Synthesis of Regioselectively Functionalized Pyrenes via Transition-Metal-Catalyzed Electrocyclization

D. Barney Walker, Joshua Howgego, Anthony P. Davis*

School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK
Fax +44(117)9298611; E-mail: Anthony.Davis@bristol.ac.uk

Received 14 July 2010

Abstract: Transition-metal-catalyzed electrocyclic rearrangement of 2,6-diethynyl-1,1′-biphenyl precursors to form polysubstituted pyrenes is described. This method is useful for the preparation of pyrenes with uncommon substitution patterns, and selective integration of functional groups at the 1-, 2-, 3-, 5-, 7- and 9-positions is demonstrated.

Key words: pyrene, electrocyclic reactions, arenes, rearrangements, alkynes

Pyrene and its derivatives are well known to be efficient fluorophores[1] and have been extensively investigated as key components of biological probes,[2] liquid crystals,[3] and chemosensors.[4] In addition, the extended planar π-system of pyrene makes it useful for noncovalent functionalization of carbon nanotubes.[5] Our own interest in pyrene scaffolds was prompted whilst investigating large aromatic surfaces as supramolecular building blocks. Pyrenes seemed promising components, but they suffered from a lack of methods for controlled and regioselective functionalization. We therefore investigated alternative protocols for their assembly. Here, we describe a convenient method for the selective synthesis of polysubstituted pyrene rings based on electrocyclic isomerization of 2,6-diethynyl-1,1′-biphenyl precursors.

Typically, pyrene is functionalized via electrophilic aromatic substitution, yielding products substituted almost exclusively at the 1-, 3-, 6-, and 8-positions (Figure 1).[6] Whilst direct substitution at the 2- and 7-positions is limited to bulky electrophiles,[7] the preparation of 2,7-disubstituted pyrenes has been achieved previously by valence isomerization–dehydrogenation of *m*-cyclophanes,[8] photochemical cyclization of 2,2′-divinylbiphenyls,[9] thermal annulation of labile 2,2′-disubstituted dithiobenzoylbiphenyls,[10] and aromatization of substituted 4,5,9,10-tetrahydropyrenes.[11] These elegant methods have provided access to some elaborate pyrene-based molecular architectures.[12] However, our purposes required a method that allowed the selective introduction of sensitive functionality in a fashion that differentiated between the two ends of the pyrene system (Figure 1). For this reason we sought to build on the work of Swager,[13] Larock,[14] and Fürstner[15] in fusing polycyclic aromatics via electrocyclization of ethynyl-1,1′-biphenyl systems. In particular, Fürstner has demonstrated a versatile route to substituted phenanthrenes using transition-metal catalysts to activate the terminal alkyne for subsequent cyclization (Scheme 1). These methodologies have been employed by others to prepare complex polycyclic aromatic systems[16] but have not been applied to pyrene synthesis. We envisaged that a route to substituted pyrenes based on this chemistry would allow facile access to derivatives selectively substituted in almost all the available positions.

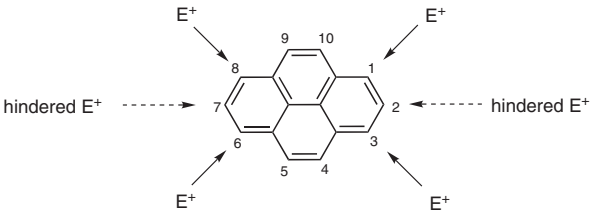
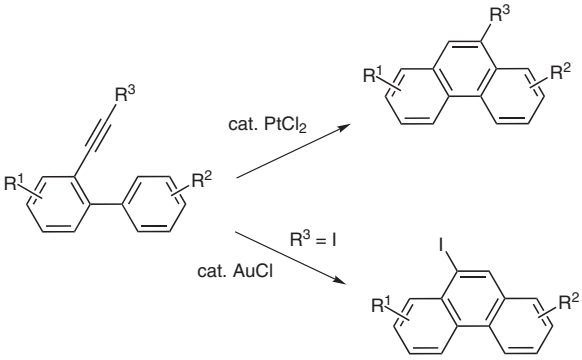


Figure 1 Approaches to substituted pyrenes; few methods are available for controlled differentiation between the left and right halves of the molecule

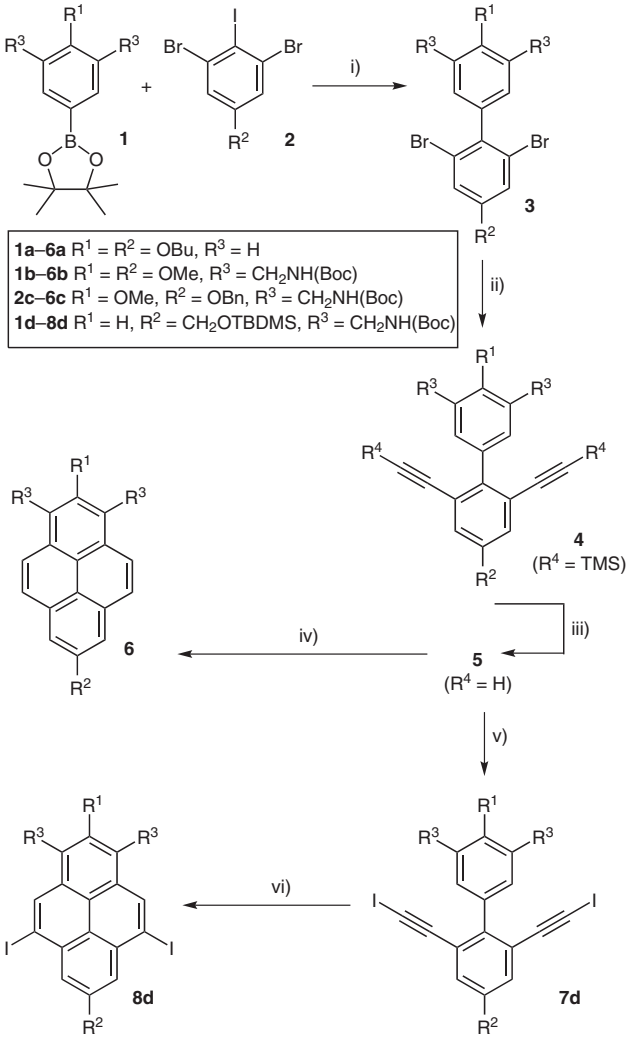


Scheme 1 Fürstner's phenanthrene syntheses

To first investigate the efficacy of this methodology for the formation of pyrenes, a model biphenyl 2,6-dialkyne was prepared in a three-step sequence. As shown in Scheme 2, the selective Suzuki coupling of boronic ester **1a** with iodide **2a** furnished dibromide **3a** in 67% yield. This was followed by a Sonagashira reaction with ethynyltrimethylsilane to give **4a** and subsequent cleavage of the terminal silicon groups with tetrabutylammonium fluoride (TBAF), to give the target bisalkyne **5a** in 67% yield over two steps. In the key transformation, heating a toluene solution of **5a** with 10 mol% platinum(II) chloride

SYNTHESIS 2010, No. 21, pp 3686–3692
Advanced online publication: 01.09.2010
DOI: 10.1055/s-0030-1258238; Art ID: P11310SS

overnight resulted in complete conversion of the starting material into pyrene **6a** with an isolated yield of 78%. Importantly, the preference for 6-*endo*-dig cyclization over the plausible 5-*exo* mode was maintained in this reaction, as observed previously for the formation of phenanthrenes.[15]



Scheme 2 Synthesis of functionalized pyrenes **6a–c** and **8d**. *Reagents and conditions*: (i) $Pd(dppf)Cl_2$, 2 M Na_2CO_3, DMSO, 50 °C, 16 h, 67–71%; (ii) TMSCCH, $Pd(PPh_3)_4$, CuI, Et_3N, piperidine, 80 °C, 16 h, 72–83%; (iii) TBAF, THF, 5 min, r.t., 89–93% (**4a–c**), or NaOH, MeOH, 5 min, r.t., 85% (**4d**); (iv) $PtCl_2$, toluene, 80 °C, 16 h, 62–78%; (v) I_2, DMAP, CH_2Cl_2, 42 °C, 16 h, 89%; AuCl, toluene, 60 °C, 38%.

