Supporting Information


Martin Tlustý,† Martin Babor,‡ Václav Eigner,∫ Michal Kohout† and Pavel Lhoták‡*

†Department of Organic Chemistry, University of Chemistry and Technology, Prague (UCTP), Technicka 5, 166 28 Prague 6, Czech Republic
‡ Department of Solid State Chemistry, UCTP, Technicka 5, 166 28 Prague 6, Czech Republic
∫ Department of Structure Analysis, Institute of Physics of Czech Academy of Sciences, Na Slovance 1999, 182 21 Prague 8, Czech Republic

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1. Spectral characterization of compounds

![Image of compound structure]

**Figure 1:** $^1$H NMR of compound 6a (CDCl$_3$, 400 MHz).

![13C(APT) NMR spectrum]

**Figure 2:** $^{13}$C(APT) NMR of compound 6a (CDCl$_3$, 100 MHz).
Figure 3: HRMS of compound 6a (ESI+).

Figure 4: IR of compound 6a (KBr).
Figure 5: $^1$H NMR of compound 6b (CDCl$_3$, 400 MHz).

Figure 6: $^{13}$C(APT) NMR of compound 6b (CDCl$_3$, 100 MHz).
Figure 7: HRMS of compound 6b (ESI+).

Figure 8: IR of compound 6b (KBr).
Figure 9: $^1$H NMR of compound 6c (CDCl$_3$, 400 MHz).

Figure 10: $^{13}$C(APT) NMR of compound 6c (CDCl$_3$, 100 MHz).
Figure 11: HRMS of compound 6c (ESI+).

Figure 12: IR of compound 6c (KBr).
Figure 13: $^1$H NMR of compound 6d (CDCl$_3$, 400 MHz).

Figure 14: $^{13}$C(APT) NMR of compound 6d (CDCl$_3$, 100 MHz).
Figure 15: HRMS of compound 6d (ESI+).

Figure 16: IR of compound 6d (KBr).
Figure 17: $^1$H NMR of compound 6e (CDCl$_3$, 400 MHz).

Figure 18: $^{13}$C(APT) NMR of compound 6e (CDCl$_3$, 100 MHz).
Figure 19: HRMS of compound 6e (ESI+).

Figure 20: IR of compound 6e (KBr).
Figure 21: $^1$H NMR of compound 6f (CDCl$_3$, 400 MHz).

Figure 22: $^{13}$C(APT) NMR of compound 6f (CDCl$_3$, 100 MHz).
Figure 23: HRMS of compound 6f (ESI+).

Figure 24: IR of compound 6f (KBr).
Figure 25: $^1$H NMR of compound 7a (CDCl$_3$, 400 MHz).

Figure 26: $^{13}$C(APT) NMR of compound 7a (CDCl$_3$, 100 MHz).
Figure 27: HRMS of compound 7a (ESI+).

Figure 28: IR of compound 7a (KBr).
Figure 29: $^1$H NMR of compound 7b (CDCl$_3$, 400 MHz).

Figure 30: $^{13}$C(APT) NMR of compound 7b (CDCl$_3$, 100 MHz).
Figure 31: HRMS of compound 7b (ESI+).

Figure 32: IR of compound 7b (KBr).
Figure 33: $^1$H NMR of compound 7c (CDCl$_3$, 400 MHz).

Figure 34: HRMS of compound 7c (ESI$^+$).
Figure 35: HRMS of compound 7e (ESI+).
Figure 36: $^1$H NMR of compound 8a (CDCl$_3$, 400 MHz).

Figure 37: HRMS of compound 8a (ESI+).
Figure 38: IR of compound 8a (KBr).
Figure 39: $^1$H NMR of compound 8b (CDCl$_3$, 400 MHz).

Figure 40: $^{13}$C(APT) NMR of compound 8b (CDCl$_3$, 100 MHz).
Figure 41: HRMS of compound 8b (ESI+).

Figure 42: IR of compound 8b (KBr).
Figure 43: $^1$H NMR of compound 11 (CDCl$_3$, 400 MHz).

