

Towards a real knotaxane

*Torben Duden and Ulrich Lüning**

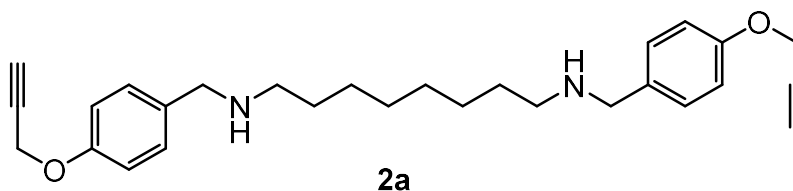
Supporting information

The following compounds have been purchased:

ammonium hexafluorophosphate (97 %, abcr), 4-benzyloxyphenol (97 %, Alfa Aesar), 1,10-diaminodecane (97 %, Sigma Aldrich), 1,8-diaminooctane (98 %, abcr), 2,6-dimethylpyridine (99%, Sigma Aldrich), phosphorus tribromide (98 %, Merck), sodium azide (99 %, Merck), sodium borohydrid (97 %, abcr), DB24C8 (98 %, TCI), tetrakis(acetonitrile)copper(I) hexafluorophosphate (97 %, TCI), methyl iodide (99 %, Sigma Aldrich)

The synthetic procedures for compounds which are not described in the literature are listed below. In the assignments of NMR signals, the following abbreviations have been used: Ar = aryl ring, further identification by prefix or indices, see drawings; Ar_{crown} = benzene ring of DB24C8; Tri = triazol/ium ring.

***N,N'*-Bis[4-(prop-2-inyloxy)phenylmethyl]octane-1,8-diylidamine (2a)**



Under nitrogen atmosphere, 1,8-diaminooctane (900 mg, 6.25 mmol) and 4-(prop-2-inyloxy)benzaldehyde [1] **1** (2.00 g, 12.5 mmol) were dissolved in dry methanol (80 mL). The solution was stirred at room temp. for 2 h resulting in a precipitation of a colorless solid. Next, sodium borohydride (3.91 g, 103 mmol) was added in portions at 0 °C. The mixture was stirred for 4 h at 0 °C and then for another 16 h at room temp. The clear solution was carefully mixed with water (30 mL) and the solvent was removed in vacuo. The aqueous layer was extracted with dichloromethane (3 x50 mL). The organic layer was dried with magnesium sulfate and the solvent was removed in vacuo. A pale yellow solid was obtained.

Yield: 2.58 g (5.91 mmol, 95 %).

Meltingpoint: 63 °C.

¹H-NMR (500 MHz, CDCl₃): δ = 7.27-7.23 (m, 4 H, Ar-*H*-2,6), 6.95-6.91 (m, 4 H, Ar-*H*-3,5), 4.68 (d, ⁴*J* = 2.4 Hz, 4 H, Ar-OCH₂), 3.73 (s, 4 H, Ar-CH₂), 2.60 (t, ³*J* = 7.1 Hz, 4 H, Ar-CH₂NHCH₂), 2.51 (t, ⁴*J* = 2.4 Hz, 2 H, CH), 1.53-1.45 (m, 4 H, NHCH₂CH₂), 1.35-1.22 (m, 8 H, NHCH₂CH₂CH₂CH₂) ppm.

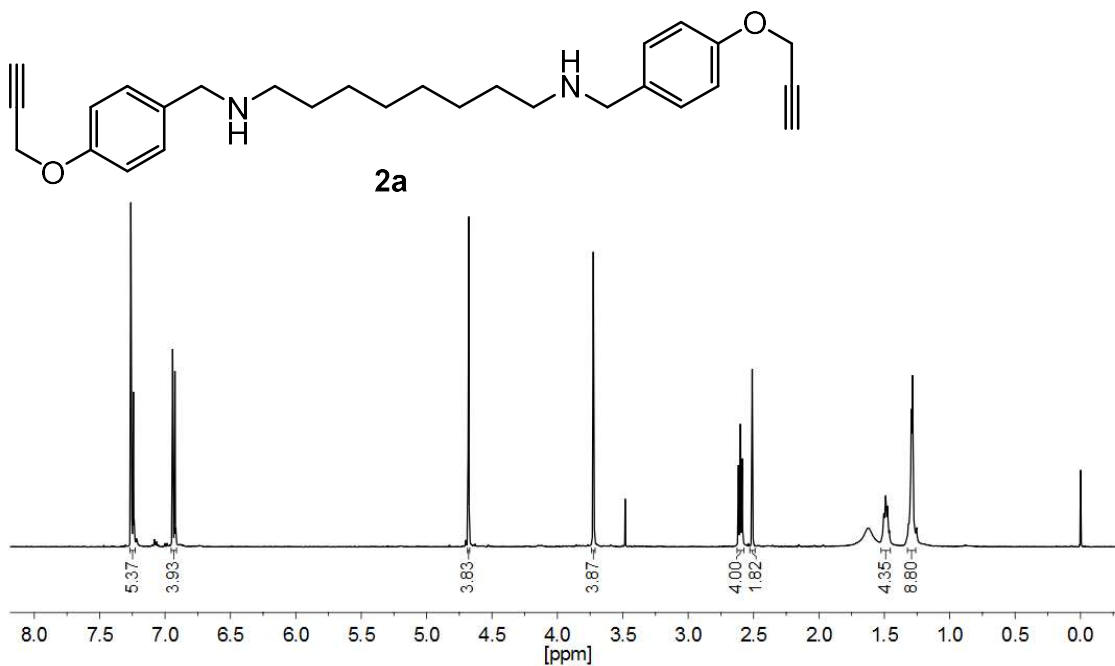
¹³C-NMR (125 MHz, CDCl₃): δ = 156.7 (s, Ar-C-4), 133.5 (s, Ar-C-1), 129.5 (d, Ar-C-2,6), 115.0 (d, Ar-C-3,5), 78.8 (s, CCH), 75.6 (d, CH), 56.0 (t, OCH₂), 53.6 (t, Ar-CH₂), 49.5 (t, Ar-CH₂NHCH₂), 30.1 (t, NHCH₂CH₂), 29.6 (t, NHCH₂CH₂CH₂CH₂), 27.4 (t, NHCH₂CH₂CH₂) ppm.

IR (ATR): $\tilde{\nu}$ = 3288 (w, C≡CH), 3260 (m, NH), 2921 (m, aliph. CH), 2162 (w, C≡C), 1507, 1451 (s, arom.), 1232, 1022 (s, CO), 809 (s, 1,4-disubst.) cm⁻¹.

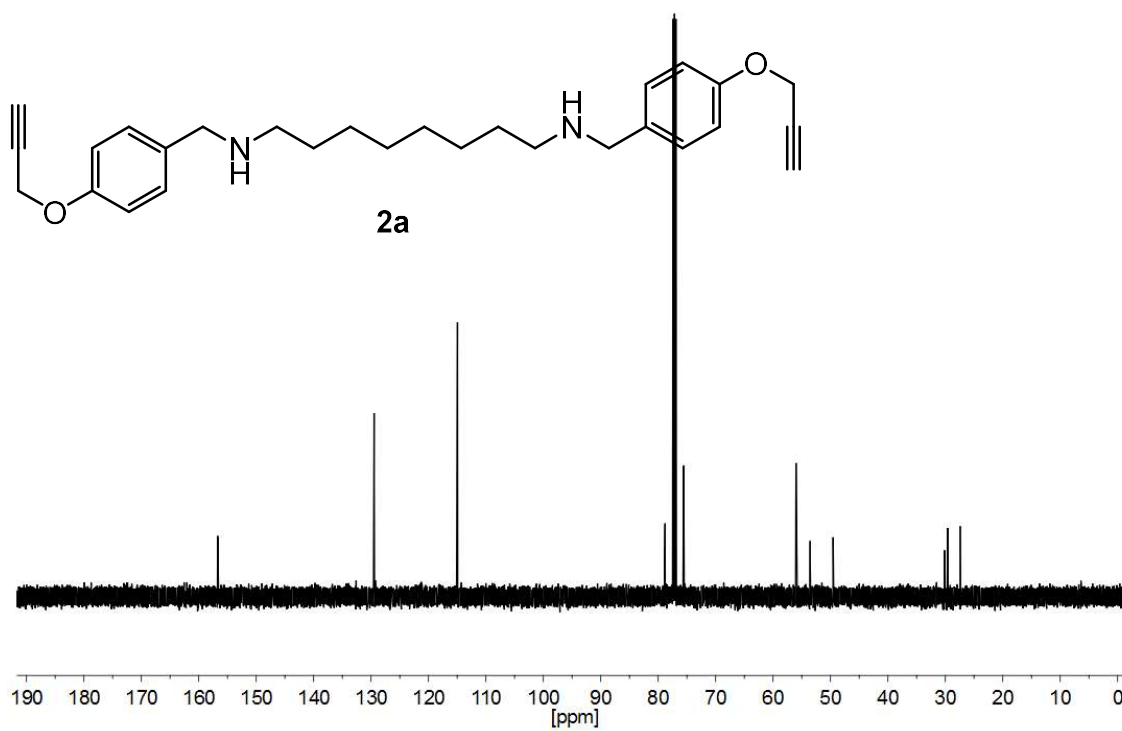
MS (HR-ESI): C₂₈H₃₇N₂O₂ calcd. *m/z* = 433.2850, found *m/z* = 433.2847 (Δ = -0.56 ppm).

Elemental analysis: C₂₈H₃₆N₂O₂•0.2 H₂O: calc.C 76.94, H 8.42, N 6.41, found C 76.66, H 8.42, N 6.43.

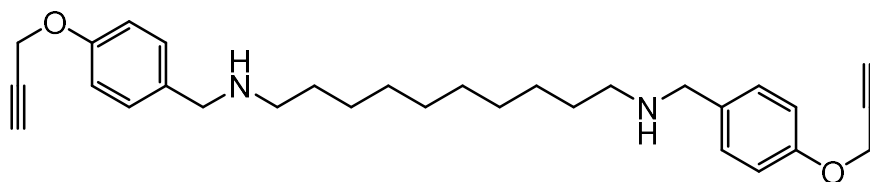
20180518-15-L505Duden_7438
 Position 15, Mitarbeiter Duden , Sample TD-P-230F2, Menge 5 mg / CDCl₃, Re kein



20180518-15-L505Duden_7438
 Position 15, Mitarbeiter Duden , Sample TD-P-230F2, Menge 5 mg / CDCl₃, Re kein



***N,N'*-Bis[4-(prop-2-inyloxy)phenylmethyl]decane-1,10-diyl diamine (2b)**



2b

Under nitrogen atmosphere, 1,10-diaminodecane (1.08 g, 6.25 mmol) and 4-(prop-2-inyloxy)benzaldehyde [1] **1** (2.00 g, 12.5 mmol) were dissolved in dry methanol (80 mL). The solution was stirred at room temp. for 2 h resulting in a precipitation of a colorless solid. Next sodium borohydride (3.91 g, 103 mmol) was added in portions at 0 °C. The mixture was stirred for 4 h at 0 °C and then for another 16 h at room temp. The clear solution was carefully mixed with water (30 mL) and the solvent was removed in vacuo. The aqueous layer was extracted with dichloromethane (3 x 50 mL). The organic layer was dried over magnesium sulfate and the solvent was removed in vacuo. A pale yellow solid was obtained.

Yield: 2.60 g (5.64 mmol, 90 %).

Melting point: 71 °C.

¹H-NMR (500 MHz, CDCl₃): δ = 7.29-7.20 (m, 4 H, Ar-*H*-2,6), 6.98-6.89 (m, 4 H, Ar-*H*-3,5), 4.68 (d, ⁴*J* = 2.4 Hz, 4 H, Ar-OCH₂), 3.72 (s, 4 H, Ar-CH₂), 2.60 (t, ³*J* = 7.1 Hz, 4 H, Ar-CH₂NHCH₂), 2.51 (t, ⁴*J* = 2.4 Hz, 2 H, CH), 1.57-1.39 (m, 4 H, NHCH₂CH₂), 1.25-1.26 (m, 12 H, NHCH₂CH₂CH₂CH₂CH₂) ppm.

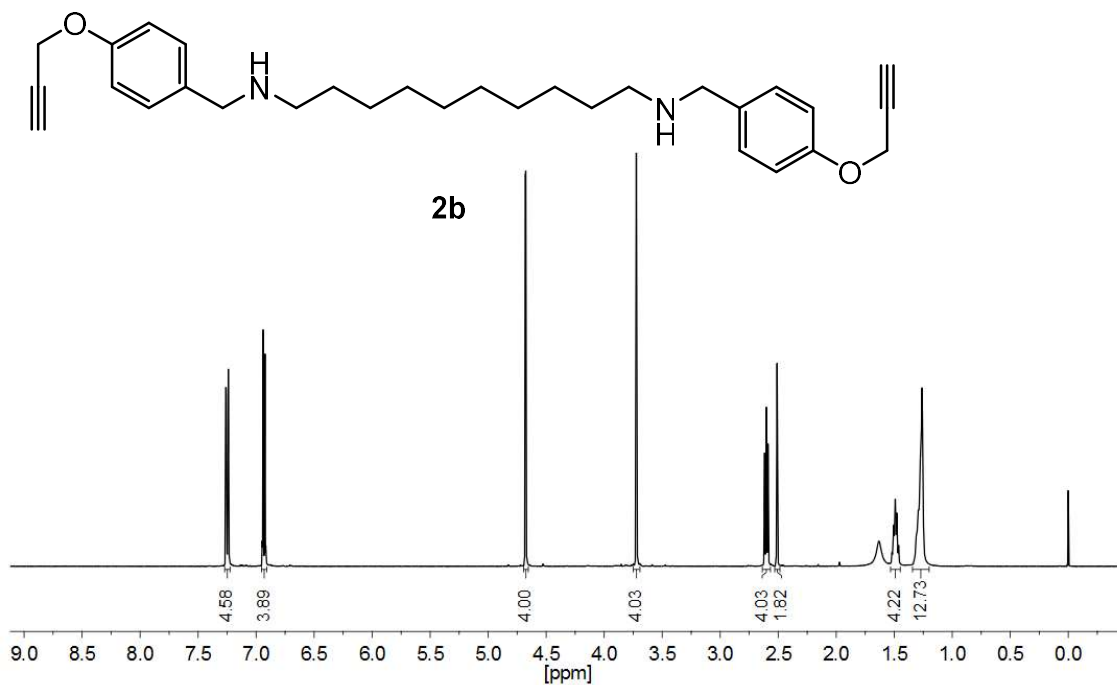
¹³C-NMR (125 MHz, CDCl₃): δ = 156.7 (s, Ar-C-4), 133.5 (s, Ar-C-1), 129.4 (d, Ar-C-2,6), 114.9 (d, Ar-C-3,5), 78.8 (s, CCH), 75.6 (d, CH), 56.0 (t, OCH₂), 53.6 (t, Ar-CH₂), 49.6 (t, Ar-CH₂NHCH₂), 30.2 (t, NHCH₂CH₂), 29.67 (t, NHCH₂CH₂CH₂CH₂), 29.65 (t, NHCH₂CH₂CH₂CH₂CH₂), 27.5 (t, NHCH₂CH₂CH₂) ppm.

IR (ATR): $\tilde{\nu}$ = 3288 (w, C≡CH), 3260 (w, NH), 2919 (m, aliph. CH), 1509, 1454 (s, arom.), 1235, 1029 (s, CO), 812 (s, 1,4-disubst.) cm⁻¹.

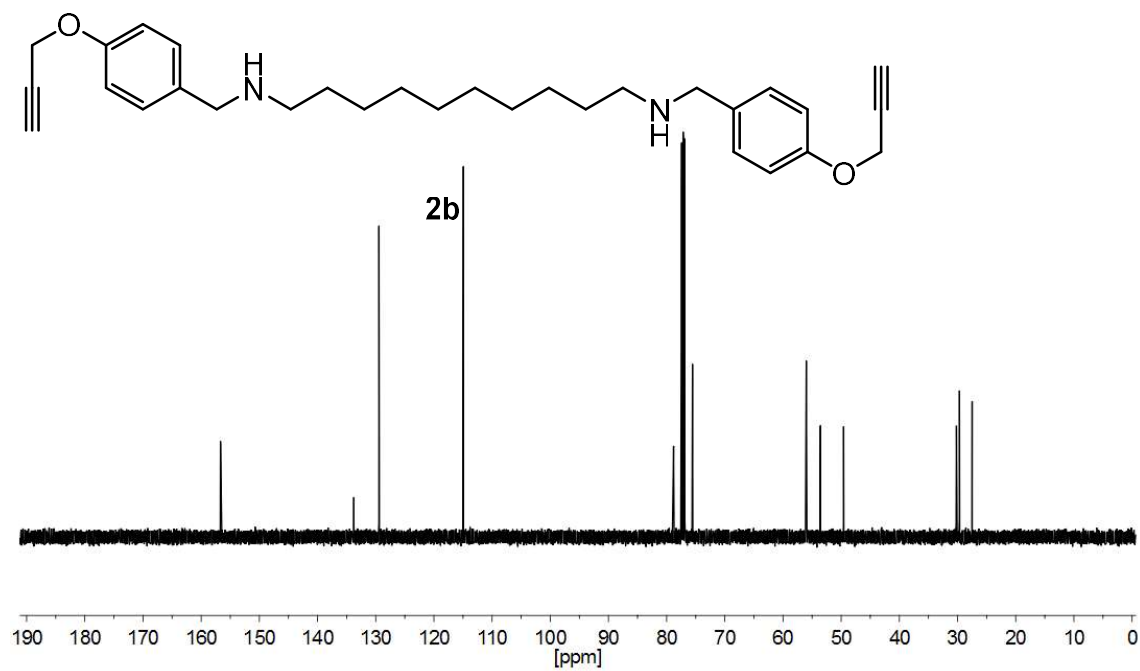
MS (HR-ESI): C₃₀H₄₁N₂O₂ calcd. *m/z* = 461.3163, found *m/z* = 461.3158 (Δ = -1.06 ppm).

Elemental analysis: C₃₀H₄₀N₂O₂•0.2 H₂O: calcd. C 77.46, H 8.77, N 6.02, found C 77.66, H 8.78, N 6.02.

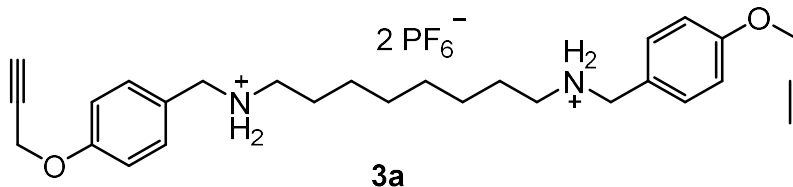
20180522-33-L505Duden_7457
 Position 33, Mitarbeiter Duden, Sample TD - P - 231, Menge ~ 9.0 mg/CDCl₃, Re kein



20180522-33-L505Duden_7457
 Position 33, Mitarbeiter Duden, Sample TD - P - 231, Menge ~ 9.0 mg/CDCl₃, Re kein



***N,N'*-Bis[4-(prop-2-ynyloxy)phenylmethyl]octane-1,8-diylidinium
bis(hexafluorophosphate) (3a)**



The secondary amine **2a** (2.47 g, 5.72 mmol) was dissolved in ethanol (50 mL) and then mixed with concentrated hydrochloric acid (5 mL). The suspension was stirred for 2 h at room temp. and then filtered. The colorless solid was dried in vacuo. The hydrochloride was suspended in acetone (75 mL) and mixed with an aqueous saturated NH_4PF_6 solution until a clear solution was obtained. The solvent was then removed in vacuo and the residue stirred in water (200 mL) for 2 h. The colorless solid was filtered and dried in vacuo.

Yield: 3.07 g (4.24 mmol, 74 %).

Melting point: 185 °C.

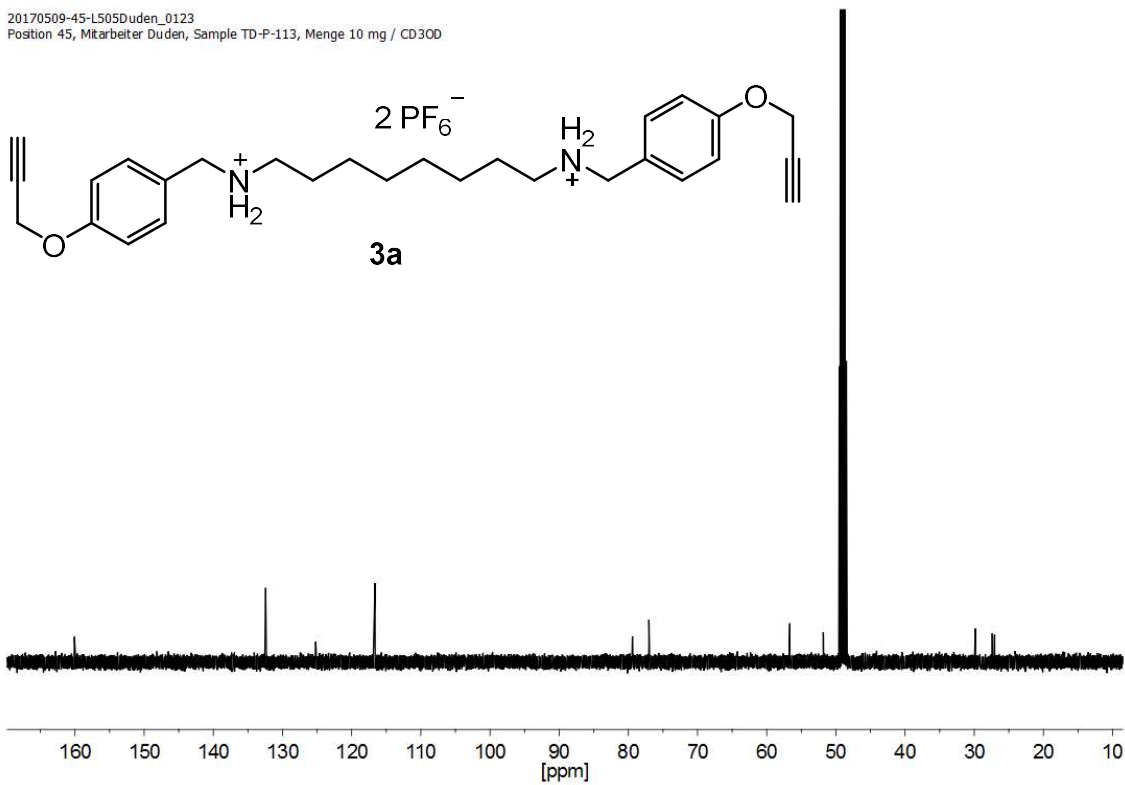
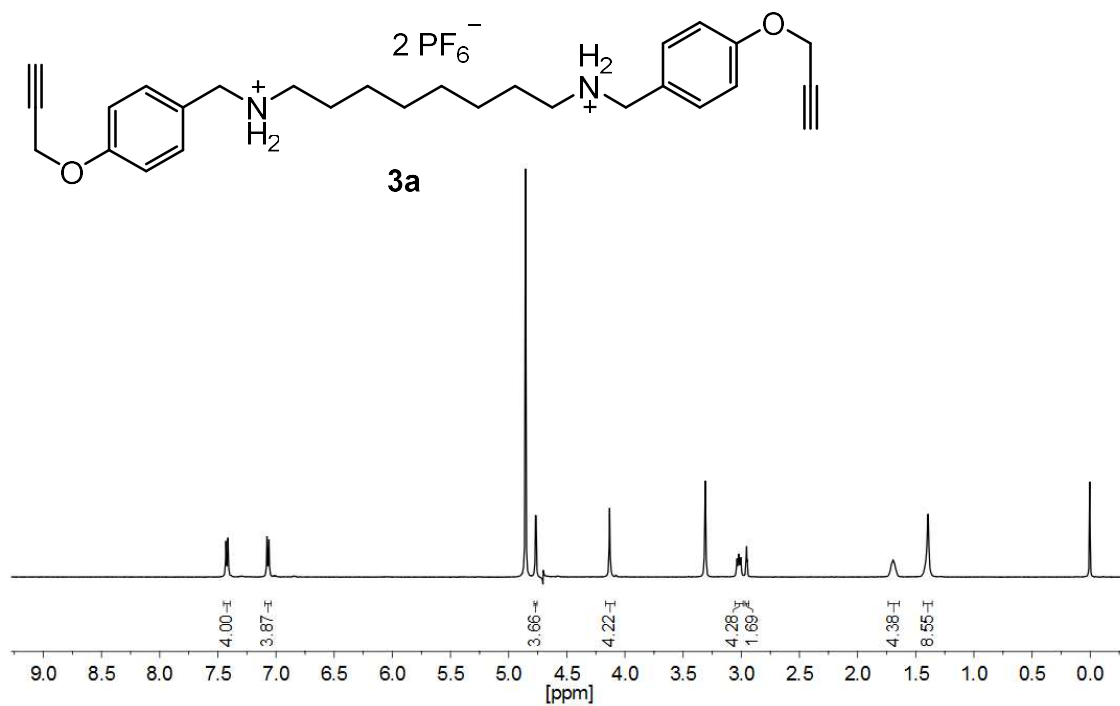
$^1\text{H-NMR}$ (500 MHz, $\text{MeOD-}d_4$): δ = 7.42 (d, 3J = 8.7 Hz, 4 H, Ar-*H*-2,6), 7.07 (d, 3J = 8.7 Hz, 4 H, Ar-*H*-3,5), 4.77 (d, 4J = 2.4 Hz, 4 H, Ar- OCH_2), 4.13 (s, 4 H, Ar- CH_2), 3.05-2.98 (m, 4 H, Ar- CH_2NHCH_2), 2.95 (t, 4J = 2.4 Hz, 2 H, CH), 1.70 (s, 4 H, NHCH_2CH_2), 1.39 (s, 8 H, $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$) ppm.

$^{13}\text{C-NMR}$ (125 MHz, $\text{MeOD-}d_4$): δ = 160.1 (s, Ar-C-4), 132.5 (d, Ar-C-2,6), 125.2 (s, Ar-C-1), 116.6 (d, Ar-C-3,5), 79.4 (s, CCH), 77.0 (d, CH), 56.7 (t, OCH_2), 51.8 (t, Ar- CH_2), 48.4 (t, Ar- CH_2NHCH_2), 29.8 (t, $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 27.4 (t, $\text{NHCH}_2\text{CH}_2\text{CH}_2$), 27.1 (t, NHCH_2CH_2) ppm.

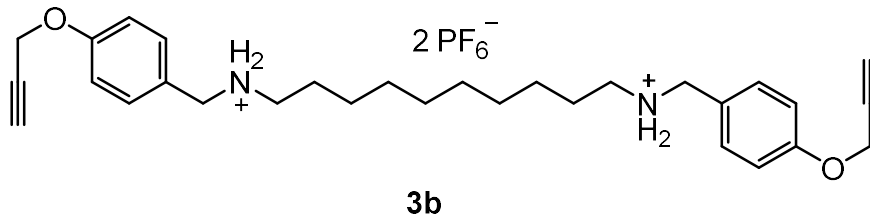
IR (ATR): $\tilde{\nu}$ = 3287 (w, $\text{C}\equiv\text{CH}$), 2936 (w, aliph. CH), 2864 (w, NH_2^+), 1517 (m, arom.), 1245, 1025 (m, CO), 829 (s, 1,4-disubst.), 556 (s, PF_6) cm^{-1} .

MS (HR-ESI): $\text{C}_{28}\text{H}_{37}\text{N}_2\text{O}_2$ calcd. m/z = 433.2850, found m/z = 433.2843 (Δ = -1.43 ppm).

Elemental analysis: $\text{C}_{28}\text{H}_{38}\text{N}_2\text{O}_2\text{P}_2$: calcd. C 46.42, H 5.29, N 3.87, found C 46.35, H 5.27, N 3.98.



***N,N'*-Bis[4-(prop-2-ynyloxy)phenylmethyl]decane-1,10-diylidinium
bis(hexafluorophosphate) (**3b**)**



The secondary amine **2b** (2.59 g, 5.62 mmol) was dissolved in ethanol (50 mL) and then mixed with concentrated hydrochloric acid (5 mL). The suspension was stirred for 2 h at room temp. and then filtered. The colorless solid was dried in vacuo. The hydrochloride was suspended in acetone (75 mL) and mixed with an aqueous saturated NH_4PF_6 solution until a clear solution was obtained. The solvent was removed in vacuo and the residue stirred in water (200 mL) for 2 h. The colorless solid was filtered and dried in vacuo.

Yield: 3.64 g (4.84 mmol, 86 %).

Melting point: 202 °C.

$^1\text{H-NMR}$ (500 MHz, $\text{MeOD-}d_4$): δ = 7.45-7.40 (m, 4 H, Ar-*H*-2,6), 7.10-7.05 (m, 4 H, Ar-*H*-3,5), 4.77 (d, 4J = 2.4 Hz, 4 H, Ar- OCH_2), 4.13 (s, 4 H, Ar- CH_2), 3.05-2.99 (m, 4 H, Ar- CH_2NHCH_2), 2.95 (t, 4J = 2.4 Hz, 2 H, CH), 1.73-1.65 (m, 4 H, NHCH_2CH_2), 1.42-1.33 (m, 12 H, $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$) ppm.

