# Chiral conflict among different helicenes suppresses formation of one enantiomorph in 2D crystallization

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**Supporting Information Figure S1.** Models for homochiral and heterochiral packing for db[5]H. If heterochiral dimers are constructed at the same packing density as for the homochiral dimer (a), one combination has *a priori* a too strong overlap (b, red ellipse). A second combination (c) can be packed with equal density, but its combinations do not fit to the experimentally observed packing (d, heterochiral arrangements are presented with higher transparency.): Although one arrangement (*P*-*M*<sub>1</sub>) fits the bright protrusions, it contradicts the STM contrast at the lower molecular edge (d, yellow ellipse). In particular, it is not possible to build an extended layer due to strong overlap among the unit cells (*P*-*M*<sub>1</sub>, red ellipse). Like for the homochiral combination the *P*-*M*<sub>2</sub> arrangement fits the STM contrast at the lower molecular edge (blue ellipses), but not the bright protrusion pattern. In order to fit into the unit cell, however, the pair of dimers has to pack so close, that the lower parts of the molecules in the middle show a too strong overlap (*P*-*M*<sub>2</sub> red ellipse). The STM image (d) is identical to the one shown as Fig. 2d (10 nm × 10 nm, U = 2.051 V, I = 28 pA).



Supporting Information Figure S2. Model of a 2 × 3 arrangement of unit cells. A single unit cell consists of two dimers, rotated by 180 degrees with respect to each other. This allows along the  $\begin{bmatrix} 1 & \overline{1} & 0 \end{bmatrix}$ direction a close arrangement by overlap to one side, but not to the other side. No overlap is observed along the  $[11\overline{2}]$  direction (*viz.* perpendicular to  $[1\overline{1}0]$ ). The transformation matrix between

adsorbate lattice and gold substrate is  $\begin{pmatrix} 6 & 2 \\ 0 & 13 \end{pmatrix}$ . A unit cell contains 4 molecules and covers 78 Au

atoms. The lengths of the unit cell vectors are 1.52 nm and 3.74 nm.



Supporting Information Figure S3. STM image ( $150 \text{ nm} \times 150 \text{ nm}$ , U = -2.725 V, I = 31 pA) of a monolayer consisting of 90% *rac*-db[5]H and 10% (*M*)-[7]H. The (*P*)-db[5]H enantiomorph (yellow) covers a smaller area than the (*M*)-db[5]H enantiomorph (blue).



**Supporting Information Figure S4.** Dependence of excess of *M*-db[5]H domains (blue) and overall ordered area (red) on the amount of [7]H mixed into the monolayer. The amount of [7]H is given in percentage of the area covered (coverage, bottom axis) and the relative molar amount of [7]H in the layer ('diastereomeric excess-de').

Supporting Information Table S1. Summary of the statistical analyses.

Coverage doping	Amount of <i>M</i> -7[H]	Nr of 200 x 200 nm images	Total area probed /nm <sup>2</sup>	Ordered area /nm <sup>2</sup>	Percentage of ordered area	Percen- tage M domains	Avg. Domain Size (M)	Avg. Domain Size (P)
0 %	0.00 %	10	400'000	17627	$44 \pm 5$	50	1091	
5 %	6.60 %	10	400'000	10876	$27 \pm 10$	54	655	498
10 %	13.20 %	10	400'000	9815	$25 \pm 8$	67	1119	714
15 %	19.80 %	10	400'000	6860	$17 \pm 11$	86	689	250
20 %	26.40 %	10	400'000	2576	$6 \pm 3$	100	447	



**Supporting Information Figure S5.** Models for diastereomeric interactions between (P)-db[5]H and (M)-[7]H (a-c) and (M)-db[5]H and (M)-[7]H (d-f). The six examples show the closest arrangements possible for P-M and M-M combinations. The largest overlap between both species is achieved for the P-M pair shown in b.

## Syntheses

$$\square_{Br}^{F} \xrightarrow{a} \bigcirc_{F}^{Br} \xrightarrow{b} \stackrel{F}{\longrightarrow} \stackrel{f}{\longrightarrow} \stackrel{c}{\longrightarrow} \stackrel{c}$$

a 1. nBuLi, THF, -78 °C 2. ZnCl<sub>2</sub> 3. Pd(PPh<sub>3</sub>)<sub>4</sub>, 1-bromo-2-iodobenzene, 50 °C, 12 h, 90 %.

b 1. nBuLi, THF, -78 °C 2. ZnCl<sub>2</sub> 3. PEPPSI-*i*Pr, 1,4-diiodobenzene, 70 °C, 13 h, 61 %.

c [/Pr<sub>3</sub>Si][CHB<sub>11</sub>H<sub>5</sub>Cl<sub>6</sub>], Me<sub>2</sub>SiMes<sub>2</sub>, PhCl, 110 °C, 8 h, 67 %.

