

# **(Deep) Blue Through-Space Conjugated TADF Emitters Based on [2.2]Paracyclophanes**

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## Additional Information

### Nomenclature of [2.2]Paracyclophanes

The IUPAC nomenclature for cyclophanes in general is confusing.<sup>1</sup> Therefore Vögtle *et al.* developed a specific cyclophane nomenclature, which is based on a core-substituent ranking.<sup>2</sup> This is exemplified in Figure S1 for the [2.2]paracyclophane.

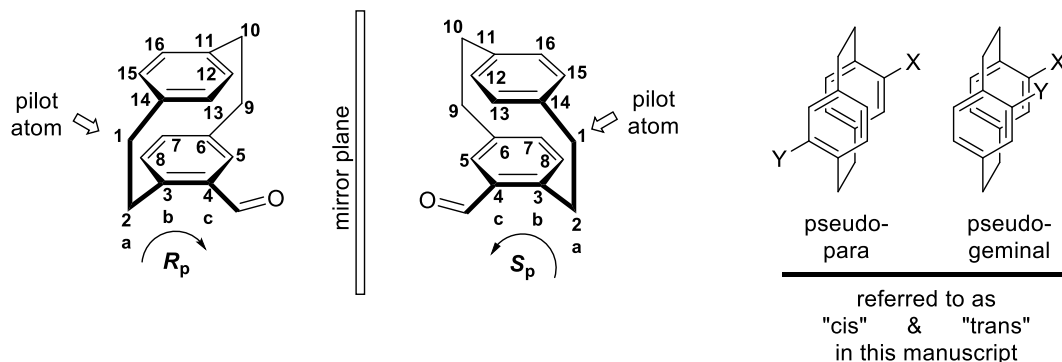


Figure S1. Entire nomenclature shown on both 4-formyl[2.2]paracyclophane enantiomers.

The core structure is named according to the length of the aliphatic bridges in squared brackets (e.g. [n.m]) and the benzene substitution patterns (ortho, meta or para). [2.2]Paracyclophane belongs to the  $D_{2h}$  symmetry, which is broken by the first substituent, resulting in two planar chiral enantiomers. They cannot be drawn in a racemic fashion. By definition, the arene bearing the substituent is set to a chirality plane, and the first atom of the cyclophane structure outside the plane and closest to the chirality center is defined as the “*pilot atom*”. If both arenes are substituted, the substituent with higher priority according to the Cahn-Ingold-Prelog (CIP) nomenclature is preferred.<sup>3</sup> The stereo descriptor is determined by the sense of rotation viewed from the pilot atom. To describe the positions of the substituents correctly, an unambiguous numeration is needed. The numbering of the arenes follows the sense of rotation determined by CIP. To indicate the planarity of the chiral center, a subscripted  $p$  is added. Unfortunately the numbering of the second arene is not consistent in the literature. Therefore another description based on the benzene substitution patterns is preferred for disubstituted [2.2]paracyclophanes. Substitution on the other ring is commonly named pseudo-(*ortho*, *meta*, *para* or *geminal*). With respect to the scope and aim of this communication pseudo-*para* (4,16) derivatives are named “*trans*” and pseudo-*geminal* (4,13) derivatives “*cis*”.

## 2. Synthesis of Compounds

### 2.1. General Remarks

NMR spectra were recorded on a *Bruker* AM 400 or a *Bruker* Avance 500 spectrometer as solutions at room temperature. Chemical shifts  $\delta$  are expressed in parts per million (ppm) downfield from tetramethylsilane (TMS). References for  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were the residual solvent peaks of chloroform ( $^1\text{H}$ :  $\delta = 7.26$  ppm), DMSO ( $^1\text{H}$ :  $\delta = 2.50$  ppm),  $\text{D}_1$ -chloroform ( $^{13}\text{C}$ :  $\delta = 77.0$  ppm) and  $\text{D}_6$ -DMSO ( $^{13}\text{C}$ :  $\delta = 39.43$  ppm). All coupling constants ( $J$ ) are absolute values and are expressed in Hertz (Hz). The description of signals includes: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet,  $m_c$  = centered multiplet, dd = doublet of doublets and ddd = double doublet of doublets and so forth. The spectra were analyzed according to first order. The assignments of the signal structure in  $^1\text{H}$  NMR were made by the multiplicity and for  $^{13}\text{C}$  NMR by DEPT 90- and DEPT 135-spectra (DEPT = distortionless enhancement by polarization transfer) and are described as follows: + = primary or tertiary C-atom (positive DEPT-signal), - = secondary C-atom (negative signal) and  $\text{C}_{\text{quart.}}$  = quaternary C-atom (no signal).

IR spectra were recorded on a FT-IR *Bruker* IFS 88 spectrometer. The compounds were measured as pure substances by ATR technique (ATR = attenuated total reflection). The position of the absorption band is given in wave numbers  $\tilde{\nu}$  in  $\text{cm}^{-1}$ . The intensities of the bands were characterized as follows: vs = very strong (0–20% T), s = strong (21–40% T), m = medium (41–60% T), w = weak (61–80% T), vw = very weak (81–100% T).

Melting points were measured using a Cambridge Instruments device, model *OptiMelt MPA 100* with a temperature increase of  $1\text{ }^\circ\text{C}/\text{min}$ .

Mass spectra were measured by EI-MS (electron impact mass spectrometry) and were recorded on a *Finnigan MAT 95*. The peaks are given as mass-to-charge-ratio ( $m/z$ ). The molecule peak is given as  $[\text{M}]^+$  and characteristic fragment peaks are given as  $[\text{M-fragment}]^+$  or  $[\text{fragment}]^+$ . The signal intensities are given in percent, relatively to the intensity of the base signal (100%). For the high resolution mass, the following abbreviations were used: calc. = calculated data, found = measured data.

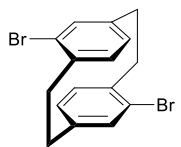
Analytical thin layer chromatography (TLC) was carried out on Merck silica gel coated aluminum plates (silica gel 60, F<sub>254</sub>), detected under UV-light at 254 nm or stained with “Seebach staining solution” (mixture of molybdate phosphoric acid, cerium(IV)-sulfate tetrahydrate, sulfuric acid and water) or basic potassium permanganate solution. Solvent mixtures are understood as volume/volume. Solvents, reagents and chemicals were purchased from *Sigma-Aldrich*, *ABCR* and *Acros Organics*. All solvents, reagents and chemicals were used as purchased unless stated otherwise.

Air- or moisture-sensitive reactions were carried out under argon atmosphere in oven-dried and previously evacuated glass ware. Liquids were transferred with plastic syringes and steel cannula. Reaction control was

performed by thin layer chromatography. If not stated otherwise, crude products were purified by flash chromatography by the procedure of Still.<sup>4</sup> Silica gel 60 (0.040 × 0.063 mm, Geduran®, Merck) was used as stationary phase and as mobile phase, solvents of p.a. quality were used.

## 2.2. Synthetic Procedures and Analytical Data

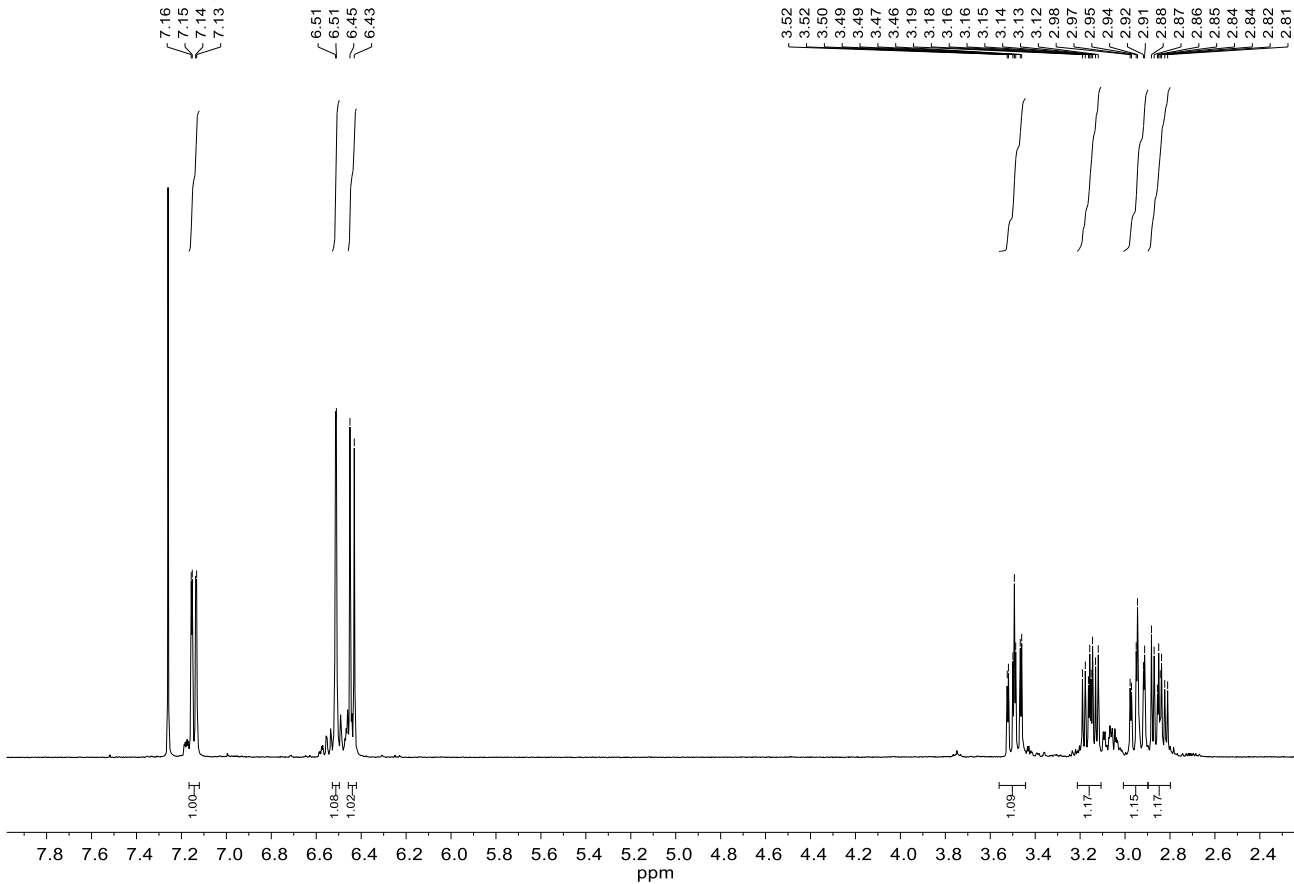
### 4,16-dibromo[2.2]paracyclophane (5):



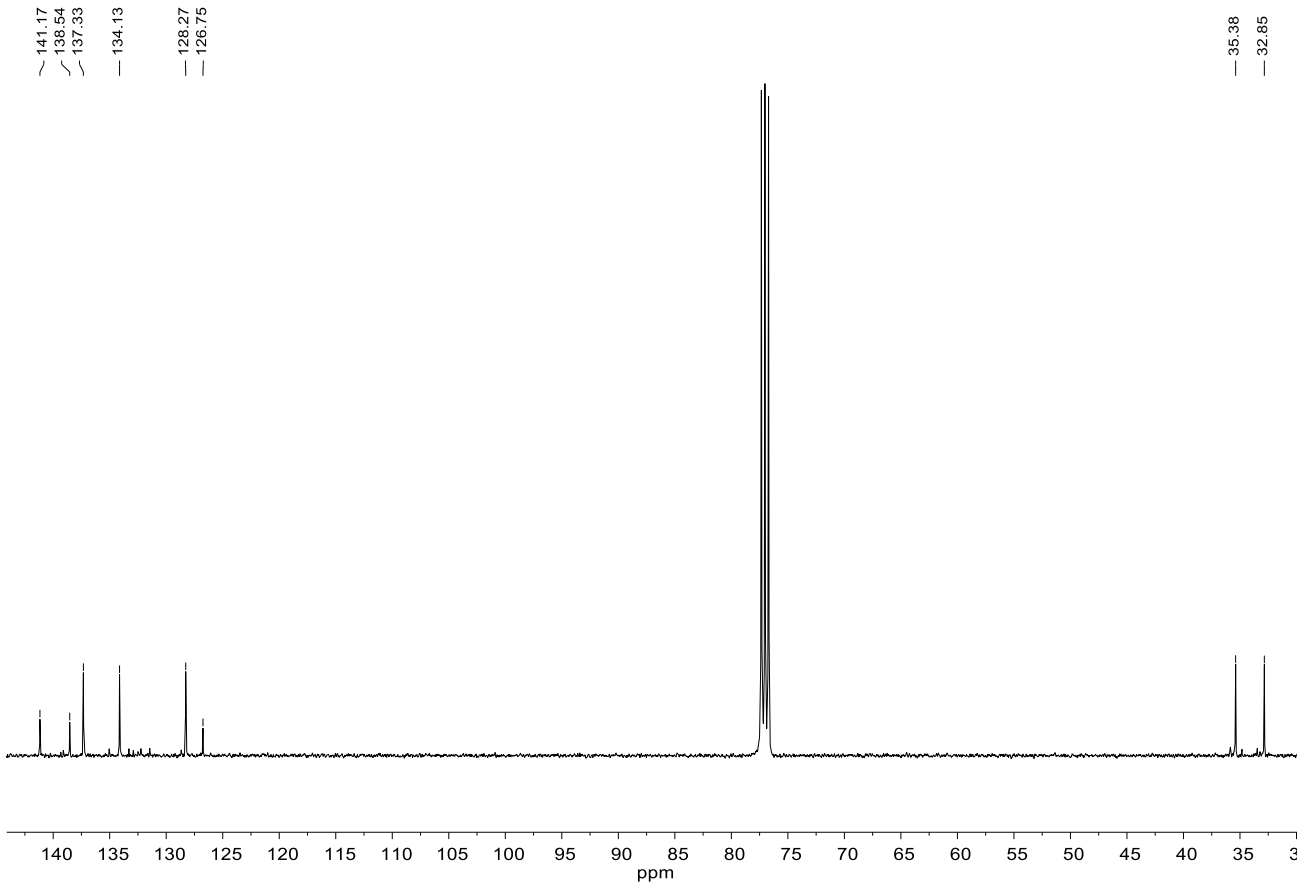
The synthesis followed a modified protocol reported in literature.<sup>5</sup> To iron powder (241 mg, 4.32 mmol, 4.50 mol%) were added 15 mL of a solution of 10.3 mL bromine (32.1 g, 201 mmol, 2.10 equiv.) in 80 mL dichloromethane. After stirring for 1 h, the reaction mixture was diluted with 100 mL dichloromethane and [2.2]paracyclophane (20.0 g, 96.0 mmol, 1.00 equiv.) were added. The mixture was stirred for further 30 min, followed by dropwise addition of the residual bromine solution over 5 h. The reaction mixture was stirred for 3 d. Then a sat. aqueous solution of Na<sub>2</sub>SO<sub>3</sub> was added to the reaction mixture, which was stirred until decoloration occurred (1 h). The organic phase was filtrated and the residual solid dried without further purification. The product was obtained in 9.52 g (26.0 mmol, 28%) as a white solid.

