

Synthesis of Dithiane-Based Photolabile Molecular Systems

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Received 1 February 2001

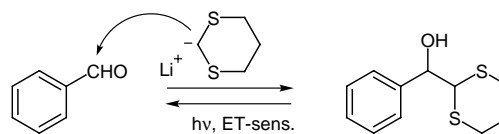
Dedicated to Howard E. Zimmerman on the occasion of his 75th birthday

Abstract: Synthesis of photolabile molecular systems based on lithiodithiane addition to carbonyl compounds is described. Dithianes of the spiro structure, e.g., 2,4,8,10-tetrathiaspiro[5.5]undecane and 2,4-dithia-8,10-dioxaspiro[5.5]undecane are utilized as tethers, thus allowing for a modular approach to building a diverse set of photocleavable molecules. A variety of carbonyl compounds ranging from simple substituted benzaldehydes to formylated benzocrown ethers, carbohydrates or calixarenes are found to be suitable for this chemistry.

Key words: photolabile molecular hosts, photoinduced electron transfer, dithiane, 2,4,8,10-tetrathiaspiro[5.5]undecane, 2,4-dithia-8,10-dioxaspiro[5.5]undecane, calix[4]arene, benzocrown ether, ribofuranose, glucopyranose, galactopyranose

Recently we reported¹ an efficient photoinduced C–C bond cleavage in α -hydroxyalkyl-1,3-dithianes (Corey–Seebach dithiane-carbonyl adducts²). The mechanism of this reaction involves photochemically induced single electron transfer from the dithiane moiety to the excited molecule of ET-photosensitizer (benzophenone), accompanied by mesolytic C–C cleavage in the generated cation-radical, which is assisted by the anion-radical of benzophenone.

In view of the remarkable efficiency for both lithiodithiane addition to substituted benzaldehydes and photo-fragmentation of such dithiane adducts, we have been investigating the applicability of these systems as molecular latches that could be used to attach various molecular and macromolecular blocks and, at the same time, could be selectively unfastened on demand.³ One of the



Scheme 1

many potential applications for these systems could be in assembling photocleavable molecular hosts capable of releasing guest molecules upon irradiation. Our specific strategy was to tether two formylated macromolecular blocks with spiro-bis-dithiane **1** (Scheme 2) or dithiane-bis-methanol **2** (Scheme 3) to produce a photolabile system equipped with one or two photocleavable C–C bonds.

A variety of compounds having a benzaldehyde fragment in their structure are suitable for such assembly. In this paper we report the synthesis of the linkers **1** and **2**, approaches to several dithiane-bearing molecular building blocks and, finally, joining these blocks together to furnish photolabile molecular systems.

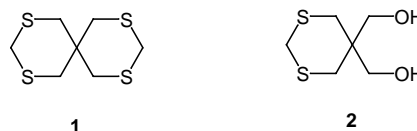
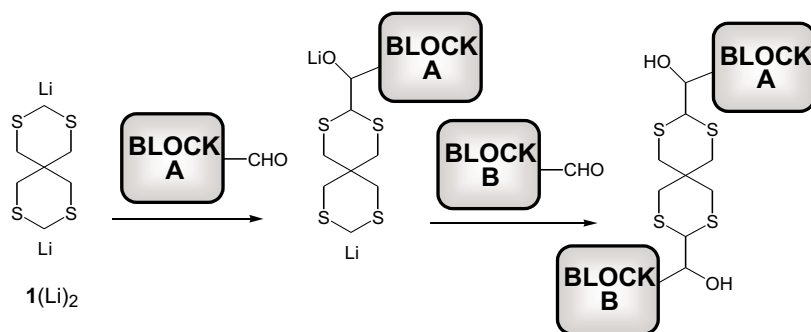


Figure 1

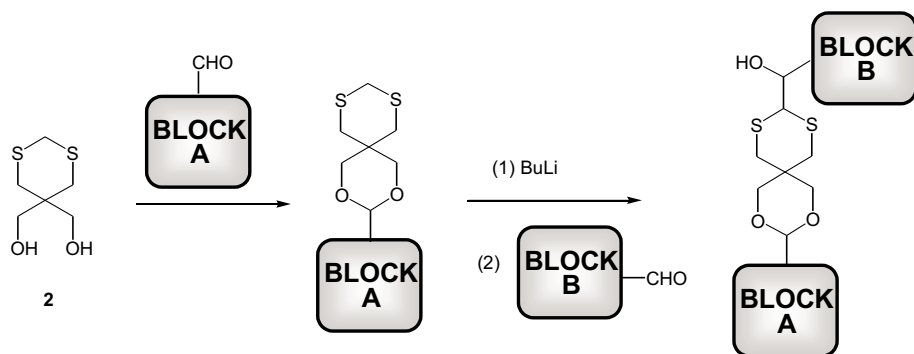
Synthesis of linkers 1 and 2: The novel spiro-bis-



Scheme 2

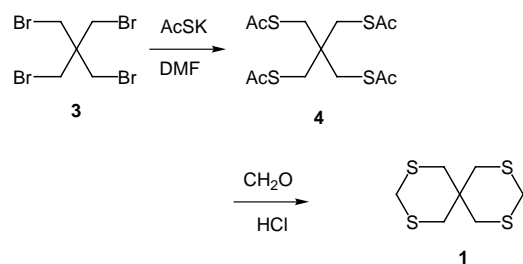
Synthesis 2001, No. 8, 18 06 2001. Article Identifier: 1437-210X,E;2001,0,08,1133,1142,ftx,en;C00801SS.pdf.
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ISSN 0039-7881

dithiane **1** was synthesized starting from commercially available pentaerythrityl tetrabromide (**3**). Nucleophilic substitution by potassium thioacetate in DMF yielded



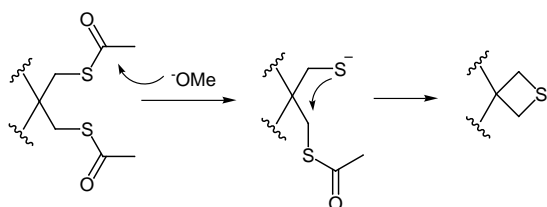
Scheme 3

87% of the corresponding tetrathioacetate **4** (Scheme 4). However, attempts to deacetylate **4** under basic conditions (MeONa/MeOH) produced the target tetra-thiol that was considerably contaminated by thietanes (Scheme 5). We rationalized that intramolecular nucleophilic displacement in this sterically hindered environment can be a significant channel to partially relieve steric strain. An alternative approach – combining both thioacetate hydrolysis and thioacetal formation in one step under acid-catalyzed conditions – was successful and the target spiro-bis-dithiane **1** was obtained in 76% isolated yield.

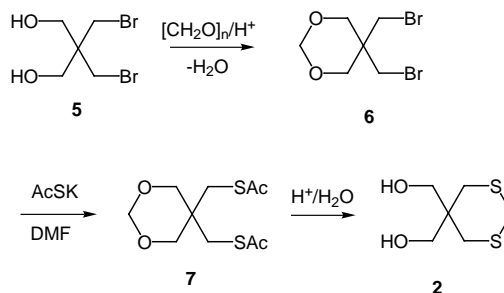


Scheme 4

Dimethanol **2** was synthesized from commercially available 2,2-bis(bromomethyl)-1,3-propanediol (**5**), which was first protected via cyclic acetal formation with formaldehyde to give **6**, and then reacted with potassium thioacetate. The critical feature of this synthetic sequence was that during the next, acid-catalyzed step no extra formaldehyde was added and therefore the deprotection of the diol and formation of the dithiane ring occurred via methylenic transfer from oxygens to sulfurs (59% yield).

