Supporting Information

Site-selective Diels-Alder reaction between a biphenylene-based polyarene and a semiconductor surface

Szymon Godlewski,‡[,a] Mads Engelund,‡[b] Diego Peña,[c] Rafał Zuzak,[a] Hiroyo Kawai,[*,d] Marek Kolmer,[a] Jorge Caeiro,[c] Enrique Guitián,[c] K. Peter C. Vollhardt,[e] Daniel Sanchez-Portal,[b] Marek Szymonski,[a] Dolores Pérez[*,c]*

[a] Centre for Nanometer-Scale Science and Advanced Materials, NANOSAM, Faculty of Physics, Astronomy and Applied Computer Science, Jagiellonian University, Lojasiewicza 11, PL 30-348 Krakow, Poland. E-mail: szymon.godlewski@uj.edu.pl
[b] Centro de Física de Materiales CSIC-UPV/EHU and DIPC, Paseo Manual de Lardizabal 5, E-20018, Donostia-San Sebastián, Spain.
[c] Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS) and Departamento de Química Orgánica, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain. E-mail: dolores.perez@usc.es
[d] Institute of Materials Research and Engineering, 2 Fusionopolis Way, Innovis, #08-03, Singapore 138634. E-mail: kawaih@imre.a-star.edu.sg
[e] Department of Chemistry, University of California at Berkeley, Berkeley, CA 94720-1460, USA.

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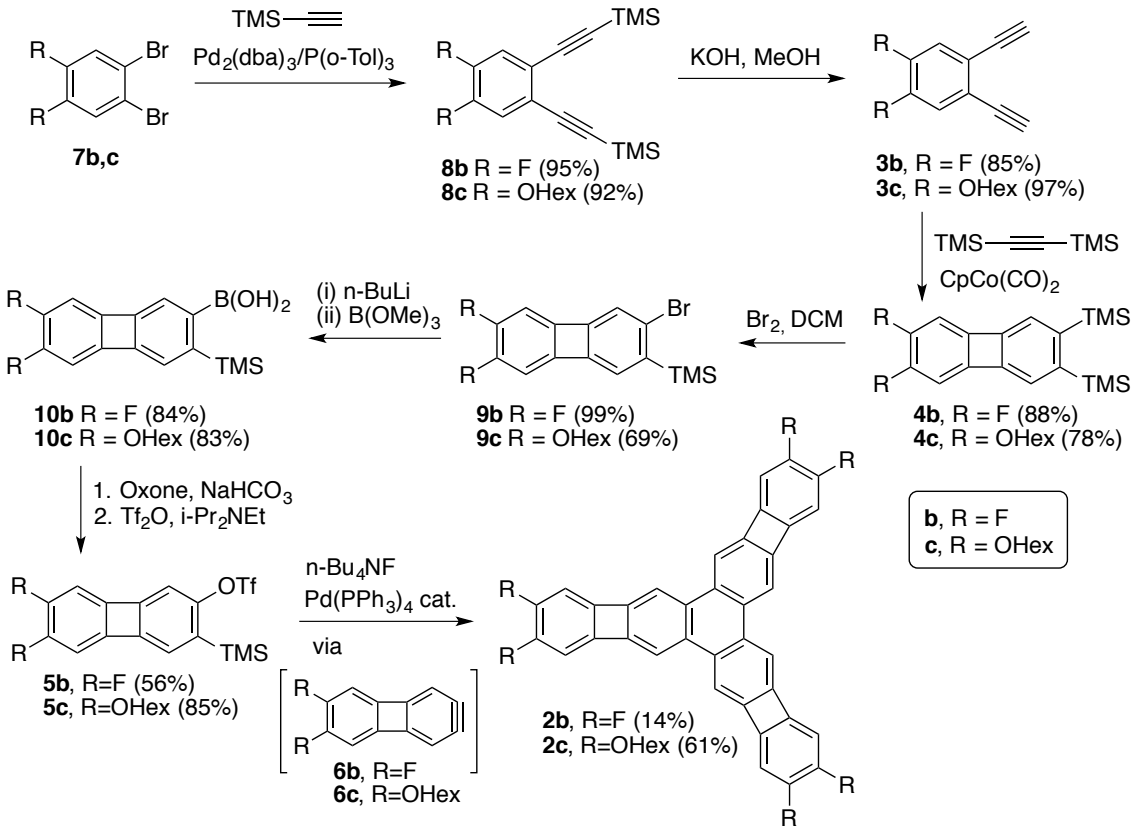
1. Experimental section for the synthesis of tribiphenylenes 2b and 2c[1]

1.1. Materials and Methods. All reactions were performed under argon atmosphere. THF, Et_2O, CH_2Cl_2 and CH_3CN were purchased from Fluka (puriss., absolute, over molecular sieve) and used as received. Acetone was dried over molecular sieve. Et_3N and *i*-Pr_2NEt were distilled under argon from CaH_2. $Pd(PPh_3)_4$ was prepared following published procedures.[2] Other commercial reagents were purchased from Aldrich Chemical Co. or ABCR and were used without further purification. TLC was performed on Merck silica gel 60 F_{254}; chromatograms were visualized with UV light (254 nm and 360 nm) and/or by treating with Hanessian reagent system followed by heating. Flash chromatography was performed on Merck silica gel 60 (ASTM 230-400 mesh). Reported melting points are uncorrected and were measured in a Büchi B-540 instrument. ^1H and ^{13}C-NMR spectra were recorded in Varian AMX 300, Varian AMX 400 or Bruker WM-500 spectrometers. LR and HR mass spectra were recorded using EI (70 eV) in a HP-5988A spectrometer and MALDI-TOF in a Bruker Autoflex spectrometer.



Scheme S1. Synthesis of trisbiphenylenes **2b** and **2c**

1.2. <u>Fluoro-substituted series</u>:

4,5-Difluoro-1,2-bis[(1-trimethylsilyl)ethynyl]benzene (8b). To a solution of 4,5-dibromo-1,2-difluorobenzene (**7b**, 5055 mg, 18.59 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (481 mg, 0.465 mmol) and P(*t*-Bu)$_3$ (232 μL, 0.930 mmol) in dry Et_3N (41 mL), trimethylsilylacetylene (TMSA, 15.45 mL, 111.55 mmol) was added and the mixture was allowed to stir for additional 96 h. Then, an aqueous solution HCl 1% (200 mL) was added, the phases were separated and the aqueous layer was extracted with Et_2O (2 x 160 mL). The combined organic phase were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2; hexanes) to afford the expected product as a light brown solid (5403 mg, 95%). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.25 (t, *J* = 9.3 Hz, 2H), 0.26 (s, 18H) ppm. ^{13}C-NMR-DEPT (75 MHz, $CDCl_3$): δ 149.8 (dd, *J* = 254.6 and 15.2 Hz, 2 x C), 123.0 (t, *J* = 5.7 Hz, 2 x C), 121.0 (dd, *J* = 12.1 and 8.1 Hz, 2 x CH), 101.1 (s, 2 x C), 99.5 (s, 2 x C), -0.1 (s, 6 x CH_3) ppm. LRMS (EI), *m*/*z* (%): 306 (M^+, 16), 291 (M^+-15, 26), 138 (13), 73 (100). HRMS (EI) for $C_{16}H_{20}F_2Si_2$, calcd: 306.1072, found: 306.1074.

1,2-Bis(ethynyl)-4,5-difluorobenzene (3b). To a solution of 4,5-difluoro-1,2-bis((1-trimethylsilyl)ethynyl)benzene (**8b**, 1987 mg, 6.483 mmol) in Et_2O (100 mL), a solution of KOH in MeOH (51.9 mL, 1.25 M, 64.829 mmol) was slowly added. The mixture was allowed to stir for additional 30 min and then the reaction was washed with H_2O (3 x 200 mL). The combined organic phase were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography quickly (SiO_2; 10 % CH_2Cl_2/hexanes) to afford the expected product as a dark red oil (895 mg, 85%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.30 (t, *J* = 9.1 Hz, 2H), 3.33 (s, 2H) ppm. ^{13}C-NMR-DEPT (100 MHz, $CDCl_3$): δ 150.1 (dd, *J* = 255.4 and 15.1 Hz, 2 x C), 122.3 (t, *J* = 5.9 Hz, 2 x C), 121.5 (m, ABX, 2 x CH), 81.9 (s, 2 x C), 76.7 (s, 2 x CH) ppm. LRMS (EI), *m*/*z* (%): 149 (M^+-13, 0.2), 73 (100). LRMS (CI), *m*/*z* (%): 163 (M^++1, 91), 149 (22), 85 (100). HRMS (CI) for $C_{10}H_4F_2$, calcd: 162.0281, found: 162.0286.

6,7-Difluoro-2,3-bis(trimethylsilyl)biphenylene (4b). A solution of 1,2-bis(ethynyl)-4,5-difluorobenzene (**3b**, 447 mg, 2,757 mmol) and $CpCo(CO)_2$ (88 μL, 0.689 mmol) in bis(trimethylsilyl)acetylene (BTMSA,13.1 mL) was added over a period of 7 h (syringe pump) to refluxing BTMSA (43.7 mL) contained in a two neck round bottom flash provided with a condenser an irradiated with a two 150 W lamp (power reduced to 75%) The resulting solution was refluxed under irradiation for an additional 2 h, allowed to reach room temperature and the solvent was distilled under reduced pressure (BTMSA in excess is recovered). After purification by flash chromatography (SiO_2; hexanes), the title compound was isolated as a yellow solid (796 mg, 88%). ^{1}H-NMR

(250 MHz, $CDCl_3$): δ 6.91 (s, 2H), 6.54 (t, *J* = 7.6 Hz, 2H), 0.33 (s, 18H) ppm. ^{13}C-NMR-DEPT (75 MHz, $CDCl_3$): δ 149.9 (dd, *J* = 249.6 and 15.4 Hz, 2 x C), 149.1 (s, 2 x C), 148.4 (t, *J* = 5.8 Hz, 2 x C), 147.3 (s, 2 x C), 122.6 (s, 2 x CH), 109.8 (m, ABX, 2 x CH), 2.1 (s, 6 x CH_3) ppm. LRMS (EI), *m*/*z* (%): 332 (M^+, 32), 317 (M^+-15, 8), 301 (M^+-30, 29), 73 (100). HRMS (EI) for $C_{18}H_{22}F_2Si_2$, calcd: 332.1228, found: 332.1224.

2-Bromo-6,7-difluoro-3-(trimethylsilyl)biphenylene (9b). A solution of Br_2 (48 μL, 0.944 mmol) in dry CH_2Cl_2 (32.0 mL) was dropwise added to a solution of 8,9-difluoro-2,3-bis(trimethylsilyl)biphenylene (**4b**, 314 mg, 0.944 mmol) in dry CH_2Cl_2 (32.0 mL) and cooled to -78ºC. The mixture was stirred at that temperature until consumption of the starting material (TLC analysis, ~ 15 min) and then a saturated aqueous solution $Na_2S_2O_5$ (10 mL) was added over the reaction still cool. Once reached room temperature, water (10 mL) was added. The phases were separated the aqueous phase extracted with CH_2Cl_2 (2 x 20 mL). The combined organic phase were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was chromatographed (SiO_2; hexanes) to afford the expected compound as a yellow solid (317 mg, 99%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.76 (s, 1H), 6.65 (s, 1H), 6.56 (d, *J* = 8.2 Hz, 1H), 6.54 (d, *J* = 8.4 Hz, 1H), 0.35 (s, 9H) ppm. ^{13}C-NMR-DEPT (100 MHz, $CDCl_3$): δ 150.5 (dd, *J* = 250.2 and 14.3 Hz, C), 150.1 (t, *J* = 2.2 Hz, C), 150.0 (dd, *J* = 249.6 and 14.4 Hz, C), 147.2 (dd, *J* = 6.5 and 5.2 Hz, C), 145.7 (t, *J* = 5.8 Hz, C), 145.8 (t, *J* = 3.8 Hz, C), 141.4 (s, C), 130.8 (s, C), 123.4 (s, CH), 122.2 (s, CH), 110.5 (m, ABX, 2 x CH), -0.5 (s, 3 x CH_3) ppm. LRMS (EI), *m*/*z* (%): 340 (M^++2, 20), 338 (M^+, 19), 325 (M^+-13, 15), 323 (M^+-15, 15), 201 (50), 58 (100). HRMS (EI) for $C_{15}H_{13}F_2Si^{81}Br$, calcd: 339.9918, found: 339.9917; for $C_{15}H_{13}F_2Si^{79}Br$, calcd: 337.9938, found: 337.9935.

[6,7-Difluoro-3-(trimethylsilyl)biphenylen-2-yl]boronic acid (10b). To a solution of 2-bromo-8,9-difluoro-3-(trimethylsilyl)biphenylene (**9b**, 538 mg, 1.586 mmol) in THF (57 mL) and cooled to -78ºC, a solution of *n*-BuLi (608 μL, 2.870 M in hexanes, 1.744 mmol) was dropwise added. The mixture was allowed to stir at this temperature for additional 1 h, and then $B(OMe)_3$ (889 μL, 7.930 mmol) was dropwise added. After of 5 min, the cooling bath was removed and the reaction was stirred for 2 h more at room temperature. Then, an aqueous solution HCl 1M (35 mL) was added, the phases were separated and the organic layer was washed with H_2O (2 x 50 mL). The combined organic phase were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography [SiO_2; i. EtOAc/hexanes (1:6), ii. EtOAc/hexanes (1:3), iii. EtOAc/hexanes (1:1)] to afford a green solid (406 mg, 84%) which was subjected to the next reaction without further purification.

6,7-Difluoro-3-(trimethylsilyl)biphenylen2-yl trifluoromethanesulphonate (5b). To a solution of the previously prepared boronic acid (**10b**, 406 mg, 1.335 mmol) in 1:10 water/acetone (27.6 mL) and cooled to 0ºC, oxone® (821 mg, 1.335 mmol) and saturated aqueous solution $NaHCO_3$ (5.8 mL) were added. Stirring was kept for 15 min and then saturated aqueous solution $Na_2S_2O_3$ (50 mL) was added. The two phases which formed were separated and the aqueous phase extracted with Et_2O (2 x 75 mL). The combined organic phase were dried over anhydrous Na_2SO_4, filtered, concentrated under reduced pressure and dried in vacuo for 30 min. The crude residue was dissolved in dry CH_2Cl_2 (33 mL) and the resulting solution cooled to -78ºC, then *i*-Pr_2NEt (255 μL, 1.469 mmol) and Tf_2O (281 μL, 1.669 mmol) were sequentially added. The mixture was allowed to stir to that temperature for 30 min. Then, saturated aqueous $NaHCO_3$ (40 mL) was added, the phases were separated once reached room temperature and the aqueous phase extracted with CH_2Cl_2 (2 x 40 mL). The combined organic phase were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2; hexanes) to afford the expected product as a yellow solid (308 mg, 56%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.68 (s, 1H), 6.63-6.56 (m, 3H), 0.33 (s, 9H) ppm. ^{13}C-NMR-DEPT (100 MHz, $CDCl_3$): δ 155.0 (s, C), 151.4 (t, *J* = 2.3 Hz, C), 150.7 (dd, *J* = 250.7 and 18.0 Hz, C), 150.6 (dd, *J* = 250.7 and 18.2 Hz, C), 146.5 (t, *J* = 2.3 Hz, C), 146.3 (dd, *J* = 6.8 and 5.4 Hz, C), 144.2 (dd, *J* = 6.9 and 5.2 Hz, C), 132.9 (s, C), 122.8 (s, CH), 118.4 c, *J* = 320.0 Hz, CF_3), 110.6 (s, CH), 110.4 (m, ABX, 2 x CH), -0.8 (s, 3 x CH_3) ppm. LRMS (EI), *m*/*z* (%): 408 (M^+, 9), 275 (M^+-135, 15), 260 (16), 201 (51), 58 (100). HRMS (EI) for $C_{16}H_{13}O_3F_5SiS$, calcd: 408.0275, found: 408.0280.

Tris[2,3-difluorobenzocyclobutadieno]triphenylene (2b). To a solution of triflate **5b** (141 mg, 0.345 mmol) and $Pd(PPh_3)_4$ (40 mg, 0.034 mmol) in dry THF (17.0 mL), placed in an Schlenk tube, a solution prepared by dilution of *n*-Bu_4NF (380 μL, 1.0 M in THF, 0.380 mmol) in THF (2.0 ml) was added at room temperature over 3 h (syringe pump). The bright yellow solid which precipitated from the reaction mixture was collected by centrifugation. Then, the product was washed by centrifugation with THF (3 x 1.5 mL), hexanes (2 x 1.5 mL) and CH_2Cl_2 (2 x 1.5 mL) to obtain the expected compound as a yellow solid (9 mg, 14%). LRMS (EI), *m*/*z* (%): 558 (M^+, 100), 279 (21).HRMS (EI) for $C_{36}H_{12}F_6$, calcd: 558.0843, found: 558.0847. LRMS (MALDI-TOF, positive), *m*/*z* (%): 558.5 (M^+, 66). LRMS (MALDI-TOF, negative), *m*/*z* (%): 1115.4 (2 x M^+, 31).

1.3. Hexyloxy-substituted series:

4,5-Bis(hexyloxy)-1,2-bis[(1-trimethylsilyl)ethynyl]benzene (8c). To a solution of 4,5-dibromo-1,2-bis(hexyloxy)benzene (**7c**, 4994 mg, 11.45 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (296 mg, 0.286 mmol) and P(*t*-Bu)$_3$ (139 μL, 0.572 mmol) in dry Et_3N (25 mL), trimethylsilylacetylene (9.52 mL, 68.7 mmol) was added and the mixture was allowed to stir for additional 190 h. Then, an aqueous solution HCl 1% (200 mL) was added, the phases were separated and the aqueous layer was extracted with Et_2O (2 x 160 mL). The combined organic phase were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2; i. 10 % CH_2Cl_2/hexanes, ii. 20 % CH_2Cl_2/hexanes) to afford the expected product as a light brown oil (4981 mg, 92%). ^{1}H-NMR (300 MHz, $CDCl_3$): ∂ 6.90 (s, 2H), 3.97 (t, *J* = 6.6 Hz, 4H), 1.84-1.76 (m, 4H), 1.49-1.42 (m, 4H), 1.37-1.31 (m, 8H), 0.90 (t, *J* = 7.0 Hz, 6H), 0.26 (s, 18H) ppm. ^{13}C-NMR-DEPT (100 MHz, $CDCl_3$): ∂ 149.1 (2 x C), 118.7 (2 x C), 116.2 (2 x CH), 103.6 (2 x C), 96.4 (2 x C), 69.1 (2 x CH_2), 31.5 (2 x CH_2), 29.0 (2 x CH_2), 25.6 (2 x CH_2), 22.6 (2 x CH_2), 14.0 (2 x CH_3), 0.1 (2 x CH_3) ppm. LRMS (EI), *m*/*z* (%): 470 (M^+, 66), 455 (M^+-15, 13), 302 (33), 287 (37), 73 (100). HRMS (EI) for $C_{28}H_{46}O_2Si_2$, calcd: 470.3036, found: 470.3052.

1,2-Diethynyl-4,5-bis(hexyloxy)benzene (3c). To a solution of 4,5-bis(hexyloxy)-1,2-bis((1-trimethylsilyl)ethynyl)benzene (**8c**, 2998 mg, 6.367 mmol) in Et_2O (19 mL), a solution of KOH in MeOH (51.0 mL, 1.25 M, 63.670 mmol) was slowly added. The mixture was allowed to stir for additional 30 min and then the reaction was washed with H_2O (3 x 200 mL). The combined organic phase were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography quickly (SiO_2; 40 % CH_2Cl_2/hexanes) to afford the expected product as a dark red oil (2022 mg, 97%). ^{1}H-NMR (300 MHz, $CDCl_3$): ∂ 6.95 (s, 2H), 3.98 (t, *J* = 6.6 Hz, 4H), 3.24 (s, 2H), 1.85-1.77 (m, 4H), 1.48-1.42 (m, 4H), 1.37-1.31 (m, 8H), 0.90 (t, *J* = 7.0 Hz, 6H) ppm. ^{13}C-NMR-DEPT (100 MHz, $CDCl_3$): ∂ 149.4 (2 x C), 117.8 (2 x C), 116.5 (2 x CH), 82.2 (2 x C), 79.4 (2 x CH), 69.2 (2 x CH_2), 31.5 (2 x CH_2), 29.0 (2 x CH_2), 25.6 (2 x CH_2), 22.6 (2 x CH_2), 14.0 (2 x CH_3) ppm. LRMS (EI), *m*/*z* (%): 326 (M^+, 17), 242 (M^+, 7), 158 (100). HRMS (EI) for $C_{22}H_{30}O_2$, calcd: 326.2246, found: 326.2238.

6,7-Bis(hexyloxy)-2,3-bis(trimethylsilyl)biphenylene (4c). A solution of 1,2-bis(ethynyl)-4,5-bis(hexyloxy)benzene (**3c**, 721 mg, 2,208 mmol) and $CpCo(CO)_2$ (70 μL, 0.552 mmol) in bis(trimethylsilyl)acetylene (BTMSA, 10.5 mL) was added over a period of 7 h (syringe pump) to refluxing BTMSA (35.0 mL) contained in a two neck round bottom flash provided with a condenser an irradiated with a two 150 W lamp (power reduced to 75%) The resulting solution was refluxed under irradiaton for an

additional 2 h, allowed to reach room temperature and the solvent was distilled under reduced pressure (BTMSA in excess is recovered). After purification by flash chromatography (SiO_2; 20% CH_2Cl_2/hexanes), the title compound was isolated as an orange oil (861 mg, 78%). ^{1}H-NMR (300 MHz, $CDCl_3$): ∂ 6.74 (s, 2H), 6.48 (s, 2H), 3.91 (t, *J* = 6.6 Hz, 4H), 1.79-1.70 (m, 4H), 1.48-1.31 (m, 12H), 0.92-0.88 (m, 6H), 0.30 (s, 18H) ppm. ^{13}C-NMR-DEPT (100 MHz, $CDCl_3$): ∂ 149.6 (2 x C), 148.8 (2 x C), 147.1 (2x C), 145.5 (2 x C), 120.7 (2 x CH), 109.2 (2 x CH), 70.2 (2 x CH_2), 31.6 (2 x CH_2), 29.5 (2 x CH_2), 25.7 (2 x CH_2), 22.6 (2 x CH_2), 14.0 (2 x CH_3), 2.1 (2 x CH_3) ppm. LRMS (EI), *m*/*z* (%): 496 (M^+, 57), 412 (3), 327 (100), 73 (39). HRMS (EI) for $C_{30}H_{48}O_2Si_2$, calcd: 496.3193, found: 496.3192.

2-Bromo-6,7-bis(hexyloxy)-3-(trimethylsilyl)biphenylene (9c). A solution of *N*-bromosuccinimide (181 mg, 1.020 mmol) in dry acetone (5.5 mL) was dropwise added to a solution of 8,9-bis(hexyloxy)-2,3-bis(trimethylsilyl)biphenylene (405 mg, 0.815 mmol) and $AgNO_3$ (42 mg, 0.245 mmol) in dry acetone (5.5 mL). The mixture was stirred at room temperature until consumption of the starting material (TLC analysis, ~ 30 min). The solvent was concentrated under reduced pressure and the residue was chromatographed (SiO_2; i. 10% CH_2Cl_2/hexanes, ii. 20% CH_2Cl_2/hexanes) to afford the expected compound as a yellow solid (282 mg, 69%). ^{1}H-NMR (300 MHz, $CDCl_3$): ∂ 6.74 (s, 2H), 6.48 (s, 2), 3.91 (t, *J* = 6.6 Hz, 4H), 1.79-1.70 (m, 4H), 1.48-1.31 (m, 12H), 0.92-0.88 (m, 6H), 0.30 (s, 18H) ppm. ^{13}C-NMR-DEPT (100 MHz, $CDCl_3$): δ 149.6 (2 x C), 148.8 (2 x C), 147.1 (2 x C), 145.5 (2 x C), 120.7 (2 x CH), 109.2 (2 x CH), 70.2 (2 x CH_2), 31.6 (2 x CH_2), 29.5 (2 x CH_2), 25.7 (2 x CH_2), 22.6 (2 x CH_2), 14.0 (2 x CH_3), 2.1 (2 x CH_3) ppm. LRMS (EI), *m*/*z* (%): 504 (M^++2, 46), 502 (M^+, 44), 420 (8), 418 (8), 335 (100), 333 (91), 196 (62). HRMS (EI) for $C_{27}H_{39}O_2Si^{81}Br$, calcd: 504.1882, found: 504.1888; for $C_{27}H_{39}O_2Si^{79}Br$, calcd: 502.1903, found: 502.1899.

[6,7-Bis(hexyloxy)-3-(trimethylsilyl)biphenylen-2-yl]boronic acid (10c). To a solution of 2-bromo-8,9-bis(hexyloxy)-3-(trimethylsilyl)biphenylene (**9c**, 463 mg, 0.919 mmol) in THF (33 mL) and cooled to -78ºC, a solution of *n*-BuLi (427 µL, 2,367 M in hexanes, 1.012 mmol) was dropwise added. The mixture was allowed to stir at this temperature for additional 1 h, and then $B(OMe)_3$ (515 µL, 4.595 mmol) was dropwise added. After of 5 min, the cooling bath was removed and the reaction was stirred for 4 h more at room temperature. Then, an aqueous solution HCl 1M (20 mL) was added, the phases were separated and the organic layer was washed with H_2O (2 x 30 mL). The combined organic phase were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography [SiO_2; i. EtOAc/hexanes 1:9, ii. EtOAc/hexanes 1:4, iii. EtOAc/hexanes 1:2) to afford the expected product as a green solid (357 mg, 83%). ^{1}H-NMR (400 MHz, DMSO-d_6): δ 7.96 (s, 2H), 6.61 (d, *J* = 2.1Hz, 2H), 6.60 (d, *J* = 1.0 Hz, 2H), 6.52 (d, *J* = 1.0 Hz, 2H),

3.86 (dt, J = 6.3 and 1.4 Hz, 4H), 1.67-1.60 (m, 4H), 1.44-1.37 (m, 4H), 1.30-1.27 (m, 8H), 0.89-0.85 (m, 6H), 0.20 (s, 9H) ppm. ^{13}C-NMR-DEPT (400 MHz, DMSO-d_6): δ 148.9 (C), 148.5 (C), 148.2 (2x C), 148.1 (C), 144.6 (C), 144.2 (C), 142.7(C), 119.2 (CH), 118.4 (CH), 109.1 (CH), 109.0 (CH), 69.1 (2 x CH_2), 30.1 (2 x CH_2), 28.8 (2 x CH_2), 25.1 (2 x CH_2), 22.0 (2 x CH_2), 13.8 (2 x CH_3), 0.3 (2 x CH_3) ppm. LRMS (EI), m/z (%): 424 (M^+-34, 26), 255 (100). LRMS (CI), m/z (%): 424 (M^+-34, 100), 409 (41), 340 (34).