$R_f = 0.72$  (CH/EA 10:1). – <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.14$  (dd,  $J = 7.8, 1.8$  Hz, 2H), 6.51 (d,  $J = 1.7$  Hz, 2H), 6.44 (d,  $J = 7.8$  Hz, 2H), 3.49 (ddd,  $J = 13.0, J = 10.4, 2.3$  Hz, 2H), 3.15 (ddd,  $J = 12.7, 10.4, 4.9$  Hz, 2H), 2.94 (ddd,  $J = 12.7, 10.7, 2.3$  Hz, 2H), 2.85 (ddd,  $J = 13.2, 10.7, 5.0$  Hz, 2H) ppm. – <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 141.3$  (C<sub>quart.</sub>), 138.7 (C<sub>quart.</sub>), 137.5 (+), 134.2 (+), 128.4 (+), 126.9 (C<sub>quart.</sub>), 35.5 (–), 33.0 (–) ppm. – IR (ATR):  $\tilde{\nu} = 2931$  (vw), 2849 (vw), 1582 (vw), 1535 (vw), 1473 (vw), 1449 (vw), 1432 (vw), 1390 (w), 1185 (vw), 1030(w), 898 (w), 855 (w), 829 (w), 706 (w), 669 (w), 648 (w), 464 (w) cm<sup>-1</sup>. – MS (70 eV, EI),  $m/z$  (%): 368/366/364 (19/38/20) [M]<sup>+</sup>, 184/182 (100/95) [M – C<sub>8</sub>H<sub>7</sub>Br]<sup>+</sup>, 103 (19) [C<sub>8</sub>H<sub>7</sub>]<sup>+</sup>. – HRMS (C<sub>16</sub>H<sub>14</sub><sup>79</sup>Br<sub>2</sub>) calc.: 363.9457; found: 363.9457. Analytical data matches that of the literature.<sup>6</sup>

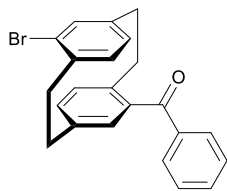
4,16-dibromo[2.2]paracyclophane



4,16-dibromo[2.2]paracyclophane



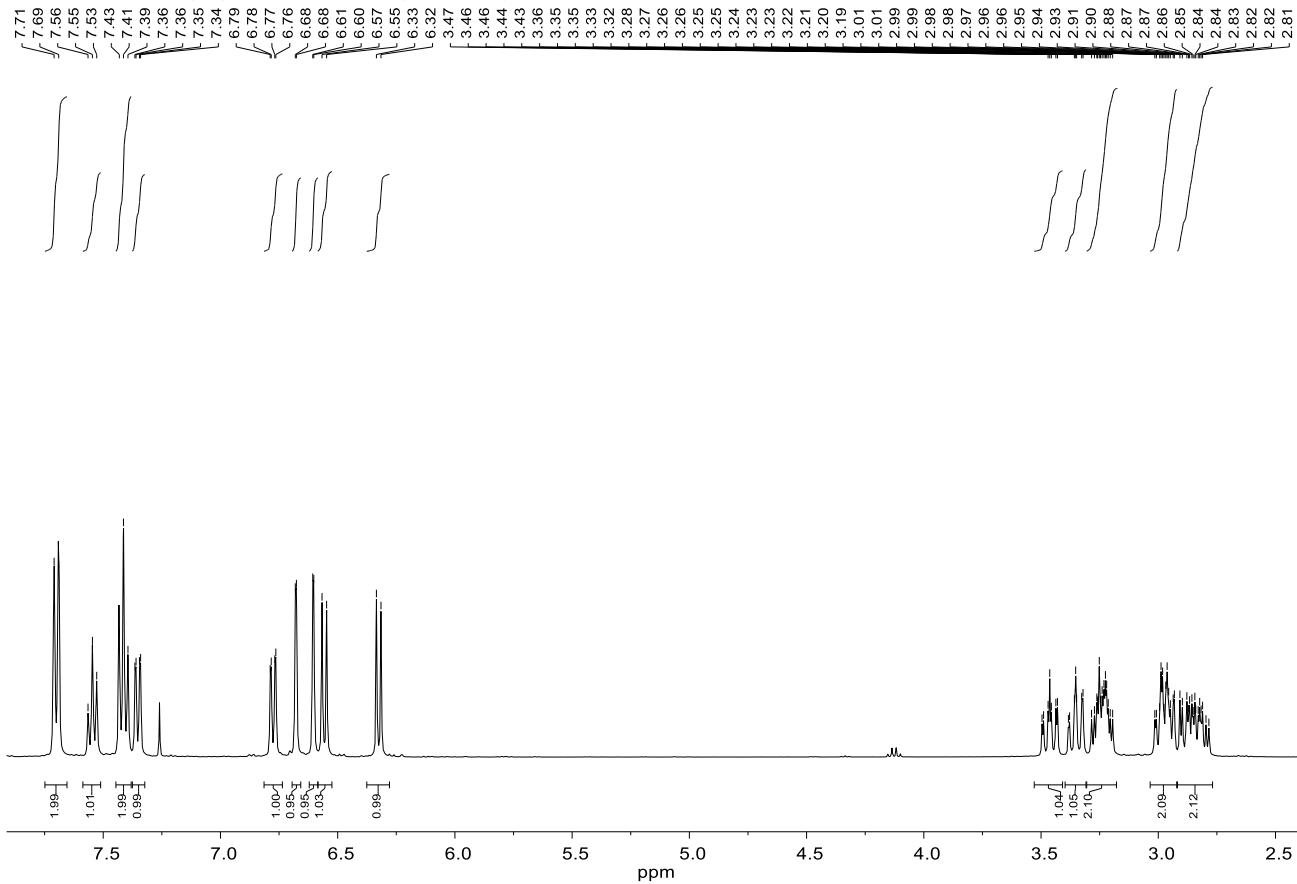
(rac, “trans”) 4 -bromo-16-benzoyl[2.2]paracyclophane (6):



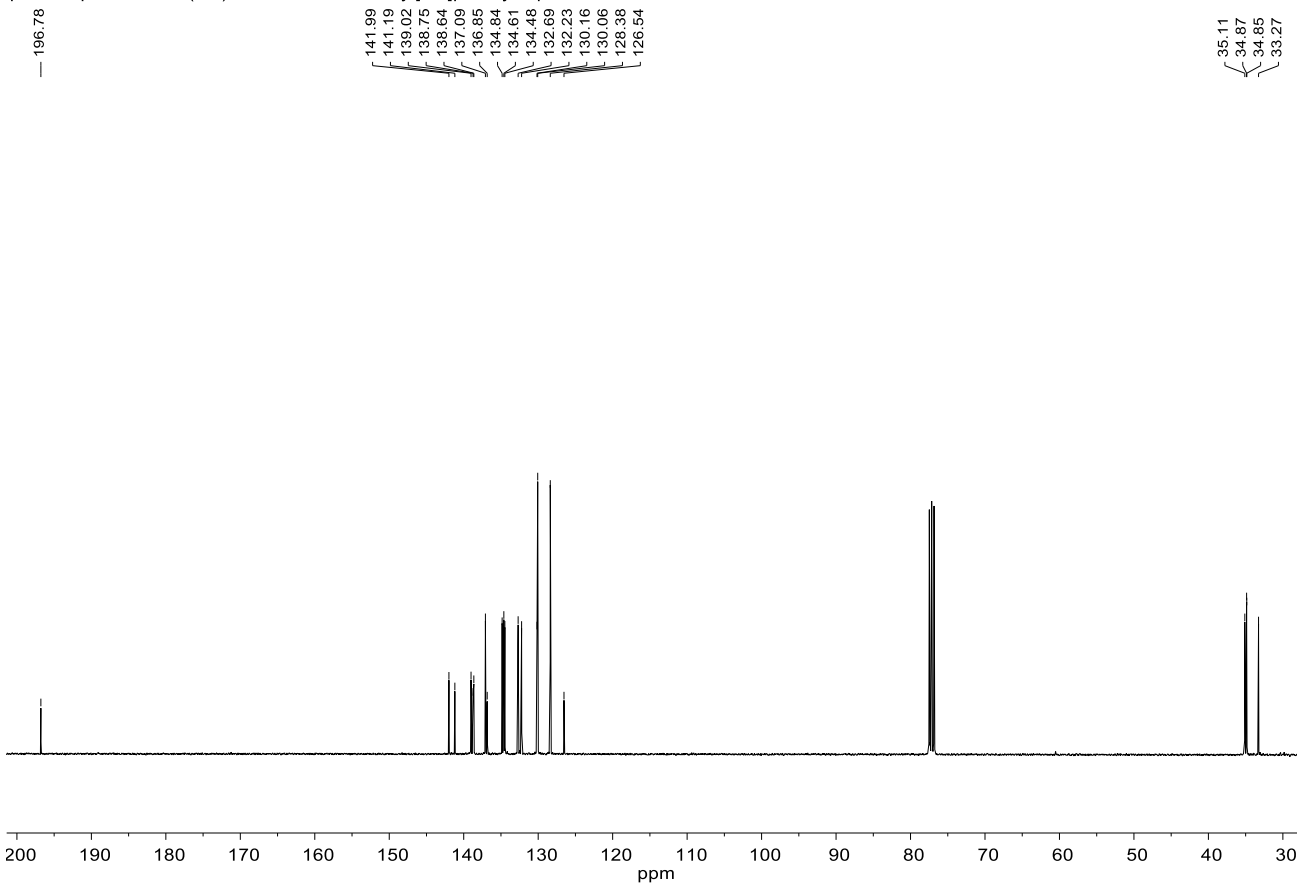
A solution of <sup>n</sup>BuLi (3.94 mL of 2.5 M in hexane, 9.84 mmol, 1.20 equiv.) was added dropwise to a solution of 4,16-dibromo[2.2]paracyclophane (**5**) (3.00 g, 8.20 mmol, 1.00 equiv.) in 150 mL dry tetrahydrofuran at  $-78\text{ }^{\circ}\text{C}$  under argon atmosphere. After stirring for 1 h, the reaction mixture was warmed up to  $0\text{ }^{\circ}\text{C}$  and 7.56 mL of benzoyl chloride (9.22 g, 65.6 mmol, 8.00 equiv.) were added quickly. The reaction mixture was warmed up to room temperature and stirred for 16 h. The reaction mixture was quenched by addition of water and was extracted with ethyl acetate (3  $\times$  100 mL). The combined organic phases were washed with sat. aqueous  $\text{NH}_4\text{Cl}$  solution (100 mL), brine (100 mL), dried over  $\text{Na}_2\text{SO}_4$  and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, cyclohexane/ethyl acetate; 50/1) to yield 4.24 g of an off-white solid (5.58 mmol, 68%).

$R_f = 0.22$  (CH/Ea 50:1). –  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.70$  (d,  $J = 7.8$  Hz, 2H), 7.55 (t,  $J = 7.4$  Hz, 1H), 7.41 (t,  $J = 7.4$  Hz, 2H), 7.35 (dd,  $J = 7.8, 1.9$  Hz, 1H), 6.78 (dd,  $J = 7.9, 1.8$  Hz, 1H), 6.68 (d,  $J = 1.9$  Hz, 1H), 6.60 (d,  $J = 1.8$  Hz, 1H), 6.56 (d,  $J = 7.8$  Hz, 1H), 6.33 (d,  $J = 7.8$  Hz, 1H), 3.46 (ddd,  $J = 13.2, 10.4, 2.7$  Hz, 1H), 3.35 (ddd,  $J = 12.5, 10.5, 2.1$  Hz, 1H), 3.28 – 3.19 (m, 2H), 3.01 – 2.93 (m, 2H), 2.92 – 2.76 (m, 2H) ppm. –  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 196.78$  ( $\text{C}_{\text{quat.}}$ , CO), 141.99 ( $\text{C}_{\text{quat.}}$ ), 141.19 ( $\text{C}_{\text{quat.}}$ ), 139.02 ( $\text{C}_{\text{quat.}}$ ), 138.75 ( $\text{C}_{\text{quat.}}$ ), 138.64 ( $\text{C}_{\text{quat.}}$ ), 137.09 (+), 136.85 ( $\text{C}_{\text{quat.}}$ ), 134.84 (+), 134.61 (+), 134.48 (+), 132.69 (+), 132.23(+), 130.16 (+), 130.06 (+), 128.38 (+), 126.54 ( $\text{C}_{\text{quat.}}$ ), 35.11 (–), 34.87 (–), 34.85 (–), 33.27 (–) ppm. – IR (ATR):  $\tilde{\nu} = 2926$  (vw), 1645 (w), 1587 (vw), 1478 (vw), 1448 (vw), 1392 (vw), 1313 (vw), 1279 (w), 1033 (vw), 989 (vw), 908 (vw), 889 (vw), 855 (vw), 822 (w), 742 (w), 722 (vw), 701 (m), 667 (w), 652 (w), 639 (w), 514 (vw), 476 (w), 458 (vw), 397 (vw)  $\text{cm}^{-1}$  – MS (FAB, 3-NBA),  $m/z$ : 391/393 [ $\text{M}(^{79}\text{Br}^{81}\text{Br})+\text{H}$ ]<sup>+</sup>, 390/392 [ $\text{M}(^{79}\text{Br}^{81}\text{Br})$ ]<sup>+</sup>. – HRMS ( $\text{C}_{23}\text{H}_{19}^{79}\text{BrO}$ ) calc.: 390.0619; found: 390.0620. – HRMS ( $\text{C}_{23}\text{H}_{19}^{79}\text{BrO}+\text{H}$ ) calc.: 391.0698; found: 391.0700.

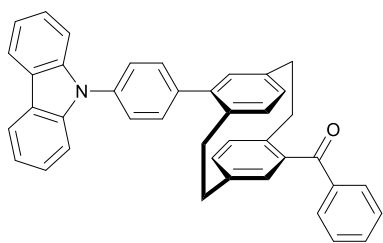
pseudo-para "trans" (rac)-4-bromo-16-benzoyl[2.2]paracyclophane



pseudo-para "trans" (rac)-4-bromo-16-benzoyl[2.2]paracyclophane



(rac, "trans") 4-Benzoyl-16-(4'-N-carbazolyl)phenyl[2.2]paracyclophane (8):

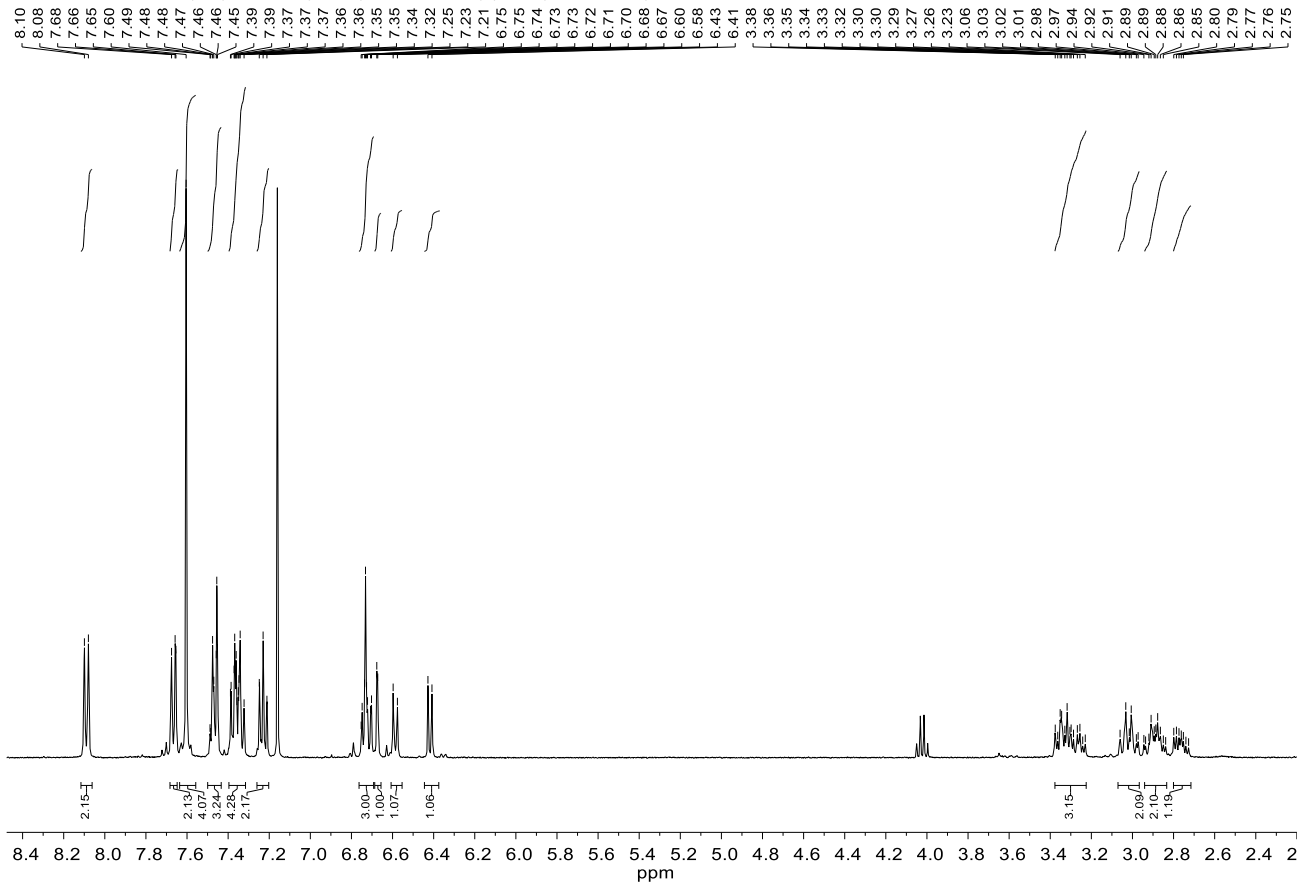


In a pressure vial were charged (*rac*)-4-bromo-16-benzoyl[2.2]paracyclophane (**6**) (97.8 mg, 250  $\mu$ mol, 1.00 equiv.), 4-(*N*-carbazolyl)phenyl boronic acid (144 mg, 500  $\mu$ mol, 2.00 equiv.), Cs<sub>2</sub>CO<sub>3</sub> (244 mg, 750  $\mu$ mol, 3.00 equiv.), and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (21.1 mg, 30.0  $\mu$ mol, 10 mol%). The sealed vial was evacuated and flushed with argon three times. Through the septum 6 mL of degassed tetrahydrofuran and 1.5 mL of degassed water were added, then heated to 75 °C and stirred for 16 h. The reaction mixture was diluted in 50 mL of ethyl acetate and washed first with sat. aqueous NH<sub>4</sub>Cl solution (3  $\times$  30 mL) and then with brine (30 mL). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, cyclohexane/ethyl acetate; 50/1) to yield 106 mg of the product as a white solid (191  $\mu$ mol, 76%).

