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Synthesis of High Refractive Spiroheterocyclic Derivatives Through Thioacetalization of Multi-Carbonyl Compounds

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Preparation of several new spirocyclic mercapto derivatives is described. Thiol protection on multi-carbonyl compounds allows of high sulfur content necessary to induce high refractive index. Condensation of 1,3-dimercapto-2-propanol and cyclohexanone followed by successive oxidation and thioacetalization affords a dispirocycle with four sulfurs. Selective *S,S*-protection of cyclohexane-1,4-dione is achieved with 1,3-dimercapto-2-propanol and 2,3-dimercapto-1-propanol to provide dispirocycles with four sulfurs. Olefine-oxidation of norbornene gives a useful dialdehyde intermediate which is transformed to 1,3-dithiolane for a linearly-bound-cyclic molecule. Refractive index of linearly-bound-cycles was below 1.60 and dispirocycles exhibited high refractive index of 1.57-1.69.

Key Words : Spiro heterocycle, High refractive index, 1,3-Dithiolane, Polyacrylate film, Dispirocycle

Introduction

Protection and deprotection of reactive functional groups are essential steps in the synthesis of polyfunctional compounds.[1] The carbonyl protection using SH often competes with nucleophilic reactions[2] and SH group is sensitive to the oxidation by dimerization and *S*-oxide formation.[1,3] 1,3-Dithiocyclic molecule (*S,S*-acetal) form an important class of carbonyl protection and unlike oxygen containing analogues, it is hydrolytically stable and tolerant to a wide pH range.[1] For example, intermediate thioacetals in the natural product synthesis[3,4] were quite stable under basic and acidic conditions.[5]

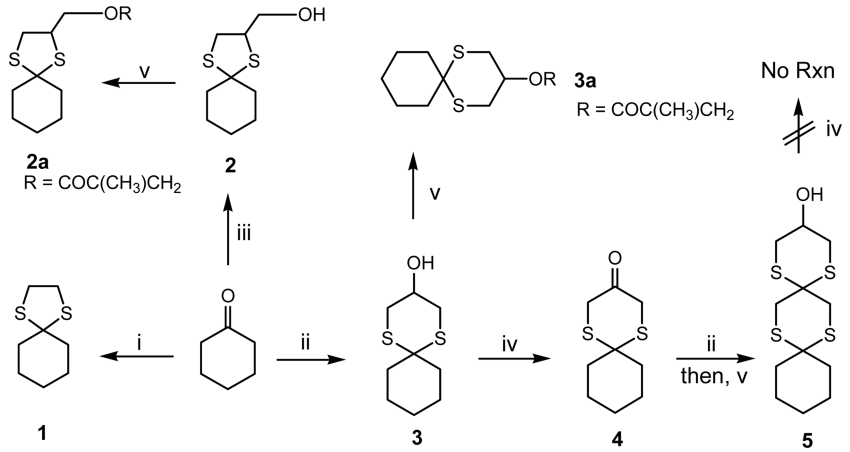
The *S,S*-acetals are also utilized as a reactive methylene anion[6] or masked methylene functions in carbon-carbon bond formation.[7] Generally, they are prepared through the condensation reaction of carbonyl compounds with thiols or dithiols in the presence of cyatalytic Lewis acid such as iodine,[8] *p*-toluenesulfonic acid (*p*-TsOH),[9] BF_3OEt_2,[10] TMSOTf[11] and $Sc(OTf)_3$.[12]

On the other hand, sulfur attached molecules have been considered as a raw material in the optical field requiring high refractive index.[13] The refractive index was controlled with a sulfur content in the material. Alkyl sulfur bonds are optically stable and transparent and thus suitable for lenses, prism, anti-refraction coating, and optical wave guide applications.[14] The refractive index is closely related with a material density because it is resulted from field interaction between a light and induced electric field of materials. A cyclic molecular structure has less molar volume than acyclic structure and it serves a high density. Thus, cyclic thio-acetals were considered for the high refractive index. The carbonyl protection with two sulfurs is valuable for a high refractive index as well as synthetic stability.

