Supporting Information for

Meta-Bridged Calix[4]arenes: A Straightforward Synthesis via Organomercurial Chemistry

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Experimental procedures and characterizations

General Experimental Procedures

All chemicals were purchased from commercial sources and used without further purification. Solvents were dried and distilled using conventional methods. Melting points were measured on Heiztisch Mikroskop – Polytherm A (Wagner & Munz, Germany). NMR spectra were performed on Varian Gemini 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz) and on Bruker Advance DRX 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) spectrometers. Deuterated solvents used are indicated in each case. Chemical shifts (δ) are expressed in ppm and are referred to the residual peak of the solvent or TMS as an internal standard; coupling constants (J) are in Hz. The mass analyses were performed using ESI technique on Q–TOF (Micromass) spectrometer. Elemental analyses were done on Perkin–Elmer 240, Elementar vario EL (Elementar, Germany) or Mitsubishi TOX–100 instruments. All samples were dried in the desiccator over P_2O_5 under vacuum (1 Torr) at 80 °C for 8 hours. The IR spectra were measured on an FT–IR spectrometer Nicolet 740 or Bruker IFS66 spectrometers equipped with a heatable Golden Gate Diamante ATR–Unit (SPECAC) in KBr. 100 Scans for one spectrum were co–added at a spectral resolution of 4 cm^{-1}. The courses of the reactions were monitored by TLC using TLC aluminum sheets with Silica gel 60 F_{254} (Merck). The column chromatography was performed using Silica gel 60 (Merck).

General remark: All organomercury derivatives are considered potentially hazardous and require special consideration!

The corresponding trifluoroacetyloxymercurio derivatives **2a**, **2b** and **2c** were not characterized as we were unable to purify them using chromatographic separation – these compounds do not move on silica gel or alumina and they are unstable upon the contact with sorbent material. From these reasons we did not isolate these derivatives and they were always directly transformed into corresponding chloromercurio derivatives **3**.

4-chloromercurio-25,26,27,28-tetrapropoxycalix[4]arene (3a)

It was prepared on a 1 g scale using procedure currently published by our group:
P. Slavik, M. Dudič, K. Flídrová, J. Sýkora, I. Císařová, S. Böhm, P. Lhoták, *Org. Lett.* **2012**, *14*, 3628-3631

4-chloromercurio-25,26,27,28-tetramethoxycalix[4]arene (3b)

A mixture of calixarene **1b** (200 mg, 0.42 mmol) and $Hg(TFA)_2$ (180 mg, 0.42 mmol) was dissolved in 30 ml of dry chloroform and stirred overnight at room temp. Brine (30 ml) was then added and the reaction mixture was stirred for 1 h. The organic layer was separated, washed three times with water and dried over $MgSO_4$. Solvent was removed under a reduced pressure, and the crude product **3b** (white powder) was used without any purification into next step. HRMS (ESI$^+$): $[M+NH_4]^+$ calcd: 734.19554, found: 734.19517 (100% int.); $[M+Na]^+$ calcd: 739.15093, found: 739.14982 (50%); $[M+K]^+$ calcd: 755.12487, found: 755.12337 (20%).

4-chloromercurio-25,26,27,28-tetraethoxycalix[4]arene (3c)

A mixture of calixarene **1c** (225 mg, 0.42 mmol) and $Hg(CF_3COO)_2$ (180 mg, 0.42 mmol) was dissolved in dry chloroform and stirred overnight at room temp. Brine (30 ml) was then added and the reaction mixture was stirred vigorously for 1 h. The organic layer was separated, washed with water and dried over $MgSO_4$. Solvent was removed under a reduced pressure to yield the crude product which was purified by column chromatography on a silica gel (eluent = CH_2Cl_2:hexane 1:1, v/v). The title compound was obtained as a white solid in 65% yield (0.210 g), m.p. 245 - 247 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz, 298 K) δ 6.83-7.12 (m, 6H, ArH), 6.22-6.39 (m, 5H, ArH), 4.70 (d, 1H, *J*=14.1 Hz, $ArCH_2Ar$), 4.46 (d, 1H, *J*=13.5 Hz, $ArCH_2Ar$), 4.45 (d, 2H, *J*=13.2 Hz, $ArCH_2Ar$), 4.08-4.23 (m, 4H, OCH_2), 3.79-3.90 (m, 4H, OCH_2), 3.18 (d, 2H, *J*=13.5 Hz, $ArCH_2Ar$), 3.16 (d, 1H, *J*=13.5 Hz, $ArCH_2Ar$), 3.03 (d, 1H, *J*=14.1 Hz, $ArCH_2Ar$), 1.36-1.50 (m, 12H, CH_3) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz, 298 K) δ 157.7, 157.5, 157.1, 155.7, 148.2, 139.0, 138.9, 137.4, 137.2, 136.7, 135.8, 134.4, 134.1, 130.5, 130.2, 129.1, 128.9, 128.7, 128.1, 127.9, 127.5, 123.8, 122.5, 122.3, 70.8, 70.6, 70.4, 69.9, 34.5, 31.6, 31.3, 31.2, 15.9, 15.5 ppm. HRMS (TOF MS ESI+): $[M+NH_4]^+$ calcd: 790.25814, found: 790.25782 (100% int.); $[M+Na]^+$ calcd: 795.21353, found: 795.21243 (60%).

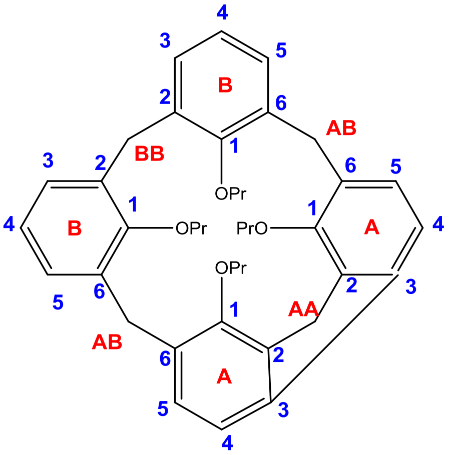
6,10-bridged-25,26,27,28-tetrapropoxycalix[4]arene (4a):

A mixture of calixarene **3a** (0.110 g, 0.13 mmol), $AsPh_3$ (0.007 g, 0.02 mmol), Cs_2CO_3 (0.040 g, 0.13 mmol), and $Pd(OAc)_2$ (0.003 g, 0.01 mmol) was put into the Schlenk flask and the whole apparatus was several times evacuated and flushed with argon. Deoxygenated toluene (7 ml bubbled with argon) was then added and the reaction mixture was stirred overnight at reflux. After cooling to room temperature 20 ml of DCM was added, the organic layer was washed with water and dried over $MgSO_4$. Solvent was removed under a reduced pressure to yield the crude product which was purified by preparative TLC on a silica gel (glass plates 20 x 20 cm, eluent = CH_2Cl_2:hexane 1:2, v/v). The title compound was obtained as a white powder in 64% yield (50 mg), m.p. 199 – 203 °C. ^{1}H NMR (600.13 MHz, $CDCl_3$, 298 K) δ 7.11 (d, 2H, *J* = 6.9 Hz, H-3 –*B*), 6.93 (dd, 2H, *J* = 1.3, 7.4 Hz, H-5 –*B*), 6.77 (dd, 2H, *J* = 7.6, 7.6 Hz, H-4 –*B*), 6.71 (d, 2H, *J* = 8.1 Hz, H -4 –*A*), 6.58 (d, 2H, *J* = 8.1 Hz, H-5 –*A*), 4.44 (d, 2H, *J* = 12.8 Hz, H-bridge –*AB*), 4.25 – 4.05 (m, 2H and 1H, $C\underline{H}_2$ – *A* and H-bridge –*BB*), 4.02 – 3.92 (m, 2H and 2H, $C\underline{H}_2$ – *A* and $C\underline{H}_2$ – *B),* 3.88 (d, 1H, *J* = 19.1 Hz, H-bridge –*AA*), 3.85 (d, 1H, *J* = 19.1 Hz, H-bridge –*AA*), 4.50 – 3.40 (m, 2H, $C\underline{H}_2$ – *B*), 3.32 (d, 2H, *J* = 12.8 Hz, H-bridge –*AB*), 2.96 (d, 1H, *J* = 12.9 Hz, H-bridge –*BB*), 2.14 – 2.04 (m, 2H, $CH_2C\underline{H}_2CH_3$-*B*), 1.98 – 1.86 (m, 6H, $CH_2C\underline{H}_2CH_3$-*A* and $CH_2C\underline{H}_2CH_3$-*B*), 1.18 and 0.97 (2 x tr, 2 x 6H, $CH_2CH_2C\underline{H}_3$ –*A* and $CH_2CH_2C\underline{H}_3$ –*B*).

^{13}C NMR (150.86 MHz, $CDCl_3$, 298 K) δ 157.5 (kv. C-1 –*A*), 156.1 (kv. C-1 –*B*), 144.8 (kv. C-2 -*A*), 138.5 (kv. C-6 -*B*), 137.5 (kv. C-3 -*A*), 134.4 (kv. C-2 -*B*), 130.2 (CH-5–*A*), 129.0 (CH-3 -*B),* 127.7 (kv. C-6 -*A*), 127.6 (CH-5 -*B*), 122.7 CH-4-*B),* 116.4 (CH-4 –*A),* 76.7 (OCH_2-*B*), 75.5 (OCH_2A)*,* 34.3 (C-

bridge –*AA*), 33.4 (C-bridge –*AB*), 25.9 (C-bridge –*BB*), 23.7 ($OCH_2\underline{C}H_2CH_3$-*A*), 23.0 ($OCH_2\underline{C}H_2CH_3$-*B*), 10.9 ($\underline{C}H_3$-*A*), 10.0 ($\underline{C}H_3$-*B*) ppm.
HRMS ESI+ *m/z* for $C_{40}H_{46}O_4$ calcd.: 591.34689 $[M+H]^+$; found: 591.34662 (5%) $[(M+H)]^+$; calcd.: 613.32883 $[M+Na]^+$; found: 613.32886 (100%) $[(M+Na)]^+$; calcd.: 629.30277 $[M+K]^+$; found: 629.30214 (5%) $[(M+K)]^+$.

Numbering for NMR spectra:



6,10-bridged-25,26,27,28-tetramethoxycalix[4]arene (4b):

Crude reaction mixture of 4-chloromercurio-25,26,27,28-tetramethoxycalix[4]arene **3b** (prepared from 0.200 g (0.42 mmol) of 25,26,27,28-tetramethoxycalix[4]arene **1b**), 0.02 g (0.08 mmol) of $AsPh_3$, 0.14 g of Cs_2CO_3 (0.42 mmol) and 0.009 g of $Pd(OAc)_2$ (0.04 mmol) were put into the Schlenk flask and the flask was filled with argon. Toluene (7 ml) was bubbled with argon for 10 min. and added to the Schlenk flask. The reaction mixture was heated to reflux overnight. After cooling, 20 ml of CH_2Cl_2 was added and the mixture was washed with water (20 ml). Organic layer was dried over $MgSO_4$, evaporated and separated on preparative TLC using CH_2Cl_2-hexane (1:1 v/v) as an eluent. Crude product was recrystalized from mixture of CH_2Cl_2 and ethyl-acetate. The title compound was obtained as colorless crystals (0.08 g, 39 %), m.p. 210-214 °C.

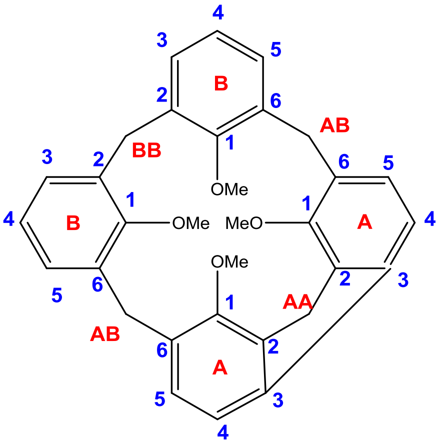
Spectra of the *1,2-alternate* conformation: ^{1}H NMR (500.13 MHz, CD_2Cl_2, 203 K) δ 7.26 (d, 2H, *J* = 6.9 Hz, H-5 –*A*), 7.14 (d, 2H, *J* = 7.8 Hz, H -4 –*A*), 7.15 – 7.05 (overlapped 4H, H-5 –*B* and H-3 –*B*), 6.81 (dd, 2H, *J* = 7.7, 7.7 Hz, H-4 –*B*), 8 x H-bridge and 8 x $OC\underline{H_2}$ overlapped by corresponding signals of the major cone conformer), 7.67 and 3.31 (2 x s, 2 x 3H, $C\underline{H_3}$.
^{13}C NMR (125.77 MHz, CD_2Cl_2, 203 K) δ 157.7 (kv. C-1 –*A*), 156.9 (kv. C-1 –*B*), 146.4 (kv. C-2 -*A*), 136.8 (kv. C-3 -*A*), 135.2 (kv. C-6 -*B*), 134.4 (kv. C-2 -*B*), 131.0 and 130.9 (CH-5–*A* and CH-3 -*B), 129.3* (CH-5 -*B*), 128.9 (kv. C-6 -*A*), 122.2 CH-4-*B),* 115.8 (CH-4 –*A),* 60.0 (2 x OCH_3), 36.8 (C-bridge –*AB*), 32.8 (C-bridge –*AA*), 25.6 (C-bridge –*BB*).

Spectra of the *cone* conformation: ^{1}H NMR (600.13 MHz, CD_2Cl_2, 203 K) δ 7.07 (d, 2H, *J* = 7.4 Hz, H-3 –*B*), 6.92 (d, 2H, *J* = 7.2 Hz, H-5 –*B*), 6.77 (dd, 2H, *J* = 7.4, 7.4 Hz, H-4 –*B*), 6.72 (d, 2H, *J* = 8.2 Hz, H -4 –*A*), 6.57 (d, 2H, *J* = 8.2 Hz, H-5 –*A*), 4.29 (d, 2H, *J* = 13.0 Hz, H-bridge –*AB*), 4.06 (d, 1H, *J* = 18.9 Hz, H-bridge –*AA*), 4.01 (s, 3H, $C\underline{H_3}$), 3.89 (d, 1H, *J* = 12.7 Hz, H-bridge –*BB*), 3.67

(overlapped 1H, H-bridge –*AA*), 3.59 (s, 3H, C$\underline{H}_3$), 3.30 (d, 2H, J = 13.0 Hz, H-bridge –*AB*), 2.98 (d, 1H, J = 12.7 Hz, H-bridge –*BB*).
^{13}C NMR (150.86 MHz, CD$_2$Cl$_2$, 203 K) δ 159.6 (kv. C-1 –*A*), 156.6 (kv. C-1 –*B*), 145.0 (kv. C-2 -*A*), 138.3 (kv. C-6 -*B*), 136.3 (kv. C-3 -*A*), 134.6 (kv. C-2 -*B*), 130.1 (CH-5–*A*), 129.0 (CH-3 -*B),* 128.0 (CH-5 -*B*), 126.8 (kv. C-6 -*A*), 123.5 CH-4-*B),* 116.6 (CH-4 –*A),* 61.6 and 60.9 (CH$_3$-*A* and CH$_3$-*B*)*,* 35.2 (C-bridge –*AA*), 32.7 (C-bridge –*AB*), 26.2 (C-bridge –*BB*).

MS ESI+ [M+NH$_4$]$^+$ calculated: 498.26389 found: 498.26433 (100% int.); [M+Na]$^+$ calculated: 503.21928 found: 503.21921 (40%); [M+K]$^+$ calculated 519.19322 found: 519.19293 (15%).

Numbering for NMR spectra:



6,10-bridged-25,26,27,28-tetraethoxycalix[4]arene (4c):

4-chloromercurio-25,26,27,28-tetraethoxycalix[4]arene **3b** (0.1 g, 0.13 mmol), Pd(OAc)$_2$ (0.003 g, 0.01 mmol), Cs$_2$CO$_3$ (0.04 g, 0.13 mmol) and AsPh$_3$ (0.008g, 0.03 mmol) were put into the Schlenk flask and the flask was flushed with argon. Toluene (10 ml) was bubbled with argon for 15 min. and added to the flask. The reaction mixture was then heated overnight at reflux. The reaction mixture was cooled to room temp., toluene was diluted with CH$_2$Cl$_2$ (20 ml) and washed with water (2x10 ml). Organic layer was dried over MgSO$_4$, evaporated and purified on preparative TLC using CH$_2$Cl$_2$:hexane (1:2 v/v) mixture as an eluent. We obtained 0.017 g (25%) of the *cone* conformer **4c**(*co*) and 0.010 g (15%) of the *1,2-alternate* conformer **4c**(*alt*).

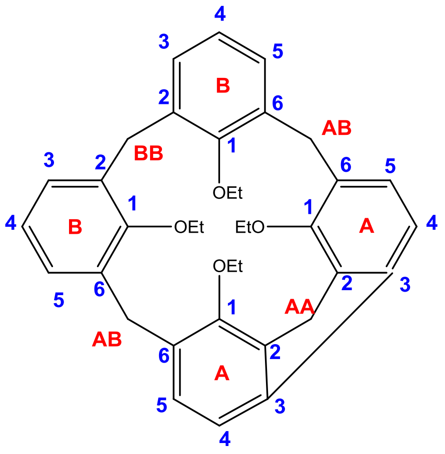
Data for **4c**(*alt*): m.p. 190-192 °C; ^{1}H NMR (500.13 MHz, C$_2$D$_2$Cl$_4$, 298 K) δ 7.28 (d, 2H, J = 7.7 Hz, H-5 –*A*), 7.18 (d, 2H, J = 8.1 Hz, H -4 –*A*), 7.16 (d, 2H, J = 7.4 Hz, H-5 –*B*), 7.10 (d, 2H, J = 7.3 Hz, H-3 –*B*), 6.82 (dd, 2H, J = 7.4, 7.4 Hz, H-4 –*B*), 4.10 – 3.85 (m, 7H, H-bridge –*AB*, H-bridge –*BB*, C$\underline{H}_2$ – *B*), 3.8 – 3.68 (m, 2H, C$\underline{H}_2$ – *A*), 3.65 (d, 2H, J = 13.8 Hz, H-bridge –*AB*), 3.50 (d, 1H, J = 19.0 Hz, H-bridge –*AA*), 3.50 – 3.38 (m, 2H, C$\underline{H}_2$ – *A*), 2.98 (d, 1H, J = 13.0 Hz, H-bridge –*BB*), 2.89 (d, 1H, J = 19.0 Hz, H-bridge –*AA*), 1.25 – 1.35 (m, 2 x 6H, CH$_2$CH$_2$C$\underline{H}_3$ –*A* and CH$_2$CH$_2$C$\underline{H}_3$ –*B*).
^{13}C NMR (125.77 MHz, C$_2$D$_2$Cl$_4$, 298 K) δ 156.6 (kv. C-1 –*A*), 156.3 (kv. C-1 –*B*), 146.2 (kv. C-2 -*A*), 137.9 (kv. C-3 -*A*), 135.4 (kv. C-6 -*B*), 134.5 (kv. C-2 -*B*), 131.6 (CH-5–*A*), 131.0 (CH-3 -*B),* 129.3 (CH-5 -*B*), 129.2 (kv. C-6 -*A*), 121.5 CH-4-*B),* 116.2 (CH-4 –*A),* 68.8 (OCH$_2$-*A*), 68.2 (OCH$_2$-*B*)*,* 37.6 (C-bridge –*AB*), 32.8 (C-bridge –*AA*), 26.2 (C-bridge –*BB*), 15.9 and 15.7 ppm ($\mathbf{\underline{C}}$H$_3$-*A*), ($\mathbf{\underline{C}}$H$_3$-*B*). MS ESI

$[M+H]^+$ calcd: 535.28429, found: 535.28484 (50% int.); $[M+NH_4]^+$ calcd: 552.31084, found: 552.31151 (100%); $[M+Na]^+$ calcd: 557.26623, found: 557.26627 (70%).