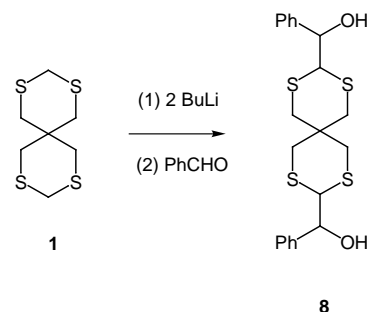


Scheme 5



Scheme 6

Symmetric photolabile bis-adducts based on 1: We first exemplified our approach by generating bis-lithiated **1** and quenching it with excess benzaldehyde to produce diol **8**.⁴

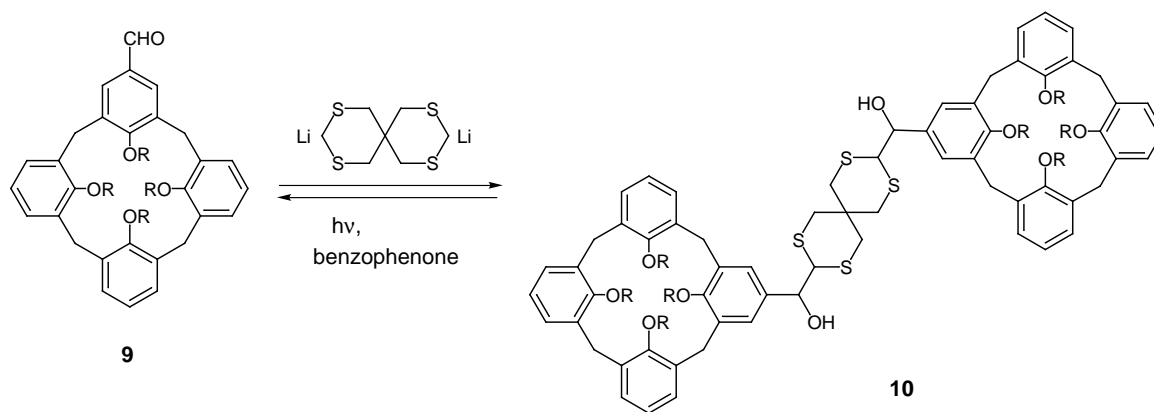


Scheme 7

More complex systems can be assembled using monoformylated calix[4]arene **9**⁵ as a building block ($R = \text{EtOCH}_2\text{CH}_2$). Its reaction with dilithiated **1** in THF furnished bis-calixarene **10** in 71% yield.

Bis-adducts **8** and **10** are photolabile molecular systems. They cleave quantitatively, regenerating benzaldehyde or calixarene **9** respectively, upon irradiation in the presence of benzophenone in acetonitrile.

Utilizing essentially the same conditions, we assembled crown ether-based hosts **11** and **12**, starting from monoformylated dibenzo-24-crown-8 and benzo-18-crown-6 ethers, respectively.



Scheme 8

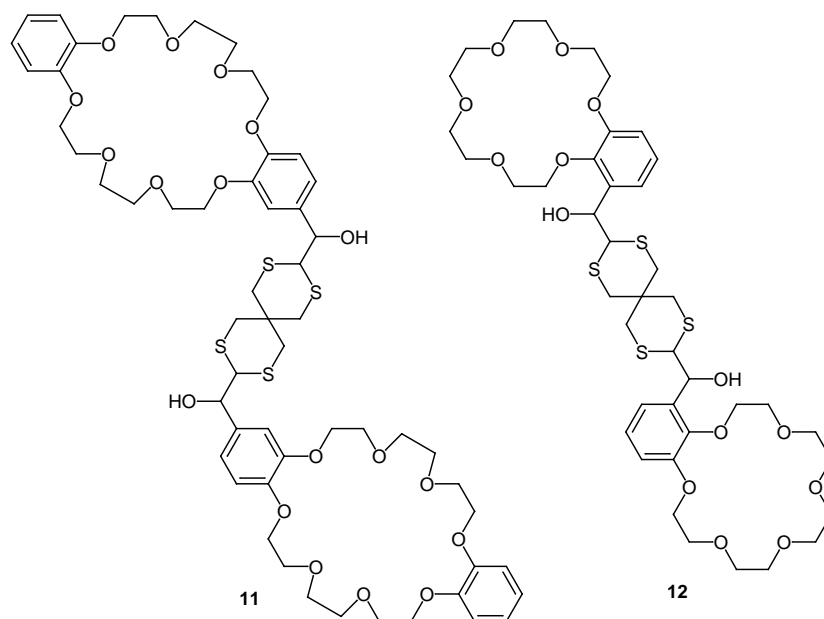


Figure 2

Complexation properties and photophysics of these and other molecular hosts described in this paper will be discussed elsewhere.

Monoadducts as building blocks for non-symmetric assemblies: In order to diversify the series of photocleavable molecular hosts containing our dithiane-based photolatching device, we synthesized a series of mono-adducts of **1** and monoacetals of **2**, which were utilized in the subsequent steps for coupling with various formyl-bearing blocks:

Thus, on reacting formyl-substituted benzocrown ethers or calix[4]arene with *mono*-lithiated spiro-bis-dithiane **1**, we synthesized **13–16**.

Bidentate precursors **17–19** were prepared from mono-lithiated **1** and bis-formylated dibenzocrowns⁶ or calix[4]arene.⁵

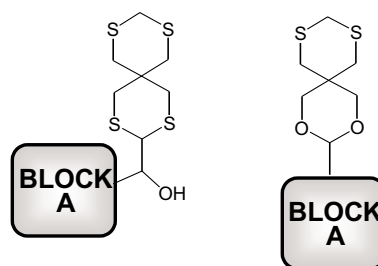
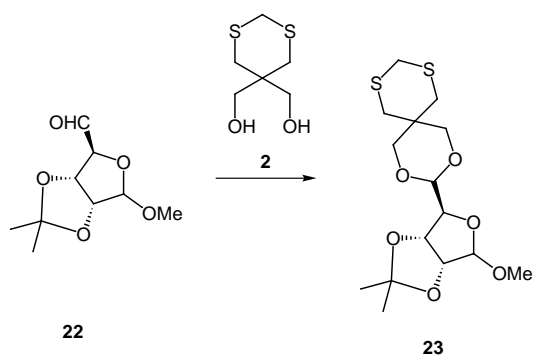
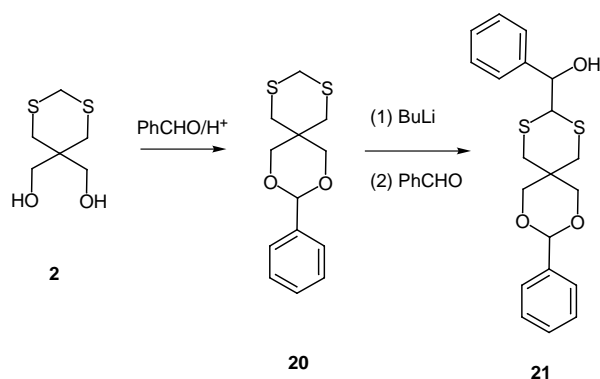


Figure 3

Similar monodithiane-containing systems can be readily obtained from diol **2** via acetal formation. The simplest illustration of this approach is the benzaldehyde acetal **20**, which upon treatment with butyl lithium and quenching with another mole of benzaldehyde produces photocleavable molecule **21**.



Scheme 9

Scheme 10

We utilized this coupling mode in order to introduce chiral auxiliary groups into the building blocks, specifically, in conjunction with carbohydrate-based formylated systems. There are several readily available formyl-bearing pyranoses or furanoses, with fully protected hydroxy groups, which are suitable for Corey–Seebach chemistry. For example, treating furanose **22** with **2** under acid-cata-

lyzed conditions furnished acetal **23** in 72% yield (Scheme 10). A similar synthetic sequence starting from D-galactose derivative **24** produced a D-galactopyranosyl-bearing dithiane **25**, although the overall yield was only 38% (Scheme 11).

