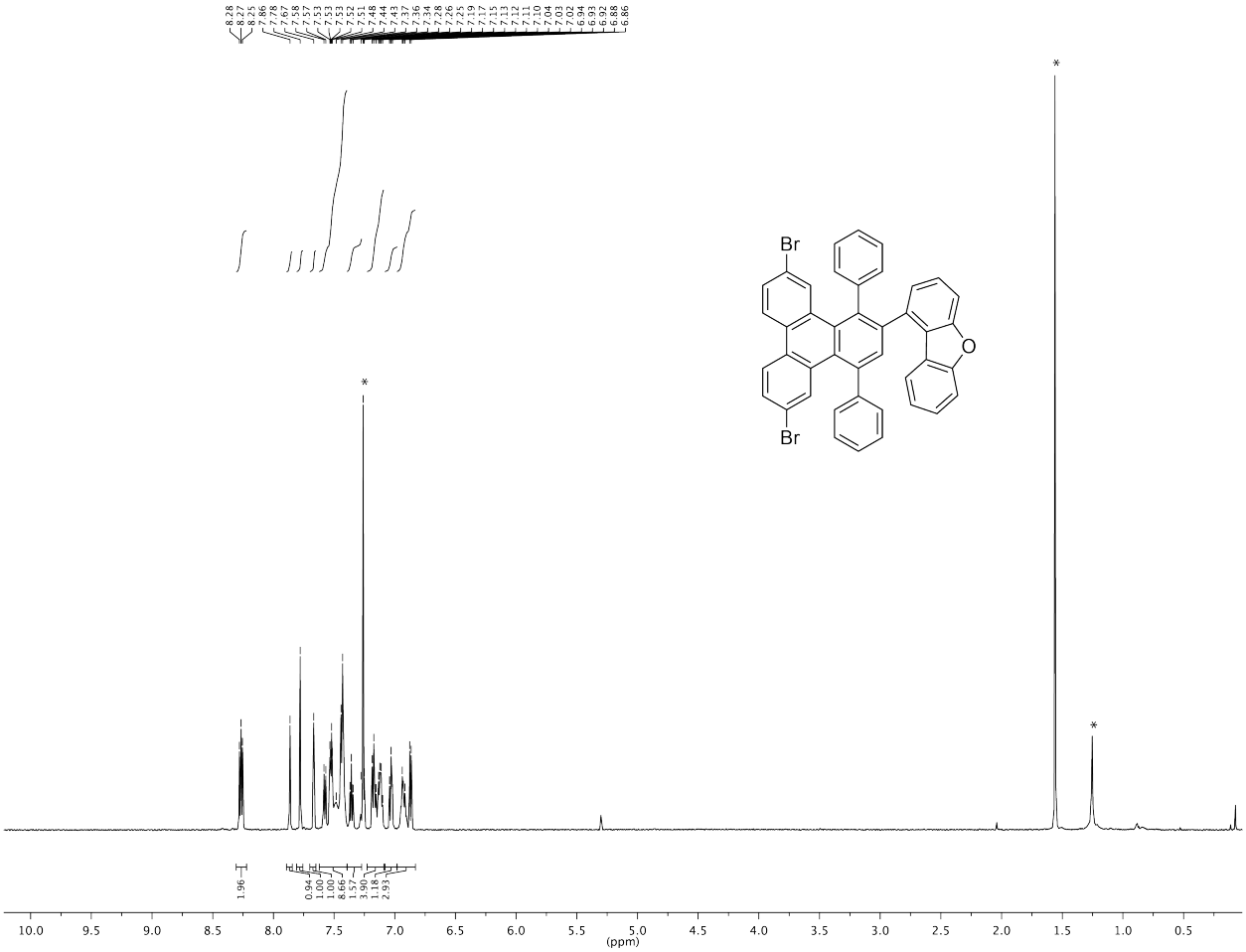


**Figure S20.** $^{1}$H NMR (500 MHz, 25 °C) spectrum of **1b** (* solvent residual peak).

