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Functionalized Nanodiamonds Part 3: Thiolation of Tertiary/Bridgehead Alcohols[||]

Boryslav A. Tkachenko,[⊥] Natalie A. Fokina,[⊥] Lesya V. Chernish,[‡] Jeremy E. P. Dahl,[§] Shenggao Liu,[§] Robert M. K. Carlson,[§] Andrey A. Fokin,*[,⊥,‡] and Peter R. Schreiner*[,⊥]

Institut für Organische Chemie, Justus-Liebig University, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany, Department of Organic Chemistry, Kiev Polytechnic Institute, pr. Pobedy 37, 03056 Kiev, Ukraine, and MolecularDiamond Technologies, Chevron Technology Ventures LLC, 100 Chevron Way, Richmond, California 94802

aaf@xtf.ntu-kpi.kiev.ua; prs@org.chemie.uni-giessen.de

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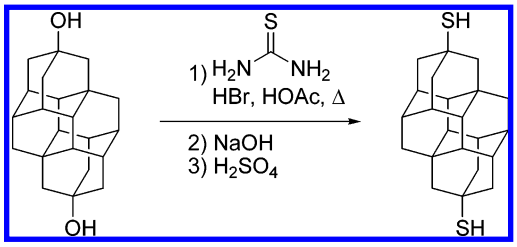
ABSTRACT



Treatment of acyclic as well as polycyclic tertiary mono- and dihydroxy hydrocarbon derivatives with thiourea in the presence of hydrobromic and acetic acid represents a convenient one-step route to the respective tertiary thiols and dithiols. This procedure was used for the preparation of diamondoid thiols of diamantane, triamantane, [121]tetramantane, and others that are prospective nanoelectronic materials.

Incorporation of thiol groups into organic molecules allows their attachment to nobel metal surfaces to form self-assembled monolayers (SAMs)[1] that have applications in molecular electronics.[2,3] Nanodiamonds functionalized with SH groups offer fascinating new possibilities for "diamond on gold" surface design in monolayer formation. The smallest nanodiamonds (also referred to as diamondoids, Figure 1), whose 1−2 nm sized carbon frameworks resemble a part of the diamond lattice, may allow more rational surface design than traditional conformationally flexible substrates.[4] Unlike

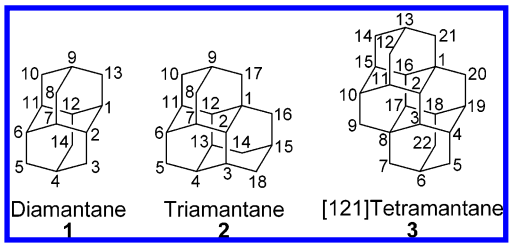


Figure 1. Structures of diamantane (**1**), triamantane (**2**), and [121]-tetramantane (**3**).

aryl[3,5] and alkyl[1] thiols that are widely utilized for the preparation of SAMs, rigid diamondoids are likely to display

[||] For parts 1 and 2, see refs 13 and 14.
[⊥] Justus-Liebig University.
[‡] Kiev Polytechnic Institute.
[§] Chevron Technology Ventures.

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unique SAM properties. The simplest thiolated diamondoid, adamantane-1-thiol, forms SAMs with fewer defects and looser bonding to the Au{111} surface than *n*-alkanethiolates.[4] Furthermore, one can achieve diversity of SAMs varying not only the three-dimensional shape of the hydrocarbon but also the position of the −SH group in the cage. This allows the preparation of coated surfaces with novel properties by varying intermolecular distance, surface structure, thickness, etc. Diamondoid dithiols are also promising building blocks for molecular conductance junctions[6] in nanoelectronic devices[7] and, because of the parallel hyperconjugated σ_{C-C} bonds, may show better conductivity than conformationally flexible *n*-alkane dithiols.[8]

Although several lower diamondoids can be prepared synthetically through elaborate multistep procedures,[9] the newly discovered natural source[10] (crude oil) makes diamantane (**1**), triamantane (**2**), and [121]tetramantane[11] (**3**) available in considerable quantities (Figure 1). Selective functionalizations of diamondoids are known[12] to be rather difficult because of the large number of tertiary C−H bonds with similar reactivity; some general approaches to solve this problem are outlined in our previous work.[13,14] Diamondoid alcohols have been chosen as starting materials for the preparation of thiols because they are readily available through the oxidations of diamondoids. Alcohols **17**−**19** and **23**−**25** (Figure 2) were prepared via oxidation with HNO_3[13,15] and **20**−**22**, **26**, and **27** through a three-step procedure that includes irradiation with diacetyl, Baeyer−Villiger oxidation of the respective acetyl derivatives to the acetates, and their base-promoted hydrolysis.[14]