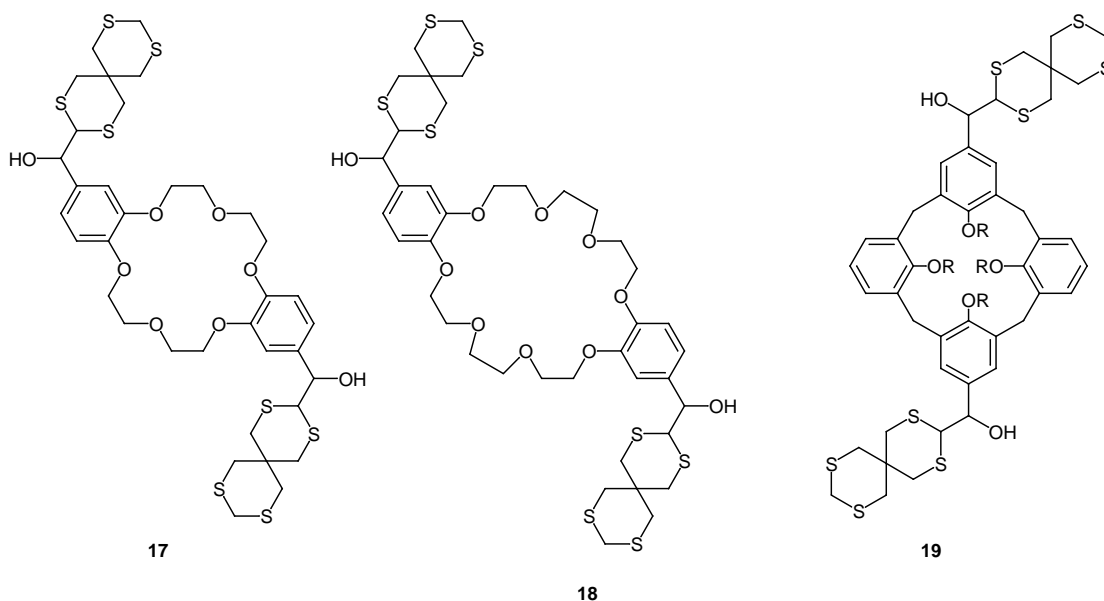
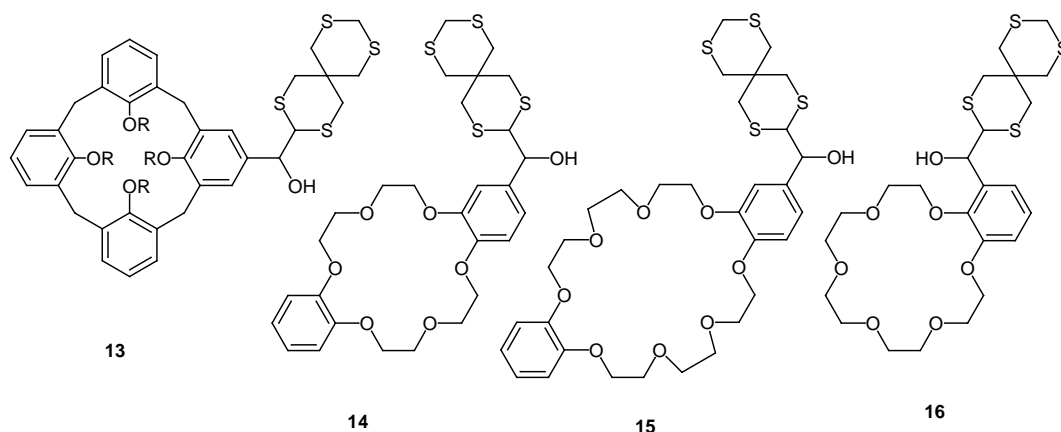
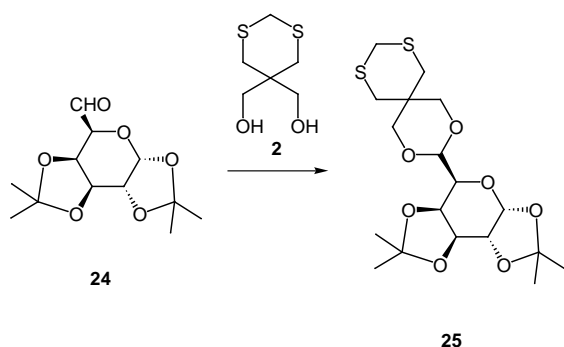
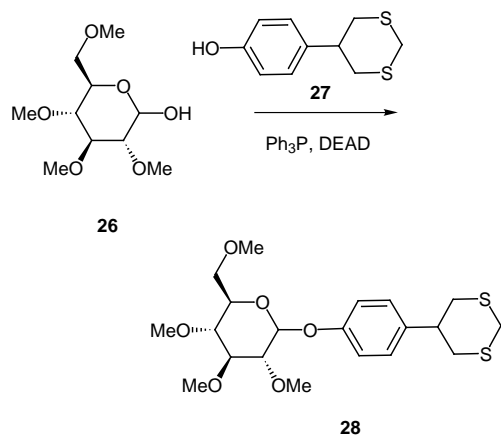


Figure 5



Scheme 11

Glycosidation of phenols bearing formyl or dithiane moieties offered yet another approach to chiral building blocks. We coupled tetramethyl glucopyranose **26** with 5-(*p*-hydroxyphenyl)-1,3-dithiane **27**⁷ to furnish dithiane-bearing permethylated glucopyranoside **28**.



Scheme 12

Various carbohydrate fragments can also be introduced in the form of glycosides of *p*-hydroxybenzaldehyde. For example, glycosidation with tetraacetylated glucopyranosyl bromide produced **29**, which we utilized as a carbonyl component.

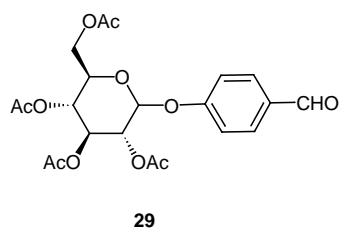


Figure 6

Building a diverse series of photolabile molecular objects: Having such a diverse assortment of precursors, we then coupled them with aromatic aldehydes, ranging in complexity from unpretentious benzaldehyde, to formylated benzocrown ethers, to calixarenes. Figure 7 shows

the photolabile (hybrid) systems that were synthesized by joining dissimilar dithiane and formyl-bearing components.

Details on experimental procedures can be found in the experimental section.

In conclusion, we have shown that the classic dithiane-carbonyl chemistry can be successfully adopted to assemble a diverse set of organic macromolecules, which are capable of photochemically induced disassembly in the presence of electron-transfer sensitizers.

Common reagents were purchased from Aldrich Chemical Co. and used without additional purification. THF was refluxed over and distilled from potassium benzophenone ketyl prior to use. ^1H and ^{13}C NMR spectra were recorded at 25 °C on a Varian Mercury 400 MHz instrument. TMS was used as an internal standard. Column chromatography was performed on silica gel, 70–230 mesh ASTM, using EtOAc–hexane mixtures (gradient from 1:20 to 1:2), unless specified. HP 6890 with MSD detector was used to analyze the compounds.

5,5-Bis(bromomethyl)-[1,3]dioxane (**6**)⁸

To a solution of 2,2-bis(bromomethyl)-1,3-propanediol (**5**, 5 g, 19.1 mmol) in formalin (7.0 mL) was added concd HCl (4 mL) at r.t. The mixture was refluxed overnight with stirring. After being cooled to r.t., it was extracted twice with CH_2Cl_2 (2×15 mL). The organic phases were combined and washed with sat. Na_2CO_3 (30 mL), dried (MgSO_4), and solvent was then removed under reduced pressure to afford the crude acetal **6** (5.0 g, 96%). It was used without further purification.

^1H NMR (CDCl_3): δ = 4.79 (s, 2H), 3.83 (s, 4H), 3.58 (s, 4H).

^{13}C NMR (CDCl_3): δ = 94.4, 71.5, 38.1, 35.2.

MS (EI): m/z (%) = 273 (M^+ , 5), 244 (15), 214 (90), 163 (50), 133 (60), 53 (100).

Pentaerythrityl tetrathioacetate (**4**)

Potassium thioacetate (31.8 g, 278 mmol) was dissolved in DMF (150 mL) and pentaerythrityl tetrabromide (**3**, 12.1 g, 31 mmol) was added to this solution. The reaction mixture was stirred under N_2 atm for 60 h at 25 °C, the solvent was then removed under vacuum. The residue was dissolved in CH_2Cl_2 (150 mL) and washed thrice with H_2O (3×100 mL). The organic phase was dried (MgSO_4) and concentrated. The crude product was recrystallized from MeOH to give the title compound (10.1 g, 87%).

^1H NMR (CDCl_3): δ = 3.04 (s, 8H), 2.36 (s, 12H)

^{13}C NMR (CDCl_3): δ = 194.0, 42.7, 34.9, 30.7.

