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Supplementary Information

Synthesis and optical resolution of an inherently chiral calix[4]arene amino acid

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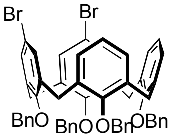
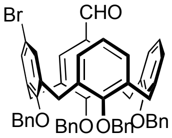
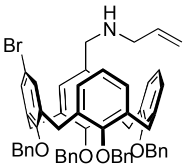
General: ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer in $CDCl_3$. Tetramethylsilane (TMS) served as the internal standard (0 ppm) for ^{1}H NMR, and $CDCl_3$ served as the internal standard (77.0 ppm) for ^{13}C NMR. IR spectra were measured with a Jasco FT/IR-700 spectrometer. Circular dichroism (CD) spectra were measured with a Jasco J-820 spectrometer. Optical rotations were measured on a Jasco DIP-1000 digital polarimeter. High performance liquid chromatography (HPLC) was performed on a Hitachi 655 Liquid Chromatograph instrument using 0.46×25 cm SUMICHIRAL OA-4800. Preparative gel-permeation chromatography (GPC) and preparative HPLC were performed using a JAI model 908 liquid chromatograph with JAIGEL-1H, 2H columns and with a SUMICHIRAL OA-4800 column (2.0×25 cm), respectively. SUMICHIRAL OA-4800 columns were pre-activated by $CHCl_3$, containing 0.2% TFA. Analytical thin-layer chromatography (TLC) and column chromatography were carried out on precoated silica gel 60 F_{254} glass plates (E. Merck) and with silica gel 60 (spherical 0.040–0.100 mm, Kanto), respectively. Tetrahydrofuran (THF) was freshly distilled from Na-benzophenone.



5,11-Dibromo-25,26,27,28-tetrabenzyloxycalix[4]arene (3). To a solution of 5,11-dibromo-25,26-dibenzyloxy-27,28-dihydroxycalix[4]arene **2**[1] (13.0 mmol) and NaH (130 mmol, 60% dispersion in paraffin liquid) in CH_3CN (300 ml) was added benzyl bromide (130 mmol) at room temperature. The reaction mixture was stirred for 2 h at room temperature, and then quenched with 1N HCl aq (150 ml). After the removal of CH_3CN by evaporation, organic materials were extracted with $CHCl_3$ (70 ml × 3) and the organic extracts were dried over $MgSO_4$. Evaporation of solvents and purification of the residue by column chromatography on silica gel ($CHCl_3$/hexane = 1/3 to 1/1 as eluent) afforded **3** in 87% yield: ^1H NMR (400 MHz, $CDCl_3$) δ 7.19–7.30 (m, 20H), 6.52–6.74 (m, 10H), 4.83–4.96 (m, 8H), 4.26 (d, J = 13.7 Hz, 1H), 4.12 (d, J = 13.7 Hz, 2H), 3.98 (d, J = 13.8 Hz, 1H), 3.02 (d, J = 13.7 Hz, 1H), 2.87 (d, J = 13.8 Hz, 2H), 2.70 (d, J = 13.9 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.24, 154.33, 137.77, 137.43, 136.87, 135.29, 134.40, 131.09, 130.44, 129.62, 129.41, 128.56, 128.05, 128.03, 127.99, 127.86, 122.60, 115.02, 76.48, 76.28, 31.21, 31.09, 30.91 ppm; IR 3061, 3029, 2916, 2866, 1457, 1210, 1190, 977, 750, 697 cm^{-1}; Anal. Calcd for $C_{56}H_{46}Br_2O_4$: C, 71.34; H, 4.92. Found: C, 71.05; H, 4.82.

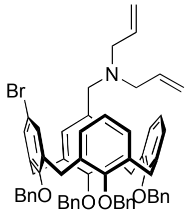


5-Bromo-11-formyl-25,26,27,28-tetrabenzyloxycalix[4]arene [(±)-4]. To a solution of 5,11-dibromo-25,26,27,28-tetrabenzyloxycalix[4]arene **3** (5.0 mmol) in THF (80 ml) was added *n*-BuLi (5.5 mmol, 1.5M in hexane) at –78 ˚C under argon atmosphere and the mixture was stirred for 15 min at this temperature. Then, dry *N*,*N*-dimethylformamide (7.5 mmol) was added, and the mixture was stirred for 15 min at –78 ˚C. The reaction mixture was quenched with 0.1N HCl aq (60 ml). After the removal of THF by evaporation, organic materials were extracted with $CHCl_3$ (30 ml × 3). The organic extracts were washed with water, and dried over $MgSO_4$. Evaporation of solvents and purification of the residue by column chromatography on silica gel ($CHCl_3$/hexane = 1/2 to 2/1 as eluent) afforded **4** in 84% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (s, 1H), 7.09–7.34 (m, 22H), 6.42–6.70 (m, 8H), 4.79–5.06 (m, 8H), 4.27 (d, *J* = 13.7 Hz, 1H), 4.21 (d, *J* = 13.8 Hz, 1H), 4.12 (d, *J* = 13.7 Hz, 1H), 4.05 (d, *J* = 13.9 Hz, 1H), 3.04 (d, *J* = 13.7 Hz, 1H), 3.02 (d, *J* = 13.9 Hz, 1H), 2.88 (d, *J* = 13.8 Hz, 1H), 2.83 (d, *J* = 14.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.67, 160.95, 155.38, 155.07, 154.18, 137.44, 137.35, 137.28, 137.03, 136.78, 136.54, 136.48, 136.24, 135.70, 134.96, 134.82, 133.96, 131.09 130.96, 130.51, 130.40, 129.86, 129.57, 129.53, 129.30, 128.73, 128.54, 128.15, 128.07, 128.00, 127.97, 127.91, 127.88, 122.75, 122.43, 115.18, 76.70, 76.53, 76.47, 76.11, 31.24, 31.14, 31.04, 31.01 ppm; IR 3061, 3029, 2917, 2865, 2725, 1688, 1456, 1191, 977, 748, 698 cm^{-1}; Anal. Calcd for $C_{57}H_{47}BrO_5$•$0.1CHCl_3$: C, 75.89; H, 5.24. Found: C, 75.81; H, 5.10.

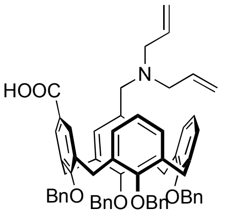


5-(*N*-Allylaminomethyl)-11-bromo-25,26,27,28-tetrabenzyloxycalix[4]arene [(±)-5]. To a solution of **4** (4.0 mmol) in THF (20 ml)-ethanol (15 ml) mixed solvents was added allylamine (20 mmol) at room temperature and the mixture was stirred for 24 h. Then, $NaBH_4$ (4.0 mmol) was added and the mixture was stirred for 30 min. The reaction mixture was quenched with sat. NH_4Cl aq. After the removal of THF and EtOH by evaporation, organic materials were extracted with $CHCl_3$ (30 ml × 3). The organic extracts were washed with water, and dried over $MgSO_4$. Evaporation of solvents and purification of the residue by column chromatography on silica gel ($CHCl_3$/AcOEt = 1/0 to 0/1 as eluent) afforded **5** in 92% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12–7.52 (m, 20H), 6.61–6.74 (m, 6H), 6.39–6.46 (m, 4H), 5.89–5.99 (m, 1H), 5.17–5.22 (m, 2H), 4.78–5.00 (m, 8H), 4.23 (d, *J* = 13.5 Hz, 1H), 4.21 (d, *J* = 13.5 Hz, 1H), 4.08 (d, *J* = 13.5 Hz, 1H), 4.05 (d, *J* = 13.5 Hz, 1H), 3.66 (s, 2H), 3.19 (d, *J* = 6.2 Hz, 2H), 2.99 (d, *J* = 13.7 Hz, 1H), 2.97 (d, *J* = 13.7 Hz, 1H), 2.82 (d, *J* = 13.6 Hz, 1H), 2.80 (d, *J* = 13.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz,

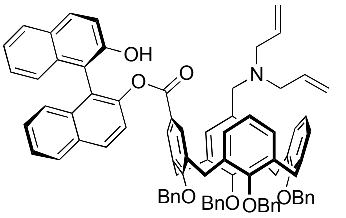
$CDCl_3$) δ 155.44, 155.03, 154.16, 137.61, 137.38, 137.32, 137.08, 137.02, 136.89, 136.29, 136.06, 135.40, 135.17, 134.52, 134.35, 134.12, 130.54, 130.51, 129.80, 129.78, 129.43, 129.19, 129.15, 128.77, 128.54, 128.15, 128.02, 127.98, 127.94, 127.87, 127.83, 122.55, 122.15, 118.38, 115.02, 76.67, 76.54, 76.14, 76.00, 51.54, 50.15, 31.22, 31.08 ppm; IR 3423, 3061, 3029, 2975, 2916, 2865, 1456, 1211, 1190, 981, 753, 697 cm^{-1}; Anal. Calcd for $C_{60}H_{54}BrNO_4$•$0.5CHCl_3$: C, 73.24; H, 5.49; N, 1.41. Found: C, 73.47; H, 5.45; N, 1.45.