6,7-Bis(hexyloxy)-3-(trimethylsilyl)biphenylen2-yl trifluoromethanesulphonate (5c). To a solution of the previously synthetized boronic acid (357 mg, 0.762 mmol) in 1:10 water/acetone (16.7 mL) and cooled to 0ºC, oxone® (469 mg, 0.762 mmol) and saturated aqueous solution $NaHCO_3$ (3.3 mL) were added. Stirring was kept for 15 min and then saturated aqueous solution $Na_2S_2O_3$ (30 mL) was added. The two phases which formed were separated and the aqueous phase extracted with Et_2O (2 x 50 mL). The combined organic phase were dried over anhydrous Na_2SO_4, filtered, concentrated under reduced pressure and dried under vacuum for 30 min. The crude residue was dissolved in dry CH_2Cl_2 (20 mL) and the resulting solution cooled to -78ºC, then i-Pr_2NEt (146 μL, 0.838 mmol) and Tf_2O (160 μL, 0.952 mmol) were sequentially added. The mixture was allowed to stir to that temperature for 30 min. Then, saturated aqueous $NaHCO_3$ (30 mL) was added, the phases were separated once reached room temperature and the aqueous phase extracted with CH_2Cl_2 (2 x 30 mL). The combined organic phase were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2; 20% CH_2Cl_2/hexanes) to afford triflate **3c** as a yellow oil (369 mg, 85%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 6.50 (s, 1H), 6.48 (s, 1H), 6.43 (s, 1H), 6.38 (s, 1H), 3.92 (dt, J = 6.6 and 2.6 Hz, 4H), 1.80-1.71 (m, 4H), 1.49-1.30 (m, 12H), 0.93-0.88 (m, 6H), 0.29 (s, 9H) ppm. ^{13}C-NMR-DEPT (100 MHz, $CDCl_3$): δ 154.5 (C), 154.1 (C), 150.0 (C), 149.7 (C), 148.8 (C), 143.4 (C), 140.1(C), 130.3 (C), 120.0 (CH), 118.4 (c, J = 320.0 Hz, CF_3), 109.5 (CH), 108.7 (2 x CH), 70.2 (2 x CH_2), 70.1 (2 x CH_2), 31.6 (2 x CH_2), 29.4 (2 x CH_2), 25.6 (2 x CH_2), 22.6 (2 x CH_2), 14.0 (2 x CH_3), -0.7 (2 x CH_3) ppm. LRMS (EI), m/z (%): 572 (M^+, 18), 439 (89), 355 (25), 255 (100). HRMS (EI) for $C_{28}H_{39}O_5F_3SiS$, calcd: 572.2240, found: 572.2236.

Tris[2,3-bis(hexyloxy)benzocyclobutadieno]triphenylene (2c). To a solution of triflate **3c** (302 mg, 0.527 mmol) and $Pd_2(dba)_3 \cdot CHCl_3$ (55 mg, 0.053 mmol) in a mixture of THF/CH_3CN (1:6) (52 mL), placed in an Schlenk tube, finely powdered anhydrous CsF (480 mg, 3.162 mmol) was added. The resulting suspension was stirred at room temperature for 15 h, concentrated under reduced pressure and the residue was chromatographied (SiO_2; i. 20% CH_2Cl_2/hexanes, ii. 40% CH_2Cl_2/hexanes, iii. 50% CH_2Cl_2/hexanes) to afford the expected compound as yellow solid (113 mg, 61%). ^{1}H-

NMR (400 MHz, $CDCl_3$): δ 7.27 (s, 6H), 6.61 (s, 6H), 3.97 (t, *J* = 6.6 Hz, 12H), 1.84-1.76 (m, 12H), 1.52-1.45 (m, 12H), 1.37-1.33 (m, 24H), 0.94-0.90 (m, 18H) ppm. ^{13}C-NMR-DEPT (100 MHz, $CDCl_3$): δ 150.2 (4 x C), 147.2 (4 x C), 143.6 (4 x C), 130.6 (4 x C), 108.7 (4 x CH), 108.4 (4 x CH), 70.0 (4 x CH_2), 31.6 (4 x CH_2), 29.4 (4 x CH_2), 25.7 (4 x CH_2), 22.6 (4 x CH_2), 14.0 (4 x CH_3) ppm. LRMS (MALDI-TOF), *m*/*z* (%): 1050.7 (M^+, 2223). HRMS (MALDI-TOF) for $C_{72}H_{90}O_6$, calcd: 1050.6732, found: 1050.6738.

2. ^{1}H and ^{13}C NMR spectra

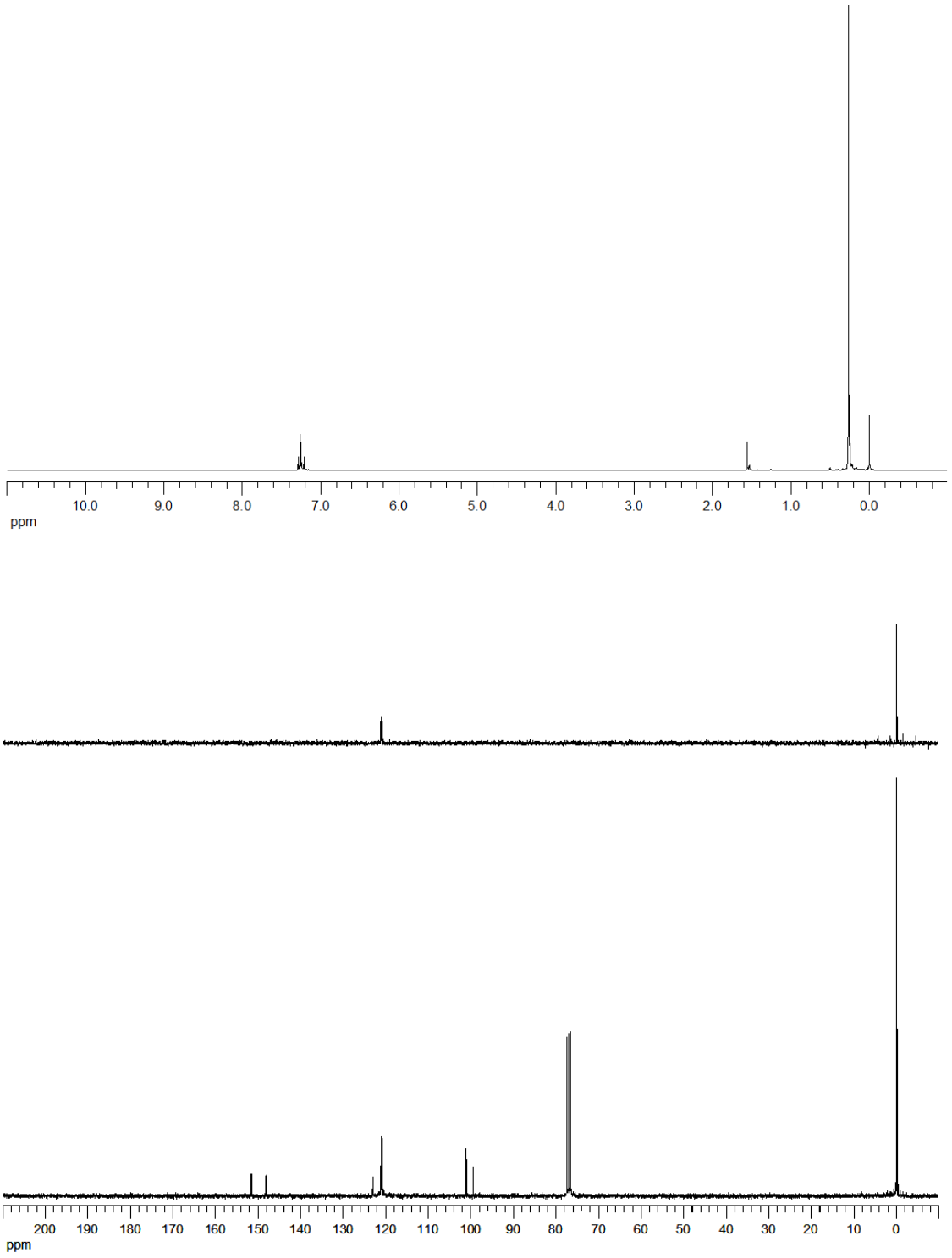


Figure S1. ^{1}H (250 MHz) and ^{13}C NMR (75 MHz) spectra of compound **8b** ($CDCl_3$).

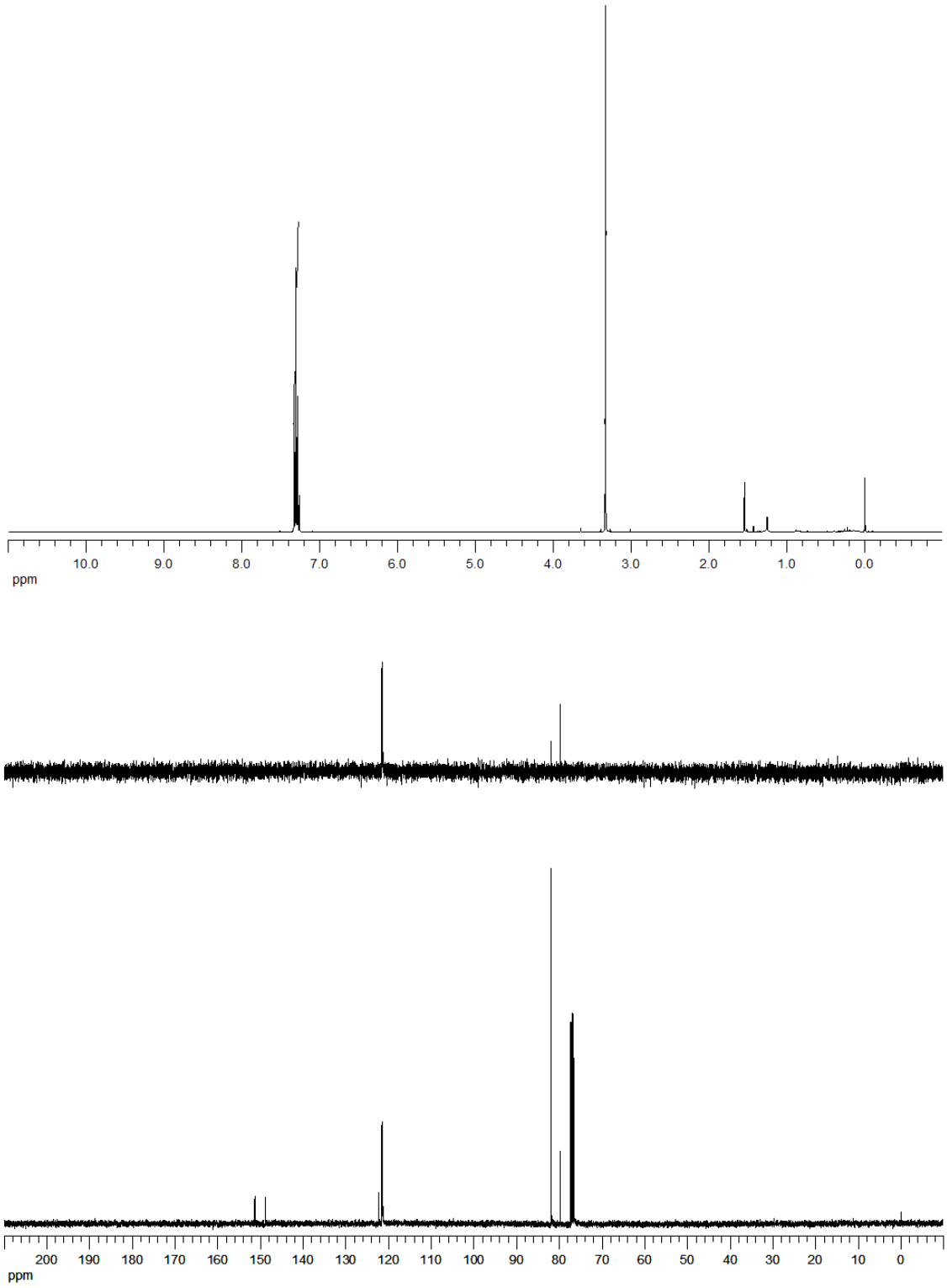


Figure S2. ^{1}H (300 MHz) and ^{13}C NMR (100 MHz) spectra of compound **3b** ($CDCl_3$).

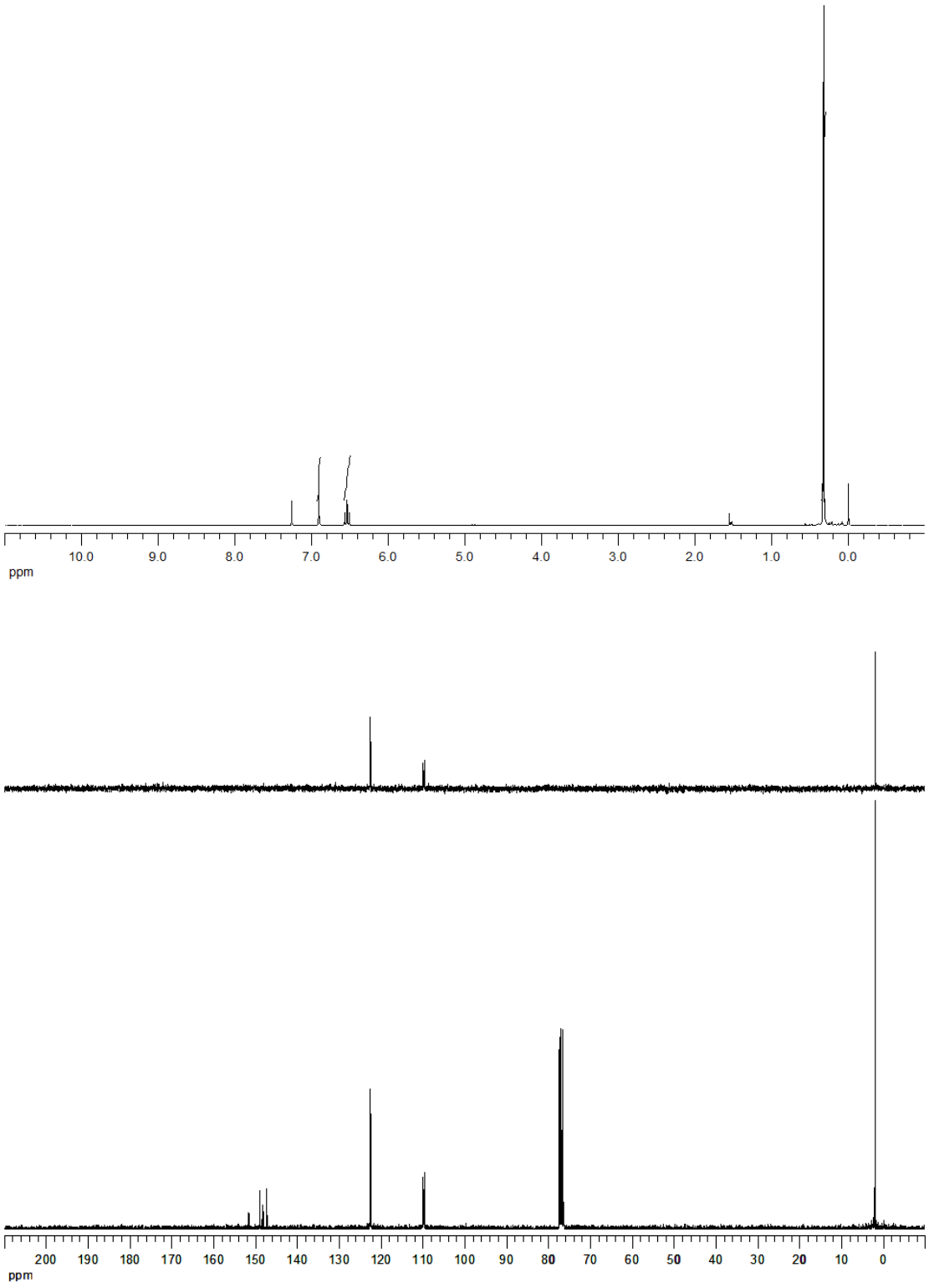


Figure S3. ^{1}H (250 MHz) and ^{13}C NMR (75 MHz) spectra of compound **4b** ($CDCl_3$).

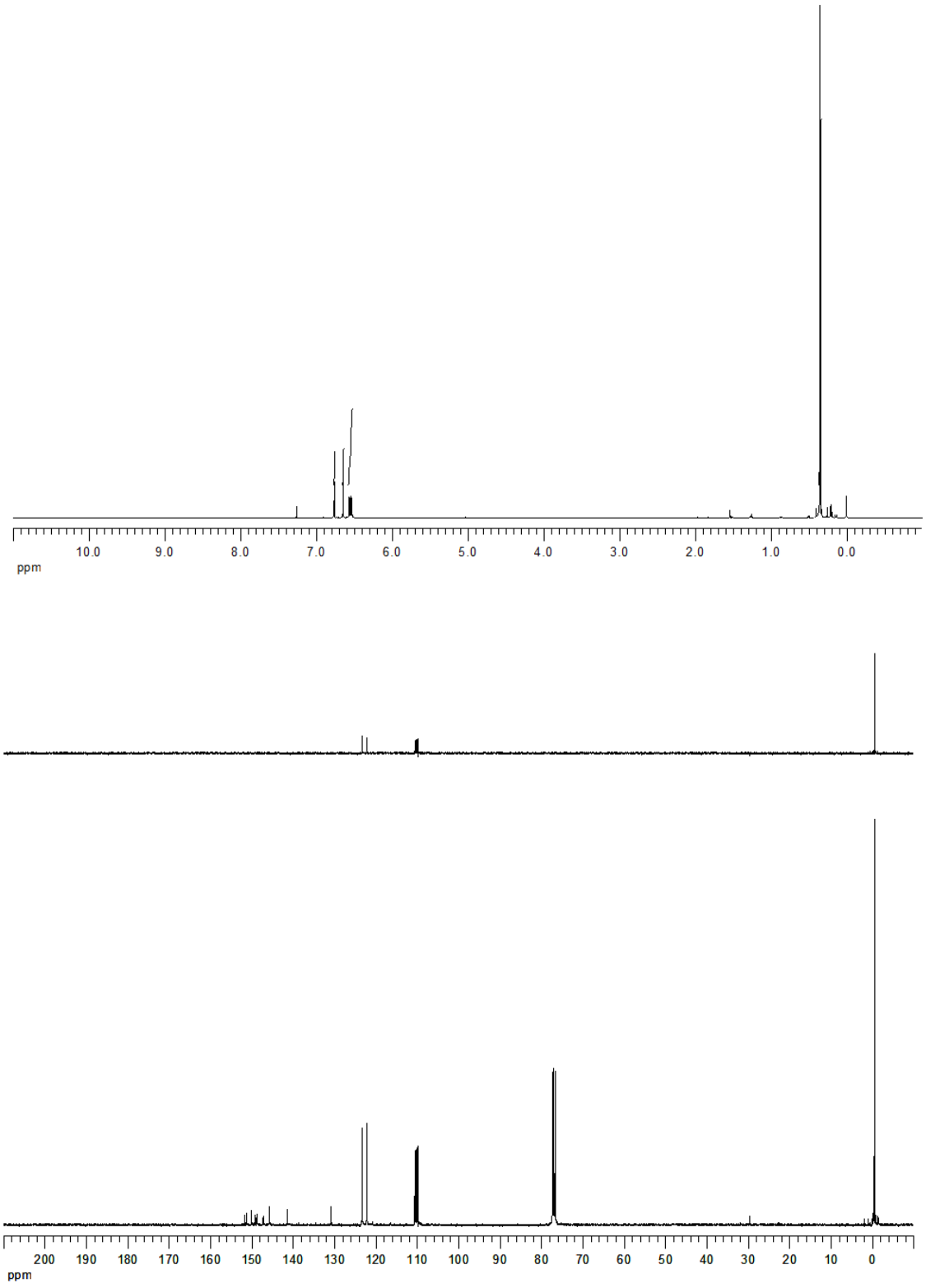


Figure S4. ^{1}H (400 MHz) and ^{13}C NMR (125 MHz) spectra of compound **9b** ($CDCl_3$).

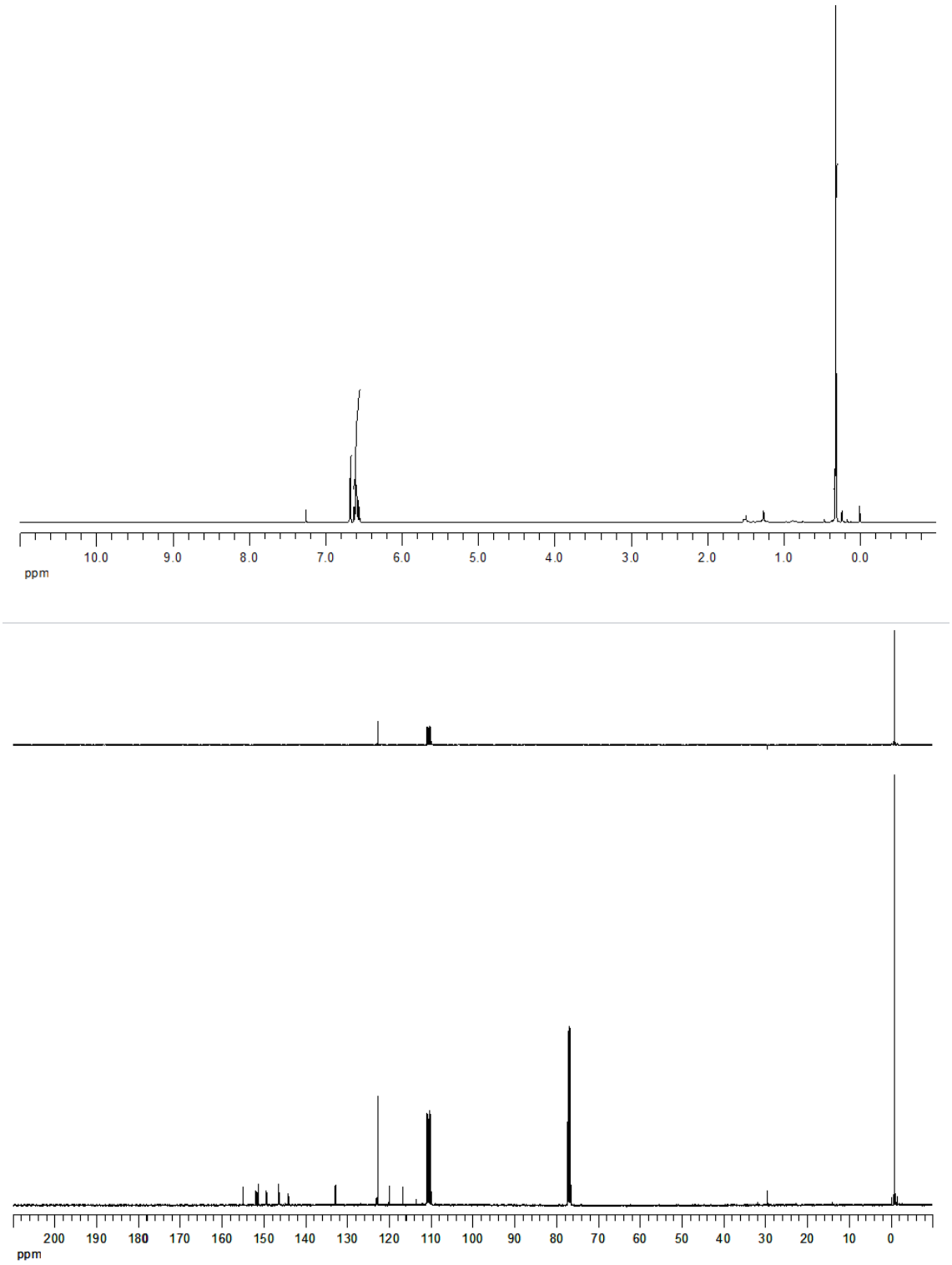


Figure S5. ^{1}H (400 MHz) and ^{13}C NMR (125 MHz) spectra of compound **5b** ($CDCl_3$).

