

Supporting Information

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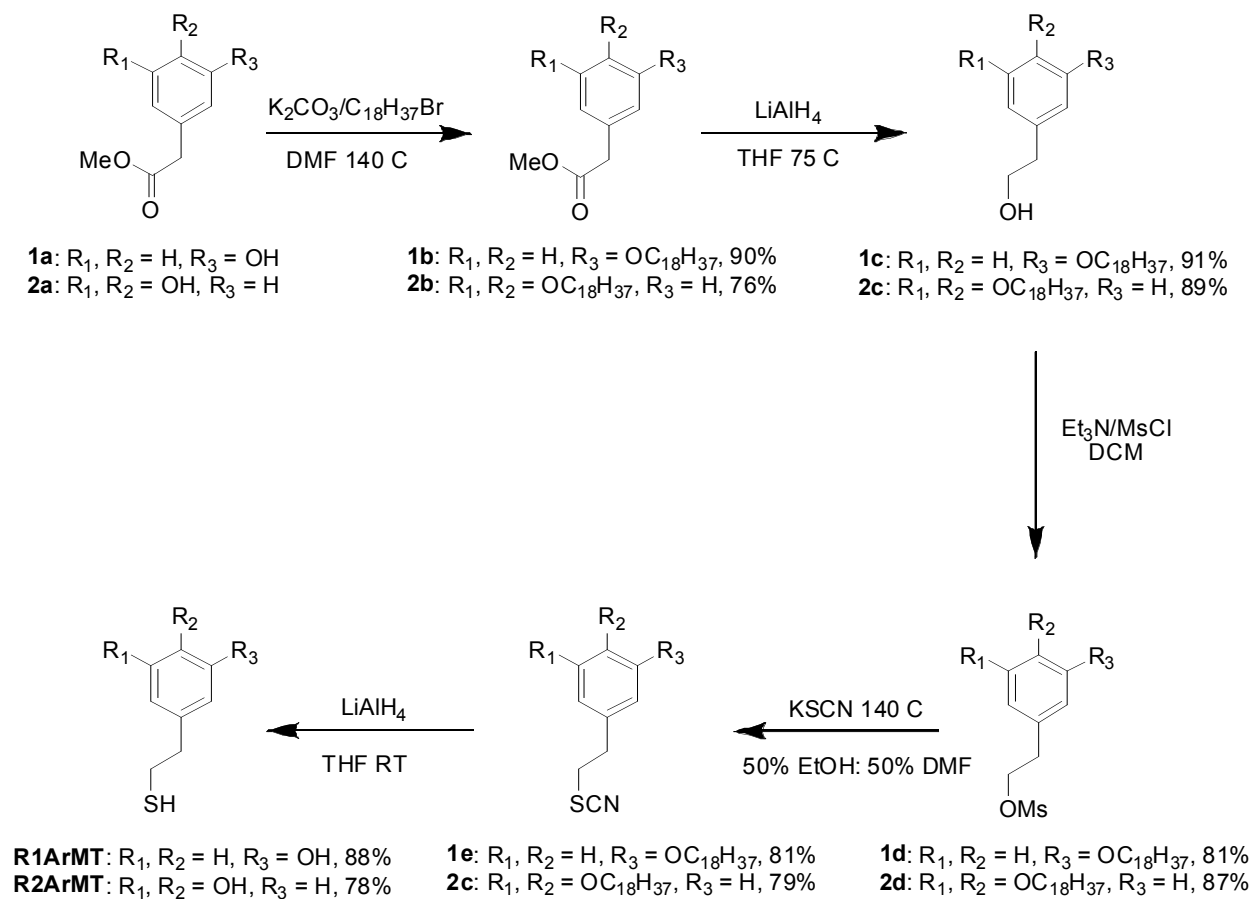
Self-Assembled Monolayers Derived from Alkoxyphenylethanethiols Having One, Two, and Three Pendant Chains

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Scheme S1. Synthesis Route Used to Prepare **R1ArMT** and **R2ArMT**



4-Octadecyloxyphenylacetate (1b). A mixture of K_2CO_3 (8.31 g, 60.2 mmol), methyl 4-hydroxy-phenylacetate (5.00 g, 30.0 mmol) and 1-bromooctadecane (13.04 g, 39.11 mmol) in DMF (80 mL) was stirred at 140 °C overnight. After cooling to rt, the residual K_2CO_3 was removed by filtration, and the filtrate was diluted with H_2O and acidified with 2 M HCl. The aqueous layer was extracted with CH_2Cl_2 (3×250 mL). The organic layers were combined and washed with water (3×50 mL), dried over $MgSO_4$, and concentrated to dryness to afford the crude product. The crude product was taken up in CH_2Cl_2 and added to cold MeOH to precipitate **1b** (11.30 g, 27.01 mmol, 90%) as a white powder. 1H NMR (500 MHz, $CDCl_3$): δ 0.87 (t, $J = 6.9$ Hz, $ArOCH_2CH_2(CH_2)_{15}CH_3$, 3H), 1.26-1.41 (m, $ArOCH_2CH_2(CH_2)_{15}CH_3$, 30H), 1.73 (pent, $J = 7.4$ Hz, $ArOCH_2CH_2(CH_2)_{15}CH_3$, 2H), 3.56 (s, $ArCH_2COOCH_3$, 2H), 3.68 ($ArCH_2COOCH_3$, 3H), 3.93 (t, $J = 6.9$ Hz, $ArOCH_2CH_2(CH_2)_{15}CH_3$, 2H), 6.85 (d, $J = 8.6$ Hz, ArH , 2H), 7.17 (d, $J = 8.6$ Hz, ArH , 2H).

2-(4-(Octadecyloxy)phenyl)ethanol (1c). To a suspension of $LiAlH_4$ (0.45 g, 12 mmol) in THF (25 mL) was added dropwise a solution of **1b** (2.00 g, 4.78 mmol) in THF (20 mL). The mixture was refluxed for 6 h under argon, quenched with water, and acidified with 2 M HCl. After being stirred for 10 min, the resultant mixture was extracted with CH_2Cl_2 (3×150 mL). The combined organic layers were washed subsequently with brine (3×50 mL) and water (3×50 mL), dried over $MgSO_4$, and evaporated to dryness to give (1.70 g, 4.35 mmol, 91%) of **1c**. 1H NMR (500 MHz, $CDCl_3$): δ 0.87 (t, $J = 6.9$ Hz, $ArOCH_2CH_2(CH_2)_{15}CH_3$, 3H), 1.25-1.47 (m, $ArOCH_2CH_2(CH_2)_{15}CH_3$, 30H), 1.76 (pent, $J = 7.4$ Hz, $ArOCH_2CH_2(CH_2)_{15}CH_3$, 2H), 2.80 (t, $J = 6.9$ Hz, $ArCH_2CH_2OH$), 3.64 (t, $J = 6.9$ Hz, $ArCH_2CH_2OH$, 2H), 3.81 (t, $J = 6.9$ Hz, $ArCH_2CH_2OH$, 1H), 3.92 (t, $J = 7.4$ Hz, $ArOCH_2CH_2(CH_2)_{15}CH_3$, 2H), 6.84 (d, $J = 8.6$ Hz, ArH , 2H), 7.12 (d, $J = 8.6$ Hz, ArH , 2H).

