SYNTHESIS OF AROMATIC TRIYNES AS PRECURSORS TO HELICENE DERIVATIVES

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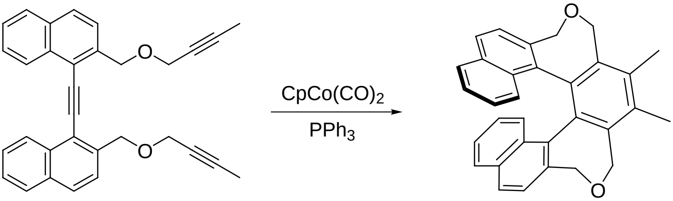
Dedicated to Professor Otakar Červinka on the occasion of his 75th birthday.

A general and versatile synthetic approach to a broad series of aromatic triynes as precursors to helicene derivatives has been developed. Employing a set of simple tools, triynes comprising the (phenylethynyl)benzene, 1-(phenylethynyl)naphthalene, and 1-(1-naphthylethynyl)-naphthalene moiety have been prepared in good to excellent yields throughout the whole reaction sequence. The methodology allows constructing various types of a junction between the central diarylacetylene moiety and the attached acetylene units to get the target triynes of general formula $R–C≡C–CH_2–X–CH_2–Ar–C≡C–Ar'–CH_2–X–CH_2–C≡C–R$ or $R–C≡C–CH_2CH_2–Ar–C≡C–Ar'–CH_2CH_2–C≡C–R$ (R = H, CH_3, TMS, or TIPS; X = O, NTs, or $C(CO_2CH_3)_2$; Ar/Ar′ = 2-phenylene or 2-naphthylene).

Key words: Acetylenes; Alkynes; Arenes; Ethers; Helicenes; Sonogashira reaction; Triynes; Cyclotrimerizations; Cross-coupling reactions.

During the last decade, a growing attention has been paid to helicene chemistry being induced by a general interest in artificial chiral molecules[1] and their exploitation[2]. However, fascinating helicenes[3] had earned a bad reputation in the past as hardly attainable molecules. The situation dramatically changed in the nineties namely due to a breakthrough in their synthesis made by Katz in 1990 (ref.[4]). His original methodology involving Diels–Alder cycloaddition of 1,4-benzoquinone to divinyl aromatics, which is surprisingly easy and general, has gradually become the first practical method for multigram-scale preparation of various substituted carbohelicenes[5] as well as heterohelicenes[6].

The discovery of Katz has inspired other groups to search for alternative nonphotochemical strategies to synthesize helicenes[7]. Recently, we have published a novel *organometallic* approach to helicene-like molecules as well as parent carbohelicenes based on intramolecular [2+2+2] cyclotrimerization of aromatic triynes under Co(I) or Ni(0) catalysis[8] (Scheme 1). We have shown that our *de novo* construction of a helical scaffold exhibits remarkable flexibility allowing synthesis of a series of products with five, six, and seven *ortho*-fused carbo- and/or heterocycles. However, the success of this methodology depends on the facile accessibility of the key aromatic triynes. Herein, we report simple and versatile methods for an assembly of the various aromatic triynes as precursors to helicene derivatives. To diversify the skeleton of target helices, we have altered aromatic parts, linkers, and terminal alkyne substituents at the aromatic triynes.



SCHEME 1

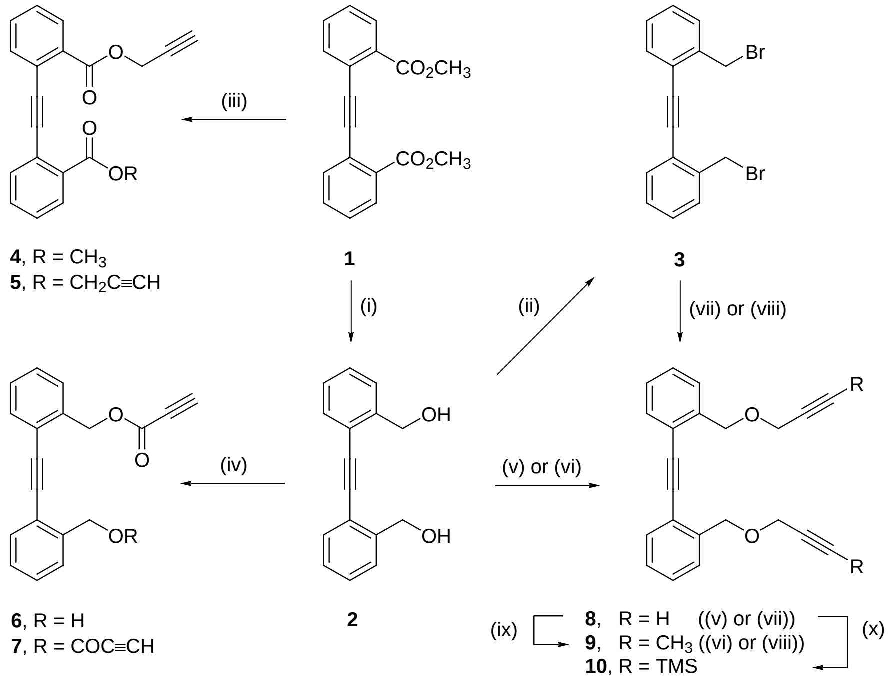
RESULTS AND DISCUSSION

Synthesis of Triynes Containing the (Phenylethynyl)benzene Moiety

Triynes comprising the (phenylethynyl)benzene moiety with two tethered acetylene units are designed as precursors of pentacyclic helical molecules. All triyne variations may be derived from three substituted (phenylethynyl)benzenes **1**–**3** that are readily available from commercial chemicals[9] (Scheme 2).

In order to attach the acetylene units to the (phenylethynyl)benzene moiety by an oxygen-containing three-atom ester-type tether, diester **1** was treated with excess of prop-2-yn-1-ol under basic conditions. Although some transesterification proceeded, the desired triyne **5** was obtained in low yield along with the minor diyne **4** (Scheme 2). Similarly, the attempt to connect the acetylene units by a complementary ester-type tether provided discouraging results because condensation of diol **2** with propiolic acid led only to a small amount of triyne **7** beside the major diyne **6**.

