SUPPORTING INFORMATION

Substitution Pattern Controlled Quantum Interference in [2.2]Paracyclophane-Based Single-Molecule Junctions

Ksenia Reznikova,†,# Chunwei Hsu,‡,# Werner M. Schosser,§,# Almudena Gallego,† Katawoura Beltako,§ Fabian Pauly,*,# Herre S. J. van der Zant,*,‡ Marcel Mayor*,†,¶,¤

†Department of Chemistry, University of Basel, St. Johannis-Ring 19, 4056 Basel (Switzerland)
‡Kavli Institute of Nanoscience, Delft University of Technology, Lorentzweg 1, Delft 2628 CJ (The Netherlands)
§Institute of Physics, University of Augsburg, Universitätsstraße 1, 86159 Augsburg (Germany)
¶Institute for Nanotechnology, Karlsruhe Institute of Technology (KIT), P. O. Box 3640, 76021 Karlsruhe (Germany)
¤Lehn Institute of Functional Materials, School of Chemistry, Sun Yat-Sen University, Guangzhou 510274 (China)

*To whom correspondence should be addressed, Email: fabian.pauly@uni-a.de, h.s.j.vanderzant@tudelft.nl, marcel.mayor@unibas.ch

# These authors contributed equally to this work.
# Table of Contents

1. Synthesis and Characterization ........................................................................................................ 3
   1.1 Experimental Procedures .................................................................................................................. 4
   1.2 Characterization .............................................................................................................................. 10
   1H, 13C{1H} NMR (CDCl₃, 500/126 MHz) and HR-MS spectra of ps-para(para StBu PCP (9) .......... 10
   1H, 13C{1H} NMR (CDCl₃, 500/126 MHz) and HR-MS spectra of ps-para(para PCP (1a) ............. 14
   1H, 13C{1H} NMR (CDCl₃, 500/126 MHz) and HR-MS spectra of ps-para-meta StBu PCP (10) ....... 18
   1H, 13C{1H} NMR (CDCl₃, 500/126 MHz) and HR-MS spectra of ps-para-meta PCP (3a) .......... 22
   1H, 13C{1H} NMR (CDCl₃, 500/126 MHz) and HR-MS spectra of ps-meta-para StBu PCP (11) ....... 26
   1H, 13C{1H} NMR (CDCl₃, 500/126 MHz) and HR-MS spectra of ps-meta-para PCP (2a) ............. 30
   1H, 13C{1H} NMR (CDCl₃, 500/126 MHz) and HR-MS spectra of ps-meta-meta StBu PCP (12) ....... 34
   1H, 13C{1H} NMR (CDCl₃, 500/126 MHz) and HR-MS spectra of ps-meta-meta PCP (4a) ............. 38

2. Transport Measurements .................................................................................................................... 42
   2.1 Mechanically Controlled Break Junction ....................................................................................... 42
   2.2 Fast-Breaking Measurements ......................................................................................................... 42
   2.3 Distance-Modulation Measurements ............................................................................................. 43
   2.4 Estimation of the Gauge Factor ..................................................................................................... 44
   2.5 Stick-Slip Motion in Molecular Junctions ....................................................................................... 45

3. Transport Calculations ...................................................................................................................... 46
   3.1 DFT Calculation Setup .................................................................................................................. 46
   3.2 Transmission Maps and Stick-Slip Motion in the Top-Top Configuration .................................... 47
   3.3 Quantum Interference Effects and Symmetry Rules ..................................................................... 50
   3.4 Transmission Eigenchannels ......................................................................................................... 51

4. References ......................................................................................................................................... 52
1. Synthesis and Characterization

**General Remarks:** All commercially available compounds were purchased from Sigma-Aldrich, Acros, Apollo Scientific, Alfa Aesar, and Fluorochem and used without further purification. Anhydrous solvents were purchased from Sigma-Aldrich and stored over molecular sieves (4 Å). All reactions with reagents that are easily oxidized or hydrolyzed were performed under argon using Schlenk techniques with anhydrous solvents in oven-dried glassware. Column chromatography was performed on silica gel P60 (40-63 µm) from Silicycle™ using technical grade solvents. TLC was performed with silica gel 60 F254 aluminum sheets with a thickness of 0.25 mm purchased from Merck. Melting points were measured on a Büchi M-565 melting point apparatus and are uncorrected. $^1$H-NMR and $^{13}$C{$^1$H} NMR experiments were performed on Bruker Avance III NMR spectrometers operating at 500 MHz and 126 MHz proton frequencies, respectively. The instruments were equipped with an indirect-detection 5 mm BBI probe and with actively shielded z-gradients. The chemical shifts are reported in parts per million (ppm) referenced to the residual solvent peak, and the coupling constants ($J$) are given in hertz (Hz). All spectra were recorded at 298.15 K. For high-resolution mass spectra (HR-MS), a HR-ESI-ToF-MS measurement on a maXis™ 4G instrument from Bruker was used. Since the synthesized compounds 1a-4a as well as 9-12 shown in this publication were less prone to form adducts with common ions like H$^+$, NH$_4^+$, K$^+$ or Na$^+$, the characteristic binding of silver ions to aromatic hydrocarbons$^{1,2}$ was used to increase the signal intensity in the HR-ESI-ToF-MS analysis.
1.1 Experimental Procedures

Scheme S1: Synthesis Overview: i) boronic acid 7 or 8, K$_2$CO$_3$, Pd(PPh$_3$)$_4$, toluene/H$_2$O (6:1), 110 °C, 16 h; b) Bi(OTf)$_3$, AcCl, dry toluene/MeCN (1:1), RT, 2-3 h. The substitution patterns of the molecules in both the central PCP subunit and in the peripheral subunits are labeled in red and blue for para- and meta-substitution, respectively. For simplicity, the naming of structures was done according to the prefixes with ps as an abbreviation for pseudo, followed by the prefix referring to the substitution pattern of the central PCP subunit and the second one to the substitution pattern of the thiol anchoring group in the phenyl subunits.

Pseudo-para-dibromo[2.2]paracyclophane 5 and pseudo-meta-dibromo[2.2]paracyclophane 6 were synthesized over the bromination of [2.2]paracyclophane according to literature known procedure.$^3$ (3-((Tert-butylthio)phenyl)boronic acid 8 was commercially available. (4-((Tert-butylthio)phenyl)boronic acid 7 was prepared according to literature known procedures, starting from the respective 4-bromothiophenol and tert-butyl chloride in the presence of AlCl$_3$ to give the desired thioether,$^4$ followed by lithium-halogen exchange, reacting with B(OMe)$_3$ and hydrolysis to the desired boronic acid 7.$^5$

**General Procedure 1: Suzuki Cross-Coupling Reaction**

Dibromo[2.2]paracyclophane 5 or 6 (1.0 eq.), boronic acid 7 or 8 (2.4 eq.), and potassium carbonate (2.0 eq.) were dissolved in toluene/water (6:1). The reaction mixture was sparged with argon for 20 min. Pd(PPh$_3$)$_4$ (10 mol%) was added, and the reaction mixture was heated to 110 °C for 16 h. Afterward, the reaction mixture was cooled to room temperature, diluted with toluene and washed with water (3x), brine (1x), dried over Na$_2$SO$_4$, and filtered. The solvent was removed under reduced pressure, and the crude product was purified by flash column chromatography.

**General Procedure 2: Transprotection Reaction**

This reaction procedure was adopted from literature.$^6$
Previously prepared compounds 9 – 12 (1.0 eq.) and acetyl chloride (50 eq.) were dissolved in dry toluene/MeCN (1:1) under argon atmosphere. Bismuth(III)trifluoromethanesulfonate (3.0 eq.) was added and the reaction mixture was stirred at room temperature till full conversion was observed by TLC (2-3 h). Then, water was added, and the aqueous layer was extracted with CH₂Cl₂ (3x). The combined organic layers were dried over Na₂SO₄ and filtered. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography.

**Pseudo-para-bis((4'-tert-butylthio)phenyl)[2.2]paracyclopahne (ps-para-para StBu PCP 9):**

Compound 9 was synthesized according to general procedure 1 using pseudo-para-dibromo[2.2]paracyclophane 5 (200 mg, 546 µmol, 1.0 eq.), (4-(tert-butylthio)phenyl)boronic acid 7 (275 mg, 1.31 mmol, 2.4 eq.), K₂CO₃ (151 mg, 1.09 mmol, 2.0 eq.), Pd(PPh₃)₄ (63 mg, 54.6 µmol, 10 mol%), toluene (12 mL) and water (2 mL). The crude was purified by flash column chromatography (cyclohexane/CH₂Cl₂ 2:1) to give ps-para-para StBu PCP 9 (201 mg, 386 µmol, 69%) as a white solid.

**TLC (SiO₂, cyclohexane/CH₂Cl₂ 2:1):** Rf=0.15

**m.p.** > 270 °C (decomposition)

**¹H NMR (500 MHz, CDCl₃):** δ 7.68 – 7.62 (m, 4H, Ar-H), 7.51 – 7.47 (m, 4H, Ar-H), 6.69 – 6.64 (m, 4H, PCPAr-H), 6.60 (dd, J = 7.7, 1.9 Hz, 2H, PCPAr-H), 3.45 (ddd, J = 13.9, 9.9, 4.3 Hz, 2H, CH₂), 3.04 (ddd, J = 13.9, 10.0, 4.7 Hz, 2H, CH₂), 2.87 (ddd, J = 14.1, 10.0, 4.2 Hz, 2H, CH₂), 2.78 (ddd, J = 13.7, 9.9, 4.7 Hz, 2H, CH₂), 1.36 (s, 18H, tBu-H) ppm.

**¹³C{¹H} NMR (126 MHz, CDCl₃):** δ 141.8, 141.5, 140.1, 137.7, 137.0, 135.0, 132.5, 131.4, 129.9, 129.6, 46.2, 34.9, 34.0, 31.2 ppm.

**HR-MS (ESI, +):** m/z calcd. for C₃₆H₄₀S₂Ag [M+Ag]⁺ 643.1617; found: 643.1604.

**Pseudo-para-bis((4'-acetylthio)phenyl)[2.2]paracyclophane (ps-para-para PCP 1a):**

Compound 1a was synthesized according to general procedure 2 using compound 9 (51 mg, 95 µmol, 1.0 eq.), acetyl chloride (0.34 mL, 4.75 mmol, 50 eq.), bismuth(III)trifluoromethanesulfonate (189 mg, 282 µmol, 3.0 eq.), toluene (10 mL) and acetonitrile (10 mL). The crude was purified by flash column chromatography (cyclohexane/CH₂Cl₂ 1:4) to give ps-para-para PCP 1a (41 mg, 81 µmol, 85%) as a white solid.
TLC (SiO₂, cyclohexane/CH₂Cl₂ 1:4): Rf=0.19

m.p. > 290 °C (decomposition)

¹H NMR (500 MHz, CDCl₃): 7.59 – 7.52 (m, 8H, Ar-H), 6.68 – 6.64 (m, 4H, PCPAr-H), 6.59 (dd, J = 7.8, 1.9 Hz, 2H, PCPAr-H), 3.44 (ddd, J = 14.0, 9.9, 4.4 Hz, 2H, CH₂), 3.05 (ddd, J = 14.0, 9.9, 4.8 Hz, 2H, CH₂), 2.90 – 2.78 (m, 4H, CH₂), 2.48 (s, 6H, SAc-H) ppm.

¹³C{¹H} NMR (126 MHz, CDCl₃): δ 194.2, 142.5, 141.2, 140.2, 137.1, 135.1, 134.6, 132.5, 130.6, 129.8, 126.6, 34.9, 33.9, 30.4 ppm.

HR-MS (ESI, +): m/z calcd. for C₃₂H₂₈O₂S₂Ag [M+Ag]+ 615.0576; found: 615.0572.

Pseudo-para-bis((3’-tert-butylthio)phenyl)[2.2]paracyclophane (ps-para-meta SrBu PCP 10):

Compound 10 was synthesized according to general procedure 1 using pseudo-para-dibromo[2.2]paracyclophane 5 (150 mg, 410 µmol, 1.0 eq.), (3-(tert-butylthio)phenyl)boronic acid 8 (207 mg, 984 µmol, 2.4 eq.), K₂CO₃ (113 mg, 820 µmol, 2.0 eq.), Pd(PPh₃)₄ (47 mg, 41 µmol, 10 mol%), toluene (12 mL) and water (2 mL). The crude was purified by flash column chromatography (cyclohexane/CH₂Cl₂ 3:1) to give ps-para-meta SrBu PCP 10 (154 mg, 287 µmol, 70%) as a white solid.

TLC (SiO₂, cyclohexane/CH₂Cl₂ 3:1): Rf=0.15

m.p.: 168 – 170 °C

¹H NMR (500 MHz, CDCl₃): δ 7.72 (t, J = 1.7 Hz, 2H, Ar-H), 7.55 (m, 4H, Ar-H), 7.46 (t, J = 7.6 Hz, 2H, Ar-H), 6.69 – 6.66 (m, 4H, PCPAr-H), 6.60 (dd, J = 7.9, 1.9 Hz, 2H, PCPAr-H), 3.45 (ddd, J = 13.9, 10.0, 4.3 Hz, 2H, CH₂), 3.05 (ddd, J = 14.0, 10.0, 4.7 Hz, 2H, CH₂), 2.87 (ddd, J = 14.1, 10.0, 4.3 Hz, 2H, CH₂), 2.79 (ddd, J = 13.7, 9.9, 4.7 Hz, 2H, CH₂), 1.38 (s, 18H, tBu-H) ppm.

¹³C{¹H} NMR (126 MHz, CDCl₃): δ 141.7, 141.5, 140.1, 138.9, 137.0, 136.0, 135.0, 133.0, 132.4, 130.4, 129.5, 128.8, 46.3, 34.9, 33.9, 31.2 ppm.