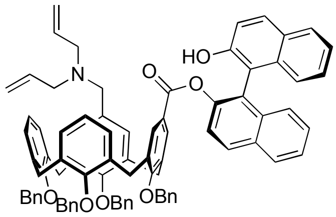
5-Bromo-11-(*N*,*N*-diallylaminomethyl)-25,26,27,28-tetrabenzyloxycalix[4]arene [(±)-6]. To a mixture of **5** (3.0 mmol), K_2CO_3 (6.0 mmol), and CH_3CN (60 ml) was added allyl bromide (3.3 mmol) and the mixture was heated at 50 ˚C for 15 h. The reaction mixture was cooled to room temperature and the mixture was quenched with water. After the removal of CH_3CN by evaporation, organic materials were extracted with $CHCl_3$ (30 ml × 3) and the organic extracts were dried over $MgSO_4$. Evaporation of solvents and purification of the residue by column chromatography on silica gel ($CHCl_3$/AcOEt = 30/1 to 15/1 as eluent) afforded **6** in 90% yield: ^1H NMR (400 MHz, $CDCl_3$) δ 7.10–7.38 (m, 20H), 6.59–6.77 (m, 6H), 6.34–6.41 (m, 4H), 5.81–5.90 (m, 2H), 5.13–5.18 (m, 4H), 4.80–5.15 (m, 8H), 4.23 (d, J = 13.6 Hz, 1H), 4.21 (d, J = 13.5 Hz, 1H), 4.07 (d, J = 13.5 Hz, 1H), 4.05 (d, J = 13.5 Hz, 1H), 3.39 (s, 2H), 2.94–3.00 (m, 6H), 2.81 (d, J = 13.7 Hz, 1H), 2.78 (d, J = 13.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.39, 154.96, 154.51, 154.09, 137.68, 137.40, 137.09, 136.96, 136.11, 135.81, 135.23, 134.98, 134.41, 130.53, 130.41, 129.88, 129.70, 129.39, 129.16, 129.05, 128.78, 128.16, 128.15, 128.00, 127.83, 127.80, 122.54, 122.28, 117.70, 115.04, 76.65, 76.56, 76.03, 56.82, 56.15, 31.26, 31.21, 31.11, 31.08 ppm; IR 3062, 3029, 2975, 2917, 2867, 2807, 1458, 1211, 1190, 979, 916, 697 cm^{-1}; Anal. Calcd for $C_{63}H_{58}BrNO_4$•$0.1CHCl_3$: C, 76.95; H, 5.94; N, 1.42. Found: C, 76.75; H, 5.89; N, 1.23.



5-Carboxy-11-(*N*,*N*-diallylaminomethyl)-25,26,27,28-tetrabenzyloxycalix[4]arene [(±)-7]. To a solution of **6** (2.0 mmol) in THF (50 ml) was added *n*-BuLi (3.0 mmol, 1.5M in hexane) at –78 ˚C under argon atmosphere and the mixture was stirred for 15 min at this temperature. Then, CO_2 gas was bubbled *via* a needle for 15 min at –78 ˚C. The reaction mixture was quenched with 0.1N HCl aq (40 ml). After removal of THF by evaporation, organic materials were extracted with $CHCl_3$ (20 ml × 3). The organic extracts were washed with water, and dried over $MgSO_4$. Evaporation of solvents and purification of the residue by column chromatography on silica gel ($CHCl_3$/MeOH = 40/1 to 10/1 as eluent) afforded **7** in 78% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.03 (br s, 1H), 7.19–7.44 (m, 22H), 6.41–6.73 (m, 8H), 6.03–6.13 (m, 2H), 5.39–5.42 (m, 2H), 5.01–5.15 (m, 6H), 4.78–4.88 (m, 4H), 4.23 (d, *J* = 13.4 Hz, 1H), 4.18 (d, *J* = 13.4 Hz, 1H), 4.16 (d, *J* = 13.4 Hz, 1H), 4.10 (d, *J* = 13.6 Hz, 1H), 3.83 (d, *J* = 13.6 Hz, 1H), 3.76 (d, *J* = 13.5 Hz, 1H), 3.01–3.18 (br m, 2H), 2.98 (d, *J* = 13.5 Hz, 1H), 2.96 (d, *J* = 14.1 Hz, 1H), 2.93 (d, *J* = 14.4 Hz, 1H), 2.89 (d, *J* = 14.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.85, 159.82, 156.13, 155.11, 155.07, 137.25, 136.99, 136.64, 136.56, 136.40, 136.03, 135.84, 135.32, 135.22, 134.75, 134.04, 131.48, 130.98, 130.73, 130.16, 129.79, 129.75, 129.47, 129.44, 128.72, 128.28, 128.16, 128.14, 128.09, 128.03, 127.92, 127.71, 127.28, 124.61, 124.09, 122.65, 122.23, 121.20, 77.03, 76.82, 76.11, 76.01, 53.86, 53.68, 31.17 ppm; IR 3422, 3060, 3029, 2920, 2868, 2526, 1703, 1455, 1212, 1189, 979, 763, 698 cm^{-1}; Anal. Calcd for $C_{64}H_{59}NO_6{\bullet}0.7CHCl_3$: C, 76.11; H, 5.82; N, 1.37. Found: C, 76.14; H, 5.89; N, 1.38.



8a or **8b**

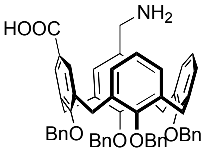


8b or **8a**

Diastereomers 8a and 8b. To a solution of **7** (2.0 mmol), DCC (3.0 mmol), and DMAP (1.0 mmol) in CH_2Cl_2 (30 ml) was added (*R*)-BINOL (2.2 mmol) at room temperature and the mixture was stirred for 6 h. The reaction mixture was filtrated over celite and the filtrate was dried over $MgSO_4$. Evaporation of CH_2Cl_2 and purification of the residue by column chromatography on silica gel ($CHCl_3$/AcOEt = 30/1 to 5/1 as eluent) afforded the ~1:1 mixture of diastereomers **8a** and **8b** in 92% yield.

8a. $[\alpha]^{25}_{D}$ +49.3 (*c* 1.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.9 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.9 Hz, 1H), 7.50 (dt, *J* = 1.5, 7.3 Hz, 1H), 7.09–7.36 (m, 26H), 6.90–6.94 (m, 2H), 6.37–6.59 (m, 6H), 6.23–6.25 (m, 2H), 6.12 (br s, 1H), 5.66–5.76 (m, 2H), 4.98–5.06 (m, 8H), 4.76–4.86 (m, 4H), 4.17 (d, *J* = 13.5 Hz, 1H), 4.16 (d, *J* = 13.5 Hz, 1H), 4.00 (d, *J* = 13.4 Hz, 1H), 3.98 (d, *J* = 13.5 Hz, 1H), 3.24 (d, *J* = 13.7 Hz, 1H), 3.16 (d, *J* = 13.8 Hz, 1H), 2.93 (d, *J* = 13.5 Hz, 1H+1H), 2.77 (d, *J* = 6.1 Hz, 4H), 2.68 (d, *J* = 13.6 Hz, 1H), 2.63 (d, *J* = 13.7 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.57, 160.04, 155.20, 154.89, 153.95, 151.90, 148.22, 137.59, 137.36, 136.94, 135.93, 135.91, 135.64, 135.60, 135.42, 135.33, 134.52, 134.30, 133.78, 133.75, 133.53, 133.45, 131.84, 130.56, 130.26, 130.00, 129.86, 129.68, 129.60, 129.44, 128.87, 128.69, 128.43, 128.35, 128.24, 128.19, 128.16, 128.04, 128.01, 127.97, 127.95, 127.87, 127.82, 127.75, 127.00, 126.47, 125.81, 124.79, 123.12, 122.61, 122.31, 122.23, 121.95, 118.23, 117.70, 114.28, 76.73, 76.62, 76.04, 75.89, 56.77, 56.20, 31.25, 31.18, 31.05, 31.02 ppm; IR 3525, 3446, 3060, 3030, 2976, 2918, 2867, 2816, 1730, 1457, 1303, 1211, 1171, 980, 747, 698 cm^{-1}; Anal. Calcd for $C_{84}H_{71}NO_7$•$0.1CHCl_3$: C, 82.91; H, 5.87; N, 1.15. Found: C, 82.60; H, 5.74; N, 0.93.