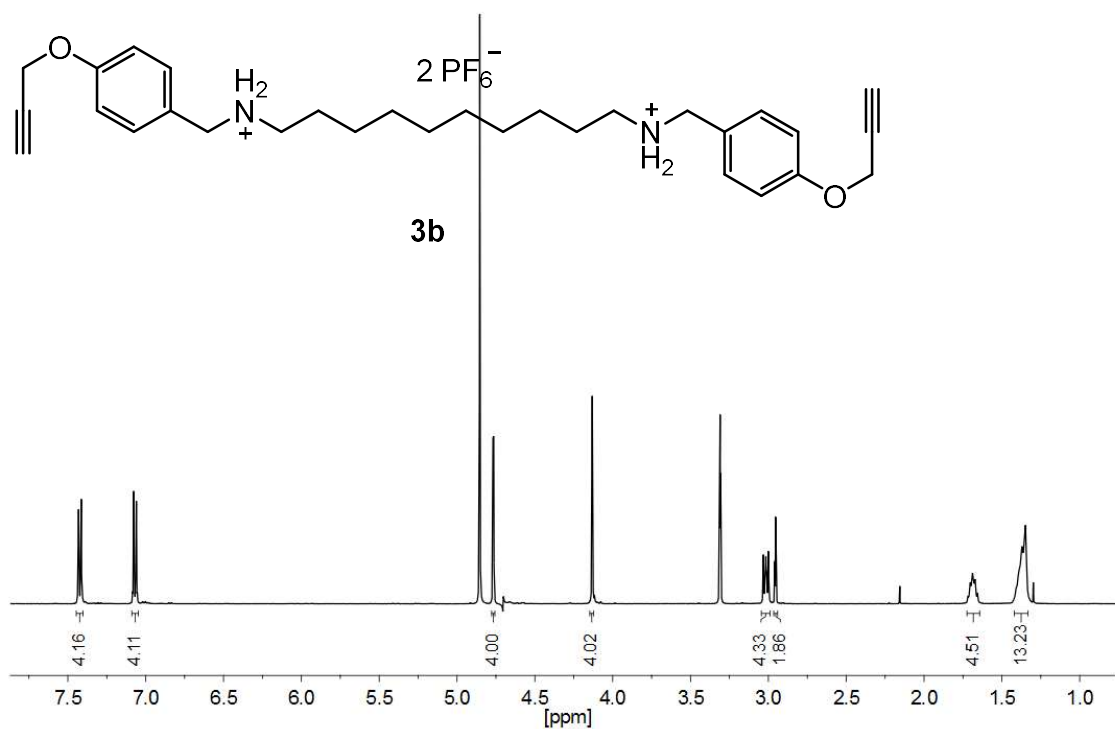
$^{13}\text{C-NMR}$ (125 MHz, $\text{MeOD-}d_4$): δ = 160.1 (s, Ar-C-4), 132.4 (d, Ar-C-2,6), 125.2 (s, Ar-C-1), 116.6 (d, Ar-C-3,5), 79.4 (s, CCH), 77.0 (d, CH), 56.7 (t, OCH_2), 51.8 (t, Ar- CH_2), 48.5 (t, Ar- CH_2NHCH_2), 30.3 (t, $\text{NHCH}_2\text{CH}_2\text{CH}_2$), 30.1 (t, $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 27.6 (t, $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 27.1 (t, NHCH_2CH_2) ppm.

IR (ATR): $\tilde{\nu}$ = 3288 (w, $\text{C}\equiv\text{CH}$), 2925 (w, aliph. CH), 2856 (w, NH_2^+), 1519 (m, arom.), 1226, 1029 (m, CO), 815 (s, 1,4-disubst.), 556 (s, PF_6) cm^{-1} .

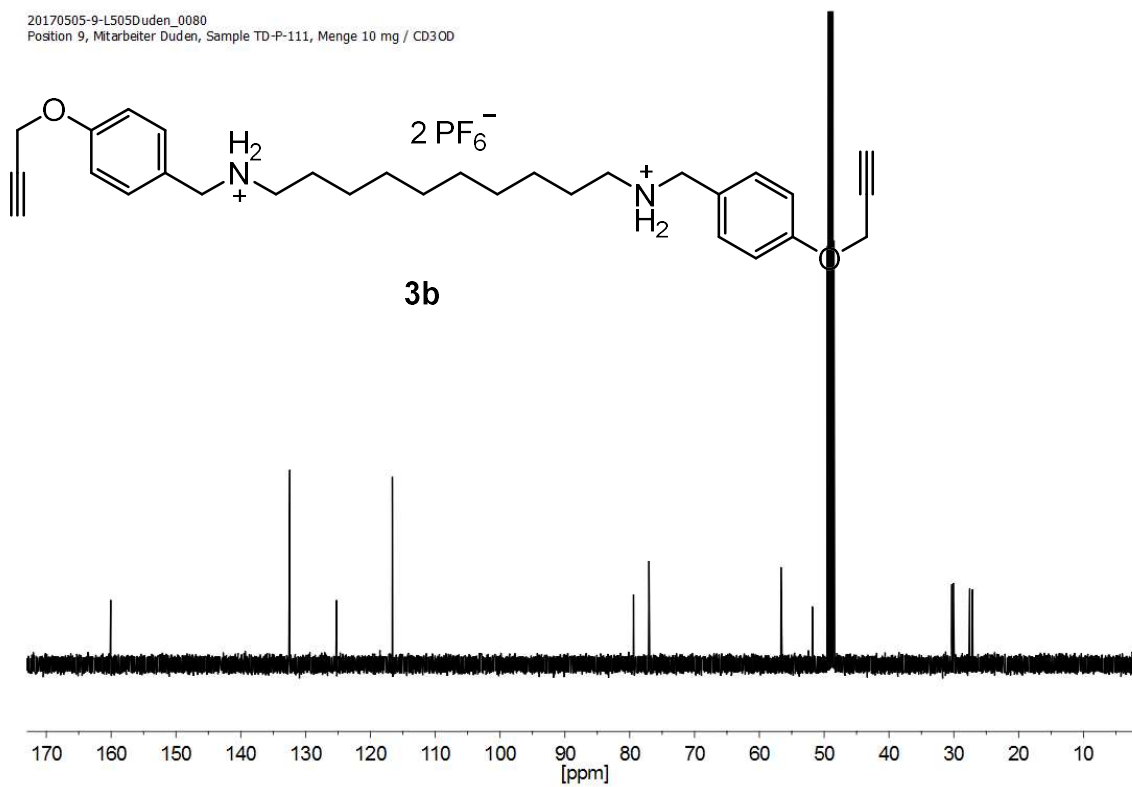
MS (HR-ESI): $\text{C}_{30}\text{H}_{41}\text{N}_2\text{O}_2$ calcd. m/z = 461.3163, found m/z = 461.3156 (Δ = -1.42 ppm).

Elemental analysis: $\text{C}_{30}\text{H}_{42}\text{N}_2\text{O}_2\text{P}_2$: calcd. C 47.88, H 5.63, N 3.72, found C 48.16, H 5.73, N 3.81.

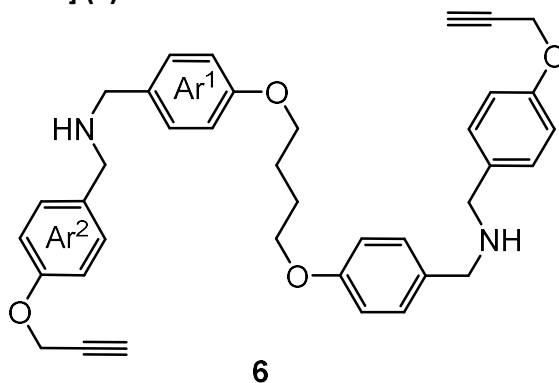
20170505-9-L505Duden_0080
 Position 9, Mitarbeiter Duden, Sample TD-P-111, Menge 10 mg / CD300



20170505-9-L505Duden_0080
 Position 9, Mitarbeiter Duden, Sample TD-P-111, Menge 10 mg / CD300



***N,N'*-{4,4'-[Butane-1,4-diylbis(oxy)]bis(4,1-phenylmethyl)}bis[4-(prop-2-inyloxy)phenylmethanamine] (6)**



Under nitrogen atmosphere, 4-(prop-2-inyloxy)benzylamine [2] (**5**, 1.30 g, 8.06 mmol) and 1,4-bis(4-formylphenoxy)butane [3] (**4**, 1.20 g, 4.03 mmol) were dissolved in dry methanol (75 mL) and stirred under reflux for 3 h. The suspension was then cooled down to 0 °C and mixed with portions of sodium borohydride (total: 2.40 g, 63.0 mmol). The suspension was stirred for 1 h at 0 °C and then for 16 h at room temp. Water (25 mL) was added and methanol was removed in vacuo. The aqueous layer was extracted with dichloromethane (4 x 75 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was removed in vacuo. A colorless oil was obtained.

Yield: 2.10 g (3.57 mmol, 89 %).

¹H-NMR (500 MHz, CDCl₃): δ = 7.32-7.17 (m, 8 H, Ar¹-H-2,6, Ar²-H-2,6), 6.96-6.91 (m, 4 H, Ar¹-H-3,5), 6.89-6.83 (m, 4 H, Ar²-H-3,5), 4.68 (d, ⁴J = 2.4 Hz, 4 H, OCH₂CCH), 4.06-3.99 (m, 4 H, OCH₂CH₂), 3.74-3.71 (m, 8 H, CH₂NHCH₂), 2.51 (t, ⁴J = 2.4 Hz, 2 H, CCH), 1.99-1.95 (m, 4 H, OCH₂CH₂) ppm.

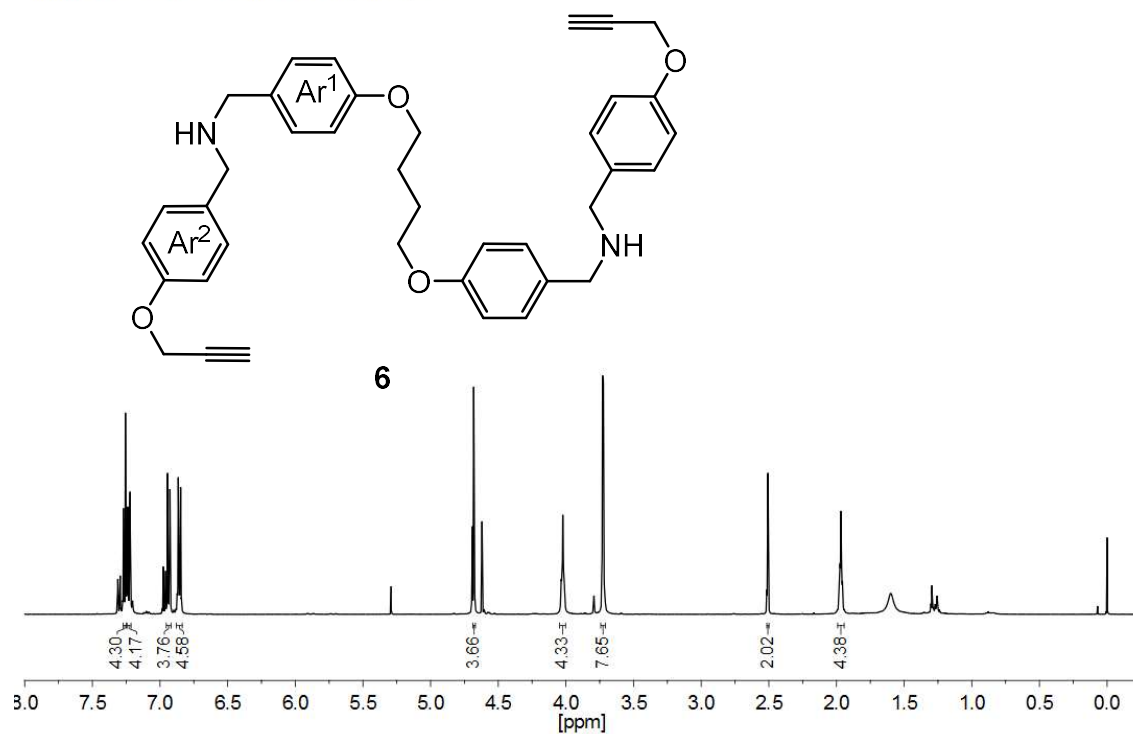
¹³C-NMR (125 MHz, CDCl₃): δ = 158.2 (s, Ar¹-C-4), 156.7 (s, Ar²-C-4), 133.6 (s, Ar²-C-1), 132.5 (s, Ar¹-C-1), 129.5 (d, Ar¹-C-2,6, Ar²-C-2,6), 114.9 (d, Ar²-C-3,5), 114.5 (d, Ar¹-C-3,5), 78.8 (s, CCH), 75.6 (d, CCH), 67.6 (t, OCH₂CH₂), 56.0 (t, OCH₂CCH), 52.6 (t, CH₂NHCH₂), 52.5 (t, CH₂NHCH₂), 26.2 (CH₂CH₂) ppm.

IR (ATR): $\tilde{\nu}$ = 3292 (s, C≡CH), 2929, 2874, 2823 (m, aliph. CH), 2134 (w, C≡C), 1609, 1508 (s, arom.), 1234, 1214, 1166, 1026 (s, CO), 820 (s, 1,4-disubst.) cm⁻¹.

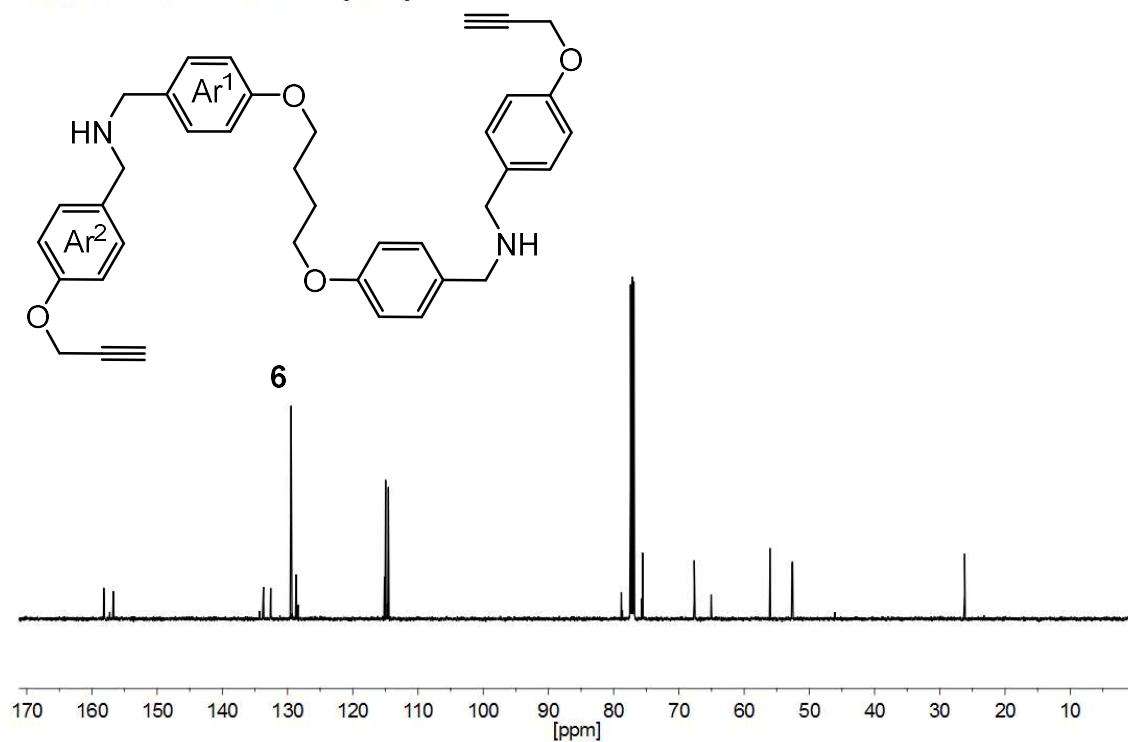
MS (HR-ESI): C₃₈H₄₃N₂O₄ calcd. *m/z* = 589.3061, found *m/z* = 589.3061 (Δ = -0.03 ppm).

Elemental analysis: C₃₈H₄₂N₂O₄•0.2 H₂O: calcd. C 76.93, H 6.88, N 4.72, found C 76.80, H 6.94, N 4.42.

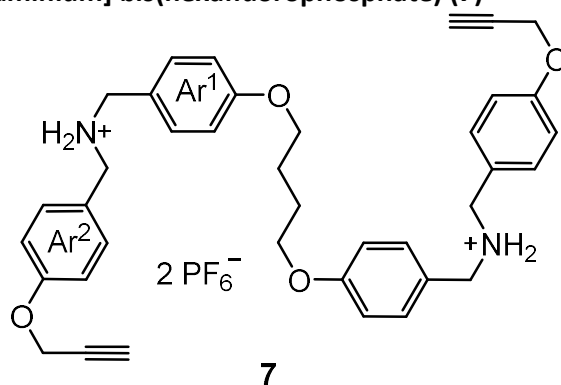
170302-19-L503Dude_1842
 Position 19, Mitarbeiter Duden, Probe TD - P - 76, Menge 10.0 mg/CDCl₃



170302-19-L503Dude_1842
 Position 19, Mitarbeiter Duden, Probe TD - P - 76, Menge 10.0 mg/CDCl₃



***N,N'*-{4,4'-[Butane-1,4-diylbis(oxy)]bis(4,1-phenylmethyl)}bis[4-(prop-2-inyloxy)phenylmethylinium] bis(hexafluorophosphate) (7)**



Amine **6** (1.54 g, 2.62 mmol) was dissolved in ethanol (100 mL) and mixed with concentrated hydrochloric acid (4 mL). The resulting suspension was stirred for 2 h at room temp. and was then filtered. The colorless solid was dried in vacuo, then suspended in acetone (100 mL) and treated with aqueous saturated NH_4PF_6 solution until a clear solution was obtained. The solvent was then removed in vacuo. The residue was suspended in water (100 mL) and stirred at room temp. for 1 h. Filtration gave a colorless solid which was dried in vacuo.

Yield: 2.30 mg (2.60 mmol, 99 %).

Melting point: 200 °C.

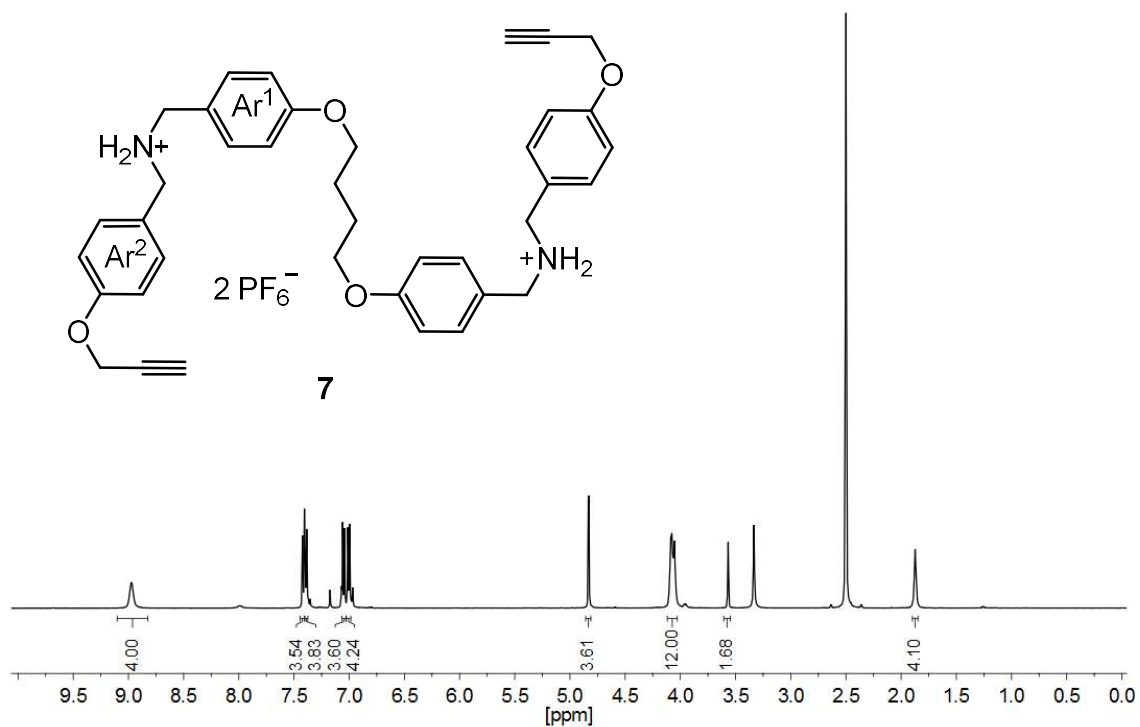
$^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$): δ = 8.97 (s, 4 H, NH_2), 7.41 (d, 3J = 8.8 Hz, 4 H, $\text{Ar}^2\text{-H-2,6}$), 7.39 (d, 3J = 8.8 Hz, 4 H, $\text{Ar}^1\text{-H-2,6}$), 7.05 (d, 3J = 8.8 Hz, 4 H, $\text{Ar}^2\text{-H-3,5}$), 7.00 (d, 3J = 8.8 Hz, 4 H, $\text{Ar}^1\text{-H-3,5}$), 4.83 (d, 4J = 2.3 Hz, 4 H, OCH_2CCH), 4.11-4.03 (m, 12 H, $\text{H}_2\text{CNH}_2\text{CH}_2$, OCH_2CH_2), 3.57 (t, 4J = 2.3 Hz, 2 H, CCH), 1.87 (s, 4 H, OCH_2CH_2) ppm.

$^{13}\text{C-NMR}$ (125 MHz, $\text{DMSO-}d_6$): δ = 159.1 (s, $\text{Ar}^1\text{-C-4}$), 157.6 (s, $\text{Ar}^2\text{-C-4}$), 131.54 (d, $\text{Ar}^1\text{-C-2,6}$), 131.47 (d, $\text{Ar}^2\text{-C-2,6}$), 124.4 (s, $\text{Ar}^2\text{-C-1}$), 123.5 (s, $\text{Ar}^1\text{-C-1}$), 115.0 (d, $\text{Ar}^2\text{-C-3,5}$), 114.5 (d, $\text{Ar}^1\text{-C-3,5}$), 79.0 (s, CCH), 78.3 (d, CCH), 67.3 (t, OCH_2CH_2), 55.4 (t, OCH_2CCH), 49.5 (t, $\text{Ar}^2\text{-CH}_2\text{NH}_2$), 48.3 (t, $\text{Ar}^1\text{-CH}_2\text{NH}_2$), 25.4 (t, OCH_2CH_2) ppm.

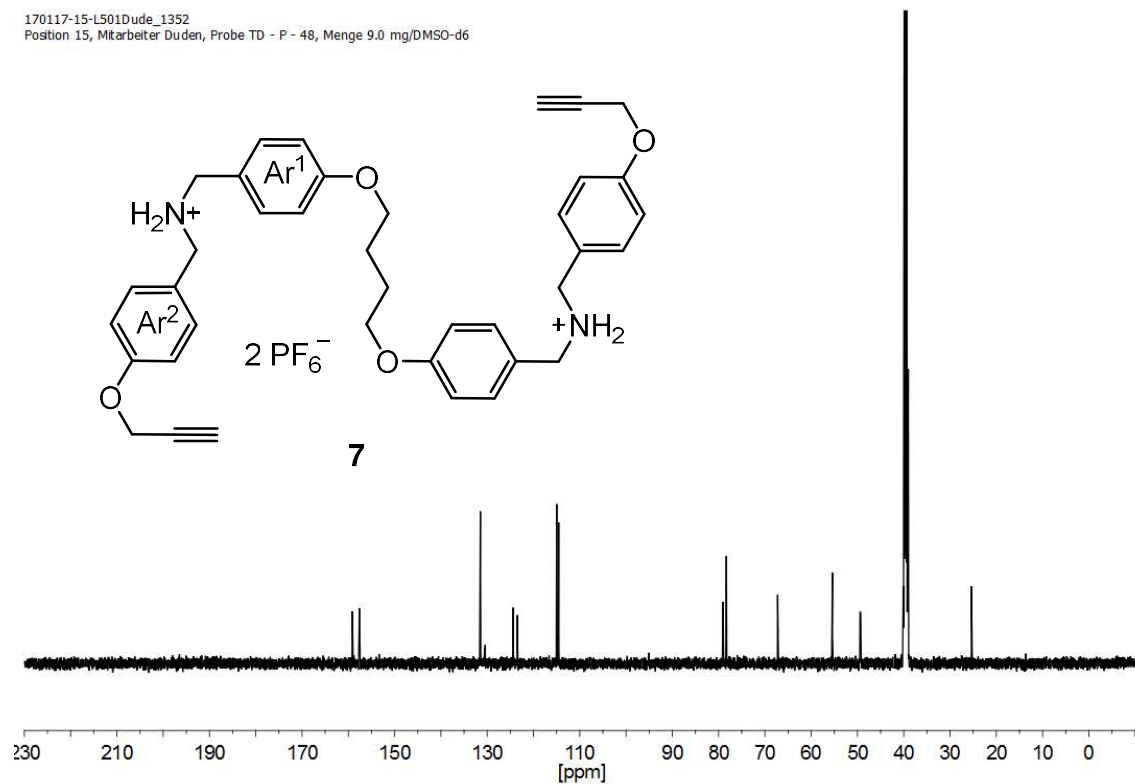
IR (ATR): $\tilde{\nu}$ = 3259 (w, $\text{C}\equiv\text{CH}$), 1613, 1516 (m, arom.), 1249, 1183, 1024 (s, CO), 826 (s, 1,4-disubst.), 557 (s, PF_6) cm^{-1} .

MS (MALDI): $m/z(\%)$ = 735.8 (5) $[\text{M} - \text{PF}_6]^+$, 613 (100), 589.8 (21) $[\text{M} - 2\text{PF}_6 - \text{H}^+]^+$.

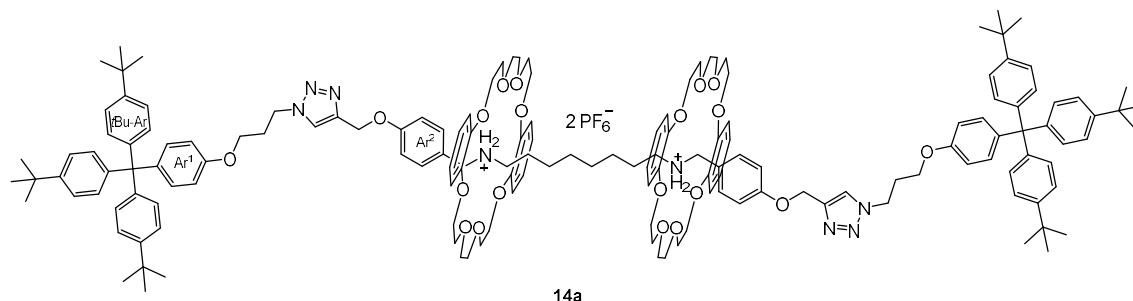
170117-15-L501Dude_1352
 Position 15, Mitarbeiter Duden, Probe TD - P - 48, Menge 9.0 mg/DMSO-d6



170117-15-L501Dude_1352
 Position 15, Mitarbeiter Duden, Probe TD - P - 48, Menge 9.0 mg/DMSO-d6



[3]-*N,N'*-(Octane-1,8-diyl)-*N,N'*-bis{[4-({1-[3-(4-{tris[4-(dimethylethyl)phenyl]methyl}phenoxy)propyl]-1*H*-1,2,3-triazol-4-yl]methoxy}phenyl]methanaminium}-rotaxa-bis(1,12-[1,2]dibenzena-2,5,8,11,13,16,19,22-octaoadococaphan) bis(hexafluorophosphate) (14a)



Under nitrogen atmosphere, axis **3a** (92.4 mg, 128 μmol) and DB24C8 (**13**, 144 mg, 321 μmol) were suspended in dry dichloromethane (50 mL). The suspension was stirred at room temp. until a clear solution was obtained. Then, stopper **11** [4] (150 mg, 255 μmol), tetrakis(acetonitrile)copper(I) hexafluorophosphate (95.1 mg, 255 μmol) and 2,6-dimethylpyridine (ca. 60 μL) were added. The yellow solution was stirred for 1 d at room temp. and then water (20 mL) was added. The aqueous layer was extracted with dichloromethane (3 x 30 mL) and the solvent was removed in vacuo. The residue was filtered through silica gel [dichloromethane/methanol (80 : 20)]. The solvent of the filtrate was removed in vacuo and the residue was purified by chromatography using silica gel [dichloromethane/methanol (1 : 0) \rightarrow (24 : 1), R_f = 0.05]. The yellow solid was dissolved in very little ethyl acetate and DB24C8 (**13**) precipitated. The solid was filtered off and the process repeated. Finally, the residue was cleaned again by chromatography on silica gel [dichloromethane/methanol (1 : 0) \rightarrow (24 : 1), R_f = 0.05]. A pale yellow solid was obtained.

Yield: 123 mg (43.9 μmol , 34 %).

Melting point: 199 $^{\circ}\text{C}$.

