Synthesis of Unsymmetrical 1,4-Diarylbutadiynes by Stille Coupling

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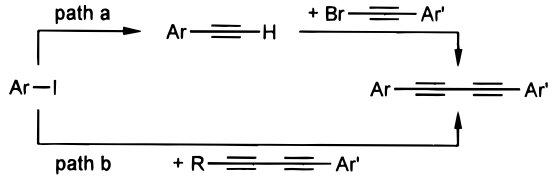
In the context of catenane synthesis we are interested in shape persistent,[1] angular molecules like **9**, containing substituted arylbutadiyne moieties attached to a central phenylene ring. A common method for the synthesis of such unsymmetrically substituted 1,4-diarylbutadiynes uses the Cadiot−Chodkiewicz coupling of arylethyne with 1-aryl-2-bromoethyne (Scheme 1, path a).[2,3] The yields are often moderate to good, depending on the actual substituents at the arylethyne and the bromoethyne. In a well known side reaction the bromoethyne dimerizes to give symmetrical 1,4-diarylbutadiyne. To no surprise, the reaction of 3,5-diethynyl-4-[(4-methoxybenzyl)oxy]-benzoic acid with 1-(4-iodophenyl)-2-bromoethyne under the typical Cadiot−Chodkiewicz conditions gave a considerable amount of 1,4-bis(4-iodophenyl)butadiyne. Use of 1-(4-iodophenyl)-2-*iodo*ethyne instead of 1-(4-iodophenyl)-2-*bromo*ethyne under conditions[5,6] reported not to give the dimerization product of the iodoethyne component resulted in a mixture of products including the dimerization product 1,4-bis(4-iodophenyl)butadiyne. This waste of rather precious arylethyne, troubles with the separation of the desired product from the dimerization product when working on a large scale, and the inherent problems of using reactions with only moderate yields on molecules with two to-be-transformed functionalities made us search for a better approach. Alternatively to the alkyne−alkyne coupling reaction, as in the mentioned Cadiot−Chodkiewicz coupling, one can consider an aryl−alkadiyne coupling to form diarylbutadiyne (Scheme 1, path b). Proper substituents R at the arylbutadiyne unit may be for example H, Cu, ZnCl, SnR'_3. Those substituents are known to allow for the coupling of arylethynes with aryl halides to give diarylethynes.[7−10] Little is known about such coupling reactions using the corresponding arylbutadiynes.[1e,11] This paper reports on the synthesis of the appropriate arylbutadiynes and their use in the formation of the angular molecules **9**.

Scheme 1. Formation of Unsymmetrical Diarylbutadiynes (R = e.g. H, Cu, ZnCl, SnR'_3)



Results and Discussion

The approach outlined in Scheme 1 as path b requires arylbutadiynes as prefabricated building blocks. These were synthesized starting from *para*-substituted aryl halides **1** (Scheme 2). In a first step the aryl halides **1** were coupled with propargyl alcohol or with (trimethylsilyl)acetylene to give the disubstituted acetylenes **2** and **3**, respectively.[7] The monosubstituted acetylenic compounds **4** were formed by reaction of compounds **2** with MnO_2 and KOH[12] or by reaction of compounds **3** with K_2CO_3 or NaOH. The acetylenes **4** were subsequently coupled with 3-bromoprop-2-ynol under the conditions of the Cadiot−Chodkiewicz reaction[2,13] to give diacetylenes **5**. The conversion of **4** was found to be nearly quantitative only when a large excess (3 equiv) of 3-bromoprop-2-ynol had been used. This is partly due to the unavoidable formation of the dimerization product hexa-2,4-diyne-1,6-diol. However, 3-bromoprop-2-ynol is a rather inexpensive reagent and separation of hexa-2,4-diyne-1,6-diol was easily achieved either by chromatography, distillation, or recrystallization. The reverse reaction of propargyl alcohol with 1-aryl-2-bromoethyne is possible, as tested for **5a**,**b**. However, as expected, in this case part of the valuable 1-bromo-2-(4-bromophenyl)ethyne or 1-bromo-2-tolylethyne was consumed by dimerization, and the isolation of pure **5a**,**b** became more tedious.