MS (EI): m/z (%) = 325 ($[\text{M} - \text{CH}_3\text{CO}]^+$, 100), 283 (40), 241 (90), 223 (45), 119 (30).

5,5-Bis(acetylthiomethyl)-[1,3]dioxane (**7**)

Potassium thioacetate (6.25 g, 54.7 mmol) was dissolved in DMF (40 mL) and 5,5-bis(bromomethyl)-[1,3]dioxane (**6**, 5.0 g, 18.3 mmol) was added to this solution. The reaction mixture was stirred for one day at r.t. The solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2 (50 mL), washed with H_2O (50 mL), brine (50 mL), and dried (MgSO_4). The organic layer was concentrated to afford the crude product **7** (4.0 g, 82%). It was used without further purification.

^1H NMR (CDCl_3): δ = 4.78 (s, 2H), 3.66 (s, 4H), 3.09 (s, 4H), 2.36 (s, 6H).

^{13}C NMR (CDCl_3): δ = 194.4, 94.1, 72.5, 37.7, 31.4, 30.7.

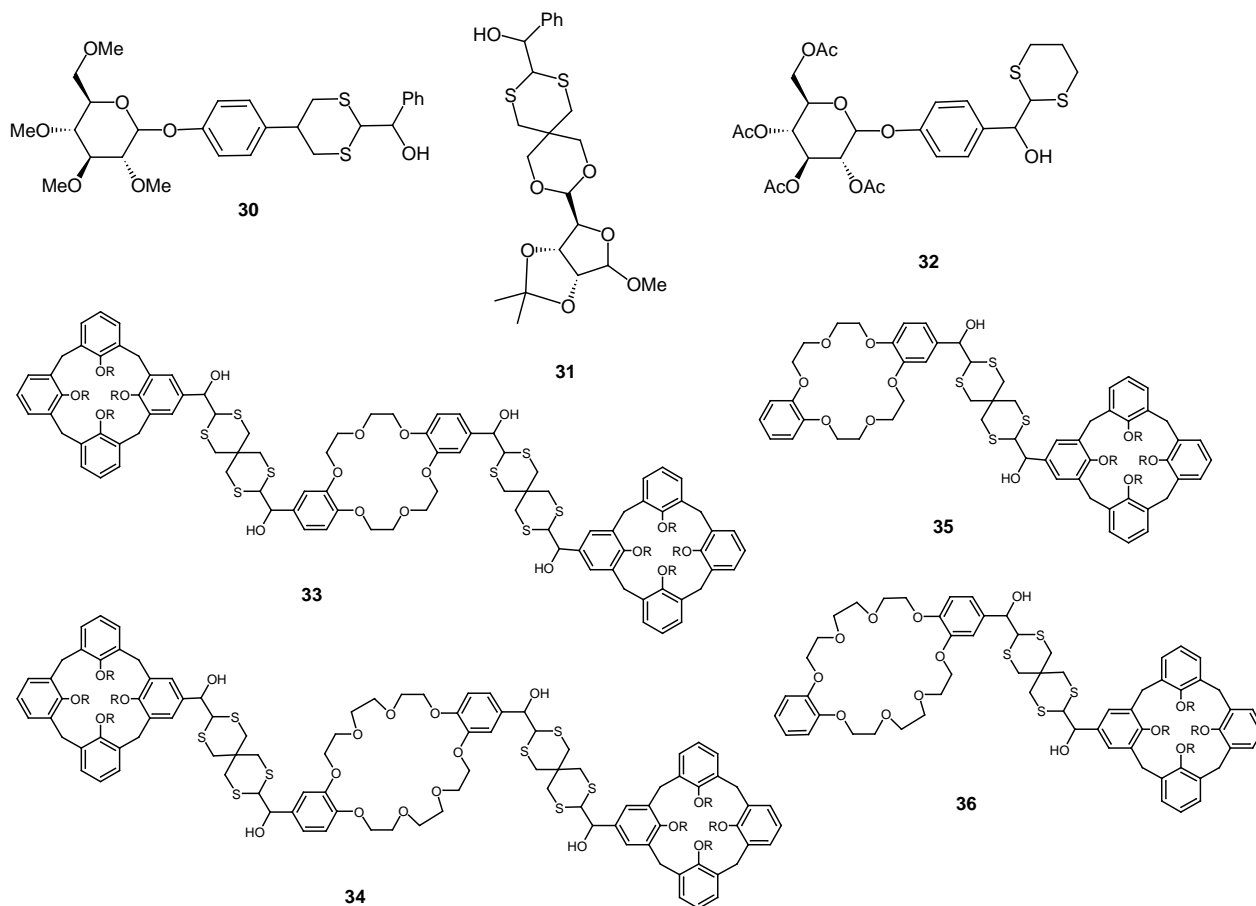


Figure 7 Photolabile hybrids assembled by coupling different dithiane- and formyl-bearing building blocks

MS (EI): m/z (%) = 264 (M^+ , 2), 221 (100), 191 (10), 179 (10), 131 (15), 117 (20), 99 (14), 85 (22).

2,4,8,10-Tetrathiaspiro[5.5]undecane (1)

Pentaerythrityl tetrathioacetate (**4**, 3 g, 8.15 mmol) was suspended in a formalin–HCl mixture (53 mL of 40% formalin, 8 mL of 37% HCl) and the reaction mixture was refluxed for 16 h. It was neutralized with sat. Na_2CO_3 after being cooled to r. t. The product was extracted with CH_2Cl_2 (50 mL), the organic layer was dried (MgSO_4), and concentrated. Crude product was recrystallized from a CHCl_3 –MeOH mixture. Decolorization when boiling with activated carbon in CHCl_3 –MeOH (70:30) for 1 h gave white crystals **1** (1.39 g, 76%), mp 163–164 °C.

^1H NMR (CDCl_3): δ = 3.66 (s, 4H), 2.95 (s, 8H).

^{13}C NMR (CDCl_3): δ = 38.6, 32.2, 24.9.

MS (EI): m/z (%) = 224 (M^+ , 100), 177 (30), 131 (40), 99 (60), 85 (50).

Anal. Calcd for $\text{C}_7\text{H}_{12}\text{S}_4$: C, 37.46; H, 5.39. Found: C, 37.28; H, 5.53.

5,5-Bis(hydroxymethyl)-[1,3]dithiane (2)

To a solution of 2 N HCl (20 mL) was added dithioacetate (**7**, 1 g, 3.8 mmol), and the reaction mixture was refluxed for one day. The dark oil residue was discarded. The reaction mixture was cooled, neutralized with Na_2CO_3 , then extracted with CH_2Cl_2 (4 \times 30 mL). The organic layer was dried (MgSO_4), and concentrated to give

crude product **2** (0.40 g, 59%). Recrystallization from CH_2Cl_2 afforded pure compound as white crystals, mp 100.5–101 °C.

^1H NMR (CDCl_3): δ = 3.90 (s, 4H), 3.77 (s, 1H), 3.69 (s, 2H), 2.96 (s, 1H), 2.72 (s, 4H).

^{13}C NMR (CDCl_3): δ = 67.6, 67.3, 44.4, 34.6, 33.4, 32.1.

MS (EI): m/z (%) = 180 (M^+ , 95), 115 (30), 85 (100), 71 (45), 57 (60).

Anal. Calcd for $\text{C}_6\text{H}_{12}\text{O}_2\text{S}_2$: C, 39.97; H, 6.71. Found: C, 39.72; H, 6.77.

Acetal Preparation with 2:3-Phenyl-2,4-dioxo-8,10-dithiaspiro[5.5]undecane (20); Typical Procedure

To a solution of benzaldehyde (106 mg, 1.0 mmol) and 5,5-bis(hydroxymethyl)-[1,3]dithiane (**2**, 180 mg, 1.0 mmol) in benzene (20 mL) was added toluene sulfonic acid monohydrate (20 mg). H_2O was removed by azeotrope formation during 3 h. The reaction mixture was cooled to r. t. and washed with sat. NaHCO_3 (20 mL). The aqueous layer was extracted twice with benzene (2 \times 20 mL), the organic phases were combined, dried (MgSO_4), and concentrated to give **20** (256 mg, 96%).