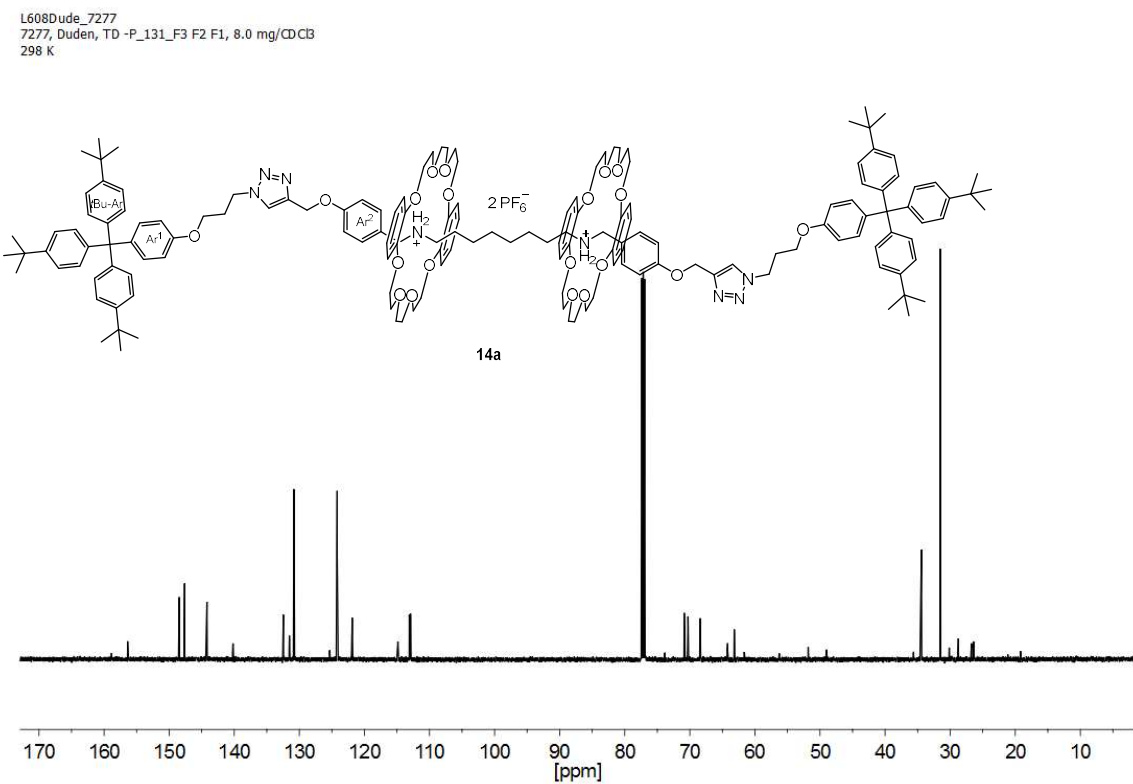
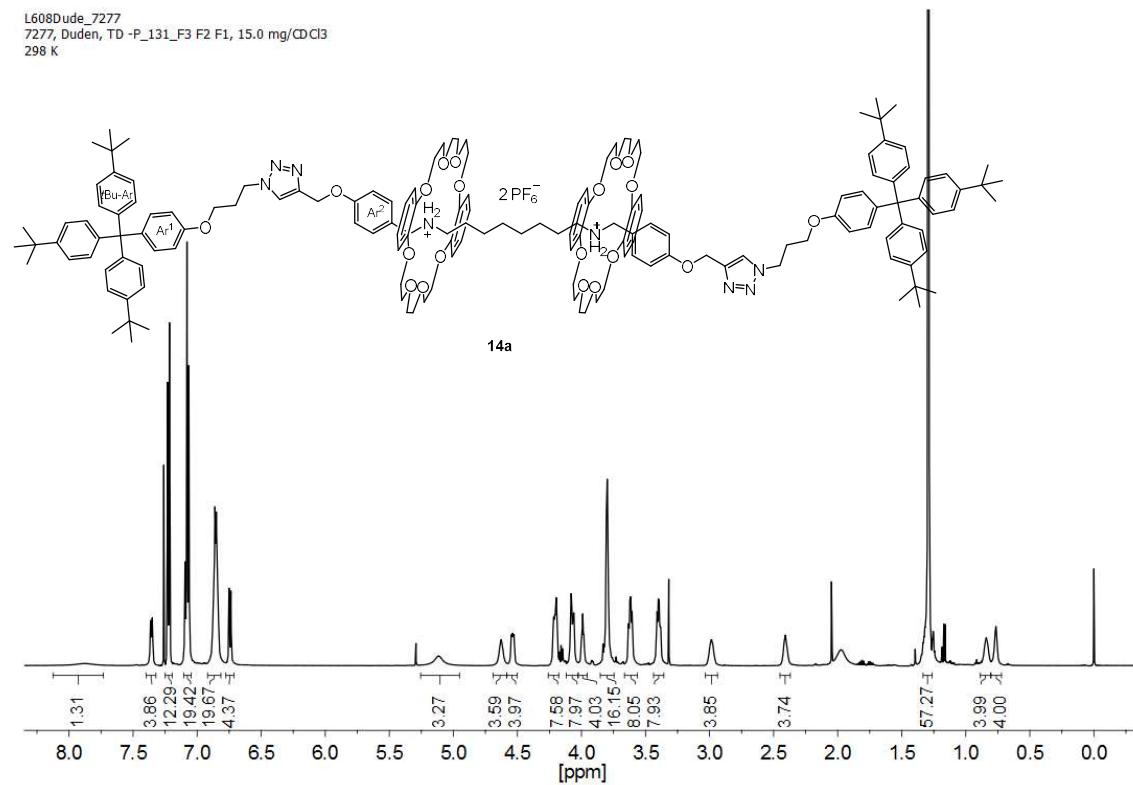
$^1\text{H-NMR}$ (600 MHz, CDCl_3): δ = 7.99 (br. s, 2 H, H_{Tri}), 7.36 (d, 3J = 7.8 Hz, 4 H, $\text{Ar}^2\text{-H-2,6}$), 7.22 (d, 3J = 8.6 Hz, 12 H, $t\text{BuAr-H-3,5}$), 7.12-7.04 (m, 18 H, $t\text{BuAr-H-2,6}$, $\text{Ar}^1\text{-H-2,6}$), 6.92-6.81 (m, 20 H, $\text{Ar}^2\text{-H-3,5}$, $\text{Ar}_{\text{crown}}\text{-H-3,4,5,6}$), 6.75 (d, 3J = 8.8 Hz, 4 H, $\text{Ar}^1\text{-H-3,5}$), 5.12 (br. s, 4 H, $\text{Ar}^2\text{-O-CH}_2$), 4.63 (br. s, 4 H, $\text{Tri-CH}_2\text{CH}_2$), 4.55-4.53 (m, 4 H, $\text{Ar}^2\text{-CH}_2$), 4.25-4.18 (m, 8 H, $\text{CH}_2\text{-crown}$), 4.10-4.05 (m, 8 H, $\text{CH}_2\text{-crown}$), 3.99 (t, 3J = 5.2 Hz, 4 H, $\text{Ar}^1\text{-OCH}_2$), 3.82-3.77 (m, 16 H, $\text{CH}_2\text{-crown}$), 3.65-3.58 (m, 8 H, $\text{CH}_2\text{-crown}$), 3.43-3.38 (m, 8 H, $\text{CH}_2\text{-crown}$), 3.02-2.95 (m, 4 H, $\text{NH}_2\text{CH}_2\text{CH}_2$), 2.44-2.38 (m, 4 H, $\text{Tri-CH}_2\text{CH}_2$), 1.34-1.26 (m, 58 H, CH_3 , $\text{NH}_2\text{CH}_2\text{CH}_2$), 0.87-0.81 (m, 4 H, $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 0.78-0.75 (m, 4 H, $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$) ppm.

$^{13}\text{C-NMR}$ (150 MHz, CDCl_3): δ = 158.9 (s, $\text{Ar}^2\text{-C-1}$), 156.4 (s, $\text{Ar}^1\text{-C-1}$), 148.5 (s, $t\text{BuAr-C-4}$), 147.6 (s, $\text{Ar}_{\text{crown}}\text{-C-1,2}$), 144.2 (s, $t\text{BuAr-C-1}$), 140.2 (s, $\text{Ar}^1\text{-C-4}$), 132.5 (d, $t\text{BuAr-C-2,6}$), 131.5 (d, $\text{Ar}^2\text{-C-3,5}$), 130.8 (d, $\text{Ar}^1\text{-C-3,5}$), 125.3 (s, $\text{Ar}^2\text{-C-4}$), 124.2 (d, $t\text{BuAr-C-3,5}$), 121.9 (d, $\text{Ar}_{\text{crown}}\text{-C-4,5}$), 114.9 (d, $\text{Ar}^2\text{-C-2,6}$), 113.1 (d, $\text{Ar}^1\text{-C-2,6}$), 112.9 (d, $\text{Ar}_{\text{crown}}\text{-C-3,6}$), 70.9 (t, $\text{CH}_2\text{-crown}$), 70.3 (t, $\text{CH}_2\text{-crown}$), 68.4 (t, $\text{CH}_2\text{-crown}$), 64.2 (s, $\text{C}(t\text{BuAr})_3\text{Ar}^1$), 63.2 (t, $\text{Ar}^1\text{-OCH}_2$), 61.7 (t, $\text{Ar}^2\text{-OCH}_2$), 51.8 (t, $\text{Ar}^2\text{-CH}_2$), 49.0 (t, $\text{NH}_2\text{CH}_2\text{CH}_2$), 47.4 (t, $\text{Tri-CH}_2\text{CH}_2$), 34.4 (s, CCH_3), 31.5 (q, CH_3), 30.1 (t, $\text{Ar}^1\text{-OCH}_2\text{CH}_2$), 28.7 (t, $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 26.7 (t, $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 26.4 (t, $\text{NH}_2\text{CH}_2\text{CH}_2$) ppm.

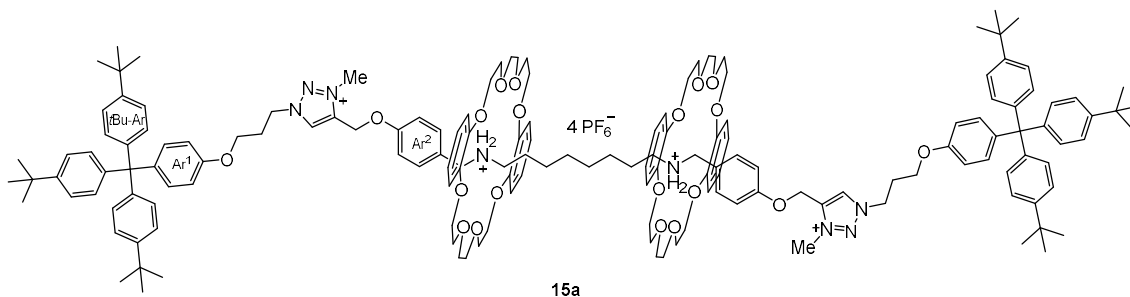
The signals Tri-C-4, 5 could not be found.

IR (ATR): $\tilde{\nu}$ = 2955 (w, aliph. CH), 2870 (w, NH_2^+), 1504, 1454 (m, arom.), 1249, 1107, 1054 (m, CO), 837 (s, 1,4-disubst.), 745 (m, 1,2-disubst.), 557 (s, PF_6^-) cm^{-1} .

MS (HR-ESI): $\text{C}_{156}\text{H}_{200}\text{N}_8\text{O}_{20}$ calcd. m/z = 1252.7434, found m/z = 1252.7434 (Δ = 0.02 ppm).



[3]-4,4'-[Octane-1,8-diylbis(azaniumdiylmethylene-4,1-phenylenoxymethylene)]-bis{3-methyl-1-[3-(4-{tris[4-(dimethylethyl)phenyl]methyl}phenoxy)propyl]-1*H*-1,2,3-triazol-3-ium}-rotaxa-bis(1,12-[1,2]dibenzena-2,5,8,11,13,16,19,22-octaoxadocosaphan) tetrakis(hexafluorophosphate) (15a**)**



Rotaxane **14a** (30.0 mg, 10.7 μmol) was dissolved in methyl iodide (2 mL) and stirred for 4 d at room temp. The solvent was removed in vacuo and the residue was dissolved in dichloromethane (3 mL). An identical volume of saturated aqueous ammonium hexafluorophosphate solution was added and the mixture was stirred vigorously for 3 h at room temp. The aqueous layer was extracted with dichloromethane (2 x 10 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was removed in vacuo. A pale yellow solid was obtained.

Yield: 33.6 mg (10.7 μmol , quant.).

Melting point: 235 $^{\circ}\text{C}$.

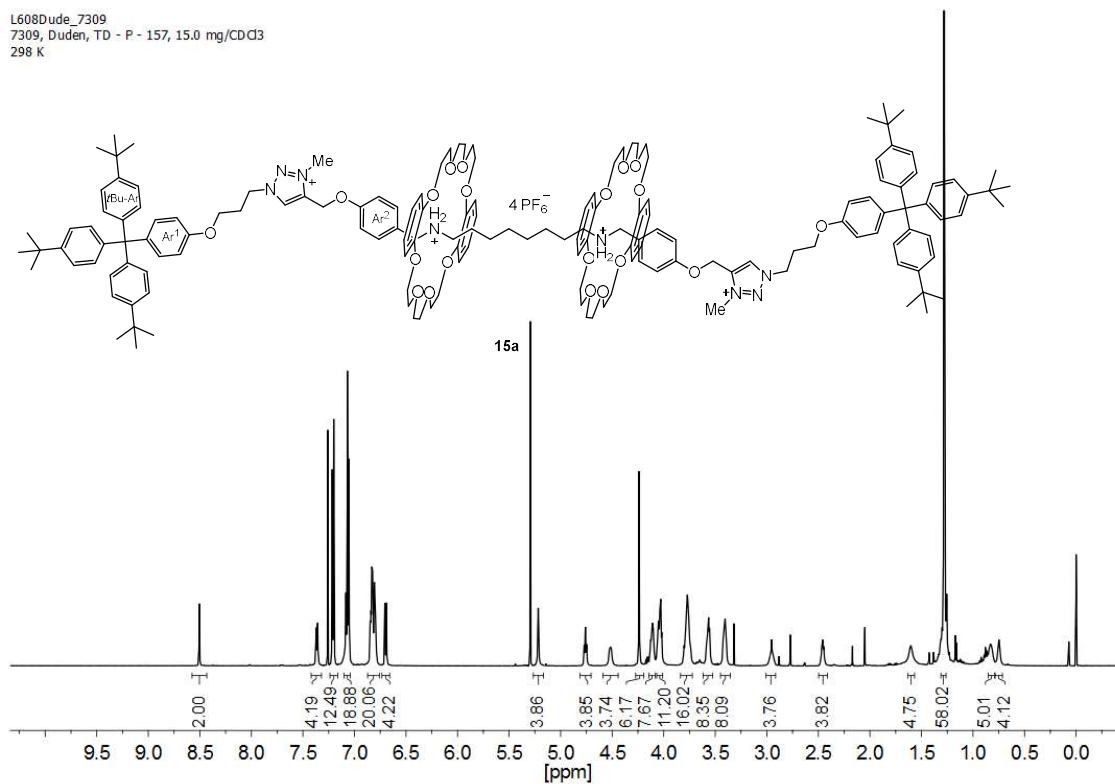
$^1\text{H-NMR}$ (600 MHz, CDCl_3): δ = 8.51 (s, 2 H, H_{Tri}), 7.37 (d, 3J = 8.2 Hz, 4 H, $\text{Ar}^2\text{-H-2,6}$), 7.21 (d, 3J = 8.7 Hz, 12 H, $t\text{BuAr-H-3,5}$), 7.10-7.04 (m, 18 H, $t\text{BuAr-H-2,6}$, $\text{Ar}^1\text{-H-2,6}$), 6.86-6.78 (m, 20 H, $\text{Ar}^2\text{-H-3,5}$, $\text{Ar}_{\text{crown}}\text{-H-3,4,5,6}$), 6.70 (d, 3J = 8.8 Hz, 4 H, $\text{Ar}^1\text{-H-3,5}$), 5.22 (s, 4 H, $\text{Ar}^2\text{-O-CH}_2$), 4.76 (t, 3J = 7.0 Hz, 4 H, $\text{Tri-CH}_2\text{CH}_2$), 4.52 (br. s, 4 H, $\text{Ar}^2\text{-CH}_2$), 4.24 (s, 6 H, CH_3Tri), 4.14-4.08 (m, 8 H, $\text{CH}_2\text{-crown}$), 4.07-4.01 (m, 12 H, $\text{CH}_2\text{-crown}$, $\text{Ar}^1\text{-OCH}_2$), 3.82-3.72 (m, 16 H, $\text{CH}_2\text{-crown}$), 3.60-3.53 (m, 8 H, $\text{CH}_2\text{-crown}$), 3.44-3.37 (m, 8 H, $\text{CH}_2\text{-crown}$), 2.99-2.92 (m, 4 H, $\text{NH}_2\text{CH}_2\text{CH}_2$), 2.49-2.43 (m, 4 H, $\text{Tri-CH}_2\text{CH}_2$), 1.32-1.25 (m, 58 H, $\text{C}(\text{CH}_3)_3$, $\text{NH}_2\text{CH}_2\text{CH}_2$), 0.85-0.79 (m, 4 H, $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 0.77-0.73 (m, 4 H, $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$) ppm.

$^{13}\text{C-NMR}$ (150 MHz, CDCl_3): δ = 157.6 (s, $\text{Ar}^2\text{-C-1}$), 156.1 (s, $\text{Ar}^1\text{-C-1}$), 148.5 (s, $t\text{BuAr-C-4}$), 147.6 (s, $\text{Ar}_{\text{crown}}\text{-C-1,2}$), 144.2 (s, $t\text{BuAr-C-1}$), 140.32 (s, $\text{Ar}^1\text{-C-4}$), 140.30 (s, Tri-C-4), 132.5 (d, $t\text{BuAr-C-2,6}$), 131.8 (d, $\text{Ar}^2\text{-C-3,5}$), 130.8 (d, $\text{Ar}^1\text{-C-3,5}$), 129.7 (d, Tri-C-5), 126.5 (s, $\text{Ar}^2\text{-C-4}$), 124.2 (d, $t\text{BuAr-C-3,5}$), 121.8 (d, $\text{Ar}_{\text{crown}}\text{-C-4,5}$), 115.0 (d, $\text{Ar}^2\text{-C-2,6}$), 113.1 (d, $\text{Ar}^1\text{-C-2,6}$), 112.9 (d, $\text{Ar}_{\text{crown}}\text{-C-3,6}$), 70.8 (t, $\text{CH}_2\text{-crown}$), 70.3 (t, $\text{CH}_2\text{-crown}$), 68.4 (t, $\text{CH}_2\text{-crown}$), 63.7 (s, $\text{C}(t\text{BuAr})_3\text{Ar}^1$), 63.2 (t, $\text{Ar}^1\text{-OCH}_2$), 58.3 (t, $\text{Ar}^2\text{-OCH}_2$), 51.8 (t, $\text{Ar}^2\text{-CH}_2$, t, $\text{Tri-CH}_2\text{CH}_2$), 48.9 (t, $\text{NH}_2\text{CH}_2\text{CH}_2$), 38.7 (q, CH_3Tri), 34.4 (s, $\text{C}(\text{CH}_3)_3$), 31.5 (q, $\text{C}(\text{CH}_3)_3$), 29.2 (t, $\text{Ar}^1\text{-OCH}_2\text{CH}_2$), 28.7 (t, $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 26.7 (t, $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2$) 26.4 (t, $\text{NH}_2\text{CH}_2\text{CH}_2$) ppm.

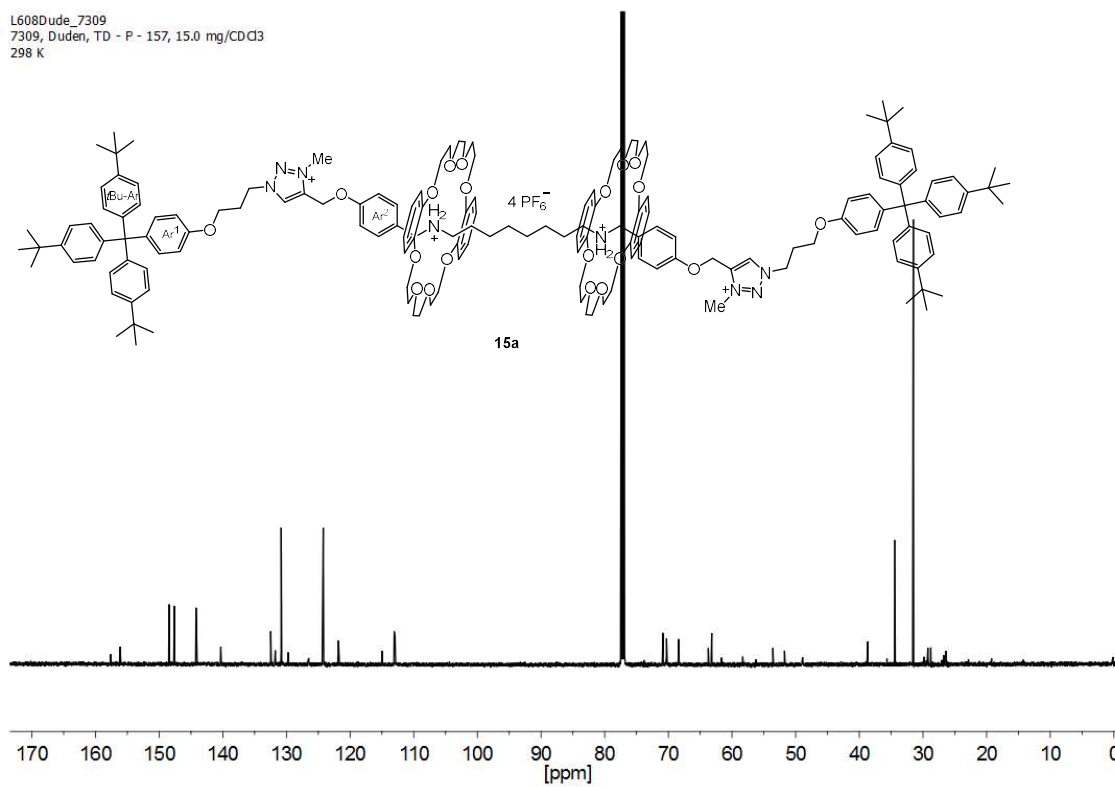
IR (ATR): $\tilde{\nu}$ = 2961 (w, aliph. CH), 1504, 1456 (m, arom.), 1246, 1228, 1105, 1055 (m, CO), 835 (s, 1,4-disubst.), 742 (m, 1,2-disubst.), 557 (s, PF_6) cm^{-1} .

MS (HR-ESI): $\text{C}_{158}\text{H}_{206}\text{N}_8\text{O}_{20}$ calcd. m/z = 633.8832, found m/z = 633.8838 (Δ = +1.00 ppm), $\text{C}_{158}\text{H}_{206}\text{F}_6\text{N}_8\text{O}_{20}\text{P}$ calcd. m/z = 893.4991, found m/z = 893.4977 (Δ = -0.61 ppm).

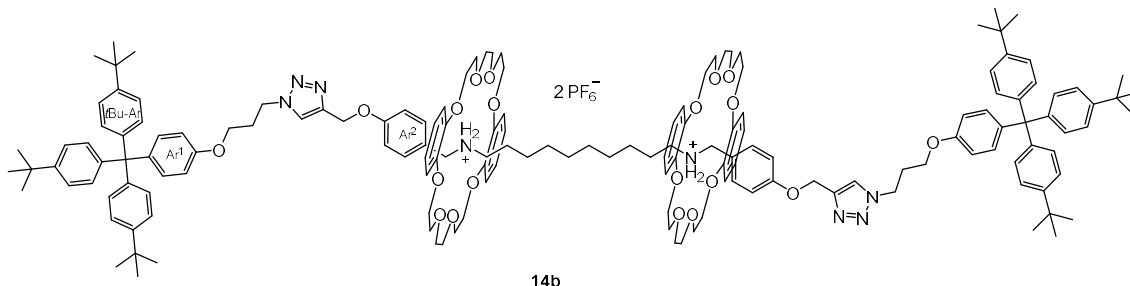
L608Dude_7309
7309, Duden, TD - P - 157, 15.0 mg/CDCl₃
298 K



L608Dude_7309
7309, Duden, TD - P - 157, 15.0 mg/CDCl₃
298 K



[3]-*N,N'*-(Decane-1,10-diyl)-*N,N'*-bis{[4-({1-[3-(4-{tris[4-(dimethylethyl)phenyl]methyl}phenoxy)propyl]-1*H*-1,2,3-triazol-4-yl]methoxy}phenyl]methanaminium}-rotaxa-bis(1,12-[1,2]dibenzena-2,5,8,11,13,16,19,22-octaoadoccosaphan) bis(hexafluorophosphate) • dibenzo-24-crown-8 (14b**•**13**)**



Under nitrogen atmosphere, axis **3b** (96.2 mg, 128 μ mol) and DB24C8 (**13**, 144 mg, 321 μ mol) were suspended in dry dichloromethane (50 mL). The suspension was stirred at room temp. until a clear solution was obtained. Then stopper **11** [4] (150 mg, 255 μ mol), tetrakis(acetonitrile)copper(I) hexafluorophosphate (95.1 mg, 255 μ mol) and 2,6-dimethylpyridine (ca. 60 μ L) were added. The yellow solution was stirred for 1 d at room temp. and then water (20 mL) was added. The aqueous layer was extracted with dichloromethane (3 x 30 mL) and the solvent was removed in vacuo. The residue was filtered through silica gel [dichloromethane/methanol (80 : 20)]. The solvent of the filtrate was removed in vacuo and the residue was purified by chromatography using silica gel [dichloromethane/methanol (1 : 0) \rightarrow (24 : 1), R_f = 0.05]. The yellow solid was dissolved in very little ethyl acetate and DB24C8 (**13**) precipitated. The solid was filtered off and the process was repeated. Finally, the residue was cleaned again by chromatography on silica gel [dichloromethane/methanol (1 : 0) \rightarrow (24 : 1), R_f = 0.05]. A pale yellow solid was obtained which consisted of rotaxane **14b** and one additional equivalent of macrocycle **13**. The analytical data below have been obtained from this adduct **14b**•**13**.

Yield: 160 mg (48,9 μ mol, 38 %).

Melting point: 175 $^{\circ}$ C.

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 7.86 (br. s, 2 H, H_{Tri}), 7.37 (d, 3J = 8.4 Hz, 4 H, $\text{Ar}^2\text{-H-2,6}$), 7.24-7.20 (m, 12 H, $t\text{BuAr-H-3,5}$), 7.12-7.04 (m, 24 H, $t\text{BuAr-H-2,6}$, $\text{Ar}^1\text{-H-2,6}$, $\text{Ar}_{\text{crown-H-3,4,5,6}}$), 6.90-6.83 (m, 20 H, $\text{Ar}^2\text{-H-3,5}$, $\text{Ar}_{\text{crown-H-3,4,5,6}}$), 6.74 (d, 3J = 8.9 Hz, 4 H, $\text{Ar}^1\text{-H-3,5}$), 5.12 (br. s, 4 H, $\text{Ar}^2\text{O-CH}_2$), 4.60 (t, 3J = 6.8 Hz, 4 H, $\text{Tri-CH}_2\text{CH}_2$), 4.56-4.52 (m, 4 H, $\text{Ar}^2\text{-CH}_2$), 4.33-4.25 (m, 8 H, $\text{CH}_2\text{-crown}$), 4.25-4.17 (m, 8 H, $\text{CH}_2\text{-crown}$), 4.12-4.05 (m, 8 H, $\text{CH}_2\text{-crown}$), 3.99 (t, 3J = 5.2 Hz, 4 H, $\text{Ar}^1\text{-OCH}_2$), 3.84-3.75 (m, 24 H, $\text{CH}_2\text{-crown}$), 3.65-3.56 (m, 16 H, $\text{CH}_2\text{-crown}$), 3.43-3.35 (m, 8 H, $\text{CH}_2\text{-crown}$), 3.01-2.94 (m, 4 H, $\text{NH}_2\text{CH}_2\text{CH}_2$), 2.42-2.36 (m, 4 H, $\text{Tri-CH}_2\text{CH}_2$), 1.39-1.32 (m, 4 H, $\text{NH}_2\text{CH}_2\text{CH}_2$), 1.29 (s, 54 H, CH_3), 0.96-0.86 (m, 12 H, $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$) ppm.

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ = 158.5 (s, $\text{Ar}^2\text{-C-1}$), 156.4 (s, $\text{Ar}^1\text{-C-1}$), 148.4 (s, $t\text{BuAr-C-4}$), 147.6 (s, $\text{Ar}_{\text{crown-C-1,2}}$), 144.2 (s, $t\text{BuAr-C-1}$), 140.1 (s, $\text{Ar}^1\text{-C-4}$), 132.4 (d, $t\text{BuAr-C-2,6}$), 131.6 (d, $\text{Ar}^2\text{-C-3,5}$), 130.8 (d, $\text{Ar}^1\text{-C-3,5}$), 125.3 (s, $\text{Ar}^2\text{-C-4}$), 124.2 (d, $t\text{BuAr-C-3,5}$), 121.9 (d, $\text{Ar}_{\text{crown-C-4,5}}$), 114.7 (d, $\text{Ar}^2\text{-C-2,6}$), 113.1 (d, $\text{Ar}^1\text{-C-2,6}$), 113.0 (d, $\text{Ar}_{\text{crown-C-3,6}}$), 70.8 (t, $\text{CH}_2\text{-crown}$), 70.3 (t, $\text{CH}_2\text{-crown}$), 68.4 (t, $\text{CH}_2\text{-crown}$), 64.1 (t, $\text{Ar}^1\text{-OCH}_2$), 63.2 (s, $\text{C}(t\text{BuAr})_3\text{Ar}^1$), 61.7 (t, $\text{Ar}^2\text{-OCH}_2$),

51.6 (t, Ar²-CH₂), 48.8 (t, NH₂CH₂CH₂), 47.4 (t, Tri-CH₂CH₂), 34.4 (s, CCH₃), 31.5 (q, CH₃), 29.9 (t, Ar¹-OCH₂CH₂), 28.8 (t, NH₂CH₂CH₂CH₂CH₂CH₂), 26.4 (t, NH₂CH₂CH₂CH₂), 26.3 (t, NH₂CH₂CH₂) ppm.

The signals Tri-C-4, 5 could not be found.