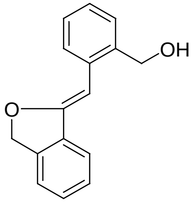
By contrast, a three-atom ether-type tether could be prepared more effectively. It may be constructed by alkylation of dialkoxide derived from diol **2** or, alternatively, by displacement of bromine atoms in dibromide **3** with alkoxides. To pursue the former approach, deprotonation of diol **2** with sodium hydride had to be carried out in THF at 0 °C otherwise, at higher temperature, the addition of an internal alkoxide nucleophile across the triple bond yielded the undesirable enol ether **11** (ref.[13]). The subsequent alkylation with prop-2-yn-1-yl bromide afforded triyne **8** in excellent yield but the same reaction with 1-bromobut-2-yne furnished triyne **9** in unsatisfactory yield (Scheme 2). In a complementary approach, benzylic substitu-



(i) $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ (1.2 equiv.), toluene, 0 °C, 15 min, 87%
(ii) PBr_3 (1.0 equiv.), THF, 0 °C, 30 min, 87%
(iii) $HOCH_2C{\equiv}CH$ (95 equiv.), K_2CO_3 (1.2 equiv.), 50 °C, overnight, 12% of **4**, 21% of **5**
(iv) $HC{\equiv}CCO_2H$ (2.0 equiv.), DCC (2.0 equiv.), DMAP (28 mole %), ether-THF (5 : 1), rt, overnight, 31% of **6**, 12% of **7**
(v) NaH (2.7 equiv.), THF, 0 °C, 30 min, then $BrCH_2C{\equiv}CH$ (4.3 equiv.), 0 °C to rt, overnight, 91%
(vi) NaH (2.4 equiv.), THF, 0 °C, 1 h, then $BrCH_2C{\equiv}CCH_3$ (4.1 equiv.), 0 °C to rt, overnight, 24%
(vii) $NaOCH_2C{\equiv}CH$ (2.4 equiv.), DMF, rt, 15 min, 79%
(viii) $NaOCH_2C{\equiv}CCH_3$ (2.2 equiv.), DMF, rt, overnight, 69% of **9**, 5% of **14**
(ix) BuLi (2.1 equiv.), THF, -78 °C, 10 min, then CH_3I (3.0 equiv.), -78 °C to rt, overnight, 62%
(x) BuLi (2.1 equiv.), THF, -78 °C, 10 min, then TMSCl (2.4 equiv.), -78 °C to rt, overnight, 71%

SCHEME 2

tion in dibromide **3** with sodium alkoxides derived from prop-2-yn-1-ol as well as but-2-yn-1-ol resulted in the formation of the desired triynes **8** and **9**, respectively, in good and comparable yields[14] (Scheme 2).



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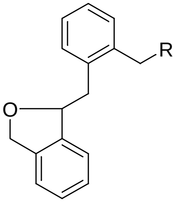
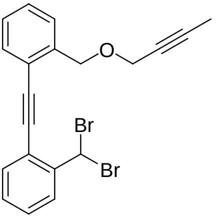


12, R = OH
13, R = H



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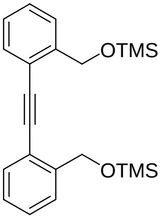

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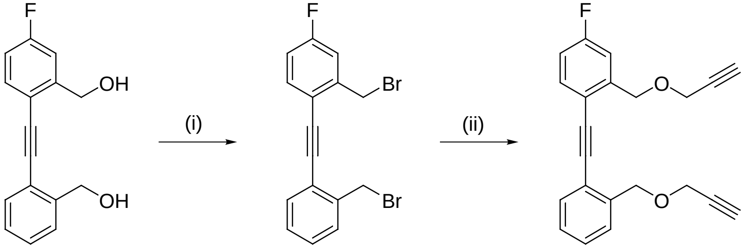
Triyne **8** with the terminal acetylene units has been shown to be a suitable substrate for further modifications. Generating the double lithium acetylide from **8** with butyllithium, the following reaction with methyl iodide or trimethylsilyl chloride gave rise to triynes **9** and **10** with the methyl or trimethylsilyl groups at the alkyne termini[16] (Scheme 2).

Owing to an increased susceptibility of the fluorinated diol **16** (ref.[10b]) to nucleophilic addition across the triple bond, the generation of dialkoxide from **16** was not possible (Scheme 3). Therefore, dibromide **17** was prepared and transformed in good yield by reaction with sodium prop-2-yn-1-olate to the fluorinated triyne **18**.

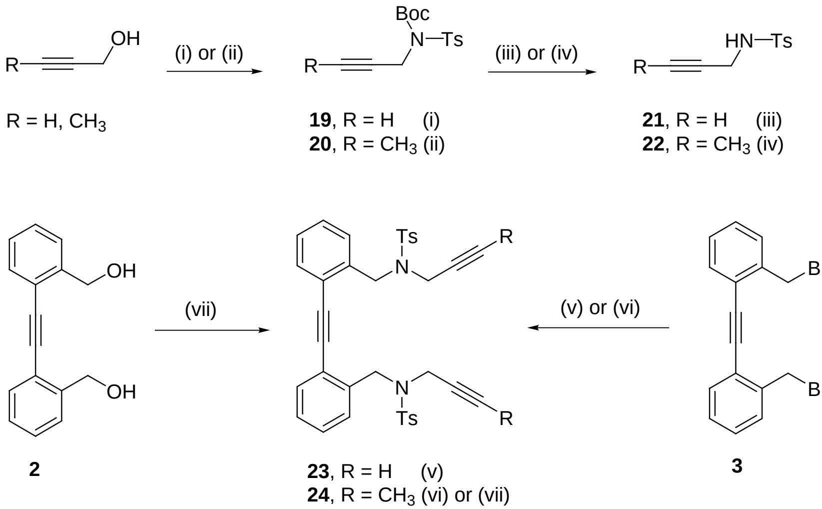


16 **17** **18**

(i) CBr_4 (2.3 equiv.), PPh_3 (2.1 equiv.), acetonitrile, rt, overnight, 80%
(ii) $NaOCH_2C{\equiv}CH$ (2.2 equiv.), DMF, rt, 10 min, 78%