Although the most obvious method for the incorporation of an SH group is the substitution of halogen or hydroxyl functions, these transformations turned out to be a difficult task for diamondoids. Despite a number of thiolation reagents widely used for *primary* and *secondary* substrates (mostly bromides), model reactions with 1-bromoadamantane (for example, involving hydrogen sulfide,[16] organolithium reagents with elemental sulfur,[17] potassium thioacetate[18] and ethyl xanthogenate,[19] sodium dimethyldithiocarbamate,[20] hydrosulfide,[21] and thiosulfate[22]) resulted in no conversion or proceeded in unsatisfactory yields of the respective adamantane-1-thiol; only the reaction with thiourea[23] gave a satisfactory yield. This is likely to be a consequence of the steric shielding of the tertiary bridgehead position that prevents the backside attack of the reagent.

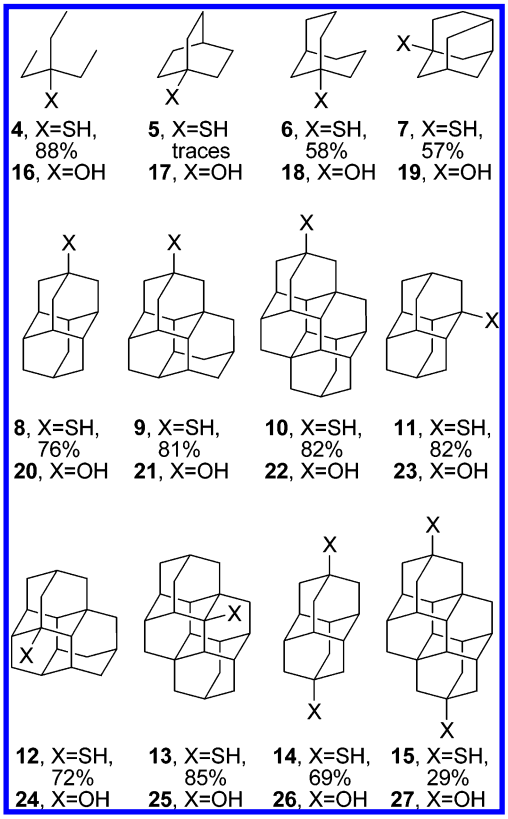

Figure 2. Selected thiols and dithiols prepared from the respective hydroxy derivatives (yields of thiols are preparative).

Condensation of the bromides in ethanol with thiourea followed by hydrolysis of the thiouronium salt intermediate under basic conditions is considered to be a good thiolation method for various bromides and is widely utilized for the preparation of primary and secondary thiols. For 1-bromoadamantane, we found that ethanol (used as the solvent) reacts with the intermediate cation to give 1-ethoxyadamantane in quantities comparable to those for the desired product. Replacing the solvent with polar aprotic DMSO, which is known to facilitate this reaction considerably for primary and secondary derivatives,[24] gave no conversion. We developed a procedure that utilizes the diamondoid alcohols

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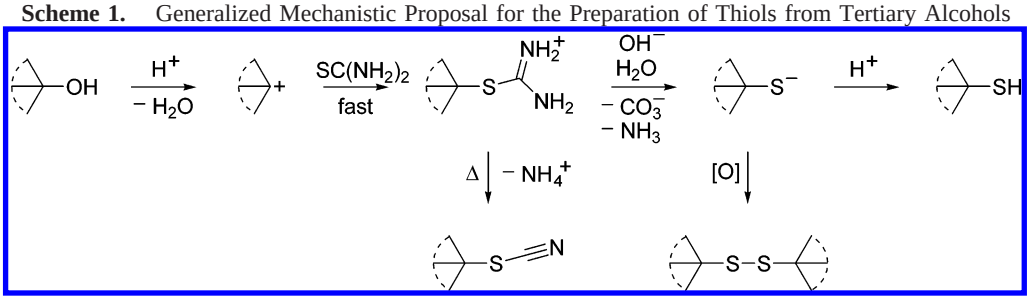
Scheme 1. Generalized Mechanistic Proposal for the Preparation of Thiols from Tertiary Alcohols