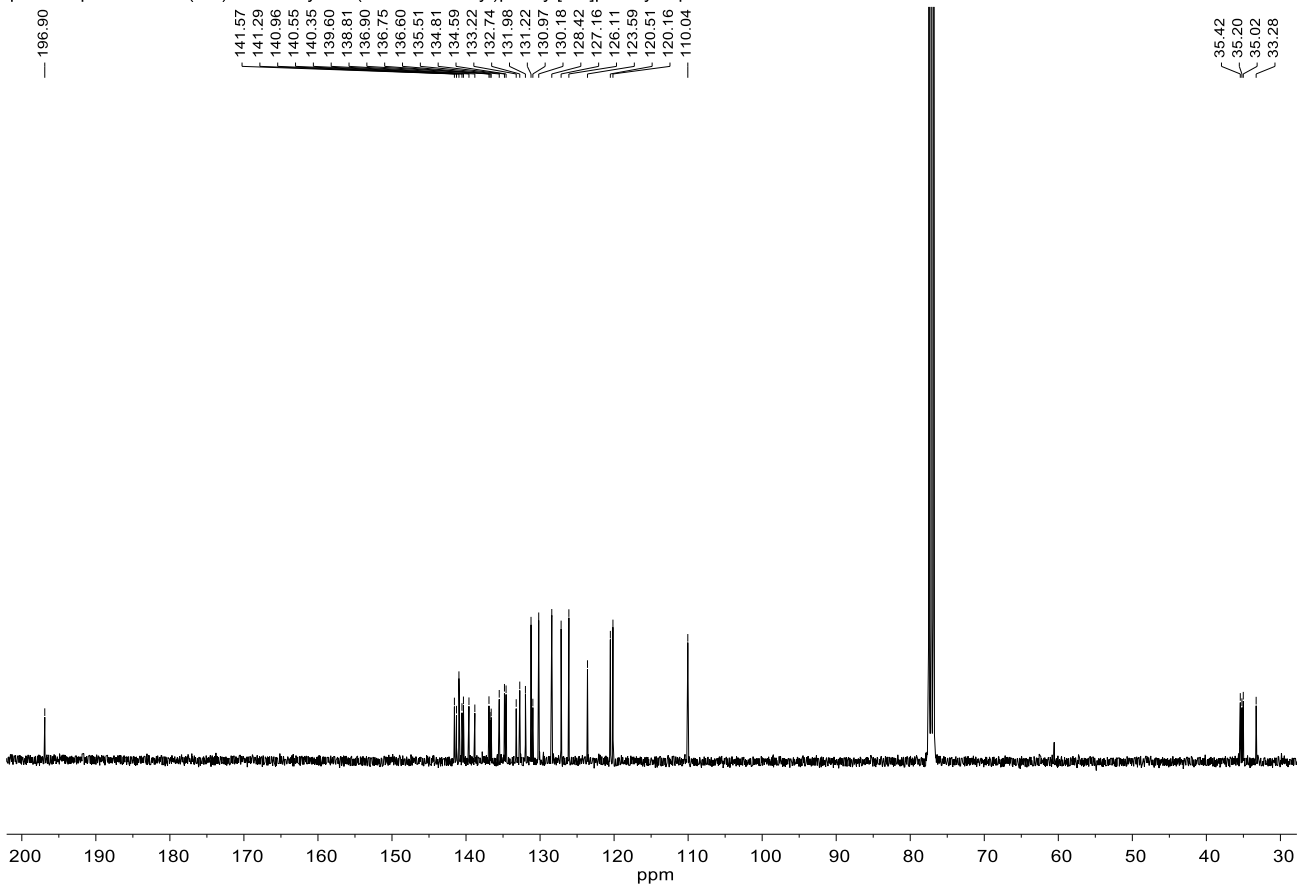
$R_f = 0.14$  (CH/EA 50:1). – <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.09 (d,  $J = 7.8$  Hz, 2H), 7.70 – 7.64 (m, 2H), 7.60 (s, 4H), 7.49 – 7.45 (m, 3H), 7.41 – 7.31 (m, 4H), 7.25 – 7.21 (m, 2H), 6.77 – 6.69 (m, 3H), 6.67 (d,  $J = 1.9$  Hz, 1H), 6.59 (d,  $J = 8.3$  Hz, 1H), 6.42 (d,  $J = 7.8$  Hz, 1H), 3.44 – 3.18 (m, 3H), 3.06 – 2.97 (m, 2H), 2.96 – 2.83 (m, 2H), 2.76 (ddd,  $J = 14.3, 10.2, 5.2$  Hz, 1H) ppm. – <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 196.90 (C<sub>quat.</sub>, CO), 141.57 (C<sub>quat.</sub>), 141.29 (C<sub>quat.</sub>), 140.96 (C<sub>quat.</sub>), 140.55 (C<sub>quat.</sub>), 140.35 (C<sub>quat.</sub>), 139.60 (C<sub>quat.</sub>), 138.81 (C<sub>quat.</sub>), 136.90 (C<sub>quat.</sub>), 136.75 (C<sub>quat.</sub>), 136.60 (C<sub>quat.</sub>), 135.51 (+), 134.81 (+), 134.59 (+), 133.22 (+), 132.74 (+), 131.98 (+), 131.22 (+), 130.97 (+), 130.18 (+), 128.42 (+), 127.16 (+), 126.11(+), 123.59 (C<sub>quat.</sub>), 120.51 (+), 120.16 (+), 110.04 (+), 35.42 (–), 35.20 (–), 35.02 (–), 33.28 (–) ppm. – Mp : 145-150 °C. – IR (ATR):  $\tilde{\nu}$  = 3045 (vw), 2922 (vw), 2852 (vw), 1651 (w), 1596 (vw), 1514 (w), 1478 (vw), 1449 (w), 1335 (vw), 1315 (vw), 1269 (w), 1228 (w), 1171 (vw), 1026 (vw), 913 (vw), 838 (vw), 748 (w), 723 (w), 701 (w), 656 (vw), 565 (vw), 489 (vw), 423 (vw) cm<sup>-1</sup>. – MS (FAB, 3-NBA),  $m/z$ : 554 [M+H]<sup>+</sup>, 553 [M]<sup>+</sup>. – HRMS (C<sub>41</sub>H<sub>31</sub>NO) calc.: 553.2406; found: 553.2403.



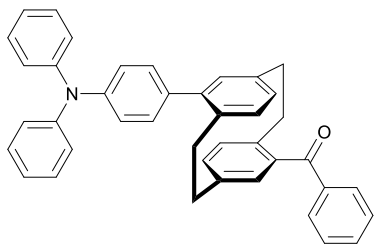
pseudo-para "trans" (rac)-4-Benzoyl-16-(4'-N-carbazolyl)phenyl[2.2]paracyclophane



pseudo-para "trans" (rac)-4-Benzoyl-16-(4'-N-carbazolyl)phenyl[2.2]paracyclophane



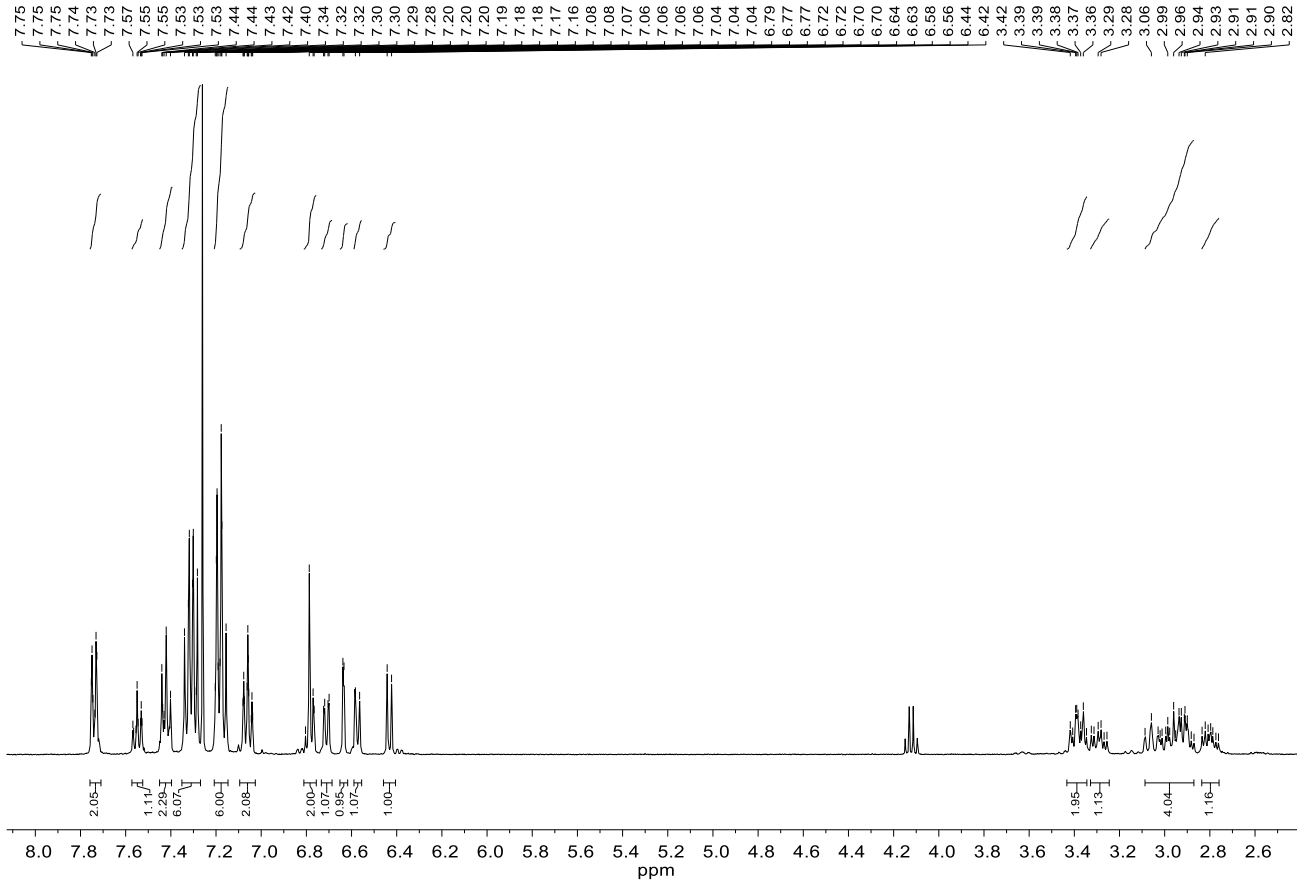
(rac, "trans") 4-Benzoyl-16-(4'-N-diphenylamino)phenyl[2.2]paracyclophane (7):



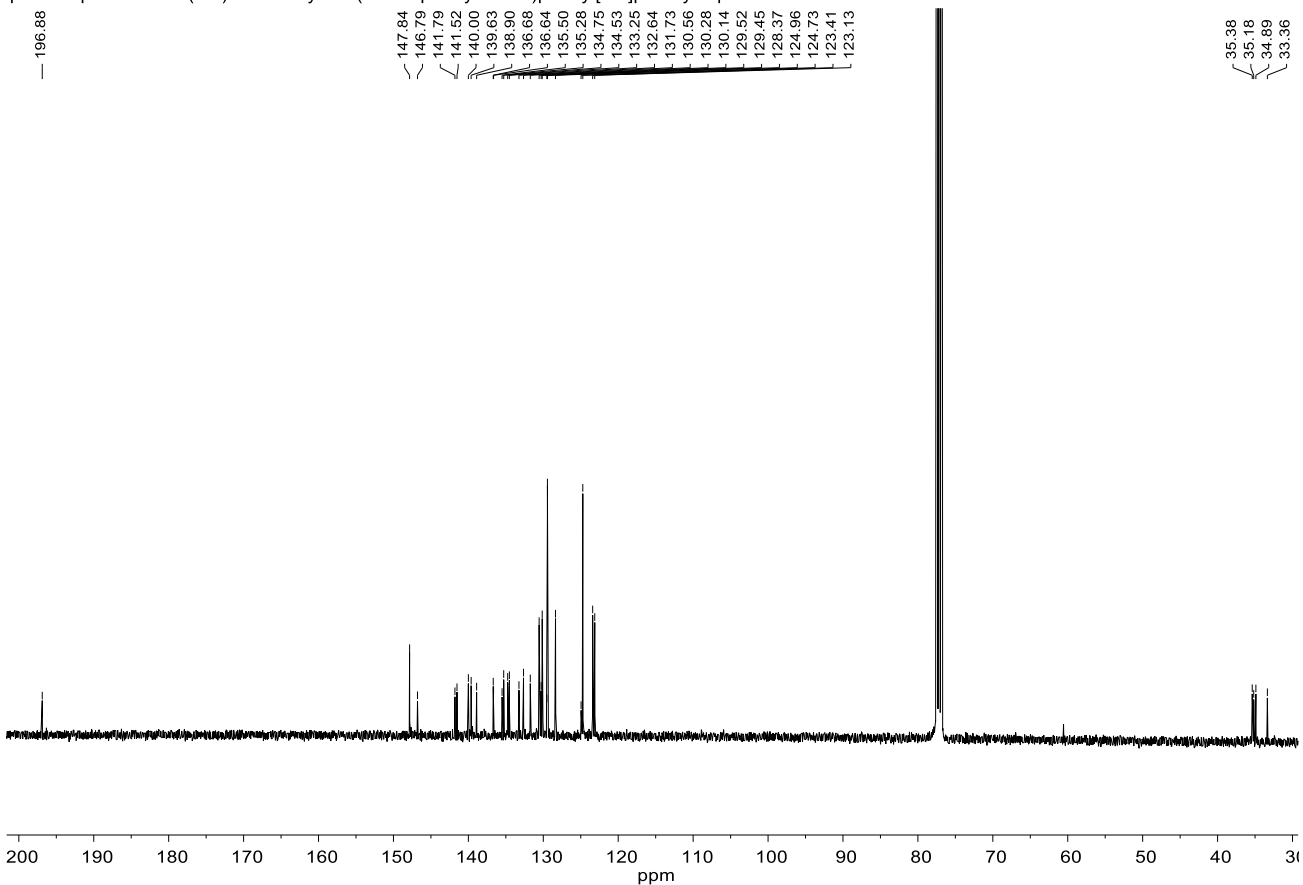
In a pressure vial were charged (*rac*)-4-bromo-16-benzoyl[2.2]paracyclophane (**6**) (97.8 mg, 250  $\mu$ mol, 1.00 equiv.), 4-(*N*-diphenylamino)phenyl boronic acid (144 mg, 500  $\mu$ mol, 2.00 equiv.), Cs<sub>2</sub>CO<sub>3</sub> (244 mg, 750  $\mu$ mol, 3.00 equiv.), and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (21.1 mg, 30.0  $\mu$ mol, 10 mol%). The sealed vial was evacuated and flushed with argon three times. Through the septum 6 mL of degassed tetrahydrofuran and 1.5 mL of degassed water were added, then heated to 75 °C and stirred for 16 h. The reaction mixture was diluted in 50 mL of ethyl acetate and washed first with sat. aqueous NH<sub>4</sub>Cl solution (3  $\times$  30 mL) and then with brine (30 mL). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, cyclohexane/ethyl acetate; 50/1) to yield 92.2 mg of the product as an off-white solid (65%, 166  $\mu$ mol).