Treatment of **5** with suspended MnO_2 and KOH[12,13] for about 1 h gave the deprotected butadiynes **6** in a clean and quantitative reaction. Therefore storable compounds **5** appear to be valuable precursors for compounds **6**, which turned out to be rather instable when isolated free of solvent. The transformation is compatible with a variety of functionalities and protecting groups (Scheme 2). This synthesis of arylbutadiynes **6** via **5** starting from arylethynes **4** is a suitable alternative to the synthesis of butadiynes by cross-coupling of alkynes with 1-chloro-2-iodoethylene or 1,2-dichloroethylene followed by HCl-elimination from the 1-chloro-1-buten-3-yne derivatives by $NaNH_2/NH_3$[14] or Bu_4NF.[15] Compound **6a** and phenylbutadiyne were isolated free of solvent by filtering the reaction suspension of the acetylene deprotection step

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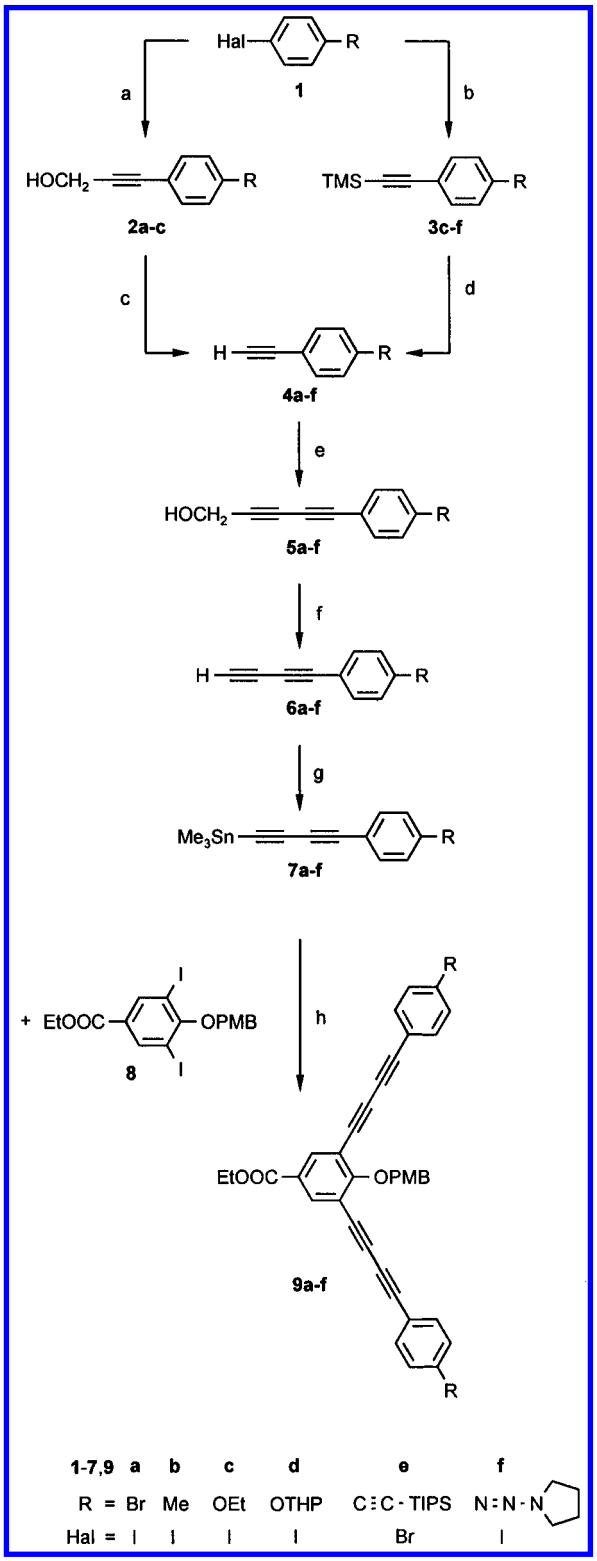
S0022-3263(97)00549-5 CCC: $14.00

Scheme 2[a]