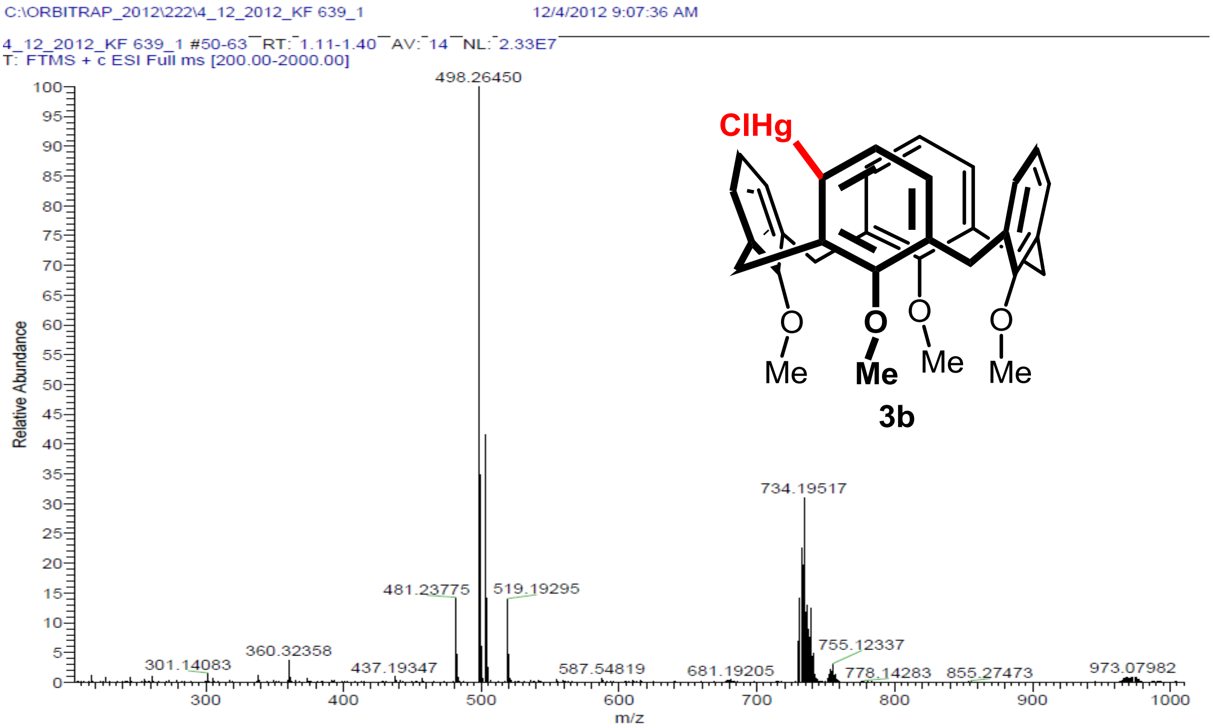
Data for **4c**(*co*): m.p. 226-229 °C; ^{1}H NMR (500.13 MHz, $C_2D_2Cl_4$, 298 K) δ 7.10 (d, 2H, *J* = 7.6 Hz, H-3 –*B*), 6.95 (d, 2H, *J* = 7.1 Hz, H-5 –*B*), 6.77 (dd, 2H, *J* = 7.7, 7.7 Hz, H-4 –*B*), 6.70 (d, 2H, *J* = 8.1 Hz, H -4 –*A*), 6.59 (d, 2H, *J* = 8.1 Hz, H-5 –*A*), 4.42 (d, 2H, *J* = 12.8 Hz, H-bridge –*AB*), 4.39 – 3.29 (m, 2H, $C\underline{H}_2$ – *A*), 4.17 (d, 1H, *J* = 12.9 Hz, H-bridge –*BB*), 4.15 – 4.05 (m, 4H, $C\underline{H}_2$ – *A* and $C\underline{H}_2$ – *B*), 3.92 (d, 1H, *J* = 19.6 Hz, H-bridge –*AA*), 3.86 (d, 1H, *J* = 19.6 Hz, H-bridge –*AA*), 3.65 – 3.58 (m, 2H, $C\underline{H}_2$ – *B*), 3.33 (d, 2H, *J* = 12.9 Hz, H-bridge –*AB*), 2.97 (d, 1H, *J* = 12.9 Hz, H-bridge –*BB*), 1.54 (tr, 2 x 6H, $CH_2CH_2C\underline{H}_3$ –*A* and $CH_2CH_2C\underline{H}_3$ –*B*).

^{13}C NMR (125.77 MHz, $C_2D_2Cl_4$, 298 K) δ 157.1 (kv. C-1 –*A*), 155.7 (kv. C-1 –*B*), 144.3 (kv. C-2 -*A*), 138.4 (kv. C-6 -*B*), 137.3 (kv. C-3 -*A*), 134.4 (kv. C-2 -*B*), 129.9 (CH-5–*A*), 128.7 (CH-3 -*B),* 127.6 (kv. C-6 -*A*), 127.3 (CH-5 -*B*), 122.4 CH-4-*B),* 116.6 (CH-4 –*A),* 69.8 (OCH_2-*A*), 68.9 (OCH_2-*B*)*,* 34.3 (C-bridge –*AA*), 33.2 (C-bridge –*AB*), 25.7 (C-bridge –*BB*), 15.8 and 15.6 ($\underline{\mathbf{C}}H_3$-*A*), ($\underline{\mathbf{C}}H_3$-*B*). ppm. MS ESI $[M+H]^+$ calcd: 535.28429, found: 535.28452 (100% int.); $[M+NH_4]^+$ calcd: 552.31084, found: 552.31120 (90%); $[M+Na]^+$ calcd: 557.26623, found: 557.26631 (30%); $[M+K]^+$ calcd: 573.24017, found: 573.24005 (50%).

Numbering for NMR spectra:



Compound 3b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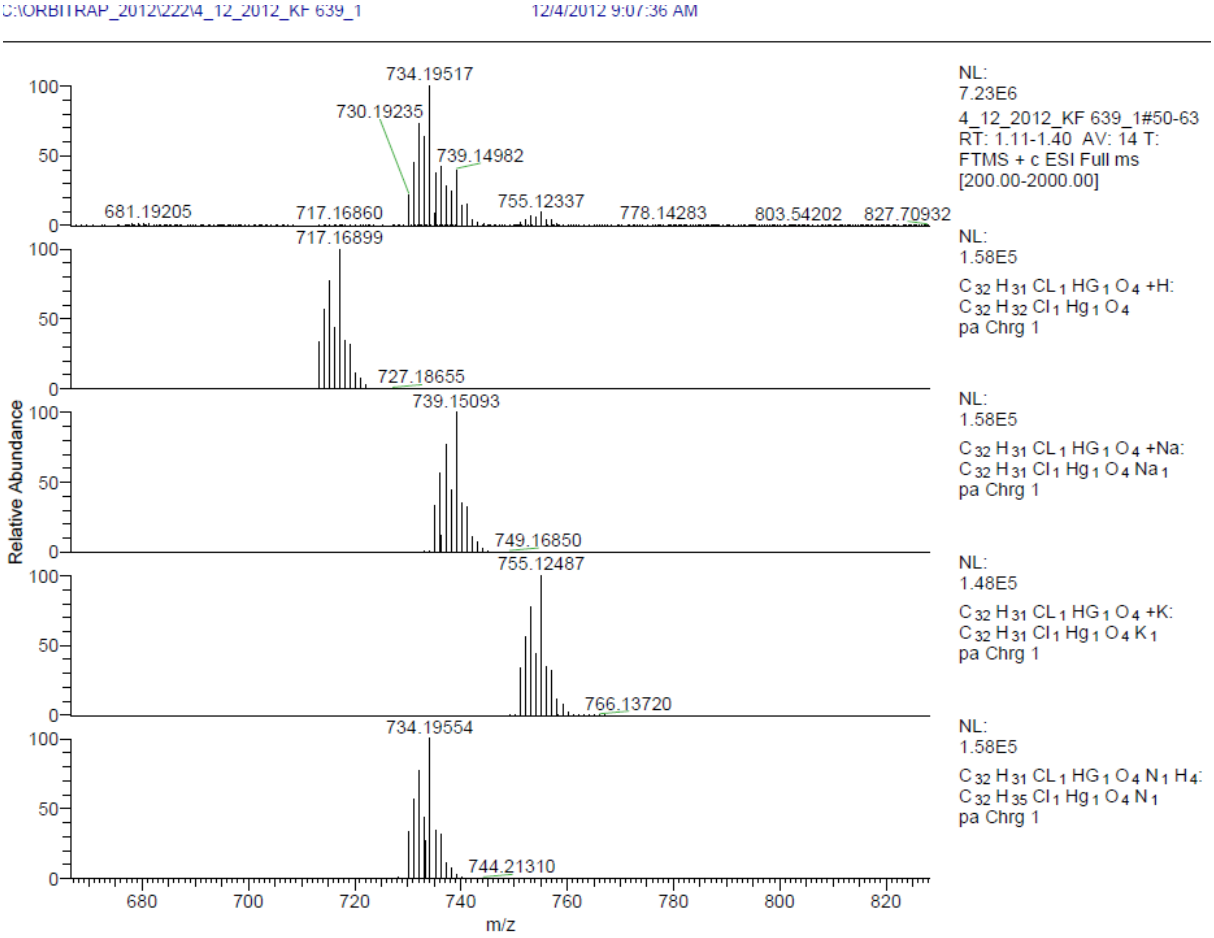
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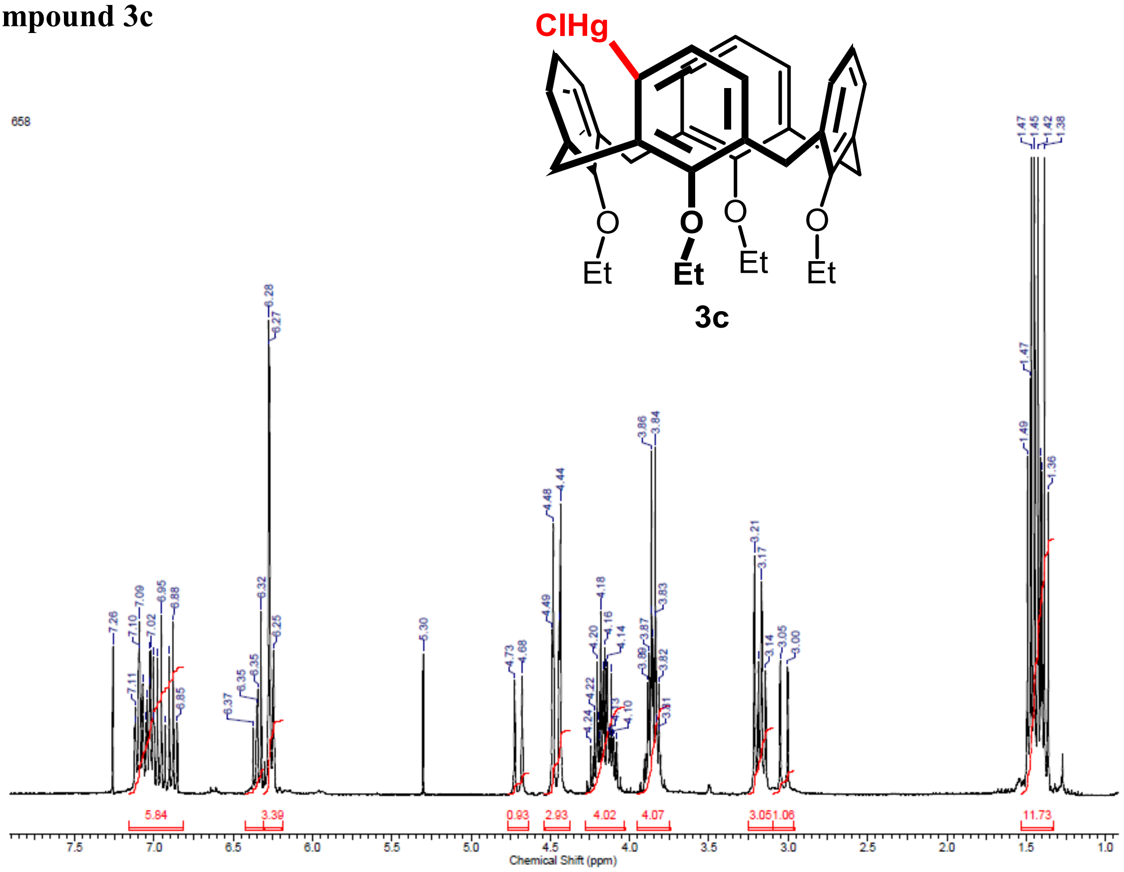
Compound 3c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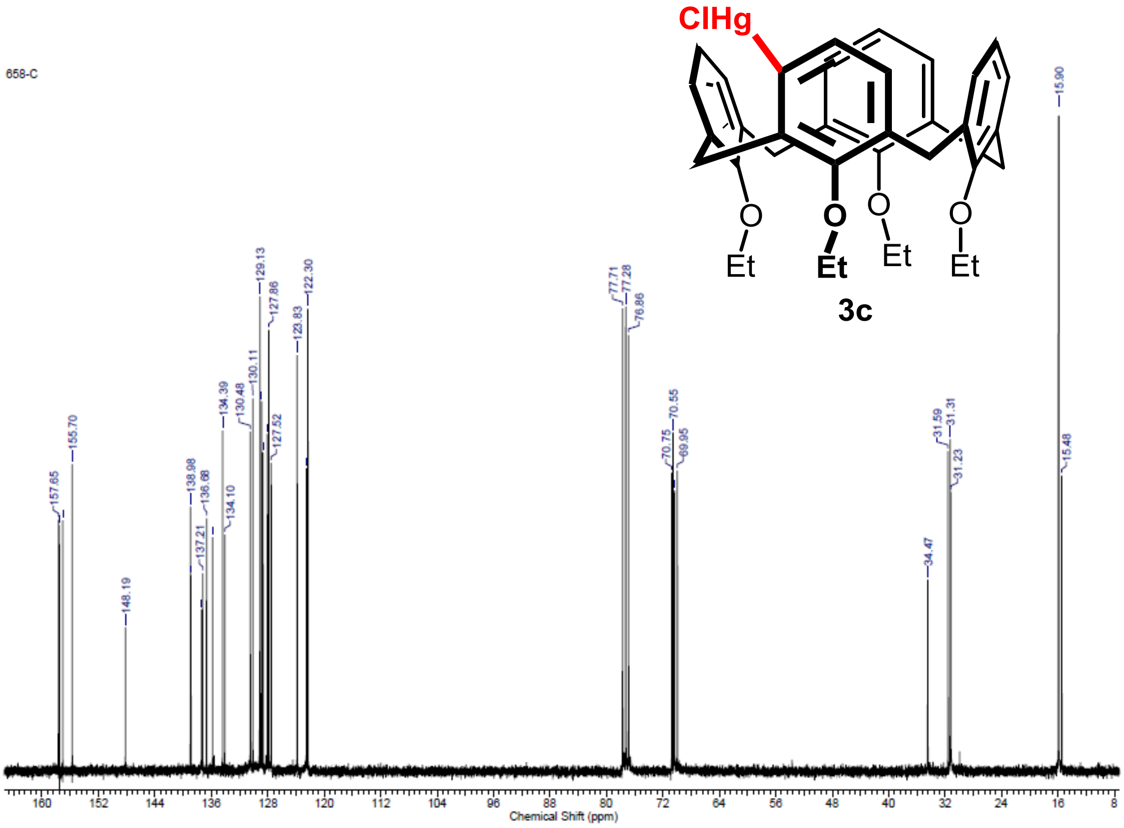
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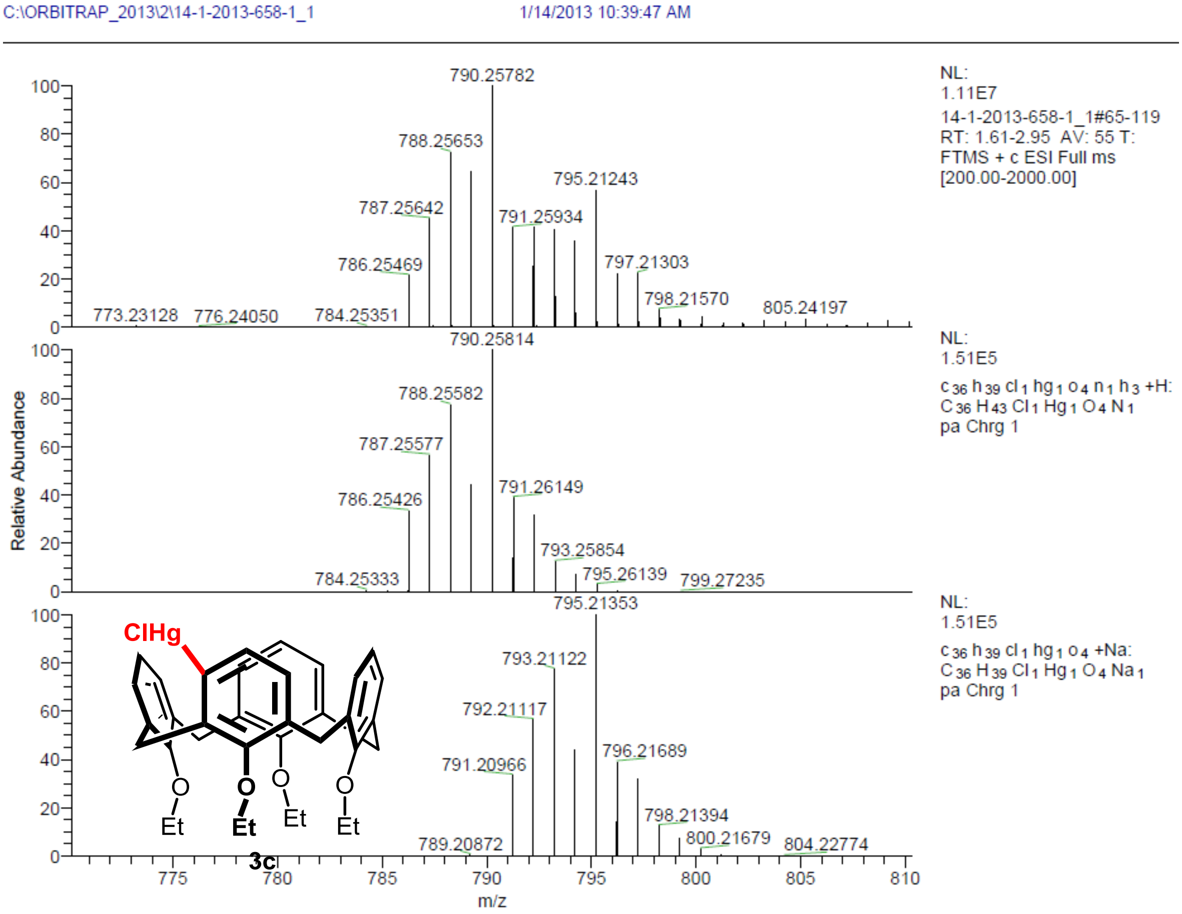
Chemical Shift (ppm)

