Syntheses and Structures of Isomeric [6.6]- and [8.8]Cyclophanes with 1,4-Dioxabut-2-yne and 1,6-Dioxahexa-2,4-diyne Bridges†

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All three isomers (*ortho, meta,* and *para*) of [8.8]cyclophane bearing 1,6-dioxahexa-2,4-diyne bridges have been synthesized and structually characterized by single-crystal X-ray crystallography to determine the conformation of the cyclophanes and their cavity dimensions. The three isomeric [6.6]cyclophanes bearing 1,4-dioxabut-2-yne bridges have also been synthesized from but-2-yne-1,4-diol ditosylate and the isomeric dihydroxybenzenes. The [6.6]orthocyclophane has been structurally characterized by single-crystal X-ray crystallography. The energy-minimized structures from the semiempirical AM1 calculations of these cyclophanes compare very well with the structures obtained by X-ray crystallography.

Introduction

The design and synthesis of cyclophanes possessing rigidly defined cavities and shape-persistent structures of molecular dimensions is of interest as molecular hosts in the areas of host−guest and electron donor−acceptor complexes.[1] The dimensions of the cavity depend on the spacer group and its connectivity to the arene units. Acetylenic units as bridges impart rigidity to the cyclophanes, and the number of acetylenic units in the bridge and its connectivity to the arene units control the size of the cavity possessed by the cyclophane. Two such readily available units are 1,4-dioxabut-2-yne and 1,6-dioxahexa-2,4-diyne. Whitlock has used the latter unit for the construction of several [8.8]paracyclophanes, which are substituted derivatives of **2c**.[2] However, the parent cyclophane, namely **2c**, has not been reported so far. Breslow has reported a triply bridged [8.8.8]cyclophane consisting of the 1,6-dioxahexa-2,4-diyne units bridging two triphenylmethyl moieties.[3] Similarly, Vögtle has also reported the synthesis of an [8.8.8]cyclophane connecting two triphenylmethyl cations as the arene units.[4] The use of 1,4-dioxabut-2-yne moiety as the bridging unit in the synthesis of cyclophanes has been rare. Recently, Gokel has reported the synthesis and selective ion complexing ability of [6.6]paracyclophane **1c**.[5] Our interest in the area of cyclophanes bearing acetylenic bridging units[6] is to study the structure, conformation and cavity dimensions of these cyclophanes for their use as donors to form electron donor−acceptor complexes with acceptors of suitable dimensions. Herein we report the syntheses and X-ray crystal structures of isomeric [8.8]cyclophanes and also the syntheses of isomeric [6.6]cyclophanes and the X-ray crystal structure of the *ortho* isomer **1a** (Scheme 1). The energy-minimized structures based on semiempirical AM1 calculations[7] are also reported and compared with the structures from the X-ray crystallography.

Results and Discussion:

Syntheses of [8.8]Cyclophanes. The isomeric [8.8]-cyclophanes (**2a**−**c**) (Scheme 1) were synthesized from the corresponding benzenediols (**3a**−**c**) by a two-step procedure (Scheme 2).

Propargylation of the benzenediols proceeded cleanly to yield the corresponding isomeric bispropargyl ethers (**4a**−**c**) in good yields. When the bispropargyl ethers were subjected to Glaser−Eglington coupling, the cyclophanes were obtained in rather poor yields. In an attempt to improve the overall yield, an alternative route involving the stepwise construction of the bridges was attempted

† Dedicated to Prof. H. W. Whitlock, Jr., on the occasion of his 65th birthday.

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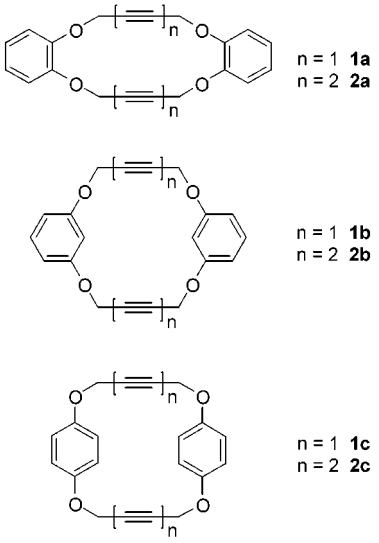
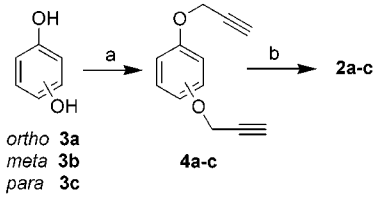
Scheme 1

