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Sulfur-Incorporating Cyclotriveratrylene Analogues: The Synthesis of Cyclotrithioguaiacylene

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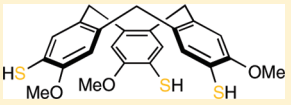
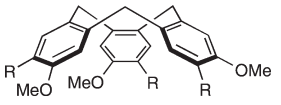
Supporting Information

ABSTRACT: Cyclotriguaiacylene **1** is the universal precursor of cryptophanes, and represents an important intermediate for the preparation of functionalized cavitands of the cyclotriveratrylene family. Its thio analogue (cyclotrithioguaiacylene **3**) was synthesized by two different routes, involving either the Newman−Kwart or the Pummerer rearrangement. The latter, performed starting from a trisulfoxide precursor, produced a purer compound in higher overall yield.



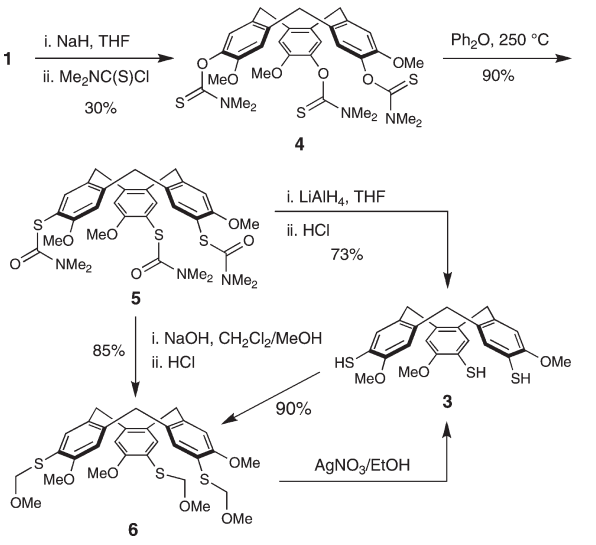
Cryptophanes are spherical, hollow, and chiral molecules built by triple bridging of two (C_3)-cyclotriveratrylene (CTV) concave subunits with chains of various nature, usually methylenic.[1] Their lipophilic cavity can bind stereospecifically various substrates by van der Waals and/or cation−π interactions: methane[2] and its halogenated derivatives,[3] acetylcholine and related quaternary ammonium salts,[4] and xenon gas.[5] With few exceptions, most of the known cryptophanes are synthesized from cyclotriguaiacylene (**1**), a CTV analogue featuring hydroxy functions that alternate with methoxy substituents.[6] Other useful functional groups that could be incorporated either directly or by a series of chemical transformations are the halogeno (Br,[7] I[8]), the triflate,[9] the amino,[10] and the methylthio (CTV **2**)[11] substituents. However, the synthesis of the thio analogue, in which SH groups replace the OH groups of cyclotriguaiacylene, has not been reported. The significance of this trithiol CTV derivative (**3**) stems from the fact that it could be used to advantage as a building block for the self-assembly of cryptophanes using disulfide bond formation, by analogy with systems made from α-cyclodextrin[12] or other tripodal building blocks,[13] or for performing dynamic combinatorial chemistry experiments,[14] using the thiol disulfide exchange.[15]



1: R = OH
2: R = SCH_3
3: R = SH

The Newman−Kwart rearrangement[16] is a well-established method for converting phenols to thiophenols, which was employed, in particular, for the preparation of *p-tert*-butylcalix[4]arenethiols from *p-tert*-butylcalix[4]arene.[17] Therefore, it seemed perfectly adapted for the synthesis of **3** from **1**

Scheme 1. The Newman−Kwart Route to Cyclotrithioguaiacylene (3)



(Scheme 1). Accordingly, **1** was reacted at first with an excess of NaH in THF followed by *N*,*N*-dimethylthiocarbamoyl chloride, and the reaction mixture was heated at reflux. The trifunctionalized *O*-aryl *N*,*N*-dimethylthiocarbamate CTV derivative (**4**) was separated from the mono- and difunctionalized products by flash column chromatography and obtained in 30% yield. Subsequent thermic rearrangement in diphenyl ether at 250 °C afforded the *S*-aryl *N*,*N*-dimethylthiocarbamate CTV isomer **5** in 90% yield as a brown solid. Cyclotrithioguaiacylene **3** was finally

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obtained by $LiAlH_4$ reduction of **5** in THF followed by acidic workup, in 73% yield. However, the purity of the rearranged products (**3** and **5**) was not fully satisfactory (Figures S3 and S13, Supporting Information). Another drawback of this route was the low yield of the carbamoylation reaction (30%).