Compound 3c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ClHg
O
Et
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m/z
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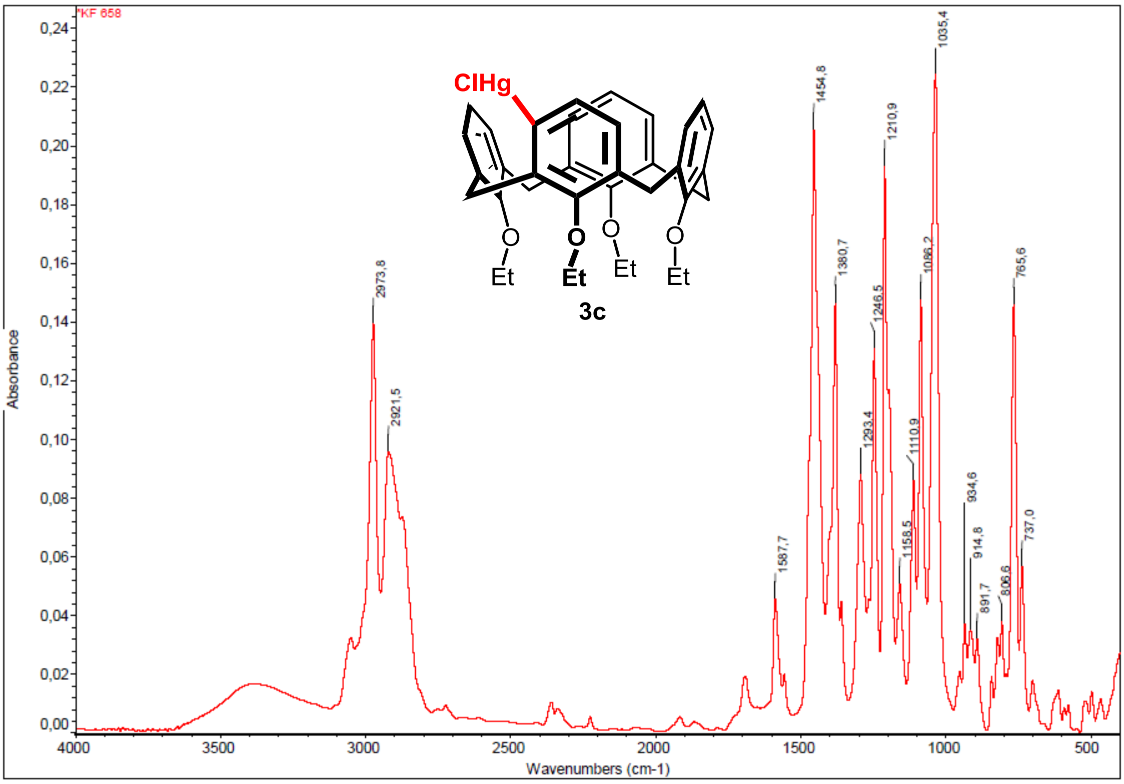
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Et
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1210,9
1158,5
1110,9
1086,2
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914,8
891,7
806,6
765,6
737,0
Absorbance
Wavenumbers (cm-1)
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0,02
0,04
0,06
0,08
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0,12
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3000
2500
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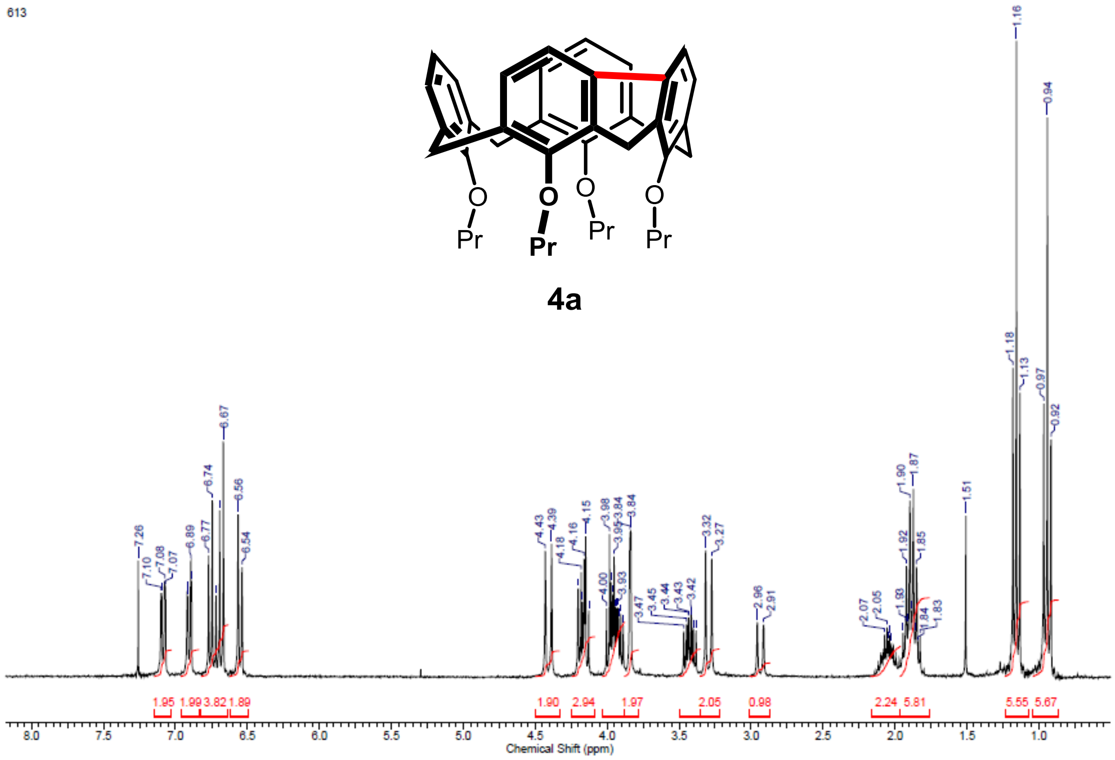
1500
1000
500

Compound 4a


613
O
Pr
4a
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7.10
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6.56
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4.39
4.18
4.16
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3.95
3.93
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3.47
3.45
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3.43
3.42
3.32
3.27
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2.91
2.07
2.05
1.93
1.92
1.90
1.87
1.85
1.84
1.83
1.51
1.18
1.16
1.13
0.97
0.94
0.92
1.95
1.99
3.82
1.89
1.90
2.94
1.97
2.05
0.98
2.24
5.81
5.55
5.67
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7.5
7.0
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2.0
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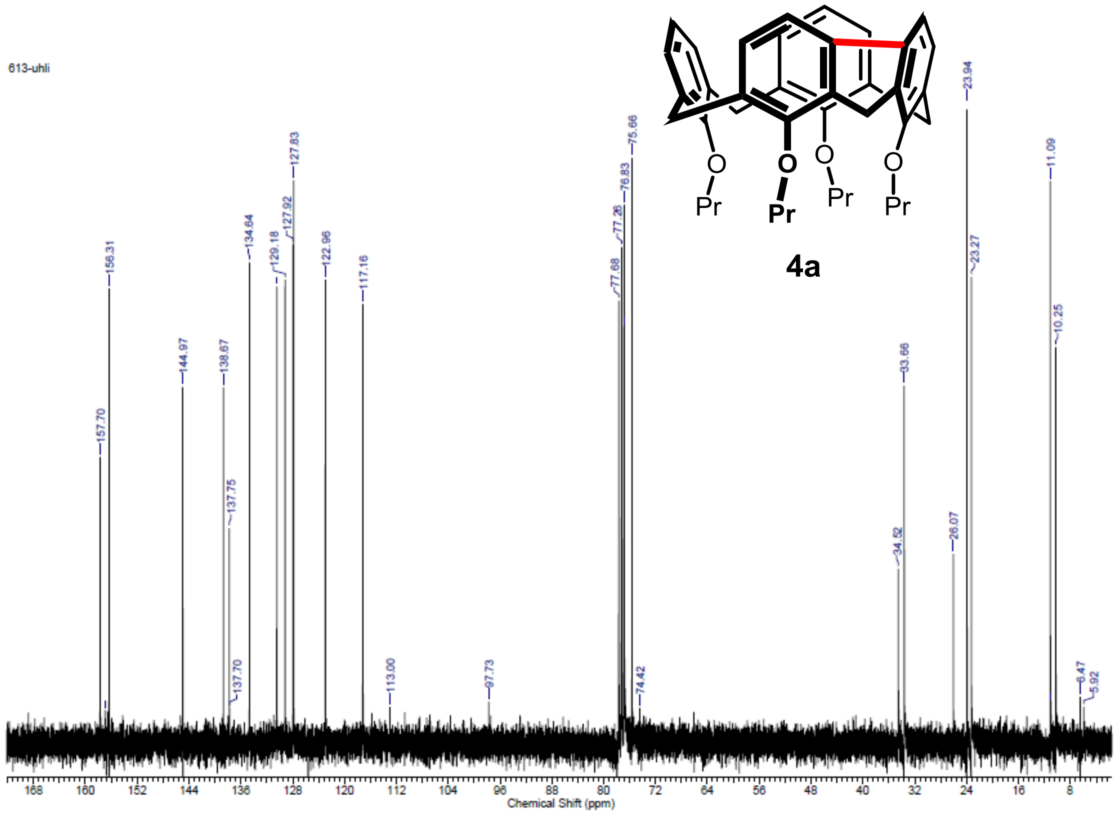
1.0
Chemical Shift (ppm)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122.96
117.16
113.00
97.73
77.68
77.26
76.83
75.66
74.42
34.52
33.66
26.07
23.94
23.27
11.09
10.25
6.47
5.92
168
160
152
144
136
128
120
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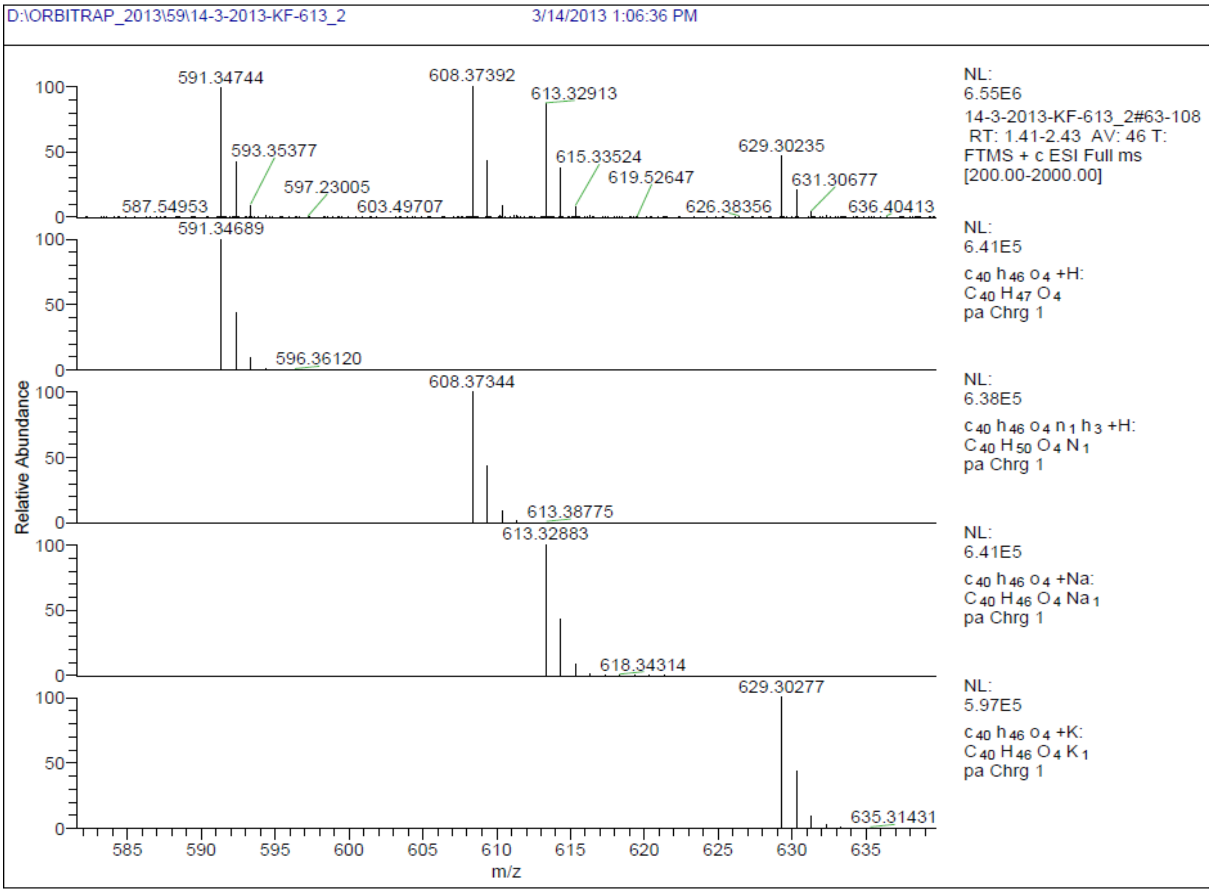
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