Figure 44: $^{13}$C(APT) NMR of compound 11 (CDCl$_3$, 100 MHz).
Figure 45: HRMS of compound 11 (ESI+).

Figure 46: IR of compound 11 (KBr).
Figure 47: $^1$H NMR of compound 12a (CDCl$_3$, 400 MHz).

Figure 48: $^{13}$C(APT) NMR of compound 12a (CDCl$_3$, 100 MHz).
Figure 49: HRMS of compound 12a (ESI+).

Figure 50: IR of compound 12a (KBr).
Figure 51: $^1$H NMR of compound 12b (CDCl$_3$, 400 MHz).

Figure 52: $^{13}$C(APT) NMR of compound 12b (CDCl$_3$, 100 MHz).
Figure 53: HRMS of compound 12b (ESI+).

Figure 54: IR of compound 12b (KBr).
Figure 55: $^1$H NMR of compound 13a (CDCl$_3$, 400 MHz).

Figure 56: $^{13}$C(APT) NMR of compound 13a (CDCl$_3$, 100 MHz).
Figure 57: HRMS of compound 13a (ESI+).

Figure 58: IR of compound 13a (KBr).
Figure 59: $^1$H NMR of compound 13b (CDCl$_3$, 400 MHz).

Figure 60: $^{13}$C(APT) NMR of compound 13b (CDCl$_3$, 100 MHz).
Figure 61: HRMS of compound 13b (ESI+).

Figure 62: IR of compound 13b (KBr).
Figure 63: $^1$H NMR of compound 13c (CDCl$_3$, 400 MHz).

Figure 64: $^{13}$C(APT) NMR of compound 13c (CDCl$_3$, 100 MHz).
Figure 65: HRMS of compound 13c (ESI+).

Figure 66: IR of compound 13c (KBr).
**Figure 67:** $^1$H NMR of compound 13d (CDCl$_3$, 400 MHz).

**Figure 68:** $^{13}$C(APT) NMR of compound 13d (CDCl$_3$, 100 MHz).
Figure 69: HRMS of compound 13d (ESI+).

Figure 70: IR of compound 13d (KBr).
Figure 71: $^1$H NMR of compound 13e (CDCl$_3$, 400 MHz).

Figure 72: $^{13}$C(APT) NMR of compound 13e (CDCl$_3$, 100 MHz).
Figure 73: HRMS of compound 13e (ESI+).

Figure 74: IR of compound 13e (KBr).
Figure 75: $^1$H NMR of compound 13f (CDCl$_3$, 400 MHz).

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Figure 77: HRMS of compound 13f (ESI+).

Figure 78: IR of compound 13f (KBr).
Figure 79: $^1$H NMR of compound 14a (CDCl$_3$, 400 MHz).

Figure 80: $^{13}$C(APT) NMR of compound 14a (CDCl$_3$, 100 MHz).
Figure 81: HRMS of compound 14a (ESI+).

Figure 82: IR of compound 14a (KBr).
**Figure 83:** $^1$H NMR of compound 14b (CDCl$_3$, 400 MHz).

**Figure 84:** $^{13}$C(APT) NMR of compound 14b (CDCl$_3$, 100 MHz).
Figure 85: HRMS of compound 14b (ESI+).

Figure 86: IR of compound 14b (KBr).
Figure 87: $^1$H NMR of compound $14c$ (CDCl$_3$, 400 MHz).

Figure 88: $^{13}$C(APT) NMR of compound $14c$ (CDCl$_3$, 100 MHz).
Figure 89: HRMS of compound 14c (ESI+).

Figure 90: IR of compound 14c (KBr).
Figure 91: $^1$H NMR of compound 14d (CDCl$_3$, 400 MHz).

Figure 92: $^{13}$C(APT) NMR of compound 14d (CDCl$_3$, 100 MHz).
Figure 93: HRMS of compound 14d (ESI+).

Figure 94: IR of compound 14d (KBr).
Figure 95: $^1$H NMR of compound 14e (CDCl$_3$, 400 MHz).