[a] Key: PMB = 4-Methoxybenzyl; (a) $HOCH_2CCH$, $Pd(PPh_3)_2Cl_2$, CuI, piperidine, THF, 0 °C → rt, 83−88%; (b) for **3c**: **1c**, TMSCCH, $Pd(PPh_3)_2Cl_2$, CuI, piperidine, rt, 86%; for **3d**,**f**: **1d**, **f**, TMSCCH, $Pd(PPh_3)_2Cl_2$, CuI, Et_2NH, rt, 78% and 67%, respectively; for **3e**: (1) **1a**, TMSCCH, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, piperidine, 0 °C → rt; (2) TIPSCCH, 60 °C, 72%; (c) MnO_2, KOH, Et_2O, 77−85%; (d) K_2CO_3 or KOH, MeOH, 81−86%; (e) CuCl, $NH_2OH{\cdot}HCl$, 70% aqueous $EtNH_2$, MeOH, additional THF in the case of **4f**, for yields see Table 1; (f) MnO_2, KOH, Et_2O, additional CH_2Cl_2 in the case of **5c** and **f**; (g) Me_3SnNEt_2, Et_2O, additional CH_2Cl_2 in the case of **5c** and **f**, for yields see Table 1; (h) $Pd_2(dba)_3$, $AsPh_3$, THF, 60 °C, for yields see Table 1.

Table 1. Isolated Yields (%) of the Key Compounds 5, 7, and 9

	a	b	c	d	e	f
5	65	47	64	89	53	64
7[a]	47[b]	83	79	79	80	82
9	70	70	88	85	43[c]	31[d]

[a] Overall yield starting from **5**. [b] One reaction out of six gave a yield of 60%. [c] The reaction of **7e** with **8** was incomplete (ca. 80% conversion, estimated from the ^1H NMR spectrum). Therefore the isolation of pure **9e** resulted in a relatively low yield. [d] Compound **9f** was synthesized only once. The not optimized workup may account for the low yield.

and fractional distillation of the filtrate. The products were stored under argon in a freezer and used the next day for the coupling reaction. At room temperature the pure compounds turned partly insoluble within few hours.

For the synthesis of tolanes the most convenient method is the Pd/Cu-catalyzed coupling of arylethynes with aryl halides.[7] The analogous reaction of an arylbutadiyne (Scheme 1: R = H) with an aryl iodide had been reported.[11] However, the reaction of **6a** with **8** at room temperature in piperidine with $Pd(PPh_3)_2Cl_2$ and CuI as catalysts yielded starting material **8** and a considerable amount of olefinic products instead of product **9a**. The model reaction of phenylbutadiyne with the simple aryl iodide **1b** under the same conditions gave also a mixture of several products including alkenes.

As an alternative, the Stille coupling[10] between 1-aryl-2-(trimethylstannyl)butadiyne and aryl halide is suggested by the work of Bunz *et al.*[1e] The syntheses of stannylbutadiynes **7** were accomplished by treatment of **6** with (*N*,*N*-dimethylamino)trimethylstannane[10] using the filtrate of the conversion reaction of **5** to **6**. The possibility to skip aqueous workup prior to addition of an air- and water-sensitive reagent renders this procedure convenient and advantageous to other reported methods for the preparation of **6**.[14,15] The stannylbutadiynes **7** can be used either directly after removing the solvent or after distillation. The stannanes **7** were isolated in good yields with the exception of **7a** (Table 1). For unknown reasons, compound **7a** was reproducibly isolated in comparatively low yields. One factor might be the greater acidity of the acceptor-substituted arylbutadiyne **6a** compared to the other arylbutadiynes **6b**−**f**. Because no byproducts could be detected in the solution of **6a**, the compounds **5a** or **6a** must have been either partially trapped in the MnO_2/KOH precipitate or turned into insoluble material during the acetylene deprotection step. The stannylbutadiynes were stored in a freezer under argon for several months without any sign of decomposition. They also proofed stable at room temperature for several days when stored under argon. Reaction of the stannanes **7** with the diiodide **8** in THF in the presence of $Pd_2(dba)_3$/$AsPh_3$[16] gave the angular molecules **9** usually in good yields (Table 1). The reaction of **7a** with **8** shows that the iodide−bromide-selectivity,[17] used for the synthesis of **1e** and **2a**, works as well in this case of the Stille coupling. Other reaction conditions that had been reported for the Stille coupling,[10a,18] e.g. DMF instead of THF or $Pd(CH_3CN)_2Cl_2$ instead of $Pd_2(dba)_3$/$AsPh_3$, resulted in a very slow formation of **9**.

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In this paper a convenient and general way to a variety of arylbutadiynes **6** and their stannane derivatives **7** is described. The latter proved to be useful arylbutadiyne construction blocks for the synthesis of unsymmetrical 1,4-diarylbutadiynes as in compound **9**. The reported synthetic strategy is efficient, feasible on the gram scale, and compatible with a range of functionalities.