With a straightforward synthetic sequence established, substituted pyrene precursors **5b** and **5c** were prepared in practical yields and subjected to the same platinum(II)-mediated electrocyclization reaction conditions. As with the model compound, isomerization proceeded cleanly and 1,2,3,7-substituted pyrenes **6b** and **6c** were produced in 62% and 63% yields, respectively. The extension of Fürstner's protocol to the synthesis of pyrenes offers several advantages over existing methods. Firstly, the introduction of functional groups that are suitable for further modification (in this case *tert*-butyl carbamate protected aminomethyl groups) proceeds without incident. Secondly, unlike methodologies that start from pyrene itself, functionality can readily be introduced to the 2- and 7-positions. Finally, the functional groups attached to the 2- and 7-positions can be varied independently of one another, as demonstrated in the preparation of **6c** (illustrated in this case with an *O*-methyl attached between CH_2NHBoc groups, and an *O*-benzyl group tethered to the opposite end of the molecule).

In the course of our research, the preparation of a pyrene that was substituted selectively in the 1,3,5,7,9-positions also became relevant. We envisioned that a further development of Fürstner's work, this time employing the gold(I)-mediated cyclization of 2,6-bisiodoalkynes (Scheme 1), could be used for this purpose. It has previously been observed that using AuCl as a catalyst in this type of reaction facilitates formation of a vinylidene intermediate via a concomitant 1,2-halide shift. In this case, such a rearrangement would promote the formation of a 5,9-diiodopyrene.

Compound **2d** was subjected to sequential Suzuki and Sonagashira coupling reaction conditions and the terminal alkyne groups were desilylated using sodium hydroxide, to furnish **5d** (37% yield over three steps). Treatment of **5d** with 4-(*N*,*N*-dimethylamino)pyridine (DMAP) and I_2 in refluxing dichloromethane for six hours resulted in clean conversion into the diiodo alkyne **7d**. Finally, overnight heating of **7d** with gold(I) chloride in toluene at 60 °C resulted in the formation of its fully aromatized isomer **8d** in 38% yield. The substitution pattern of **8d** was confirmed by a NOESY NMR experiment that proved that the anticipated regioisomer was formed in the reaction.

In conclusion, we have demonstrated a convenient protocol for the synthesis of polyfunctionalized pyrenes based on the cycloisomerization of diethynyl biphenyl precursors using either platinum or gold salts as catalysts. The procedure allows access to substitution patterns not readily available when starting with pyrene directly and has the potential to allow access to a wide range of highly functionalized pyrene derivatives.

^1H and ^{13}C NMR spectra were recorded at 400 MHz with a Delta/GX 400 spectrometer, an Eclipse 400 spectrometer, or a Varian 400-MR spectrometer, or at 500 MHz with a Varian System 500A spectrometer. Chemical shifts are reported in ppm downfield from TMS. Mass spectra (electron impact and chemical ionization), were recorded with a VG Analytical Autospec (EI), VG Analytical Quattro (ESI), or with an Applied Biosystems 4700 spectrometer. All commercially available compounds were purchased from Aldrich, Alfa-Aesar, or Sigma and were used without further purification except where stated. Solvents for synthesis were dried by passing through a modified Grubbs system,[17] manufactured by Anhydrous Engineering. Routine monitoring of reactions was performed using precoated silica gel TLC plates (Merck silica gel 60 F254). Spots were visualized by either UV light, or by staining with an ethanolic solution of phosphomolybdic acid, potassium permanganate, or ninhydrin. Flash column chromatography[18] was performed using silica gel (Fisher brand silica 60 Å particle size 35–70

micron) as the absorbent. Compounds **1a**,[19] **1b**,[20] and **1d**[21] were prepared according to literature procedures.

1,3-Dibromo-5-butoxy-2-iodobenzene (2a)
To a solution of 3,5-dibromo-4-iodophenol[22] (500 mg, 1.32 mmol) and 1-bromobutane (160 μL, 1.45 mmol) in MeCN (50 mL), were added K_2CO_3 (910 mg, 6.6 mmol) and NaI (5 mg, 0.03 mmol). The suspension was heated at reflux for 18 h, filtered, and the organic filtrate was concentrated under reduced pressure. The resultant oil was re-dissolved in CH_2Cl_2 (50 mL) and washed with H_2O (2 × 25 mL) and brine (25 mL). The aqueous layers were combined and extracted with CH_2Cl_2 (2 × 25 mL). The combined organic layers were dried over anhydrous Na_2SO_4, concentrated under reduced pressure and the crude product was purified by column chromatography (hexanes–CH_2Cl_2, 4:1) to yield **2a**.

Yield: 407 mg (71%); colorless solid; mp 43–44 °C; R_f = 0.69 (hexanes–CH_2Cl_2, 4:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.98 (t, J = 7.5 Hz, 3 H, -CH_2CH_3), 1.48 (m, 2 H, -CH_2CH_3), 1.75 (m, 2 H, -OCH_2CH_2-), 3.92 (t, J = 6.4 Hz, 2 H, -OCH_2CH_2-), 7.16 (s, 2 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.7 (-CH_2CH_3), 19.1 (-CH_2CH_3), 31.0 (-OCH_2CH_2-), 68.5 (-OCH_2CH_2-), 97.4 (ArC_q), 118.2 (ArCH), 130.9 (ArC_q), 159.8 (ArC_q).

HRMS (CI$^+$): m/z [M]$^+$ calcd for $C_{10}H_{11}O_2{}^{79}Br_2I$: 431.8221; found: 431.8216.

Anal. Calcd for $C_{10}H_{11}O_2{}^{79}Br_2I$: C, 27.68; H, 2.56. Found: C, 27.78; H, 2.31.

1,3-Dibromo-2-iodo-5-methoxybenzene (2b)
Prepared as described for **2a** using Me_2SO_4.

Yield: 756 mg (73%); colorless solid; mp 101–102 °C; R_f = 0.56 (hexanes–CH_2Cl_2, 4:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.79 (s, 3 H, -OCH_3), 7.17 (s, 2 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 55.9 (-OCH_3), 97.8 (ArC_q), 117.7 (ArCH), 131.0 (ArC_q), 160.2 (ArC_q).

