Experimental details for the extraction, isolation, structure determination and synthesis of compound 1: 2',5,6'-trichloro-2,3'-dihydroxybibenzyl

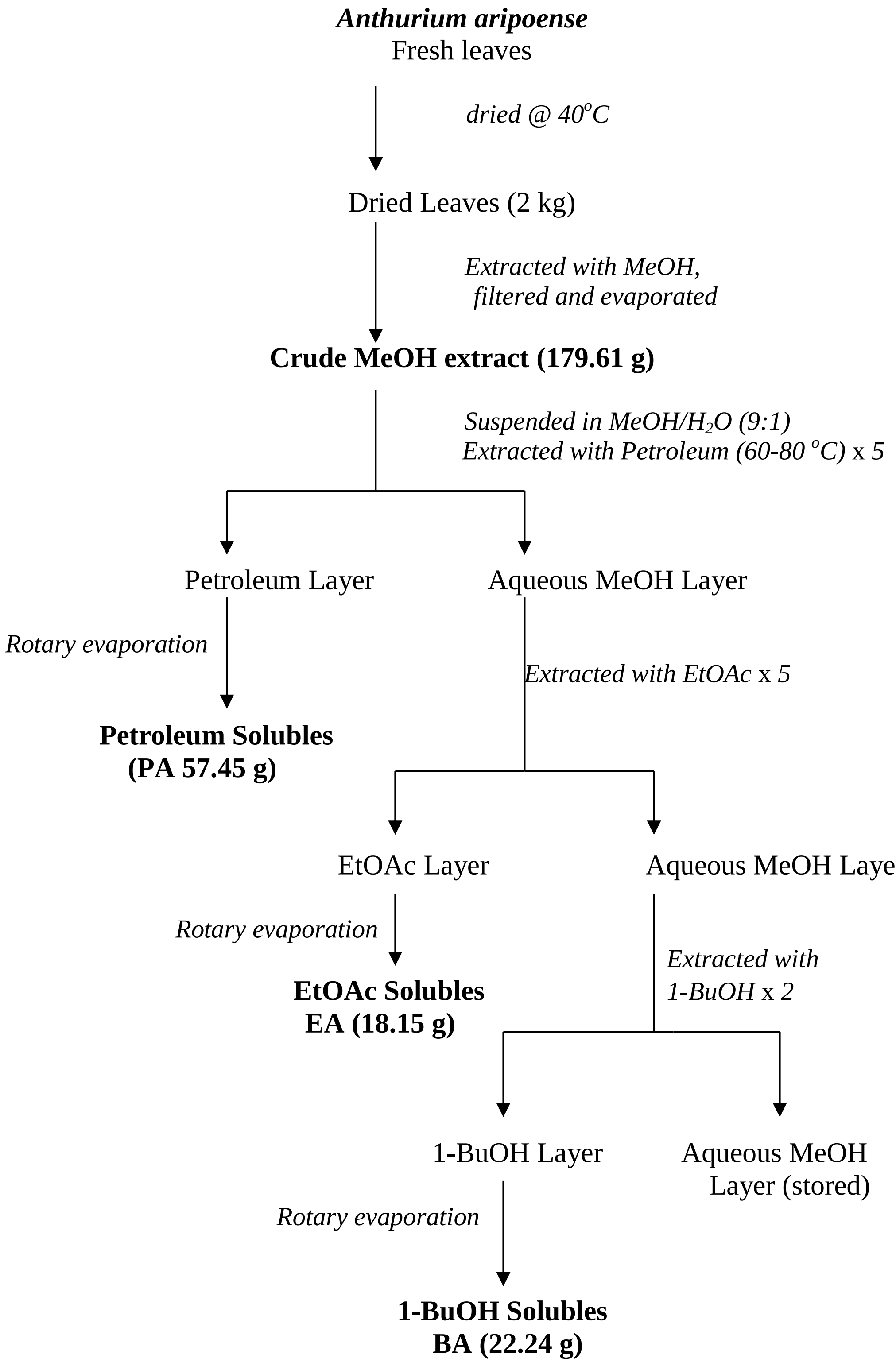
Collection and Extraction

Leaves of *Anthruium aripoense* were collected at an altitude of 750 m in the northern highlands of Trinidad by R. Ramsewak, J. Frank, W. Johnson and G. Beepath and identified by Mr Winston Johnson (National Herbarium of Trinidad and Tobago). A voucher specimen has been lodged at the National Herbarium of Trinidad and Tobago (No. TRIN 36517). The fresh leaves were oven dried at 40 °C for 3 days. The dried leaves (2.00 kg) were macerated in a Waring blender with MeOH (12 dm^3). The mixture was left to soak for 24 h, and extracted exhaustively with MeOH. The methanolic mixture was filtered and the filtrate was concentrated under reduced pressure to give a crude dark green, gummy extract (179.61 g).