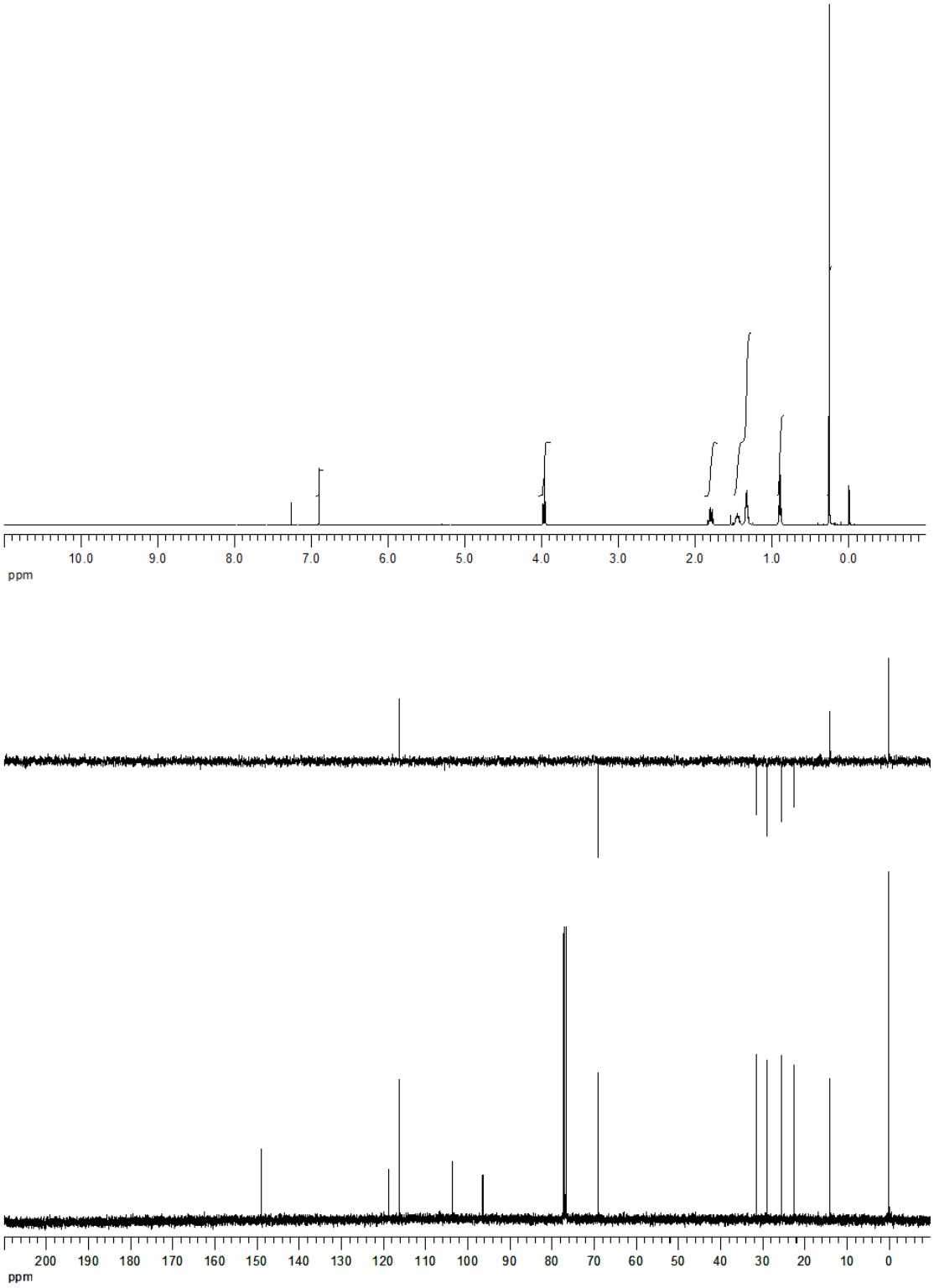


Figure S6. ^{1}H (300 MHz) and ^{13}C NMR (100 MHz) spectra of compound **8c** ($CDCl_3$).

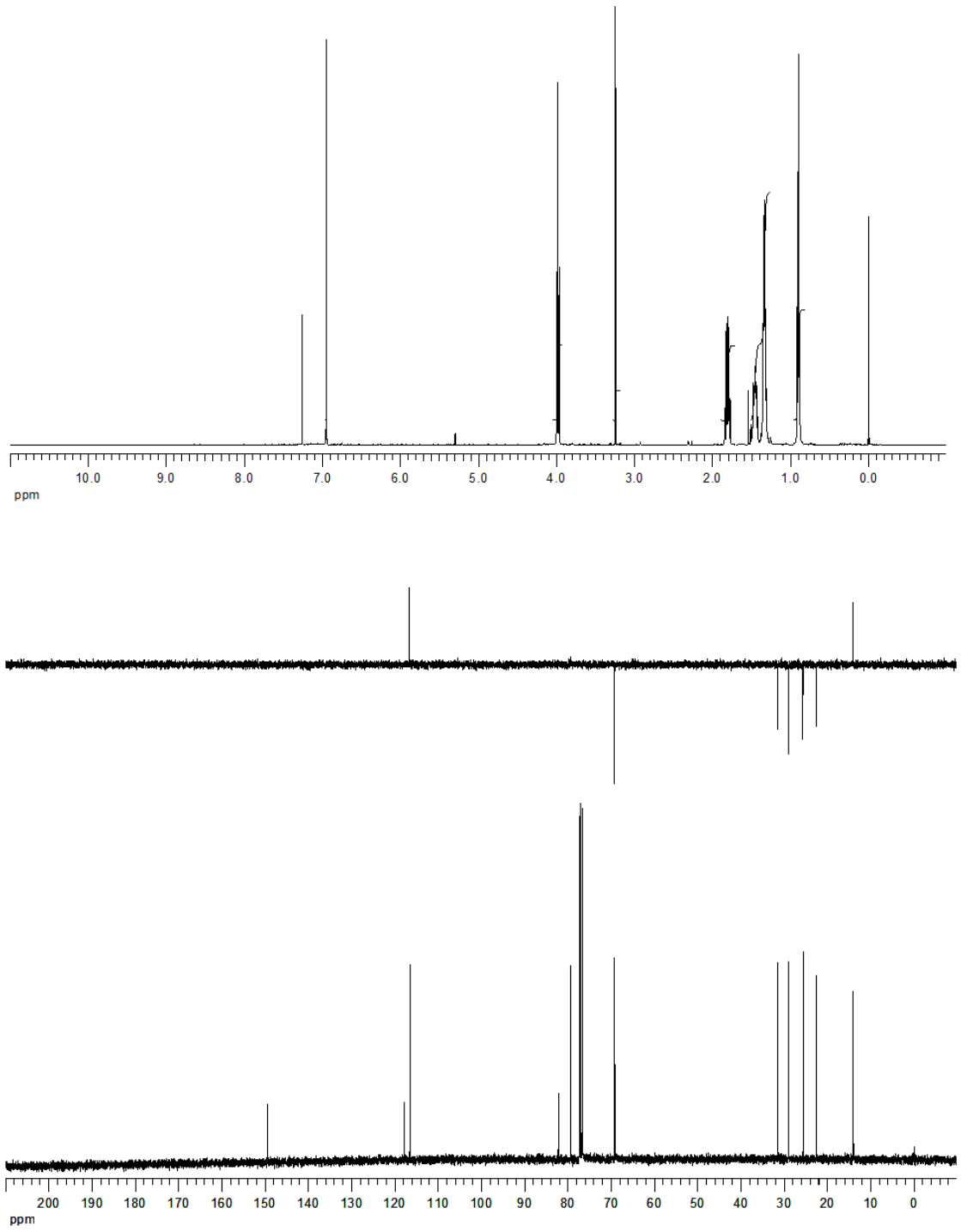


Figure S7. ^{1}H (300 MHz) and ^{13}C NMR (100 MHz) spectra of compound **3c** ($CDCl_3$).

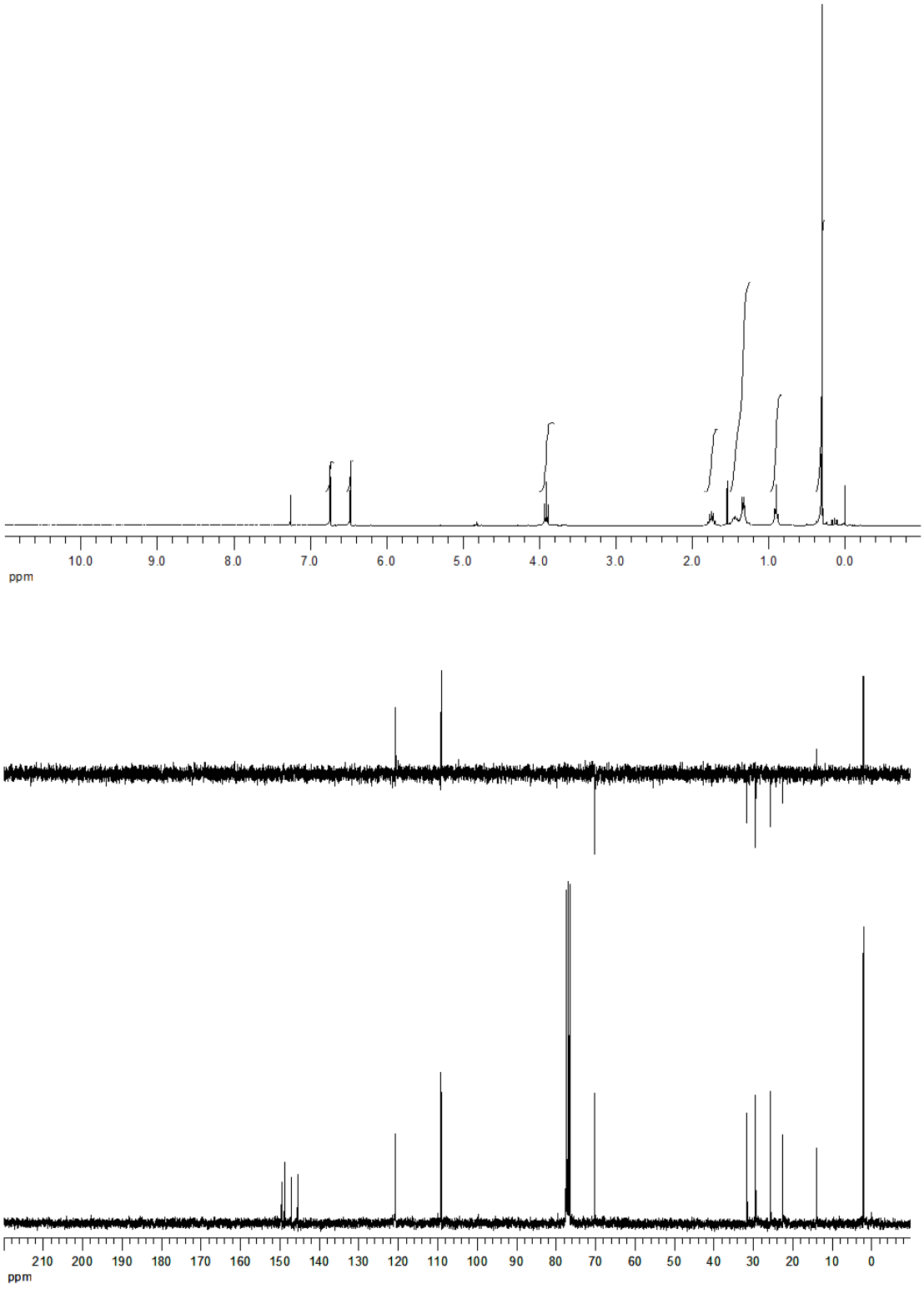


Figure S8. ^{1}H (300 MHz) and ^{13}C NMR (100 MHz) spectra of compound **4c** ($CDCl_3$).

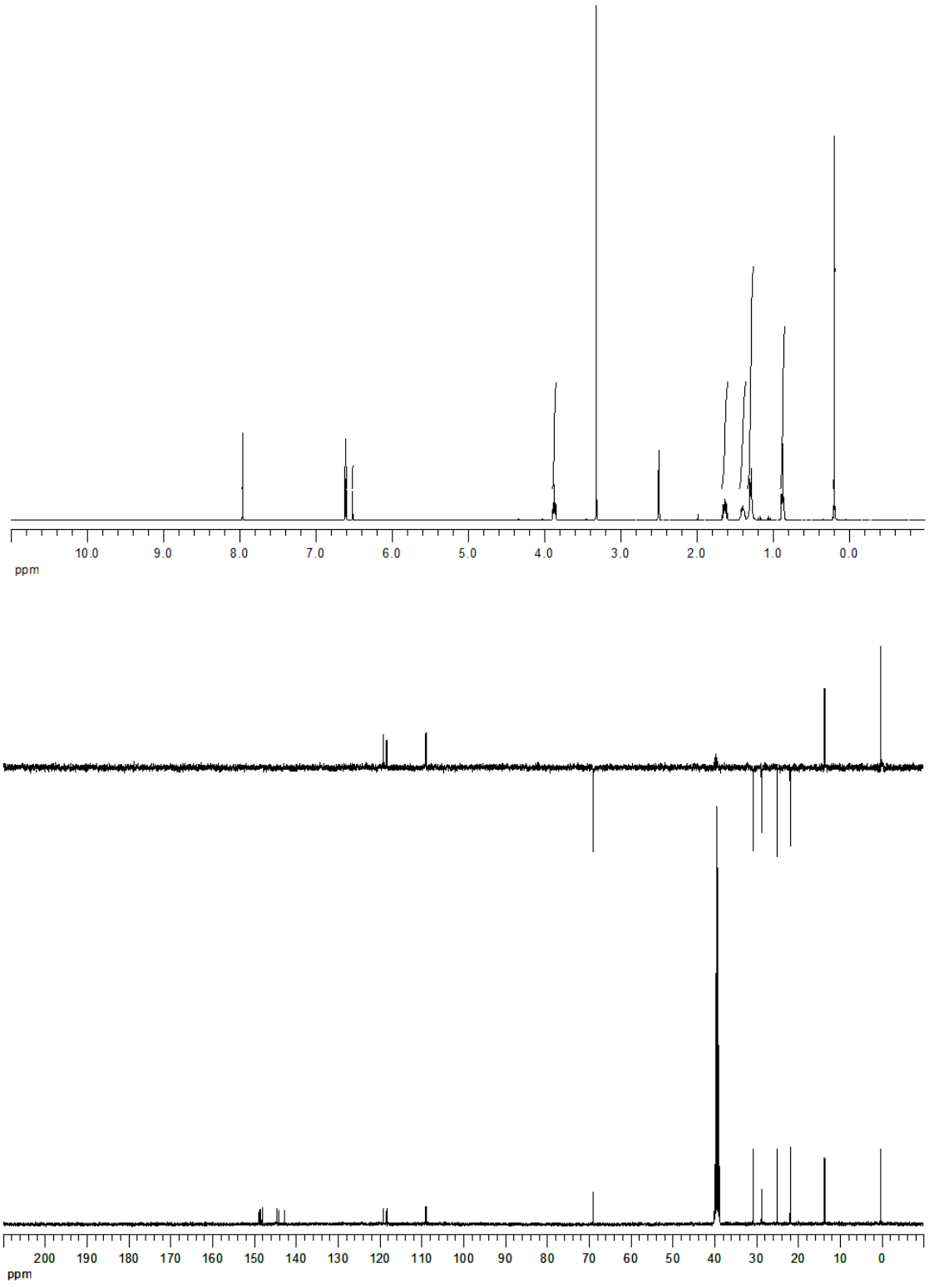


Figure S9. ^{1}H (400 MHz) and ^{13}C NMR (125 MHz) spectra of compound **10c** ($CDCl_3$).

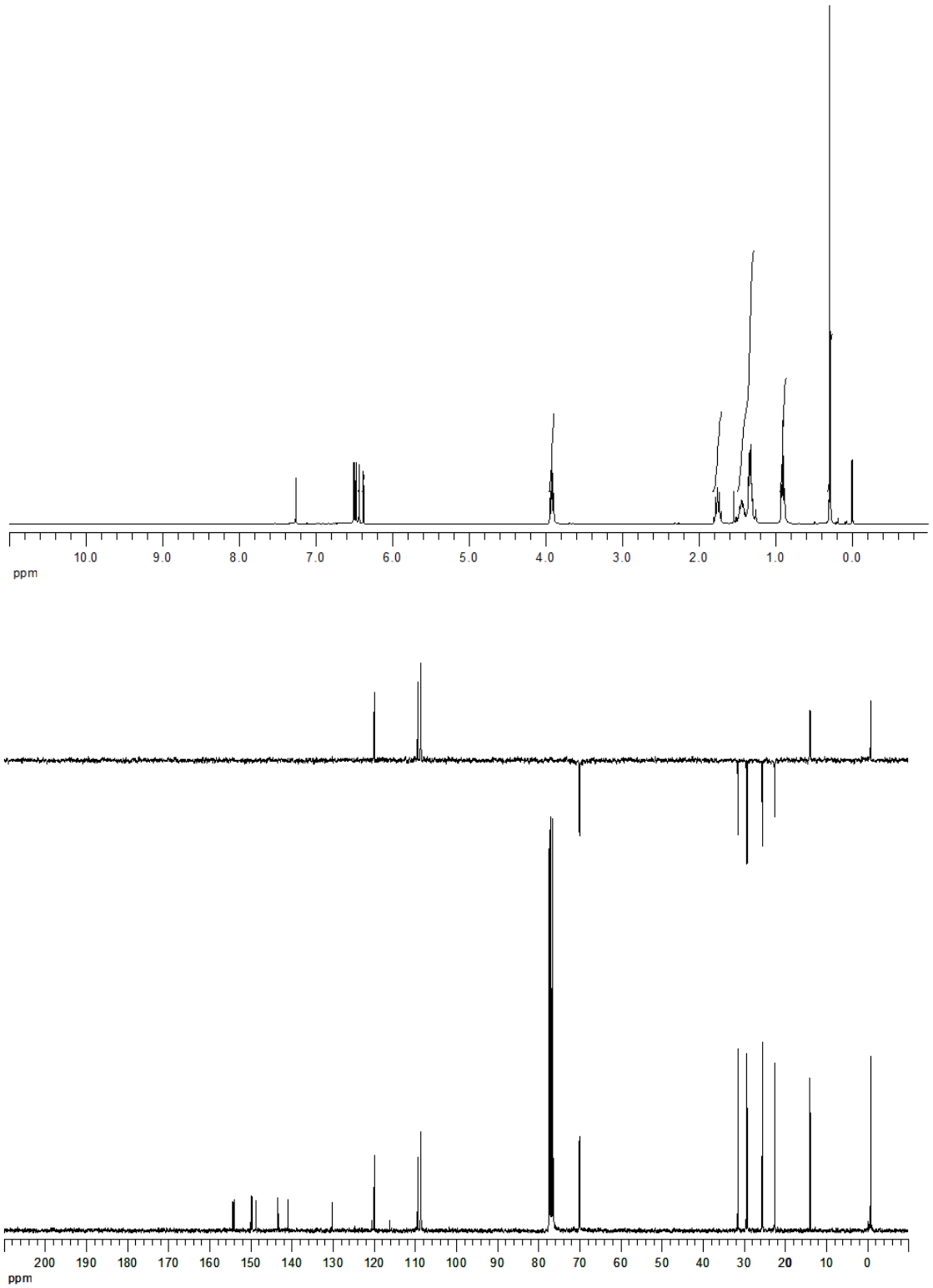


Figure S10. ^{1}H (300 MHz) and ^{13}C NMR (100 MHz) spectra of compound **5c** ($CDCl_3$).

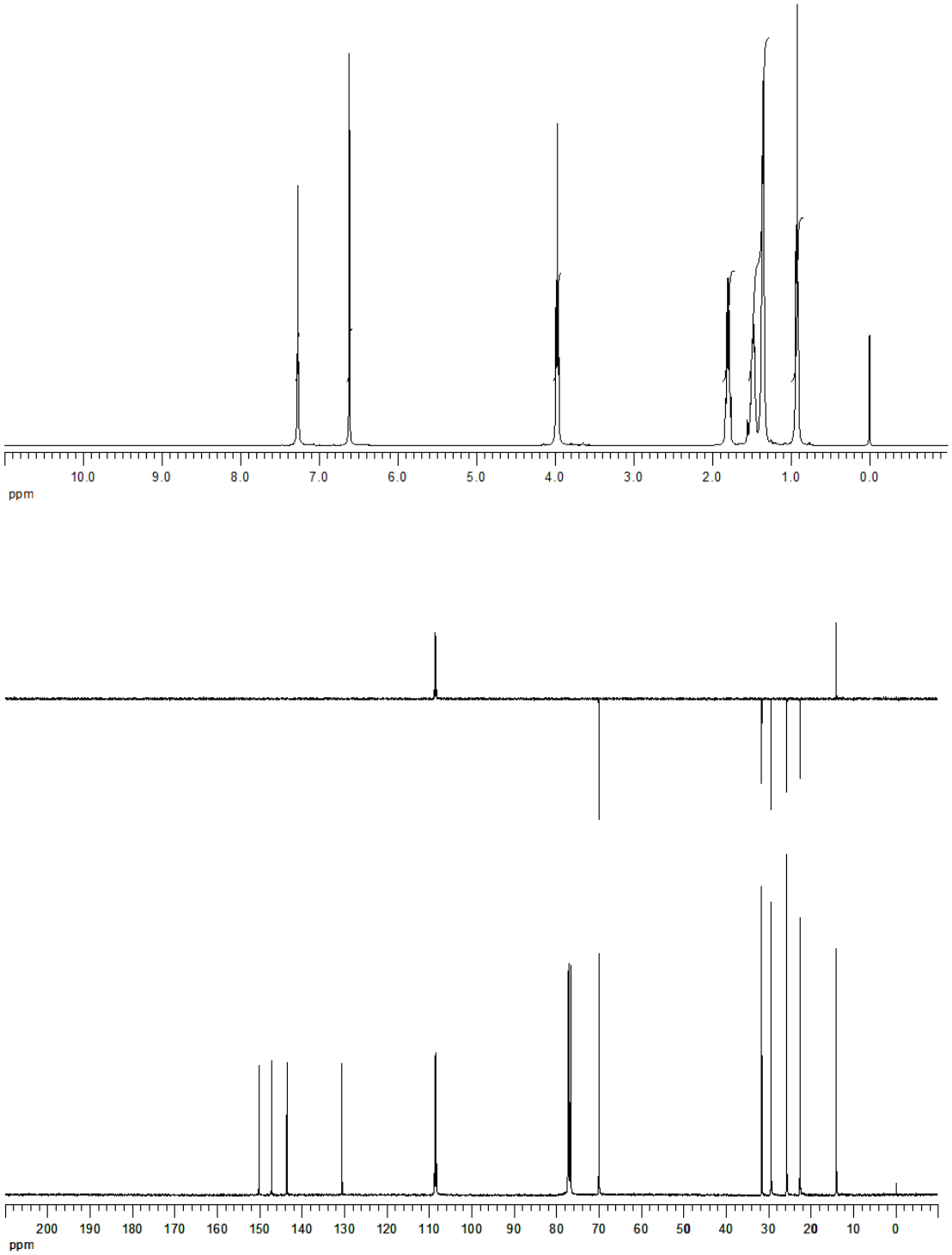
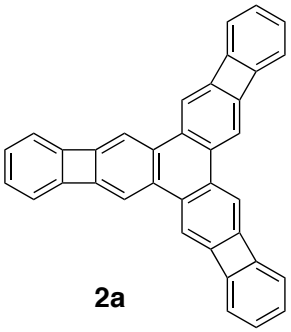
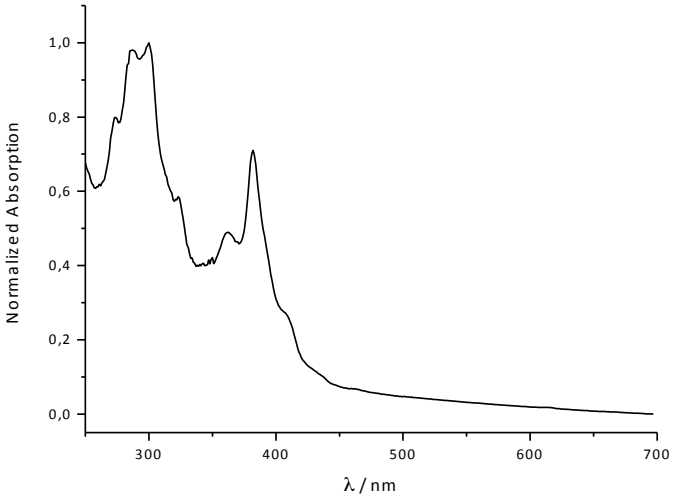


Figure S11. ^{1}H (400 MHz) and ^{13}C NMR (125 MHz) spectra of compound **2b** ($CDCl_3$)..