4-(Octadecyloxy)phenethylmethanesulfonate (1d). To a stirred solution of **1c** (2.00 g, 4.75 mmol) and triethylamine (1.99 mL, 14.3 mmol) in anhydrous THF (25 mL) was added dropwise methanesulfonyl chloride (1.11 mL, 14.3 mmol) over 5 min. Stirring of the mixture was continued at rt for 4 h under argon. Ice-cold water was poured into the reaction flask to destroy any remaining methanesulfonyl chloride. The mixture was extracted with diethyl ether (3 × 100 mL). The combined organic phase were washed successively with 2 M HCl (1 × 100 mL) and water (1 × 100 mL), dried over MgSO₄, and concentrated to dryness. A minimum volume of CH₂Cl₂ was used to dissolve the crude product, and then MeOH was added to the solution to obtain the crude mesylate **1d** (1.80 g, 3.84 mmol, 81%). The crude product was used in the next step without any purification. ¹H NMR (500 MHz, CDCl₃): δ 0.87 (t, *J* = 6.9 Hz, ArOCH₂CH₂(CH₂)₁₅CH₃, 3H), 1.25-1.47 (m, ArOCH₂CH₂(CH₂)₁₅CH₃, 30H), 1.76 (pent, *J* = 7.8 Hz, ArOCH₂CH₂(CH₂)₁₅CH₃, 2H), 2.84 (s, ArCH₂CH₂SO₂CH₃, 3H), 2.98 (t, *J* = 6.9 Hz, ArCH₂CH₂SO₂CH₃, 2H), 3.92 (t, *J* = 6.9 Hz, ArOCH₂CH₂(CH₂)₁₅CH₃, 2H), 4.37 (t, *J* = 6.9 Hz, ArCH₂CH₂SO₂CH₃, 2H), 6.83 (d, *J* = 8.7 Hz, ArH, 2H), 7.12 (d, *J* = 8.7 Hz, ArH, 2H).

1-(Octadecyloxy)-4-(2-thiocyanatethyl)benzene (1e). A mixture of **1d** (1.00 g, 2.13 mmol) and KSCN (2.07 g, 21.3 mmol) in the mixture of EtOH (10 mL) and DMF (10 mL) was stirred at 140° C for 24 h. The resulting mixture was poured into cold water. The precipitate formed was filtered, washed with water, and then dissolved in CH₂Cl₂ (250 mL). The organic layer was washed with saturated brine (1 × 50 mL), dried over MgSO₄, and concentrated to dryness. The crude product was purified by column chromatography on silica gel eluting with CH₂Cl₂ to afford **1e** (0.75 g, 1.7 mmol, 81%). ¹H NMR (500 MHz, CDCl₃): δ 0.87 (t, *J* = 6.9 Hz, ArOCH₂CH₂(CH₂)₁₅CH₃, 3H), 1.20-1.48 (m, ArOCH₂CH₂(CH₂)₁₅CH₃, 30H), 1.76 (pent, *J* = 6.9 Hz, ArOCH₂CH₂(CH₂)₁₅CH₃, 2H), 3.05 (t, *J* = 7.4 Hz, ArCH₂CH₂SCN), 3.13 (t, *J* = 7.4 Hz, ArCH₂CH₂SCN, 2H), 3.92 (t, *J* = 6.9 Hz, ArOCH₂CH₂(CH₂)₁₅CH₃, 2H), 6.84 (d, *J* = 8.6 Hz, ArH, 2H), 7.10 (d, *J* = 8.6 Hz, ArH, 2H).

2-(4-Octadecyloxy)phenyl)etanethiol (R1ArMT). To a suspension LiAlH₄ (0.22 g, 5.8 mmol) in THF (25 mL) was added dropwise a solution of **1e** (1.00 g, 2.31 mmol) in THF (20 mL). The reaction was stirred at rt for 6 h under argon and then quenched with water and acidified to pH ~1 by carefully adding conc. HCl. The mixture was extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layers were washed subsequently with brine (1 × 50 mL) and water (1 × 50 mL), dried over MgSO₄, and evaporated to dryness to give **R1ArMT** (0.83 g, 0.20 mmol, 88%). ¹H NMR (500 MHz, CDCl₃): δ 0.87 (t, *J* = 6.8 Hz, ArOCH₂CH₂(CH₂)₁₅CH₃, 3H), 1.21-1.50 (m, ArOCH₂CH₂(CH₂)₁₅CH₃, and ArCH₂CH₂SH, 31H), 1.75 (pent, *J* = 6.8 Hz, ArOCH₂CH₂(CH₂)₁₅CH₃, 2H), 2.74 (m, ArCH₂CH₂SH), 2.83 (t, *J* = 7.4 Hz, ArCH₂CH₂SH, 2H), 3.92 (t, *J* = 6.9 Hz, ArOCH₂CH₂(CH₂)₁₅CH₃, 2H), 6.83 (d, *J* = 8.6 Hz, ArH, 2H), 7.09 (d, *J* = 8.6 Hz, ArH, 2H). ¹³CNMR (125 MHz, CDCl₃): δ 14.22, 22.78, 26.14, 26.44, 29.45, 29.78, 32.01, 39.46, 68.10, 114.56, 129.66, 131.76, 157.93.

Methyl-2-(3,3-bis(octadecyloxy)phenyl)acetate (2b). Following the procedure described for **1b**, methyl-2-(3,5-dihydroxyphenyl)acetate (2.50 g, 13.7 mmol) was treated with K₂CO₃ (18.97 g, 137.2 mmol) and 1-bromooctadecane (13.73 g, 41.16 mmol) in DMF (150 mL) at 120 °C to give a pale yellow crude product. The crude product was purified by column chromatography using CH₂Cl₂:hexane (3:2) as the eluent to afford a white powder product **2b** (7.21 g, 10.5 mmol, 76%). ¹H NMR (400 MHz, CDCl₃): δ 0.87 (t, *J* = 6.9 Hz, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₂, 6H), 1.24-1.43 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₂, 60H), 1.74 (pent, *J* = 7.8 Hz, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₂, 4H), 3.53 (s, ArCH₂COOCH₃, 2H), 3.70 (s, ArCH₂COOCH₃, 3H), 3.90 (t, *J* = 6.9 Hz, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₂, 4H), 6.35 (s, ArH, 1H), 6.39 (s, ArH, 2H).