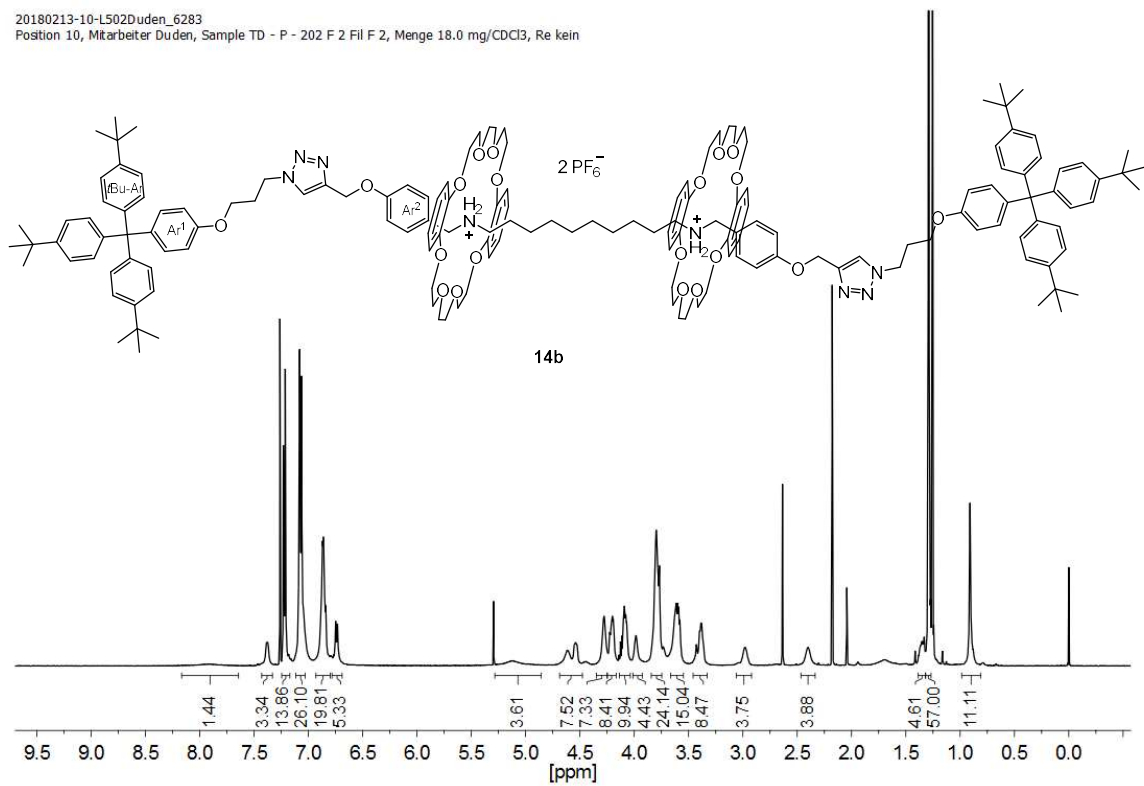
In addition, signals of an additional ring were observed. Intergration estimated approx. one equivalent.

IR (ATR): $\tilde{\nu}$ = 2960 (w, aliph. CH), 2873 (w, NH₂⁺), 1501, 1451 (m, arom.), 1249, 1121, 1053 (m, CO), 834 (s, 1,4-disubst.), 743 (m, 1,2-disubst.), 556 (s, PF₆) cm⁻¹.

MS (HR-ESI): C₁₅₈H₂₀₄N₈O₂₀ calcd. m/z = 1266.7591, found m/z = 1266.7589 (Δ = -0.08 ppm).

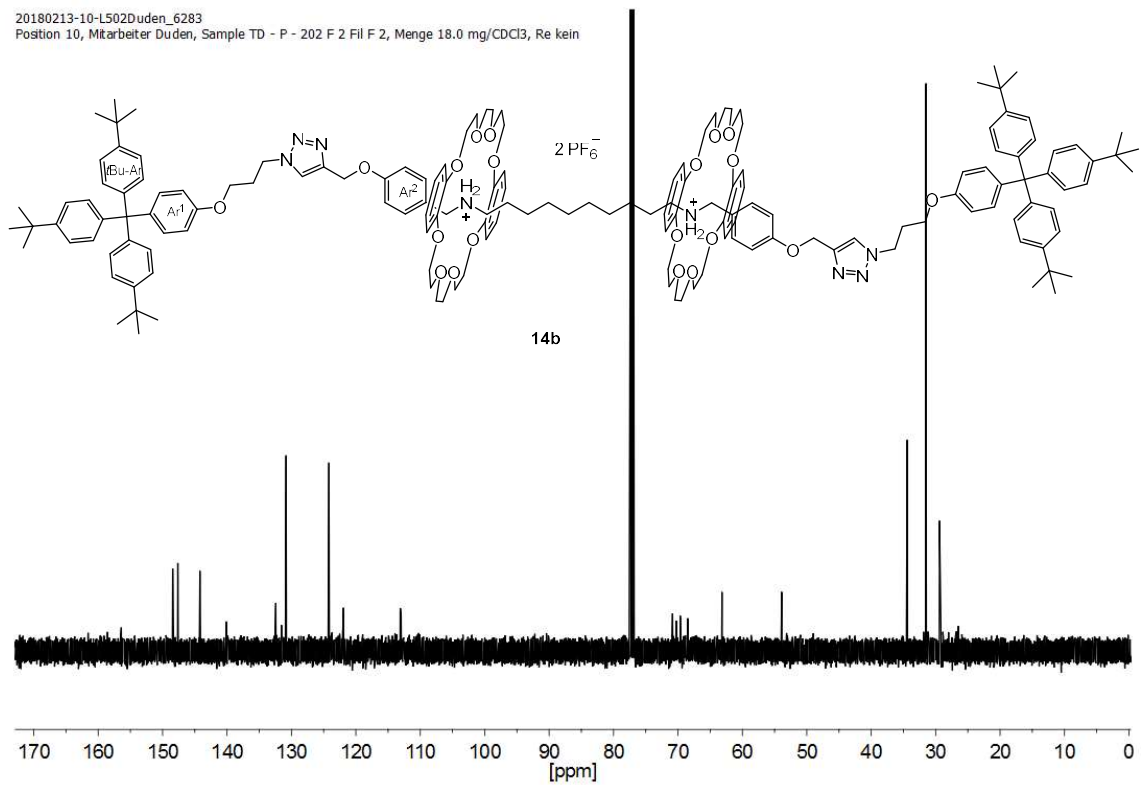
20180213-10-L502Duden_6283

Position 10, Mitarbeiter Duden, Sample TD - P - 202 F 2 Fil F 2, Menge 18.0 mg/CDCl₃, Re kein

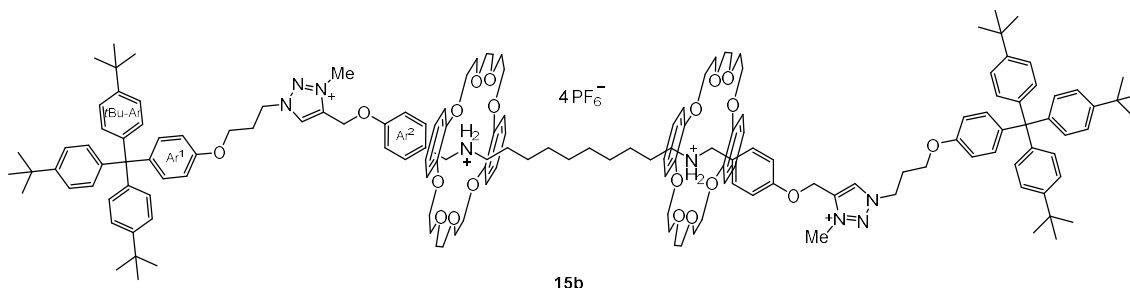


20180213-10-L502Duden_6283

Position 10, Mitarbeiter Duden, Sample TD - P - 202 F 2 Fil F 2, Menge 18.0 mg/CDCl₃, Re kein



[3]-4,4'-[Decane-1,10-diylbis(azaniumdiylmethylene-4,1-phenylenoxymethylene)]-bis{3-methyl-1-[3-(4-{tris[4-(dimethylethyl)phenyl]methyl}phenoxy)propyl]-1*H*-1,2,3-triazol-3-ium}-rotaxa-bis(1,12-[1,2]dibenzena-2,5,8,11,13,16,19,22-octaoxadocosaphan) tetrakis(hexafluorophosphate) • dibenzo-24-crown-8 (15b•13**)**



Rotaxane **14b•13** (50.0 mg, 15.3 μ mol) was dissolved in methyl iodide (2 mL) and stirred for 4 d at room temp. The solvent was removed in vacuo and the residue was dissolved in dichloromethane (3 mL). An identical volume of saturated aqueous ammonium hexafluorophosphate solution was added and the mixture was stirred vigorously for 3 h at room temp. The aqueous layer was extracted with dichloromethane (2 x 10 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was removed in vacuo. A pale yellow solid was obtained which consisted of rotaxane **15b** and one additional equivalent of macrocycle **13**. The analytical data below have been obtained from this adduct **15b•13**.

Yield: 54.0 mg (15.0 μ mol, 98 %).

Melting point: 204 °C.

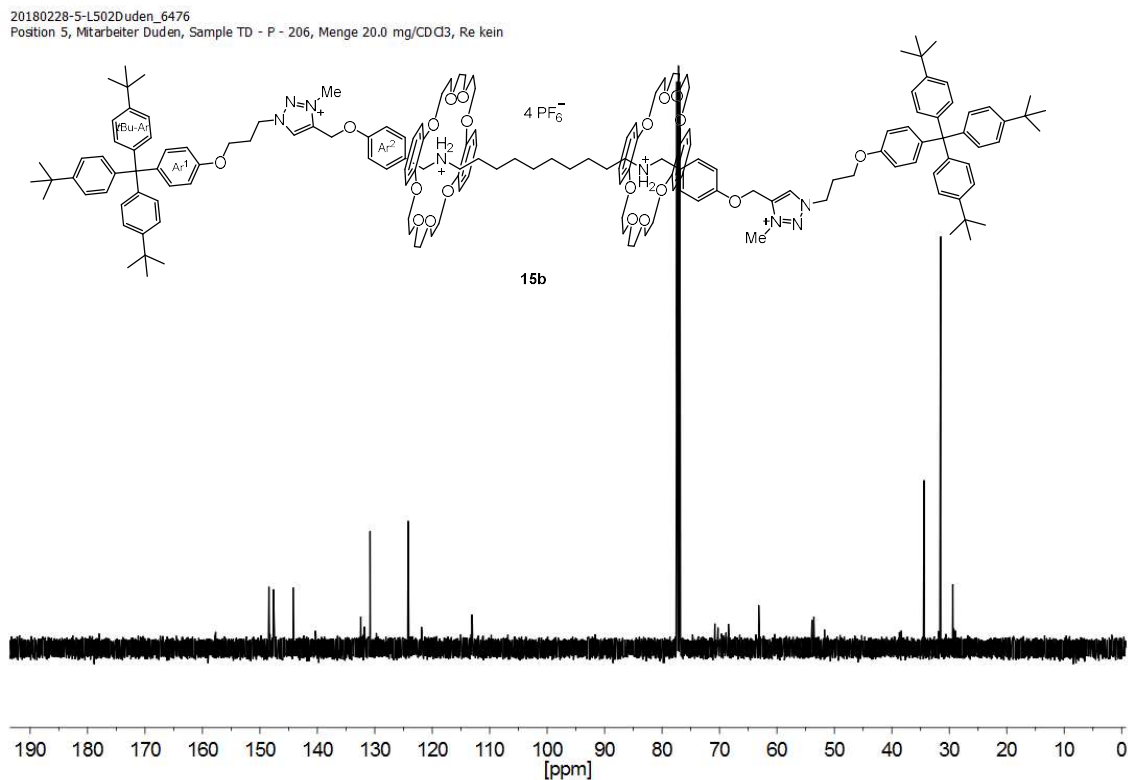
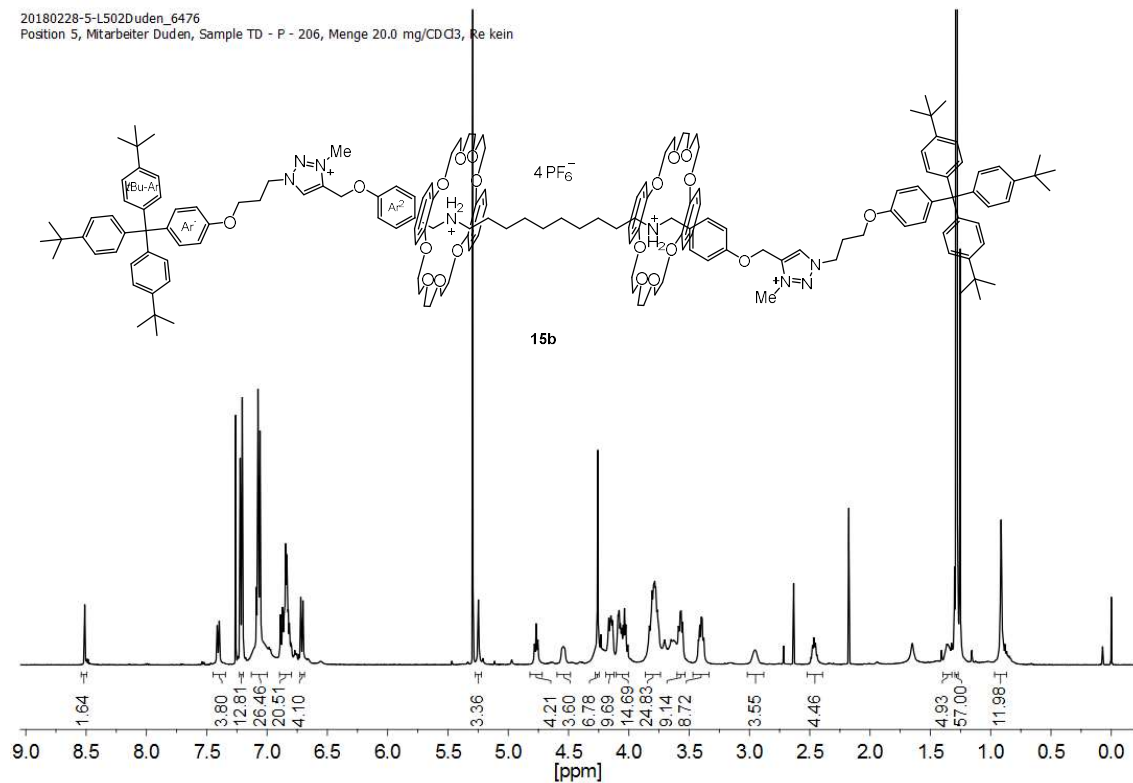
¹H-NMR (500 MHz, CDCl₃): δ = 8.51 (s, 2 H, *H*_{Tri}), 7.40 (d, ³*J* = 8.6 Hz, 4 H, Ar²-*H*-2,6), 7.21 (d, ³*J* = 8.7 Hz, 12 H, *t*BuAr-*H*-3,5), 7.10-7.04 (m, 26 H, *t*BuAr-*H*-2,6, Ar¹-*H*-2,6, Ar_{crown}-*H*-3,4,5,6), 6.90-6.79 (m, 20 H, Ar²-*H*-3,5, Ar_{crown}-*H*-3,4,5,6), 6.70 (d, ³*J* = 8.7 Hz, 4 H, Ar¹-*H*-3,5), 5.25 (s, 4 H, Ar²O-CH₂), 4.77 (t, ³*J* = 7.1 Hz, 4 H, Tri-CH₂CH₂), 4.54 (br. s, 4 H, Ar²-CH₂), 4.26 (s, 6 H, CH₃Tri), 4.19-4.12 (m, 8 H, CH₂-crown), 4.11-3.98 (m, 16 H, CH₂-crown, Ar¹OCH₂), 3.86-3.74 (m, 24 H, CH₂-crown), 3.60-3.53 (m, 8 H, CH₂-crown), 3.44-3.36 (m, 8 H, CH₂-crown), 3.00-2.91 (m, 4 H, NH₂CH₂CH₂), 2.52-2.43 (m, 4 H, Tri-CH₂CH₂), 1.39-1.33 (m, 4 H, NH₂CH₂CH₂), 1.28 (m, 54 H, C(CH₃)₃), 0.95-0.89 (m, 12 H, NH₂CH₂CH₂CH₂CH₂CH₂) ppm.

¹³C-NMR (125 MHz, CDCl₃): δ = 157.5 (s, Ar²-C-1), 156.0 (s, Ar¹-C-1), 148.4 (s, *t*BuAr-C-4), 147.6 (s, Ar_{crown}-C-1,2), 144.2 (s, *t*BuAr-C-1), 140.2 (s, Tri-C-4), 140.0 (s, Ar¹-C-4), 132.5 (d, *t*BuAr-C-2,6), 131.8 (d, Ar²-C-3,5), 130.8 (d, Ar¹-C-3,5), 129.5 (d, Tri-C-5), 126.3 (s, Ar²-C-4), 124.2 (d, *t*BuAr-C-3,5), 121.9 (d, Ar_{crown}-C-4,5), 114.9 (d, Ar²-C-2,6), 113.1 (d, Ar¹-C-2,6), 112.8 (d, Ar_{crown}-C-3,6), 70.8 (t, CH₂-crown), 70.3 (t, CH₂-crown), 68.4 (t, CH₂-crown), 63.5 (t, Ar¹-OCH₂), 63.2 (s, C(*t*BuAr)₃Ar¹), 58.2 (t, Ar²-OCH₂), 51.7 (t, Ar²-CH₂, t, Tri-CH₂CH₂), 48.8 (t, NH₂CH₂CH₂), 38.4 (q, CH₃Tri), 34.4 (s, C(CH₃)₃), 31.5 (q, C(CH₃)₃), 29.4 (t, Ar¹-OCH₂CH₂), 28.8 (t, NH₂CH₂CH₂CH₂), 26.6 (t, NH₂CH₂CH₂), 26.3 (t, NH₂CH₂CH₂CH₂CH₂, t, NH₂CH₂CH₂CH₂CH₂CH₂) ppm.

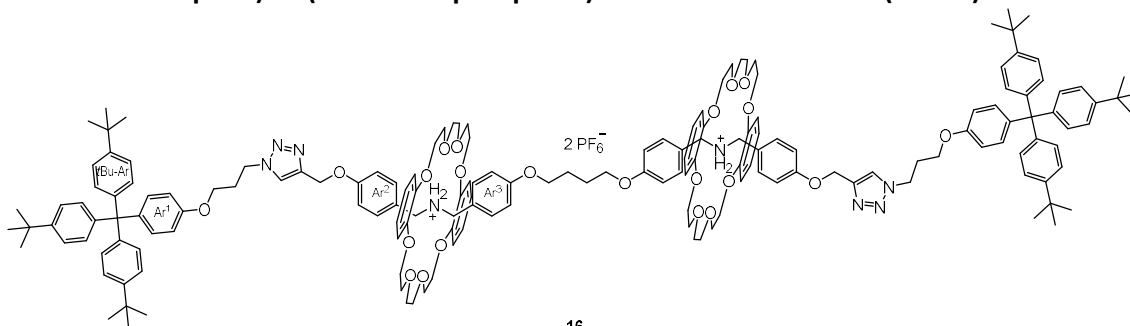
In addition, signals of an additional ring were observed. Intergration estimated approx. one equivalent.

IR (ATR): $\tilde{\nu}$ = 2950 (w, aliph. CH), 1504, 1455 (m, arom.), 1247, 1106, 1055 (m, CO), 837 (s, 1,4-disubst.), 742 (m, 1,2-disubstit.), 557 (s, PF₆) cm⁻¹.

MS (HR-ESI): $C_{160}H_{210}N_8O_{20}$ calcd. $m/z = 640.8910$, found $m/z = 640.8900$ ($\Delta = -1.52$ ppm),
 $C_{160}H_{210}F_6N_8O_{20}P$ calcd. $m/z = 902.8429$, found $m/z = 902.8410$ ($\Delta = -2.10$ ppm),
 $C_{160}H_{210}F_{12}N_8O_{20}P_2$ calcd. $m/z = 1426.7467$, found $m/z = 1426.7446$ ($\Delta = -1.47$ ppm).



[3]-*N,N'*-[Butane-1,4-diylbis(oxy-4,1-phenylenemethylene)]-*N,N'*-bis{[4-({1-[3-(4-{tris[4-(dimethylethyl)phenyl]methyl}phenoxy)propyl]-1*H*-1,2,3-triazol-4-yl)methoxy}phenyl]methanaminium}-rotaxa-bis(1,12-[1,2]dibenzena-2,5,8,11,13,16,19,22-octaoadococaphan) bis(hexafluorophosphate) • dibenzo-24-crown-8 (16•13)



16

Under nitrogen atmosphere, Axis **7** (100 mg, 114 μmol) and DB24C8 (**13**, 102 mg, 227 μmol) were suspended in dry dichloromethane (50 mL). The suspension was stirred at room temp. until a clear solution was obtained. Then stopper **11** [4] (146 mg, 250 μmol), tetrakis(acetonitrile)copper(I) hexafluorophosphate (93.0 mg, 250 μmol) and 2,6-dimethylpyridine (ca. 60 μL) were added. The yellow solution was stirred for 1 d at room temp. and then water (20 mL) was added. The aqueous layer was extracted with dichloromethane (3 x 30 mL) and the solvent was removed in vacuo. The residue was filtered through silica gel [dichloromethane/methanol (80 : 20)]. The solvent of the filtrate was removed in vacuo and the residue was purified by chromatography using silica gel [dichloromethane/methanol (1 : 0) \rightarrow (24 : 1), $R_f = 0.05$]. The yellow solid was dissolved in very little ethyl acetate and DB24C8 (**13**) precipitated. The solid was filtered off and the process was repeated. Finally, the residue was purified again by chromatography on silica gel [dichloromethane/methanol (1 : 0) \rightarrow (24 : 1), $R_f = 0.05$]. A pale yellow solid was obtained which consisted of rotaxane **16** and one additional equivalent of macrocycle **13**. The analytical data below have been obtained from this adduct **16•13**.

Yield: 22.0 mg (6.47 μmol , 6 %).

Melting point: 178 $^{\circ}\text{C}$.

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 7.84 (br. s, 2 H, H_{Tri}), 7.46-7.40 (m, 4 H, $\text{Ar}^2\text{-H-2,6}$), 7.24-7.17 (m, 16 H, $t\text{BuAr-H-3,5}$, $\text{Ar}^3\text{-H-2,6}$), 7.10-7.04 (m, 20 H, $t\text{BuAr-H-2,6}$, $\text{Ar}^1\text{-H-2,6}$, $\text{Ar}_{\text{crown-H-3,4,5,6}}$), 6.98-6.72 (m, 28 H, $\text{Ar}^2\text{-H-3,5}$, $\text{Ar}^3\text{-H-3,5}$, $\text{Ar}^1\text{-H-3,5}$, $\text{Ar}_{\text{crown-H-3,4,5,6}}$), 5.11 (br. s, 4 H, $\text{Ar}^2\text{O-CH}_2$), 4.58 (t, $^3J = 7.5$ Hz, 4 H, $\text{Tri-CH}_2\text{CH}_2$), 4.48-4.42 (m, 8 H, $\text{Ar}^2\text{-CH}_2$, $\text{Ar}^3\text{-CH}_2$), 4.13-4.06 (m, 16 H, $\text{CH}_2\text{-crown}$), 4.02-3.96 (m, 8 H, $\text{Ar}^1\text{-OCH}_2$, $\text{Ar}^3\text{-OCH}_2$), 3.76-3.69 (m, 16 H, $\text{CH}_2\text{-crown}$), 3.47-3.36 (m, 16 H, $\text{CH}_2\text{-crown}$), 3.84-3.75 (m, 24 H, $\text{CH}_2\text{-crown}$), 3.43-3.35 (m, 8 H, $\text{CH}_2\text{-crown}$), 2.41-2.34 (m, 4 H, $\text{Tri-CH}_2\text{CH}_2$), 1.96-1.92 (m, 4 H, $\text{Ar}^3\text{-OCH}_2\text{CH}_2$), 1.29 (s, 54 H, CH_3) ppm.

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ = 159.7 (s, $\text{Ar}^3\text{-C-1}$), 158.7 (s, $\text{Ar}^2\text{-C-1}$), 156.4 (s, $\text{Ar}^1\text{-C-1}$), 148.4 (s, $t\text{BuAr-C-4}$), 147.6 (s, $\text{Ar}_{\text{crown-C-1,2}}$), 144.2 (s, $t\text{BuAr-C-1}$), 140.1 (s, $\text{Ar}^1\text{-C-4}$), 132.4 (d, $t\text{BuAr-C-2,6}$), 130.94 (d, $\text{Ar}^2\text{-C-3,5}$), 130.90 (d, $\text{Ar}^3\text{-C-3,5}$), 130.8 (d, $\text{Ar}^1\text{-C-3,5}$), 124.3 (s, $\text{Ar}^2\text{-C-4}$), 124.2 (d, $t\text{BuAr-C-3,5}$), 123.6 (s, $\text{Ar}^3\text{-C-4}$), 121.8 (d, $\text{Ar}_{\text{crown-C-4,5}}$), 115.0 (d, $\text{Ar}^3\text{-C-2,6}$), 114.7 (d, $\text{Ar}^2\text{-C-2,6}$), 113.1 (d, $\text{Ar}^1\text{-C-2,6}$), 112.9 (d, $\text{Ar}_{\text{crown-C-3,6}}$), 70.8 (t, $\text{CH}_2\text{-crown}$), 70.3 (t, $\text{CH}_2\text{-crown}$),

68.4 (t, CH₂-crown), 67.2 (t, Ar³-OCH₂), 64.1 (t, Ar¹-OCH₂), 63.2 (s, C(tBuAr)₃Ar¹), 61.5 (t, Ar²-OCH₂), 51.9 (t, Ar²-CH₂, Ar³-CH₂), 47.4 (t, Tri-CH₂CH₂), 34.4 (s, CCH₃), 31.5 (q, CH₃), 30.2 (t, Ar¹-OCH₂CH₂), 25.7 (t, Ar³-OCH₂CH₂) ppm.

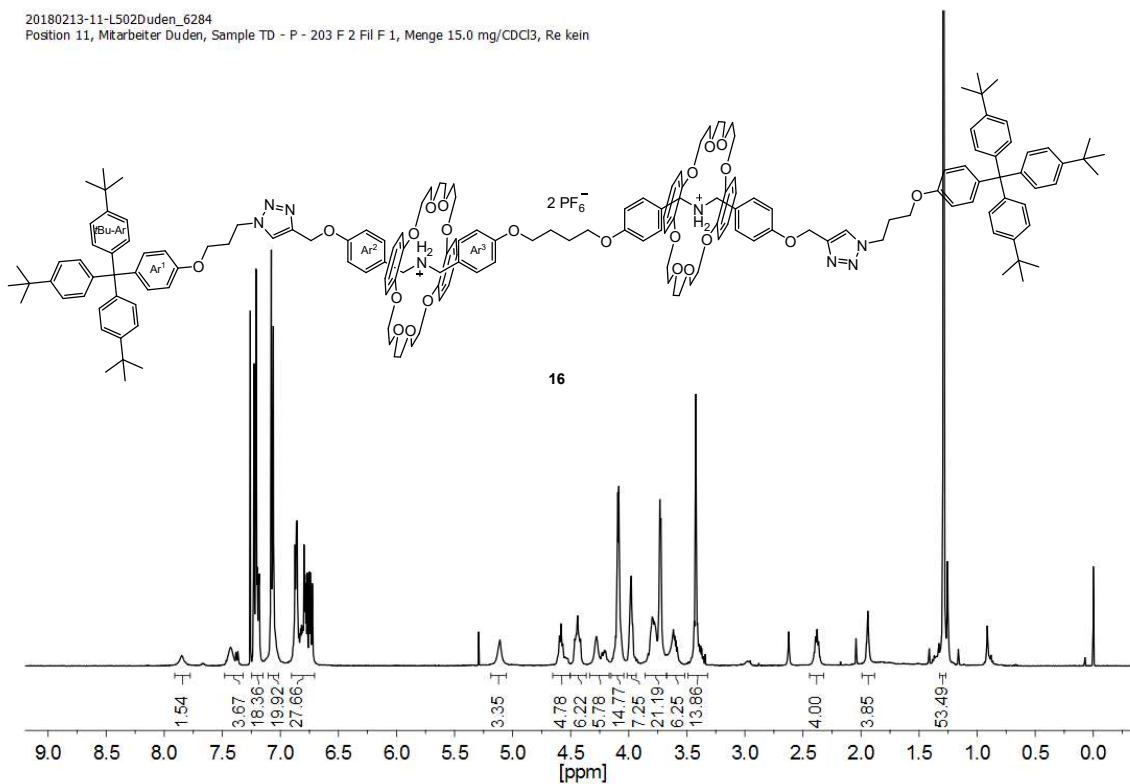
The signals for Tri-C-4,5 and Ar²-C-1,4 could not be found.

In addition, signals of an additional ring were observed. Intergration estimated approx. one equivalent.