The crude methanolic extract was suspended in MeOH/H_2O (9:1, 500 cm^3) and extracted sequentially with petroleum (5 × 700 cm^3), EtOAc (5 × 700 cm^3) and 1-BuOH (2 × 700 cm^3). Anhydrous sodium sulfate was used as the drying agent, the extracts were filtered, and the solvents were removed under reduced pressure. This resulted in petroleum solubles (PA, 57.45 g), EtOAc solubles (EA, 18.15 g), and 1-BuOH solubles (BA, 22.24 g) **(Scheme 1)**.

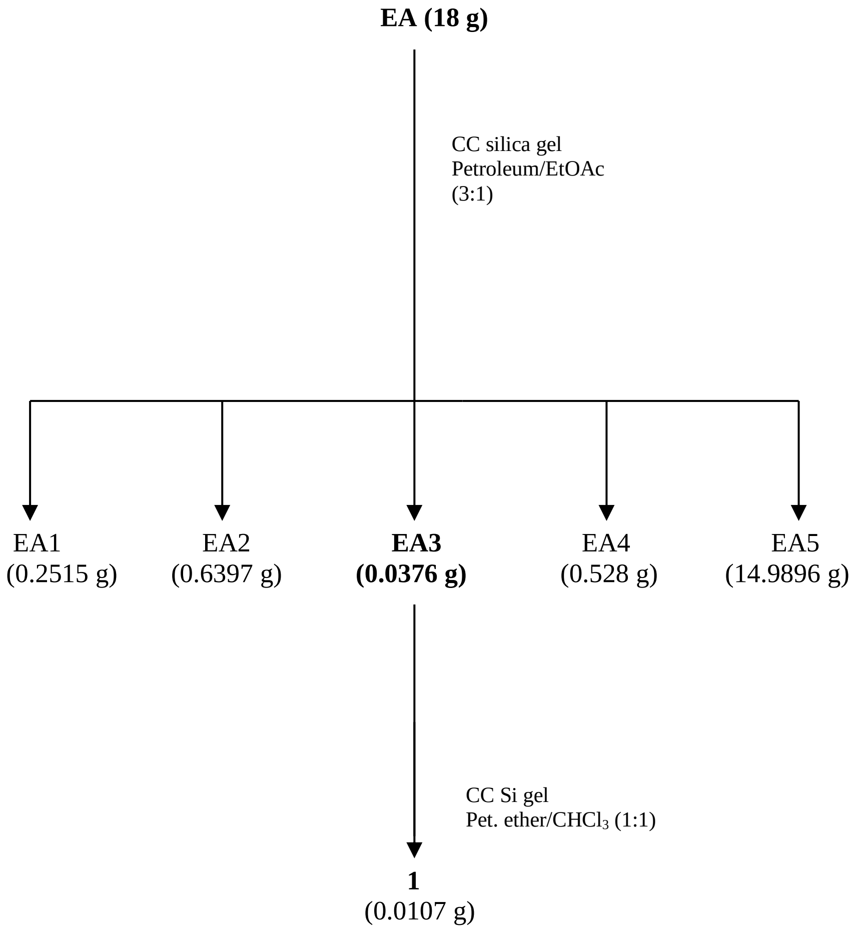
Isolation

The EtOAc extract (EA, 18 g) was subjected to isocratic silica gel column chromatography, eluting with petroleum/EtOAc (3:1). Seventy fractions were collected and combined on the basis of their TLC profiles on silica gel to obtain five combined fractions (EA1 to EA5).

Fraction EA3 was isocratically chromatographed over silica gel using petroleum/$CHCl_3$ (1:1) as the eluting solvent. There were three combined fractions (EA3-I to EA3-III) based on TLC evidence. Fraction EA3-II was identified as 2',5,6'-trichloro-2,3'-dihydroxybibenzyl **1** (0.0107 g) **(Scheme 2)**.



