Highly Bent Crystals Formed by Restrained π-Stacked Columns Connected via Alkylene Linkers with Variable Conformations

Chih-Ming Chou, Shunpei Nobusue, Shohei Saito,* Daishi Inoue, Daisuke Hashizume and Shigehiro Yamaguchi*

Department of Chemistry, Graduate School of Science, and Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, Furo, Chikusa, Nagoya 464-8602, Japan.
Materials Characterization Support Unit, RIKEN Center for Emergent Matter Science (CEMS), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

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I. Experimental details

**General.** $^1$H and $^{13}$C NMR spectra were recorded with a JEOL AL-400 MHz spectrometer (400 MHz for $^1$H and 100 MHz for $^{13}$C). Chemical shifts are reported in δ ppm using CHCl$_3$ (7.26 ppm) for $^1$H NMR, and CDCl$_3$ (77.16 ppm) for $^{13}$C NMR as an internal standard. Mass spectrometry was measured with a Bruker Daltonics MicroTOF focus using a positive-mode APCI-TOF method in a toluene solution and a Bruker Daltonics Ultraflex III TOF/TOF (MALDI-TOF-MS). Melting points (Mp.) were measured on a Yanaco MP-S3 instrument. Single crystal X-ray diffraction measurements were performed with Rigaku X-ray diffractometers. For the 1a and 1c·prism crystals, the diffractometer equipped with a molybdenum MicroMax-007 generator, VariMax-Mo optics, and Saturn70 CCD detector was used. For the 1b crystal, the diffractometer equipped with a molybdenum FR-X generator, VariMax-Mo optics, and a PILATUS 200K detector was used. For 1c·bent, the diffractometer equipped with a copper MicroMax-007 microfocus generator, VariMax-Cu optics, and a RAPID IP detector was used. Temperature varied powder X-ray diffraction patterns were measured with a Rigaku SmartLab X-ray diffractometer, equipped with AnthonPaar DCS 350 temperature controller, using Cu Kα radiation in 2θ / θ mode at the rate of 2 ° min$^{-1}$. Temperature was varied at 2 °C min$^{-1}$, and annealed 5 min before diffraction measurements at each temperature. The pattern resolution and unit-cell refinement of powder X-ray diffraction was performed by Pawley method with Rigaku PDXL2. For scanning electron microscopy, the crystals of 1 in 1,2-dichloroethane solution were dried on a silicon-wafer, and were coated with osmium using Filgen, OPC80N osmium coater. Secondary electron images were observed using a JEOL JSM-6330F scanning electron microscope at accelerating voltage of 3 kV with 45° tilting of the sample stage. Fluorescence spectra of the crystals were measured with a Hitachi F-4500 spectrometer in spectral grade solvents. Column chromatography was performed using neutral silica gel PSQ 60B or PSQ100B (Fuji Silysia Chemical). All reactions were performed under a nitrogen atmosphere, unless stated otherwise. Commercially available solvents and reagents were used without further
puriﬁcation unless otherwise mentioned. Dry ether, toluene, tetrahydrofuran (THF) and
diisopropylamine were purchased from Kanto Chemical. Compounds 2a, 2b, and
9-bromo-10-iodoanthracene were prepared according to the literature methods.1,2

A general procedure for the Sonogashira coupling/desilylation reaction (I).

To a 100 mL two-necked flask 1,6-bis(2-bromo-3-thienyl)hexane or 1,7-bis(2-bromo-3-thienyl)heptane (1.0 equiv.), trimethylsilylacetylene (2.3 equiv.), Pd(PPh₃)₄ (5.0 mol%) and CuI (5.0 mol%) in dry toluene/diisopropylamine (3:1) were added. The resulting mixture was stirred at 80 °C under a nitrogen atmosphere for 12 h. The resulting mixture was extracted with CH₂Cl₂, washed with water and dried over anhydrous MgSO₄. After the solvent was removed under reduced pressure, the reaction mixture was treated with K₂CO₃ (3.0 equiv.) in MeOH/THF and stirred at room temperature. After the reaction completed, water was added and the mixture was extracted with ether. The combined organic layer was washed with water and brine dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel afforded the corresponding terminal alkyne products.