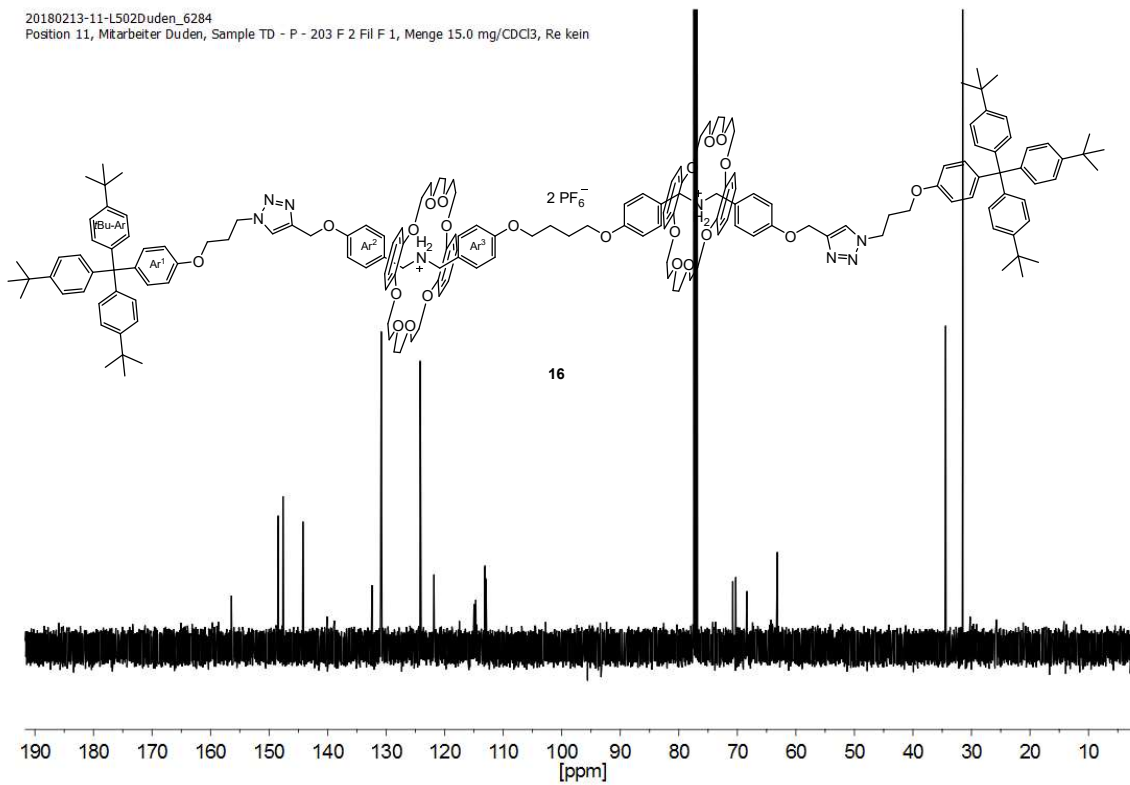
IR (ATR): $\tilde{\nu}$ = 2963 (w, aliph. CH), 2879 (w, NH₂⁺), 1501, 1453 (m, arom.), 1252, 1124, 1050 (m, CO), 834 (s, 1,4-disubst.), 743 (m, 1,2-disubst.), 556 (s, PF₆) cm⁻¹.

MS (HR-ESI): C₁₆₆H₂₀₄N₈O₂₂ calcd. m/z = 1330.7540, found m/z = 1330.7541 (Δ = -0.01 ppm).

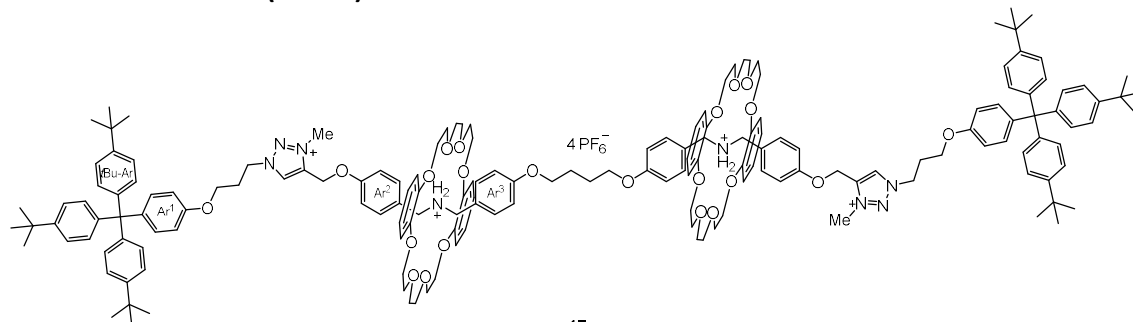
20180213-11-L502Duden_6284
 Position 11, Mitarbeiter Duden, Sample TD - P - 203 F 2 Fil F 1, Menge 15.0 mg/CDCl₃, Re kein



20180213-11-L502Duden_6284
 Position 11, Mitarbeiter Duden, Sample TD - P - 203 F 2 Fil F 1, Menge 15.0 mg/CDCl₃, Re kein



[3]-4,4'-[Butane-1,4-diylbis(oxy-4,1-phenylenemethyleneazaniumdiylmethylene-4,1-phenyleneoxymethylene)]-bis{3-methyl-1-[3-(4-{tris[4-(dimethylethyl)phenyl]methyl}phenoxy)propyl]-1*H*-1,2,3-triazol-3-ium}-rotaxabis(1,12-[1,2]dibenzena-2,5,8,11,13,16,19,22-octaodocosa-phan) tetrakis(hexafluorophosphate) • dibenzo-24-crown-8 (17•13**)**



17

Rotaxane **16•13** (33.0 mg, 9.70 μmol) was dissolved in methyl iodide (2 mL) and stirred for 4 d at room temp. The solvent was removed in vacuo and the residue was dissolved in dichloromethane (3 mL). An identical volume of saturated aqueous ammonium hexafluorophosphate solution was added and the mixture was stirred vigorously for 3 h at room temp. The aqueous layer was extracted with dichloromethane (2 x 10 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was removed in vacuo. A pale yellow solid was obtained which consisted of rotaxane **17** and one additional equivalent of macrocycle **13**. The analytical data below have been obtained from this adduct **17•13**.

Yield: 36.0 mg (9.67 μmol , quant.).

Melting point: 140 °C.

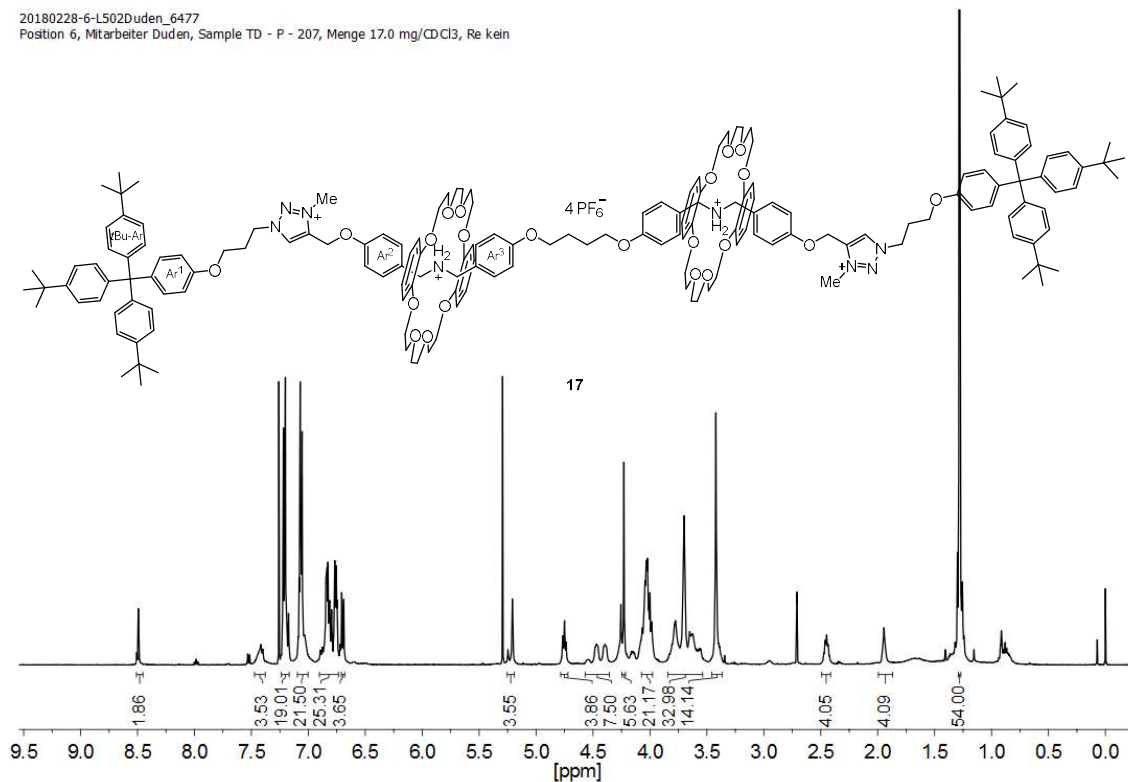
$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 8.49 (br. s, 2 H, H_{Tri}), 7.48-7.39 (m, 4 H, $\text{Ar}^2\text{-H-2,6}$), 7.24-7.16 (m, 16 H, $t\text{BuAr-H-3,5}$, $\text{Ar}^3\text{-H-2,6}$), 7.19-7.04 (m, 24 H, $t\text{BuAr-H-2,6}$, $\text{Ar}^1\text{-H-2,6}$, $\text{Ar}_{\text{crown-H-3,4,5,6}}$), 6.98-6.74 (m, 28 H, $\text{Ar}^2\text{-H-3,5}$, $\text{Ar}^3\text{-H-3,5}$, $\text{Ar}_{\text{crown-H-3,4,5,6}}$), 6.71-6.68 (m, 4 H, $\text{Ar}^1\text{-H-3,5}$), 5.21 (s, 4 H, $\text{Ar}^2\text{-O-CH}_2$), 4.75 (t, 3J = 7.0 Hz, 4 H, $\text{Tri-CH}_2\text{CH}_2$), 4.49-4.47 (m, 8 H, $\text{Ar}^2\text{-CH}_2$, $\text{Ar}^3\text{-CH}_2$), 4.23 (s, 6 H, $\text{CH}_{3\text{Tri}}$), 4.11-3.96 (m, 24 H, $\text{CH}_2\text{-crown}$, $\text{Ar}^1\text{-OCH}_2$, $\text{Ar}^3\text{-OCH}_2$), 3.84-3.54 (m, 32 H, $\text{CH}_2\text{-crown}$), 3.45-3.38 (m, 16 H, $\text{CH}_2\text{-crown}$), 2.38-2.34 (m, 4 H, $\text{Tri-CH}_2\text{CH}_2$), 1.96-1.92 (m, 4 H, $\text{Ar}^3\text{-OCH}_2\text{CH}_2$), 1.29 (s, 54 H, CH_3) ppm.

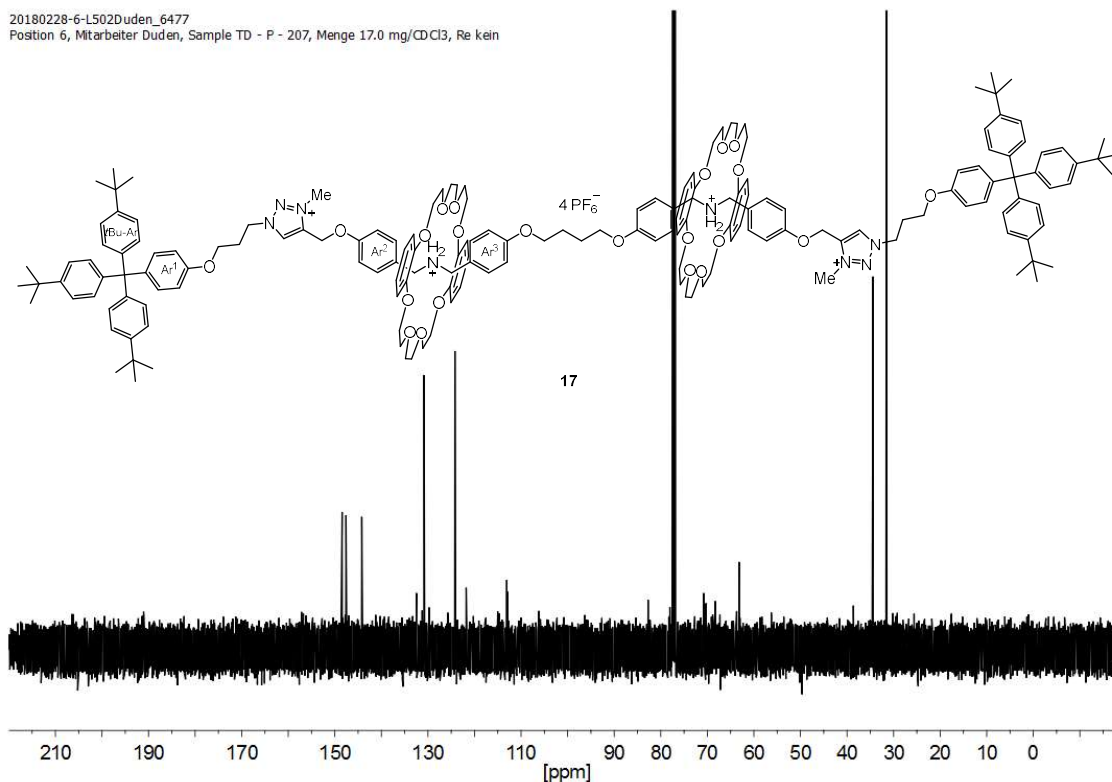
$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ = 159.5 (s, $\text{Ar}^3\text{-C-1}$), 157.4 (s, $\text{Ar}^2\text{-C-1}$), 156.0 (s, $\text{Ar}^1\text{-C-1}$), 148.4 (s, $t\text{BuAr-C-4}$), 147.6 (s, $\text{Ar}_{\text{crown-C-1,2}}$), 144.2 (s, $t\text{BuAr-C-1}$), 140.04 (s, Tri-C-4), 140.03 (s, $\text{Ar}^1\text{-C-4}$), 132.3 (d, $t\text{BuAr-C-2,6}$), 131.7 (d, $\text{Ar}^2\text{-C-3,5}$), 131.1 (d, $\text{Ar}^3\text{-C-3,5}$), 130.8 (d, $\text{Ar}^1\text{-C-3,5}$), 129.5 (d, Tri-C-5), 125.5 (s, $\text{Ar}^2\text{-C-4}$), 124.2 (d, $t\text{BuAr-C-3,5}$), 123.5 (s, $\text{Ar}^3\text{-C-4}$), 121.8 (d, $\text{Ar}_{\text{crown-C-4,5}}$), 114.8 (d, $\text{Ar}^2\text{-C-2,6}$), 114.5 (d, $\text{Ar}^3\text{-C-2,6}$), 113.1 (d, $\text{Ar}^1\text{-C-2,6}$), 112.8 (d, $\text{Ar}_{\text{crown-C-3,6}}$), 70.8 (t, $\text{CH}_2\text{-crown}$), 70.3 (t, $\text{CH}_2\text{-crown}$), 68.3 (t, $\text{CH}_2\text{-crown}$), 67.1 (t, $\text{Ar}^3\text{-OCH}_2$), 63.5 (t, $\text{Ar}^1\text{-OCH}_2$), 63.2 (s, $\text{C}(t\text{BuAr})_3\text{Ar}^1$), 58.1 (t, $\text{Ar}^2\text{-OCH}_2$), 51.9 (t, $\text{Ar}^2\text{-CH}_2$), 51.7 (t, $\text{Ar}^3\text{-CH}_2$), 51.5 (t, $\text{Tri-CH}_2\text{CH}_2$), 38.4 (q, $\text{CH}_{3\text{Tri}}$), 34.4 (s, $\text{C}(\text{CH}_3)_3$), 31.5 (q, $\text{C}(\text{CH}_3)_3$), 29.0 (t, $\text{Ar}^1\text{-OCH}_2\text{CH}_2$), 25.4 (t, $\text{Ar}^3\text{-OCH}_2\text{CH}_2$) ppm.

In addition, signals of an additional ring were observed. Intergration estimated approx. one equivalent.

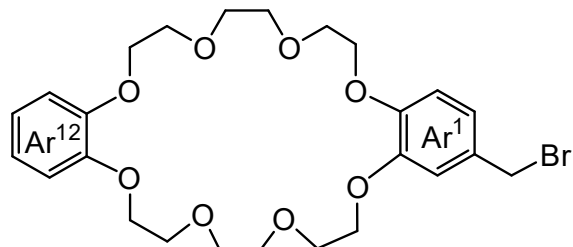
IR (ATR): $\tilde{\nu}$ = 2952 (w, aliph. CH), 1506, 1453 (m, arom.), 1246, 1102, 1053 (m, CO), 837 (s, 1,4-disubst.), 742 (m, 1,2-disubst.), 557 (s, PF₆) cm⁻¹.

MS (HR-ESI): C₁₆₈H₂₁₀N₈O₂₀ calcd. m/z = 672.8885, found m/z = 640.8900 (Δ = -1.4 ppm),
 C₁₆₀H₂₁₀F₆N₈O₂₀P calcd. m/z = 945.5060, found m/z = 945.5042 (Δ = -1.89 ppm),
 C₁₆₀H₂₁₀F₁₂N₈O₂₀P₂ calcd. m/z = 1490.7413, found m/z = 1490.7394 (Δ = -1.31 ppm).





1⁴-(Bromomethyl)-1,12-[1,2]dibenzena-2,5,8,11,13,16,19,22-octaoxadocosaphan (DB24C8-CH₂Br) (24)



24

Under nitrogen atmosphere, DB24C8-CH₂OH [5] (**23**, 500 mg, 1.05 mmol) was added in dry. Dichloromethane (20 mL) was dissolved and phosphorus tribromide (150 μ L, 1.57 mmol) dissolved in dry dichloromethane (10 mL) was added under ice cooling. The solution was stirred for 2 h at room temp. and then water (15 mL) was added. The phases were separated and the aqueous phase extracted with dichloromethane (3 x 10 mL each). The organic phases were washed with saturated sodium chloride solution (50 mL), dried over sodium sulfate, filtered and the solvent was removed under vacuum. A pale yellow solid was obtained.

Yield: 572 mg (1.05 mmol, quant).

Meltingpoint: 94 °C.

¹H-NMR (600 MHz, CDCl₃): δ = 6.95-6.85 (m, 6 H, Ar¹-H-3,5, Ar¹²-H-3,4,5,6), 6.79 (d, ³J = 8.1 Hz, 1 H, Ar¹-H-6), 4.46 (s, 2 H, CH₂Br), 4.19-4.12 (m, 8 H, CH₂), 3.94-3.88 (m, 8 H, CH₂), 3.83-3.82 (m, 8 H, CH₂) ppm.

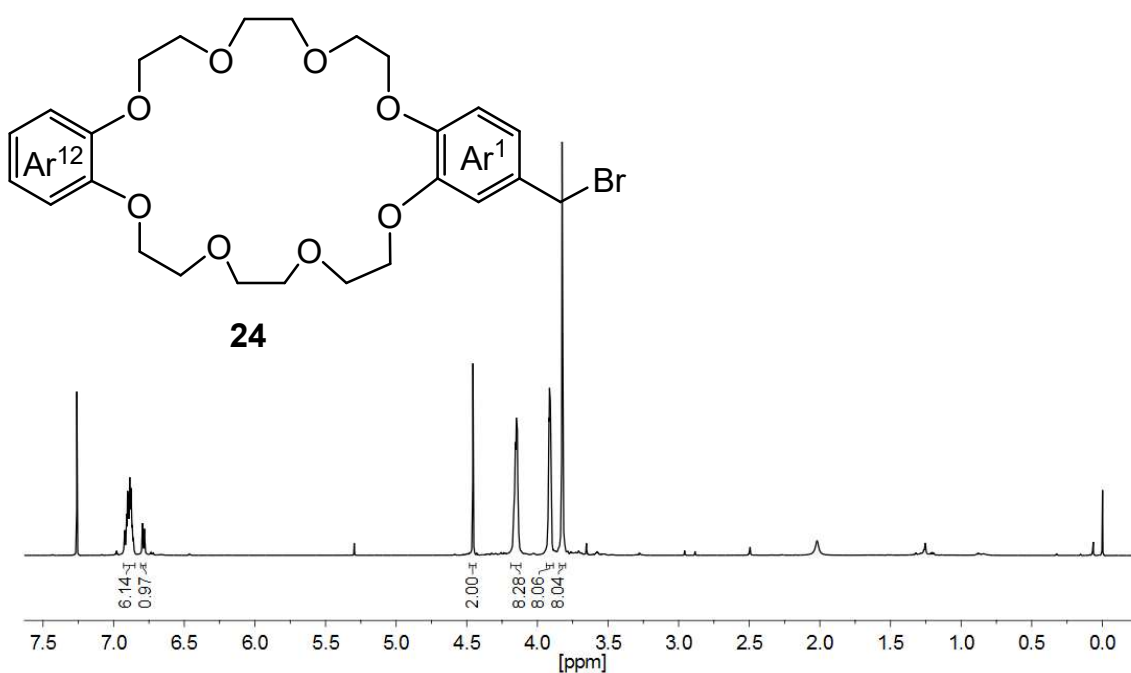
^{13}C -NMR (150 MHz, CDCl_3): δ = 149.3 (s, $\text{Ar}^1\text{-C-1}$), 149.1 (s, $\text{Ar}^{12}\text{-C-1,2}$), 149.0 (s, $\text{Ar}^1\text{-C-2}$), 130.9 (s, $\text{Ar}^1\text{-C-4}$), 122.2 (d, $\text{Ar}^1\text{-C-5}$), 121.6 (d, $\text{Ar}^{12}\text{-C-4,5}$), 114.8 (d, $\text{Ar}^1\text{-C-3}$), 114.2 (d, $\text{Ar}^{12}\text{-C-3,6}$), 113.6 (d, $\text{Ar}^1\text{-C-6}$), 71.4 (t, CH_2), 70.1 (t, CH_2), 69.92 (t, CH_2), 69.91 (t, CH_2), 69.61 (t, CH_2), 69.58 (t, CH_2), 69.53 (t, CH_2), 69.51 (t, CH_2), 34.4 (t, CH_2Br) ppm.

IR (ATR): $\tilde{\nu}$ = 2928, 2870 (m, aliph. CH), 1506 (s, arom.), 1124, 1102 (s. CO), 727 (s, 1,2-disubst.) cm^{-1} .

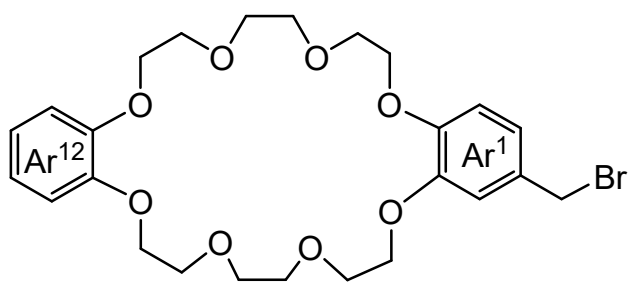
MS (HR-El): $\text{C}_{25}\text{H}_{33}^{79}\text{BrO}_8$ bzw. $\text{C}_{25}\text{H}_{33}^{81}\text{BrO}_8$ calcd. m/z = 540.1359 or 542.1338, found m/z = 440.1351 or 542.1335 (Δ = -1.51 or -0.70 ppm).

Elemental analysis: $\text{C}_{25}\text{H}_{33}\text{BrO}_8$: calcd. C 55.46, H 6.14, found C 55.84, H 6.65.

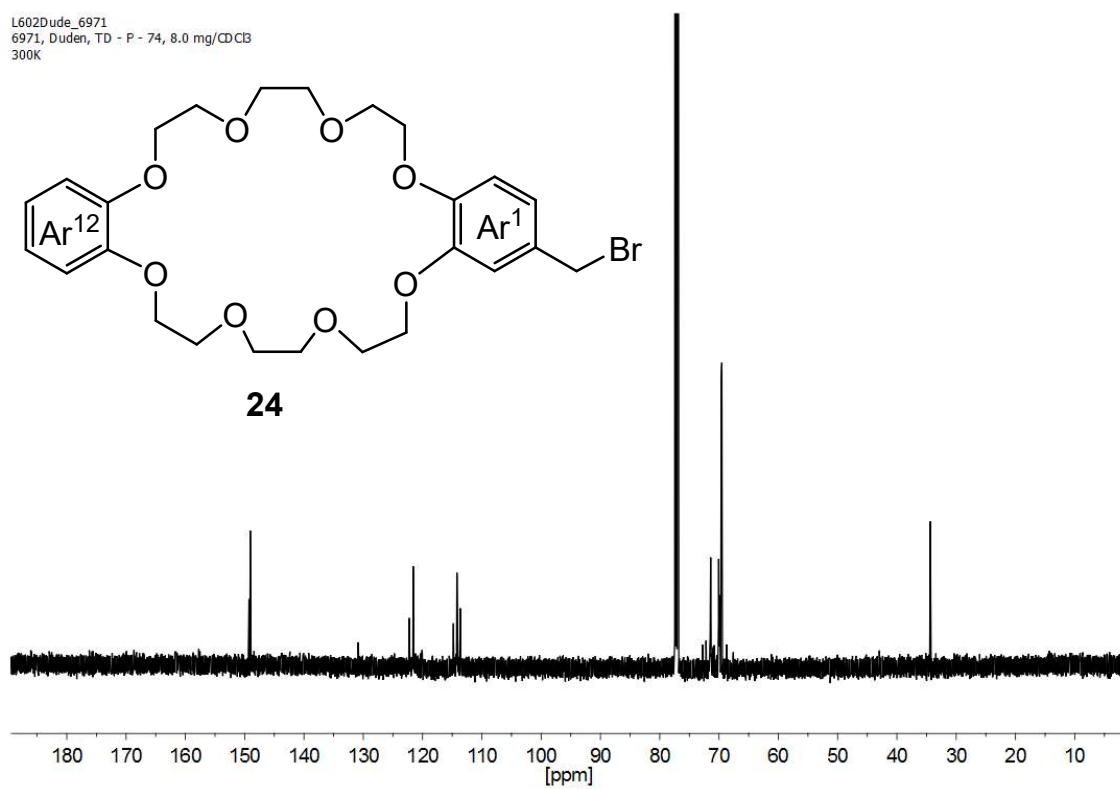
L602Dude_6971
6971, Duden, TD - P - 74, 8.0 mg/ CDCl_3
300K

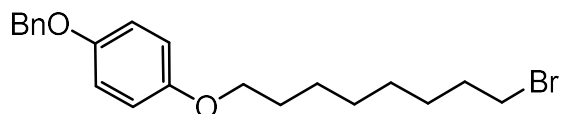


L602Dude_6971
6971, Duden, TD - P - 74, 8.0 mg/CDCl₃
300K



24



1-(Benzyloxy)-4-(8-bromooctyloxy)benzene (26d)**26d**

Under nitrogen atmosphere, 4-benzyloxyphenol **25** (8.00 g, 40.0 mmol) and potassium carbonate (11.0 g, 80.0 mmol) were suspended in acetonitrile (100 mL) and 1,8-dibromooctane (32.6 g, 120 mmol) was added. The suspension was stirred under reflux for 20 h and then filtered. The solvent was removed in vacuo and the residue was dissolved with dichloromethane (200 mL). The organic layer was washed with 10% aqueous sodium hydroxide solution (4 x 50 mL), dried with magnesium sulfate and filtered. The solvent was removed in vacuo and the residue was recrystallized from *n*-hexane. A colorless solid was obtained.

Yield: 11.8 g (30.1 mmol, 75 %).

Melting point: 78 °C.

¹H-NMR (500 MHz, CDCl₃): δ = 7.42 (d, ³*J* = 7.4 Hz, 2 H, Bn-*H*-2,6), 7.40-7.35 (m, 2 H, Bn-*H*-3,5), 7.34-7.29 (m, 1 H, Bn-*H*-4), 6.92-6.87 (m, 2 H, Ar-*H*-2,6), 6.85-6.79 (m, 2 H, Ar-*H*-3,5), 5.01 (s, 2 H, PhCH₂O), 3.90 (t, ³*J* = 6.5 Hz, 2 H, OCH₂CH₂), 3.41 (t, ³*J* = 6.8 Hz, 2 H, CH₂Br), 1.90-1.82 (m, 2 H, CH₂CH₂Br), 1.79-1.71 (m, 2 H, OCH₂CH₂), 1.49-1.41 (m, 4 H, OCH₂CH₂CH₂, CH₂CH₂CH₂Br), 1.39-1.30 (m, 4 H, OCH₂CH₂CH₂CH₂, CH₂CH₂CH₂CH₂Br) ppm.

