Supporting Information

Author: Hirohito Tsue,* Kazutaka Enyo, and Ken-ichi Hirao

Title: Fragmentation Reaction via an ipso-Attack in the Multi-step Synthesis of Regioselectively Functionalized Calix[8]arene

Contents:

Experimental Section

General. Melting points were measured on a Yanagimoto MP-500D micro-melting point apparatus and were uncorrected. ^{1}H-NMR spectra were recorded on a JEOL EX-400 in $CDCl_3$ solution using Me_4Si as an internal standard. Mass spectra were obtained on a JEOL JMS-DX303 and/or JEOL JMS-01SG-2. IR spectra were measured on a JEOL FT/IR-230 as KBr discs. Elemental analyses were performed on a Yanako MT-5. Silica gel of Merck Kieselgel 60 was used for chromatography. Organic solvents were purified by the standard procedure. Compounds **2**[1] and **3**[2] were prepared according to the descriced procedure.

Initial step 2 + 3 → 4. A suspension of **2** (6.36 g, 13.4 mmol), **3** (1.0015 g, 4.4269 mmol), and *p*-TsOH (69.5 mg, 404 μmol) in anhydrous benzene (185 ml) was refluxed for 24 h; the suspension changed into a pale yellow solution before reflux began. After cooling to room temperature, the reaction mixture was washed with saturated aqueous $NaHCO_3$, saturated aqueous NaCl, and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave 6.84 g of pale yellow solid, which was carefully purified by repetitive flash column chromatography on SiO_2 with eluents of which the polarities were ranging from 40% hexane–$CHCl_3$ to 20% EtOAc–$CHCl_3$. Unreacted **2** (2.3226 g) was recovered, and **4** (1.0093 g, 20.0%) was obtained along with compounds **1** (23.0 mg, 0.78%), **5** (261.4 mg, 12.0%), **6**

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[1] Dhawan, B.; Gutsche, C. D. *J. Org. Chem.* **1983**, *48*, 1536.

[2] Zinke, A.; Ott, R.; Leggewire, E.; Hassanein, A.; Zankl, G. *Monatsh. Chem.* **1956**, *87*, 552; *Chem. Abst.* **1957**, *51*, 2845c.

(818.1 g, 22.7%), **7** (901.8 mg, 25.5%), **8** (201.1 g, 8.1%), **9** (9.3 mg, 0.31%), **10** (8.4 mg, 0.53%), **11** (10.2 mg, 0.53%), **12** (69.8 mg, 3.2%), **13** (3.4 mg, 0.24%), and **14** (14.4 mg, 0.49%). Spectral and microanalytical data of these compounds are summarized below.

Second step 3 + 4 → 1. A suspension of **3** (198.2 mg, 876.1 μmol), **4** (1.0074 mg, 884.0 μmol), and *p*-TsOH (6.3 mg, 37 μmol) in anhydrous benzene (90 ml) was heated under reflux for 24.5 h; the suspension turned into a yellow solution before reflux started. After cooling to room temperature, the solvent was evaporated to dryness, and the resulting residue was dissolved in $CHCl_3$ (100 ml). The solution was washed with saturated aqueous $NaHCO_3$, saturated aqueous NaCl, and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave 1.23 g of pale yellow solid, which was carefully purified by repetitive flash column chromatography on SiO_2 with eluents of which the polarities were ranging from 30% hexane–$CHCl_3$ to 5% EtOAc–$CHCl_3$. Unreacted **4** (385.7 mg) was recovered, and **1** (99.5 mg, 8.5%) was obtained along with compound **12** (118.4 mg, 13.7%) and **15** (65.1 g, 35.7%). Spectral and microanalytical data of these compounds are given below.

Diethyl 11,17,23,35,41,47-hexa-*tert*-butyl-49,50,51,52,53,54,55,56-octahydroxycalix[8]arene-5,29-dicarboxylate (1). Colorless fine powder from chloroform—hexane, mp >450 °C (dec.); MS (FAB) *m/z* 1328 (M^+); IR (KBr) 3232 ($\nu_{O\text{-}H}$), 1718 ($\nu_{C=O}$) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.25 (s, 18H, *tert*-Bu), 1.26 (s, 36H, *tert*-Bu), 1.36 (t, J=7.1 Hz, 6H, CH_2CH_3), 3.54 (br s, 8H, $ArCH_2$), 4.33 (br s, 12H, $ArCH_2$ and CH_2CH_3), 7.19 (s, 4H, Ar-H), 7.20 (d, J=2.4 Hz, 4H, Ar-H), 7.22 (d, J=2.4 Hz, 4H, Ar-H), 7.87 (s, 4H, Ar-H), 9.3 (br s, 4H, OH), 9.37 (s, 2H, OH), 10.21 (s, 2H, OH); Anal. Calcd for $C_{86}H_{104}O_{12}$: C, 77.68; H, 7.88%. Found: C, 77.51; H, 7.93%.

4-*tert*-Butyl-3,5-bis[(5-*tert*-butyl-2-hydroxyphenyl)methyl]phenol (2). Colorless solid from benzene, mp 220—221 °C (lit.[1] 219—221 °C).

Ethyl 3,5-bis(hydroxymethyl)-4-hydroxybenzoate (3). Colorless solid from $CHCl_3$, mp 137—138 °C (lit.[2] 139 °C).

Ethyl 3,5-bis[[5-*tert*-butyl-3-[[5-*tert*-butyl-3-[(5-*tert*-butyl-2-hydroxyphenyl)methyl]-2-hydroxyphenyl]methyl]-2-hydroxyphenyl]methyl]-4-hydroxybenzoate (4). Colorless solid from benzene—hexane, mp 181.5—184.3 °C (dec.); MS (FAB) *m/z* 1138 (M^+); IR (KBr) 3274 ($\nu_{O\text{-}H}$), 1685 ($\nu_{C=O}$) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.25 (s, 18H, *tert*-Bu), 1.28 (s, 18H, *tert*-Bu), 1.29 (s, 18H, *tert*-Bu), 1.35 (t, J=7.1 Hz, 3H, CH_2CH_3), 3.92 (br s, 8H, $ArCH_2$), 4.00 (br s, 4H, $ArCH_2$), 4.32 (q, J=7,1 Hz, 2H, CH_2CH_3), 6.75 (d, J=8.5 Hz, 2H, Ar-H), 7.02 (d, J=2.4 Hz, 2H, Ar-H), 7.31 (d, J=2.2 Hz, 2H, Ar-H), 7.85 (s, 2H, Ar-H), 9.41 (s, 2H, OH), 9.74 (s, 2H, OH), 9.98 (s, 2H, OH), 10.92 (s, 1H, OH); Anal. Calcd for $C_{75}H_{94}O_9$: C, 79.05; H, 8.31%. Found: C, 78.96; H, 8.30%.

Ethyl 3,5-bis[(5-*tert*-butyl-2-hydroxyphenyl)methyl]-4-hydroxybenzoate (5). Colorless solid from benzene—hexane, mp 172—175 °C (lit.[3] 170 °C).