Scheme 1 Extraction Procedure for *Anthurium aripoense* leaves



Scheme 2 Isolation of Compound **1**

General Experimental Details (isolation and identification)

Melting point was determined on a Reichert melting point apparatus. IR spectra were acquired on a Perkin Elmer FTIR RX1 spectrophotometer and the sample was prepared as a concentrated solution. The UV-visible spectrum was recorded on a Varian CARY 50 UV-visible spectrophotometer using $CHCl_3$ as the solvent. The 1D and 2D NMR data, namely ^1H, ^{13}C, DEPT, COSY, HSQC, HMBC, and T-ROESY, were obtained from a Varian Unity-500 spectrometer at 500 MHz (^1H) and at 125 MHz (^{13}C). The sample was prepared in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. The chemical shift (δ) values are quoted in parts per million (ppm) and are to high frequency relative to the TMS signal. Mass spectral data were obtained from a Bruker Daltonics microTOF-Q ESI mass spectrometer.

Thin Layer Chromatography (TLC) were performed on a 0.25 mm thick Merck silica gel 60 F_{254} aluminium-backed plates. The chromatograms were visualized under UV light at 254 nm (short wave radiation) and 365 nm (long wave radiation). Ammonium molybdate (5 g ammonium molybdate in 10% sulfuric acid) was used as the spraying reagent for the TLC chromatograms.

Column chromatography was performed under gravity using Merck silica gel 60 (70-230 mesh). The solvents used were petroleum (bp 60-80 °C), $CHCl_3$, EtOAc, MeOH, and 1-

BuOH. All solvents used in the extraction, isolation and purification of compounds were distilled prior to use.

Identification of compound 1

Compound **1** was isolated as an off-white solid, mp 121–123 °C (value lowered by the presence of slight impurities). The IR spectrum exhibited absorption bands at 3375 cm^{-1} (OH), and 1592 cm^{-1} (C=C), whilst in the UV-vis spectrum, an absorbance at λ_{max} 285 nm (3.70) was observed.

HRESIMS of compound **1** showed an isotope pattern of $[M + H]^+$ ions (*m/z* 316.9863/318.9824/320.9777/322.9739) characteristic of a trichlorinated derivative. The molecular formula was deduced to be $C_{14}H_{11}O_2Cl_3$, which required eight double bond equivalents.

The ^{1}H NMR spectrum revealed the presence of nine protons; five of which were aromatic proton signals at δ 6.73 (d, J = 8.6 Hz, H-3'), δ 7.07 (dd, J = 8.6, 2.6 Hz, H-4'), δ 7.12 (d, J = 2.6 Hz, H-6'), δ 6.88 (d, J = 8.8 Hz, H-4") and δ 7.21 (d, J = 8.8 Hz, H-5"). There were two sets of methylene proton signals at δ 2.81 (m, H-1) and δ 3.17 (m, H-2).

Fourteen carbon atom signals were observed in the ^{13}C NMR spectrum. There were twelve aromatic carbon signals of which five CH signals were observed at δ 116.6 (C-3'), δ 127.4 (C-4'), δ 130.0 (C-6'), δ 114.8 (C-4"), and δ 128.7 (C-5"); seven quaternary aromatic carbon signals were observed at δ 128.8 (C-1'), δ 152.5 (C-2'), δ 125.4 (C-5'), δ 137.1 (C-1"), δ 121.2 (C-2"), δ 150.5 (C-3") and δ 125.9 (C-6"). Two carbon signals were attributed to methylene carbons at δ 28.5 (C-1) and δ 31.9 (C-2).

The chemical shift of the proton signals at δ 2.81 (m, H-1) and δ 3.17 (m, H-2) along with the DEPT, COSY and HMBC spectra revealed the presence of a $–CH_2–CH_2–$ group, of which each methylene carbon was attached to an aromatic ring. In the COSY spectrum, the methylene protons at δ 2.81 (m, H-1) correlated to the other methylene protons at δ 3.17 (m, H-2), and showed weak correlation to the aromatic proton at δ 7.12 (d, J = 2.6 Hz, H-6'). In the HMBC spectrum, the methylene protons at δ 2.81 (m, H-1) correlated to the methylene carbon at δ 31.9 (C-2) and four aromatic carbon signals at δ 128.8 (C-1')), δ 125.4 (C-5'), δ 130.0 (C-6') and δ 137.1 (C-1"); and the other methylene protons at δ 3.17 (m, H-2) showed long range correlations to the methylene carbon at δ 28.47 (C-1) and the aromatic signals at δ 137.1 (C-1"), δ 121.2 (C-2"), δ 128.7 (C-5") and δ 125.9 (C-6"). These results confirmed that the methylene carbon at δ 28.5 (C-1) was directly attached to the quaternary aromatic carbon at δ 128.8 (C-1'), and the other methylene carbon at δ 31.9 (C-2) was directly attached to the quarternary aromatic carbon at δ 137.1 (C-1") **(Figure 1)**.

