

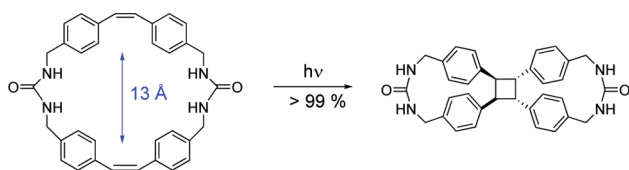
Control of the Intramolecular [2+2] Photocycloaddition in a Bis-Stilbene Macrocycle

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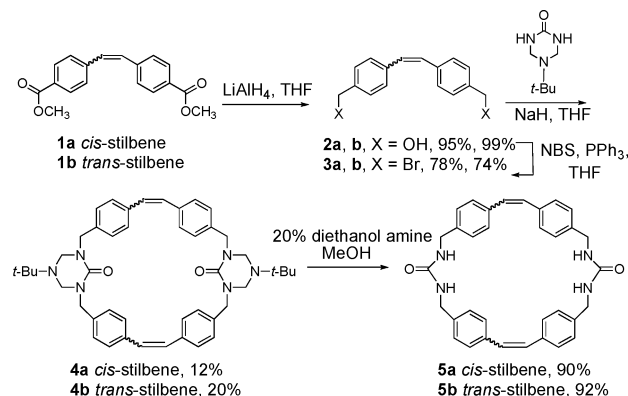
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The intramolecular [2+2] photocyclization of a bis-stilbene macrocycle was studied. The reaction can be controlled by the insertion and removal of urea protecting groups. Upon UV-irradiation in both the solid state and DMSO solution, the free urea macrocycle undergoes a *cis*–*trans* photoisomerization that is followed by a [2+2] cycloaddition to afford a single product in high yield. The presence of the triazinanone urea protecting groups does not alter the *cis*–*trans* photoisomerization but greatly decreases the selectivity of the photocycloaddition step.

The [2+2] cycloaddition reaction has been one of the most efficient and stereoselective methods for synthesizing cyclobutane derivatives in the solid state.¹ However, in solution it is more difficult to control both yield and stereoselectivity of the process. Olefins such as stilbene typically afford a mixture of products upon UV-irradiation in solution.² Supramolecular³ and

SCHEME 1. Synthesis of Bis-Urea Stilbene Macrocycles



covalent approaches, which fix two stilbene units within macrocyclic frameworks,⁴ have the potential to exert greater control over the photodimerization of stilbene derivatives. We report herein that subtle conformational effects can be used to control the selectivity of an intramolecular [2+2] photoaddition of stilbenes in solution. This paper describes the synthesis of a bis-urea macrocycle containing two *cis*-stilbenes. The presence or absence of a triazinanone urea protecting group exerts surprising effects on the reaction of these macrocycles. Upon UV irradiation both macrocycles appear to undergo a *cis*–*trans* photoisomerization. However, only the unprotected urea macrocycle affords a single product for the subsequent [2+2] cycloaddition, the *cis,trans,cis*-cycloadduct in high conversion. In contrast, UV irradiation of the triazinanone protected urea macrocycle gives a complex mixture of products. We study the reasons for this marked difference in selectivity.

Bis-stilbene macrocycle **5a** was synthesized from commercial dimethyl *cis*-stilbene-4,4'-dicarboxylate **1a** (Scheme 1). First, the diester **1a** was reduced to diol **2a**. Bromination of diol **2a** with NBS/PPh₃ yielded dibromide **3a**.⁵ The dibromide **3a** was cyclized with the triazinanone in NaH/THF to afford the protected *cis*-macrocycle **4a**.⁶ The protecting group was removed with use of diethanolamine in methanol to yield target macrocycle **5a**.⁷ The *trans*-stilbene macrocycle was prepared by a similar route starting with *trans*-stilbene **1b**.

We used X-ray crystallography to compare the solid state structures of compounds **4a** and **5a**. Single crystals of **4a** were obtained by slow diffusion of hexane into a THF solution of **4a**. In the X-ray crystal structure (Figure 1a), the *tert*-butyls of the protecting groups are positioned above and below the macrocyclic plane. The two urea groups are aligned in opposite directions, which minimizes the dipole interactions. The distance between the two stilbene double bonds was 13.4 Å, which should be too distant for an intramolecular [2+2] cycloaddition.