Ethyl 5-[(5-*tert*-butyl-2-hydroxyphenyl)methyl]-3-[[5-*tert*-butyl-3-[[5-*tert*-butyl-3-[(5-*tert*-butyl-2-hydroxyphenyl)methyl]-2-hydroxyphenyl]methyl]-2-hydroxyphenyl]methyl]-4-hydroxybenzoate (6). Colorless solid from benzene—hexane, mp 138—140 °C; MS (FD) *m/z* 814 (M^+); IR (KBr) 3253 ($\nu_{O\text{-}H}$), 1695 ($\nu_{C=O}$) cm^{-1}; ^1H-NMR ($CDCl_3$) δ 1.24 (s, 9H, *tert*-Bu), 1.26 (s, 9H, *tert*-Bu), 1.27 (s, 9H, *tert*-Bu), 1.28 (s, 9H, *tert*-Bu), 1.37 (t, J=7.1 Hz, 3H, $\mathrm{CH_2C}\mathit{H}_3$), 3.82 (s, 2H, $ArCH_2$), 3.85 (s, 2H, $ArCH_2$), 3.89 (s, 2H, $ArCH_2$), 3.90 (s, 2H, $ArCH_2$), 4.34 (q, J=7.1 Hz, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 6.79 (d, J=8.5 Hz, 1H, Ar-H), 6.89 (d, J=8.5 Hz, 1H, Ar-H), 7.07 (dd, J=2.3, 8.5 Hz, 1H, Ar-H), 7.12 (d, J=2.2 Hz, 1H, Ar-H), 7.16 (m, 3H, Ar-H), 7.20 (d, J=2.4 Hz, 1H, Ar-H), 7.32 (m, 2H, Ar-H), 7.85 (d, J=1.9 Hz, 1H, Ar-H), 7.89 (d, J=2.2 Hz, 1H, Ar-H), 8.57 (s, 1H, OH), 9.13 (s, 1H, OH), 9.22 (s, 1H, OH), 10.05 (s, 1H, OH); Anal. Calcd for $C_{53}H_{66}O_7\cdot1.5H_2O$: C, 75.59; H, 8.26%. Found: C, 75.76; H, 8.39%.

4-*tert*-Butyl-2,6-bis[[5-*tert*-butyl-3-[(5-*tert*-butyl-2-hydroxyphenyl)methyl]-2-hydroxyphenyl]methyl]phenol (7). Colorless solid from benzene—hexane, mp 218—221 °C (lit.[4] 217—218 °C).

4-*tert*-Butyl-2,6-bis[[5-*tert*-butyl-3-[[5-*tert*-butyl-3-[(5-*tert*-butyl-2-hydroxyphenyl)methyl]-2-hydroxyphenyl]methyl]-2-hydroxyphenyl]methyl]phenol (8). Colorless solid from benzene—hexane, mp 253—256 °C (lit.[4] 252—254 °C).

Ethyl 3-(hydroxymethyl)-5-[[5-*tert*-butyl-3-[[5-*tert*-butyl-3-[(5-*tert*-butyl-2-hydroxyphenyl)methyl]-2-hydroxyphenyl]methyl]-2-hydroxyphenyl]methyl]-4-hydroxybenzoate (9). Colorless solid from chloroform—hexane, mp 191—193 °C; MS (FD) *m/z* 682 (M^+); IR (KBr) 3376 ($\nu_{O\text{-}H}$), 1685 ($\nu_{C=O}$) cm^{-1}; ^1H-NMR ($CDCl_3$) δ 1.22 (s, 9H, *tert*-Bu), 1.23 (s, 9H, *tert*-Bu), 1.26 (s, 9H, *tert*-Bu), 1.31 (t, J=7.2 Hz, 3H, $\mathrm{CH_2C}\mathit{H}_3$), 3.78 (s, 2H, $ArCH_2$), 3.84 (s, 2H, $ArCH_2$), 3.90 (s, 2H, $ArCH_2$), 4.27 (q, J=7.1 Hz, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 5.00 (br s, 1H, $\mathrm{CH_2O}\mathit{H}$), 5.04 (d, J=5.1 Hz, 2H, $\mathrm{C}\mathit{H}_2\mathrm{OH}$), 6.48 (d, J=8.3 Hz, 1H, Ar-H), 7.01 (dd, J=2.4, 8.5 Hz, 1H, Ar-H), 7.09 (d, J=2.4 Hz, 1H, Ar-H), 7.14 (m, 2H, Ar-H), 7.18 (d, J=2.4 Hz, 1H, Ar-H), 7.22 (d, J=2.4 Hz, 1H, Ar-H), 7.68 (d, J=2.0 Hz, 1H, Ar-H), 7.85 (d, J=2.0 Hz, 1H, Ar-H), 8.82 (s, 1H, OH), 9.06 (s, 1H, OH), 9.19 (s, 1H, OH), 10.17 (s, 1H, OH); Anal. Calcd for $C_{43}H_{54}O_7\cdot0.5H_2O$: C, 74.65; H, 8.01%. Found: C, 74.75; H, 8.07%.

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3) de Mendoza, J.; Nieto, P. M.; Prados, P.; Sánchez, C. *Tetrahedron* **1990**, *46*, 671.

4) Casiraghi, G.; Cornia, M.; Ricci, G.; Balduzzi, G.; Casnari, G.; Andreetti, G. D. *Makromol. Chem.* **1983**, *184*, 1363.

Ethyl 3-(hydroxymethyl)-5-[(5-*tert*-butyl-2-hydroxyphenyl)methyl]-4-hydroxybenzoate (10). Colorless solid from chloroform—hexane, mp 114—117 °C; MS (FD) *m/z* 358 (M^+); IR (KBr) 3367 (ν_{O-H}), 3248 (ν_{O-H}), 1693 ($\nu_{C=O}$) cm^{-1}; ^1H-NMR ($CDCl_3$) δ 1.28 (s, 9H, *tert*-Bu), 1.36 (t, J=7.2 Hz, 3H, CH_2CH_3), 2.52 (t, J=3.9 Hz, 1H, CH_2OH), 3.95 (s, 2H, $ArCH_2$), 4.33 (q, J=7.2 Hz, 2H, CH_2CH_3), 4.91 (d, J=3.9 Hz, 2H, CH_2OH), 6.68 (br s, 1H, ArOH), 6.78 (d, J=8.5 Hz, 1H, Ar-H), 7.13 (dd, J=8.5, 2.5 Hz, 1H, Ar-H), 7.29 (d, J=2.5 Hz, 1H, Ar-H), 7.63 (d, J=2.1 Hz, 1H, Ar-H), 7.96 (d, J=2.1 Hz, 1H, Ar-H), 9.02 (br s, 1H, ArOH); Anal. Calcd for $C_{21}H_{26}O_5 \cdot 0.05CHCl_3$: C, 69.38; H, 7.21; Cl, 1.46%. Found: C, 69.12; H, 7.20; Cl, 1.42%.

