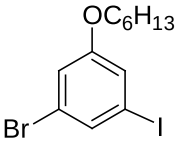
7.2 Syntheses

Compounds **34a**,[31] **34c**,[31] **35**,[31] **36**,[31] **37a**,[31] **37b** (with benzene replaced by toluene),[112] **38a**,[30] **38c**,[30] **42a**,[32] **43a**,[31] **44a**,[32] **45a**,[32] **50**,[29] **52**,[125] **53**,[27] **54**,[131] **55**,[27] **56**,[27] **57**,[27] **58**,[30] **59**,[31] **64**,[125] **65**,[125] **68**,[27] **71**,[69] **72**,[69] **75**,[137] **76**,[137] **77**,[67] **78**,[67] **96**,[28] **98**,[31] **107**,[70] **108**,[70] **114**,[175] and **115**[176] were prepared according to literature procedures. I am grateful to F. Kutzner for providing **108**.

7.2.1 Compounds of Chapter 4.3

*1-Bromo-3-hexoxy-5-iodobenzene **34b***

$C_{12}H_{16}BrIO$, M = 383. 07



To a solution of **39** (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 **34b** (46.4 g, 121 mmol, 97 %) as a colorless sirup.

R_f = 0.50 (hexane).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.39 (t, 1 H, ^4J = 1.4 Hz, aryl-H), 7.15 (dd, 1 H, ^4J = 1.5 Hz, ^4J = 2.2 Hz, aryl-H), 6.98 (t, 1 H, ^4J = 2.0 Hz, aryl-H), 3.87 (t, 2 H, ^3J = 6.5 Hz, α-CH_2), 1.73 (quintet, 2 H, ^3H ≈ 7 Hz, β-CH_2), 1.30-1.33 (m, 6 H, γ-, δ-, ε-CH_2), 0.90 (t, 3 H, ^3J = 6.6 Hz, -CH_3).

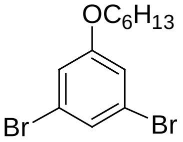
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 160.07, 131.68, 123.04, 122.70, 117.54, 94.18, 68.49, 31.44, 28.94, 25.56, 22.55, 14.01.

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) $[M-C_5H_{11}]^+$, 302 (0.7), 301 (7.5), 300 (97.7), 299 (8.9), 298 (100) $[M-C_6H_{12}]^+$, 284 (0.5), 283 (5.9), 282 (0.7), 281 (5.9) $[M-C_5H_{11}–CH_2O]^+$, 271 (2.2), 270 (0.3), 269 (2.2) $[M-C_6H_{12}–CHO]^+$.

HRMS:	Calc.:	381.94293
	Found:	381.94565.

1,3-Dibromo-5-hexoxybenzene ***38b***

$C_{12}H_{16}Br_2O$, M = 336.07



A mixture of **37b**[112] (45.07 g, 179 mmol), *n*-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 down, 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 **38b** as a colorless liquid (58.39 g, 174 mmol, 97 %).

R_f = 0.79 (hexane).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.20 (t, 1 H, ^3J = 1.5 Hz, 4-H), 6.96 (d, 2 H, ^3J = 1.6 Hz, 2,6-H), 3.89 (t, 2 H, ^3J = 6.5 Hz, α-CH_2), 1.74 (quintet, 2 H, $^3H \approx 7$ Hz, β-CH_2), 1.28-1.42 (m, 6 H, γ-, δ-, ε-CH_2), 0.89 (t, 3 H, ^3J = 6.7 Hz, -CH_3).

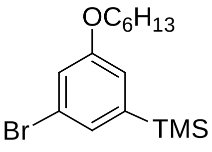
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 160.36, 126.12, 123.03, 116.91, 68.61, 31.45, 28.93, 25.56, 22.54, 13.98.

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 ***39***

$C_{15}H_{25}BrOSi$, M = 329.35



To a solution of **38b** (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 phase 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 **39** (51.35 g, 156 mmol, 90 %) as a colorless oil.

R_f = 0.45 (hexane).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.16 (t, 1 H, ^4J = 1.0 Hz, aryl-H), 7.00 (t, 1 H, ^4J = 2.0 Hz, aryl-H), 6.94 (dd, 1 H, ^4J = 0.8 Hz, ^4J = 2.4 Hz, aryl-H), 3.92 (t, 2 H, ^3J = 6.5 Hz, α-CH_2), 1.74-1.77 (quintet, 2 H, ^3H ≈ 7 Hz, β-CH_2), 1.31-1.35 (m, 6 H, γ-, δ-, ε-CH_2), 0.90 (t, 3 H, ^3J = 6.9 Hz, hexyl-CH_3), 0.25 (s, 9 H, silyl-CH_3).