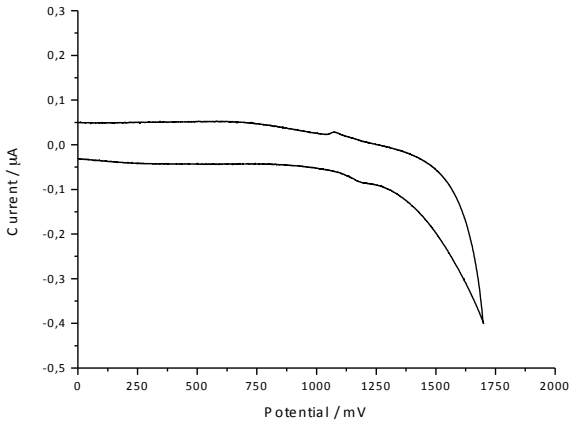
3. UV-Vis spectra ($CDCl_3$) and cyclic voltamograms of trisbenzotriphenylenes 2a and 2c[I]



2a

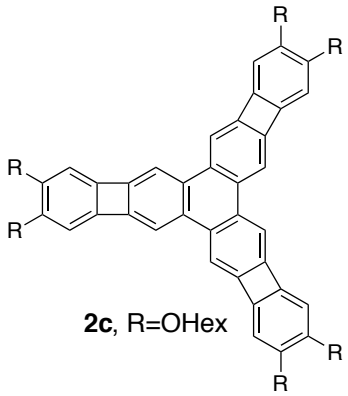


λ_{onset} = 415nm
Optical Gap = 2.99 eV

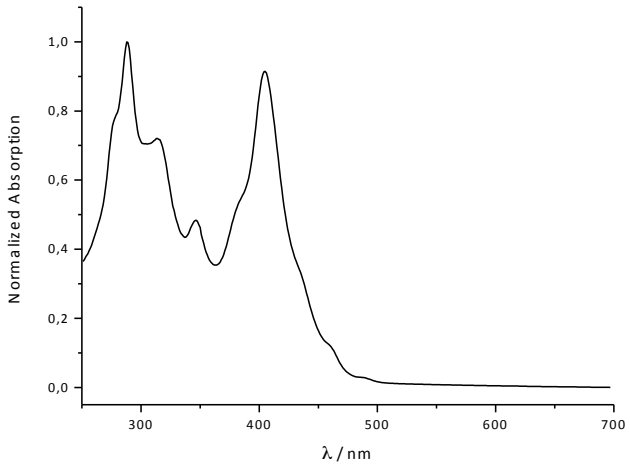


E_{ox} = 1.14 V

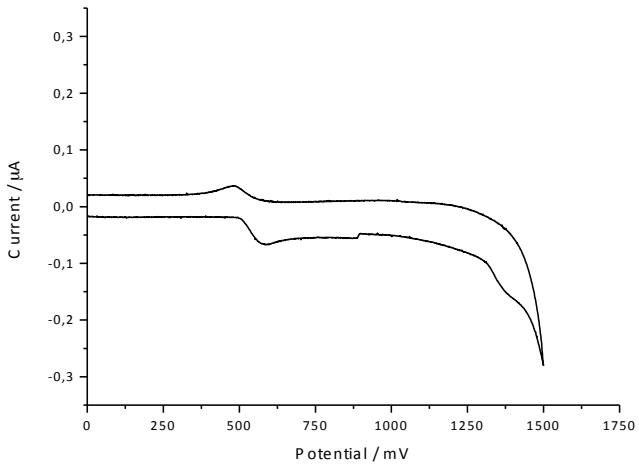
[I] Characterization of **2b** in solution was precluded due to its insolubility in common organic solvents



2c, R=OHex



λ_{onset} = 463nm
Optical Gap = 2.68 eV

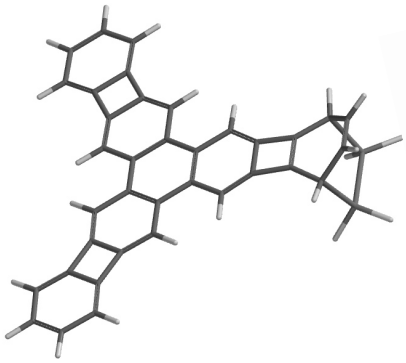


E_{ox} = 0.53 V

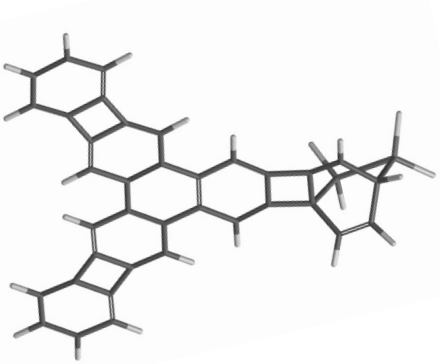
4. Preliminary estimation of the relative stabilitities of the [4+2] cycloadducts of 2a and 2b with digermene ($H_2Ge=GeH_2$)[II]

The initial minimization of structures was achieved by using the MM2 method followed by calculation of the equilibrium geometry using DFT at the B3LYP 6-31G(D) level. These computations were performed by using Spartan 10 package program at standard conditions of 298.15 K and 1.00 atm.[3]

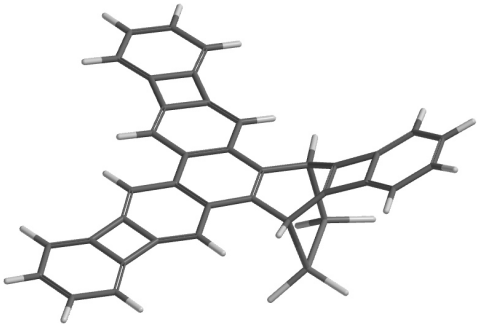
4.a.Cycloadducts of **2a**



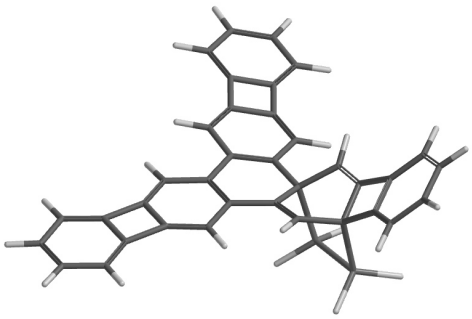
Trisbiphenylene ADA 1: -5538.43880 au
-3475423.5605 kcal/mol



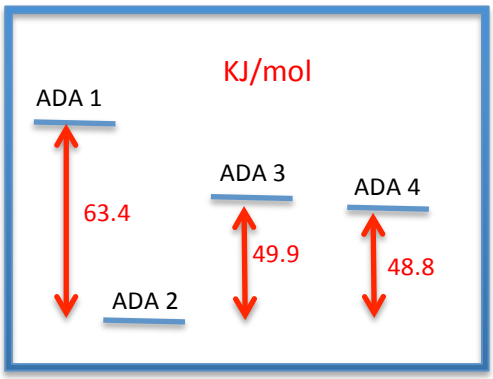
Trisbiphenylene ADA 2: -5538.46297 au
-3475438.7274 kcal/mol



Trisbiphenylene ADA 3: -5538.44395 au
-3475426.7922 kcal/mol



Trisbiphenylene ADA 4: -5538.44438 au
-3475427.062 kcal/mol



[II] For comparison, a similar analysis for trinaphthylene **1** is included in page S34

Tribiphenylene ADA 1 Energy: -5538.438802 au

Cartesian Coordinates (Angstroms)

Atom	X	Y	Z
1 C C1	2.8602594	0.0547862	-0.7222103
2 C C2	1.6282384	0.2201080	-1.4352152
3 C C3	0.3903292	0.3813510	-0.7113942
4 C C4	0.3903292	0.3813510	0.7113942
5 C C5	1.6282384	0.2201080	1.4352152
6 C C6	2.8602594	0.0547862	0.7222103
7 C C7	-0.8646798	0.5475176	-1.4380330
8 H H9	-0.8846802	0.5321632	-2.5192594
9 C C8	-1.9931151	0.7177708	-0.7201861
10 C C9	-1.9931151	0.7177708	0.7201861
11 C C10	-0.8646798	0.5475176	1.4380330
12 H H10	-0.8846802	0.5321632	2.5192594
13 C C11	1.6316590	0.2266013	2.8818833
14 H H13	0.7131852	0.3575072	3.4379931
15 C C12	2.8176778	0.0694303	3.5197930
16 C C13	4.0490762	-0.0973208	2.8059943
17 C C14	4.0980373	-0.1077839	1.4507848
18 H H14	5.0364780	-0.2338111	0.9277953
19 C C15	4.0980373	-0.1077839	-1.4507848
20 H H17	5.0364780	-0.2338111	-0.9277953
21 C C16	4.0490762	-0.0973208	-2.8059943
22 C C17	2.8176778	0.0694303	-3.5197930
23 C C18	1.6316590	0.2266013	-2.8818833
24 H H18	0.7131852	0.3575072	-3.4379931
25 C C21	3.5634154	-0.0235857	4.8189029
26 C C22	4.7873913	-0.1890833	4.1089871
27 C C23	4.7873913	-0.1890833	-4.1089871
28 C C24	3.5634154	-0.0235857	-4.8189029
29 C C29	3.5092896	-0.0094507	6.1948613
30 H H7	2.5865950	0.1160360	6.7543400
31 C C30	4.7470352	-0.1697283	6.8630218
32 H H12	4.7640118	-0.1666722	7.9497529
33 C C31	5.9449421	-0.3313631	6.1682150
34 H H8	6.8680223	-0.4508654	6.7294169
35 C C32	5.9943829	-0.3450661	4.7534909
36 H H20	6.9377842	-0.4725092	4.2302408
37 C C33	5.9943829	-0.3450661	-4.7534909
38 H H3	6.9377842	-0.4725092	-4.2302408
39 C C34	5.9449421	-0.3313631	-6.1682150
40 H H22	6.8680223	-0.4508654	-6.7294169
41 C C35	4.7470352	-0.1697283	-6.8630218
42 H H21	4.7640118	-0.1666722	-7.9497529
43 C C36	3.5092896	-0.0094507	-6.1948613
44 H H24	2.5865950	0.1160360	-6.7543400
45 C C19	-4.7476597	0.9916695	-1.4484355
46 H H2	-4.6586625	1.2547650	-2.5035169
47 C C20	-4.7476597	0.9916695	1.4484355
48 H H11	-4.6586625	1.2547650	2.5035169
49 C C25	-5.7058950	1.8732686	-0.6728835
50 H H15	-6.4153870	2.4773167	-1.2322188
51 C C26	-5.7058950	1.8732686	0.6728835
52 H H16	-6.4153870	2.4773167	1.2322188
53 GeGe1	-5.5464227	-0.9002730	-1.2263094
54 H H1	-4.6166888	-1.9601797	-1.8708219
55 H H4	-6.9521615	-0.9817286	-1.8770731

56 Ge Ge2	-5.5464227	-0.9002730	1.2263094
57 H H5	-4.6166888	-1.9601797	1.8708219
58 H H23	-6.9521615	-0.9817286	1.8770731
59 C C27	-3.4846997	0.9235409	0.6826726
60 C C28	-3.4846997	0.9235409	-0.6826726

Tribiphenylene ADA 2 Energy: -5538.462966 au

Atom	X	Y	Z
1 C C1	1.5345439	-1.3728099	0.1912483
2 C C2	2.7944538	-0.7124589	0.0849159
3 C C3	2.8567022	0.7401548	0.0578842
4 C C4	1.6555118	1.5074282	0.0821763
5 C C5	0.3658922	0.8389899	0.1925185
6 C C6	0.3089696	-0.5938473	0.2753506
7 C C7	4.1361197	1.4073521	0.0000567
8 H H9	5.0580074	0.8417673	0.0078025
9 C C8	4.1484546	2.7638532	-0.0524074
10 C C9	2.9425506	3.5314143	-0.0510105
11 C C10	1.7187205	2.9465977	0.0160832
12 H H10	0.8166619	3.5437086	0.0233163
13 C C11	-0.8393633	1.6029221	0.2435123
14 H H13	-0.8193326	2.6831954	0.1888441
15 C C12	-2.0272959	0.9323555	0.3825981
16 C C13	-2.0814197	-0.4799982	0.4758036
17 C C14	-0.9546277	-1.2495672	0.4319162
18 H H14	-1.0152482	-2.3264497	0.5230604
19 C C15	1.4743914	-2.8143883	0.2010187
20 H H17	0.5250289	-3.3295059	0.2601822
21 C C16	2.6409417	-3.5039312	0.1156589
22 C C17	3.9042488	-2.8426017	0.0115980
23 C C18	4.0076955	-1.4889818	-0.0096010
24 H H18	4.9702939	-1.0060282	-0.1092465
25 C C19	4.9520094	4.0316976	-0.1178426
26 C C20	3.7498930	4.7958132	-0.1191325
27 C C21	-3.4847883	1.0473188	0.5656260
28 C C23	3.3348871	-4.8343076	0.0502661
29 C C24	4.5935416	-4.1755007	-0.0526857
30 C C25	6.1954614	4.6198910	-0.1665880
31 H H2	7.1232237	4.0549575	-0.1654535
32 C C26	6.2068998	6.0352390	-0.2198342
33 H H4	7.1613243	6.5534273	-0.2605163
34 C C27	5.0306607	6.7827103	-0.2213852
35 H H1	5.0945498	7.8668107	-0.2630892
36 C C28	3.7541026	6.1711747	-0.1700264
37 H H6	2.8487716	6.7713747	-0.1714735
38 C C29	-4.5200934	1.8282361	0.8954488
39 H H7	-4.4817365	2.9118841	0.9662734
40 C C33	3.2222858	-6.2061920	0.0485350
41 H H3	2.2721487	-6.7271254	0.1244885
42 C C34	4.4379842	-6.9247056	-0.0599293
43 H H22	4.4093275	-8.0111230	-0.0657495
44 C C35	5.6695171	-6.2799385	-0.1604923
45 H H21	6.5730581	-6.8782745	-0.2424614
46 C C36	5.7782637	-4.8677956	-0.1601140
47 H H24	6.7473307	-4.3838703	-0.2411455
48 C C22	-3.6060650	-0.4880590	0.5774853
49 C C30	-5.7918257	1.0887136	1.2536874

50 H H19	-6.5175280	1.7351179	1.7513206
51 C C31	-4.4302228	-0.9261437	1.7487196
52 H H20	-4.1932373	-1.8376995	2.2915507
53 C C32	-5.4956576	-0.1599157	2.0546464
54 H H23	-6.1798337	-0.4344891	2.8540459
55 Ge Ge1	-4.6622058	-0.9978699	-1.0817817
56 H H5	-4.9208742	-2.5253357	-1.1340290
57 H H8	-3.9120727	-0.5574337	-2.3644680
58 Ge Ge2	-6.5908983	0.4000440	-0.5015219
59 H H15	-6.8519130	1.5685035	-1.4900604
60 H H16	-7.9326388	-0.3358332	-0.2356585

Tribiphenylene ADA 3 Energy: -5538.443951 au

Atom	X	Y	Z
1 C C1	-0.6680629	-0.2104706	1.4324668
2 C C2	-1.9119758	-0.3019074	0.7203091
3 C C3	-1.9119758	-0.3019074	-0.7203091
4 C C4	-0.6680629	-0.2104706	-1.4324668
5 C C5	0.5636587	-0.1703231	-0.6992804
6 C C6	0.5636587	-0.1703231	0.6992804
7 C C7	-3.1551558	-0.3726875	-1.4554388
8 H H9	-4.1015783	-0.4523995	-0.9373390
9 C C8	-3.0992560	-0.3293329	-2.8095604
10 C C9	-1.8581303	-0.2133904	-3.5194098
11 C C10	-0.6648638	-0.1541659	-2.8785110
12 H H10	0.2629209	-0.0545085	-3.4266851
13 C C15	-0.6648638	-0.1541659	2.8785110
14 H H17	0.2629209	-0.0545085	3.4266851
15 C C16	-1.8581303	-0.2133904	3.5194098
16 C C17	-3.0992560	-0.3293329	2.8095604
17 C C18	-3.1551558	-0.3726875	1.4554388
18 H H18	-4.1015783	-0.4523995	0.9373390
19 C C19	-3.8391447	-0.3323746	-4.1151144
20 C C20	-2.6068733	-0.2144647	-4.8192044
21 C C21	4.2614197	-1.5443328	-0.7155124
22 C C22	4.2614197	-1.5443328	0.7155124
23 C C23	-2.6068733	-0.2144647	4.8192044
24 C C24	-3.8391447	-0.3323746	4.1151144
25 C C25	-5.0524641	-0.3926052	-4.7641640
26 H H2	-6.0026731	-0.4826259	-4.2456630
27 C C26	-4.9994660	-0.3297333	-6.1770283
28 C C27	-3.7926763	-0.2139048	-6.8663280
29 C C28	-2.5489749	-0.1521209	-6.1937595
30 H H6	-1.6194707	-0.0606715	-6.7483350
31 C C29	5.2911791	-2.0551894	-1.4464646
32 H H7	5.3186202	-2.0501034	-2.5324849
33 C C30	6.3777038	-2.6123874	-0.6892541
34 C C31	6.3777038	-2.6123874	0.6892541
35 C C32	5.2911791	-2.0551894	1.4464646
36 H H20	5.3186202	-2.0501034	2.5324849
37 C C33	-2.5489749	-0.1521209	6.1937595
38 H H3	-1.6194707	-0.0606715	6.7483350
39 C C34	-3.7926763	-0.2139048	6.8663280
40 C C35	-4.9994660	-0.3297333	6.1770283
41 C C36	-5.0524641	-0.3926052	4.7641640
42 H H24	-6.0026731	-0.4826259	4.2456630
43 C C11	2.9134610	-0.8376324	-0.6770017

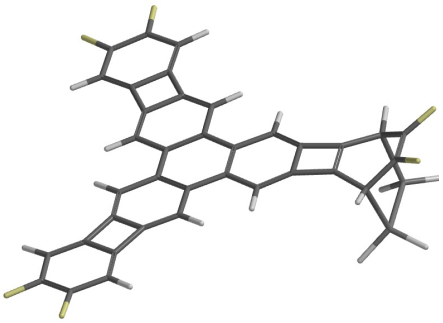
44 C C12	2.9134610	-0.8376324	0.6770017
45 C C13	1.9005553	-0.0800523	1.4318723
46 H H5	1.8466466	-0.3402419	2.4855805
47 C C14	1.9005553	-0.0800523	-1.4318723
48 H H23	1.8466466	-0.3402419	-2.4855805
49 Ge Ge2	2.4807605	1.8891454	-1.2223331
50 H H14	1.4551506	2.8468303	-1.8813644
51 H H15	3.8741744	2.1006682	-1.8671396
52 Ge Ge1	2.4807605	1.8891454	1.2223331
53 H H13	1.4551506	2.8468303	1.8813644
54 H H16	3.8741744	2.1006682	1.8671396
55 H H35	-5.9268593	-0.3731460	6.7419501
56 H H36	-3.8078698	-0.1695508	7.9520905
57 H H37	-5.9268593	-0.3731460	-6.7419501
58 H H38	-3.8078698	-0.1695508	-7.9520905
59 H H39	7.2198576	-3.0435010	-1.2240850
60 H H40	7.2198576	-3.0435010	1.2240850

Tribiphenylene ADA 4 Energy: -5538.444378 au

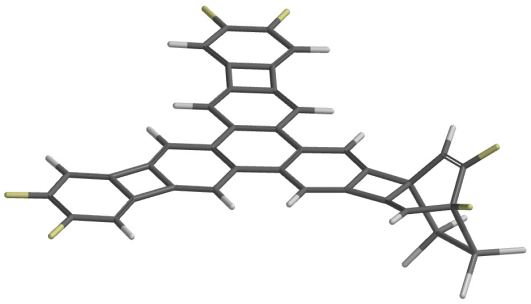
Atom	X	Y	Z
1 C C1	-0.7825891	-1.3049483	-0.0429462
2 C C2	-1.8846585	-0.4591212	-0.2845050
3 C C3	-1.7189823	1.0085319	-0.2547212
4 C C4	-0.4282850	1.5902866	-0.2031040
5 C C7	-2.8831728	1.8483835	-0.2462526
6 H H9	-3.8760130	1.4177790	-0.2262538
7 C C8	-2.6978793	3.1993062	-0.2255052
8 C C9	-1.3995560	3.7815316	-0.1787010
9 C C10	-0.2725026	3.0150910	-0.1479936
10 H H10	0.7148771	3.4503471	-0.0530975
11 C C15	-0.9480959	-2.7220735	0.0510831
12 H H17	-0.0945097	-3.3504780	0.2849272
13 C C16	-2.1985384	-3.2314186	-0.1614039
14 C C17	-3.3002665	-2.3890811	-0.4744150
15 C C18	-3.1775576	-1.0317508	-0.5385958
16 H H18	-4.0198852	-0.4025464	-0.7971922
17 C C19	-3.3150136	4.5701889	-0.1700032
18 C C20	-2.0160049	5.1529000	-0.1218692
19 C C23	-3.0863649	-4.4406712	-0.2720277
20 C C24	-4.1898702	-3.5992748	-0.5946998
21 C C25	-4.4611207	5.3291525	-0.1441796
22 H H2	-5.4601776	4.9040691	-0.1769911
23 C C26	-4.2705279	6.7327807	-0.0707512
24 C C27	-3.0011669	7.3021302	-0.0225772
25 C C28	-1.8233602	6.5120307	-0.0448957
26 H H6	-0.8413219	6.9743887	-0.0036696
27 C C33	-3.2016418	-5.8083843	-0.2001859
28 H H3	-2.3720120	-6.4656447	0.0439921
29 C C34	-4.4917630	-6.3343711	-0.4695640
30 C C35	-5.5690505	-5.5129316	-0.7868018
31 C C36	-5.4414285	-4.1011752	-0.8588069
32 H H24	-6.2948236	-3.4775261	-1.1091291
33 C C13	0.6107975	-0.7516979	0.1110696
34 C C14	3.1913957	0.3196241	-0.1666638
35 Ge Ge2	3.4007794	0.0814963	1.8409878
36 H H14	3.6628130	1.4418245	2.5346531
37 H H15	4.5536768	-0.9021400	2.1669353

38 Ge Ge1	1.1694368	-0.8757148	2.1124992
39 H H13	0.1497300	-0.0897005	2.9765231
40 H H16	1.1621658	-2.3631284	2.5523797
41 C C5	0.7717781	0.7376494	-0.1911533
42 C C6	2.0318398	1.2301850	-0.3615253
43 H H38	2.2128226	2.2738457	-0.5948958
44 C C11	1.6421318	-1.5742903	-0.6572495
45 H H36	1.3276394	-2.4849457	-1.1555980
46 C C12	2.8656340	-1.0535659	-0.7600348
47 C C21	4.4474639	0.2542215	-1.0388346
48 C C22	4.1462280	-1.0480360	-1.4910542
49 C C29	4.9808274	-1.7420147	-2.3569055
50 H H7	4.7636498	-2.7450515	-2.7131662
51 C C30	6.1417914	-1.0642185	-2.7633552
52 C C31	6.4335847	0.2343788	-2.3233834
53 C C32	5.5840440	0.9305044	-1.4428178
54 H H11	5.8259926	1.9375164	-1.1129697
55 H H25	-5.1417376	7.3821736	-0.0509959
56 H H26	-2.9091344	8.3835161	0.0340430
57 H H27	-6.5374245	-5.9645303	-0.9854026
58 H H28	-4.6414136	-7.4099415	-0.4271139
59 H H29	6.8342144	-1.5571560	-3.4407043
60 H H30	7.3437587	0.7149133	-2.6728317

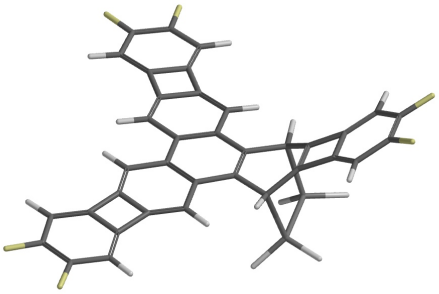
4.b.Cycloadducts of **2b**



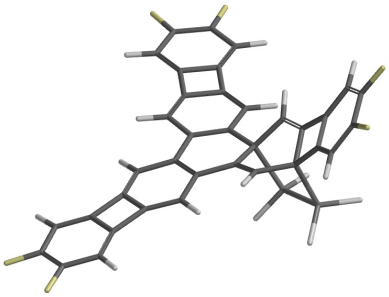
6F-Trisbiphenylene ADA 1: -6133.81249 au
-3849026.2713 kcal/mol



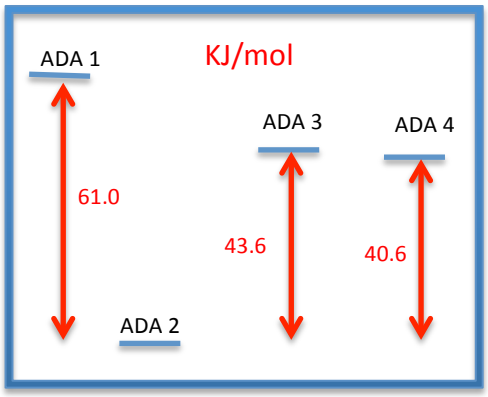
6F-Trisbiphenylene ADA 2: -6133.85573 au
-3849053.4048 kcal/mol



6F-Trisbiphenylene ADA 3: -6133.81915 au
-3849030.4505 kcal/mol



6F-Trisbiphenylene ADA 4: -6133.82028 au
-3849031.1596 kcal/mol



4F-Trisbiphenylene ADA 1 Energy: -6133.812494 au

Atom	X	Y	Z
1 C C1	2.5961231	0.0755787	-0.7219109
2 C C2	1.3635514	0.2378150	-1.4346123
3 C C3	0.1210538	0.3538190	-0.7114361
4 C C4	0.1210538	0.3538190	0.7114361
5 C C5	1.3635514	0.2378150	1.4346123
6 C C6	2.5961231	0.0755787	0.7219109
7 C C7	-1.1394419	0.4642070	-1.4386923

8 H H9	-1.1611162	0.4272437	-2.5193207
9 C C8	-2.2721533	0.5953491	-0.7200748
10 C C9	-2.2721533	0.5953491	0.7200748
11 C C10	-1.1394419	0.4642070	1.4386923
12 H H10	-1.1611162	0.4272437	2.5193207
13 C C11	1.3694789	0.2826005	2.8808222
14 H H13	0.4535724	0.4343568	3.4356660
15 C C12	2.5575522	0.1436602	3.5174286
16 C C13	3.7873132	-0.0408589	2.8047789
17 C C14	3.8361322	-0.0739135	1.4506412
18 H H14	4.7745622	-0.2050253	0.9291965
19 C C15	3.8361322	-0.0739135	-1.4506412
20 H H17	4.7745622	-0.2050253	-0.9291965
21 C C16	3.7873132	-0.0408589	-2.8047789
22 C C17	2.5575522	0.1436602	-3.5174286
23 C C18	1.3694789	0.2826005	-2.8808222
24 H H18	0.4535724	0.4343568	-3.4356660
25 C C21	3.3060424	0.0835381	4.8148455
26 C C22	4.5270661	-0.1040473	4.1070866
27 C C23	4.5270661	-0.1040473	-4.1070866
28 C C24	3.3060424	0.0835381	-4.8148455
29 C C29	3.2494104	0.1338601	6.1908613
30 H H7	2.3460692	0.2770469	6.7743286
31 C C30	4.4848097	-0.0171405	6.8462329
32 C C31	5.6801455	-0.2043639	6.1534491
33 C C32	5.7377248	-0.2527192	4.7487402
34 H H20	6.6925201	-0.4000717	4.2551956
35 C C33	5.7377248	-0.2527192	-4.7487402
36 H H3	6.6925201	-0.4000717	-4.2551956
37 C C34	5.6801455	-0.2043639	-6.1534491
38 C C35	4.4848097	-0.0171405	-6.8462329
39 C C36	3.2494104	0.1338601	-6.1908613
40 H H24	2.3460692	0.2770469	-6.7743286
41 C C19	-5.0384135	0.6525850	-1.4471622
42 H H2	-5.0028800	0.9573141	-2.4938725
43 C C20	-5.0384135	0.6525850	1.4471622
44 H H11	-5.0028800	0.9573141	2.4938725
45 C C25	-6.0688927	1.4260676	-0.6713258
46 C C26	-6.0688927	1.4260676	0.6713258
47 Ge Ge1	-5.6352350	-1.3195561	-1.2289941
48 H H1	-4.6158334	-2.2830028	-1.8861831
49 H H4	-7.0358546	-1.5147882	-1.8604325
50 Ge Ge2	-5.6352350	-1.3195561	1.2289941
51 H H5	-4.6158334	-2.2830028	1.8861831
52 H H23	-7.0358546	-1.5147882	1.8604325
53 C C27	-3.7720052	0.7237125	0.6823139
54 C C28	-3.7720052	0.7237125	-0.6823139
55 F F1	-7.0390496	2.0328537	1.3823005
56 F F2	-7.0390496	2.0328537	-1.3823005
57 F F3	4.5274910	0.0176570	8.1899426
58 F F4	6.8119197	-0.3467103	6.8655309
59 F F5	6.8119197	-0.3467103	-6.8655309
60 F F6	4.5274910	0.0176570	-8.1899426