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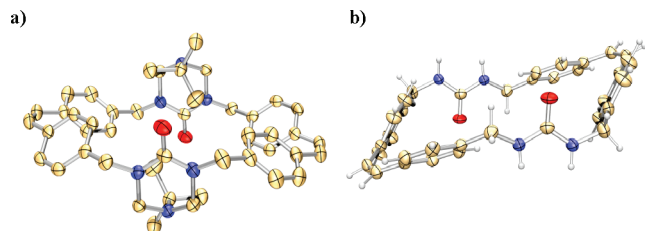
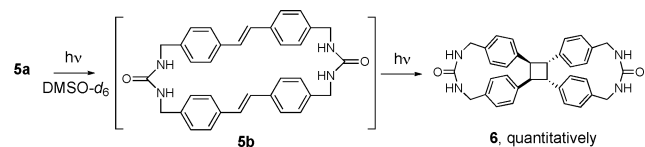


FIGURE 1. Views from the X-ray structures: (a) triazinanone protected stilbene macrocycle **4a** and (b) bis-urea stilbene macrocycle **5a**.

SCHEME 2. Proposed Reaction Pathway for **5a**



Single crystals of bis-urea **5a** (Figure 1b) were obtained upon slow cooling of a MeOH/H₂O solution from 85 °C to room temperature overnight. Similar to **4a**, the two urea groups are oriented oppositely.⁸ The distance between the two double bonds within the macrocycle was again quite large (12.9 Å). Therefore, we did not expect to observe the intramolecular [2+2] reaction in either case, and we were interested to see if two macrocycles could be coupled via a [2+2] photoaddition to give dimers. Macrocycle **5a** self-assembles in the crystal into an offset structure through typical urea–urea hydrogen bonds with NH⋯O distances of 2.88 to 2.89 Å. This offset assembly brings the stilbene double bonds of adjacent macrocycles closer resulting in several contacts at ~4.9 Å.

Stilbene and its derivatives are known to undergo three types of photochemical conversions, including *cis*–*trans* isomerization,^{9,10} photodimerization or cross-photocycloaddition with alkenes and arenes,¹¹ and photochemical conversion to phenanthrenes.¹² Given the large separation of the reactive double bonds in the solid state structures of **4a** and **5a**, the intramolecular cycloadditions were expected to be disfavored over intermolecular reactions.¹³ We first investigated the photochemistry of macrocycles **4a** and **5a** in solution (DMSO-*d*₆) as a control. Our hypothesis was that these compounds should show unselective reactions to afford multiple products. Indeed, when the triazinanone protected urea **4a** was irradiated under UV light at room temperature with a Hanovia 450 W medium pressure mercury arc lamp, a complex mixture of products was observed. In contrast, similar UV-irradiation of the unprotected urea **5a** (7.58 mM in DMSO-*d*₆) gave a single product the *cis,trans,cis*-

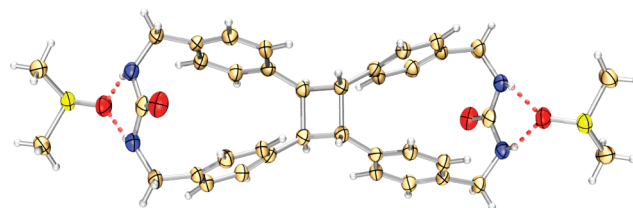


FIGURE 2. Single-crystal X-ray structure confirmed assignment of **6**, which crystallized as a bis(DMSO) solvate complex.

cycloadduct **6** in high yield (Scheme 2). The ¹H NMR spectra in DMSO-*d*₆ shows the cyclobutane CH's at 4.5 ppm, consistent with literature reports for the stereochemistry of the cyclobutane ring in **6**.^{4,13} This product does not have the expected stereochemistry for the [2+2] photoaddition of the *cis*-stilbene (**5a**) starting material. Photoisomerization of the double bonds of one of the *cis*-stilbene units to give a mixed *cis,trans*-intermediate and subsequent [2+2] photocyclization would also give the wrong stereochemistry. Indeed, the formation of product **6** is most easily rationalized by the intramolecular *syn* addition of the *trans,trans*-intermediate **5b** (Scheme 2).