Supporting Scheme 1. Scheme of synthesis of db[5]H.

## **Reaction Conditions and Chemicals**

The C–F activation reaction was set up in an MBraun glovebox under a nitrogen atmosphere with  $O_2$ ,  $H_2O < 0.1$  ppm. The reaction mixture was heated outside the glovebox, but still under a nitrogen atmosphere. All glassware was dried at 150 °C for at least 12 hrs and allowed to cool *in vacuo*. The substrates and reagents used for the C–F activation reaction were synthesized and purified. Chlorobenzene was filtered through dry  $Al_2O_3$  and stored over 4 Å molecular sieves. The Negishi cross-coupling reactions were conducted in water- and oxygen-free atmosphere. Dry THF from the solvent system was used, ZnCl<sub>2</sub> was melted under vacuum in order to eliminate water residue, Palldium catalysts were synthesized in the Siegel group. For work-up and purification outside the glovebox, distilled solvents of technical grade were used.

Compound	Quality	Supplier
chlorobenzene	puriss.	Fluka
1-bromo-2-iodobenzene	99 %	Fluorochem
<i>n</i> -BuLi (2.5 M in hexane)		Acros
1,4-diiodobenzene	99 %	Aldrich
1-fluoro-2-bromobenzene	99 %	Alfa Aesar
zinc chloride	puriss.	Sigma Aldrich

 Table S1. Suppliers and grade of used chemicals.

## Instruments

**NMR spectra** were recorded on Bruker AV-400 (<sup>19</sup>F), and Bruker AV-500 (<sup>1</sup>H, <sup>13</sup>C) instruments. <sup>13</sup>C NMR spectra are proton decoupled. Data are reported as follows: chemical shift in ppm, multiplicity (s = singlet, d = doublet, m = multiplet, ddd = doublet of doublet of doublet, etc.), coupling constant <sup>a</sup>J in Hz, and integration. The signals were referenced against solvent peaks (<sup>1</sup>H: residual CHCl<sub>3</sub> 7.26 ppm; <sup>13</sup>C, CDCl<sub>3</sub> 77.16 ppm) or external standards (<sup>19</sup>F: CCl<sub>3</sub>F in CDCl<sub>3</sub> 0 ppm).

Mass spectra were recorded by the Laboratory for Mass Spectroscopy of the Organic

Chemistry Institute of the University of Zurich on a Finnigan MAT95 instrument or on a Finnigan Trace DSQ GC-MS. Data are reported as follows: m/z (% relative intensity).

## **Syntheses**

**2-fluoro-2'-bromobiphenyl**: To a solution of 1-fluoro-2-bromobenzene (1.12 g, 6.40 mmol) in THF (10 mL) nBuLi (2.7 mL, 2.5 M in hexane, 6.75 mmol) was added at -78 °C. The slightly yellow solution was stirred for 30 min. When ZnCl<sub>2</sub> (952 mg, 6.99 mmol) in THF (8 mL) was added the solution turned colorless and was allowed to warm to 0 °C. It was then transferred to a flask charged with 1-bromo-2-iodobenzene (1.65 g, 5.83 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (67 mg, 0.06 mmol) and THF (10 mL). The solution was then heated to 50 °C and stirred for 12 h. The reaction was quenched with water. The water was then extracted with DCM (3x), the combined organic phases were dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo. Flash column chromatography (Hex/DCM 99:1) afforded the desired product as a colorless oil (1.32 g, 90 %).

 $R_{f}$  (silica, Hexane)= 0.26.

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.69 (dd, J = 8.0, 1.5 Hz, 1 H), 7.41–7.35 (m, 2 H), 7.33–7.20 (m, 3 H), 7.15 (ddd, J = 10, 8.5, 1.5 Hz, 1 H).

<sup>13</sup>C-NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta = 159.70$  (d, <sup>1</sup> $J_{C-F} = 247.3$  Hz), 137.35, 133.01, 131.76, 131.71 (d, <sup>3</sup> $J_{C-F} = 3.1$  Hz), 129.97 (d, <sup>3</sup> $J_{C-F} = 8.0$  Hz), 129.55, 129.03 (d, <sup>2</sup> $J_{C-F} = 16.1$  Hz), 127.31, 123.99, 123.93 (d, <sup>4</sup> $J_{C-F} = 3.6$  Hz), 115.78 (d, <sup>2</sup> $J_{C-F} = 22.1$  Hz).