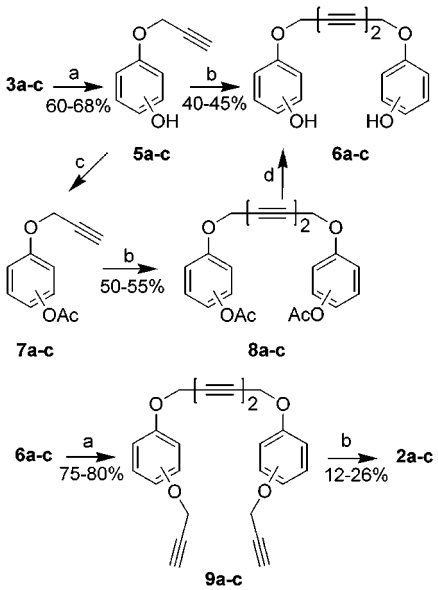


Scheme 2[a]



[a] Key: (a) propargyl bromide, K_2CO_3, acetone, reflux, 22 h, 80−89%; (b) $Cu(OAc)_2 \cdot H_2O$, CH_3CN, pyridine, 60 °C, 2 h, 8−11%.

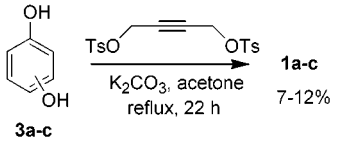
Scheme 3[a]



[a] Key: (a) propargyl bromide, K_2CO_3, acetone, reflux, 22 h; (b) $Cu(OAc)_2 \cdot H_2O$, CH_3CN, py, 60 °C, 2 h; (c) Ac_2O, py, CH_2Cl_2, rt, 5 h, 70−75%; (d) Na_2CO_3, MeOH, rt, 1 day, 60−70%.

(Scheme 3). The benzenediols were first converted into the monopropargyl ethers (**5a**−**c**) followed by the Glaser−Eglington coupling to give the singly bridged precursors (**6a**−**c**). Further propargylation followed by coupling of the terminal acetylene units in **9a**−**c** yielded the isomeric cyclophanes (**2a**−**c**), again in poor yields. A slight improvement in the yield was observed when the monopropargyl ethers (**5a**−**c**) were first converted to the corresponding acetates (**7a**−**c**) and the coupling of the acetates was carried out to give the singly bridged precursor acetates (**8a**−**c**).

Scheme 4



In spite of carrying out the coupling reaction under a variety of literature reported conditions[8] and also under high dilution conditions, the yields of the cyclophanes could not be improved. Thus, in Schemes 2 and 3 the bottleneck has been the Glaser−Eglington coupling step. In spite of the low yields, the cyclophanes were isolated and purified by column chromatography and repeated crystallization and were thoroughly characterized by spectroscopic, analytical, and single-crystal X-ray crystallographic data.

Syntheses of [6.6]Cyclophanes. The isomeric [6.6]-cyclophanes (**1a**−**c**) were synthesized starting from the corresponding benzenediols (**3a**−**c**) by a single step using buta-2-yne-1,4-diol ditosylate (Scheme 4). Although the desired cyclophanes were formed in poor yields, they were isolated and purified by column chromatography and repeated crystallization. The cyclophanes were fully characterized by spectroscopic and analytical data. The *ortho* isomer has also been characterized by single-crystal X-ray crystallographic data.