$R_f = 0.14$  (CH/EA 50:1). – <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 7.79 - 7.69$  (m, 2H), 7.59 – 7.51 (m, 1H), 7.42 (t,  $J = 7.7$  Hz, 2H), 7.35 – 7.27 (m, 6H), 7.21 – 7.14 (m, 6H), 7.10 – 7.02 (m, 2H), 6.81 – 6.75 (m, 2H), 6.71 (dd,  $J = 7.8, 1.9$  Hz, 1H), 6.64 (d,  $J = 1.9$  Hz, 1H), 6.57 (d,  $J = 7.5$  Hz, 1H), 6.43 (d,  $J = 7.8$  Hz, 1H), 3.44 – 3.34 (m, 2H), 3.34 – 3.24 (m, 1H), 3.11 – 2.86 (m, 4H), 2.85 – 2.74 (m, 1H) ppm. – <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta = 196.88$  (C<sub>quat.</sub>, CO), 147.84 (C<sub>quat.</sub>), 146.79 (C<sub>quat.</sub>), 141.79 (C<sub>quat.</sub>), 141.52 (C<sub>quat.</sub>), 140.00 (C<sub>quat.</sub>), 139.63 (C<sub>quat.</sub>), 138.90 (C<sub>quat.</sub>), 136.68 (C<sub>quat.</sub>), 136.64 (C<sub>quat.</sub>), 135.50 (C<sub>quat.</sub>), 135.28 (+), 134.75 (+), 134.53 (+), 133.25 (+), 132.64 (+), 131.73 (+), 130.56 (+), 130.28 (+), 130.14 (+), 129.52 (+), 129.45 (+), 128.37 (+), 124.96 (+), 124.73 (+), 123.41 (+), 123.13 (+), 35.38 (–), 35.18 (–), 34.89 (–), 33.36 (–) ppm. – Mp : 125-130 °C. – IR (ATR):  $\tilde{\nu} = 3058$  (vw), 3032 (vw), 2923 (w), 2853 (vw), 2258 (vw), 1715 (vw), 1652 (w), 1589 (w), 1487 (w), 1447 (vw), 1270 (m), 1151 (w), 1110 (w), 1024 (m), 819 (w), 753 (w), 695 (m), 617 (w), 510 (w), 483 (w), 426 (vw) cm<sup>-1</sup>. – MS (FAB, 3-NBA),  $m/z$ : 556 [M+H]<sup>+</sup>, 555 [M]<sup>+</sup>. – HRMS (C<sub>41</sub>H<sub>33</sub>NO) calc.: 555.2562; found: 555.2564.

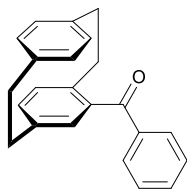
pseudo-para "trans" (rac)-4-Benzoyl-16-(4'-N-diphenylamino)phenyl[2.2]paracyclophane



pseudo-para "trans" (rac)-4-Benzoyl-16-(4'-N-diphenylamino)phenyl[2.2]paracyclophane



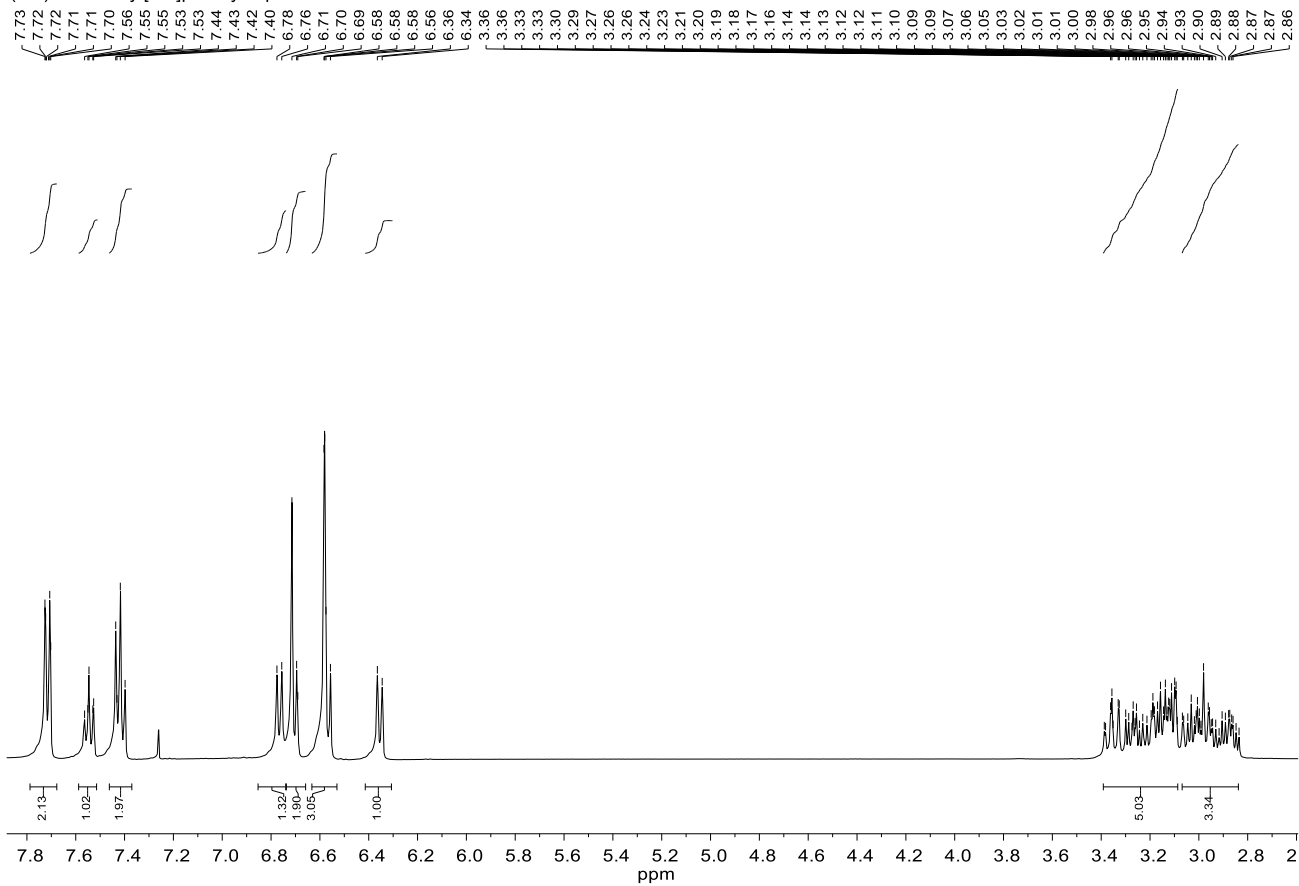
(rac)-4-Benzoyl[2.2]paracyclophane (1)



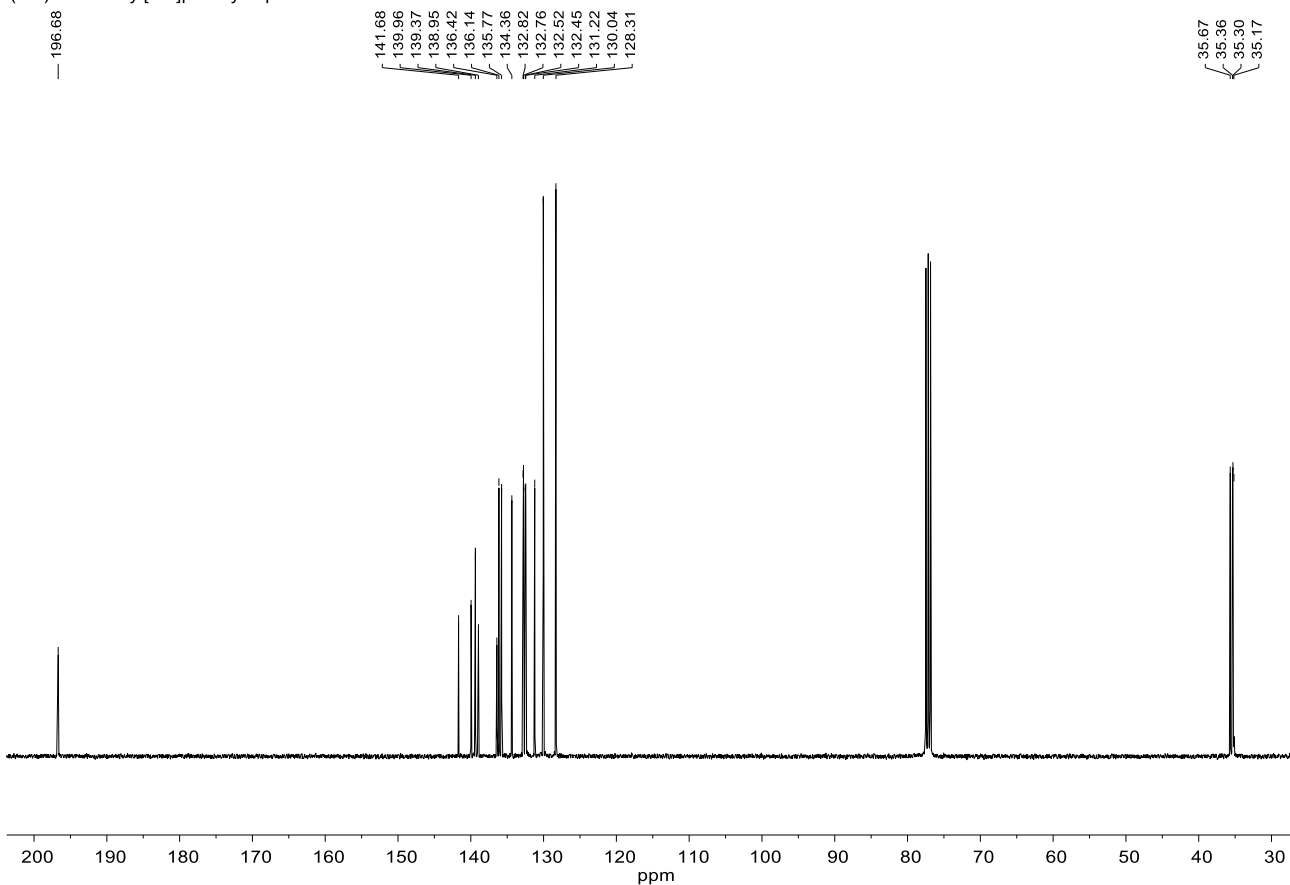
In a 250 mL flask, [2.2]paracyclophane (10.4 g, 50.0 mmol, 1.00 equiv.) was dissolved in 100 mL of dichloromethane and cooled to  $-10\text{ }^{\circ}\text{C}$ . A solution of benzoyl chloride (11.5 mL, 14.1 g, 100 mmol, 2.00 equiv.) and  $\text{AlCl}_3$  (11.7 g, 88.0 mmol, 1.75 equiv.) in 50 mL of dichloromethane were added and stirred for 1 h. The reaction mixture was filtered through glass wool and hydrolyzed with ice. Extraction was carried out with dichloromethane (200 mL), afterwards the organic layer was washed with aqueous  $\text{NaHCO}_3$  (200 mL) solution and brine (200 mL), then dried over  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated under reduced pressure and the residue was recrystallized in ethanol to yield 12.4 g (39.7 mmol, 79%) of colorless crystals.

$R_f = 0.53$  (CH/EA 40:1) –  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.72$  (d,  $J = 7.8$  Hz, 2H), 7.56 – 7.53 (m, 1H), 7.42 (t,  $J = 7.7$  Hz, 2H), 6.77 (d,  $J = 7.9$  Hz, 1H), 6.71 – 6.69 (m, 2H), 6.58 – 6.55 (m, 3H), 6.35 (d,  $J = 7.9$  Hz, 1H), 3.39 – 3.09 (m, 5H), 3.07 – 2.84 (m, 3H) ppm. –  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta = 196.68$  ( $\text{C}_{\text{quat.}}$ , CO), 141.68 ( $\text{C}_{\text{quat.}}$ ), 139.96 ( $\text{C}_{\text{quat.}}$ ) 139.37 ( $\text{C}_{\text{quat.}}$ ), 138.95 ( $\text{C}_{\text{quat.}}$ ), 136.42 ( $\text{C}_{\text{quat.}}$ ), 136.14 (+), 135.77 (+), 134.36 (+), 132.82 (+), 132.76 (+), 132.52 (+), 132.45 (+), 131.22 (+), 130.04 (+), 128.31 (+), 35.67 (–), 35.36 (–), 35.30 (–), 35.17 (–) ppm. – IR (ATR)  $\tilde{\nu} = 2919$  (w), 2848 (vw), 1649 (m), 1594 (w), 1446 (w), 1411 (vw), 1318 (w), 1294 (w), 1269 (w), 1196 (w), 976 (w), 941 (w), 907 (w), 891 (w), 835 (w), 803 (w), 726 (w), 700 (m), 656 (w), 634 (m), 509 (m), 454 (vw)  $\text{cm}^{-1}$ . – MS (EI, 70 eV)  $m/z$  [%] = 313 (25)  $[\text{M}+\text{H}]^+$ , 312 (100)  $[\text{M}]^+$ , 208 (86)  $[\text{M}-\text{C}_8\text{H}_8]^+$ , 207 (73)  $[\text{M}-\text{C}_8\text{H}_9]^+$ , 105 (11)  $[\text{C}_8\text{H}_9]^+$ , 104 (29)  $[\text{C}_8\text{H}_8]^+$ . – HRMS ( $\text{C}_{23}\text{H}_{20}\text{O}$ ) calc. 312.1509; found 312.1510. The analytical data matches that of the literature.<sup>7</sup>

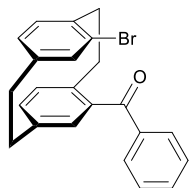
(rac)-4-Benzoyl[2.2]paracyclophane



(rac)-4-Benzoyl[2.2]paracyclophane



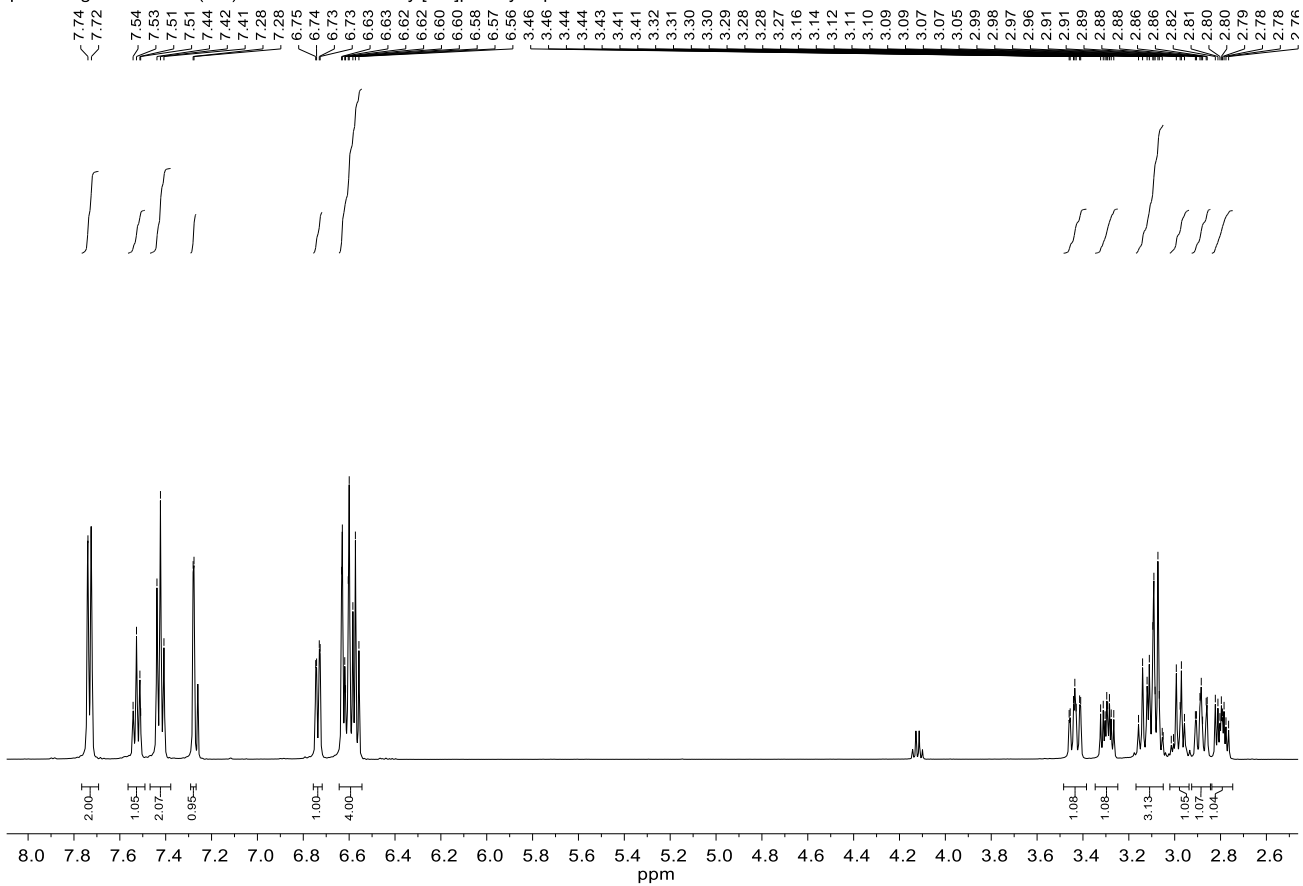
(rac, “cis”)-4-Bromo-13-benzoyl[2.2]paracyclophane (2)



