Synthesis of Tripodal Trifluoroacetophenone Derivatives and Their Evaluation as Ion-Selective Electrode Membranes

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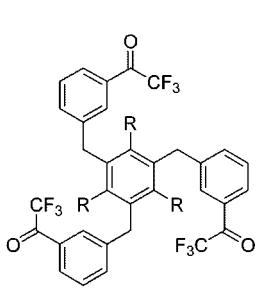
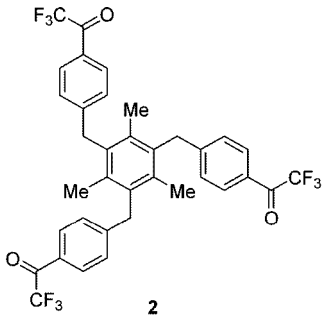
New, C_3 symmetric, tripodal trifluoroacetophenone derivatives **1-3** have been synthesized as anion ionophores. Evaluation of their ion selectivity has been carried out through ion-selective electrode membranes. The selectivity coefficients for the carbonate electrode toward various anions are dependent on the composition of the membranes and the lipophilicity of the ionophores. The tripodal ionophore **1a** showed an improved selectivity toward salicylate when 90 mol% of a lipophilic additive was used, compared to that of *p*-dodecyltrifluoroacetophenone.

Key Words : Tripodal ionophores, Trifluoroacetophenone, Carbonate anion, Ion-selective electrode

Recently selective recognition and sensing of anions by artificial receptors have attracted a considerable research interest in view of their potential applications in various areas.[1] To develop an artificial receptor that is selective toward a specific analyte, multiple interactions between host and guest in a complementary fashion may be considered. We have been interested in C_3 symmetric tripodal receptors that provide multiple interaction sites toward given analytes.[2] Among various anions, oxoanions such as carbonates, phosphates, or chlorates may participate in trigonal interactions with suitably designed tripodal receptors because these anions have trigonal or tetragonal structural features.[2d] As a recognition motif, we were particularly interested in the trifluoroacetophenone group, which has been successfully used in the carbonate-selective electrode membranes.[3] Selective recognition and sensing of carbonate ions are of importance in clinical diagnostics, environmental monitoring, and industrial purposes.[4] It is known that trifluoroacetyl group reacts with carbonates (CO_3^{2-}, HCO_3^-) to generate carbonyl adducts.[5] Therefore, it may result in an ideal receptor system if we introduce three trifluoroacetyl (TFA) groups in the receptor[6] positioned suitably to interact with the oxoanions of trigonal or tetrahedral guests. Herein, we wish to report the synthesis of C_3 symmetric trifluoroacetophenones **1-3** and their evaluation as recognition components in ion-selective electrode membranes.



1a: R = Me
1b: R = Et



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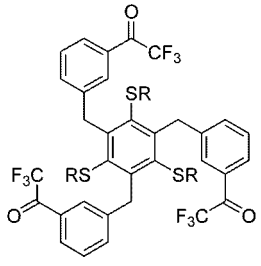

3: R = *n*-$C_{12}H_{25}$

Synthesis of the ionophores 1-3. The benzene-based tripodal receptor system has been designed based on the fact that three trifluoroacetophenone groups can have a conformational preference of "all-syn" conformer over others.[7] A molecular modeling study on the benzene-based tripodal trifluoroacetophenone receptors (BTTFAs) suggested that the position of TFA groups, *meta* and *para*, seems to affect the relative strain of the host-guest adducts depending on different guests. During the synthesis of receptors **1**, we found that introduction of the TFA groups was problematic. After examining several routes, finally the TFA groups could be introduced through the addition of CF_3^- anion to the aldehyde function[8] and subsequent oxidation. The established procedures for BTTFAs **1a** and **1b** are illustrated in Scheme 1. The synthesis of tris(1,3-dioxane) **6a** was achieved by generation of the Grignard reagent from bromobenzene **4** and subsequent CuI-catalyzed coupling with tris(1,3,5-bromomethyl)-2,4,6-trimethylbenzene **5a** at 60 °C in THF in 89% yield.[9] A lower yield (65%) was obtained in the synthesis of **6b** from tribromide **5b**, probably owing to increased steric strain. Regeneration of the aldehyde function gave **7a**, and subsequent addition of "CF_3^-" followed by oxidation of the corresponding alcohol **8a** with the Dess-