HR-MS (ESI, +): m/z calcd. for C₃₆H₄₀S₂Ag [M+Ag]+ 643.1617; found: 643.1610.
Pseudo-para-bis((3′-acetylthio)phenyl)[2.2]paracycophane (ps-para-meta PCP 3a):

Compound 3a was synthesized according to general procedure 2 using compound 10 (50 mg, 93.1 µmol, 1.0 eq.), acetyl chloride (0.33 mL, 4.66 mmol, 50 eq.), bismuth(III)trifluoromethane-sulfonate (187 mg, 279 µmol, 3.0 eq.), toluene (4 mL) and acetonitrile (4 mL). The crude was purified by flash column chromatography (cyclohexane/CH₂Cl₂ 1:2) to give ps-para-meta PCP 3a (30 mg, 59 µmol, 63%) as a white amorphous solid.

TLC (SiO₂, cyclohexane/CH₂Cl₂ 1:2): Rₜ=0.15

¹H NMR (500 MHz, CDCl₃): δ 7.59 – 7.56 (m, 4H, Ar-H), 7.54 (t, J = 7.8 Hz, 2H, Ar-H), 7.43 (dt, J = 7.4, 1.6 Hz, 2H, Ar-H), 6.67 – 6.62 (m, 6H, PCPAr-H), 3.48 (ddd, J = 13.8, 9.9, 4.2 Hz, 2H, CH₂), 3.04 (ddd, J = 14.0, 10.0, 4.9 Hz, 2H, CH₂), 2.92 – 2.78 (m, 4H, CH₂), 2.49 (s, 6H, SAc-H) ppm.

¹³C{¹H} NMR (126 MHz, CDCl₃): δ 194.0, 142.4, 141.1, 140.2, 137.1, 136.0, 135.0, 132.5, 132.4, 130.9, 129.7, 129.5, 128.3, 34.8, 33.8, 30.5 ppm.

HR-MS (ESI, +): m/z calcd. for C₃₂H₂₈O₂S₂Ag [M+Ag]⁺ 615.0576; found: 615.0576.

Pseudo-meta-bis((4′-tert-butythio)phenyl)[2.2]paracycophane (ps-meta-para SrBu PCP 11):

Compound 11 was synthesized according to general procedure 2 using pseudo-meta-dibromo[2.2]paracycophane 6 (200 mg, 546 µmol, 1.0 eq.), (4-(tert-butythio)phenyl)boronic acid 7 (275 mg, 1.31 mmol, 2.4 eq.), K₂CO₃ (151 mg, 1.09 mmol, 2.0 eq.), Pd(PPh₃)₄ (63 mg, 54 µmol, 2.0 eq.), toluene (12 mL) and water (2 mL). The crude was purified by flash column chromatography (cyclohexane/CH₂Cl₂ 3:1). The remaining impurities were precipitating in CH₂Cl₂ by adding MeOH, followed by filtration and evaporation of mother liquor to give ps-meta-para PCP 11 (175 mg, 344 µmol, 60%) as a colorless oil.

TLC (SiO₂, cyclohexane/CH₂Cl₂ 2:1): Rₜ=0.23

¹H NMR (500 MHz, CDCl₃): δ 7.65 – 7.61 (m, 4H, Ar-H), 7.48 – 7.44 (m, 4H, Ar-H), 6.72 (d, J = 1.9 Hz, 2H, PCPAr-H), 6.69 (d, J = 7.8 Hz, 2H, PCPAr-H), 6.58 (dd, J = 7.7, 1.9 Hz, 2H, PCPAr-H), 3.28 – 3.06 (m, 6H, CH₂), 2.56 – 2.48 (m, 2H, CH₂), 1.35 (s, 18H, tBu-H) ppm.

¹³C{¹H} NMR (126 MHz, CDCl₃): δ 141.9, 141.6, 139.8, 137.7, 137.5, 132.5, 132.0, 131.6, 131.4, 129.8, 46.2, 35.3, 33.6, 31.2 ppm.

HR-MS (ESI, +): m/z calcd. for C₃₆H₄₀AgS₂ [M+Ag]⁺ 643.1617; found: 643.1615.
Pseudo-meta-bis((4'-tert-acetylthio)phenyl)[2.2]paracyclophane (ps-meta-para PCP 2a):

Compound 2a was synthesized according to general procedure 2 using compound 11 (20 mg, 37.3 µmol, 1.0 eq.), acetyl chloride (0.13 mL, 1.86 mmol, 50 eq.), bismuth(III)trifluoromethane-sulfonate (74.9 mg, 112 µmol, 3.0 eq.), toluene (2 mL) and acetonitrile (2 mL). The crude was purified by flash column chromatography (cyclohexane/CH$_2$Cl$_2$ 1:2) to give ps-meta-para PCP 2a (13.6 mg, 33 µmol, 72%) as a white amorphous solid.

TLC (SiO$_2$, cyclohexane/CH$_2$Cl$_2$ 1:2): $R_f$=0.32

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.54 – 7.50 (m, 8H, Ar-$H$), 6.72 (d, $J$ = 1.9 Hz, 2H, PCPAr-$H$), 6.67 (d, $J$ = 7.9 Hz, 2H, PCPAr-$H$), 6.57 (dd, $J$ = 7.8, 1.9 Hz, 2H, PCPAr-$H$), 3.27 – 3.07 (m, 4H, CH$_2$), 2.62 – 2.54 (m, 2H, CH$_2$), 2.47 (s, 6H, SAc-$H$) ppm.

$^{13}$C{$^1$H} NMR (126 MHz, CDCl$_3$): $\delta$ 194.2, 142.4, 141.7, 139.9, 137.6, 134.6, 132.6, 132.1, 131.8, 130.5, 126.6, 35.3, 33.5, 30.4 ppm.

HR-MS (ESI, +): $m/z$ calcd. for C$_{32}$H$_{28}$O$_2$S$_2$Ag [M+Ag]$^+$ 615.0576; found: 615.0583.

Pseudo-meta-bis((3'-tert-butylthio)phenyl)[2.2]paracyclophane (ps-meta-meta StBu PCP 12):

Compound 12 was synthesized according to general procedure 2 using pseudo-meta-dibromo[2.2]paracyclophane 6 (150 mg, 410 µmol, 1.0 eq.), (3-(tert-butylthio)phenyl)boronic acid 8 (200 mg, 952 µmol, 2.4 eq.), K$_2$CO$_3$ (113 mg, 820 µmol, 2.0 eq.), Pd(PPh$_3$)$_4$ (47.4 mg, 41 µmol, 10 mol%), toluene (12 mL) and water (2 mL). The crude was purified by flash column chromatography (cyclohexane/CH$_2$Cl$_2$ 4:1). The remaining impurities were precipitating in CH$_2$Cl$_2$ by adding MeOH, followed by filtration and evaporation of mother liquor to give ps-meta-meta StBu PCP 12 (149 mg, 278 kµmol, 68 %) as a colorless oil.

TLC (SiO$_2$, cyclohexane/CH$_2$Cl$_2$ 4:1): $R_f$=0.13

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.68 (t, $J$ = 1.7 Hz, 2H, Ar-$H$), 7.54 (dt, $J$ = 7.5, 1.5 Hz, 2H, Ar-$H$), 7.49 (dt, $J$ = 7.7, 1.5 Hz, 2H, Ar-$H$), 7.44 (t, $J$ = 7.6 Hz, 2H, Ar-$H$), 6.72 (d, $J$ = 1.9 Hz, 2H, PCPAr-$H$), 6.68 (d, $J$ = 7.8 Hz, 2H, PCPAr-$H$), 6.59 (dd, $J$ = 7.8, 1.9 Hz, 2H, PCPAr-$H$), 3.27 – 3.06 (m, 6H, CH$_2$), 2.58 – 2.49 (m, 2H, CH$_2$), 1.36 (s, 18H, tBu-$H$) ppm.

$^{13}$C{$^1$H} NMR (126 MHz, CDCl$_3$): $\delta$ 141.9, 141.6, 139.9, 138.7, 137.5, 136.0, 133.0, 132.4, 132.0, 131.6, 130.2, 128.8, 46.3, 35.3, 33.6, 31.2 ppm.

HR-MS (ESI, +): $m/z$ calcd. for C$_{36}$H$_{40}$AgS$_2$ [M+Ag]$^+$ 643.1617; found: 643.1604.
**Pseudo-meta-bis((3'-tert-acetylthio)phenyl)[2.2]paracyclophane (ps-meta-meta PCP 4a):**

Compound 4a was synthesized according to general procedure 2 using compound 12 (50 mg, 93.1 µmol, 1.0 eq.), acetyl chloride (0.33 mL, 4.66 mmol, 50 eq.), bismuth(III)trifluoromethanesulfonate (187 mg, 279 µmol, 3.0 eq.), toluene (4 mL) and acetonitrile (4 mL). The crude was purified by flash column chromatography (cyclohexane/CH2Cl2 1:2) to give ps-meta-meta PCP 4a (31 mg, 61 µmol, 66%) as a white amorphous solid.

**TLC** (SiO2, cyclohexane/CH2Cl2 1:2): Rf = 0.26

**1H NMR (500 MHz, CDCl3):** δ 7.56 – 7.49 (m, 6H, Ar-H), 7.41 (dt, J = 6.7, 1.9 Hz, 2H, Ar-H), 6.73 (d, J = 7.8 Hz, 2H, PCPAr-H), 6.69 (d, J = 1.9 Hz, 2H, PCPAr-H), 6.58 (dd, J = 7.8, 1.9 Hz, 2H, PCPAr-H), 3.27 – 3.16 (m, 4H, CH2), 3.14 – 3.06 (m, 2H, CH2), 2.60 – 2.51 (m, 2H, CH2), 2.47 (s, 6H, SAc-H) ppm.

**13C{1H} NMR (126 MHz, CDCl3):** δ 194.0, 142.2, 141.5, 139.8, 137.7, 135.7, 132.6, 132.5, 132.0, 131.7, 130.8, 129.5, 128.3, 35.2, 33.5, 30.5 ppm.

**HR-MS (ESI, +):** m/z calcd. for C32H28O2S2Ag [M+Ag]+ 615.0576; found: 615.0577.
1.2 Characterization

$^1$H, $^{13}$C($^1$H) NMR (CDCl$_3$, 500/126 MHz) and HR-MS spectra of ps-para-para StBu PCP (9)
# High Resolution Mass Spectrometry Report

## Measured m/z vs. theoretical m/z

| #  | m/z    | I % | I   |
|----|--------|-----|-----|
| 1  | 106.9052 | 1.2 | 20279 |
| 2  | 108.9048 | 1.4 | 23458 |
| 3  | 147.9515 | 96.0 | 1581629 |
| 4  | 148.9345 | 1.5 | 26334 |
| 5  | 149.9312 | 100.0 | 1647776 |
| 6  | 150.9339 | 1.7 | 28649 |
| 7  | 165.9418 | 1.6 | 27351 |
| 8  | 167.9415 | 1.7 | 27860 |
| 9  | 188.9575 | 1.6 | 263703 |
| 10 | 189.9602 | 0.8 | 13354 |
| 11 | 190.9572 | 15.6 | 257458 |
| 12 | 275.7969 | 7.4 | 121156 |
| 13 | 277.7965 | 14.0 | 250602 |
| 14 | 279.7962 | 8.5 | 107139 |
| 15 | 316.8237 | 17.6 | 280533 |
| 16 | 318.8236 | 35.9 | 595526 |
| 17 | 320.8230 | 15.2 | 256711 |
| 18 | 357.8499 | 4.4 | 72285 |
| 19 | 358.8499 | 8.6 | 141120 |
| 20 | 361.8494 | 4.1 | 66776 |
| 21 | 396.5457 | 1.3 | 20963 |
| 22 | 396.5457 | 2.4 | 39104 |
| 23 | 397.5457 | 1.1 | 18085 |
| 24 | 397.5457 | 1.5 | 24121 |
| 25 | 405.5510 | 0.8 | 13571 |
| 26 | 416.5058 | 2.5 | 41310 |
| 27 | 416.5060 | 1.2 | 19402 |
| 28 | 417.5059 | 5.1 | 84232 |
| 29 | 417.5062 | 2.4 | 38666 |
| 30 | 418.5068 | 3.0 | 50053 |
| 31 | 418.5060 | 1.3 | 21243 |
| 32 | 446.6859 | 1.3 | 21215 |
| 33 | 446.6855 | 1.2 | 20346 |
| 34 | 479.6921 | 2.1 | 33840 |
| 35 | 480.6926 | 0.9 | 14740 |
| 36 | 480.6922 | 6.2 | 102317 |
| 37 | 481.6925 | 2.7 | 44129 |
| 38 | 481.6921 | 6.2 | 101927 |
| 39 | 482.6933 | 2.7 | 44896 |
| 40 | 482.6919 | 2.6 | 42563 |
| 41 | 483.6932 | 1.0 | 16473 |
| 42 | 485.7161 | 2.6 | 43245 |
| 43 | 487.7160 | 7.2 | 117673 |
| 44 | 488.7159 | 6.6 | 108605 |
| 45 | 491.7152 | 2.0 | 33477 |
| 46 | 501.5051 | 1.2 | 18999 |
| 47 | 502.5052 | 1.2 | 20438 |
| 48 | 517.2947 | 1.8 | 26444 |
| 49 | 519.2945 | 1.8 | 25673 |
| 50 | 526.7423 | 0.8 | 13269 |
| 51 | 528.7423 | 2.2 | 37020 |
| 52 | 530.7422 | 2.1 | 34571 |
| 53 | 565.8363 | 2.0 | 33770 |
| 54 | 565.8365 | 0.9 | 14453 |
| 55 | 566.8344 | 3.0 | 48686 |
| 56 | 566.8366 | 1.3 | 22132 |
| 57 | 567.8363 | 2.2 | 35497 |
| 58 | 567.8365 | 0.9 | 14124 |
| 59 | 612.4247 | 0.8 | 13127 |
| 60 | 637.3733 | 3.2 | 53324 |
| 61 | 638.3763 | 1.3 | 20631 |
| 62 | 639.3734 | 3.2 | 52999 |

