Buttressing Effects Rerouting the Deprotonation and Functionalization of 1,3-Dichloro- and 1,3-Dibromobenzene

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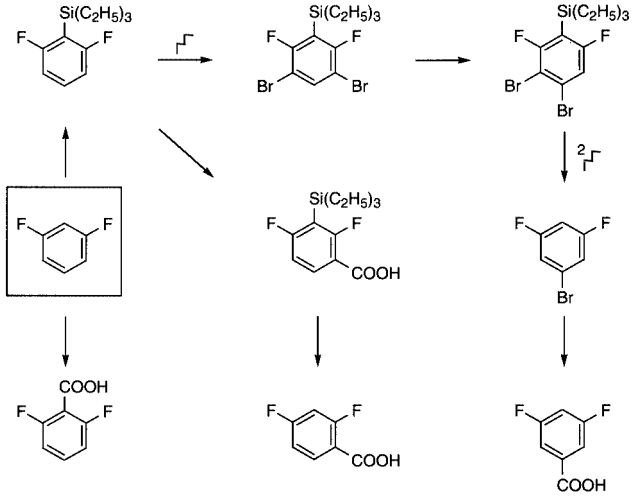
A systematic comparison between 1,3-difluorobenzene, 1,3-dichlorobenzene, and 1,3-dibromobenzene did not reveal major differences in their behavior towards strong bases such as lithium diisopropylamide or lithium 2,2,6,6-tetramethylpiperidide. Thus, all 2,6-dihalobenzoic acids **1** are directly accessible by consecutive treatment with a suitable base and dry ice. In contrast, (2,6-dichlorophenyl)- and (2,6-bromophenyl)triethylsilane (**2a** and **2b**) were found to undergo deprotonation at the 5-position (affording acids **3** and, after deprotection, **4**), whereas the 1,3-difluoro analog is known to react at the 4-position. The 2,4-dihalobenzoic acids **7** were selectively prepared from either the silanes **2** (by bromination at the 4-position, metalation and carboxylation of the neighboring position, followed by desilylation and debromination) or the 1,3-dihalo-2-iodobenzenes **8** (by base-promoted migration of iodine to the 4-position followed by iodine/magnesium permutation and subsequent carboxylation).

Introduction

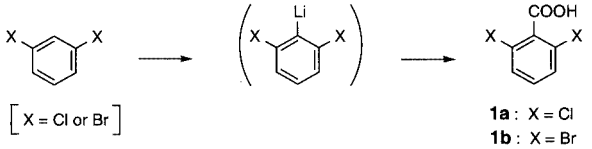
We have previously shown how 1,3-difluorobenzene can be elaborated to the three conceivable benzoic acids.[1] The 2,6-difluoro isomer was obtained in one step by the metalation of the starting material with *sec*-butyllithium followed by carboxylation. The preparation of the 2,4-difluoro isomer was also straightforward. The most acidic 2-position having been blocked with a trialkylsilyl group, the attack of the organometallic base was deflected to the next reactive 4-position. All that remained to be done after carboxylation was to remove the protective substituent. The route leading to the 3,5-difluoro isomer passed through six isolable intermediates. Despite its length, it was found to be economical and expedient.

An extension of this study to 1,3-dichlorobenzene and 1,3-dibromobenzene did not promise much excitement. We nevertheless embarked on this project, because it was not clear at the outset how one could convert 1,3-dibromobenzene into 3,5-dibromobenzoic acid without triggering "halogen scrambling" processes.[2] The 3,5-dibromobenzoic acid could, of course, be most conveniently prepared starting



from the commercial 1,3,5-tribromobenzene. One would simply have to treat this compound consecutively with butyllithium and carbon dioxide. However, our ambition was to derive all targeted acids from the same two substrates, namely 1,3-dichlorobenzene and 1,3-dibromobenzene.

It caused no trouble at all to obtain the 2,6-dichlorobenzoic acid (**1a**; 95%) and 2,6-dibromobenzoic acid (**1b**; 87%). The substrates were just deprotonated with lithium 2,2,6,6-tetramethylpiperidide (LITMP),[3] carboxylated with dry ice and isolated after neutralization.