SCHEME 3

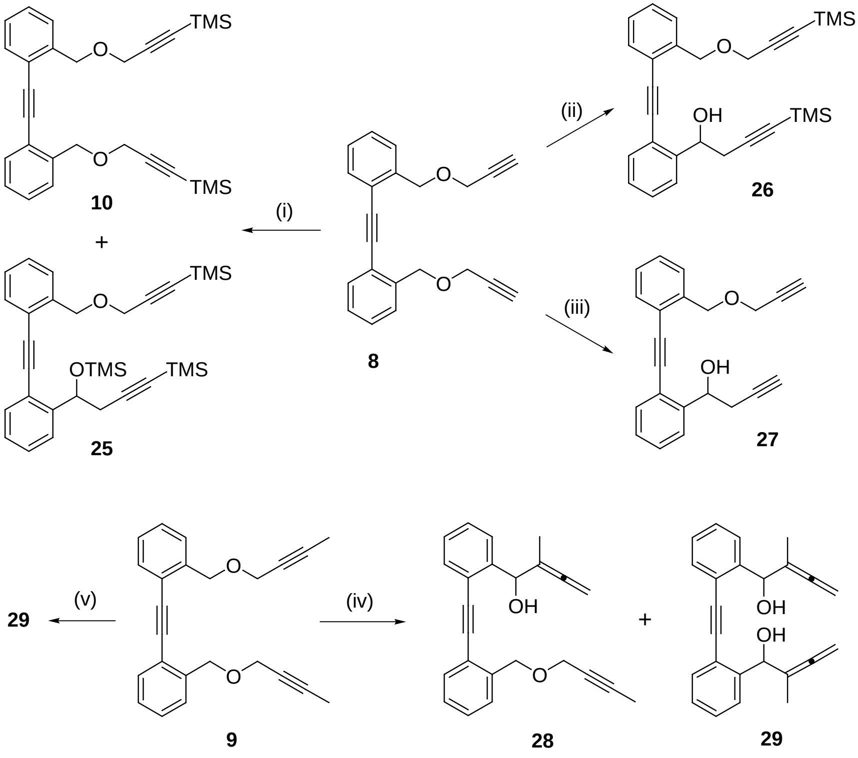
In order to attach acetylene units to the (phenylethynyl)benzene moiety by a nitrogen-containing three-atom amide-type tether, dibromide **3** was treated with sodium salt of *N*-(prop-2-yn-1-yl)sulfonamide **21** (ref.[17]) as well as *N*-(but-2-yn-1-yl)sulfonamide[18] (**22**) (Scheme 4). The reactions gave triyne **23** in low yield and triyne **24** in moderate yield. The latter compound was prepared alternatively by the Mitsunobu reaction from diol **2** and *N*-(but-2-yn-1-yl)sulfonamide (**22**) in better yield.



(i) BocNHTs (1.5 equiv.), DEAD (2.5 equiv.), PPh_3(3.0 equiv.), THF, rt, overnight, 76%
(ii) BocNHTs (1.4 equiv.), DEAD (2.4 equiv.), PPh_3(2.9 equiv.), THF, rt, overnight, 78%
(iii) CF_3CO_2H (3.0 equiv.), CH_2Cl_2, rt, 45 min, 87%
(iv) CF_3CO_2H (3.3 equiv.), CH_2Cl_2, rt, 4 h, 88%
(v) **21** (2.0 equiv.), NaH (2.1 equiv.), DMF, 0 ^oC to rt, overnight, 27%
(vi) **22** (2.0 equiv.), NaH (2.6 equiv.), THF-DMF (6 : 1), 65 ^oC, 20 min, 63%
(vii) **22** (2.0 equiv.), DEAD (2.6 equiv.), PPh_3 (3.0 equiv.), THF, rt, 1 h, 72%

SCHEME 4

The tethers in triynes **8** and **9** called for the Wittig rearrangement[21] to contract the three-atom junction to the two-atom junction and, therefore, to diversify further the family of triynes. Therefore triynes **8** and **9** were treated with a strong base and subsequently with an electrophile (Scheme 5). In the case of triyne **8** with the terminal acetylene units, a single [1,2] rearrangement proceeded being initialized by deprotonation uniformly at the benzylic position. Triynes **25**–**27** bearing only one contracted tether were isolated in low or modest yield. By contrast, triyne **9** with the methylated acetylene units exhibited a different behavior. The proton abstraction also took place at the benzylic position but the rearrangement proceeded in a [1,4] fashion involving the propargylic shift. Hence, a 2 : 1 mixture of bisallene **29** and monoallene **28** was obtained in moderate yield. Under different conditions, bisallene **29** was formed as the main product in modest yield.



(i) BuLi (2.4 equiv.), THF, -78 ^{o}C, 40 min, then TMSCl (2.6 equiv.), -78 ^{o}C to rt, overnight, 48% of **10**, 22% of **25**, 22% recovery of **8**

(ii) BuLi (4.9 equiv.), THF, -78 ^{o}C, 1.5 h, then TMSCl (5.1 equiv.), -78 ^{o}C to rt, overnight, 23%

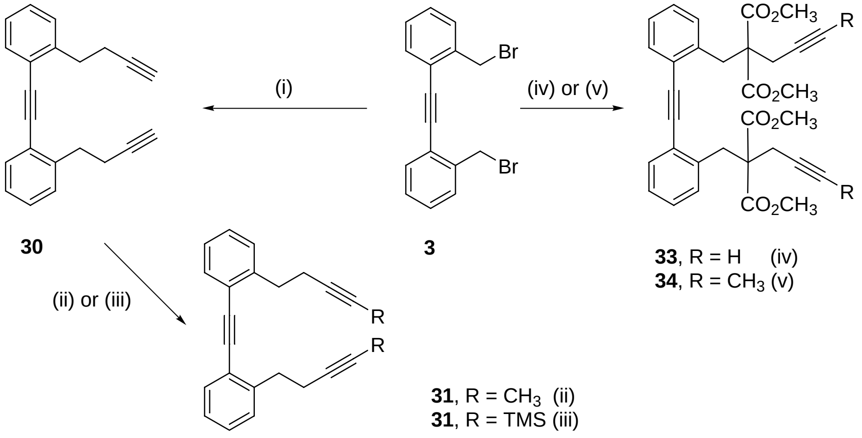
(iii) BuLi (5.0 equiv.), THF, -78 ^{o}C, 30 min, then CH_3I (5.6 equiv.), -78 ^{o}C to rt, 3 h, 31%

(iv) BuLi (2.6 equiv.), THF, -78 ^{o}C, 30 min, then CH_3I (3.4 equiv.), -78 ^{o}C to rt, 3 h, 14% of **28**, 28% of **29** as a 1 : 1 mixture of the (*R*,R**) and (*R*,S**) diastereoisomers (^{1}H NMR)

(v) *tert*-BuLi (2.5 equiv.), THF, -78 ^{o}C, 2 h, then H_2O (excess), -78 ^{o}C to rt, overnight, 31%, a 1 : 1 mixture of the (*R*,R**) and (*R*,S**) diastereoisomers (^{1}H NMR)