Figure 96: $^{13}$C(APT) NMR of compound 14e (CDCl$_3$, 100 MHz).
Figure 97: HRMS of compound 14e (ESI+).

Figure 98: IR of compound 14e (KBr).
2. Chiral separation and ECD spectra

Figure 99: Preparative enantioseparation of 7b on Chiralpak IA (250×20 mm i.d., 5 μm).

Figure 100: Preparative enantioseparation of 14b on Chiralpak IA (250×20 mm i.d., 5 μm).
The enantiomeric nature of the separated substances was confirmed by ECD spectroscopy using Jasco J-810 (Jasco).

**Figure 101:** ECD spectra of both separated enantiomers of 7b in MeOH, the first eluting enantiomer 7b₁ full (blue) line, the second eluting enantiomer 7b₂ dashed (orange) line.

**Figure 102:** ECD spectra of both separated enantiomers of 14b in MeOH, the first eluting enantiomer 14b₁ full (blue) line, the second eluting enantiomer 14b₂ dashed (orange) line.
3. Crystallographic data

Crystallographic data for 7b-1

The structure of 7b was measured using D8 VENTURE equipped with Photon CMOS detector with Cu-Kα (λ = 1.54178 Å) radiation at 180 K. The structure was in hexagonal system, P61 space group with lattice parameters a=14.5403(3) Å, b=14.5403(3) Å, c=36.4429(8) Å, α=90° β=90° γ=120°, Z = 6, V = 6672.5(4) Å³, Dc = 1.199 g/cm³, μ (Cu-Kα) = 0.713 mm⁻¹. The data reduction and absorption correction were done with Apex3 software. The structure was solved by charge-flipping methods using SIR92 software and refined by full matrix least squares on F squared value using Crystals software to final values R = 0.0438 and wR = 0.1004 using 8653 independent reflections (Θmax = 72.100°), 609 parameters and 42 restraint. MCE software was used for visualization of residual electron density maps. According to common practice the hydrogen atoms attached to carbon atoms were placed geometrically with Uiso(H) in range 1.2–1.5 Ueq of parent atom (C). The crystal is a solid solution of two chemical entities. The difference between them is the chlorine atom bonded in the para position to the one of propoxy group. The occupancy of the molecule, which contains chlorine, is 0.23. The ordering is random, there are no peaks in the pattern which can show the supercell. The disordered functional groups were refined with restrained geometry and occupancy constrained to full for each atomic position. The structure was deposited into Cambridge Structural Database under number CCDC 1918213.

Figure 103: X-ray structure of compound 7b-1.
Crystallographic data for 8b

Larger prism crystal of 8b was selected, immersed in high viscosity PEG oil and cut to size appropriate for data collection. Data were collected at 180 (2) K on a D8 Venture Photon CMOS diffractometer with Incoatec microfocus sealed tube Cu-Kα radiation. The crystal s found to be in monoclinic space group P21/c with lattice parameters \( a = 12.0248 (3) \, \text{Å} \), \( b = 20.0249 (4) \, \text{Å} \), \( c = 40.0398 (9) \, \text{Å} \), \( \beta = 93.8505 (12) ^{\circ} \), \( V = 9619.6 (4) \, \text{Å}^3 \), \( Z = 8 \). The structure was solved by charge flipping\(^{[x2]}\) and anisotropically refined by full matrix least squares on \( F^2 \) using the CRYSTALS suite of programs\(^{[x3]}\) to final value \( R = 0.064 \) and \( wR = 0.153 \) using 17623 independent reflections (\( \Theta_{\text{max}} = 68.5^{\circ} \)), 1456 parameters and 491 restraints. The disordered propoxy groups and solvent were refined with restrained geometry and thermal parameters. The sum occupancy of disordered positions was restrained to 1 for each group. The hydrogen atoms attached to carbon atoms were placed in calculated positions. The hydrogen atoms attached to oxygen and nitrogen atoms were found in difference electron density maps. In both cases were the hydrogen atoms refined with riding constrains after initial refinement of geometry. The MCE program\(^{[x4]}\) was used for visualization of residual electron density maps. The structure was deposited into Cambridge Structural Database under number CCDC 1918371.