Crystal Structures of the Cyclophanes, Their Conformations, and Their Cavity Dimensions. The crystal structures of all the three isomers of the [8.8]-cyclophanes (**2a**−**c**) are shown in Figure 1. The cavities in these cyclophanes can be approximated to be a rectangular box, and the cavity dimensions mentioned herein are the center-to-center distance between bridges and the distance between the two arene units. In the case of [8.8]orthocyclophane (**2a**), there are two independent molecules in the unit cell stacked alternatively along the crystallographic *b* axis. Each of the independent molecules possesses a center of symmetry. The cavity dimensions are 4.1 × 10. 2 Å. The structure of the *meta* isomer **2b** corresponds to an elongated *anti*-chair conformation, and the structure possesses an inversion center. The cavity dimensions are 4.4 × 10.4 Å. The distance between the intraannular aromatic hydrogens is 6.705 Å. The structure of the *para* isomer **2c** in the crystal corresponds to an *anti*-chair conformation with the two arene units parallel to each other and forming an angle of 55° with the plane connecting the sp-carbons of the two bridges. The cavity dimensions are 7.0 × 7.9 Å. The center-to-center distance between the aromatic units is 7.87 Å. The molecular structure of [6.6]orthocyclophane (**1a**) in the crystal is very similar to that of **2a**, possessing a center of symmetry (Figure 2). Of the four structures presented here, only in the *ortho*-cyclophane **1a** are the molecules stacked on top of each other in a crystal lattice forming

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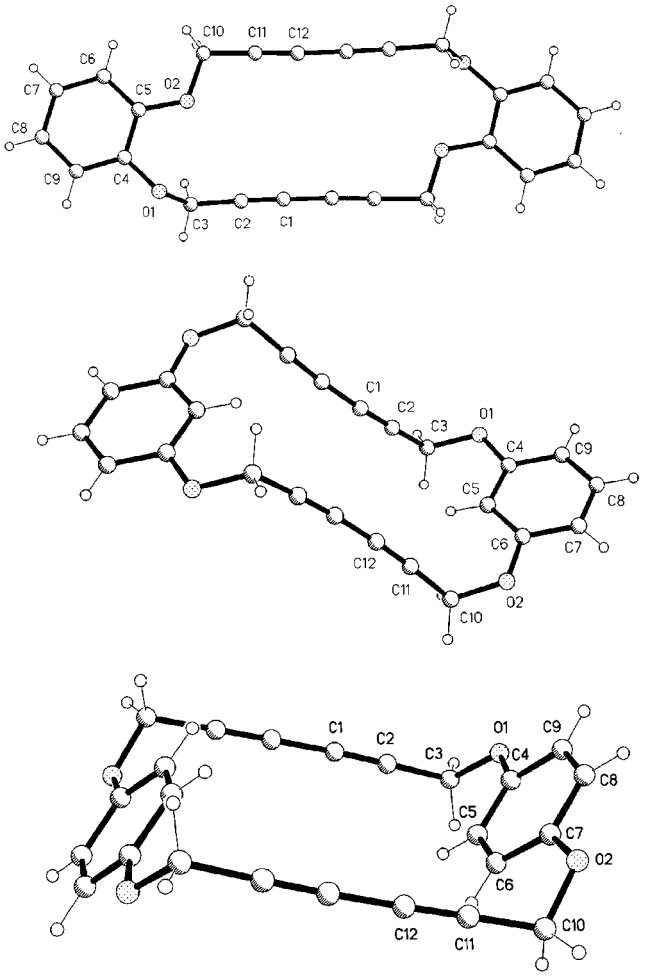

Figure 1. Structures of cyclophanes **2a**−**c** (top to bottom, respectively) in the crystal.

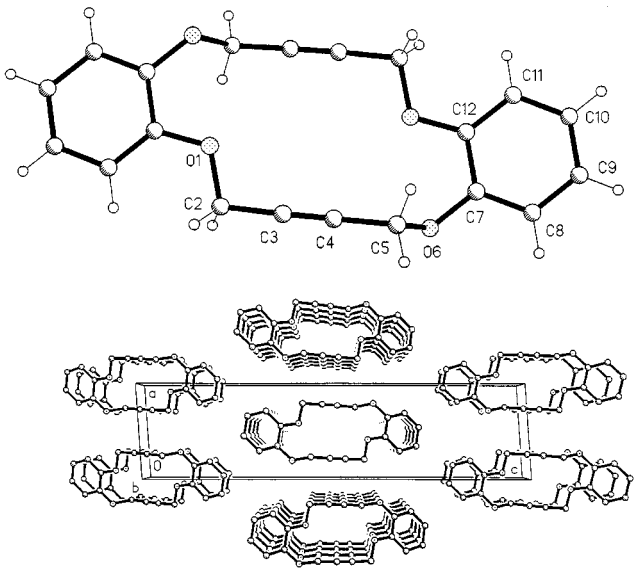

Figure 2. Structure of **1a** in the crystal (top) and packing diagram of **1a** in the crystal (bottom).

