Shape-Persistent Macrocycles with Terpyridine Units: Synthesis, characterization, and structure in the crystal

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Supporting Information

Experimental Section

General Information

All commercially available substances were purchased from Aldrich, Merck, Lancaster, ABR or Acros, and used without further purification. Solvents were purified and dried – if necessary – according to standard methods.[1] The catalyst $Pd(PPh_3)_4$ was synthesized according to literature[2] and stored in the dry-box. For reactions with this catalyst, the solvents, solutions or suspensions were degassed by a repeated cycle of evacuation and gasing with nitrogen. The nitrogen was purchased from Messer-Griesheim as Nitrogen 4.0 or 5.0.

NMR spectrometry: The spectra were recorded on a Bruker WH 270 MHz or AC 500 MHz with the solvent itself as inner standard. If not stated otherwise, measurements were done at room temperature. All shifts are given in ppm. The deuterated solvents were purchased from Merck or Deutero GmbH. **EI and FAB(+) mass spectrometry:** Spectra were recorded with a Varian MAT 771 or MAT 112 S spectrometer. **MALDI-TOF mass spectrometry:** Spectra were recorded with a Kratos MALDI 3 from Shimadzu. Please note that values given for signals in MALDI generally refer to the lowest mass isotope of a specific ion (not for the isotope with highest intensity!). **Elemental analysis:** It was used a Perkin-Elmer EA 240. **Melting points:** They were recorded using Büchi 510 (open capillaries, uncorrected values). **Analytical TLC:** Reactions were checked by TLC with TLC-ready charts by Merck (no. 5554, aluminium sheets with silica gel Si 60 with fluorescence indicator F_{254}), or TLC-ready charts by Macherey-Nagel (Polygram Alox N/UV_{254}, ready foils with 0.2 mm aluminium oxide with fluorescent indicator F_{254}). Detection was in UV light with wavelength λ = 254 or λ = 366 nm. If not stated otherwise, silica gel TLC charts were used. **Preparative column chromatography:** The chromatography was run with Merck flash silica gel (230-400 mesh ASTM, grain size 40-60 pm), Machery-Nagel silica gel 60 M (230-400 mesh ASTM, grain size 40-63 pm), or Fluka aluminium oxide neutral (Typ 507 C, 0.05-0.15 mm). **Analytical GPC:** Measurements were performed with a Waters Assoc.

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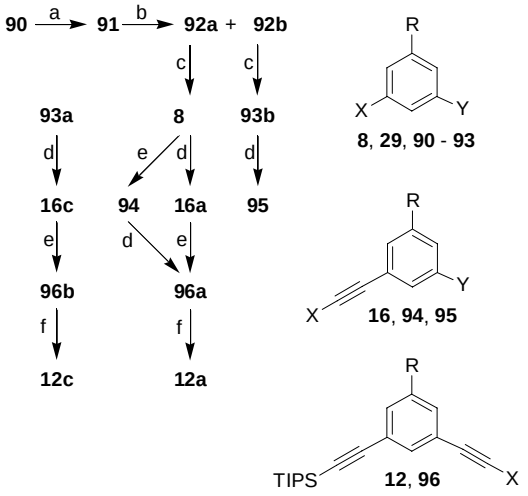
[1] (1a) Tietze, L. F.; Eicher, T. *Reaktionen und Synthesen im organisch-chemischen Praktikum und Forschungslaboratorium*, Thieme-Verlag, Stuttgart **1991**; (1b) *Organikum, organisch-chemisches Grundpraktikum*, 20.ed., Johann Ambrosius Barth Verlag, Stuttgart **1996**

[2] Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121-124.

150-c Alc/GPC chromatograph by using the column set Waters Styragel HR columns. As mobile phase, THF was used. Detection was by a Waters 410 RI detector or a 484 UV/VIS detector against polystyrene as calibration standard. **Preparative GPC:** Separation was by using a Waters machine with UV detection; the mobile phase was THF. Separation columns were Waters Styragel HR columns. In some cases, material was contaminated with THF oligomers after preparative GPC;[3] the material could be purified by precipitation as described in the corresponding procedures.

Schemes 8 and 9

Scheme 8. Synthesis and/or structure of basic compounds **8**, **12**, **16**, **29**, **90**-**96**

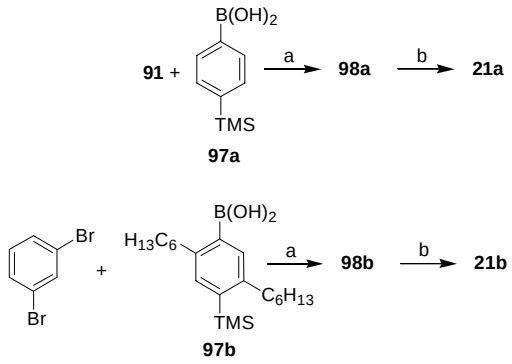


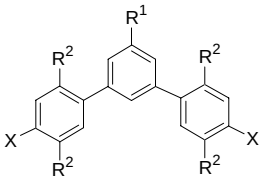
	R	X	Y	Yield
8	OC_6H_{13}	Br	I	97 %
12a	OC_6H_{13}	H	-	99 %
12b	$CH_2OC_6H_{13}$	H	-	-
12c	CH_2OTHP	H	-	98 %
16a	OC_6H_{13}	TMS	Br	97 %
16b	$CH_2OC_6H_{13}$	TMS	Br	-
16c	CH_2OTHP	TMS	Br	85 %
29	$CH_2OC_6H_{13}$	I	I	-
90	OH	Br	Br	-
91	OC_6H_{13}	Br	Br	97 %
92a	OC_6H_{13}	Br	TMS	90 %
92b	OC_6H_{13}	TMS	TMS	11 %
93a	CH_2OTHP	Br	I	-
93b	OC_6H_{13}	I	I	93 %
94	OC_6H_{13}	TIPS	Br	79 %
95	OC_6H_{13}	TMS	I	56 %
96a	OC_6H_{13}	TMS	-	84 % (**16a**)
				91 % (**94**)
96b	CH_2OTHP	TMS	-	72 %

Reagents and conditions: (a) $C_6H_{13}Br$, K_2CO_3, 18-crown-6, diethylketone. (b) 1.*n*-BuLi 2.TMSCl, ether. (c) ICl, CH_2Cl_2. (d) TMS-acetylene, Pd^0/CuI, TEA. (e) TIPS-acetylene, Pd^0/CuI, TEA. (f) NaOH, methanol/CH_2Cl_2.

[3] This is described in: Beinhoff, M. PhD thesis, FU Berlin, Germany **2002**, http://www.diss.fu-berlin.de/2002/13

Scheme 9. Synthesis of the terphenyl units **21a**, **b**





	R^1	R^2	X	Yield
21a	OC_6H_{13}	H	I	93 %
21b	H	C_6H_{13}	I	89 %
98a	OC_6H_{13}	H	TMS	86 %
98b	H	C_6H_{13}	TMS	81 %

Reagents and conditions: (a) Pd^0, toluene / $Na_2CO_{3(aqu.)}$. (b) ICl, CH_2Cl_2.

Synthetic procedures

For those compounds mentioned in the Main Article which were prepared according to literature procedures, see there. The following compounds, which only appear in this SI part, have been prepared according to literature procedures: **90** (solvent benzene replaced by toluene),[4] **93a**,[5] **97a**,[6] and **97b**.[7]

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[4] (a) Kraus, R.; Spiteller, G. *Org. Mass. Spectrom.* **1989**, *24*, 861-865. (b) For a short overview over recent trends in hydro-de-bromination, see: Effenberger, F. *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 1699-1700. (c) For a recent procedure to generate the related compound 1,3-diiodo phenol, see: Höger, S.; Bonrad, K.; Mourran, A.; Beginn, U.; Möller, M. *J. Am. Chem. Soc.* **2001**, *123*, 5651-5659.

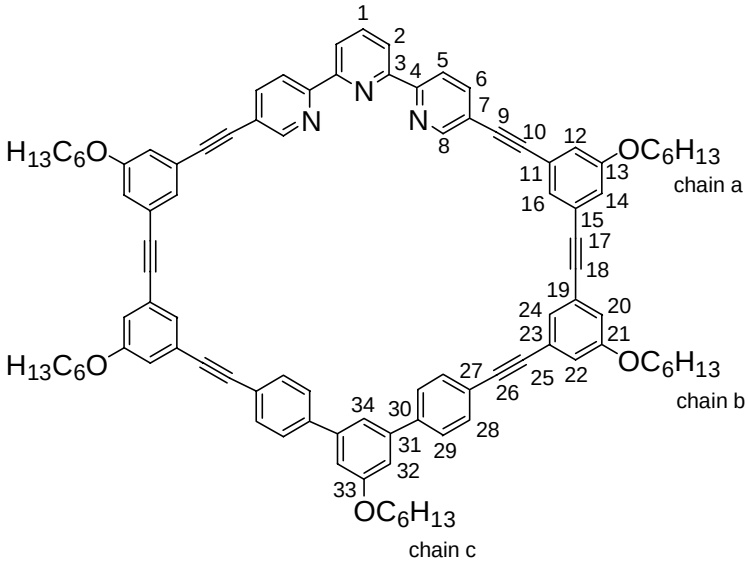
[5] Henze, O. PhD thesis **2000**, FU Berlin, Germany, http://www.diss.fu-berlin.de/2000/47/.

[6] Lützow, K. PhD thesis **1997**, FU Berlin, Germany.

[7] Hensel, V.; Schlüter, A. D. *Liebigs Ann./Recueil* **1997**, *130*, 303-309.

15,22,33,44,51-Pentakis(hexyloxy)-8,58,72-triaza-undecacyclo[54.2.2.1^{2,6}.2^{2,7}.1^{13,17}.1^{20,24}.2^{27,30}.1^{31,35}.2^{36,39}.1^{42,46}.1^{49,53}]diheptaconta-1(58),2,4,6(72),7,9,13,15,17(69),20,22,24(68),27,29,31,33,35(65),36,38,42,44,46(62),49,51,53(61),56,59,63,66,70-triacontaen-11,18,25,40,47,54-hexayne, $C_{99}H_{97}N_3O_5$, M = 1408.87, ***1a***

A solution of **20a** (90 mg, 0.083 mmol) and **21a** (48 mg, 0.083 mmol) in dried toluene/ triethylamine (60 ml, 1:1) was freeze-degassed twice. $Pd[P(Ph_3)]_4$ (8 mg, 0.007 mmol) and CuI (1.3 mg, 0.007 mmol) were added, the mixture degassed again and stirred at 60°C in a sealed flask for 4 days, and at 80°C for one more day. The mixture was allowed to cool down and stirred with an aqueous solution of KCN (50 mg KCN, 50 ml H_2O) for 30 mins. The phases were separated, the aqueous phase was extracted with toluene (50 ml), the combined organic phases with water (100 ml), and dried over $MgSO_4$. The solvent was evaporated in vacuo to yield a brownish raw product (110 mg, solid after freeze-drying). From this, cycle **1a** was isolated as a yellow, amorphous material (25 mg, 0.018 mmol, 21 %) by preparative GPC, and likewise **[1a]$_2$** (14 mg, 0.005 mmol, 12 %).



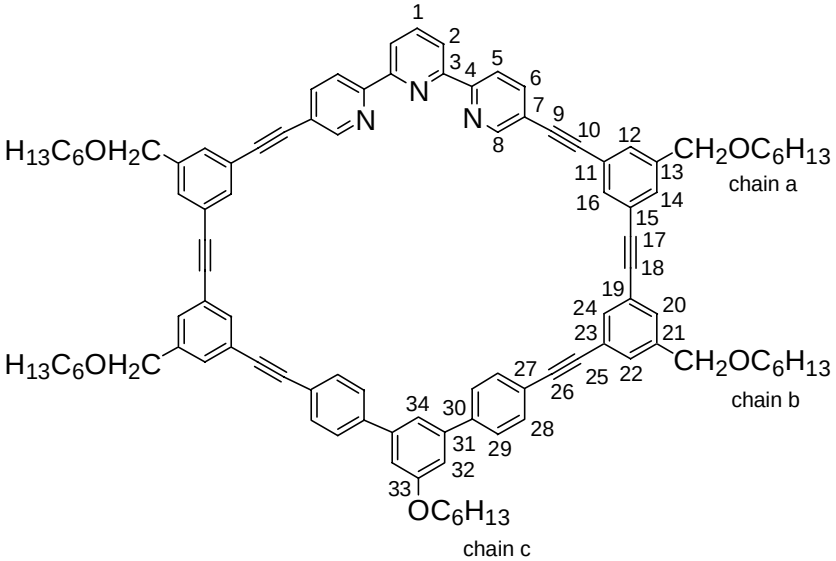
^{1}H-NMR (500 MHz, d^8-THF, 320 K): δ = 8.95 (d, 2 H, ^{4}J = 1.5 Hz, 8-H), 8.90 (d, 2 H, ^{3}J = 8.0 Hz, 5-H), 8.70 (d, 2 H, ^{3}J = 7.5 Hz, 2-H), 8.18 (dd, 2 H, ^{3}J = 8.0 Hz, ^{4}J = 2.0 Hz, 6-H), 8.15 (t, 1 H, ^{3}J = 7.5 Hz, 1-H), 7.94 (d, 4 H, ^{3}J = 8.5 Hz, 29-H), 7.77 (d, 4 H, ^{3}J = 8.5 Hz, 28-H), 7.75 (m, 1 H, 34-H), 7.53 and 7.50 (2 s, 4 H, H-16, H-24), 7.38 (s, 2 H, 32-H), 7.29, 7.25, 7.24 and 7.20 (4 s, 8 H, 12-H, 14-H, 20-H, 22-H), 4.29 (t, 2 H, ^{3}J = 6.0 Hz, α-CH_2 (c-chain)), 4.23 and 4.21 (2 t, 8 H, ^{3}J = 6.5 Hz, α-CH_2 (a,b-chain)), 1.97-2.01 (m, 10 H, β-CH_2 (a,b,c-chain)), 1.70 (s br, 10 H, γ-CH_2 (a,b,c-chain)), 1.57 (s br, 20 H, δ,ε-CH_2 (a,b,c-chain)), 1.11 (t, 15 H, ^{3}J = 7.0 Hz, -CH_3 (a,b,c-chain)). **^{13}C-NMR** (125.8 MHz, d^8-THF, 320 K): δ = 161.31 (33-C), 160.15 (13-C, 21-C), 155.79 (4-C), 155.57 (3-C), 152.06 (8-C), 142.59 (31-C), 141.67 (30-C), 140.04 (6-C), 138.43 (1-C), 132.69 (28-C), 128.52 and 128.39 (16-C, 24-C), 127.73 (29-C), 125.59, 125.33, 125.10 and 124.93 (11-C, 15-C, 19-C, 23-C), 123.06 (27-C), 122.10 (2-C),

120.94 (5-C), 118.57, 118.30 and 118.13 (12-C, 14-C, 20-C, 22-C, 34-C), 113.06 (32-C), 93.32, 89.91, 89.79 and 89.48 (10-C, 17-C, 18-C, 25-C), 90.33 (26-C), 87.50 (9-C), 69.11 (α-C (a,b-hexyl)), 68.83 (α-C (c-hexyl)), 32.40 (δ-C (a,b,c-hexyl)), 30.25 (β-C (c-hexyl)), 30.01 (β-C (a,b-hexyl)), 26.62 (γ-C (c-hexyl)), 26.49 (γ-C (a,b-hexyl)), 23.35 (ε-C (a,b,c-hexyl)), 14.17 (methyl-C (a,b,c-hexyl)); 7-C could not be assigned. **MS** (**FAB(+)**, MNBA/CH_2Cl_2-Matrix): m/z (%) = 1409 $[M+H]^+$.

Cyclic oligomer, $C_{198}H_{194}N_6O_{10}$, M = 2817.74, ***[1a]₂***

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.75 (s, 4 H), 8.57 (d, 4 H, ^{3}J = 8.2 Hz), 8.42 (d, 4 H, ^{3}J = 8.0 Hz), 7.91-7.93 (m, 6 H), 7.60 (s br, 16 H), 7.33 (m, 6 H), 7.27 (s br, 4 H), 7.24 (s, 4 H), 7.00-7.07 (m, 16 H), 3.96 (m, 20 H), 1.78 (s br, 20 H), 1.46 (s br, 20 H), 1.23-1.34 (m, 40 H), 0.90 (s br, 30 H). **^{13}C-NMR** (125.8 MHz, $CDCl_3$): δ = 159.98, 158.81, 154.73, 154.57, 151.54, 142.19, 140.89, 139.31, 137.88, 132.12, 127.44, 127.15, 124.43, 124.24, 124.09, 123.72, 122.15, 121.44, 120.36, 120.07, 118.36, 118.09, 117.72, 112.40, 92.78, 89.48, 89.08, 88.77, 86.68, 68.25, 31.55, 29.69, 29.11, 25.68, 22.62, 22.00, 14.07. **MS** (**MALDI**, THA): m/z (%) = 2943.81 $[M+CH_3]^+$, 2929.02 $[M+H]^+$.

33-Hexoxy-15,22,44,51-tetrakis(hexoxymethyl)-8,58,72-triazaundecacyclo[54.2.2.1^{2,6}.2^{2,7}.1^{13,17}.1^{20,24}.2^{27,30}.1^{31,35}.2^{36,39}.1^{42,46}.1^{49,53}]diheptaconta-1(58),2,4,6(72),7,9,13,15,17(69),20,22,24(68),27,29,31,33,35(65),36,38,42,44,46(62),49,51,53(61),56,59,63,66,70-triacontaen-11,18,25,40,47,54-hexayne, $C_{103}H_{105}N_3O_5$, M = 1464.98, ***1b***



The procedure was analogous to that described for **1a** (**20b**: 1.08 g, 0.944 mmol; **21a**: 549 mg, 0.944 mmol; $Pd[P(Ph_3)]_4$: 87 mg, 0.076 mmol; CuI: 14 mg, 0.076 mmol; toluene/triethylamine: 700 ml, 1:1). The raw product (1.48 g, solid after freeze-drying) was worked up by preparative GPC to give cycle **1b** (290 mg, 0.20 mmol, 21 %) and cyclic oligomer **$[1b]_2$** (132 mg, 0.043 mmol, 9 %) as yellow, amorphous materials after freeze-drying. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 8.64 (s, 2 H, 8-H), 8.48 (d, 2 H, ^{3}J = 7.5 Hz, 5-H), 8.33 (d, 2 H, ^{3}J = 7.5 Hz, 2-H), 7.82 (t, 1 H, ^{3}J = 8.0 Hz, 1-H), 7.79 (d, 2 H, ^{3}J = 7.0 Hz, 6-H), 7.53 (d, 4 H, ^{3}J = 7.5 Hz, 29-H), 7.50 (s, 4 H, H-16, H-24), 7.45 (d, 4 H, ^{3}J = 7.5 Hz, 28-H), 7.37 (s, 1 H, 34-H, overlayed with H-12 etc.), 7.37, 7.31, 7.26 (3 s, 8 H, 12-H, 14-H, 20-H, 22-H), 6.95 (s, 2 H, 32-H), 4.47, 4.37 (2s, 8 H, aryl-CH_2 (a,b-chain)), 3.97 (t, 2 H, ^{3}J = 6.5 Hz, α-CH_2 (c-chain)), 3.54, 3.51 (2 t, 8 H, ^{3}J = 6.5 Hz, α-CH_2 (a,b-chain)), 1.82 (quintet, 2 H, ^{3}J = 7.0 Hz, β-CH_2 (c-chain)), 1.69 (sextet, 8 H, ^{3}J ≈ 6 Hz, β-CH_2 (a,b-chain)), 1.48 (quintet, 2 H, ^{3}J ≈ 7 Hz, γ-CH_2 (c-chain)), 1.36-1.48 (m, 28 H, γ-CH_2 (a,b-chain), δ,ε-CH_2 (a,b,c-chain)), 0.93-0.98 (m, 15 H, -CH_3 (a,b,c-chain)). **^{13}C-NMR** (125.8 MHz, $CDCl_3$): δ = 159.89 (33-C), 154.42, 154.24 (3-C, 4-C), 151.16 (8-C), 141.38 (31-C), 140.14 (30-C), 139.41, 139.25 (13-C, 21-C), 139.18 (6-C), 137.52 (1-C), 134.18, 134.09 (16-C, 24-C), 131.97 (28-C), 130.19, 129.95 (2 signals), 129.76 (12-C, 14-C, 20-C, 22-C), 126.67 (29-C), 123.61, 123.46, 123.21, 122.98 (11-C, 15-C, 19-C, 23-C), 122.10 (27-C), 121.15 (2-C), 120.18 (5-C), 119.98 (7-C), 117.50 (34-C), 111.98 (32-C), 92.70, 89.40, 89.29, 89.01 (10-C, 17-C, 18-C, 25-C), 89.80 (26-C), 87.06 (9-C), 71.94, 71.89 (aryl-CH_2 (a,b-chain)), 70.92, 70.84 (α-C (a,b-chain)), 68.06 (α-C (c-chain)), 31.70 (δ-C (a,b-chain)), 31.66 (δ-C (c-chain)), 29.72 (β-C (a,b-chain)), 29.36 (β-C (c-chain)), 25.88 (γ-C (a,b-chain)), 25.80 (γ-C (c-chain)), 22.63 (ε-C (a,b,c-chain)), 14.04 (methyl-C (a,b,c-chain)). **MS** (**FAB(+)**, MNBA/CH_2Cl_2-Matrix): m/z (%) = 1465 $[M+H]^+$. **MS** (**MALDI**, THA): m/z (%) = 1478.86 $[M+CH_3]^+$, 1464.90 $[M+H]^+$, 1392.77 $[M-C_5H_{11}]^+$, 1378.78 $[M-C_6H_{13}]^+$.

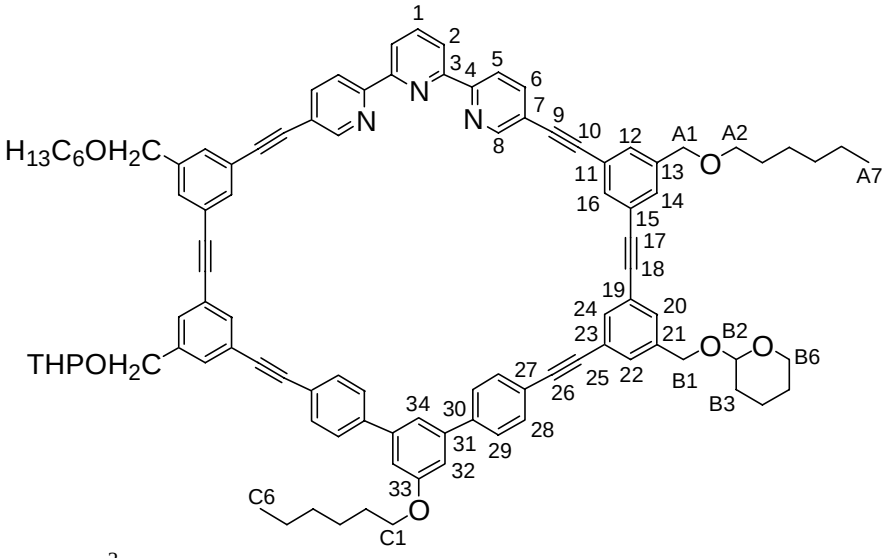
Cyclic oligomer $C_{206}H_{210}N_6O_{10}$, M = 2929.96, ***$[1b]_2$***

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.79 (s, 4 H), 8.61 (d, 4 H, ^{3}J = 8.0 Hz), 8.45 (d, 4 H, ^{3}J = 7.5 Hz), 7.92-7.95 (m, 6 H), 7.61-7.65 (m, 24 H), 7.46-7.49 (m, 8 H), 7.38 (s, 4 H), 7.10 (s, 6 H), 4.50 (s, 8 H), 4.49 (s, 8 H), 4.05 (t, 4 H, ^{3}J = 6.0 Hz), 3.50 (t, 8 H, ^{3}J = 6.5 Hz), 3.49 (t, 8 H, ^{3}J = 6.5 Hz), 1.82 (quintett, 4 H, ^{3}J = 7.0 Hz), 1.63-1.68 (m, 16 H), 1.47-1.49 (m, 4 H), 1.27-1.47 (m, 56 H), 0.87-0.91 (m, 30 H). **^{13}C-NMR** (125.8 MHz, $CDCl_3$): δ = 160.04, 154.85, 154.66, 151.58,

142.22, 140.95, 139.68, 139.57, 139.27, 137.89, 133.83, 132.08, 130.67, 130.42, 130.25, 127.15, 123.71, 123.54, 123.37, 123.03, 122.21, 121.49, 120.38, 120.11, 118.35, 112.51, 92.70, 89.92, 89.34, 88.98, 87.01, 71.91, 71.86, 70.90, 70.85, 68.25, 31.66, 31.57, 29.68, 29.29, 25.84, 25.74, 22.61, 14.03. **MS** (**MALDI**, THA): m/z (%) = 2952.60 $[M+Na]^+$, 2944.66 $[M+CH_3]^+$, 2930.77 $[M+H]^+$, 2844.89 $[M-C_6H_{13}]^+$.

15,51-Bis(hexoxymethyl)-22,24-di-(tetrahydropyran-2-yloxymethyl)-8,58,72-triaza-undecacyclo [54.2.2.2.1^{2,6}.2^{2,7}.1^{13,17}.1^{20,24}.2^{27,30}.1^{31,35}.2^{36,39}.1^{42,46}.1^{49,53}]diheptaconta-1(58),2,4,6(72),7,9,13,15, 17(69),20,22,24(68),27,29,31,33,35(65),36,38,42,44,46(62),49,51,53(61),56,59,63,66,70-triacontaen-11,18,25,40,47,54-hexayne, $C_{101}H_{97}N_3O_7$, M = 1464.89, ***1c***

The procedure was analogous to that described for **1a** (**20c**: 600 mg, 0.527 mmol; **21a**: 307 mg, 0.527 mmol; toluene/triethylamine: 260 ml/260 ml; $Pd[P(Ph_3)]_4$: 49 mg, 0.042 mmol; CuI: 8 mg, 0.042 mmol). From the brownish raw product (850 mg, solid after freeze-drying), cycle **1c** and oligomer **[1c]$_2$** were isolated by preparative GPC. These were dissolved in THF (ca. 5 ml), precipitated with methanol (ca. 8 ml), centrifugated, and the solvent layer taken off. This procedure was repeated once, to afford **1c** (135 mg, 0.092 mmol, 18 %) and **[1c]$_2$** (38 mg, 0.013 mmol, 5 %) as yellow, amorphous materials after freeze-drying.



^{1}H-NMR (500 MHz, $CDCl_3$, 293 K): δ = 8.53 (s, 2 H, 8-H), 8.37 (d, 2 H, ^{3}J = 7.5 Hz, 5-H), 8.24 (d, 2 H, ^{3}J = 7.5 Hz, 2-H), 7.74 (t, 1 H, ^{3}J = 7.5 Hz, 1-H), 7.67 (d, 2 H, ^{3}J = 7.5 Hz, 6-H), 7.45 (d, 4 H, ^{3}J = 7.2 Hz, 29-H), 7.38 (s, 4 H, H-16, H-24), 7.35 (d, 4 H, ^{3}J = 7.2 Hz, 28-H), 7.31 (s, 3 H, 34-H and 12-H or 14-H), 7.28 and 7.29 (2 s, 4 H, 12-H or 14-H, and 20-H or 22-H), 7.23 (s, 2 H, 20-H or 22-H), 6.85 (s, 2 H, 32-H), 4.73 (t, 2 H, ^{3}J = 2.5 Hz, B2-H), 4.68 (d, 2 H, ^{2}J = 12.0 Hz, B1-H), 4.38 (d, 2 H, ^{2}J = 12.0 Hz, B1'-H), 4.42 (s, 4 H, A1-H), 3.94 (dt, 2 H, ^{2}J = 10.0 Hz, ^{3}J = 2.2 Hz, B6-H), 3.58-3.61 (m, 2 H, B6'-H), 3.89 (t, 2 H, ^{3}J = 5.5 Hz, C1-H), 3.51 (t, 4 H, ^{3}J = 6.5 Hz, A2-H), 1.92-1.94 (m, 2 H, B3-H), 1.72-1.82 (m,

6 H, B3'-H, C2-H, B4-H,), 1.65-1.74 (m, 6 H, A3-H, B5-H), 1.60-1.65 (m, 6 H, B4'-H, B5'-H, C3-H), 1.45-1.49 (m, 2 H, C4-H), 1.34-1.45 (m, 14 H, A4-H, A5-H, A6-H, C5-H), 0.90-0.97 (m, 9 H, A7-H, C6-H). **^{13}C-NMR** (125.8 MHz, $CDCl_3$, 293 K): δ = 159.75 (33-C), 154.07 and 154.24 (3-C, 4-C), 151.04 (8-C), 141.10 (27-C or 31-C), 139.90 (30-C), 139.23 (13-C), 138.97 (6-C), 138.64 (21-C), 137.31 (1-C), 133.98 and 134.04 (16-C, 24-C), 131.88 (28-C), 129.81 and 130.06 (12-C, 14-C, 20-C, 22-C), 126.48 (29-C), 122.91, 123.10, 123.33 and 123.53 (11-C, 15-C, 19-C, 23-C), 121.97 (27-C or 31-C), 120.97 (2-C), 120.00 (5-C), 119.84 (7-C), 117.18 (34-C), 111.80 (32-C), 97.81 (B2-C), 88.95 and 92.59 (10-C, 17-C), 89.74 (26-C), 89.21 and 89.30 (18-C, 25-C), 87.04 (9-C), 71.85 (A1-C), 70.86 (A2-C), 67.85 (B1-C, C1-C), 62.02 (B6-C), 31.66 (A5-C, C5-C), 30.48 (B3-C), 29.67 (A3-C), 29.33 (C2-C), 25.83 (A4-C), 25.76 (C3-C), 25.42 (B5-C), 22.60 (A6-C, C4-C), 19.27 (B4-C), 14.01 (A7-C, C6-C). **MS** (**MALDI**, THA): m/z (%) = 1562.58 $[M+C_5H_7O_2]^+$, 1486.68 $[M+Na]^+$, 1464.51 $[M+H]^+$.

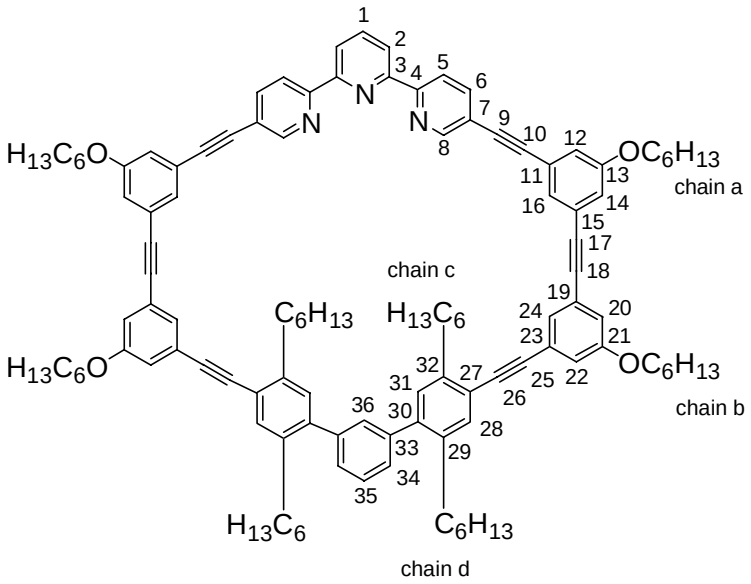
Cyclic oligomer, $C_{202}H_{194}N_6O_{14}$, M = 2929.78, ***[1c]$_2$***

^{1}H-NMR (500 MHz, $CDCl_3$,): δ = 8.78 (d, 2 H, ^{4}J = 1.5 Hz), 8.60 (d, 2 H, ^{3}J = 7.5 Hz), 8.46 (d, 2 H, ^{3}J = 7.5 Hz), 7.93-7.98 (m, 3 H), 7.66 (t, 2 H, ^{4}J = 1.5 Hz), 7.57-7.65 (m, 10 H), 7.51 (s br, 2 H), 7.44-7.49 (m, 6 H), 7.37 (t, 1 H, ^{4}J = 1.0 Hz), 7.09 (d, 2 H, ^{4}J = 1.5 Hz), 4.77 (d, 2 H, ^{2}J = 12.0 Hz), 4.73 (t, 2 H, ^{3}J = 3.5 Hz), 4.49 (s, 4 H), 4.48 (d, 2 H, ^{2}J = 13.0 Hz), 4.04 (t, 2 H, ^{3}J = 6.5 Hz), 3.91 (dt, 2 H, ^{2}J = 10.0 Hz, ^{3}J = 2.5 Hz), 3.55-3.59 (m, 2 H), 3.48 (t, 4 H, ^{3}J = 7.0 Hz), 1.85-1.91 (m, 2 H), 1.54-1.83 (m, 18 H), 1.44-1.52 (m, 2 H), 1.27-1.40 (m, 14 H), 0.87-0.92 (m, 9 H). **MS** (**MALDI**, THA): m/z (%) = 2990.44 $[M+Cu]^+$, 2950.45 $[M+Na]^+$, 2928.55 $[M+H]^+$.