Single crystals of **6** were obtained from a DMSO-*d*₆ solution (2 mg/0.5 mL). The X-ray structure in Figure 2 provides clear confirmation of the *cis,trans,cis* arrangement of the cyclobutane ring, which is usually characterized by the chemical shift of the cyclobutane hydrogens alone.^{4,13} Crystallization of this compound is aided by the urea groups and the molecule crystallized as a bis(DMSO) solvate complex. The regiochemistry of the cyclobutane results in close contacts between the two *cis* phenyl rings, which show centroid–centroid distances of 3.66 Å.

To gain insight into the mechanism of this transformation, the reaction was monitored by UV–vis spectroscopy. During the first hour of UV-irradiation, the absorption maxima of the solution of **5a** (2.5×10^{-5} M in CHCl₃) shifted from $\lambda_{\text{max}} = 282$ nm ($\epsilon = 50\,000$) to $\lambda_{\text{max}} = 289$ nm and the intensity of this band increased (Figure 3a). Further UV-irradiation resulted in a continued red shift and the slow decay of this band (Figure 3b).

These absorption bands correspond to the $\pi \rightarrow \pi^*$ transition of the stilbene double bond. The observed red shift is consistent with the isomerization of the *cis*-stilbene to the *trans*-isomer (intermediate **5b**). Indeed, the parent *cis*-stilbene displays a $\pi \rightarrow \pi^*$ transition at $\lambda_{\text{max}} = 282$ nm ($\epsilon = 12\,300$) while *trans*-stilbene shows this transition at longer wavelength ($\lambda_{\text{max}} = 295$ nm) and has a larger extinction coefficient ($\epsilon = 25\,000$).¹⁴ Product **6** lacks the stilbene double bond and has no absorption in this region. We synthesized **5b** (Scheme 1) and found that it displayed a similar absorption band at 292 nm (Figure 3b, inset). It is likely that the slow steps of this process are the photoisomerizations, first to a mixed *cis,trans*-intermediate, which does not appear to cyclize given the stereochemistry of the observed product. Further photoisomerization likely affords the *trans,trans*-intermediate **5b**. Under UV-irradiation, pure **5b** undergoes a [2+2] cycloaddition to form product **6** exclusively. The reaction of **5a** was also monitored by using ¹H NMR, which indicated that after 2 h of UV-irradiation the major resonances correspond to starting material **5a** and product **6**. Also visible in low concentration were resonances that were consistent with the formation of **5b** (Supporting Information).

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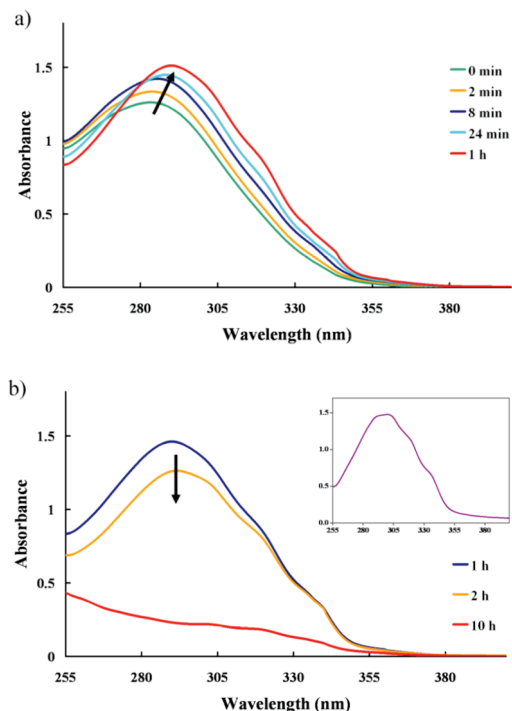


FIGURE 3. The UV–visible absorption spectra of **5a** (2.5×10^{-5} M in CHCl_3) was monitored over the course of the reaction: (a) 0 min to 1 h and (b) 1 to 10 h. Inset: Absorption spectra of the *trans*-stilbene **5b** (2.5×10^{-5} M in CHCl_3), which was synthesized independently.