Results and Discussion

In the course of our continuous research[15] for the sulfur containing acrylates, a spirocyclic alcohol was considered. Thiol-protection of multi-carbonyl compounds affords the spirocyclic structure allowing of high sulfur content in a molecule. To begin with, cyclohexanone was converted to 1,4-dithiaspiro[4.5]decane (**1**) by treatment with 1,2-ethane-dithiol in refluxing benzene containing *p*-TsOH. Under the same condition, alcohol derivatives (**2**-**3**) were predominantly formed through selective *S,S*-cyclization with 1,3- and 2,3-dimercaptopropanols. Competitive *O,S*-cyclization was not detected as shown in Scheme 1. 1,3-Dimercapto-2-propanol was prepared through a reductive cleavage of a S-S bonded polymeric mixture which was preformed from 1,3-dichloro-2-propanol and disodium disulfide.[16] The oxidation of alcohol **3** was carried out with oxalyl chloride, DMSO, and TEA at −78 °C.[17] The ketone **4** was isolated in a 68% yield and IR spectrum indicated the formation of a carbonyl group with strong absorption. The carbonyl protection of compound **4** with 1,3-dimercapto-2-propanol afforded dispirocyclic alcohol **5** in 48% yield. Further oxidation of **5** did not occur due to its low solubility in the oxidation condition and starting material **5** was recovered unchanged. Acrylic derivation of alcohols **2** and **5** was performed with methacrylic anhydride to give **2a** and **3a** in 75 and 90% yields, respectively, which would be a useful monomer for the transparent optical polymer film with high refractive index.

For a convenient synthesis of dispirocycles, a multiple protection of cyclic diketones was considered. Cyclohexane-1,4-dione was treated with two equivalents of 1,2-ethane-dithiol in the presence of *p*-TsOH for 6 hrs in refluxing benzene to give dispirocycle (Scheme 2). Similar conversion

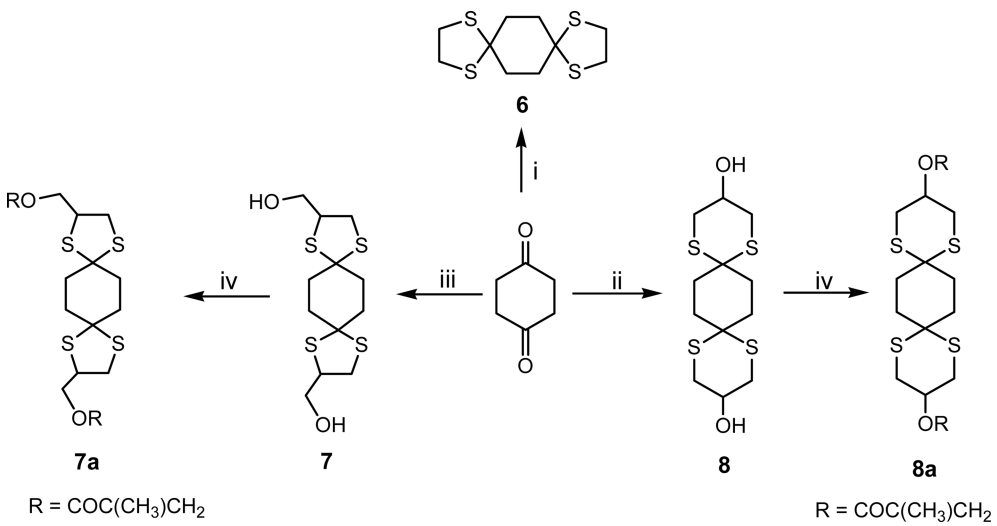


Scheme 1. Synthesis of spirocyclic derivatives. *Reagents and conditions:* (i) 1,2-ethanedithiol, *p*-TsOH, refluxing benzene, 1 h, 86%; (ii) 1,3-dimercapto-2-propanol, *p*-TsOH, refluxing benzene, 3-4 h, 78%; (iii) 2,3-dimercapto-1-propanol, *p*-TsOH, refluxing benzene, 3 h, 65%; (iv) oxalyl chloride/DMSO/TEA, CH_2Cl_2, 78 °C, 2 h; (v) methacrylic anhydride, TEA, CH_2Cl_2, rt, 5 h.