^1H NMR (CDCl_3): δ = 7.50–7.44 (m, 2H), 7.40–7.32 (m, 3H), 5.43 (s, 1H), 4.53 (d, 2H, J = 12 Hz), 3.70 (s, 2H), 3.66 (d, 2H, J = 12 Hz), 3.16 (s, 2H), 2.50 (s, 2H).

^{13}C NMR (CDCl_3): δ = 137.6, 128.9, 128.2, 125.9, 102.3, 73.9, 34.7, 34.6, 32.4, 28.4.

MS (EI): m/z (%) = 268 (M^+ , 100), 132 (50), 99 (55), 85 (55).

3-(6-Methoxy-2,2-dimethyl-tetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-2,4-dioxo-8,10-dithiaspiro[5.5]undecane (23)

Methyl 2,3-*O*-isopropylidene-5-aldehyde- β -D-ribofuranoside⁹ (**22**, 500 mg, 2.5 mmol), **2** (490 mg, 2.7 mmol) and TsOH·H₂O (30 mg) in benzene were reacted, as described above for **20**, to give 646 mg (72%) of **23**.

¹H NMR (CDCl₃): δ = 5.00 (s, 1H), 4.80 (d, 1H, *J* = 5 Hz), 4.53 (d, 1H, *J* = 5 Hz), 4.45 (d, 2H, *J* = 12 Hz), 4.37 (d, 1H, *J* = 8 Hz), 4.11 (d, 1H, *J* = 8 Hz), 3.67 (s, 2H), 3.42 (d, 2H, *J* = 12 Hz), 3.34 (s, 3H), 3.05 (s, 2H), 2.42 (s, 2H), 1.48 (s, 3H), 1.32 (s, 3H).

¹³C NMR (CDCl₃): δ = 112.5, 108.9, 101.2, 86.8, 84.7, 80.9, 73.3, 73.2, 54.7, 34.5, 34.4, 32.3, 28.5, 26.5, 25.2.

HRMS: *m/z* calcd for C₁₅H₂₅O₆S₂ [MH⁺]: 365.1093. Found: 365.1100.

5-(2,4-Dioxo-8,10-dithiaspiro[5.5]undec-3-yl)-2,2,7,7-tetramethyl-tetrahydro-bis[1,3]dioxolo[4,5-*b*;4',5'-*d*]pyran (25)

1,2:3,4-Di-*O*-isopropylidene-6-aldehyde- α -D-galactopyranose^{9,10} (**24**, 997 mg, 3.8 mmol), **2** (759 mg, 4.7 mmol) and TsOH·H₂O (40 mg) in benzene were reacted as described above and purified by column chromatography (silica gel; EtOAc–hexane) (620 mg, 38%).

¹H NMR (CDCl₃): δ = 5.56 (d, 1H, *J* = 5 Hz), 4.66 (d, 1H, *J* = 7 Hz), 4.60 (dd, 1H, *J* = 12, 2 Hz), 4.58 (dd, 1H, *J* = 8, 2 Hz), 4.37 (dd, 1H, *J* = 12, 2 Hz), 4.29 (dd, 1H, *J* = 5, 2 Hz), 4.27 (dd, 1H, *J* = 12, 2 Hz), 3.76–3.74 (m, 2H), 3.67 (d, 1H, *J* = 14 Hz), 3.49 (dd, 2H, *J* = 12, 8 Hz), 3.13 (d, 1H, *J* = 14 Hz), 2.96 (d, 1H, *J* = 14 Hz), 2.48 (d, 1H, *J* = 14 Hz), 2.37 (d, 1H, *J* = 14 Hz), 1.54 (s, 3H), 1.46 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H).

¹³C NMR (CDCl₃): δ = 109.2, 108.7, 100.0, 96.3, 74.0, 72.7, 70.6, 70.5, 70.3, 68.8, 34.6, 34.5, 32.4, 28.6, 26.3, 26.1, 25.0, 24.6.

HRMS: *m/z* calcd for C₁₈H₂₉O₇S₂ [MH⁺]: 421.1355. Found: 421.12998.

Dithiane–Carbonyl Adducts: Phenyl-(3-phenyl-2,4-dioxo-8,10-dithiaspiro[5.5]undeca-9-yl)methanol (21); Typical Procedure

A solution of 3-phenyl-2,4-dioxo-8,10-dithia-spiro[5.5]undecane (**20**, 244 mg, 0.91 mmol) in freshly distilled THF (10 mL) was cooled to –25 °C under N₂. Then *n*-BuLi (1.6 M solution in hexanes, 1.46 mmol, 0.91 mL) was added drop-wise with stirring. The resulting mixture was stirred for 2 h at –25 °C to complete lithiation. The resulting solution of the anion was cooled to –78 °C, and a solution of benzaldehyde (155 mg, 1.46 mmol) in THF (2 mL) was added drop-wise with stirring. The reaction mixture was stirred for 1 h at this temperature and then stored in a freezer at –25 °C overnight. It was quenched with a sat. NH₄Cl, extracted twice with Et₂O (2 × 10 mL), and the combined organic extracts were dried (MgSO₄). The solvent was then removed under reduced pressure. The residue was purified on a silica gel column (EtOAc–hexane) to give two pairs of diastereomers (270 mg, 79%).

Diastereomers 21a

¹H NMR (CDCl₃): δ = 7.50–7.30 (m, 10H), 5.40 (s, 1H), 4.86 (dd, 1H, *J* = 3, 8 Hz), 4.51 (dd, 1H, *J* = 3, 11 Hz), 4.36 (dd, 1H, *J* = 3, 11 Hz), 4.03 (d, 1H, *J* = 8 Hz), 3.65 (d, 1H, *J* = 11 Hz), 3.63 (d, 1H, *J* = 11 Hz), 3.29 (d, 1H, *J* = 14 Hz), 3.02 (d, 1H, *J* = 14 Hz), 3.02 (d, 1H, *J* = 3 Hz), 2.50 (d, 1H, *J* = 14 Hz), 2.38 (d, 1H, *J* = 14 Hz).

¹³C NMR (CDCl₃): δ = 139.7, 137.5, 128.9, 128.4, 128.19, 128.18, 126.7, 125.9, 102.2, 74.4, 73.6, 52.9, 32.5, 31.9, 28.5.

Diastereomers 21b

¹H NMR (CDCl₃): δ = 7.50–7.30 (m, 10H), 5.40 (s, 1H), 4.91 (dd, 1H, *J* = 3, 7 Hz), 4.56 (dd, 1H, *J* = 3, 12 Hz), 4.32 (dd, 1H, *J* = 3, 12 Hz), 4.08 (d, 1H, *J* = 7 Hz), 3.70 (d, 1H, *J* = 12 Hz), 3.63 (d, 1H, *J* = 12 Hz), 3.31 (d, 1H, *J* = 14 Hz), 2.99 (d, 1H, *J* = 14 Hz), 2.88 (d, 1H, *J* = 3 Hz), 2.58 (d, 1H, *J* = 14 Hz), 2.37 (d, 1H, *J* = 14 Hz).

¹³C NMR (CDCl₃): δ = 139.8, 137.5, 129.0, 128.4, 128.21, 128.18, 126.6, 125.9, 102.3, 74.7, 74.2, 73.0, 53.3, 33.1, 32.0, 28.5.

HRMS: *m/z* calcd for C₂₀H₂₃O₃S₂ [MH⁺]: 375.1089. Found: 375.1096.

[9-(Hydroxy-phenyl-methyl)-2,4,8,10-tetrathiaspiro[5.5]undec-3-yl]-phenyl-methanol (8)

2,4,8,10-Tetrathiaspiro[5.5]undecane (**1**, 64 mg, 0.30 mmol), BuLi (0.86 mmol) and benzaldehyde (91 mg, 0.86 mmol) were reacted as described above for **21**. Column chromatography yielded **8** as a mixture of diastereomers (78 mg, 63%).

¹H NMR (CDCl₃): δ = 7.42–7.28 (m, 10H), 4.88–4.81 (m, 2H), 4.03–3.96 (m, 2H), 3.12–2.62 (m, 10H).