HRMS (EI$^+$): m/z [M]$^+$ calcd for $C_7H_5O^{79}Br_2I$: 389.7752; found: 389.7765.

Anal. Calcd for $C_7H_5OBr_2I$: C, 21.46; H, 1.29. Found: C, 21.78; H, 1.39.

5-(Benzyloxy)-1,3-dibromo-2-iodobenzene (2c)
Prepared as described for **2a** using benzyl bromide.

Yield: 1.48 g (91%); colorless solid; mp 57–59 °C; R_f = 0.54 (hexanes–CH_2Cl_2, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.02 (s, 2 H, -OCH_2-), 7.25 (s, 2 H, ArH), 7.40 (m, 5 H, BnH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 70.6 (-OCH_2-), 98.2 (ArC_q), 118.5 (ArCH), 127.5 (ArCH), 128.5 (ArCH), 128.8 (ArCH), 131.1 (ArC_q), 135.4 (ArC_q), 159.3 (ArC_q).

HRMS (CI$^+$): m/z [M]$^+$ calcd for $C_{13}H_9O^{79}Br_2I$: 465.8065; found: 465.8058.

***tert*-Butyl[(3,5-dibromo-4-iodobenzyl)oxy]dimethylsilane (2d)**
(i) To a solution of ethyl 3,5-dibromo-4-iodobenzoate[23] (7.89 g, 18 mmol) in anhydrous CH_2Cl_2 (100 mL) cooled to –78 °C under an atmosphere of nitrogen, was added DIBAL-H (40 mL, 1 M, 4 mmol) dropwise over 10 min and the resulting suspension was stirred for 2 h whilst slowly warming to r.t. The clear solution was then cooled to 0 °C and sat. aq NH_4Cl (10 mL) was added dropwise over 10 min. The slurry formed was filtered and the organic layer was separated. The precipitate was extracted with THF (3 × 50 mL) and the combined organic washings were dried over anhydrous Na_2SO_4, concentrated under reduced pressure and washed with CH_2Cl_2 (5 mL) to furnish a white solid.

Yield: 6.52 g (92%); mp 127–129 °C; R_f = 0.72 (CH_2Cl_2–MeOH, 97:3).

^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ = 4.44 (d, ^3J = 5.8 Hz, 2 H, CH_2OH), 5.44 (t, ^3J = 5.8 Hz, 1 H, CH_2OH), 7.62 (s, 2 H, ArH).

^{13}C NMR (125 MHz, DMSO-d_6, 298 K): δ = 61.0 (-CH_2OH), 107.2 (ArC_q), 129.1 (ArCH), 130.3 (ArC_q), 146.5 (ArC_q).

HRMS (EI$^+$): m/z [M]$^+$ calcd for $C_7H_5OBr_2I$: 389.7752; found: 389.7753.

(ii) To a solution of several batches of the compound isolated as described in step (i) above (9.00 g, 23.0 mmol) dissolved in DMF (15 mL) were added TBDMSCl (4.39 g, 29.9 mmol, 1.3 equiv) and imidazole (2.04 g, 29.9 mmol, 1.3 equiv). The reaction mixture was stirred for 16 h at r.t. and then poured into ice water (100 mL). The resulting mixture was extracted with CH_2Cl_2 (2 × 150 mL) and the organic layer was then washed with sat. aq $NaHCO_3$ (150 mL), brine (50 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude oil obtained was purified using flash chromatography (CH_2Cl_2) to yield **2d**.

Yield: 11.4 g (98%); colorless oil; R_f = 0.73 (hexanes–CH_2Cl_2, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.11 [s, 6 H, -$Si(CH_3)_2$], 0.95 [s, 9 H, -$C(CH_3)_3$], 4.63 (-CH_2O-), 7.72 (s, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –5.3 [-$Si(CH_3)_2$], 18.3 (-SiC-), 25.9 [-$C(CH_3)_3$], 63.1 (-CH_2O-), 106.5 (ArC_q), 128.6 (ArCH), 131.0 (ArC_q), 144.7 (ArC_q).

HRMS (EI$^+$): m/z [M]$^+$ calcd for $C_{13}H_{19}O^{79}Br_2ISi$: 503.8617; found: 503.8612.

2,6-Dibromo-4,4′-dibutoxy-1,1′-biphenyl (3a)
1a (450 mg, 1.04 mmol) and **2a** (272 mg, 0.98 mmol) were dissolved in DMSO (10 mL) and the solution was degassed for 30 min before being purged with argon. To the resulting clear solution were added Pd(dppf)Cl_2 (43 mg, 52 μmol, 0.05 equiv) and aq $NaHCO_3$ (2.1 mL, 2 M, 4.2 mmol, 4 equiv). The reaction mixture was heated at 50 °C for 18 h then dissolved in EtOAc (50 mL), washed with H_2O (2 × 30 mL) and dried over anhydrous Na_2SO_4. The aqueous phase was extracted with EtOAc (2 × 30 mL) and the combined organic washes were concentrated under reduced pressure. The resultant solid was purified by flash chromatography (hexanes–CH_2Cl_2, 4:1) to give **3a**.

Yield: 301 mg (67%); colorless oil; R_f = 0.41 (hexanes–CH_2Cl_2, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (m, 6 H, -CH_2CH_3), 1.51 (m, 4 H, -CH_2CH_3), 1.79 (m, 4 H, -OCH_2CH_2-), 3.99 (m, 4 H, -OCH_2CH_2-), 6.96 (d, J = 8.6 Hz, 2 H, ArH), 7.12 (d, J = 8.6 Hz, 2 H, ArH), 7.19 (s, 2 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8 (-CH_2CH_3), 13.9 (-CH_2CH_3), 19.1 (-CH_2CH_3), 19.3 (-CH_2CH_3), 31.1 (-OCH_2CH_2), 31.4 (-OCH_2CH_2), 67.6 (-OCH_2CH_2), 68.4 (-OCH_2CH_2), 113.8 (ArCH), 118.1 (ArCH), 124.9 (ArC_q), 130.9 (ArCH), 133.2 (ArC_q), 134.9 (ArC_q), 158.7 (2 × ArC_q).

HRMS (EI$^+$): m/z [M]$^+$ calcd for $C_{20}H_{24}O_2{}^{79}Br_2$: 454.0143; found: 454.0152.

Di-*tert*-butyl {[2′,6′-Dibromo-4,4′-dimethoxy-(1,1′-biphenyl)-3,5-diyl]bis(methylene)}dicarbamate (3b)
Prepared as described for **3a** using **1b** and **2b**.

Yield: 833 mg (71%); colorless solid; R_f = 0.54 (CH_2Cl_2–EtOAc, 9:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.45 [s, 18 H, $C(CH_3)_3$], 3.82 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3),4.41 (m, 4 H, CH_2NH), 4.93 (m, 2 H, CH_2NH), 7.07 (s, 2 H, ArH), 7.18 (s, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.4 [-C(CH_3)$_3$], 39.7 (-CH_2NH-), 55.8 (-OCH_3), 61.5 (-OCH_3), 79.4 [-C(CH_3)$_3$], 117.7 (ArCH), 124.4 (ArCH), 129.7 (ArC_q), 130.1 (ArC_q), 131.6 (ArC_q), 134.5 (ArC_q), 137.0 (ArC_q), 155.8 (ArC_q), 159.3 (-CONH).

HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{26}H_{34}O_6N_2{}^{79}Br_2Na$: 651.0676; found: 651.0693.

Di-*tert*-Butyl {[4′-(Benzyloxy)-2′,6′-dibromo-4-methoxy-(1,1′-biphenyl)-3,5-diyl]bis(methylene)}dicarbamate (3c)

Prepared as described for **3a** using **1c** and **2c**.

Yield: 1.29 g (63%); colorless solid; mp 158–159 °C; R_f = 0.30 (CH_2Cl_2–EtOAc, 9:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.45 [s, 18 H, -C(CH_3)$_3$], 3.86 (s, 3 H, -OCH_3), 4.41 (d, ^3J = 5.6 Hz, 4 H, -CH_2NH-), 4.92 (m, 2 H, -CH_2NH-), 5.07 (s, 2 H, -OCH_2-), 7.08 (s, 2 H, ArH), 7.27 (s, 2 H, ArH), 7.43 (m, 5 H, BnH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.4 [-C(CH_3)$_3$], 39.7 (-CH_2NH-), 61.6 (-OCH_3), 70.6 (-OCH_2Bn), 79.5 [-C(CH_3)$_3$], 118.6 (ArCH), 124.5 (ArC_q), 127.5 (ArCH), 128.4 (ArCH), 128.7 (2 × ArCH), 130.1 (ArC_q), 131.7 (ArC_q), 134.8 (ArC_q), 135.8 (ArC_q), 136.9 (ArC_q), 155.8 (ArC_q), 158.4 (-CONH-).

HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{32}H_{38}N_2O_6{}^{79}Br_2Na$: 727.0989; found: 727.0982.

Anal. Calcd for $C_{32}H_{38}N_2O_6Br_2$: C, 54.40; H, 5.42; N, 3.87. Found: C, 54.96; H, 5.20; N, 3.88.

Di-*tert*-Butyl {[2′,6′-Dibromo-4′-(*tert*-butyldimethylsilyloxymethyl)-(1,1′-biphenyl)-3,5-diyl]bis(methylene)}dicarbamate (3d)

Prepared as described for **3a** using **1d** and **2d**.

Yield: 1.28 g (55%); colorless solid; mp 130–131 °C; R_f = 0.43 (CH_2Cl_2–EtOAc, 9:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.14 [s, 6 H, -Si(CH_3)$_2$], 0.97 [s, 9 H, -SiC(CH_3)$_3$], 1.47 [s, 18 H, -OC(CH_3)$_3$], 4.37 (m, 4 H, -CH_2NH-), 4.72 (s, 2 H, -CH_2O-), 4.87 (m, 2 H, -CH_2NH-), 7.04 (m, 1 H, ArH), 7.24 (m, 2 H, ArH), 7.58 (s, 2 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –5.3 [-Si(CH_3)$_2$], 18.4 (-SiC-), 25.9 [-SiC(CH_3)$_3$], 28.4 [-C(CH_3)$_3$], 44.5 (-CH_2NH-), 63.3 (-CH_2O-), 79.6 [-C(CH_3)$_3$], 124.1 (ArCH), 126.1 (ArCH), 127.5 (ArC_q), 129.2 (ArCH), 139.3 (ArC_q), 140.7 (ArC_q), 141.6 (ArC_q), 144.0 (ArC_q), 155.8 (-CONH-).

HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{31}H_{46}O_5N_2{}^{79}Br_2SiNa$: 735.1435; found: 735.1425.

{[4,4′-Dibutoxy(1,1′-biphenyl)-2,6-diyl]bis(ethyne-2,1-diyl)}bis(trimethylsilane) (4a)

3a (50 mg, 109 μmol) was added to a Schlenk tube and dissolved in anhydrous Et_3N (2 mL). To the resulting clear solution was added anhydrous piperidine (0.5 mL), $Pd(PPh_3)_4$ (13 mg, 10.9 μmol, 0.1 equiv), CuI (2 mg, 5.5 μmol, 0.05 equiv) and ethynyltrimethylsilane (310 μL, 2.18 mmol, 20 equiv). The mixture was heated at 80 °C for 18 h under argon, cooled to r.t. and partitioned between CH_2Cl_2 (30 mL) and sat. aq NH_4Cl (20 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 15 mL) and the combined organic layers were dried over anhydrous Na_2SO_4, concentrated under reduced pressure and the crude residue was purified by flash chromatography (hexanes–CH_2Cl_2, 4:1) to give **4a**.

Yield: 39 mg (72%); colorless oil; R_f = 0.28 (hexanes–CH_2Cl_2, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.08 [s, 18 H, -Si(CH_3)$_3$], 0.99 (m, 6 H, -CH_2CH_3), 1.51 (m, 4 H, -CH_2CH_3), 1.78 (m, -OCH_2CH_2-), 4.00 (m, 4 H, -OCH_2CH_2-), 6.88 (d, ^3J = 8.6 Hz, 2 H, ArH), 7.05 (s, 2 H, ArH), 7.39 (d, ^3J = 8.6 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.4 [-Si(CH_3)$_3$], 13.8 (2 × CH_2CH_3), 19.2 (2 × CH_2CH_3), 31.1 (2 × OCH_2CH_2), 67.8 (-OCH_2CH_2-), 68.0 (-OCH_2CH_2-), 97.5 (-CCSi-), 104.4 (-CCSi-), 113.2 (ArCH), 119.1 (ArCH), 123.7 (ArC_q), 130.5 (ArC_q), 131.6 (ArCH), 139.7 (ArC_q), 157.0 (ArC_q), 158.3 (ArC_q).

HRMS (EI$^+$): m/z [M]$^+$ calcd for $C_{30}H_{42}O_2Si_2$: 490.2723; found: 490.2709.

Di-*tert*-Butyl {[4,4′-Dimethoxy-2′,6′-bis(trimethylsilylethynyl)-(1,1′-biphenyl)-3,5-diyl]bis(methylene)}dicarbamate (4b)

Prepared as described for **4a** using **3b**.

Yield: 607 mg (83%); colorless solid; R_f = 0.85 (CH_2Cl_2–EtOAc, 9:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.06 [s, 18 H, Si(CH_3)$_3$], 1.45 [s, 18 H, -C(CH_3)$_3$], 3.81 (s, 3 H, -OCH_3), 3.82 (s, 3 H, -OCH_3), 4.42 (m, 4 H CH_2NH), 4.86 (m, 2 H, CH_2NH), 7.04 (s, 2 H, ArH), 7.29 (s, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –0.01 [-Si(CH_3)$_3$], 28.7 [-C(CH_3)$_3$], 40.4 (-CH_2NH-), 55.9 (-OCH_3), 61.8 (-OCH_3), 79.7 [-C(CH_3)$_3$], 98.3 (-CCSi-), 104.2 (-CCSi-), 118.8 (ArCH), 124.1 (ArCH), 130.1 (ArC_q), 130.6 (ArC_q), 131.3 (ArC_q), 135.3 (ArC_q), 139.4 (ArC_q), 156.0 (ArC_q), 158.1 (-CONH).

HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{36}H_{52}O_6N_2Si_2Na$: 687.3256; found: 687.3264.

Di-*tert*-Butyl {[4′-(Benzyloxy)-4-methoxy-2′,6′-bis(trimethylsilylethynyl)-(1,1′-biphenyl)-3,5-diyl]bis(methylene)}dicarbamate (4c)

Prepared as described for **4a** using **3c**.

Yield: 565 mg (62%); colorless foam; R_f = 0.57 (CH_2Cl_2–EtOAc, 9:1).

^{1}H NMR (500 MHz): δ = 0.06 [s, 18 H, -Si(CH_3)$_3$], 1.46 [s, 18 H, -C(CH_3)$_3$], 3.81 (s, 3 H, -OCH_3), 4.43 (m, 4 H, -CH_2NH-), 4.85 (m, 2 H, -CH_2NH-), 5.08 (s, 2 H, -OCH_2-), 7.14 (s, 2 H, ArH), 7.30 (s, 2 H, ArH), 7.41 (m, 5 H, BnH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –0.3 [-Si(CH_3)$_3$], 28.4 [-C(CH_3)$_3$], 40.0 (-CH$_2$NH-), 61.5 (-OCH_3), 70.2 (-OCH_2Bn), 79.4 [-C(CH_3)$_3$], 98.0 (-CCSi-), 103.8 (-CCSi-), 119.4 (ArCH), 123.8 (ArC_q), 127.4 (ArCH), 128.1 (ArCH), 128.6 (ArCH), 130.3 (ArC_q), 130.9 (ArC_q and ArCH), 135.0 (ArC_q), 136.4 (ArC_q), 139.4 (ArC_q), 155.7 (ArC_q), 157.0 (-CONH-).

HRMS (ESI$^+$): m/z [M + Na]$^+$ calcd for $C_{42}H_{56}O_6N_2Si_2Na$: 763.3569; found: 763.3597.

Di-*tert*-Butyl {[4′-(*tert*-Butyldimethylsilyloxymethyl)-2′,6′-bis(trimethylsilylethynyl)-(1,1′-biphenyl)-3,5-diyl]bis(methylene)}dicarbamate (4d)

Prepared as described for **4a** using **3d**.

Yield: 845 mg (80%); colorless foam; R_f = 0.70 (CH_2Cl_2–EtOAc, 9:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.06 [s, 9 H, -Si(CH_3)$_3$], 0.13 [s, 6 H, -Si(CH_3)$_2$], 0.96 [s, 9 H, -SiC(CH_3)$_3$], 1.47 [s, 18 H, -OC(CH_3)$_3$], 4.36 (m, 4 H, -CH_2NH-), 4.69 (s, 2 H, -CH_2O-), 4.75 (m, 2 H, -CH_2NH-), 7.22 (m, 1 H, ArH), 7.27 (m, 2 H, ArH), 7.46 (s, 2 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –5.2 [-Si(CH_3)$_2$], –0.3 [-CCSi(CH_3)$_3$], 18.5 (-SiC-), 26.0 [-SiC(CH_3)$_3$], 28.4 [-C(CH_3)$_3$], 44.7 (-CH_2NH-), 64.0 (-CH_2O-), 79.5 [-C(CH_3)$_3$], 97.9 [CCSi(CH_3)$_3$], 104.1

[*C*CSi(CH$_3$)$_3$], 122.7 (Ar*C*H), 125.7 (Ar*C*H), 128.5 (ArC_q), 130.7 (Ar*C*H), 138.0 (ArC_q), 139.3 (ArC_q), 140.5 (ArC_q), 145.0 (ArC_q), 155.8 (-CONH-).

HRMS (ESI$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_{41}H_{64}O_5N_2Si_3Na$: 771.4015; found: 771.4013.

4,4′-Dibutoxy-2,6-diethynyl-1,1′-biphenyl (5a)

4a (18 mg, 37 μmol) was dissolved in CH_2Cl_2 (1 mL) and a solution of TBAF (0.1 mL, 1 M in THF, 100 μmol, 3.5 equiv) was added dropwise. After 15 min the mixture was partitioned between H_2O (5 mL) and CH_2Cl_2 (5 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL) and the combined organic fractions were washed with brine (10 mL), dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash chromatography (hexanes–CH_2Cl_2, 4:1) to give **5a**.

Yield: 12 mg (93%); colorless foam; R_f = 0.19 (hexanes–CH_2Cl_2, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (m, 6 H, -CH_2CH_3), 1.52 (m, 4 H, -CH_2CH_3), 1.80 (m, 4 H, -OCH_2CH_2-), 2.95 (s, 2 H, -CCH), 4.00 (m, 4 H, -OCH_2CH_2-), 6.93 (d, ^3J = 8.6 Hz, 2 H, ArH), 7.13 (s, 2 H, ArH), 7.38 (d, ^3J = 8.6 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8 (-CH_2CH_3), 13.9 (-CH_2CH_3), 19.2 (-CH_2CH_3), 19.3 (-CH_2CH_3), 31.2 (-OCH_2CH_2-), 31.4 (-OCH_2CH_2-), 67.5 (-OCH_2CH_2-), 68.0 (-OCH_2CH_2-), 80.2 (-C*C*H), 82.6 (-*C*CH), 113.4 (Ar*C*H), 120.0 (Ar*C*H), 123.0 (ArC_q), 130.1 (ArC_q), 131.4 (Ar*C*H), 139.6 (ArC_q), 157.1 (ArC_q), 158.6 (ArC_q).

HRMS (ESI$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_{24}H_{26}O_2Na$: 369.1825; found: 369.1833.

Di-*tert*-Butyl {[2′,6′-Diethynyl-4,4′-dimethoxy(1,1′-biphenyl)-3,5-diyl]bis(methylene)}dicarbamate (5b)

Prepared as described for **5a** using **4b**.

Yield: 423 mg (89%); colorless foam; R_f = 0.39 (CH_2Cl_2–EtOAc, 9:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.45 [s, 18 H, -C(CH$_3$)$_3$], 2.97 (s, 2 H, CCH), 3.84 (br s, 6 H, 2 × OCH_3), 4.42 (m, 4 H CH_2NH), 4.89 (m, 2 H, CH_2NH), 7.12 (s, 2 H, ArH), 7.39 (s, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.4 [-C(*C*H$_3$)$_3$], 39.6 (-CH_2NH-), 55.5 (-OCH_3), 61.6 (-OCH_3), 79.4 [-*C*(CH$_3$)$_3$], 80.8 (-C*C*H), 82.3 (-*C*CH), 119.5 (Ar*C*H), 122.9 (Ar*C*H), 130.7 (ArC_q), 130.9 (ArC_q), 133.8 (ArC_q), 138.8 (ArC_q), 155.6 (ArC_q), 155.8 (ArC_q), 157.8 (-CONH-).

HRMS (ESI$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_{30}H_{36}O_6N_2Na$: 543.2466; found: 543.2466.

Di-*tert*-Butyl {[4′-(Benzyloxy)-2′,6′-diethynyl-4-methoxy(1,1′-biphenyl)-3,5-diyl]bis(methylene)}dicarbamate (5c)

Prepared as described for **5a** using **4c**.