Experimental Section

General. All experiments were carried out under inert atmosphere (argon or nitrogen). Piperidine and dichloromethane were distilled from CaH_2. THF and diethyl ether were dried over sodium/benzophenone. The petroleum ether used had a boiling range of 30−40 °C. Activated MnO_2, $Pd_2(dba)_3$, and $AsPh_3$ were purchased from Aldrich. Me_3Sn-NEt_2[19] and 3-bromoprop-2-ynol[2a] were synthesized according to the literature. For flash chromatography, Merck silica gel (mesh 70−230) was used. TLC was performed on silica gel coated aluminum foil (Merck aluminum foils 60 F_{254}). If not otherwise mentioned, ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ as solvent and internal standard on a 300 MHz spectrometer. DEPT experiments were run to determine the multiplicity in the ^{13}C NMR spectra.

General Procedure for the Preparation of 5-Arylpenta-2,4-diynols 5a−f. The reactions were carried out using 2−10 g of starting material **4**.

Arylethyne **4** (10 mmol) was added to a degassed mixture of hydroxylamine hydrochloride (12 mmol) and CuCl (0.4 mmol) in methanol (5.5 mL) and aqueous 70% ethylamine (2.9 mL). In the case of **4f**, THF (4 mL) was added. To this intensely yellow suspension 3-bromoprop-2-ynol (30 mmol) diluted with methanol (36 mL) was added over the course of 20−30 min. The inside temperature was kept at 15−20 °C with the help of an dry ice/2-propanol bath. In case that the color changed to greenish, some additional hydroxylamine hydrochloride was added. After complete addition of 3-bromoprop-2-ynol, the cooling bath was removed and the suspension was stirred at rt for another 4 h. For workup, the suspension was poured into saturated aqueous NH_4Cl, the aqueous phase was extracted with diethyl ether (**5b**−**f**) or methylene chloride (**5a**), and the combined organic phases were washed with saturated aqueous NH_4Cl, dried (Na_2SO_4), and filtered. After removal of the solvent *in vacuo*, the residue was purified by flash chromatography (**5a,b**: methylene chloride; **5c**−**f**: petroleum ether/diethyl ether 1:1 v/v). The first fraction contained unreacted **4** and the second the diyne **5**.

5-(4-Bromophenyl)penta-2,4-diynol (5a). Heating of the second eluted fraction under vacuum (70 °C/0.01 mbar) to remove hexa-2,4-diyne-1,6-diol gave **5a** (65%) as a pale yellow solid residue: mp 138 °C (lit.[13]: 128−130 °C); ^1H NMR δ 1.83 (br s, 1H), 4.41 (s, 2H), 7.33, 7.45 (AA′BB′, 2H each); ^{13}C NMR (DMSO-d_6) δ 49.5, 67.8, 74.4, 76.3, 84.7, 119.7, 123.4, 131.9, 134.2. Anal. Calcd for $C_{11}H_7BrO$: C, 56.20; H, 3.00. Found: C, 56.14; H, 2.94.

5-(4-Methylphenyl)penta-2,4-diynol (5b). Recrystallization of the second eluted fraction from petroleum ether containing a small amount of diethyl ether gave **5b** (47%) as pale yellow flaky crystals: mp 82 °C; ^1H NMR δ 1.95 (s, 1H), 2.34 (s, 3H), 4.41 (s, 2H), 7.11 and 7.37 (AA′BB′, 2H each); ^{13}C NMR δ 21.6, 51.6, 70.6, 72.6, 78.9, 80.1, 118.2, 129.2, 132.5, 139.8. Anal. Calcd for $C_{12}H_{10}O$: C, 84.68; H, 5.92. Found: C, 84.72; H, 5.91.

5-[4-(Ethyloxy)phenyl]penta-2,4-diynol (5c). The diyne **5c** (64%) was obtained as a brownish solid: mp 109−110 °C; ^1H NMR δ 1.40 (t, J = 7.0 Hz, 3H), 1.86 (br s, 1H), 4.02 (q, J = 7.0 Hz, 2H), 4.40 (s, 2H), 6.81 and 7.40 (AA′BB′, 2H each); ^{13}C NMR δ 14.7, 51.7, 63.6, 70.8, 72.0, 79.0, 79.8, 113.1, 114.6, 134.2, 159.9. Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.94, H, 6.00.