In comparison, the presence of the triazinanone protecting group did not appear to alter the *cis*–*trans* photoisomerization step but greatly diminished the selectivity of the subsequent [2+2] photocycloaddition. Similar to the bis-urea **5a**, the triazinanone protected macrocycle **4a** showed a red shift from 284 to 292 nm after 2 h, consistent with its photoisomerization to a *trans*-stilbene **4b**. This band subsequently decayed as the double bond further reacts to give a mixture of cyclobutane isomers. The product distribution from **4a** was analyzed by using LC-MS, which showed six products with *m/z* 723 (Supporting Information). This molecular weight could correlate with the starting materials, intermediates, or the [2+2] cycloaddition products as well as doubly charged intermolecular dimers. Closer analysis indicated that only one of these products corresponded to a doubly charged intermolecular dimer and that the major products are due to intramolecular cycloadditions. Given that our UV–vis studies suggest that **4a** undergoes a *cis*–*trans* photoisomerization followed by loss of the stilbene double bond, we assume that the major products are a mixture of cyclobutane stereoisomers, which were not further characterized. Experimentally, it appears that the presence of the triazinanone protecting group adversely affected the selectivity of the [2+2] photocycloaddition.

We next investigated if this *cis*–*trans* photoisomerization and subsequent [2+2] cycloaddition also occurred in the solid state. We predicted that the reaction would favor intermolecular [2+2] photodimers instead of **6**, because the photoisomerization of the stilbene requires large spatial displacements of atoms. A crystalline sample of **5a** (4 mg) was placed between two Pyrex microscope slides. Surprisingly, irradiation of **5a** at room temperature for 14 h afforded **6** as the only product in high conversion (85%). Although the reaction was slightly slower in the solid state, it appears that crystalline constraints had no influence on the products observed. The free ureas (**5a** and **5b**)

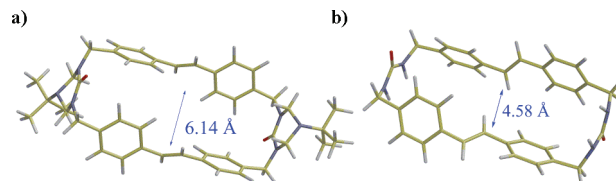


FIGURE 4. Models of the *trans*-stilbene intermediates were constructed with Spartan.¹⁵ Monte Carlo searches of the conformer distribution at ground state with Molecular Mechanics (MMFF) suggest these are the lowest energy structures of (a) **4b** and (b) **5b**.

afforded **6** exclusively in solution and in the solid state. In contrast, both the protected macrocycles (**4a** and **4b**) produced a mixture of products upon UV-irradiation.

The differences in product selectivity of the photodimerization reaction of protected **4a** versus unprotected **5a** may be explained as the diminishing of distances between two double bonds. In both cases the observed shifts in the UV-absorption spectra and ¹H NMR data suggested that photoisomerization (**4a** and **5a**) proceeded to give the *trans,trans*-isomers (**4b** and **5b**). Since neither of these *trans,trans*-intermediates have yet afforded crystals, we used Spartan to model their ground state conformations.¹⁵ The models suggest that the *trans*-intermediate **5b** adopts a shorter distance between stilbene double bonds than the corresponding *trans*-intermediate in protected **4b**. Although neither of these lowest energy structures (Figure 4) have the olefins preorganized at the <4.2 Å preferred for [2+2] cycloaddition,^{13c} the alkenes are significantly closer in **5b** (4.6 Å vs. 6.1 Å). In solution under UV-irradiation, both structures should be able to access a number of higher energy conformations; however, the triazinanone ring in **4b** introduces further rigidity and enforces a more linear arrangement of the urea, which effectively pushes the alkenes further apart. In contrast, **5b** is more flexible and may access additional conformations that decrease the distance between the alkenes. Indeed, experimental evidence suggests that **5b** adopts a conformation that enables the selective formation of **6**.

In summary, the immobilization of two *cis*-stilbenes within a bis-urea macrocycle facilitated the *cis*–*trans* photoisomerization and subsequent highly selective [2+2] photocycloaddition to yield a single cyclobutane adduct quantitatively. This is in contrast to the photochemistry of the triazinanone protected macrocycle, which also underwent the *cis*–*trans* photoisomerization but does not show any selectivity in the subsequent [2+2] cycloaddition. We are currently investigating the feasibility of using carbonates instead of ureas to see if they exhibit similar selectivity. Carbonates would be synthetically useful as they are readily hydrolyzed and could provide a handle for further structural elaboration.