SCHEME 5

As the attempt to prepare triynes with all-carbon-atom tethers *via* the Wittig rearrangement failed due to insufficient yields, alternative and more efficient approaches to the construction of an ethane or propane junction were developed (Scheme 6). Concerning a two-carbon-atom tether, displacement of bromine in dibromide **3** with $LiCH_2C{\equiv}CTMS$ (generated *in situ* from trimethyl(prop-1-yn-1-yl)silane and butyllithium) proceeded smoothly to build up a triyne framework, however, with partially desilylated terminal alkyne units. Therefore, the reaction mixture was instantly treated with an excess of Bu_4NF and this one-pot procedure afforded triyne **30** with the terminal acetylene units in good yield[8c]. Deprotonation of **30** with butyllithium and the subsequent reactions of the double lithium acetylide with electrophiles cleanly provided triynes **31** and **32** with the methyl or trimethylsilyl groups at the acetylene termini. Similarly, the reactions of dibromide **3** with stabilized carbon nucleophiles generated *in situ* from dimethyl 2-(prop-2-yn-1-yl)malonate[22] or dimethyl 2-(but-2-yn-1-yl)-malonate[23] by sodium hydride led to triynes **33** and **34** in good or high yield to demonstrate an efficient approach to a three-carbon-atom tether.



(i) $LiCH_2C{\equiv}CTMS$ (2.1 equiv.), THF, -78 °C, 1 h, then Bu_4NF (8.0 equiv.) in THF, rt, 16 h, 67%

(ii) BuLi (2.2 equiv.), THF, -78 °C, 10 min, then CH_3I (2.2 equiv.), -78 °C, 15 min, 91%

(iii) BuLi (2.1 equiv.), THF, -78 °C, 10 min, then TMSCl (2.1 equiv.), -78 °C, 15 min, 98%

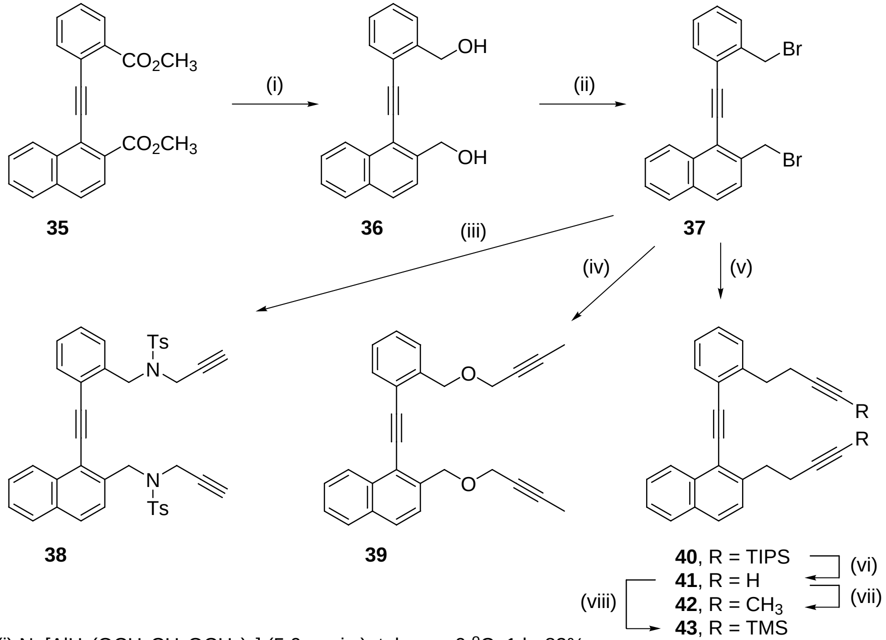
(iv) $(HC{\equiv}CCH_2)NaC(CO_2CH_3)_2$ (2.1 equiv.), THF, rt, 30 h, 60%

(v) $(CH_3C{\equiv}CCH_2)NaC(CO_2CH_3)_2$ (2.2 equiv.), THF, rt, 1 h, 86%

SCHEME 6

Synthesis of Triynes Containing the 1-(Phenylethynyl)naphthalene Moiety

Triynes comprising the 1-(phenylethynyl)naphthalene moiety with two tethered acetylene units are designed as precursors to the hexacyclic helical molecules. The chemistry of the 1-(phenylethynyl)naphthalene-derived triynes **38**–**43** exhibits almost the same features as the chemistry of their (phenylethynyl)benzene counterparts (Scheme 7). Accordingly, the synthesis started with diester **35** which is available from the corresponding aromatic building blocks by employing the aryl-alkynyl coupling methodology[11]. Diester **35** was routinely reduced to diol **36** and then converted to dibromide **37** that was a common substrate for all branches of the uniform reaction scheme.



(i) $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ (5.0 equiv.), toluene, 0 °C, 1 h, 82%

(ii) PBr_3 (1.4 equiv.), THF, 0 °C, 2 h, 65%

(iii) **21** (2.6 equiv.), NaH (2.8 equiv.), DMF, 0 °C to rt, overnight, 99%

(iv) $NaOCH_2C{\equiv}CCH_3$ (2.2 equiv.), DMF, rt, 2 h, 68%

(v) $LiCH_2C{\equiv}CTIPS$ (2.3 equiv.), THF, -78 °C, 1 h, 74%

(vi) Bu_4NF (4.9 equiv.), THF, rt, 1 h, 97%

(vii) BuLi (2.2 equiv.), THF, -78 °C, 10 min, then CH_3I (2.5 equiv.), -78 °C, 20 min, 93%

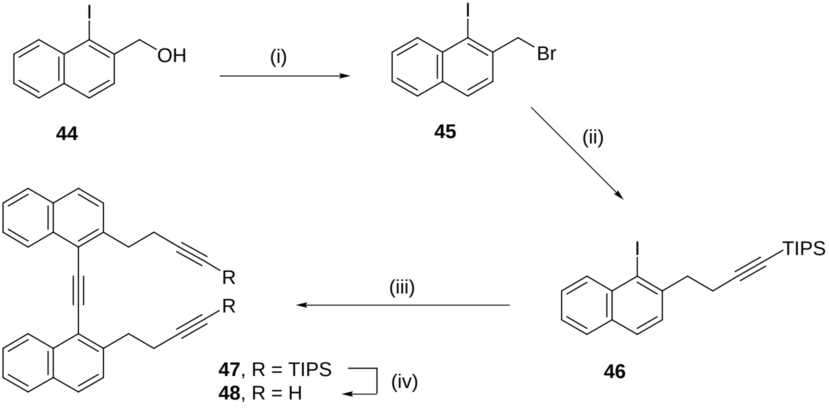
(viii) BuLi (2.2 equiv.), THF, -78 °C, 10 min, then TMSCl (2.7 equiv.), -78 °C, 20 min, 93%