Compound 4a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619.52647
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631.30677
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636.40413
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596.36120
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608.37344
613.38775
NL: 6.38E5
c 40 h 46 o 4 n 1 h 3 +H: C 40 H 50 O 4 N 1 pa Chrg 1
613.32883
618.34314
NL: 6.41E5
c 40 h 46 o 4 +Na: C 40 H 46 O 4 Na 1 pa Chrg 1
629.30277
635.31431
NL: 5.97E5
c 40 h 46 o 4 +K: C 40 H 46 O 4 K 1 pa Chrg 1
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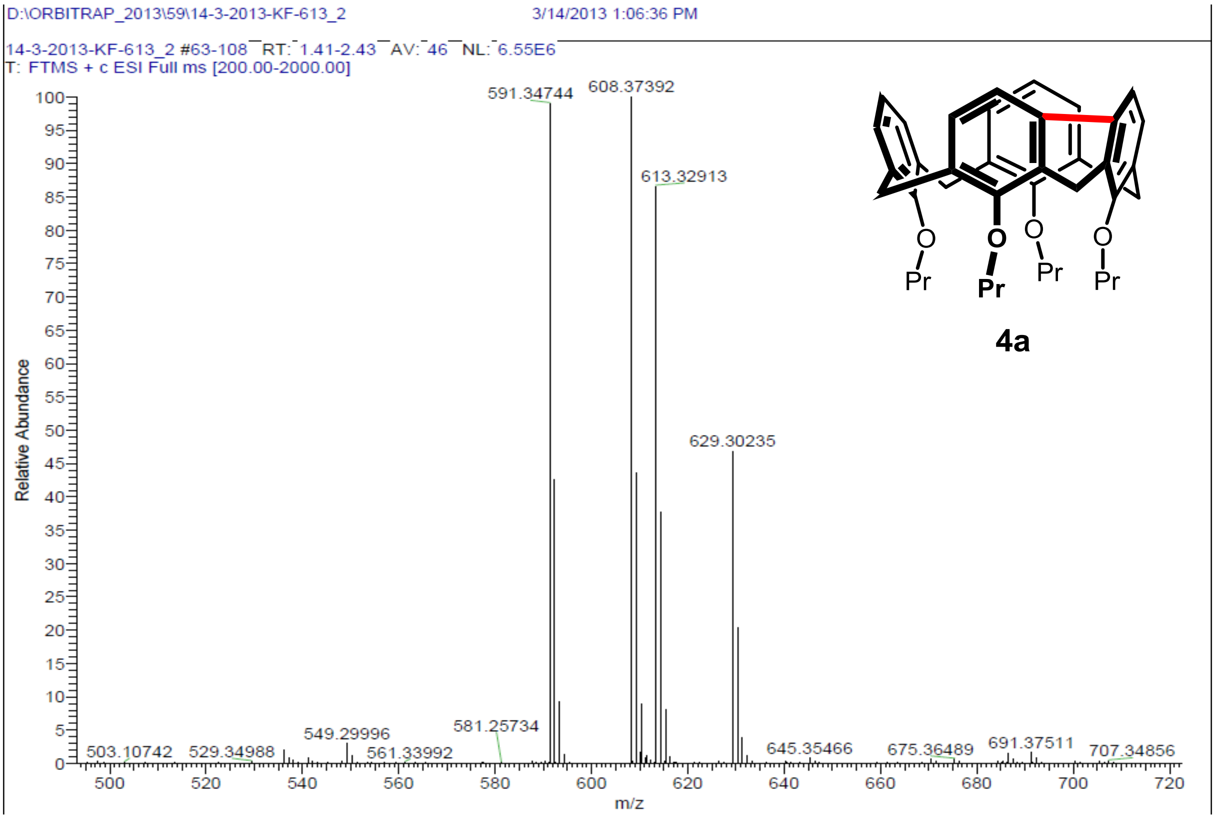
595
600
605
610
615
620
625
630
635
m/z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14-3-2013-KF-613_2 #63-108 RT: 1.41-2.43 AV: 46 NL: 6.55E6
T: FTMS + c ESI Full ms [200.00-2000.00]
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613.32913
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549.29996
561.33992
581.25734
645.35466
675.36489
691.37511
707.34856
Relative Abundance
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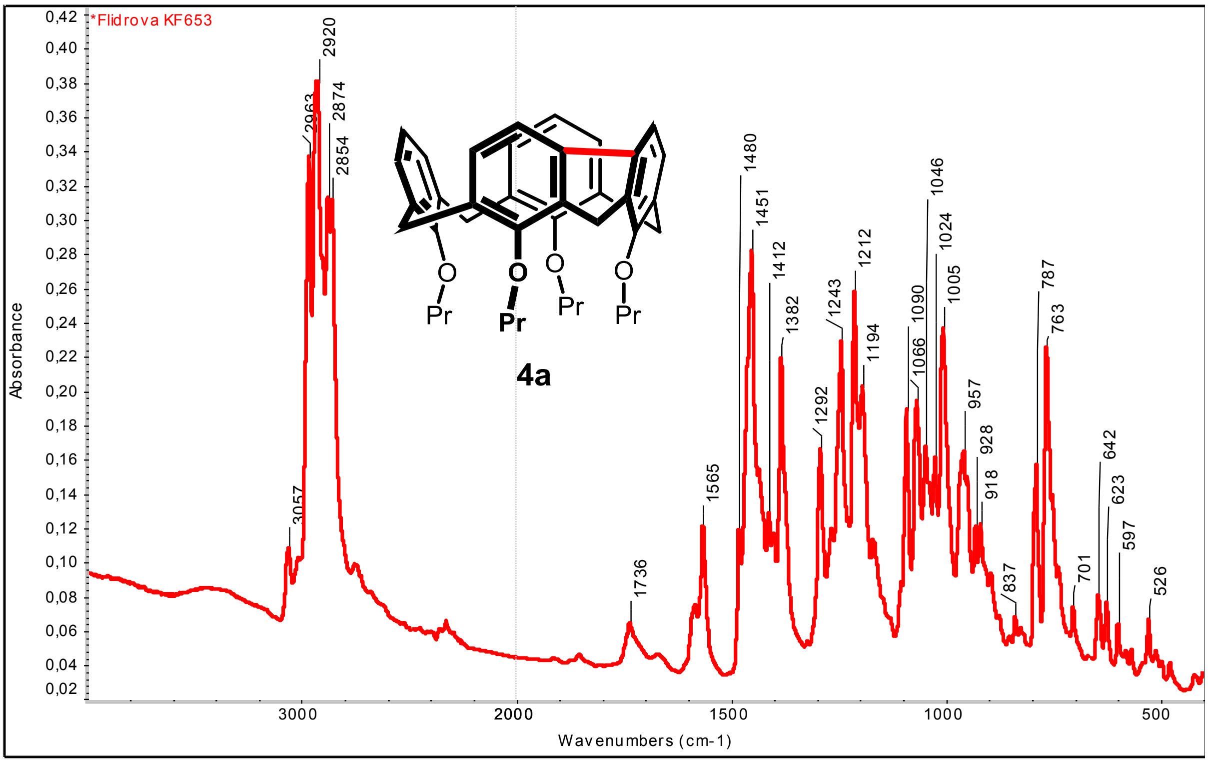
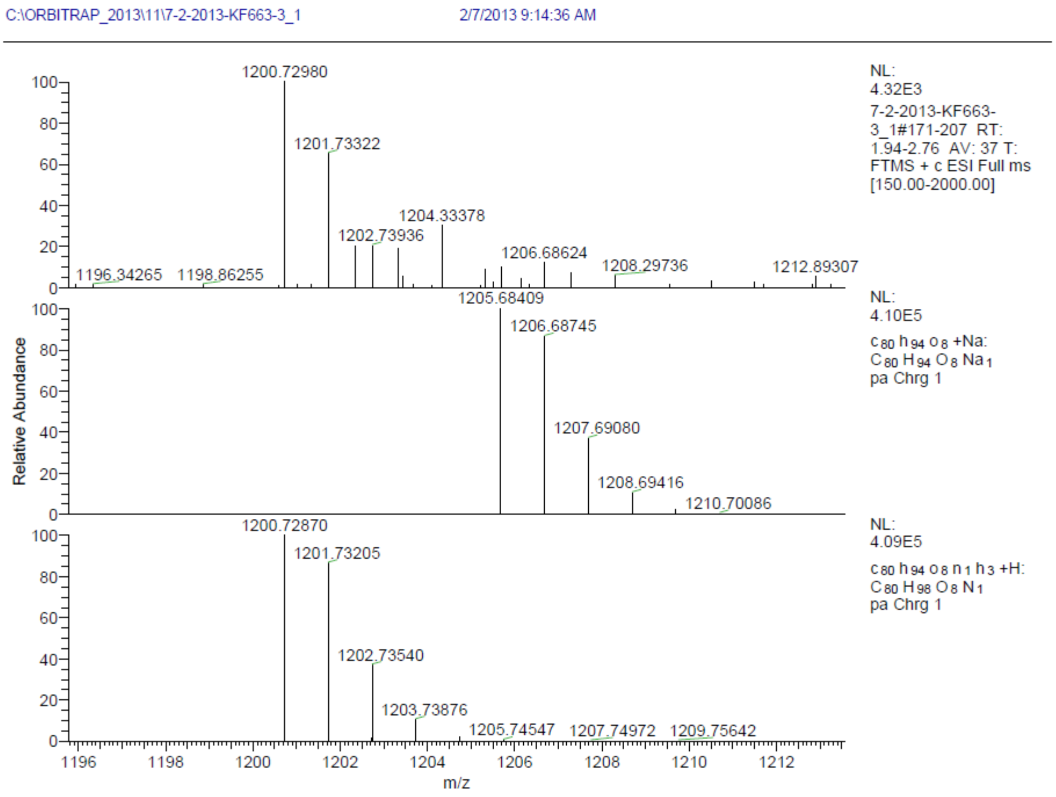
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
500
520
540
560
580
600
620
640
660
680
700
720
m/z
O
Pr
O
Pr
O
Pr
O
Pr
4a

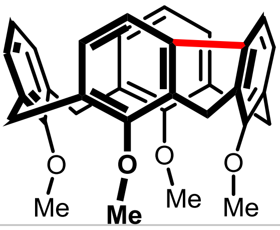
Compound 4a

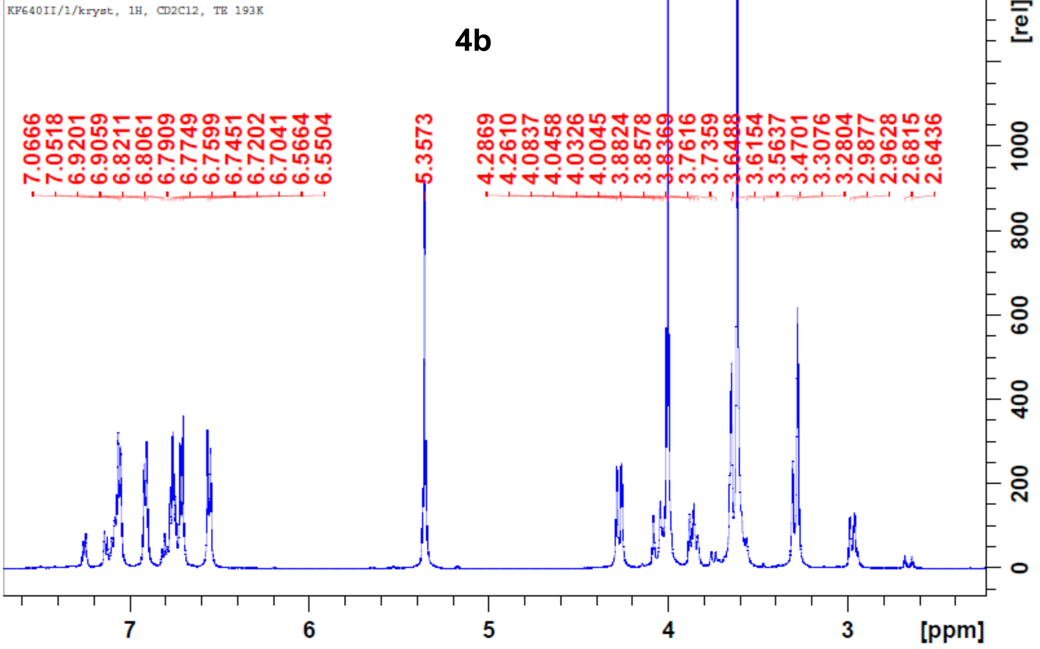


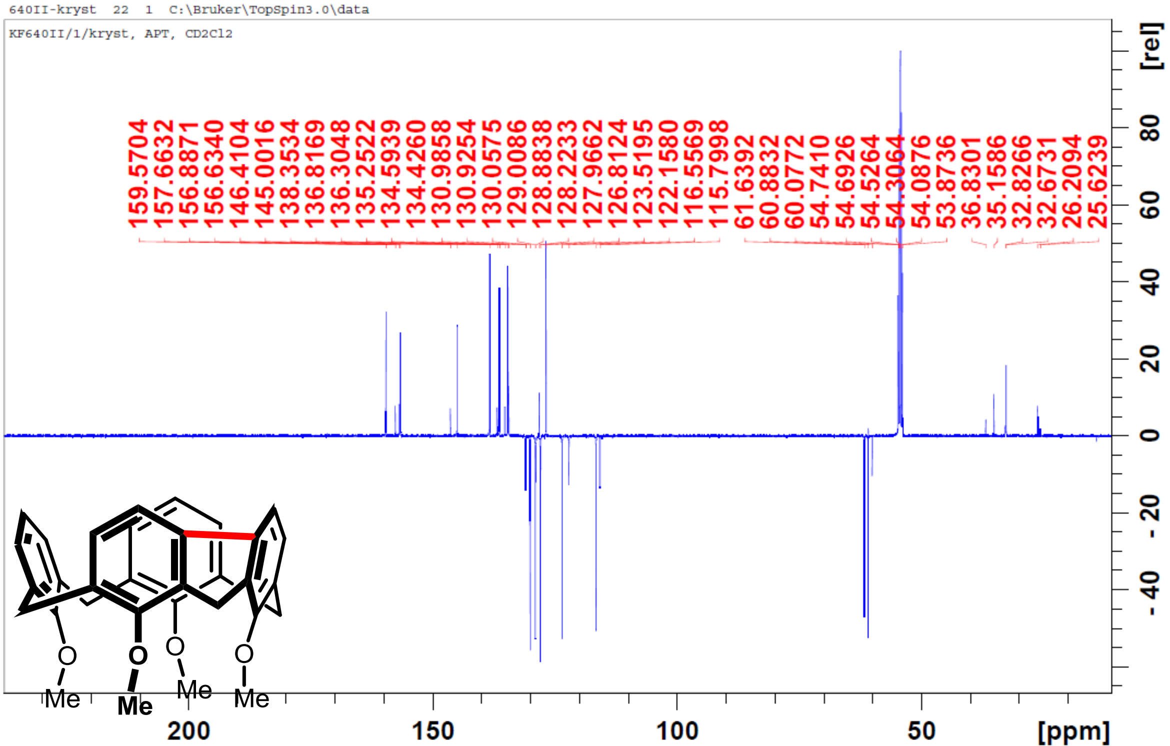
Compound 5a (dimer)