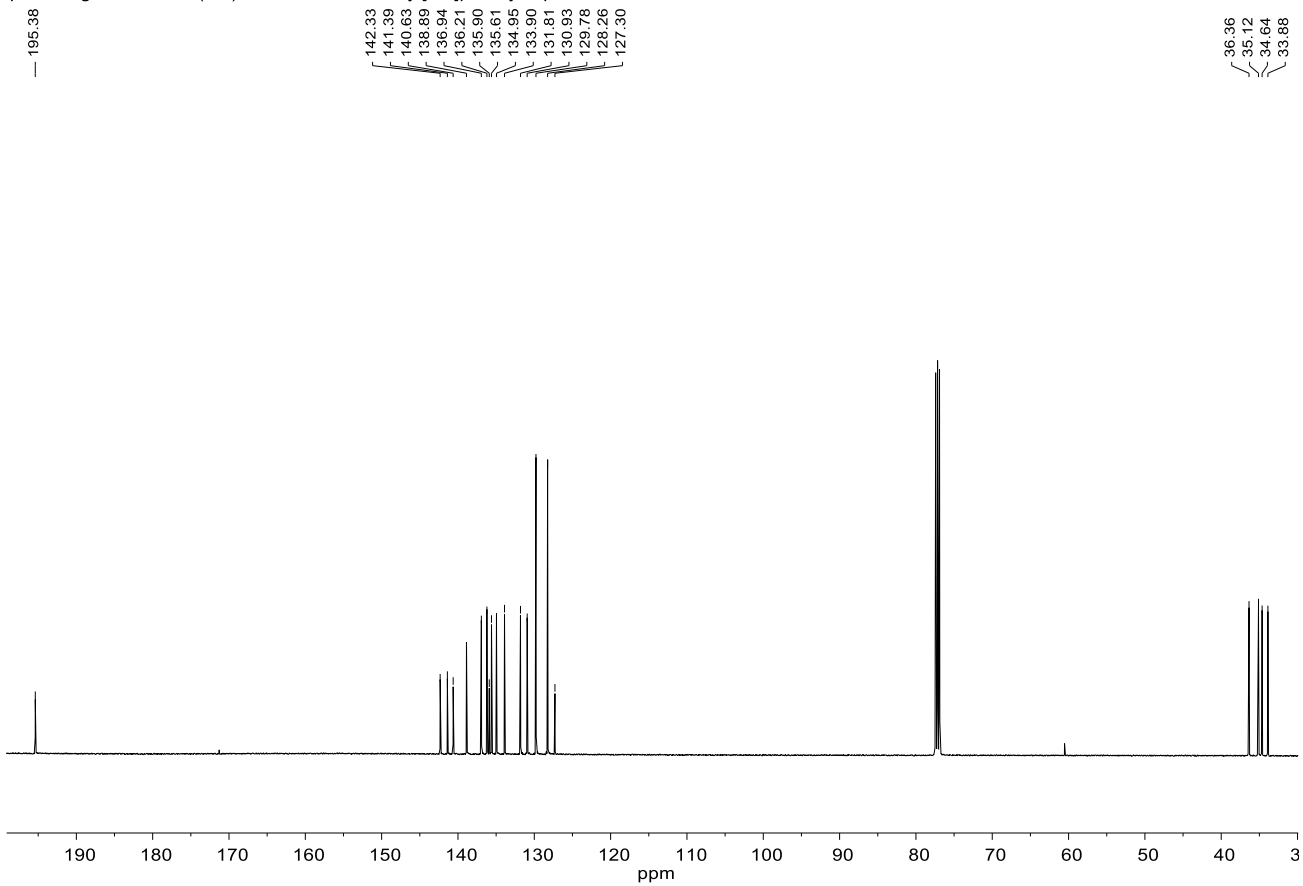
A solution of 2.51 mL bromine (7.82 g, 49.0 mmol, 1.02 equiv.) in 60 mL of dichloromethane was prepared in a dropping funnel and 5 mL of this solution were added to iron filings (50.0 mg, 960  $\mu$ mol, 2 mol%) in a 500 mL three neck flask and stirred for 1 h at room temperature. Then 100 mL of dichloromethane and (*rac*)-4-benzoyl[2.2]paracyclophane (**1**) (15.0 g, 48.0 mmol, 1.00 equiv.) were added and stirred for another 30 min. The remainder of the bromine solution was added dropwise over a period of 5 h and the mixture was stirred for 3 days. The reaction was quenched with a saturated sodium sulfite solution (200 mL) and stirred for 30 min until full discoloration of the mixture. The organic phase was separated, washed with brine (200 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. The filtrate was evaporated and the residue was purified by flash chromatography (silica, 40:1 cyclohexane:ethyl acetate) to yield 8.60 g (21.9 mmol, 46%) of a white solid.

R<sub>f</sub> = 0.23 (CH/EA 40:1) – <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.73 (d, *J* = 7.7 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 1.9 Hz, 1H), 6.74 (dd, *J* = 7.7, 1.9 Hz, 1H), 6.68 – 6.53 (m, 4H), 3.44 (ddd, *J* = 12.8, 9.6, 2.3 Hz, 1H), 3.29 (ddd, *J* = 13.2, 9.6, 5.7 Hz, 1H), 3.18 – 3.04 (m, 3H), 3.02 – 2.94 (m, 1H), 2.88 (ddd, *J* = 12.9, 10.0, 2.3 Hz, 1H), 2.79 (ddd, *J* = 13.2, 10.0, 5.7 Hz, 1H) ppm – <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 195.38 (C<sub>quat.</sub>, CO), 142.33 (C<sub>quat.</sub>), 141.39 (C<sub>quat.</sub>), 140.63 (C<sub>quat.</sub>), 138.89 (C<sub>quat.</sub>), 136.94 (+), 136.21 (+), 135.90 (C<sub>quat.</sub>), 135.61 (+), 134.95 (+), 133.90 (+), 131.81 (+), 130.93 (+), 129.78 (+), 128.26 (+), 127.30 (C<sub>quat.</sub>), 36.36 (–), 35.12 (–), 34.64 (–), 33.88 (–) ppm. – IR (ATR)  $\tilde{\nu}$  = 2927 (w), 1742 (w), 1649 (m), 1587 (w), 1471 (w), 1445 (w), 1388 (w), 1268 (m), 1240 (w), 1205 (w), 1030 (w), 981 (w), 951 (w), 890 (w), 836 (w), 800 (w), 735 (m), 700 (m), 652 (w), 637 (w), 604 (w), 519 (w), 479 (w), 390 (vw) cm<sup>-1</sup>. – MS (EI, 70 eV) *m/z* [%] = 393 (12) [M(<sup>81</sup>Br)+H]<sup>+</sup>, 392 (50) [M(<sup>81</sup>Br)]<sup>+</sup>, 391 (12) [M(<sup>79</sup>Br)+H]<sup>+</sup>, 390 (47) [M(<sup>79</sup>Br)]<sup>+</sup>, 208 (100) [M–C<sub>8</sub>H<sub>7</sub>Br]<sup>+</sup>, 207 (91) [M–C<sub>8</sub>H<sub>8</sub>Br]<sup>+</sup>, 106 (39) [CHOPh]<sup>+</sup>. – HRMS (C<sub>23</sub>H<sub>19</sub><sup>79</sup>BrO) calc. 390.0614; found 390.0612.

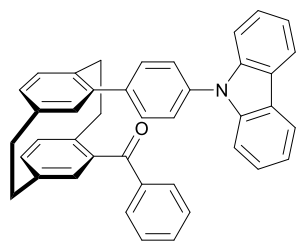
pseudo-geminal "cis" (rac)-4-Bromo-13-benzoyl[2.2]paracyclophane



pseudo-geminal "cis" (rac)-4-Bromo-13-benzoyl[2.2]paracyclophane



(rac, "cis") 4-Benzoyl-13-(4'-N-carbazolyl)phenyl[2.2]paracyclophane (4):



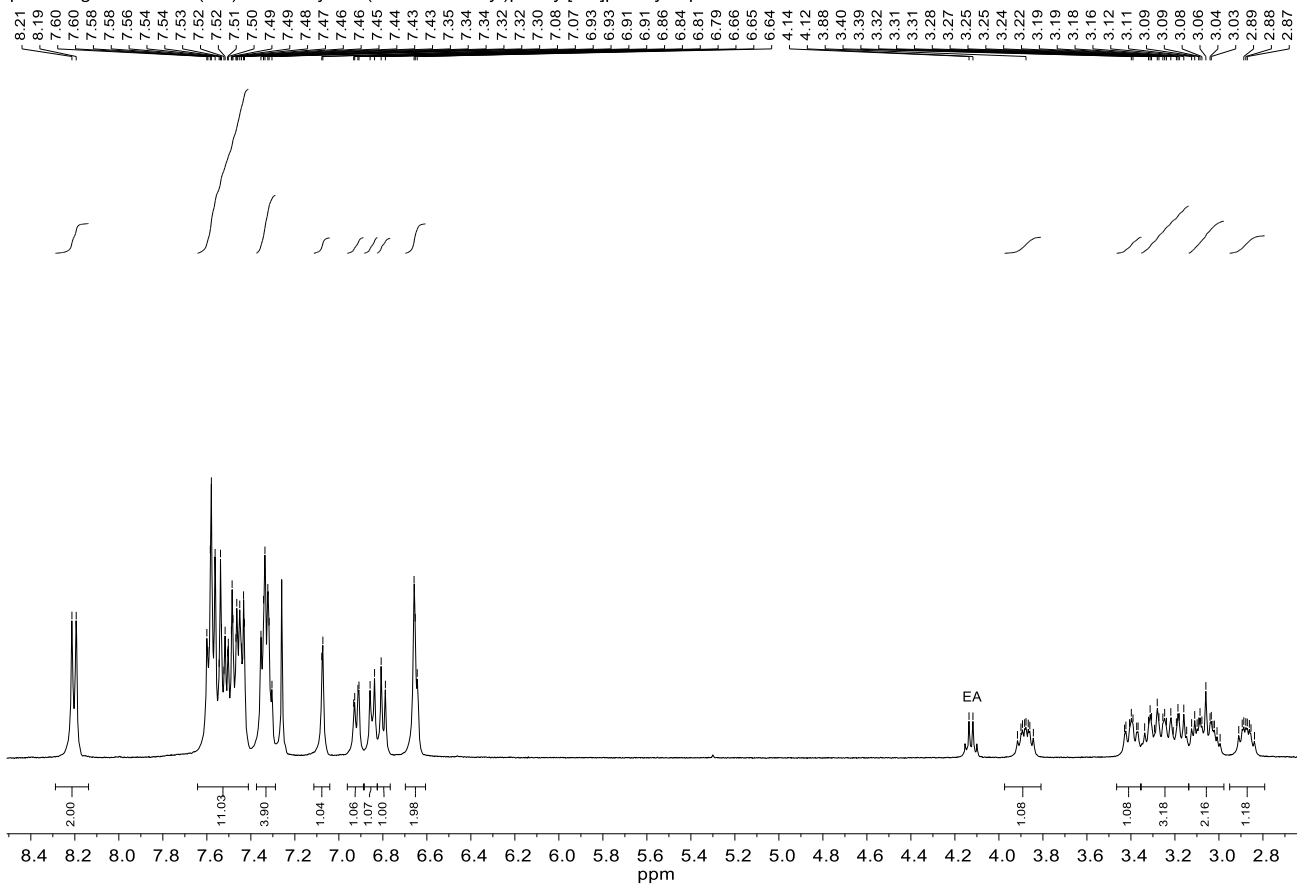
In a pressure vial were charged with (*rac*)-4-bromo-13-benzoyl[2.2]paracyclophane (**2**) (156.5 mg, 400  $\mu$ mol, 1.00 equiv.), 4-(*N*-carbazolyl)phenyl boronic acid (229 mg, 800  $\mu$ mol, 2.00 equiv.),  $K_3PO_4$  (170 mg, 800  $\mu$ mol, 2.00 equiv.),  $Pd(OAc)_2$  (8.98 mg, 40.0  $\mu$ mol, 10 mol%) and 2-dicyclohexylphosphino-2,6-diisopropoxybiphenyl ("RuPhos") (37.3 mg, 80.0  $\mu$ mol, 20 mol%). The sealed vial was evacuated and flushed

with argon three times. Through the septum 7 mL of degassed toluene and 1 mL of degassed water were added, then heated to 75 °C and stirred for 16 h. The reaction mixture was diluted in 50 mL of ethyl acetate and washed first with sat. aqueous  $NH_4Cl$  solution (3  $\times$  30 mL) and then with brine (30 mL). The organic layer was dried over  $Na_2SO_4$  and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, cyclohexane/ethyl acetate; 20/1) to yield 126 mg of the product as a white solid (227  $\mu$ mol, 57%).