SCHEME 7

Dibromide **37** allowed building up the triyne framework in one step regardless of the tether type that it comprised. Reaction with *N*-(prop-2-yn-1-yl)sulfonamide (**21**) in the presence of a base afforded triyne **38** with the three-atom nitrogen-containing tethers in excellent yield. The base-mediated alcoholysis with but-2-yn-1-ol furnished triyne **39** with the three-atom oxygen-containing tethers in good yield. On treatment with $LiCH_2C{\equiv}CTIPS$ (generated *in situ* from triisopropyl(prop-1-yn-1-yl)silane and butyllithium), the bis-silylated triyne **40** containing the two-carbon-atom tethers was obtained in good yield[8c]. The stable TIPS groups, being untouched by the lithium reagent, were easily removed by Bu_4NF to get triyne **41** with the terminal acetylene units in nearly quantitative yield[8c]. The latter compound was further modified at the alkyne termini by deprotonation followed by a quench with an electrophile to afford triynes **42** and **43** in excellent yields.

Synthesis of Triynes Containing the 1-(1-Naphthylethynyl)naphthalene Moiety

Triynes comprising the 1-(1-naphthylethynyl)naphthalene moiety with two tethered acetylene units are designed as precursors to the heptacyclic helical molecules. The synthesis of triynes **47** and **48** relied on a slightly different strategy (Scheme 8). The readily available alcohol **44** (ref.[11]) was



(i) PBr_3 (0.5 equiv.), THF, 0 °C, 1 h, 94%

(ii) $LiCH_2C{\equiv}CTIPS$ (1.2 equiv.), THF, -78 °C, 2.5 h, 69%

(iii) $HC{\equiv}CH_{(g)}$, $Pd(PPh_3)_4$ (6 mole %), CuI (10 mole %), piperidine, 80 °C, 2 h, 77%

(iv) Bu_4NF (4.3 equiv.), THF, rt, 1 h, 70%

SCHEME 8

converted to bromide **45** which on reaction with $LiCH_2C≡CTIPS$ allowed the attachment of a side arm with a protected alkyne unit to obtain iodide **46** in good yield. The naphthalene building block was coupled with gaseous acetylene under Pd(0)/Cu(I) catalysis to give triyne **47** with the two-carbon-atom tethers in good yield. Desilylation with Bu_4NF gave triyne **48** in good yield as well.

CONCLUSION

Employing a set of simple synthetic tools, a broad series of triynes derived from the (phenylethynyl)benzene, 1-(phenylethynyl)naphthalene, and 1-(1-naphthylethynyl)naphthalene moiety has been prepared. Effective methods have been developed to construct various types of a junction between the central diarylacetylene moiety and the attached acetylene units comprising the three-atom oxygen-, nitrogen-, and all-carbon-containing tethers as well as the two-carbon-atom tether. The target triynes have been obtained in good to excellent yields throughout the whole reaction sequence enabling also a multigram-scale preparation.

EXPERIMENTAL

General

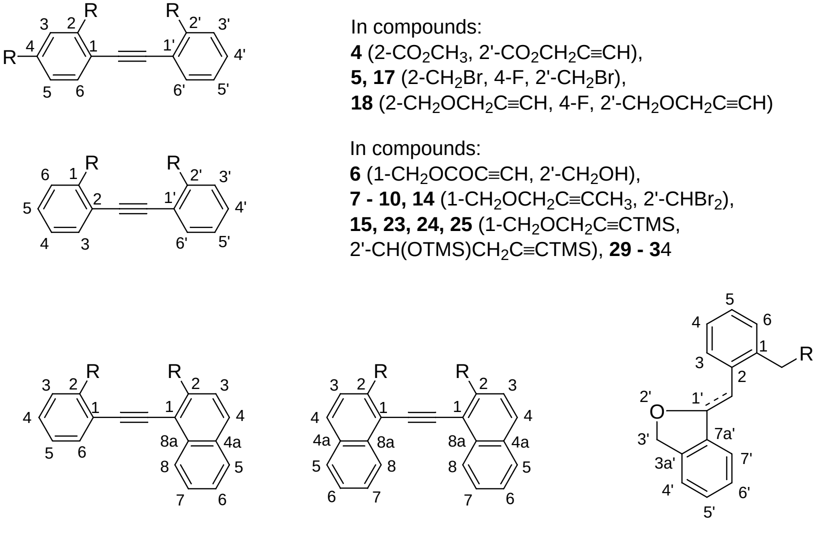
Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. ^{1}H NMR spectra were measured at 499.8 or 200.0 MHz, ^{13}C NMR spectra at 125.7 MHz, in $CDCl_3$ with TMS as an internal standard or in acetone-d_6 (referenced to acetone). ^{19}F NMR spectra were measured at 470.3 MHz in $CDCl_3$ with $CFCl_3$ as an internal standard. Chemical shifts are given in δ-scale, coupling constants J are given in Hz (Fig. 1). HMBC experiments were setup for J_{C-H} = 5 Hz. For correct assignment of both ^{1}H and ^{13}C NMR spectra of key compounds, the HCOSY and HMQC experiments were performed. For all the other compounds, the general semiempirical equations were applied to the chemical shift assignments. IR spectra were measured in $CHCl_3$ or CCl_4. EI MS spectra were determined at an ionizing voltage of 70 eV. FAB MS spectra were measured using the thioglycerol–glycerol 3 : 1, dithiothreitol–dithioerythritol 5 : 1 or bis(2-hydroxyethyl)disulfide matrix. HR MS spectra were obtained by the EI or FAB technique. GC MS analyses were carried out on a DB-5 column (0.25 × 30 m × 0.25 μm). All reactions were performed under argon. Reagent grade materials purchased from Sigma–Aldrich, Fluka, Merck, and Avocado were used as received. THF and ether were freshly distilled from sodium/benzophenone under nitrogen; piperidine was distilled from calcium hydride under argon and degassed by three freeze-pump-thaw cycles before use; toluene was freshly distilled from phosphorus pentoxide under argon; dichloromethane was freshly distilled from calcium hydride under argon; acetonitrile was distilled from calcium hydride under argon and stored over 4Å molecular sieves; DMF was distilled from calcium hydride under reduced pressure and stored over 4Å molecular sieves. The reactions with gaseous acetylene under 1 atm pressure were performed in a vessel connected to a rubber balloon filled with acetylene directly from a cylinder. TLC was performed on Silica gel 60 F_{254}-coated aluminium sheets (Merck) and spots were detected by the solution of $Ce(SO_4)_2 \cdot 4H_2O$ (1%) and $H_3P(Mo_3O_{10})_4$ (2%) in sulfuric acid (10%). Flash chromatography was performed on Silpearl silica gel (Kavalier Votice, Czech Republic) or Silica gel 60 (0.040–0.063 mm or <0.063 mm, Merck). Semipreparative HPLC was carried out on a silica gel column (Partisil M9, Whatman 10/50, 500 mm × 10 mm; sample injections on a 10–20 mg scale) using a refractometric detector.