instead of the bromides (comparative reactions of bromides produced thiols in poor yields). Previous attempts to obtain adamantane-1-thiol from 1-hydroxyadamantane[25] with Lawesson's reagent {2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide} gave only 30% of the desired product. The reaction with thiourea in a CH_3COOH/HBr_{aq} mixture resulted in the direct conversion of various tertiary alcohols to the respective thiols (as generalized in Scheme 1). Workup requires some attention as disulfides (formed by air oxidation of the aqueous thiolates; Scheme 1), as well as thiocyanates (products of the thermal decomposition of the intermediate thiouronium salts), form. This makes the isolation of pure thiols somewhat tedious; this is especially critical for increasingly larger diamondoid thiols.

The use of such polar solvents implies that tertiary bridgehead carbocations form as intermediates in the course of the reaction. In our previous work,[13] we found that the diamondoid apical cations are less stable than the medial ones. For instance, the diamantyl-1-cation is 3.1 kcal mol^{-1} more stable than the diamantyl-4-cation, and one would expect the formation of mixtures of isomeric thiols, as previously found for the equilibration of 1- and 4-diamantanols in acidic media.[26] However, we did not find any isomerization products en route from the alcohols to the respective thiols (Scheme 1; see Supporting Information for details). For instance, the reaction of 4-hydroxy diamantane (**20**) produces 4-derivatives exclusively. Hence, nucleophilic trapping of the diamandoidyl cation by thiourea is faster than bimolecular exchange reactions that would give the thermodynamically most stable cation.

To probe the applicability of our method to simpler cage and acyclic alcohols, the reaction was also performed with 3-ethylpentane-3-ol (**16**), bicyclo[3.3.1]nonane-1-ol (**18**), and protoadamantane-6-ol (**19**), which all gave good yields of the respective thiols (**4**−**7**).[27] The very low yield of the thiol from bicyclo[2.2.2]octane-1-ol (**17**) can readily be explained by the instability of the respective carbocation intermediate. Thiolation of diamondoid alcohols requires longer reaction times (3 h) than for **16**, **18**, and **19**; the apical derivatives (**20**−**22**) are generally more reactive than the medial (**23**−**25**) ones (reactions complete in approximately 10 h). Incorporation of two SH groups (thiols **14** and **15**) requires longer reaction times.

Similar to the fused polyadamantane diamondoids, oligo-1,3-adamantanes also can be recognized as repeating units of the diamond lattice[28] with 1,1'-diadamantyl (**28**) being