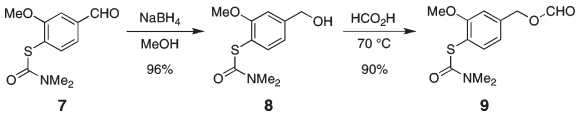
In fact, we had earlier attempted to cleave the carbamate functions of **5** by hydrolysis in basic conditions (NaOH). As the reaction did not proceed in pure methanol, we employed a 1:1 mixture of methanol and dichloromethane as solvent (Scheme 1). Unexpectedly, this reaction resulted in the trans-protection of the thiol groups of **3**, by exchange of the carbamate functions of **5** with the MOM functions of **6**, in 85% yield after chromatography. Although extensively used for the protection of alcohols and phenols,[18] the MOM group has been very scarcely employed for the protection of their thio analogues. Classical conditions involve MOMCl/base in THF.[19] Actually, reaction of **3** in the conditions used for the conversion of **5** into **6** also produced **6**, in 90% yield. This suggests that the thiolate functions released in the hydrolysis of **5** then react with CH_2Cl_2/MeOH. Noticeably, a very similar MOM protection of an arylthiol by reaction with CH_2BrCl in methanol in the presence of powdered KOH and a phase transfer catalyst has been reported.[20] The reaction was suggested to proceed via methanolysis of the intermediate sulfonium cation resulting from chloride elimination of the intermediate chloromethyl sulfide. This roundabout potential route to **3** was quite interesting, as purification of **6** was very easy, contrary to that of **5**. However, attempts to remove the MOM protection with the established method ($AgNO_3$/EtOH)[19b,19d] failed to afford a clean product. Therefore we sought for other routes.

(C_3)-CTV′s are synthesized by acid-catalyzed regiospecific cyclodehydration of 3,4-disubstituted benzyl alcohol derivatives.[21] Procedures developed recently use milder conditions (catalytic $Sc(OTf)_3$ in acetonitrile).[9] Both 3- and 4-substituents must be ortho−para directing, and the former strongly activating toward electrophilic aromatic substitution (electron-donor).[10] In spite of these limitations, we attempted the direct formation of CTV **4** from 4-(*N*,*N*-dimethylcarbamoylthio)-3-methoxybenzene methanol (**8**), obtained in 96% yield by $NaBH_4$ reduction of the known aldehyde (**7**).[11] However, heating of **8** in HCO_2H at 70 °C produced the corresponding ester **9** (Scheme 2). Therefore we finally concentrated our efforts on presynthesized, sulfur-substituted CTV platforms.

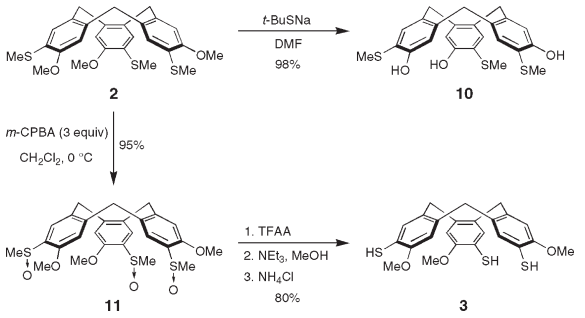
The known methylthio-substituted CTV **2** represents another interesting and easily accessible starting compound.[11] Unfortunately, as reported by Collet and co-workers, attempts to selectively S-demethylate **2** with Na/HMPA at 100 °C failed.[22] We obtained similar results by employing sodium diethylamide in refluxing HMPT/xylene.[22] In addition, reaction with *t*-BuSNa in refluxing DMF, which has also been efficiently used for the cleavage of the C−S bond,[23] gave the known *O*-demethylated product (**10**),[11] a result that could have been predicted from precedent.[11,25]