8b. $[\alpha]^{23}_{D}$ +77.3 (*c* 0.88, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.9 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.76–7.80 (m, 2H), 7.51 (dt, *J* = 1.1, 7.4 Hz, 1H), 7.47 (d, *J* = 8.9 Hz, 1H), 7.12–7.36 (m, 26H), 6.89–6.95 (m, 2H), 6.37–6.61 (m, 6H), 6.12–6.19 (m, 2H), 5.70–5.80 (m, 2H), 5.48 (br s, 1H), 4.91−5.12 (m, 8H), 4.75–4.87 (m, 4H), 4.18 (d, *J* = 13.4 Hz, 1H), 4.16 (d, *J* = 13.3 Hz, 1H), 3.98 (d, *J* = 13.5 Hz, 1H), 3.97 (d, *J* = 13.5 Hz, 1H), 3.26 (d, *J* = 13.4 Hz, 1H), 3.19 (d, *J* = 13.4 Hz, 1H), 2.94 (d, *J* = 13.6 Hz, 1H+1H), 2.86 (dd, *J* = 6.3, 13.9 Hz, 2H), 2.78 (dd, *J* = 7.1, 13.8 Hz, 2H), 2.66 (d, *J* = 13.7 Hz, 1H), 2.64 (d, *J* = 13.7 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.84, 160.12, 155.23, 154.90, 154.02, 151.79, 148.43, 137.58, 137.35, 136.88, 135.93, 135.58, 135.48, 135.21, 135.16, 134.57, 134.44, 133.75, 133.58, 133.51, 133.34, 131.98, 130.48, 130.36, 130.32, 130.00, 129.61, 129.59, 129.46, 129.40, 129.07, 128.82, 128.68, 128.33, 128.26, 128.19, 128.02, 127.98, 127.95, 127.90, 127.86, 127.76, 127.71, 127.24, 126.54, 125.99, 125.61, 124.62, 123.27, 123.13, 122.27, 122.17, 121.85, 118.30, 117.66, 114.25, 76.69, 76.55, 76.17, 75.80, 56.33, 55.87, 31.21, 31.14, 31.05 ppm; IR 3522, 3446, 3060, 3030, 3006, 2976, 2917, 2867, 2814, 1728, 1457, 1303, 1210, 1171, 979, 763, 747, 698 cm^{-1}; Anal. Calcd for $C_{84}H_{71}NO_7$: C, 83.62; H, 5.93; N, 1.16. Found: C, 83.69; H, 5.83; N, 1.28.



5-(Aminomethyl)-11-carboxy-25,26,27,28-tetrabenzyloxycalix[4]arene [(+)-1 or (–)-1]. The mixture of **8a** or **8b** (0.50 mmol), *N*,*N*'-dimethylbarbituric acid [NDMBA (2.5 mmol)], $Pd(OAc)_2$ (0.10 mmol), and PPh_3 (0.40 mmol) in CH_2Cl_2 (20 ml) was stirred for 8 h at 35 ˚C. After the removal of CH_2Cl_2 by evaporation, the solvent was replaced by benzene (20 ml). The benzene solution was washed with sat. $NaHCO_3$ aq (10 ml × 3), and dried over $MgSO_4$. Evaporation of solvents and purification of the residue by column chromatography on silica gel ($CHCl_3$/MeOH = 30/1 to 5/1 as eluent) afforded the de-*N*-allylated product. The de-*N*-allylated product in THF (5 ml)-ethanol (3 ml) mixed solvents was treated with 1M NaOH aq (1.5 ml), and the mixture was heated at 60 ˚C for 6 h. Then, the reaction mixture was cooled to 0 ˚C and neutralized with 1N HCl aq (1.6 ml). After removal of THF and ethanol by evaporation, organic materials were extracted with $CHCl_3$ (10 ml × 3). The organic extracts were washed with water, and dried over $MgSO_4$. Evaporation of solvents and purification of the residue by column chromatography on silica gel ($CHCl_3$/MeOH =

15/1 to 3/1 as eluent) afforded $(-)_{298}$-**1** or $(+)_{298}$-**1** in 43% and 41% yields, respectively: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (br s, 3H), 6.20–7.28 (m, 30H), 4.69–4.97 (m, 8H), 3.91–4.17 (m, 6H), 2.79–2.94 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.16, 159.80, 156.05, 155.33, 154.84, 137.55, 137.40, 137.26, 136.98, 136.61, 136.12, 135.28, 134.98, 134.78, 134.14, 133.83, 130.67, 130.18, 129.69, 129.60, 129.04, 128.84, 128.48, 128.25, 128.09, 127.97, 127.82, 127.76, 127.74, 126.41, 123.79, 122.52, 122.17, 76.59, 76.49, 75.96, 43.11, 31.15, 31.04, 30.87 ppm; IR 3398, 3060, 3030, 2974, 2916, 2868, 2610, 1685, 1602, 1455, 1376, 1281, 1213, 1191, 983, 762, 734, 698 cm^{-1}; Anal. Calcd for $C_{58}H_{51}NO_6$•$0.5CHCl_3$: C, 76.60; H, 5.60; N, 1.53. Found: C, 76.54; H, 5.81; N, 1.50.

Resolution of calix[4]arenes 8a and 8b by preparative HPLC. Resolution of diastereomers **8a** and **8b** was carried out by preparative HPLC using a SUMICHIRAL OA-4800 column (2.0 × 25 cm) with $CHCl_3$ as the eluent. The diastereomeric mixture of **8a** and **8b** (~1:1) (300 mg) was loaded onto the preparative column. The $CHCl_3$ solutions of separated diastereomers were washed with sat. $NaHCO_3$ aq, and pure calix[4]arenes **8a** (first fraction) (~100 mg) and **8b** (second fraction) (~100 mg) were obtained. The diastereomeric purity of the calix[4]arene **8a** and **8b** was determined by HPLC analysis (Fig. S1).

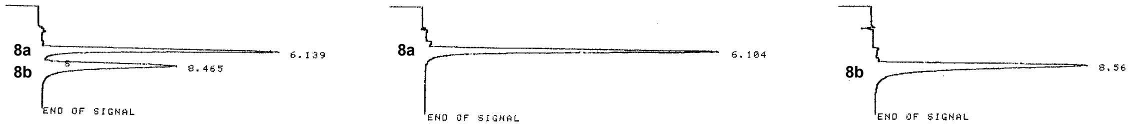
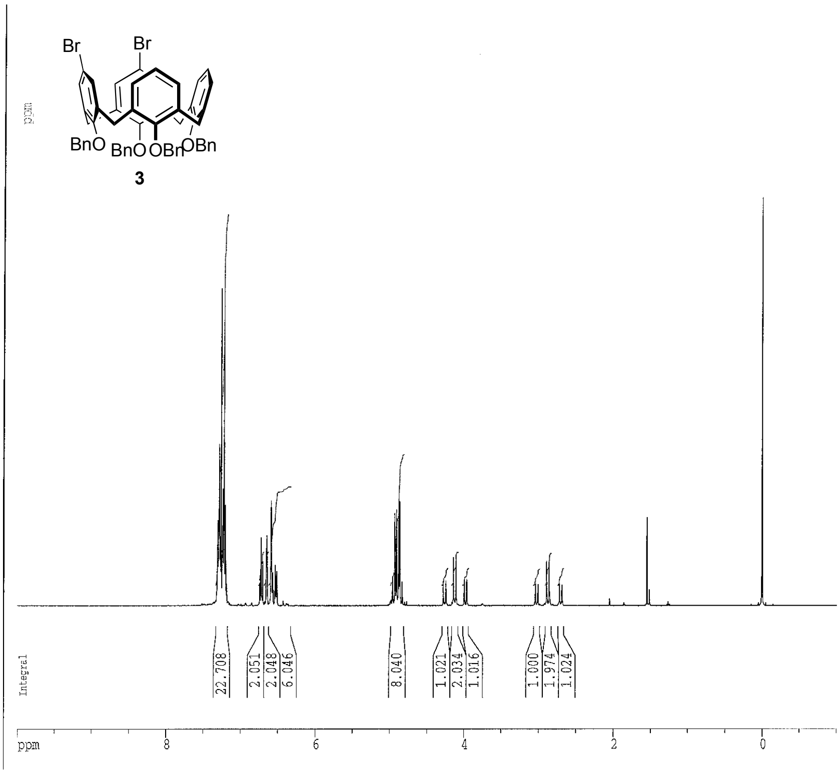


Fig. S1 HPLC chromatogram of calix[4]arene **8a** and **8b** [SUMICHIRAL OA-4800 (0.46 × 25 cm), $CHCl_3$/hexane = 80/20, 1.0 ml/min].

(1) S. Shimizu, A. Moriyama, K, Kito and Y. Sasaki, *J. Org. Chem.*, 2003, **68**, 2187.