**Figure 104:** X-ray structure of compound 8b.
Crystalllographic data for 14a

Larger prism crystal of 14a was selected, immersed in high viscosity PEG oil and cut to size appropriate for data collection. Data were collected at 180 (2) K on a D8 Venture Photon CMOS diffractometer with Incoatec microfocus sealed tube Cu-Kα radiation. The crystal s found to be in monoclinic space group P2₁/c with lattice parameters a = 13.9434 (6) Å, b = 17.1880 (8) Å, c = 17.1967 (8) Å, β = 105.4889 (17) °, V = 3971.7 (3) Å³, Z = 4. The structure was solved by charge flipping and anisotropically refined by full matrix least squares on F squared using the CRYSTALS suite of programs to final value R = 0.045 and wR = 0.113 using 7210 independent reflections (Θmax = 68.4°), 546 parameters and 58 restraints. The disordered propoxy groups were refined with restrained geometry and thermal parameters. The sum occupancy of disordered positions was restrained to 1 for each group. The hydrogen atoms attached to carbon atoms were placed in calculated positions. The hydrogen atoms attached to nitrogen atoms were found in difference electron density maps. In both cases were the hydrogen atoms refined with riding constrains after initial refinement of geometry. The MCE program was used for visualization of residual electron density maps. The structure was deposited into Cambridge Structural Database under number CCDC 1918372.

Figure 105: X-ray structure of compound 14a.

4. Titration experiments

Nitromethane was mixed with specified amount of CDCl$_3$. 0.5 ml of nitromethane solution was put in NMR tube. To 0.12 ml of the nitromethane solution a specific amount of calixarene 7a was added. The aliquots of 7a were gradually added to NMR tube to achieve different guest / calixarene ratios (1:0.000-150.714), ensuring constant guest concentration during the experiment. The complexation constants were determined by analyzing CIS of protons of the guest molecule using nonlinear curve-fitting procedure (program BindFit).

![Table of values]

**Figure 106:** $^1$H NMR titration of compound 7a with nitromethane (CDCl$_3$, 400 MHz).
Calixarene 7b-1 was dissolved in specified amount of 1,1,2,2-tetrachloroethane. 0.5 ml of calixarene solution was put in NMR tube. To 0.6 ml of the calixarene solution a specific amount of (S)-N-methylnicotinium iodide (NMNI) was added. The aliquots of NMNI were gradually added to NMR tube to achieve different calixarene/guest ratios (1:0.000-11.896), ensuring constant host concentration during the experiment. The complexation constants were determined by analyzing CIS of protons of the host molecule using nonlinear curve-fitting procedure (program BindFit).

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**Figure 107:** $^{1}$H NMR titration of compound 7b-1 with NMNI (C$_2$D$_2$Cl$_4$, 400 MHz).
Calixarene 7b-2 was dissolved in specified amount of 1,1,2,2-tetrachloroethane. 0.5 ml of calixarene solution was put in NMR tube. To 0.6 ml of the calixarene solution a specific amount of (S)-N-methylnicotinium iodide (NMNI) was added. The aliquots of NMNI were gradually added to NMR tube to achieve different calixarene/guest ratios (1:0.000-11.715), ensuring constant host concentration during the experiment. The complexation constants were determined by analyzing CIS of protons of the host molecule using nonlinear curve-fitting procedure (program BindFit).

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Figure 108: $^1$H NMR titration of compound 7b-2 with NMNI (C₂D₂Cl₄, 400 MHz).
Calixarene 11 was dissolved in specified amount of CDCl₃. 0.5 ml of calixarene solution was put in NMR tube. To 0.6 ml of the calixarene solution a specific amount of tetrabutylammonium acetate (TBAA) was added. The aliquots of TBAA were gradually added to NMR tube to achieve different calixarene/guest ratios (1:0.000-39.765), ensuring constant host concentration during the experiment. The complexation constants were determined by analyzing CIS of fluorines of the host molecule using nonlinear curve-fitting procedure (program BindFit).