Bruker Compass DataAnalysis 4.0  Acquisition Date 04.02.2021 15:44:33  Page 2 of 3
### High Resolution Mass Spectrometry Report

| # | m/z | % | I |
|---|-----|---|---|
| 63 | 640.3765 | 1.2 | 19479 |
| 64 | 658.6079 | 0.8 | 13811 |
| 65 | 684.6178 | 2.9 | 478559 |
| 66 | 685.1907 | 11.7 | 192316 |
| 67 | 686.1878 | 33.2 | 547250 |
| 68 | 687.1903 | 12.4 | 205018 |
| 69 | 688.1882 | 5.8 | 95824 |
| 70 | 689.1869 | 1.8 | 29673 |
| 71 | 690.1874 | 1.2 | 19446 |
| 72 | 728.6070 | 2.2 | 35542 |
| 73 | 729.1084 | 1.8 | 29678 |
| 74 | 729.6072 | 2.7 | 45273 |
| 75 | 730.1081 | 1.9 | 31479 |
| 76 | 730.6076 | 1.5 | 25081 |
| 77 | 731.1090 | 0.9 | 14483 |
| 78 | 812.0534 | 6.7 | 110291 |
| 79 | 813.0553 | 4.1 | 67769 |
| 80 | 813.5548 | 1.4 | 22500 |
| 81 | 814.0537 | 16.4 | 270106 |
| 82 | 814.5546 | 2.0 | 33543 |
| 83 | 815.0555 | 7.5 | 124269 |
| 84 | 815.5542 | 1.5 | 25068 |
| 85 | 816.0535 | 8.6 | 141865 |
| 86 | 817.0554 | 3.1 | 50592 |
| 87 | 818.0534 | 1.0 | 16277 |
| 88 | 886.4994 | 1.3 | 20785 |
| 89 | 896.0099 | 1.0 | 16009 |
| 90 | 896.4969 | 1.4 | 23965 |
| 91 | 900.0006 | 1.0 | 16252 |
| 92 | 900.5002 | 0.9 | 15574 |
| 93 | 900.9450 | 1.3 | 21169 |
| 94 | 982.8453 | 4.2 | 68581 |
| 95 | 983.8475 | 2.2 | 35753 |
| 96 | 984.8452 | 4.5 | 73800 |
| 97 | 985.9470 | 1.8 | 30258 |
| 98 | 986.8451 | 1.6 | 27070 |
| 99 | 1153.8370 | 1.2 | 26362 |
| 100 | 1155.8374 | 0.9 | 14825 |

#### Acquisition Parameter

**General**
- Fore Vacuum: 2.4e-100 mBar
- Scan Begin: 75 mV

**Source**
- Set Nebulizer: 0.4 Bar
- Set Dry Heater: 180 °C

**Quadrupole**
- Set Ion Energy (MS only): 4.0 eV

**Coll. Cell**
- Collision Energy: 8.0 eV
- Set Collison Cell RF: 350.0 Vpp

**Ion Cooler**
- Set Ion Cooler Transfer Time: 75.0 μs
- Set Ion Cooler Pre Pulse Storage Time: 10.0 μs

**High Vacuum**
- Scan End: 170 mV
- Set Capillary: 3600 V
- Set End Plate Offset: -500 V

**Source Type**
- Ion Polarity: Positive
- ESI: 4.0 l/min

**Acquisition Date**
- 04.02.2021 15:44:33

---

Bruker Compass DataAnalysis 4.0

Page 3 of 3
$^1$H, $^{13}$C($^1$H) NMR (CDCl$_3$, 500/126 MHz) and HR-MS spectra of ps-para-para PCP (1a)
# Measured m/z vs. theoretical m/z

| Mass list | m/z | l % | l |
|-----------|-----|-----|---|
| 1         | 106.9050 | 1.9 | 23460 |
| 2         | 108.9047 | 2.2 | 27107 |
| 3         | 147.9313 | 94.4 | 1187570 |
| 4         | 148.9341 | 1.0 | 20441 |
| 5         | 148.9310 | 100.0 | 1257418 |
| 6         | 150.9336 | 1.9 | 24031 |
| 7         | 165.9417 | 1.5 | 18271 |
| 8         | 167.9414 | 1.4 | 18231 |
| 9         | 188.9573 | 13.2 | 165846 |
| 10        | 150.9570 | 13.2 | 166362 |
| 11        | 275.7965 | 10.4 | 130154 |
| 12        | 277.7966 | 20.3 | 255627 |
| 13        | 278.7961 | 8.5 | 119201 |
| 14        | 301.9602 | 2.2 | 27602 |
| 15        | 303.9697 | 2.1 | 26151 |
| 16        | 316.8234 | 15.5 | 184421 |
| 17        | 318.8234 | 31.3 | 393286 |
| 18        | 320.8227 | 13.4 | 160063 |
| 19        | 333.0967 | 1.5 | 19119 |
| 20        | 335.0968 | 1.5 | 18664 |
| 21        | 347.1123 | 1.6 | 19536 |
| 22        | 349.1124 | 1.5 | 18008 |
| 23        | 357.8497 | 3.4 | 43273 |
| 24        | 359.8495 | 6.7 | 83500 |
| 25        | 361.1284 | 13.4 | 168196 |
| 26        | 361.6491 | 3.2 | 40623 |
| 27        | 362.1314 | 2.4 | 30025 |
| 28        | 363.1283 | 12.8 | 160916 |
| 29        | 364.1313 | 2.1 | 26811 |
| 30        | 365.1430 | 2.1 | 26027 |
| 31        | 375.1436 | 2.7 | 35555 |
| 32        | 377.1435 | 2.4 | 30415 |
| 33        | 387.1430 | 2.8 | 34911 |
| 34        | 389.1592 | 12.4 | 156450 |
| 35        | 390.1668 | 2.3 | 29459 |
| 36        | 391.1595 | 10.9 | 137667 |
| 37        | 392.1627 | 2.3 | 28500 |
| 38        | 394.1494 | 1.8 | 22241 |
| 39        | 396.1492 | 1.7 | 21400 |
| 40        | 446.6869 | 2.6 | 32334 |
| 41        | 448.6868 | 2.4 | 30221 |
| 42        | 485.7158 | 2.4 | 29742 |
| 43        | 487.7157 | 6.4 | 80979 |
| 44        | 489.7153 | 6.4 | 79082 |
| 45        | 491.7148 | 1.9 | 24464 |
| 46        | 517.2946 | 6.6 | 82573 |
| 47        | 518.2979 | 2.2 | 27284 |
| 48        | 519.2945 | 6.3 | 78621 |
| 49        | 520.2973 | 2.1 | 26123 |
| 50        | 528.7421 | 1.7 | 21944 |
| 51        | 530.7417 | 1.7 | 21017 |
| 52        | 531.2566 | 3.1 | 38050 |
| 53        | 533.2560 | 3.1 | 38504 |
| 54        | 533.2855 | 3.5 | 44438 |
| 55        | 534.2900 | 1.3 | 16894 |
| 56        | 535.2891 | 3.4 | 42412 |
| 57        | 549.2845 | 2.5 | 31006 |
| 58        | 551.2844 | 2.2 | 27551 |
| 59        | 581.2738 | 1.4 | 17629 |
| 60        | 583.2736 | 1.3 | 16908 |
| 61        | 613.4089 | 1.4 | 18135 |
| 62        | 615.0572 | 31.7 | 397975 |

Bruker Compass Data Analysis 4.0

Acquisition Date: 04.02.2021 15:51:00

Page 2 of 3
### High Resolution Mass Spectrometry Report

| #  | m/z | %  | I   |
|----|-----|----|-----|
| 63 | 616.0597 | 11.4 | 143376 |
| 64 | 617.0569 | 31.9 | 400812 |
| 65 | 618.0566 | 11.2 | 140297 |
| 66 | 619.0563 | 3.3  | 41226  |
| 67 | 639.4242 | 1.7  | 21173  |
| 68 | 641.4300 | 1.8  | 20709  |
| 69 | 656.0635 | 24.3 | 304927 |
| 70 | 657.0661 | 8.8  | 110302 |
| 71 | 658.0634 | 25.1 | 315445 |
| 72 | 659.0556 | 9.1  | 114072 |
| 73 | 660.0634 | 3.0  | 36024  |
| 74 | 666.1575 | 5.9  | 74801  |
| 75 | 687.1904 | 2.1  | 26466  |
| 76 | 688.1876 | 11.1 | 139410 |
| 77 | 688.1900 | 3.7  | 46240  |
| 78 | 690.1675 | 5.2  | 65533  |
| 79 | 691.1900 | 1.7  | 21000  |
| 80 | 704.1518 | 2.5  | 31394  |
| 81 | 783.9490 | 5.5  | 69485  |
| 82 | 784.9517 | 2.1  | 26566  |
| 83 | 785.9491 | 11.1 | 136398 |
| 84 | 786.9515 | 4.0  | 49781  |
| 85 | 787.9487 | 6.2  | 78496  |
| 86 | 788.9512 | 2.2  | 27129  |
| 87 | 857.0797 | 1.4  | 17593  |
| 88 | 952.8408 | 1.8  | 20109  |
| 89 | 954.8413 | 4.6  | 57476  |
| 90 | 955.8442 | 1.7  | 21906  |
| 91 | 956.8412 | 4.6  | 57220  |
| 92 | 957.8440 | 1.7  | 21358  |
| 93 | 958.8405 | 1.8  | 22896  |
| 94 | 1123.2074 | 2.3  | 29368  |
| 95 | 1124.2112 | 1.7  | 21832  |
| 96 | 1125.2066 | 3.0  | 38040  |
| 97 | 1126.2109 | 2.0  | 25531  |
| 98 | 1284.1004 | 2.8  | 34807  |
| 99 | 1295.1035 | 1.9  | 23596  |
| 100 | 1296.1016 | 2.1  | 26333  |

### Acquisition Parameters

- **General**
  - Fore Vacuum: 2.44e+000 mBar
  - Scan Begin: 75 mV

- **Source**
  - Set Nebulizer: 0.4 Bar
  - Set Dry Heater: 180 °C

- **Quadrupole**
  - Set Ion Energy (MS only): 4.0 eV

- **Coll. Cell**
  - Collision Energy: 8.0 eV
  - Set Collision Cell RF: 350.0 Vpp

- **Ion Cooler**
  - Set Ion Cooler Transfer Time: 75.0 μs
  - Set Ion Cooler Pre Pulse Storage Time: 10.0 μs

**Source Type**: 1.14e-007 mBar
**Ion Polarity**: 1700 mV
**ESI**: 3800 V
**Gas**: -500 V
**Offset**: 4.0 l/min

**Bruker Compass Data Analysis 4.0**
**Acquisition Date**: 04.02.2021 15:51:00
**Page**: 3 of 3
$^{1}H$, $^{13}C$($^{1}H$) NMR (CDCl$_3$, 500/126 MHz) and HR-MS spectra of ps-para-meta StBu PCP (10)
High Resolution Mass Spectrometry Report

Sample Name: KR-168
Comment: in MeOH+ AgNO3 (1mM)
Instrument: maXis 4G
Method: 22 Direct_pos_mid.m

![Mass Spectral Diagram]

---

Bruker Compass DataAnalysis 4.0  Acquisition Date: 04.02.2021 15:40:49  Page 1 of 3
High Resolution Mass Spectrometry Report

| Measured m/z vs. theoretical m/z | Mass list |
|----------------------------------|-----------|
| Meas. m/z                        | #         | m/z     | %     | I     |
| 643.1610                         | 1         | 147.5312| 16.5  | 389266|
| 438.4350                         | 2         | 149.5399| 21.6  | 451621|
| 388.3873                         | 3         | 188.6573| 3.4   | 50271 |
| 310.6669                         | 4         | 190.9569| 3.5   | 71482 |
| 278.7666                         | 5         | 275.7696| 1.3   | 286288|
| 277.7693                         | 6         | 277.7693| 2.4   | 49709 |
| 266.7608                         | 7         | 316.8223| 2.9   | 59523 |
| 268.7631                         | 8         | 318.8231| 5.7   | 116904|
| 258.7553                         | 9         | 320.8227| 7.5   | 51805 |
| 250.7853                         | 10        | 359.8496| 1.5   | 30367 |
| 250.7853                         | 11        | 517.2948| 1.7   | 35064 |
| 250.7853                         | 12        | 519.2946| 1.6   | 33150 |
| 250.7853                         | 13        | 525.2118| 1.4   | 28896 |
| 250.7853                         | 14        | 527.2118| 1.4   | 28863 |
| 250.7853                         | 15        | 637.3723| 1.9   | 30343 |
| 250.7853                         | 16        | 639.3734| 1.8   | 37374 |
| 250.7853                         | 17        | 643.1610| 4.6   | 94368 |
| 250.7853                         | 18        | 643.6629| 3.2   | 63222 |
| 250.7853                         | 19        | 644.1617| 9.0   | 165578|
| 250.7853                         | 20        | 644.6627| 6.6   | 139846|
| 250.7853                         | 21        | 645.1618| 7.7   | 159043|
| 250.7853                         | 22        | 645.6625| 4.4   | 90336 |
| 250.7853                         | 23        | 646.1620| 2.4   | 49784 |
| 250.7853                         | 24        | 684.1857| 91.4  | 1890306|
| 250.7853                         | 25        | 685.1314| 34.9  | 722384|
| 250.7853                         | 26        | 688.1857| 100.0 | 2068073|
| 250.7853                         | 27        | 687.1910| 37.8  | 781310|
| 250.7853                         | 28        | 688.1890| 11.2  | 232171|
| 250.7853                         | 29        | 689.1855| 3.3   | 88240 |
| 250.7853                         | 30        | 727.6072| 3.0   | 61701 |
| 250.7853                         | 31        | 728.1059| 2.4   | 51547 |
| 250.7853                         | 32        | 728.6090| 9.9   | 204185|
| 250.7853                         | 33        | 729.1092| 7.4   | 152583|
| 250.7853                         | 34        | 729.6083| 12.2  | 252757|
| 250.7853                         | 35        | 730.1091| 6.4   | 174569|
| 250.7853                         | 36        | 730.6083| 6.7   | 137821|
| 250.7853                         | 37        | 731.1089| 3.7   | 77529 |
| 250.7853                         | 38        | 731.6082| 1.9   | 38610 |
| 250.7853                         | 39        | 812.0542| 22.5  | 466646|
| 250.7853                         | 40        | 813.0566| 10.1  | 297226|
| 250.7853                         | 41        | 814.0545| 54.0  | 1118475|
| 250.7853                         | 42        | 814.5542| 1.7   | 34172 |
| 250.7853                         | 43        | 815.0569| 20.1  | 415004|
| 250.7853                         | 44        | 815.5545| 1.3   | 27161 |
| 250.7853                         | 45        | 816.0541| 27.3  | 858402|
| 250.7853                         | 46        | 817.0560| 9.3   | 102027|
| 250.7853                         | 47        | 818.0539| 3.1   | 64765 |
| 250.7853                         | 48        | 980.8454| 3.5   | 73172 |
| 250.7853                         | 49        | 981.8460| 1.6   | 32870 |
| 250.7853                         | 50        | 982.9458| 10.7  | 220544|
| 250.7853                         | 51        | 983.9458| 4.3   | 88579 |
| 250.7853                         | 52        | 984.9457| 11.6  | 233574|
| 250.7853                         | 53        | 985.9479| 4.3   | 86971 |
| 250.7853                         | 54        | 986.9453| 4.6   | 95619 |
| 250.7853                         | 55        | 987.9474| 1.6   | 33557 |
| 250.7853                         | 56        | 1082.1618| 1.8  | 37301 |
| 250.7853                         | 57        | 1082.6227| 1.7  | 35271 |
| 250.7853                         | 58        | 1083.1522| 1.9  | 39448 |
| 250.7853                         | 59        | 1083.6524| 1.6  | 32687 |
| 250.7853                         | 60        | 1185.6273| 1.4  | 34661 |
| 250.7853                         | 61        | 1186.6287| 1.5  | 31878 |
| 250.7853                         | 62        | 1186.6260| 3.3  | 88509 |