Ethyl 11,17,23,29,35,41,47-hepta-*tert*-butyl-49,50,51,52,53,54,55,56-octahydroxycalix[8]arene-5-carboxylate (11). Colorless solid from chloroform—hexane, mp >400 °C (dec.); MS (FD) *m/z* 1312 (M^+); IR (KBr) 3219 (ν_{O-H}), 1718 ($\nu_{C=O}$) cm^{-1}; ^1H-NMR ($CDCl_3$) δ 1.25 (s, 45H, *tert*-Bu), 1.26 (s, 18H, *tert*-Bu), 1.36 (t, J=7.1 Hz, 3H, CH_2CH_3), 3.55 (br s, 8H, $ArCH_2$), 4.35 (br s, 10H, $ArCH_2$ and CH_2CH_3), 7.17 (s, 8H, Ar-H), 7.18 (s, 2H, Ar-H), 7.20 (d, J=2.4 Hz, 2H, Ar-H), 7.21 (d, J=2.4 Hz, 2H, Ar-H), 7.87 (s, 2H, Ar-H), 9.58 (br s, 6H, OH), 10.22 (br s, 1H, OH), 10.51 (br s, 1H, OH); HRMS (FD) Calcd for $C_{87}H_{108}O_{10}$: *m/z* 1312.795. Found: *m/z* 1312.798. Anal. Calcd for $C_{87}H_{108}O_{10} \cdot H_2O$: C, 78.59; H, 8.40%. Found: C, 78.46; H, 8.32%.

Ethyl 11,17,23,29,35-penta-*tert*-butyl-37,38,39,40,41,42-hexahydroxycalix[6]arene-5-carboxylate (12). Colorless powder from chloroform—hexane, mp >400 °C (dec.); MS (FD) *m/z* 988 (M^+); IR (KBr) 3137 (ν_{O-H}), 1714 ($\nu_{C=O}$) cm^{-1}; ^1H-NMR ($CDCl_3$) δ 1.25 (s, 18H, *tert*-Bu), 1.26 (s, 18H, *tert*-Bu), 1.27 (s, 9H, *tert*-Bu), 1.37 (t, J=7.1 Hz, 3H, CH_2CH_3), 3.88 (br s, 12H, $ArCH_2$), 4.33 (q, J=7.1 Hz, 2H, CH_2CH_3), 7.15 (d, J=2 Hz, 2H, Ar-H), 7.16 (s, 6H, Ar-H), 7.17 (d, J=2 Hz, 2H, Ar-H), 10.25 (br s, 1H, OH), 10.48 (br s, 4H, OH), 11.07 (br s, 1H, OH); Anal. Calcd for $C_{65}H_{80}O_8 \cdot 1.1CHCl_3$: C, 70.84; H, 7.29; Cl, 10.44%. Found: C, 71.09; H, 7.53; Cl, 10.16%.

5,11,17,23,29,35-Hexa-*tert*-butyl-37,38,39,40,41,42-hexahydroxycalix[6]arene (13). Colorless solid from chloroform—hexane, mp >300 °C (lit.[5] 372—374 °C).

Ethyl 11,17,23-tri-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene-5-carboxylate (14). Colorless powder from chloroform—hexane, mp >300 °C; MS (FD) *m/z* 664 (M^+); IR (KBr) 3175 (ν_{O-H}), 1717 ($\nu_{C=O}$) cm^{-1}; ^1H-NMR ($CDCl_3$) δ 1.19 (s, 9H, *tert*-Bu), 1.22 (s, 18H, *tert*-Bu), 1.30 (t, J=7.1 Hz, 3H, CH_2CH_3), 3.49 (br d, J=13.7 Hz, 2H, $ArCH_2$), 3.58 (br d, J=14.2 Hz, 2H, $ArCH_2$), 4.25 (br s, 4H, $ArCH_2$), 4.29 (q, J=7.1 Hz, 2H, CH_2CH_3), 7.03 (s, 2H, Ar-H), 7.08 (d, J=2.7 Hz, 2H, Ar-H) 7.09 (d,

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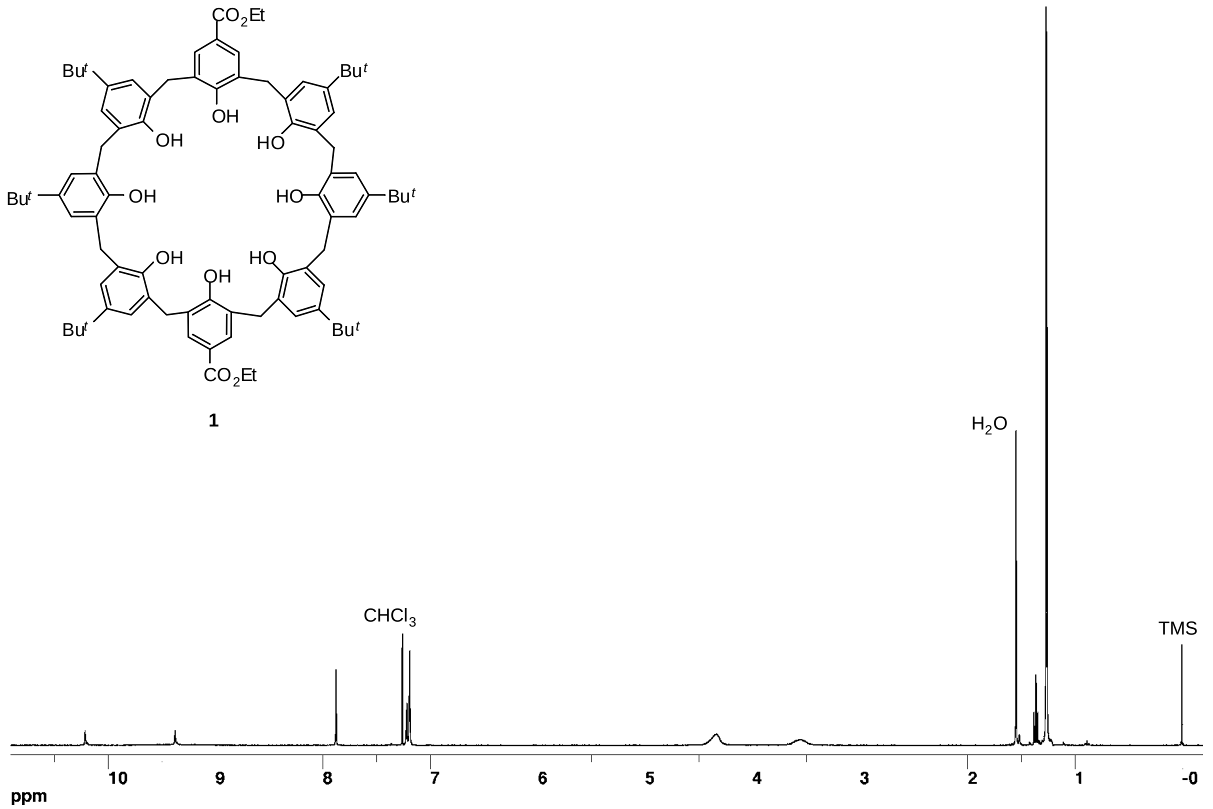
5) Gutsche, C. D.; Dhawan, B.; Leonis, M.; Stewart, D. *Org. Syn.* **1990**, *68*, 238.