Yield: 363 mg (85%); colorless solid; R_f = 0.18 (CH_2Cl_2–EtOAc, 9:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.46 [s, 18 H, -C(CH$_3$)$_3$], 2.97 (s, 2 H, -CCH), 3.85 (s, 3 H, -OCH_3), 4.42 (m, 4 H, -CH_2NH-), 4.89 (m, 2 H, -CH_2NH-), 5.10 (s, 2 H, -OCH_2-), 7.21 (s, 2 H, ArH), 7.41 (m, 7 H, ArH and BnH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.4 [-C(*C*H$_3$)$_3$], 39.6 (-CH_2NH-), 61.6 (-OCH_3), 70.3 (-OCH_2Bn), 79.4 [-*C*(CH$_3$)$_3$], 80.9 (-C*C*H), 82.3 (-*C*CH), 120.4 (Ar*C*H), 123.0 (ArC_q), 127.5 (Ar*C*H), 128.2 (Ar*C*H), 128.7 (Ar*C*H), 130.7 (Ar*C*H), 130.9 (ArC_q), 133.8 (ArC_q), 136.2 (ArC_q), 139.1 (ArC_q), 155.6 (ArC_q), 155.8 (ArC_q), 157.0 (-CONH-).

HRMS (ESI$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_{36}H_{40}O_6N_2Na$: 619.2779; found: 619.2797.

Di-*tert*-Butyl {[4′-(*tert*-Butyldimethylsilyloxymethyl)-2′,6′-diethynyl(1,1′-biphenyl)-3,5-diyl]bis(methylene)}dicarbamate (5d)

4d (839 mg, 1.12 mmol) was dissolved in CH_2Cl_2 (20 mL) and a solution of NaOH (10 mL, 5% by mass) was added dropwise. After 10 min the mixture was partitioned between H_2O (10 mL) and CH_2Cl_2 (50 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL) and the combined organic fractions were washed with brine (20 mL), dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash chromatography (CH_2Cl_2–EtOAc, 19:1) to give **5d**.

Yield: 576 mg (85%); colorless solid; mp 72–73 °C; R_f = 0.27 (CH_2Cl_2–EtOAc, 9:1).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 0.14 [s, 6 H, -Si(CH$_3$)$_2$], 0.97 [s, 9 H, -SiC(CH$_3$)$_3$], 1.47 [s, 18 H, -OC(CH$_3$)$_3$], 2.96 (s, 2 H, -CCH), 4.38 (m, 4 H, -CH_2NH-), 4.72 (s, 2 H, -CH_2O-), 4.84 (m, 2 H, -CH_2NH-), 7.20 (m, 1 H, ArH), 7.32 (m, 2 H, ArH), 7.54 (s, 2 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = –5.3 [-Si(CH$_3$)$_2$], 18.4 (-SiC-), 26.0 [-SiC(*C*H$_3$)$_3$], 28.4 [-C(*C*H$_3$)$_3$], 44.5 (-CH_2NH-), 63.8 (-CH_2O-), 79.5 [-*C*(CH$_3$)$_3$], 80.7 (-C*C*H), 82.4 (-*C*CH), 121.9 (Ar*C*H), 125.9 (ArC_q), 128.3 (Ar*C*H), 131.4 (Ar*C*H), 138.4 (ArC_q), 138.7 (ArC_q), 140.7 (ArC_q), 145.0 (ArC_q), 155.8 (-CONH).

HRMS (ESI$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_{35}H_{48}O_5N_2SiNa$: 627.3225; found: 627.3243.

2,7-Dibutoxypyrene (6a)

To a solution of **5a** (9 mg, 24.5 μmol) dissolved in anhydrous toluene (0.7 mL) was added $PtCl_2$ (1 mg, 2.45 μmol, 0.1 equiv) and the mixture was degassed, purged with argon and heated at 80 °C for 16 h. The solution was then concentrated under reduced pressure and purified by flash chromatography (hexanes–CH_2Cl_2, 7:3) to give **6a**.

Yield: 7 mg (78%); colorless solid; mp 145–146 °C; R_f = 0.51 (hexanes–CH_2Cl_2, 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.05 (t, J = 7.5 Hz, 6 H, -CH_2CH_3), 1.60 (m, 4 H, -CH_2CH_3), 1.92 (m, 4 H, -OCH_2CH_2-), 4.26 (t, J = 6.5 Hz, 4 H, -OCH_2CH_2-), 7.69 (s, 4 H, ArH), 7.95 (s, 4 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (-CH_2CH_3), 19.4 (-CH_2CH_3), 31.5 (-OCH_2CH_2-), 68.3 (-OCH_2CH_2-), 111.3 (Ar*C*H), 120.1 (ArC_q), 127.4 (Ar*C*H), 131.6 (ArC_q), 156.7 (ArC_q).

HRMS (ESI$^+$): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{27}O_2$: 347.2006; found: 347.2014.

Di-*tert*-Butyl [(2,7-Dimethoxypyrene-1,3-diyl)bis(methylene)]dicarbamate (6b)

Prepared as described for **6a** using **5b**.

Yield: 231 mg (62%); colorless solid; mp 221–222 °C; R_f = 0.56 (CH_2Cl_2–EtOAc, 9:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.47 [s, 18 H, -C(CH$_3$)$_3$], 4.00 (s, 3 H, -OCH_3), 4.09 (s, 3 H, -OCH_3), 4.93 (m, 2 H, CH_2NH), 5.06 (m, 4 H CH_2NH), 7.72 (s, 2 H, ArH), 8.06 (d, ^3J = 9.3 Hz, 2 H, ArH), 8.33 (d, ^3J = 9.3 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.4 [-C(*C*H$_3$)$_3$], 36.2 (-CH_2NH), 55.7 (-OCH_3), 63.6 (-OCH_3), 79.5 [-C(*C*H$_3$)$_3$], 111.2 (Ar*C*H), 119.9 (ArC_q), 122.6 (ArC_q), 123.9 (ArC_q), 125.2 (ArC_q), 128.3 (Ar*C*H), 129.9 (ArC_q), 131.9 (Ar*C*H); 155.0 (ArC_q), 155.6 (ArC_q), 157.7 (-CONH-).

HRMS (ESI$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_{30}H_{36}O_6N_2Na$: 543.2466; found: 543.2487.

Di-*tert*-Butyl {[7-(Benzyloxy)-2-methoxypyrene-1,3-diyl]bis(methylene)}dicarbamate (6c)
Prepared as described for **6a** using **5c**.