A general procedure for the Sonogashira coupling reaction (II).

To a 100 mL two-necked flask 1,6-bis(2-ethynyl-3-thienyl)hexane or 1,7-bis(2-ethynyl-3-thienyl)heptane (1.0 equiv.), 9-bromo-10-iodoanthracene (2.0 equiv.), Pd(PPh₃)₄ (5.0 mol%) and CuI (5.0 mol%) in dry toluene/diisopropylamine were added and stirred at room temperature under a
nitrogen atmosphere for overnight. After addition of water, the reaction mixture was extracted with CHCl₃. The combined organic layer was washed with water and brine, dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure to afford the desired coupling product and was used without further purification.

**A general procedure for the Sonogashira coupling reaction (III).**

To a 200 mL three-necked flask the 1,6-bis(2-ethynyl-3-thienyl)hexane or 1,7-bis(2-ethynyl-3-thienyl)heptane (1.0 equiv.), Pd(PPh₃)₄ (5.0 mol%) and CuI (5.0 mol%) was placed. Aryl bromide (1.0 equiv.) in dry diisopropylamine/THF was slowly added to the reaction mixture at room temperature and then heated at 60 °C with stirring under a nitrogen atmosphere for 18 h. After removal of the solvents under reduced pressure, water was added and the mixture was extracted with CHCl₃. The combined organic layer was water and brine, dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel afforded the desired coupling product.

**1,6-Bis(2-ethynyl-3-thienyl)hexane (3a):** According to the general procedure I: Step 1: 2a (8.30 g, 20.3 mmol), trimethylsilylacetylene (8.5 mL, 60 mmol), Pd(PPh₃)₄ (1.15 g, 1.00 mmol) and CuI (190 mg, 1.00 mmol) in diisopropylamine (20 mL) and toluene (60 mL). Step 2: K₂CO₃ (8.28 g, 59.9 mmol) in MeOH (100 mL) and THF (20 mL). Purification by flash column chromatography (CH₂Cl₂/hexane = 1:9, Rₜ = 0.50) gave 3a (4.06 g, 13.6 mmol) in 65% as a yellow liquid: ¹H NMR (400 MHz, CDCl₃): δ 7.15 (d, J = 5.2 Hz, 2H), 7.84 (d, J = 5.2 Hz, 2H), 3.42 (s, 2H), 2.70 (t, J = 7.6 Hz), 1.50-1.70 (m, 4H), 1.30-1.45 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 148.9, 128.0, 126.2, 117.1, 83.2, 76.8, 30.1, 29.3, 28.9; HRMS (APCI, positive) calculated for C₁₉H₁₈S₂ ([M]⁺): 299.0923. Found: 299.0935.

**1,7-Bis(2-ethynyl-3-thienyl)heptane (3b):** According to the general procedure I: Step 1: 2b (1.09 g,
2.58 mmol), trimethylsilylacetylene (0.85 mL, 6.0 mmol), Pd(PPh₃)₄ (120 mg, 0.104 mmol) and CuI (19.7 mg, 0.103 mmol) in diisopropylamine (4 mL) and toluene (12 mL). Step 2: K₂CO₃ (1.09 g, 7.89 mmol) in MeOH (10 mL) and THF (2 mL). Purification by flash column chromatography (CH₂Cl₂/hexane = 1:9, Rₜ = 0.50) gave 3b (475 mg, 1.52 mmol) in 58% as a yellow liquid: ¹H NMR (400 MHz, CDCl₃): δ 7.15 (d, J = 5.2 Hz, 2H), 6.84 (d, J = 5.2 Hz, 2H), 3.43 (s, 2H), 2.71 (t, J = 7.8 Hz, 4H), 1.55-1.68 (m, 4H), 1.30-1.40 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 149.0, 128.0, 126.2, 116.97, 83.2, 76.7, 30.1, 29.3, 29.06, 29.05; HRMS (APCI, positive) calculated for C₁₉H₂₀S₂ ([M⁺]): 312.1001. Found: 312.1006.

