



# [1.1]*meta*-Stilbenophanes as calixarene analogs: preparation, crystal structure, and cis–trans photoisomerization

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**Abstract**—Three isomers of [1.1]*meta*-stilbenophane were synthesized by the McMurry reaction of diarylmethane dialdehyde and their crystal structures and photochemical properties were investigated. X-ray crystallographic analyses of these isomers revealed that they were assigned to a trans–trans (t–t) form with a 1,3-alternate conformation, a cis–trans (c–t) form with a distorted-cone conformation, and a cis–cis (c–c) form with a 1,2-alternate conformation. A  $^1\text{H}$  NMR study indicated that a t–t isomer could be completely transformed into a 35:65 mixture of c–t and c–c isomers by photoirradiation at 254 nm.

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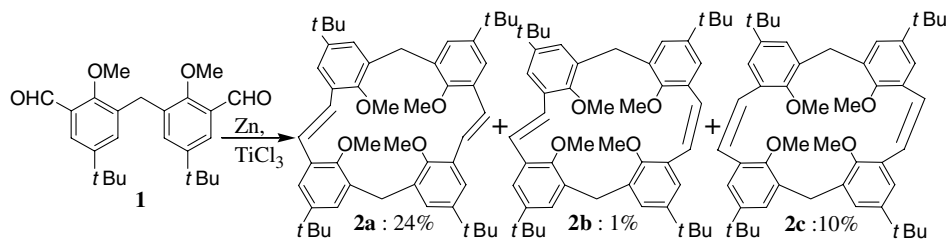
## 1. Introduction

Calixarenes and their analogs have attracted considerable attention because of their design possibilities as a host molecule in supramolecular chemistry.<sup>1</sup> One of the characteristic properties of calixarenes is a conformational variety. For example, calix[4]arenes can assume four types of conformations, namely, cone, partial-cone, 1,3-alternate, and 1,2-alternate; 1,3-alternate isomers of calix[4]arene derivatives can then be used for a heterobimolecular complexation.<sup>2</sup> By using their conformational variety and design possibilities, calixarenes and their analogs can be applied as a basic skeleton for molecular device units in molecular nanotechnology.<sup>3</sup> On the other hand, the cis–trans photoisomerization of azobenzene or stilbene is one of the typical photochromic reactions, and their potential in light-driven functional molecules and materials is of interest.<sup>4</sup> There have been some reports about calixarene derivatives that have azobenzene moieties as photoresponsive substituents.<sup>5</sup> Recently, Tamaoki reported the synthesis and cis–trans photoisomerization properties of [1.1](3.3')azobenzenophanes;<sup>6</sup> their conformation depends on the cis–trans isomerization of an azobenzene unit in a basic ring skeleton and their photoisomerization reactions are affected by steric effects

such as a macrocyclic structure.<sup>6c</sup> [1.1](3.3')Azobenzenophane can be considered to be a calixarene analog that has light-driven functional moieties in the basic ring skeleton, and not as a substituent. With regard to stilbenophane, there have been some reports on the use of stilbene units as a photoresponsive substituent.<sup>7</sup> For example, Mizuno reported the intramolecular photocycloaddition and cis–trans photoisomerization of stilbenophanes bonded by silyl chains.<sup>8</sup> Although some calixarene analogs having stilbene units as substituents<sup>9</sup> have been studied, there have been few reports on the photochemical properties of calixarene analogs that have a stilbene unit in the basic ring skeleton. Here, we examined the preparation and cis–trans photoisomerization of [1.1]*meta*-stilbenophanes **2a**, **2b**, and **2c**. This is the first report on the cis–trans photoisomerization and isolation of *meta*-stilbenophanes, which are trans–trans (t–t), cis–trans (c–t), and cis–cis (c–c) isomers. We also determined the crystal structures of the t–t, c–t, and c–c isomers of *meta*-stilbenophanes **2a**, **2b**, and **2c** by X-ray crystallography, and investigated their cis–trans photoisomerization properties by means of the UV–vis absorption spectra and  $^1\text{H}$  NMR spectra.