5-[4-(Tetrahydropyran-2-yloxy)phenyl]penta-2,4-diynol (5d). Diyne **5d** (89%) was obtained as an off-white solid: mp 97 °C; ^1H NMR δ 1.5−2.1 (m, 6H), 3.59 (m, 1H), 3.84 (m, 1H), 4.39 (d, J = 6.2 Hz, 2H), 5.43 (t, J = 3.1 Hz, 1H), 6.98 and 7.41 (AA′BB′, 2H each); ^{13}C NMR δ 18.5, 25.0, 30.1, 51.5, 62.0, 70.5, 72.1, 78.7, 80.0, 96.1, 114.1, 116.4, 134.1, 157.8. Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.92, H, 6.25.

5-[4-[2-(Triisopropylsilyl)ethynyl]phenyl]penta-2,4-diynol (5e). Heating of the second eluted fraction under vacuum (60 °C/0.01 mbar) to remove hexa-2,4-diyne-1,6-diol gave **5d** (53%) as a brown oily residue: ^1H NMR δ 1.10 (s, 21H), 2.04 (br s, 1H), 4.40 (s, 2H), 7.39 (s, 4H); ^{13}C NMR δ 11.3, 18.6, 51.6, 70.3, 74.9, 78.1, 81.4, 93.9, 106.3, 121.1, 124.5, 132.0, 132.3. Anal. Calcd for $C_{22}H_{28}OSi$: C, 78.51; H, 8.39. Found: C, 78.57, H, 8.29.

5-[4-(3,3-Tetramethylenetriazeno)phenyl]penta-2,4-diynol (5f). Recrystallization of the second eluted fraction from ethanol gave **5f** (64%) as yellow needles: mp 144 °C; ^1H NMR[20] δ 2.02 (br t, 4H), 2.23 (br s, 1H), 3.78 (br s, 4H), 4.38 (s, 2H), 7.35 and 7.44 (AA′BB′, 2H each); ^{13}C NMR δ 23.7, 47 and 51 (very broad signals[20]), 51.5, 70.6, 73.0, 79.3, 80.5, 117.3, 120.3, 133.4, 152.0. Anal. Calcd for $C_{15}H_{15}N_3O$: C, 71.13; H, 5.97; N, 16.59. Found: C, 71.09, H, 6.09; N, 16.66.

General Procedure for the Preparation of (4-Arylbuta-1,3-diynyl)trimethylstannanes 7a−f. The reactions were carried out starting from 3−5 g of compounds **5**.

Compounds **5a,b,d,e** (10 mmol) were dissolved in diethyl ether (47 mL), **5c** (10 mmol) was dissolved in diethyl ether (14 mL) and methylene chloride (41 mL), and **5f** (10 mmol) was dissolved in diethyl ether (38 mL) and methylene chloride (19 mL). These solutions were cooled in an ice bath, and MnO_2 (100 mmol) and powdered KOH (50 mmol) were added. The suspensions were stirred well at rt, and the reactions were monitored by TLC (petroleum ether/diethyl ether 1:1). Usually they were complete after 1 h. If not, some more MnO_2 (10−50 mmol) and powdered KOH (5−25 mmol) were added. Upon completion of the reactions (usually after further 15 min), the precipitates were filtered off under inert atmosphere by use of a double-ended frit and washed several times with diethyl ether. (*N*,*N*-Diethylamino)trimethylstannane (11−13 mmol) was added to the slightly yellow filtrates. After 1 h of stirring at rt, the solvent was distilled off giving brown solids (**7a**−**d**,**f**) or a brown, very viscous oil (**7e**).

[4-(4-Bromophenyl)buta-1,3-diynyl]trimethylstannane (7a). Distillation (150 °C bath temp/0.001 mbar) gave **7a** (47%; one reaction out of six gave a yield of 60%) as a pale yellow solid: mp 80 °C; ^1H NMR δ 0.35 (s with Sn satellites,[21] 9H), 7.31 and 7.42 (AA′BB′, 2H each); ^{13}C NMR δ −7.68 (signal with Sn satellites[21]), 73.06, 75.53, 90.98, 93.27, 120.79, 123.47, 131.69, 133.98. Anal. Calcd for $C_{13}H_{13}BrSn$: C, 42.45; H, 3.56. Found: C, 42.15; H, 3.02.