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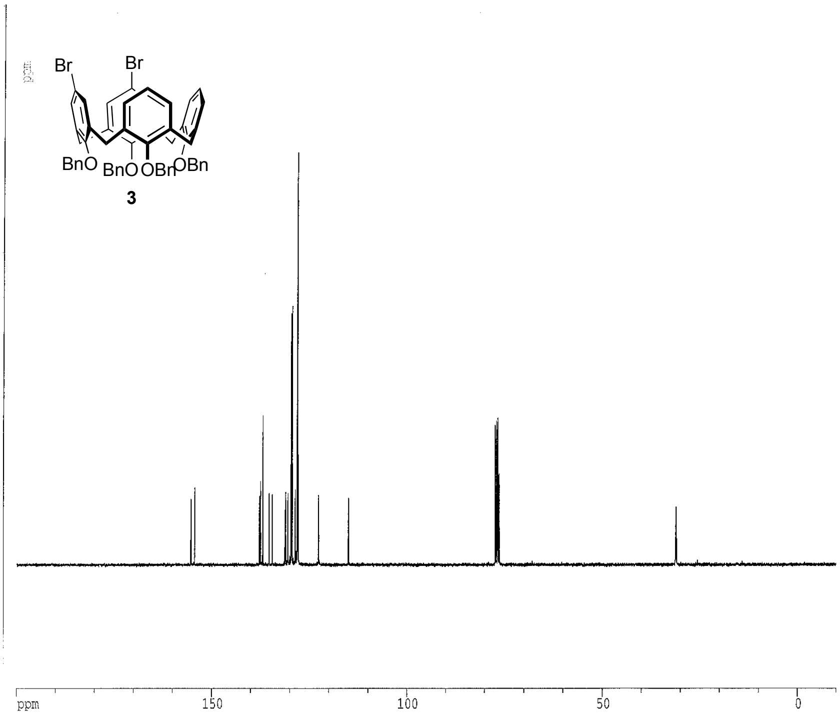
Current Data Parameters
NAME          Dec11-2007
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20071211
Time                9.05
INSTRUM           dpx400
PROBHD   5 mm QNP 1H/1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                   362
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec

============ CHANNEL f1 ============
NUC1                  1H
P1                  8.90 usec
PL1                -2.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300101 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P               10.000 ppm
F1               4001.30 Hz
F2P               -1.000 ppm
F2               -400.13 Hz
PPMCM            0.55000 ppm/cm
HZCM           220.07150 Hz/cm
```



```
Current Data Parameters
NAME          Dec11-2007
EXPNO                 10
PROCNO                 1

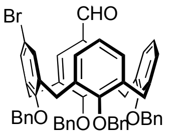
F2 - Acquisition Parameters
Date_           20071211
Time                8.41
INSTRUM           dpx400
PROBHD   5 mm QNP 1H/1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   237
DS                     2
SWH            25125.629 Hz
FIDRES          0.383387 Hz
AQ             1.3042164 sec
RG                3649.1
DW                19.900 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec

============ CHANNEL f1 ============
NUC1                 13C
P1                  8.00 usec
PL1                -2.00 dB
SFO1         100.6237959 MHz

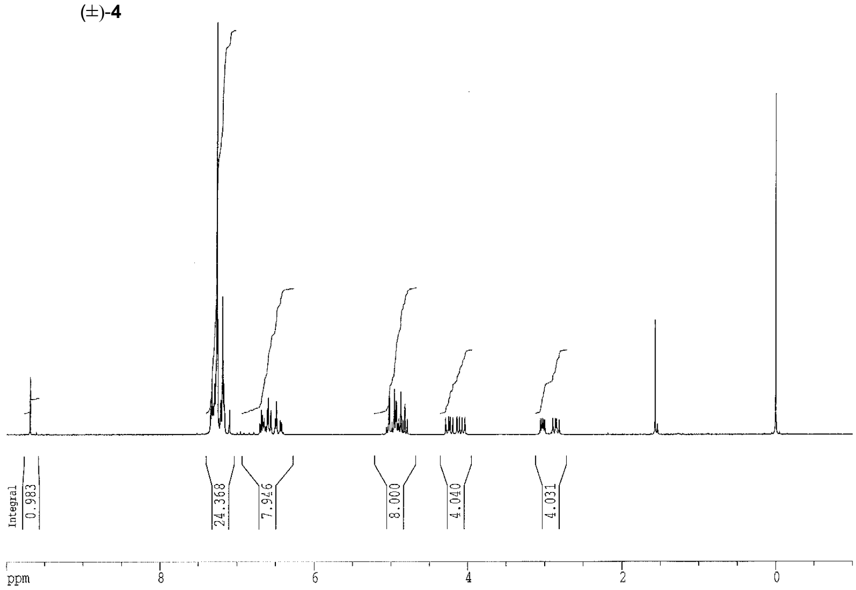
============ CHANNEL f2 ============
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -2.00 dB
PL12               18.00 dB
PL13               18.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127930 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P              200.000 ppm
F1              20122.56 Hz
F2P              -10.000 ppm
F2              -1006.13 Hz
PPMCM           10.50000 ppm/cm
HZCM          1056.43433 Hz/cm
```



(±)-**4**



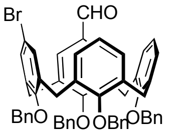
```
Current Data Parameters
NAME         Feb13-2008
EXPNO                30
PROCNO                1

F2 - Acquisition Parameters
Date_          20080213
Time               8.56
INSTRUM          dpx400
PROBHD    5 mm QNP 1H/1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                645.1
DW               60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           1.00000000 sec

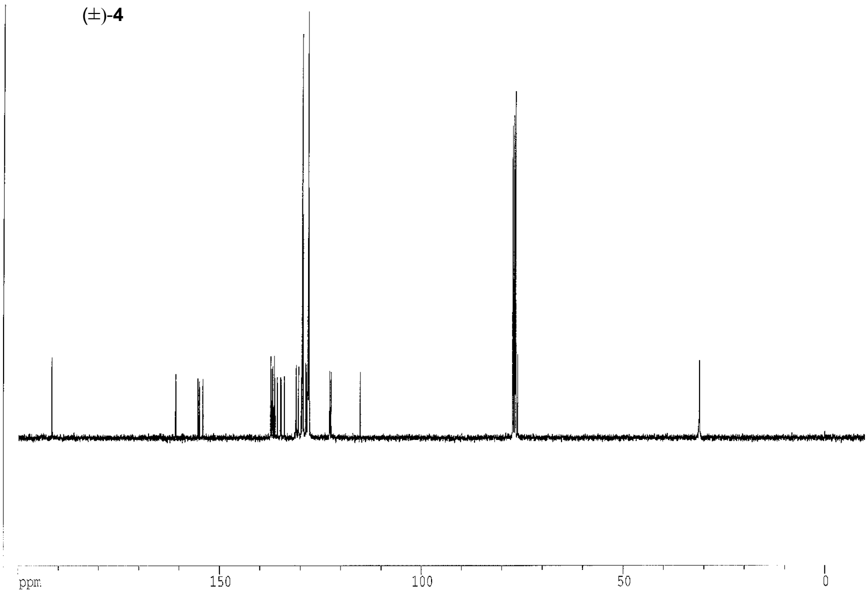
============ CHANNEL f1 =============
NUC1                 1H
P1                 8.90 usec
PL1               -2.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300088 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P              10.000 ppm
F1              4001.30 Hz
F2P              -1.000 ppm
F2              -400.13 Hz
PPMCM           0.55000 ppm/cm
HZCM          220.07150 Hz/cm
```



(±)-**4**



```
Current Data Parameters
NAME         Feb13-2008
EXPNO                10
PROCNO                1