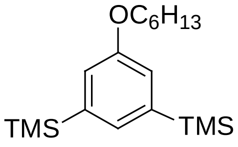
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 159.38, 144.34, 127.84, 123.01, 118.55, 117.37, 68.15, 31.55, 29.16, 25.68, 22.58, 14.01, -1.29.

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 ***40***

$C_{18}H_{34}OSi_2$, M = 322.64



40 was isolated as a side product from one batch of synthesis of **39** (**38b**: 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: **39**: 59.53 g, 181 mmol, 80 %; **40**: 8.30 g; 25.7 mmol, 11 %; as colorless oils).

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, ^4J = 0.8 Hz, 2,6-H), 4.05 (t, 2 H, ^3J = 6.5 Hz, α-CH_2), 1.86 (quintet, 2 H, ^3H ≈ 7 Hz, β-CH_2), 1.38-1.58 (m, 6 H, γ-, δ-, ε-CH_2), 0.98 (t, 3 H, ^3J = 7.1 Hz, hexyl-CH_3), 0.34 (s, 18 H, silyl-CH_3).

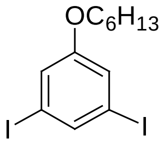
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 157.98, 141.25, 130.20, 119.68, 67.70, 31.65, 29.44, 25.81, 22.62, 14.02, -1.10.

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 ***41***

$C_{12}H_{16}I_2O$, M = 430.07



The procedure was analogous to that described for **34b** (**40**: 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 **41** (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, ^4J = 1.3 Hz, 4,6-H), 3.86 (t, 2 H, ^3J = 6.5 Hz, α-CH_2), 1.72 (quintet, 2 H, $^3H \approx 7$ Hz, β-CH_2), 1.27-1.43 (m, 6 H, γ-, δ-, ε-CH_2), 0.89 (t, 3 H, ^3J = 6.6 Hz, -CH_3).

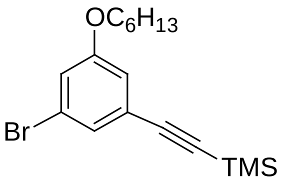
^{13}**C-NMR** (67.9 MHz, $CDCl_3$): δ = 159.93, 137.26, 123.43, 94.55, 68.49, 31.46, 28.96, 25.57, 22.55, 13.99.

MS (**EI**, 80 eV, 90°C): m/z (%) = 432 (0.8), 431 (9.7), 430 (77.2) $[M]^+$, 359 (1.2) $[M-C_5H_{11}]^+$, 347 (6.7), 346 (100.0) $[M-C_6H_{12}]^+$, 329 (3.9) $[M-C_5H_{11}–CH_2O]^+$.

EA:	Calc.:	C: 33.51	H: 3.75
	Found:	C: 33.41	H: 3.74.

1-Bromo-3-hexoxy-5-[(trimethylsilyl)ethynyl]benzene ***42b***

$C_{17}H_{25}BrOSi$, M = 353.37



Under N_2, to a degassed solution of **34b** (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 very 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 **42b** (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, ^4J = 1.4 Hz, aryl-H), 6.99 (t, 1 H, ^4J = 2.1 Hz, aryl-H), 6.89 (dd, 1 H, ^4J = 1.3 Hz, ^4J = 2.2 Hz, aryl-H), 3.88 (t, 2 H, ^3J = 6.5 Hz, α-CH_2), 1.73 (quintet, 2 H, $^3H \approx 7$ Hz, β-CH_2), 1.30-1.42 (m, 6 H, γ-, δ-, ε-CH_2), 0.90 (t, 3 H, ^3J = 6.6 Hz, -CH_3), 0.24 (s, 9 H, silyl-H).

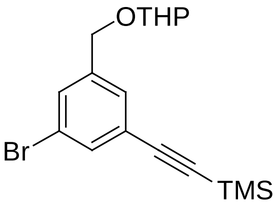
^{13}**C-NMR** (67.9 MHz, $CDCl_3$): δ = 159.34, 126.86, 125.36, 122.29, 118.76, 116.30, 103.37, 95.29, 68.30, 31.47, 28.99, 25.59, 22.57, 14.02, -0.17.