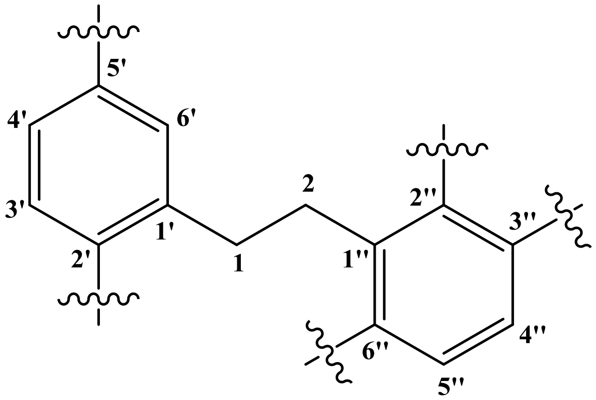


Figure 1 Partial Structure A

In the ^{1}H NMR spectrum, aromatic proton signals at δ 6.73 (d, *J* = 8.6 Hz, H-3'), δ 7.07 (dd, *J* = 8.6, 2.6 Hz, H-4') and δ 7.12 (d, *J* = 2.6 Hz, H-6') indicated the presence of a 1,2,5-trisubstituted aromatic ring. In the HMBC spectrum, the aromatic proton at δ 6.73 (d, *J* = 8.6 Hz, H-3') correlated to the quaternary aromatic carbons at δ 128.8 (C-1'), δ 152.5 (C-2') and δ 125.4 (C-5'); the aromatic proton signal at δ 7.07 (dd, *J* = 8.6, 2.6 Hz, H-4') showed long range correlations to the aromatic carbons at δ 152.5 (C-2'), δ 125.4 (C-5') and δ 130.0 (C-6'); and the aromatic proton at δ 7.12 (d, *J* = 2.6 Hz, H-6') correlated to the methylene carbon at δ 28.5 (C-1) and the aromatic carbons at δ 152.5 (C-2'), δ 127.4 (C-4') and δ 125.4 (C-5'). These results, as well as the DEPT spectrum, indicated that the carbon atoms at δ 128.8 (C-1'), δ 152.5 (C-2') and δ 125.4 (C-5') were the substituted carbon atoms **(Figure 1)**.

In theory the ^{13}C chemical shifts of aromatic carbon atoms directly attached to various substituents have been correlated with substituent electronegativity after correcting for magnetic anisotropic effects (relative to benzene as standard at 128.5 ppm). Chemical shifts for polysubstituted aromatic compounds can be predicted on the basis of the additivity of the chemical shifts of monosubstituted benzenes. It should be noted that the carbon atoms *ortho* and *para* to a carbon bearing an attached hydroxyl substituent are more shielded due to the mesomeric effect and, therefore, possess a more upfield chemical shift. The ^{13}C chemical shifts for Cl and OH substituted aromatic carbon atoms of monosubstituted benzenes are illustrated in **Table 1**.

Table 1 Selected ^{13}C substituent effects of monosubstituted benzenes[1,a]

Substituent	**Position**			
	C-1 ***ipso*** **(Attachment)**	**C-2** ***ortho***	**C-3** ***meta***	**C-4** ***para***
OH	+26.6	-12.7	+1.6	-7.3
Cl	+6.4	+0.2	+1.0	-2.0

[a] ^{13}C chemical shifts are in ppm and relative to TMS as the internal standard and benzene at 128.5 ppm

Therefore, the quaternary aromatic carbon atom at δ 152.5 (C-2') was attributed to an attached OH substituent whereas the quaternary aromatic carbon atom at δ 125.4 (C-5') was attributed to an attached Cl substituent.

The COSY spectrum confirmed the correlation between the two aromatic protons at δ 6.88 (d, *J* = 8.8 Hz, H-4'') and δ 7.21 (d, *J* = 8.8 Hz, H-5''). In the HMBC spectrum, the aromatic proton at δ 6.88 (d, *J* = 8.8 Hz, H-4") correlated to the quaternary aromatic carbons at δ 121.2 (C-2"), δ 150.5 (C-3") and δ 125.9 (C-6"); and the aromatic proton at δ 7.21 (d, *J* = 8.8 Hz, H-5") showed long range correlations to the aromatic carbons at δ 137.1 (C-1"), δ 150.5 (C-3") and δ 125.9 (C-6"). By referring to **Table 1**, it was confirmed that the quaternary aromatic carbon at δ 150.5 (C-3") was attributed to an attached OH substituent whereas the quaternary aromatic carbon atoms at δ 121.2 (C-2") and δ 125.9 (C-6") were attributed to attached Cl substituents **(Figure 1)**.