¹³C NMR (CDCl₃): δ = 139.7, 128.4, 128.2, 126.63, 126.60, 74.5, 74.4, 53.0, 52.8, 52.7, 36.9, 36.8, 36.3, 36.0, 35.9, 35.2, 35.0, 25.3.

HRMS: *m/z* calcd for C₂₁H₂₅O₂S₄ [MH⁺]: 437.0737. Found: 437.0695.

Calixarene Bis-adduct (10)

A solution of 2,4,8,10-tetrathiaspiro[5.5]undecane (**1**, 50 mg, 0.22 mmol) in THF (10 mL) was cooled to –78 °C under N₂. Then *n*-BuLi (1.6 M solution in hexanes, 0.80 mmol, 0.50 mL) was added drop-wise with stirring. The resulting mixture was stirred for 2 h at –25 °C and reacted as described above for **21** with 5-formyl-25,26,27,28-tetrakis(2-ethoxyethoxy)calix[4]-arene⁵ (**9**, 330 mg, 0.45 mmol). After column separation, the title compound was obtained (270 mg, 71%).

¹H NMR (CDCl₃): δ = 6.70–6.42 (m, 22H), 4.52–4.39 (m, 10H), 4.18–4.04 (m, 16H), 3.93–3.87 (m, 2H), 3.86–3.80 (m, 16H), 3.57–3.49 (m, 16H), 3.18–3.06 (m, 10H), 2.90–2.57 (m, 6H), 2.02–1.92 (m, 2H), 1.25–1.15 (m, 24H).

HRMS: *m/z* calcd for C₉₇H₁₂₃O₁₇S₄ [MH – H₂O]⁺: 1687.7640. Found: 1687.7696.

Mono-adduct of 1 with Calixarene; Compound 13

A solution of **1** (430 mg, 1.92 mmol) in THF (20 mL) was treated with *n*-BuLi (1.6 M solution in hexanes, 1.92 mmol, 1.20 mL) and reacted with 5-formyl-25,26,27,28-tetrakis(2-ethoxyethoxy)calix[4]arene (370 mg, 0.5 mmol) as described above for **21**. After column separation, the title compound was obtained (416 mg, 86%).

¹H NMR (CDCl₃): δ = 6.70–6.48 (m, 11H), 4.53–4.43 (m, 5H), 4.17–4.05 (m, 8H), 3.94 (d, 1H, *J* = 7 Hz), 3.86–3.81 (m, 8H), 3.64 (s, 2H), 3.58–3.51 (m, 8H), 3.18–2.66 (m, 12H), 2.02 (s, 1H), 1.25–1.16 (m, 12H).

Anal. Calcd for C₅₂H₆₈O₉S₄: C, 64.70; H, 7.10. Found: C, 64.83; H, 7.24.

Mono-adduct of 1 with 4-formyldibenzo-18-crown-6; Compound 14

A solution of **1** (462 mg, 2.06 mmol) in THF (50 mL) was treated with *n*-BuLi (1.6 M solution in hexanes, 6.19 mmol, 3.87 mL), and reacted with 4-formyldibenzo-18-crown-6¹¹ (370 mg, 0.5 mmol) as described above for **21**. After column separation (silica gel; CHCl₃–MeOH; 19:1), the title compound was obtained (512 mg, 81%).

¹H NMR (CDCl₃): δ = 6.96–6.78 (m, 7H), 4.77 (d, 1H, *J* = 7 Hz), 4.24–4.12 (m, 8H), 4.06–3.96 (m, 9H), 3.62 (s, 2H), 3.26–2.64 (m, 9H).

¹³C NMR (CDCl₃): δ = 148.61, 148.57, 148.4, 132.8, 121.2, 119.6, 113.6, 112.7, 111.8, 74.5, 70.0, 69.9, 68.9, 68.8, 53.4, 38.8, 37.5, 37.1, 36.1, 32.0, 25.2.

HRMS: *m/z* calcd for C₂₈H₃₅O₆S₄ [MH – H₂O]⁺: 595.1317. Found: 595.1289.

Bidentate Precursor 19; Typical Procedure

A solution of **1** (1.2 g, 5.35 mmol) in freshly distilled THF (20 mL) was cooled to -78°C under N_2 . Then *n*-BuLi (1.6 M solution in hexanes, 5.76 mmol, 3.6 mL) was added drop-wise with stirring. The resulting mixture was allowed to stand for 2 h at -20°C . Then 5,17-diformyl-25,26,27,28-tetrakis(2-ethoxyethoxy)calix[4]arene⁵ (0.62 g, 0.8 mmol) was added and the reaction mixture was stirred overnight at r.t. The reaction mixture was quenched with sat. NH_4Cl , evaporated, and extracted with CHCl_3 . The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc –hexane, 2:3) to afford 0.484 g of **19** (49.7%).

Calixarenic Bidentate Precursor 19

^1H NMR (CDCl_3) δ = 6.29–6.86 (m, 10H), 4.46–4.52 (m, 4H), 4.34–4.39 (m, 2H), 4.18–4.21 (m, 4H), 4.00–4.07 (m, 4H), 3.78–3.89 (m, 10H), 3.63 (s, 2H), 3.49–3.58 (m, 8H), 2.67–3.17 (m, 20H), 2.04 (s, 2H), 1.14–1.23 (m, 12H).

Anal. Calcd for $\text{C}_{60}\text{H}_{80}\text{O}_{10}\text{S}_8$: C, 59.18; H, 6.62. Found: C, 58.77; H, 6.84.

Dibenzo-24-crown-8 based Bidentate Precursor 18

^1H NMR (CDCl_3) δ = 6.79–6.96 (m, 6H), 4.74–4.79 (m, 2H), 4.11–4.28 (m, 8H), 4.00 (d, 2H, J = 7.3 Hz), 3.86–3.90 (m, 8H), 3.79–3.82 (m, 8H), 3.64 (s, 4H), 2.73–3.09 (m, 16H), 2.00 (s, 2H).

Dibenzo-18-crown-6 based Bidentate Precursor 17

^1H NMR ($\text{DMSO}-d_6$) δ = 6.82–6.95 (m, 6H), 4.63 (d, 2H), 4.18 (d, 2H), 4.01–4.07 (m, 8H), 3.79–3.85 (m, 8H), 3.70 (s, 4H), 2.67–3.10 (m, 16H).

Adduct of 23 with Benzaldehyde; Compound 31

A solution of **23** (287 mg, 0.79 mmol), *n*-BuLi (1.6 M solution in hexanes, 1.3 mmol, 0.79 mL), and benzaldehyde (134 mg, 1.3 mmol) was reacted as described above for **21**. Purification by column chromatography produced diastereomers **31** (160 mg, 43%).

Diastereomers 31a

^1H NMR (CDCl_3) δ = 7.41–7.29 (m, 5H), 5.00 and 4.99 (two s, 1H), 4.86 (dd, 1H, J = 3, 8 Hz), 4.78 (d, 1H, J = 6 Hz), 4.52 (d, 1H, J = 6 Hz), 4.56–4.39 (m, 1H), 4.36 (d, 1H, J = 8 Hz), 4.33–4.27 (m, 1H), 4.11 (d, 1H, J = 8 Hz), 4.02 and 4.00 (two d, 1H, J = 7 Hz), 3.41 (dd, 2H, J = 8, 12 Hz), 3.33 and 3.32 (two s, 3H), 3.20 (dd, 1H, J = 3, 15 Hz), 3.00 (dd, 1H, J = 3, 7 Hz), 2.93 (d, 1H, J = 15 Hz), 2.43 (dd, 1H, J = 4, 14 Hz), 2.31 (dd, 1H, J = 8, 14 Hz), 1.48 (s, 3H), 1.31 (s, 3H).

^{13}C NMR (CDCl_3) δ = 139.8, 128.4, 128.2, 126.69, 126.66, 112.57, 112.56, 109.0, 108.9, 101.2, 86.84, 86.80, 84.7, 80.9, 74.5, 74.4, 73.1, 73.0, 72.9, 54.73, 54.70, 53.0, 52.8, 32.5, 32.3, 31.9, 31.8, 28.7, 26.5, 25.2.