1,6-Bis[2-(10-bromo-9-anthryl)ethynyl]-3-thienyl|hexane (4a): According to the general procedure II: 3a (624 mg, 2.09 mmol), 9-bromo-10-iodoanthracene (1.60 g, 4.18 mmol), Pd(PPh₃)₄ (116 mg, 0.100 mmol) and CuI (19 mg, 0.10 mmol) in diisopropylamine (10 mL) and toluene (10 mL) to give 4a (1.47 g, 1.82 mmol) in 91% as a yellow solid: Mp.: 165–166 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.43–8.55 (m, 8H), 7.50–7.55 (m, 12H), 7.25 (d, J = 5.2 Hz, 2H), 6.89 (d, J = 5.2 Hz, 2H), 2.92 (t, J = 7.8 Hz, 4H), 1.78–1.85 (m, 4H), 1.53–1.60 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 147.9, 132.5, 130.2, 128.5, 127.3, 127.0, 126.73, 126.70, 123.98, 118.5, 118.2, 94.7, 92.1, 30.5, 30.0, 29.3; HRMS (APCI, positive) calculated for C₄₆H₃₂Br₂S₂ ([M⁺]): 806.0307. Found: 806.0312.

1,7-Bis[2-(10-bromo-9-anthryl)ethynyl]-3-thienyl|heptane (4b): According to the general procedure II: 3b (1.56 g, 4.99 mmol), 9-bromo-10-iodoanthracene (3.82 g, 9.97 mmol), Pd(PPh₃)₄ (289 mg, 0.250 mmol) and CuI (47 mg, 0.25 mmol) in diisopropylamine (10 mL) and toluene (30 mL) to give 4b (3.60 g, 4.38 mmol) in 88% as a yellow solid: Mp.: 191–192 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.40–8.60 (m, 8H), 7.49–7.62 (m, 8H), 7.27 (d, J = 5.2 Hz, 2H), 6.89 (d, J = 5.2 Hz, 2H), 2.88 (t, J = 7.6 Hz, 4H), 1.69–1.81 (m, 4H), 1.45–1.58 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 148.0, 132.5, 130.2, 128.5, 128.2, 127.3, 127.0, 126.72, 126.69, 123.9, 118.5, 118.2, 94.8, 92.0, 30.5, 29.9, 29.3, 29.1; HRMS (APCI, positive) calculated for C₄₇H₃₄Br₂S₂ ([M⁺]): 820.0463. Found:
820.0473.

**Macrocyclic dimer 1a:** According to the general procedure III: 3a (267 mg, 0.895 mmol), 4a (710 mg, 0.878 mmol), Pd(PPh₃)₄ (50.8 mg, 0.0440 mmol) and CuI (8.3 mg, 0.044 mmol) in diisopropylamine (30 mL) and THF (100 mL). Purification by flash column chromatography (CH₂Cl₂/hexane = 1:2, Rf = 0.40) gave 1a (124 mg, 0.131 mmol) in 15% as an orange solid: Mp. > 280 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.30–8.38 (m, 8H), 7.27–7.39 (m, 12H), 6.99 (d, J = 5.2 Hz, 4H), 2.96 (t, J = 7.6 Hz, 8H), 1.80–1.92 (m, 8H), 1.59–1.68 (m, 8H); ¹³C NMR (100 MHz, CDCl₃): δ 147.7, 131.4, 128.5, 126.8, 126.7, 126.6, 118.9, 118.0, 95.1, 92.8, 30.5, 30.1, 29.2; HRMS (APCI, positive) calculated for C₆₄H₉₀S₄ ([M+H]⁺): 945.2712. Found: 945.2717.