28,37,63,66-Tetrahexyl-15,22,44,51-tetrakis(hexoxy)-8,58,72-triazaundecacyclo[54.2.2.1^{2,6}.2^{2,7}.1^{13,17}.1^{20,24}.2^{27,30}.1^{31,35}.2^{36,39}.1^{42,46}.1^{49,53}]diheptaconta-1(58),2,4,6(72),7,9,13,15,17(69),20,22,24(68),27,29,31,33,35(65),36,38,42,44,46(62),49,51,53(61),56,59,63,66,70-triacontaen-11,18,25,40,47,54-hexayne, $C_{117}H_{133}N_3O_4$, M = 1645.35, ***1d***

The procedure was analogous to that described for **1a** (**20a**: 160 mg, 0.15 mmol; **21b**: 121 mg, 0.15 mmol; CuI: 2.3 mg, 0.01 mmol; $Pd[P(Ph_3)]_4$: 14 mg, 0.01 mmol; toluene: 150 ml; triethylamine: 150 ml; 4 days at 60°C, 2 days at 75°C). Cycle **1d** was isolated as a yellow, amorphous material (42 mg, 0.026 mmol, 17 %) by preparative GPC. **^{1}H-NMR** (500 MHz, $CDCl_3$, 310 K): δ = 8.82 (dd, 2 H, ^{4}J = 1.0 Hz, ^{5}J = 0.5 Hz, 8-H), 8.64 (d, 2 H, ^{3}J = 8.5 Hz, ^{4}J = 1.0 Hz, 5-H), 8.48 (d, 2 H, ^{3}J = 8.0 Hz, 2-H), 7.96 (dd, 2 H, ^{3}J = 8.0 Hz, ^{4}J = 2.0 Hz, 6-H), 7.95 (t,

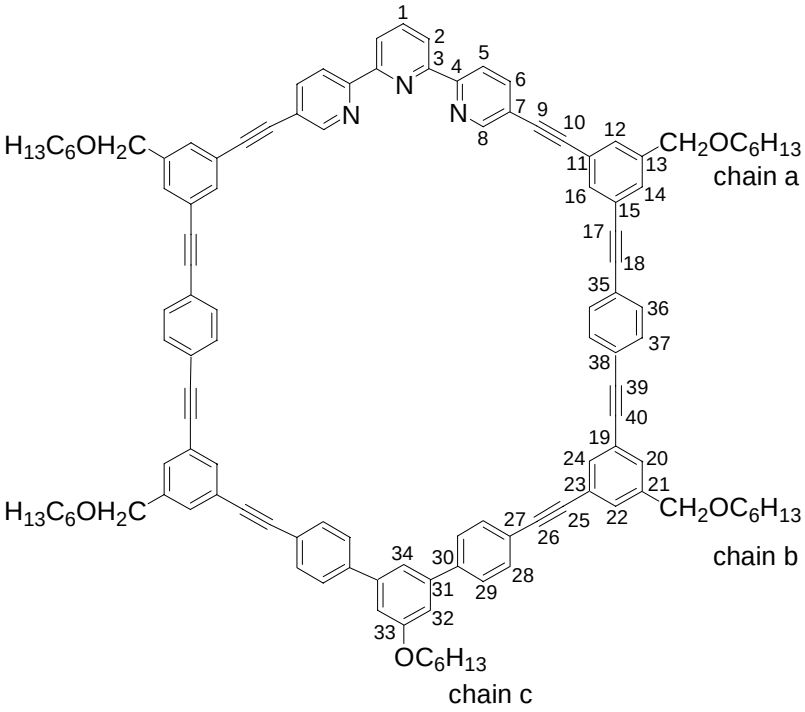
1 H, ^3J = 8.0 Hz, 1-H), 7.45 (s, 2 H, 28-H; t, 1 H, ^3J = 7.5 Hz, 35-H), 7.39 (t, 2 H, ^4J = 1.5 Hz, 16-H), 7.34 (t, 2 H, ^4J = 1.3 Hz, 24-H), 7.33 (dd, 2 H, ^3J = 7.3 Hz, ^4J = 1.8 Hz, 34-H), 7.26 (t, 1 H, ^4J = 2.0 Hz, 36-H), 7.12 (s, 2 H, 31-H), 7.08 (dd, 2 H, ^4J = 1.5 Hz, ^4J = 2.5 Hz, 14-H), 7.06 (dd, 2 H, ^4J = 1.5 Hz, ^4J = 2.5 Hz, 12-H), 7.05 (dd, 2 H, ^4J = 1.0 Hz, ^4J = 2.5 Hz, 22-H), 7.03 (dd, 2 H, ^4J = 1.5 Hz, ^4J = 2.5 Hz, 14-H), 4.01 (2 t, 8 H, ^3J = 6.5 Hz, α-CH_2 (a,b-chain)), 2.85 (t, 4 H, ^3J = 7.5 Hz, α-CH_2 (c-chain)), 2.62 (t, 4 H, ^3J = 7.5 Hz, α-CH_2 (d-chain)), 1.83 (2 quintets, 8 H, ^3J = 6.5 Hz, β-CH_2 (a,b-chain)), 1.79 (quintet, 4 H, ^3J = 7.5 Hz, β-CH_2 (c-chain)), 1.42-1.52 (m, 16 H, γ-CH_2 (a,b,c-chain), β-CH_2 (d-chain)), 1.32-1.40 and 1.18-1.28 (m, 20 H, and m, 16 H, all other -CH_2), 0.93 (t, 12 H, ^3J = 7.5 Hz, 4 -CH_3), 0.90 (t, 6 H, ^3J = 7.0 Hz, 2 -CH_3), 0.84 (t, 6 H, ^3J = 7.0 Hz, 2 -CH_3).



^{13}C-NMR (125.8 MHz, $CDCl_3$, 293 K): δ = 158.90 and 158.87 (13-C and 21-C), 154.67 (4-C), 154.44 (3-C), 151.25 (8-C), 142.38 (32-C), 141.92 (30-C), 141.34 (33-C), 139.62 (6-C), 137.97 (1-C), 137.70 (29-C), 132.96 (28-C), 130.51 (31-C), 130.14 (36-C), 128.04 (16-C), 127.82 (24-C), 127.65 (35-C), 127.51 (34-C), 124.87 and 124.00 (19-C and 23-C), 124.27 and 123.72 (11-C and 15-C), 121.44 (2-C), 121.14 (27-C), 120.49 (5-C), 120.13 (7-C), 117.86 (14-C), 117.48 (12-C), 117.39 (20-C), 117.04 (22-C), 92.90 (10-C), 91.60 (25-C), 89.18 (18-C), 88.74 (17-C and 26-C), 86.67 (9-C), 68.29 and 68.22 (α-C (a,b-chain)), 34.38 (α-C (c-chain)), 32.54 (α-C (d-chain)), 31.78, 31.53, 31.21, 30.88, 29.40, 29.14, 29.10, 25.66, 22.71, 22.60, 22.49 (all other CH_2-C), 14.18, 14.06, 14.05 (methyl-C (a,b,c,d-chain)). **MS** (**FAB(+)**, MNBA/DMSO/CH_2Cl_2-Matrix): m/z (%) = 1646 $[M+H]^+$

39-Hexoxy-15,28,50,63-tetrakis(hexoxymethyl)tridecacyclo[66.2.2.1^{2,6}.2^{7,10}.1^{13,17}.2^{20,23}.1^{26,30}.2^{33,36}.1^{37,41}.2^{42,45}.1^{48,52}.2^{55,58}.1^{61,65}]octaoctaconta-1(70),2,4,6(88),7,9,13,15,17(85),20,22,26,28,30(82),33,35,37,39,41(79),42,44,48,50,52(76),55,57,61,63,65(73),68,71,74,77,80,83,86-hexatriacontaen-11,18,24,31,46,53,59,66-octayne, $C_{119}H_{113}N_3O_5$, M = 1665.22, **2**

The procedure was analogous to that described for **1a**. **21a** (430 mg, 0.739 mmol), **26b** (989 mg, 0.739 mmol), toluene/triethylamine (350 ml/ 350 ml), $Pd[P(Ph_3)]_4$ (68 mg, 0.059 mmol), CuI (11 mg, 0.059 mmol). From the brownish raw product (1.17 g), cycle **2** and oligomer **[2]$_2$** were isolated by preparative GPC. These were dissolved in THF (ca. 5 ml), precipitated with methanol (ca. 8 ml), centrifuged, and the solvent layer taken off. This procedure was repeated once, to afford **2** (216 mg, 0.13 mmol, 18 %) and **[2]$_2$** (83 mg, 0.025 mmol, 7 %) as yellow, amorphous materials after freeze-drying. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 8.59 (s, 2 H, 8-H), 8.38 (d, 2 H, ^{3}J = 7.5 Hz, 5-H), 8.31 (d, 2 H, ^{3}J = 7.5 Hz, 2-H), 7.80 (t, 1 H, ^{3}J = 7.5 Hz, 1-H), 7.72 (d, 2 H, ^{3}J = 7.5 Hz, 6-H), 7.44 (d, 4 H, ^{3}J = 7.5 Hz, 29-H), 7.43, 7.39 (2 s, 4 H, H-16, H-24), 7.41 (d, 4 H, ^{3}J = 7.5 Hz, 28-H), 7.30 (s, 8 H, 36-H, 37-H), 7.21-7.30 (m, 9 H, 12-H, 14-H, 20-H, 22-H, 34-H), 6.95 (s, 2 H, 32-H), 4.38, 4.36 (2s, 8 H, aryl-CH_2 (a,b-chain)), 4.00 (t, 2 H, ^{3}J = 6.0 Hz, α-CH_2 (c-chain)), 3.49, 3.47 (2 t, 8 H, ^{3}J = 6.5 Hz, α-CH_2 (a,b-chain)), 1.84 (quintet, 2 H, ^{3}J = 7.0 Hz, β-CH_2 (c-chain)), 1.66 (m, 8 H, β-CH_2 (a,b-chain)), 1.52 (quintet, 2 H, ^{3}J ≈ 7 Hz, γ-CH_2 (c-chain)), 1.29-1.45 (m, 28 H, γ-CH_2 (a,b-chain), δ,ε-CH_2 (a,b,c-chain)), 0.91-0.99 (m, 15 H, -CH_3 (a,b,c-chain)). **^{13}C-NMR** (125.8 MHz, $CDCl_3$): δ = 159.72 (33-C), 154.13 (3-C, 4-C), 151.00 (8-C), 141.07 (31-C), 139.65 (30-C), 139.16, 139.03 (13-C, 21-C), 138.83 (6-C), 137.05 (1-C), 133.67, 133.56 (16-C, 24-C), 131.85 (28-C), 131.30 (36,37), 129.93, 129.67 (2 signals), 129.58 (12-C, 14-C, 20-C, 22-C), 126.34 (29-C), 123.53, 123.38, 123.25, 122.88 (11-C,



15-C, 19-C, 23-C), 122.75, 122.60 (35-C, 38-C), 121.99 (27-C), 120.87 (2-C), 119.86 (5-C), 119.84 (7-C), 117.04 (34-C), 111.82 (32-C), 92.65, 90.59, 90.36, 89.78 (2 signals), 89.29 (10-C, 17-C, 18-C, 25-C, 39-C, 40-C), 89.57 (26-C), 87.07 (9-C), 71.91, 71.85 (aryl-CH_2 (a,b-chain)), 70.92, 70.82 (α-C (a,b-chain)), 68.06 (α-C (c-chain)), 31.74 (δ-C (a,b,c-chain)), 29.74 (β-C (a,b-chain)), 29.46 (β-C (c-chain)), 25.92 (γ-C (a,b-chain)), 25.85 (γ-C (c-chain)), 22.64 (ε-C (a,b,c-chain)), 14.03 (methyl-C (a,b,c-chain)). **MS** (**MALDI**, THA): m/z (%) = 1692.79 $[M+C_2H_5]^+$, 1686.79 $[M+Na]^+$, 1678.80 $[M+CH_3]^+$, 1664.84 $[M+H]^+$, 1592.83 $[M-C_5H_{11}]^+$, 1578.73 $[M-C_6H_{13}]^+$.

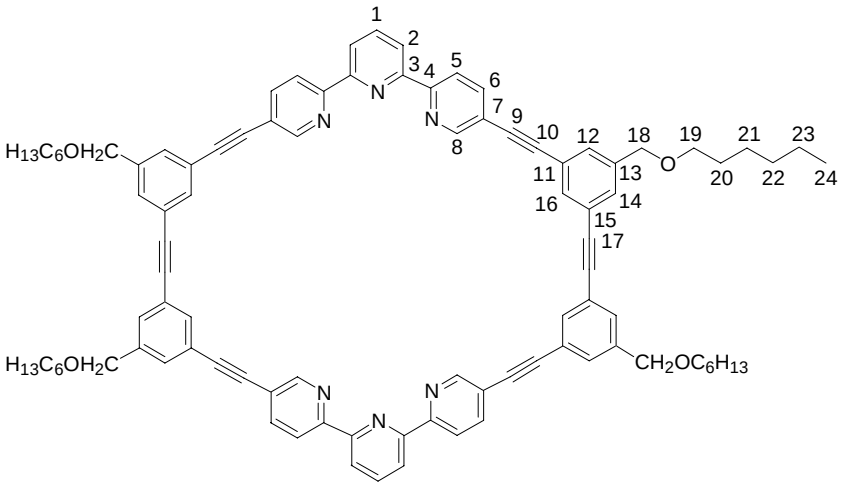
Cyclic oligomer, $C_{238}H_{226}N_6O_{10}$, M = 3330.44, ***[2]₂***

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.80 (dd, ^{4}J = 2.0 Hz, ^{5}J = 0.8 Hz, 4 H, 8-H), 8.60 (dd, 4 H, ^{3}J = 8.2 Hz, ^{4}J = 0.6 Hz, 5-H), 8.47 (d, 4 H, ^{3}J = 7.8 Hz, 2-H), 7.96 (t, 2 H, ^{3}J = 8.0 Hz, 1-H), 7.93 (d, 4 H, ^{3}J = 8.0 Hz, 6-H), 7.66 (t, 4 H, ^{4}J = 1.5 Hz), 7.64 (t, 4 H, ^{4}J = 1.5 Hz), 7.58-7.63 (m, 16 H), 7.48-7.52 (m, 28 H), 7.46 (t, 4 H, ^{4}J = 1.5 Hz), 7.38 (t, 2 H, ^{4}J = 1.5 Hz), 7.11 (d, 4 H, ^{4}J = 1.5 Hz), 4.50 (s, 8 H), 4.49 (s, 8 H), 4.06 (t, 4 H, ^{3}J = 6.5 Hz), 3.50 (t, 8 H, ^{3}J = 6.6 Hz), 3.49 (t, 8 H, ^{3}J = 6.5 Hz), 1.83 (quintet, 4 H, ^{3}J = 7.0 Hz), 1.61-1.65 (m, 16 H), 1.50 (m, 4 H), 1.27-1.42 (m, 56 H), 0.88-0.93 (m, 30 H). **^{13}C-NMR** (125.8 MHz, $CDCl_3$): δ = 160.09, 154.94, 154.74, 151.61, 142.26, 140.99, 139.78, 139.63, 139.30, 137.91, 133.78, 132.10, 131.63, 130.68, 130.43, 130.25, 127.17, 123.76, 123.61, 123.46, 123.16, 123.10, 122.98, 122.26, 121.54, 120.40, 120.12, 118.38, 112.58, 92.72, 90.64, 90.41, 89.95, 89.86, 89.63, 89.40, 87.08, 71.95, 71.88, 70.95, 70.88, 68.33, 31.69, 31.60, 29.71, 29.33, 25.87, 25.77, 22.63, 14.03. **MS** (**MALDI**, THA): m/z (%) = 3328.60 $[M+H]^+$ (signal with highest intensity); a number of signals with lower intensity at higher m/z values could not be assigned.

15,22,44,51-Tetrakis(hexoxymethyl)-8,29,37,58,65,72-hexaazaundecacyclo[54.2.2.1^{2,6}.2^{2,7}.1^{13,17}.1^{20,24}.2^{27,30}.1^{31,35}.2^{36,39}.1^{42,46}.1^{49,53}]diheptaconta-1(58),2,4,6(72),7,9,13,15,17(69),20,22,24(68),27,29,31,33,35(65),36,38,42,44,46(62),49,51,53(61),56,59,63,66,70-triacontaen-11,18,25,40,47,54-hexayne, $C_{94}H_{90}N_6O_4$, M = 1367.78, ***3***

A solution of **30** (100 mg, 0.109 mmol) and **33b** (78 mg, 0.109 mmol) in dried toluene/ triethylamine (100 ml, 1:1) was freeze-degassed twice. $Pd[P(Ph_3)]_4$ (10 mg, 0.0087 mmol) and CuI (1.7 mg, 0.0087 mmol) were added, the mixture degassed again and stirred at 60°C in a

sealed flask for 4 days, and at 80°C for one more day. The mixture was allowed to cool down and stirred with an aqueous solution of KCN (50 mg KCN, 50 ml H_2O) for 30 mins. The phases were separated, the aqueous phase was extracted with toluene (50 ml), the combined organic phases with water (100 ml), and dried over $MgSO_4$. The solvent was evaporated in vacuo to yield a brownish raw product (120 mg, solid after freeze-drying). From this, cycle **3** was isolated as a yellow, amorphous material (40 mg, 0.029 mmol, 27 %) by preparative GPC, and likewise **[3]$_2$** (9 mg, 0.0032 mmol, 6 %).

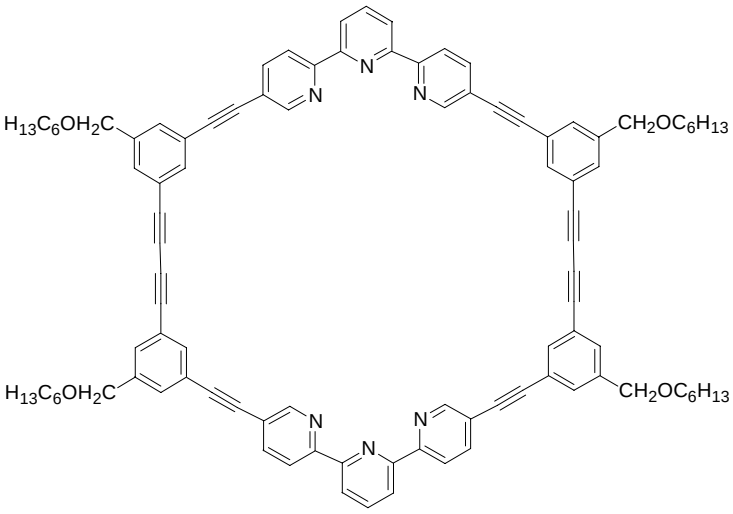


^{1}H-NMR (500 MHz, $CDCl_3$, 293 K): δ = 8.48 (s, 4 H, 8-H), 8.40 (d, 4 H, ^{3}J = 8.5 Hz, 5-H), 8.19 (d, 4 H, ^{3}J = 7.5 Hz, 2-H), 7.72 (d, 8 H, ^{3}J = 8.0 Hz, 6-H), 7.71 (t, 2 H, ^{3}J = 8.0 Hz, 1-H), 7.38, 7.28, 7.24 (3 s, 18 H, 12-H, 14-H, 16-H), 4.41 (s, 8 H, 18-H), 3.52 (t, 8 H, ^{3}J = 6.5 Hz, 19-H), 1.68 (quintet, 8 H, ^{3}J = 7.0 Hz, 20-H), 1.43 (quintet, 8 H, ^{3}J = 7.0 Hz, 21-H), 1.24-1.39 (m, 16 H, 22-H, 23-H), 0.93 (t, 12 H, ^{3}J = 7.0 Hz, 24-H). **MS** (**MALDI**, THA): m/z (%) = 1465.85 $[M+CH_3+C_6H_{12}]^+$, 1389.94 $[M+Na]^+$, 1367.95 $[M+H]^+$.

Cyclic compound, $C_{188}H_{180}N_{12}O_8$, M = 2735.56, ***[3]$_2$***

^{1}H-NMR (500 MHz, $CDCl_3$, 293 K): δ = 8.81 (d, 8 H, ^{4}J = 2.0 Hz, 8-H), 8.60 (d, 8 H, ^{3}J = 8.0 Hz, 5-H), 8.44 (d, 8 H, ^{3}J = 8.0 Hz, 2-H), 7.95 (dd, 8 H, ^{3}J = 8.0 Hz, ^{4}J = 2.0 Hz, 6-H), 7.92 (t, 4 H, ^{3}J = 8.0 Hz, 1-H), 7.65 (s, 8 H, 16-H), 7.48 and 7.50 (2 s, 16 H, 12-H, 14-H), 4.49 (s, 16 H, 18-H), 3.50 (t, 16 H, ^{3}J = 7.0 Hz, 19-H), 1.64 (t, 16 H, ^{3}J = 7.0 Hz, 20-H), 1.36-1.42 (m, 16 H, 21-H), 1.27-1.35 (m, 32 H, 22-H, 23-H), 0.89 (t, 24 H, ^{3}J = 7.0 Hz, 24-H). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 154.93 (4-C), 154.71 (3-C), 151.63 (8-C), 141.82 (13-C), 139.34 (6-C), 137.94 (1-C), 133.93 (16-C), 131.88 (28-C), 130.45 and 130.70 (12-C, 14-C), 123.09 and 123.52 (11-C, 15-C), 120.54 (2-C), 120.43 (5-C), 120.13 (7-C), 89.21 and 92.72 (10-C, 17-C), 87.09 (9-C), 71.90 (C-18), 69.18 (C-19), 31.70 (C-22), 29.73 (C-20), 25.98 (C-21); 19.87 (C-23); 14.06 (C-24). **MS** (**MALDI**, THA): m/z (%) = 2756.7 $[M+Na]^+$, 2748.8 $[M+CH_3]^+$, 2734.8 $[M+H]^+$.

15,24,46,55-Tetrakis(hexyloxymethyl)-8,31,39,62,69,76-hexaaza-undecacyclo[58.2.2.1^{2,6}.2^{7,10}.1^{13,17}.1^{22,26}.2^{29,32}.1^{33,37}.2^{38,41}.1^{44,48}.1^{53,57}]hexaheptaconta-1(62),2,4,6(76),7,9,13,15,17(73),22,24,26(72),29,31,33,35,37(69),38,40,44,46,48(66),53,55,57(65),60,63,67,70,74-triacontaen-11,18,20,27,42,49,51,58-octayne, $C_{98}H_{90}N_6O_4$, M = 1415.83, **4**



To a solution of $PdCl_2(PPh_3)_2$ (30 mg, 0.043 mmol) and CuI (8 mg, 0.043 mmol) in piperidine/THF (100 ml / 150 ml), a solution of **33b** (344 mg, 485 mmol) in THF (25 ml) was added over a period of 4 days under stirring on air. It was stirred for two more days, the solvent evaporated, the soluble part of the residue dissolved in CH_2Cl_2, extracted with water (50 ml) and the aqueous phase again extracted with CH_2Cl_2 (50 ml). The combined organic phases were dried over $MgSO_4$, the solvent evaporated and the residue freeze-dried to give 1.00 g of a brownish solid material. By preparative GPC, cycle **4** (28 mg, 0.020 mmol, 8 %), oligomer $\mathbf{[4]_{1.5}}$ (26 mg, 0.012 mmol, 8 %), and oligomer $\mathbf{[4]_2}$ (11 mg, 0.004 mmol, 3 %) were isolated as yellow, amorphous materials. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 8.44 (s, 4 H, tpy-6,6''-H), 8.37 (s br, 4 H, tpy-3,3''-H), 8.14 (d, 4 H, ^{3}J = 7.0 Hz, tpy-3',5'-H), 7.72 (s br, 4 H, tpy-4,4''-H), 7.66 (t, 2 H, ^{3}J = 7.5 Hz, tpy-4'-H), 7.29 (s, 4 H, phenyl-H), 7.17 (s, 8 H, phenyl-H), 4.33 (s, 8 H, benzyl-H), 3.49 (t, 8 H, ^{3}J = 6.7 Hz, α-CH_2), 1.67 (quintet, 8 H, hexyl-β-CH_2), 1.34-1.44 (m, 24 H, γ-, δ-, ε-CH_2), 0.94 (t, 3 H, ^{3}J = 6.8 Hz, hexyl-CH_3). **MS** (**MALDI**, THA): m/z (%) = 1513.81 $[M+CH_3+C_6H_{12}]^+$, 1477.82 $[M+Na+K]^+$, 1453.90 $[M+K]^+$, 1437.89 $[M+Na]^+$, 1429.90 $[M+CH_3]^+$, 1415.90 $[M+H]^+$, 1329.78 $[M-C_6H_{13}]^+$.

Cyclic oligomer, $C_{147}H_{135}N_9O_6$, M = 2123.74***, [4]$_{1.5}$***

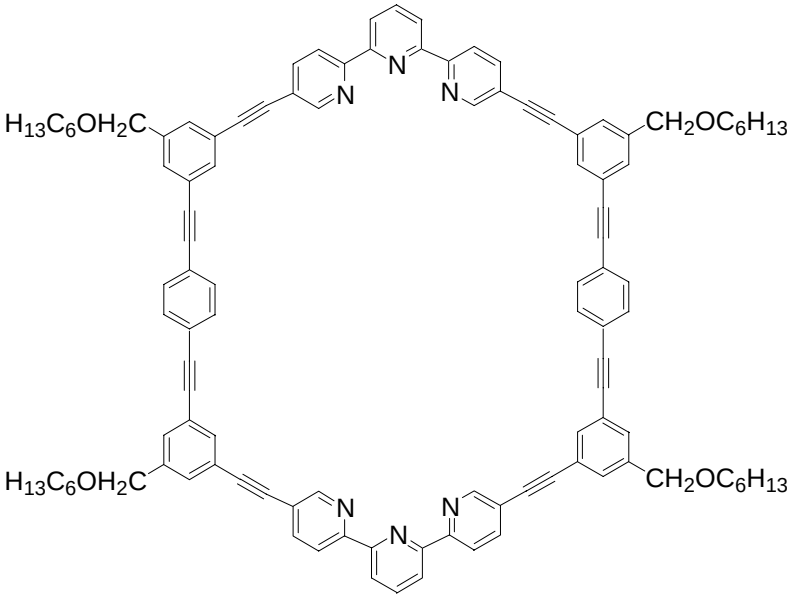
MS (**MALDI**, THA): m/z (%) = 2145.34 $[M+Na]^+$, 2137.28 $[M+CH_3]^+$, 2123.32 $[M+H]^+$.

Cyclic oligomer, $C_{196}H_{180}N_{12}O_8$, M = 2831.66***, [4]$_2$***

MS (**MALDI**, THA): m/z (%) = 2908.92 $[M+Cu+CH_3]^+$, 2894.92 $[M+Cu]^+$, 2846.82 $[M+CH_3]^+$, 2832.42 $[M+H]^+$, 2761.53 $[M-C_5H_{11}]^+$, 2746.76 $[M-C_6H_{12}]^+$, 2675.88 $[M-C_5H_{11}-C_6H_{12}]^+$, 2660.95

$[M-2C_6H_{12}]^+$. Only a spectrum in the linear mode (i.e., with less resolution than in the reflector mode) could be obtained. The different isotopes could therefore not be resolved.

15,28,50,63-Tetrakis(hexyl-oxymethyl)-8,35,43,70,79,88-hexaaza-tridecacyclo[66.2.2.1^{2,6}.2^{7,10}.1^{13,17}.2^{20,23}.1^{26,30}.2^{33,3}.1^{37,41}.2^{42,45}.1^{48,52}.2^{55,58}.1^{61,65}]-octaoctaconta-1(70),2,4,6(88),7,9,13,15,17(85),20,22,26,28,30(82),33,35,37,39,41(79),42,44,48,50,52(76),55,57,61,63,65(73),68,71,74,77,80,83,86-hexatriacontaen-11,18,24,31,46,53,59,66-octayne,



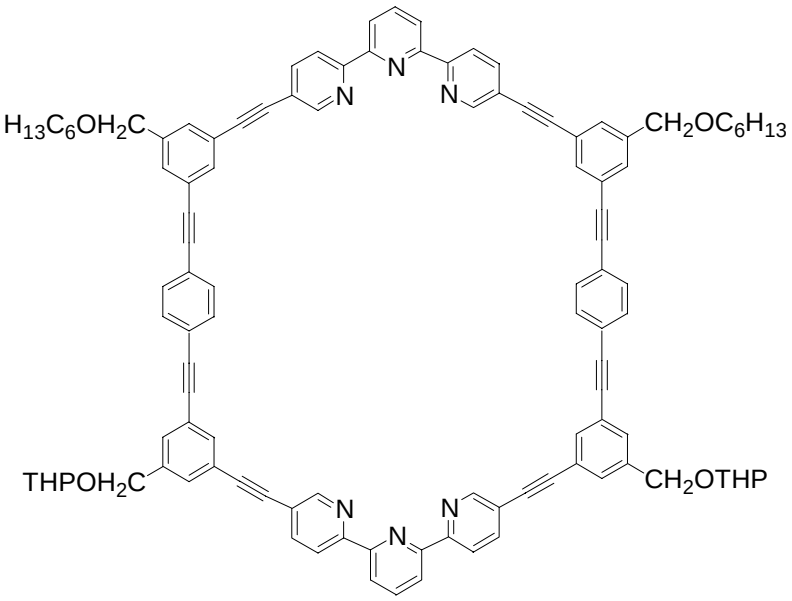
$C_{110}H_{98}N_6O_4$, M = 1568.02, ***5a***

The procedure was analogous to that described for **1a** (**33b**: 727 mg, 1.02 mmol; **35a**: 1.14 g, 1.02 mmol; toluene/triethylamine: 350 ml/ 350 ml; $Pd[P(Ph_3)]_4$: 95 mg, 0.082 mmol; CuI: 16 mg, 0.082 mmol). Raw product: 1.15 g brownish solid after freeze-drying. During preparative GPC, a colorless material precipitated from the THF solution of the raw product, was collected, dissolved again and likewise separated by GPC. There, another precipitate formed and was treated the same way. As combined fractions from the three preparative GPC runs, cycle **5a** (181 mg, 0.115 mmol, 11 %) and oligomer **[5a]$_2$** (94 mg, 0.030 mmol, 6 %) were isolated as yellow, amorphous materials after freeze-drying. The solution NMR spectra of **5a** gave only extremely broad signals which could not be used to support the proposed structure. **MS** (**FAB(+)**, MNBA/DMSO/CH_2Cl_2-Matrix): m/z (%) = 1566 (37.3), 1567 (52.9), 1568 (86.3), 1569 (80.4), 1570 (51.0), 1571 (33.3) $[M/M+H]^+$, 1636 (21.6), 1637 (62.8), 1638 (70.6), 1639 (100.0), 1640 (66.7), 1641 (62.8), 1642 (37.3), 1643 (21.6) $[M+C_5H_{11}]^+$. **MS** (**MALDI**, THA): m/z (%) = 1637.57 $[M+C_5H_{11}]^+$, 1581.60 $[M+CH_3]^+$, 1567.62 $[M+H]^+$, 1495.50 $[M-C_5H_{11}]^+$, 1481.53 $[M-C_6H_{13}]^+$.