Diastereomers 31b

^1H NMR (CDCl_3) δ = 7.42–7.30 (m, 5H), 4.991 and 4.985 (two s, 1H), 4.89 (dd, 1H, J = 3, 7 Hz), 4.80–4.76 (m, 1H), 4.52 (d, 1H, J = 6 Hz), 4.50–4.45 (m, 1H), 4.36 (d, 1H, J = 7 Hz), 4.28–4.23 (m, 1H), 4.10–4.03 (m, 2H), 3.47 (d, 1H, J = 12 Hz), 3.40 (d, 1H, J = 12 Hz), 3.334 and 3.325 (two s, 3H), 3.20 (dd, 1H, J = 4, 14 Hz), 2.90 (d, 1H, J = 14 Hz), 2.84 (dd, 1H, J = 3, 7 Hz), 2.50 (dd, 1H, J = 6, 14 Hz), 2.30 (dd, 1H, J = 6, 14 Hz), 1.47 (s, 3H), 1.31 and 1.30 (two s, 3H).

^{13}C NMR (CDCl_3) δ = 139.8, 128.4, 128.2, 126.64, 126.59, 112.6, 109.00, 108.97, 101.28, 101.25, 86.84, 86.82, 84.8, 80.94, 80.93, 74.7, 74.6, 73.7, 73.6, 72.5, 72.4, 54.8, 54.7, 53.4, 53.2, 33.0, 32.9, 32.0, 31.8, 28.7, 26.6, 25.2.

HRMS: m/z calcd for $\text{C}_{22}\text{H}_{29}\text{O}_6\text{S}_2$ [$\text{MH} - \text{H}_2\text{O}$]⁺: 453.1406. Found: 453.1406.

2-(4-[1,3]Dithian-5-yl-phenoxy)-6-methoxymethyl-3,4,5-trimethoxy-tetrahydropyran (28)

To a stirred solution of 2,3,4,6-tetra-*O*-methyl-D-glucopyranose **26**¹² (400 mg, 1.69 mmol) and 4-[1,3]dithian-5-yl-phenol (**27**, 358 mg, 1.69 mmol) in THF (6 mL) at 0°C were added Ph_3P (443 mg, 1.69 mmol) and a solution of diethyl azodicarboxylate (294 mg, 1.69 mmol) in THF (3 mL). The mixture was stirred at r.t. overnight. It was concentrated and the product was isolated by column chromatography to afford **28** (510 mg, 70%).

^1H NMR (CDCl_3): δ = 7.09 (d, 2H, J = 8 Hz), 6.97 (d, 2H, J = 8 Hz), 4.80 (d, 1H, J = 7 Hz), 4.09 (d, 1H, J = 14 Hz), 3.67–3.64 (m, 1H), 3.65 (s, 3H), 3.64 (s, 3H), 3.59–3.55 (m, 1H), 3.55 (s, 3H), 3.49–3.39 (m, 2H), 3.38 (s, 3H), 3.30–3.20 (m, 3H), 3.16–3.08 (m, 1H), 3.05–2.95 (m, 2H), 2.82–2.75 (m, 2H).

^{13}C NMR (CDCl_3): δ = 156.1, 139.2, 127.4, 116.8, 101.2, 86.2, 83.3, 79.0, 74.7, 71.1, 60.9, 60.5, 60.4, 59.3, 43.1, 35.9, 35.8, 31.1.

Adduct of 28 with Benzaldehyde; Compound 30

A solution of glycoside **28** (190 mg, 0.44 mmol), *n*-BuLi (1.6 M solution in hexanes, 0.71 mmol, 0.44 mL), and benzaldehyde (75 mg, 0.71 mmol) was reacted as described above for **21**. The product was purified by column chromatography. (76 mg, 32%).

^1H NMR (CDCl_3): δ = 7.46–7.32 (m, 5H), 7.07 (d, 2H, J = 8 Hz), 6.95 (d, 2H, J = 8 Hz), 4.91 (dd, 1H, J = 4, 7 Hz), 4.77 (d, 1H, J = 6 Hz), 4.48 (d, 1H, J = 6 Hz), 3.65–3.63 (m, 1H), 3.64 (s, 3H), 3.63 (s, 3H), 3.58–3.54 (m, 1H), 3.54 (s, 3H), 3.40–3.37 (m, 1H), 3.37 (s, 3H), 3.28–3.18 (m, 3H), 3.07–2.94 (m, 3H), 2.90–2.80 (m, 2H), 2.72 (d, 1H, J = 4 Hz).

^{13}C NMR (CDCl_3): δ = 156.2, 139.9, 138.4, 128.4, 128.2, 127.5, 126.3, 116.9, 101.3, 86.3, 83.4, 79.1, 75.8, 74.8, 71.2, 60.9, 60.6, 60.5, 59.4, 54.9, 42.6, 36.6, 36.2.

HRMS: m/z calcd for $\text{C}_{27}\text{H}_{35}\text{O}_6\text{S}_2$ [$\text{MH} - \text{H}_2\text{O}$]⁺: 519.1875. Found: 519.1856.

Adduct of 29 with Dithiane; Compound 32

A solution of 1,3-dithiane (100 mg, 0.83 mmol) in THF (15 mL) was cooled to -25°C under N_2 . Then *n*-BuLi (1.6 M solution in hexanes, 1.0 mmol, 0.63 mL) was added drop-wise with stirring. The resulting mixture was stirred for 2 h at -25°C . It was then added slowly into a solution of 4-*O*-[tetra-*O*-acetyl- β -D-glucopyranosyl]benzaldehyde **29**¹³ (377 mg, 0.83 mmol) in THF (20 mL) at -78°C with vigorous stirring. The reaction mixture was stirred for 1 h at this temperature and then stored in a freezer at -25°C overnight. The work-up procedure was the same as for **21**. The product was purified by column chromatography (250 mg, 52%).

^1H NMR (CDCl_3): δ = 7.35 (d, 2H, J = 9 Hz), 6.98 (d, 2H, J = 9 Hz), 5.32–5.23 (m, 2H), 5.16 (m, 1H), 5.09 (dd, 1H, J = 3, 6 Hz), 4.88 (d, 1H, J = 6 Hz), 4.27 (dd, 1H, J = 6, 12 Hz), 4.16 (d, 1H, J = 12 Hz), 4.04 (dd, 1H, J = 3, 8 Hz), 3.89–3.82 (m, 1H), 3.02–2.88 (m, 2H), 2.78–2.68 (m, 2H), 2.05–1.95 (m, 2H), 2.08 (s, 3H), 2.051 (s, 3H), 2.046 (s, 3H), 2.03 (s, 3H).

^{13}C NMR (CDCl_3): δ = 170.3, 170.0, 169.1, 169.0, 156.6, 134.9, 128.0, 116.53, 116.50, 98.9, 98.8, 74.13, 74.07, 72.7, 72.1, 71.1, 68.3, 62.0, 52.9, 28.3, 27.7, 25.4, 20.84, 20.78, 20.74, 20.72.

HRMS: m/z calcd for $\text{C}_{25}\text{H}_{33}\text{O}_{11}\text{S}_2$ [MH^+]: 573.1464. Found: 573.1441.

Monoadduct of 1 with 4-Formyldibenzo-24-crown-8; Compound 15

A solution of **1** (611 mg, 2.73 mmol) in THF (50 mL) was treated with *n*-BuLi (1.6 M solution in hexanes, 3.27 mmol, 2.04 mL) and reacted with 4-formyldibenzo-24-crown-8¹⁴ (1 g, 2.1 mmol in 25 mL of THF) as described above for **21**. The reaction mixture was quenched with sat. NH_4Cl and extracted twice with Et_2O (2×10

mL). The combined organic extracts were dried (MgSO_4), and the solvent was then removed under vacuum. The residue was purified by column chromatography (gradient elution with CHCl_3 – CH_3OH , 100:0 to 95:5) to give **15** (1.1 g, 68%).

^1H NMR (CDCl_3): δ = 6.98–6.78 (m, 7H), 4.76 (dd, 1H, J = 3.0, 7.54 Hz), 4.21–4.09 (m, 8H), 4.00 (d, 1H, J = 7.8 Hz), 3.94–3.87 (m, 8H), 3.85–3.79 (m, 8H), 3.66–3.59 (s, 2H), 3.11–2.68 (m, 8H).