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 ***42c***

$C_{17}H_{23}BrO_2Si$, M = 253.21



The procedure was analogous to that described for **42b** (**34c**:[31] 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 **42c** (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) $[M\text{-}CH_3]^+$, 300 (0.6), 299 (0.5), 298 (1.5), 297 (7.2), 296 (1.7), 295 (7.5) $[M\text{-}C_4H_7O]^+$, 270 (7.4), 269 (31.6), 268 (89.6), 267 (96.8), 266 (86.3), 265 (71.0) $[M\text{-}C_5H_8O_2]^+/[M\text{-}C_5H_9O_2]^+$, 254 (11.8), 253 (24.9), 252 (37.1), 251 (24.4), 250 (28.2) $[M\text{-}C_5H_8O_2\text{-}CH_3]^+/[M\text{-}C_5H_9O_2\text{-}CH_3]^+$.

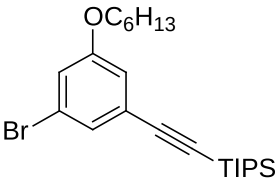
EA: Calc.: C:55.58 H:6.31
Found: C:55.61 H:6.07.

1-Bromo-3-hexoxy-5-[(triisopropylsilyl)ethynyl]benzene ***43b***

$C_{23}H_{37}BrOSi$, M = 437.53

A solution of **34b**[31] (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 **43b** (42.0 g, 96.0 mmol, 79 %) as a slightly yellow oil.

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$_3$).

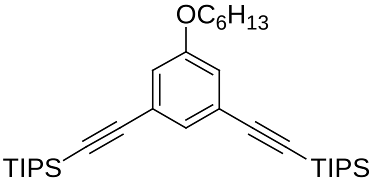
^{13}C-NMR (67.9 MHz, CDCl$_3$): δ = 159.46, 126.96, 125.80, 122.32, 118.30, 116.77, 105.38, 91.84, 68.35, 31.52, 29.06, 25.64, 22.59, 18.63, 14.02, 11.26.

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-C$_3$H$_7$]$^+$, 369 (1.1), 368 (3.9), 367 (16.0), 366 (4.3), 365 (15.7) [M-C$_5$H$_{11}$]$^+$, 357 (0.8), 356 (1.0), 355 (1.9), 354 (5.1), 353 (19.0), 352 (5.2), 351 (18.8) [M-C$_6$H$_{13}$]$^+$, 342 (1.1), 341 (3.1), 340 (5.3), 339 (20.1), 338 (4.8), 337 (18.2) [M-C$_6$H$_{12}$-CH$_3$]$^+$, 327 (1.6), 326 (5.3), 325 (24.4), 324 (5.6), 323 (23.1) [M-C$_5$H$_{11}$-C$_3$H$_6$]$^+$.

HRMS:	Calc.: 436.17971 [M]$^+$	Calc.: 393.12493 [M – C$_3$H$_7$]$^+$
	Found: 436.17733	Found: 393.12722.

*1-Hexyloxy-3,5-bis[(triisopropylsilyl)ethynyl]benzene **43x***

C$_{34}$H$_{58}$OSi$_2$, M = 539.00



This compound was isolated as a side product from the column chromatography of **43b** (110 mg, 0.20 mmol, 0.2 %) as a colorless oil.

R$_f$ = 0.31 (hexane)

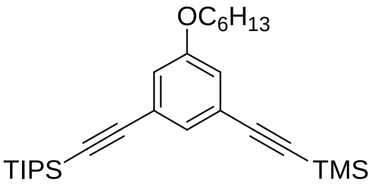
^{1}H-NMR (270 MHz, CDCl$_3$): δ = 7.14 (t, 1 H, ^{4}J = 1.4 Hz, 4-H), 6.93 (d, 2 H, ^{4}J = 1.4 Hz, 2,6-H), 3.93 (t, 2 H, ^{3}J = 6.5 Hz, α-CH$_2$), 1.75 (quintet, 2 H, ^{3}J ≈ 7 Hz, β-CH$_2$), 1.29-1.47 (m, 6 H, γ-, δ-, ε-CH$_2$), 1.12 (s, 42 H, silyl-H), 0.90 (t, 3 H, ^{3}J = 6.8 Hz, hexyl-CH$_3$).

^{13}C-NMR (67.9 MHz, CDCl$_3$): δ = 158.58, 127.78, 124.55, 118.30, 106.17, 90.85, 68.16, 31.56, 29.17, 25.69, 22.60, 18.66, 14.03, 11.30.

MS (**EI**, 80 eV, 130°C): m/z (%) = 541 (1.0), 540 (3.9), 539 (10.4), 538 (21.8) $[M]^+$, 499 (0.8), 498 (4.0), 497 (16.0), 496 (43.1), 495 (100.0) $[M-C_3H_7]^+$, 469 (1.2), 468 (3.0), 467 (7.0) $[M-C_5H_{11}]^+$, 457 (0.9), 456 (1.7), 455 (2.7), 454 (4.2), 453 (9.5) $[M-C_6H_{13}]^+$.