[4-(4-Methylphenyl)buta-1,3-diynyl]trimethylstannane (7b). Distillation (104 °C bath temp/0.001 mbar) gave **7b** (83%) as a pale yellow solid: mp 62 °C; ^1H NMR δ 0.35 (s with Sn satellites,[21] 9H), 2.34 (s, 3H), 7.10 and 7.36 (AA′BB′, 2H each); ^{13}C NMR δ −7.7 (signal with Sn satellites[21]), 21.6, 73.7, 74.6, 91.3, 91.7, 118.5, 129.1, 132.5, 139.4. Anal. Calcd for $C_{14}H_{16}Sn$: C, 55.50; H, 5.32. Found: C, 55.61; H, 5.26.

[4-[4-(Ethyloxy)phenyl]buta-1,3-diynyl]trimethylstannane (7c). Distillation (160−170 °C bath temp/0.001 mbar) gave **7c** (79%) as a colorless solid: mp 66 °C; ^1H NMR δ 0.33 (s with Sn satellites,[21] 9H), 1.37 (t, J = 7.0 Hz, 3H), 3.98 (q, J = 7.0 Hz, 2H), 6.77 and 7.36 (AA′BB′, 2H each); ^{13}C NMR δ −7.68 (signal with Sn satellites[21]), 14.7, 63.5, 73.2, 74.6, 91.2, 91.7, 113.4, 114.6, 134.2, 159.7. Anal. Calcd for $C_{15}H_{18}OSn$: C, 54.10; H, 5.45. Found: C, 54.46, H, 5.37.

[4-[4-(Tetrahydropyran-2-yloxy)phenyl]buta-1,3-diynyl]trimethylstannane (7d). Distillation (175 °C bath temp/0.001 mbar) gave **7d** (79%) as a slightly yellow solid: mp 107 °C; ^1H NMR δ 0.34 (s with Sn satellites,[21] 9H), 1.5−2.1 (m, 6H), 3.59 (m, 1H), 3.84 (m, 1H), 5.41 (t, J = 3.0 Hz, 1H), 6.96 and 7.39 (AA′BB′, 2H each); ^{13}C NMR δ −7.7 (signal with Sn satellites[21]), 18.6, 25.1, 30.2, 62.0, 73.2, 74.5, 91.3, 91.5, 96.2,

(19) Jones, K.; Lappert, M. F. *J. Chem. Soc.* **1965**, 1944.

(20) Temperature dependent measurements of **3f** in $C_2D_2Cl_4$ revealed coalescence of the two signals at 47 and 51 ppm at higher temperature. At 80 °C they give a rather sharp signal with δ = 49.0. Furthermore the signal at 24 ppm sharpens when the temperature is raised. Similarly, the ^1H signals at 2 and 4 ppm get considerably narrower with temperature increase. This observation is explained with the conformational flexibility of the pyrrolidine ring.

(21) The satellites showed the expected coupling constants of 58 and 60 Hz for ^2J(H, Sn) and 388 and 406 Hz for $^1J(CH_3, Sn)$. The signal to noise ration of the ^{13}C NMR spectra was usually too low for detection of the Sn satellites of the alkyne signal.

114.4, 116.4, 134.1, 157.7. Anal. Calcd for $C_{18}H_{22}O_2Sn$: C, 55.57; H, 5.70. Found: C, 55.61, H, 5.73.

[4-[4-[2-(Triisopropylsilyl)ethynyl]phenyl]buta-1,3-diynyl]trimethylstannane (7e). The brown oil was heated to 80 °C/0.001 mbar in order to remove excess stannane reagent and trapped solvent. Product **7d** (80%) was obtained as a very viscous, black oil which was used without further purification: ^{1}H NMR δ 0.35 (s with Sn satellites,[21] 9H), 1.11 (s, 21 H), 7.39 (s, 4H); ^{13}C NMR δ −7.7 (signal with Sn satellites[21]), 11.3, 18.6, 73.8, 76.1, 91.1, 93.5, 93.7, 106.4, 121.6, 124.2, 131.9, 132.4. Anal. Calcd for $C_{24}H_{34}SiSn$: C, 61.42; H, 7.30. Found: C, 61.39, H, 7.33.