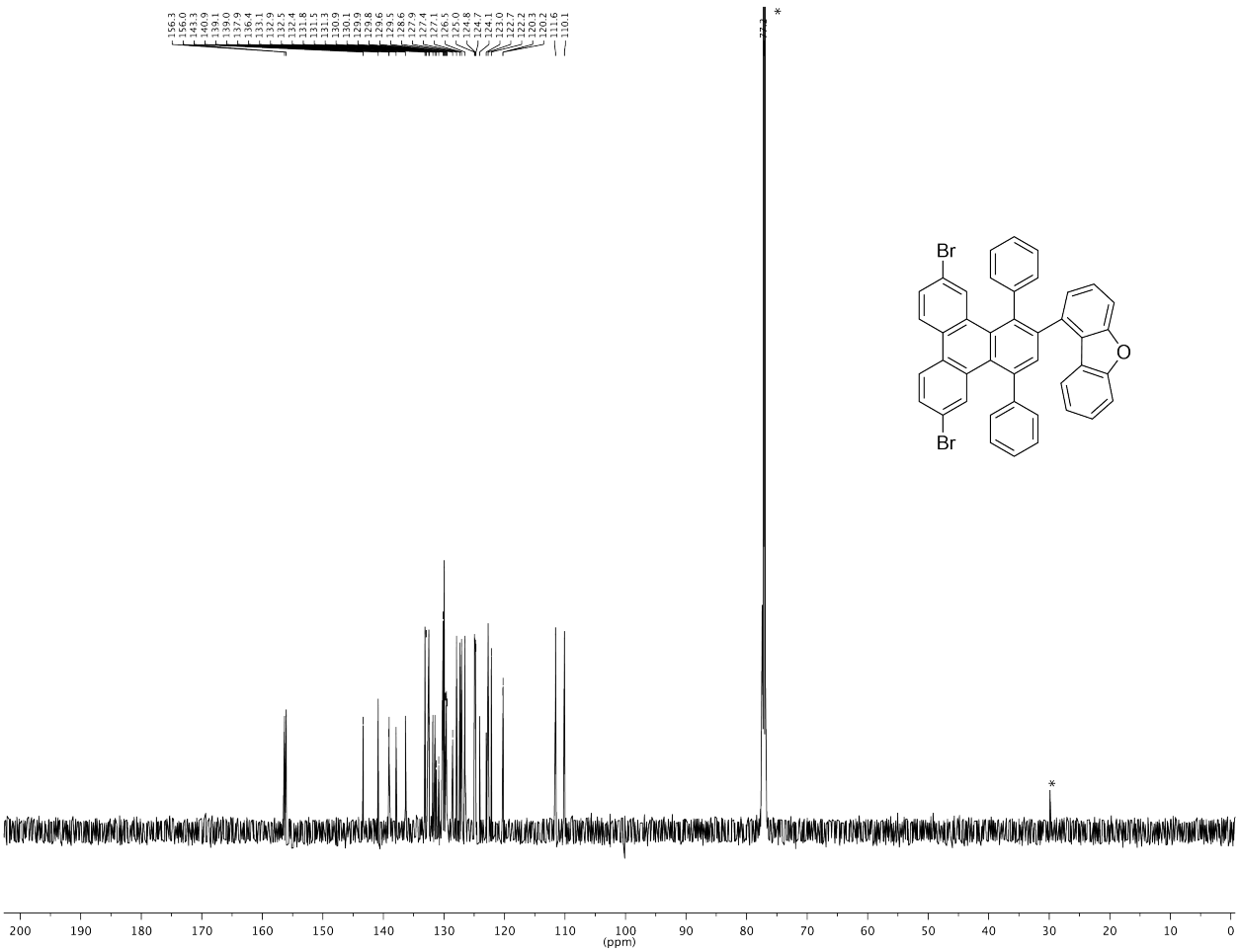


**Figure S21.** $^{13}$C NMR (151 MHz, 25 °C) spectrum of **1b** (* solvent residual peak).

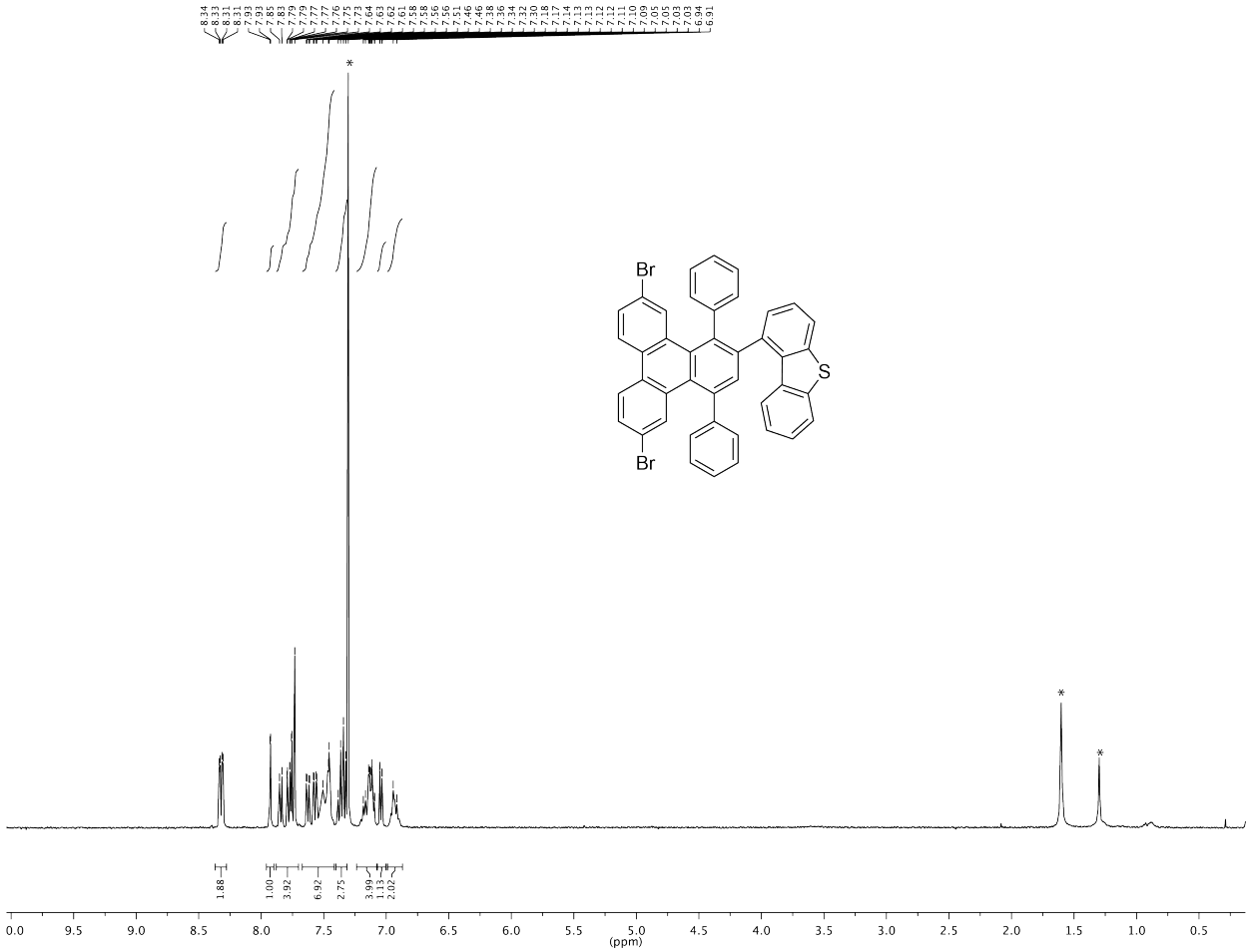