4F-Tribiphenylene ADA 2 Energy: -6133.835733 au

Atom	X	Y	Z
1 C C1	-1.2683277	-1.4139600	-0.1393258
2 C C2	-2.5450157	-0.7785549	-0.1084647
3 C C3	-2.6374796	0.6721273	-0.0824583
4 C C4	-1.4523682	1.4641895	-0.0710518
5 C C5	-0.1464930	0.8222839	-0.1296621
6 C C6	-0.0558551	-0.6113388	-0.1661789
7 C C7	-3.9321751	1.3125062	-0.0576567
8 H H9	-4.8424205	0.7292017	-0.0788509
9 C C8	-3.9717473	2.6676414	-0.0085618
10 C C9	-2.7825257	3.4602091	0.0236105
11 C C10	-1.5456069	2.9023023	-0.0050228
12 H H10	-0.6563041	3.5170329	0.0276608
13 C C11	1.0421410	1.6121157	-0.1671722
14 H H13	0.9966467	2.6928247	-0.1714131
15 C C12	2.2479125	0.9619834	-0.2222590
16 C C13	2.3369928	-0.4499407	-0.2434959
17 C C14	1.2270089	-1.2441940	-0.2292653
18 H H14	1.3163530	-2.3217385	-0.2733217
19 C C15	-1.1778247	-2.8544548	-0.1424821
20 H H17	-0.2173210	-3.3511233	-0.1519893
21 C C16	-2.3333574	-3.5651970	-0.1238688
22 C C17	-3.6137840	-2.9294793	-0.0987723
23 C C18	-3.7471580	-1.5791145	-0.0893046
24 H H18	-4.7245204	-1.1172378	-0.0615082
25 C C19	-4.8018294	3.9166198	0.0460623
26 C C20	-3.6174318	4.7053927	0.0808538
27 C C21	3.7080057	1.1010724	-0.3540639
28 C C23	-3.0020589	-4.9074854	-0.1071659
29 C C24	-4.2773379	-4.2755851	-0.0824514
30 C C25	-6.0614370	4.4732549	0.0735913
31 H H2	-6.9917567	3.9157845	0.0490259
32 C C26	-6.0929574	5.8786643	0.1397495
33 C C27	-4.9333172	6.6510184	0.1745368
34 C C28	-3.6467945	6.0809521	0.1458683
35 H H6	-2.7737997	6.7242259	0.1756582
36 C C29	4.7330557	1.8859407	-0.6998293
37 H H7	4.7081092	2.9594020	-0.8597943
38 C C33	-2.8552376	-6.2770475	-0.1044678
39 H H3	-1.9072926	-6.8041642	-0.1219473
40 C C34	-4.0577862	-7.0072982	-0.0758168
41 C C35	-5.3066256	-6.3889394	-0.0508911
42 C C36	-5.4552036	-4.9893277	-0.0533427
43 H H24	-6.4492585	-4.5554046	-0.0324760
44 C C22	3.8647418	-0.4287280	-0.2670228
45 C C30	6.0375713	1.1561061	-0.9240510
46 C C31	4.7447891	-0.9289270	-1.3715499
47 H H20	4.6041871	-1.8950894	-1.8445620
48 C C32	5.7853229	-0.1363810	-1.6707039
49 Ge Ge1	4.8414642	-0.8123748	1.4803226
50 H H5	5.1425708	-2.3252239	1.6231942
51 H H8	4.0222246	-0.3243167	2.7015499
52 Ge Ge2	6.7741081	0.5918398	0.9098861
53 H H15	6.9588748	1.8469090	1.7971863
54 H H16	8.1316124	-0.1284921	0.7188922
55 F F1	-4.0114017	-8.3508483	-0.0714105
56 F F2	-6.4020593	-7.1681688	-0.0221382

57 F F3	-7.2798603	6.5095954	0.1720854
58 F F4	-5.0611226	7.9878145	0.2392344
59 F F5	6.7315137	-0.4748904	-2.5611392
60 F F6	6.9433108	1.9513258	-1.6138947

4F-Tribiphenylene ADA 3 Energy: -6133.819145 au

Atom	X	Y	Z
1 C C1	-0.5458991	-0.0314439	1.4317714
2 C C2	-1.7726896	-0.2565732	0.7200582
3 C C3	-1.7726896	-0.2565732	-0.7200582
4 C C4	-0.5458991	-0.0314439	-1.4317714
5 C C5	0.6761802	0.1221497	-0.6995014
6 C C6	0.6761802	0.1221497	0.6995014
7 C C7	-3.0021967	-0.4583705	-1.4546749
8 H H9	-3.9338378	-0.6436465	-0.9369223
9 C C8	-2.9506624	-0.4001318	-2.8076699
10 C C9	-1.7308227	-0.1407694	-3.5167276
11 C C10	-0.5498541	0.0405565	-2.8777072
12 H H10	0.3605742	0.2475630	-3.4246751
13 C C15	-0.5498541	0.0405565	2.8777072
14 H H17	0.3605742	0.2475630	3.4246751
15 C C16	-1.7308227	-0.1407694	3.5167276
16 C C17	-2.9506624	-0.4001318	2.8076699
17 C C18	-3.0021967	-0.4583705	1.4546749
18 H H18	-3.9338378	-0.6436465	0.9369223
19 C C19	-3.6860073	-0.4727846	-4.1118064
20 C C20	-2.4766182	-0.2099351	-4.8144086
21 C C21	4.4561957	-0.9679918	-0.7156752
22 C C22	4.4561957	-0.9679918	0.7156752
23 C C23	-2.4766182	-0.2099351	4.8144086
24 C C24	-3.6860073	-0.4727846	4.1118064
25 C C25	-4.8887949	-0.6645005	-4.7569848
26 H H2	-5.8352168	-0.8688250	-4.2676495
27 C C26	-4.8345382	-0.5801752	-6.1597735
28 C C27	-3.6497217	-0.3197288	-6.8478889
29 C C28	-2.4228856	-0.1248142	-6.1890173
30 H H6	-1.5279053	0.0752884	-6.7685746
31 C C29	5.5078755	-1.4281781	-1.4492795
32 H H7	5.5631654	-1.4400035	-2.5327921
33 C C30	6.6108098	-1.9237131	-0.6877235
34 C C31	6.6108098	-1.9237131	0.6877235
35 C C32	5.5078755	-1.4281781	1.4492795
36 H H20	5.5631654	-1.4400035	2.5327921
37 C C33	-2.4228856	-0.1248142	6.1890173
38 H H3	-1.5279053	0.0752884	6.7685746
39 C C34	-3.6497217	-0.3197288	6.8478889
40 C C35	-4.8345382	-0.5801752	6.1597735
41 C C36	-4.8887949	-0.6645005	4.7569848
42 H H24	-5.8352168	-0.8688250	4.2676495
43 C C11	3.0707329	-0.3413442	-0.6768533
44 C C12	3.0707329	-0.3413442	0.6768533
45 C C13	2.0006605	0.3293145	1.4332594
46 H H5	1.9701546	0.0640287	2.4865974
47 C C14	2.0006605	0.3293145	-1.4332594
48 H H23	1.9701546	0.0640287	-2.4865974
49 Ge Ge2	2.4114747	2.3416446	-1.2225088

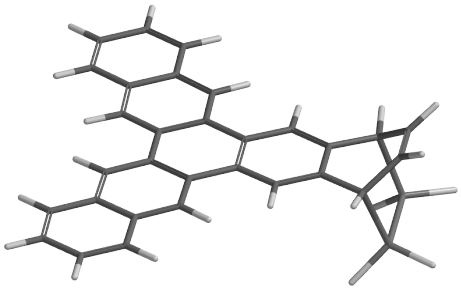
50 H H14	1.3008526	3.1999504	-1.8785595
51 H H15	3.7787788	2.6723684	-1.8713872
52 Ge Ge1	2.4114747	2.3416446	1.2225088
53 H H13	1.3008526	3.1999504	1.8785595
54 H H16	3.7787788	2.6723684	1.8713872
55 F F1	-3.6958459	-0.2548738	8.1897638
56 F F2	-5.9585331	-0.7571371	6.8751640
57 F F3	7.6807285	-2.4088614	1.3486851
58 F F4	7.6807285	-2.4088614	-1.3486851
59 F F5	-5.9585331	-0.7571371	-6.8751640
60 F F6	-3.6958459	-0.2548738	-8.1897638

4F-Tribiphenylene ADA 4 Energy: -6133.820280 au

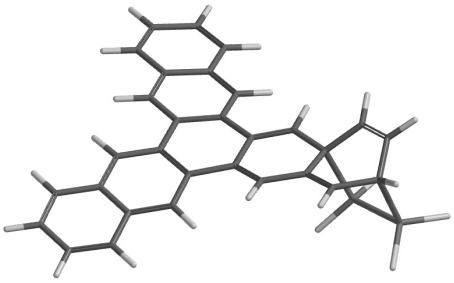
Atom	X	Y	Z
1 C C1	-1.0987291	-1.0470821	0.1347748
2 C C2	-1.8249110	0.1045368	-0.2321843
3 C C3	-1.1683279	1.4272123	-0.2449598
4 C C4	0.2376700	1.5365755	-0.1174531
5 C C7	-1.9743887	2.6108142	-0.3502352
6 H H9	-3.0537660	2.5432002	-0.3900220
7 C C8	-1.3379434	3.8160498	-0.3584811
8 C C9	0.0759631	3.9235387	-0.2317915
9 C C10	0.8695584	2.8243507	-0.0942311
10 H H10	1.9384167	2.9056482	0.0624288
11 C C15	-1.7486785	-2.3131952	0.2784008
12 H H17	-1.1823379	-3.1775129	0.6094703
13 C C16	-3.0819977	-2.3771898	-0.0121677
14 C C17	-3.8033639	-1.2337869	-0.4524214
15 C C18	-3.2177148	-0.0076734	-0.5663528
16 H H18	-3.7729332	0.8508750	-0.9220362
17 C C19	-1.4496296	5.3142244	-0.3911662
18 C C20	-0.0359609	5.4222745	-0.2616770
19 C C23	-4.3240815	-3.2139391	-0.1394414
20 C C24	-5.0457297	-2.0717691	-0.5893041
21 C C25	-2.2702969	6.4152535	-0.4747114
22 H H2	-3.3503047	6.3846508	-0.5725122
23 C C26	-1.6097514	7.6594813	-0.4278971
24 C C27	-0.2281526	7.7654537	-0.2987258
25 C C28	0.6101607	6.6358272	-0.2080200
26 H H6	1.6817453	6.7701159	-0.1053198
27 C C33	-4.9075305	-4.4530360	-0.0112016
28 H H3	-4.4013402	-5.3509084	0.3271561
29 C C34	-6.2732594	-4.5112706	-0.3571931
30 C C35	-6.9772394	-3.3961483	-0.7993123
31 C C36	-6.3762847	-2.1267256	-0.9306610
32 H H24	-6.9681485	-1.2875542	-1.2804191
33 C C13	0.3887745	-0.9930383	0.3665799
34 C C14	3.1910079	-0.8828704	0.2207088
35 Ge Ge2	3.2085126	-1.0328171	2.2464764
36 H H14	3.8701427	0.2154957	2.8800462
37 H H15	3.9514982	-2.3127349	2.7057756
38 Ge Ge1	0.7696052	-1.1550738	2.4121125
39 H H13	0.0451036	-0.0022395	3.1527255
40 H H16	0.2228653	-2.5122371	2.9279719
41 C C5	1.0678014	0.3281054	0.0097455
42 C C6	2.4263157	0.3510873	-0.1001181

43 H H38	2.9655787	1.2535008	-0.3669636
44 C C11	1.1127885	-2.1687841	-0.2841032
45 H H36	0.5316669	-2.9538393	-0.7557466
46 C C12	2.4440403	-2.1011342	-0.3263157
47 C C21	4.3880262	-1.4317295	-0.5563248
48 C C22	3.6816729	-2.5820089	-0.9631714
49 C C29	4.2647235	-3.5826192	-1.7323155
50 H H7	3.7604999	-4.4829743	-2.0670566
51 C C30	5.5987581	-3.3630410	-2.0767766
52 C C31	6.2964005	-2.2128603	-1.6814783
53 C C32	5.7090046	-1.2087046	-0.9052102
54 H H11	6.2900029	-0.3363398	-0.6232217
55 F F1	-2.3323712	8.7904282	-0.5141706
56 F F2	0.3171013	8.9941999	-0.2627621
57 F F3	-8.2780987	-3.5418426	-1.1078785
58 F F4	-6.9270929	-5.6824544	-0.2566937
59 F F5	7.5774026	-2.0921112	-2.0714554
60 F F6	6.2580193	-4.2710462	-2.8189121

4.c.Cycloadducts of **1** (for comparison)



Trinaphthylene ADA 1: -5310.06837 au
-3332118.9215 kcal/mol



Trinaphthylene ADA 2: -5310.01824 au
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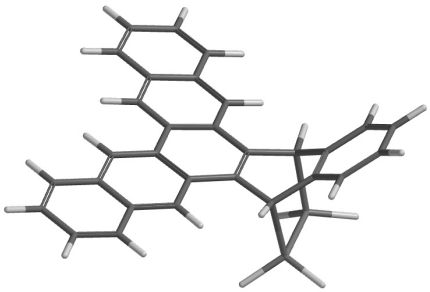
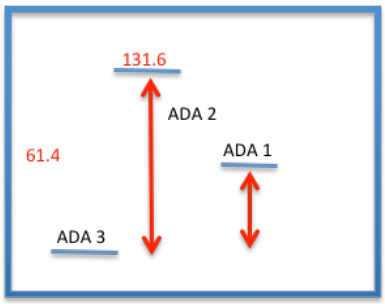


Trinaphthylene ADA 3: -5310.04497 au
-3332104.2377kcal/mol



Trinaphthylene ADA 1 Energy: -5310.068371 au

Atom	X	Y	Z
1 C C1	0.2703623	0.4176480	-0.7096675
2 C C2	0.2703623	0.4176480	0.7096675
3 C C3	1.5297934	0.2317633	1.4543397
4 C C4	2.7652651	0.0446985	0.7382193
5 C C5	2.7652651	0.0446985	-0.7382193
6 C C6	1.5297934	0.2317633	-1.4543397
7 C C7	1.5610935	0.2303171	2.8463339
8 H H9	0.6485062	0.3718275	3.4148582
9 C C8	2.7466763	0.0525835	3.5878484
10 C C9	3.9740210	-0.1341966	2.8759114
11 C C10	3.9381350	-0.1309842	1.4667785
12 H H10	4.8832981	-0.2750318	0.9546756
13 C C11	2.7686724	0.0520731	5.0129121
14 H H13	1.8348782	0.1950425	5.5529739
15 C C12	3.9499686	-0.1253471	5.6969367
16 H H5	3.9559239	-0.1241344	6.7839607
17 C C13	5.1694475	-0.3112832	4.9893037
18 H H15	6.0945966	-0.4510708	5.5426570
19 C C14	5.1802586	-0.3154414	3.6128359
20 H H14	6.1115021	-0.4582972	3.0684471
21 C C15	3.9381350	-0.1309842	-1.4667785
22 H H17	4.8832981	-0.2750318	-0.9546756
23 C C16	3.9740210	-0.1341966	-2.8759114
24 C C17	2.7466763	0.0525835	-3.5878484
25 C C18	1.5610935	0.2303171	-2.8463339
26 H H18	0.6485062	0.3718275	-3.4148582
27 C C19	5.1802586	-0.3154414	-3.6128359
28 H H21	6.1115021	-0.4582972	-3.0684471
29 C C20	5.1694475	-0.3112832	-4.9893037
30 H H7	6.0945966	-0.4510708	-5.5426570
31 C C21	3.9499686	-0.1253471	-5.6969367
32 H H23	3.9559239	-0.1241344	-6.7839607
33 C C22	2.7686724	0.0520731	-5.0129121
34 H H22	1.8348782	0.1950425	-5.5529739
35 C C23	-0.9574046	0.6010040	-1.3801380
36 H H25	-0.9861989	0.6090698	-2.4644056
37 C C24	-2.1582647	0.7768891	-0.7067888
38 C C25	-2.1582647	0.7768891	0.7067888
39 C C26	-0.9574046	0.6010040	1.3801380
40 H H26	-0.9861989	0.6090698	2.4644056
41 C C27	-3.4830965	0.9539768	1.4036667
42 H H3	-3.3614673	1.1946296	2.4628444
43 C C28	-3.4830965	0.9539768	-1.4036667
44 H H6	-3.3614673	1.1946296	-2.4628444
45 C C29	-4.3450326	1.9460501	-0.6729648
46 H H11	-4.9780884	2.6206832	-1.2444754
47 C C30	-4.3450326	1.9460501	0.6729648
48 H H8	-4.9780884	2.6206832	1.2444754
49 Ge Ge1	-4.4562845	-0.8381742	-1.2223967
50 H H2	-5.8510406	-0.7574706	-1.8935791
51 H H4	-3.6242204	-1.9712029	-1.8761260
52 Ge Ge2	-4.4562845	-0.8381742	1.2223967
53 H H12	-5.8510406	-0.7574706	1.8935791
54 H H16	-3.6242204	-1.9712029	1.8761260

Trinaphthylene ADA 2 Energy: -5310.018244 au

Atom	X	Y	Z
1 C C1	2.6813413	0.8313708	0.2355220
2 C C2	1.4145465	1.5170323	0.2424113
3 C C5	1.4933995	-1.4016116	0.1611124
4 C C6	2.7209870	-0.6506581	0.2077949
5 C C15	1.5600448	-2.7734079	-0.0503928
6 H H17	0.6482257	-3.3534004	-0.1529744
7 C C16	2.7790681	-3.4779207	-0.1500654
8 C C17	3.9997223	-2.7424876	-0.0288310
9 C C18	3.9245678	-1.3421987	0.1381405
10 H H18	4.8667037	-0.8073752	0.1899215
11 C C19	2.8382618	-4.8844107	-0.3634490
12 H H21	1.9083708	-5.4410293	-0.4606976
13 C C20	4.0515454	-5.5318722	-0.4443816
14 H H7	4.0864029	-6.6060319	-0.6075844
15 C C21	5.2640915	-4.8025362	-0.3165024
16 H H23	6.2144467	-5.3259894	-0.3828024
17 C C22	5.2379363	-3.4401010	-0.1132239
18 H H22	6.1651939	-2.8785350	-0.0188789
19 C C23	3.8430283	1.5907423	0.1718916
20 H H25	4.8144715	1.1080797	0.1774082
21 C C24	3.8373086	2.9995997	0.0639006
22 C C25	2.5766345	3.6719955	-0.0110648
23 C C26	1.3997213	2.8975037	0.0786195
24 H H26	0.4524088	3.4221296	0.0026508
25 C C27	5.0341261	3.7667807	-0.0081392
26 H H29	5.9916049	3.2535641	0.0519777
27 C C28	4.9841491	5.1357106	-0.1568215
28 H H3	5.9040757	5.7119700	-0.2130731
29 C C29	3.7325615	5.8021849	-0.2413313
30 H H31	3.7066700	6.8821297	-0.3624099
31 C C30	2.5571276	5.0866488	-0.1714803
32 H H30	1.5975671	5.5957881	-0.2346284
33 C C3	0.1955764	-0.7151222	0.3534024
34 C C4	0.1634103	0.7578793	0.4336982
35 C C7	-1.0069634	1.3841487	0.7695975
36 H H4	-1.0156266	2.4536288	0.9570638
37 C C10	-0.9637345	-1.4063612	0.5303247
38 H H10	-0.9555477	-2.4918874	0.5576505
39 C C13	-4.3817788	-0.8702446	1.9734055
40 H H13	-5.1056922	-1.3540991	2.6243818
41 C C14	-3.2548292	-1.4921137	1.5876888
42 H H12	-3.0147318	-2.5023760	1.9112633
43 C C8	-2.2924746	-0.7818894	0.6740859
44 C C9	-4.6707684	0.5096147	1.4538917
45 H H8	-5.4575429	1.0224718	2.0109091
46 C C11	-2.2590575	0.6994193	0.9558491
47 C C12	-3.4159788	1.3116145	1.3375135
48 H H14	-3.4510979	2.3857136	1.5050599
49 Ge Ge1	-3.2475372	-0.8844500	-1.2037747
50 H H2	-2.3726927	-0.1290975	-2.2329283
51 H H5	-3.3833554	-2.3727851	-1.6162333
52 Ge Ge2	-5.3021214	0.2120516	-0.4852441
53 H H9	-6.5491699	-0.7089220	-0.5257954
54 H H11	-5.6230241	1.5649395	-1.1691466

Trinaphthylene ADA 3 Energy: -5310.044969 au

Atom	X	Y	Z
1 C C1	2.0452445	0.2330220	-0.7347739
2 C C2	0.7870732	0.2172884	-1.4432902
3 C C3	-0.4593691	0.2531546	-0.6873703
4 C C4	-0.4593691	0.2531546	0.6873703
5 C C5	0.7870732	0.2172884	1.4432902
6 C C6	2.0452445	0.2330220	0.7347739
7 C C11	-3.6796053	1.9862639	-1.3957466
8 H H13	-3.6722459	1.9915182	-2.4836756
9 C C12	-4.5736272	2.7992174	-0.6985168
10 H H5	-5.2649945	3.4359128	-1.2439808
11 C C13	-4.5736272	2.7992174	0.6985168
12 H H15	-5.2649945	3.4359128	1.2439808
13 C C14	-3.6796053	1.9862639	1.3957466
14 H H14	-3.6722459	1.9915182	2.4836756
15 C C15	0.8048177	0.1695834	2.8361951
16 H H17	-0.1241104	0.1370579	3.3944867
17 C C16	1.9982904	0.1560990	3.5833989
18 C C17	3.2453220	0.1962354	2.8806242
19 C C18	3.2236383	0.2309039	1.4727174
20 H H18	4.1836873	0.2498996	0.9679347
21 C C19	2.0111230	0.1085350	5.0065854
22 H H21	1.0626944	0.0757394	5.5380590
23 C C20	3.1990191	0.1048582	5.6977139
24 H H7	3.1975513	0.0690187	6.7837917
25 C C21	4.4363812	0.1479617	5.0003988
26 H H23	5.3672723	0.1452041	5.5608846
27 C C22	4.4579569	0.1924810	3.6270229
28 H H22	5.4030110	0.2249000	3.0897091
29 C C23	3.2236383	0.2309039	-1.4727174
30 H H25	4.1836873	0.2498996	-0.9679347
31 C C24	3.2453220	0.1962354	-2.8806242
32 C C25	1.9982904	0.1560990	-3.5833989
33 C C26	0.8048177	0.1695834	-2.8361951
34 H H26	-0.1241104	0.1370579	-3.3944867
35 C C27	4.4579569	0.1924810	-3.6270229
36 H H29	5.4030110	0.2249000	-3.0897091
37 C C28	4.4363812	0.1479617	-5.0003988
38 H H3	5.3672723	0.1452041	-5.5608846
39 C C29	3.1990191	0.1048582	-5.6977139
40 H H31	3.1975513	0.0690187	-6.7837917
41 C C30	2.0111230	0.1085350	-5.0065854
42 H H30	1.0626944	0.0757394	-5.5380590
43 C C7	-1.7990362	0.2570577	1.3861626
44 H H1	-1.7264385	0.5090034	2.4429150
45 C C8	-1.7990362	0.2570577	-1.3861626
46 H H9	-1.7264385	0.5090034	-2.4429150
47 C C9	-2.7833687	1.1662771	0.7025651
48 C C10	-2.7833687	1.1662771	-0.7025651
49 Ge Ge1	-2.5325499	-1.6435422	-1.2184969
50 H H2	-1.5603003	-2.6529620	-1.8792283
51 H H4	-3.9236346	-1.7482782	-1.8935385
52 Ge Ge2	-2.5325499	-1.6435422	1.2184969
53 H H10	-3.9236346	-1.7482782	1.8935385
54 H H11	-1.5603003	-2.6529620	1.8792283

5. Calculated geometries

In Figure S12 optimized structures for both tribiphenylene and hexafluorotribiphenylene molecules interacting with the surface dangling bond (DB) dimer are displayed. It is shown that for both molecules the most stable configuration is found when the chemical bonds are formed between the DB dimer and the outer phenyl ring, as indicated in panels (b) and (g), respectively. Lower binding energies are found for the molecule attached by the inner phenyl ring shown in panels (c) and (h). Even lower binding energies are calculated for the configuration, in which the bonds with the surface are formed by the phenyl ring located within the molecule branch pointing along surface reconstructed rows, i.e. in the configuration similar to the one observed for trinaphthylenes. These structures are visualized in Figure S12 panels (a) and (f) for tribiphenylene and the fluorine substituted derivative, respectively. We calculate also the optimized structures and binding energies for molecules located over the DB dimer, but rotated by 90°. It is found that in such configuration there are no chemical bonds between the molecule and the surface and the DB dimer remains in a buckled state, however, the buckling angle is influenced by the interaction with the molecule. The structures are shown in Figure S12, panels (d,e) and (i,j). These configurations are similar to the ones obtained for trinaphthylene molecules (see Figure S4, c,d), which were observed experimentally.[4,5]

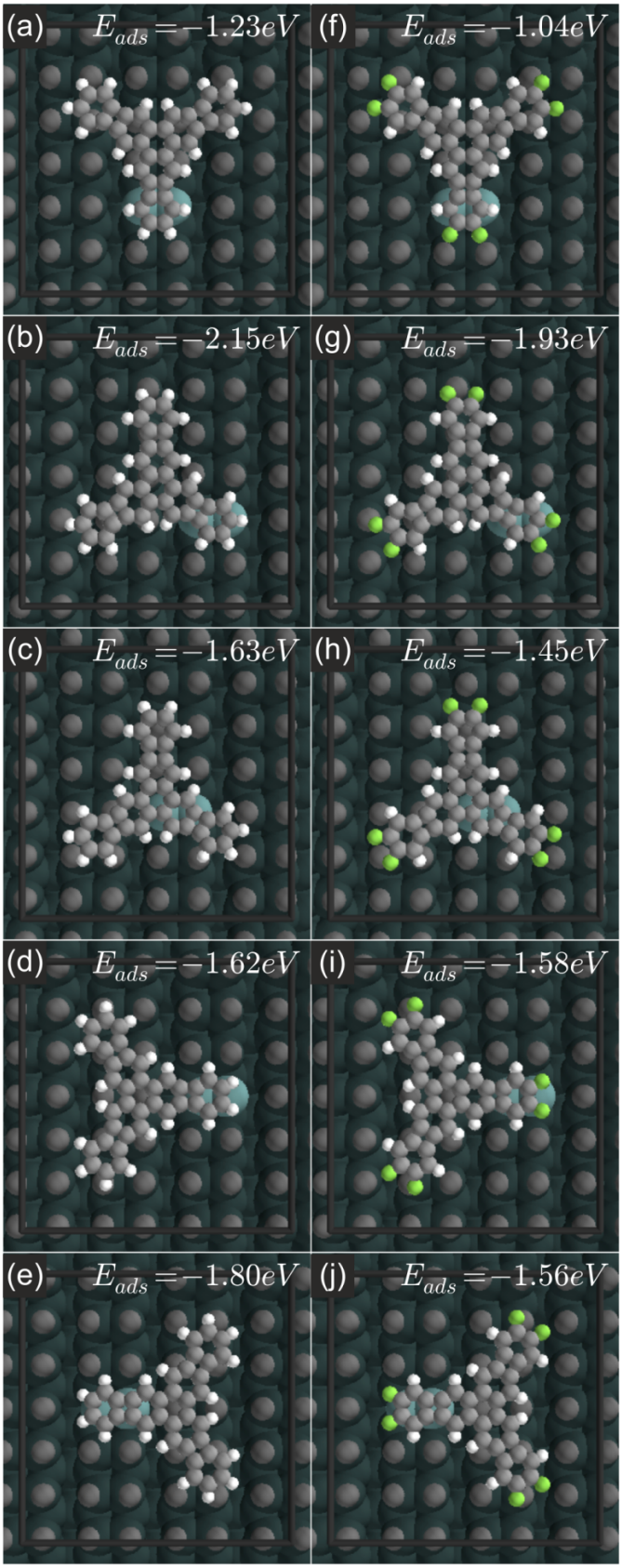


Figure S12. Optimized structures and adsorption energies obtained for tribiphenylene (a-e) and hexafluorotribiphenylene (f-j) molecules interacting with the surface DB dimer; panels (a-c) and (f-h) show molecules attached chemically to the DB dimer, panels (d-e) and (i-j) show configurations in which no bonds between the molecule and the surface are formed.