[4-[4-(3,3-Tetramethylenetriazeno)phenyl]buta-1,3-diynyl]trimethylstannane (7f). The crude material (82%) was used for further reactions. For elemental analysis a small portion was distilled (140 °C bath temp/0.001 mbar) to yield a yellow-brown solid: mp 128 °C; ^{1}H NMR[20] δ 0.33 (s with Sn-satellites,[21] 9H), 2.00 (br s, 4H), 3.78 (br m, 4H), 7.31 and 7.41 (AA′BB′, 2H each); ^{13}C NMR δ −7.8 (signal with Sn-satellites[21]), 23.6, 47 and 51 (very broad signals[20]), 74.1, 75.1, 91.5, 91.9, 117.7, 120.4, 133.5, 152.0. Anal. Calcd for $C_{17}H_{21}N_3Sn$: C, 52.89; H, 5.48; N, 10.88. Found: C, 52.93, H, 5.48; N, 10.79.

General Procedure for the Synthesis of the Angular Molecules 9a−f. The reactions were carried out using 1.6−3.5 g of starting compound **8**.

To a cooled (ice bath) solution of **8** (1 mmol) in THF (6.5 mL) were added $Pd_2(dba)_3$ (0.02 mmol) and $AsPh_3$ (0.16 mmol). The ice bath was removed, and the deep red mixture was stirred at rt until all of the catalyst had dissolved and the color had turned green. This solution was again cooled with an ice bath, and stannane **7** (2.1−2.2 mmol) was added. The reaction mixture was heated to 60 °C for 11−15 h whereupon it turned black. The solvent and most of the trimethyliodostannane were removed *in vacuo*. In the case of **9a**, the black residue was dissolved in THF (7.7 mL), and the product was precipitated by addition of diethyl ether. In the cases of **9b−f** the black residue was suspended in ethanol (2−5.4 mL; compound **9e** solidified in ethanol after cooling for some time to −18 °C), and the brown solid was isolated.

Angular Molecule 9a. Compound **9a** (70%) was obtained as a brownish solid: mp 170 °C; ^{1}H NMR δ 1.38 (t, J = 7.1 Hz, 3H), 3.78 (s, 3H), 4.35 (q, J = 7.1 Hz, 2H), 5.38 (s, 2H), 6.89 and 7.46 (AA′BB′, 2H each), 7.39 and 7.49 (AA′BB′, 4H each), 8.12 (s, 2H); ^{13}C NMR δ 14.3, 55.2, 61.5, 74.8, 76.0, 77.1, 79.1, 82.0, 113.8, 116.7, 120.4, 124.0, 126.0, 128.2, 130.4, 131.8, 133.9, 136.5, 159.8, 164.4, 165.9. Anal. Calcd for $C_{37}H_{24}Br_2O_4$: C, 64.18; H, 3.49. Found: C, 63.94, H, 3.69.

Angular Molecule 9b. The solid was purified by flash chromatography (methylene chloride) and then recrystallized from ethyl acetate giving **9b** (70%) as brownish needles: mp 127−128 °C; ^{1}H NMR δ 1.38 (t, J = 7.1 Hz, 3H), 2.38 (s, 6H), 3.77 (s, 3H), 4.35 (q, J = 7.1 Hz, 2H), 5.39 (s, 2H), 6.91 and 7.50 (AA′BB′, 2H each), 7.16 and 7.45 (AA′BB′, 4H each), 8.12 (s, 2H); ^{13}C NMR δ 14.2, 21.6, 55.2, 61.4, 73.1, 75.9, 76.2, 79.5, 83.5, 113.8, 116.9, 118.4, 125.9, 128.3, 129.3, 130.5, 132.5, 136.2, 139.9, 159.8, 164.5, 165.8. Anal. Calcd for $C_{39}H_{30}O_4$: C, 83.25; H, 5.37. Found: C, 82.85, H, 5.33.

Angular Molecule 9c. Filtration through silica gel (methylene chloride/petroleum ether 1:1 v/v) yielded **9c** (88%) as a brown solid: mp 120 °C; ^{1}H NMR δ 1.37 (t, J = 7.1 Hz, 3H), 1.42 (t, J = 7.0 Hz, 6H), 3.78 (s, 3H), 4.04 (q, J = 7.0 Hz, 4H), 4.35 (q, J = 7.1 Hz, 2H), 5.38 (s, 2H), 6.85 and 7.48 (AA′BB′, 4H each), 6.90 and 7.50 (AA′BB′, 2H each), 8.10 (s, 2H); ^{13}C NMR δ 14.3, 14.7, 55.2, 61.4, 63.6, 72.6, 75.8, 76.1, 79.7, 83.6, 113.2, 113.8, 114.7, 117.1, 126.0, 128.4, 130.5, 134.2, 136.1, 159.8, 160.0, 164.5, 165.7. Anal. Calcd for $C_{41}H_{34}O_6$: C, 79.08; H, 5.50. Found: C, 78.96, H, 5.51.