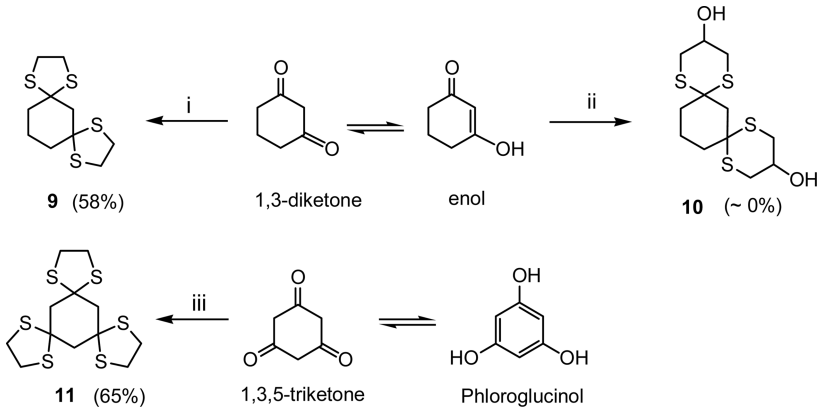
of the 1,4-diketone was achieved with 2,3-dimercapto-1-propanol and 1,3-dimercapto-2-propanol to give alcohols **7** and **8**, respectively, as isomeric mixture in a moderate yield of 40-50%. The conversion yield was not enhanced above 50% due to the formation of unknown insoluble precipitate during the reaction. The reaction was testified with various catalysts such as iodine, BF_3OEt_2 and TMSOTf under several solvents and temperature conditions. The unknown white precipitation was observed at all attempts with no progress. Reaction of cyclohexane-1,4-dione with 2-trimethylsilanyloxy-1,3-bistrimethyl-silanylsulfanylpropane, which was prepared by reaction of 2,3-dimercapto-1-propanol with TMSCl, in the presence of TMSOTf or BF_3OEt_2 at −50 ºC followed by deprotection of TMS group with aqueous K_2CO_3 afforded **7** in 39% yield. The further oxidation of **8** failed to generate a diketone analogue due to its low solubility in the oxidation condition. Starting material **8** was recovered together with a trace amount of partially oxidized product after reaction. Acrylation of compound **7** and **8** yielded methacrylic derivatives **7a** and **8a** in 65 and 78% yields, respectively, which would be useful monomer for UV-curable thin film application.[18]

The above synthetic approach was applied to the transformation of cyclohexane-1,3-dione, which is in equilibrium of an enol tautomer.[19] The reaction did not give any cyclized product **10**, even though it was completely consumed to generate an unknown precipitate. The similar reaction with 1,2-ethanedithiol formed dispirocycle **9** in 58% yield without any precipitation as shown in Scheme 3. Reaction of 1,3,5-cyclohexanetrione of a phloroglucin tautomer[20] with 1,2-ethanedithiol formed a trispirocycle in the presence of catalytic BF_3OEt_2. The symmetric molecule **11** was isolated as a solid and exhibited low solubility in common organic solvents.

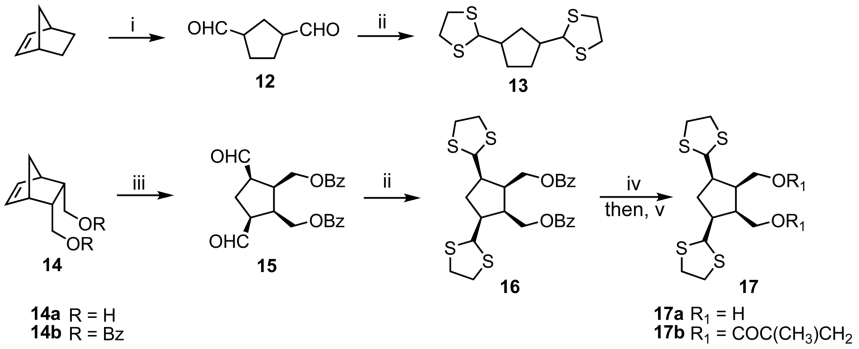
On the basis of the above results, our attention was focused on the construction of multicyclic acetals. Dialdehyde **12** was prepared from $KMnO_4$ oxidation of norbornene.[21] *cis*-Configuration was isomerized under the metallic oxidant