Experimental Section

***cis*-Stilbene Diol 2a.** A solution of LAH (0.274 g, 6.87 mmol) was stirred in 30 mL of THF at 0 °C in a 250 mL round-bottomed flask fitted with an addition funnel. The addition funnel was charged with dimethyl *cis*-stilbene-4,4'-dicarboxylate **1a** (0.925 g, 3.12 mmol) in 50 mL of THF. The mixture was added dropwise to the LAH solution and the reaction was stirred for 6 h. The reaction was quenched by 0.3 mL of H₂O, 0.6 mL of 1 N NaOH, and then 0.9 mL of H₂O. The mixture was filtered to remove precipitate, dried over Na₂SO₄, and reduced in vacuo. A white solid was obtained (0.71 g, 95%). Mp 116–119 °C; ¹H NMR (300 MHz,

(15) Spartan 04 for Macintosh, v. 1.1.1; Wavefunction, Inc., Irvine, CA, 2007.

DMSO- d_6) δ 4.44 (d, $J = 6.0$ Hz, 4H), 5.15 (t, $J = 6.0$ Hz, 2H), 6.57 (s, 2H), 7.18 (s, 8H); ^{13}C NMR (75 MHz, DMSO- d_6) δ 63.3, 127.1, 128.9, 130.3, 135.9, 142.3; MS (EI) m/z 179, 193, 221, 240 (M^+); HRMS (EI) calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2$ 240.1150, found 240.1147.

cis-Stilbene Dibromide 3a. The diol **2a** (0.50 g, 2.08 mmol) was stirred in 40 mL of THF and PPh_3 (1.20 g, 4.58 mmol) and NBS (0.815 g, 4.58 mmol) were added. The reaction mixture was stirred overnight and then was quenched with saturated sodium bicarbonate (3 mL) and diluted with H_2O (40 mL). The solution was reduced to half its volume in vacuo and was extracted with CH_2Cl_2 (3×30 mL). The organic layer was separated then dried over MgSO_4 , and the volatiles were removed under vacuum. The crude mixture was loaded onto a silica gel and eluted with 1:6 EtOAc/hexanes to afford the dibromide **3a** (0.59 g, 78%). Mp 108–112 °C; ^1H NMR (300 MHz, CDCl_3) δ 4.47 (s, 4H), 6.58 (s, 2H), 7.20–7.28 (m, 8H); ^{13}C NMR (75 MHz, CDCl_3) δ 33.6, 129.3, 129.5, 130.4, 136.9, 137.5; MS (EI) m/z 89, 103, 206, 287, 366 (M^+), 370 (M^{+4}); HRMS (EI) calcd for $\text{C}_{16}\text{H}_{14}\text{Br}_2$ 363.9462, found 363.9464.

4,4'-cis-Bis(triazinanone)stilbenophane (4a). Triazinanone (0.504 g, 1.38 mmol) was weighed into an oven-dried 100 mL round-bottomed flask under N_2 (g) and dissolved in 20 mL of THF. Next, NaH (0.165 g, 4.13 mmol) was added and the reaction was heated at 80 °C for 30 min. The solution was cooled, **3a** (0.504 g, 1.38 mmol in 20 mL of THF) was added, and the mixture was heated at 80 °C overnight. The reaction was quenched with H_2O (30 mL) and reduced to half its original volume under vacuum. The remaining aqueous solution was extracted with CH_2Cl_2 (3×30 mL). The organic layer was separated, dried over Na_2SO_4 , and evaporated. The residue was purified by column chromatography (silica gel, eluent = 1:2 acetone:hexanes) to afford a white precipitate (0.11 g, 12%). Mp 328–330 °C dec; ^1H NMR (400 MHz, DMSO- d_6) δ 0.75 (s, 18 H), 4.20 (s, 8 H), 4.30 (s, 8 H), 6.59 (s, 4 H), 7.13 (d, $J = 8.0$ Hz, 8 H), 7.24 (d, $J = 8.1$ Hz, 8H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 27.8, 46.7, 53.8, 60.5, 128.4, 129.0, 129.7, 135.9, 137.5, 155.5; MS (EI) m/z 191, 206, 234, 248, 263, 290, 389, 552, 580, 665, 722 (M^+); HRMS (EI) calcd for $\text{C}_{46}\text{H}_{54}\text{N}_6\text{O}_2$ 722.4308, found 722.4312.