a columnar structure along the crystallographic *b* axis (Figure 2). The cavity dimensions of **1a** are 4.0 × 7.5 Å. Recently, Gokel[5] has reported the X-ray crystal structure of the [6.6]paracyclophane **1c**, and in the solid state the molecule exists in the chair conformation just as in the case of **2c** reported herein. Although the structure of the *meta* isomer **2b** in the solid state is *anti*, in solution it could exist as a mixture of *syn* and *anti* conformers. To investigate this possibility, the ^{1}H NMR spectrum of **2b** was recorded in the temperature range of −95 to +135 °C. Under these conditions, the NMR spectrum remained unchanged, and no coalescence (or decoalescence) of the NMR signals could be observed. We conclude that the cavity dimensions of **2b** are large enough for a rapid *syn*−*anti* interconversion in solution even at −95 °C.

Table 1. Comparison of the Cavity Dimensions (in Å) of the Cyclophanes[a]

cyclophane	exptl	calcd
1a	4.0 × 7.9	4.0 × 7.6
1b		4.9 × 8.0 (3.8)
1c	5.5 × 7.0	5.5 × 7.0
2a	4.1 × 10.2	4.1 × 9.7
2b	4.4 × 10.4 (6.7)	4.8 × 10.2 (6.30)
2c	7.0 × 7.9	7.7 × 7.9

[a] The dimensions are the center-to-center distance between bridges and the distance between the two arene units, respectively, in Å. The numbers in the parentheses are the distance between the intraannular hydrogens of the metacyclophanes. The experimental data for **1c** is from ref 5a.

Figure 3. Calculated energy-minimized structure of **1b**.

Calculation of Energy-Minimized Conformation of the Cyclophanes.[7] The energy minimization calculations were carried out by semiempirical AM1 methods. Although the energy-minimized conformation/geometry highly depends on the local geometry from the starting model, we find that the energy-minimized structures in the case of **2a**−**c** and **1a** are in good agreeement with the X-ray structures in terms of the conformation cyclophanes and their cavity dimensions. For example, cyclophanes **1c** and **2c** that exist in an elongated chair conformation in the solid state (crystal) show the same conformation in the calculated energy-minimized structure as well. Similarly, cyclophane **2b**, which exists in an *anti* chair conformation in the solid state (crystal), shows an identical conformation in the calculated energy-minimized structure. The cavity dimensions from the calculations and the X-ray structures are compared in Table 1. Cyclophane **1b** is the only member of this series for which the X-ray crystal structure is not known. The calculated energy-minimized structure of **1b** (Figure 3) clearly shows an *anti* chair conformation similar to the larger cyclophane **2b**. From the AM1 calculations, we have estimated the differences in the heat of formation between the *syn* and *anti* conformations of **1b** and **2b** to be approximately 1.27 and 0.33 kcal/mol, respectively.

Formation of Charge-Transfer (CT) Complexes. The cyclophanes **1a**−**c** and **2a**−**c** are good electron donors

Table 2. Absorption Maximum (in nm) of the Charge-Transfer Complexes in CH_2Cl_2

	acceptor		
donor	TCNE	TCNQ[a]	DDQ
1a	420, 520	460−700	560
1b	420, 520	460−700	560
1c	400, 560	560	650
2b	400, 500	440−700	540
4a	410, 520	460−700	560
4b	420, 500	460−700	570
4c	380, 550	540	630

[a] Except for **1c** and **4c** no distinct absorption maximum was observed. The range given is the tail portion of the CT band in the visible region.

due to the electron-rich dialkoxyarene units. The formation of CT complexes of the cyclophanes was studied with TCNE, TCNQ, and DDQ as the acceptors in dichloromethane using electronic spectroscopy.[9] The bispropargyloxybenzenes **4a**−**c** were also studied for comparison. Formation of purple CT complexes was observed with TCNE with all the substrates studied. The formation of the CT complexes was accompanied by the observation of a new CT band in the visible region of the electronic spectra of the solutions containing the donor and TCNE. The CT complexes of TCNE showed multiple CT bands with two absorption maxima, which is a very characteristic feature of the TCNE complexes with arene donors.[10] The CT complexes of TCNQ were dark yellow in color, and they did not display any characteristic absorption maximum in the visible region of the electronic spectra, rather a broad tail absorption in the region of 460−700 nm was observed in all the cases. The CT complexes of DDQ were greenish yellow in color, and they showed a broad featureless CT band in the electronic spectra. The absorption spectral data of the CT complexes are given in Table 2.