<sup>19</sup>F-NMR (376.5 MHz, CDCl<sub>3</sub>):  $\delta = -114.68$ .

MS (EI): *m/z* (%): 251.9 (80), 249.9 (84), 171.0 (42), 170.0 (100), 151.0 (20), 85.0 (24), 75.0 (20).

**1,4-bis**(**2,2'-difluorobiphenyl-2-yl)benzene**: To a solution of 2-fluoro-2'-bromobiphenyl (599 mg, 2.39 mmol) in THF (12 mL) nBuLi (1.1 mL, 2.5 M in hexane, 2.75 mmol) was added at – 78 °C . The yellow solution was stirred for 30 min. When  $\text{ZnCl}_2$  (386 mg, 2.83 mmol) in THF (4 mL) was added the solution turned almost colorless and was allowed to warm to 0 °C. It was then transferred to a flask charged with 1,4-diiodobenzene (360 mg, 1.09 mmol) and PEPPSI-iPr (21 mg, 0.03 mmol) and THF (4 mL). The solution was then heated to 70 °C and stirred for 13 h. The reaction was quenched with an aqueous solution of NaHCO<sub>3</sub> (10 %). The water phase was then extracted with DCM (3x), the combined organic phases were dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo. Flash column chromatography (Hex/DCM 98:2 to 90:10) afforded the desired product as a white solid (276 mg, 61 %).

 $R_{f}$  (silica, Hex/DCM 9:1) = 0.17.

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.46–7.37 (m, 8 H), 7.22–7.16 (m, 2 H), 7.07 (ddd, J = 7.5,

7.5, 2.0 Hz, 2 H), 7.01 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 2 H), 6.97 (s, 4 H), 6.91 (ddd, *J* = 10.0, 8.0, 1.0 Hz, 2 H).

<sup>13</sup>C-NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta = 159.55$  (d, <sup>1</sup> $J_{C-F} = 246.6$  Hz), 141.43, 139.61, 134.51, 132.24 (d, <sup>3</sup> $J_{C-F} = 3.5$  Hz), 131.09, 130.16, 129.18 (d, <sup>2</sup> $J_{C-F} = 15.6$  Hz), 128.83 (d, <sup>3</sup> $J_{C-F} = 7.8$  Hz), 128.83 (2 C), 128.26, 127.24, 123.79 (d, <sup>4</sup> $J_{C-F} = 3.6$  Hz), 115.58 (d, <sup>2</sup> $J_{C-F} = 22.5$  Hz).

<sup>19</sup>F-NMR (376.5 MHz, CDCl<sub>3</sub>):  $\delta = -115.44$ .

MS (EI): *m/z* (%): 418.2 (100), 398.2 (19), 246.1 (20), 207.1 (21), 188.1 (30).

[5,6, 9,10]-dibenzopentahelicene: In the glove box, a vial was charged with 1,4-bis(2,2'-difluorobiphenyl-2-yl)benzene (23 mg, 0.055 mmol),  $[iPr_3Si][CHB_{11}H_3Cl_6]$  (6 mg, 0.011 mmol) and Me<sub>2</sub>SiMes<sub>2</sub> (44 mg, 0.148 mmol). The mixture was dissolved in chlorobenzene (1 mL), heated to 110 °C and stirred for 8 h. The reaction was quenched with ethyl acetate and the solvents were evaporated. Flash column chromatography afforded the product as a white solid (14 mg, 67 %).

 $R_{f}$  (silica, Hex/DCM 4:1) = 0.12.

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.68 (m, 6 H), 8.58 (d, *J* = 8.0 Hz, 2 H), 8.27 (d, *J* = 8.0 Hz, 2 H), 7.74 (m, 4 H), 7.53 (ddd, *J* = 8.0, 7.0, 1.5 Hz, 2 H), 7.53 (ddd, *J* = 8.0, 6.5, 1.0 Hz, 2 H).

<sup>13</sup>C-NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta$  = 131.13, 131.04, 130.53, 130.44, 130.05, 129.71, 127.84, 127.64, 127.44, 127.06, 125.37, 123.85, 123.66, 123.37, 121.96.

HR-MS (ESI): m/z: Calculated for C<sub>30</sub>H<sub>19</sub> [M+H]<sup>+</sup>: 379.14813, found: 379.14830.

**Crystal-Structure Determination.** – A crystal of  $C_{30}H_{18}$  was mounted on a glass fibre and used for a low-temperature X-ray structure determination. All measurements were made on an *Agilent Technologies SuperNova* area-detector diffractometer<sup>2</sup> using Cu K $\alpha$  radiation ( $\lambda = 1.54184$  Å) from a micro-focus X-ray source and an *Oxford Instruments Cryojet XL* cooler. The unit cell constants and an orientation matrix for data collection were obtained from a least-squares refinement of the setting angles of 10218 reflections in the range 4° < 20 < 148°. A total of 1884 frames were collected using  $\omega$  scans with  $\kappa$  offsets, 1.5-10.0 seconds exposure time and a rotation angle of 1.0° per frame, and a crystal-detector distance of 55.0 mm.