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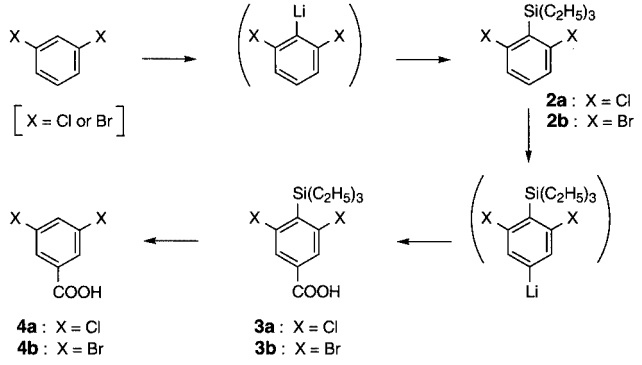
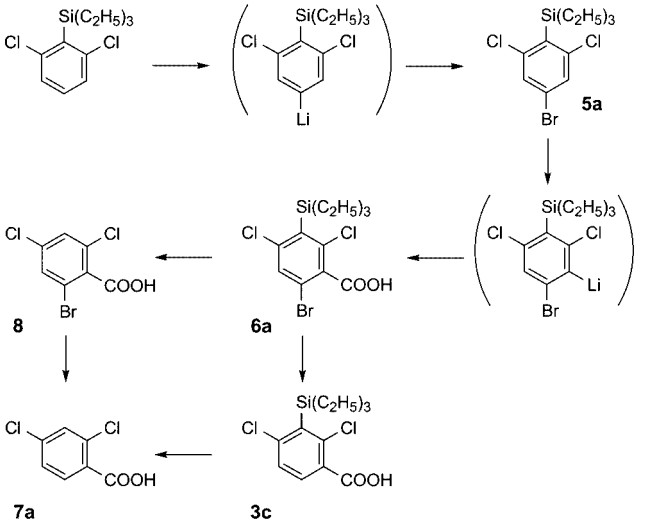
The silanes **2a** (89%) and **2b** (78%) were obtained analogously. Then (2,6-dichlorophenyl)triethylsilane (**2a**) was deprotonated with LITMP before pouring the mixture onto freshly crushed dry ice. To our great surprise, the reaction product turned out to be 3,5-dichloro-4-(triethylsilyl)benzoic acid (**3a**; 71%) rather than the expected 2,4,3-isomer. The same compound was formed in 52% and 61% yields, respectively, when LITMP was replaced by lithium diisopropylamide (LIDA) or *sec*-butyllithium. (2,6-Dichlorophenyl)tri*methyl*silane, when treated consecutively with *sec*-butyllithium and dry ice, gave the 3,5-dichloro-4-(trimethylsilyl)benzoic acid (59%) again as the sole derivative. To achieve the deprotonation of (2,6-dibromophenyl)triethylsilane (**2b**) one had to employ the "Faigl mix"[4] (LITMP in the presence of potassium *tert*-butoxide and *N*,*N*′,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine) as the base. Carboxylation provided the isomerically uncontaminated 3,5-dibromo-4-(triethylsilyl)benzoic acid (**3b**; 42%). Desilylation to the 3,5-dichlorobenzoic acid (**4a**; 91%) and the 3,5-dibromobenzoic acid (**4b**; 90%) was accomplished with potassium hydroxide.

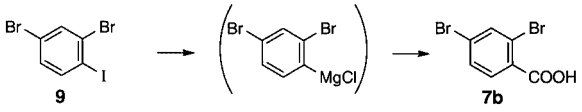


The unforeseen site selectivity in favor of the halogen remote position simplified the task of preparing the remaining 2,4-dihalobenzoic acids **7a** and **7b**. The (4-bromo-2,6-dichlorophenyl)triethylsilane (**5a**) was made by the consecutive treatment of silane **2a** with *sec*-butyllithium and bromine. Deprotonation with LITMP and carboxylation afforded 6-bromo-2,4-dichloro-3-(triethylsilyl)benzoic acid (**6a**; 93%) and, after base-promoted desilylation and subsequent reductive debromination, respectively 2-bromo-4,6-dichlorobenzoic acid (**8**; 98%) and 2,4-dichlorobenzoic acid (**7a**; 98%). The acid **7a** was also obtained *via* the intermediate **3c** by simple inversion of the debromination and desilylation steps.