Cyclic oligomer, $C_{220}H_{196}N_{12}O_8$, M = 3136.04**, *[5a]₂***

This compound could not be characterized according to common standards. The NMR spectra showed extremely broad signals and the maldi tof spectra could not be obtained under conditions allowing for a reliable interpretation. Analytical GPC, however, suggests it to be a cyclic tetramer like those described for the other macrocycles.

15,63-Bis(hexyloxymethyl)-28, 50-bis(tetrahydro-pyran-2-yloxymethyl)-8,35,43,70,79, 88-hexaazatridecacyclo[66.2.2.1^{2,6}.2^{7,10}.1^{13,17}.2^{20,23}.1^{26,30}.2^{33,36}.1^{37,41}.2^{42,45}.1^{48,52}.2^{55,58}.1^{61,65}] octaoctaconta-1(70),2,4,6(88),7, 9,13,15,17(85),20,22,26,28,30 (82),33,35,37,39,41(79),42,44, 48,50,52(76),55,57,61,63, 65(73),68,71,74,77, 80,83,86-hexatriacontaen-11,18,24,31, 46,53,59,66-octayne, $C_{108}H_{90}N_6O_6$, M = 1567.93, ***5b***

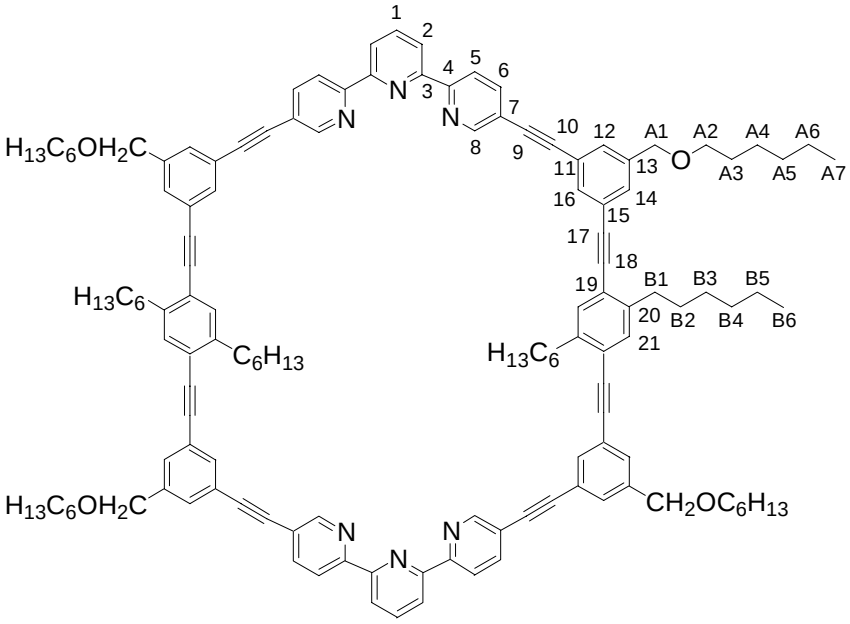


The procedure was analogous to that described for **1a** (**33c**: 108 mg, 0.153 mmol; **35a**: 170 mg, 0.153 mmol; toluene/triethyl-amine: 60 ml/ 60 ml; $Pd[P(Ph_3)]_4$: 14 mg, 0.012 mmol; CuI: 2.3 mg, 0.012 mmol). Raw product: 150 mg brownish solid after freeze-drying. By preparative GPC, cycle **5b** (46 mg, 0.030 mmol, 19 %) and oligomer **[5b]₂** (32 mg, 0.010 mmol, 13 %) were isolated as yellow, amorphous materials after freeze-drying. The solution NMR spectra of **5b** showed extremely broad signals and can, therefore, not be used to support the proposed structure. **MS** (**MALDI**, THA): m/z (%) = 1637.57 $[M+C_5H_{11}]^+$, 1581.60 $[M+CH_3]^+$, 1567.88 $[M+H]^+$, 1494.50 $[M-C_5H_{11}]^+$, 1481.76 $[M-C_6H_{13}]^+$.

Cyclic oligomer, $C_{216}H_{180}N_{12}O_{12}$, M = 3135.86, ***[5b]₂***

MS (**MALDI**, THA): m/z (%) = 3196.78 $[M+Cu]^+$, 3156.82 $[M+Na]^+$.

21,56,83,74-Tetrahexyl-15,28,50,63-tetrakis(hexyloxymethyl)-8,35,43,70,79,88-hexaaza-tridecacyclo[66.2.2.1^{2,6}.2^{7,10}.1^{13,17}.2^{20,23}.1^{26,30}.2^{33,36}.1^{37,41}.2^{42,45}.1^{48,52}.2^{55,58}.1^{61,65}]octaoctaconta-1(70),2,4,6(88),7,9,13,15,17(85),20,22,26,28,30(82),33,35,37,39,41(79),42,44,48,50,52(76), 55,57,61,63,65(73),68,71,74,77,80,83,86-hexatriacontaen-11,18,24,31,46,53,59,66-octayne, $C_{134}H_{146}N_6O_4$, M = 1904.66, ***5c***



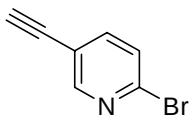
The procedure was analogous to that described for **1a** (**33b**: 147 mg, 0.207 mmol; **35b**: 300 mg, 0.207 mmol; toluene/ triethylamine: 80 ml/ 80 ml; $Pd[P(Ph_3)]_4$: 19 mg, 0.017 mmol; CuI: 3 mg, 0.02 mmol). Raw product: 420 mg brownish solid after freeze-drying. By preparative GPC, cycle **5c** (45 mg, 0.024 mmol, 11 %) and oligomer **[5c]$_2$** (24 mg, 0.006 mmol, 6 %) were isolated as yellow, amorphous materials. The ^{1}H NMR spectrum indicated **5c** not to be an absolutely pure compound. **^{1}H-NMR** (500 MHz, $CDCl_3$/d-TFA ca. 3:1, 300 K): δ = 9.28 (s, 4 H, ^{4}J = 1.5 Hz, 8-H), 8.77 (d, 4 H, ^{3}J = 8.0 Hz, ^{4}J = 1.5 Hz, 6-H), 8.70 (d, 4 H, ^{3}J = 8.5 Hz, 5-H), 8.54 (d, 4 H, ^{3}J = 7.5 Hz, 2-H), 8.47 (t, 2 H, ^{3}J = 7.0 Hz, 1-H), 7.81 (s br, 4 H, H-16), 7.62 (s br, 8 H, 12-H, 14-H), 7.44 (s br, 4 H, 21-H), 4.74 (s, 8 H, H-A1), 3.72 (t, 8 H, ^{3}J = 7.0 Hz, H-A2), 2.87 (s br, 8 H, B1-H), 1.75 (quintet, 8 H, ^{3}J = 7.0 Hz, B2-H), 1.72 (quintet, 8 H, ^{3}J = 7.5 Hz, A3-H), 1.31-1.46 (m, 48 H, A4-H, A5-H, A6-H, B3-H, B4-H, B5-H, 24 H), 0.87-0.92 (m, 30 H, A7-H, B6-H). The spectrum shows a number of impurities. **^{13}C-NMR** (125.8 MHz, $CDCl_3$/d-TFA ca. 3:1, 300 K): δ = 149.41 (6-C), 146.64 (3-C), 144.79 (8-C), 144.65 (4-C), 142.90 (20-C), 142.38 (1-C), 137.58 (13-C), 134.89 (16-C), 135.58, 131.73 (12-C, 14-C), 132.94 (21-C), 126.23 (2-C), 125.98 (7-C), 125.41 (11-C or 15-C), 124.71 (5-C), 122.64 (19-C), 121.45 (11-C or 15-C), 100.40, 90.60 (10-C, 17-C), 91.98 (18-C), 82-01 (9-C), 71.75 (A1-C), 71.60 (A2-C), 34.18 (B1-C), 31.89, 31.60 (A5-C, B4-C), 30.76 (B2-C), 29.27 (B3-C), 28.77 (A3-C), 25.44 (A4-C), 22.69, 22.54 (A6-C, B5-C),

13.86, 13.63 (A7-C, B6-C). **MS** (**MALDI**, THA): m/z (%) = 2044.11 $[M+C_5H_{10}+C_5H_{11}]^+$, 1974.16 $[M+C_5H_{11}]^+$, 1904.22 $[M+H]^+$.

Cyclic oligomer, $C_{268}H_{252}N_{12}O_8$, M = 3809.32, ***[5c]$_2$***

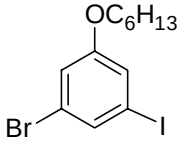
This compound could not be obtained in pure form. By applying the HETCOR NMR pulse sequence and comparing the spectra with that of similar substances, the NMR signals of **[5c]$_2$** could nevertheless be unambiguously assigned. **^{1}H-NMR** (500 MHz, $CDCl_3$, 300 K): δ = 8.83 (s br, 8 H, ^{4}J = 1.5 Hz, 8-H), 8.63 (dd, 8 H, ^{3}J = 8.5 Hz, ^{5}J = 2.5 Hz, 5-H), 8.48 (d, 8 H, ^{3}J = 8.0 Hz, 2-H), 7.96-7.98 (m, 12 H, 1-H, 6-H), 7.63 (s br, 8 H, H-16), 7.52, 7.49 (2 s br, 16 H, 12-H, 14-H), 7.40 (s br, 8 H, 21-H), 4.51 (s, 16 H, H-A1), 3.51 (t, 16 H, ^{3}J = 7.0 Hz, H-A2), 2.81 (t, 16 H, ^{3}J = 7.5 Hz, H-B1), 1.72 (quintet, 16 H, ^{3}J = 7.0 Hz, B2-H), 1.64 (quintet, 16 H, ^{3}J = 7.0 Hz, A3-H), 1.31-1.42 (m, 96 H, A4-H, A5-H, A6-H, B3-H, B4-H, B5-H, 24 H), 0.90 (t, 60 H, ^{3}J = 6.5 Hz, A7-H, B6-H). **^{13}C-NMR** (125.8 MHz, $CDCl_3$, 300 K): δ = 154.97 (4-C), 154.65 (3-C), 151.60 (8-C), 142.39 (20-C), 139.74 (13-C), 139.45 (6-C), 138.07 (1-C), 133.52 (16-C), 132.48 (21-C), 130.68, 130.41 (12-C, 14-C), 124.04, 123.04 (11-C, 15-C), 122.49 (19-C), 121.69 (2-C), 121.53 (5-C), 120.24 (7-C), 93.03, 92.86 (10-C, 17-C), 89.20 (18-C), 86.90 (9-C), 71.92 (A1-C), 70.94 (A2-C), 34.10 (B1-C), 31.77, 31.68 (A5-C, B4-C), 30.62 (B2-C), 29.70 (A3-C), 29.23 (B3-C), 25.86 (A4-C), 22.63 (A6-C, B5-C), 14.14, 14.05 (A7-C, B6-C).

2-Bromo-5-ethynylpyridine, C_7H_4BrN, M = 182.08, ***7***



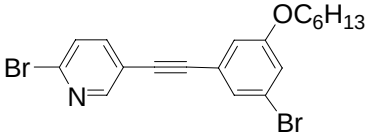
The procedure was analogous to that described for **16a** (**6**: 23 g, 81.0 mmol; TMS-acetylene: 8.51 g, 86.7 mmol). The crude product was refluxed for 20 mins in methanol (30 ml) and purified by column chromatography (hexane/ethyl acetate) to give **7** (11.8 g, 65.2 mmol, 81 %) as a sandy colored, crystalline solid, m.p. = 83°C. **R_f** = 0.29 (hexane/ethyl acetate 30:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 8.41 (d, 1 H, ^{4}J = 2.2 Hz, 6-H), 7.55 (dd, 1 H, ^{3}J = 8.1 Hz, ^{4}J = 2.2 Hz, 4-H), 7.41 (d, 1 H, ^{3}J = 8.2 Hz, 3-H), 3.25 (s, 1 H, ethynyl-H). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 152.58, 141.68, 141.06, 127.58, 118.43, 82.00, 79.07. **MS** (**EI**, 80 eV, 40°C): m/z (%) = 184 (7.7), 183 (97.4), 182 (8.8), 181 (100.0), 180 (0.8) $[M]^+$, 103 (6.2), 102 (81.4) $[M-Br]^+$. **EA**: Calc.: C:46.18, H:2.21, N:7.69; Found: C:46.18, H:2.27, N:7.55.

1-Bromo-3-hexoxy-5-iodobenzene, $C_{12}H_{16}BrIO$, M = 383. 07, ***8*** (Scheme 8)



To a solution of **92a** (41 g, 125 mmol) in dichloromethane (450 ml), a solution of iodine chloride (22.2 g, 137 mmol) in dichloromethane (50 ml) was added dropwise under N_2 at –78°C. After stirring at this temperature for 30 mins, the reaction was stopped by an aqueous solution of sodium disulfite (500 ml) and the phases were separated. The aqueous phase was washed twice with dichloromethane (200 ml/100 ml). The combined organic phases were dried over $MgSO_4$ and the solvent removed in vacuo to afford a brownish oil (46.5 g). Chromatographic separation through silica gel with hexane gave **8** (46.4 g, 121 mmol, 97 %) as a colorless sirup. $\mathbf{R_f}$ = 0.50 (hexane). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 7.39 (t, 1 H, ^{4}J = 1.4 Hz, aryl-H), 7.15 (dd, 1 H, ^{4}J = 1.5 Hz, ^{4}J = 2.2 Hz, aryl-H), 6.98 (t, 1 H, ^{4}J = 2.0 Hz, aryl-H), 3.87 (t, 2 H, ^{3}J = 6.5 Hz, α-CH_2), 1.73 (quintet, 2 H, ^{3}H ≈ 7 Hz, β-CH_2), 1.30-1.33 (m, 6 H, γ-, δ-, ε-CH_2), 0.90 (t, 3 H, ^{3}J = 6.6 Hz, -CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 160.07, 131.68, 123.04, 122.70, 117.54, 94.18, 68.49, 31.44, 28.94, 25.56, 22.55, 14.01. **MS** (**EI**, 80 eV, 60°C): m/z (%) = 386 (0.7), 385 (6.0), 384 (42.6), 383 (6.9), 382 (43.8) $[M]^+$, 314 (0.3), 313 (2.5), 312 (0.3), 311 (2.4) $[M\text{-}C_5H_{11}]^+$, 302 (0.7), 301 (7.5), 300 (97.7), 299 (8.9), 298 (100) $[M\text{-}C_6H_{12}]^+$, 284 (0.5), 283 (5.9), 282 (0.7), 281 (5.9) $[M\text{-}C_5H_{11}\text{–}CH_2O]^+$, 271 (2.2), 270 (0.3), 269 (2.2) $[M\text{-}C_6H_{12}\text{–}CHO]^+$. **HRMS**: Calc.: 381.94293; Found: 381.94565.

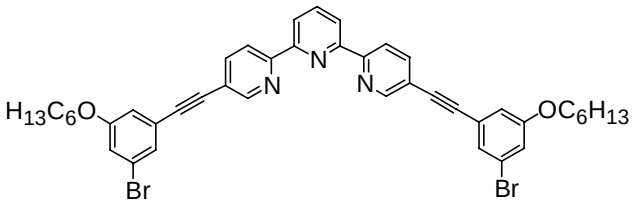
2-Bromo-5-[(3-bromo-5-hexoxyphenyl)ethynyl]pyridine, $C_{19}H_{19}Br_2NO$, M = 437.17, **9**



The procedure was analogous to that described for **94** (**7**: 6.17 g, 33.9 mmol; **8**: 13.0 g, 33.9 mmol; CuI: 194 mg, 1.02 mmol; $Pd[P(Ph_3)]_4$: 1.18 g, 1.02 mmol; triethylamine/toluene: 200 ml/50 ml). The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate) to afford **9** (12.16 g, 27.8 mmol, 82 %) as a yellow sirup which, in the course of weeks, slowly started to crystallize. $\mathbf{R_f}$ = 0.50 (hexane/ethyl acetate 20:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 8.45 (d, 1 H, ^{4}J = 2.3 Hz, py-6-H), 7.57 (dd, 1 H, ^{3}J = 8.2 Hz, ^{4}J = 2.2 Hz, py-4-H), 7.43 (d, 1 H, ^{3}J = 8.3 Hz, py-3-H), 7.20 (t, 1 H, ^{4}J = 1.3, phenyl-H), 7.02 (t, 1 H, ^{4}J = 1.9, phenyl-H), 6.92-6.93 (dd, 1 H, ^{4}J = 1.3, ^{4}J = 2.2, phenyl-H), 3.89 (t, 2 H, ^{3}J = 6.5 Hz, α-CH_2), 1.68-1.76 (quintet, 2 H, ^{3}H ≈ 7 Hz, β-CH_2), 1.26-1.43 (m, 6 H, γ-, δ-, ε-CH_2), 0.87 (t, 3 H, ^{3}J = 6.5, -CH_3). **^{13}C-NMR** (67.9 MHz,

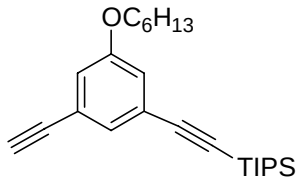
$CDCl_3$): δ = 159.52, 152.29, 141.32, 140.44, 127.61, 126.44, 124.33, 122.55, 119.08, 116.14, 92.33, 85.44, 68.41, 31.41, 28.92, 25.53, 22.51, 13.97. **MS** (**EI**, 80 eV, 185°C): m/z (%) = 440 (2.20), 439 (25.4), 438 (11.6), 437 (50.8), 436 (7.0), 435 (25.2) $[M]^+$, 356 (8.6), 355 (49.6), 354 (20.0), 353 (100.0), 352 (10.1), 351 (50.6), 350 (1.5) $[M\text{-}C_6H_{12}]^+$, 327 (1.9), 326 (6.1), 325 (3.6), 324 (11.3), 323 (2.0), 322 (5.8) $[M\text{-}C_5H_{11}\text{–}CH_2O]^+$, 275 (2.1), 274 (8.3), 273 (5.2), 272 (8.1), 271 (3.4) $[M\text{-Br-}C_6H_{12}]^+$, 257 (3.3), 256 (1.3), 255 (2.9) $[M\text{-}C_5H_{11}\text{–}CH_2O\text{-Br}]^+$, 246 (4.2), 245 (2.7), 244 (5.2), 243 (2.1) $[M\text{-Br-}COC_6H_{12}]^+$, 194 (4.9), 193 (26.9) $[M\text{-2Br-}C_6H_{12}]^+$, 167 (1.3), 166 (2.3), 165 (9.3), 164 (38.2), 163 (4.0) $[M\text{-}C_5H_{11}\text{–}CH_2O\text{-2Br}]^+$. **EA**: Calc.: C: 52.20, H: 4.38, N: 3.20; Found: C: 52.29, H: 4.37, N: 3.10.

5,5‘‘-Bis[(3-bromo-5-hexoxyphenyl)ethynyl]-2,2‘:6‘,2‘‘-terpyridine, $C_{43}H_{41}Br_2N_3O_2$, M = 791.62, ***11***



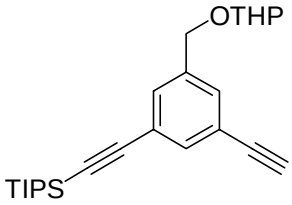
The procedure was analogous to that described for **28a** (**9**: 2.06 g, 4.71 mmol; **10**: 0.95 g, 2.35 mmol; $Pd[P(Ph_3)]_4$: 112 mg, 0.097 mmol; toluene : 50 ml). The crude product was purified by column chromatography (hexane/ethyl acetate) to afford **11** (1.07 g, 1.35 mmol, 58 %) as a yellow sirup. $\mathbf{R_f}$ = 0.55 (hexane/ethyl acetate 4:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 8.75 (s, 2 H, tpy-6,6‘‘-H), 8.53 (d, 2 H, ^3J = 8.2 Hz, tpy-3,3‘‘-H), 8.41 (d, 2 H, ^3J = 7.8 Hz, tpy-3’,5’-H), 7.88 (t, 1 H, $^3J \approx 9$ Hz, tpy-4’-H), 7.86 (dd, 2 H, ^3J = 8.3 Hz, ^4J = 2.0 Hz, tpy-4,4‘‘-H), 7.24 (s, 2 H, phenyl-H), 7.01 (s, 2 H, phenyl-H), 6.96 (s, 2 H, phenyl-H), 3.89 (t, 4 H, ^3J = 6.4 Hz, α-CH_2), 1.69 (quintet, 4 H, $^3J \approx 7$ Hz, β-CH_2), 1.23-1.43 (m, 12 H, γ-,δ-,ε-CH_2), 0.89 (t, 6 H, ^3J = 6.3 Hz, -CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 159.52, 154.82, 154.48, 151.57, 139.19, 137.84, 126.53, 124.79, 122.54, 121.50, 120.26, 119.77, 118.86, 116.16, 92.01, 87.19, 68.40, 31.48, 28.99, 25.59, 22.56, 14.02. **MS** (**EI**, 80 eV, 260°C): m/z (%) = 794 (0.8), 793 (1.5), 792 (1.0), 790 (0.6), 789 (1.2) $[M]^+$, 707 (0.7) $[M\text{-}C_6H_{12}]^+$, 623 (0.7) $[M\text{-}2C_6H_{12}]^+$. **EA**: Calc.: C:65.24, H:5.22, N:5.31; Found: C:65.42, H:5.39, N:5.04.

1-Ethynyl-3-hexoxy-5-[(triisopropylsilyl)ethynyl]benzene, $C_{25}H_{38}SiO$, M = 382.66, ***12a*** (Scheme 8)



96a (28.28 g, 62.17 mmol) was dissolved in a mixture of CH_2Cl_2 (300 ml) and MeOH (300 ml), and a few drops of 2 N NaOH were added. After stirring overnight, the solvent was evaporated and the crude mixture purified by chromatography over silica gel (hexane) to afford **12a** (23.56 g, 61.57 mmol, 99 %) as a slightly yellow oil. $\mathbf{R_f}$ = 0.34 (hexane). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 7.17 (d, 1 H, ^{4}J = 1.2 Hz, 4-H), 6.94-6.97 (m, 2 H, 2,6-H), 3.91 (t, 2 H, ^{3}J = 6.4 Hz, α-CH_2), 3.03 (s, 1 H, ethynyl-H), 1.74 (quintet, 2 H, ^{3}J ≈ 8 Hz, β-CH_2), 1.28-1.45 (m, 6 H, γ-, δ-, ε-CH_2), 1.11 (s, 21 H, silyl-H), 0.89 (t, 3 H, ^{3}J = 7.0 Hz, hexyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 158.64, 128.07, 124.70, 123.10, 118.81, 118.11, 105.95, 91.13, 82.83, 77.31, 68.20, 31.52, 29.10, 25.65, 22.58, 18.63, 14.01, 11.26. **MS** (**EI**, 80 eV, 120°C): m/z (%) = 384 (2.3), 383 (8.4), 382 (25.0) $[M]^+$, 342 (1.4), 341 (7.9), 340 (29.4), 339 (100.0), 338 (1.9) $[M\text{-}C_3H_7]^+$, 312 (3.8), 311 (12.5), $[M\text{-}C_5H_{11}]^+$, 299 (1.4), 298 (4.5), 297 (16.8) $[M\text{-}C_6H_{13}]^+$, 285 (2.5), 284 (5.1), 283 (19.2) $[M\text{-}C_5H_{11}\text{-}C_2H_4]^+$, 271 (1.7), 270 (6.0), 269 (24.8) $[M\text{-}C_6H_{13}\text{-}C_2H_4]^+$. **EA**: Calc.: C:78.47, H:10.01; Found: C:78.19, H: 9.89.

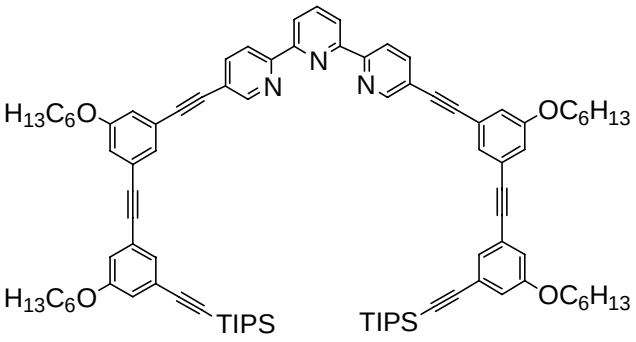
1-Ethynyl-3-(tetrahydropyran-2-yloxymethyl)-5-[(triisopropylsilyl)ethynyl]benzene, $C_{25}H_{36}O_2Si$, M = 396.64, ***12c*** (Scheme 8)



The procedure was analogous to that described for **12a** (**96b**: 24.52 g, 52.30 mmol; dichloromethane: 125 ml; methanol: 125 ml). The crude product was purified by chromatography over a short silica gel column (hexane/ethyl acetate + a few drops of triethylamine) to afford **12c** (20.30 g, 51.18 mmol, 98 %) as a yellow sirup. $\mathbf{R_f}$ = 0.52 (hexane/ethyl acetate 30:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 7.50 (s, 1 H, aryl-4-H), 7.42 (s, 2 H, aryl-2,6-H), 4.66-4.72 (m, 2 H, benzyl-H, THP-2-H), 4.40 (d, 1 H, ^{2}J = 12.3 Hz, benzyl-H'), 3.83-3.90 (m, 1 H, THP-6-H), 3.51-3.57 m, 1 H, THP-6-H), 3.05 (s, 1 H, ethynyl-H), 1.50-1.86 (m, 6 H, THP-3,3',4,4',5,5'-H), 1.10 (s, 21 H, silyl-H). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 138.85, 134.56, 131.36, 131.02, 123.84, 122.34, 105.84, 97.77, 91.46, 82.70, 77.68, 67.70, 62.02, 30.40, 25.37, 19.21, 18.59, 11.22. **MS** (**EI**, 80 eV, 120°C): m/z (%) =

397 (0.6), 396 (1.7) $[M]^+$, 357 (0.4), 356 (1.8), 355 (8.8), 354 (30.5), 353 (100.0) $[M-C_3H_7]^+$. **EA**: Calc.: C:75.70, H:9.15; Found: C:75.73, H:9.44.

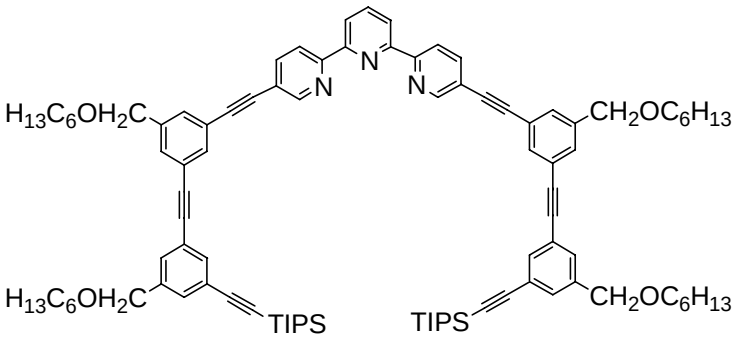
5,5‘‘-Bis{[3-({3-[(triisopropylsilyl)ethynyl]-5-hexoxyphenyl}ethynyl)-5-hexoxyphenyl]-ethynyl}-2,2‘:6‘,2‘‘-terpyridine, $C_{93}H_{115}N_3O_4Si_2$, M = 1395.12, ***14a***



The procedure was analogous to that described for **28a** (Scheme 2; **10**: 2.00 g, 4.95 mmol; **19a**: 7.32 g, 9.91 mmol; $Pd[P(Ph_3)]_4$: 344 mg, 0.30 mmol; toluene: 125 ml). The crude product was purified by column chromatography (dichloromethane) to afford **14a** (3.00 g, 2.15 mmol, 43 %) as a yellow resin. $\mathbf{R_f}$ = 0.53 (hexane/ethyl acetate 4:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 8.81 (d, 2 H, ^4J = 1.8 Hz, tpy-6,6‘‘-H), 8.60 (d, 2 H, ^3J = 8.3 Hz, tpy-3,3‘‘-H), 8.46 (d, 2 H, ^3J = 7.8 Hz, tpy-3’,5’-H), 7.97 (t, 1 H, $^3J \approx 9$ Hz, tpy-4’-H), 7.95 (dd, 2 H, ^3J = 8.3 Hz, ^4J = 2.0 Hz, tpy-4,4‘‘-H), 7.33 (s, 2 H, phenyl-H), 7.23 (d, 2 H, ^4J = 2.4 Hz, phenyl-H), 7.05 (dd, 4 H, ^4J = 1.0 Hz, ^4J = 4.7 Hz, phenyl-H), 6.98 (dd, 4 H, ^4J = 1.0 Hz, ^4J = 3.9 Hz, phenyl-H), 3.98 (t, 4 H, ^3J = 6.5 Hz, α-CH_2), 3.95 (t, 4 H, ^3J = 6.6 Hz, α-CH_2), 1.76 (quintet, 8 H, $^3J \approx 7$ Hz, β-CH_2), 1.31-1.45 (m, 24 H, γ-,δ-,ε-CH_2), 1.12 (s, 42 H, silyl-H), 0.90 (m, 12 H, hexyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 158.93, 158.76, 154.92, 154.77, 151.68, 139.35, 138.01, 127.72, 127.30, 124.77, 124.37, 123.94, 123.79, 121.59, 120.48, 120.17, 118.62, 118.27, 118.01, 117.60, 106.10, 92.81, 91.14, 89.10, 88.63, 86.63, 68.37, 68.28, 31.53, 29.12, 25.66, 22.59, 18.66, 14.01, 11.30. **MS** (**EI**, 80 eV, 320°C): m/z (%) = 1397 (0.2), 1396 (0.3), 1395 (0.5), 1394 (0.4), 1393 (0.4) $[M]^+$, 1355 (0.4), 1354 (0.9), 1353 (2.0), 1352 (3.8), 1351 (3.5), 1350 (2.5) $[M-C_3H_7]^+$, 1314 (0.2), 1313 (0.4), 1312 (1.1), 1311 (2.5), 1310 (4.6), 1309 (10.9), 1308 (6.4), 1307 (5.8), 1306 (0.2) $[M-2C_3H_7]^+$, 1271 (0.3), 1270 (0.9), 1269 (1.7), 1268 (2.5), 1267 (2.8), 1266 (3.4), 1265 (0.3) $[M-3C_3H_7]^+$. **EA**: Calc.: C:80.07, H:8.31, N:3.01; Found: C:79.82, H:8.26, N:2.93.

5,5‘‘-Bis{[3-hexoxymethyl-5-({3-hexoxymethyl-5-[(triisopropylsilyl)ethynyl]phenyl}ethynyl)-phenyl]ethynyl}-2,2‘:6‘,2‘‘-terpyridine, $C_{97}H_{123}N_3O_4Si_2$, M = 1451.23, ***14b***

The procedure was analogous to that described for **28a** (**10**: 847 mg, 2.09 mmol; **19b**: 3.21 g, 4.19 mmol; $Pd[P(Ph_3)]_4$: 150 mg, 0.130 mmol, toluene: 50 ml, reaction time: 60 hrs). For the chromatographic purification, dichloromethane was used as eluent to afford **14b** (1.67 g, 1.15 mmol, 55 %) as a yellow sirup. $\mathbf{R_f}$ = 0.50 (hexane/ethyl acetate 10:1, aluminium oxide).