Scheme 2. Synthesis of dispiroheterocycles. *Reagents and conditions:* (i) 1,2-ethanedithiol, *p*-TsOH, refluxing benzene, 6 h, 98%; (ii) 1,3-dimercapto-2-propanol, *p*-TsOH, refluxing benzene, 6 h, 45%; (iii) TMS-protected 2,3-dimercapto-1-propanol, TMSOTf or BF_3OEt_2, THF, 3 h; (iv) methacrylic anhydride, TEA, CH_2Cl_2, 5 h.



Scheme 3. Synthesis of di- and trispirocyclic derivatives. *Reagents and conditions:* (i) 1,2-ethanedithiol, *p*-TsOH, refluxing benzene, 2 h; (ii) 1,3-dimercapto-2-propanol, PTSA, refluxing benzene, 6 h; (iii) 1,2-ethanedithiol, BF_3OEt_2, refluxing acetic acid, 10 h.



Scheme 4. Synthesis of multicyclic acetal derivatives. *Reagents and conditions:* (i) $KMnO_4/CuSO_4$-$5H_2O$, CH_2Cl_2/^{t}BuOH, 42%; (ii) 1,2-ethanedithiol, *p*-TsOH, refluxing benzene, 2 h, 80-85%; for **14b** from **14a**, benzoyl chloride, TEA, CH_2Cl_2, 5 h, 82%; (iii) O_3, CH_2Cl_2/MeOH (1:1, v/v), 78 °C/2 h, then Me_2S, rt/5 h, 75%; (iv) KOH, THF/MeOH (1:1), 1 h, 92% (**17a**); (v) methacrylic anhydride, TEA, CH_2Cl_2, rt, 3 h (**17b**).

and condensed with 1,2-ethanedithiol to yield a linearly-bound-cyclic molecule **13**. *cis*-Dialdehyde **15** was prepared by ozonolysis[2] of **14b** to maintain *cis*-configuration. Bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic anhydride was treated with lithium aluminum hydride followed by protection of alcohol group with benzoyl chloride to give **14b**. After the condensation of **15** with 1,2-ethanedithiol, alcohol group for **17a** was regenerated by a cleavage of benzoyl group in 92% yield. Methacrylate **17b** was prepared by reaction of **17a** with methacrylic anhydride in 78% yield for UV-curable polymer.[18] Scheme 4 shows the synthesis of multicyclic thioacetal from norborene derivatives.

Diacrylates were irradiated with UV light for polymer films. Polymerization was accelerated by using photoinitiator (IRG 819). Refractive index of the polymer films was measured using Abbe refractometer. Table 1 summarizes refractive index of polymer films and several cyclic thioacetals. Refractive index of dispirocyclic thioacetal **8** is evidently higher than spirocyclic thioacetal **3**. The spirocycles exhibited higher refractive index than linearly-bound-cyclic thioacetal.

Summary

Several useful spiroheterocyclic derivatives were prepared by 1,2- or 1,3-dithiol protection of ketones and aldehydes. Selective *S,S*-protection of cyclohexane-1,4-dione was achieved with 1,3-dimercapto-2-propanol and 2,3-dimercapto-1-propanol. A tricyclic diacrylate was conveniently synthesized from norbornene derivative. The spirocycles exhibited higher refractive index than linearly-bound-cyclic thioacetal. The multicyclic structure including dithiolane is a practical synthetic approach for high sulfur content necessary to achieve high refractive index.