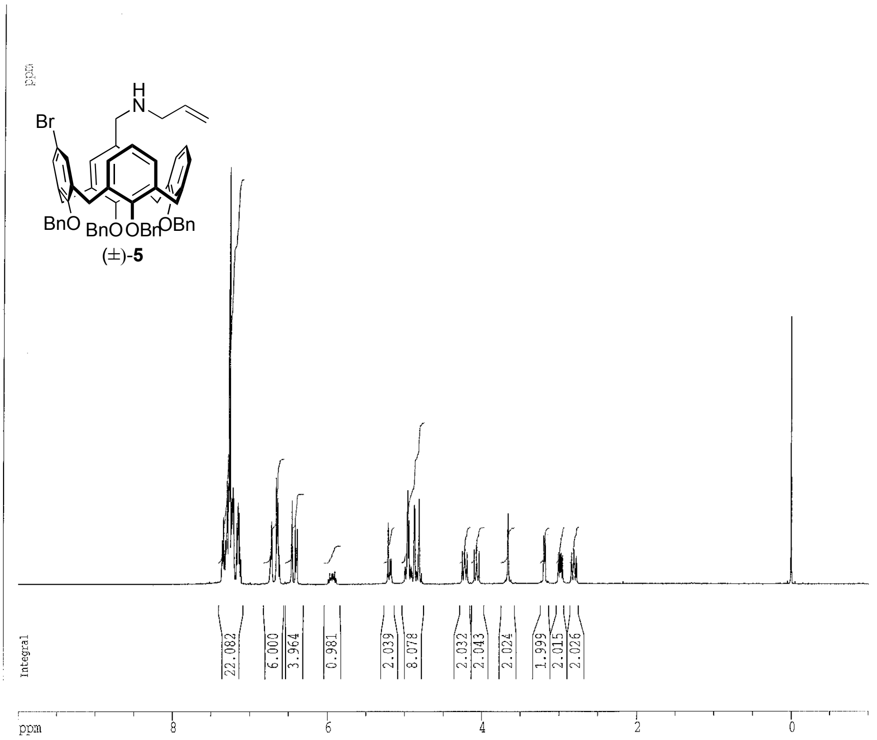
F2 - Acquisition Parameters
Date_          20080213
Time               8.24
INSTRUM          dpx400
PROBHD    5 mm QNP 1H/1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  266
DS                    2
SWH           25125.629 Hz
FIDRES         0.383387 Hz
AQ            1.3042164 sec
RG               9195.2
DW               19.900 usec
DE                 6.00 usec
TE                300.0 K
D1           2.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec

============ CHANNEL f1 =============
NUC1                13C
P1                 8.00 usec
PL1               -2.00 dB
SFO1        100.6237959 MHz

============ CHANNEL f2 =============
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -2.00 dB
PL12              18.00 dB
PL13              18.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127869 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
F1P             200.000 ppm
F1             20122.56 Hz
F2P             -10.000 ppm
F2             -1006.13 Hz
PPMCM          10.50000 ppm/cm
HZCM         1056.43420 Hz/cm
```



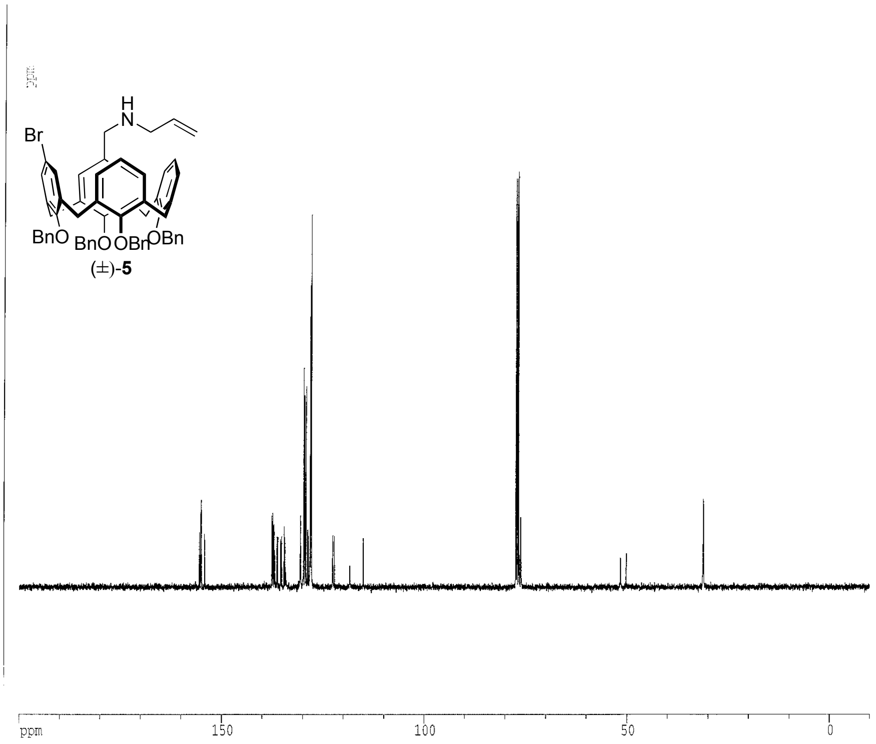
```
Current Data Parameters
NAME         Feb14-2008
EXPNO                30
PROCNO                1

F2 - Acquisition Parameters
Date_          20080214
Time               9.11
INSTRUM          dpx400
PROBHD    5 mm QNP 1H/1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                  362
DW               60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           1.00000000 sec

============ CHANNEL f1 =============
NUC1                 1H
P1                 8.90 usec
PL1               -2.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300098 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P              10.000 ppm
F1              4001.30 Hz
F2P              -1.000 ppm
F2              -400.13 Hz
PPMCM           0.55000 ppm/cm
HZCM          220.07150 Hz/cm
```



```
Current Data Parameters
NAME         Feb14 2008
EXPNO                10
PROCNO                1

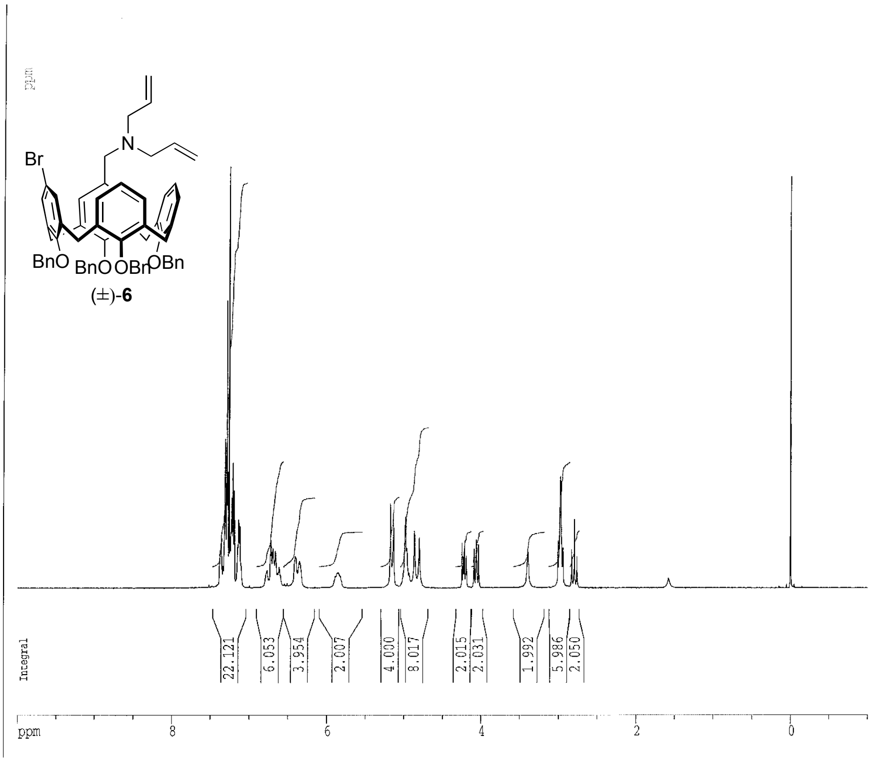
F2 - Acquisition Parameters
Date_          20080214
Time               8.28
INSTRUM          dpx400
PROBHD    5 mm QNP 1H/1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  427
DS                    2
SWH           25125.629 Hz
FIDRES         0.383387 Hz
AQ            1.3042164 sec
RG              11585.2
DW               19.900 usec
DE                 6.00 usec
TE                300.0 K
D1           2.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec

============ CHANNEL f1 =============
NUC1                13C
P1                 8.00 usec
PL1               -2.00 dB
SFO1        100.6237959 MHz