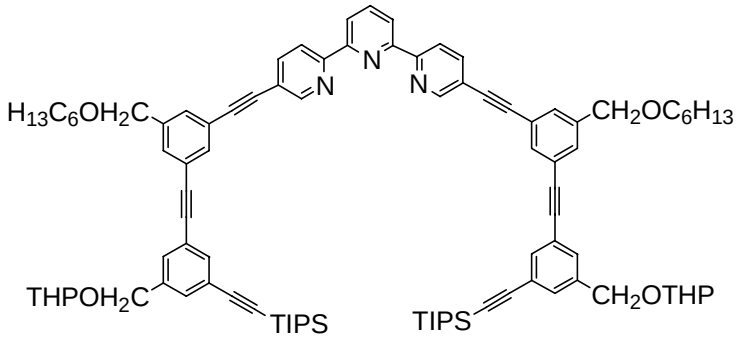


^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.81 (dd, 2 H, ^4J = 1.8 Hz, ^5J = 0.6 Hz, tpy-6,6‘‘-H), 8.60 (d, 2 H, ^3J = 8.3 Hz, tpy-3,3‘‘-H), 8.47 (d, 2 H, ^3J = 7.8 Hz, tpy-3‘,5‘-H), 7.95 (t, 1 H, ^3J = 7.8 Hz, tpy-4‘-H), 7.95 (dd, 2 H, ^3J = 8.2 Hz, ^4J = 2.2 Hz, tpy-4,4‘‘-H), 7.64 (s, 2 H, phenyl-H), 7.55 (t, 2 H, ^4J = 1.3 Hz, phenyl-H), 7.50 (d, 2 H, ^4J = 1.3 Hz, phenyl-H), 7.48 (s, 2 H, phenyl-H), 7.44 (s, 2 H, phenyl-H), 7.40 (s, 2 H, phenyl-H), 4.49 (s, 4 H, aryl-CH_2-O-), 4.45 (s, 4 H, aryl-CH_2-O-), 3.49 (t, 4 H, ^3J = 6.5 Hz, α-CH_2), 3.46 (t, 4 H, ^3J = 6.5 Hz, α-CH_2), 1.59-1.66 (m, 8 H, β-CH_2), 1.29-1.38 (m, 24 H, γ-,δ-,ε-CH_2), 1.12 (s, 42 H, silyl-H), 0.89 (t, 6 H, ^3J =6.6 Hz, hexyl-CH_3), 0.88 (t, 6 H, ^3J =6.5 Hz, hexyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 154.89, 154.71, 151.66, 139.68, 139.37, 139.24, 137.92, 134.13, 133.69, 130.91, 130.78, 130.38, 123.95, 123.56, 123.15, 123.02, 121.54, 120.36, 120.10, 106.02, 92.67, 91.42, 89.30, 88.86, 86.98, 71.87, 70.87, 70.80, 31.66, 29.67, 25.83, 22.61, 18.64, 14.03, 11.27. **MS** (**FAB(+)**, MNBA/CH_2Cl_2-Matrix): m/z (%) = 1453 (7.2), 1452 (8.5), 1451 (7.6) $[M+H]^+$, 1367 (4.1), 1366 (4.0), 1365 (4.3) $[M-C_6H_{12}]^+/[M-C_6H_{14}]^+$. **EA**: Calc.: C:80.28, H:8.54, N:2.90; Found: C:80.39, H:8.26, N:2.68.

5,5‘‘-Bis{[3-hexyloxymethyl-5-({3-(tetrahydropyran-2-yloxymethyl)-5-[(triisopropylsilyl)-ethynyl]phenyl}ethynyl)phenyl]ethynyl} -2,2‘:6‘,2‘‘-terpyridine, $C_{95}H_{115}N_3O_6Si_2$, M = 1451.14, **14c**

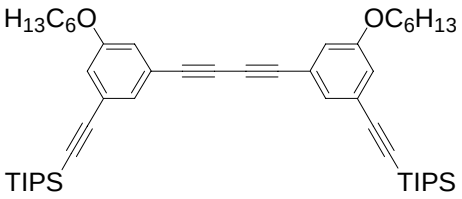
The procedure was analogous to that described for **28a** (**10**: 1.61 g, 3.98 mmol; **19c**: 6.10 g, 7.95 mmol; $Pd[P(Ph_3)]_4$: 276 mg, 0.23 mmol, toluene: 120 ml, reaction time: 72 hrs). The crude product was purified by column chromatography (aluminium oxide, hexane/ethyl acetate 15:1) to

afford **14c** (1.80 g, 1.24 mmol, 31 %) as a colorless resin. $\mathbf{R_f}$ = 0.29 (hexane/ethyl acetate 20:1, aluminium oxide).



^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.82 (dd, 2 H, ^{4}J = 1.7 Hz, ^{5}J = 0.7 Hz, tpy-6,6''-H), 8.62 (d, 2 H, ^{3}J = 8.3 Hz, tpy-3,3''-H), 8.47 (d, 2 H, ^{3}J = 7.8 Hz, tpy-3',5'-H), 7.97 (t, 1 H, ^{3}J = 7.7 Hz, tpy-4'-H), 7.95 (dd, 2 H, ^{3}J = 8.3 Hz, ^{4}J = 2.3 Hz, tpy-4,4''-H), 7.66 (t, 2 H, ^{4}J = 1.4 Hz, phenyl-H), 7.56 (t, 2 H, ^{4}J = 1.4 Hz, phenyl-H), 7.52 (s, 2 H, phenyl-H), 7. t, 2 H, ^{4}J = 1.2 Hz, phenyl-H), 7.48 (s, 2 H, phenyl-H), 7.42 (s, 2 H, phenyl-H), 4.69-4.76 (m, 4 H, benzyl (THP)-H, THP-2-H), 4.50 (s, 4 H, benzyl (hexyl)-H), 4.45 (d, 2 H, ^{2}J ≈ 12 Hz, benzyl (THP)-H'), 3.85-3.94 (m, 2 H, THP-6-H), 3.51-3.59 (m, 2 H, THP-6'-H), 3.49 (t, 4 H, ^{3}J = 6.6 Hz, hexyl-α-CH_2), 1.52-1.85 (m, 16 H, THP-3,3',4,4',5,5'-H, hexyl-β-CH_2), 1.29-1.41 (m, 12 H, hexyl-γ-, δ-, ε-CH_2), 1.12 (s, 42 H, silyl-H), 0.89 (t, 3 H, ^{3}J = 6.8 Hz, hexyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 154.86, 154.68, 151.64, 139.66, 139.23, 138.92, 137.92, 134.18, 133.68, 131.10, 130.77, 130.57, 130.44, 123.93, 123.52, 123.17, 123.00, 121.52, 120.35, 120.08, 105.98, 97.83, 92.66, 91.47, 89.27, 88.87, 86.97, 71.83, 70.85, 67.82, 62.09, 31.65, 30.44, 29.66, 25.82, 25.39, 22.61, 19.25, 18.63, 14.03, 11.25. **MS** (**EI**, 80 eV, 350°C, decomposition): m/z (%) = 1452 (20.4), 1451 (25.4) $[M]^+$, 1410 (25.8), 1409 (28.2), 1408 (35.9), 1407 (34.0) $[M\text{-}C_3H_7]^+$, 1369 (27.1), 1368 (43.5), 1367 (59.7), 1366 (94.3), 1365 (100.0), 1364 (80.7) $[M\text{-}C_6H_{13}]^+$, 1327 (17.9), 1326 (26.0), 1325 (57.4), 1324 (48.5), 1323 (52.6) $[M\text{-}C_6H_{13}\text{-}C_3H_7]^+$, 1282 (26.5), 1280 (47.2) $[M\text{-}C_6H_{13}\text{-}C_6H_{12}]^+$. **MS** (**FAB(+)**, CH_2Cl_2/MNBA-Matrix): m/z (%) = 1455 (4.8), 1454 (9.5), 1453 (10.6), 1452 (13.5) $[M+H]^+$, 1370 (2.8), 1369 (3.8), 1368 (6.3) $[M+H\text{-}C_6H_{12}]^+$. **EA**: Calc.: C:78.63, H:7.99, N:2.90; Found: C:78.78, H:7.87, N:3.00.

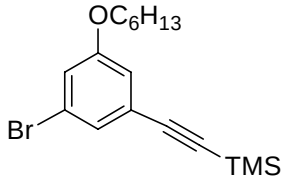
1,4-Bis{3-hexoxy-5-[(triisopropylsilyl)ethynyl]}buta-1,3-diyne, $C_{50}H_{74}O_2Si_2$, M = 762.50, ***15***



This compound was isolated as a side product from the synthesis of **14a** according to Scheme 1. This was analogous to that described for **94** (**11**: 140 mg, 0.177 mmol; **12a**: 405 mg, 1.06 mmol; CuI: 10 mg,

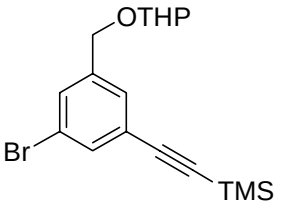
0.05 mmol; $Pd[P(Ph_3)]_4$: 61 mg, 0.05 mmol; triethylamine: 25 ml; toluene: 25 ml; reaction temperature: 70°C; reaction time: 72 hrs). The crude product was purified by chromatography over silica gel (hexane) to afford the desired product (**14a**) as impure material (130 mg) and **15** (260 mg, 0.34 mmol, 64 %). $\mathbf{R_f}$ = 0.16 (hexane). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 7.22 (t, 2 H, ^{4}J = 1.2 Hz, aryl-H), 6.97-7.00 (m, 4 H, aryl-H), 3.92 (t, 4 H, ^{3}J = 6.4 Hz, α-CH_2), 1.75 (quintet, 4 H, ^{3}J ≈ 7 Hz, β-CH_2), 1.28-1.44 (m, 12 H, γ-, δ-, ε-CH_2), 1.12 (s, 42 H, silyl-H), 0.91 (t, 3 H, ^{3}J = 6.3 Hz, hexyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 158.71, 128.50, 124.91, 122.68, 119.46, 118.12, 105.76, 91.15, 80.92, 73.90, 68.28, 31.52, 29.08, 25.65, 22.59, 18.63, 14.01, 11.28. **MS** (**EI**, 80 eV, 270°C): m/z (%) = 765 (5.4), 764 (13.9), 763 (26.7), 762 (39.6) $[M]^+$, 723 (5.7), 722 (13.1), 721 (30.1), 720 (64.0), 719 (100.0) $[M\text{-}C_3H_7]^+$, 679 (8.0), 678 (13.4), 677 (15.7) $[M\text{-}C_6H_{13}]^+$, 639 (7.6), 638 (9.6), 637 (11.2), 636 (11.5), 635 (16.0) $[M^+\text{-}C_3H_7\text{-}C_6H_{12}]^+$.

1-Bromo-3-hexoxy-5-[(trimethylsilyl)ethynyl]benzene, $C_{17}H_{25}BrOSi$, M = 353.37, ***16a*** (Scheme 8)



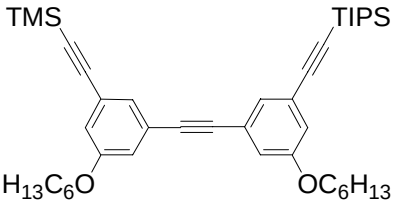
Under N_2, to a degassed solution of **8** (18.24, 47.6 mmol) in dry triethylamine (250 ml) were added CuI (272 mg, 1.42 mmol), $[Pd(PPh_3)_4]$ (1.65 g, 1.42 mmol) and TMS-acetylene (4.77 mg, 48.6 mmol). The mixture was shortly evacuated and stirred for 72 hrs at 60°C in a sealed flask. The solvent was evaporated in vacuo and the residue filtered through a short silica gel column (hexane) to give **16a** (16.4 g, 46.4 mmol, 97 %) as a slightly yellow oil. $\mathbf{R_f}$ = 0.40 (hexane). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 7.18 (t, 1 H, ^{4}J = 1.4 Hz, aryl-H), 6.99 (t, 1 H, ^{4}J = 2.1 Hz, aryl-H), 6.89 (dd, 1 H, ^{4}J = 1.3 Hz, ^{4}J = 2.2 Hz, aryl-H), 3.88 (t, 2 H, ^{3}J = 6.5 Hz, α-CH_2), 1.73 (quintet, 2 H, ^{3}H ≈ 7 Hz, β-CH_2), 1.30-1.42 (m, 6 H, γ-, δ-, ε-CH_2), 0.90 (t, 3 H, ^{3}J = 6.6 Hz, -CH_3), 0.24 (s, 9 H, silyl-H). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 159.34, 126.86, 125.36, 122.29, 118.76, 116.30, 103.37, 95.29, 68.30, 31.47, 28.99, 25.59, 22.57, 14.02, -0.17. **MS** (**EI**, 80 eV, 50°C): m/z (%) = 356 (5.8), 355 (23.3), 354 (96.8), 353 (24.6), 352 (94.3) $[M]^+$, 341 (4.5), 340 (16.9), 339 (72.3), 338 (17.3), 337 (70.7) $[M\text{-}CH_3]^+$, 272 (1.6), 271 (5.6), 270 (29.7), 269 (7.0), 268 (29.7), 267 (2.4) $[M\text{-}C_6H_{12}]^+$, 257 (4.9), 256 (16.5), 255 (99.7), 254 (20.6), 253 (100.0), 252 (4.9), 251 (2.3) $[M\text{-}C_6H_{12}\text{-}CH_3]^+$. **EA**: Calc.: C:57.78, H:7.13; Found: C:57.60, H:6.88.

1-Bromo-3-(tetrahydropyran-2-yloxymethyl)-5-[(trimethylsilyl)ethynyl]benzene, $C_{17}H_{23}BrO_2Si$, M = 253.21, ***16c*** (Scheme 8)



The procedure was analogous to that described for **16a** (**93a**: 21.72 g, 54.7 mmol; TMS-acetylene: 5.48 g, 55.8 mmol; CuI: 319 mg, 1.68 mmol; $[Pd(PPh_3)_4]$: 1.94 g, 1.68 mmol; triethylamine: 300 ml; reaction time: 4 days). The crude product was purified by chromatography over silica gel (hexane/toluene) to afford **16c** (17.05 g, 46.4 mmol, 85 %) as a yellow sirup. $\mathbf{R_f}$ = 0.81 (hexane/ethyl acetate 10:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 7.49 (s, 1 H, aryl-H), 7.44 (s, 1 H, aryl-H), 7.30 (s, 1 H, aryl-H), 4.65-4.70 (m, 2 H), 4.39 (d, 1 H, ^3J = 12.5 Hz), 3.80-3.85 (m, 1 H), 3.50-3.54 (m, 1 H), 1.53-1.82 (m, 6 H), 0.22 (s, 9 H, silyl-H). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 140.53, 133.52, 130.60, 129.45, 124.90, 121.93, 103.24, 97.76, 95.67, 67.38, 61.95, 30.34, 25.32, 19.13, -0.22. **MS** (**EI**, 80 eV, 40-50°C): m/z (%) = 368 (0.4), 366 (0.5) $[M]^+$, 353 (0.9), 351 (0.9) $[M-CH_3]^+$, 300 (0.6), 299 (0.5), 298 (1.5), 297 (7.2), 296 (1.7), 295 (7.5) $[M-C_4H_7O]^+$, 270 (7.4), 269 (31.6), 268 (89.6), 267 (96.8), 266 (86.3), 265 (71.0) $[M-C_5H_8O_2]^+$/$[M-C_5H_9O_2]^+$, 254 (11.8), 253 (24.9), 252 (37.1), 251 (24.4), 250 (28.2) $[M-C_5H_8O_2-CH_3]^+$/$[M-C_5H_9O_2-CH_3]^+$. **EA**: Calc.: C:55.58, H:6.31; Found: C:55.61, H:6.07.

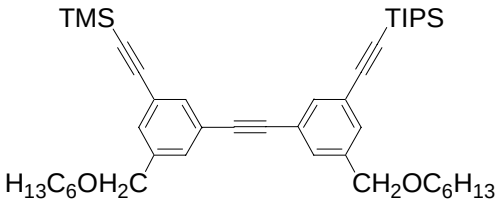
1-Hexoxy-3-({3-hexoxy-5-[(trimethylsilyl)ethynyl]phenyl}ethynyl)-5-[(triisopropylsilyl) ethynyl]benzene, $C_{42}H_{62}O_2Si_2$, M = 655.12, ***17a***



The procedure was analogous to that described for **94** (**12a**: 8.00 g, 20.9 mmol;**16a**: 7.43 g, 20.9 mmol; CuI: 119 mg, 0.63 mmol; $Pd[P(Ph_3)]_4$: 725 mg, 0.63 mmol; triethylamine: 150 ml; reaction temperature: 70°C; reaction time: 4 days). The crude product was purified by chromatography over silica gel (hexane/toluene) to afford **17a** (10.22 g, 15.6 mmol, 75 %) as a yellow sirup.$\mathbf{R_f}$ = 0.79 (hexane/ethyl acetate 100:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 7.19-7.20 (m, 2 H, aryl-H), 6.94-7.00 (m, 4 H, aryl-H), 3.90-3.96 (2 t, 4 H, ^3J = 6.5 Hz, α-CH_2), 1.70-1.78 (quintet, 4 H, $^3J \approx 7$ Hz, β-CH_2), 1.31-1.43 (m, 12 H, γ-,δ-,ε-CH_2), 1.11 (s, 21 H, TIPS-H), 0.89 (t, 6 H, ^3J = 6.6 Hz, hexyl-CH_3), 0.23 (s, 9 H, TMS-H). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 158.72, 127.66, 124.71, 124.32, 124.03, 118.55, 118.15, 118.03, 117.50, 106.12, 104.15, 94.58,

91.03, 88.80, 88.74, 68.22, 31.53, 29.11, 25.66, 22.59, 18.65, 14.01, 11.29, -0.12. **MS** (**EI**, 80 eV, 180°C): m/z (%) = 657 (2.4), 656 (7.8), 655 (16.5), 654 (33.0) $[M]^+$, 639 (1.6) $[M\text{-}CH_3]^+$, 615 (2.2), 614 (6.3), 613 (22.3), 612 (54.1), 611 (100.0) $[M\text{-}C_3H_7]^+$, 585 (2.1), 584 (5.3), 583 (11.5) $[M\text{-}C_5H_{11}]^+$, 571 (3.6), 570 (8.0), 569 (15.5) $[M\text{-}C_6H_{13}]^+$. **EA**: Calc.: C:77.00, H:9.54; Found: C:77.00, H:9.58.

1-Hexoxymethyl-3-({3-hexoxymethyl-5-[(trimethylsilyl)ethynyl]phenyl}ethynyl)-5-[(triisopropylsilyl)ethynyl]benzene, $C_{44}H_{66}O_2Si_2$, M = 683.17, **17b**

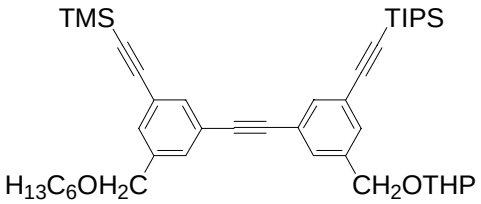


The procedure was analogous to that described for **94** (**12b**: 14.16 g, 35.7 mmol; **16b**: 13.11 g, 35.7 mmol; CuI: 204 mg, 1.07 mmol; $Pd[P(Ph_3)]_4$: 1.24 g, 1.07 mmol; triethylamine: 500 ml; reaction time: 3 days; reaction temperature: 70°C). The crude product was purified by column chromatography (silica gel, hexane/toluene) to afford **17b** (18.50 g, 27.1 mmol, 76 %) as a yellow oil. $\mathbf{R_f}$ = 0.36 (hexane/ethyl acetate 50:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 7.53 (d, 2 H, ^4J = 1.7 Hz, aryl-H), 7.42 (d, 2 H, ^4J = 1.4 Hz, aryl-H), 7.39 (s, 2 H, aryl-H), 4.44 (2 s, 4 H, benzyl-H), 3.45 (t, 2 H, ^3J = 6.6 Hz, α-CH_2), 3.44 (t, 2 H, ^3J = 6.6 Hz, α-CH_2), 1.58-1.60 (m, 4 H, β-CH_2), 1.28-1.35 (m, 12 H, γ-,δ-,ε-CH_2), 1.11 (s, 21 H, TIPS-H), 0.88 (t, 6 H, ^3J =6.8 Hz, hexyl-CH_3), 0.22 (s, 9 H, TMS-H). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 139.34, 134.10, 134.02, 130.75, 130.47, 130.34, 123.92, 123.52, 123.24, 106.04, 104.05, 94.91, 91.34, 89.00, 88.95, 71.86, 70.76, 31.65, 29.65, 25.82, 22.60, 18.63, 14.02, 11.27, -0.14. **MS** (**EI**, 80 eV, 180°C): m/z (%) = 685 (7.7), 684 (23.6), 683 (54.9), 682 (100.0) $[M]^+$, 641 (16.3), 640 (37.7), 639 (70.4) $[M\text{-}C_3H_7]^+$, 583 (10.9), 582 (20.9) $[M\text{-}OC_6H_{13}]^+$, 540 (8.1), 539 (16.3) $[M\text{-}C_3H_7\text{-}OC_6H_{13}]^+$. **EA**: Calc.: C:77.36, H:9.74; Found: C:77.13, H:9.51.

1-Hexoxymethyl-3-({3-(tetrahydropyran-2-yloxymethyl)-5-[(triisopropylsilyl)ethynyl]phenyl}-ethynyl)-5-[(trimethylsilyl)ethynyl]benzene, $C_{43}H_{62}O_3Si_2$, M = 683.13, ***17c***

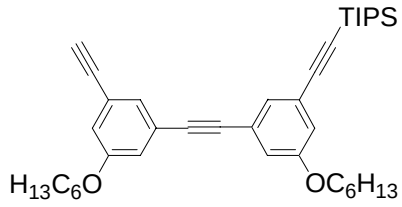
The procedure was analogous to that described for **94** (**12c**: 7.00 g, 17.6 mmol; **16b**: 6.50 g, 17.6 mmol; CuI: 100 mg, 0.530 mmol; $Pd[P(Ph_3)]_4$: 610 mg, 0.530 mmol; triethylamine: 150 ml; reaction time: 3 days; reaction temperature: 70°C). The crude product was purified by column

chromatography (silica gel, hexane/toluene) to afford **17c** (7.38 g, 10.8 mmol, 61 %) as a brownish foam. $\mathbf{R_f}$ = 0.24 (hexane/ethyl acetate 20:1).



^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.53 (d, 2 H, ^{4}J = 1.6 Hz, aryl-H), 7.38-7.44 (m, 4 H, aryl-H), 4.68-4.75 (m, 2 H, benzyl (THP)-H, THP-2-H), 4.42-4.47 (m, 3 H, benzyl (THP)-H', benzyl (hexyl)-H), 3.85-3.93 (m, 1 H, THP-6-H), 3.50-3.58 (m, 1 H, THP-6'-H), 3.44 (t, 2 H, ^{3}J = 6.6 Hz, hexyl-α-CH_2), 1.52-1.85 (m, 8 H, THP-3,3',4,4',5,5'-H, hexyl-β-CH_2), 1.24-1.38 (m, 6 H, hexyl-γ-, δ-, ε-CH_2), 1.11 (s, 21 H, TIPS-H), 0.88 (t, 3 H, ^{3}J = 6.7 Hz, hexyl-CH_3), 0.23 (s, 9 H, TMS-H). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 139.36, 138.90, 134.18, 134.04, 131.03, 130.78, 130.52, 123.92, 123.52, 123.26, 106.02, 104.05, 97.83, 94.94, 91.44, 88.99, 71.86, 70.74, 67.85, 62.11, 31.65, 30.46, 29.66, 25.82, 25.41, 22.61, 19.26, 18.64, 14.03, 11.28, -0.13. **MS** (**EI**, 80 eV, 220°C): m/z (%) = 683 (5.9), 682 (10.4), 681 (9.0) $[M]^+$, 642 (5.5), 641 (18.9), 640 (44.8), 639 (77.9), 638 (42.5) $[M-C_3H_7]^+$, 598 (8.2), 597 (8.8) $[M-C_3H_7-C_3H_6]^+$, 585 (7.7), 584 (23.6), 583 (56.9), 582 (100.0), 581 (4.9) $[M-C_5H_8O_2]^+$, 540 (4.9), 539 (8.9) $[M-C_5H_8O_2-C_3H_7]^+$. **EA**: Calc.: C:75.60, H:9.15; Found: C:75.59, H:9.35.

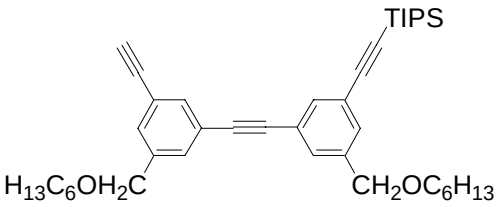
1-Hexoxy-3-[1-(3-hexoxy-5-ethynylphenyl)ethynyl]-5-[(triisopropylsilyl)ethynyl]benzene, $C_{39}H_{54}O_2Si$, M = 582.94, ***18a***



The procedure was analogous to that described for **12a** (**17a**: 10.2 g, 15.6 mmol; methanol: 70 ml; dichloromethane: 70 ml). The crude product was dissolved in dichloromethane (100 ml), washed with water (100 ml) and the aqueous phase extracted with dichloromethane (2 × 100 ml). The combined organic phases were dried over $MgSO_4$, and the solvent was evaporated to afford **18a** (8.87 g, 15.2 mmol, 98 %) as a brownish sirup, which crystallized to a slightly colored amorphous material. $\mathbf{R_f}$ = 0.21 (hexane). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 7.21 (m, 2 H, aryl-H), 6.97-7.01 (m, 4 H, aryl-H), 3.91-3.96 (2 t, 4 H, ^{3}J ≈ 7 Hz, α-CH_2), 3.04 (s, 1 H, ethynyl-H), 1.75 (quintet, 4 H, ^{3}J ≈ 7 Hz, β-CH_2), 1.32-1.43 (m, 12 H, γ-,δ-,ε-CH_2), 1.11 (s, 21 H, silyl-H), 0.89 (t, 6 H, ^{3}J = 6.8 Hz, hexyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 158.74, 127.64, 124.73, 124.20, 123.92, 123.30, 118.60, 118.21, 117.56, 106.08, 91.10, 88.95, 88.58, 82.77, 68.28, 31.52, 29.12, 25.65, 22.58,

18.65, 14.01, 11.29. **MS** (**EI**, 80 eV, 150°C): m/z (%) = 583 (8.0), 582 (13.6) $[M]^+$, 541 (22.2), 540 (55.4), 539 (100.0) $[M\text{-}C_3H_7]^+$, 512 (6.9), 511 (15.0) $[M\text{-}C_5H_{11}]^+$, 498 (9.8), 497 (21.7) $[M\text{-}C_6H_{13}]^+$, 484 (6.7), 483 (11.8) $[M\text{-}C_5H_{11}\text{-}C_2H_4]^+$, 469 (15.3) $[M\text{-}C_6H_{13}\text{-}C_2H_4]^+$. **EA**: Calc.: C:80.36, H:9.34; Found: C:80.08, H:9.12.

1-Hexoxymethyl-3-[1-(3-hexoxymethyl-5-ethynylphenyl)ethynyl]-5-[(triisopropylsilyl)ethynyl] -benzene, $C_{41}H_{58}O_2Si$, M = 610.99, ***18b***

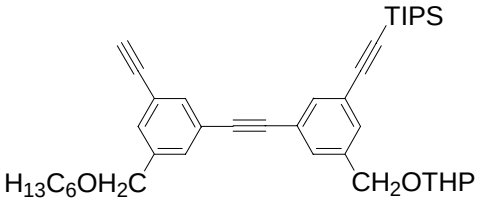


The procedure was analogous to that described for **12a** (**17b**: 18.50 g, 27.08 mmol; dichloromethane: 250 ml; methanol: 250 ml). The solvent was evaporated and the crude product dissolved in dichloromethane (200 ml) and washed with aqueous NaCl (200 ml). The aqueous phase was extracted with dichloromethane (100/50 ml), the combined organic phases are dried over $MgSO_4$ and the solvent was evaporated to afford **18b** (16.08 g, 26.32 mmol, 97 %) as a brownish oil. Alternatively, the crude product was purified by chromatography over silica gel (hexane/toluene). $\mathbf{R_f}$ = 0.67 (hexane/ethyl acetate 40:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 7.54 (d, 2 H, ^4J = 1.4 Hz, aryl-H), 7.46 (s, 1 H, aryl-H), 7.40-7.43 (m, 3 H, aryl-H), 4.45 (s, 4 H, aryl-CH_2-O-), 3.46 (t, 2 H, ^3J = 6.6 Hz, α-CH_2), 3.45 (t, 2 H, ^3J = 6.6 Hz, α-CH_2), 3.07 (s, 1 H, ethynyl-H), 1.59 (quintet, 4 H, $^3J \approx 7$ Hz, β-CH_2), 1.26-1.39 (m, 12 H, γ-,δ-,ε-CH_2), 1.21 (s, 21 H, silyl-H), 0.88 (t, 6 H, ^3J =6.8 Hz, hexyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 139.51, 139.34, 134.09, 130.89, 130.36, 123.93, 123.39, 123.14, 122.52, 106.01, 91.38, 89.15, 88.80, 82.69, 77.72, 71.87, 71.78, 70.79, 31.65, 29.65, 25.82, 22.60, 18.63, 14.02, 11.26. **MS** (**EI**, 80 eV, 160°C): m/z (%) = 612 (12.7), 611 (44.3), 610 (100.0) $[M]^+$, 569 (8.1), 568 (29.6), 567 (75.1) $[M\text{-}C_3H_7]^+$, 525 (9.4) $[M\text{-}C_6H_{13}]^+$, 511 (7.3), 510 (20.7) $[M\text{-}OC_6H_{13}]^+$, 468 (6.7), 467 (20.3) $[M\text{-}C_3H_7\text{-}OC_6H_{13}]^+$. **EA**: Calc.: C:80.60, H:9.57; Found: C:80.51, H:9.45.

1-Hexoxymethyl-3-({3-(tetrahydropyran-2-yloxymethyl)-5-[(triisopropylsilyl)ethynyl]phenyl}ethynyl)-5-ethynylbenzene, $C_{40}H_{54}O_3Si$, M = 610.95, ***18c***

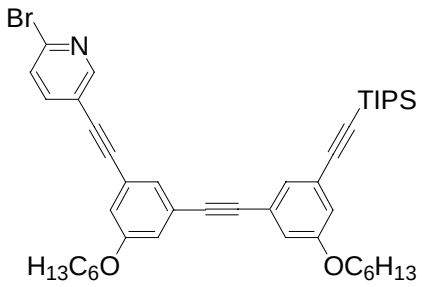
The procedure was analogous to that described for **12a** (**17c**: 7.38 g, 10.80 mmol; dichloromethane: 125 ml; methanol: 125 ml). The solvent was evaporated, the crude product

dissolved in dichloromethane (200 ml) and washed with aqueous NaCl (200 ml). The crude product was purified by chromatography over silica gel (hexane/ethyl acetate + a few drops of triethylamine) to afford **18c** (5.69 g, 9.33 mmol, 86 %) as a yellow sirup. $\mathbf{R_f}$ = 0.63 (hexane/ethyl acetate 10:1).