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(27) Characterization of thiols. **3-Ethylpentane-3-thiol (4)**, yield 88%, colorless liquid. ^{1}H NMR: 1.58 (q, 6H, J = 7.4 Hz), 1.30 (s, 1H), 0.91 (t, 9H, J = 7.4 Hz). ^{13}C NMR: 52.7 (C), 32.8 (CH_2), 8.5 (CH_3). MS (*m*/*z*): 132 (16%), 103 (16%), 99 (18%), 69 (28%), 61 (30%), 57 (100%), 55 (10%). HR-MS (*m*/*z*): found, 132.0981; calcd for $C_7H_{16}S$, 132.0973. **Bicyclo[2.2.2]octane-1-thiol (5)** was not isolated. After workup, yellow oil was isolated that cointained ∼4% of the product. MS (*m*/*z*): 142 (87%), 115 (43%), 109 (100%), 86 (90%), 79 (42%), 67 (78%), 55 (18%). **Bicyclo-[3.3.1]nonane-1-thiol (6)**, yield 58%, white solid, mp = 32−35 °C. ^{1}H NMR: 2.15−1.45 (m, 16H). ^{13}C NMR: 45.8 (CH_2), 44.8 (C), 41.6 (CH_2), 30.8 (CH), 29.8 (CH_2), 23.7 (CH_2). MS (*m*/*z*): 156 (20%), 123 (100%), 113 (10%), 81 (88%), 67 (45%), 55 (17%). HR-MS (*m*/*z*): found, 156.0968; calcd for $C_9H_{16}S$, 156.0973. **Protoadamantane-6-thiol (7)**, yield 57%, white solid, mp = 36−40 °C. ^{1}H NMR: 2.35−1.25 (m, 16H). ^{13}C NMR: 50.7 (CH_2), 44.2 (C), 44.0 (CH_2), 41.0 (CH_2), 37.4 (CH_2), 36.3 (CH_2), 36.2 (CH), 36.0 (CH), 32.7 (CH), 24.7 (CH_2). MS (*m*/*z*): 168 (12%), 135 (100%), 107 (9%), 93 (23%), 79 (31%), 67 (18%), 55 (7%). HR-MS (*m*/*z*): found, 168.0970; calcd for $C_{10}H_{16}S$, 168.0973. **Diamantane-4-thiol (8)**, yield 76%, white solid, mp = 63−64 °C. ^{1}H NMR: 1.89 (m, 6H), 1.84 (bs, 3H), 1.78 (bs, 1H), 1.75−1.68 (m, 9H), 1.62 (s, 1H). ^{13}C NMR: 48.2 (CH_2), 41.6 (C), 39.3 (CH), 37.3 (CH_2), 35.9 (CH), 25.4 (CH). MS (*m*/*z*): 220 (7%), 187 (100%), 159 (1%), 145 (4%), 131 (6%), 117 (2%), 105 (6%), 91 (8%), 79 (7%), 77 (4%). HR-MS (*m*/*z*): found, 220.1264; calcd for $C_{14}H_{20}S$, 220.1286. **Triamantane-9-thiol (9)**, yield 81%, white solid, mp = 77−79 °C. ^{1}H NMR: 1.97−1.81 (m, 5H), 1.78 (bs, 2H), 1.75−1.58 (m, 11H), 1.47 (s, 2H), 1.42 (bs, 2H), 1.29 (m, 2H). ^{13}C NMR: 55.0 (CH_2), 47.9 (CH_2), 45.2 (CH), 44.7 (CH_2), 42.7 (C), 39.9 (CH), 37.8 (CH_2), 37.6 (CH_2), 37.4 (CH), 35.4 (C), 34.8 (CH), 33.6 (CH), 27.3 (CH). MS (*m*/*z*): 272 (3%), 256 (5%), 239 (100%), 197 (1%), 183 (2%), 157 (4%), 143 (10%), 129 (10%), 128 (6%), 119 (8%), 105 (11%), 91 (24%), 79 (11%), 77 (10%), 67 (7%). HR-MS (*m*/*z*): found, 272.1594; calcd for $C_{18}H_{24}S$, 272.1599. **[121]Tetramantane-6-thiol (10)**, yield 82%, white solid, mp = 109−112 °C. ^{1}H NMR: 1.88 (bs, 4H), 1.78 (bs, 2H), 1.72−1.63 (m, 8H), 1.57 (s, 2H), 1.52 (s, 2H), 1.43 (bs, 2H), 1.35 (bs, 2H), 1.30 (d, J = 2.9 Hz, 2H), 1.26 (m, 4H). ^{13}C NMR: 54.1 (CH_2), 47.8 (CH_2), 46.7 (CH), 45.7 (CH), 45.2 (CH_2), 44.9 (CH_2), 44.1 (CH_2), 42.9 (C), 39.9 (CH), 38.0 (CH), 37.8 (CH_2), 36.6 (CH), 35.3 (CH), 33.4 (C), 31.1 (C), 27.8 (CH). MS (*m*/*z*): 324 (3%), 308 (10%), 291 (100%), 169 (3%), 155 (11%), 145 (20%), 141 (8%), 129 (7%), 105 (6%), 91 (10%). HR-MS (m/z): found, 324.1897; calcd for $C_{22}H_{28}S$, 324.1912. **Diamantane-1-thiol (11)**, yield 82%, white solid, mp = 227−229 °C. ^{1}H NMR: 2.31 (d, J = 12.8 Hz, 2H), 1.97 (m, 2H), 1.90 (bs, 3H), 1.83−1.64 (m, 10H), 1.58 (s, 1H), 1.52 (d, J = 12.8 Hz, 2H). ^{13}C NMR: 51.2 (C), 50.7 (CH_2), 44.4 (CH), 39.3 (CH), 38.4 (CH_2), 37.7 (CH_2), 36.5 (CH), 34.0 (CH_2), 29.4 (CH), 25.5 (CH). MS (*m*/*z*): 220 (5%), 187 (100%), 159 (2%), 145 (3%), 131 (6%), 117 (4%), 105 (9%), 91 (14%), 79 (7%), 77 (6%). HR-MS (*m*/*z*): found, 220.1272; calcd for $C_{14}H_{20}S$, 220.1286. **Triamantane-3-thiol (12)**, yield 72%, white solid, mp = 145−146 °C. ^{1}H NMR: 2.32−2.23 (m, 2H), 2.06−1.97 (m, 2H), 1.95 (m, 1H), 1.88−1.59 (m, 11H), 1.55 (s, 1H), 1.53−1.39 (m, 3H), 1.37−1.22 (m, 4H). ^{13}C NMR: 53.4 (CH), 51.9 (C), 50.7 (CH_2), 45.8 (CH), 45.0 (CH_2), 44.9 (CH_2), 42.3 (CH), 39.6 (CH), 37.8 (CH_2), 37.7 (CH), 37.6 (CH_2), 37.6 (CH_2), 35.7 (C), 35.0 (CH), 34.6 (CH_2), 33.6 (CH), 30.3 (CH), 27.7 (CH). MS (*m*/*z*): 272 (2%), 239 (100%), 167 (9%), 143 (17%), 129 (20%), 128 (9%), 105 (10%), 91 (23%), 67 (6%). HR-MS (*m*/*z*): found, 272.1600; calcd for $C_{18}H_{24}S$, 272.1599. **[121]Tetramantane-2-thiol (13)**, yield 85%, white solid, mp = 102−105 °C. ^{1}H NMR: 2.53−2.45 (m, 2H), 1.98−1.82 (m, 5H), 1.80−1.60 (m, 10H), 1.58 (m, 1H), 1.56−1.52 (m, 2H), 1.47 (bs, 1H), 1.41 (bs, 1H), 1.39−1.23 (m, 4H), 1.10−1.03 (m, 1H), 1.00−0.94 (m, 1H). ^{13}C NMR: 60.6 (C), 55.3 (CH), 49.4 (CH), 47.5 (CH), 46.7 (CH), 45.5 (CH_2), 44.3 (CH_2), 41.3 (CH_2), 39.7 (CH_2), 39.3 (CH), 38.7 (CH_2),