Bruker Compass DataAnalysis 4.0  Acquisition Date 04.02.2021 15:40:49  Page 2 of 3
# High Resolution Mass Spectrometry Report

| #  | m/z  | I % | I |
|----|------|-----|---|
| 83 | 1187.1286 | 3.4 | 71673 |
| 84 | 1187.6294 | 4.5 | 32192 |
| 85 | 1186.1291 | 4.0 | 81840 |
| 86 | 1188.6287 | 3.7 | 75807 |
| 87 | 1189.1287 | 2.7 | 55121 |
| 88 | 1189.6286 | 1.9 | 38961 |
| 89 | 1251.0740 | 2.1 | 43455 |
| 70 | 1251.5746 | 2.1 | 44035 |
| 71 | 1252.0743 | 3.5 | 72679 |
| 72 | 1252.5750 | 3.3 | 97484 |
| 73 | 1253.0750 | 3.5 | 73925 |
| 74 | 1253.5752 | 2.9 | 60775 |
| 75 | 1254.0745 | 2.4 | 49800 |
| 76 | 1254.5745 | 1.7 | 34783 |
| 77 | 1338.5209 | 2.2 | 44568 |
| 78 | 1337.0211 | 2.1 | 43377 |
| 79 | 1337.5204 | 2.6 | 57166 |
| 80 | 1338.0212 | 2.3 | 48449 |
| 81 | 1338.5205 | 2.3 | 47646 |
| 82 | 1339.0212 | 1.7 | 36012 |
| 83 | 1339.5213 | 1.4 | 29793 |
| 84 | 1350.3075 | 2.6 | 53354 |
| 85 | 1351.3065 | 2.0 | 42288 |
| 86 | 1352.3077 | 2.1 | 42464 |
| 87 | 1353.3093 | 1.3 | 27181 |
| 88 | 1421.9673 | 1.3 | 26904 |
| 89 | 1517.1988 | 2.0 | 41465 |
| 90 | 1518.2023 | 1.7 | 35710 |
| 91 | 1519.1994 | 6.6 | 139915 |
| 92 | 1520.2019 | 5.3 | 108961 |
| 93 | 1521.2004 | 8.2 | 196819 |
| 94 | 1522.2019 | 5.7 | 118840 |
| 95 | 1523.2006 | 4.8 | 99479 |
| 96 | 1524.2012 | 2.7 | 56863 |
| 97 | 1525.2011 | 1.3 | 27609 |
| 98 | 1690.0027 | 2.2 | 46919 |
| 99 | 1691.0052 | 1.9 | 38978 |
| 100 | 1692.0036 | 2.0 | 41471 |

**Acquisition Parameter**

- **General**
  - Fore Vacuum: 2.48e+000 mBar
  - Scan Begin: 75 m/z
  - Scan End: 1.14e-007 mBar
  - Source Type: ESI
  - ESI Polarit: Positive

- **Source**
  - Set Nebulizer: 0.4 Bar
  - Set Dry Heater: 160 °C

- **Quadrupole**
  - Set Ion Energy: 4.0 eV

- **Coll. Cell**
  - Collision Energy: 8.0 eV

- **Ion Cooler**
  - Set Ion Cooler Transfer Time: 75.0 µs
  - Set Ion Cooler Pre Pulse Storage Time: 10.0 µs

---

Bruker Compass DataAnalysis 4.0  
Acquisition Date: 04.02.2021 16:40:49  
Page 3 of 3
$^1$H, $^{13}$C($^1$H) NMR (CDCl$_3$, 500/126 MHz) and HR-MS spectra of ps-para-meta PCP (3a)
## High Resolution Mass Spectrometry Report

### Measured m/z vs. theoretical m/z

| Mass list | # | m/z   | %N | I  |
|-----------|---|-------|----|----|
| 1         | 275.7970  | 12.3 | 23666 |
| 2         | 277.7967  | 22.7 | 43541 |
| 3         | 279.7964  | 10.9 | 20989 |
| 4         | 301.8333  | 4.7  | 8952 |
| 5         | 316.8238  | 38.0 | 72643 |
| 6         | 318.8237  | 70.5 | 135252 |
| 7         | 320.8232  | 35.5 | 67977 |
| 8         | 357.8505  | 14.6 | 28038 |
| 9         | 359.8501  | 27.5 | 52648 |
| 10        | 361.8498  | 12.7 | 24275 |
| 11        | 367.8210  | 4.5  | 8543 |
| 12        | 369.8206  | 7.7  | 14737 |
| 13        | 388.1575  | 7.2  | 13897 |
| 14        | 390.1755  | 6.9  | 13274 |
| 15        | 399.1079  | 11.2 | 21421 |
| 16        | 401.1076  | 11.6 | 22306 |
| 17        | 415.1025  | 7.1  | 13561 |
| 18        | 417.1030  | 7.1  | 13948 |
| 19        | 437.1613  | 24.4 | 46812 |
| 20        | 438.1645  | 5.5  | 10580 |
| 21        | 439.1610  | 21.5 | 41285 |
| 22        | 440.1843  | 4.0  | 9146 |
| 23        | 448.6968  | 6.4  | 12260 |
| 24        | 448.6964  | 6.1  | 11629 |
| 25        | 465.6125  | 22.4 | 42681 |
| 26        | 466.2157  | 5.2  | 9877 |
| 27        | 487.2123  | 21.6 | 41457 |
| 28        | 488.2157  | 5.2  | 9938 |
| 29        | 485.7166  | 10.9 | 20803 |
| 30        | 487.7165  | 28.1 | 53844 |
| 31        | 489.7163  | 25.6 | 49623 |
| 32        | 491.7158  | 8.8  | 16911 |
| 33        | 517.2954  | 13.7 | 26100 |
| 34        | 516.2087  | 5.0  | 9673 |
| 35        | 519.2050  | 13.8 | 26220 |
| 36        | 528.7429  | 9.3  | 17923 |
| 37        | 530.7430  | 8.9  | 17110 |
| 38        | 615.5076  | 95.3 | 182681 |
| 39        | 616.0006  | 34.5 | 69068 |
| 40        | 617.0575  | 100.0 | 191719 |
| 41        | 618.0600  | 34.1 | 65355 |
| 42        | 619.0570  | 11.9 | 22541 |
| 43        | 655.0355  | 24.7 | 47436 |
| 44        | 657.0668  | 10.1 | 19450 |
| 45        | 658.0366  | 26.2 | 50185 |
| 46        | 659.0686  | 9.6  | 18720 |
| 47        | 684.1877  | 11.5 | 21983 |
| 48        | 685.1967  | 4.7  | 9991 |
| 49        | 686.1580  | 16.1 | 30859 |
| 50        | 687.1912  | 6.5  | 12424 |
| 51        | 688.1866  | 10.5 | 20116 |
| 52        | 690.1866  | 4.5  | 8541 |
| 53        | 789.3519  | 15.1 | 28960 |
| 54        | 770.3546  | 7.4  | 14242 |
| 55        | 771.3516  | 15.7 | 30076 |
| 56        | 772.3543  | 6.8  | 12985 |
| 57        | 793.6514  | 9.3  | 17546 |
| 58        | 795.6511  | 18.3 | 35043 |
| 59        | 796.8539  | 7.0  | 13439 |
| 60        | 787.6507  | 10.5 | 20142 |
| 61        | 789.4991  | 31.0 | 59366 |
| 62        | 790.5021  | 14.3 | 27368 |

Bruker Compass Data Analysis 4.0  Acquisition Date  17.03.2020 12:15:39  Page 2 of 3
High Resolution Mass Spectrometry Report

| #  | m/z  | l %  | l   |
|----|------|------|-----|
| 63 | 791.4693 | 31.0 | 59338 |
| 64 | 792.5016 | 14.3 | 27416 |
| 65 | 793.5031 | 4.6  | 9112  |
| 66 | 805.4936 | 5.1  | 9735  |
| 67 | 807.4933 | 5.3  | 10187 |
| 68 | 812.0556 | 7.7  | 14702 |
| 69 | 814.0559 | 15.6 | 30282 |
| 70 | 815.0564 | 6.4  | 12320 |
| 71 | 816.0558 | 9.3  | 17882 |
| 72 | 945.3382 | 5.6  | 11083 |
| 73 | 947.3400 | 6.7  | 12824 |
| 74 | 954.6482 | 4.9  | 9299  |
| 75 | 956.8479 | 5.0  | 9552  |
| 76 | 973.3714 | 5.4  | 100322 |
| 77 | 975.3718 | 6.7  | 12895 |
| 78 | 982.9529 | 5.1  | 9782  |
| 79 | 984.9532 | 5.7  | 10070 |
| 80 | 1023.5182 | 4.5  | 8544  |
| 81 | 1025.5198 | 4.8  | 9255  |
| 82 | 1123.2227 | 13.6 | 26119 |
| 83 | 1124.2248 | 10.5 | 20112 |
| 84 | 1125.2229 | 17.6 | 34134 |
| 85 | 1126.2255 | 11.7 | 22372 |
| 86 | 1127.2249 | 6.5  | 12370 |
| 87 | 1277.5239 | 8.8  | 16794 |
| 88 | 1278.5268 | 7.7  | 14792 |
| 89 | 1279.5247 | 11.6 | 22334 |
| 90 | 1280.5264 | 8.3  | 15920 |
| 91 | 1294.1245 | 6.2  | 11821 |
| 92 | 1295.1262 | 4.9  | 9423  |
| 93 | 1297.6717 | 7.4  | 14116 |
| 94 | 1298.6742 | 5.9  | 11274 |
| 95 | 1299.6735 | 10.1 | 10295 |
| 96 | 1300.6760 | 6.8  | 13109 |
| 97 | 1451.9765 | 5.2  | 9917  |
| 98 | 1452.9797 | 4.7  | 8668  |
| 99 | 1453.9773 | 7.0  | 13492 |
| 100 | 1454.9801 | 5.5  | 10472 |

Acquisition Parameter

- **General**
  - Fore Vacuum Scan Begin: 2.5e-+000 mBar 75 m/z
  - Source Scan End: 0.4 Bar
  - Source Set Dry Heater: 160 °C

- **Source**
  - Set Nebulizer: 0.4 Bar
  - Set Dry Heater: 160 °C
  - Set Capillary: 3600 V
  - Set End Plate Offset: -500 V

- **Quadrupole**
  - Set Ion Energy (MS only): 4.0 eV

- **Collision**
  - Collision Energy: 8.0 eV
  - Set Collision Cell RF: 500.0 Vpp

- **Ion Cooler**
  - Set Ion Cooler Transfer Time: 100.0 μs
  - Set Ion Cooler Pre Pulse Storage Time: 18.0 μs