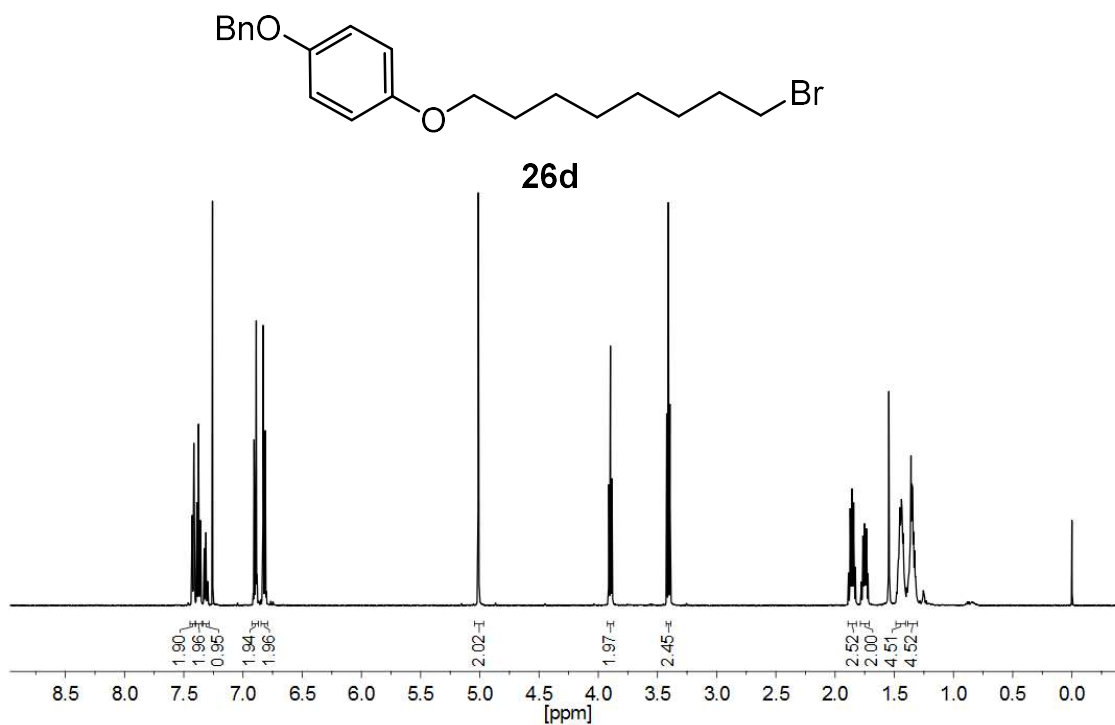
¹³C-NMR (125 MHz, CDCl₃): δ = 153.6 (s, Ar-C-1), 153.0 (s, Ar-C-4), 137.5 (s, Bn-C-1), 128.7 (d, Bn-C-3,5), 128.0 (d, Bn-C-4), 127.6 (d, Bn-C-2,6), 116.0 (d, Ar-C-2,6), 115.5 (d, Ar-C-3,5), 70.8 (t, PhCH₂O), 68.6 (t, OCH₂CH₂), 34.1 (t, CH₂Br), 32.9 (t, CH₂CH₂Br), 29.3 (t, OCH₂CH₂), 28.8 (t, OCH₂CH₂CH₂), 28.2 (t, CH₂CH₂CH₂Br), 26.1 (t, CH₂CH₂CH₂CH₂Br), 25.5 (t, OCH₂CH₂CH₂CH₂) ppm.

IR (ATR): $\tilde{\nu}$ = 2934, 2859 (w, aliph. CH), 1507, 1464, 1454 (s, arom.), 1226, 1022 (s, CO), 824 (s, 1,4-disubst.), 737 (s, monosubst.), 694 (s, monosubst.) cm⁻¹.

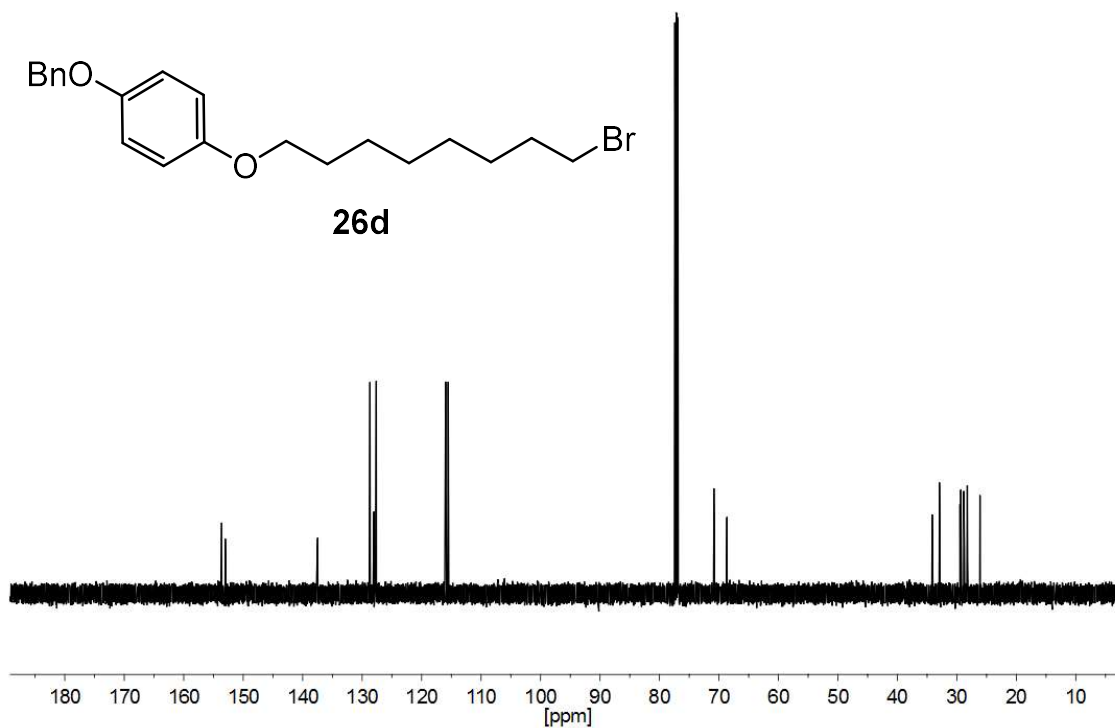
MS (HR-EI): C₂₁H₂₇⁷⁹BrO₂ calcd. *m/z* = 390.1194, found *m/z* = 390.1188 (Δ = -1.59 ppm). C₂₁H₂₇⁸¹BrO₂ calcd. *m/z* = 392.1174, found *m/z* = 392.1170 (Δ = -0.93 ppm).

Elemental analysis: C₂₁H₂₇BrO₂: calcd. C 64.45, H 6.95, found C 64.43, H 6.96.

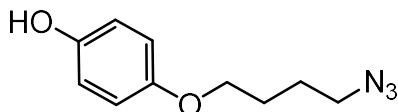
20180712-13-L507Duden_8062
 Position 13, Mitarbeiter Duden, Sample TD - P - 254, Menge 10.0 mg/CDCl₃, Re kein



20180712-13-L507Duden_8062
 Position 13, Mitarbeiter Duden, Sample TD - P - 254, Menge 10.0 mg/CDCl₃, Re kein



4-(4-Azidobutyloxy)phenol (28b)



28b

Bromide **27b** (4.38 g, 17.9 mmol) was dissolved in dimethylsulfoxide (20 mL), sodium azide (3.49 g, 53.7 mmol) was added and the mixture was stirred at room temp. for 18 h. Water (20 mL) was added and the aqueous layer was extracted with diethyl ether (3 x 20 mL). The organic layer was dried with magnesium sulfate, filtered and the solvent was removed in vacuo. The crude product was purified by chromatography using silica gel [dichloromethane → dichloromethane/methanol (93 : 7); R_f = 0.3] cleaned. A colorless oil was obtained.

Yield: 2.56 g (12.3 mmol, 69 %).

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 6.80-6.73 (m, 4 H, Ar-*H*-2,3,5,6), 4.66 (s, 1 H, OH), 3.93 (t, 3J = 5.9 Hz, 2 H, OCH_2), 3.36 (t, 3J = 6.6 Hz, 2 H, CH_2N_3), 1.88-1.75 (m, 4 H, $\text{CH}_2\text{CH}_2\text{N}_3$), OCH_2CH_2) ppm.

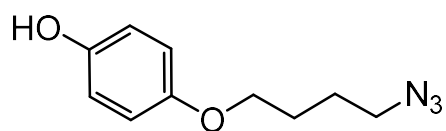
$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ = 153.2 (s, Ar-C-4), 149.7 (s, Ar-C-1), 116.2 (d, Ar-C-2,6), 115.7 (d, Ar-C-3,5), 68.0 (t, OCH_2), 51.4 (t, CH_2N_3), 28.1 (t, $\text{CH}_2\text{CH}_2\text{N}_3$), 26.7 (t, OCH_2CH_2) ppm.

IR (ATR): $\tilde{\nu}$ = 3394 (br. m, OH), 2955, 2928, 2904, 2869 (w, aliph. CH), 2102 (s, azide), 1506, 1451 (s, arom.), 1223, 1058 (s, CO), 821 (s, 1,4-disubst.) cm^{-1} .

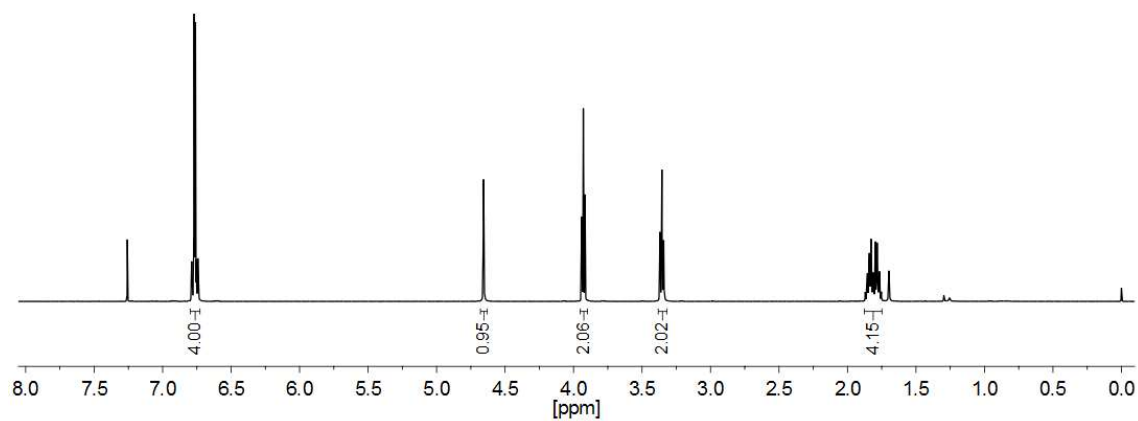
MS (HR-El): $\text{C}_{10}\text{H}_{13}\text{N}_3\text{O}_2$ calcd. m/z = 207.1008, found m/z = 207.1011 (Δ = 1.30 ppm).

Elemental analysis: $\text{C}_{10}\text{H}_{13}\text{N}_3\text{O}_2 \cdot 0.2 \text{ H}_2\text{O}$: calcd. C 56.73, H 6.43, N 19.85, found C 56.87, H 6.22, N 19.63.

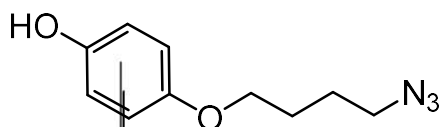
20180718-17-L507Duden_8120
 Position 17, Mitarbeiter Duden, Sample TD - P - 258, Menge 11.0 mg/CDCl₃, Re kein



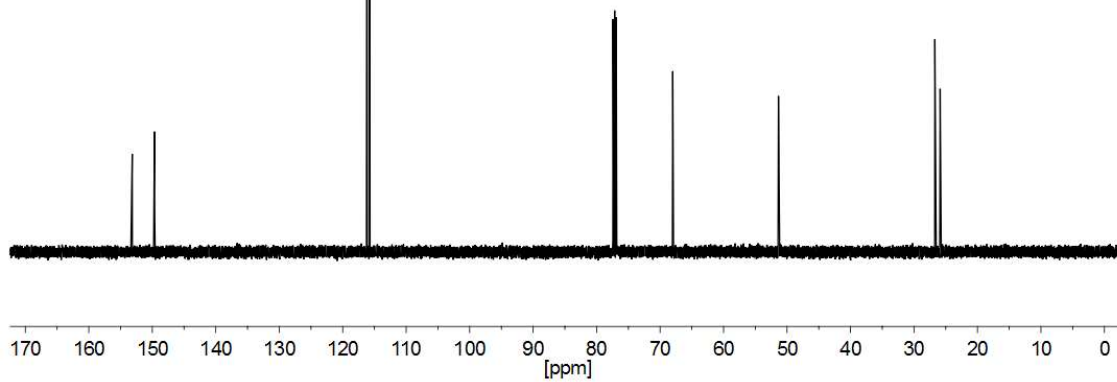
28b

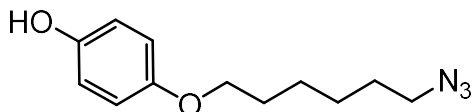


20180718-17-L507Duden_8120
 Position 17, Mitarbeiter Duden, Sample TD - P - 258, Menge 11.0 mg/CDCl₃, Re kein



28b



4-(6-Azidohexyloxy)phenol (28c)**28c**

Bromide **27c** (1.61 g, 5.92 mmol) was dissolved in dimethylsulfoxide (20 mL), sodium azide (1.54 g, 23.7 mmol) was added and the mixture was stirred at room temp. for 18 h. Water (20 mL) was added and the aqueous layer was extracted with diethyl ether (3 x 20 mL). The organic layer was dried with magnesium sulfate, filtered and the solvent was removed in vacuo. The crude product was purified by chromatography using silica gel [dichloromethane → dichloromethane/methanol (93 : 7); R_f = 0.3] cleaned. A colorless oil was obtained.

Yield: 845 mg (3.84 mmol, 65 %).

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 6.80-6.72 (m, 4 H, Ar-*H*-2,3,5,6), 4.79 (s, 1 H, OH), 3.90 (t, 3J = 6.4 Hz, 2 H, OCH_2), 3.28 (t, 3J = 6.9 Hz, 2 H, CH_2N_3), 1.82-1.71 (m, 2 H, OCH_2CH_2), 1.67-1.59 (m, 2 H, $\text{CH}_2\text{CH}_2\text{N}_3$), 1.55-1.38 (m, 4 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}_3$) ppm.

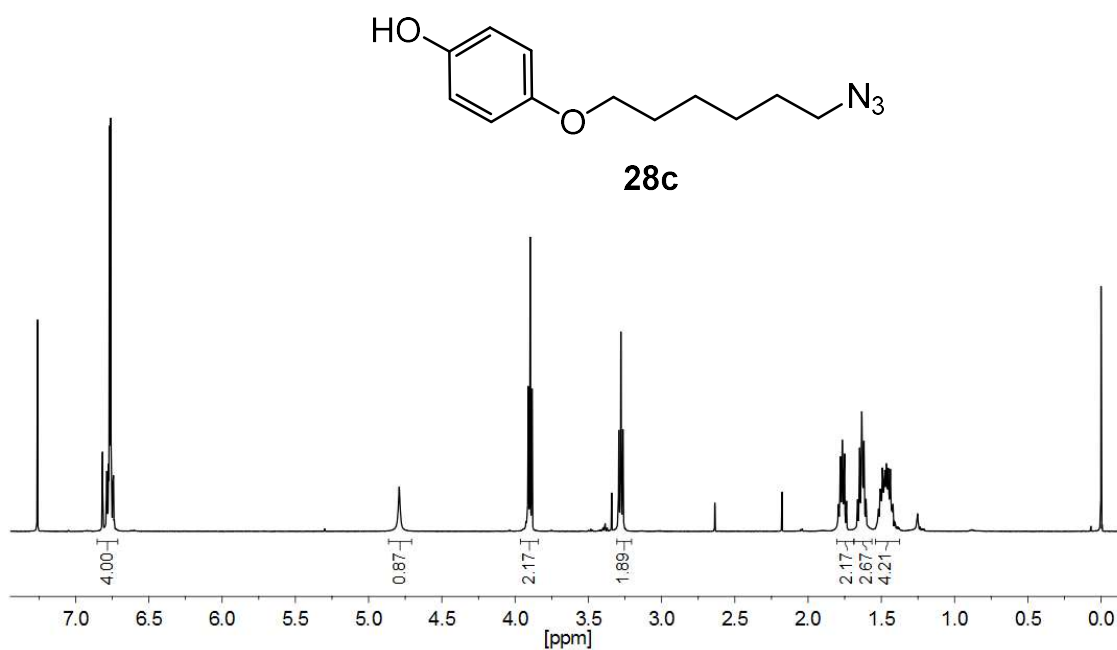
$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ = 153.3 (s, Ar-*C*-4), 149.7 (s, Ar-*C*-1), 116.2 (d, Ar-*C*-2,6), 115.7 (d, Ar-*C*-3,5), 68.6 (t, OCH_2), 51.5 (t, CH_2N_3), 29.4 (t, OCH_2CH_2), 28.9 (t, $\text{CH}_2\text{CH}_2\text{N}_3$), 26.7 (t, $\text{CH}_2\text{CH}_2\text{CH}_2\text{N}_3$), 25.8 (t, $\text{OCH}_2\text{CH}_2\text{CH}_2$) ppm.

IR (ATR): $\tilde{\nu}$ = 3369 (br. m, OH), 2937, 2862 (m, aliph. CH), 2092 (s, azide), 1508, 1446 (s, arom.), 1207, 1027 (CO), 825 (s, 1,4-disubst.) cm^{-1} .

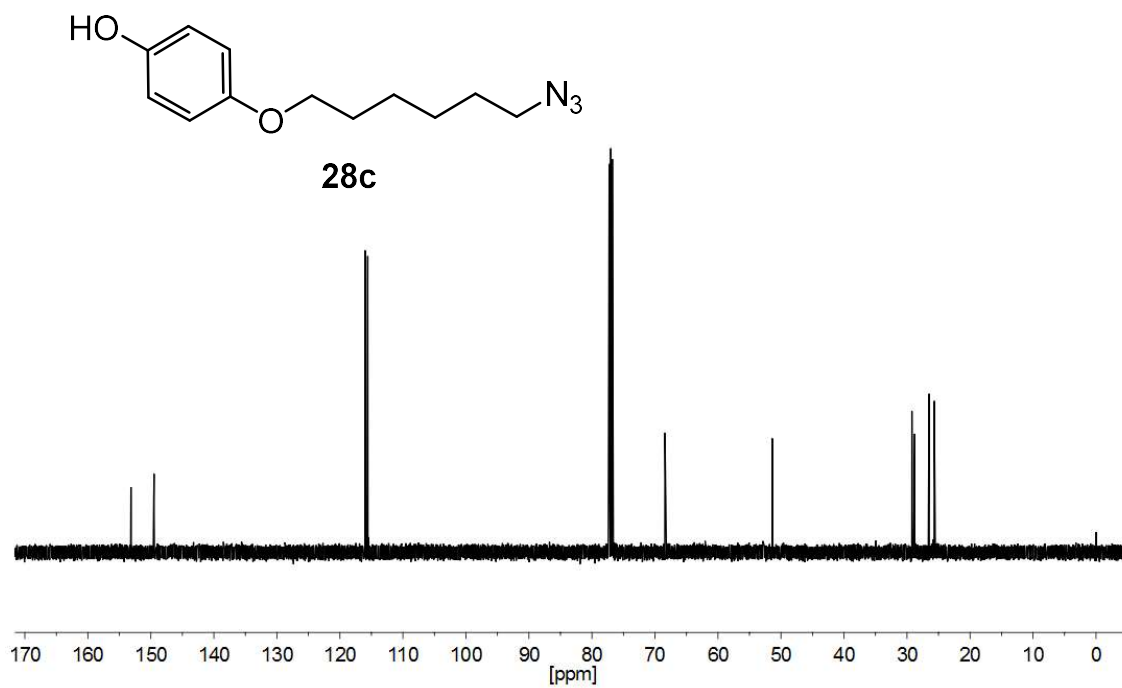
MS (HR-El): $\text{C}_{12}\text{H}_{17}\text{N}_3\text{O}_2$ calcd. m/z = 235.1321, found m/z = 235.1329 (Δ = 3.40 ppm).

Elemental analysis: $\text{C}_{12}\text{H}_{17}\text{N}_3\text{O}_2$: calcd. C 61.26, H 7.28, N 17.86, found C 61.38, H 7.42, N 17.59.

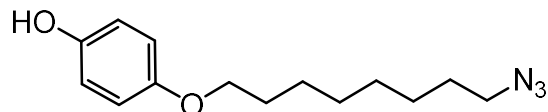
20180119-3-P501Paschelke_5917
 Position 3, Mitarbeiter Paschelke, Sample TP 005 a, Menge 6.0 mg/CDCl₃, Re kein



20180119-3-P501Paschelke_5917
 Position 3, Mitarbeiter Paschelke, Sample TP 005 a, Menge 6.0 mg/CDCl₃, Re kein



4-(8-Azidoctyloxy)phenol (**28d**)



28d

Bromide **27d** (5.00 g, 16.6 mmol) was dissolved in dimethylsulfoxide (20 mL), sodium azide (3.23 g, 50.0 mmol) was added and the mixture was stirred at room temp. for 18 h. Water (20 mL) was added and the aqueous layer was extracted with diethyl ether (3 x 20 mL). The organic layer was dried with magnesium sulfate, filtered and the solvent was removed under vacuum. The crude product was purified by chromatography using silica gel [dichloromethane → dichloromethane/methanol (93 : 7); R_f = 0.3] cleaned. A colorless oil was obtained.

Ausbeute: 3.91 g (14.9 mmol, 90 %).

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 6.81-6.71 (m, 4 H, Ar-*H*-2,3,5,6), 5.04 (s, 1 H, OH), 3.89 (t, 3J = 6.6 Hz, 2 H, OCH_2), 3.25 (t, 3J = 7.0 Hz, 2 H, CH_2N_3), 1.79-1.70 (m, 2 H, OCH_2CH_2), 1.64-1.55 (m, 2 H, $\text{CH}_2\text{CH}_2\text{N}_3$), 1.49-1.41 (m, 2 H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.40-1.29 (m, 6 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{N}_3$, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}_3$) ppm.

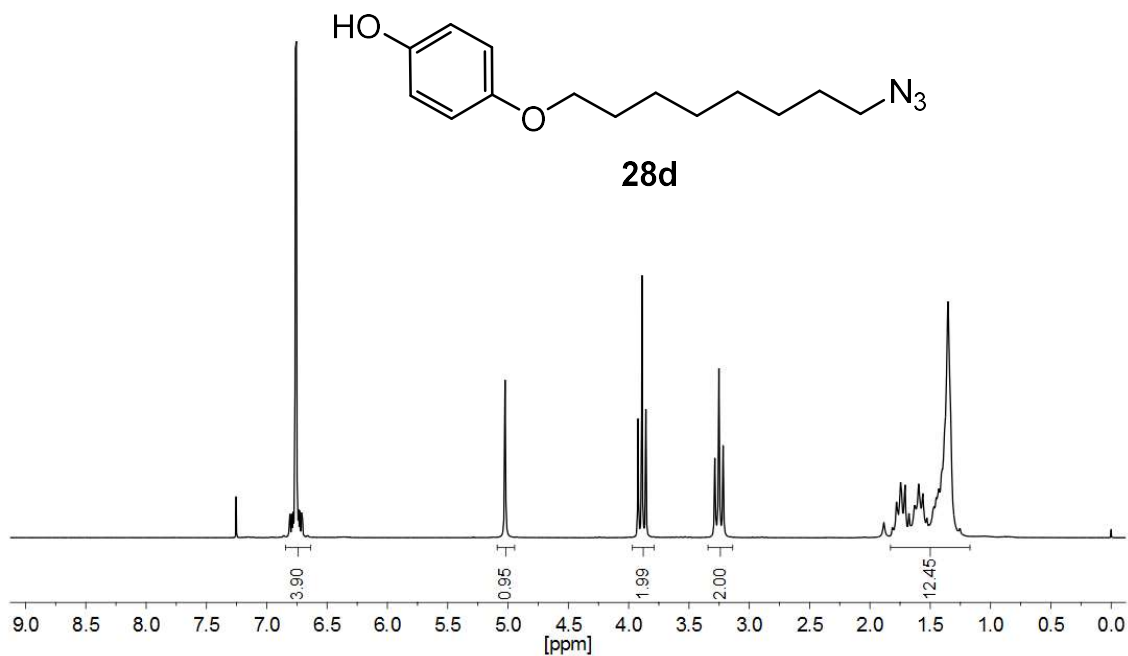
$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ = 153.3 (s, Ar-C-4), 149.6 (s, Ar-C-1), 116.2 (d, Ar-C-2,6), 115.8 (d, Ar-C-3,5), 68.9 (t, OCH_2), 51.6 (t, CH_2N_3), 29.4 (t, OCH_2CH_2), 29.3 (t, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 29.2 (t, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}_3$), 28.9 (t, $\text{CH}_2\text{CH}_2\text{N}_3$), 26.7 (t, $\text{CH}_2\text{CH}_2\text{CH}_2\text{N}_3$), 26.0 (t, $\text{OCH}_2\text{CH}_2\text{CH}_2$) ppm.

IR (ATR): $\tilde{\nu}$ = 3419 (br. s, OH), 2930, 2854 (s, aliph. CH), 2117 (s, azide), 1510, 1453 (s, arom.), 1229, 1034 (CO), 822 (s, 1,4-disubst.) cm^{-1} .

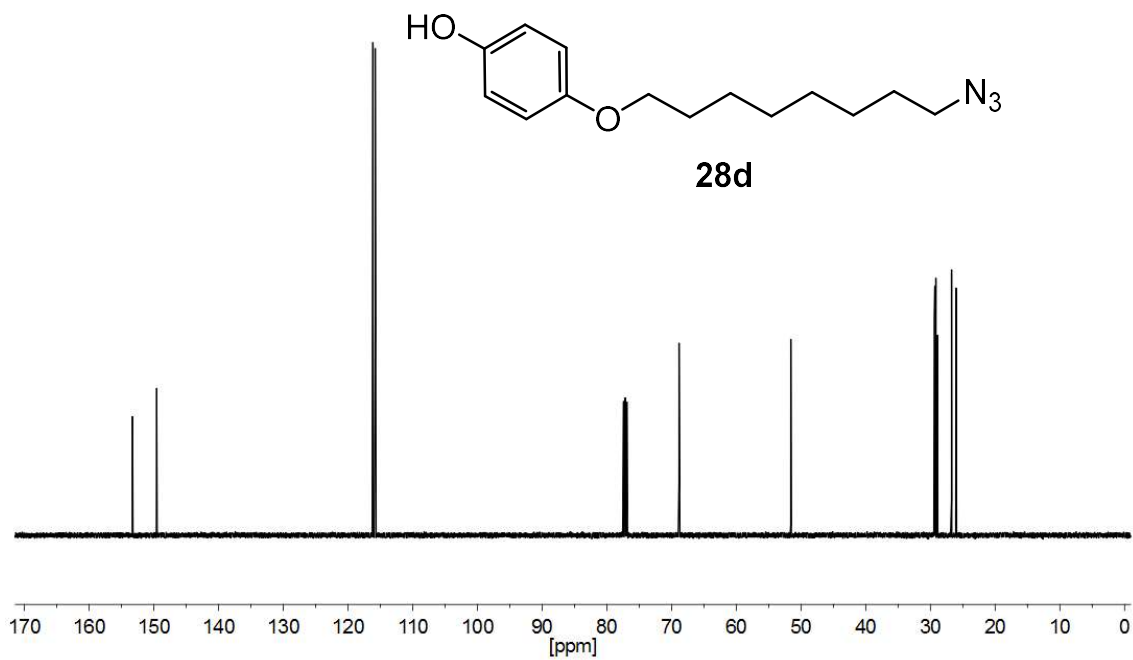
MS (HR-EI): $\text{C}_{14}\text{H}_{21}\text{N}_3\text{O}_2$ calcd. m/z = 263.1634, found m/z = 263.1647 (Δ = 4.84 ppm).

Elemental analysis: $\text{C}_{14}\text{H}_{21}\text{N}_3\text{O}_2$: calcd. C 63.85, H 8.04, N 15.96, found C 63.67, H 8.03, N 15.94.

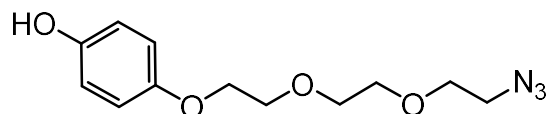
180815-41-L208Duden
 Praktikant/Mitarbeiter Duden, Substanz TD-P-270 F1, Menge 12 mg
 1H64-noplot CDCl3 {D:\uen\18\08} nmrsu 41



20180815-28-L508Duden_8465
 Position 28, Mitarbeiter Duden, Sample TD - P - 270 F 1, Menge 12.0 mg/CDCl3, Re kein



4-{2-[2-(2-Azidoethoxy)ethoxy]ethoxy}phenol (**32**)



32

Under nitrogen atmosphere, 4-(2-{2-[2-(4'-methylbenzenesulfonyloxy)ethoxy]ethoxy}ethoxy)phenol **31** [6] (2.10 g, 5.30 mmol) and sodium azide (4.00 g, 61.5 mmol) were suspended in dry dimethylformamide (20 mL) and stirred at 70 °C for 2 d. Water (50 mL) was added to the suspension and the aqueous phase was extracted with dichloromethane (4 x 50 mL). The organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The raw product was cleaned on silica gel [cyclohexane : ethyl acetate (1 : 1); R_f = 0.5] cleaned. A colourless oil was obtained.

Yield: 1.16 g (4.35 mmol, 84 %).

$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 6.79-6.71 (m, 4 H, Ar-*H*-2,3,5,6), 4.09-4.02 (m, 2 H, Ar- OCH_2), 3.87-3.82 (m, 2 H, Ar- OCH_2CH_2), 3.77-3.72 (m, 2 H, Ar- $\text{OCH}_2\text{CH}_2\text{OCH}_2$), 3.72-3.64 (m, $\text{CH}_2\text{OCH}_2\text{CH}_2\text{N}_3$), 3.41-3.35 (m, 2 H, CH_2N_3) ppm.

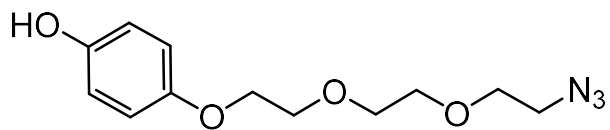
$^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ = 152.9 (s, Ar-*C*-4), 150.0 (s, Ar-*C*-1), 116.2 (d, Ar-*C*-2,6), 115.9 (d, Ar-*C*-3,5), 70.9 (t, Ar- $\text{OCH}_2\text{CH}_2\text{OCH}_2$), 70.8 (t, $\text{CH}_2\text{OCH}_2\text{CH}_2\text{N}_3$), 70.2 (t, $\text{CH}_2\text{CH}_2\text{N}_3$), 70.1 (t, Ar- OCH_2CH_2), 68.2 (t, Ar- OCH_2), 50.8 (t, CH_2N_3) ppm.