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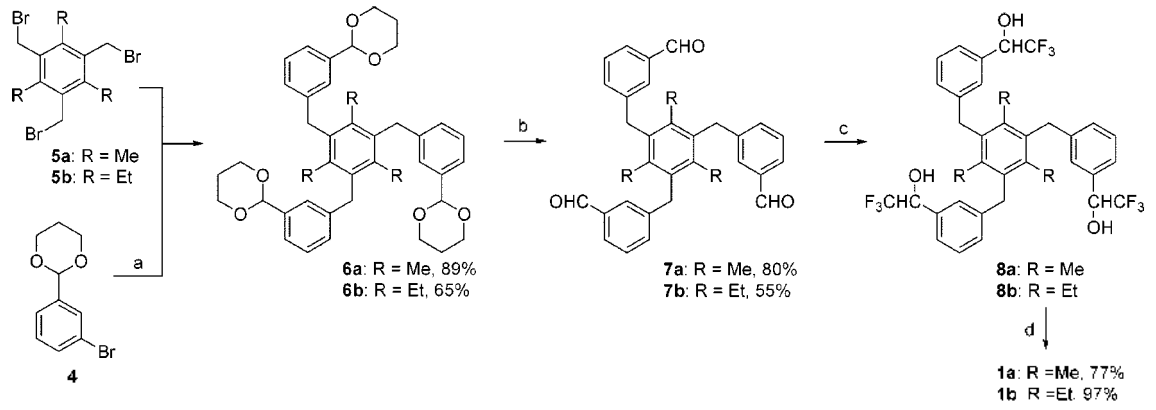
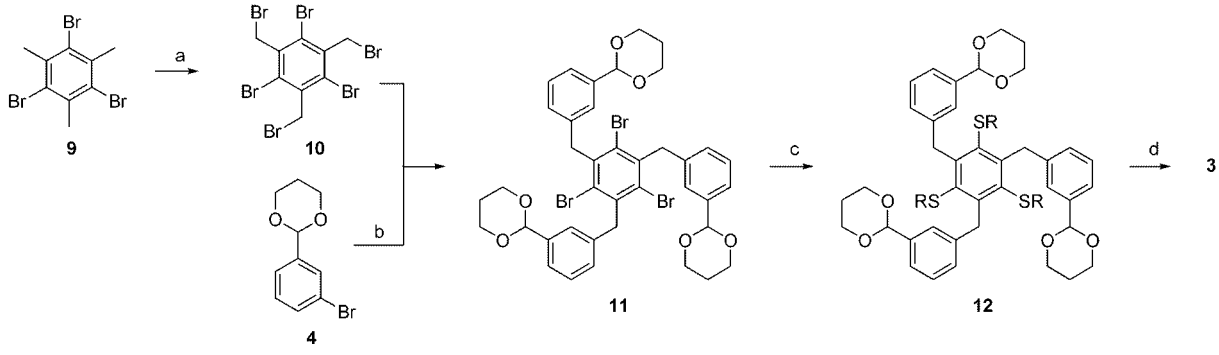


Scheme 1. [a]Reagents and conditions: (a) Mg, 15 mol% CuI, THF, 60 °C; (b) aq. HCl, acetone; (c) $TMSCF_3$, cat. CsF, DMF, r.t.; (d) Dess-Martin periodinane, CH_2Cl_2, r.t.

Martin periodiane[10] afforded the final product **1a**. Also. **1b** and a *para* analog **2** were synthesized similarly. The tripodal receptors **1** and **2** exhibited C_3 symmetric structures by NMR analyses.

To evaluate whether increasing lipophilicity of the receptor leads to an enhanced ISE performance of the membrane. we also synthesized receptor **3**. 1,3,5-Tribromo-2,4,6-tris(bromomethyl)benzene **10**,[11] prepared from 2,4,6-(tribromo)mesitylene **9**[12] *via* radical bromination. was subjected to the CuI-catalyzed Grignard coupling to afford tribromide **11**. albeit in a lower yield. Introduction of a long lipophilic chain could be achieved by a direct nucleophilic substitution reaction with 1-dodecanethiol *via* a thiolate anion.[13] Because of steric hindrance. other attempts to introduce a long alkyl chain such as transition metal-catalyzed coupling reactions were not successful. From thioether **12**. BTTFA **3** was synthesized following the same reactions as described above (Scheme 2).