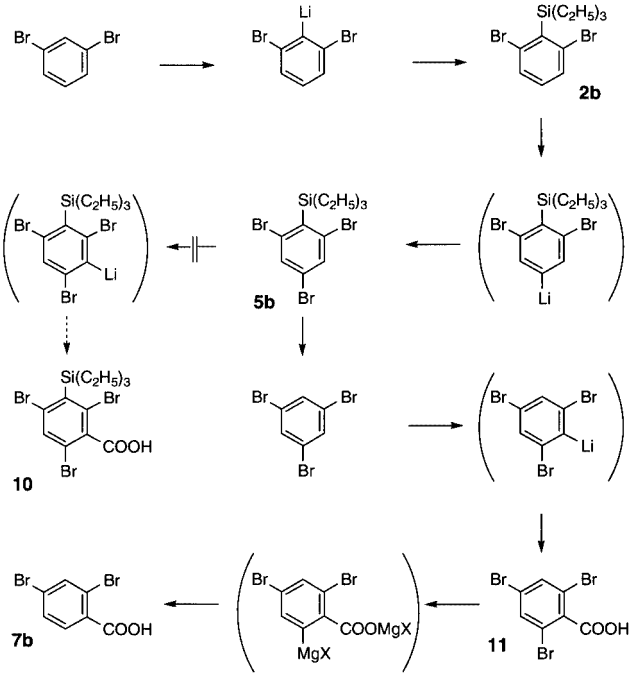
The 2,4-dibromobenzoic acid (**7b**) was prepared from the readily accessible [5] 2,4-dibromo-1-iodobenzene (**9**) by iodine/metal permutation using isopropylmagnesium chloride followed by carboxylation and neutralization in a 91% yield. The reaction was less clean when butyllithium was employed as the base.

For reasons of thematic coherence, we also wanted to make the acid **7b** starting from 1,3-dibromobenzene. Upon consecutive treatment with LITMP, chlorotriethylsilane,

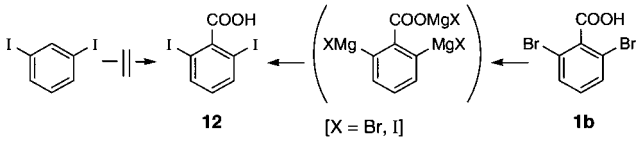




again LITMP and 1,2-dibromo-1,1,2,2-tetrafluoroethane, the (2,4,6-tribromophenyl)triethylsilane (**5b**; 47%) was obtained. This silane, being totally inert towards bases,[6] could not be subjected to the standard deprotonation/carboxylation sequence to give acid **10**. Therefore, silane **5b** was deprotected to give 1,3,5-tribromobenzene, a commercial and expensive product. Subsequent deprotonation and carboxylation afforded the 2,4,6-tribromobenzoic acid **11**[6] (88%). The selective removal of one *ortho*-bromo substituent was accomplished with lithium tributylmagnesiate,[7–9] the acid **7b** being isolated in a 92% yield.



The reaction sequences starting from 1,3-dichlorobenzene and 1,3-dibromobenzene could not be extended to 1,3-diiodobenzene. Lacking sufficient acidity, the latter substrate was not amenable to deprotonation. The 2,6-diiodobenzoic acid (**12**) was found to be accessible by subjecting the dibromo analogous compound **1b** to a double magnesiate-promoted halogen/metal permutation, followed by treatment with elemental iodine.



The metalation of the 2,6-dichloro- and 2,6-dibromosilanes (**2a** and **2b)** at a position not adjacent to, but remote from, an "*ortho*-directing" group is without precedent. The related case of 1,3-bis(trifluoromethyl)benzene has already received much attention. Whereas the superbasic mixture of butyllithium and potassium *tert*-butoxide abstracts a proton exclusively from the most activated 2-position[10] and LITMP cleanly from the 4-position,[11] *tert*-butyllithium produces a 1:1 mixture of 4- and 5-lithiated species.[11] This result, a singular exception, can be confidently attributed to a steric bias against the proximity between a bulky substituent and a bulky reagent. The behavior of the (2,6-dichlorophenyl)triethylsilane (**2a**) and (2,6-dibromophenyl)triethylsilane falls into another category. If once again a "buttressing effect" manifests itself, it cannot be one of the familiar kind.[12–18] At the moment we have to content ourselves to draw attention to the phenomenon rather than to fathom its origins.