1-Hexyloxy-3-[(triisopropylsilyl)ethynyl]-5-[(trimethylsilyl)ethynyl]benzene ***44b***

$C_{28}H_{46}Si_2O$, M = 454.84



Method A:

The procedure was analogous to that described for **43b** (**42b**: 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 **44b** (17.64 g, 38.78 mmol, 84 %) as a slightly yellow oil.

Method B:

The procedure was analogous to that described for **42b** (**43b**: 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 **44b** (39.74 g, 87.4 mmol, 91 %) as a slightly yellow oil.

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).

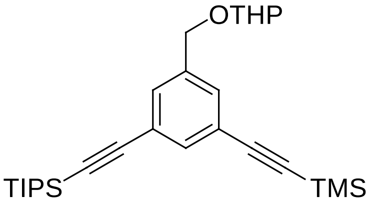
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 158.59, 127.93, 124.57, 124.11, 118.76, 117.77, 106.10, 104.21, 94.43, 90.87, 68.18, 31.52, 29.12, 25.66, 22.59, 18.65, 14.02, 11.28, -0.98.

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) $[M-CH_3]^+$, 414 (3.2), 413 (13.8), 412 (38.5), 411 (100.0), 410 (2.4), 409 (1.1) $[M-C_3H_7]^+$, 385 (1.5), 384 (3.8), 383 (10.6), 382 (1.8) $[M-C_5H_{11}]^+$, 372 (1.2), 371 (2.1), 370 (4.8), 369 (13.7), 368 (1.1), 367 (1.2) $[M-C_6H_{13}]^+$.

High resolution MS: calc.: 454.30872
found: 454.30642.

1-(Tetrahydropyran-2-yloxymethyl)-3-[(triisopropylsilyl)ethynyl]-5-[(trimethylsilyl)ethynyl]-benzene ***44c***

$C_{28}H_{44}O_2Si_2$, M = 468.82



The procedure was analogous to that described for **43b** (**42c**: 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 **44c** (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, ^2J = 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) $[M-CH_3]^+$, 432 (0.1), 431 (0.2), 430 (0.7), 429 (1.6), 428 (9.8), 427 (15.7), 426 (40.5), 425 (100.0) $[M-C_3H_7]^+$, 370 (14.6), 369 (40.0), 368 (87.2), 367 (13.1) $[M-C_5H_8O_2]^+$, 342 (7.2), 341 (20.9) $[M-C_7H_{11}O_2]^+$, 326 (8.5), 325 (16.4) $[M-C_5H_8O_2-C_3H_7]^+$, 297 (13.7) $[M-C_7H_{11}O_2-C_3H_8]^+$, 284 (7.5), 283 (21.8) $[M-C_5H_8O_2-C_3H_7-C_3H_6]^+$, 271 (10.2), 270 (10.0), 269 (24.2), 268 (9.1) $[M-C_7H_{11}O_2-C_3H_8–C_2H_4]^+$, 257 (5.7), 256 (10.5), 255 (30.6), 254 (15.3) $[M-C_7H_{11}O_2-C_3H_8-C_3H_7]^+$.

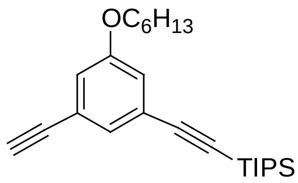
Microanalysis	Calc.:	C:71.73	H:9.46
	Found:	C:71.54	H:9.74.

1-Ethynyl-3-hexoxy-5-[(triisopropylsilyl)ethynyl]benzene ***45b***

$C_{25}H_{38}SiO$, M = 382.66

44b (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 **45b** (23.56 g, 61.57 mmol, 99 %) as a slightly yellow oil.

R_f = 0.34 (hexane)



^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.17 (d, 1 H, ^4J = 1.2 Hz, 4-H), 6.94-6.97 (m, 2 H, 2,6-H), 3.91 (t, 2 H, ^3J = 6.4 Hz, α-CH_2), 3.03 (s, 1 H, ethynyl-H), 1.74 (quintet, 2 H, $^3J \approx$ 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, ^3J = 7.0 Hz, hexyl-CH_3).

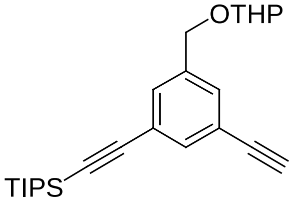
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 158.64, 128.07, 124.70, 123.10, 118.81, 118.11, 105.95, 91.13, 82.83, 77.31, 68.20, 31.52, 29.10, 25.65, 22.58, 18.63, 14.01, 11.26.