^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.54 (d, 2 H, ^{4}J = 1.3 Hz, aryl-H), 7.45 (s, 2 H, aryl-H), 7.40 (m, 2 H, aryl-H), 4.68-4.75 (m, 2 H, benzyl (THP)-H, THP-2-H), 4.43-4.52 (m, 3 H, benzyl (THP)-H', benzyl (hexyl)-H), 3.85-3.93 (m, 1 H, THP-6-H), 3.51-3.57 (m, 1 H, THP-6'-H), 3.45 (t, 2 H, ^{3}J = 6.7 Hz, hexyl-α-CH_2), 3.07 (s, 1 H, ethynyl-H), 1.58-1.84 (m, 8 H, THP-3,3',4,4',5,5'-H, hexyl-β-CH_2), 1.29-1.40 (m, 6 H, hexyl-γ-, δ-, ε-CH_2), 1.11 (s, 21 H, TIPS-H), 0.88 (t, 3 H, ^{3}J = 6.6 Hz, hexyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 139.52, 138.92, 134.15, 134.08, 131.08, 130.89, 130.82, 130.57, 123.92, 123.37, 123.17, 122.52, 105.99, 97.83, 91.45, 89.14, 88.82, 82.68, 77.74, 71.77, 70.80, 67.82, 62.08, 31.64, 30.45, 29.65, 25.81, 25.40, 22.59, 19.25, 18.63, 14.01, 11.26. **MS** (**EI**, 80 eV, 230°C): m/z (%) = 610 (3.7), 609 (5.7) $[M-H]^+$, 569 (13.0), 568 (39.5), 567 (84.7), 566 (32.2), 565 (1.9) $[M-C_3H_7]^+$, 512 (5.4), 511 (14.2), 510 (45.2), 509 (100.0), 508 (2.3) $[M-C_5H_9O_2]^+$. **EA**: Calc.: C:78.64, H:8.91; Found: C:78.81, H:8.67.

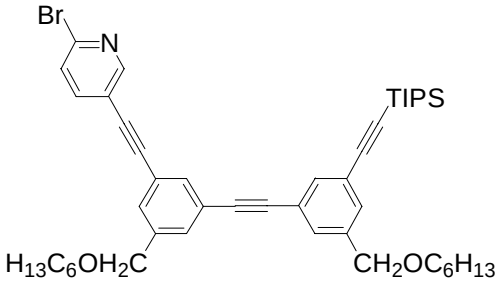
2-Bromo-5-{[3-hexoxy-5-({3-hexoxy-5-[(triisopropylsilyl)ethynyl]phenyl}ethynyl)phenyl]-ethynyl}pyridine, $C_{44}H_{56}BrNO_2Si$, M = 738.92, ***19a***



The procedure was analogous to that described for **94** (**6**: 4.32 g, 15.2 mmol; **18a**: 8.87 g, 15.2 mmol; CuI: 87 mg, 0.46 mmol; $Pd[P(Ph_3)]_4$: 527 mg, 0.46 mmol; triehtylamine: 150 ml; reaction time: 3 days). The crude product was purified by column chromatography (silica gel, hexane/toluene) to afford **19a** (9.88 g, 13.88 mmol, 88 %) as a yellow sirup, which crystallized to an amorphous material. $\mathbf{R_f}$ = 0.48 (hexane/ethyl acetate 30:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 8.48 (d, 1 H, ^{4}J = 2.3 Hz, py-6-H), 7.62 (dd, 1 H, ^{3}J = 8.3 Hz, ^{4}J = 2.4 Hz, py-4-H), 7.45 (d, 1 H, ^{3}J = 8.3 Hz, py-3-H), 7.27 (s, 1 H, phenyl-H), 7.21 (s, 1 H, phenyl-H), 6.97-7.04 (m, 4 H, phenyl-H), 3.96 (t, 2 H, ^{3}J = 6.3 Hz, α-CH_2), 3.94 (t, 2 H, ^{3}J = 6.3 Hz, α-CH_2), 1.77 (m, 4 H, β-CH_2), 1.32-1.46 (m, 12 H, γ-, δ-, ε-CH_2), 1.11 (s, 21 H, silyl-H),

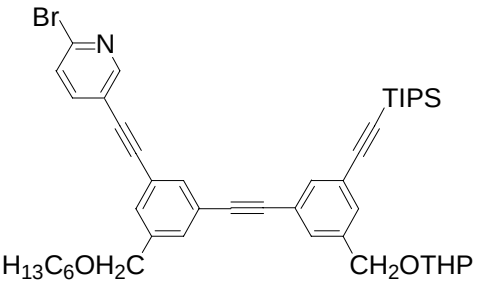
0.89 (t, 6 H, ^3J = 6.7, -CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 158.90, 158.74, 152.39, 141.23, 140.52, 127.68, 127.19, 124.75, 124.42, 123.85, 119.47, 118.60, 118.40, 117.95, 117.58, 106.05, 92.12, 91.14, 89.17, 88.48, 84.92, 68.34, 68.25, 31.51, 29.10, 25.64, 22.58, 18.64, 14.01, 11.27. **MS** (**EI**, 80 eV, 100°C): m/z (%) = 741 (2.6), 740 (6.3), 739 (13.1), 738 (7.3), 737 (12.5) $[M]^+$, 699 (3.8), 698 (17.9), 697 (48.7), 696 (100.0), 695 (43.1), 694 (84.8) $[M\text{-}C_3H_7]^+$, 668 (3.9), 666 (4.0) $[M\text{-}C_5H_{11}]^+$, 655 (2.9), 654 (8.2), 653 (3.9), 652 (6.5) $[M\text{-}C_6H_{13}]^+$, 640 (3.9), 638 (3.5) $[M\text{-}C_6H_{13}\text{-}C_2H_4]^+$. **EA**: Calc.: C:71.52, H:7.64, N:1.90; Found: C:71.34, H:7.74, N:1.65.

2-Bromo-5-{[3-hexoxymethyl-5-({3-hexoxymethyl-5-[(triisopropylsilyl)ethynyl]phenyl}ethynyl) phenyl]ethynyl}pyridine, $C_{46}H_{60}BrNO_2Si$, M = 766.97, ***19b***



The procedure was analogous to that described for **94** (**6**: 7.47 g, 26.32 mmol; **18b**: 16.08 g, 26.32 mmol; CuI: 150 mg, 0.79 mmol; $Pd[P(Ph_3)]_4$: 912 mg, 0.79 mmol, triethylamine: 270 ml; reaction time: 3 days). The crude product was purified by column chromatography (silica gel, hexane/toluene) to afford **19b** (14.79 g, 19.28 mmol, 73 %) as a yellow sirup, which slowly crystallized. $\mathbf{R_f}$ = 0.13 (hexane/ethyl acetate 50:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 8.49 (d, 1 H, ^4J = 2.1 Hz, py-6-H), 7.62 (dd, 1 H, ^3J = 8.3 Hz, ^4J = 2.3 Hz, py-4-H), 7.59 (t, 1 H, ^4J = 1.2 Hz, phenyl-H), 7.53 (s, 1 H, phenyl-H), 7.45-7.48 (m, 3 H, py-2-H, 2 phenyl-H), 7.43 (s, 1 H, phenyl-H), 7.40 (s, 1 H, phenyl-H) 4.47 (s, 2 H, aryl-CH_2-O-), 4.44 (s, 2 H, aryl-CH_2-O-), 3.47 (t, 2 H, ^3J = 6.6 Hz, α-CH_2), 3.46 (t, 2 H, ^3J = 6.6 Hz, α-CH_2), 1.58-1.64 (m, 4 H, β-CH_2), 1.28-1.39 (m, 12 H, γ-,δ-,ε-CH_2), 1.11 (s, 21 H, silyl-H), 0.87 (t, 6 H, ^3J =6.8 Hz, hexyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 152.34, 141.21, 120.46, 139.74, 139.36, 134.08, 133.59, 130.94, 130.32, 127.64, 123.93, 123.59, 123.06, 122.56, 119.43, 105.96, 93.03, 91.42, 89.38, 88.68, 85.21, 71.84, 71.75, 70.87, 70.78, 31.62, 29.63, 25.80, 22.58, 18.61, 14.00, 11.24. **MS** (**EI**, 80 eV, 155°C): m/z (%) = 769 (1.5), 768 (4.7), 767 (9.1), 766 (4.3), 765 (7.1) $[M]^+$, 727 (3.6), 726 (14.5), 725 (44.3), 724 (100.0), 723 (47.6), 723 (83.6) $[M\text{-}C_3H_7]^+$, 696 (1.6), 694 (1.5) $[M\text{-}C_5H_{11}]^+$, 683 (1.8), 682 (3.9), 681 (2.1), 680 (4.1) $[M\text{-}C_6H_{13}]^+$, 668 (1.0), 667 (1.7), 666 (1.1), 665 (1.2) $[M\text{-}OC_6H_{13}]^+$. **EA**: Calc.: C:72.04, H:7.88, N:1.83; Found: C:72.00, H:7.63, N:1.72.

2-Bromo-5-{[3-hexoxymethyl-5-({3-(tetrahydropyran-2-yloxymethyl)-5-[(triisopropylsilyl)ethynyl]phenyl}ethynyl)phenyl]ethynyl}pyridine, $C_{45}H_{56}BrO_3NSi$, M = 766.93, ***19c***

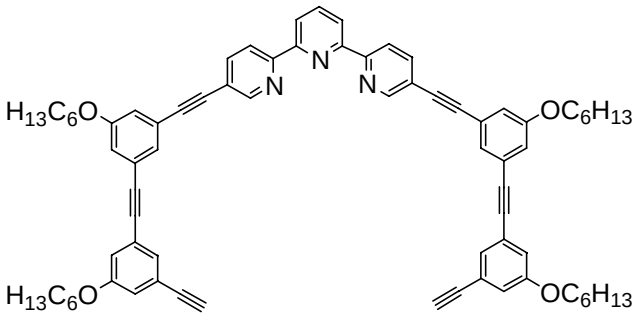


The procedure was analogous to that described for **94** (**6**: 2.54 g, 8.94 mmol; **18c**: 5.46 g, 8.94 mmol; CuI: 51 mg, 0.27 mmol; $Pd[P(Ph_3)]_4$: 310 mg, 0.27 mmol; triethylamine: 100 ml; reaction time: 3 days; reaction temperature: 60°C). The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate) to afford **19c** (6.37 g, 8.31 mmol, 93 %) as a yellow sirup. $\mathbf{R_f}$ = 0.42 (hexane/ethyl acetate 10:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 8.49 (d, 1 H, ^{4}J = 2.4 Hz, py-6-H), 7.62 (dd, 1 H, ^{3}J = 8.3 Hz, ^{4}J = 2.4 Hz, py-4-H), 7.60 (t, 1 H, ^{4}J = 1.4 Hz, phenyl-H), 7.54 (t, 1 H, J = 1.3 Hz, phenyl-H), 7.46-7.49 (m, 4 H, py-3-H, phenyl-H), 7.41 (s, 1 H, phenyl-H), 4.68-4.75 (m, 2 H, benzyl (THP)-H, THP-2-H), 4.47 (s, 2 H, benzyl (hexyl)-H), 4.45 (d, 1 H, ^{2}J ≈ 13 Hz, benzyl (THP)-H'), 3.85-3.94 (m, 1 H, THP-6-H), 3.51-3.59 (m, 1 H, THP-6'-H), 3.47 (t, 2 H, ^{3}J = 6.6 Hz, hexyl-α-CH_2), 1.52-1.84 (m, 8 H, THP-3,3',4,4',5,5'-H, hexyl-β-CH_2), 1.29-1.39 (m, 6 H, hexyl-γ-, δ-, ε-CH_2), 1.11 (s, 21 H, silyl-H), 0.87 (t, 3 H, ^{3}J = 6.8 Hz, hexyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 152.29, 141.17, 140.41, 139.71, 138.90, 134.10, 133.55, 131.07, 130.91, 130.50, 130.28, 127.59, 123.89, 123.53, 123.05, 122.52, 119.38, 105.91, 97.79, 92.99, 91.45, 89.33, 88.68, 85.19, 71.70, 70.83, 67.76, 62.04, 31.58, 30.49, 29.59, 25.76, 25.23, 22.55, 19.21, 18.58, 13.97, 11.21. **MS** (**EI**, 80 eV, 120°C): m/z (%) = 767 (0.2), 766 (0.5), 765 (0.3), 764 (0.4) $[M]^+/[M-H]^+$, 727 (0.4), 726 (2.1), 725 (6.6), 724 (21.5), 723 (42.3), 722 (20.9), 721 (43.9) $[M-C_3H_7]^+/[M-H-C_3H_7]^+$, 682 (10.2), 681 (6.4), 680 (10.1) $[M-C_6H_{13}]^+$, 667 (11.2), 666 (24.6), 665 (12.5), 664 (22.3) $[M-C_5H_8O_2]^+/[M-H-C_5H_8O_2]^+$, 641 (13.1), 640 (42.3), 639 (99.2), 638 (45.0), 637 (100.0) $[M-C_7H_{11}O_2]^+/[M-H-C_7H_{11}O_2]^+$. **EA**: Calc.: C:70.48, H:7.35, N:1.83; Found: C:70.35, H:7.30, N:1.72.

5,5''-Bis({3-[(3-ethynyl-5-hexoxyphenyl)ethynyl]-5-hexoxyphenyl}ethynyl)-2,2':6',2''-terpyridine, $C_{75}H_{75}N_3O_4$, M = 1082.43, ***20a***

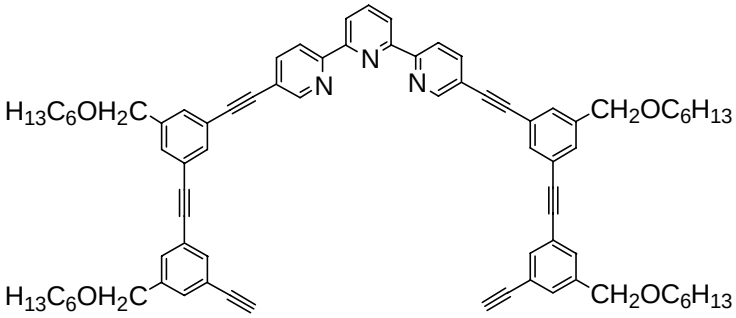
The procedure was analogous to that described for **33b** (**14a**: 300 mg, 0.215 mmol; tetra-*n*-butylammonium fluoride trihydrate: 220 mg, 0.70 mmol; THF: 10 ml). The crude product was

purified by chromatography over silica gel (hexane/ethyl acetate) to afford **20a** as a yellow sirup (190 mg, 82 % after freeze-drying). $\mathbf{R_f}$ = band (hexane/ethyl acetate 4:1).



^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.81 (dd, 2 H, ^{4}J = 2.4 Hz, ^{5}J = 0.7 Hz, tpy-6,6''-H), 8.61 (d, 2 H, ^{3}J = 8.3 Hz, tpy-3,3''-H), 8.47 (d, 2 H, ^{3}J = 7.8 Hz, tpy-3',5'-H), 7.97 (t, 1 H, ^{3}J ≈ 9 Hz, tpy-4'-H), 7.95 (dd, 2 H, ^{3}J = 8.3 Hz, ^{4}J = 1.9 Hz, tpy-4,4''-H), 7.32 (t, 2 H, ^{4}J = 1.3 Hz, phenyl-H), 7.23 (m, 2 H, phenyl-H), 6.98-7.08 (m, 8 H, phenyl-H), 3.98 (t, 4 H, ^{3}J = 6.5 Hz, α-CH_2), 3.94 (t, 4 H, ^{3}J = 6.6 Hz, α-CH_2), 3.06 (s, 2 H, ethynyl-H), 1.78 (quintet, 8 H, ^{3}J ≈ 7 Hz, β-CH_2), 1.23-1.46 (m, 24 H, γ-,δ-,ε-CH_2), 0.81-0.96 (m, 12 H, hexyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 158.95, 158.82, 154.96, 154.79, 151.71, 139.34, 138.01, 127.66, 127.31, 124.31, 124.16, 123.84, 123.36, 121.60, 120.43, 120.15, 118.65, 118.32, 118.05, 92.76, 88.88, 86.70, 82.79, 77.21, 68.35, 31.54, 29.11, 25.67, 22.60, 14.02. **MS** (**FAB(+)**, DMSO/MNBA-Matrix): m/z (%) = 1105 (0.4), 1104 (0.4) $[M+Na]^+$, 1085 (0.7), 1084 (1.8), 1083 (3.0), 1082 (3.1), 1081 (2.4), 1080 (1.0) $[M+H]^+$. **EA**: Calc.: C:83.22, H:6.98, N:3.88; Found: C:83.14, H:7.28, N:3.74.

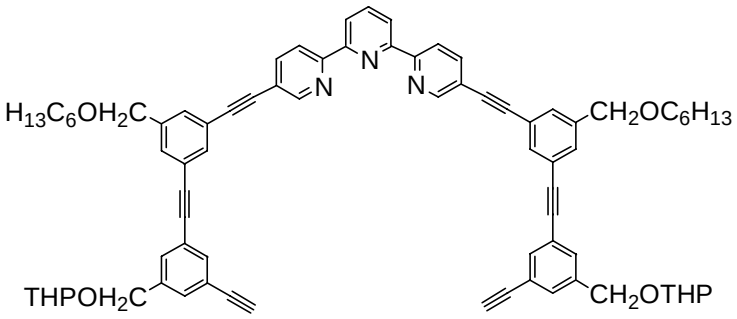
5,5''-Bis({3-[(3-ethynyl-5-hexoxymethylphenyl)ethynyl]-5-hexoxymethylphenyl}ethynyl)-2,2':6',2''-terpyridine, $C_{79}H_{83}N_3O_4$, M = 1138.54, ***20b***



The procedure was analogous to that described for **33b** (**14b**: 1.66 g, 1.14 mmol; tetra-*n*-butylammonium fluoride trihydrate: 1.18 g, 3.70 mmol; THF: 50 ml). The crude product was purified by chromatography over silica gel (dichloromethane/methanol) to afford **20b** (1.09 g, 0.957 mmol, 84 %) as a yellow resin which could not be solidified even after freeze-drying from benzene. $\mathbf{R_f}$ = 0.27 (hexane/ethyl acetate 10:1, aluminium oxide). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 8.82 (d, 2 H, ^{4}J = 1.7 Hz, tpy-6,6''-H), 8.61 (d, 2 H, ^{3}J = 8.2 Hz, tpy-3,3''-H), 8.47 (d, 2 H, ^{3}J = 7.9 Hz,

tpy-3',5'-H), 7.97 (t, 1 H, $^3J \approx 8$ Hz, tpy-4'-H), 7.95 (dd, 2 H, $^3J = 8.2$ Hz, $^4J = 2.3$ Hz, tpy-4,4''-H), 7.65 (s, 2 H, phenyl-H), 7.55 (s, 2 H, phenyl-H), 7.52 (s, 2 H, phenyl-H), 7.48 (d, 4 H, ^4J = 1.3 Hz, phenyl-H), 7.43 Hz (s, 2 H, phenyl-H), 4.50 (s, 4 H, aryl-CH_2-O-), 4.46 (s, 4 H, aryl-CH_2-O-), 3.49 (t, 4 H, $^3J = 6.8$ Hz, α-CH_2), 3.46 (t, 4 H, $^3J = 6.7$ Hz, α-CH_2), 3.08 (s, 2 H, ethynyl-H), 1.59-1.66 (m, 8 H, β-CH_2), 1.29-1.39 (m, 24 H γ-,δ-,ε-CH_2), 0.89 (t, 6 H, ^3J =6.5 Hz, hexyl-CH_3), 0.88 (t, 6 H, ^3J =6.5 Hz, hexyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 154.81, 154.62, 151.60, 139.65, 139.51, 139.20, 137.87, 134.05, 133.63, 130.93, 130.78, 130.44, 123.42, 123.28, 122.98, 122.51, 121.49, 120.31, 120.03, 92.62, 89.06, 88.99, 86.99, 82.66, 77.80, 71.74, 70.81, 31.63, 29.63, 25.80, 22.58, 14.01. **MS** (**FAB(+)**, MNBA/DMSO-Matrix): m/z (%) = 1160 (0.5) $[M+Na]^+$, 1140 (0.4), 1139 (1.8), 1138 (2.3), 1137 (1.6) $[M+H]^+$. **EA**: Calc.: C:83.34, H:7.35, N:3.69; Found: C:83.31, H:7.18, N:3.63.

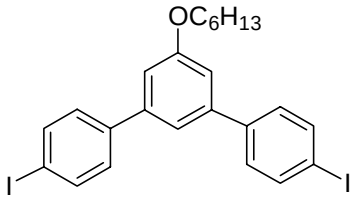
5,5''-Bis[(3-{[3-ethynyl-5-(tetrahydropyran-2-yloxymethyl)phenyl]ethynyl}-5-hexoxymethylphenyl)ethynyl]-2,2':6',2''-terpyridine, $C_{77}H_{75}N_3O_6Si_2$, M = 1138.45, ***20c***



The procedure was analogous to that described for **33b** (**14c**: 1.56 g, 1.08 mmol; tetra-*n*-butylammonium fluoride trihydrate: 1.02 g, 3.23 mmol; THF: 50 ml). The crude product was purified by chromatography over aluminium oxide (hexane/ethyl acetate) to afford **20c** (1.14 g, 1.00 mmol, 93 %) as a yellow resin which could not be solidified even after freeze-drying from benzene. $\mathbf{R_f}$ = 0.52 (hexane/ethyl acetate 4:1, aluminium oxide). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 8.80 (d, 2 H, $^4J = 1.9$ Hz, tpy-6,6''-H), 8.60 (d, 2 H, $^3J = 8.3$ Hz, tpy-3,3''-H), 8.45 (d, 2 H, $^3J = 7.9$ Hz, tpy-3',5'-H), 7.94 (t, 1 H, ^3J = 7.8 Hz, tpy-4'-H), 7.94 (dd, 2 H, $^3J = 8.3$ Hz, $^4J = 2.0$ Hz, tpy-4,4''-H), 7.64 (t, 2 H, $^4J = 1.3$ Hz, phenyl-H), 7.55 (t, 2 H, $^4J = 1.2$ Hz, phenyl-H), 7.48-7.50 (m, 6 H, phenyl-H), 7.45 (s, 2 H, phenyl-H), 4.69-4.76 (m, 4 H, benzyl (THP)-H, THP-2-H), 4.48 (s, 4 H, benzyl (hexyl)-H), 4.45 (d, 2 H, $^2J \approx 12$ Hz, benzyl (THP)-H'), 3.84-3.93 (m, 2 H, THP-6-H), 3.52-3.59 (m, 2 H, THP-6'-H), 3.48 (t, 4 H, $^3J = 6.7$ Hz, hexyl-α-CH_2), 3.09 (s, 1 H, ethynyl-H), 1.52-1.85 (m, 16 H, THP-3,3',4,4',5,5'-H, hexyl-β-CH_2), 1.26-1.43 (m, 12 H, hexyl-γ-, δ-, ε-CH_2), 0.88 (t, 3 H, $^3J = 6.8$ Hz,

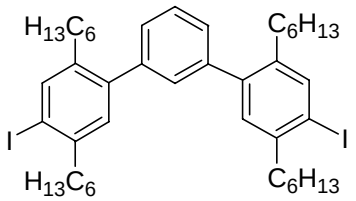
hexyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 154.70, 154.49, 151.51, 139.59, 139.08, 137.74, 134.01, 133.56, 130.99, 130.84, 130.64, 130.36, 123.33, 123.23, 122.91, 122.47, 121.41, 120.21, 119.94, 97.80, 92.57, 88.99, 86.97, 82.63, 77.86, 71.70, 70.78, 67.62, 61.95, 31.57, 30.35, 29.59, 25.76, 25.30, 22.54, 19.14, 13.98. **MS** (**FAB(+)**, DMSO/MNBA-Matrix): m/z (%) = 1141 (0.6), 1140 (0.9), 1139 (1.3), 1138 (1.4) $[M+H]^+$. **EA**: Calc.: C:81.24, H:6.64, N:3.69; Found: C:81.32, H:6.73, N:3.68.

4,4‘‘-Diiodo-5‘-hexoxy-1,1‘:3‘,1‘‘-terphenyl, $C_{24}H_{24}I_2O$, M = 582.26, ***21a*** (Scheme 9)



The procedure was analogous to that described for **8** (**98a**: 3.12 g, 6.57 mmol; iodine chloride: 2.67 g, 16.4 mmol; dichloromethane: 200 ml/50 ml). The crude product (4.18 g of a yellow oil) was purified by chromatography (silica gel; hexane) to afford **21a** (5.19 g, 12.1 mmol, 93 %) as colorless crystals. $\mathbf{R_f}$ = 0.65 (hexane/ethyl acetate 30:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 7.75 (d, 4 H, ^{3}J = 8.2 Hz, 3,5,3‘‘,5‘‘-H), 7.33 (d, 4 H, ^{3}J = 8.2 Hz, 2,6,2‘‘,6‘‘-H), 7.25 (t, 1 H, ^{4}J = 1.4 Hz, 2’-H), 7.04 (d, 2 H, ^{4}J = 1.4 Hz, 4’,6’-H), 4.04 (t, 2 H, ^{3}J = 6.6 Hz, α-CH_2), 1.81 (quintet, 2 H, ^{3}H ≈ 7 Hz, β- CH_2), 1.31-1.55 (m, 6 H, γ-, δ-, ε-CH_2), 0.89 (t, 3 H, ^{3}J ≈ 7 Hz., -CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 160.01, 142.03, 140.40, 137.81, 129.02, 117.94, 112.36, 93.37, 68.23, 31.55, 29.24, 25.72, 22.58, 14.03, 1.00. **MS** (**EI**, 80 eV, 210°C): m/z (%) = 584 (5.3), 583 (30.0), 582 (100.0) $[M]^+$, 500 (3.3), 499 (22.4), 498 (89.6)$[M-C_6H_{12}]^+$, 471 (2.4), 470 (13.3), 469 (25.6) $[M-C_6H_{12}-CHO]^+$, 457 (2.4), 456 (8.4), 455 (10.4) $[M-I]^+$, 373 (3.1), 372 (12.7), 371 (12.2), 370 (6.9) $[M-C_6H_{12}-I]^+$. **EA**: Calc.: C: 49.51, H: 4.15; Found: C: 49.44, H: 4.26.

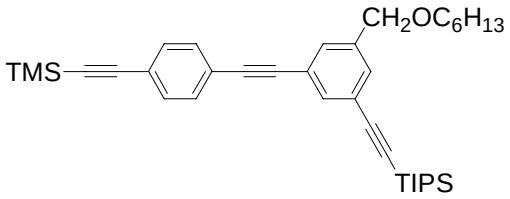
4,4‘‘-Diiodo-2,5,2‘‘,5‘‘-tetrahexyl-1,1‘:3‘,1‘‘-terphenyl, $C_{42}H_{60}I_2$, M = 818.75, ***21b*** (Scheme 9)



The procedure was analogous to that described for **8** (**98b**: 4.95 g, 6.96 mmol; iodine chloride: 2.49 g, 15.31 mmol; dichloromethane: 100 ml/50 ml). Chromatographic separation through silica gel with hexane gave **21b** (5.08 g, 6.20 mmol, 89 %) as a colorless sirup. $\mathbf{R_f}$ = 0.52 (hexane). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 7.72 (s, 2 H, 6,6‘‘-H), 7.43 (t, 1 H, ^{3}J ≈

8 Hz, 5'-H), 7.29-7.31 (m, 3 H, 2',4',6'-H), 7.04 (s, 2 H, 3,3''-H), 2.70 (t, 4 H, $^3J \approx 8$ Hz, α-CH_2), 2.61 (t, 4 H, $^3J \approx 8$ Hz, α-CH_2), 1.19-1.62 (m, 32 H, β-, γ-, δ-, ε-CH_2), 0.89 (t, 6 H, $^3J = 6.8$ Hz, hexyl-CH_3), 0.82 (t, 6 H, $^3J = 6.8$ Hz, hexyl-CH_3), 0.36 (s, 18 H, silyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 142.60, 141.69, 140.94, 139.83, 130.59, 129.69, 127.87, 127.65, 99.48, 40.33, 32.27, 31.63, 31.47, 31.16, 30.36, 29.10, 22.60, 22.47, 14.06, 14.02. **MS** (**EI**, 80 eV, 60°C): m/z (%) = 820 (13.4), 819 (61.8), 820 (100.0) $[M]^+$, 748 (5.8), 747 (11.5) $[M-C_5H_{11}]^+$, 693 (13.5), 692 (30.7) $[M-I]^+$, 622 (7.6), 621 (24.5), 620 (35.5) $[M-C_5H_{11}-HI]^+$. **EA**: Calc.: C: 61.61, H: 7.39; Found: C: 61.74, H: 7.63.

1-Hexoxymethyl-3-({4-[(trimethylsilyl)ethynyl]phenyl}ethynyl)-5-[(triisopropylsilyl)ethynyl]-benzene, $C_{37}H_{52}OSi_2$, M = 568.99, ***23a***

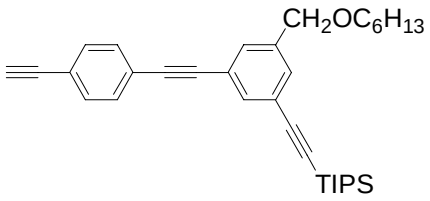


The procedure was analogous to that described for **94** (**12b**: 13.50 g, 34.1 mmol; **22**: 8.62 g, 34.1 mmol; CuI: 194 mg, 1.02 mmol; $Pd[P(Ph_3)]_4$: 1.18 g, 1.02 mmol; triethylamine: 250 ml; reaction time: 3 days; reaction temperature: 70°C). The crude product was purified by column chromatography (silica gel, hexane/toluene) to afford **23a** (15.11 g, 26.56 mmol, 78 %) as a yellow sirup. $\mathbf{R_f}$ = 0.71 (hexane/ethyl acetate 40:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 7.53 (t, 1 H, $^4J = 1.3$ Hz, aryl-H), 7.42 (s, 5 H, aryl-H), 7.39 (d, 1 H, ^4J = 1.3 Hz, aryl-H), 4.44 (s, 2 H, benzyl-H), 3.45 (t, 2 H, $^3J = 6.6$ Hz, α-CH_2), 1.55-1.63 (quintet, 2 H, $^3J \approx 7$ Hz, β-CH_2), 1.28-1.38 (m, 6 H, γ-,δ-,ε-CH_2), 1.11 (s, 21 H, TIPS-H), 0.87 (t, 3 H, ^3J = 6.7 Hz, hexyl-CH_3), 0.24 (s, 9 H, TMS-H). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 139.35, 134.07, 131.88, 131.34, 130.91, 130.35, 123.95, 123.22, 123.07, 106.03, 104.58, 96.35, 91.40, 90.43, 89.47, 71.90, 70.79, 31.66, 29.66, 25.84, 22.61, 18.65, 14.03, 11.28, -0.11. **MS** (**EI**, 80 eV, 180°C): m/z (%) = 571 (7.5), 570 (21.2), 569 (40.8), 568 (62.0) $[M]^+$, 527 (19.8), 526 (47.9), 525 (100) $[M-C_3H_7]^+$, 497 (9.5) $[M-C_5H_{11}]^+$. **EA**: Calc.: C:78.10, H:9.21; Found: C:77.82, H:8.99.

1-Hexoxymethyl-3-[(4-ethynylphenyl)ethynyl]-5-[(triisopropylsilyl)ethynyl]benzene, $C_{34}H_{44}OSi$, M = 496.81, ***23b***

The procedure was analogous to that described for **12a** (**23a**: 11.58 g, 20.35 mmol; dichloromethane: 70 ml; methanol: 70 ml). The solvent was evaporated, the crude product

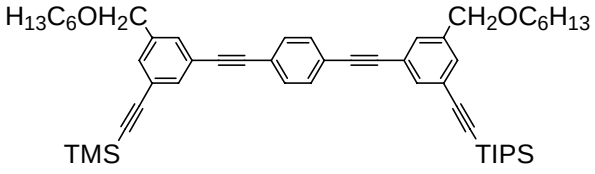
dissolved in dichloromethane (100 ml), and washed with water (100 ml). The aqueous phase was extracted with dichloromethane (2 × 100 ml), the combined organic layers were dried over $MgSO_4$ and the solvent evaporated to afford **23b** (9.98 g, 20.09 mmol, 99 %) as a yellow sirup.