Experimental Section

Working practices and abbreviations are specified in previous articles from this laboratory.[19–21] ^{1}H and ^{1}H-decoupled ^{13}C NMR spectra were recorded of samples dissolved in deuteriochloroform at 400 and 101 MHz, respectively, relative to the internal standard tetramethylsilane (chemical shift $\delta = 0.00$ ppm).

1. Halobenzoic Acids

2,6-Dichlorobenzoic Acid (1a): 1,3-Dichlorobenzene (3.0 mL, 3.7 g, 25 mmol) was added to a solution of butyllithium (25 mmol) in hexanes (15.8 mL) and tetrahydrofuran (30 mL) kept in a dry-ice bath for 45 min before being poured on an excess of freshly crushed dry ice. The mixture was briefly stirred before an ethereal solution (15 mL) of 2.0 M hydrogen chloride (30 mmol) was added under shaking. The volatiles were evaporated and the residue was extracted with boiling ethyl acetate (3 × 15 mL). Upon filtration and concentration of the combined organic layers, the product crystallized as tiny colorless needles (from hexanes); m.p. 142–144 °C (ref.[22] m.p. 147 °C); yield: 4.54 g (95%). ^{1}H NMR: $\delta = 7.3$ (m) ppm.

2,6-Dibromobenzoic Acid (1b): 2,2,6,6-Tetramethylpiperidine (4.1 mL, 3.5 g, 25 mmol) and 1,3-dibromobenzene (3.1 mL, 5.9 g, 25 mmol) were added consecutively to a solution of butyllithium (25 mmol) in hexanes (16 mL) and tetrahydrofuran (40 mL) kept in a methanol/dry ice bath. After 2 h at −75 °C, the mixture was poured on an excess of freshly crushed solid carbon dioxide and worked up as described in the preceding paragraph, giving colorless needles (from hexanes); m.p. 144–146 °C (ref.[23] 146.5 °C); yield: 6.02 g (87%). ^{1}H NMR: $\delta = 7.59$ (d, $J = 8.0$ Hz, 2 H), 7.18 (t, $J = 8.0$ Hz, 1 H) ppm.

2,6-Diiodobenzoic Acid (12): 2,6-Dibromobenzoic acid (**1b**; 4.2 g, 15 mmol) in tetrahydrofuran (15 mL) was added to a solution of butyllithium (15 mmol) and butylmagnesium chloride (10 mmol) in tetrahydrofuran (70 mL) and hexanes (16 mL) at 0 °C. After 45 min at 0 °C, iodine (7.6 g, 30 mmol) in tetrahydrofuran (25 mL) was added. The reaction mixture was acidified with 2.0 M hydrochloric acid (10 mL) and washed with a saturated aqueous sodium sulfite solution (30 mL). The product was extracted with hexanes (3 × 50 mL). Crystallization from chloroform (30 mL) afforded tiny needles; m.p. 182–184 °C; (ref.[24] 184–187 °C); yield: 5.05 g (90%). ^{1}H NMR: $\delta = 7.87$ (d, $J = 8.0$ Hz, 2 H), 6.81 (t, $J = 7.9$ Hz, 1 H) ppm.

3,5-Dichlorobenzoic Acid (4a): 3,5-Dichloro-4-(triethylsilyl)benzoic acid (**3a**; 7.6 g, 25 mmol) and potassium hydroxide (5.5 g, 0.10 mol) were heated under reflux in a 4:1 (v/v) mixture of methanol and water (50 mL). After 2 h, the solvents were evaporated and the residue was acidified with an aqueous 2.0 M hydrochloric acid (5 mL) solution. The acid was extracted with diethyl ether (3 × 20 mL). Crystallization from hexanes (50 mL) gave colorless needles; m.p. 183–185 °C (ref.[25] m.p. 182.5–183.0 °C); yield: 4.34 g (91%). ^{1}H NMR: $\delta = 7.96$ (d, $J = 1.9$ Hz, 2 H), 7.59 (d, $J = 2.0$ Hz, 1 H) ppm.