============ CHANNEL f2 =============
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -2.00 dB
PL12              18.00 dB
PL13              18.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127830 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
F1P             200.000 ppm
F1             20122.56 Hz
F2P             -10.000 ppm
F2             -1006.13 Hz
PPMCM          10.50000 ppm/cm
HZCM         1056.43420 Hz/cm
```



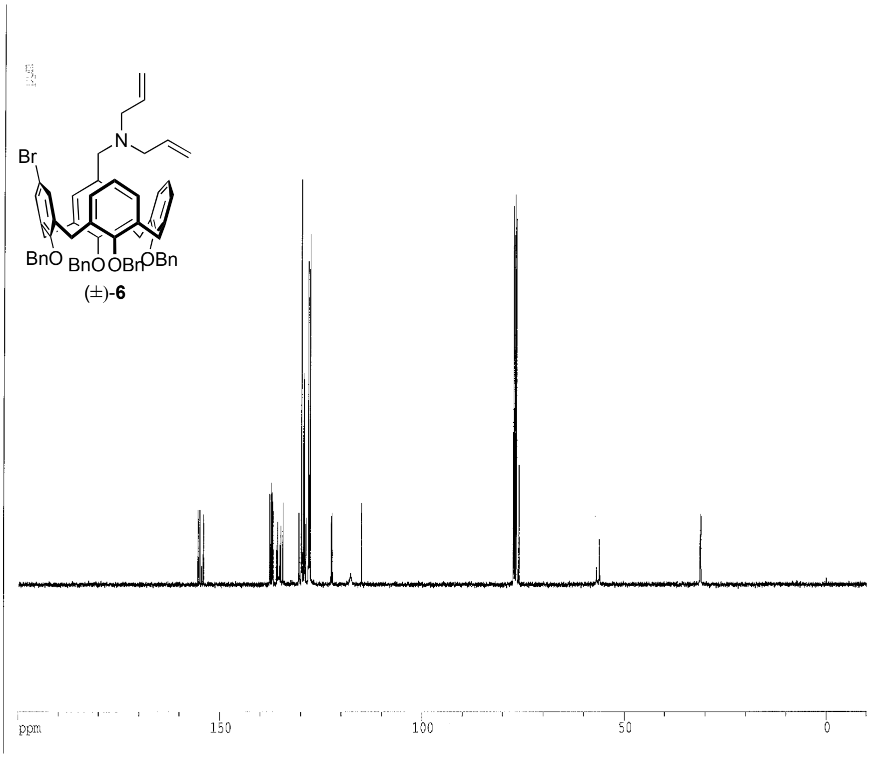
```
Current Data Parameters
NAME          Feb15-2008
EXPNO                 30
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080215
Time                9.11
INSTRUM           dpx400
PROBHD    5 mm QNP 1H/1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                   362
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec

============ CHANNEL f1 =============
NUC1                  1H
P1                  8.90 usec
PL1                -2.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300100 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P               10.000 ppm
F1               4001.30 Hz
F2P               -1.000 ppm
F2               -400.13 Hz
PPMCM            0.55000 ppm/cm
HZCM           220.07150 Hz/cm
```



```
Current Data Parameters
NAME          Feb15-2008
EXPNO                 10
PROCNO                 1

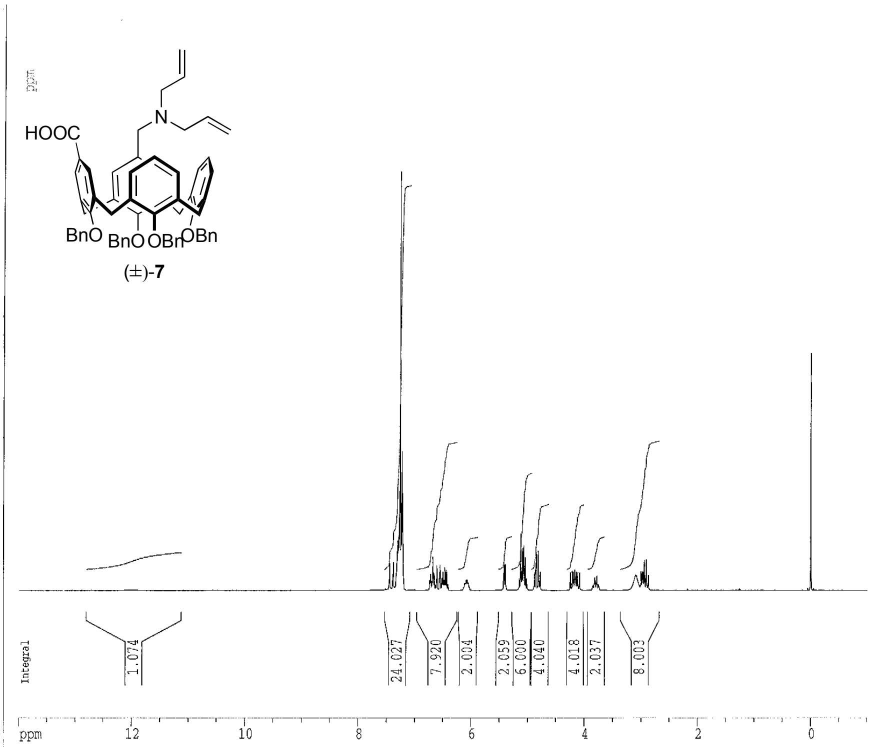
F2 - Acquisition Parameters
Date_           20080215
Time                8.23
INSTRUM           dpx400
PROBHD    5 mm QNP 1H/1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   490
DS                     2
SWH            25125.629 Hz
FIDRES          0.383387 Hz
AQ             1.3042164 sec
RG                  6502
DW                19.900 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec

============ CHANNEL f1 =============
NUC1                 13C
P1                  8.00 usec
PL1                -2.00 dB
SFO1         100.6237959 MHz

============ CHANNEL f2 =============
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -2.00 dB
PL12               18.00 dB
PL13               18.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127861 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P              200.000 ppm
F1              20122.56 Hz
F2P              -10.000 ppm
F2              -1006.13 Hz
PPMCM           10.50000 ppm/cm
HZCM          1056.43420 Hz/cm
```



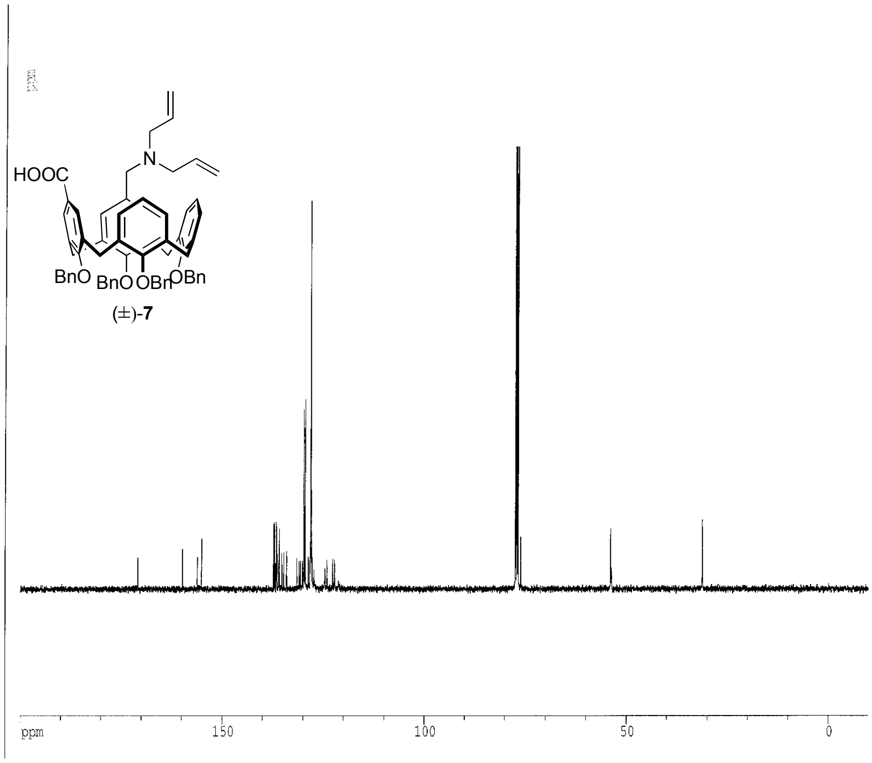
```
Current Data Parameters
NAME          Feb13-2008
EXPNO                 60
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080213
Time                9.49
INSTRUM           dpx400
PROBHD    5 mm QNP 1H/1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                   362
DW                60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec

============ CHANNEL f1 =============
NUC1                  1H
P1                  8.90 usec
PL1                -2.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300081 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P               14.000 ppm
F1               5601.82 Hz
F2P               -1.000 ppm
F2               -400.13 Hz
PPMCM            0.75000 ppm/cm
HZCM           300.09750 Hz/cm
```



```
Current Data Parameters
NAME          Feb13-2008
EXPNO                 40
PROCNO                 1