Evaluation of BTTFAs 1-3 as ISE membranes toward various anions. Evaluation of ion selectivity through ion-selective membrane electrodes has several advantages such as very short response time. independent behavior towards colored or turbid samples. simple preparation of the membranes. and lower cost compared to other methods. ISE membranes from the BTTFAs were prepared according to the established procedure[14] using 4.2 mg of a BTTFA (5.2 wt%). 30 mg of poly(vinyl chloride) (37.3 wt%) as the matrix. 46.3 mg of bis(2-ethylhexyl)adipate (57.5 mol%) as the plasticizer. and a varying amount of tridodecyl(methyl)-ammonium chloride (TDMACl) as the lipophilic additive (30-90 mol% with respect to that of the ionophore). Potential differences were measured between the ion-selective electrodes and a double junction Ag|AgCl reference electrode. The response slopes of the ISE membranes were evaluated in 0.1 M Tris-H_2SO_4, pH 8.6. As can be seen from Figure 1a. the BTTFA **1a**-doped membrane (with 90 mol% of the additive) shows a similar response behavior toward selected ions as that of *p*-dodecyltrifluoroacetophenone (TFADB), a reference membrane. The membranes of other BTTFAs also showed similar response patterns. The pH response of BTTFA **1a**-doped membrane shows a relatively insensitive range pH 6-9. as observed in the case of TFADB (Figure 1b). The ion selectivity coefficients of the BTTFA-doped membranes under different composition were examined by using the separate solution method (IUPAC SSM II method) at an interfering ion concentration of 0.1 M. and the results are listed in Table 1. Anions other than oxoanions including salicylate (Sal^-) have been studied. Positive values mean higher response toward the ions compared to carbonate ions and negative values mean lower response. The relative ion selectivity in the case of BTTFA **1a**-doped membrane is as follows: $Sal^- > ClO_4^- > SCN^- > (CO_3^{2-}, HCO_3^-) > NO_3^- > NO_2^- > Br^- > Cl^- > HPO_4^{2-}$. This trend has a correlation with



Scheme 2. [a]Reagents and conditions: (a) cat. $(PhCO_2)_2$, NBS, CCl_4, reflux, 85%; (b) Mg, 15 mol% CuI, THF, 60 °C, 24%; (c) n-$C_{12}H_{25}SH$, NaH, *N,N*-dimethylimidazolidinone, reflux, 44%; (d) aq. HCl, acetone, 88%; $TMSCF_3$, cat. CsF, DME, r.t., 84%; Dess-Martin periodinane, CH_2Cl_2, 100%.

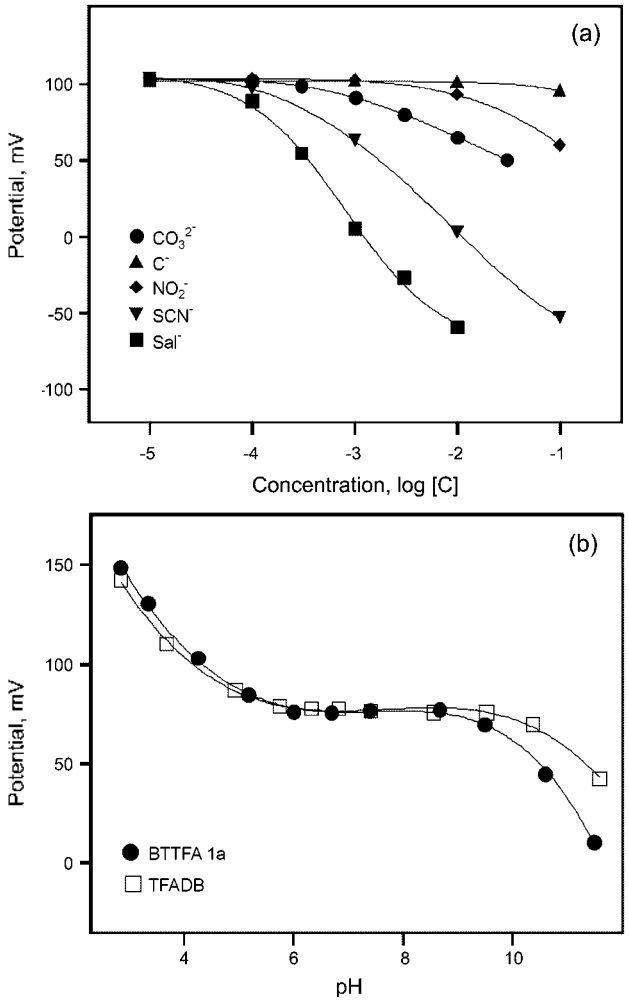


Figure 1. (a) Calibration curve for BTTFA **1a**-based electrode to various anions. (b) pH Response of the electrodes based on BTTFA **1a**-90 mol% TDMACl and TFADB.