Bruker Compass DataAnalysis 4.0
Acquisition Date: 17.03.2020 12:15:30
Page 3 of 3
$^1$H, $^{13}$C($^1$H) NMR (CDCl$_3$, 500/126 MHz) and HR-MS spectra of ps-meta-para StBu PCP (11)
## High Resolution Mass Spectrometry Report

| Measured m/z vs. theoretical m/z |
|----------------------------------|
| **Mass list**                    |

| # | m/z   | Int % | Score | m/z | err [mDa] | err [ppm] | mSigma | ndb | e° | Conf | z |
|---|-------|-------|-------|-----|----------|-----------|--------|-----|----|------|---|
| 1 | 366.1743 | 6.2 | 100.00 | 643.1615 | 0.2 | 0.3 | 320.0 | 16.5 | even | 1+ |
| 2 | 390.1744 | 6.1 | 469.94 | | | | | | |
| 3 | 395.5449 | 5.3 | 40379 | | | | | | |
| 4 | 396.5450 | 10.6 | 61329 | | | | | | |
| 5 | 397.0485 | 4.7 | 35889 | | | | | | |
| 6 | 397.5449 | 6.1 | 46752 | | | | | | |
| 7 | 399.0485 | 5.3 | 40724 | | | | | | |
| 8 | 401.0485 | 5.1 | 33680 | | | | | | |
| 9 | 416.0588 | 8.6 | 67005 | | | | | | |
| 10 | 416.0588 | 4.1 | 31707 | | | | | | |
| 11 | 417.0588 | 17.3 | 132215 | | | | | | |
| 12 | 417.5602 | 7.9 | 60564 | | | | | | |
| 13 | 418.0588 | 10.2 | 77737 | | | | | | |
| 14 | 419.5599 | 4.4 | 33689 | | | | | | |
| 15 | 437.1806 | 7.5 | 57435 | | | | | | |
| 16 | 439.1804 | 6.9 | 16038 | | | | | | |
| 17 | 465.2119 | 6.1 | 64646 | | | | | | |
| 18 | 467.2120 | 5.9 | 44976 | | | | | | |
| 19 | 480.9294 | 5.0 | 38265 | | | | | | |
| 20 | 481.9293 | 5.3 | 40557 | | | | | | |
| 21 | 463.1616 | 31.5 | 241523 | | | | | | |
| 22 | 443.6631 | 22.5 | 172602 | | | | | | |
| 23 | 444.1621 | 75.0 | 574070 | | | | | | |
| 24 | 444.6633 | 51.3 | 350998 | | | | | | |
| 25 | 445.1623 | 59.1 | 452473 | | | | | | |
| 26 | 445.6630 | 32.0 | 245089 | | | | | | |
| 27 | 446.1627 | 17.0 | 159443 | | | | | | |
| 28 | 446.6624 | 6.4 | 49310 | | | | | | |
| 29 | 661.1481 | 6.1 | 46837 | | | | | | |
| 30 | 661.6483 | 4.9 | 37644 | | | | | | |
| 31 | 662.1483 | 13.3 | 100307 | | | | | | |
| 32 | 662.6484 | 9.6 | 74789 | | | | | | |
| 33 | 663.1485 | 10.0 | 37643 | | | | | | |
| 34 | 663.6485 | 6.4 | 46658 | | | | | | |
| 35 | 670.1454 | 6.5 | 49687 | | | | | | |
| 36 | 670.6456 | 4.9 | 37150 | | | | | | |
| 37 | 671.1456 | 4.9 | 37375 | | | | | | |
| 38 | 679.1340 | 4.6 | 35133 | | | | | | |
| 39 | 681.1340 | 5.0 | 36989 | | | | | | |
| 40 | 684.1878 | 90.9 | 696002 | | | | | | |
| 41 | 685.1908 | 32.8 | 256845 | | | | | | |
| 42 | 686.1877 | 100.0 | 765771 | | | | | | |
| 43 | 687.1802 | 35.0 | 268172 | | | | | | |
| 44 | 698.1863 | 11.5 | 87696 | | | | | | |
| 45 | 722.1605 | 3.7 | 28313 | | | | | | |
| 46 | 727.6801 | 8.5 | 65380 | | | | | | |
| 47 | 728.1006 | 7.4 | 55052 | | | | | | |
| 48 | 728.6806 | 28.5 | 216196 | | | | | | |
| 49 | 729.1006 | 21.4 | 164250 | | | | | | |
| 50 | 729.6800 | 26.8 | 281730 | | | | | | |
| 51 | 730.1099 | 24.6 | 169725 | | | | | | |
| 52 | 730.6091 | 16.9 | 151516 | | | | | | |
| 53 | 731.1095 | 11.1 | 85183 | | | | | | |
| 54 | 731.6091 | 5.6 | 42881 | | | | | | |
| 55 | 748.5960 | 5.2 | 40055 | | | | | | |
| 56 | 747.9684 | 4.2 | 32029 | | | | | | |
| 57 | 747.9564 | 6.2 | 47777 | | | | | | |
| 58 | 749.9562 | 4.4 | 35854 | | | | | | |
| 59 | 749.9555 | 3.6 | 27335 | | | | | | |
| 60 | 755.1013 | 3.8 | 29471 | | | | | | |
| 61 | 755.5566 | 3.5 | 30160 | | | | | | |
| 62 | 789.4979 | 13.8 | 105944 | | | | | | |

**Bruker Compass DataAnalysis 4.0**

**Acquisition Date:** 17.03.2020 12:00:18

Page 2 of 3
High Resolution Mass Spectrometry Report

| # | m/z  | I % | I  |
|---|------|-----|----|
| 63 | 790.5011 | 6.3 | 45168 |
| 64 | 791.4684 | 14.6 | 111681 |
| 65 | 792.5068 | 6.2 | 47337 |
| 66 | 812.0555 | 8.3 | 63347 |
| 67 | 813.0570 | 8.6 | 60615 |
| 68 | 813.5575 | 4.6 | 35135 |
| 69 | 814.0561 | 24.0 | 183512 |
| 70 | 814.5574 | 7.1 | 54699 |
| 71 | 815.0575 | 13.9 | 106166 |
| 72 | 815.5572 | 5.6 | 42509 |
| 73 | 816.0559 | 11.5 | 57919 |
| 74 | 817.0572 | 4.0 | 20375 |
| 75 | 996.7461 | 6.9 | 52893 |
| 76 | 997.2474 | 7.4 | 56039 |
| 77 | 997.7468 | 10.6 | 81094 |
| 78 | 998.2476 | 9.2 | 70089 |
| 79 | 998.7474 | 7.9 | 60636 |
| 80 | 999.2476 | 5.0 | 42789 |
| 81 | 1015.7345 | 4.6 | 33450 |
| 82 | 1016.2355 | 4.1 | 31513 |
| 83 | 1081.1986 | 3.6 | 27249 |
| 84 | 1081.7001 | 4.1 | 31708 |
| 85 | 1082.1988 | 6.8 | 52334 |
| 86 | 1082.7001 | 6.7 | 51416 |
| 87 | 1083.1985 | 7.3 | 50658 |
| 88 | 1083.7001 | 6.1 | 49619 |
| 89 | 1084.1987 | 4.5 | 34534 |
| 90 | 1187.6527 | 4.2 | 32220 |
| 91 | 1188.1536 | 3.7 | 27936 |
| 92 | 1307.6452 | 3.7 | 28642 |
| 93 | 1325.7573 | 6.3 | 48824 |
| 94 | 1326.7968 | 5.6 | 43181 |
| 95 | 1327.7948 | 9.3 | 70911 |
| 96 | 1328.7971 | 6.6 | 50597 |
| 97 | 1350.3554 | 3.8 | 29426 |
| 98 | 1351.3569 | 3.8 | 26965 |
| 99 | 1454.0005 | 3.7 | 26462 |
| 100 | 1474.1527 | 4.6 | 35176 |

Acquisition Parameter

| General | Fore Vacuum | 2.58e+000 mBar | High Vacuum | 9.68e-008 mBar | Source Type | Ion Pointly | ESI | Positive | 4.0 l/min |
|---------|-------------|----------------|-------------|----------------|-------------|------------|-----|----------|-----------|
| Source  | Scan Begin  | 76 m/z         | Scan End    | 1700 m/z       |             |            |     |          |           |
|         | 0.4 Bar     |                | Set Capillary | 3800 V         | Set Dry Gas |            |     |          |           |
|         | 160 °C      |                | Set End Plate Offset | -500 V |            |            |     |          |           |
| Quadrupole | Set Ion Energy (MS only) | 4.0 eV | Set Collision Cell RF | 500.0 Vpp |
| Coll. Cell | Collision Energy | 8.0 eV |            |            |            |            |     |          |           |
| Ion Cooler | Set Ion Cooler Transfer Time | 100.0 μs | Set Ion Cooler Pre Pulse Storage Time | 18.0 μs |
$^1$H, $^{13}$C{$^1$H} NMR (CDCl$_3$, 500/126 MHz) and HR-MS spectra of ps-meta-para PCP (2a)
### High Resolution Mass Spectrometry Report

#### Measured m/z vs. theoretical m/z

| #  | m/z     | %     | I     | I     |
|----|---------|-------|-------|-------|
| 1  | 275.7866| 2.9   | 15572 |       |
| 2  | 277.7866| 5.6   | 29917 |       |
| 3  | 279.7862| 2.7   | 14576 |       |
| 4  | 316.8237| 9.2   | 48685 |       |
| 5  | 318.8235| 17.7  | 94297 |       |
| 6  | 320.8231| 8.7   | 46407 |       |
| 7  | 357.8504| 3.5   | 18553 |       |
| 8  | 359.8501| 6.6   | 30550 |       |
| 9  | 381.8498| 3.2   | 17014 |       |
| 10 | 389.8288| 2.0   | 10059 |       |
| 11 | 399.8180| 2.1   | 10943 |       |
| 12 | 401.8178| 2.1   | 11011 |       |
| 13 | 409.8476| 2.9   | 15296 |       |
| 14 | 410.9469| 2.8   | 14946 |       |
| 15 | 437.1011| 2.6   | 13353 |       |
| 16 | 439.1810| 2.4   | 12353 |       |
| 17 | 485.2123| 2.9   | 15522 |       |
| 18 | 487.2123| 2.8   | 14650 |       |
| 19 | 485.7170| 2.4   | 12257 |       |
| 20 | 487.7167| 6.4   | 33554 |       |
| 21 | 489.7162| 6.0   | 31672 |       |
| 22 | 491.7158| 2.0   | 10727 |       |
| 23 | 517.2655| 3.2   | 17090 |       |
| 24 | 519.2653| 3.0   | 15974 |       |
| 25 | 528.7431| 2.4   | 12655 |       |
| 26 | 530.7431| 2.3   | 11977 |       |
| 27 | 549.1231| 69.1  | 367566|       |
| 28 | 550.1258| 19.0  | 100959|       |
| 29 | 551.1229| 67.6  | 359033|       |
| 30 | 552.1254| 18.7  | 99249 |       |
| 31 | 553.1240| 4.7   | 25226 |       |
| 32 | 615.0585| 94.5  | 50224 |       |
| 33 | 616.0510| 31.0  | 126735|       |
| 34 | 617.0581| 100.0 | 53163 |       |
| 35 | 618.0568| 31.4  | 168745|       |
| 36 | 619.0574| 10.3  | 54331 |       |
| 37 | 620.0578| 3.0   | 15970 |       |
| 38 | 656.0646| 23.4  | 30017 |       |
| 39 | 657.0675| 25.5  | 130747|       |
| 40 | 658.0646| 76.4  | 404282|       |
| 41 | 659.0671| 28.9  | 143168|       |
| 42 | 660.0643| 9.3   | 46519 |       |
| 43 | 661.0646| 2.6   | 13316 |       |
| 44 | 668.1962| 3.0   | 10134 |       |
| 45 | 668.1866| 3.0   | 15711 |       |
| 46 | 716.1053| 2.9   | 15295 |       |
| 47 | 720.0153| 5.4   | 28914 |       |
| 48 | 722.0154| 3.1   | 16334 |       |
| 49 | 789.3753| 2.0   | 10386 |       |
| 50 | 783.9518| 7.4   | 26921 |       |
| 51 | 784.9548| 2.8   | 15080 |       |
| 52 | 795.9520| 14.7  | 18355 |       |
| 53 | 798.9543| 5.5   | 29777 |       |
| 54 | 787.9513| 8.3   | 44202 |       |
| 55 | 788.9538| 3.0   | 15737 |       |
| 56 | 789.4897| 4.1   | 21936 |       |
| 57 | 790.5015| 2.1   | 10899 |       |
| 58 | 791.4890| 4.6   | 24343 |       |
| 59 | 792.0200| 2.1   | 10963 |       |
| 60 | 836.8448| 1.9   | 10349 |       |
| 61 | 954.8485| 3.5   | 15020 |       |
| 62 | 956.8483| 3.6   | 19338 |       |

*Bruker Compass DataAnalysis 4.0*  
*Acquisition Date: 17.03.2020 12:29:57*  
*Page 2 of 3*
High Resolution Mass Spectrometry Report

| #  | m/z   | I    | I%  |
|----|-------|------|-----|
| 63 | 993.3463 | 2.1 | 11403 |
| 64 | 1057.2832 | 3.7 | 19418 |
| 65 | 1058.2867 | 2.5 | 13131 |
| 66 | 1059.2844 | 4.8 | 25481 |
| 67 | 1080.2867 | 2.6 | 14742 |
| 68 | 1123.2219 | 14.6 | 77491 |
| 69 | 1124.2250 | 10.9 | 57899 |
| 70 | 1125.2226 | 19.6 | 100219 |
| 71 | 1126.2246 | 12.5 | 69548 |
| 72 | 1127.2239 | 6.6 | 34531 |
| 73 | 1128.2242 | 3.0 | 19696 |
| 74 | 1182.2461 | 3.2 | 17017 |
| 75 | 1184.2462 | 2.2 | 11530 |
| 76 | 1211.5842 | 2.1 | 11396 |
| 77 | 1213.3855 | 2.7 | 14210 |
| 78 | 1228.1846 | 3.7 | 19687 |
| 79 | 1229.1874 | 2.2 | 11647 |
| 80 | 1230.1847 | 2.6 | 13526 |
| 81 | 1231.7312 | 2.6 | 13719 |
| 82 | 1232.7342 | 2.0 | 10898 |
| 83 | 1233.7322 | 3.2 | 17227 |
| 84 | 1234.7355 | 2.2 | 11817 |
| 85 | 1279.5236 | 2.0 | 10391 |
| 86 | 1292.1233 | 4.8 | 25440 |
| 87 | 1293.1259 | 3.6 | 10259 |
| 88 | 1294.1296 | 10.9 | 57060 |
| 89 | 1295.1266 | 7.6 | 40302 |
| 90 | 1296.1241 | 6.1 | 45236 |
| 91 | 1297.1257 | 5.0 | 20329 |
| 92 | 1298.1258 | 0.4 | 13353 |
| 93 | 1587.4865 | 2.2 | 11944 |
| 94 | 1569.4704 | 2.0 | 10387 |
| 95 | 1631.4078 | 6.0 | 32062 |
| 96 | 1632.4114 | 6.6 | 34019 |
| 97 | 1633.4101 | 10.4 | 55447 |
| 98 | 1634.4121 | 9.1 | 45383 |
| 99 | 1635.4116 | 6.0 | 31975 |
| 100 | 1636.4123 | 3.4 | 16131 |