[Ethynediylbis(2,1-phenylene)]dimethanol (**2**)

$Na[AlH_2(OCH_2CH_2OCH_3)_2]$ (3.5 M solution in toluene, 3.5 ml, 12.25 mmol, 1.2 equivalent) was added dropwise during a 5 min period to a solution of diester **1** (ref.[10]) (1.5 g, 5.097 mmol) in dry toluene (15 ml) under argon at 0 °C. After stirring at room temperature for 15 min, the unreacted hydride reagent was carefully decomposed by adding saturated aqueous solution of Na_2SO_4. The reaction mixture was filtered through a short pad of silica gel using acetone, the solvents were evaporated *in vacuo* and the residue was crystallized from petroleum ether–acetone to get diol **2** (1.05 g, 87%). ^{1}H NMR (200 MHz, acetone-d_6) spectrum was in accord with the literature data[11].

Bis[2-(bromomethyl)phenyl]acetylene (**3**)

Phosphorus tribromide (280 μl, 2.95 mmol, 1.0 equivalent) was added to diol **2** (ref.[11]) (703 mg, 2.95 mmol) in dry THF (5 ml) at 0 °C under nitrogen. After stirring at 0 °C for 30 min, the solvent was removed *in vacuo*. Flash chromatography on silica gel (petroleum



In compounds:
4 (2-CO_2CH_3, 2'-$CO_2CH_2C{\equiv}CH$),
5, 17 (2-CH_2Br, 4-F, 2'-CH_2Br),
18 (2-$CH_2OCH_2C{\equiv}CH$, 4-F, 2'-$CH_2OCH_2C{\equiv}CH$)

In compounds:
6 (1-$CH_2OCOC{\equiv}CH$, 2'-CH_2OH),
7 - 10, 14 (1-$CH_2OCH_2C{\equiv}CCH_3$, 2'-$CHBr_2$),
15, 23, 24, 25 (1-$CH_2OCH_2C{\equiv}CTMS$,
2'-$CH(OTMS)CH_2C{\equiv}CTMS$), **29 - 3**4

In compounds: **36 - 43**

In compounds: **47, 48**

In compounds: **11 -13**

FIG. 1
Numbering of aromatics as utilized in 1H and 13 C NMR spectra signal assignments

ether–ether–acetone 80 : 10 : 10) gave dibromide **3** (929 mg, 87%) as a white solid. ^{1}H NMR (200 MHz, acetone-d_6) spectrum was in accord with the literature data[12a].

Methyl Prop-2-yn-1-yl 2,2′-Ethynediyldibenzoate (**4**)

Dimethyl ester **1** (ref.[10]) (53 mg, 0.180 mmol) and anhydrous potassium carbonate (30 mg, 0.217 mmol, 1.2 equivalent) in prop-2-yn-1-ol (1 ml, 17.18 mmol, 95 equivalents) were stirred in a tightly stoppered flask at 50 °C overnight. The mixture was cooled to room temperature and evaporated to dryness under vacuum of the oil pump. The residue was partitioned between ether and water, the ethereal phase was separated and the aqueous phase was extracted with ether (4×). The ethereal portions were combined, washed with brine (1×), dried over Na_2SO_4 and evaporated *in vacuo*. Repeated preparative HPLC on silica gel (petroleum ether–acetone 85 : 15 and 87 : 13, respectively) gave methyl prop-2-yn-1-yl ester **4** (7 mg, 12%) as an oil and the more polar di(prop-2-yn-1-yl) ester **5** (13 mg, 21%) as a white solid. Compound **4**: IR (CCl_4): 3 392 w, 3 313 m, 3 070 w, 3 022 vw, 2 133 vw, 1 735 vs, 1 722 s, 1 597 w, 1 568 w, 1 493 m, 1 448 m, 1 434 w, 1 367 w, 1 291 s, 1 264 m, 1 251 vs, 1 247 vs, 1 191 w, 1 163 w, 1 129 m, 1 078 m, 1 069 m, 700 w, 673 w, 665 w, 632 w. ^{1}H NMR (500 MHz, $CDCl_3$): 2.47 (d, 1 H, *J* = 2.4, HC≡C); 3.96 (s, 3 H, CH_3); 4.97 (d, 2 H, *J* = 2.4, CH_2); 7.40 (ddd, 1 H, *J* = 7.9, 7.5, 1.3, 4-H); 7.41 (ddd, 1 H, *J* = 7.9, 7.5, 1.4, 4′-H); 7.51 (dt, 1 H, *J* = 7.5, 7.5, 1.4, 5-H); 7.54 (dt, 1 H, *J* = 7.5, 7.5, 1.4, 5′-H); 7.74 (ddd, 1 H, *J* = 7.7, 1.3, 0.6, 6′-H); 7.78 (ddd, 1 H, *J* = 7.6, 1.4, 0.6, 6-H); 7.99 (ddd, 1 H, *J* = 7.9, 1.4, 0.6, 3-H); 8.04 (ddd, 1 H, *J* = 7.9, 1.3, 0.6, 3′-H). ^{13}C NMR ($CDCl_3$): 52.19 (q, CH_3), 52.56 (t, CH_2), 75.06 (d, HC≡C), 77.76 (s, HC≡C), 92.87 (s, ArC≡CAr′), 93.54 (s, ArC≡CAr′), 123.80 (s, C-2), 124.21 (s, C-2′), 128.15 (d, C-4′), 128.18 (d, C-4), 130.44 (d, C-3), 130.73 (d, C-3′), 130.90 (s, C-1′), 131.70 (d, C-5), 131.83 (s, C-1), 132.15 (d, C-5′), 134.42 (d, C-6′), 134.47 (d, C-6), 165.26 (s, CO_2CH_2), 166.62 (s, CO_2CH_3). EI MS (*m/z*, rel.%): 287 ($(M - CH_3O)^+$, 3), 279 (100), 264 (27), 248 (11), 235 (5), 220 (17), 180 (8), 176 (7), 163 (10), 152 (5), 132 (3), 88 (5), 39 (5), 28 (8). FAB MS (*m/z*, thioglycerol–glycerol matrix): 319 ($(M + H)^+$), 287, 279, 263, 248, 220, 189, 186, 176, 163, 151, 115, 77. HR FAB MS: calculated for $C_{20}H_{15}O_4$ (M + H) 319.0970, found 319.0883.