the lipophilicity of anions.[15] The selective recognition involves a partition process of the anions into the organic solvent of the membrane phase, which is assisted by the lipophilic quaternary ammonium species, TDMACl. The trend of ion selectivity, however, is changed in the case of BTTFA **1b** when the mol% of [TDMACl]/[**1b**] was 90%. In this case, the selectivity coefficients of lipophilic anions increased much, and perchlorate anion showed a larger selectivity coefficient than that of salicylate anion. Among the ionophores **1-3**, the most lipophilic **3** shows increased selectivity toward more lipophilic anions and vice versa. Regarding to the carbonate selectivity toward the lipophilic anions, a better selectivity was observed in the case of BTTFA **1a** with 90% of the additive, compared to that of the TFADB membrane. A considerable effort has been focused in the development of a carbonate-selective membrane, particularly that has selectivity toward the most interfering salicylate anion. The selectivity coefficient data of our tripodal TFA analogs suggests that in addition to multiple interactions other factors such as lipophilicity, steric and electronic factors have to be optimized as well as membrane properties. A significant progress has been made recently in the carbonate-selective membranes composed of three TFA groups,[6] which augur for the development of new tripodal carbonate sensors.

In summary, we have synthesized a new type of C_3 symmetric, tripodal trifluoroacetophenone derivatives. The ion selectivity of the ionophores has been evaluated toward several anions through the corresponding ion-selective electrode membranes. The ion selectivity coefficients show that the selectivity is dependent on the composition of the membranes, particularly on the mol% of the lipophilic additive and the lipophilicity of ionophores. A better selectivity pattern as a carbonate-selective electrode membrane was observed in the case of BTTFA **1a** with 90 mol% of the additive. A further structural optimization of the ionophores capable of multiple interactions is under investigation.

Experimental Section

2-(3-Bromophenyl)-[1,3]-dioxane (4). To a mixture of 3-bromobenzaldehyde (2.33 mL, 20 mmol), 1,3-propanediol (1.9 mL, 26.0 mmol) and *p*-toluenesulfonic acid mono-

Table 1. Selectivity coefficients of membrane electrodes of ionophores **1-3** toward various anions relative to carbonate ions

Electrode-type[b]	Selectivity coefficient								Slope (mV dec.)	Detection limit (log[C])
	Cl^-	Br^-	NO_2^-	HPO_4^{2-}	NO_3^-	SCN^-	ClO_4^-	SaI^-		
TFADB - 13 mol%	-4	-0.8	-0.47	–	0.36	1.79	2.56	2.47	-30.3	-3.36
BTTFA **1a**-30 mol%	-2.77	-1.75	-1.06	-4	-0.26	1.10	1.91	2.14	-30.0	-3.24
BTTFA **1a**-60 mol%	-2.68	-1.65	-1.00	-4	-0.16	1.16	1.97	2.13	-29.3	-3.33
BTTFA **1a**-90 mol%	-2.33	1.30	-0.82	-4	-0.04	1.27	1.64	1.96	-29.9	-3.31
BTTFA **1b**-30 mol%	-4.00	-3.34	-1.47	-3.30	-0.31	1.10	1.91	2.12	-29.6	-3.37
BTTFA **1b**-60 mol%	-4.00	-1.74	-1.25	-3.28	-0.07	1.35	2.07	2.12	-31.2	-3.42
BTTFA **1b**-90 mol%	-1.61	-0.11	-0.13	-2.35	0.89	2.19	2.47	2.31	-30.1	-3.11
BTTFA **2**-30 mol%	-4.00	-1.46	-0.81	-2.60	0.17	1.60	2.41	2.47	-29.7	-3.29
BTTFA **2**-60 mol%	-4.00	-1.51	-0.94	-2.67	0.15	1.61	2.38	2.37	-29.9	-3.27
BTTFA **2**-90 mol%	-4.00	-1.59	-1.07	-2.76	0.07	1.48	2.23	2.29	-29.8	-3.27
BTTFA **3**[c]	-2.45	-0.79	-0.44	-3.63	0.25	1.8	2.76	2.46	-30.2	-3.60