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) $[M-C_3H_7]^+$, 312 (3.8), 311 (12.5), $[M-C_5H_{11}]^+$, 299 (1.4), 298 (4.5), 297 (16.8) $[M-C_6H_{13}]^+$, 285 (2.5), 284 (5.1), 283 (19.2) $[M-C_5H_{11}-C_2H_4]^+$, 271 (1.7), 270 (6.0), 269 (24.8) $[M-C_6H_{13}-C_2H_4]^+$.

Microanalysis	Calc.:	C:78.47	H:10.01
	Found:	C:78.19	H: 9.89.

1-Ethynyl-3-(tetrahydropyran-2-yloxymethyl)-5-[(triisopropylsilyl)ethynyl]benzene ***45c***

$C_{25}H_{36}O_2Si$, M = 396.64



The procedure was analogous to that described for **45b** (**44c**: 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 **45c** (20.30 g, 51.18 mmol, 98 %) as a yellow sirup.

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, ^2J = 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).

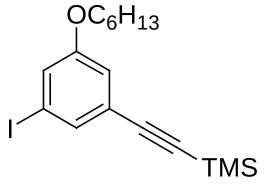
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 138.85, 134.56, 131.36, 131.02, 123.84, 122.34, 105.84, 97.77, 91.46, 82.70, 77.68, 67.70, 62.02, 30.40, 25.37, 19.21, 18.59, 11.22.

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.

1-Hexoxy-3-iodo-5-[(trimethylsilyl)ethynyl]benzene ***46***

$C_{17}H_{25}IOSi$, M = 400.37



The procedure was analogous to that described for **42b** (**41**: 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 **46** (2.70 g, 6.74 mmol, 56 %) as a slightly yellow oil.

R

R_f = 0.36 (hexane).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.37 (t, 1 H, ^4J = 0.7 Hz, aryl-H), 7.19 (t, 1 H, ^4J = 1.0 Hz, aryl-H), 6.91 (t, 1 H, ^4J = 1.1 Hz, aryl-H), 3.88 (t, 2 H, ^3J = 6.5 Hz, α-CH_2), 1.73 (quintet, 2 H, $^3H \approx 7$ Hz, β-CH_2), 1.28-1.57 (m, 6 H, γ-, δ-, ε-CH_2), 0.89 (t, 3 H, ^3J = 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) $[M-CH_3]^+$, 329 (2.7), 328 (15.2) $[M-C_5H_{12}]^+$, 318 (1.8), 317 (6.1), 316 (33.0) $[M-C_6H_{13}]^+$, 304 (1.6), 303 (5.5), 302 (18.7), 301 (91.5), 300 (2.8), 299 (1.0) $[M-C_6H_{12}-CH_3]^+$.

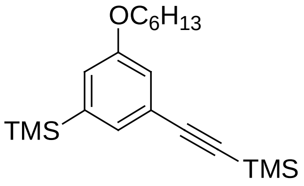
EA:	Calc.:	C:51.00	H:6.29
	Found:	C:51.07	H:6.06.

1-Hexoxy-3-trimethylsilyl-5-[(trimethylsilyl)ethynyl]benzene ***47***

$C_{20}H_{34}Si_2O$, M = 346.66

The procedure was analogous to that described for **42b** (**39**: 15.0 g, 45.5 mmol; TMS-acetylene: 5.37 g, 54.7 mmol; CuI: 260 mg, 1.37 mmol; $[Pd(PPh_3)_4]$: 1.58 g, 1.37 mmol; triethylamine: 100 ml; reaction time: 3 days). The crude product was purified by column chromatography (hexane) to afford **47** (15.16 g, 43.7 mmol, 96 %) as a colorless oil.

R_f = 0.17 (hexane) / 0.63 (hexane/ethyl acetate 40:1).



^{1}H-NMR (270 MHz, CDCl$_3$): δ = 7.19 (s, 1 H, phenyl-H), 7.00 (d, 1 H, ^{4}J = 2.4 Hz, phenyl-H), 6.95 (t, 1 H, ^{4}J = 2.3 Hz, phenyl-H), 3.94 t, 2 H, ^{3}J = 6.6 Hz, α-CH$_2$), 1.77 (quintet, 2 H, ^{3}J ≈ 7 Hz, β-CH$_2$), 1.30-1.46 (m, 6 H, γ-, δ-, ε-CH$_2$), 0.91 (t, 3 H, ^{3}J = 6.7 Hz, hexyl-CH$_3$), 0.25 (s, 18 H, silyl-CH$_3$).