Data reduction was performed with *CrysAlisPro<sup>2</sup>*. The intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction using spherical harmonics<sup>2</sup> was applied. The space group was uniquely determined by the systematic absences. Equivalent reflections were merged. The data collection and refinement parameters are given in

Table 1. A view of the molecule is shown in the Figure.

The structure was solved by direct methods using *SHELXS97*<sup>3</sup>, which revealed the positions of all non-hydrogen atoms. The non-hydrogen atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined by using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to  $1.2U_{eq}$  of its parent atom. The refinement of the structure was carried out on  $F^2$  by using full-matrix least-squares procedures, which minimised the function  $\Sigma w (F_0^2 - F_c^2)^2$ . The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. Plots of  $\Sigma w (F_0^2 - F_c^2)^2$  versus  $F_c/F_c(\max)$  and resolution showed no unusual trends. A correction for secondary extinction was applied.

Neutral atom scattering factors for non-hydrogen atoms were taken from Maslen, Fox and O'Keefe<sup>4a</sup>, and the scattering factors for H-atoms were taken from Stewart, Davidson and Simpson<sup>5</sup>. Anomalous dispersion effects were included in  $F_c^6$ ; the values for f' and f'' were those of Creagh and McAuley<sup>4b</sup>. The values of the mass attenuation coefficients are those of Creagh and Hubbel<sup>4c</sup>. The *SHELXL97* program<sup>3</sup> was used for all calculations.



*ORTEP*<sup>1</sup> representation of the molecule (50% probability ellipsoids; H-atoms given arbitrary displacement parameters for clarity)

#### **Definition of Terms**

Function minimized:  $\Sigma w (F_0^2 - F_c^2)^2$  where

$$w = [\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP]^{-1} \text{ and } P = (F_{o}^{2} + 2F_{c}^{2})/3$$

$$F_{o}^{2} = S(C - RB)/Lp$$
and  $\sigma^{2}(F_{o}^{2}) = S^{2}(C + R^{2}B)/Lp^{2}$ 

$$S = Scan rate$$

$$C = Total integrated peak count$$

$$R = Ratio of scan time to background counting time$$

$$B = Total background count$$

$$Lp = Lorentz-polarization factor$$

R-factors:  $R_{int} = \Sigma |\langle F_0^2 \rangle - F_0^2 | / \Sigma F_0^2$  summed only over reflections for which more than one symmetry equivalent was measured.  $R(F) = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$  summed over all observed reflections.  $wR(F^2) = [\Sigma w(F_0^2 - F_c^2)^2 / \Sigma w(F_0^2)^2]^{1/2}$  summed over all reflections. Standard deviation of an observation of unit weight (goodness of fit):  $[\Sigma w(F_0^2 - F_c^2)^2 / (N_0 - N_v)]^{1/2}$  where  $N_0$  = number of observations;  $N_v$  = number of variables

### References

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# Crystallographic data

Crystallised from		?				
Empirical formula		C <sub>30</sub> H <sub>18</sub>				
Formula weight [g mol <sup>-1</sup> ]		378.47				
Crystal colour, habit		colorless, plate				
Crystal dimensions [	mm]	$0.04 \cdot 0.28 \cdot 0.44$				
Temperature [K]		100(1)				
Crystal system		monoclinic				
Space group		<i>P</i> 2 <sub>1</sub> / <i>n</i> (#14)				
Ζ		4				
Reflections for cell d	etermination	10218				
2θ range for cell dete	ermination [°]	4-148				
Unit cell parameters	<i>a</i> [Å]	19.3549(3)				
	<i>b</i> [Å]	5.12886(5)				
	<i>c</i> [Å]	19.9604(3)				
	α [°]	90				
	β [°]	115.0553(19)				
	γ [°]	90				
	V[Å <sup>3</sup> ]	1794.99(4)				
<i>F</i> (000)		792				
$D_x [{ m g \ cm^{-3}}]$		1.400				
μ(Cu <i>K</i> α) [mm <sup>-1</sup> ]		0.604				
Scan type		ω				
2θ <sub>(max)</sub> [°]		148.0				
Transmission factors	(min; max)	0.208; 1.000				
Total reflections mea	sured	18317				
Symmetry independe	ent reflections	774977329				
R <sub>int</sub>		0.018				
Reflections with $I > 2$	$2\sigma(I)$	3308				
Reflections used in refinement		3588				
Parameters refined		272				
Final $R(F)$ [ $I > 2\sigma(I)$	) reflections]	0.0326				
$wR(F^2)$ (all da	ta)	0.0894				
Weights:	$w = [\sigma^2(F_0^2) +$	$(0.0456P)^2 + 0.6114P]^{-1}$ where $P = (F_0^2 + 2F_c^2)/3$				