Yield: 211 mg (63%); colorless solid; mp 204–205 °C; R_f = 0.34 (CH_2Cl_2–EtOAc, 9:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.47 [s, 18 H, -C(CH_3)$_3$], 4.00 (s, 3 H, -OCH_3), 4.92 (m, 2 H, -CH_2N*H*-), 5.02 (m, 4 H, -C*H*$_2$NH-), 5.38 (s, 2 H, -OCH_2-), 7.38 (m, 1 H, BnH), 7.45 (m, 2 H, BnH), 7.57 (m, 2 H, BnH), 7.81 (s, 2 H, ArH), 8.07 (d, ^3J = 9.3 Hz, 2 H, ArH), 8.33 (d, ^3J = 9.3 Hz, 2 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 28.4 [-C(*C*H_3)$_3$], 36.2 (-CH_2NH-), 63.6 (-OCH_3), 70.5 (-OCH_2Bn), 79.5 [-*C*(CH_3)$_3$], 112.1 (Ar*C*H), 120.1 (ArC_q), 122.6 (ArC_q), 123.9 (ArC_q), 125.3 (ArC_q), 127.6 (Ar*C*H), 128.1 (Ar*C*H), 128.3 (ArC_q), 128.7 (Ar*C*H), 129.9 (ArC_q), 131.9 (Ar*C*H), 136.9 (Ar*C*H), 155.1 (ArC_q), 155.6 (ArC_q), 156.9 (-CONH-).

HRMS (ESI$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_{36}H_{40}N_2O_6Na$: 619.2779; found: 619.2795.

Di-*tert*-Butyl {[4′-(*tert*-Butyldimethylsilyloxymethyl)-2′,6′-bis(iodoethynyl)-(1,1′-biphenyl)-3,5-diyl]bis(methylene)}dicarbamate (7d)
To a solution of **5d** (50 mg, 82.6 μmol) dissolved in anhydrous CH_2Cl_2 was added I_2 (46 mg, 180 μmol, 2.2 equiv) and DMAP (22 mg, 180 μmol, 2.2 equiv), and the reaction mixture was heated at 40 °C for 6 h. The solution was partitioned between CH_2Cl_2 (20 mL) and sat. aq $Na_2S_2O_3$ (20 mL). The aqueous phase was re-extracted with CH_2Cl_2 (2 × 30 mL) and the combined organic layers were washed with brine (10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash chromatography (CH_2Cl_2–EtOAc, 19:1) and then washed with hexane (5 mL) and filtered to give **7d**.

Yield: 63 mg (89%); colorless solid; mp 138–139 °C; R_f = 0.27 (CH_2Cl_2–EtOAc, 9:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.13 [s, 6 H, -Si(CH_3)$_2$], 0.96 [s, 9 H, -SiC(CH_3)$_3$], 1.49 [s, 18 H, -OC(CH_3)$_3$], 4.40 (m, 4 H, -C*H*$_2$NH-), 4.68 (s, 2 H, -CH_2O-), 4.82 (m, 2 H, -CH_2N*H*-), 7.22 (m, 1 H, ArH), 7.35 (m, 2 H, ArH), 7.46 (s, 2 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –5.3 [-Si(CH_3)$_2$], 18.4 (-SiC-), 26.0 [-SiC(*C*H_3)$_3$], 28.5 [-C(*C*H_3)$_3$], 44.7 (-CH_2NH-), 63.9 (-CH_2O-), 79.5 [-*C*(CH_3)$_3$], 80.7 (-*C*CI), 93.2 (-C*C*I), 122.8 (Ar*C*H), 126.3 (Ar*C*H), 128.7 (ArC_q), 131.5 (Ar*C*H), 138.0 (ArC_q), 138.3 (ArC_q), 140.6 (ArC_q), 145.5 (ArC_q), 155.9 (-CONH).

HRMS (ESI$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_{35}H_{46}O_5N_2SiI_2Na$: 879.1158; found: 879.1123.

Di-*tert*-Butyl {[7-(*tert*-Butyldimethylsilyloxymethyl)-5,9-diiodopyrene-1,3-diyl]bis(methylene)}dicarbamate (8d)
To a solution of **7d** (32 mg, 37.3 μmol) dissolved in anhydrous toluene (5 mL), was added AuCl (3.5 mg, 14.9 μmol, 0.4 equiv) and the mixture was degassed, purged with argon and stirred at r.t. for 16 h. The solution was then concentrated under reduced pressure and purified by flash chromatography (CH_2Cl_2–EtOAc, 19:1) to give **8d**.

Yield: 12 mg (38%); pale-yellow solid; mp 176–177 °C; R_f = 0.40 (CH_2Cl_2–EtOAc, 9:1).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 0.25 [s, 6 H, -Si(CH_3)$_2$], 1.09 [s, 9 H, -SiC(CH_3)$_3$], 1.53 [s, 18 H, -OC(CH_3)$_3$], 4.97 (m, 4 H, -C*H*$_2$NH-), 5.04 (m, 2 H, -CH_2N*H*-), 5.27 (s, 2 H, -CH_2O-), 7.88 (s, 1 H, CH_a), 8.50 (s, 2 H, CH_c), 8.89 (s, 2 H, CH_b).

^{13}C NMR (125 MHz, CD_2Cl_2): δ = –4.8 [-Si(CH_3)$_2$], 18.9 (-SiC-), 26.5 [-SiC(*C*H_3)$_3$], 28.8 [-C(*C*H_3)$_3$], 43.1 (-CH_2NH_2-), 65.2 (-CH_2O-), 80.2 [-*C*(CH_3)$_3$], 100.3 (ArC_q), 123.8 (ArC_q), 124.7 (ArC_q), 126.6 (Ar*C*H), 129.1 (ArC_q), 129.6 (Ar*C*H), 131.5 (ArC_q), 133.0 (ArC_q), 135.2 (Ar*C*H), 141.8 (ArC_q), 156.3 (-CONH-).

HRMS (ESI$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_{35}H_{46}O_5N_2SiI_2Na$: 879.1158; found: 879.1181.

Acknowledgment

This work was supported by the Engineering and Physical Sciences Research Council (grant EP/D060192/1).

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

References

(1) (a) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*; Academic Press: New York, **1971**. (b) Winnik, F. M. *Chem. Rev.* **1993**, *93*, 587.

(2) (a) Kalyanasundaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 2039. (b) Lewis, F. D.; Zhang, Y. F.; Letsinger, R. L. *J. Am. Chem. Soc.* **1997**, *119*, 5451. (c) Wojczewski, C.; Stolze, K.; Engels, J. W. *Synlett* **1999**, 1667. (d) Okamoto, A.; Kanatani, K.; Saito, I. *J. Am. Chem. Soc.* **2004**, *126*, 4820. (e) Ziessel, R.; Goze, C.; Ulrich, G. *Synthesis* **2007**, 936. (f) Zhang, R. X.; Tang, D.; Lu, P.; Yang, X. Y.; Liao, D. L.; Zhang, Y. J.; Zhang, M. J.; Yu, C.; Yam, V. W. W. *Org. Lett.* **2009**, *11*, 4302.

(3) (a) Bock, H.; Helfrich, W. *Liq. Cryst.* **1995**, *18*, 387. (b) Benning, S. A.; Haßheider, T.; Keuker-Baumann, S.; Bock, H.; Della Sala, F.; Frauenheim, T.; Kitzerow, H.-S. *Liq. Cryst.* **2001**, *28*, 1105. (c) de Halleux, V.; Calbert, J. P.; Brocorens, P.; Cornil, J.; Declercq, J. P.; Brédas, J. L.; Geerts, Y. *Adv. Funct. Mater.* **2004**, *14*, 649. (d) Hayer, A.; de Halleux, V.; Köhler, A.; El-Garoughy, A.; Meijer, E. W.; Barberá, J.; Tant, J.; Levin, J.; Lehmann, M.; Gierschner, J.; Cornil, J.; Geerts, Y. H. *J. Phys. Chem. B* **2006**, *110*, 7653. (e) Sienkowska, M. J.; Farrar, J. M.; Zhang, F.; Kusuma, S.; Heiney, P. A.; Kaszynski, P. *J. Mater. Chem.* **2007**, *17*, 1399. (f) Diring, S.; Camerel, F.; Donnio, B.; Dintzer, T.; Toffanin, S.; Capelli, R.; Muccini, M.; Ziessel, R. *J. Am. Chem. Soc.* **2009**, *131*, 18177.