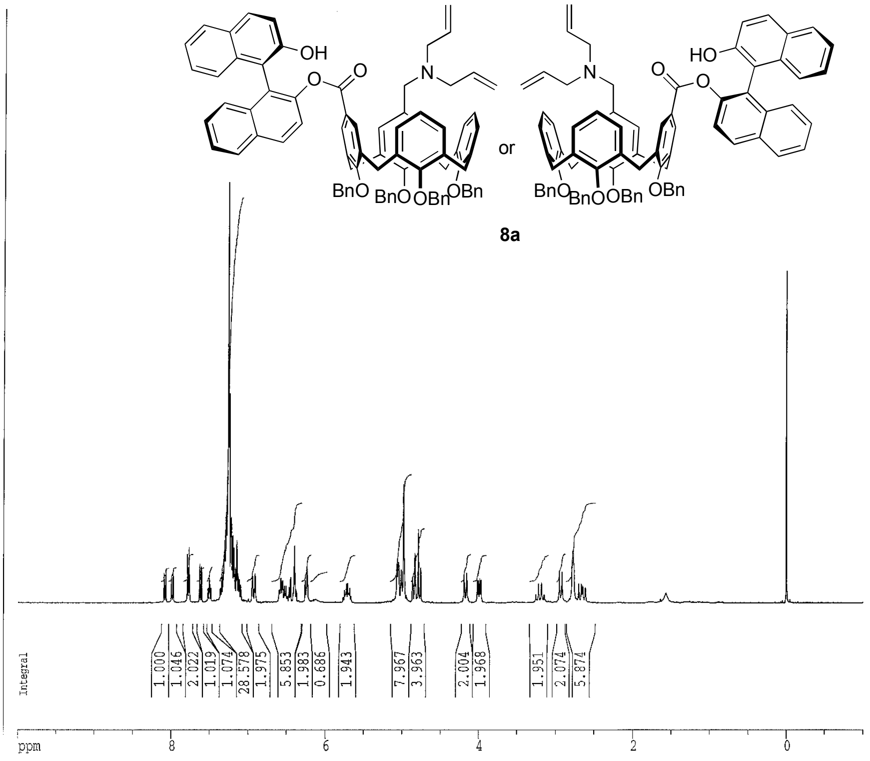
F2 - Acquisition Parameters
Date_           20080213
Time                9.09
INSTRUM           dpx400
PROBHD    5 mm QNP 1H/1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   428
DS                     2
SWH            25125.629 Hz
FIDRES          0.383387 Hz
AQ             1.3042164 sec
RG                 16384
DW                19.900 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec

============ CHANNEL f1 =============
NUC1                 13C
P1                  8.00 usec
PL1                -2.00 dB
SFO1         100.6237959 MHz

============ CHANNEL f2 =============
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -2.00 dB
PL12               18.00 dB
PL13               18.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127884 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P              200.000 ppm
F1              20122.56 Hz
F2P              -10.000 ppm
F2              -1006.13 Hz
PPMCM           10.50000 ppm/cm
HZCM          1056.43420 Hz/cm
```



8a

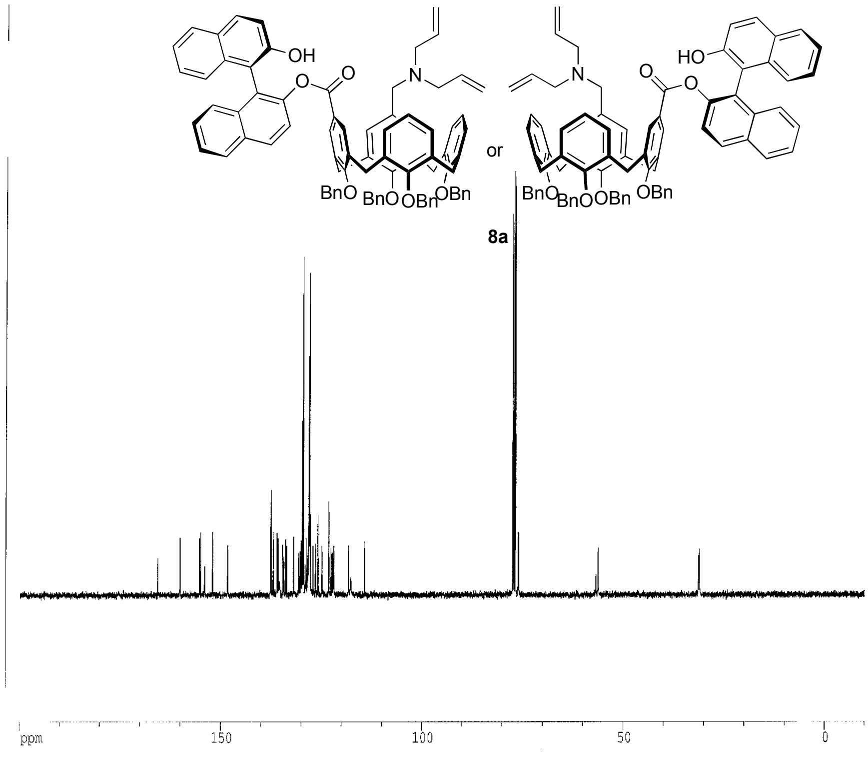
```
Current Data Parameters
NAME           Dec22-2007
EXPNO                  50
PROCNO                  1

F2 - Acquisition Parameters
Date_            20071222
Time                10.15
INSTRUM            dpx400
PROBHD   5 mm QNP 1H/1
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                    362
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec

============ CHANNEL f1 =============
NUC1                   1H
P1                   8.90 usec
PL1                 -2.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300108 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                10.000 ppm
F1                4001.30 Hz
F2P                -1.000 ppm
F2                -400.13 Hz
PPMCM             0.55000 ppm/cm
HZCM            220.07150 Hz/cm
```



8a

```
Current Data Parameters
NAME           Dec22-2007
EXPNO                  10
PROCNO                  1

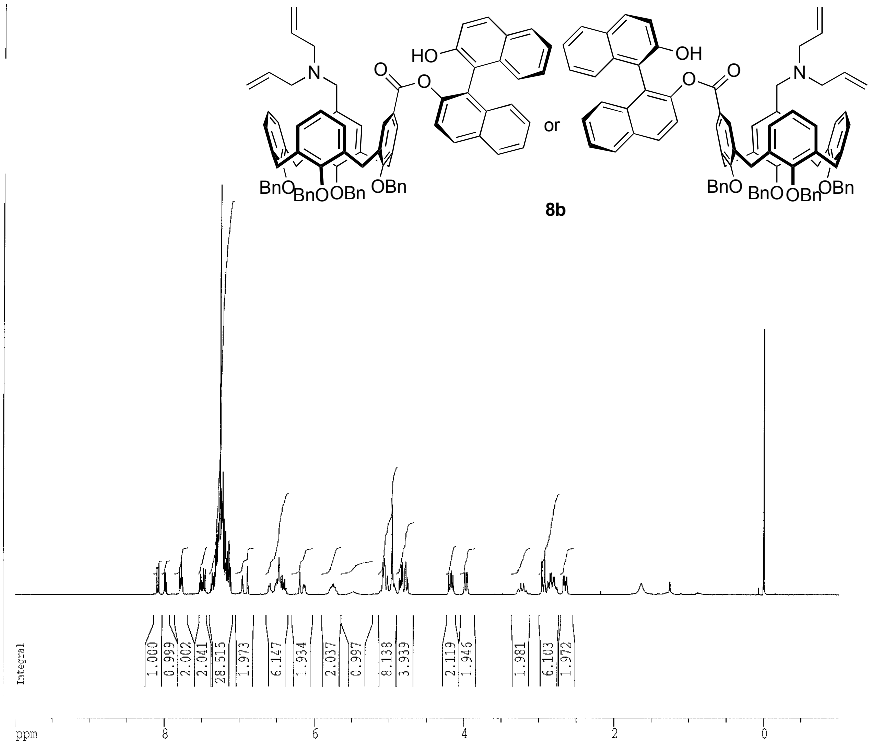
F2 - Acquisition Parameters
Date_            20071222
Time                 8.39
INSTRUM            dpx400
PROBHD   5 mm QNP 1H/1
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    355
DS                      2
SWH             25125.629 Hz
FIDRES           0.383387 Hz
AQ              1.3042164 sec
RG                   8192
DW                 19.900 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
D11            0.03000000 sec
D12            0.00002000 sec

============ CHANNEL f1 =============
NUC1                  13C
P1                   8.00 usec
PL1                 -2.00 dB
SFO1          100.6237959 MHz