Compound 4b

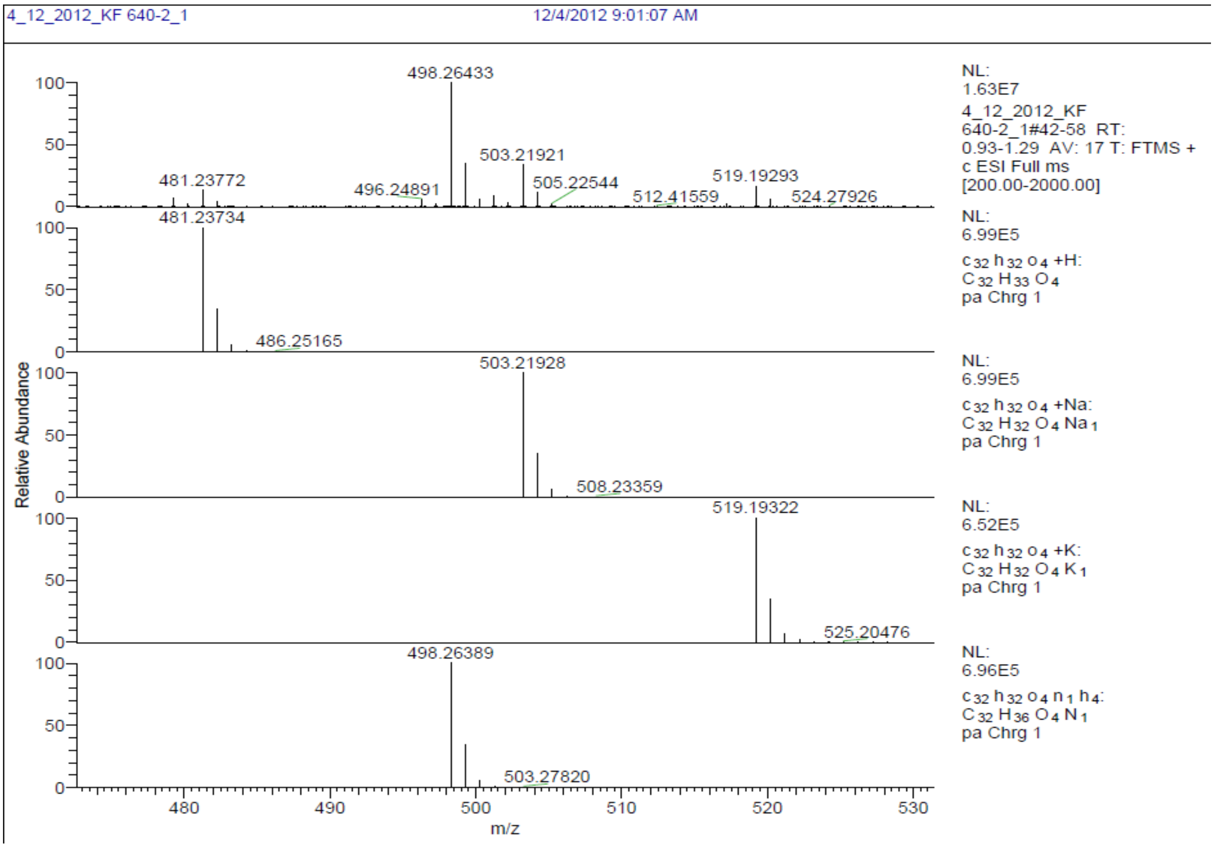






4b

Compound 4b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481.23772
496.24891
505.22544
512.41559
519.19293
524.27926
NL: 1.63E7
4_12_2012_KF 640-2_1#42-58 RT: 0.93-1.29 AV: 17 T: FTMS + c ESI Full ms [200.00-2000.00]
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486.25165
NL: 6.99E5
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503.21928
508.23359
NL: 6.99E5
c 32 h 32 o 4 +Na: C 32 H 32 O 4 Na 1
pa Chrg 1
519.19322
525.20476
NL: 6.52E5
c 32 h 32 o 4 +K: C 32 H 32 O 4 K 1
pa Chrg 1
498.26389
503.27820
NL: 6.96E5
c 32 h 32 o 4 n 1 h 4: C 32 H 36 O 4 N 1
pa Chrg 1
Relative Abundance
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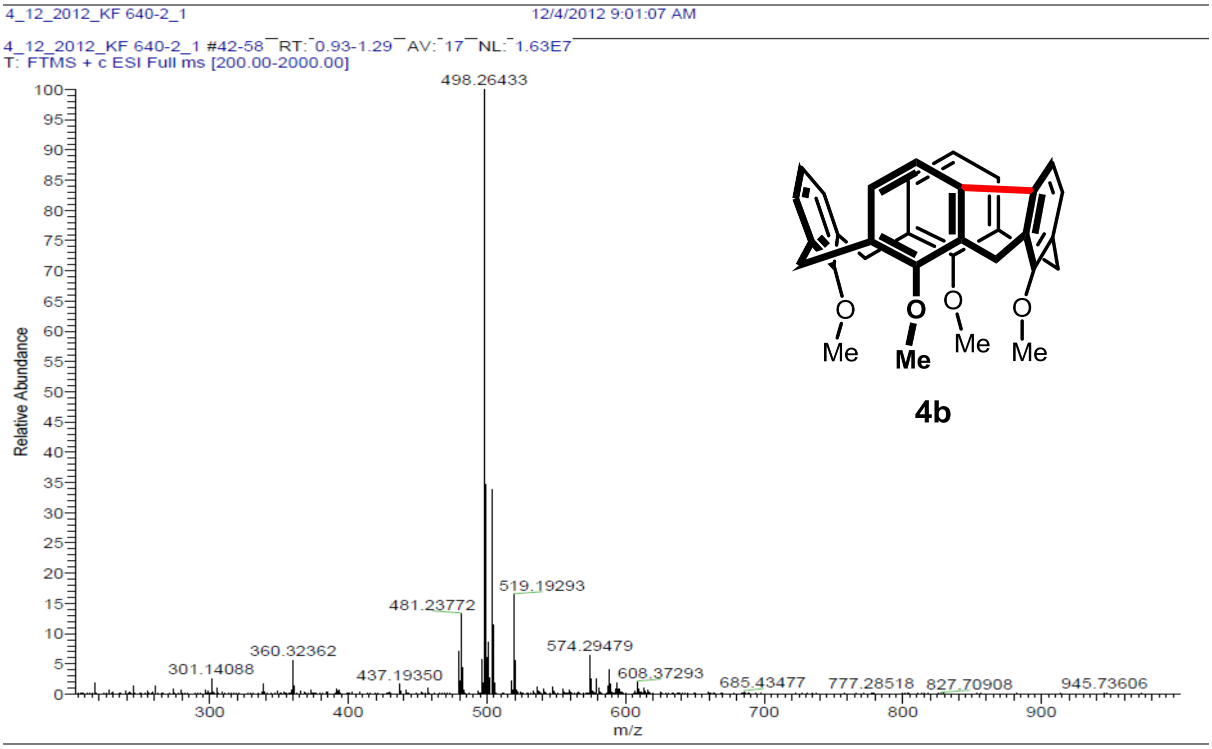
100
480
490
500
510
520
530
m/z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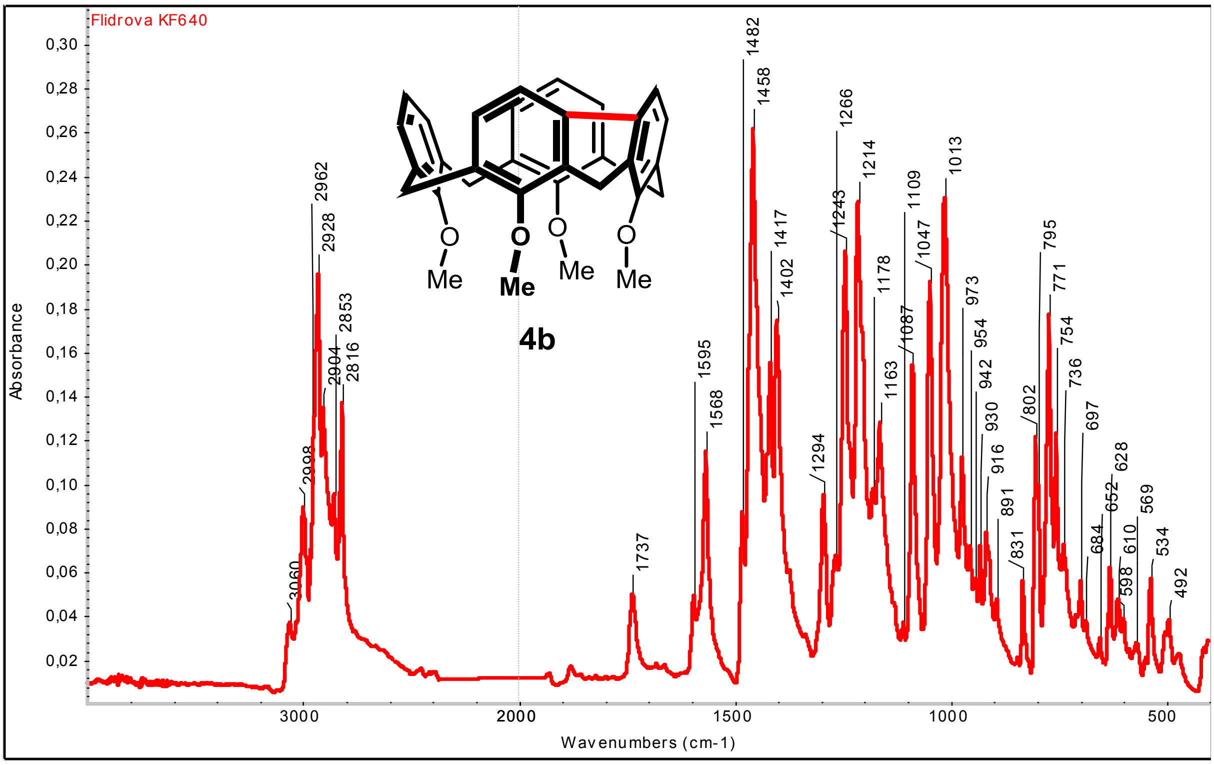
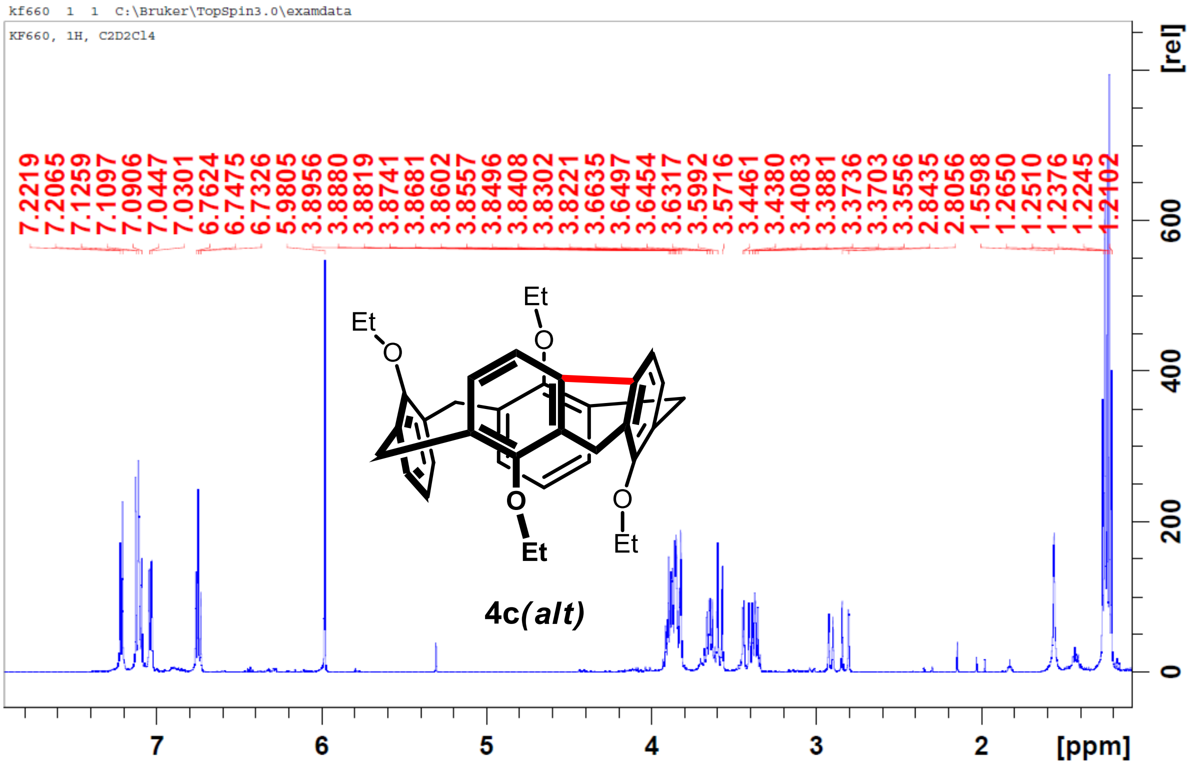
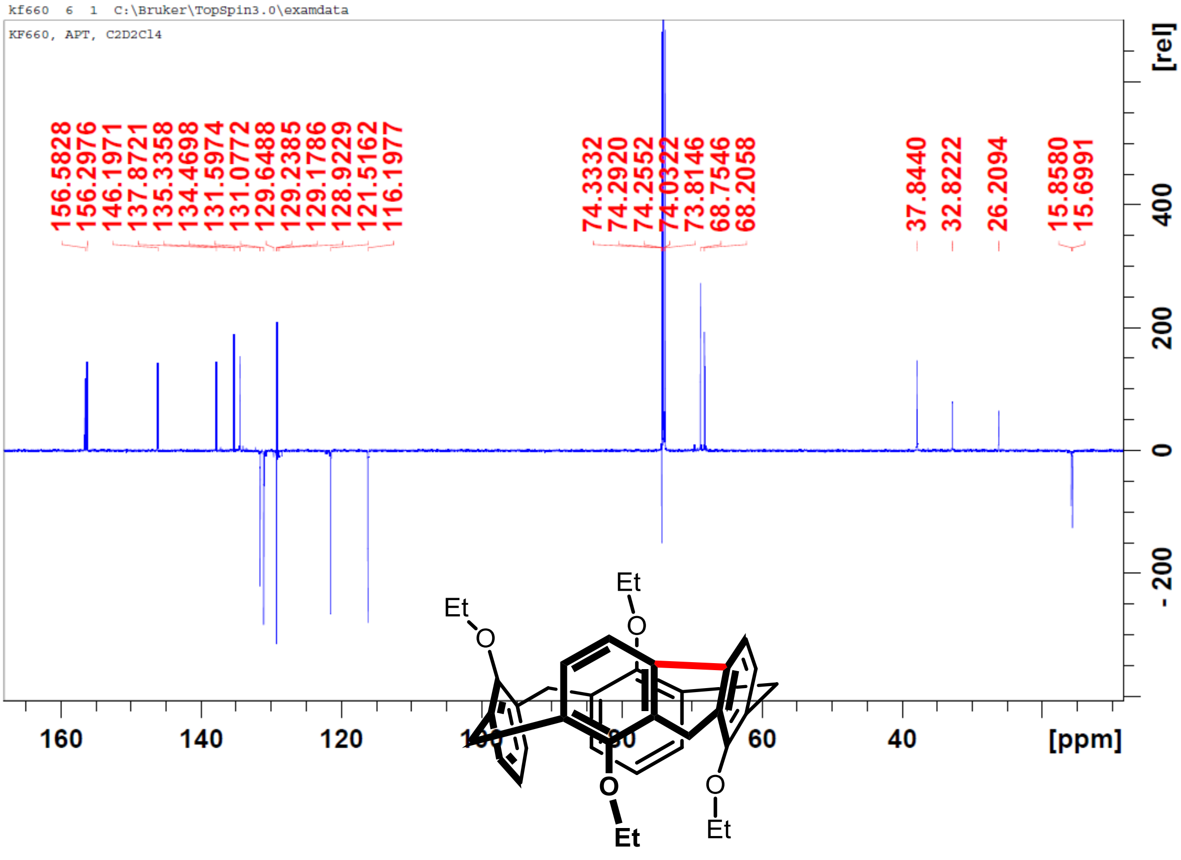
12/4/2012 9:01:07 AM
4_12_2012_KF 640-2_1 #42-58 RT: 0.93-1.29 AV: 17 NL: 1.63E7
T: FTMS + c ESI Full ms [200.00-2000.00]
498.26433
519.19293
481.23772
574.29479
360.32362
301.14088
437.19350
608.37293
685.43477
777.28518
827.70908
945.73606
Relative Abundance
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
300
400
500
600
700
800
900
m/z
O
Me
O
Me
O
Me
O
Me
4b

Compound 4b


Flidrova KF640
Absorbance
0,30
0,28
0,26
0,24
0,22
0,20
0,18
0,16
0,14
0,12
0,10
0,08
0,06
0,04
0,02
3000
2000
1500
1000
500
Wavenumbers (cm-1)
O
Me
O
Me
O
Me
O
Me
4b
3060
2998
2962
2928
2904
2853
2816
1737
1595
1568
1482
1458
1417
1402
1294
1266
1243
1214
1178
1163
1109
1087
1047
1013
973
954
942
930
916
891
831
802
795
771
754
736
697
684
652
628
610
598
569
534
492

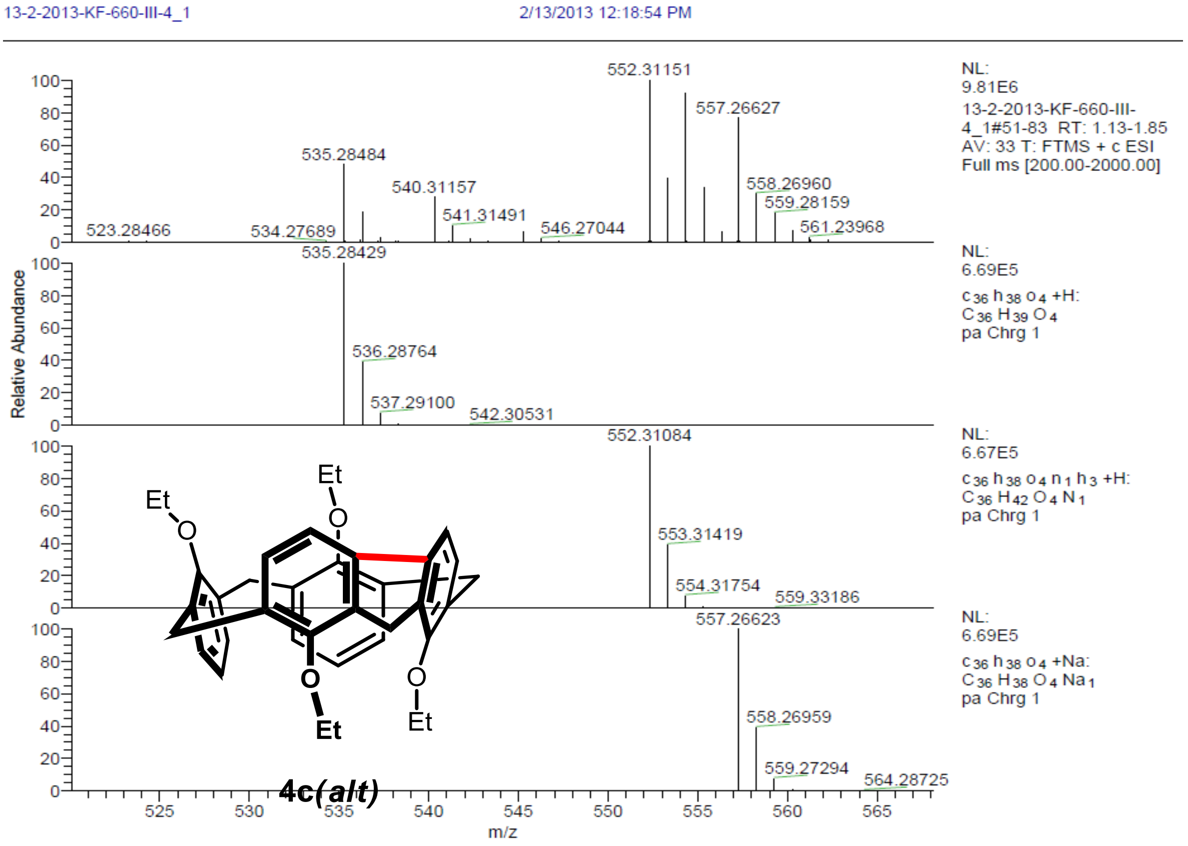
Compound 4c(*alt*)

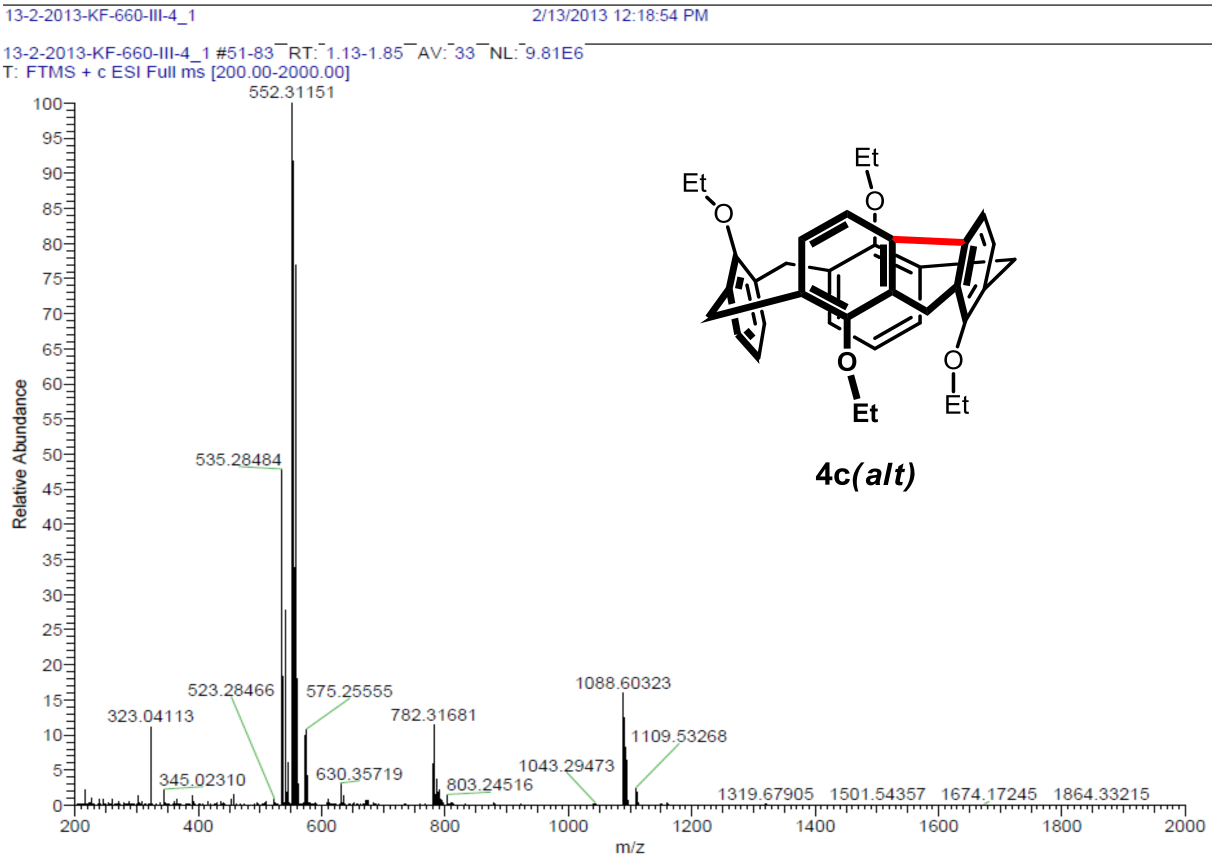


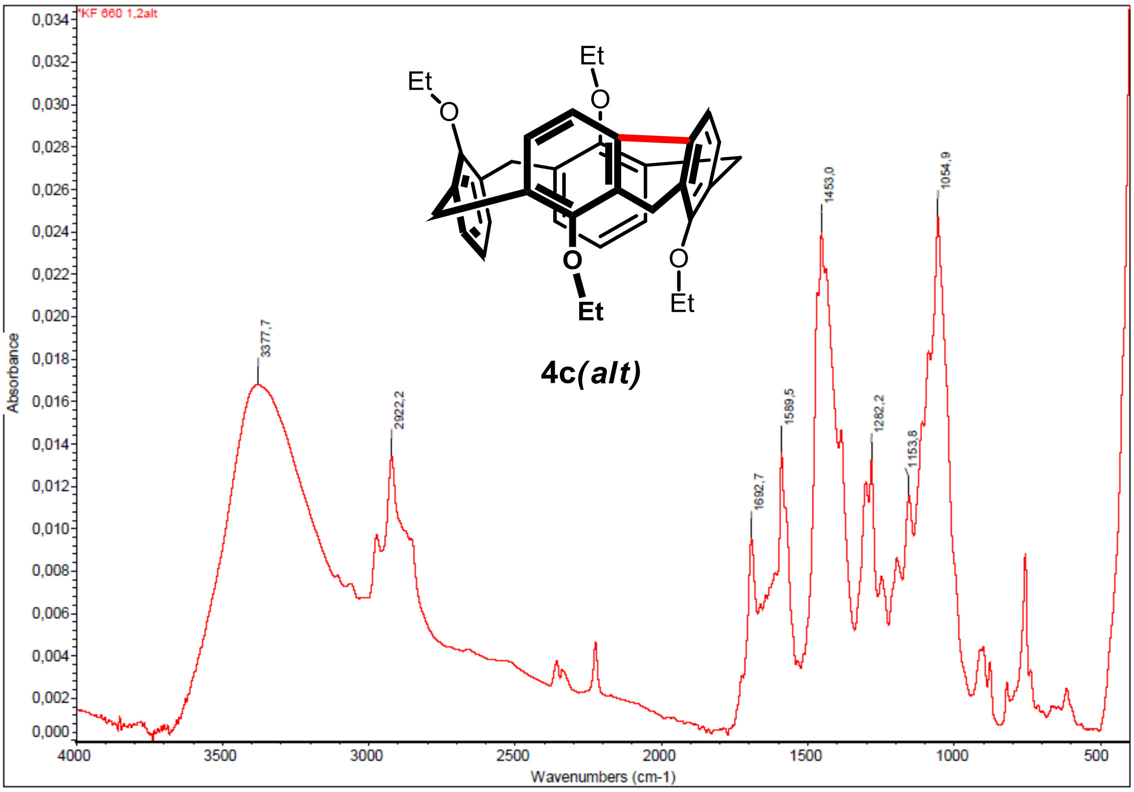


4c(*alt*)