[a]The membrane electrodes were prepared using 4.2 mg of ionophore, 30 mg of PVC, 46.3 mg of the plasticizer, and 30-90 mol% of the additive. [b]The mol% means that of the additive with respect to the ionophore. [c]8.3 mg of the ionophore and 1 mg of the additive were used.

hydrate (380 mg, 0.2 mmol) was added benzene (40 mL) and the reaction vessel was equipped with a Dean-Stark apparatus with reflux condenser. The reaction mixture was refluxed for 5 h with stirring. After being cooled to room temperature, the mixture was concentrated. Extractive workup with ethyl acetate and purification by column chromatography (hexane : EtOAc, 5 : 1) afforded **4** (5.6 g, 100%) as a colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.41 (m, 0.5H), 1.45-1.48 (m, 0.5H), 2.13-2.29 (m, 1H), 3.92-4.01 (m, 2H), 4.22-4.29 (m, 2H), 5.46 (s, 1H), 7.24 (d, J = 7.8 Hz, 1H), 7.38-7.41 (m, 1H), 7.41-7.48 (m, 1H), 7.66 (t, J = 1.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.5, 132.5, 130.5, 129.9, 125.4, 123.0, 101.0, 68.0, 26.; MS (EI) *m/z*: calcd. for $C_{10}H_{11}BrO_2$ 241.99 $[M]^+$, found 241.02.

2,4,6-Tris[{3-([1,3]-dioxan-2-yl)methyl}phenyl]-1,3,5-trimethylbenzene (6a). To a stirred solution of magnesium powder (183 mg, 7.5 mmol) in THF (5 mL) was added **4** (1.22 g, 5 mmol) and 1,2-dibromoethane (cat.) at room temperature under an argon atmosphere. The resulting mixture was stirred for additional 1 h. To this Grignard solution was added dropwise a THF (5 mL) solution of 1,3,5-tris(bromomethyl)mesitylene **5** (399 mg, 1.0 mmol) and copper iodide (19 mg, 0.1 mmol) at 60 °C. After being stirred for additional 12 h, the reaction mixture was allowed to cool to room temperature, and it was quenched with saturated aqueous $NaHCO_3$ (10 mL) solution. The resulting solution was diluted with ethyl acetate (10 mL), washed with brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. Purification of the residue by column chromatography (hexane : EtOAc, 3 : 2) afforded dioxane **6a** (579.4 mg, 89%) as a white solid: mp 60-62 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.41-1.46 (m, 3H), 2.01 (s, 9H), 2.12-2.28 (m, 3H), 3.97 (dt, J = 2.4, 12.2 Hz, 6H), 4.13, (s, 3H), 4.26 (dd, J = 4.9, 11.0 Hz, 6H), 5.46 (s, 3H), 6.83 (d, J = 7.5 Hz, 3H), 7.20 (t, J = 7.5 Hz, 3H), 7.31-7.36 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.0, 139.3, 135.5, 135.2, 129.1, 128.4, 126.3, 124.1, 102.5, 68.0, 36.8, 26.4, 17.5; MS (FAB) *m/z*: calcd. for $C_{42}H_{48}O_6$ 649.35 $[M+1]^+$, found 649.35.

2,4,6-Tris[{3-([1,3]-dioxan-2-yl)methyl}phenyl]-1,3,5-triethylbenzene (6b). This compound was prepared following the same procedure as for **6a**, using dioxane **4** (1.11 g, 4.6 mmol) and 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene **5b** (441 mg, 1.0 mmol) and copper iodide (57 mg, 0.3 mmol). Purification by column chromatography (hexane : EtOAc, 3 : 2) afforded **6b** (449 mg, 65%) as a white solid: mp 100-102 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.05 (t, J = 7.5 Hz, 9H), 1.41-1.46 (m, 3H), 2.13-2.22 (m, 3H), 2.36 (q, J = 7.5 Hz, 6H), 3.97 (dt, J = 2.4, 12.2 Hz, 6H), 4.13, (s, 6H), 4.26 (dd, J = 4.9, 10.8 Hz, 6H), 5.46 (s, 3H), 6.77 (d, J = 7.5 Hz, 3H), 7.18 (t, J = 7.6 Hz, 3H), 7.24-7.32 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.1, 141.0, 139.1, 134.2, 129.0, 128.3, 126.4, 124.1, 102.4, 68.0, 35.1, 26.4, 24.3, 15.8; MS (FAB) *m/z*: calcd. for $C_{45}H_{54}O_6$ 690.39 $[M+1]^+$, found 691.38.