Figure 109: $^{19}$F NMR titration of compound 11 with TBBA (CDCl₃, 376 MHz).
Calixarene 12a was dissolved in specified amount of CDCl$_3$. 0.5 ml of calixarene solution was put in NMR tube. To 0.6 ml of the calixarene solution a specific amount of tetrabutylammonium acetate (TBAA) was added. The aliquots of TBAA were gradually added to NMR tube to achieve different calixarene/guest ratios (1:0.000-82.716), ensuring constant host concentration during the experiment. The complexation constants were determined by analyzing CIS of fluorines of the host molecule using nonlinear curve-fitting procedure (program BindFit).

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<td>0.001623</td>
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</tr>
</tbody>
</table>

Figure 110: $^{19}$F NMR titration of compound 12a with TBBA (CDCl$_3$, 376 MHz).
Calixarene 14b was dissolved in specified amount of CDCl₃. 0.5 ml of calixarene solution was put in NMR tube. To 0.6 ml of the calixarene solution a specific amount of acetonitrile (ACN) was added. The aliquots of ACN were gradually added to NMR tube to achieve different calixarene/guest ratios (1:0.000-101.038), ensuring constant host concentration during the experiment. The complexation constants were determined by analyzing CIS of protons of the host molecule using nonlinear curve-fitting procedure (program BindFit).

<table>
<thead>
<tr>
<th>V(ACN)</th>
<th>0.008 ml</th>
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<tbody>
<tr>
<td>M(ACN)</td>
<td>41.05 g/mol</td>
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<tr>
<td>m(ACN)</td>
<td>0.006238 g</td>
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<tr>
<td>c(ACN)</td>
<td>0.255296417 mol/l</td>
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<tr>
<td>V(CHCl₃_14b)</td>
<td>0.6 ml</td>
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<tr>
<td>p(ACN)</td>
<td>0.786 g/ml</td>
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<tr>
<td>M(14b)</td>
<td>804.93 g/mol</td>
</tr>
<tr>
<td>m(14b)</td>
<td>0.001218 g</td>
</tr>
<tr>
<td>c(14b)</td>
<td>0.001261 mol/l</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>V (total)</th>
<th>n V (addition, total)</th>
<th>[n V (addition) [ml]]</th>
<th>c(ACN)</th>
<th>[mol/l]</th>
<th>c(14b)</th>
<th>[mol/l]</th>
<th>K(14b)/c(ACN) shift [Hz]</th>
<th>shift 2 [Hz]</th>
<th>shift 3 [Hz]</th>
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<td>0.000000</td>
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<td>0.000000</td>
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<td>0.000900</td>
<td>0.000300</td>
<td>0.000459</td>
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<td>101.037520</td>
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<td>3133.42</td>
<td>2824.31</td>
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</tbody>
</table>

K = 71.92 M⁻¹
Error = 4.55908072 M⁻¹

**Figure 111:** ¹H NMR titration of compound 14b with ACN (CDCl₃, 400 MHz).
Calixarene 14b was dissolved in specified amount of 1,1,2,2-tetrachloroethane. 0.5 ml of calixarene solution was put in NMR tube. To 0.6 ml of the calixarene solution a specific amount of N-methylpyridinium iodide (NMPI) was added. The aliquots of NMPI were gradually added to NMR tube to achieve different calixarene/guest ratios (1:0.000-11.955), ensuring constant host concentration during the experiment. The complexation constants were determined by analyzing CIS of protons of the host molecule using nonlinear curve-fitting procedure (program BindFit).