The ^{1}H and ^{13}C NMR data for **1** are represented in **Table 2**. Compound **1** was identified as **2',5,6'-trichloro-2,3'-dihydroxybibenzyl**.

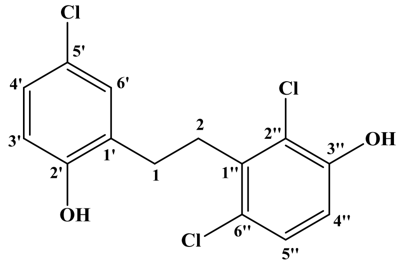


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Table 2 NMR data for Compound **1** [a]

Position	δ_C	δ_H	COSY	HMBC
1	28.5	2.81 (m)	H-2, H-6'	C-2, C-1', C-5', C-6', C-1"
2	31.9	3.17 (m)	H-1	C-1, C-1", C-2", C-5", C-6"
1'	128.8	--------	--------	--------
2'	152.5	--------	--------	--------
3'	116.6	6.73 (d, 8.6)	H-4'	C-1', C-2', C-5'
4'	127.4	7.07 (dd, 8.6, 2.6)	H-3', H-6'	C-2', C-5', C-6'
5'	125.4	--------	--------	--------
6'	130.0	7.12 (d, 2.6)	H-1, H-4'	C-1, C-2', C-4', C-5'
1"	137.1	--------	--------	--------
2"	121.2	--------	--------	--------
3"	150.5	--------	--------	--------
4"	114.8	6.88 (d, 8.8)	H-5"	C-2", C-3", C-6"
5"	128.7	7.21 (d, 8.8)	H-4"	C-1", C-3", C-6"
6"	125.9	--------	--------	--------

[a] Data acquired at 500 MHz (^{1}H) and 125 MHz (^{13}C) in $CDCl_3$ with TMS as the internal standard. Multiplicities and coupling constants (in Hz) are in parentheses.

Synthesis of 1

General Experimental Details (synthesis)

Infrared spectra were recorded for Nujol mulls on a Perkin Elmer 1420 instrument. NMR spectra were obtained for ^{1}H at either 300 or 400 MHz and for ^{13}C at 75 or 100 MHz using a Bruker Avance 500 instrument. All spectra were run in $CDCl_3$ with TMS as reference. Chemical shifts are reported in parts per million to high frequency of the reference and coupling constants *J* are in hertz. Mass spectra were obtained on a Micromass GCT mass spectrometer using Electrospray (ES) or Chemical Ionisation (CI). Melting points were determined using a Reichert hot-stage microscope. Microanalysis for carbon and hydrogen was carried out on a Carlo-Erba 1106 elemental analyser. Column chromatography was performed using silica gel of 40-63 μm particle size. TLC was performed using 0.2 mm layers of silica (Merck, Kieselgel 60F$_{254}$) on aluminium sheets. The components were observed under UV light.

5-Chloro-2-hydroxybenzaldehyde
A solution of 2-hydroxybenzaldehyde (44.9 g, 368 mmol) in acetic acid (150 cm^3) was stirred at RT while chlorine gas, generated by addition of conc HCl to potassium permanganate, was passed through it over 1.5 h. The mixture was stirred for a further 30 min and then the resulting solid was filtered off to give the title product (30.4 g, 53%) as colourless crystals, mp 99–101 °C (lit.,[2] 98 °C); δ_H 10.92 (1 H, s, OH), 9.85 (1 H, s, CHO), 7.54 (1 H, d, *J* 2.4), 7.48 (1 H, dd, *J* 8.8, 2.4) and 6.97 (1 H, d, *J* 8.8)

2-Benzyloxy-5-chlorobenzaldehyde 2
A solution of potassium hydroxide (11.1 g, 198 mmol) in ethanol (40 cm^3) was stirred while 5-chloro-2-hydroxybenzaldehyde (30.0 g, 192 mmol) was added, followed by a solution of benzyl bromide (23.0 cm^3, 33.0 g, 193 mmol) in ethanol (80 cm^3). The mixture was heated under reflux for 2 h and then allowed to cool and added to water (370 cm^3). The resulting solid was filtered off to give **2** (30.7 g, 65%) as a yellow solid, mp 78–80 °C (lit.,[3] 78–79 °C); δ_H 10.48 (1 H, s, CHO), 7.81 (1 H, d, *J* 2.8), 7.47 (1 H, dd, *J* 8.8, 2.8), 7.42–7.36 (5 H, m), 7.00 (1 H, d, *J* 8.8) and 5.19 (2 H, s).