2,4,6-Tris[{(3-formyl)phenyl}methyl]-1,3,5-trimethylbenzene (7a). To an acetone (5 mL) solution of tris-[1,3]-dioxane **6a** (570 mg, 0.878 mmol) was added 2.5% aqueous HCl solution (1 mL) at room temperature. After being stirred for several hours, the mixture was treated with saturated aqueous $NaHCO_3$ (15 mL) solution and diluted with ethyl acetate (15 mL). Extractive workup and purification by column chromatography (hexane : EtOAc, 3 : 2) afforded **7a** (331.4 mg, 80%) as a white solid: mp 125-127 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.14 (s, 9H), 4.25, (s, 6H), 7.33 (d, J = 7.7 Hz, 3H), 7.45 (t, J = 7.6 Hz, 3H), 7.55 (s, 3H), 7.69 (d, J = 7.5 Hz, 3H), 9.96 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.2, 142.0, 137.3, 135.6, 135.1, 134.6, 129.8, 129.2, 128.4, 36.5, 17.5; MS (FAB) *m/z*: calcd. for $C_{33}H_{30}O_3$ 475.22 $[M+1]^+$, found 475.38.

2,4,6-Tris[{(3-formyl)phenyl}methyl]-1,3,5-triethylbenzene (7b). This compound was prepared following the same procedure as for **7a** using dioxane **6b** (324.5 mg, 0.5 mmol). Purification by column chromatography (hexane : EtOAc, 7 : 3) afforded **7b** (142 mg, 55%) as a viscous oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10 (t, J = 7.5 Hz, 9H), 2.40 (q, J = 7.5 Hz, 6H), 4.24 (s, 9H), 7.33 (d, J = 7.6 Hz, 3H), 7.46 (t, J = 7.5 Hz, 3H), 7.51 (s, 3H), 7.68 (d, J = 7.5 Hz, 3H), 9.96 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.4, 193.0, 142.9, 142.3, 137.3, 137.3, 134.5, 134.2, 129.8, 129.1, 128.9, 128.6, 128.4, 34.8, 24.4, 15.9.

2,4,6-Tris[{3-(2,2,2-trifluoroacetyl)phenyl}methyl]-1,3,5-trimethylbenzene (1a). To a DME (10 mL) solution of trialdehyde **7a** (247 mg, 0.52 mmol) and carefully dried cesium fluoride (cat.) was added $TMSCF_3$ (0.5 M solution in THF, 6 mL, 2.6 mmol) at 0 °C under an argon atmosphere. After l being stirred for additiona 12 h at room temperature, the reaction mixture was treated with 10% aqueous HCl (1 mL) solution and diluted with ethyl acetate (20 mL). Extractive workup and purification by column chromatography (hexane : EtOAc, 3 : 2) afforded alcohol **8a** (320.4 mg, 90 %) as a viscous oil. To a stirred solution of Dess-Martin periodinane (2.08 g, 4.9 mmol) in dry CH_2Cl_2 (30 mL, 0.16 M) was added a CH_2Cl_2 (1 mL) solution of the alcohol **8a** (280.4 mg, 0.41 mmol) at room temperature. After being stirred for 12 h, the resulting reaction mixture was diluted with diethyl ether (40 mL), and it was poured into a sodium thiosulfate solution (40 mL, 0.26 M in saturated aqueous sodium bicarbonate). Extractive workup with diethyl ether and purification by column chromatography (hexane : EtOAc, 3 : 2) afforded **1a** (238.9 mg, 86%) as a white solid. An analytically pure sample was obtained after recrystallization from CH_2Cl_2-hexane: mp 89-90 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.14 (s, 9H), 4.26 (s, 6H), 7.24 (d, J = 8.3 Hz, 6H), 8.01 (d, J = 7.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.9, 181.4, 180.9, 180.5 (q, J = 34.7 Hz, -$\underline{C}$OCF$_3$), 142.1, 135.8, 135.5, 134.9, 130.8, 130.8, 130.0, 128.5, 123.1, 119.2, 115.4, 111.5 (q, J = 289.6 Hz, -$\underline{C}$F$_3$), 36.5, 17.5; ^{19}F NMR (300 MHz, $CDCl_3$) δ 5.05; HRMS (EI) *m/z*: calcd. for $C_{36}H_{27}F_9O_3$ 677.1816 $[M]^+$, found 677.1812.