**Macrocyclic dimer 1b:** According to the general procedure III: 3a (152 mg, 0.509 mmol), 4b (410 mg, 0.498 mmol), Pd(PPh₃)₄ (29.0 mg, 0.0251 mmol) and CuI (4.7 mg, 0.025 mmol) in diisopropylamine (10 mL) and THF (90 mL). Purification by flash column chromatography (CH₂Cl₂/hexane = 1:2, Rf = 0.40) gave 1b (86 mg, 0.090 mmol) in 18% as a deep orange solid: Mp. > 280 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.30–8.39 (m, 8H), 7.34–7.42 (m, 8H), 7.28–7.34 (m, 4H), 6.97–7.01 (m, 4H), 2.90–3.01 (m, 8H), 1.78–1.93 (m, 8H), 1.62–1.68 (m, 4H), 1.52–1.62 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 147.8, 147.7, 131.4, 131.30, 128.54, 128.51, 126.85, 126.83, 126.71, 126.65, 126.59, 118.9, 118.0, 117.9, 95.2, 95.1, 92.9, 92.8, 30.7, 30.6, 30.1, 30.0, 29.5, 29.3, 29.1; HRMS (APCI, positive) calculated for C₆₅H₉₁S₄ ([M+H]⁺): 959.2868. Found: 959.2872.

**Macrocyclic dimer 1c:** According to the general procedure III: 3b (95.0 mg, 0.304 mmol), 4b (246 mg, 0.299 mmol), Pd(PPh₃)₄ (17.3 mg, 0.0150 mmol,) and CuI (2.8 mg, 0.015 mmol,) in diisopropylamine (5 mL) and THF (60 mL). Purification by flash column chromatography (CH₂Cl₂/hexane = 1:2, Rf = 0.40) gave 1c (60 mg, 0.616 mmol) in 21% as a deep orange solid: Mp. > 280 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.26–8.32 (m, 8H), 7.36–7.43 (m, 8H), 7.33 (d, J = 5.2 Hz,
4H), 7.00 (d, J = 5.2 Hz, 4H), 2.93 (t, J = 7.6 Hz, 8H), 1.77–1.94 (m, 8H), 1.54–1.68 (m, 8H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \( \delta \) 147.7, 131.1, 128.5, 126.8, 126.7, 126.5, 119.0, 117.8, 95.1, 93.0, 30.8, 30.0, 29.5, 29.2; HRMS (APCI, positive) calculated for C\textsubscript{66}H\textsubscript{52}S\textsubscript{4} ([M\textsuperscript{+}]): 972.2946. Found: 972.2956.
II. Crystallographic data, mechanical bending behavior, SEM images, powder X-ray diffraction patterns, and DSC profiles

The structure was solved by direct methods (SHELXS-97 or SHELXS-2013)\(^3\) and refined by least-squares calculations on \(F^2\) for all independent reflections (SHELXL-97 or SHELXL-2013). All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in idealized positions and refined by applying riding models with the relative isotropic displacement parameters. Crystal morphology calculation of \(1a\) and \(1b\) based on their crystal structures using the Bravais-Friedel-Donay-Harker (BFDH) method was conducted by the Morphology module in the Materials Studio 7.0 simulation package distributed by Accelrys Inc., San Diego CA (2014).

![Fig. S1. X-ray crystal structure of \(1b\). Molecular structure (left) and packing structure (right). Thermal ellipsoids are drawn at the 50% probability level.](image)

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**Fig. S2.** Face index analysis of 1a and 1b based on the X-ray crystallography.

**Fig. S3.** Crystal morphology calculation of 1a and 1b using the Bravais-Friedel-Donnay-Harker (BFDH) method.
Fig. S4. Mechanical bending of macrocyclic dimer 1b by a metallic pin at ambient temperature. The scale bar represents 500 µm.
**Figure S5.** X-ray crystal structure of 1c-prism. Molecular structure (left) and crystal packing (right). Thermal ellipsoids are drawn at the 50% probability level.

**Fig. S6.** Scanning electron micrograph of 1c-bent.
Fig. S7. Observed diffraction spots of 1c·bent a) before and b) after the annealing process. The straight part of the crystal, which was cut into small pieces, was used for the X-ray diffraction experiment.