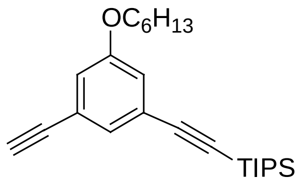
^{13}C-NMR (67.9 MHz, CDCl$_3$): δ = 158.13, 142.18, 129.11, 123.53, 120.92, 116.87, 105.46, 93.56, 67.90, 31.57, 29.25, 25.72, 22.60, 14.03, 0.01, -1.26.

MS (**EI**, 80 eV, 30°C): m/z (%) = 348 (12.0), 347 (31.6), 346 (100.0) [M]$^+$, 333 (6.2), 332 (18.3), 331 (58.4) [M-CH$_3$]$^+$.

HRMS:	Calc.:	346.21462
	Found:	346.21371.

1-Ethynyl-3-hexoxy-5-(triisopropylsilyl)benzene ***48***

$C_{17}H_{26}SiO$, M = 274.48



The procedure was analogous to that described for **45b** (**47**: 5.37 g, 15.49 mmol; methanol: 50 ml; dichloromethane: 20 ml). The crude product was purified by chromatography over silica gel (hexane) to afford **48** (4.17 g, 15.2 mmol, 98 %) as a slightly yellow oil.

R$_f$ = 0.25 (hexane).

^{1}H-NMR (270 MHz, CDCl$_3$): δ = 7.24 (s, 1 H, phenyl-H), 7.06 (d, 1 H, ^{4}J = 2.3 Hz, phenyl-H), 7.00 (dd, 1 H, ^{4}J = 1.3 Hz, ^{4}J = 2.4 Hz, phenyl-H), 3.96 (t, 2 H, ^{3}J = 6.6 Hz, α-CH$_2$), 3.06 (s, 1 H, ethynyl-H), 1.79 (quintet, 2 H, ^{3}J ≈ 7 Hz, β-CH$_2$), 1.32-1.50 (m, 6 H, γ-, δ-, ε-CH$_2$), 0.92 (t, 3 H, ^{3}J = 6.7 Hz, hexyl-CH$_3$), 0.27 Hz (s, 9 H, silyl-CH$_3$).

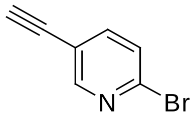
^{13}C-NMR (67.9 MHz, CDCl$_3$): δ = 158.21, 142.38, 129.24, 122.56, 120.98, 117.21, 83.98, 76.69, 67.93, 31.57, 29.22, 25.71, 22.58, 14.01, -1.31.

MS (**EI**, 80 eV, 20°C): m/z (%) = 276 (6.7), 275 (28.5), 274 (97.3) [M]$^+$, 261 (5.4), 260 (21.2), 259 (67.5) [M-CH$_3$]$^+$, 191 (7.0), 190 (37.8) [M-C$_6$H$_{12}$]$^+$, 177 (7.9), 176 (24.2), 175 (100.0), 174 (5.1), 173 (5.3) [M-C$_6$H$_{12}$-CH$_3$]$^+$.

EA:	Calc.:	C:74.39	H:9.55
	Found:	C:74.31	H:9.35.

2-Bromo-5-ethynylpyridine ***60***

C_7H_4BrN, M = 182.08



The procedure was analogous to that described for **42b**.(**59**:[31] 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 **60** (11.8 g, 65.2 mmol, 81 %) as a sandy colored, crystalline solid, m.p. = 83°C. The side product **60x** (140 mg, 1.10 mmol, 1 %) was isolated as brownish solid.

R$_f$ = 0.29 (hexane/ethyl acetate 30:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.41 (d, 1 H, ^4J = 2.2 Hz, 6-H), 7.55 (dd, 1 H, ^3J = 8.1 Hz, ^4J = 2.2 Hz, 4-H), 7.41 (d, 1 H, ^3J = 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) $[M-Br]^+$.

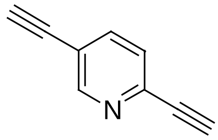
EA:	Calc.:	C:46.18	H:2.21	N:7.69
	Found:	C:46.18	H:2.27	N:7.55.

2,5-Diethynylpyridine ***60x***

C_9H_5N, M = 127.15

60x was isolated as a a side product from the synthesis of **60**.

R$_f$ = 0.12 (hexane/ethyl acetate 30:1).



^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.65 (s, 1 H, 6-H), 7.71 (dd, 1 H, ^3J = 8.2 Hz, ^4J = 1.9 Hz, 4-H), 7.40 (d, 1 H, ^3J = 8.1 Hz, 3-H), 3.28 (s, 1 H, ethynyl-H), 3.23 (s, 1 H, ethynyl-H).

^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 152.73, 141.32, 139.02, 126.55, 118.84, 82.40, 82.16, 79.79, 79.10.