Acquisition Parameter

**General**
- Fore Vacuum: 2.58e+000 mBar
- Scan Begin: 75 m/z
- Scan End: 3000 m/z
- Set Capillary: 3800 V
- Set End Plate Offset: -500 V
- ESI Positive: 4.0 l/min

**Source**
- Set Nebulizer: 0.4 Bar
- Set Dry Heater: 180 °C
- Set Collision Cell RF: 500.0 Vpp
- Set Ion Cooler Pre Pulse Storage Time: 18.0 μs

**Quadrupole**
- Set Ion Energy (MS only): 4.0 eV

**Coll. Cell**
- Collision Energy: 8.0 eV

**Ion Cooler**
- Set Ion Cooler Transfer Time: 100.0 μs

Bruker Compass Data Analysis 4.0

Acquisition Date: 17.03.2020 12:29:57

Page 3 of 3
$^1$H, $^{13}$C{\textsuperscript{1}H} NMR (CDCl$_3$, 500/126 MHz) and HR-MS spectra of ps-meta-meta StBu PCP (12)
# High Resolution Mass Spectrometry Report

| Mass list | Formula | Score | m/z | err (mDa) | err (ppm) | mSigma | nb | e'’ Conf | z |
|-----------|---------|-------|-----|-----------|-----------|--------|----|-----------|---|
| 643.1604  | C36 H 40 Ag S 2 | 100.00 | 643.1617 | 1.3 | 2.0 | 117.6 | 16.5 | even | 1+ |

| # | m/z   | f%   | 1   |
|---|-------|-----|-----|
| 1 | 316.8236 | 4.6 | 24566 |
| 2 | 318.8234 | 6.3 | 46904 |
| 3 | 320.8227 | 4.3 | 23530 |
| 4 | 388.1756 | 3.9 | 21376 |
| 5 | 390.1753 | 3.6 | 19860 |
| 6 | 398.5457 | 3.8 | 20814 |
| 7 | 399.1078 | 10.0 | 54308 |
| 8 | 401.1076 | 9.5 | 52179 |
| 9 | 415.1027 | 5.6 | 30046 |
| 10 | 417.0566 | 5.6 | 30033 |
| 11 | 417.1026 | 5.7 | 30925 |
| 12 | 437.1809 | 10.5 | 57229 |
| 13 | 439.1907 | 9.6 | 53998 |
| 14 | 465.2122 | 6.7 | 47004 |
| 15 | 467.2122 | 6.3 | 45137 |
| 16 | 517.2651 | 4.2 | 21777 |
| 17 | 519.2651 | 4.3 | 23572 |
| 18 | 643.1804 | 14.6 | 79995 |
| 19 | 644.1622 | 12.0 | 65718 |
| 20 | 644.6622 | 5.1 | 27922 |
| 21 | 645.1669 | 5.1 | 96801 |
| 22 | 645.6625 | 3.6 | 19877 |
| 23 | 646.1629 | 6.6 | 35912 |
| 24 | 684.1881 | 69.0 | 377318 |
| 25 | 685.1908 | 28.2 | 104382 |
| 26 | 686.1879 | 76.9 | 420044 |
| 27 | 697.1903 | 29.2 | 159770 |
| 28 | 688.1884 | 12.3 | 67288 |
| 29 | 689.1888 | 3.9 | 21402 |
| 30 | 727.6882 | 5.9 | 32090 |
| 31 | 728.1098 | 4.6 | 25168 |
| 32 | 728.6089 | 17.2 | 94229 |
| 33 | 728.1099 | 14.0 | 79957 |
| 34 | 729.6088 | 22.1 | 120686 |
| 35 | 730.1105 | 15.1 | 82433 |
| 36 | 730.6092 | 12.3 | 67078 |
| 37 | 731.1092 | 7.7 | 41925 |
| 38 | 731.6094 | 3.6 | 20790 |
| 39 | 789.4978 | 14.4 | 79770 |
| 40 | 790.5009 | 6.9 | 37825 |
| 41 | 791.4983 | 13.9 | 70074 |
| 42 | 792.5008 | 6.6 | 35842 |
| 43 | 797.0640 | 5.3 | 28620 |
| 44 | 812.0559 | 46.1 | 262717 |
| 45 | 813.0585 | 18.7 | 102460 |
| 46 | 814.0585 | 100.0 | 546516 |
| 47 | 815.0584 | 37.2 | 203105 |
| 48 | 816.0556 | 52.3 | 250774 |
| 49 | 817.0577 | 21.2 | 119030 |
| 50 | 818.0548 | 6.9 | 37945 |
| 51 | 683.0527 | 3.5 | 19289 |
| 52 | 885.0531 | 6.7 | 38559 |
| 53 | 887.0524 | 4.1 | 22872 |
| 54 | 980.0515 | 9.1 | 49798 |
| 55 | 981.0555 | 3.9 | 21308 |
| 56 | 982.0522 | 24.7 | 135017 |
| 57 | 983.0550 | 10.5 | 57292 |
| 58 | 984.0522 | 26.8 | 146340 |
| 59 | 985.0546 | 10.5 | 57646 |
| 60 | 986.0519 | 11.0 | 59998 |
| 61 | 987.0546 | 4.5 | 24795 |
| 62 | 1033.8503 | 4.0 | 21597 |

Bruker Compass DataAnalysis 4.0  Acquisition Date 17.03.2020 12:12:52  Page 2 of 3
# High Resolution Mass Spectrometry Report

| #  | m/z  | I %  | I  |
|----|------|------|----|
| 63 | 1035.9504 | 4.0 | 21608 |
| 64 | 1166.9423 | 5.4 | 20345 |
| 65 | 1167.9446 | 5.6 | 31622 |
| 66 | 1167.9432 | 7.0 | 38389 |
| 67 | 1168.9436 | 6.1 | 33314 |
| 68 | 1168.9431 | 6.2 | 33679 |
| 69 | 1169.9443 | 4.6 | 25312 |
| 70 | 1251.9844 | 5.4 | 20924 |
| 71 | 1251.9848 | 5.4 | 25070 |
| 72 | 1252.9845 | 8.1 | 44178 |
| 73 | 1252.9846 | 7.4 | 40386 |
| 74 | 1253.9841 | 9.1 | 49640 |
| 75 | 1253.9848 | 7.0 | 38241 |
| 76 | 1254.9850 | 6.0 | 35916 |
| 77 | 1254.9848 | 4.2 | 23118 |
| 78 | 1336.9457 | 5.3 | 29085 |
| 79 | 1337.9462 | 5.1 | 27894 |
| 80 | 1337.9469 | 6.4 | 35244 |
| 81 | 1338.9469 | 6.0 | 33681 |
| 82 | 1338.9467 | 5.5 | 39699 |
| 83 | 1339.9456 | 4.4 | 24125 |
| 84 | 1339.9456 | 3.6 | 19556 |
| 85 | 1350.9331 | 5.9 | 32257 |
| 86 | 1351.9337 | 4.7 | 25724 |
| 87 | 1352.9338 | 4.3 | 25570 |
| 88 | 1453.9726 | 3.8 | 29621 |
| 89 | 1517.2373 | 4.8 | 26472 |
| 90 | 1518.2314 | 4.2 | 22788 |
| 91 | 1519.2396 | 15.3 | 83590 |
| 92 | 1520.2410 | 12.7 | 69337 |
| 93 | 1521.2398 | 10.3 | 16538 |
| 94 | 1522.2412 | 15.7 | 14844 |
| 95 | 1523.2403 | 11.5 | 62782 |
| 96 | 1524.2408 | 6.5 | 35322 |
| 97 | 1525.2428 | 3.7 | 20461 |
| 98 | 1690.1485 | 5.6 | 30777 |
| 99 | 1691.1477 | 4.4 | 24241 |
| 100 | 1692.1488 | 4.7 | 25510 |

## Acquisition Parameter

| General | Fore Vacuum | 2.59e+000 mBar | High Vacuum | 9.68e-008 mBar | Source Type | Ion Pointly | ESI | Positive | 4.0 l/min |
|---|---|---|---|---|---|---|---|---|---|
| Scan Begin | 75 m/z | Scan End | 1700 m/z | Source Type | 4000 V | Set Dry Gas | -500 V |
| Set Nebulizer | 0.4 Bar | Set Capillary | | | Set Dry Gas | |
| Dry Heater | 260 °C | Set End Plate Offset | | | | |
| Quadrupole | Set Ion Energy (MS only) | 4.0 eV | | | | |
| Coll. Cell | Collision Energy | 8.0 eV | | | | |
| Ion Cooler | Set Ion Cooler Transfer Time | 100.0 μs | | | Set Ion Cooler Pre Pulse Storage Time | 18.0 μs |

Bruker Compass Data Analysis 4.0  Acquisition Date  17.03.2020 12:12:52  Page 3 of 3
$^1$H, $^{13}$C$^1$H NMR (CDCl$_3$, 500/126 MHz) and HR-MS spectra of ps-meta-meta PCP (4a)
# High Resolution Mass Spectrometry Report

| # | m/z | % | Form | Score | m/z | err [mDa] | err [ppm] | mSigma | nobs | e-Conf | z |
|---|-----|---|------|-------|-----|----------|----------|--------|------|--------|---|
| 1 | 275.7962 | 15.4 | 1 C 32 H 28 Ag O 2 S 2 | 100.00 | 615.0576 | -0.1 | -0.2 | 15.3 | 18.5 | even | 1+ |
| 2 | 277.7960 | 29.0 | 49892 | | | | | | | | |
| 3 | 279.7987 | 14.2 | 24413 | | | | | | | | |
| 4 | 316.8265 | 51.4 | 83348 | | | | | | | | |
| 5 | 318.8265 | 100.0 | 179159 | | | | | | | | |
| 6 | 320.8259 | 47.4 | 81549 | | | | | | | | |
| 7 | 333.8268 | 4.0 | 6807 | | | | | | | | |
| 8 | 357.8331 | 19.5 | 33557 | | | | | | | | |
| 9 | 359.8329 | 36.7 | 63055 | | | | | | | | |
| 10 | 361.8314 | 4.0 | 6819 | | | | | | | | |
| 11 | 361.8525 | 17.7 | 30482 | | | | | | | | |
| 12 | 363.8531 | 4.1 | 7072 | | | | | | | | |
| 13 | 367.8529 | 5.2 | 9026 | | | | | | | | |
| 14 | 369.8523 | 10.0 | 17274 | | | | | | | | |
| 15 | 371.8529 | 4.6 | 7919 | | | | | | | | |
| 16 | 377.8469 | 3.1 | 5314 | | | | | | | | |
| 17 | 371.8397 | 3.6 | 6591 | | | | | | | | |
| 18 | 381.8248 | 10.0 | 17203 | | | | | | | | |
| 19 | 389.8232 | 5.0 | 8685 | | | | | | | | |
| 20 | 390.8278 | 10.3 | 17783 | | | | | | | | |
| 21 | 391.8265 | 4.4 | 7637 | | | | | | | | |
| 22 | 399.8100 | 12.6 | 21699 | | | | | | | | |
| 23 | 401.8100 | 11.4 | 19679 | | | | | | | | |
| 24 | 403.8031 | 4.1 | 7036 | | | | | | | | |
| 25 | 415.8050 | 8.2 | 14093 | | | | | | | | |
| 26 | 417.8048 | 7.7 | 13228 | | | | | | | | |
| 27 | 437.8333 | 32.3 | 55554 | | | | | | | | |
| 28 | 438.8185 | 6.9 | 11904 | | | | | | | | |
| 29 | 439.8300 | 29.9 | 51439 | | | | | | | | |
| 30 | 440.8162 | 6.2 | 10980 | | | | | | | | |
| 31 | 444.6914 | 3.4 | 5930 | | | | | | | | |
| 32 | 446.6916 | 8.6 | 15122 | | | | | | | | |
| 33 | 449.6913 | 5.0 | 13787 | | | | | | | | |
| 34 | 465.6141 | 29.6 | 50825 | | | | | | | | |
| 35 | 466.6172 | 7.2 | 12390 | | | | | | | | |
| 36 | 487.6238 | 28.1 | 45272 | | | | | | | | |
| 37 | 488.6217 | 6.5 | 11138 | | | | | | | | |
| 38 | 485.6180 | 13.6 | 23713 | | | | | | | | |
| 39 | 487.7178 | 36.3 | 65811 | | | | | | | | |
| 40 | 489.7174 | 34.3 | 56889 | | | | | | | | |
| 41 | 491.7172 | 10.7 | 18521 | | | | | | | | |
| 42 | 517.7263 | 14.3 | 24580 | | | | | | | | |
| 43 | 518.7266 | 4.7 | 8097 | | | | | | | | |
| 44 | 519.7263 | 13.0 | 22329 | | | | | | | | |
| 45 | 520.2690 | 4.3 | 7458 | | | | | | | | |
| 46 | 526.7442 | 4.7 | 8168 | | | | | | | | |
| 47 | 528.7439 | 12.4 | 21545 | | | | | | | | |
| 48 | 530.7434 | 11.7 | 20151 | | | | | | | | |
| 49 | 532.7430 | 4.1 | 6979 | | | | | | | | |
| 50 | 608.0739 | 3.4 | 5545 | | | | | | | | |
| 51 | 615.0577 | 21.8 | 37519 | | | | | | | | |
| 52 | 615.4221 | 4.0 | 6602 | | | | | | | | |
| 53 | 616.0610 | 7.8 | 13376 | | | | | | | | |
| 54 | 617.0576 | 22.9 | 39358 | | | | | | | | |
| 55 | 617.4256 | 3.4 | 5845 | | | | | | | | |
| 56 | 618.0605 | 8.2 | 14182 | | | | | | | | |
| 57 | 643.4553 | 4.0 | 6958 | | | | | | | | |
| 58 | 656.6103 | 3.1 | 5342 | | | | | | | | |
| 59 | 658.6102 | 4.5 | 7730 | | | | | | | | |
| 60 | 686.1853 | 7.3 | 12564 | | | | | | | | |
| 61 | 698.1850 | 8.6 | 15198 | | | | | | | | |
| 62 | 689.1927 | 3.2 | 5437 | | | | | | | | |