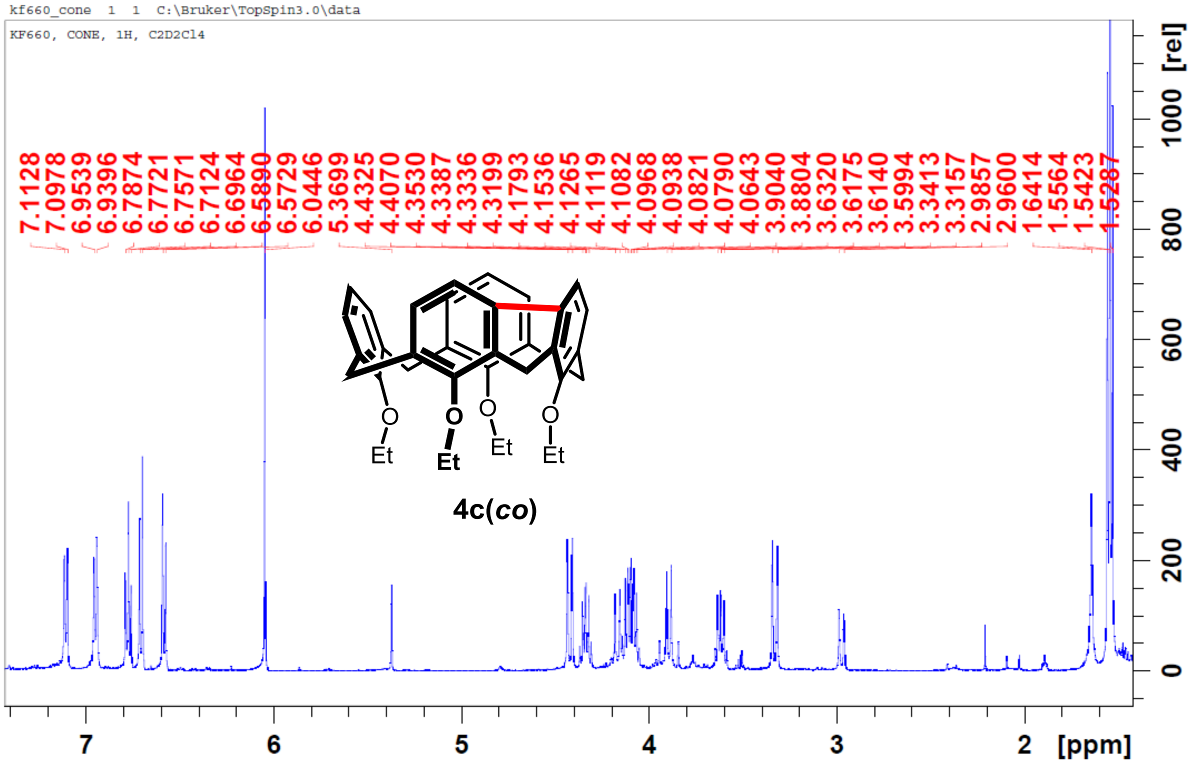
Compound 4c(*alt*)

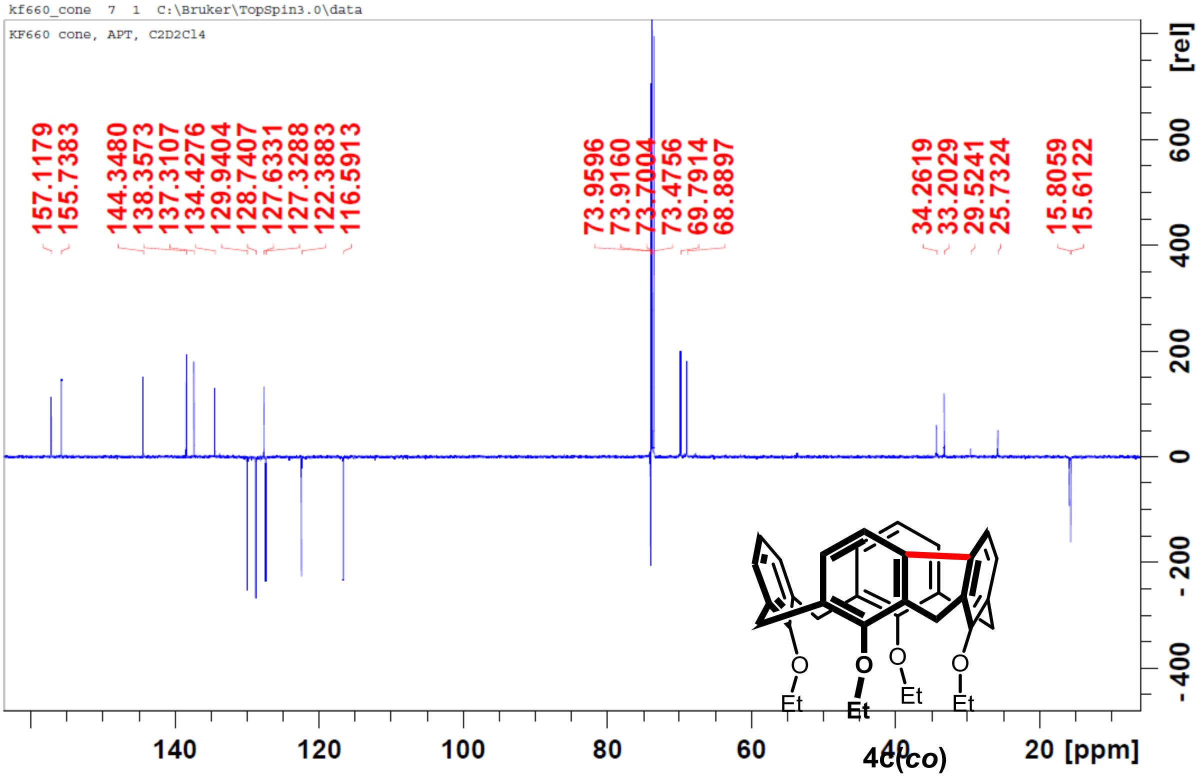




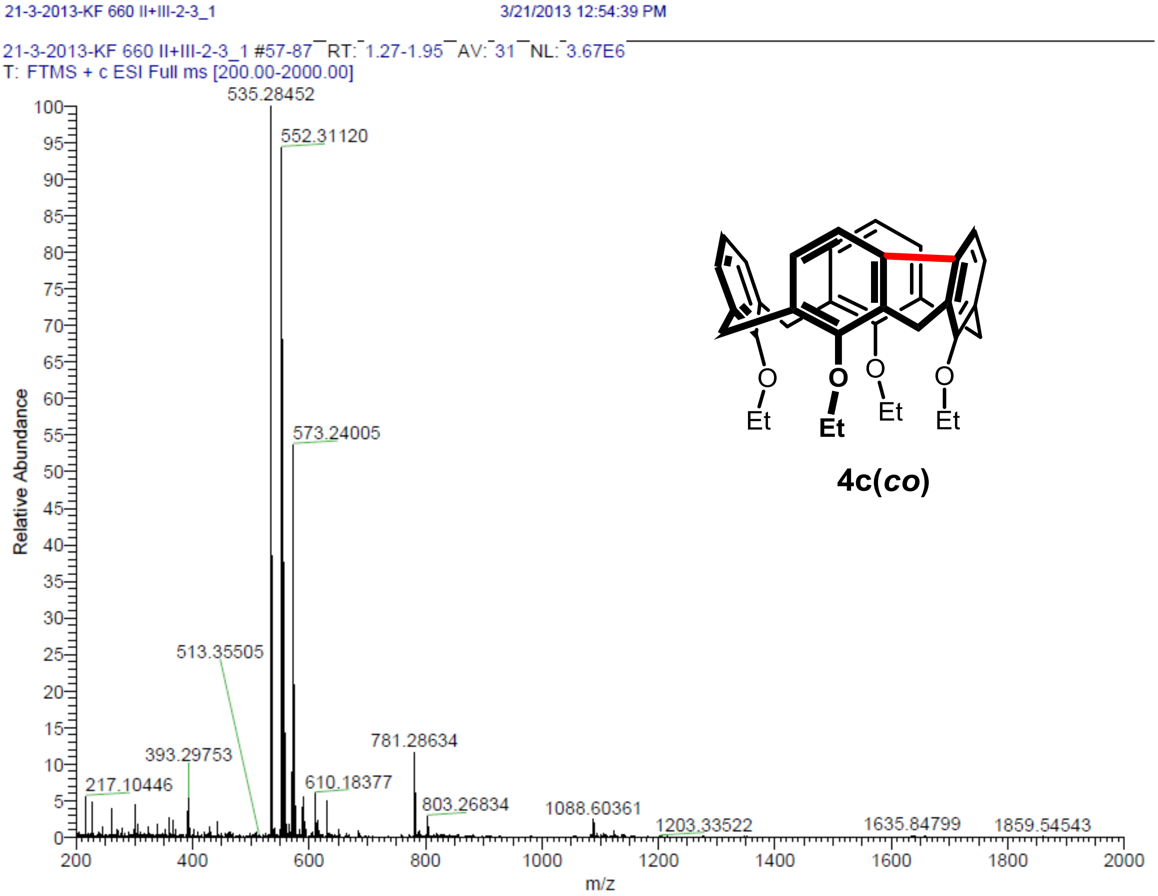

*KF 660 1,2alt
Et
O
Et
O
O
Et
O
Et
4c(alt)
3377,7
2922,2
1692,7
1589,5
1453,0
1282,2
1153,8
1054,9
Absorbance
0,034
0,032
0,030
0,028
0,026
0,024
0,022
0,020
0,018
0,016
0,014
0,012
0,010
0,008
0,006
0,004
0,002
0,000
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

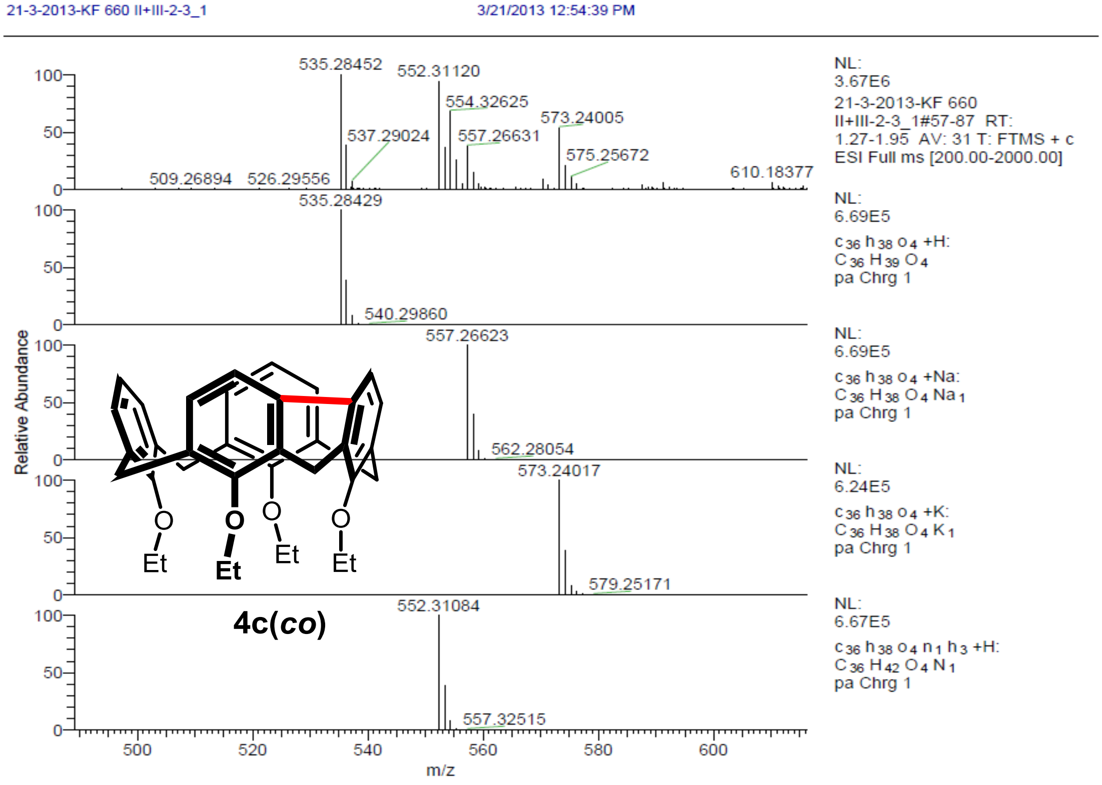
Compound 4c(*co*)



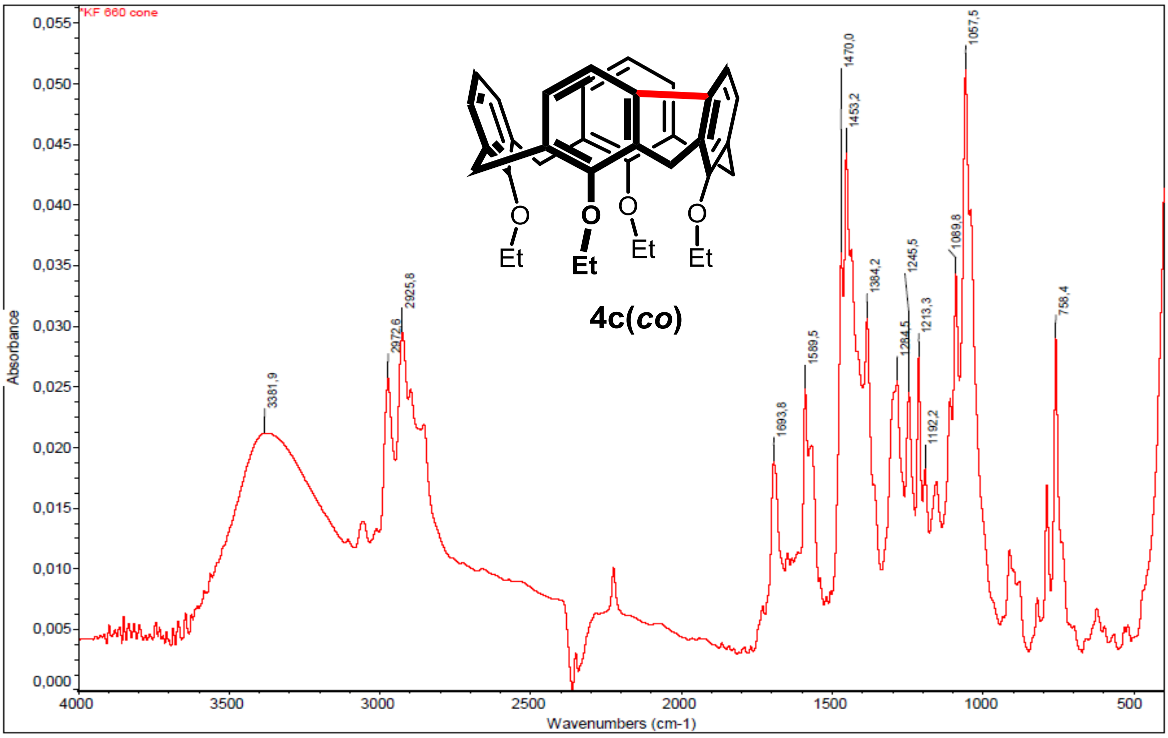


Compound 4c(*co*)