The preparation of [1.1]*meta*-stilbenophanes **2a**, **2b**, and **2c** is shown in Scheme 1. Diarylmethane dialdehyde **1** was prepared by the Kröhnke reaction of bis(chloromethyl)biphenylmethane.<sup>10</sup> The McMurry reaction<sup>11</sup> was performed by using titanium tetrachloride and zinc

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Scheme 1.

powder. A dry THF solution of titanium tetrachloride was added to the suspension of zinc powder in dry THF under nitrogen. Then, a solution of diarylmethane dialdehyde **1** in dry THF was added dropwise under nitrogen. Three isomers—**2a**, **2b**, and **2c**—of [1.1]meta-stilbenophane were produced after refluxing for 48 h in THF, and they were isolated by column chromatography (silica gel) in 24%, 1%, and 10% yields, respectively. The other products included a complex mixture of linear chains or cyclic polymers.

X-ray crystal structure analysis revealed that isomers **2a**, **2b**, and **2c** are t-t, c-t, and c-c isomers of [1.1]meta-stilbenophane, respectively. Isomer **2a** was determined to have a 1,3-alternate conformation (Fig. 1).<sup>12</sup> The torsion angles of the C=C double bonds in the stilbene units are 163.7° and 153.6°, and the dihedral angles of the aromatic plane in a stilbene structure are 88.1° and 81.0°. Therefore, all stilbene structures in **2a** appear to vary from a plane and there are no resonance interactions between the aromatic planes and the C=C double bond. The cavity diameters of **2a** were 9.27 Å and 5.87 Å, and a column structure of **2a** along the *c*-axial direction is observed in a unit cell. Based on these results, it may be possible to apply the 1,3-alternate conformer **2a** as a host molecule in the solid state. In the solution, it was expected that **2a** would move rapidly due to the sharp <sup>1</sup>H NMR singlet of protons at CH<sub>2</sub> and HC=CH in the bridge moieties. In order to obtain details about the conformational properties of **2a** in a solution, fur-

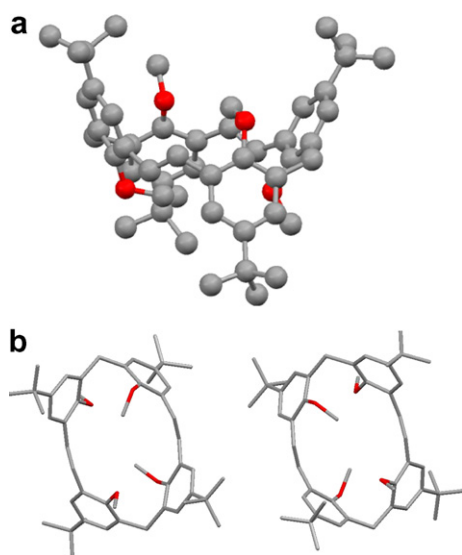
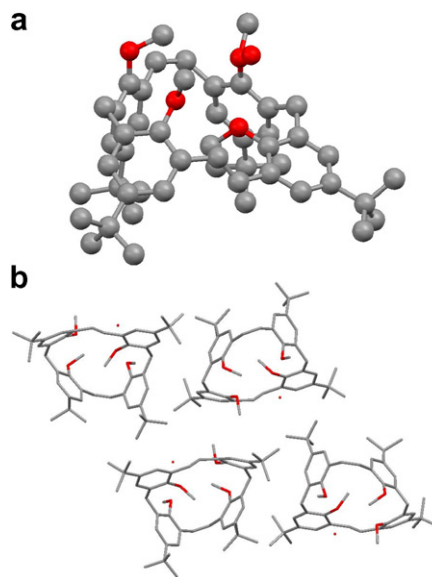
ther investigations using methods such as dynamic NMR spectroscopy would be required.

The X-ray crystallography of c-t isomer **2b** revealed that it forms a complex with H<sub>2</sub>O in a 1:1 ratio (Fig. 2).<sup>13</sup> A crystal of **2b** was obtained from EtOAc by recrystallization, and H<sub>2</sub>O molecules can be obtained from moisture in the air. Isomer **2b** was determined to have a distorted-cone-type conformation in which an aromatic plane tilts within a cavity. The distances between the methoxy oxygen and the H<sub>2</sub>O oxygen atoms are 2.92, 3.08, 3.48, and 4.90 Å. Since the distances between two pairs of oxygen atoms are less than 3.1 Å, they are expected to form hydrogen bonds.