HRMS: m/z calcd for $\text{C}_{32}\text{H}_{43}\text{O}_8\text{S}_4$ [$\text{MH} - \text{H}_2\text{O}$] $^+$ 683.1841. Found: 683.1840.

Monoadduct of **1** with 3-Formylbenzo-18-crown-6;¹⁵

Compound 16

Yield = 94%.

^1H NMR (CDCl_3): δ = 6.82–7.02 (m, 3H), 5.00–5.08 (m, 1H), 4.31–4.46 (m, 3H), 4.12–4.21 (m, 2H), 3.91–4.05 (m, 2H), 3.83–3.90 (m, 3H), 3.57–3.78 (m, 14H), 2.59–3.10 (m, 8H).

Bis-adduct of **1** with 4-Formyldibenzo-24-crown-8; Compound 11

A solution of **1** (353 mg, 1.57 mmol) in THF (50 mL) was treated with *n*-BuLi (1.6 M solution in hexanes, 3.78 mmol, 2.4 mL) and reacted with 4-formyldibenzo-24-crown-8¹⁴ (1.6 g, 3.36 mmol in 25 mL of THF) as described above for **21**. The reaction mixture was quenched with sat. NH_4Cl and extracted twice with Et_2O (2×10 mL). The combined organic extracts were dried (MgSO_4), and the solvent was then removed under vacuum. The residue was purified by column chromatography (gradient elution with CHCl_3 – CH_3OH , 100:0 to 97:3) to give **11** (1.2 g, 61%).

^1H NMR (CDCl_3): δ = 7.04–6.78 (m, 14H), 4.86–4.74 (m, 2H), 4.24–4.06 (m, 16H), 4.04–3.96 (m, 2H), 3.96–3.70 (m, 32H), 3.15–2.58 (m, 8H).

HRMS (characterized in a form of mono-sodium molecular ion): m/z calcd for $\text{C}_{57}\text{H}_{76}\text{O}_{18}\text{S}_4\text{Na}$ [MNa^+]: 1199.3812. Found: 1199.3856.

Bis-adduct of **1** with Benzo-18-crown-6; Compound 12

Yield = 46%.

^1H NMR (CDCl_3): δ = 6.81–7.01 (m, 6H), 5.00–5.09 (m, 2H), 4.25–4.48 (m, 6H), 4.12–4.19 (m, 4H), 3.57–4.02 (m, 34H), 2.56–3.24 (m, 8H).

HRMS (characterized in a form of mono-sodium molecular ion): m/z calcd for $\text{C}_{41}\text{H}_{60}\text{O}_{14}\text{S}_4\text{Na}$ [MNa^+]: 927.2764. Found: 927.2732.

Calixarene Adduct with 4-Formyl-dibenzo-18-crown-6:

Compound 35; Typical Procedure

A solution of **9** (387 mg, 0.4 mmol) in freshly distilled THF (20 mL) was cooled to -78°C under N_2 . *n*-BuLi (1.6 M solution in hexanes, 0.88 mmol, 0.55 mL) was added drop-wise with stirring. The resulting mixture was allowed to stand for 2 h at -20°C . 4-Formyldibenzo-18-crown-6 (105 mg, 0.27 mmol) was added and reaction mixture was stirred at r.t. overnight. The reaction mixture was quenched with sat. NH_4Cl , concentrated by evaporation, and extracted with CHCl_3 . The solvent was removed in vacuum and the residue was purified by column chromatography, eluting first with CHCl_3 – MeCN (1:1) to remove starting materials and then with CHCl_3 – MeOH (98:2) to afford **35** (198 mg, 54%).

^1H NMR (CDCl_3): δ = 6.93–6.80 (m, 7H), 6.70–6.45 (m, 11H), 4.80–4.74 (m, 1H), 4.52–4.46 (m, 4H), 4.45–4.41 (m, 1H), 4.20–

4.00 (m, 24H), 4.00–3.95 (m, 1H), 3.94–3.87 (m, 1H), 3.84–3.80 (m, 8H), 3.57–3.49 (m, 8H), 3.18–2.60 (m, 12H), 2.00–1.94 (m, 1H), 1.17–1.28 (m, 12H).

MS [MNa^+]: m/z = 1374.9, 1375.9, 1376.9 (in agreement with isotope pattern calculated for $\text{C}_{73}\text{H}_{92}\text{O}_{16}\text{S}_4\text{Na}$: m/z = 1374.5, 1375.5, 1376.5).

Calixarene Adduct with 4-Formyl-dibenzo-24-crown-8;

Compound 36

Yield = 58%.

^1H NMR (CDCl_3): δ = 6.93–6.80 (m, 7H), 6.70–6.45 (m, 11H), 4.80–4.73 (m, 1H), 4.52–4.45 (m, 4H), 4.45–4.42 (m, 1H), 4.18–4.04 (m, 16H), 4.02–3.94 (m, 1H), 3.93–3.88 (m, 9H), 3.86–3.80 (m, 16H), 3.57–3.49 (m, 8H), 3.18–2.60 (m, 12H), 1.98–1.92 (m, 1H), 1.28–1.17 (m, 12H).

MS [MNa^+]: m/z = 1462.9, 1463.9, 1464.9 (in agreement with isotope pattern calculated for $\text{C}_{77}\text{H}_{100}\text{O}_{18}\text{S}_4\text{Na}$: m/z = 1462.6, 1463.6, 1464.6).

Bis-Calixarene Adduct with 4,4'-Diformyldibenzo-18-crown-6;

Compound 33

Yield = 18%.

^1H NMR (CDCl_3): δ = 6.91–6.78 (m, 6H), 6.70–6.45 (m, 22H), 4.80–4.73 (m, 2H), 4.52–4.45 (m, 8H), 4.19–3.94 (m, 34H), 3.93–3.85 (m, 2H), 3.84–3.79 (m, 16H), 3.56–3.49 (m, 16H), 3.19–2.60 (m, 24H), 2.02–1.95 (m, 2H), 1.28–1.17 (m, 24H).

MS [MNa^+]: m/z = 2367.5, 2368.5, 2369.5, 2370.5 (in agreement with isotope pattern calculated for $\text{C}_{126}\text{H}_{160}\text{O}_{26}\text{S}_8\text{Na}$: m/z = 2367.9, 2368.9, 2369.9, 2370.9).

Bis-Calixarene Adduct with 4,4'-Diformyldibenzo-24-crown-8;

Bis-adduct 34

Yield = 27%.

^1H NMR (CDCl_3): δ = 6.92–6.78 (m, 6H), 6.70–6.46 (m, 22H), 4.78–4.72 (m, 2H), 4.52–4.45 (m, 8H), 4.45–4.41 (m, 2H), 4.18–4.02 (m, 24H), 4.00–3.95 (m, 2H), 3.93–3.87 (m, 10H), 3.86–3.79 (m, 24H), 3.57–3.48 (m, 16H), 3.19–2.60 (m, 24H), 2.01–1.96 (m, 2H), 1.25–1.17 (m, 24H).

MS [MNa^+]: m/z = 2454.9, 2455.9, 2456.9, 2457.9, 2458.9 (in agreement with isotope pattern calculated for $\text{C}_{130}\text{H}_{167}\text{O}_{28}\text{S}_8\text{Na}$: m/z = 2454.9, 2455.9, 2456.9, 2457.9, 2458.9).

Photofragmentation; Typical Procedure

A solution of the appropriate α -hydroxyalkyl-1,3-dithiane, for example, [9-(hydroxy-phenyl-methyl)-2,4,8,10-tetrathiaspiro[5,5]undec-3-yl]-phenyl-methanol (**8**, 8 mg, 0.02 mmol) and benzophenone (7 mg, 0.04 mmol), in CD_3CN (0.6 mL) was degassed by four freeze-pump-thaw cycles and sealed in a Pyrex NMR tube. Irradiations were carried out in a carousel Rayonet photoreactor, with reaction progress monitored by NMR by disappearance of the starting material and appearance of the aldehyde signal. After 1 h of irradiation the conversion was about 80%.

Acknowledgement

Support of this research by the National Science Foundation (Career Award CHE-9876389) is gratefully acknowledged.

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