Tribiphenylene (gas phase)

X	Y	Z		
-5.18645813	-0.71739403	-0.00000001	1	C.blyp
-5.18996042	0.71659883	-0.00000001	2	C.blyp
-6.36730351	1.45365288	-0.00000002	3	C.blyp
-6.38994632	2.55484101	-0.00000001	4	H.opt88
-7.56985981	0.69223988	-0.00000002	5	C.blyp
-8.53801847	1.21869251	-0.00000002	6	H.opt88
-7.56512351	-0.71334773	-0.00000000	7	C.blyp
-8.52887274	-1.24811195	-0.00000000	8	H.opt88
-6.35672317	-1.46467510	-0.00000001	9	C.blyp
-6.36697707	-2.56614592	-0.00000000	10	H.opt88
-3.68373896	-0.71783473	-0.00000000	11	C.blyp
-3.68466640	0.72145850	-0.00000000	12	C.blyp
-2.52286720	1.44772123	-0.00000001	13	C.blyp
-2.54751938	2.54465965	-0.00000002	14	H.opt88
-1.26915381	0.71972515	-0.00000001	15	C.blyp
-1.26977884	-0.72206858	-0.00000001	16	C.blyp
-2.52412761	-1.44668054	-0.00000000	17	C.blyp
-2.55197093	-2.54338101	-0.00000000	18	H.opt88
1.95274810	4.83497298	-0.00000000	19	C.blyp
3.19635434	4.12082572	-0.00000001	20	C.blyp
4.42365325	4.77132537	-0.00000001	21	C.blyp
5.38860905	4.23993963	-0.00000001	22	H.opt88
4.36562150	6.19344029	-0.00000001	23	C.blyp
5.30549593	6.76870714	-0.00000001	24	H.opt88
3.14614289	6.89235127	-0.00000000	25	C.blyp
3.16531196	7.99422290	-0.00000001	26	H.opt88
1.89109974	6.22207685	-0.00000000	27	C.blyp
0.94247071	6.78188181	-0.00000000	28	H.opt88
1.20091133	3.53374170	-0.00000001	29	C.blyp
2.44773996	2.81487914	-0.00000001	30	C.blyp
2.49601730	1.44550090	-0.00000002	31	C.blyp
3.45858152	0.91845502	-0.00000001	32	H.opt88
1.23870779	0.72323565	-0.00000002	33	C.blyp
-0.00970390	1.44466910	-0.00000002	34	C.blyp
-0.00992945	2.89347418	-0.00000001	35	C.blyp
-0.94600634	3.46568322	-0.00000000	36	H.opt88
3.19156995	-4.12473511	-0.00000001	37	C.blyp
1.95137808	-4.84472763	-0.00000002	38	C.blyp
1.90165410	-6.23278316	-0.00000001	39	C.blyp
0.95899497	-6.80235198	-0.00000000	40	H.opt88
3.16225183	-6.89347046	-0.00000002	41	C.blyp
3.19061202	-7.99519034	-0.00000001	42	H.opt88
4.37707103	-6.18649478	-0.00000002	43	C.blyp
5.32178487	-6.75385160	-0.00000002	44	H.opt88
4.42400010	-4.76447937	-0.00000002	45	C.blyp
5.38333589	-4.22304721	-0.00000003	46	H.opt88
2.44047316	-2.82311746	-0.00000001	47	C.blyp
1.19448659	-3.54355597	-0.00000001	48	C.blyp
-0.01541967	-2.90031617	-0.00000000	49	C.blyp
-0.95311918	-3.47034363	-0.00000000	50	H.opt88
-0.01222771	-1.45039369	-0.00000001	51	C.blyp
1.23676975	-0.73008251	-0.00000002	52	C.blyp
2.49161921	-1.45430796	-0.00000002	53	C.blyp
3.45525667	-0.92952328	-0.00000001	54	H.opt88

Tribiphenylene on DB dimer (b, in Figure S12)

X	Y	Z		
-10.47321535	-11.05774585	-8.09437181	1	H.opt88
-5.93319796	-11.05801420	-8.09544306	2	H.opt88
-2.28122154	-11.05774585	-8.09437181	3	H.opt88
2.25879585	-11.05801420	-8.09544306	4	H.opt88
5.91077228	-11.05774585	-8.09437181	5	H.opt88
10.45078967	-11.05801420	-8.09544306	6	H.opt88
-10.48045885	-9.41981148	-8.12242221	7	H.opt88
-5.92611747	-9.42024850	-8.12421017	8	H.opt88
-2.28846504	-9.41981148	-8.12242221	9	H.opt88
2.26587635	-9.42024850	-8.12421017	10	H.opt88
5.90352878	-9.41981148	-8.12242221	11	H.opt88
10.45787016	-9.42024850	-8.12421017	12	H.opt88
-10.47321535	-6.96174895	-8.09437181	13	H.opt88
-5.93319796	-6.96201730	-8.09544306	14	H.opt88
-2.28122154	-6.96174895	-8.09437181	15	H.opt88
2.25879585	-6.96201730	-8.09544306	16	H.opt88
5.91077228	-6.96174895	-8.09437181	17	H.opt88
10.45078967	-6.96201730	-8.09544306	18	H.opt88
-10.48045885	-5.32381458	-8.12242221	19	H.opt88
-5.92611747	-5.32425160	-8.12421017	20	H.opt88
-2.28846504	-5.32381458	-8.12242221	21	H.opt88
2.26587635	-5.32425160	-8.12421017	22	H.opt88
5.90352878	-5.32381458	-8.12242221	23	H.opt88
10.45787016	-5.32425160	-8.12421017	24	H.opt88
-10.47321535	-2.86575204	-8.09437181	25	H.opt88
-5.93319796	-2.86602039	-8.09544306	26	H.opt88
-2.28122154	-2.86575204	-8.09437181	27	H.opt88
2.25879585	-2.86602039	-8.09544306	28	H.opt88
5.91077228	-2.86575204	-8.09437181	29	H.opt88
10.45078967	-2.86602039	-8.09544306	30	H.opt88
-10.48045885	-1.22781767	-8.12242221	31	H.opt88
-5.92611747	-1.22825469	-8.12421017	32	H.opt88
-2.28846504	-1.22781767	-8.12242221	33	H.opt88
2.26587635	-1.22825469	-8.12421017	34	H.opt88
5.90352878	-1.22781767	-8.12242221	35	H.opt88
10.45787016	-1.22825469	-8.12421017	36	H.opt88
-10.47321535	1.23024487	-8.09437181	37	H.opt88
-5.93319796	1.22997652	-8.09544306	38	H.opt88
-2.28122154	1.23024487	-8.09437181	39	H.opt88
2.25879585	1.22997652	-8.09544306	40	H.opt88
5.91077228	1.23024487	-8.09437181	41	H.opt88
10.45078967	1.22997652	-8.09544306	42	H.opt88
-10.48045885	2.86817924	-8.12242221	43	H.opt88
-5.92611747	2.86774222	-8.12421017	44	H.opt88
-2.28846504	2.86817924	-8.12242221	45	H.opt88
2.26587635	2.86774222	-8.12421017	46	H.opt88
5.90352878	2.86817924	-8.12242221	47	H.opt88
10.45787016	2.86774222	-8.12421017	48	H.opt88
-10.47321535	5.32624178	-8.09437181	49	H.opt88
-5.93319796	5.32597343	-8.09544306	50	H.opt88
-2.28122154	5.32624178	-8.09437181	51	H.opt88
2.25879585	5.32597343	-8.09544306	52	H.opt88
5.91077228	5.32624178	-8.09437181	53	H.opt88
10.45078967	5.32597343	-8.09544306	54	H.opt88
-10.48045885	6.96417615	-8.12242221	55	H.opt88

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5.90352878 11.06017305 -8.12242221 71 H.opt88
10.45787016 11.05973603 -8.12421017 72 H.opt88
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-6.05837674 -12.29850310 -7.16274428 74 Ge.blyp.re
-2.15512266 -12.29780175 -7.16249157 75 Ge.blyp.re
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-6.90067297 8.16175466 -1.61027347248 Ge.blyp.re
-1.28463985 8.15558365 -1.61657011249 Ge.blyp.re
1.25522649 8.17010928 -1.60725377250 Ge.blyp.re
6.91415374 8.17129145 -1.60020019251 Ge.blyp.re
9.45354653 8.17176816 -1.59948975252 Ge.blyp.re
-10.01041685 -12.30656519 -0.11740169253 H.opt88
-6.34977921 -12.26964065 -0.15138450254 H.opt88
-1.85651616 -12.32049039 -0.12041084255 H.opt88
1.81965159 -12.31242980 -0.12336797256 H.opt88
6.35191428 -12.30908024 -0.12662832257 H.opt88
10.01476652 -12.30801471 -0.12740184258 H.opt88
-10.03002268 -8.21268073 -0.12659789259 H.opt88
-6.36736926 -8.22434841 -0.13173668260 H.opt88
-1.84518390 -8.20792264 -0.13031635261 H.opt88
1.82034953 -8.20971784 -0.13186717262 H.opt88
6.35132190 -8.21303081 -0.12645805263 H.opt88
10.01399202 -8.21400773 -0.12670618264 H.opt88
-10.04522784 -4.09395680 -0.12416175265 H.opt88
-6.37312894 -4.08128279 -0.12478750266 H.opt88
-1.85052843 -4.19295724 -0.11333840267 H.opt88
1.82344959 -4.19287378 -0.11553401268 H.opt88
6.34974722 -4.11329950 -0.12456316269 H.opt88
10.02447971 -4.10611528 -0.12309694270 H.opt88
-10.07991151 0.00444920 -0.19165854271 H.opt88
-6.38233929 -0.03848002 -0.18686079272 H.opt88
6.34071679 -0.02089078 -0.13067088273 H.opt88
10.00891867 -0.01743843 -0.13156604274 H.opt88
-10.02444566 4.05536605 -0.11096715275 H.opt88
-6.28672100 4.08603838 -0.16727656276 H.opt88
-1.87716084 4.25761019 -0.18702020277 H.opt88
1.79880100 4.16238805 -0.12069160278 H.opt88
6.35093662 4.07244493 -0.12614463279 H.opt88
10.02235561 4.06404059 -0.12364171280 H.opt88
-9.99119102 8.16719372 -0.10417101281 H.opt88
-6.30984718 8.15712848 -0.16380338282 H.opt88
-1.85648770 8.10729835 -0.14611104283 H.opt88
1.81671992 8.15700091 -0.13392124284 H.opt88
6.35213558 8.17051173 -0.12763409285 H.opt88
10.01419472 8.17241742 -0.12607040286 H.opt88
-0.64704751 1.23124532 0.92826933287 C.blyp
-1.42792122 -0.02271091 0.50195137288 C.blyp
-0.73823599 -1.26780192 0.94092331289 C.blyp
-1.30768076 -2.16265617 1.24488324290 H.opt88
0.62918116 -1.25376946 0.91832317291 C.blyp

1.20637513	-2.15517797	1.18790237292	H.opt88
1.38798352	-0.01765744	0.51352625293	C.blyp
2.46256544	-0.05901079	0.77977514294	H.opt88
0.71199304	1.25420339	0.95278499295	C.blyp
1.30950928	2.10794201	1.31433614296	H.opt88
-1.90809506	1.86647798	1.36407252297	C.blyp
-2.65237796	0.67879883	1.08597213298	C.blyp
-4.00251784	0.58419562	1.36027413299	C.blyp
-4.55590513	-0.35092705	1.18659188300	H.opt88
-4.67448619	1.77279072	1.82077872301	C.blyp
-3.95079399	3.02230839	1.92436990302	C.blyp
-2.52295237	3.03130342	1.79888885303	C.blyp
-1.93803317	3.93390046	2.02388652304	H.opt88
-9.45183898	-0.27436446	2.24646745305	C.blyp
-10.18915561	0.95692968	2.21362254306	C.blyp
-11.56612112	0.99093578	2.02649600307	C.blyp
-12.14531187	1.92761407	1.95885856308	H.opt88
-12.20086509	-0.27799933	1.89756509309	C.blyp
-13.29373991	-0.31881080	1.75607410310	H.opt88
-11.47942344	-1.48505642	1.93832524311	C.blyp
-12.02777679	-2.43531490	1.81955348312	H.opt88
-10.06561359	-1.51452317	2.11287473313	C.blyp
-9.50953950	-2.46669767	2.11368171314	H.opt88
-8.16134289	0.49847882	2.28531646315	C.blyp
-8.90009449	1.73319224	2.28330792316	C.blyp
-8.27707752	2.95739066	2.31041792317	C.blyp
-8.86127063	3.88743894	2.33335947318	H.opt88
-6.82847446	2.97826744	2.26426977319	C.blyp
-6.10189088	1.74494444	2.11412824320	C.blyp
-6.79035652	0.47473998	2.20317468321	C.blyp
-6.22975618	-0.47142545	2.20574218322	H.opt88
-6.16980314	8.17024484	2.29695217323	C.blyp
-4.76770542	8.19301991	1.99300839324	C.blyp
-4.08731869	9.37566649	1.72307619325	C.blyp
-3.01426046	9.41318393	1.47206563326	H.opt88
-4.86836149	10.56401933	1.78905318327	C.blyp
-4.38250610	11.53475860	1.58865106328	H.opt88
-6.23889593	10.54200482	2.10936944329	C.blyp
-6.78832211	11.49698474	2.15938554330	H.opt88
-6.93545764	9.32838385	2.36874797331	C.blyp
-8.01422188	9.32668435	2.59735762332	H.opt88
-6.13888503	6.66560162	2.33541232333	C.blyp
-4.72570065	6.68907605	2.06206599334	C.blyp
-3.98696919	5.53608812	1.95239092335	C.blyp
-2.91286575	5.57159505	1.71828720336	H.opt88
-4.68423870	4.27370597	2.09490075337	C.blyp
-6.11214277	4.25010406	2.27876607338	C.blyp
-6.84451127	5.49202379	2.43171026339	C.blyp
-7.92849485	5.49785450	2.61235063340	H.opt88

Hexafluororibophenylene (2b, gas phase)

X	Y	Z		
-5.18645813	-0.71739403	-0.00000001	1	C.blyp
-5.18996042	0.71659883	-0.00000001	2	C.blyp
-6.36730351	1.45365288	-0.00000002	3	C.blyp
-6.38994632	2.55484101	-0.00000001	4	H.opt88
-7.56985981	0.69223988	-0.00000002	5	C.blyp

-8.53801847	1.21869251	-0.00000002	6	H.opt88
-7.56512351	-0.71334773	-0.00000000	7	C.blyp
-8.52887274	-1.24811195	-0.00000000	8	H.opt88
-6.35672317	-1.46467510	-0.00000001	9	C.blyp
-6.36697707	-2.56614592	-0.00000000	10	H.opt88
-3.68373896	-0.71783473	-0.00000000	11	C.blyp
-3.68466640	0.72145850	-0.00000000	12	C.blyp
-2.52286720	1.44772123	-0.00000001	13	C.blyp
-2.54751938	2.54465965	-0.00000002	14	H.opt88
-1.26915381	0.71972515	-0.00000001	15	C.blyp
-1.26977884	-0.72206858	-0.00000001	16	C.blyp
-2.52412761	-1.44668054	-0.00000000	17	C.blyp
-2.55197093	-2.54338101	-0.00000000	18	H.opt88
1.95274810	4.83497298	-0.00000000	19	C.blyp
3.19635434	4.12082572	-0.00000001	20	C.blyp
4.42365325	4.77132537	-0.00000001	21	C.blyp
5.38860905	4.23993963	-0.00000001	22	H.opt88
4.36562150	6.19344029	-0.00000001	23	C.blyp
5.30549593	6.76870714	-0.00000001	24	H.opt88
3.14614289	6.89235127	-0.00000000	25	C.blyp
3.16531196	7.99422290	-0.00000001	26	H.opt88
1.89109974	6.22207685	-0.00000000	27	C.blyp
0.94247071	6.78188181	-0.00000000	28	H.opt88
1.20091133	3.53374170	-0.00000001	29	C.blyp
2.44773996	2.81487914	-0.00000001	30	C.blyp
2.49601730	1.44550090	-0.00000002	31	C.blyp
3.45858152	0.91845502	-0.00000001	32	H.opt88
1.23870779	0.72323565	-0.00000002	33	C.blyp
-0.00970390	1.44466910	-0.00000002	34	C.blyp
-0.00992945	2.89347418	-0.00000001	35	C.blyp
-0.94600634	3.46568322	-0.00000000	36	H.opt88
3.19156995	-4.12473511	-0.00000001	37	C.blyp
1.95137808	-4.84472763	-0.00000002	38	C.blyp
1.90165410	-6.23278316	-0.00000001	39	C.blyp
0.95899497	-6.80235198	-0.00000000	40	H.opt88
3.16225183	-6.89347046	-0.00000002	41	C.blyp
3.19061202	-7.99519034	-0.00000001	42	H.opt88
4.37707103	-6.18649478	-0.00000002	43	C.blyp
5.32178487	-6.75385160	-0.00000002	44	H.opt88
4.42400010	-4.76447937	-0.00000002	45	C.blyp
5.38333589	-4.22304721	-0.00000003	46	H.opt88
2.44047316	-2.82311746	-0.00000001	47	C.blyp
1.19448659	-3.54355597	-0.00000001	48	C.blyp
-0.01541967	-2.90031617	-0.00000000	49	C.blyp
-0.95311918	-3.47034363	-0.00000000	50	H.opt88
-0.01222771	-1.45039369	-0.00000001	51	C.blyp
1.23676975	-0.73008251	-0.00000002	52	C.blyp
2.49161921	-1.45430796	-0.00000002	53	C.blyp
3.45525667	-0.92952328	-0.00000001	54	H.opt88

Hexafluorotribiphenylene on DB dimer (g, in Figure S12)

X	Y	Z		
-10.47321535	-11.05774585	-8.09437181	1	H.opt88
-5.93319797	-11.05801420	-8.09544306	2	H.opt88
-2.28122154	-11.05774585	-8.09437181	3	H.opt88
2.25879585	-11.05801420	-8.09544306	4	H.opt88
5.91077227	-11.05774585	-8.09437181	5	H.opt88
10.45078966	-11.05801420	-8.09544306	6	H.opt88
-10.48045885	-9.41981148	-8.12242221	7	H.opt88
-5.92611747	-9.42024849	-8.12421017	8	H.opt88
-2.28846504	-9.41981148	-8.12242221	9	H.opt88
2.26587635	-9.42024849	-8.12421017	10	H.opt88
5.90352878	-9.41981148	-8.12242221	11	H.opt88
10.45787016	-9.42024849	-8.12421017	12	H.opt88
-10.47321535	-6.96174894	-8.09437181	13	H.opt88
-5.93319797	-6.96201729	-8.09544306	14	H.opt88
-2.28122154	-6.96174894	-8.09437181	15	H.opt88
2.25879585	-6.96201729	-8.09544306	16	H.opt88
5.91077227	-6.96174894	-8.09437181	17	H.opt88
10.45078966	-6.96201729	-8.09544306	18	H.opt88
-10.48045885	-5.32381457	-8.12242221	19	H.opt88
-5.92611747	-5.32425159	-8.12421017	20	H.opt88
-2.28846504	-5.32381457	-8.12242221	21	H.opt88
2.26587635	-5.32425159	-8.12421017	22	H.opt88
5.90352878	-5.32381457	-8.12242221	23	H.opt88
10.45787016	-5.32425159	-8.12421017	24	H.opt88
-10.47321535	-2.86575203	-8.09437181	25	H.opt88
-5.93319797	-2.86602038	-8.09544306	26	H.opt88
-2.28122154	-2.86575203	-8.09437181	27	H.opt88
2.25879585	-2.86602038	-8.09544306	28	H.opt88
5.91077227	-2.86575203	-8.09437181	29	H.opt88
10.45078966	-2.86602038	-8.09544306	30	H.opt88
-10.48045885	-1.22781766	-8.12242221	31	H.opt88
-5.92611747	-1.22825468	-8.12421017	32	H.opt88
-2.28846504	-1.22781766	-8.12242221	33	H.opt88
2.26587635	-1.22825468	-8.12421017	34	H.opt88
5.90352878	-1.22781766	-8.12242221	35	H.opt88
10.45787016	-1.22825468	-8.12421017	36	H.opt88
-10.47321535	1.23024488	-8.09437181	37	H.opt88
-5.93319797	1.22997653	-8.09544306	38	H.opt88
-2.28122154	1.23024488	-8.09437181	39	H.opt88
2.25879585	1.22997653	-8.09544306	40	H.opt88
5.91077227	1.23024488	-8.09437181	41	H.opt88
10.45078966	1.22997653	-8.09544306	42	H.opt88
-10.48045885	2.86817925	-8.12242221	43	H.opt88
-5.92611747	2.86774223	-8.12421017	44	H.opt88
-2.28846504	2.86817925	-8.12242221	45	H.opt88
2.26587635	2.86774223	-8.12421017	46	H.opt88
5.90352878	2.86817925	-8.12242221	47	H.opt88
10.45787016	2.86774223	-8.12421017	48	H.opt88
-10.47321535	5.32624178	-8.09437181	49	H.opt88
-5.93319797	5.32597343	-8.09544306	50	H.opt88
-2.28122154	5.32624178	-8.09437181	51	H.opt88
2.25879585	5.32597343	-8.09544306	52	H.opt88
5.91077227	5.32624178	-8.09437181	53	H.opt88
10.45078966	5.32597343	-8.09544306	54	H.opt88
-10.48045885	6.96417615	-8.12242221	55	H.opt88

-5.92611747 6.96373913 -8.12421017 56 H.opt88
-2.28846504 6.96417615 -8.12242221 57 H.opt88
2.26587635 6.96373913 -8.12421017 58 H.opt88
5.90352878 6.96417615 -8.12242221 59 H.opt88
10.45787016 6.96373913 -8.12421017 60 H.opt88
-10.47321535 9.42223869 -8.09437181 61 H.opt88
-5.93319797 9.42197034 -8.09544306 62 H.opt88
-2.28122154 9.42223869 -8.09437181 63 H.opt88
2.25879585 9.42197034 -8.09544306 64 H.opt88
5.91077227 9.42223869 -8.09437181 65 H.opt88
10.45078966 9.42197034 -8.09544306 66 H.opt88
-10.48045885 11.06017306 -8.12242221 67 H.opt88
-5.92611747 11.05973604 -8.12421017 68 H.opt88
-2.28846504 11.06017306 -8.12242221 69 H.opt88
2.26587635 11.05973604 -8.12421017 70 H.opt88
5.90352878 11.06017306 -8.12242221 71 H.opt88
10.45787016 11.05973604 -8.12421017 72 H.opt88
-10.34739388 -12.29812700 -7.16253951 73 Ge.blyp.re
-6.05896316 -12.29828835 -7.16318891 74 Ge.blyp.re
-2.15457351 -12.29779687 -7.16348079 75 Ge.blyp.re
2.13283776 -12.29859333 -7.16261013 76 Ge.blyp.re
6.03716701 -12.29783891 -7.16153169 77 Ge.blyp.re
10.32807323 -12.29857352 -7.16157482 78 Ge.blyp.re
-10.35059698 -8.20004142 -7.16262207 79 Ge.blyp.re
-6.06097880 -8.20163400 -7.16339552 80 Ge.blyp.re
-2.15664935 -8.20157393 -7.16382165 81 Ge.blyp.re
2.13448922 -8.20294851 -7.16248438 82 Ge.blyp.re
6.03855103 -8.20194702 -7.16114371 83 Ge.blyp.re
10.32599576 -8.20216229 -7.16181484 84 Ge.blyp.re
-10.35172671 -4.10652591 -7.16246897 85 Ge.blyp.re
-6.06009949 -4.10653514 -7.16379786 86 Ge.blyp.re
-2.15423111 -4.10549322 -7.16179253 87 Ge.blyp.re
2.13266837 -4.10618582 -7.16204524 88 Ge.blyp.re
6.03886364 -4.10631651 -7.16233346 89 Ge.blyp.re
10.32429698 -4.10661653 -7.16336306 90 Ge.blyp.re
-10.34791137 -0.00931189 -7.16270477 91 Ge.blyp.re
-6.05622468 -0.01065709 -7.16099716 92 Ge.blyp.re
-2.15032826 -0.01055488 -7.15736933 93 Ge.blyp.re
2.13043557 -0.01054340 -7.15740996 94 Ge.blyp.re
6.03307518 -0.00976374 -7.15895248 95 Ge.blyp.re
10.32443738 -0.00987964 -7.16305896 96 Ge.blyp.re
-10.35028205 4.08672822 -7.16342857 97 Ge.blyp.re
-6.06027344 4.08631459 -7.16629644 98 Ge.blyp.re
-2.15296204 4.08569673 -7.16425621 99 Ge.blyp.re
2.13317461 4.08457483 -7.16402520100 Ge.blyp.re
6.03942250 4.08626864 -7.16254020101 Ge.blyp.re
10.32635594 4.08664157 -7.16292683102 Ge.blyp.re
-10.34510589 8.18263975 -7.16161470103 Ge.blyp.re
-6.06264793 8.18266642 -7.16487430104 Ge.blyp.re
-2.15441443 8.18337673 -7.16507751105 Ge.blyp.re
2.13950270 8.18398572 -7.16549204106 Ge.blyp.re
6.04063541 8.18279312 -7.16232560107 Ge.blyp.re
10.33087438 8.18173020 -7.16049221108 Ge.blyp.re
-12.29573473 -12.30933863 -5.59721205109 Ge.blyp.re
-8.20464952 -12.30955636 -5.92041605110 Ge.blyp.re
-4.10468629 -12.30561279 -5.60555708111 Ge.blyp.re
-0.01224512 -12.31260960 -5.91831429112 Ge.blyp.re
4.08453325 -12.30770979 -5.60109923113 Ge.blyp.re
8.18264006 -12.31023269 -5.91889815114 Ge.blyp.re