============ CHANNEL f2 =============
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                 -2.00 dB
PL12                18.00 dB
PL13                18.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF            100.6127945 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                  20.00 cm
F1P               200.000 ppm
F1               20122.56 Hz
F2P               -10.000 ppm
F2               -1006.13 Hz
PPMCM            10.50000 ppm/cm
HZCM           1056.43433 Hz/cm
```



8b

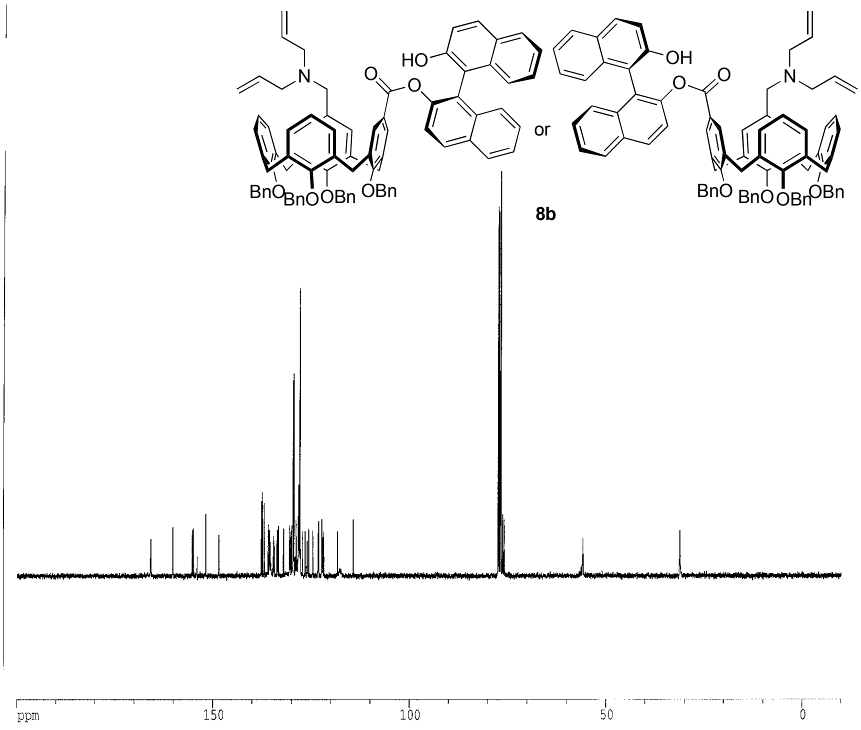
```
Current Data Parameters
NAME          Feb23-2008
EXPNO                130
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080223
Time               13.42
INSTRUM           dpx400
PROBHD   5 mm QNP 1H/1
PULPROG             zg30
TD                 65536
SOLVENT            CDC13
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                 574.7
DW                62.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec

============ CHANNEL f1 =============
NUC1                  1H
P1                  8.80 usec
PL1                -1.20 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300100 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P               10.000 ppm
F1               4001.30 Hz
F2P               -1.000 ppm
F2               -400.13 Hz
PPMCM            0.55000 ppm/cm
HZCM           220.07150 Hz/cm
```



8b

```
Current Data Parameters
NAME          Dec22-2007
EXPNO                 30
PROCNO                 1

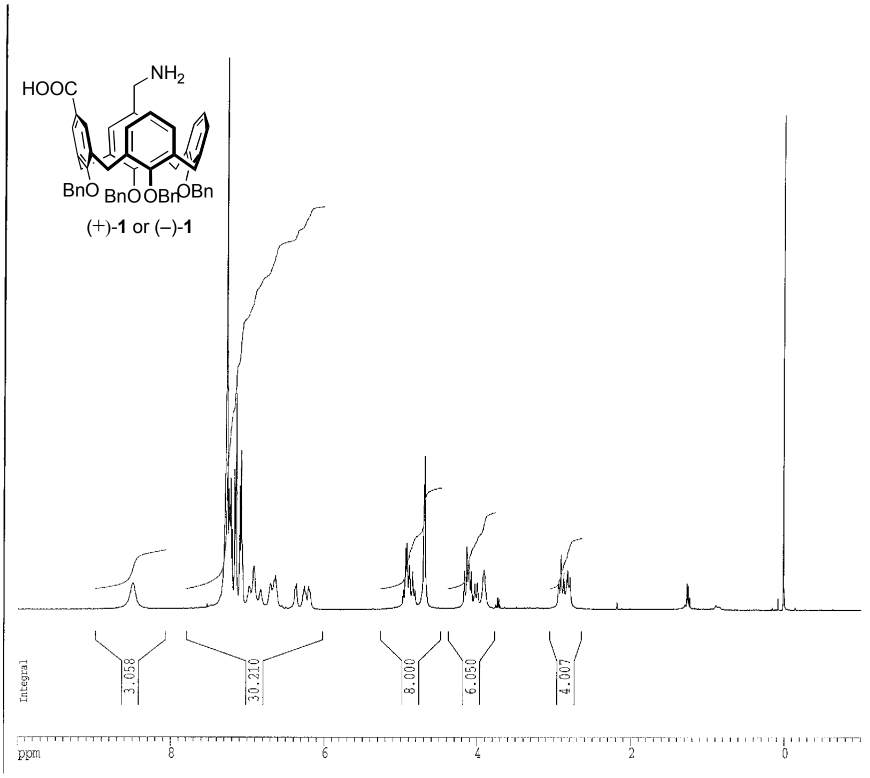
F2 - Acquisition Parameters
Date_           20071222
Time                9.30
INSTRUM           dpx400
PROBHD   5 mm QNP 1H/1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDC13
NS                   391
DS                     2
SWH            25125.629 Hz
FIDRES          0.383387 Hz
AQ             1.3042164 sec
RG                4597.6
DW                19.900 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec

============ CHANNEL f1 =============
NUC1                 13C
P1                  8.00 usec
PL1                -2.00 dB
SFO1         100.6237959 MHz

============ CHANNEL f2 =============
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -2.00 dB
PL12               18.00 dB
PL13               18.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127968 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P              200.000 ppm
F1              20122.56 Hz
F2P              -10.000 ppm
F2              -1006.13 Hz
PPMCM           10.50000 ppm/cm
HZCM          1056.43445 Hz/cm
```



(+)-**1** or (–)-**1**

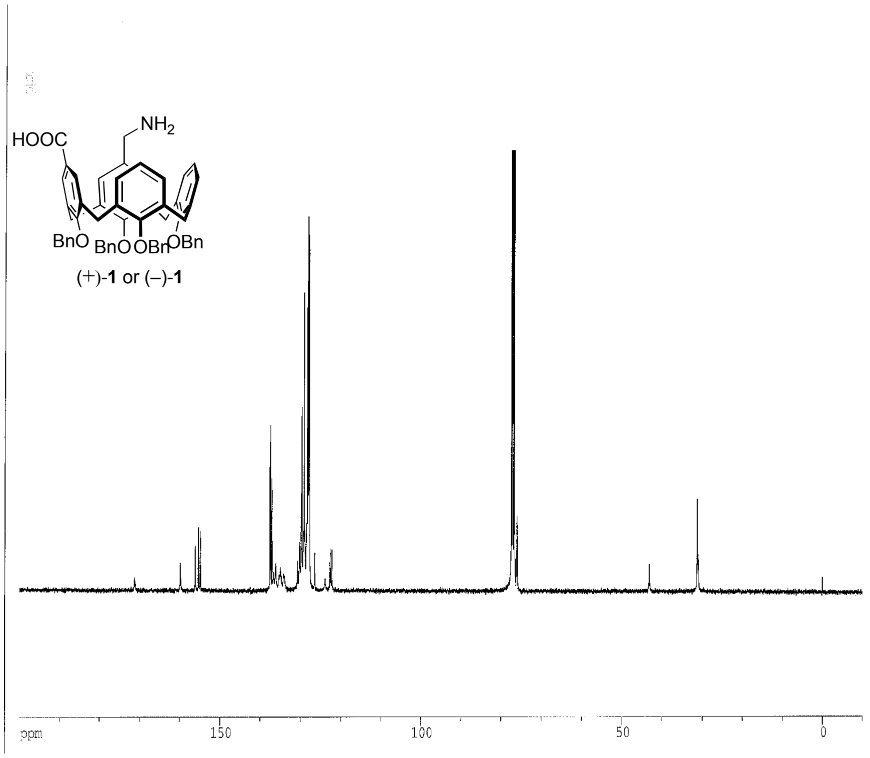
```
Current Data Parameters
NAME          Oct31-2007
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20071031
Time                9.54
INSTRUM           dpx400
PROBHD    5 mm QNP 1H/1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                   256
DW                62.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec

============ CHANNEL f1 ============
NUC1                  1H
P1                  8.80 usec
PL1                -1.20 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300058 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P               10.000 ppm
F1               4001.30 Hz
F2P               -1.000 ppm
F2               -400.13 Hz
PPMCM            0.55000 ppm/cm
HZCM           220.07150 Hz/cm
```



(+)-**1** or (–)-**1**

```
Current Data Parameters
NAME          Mar05-2008
EXPNO                260
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080305
Time               21.52
INSTRUM           dpx400
PROBHD    5 mm QNP 1H/1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                 11240
DS                     2
SWH            25125.629 Hz
FIDRES          0.383387 Hz
AQ             1.3042164 sec
RG                7298.2
DW                19.900 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec

============ CHANNEL f1 ============
NUC1                 13C
P1                  8.00 usec
PL1                -2.00 dB
SFO1         100.6237959 MHz

============ CHANNEL f2 ============
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -2.00 dB
PL12               18.00 dB
PL13               18.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127823 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P              200.000 ppm
F1              20122.56 Hz
F2P              -10.000 ppm
F2              -1006.13 Hz
PPMCM           10.50000 ppm/cm
HZCM          1056.43420 Hz/cm
```