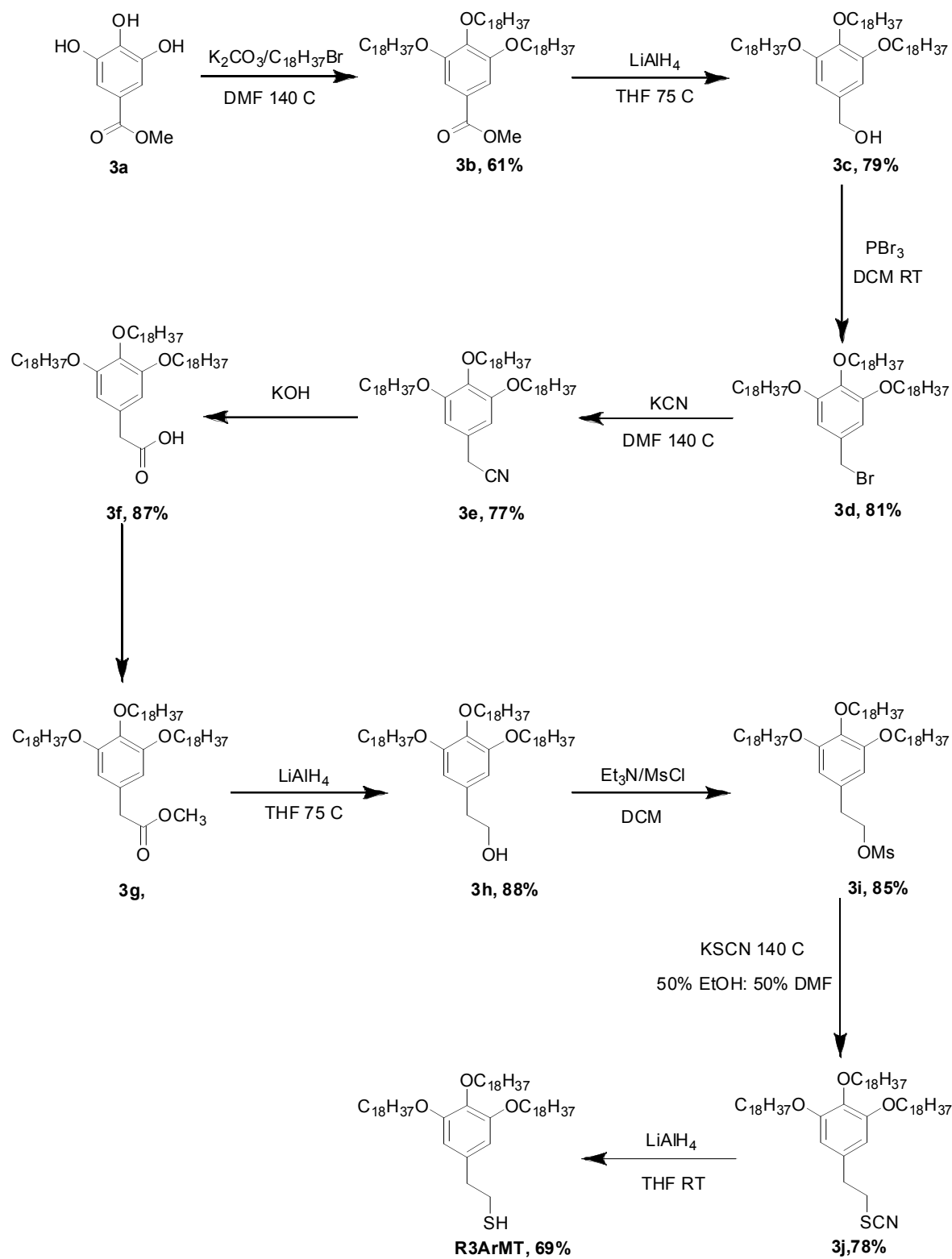
2-(3,5-Bis(octadecyloxy)phenyl)ethanol (2c). Following the procedure described for **1c**, a solution of **2b** (2.00 g, 2.91 mmol) in THF (15 mL) was added to a suspension of LiAlH₄ (0.28 g, 7.2 mmol) in THF (10 mL) to obtain **2c** (1.70 g, 2.58 mmol, 89%). ¹H NMR (300 MHz, CDCl₃): δ 0.88 (t, *J* = 6.3 Hz, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₂, 6H), 1.24-1.43 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₂, 60H), 1.76 (pent, *J* = 6.3 Hz, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₂, 4H), 2.79 (t, *J* = 6.3 Hz, ArCH₂CH₂OH, 2H), 3.83-3.890 (m, ArCH₂CH₂OH, and ArCH₃CH₂OH, 3H), 3.91 (t, *J* = 6.6 Hz, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₂, 4H), 6.35 (s, ArH, 1H), 6.36 (s, ArH, 2H).

3,5-Bis(octadecyloxy)phenethylmethanesulfonate (2d). Following the procedure described for **1d**, a mixture of **2c** (2.00 g, 3.03 mmol) and triethylamine (1.27 mL, 9.10 mmol) in THF (30 mL) was treated with methansulfonyl chloride (0.71 mL, 9.1 mmol) to obtain the crude mesylate **2d** (1.94 g, 2.65 mmol, 87%) as a white powder. ¹H NMR (300 MHz, CDCl₃): δ 0.88 (t, *J* = 6.3 Hz, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₂, 6H), 1.20-1.42 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₂, 60H), 1.76 (pent, *J* = 6.6 Hz, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₂, 4H), 2.88 (s, ArCH₂CH₂SO₂CH₃, 3H), 2.97 (t, *J* = 6.6 Hz, ArCH₂CH₂SO₂CH₃, 2H), 3.91 (t, *J* = 6.6 Hz, ArOCH₂CH₂(CH₂)₁₅CH₃, 2H), 4.40 (t, *J* = 6.6 Hz, ArCH₂CH₂SO₂CH₃, 2H), 6.63 (s (br), ArH, 3H).

1,3-Bis(octadecyloxy)-5-(2-thiocyanatoethyl)benzene (2e). Following the procedure described for **1e**, **2d** (2.00 g, 2.73 mmol) was treated with KSCN (2.66 g, 27.3 mmol) dissolved in a mixture of EtOH (10 mL) and DMF (10 mL). The crude product was purified by column chromatography using CH₂Cl₂:hexane (3:2) as the eluent to afford **2e** (1.52 g, 2.17 mmol, 79%). ¹H NMR (500 MHz, CDCl₃): δ 0.88 (t, *J* = 6.9 Hz, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₂, 6H), 1.21-1.49 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₂, 60H), 1.77 (pent, *J* = 6.9 Hz, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₂, 4H), 3.02 (t, *J* = 6.9 Hz, ArCH₂CH₂SCN, 2H), 3.16 (t, *J* = 6.8 Hz, ArCH₂CH₂SCN, 2H), 3.92 (t, *J* = 6.9 Hz, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₂, 4H), 6.32 (s, ArH, 2H), 6.34 (s, ArH, 1H).