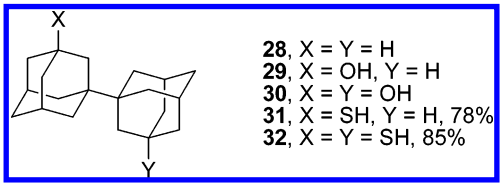

Figure 3. 1,1′-Diadamantyl **28**, its alcohols (**29**, **30**), and corresponding thiols (**31**, **32**) (yields of thiols are preparative).

the smallest representative hydrocarbon (Figure 3). Our thiolation protocol works well for both the mono- (**29**)[29] and the dihydroxy (**30**)[30] derivatives, and the corresponding monothiol (**31**) and dithiol (**32**) products were obtained in good yields.

We have developed a straightforward one-pot method for the synthesis of tertiary thiols from their corresponding alcohols. The thiolation procedure can be applied to a large range of tertiary alcohols that are able to form tertiary cations. The position and number of hydroxy groups in the diamondoid cages have a considerable influence on the reaction time. To the best of our knowledge, the method described here is the only path to nanodiamond thiols as well as to many related tertiary cage hydrocarbon thiols.

General Procedure for the Preparation of Thiols. To a stirred solution of thiourea (11.40 g, 150 mmol) in glacial acetic acid (50 mL) and 48% aqueous HBr (25 mL) was added the respective hydroxy diamondoid (1 mmol). The mixture was homogenized within about 30 min and was refluxed under argon for 3 h (in the case of alcohols **16**, **18**, **19**, **29**), 6 h (alcohols **20**−**22**, **30**), 10 h (alcohols **23**−**25**), and 48 h (alcohols **17**, **26**, **27**). The hot reaction mixture was poured in small portions into a cold (ice bath) 15% aqueous NaOH solution (600 mL) and was stirred overnight at room temperature. The resulting sodium thiolate suspension/solution was cooled (ice bath) and was acidified with 50% aqueous H_2SO_4 to pH = 2−3 while maintaining the temperature below 10 °C. The crude product was extracted with chloroform (5 × 15 mL), and the combined extracts were washed with aqueous $NaHCO_3$ solution (10 mL) and brine and dried over Na_2SO_4. Solvent removal gave the crude thiol which was purified via column chromatography on silica gel (CCl_4).

