SUPPORTING INFORMATION

Title: Broad Functionalization of Deep-Cavity Cavitands by Directed ortho Metalation
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Ref. No.: O200800206
<table>
<thead>
<tr>
<th>General Experimental Methods and Data for 6/7, 15, 17, 19 and 23</th>
<th>S2-S4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H NMR, $^{13}$C NMR and MALDI-TOF MS spectra of 2</td>
<td>S5-S7</td>
</tr>
<tr>
<td>$^1$H NMR, $^{13}$C NMR and MALDI-TOF MS spectra of 3</td>
<td>S8-S10</td>
</tr>
<tr>
<td>$^1$H NMR, $^{13}$C NMR and MALDI-TOF MS spectra of 4</td>
<td>S11-S13</td>
</tr>
<tr>
<td>$^1$H NMR, $^{13}$C NMR and MALDI-TOF MS spectra of 5</td>
<td>S14-S16</td>
</tr>
<tr>
<td>$^1$H NMR, $^{13}$C NMR and MALDI-TOF MS spectra of 6/7</td>
<td>S17-S19</td>
</tr>
<tr>
<td>$^1$H NMR, $^{13}$C NMR and MALDI-TOF MS spectra of 8</td>
<td>S20-S22</td>
</tr>
<tr>
<td>$^1$H NMR, $^{13}$C NMR and MALDI-TOF MS spectra of 9</td>
<td>S23-S25</td>
</tr>
<tr>
<td>$^1$H NMR, $^{13}$C NMR and MALDI-TOF MS spectra of 10</td>
<td>S26-S28</td>
</tr>
<tr>
<td>$^1$H NMR, $^{13}$C NMR and MALDI-TOF MS spectra of 11</td>
<td>S29-S31</td>
</tr>
<tr>
<td>$^1$H NMR, $^{13}$C NMR and MALDI-TOF MS spectra of 12</td>
<td>S32-S34</td>
</tr>
<tr>
<td>$^1$H NMR, $^{13}$C NMR and MALDI-TOF MS spectra of 13</td>
<td>S35-S37</td>
</tr>
<tr>
<td>$^1$H NMR, $^{13}$C NMR and MALDI-TOF MS spectra of 14</td>
<td>S38-S40</td>
</tr>
<tr>
<td>$^1$H NMR, $^{13}$C NMR and MALDI-TOF MS spectra of 15</td>
<td>S41-S43</td>
</tr>
<tr>
<td>$^1$H NMR, $^{13}$C NMR and MALDI-TOF MS spectra of 16</td>
<td>S44-S46</td>
</tr>
</tbody>
</table>
General Experimental methods. All reagents were purchased from various commercial sources and used without further purification. At frequent intervals, solutions of butyllithiums were titrated using diphenyl acetic acid. All reactions were run under a nitrogen atmosphere. The synthesis of 1 has been reported previously.8a,b Flash chromatography (silica gel 60 Å, 230-400 mesh; Natland International) was used for product purification. Melting points were determined on a Mel-Temp II apparatus and are uncorrected. The NMR spectra were recorded on a Varian 300 MHz, 400 MHz or 500 MHz spectrometers. Mass spectra were recorded on a Voyager-DE Elite or 4700 Reflector MALDI-TOF mass spectrometers. Elemental analyses were performed by Atlantic Microlab Inc.

A/C- and A/B-exo diester 6 and 7 (inseparable): Yield = 23%. m.p. > 250 °C. 1H NMR (500 MHz, CDCl₃, 25 °C): δ = 2.58 (m, 16H), 3.95 (m, 6H), 4.54 (m, 4H), 4.84 (m, 4H₂), 5.94 (s, 2H), 5.98 (s, 4H), 6.02 (s, 2H), 6.49 (brs, 4H), 6.52 (brs, 2H), 6.56 (brs, 2H), 6.60 (brs, 4H), 6.66 (t, 1H, J = 2.0 Hz), 6.70 (t, 4H, J = 2.0 Hz), 6.72 (t, 1H, J = 2.0 Hz), 6.99 (t, 2H, J = 2.0 Hz), 7.01 (t, 2H, J = 2.0 Hz), 7.13 (m, 8H), 7.19-7.30 (m, 24H), 7.59 (t, 4H, J = 8.0 Hz) ppm. 13C NMR (100 MHz, CDCl₃, 25 °C): δ = 33.02, 34.55, 36.84, 53.14, 105.67, 105.85, 106.09, 106.23, 106.33, 107.82, 109.47, 109.94, 115.10, 115.55,
115.98, 120.79, 120.91, 121.20, 122.40, 126.48, 128.58, 128.92, 131.48, 136.89, 137.00, 137.11, 137.21, 139.33, 140.38, 141.52, 156.47, 156.57, 156.77, 156.79, 158.21, 161.43, 165.41 ppm. MS (MALDI-TOF): calcd. for $[C_{116}H_{84}O_{20} + Ag]^+$ 1905.76; found 1905.04.