J=2.7 Hz, 2H, Ar-H), 7.76 (s, 2H, Ar-H), 10.25 (br s, 4H, OH); Anal. Calcd for $C_{43}H_{52}O_6{\cdot}0.4CHCl_3$ C, 73.15; H, 7.41; Cl, 5.97%. Found: C, 73.44; H, 7.57; Cl, 6.06%.

Triethyl 25,26,27-trihydroxy-2,3,10,11,18,19-hexahomo-3,11,19-trioxacalix[3]arene-7,15,23-tricarboxylate (15). Colorless fine powder from benzene—hexane, mp 223—225 °C; MS (FD) *m/z* 624 (M^+); IR (KBr) 3329 ($\nu_{O\text{-}H}$), 1720 ($\nu_{C=O}$) cm^{-1}; ^1H-NMR ($CDCl_3$) δ 1.37 (t, 9H, J=7.1 Hz, CH_2CH_3), 4.33 (q, 6H, J=7.1 Hz, CH_2CH_3), 4.76 (s, 12H, $ArCH_2$), 7.86 (s, 6H, Ar-H), 9.19 (s, 3H, OH); Anal. Calcd for $C_{33}H_{36}O_{12}$: C, 63.45; H, 5.81%. Found: C, 63.51; H, 5.91%.