Di(prop-2-yn-1-yl) 2,2′-ethynediyldibenzoate (**5**). M.p. 112.5–113.5 °C (methanol). IR (CCl_4): 3 392 w, 3 313 m, 3 070 w, 2 133 vw, 1 738 s, 1 724 m, 1 597 w, 1 568 w, 1 493 w, 1 448 w, 1 367 w, 1 287 m, 1 265 w, 1 248 vs, 1 163 w, 1 128 m, 1 072 s, 699 w, 674 w, 632 w. ^{1}H NMR (500 MHz, $CDCl_3$): 2.47 (t, 2 H, *J* = 2.6, 2 × HC≡); 4.97 (d, 4 H, *J* = 2.6, 2 × CH_2); 7.41 (dt, 2 H, *J* = 7.6, 7.6, 1.2, 4,4′-H); 7.54 (dt, 2 H, *J* = 7.6, 7.6, 1.4, 5,5′-H); 7.79 (dd, 2 H, *J* = 7.8, 1.2, 6,6′-H); 8.04 (dd, 2 H, *J* = 7.9, 1.4, 3,3′-H). ^{13}C NMR ($CDCl_3$): 52.57 (t, 2 × CH_2), 75.07 (d, 2 × HC≡C), 77.76 (s, 2 × HC≡C), 93.28 (s, ArC≡CAr), 124.11 (s, C-2,2′), 128.20 (d, C-5,5′), 130.70 (d, C-6,6′), 130.87 (s, C-1,1′), 132.10 (d, C-3,3′), 134.54 (d, C-4,4′), 165.23 (s, 2 × C=O). EI MS (*m/z*, rel.%): 303 ($(M - C_3H_3)^+$, 59), 275 (8), 264 (100), 248 (13), 231 (6), 220 (11), 208 (22), 180 (24), 176 (14), 163 (26), 152 (16), 137 (4), 104 (5), 88 (8), 76 (8), 63 (5), 39 (18). FAB MS (*m/z*, thioglycerol–glycerol matrix): 343 ($(M + H)^+$), 303, 287, 265, 249, 179, 165, 147, 91, 87, 73, 61, 57. HR FAB MS: calculated for $C_{22}H_{15}O_4$ (M + H) 343.0970, found 343.1022.

2-{[2-(Hydroxymethyl)phenyl]ethynyl}benzyl Propiolate (**6**)

N,*N*-Dimethylpyridin-4-amine (7 mg, 0.057 mmol, 28 mole %) in dry ether (1 ml) was added to propiolic acid (27 μl, 0.433 mmol, 2.0 equivalents) in dry ether (1 ml) at room temperature under argon. The yellowish suspension was formed and then diol **2** (ref.[11]) (50 mg, 0.210 mmol) in a mixture of dry ether–THF (3 ml, 2 : 1) and *N,N′*-dicyclohexylcarbodiimide (87 mg, 0.420 mmol, 2.0 equivalents) in dry ether (1 ml) were added. The reaction mixture was stirred at room temperature overnight. The orange precipitate was filtered off, the filtrate was evaporated to dryness and the residue was passed through a short pad of silica gel (petroleum ether–acetone 75 : 25). The crude product was purified by preparative HPLC (petroleum ether–acetone 75 : 25) to get diester **7** (8 mg, 12%) and more polar monoester **6** (19 mg, 31%) as amorphous solids. Compound **6**: IR (CCl_4): 3 617 w, 3 463 vw, 3 306 w, 3 069 w, 3 027 w, 2 942 m, 2 928 w (sh), 2 859 w, 2 125 w, 1 722 m, 1 687 m, 1 612 s, 1 575 vw, 1 491 w, 1 460 vw, 1 377 w, 1 338 w, 1 230 w (sh), 1 221 m, 1 151 m, 1 114 m, 1 019 w, 690 vw, 655 vw. ^{1}H NMR (500 MHz, $CDCl_3$): 2.17 (brs, 1 H, OH); 2.91 (s, 1 H, HC≡C); 4.92 (brs, 2 H, CH_2Ar'); 5.48 (s, 2 H, CH_2Ar); 7.31 (dt, 1 H, J = 7.6, 7.6, 1.5, 5′-H); 7.37 (brdt, 1 H, J = 7.6, 7.6, 2.0, 4′-H); 7.37–7.41 (m, 2 H, 4,5-H); 7.47–7.49 (m, 1 H, 6-H); 7.50 (brd, 1 H, J = 7.7, 6′-H); 7.57 (dt, 1 H, J = 7.6, 7.6, 1.5, 3′-H); 7.58–7.60 (m, 1 H, 3-H). ^{13}C NMR ($CDCl_3$): 63.96 (t, CH_2Ar'), 66.42 (t, CH_2Ar), 75.27 (d, HC≡C), 90.88 (s, ArC≡CAr′), 92.06 (s, ArC≡CAr′), 121.15 (s, C-1′), 122.91 (s, C-2), 127.56 (d, C-3′), 127.59 (d, C-5′), 128.74 (d, C-4), 128.83 (d, C-6), 129.09 (d, C-4′, 5), 132.46 (d, C-3), 132.47 (d, C-6′), 135.85 (s, C-1), 142.51 (s, C-2′), 152.57 (s, CO); signal of HC≡C was not identified. EI MS (*m/z*, rel.%): 290 ($M^{+\bullet}$, 15), 259 (6), 237 (11), 220 (100), 202 (19), 191 (84), 178 (29), 165 (34), 119 (15), 115 (34), 105 (13), 94 (29), 77 (26), 69 (15), 63 (14), 53 (56), 43 (24). FAB MS (*m/z*, thioglycerol–glycerol matrix): 291 ($(M + H)^+$), 273, 253, 245, 221, 219, 203, 191, 178, 165, 149, 135, 115, 105. HR EI MS: calculated for $C_{19}H_{14}O_3$ 290.0943, found 290.0893.