IR (ATR): $\tilde{\nu}$ = 3366 (br. m, OH), 2873 (m, aliph. CH), 2100 (s, azide), 1509, 1444 (s, arom.), 1211, 1101, 1062 (s, CO.), 826 (s, 1,4-disubst.) cm^{-1} .

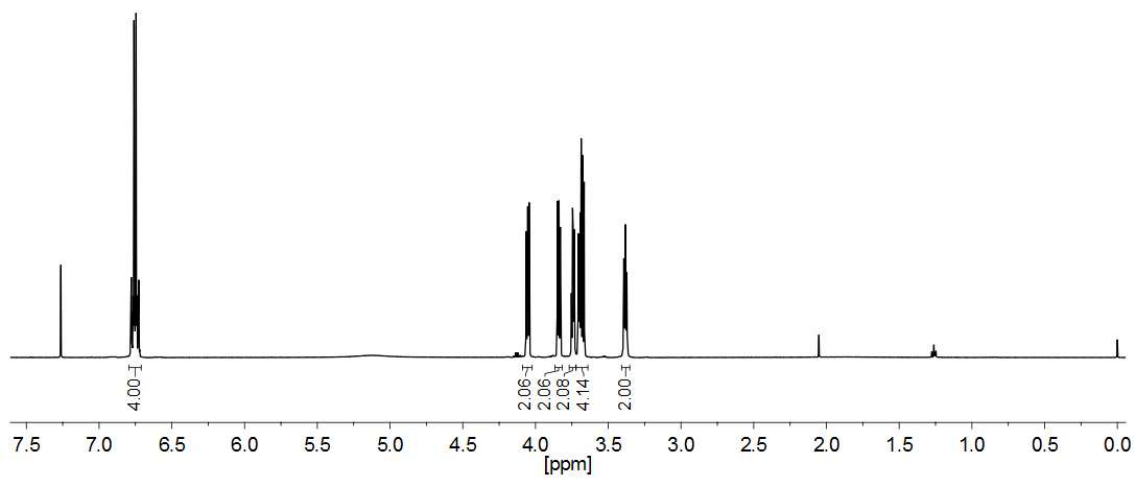
MS (HR-ESI): $\text{C}_{12}\text{H}_{17}\text{N}_3\text{NaO}_3$ calcd. m/z = 290.1111, found m/z = 290.1110 (Δ = -0.53 ppm)

Elemental analysis: $\text{C}_{12}\text{H}_{17}\text{N}_3\text{O}_3$: calcd. C 53.92, H 6.41, N 15.72, found C 53.99, H 6.46, N 15.69.

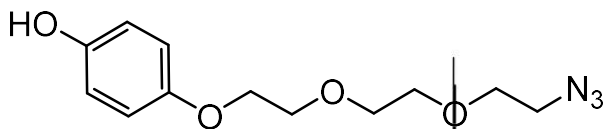
20181102-26-LS11Duden_9534
 Position 26, Mitarbeiter Duden, Sample TD - P -302, Menge 11.0 mg/CDCl₃, Re kein



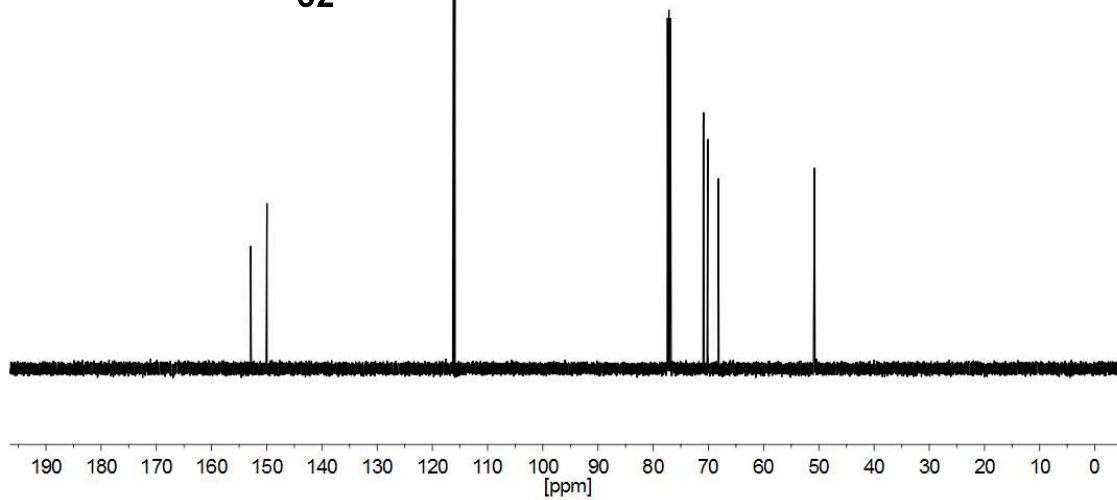
32



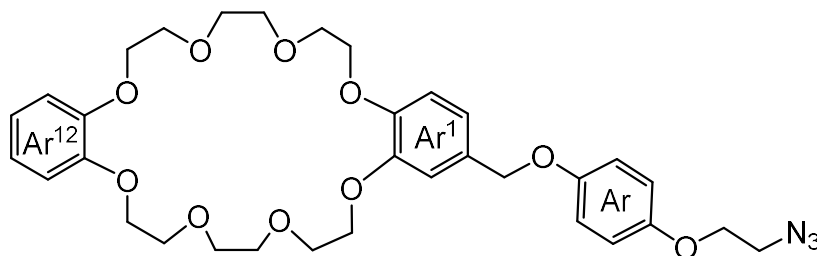
20181102-26-LS11Duden_9534
 Position 26, Mitarbeiter Duden, Sample TD - P -302, Menge 11.0 mg/CDCl₃, Re kein



32



1⁴-[4-(2-Azidoethoxy)phenoxy]methyl]-1,12-[1,2]dibenzena-2,5,8,11,13,16,19,22-octaoxadocosaphan (33a)



33a

Under nitrogen atmosphere, phenol **28a** [7] (200 mg, 1.11 mmol) and cesium carbonate (723 mg, 2.22 mmol) were suspended in dry acetone (100 mL) and stirred under reflux for 2 h. A catalytic amount of potassium iodide and DB24C8-CH₂Br (**24**, 850 mg, 1.57 mmol) were then added and stirred for 16 h under reflux. After cooling, water (50 mL) was added and the aqueous phase extracted with dichloromethane (3 x 50 mL each). The organic phase was dried over magnesium sulphate, filtered and the solvent removed in a vacuum. The raw product was cleaned on silica gel [dichloromethane : acetonitrile (1 : 0) → (3 : 1)]. The colorless solids were recrystallized from *n*-hexane/chloroform.

Yield: 404 mg (632 μmol, 57 %).

Meltingpoint: 84 °C.

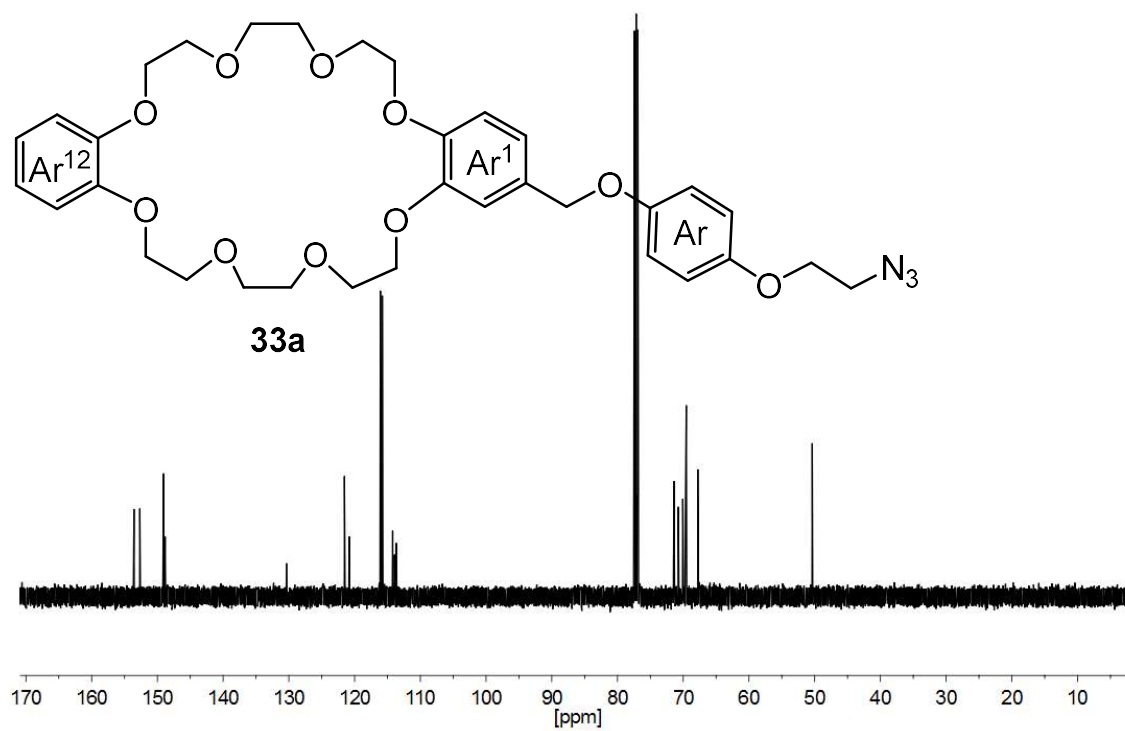
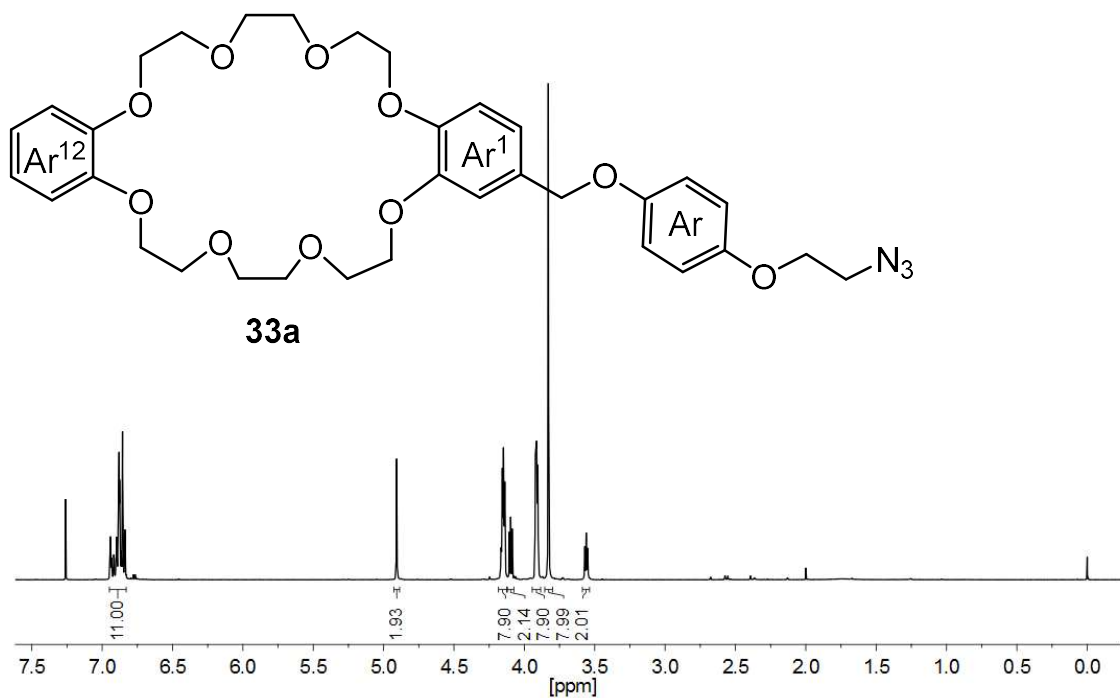
¹H-NMR (500 MHz, CDCl₃): δ = 6.95-6.82 (m, 11 H, Ar¹-H-3,5,6, Ar¹²-H-3,4,5,6, Ar-H-2,3,5,6), 4.91 (s, 2 H, Ar¹-CH₂), 4.16-4.12 (m, 8 H, Ar¹-OCH₂, Ar¹²-OCH₂), 4.10 (t, ³J = 5.3 Hz, 2 H, CH₂CH₂N₃), 3.94-3.88 (m, 8 H, Ar¹-OCH₂CH₂, Ar¹²-OCH₂CH₂), 3.83 (s, 8 H, Ar¹-OCH₂CH₂OCH₂, Ar¹²-OCH₂CH₂OCH₂), 3.56 (t, ³J = 5.3 Hz, 2 H, CH₂N₃) ppm.

¹³C-NMR (125 MHz, CDCl₃): δ = 153.6 (s, Ar-C-1), 152.7 (s, Ar-C-4), 149.2 (s, Ar¹-C-2), 149.1 (s, Ar¹²-C-1,2), 148.8 (s, Ar¹-C-1), 130.3 (s, Ar¹-C-4), 121.6 (d, Ar¹²-C-4,5), 120.8 (d, Ar¹-C-5), 116.1 (d, Ar-C-2,6), 115.8 (s, Ar-C-3,5), 114.2 (d, Ar¹²-C-3,6), 113.9 (d, Ar¹-C-6), 113.6 (d, Ar¹-C-3), 71.43 (t, CH₂), 71.41 (t, CH₂), 70.8 (Ar¹-CH₂), 70.1 (t, CH₂), 70.01 (t, CH₂), 70.00 (t, CH₂), 69.7 (t, CH₂), 69.6 (t, CH₂), 69.5 (t, CH₂), 67.8 (t, CH₂CH₂N₃), 50.4 (t, CH₂N₃) ppm.

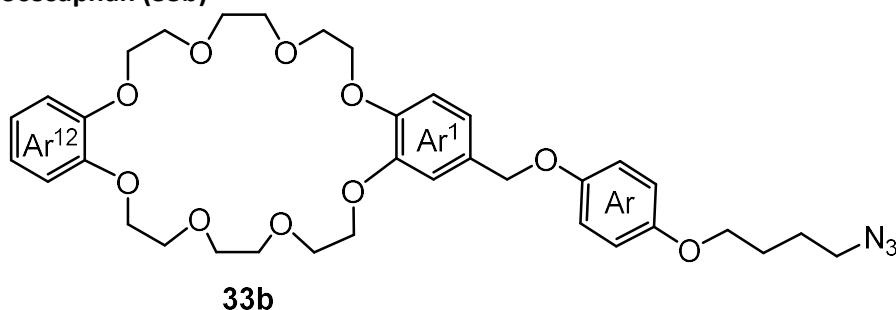
IR (ATR): $\tilde{\nu}$ = 2865 (m, aliph. CH), 2107 (s, azide), 1506, 1452 (s, arom.), 1257, 1214, 1123, 1054 (s, CO), 821 (s, 1,4-disubst.), 736 (s, 1,2-disubst.) cm⁻¹.

MS (HR-ESI): C₃₃H₄₁N₃NaO₁₀ calcd. *m/z* = 662.2684, found *m/z* = 662.2670 (Δ = -1.42 ppm).

Elemental analysis: C₃₃H₄₁N₃O₁₀: calcd. C 61.96, H 6.46, N 6.57, found C 61.89, H 6.47, N 6.88.



1⁴-[4-(4-Azidobutyloxy)phenoxy]methyl]-1,12-[1,2]dibenzena-2,5,8,11,13,16,19,22-octaoxadocosaphan (33b)



Under nitrogen atmosphere, phenol **28b** (842 mg, 4.07 mmol) and cesium carbonate (3.97 g, 12.2 mmol) were suspended in dry acetone (100 mL) and stirred under reflux for 2 h. A catalytic amount of potassium iodide and DB24C8-CH₂Br (**24**, 2.00 g, 3.70 mmol) were then added and stirred for 16 h under reflux. After cooling, water (50 mL) was added and the aqueous phase extracted with dichloromethane (3 x 50 mL). The organic phase was dried over magnesium sulphate, filtered and the solvent removed in a vacuum. The raw product was cleaned on silica gel [dichloromethane : acetonitrile (1 : 0) → (3 : 1)]. The colorless solid was recrystallized from *n*-hexane/chloroform.

Ausbeute: 832 mg (1.25 mmol, 34 %).

Schmelzpunkt: 86 °C.

¹H-NMR (500 MHz, CDCl₃): δ = 6.96-6.76 (m, 11 H, Ar¹-H-3,5,6, Ar¹²-H-3,4,5,6, Ar-H-2,3,5,6), 4.90 (s, 2 H, Ar¹-CH₂), 4.18-4.12 (m, 8 H, Ar¹-OCH₂, Ar¹²-OCH₂), 3.96-3.89 (m, 10 H, Ar-OCH₂CH₂, Ar¹-OCH₂CH₂, Ar¹²-OCH₂CH₂), 3.83 (s, 8 H, Ar¹-OCH₂CH₂OCH₂, Ar¹²-OCH₂CH₂OCH₂), 3.35 (t, ³J = 6.6 Hz, 2 H, CH₂N₃), 1.88-1.74 (m, 4 H, CH₂CH₂CH₂N₃) ppm.

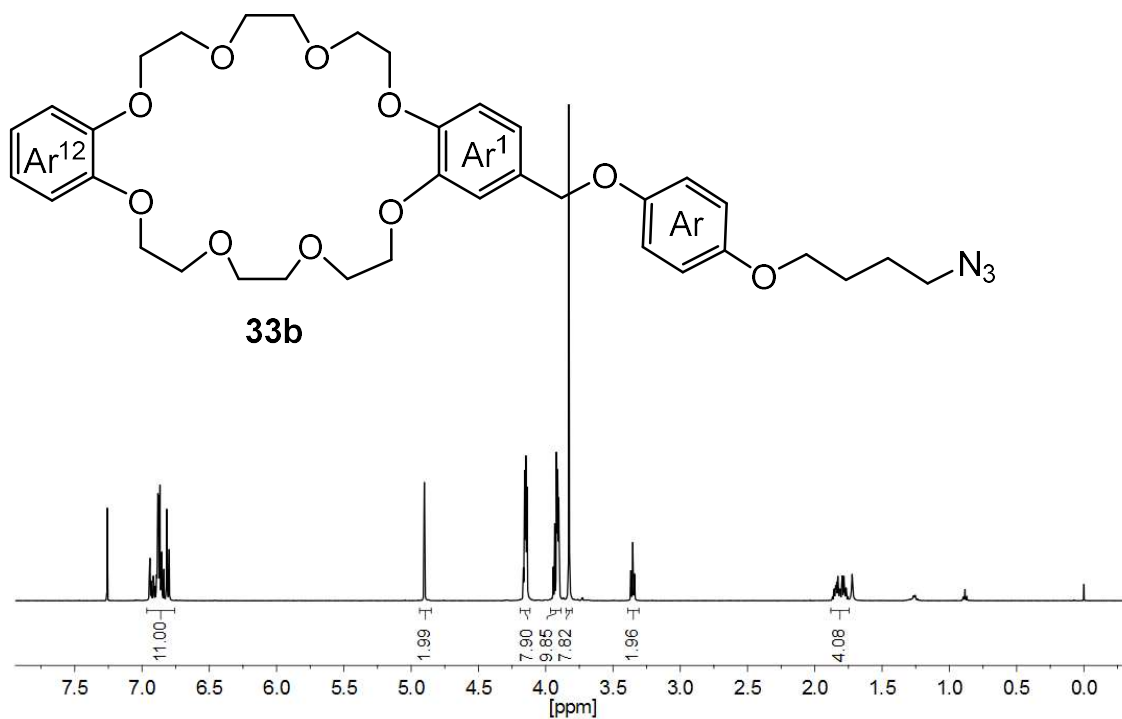
¹³C-NMR (125 MHz, CDCl₃): δ = 153.3 (s, Ar-C-1), 153.1 (s, Ar-C-4), 149.2 (s, Ar¹-C-2), 149.1 (s, Ar¹²-C-1,2), 148.8 (s, Ar¹-C-1), 130.5 (s, Ar¹-C-4), 121.6 (d, Ar¹²-C-4,5), 120.8 (d, Ar¹-C-5), 116.1 (d, Ar-C-2,6), 115.5 (s, Ar-C-3,5), 114.25 (d, Ar¹²-C-3,6), 114.0 (d, Ar¹-C-6), 113.7 (d, Ar¹-C-3), 71.41 (t, CH₂), 71.39 (t, CH₂), 70.8 (t, Ar¹-CH₂), 70.1 (t, CH₂), 70.01 (t, CH₂), 70.00 (t, CH₂), 69.7 (t, CH₂), 69.6 (t, CH₂), 69.5 (t, CH₂), 67.9 (t, Ar-OCH₂CH₂), 51.4 (t, CH₂N₃), 26.7 (t, CH₂CH₂CH₂N₃), 25.9 (t, CH₂CH₂N₃) ppm.

IR (ATR): $\tilde{\nu}$ = 2928 (w, aliph. CH.), 2102 (s, azide), 1507, 1452 (s, arom.), 1219, 1123, 1101, 1052 (s, CO), 823 (s, 1,4-disubst.), 739 (s, 1,2-disubst.) cm⁻¹.

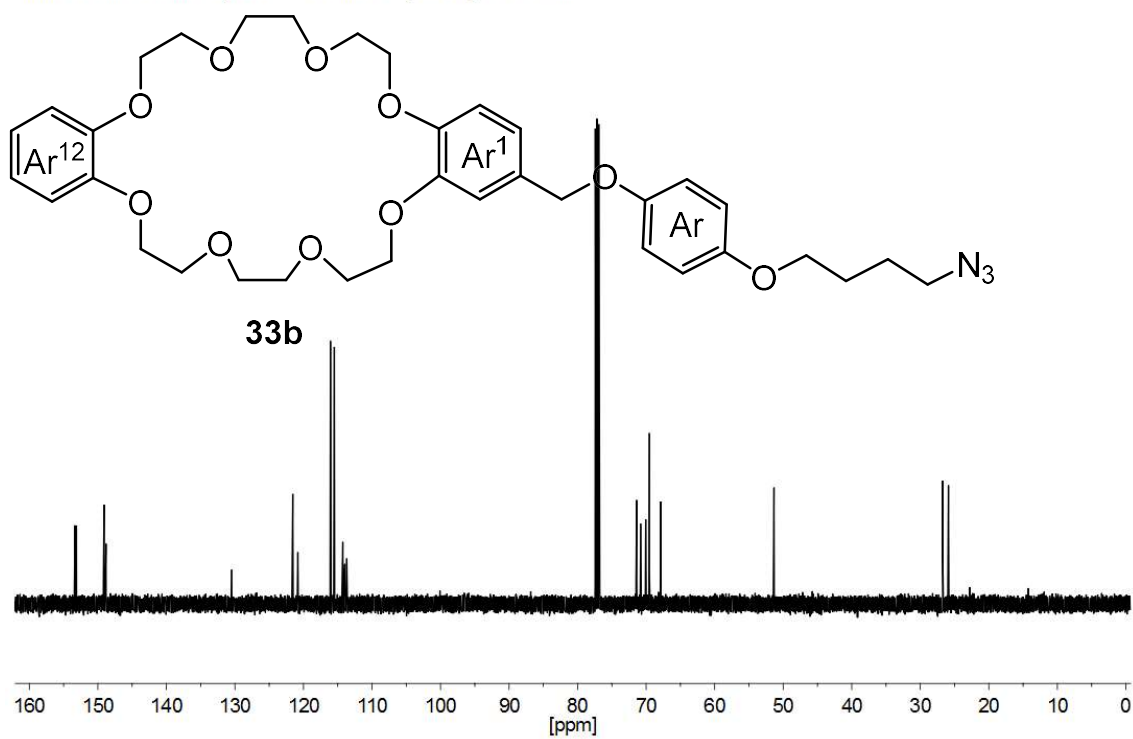
MS (HR-ESI): C₃₅H₄₅N₃NaO₁₀ calcd. *m/z* = 690.2997, found *m/z* = 690.2988 (Δ = -1.30 ppm).

Elemental analysis: C₃₅H₄₅N₃O₁₀: calcd. C 62.95, H 6.79, N 6.29, found C 62.84, H 6.96, N 6.36.

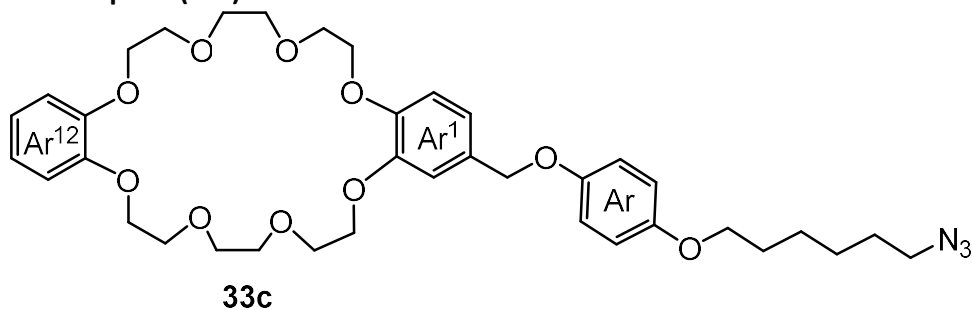
20180815-27-L508Duden_8464
 Position 27, Mitarbeiter Duden, Sample TD - P -262 F 2 umkr, Menge 15.0 mg/CDCl₃, Re kein



20180815-27-L508Duden_8464
 Position 27, Mitarbeiter Duden, Sample TD - P -262 F 2 umkr, Menge 15.0 mg/CDCl₃, Re kein



1⁴-[4-(6-Azidohexyloxy)phenoxyethyl]-1,12-[1,2]dibenzena-2,5,8,11,13,16,19,22-octaoxadocosaphan (33c)



Under nitrogen atmosphere, phenol **28c** (477 mg, 2.03 mmol) and cesium carbonate (2.00 g, 6.06 mmol) were suspended in dry acetone (100 mL) and stirred under reflux for 2 h. A catalytic amount of potassium iodide and DB24C8-CH₂Br (**24**, 1.00 g, 1.85 mmol) were then added and stirred for 16 h under reflux. After cooling, water (50 mL) was added and the aqueous phase extracted with dichloromethane (3 x 50 mL). The organic phase was dried over magnesium sulphate, filtered and the solvent removed in a vacuum. The raw product was cleaned on silica gel [dichloromethane : acetonitrile (1 : 0) → (3 : 1)]. The colorless solid was recrystallized from *n*-hexane/chloroform.

Yield: 968 mg (1.39 mmol, 75 %).

Meltingpoint: 66 °C.

¹H-NMR (500 MHz, CDCl₃): δ = 6.96-6.79 (m, 11 H, Ar¹-H-3,5,6, Ar¹²-H-3,4,5,6, Ar-H-2,3,5,6), 4.90 (s, 2 H, Ar¹-CH₂), 4.18-4.12 (m, 8 H, Ar¹-OCH₂, Ar¹²-OCH₂), 3.94-3.88 (m, 10 H, Ar-OCH₂CH₂, Ar¹-OCH₂CH₂, Ar¹²-OCH₂CH₂), 3.83 (s, 8 H, Ar¹-OCH₂CH₂OCH₂, Ar¹²-OCH₂CH₂OCH₂), 3.28 (t, ³J = 6.9 Hz, 2 H, CH₂N₃), 1.81-1.73 (m, 2 H, Ar-OCH₂CH₂), 1.66-1.60 (m, 2 H, CH₂CH₂N₃), 1.54-1.40 (m, 4 H, Ar-OCH₂CH₂CH₂, CH₂CH₂CH₂N₃) ppm.