-12.29931617 -8.21213480 -5.59760702115 Ge.blyp.re
-8.20819324 -8.20535704 -5.92223872116 Ge.blyp.re
-4.10765956 -8.20716295 -5.60520277117 Ge.blyp.re
-0.01321663 -8.22299879 -5.92370518118 Ge.blyp.re
4.08719047 -8.21482129 -5.60020374119 Ge.blyp.re
8.18291368 -8.21130776 -5.91441282120 Ge.blyp.re
-12.30319816 -4.11503224 -5.60008095121 Ge.blyp.re
-8.20705556 -4.12186397 -5.92553255122 Ge.blyp.re
-4.10769698 -4.11787621 -5.60389426123 Ge.blyp.re
-0.01142865 -4.11132039 -5.91447721124 Ge.blyp.re
4.08737278 -4.12017404 -5.60395245125 Ge.blyp.re
8.18199230 -4.11828723 -5.91691849126 Ge.blyp.re
-12.29988798 -0.01595159 -5.60166893127 Ge.blyp.re
-8.20410422 -0.02056910 -5.92102189128 Ge.blyp.re
-4.10174920 -0.02196122 -5.59623150129 Ge.blyp.re
-0.00989779 -0.02558378 -5.89117014130 Ge.blyp.re
4.08044021 -0.02264055 -5.59100573131 Ge.blyp.re
8.17985371 -0.02356669 -5.91827040132 Ge.blyp.re
-12.30003035 4.08091132 -5.59963708133 Ge.blyp.re
-8.20535932 4.07999332 -5.92933281134 Ge.blyp.re
-4.10683023 4.07370255 -5.61220671135 Ge.blyp.re
-0.00962071 4.06008258 -5.92061793136 Ge.blyp.re
4.08676300 4.07735480 -5.60537926137 Ge.blyp.re
8.18321359 4.07210179 -5.91830610138 Ge.blyp.re
-12.29215862 8.17323845 -5.59437186139 Ge.blyp.re
-8.20395045 8.17181879 -5.91380942140 Ge.blyp.re
-4.10910350 8.17806856 -5.61285772141 Ge.blyp.re
-0.00523377 8.18165055 -5.93364368142 Ge.blyp.re
4.08938362 8.17558772 -5.60220906143 Ge.blyp.re
8.18545362 8.16863492 -5.91799990144 Ge.blyp.re
-12.29646549 -10.26126410 -4.13856079145 Ge.blyp.re
-8.21563326 -10.25345302 -4.52534061146 Ge.blyp.re
-4.10602699 -10.25469529 -4.15496436147 Ge.blyp.re
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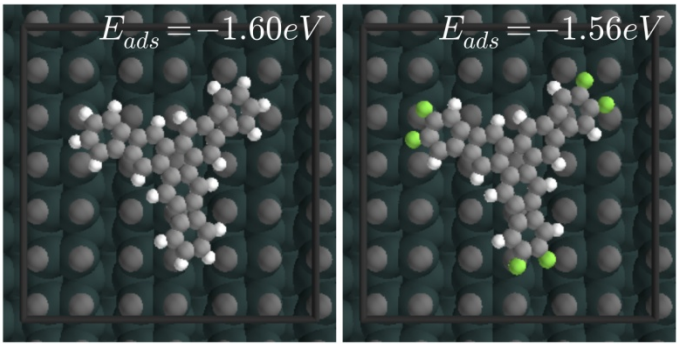

Figure S13. Optimized structures and adsorption energies obtained for tribiphenylene (left panel) and hexafluorotribiphenylene (right panel) located on the perfectly hydrogenated Ge(001):H surface.

In Figure S13 we show the calculated structures for the tribiphenylene and hexafluorotribiphenylene molecules located on the perfectly hydrogenated Ge(001):H surface.

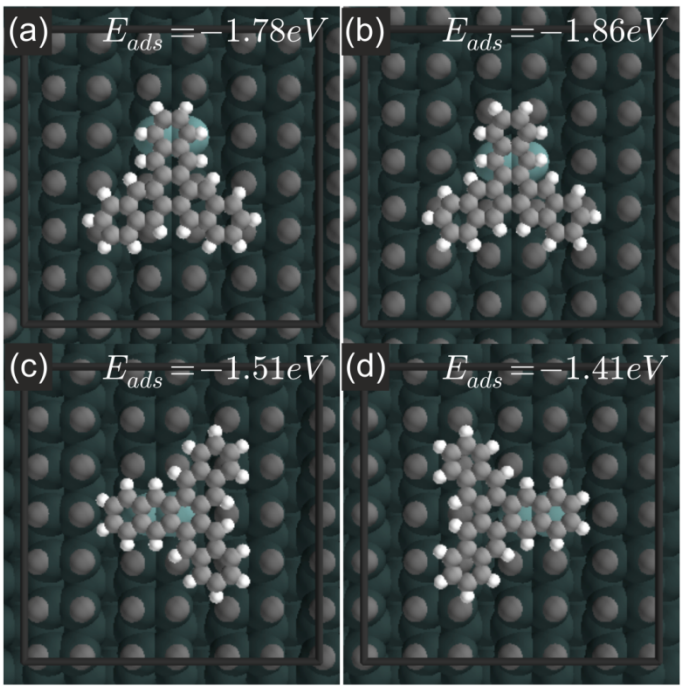

Figure S14. Optimized structures obtained for trinaphthylene on a DB dimer; (a) and (b) show molecule attached chemically by the outer and inner phenyl ring, respectively; (c) and (d) visualize molecule rotated by 90° and located over the buckled DB dimer, these configurations refer to experimentally observed in previous reports.[4,5]

For comparison Figure S14 shows optimized structures obtained for trinaphthylene located over the surface DB dimer. Configurations in which chemical bonds are formed by the outer and inner phenyl rings are visualized in panels (a) and (b), respectively. In Figure S14 (c,d) the optimized structures with no chemical bonds are shown. These configurations were reported experimentally[4,5] and are similar to those calculated for tribiphenylene and hexafluorotribiphenylene molecules (see Figure S12 (d,e) and (i,j)).

6. Tribiphenylenes on fully hydrogenated Ge(001):H

The molecules covalently attached to surface DB dimers are quite sensitive to STM imaging and could be easily detached from the surface DB dimers. Such unintentional events were frequently observed during filled state imaging, and probing empty states was even more unstable, always leading to bond cleavage and molecule displacement. After removal from the DB dimer, the molecule adopts a much more planar geometry over the hydrogenated surface rows, most often found in the configuration shown in Figure S15, slightly rotated with respect to surface reconstruction rows. Figure 6a shows the experimentally recorded high resolution filled state STM image of the molecule, and Figure S15b displays the calculated STM appearance. Good agreement between the calculated and experimentally recorded STM images confirms the correct assignment of molecule conformation and weak van der Waals interaction with the hydrogenated surface. The calculated adsorption energy reaches 1.60 eV.

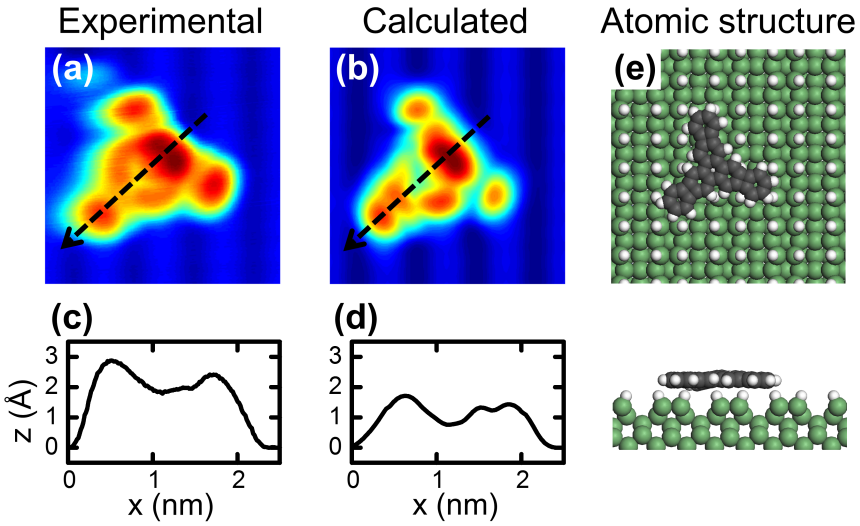

Figure S15. Tribiphenylene (2a) physisorbed on a Ge(001):H surface. (a) Filled state STM image, tunnelling current: 2 pA, bias voltage: –2.2 V; (b) calculated STM topography, tunnelling current: 2 pA, bias voltage: –1.2 V; (c) and (d) cross sections over the experimental and calculated images, respectively; (e) schematic structural image.

7. Hexakys(hexyloxy)tribiphenylene

In Figure S16 we show the typical filled state STM image of the molecular derivatives functionalized with the peripheral hexyloxy chains. The molecules are marked with white, dashed circles. One can clearly note that molecules are differently oriented and some kind of streaky/ghost features around the molecule branches appear, which are most likely originating from the flexible and long side hexyloxy chains. The molecules were found to be stable and no controlled manipulation events were recorded. Therefore it was impossible to unambiguously determine the defects located underneath the molecules.

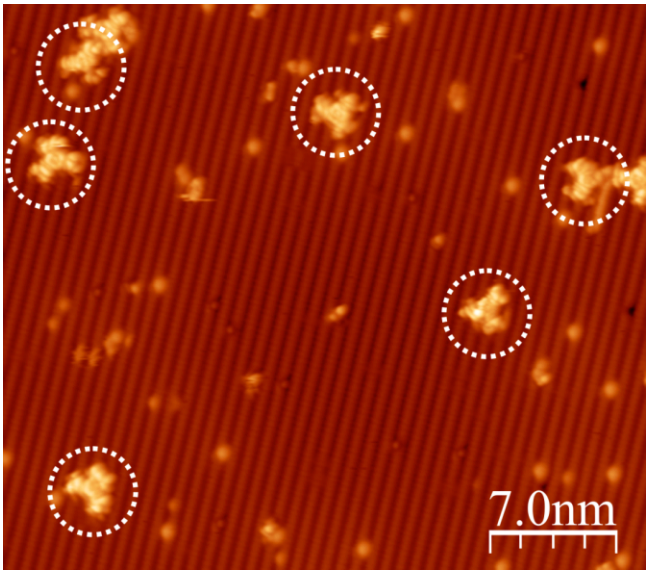

Figure S16. Typical filled state STM image of the tribiphenylene derivative functionalized with hexylkoxy chains. White, dashed circles mark the molecules, tunneling current 10 pA, bias voltage -2.0 V.

8. Molecule Structures and Orbitals

In Figure S17 and S18 schematic image of the tribiphenylene and hexafluorotribiphenylene molecules together with molecular orbitals calculated using the Extended Hückel Model Orbital (EHMO) approach are shown.

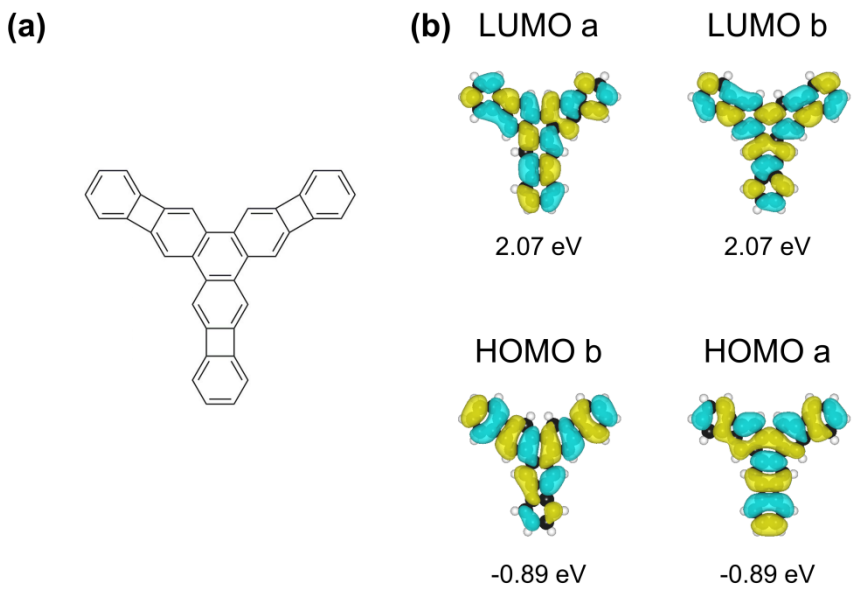

Figure S17. Tribiphenylene structural image (a) and molecular orbitals (b).

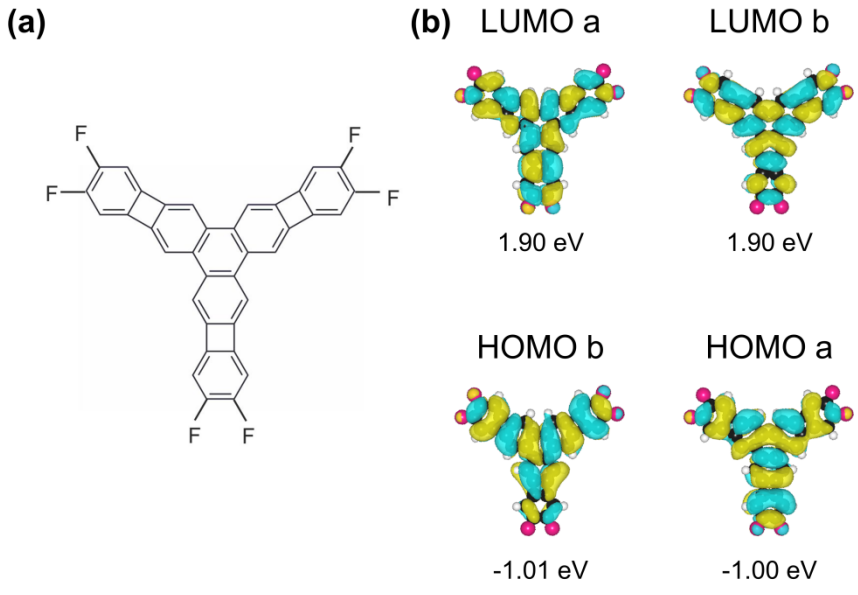

Figure S18. Hexafluorotribiphenylene structural image (a) and molecular orbitals (b).

9. Attachment Path Calculated For the Hexafluorotribiphenylene

In Figure S19 we analyze the attachment path calculated for the hexafluorotribiphenylene. This was done using Nudged-Elastic-Band (NEB) calculations to investigate the adsorption/desorption path of the hexafluorotribiphenylene molecule attached to the DB dimer site. Visualization displays the molecule configurations with the calculated energies. In this approach we followed the method described for the tribiphenylene molecules and studied the path from the attached configuration (geometry number 13 on the right, Figure S19) to the physisorbed state located nearby on a hydrogenated Ge(001):H surface (geometry number 1 on the left, Figure S19). The diagram shows that the attachment proceeds through a transition state with the calculated energy barrier of approximately 0.82 eV (1.37 eV for molecule detachment) with no additional intermediate states. Such finding promotes the simultaneous formation of both Ge-C bonds and the concerted reaction mechanism, which strongly supports the anticipated Diels-Alder [4+2] cycloaddition reaction.

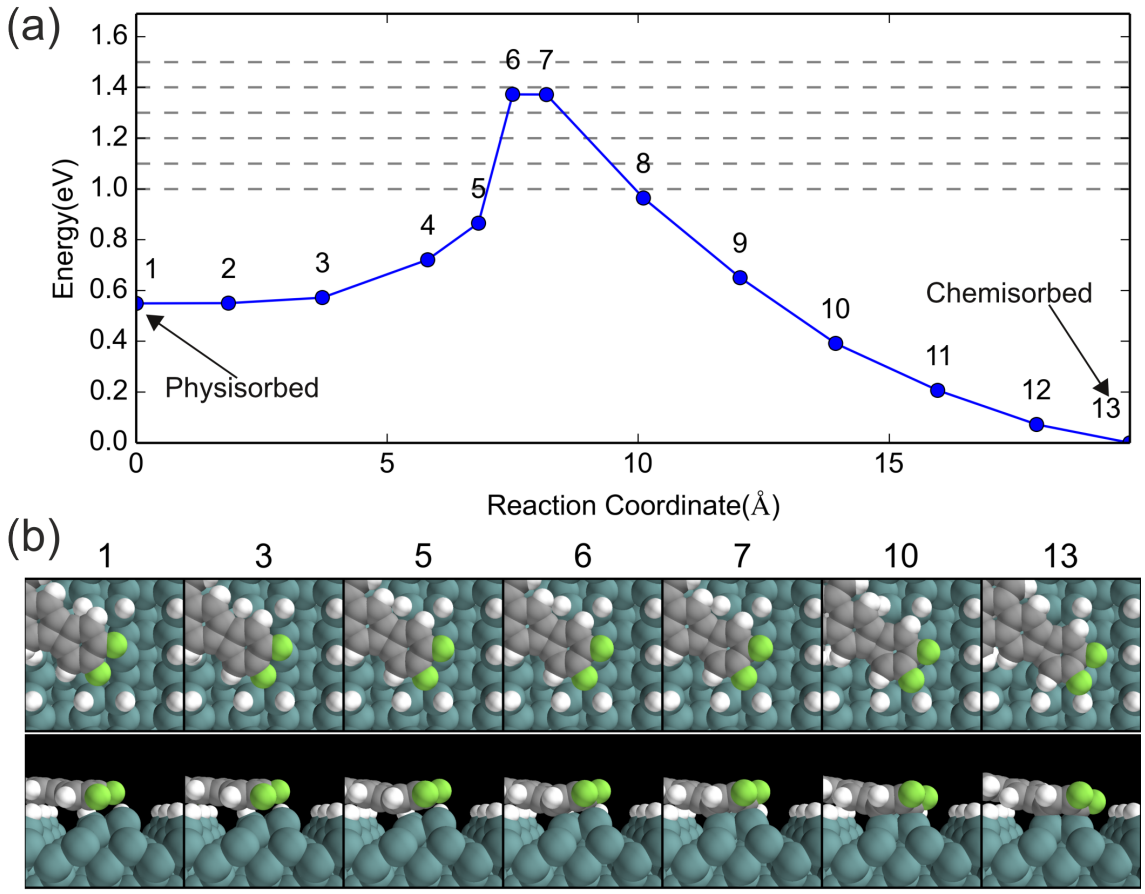

Figure S19. (a) Calculated attachment path of the hexafluorotribiphenylene on a DB dimer. Energies are plotted against a collective reaction coordinate. The distance is given the Euclidian distance between the total position vectors (running over all atoms) of subsequent configurations. (b) Selected configurations of the molecule on the attachment path.

10. Additional STM image of F Substituted Tribiphenylene Derivative

In Figure S20 we show the additional experimental and calculated STM images of hexafluorotribiphenylene attached chemically on a DB dimer. The images show that a better resolved intramolecular contrast is obtained for higher tunneling currents (Figure S20 (c,d)). However, the molecules are instable against measurements in such conditions, which is indicated by the streaky pattern at the bottom of Figure S20 (c) resulting from the uncontrolled detachment of the molecule from the DB dimer site and further manipulation of the molecule on a surface.

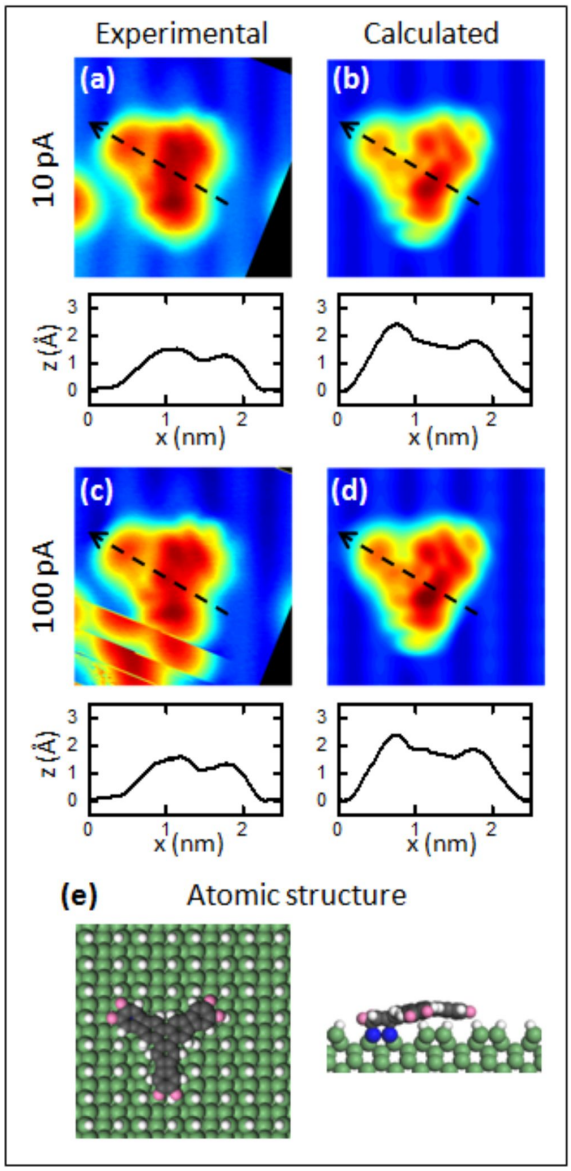

Figure S20. Hexafluorotribiphenylene attached chemically to the surface DB dimer on a Ge(001):H surface. (a) and (c) filled state STM images, tunneling current: 10pA and 100pA, respectively, bias voltage: -2.0V; (b) and (d) calculated STM topographies, tunneling current: 10pA and 100pA, respectively, bias voltage: -1.2V; (e) structural image.

11. Electronic Properties of Hexafluorotribiphenylene Molecules

In Figure S21 we show the state interaction diagram for hexafluorotribiphenylene molecules. The results are very similar to those obtained for tribiphenylenes. The differences arise mainly from different energies of molecule orbitals.

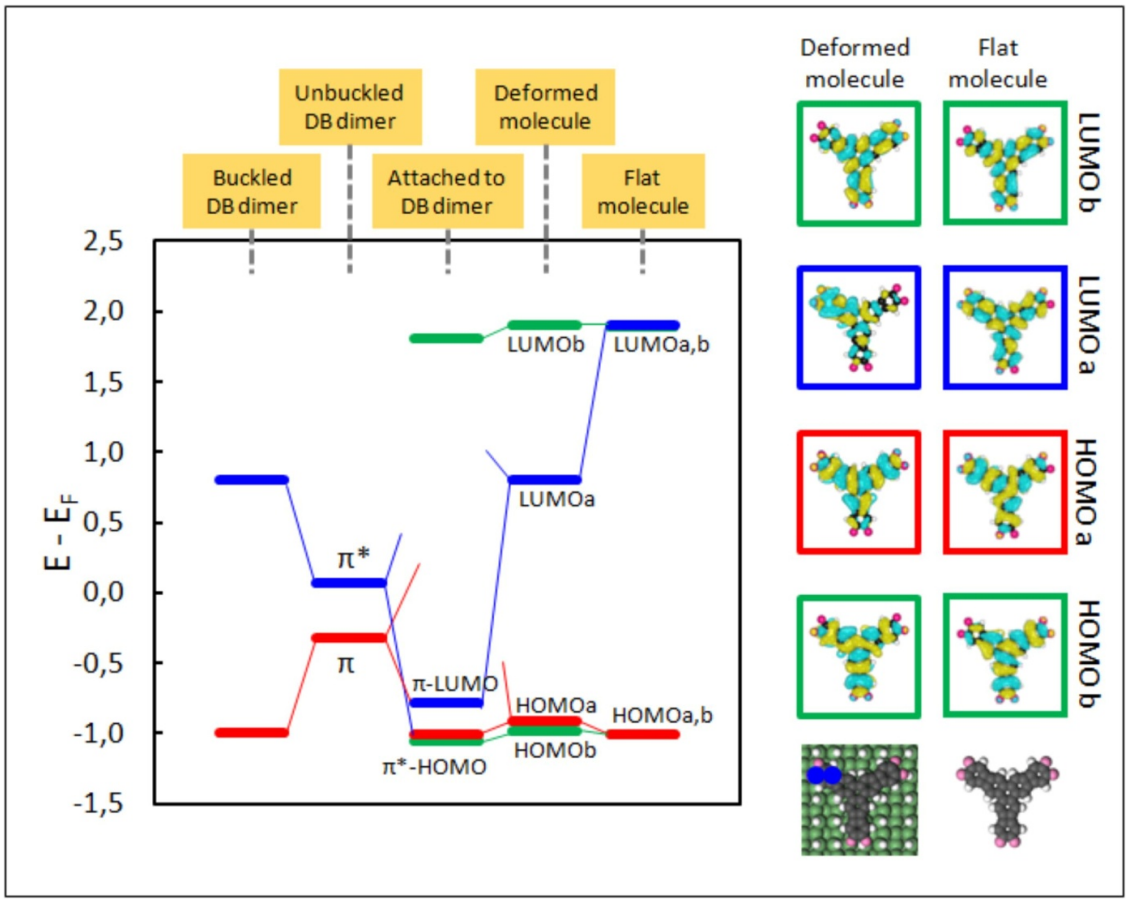

Figure S21. State interaction diagram calculated for the hexafluorotribiphenylene attached to the DB dimer on a Ge(001):H surface; left column shows the molecular orbital diagram with states of the buckled DB dimer (left), unbuckled DB dimer (second left), molecule attached chemically to the DB dimer (middle), deformed molecule (second middle) and the flat molecule (right), right column presents EHMO calculated molecular orbitals of the molecule deformed to the attachment configuration (left) and the flat molecule (right), colors match the orbitals shown in the right column with the diagram on the left; for the attached to the DB dimer configuration the antibonding π*-HOMO and π-LUMO states are not shown, since they exhibit a large dispersion in the band structure and do not appear apparently in the projected density of states (PDOS) and T(E).