Fig. S8. Macroscopic motion during the annealing process of 1c·bent at 100 °C.
Fig. S9. Powder X-ray diffraction patterns of 1c·bent in the first cooling process from 100 °C to −80 °C, in which Cu Kα radiation was used.
Fig. S10. Powder X-ray diffraction patterns of 1c-bent in the second heating process from −80 °C to 100 °C, in which Cu Kα radiation was used.
Fig. S11. DSC profiles of 1a, 1b, and 1c·bent.
**Table S1.** Crystallographic Data of 1c-prism and 1c-bent Before the Annealing Process

<table>
<thead>
<tr>
<th></th>
<th>1c-prism</th>
<th>1c-bent (before annealing)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₆₀H₁₂S₅·C₂H₄Cl₂</td>
<td>C₆₀H₁₂S₄</td>
</tr>
<tr>
<td>T (°C)</td>
<td>−170</td>
<td>20</td>
</tr>
<tr>
<td>Crystal System</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space Group</td>
<td>P2₁/c</td>
<td>P2₁/n</td>
</tr>
<tr>
<td>a (Å)</td>
<td>7.6706(11)</td>
<td>21.62(8)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>17.4871(15)</td>
<td>5.283(16)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>20.506(3)</td>
<td>24.82(8)</td>
</tr>
<tr>
<td>β (°)</td>
<td>100.272(5)</td>
<td>111.57(7)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>2706.5(6)</td>
<td>2837(15)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>GOF</td>
<td>1.116</td>
<td>1.356</td>
</tr>
<tr>
<td>R_{int}</td>
<td>0.0220</td>
<td>0.0497</td>
</tr>
<tr>
<td>R(F)</td>
<td>0.0376</td>
<td>0.1070</td>
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<tr>
<td>wR(F²)</td>
<td>0.1202</td>
<td>0.3841</td>
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<tr>
<td>CCDC</td>
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**Table S2.** Crystal Lattices Determined by X-ray Crystallographic Analysis at Various Temperatures[^a]

<table>
<thead>
<tr>
<th>Temp / °C</th>
<th>a / Å</th>
<th>b / Å</th>
<th>c / Å</th>
<th>β / °</th>
<th>Cell volume / Å³</th>
</tr>
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<tbody>
<tr>
<td>−40[^b]</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>−60</td>
<td>20.21</td>
<td>5.27</td>
<td>24.70</td>
<td>109.1</td>
<td>2485</td>
</tr>
<tr>
<td>−80</td>
<td>20.19</td>
<td>5.26</td>
<td>24.66</td>
<td>109.2</td>
<td>2475</td>
</tr>
<tr>
<td>−20</td>
<td>21.60</td>
<td>5.31</td>
<td>24.31</td>
<td>111.9</td>
<td>2587</td>
</tr>
<tr>
<td>0</td>
<td>21.54</td>
<td>5.29</td>
<td>24.60</td>
<td>111.8</td>
<td>2598</td>
</tr>
<tr>
<td>20</td>
<td>21.52</td>
<td>5.25</td>
<td>24.81</td>
<td>111.8</td>
<td>2599</td>
</tr>
</tbody>
</table>

[^a]: The crystal was annealed at 100 °C for 30 min and then slowly cooled down to corresponding temperatures (ΔT/Δt = 2 °C/min). The temperature was kept for 5 min before the measurements.  
[^b]: The lattice parameter at −40 °C was not able to be determined probably due to the serious conformational heterogeneity in the transition period.
Fig. S12. X-ray crystal structure of 1c·bent at 20 °C. Molecular structure (left) and crystal packing (right). Thermal ellipsoids are drawn at the 50% probability level.

Fig. S13. X-ray crystal structure of 1c·bent at ~150 °C. Molecular structure (left) and crystal packing (right). Thermal ellipsoids are drawn at the 50% probability level.