Table 1. Refractive index of cyclic acetals and their polymer films

Sample[a]	**3**	**3a**	**6**	**8**	**8a**[b]	**13**	**17a**	**17b**[b]
λ = 486 nm	1.583	1.573	-	1.652	-	1.608	1.612	1.615
λ = 589 nm	1.574	1.561	1.688	1.641	1.645	1.595	1.597	1.599

[a]Refractive indices were measured using Abbe refractometer and calculated from cyclohexanone solutions. [b]UV-cured polyacrylate films

Experimental Section

General. All reagents were purchased from Sigma-Aldrich Chemical Co. and the reagent-grade solvents were dried when necessary and purified by vacuum distillation. Column chromatography was performed using silica gel (Merck, 250-430 mesh). ^{1}H-NMR spectroscopy experiments (Bruker AM-300 spectrometer) using tetramethylsilane (TMS; δ 0) as internal standard. A MAGNA-IR 750 spectrometer (Nicolet Instrument Co., USA) recorded the FT-IR spectra. The mass spectra were recorded on an Agilent 1200LC/1100 MSD SL mass spectrometer.

Preparation of the Spirocyclic Acetal Derivative. To a flask charged with a carbonyl compounds (1.0 mmol) in benzene were successively added thiol reagents (1.1 or 2.2 mmol) and catalytic amount of *p*-toluenesulfonic acid. The reaction mixture was refluxed using Dean-Stark apparatus. The reaction was monitored by TLC and upon completion the reaction mixture was extracted with ethyl acetate, washed with water and brine and dried over anhydrous $MgSO_4$. The concentrated residue was subjected to column chromatography on silica gel using ethyl acetate/hexane as eluent to give a corresponding product.

Ozonolysis of 14b. A solution of norbornen derivative (**14**) (10.0 mmol, 3.62 g) in MeOH/CH_2Cl_2 (15.0 mL/15.0 mL) was kept at −78 °C and treated with excess O_3 bubble until the solution color turned to pale blue for 2 hrs. After being added dimethyl sulfide (5 mL), the mixture was stirred for 5 hrs at 25 °C. The resulting mixture was extracted with CH_2Cl_2, washed with water and dried over anhydrous $MgSO_4$. The concentrated residue was subjected to column chromatography on silica gel using ethyl acetate/hexane as eluent to give corresponding dialdehyde **15** in 75% yield.

UV-Polymerization. Diacrylate (1.0 g) was dissolved in 1,2,3-trichloropropane (2.0 mL) and mixed with Irg 819 (5.0 mg). The solution was filtered through a 0.45 μm-PTFE syringe filter and kept for 2 hrs to remove air bubble. Diacrylate solution was spin-coated on a glass plate and then illuminated with a mercury lamp for 10 min under nitrogen condition. The resulting film was baked for 5 min in the vacuum oven set at 100 °C.

Compound 1: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.18-1.24 (m, 2H), 1.48-1.59 (m, 4H), 1.99-2.09 (m, 4H), 3.20 (s, 4H); LC-MS, *m*/*z* 174.05 $[M]^+$.

Compound 2: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.26-1.39 (m, 2H), 1.30-1.78 (m, 4H), 1.82-2.11 (m, 5H), 3.31 (m, 2H), 3.65 (m, 1H), 3.75 (m, 1H), 3.92(m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.5, 25.9, 33.7, 35.3, 37.2, 37.6, 52.5, 58.4; IR (KBr): ν_{max} 3351 (br), 2925, 2853, 1448, 1001, 768 cm^{-1}; LC-MS, *m*/*z* 205.07 $[M+1]^+$.

Compound 2a: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.38 (m, 2H), 1.61 (m, 4H), 1.97 (s, 3H), 1.99-2.05 (m, 4H), 3.21-3.39 (m, 2H), 3.95 (m, 1H), 4.12-4.35 (m, 2H), 5.58 (s, 1H), 6.12 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.6, 25.1, 25.8, 26.9, 39.3, 42.7, 43.6, 52.5, 65.5, 69.1, 126.2, 136.2, 167.1; IR (KBr): ν_{max} 2938, 2854, 1717, 1633, 1450, 1148, 772.