$C_{116}H_{84}O_{20} \cdot 1/2CHCl_3$ (1857.59): calcd. C 75.49, H 4.56; found C 75.36, H 4.56.

A/B/C-exo triphenol 15: Yield = 10%. m.p. > 250 °C. $^1H$ NMR (400 MHz, CDCl$_3$, 25 °C): (contaminated with < 2% impurities) $\delta$ = 2.47-2.63 (m, 16H), 4.53 (s, 3H), 4.55 (s, 1H), 4.81-4.85 (m, 4H), 5.85 (brs, 3H), 5.99 (s, 4H), 6.52 (distorted d, 2H), 6.54 (distorted s, 2H), 6.55 (s, 4H), 6.67 (t, 2H, $J = 2.0$ Hz), 6.70 (t, 2H, $J = 2.2$ Hz), 7.00 (distorted t, 1H), 7.10-7.12 (m, 8H), 7.17-7.29 (m, 24H), 7.57-7.63 (m, 4H) ppm. $^{13}C$ NMR (100 MHz, CDCl$_3$, 25 °C): $\delta$ = 33.02, 34.55, 36.85, 105.85, 106.39, 106.48, 106.54, 109.85, 109.99, 114.35, 115.54, 115.81, 115.86, 120.85, 121.09, 122.30, 126.42, 128.16, 128.55, 128.87, 131.51, 131.58, 135.75, 136.92, 136.90, 139.47, 141.54, 148.07, 148.10, 148.17, 156.53, 156.69, 156.80, 161.30 ppm. MS (MALDI-TOF): calcd. for $[C_{112}H_{80}O_{19} + Ag]^+$ 1837.69; found 1837.73.

Tetra-exo, mono-endo phenol 17: Yield = 21%. m.p. > 250 °C. $^1H$ NMR (400 MHz, CDCl$_3$, 25 °C): (contaminated with ∼ 5% impurities) $\delta$ = 2.47-2.63 (m, 16H), 4.51 and 4.52 (2 × s, 4H), 4.74 (brs, 1H), 4.80-4.85 (m, 4H), 5.96, 5.97 and 5.98 (3 × s, 4H), 6.50 (s, 2H), 6.57 (s, 2H), 6.59 and 6.60 (2 × s, 4H), 6.67 (distorted t, 1H), 6.76 (distorted t, 2H), 7.10-7.12 (m, 32H), 7.57-7.62 (m, 4H) ppm. $^{13}C$ NMR (100 MHz, CDCl$_3$, 25 °C): $\delta$ = 33.04, 34.55, 36.84, 105.25, 106.34, 106.66, 109.92, 115.35, 115.86, 121.17, 122.31, 122.47, 126.41, 128.18, 128.27, 128.55, 128.87, 131.48, 135.31, 135.82, 136.94, 141.56, 142.92, 147.52, 148.23, 148.38, 156.44, 156.52, 156.60, 156.66, 156.78 ppm. MS (MALDI-TOF): calcd. for $[C_{112}H_{80}O_{21} + Ag]^+$ 1869.69; found 1869.69.