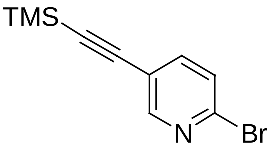
MS (**EI**, 80 eV, 40°C): m/z (%) = 130 (1.2), 129 (1.0), 128 (13.4), 127 (100.0), 126 (1.9) $[M]^+$.

2-Bromo-5-[(trimethylsilyl)ethynyl]pyridine ***61***

$C_{10}H_{12}BrNSi$, M = 254.20

The procedure was analogous to that described for **42b** (**59**[31]: 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 **61** 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).

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).

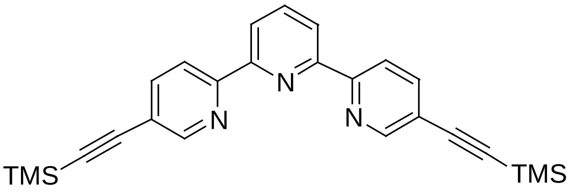
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 152.64, 141.10, 140.83, 127.40, 119.43, 99.97, 99.82, -0.37.

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 ***62***

$C_{25}H_{27}N_3Si_2$, M = 425.68



A solution of **52**[125] (7.0 g, 17.3 mmol) and **61** (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 **62** (5.12 g, 12.0 mmol, 70 %) as a colorless solid, m.p. = 215°C.

R_f = 0.70 (hexane/ethyl acetate 4:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.73 (dd, 2 H, ^4J = 2.0 Hz, ^5J = 0.8 Hz, 6,6’’-H), 8.52 (dd, 2 H, ^3J = 8.3 Hz, ^4J = 0.7 Hz, 3,3’’-H), 8.41 (d, 2 H, ^3J = 7.8 Hz, 3’,5’-H), 7.91 (t, 1 H, ^3J = 8.0 Hz, 4’-H), 7.87 (dd, 2 H, ^3J = 8.3 Hz , ^4J = 2.0 Hz, 4,4’’-H), 0.28 (s, 18 H, silyl-CH_3).

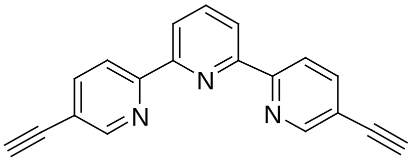
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 154.78, 154.65, 152.01, 139.64, 137.92, 121.55, 120.16, 101.83, 99.17, -0.16.

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 **63***

$C_{19}H_{11}N_3$, M = 281.32



A solution of **62** (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 **63** (2.32 g, 8.25 mmol, 90 %) as slightly yellow crystals (decomposition at 165-168°C).

R_f = 0.23 (hexane/ethyl acetate 4:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.76 (d, 2 H, ^4J = 2.0 Hz, 6,6''-H), 8.54 (d, 2 H, ^3J = 8.3 Hz, 3,3''-H), 8.43 (d, 2 H, ^3J = 7.8 Hz, 3',5'-H), 7.92 (t, 1 H, ^3J = 7.9 Hz, 4'-H), 7.87 (dd, 2 H, ^3J = 8.2 Hz , ^4J = 2.1 Hz, 4,4''-H), 3.29 (s, 2 H, ethynyl-H).

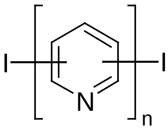
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 155.22, 154.55, 152.14, 139.88, 137.97, 121.62, 120.24, 119.14, 81.35, 80.69.

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.

*Attempt to 5,5''-Diiodo-2,2':6',2''-terpyridine **67$_3$***

$C_{15}H_9I_2N_3$, M = 485.07



A solution of **52**[125] (3.06 g, 7.56 mmol) and **65**[125] (5.00 g, 15.1 mmol) in dry toluene (50 ml) was degassed. After addition of $Pd[P(Ph_3)]_4$ (350 mg, 0.30 mmol), it was degassed again, then refluxed for 72 hrs under nitrogen. The precipitate was filtered and washed with toluene. It was found to be insoluble in comon organic solvents, but only in hot DMSO or pyridine. Analysis by EI-mass spectrometry revealed a mixture of different iodo functionalized oligopyridines **67$_n$**.

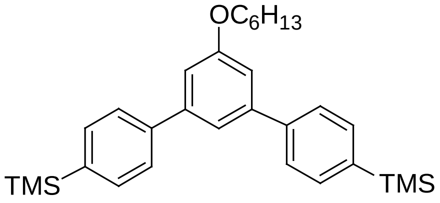
HRMS:

n = 3:	**n** = 4:	**n** = 5:
Calc.: 454.30872	Calc.: 561.91515	Calc.: 638.94170
Found: 454.30642	Found: 561.91723	Found: 638.94433

n = 6:	**n** = 7:
Calc.: 715.96825	Calc.: 792.99450
Found: 715.96570	Found: 792.99731.