2-(3,3-Bis(octadecyloxy)phenyl)ethanethiol (R2ArMT). Following the procedure described for **R1ArMT**, a solution of **2e** (2.00 g, 2.91 mmol) in THF (15 mL) was added dropwise to a suspension of LiAlH₄ (0.28 g, 7.2 mmol) in THF (10 mL) to give **R2ArMT** (0.75 g, 1.1 mmol, 78%). ¹H NMR (500 MHz, CDCl₃): δ 0.87 (t, *J* = 6.9 Hz, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₂, 6H), 1.21-1.50 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₂, and ArCH₂CH₂SH, 61H), 1.75 (pent, *J* = 6.9 Hz, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₂, 4H), 2.76 (m, ArCH₂CH₂SH, 2H), 2.83 (t, *J* = 6.9 Hz, ArCH₂CH₂SH, 2H), 3.90 (t, *J* = 6.9 Hz, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₂, 4H), 6.32 (s, ArH, 3H). ¹³CNMR (125 MHz, CDCl₃): δ 14.22, 22.79, 25.94, 26.15, 29.59, 29.70, 29.78, 32.02, 40.67, 68.08, 99.34, 107.22, 142.01, 160.46.

Scheme S2. Synthesis Route Used to Prepare **R3ArMT**



Methyl-3,4,4-tris(octadecyloxy)benzoate (3b). Following the procedure described for **1b**, methyl-3,4,5-trihydroxybenzoate (2.00 g, 10.8 mmol) was treated with K₂CO₃ (22.53 g, 163.0 mmol) and 1-bromooctadecane (16.30 g, 48.90 mmol) in DMF (250 mL) at 140 °C to give a pale yellow crude product. The crude product was purified by column chromatography using EtOAc:hexane (1:4) as the eluent to afford **3b** as a white powder (6.20 g, 6.58 mmol, 61%). ¹H NMR (500 MHz, CDCl₃): δ 0.87 (t, *J* = 7.2 Hz, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 9H), 1.24-1.48 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 90H), 1.68-1.81 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 6H), 3.87 (s, ArCOCH₃, 3H), 3.98-4.01 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 6H), 7.24 (s, ArH, 2H).

(3,4,5-Tris(octadecyloxy)phenyl)methanol (3c). Following the procedure described for **1c**, a solution of **3b** (6.00 g, 5.03 mmol) in THF (20 mL) was added to a suspension of LiAlH₄ (0.60 g, 16 mmol) in THF (15 mL) to obtain **3c** (5.30 g, 5.80 mmol, 91%). ¹H NMR (500 MHz, CDCl₃): δ 0.87 (t, *J* = 7.2 Hz, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 9H), 1.24-1.47 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 90H), 1.68-1.81 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 6H), 3.63 (br, ArCH₂OH, 1H), 3.92-3.97 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 6H), 4.59 (d, *J* = 5.7, ArCH₂OH, 2H), 6.55 (s, ArH, 2H).

5-(Bromomethyl)-1,2,3-tris(octadecyloxy)benzene (3d). A solution of PBr₃ (1.42 mL, 15.1 mmol) in CH₂Cl₂ (10 mL) was added slowly to a stirred solution of **3c** (4.60 g, 5.30 mmol) in CH₂Cl₂ (100 mL) at rt. The mixture was then stirred for 3 h under argon, quenched with H₂O (25 mL), and extracted with CH₂Cl₂ (3 × 100 mL). The combined organic layers were washed subsequently with brine (1 × 100 mL), water (1 × 100 mL), and dried over MgSO₄. Removal the solvents afforded **3d** (4.00 g, 4.10 mmol, 81%) as a white powder. ¹H NMR (500 MHz, CDCl₃): δ 0.87 (t, *J* = 6.9 Hz, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 9H), 1.24-1.47 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 90H), 1.68-1.81 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 6H), 3.92-3.96 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 6H), 4.43 (s, ArCH₂Br, 2H), 6.56 (s, ArH, 2H).

2-(3,4,5-Tris(octadecyloxy)phenyl)acetonitrile (3e). To a solution of **3d** (4.20 g, 4.30 mmol) in DMF (150 mL) was added a solution of NaCN (1.05 g, 21.5 mmol) in water (15 mL). The mixture was heated at 140 °C for 72 h, quenched with water (50 mL), and extracted with CH₂Cl₂ (3 × 100 mL). The combined organic layers were washed with brine (1 × 100 mL) and water (1 × 100 mL), and dried over MgSO₄. The solvent was evaporated to dryness to obtain the crude product. The crude product was dissolved in a minimum volume of CH₂Cl₂, and cold MeOH was added to precipitate **3e** (3.13 g, 3.39 mmol, 79%) as a white powder. ¹H NMR (500 MHz, CDCl₃): δ 0.88 (t, *J* = 6.9 Hz, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 9H), 1.24-1.47 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 90H), 1.68-1.81 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 6H), 3.65 (s, ArCH₂CN, 2H), 3.92-3.96 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 6H), 6.47 (s, ArH, 2H).

2-(3,4,5-Tris(octadecyloxy)phenyl) acetic acid (3f). To a suspension of nitrile **3e** (2.00 g, 2.19 mmol) in methanol (150 mL) was added NaOH (30.0 g, 750 mmol) in water (20 mL). The mixture was heated to reflux for 72 h. When the reaction was cooled to rt, H₂O (100 mL) was poured to dilute the solution. The mixture was acidified by slowly adding conc. HCl to pH ~1 and then extracted with CH₂Cl₂ (3 × 150 mL). After washing the combined organic layers with brine (2 × 100 mL) and water (1 × 100 mL), the organic phase was dried over MgSO₄ and evaporated to give the crude product. The crude product was taken up in CH₂Cl₂, and cold MeOH was added to precipitate **3f** (1.80 g, 1.91 mmol, 87%) as a white powder. The product was used in the next step without further purification. ¹H NMR (500 MHz, CDCl₃): δ 0.87 (t, *J* = 7.4 Hz, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 9H), 1.24-1.49 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 90H), 1.69-1.81 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 6H), 3.48 (s, ArCH₂COOH, 2H), 3.89-3.94 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 6H), 6.45 (s, ArH, 2H).