2-Benzyloxy-5-chlorobenzyl alcohol 3
A solution of sodium borohydride (3.45 g, 91.2 mmol) in water (125 cm^3) was added dropwise to a solution of 2-benzyloxy-5-chlorobenzaldehyde (15.05 g, 60.8 mmol) in methanol (300 cm^3) stirred at RT. After 2 h, the mixture was acidified to pH 2 with 2 M HCl and partly evaporated under reduced pressure. The aqueous residue was extracted with CH_2Cl_2 (2 × 100 cm^3) and the combined extract was dried and evaporated to give the product **3** (13.82 g, 80%) as colourless crystals, mp 55–57 °C (HRMS (ES$^+$): found, 271.0508. $C_{14}H_{13}ClO_2Na$ (M+Na) requires 271.0502); ν_{max} 3370, 1605, 1487, 1240, 1127, 1021, 800, 732 and 695 cm^{-1}; δ_H 7.41–7.31 (5 H, m), 7.30 (1 H, d, *J* 2.8), 7.18 (1 H, dd, *J* 8.8, 2.8), 6.83 (1 H, d, *J* 8.8), 5.08 (2 H, s), 4.68 (2 H, s) and 2.15 (1 H, br s, OH) [agrees with lit.,[4]]; δ_C 154.8 (C), 136.3 (C), 131.3 (C), 128.7 (2CH), 128.3 (CH), 128.20 (CH), 128.18 (CH), 127.2 (2CH), 125.9 (C), 112.8 (CH), 70.4 (CH_2) and 61.2 (CH_2); *m/z* (ES) 270.88 (M+Na).

2-Benzyloxy-5-chlorobenzyl bromide 4
A solution of 2-benzyloxy-5-chlorobenzyl alcohol (5.36 g, 21.5 mmol) in toluene (90 cm^3) was stirred at RT while phosphorus tribromide (0.71 cm^3, 2.03 g, 7.5 mmol) was added. After stirring for 12 h the solution was washed with water (3 × 35 cm^3), dried and evaporated to give the product **4** (6.56 g, 98%) as pale yellow crystals, mp 61–62 °C (HRMS (CI): found, 231.0568. $C_{14}H_{12}ClO$ (M–Br) requires 231.0577); δ_H 7.45–7.28 (5 H, m), 7.26 (1 H, d, *J* 2.8), 7.13 (1 H, dd, *J* 8.8, 2.8), 6.75 (1 H, d, *J* 8.8), 5.04 (2 H, s) and 4.46 (2 H, s) [agrees with lit.,[4]]; δ_C 154.9 (C), 136.2 (C), 130.5 (CH), 129.6 (CH), 128.5 (2CH), 128.00 (C), 127.97 (CH), 127.0 (2CH), 125.4 (C), 113.4 (CH), 70.2 (CH_2) and 27.7 (CH_2); *m/z* (CI) 311.98 (^{81}Br-M$^+$, 3%), 231.05 (M–Br, 100).

2,6-Dichloro-3-hydroxybenzaldehyde
A solution of 3-hydroxybenzaldehyde (22.4 g, 184 mmol) in acetic acid (75 cm^3) was stirred at RT while chlorine gas, generated by addition of conc HCl to potassium permanganate, was passed through it over 1.5 h. The mixture was stirred for a further 30 min and then the resulting solid was filtered off and recrystallized from water to give the title product (20.3 g,

58%) as pale yellow crystals, mp 138–140 °C (lit.,[5] 140.5 °C); δ_H 10.46 (1 H, s, CHO), 7.32 (1 H, d, *J* 8.8), 7.19 (1 H, d, *J* 8.8) and 5.98 (1 H, s, OH).