5‘-Hexoxy-4,4‘‘-bis(trimethylsilyl)-1,1‘:3‘,1‘‘-terphenyl ***73a***

$C_{30}H_{42}Si_2O$, M = 474.83



A mixture of **38b** (2.71 g, 8.10 mmol), **72**[69] (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 **73a** (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, ^4J = 1.3 Hz, 2’-H), 7.10 (d, 2 H, ^4J = 1.3 Hz, 4’,6’-H), 4.06 (t, 2 H, ^3J = 6.5 Hz, α- CH_2), 1.83 (quintet, 2 H, $^3H \approx 7$ Hz, β- CH_2), 1.32-1.53 (m, 6 H, γ-, δ-, ε-CH_2), 0.90 (t, 3 H, ^3J = 6.9 Hz., hexyl-CH_3), 0.32 (s, 16 H, silyl-CH_3).

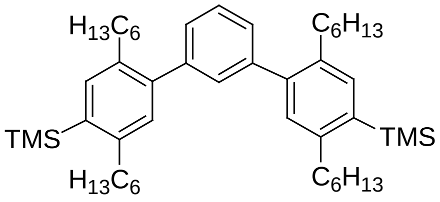
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 159.86, 143.03, 141.59, 139.54, 133.80, 126.60, 118.70, 112.44, 68.21, 31.60, 29.32, 25.77, 22.62, 14.04, -1.09.

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) $[M-CH_3]^+$, 392 (1.7), 391 (3.8), 390 (8.4), 389 (2.2) $[M-C_6H_{12}]^+$, 378 (1.7), 377 (6.2), 376 (16.1), 375 (43.0), 374 (4.0), 373 (3.0) $[M-C_6H_{12}-CH_3]^+$, 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 **73b***

$C_{48}H_{78}Si_2$, M = 711.31



The procedure was analogous to that described for **73a** (**78**[67]: 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 **73b** (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, ^3J = 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, ^3J ≈ 8 Hz, α-CH_2), 2.61 (t, 4 H, ^3J ≈ 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).

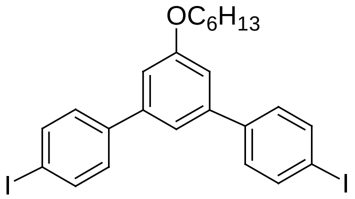
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 145.97, 142.42, 141.77, 136.62, 136.51, 135.66, 130.21, 130.02, 127.51, 36.01, 32.81, 32.60, 31.80, 31.55, 31.47, 29.74, 29.28, 22.62, 22.54, 14.05, 0.59.

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) $[M-CH_3]^+$.

EA:	Calc.:	C: 81.05	H: 11.05
	Found:	C: 81.01	H: 11.22.

*4,4''-Diiodo-5'-hexoxy-1,1':3',1''-terphenyl **74a***

$C_{24}H_{24}I_2O$, M = 582.26



The procedure was analogous to that described for **34b** (**73a**: 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 **41** (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, ^3J = 8.2 Hz, 3,5,3’’,5’’-H), 7.33 (d, 4 H, ^3J = 8.2 Hz, 2,6,2’’,6’’-H), 7.25 (t, 1 H, ^4J = 1.4 Hz, 2’-H), 7.04 (d, 2 H, ^4J = 1.4 Hz, 4’,6’-H), 4.04 (t, 2 H, ^3J = 6.6 Hz, α- CH_2), 1.81 (quintet, 2 H, ^3H ≈ 7 Hz, β- CH_2), 1.31-1.55 (m, 6 H, γ-, δ-, ε-CH_2), 0.89 (t, 3 H, ^3J ≈ 7 Hz., -CH_3).

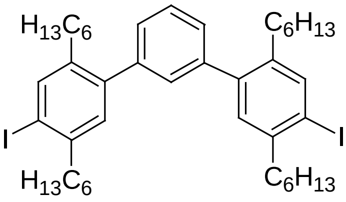
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 160.01, 142.03, 140.40, 137.81, 129.02, 117.94, 112.36, 93.37, 68.23, 31.55, 29.24, 25.72, 22.58, 14.03, 1.00.

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 ***74b***

$C_{42}H_{60}I_2$, M = 818.75



The procedure was analogous to that described for **34b** (**73b**: 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 **74b** (5.08 g, 6.20 mmol, 89 %) as a colorless sirup.

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, ^3J ≈ 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 ≈ 8 Hz, α-CH_2), 2.61 (t, 4 H, ^3J ≈ 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.