2,4,6-Tris[{3-(2,2,2-trifluoroacetyl)phenyl}methyl]-1,3,5-triethylbenzene (1b). This compound was prepared following the same procedure as for **1a** using trialdehyde **7b** (83.1 mg, 0.16 mmol). Purification by column chromatography (hexane : EtOAc, 7 : 3) afforded **1b** (97.3 mg, 97% for two steps) as a viscous liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ

1.15 (t, J = 7.5 Hz, 9H), 2.40 (q, J = 7.5 Hz, 6H), 4.24 (s, 6H), 7.38 (d, J = 7.7 Hz, 3H), 7.48 (t, J = 7.7 Hz, 3H), 7.74 (s, 3H), 7.88 (d, J = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.8, 181.4, 180.9, 180.4 (q, J = 34.6 Hz, -$\underline{C}OCF_3$), 142.9, 142.5, 135.5, 134.0, 130.8, 130.0, 129.9, 129.7, 128.7, 128.4, 123.1, 119.2, 115.4, 111.5 (q, J = 289.6 Hz, -CF_3), 34.9, 24.4, 15.8; ^{19}F NMR (300 MHz, $CDCl_3$) δ 5.02; HRMS (EI) m/z: calcd for $C_{39}H_{33}F_9O_3$ 720.2286 $[M]^+$, found 720.2288.

2,4,6-Tris[{4-(2,2,2-trifluoroacetyl)phenyl}methyl]-1,3,5-trimethylbenzene (2). This compound was prepared following the same procedure as for **1a**: mp 160-163 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.14 (s, 9H), 4.26 (s, 6H), 7.24 (d, J = 8.3 Hz, 6H), 8.01 (d, J = 7.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.4, 180.9, 180.5, 180.0 (q, J = 34.7 Hz, -$\underline{C}OCF_3$), 149.7, 135.9, 134.7, 131.2, 129.2, 128.6, 123.2, 119.3, 115.5, 111.6 (q, J = 289.6 Hz, -CF_3), 37.3, 17.6; ^{19}F NMR (300 MHz, $CDCl_3$) δ 5.05; HRMS (EI) m/z: calcd. for $C_{36}H_{27}F_9O_3$ 677.1816 $[M]^+$, found 678.1809.

1,3,5-Tribromo-2,4,6-tris(bromomethyl)benzene (10). This compound was prepared from known 2,4,6-tribromomesitylene. The mixture of 2,4,6-tribromomesitylene **9** (3.57 g, 10 mmol), *N*-bromosuccinimide (6.4 g, 36 mmol) and benzoyl peroxide (121 mg, 0.5 mmol) in carbon tetrachloride (70 mL) was refluxed under a sun lamp (250 W) for 20 h. The reaction mixture was allowed to cool to room temperature and filtered through Celite. The filtered solid dissolved in acetone was heated to dissolve succinimide, and it was kept in a refrigerator for 12 h. The solid product was collected by filteration, washed with cold acetone, and dried *in vacuo* to afford **10** (2.53 g, 85%) as a white solid. This compound was analytically pure and needs no further purification: mp 231-233 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.92 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 129.2, 36.2; MS (EI) m/z: calcd. for $C_9H_6Br_6$ 587.56 $[M]^+$, found 587.56 $[M]^+$, 589.59 [5 ^{79}Br + ^{81}Br], 591.59 [4 ^{79}Br + 2 ^{81}Br], 593.59 [3 ^{79}Br + 3 ^{81}Br], 595.58 [2 ^{79}Br + 4 ^{81}Br], 597.57 [^{79}Br + 5 ^{81}Br], 599.57 [6 ^{81}Br].