^{1}H-NMR spectra of all new compounds



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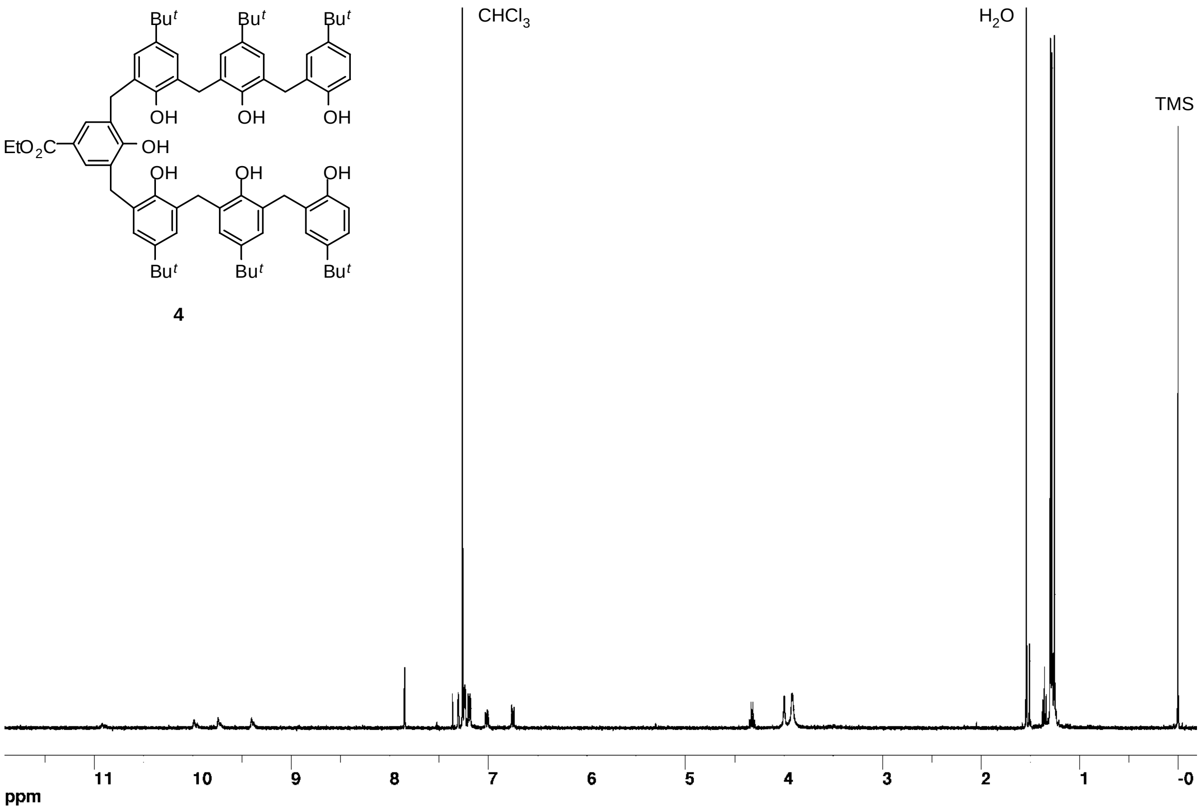
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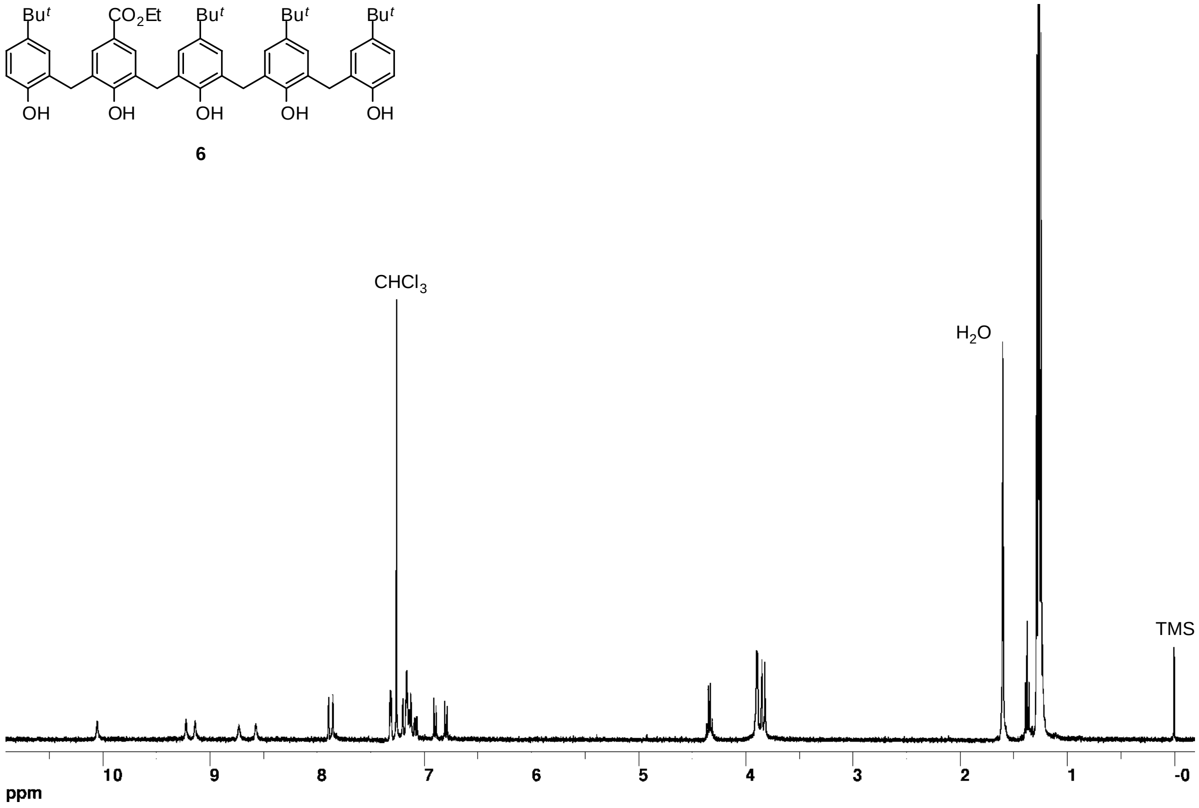
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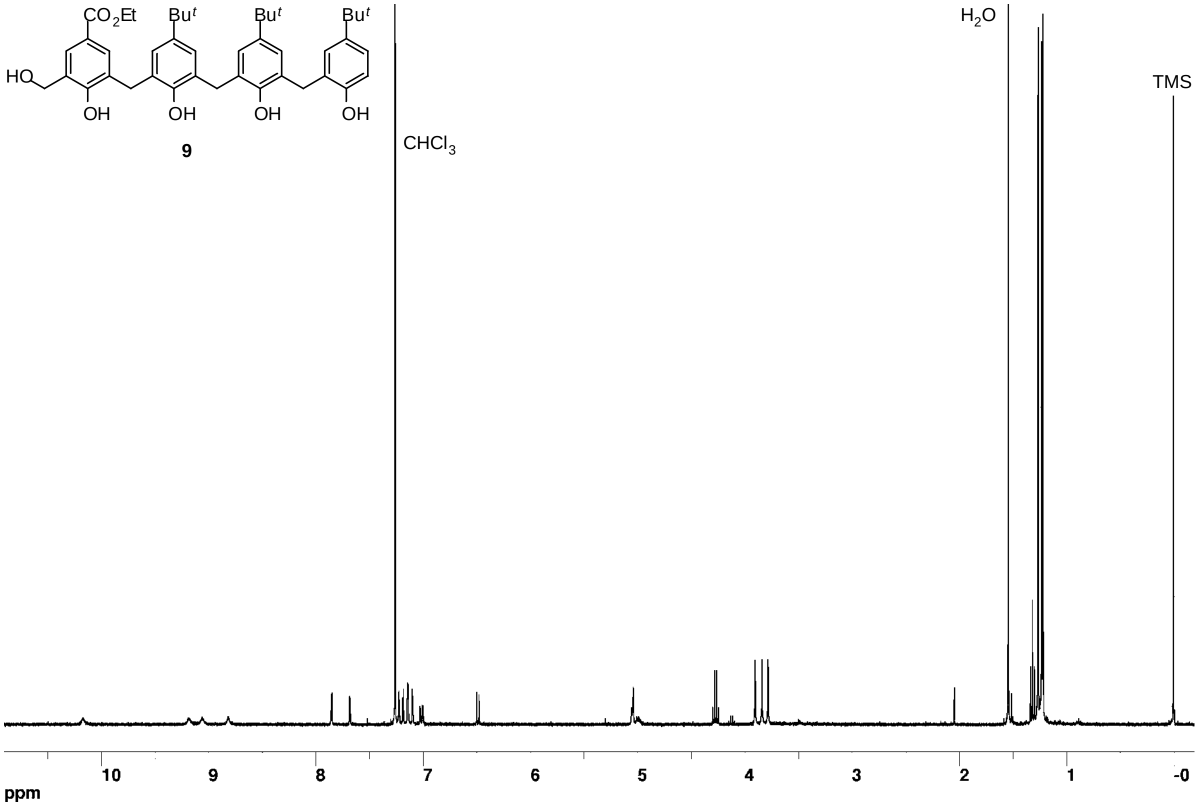
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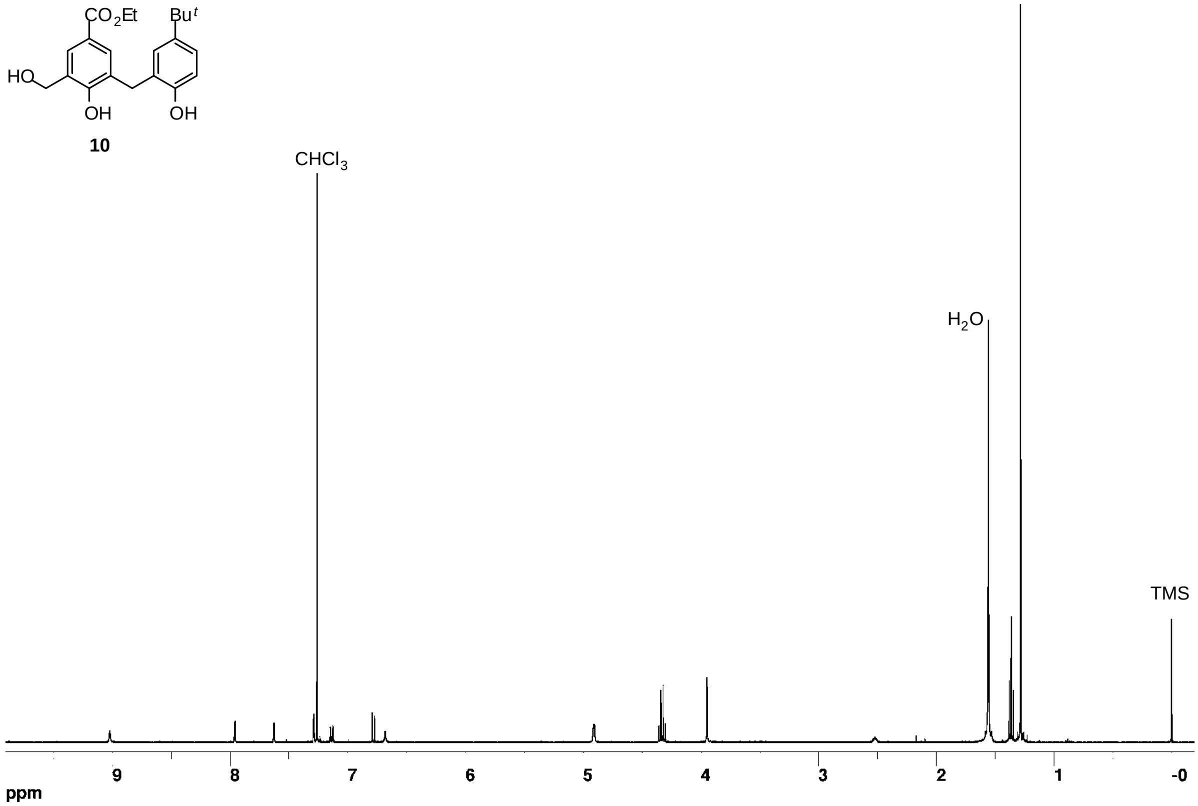
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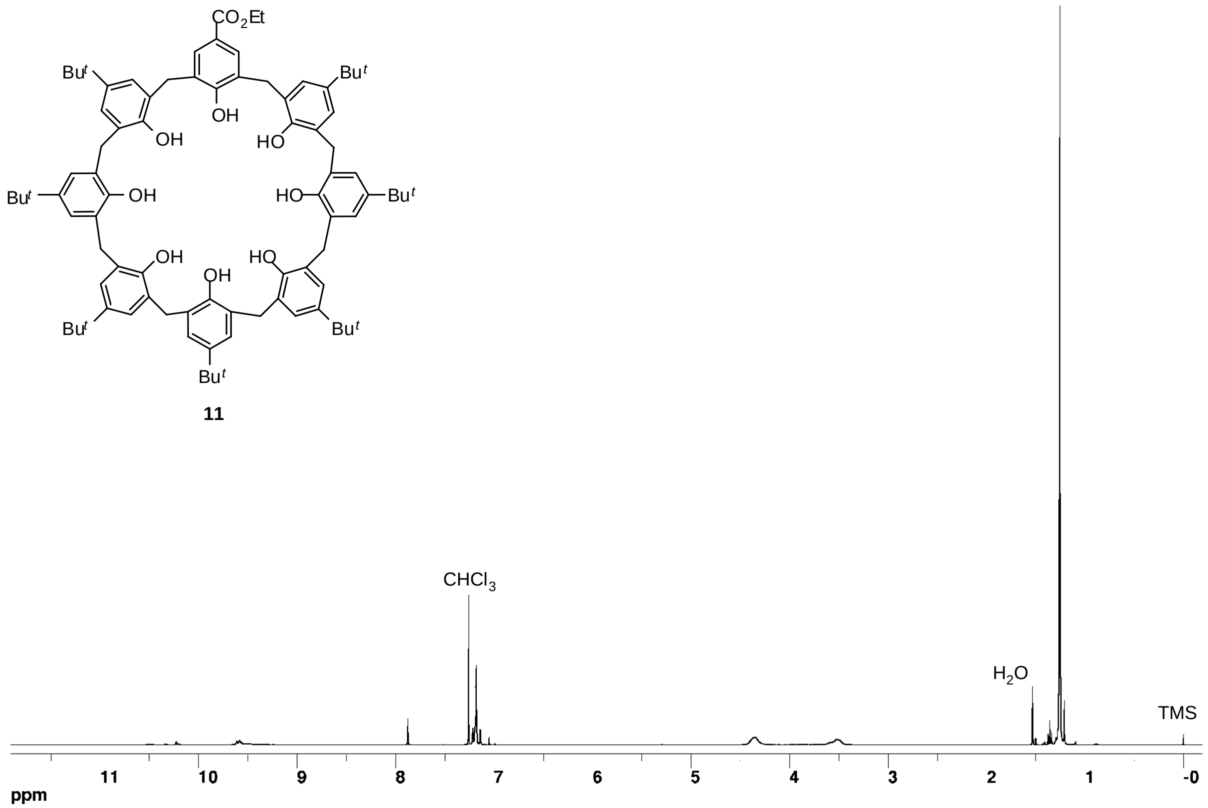