The torsion angle between the aromatic plane and the C=C double bond was 140.0° in the *trans*-stilbene unit, and 94.3° and 128.7° in the *cis*-stilbene unit. The torsion angles of the *cis*-stilbene units were distorted to a greater extent than those of **2a**. This distortion depended on the ring structure of [1.1]meta-stilbenophane, and it may have affected the *cis*-*trans* photoisomerization process between **2a** and **2b**.

## 2. Results and discussion

The X-ray crystal structure of **2c** indicated that both stilbene moieties are *cis*-isomers and they assume a

Figure 1. Crystal structure of **2a**: (a) side view; (b) in unit cell.Figure 2. Crystal structure of **2b**: (a) side view; (b) in unit cell.

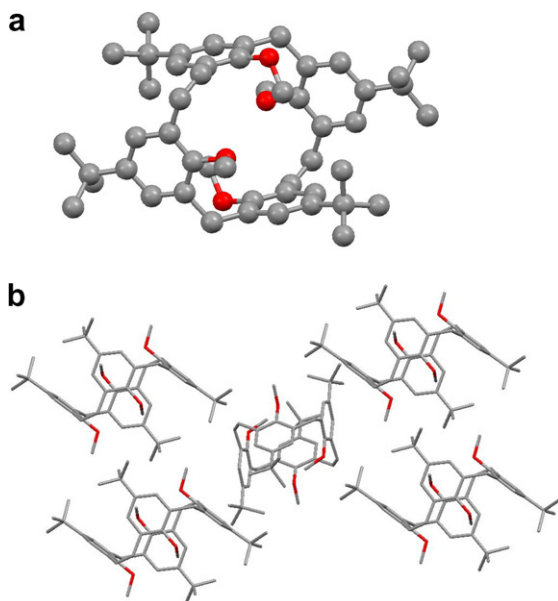


Figure 3. Crystal structure of **2c**: (a) side view; (b) in unit cell.

1,2-alternate conformation (Fig. 3).<sup>14</sup> The torsion angles between the aromatic plane and the C=C double bond of **2c** were determined to be 102.2° and 140.0°, and these values were significantly smaller than those of the *cis*-stilbene unit in **2b**. Isomer **2c** assumes a 1,2-alternate conformation in which the dihedral angles of the diagonal aromatic planes were approximately 0°. Therefore, *c-c* isomer **2c** can be considered to produce a tube-type structure. <sup>1</sup>H NMR peaks at the methoxy protons of **2a** and **2b** were observed as sharp singlets; however, those of **2c** were observed as a broad singlet. These results suggest that *c-c* isomer **2c** has a flexible structure but its motion is slow as compared to **2a** and **2b**. In fact, the <sup>1</sup>H NMR peak of **2a** at -80°C in toluene-*d*<sub>8</sub> was observed as a broad singlet similar to that of **2c** due to its slower molecular motion at low temperature. It is suggested that this difference in flexibility will influence the *cis*-*trans* photoisomerization properties between **2b** and **2c**.

The UV spectra of [1.1]*meta*-stilbenophanes **2a**, **2b**, and **2c** are shown in Figure 4. The absorption maximum and the molar absorbance coefficients of **2a**, **2b**, and **2c** were detected as 274 nm and  $2.42 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ , 283 nm and  $1.2 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ , and 274 nm and  $1.79 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ , respectively.

The *cis*-*trans* photoisomerization of **2a** was examined by using a low-pressure mercury lamp (TOSHIBA Lighting & Technology Corporation, GL10-A, 10 W). It emits light with a specific wavelength of 254 nm without the use of a UV filter. The UV-vis spectral change of **2a** was observed under photoirradiation at 254 nm using a low-pressure mercury lamp in cyclohexane (Fig. 5). The intensities at 280 nm decreased with photoirradiation for less than 1 min; however, the spectrum did not change after more than 1 min. Since the molar absorbance coefficient of **2a** was higher than that of **2b** or **2c**, the *cis*-*trans* photoisomerization would reach the photostationary state in 1 min. The photoirradiation of **2b** and **2c** was also examined, and these spectra were

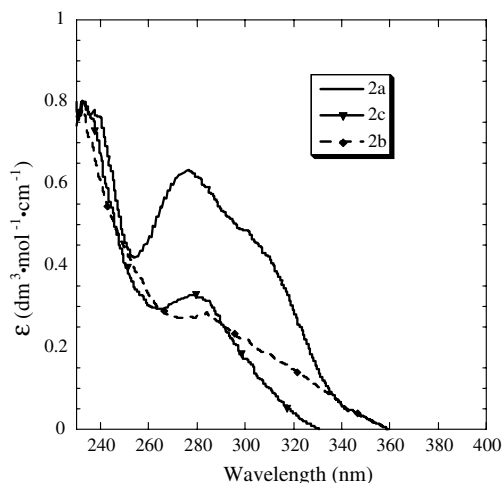


Figure 4. UV spectra of **2a**, **2b**, and **2c** in cyclohexane.