2,4,6-Tris[{3-([1,3]-dioxan-2-yl)phenyl}methyl]-1,3,5-tribromobenzene (11). This compound was prepared following the same procedure as for **6a**, using dioxane **4** (1.09 g, 4.5 mmol), 1,3,5-tribromo-2,4,6-tris(bromomethyl)benzene **10** (490 mg, 0.825 mmol), and copper iodide (57 mg, 0.3 mmol). Purification by column chromatography (hexane : EtOAc, 3 : 2) afforded dioxane **11** (170.7 mg, 24.2%) as a white solid: mp 102-104 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.41-1.46 (m, 3H), 2.13-2.30 (m, 3H), 3.93 (dt, J = 2.1, 12.2 Hz, 6H), 4.25 (dd, J = 4.9, 9.6 Hz, 6H), 4.60 (s, 3H), 5.46 (s, 3H), 6.93 (d, J = 7.5 Hz, 3H), 7.19-7.40 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.6, 139.7, 139.4, 138.1, 129.1, 129.0, 128.6, 126.9, 124.6, 102.3, 68.0, 45.3, 26.4; MS (FAB) m/z: calcd. for $C_{39}H_{39}Br_3O_6$ 841.03 $[M+1]^+$, found 841.15 $[M + 1]^+$, 844.96 [^{79}Br + 2 ^{81}Br], 846.87 [3 ^{81}Br].

2,4,6-Tris[{3-([1,3]-dioxan-2-yl)phenyl}methyl]-1,3,5-tris(dodecylsulfanyl)benzene (12). To a DME (1 mL) solution of **11** (200 mg, 0.237 mmol) and 1-dodecanthiol (0.455 mL, 1.89 mmol) was added sodium hydride (60% dispersion in mineral oil, 71 mg, 1.78 mmol) at 0 °C under an argon atmosphere. After 30 minutes at room temperature, the reaction mixture was heated at 70-80 °C for 9 h. After being cooled to room temperature, the reaction mixture was quenched with saturated aqueous ammonium chloride solution (5 mL), and diluted with ethyl acetate (5 mL). Extractive workup and purification by column chromatography (hexane : EtOAc, 4 : 1) afforded **12** (124.5 mg, 44%) as a viscous oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, J = 6.9 Hz, 9H), 1.09-1.30 (m, 60H), 1.40-1.46 (m, 3H), 2.13-2.27 (m, 9H), 3.96 (dt, J = 2.3, 12.2 Hz, 6H), 4.24 (dd, J = 4.9, 10.7 Hz, 6H), 4.93 (s, 6H), 5.44 (s, 3H), 6.81 (d, J = 7.4 Hz, 3H), 7.17 (t, J = 7.6 Hz, 3H), 7.24-7.30 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.4, 142.4, 139.1, 137.5, 128.9, 128.6, 127.1, 123.8, 102.5, 68.0, 41.7, 38.3, 32.6, 30.3, 30.2, 30.0, 30.0, 29.9, 29.6, 26.5, 23.4, 14.8; MS (FAB) m/z: calcd. for $C_{75}H_{114}O_6S_3$ 1206.78 $[M+1]^+$, found 1208.06.

2,4,6-Tris[{3-(2,2,2-trifluoroacetyl)phenyl}methyl]-1,3,5-tris(dodecylsulfanyl)benzene (3): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, J = 6.9 Hz, 9H), 1.10-1.30 (m, 60H), 2.29 (t, J = 7.4 Hz, 6H), 5.00 (s, 6H), 7.37-7.48 (m, 6H), 7.73 (s, 3H), 7.87 (d, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.8, 181.3, 180.9, 180.4 (q, J = 34.6 Hz, -$\underline{C}OCF_3$), 152.1, 143.4, 138.1, 136.1, 130.5, 130.4, 129.7, 128.4, 123.1, 119.3, 115.4, 111.5 (q, J = 289.7 Hz, -CF_3), 41.4, 38.7, 32.6, 30.3, 30.2, 30.1, 30.0, 29.9, 29.8, 29.6, 23.4, 14.8; ^{19}F NMR (300 MHz, $CDCl_3$) δ 5.08; HRMS (FAB) m/z: calcd. for $C_{69}H_{93}F_9O_3S_3$ 1237.6143 $[M+1]^+$, found 1237.5906.

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