R_f = 0.56 (hexane/ethyl acetate 40:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.54 (t, 1 H, ^4J = 1.4 Hz, aryl-H), 7.45 (s, 4 H, aryl-H), 7.43 (s, 1 H), 7.40 (t, 1 H, ^4J = 1.3 Hz, aryl-H), 4.45 (s, 2 H, benzyl-H), 3.46 (t, 2 H, ^3J = 6.7 Hz, α-CH_2), 3.16 (s, 1H, ethynyl-H), 1.56-1.63 (quintet, 2 H, $^3J \approx 7$ Hz, β-CH_2), 1.30-1.41 (m, 6 H, γ-,δ-,ε-CH_2), 1.11 (s, 21 H, TIPS-H), 0.87 (t, 3 H, ^3J = 6.7 Hz, hexyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 139.36, 134.04, 132.03, 131.45, 130.92, 130.34, 123.94, 123.45, 123.15, 122.06, 106.01, 91.39, 90.49, 89.26, 83.18, 78.98, 71.86, 70.77, 31.64, 29.64, 25.82, 22.59, 18.62, 14.01, 11.26. **MS** (**EI**, 80 eV, 160°C): m/z (%) = 498 (5.6), 497 (15.5), 496 (34.6) $[M]^+$, 455 (12.8), 454 (43.6), 453 (100.0), 452 (3.0) $[M\text{-}C_3H_7]^+$, 426 (3.6), 425 (10.5) $[M\text{-}C_5H_{11}]^+$, 412 (4.3), 411 (10.2) $[M\text{-}C_6H_{13}]^+$. **EA**: Calc.: C:82.19, H:8.93; Found: C:81.99, H:9.04.

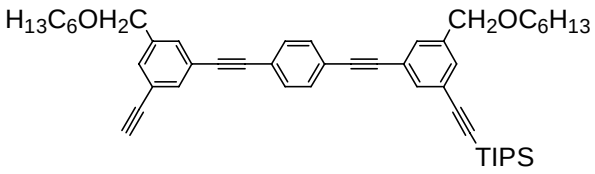
1-Hexoxymethyl-3-{[4-({3-hexoxymethyl-5-[(trimethylsilyl)ethynyl]phenyl}ethynyl) phenyl]ethynyl}-5-[(triisopropylsilyl)ethynyl]benzene, $C_{52}H_{70}O_2Si_2$, M = 783.29, ***24a***



The procedure was analogous to that described for **94** (**16b**: 8.85 g, 24.1 mmol; **23b**: 11.97 g, 24.1 mmol; CuI: 138 mg, 0.723 mmol; $Pd[P(Ph_3)]_4$: 835 mg, 0.723 mmol; triethylamine: 150 ml; reaction time: 3 days; reaction temperature: 80°C). The crude product was purified by column chromatography (silica gel, hexane/toluene) to afford **24a** (13.38 g, 17.1 mmol, 71 %) as a yellow sirup. **R_f** = 0.41 (hexane/ethyl acetate 40:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 7.54 (d, 2 H, ^4J = 1.4 Hz, aryl-H), 7.47 (s, 4 H, aryl-H), 7.44 (s, 2 H, aryl-H), 7.39 (d, 2 H, ^4J = 1.0 Hz, aryl-H), 4.45 (s, 2 H, benzyl-H), 4.44 (s, 2 H, benzyl-H), 3.46 (t, 2 H, ^3J = 6.6 Hz, α-CH_2), 3.44 (t, 2 H, ^3J = 6.6 Hz, α-CH_2), 1.58-1.63 (m, 4 H, β-CH_2), 1.28-1.38 (m, 12 H, γ-,δ-,ε-CH_2), 1.12 (s, 42 H, TIPS-H), 0.88 (t, 6 H, ^3J = 6.7 Hz, hexyl-CH_3), 0.24 (s, 9 H, TMS-H). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 139.38, 134.04, 133.99, 131.55, 130.89, 130.81, 130.46, 130.58, 123.95, 123.55, 123.25, 123.00, 106.04, 104.05, 94.97, 91.39, 90.49, 90.45,

89.51, 71.87, 70.77, 31.65, 29.65, 25.83, 22.60, 18.64, 14.03, 11.28, -0.13. **MS** (**FAB(+)**, MNBA/CH_2Cl_2-Matrix): m/z (%) = 785 (8.1), 784 (12.7), 783 (22.9), 782 (50.3), 781 (73.8), 780 (40.4), 779 (13.3), 778 (8.7) $[M-2H]^+$, 741 (9.9), 740 (18.4), 739 (30.1), 738 (41.2) $[M-2H-C_3H_7]^+$, 696 (5.5) $[M-C_6H_{13}]^+$, 682 (41.7), 681 (67.1), 680 (100.0) $[M-CH_3-2C_3H_7]^+$. **EA**: Calc.: C:79.74, H:9.00; Found: C:79.54, H:8.76.

1-Hexoxymethyl-3-({4-[(3-ethynyl-5-hexoxymethylphenyl)ethynyl]phenyl}ethynyl)-5-[(triisopropylsilyl)ethynyl]benzene, $C_{49}H_{62}O_2Si$, M = 711.11, ***24b***

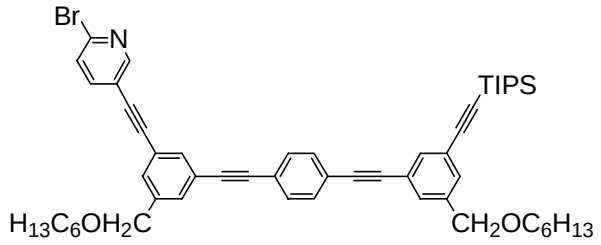


The procedure was analogous to that described for **12a** (**24a**: 12.59 g, 16.10 mmol; dichloromethane: 100 ml; methanol: 70 ml). The crude product was purified by chromatography over silica gel (hexane/toluene) to afford **24b** (8.53 g, 12.0 mmol, 75 %) as a yellow sirup. $\mathbf{R_f}$ = 0.26 (hexane/ethyl acetate 10:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 7.54-7.56 (m, 2 H, aryl-H), 7.48 (s, 5 H, aryl-H), 7.42-7.44 (m, 2 H, aryl-H), 7.40 (t, 1 H, ^4J = 1.4 Hz, aryl-H), 4.45 (s, 4 H, benzyl-H), 3.46 (t, 2 H, ^3J = 6.6 Hz, α-CH_2), 3.08 (s, 1 H, ethynyl-H), 1.61 (quintet, 4 H, $^3J \approx 7$ Hz, β-CH_2), 1.20-1.41 (m, 12 H, γ-,δ-,ε-CH_2), 1.12 (s, 21 H, silyl-H), 0.88 (t, 6 H, ^3J =6.6 Hz, hexyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 139.54, 139.36, 134.04, 131.55, 130.91, 130.77, 130.34, 123.93, 123.39, 123.20, 123.05, 122.90, 122.54, 106.02, 91.38, 90.52, 90.23, 89.65, 89.48, 82.68, 77.78, 71.86, 71.76, 70.79, 31.64, 29.65, 25.82, 22.60, 18.63, 14.02, 11.26. **MS** (**EI**, 80 eV, 240°C): m/z (%) = 713 (9.1), 712 (27.2), 711 (61.7), 710 (95.6), 709 (83.5) $[M]^+$, 669 (23.3), 668 (58.5), 667 (100.0), 666 (89.7) $[M-C_3H_7]^+$. **EA**: Calc.: C:82.76, H:8.79; Found: C:82.62, H:8.71.

2-Bromo-5-[(3-hexoxymethyl-5-{[4-({3-hexoxymethyl-5-[(triisopropylsilyl)ethynyl]phenyl}-ethynyl)phenyl]ethynyl}phenyl)ethynyl]pyridine, $C_{54}H_{64}BrO_2NSi$, M = 867.09, ***25***

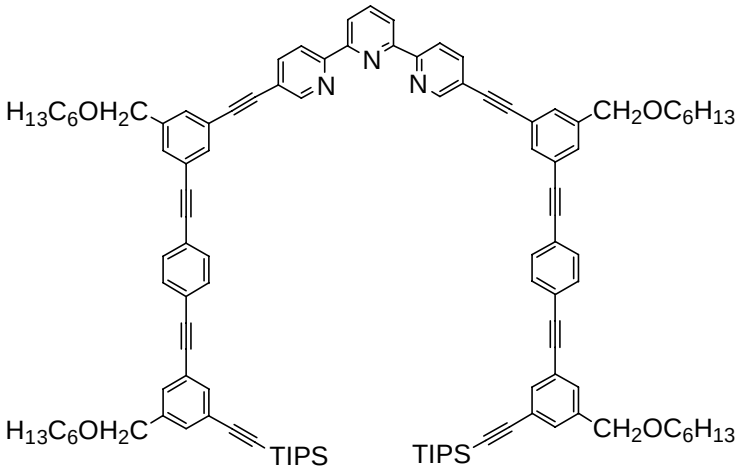
The procedure was analogous to that described for **94** (**6**: 4.30 g, 15.2 mmol; **24b**: 10.77 g, 15.15 mmol; CuI: 86 mg, 0.452 mmol; $Pd[P(Ph_3)]_4$: 520 mg, 0.452 mmol; triethylamine: 250 ml; reaction time: 3 days; reaction temperature: 60°C). The crude product was purified by column chromatography (silica gel, hexane/toluene) to afford **25** (11.10 g, 12.8 mmol, 84 %) as a brown sirup. $\mathbf{R_f}$ = 0.60 (hexane/ethyl acetate 10:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 8.50 (d, 1 H, ^4J =

2.2 Hz, py-6-H), 7.62 (dd, 1 H, ^3J = 8.3 Hz, ^4J = 2.3 Hz, py-4-H), 7.61 (t, 1 H, ^4J = 1.5 Hz, phenyl-H), 7.54 (t, 1 H, ^4J = 1.4 Hz, phenyl-H), 7.46-7.48 (m, 7 H, 6 phenyl-H, py-2-H), 7.44 (s, 1 H, phenyl-H), 7.40 (s, 1 H, phenyl-H), 4.48 (s, 2 H, benzyl-H), 4.45 (s, 2 H, benzyl-H), 3.48 (t, 2 H, ^3J = 6.5 Hz, α-CH_2), 3.46 (t, 2 H, ^3J = 6.6 Hz, α-CH_2), 1.56-1.65 (m, 4 H, β-CH_2), 1.25-1.39 (m, 12 H, γ-,δ-,ε-CH_2), 1.11 (s, 21 H, silyl-H), 0.87 (t, 6 H, ^3J = 6.6 Hz, hexyl-CH_3).



^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 152.34, 141.23, 140.45, 139.77, 139.36, 134.03, 133.56, 131.55, 130.93, 130.34, 127.64, 123.93, 123.60, 123.16, 122.80, 122.59, 119.42, 106.00, 93.02, 91.40, 90.59, 90.15, 89.87, 89.44, 85.26, 71.85, 71.75, 70.89, 70.78, 31.63, 29.63, 25.81, 22.59, 18.62, 14.01, 11.25. **MS** (**FAB(+)**, CH_2Cl_2 /DMSO/MNBA-Matrix)): m/z (%) = 870 (26.10), 869 (57.5), 868 (100.0), 867 (78.8), 866 (96.4) $[M+H]^+$. **EA**: Calc.: C:74.80, H:7.44, N:1.55; Found: C:74.89, H:7.34, N:1.55.

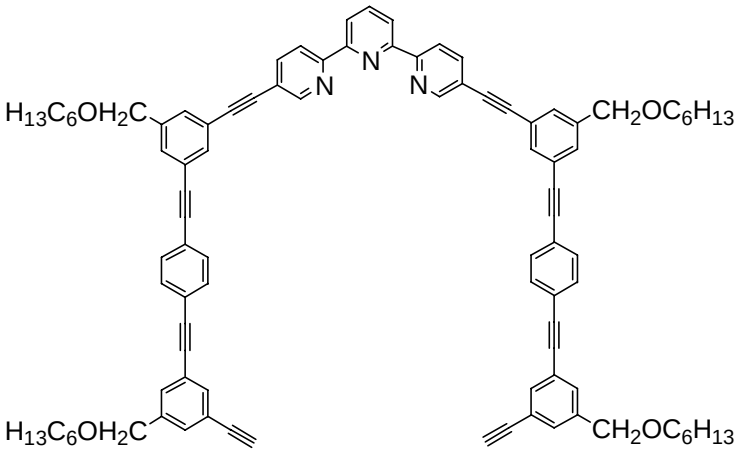
5,5‘‘-Bis[(3-hexoxymethyl-5-{[4-({3-hexoxymethyl-5-[(triisopropylsilyl)ethynyl]phenyl}-ethynyl)phenyl]ethynyl}phenyl)ethynyl]-2,2‘:6‘,2‘‘-terpyridine, $C_{113}H_{131}N_3O_4Si_2$, M = 1651.47, ***26a***



The procedure is analogous to that described for **28a** (**10**: 2.54 g, 6.29 mmol; **25**: 10.90 g, 12.57 mmol; $Pd[P(Ph_3)]_4$: 436 mg, 0.377 mmol, toluene: 150 ml, reaction time: 48 hrs). The crude product was purified by repeated column chromatography (hexane/ dichloromethane on aluminium oxide, hexane/ethyl acetate on silica gel) to afford **26a** (4.27 g, 2.59 mmol, 41 %) as a yellow resin. $\mathbf{R_f}$ = 0.73 (hexane/ethyl acetate 4:1, aluminium oxide). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 8.82 (d, 2 H, ^4J = 1.6 Hz, tpy-6,6‘‘-H), 8.62 (d, 2 H, ^3J = 8.3 Hz, tpy-3,3‘‘-H), 8.47 (d, 2 H, ^3J = 7.8 Hz, tpy-3’,5’-H), 7.98 (t, 1 H, ^3J = 7.8 Hz,

tpy-4'-H), 7.96 (dd, 2 H, ^{3}J = 8.2 Hz, ^{4}J = 2.2 Hz, tpy-4,4''-H), 7.67 (s, 2 H, phenyl-H), 7.55 (t, 2 H, ^{4}J = 1.3 Hz, phenyl-H), 7.52 (s, 2 H, phenyl-H), 7.50 (s, 10 H, phenyl-H), 7.44 (s, 2 H, phenyl-H), 7.40 (s, 2 H, phenyl-H), 4.50 (s, 4 H, aryl-CH_2-O-), 4.45 (s, 4 H, aryl-CH_2-O-), 3.50 (t, 4 H, ^{3}J = 6.6 Hz, α-CH_2), 3.46 (t, 4 H, ^{3}J = 6.7 Hz, α-CH_2), 1.56-1.69 (m, 8 H, β-CH_2), 1.25-1.44 (m, 24 H, γ-,δ-,ε-CH_2), 1.12 (s, 42 H, silyl-H), 0.89 (t, 6 H, ^{3}J =6.5 Hz, hexyl-CH_3), 0.87 (t, 6 H, ^{3}J =6.8 Hz, hexyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 154.84, 154.65, 151.62, 139.67, 139.35, 139.20, 137.87, 134.04, 133.63, 131.56, 130.90, 130.72, 130.33, 123.93, 123.54, 123.19, 123.06, 122.90, 121.52, 120.33, 120.06, 106.03, 92.66, 91.38, 90.56, 90.34, 89.79, 89.49, 87.02, 71.85, 70.88, 70.78, 31.65, 29.66, 25.83, 22.60, 18.63, 14.03, 11.26. **MS** (**FAB(+)**, MNBA/CH_2Cl_2-Matrix): m/z (%) = 1655 (21.4), 1654 (31.4), 1653 (50.0), 1652 (52.8), 1651 (46.4) $[M+H]^+$, 1568 (20.5), 1567 (23.7), 1566 (22.9) $[M-C_6H_{12}]^+$. **EA**: Calc.: C:82.18, H:7.99, N:2.54; Found: C:82.20, H:7.91, N:2.46.

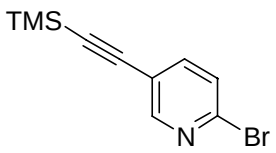
5,5''-Bis{[3-hexyloxymethyl-5-({4-[(3-ethynyl-5-hexoxymethylphenyl)ethynyl]phenyl}-ethynyl)phenyl]ethynyl}-2,2':6',2''-terpyridine, $C_{95}H_{91}N_3O_4$, M = 1338.78, ***26b***



The procedure was analogous to that described for **33b** (**26a**: 4.08 g, 2.47 mmol; tetra-*n*-butylammonium fluoride trihydrate: 3.12 g, 9.88 mmol; THF: 50 ml). The crude product was purified by chromatography over aluminium oxide (hexane/ethyl acetate) to afford **26b** (2.04 g, 1.52 mmol, 62 %) as a yellow resin which could not be solidified even after freeze-drying from benzene. $\mathbf{R_f}$ = 0.63 (hexane/ethyl acetate 4:1, aluminium oxide). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 8.82 (d, 2 H, ^{4}J = 1.9 Hz, tpy-6,6''-H), 8.61 (d, 2 H, ^{3}J = 8.3 Hz, tpy-3,3''-H), 8.47 (d, 2 H, ^{3}J = 7.8 Hz, tpy-3',5'-H), 7.96 (t, 1 H, ^{3}J ≈ 8 Hz, tpy-4'-H), 7.95 (dd, 2 H, ^{3}J = 8.2 Hz, ^{4}J = 2.2 Hz, tpy-4,4''-H), 7.66 (s, 2 H, phenyl-H), 7.59 (s, 2 H, phenyl-H), 7.52 (s, 2 H, phenyl-H), 7.49 (s, 10 H, phenyl-H), 7.48 (s, 2 H, phenyl-H), 7.42 (s, 2 H, phenyl-H), 4.50 (s, 4 H, aryl-CH_2-O-), 4.45 (s, 4 H, aryl-CH_2-O-), 3.48 (t, 4 H, ^{3}J = 6.6 Hz, α-CH_2), 3.46 (t, 4 H, ^{3}J = 6.7 Hz, α-CH_2), 3.08 (s, 2 H,

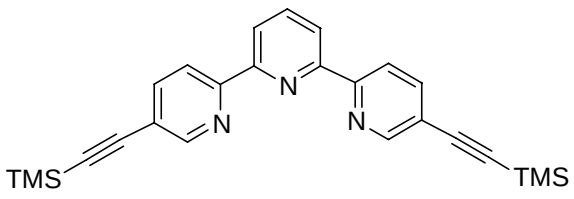
ethynyl-H), 1.56-1.69 (m, 8 H, β-CH_2), 1.25-1.44 (m, 24 H γ-,δ-,ε-CH_2), 0.89 (t, 6 H, ^3J =6.7 Hz, hexyl-CH_3), 0.88 (t, 6 H, ^3J =6.7 Hz, hexyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 154.73, 154.52, 151.54, 139.63, 139.49, 139.09, 137.74, 134.05, 133.97, 133.55, 131.51, 130.85, 130.67, 130.37, 123.44, 123.30, 122.91, 122.48, 121.44, 120.22, 119.97, 92.63, 90.37, 90.33, 89.73, 89.60, 87.02, 82.67, 77.82, 71.73, 71.68, 70.82, 70.76, 31.61, 29.62, 25.78, 22.57, 14.00. **MS** (**FAB(+)**, MNBA/CH_2Cl_2-Matrix): m/z (%) = 1342 (0.07), 1341 (0.09), 1340 (0.18), 1339 (0.16) $[M+H]^+$. **EA**: Calc.: C:85.23, H:6.85, N:3.14; Found: C:85.35, H:6.88, N:3.03.

2-Bromo-5-[(trimethylsilyl)ethynyl]pyridine, $C_{10}H_{12}BrNSi$, M = 254.20, ***27***



The procedure was analogous to that described for **16a** (**6**: 23.8 g, 83.8 mmol; TMS-acetylene: 8.80 g, 89.7 mmol; CuI: 480 mg, 2.51 mmol; $[Pd(PPh_3)_4]$: 2.90 g, 2.51 mmol; triethylamine/toluene: 175 ml/40 ml; reaction time: 48 hrs). The crude product was purified by chromatography over silica gel (hexane/ethyl acetate) to give **27** as colorless crystals (14.79 g, 58.2 mmol, 69 %, m.p. = 68-71°C). A small fraction was further purified by sublimation (50°C, 7×10^{-2} mbar, m.p. = 73°C). $\mathbf{R_f}$ = 0.48 (hexane/ethyl acetate 20:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 8.40 (d, 1 H, ^4J = 2.4 Hz, 6-H), 7.55 (dd, 1 H, ^3J = 8.3 Hz, ^4J = 2.4 Hz, 4-H), 7.40 (d, 1 H, 3J = 8.4 Hz, 3-H), 0.23 (s, 9 H). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 152.64, 141.10, 140.83, 127.40, 119.43, 99.97, 99.82, -0.37. **MS** (**EI**, 80 eV, 60°C): m/z (%) = 257 (1.1), 256 (4.2), 255 (26.1), 254 (7.1), 253 (25.9), 252 (3.0) $[M]^+$, 242 (4.4), 241 (15.5), 240 (100.0), 239 (16.0), 238 (98.9) $[M-CH_3]^+$. **EA**: Calc.: C:47.25, H:4.76, N:5.51; Found: C:47.30, H:4.68, N:5.32.

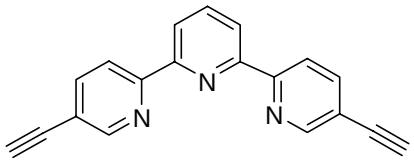
5,5‘‘-Bis[(trimethylsilanyl)ethynyl]-2,2‘:6‘,2‘‘-terpyridine, $C_{25}H_{27}N_3Si_2$, M = 425.68, ***28a***



Caution: Trimethyltin derivatives are highly toxic! A solution of **10** (7.0 g, 17.3 mmol) and **27** (8.79 g, 34.6 mmol) in dry toluene (150 ml) was degassed. After addition of $Pd[P(Ph_3)]_4$ (0.8 g, 0.7 mmol), it was degassed again, then refluxed for 24 hrs under nitrogen. The dark colored reaction mixture was poured into an aqueous KF solution (150 ml) and stirred for 30 mins. It was filtered from the dark green precipitate,

washed with toluene, the phases were separated and the aqueous phase extracted with toluene (2 × 150 ml). The combined organic layers were dried over $MgSO_4$, the solvent removed in vacuo and the crude product purified by column chromatography (hexane/ethyl acetate) to afford **28a** (5.12 g, 12.0 mmol, 70 %) as a colorless solid, m.p. = 215°C. $\mathbf{R_f}$ = 0.70 (hexane/ethyl acetate 4:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 8.73 (dd, 2 H, ^{4}J = 2.0 Hz, ^{5}J = 0.8 Hz, 6,6''-H), 8.52 (dd, 2 H, ^{3}J = 8.3 Hz, ^{4}J = 0.7 Hz, 3,3''-H), 8.41 (d, 2 H, ^{3}J = 7.8 Hz, 3',5'-H), 7.91 (t, 1 H, ^{3}J = 8.0 Hz, 4'-H), 7.87 (dd, 2 H, ^{3}J = 8.3 Hz , ^{4}J = 2.0 Hz, 4,4''-H), 0.28 (s, 18 H, silyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 154.78, 154.65, 152.01, 139.64, 137.92, 121.55, 120.16, 101.83, 99.17, -0.16. **MS** (**EI**, 80 eV, 190°C): m/z (%) = 428 (3.4), 427 (14.1), 426 (37.0), 425 (94.4), 424 (5.2), 423 (1.6) $[M]^+$, 413 (3.8), 412 (14.8), 411 (39.0), 410 (100.0), 408 (3.0), 407 (1.4) $[M\text{-}CH_3]^+$. **EA**: Calc.: C:70.54, H:6.39, N:9.87; Found: C:70.29, H:6.12, N:9.78.

5,5''-Diethynyl-2,2':6',2''-terpyridine, $C_{19}H_{11}N_3$, M = 281.32, ***28b***

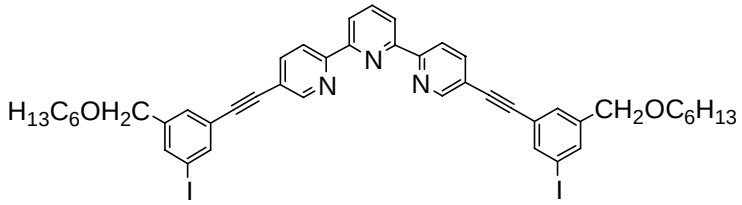


A solution of **28a** (3.89 g, 9.14 mmol) in dichloromethane/methanol (50 ml/100 ml) was refluxed for 2 hrs after addition of 2 N aqueous NaOH (5 drops). The solvent was evaporated and the crude product purified by filtration chromatography (hexane/acetone 5-10 %) to give **28b** (2.32 g, 8.25 mmol, 90 %) as slightly yellow crystals (decomposition at 165-168°C). $\mathbf{R_f}$ = 0.23 (hexane/ethyl acetate 4:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 8.76 (d, 2 H, ^{4}J = 2.0 Hz, 6,6''-H), 8.54 (d, 2 H, ^{3}J = 8.3 Hz, 3,3''-H), 8.43 (d, 2 H, ^{3}J = 7.8 Hz, 3',5'-H), 7.92 (t, 1 H, ^{3}J = 7.9 Hz, 4'-H), 7.87 (dd, 2 H, ^{3}J = 8.2 Hz , ^{4}J = 2.1 Hz, 4,4''-H), 3.29 (s, 2 H, ethynyl-H). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 155.22, 154.55, 152.14, 139.88, 137.97, 121.62, 120.24, 119.14, 81.35, 80.69. **MS** (**EI**, 80 eV, 70°C): m/z (%) = 283 (2.46), 282 (22.1), 281 (100.0), 280 (9.3), 279 (2.2), 278 (1.2) $[M]^+$. **EA**: Calc.: C:81.12, H:3.94, N:14.94; Found: C:81.13, H:4.03, N:14.77.

5,5''-Bis[3-hexoxymethyl-5-iodophenyl)ethynyl]-2,2':6',2''-terpyridine, $C_{45}H_{45}I_2N_3O_2$, M = 913.68, ***30***

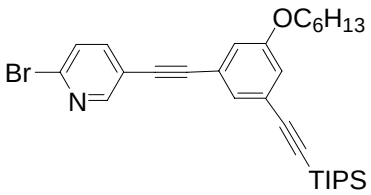
The procedure was analogous to that described for **94** (**28b**: 191 mg, 0.68 mmol; **29**: 3.0 g, 6.82 mmol; CuI: 13 mg, 0.068 mmol; $Pd[P(Ph_3)]_4$: 79 mg, 0.068 mmol; triethylamine: 30 ml;

toluene: 30 ml; reaction time: 3 days; reaction temperature: 60°C). The crude product was purified by column chromatography (aluminium oxide, hexane/ethyl acetate) to afford **30** (370 mg, 0.40 mmol, 60 %) as a yellow amorphous material. Most of **29** (2.33 g, 5.29 mmol, 78 %) was regained. $\mathbf{R_f}$ = 0.44 (hexane/ethyl acetate 10:1, aluminium oxide).



^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.79 (d, 2 H, ^{4}J = 1.7 Hz, tpy-6,6''-H), 8.60 (d, 2 H, ^{3}J = 8.3 Hz, tpy-3,3''-H), 8.46 (d, 2 H, ^{3}J = 7.8 Hz, tpy-3',5'-H), 7.96 (t, 1 H, ^{3}J = 7.8 Hz, tpy-4'-H), 7.93 (dd, 2 H, ^{3}J = 8.3 Hz, ^{4}J = 2.1 Hz, tpy-4,4''-H), 7.83 (t, 2 H, ^{4}J = 1.3 Hz, phenyl-H), 7.68 (s, 2 H, phenyl-H), 7.49 (s, 2 H, phenyl-H), 4.44 (s, 4 H, benzyl-H), 3.47 (t, 4 H, ^{3}J = 6.6 Hz, α-CH_2), 1.62 (quintet, 4 H, ^{3}J ≈ 7 Hz, β-CH_2), 1.23-1.42 (m, 12 H, γ-,δ-,ε-CH_2), 0.88 (t, 6 H, ^{3}J = 6.8 Hz, -CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 154.56, 154.22, 151.36, 140.98, 138.84, 137.56, 136.33, 129.46, 124.25, 121.32, 120.03, 119.58, 93.70, 91.63, 87.48, 71.15, 70.76, 31.49, 29.47, 25.67, 22.48, 13.97. **MS** (**EI**, 80 eV, 140°C): m/z (%) = 915 (13.3), 914 (49.6), 913 (100.0) $[M]^+$, 828 (7.7) $[M\text{-}C_6H_{13}]^+$, 814 (9.7), 813 (21.4) $[M\text{-}OC_6H_{12}]^+$, 787 (7.0) $[M\text{-}I]^+$. **EA**: Calc.: C:59.16, H:4.96, N:4.60; Found: C:59.12, H:4.77, N:4.62.

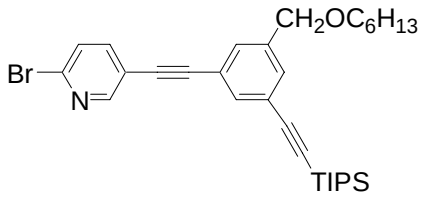
2-Bromo-5-({3-hexoxy-5-[(triisopropylsilyl)ethynyl]phenyl}ethynyl)pyridine, $C_{30}H_{40}BrNOSi$, M = 538.64, ***31a***



The procedure was analogous to that described for **94** (**6**: 556 mg, 1.96 mmol; **12a**: 750 mg, 1.96 mmol; CuI: 37 mg, 0.20 mmol; $Pd[P(Ph_3)]_4$: 226 mg, 0.20 mmol; triethylamine/toluene: 30 ml/20 ml). The crude product was purified by chromatography over aluminium oxide (hexane/ethyl acetate) to afford **31a** (690 mg, 1.28 mmol, 65 %) as a slightly yellow oil. $\mathbf{R_f}$ = 0.13 (hexane, aluminium oxide). **^{1}H-NMR** (270 MHz, DMSO): δ = 8.48 (d, 1 H, ^{4}J = 2.3 Hz, tpy-6-H), 7.61 (dd, 2 H, ^{3}J = 8.2 Hz, ^{4}J = 2.3 Hz, tpy-4-H), 7.45 (d, 2 H, ^{3}J = 8.3 Hz, tpy-3-H), 7.22 (t, 1 H, ^{4}J = 1.1 Hz, phenyl-2-H), 6.98 (d, 2 H, ^{3}J = 0.8 Hz, phenyl-4,6-H), 3.94 (t, 2 H, ^{3}J = 6.5 Hz, α-CH_2), 1.76 (quintett,2 H, ^{3}J ≈ 7 Hz, β-CH_2), 1.28-1.46 (m, 6 H, γ-, δ-, ε-CH_2), 1.11 (s, 21 H, silyl-H), 0.87 (t, 3 H, ^{3}J = 6.9 Hz, hexyl-CH_3). **^{13}C-NMR** (67.9 MHz, DMSO): δ =

158.79, 152.38, 141.20, 140.51, 127.61, 124.91, 123.13, 119,47, 119.06, 117.53, 105.81, 93.17, 91.43, 84.82, 68.28, 31.50, 29.09, 25.64, 22.57, 18.63, 14.00, 11.68, 11.25. **MS** (**EI**, 80 eV, 150°C): m/z (%) = 540 (4.5), 539 (11.8), 538 (4.0), 537 (10.8) $[M]^+$, 499 (1.4), 498 (8.2), 497 (30.1), 496 (100.0), 495 (33.4), 494 (86.1) $[M\text{-}C_3H_7]^+$, 470 (1.5), 469 (5.8), 468 (19.3), 467 (7.3), 466 (18.5) $[M\text{-}C_5H_{11}]^+$, 456 (2.4), 455 (7.5), 454 (25.1), 453 (9.8), 452 (24.7), $[M\text{-}C_6H_{13}]^+$. **EA**: Calc.: C:66.90, H:7.48, N:2.60; Found: C:66.88, H:7.25, N:2.45.