The CT spectra of the cyclophanes were nearly identical to the CT spectra of the model substrates **4a**−**c**. From the data it is evident that the dialkoxyarene unit is responsible for the formation of the CT complexes with various acceptors. The determination of the formation constant of the CT complexes using the Benesi−Hildebrand method[11] was attempted. The magnitude of the association constants was in the range of 0.3−10 M^{-1}.

Conclusions

The synthesis of the three isomers of [6.6]- and [8.8]-cyclophanes bearing 1,4-dioxabut-2-yne and 1,6-dioxahexa-2,4-diyne bridges, respectively, has been reported. The three isomers of the [8.8]cyclophane and the *ortho* isomer of the [6.6]cyclophane have been structurally characterized by single-crystal X-ray diffraction. The energy-minimized structures obtained by semiempirical AM1 calculations are in good agreement with the crystal structures of these cyclophanes. The cyclophanes form colored CT complexes with electron acceptors such as TCNE, TCNQ, and DDQ due to the electron-rich dialkoxyarene units.

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Experimental Section

General Procedure for the Glaser−Eglington Coupling of the Bis-Propargyl Ethers 4a−c. To a suspension of cupric acetate monohydrate (6.78 g, 34.0 mmol) in a mixture of acetonitrile (240 mL) and pyridine (60 mL) at 60 °C was added a solution of the bis propargyl ether (**4a**−**c**) (3.0 g, 15.8 mmol) in acetonitrile (20 mL). The color of the solution changed from deep blue to green. The mixture was stirred for 2 h, during which time the reaction was monitored by TLC. The reaction mixture was cooled to room temperature, and water was added (500 mL). The mixture was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic phase was washed with 4 N HCl (2 × 100 mL), saturated $NaHCO_3$ (200 mL), water (2 × 200 mL), and saturated brine (200 mL). The organic layer was dried over anhydrous Na_2SO_4 and filtered, and the solvent was removed. The crude product was chromatographed on silica gel and eluted with a hexane/ethyl acetate (7:3 v/v) mixture to afford the cyclophanes **2a**−**c** as colorless solids.

General Procedure for the Synthesis of [6.6]Cyclophanes (1a−c). To a solution of the benzenediol (**3a**−**c**) (0.5 g, 4.54 mmol) in dry acetone (30 mL) was added anhydrous K_2CO_3 (3.14 g, 22.7 mmol), and the mixture was refluxed for 0.5 h. To the mixture was added dropwise a solution of 2-butyne-1,4-diol ditosylate (1.8 g, 4.54 mmol) in dry acetone (10 mL) over a period of 0.5 h. The resulting mixture was stirred and refluxed for an additional 20 h. The mixture was cooled and filtered, and the filtrate was evaporated. The residue was dissolved in CH_2Cl_2 (100 mL) and washed with water (2 × 100 mL) and saturated brine (100 mL). The organic layer was dried over Na_2SO_4, and removal of the solvent yielded a white solid. The crude product was chromatographed on silica gel and eluted with a mixture of hexane/ethyl acetate (4:1 v/v) to afford the cyclophanes **1a**−**c** as colorless solids.

Spectroscopic Characterization of the Cyclophanes. 1,6,13,18-Tetraoxa[6.6]orthocyclophane-3,15-diyne (**1a**): yield 0.084 g (0.26 mmol) (11.6% from 0.5 g, 4.5 mmol of **3a**); colorless crystalline solid; mp 174−176 °C; IR (KBr) 1600, 1497 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.82−6.72 (AA′BB′ multiplet, 8H), 4.70 (s, 8H); ^{13}C NMR($CDCl_3$, 100 MHz) δ 147.89 (s), 122.79 (d), 117.40 (d), 82.09 (s), 57.79 (t); MS (EI, 70 eV) 321(18), 320 (M^+, 92), 160 (100); HRMS calcd for $C_{20}H_{16}O_4$ 320.10486, found 320.1042. Anal. Calcd: C, 74.97; H, 5.03. Found: C, 74.67; H, 5.03.