Methyl-2-(3,4,5-tris(octadecyloxy)phenyl)acetate (3g). A solution of 50% w/w BF₃ in MeOH (2.00 ml, 24.0 mmol) was added slowly under argon to a stirred solution of **3f** (4.00 g, 4.38 mmol) dissolved in a mixture of MeOH (50 mL) and THF (150 mL). The mixture was heated to reflux for 48 h. After cooling to rt, H₂O (50 mL) was added, and the mixture was extracted with CH₂Cl₂ (3 × 150 mL). The collected organic layers were washed with brine (1 × 100 mL) and water (1 × 100 mL), dried over MgSO₄, and evaporated to obtain ester **3g** as a pale yellow powder. Further purification by column chromatography with CH₂Cl₂:hexane (3:2) as the eluent afforded **3g** (2.20 g, 2.30 mmol, 52%) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 0.86 (t, *J* = 6.9 Hz, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 9H), 1.18-1.50 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 90H), 1.69-1.81 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 6H), 3.51 (s, ArCH₂COOCH₃, 2H), 3.69 (s, ArCH₂COOCH₃, 3H), 3.89-3.96 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 6H), 6.44 (s, ArH, 2H).

2-(3,4,5-Tris(octadecyloxy)phenyl)ethanol (3h). Following the procedure described for **1c**, a solution of **3g** (2.00 g, 2.09 mmol) in THF (15 mL) was added dropwise to a suspension of LiAlH₄ (0.20 g, 5.2 mmol) in THF (10 mL) to give **3h** (1.70 g, 1.83 mmol, 88%). ¹H NMR (400 MHz, CDCl₃): δ 0.87 (t, *J* = 7.4 Hz, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 9H), 1.25-1.45 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 90H), 1.65-1.87 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃, 6H), 2.76 (t, *J* = 8.0 Hz, ArCH₂CH₂OH, 2H), 3.85 (m, ArCH₂CH₂OH, 1H), 3.92-3.96 (m, Ar(OCH₂CH₂(CH₂)₁₅CH₃)₃ and ArCH₂CH₂OH, 8H), 6.37 (s, ArH, 2H).

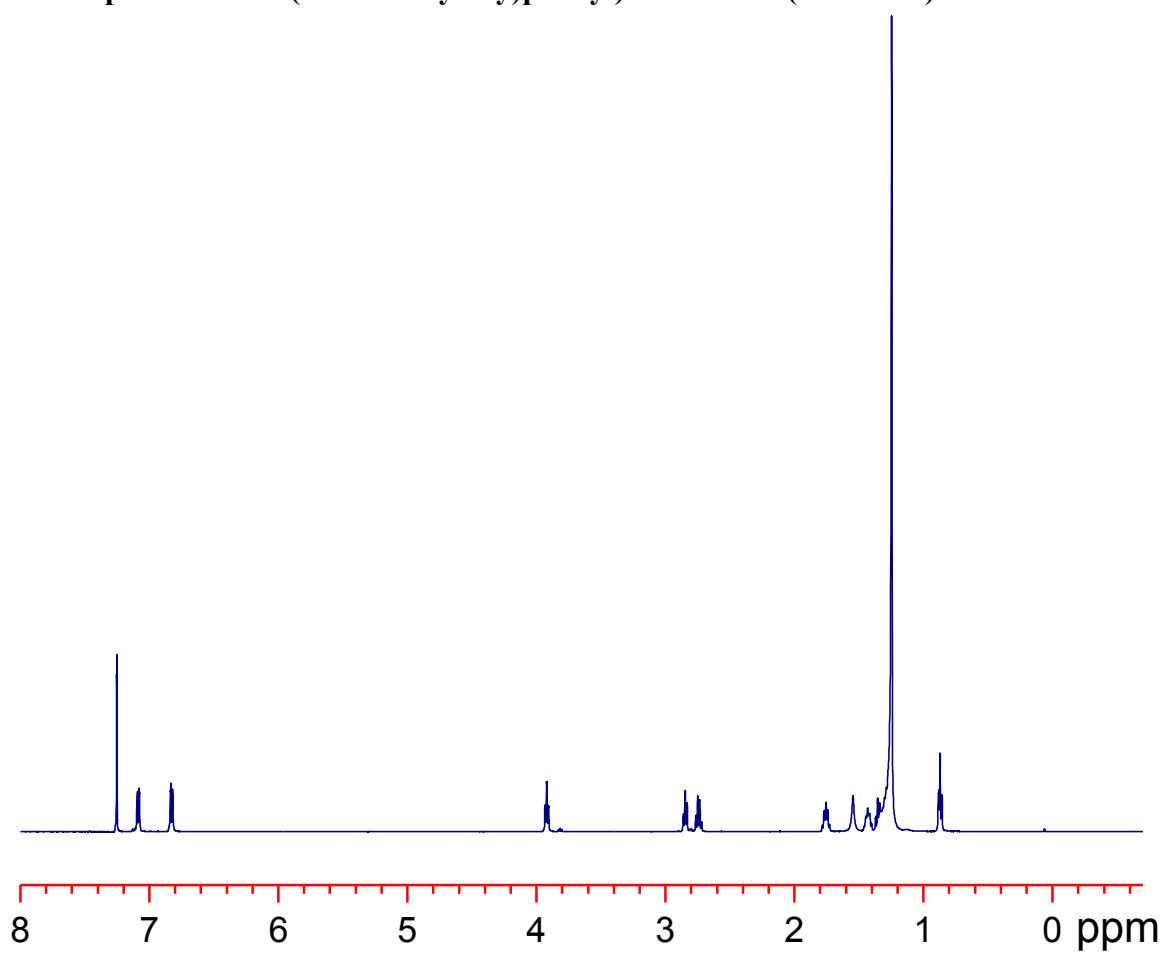
3,4,5-Tris(octadecyloxy)phenylmethanesulfonate (3i). Following the procedure described for **1d**, a mixture of **3h** (1.50 g, 1.62 mmol) and triethylamine (0.68 mL, 4.8 mmol) in THF (30 mL) was treated with methanesulfonyl chloride (0.38 mL, 4.8 mmol) to obtain the crude mesylate **3i**. The crude product was dissolved in a minimum volume of CH₂Cl₂, and MeOH was added to precipitate **3i** (1.38 g, 1.37 mmol, 85%) as a white powder. ¹H NMR (500 MHz, CDCl₃): δ 0.87

(t, $J = 7.4$ Hz, $\text{Ar}(\text{OCH}_2\text{CH}_2(\text{CH}_2)_{15}\text{CH}_3)_3$, 9H), 1.20-1.48 (m, $\text{Ar}(\text{OCH}_2\text{CH}_2(\text{CH}_2)_{15}\text{CH}_3)_3$, 90H), 1.69-1.80 (m, $\text{Ar}(\text{OCH}_2\text{CH}_2(\text{CH}_2)_{15}\text{CH}_3)_3$, 6H), 2.85 (s, $\text{ArCH}_2\text{CH}_2\text{SO}_2\text{CH}_3$, 3H), 2.95 (t, $J = 7.4$ Hz, $\text{ArCH}_2\text{CH}_2\text{SO}_2\text{CH}_3$, 2H), 3.90-3.96 (m, $\text{Ar}(\text{OCH}_2\text{CH}_2(\text{CH}_2)_{15}\text{CH}_3)_3$, 6H), 4.38 (t, $J = 7.4$ Hz, $\text{ArCH}_2\text{CH}_2\text{SO}_2\text{CH}_3$, 2H), 6.37 (s, ArH , 2H).