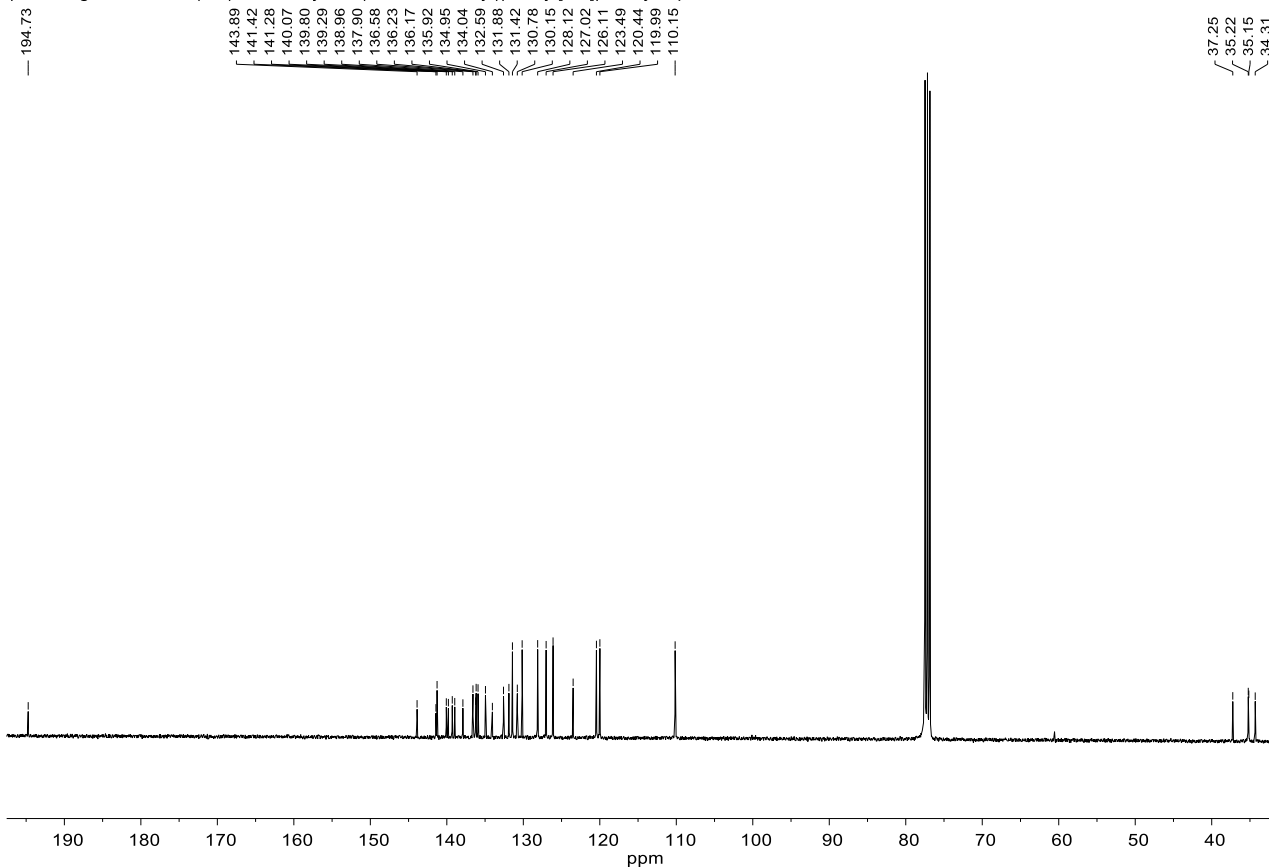
$R_f = 0.34$  (CH/EA 20:1). –  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta = 8.20$  (d,  $J = 7.8$  Hz, 2H), 7.64 – 7.40 (m, 11H), 7.33 (td,  $J = 7.4, 4.9$  Hz, 4H), 7.08 (d,  $J = 2.0$  Hz, 1H), 6.92 (dd,  $J = 7.8, 1.9$  Hz, 1H), 6.85 (d,  $J = 8.1$  Hz, 1H), 6.80 (d,  $J = 7.7$  Hz, 1H), 6.66 (d,  $J = 2.1$  Hz, 2H), 3.88 (ddd,  $J = 13.4, 9.3, 6.4$  Hz, 1H), 3.40 (ddd,  $J = 12.3, 9.2, 2.5$  Hz, 1H), 3.35 – 3.14 (m, 3H), 3.14 – 2.95 (m, 2H), 2.87 (ddd,  $J = 13.0, 9.2, 6.3$  Hz, 1H) ppm. –  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta = 194.73$  ( $C_{quat.}, CO$ ), 143.89 ( $C_{quat.}$ ), 141.42 ( $C_{quat.}$ ), 141.28 ( $C_{quat.}$ ), 140.07 ( $C_{quat.}$ ), 139.80 ( $C_{quat.}$ ), 139.29 ( $C_{quat.}$ ), 138.96 ( $C_{quat.}$ ), 137.90 ( $C_{quat.}$ ), 136.58 (+), 136.23 ( $C_{quat.}$ ), 136.17 (+), 135.92 (+), 134.95 (+), 134.04 ( $C_{quat.}$ ), 132.59 (+), 131.88 (+), 131.42 (+), 130.78 (+), 130.15 (+), 128.12 (+), 127.02 (+), 126.11 (+), 123.49 ( $C_{quat.}$ ), 120.44 (+), 119.99 (+), 110.15 (+), 37.25 (–), 35.22 (–), 35.15 (–), 34.31 (–) ppm. – Mp : 165-175 °C. – IR (ATR):  $\tilde{\nu} = 2922$  (vw), 1733 (vw), 1650 (vw), 1595 (vw), 1515 (vw), 1477 (vw), 1450 (w), 1334 (vw), 1315 (vw), 1269 (vw), 1230 (w), 978 (vw), 914 (vw), 837 (vw), 749 (vw), 723 (w), 700 (w), 632 (vw), 566 (vw), 525 (vw), 487 (vw), 424 (vw)  $cm^{-1}$  – MS (FAB, 3-NBA),  $m/z$ : 554  $[M+H]^+$ , 553  $[M]^+$ . – HRMS ( $C_{41}H_{31}NO$ ) calc.: 553.2406; found: 553.2405.



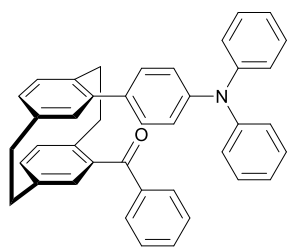
pseudo-geminal "cis" (rac)-4-Benzoyl-13-(4'-N-carbazolyl)phenyl[2.2]paracyclophane



pseudo-geminal "cis" (rac)-4-Benzoyl-13-(4'-N-carbazolyl)phenyl[2.2]paracyclophane



(rac, "cis") 4-Benzoyl-13-(4'-N-diphenylamino)phenyl[2.2]paracyclophane (3):

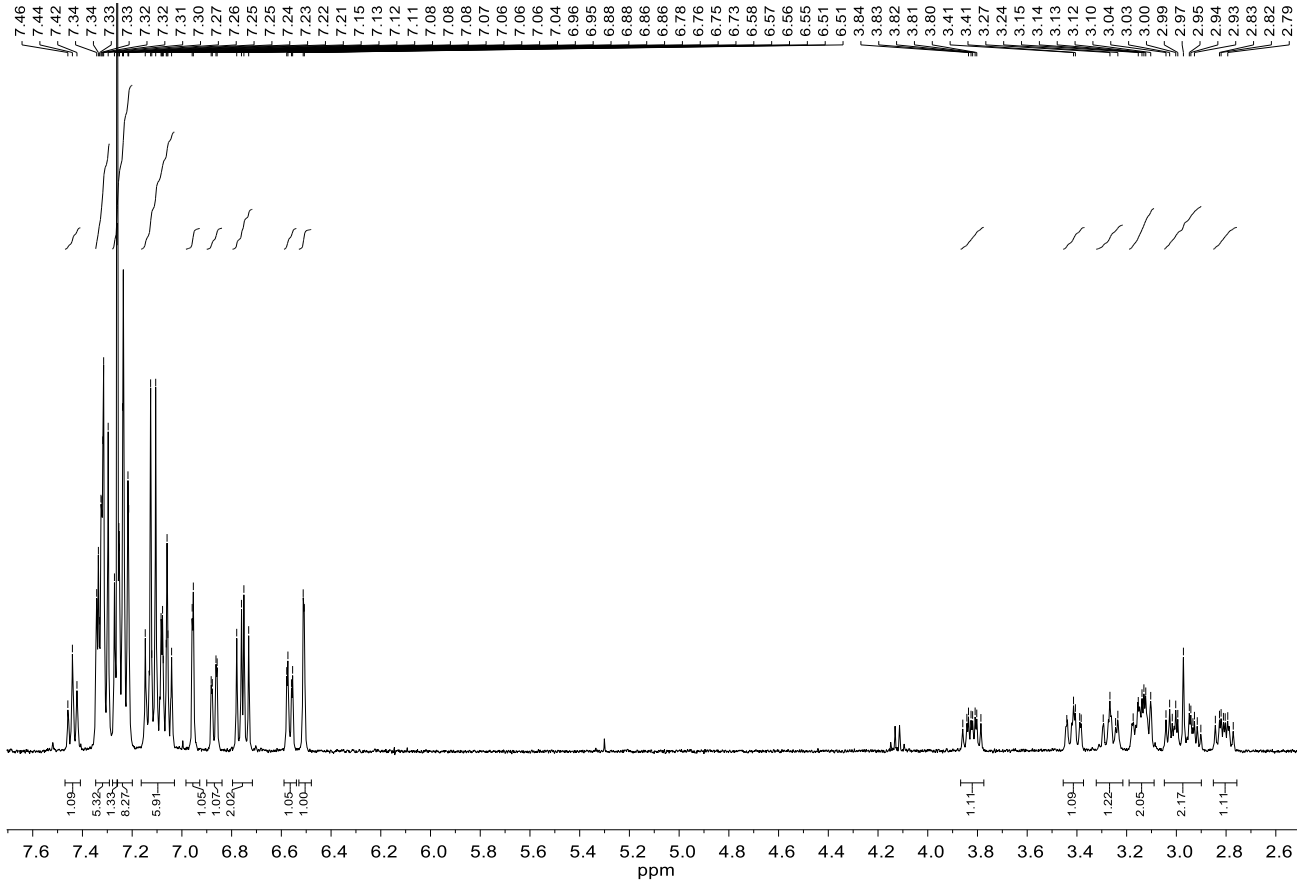


In a pressure vial were charged with (*rac*)-4-bromo-13-benzoyl[2.2]paracyclophane (**2**) (156.5 mg, 400  $\mu$ mol, 1.00 equiv.), 4-(*N*-diphenylamino)phenyl boronic acid (231 mg, 800  $\mu$ mol, 2.00 equiv.),  $K_3PO_4$  (170 mg, 800  $\mu$ mol, 2.00 equiv.),  $Pd(OAc)_2$  (4.50 mg, 20.0  $\mu$ mol, 5 mol%) and 2-dicyclohexylphosphino-2,6-diisopropoxybiphenyl ("RuPhos") (18.7 mg, 40.0  $\mu$ mol, 10 mol%). The sealed vial was evacuated and flushed

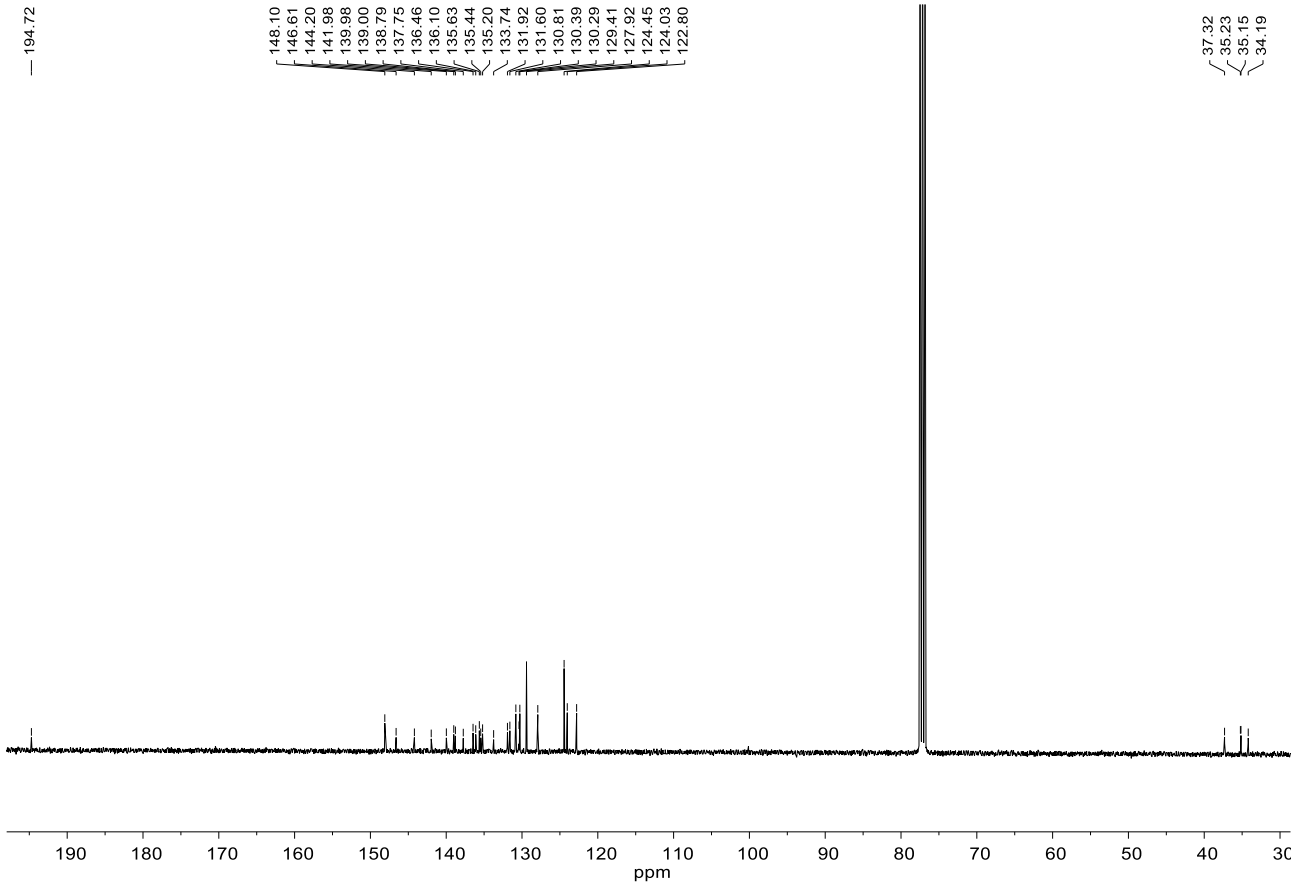
with argon three times. Through the septum 7 mL of degassed toluene and 1 mL of degassed water were added, then heated to 75 °C and stirred for 16 h. The reaction mixture was diluted in 50 mL of ethyl acetate and washed first with sat. aqueous  $NH_4Cl$  solution (3  $\times$  30 mL) and then with brine (30 mL). The organic layer was dried over  $Na_2SO_4$  and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, gradient of cyclohexane/ethyl acetate; 50/1 to 20/1) to yield 145 mg of the product as an off-white solid (261  $\mu$ mol, 65%).

$R_f=0.26$  (CH/EA 20:1) = 0.26. –  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  = 7.44 (t,  $J$  = 7.3 Hz, 1H), 7.36 – 7.29 (m, 5H), 7.28 – 7.20 (m, 7H), 7.16 – 7.02 (m, 6H), 6.96 (d,  $J$  = 1.9 Hz, 1H), 6.87 (dd,  $J$  = 7.7, 1.8 Hz, 1H), 6.76 (dd,  $J$  = 11.6, 7.7 Hz, 2H), 6.57 (dd,  $J$  = 7.6, 1.9 Hz, 1H), 6.51 (d,  $J$  = 1.9 Hz, 1H), 3.82 (ddd,  $J$  = 13.3, 9.2, 6.6 Hz, 1H), 3.47 – 3.35 (m, 1H), 3.33 – 3.22 (m, 1H), 3.20 – 3.08 (m, 2H), 3.07 – 2.89 (m, 2H), 2.87 – 2.73 (m, 1H) ppm. –  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  = 194.72 ( $C_{quat.}$ , CO), 148.10 ( $C_{quat.}$ ), 146.61 ( $C_{quat.}$ ), 144.20 ( $C_{quat.}$ ), 141.98 ( $C_{quat.}$ ), 139.98 ( $C_{quat.}$ ), 139.00 ( $C_{quat.}$ ), 138.79 ( $C_{quat.}$ ), 137.75 ( $C_{quat.}$ ), 136.46 (+), 136.10 (+), 135.63 (+), 135.44 ( $C_{quat.}$ ), 135.20 (+), 133.74 ( $C_{quat.}$ ), 131.92 (+), 131.60 (+), 130.81 (+), 130.39 (+), 130.29 (+), 129.41 (+), 127.92 (+), 124.45 (+), 124.03 (+), 122.80 (+), 37.32 (–), 35.23 (–), 35.15 (–), 34.19 (–) ppm. – Mp : 91-95 °C. – IR (ATR):  $\tilde{\nu}$  = 2922 (vw), 1736 (w), 1649 (w), 1588 (w), 1509 (w), 1486 (w), 1445 (w), 1316 (w), 1268 (m), 1175 (w), 1074 (vw), 1046 (vw), 977 (vw), 916 (vw), 834 (w), 800 (vw), 751 (w), 696 (m), 661 (w), 648 (w), 634 (w), 550 (vw), 512 (w), 489 (vw)  $cm^{-1}$ . – MS (FAB, 3-NBA),  $m/z$ : 556  $[M+H]^+$ , 555  $[M]^+$ . – HRMS ( $C_{41}H_{33}NO$ ) calc.: 555.2562; found: 555.2561.

pseudo-geminal "cis" (rac)-4-Benzoyl-13-(4'-N-diphenylamino)phenyl[2.2]paracyclophane



pseudo-geminal "cis" (rac)-4-Benzoyl-13-(4'-N-diphenylamino)phenyl[2.2]paracyclophane



### 3. Photophysical Characterization

*Photophysical measurements.* Optically dilute solutions of concentrations in the order of  $10^{-5}$  or  $10^{-6}$  M were prepared in HPLC grade solvent for absorption and emission analysis. Absorption spectra were recorded at room temperature on a Shimadzu UV-1800 double beam spectrophotometer. Aerated solutions were bubbled with compressed air for 5 minutes whereas degassed solutions were prepared via three freeze-pump-thaw cycles prior to emission analysis using an in-house adapted fluorescence cuvette, itself purchased from Starna. Steady-state emission and time-resolved emission spectra were recorded at 298 K using an Edinburgh Instruments F980 fluorimeter. Samples were excited at 360 nm for steady-state measurements and at 378 nm for time-resolved measurements. Photoluminescence quantum yields for solutions were determined using the optically dilute method<sup>8</sup> in which four sample solutions with absorbance at 360 nm being ca. 0.10, 0.080, 0.060 and 0.040 were used. Their emission intensities were compared with those of a reference, quinine sulfate, whose quantum yield ( $\Phi_r$ ) in 1 N H<sub>2</sub>SO<sub>4</sub> was determined to be 54.6% using absolute method.<sup>9</sup> The quantum yield of sample,  $\Phi_{PL}$ , can be determined by the equation  $\Phi_{PL} = \Phi_r(A_r/A_s)((I_s/I_r)(n_s/n_r)^2)$ , where A stands for the absorbance at the excitation wavelength ( $\lambda_{exc}$ : 360 nm), I is the integrated area under the corrected emission curve and n is the refractive index of the solvent with the subscripts “s” and “r” representing sample and reference respectively. An integrating sphere was employed for quantum yield measurements for thin film samples.