Racemate A-exo, B(C)-endo dithioether 19 (and its enantiomer): Yield = 35%. m.p. > 250 °C. $^1H$ NMR (400 MHz, CDCl$_3$, 25 °C): (contaminated with ∼ 8% isomeric compounds) $\delta$ = 2.26 (s, 3H), 2.47-2.63 (m, 19H), 4.54-4.57 (m, 4H), 4.81-4.86 (m, 4H), 5.95 (s, 1H), 5.98-6.01(m, 3H), 6.40 (d, 2H, $J = 0.8$ Hz), 6.48-6.64 (m, 7H), 6.69-6.71 (m, 2H), 6.97 (t, 1H, $J = 2.4$ Hz), 7.05-7.06 (m, 2H), 7.10-7.12 (m, 8H), 7.17-7.31 (m,
A/B/C-tri-exo, C/D-di-endo thioether 23: Yield = 22%. m.p. > 250 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\), 25 °C): (contaminated with ~ 7 % impurities) \(\delta = 2.14\) (s, 6H), 2.49-2.62 (m, 25H), 4.52-4.58 (m, 4H), 4.79-4.86 (m, 4H), 5.94 (s, 2H), 5.96 (s, 2H), 6.45-6.47 (m, 4H), 6.57 (m, 4H), 6.64 (t, 2H, \(J = 2.2\) Hz), 7.09-7.33 (m, 32H), 7.52-7.63 (m, 4H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\), 25 °C): \(\delta = 18.06, 18.35, 33.01, 34.53, 36.79, 104.83, 104.95, 106.02, 106.32, 109.57, 115.52, 115.79, 120.88, 122.31, 122.46, 125.00, 126.43, 128.54, 128.88, 130.34, 131.54, 136.91, 136.98, 137.02, 137.07, 137.85, 137.98, 138.96, 141.49, 156.63, 156.90, 156.94, 157.33, 157.48, 161.17, 161.49 ppm. MS (MALDI-TOF): calcd. for [C\(_{117}\)H\(_{96}\)O\(_{16}\)S\(_5\) + Ag]\(^+\) 2020.16; found 2018.30. An alternative structure, namely A/B/C-tri-exo A/B-di-endo, also fits the above data. We discount this possible interpretation on account of: 1) the up field position of endo-thio ether protons (\(\delta 2.14\)) as compared to endo-thio ether protons in 18, 19 and 21 (\(\delta 2.26-2.27\)); it may also be noted that endo-thio ether protons in 24, located in between two exo-thio ether protons appear down field at \(\delta 2.39\). 2) The charge density in the polyanion intermediate would be very high.
$^1$H NMR spectrum of 2
$^{13}$C NMR spectrum of 2
MALDI-TOF MS spectrum of 2
$^1$H NMR spectrum of 3
$^{13}$C NMR spectrum of 3
MALDI-TOF MS spectrum of 3
$^1$H NMR spectrum of 4
$^{13}$C NMR spectrum of 4
MALDI-TOF MS spectrum of 4
$^1$H NMR spectrum of 5
$^{13}$C NMR spectrum of 5
MALDI-TOF MS spectrum of 5
$^1$H NMR spectrum of 6/7
$^{13}$C NMR spectrum of 6/7
MALDI-TOF MS spectrum of 6/7
$^1$H NMR spectrum of 8
$^{13}\text{C}$ NMR spectrum of 8
MALDI-TOF MS spectrum of 8
$^1$H NMR spectrum of 9
$^{13}$C NMR spectrum of 9
MALDI-TOF MS spectrum of 9
$^1$H NMR spectrum of 10
$^{13}$C NMR spectrum of 10
MALDI-TOF MS spectrum of 10
$^1$H NMR spectrum of 11
$^{13}\text{C}$ NMR spectrum of 11
MALDI-TOF MS spectrum of 11
$^1$H NMR spectrum of 12
$^{13}$C NMR spectrum of 12
MALDI-TOF MS spectrum of 12
$^1$H NMR spectrum of 13
$^{13}$C NMR spectrum of 13
MALDI-TOF MS spectrum of 13
$^1$H NMR spectrum of 14
$^{13}$C NMR spectrum of 14
MALDI-TOF MS spectrum of 14
$^1$H NMR spectrum of 15 (impurity < 2%)
$^{13}$C NMR spectrum of 15
MALDI-TOF MS spectrum of 15
$^1$H NMR spectrum of 16
$^{13}$C NMR spectrum of 16
MALDI-TOF MS spectrum of 16
$^1$H NMR spectrum of 17 (impurity ~ 5%)
$^{13}$C NMR spectrum of 17
MALDI-TOF MS spectrum of 17
$^{1}$H NMR spectrum of 18
$^{13}$C NMR spectrum of 18
MALDI-TOF MS spectrum of 18
$^1$H NMR spectrum of 19 (impurity ~ 8%)
$^{13}$C NMR spectrum of 19
MALDI-TOF MS spectrum of 19
$^1$H NMR spectrum of 20
$^{13}$C NMR spectrum of 20
MALDI-TOF MS spectrum of 20
$^1$H NMR spectrum of 21
$^{13}$C NMR spectrum of 21
MALDI-TOF MS spectrum of 21
\(^1\)H NMR spectrum of 22
$^{13}$C NMR spectrum of 22
MALDI-TOF MS spectrum of 22
$^1$H NMR spectrum of 23 (impurity ~ 7%)
$^{13}$C NMR spectrum of 23
MALDI-TOF MS spectrum of 23
$^1$H NMR spectrum of 24
$^{13}$C NMR spectrum of 24
MALDI-TOF MS spectrum of 24
$^1$H NMR spectrum of 25
$^{13}$C NMR spectrum of 25
MALDI-TOF MS spectrum of 25