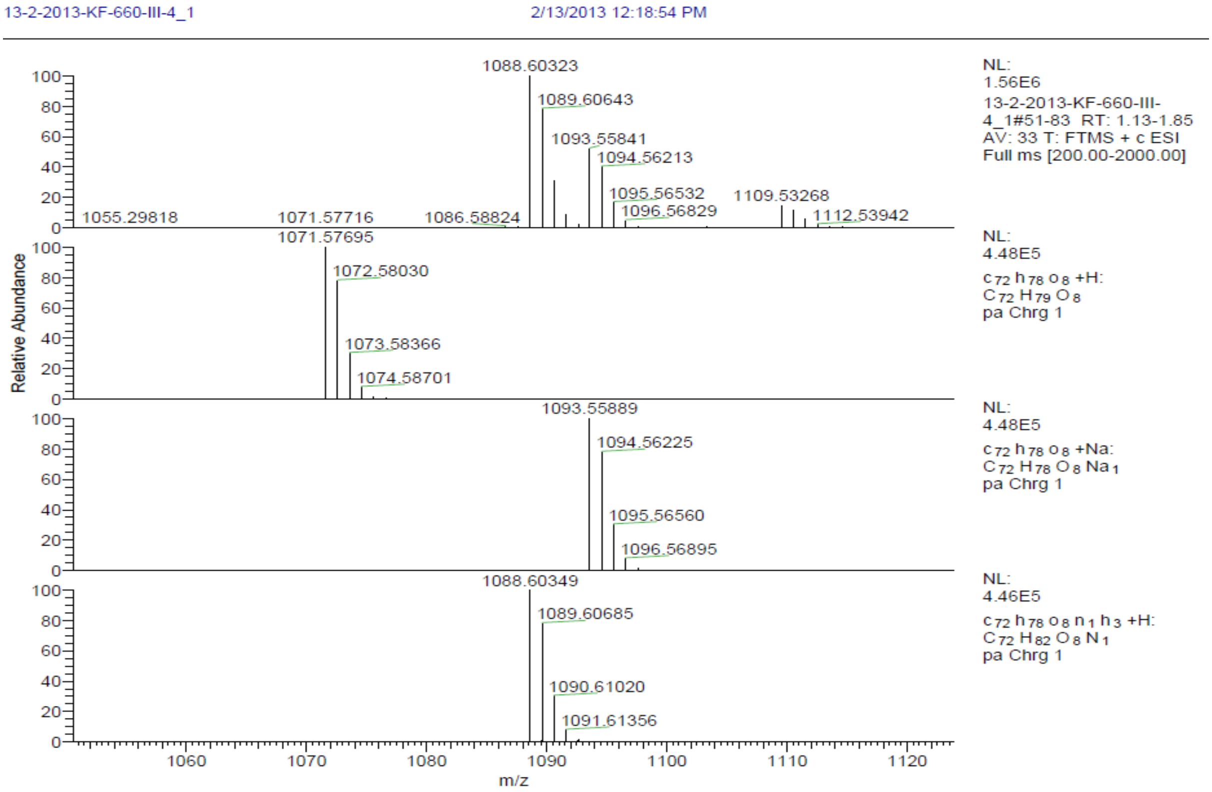




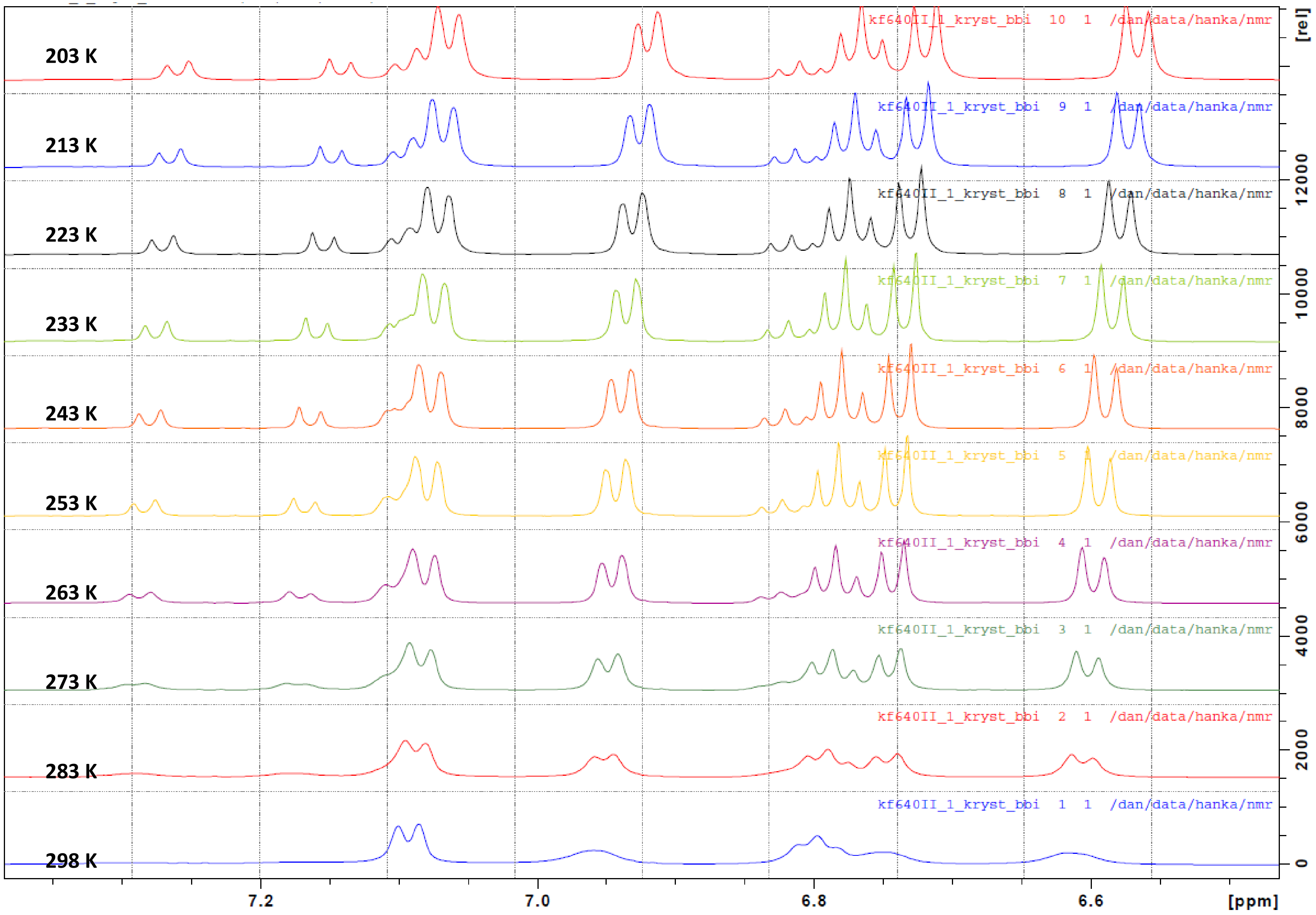
Compound 4c(*co*)



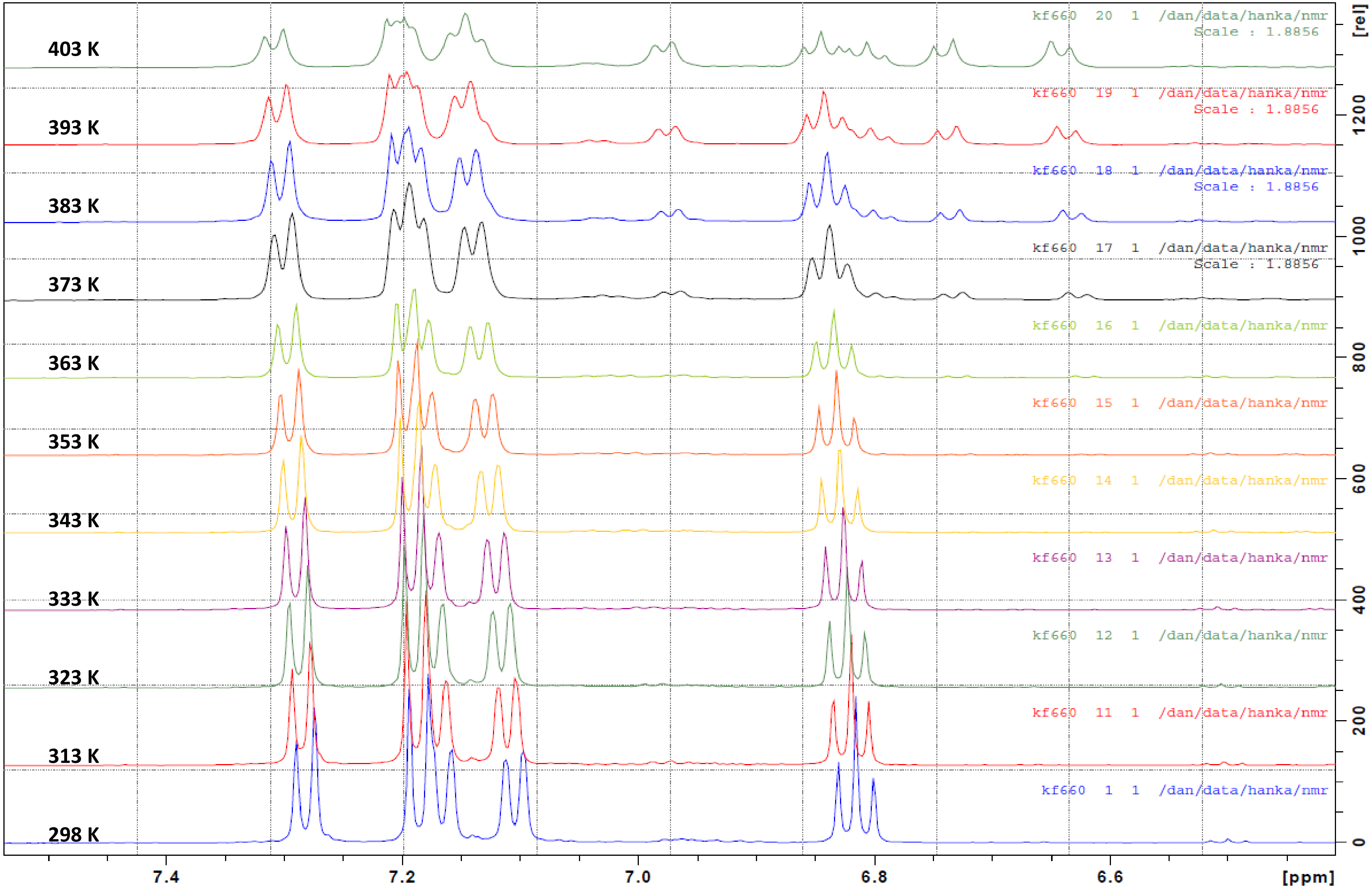
Dimer 5c



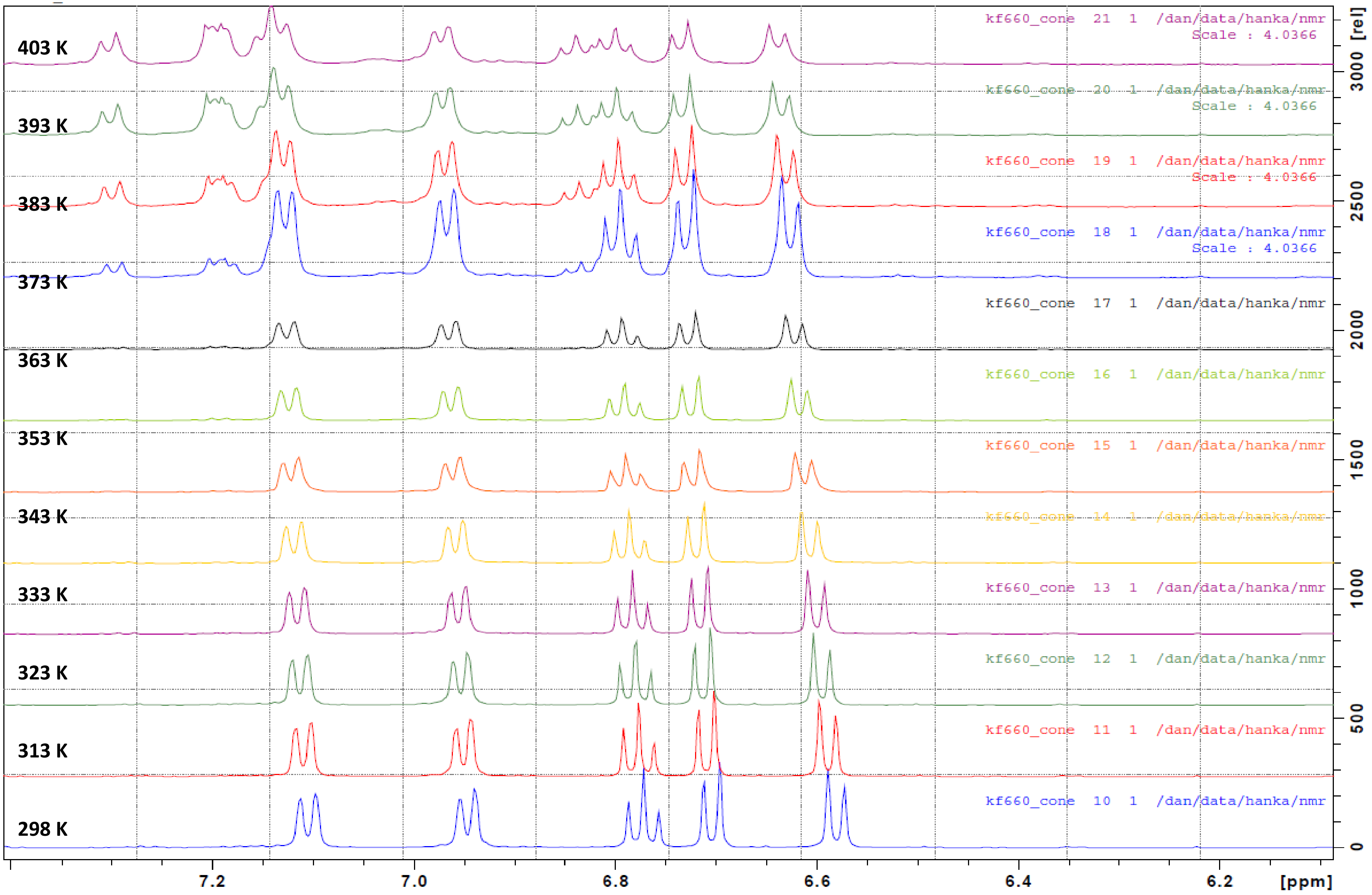
^{1}H NMR spectra of 4b (500 MHz, CD_2Cl_2, 298 to 203 K)

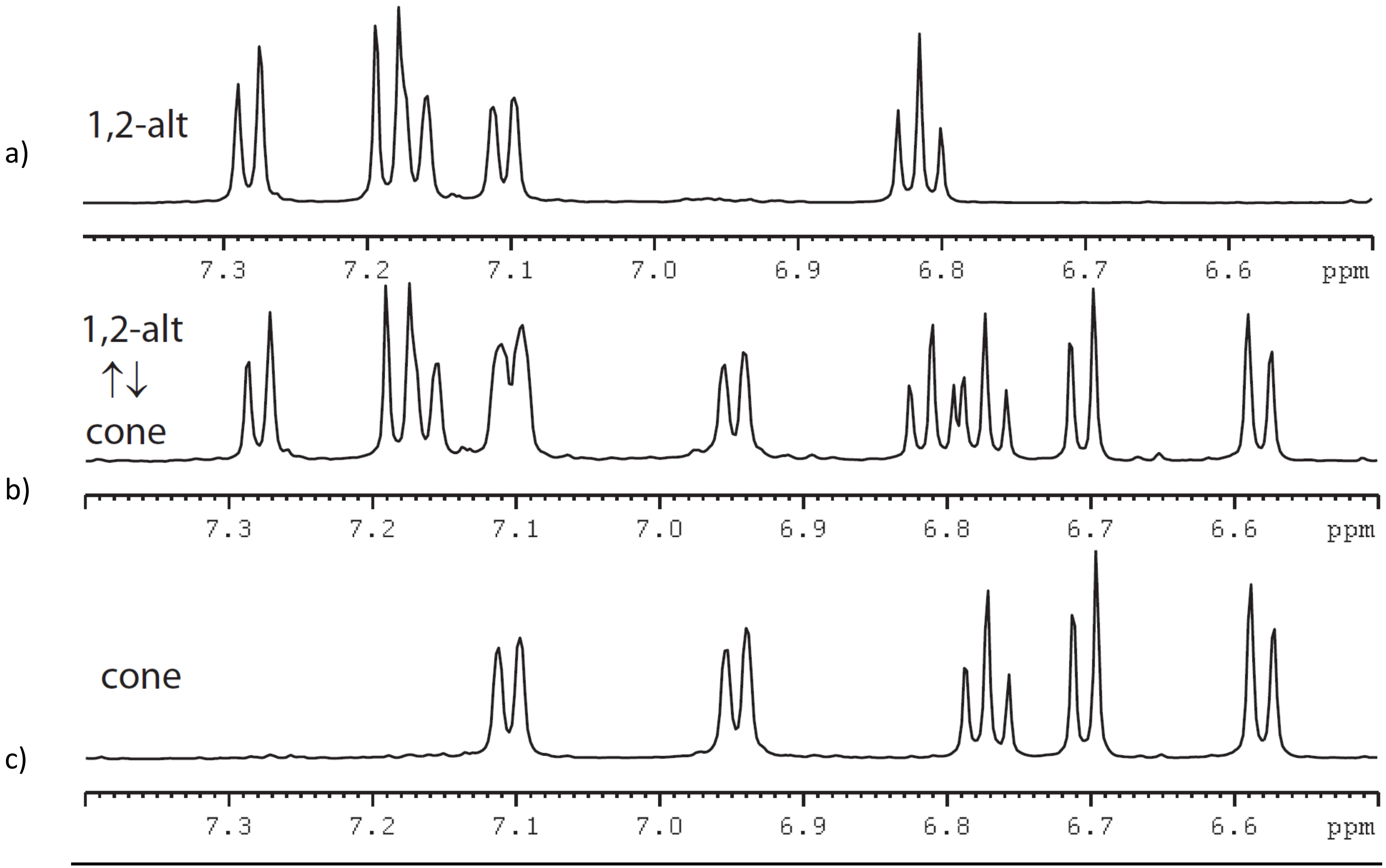


^{1}H NMR spectra of 4b(*alt*) (500 MHz, $CDCl_2$-$CDCl_2$, 298 to 403 K).



^{1}H NMR spectra of 4b(*co*) (500 MHz, $CDCl_2$-$CDCl_2$, 298 to 403 K).





a) ^{1}H NMR spectrum of pure isomer **4c**(*alt*), c) ^{1}H NMR spectrum of pure isomer **4c**(*co*), b) spectrum of thermodynamic equilibrium after 3 h heating of **4c**(*alt*) or **4c**(*co*) to 130 °C (500 MHz, CD_2Cl-CD_2Cl).

Crystallographic data

Derivative **4a** (*cone*) (KF_609):

Formula: $C_{40}H_{46}O_4$, $M_r = 590.8$, crystal dimension 0.50 × 0.32 × 0.19 mm, crystal system Triclinic, space group P-1, $a = 10.6165$ (2) Å, $b = 11.7880$ (3) Å, $c = 14.3411$ (3) Å, $\alpha = 100.7475$ (19)°, $\beta = 110.181$ (2)°, $\gamma = 92.2470$ (19)°, V = 1644.55 (7) $Å^3$, Z = 2, $\rho_{calc} = 1193$ kgm^{-3}, $\mu = 0.59$ mm^{-1}, Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å, $T = 120$ K, $2\Theta_{max}$, = 134.2, 31302/5780 measured/independent reflections, $R_{int} = 0.024$, $R = 0.041$, $wR = 0.127$, $\Delta\rho_{max} = 0.53$ $eÅ^{-3}$, $\Delta\rho_{min} = -0.25$ $eÅ^{-3}$. The data were collected on Gemini Ultradiffractometer with Atlas CCD detector and graphite monochromator. The structure was solved using charge flipping methods[3] and refined using the Jana2006 suite of programs[4]. All non-hydrogen atoms were refined using harmonic refinement. The hydrogen atoms were located in Fourier difference maps, but according to common practice they were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93-0.98 Å) and U_{iso} (H) (in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints. The structure was deposited into Cambridge Structural Database under number CCDC 930504.

Derivative **4c** (*1,2-alternate*) (KF_660):

Formula: $C_{36}H_{38}O_4$, $M_r = 534.69$, crystal dimension 0.37 × 0.29 × 0.11 mm, crystal system Monoclinic, space group $P2_1/n$, $a = 11.09428$ (16) Å, $b = 15.33790$ (18) Å, $c = 17.4781$ (2) Å, $\beta = 91.8464$ (12)°, V = 2972.58 (7) $Å^3$, Z = 4 , $\rho_{calc} = 1195$ kgm^{-3}, $\mu = 0.60$ mm^{-1}, Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å, $T = 293$ K, $2\Theta_{max}$, = 151.6, 61451/6069 measured/independent reflections, $R_{int} = 0.033$, $R = 0.065$, $wR = 0.124$, $\Delta\rho_{max} = 0.31$ $eÅ^{-3}$, $\Delta\rho_{min} = -0.30$ $eÅ^{-3}$. The data were collected on Xcalibur PX diffractometer with Onyx CCD detector and graphite monochromator. The structure was solved using direct methods[1] and refined using the Crystals suite of programs[2]. All non-hydrogen atoms were refined using harmonic refinement. The hydrogen atoms were located in Fourier difference maps, but according to common practice they were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93-0.98 Å) and U_{iso} (H) (in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints. The structure was deposited into Cambridge Structural Database under number CCDC 930506.