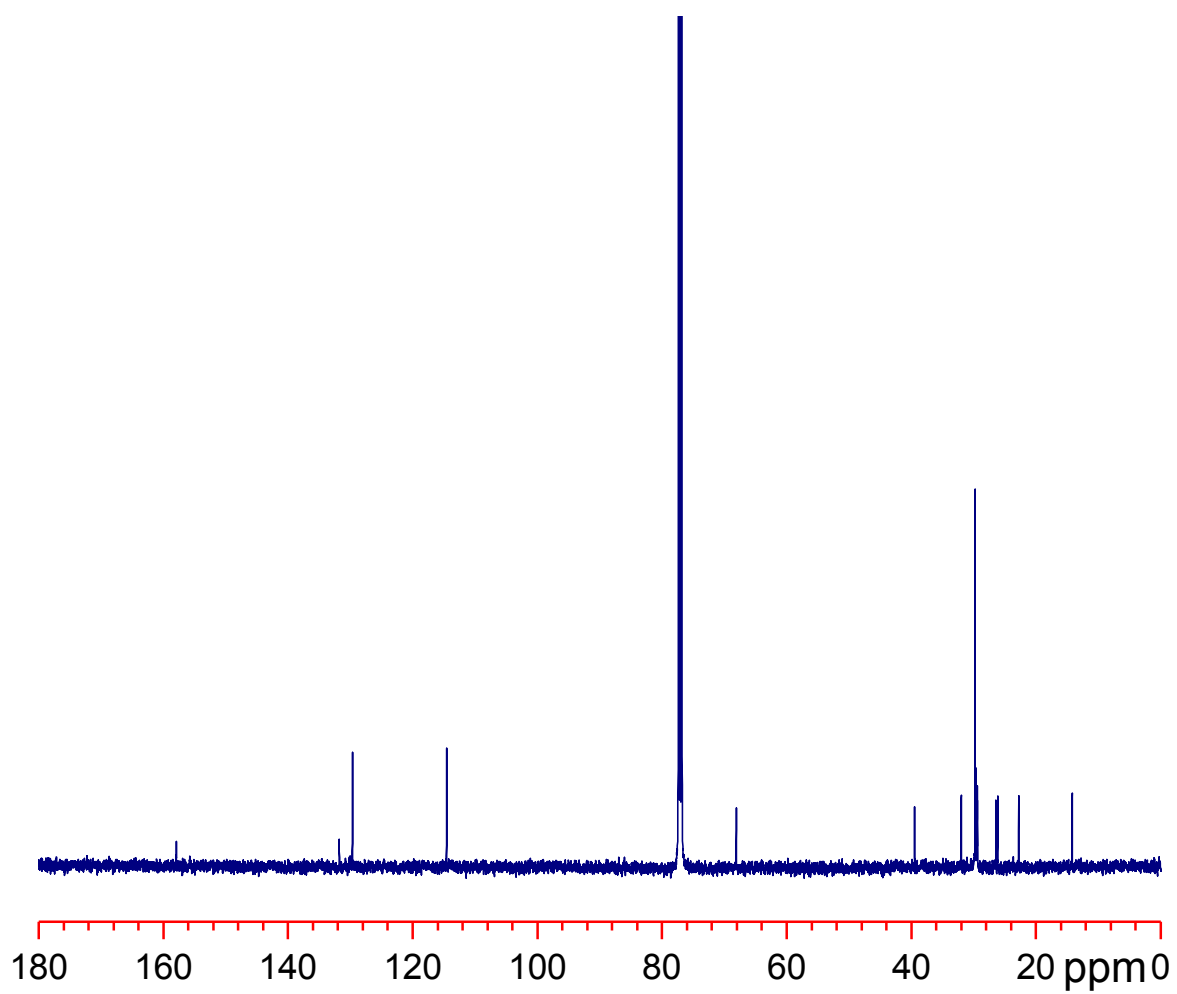
1,2,3-Tris(octadecyloxy(-5-(2-thiocyanatoethyl)benzene (3j). Following the procedure described for **1e**, **3i** (2.00 g, 1.99 mmol) was treated with KSCN (1.93 g, 19.9 mmol) dissolved in a mixture of EtOH (10 mL) and DMF (10 mL). The crude product was purified by column chromatography using CH_2Cl_2 :hexane (3:2) as the eluent to afford **3j** (1.50 g, 1.54 mmol, 78%). ^1H NMR (400 MHz, CDCl_3): δ 0.87 (t, $J = 6.9$ Hz, $\text{Ar}(\text{OCH}_2\text{CH}_2(\text{CH}_2)_{15}\text{CH}_3)_3$, 9H), 1.24-1.49 (m, $\text{Ar}(\text{OCH}_2\text{CH}_2(\text{CH}_2)_{15}\text{CH}_3)_3$, 90H), 1.75-1.81 (m, $\text{Ar}(\text{OCH}_2\text{CH}_2(\text{CH}_2)_{15}\text{CH}_3)_3$, 6H), 3.06 (t, $J = 7.4$ Hz, $\text{ArCH}_2\text{CH}_2\text{SCN}$, 2H), 3.14 (t, $J = 7.4$ Hz, $\text{ArCH}_2\text{CH}_2\text{SCN}$, 2H), 3.92 (m, $\text{Ar}(\text{OCH}_2\text{CH}_2(\text{CH}_2)_{15}\text{CH}_3)_3$, 6H), 6.37 (s, ArH , 2H).