Sulfoxides, which are obtained by controlled oxidation of thioethers, are easily converted to thiols by the Pummerer rearrangement upon reaction with trifluoroacetic anhydride (TFAA) in the presence of a base (Et_3N).[26] Accordingly, **2** was reacted with the stoichiometric amount of *m*-CPBA in CH_2Cl_2 at 0 °C (Scheme 3). The trisulfoxide **11** derivative of **2** was obtained in 95% yield as a mixture of diastereomers that could not be separated by chromatography.[27] Indeed, its ^1H NMR spectrum showed complex patterns. In particular, several

Scheme 2. Attempted Direct Preparation of 4



Scheme 3. The Pummerer Route to Cyclotrithioguaiacylene



singlets for the CH_3S protons could be identified, with a maximum of seven in $CDCl_3$ (Figure S25, Supporting Information). (C_3)-CTV's are intrinsically chiral compounds because of their conical (crown) shape and arrangement of substituents, and exist as a mixture of *P* and *M* conformers.[28] Therefore, as three stereocenters are generated by oxidation of the methyl thioether substituents, **11** is expected to exist in the form of four pairs of diastereomers, C_3-symmetric P,R,R,R/M,S,S,S and P,S,S,S/M,R,R,R, and asymmetric P,R,R,S/M,S,S,R and P,R,S,S/M,S,R,R. The CH_3S protons show up as one singlet each for the former, and as three singlets each for the latter. Therefore, the maximum number of signals for these protons is eight. This arithmetical analysis shows that *m*-CPBA oxidation of **2** to trisulfoxide **11** is likely to produce all the possible diastereomers. The Pummerer rearrangement was carried out by reaction of **11** with 3 equiv of trifluoroacetic anhydride in CH_2Cl_2, followed by aminolysis of the thioacetate intermediate by NEt_3/CH_3OH. In this way pure **3** was obtained in 80% yield after purification by column chromatography as a colorless solid material. In addition to the expected singlets for the α (6.77 ppm) and α′ (7.21 ppm) protons, and the pairs of doublets for the equatorial (3.52 ppm) and axial (4.66 ppm) methylenic protons, its ^1H NMR spectrum showed the signature of the thiol protons as a singlet at 3.72 ppm.

Clearly, trisulfoxide **11** was obtained as a mixture of diastereomers. However, complete oxidation to the trisulfone should afford a single product. Accordingly, reaction of **2** with 7.5 equiv of *m*-CPBA at room temperature afforded trisulfone **12** in 89% yield (Scheme 4). Its ^1H NMR spectrum in $CDCl_3$ showed only one set of signals, and was left unchanged upon switching to other solvents. Heating of **12** in $C_2D_2Cl_4$ up to 110 °C caused a slight downfield shift of the signals of the cone conformation and the development of a new set of signals corresponding to the rarely observed saddle conformation, the most characteristic ones being the singlet of the methylene protons at 4.06 ppm.[29] Interestingly, prolonged heating at 100 °C (Figure 1) did not change the ratio between the cone and saddle conformers (6:1).

Slow evaporation of CH_2Cl_2/heptane solutions of trisulfone **12** left X-ray quality needle-shaped colorless crystals. The ORTEP view of Figure 2 shows the cone-shaped structure of

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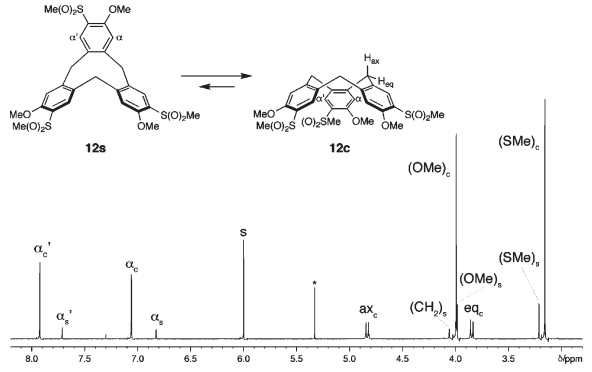


Figure 1. Monitoring of the equilibrium between the saddle (s) and the crown (c) conformations of (C_3)-CTV **12** by ^{1}H NMR (600 MHz, 298 K) in $C_2D_2Cl_4$ after prolonged heating at 100 °C. The peak marked with an asterisk is due to residual CH_2Cl_2.