1,6,13,18-Tetraoxa[6.6]metacyclophane-3,15-diyne (**1b**): yield 0.053 g (0.17 mmol) (7.3% from 0.5 g, 4.5 mmol of **3b**); colorless crystalline solid; mp 157−158 °C; IR (KBr): 1616, 1491, 1146 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.14 (t, 2H, J = 8.2 Hz), 6.54 (dd, 4H, J = 8.2, 2.4 Hz), 6.20 (t, 2H, J = 2.4 Hz), 4.69 (s, 8H); ^{13}C NMR($CDCl_3$, 100 MHz) δ 158.59 (s), 130.01 (d), 108.52 (d). 102.25 (d), 82.54 (s), 56.05 (t); MS (EI, 70 eV) 321 (12), 320 (M^+, 64), 160 (100); HRMS calcd for $C_{20}H_{16}O_4$ 320.10486, found 320.1042. Anal. Calcd: C, 74.97; H, 5.03. Found: C, 75.44; H, 5.00.

1,6,13,18-Tetraoxa[6.6]paracyclophane-3,15-diyne (**1c**): yield 0.048 g (0.15 mmol) (6.6% from 0.5 g, 4.5 mmol of **3c**); colorless crystalline solid; mp 190−192 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.84 (s, 8H), 4.67 (s, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.10 (s), 116.26 (d), 82.65 (s), 56.61 (t); MS (EI, 70 eV) 321 (10), 320 (M^+, 56), 52 (100); HRMS calcd for $C_{20}H_{16}O_4$ 320.10486, found 320.1048.

1,8,15,22-Tetraoxa[8.8]orthocyclophane-3,5,17,19-tetrayne (**2a**): yield 0.39 g (1.0 mmol) (7.9% from 5.0 g, 27.0 mmol of **4a**); colorless solid; mp 170−172 °C; IR (KBr) 1587, 1468, 1235, 1116, 1011 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.98 (AA′BB′ multiplet, 8H), 4.82 (s, 8H); ^{13}C NMR($CDCl_3$, 100 MHz) δ 148.13 (s), 123.35 (d), 117.68 (d), 74.21 (s), 71.25 (s), 58.53 (t); MS (EI, 70 eV) 368 (M^+, 40), 76 (100); HRMS calcd for $C_{24}H_{16}O_4$ 368.1049, found 368.1040.

1,8,15,22-Tetraoxa[8.8]metacyclophane-3,5,17,19-tetrayne (**2b**): yield 0.28 g (0.76 mmol) (7.1% from 4.0 g, 21.5 mmol of **4b**); colorless solid; mp 192−194 °C; IR (KBr) 1590, 1484, 1020 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ_7.18 (t, J = 8.30 Hz, 2H), 6.66 (t, J = 1.96 Hz, 2H), 6.58 (dd, J = 8.30 and 2.45 Hz, 4H), 4.78 (s, 8H); ^{13}C NMR($CDCl_3$, 100 MHz) δ 158.28 (s), 130.06

(d), 109.62 (d), 101.49 (d), 74.57 (s), 71.14 (s), 56.02 (t); MS (EI, 70 eV) 368 (M^+, 25), 202 (100); HRMS calcd for $C_{24}H_{16}O_4$ 368.1049, found 368.1018.

1,8,15,22-Tetraoxa[8.8]paracyclophane-3,5,17,19-tetrayne (**2c**): yield 0.54 g (1.4 mmol) (10.8% from 5.0 g, 27.0 mmol of **4c**); colorless solid; mp 165−166 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.90 (s, 8H), 4.72 (s, 8H); ^{13}C NMR($CDCl_3$, 100 MHz) δ 152.23 (s), 116.12 (d), 74.79 (s), 71.08 (s), 56.85 (t); MS (EI, 70 eV) 368 (M^+, 100), 292 (25), 183 (20); HRMS calcd for $C_{24}H_{16}O_4$ 368.1049, found 368. 1044.

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Supporting Information Available: Crystal structure data for compounds **1a** and **2a**−**c**. General experimental procedures for the syntheses of **4a**−**c**, **5a**−**c**, **6a**−**c**, and **7a**−**c**. Spectroscopic and analytical data for compounds **5b**,**c**, **7a**, **6a**−**c**, **8a**−**c**, and **9b**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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