Derivative **4b** (KF_640):

Formula: $C_{32}H_{30}O_4$, $M_r = 478.56$, crystal dimension 0.61 × 0.38 × 0.33 mm, crystal system Monoclinic, space group $P2_1/n$, $a = 7.33245$ (16) Å, $b = 33.2368$ (5) Å, $c = 10.52859$ (18) Å, $\beta = 101.6960$ (19)°, V = 2512.62 (8) $Å^3$, Z = 4 , $\rho_{calc} = 1265$ kgm^{-3}, $\mu = 0.66$ mm^{-1}, Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å, $T = 190$ K, $2\Theta_{max}$, = 154.2, 20567/5223 measured/independent reflections, $R_{int} = 0.021$, $R = 0.044$, $wR = 0.143$, $\Delta\rho_{max} = 0.28$ $eÅ^{-3}$,$\Delta\rho_{min} = -0.22$ $eÅ^{-3}$.The data were collected on Xcalibur PX diffractometer with Onyx CCD detector and graphite monochromator. The structure was solved using direct methods[1] and refined using the Crystals suite of programs[2]. All non-hydrogen atoms were refined using harmonic refinement. The hydrogen atoms were located in Fourier difference maps,but according to common practice they were repositioned geometrically.The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93-0.98 Å) and U_{iso}(H) (in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.The structure was deposited into Cambridge Structural Database under number CCDC 930505.

Literature:

[1] Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M.C., Polidori, G. and Camalli, M., SIRPOW.92 - a program for automatic solution of crystal structures by direct methods optimized for powder data, (1994). J. Appl. Cryst. 27, 435.

[2] Betteridge, P.W., Carruthers, J.R., Cooper, R.I., Prout, K. and Watkin, D.J., CRYSTALS version 12: software for guided crystal structure analysis, (2003). J. Appl. Cryst. 36, 1487.

[3] Palatinus L. and Chapuis G., SUPERFLIP - a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions,(2007). J. Appl. Cryst. 40, 786-790.

[4] Petricek, V., Dusek, M. and Palatinus L. (2006). Jana2006. Structure Determination Software Programs. Institute of Physics, Praha, Czech Republic.

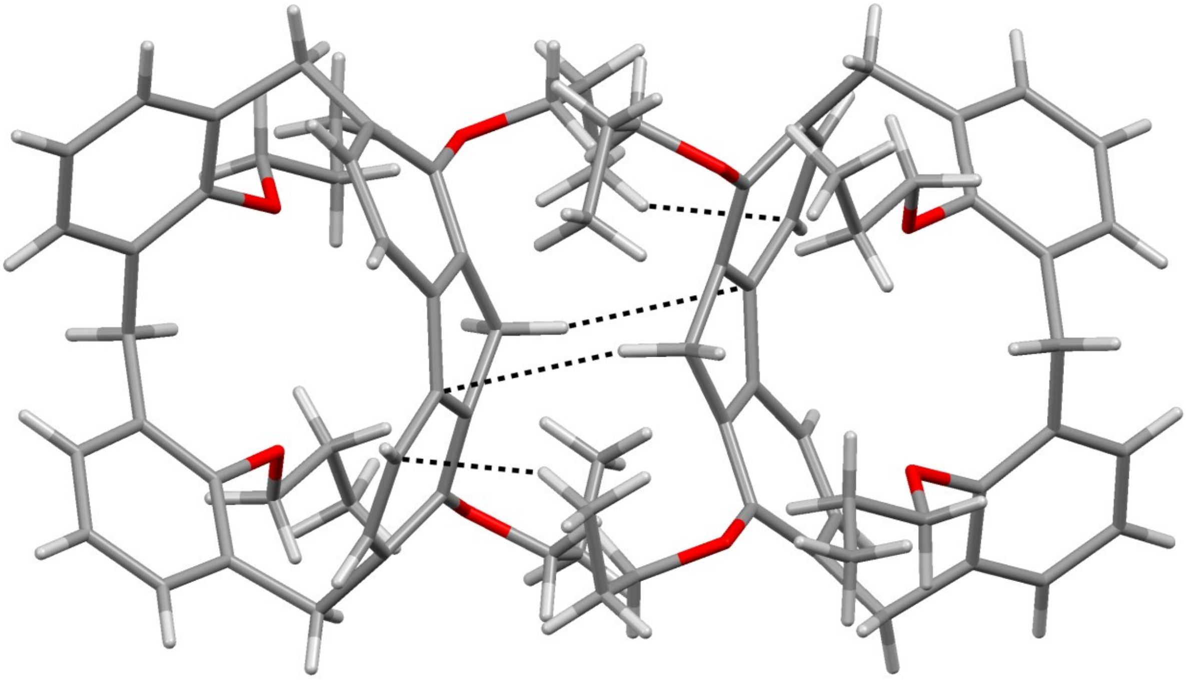


Figure S1. Molecular packing of compound **4a**. The intermolecular interactions of fluorene moiety are represented by dashed line.

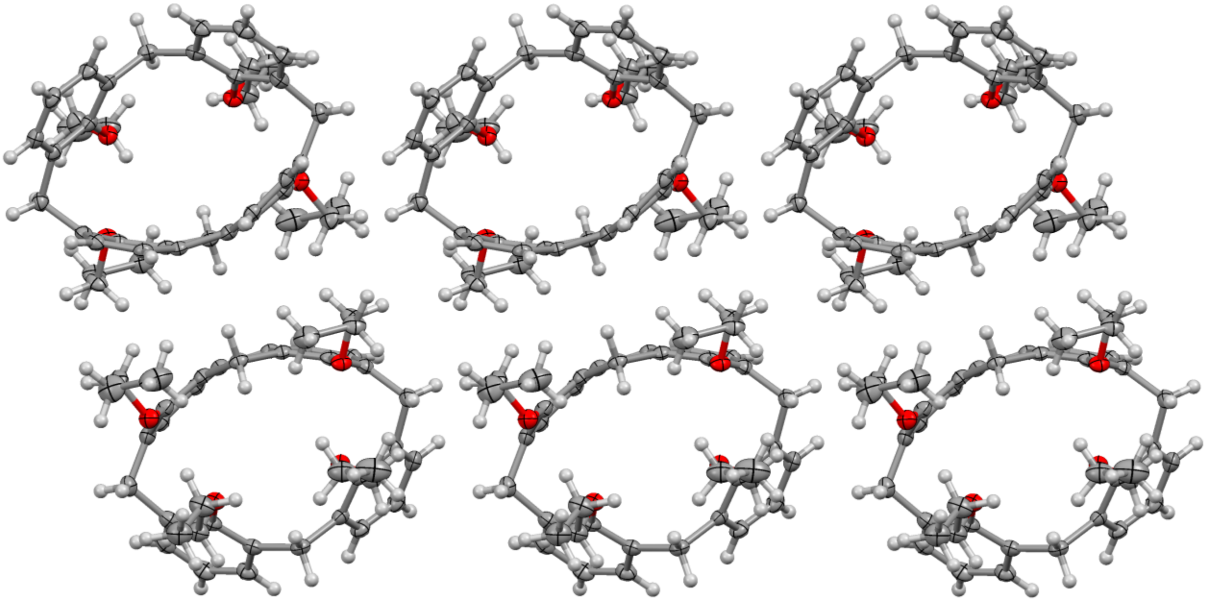


Figure S2. Molecular packing in the crystal structure of **4a** (thermal ellipsoids at the 50% probability level).

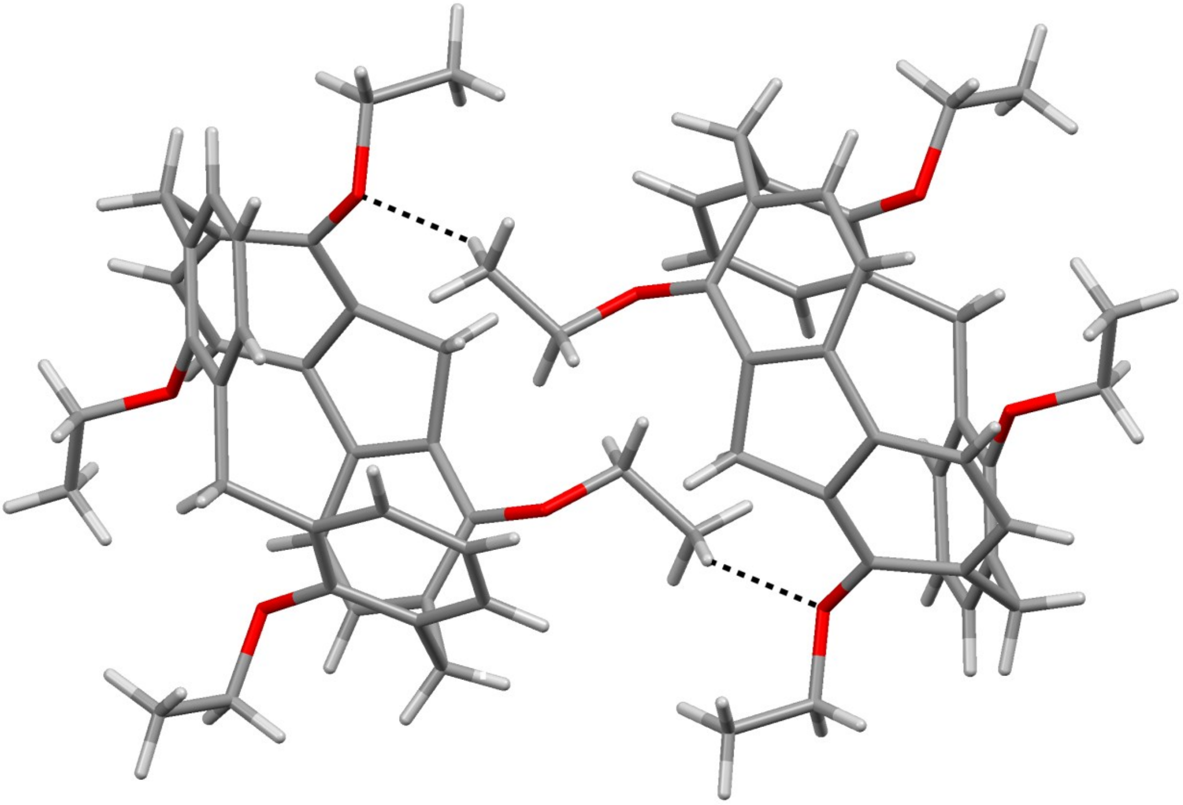


Figure S3. Molecular packing of compound **4b(*alt*)**. The intermolecular interactions are represented by dashed line.

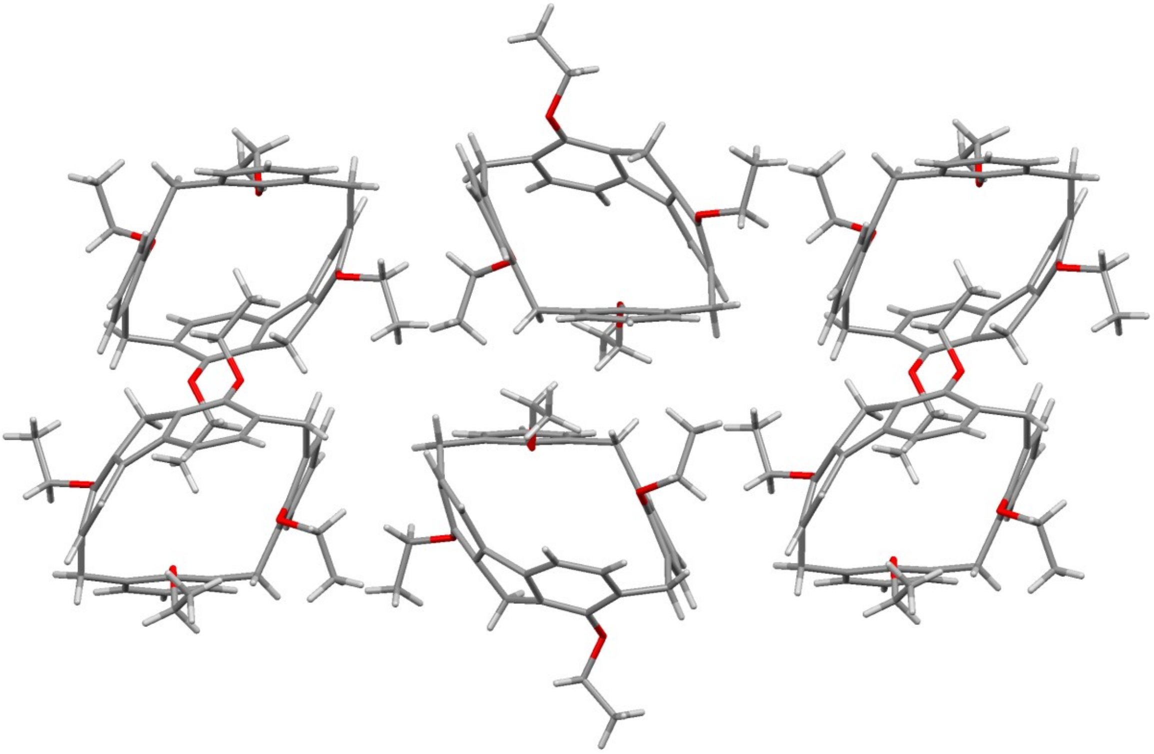


Figure S4. Molecular packing of compound **4b(*alt*)**.

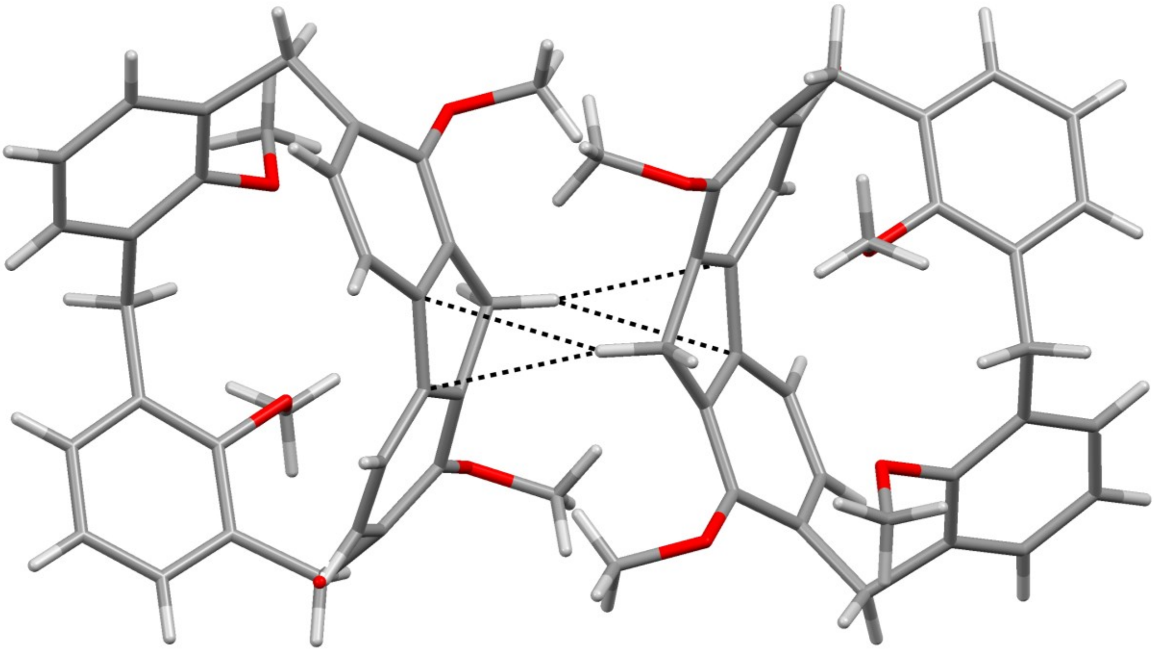


Figure S5. Molecular packing of compound **4b**. The intermolecular interactions of fluorene moieties are represented by dashed line.

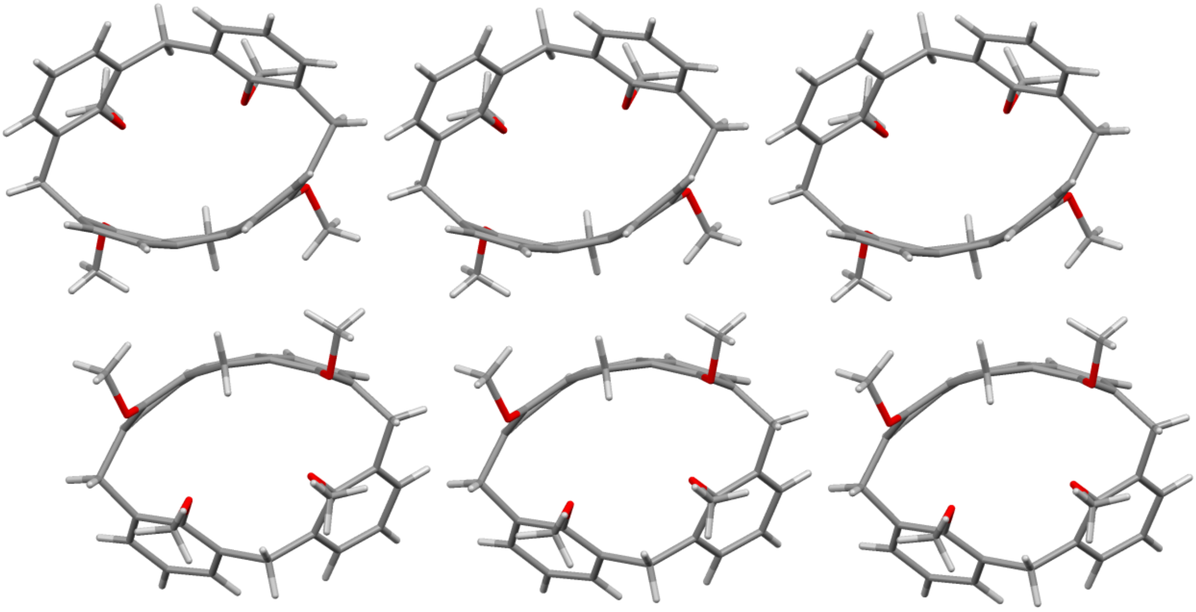


Figure S6. Molecular packing in the crystal structure of **4c**.