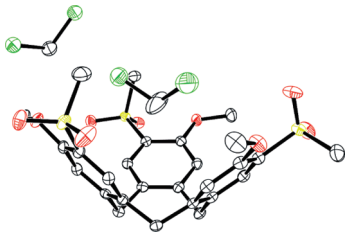
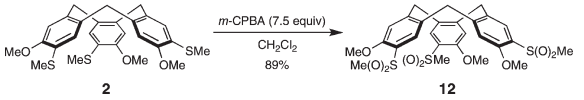


Figure 2. ORTEP view of **12** with two co-crystallized solvent molecules. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Scheme 4. Formation of Trisulfone 12



12 with two co-crystallized CH_2Cl_2 molecules, one of them being trapped within the molecular cavity. The hydrogen atoms of the latter enjoy edge-to-face CH···π interactions with the receptor, their distances to the centroids of the closest phenyl moieties being both equal to 2.81 Å. In addition, while one of the Cl-atoms exhibits two CH···Cl contacts at 2.97 and 3.21 Å, the other makes a long O···Cl interaction (3.80 Å) with a sulfonyl oxygen atom (Figure S2, Supporting Information).

This work adds a new member to the family of thiol-functionalized (C_3)-CTV's.[30] It contrasts with the reported ones by the direct connection of the SH group to the cyclophane backbone. As a result cyclotrithioguaiacylene **3** is highly preorganized to form a cryptophane capsule by oxidative dimerization. Studies along these lines will be reported in due course.

EXPERIMENTAL SECTION

2,7,12-Trimethoxy-3,8,13-tri(*N*,*N*-dimethylamino)thioxo-methoxydihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (4). NaH (1.80 g, 75.0 mmol) was added to a solution of **1** (1.00 g, 2.45 mmol) in THF (50 mL) and the resulting mixture heated at reflux for 1 h. After addition of *N*,*N*-dimethylthiocarbamoyl chloride (0.900 g, 7.35 mmol) at 0 °C, the reaction mixture was heated at reflux for 12 h. This operation was repeated once. The reaction mixture was quenched by addition of 10% aqueous HCl at 0 °C and extracted into CH_2Cl_2. The combined organic layers were concentrated to dryness. Purification of the residue by flash column chromatography (silica gel; CH_2Cl_2) afforded **4** (0.500 g, 0.75 mmol) in 30% yield. Mp 135−136 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.27 (s, 9H; NCH_3), 3.43 (s, 9H; NCH_3), 3.65 (d, ^2J = 13.8 Hz, 3H; *eq*-H), 3.78 (s, 9H; OCH_3), 4.76 (d, ^2J = 13.8 Hz, 3H; *ax*-H), 6.89 (s, 3H; α-H), 7.04 (s, 3H; α′-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 36.5 (CH_2), 38.7 (NCH_3), 43.3 (NCH_3), 56.4 (OCH_3), 114.4 (α-C), 125.3 (α′-C), 131.4 (β'-C), 138.0 (β-C), 141.4 (γ'-C), 150.0 (γ-C), 187.8 (CS) ppm; IR (ATR) ν 1507 (C═S) cm^{-1}; ESI-HRMS found, 670.20766, 692.19937, calcd for [M + H$^+$] 670.20737 and for [M + Na$^+$] 692.18932.