Goodness of fit

Secondary extinction coefficient	0.0007(2)
Final $\Delta_{max}/\sigma$	0.004
$\Delta \rho$ (max; min) [e Å <sup>-3</sup> ]	0.24; -0.17
$\sigma(d_{(C-C)})$ [Å]	0.001 - 0.002

TABLE S2. Bond lengths (Å) with standard uncertainties in parentheses.

C(1)	-C(2)	1.3745(15)	C(11) -C(12)	1.3772(16)
C(1)	-C(16)	1.4108(15)	C(12) -C(21)	1.4056(15)
C(2)	-C(3)	1.3936(16)	C(13) -C(14)	1.3634(15)
C(3)	-C(4)	1.3768(15)	C(13) -C(20)	1.4123(14)
C(4)	-C(17)	1.4077(15)	C(14) -C(15)	1.4132(14)
C(5)	-C(30)	1.4098(15)	C(15) -C(18)	1.4076(14)
C(5)	-C(6)	1.4144(15)	C(15) -C(16)	1.4612(14)
C(5)	-C(17)	1.4624(15)	C(16) -C(17)	1.4115(15)
C(6)	-C(27)	1.4142(14)	C(18) -C(19)	1.4411(14)
C(6)	-C(18)	1.4690(14)	C(19) -C(20)	1.4059(14)
C(7)	-C(8)	1.4112(15)	C(20) -C(21)	1.4629(15)
C(7)	-C(26)	1.4134(15)	C(21) -C(22)	1.4133(15)
C(7)	-C(19)	1.4666(14)	C(23) -C(24)	1.3732(16)
C(8)	-C(23)	1.4129(15)	C(24) -C(25)	1.3990(17)
C(8)	-C(22)	1.4586(15)	C(25) -C(26)	1.3750(15)
C(9)	-C(10)	1.3759(16)	C(27) -C(28)	1.3793(15)
C(9)	-C(22)	1.4097(15)	C(28) -C(29)	1.3946(16)
C(10)	-C(11)	1.3942(16)	C(29) -C(30)	1.3799(16)

TABLE S3. Bond angles (°) with standard uncertainties in parentheses.

C(2)	-C(1)	-C(16)	121.48(10)	C(17)	-C(16) -C(15)	120.12(9)
C(1)	-C(2)	-C(3)	119.96(10)	C(4)	-C(17) -C(16)	118.80(10)
C(4)	-C(3)	-C(2)	119.77(10)	C(4)	-C(17) -C(5)	122.30(10)
C(3)	-C(4)	-C(17)	121.46(10)	C(16)	-C(17) -C(5)	118.88(9)
C(30)	-C(5)	-C(6)	118.78(10)	C(15)	-C(18) -C(19)	118.40(9)
C(30)	-C(5)	-C(17)	120.97(10)	C(15)	-C(18) -C(6)	117.93(9)
C(6)	-C(5)	-C(17)	120.17(9)	C(19)	-C(18) -C(6)	123.36(9)
C(27)	-C(6)	-C(5)	118.21(9)	C(20)	-C(19) -C(18)	118.99(9)
C(27)	-C(6)	-C(18)	121.25(9)	C(20)	-C(19) -C(7)	117.05(9)