2-Bromo-5-({3-hexoxymethyl-5-[(triisopropylsilyl)ethynyl]phenyl}ethynyl)pyridine, $C_{31}H_{42}BrNOSi$, M = 552.66, ***31b***

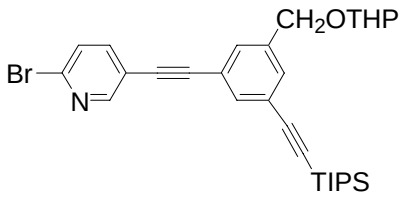


The procedure was analogous to that described for **94** (**6**: 15.64 g, 55.09 mmol; **12b**: 22.21 g, 56.00 mmol; CuI: 314 mg, 1.65 mmol; $Pd[P(Ph_3)]_4$: 1.91 g, 1.65 mmol; triethylamine: 160 ml; reaction time: 3 days; reaction temperature: 60°C). The crude product was purified by column chromatography (silica gel, hexane/toluene) to afford **31b** (25.88 g, 46.83 mmol, 85 %) as a yellow sirup. $\mathbf{R_f}$ = 0.70 (hexane/ethyl acetate 10:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 8.48 (d, 1 H, ^4J = 2.3 Hz, py-6-H), 7.62 (dd, 1 H, ^3J = 8.3 Hz, ^4J = 2.4 Hz, py-4-H), 7.54 (t, 1 H, ^4J = 1.4 Hz, phenyl-H), 7.46 (d, 1 H, ^3J = 8.5 Hz, py-3-H), 7.44 (s, 1 H, phenyl-H), 7.42 (s, 1 H, phenyl-H), 4.45 (s, 2 H, benzyl-H), 3.46 (t, 2 H, ^3J = 6.6 Hz, α-CH_2), 1.61 (quintet, 2 H, $^3H \approx$ 7 Hz, β-CH_2), 1.27-1.30 (m, 6 H, γ-, δ-, ε-CH_2), 1.11 (s, 21 H, TIPS-H), 0.87 (t, 3 H, ^3J = 6.8, -CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 152.29, 141.16, 140.43, 139.51, 134.00, 131.36, 130.26, 127.60, 124.04, 122.34, 119.42, 105.72, 93.05, 91.69, 85.10, 71.73, 70.81, 31.59, 29.59, 25.78, 22.55, 18.59, 13.98, 11.21. **MS** (**EI**, 80 eV, 150°C): m/z (%) = 554 (3.4), 553 (9.7), 552 (19.8), 551 (9.7) $[M]^+$, 550 (18.3) $[M\text{-}H]^+$, 512 (3.7), 511 (11.5), 510 (37.0), 509 (100.0), 508 (38.14) $[M^+\text{-}C_3H_7]$, 507 (93.9) $[M\text{-}H\text{-}C_3H_7]^+$. **EA**: Calc.: C:67.37, H:7.66, N:2.53; Found: C:67.42, H:7.86, N:2.46.

2-Bromo-5-({3-[(triisopropylsilyl)ethynyl]-5-(tetrahydropyran-2-yloxymethyl)phenyl}ethynyl) – pyridine, $C_{30}H_{38}BrNO_2Si$, M = 552.66, ***31c***

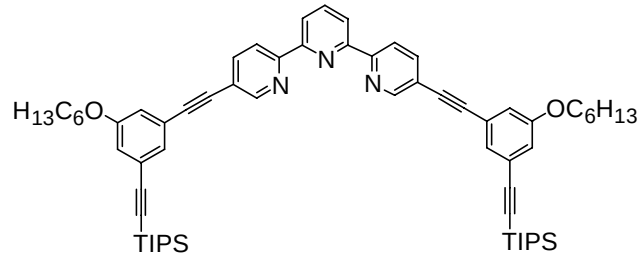
The procedure was analogous to that described for **94** (**6**: 5.00 g, 17.6 mmol; **12c**: 7.00 g, 17.6 mmol; CuI: 101 mg, 0.530 mmol; $Pd[P(Ph_3)]_4$: 611 mg, 0.530 mmol; triethylamine: 150 ml;

reaction time: 3 days; reaction temperature: 60°C). The crude product was purified by column chromatography (silica gel, hexane/toluene) to afford **31c** (12.14 g, 21.97 mmol, 87 %) as a yellow sirup. $\mathbf{R_f}$ = 0.16 (hexane/ethyl acetate 30:1).



^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.48 (d, 1 H, ^{4}J = 2.2 Hz, py-6-H), 7.62 (dd, 1 H, ^{3}J = 8.2 Hz, ^{4}J = 2.3 Hz, py-4-H), 7.55 (t, 1 H, ^{4}J = 1.2, phenyl-H), 7.48 (s, 1 H, phenyl-H), 7.45 (d, 1 H, ^{3}J = 8.6 Hz, py-3-H), 7.44 (s, 1 H, phenyl-H), 4.68-4.75 (m, 2 H, benzyl-H, THP-2-H), 4.45 (d, 1 H, ^{2}J = 12.4 Hz, benzyl-H'), 3.84-3.92 (m, 1 H, THP-6-H), 3.50-3.58 (m, 1 H, THP-6'-H), 1.51-1.84 (m, 6 H, THP-3,3',4,4',5,5'-H), 1.11 (s, 21 H, TIPS-H). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 152.30, 141.17, 140.44, 139.07, 134.06, 131.58, 130.50, 127.60, 124.04, 122.37, 119.40, 105.70, 97.85, 93.03, 91.75, 85.13, 67.71, 62.09, 30.40, 25.34, 19.22, 18.58, 11.20. **MS** (**EI**, 80 eV, 80 - 100°C): m/z (%) = 554 (1.3), 553 (3.4), 552 (3.4), 551 (3.2), 550 (3.3) $[M]^+/[M-H]^+$, 513 (2.0), 512 (8.2), 511 (28.6), 510 (82.3), 509 (100.0), 508 (76.5), 507 (94.8) $[M-C_3H_7]^+/[M-H-C_3H_7]^+$, 454 (30.5), 453 (83.2), 452 (79.9), 451 (72.9), 450 (89.9) $[M-C_5H_8O_2]^+/[M-H-C_5H_8O_2]^+$, 426 (18.1), 425 (21.3), 424 (17.1), 423 (21.4) $[M-C_7H_{11}O_2]^+/[M-H-C_7H_{11}O_2]^+$, 410 (15.8), 408 (16.9), 407 (16.3) $[M-C_5H_8O_2-C_3H_7]^+/[M-H-C_5H_8O_2-C_3H_7]^+$, 382 (15.9), 380 (16.2) $[M-C_7H_{11}O_2-C_3H_7]^+/[M-H-C_7H_{11}O_2-C_3H_7]^+$, 368 (17.4), 367 (19.0), 366 (17.7), 365 (23.3) $[M-C_5H_8O_2-C_3H_7-C_3H_6]^+/[M-C_5H_8O_2-2C_3H_7]^+$. **EA**: Calc.: C:65.20, H:6.93, N:2.53; Found: C:65.40, H:7.03, N:2.40.

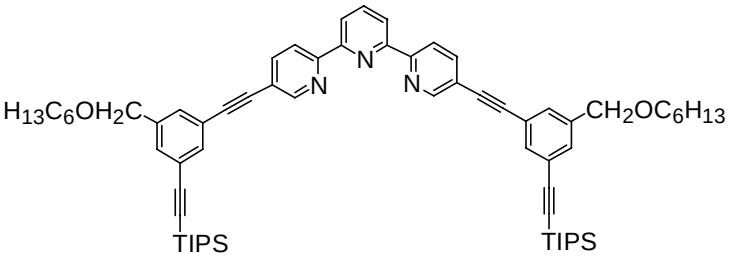
5,5'-Bis({3-hexoxy-5-[(triisopropylsilyl)ethynyl]phenyl}ethynyl)-2,2':6',2''-terpyridine,
$C_{65}H_{83}N_3O_2Si_2$, M = 994.56, ***32a***



The procedure was analogous to that described for **28a** (**10**: 225 mg, 0.56 mmol; **31a**: 600 mg, 1.1 mmol; $Pd[P(Ph_3)]_4$: 39 mg, 0.033 mmol; toluene: 25 ml; reaction time: 5 days). The crude product was purified by column chromatography (hexane/ethyl acetate, silica gel) to afford **32a** (280 mg, 0.28 mmol, 50 %) as a yellow foam. $\mathbf{R_f}$ = 0.20 (hexane/ethyl acetate 30:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 8.81 (d, 2 H, ^{4}J = 1.6 Hz, tpy-6,6''-H), 8.60 (dd, 2 H, ^{3}J = 8.3 , ^{5}J = 0.6 Hz, tpy-3,3''-H), 8.47 (d, 2 H, ^{3}J = 7.8 Hz, tpy-

3',5'-H), 7.96 (t, 1 H, $^3J \approx 8$ Hz, 4'-H), 7.94 (dd, 2 H, $^3J = 8.2$ Hz , $^4J = 2.0$ Hz, 4,4''-H), 7.27 (t, 2 H, $^4J = 1.3$ Hz, phenyl-H), 7.03 (dd, 2 H, $^4J = 0.9$ Hz, $^4J = 1.3$ Hz, phenyl-H), 7.00 (dd, 2 H, $^4J = 1.1$ Hz, phenyl-H), 3.96 (t, 4 H, $^3J = 6.4$ Hz, α-CH_2), 1.77 (quintet, 4 H, $^3J \approx 7$ Hz, β-CH_2), 1.33-1.35 (m, 12 H, γ-,δ-,ε-CH_2), 1.12 (s, 42 H, silyl-H), 0.90 (t, 6 H, $^3J = 6.8$ Hz, hexyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 158.79, 154.84, 154.72, 151.63, 139.32, 137.98, 127.66, 124,86, 123.57, 121.57, 120.40, 120.14, 118.92, 117.58, 105.96, 92.83, 91.29, 86.52, 68.28, 31.52, 29.12, 25.66, 22.58, 18.65, 14.01, 11.28. **MS** (**FAB(+)**, DMSO/CH_2Cl_2-Matrix): m/z (%) = 997 (26.0), 996 (50.6), 995 (82.0), 994 (100.0) $[M+H]^+$. **EA**: Calc.: C:78.50, H:8.41, N:4.22; Found: C:78.22, H:8.24, N:4.08.

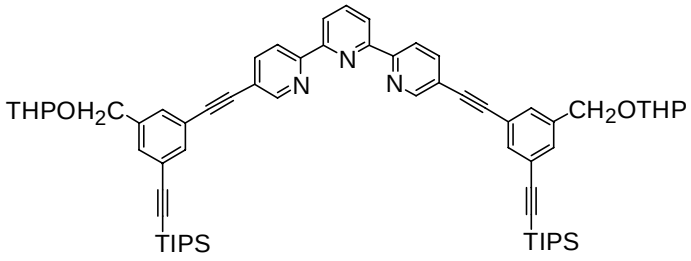
5,5'-Bis({3-hexoxymethyl-5-[(triisopropylsilyl)ethynyl]phenyl}ethynyl)-2,2':6',2''-terpyridine, $C_{67}H_{87}N_3O_2Si_2$, M = 1022.61, ***32b***



The procedure was analogous to that described for **28a** (**10**: 9.48 g, 23.5 mmol; **31b**: 25.88 g, 46.83 mmol; $Pd[P(Ph_3)]_4$: 1.62 g, 1.40 mmol; toluene: 500 ml; reaction time: 36 hrs). The crude product was purified by repeated column chromatography (hexane/dichloromethane on aluminium oxide, hexane/ethyl acetate on silica gel) to afford **32b** (13.15 g, 12.86 mmol, 55 %) as a yellow resin which could not be solidified even after freeze-drying from benzene. $\mathbf{R_f}$ = 0.78 (hexane/ethyl acetate 10:1, aluminium oxide). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 8.81 (d, 2 H, $^4J = 1.7$ Hz, tpy-6,6''-H), 8.61 (d, 2 H, $^3J = 8.3$, tpy-3,3''-H), 8.47 (d, 2 H, $^3J = 7.8$ Hz, tpy-3',5'-H), 7.96 (t, 1 H, $^3J \approx 8$ Hz, 4'-H), 7.95 (dd, 2 H, $^3J = 8.3$ Hz , $^4J = 2.0$ Hz, 4,4''-H), 7.60 (t, 2 H, $^4J = 1.4$ Hz, phenyl-H), 7.49 (s, 2 H, phenyl-H), 7.43 (s, 2 H, phenyl-H), 4.47 (s, 4 H, benzyl-H), 3.48 (t, 4 H, $^3J = 6.6$ Hz, α-CH_2), 1.62 (quintet, 4 H, $^3J \approx 7$ Hz, β-CH_2), 1.26-1.42 (m, 12 H, γ-,δ-,ε-CH_2), 1.12 (s, 42 H, silyl-H), 0.88 (t, 6 H, $^3J = 6.7$ Hz, hexyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 154.90, 154.76, 151.66, 139.48, 139.28, 137.97, 134.11, 131.27, 130.44, 124.07, 122.84, 121.56, 120.39, 120.14, 105.91, 92.72, 91.62, 86.87, 71.88, 70.86, 31.66, 29.66, 25.84, 22.61, 18.65, 14.03, 11.28. **MS** (**EI**, 80 eV, 250 - 300°C): m/z (%) = 1024 (3.2), 1023 (7.9), 1022 (14.1), 1021 (16.3) $[M]^+$, 982 (4.6), 981 (14.0),

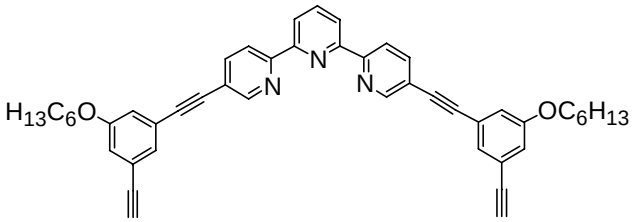
980 (36.3), 979 (74.7), 978 (100.0) $[M\text{-}C_3H_7]^+$, 951 (1.7), 950 (2.4) $[M\text{-}C_5H_{11}]^+$, 939 (2.6), 938 (6.6), 937 (14.5), 936 (23.5), 935 (23.0) $[M\text{-}C_6H_{13}]^+/[M\text{-}C_5H_{11}\text{-}CH_3]^+$. **EA**: Calc.: C:78.69, H:8.57, N:4.11; Found: C:78.82, H:8.77, N:3.88.

5,5‘-Bis({3-(tetrahydropyran-2-yloxymethyl)-5-[(triisopropylsilyl)ethynyl]phenyl} ethynyl)-2,2‘:6‘,2‘‘-terpyridine, $C_{65}H_{79}N_3O_4Si_2$, M = 1022.53, ***32c***



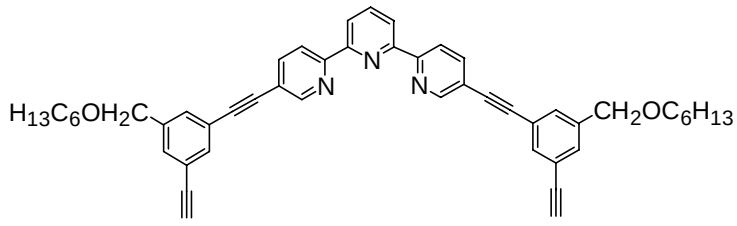
The procedure was analogous to that described for **28a** (**10**: 2.12 g, 5.23 mmol; **31c**: 5.78 g, 10.5 mmol; $Pd[P(Ph_3)]_4$: 363 mg, 0.314 mmol; toluene: 120 ml; reaction time: 48 hrs). The crude product was purified by repeated column chromatography (ethyl acetate + triethylamine, silica gel) to afford **32c** (2.41 g, 2.36 mmol, 45 %) as a colorless foam. $\mathbf{R_f}$ = 0.60 (hexane/ethyl acetate 4:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 8.81 (dd, 2 H, ^4J = 1.6 Hz, ^5J = 0.6 Hz, tpy-6,6‘‘-H), 8.61 (d, 2 H, ^3J = 8.2 , tpy-3,3‘‘-H), 8.47 (d, 2 H, ^3J = 7.8 Hz, tpy-3‘,5‘-H), 7.96 (t, 1 H, $^3J \approx 8$ Hz, 4‘-H), 7.95 (dd, 2 H, ^3J = 8.2 Hz , ^4J = 2.1 Hz, 4,4‘‘-H), 7.60 (t, 2 H, ^4J = 1.2 Hz, phenyl-H), 7.52 (s, 2 H, phenyl-H), 7.45 (s, 2 H, phenyl-H), 4.70-4.78 (m, 4 H, benzyl-H, THP-2-H), 4.47 (d, 2 H, ^2J = 12.3 Hz, benzyl-H‘), 3.86-3.95 (m, 2 H, THP-6-H), 3.52-3.60 (m, 2 H, THP-6‘-H), 1.52-1.89 (m, 12 H, THP-3,3‘,4,4‘,5,5‘-H), 1.12 (s, 42 H, silyl-H). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 154.85, 154.69, 151.62, 139.21, 139.01, 137.89, 134.13, 131.43, 130.63, 124.02, 122.84, 121.52, 120.32, 120.06, 105.88, 97.85, 92.67, 91.63, 86.89, 67.80, 62.12, 30.44, 25.38, 19.26, 18.62, 11.25. **MS** (**FAB(+)**, MNBA/CH_2Cl_2-Matrix): m/z (%) = 1025 (10.0), 1024 (21.6), 1023 (46.9), 1022 (83.9), 1021 (100.0), 1020 (12.4), 1019 (13.9) $[M]^+$, 979 (10.5), 978 (11.4), 977 (10.8) $[M\text{-}C_3H_7]^+$, 965 (11.0) $[M\text{-}C_3H_7 –CH_3]^+$, 938 (14.8), 937 (20.3), 936 (21.9), 935 (26.4), 934 (9.9), 933 (9.7) $[M\text{-}2C_3H_7]^+$, 923 (11.1), 922 (15.8), 921 (23.3), 920 (23.7), 919 (10.6) $[M\text{-}2C_3H_7\text{-}CH_3]^+$. **EA**: Calc.: C:76.35, H:7.79, N:4.11; Found: C:76.36, H:7.69, N:4.02.

5,5‘‘-Bis[(3-ethynyl-5-hexoxyphenyl)ethynyl]-2,2‘:6‘,2‘‘-terpyridine, $C_{47}H_{43}N_3O_2$, M = 681.88, ***33a***



The procedure was analogous to that described for **33b** (**32a**: 270 mg, 0.27 mmol; tetra-*n*-butylammonium fluoride trihydrate: 260 mg, 0.82 mmol; THF :10 ml. The crude mixture was purified by chromatography over silica gel (hexane/ethyl acetate) to afford **33a** (150 mg, 0.22 mmol, 81 %) as a slightly yellow sirup. $\mathbf{R_f}$ = 0.50 (hexane/ethyl acetate 4:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 8.79 (dd, 2 H, ^{4}J = 1.9 Hz, ^{4}J = 0.7 Hz, tpy-6,6’’-H), 8.58 (d, 2 H, ^{3}J = 8.3 Hz, tpy-3,3’’-H), 8.45 (d, 2 H, ^{3}J = 7.9 Hz, tpy-3’,5’-H), 7.93 (t, 1 H, ^{3}J ≈ 8 Hz, tpy-4’-H), 7.91 (dd, 2 H, ^{3}J = 8.1 Hz, ^{4}J = 2.0 Hz, tpy-4,4’’-H), 7.27 (t, 2 H, ^{4}J = 1.1 Hz, phenyl-H), 7.06 (dd, 2 H, ^{4}J = 1.4 Hz, ^{4}J = 2.2 Hz, phenyl-H), 7.00 (dd, 2 H, ^{4}J = 1.3 Hz, ^{4}J = 2.3 Hz, phenyl-H),3.94 (t, 4 H, ^{3}J = 6.5 Hz, α-CH_2), 3.01 (s, 2 H, ethynyl-H), 1.76 (quintet, 4 H, ^{3}J ≈ 8 Hz, β-CH_2), 1.23-1.46 (m, 12 H, γ-,δ-,ε-CH_2), 0.90 (t, 3 H, ^{3}J = 6.8 Hz, -CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 158.81, 154.86, 154.66, 151.62, 139.28, 137.94, 127.64, 123.77, 123.42, 121.55, 120.35, 120.03, 118.85, 118.24, 92.59, 86.70, 82.67, 77.62, 68.32, 31.51, 29.06, 25.63, 22.58, 14.01. **MS** (**EI**, 80 eV, 300°C): m/z (%) = 684 (5.5), 683 (8.7), 682 (55.2), 681 (100.0) $[M]^+$, 598 (21.5), 597 (30.6) $[M\text{-}C_6H_{12}]^+$, 514 (21.8), 513 (50.3) $[M\text{-}2C_6H_{12}]^+$. **EA**: Calc.: C:82.79, H:6.36, N:6.16; Found: C:82.97, H:6.33, N:5.88.

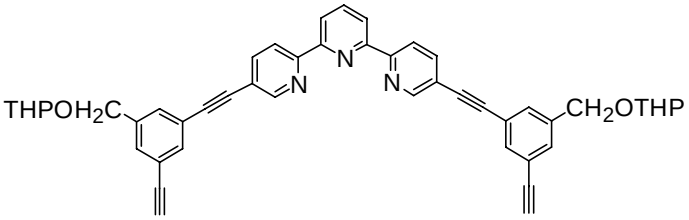
5,5‘-Bis{[3-ethynyl-5-(hexoxymethyl)phenyl]ethynyl}-2,2‘:6‘,2‘‘-terpyridine, $C_{99}H_{47}N_3O_2$, M = 709.93, ***33b***



32b (13.15 g, 12.86 mmol) was dissolved in THF (150 ml) and tetra-*n*-butylammonium fluoride trihydrate (12.2 g, 38.5 mmol) was added. After stirring overnight, the solvent was evaporated and the crude mixture purified by chromatography over aluminium oxide (hexane/ethyl acetate) to afford **33b** (6.87 g, 9.68 mmol, 75 %) as a slightly yellow solid, mp 97-98°C. $\mathbf{R_f}$ = 0.50 (hexane/ethyl acetate 4:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 8.80 (d, 2 H, ^{4}J = 1.7 Hz, tpy-6,6’’-H), 8.59 (d, 2 H, ^{3}J = 8.3 , tpy-3,3’’-H), 8.46 (d, 2 H, ^{3}J = 7.8 Hz, tpy-3’,5’-H),

7.96 (t, 1 H, $^3J \approx 8$ Hz, 4'-H), 7.95 (dd, 2 H, $^3J = 8.4$ Hz, $^4J = 1.8$ Hz, 4,4''-H), 7.60 (s, 2 H, phenyl-H), 7.52 (s, 2 H, phenyl-H), 7.45 (s, 2 H, phenyl-H), 4.47 (s, 4 H, benzyl-H), 3.48 (t, 4 H, $^3J = 6.5$ Hz, α-CH_2), 3.09 (s, 2 H, ethynyl-H), 1.62 (quintet, 4 H, $^3J \approx 7$ Hz, β-CH_2), 1.26-1.42 (m, 12 H, γ-,δ-,ε-CH_2), 0.88 (t, 6 H, $^3J = 6.7$ Hz, hexyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 154.81, 154.58, 151.58, 139.62, 139.17, 137.83, 134.09, 131.19, 130.77, 122.94, 122.60, 121.49, 120.27, 119.96, 92.46, 87.00, 82.59, 77.94, 71.69, 70.84, 31.61, 29.62, 25.79, 22.57, 14.00. **MS** (**EI**, 80 eV, 180°C): m/z (%) = 711 (28.7), 710 (65.05), 709 (100.0) $[M]^+$, 624 (23.4) $[M\text{-}C_6H_{13}]^+$, 611 (20.2), 610 (42.3), 609 (64.9) $[M\text{-}OC_6H_{12}]^+$, 524 (24.5), 523 (19.8) $[M\text{-}C_6H_{13}\text{-}OC_6H_{12/13}]^+$, 510 (23.6), 509 (45.8), 508 (32.4), 507 (19.8), 506 (20.9), 505 (17.8) $[M–2OC_6H_{12/13}]^+$. **EA**: Calc.: C:82.90, H:6.67, N:5.92; Found: C:82.87, H:6.39, N:5.74.

5,5'-Bis{[3-ethynyl-5-(tetrahydropyran-2-yloxymethyl)phenyl]ethynyl}-2,2':6',2''-terpyridine, $C_{47}H_{39}N_3O_4$, M = 709.84, ***33c***



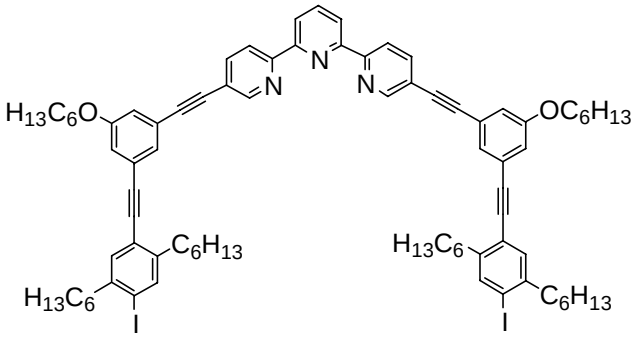
The procedure was analogous to that described for **33b** (**32c**: 2.26 g, 2.20 mmol; tetra-n-butylammonium fluoride trihydrate: 2.3 g, 7.1 mmol; THF: 60 ml). The crude product was purified by chromatography over silica gel (hexane/ethyl acetate) to afford **33c** (1.22 g, 1.72 mmol, 78 %) as a yellow resin which could not be solidified by freeze-drying from benzene. $\mathbf{R_f}$ = 0.20 (hexane/ethyl acetate 4:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 8.80 (dd, 2 H, ^4J = 1.7 Hz, $^5J = 0.6$ Hz, tpy-6,6''-H), 8.61 (d, 2 H, $^3J = 8.2$, tpy-3,3''-H), 8.46 (d, 2 H, $^3J = 7.8$ Hz, tpy-3',5'-H), 7.95 (t, 1 H, $^3J \approx 8$ Hz, 4'-H), 7.94 (dd, 2 H, $^3J = 8.2$ Hz , $^4J = 2.0$ Hz, 4,4''-H), 7.61 (t, 2 H, $^4J = 1.3$ Hz, phenyl-H), 7.54 (s, 2 H, phenyl-H), 7.48 (s, 2 H, phenyl-H), 4.70-4.78 (m, 4 H, benzyl-H, THP-2-H), 4.47 (d, 2 H, $^2J = 12.3$ Hz, benzyl-H'), 3.85-3.93 (m, 2 H, THP-6-H), 3.51-3.59 (m, 2 H, THP-6'-H), 3.10 (s, 2 H, ethynyl-H), 1.52-1.92 (m, 12 H, THP-3,3',4,4',5,5'-H). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 154.74, 154.51, 151.52, 139.16, 137.78, 134.08, 131.31, 130.88, 122.90, 122.56, 121.44, 120.22, 119.88, 97.84, 92.41, 87.00, 82.56, 77.99, 67.63, 62.01, 30.37, 25.31, 19.17. **MS** (**FAB(+)**, DMSO/CH_2Cl_2-Matrix): m/z (%) = 713 (6.5), 712 (20.3), 711 (55.8), 710 (100.0) $[M+H]^+$, 628 (7.3), 627 (12.2), 626 (9.6), 625 (13.8) $[M\text{-}C_5H_8O]^+$, 612 (5.8),

611 (14.4), 610 (21.1), 609 (7.8) $[M\text{-}C_5H_7O_2]^+/[M\text{-}C_5H_8O_2]^+$. **EA**: Calc.: C:79.53, H:5.54, N:5.92; Found: C:79.33, H:5.67, N:5.76.

5,5‘-Bis({3-hexoxymethyl-5-[(4-iodophenyl)ethynyl]phenyl}ethynyl)-2,2‘:6‘,2‘‘-terpyridine, $C_{61}H_{53}I_2N_3O_2$, M = 1113.92, ***35a***

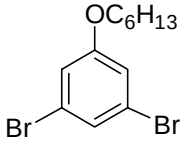
The procedure was analogous to that described for **94** (**33b**: 100 mg, 0.14 mmol; *p*-diiodobenzene: 0.924 mg, 2.80 mmol; CuI: 3 mg, 0.016 mmol; $Pd[P(Ph_3)]_4$: 16 mg, 0.016 mmol; triethylamine: 10 ml; toluene: 10 ml; reaction time: 3 days; reaction temperature: 60°C). The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate) to afford **35a** (100 mg, 0.089 mmol, 64 %) as a colorless amorphous material, m.p. 150-153°C. $\mathbf{R_f}$ = 0.20 (hexane/ethyl acetate 4:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 8.81 (d, 2 H, ^4J = 1.8 Hz, tpy-6,6‘‘-H), 8.61 (d, 2 H, ^3J = 8.3, tpy-3,3‘‘-H), 8.47 (d, 2 H, ^3J = 7.8 Hz, tpy-3’,5’-H), 7.96 (t, 1 H, $^3J \approx 8$ Hz, 4’-H), 7.95 (dd, 2 H, ^3J = 8.2 Hz , ^4J = 2.2 Hz, 4,4‘‘-H), 7.67 (d, 4 H, ^3J = 8.3 Hz, iodophenyl-3,5-H), 7.64 (t, 2 H, ^3J = 1.4 Hz, phenyl-H), 7.51 (s, 2 H, phenyl-H), 7.48 (s, 2 H, phenyl-H), 7.22 (d, 4 H, ^3J = 8.3 Hz, iodophenyl-2,6-H), 4.49 (s, 4 H, benzyl-H), 3.49 (t, 4 H, ^3J = 6.6 Hz, α-CH_2), 1.64 (quintet, 4 H, $^3J \approx 7$ Hz, β-CH_2), 1.23-1.43 (m, 12 H, γ-,δ-,ε-CH_2), 0.88 (t, 6 H, ^3J = 6.7 Hz, hexyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 154.67, 154.46, 151.49, 139.60, 139.14, 137.79, 137.47, 133.52, 133.00, 130.60, 130.40, 123.34, 122.93, 122.33, 121.46, 120.26, 119.96, 94,41, 92.61, 89.76, 89.12, 86.98, 71.73, 70.82, 31.60, 29.61, 25.78, 22.57, 14.03. **MS** (**FAB(+)**, CH_2Cl_2/DMSO/MNBA-Matrix): m/z (%) = 1118 (4.0), 1117 (9.10), 1116 (27.1), 1115 (67.5), 1114 (100.0) $[M+H]^+$, 1031 (4.7), 1030 (7.2), 1029 (11.3), 1028 (13.1) $[M\text{-}C_6H_{13}]^+$, 1016 (4.6), 1015 (6.4), 1014 (12.9), 1013 (16.3) $[M\text{-}C_6H_{12}O]^+$. **EA**: Calc.: C:65.77, H:4.80, N:3.77; Found: C:65.84, H:4.71, N:3.60.