3,5-Dibromobenzoic Acid (4b): 3,5-Dibromo-4-(triethylsilyl)benzoic acid (**3b**, 3.9 g, 10 mmol) was analogously protodesilylated as the acid **4a**; colorless needles; m.p. 218–220 °C (ref.[26] m.p. 213–214 °C); yield: 2.52 g (90%). ^{1}H NMR: $\delta = 8.18$ (d, $J = 1.8$ Hz, 2 H), 7.92 (t, $J = 1.8$ Hz, 1 H) ppm.

2,4-Dichlorobenzoic Acid (7a): 2-Bromo-3,5-dichlorobenzoic acid (**8a**; 2.7 g, 10 mmol) and zinc dust (2.6 g, 40 mmol) in a 10% aqueous sodium hydroxide solution (5 mL) were stirred at 25 °C. After 2 h, a 2.0 M aqueous hydrochloric acid solution (5 mL) was added and the acid was extracted with diethyl ether (3 × 30 mL). Upon crystallization from hexanes (10 mL), colorless needles were obtained; m.p. 158–160 °C (ref.[25] 159–160 °C); yield: 1.86 g (98%). ^{1}H NMR: $\delta = 8.00$ (d, $J = 8.5$ Hz, 1 H); 7.52 (d, $J = 2.0$ Hz, 1 H); 7.36 (dd, $J = 8.5, 2.0$ Hz, 1 H) ppm. The acid **7a** was independently obtained in 92% yield by protodesilylation of 2,4-dichloro-3-(triethylsilyl)benzoic acid (**3c**, 1.53 g, 5.0 mmol) according to the standard protocol (see the preparation of acid **4a**).

2,4-Dibromobenzoic Acid (7b): 2,4,6-Tribromobenzoic acid (**10**; 5.4 g, 15 mmol) in tetrahydrofuran (15 mL) was added to a solution of butyllithium (20 mmol) and butylmagnesium chloride (10 mmol) in tetrahydrofuran (9 mL), hexanes (13 mL) and toluene (40 mL) at 0 °C. After 45 min at 0 °C, methanol (0.7 mL, 0.6 g, 18 mmol) was added. The reaction mixture was worked up as described for acid **1**. Crystallization from dichloromethane (10 mL) gave the acid **7b** as colorless needles; m.p. 168–170 °C (ref.[27] m.p. 166.5 °C); yield: 3.85 g (92%). ^{1}H NMR: $\delta = 7.91$ (d, $J = 8.4$ Hz, 1 H), 7.90 (d, $J = 2.0$ Hz, 1 H), 7.57 (dd, $J = 8.4, 2.0$ Hz, 1 H) ppm. The acid **7b** was also formed in a 91% yield when 2,4-dibromo-1-iodobenzene [5] (**9**, 9.0 g, 25 mmol) was added to a solution of butyllithium in hexanes (13 mL) and diethyl ether (60 mL) at −100 °C before 15 min later the mixture was treated with freshly crushed dry ice and was worked up (as described for acid **1)**.

3,5-Dichloro-4-(triethylsilyl)benzoic Acid (3a): (2,6-Dichlorophenyl)triethylsilane (**2a**, see Section 2; 11 mL, 13 g, 50 mmol) was added to a solution of *sec*-butyllithium (50 mmol) in cyclohexane (36 mL) and tetrahydrofuran (0.10 L) kept in a dry-ice bath. After 45 min at −75 °C, the reaction mixture was treated with an excess of freshly crushed dry ice and worked up as described for the acid **1**; colorless needles (from hexanes); m.p. 133−135 °C; yield: 10.8 g (71%). ^{1}H NMR: δ = 7.93 (s, 2 H), 1.1 (m, 6 H), 1.0 (m, 9 H) ppm. ^{13}C NMR: δ = 170.0, 142.7, 142.4, 131.5, 129.8, 7.5, 6.1 ppm. $C_{13}H_{18}Cl_2O_2Si$ (305.11): calcd. C 51.17, H 5.90; found C 51.28, H 5.85.

3,5-Dichloro-4-(trimethylsilyl)benzoic Acid: Analogously from (2,6-dichlorophenyl)trimethylsilane (**6**, 5.5 g, 25 mmol); colorless platelets after recrystallization from toluene; m.p. 148−149 °C; yield: 3.91 g (59%). ^{1}H NMR: δ = 7.93 (s, 2 H), 0.53 (s, 9 H) ppm. ^{13}C NMR: δ = 169.9, 143.8, 142.1, 131.5, 129.7, 2.6 ppm. $C_{10}H_{12}Cl_2O_2Si$ (263.20): calcd. C 45.64, H 4.60; found C 45.58, H 4.66.