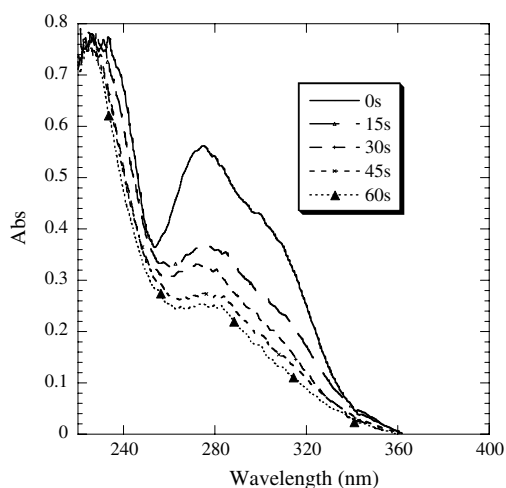
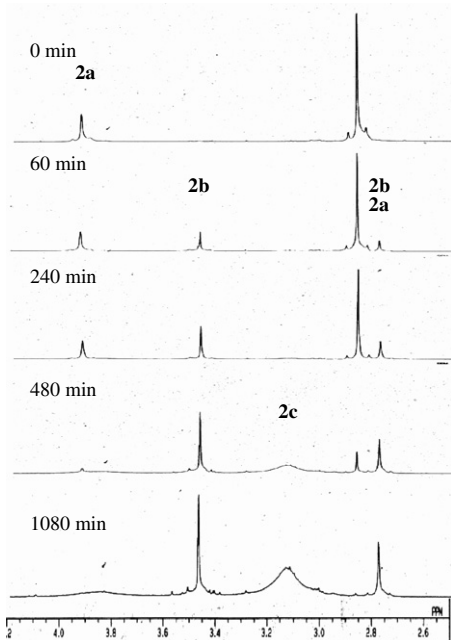


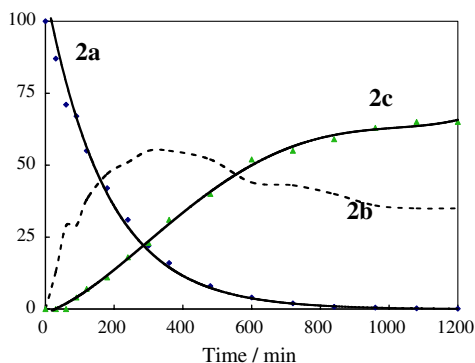
Figure 5. UV-vis spectral change of **2a** under photoirradiation of 254 nm.

observed to be the same as the photoirradiation spectrum of **2a** for 1 min.

The <sup>1</sup>H NMR spectral change under photoirradiation using a low-pressure mercury lamp is shown in Figure 6. The <sup>1</sup>H NMR spectra were measured after photoirradiation for 60, 240, 480, and 1080 min. The integration value of the methoxy peak of **2a** decreased with photoirradiation and disappeared after photoirradiation for 18 h. On the other hand, those of **2b** and **2c** increased with photoirradiation. Since the C<sub>6</sub>D<sub>6</sub> solvent inhibited the *cis*-*trans* isomerization by absorbing UV light, the time required for reaching the photostationary state with NMR monitoring was significantly longer than that with UV-vis spectroscopy. The integration ratios of the methoxy peaks of **2a**, **2b**, and **2c** are shown in Figure 7. After photoirradiation for 5 h, **2b** exhibited the maximum integration ratio of 55%. After photoirradiation for 18 h, the *cis*-*trans* isomerization attained the photostationary state in which the ratios of **2a**, **2b**, and **2c** were 0:35:65. We predicted that a mixture of **2a**, **2b**, and **2c** would be detected in the photostationary state; however, only **2b** and **2c** were obtained as a mixture.