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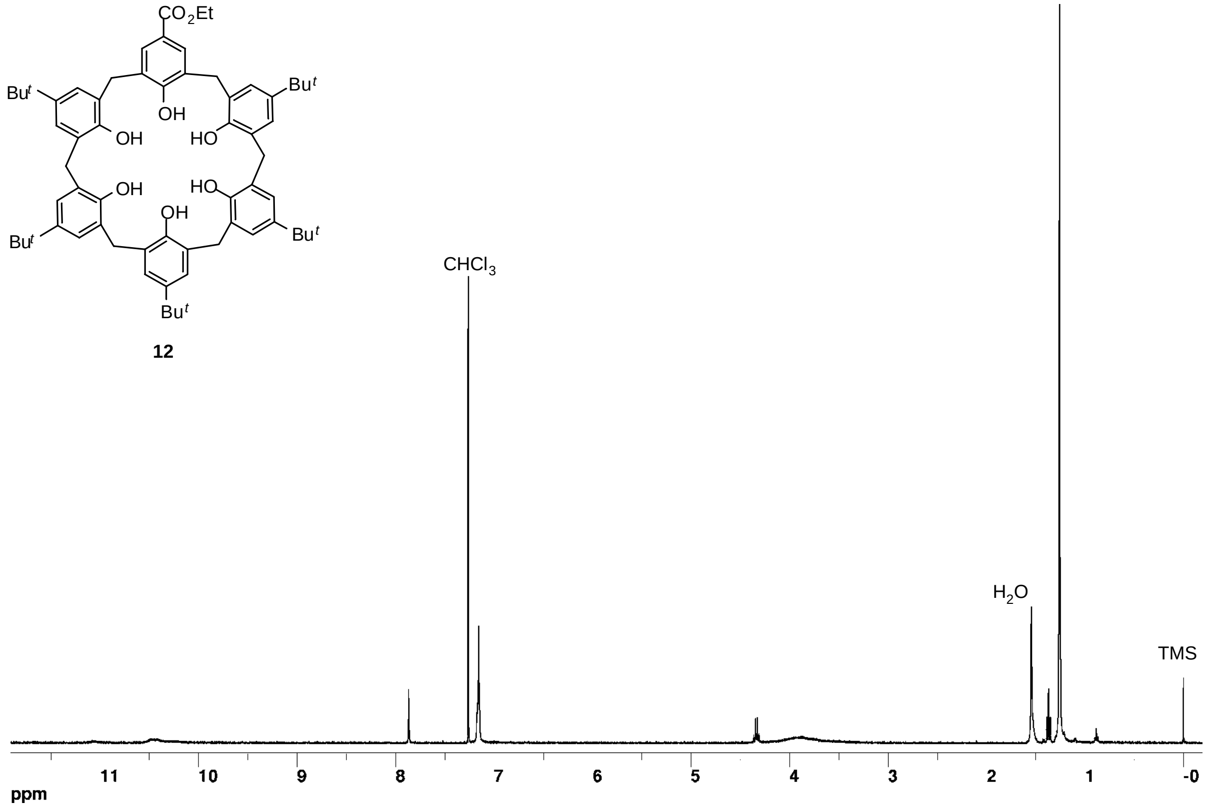