2,7,12-Trimethoxy-3,8,13-tri(*N*,*N*-dimethylamino)oxo-methylthiodihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (5). A solution of **4** (0.100 g, 0.15 mmol) in diphenyl ether (50 mL) was heated at 250 °C for 6 h. After cooling to room temperature, the reaction mixture was poured into pentane (250 mL). The resulting precipitate was isolated by filtration and purified by flash column chromatography (silicagel, CH_2Cl_2 then CH_2Cl_2/CH_3OH 95:5) to afford **5** (0.090 g; 0.134 mmol) as a brown solid in 90% yield. Mp 172−173 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.00 (br s, 9H; NCH_3), 3.09 (br s, 9H; NCH_3), 3.69 (d, ^2J = 13.8 Hz, 3H; *eq*-H), 3.85 (s, 9H; OCH_3), 4.74 (d, ^2J = 13.8 Hz, 3H; *ax*-H), 6.90 (s, 3H; α-H), 7.45 (s, 3H; α′-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 36.4 (CH_2), 36.9 (NCH_3), 56.3 (OCH_3), 113.0 (α-C), 114.9 (γ'-C), 131.2 (β'-C), 139.3 (α′-C), 143.0 (β-C), 158.6 (γ-C), 166.3 (CO); IR (ATR) ν 1658 (C═O) cm^{-1}; ESI-HRMS found 692.18985, calcd for [M + Na$^+$] 692.18932.

2,7,12-Trimethoxy-3,8,13-tri(methoxymethylthio)dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (6). From **5**: A solution of NaOH (0.500 g, 12.5 mmol) in water (2 mL) was added to a solution of **5** (0.100 g, 0.15 mmol) in a mixture of CH_2Cl_2 and CH_3OH (1:1; 60 mL). The reaction mixture was heated at reflux for 24 h. After cooling to room temperature, it was quenched by the addition of 5% aq HCl (50 mL). Extraction with CH_2Cl_2 (3 × 50 mL) followed by concentration to dryness afforded a crude material, which was purified by flash column chromatography (silicagel, CH_2Cl_2 then CH_2Cl_2/CH_3OH 98:2) to afford **6** (0.075 g, 0.127 mmol) in 85% yield. From **3**: The same procedure was employed starting from NaOH (0.0065 g, 0.163 mmol) and **3** (0.025 g, 0.055 mmol). After chromatographic purification **6** was obtained in 90% yield (0.029 g, 0.0493 mmol). Mp 129−130 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.39 (s, 9H; CH_2OCH_3), 3.64 (d, ^2J = 13.8 Hz, 3H; *eq*-H), 3.86 (s, 9H; OCH_3), 4.72 (d, ^2J = 13.8 Hz, 3H; *ax*-H), 4.83 (d, ^2J = 11.4 Hz, 3H; SCH_2), 5.01 (d, ^2J = 11.4 Hz, 3H; SCH_2), 6.83 (s, 3H; α-H), 7.52 (s, 3H; α′-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 36.5 (CH_2), 55.9 (CH_3), 56.0 (CH_3), 76.4 (OCH_2), 112.0 (α-H), 122.2 (γ'-H), 131.9 (β'-H), 132.2 (α′-H), 139.4 (β-H), 156.2 (γ-H) ppm; ESI-HRMS found 611.15486, calcd for [M + Na$^+$] 611.15662.

2,7,12-Trimethoxy-3,8,13-trimethylsulfinyldihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (11). *m*-CPBA (70−75%, 0.741 g 3.00 mmol) was added to a solution of **2** (0.500 g, 1.00 mmol) in CH_2Cl_2 (25 mL) at −30 °C. Stirring of the reaction mixture for 6 h at 0 °C was followed by addition of aqueous $NaHCO_3$ (100 mL). The resulting aqueous phase was extracted with CH_2Cl_2 and the combined organic layers concentrated to dryness. Flash column chromatography of the residue (silica gel; CH_2Cl_2/CH_3OH, 95:5) afforded **11** (0.520 g, 0.95 mmol) in 95% yield as a colorless solid, as a mixture of diastereomers (see the Supporting Information for a copy of the ^{1}H and ^{13}C NMR spectra); ESI-HRMS found 569.11384, calcd for [M + Na$^+$] 569.10967. Anal. Calcd for $C_{27}H_{30}O_6S_3 \cdot {}^5/_2H_2O$ (546.73): C, 54.8; H, 6.0; S, 16.3. Found: C, 54.9; H, 5.8; S, 16.1.