Compound 3: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.40-1.52 (m, 2H), 1.57-1.71 (m, 4H), 1.88-1.809 (m, 2H), 2.02-2.13 (m, 2H), 2.68 (dd, *J* = 5 Hz, *J* = 16 Hz, 2H), 3.155 (d, *J* = 16 Hz, 2H), 3.57 (s, 0.5H), 3.59 (s, 0.5H), 3.85-3.95 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.8, 23.1, 26.0, 33.3, 38.9, 58.2; IR (KBr): ν_{max} 3416 (br), 2930, 2851, 1454, 1028 cm^{-1}; LC-MS, *m*/*z* 205.07 $[M+1]^+$.

Compound 3a: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.40-1.51 (m, 2H), 1.58-1.71 (m, 4H), 1.82 (m, 2H), 1.90 (s, 3H), 2.09-2.18 (m, 2H), 2.80-3.04 (m, 4H), 5.09-5.19 (m, 1H), 5.61 (s, 1H), 6.16 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.3, 22.9, 23.0, 25.8, 29.6, 37.0, 38.0, 70.4, 126.5, 136.8, 166.2.

Compound 4: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.40-1.47 (m, 2H), 1.51 (s, 2H), 1.60-1.78 (m, 2H), 2.01-2.18 (m, 4H), 3.42 (s, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.3, 25.2, 35.9, 40.3, 60.4; IR (KBr): ν_{max} 2945, 2862, 1717, 1449, 1223, 763.

Compound 5: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.45 (s, 2H), 1.59-1.170 (m, 4H), 1.95-2.04 (m, 4H), 2.76 (dd, *J* = 6.3 Hz, 2H), 3.08-3.12 (m, 2H), 3.09 (s, 2H), 3.29 (s, 2H), 3.40 (m, 1H), 3.98-3.95 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.9, 33.7, 35.3, 37.3, 37.6, 47.1, 52.4, 58.5; IR (KBr): ν_{max} 3402, 2921, 2859, 1438, 1402, 1033, 899, 729 cm^{-1}; LC-MS, *m*/*z* 309.07 $[M+1]^+$.

Compound 6: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.29 (s, 8H), 2.20 (s, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 38.8, 42.4, 66.5.

Compound 7(isomers)**:** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.91-2.12 (m, 8H), 2.95-3.08 (s, 2H), 3.25 (s, 2H), 3.44-3.60 (m, 2H), 3.75-3.85 (m, 2H), 4.01-4.20 (m 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 39.0, 40.0, 40.8, 53.1, 56.8, 64.3, 67.2, 72.5; IR (KBr): ν_{max} 3418, 2934, 2868, 1441, 1228, 1063; LC-MS, *m*/*z* 325.06 $[M+1]^+$.

Compound 7a: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.98 (s, 6H), 2.22-2.38 (m, 4H), 2.45-2.60 (m, 4H), 3.22-3.38 (m, 2H), 3.41-3.55 (m, 2H), 4.03-4.17 (m, 2H), 4.22-4.34 (m, 2H), 4.44-4.50 (m, 2H), 5.62 (s, 2H), 6.09 (s, 2H).

Compound 8: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.98-2.09 (m, 4H), 2.21-2.30 (m, 4H), 2.62-2.80 (m, 4H), 3.01-3.20 (m, 4H), 3.44 (d, *J* = 6.5 Hz, 1H), 3.56 (d, *J* = 6.3 Hz, 1H), 3.81-4.03 (m, 2H); IR (KBr): ν_{max} 3437(br), 2919, 2842, 1638, 1431, 1250, 1036; LC-MS, *m*/*z* 325.04 $[M+1]^+$.

Compound 8a: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.98 (s, 6H), 2.22-2.78 (m, 8H), 3.25-3.51 (m, 4H), 4.10 (m, 2H), 4.21-4.41 (m, 4H), 5.60 (s, 2H), 6.08 (s, 2H).

Compound 9: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.88-1.96 (m, 2H), 1.99-2.16 (m, 2H), 2.76-2.80 (m, 4H), 3.22-3.41 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.7, 39.1, 42.7, 54.6, 68.0; LC-MS, *m*/*z* 264.0 $[M]^+$.