4,4'-trans-Bis(triazinanone)stilbenophane (4b). Mp 305–307 °C dec; ^1H NMR (400 MHz, CDCl_3) δ 1.25 (s, 9 H), 1.26 (s, 9 H), 3.49 (t, $J = 14.8$ Hz, 4 H), 4.10–4.20 (m, 4 H), 4.22 (s, 4H), 5.38–5.46 (m, 4H), 7.00 (s, 2H), 7.02 (s, 2H), 7.13 (d, $J = 8.0$ Hz, 4 H), 7.19 (d, $J = 8.0$ Hz, 4 H), 7.29 (d, $J = 8.0$ Hz, 4 H), 7.32 (d, $J = 8.0$ Hz, 4 H); ^{13}C NMR (100 MHz, CDCl_3) δ 28.80, 28.82, 49.2, 49.3, 54.29, 54.31, 62.5, 62.8, 126.4, 126.5, 128.3, 128.6, 128.7, 136.28, 136.3, 137.3, 157.4, 157.4; MS (EI) m/z 161, 178, 206, 234, 248, 290, 722 (M^+); HRMS (EI) calcd for $\text{C}_{46}\text{H}_{54}\text{N}_6\text{O}_2$ 722.4308, found 722.4322.

4,4'-cis-Bis(urea)stilbenophane (5a). Compound **4a** (0.078 g, 0.108 mmol) was dissolved in MeOH (15 mL) and a solution of 20% diethanol amine in H_2O (5 mL, pH \sim 2, previously adjusted with conc. HCl) was added. The mixture was heated at 85 °C overnight. A milky precipitate formed, which was filtered and washed with H_2O (5 mL) and MeOH (5 mL) to afford the macrocycle **5a** in 90% yield. Mp 340–342 °C dec; ^1H NMR (400 MHz, DMSO- d_6) δ 4.18 (d, $J = 6.0$ Hz, 8 H), 6.39 (t, $J = 6.0$ Hz, 4 H), 6.56 (s, 4 H), 7.10–7.16 (m, 16 H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 42.7, 127.1, 128.4, 129.6, 135.3, 139.6, 157.9; MS (EI) m/z 129, 226, 254, 264, 290, 528 (M^+); HRMS (EI) calcd for $\text{C}_{34}\text{H}_{32}\text{N}_4\text{O}_2$ 528.2525, found 528.2520.

4,4'-trans-Bis(urea)stilbenophane (5b). Mp 318–320 °C dec; ^1H NMR (400 MHz, DMSO- d_6) δ 4.10 (s, 8 H), 6.46 (t, $J = 6.8$ Hz, 4 H), 7.06 (d, $J = 8.0$ Hz, 8 H), 7.07 (s, 4 H), 7.34 (d, $J = 8.0$ Hz, 8 H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 43.2, 126.0, 127.4, 127.8, 135.3, 140.6, 159.4; MS (EI) m/z 115, 178, 191, 220, 248, 264, 290, 528 (M^+); HRMS (EI) calcd for $\text{C}_{34}\text{H}_{32}\text{N}_4\text{O}_2$ 528.2525, found 528.2520.

(4,4',4'',4'''-((1R,2R,3S,4S)-Cyclobutane-1,2,3,4-tetrayl)tetrakis(benzene-4,1-diyl))tetrakis(methylene)bisurea (6). A DMSO- d_6 (1 mL) solution of macrocycle **5a** (4 mg) was irradiated with a 450 W Hannoveria high pressure mercury vapor lamp at room temperature. Product **6** was obtained quantitatively. ^1H NMR (400 MHz, DMSO- d_6) δ 3.79 (d, $J = 6.8$ Hz, 8H), 4.48 (s, 4H), 5.91 (t, $J = 6.4$ Hz, 4H), 6.66 (dd, $J = 8.4, 1.6$ Hz, 4H), 6.76 (dd, $J = 8.4, 1.6$ Hz, 4H), 6.86 (d, $J = 8.4$ Hz, 4 H), 7.05 (d, $J = 8.4$ Hz, 4 H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 44.4, 45.1, 126.4, 127.8, 128.0, 130.2, 138.2, 138.6, 160.2; MS (EI) m/z 178, 204, 219, 230, 249, 260, 290, 528 (M^+).

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Supporting Information Available: NMR spectra for new compounds, X-ray reports, and CIF files of **4a**, **5a**, and **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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