2-(3,4,5-Tris(octadecyloxy)phenyl)ethanethiol (R3ArMT). Following the procedure described for **R1ArMT**, a solution of **3j** (1.00 g, 1.03 mmol) in THF (15 mL) was added dropwise to a suspension of LiAlH_4 (0.10 g, 2.6 mmol) in THF (10 mL) to give the crude product. Purification was performed by column chromatography with CH_2Cl_2 :hexane (3:2) as the eluent to afford pure **R3ArMT** (0.67 g, 0.71 mmol, 69%) as a white powder. ^1H NMR (500 MHz, CDCl_3): δ 0.87 (t, $J = 6.9$ Hz, $\text{Ar}(\text{OCH}_2\text{CH}_2(\text{CH}_2)_{15}\text{CH}_3)_3$, 9H), 1.25-1.49 (m, $\text{Ar}(\text{OCH}_2\text{CH}_2(\text{CH}_2)_{15}\text{CH}_3)_3$ and $\text{ArCH}_2\text{CH}_2\text{SH}$, 91H), 1.75-1.81 (m, $\text{Ar}(\text{OCH}_2\text{CH}_2(\text{CH}_2)_{15}\text{CH}_3)_3$, 6H), 2.76 (m, $\text{ArCH}_2\text{CH}_2\text{SH}$, 2H), 2.80 (t, $J = 6.9$ Hz, $\text{ArCH}_2\text{CH}_2\text{SCN}$, 2H), 3.90 (m, $\text{Ar}(\text{OCH}_2\text{CH}_2(\text{CH}_2)_{15}\text{CH}_3)_3$, 6H), 6.36 (s, ArH , 2H). ^{13}C NMR (500 MHz, CDCl_3): 14.22, 22.79, 26.21, 26.24, 29.47, 29.54, 29.75, 29.81, 30.43, 32.02, 40.70, 62.23, 73.51, 107.25, 135.00, 136.92, 153.17.

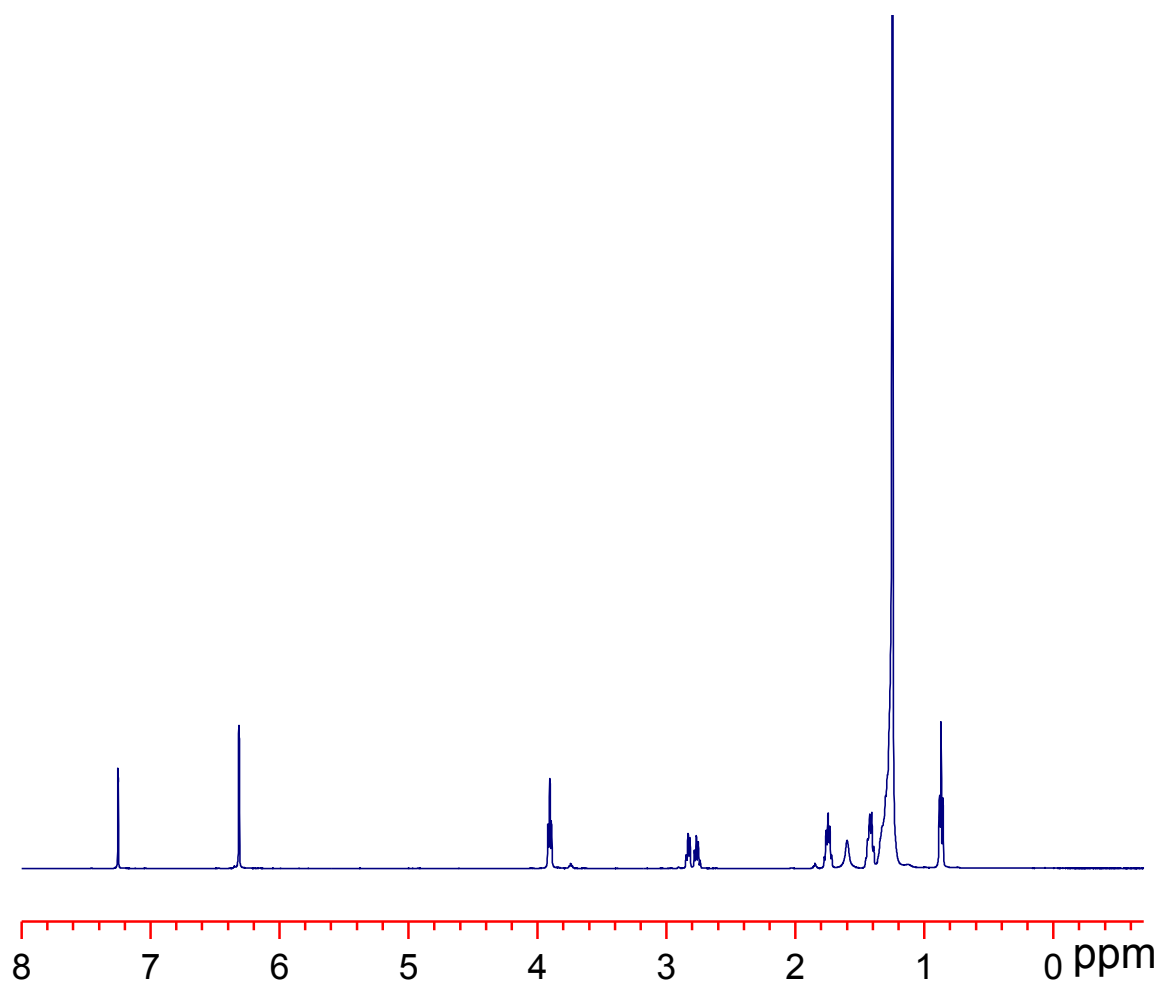
^1H NMR Spectrum of 2-(4-Octadecyloxy)phenyl)ethanethiol (R1ArMT)