3,5-Dibromo-4-(triethylsilyl)benzoic Acid (3b): 2,2,6,6-Tetramethylpiperidine (4.3 mL, 3.5 g, 25 mmol), potassium *tert*-butoxide (2.8 g, 25 mmol), *N*,*N*′,*N*′,*N*′′,*N*′′-(pentamethyl)diethylenetriamine (4.3 g, 25 mmol) and (2,6-dibromophenyl)triethylsilane (**2b**, 6.2 mL, 8.8 g, 25 mmol) were consecutively added to a solution of butyllithium (25 mmol) in hexanes (11 mL) and tetrahydrofuran (40 mL) at −100 °C. After 2 h, freshly crushed dry ice was added and the reaction mixture was worked up as described for the acid **1**; colorless needles (from hexanes); m.p. 157−159 °C; yield: 5.1 g (52%). ^{1}H NMR: δ = 8.20 (s, 2 H), 1.13 (q, *J* = 7.8 Hz, 6 H), 1.01 (t, *J* = 7.8 Hz, 9 H) ppm. ^{13}C NMR: δ = 170.4, 170.3, 147.0, 134.5, 131.8, 8.2, 6.8 ppm. $C_{13}H_{18}Br_2O_2Si$ (394.18): calcd. C 39.61, H 4.60; found C 39.96, H 4.48.

2,4-Dichloro-3-(triethylsilyl)benzoic Acid (3c): 6-Bromo-2,4-dichloro-3-(triethylsilyl)benzoic acid (see following paragraph; **6a**, 23 g, 60 mmol) was treated (0.12 L) with potassium carbonate (12 g, 15 mmol) and iodomethane (85 g, 40 mL, 60 mmol) at 60 °C during 12 h. Upon filtration of the salts and evaporation of the solvents, the methyl ester was obtained. Tributyltin hydride (11 mL, 12 g, 40 mmol) was added dropwise over a 15 min period to the methyl ester (16 g, 40 mmol) in benzene (40 mL). Then, α,α′-azobis(isobutyronitrile) (0.70 g, 4.0 mmol) was added in several portions over 10 min. After 3 h at 60 °C, toluene (30 mL) was added and the organic layer was washed with brine (2 × 25 mL) before being dried and evaporated. Distillation afforded a colorless oil; b.p. 114−115 °C/0.8 Torr; yield: 9.5 g (74%). The methyl ester (3.2 g, 10 mmol) was treated with potassium hydroxide (1.6 g, 20 mmol) in a 4:1 (v/v) mixture of ethanol and water (10 mL). After 2 h at 25 °C, the solvent was evaporated. A 2.0 M aqueous hydrochloric acid solution (5.0 mL) was added and the acid was extracted with diethyl ether (3 × 20 mL). After evaporation of the volatiles, a crystallization from hexanes (10 mL) gave colorless needles; m.p. 87−89 °C; yield: 2.78 g (91%). ^{1}H NMR: δ = 7.71 (d, *J* = 8.6 Hz, 1 H), 7.33 (d, *J* = 8.6 Hz, 1 H), 1.09 (q, *J* = 7.8 Hz, 6 H), 0.99 (t, *J* = 7.8 Hz, 9 H) ppm. ^{13}C NMR: δ = 171.6, 146.3, 141.3, 138.0, 132.3, 129.1, 128.5, 8.0, 6.5 ppm. $C_{13}H_{18}Cl_2O_2Si$ (305.10): calcd. C 51.17, H 5.90; found C 51.33, H 5.97.