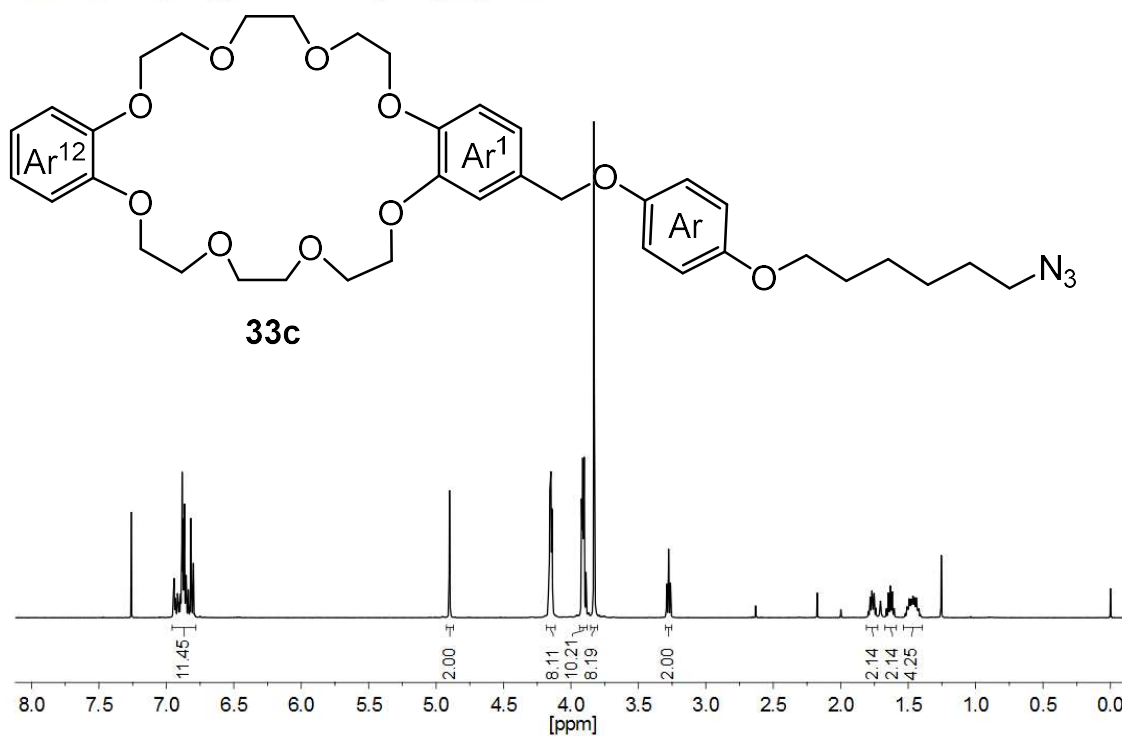
¹³C-NMR (125 MHz, CDCl₃): δ = 153.5 (s, Ar-C-1), 153.0 (s, Ar-C-4), 149.14 (s, Ar¹-C-2), 149.08 (s, Ar¹²-C-1,2), 148.8 (s, Ar¹-C-1), 130.3 (s, Ar¹-C-4), 121.6 (d, Ar¹²-C-4,5), 120.8 (d, Ar¹-C-5), 116.0 (d, Ar-C-2,6), 115.5 (s, Ar-C-3,5), 114.2 (d, Ar¹²-C-3,6), 113.9 (d, Ar¹-C-6), 113.7 (d, Ar¹-C-3), 71.4 (t, CH₂), 70.8 (t, Ar¹-CH₂), 70.1 (t, CH₂), 70.0 (t, CH₂), 69.7 (t, CH₂), 69.6 (t, CH₂), 69.5 (t, CH₂), 68.4 (t, Ar-OCH₂CH₂), 51.5 (t, CH₂N₃), 29.4 (t, Ar-OCH₂CH₂), 28.9 (t, CH₂CH₂N₃), 26.6 (t, CH₂CH₂CH₂N₃), 25.8 (Ar-OCH₂CH₂CH₂) ppm.

IR (ATR): $\tilde{\nu}$ = 2900, 2864 (s, aliph. CH), 2097 (s, azide), 1506, 1451 (s, arom.), 1258, 1221, 1123, 1105, 1055 (s, CO), 820 (m, 1,4-disubst.), 739 (m, 1,2-disubst.) cm⁻¹.

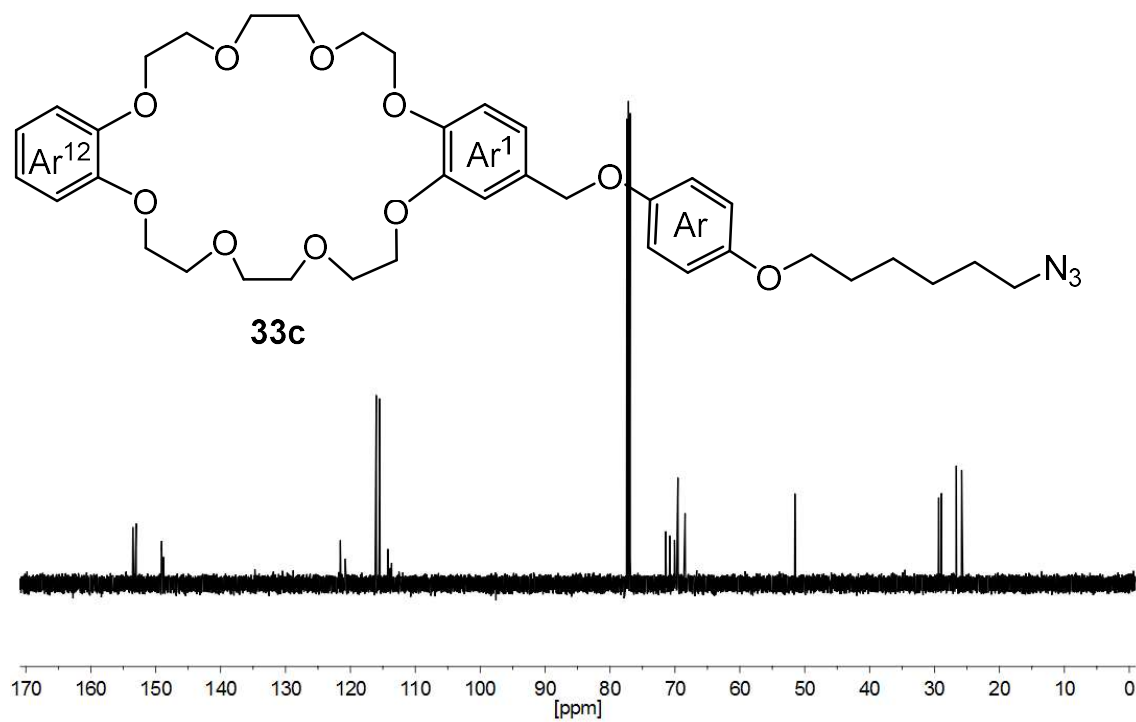
MS (HR-ESI): C₃₇H₄₉N₃NaO₁₀ calcd. *m/z* = 718.3310, found *m/z* = 718.3299 (Δ = -1.57 ppm).

Elemental analysis: C₃₇H₄₉N₃O₁₀: calcd. C 63.87, H 7.10, N 6.04, found C 63.68, H 7.13, N 6.04.

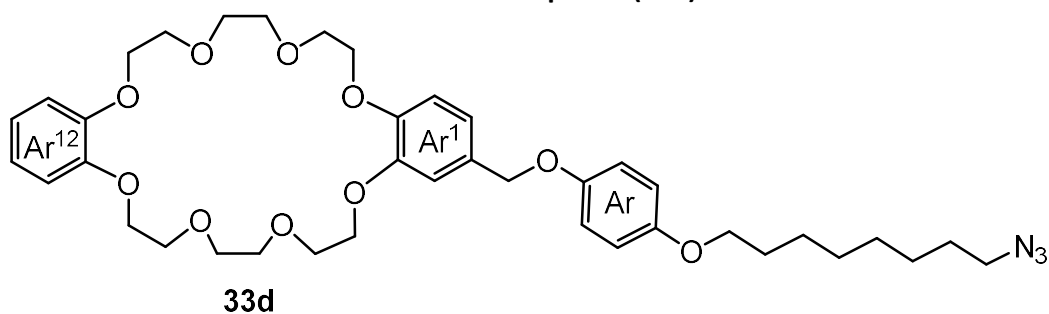
20180208-36-L502Duden_6204
 Position 36, Mitarbeiter Duden, Sample TD - P -205_F 3, Menge 12.0 mg/CDCl3, Re kein



20180208-36-L502Duden_6204
 Position 36, Mitarbeiter Duden, Sample TD - P -205_F 3, Menge 12.0 mg/CDCl3, Re kein



1⁴-[4-(8-Azidooctyloxy)phenoxyethyl]-1,12-[1,2]dibenzena-2,5,8,11,13,16,19,22-octaoxadocosaphane (33d)



Under nitrogen atmosphere, the phenol **28d** (1.07 g, 4.06 mmol) and cesium carbonate (4.00 g, 12.2 mmol) were suspended in dry acetone (100 mL) and stirred under reflux for 2 h. A catalytic amount of potassium iodide and DB24C8-CH₂Br (**24**, 2.00 g, 3.69 mmol) were then added and stirred for 16 h under reflux. After cooling, water (50 mL) was added and the aqueous phase extracted with dichloromethane (3 x 50 mL). The organic phase was dried over magnesium sulphate, filtered and the solvent removed in a vacuum. The raw product was cleaned on silica gel [dichloromethane : acetonitrile (1 : 0) → (3 : 1)]. The colorless solid was recrystallized from *n*-hexane/chloroform.

Ausbeute: 684 mg (946 μmol, 26 %).

Meltingpoint: 65 °C.

¹H-NMR (500 MHz, CDCl₃): δ = 6.96-6.79 (m, 11 H, Ar¹-H-3,5,6, Ar¹²-H-3,4,5,6, Ar-H-2,3,5,6), 4.90 (s, 2 H, Ar¹-CH₂), 4.18-4.11 (m, 8 H, Ar¹-OCH₂, Ar¹²-OCH₂), 3.94-3.87 (m, 10 H, Ar-OCH₂CH₂, Ar¹-OCH₂CH₂, Ar¹²-OCH₂CH₂), 3.83 (s, 8 H, Ar¹-OCH₂CH₂OCH₂, Ar¹²-OCH₂CH₂OCH₂), 3.26 (t, ³J = 7.0 Hz, 2 H, CH₂N₃), 1.79-1.71 (m, 2 H, Ar-OCH₂CH₂), 1.64-1.56 (m, 2 H, CH₂CH₂N₃), 1.49-1.41 (m, 2 H, Ar-OCH₂CH₂CH₂), 1.41-1.31 (m, 6 H, CH₂CH₂CH₂CH₂CH₂N₃) ppm.

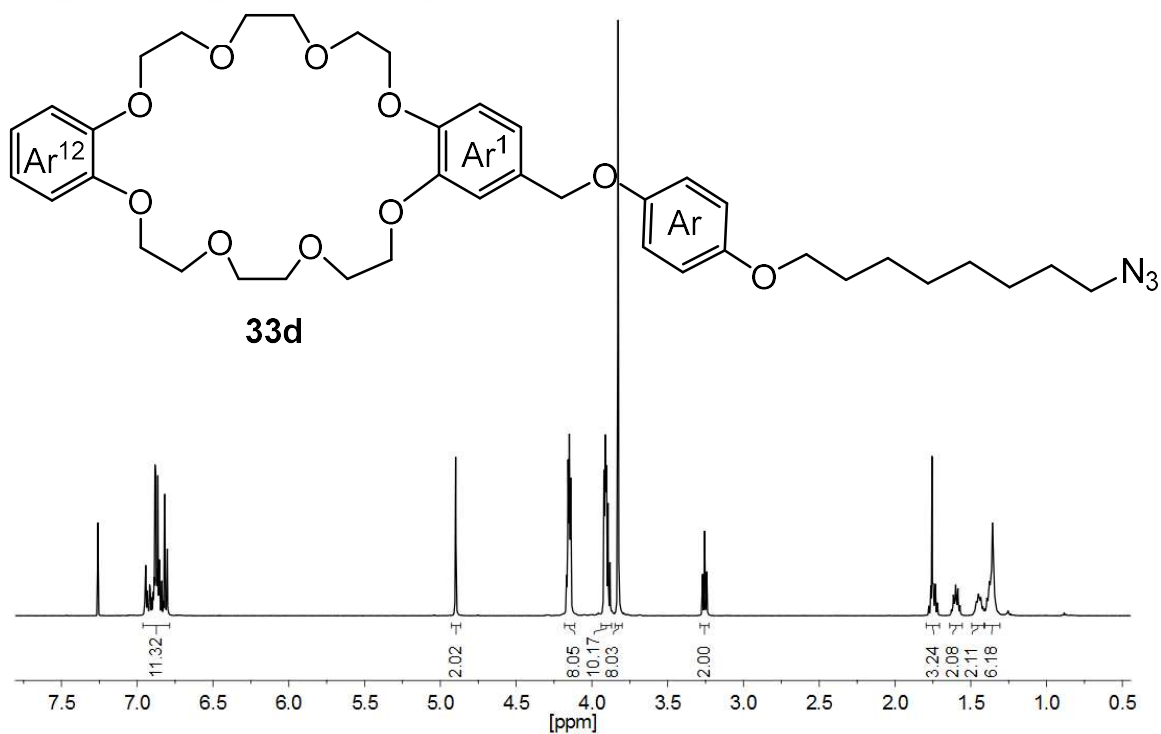
¹³C-NMR (125 MHz, CDCl₃): δ = 153.6 (s, Ar-C-1), 153.0 (s, Ar-C-4), 149.11 (s, Ar¹-C-2), 149.06 (s, Ar¹²-C-1,2), 148.8 (s, Ar¹-C-1), 130.5 (s, Ar¹-C-4), 121.6 (d, Ar¹²-C-4,5), 120.8 (d, Ar¹-C-5), 116.0 (d, Ar-C-2,6), 115.5 (s, Ar-C-3,5), 114.2 (d, Ar¹²-C-3,6), 113.9 (d, Ar¹-C-6), 113.7 (d, Ar¹-C-3), 71.4 (t, CH₂), 70.8 (t, Ar¹-CH₂), 70.04 (t, CH₂), 69.98 (t, CH₂), 69.6 (t, CH₂), 69.54 (t, CH₂), 69.51 (t, CH₂), 68.6 (t, Ar-OCH₂CH₂), 51.6 (t, CH₂N₃), 29.5 (t, Ar-OCH₂CH₂), 29.4 (t, Ar-OCH₂CH₂CH₂CH₂), 29.2 (CH₂CH₂CH₂CH₂N₃), 28.9 (t, CH₂CH₂N₃), 26.8 (t, CH₂CH₂CH₂N₃), 26.1 (t, Ar-OCH₂CH₂CH₂) ppm.

IR (ATR): $\tilde{\nu}$ = 2926, 2853 (m, aliph. CH), 2094 (s, azide), 1507, 1451 (s, arom.), 1258, 1217, 1137, 1126, 1055 (s, CO), 821 (s, 1,4-disubst.), 739 (s, 1,2-disubst.) cm⁻¹.

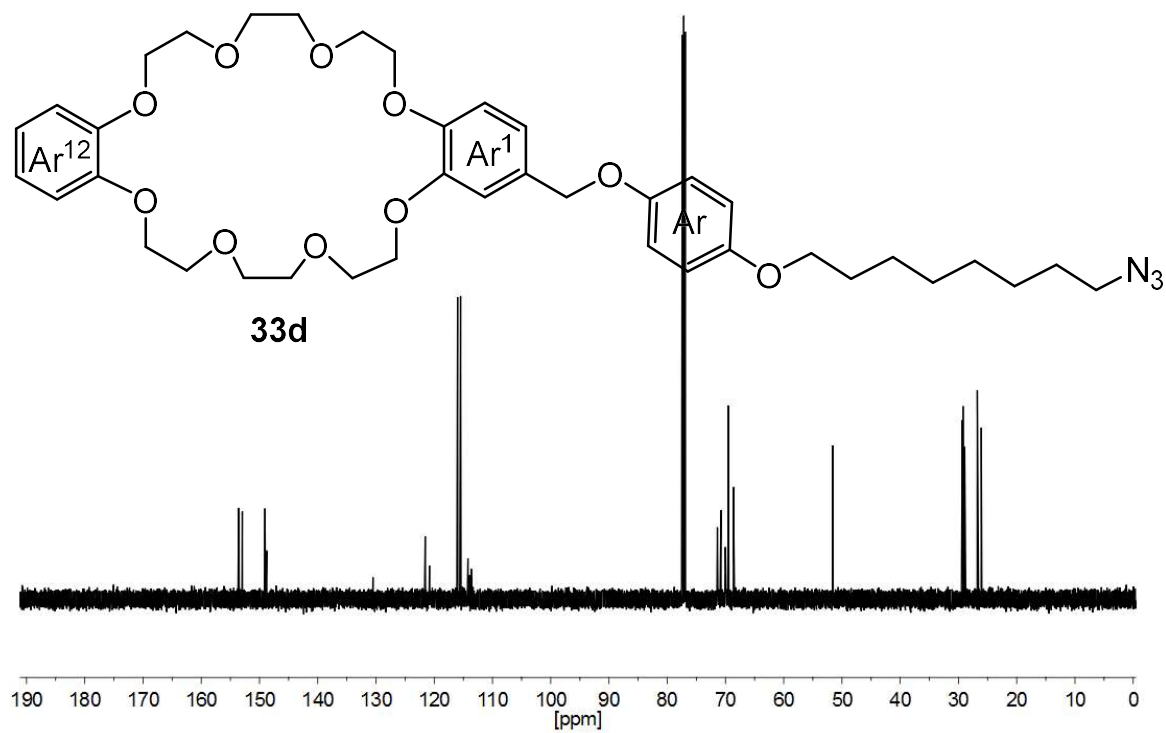
MS (HR-ESI): C₃₉H₅₃N₃NaO₁₀ calcd. *m/z* = 746.3623, found *m/z* = 746.3623 (Δ = -0.05 ppm).

Elemental analysis: C₃₉H₅₃N₃O₁₀: calcd. C 64.71, H 7.38, N 5.81, found C 64.76, H 7.20, N 5.95.

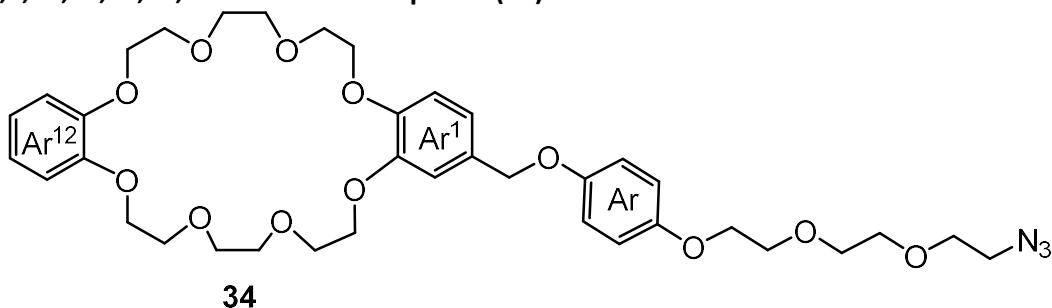
20180822-18-L508Duden_8617
 Position 18, Mitarbeiter Duden, Sample TD - P -274 F 3, Menge 15.0 mg/CDCl₃, Re kein



20180822-18-L508Duden_8617
 Position 18, Mitarbeiter Duden, Sample TD - P -274 F 3, Menge 15.0 mg/CDCl₃, Re kein



1⁴-(4-{2-[2-(2-Azidoethoxy)ethoxy]ethoxy}phenoxy)methyl)-1,12-[1,2]dibenzena-2,5,8,11,13,16,19,22-octaoxadocosaphane (34)



Under nitrogen atmosphere, phenol **32** (1.26 g, 4.72 mmol) and cesium carbonate (4.60 g, 14.0 mmol) were suspended in dry acetone (100 mL) and stirred under reflux for 2 h. A catalytic amount of potassium iodide and DB24C8-CH₂Br (**24**, 2.43 g, 4.48 mmol) were then added and stirred for 16 h under reflux. After cooling, water (50 mL) was added and the aqueous phase extracted with dichloromethane (3 x 50 mL). The organic phase was dried over magnesium sulphate, filtered and the solvent removed in a vacuum. The raw product was cleaned on silica gel [dichloromethane : acetonitrile (1 : 0) → (3 : 1)]. The colorless solid was recrystallized from *n*-hexane/chloroform.

Yield: 1.22 g (1.77 mmol, 37 %).

Meltingpoint: 62 °C.

¹H-NMR (500 MHz, CDCl₃): δ = 6.96-6.81 (m, 11 H, Ar¹-H-3,5,6, Ar¹²-H-3,4,5,6, Ar-H-2,3,5,6), 4.90 (s, 2 H, Ar¹-CH₂), 4.17-4.13 (m, 8 H, Ar¹-OCH₂, Ar¹²-OCH₂), 4.08 (t, ³J = 5.2 Hz, 2 H, Ar-OCH₂CH₂), 3.93-3.89 (m, 8 H, Ar¹-OCH₂CH₂, Ar¹²-OCH₂CH₂), 3.86-3.81 (m, 10 H, Ar¹-OCH₂CH₂OCH₂, Ar¹²-OCH₂CH₂OCH₂, Ar-OCH₂CH₂), 3.75-3.71 (m, 2 H, Ar-OCH₂CH₂OCH₂), 3.70-3.66 (m, 4 H, CH₂OCH₂CH₂N₃), 3.38 (t, ³J = 5.1 Hz, 2 H, CH₂N₃) ppm.

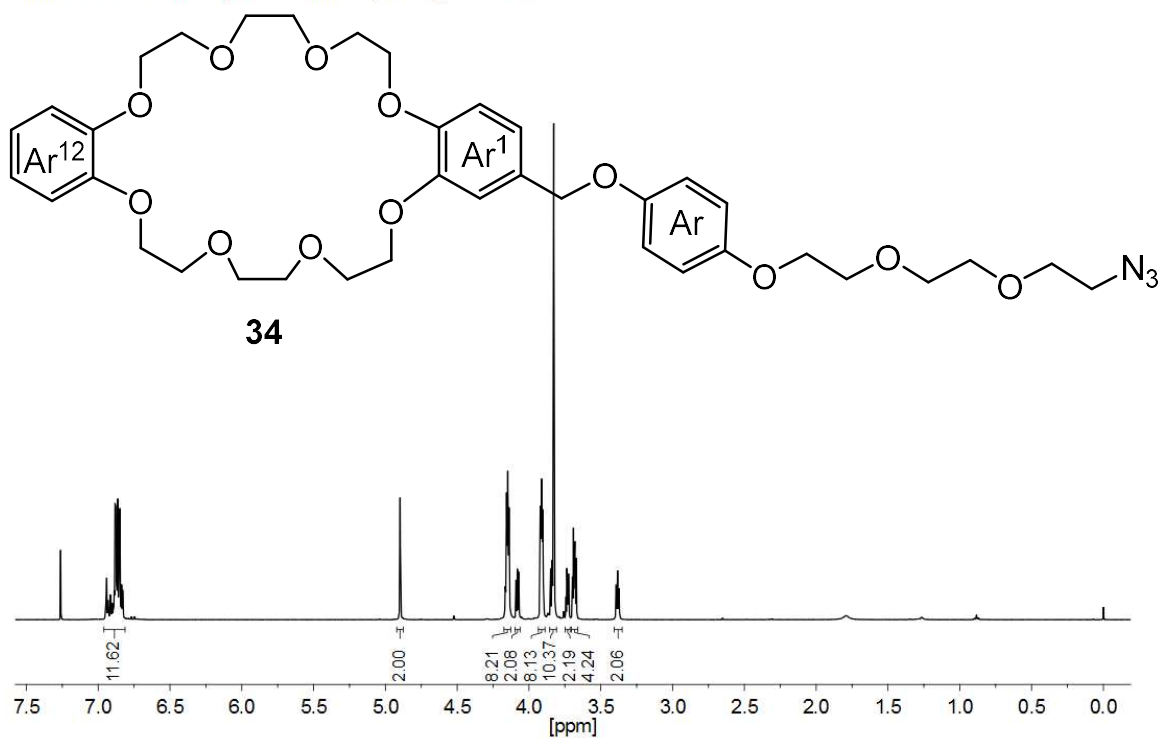
¹³C-NMR (125 MHz, CDCl₃): δ = 153.24 (s, Ar-C-1), 153.21 (s, Ar-C-4), 149.12 (s, Ar¹-C-2), 149.07 (s, Ar¹²-C-1,2), 148.8 (s, Ar¹-C-1), 130.4 (s, Ar¹-C-4), 121.5 (d, Ar¹²-C-4,5), 120.8 (d, Ar¹-C-5), 116.0 (d, Ar-C-2,6), 115.7 (s, Ar-C-3,5), 114.2 (d, Ar¹²-C-3,6), 113.9 (d, Ar¹-C-6), 113.6 (d, Ar¹-C-3), 71.4 (t, CH₂), 71.0 (t, CH₂), 70.9 (t, CH₂), 70.7 (t, Ar¹-CH₂), 70.2 (t, CH₂), 70.08 (t, CH₂), 70.05 (t, CH₂), 70.00 (t, CH₂), 69.98 (t, CH₂), 69.7 (t, CH₂), 69.6 (t, CH₂), 69.5 (t, CH₂), 68.2 (t, Ar-OCH₂CH₂), 50.8 (t, CH₂N₃) ppm.

IR (ATR): $\tilde{\nu}$ = 2875 (m, aliph. CH), 2101 (s, azide), 1508, 1447 (s, arom.), 1229, 1104, 1062 (s, CO), 834 (s, 1,4-disubst.), 750 (s, 1,2-disubst.) cm⁻¹.

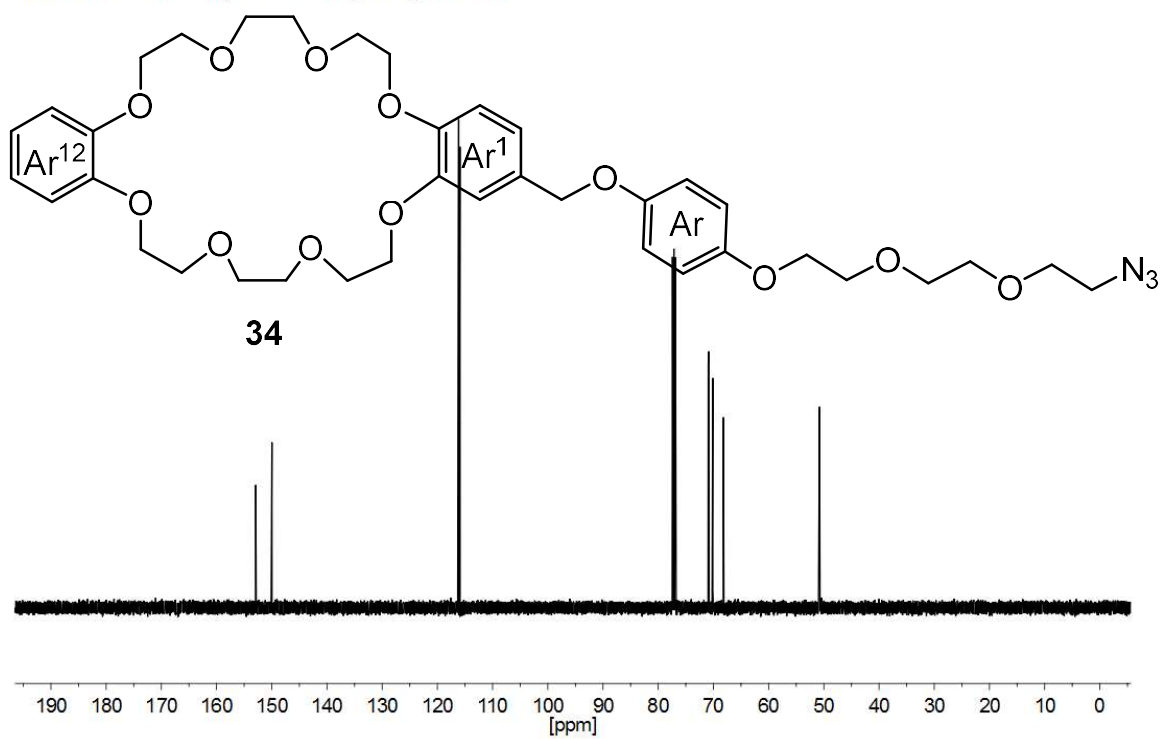
MS (HR-ESI): C₃₇H₄₉N₃NaO₁₂ calcd. *m/z* = 750.3208, found *m/z* = 750.3204 (Δ = -0.62 ppm).

Elemental analysis: C₃₇H₄₉N₃O₁₂: calcd. C 61.06, H 6.79, N 5.77, found C 60.70, H 6.76, N 5.73.

20181108-37-LS11Duden_9620
Position 37, Mitarbeiter Duden, Sample TD - P - 308 cm, Menge 20.0 mg/CDCl₃, Re kein



20181102-26-LS11Duden_9534
Position 26, Mitarbeiter Duden, Sample TD - P - 302, Menge 11.0 mg/CDCl₃, Re kein



References

1. Chavez-Acevedo, L.; Miranda, L. D. Synthesis of novel tryptamine-based macrocycles using an Ugi 4-CR/microwave assisted click-cycloaddition reaction protocol, *Org. Biomol. Chem.* **2015**, *13*, 4408-4412.
2. Talotta, C.; Gaeta, C.; Pierro, T.; Neri, P., Sequence stereoisomerism in calixarene-based pseudo[3]rotaxanes, *Org. Lett.* **2011**, *13*, 2098-2101.
3. Zhang, Y., Lai, L.; Cai, P.; Cheng, G.-Z.; Xuc, X.-M.; Liua, Y. Synthesis, characterization and anticancer activity of dinuclear ruthenium(ii) complexes linked by an alkyl chain, *New J. Chem.* **2015**, *39*, 5805-5812.
4. Aucagne, V.; Hänni, K.D.; Leigh, D.A.; Lusby, P.J.; Walke, D.B. Catalytic click rotaxanes: a substoichiometric metal-template pathway to mechanically interlocked architectures, *J. Am. Chem. Soc.* **2006**, *128*, 2186-2187.
5. Yamaguchi, N.; Gibson, H.W. Formation of supramolecular polymers from homoditopic molecules containing secondary ammonium ions and crown ether moieties, *Angew. Chem.* **1999**, *111*, 195-199; *Angew. Chem. Int. Ed.* **1999**, *38*, 143-147.
6. Yang, Y.; Fu, H.; Cui, M.; Peng, C.; Liang, Z.; Dai, J.; Zhang, Z.; Lin, C.; Liu, B. Preliminary evaluation of fluoro-pegylated benzyloxybenzenes for quantification of β -amyloid plaques by positron emission tomography, *Eur. J. Med. Chem.* **2015**, *104*, 86-96.
7. Lim, J.Y.C.; Marques, I.; Thompson, A.L.; Christensen, K.E.; Félix, V.; Beer, P.D. Chalcogen bonding macrocycles and [2]rotaxanes for anion recognition, *J. Am. Chem. Soc.* **2017**, *139*, 3122-3133.