**Figure 6.**  $^1\text{H}$  NMR spectral change of **2a** under photoirradiation in  $\text{C}_6\text{D}_6$ .



**Figure 7.** Photoirradiation times and conformer ratios as determined by  $^1\text{H}$  NMR spectra.

Since the molar absorbance coefficient of **2a** is higher than that of **2b** or **2c** at 254 nm, the photoisomerization rate from **2a** to **2b** or **2c** could be very high. However, the details of these systems are still being investigated.

### 3. Conclusion

In this Letter, we have described the preparation, crystal structure, and *cis*–*trans* photoisomerization properties of [1.1]*meta*-stilbenophanes **2a**, **2b**, and **2c**. These *meta*-stilbenophanes can be considered to be a calixarene analogs that have a stilbene unit in the basic ring skeleton. From this investigation, we have obtained some evidence indicating that the conformational varieties of calixarene analogs having stilbene units can be controlled by photoirradiation using weak UV light. In particular, a one-way isomerization process from **2a** to **2b** is of interest for the applications of this system in molecular devices. Further investigations are being conducted

to obtain details about the conformational properties of [1.1]*meta*-stilbenophanes **2a**, **2b**, and **2c** in a solution and the effect of their functional groups on *cis*–*trans* photoisomerization.

### 4. Experimental

#### McMurry reaction of bis(2-methoxy-3-formyl-4-*tert*-butylphenyl)methane **1** by using titanium chloride

A suspension of zinc powder (2.2 g, 34.3 mmol) in dry THF (50 ml) was stirred at 25 °C under nitrogen. Titanium chloride (1.4 g, 8.0 mmol) was slowly added to the mixture. The mixture was stirred at 55 °C under nitrogen for 2 h. Then, a solution of bis(2-methoxy-3-formyl-5-*tert*-butylphenyl)methane **1** (500 mg, 1.3 mmol) in dry THF (50 ml) was added dropwise and the mixture was stirred at 55 °C under nitrogen for 48 h. The reaction mixture was quenched with 10% aq potassium carbonate (50 ml) and was filtered. The filtrate was extracted using  $\text{CHCl}_3$  (50 ml  $\times$  3). The extract was washed with water, dried over  $\text{MgSO}_4$ , and evaporated in vacuo, leaving a residue that was subjected to column chromatography (silica gel) (Waco-gel, C-300, eluent; hexane:dichloromethane = 8:2) to obtain *t*–*t* isomer **2a** (165 mg, 36.0%), *c*–*t* isomer **2b**, and *c*–*c* isomer **2c** (91 mg, 20.0%).

*t*–*t* isomer **2a** (24%): colorless plate crystals, mp 221–225 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.33 (s, 36H), 2.99 (s, 12H), 3.96 (s, 4H), 6.51 (s, 4H), 7.18 (s, 8H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  155.24, 146.15, 133.42, 133.11, 131.30, 127.36, 120.69, 60.67, 38.53, 34.60, 31.87; MS (MALDI-TOF)  $m/z = 729$  ( $\text{M}^+$ ); UV–vis (cyclohexane)  $\lambda_{\text{max}}(\epsilon)$ : 274 nm (17934); Anal. Calcd for  $\text{C}_{50}\text{H}_{64}\text{O}_4 + 1/5\text{H}_2\text{O}$ : C, 81.97; H, 8.86. Found: C, 81.99; H, 9.03.

*c*–*t* isomer **2b** (1%): colorless plate crystals, mp 204–209 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.10 (s, 18H), 1.33 (s, 18H), 2.79 (s, 6H), 3.43 (s, 6H), 3.48 (m, 2H), 4.23 (m, 2H), 6.48 (s, 2H), 6.80 (d,  $J = 2.5$  Hz, 2H), 6.82 (s, 2H), 7.12 (d,  $J = 2.5$  Hz, 2H), 7.17 (d,  $J = 2.5$  Hz, 2H), 7.18 (d,  $J = 2.5$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  155.31, 154.56, 145.67, 144.04, 135.15, 133.93, 132.64, 129.46, 129.39, 128.43, 127.08, 126.06, 125.72, 121.31, 61.33, 61.31, 59.23, 59.19, 34.31, 33.97, 31.61, 31.48; MS (MALDI-TOF)  $m/z = 729$  ( $\text{M}^+$ ); UV–vis (cyclohexane)  $\lambda_{\text{max}}(\epsilon)$ : 283 nm (12580); Anal. Calcd for  $\text{C}_{50}\text{H}_{64}\text{O}_4 + 2/3\text{H}_2\text{O}$ : C, 80.99; H, 9.03. Found: C, 81.04; H, 8.89.