6-Bromo-2,4-dichloro-3-(triethylsilyl)benzoic Acid (6a): 2,2,6,6-Tetramethylpiperidine (17 mL, 14 g, 0.10 mol) and 4-bromo-2,6-(dichlorophenyl)triethylsilane (**5a**, 26 mL, 34 g, 0.10 mol) were consecutively added to a solution of butyllithium (0.10 mol) in hexanes (53 mL) and tetrahydrofuran (0.15 L) at −75 °C. After 2 h, freshly crushed dry ice was added. The reaction mixture was worked up as described for the acid **1**; colorless needles (from hexanes); m.p. 119−122 °C; yield: 35.7 g (93%). ^{1}H NMR: δ = 7.55 (s, 1 H), 1.1 (m, 6 H), 1.0 (m, 9 H) ppm. ^{13}C NMR: δ = 169.9, 143.3, 138.3, 135.7, 134.8, 132.1, 120.0, 7.7, 6.0 ppm. $C_{13}H_{17}BrCl_2O_2Si$ (384.17): calcd. C 40.69, H 4.46; found C 40.47, H 4.21.

2-Bromo-4,6-dichlorobenzoic Acid (8): 6-Bromo-2,4-dichloro-3-(triethylsilyl)benzoic acid (**6a**, 7.7 g, 20 mmol) was protodesilylated analogously as the acid **4a**; colorless needles (from hexanes); m.p. 159−161 °C; yield: 4.89 g (90%). ^{1}H NMR: δ = 7.58 (d, *J* = 1.9 Hz, 1 H), 7.43 (d, *J* = 1.9 Hz, 1 H) ppm. ^{13}C NMR: δ = 168.5, 136.5, 132.8, 132.0, 130.6, 128.1, 119.8 ppm. $C_7H_3BrCl_2O_2$ (269.86): calcd. C 31.15, H 1.11; found C 31.37, H 1.17.

2,4,6-Tribromobenzoic Acid (11): Diisopropylamine (7.4 mL, 5.1 g, 50 mmol) and 1,3,5-tribromobenzene (16 g, 50 mmol) were consecutively added to a solution of butyllithium (50 mmol) in hexanes (22 mL) and tetrahydrofuran (80 mL). After 2 h, freshly crushed dry ice was added. The reaction was worked up in the same manner as described for the acid **1**; colorless needles (from chloroform); m.p. 188−190 °C (ref.[28] m.p. 189−190 °C); yield: 15.9 g (88%). ^{1}H NMR: δ = 7.89 (s) ppm.

2. Miscellaneous

(2,6-Dichlorophenyl)triethylsilane (2a): 1,3-Dichlorobenzene (23 mL, 29 g, 0.20 mol) was added to a solution of *sec*-butyllithium (0.20 mol) in cyclohexane (0.12 L) and tetrahydrofuran (0.18 L) at −75 °C. After 45 min at −75 °C, chlorotriethylsilane (34 mL, 30 g, 0.20 mol) was added to the mixture. After 45 min at −75 °C, the reaction mixture was distilled without prior workup to afford a colorless oil; b.p. 143−145 °C/8 Torr; n_D^{20} = 1.4781; d_4^{20}= 1.195; yield: 46.5 g (89%). ^{1}H NMR: δ = 7.3 (m, 2 H), 7.1 (m, 1 H), 1.1 (m, 6 H), 1.0 (m, 9 ppm. ^{13}C NMR: δ = 142.3, 135.1, 130.0, 128.6, 7.9, 6.1 ppm. $C_{12}H_{18}Cl_2Si$ (261.11): calcd. C 55.19, H 6.89; found C 55.26, H 6.91.

(2,6-Dichlorophenyl)trimethylsilane: Analogously from 1,3-dichlorobenzene (5.7 mL, 7.4 g, 50 mmol) using chlorotrimethylsilane (6.3 mL, 5.4 g, 50 mmol); colorless liquid after distillation of the reaction mixture; b.p. 79−81 °C/4 Torr (ref.[29]: b.p. 52 °C/0.3 Torr); n_D^{20} = 1.5432 (ref. [29]: n_D^{20} = 1.5427); yield: 4.69 g (79%). ^{1}H NMR: δ = 7.22 (d, *J* = 7.9 Hz, 2 H), 7.13 (t, *J* = 7.9 Hz, 1 H), 0.51 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 142.6, 137.2, 131.5, 129.6, 3.8 ppm.