3-Benzyloxy-2,6-dichlorobenzaldehyde 5

A solution of potassium hydroxide (6.3 g, 112 mmol) in ethanol (22 cm^3) was stirred while 2,6-dichloro-3-hydroxybenzaldehyde (20.0 g, 105 mmol) was added, followed by a solution of benzyl bromide (12.8 cm^3, 18.45 g, 108 mmol) in ethanol (44 cm^3). The mixture was heated under reflux for 2 h and then allowed to cool and added to water (210 cm^3). The resulting solid was filtered off to give **5** (19.4 g, 66%) as a yellow solid, mp 74–76 °C (HRMS (CI): found, 281.0128 (M+H). $C_{14}H_{11}{}^{35}Cl_2O_2$ (M+H) requires, 281.0136); ν_{max} 1687, 1556, 1287, 1038 and 739 cm^{-1}; δ_H 10.47 (1 H, s, CHO), 7.48–7.31 (5 H, m), 7.28 (1 H, d, *J* 8.8), 7.05 (1 H, d, *J* 8.8) and 5.19 (2 H, s); δ_C 189.1 (CO), 153.6 (C), 135.5 (C), 131.5 (C), 129.5 (CH), 128.7 (2CH), 128.3 (CH), 127.1 (C), 127.0 (2CH), 126.1 (C) and 71.4 (CH_2); *m/z* (CI) 285/283/281 (M+H$^+$, 3/48/100%).

3-Benzyloxy-2,6-dichlorobenzyl alcohol 6

A solution of sodium borohydride (3.63 g, 96.0 mmol) in water (130 cm^3) was added dropwise to a solution of 3-benzyloxy-2,6-dichlorobenzaldehyde (18.0 g, 64.0 mmol) in methanol (320 cm^3) stirred at RT. After 2 h, the mixture was acidified to pH 2 with 2 M HCl and partly evaporated under reduced pressure. The aqueous residue was extracted with CH_2Cl_2 (2 × 100 cm^3) and the combined extract was dried and evaporated to give the product **6** (16.25 g, 90%) as a yellow oil; (HRMS (ES$^+$): found, 305.0108. $C_{14}H_{12}Cl_2O_2Na$ (M+Na) requires 305.0112); ν_{max} 3385, 1570, 1290, 1270, 1009, 1021, 800, 739 and 690 cm^{-1}; δ_H 7.45–7.30 (5 H, m), 7.21 (1 H, d, *J* 8.7), 6.85 (1 H, d, *J* 8.7), 5.14 (2 H, s), 4.98 (2 H, s) and 2.05 (1 H, br s, OH); δ_C 153.3 (C), 136.7 (C), 136.0 (C), 128.6 (2CH), 128.15 (CH), 128.08 (CH), 127.02 (2CH), 126.99 (C), 125.1 (C), 114.2 (CH), 71.2 (CH_2) and 60.5 (CH_2); *m/z* (ES) 304.82 (M+Na).

3-Benzyloxy-2,6-dichlorobenzyl bromide 7

A solution of 3-benzyloxy-2,6-dichlorobenzyl alcohol (7.35 g, 27.0 mmol) in toluene (125 cm^3) was stirred at RT while phosphorus tribromide (0.86 cm^3, 2.45 g, 9.04 mmol) was added. After stirring for 12 h the solution was washed with water (3 × 35 cm^3), dried and evaporated to give the product **7** (8.53 g, 91%) as a yellow oil (HRMS (CI): found, 343.9386. $C_{14}H_{11}{}^{79}Br^{35}Cl_2O$ (M$^+$) requires 343.9370); δ_H 7.48–7.32 (5 H, m), 7.24 (1 H, d, *J* 9.0), 6.88 (1 H, d, *J* 9.0), 5.15 (2 H, s) and 4.78 (2 H, s); δ_C 153.4 (C), 135.9 (C), 134.6 (C), 128.7 (2CH), 128.2 (CH), 128.1 (CH), 127.0 (2CH), 126.9 (2C), 114.4 (CH), 71.2 (CH_2) and 27.9 (CH_2); *m/z* (CI) 347.94/345.94/343.94 (M$^+$, 10/18/14%), 267.01/265.01 (M–Br, 38/100).

Coupling reaction

To a solution of methylmagnesium iodide (45 mmol) in dry diethyl ether (50 cm^3), prepared from magnesium turnings (1.5 g, 62 mmol) and iodomethane (6.39 g, 45 mmol) and stirred under nitrogen, a solution of 2-benzyloxy-5-chlorobenzyl bromide **4** (4.95 g, 15.9 mmol) and 3-benzyloxy-2,6-dichlorobenzyl bromide **7** (5.50 g, 15.9 mmol) in dry diethyl ether (100 cm^3) was added slowly leading to an exothermic reaction. After the addition the mixture was heated under reflux for 1 h and then cooled. It was poured into dilute HCl and the organic layer was separated, washed with water, dried and evaporated to afford the crude product (6.76 g). This was subjected to chromatography on silica gel (petroleum/diethyl ether, 95:5) to give two incompletely separated products:

2,2'-Bis(benzyloxy)-5,5'-dichlorobibenzyl **8** (1.59 g, 43%); δ_H 7.38–7.32 (10 H, m), 7.09 (2 H, dd, *J* 8.7, 2.7), 7.03 (2 H, d, *J* 2.7), 6.77 (2 H, d, *J* 8.7), 4.98 (4 H, s) and 2.90 (4 H, s); δ_C 155.2 (2C), 137.0 (2C), 132.5 (2C), 129.9 (2CH), 128.6 (4CH), 127.9 (2CH), 127.0 (4CH), 126.7 (2C), 125.3 (2C), 112.7 (2CH), 70.1 (2CH_2) and 30.7 (2 CH_2) and

2,3'-Bis(benzyloxy)-2',5,6'-trichlorobibenzyl **9** (2.23 g, 28%) (still containing some **8**); δ_H 7.48–7.25 (10 H, m), 7.166 (1 H, d, *J* 2.7), 7.156 (1 H, d, *J* 9.0), 7.14 (1 H, dd, *J* 8.4, 2.7), 6.83 (1 H, d, *J* 8.4), 6.76 (1 H, d, *J* 9.0), 5.13 (2 H, s), 5.07 (2 H, s), 3.25–3.19 (2 H, m) and 2.91–2.85 (2 H, m).

In addition a small amount (0.16 g) of 2-benzyloxy-5-chloroethylbenzene was isolated; δ_H 7.48–7.30 (5 H, m), 7.14 (1 H, d, *J* 2.7), 7.08 (1 H, dd, *J* 8.7, 2.7), 6.79 (1 H, d, *J* 8.7), 5.05 (2 H, s), 2.67 (2 H, q, *J* 7.5) and 1.20 (3 H, t, *J* 7.5).

5,5'-dichloro-2,2'-dihydroxybibenzyl 10

A solution of 2,2'-bis(benzyloxy)-5,5'-dichlorobibenzyl **8** (83 mg, 0.18 mmol) in a mixture of THF (2.5 cm^3) and ethanol (2.5 cm^3) was stirred while Raney® nickel (2 g) was added and the mixture was heated under reflux for 5 h. The mixture was hot-filtered through Celite which was washed with ethanol, and the combined filtrate was evaporated to give the product **10** (46 mg, 55%) as colourless crystals, mp 195–197 °C (lit.,[6] 163–164 °C) (HRMS (ES^-)): found, 281.0133. $C_{14}H_{11}Cl_2O_2$ (M–H) requires 281.0136); ν_{max} 3254, 1237, 1176, 1111, 810 and 722 cm^{-1}; δ_H 7.12 (2 H, d, *J* 2.4), 7.10 (2 H, dd, *J* 8.4, 2.4), 6.78 (2 H, d, *J* 8.4) and 2.79 (4 H, s); δ_C 152.1 (C), 129.8 (CH), 129.0 (C), 127.6 (CH), 125.6 (C), 116.7 (CH) and 31.1 (CH_2); *m/z* (ES^-) 282.9 (85%) and 280.9 (100).

2',5,6'-trichloro-2,3'-dihydroxybibenzyl 1

A solution of crude 2,3'-bis(benzyloxy),2',5,6'-trichlorobibenzyl **9** (1.30 g, 4.09 mmol) in a mixture of THF (38 cm^3) and ethanol (38 cm^3) was stirred while Raney® nickel (26 g) was added and the mixture was heated under reflux for 5 h. The mixture was hot-filtered through celite, which was washed with ethanol, and the combined filtrate was evaporated to give the product **1** as a pale yellow solid (0.40 g, 48%). Repeated column chromatography and preparative TLC on silica gel (petroleum/diethyl ether, 60:40) gave the pure product (55 mg, 7%) as a very pale brown solid, mp 157–159 °C (Found: C, 52.97; H, 3.23. $C_{14}H_{11}Cl_3O_2$ requires C, 52.94; H, 3.49%); ν_{max} 3355, 1418, 1262, 1169, 808 and 798 cm^{-1}; δ_H 7.22 (1 H, d, *J* 8.7), 7.13 (1 H, d, *J* 2.7), 7.08 (1 H, dd, *J* 8.4, 2.7), 6.89 (1 H, d, *J* 8.7), 6.72 (1 H, d, *J* 8.4), 5.59 (1 H, s), 4.84 (1 H, s), 3.16 (2 H, m) and 2.80 (2 H, m); δ_C 152.3 (C), 150.5 (C), 137.0 (C), 130.0 (CH), 128.7 (CH), 128.6 (C), 127.4 (CH), 125.9 (C), 125.5 (C), 121.1 (C), 116.6 (CH), 114.7 (CH), 31.9 (CH_2) and 28.4 (CH_2).

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