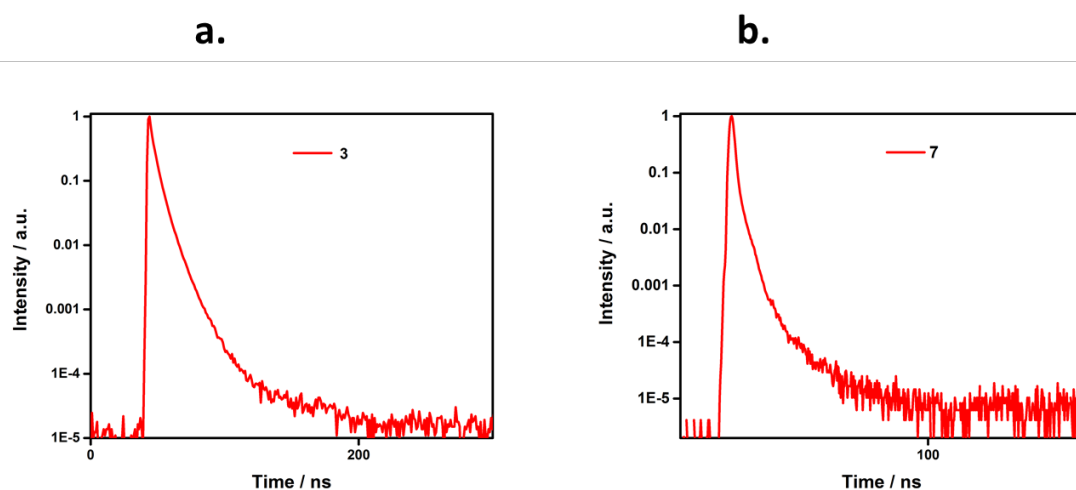


Figure S1. Transient PL decay profiles of a.) 3 and b.) 7 in degassed PhMe ( $\lambda_{exc} = 378$  nm).

### 3.1 Evaluation of lifetimes.

Prompt and delayed lifetimes were determined by a bi-exponential fit of the decay curves using the following parameters:

$$y = ae^{-t/\tau_p} + be^{-t/\tau_d}$$

where, a and b are the pre exponential factors,  $\tau_p$  and  $\tau_d$  are the prompt and delayed components and t, time is the variable parameter.

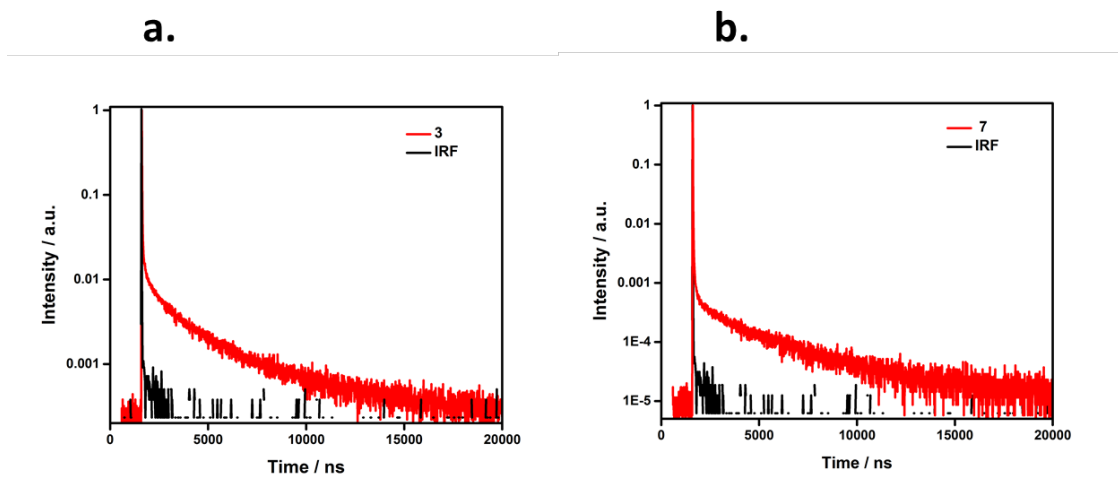


Figure S2. Transient PL decay profiles of a.) **3** and b.) **7** in 15 wt.% doped films in mCP ( $\lambda_{\text{exc}}$  378 nm), where IRF is the instrument response function.

Table S1. Absolute  $\Phi_{\text{PL}}$  measurements of doped films of **3** and **7** in different host materials as a function of doping concentrations.

Host Material <sup>a</sup>	$\Phi_{\text{PL}} / \%$	
	<b>3</b>	<b>7</b>
1 wt. % DPEPO	4.0	3.8
3 wt. % DPEPO	4.2	4.4
5 wt. % DPEPO	5.0	4.5
7 wt. % PPT	7.0	8.3

1 wt. % CzSi	7.7	7.6
3 wt. % CzSi	7.8	8.8
10 wt. % CzSi	8.6	9.3
1 wt. % mCP	7.0	7.0
3 wt. % mCP	7.4	7.7
15 wt. % mCP	12.2	15.0
20 wt. % mCP	5.0	4.3
25 wt.% mCP	2.1	3.6

<sup>a</sup> Thin films were prepared by vacuum deposition and values were determined using an integrating sphere ( $\lambda_{\text{exc}} = 360 \text{ nm}$ ); degassing was done by  $\text{N}_2$  purge.

### 3.2 Evaluation of rate constants.

The absolute rate constants for a radiative and non-radiative processes can only be explicitly calculated for a monoexponential decay. For a bi- or multiexponential decay, we assumed that the  $k_{\text{nr}}^{\text{S}}$  approaches zero and therefore the intersystem crossing can be defined as  $\Phi_{\text{ISC}} = 1 - \Phi_{\text{p}}$ .<sup>14</sup> following the method described by Masui *et al.*<sup>14</sup> The rate constants ( $k_{\text{r}}^{\text{S}}$ ,  $k_{\text{nr}}^{\text{T}}$ ,  $k_{\text{ISC}}$ ,  $k_{\text{rISC}}$ ) associated with **3** and **7** were evaluated as follows, where

$k_{\text{p}}$  and  $k_{\text{d}}$  represent the prompt and delayed fluorescence rates which were calculated from the experimentally measured prompt and delayed lifetimes:

$$k_{\text{p}} = 1 / \tau_{\text{p}}, \quad k_{\text{d}} = 1 / \tau_{\text{d}}.$$

The prompt and delayed fluorescence quantum efficiencies,  $\Phi_{\text{p}}$  and  $\Phi_{\text{d}}$  were determined by integrating the transient PL signal from 0 to 500 ns as the prompt components and from 500 ns to 20  $\mu\text{s}$  as the delayed components.<sup>14</sup>

Therefore,

$$k_{\text{r}}^{\text{S}} = \Phi_{\text{p}} k_{\text{p}}; \quad k_{\text{ISC}} = (1 - \Phi_{\text{p}}) k_{\text{p}}.$$

$$k_{\text{rISC}} = (k_{\text{p}} k_{\text{d}} / k_{\text{ISC}}) * \Phi_{\text{d}} / \Phi_{\text{p}}.$$

$$k_{\text{nr}}^{\text{T}} = k_{\text{d}} - \Phi_{\text{p}} k_{\text{rISC}}$$

where  $k_r^S$  is the radiative decay rate of the singlet state,  $k_{ISC}$  is the intersystem crossing rate,  $k_{rISC}$  is the reverse intersystem crossing rate, and  $k_{nr}^T$  is non-radiative decay rate of the triplet state.

Table S2. Rate constants of isomers **3** and **7**, determined in PhMe and 15 wt.% doped films in mCP.

<b>Material</b>	$k_r^S$ <sup>a</sup> / x 10 <sup>6</sup> s <sup>-1</sup>	$k_r^S$ <sup>b</sup> / x 10 <sup>6</sup> s <sup>-1</sup>	$k_{rISC}$ <sup>a</sup> / x 10 <sup>5</sup> s <sup>-1</sup>	$k_{ISC}$ <sup>b</sup> / x 10 <sup>7</sup> s <sup>-1</sup>	$k_{ISC}$ <sup>a</sup> / x 10 <sup>7</sup> s <sup>-1</sup>	$k_{nr}^T$ <sup>a</sup> / x 10 <sup>5</sup> s <sup>-1</sup>
<b>3</b>	6.3	63	7.0	5.2	71	4.7
<b>7</b>	18	174	3.1	11.0	11	2.4

<sup>a</sup>Calculated from the transient PL spectra measured in 15 wt.% doped films in mCP. <sup>b</sup>Calculated from the transient PL spectra measured in degassed PhMe solution.

## 4. DFT modelling.

### Computational methodology

The calculations were performed with the Gaussian 09<sup>10</sup> revision D.018 suite. Initially the geometries of all the derivatives were fully optimized using a DFT methodology employing the PBE0<sup>11</sup> functional with the standard Pople<sup>12</sup> 6-31G(d,p) basis set and Tamm–Dancoff approximation (TDA) was treated as a variant of Time-dependent density functional theory (TD-DFT). The molecular orbitals were visualized using GaussView 5.0 software<sup>13</sup>.

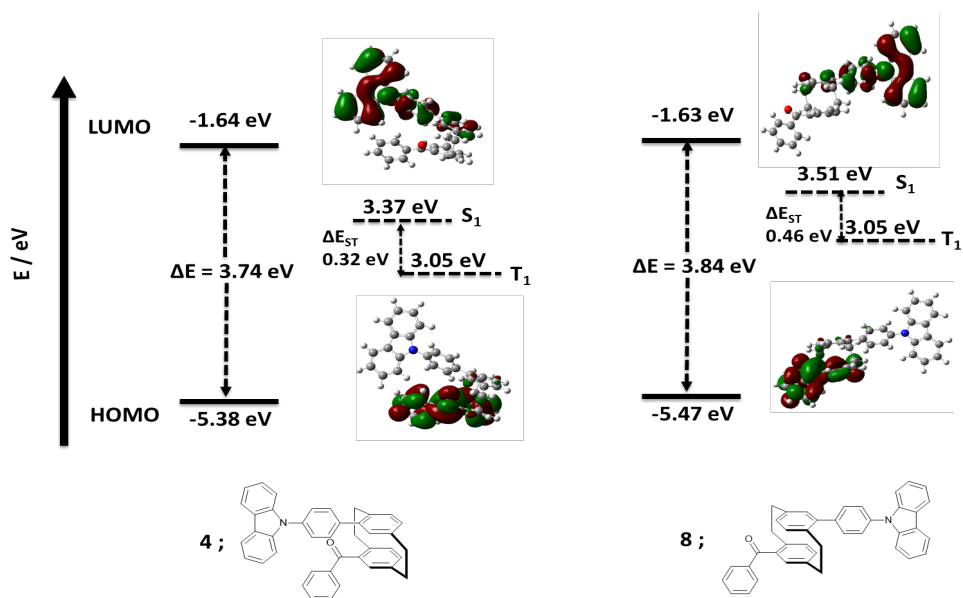


Figure S3. HOMO-LUMO profiles and excited state dynamics of cis and trans isomers **4** and **8**, respectively (PBE0/6-31G(d,p)).

Table S3. Optimized atomic coordinates of isomer **3** obtained from DFT calculations.

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.933515	-1.932747	0.211264
2	6	0	2.754054	-2.283639	1.305525
3	6	0	4.031951	-2.772284	1.015989
4	6	0	4.606983	-2.638072	-0.240321
5	6	0	3.898334	-1.995732	-1.256698
6	6	0	2.535774	-1.798333	-1.049342
7	1	0	5.653281	-2.897477	-0.383184
8	1	0	1.951976	-1.355286	-1.850336

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9	6	0	4.596044	-1.280430	-2.383054
10	1	0	3.888438	-1.101920	-3.194878
11	1	0	5.421765	-1.881722	-2.778185
12	6	0	2.455727	-1.942875	2.743274
13	6	0	5.183350	0.126740	-1.938155
14	1	0	4.910269	0.855868	-2.703164
15	1	0	6.275640	0.055945	-1.911511
16	6	0	2.873261	-0.452653	3.128129
17	1	0	1.978040	0.111919	3.410601
18	1	0	3.503982	-0.496754	4.021666
19	6	0	4.713635	0.545715	-0.570025
20	6	0	5.509555	0.227322	0.532520
21	6	0	3.423736	1.043487	-0.290417
22	6	0	4.962823	0.066511	1.800231
23	1	0	6.544260	-0.060721	0.364232
24	6	0	2.891262	0.899397	0.997373
25	6	0	3.596014	0.253655	2.011517
26	1	0	5.579585	-0.343077	2.596866
27	1	0	1.847181	1.154813	1.151404
28	6	0	2.511946	1.500431	-1.371354
29	8	0	2.561132	1.028693	-2.500480
30	6	0	1.487406	2.544771	-1.063668
31	6	0	1.681834	3.532153	-0.093136

32	6	0	0.323762	2.561320	-1.839562
33	6	0	0.724780	4.523827	0.095696
34	1	0	2.592091	3.532360	0.498109
35	6	0	-0.638114	3.542066	-1.639500
36	1	0	0.199605	1.793859	-2.596678
37	6	0	-0.434853	4.528498	-0.674141
38	1	0	0.887459	5.297410	0.840051
39	1	0	-1.545344	3.544291	-2.236414
40	1	0	-1.177933	5.307982	-0.530279
41	1	0	3.024169	-2.623315	3.384473
42	1	0	1.400291	-2.090254	2.987970
43	1	0	4.641692	-3.141482	1.837742
44	6	0	0.492974	-1.595374	0.292553
45	6	0	-0.356923	-2.047110	-0.729706
46	6	0	-0.090434	-0.800436	1.287743
47	6	0	-1.698235	-1.705355	-0.777573
48	1	0	0.054022	-2.680043	-1.510601
49	6	0	-1.437396	-0.469281	1.264657
50	1	0	0.512120	-0.406142	2.094485
51	6	0	-2.261020	-0.902854	0.222017
52	1	0	-2.321113	-2.061717	-1.591437
53	1	0	-1.853279	0.151882	2.050992
54	7	0	-3.618696	-0.535739	0.174984

55	6	0	-4.578787	-1.444679	-0.319634
56	6	0	-4.023574	0.746209	0.602151
57	6	0	-5.592978	-1.004519	-1.177006
58	6	0	-4.526677	-2.795578	0.040783
59	6	0	-5.227927	0.909676	1.296551
60	6	0	-3.228919	1.868764	0.340735
61	6	0	-6.540304	-1.900852	-1.655461
62	1	0	-5.630869	0.042582	-1.459721
63	6	0	-5.467131	-3.687826	-0.458902
64	1	0	-3.742707	-3.135976	0.709718
65	6	0	-5.630485	2.173289	1.710092
66	1	0	-5.842445	0.040037	1.505386
67	6	0	-3.631048	3.123650	0.778868
68	1	0	-2.293395	1.753011	-0.196996
69	6	0	-6.481679	-3.247415	-1.305040
70	1	0	-7.321992	-1.544627	-2.320121
71	1	0	-5.413178	-4.733872	-0.171577
72	1	0	-6.568295	2.282612	2.247098
73	6	0	-4.834360	3.288060	1.460264
74	1	0	-2.994638	3.979507	0.574803
75	1	0	-7.218880	-3.946345	-1.687467
76	1	0	-5.147244	4.272299	1.794507