Compound 11: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.68 (s, 6H), 3.28 (s, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 38.8, 54.3, 66.9.

Compound 12: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.85-1.90 (m, 4H), 1.95-2.05 (m, 1H), 2.19-2.28 (m, 1H), 2.79-2.89 (m, 2H), 9.62 (d, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.4, 40.1, 51.6, 203.3; IR (KBr): ν_{max} 2954, 2866, 2814, 2710, 1720, 1365, 1075.

Compound 13: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.44-1.50 (m, 1H), 1.58-1.65 (m, 1H), 1.82-1.89 (m, 1H), 2.03-2.12

(m, 1H), 2.19-2.28 (m, 1H), 2.64 (d, J = 6.3 Hz, 2H), 2.82 (s, 1H), 3.06-3.38 (m, 8H), 4.58 (d, J = 6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.4, 38.9, 39.3, 48.2, 59.3; LC-MS, *m/z* 278.01 $[M]^+$.

Compound 14a: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.36 (s, 2H), 2.43 (s, 2H), 2.78 (s, 2H), 3.21-3.38 (m, 2H), 3.42-3.60 (m, 2H), 4.65 (br, 2H), 6.00 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 45.2, 46.7, 50.1, 63.5, 135.0; IR (KBr): ν_{max} 3323 (br), 3057, 2964, 1748, 1434, 1049 cm^{-1}.

Compound 14b: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.41-1.63 (m, 2H), 2.78 (s, 2H), 3.02 (s, 2H), 4.15-4.28 (m, 4H), 6.30 (s, 2H), 7.40-7.56 (m, 6H), 8.01-8.08 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 41.0, 45.9, 49.4, 65.4, 128.6, 129.8, 131.9, 133.2, 135.8, 166.7; IR (KBr): ν_{max} 2983, 2894, 1708, 1603, 1454, 1323, 1268, 1117 cm^{-1}.

Compound 15: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.19-2.40 (m, 2H), 2.82-3.02 (m, 4H), 4.21-4.38 (m, 2H), 4.42-4.59 (m, 2H), 7.28-7.40 (m, 5H), 7.44-7.58 (m, 2H), 7.78-7.99 (m, 3H), 9.71 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 44.0, 52.4, 61.8, 77.0, 128.7, 129.3, 129.8, 133.5, 166.1, 201.7; IR (KBr): ν_{max} 3069, 2968, 2830, , 2728, 1714, 1272, 1105, 714 cm^{-1}.

Compound 16: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.63-1.78 (m, 2H), 2.23-2.30 (m, 2H), 2.51-2.48 (m, 4H), 2.99-3.29 (m, 8H), 4.43-4.54 (m, 2H), 4.78 (d, J = 6.5 Hz, 2H), 7.27-7.40 (m, 5H), 7.43-7.55 (m, 2H), 7.83-8.00 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.9, 31.8, 39.0, 39.3, 43.9, 48.4, 55.3, 128.6, 129.8, 129.9, 133.2, 166.5.

Compound 17a: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.38-1.51 (m, 2H), 1.96-2.22 (m, 4H), 2.98-3.28 (m, 8H), 3.61-3.78 (m, 4H), 3.82-3.99 (m, 2H), 4.63-5.98 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 34.9, 35.3, 43.4, 46.1, 59.4, 61.7; LC-MS, *m/z* 339.07 $[M+1]^+$.

Compound 17b: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.99 (s, 6H), 2.12-2.19 (m, 2H), 2.30-2.42 (m, 4H), 3.14-3.29 (m, 8H), 4.18-4.32 (m, 4H), 4.63-4.79 (m, 2H), 5.58 (s, 2H), 6.08 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.7, 34.0, 39.1, 45.6, 47.6, 57.5, 64.9, 126.2, 136.2,167.3; IR (KBr): ν_{max} 3088, 2959, 2913, 1705, 1629, 1447, 1295, 1158, 717.

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