(4) (a) Yang, J. S.; Lin, C. S.; Hwang, C. Y. *Org. Lett.* **2001**, *3*, 889. (b) Kim, S. K.; Lee, S. H.; Lee, J. Y.; Bartsch, R. A.; Kim, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 16499. (c) Kim, S. K.; Bok, J. H.; Bartsch, R. A.; Lee, J. Y.; Kim, J. S. *Org. Lett.* **2005**, *7*, 4839. (d) Zhou, Y.; Zhu, C. Y.; Gao, X. S.; You, X. Y.; Yao, C. *Org. Lett.* **2010**, *12*, 2566. (e) Martínez, R.; Espinosa, A.; Tárraga, A.; Molina, P. *Tetrahedron* **2010**, *66*, 3662.

(5) (a) Nakashima, N.; Tomonari, Y.; Murakami, H. *Chem. Lett.* **2002**, 638. (b) Guldi, D. M.; Rahman, G. M. A.; Jux, N.; Balbinot, D.; Hartnagel, U.; Tagmatarchis, N.; Prato, M. *J. Am. Chem. Soc.* **2005**, *127*, 9830. (c) Tasis, D.; Tagmatarchis, N.; Bianco, A.; Prato, M. *Chem. Rev.* **2006**, *106*, 1105. (d) Ehli, C.; Rahman, G. M. A.; Jux, N.; Balbinot, D.; Guldi, D. M.; Paolucci, F.; Marcaccio, M.; Paolucci, D.; Melle-Franco, M.; Zerbetto, F.; Campidelli, S.; Prato, M. *J. Am. Chem. Soc.* **2006**, *128*, 11222.

(6) (a) Vollmann, H.; Becker, H.; Corell, M.; Streeck, H. *Justus Liebigs Ann. Chem.* **1937**, *531*, 1. (b) Ogino, K.; Iwashima, S.; Inokuchi, H.; Harada, Y. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 473.

(7) (a) Buu-Hoi, N. P.; Cagniant, P. *Ber. Dtsch. Chem. Ges. B* **1944**, *77*, 121. (b) Berg, A.; Jakobsen, H. J.; Johansen, S. R. *Acta Chem. Scand.* **1969**, *23*, 567.

(8) (a) Mitchell, R. H.; Boekelheide, V. *J. Am. Chem. Soc.* **1970**, *92*, 3510. (b) Umemoto, T.; Satani, S.; Sakata, Y.; Misumi, S. *Tetrahedron Lett.* **1975**, *36*, 3159. (c) Yamato, T.; Ide, S.; Tokuhisa, K.; Tashiro, M. *J. Org. Chem.* **1992**, *57*, 271. (d) Bodwell, G. J.; Miller, D. O.; Vermeij, R. J. *Org. Lett.* **2001**, *3*, 2093.
(9) (a) Kreyenschmidt, M.; Baumgarten, M.; Tyutyulkov, N.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1957. (b) Kreyenschmidt, M.; Uckert, F.; Müllen, K. *Macromolecules* **1995**, *28*, 4577.
(10) Kawano, S.-i.; Yang, C.; Ribas, M.; Baluschev, S.; Baumgarten, M.; Müllen, K. *Macromolecules* **2008**, *41*, 7933.
(11) (a) Bolton, R. *J. Chem. Soc.* **1964**, 4637. (b) Connor, D. M.; Allen, S. D.; Collard, D. M.; Liotta, C. L.; Schiraldi, D. A. *J. Org. Chem.* **1999**, *64*, 6888.
(12) (a) Bodwell, G. J.; Fleming, J. J.; Mannion, M. R.; Miller, D. O. *J. Org. Chem.* **2000**, *65*, 5360. (b) Kimball, D. B.; Haley, M. M.; Mitchell, R. H.; Ward, T. R. *Org. Lett.* **2001**, *3*, 1709. (c) Tsuji, T. *Modern Cyclophane Chemistry*; Gleiter, R.; Hopf, H., Eds.; Wiley-VCH: Weinheim, **2004**, 81. (d) Zhang, B.; Manning, G. P.; Dobrowolski, M. A.; Cyrański, M. K.; Bodwell, G. J. *Org. Lett.* **2008**, *10*, 273. (e) Merner, B. L.; Dawe, L. N.; Bodwell, G. J. *Angew. Chem. Int. Ed.* **2009**, *48*, 5487.
(13) Goldfinger, M. B.; Crawford, K. B.; Swager, T. M. *J. Am. Chem. Soc.* **1997**, *119*, 4578.
(14) Yao, T.; Campo, M. A.; Larock, R. C. *J. Org. Chem.* **2005**, *70*, 3511.
(15) (a) Fürstner, A.; Mamane, V. *J. Org. Chem.* **2002**, *67*, 6264. (b) Mamane, V.; Hannen, P.; Fürstner, A. *Chem. Eur. J.* **2004**, *10*, 4556.
(16) (a) Li, C.-W.; Wang, C.-I.; Liao, H.-Y.; Chaudhuri, R.; Liu, R.-S. *J. Org. Chem.* **2007**, *72*, 9203. (b) Feng, X.; Pisula, W.; Müllen, K. *Pure Appl. Chem.* **2009**, *81*, 2203. (c) Chan, J. M. W.; Tischler, J. R.; Kooi, S. E.; Bulović, V.; Swager, T. M. *J. Am. Chem. Soc.* **2009**, *131*, 5659. (d) Mukherjee, A.; Pati, K.; Liu, R.-S. *J. Org. Chem.* **2009**, *74*, 6311. (e) Storch, J.; Sýkora, J.; Čermák, J.; Karban, J.; Císařová, I.; Růžička, A. *J. Org. Chem.* **2009**, *74*, 3090. (f) Storch, J.; Čermák, J.; Karban, J.; Císařová, I.; Sýkora, J. *J. Org. Chem.* **2010**, *75*, 3137.
(17) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
(18) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(19) Burn, P. L.; Samuel, I. D. W.; Lo, S.-C. Int. Patent WO 02067343, **2002**.
(20) Barwell, N. P.; Crump, M. P.; Davis, A. P. *Angew. Chem. Int. Ed.* **2009**, *48*, 7673.
(21) Challinor, L.; Klein, E.; Davis, A. P. *Synlett* **2008**, 2137.
(22) Yamada, K.; Kurokawa, T.; Tokuyama, H.; Fukuyama, T. *J. Am. Chem. Soc.* **2003**, *125*, 6630.
(23) Modrakowski, C.; Flores, S. C.; Beinhoff, M.; Schlüter, A. D. *Synthesis* **2001**, 2143.