5,5‘-Bis({3-hexoxymethyl-5-[(2,5-dihexyl-4-iodophenyl)ethynyl]phenyl}ethynyl)-2,2‘:6‘,2‘‘-terpyridine, $C_{85}H_{101}I_2N_3O_2$, M = 1450.56, ***35b***



The procedure was analogous to that described for **94** (**33b**: 500 mg, 0.70 mmol; **34**: 7.02 g, 14.1 mmol; CuI: 8 mg, 0.042 mmol; $Pd[P(Ph_3)]_4$: 50 mg, 0.042 mmol; triethylamine: 40 ml; toluene: 40 ml; reaction time: 3 days; reaction temperature: 60°C). The crude product was purified by repeated column chromatography (silica gel, hexane / ethyl acetate and aluminium oxide, hexane/ethyl acetate) to afford **35b** (520 mg, 0.358 mmol, 51 %) as a colorless amorphous material. Most of **34** (6.28 g, 12.6 mmol, 89 %) was regained. $\mathbf{R_f}$ = 0.35 (hexane/ethyl acetate 4:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 8.83 (d, 2 H, ^{4}J = 1.7 Hz, tpy-6,6’’-H), 8.63 (d, 2 H, ^{3}J = 8.3 , tpy-3,3’’-H), 8.48 (d, 2 H, ^{3}J = 7.8 Hz, tpy-3’,5’-H), 7.98 (t, 1 H, ^{3}J ≈ 8 Hz, 4’-H), 7.96 (dd, 2 H, ^{3}J = 8.3 Hz , ^{4}J = 2.0 Hz, 4,4’’-H), 7.66 (s, 2 H, iodophenyl-3-H), 7.63 (t, 2 H, ^{4}J = 1.4 Hz, phenyl-H), 7.52 (t, 2 H, ^{4}J = 1.3 Hz, phenyl-H), 7.48 (t, 2 H, ^{4}J = 1.2 Hz, phenyl-H), 7.30 (s, 2 H, iodophenyl-6-H), 4.50 (s, 4 H, benzyl-H), 3.50 (t, 4 H, ^{3}J = 6.6 Hz, α-OCH_2), 2.74 (t, 4 H, ^{3}J = 8 Hz, α-CH_2), 2.64 (t, 4 H, ^{3}J = 8 Hz, α-CH_2), 1.52-1.67 (m, 8 H, β-CH_2), 1.23-1.41 (m, 40 H, γ-,δ-,ε-CH_2), 0.86-0.91 (m, 18 H, -CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 154.90, 154.72, 151.66, 144.12, 142.79, 139.70, 139.50, 139.26, 137.96, 133.45, 132.29, 130.61, 130.36, 123.91, 123.04, 122.36, 121.60, 120.38, 120.10, 101.23, 92.69, 92.42, 88.56, 86.97, 71.88, 70.91, 40.19, 33.79, 31.67, 30.60, 30.14, 29.68, 29.17, 29.01, 25.84, 22.62, 14.08. **MS** (**EI**, 80 eV, 350°C): m/z (%) = 1451 (7.8), 1450 (9.0) $[M]^+$. **EA**: Calc.: C:70.38, H:7.02, N:2.90; Found: C:70.43, H:6.81, N:2.76.

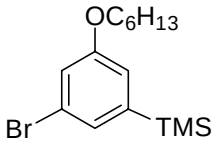
1,3-Dibromo-5-hexoxybenzene, $C_{12}H_{16}Br_2O$, M = 336.07, ***91*** (Scheme 8)



A mixture of **90** (45.07 g, 179 mmol), hexyl bromide (38 ml, 44.3 g, 268 mmol) and K_2CO_3 (30 g, 215 mmol) in diethyl ketone (500 ml) was refluxed for 18 hrs. After cooling, the suspension was extracted with water (500 ml) and the aqueous phase twice with ethyl acetate (300/200 ml). The combined organic phases were dried over $MgSO_4$ and the solvent removed in

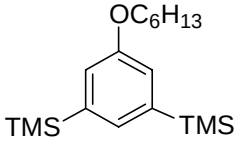
vacuum to afford a brown oil (61 g). Chromatographic filtration over a short silica gel column gave **91** as a colorless liquid (58.39 g, 174 mmol, 97 %). $\mathbf{R_f}$ = 0.79 (hexane). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 7.20 (t, 1 H, ^{3}J = 1.5 Hz, 4-H), 6.96 (d, 2 H, ^{3}J = 1.6 Hz, 2,6-H), 3.89 (t, 2 H, ^{3}J = 6.5 Hz, α-CH_2), 1.74 (quintet, 2 H, ^{3}H ≈ 7 Hz, β-CH_2), 1.28-1.42 (m, 6 H, γ-, δ-, ε-CH_2), 0.89 (t, 3 H, ^{3}J = 6.7 Hz, -CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 160.36, 126.12, 123.03, 116.91, 68.61, 31.45, 28.93, 25.56, 22.54, 13.98. **MS** (**EI**, 80 eV, 60°C): m/z (%) = 339 (1.8), 338 (12.6), 337 (3.7), 336 (26.0), 335 (2.2), 334 (13.2) $[M]^+$, 267 (1.4), 265 (2.8), 263 (1.5) $[M\text{-}C_5H_{11}]^+$, 255 (4.3), 254 (48.1), 253 (9.0), 252 (100.0), 251 (5.4), 250 (50.8) $[M\text{-}C_6H_{12}]^+$, 237 (2.9), 235 (5.7), 233 (2.7), $[M\text{-}C_5H_{11}\text{–}CH_2O]^+$, 225 (2.0), 223 (4.1), 221 (2.1) $[M\text{-}C_6H_{12}\text{-}CHO]^+$. **EA**: Calc.: C: 42.88, H: 4.80; Found: C: 42.60 H: 4.58.

1-Bromo-3-hexoxy-5-trimethylsilylbenzene, $C_{15}H_{25}BrOSi$, M = 329.35, ***92a*** (Scheme 8)



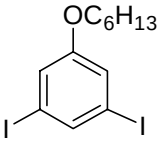
To a solution of **91** (58.39 g, 174 mmol) in diethylether (500 ml) at -78°C, a 1.6 M solution of *n*-butyl lithium in hexane (120 ml, 191 mmol) was added under N_2 over a period of 30 min. The solution was stirred for 90 min and trimethylchlorosilane (33 ml, 261 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and poured into water (800 ml). The phases were separated and the aqueous one extracted with ether (2 × 300 ml). The combined organic phases were dried over $MgSO_4$ and the solvent was removed in vacuo to afford a yellowish oil (56.62 g). Chromatographic separation through silica gel with hexane gave **92a** (51.35 g, 156 mmol, 90 %) as a colorless oil. $\mathbf{R_f}$ = 0.45 (hexane). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 7.16 (t, 1 H, ^{4}J = 1.0 Hz, aryl-H), 7.00 (t, 1 H, ^{4}J = 2.0 Hz, aryl-H), 6.94 (dd, 1 H, ^{4}J = 0.8 Hz, ^{4}J = 2.4 Hz, aryl-H), 3.92 (t, 2 H, ^{3}J = 6.5 Hz, α-CH_2), 1.74-1.77 (quintet, 2 H, ^{3}H ≈ 7 Hz, β-CH_2), 1.31-1.35 (m, 6 H, γ-, δ-, ε-CH_2), 0.90 (t, 3 H, ^{3}J = 6.9 Hz, hexyl-CH_3), 0.25 (s, 9 H, silyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 159.38, 144.34, 127.84, 123.01, 118.55, 117.37, 68.15, 31.55, 29.16, 25.68, 22.58, 14.01, -1.29. **MS** (**EI**, 80 eV, 80°C): m/z (%) = 332 (3.7), 331 (14.0), 330 (69.0), 329 (14.5), 328 (67.5) $[M]^+$, 317 (2.4), 316 (9.0), 315 (45.5), 314 (9.5), 313 (43.7) $[M\text{-}CH_3]^+$, 247 84.0), 246 (27.1), 245 (5.0), 244 (26.4), 243 (2.3) $[M\text{-}C_6H_{12}]^+$, 233 (4.0), 232 (11.0), 231 (98.6), 230 (17.0), 229 (100.0), 228 (4.6), 227 (4.6) $[M\text{-}CH_3\text{-}C_6H_{12}]^+$. **EA**: Calc.: C: 54.70, H: 7.65; Found: C: 54.61, H: 7.45

1-Hexoxy-3,5-bis(trimethylsilyl)benzene, $C_{18}H_{34}OSi_2$, M = 322.64, ***92b*** (Scheme 8)



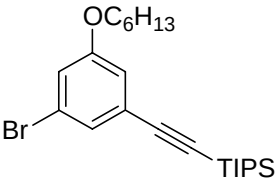
92b was isolated as a side product from one batch of synthesis of **92a** (**91**: 76.20 g, 227 mmol; diethylether: 500 ml; 1.6 M *n*-butyl lithium in hexane: 170 ml, 272 mmol; trimethylchlorosilane: 43 ml, 340 mmol; yields: **92a**: 59.53 g, 181 mmol, 80 %; **92b**: 8.30 g; 25.7 mmol, 11 %; as colorless oils). $\mathbf{R_f}$ = 0.40 (hexane). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 7.30 (s, 1 H, 4-H), 7.11 (d, 2 H, ^{4}J = 0.8 Hz, 2,6-H), 4.05 (t, 2 H, ^{3}J = 6.5 Hz, α-CH_2), 1.86 (quintet, 2 H, ^{3}H ≈ 7 Hz, β-CH_2), 1.38-1.58 (m, 6 H, γ-, δ-, ε-CH_2), 0.98 (t, 3 H, ^{3}J = 7.1 Hz, hexyl-CH_3), 0.34 (s, 18 H, silyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 157.98, 141.25, 130.20, 119.68, 67.70, 31.65, 29.44, 25.81, 22.62, 14.02, -1.10. **MS** (**EI**, 80 eV, 80°C): m/z (%) = 325 (10.6), 324 (21.4), 323 (100.0), 322 (42.2) $[M]^+$, 310 (7.6), 309 (22.4), 308 (74.7), 307 (34.1) $[M\text{-}CH_3]^+$, 226 (4.6), 225 (12.8), 224 (54.9), 223 (21.7), 222 (9.4) $[M\text{-}CH_3\text{-}C_6H_{12}]^+$. **EA**: Calc.: C: 67.10, H: 10.62; Found: C: 66.77, H: 10.66.

1,3-Diiodo-5-hexoxybenzene, $C_{12}H_{16}I_2O$, M = 430.07, ***93b*** (Scheme 8)



The procedure was analogous to that described for **8** (**92b**: 4.17 g, 12.9 mmol; iodine chloride: 5.45 g, 33.59 mmol; dichloromethane: 100 ml). The crude product was purified by chromatography (silica gel; hexane) to afford **93b** (5.19 g, 12.1 mmol, 93 %) as colorless crystals. $\mathbf{R_f}$ = 0.84 (hexane). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 7.58 (s, 1 H, 2-H), 7.18 (d, 1 H, ^{4}J = 1.3 Hz, 4,6-H), 3.86 (t, 2 H, ^{3}J = 6.5 Hz, α-CH_2), 1.72 (quintet, 2 H, ^{3}H ≈ 7 Hz, β-CH_2), 1.27-1.43 (m, 6 H, γ-, δ-, ε-CH_2), 0.89 (t, 3 H, ^{3}J = 6.6 Hz, -CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 159.93, 137.26, 123.43, 94.55, 68.49, 31.46, 28.96, 25.57, 22.55, 13.99. **MS** (**EI**, 80 eV, 90°C): m/z (%) = 432 (0.8), 431 (9.7), 430 (77.2) $[M]^+$, 359 (1.2) $[M\text{-}C_5H_{11}]^+$, 347 (6.7), 346 (100.0) $[M\text{-}C_6H_{12}]^+$, 329 (3.9) $[M\text{-}C_5H_{11}\text{–}CH_2O]^+$. **EA**: Calc.: C: 33.51, H: 3.75; Found: C: 33.41, H: 3.74.

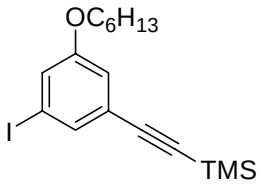
1-Bromo-3-hexoxy-5-[(triisopropylsilyl)ethynyl]benzene, $C_{23}H_{37}BrOSi$, M = 437.53, ***94*** (Scheme 8)



A solution of **8** (46.4 g, 121 mmol) and TIPS-acetylene (23.4 g, 128 mmol) in dry triethylamine (300 ml) was degassed three times by being frozen with liquid nitrogen, evacuated under warming up and washed with N_2. $Pd[P(Ph_3)]_4$ (4.19 g, 3.6 mmol) and CuI (700 mg,

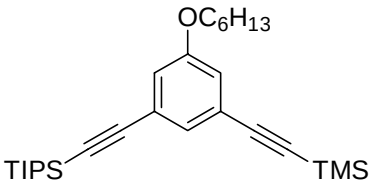
3.6 mmol) were added, the mixture was degassed again and stirred at 60°C in a sealed flask for 36 hrs. The solvent was evaporated and the crude product purified by chromatography over silica gel (hexane) to afford **94** (42.0 g, 96.0 mmol, 79 %) as a slightly yellow oil. $\mathbf{R_f}$ = 0.45 (hexane). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 7.18 (t, 1 H, ^{4}J = 1.3 Hz, aryl-H), 6.99 (t, 1 H, ^{4}J = 2.1 Hz, aryl-H), 6.90 (dd, 1 H, ^{4}J = 0.9 Hz, ^{4}J = 1.8 Hz, aryl-H), 3.90 (t, 2 H, ^{3}J = 6.4 Hz, α-CH_2), 1.74 (quintet, 2 H, ^{3}J ≈ 7 Hz, β-CH_2), 1.29-1.48 (m, 6 H, γ-, δ-, ε-CH_2), 1.12 (s, 21 H, silyl-H), 0.90 (t, 3 H, ^{3}J = 6.6 Hz, hexyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 159.46, 126.96, 125.80, 122.32, 118.30, 116.77, 105.38, 91.84, 68.35, 31.52, 29.06, 25.64, 22.59, 18.63, 14.02, 11.26. **MS** (**EI**, 80 eV, 120°C): m/z (%) = 440 (1.2), 439 (4.7), 438 (16.2), 437 (5.0), 436 (15.4) $[M]^+$, 398 (1.0), 397 (6.5), 396 (25.7), 395 (100.0), 394 (27.1), 393 (96.6) $[M\text{-}C_3H_7]^+$, 369 (1.1), 368 (3.9), 367 (16.0), 366 (4.3), 365 (15.7) $[M\text{-}C_5H_{11}]^+$, 357 (0.8), 356 (1.0), 355 (1.9), 354 (5.1), 353 (19.0), 352 (5.2), 351 (18.8) $[M\text{-}C_6H_{13}]^+$, 342 (1.1), 341 (3.1), 340 (5.3), 339 (20.1), 338 (4.8), 337 (18.2) $[M\text{-}C_6H_{12}\text{-}CH_3]^+$, 327 (1.6), 326 (5.3), 325 (24.4), 324 (5.6), 323 (23.1) $[M\text{-}C_5H_{11}\text{-}C_3H_6]^+$. **HRMS**: Calc.: 436.17971 $[M]^+$; 393.12493 $[M - C_3H_7]^+$; Found: 436.17733; 393.12722.

1-Hexoxy-3-iodo-5-[(trimethylsilyl)ethynyl]benzene, $C_{17}H_{25}IOSi$, M = 400.37, ***95*** (Scheme 8)



The procedure was analogous to that described for **16a** (**93b**: 5.19 g, 12.1 mmol; TMS-acetylene: 1.24 mg, 12.7 mmol; CuI: 72 mg, 0.38 mmol; $Pd[P(Ph_3)]_4$: 439 mg, 0.38 mmol; triethylamine: 120 ml). The crude product was purified by chromatography over silica gel (hexane) to afford **95** (2.70 g, 6.74 mmol, 56 %) as a slightly yellow oil. $\mathbf{R_f}$ = 0.36 (hexane). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 7.37 (t, 1 H, ^{4}J = 0.7 Hz, aryl-H), 7.19 (t, 1 H, ^{4}J = 1.0 Hz, aryl-H), 6.91 (t, 1 H, ^{4}J = 1.1 Hz, aryl-H), 3.88 (t, 2 H, ^{3}J = 6.5 Hz, α-CH_2), 1.73 (quintet, 2 H, ^{3}H ≈ 7 Hz, β-CH_2), 1.28-1.57 (m, 6 H, γ-, δ-, ε-CH_2), 0.89 (t, 3 H, ^{3}J = 6.5 Hz, -CH_3), 0.23 (s, 9 H, silyl-H). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 159.13, 132.81, 125.41, 124.67, 116.99, 103.14, 95.37, 93.60, 68.27, 31.48, 29.01, 25.60, 22.57, 14.02, -0.15. **MS** (**EI**, 80 eV, 80°C): m/z (%) = 403 (1.1), 402 (7.9), 401 (30.4), 400 (100.0) $[M]^+$, 387 (6.3), 386 (24.5), 385 (97.5) $[M\text{-}CH_3]^+$, 329 (2.7), 328 (15.2) $[M\text{-}C_5H_{12}]^+$, 318 (1.8), 317 (6.1), 316 (33.0) $[M\text{-}C_6H_{13}]^+$, 304 (1.6), 303 (5.5), 302 (18.7), 301 (91.5), 300 (2.8), 299 (1.0) $[M\text{-}C_6H_{12}\text{-}CH_3]^+$. **EA**: Calc.: C:51.00, H:6.29; Found: C:51.07, H:6.06.

1-Hexyloxy-3-[(triisopropylsilyl)ethynyl]-5-[(trimethylsilyl)ethynyl]benzene, $C_{28}H_{46}Si_2O$, M = 454.84, ***96a*** (Scheme 8)

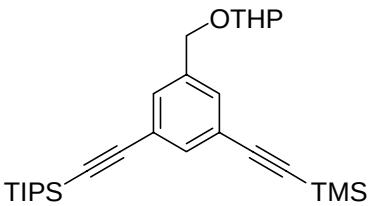


Method A: The procedure was analogous to that described for **94** (**16a**: 16.39 g, 46.38 mmol; TIPS-acetylene: 12.7 g, 69.6 mmol; CuI: 265 mg, 1.39 mmol; $Pd[P(Ph_3)]_4$: 1.61 g, 1.39 mmol; triethylamine: 250 ml). The crude product was purified by chromatography over silica gel (hexane) to afford **96a** (17.64 g, 38.78 mmol, 84 %) as a slightly yellow oil.

Method B: The procedure was analogous to that described for **16a** (**94**: 41.95 g, 95.88 mmol; TMS-acetylene: 14.2 g, 144 mmol; CuI: 548 mg, 2.5 mmol; $Pd[P(Ph_3)]_4$: 2.9 g, 2.5 mmol; triethylamine: 600 ml). The crude product was purified by chromatography over silica gel (hexane) to afford **96a** (39.74 g, 87.4 mmol, 91 %) as a slightly yellow oil.

$\mathbf{R_f}$ = 0.34 (hexane). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 7.16 (t, 1 H, ^4J = 1.3 Hz, 4-H), 6.92 (m, 2 H, 2,6-H), 3.91 (t, 2 H, ^3J = 6.4 Hz, α-CH_2), 1.73 (quintet, 2 H, $^3J \approx 7$ Hz, β-CH_2), 1.28-1.45 (m, 6 H, γ-, δ-, ε-CH_2), 1.10 (s, 21 H, TIPS-H), 0.89 (t, 3 H, ^3J = 6.7 Hz, hexyl-CH_3), 0.23 (s, 9 H, TMS-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 158.59, 127.93, 124.57, 124.11, 118.76, 117.77, 106.10, 104.21, 94.43, 90.87, 68.18, 31.52, 29.12, 25.66, 22.59, 18.65, 14.02, 11.28, -0.98. **MS** (**EI**, 80 eV, 270°C): m/z (%) = 457 (1.0), 456 (4.2), 455 (11.5), 454 (27.5), 453 (1.3) $[M]^+$, 440 (1.3), 439 (3.3) $[M\text{-}CH_3]^+$, 414 (3.2), 413 (13.8), 412 (38.5), 411 (100.0), 410 (2.4), 409 (1.1) $[M\text{-}C_3H_7]^+$, 385 (1.5), 384 (3.8), 383 (10.6), 382 (1.8) $[M\text{-}C_5H_{11}]^+$, 372 (1.2), 371 (2.1), 370 (4.8), 369 (13.7), 368 (1.1), 367 (1.2) $[M\text{-}C_6H_{13}]^+$. **High resolution MS**: calc.: 454.30872; found: 454.30642.

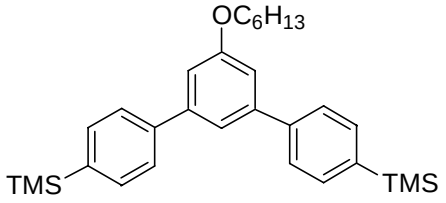
1-(Tetrahydropyran-2-yloxymethyl)-3-[(triisopropylsilyl)ethynyl]-5-[(trimethylsilyl)ethynyl]-benzene, $C_{28}H_{44}O_2Si_2$, M = 468.82, ***96b*** (Scheme 8)



The procedure was analogous to that described for **94** (**16b**: 27.16 g, 73.93 mmol; TIPS-acetylene: 20.2 g, 111 mmol; CuI: 422 mg, 2.22 mmol; $Pd[P(Ph_3)]_4$: 2.56 g, 2.22 mmol; 500 ml triethylamine, reaction time: 3 days; reaction temperature: 80°C). The solvent was evaporated, the residue was dissolved in dichloromethane (200 ml), washed with water (200 ml) and

the aqueous phase was extracted with dichloromethane (2 × 100 ml). The combined organic phases were dried over $MgSO_4$, the solvent was evaporated and the crude product purified by chromatography over silica gel (hexane/toluene) to afford **96b** (24.79 g, 52.90 mmol, 72 %) as a slightly yellow sirup. $\mathbf{R_f}$ = 0.74 (hexane/ethyl acetate 30:1) **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 7.47 (d, 1 H, 4J = 1.1 Hz, aryl-4-H), 7.38 (s, 2 H, aryl-2,6-H), 4.65-4.70 (m, 2 H, benzyl-H, THP-2-H), 4.40 (d, 1 H, ^{2}J = 12.3 Hz, benzyl-H'), 3.83-3.91 (m, 1 H, THP-6-H), 3.49-3.57 (m, 1 H, THP-6'-H), 1.50-1.83 (m, 6 H, THP-3,3',4,4',5,5'-H), 1.10 (s, 21 H, TIPS-H), 0.22 (s, 9 H, TMS-H). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 138.66, 134.42, 131.17, 130.97, 123.75, 123.34, 106.00, 104.08, 97.72, 94.77, 91.21, 67.79, 62.03, 30.42, 25.39, 19.23, 18.61, 11.24, -0.14. **MS** (**EI**, 80 eV, 120°C): m/z (%) = 470 (0.2), 469 (0.4), 468 (0.5), 467 (0.1) $[M]^+$, 456 (0.3), 455 (0.9), 454 (2.0), 453 (3.2), 452 (0.1) $[M\text{-}CH_3]^+$, 432 (0.1), 431 (0.2), 430 (0.7), 429 (1.6), 428 (9.8), 427 (15.7), 426 (40.5), 425 (100.0) $[M\text{-}C_3H_7]^+$, 370 (14.6), 369 (40.0), 368 (87.2), 367 (13.1) $[M\text{-}C_5H_8O_2]^+$, 342 (7.2), 341 (20.9) $[M\text{-}C_7H_{11}O_2]^+$, 326 (8.5), 325 (16.4) $[M\text{-}C_5H_8O_2\text{-}C_3H_7]^+$, 297 (13.7) $[M\text{-}C_7H_{11}O_2\text{-}C_3H_8]^+$, 284 (7.5), 283 (21.8) $[M\text{-}C_5H_8O_2\text{-}C_3H_7\text{-}C_3H_6]^+$, 271 (10.2), 270 (10.0), 269 (24.2), 268 (9.1) $[M\text{-}C_7H_{11}O_2\text{-}C_3H_8\text{–}C_2H_4]^+$, 257 (5.7), 256 (10.5), 255 (30.6), 254 (15.3) $[M\text{-}C_7H_{11}O_2\text{-}C_3H_8\text{-}C_3H_7]^+$. **EA**: Calc.: C:71.73, H:9.46; Found: C:71.54, H:9.74.

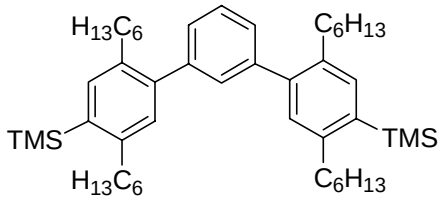
5'-Hexoxy-4,4''-bis(trimethylsilyl)-1,1':3',1''-terphenyl, $C_{30}H_{42}Si_2O$, M = 474.83, ***98a*** (Scheme 9)



A mixture of **91** (2.71 g, 8.10 mmol), **97a** (4.69 g, 24.2 mmol), toluene (100 ml) and 1 M aqueous sodium carbonate solution (100 ml) was degassed twice. After adding $Pd[P(Ph_3)]_4$ (374 mg, 0.32 mmol), the reaction mixture was degassed again and refluxed for 48 hrs under N_2. The phases were separated and the aqueous phase was extracted with toluene (2 × 100 ml). The combined organic fractions were dried over $MgSO_4$ and the solvent was removed in vacuo to give 6.5 g of a yellow sirup. Chromatographic separation through silica gel with hexane gave **98a** (3.29 g, 6.90 mmol, 86 %) as a slightly yellow sirup. $\mathbf{R_f}$ = 0.81 (hexane/ethyl acetate 40:1). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 7.61 (s, 8 H, 2,3,5,6,2'',3'',5'',6''-H), 7.39 (t, 1 H, ^{4}J = 1.3 Hz, 2'-H), 7.10 (d, 2 H, ^{4}J = 1.3 Hz, 4',6'-H), 4.06 (t, 2 H, ^{3}J = 6.5 Hz, α- CH_2), 1.83 (quintet, 2 H, ^{3}H ≈ 7 Hz, β- CH_2), 1.32-1.53 (m, 6 H, γ-, δ-, ε-CH_2), 0.90 (t, 3 H, ^{3}J = 6.9 Hz., hexyl-CH_3), 0.32 (s,

16 H, silyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 159.86, 143.03, 141.59, 139.54, 133.80, 126.60, 118.70, 112.44, 68.21, 31.60, 29.32, 25.77, 22.62, 14.04, -1.09. **MS** (**EI**, 80 eV, 180°C): m/z (%) = 477 (5.3), 476 (17.2), 475 (46.3), 474 (100.0), 473 (4.0) $[M]^+$, 462 (2.3), 461 (7.7), 460 (18.2), 459 (40.2), 458 (1.7), 457 (2.2) $[M\text{-}CH_3]^+$, 392 (1.7), 391 (3.8), 390 (8.4), 389 (2.2) $[M\text{-}C_6H_{12}]^+$, 378 (1.7), 377 (6.2), 376 (16.1), 375 (43.0), 374 (4.0), 373 (3.0) $[M\text{-}C_6H_{12}\text{-}CH_3]^+$, 73 (47.9) $[Si(CH_3)_3]^+$. **EA**: Calc.: C: 75.89, H: 8.92; Found: C: 75.89, H: 8.78.

2,5,2‘‘,5‘‘-Tetrahexyl-4,4‘‘-bis(trimethylsilyl)-1,1‘:3‘,1‘‘-terphenyl, $C_{48}H_{78}Si_2$, M = 711.31**,** ***98b*** (Scheme 9)



The procedure was analogous to that described for **98a** (**97b**: 15.15 g, 41.8 mmol; *m*-dibromobenzene: 2.0 ml, 16.7 mmol; $Pd[P(Ph_3)]_4$: 772 mg, 0.67 mmol; toluene/ 1 M aqueous Na_2CO_3: 250 ml/250 ml). The phases were separated and the aqueous phase was extracted with toluene (2 × 100 ml). The combined orange colored organic fractions were dried over $MgSO_4$ and the solvent was removed in vacuo to give 15.8 g of a dark oil. Chromatographic separation through silica gel with hexane gave **98b** (9.64 g, 13.6 mmol, 81 %) as a colorless sirup. $\mathbf{R_f}$ = 0.80 (hexane). **^{1}H-NMR** (270 MHz, $CDCl_3$): δ = 7.42 (t, 1 H, ^{3}J = 7.2 Hz, 5’-H), 7.37 (s, 2 H, 6,6’’-H), 7.29-7.31 (m, 3 H, 2’,4’,6’-H), 7.10 (s, 2 H, 3,3’’-H), 2.70 (t, 4 H, ^{3}J ≈ 8 Hz, α-CH_2), 2.61 (t, 4 H, ^{3}J ≈ 8 Hz, α-CH_2), 1.19-1.62 (m, 32 H, β-, γ-, δ-, ε-CH_2), 0.89 (t, 6 H, ^{3}J = 6.8 Hz, hexyl-CH_3), 0.82 (t, 6 H, ^{3}J = 6.8 Hz, hexyl-CH_3), 0.36 (s, 18 H, silyl-CH_3). **^{13}C-NMR** (67.9 MHz, $CDCl_3$): δ = 145.97, 142.42, 141.77, 136.62, 136.51, 135.66, 130.21, 130.02, 127.51, 36.01, 32.81, 32.60, 31.80, 31.55, 31.47, 29.74, 29.28, 22.62, 22.54, 14.05, 0.59. **MS** (**EI**, 80 eV, 200°C): m/z (%) = 714 (3.2), 713 (9.6), 711 (28.4), 710 (100.0), 708 (4.8) $[M]^+$, 697 (3.2), 696 (6.8), 695 (9.7), 693 (1.5) $[M\text{-}CH_3]^+$. **EA**: Calc.: C: 81.05, H: 11.05; Found: C: 81.01, H: 11.22.

Crystallographic Data

Table: Crystal data and structure refinement for **1a**, **1b** and **1d**.

	1a	**1b**	**1d**
Empirical formula	$C_{117}H_{115}N_3O_5$	$C_{117}H_{121}N_3O_5$	$C_{135}H_{149}N_3O_4$
Formula weight	1643.12	1649.17	1877.57
Temperature	143(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
Unit cell dimensions a	14.661(2) Å	14.493(4) Å	9.287(3) Å
b	14.909(2) Å	17.862(5) Å	22.591(7) Å
c	23.734(3) Å	20.589(6) Å	27.042(8) Å
α	107.173(2)°	97.097(7)°	101.705(7)°
β	105.122(2)°	100.914(7)°	93.268(8)°
γ	93.121(3)°	112.715(5)°	99.724(7)°
V	4735.9(9) $Å^3$	4712.13 $Å^3$	5451.02 $Å^3$
Z	2	2	2
Density (calculated)	1.152 Mg/m^3	1.162 Mg/m^3	1.144 Mg/m^3
Absorption coefficient μ	0.07 mm^{-1}	0.07 mm^{-1}	0.07 mm^{-1}
F(000)	1756	1768	2024
Crystal size	0.33×0.12×0.10 mm	0.52×0.41×0.13 mm	0.5×0. 2×0.05 mm
Theta range for data collection	$2\theta_{max}$ = 45°	$2\theta_{max}$ = 45°	$2\theta_{max}$ = 45°
Index ranges	-15≤h≤15, -16≤k≤15, -25≤l≤25	-15≤h≤15, -19≤k≤19, -22≤l≤22	-9≤h≤9, -24≤k≤23, -29≤l≤29
Reflections collected	36482	31122	43770
Independent reflections	12205 [R_{int} = 0.10]	12331 [R_{int} = 0.171]	14211 [R_{int} = 0.17]
Completeness to Θ_{max}	98.7 %	99.9 %	99.9 %
Absorption correction	none	none	none
Max. and min. transmission	-	-	-
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	12205 / 1164 / 1084	12331 / 981 / 343	14211 / 1306/1210
Goodness-of-fit on F^2	1.072	1.452	1.20
Final R indices [I>2sigma(I)]	R_1 = 0.0839, wR_2 = 0.2465	R_1 = 0.127, wR_2 = 0.246	R_1 = 0.113, wR_2 = 0.271
R indices (all data)	R_1 = 0.1617, wR_2 = 0.2869	R_1 = 0.314, wR_2 = 0.275	R_1 = 0.262, wR_2 = 0.317
Largest diff. peak and hole	0.86 and –0.48 e.$Å^{-3}$	0.33 and –0.28 e.$Å^{-3}$	0.68 and –0.51 e.$Å^{-3}$