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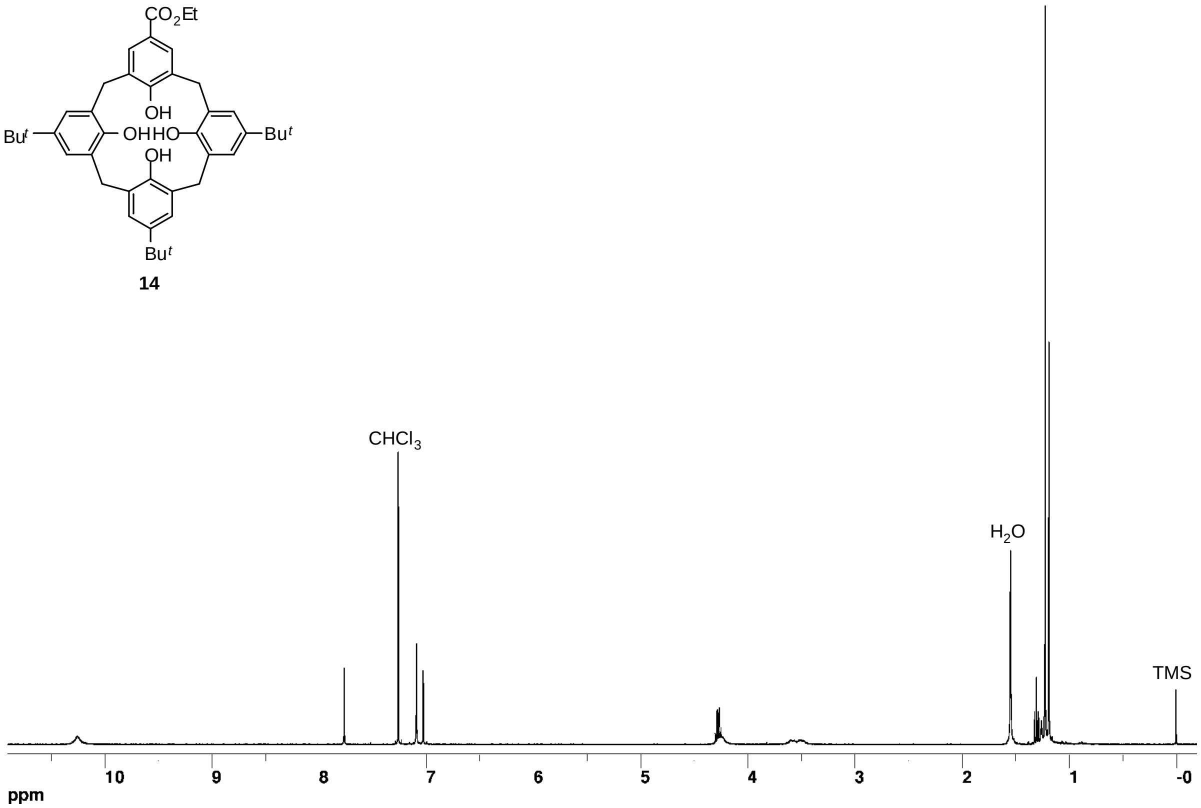

14

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Bu^t
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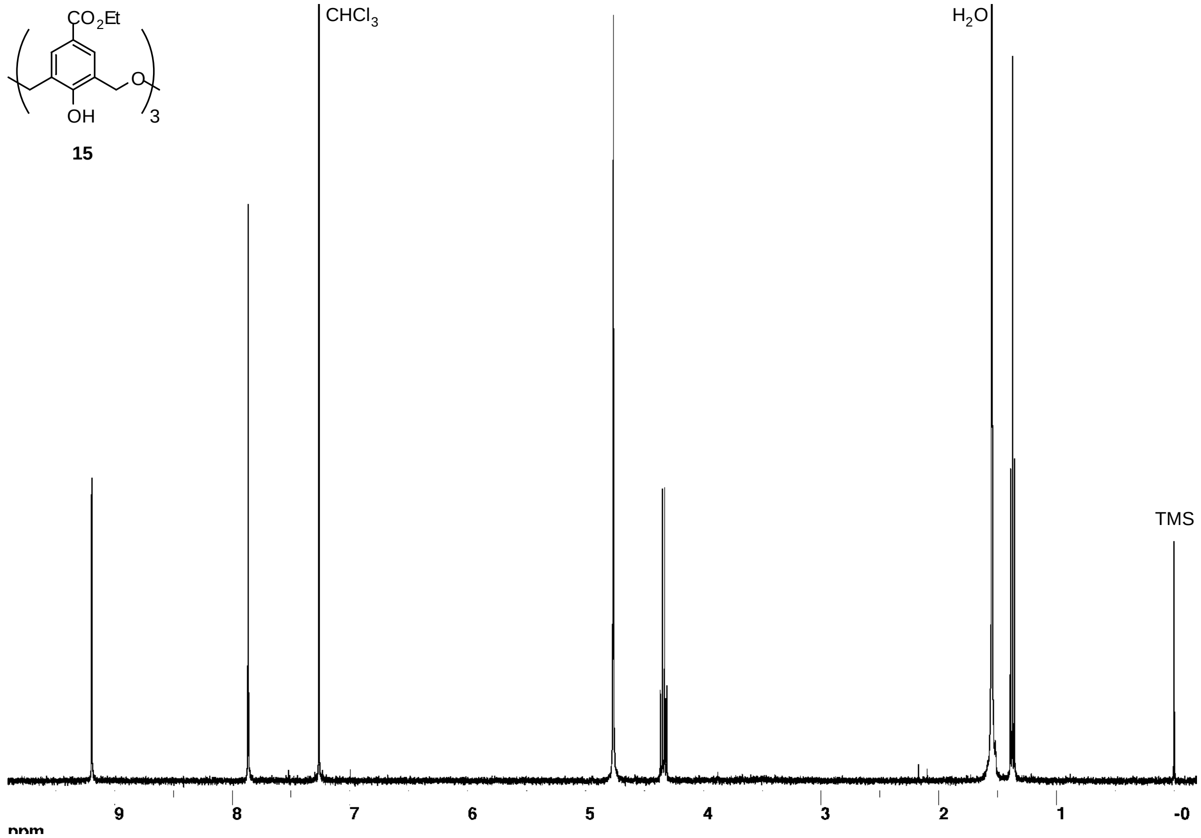