Bruker Compass DataAnalysis 4.0

Acquisition Date: 17.03.2020 16:09:30

Page 2 of 3
## High Resolution Mass Spectrometry Report

| #  | m/z   | Int. | I   |
|----|-------|------|-----|
| 63 | 690.1901 | 4.2 | 7287 |
| 64 | 783.3371 | 4.3 | 7432 |
| 65 | 765.3372 | 4.3 | 7334 |
| 66 | 789.3550 | 21.8 | 37412 |
| 67 | 770.3582 | 10.3 | 17688 |
| 68 | 771.3556 | 21.4 | 36559 |
| 69 | 772.3586 | 9.9 | 16981 |
| 70 | 785.3552 | 4.2 | 7207 |
| 71 | 789.5033 | 37.4 | 64511 |
| 72 | 790.5061 | 18.7 | 32143 |
| 73 | 791.5036 | 41.1 | 70609 |
| 74 | 792.5060 | 16.5 | 31751 |
| 75 | 793.5064 | 5.4 | 9248 |
| 76 | 805.4861 | 6.3 | 10839 |
| 77 | 806.5019 | 3.1 | 5345 |
| 78 | 807.4992 | 6.7 | 11603 |
| 79 | 810.3854 | 3.6 | 9199 |
| 80 | 812.3844 | 3.6 | 6576 |
| 81 | 1023.5381 | 6.1 | 10574 |
| 82 | 1024.5412 | 3.6 | 6541 |
| 83 | 1025.5395 | 6.3 | 10680 |
| 84 | 1026.5436 | 3.6 | 6528 |
| 85 | 1279.5086 | 3.6 | 6579 |
| 86 | 1283.7650 | 4.1 | 7072 |
| 87 | 1284.7677 | 3.3 | 5674 |
| 88 | 1285.7654 | 5.0 | 8604 |
| 89 | 1286.7686 | 3.6 | 6123 |
| 90 | 1299.7346 | 3.5 | 8903 |
| 91 | 1433.9135 | 3.9 | 6036 |
| 92 | 1452.0633 | 6.2 | 10611 |
| 93 | 1453.0679 | 5.5 | 9397 |
| 94 | 1454.0664 | 8.0 | 13748 |
| 95 | 1455.0693 | 6.0 | 10389 |
| 96 | 1456.0706 | 3.2 | 5578 |
| 97 | 1472.2177 | 3.9 | 9669 |
| 98 | 1473.2212 | 3.7 | 6396 |
| 99 | 1474.2197 | 5.5 | 9448 |
| 100 | 1475.2217 | 4.2 | 7274 |

### Acquisition Parameter

**General**
- Fore Vacuum: 2.54e+000 mBar
- Scan Begin: 75 m/z
- Source Nebulizer: 0.4 Bar
- Source Dry Heater: 180 °C

**Quadrupole**
- Set Ion Energy (MS only): 4.0 eV

**Collision Cell**
- Collision Energy: 8.0 eV
- Set Collision Cell RF: 500.0 Vpp

**Ion Cooler**
- Set Ion Cooler Transfer Time: 100.0 μs
- Set Ion Cooler Pre Pulse Storage Time: 18.0 μs

**High Vacuum**
- Scan End: 1700 m/z
- Set Capillary: 3800 V
- Set End Plate Offset: -500 V

**Source Type**
- Ion Pointify: ESI Positive

**ESI**
- 4.0 l/min
2. Transport Measurements

2.1 Mechanically Controlled Break Junction

Figure S1: Schematic illustration of the MCBJ setup.

The single-molecule measurements, described in the main text, were carried out with a mechanically controlled break junction. The MCBJ sample consists of a lithographically fabricated gold wire suspended on a flexible substrate made out of phosphor bronze (PB) with an insulating coating of polyimide (PI). The gold wire was defined with electron-beam lithography and evaporated with an electron-beam evaporator with a thickness of 80 nm together with a 3 nm titanium adhesive layer. In a typical room temperature MCBJ measurement, the gold wire is stretched through a three-point bending mechanism with a piezoelectric element and eventually ruptures, forming a nanogap between atomically sharp electrode surfaces for single-molecule characterization. During the breaking of the gold wire, the electrical conductance is recorded with or without the presence of molecules, and the closing of the junction is performed when the contact is broken, as signaled by a conductance below $10^{-6} G_0$. During the successive breaking and making of the gold contacts through the bending/unbending of the substrate, the electrical conductance is monitored, and a large number of “breaking traces” is collected. With a molecule of interest inside the junction, we can determine the single-molecule electrical conductance statistically.

2.2 Fast-Breaking Measurements

In the measurements performed for the PCP molecules, the MCBJ junctions were first characterized without the molecules for reference purposes. After the reference gold measurement, we deposited molecular solutions with concentrations ranging from 1 to 100 $\mu$M in $\text{CH}_2\text{Cl}_2$ onto the MCBJ samples. The fast-breaking measurements were performed at a constant DC bias voltage with the electrical current recorded by a homemade logarithmic current amplifier. During the fast-breaking measurements, the molecular junctions were continuously opened and closed by the piezoelectric element, creating thousands of conductance breaking traces. The thousands of breaking traces were then plotted together to form a two-dimensional conductance histogram.
Figure S2: One-dimensional histogram of a fast-breaking measurement of ps-para-para and ps-meta-para PCP.

The one-dimensional conductance histogram, which is illustrated in Figure S2, was obtained by summing the counts at a fixed conductance level across all displacement values from a two-dimensional conductance vs. displacement histogram (see Figure 2). With a log-normal fit, the most probable conductance values for the ps-para-para and ps-meta-para PCP molecules are $1.3 \times 10^{-5} G_0$ and $2.2 \times 10^{-5} G_0$, respectively.

2.3 Distance-Modulation Measurements

Figure S3: Distance-modulation traces of ps-para-para PCP. The blue lines display three different types of conductance measurements, namely in-phase, double frequency, and anti-phase, and the red line displays the voltage applied to the piezoelectric stack. Note that an increase in piezo voltage corresponds to an increase in electrode displacement. The total modulation time of the experiment is 15 seconds.
An additional set of measurements of ps-para-para PCP is presented in Figure S3. The modulation traces clearly show in-phase and anti-phase behavior for the whole duration of 15 s. Note that the ascribed double frequency signal changes to the in-phase configuration after around 8 s during the modulation experiment. There are 112 traces in total showing a clear modulation signal in this modulation experiment, and the ratio of each behavior is provided in Figure S4.

**Figure S4:** Ratio of phase response behaviors of ps-para-para PCP during the distance-modulation experiments.

The ratio between the in-phase, anti-phase, and double-frequency is 60:13:27. The in-phase case is clearly dominating the modulation behavior compared to the anti-phase case. This difference also results in much fewer counts in the negative gauge factor shown in Figure 4a. The scarceness of the anti-phase behavior can be understood by looking at the starting electrode position in the modulation experiment. There, we first opened the junction up to 7.5 Å and then started modulating the junction with an amplitude of 5 Å. The total length of the molecular plateau is about 12.5 Å according to the fast-breaking measurement shown in Figure 2. Although the modulation size in the junction may not directly transform into the deformation of the molecule, we thus expect that the modulation occurs mostly in the strained molecular state. Considering the transmission vs. displacement chart for ps-para-para PCP shown in Figure 5b and the conductance dip depicted in Figure 3e, the in-phase behavior should be prevalent for a strained molecule.

### 2.4 Estimation of the Gauge Factor

In the main text, we introduced the gauge factor to quantify the mechano-sensitivity of the molecules. We define it as:

$$ GF(f) \equiv \text{FFT}\left[\log \frac{G}{G_0}\right](f) / \text{FFT}[d/d_0](f) $$

where $GF(f)$ is the frequency-dependent gauge factor, which we evaluate at $f=5$ Hz. In Eq. (1), FFT is the amplitude of the Fast-Fourier transform, $G$ is the conductance, $G_0$ is the conductance quantum, $d$ is the electrode displacement estimated from the piezo voltage, and $d_0$ is the length of the molecule estimated from the most probable molecular length in fast-breaking measurements. Essentially, GF involves a Fast-Fourier transform of the conductance signal on a logarithmic scale and of the electrode displacement on a linear scale. The obtained FFT amplitudes at the driving frequency $f$ of 5 Hz are then taken to define GF by taking the ratio of the two. Note that the sign of GF is fixed by the phase of the signal obtained from the FFT spectra, where in-phase gives a positive GF and anti-phase a negative GF.
For example, if we use a highly mechano-sensitive molecule with mainly anti-phase behavior, we expect to see GF < 0, and a large absolute value |GF| ≠ 0 indicates a large conductance change. In the case of a non-mechano-sensitive molecule, such as ps-meta-para PCP, |GF| is close to 0, while we find |GF| > 1 for the mechano-sensitive ps-para-para PCP.

2.5 Stick-Slip Motion in Molecular Junctions

Figure S5: Individual fast-breaking traces for ps-meta-para and ps-para-para molecules.

In the fast-breaking experiment described in the main text, thousands of breaking traces for ps-meta-para and ps-para-para molecules were obtained. As suggested by Figure S2, the average conductance value of ps-meta-para is slightly larger and exhibits a narrower conductance distribution than those of ps-para-para. This is explained by the absence of DQI in the case of ps-meta-para. When the individual traces shown in Figure S5 are examined further, it is clear that ps-para-para features conductance oscillations during the displacement of electrodes, indicating the presence of DQI. However, oscillations can repeat up to 3 or 4 times instead of the single oscillation expected from crossing a DQI dip. Such a behavior was already observed in the previous experiment with OPE PCP, and we explained it by the stick-slip motion of the molecule in the junction. This stick-slip motion happens, when the molecule is strained sufficiently. As the gold-sulfur connection breaks due to the high strain, the molecule contracts before it establishes a new connection between the sulfur anchor and a nearby electrode gold atom. This process leads to multiple conductance oscillation as observed in the breaking traces. A similar motion can be conceived, if the molecule drags along with it a gold adatom or generally a smaller gold cluster that slides along a macroscopic gold surface. The stick-slip motion is discussed further in the theory section below.
3. Transport Calculations

3.1 DFT Calculation Setup

We describe electronic transport through the PCP-based single-molecule junctions as phase-coherent and elastic in terms of the Landauer scattering theory. The conductance at sufficiently low temperatures simplifies to

\[ G = G_0 \tau(E_F), \]

i.e. the product of the energy-dependent transmission function \( \tau(E) \), evaluated at the Fermi energy \( E_F \), and the conductance quantum \( G_0 = 2e^2/h \). The elastic transmission \( \tau(E) \) is computed in a parameter-free approach by combining DFT with NEGF techniques. The established theoretical methods have been discussed in detail previously.

The calculations to obtain the transmission as a function of energy and electrode displacement for the four PCP derivatives comprise the following steps: First, the molecular structures are optimized in the gas phase. Then terminal hydrogens at each sulfur atom are removed, and the molecules are placed between two tetrahedral gold leads. We distinguish “top-top” and “hollow-hollow” junction geometries, where we use either atomically sharp tips, ending with a single Au tip atom for “top-top”, or blunt tips for hollow-hollow, where the tip atoms are removed on each side. The resulting junction structures are subsequently optimized by relaxing both the molecule and the four (for top-top geometries) or three (for hollow-hollow geometries) gold atoms that are located at the top of each pyramid. The rest of the gold atoms are fixed in a face-centered cubic lattice configuration. The resulting geometries are displayed in Figure 5a of the main text for the hollow-hollow junction configuration and in Figure S6a for the top-top junction configuration. In the stretching process we separate the gold contacts in steps of 0.1 Å, optimize the geometries as described before, and keep increasing the electrode separation \( d \) until the contact ruptures. For compression we proceed in an analogous way until the molecular structure starts to strongly deform. Finally the transmission \( \tau(E, d) \) and from Eq. (1) the conductance \( G(d) \) are computed for the static geometries within the DFT-NEGF formalism.