![Figure 112: 1H NMR titration of compound 14b with NMPI (CDCl₃-CDCl₃, 400 MHz).](image-url)
Calixarene 14b was dissolved in specified amount of 1,1,2,2-tetrachloroethane. 0.5 ml of calixarene solution was put in NMR tube. To 0.6 ml of the calixarene solution a specific amount of N-methyl isoquinolinium iodide (NMII) was added. The aliquots of NMII were gradually added to NMR tube to achieve different calixarene/guest ratios (1:0.000-12.867), ensuring constant host concentration during the experiment. The complexation constants were determined by analyzing CIS of protons of the host molecule using nonlinear curve-fitting procedure (program BindFit).

\[
\begin{array}{|c|c|c|c|c|c|c|}
\hline
\text{M(NMII)} & 271.10147 \text{ g/mol} & \text{M(14b)} & 804.93 \text{ g/mol} \\
\text{m(NMII)} & 0.00524 \text{ g} & \text{m(14b)} & 0.001214 \text{ g} \\
\text{c(NMII)} & 0.03222426 \text{ mol/l} & \text{c(14b)} & 0.001257 \text{ mol/l} \\
\text{V(CDCl}_3\text{CDCl}_3) & 0.6 \text{ ml} & \text{V(CDCl}_3\text{14b)} & 1.2 \text{ ml} \\
\hline
\end{array}
\]

<table>
<thead>
<tr>
<th>K (M⁻¹)</th>
<th>Error (M⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>211.16</td>
<td>2.1686132</td>
</tr>
</tbody>
</table>

Figure 113: ¹H NMR titration of compound 14b with NMII (CDCl₃-CDCl₃, 400 MHz).
Calixarene 14b was dissolved in specified amount of 1,1,2,2-tetrachloroethane. 0.5 ml of calixarene solution was put in NMR tube. To 0.6 ml of the calixarene solution a specific amount of N-methylquinolinium iodide (NMQI) was added. The aliquots of NMQI were gradually added to NMR tube to achieve different calixarene/guest ratios (1:0.000-12.351), ensuring constant host concentration during the experiment. The complexation constants were determined by analyzing CIS of protons of the host molecule using nonlinear curve-fitting procedure (program BindFit).

![Figure 114](image)

Figure 114: $^1$H NMR titration of compound 14b with NMQI (CDCl$_2$-CDCl$_2$, 400 MHz).
Calixarene 14b-1 was dissolved in specified amount of 1,1,2,2-tetrachloroethane. 0.5 ml of calixarene solution was put in NMR tube. To 0.6 ml of the calixarene solution a specific amount of (S)-N-methyl nicotinium iodide (NMNI) was added. The aliquots of NMNI were gradually added to NMR tube to achieve different calixarene/guest ratios (1:0.000-11.008), ensuring constant host concentration during the experiment. The complexation constants were determined by analyzing CIS of protons of the host molecule using nonlinear curve-fitting procedure (program BindFit).

![Figure 115](image-url)  

**Figure 115:** $^1$H NMR titration of compound 14b-1 with NMNI (CDCl$_3$-CDCl$_2$, 400 MHz).
Calixarene 14b-2 was dissolved in specified amount of 1,1,2,2-tetrachloroethane. 0.5 ml of calixarene solution was put in NMR tube. To 0.6 ml of the calixarene solution a specific amount of (S)-N-methylnicotinium iodide (NMNI) was added. The aliquots of NMNI were gradually added to NMR tube to achieve different calixarene/guest ratios (1:0.000-12.077), ensuring constant host concentration during the experiment. The complexation constants were determined by analyzing CIS of protons of the host molecule using nonlinear curve-fitting procedure (program BindFit).

\[
\begin{array}{cccc}
M(NMNI) & 304,1755 \text{ g/mol} & M(14b-2) & 804,53 \text{ g/mol} \\
m(NMNI) & 0,00626 \text{ g} & m(14b-2) & 0,0013771 \text{ g} \\
c(NMNI) & 0,0343 \text{ mol/l} & c(14b-2) & 0,001426 \text{ mol/l} \\
V(C2D2Cl4) & 0,6 \text{ ml} & V(C2D2Cl4) & 1,2 \text{ ml} \\
\end{array}
\]

Figure 116: \(^1\)H NMR titration of compound 14b-2 with NMNI (CDCl\(_2\)-CDCl\(_2\), 400 MHz).