15

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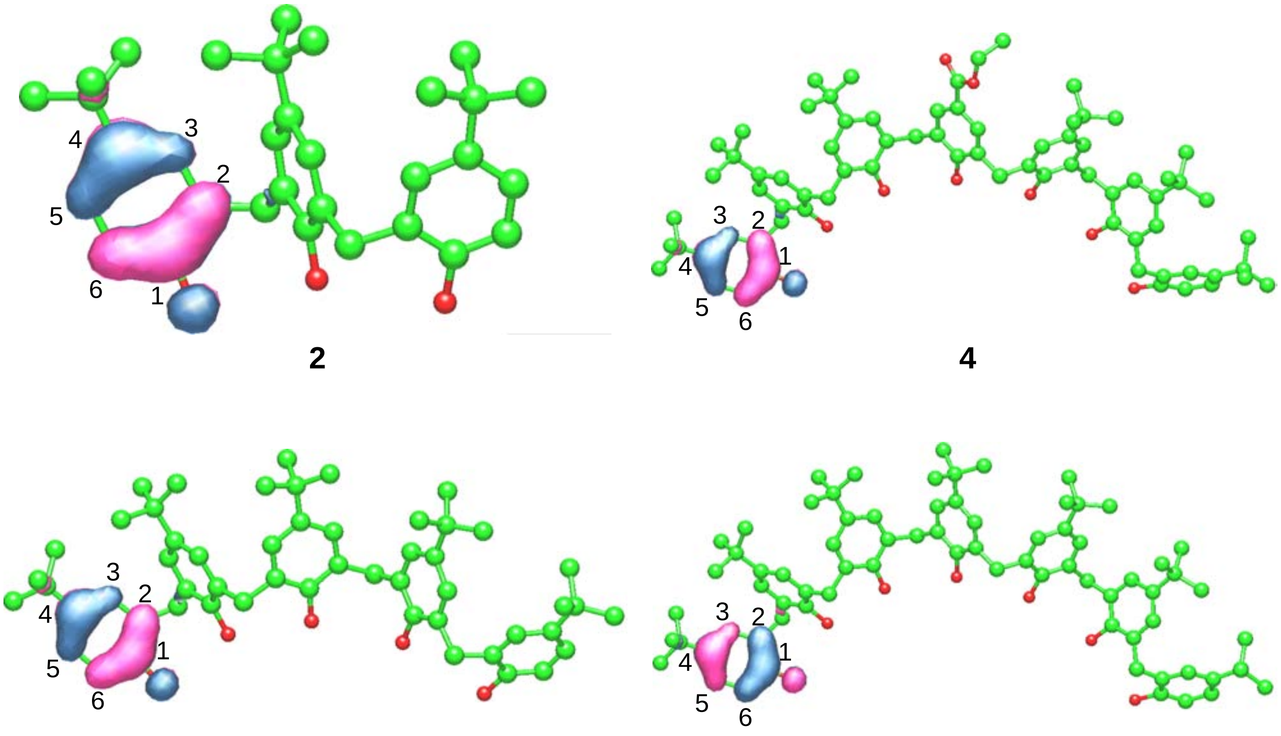
ppm

Theoretical Calculation

Semiempirical molecular orbital calculations[6] based on PM3[7] were performed in order to understand aromatic electrophilic substitution reactions between benzyl cation **16** and phenol condensates **2**, **4**, **7**, and **8**. As shown in Figure 1, the theoretical calculations demonstrated that the orbital coefficients of the HOMOs (highest occupied molecular orbitals) in the phenol condensates appeared only in one of the terminal phenol rings, the carbon atoms of which are numbered. The orbital energies, the LCAO (linear combination of atomic orbitals) coefficients, and the atomic charges at the numbered carbon atoms are summarized in Tables 1, 2, and 3, respectively. The corresponding information on the LUMO (lowest unoccupied molecular orbital) of the benzyl cation **16** is provided in Figure 2 and Table 4.



2 **4**

7 **8**

Figure 1. HOMOs of **2**, **4**, **7**, and **8** (hydrogen atoms are omitted for clarity)

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[6] The calculations were performed by using the MOPAC97 program package implemented in WinMOPAC Version 2.0, Fujitsu Limited, 1998.

[7] Stewart, J. J. P. *J. Comp. Chem.* **1989**, *10*, 209.

Table 1. Energy Levels of the HOMOs in Phenol Condensates **2**, **4**, **7**, and **8**

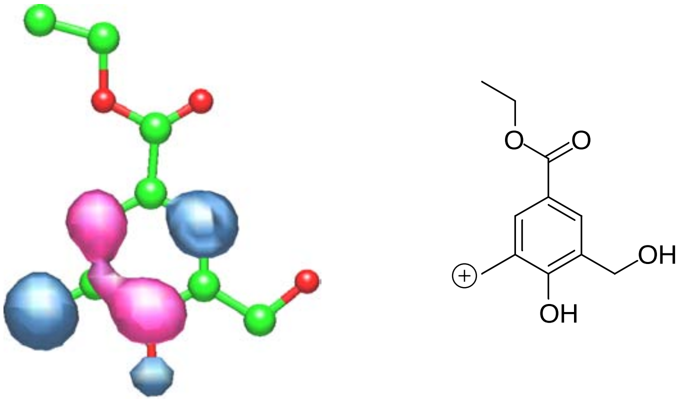
compd no.	orbital energy / eV
2	-8.748
4	-8.676
7	-8.686
8	-8.665

Table 2. LCAO Coefficients at the Numbered Carbon Atoms of **2**, **4**, **7**, and **8**

compd no.	LCAO coefficient					
	C^1	C^2	C^3	C^4	C^5	C^6
2	0.471	0.364	-0.199	-0.508	-0.239	0.307
4	0.468	0.367	-0.192	-0.504	-0.241	-0.300
7	0.468	0.368	-0.193	-0.505	-0.241	0.301
8	-0.467	-0.367	0.192	0.504	0.241	-0.301

Table 3. Atomic Charges at the Numbered Carbon Atoms of **2**, **4**, **7**, and **8**

compd no.	atomic charge / e					
	C^1	C^2	C^3	C^4	C^5	C^6
2	0.111	-0.162	-0.080	-0.109	-0.073	-0.142
4	0.111	-0.161	-0.078	-0.109	-0.075	-0.143
7	0.111	-0.161	-0.078	-0.109	-0.075	-0.143
8	0.111	-0.160	-0.078	-0.109	-0.075	-0.143



16

Figure 2. LUMO of benzyl cation **16** (hydrogen atoms are omitted for clarity)

Table 4. Orbital Energy of the LUMO in Benzyl Cation **16**, and the LCAO Coefficient and the Atomic Charge at the Carbocation Center

Orbital energy / eV	LCAO coefficient	atomic charge / e
-7.083	0.608	0.185

According to the Klopman's general perturbation equation (eq. 1),[8] perturbation energies (ΔE) between the frontier molecular orbitals of the phenol condensates and the benzyl cation were estimated.

$$\Delta E = -\frac{Q_\mathrm{A}Q_\mathrm{B}}{R_\mathrm{AB}\varepsilon} + \frac{2\left(C_\mathrm{A}C_\mathrm{B}\Delta\beta\right)^2}{\left|E_\mathrm{A} - E_\mathrm{B}\right|} \qquad (1)$$

In this equation, Q_A and Q_B are atomic charges of reactants A and B, R_AB is separation distance between them, ε is dielectric constant of reaction medium (2.27401 for benzene[9]), C_A and C_B are LCAO coefficients at one site of interaction, $\Delta\beta$ is interorbital interaction integral, and E_A and E_B are energy levels of the relevant molecular orbitals. Parameters R_AB and $\Delta\beta$ were set to be 2.5 Å and -2.63 eV,[10] respectively, since preliminary PM3-calculations on the transition states in the aromatic electrophilic substitution reactions between **2** and **16** revealed that the separation distances between them were within the range of 2.30–2.45 Å.[11] The results of the theoretical calculations are summarized in Table 5.

Table 5. Perturbation Energies between Benzyl Cation **16** and Phenol Condensates **2**, **4**, **7**, and **8**

compd no.	ΔE / eV					
	C^1	C^2	C^3	C^4	C^5	C^6
2	0.629	0.484	0.159	0.844	0.210	0.357
4	0.651	0.509	0.155	0.868	0.221	0.357
7	0.649	0.508	0.155	0.866	0.220	0.357
8	0.655	0.511	0.156	0.873	0.222	0.360

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