**Figure S22.** $^{1}$H NMR (600 MHz, 25 °C) spectrum of **1c** (***** solvent residual peak).

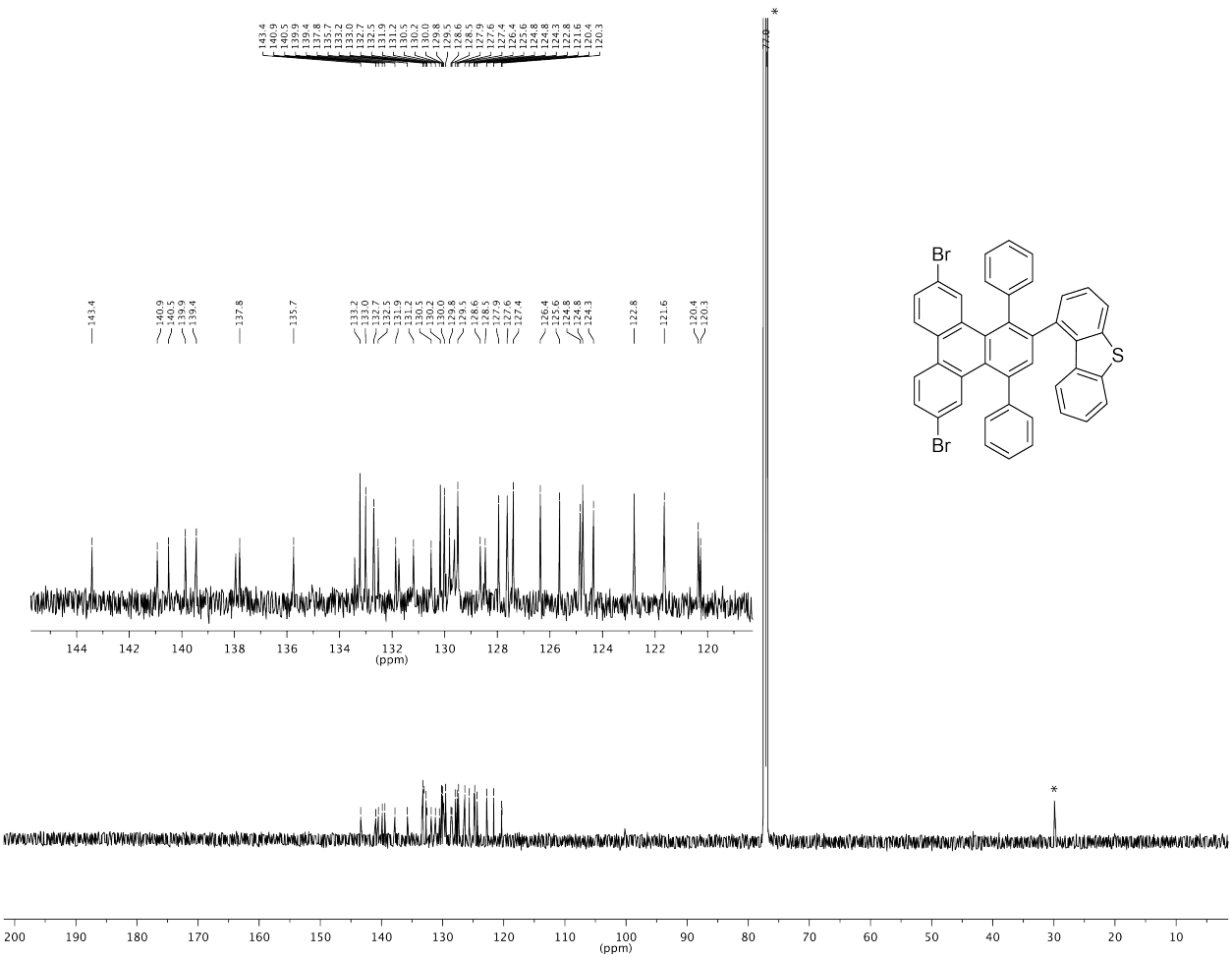


**Figure S23.** $^{13}$C NMR (151 MHz, 25 °C) spectrum of **1c** (* solvent residual peak).

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