-C(6)	-C(18)	120.04(9)	C(18) ·	-C(19)	-C(7)	123.63(9)
-C(7)	-C(26)	118.48(9)	C(19) ·	-C(20)	-C(13)	118.36(10)
-C(7)	-C(19)	120.24(9)	C(19) ·	-C(20)	-C(21)	120.08(9)
-C(7)	-C(19)	120.75(10)	C(13) ·	-C(20)	-C(21)	121.56(9)
-C(8)	-C(23)	118.83(10)	C(12)	-C(21)	-C(22)	118.52(10)
-C(8)	-C(22)	119.79(9)	C(12)	-C(21)	-C(20)	121.48(10)
-C(8)	-C(22)	121.15(10)	C(22)	-C(21)	-C(20)	119.91(9)
-C(9)	-C(22)	121.13(10)	C(9)	-C(22)	-C(21)	118.99(10)
-C(10)	-C(11)	119.87(10)	C(9)	-C(22)	-C(8)	122.37(10)
-C(11)	-C(10)	120.01(11)	C(21)	-C(22)	-C(8)	118.47(9)
-C(12)	-C(21)	121.41(10)	C(24)	-C(23)	-C(8)	121.41(10)
-C(13)	-C(20)	121.01(10)	C(23)	-C(24)	-C(25)	119.63(10)
-C(14)	-C(15)	121.24(10)	C(26)	-C(25)	-C(24)	120.16(10)
-C(15)	-C(14)	118.55(9)	C(25)	-C(26)	-C(7)	121.23(10)
-C(15)	-C(16)	120.25(9)	C(28)	-C(27)	-C(6)	121.66(10)
-C(15)	-C(16)	121.19(9)	C(27)	-C(28)	-C(29)	119.78(10)
-C(16)	-C(17)	118.53(10)	C(30) ·	-C(29)	-C(28)	119.72(10)
-C(16)	-C(15)	121.29(10)	C(29)	-C(30)	-C(5)	121.56(10)
	-C(6) -C(7) -C(7) -C(8) -C(8) -C(8) -C(8) -C(9) -C(10) -C(11) -C(12) -C(12) -C(13) -C(14) -C(15) -C(15) -C(15) -C(16)	-C(6)-C(18)-C(7)-C(26)-C(7)-C(19)-C(7)-C(19)-C(8)-C(23)-C(8)-C(22)-C(8)-C(22)-C(9)-C(22)-C(10)-C(11)-C(11)-C(10)-C(12)-C(21)-C(13)-C(20)-C(14)-C(15)-C(15)-C(14)-C(15)-C(16)-C(16)-C(17)-C(16)-C(15)	-C(6) $-C(18)$ $120.04(9)$ $-C(7)$ $-C(26)$ $118.48(9)$ $-C(7)$ $-C(19)$ $120.24(9)$ $-C(7)$ $-C(19)$ $120.75(10)$ $-C(8)$ $-C(23)$ $118.83(10)$ $-C(8)$ $-C(22)$ $119.79(9)$ $-C(8)$ $-C(22)$ $121.15(10)$ $-C(9)$ $-C(22)$ $121.13(10)$ $-C(10)$ $-C(11)$ $119.87(10)$ $-C(11)$ $-C(10)$ $120.01(11)$ $-C(12)$ $-C(21)$ $121.41(10)$ $-C(13)$ $-C(20)$ $121.01(10)$ $-C(14)$ $-C(15)$ $121.24(10)$ $-C(15)$ $-C(16)$ $120.25(9)$ $-C(16)$ $-C(17)$ $118.53(10)$ $-C(16)$ $-C(15)$ $121.29(10)$	-C(6) $-C(18)$ $120.04(9)$ $C(18)$ $-C(7)$ $-C(26)$ $118.48(9)$ $C(19)$ $-C(7)$ $-C(19)$ $120.24(9)$ $C(19)$ $-C(7)$ $-C(19)$ $120.75(10)$ $C(13)$ $-C(8)$ $-C(23)$ $118.83(10)$ $C(12)$ $-C(8)$ $-C(22)$ $119.79(9)$ $C(12)$ $-C(8)$ $-C(22)$ $121.15(10)$ $C(22)$ $-C(9)$ $-C(22)$ $121.13(10)$ $C(9)$ $-C(10)$ $-C(11)$ $119.87(10)$ $C(9)$ $-C(11)$ $-C(10)$ $120.01(11)$ $C(21)$ $-C(12)$ $-C(21)$ $121.41(10)$ $C(24)$ $-C(13)$ $-C(20)$ $121.01(10)$ $C(23)$ $-C(14)$ $-C(15)$ $121.24(10)$ $C(25)$ $-C(15)$ $-C(16)$ $120.25(9)$ $C(28)$ $-C(15)$ $-C(16)$ $121.19(9)$ $C(27)$ $-C(16)$ $-C(17)$ $118.53(10)$ $C(30)$ $-C(16)$ $-C(15)$ $121.29(10)$ $C(29)$	-C(6) $-C(18)$ $120.04(9)$ $C(18)$ $-C(19)$ $-C(7)$ $-C(26)$ $118.48(9)$ $C(19)$ $-C(20)$ $-C(7)$ $-C(19)$ $120.24(9)$ $C(19)$ $-C(20)$ $-C(7)$ $-C(19)$ $120.75(10)$ $C(13)$ $-C(20)$ $-C(7)$ $-C(19)$ $120.75(10)$ $C(12)$ $-C(21)$ $-C(8)$ $-C(23)$ $118.83(10)$ $C(12)$ $-C(21)$ $-C(8)$ $-C(22)$ $119.79(9)$ $C(12)$ $-C(21)$ $-C(8)$ $-C(22)$ $121.15(10)$ $C(22)$ $-C(21)$ $-C(9)$ $-C(22)$ $121.13(10)$ $C(9)$ $-C(22)$ $-C(10)$ $-C(11)$ $119.87(10)$ $C(9)$ $-C(22)$ $-C(11)$ $-C(10)$ $120.01(11)$ $C(21)$ $-C(22)$ $-C(11)$ $-C(10)$ $121.01(10)$ $C(24)$ $-C(23)$ $-C(13)$ $-C(20)$ $121.01(10)$ $C(26)$ $-C(25)$ $-C(15)$ $-C(16)$ $120.25(9)$ $C(28)$ $-C(27)$ $-C(15)$ $-C(16)$ $121.19(9)$ $C(27)$ $-C(28)$ $-C(16)$ $-C(17)$ $118.53(10)$ $C(30)$ $-C(29)$ $-C(16)$ $-C(15)$ $121.29(10)$ $C(29)$ $-C(30)$	-C(6) $-C(18)$ $120.04(9)$ $C(18)$ $-C(19)$ $-C(7)$ $-C(7)$ $-C(26)$ $118.48(9)$ $C(19)$ $-C(20)$ $-C(21)$ $-C(7)$ $-C(19)$ $120.75(10)$ $C(13)$ $-C(20)$ $-C(21)$ $-C(8)$ $-C(23)$ $118.83(10)$ $C(12)$ $-C(21)$ $-C(22)$ $-C(8)$ $-C(22)$ $119.79(9)$ $C(12)$ $-C(21)$ $-C(20)$ $-C(8)$ $-C(22)$ $121.15(10)$ $C(22)$ $-C(21)$ $-C(20)$ $-C(9)$ $-C(22)$ $121.13(10)$ $C(9)$ $-C(22)$ $-C(21)$ $-C(10)$ $-C(11)$ $119.87(10)$ $C(9)$ $-C(22)$ $-C(8)$ $-C(11)$ $-C(10)$ $120.01(11)$ $C(21)$ $-C(22)$ $-C(8)$ $-C(12)$ $-C(21)$ $121.01(10)$ $C(24)$ $-C(25)$ $-C(13)$ $-C(20)$ $121.01(10)$ $C(26)$ $-C(27)$ $-C(24)$ $-C(15)$ $-C(16)$ $120.25(9)$ $C(28)$ $-C(27)$ $-C(6)$ $-C(15)$ $-C(16)$ $121.19(9)$ $C(27)$ $-C(28)$ $-C(29)$ $-C(16)$ $-C(17)$ $118.53(10)$ $C(30)$ $-C(29)$ $-C(28)$