2,7,12-Trimethoxy-3,8,13-trimethylsulfonyldihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (12). *m*-CPBA (70−75%, 0.400 g 1.5 mmol) in CH_2Cl_2 (20 mL) was added to a solution of **2** (0.100 g, 0.200 mmol) in CH_2Cl_2 (50 mL) at −20 °C. The mixture was stirred at 0 °C for 6 h, then at room temperature for 12 h. The reaction was quenched by addition of a saturated aqueous solution of $NaHCO_3$. The organic layer was

separated, and the aqueous layer extracted into CH_2Cl_2 (3 × 100 mL). The combined organic layers were concentrated to dryness, and the resulting solid purified by column chromatography (silica gel; CH_2Cl_2/CH_3OH 95:5) to afford **12** (0.106 g, 0.178 mmol) in 89% yield as a colorless solid. Mp 350 °C dec; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.14 (s, 9H; $S(O)_2CH_3$), 3.83 (d, ^2J = 13.8 Hz, 3H; *eq*-H), 3.98 (s, 9H; OCH_3), 4.83 (d, ^2J = 13.8 Hz, 3H; *ax*-H), 7.06 (s, 3H; α-H), 7.96 (s, 3H; α′-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 36.5 (CH_2), 43.1 ($S(O)_2CH_3$), 56.8 (OCH_3), 113.9 (α-C), 127.5 (γ′-C), 130.3 (β′-C), 131.2 (α′-C), 147.1 (β-C), 156.2 (γ-C) ppm; IR (ATR) ν 1287 (S═O), 1139 (S═O) cm^{-1}; ESI-HRMS found 617.09300, calcd for [M + Na$^+$] 617.09442. Anal. Calcd for $C_{27}H_{30}O_9S_3$ (594.73): C, 54.5; H, 5.1. Found: C, 54.5; H, 5.2.

2,7,12-Trimethoxy-3,8,13-trithiodihydro-5*H*-tribenzo[*a*,*d*,*g*]-cyclononene (3). From **5**: $LiAlH_4$ (0.035 g, 0.9 mmol) was added to a suspension of **5** (0.050 g, 0.0746 mmol) in anhydrous THF (20 mL) at room temperature. After heating the resulting mixture at reflux for 12 h, the reaction was quenched by careful addition of ethylacetate (25 mL) followed by 10% aqueous HCl (50 mL). The reaction mixture was concentrated and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with water then dried ($MgSO_4$), and the solvents evaporated to dryness, affording **3** (0.025 g, 0.0547 mmol) in 73% yield, as a pale yellow solid. From **11**: Trifluoroacetic anhydride (0.690 mL, 4.9 mmol) was added dropwise to a solution of **11** (0.300 g, 0.55 mmol) in anhydrous CH_2Cl_2 (75 mL). The temperature was raised to 0 °C and the reaction mixture stirred at this temperature for 5 h, followed by 12 h at room temperature. The solvent was evaporated and the residue retaken in a mixture of triethylamine and methanol (1:1, 10 mL) under nitrogen. The resulting solution was stirred at room temperature for 30 min, then concentrated to dryness. The residue was dissolved in CH_2Cl_2 (100 mL), and shaken with a saturated aqueous solution of NH_4Cl (50 mL). The organic layer was separated, and the aqueous phase extracted into CH_2Cl_2. The residue obtained after evaporation of the solvent was purified by column chromatography (silica gel; CH_2Cl_2/pentane, 50:50 then 80:20), which afforded **3** (0.200 g, 0.438 mmol) in 80% yield as a colorless solid. Mp 242−244 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.52 (d, ^2J = 13.8 Hz, 3H; *eq*-H), 3.72 (s, 3H; SH), 3.87 (s, 9H; OCH_3), 4.66 (d, ^2J = 13.8 Hz, 3H; *ax*-H), 6.77 (s, 3H; α-H), 7.21 (s, 3H; α′-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 36.4 (CH_2), 56.3 (OCH_3), 112.3 (α-C), 118.8 (γ′-C), 130.8 (α′-C), 132.0 (β′-C), 138.2 (β-C), 154.0 (γ-C); ESI-HRMS found 479.07836, calcd for [M + Na$^+$] 479.07798.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. General Experimental Methods and additional experimental procedures, copies of ^{1}H and ^{13}C NMR spectra for all compounds, and a crystallographic information file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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