We note here that the state interaction diagrams (Figure 8 for tribiphenylene in the main text and S21 for hexafluorotribiphenylene in SI) exhibit an important difference when compared with the one obtained for trinaphthylene (Fig. 3 in ref. [4]). The quick look on the orbital energies for the unbuckled DB dimer and the deformed trinaphthylene molecule yields the energy difference $\Delta E(\pi\text{-LUMO}) < \Delta E(\pi^*\text{-HOMO})$, which is consistent with an important contribution of the π-LUMO interaction in the binding. But for 2a (also for 2b) the situation is reversed, namely, energy difference $\Delta E(\pi\text{-LUMOa}) >$

$\Delta E(\pi^*\text{-HOMOa})$, which would indicate the more significant role of the π^*-HOMOa mixing.

Taking into account the anticipated important π^*-HOMOa mixing we analyze the influence of the molecular orbital shifts (tribiphenylene vs. hexafluorotribiphenylene) on the attachment reaction barrier height. This is done on the basis of the frontier orbital approximation. We shall expect the higher barrier for the hexafluorotribiphenylene attaching to the surface DB dimer compared to the tribiphenylene species, due to the downshift of both HOMO and LUMO orbitals of the substituted derivative. This is in perfect agreement with the calculated slightly higher barrier for the hexafluorotribiphenylene molecule.

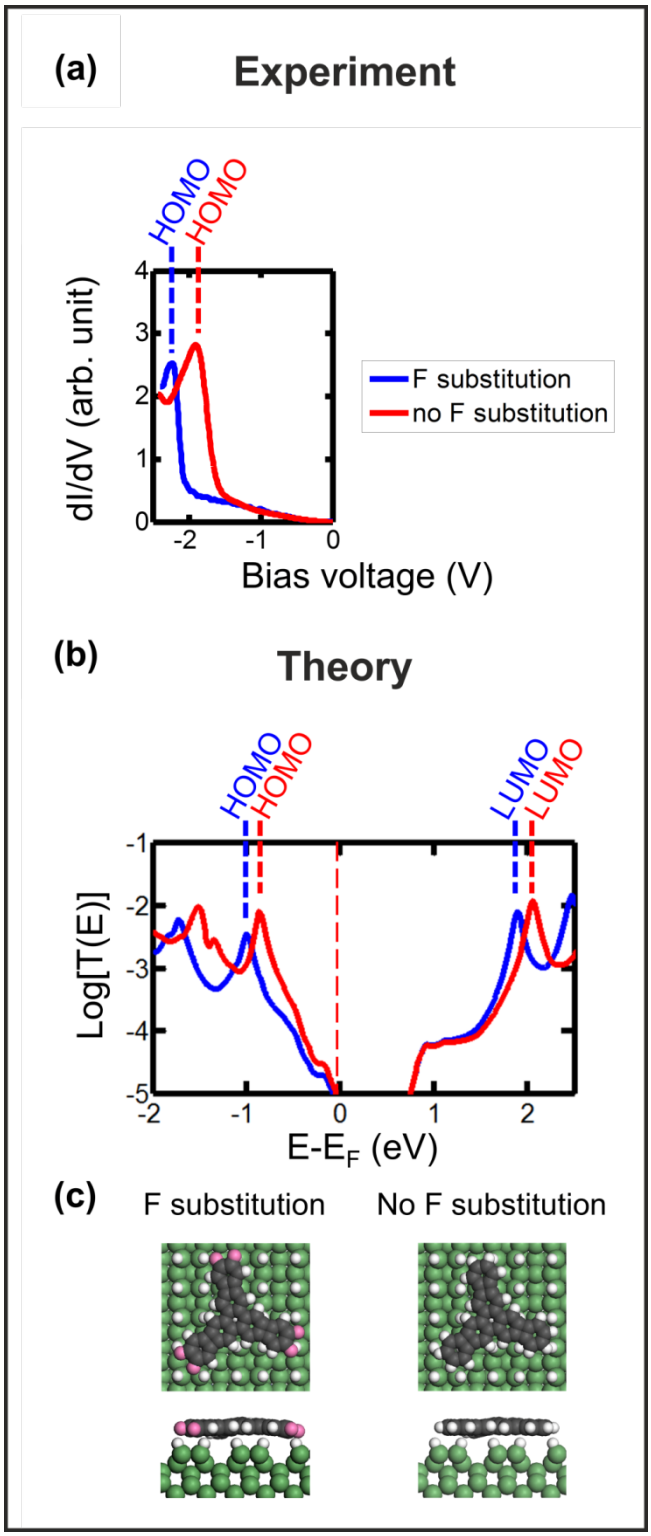

Figure S22. Comparison of the electronic structure of the tribiphenylene and the hexafluorotribiphenylene molecule. (a) Experimental dI/dV STS data recorded over the tribiphenylene and hexafluorortribiphenylene molecule physisorbed on Ge(001):H surface; (b) Calculated transmission coefficient T(E) spectra calculated the tribiphenylene and hexafluorotribiphenylene molecule physisorbed on Ge(001):H surface; (c) schematic structural images of both molecules.

Comparison of the electronic properties of the tribiphenylenes and hexafluorotribiphenylene molecules on a surface is shown in Figure S22. Panel (a) shows the STS dI/dV data recorded for both species physisorbed on the perfectly hydrogenated Ge(001):H surface. It is clearly demonstrated that the HOMO state of hexafluorotribiphenylene molecules is shifted downward by about 0.32 eV (-2.23 eV for F substituted and -1.91 eV for tribiphenylene). The calculations show a similar trend with a slightly smaller difference of 0.14 eV (-1.00 eV and -0.86 eV) as documented in panel (b). Simulations indicate that a similar difference should appear for excited states, however, it was not verified experimentally due to instabilities of the system against empty state STM probing.

12. Electronic Properties of Molecules Physisorbed on a DB Dimer

Let us now analyze the configuration observed in Figure 7b (main text) in more detail. To get deeper understanding of the structure and electronic properties we have performed STS measurements, calculated transmission coefficient T(E) spectra and made the comparison of simulated and experimental STM topographies. In Figure S23 (b) the calculated transmission coefficient T(E) spectra for the physisorbed configuration with two alternative buckling orientation of the DB dimer underneath the molecule are displayed (configurations called "down" and "up" in Figure S22). These two geometries are characterized by adsorption energies of 1.80 eV and 1.62 eV, respectively (see Figure S12 (d,e), with a small preference for the geometry "down". Due to the fact that there are obvious differences in the calculated spectra for both geometries we have analyzed the projected density of states (PDOS) to recognize the origin of observed peaks. From the analysis it becomes clear that the HOMO state of the molecule could be correlated with a pronounced resonance observed for configuration "down" at around -1.0 eV and the shoulder in the T(E) of configuration "up" recorded at the same energy range. This corresponds well to the value obtained for the HOMO resonance of the tribiphenylene molecule located on a hydrogenated Ge(001):H surface (see Figure S22 (b)). Further, the other peak observed in T(E) spectra of geometry "up" at around -0.6 eV and a shoulder in the configuration "down" could be attributed to the DB dimer π state. The comparison of the PDOS indicates that for both configurations the π state is shifted up in energy by approximately 0.1-0.2 eV when compared to the bare buckled DB dimer. This is also reflected in the T(E) spectra of the bare DB dimer, for which the broad resonance is centered at lower energies as documented by the black curve in Figure S23. Similar results are also obtained for the empty state part of the spectrum, for both geometries "down" and "up" the π^* resonance is located higher in energy compared to the bare buckled DB dimer, which is displayed in Figure S23. The shift of the DB π^* state in configuration "down" reaches even higher value of 0.5 eV, whereas for the geometry "up" the energy displacement is comparable with the filled state shift. The molecule LUMO state peaks are recorded within the same energy range as for the molecule on a Ge(001):H surface.

The experimental STS dI/dV curve recorded for the tribiphenylene molecule is displayed in Figure S23 (a) and exhibits the presence of the resonance at around -1.9 eV, in the similar range as the HOMO state of the physisorbed molecule shown in Figure S22 (a). Together with the calculations indicating almost no shift of the HOMO resonance we may conclude that the recorded peak originates from the HOMO state of the molecule.

Moreover an additional peak is recorded within the filled state part and centered at -0.7V, which is about 0.3 eV higher in energy than the π resonance of the bare buckled DB dimer.[6] We attribute this peak to the π state of the DB dimer located underneath the molecule shifted by the interaction with the polycyclic platform, in accordance with the calculations. It is important to emphasize that we expect the DB dimer to oscillate underneath the molecule during STM/STS measurements as previously described for

starphenes.[4,5] Further, the low voltage empty state part of the STS dI/dV spectrum contains another resonance recorded at +1.2 eV. This peak is attributed to the π* resonance of the buckled DB dimer shifted by approximately 0.4 eV when compared with bare DB dimer.[6] Here we emphasize that the shift of the level agrees better with the theoretically calculated for geometry "down" and reaches higher value that simulated for geometry "up". This could be understood, as there is a preference of the system to stay in geometry "down" characterized by a lower energy, therefore during STS measurements the molecules tend to expend a longer time in that configuration. As a result the experimentally measured shift has a value in between the calculated ones, although closer to that calculated for the preferred "down" geometry. However, we have to note that the simulations do not take into account the dynamics of the system and the detailed analysis is far beyond the scope of the present work and capabilities of the approach. In the light of the mentioned limitations we should emphasize that the obtained agreement is reasonable.

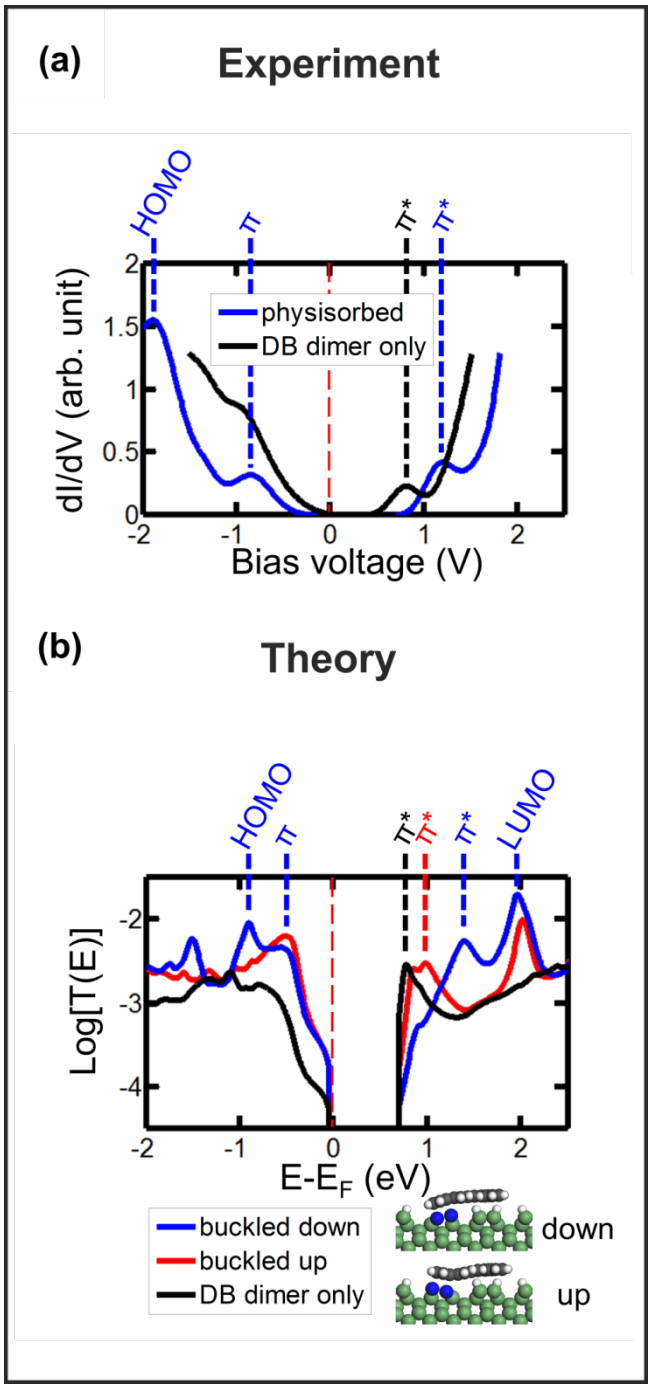

Figure S23. Experimental STS dI/dV data (a) and calculated transmission coefficient T(E) spectra (b) recorded for tribiphenylene physisorbed on a buckled DB dimer.

Our considerations indicate that the molecule is located over the buckled DB dimer and held by van der Waals forces with no chemical bonds. The conclusions are supported by the good agreement between the simulated STM topography and the calculated one. The images are shown in Figure S24. The calculated image (shown in Fig. S24 (b)) to compare with the experimental one (Figure S24 (a)) was obtained from two oppositely buckled configurations using a simplified approximation, in which we postulate that the tip height in the constant current topography is determined by the one with higher

altitude. The method was already applied before to calculate the images of a trinaphthylene molecule.[5]

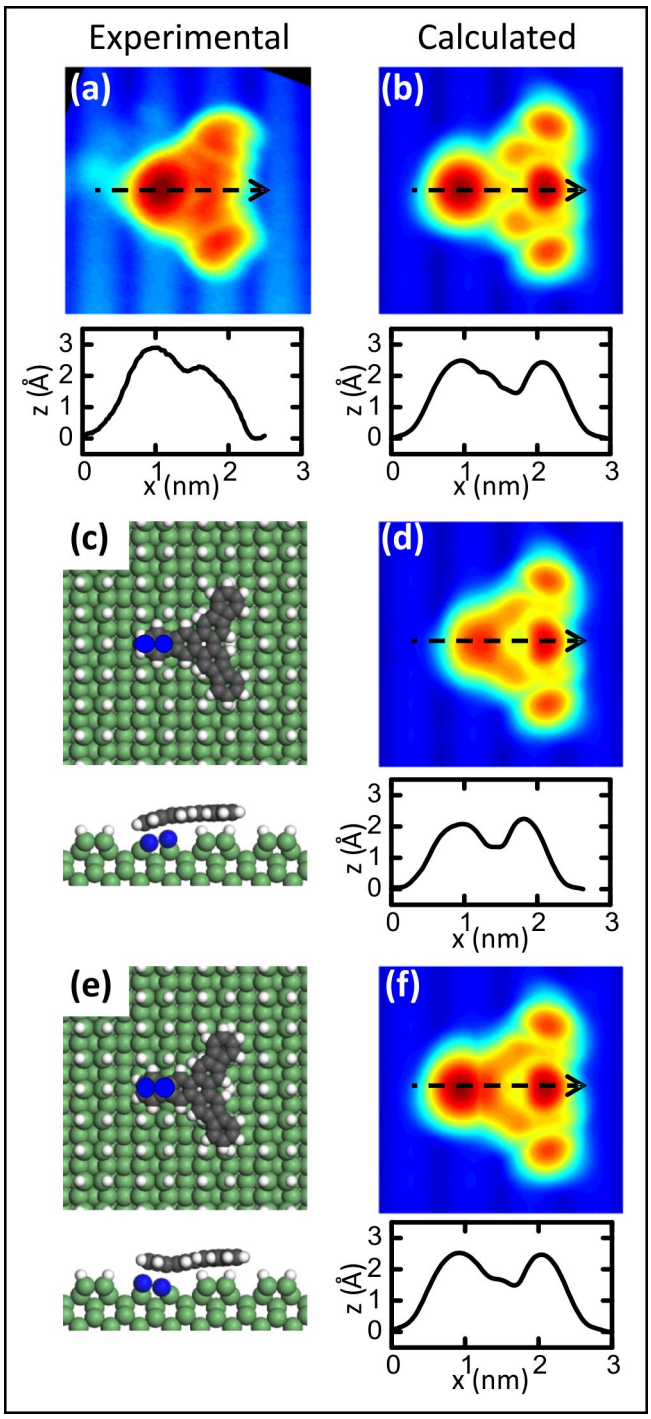

Figure S24. Experimental (a) and calculated (b) constant current STM topography of the tribiphenylene molecule located on a buckled DB dimer, (c) and (d) schematic image of configuration "down" and the calculated STM appearance, respectively, (e) and (f) schematic image of configuration "up" and the calculated STM appearance, respectively; bias voltage -2.0V (experiment, panel a) and -1.2V (calculations, panel b, d, f), tunneling current 2 pA.

The HOMO state of the molecule located on a buckled DB dimer stays almost unshifted, but the DB dimer π and π* states shift significantly due to the interaction with the molecule. The origin

of the shift lies in the displacement of Ge atoms forming the DB dimer. The atom movement results in a reduction of the buckling angle from approximately 18,5° for bare DB dimer to 12.0° for the DB dimer underneath the molecule with both Ge atoms moving slightly up and increasing their horizontal separation. Interestingly the reduction of DB dimer buckling for fully aromatic trinaphthylene molecules is much lower reaching approximately 14.4°-14.9° and consequently leading to much smaller DB dimer π and π* state shifts as already observed in previous experiments[5] and confirmed in calculations of both T(E) and PDOS (see Figure S25). We attribute the difference to the significant dissimilarities between the organic species, the fully aromatic trinaphthylene and the tribiphenylene containing non-aromatic 4-member rings. The distinct differences in the local chemical nature of the molecules results in a noticeable disparity in the DB dimer buckling and shifts of its electronic levels. The stronger interaction of the tribiphenylene molecule with a DB dimer resulting in a less buckled configuration may be responsible for the fact that we did not manage to observe the characteristic telegraph noise over the oscillating DB dimer underneath the molecule and also did not notice any streaky pattern in STM images in close vicinity of the DB dimer location. This is in contrast to trinaphthylene[4] and most likely is related to the decreased barrier for DB dimer switching and smaller buckling angle leading to more frequent flipping of the DB dimer underneath the tribiphenylene molecule, which falls out of the resolution limit of the apparatus.

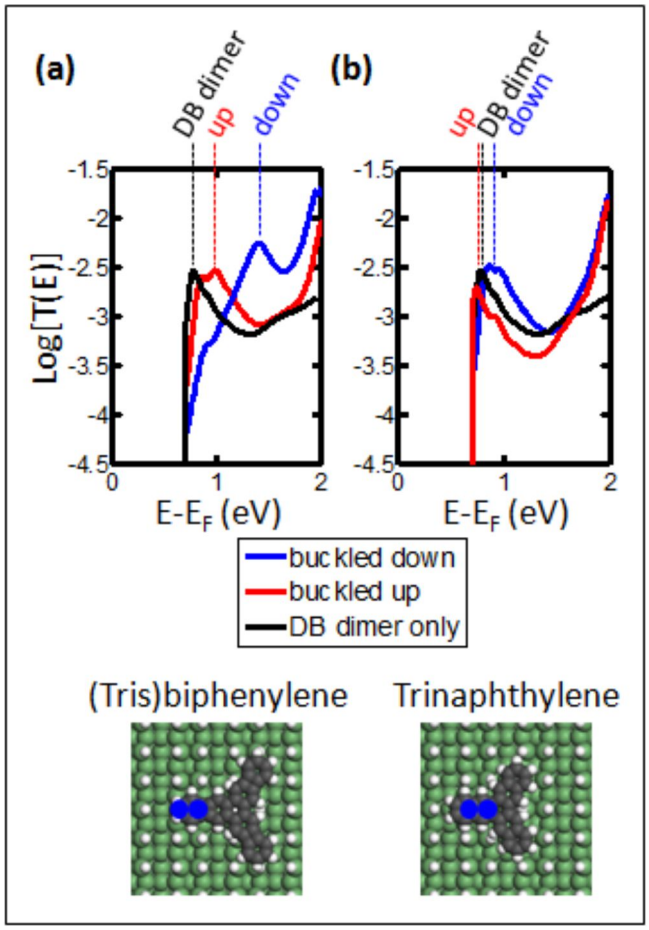

Figure S25. Comparison of the calculated position of the DB dimer resonances for bare DB dimer and the DB dimer covered by tribiphenylene and trinaphthylene.

13. Electronic Properties of Molecules on a Single DB

The experiments revealed that there are some molecules located over single DBs. We found both tribiphenylene and hexafluorotribiphenylene species interacting with single DBs. In contrast to DB dimers, which form chemical bonds with molecules, single DBs interact only weakly. The calculated structures for both species are shown in Figure S26.

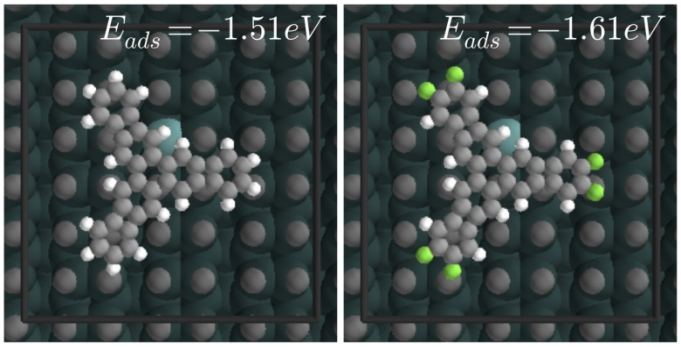

Figure S26. Calculated structures of tribiphenylene (left) and hexafluorotribiphenylene (right) interacting with a single DB.

The experimental images of tribiphenylene and hexafluorotribiphenylene located over single DBs are shown in Figure S27 (a,b). In both cases the DB site is located asymmetrically underneath the molecule, in Figure S27 (a) the position of the DB is indicated by the white crosses. The STS dI/dV spectra recorded over molecules are shown in Figure S27 (c). The HOMO resonance for the tribiphenylene molecule is recorded at approximately -1.76 V, whereas for the hexafluorotribiphenylene it appears almost 0.22 V lower in energy, around -1.98 V. This means that the downward shift of the HOMO state induced by F atoms is confirmed and preserved for molecules interacting with single DBs. Interestingly in both cases the HOMO state is located higher in energy compared to HOMO of the molecules physisorbed on a perfectly hydrogenated Ge(001):H surface. The difference reaches 0.15 V for tribiphenylene and 0.25 V for hexafluorotribiphenylene. These values correspond well to the expected band bending induced by a single electron charging of the single DB site, which may indicate that the HOMO resonances of both molecules are recorded with the presence of the negatively charged single DB underneath the molecules As described, for example, by Engelund et al.[7] changing the charge state of single DBs under the relatively large biases applied here is a frequent observation hydrogenated semiconductors. The additional resonances of the STS dI/dV curves present for both species at around -1.5 V and -0.6 V could be attributed to the DB as reported previously for trinaphthylenes located on a single DB.[8]

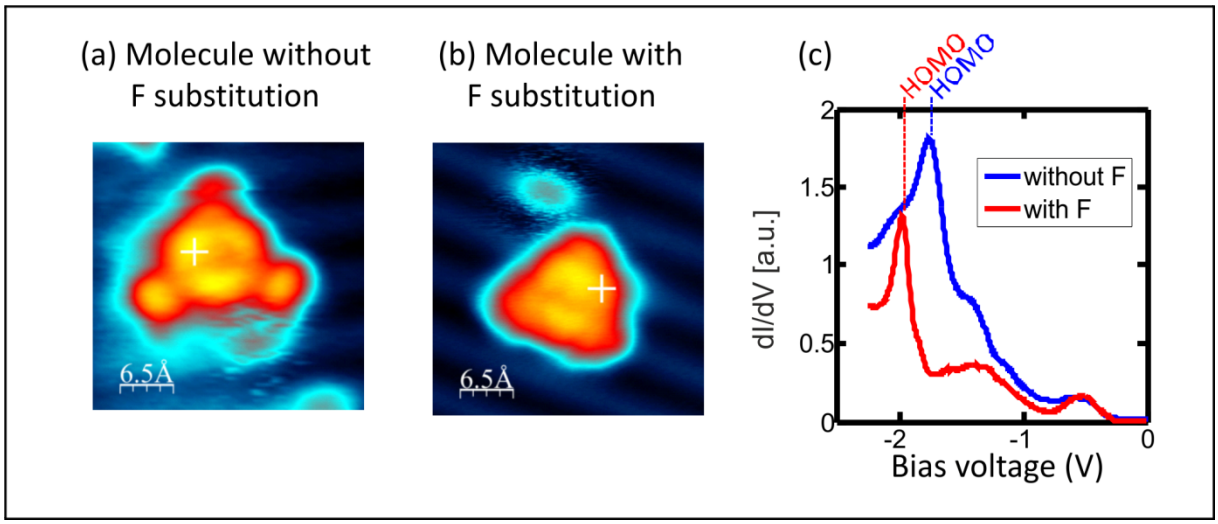

Figure S27. Tribiphenylene and hexafluorotribiphenylene molecules interacting with single DBs; filled state STM image of the tribiphenylene (a) and hexafluorotribiphenylene (b); (c) STS dI/dV data recorded over both molecules; STM image parameters: bias voltage -2.0 V, tunneling current: 2 pA.

14. References

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