The DFT calculations are performed with the quantum chemistry code TURBOMOLE, employing the def-SV(P) Gaussian basis set for all atoms and the PBE exchange-correlation functional. Total energies are converged to an accuracy of better than \( 10^{-8} \) a.u., while geometries are optimized until the change of the maximum norm of the Cartesian gradient is below \( 10^{-3} \) a.u. The transport program that we use for computing the elastic transmission is custom-built and interfaced with TURBOMOLE. For evaluating the transmission function, we employ \( 16 \times 16 \) transverse \( k \)-points to properly describe the semi-infinite gold electrodes.
3.2 Transmission Maps and Stick-Slip Motion in the Top-Top Configuration

In the main text, we discuss conduction properties of the four PCP molecules immobilized in hollow-hollow junctions. In this part we now focus on a different geometry, namely the behavior of the PCP derivatives in the top-top configuration, see Figure S6a. The conductance and the total energy of DFT are illustrated in Figure S6b for all four PCP derivatives. Considering the example of the ps-para-para PCP single-molecule junction, both quantities show pronounced jumps at certain stretching steps during the electrode displacement process. Starting from the initial junction geometry at zero displacement, conductance and total energy grow to a local maximum at 1.5 Å. At this point an anchoring sulfur slips to the next gold atom, see Figure S7a, and the molecule releases the mechanical tension that has been built up due to the mechanical stretching process. An instantaneous decrease of both conductance and energy is observed, restoring the latter to a lower value. After reaching the final tip gold atom, the junction breaks at 5.6 Å, and the molecule snaps back and loses contact to one electrode as the mechanical tension becomes too high, which leads to a sharp drop in the conductance. Molecular contacts based on the other three PCP derivatives show a similar interplay of elastic and plastic stretching stages. The sliding of the anchor group along the surface of the electrode, as presented in Figure S7 and called stick-slip motion, is evident from the experimental data in Figure S5 and has also been observed in our previous work.\(^7\)

In the two-dimensional contour maps of transmission in dependence of energy and electrode displacement, see Figure S6c, sudden geometric rearrangements in the junctions (such as the slipping of the anchor group to a neighboring gold atom) result in a discontinuous distance dependence (for ps-para-para PCP at 1.5 Å and 4.6 Å, for ps-meta-para PCP at 2.3 Å, for ps-para-meta PCP at 3.1 Å and 5.0 Å, and for ps-meta-meta PCP at 0.8 Å and 2.4 Å).

A closer look at Figure S6c reveals a similar transport behavior of the top-top molecular junctions compared to the hollow-hollow junctions of Figure 5 in the main text. Again, inside the electronic gap between the HOMO and the LUMO the ps-para-para PCP junction shows transmission valleys (blue diagonal traces) with transmission values lower than 10\(^{-6}\), which cause DQI conductance dips. In contrast the ps-meta-para PCP junction features a rather constant transmission in the range of about 10\(^{-3}\) to 10\(^{-4}\). Different from the observations in the main text, remnants of transmission valleys are faintly visible close to the LUMO for the ps-meta-meta PCP molecular junction in top-top configuration, further consolidating the hypothesis of the central ps-para PCP subunit as origin of the DQI phenomenon. Again, rather uniform transmission values are predicted in the molecule’s electronic gap for ps-meta-meta PCP as structural analogue with a central ps-meta PCP subunit.
Figure S6: (a) Illustration of the PCP derivatives 1-4, immobilized in top-top junctions between two gold electrodes. (b) Calculated conductance and total energy of the PCP molecular junctions during the gap opening. (c) Transmission maps of the four types of PCP single-molecule junctions. Horizontal red resonances in the maps arise from molecular frontier orbitals. For the ps-para-para PCP molecule, an anti-resonance is observed inside the HOMO-LUMO gap that shifts in energy as the displacement is varied. Analogous behavior can be found for the ps-para-meta PCP molecule as well, but the effect is masked by the DQI, resulting from the meta coupling at the terminal benzene rings. Tunable DQI effects are neither found in the simulations of ps-meta-para PCP junctions nor ps-meta-meta PCP junctions with central ps-meta PCP systems. The position of the Fermi energy $E_F$ is indicated as a horizontal dashed line in each plot. The conductance curves of panel b are obtained by tracing the transmission along this line.
Figure S7: Snapshots illustrating the stick-slip motion of the sulfur anchor group on the gold electrode at different electrode displacements $d$ for the (a) ps-para-para, (b) ps-meta-para, (c) ps-para-meta, and (d) ps-meta-meta PCP molecules.
3.3 Quantum Interference Effects and Symmetry Rules

We relate the valleys of low transmission in Figures 5 and S6 to DQI effects, resulting from molecular frontier orbital contributions. The appearance or absence of these valleys can be explained by using orbital symmetry rules for the molecules’ gas-phase orbitals, which are documented in the literature. For off-resonant transport inside the HOMO-LUMO gap, embedding self-energies of the electrodes can be neglected to first approximation. Therefore, the retarded Green’s function $G_{i\alpha,j\beta}^{r}(E)$ that describes the probability amplitude for the propagation of electrons from orbital $\alpha$ at atom $i$ to orbital $\beta$ at atom $j$ through the molecule can be approximated by the zeroth-order Green’s function

$$G_{i\alpha,j\beta}^{r,(0)}(E) = \sum_{k} \frac{C_{i\alpha,k} C_{j\beta,k}^{*}}{E + \eta - \epsilon_{k}}$$

with the energy $\epsilon_{k}$ of molecular orbital $k$, its coefficient $C_{i\alpha,k}$ at atom $i$ and atomic orbital $\alpha$, and a positive infinitesimal broadening parameter $\eta$. We identify the sites $i$ and $j$ with the terminal sulfur...
atoms of the respective PCPs (see Figure S9). The relation between the transmission and the Green’s function

\[ \tau(E) \propto |G_{\alpha,\beta}^{r,(0)}(E)|^2 \]  

ultimately connects transmission to molecular orbital contributions \( k \). In Eq. (3) a sum should be carried out over all orbitals \( \alpha \) and \( \beta \) that couple well to the electrodes, and there should be a weighting factor included that depends on this molecule-electrode coupling. For simplicity and under the assumption that the energy \( E \) is located between the HOMO energy \( \epsilon_{\text{HOMO}} \) and the LUMO energy \( \epsilon_{\text{LUMO}} \), we reduce the Green’s function in Eq. (2) to the largest terms and thus only consider the HOMO and LUMO contributions

\[ G_{\alpha,\beta}^{r,(0)}(E) \approx \frac{c_{\alpha,\text{HOMO}}c_{\beta,\text{HOMO}}^*}{E + i\eta - \epsilon_{\text{HOMO}}} + \frac{c_{\alpha,\text{LUMO}}c_{\beta,\text{LUMO}}^*}{E + i\eta - \epsilon_{\text{LUMO}}}. \]  

For a full description of the transmission behavior further orbital contributions \( k \) may need to be taken into account\(^{16,}\), but Eq. (4) still allows for a qualitative explanation of the occurrence or absence of DQI in the case of the studied PCP systems. We will omit the atomic orbital indices \( \alpha \) and \( \beta \) in Eqs. (2)-(4) in the following and not specify them further, similar to the presentation in the paper. They will simply be of the form of the HOMO and LUMO wavefunctions at the atoms \( i \) and \( j \). It is important though that the orbital characters of HOMO and LUMO wavefunctions are of compatible character in order to interfere as given in Eq. (4). Figure S8 reveals that this is the case here, i.e. all of the relevant HOMOs and LUMOs exhibit the same \( \pi \)-character and spatial orientation at the respective terminal sulfur atoms for each of the four PCP derivatives. The form of the Green’s function in Eq. (4) combined with Eq. (3) allows to draw the following conclusions\(^{12,13}\): First, the products of the orbital coefficients \( c_{\alpha,\text{HOMO}}c_{\beta,\text{HOMO}}^* \) of the HOMO and \( c_{\alpha,\text{LUMO}}c_{\beta,\text{LUMO}}^* \) of the LUMO need to be of decent size in order to contribute to the transmission. For this reason, the weights of HOMO and LUMO wave functions need to be sufficiently large on the anchoring atoms \( i \) and \( j \), meaning that these are delocalized orbitals. Second, the parities of the molecule’s HOMO and LUMO need to be different (\( \text{sign}(c_{\alpha,\text{HOMO}}c_{\beta,\text{HOMO}}^*) = -\text{sign}(c_{\alpha,\text{LUMO}}c_{\beta,\text{LUMO}}^*) \)) in order to achieve high transmission, as in this case the terms in Eq. (4) add up. If the parities of HOMO and LUMO are the same instead, the two terms cancel each other inside the gap, and DQI occurs, resulting in a low transmission. Figure S8 shows relevant frontier molecular orbitals and their energies, from which orbital weights on terminal sulfurs as well as their parity can be inferred. The quantities are needed to rationalize the transport behavior in Figure 5 of the main text as well as Figure S6 in terms of the orbital symmetry rules.

3.4 Transmission Eigenchannels

Figure S9 visualizes the wave function of those left-incoming transmission eigenchannels with the highest transmission for each of the four studied PCP isomers at the Fermi energy and at a particular
electrode separation $d$. We see that the amplitude of the eigenchannels decays along the propagation direction inside the molecules, as expected in an off-resonant transport situation.

The spatial distribution of the wave function is quite similar for all four molecules, exhibiting a high weight on the molecular deck that is directly connected through a sulfur anchor to the left electrode and a low weight on the molecular deck that is directly connected to the right electrode. Note the low weight of the wave function on the ethylene braces of the central paracyclophane units. It indicates that they do not contribute to the phase-coherent electronic transmission through the PCP molecules at $E_F$.

![Image](image-url)

**Figure S9:** Illustration of the wave function of the most transparent left-incoming transmission eigenchannel, evaluated at the Fermi energy $E_F$, for electron transport through (a) ps-para-para, (b) ps-meta-para, (c) ps-para-meta, and (d) ps-meta-meta PCP molecules connected to gold electrodes. The selected electrode displacement $d$ is indicated separately for each junction.

4. References

(1) Duncan, K. D.; Fang, R.; Yuan, J.; Chu, R. K.; Dey, S. K.; Burnum-Johnson, K. E.; Laneckoff, I. Quantitative Mass Spectrometry Imaging of Prostaglandins as Silver Ion Adducts with Nanospray Desorption Electrospray Ionization. *Anal. Chem.* 2018, 90 (12), 7246–7252. https://doi.org/10.1021/acs.analchem.8b00350.

(2) Munakata, M.; Wu, L. P.; Sugimoto, K.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Maeno, N.; Fujita, M. Silver(I) Complex Assemblies with Nonplanar Aromatic Compounds. *Inorg. Chem.* 1999, 38 (25), 5674–5680. https://doi.org/10.1021/ic990391m.

(3) Vorontsova, N. V.; Rozenberg, V. I.; Sergeeva, E. V.; Vorontsov, E. V.; Starikova, Z. A.; Lyssenko, K. A.; Hopf, H. Symmetrically Tetrasubstituted [2.2]Paracyclophanes: Their Systematization and Regioselective Synthesis of Several Types of Bis-Bifunctional Derivatives by Double Electrophilic Substitution. *Chem. – Eur. J.* 2008, 14 (15), 4600–4617. https://doi.org/10.1002/chem.200701683.

(4) Søndergaard, R.; Krebs, F. C. The Challenge of Synthesizing Oligomers for Molecular Wires. *Polymers* 2011, 3 (1), 545–557. https://doi.org/10.3390/polym3010054.

(5) Kahrs, C.; Wickleder, M. S.; Christoffers, J. Biphenyl Sulfonic and Disulfonic Acids with Perfluorinated Alkyl Residues. *Eur. J. Org. Chem.* 2018, 2018 (41), 5754–5762. https://doi.org/10.1002/ejoc.201800882.

(6) Jevric, M.; Petersen, A. U.; Manso, M.; Madsen, A. Ø.; Nielsen, M. B. Bismuth(III)-Promoted Acetylation of Thio-ethers into Thioacetates: Bismuth(III)-Promoted Acetylation of Thioethers into Thioacetates. *Eur. J. Org. Chem.* 2015, 2015 (21), 4675–4688. https://doi.org/10.1002/ejoc.201500420.

(7) Stefani, D.; Weiland, K. J.; Skripnik, M.; Hsu, C.; Perrin, M. L.; Mayor, M.; Pauly, F.; van der Zant, H. S. J. Large Conductance Variations in a Mechano sensitive Single-Molecule Junction. *Nano Lett.* 2018, 18 (9), 5981–5988. https://doi.org/10.1021/acs.nanolett.8b02810.

(8) Cuevas, J. C.; Scheer, E. *Molecular Electronics : An Introduction to Theory and Experiment*, 2nd ed.; World Scientific: Singapore, 2017.
(9) Pauly, F.; Viljas, J. K.; Huniar, U.; Hähner, M.; Wohlthat, S.; Bürkle, M.; Cuevas, J. C.; Schön, G. Cluster-Based Density-Functional Approach to Quantum Transport through Molecular and Atomic Contacts. New J. Phys. 2008, 10 (12), 125019. https://doi.org/10.1088/1367-2630/10/12/125019.

(10) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. Electronic Structure Calculations on Workstation Computers: The Program System Turbomole. Chem. Phys. Lett. 1989, 162 (3), 165–169. https://doi.org/10.1016/0009-2614(89)85118-8.

(11) Schäfer, A.; Horn, H.; Ahlrichs, R. Fully Optimized Contracted Gaussian Basis Sets for Atoms Li to Kr. J. Chem. Phys. 1992, 97 (4), 2571–2577. https://doi.org/10.1063/1.463096.

(12) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77 (18), 3865–3868. https://doi.org/10.1103/PhysRevLett.77.3865.

(13) Bürkle, M.; Viljas, J. K.; Vonlanthen, D.; Mishchenko, A.; Schön, G.; Mayor, M.; Wandlowski, T.; Pauly, F. Conduction Mechanisms in Biphenyl Dithiol Single-Molecule Junctions. Phys. Rev. B 2012, 85 (7), 075417. https://doi.org/10.1103/PhysRevB.85.075417.

(14) Yoshizawa, K.; Tada, T.; Staykov, A. Orbital Views of the Electron Transport in Molecular Devices. J. Am. Chem. Soc. 2008, 130 (29), 9406–9413. https://doi.org/10.1021/ja800638t.

(15) Nozaki, D.; Lucke, A.; Schmidt, W. G. Molecular Orbital Rule for Quantum Interference in Weakly Coupled Dimers: Low-Energy Giant Conductivity Switching Induced by Orbital Level Crossing. J. Phys. Chem. Lett. 2017, No. 8 (4), 727–732. https://doi.org/10.1021/acs.jpcllett.6b02989.

(16) Tsuji, Y.; Yoshizawa, K. Frontier Orbital Perspective for Quantum Interference in Alternant and Nonalternant Hydrocarbons. J. Phys. Chem. C 2017, 121 (17), 9621–9626. https://doi.org/10.1021/acs.jpcc.7b02274.