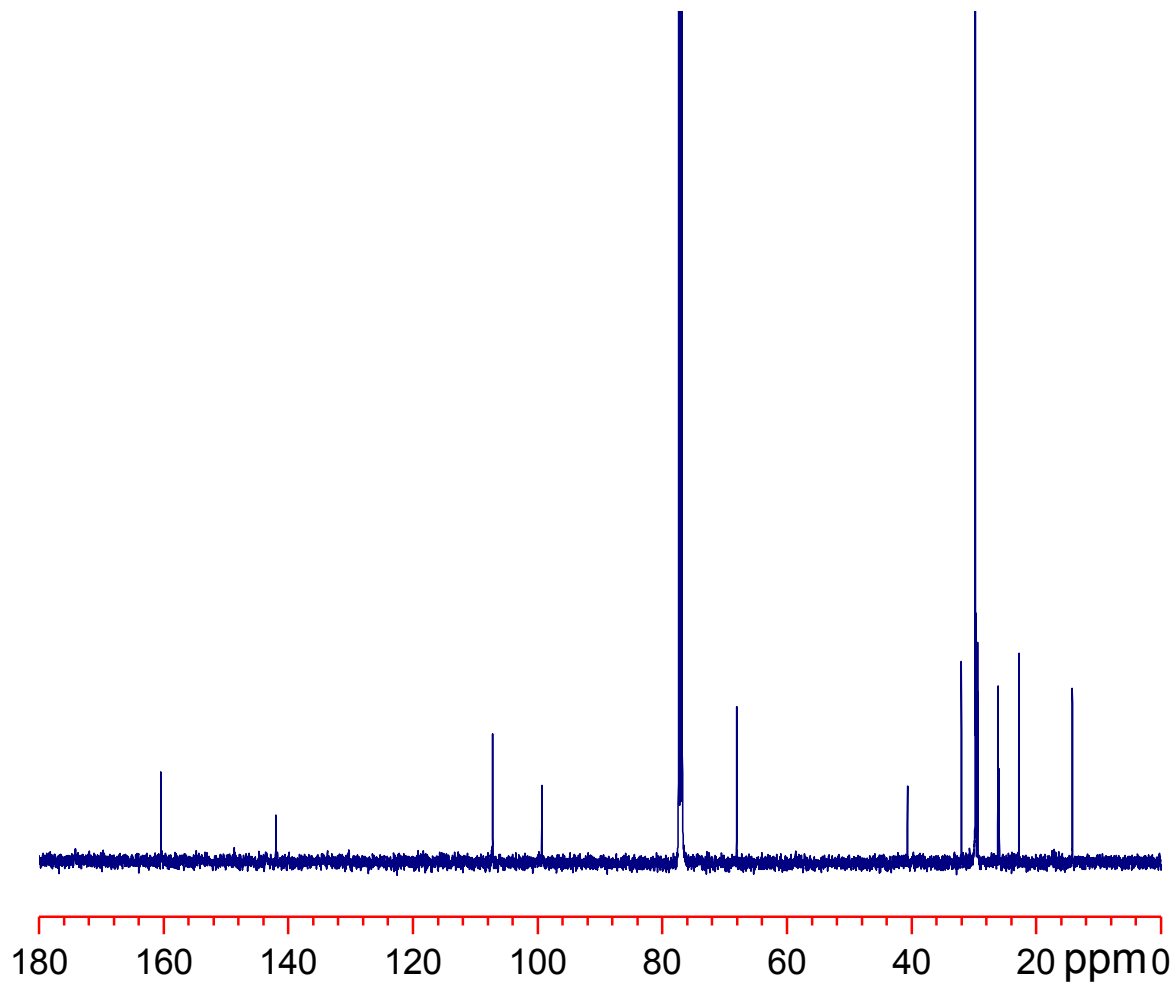
^{13}C NMR Spectrum of 2-(4-Octadecyloxy)phenyl)ethanethiol (R1ArMT)



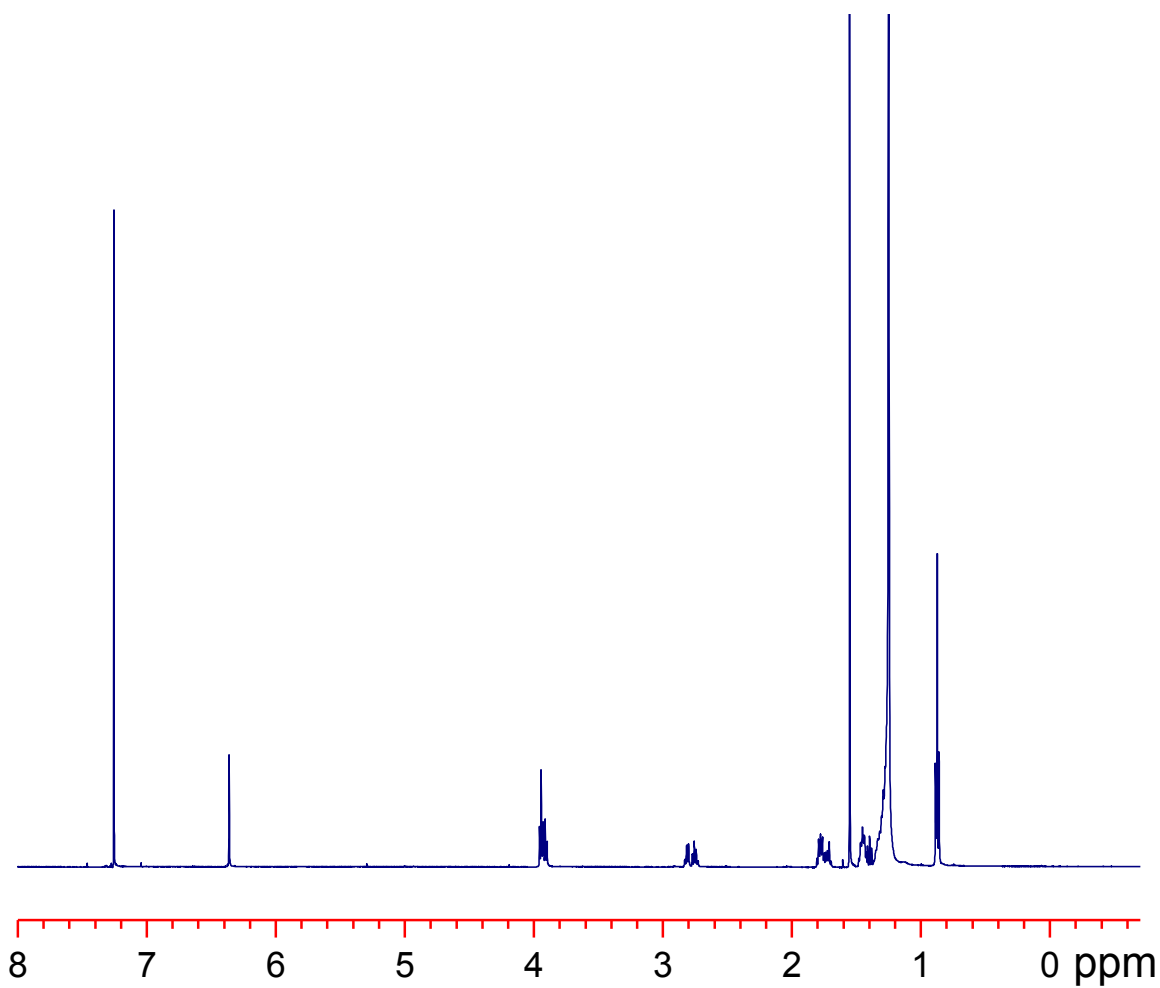
¹H NMR Spectrum of 2-(3,3-Bis(octadecyloxy)phenyl)ethanethiol (R2ArMT)



^{13}C NMR Spectrum of 2-(3,3-Bis(octadecyloxy)phenyl)ethanethiol (R2ArMT)



^1H NMR Spectrum of 2-(3,4,5-Tris(octadecyloxy)phenyl)ethanethiol (R3ArMT)



^{13}C NMR Spectrum of 2-(3,4,5-Tris(octadecyloxy)phenyl)ethanethiol (R3ArMT)