Angular Molecule 9d. Flash chromatography (methylene chloride) gave **9d** (85%) as a yellow-brown solid contaminated with catalyst, clearly to be seen in the ^{1}H NMR spectrum:[22] ^{1}H NMR δ 1.37 (t, J = 7.1 Hz, 3H), 1.5−2.1 (m, 12H), 3.61 (m, 2H), 3.78 (s, 3H); 3.86 (m, 2H), 4.35 (q, J = 7.1 Hz, 2H), 5.38 (s, 2H), 5.45 (t, J = 3.0 Hz, 2H), 6.90 and 7.50 (AA′BB′, 2H each), 7.02 and 7.48 (AA′BB′, 4H each), 8.10 (s, 2H); ^{13}C NMR δ 14.3, 18.6, 25.1, 30.2, 55.3, 61.4, 62.1, 72.7, 75.9, 76.1, 79.7, 83.5, 96.3, 113.9, 114.2, 116.6, 117.1, 126.0, 128.4, 130.5, 134.1, 136.2, 158.1, 159.8, 164.6, 165.8.

Angular Molecule 9e. Purification by flash chromatography (diethyl ether/petroleum ether 1:10 v/v) and subsequent recrystallization from ethanol containing some ethyl acetate gave **9e** (43%) as a greyish solid: mp 98 °C; ^{1}H NMR δ 1.12 (s, 42H), 1.38 (t, J = 7.1 Hz, 3H), 3.78 (s, 3H), 4.35 (q, J = 7.1 Hz, 2H), 5.39 (s, 2H), 6.89 (half of an AA′BB′ system, 2H), 7.46 (m, 10 H), 8.12 (s, 2H); ^{13}C NMR (CD_2Cl_2) δ 11.7, 14.4, 18.8, 55.6, 61.9, 75.5, 76.6, 77.8, 79.4, 83.1, 94.7, 106.7, 114.2, 117.1, 121.6, 125.1, 126.7, 128.7, 130.9, 132.4, 132.8, 136.8, 160.4, 164.6, 166.4. Anal. Calcd for $C_{59}H_{66}O_4Si_2$: C, 79.15; H, 7.43. Found: C, 78.95, H, 7.29.

Angular Molecule 9f. Purification by flash chromatography (starting with petroleum ether/diethyl ether 1:2 v/v and increasing the polarity with increasing the portion of diethyl ether) and subsequent recrystallization from acetone yielded **9f** (31%) as brown needles: mp 172 °C; ^{1}H NMR[20] δ 1.38 (t, J = 7.1 Hz, 3H), 2.03 (br s, 8H), 3.70 (br s, 4H), 3.78 (s, 3H), 3.90 (br s, 4H), 4.35 (q, J = 7.1 Hz, 2H), 5.39 (s, 2H), 6.91 (half part of an AA′BB′ system, 2H), 7.39 (half part of an AA′BB′ system, 4H), 7.50 (two half parts of two AA′BB′ systems, 6H), 8.11 (s, 2H); ^{13}C NMR[20] (CH_2Cl_2) δ 14.4, 24.1 (br), 46.9 (br), 51.7 (br), 55.6, 61.8, 73.7, 76.4, 76.9, 79.9, 84.5, 114.2, 117.37, 117.41, 120.8, 126.7, 128.8, 130.9, 133.9, 136.5, 152.9, 160.4, 164.7, 166.2. Anal. Calcd for $C_{45}H_{40}O_4N_6$: C, 74.16; H, 5.53; N, 11.53. Found: C, 73.77, H, 5.37; N, 11.35.

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Supporting Information Available: Experimental procedures and full characterization for the compounds **1**−**4** and **8** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(22) Although **9d** could not be obtained as a pure compound, **9** (R = OH) synthesized from **9d** in 91% yield was an analytically pure compound.