*c*–*c* isomer **2c** (10%): colorless plate crystals, mp 229–303 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.21 (s, 36H), 3.11 (s, 12H), 3.70 (s, 4H), 6.65 (s, 4H), 6.95 (m, 4H), 7.10 (m, 4H); MS (MALDI-TOF)  $m/z = 729$  ( $\text{M}^+$ ); UV–vis (cyclohexane)  $\lambda_{\text{max}}(\epsilon)$ : 274 nm (17934); Anal. Calcd for  $\text{C}_{50}\text{H}_{64}\text{O}_4$ : C, 82.37; H, 8.85. Found: C, 82.17; H, 9.14.

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### Supplementary data

Supplementary data regarding the preparation, X-ray crystal structure, and photoisomerization. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.09.041.

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- X-ray analysis for 2a*: C<sub>50</sub>H<sub>64</sub>O<sub>4</sub>, MW = 729.01, colorless prisms, triclinic,  $P\bar{1}$  (# 2),  $Z = 2$ ,  $a = 10.599(2)$  Å,  $b = 13.399(2)$  Å,  $c = 16.404(2)$  Å,  $\alpha = 91.656(15)^\circ$ ,  $\beta = 91.475(17)^\circ$ ,  $\gamma = 103.743(15)^\circ$ ,  $V = 2260.7(7)$  Å<sup>3</sup>,  $D_{\text{calcd}} = 1.071$  g cm<sup>-3</sup>,  $T = 298$  K,  $\mu(\text{Mo K}\alpha) = 0.66$  cm<sup>-1</sup>, Rigaku AFC7R, Mo K $\alpha$  ( $\lambda = 0.71069$  Å), 488 parameters,  $R_1 = 0.086$ ,  $R_w = 0.3331$ , GOF013, X-ray data of **2a** have been deposited with the CCDC in the CIF format with deposit No. CCDC 654566. For details about the X-ray analysis, see [Supplementary data](#).
- X-ray analysis for 2b*: C<sub>50</sub>H<sub>64</sub>O<sub>4</sub>, MW = 729.01, colorless prisms, monoclinic,  $P2_1/a$  (# 14),  $Z = 4$ ,  $a = 21.070(4)$  Å,  $b = 22.874(5)$  Å,  $c = 9.2216(12)$  Å,  $\beta = 98.401(12)^\circ$ ,  $V = 4396.7(13)$  Å<sup>3</sup>,  $D_{\text{calcd}} = 1.125$  g cm<sup>-3</sup>,  $T = 298$  K,  $\mu(\text{Mo K}\alpha) = 0.71$  cm<sup>-1</sup>, Rigaku AFC7R, Mo K $\alpha$  ( $\lambda = 0.71069$  Å), 496 parameters,  $R_1 = 0.0785$ ,  $R_w = 0.2636$ , GOF = 0.990, X-ray data of **2b** have been deposited with the CCDC in the CIF format with deposit No. CCDC 648608. For details about the X-ray analysis, see [Supplementary data](#).
- X-ray analysis for 2c*: C<sub>50</sub>H<sub>64</sub>O<sub>4</sub>, MW = 729.01, colorless prisms, monoclinic,  $P2_1/c$  (# 14),  $Z = 2$ ,  $a = 9.912(3)$  Å,  $b = 24.301(11)$  Å,  $c = 9.679(5)$  Å,  $\beta = 109.36(3)^\circ$ ,  $V = 2199.7(16)$  Å<sup>3</sup>,  $D_{\text{calcd}} = 1.101$  g cm<sup>-3</sup>,  $T = 298$  K,  $\mu(\text{Mo K}\alpha) = 0.68$  cm<sup>-1</sup>, Rigaku AFC7R, Mo K $\alpha$  ( $\lambda = 0.71069$  Å), 244 parameters,  $R_1 = 0.0913$ ,  $R_w = 0.2356$ , GOF = 0.901, X-ray data of **2c** have been deposited with the CCDC in the CIF format with deposit No. CCDC 648607. For details about the X-ray analysis, see [Supplementary data](#).