TABLE S4. Torsion angles (°) with standard uncertainties in parentheses.

C(16)	-C(1)	-C(2)	-C(3)	0.6(2)	C(15)	-C(18)	-C(19)	-C(7)	-151.2(1)
C(1)	-C(2)	-C(3)	-C(4)	-0.2(2)	C(6)	-C(18)	-C(19)	-C(7)	35.2(2)
C(2)	-C(3)	-C(4)	-C(17)	-0.1(2)	C(8)	-C(7)	-C(19)	-C(20)	20.0(1)
C(30)	-C(5)	-C(6)	-C(27)	-5.7(1)	C(26)	-C(7)	-C(19)	-C(20)	-151.5(1)
C(17)	-C(5)	-C(6)	-C(27)	171.22(9)	C(8)	-C(7)	-C(19)	-C(18)	-166.75(9)
C(30)	-C(5)	-C(6)	-C(18)	-177.71(9)	C(26)	-C(7)	-C(19)	-C(18)	21.8(2)
C(17)	-C(5)	-C(6)	-C(18)	-0.8(1)	C(18)	-C(19)	-C(20)	-C(13)	-15.0(1)
C(26)	-C(7)	-C(8)	-C(23)	-5.9(1)	C(7)	-C(19)	-C(20)	-C(13)	158.64(9)
C(19)	-C(7)	-C(8)	-C(23)	-177.56(9)	C(18)	-C(19)	-C(20)	-C(21)	165.00(9)
C(26)	-C(7)	-C(8)	-C(22)	168.70(9)	C(7)	-C(19)	-C(20)	-C(21)	-21.4(1)
C(19)	-C(7)	-C(8)	-C(22)	-3.0(1)	C(14)	-C(13)	-C(20)	-C(19)	-0.7(2)
C(22)	-C(9)	-C(10)	-C(11)	0.3(2)	C(14)	-C(13)	-C(20)	-C(21)	179.4(1)
C(9)	-C(10)	-C(11)	-C(12)	1.3(2)	C(11)	-C(12)	-C(21)	-C(22)	-1.7(2)
C(10)	-C(11)	-C(12)	-C(21)	-0.6(2)	C(11)	-C(12)	-C(21)	-C(20)	174.8(1)
C(20)	-C(13)	-C(14)	-C(15)	9.6(2)	C(19)	-C(20)	-C(21)	-C(12)	-170.4(1)
C(13)	-C(14)	-C(15)	-C(18)	-2.4(2)	C(13)	-C(20)	-C(21)	-C(12)	9.6(2)
C(13)	-C(14)	-C(15)	-C(16)	176.7(1)	C(19)	-C(20)	-C(21)	-C(22)	6.1(2)
C(2)	-C(1)	-C(16)	-C(17)	-0.7(2)	C(13)	-C(20)	-C(21)	-C(22)	-173.94(9)
C(2)	-C(1)	-C(16)	-C(15)	176.3(1)	C(10)	-C(9)	-C(22)	-C(21)	-2.5(2)