(2,6-Dibromophenyl)triethylsilane (2b): 2,2,6,6-Tetramethylpiperidine (16 mL, 14 g, 0.10 mol) and 1,3-dibromobenzene (12 mL, 23 g, 0.10 mol) were consecutively added to a solution of butyllithium (0.10 mol) in hexanes (16 mL) and tetrahydrofuran (35 mL) kept in a methanol/dry ice bath. After 2 h at −75 °C, chlorotriethylsilane (17 mL, 15 g, 0.10 mol) was added. Then, a 2.0 M aqueous hydrochloric acid solution (50 mL) was added and the product was extracted with hexanes (3 × 0.10 L). The product was distilled after it was dried and the solvents evaporated, affording a colorless oil; b.p. 97−99 °C/0.6 Torr; n_D^{20} = 1.5090; d_4^{20} = 1.420; yield: 27.3 g (78%). ^{1}H NMR: δ = 7.51 (d, *J* = 8.0 Hz, 2 H), 7.27 (t, *J* = 8.0 Hz, 1 H), 1.13 (q, *J* = 8.0 Hz, 6 H), 1.00 (t, *J* = 8.0 Hz, 9 H) ppm. ^{13}C NMR: δ = 139.3, 133.0, 131.8, 130.8, 8.3, 6.8 ppm. $C_{12}H_{18}Br_2Si$ (350.17): calcd. C 41.16, H 5.18; found C 41.50, H 5.01.

(4-Bromo-2,6-dichlorophenyl)triethylsilane (5a): (2,6-Dichlorophenyl)triethylsilane (**2a**, 22 mL, 26 g, 0.10 mol) was added to a solution of *sec*-butyllithium (0.10 mol) in cyclohexane (70 mL) and tetrahydrofuran (0.20 L) at −75 °C. After 45 min at −75 °C, bromine (5.1 mL, 16 g, 0.10 mol) was added. The reaction mixture was

washed with a saturated aqueous solution of sodium hydrogen sulfite (50 mL). Upon extraction with hexanes (3 × 50 mL), distillation afforded a colorless oil; b.p. 122−123 °C/1 Torr; n_D^{20}= 1.5353; d_4^{20} = 1.314; yield: 21.4 g (63%). ^{1}H NMR: δ = 7.41 (s, 2 H), 1.1 (m, 6 H), 1.0 (m, 9 H) ppm. ^{13}C NMR: δ = 143.0, 134.5, 131.5, 123.8, 8.3, 6.5 ppm. $C_{12}H_{18}BrCl_2Si$ (340.01): calcd. C 42.38, H 5.00; found C 42.24, H 5.08.

(2,4,6-Tribromophenyl)triethylsilane (5b): 2,2,6,6-Tetramethylpiperidine (17 mL, 14 g, 0.10 mol), potassium *tert*-butoxide (11 g, 0.10 mol), *N*,*N*′,*N*′,*N*′′,*N*′′-(pentamethyl)diethylenetriamine (21 mL, 17 g, 0.10 mol) and (2,6-dibromophenyl)triethylsilane (**2b**, 25 mL, 35 g, 0.10 mol) were consecutively added to a solution of butyllithium (0.10 mol) in hexanes (65 mL) and tetrahydrofuran (0.14 L) at −100 °C. After 2 h, 1,2-dibromotetrafluoroethane (31 g, 0.12 mol) was added. The reaction mixture was washed with an aqueous 2.0 M hydrochloric acid solution (0.10 L). After extraction with hexanes (3 × 0.10 L), a distillation afforded a colorless oil; b.p. 130−132 °C/0.4 Torr; n_D^{20} = 1.5665; d_4^{20} = 1.843; yield: 19.7 g (46%). ^{1}H NMR: δ = 7.70 (s, 2 H), 1.1 (m, 6 H), 1.0 (m, 9 H) ppm. ^{13}C NMR: δ = 134.7, 131.9, 129.5, 120.2, 4.6, 3.3 ppm. $C_{12}H_{17}Br_3Si$ (429.07): calcd. C 33.59, H 3.99; found C 34.00, H 4.39.

1,3,5-Tribromobenzene: The product **5b** (9.3 mL, 17 g, 40 mmol) and potassium fluoride (9.3 g, 0.16 mol) in a 4:1 (v/v) of tetrahydrofuran and water (40 mL) were heated under reflux during 12 h. Upon extraction with hexanes (3 × 50 mL), the product was crystallized to give colorless needles (from pentanes); m.p. 118−120 °C (ref.[30] m.p. 118.5 °C); yield: 11.5 g (91%). ^{1}H NMR: δ = 7.80 (s) ppm.

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