Table S4. Optimized atomic coordinates of isomer 4 obtained from DFT calculations.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.035728	-1.918506	-0.100288
2	6	0	2.851830	-2.426739	0.932614
3	6	0	4.142091	-2.835980	0.580587
4	6	0	4.721832	-2.484955	-0.630264
5	6	0	4.008980	-1.699514	-1.537207
6	6	0	2.639575	-1.569905	-1.317912
7	1	0	5.774638	-2.695916	-0.802052
8	1	0	2.048364	-1.021193	-2.045044
9	6	0	4.707039	-0.800936	-2.522750
10	1	0	4.005077	-0.497144	-3.301266
11	1	0	5.541923	-1.322250	-3.003049
12	6	0	2.534074	-2.331320	2.402832
13	6	0	5.277253	0.517036	-1.844733
14	1	0	4.996757	1.360939	-2.477576
15	1	0	6.370301	0.455692	-1.826694
16	6	0	2.950772	-0.929355	3.038141
17	1	0	2.053284	-0.422902	3.409628
18	1	0	3.577820	-1.124915	3.913704
19	6	0	4.799173	0.696283	-0.427820
20	6	0	5.594988	0.209564	0.611787
21	6	0	3.499422	1.119435	-0.077758
22	6	0	5.045546	-0.171582	1.830907
23	1	0	6.635132	-0.029946	0.405124
24	6	0	2.967859	0.758195	1.165997

25	6	0	3.675616	-0.040489	2.062080
26	1	0	5.665071	-0.702110	2.550266
27	1	0	1.922911	0.980224	1.357436
28	6	0	2.576168	1.724187	-1.074177
29	8	0	2.643243	1.447620	-2.265229
30	6	0	1.509810	2.656892	-0.599718
31	6	0	1.675826	3.491443	0.509946
32	6	0	0.326488	2.723523	-1.341960
33	6	0	0.668696	4.380192	0.871035
34	1	0	2.600607	3.452840	1.077137
35	6	0	-0.684988	3.598743	-0.970640
36	1	0	0.222089	2.075678	-2.206201
37	6	0	-0.512642	4.430166	0.135832
38	1	0	0.807166	5.036413	1.724950
39	1	0	-1.611693	3.630978	-1.535263
40	1	0	-1.299338	5.123039	0.420754
41	1	0	3.090082	-3.113347	2.928489
42	1	0	1.474700	-2.512038	2.603782
43	1	0	4.754202	-3.322537	1.336710
44	6	0	0.586660	-1.627404	0.022513
45	6	0	-0.253543	-1.981145	-1.045017
46	6	0	-0.001303	-0.965029	1.107634
47	6	0	-1.603903	-1.665949	-1.047341
48	1	0	0.172428	-2.508829	-1.892947
49	6	0	-1.356103	-0.660790	1.124928
50	1	0	0.601456	-0.657659	1.951156
51	6	0	-2.165121	-0.997451	0.041701
52	1	0	-2.229352	-1.923847	-1.896151
53	1	0	-1.793213	-0.152796	1.978548

54	7	0	-3.530829	-0.649926	0.042780
55	6	0	-4.034011	0.629881	0.249276
56	6	0	-4.594591	-1.515840	-0.182649
57	6	0	-3.347485	1.820849	0.477022
58	6	0	-5.444274	0.588492	0.154361
59	6	0	-4.582150	-2.892332	-0.400137
60	6	0	-5.802781	-0.783120	-0.119389
61	6	0	-4.103146	2.976381	0.627863
62	1	0	-2.264531	1.850752	0.523025
63	6	0	-6.178047	1.765475	0.310905
64	6	0	-5.805857	-3.525593	-0.574832
65	1	0	-3.651524	-3.449220	-0.423944
66	6	0	-7.018176	-1.445108	-0.298777
67	6	0	-5.502848	2.954098	0.551034
68	1	0	-3.592127	3.917328	0.810471
69	1	0	-7.261891	1.749550	0.240802
70	6	0	-7.012640	-2.813515	-0.529768
71	1	0	-5.825335	-4.597682	-0.746539
72	1	0	-7.954116	-0.895699	-0.252811
73	1	0	-6.061294	3.876448	0.676706
74	1	0	-7.950620	-3.340999	-0.671920

Table S5. Optimized atomic coordinates of isomer **6** obtained from DFT calculations.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	-0.608969	-1.578992	-0.253143
2	6	0	-1.414522	-1.287815	-1.376353

3	6	0	-2.677019	-1.880442	-1.426694
4	6	0	-3.247392	-2.484423	-0.312129
5	6	0	-2.563353	-2.487174	0.903535
6	6	0	-1.205280	-2.164887	0.867347
7	1	0	-3.289820	-1.730907	-2.312976
8	1	0	-4.285156	-2.801935	-0.341254
9	1	0	-0.610047	-2.277733	1.770971
10	6	0	-3.316702	-2.573598	2.204852
11	1	0	-2.731761	-3.112108	2.957907
12	1	0	-4.248406	-3.120619	2.048079
13	6	0	-1.131963	-0.138220	-2.317808
14	1	0	-1.836250	-0.208639	-3.152619
15	6	0	-3.689115	-1.147283	2.800101
16	1	0	-4.750397	-1.162915	3.054237
17	6	0	-1.308342	1.276033	-1.630028
18	1	0	-0.317133	1.666841	-1.380349
19	1	0	-1.745295	1.957475	-2.368320
20	6	0	-3.355132	-0.024786	1.855487
21	6	0	-4.111997	0.288909	0.706593
22	6	0	-2.116907	0.608149	1.973066
23	6	0	-3.488467	0.899911	-0.388541
24	6	0	-1.508706	1.213781	0.879809
25	6	0	-2.130318	1.212375	-0.369900

26	1	0	-4.045987	0.988966	-1.317738
27	1	0	-0.481466	1.558738	0.962701
28	1	0	-3.121774	-0.995139	3.724025
29	1	0	-1.553016	0.488961	2.895573
30	6	0	-5.510689	-0.191355	0.553319
31	8	0	-5.870689	-1.276822	0.992365
32	6	0	-6.494282	0.676499	-0.161756
33	6	0	-6.342595	2.062566	-0.274842
34	6	0	-7.640455	0.066207	-0.682720
35	6	0	-7.317667	2.821846	-0.913015
36	1	0	-5.469497	2.545374	0.151822
37	6	0	-8.605366	0.823324	-1.330904
38	1	0	-7.749132	-1.006849	-0.561581
39	6	0	-8.444296	2.203575	-1.447679
40	1	0	-7.199281	3.898476	-0.989573
41	1	0	-9.487121	0.341905	-1.743142
42	1	0	-9.201607	2.797637	-1.951006
43	6	0	0.806366	-1.156843	-0.186662
44	6	0	1.343355	-0.568831	0.965858
45	6	0	1.664625	-1.358344	-1.276149
46	6	0	2.674900	-0.180094	1.025079
47	1	0	0.703717	-0.411432	1.828254
48	6	0	2.990265	-0.951450	-1.237180



49	1	0	1.281311	-1.851303	-2.164416
50	6	0	3.503143	-0.354459	-0.083906
51	1	0	3.083586	0.259316	1.929521
52	1	0	3.636379	-1.088970	-2.098371
53	7	0	4.845677	0.071507	-0.039524
54	6	0	5.957767	-0.706412	-0.343843
55	6	0	5.275565	1.351118	0.295948
56	6	0	6.024807	-2.052670	-0.697541
57	6	0	7.121860	0.083481	-0.200057
58	6	0	4.524899	2.475512	0.634055
59	6	0	6.686045	1.398198	0.207551
60	6	0	7.282920	-2.593988	-0.928632
61	1	0	5.128405	-2.657772	-0.780810
62	6	0	8.373319	-0.486104	-0.438249
63	6	0	5.214019	3.650287	0.906463
64	1	0	3.441646	2.436614	0.675788
65	6	0	7.353096	2.591741	0.486730
66	6	0	8.446725	-1.822153	-0.806157
67	1	0	7.363707	-3.640546	-1.206833
68	1	0	9.275875	0.108856	-0.332055
69	6	0	6.612818	3.711391	0.839465
70	1	0	4.653430	4.541054	1.174025
71	1	0	8.436286	2.642266	0.423460

72	1	0	9.413423	-2.277823	-0.996101
73	1	0	7.118852	4.645767	1.061027
74	1	0	-0.129460	-0.167013	-2.750698

Table S6. Optimized atomic coordinates of isomer 7 obtained from DFT calculations.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.402561	-1.483722	0.016601
2	6	0	-1.207633	-1.483018	-1.143303
3	6	0	-2.460267	-2.092891	-1.054847
4	6	0	-3.022922	-2.419949	0.171937
5	6	0	-2.337434	-2.139129	1.356427
6	6	0	-0.986432	-1.813823	1.245428
7	1	0	-3.071859	-2.169308	-1.951585
8	1	0	-4.056622	-2.750336	0.221357
9	1	0	-0.387918	-1.702535	2.147255
10	6	0	-3.102059	-1.932928	2.637224
11	1	0	-2.523678	-2.272171	3.503233
12	1	0	-4.029671	-2.507245	2.602879
13	6	0	-0.917234	-0.591138	-2.328028
14	1	0	0.140534	-0.324801	-2.347598

15	1	0	-1.130103	-1.112700	-3.267443
16	6	0	-3.488855	-0.412837	2.870511
17	1	0	-4.510128	-0.385827	3.255751
18	6	0	-1.767901	0.750576	-2.314198
19	1	0	-1.104906	1.572189	-2.606115
20	1	0	-2.546747	0.684458	-3.080519
21	6	0	-3.328081	0.412999	1.621662
22	6	0	-4.220983	0.392120	0.532324
23	6	0	-2.109484	1.063918	1.413494
24	6	0	-3.748966	0.697096	-0.751863
25	6	0	-1.648724	1.357008	0.136900
26	6	0	-2.413434	1.020316	-0.981960
27	1	0	-4.407137	0.523895	-1.599963
28	1	0	-0.626649	1.704996	0.007457
29	1	0	-2.826367	0.002523	3.637089
30	1	0	-1.440189	1.198438	2.260017
31	6	0	-5.592842	-0.162658	0.669904
32	8	0	-5.829663	-1.117215	1.400251
33	6	0	-6.701149	0.459100	-0.115514
34	6	0	-6.646841	1.773599	-0.590665
35	6	0	-7.856885	-0.300618	-0.325677
36	6	0	-7.729523	2.312995	-1.277289
37	1	0	-5.762551	2.375347	-0.407833

38	6	0	-8.930461	0.234356	-1.022676
39	1	0	-7.885008	-1.309937	0.072344
40	6	0	-8.867448	1.543072	-1.500344
41	1	0	-7.685756	3.336926	-1.636031
42	1	0	-9.820455	-0.364206	-1.192649
43	1	0	-9.709468	1.963966	-2.042275
44	6	0	1.003877	-1.029895	-0.007186
45	6	0	1.499187	-0.129669	0.944171
46	6	0	1.901508	-1.511696	-0.969668
47	6	0	2.827027	0.272682	0.940911
48	1	0	0.827994	0.261655	1.703025
49	6	0	3.225622	-1.102237	-0.995526
50	1	0	1.547940	-2.227046	-1.706889
51	6	0	3.707758	-0.204229	-0.035699
52	1	0	3.190210	0.966962	1.691886
53	1	0	3.902385	-1.485435	-1.752479
54	7	0	5.055344	0.206837	-0.051743
55	6	0	6.072480	-0.728921	-0.334405
56	6	0	5.995494	-2.032113	0.169999
57	6	0	7.170351	-0.365744	-1.122817
58	6	0	6.995141	-2.952499	-0.118399
59	1	0	5.147137	-2.314477	0.785006
60	6	0	8.174124	-1.288359	-1.388829

61	1	0	7.228870	0.642722	-1.519386
62	6	0	8.092576	-2.587526	-0.893962
63	1	0	6.920703	-3.960087	0.280227
64	1	0	9.020285	-0.991094	-2.001513
65	1	0	8.875338	-3.307552	-1.110698
66	6	0	5.387663	1.545108	0.242524
67	6	0	6.513563	1.843325	1.018591
68	6	0	4.593255	2.593034	-0.237095
69	6	0	6.839107	3.164600	1.297881
70	1	0	7.127797	1.032663	1.396858
71	6	0	4.916778	3.909739	0.064638
72	1	0	3.723089	2.363876	-0.843819
73	6	0	6.042641	4.206071	0.828860
74	1	0	7.716345	3.379180	1.901332
75	1	0	4.289913	4.711452	-0.314962
76	1	0	6.296351	5.236667	1.056016

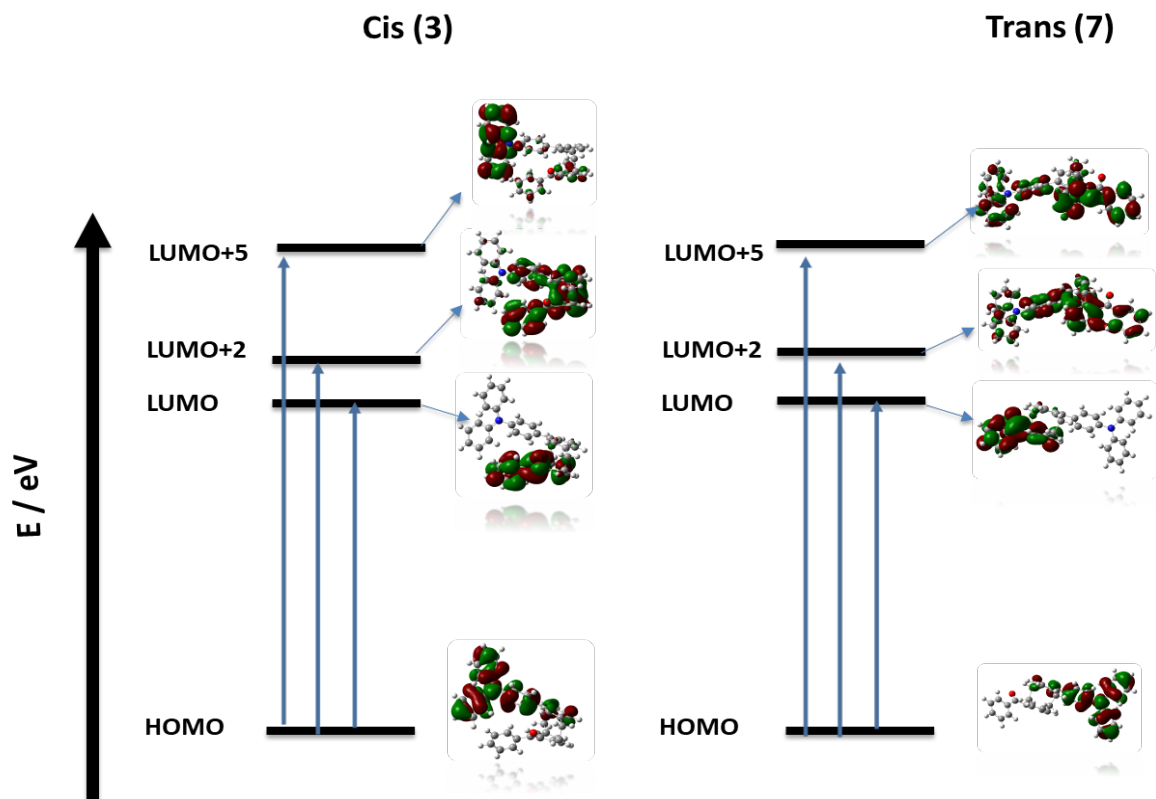


Figure S4. Natural transition orbital diagrams for the transitions H  $\rightarrow$  L, H  $\rightarrow$  L+2 and H  $\rightarrow$  L+5 in isomers **3** and **7**.

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