C(18)	-C(15)	-C(16)	-C(1) -168.10(9)	C(10)	-C(9)	-C(22)	-C(8)	172.6(1)
C(14)	-C(15)	-C(16)	-C(1) 12.9(2)	C(12)	-C(21)	-C(22)	-C(9)	3.2(2)
C(18)	-C(15)	-C(16)	-C(17) 8.8(2)	C(20)	-C(21)	-C(22)	-C(9)	-173.39(9)
C(14)	-C(15)	-C(16)	-C(17) -170.19(9)	C(12)	-C(21)	-C(22)	-C(8)	-172.15(9)
C(3)	-C(4)	-C(17)	-C(16) 0.1(2)	C(20)	-C(21)	-C(22)	-C(8)	11.3(1)
C(3)	-C(4)	-C(17)	-C(5) 178.3(1)	C(7)	-C(8)	-C(22)	-C(9)	172.16(9)
C(1)	-C(16)	-C(17)	-C(4) 0.3(1)	C(23)	-C(8)	-C(22)	-C(9)	-13.4(2)
C(15)	-C(16)	-C(17)	-C(4) -176.69(9)	C(7)	-C(8)	-C(22)	-C(21)	-12.7(1)
C(1)	-C(16)	-C(17)	-C(5) -177.95(9)	C(23)	-C(8)	-C(22)	-C(21)	161.8(1)
C(15)	-C(16)	-C(17)	-C(5) 5.0(1)	C(7)	-C(8)	-C(23)	-C(24)	3.3(2)
C(30)	-C(5)	-C(17)	-C(4) -10.3(2)	C(22)	-C(8)	-C(23)	-C(24)	-171.2(1)
C(6)	-C(5)	-C(17)	-C(4) 172.90(9)	C(8)	-C(23)	-C(24)	-C(25)	1.0(2)
C(30)	-C(5)	-C(17)	-C(16) 167.95(9)	C(23)	-C(24)	-C(25)	-C(26)	-2.7(2)
C(6)	-C(5)	-C(17)	-C(16) -8.9(1)	C(24)	-C(25)	-C(26)	-C(7)	-0.1(2)
C(14)	-C(15)	-C(18)	-C(19) -13.2(1)	C(8)	-C(7)	-C(26)	-C(25)	4.4(2)
C(16)	-C(15)	-C(18)	-C(19) 167.79(9)	C(19)	-C(7)	-C(26)	-C(25)	176.0(1)
C(14)	-C(15)	-C(18)	-C(6) 160.73(9)	C(5)	-C(6)	-C(27)	-C(28)	4.9(2)
C(16)	-C(15)	-C(18)	-C(6) -18.3(1)	C(18)	-C(6)	-C(27)	-C(28)	176.83(9)
C(27)	-C(6)	-C(18)	-C(15) -157.39(9)	C(6)	-C(27)	-C(28)	-C(29)	-0.5(2)
C(5)	-C(6)	-C(18)	-C(15) 14.4(1)	C(27)	-C(28)	-C(29)	-C(30)	-3.1(2)
C(27)	-C(6)	-C(18)	-C(19) 16.2(2)	C(28)	-C(29)	-C(30)	-C(5)	2.2(2)
C(5)	-C(6)	-C(18)	-C(19) -172.05(9)	C(6)	-C(5)	-C(30)	-C(29)	2.3(2)
C(15)	-C(18)	-C(19)	-C(20) 21.9(1)	C(17)	-C(5)	-C(30)	-C(29)	-174.6(1)
C(6)	-C(18)	-C(19)	-C(20) -151.6(1)					