Fig. S14. Space filling representation for a) the crystal structure of 1a, b) a modeled structure 1c with heptylene linkers taking all-anti conformation, and c) the crystal structure of 1c·bent at 20 °C.
Fig. S15. Observed powder X-ray diffraction pattern (red-dotted line) of freshly prepared 1c·bent crystal before annealing and its fitted pattern (blue line) as a mixture of the HT and LT phases ($R_{wp} = 0.0142$, $R_p = 0.0080$, $R_e = 0.0235$, $S = 0.6027$). The refined cell parameters were shown in Table S3. Green line demonstrates the difference between the observed and fitted patterns. The X-ray diffraction measurement was performed at room temperature (ca. 20 °C), in which Cu Kα radiation was used.

Table S3. Refined crystal lattice parameters of freshly prepared 1c·bent crystal fitted by Pawley method.

<table>
<thead>
<tr>
<th>Crystal phase</th>
<th>$a$ / Å</th>
<th>$b$ / Å</th>
<th>$c$ / Å</th>
<th>$\beta$ / °</th>
<th>$V$ / Å³</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT</td>
<td>21.821(11)</td>
<td>5.381(2)</td>
<td>25.329(13)</td>
<td>110.77(3)</td>
<td>2781(2)</td>
</tr>
<tr>
<td>LT</td>
<td>20.414(13)</td>
<td>5.303(3)</td>
<td>25.408(16)</td>
<td>108.78(3)</td>
<td>2604(3)</td>
</tr>
</tbody>
</table>
The orientation of the π stacking moieties in 1c·prism is different from those in 1a, 1b, and 1c·bent. In the crystal packing of 1c·prism, the macrocycles are slipped in the lateral direction of the bis(thienylethynyl)anthracene moieties, while those are slipped in the longitudinal direction in the other crystals (Fig. S16). As a result, an anthracene moiety in 1c·prism is stacked with three adjacent anthracene moieties, though its overlap is small. The doubly layered anthracene arrays are formed, in which the dichloroethane molecules are accommodated between them. On the other hand in 1c·bent (either in HT or LT), the single π-stacked array of the bis(thienylethynyl)anthracene moieties is formed separately. Based on these structural analyses, we propose the thermodynamic formation of 1c·prism crystal in the slower recrystallization protocol compared to that for 1c·bent. When the concentration of 1c is low and thus the recrystallization process takes a long time, the packing structure of 1c is converged to the thermodynamically more stable 1c·prism consisting of the double π-stacked arrays, while the high concentration leads to the kinetic formation of the separated but largely overlapped single π-stacked arrays.
III. Fluorescence spectra of the crystals

Fig. S17. Fluorescence spectra of the crystals 1a, 1b, 1c·prism, and 1c·bent.
IV. $^1$H and $^{13}$C NMR spectra

Fig. S18. $^1$H NMR spectrum of 3a in CDCl$_3$.

Fig. S19. $^{13}$C NMR spectrum of 3a in CDCl$_3$. 
Fig. S20. $^1$H NMR spectrum of 3b in CDCl$_3$.

Fig. S21. $^{13}$C NMR spectrum of 3b in CDCl$_3$. 
Fig. S22. $^1$H NMR spectrum of 4a in CDCl$_3$.

Fig. S23. $^{13}$C NMR spectrum of 4a in CDCl$_3$. 
Fig. S24. $^1$H NMR spectrum of 4b in CDCl$_3$.

Fig. S25. $^{13}$C NMR spectrum of 4b in CDCl$_3$. 
Fig. S26. $^1$H NMR spectrum of 1a in CDCl$_3$.

Fig. S27. $^{13}$C NMR spectrum of 1a in CDCl$_3$ (low intensity due to poor solubility).
Fig. S28. $^1$H NMR spectrum of 1b in CDCl$_3$.

Fig. S29. $^{13}$C NMR spectrum of 1b in CDCl$_3$. 
Fig. S30. $^1$H NMR spectrum of 1c in CDCl$_3$.

Fig. S31. $^{13}$C NMR spectrum of 1c in CDCl$_3$. 