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Supporting Information Available: ^{13}C NMR spectra for compounds **4**, **6**−**15**, **31**, and **32**. This material is available free of charge via the Internet at http://pubs.acs.org.

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38.5 (CH), 38.0 (CH), 37.8 (CH_2), 37.5 (CH_2), 36.9 (CH), 35.2 (C), 34.6 (C), 34.2 (CH_2), 33.5 (CH), 27.8 (CH), 27.4 (CH). MS (*m*/*z*): 324 (1%), 291 (100%), 162 (5%), 155 (14%), 145 (8%), 141 (16%), 105 (5%), 91 (8%). HR-MS (*m*/*z*): found, 324.1905; calcd for $C_{22}H_{28}S$, 324.1912. **Diamantane-4,9-dithiol (14)**, yield 69%, white solid, mp = 211.5−214.5 °C. ^1H NMR: 1.91 (bs, 12H), 1.82 (bs, 6H), 1.65 (s, 2H). ^{13}C NMR: 47.1 (CH_2), 41.0 (C), 37.5 (CH). MS (*m*/*z*): 252 (21%), 219 (100%), 203 (3%), 185 (11%), 157 (2%), 143 (7%), 129 (7%), 105 (6%), 91 (10%). HR-MS (*m*/*z*): found, 252.1014; calcd for $C_{14}H_{20}S_2$, 252.1006. **[121]Tetramantane-6,13-dithiol (15)**, yield 29%, white solid, mp = 193−195 °C. ^1H NMR: 1.94−1.84 (m, 8H), 1.79 (bs, 4H), 1.69 (m, 2H), 1.65 (s, 2H), 1.52 (bs, 4H), 1.40 (bs, 4H), 1.30 (s, 2H), 1.29 (s, 2H). ^{13}C NMR: 53.9 (CH_2), 47.7 (CH_2), 45.1 (CH), 44.3 (CH_2), 42.6 (C), 39.8 (CH), 34.9 (CH), 33.1 (C). MS (*m*/*z*): 356 (4%), 323 (100%), 155 (3%), 145 (14%), 91 (8%). HR-MS (*m*/*z*): found, 356.1632; calcd for $C_{22}H_{28}S_2$, 356.1632. **1,1'-Diadamantane-3-thiol (31)**, yield 78%, white solid, mp = 144−145.5 °C. ^1H NMR: 2.15−2.03 (m, 2H), 2.02−1.88 (m, 4H), 1.87−1.77 (m, 3H), 1.74 (bs, 3H), 1.68 (s, 1H), 1.67−1.59 (m, 5H), 1.59−1.53 (m, 8H), 1.53−1.47 (m, 4H). ^{13}C NMR: 47.3 (CH_2), 45.8 (CH_2), 44.6 (C), 39.4 (C), 37.4 (CH_2), 36.4 (C), 35.6 (CH_2), 35.3 (CH_2), 33.6 (CH_2), 30.5 (CH), 28.9 (CH). MS (*m*/*z*): 302 (2%), 269 (68%), 135 (100%), 93 (15%), 79 (15%), 67 (6%), 55 (4%). HR-MS (*m*/*z*): found, 302.2086; calcd for $C_{20}H_{30}S$, 302.2068. **1,1'-Diadamantane-3, 3'-dithiol (32)**, yield 85%, white solid, mp = 181−182 °C. ^1H NMR: 2.17−2.04 (m, 4H), 1.91 (bs, 1H), 1.85 (bs, 3H), 1.80 (bs, 3H), 1.73 (bs, 5H), 1.70 (s, 2H), 1.66−1.44 (m, 12H). ^{13}C NMR: 47.1 (CH_2), 45.8 (CH_2), 44.3 (C), 39.3 (C), 35.5 (CH_2), 33.7 (CH_2), 30.6 (CH). MS (*m*/*z*): 334 (4%), 301 (100%), 267 (3%), 167 (62%), 133 (15%), 111 (11%), 93 (19%), 79 (7%). HR-MS (*m*/*z*): found, 334.1764; calcd for $C_{20}H_{30}S_2$, 334.1789.

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