2-({2-[(Propioloyloxy)methyl]phenyl}ethynyl)benzyl propiolate (**7**). IR (CCl_4): 3 306 w, 3 254 w, 3 070 vw, 3 030 vw, 2 929 m, 2 855 w, 2 123 w, 2 115 w (sh), 1 722 vs, 1 613 w, 1 491 w, 1 371 w, 1 337 vw, 1 216 vs, 1 150 w, 1 115 w, 999 w, 965 w, 713 w, 690 w, 655 w. ^{1}H NMR (500 MHz, $CDCl_3$): 2.89 (s, 2 H, 2 × HC≡C); 5.49 (s, 4 H, 2 × CH_2); 7.37–7.39 (m, 4 H, 4,4′,5,5′-H); 7.52–7.54 (m, 2 H, 3′,6-H); 7.58–7.60 (m, 2 H, 3,6′-H). ^{13}C NMR ($CDCl_3$): 66.22 (t, 2 × CH_2), 75.16 (d, 2 × HC≡C), 91.40 (s, ArC≡CAr′), 94.78 (s, 2 × HC≡C), 122.62 (s, C-1′,2), 128.70 (d, C-4,5′), 128.89 (d, C-3′,6), 128.95 (d, C-4′,5), 132.61 (d, C-3,6′), 137.17 (s, C-1,2′), 152.49 (s, 2 × CO). EI MS (*m/z*, rel.%): 342 ($M^{+\bullet}$, 8), 243 (21), 219 (37), 215 (55), 204 (34), 202 (38), 191 (38), 189 (50), 178 (37), 165 (42), 152 (15), 139 (11), 115 (31), 101 (8), 91 (18), 77 (15), 63 (11), 53 (100), 39 (10). FAB MS (*m/z*, thioglycerol–glycerol matrix): 329, 253, 225, 205, 179, 147, 105. HR EI MS: calculated for $C_{22}H_{14}O_4$ 342.0891, found 342.1034.

Bis(2-{[(prop-2-yn-1-yl)oxy]methyl}phenyl)acetylene (**8**)

Method A. Diol **2** (ref.[11]) (258 mg, 1.08 mmol) in dry THF (2 ml) was added dropwise to sodium hydride (80% suspension in mineral oil, 89 mg, 2.97 mmol, 2.7 equivalents) in dry THF (6 ml) at 0 °C under argon. After stirring at 0 °C for 30 min, prop-2-yn-1-yl bromide (350 μl, 4.61 mmol, 4.3 equivalents) was added and the mixture was stirred at 0 °C to room temperature overnight. The solvent was removed *in vacuo* and the crude product was purified by flash chromatography on silica gel (petroleum ether–acetone 90 : 10) to obtain triyne **8** (311 mg, 91%) as a white solid.

Method B. Prop-2-yn-1-ol (430 μl, 7.39 mmol, 2.4 equivalents) was added dropwise to sodium hydride (80% suspension in mineral oil, 230 mg, 7.67 mmol, 2.4 equivalents) in dry DMF (5 ml) under argon and the mixture was stirred at room temperature for 15 min. Dibromide **3** (ref.[12]) (1.14 g, 3.14 mmol) in dry DMF (10 ml) was added. After stirring at room temperature for 15 min, the reaction mixture was partitioned between ether and water. The ethereal layer was separated and the aqueous phase was extracted with ether (2×). The ethereal portions were combined, washed with water (2×), dried over Na_2SO_4 and evaporated *in vacuo* to dryness. Flash chromatography on silica gel (petroleum ether–ether 90 : 10) afforded triyne **8** (776 mg, 79%) as a white solid, m.p. 51–53 °C (petroleum ether–ether). IR ($CHCl_3$): 3 303 m, 2 862 w, 2 120 vw, 1 606 w, 1 483 m, 1 355 m, 1 079 s, 948 w, 672 vs, 636 m. ^{1}H NMR (500 MHz, $CDCl_3$): 2.46 (t, 2 H, *J* = 2.4, 2 × HC≡C); 4.28 (d, 4 H, *J* = 2.4, 2 × HC≡CC**H**$_2$); 4.88 (s, 4 H, CH_2Ar, CH_2Ar′); 7.30 (dt, 2 H, *J* = 7.5, 7.5, 1.4, 4′,5-H); 7.37 (dt, 2 H, *J* = 7.5, 7.5, 1.5, 4,5′-H); 7.52 (brd, 2 H, *J* = 7.7, 3,6′-H); 7.56 (dd, 2 H, *J* = 7.5, 1.3, 3′,6-H). ^{13}C NMR ($CDCl_3$): 57.99 (t, 2 × HC≡CCH$_2$), 70.15 (t, CH_2Ar, CH_2Ar′), 74.97 (d, 2 × HC≡C), 79.47 (s, 2 × HC≡C), 91.72 (s, ArC≡CAr′), 122.29 (s, C-1′,2), 127.86 (d, C-4,5′), 128.20 (d, C-4′,5), 128.94 (d, C-3′,6), 132.50 (d, C-3,6′), 139.38 (s, C-1,2′). EI MS (*m/z*, rel.%): 314 (M$^{+•}$, 8), 257 (11), 245 (15), 229 (29), 219 (100), 215 (29), 203 (32), 189 (37), 178 (32), 165 (29), 115 (14), 91 (10), 71 (11), 57 (16), 43 (14). FAB MS (*m/z*, dithiothreitol–dithioerythritol matrix): 315 ((M + H)$^+$), 276, 258, 244, 229, 215, 202, 191, 178, 165, 149, 115, 86, 71. HR FAB MS: calculated for $C_{22}H_{19}O_2$ (M + H) 315.1385, found 315.1579.

Bis(2-{[(but-2-yn-1-yl)oxy]methyl}phenyl)acetylene (**9**)

Method A. Diol **2** (ref.[11]) (80 mg, 0.336 mmol) in dry THF (2 ml) was added to sodium hydride (80% suspension in mineral oil, 23 mg, 0.800 mmol, 2.4 equivalents) in dry THF (4 ml) at 0 °C under argon. After stirring at 0 °C for 1 h, 1-bromobut-2-yne (120 μl, 1.37 mmol, 4.1 equivalents) was added and the mixture was stirred at 0 °C to room temperature overnight. The solvent was removed *in vacuo* and the crude product was subsequently purified by flash chromatography on silica gel (petroleum ether–ether 90 : 10) and preparative HPLC on silica gel (petroleum ether–acetone 95 : 5) to obtain triyne **9** (28 mg, 24%) as an oil.

Method B. But-2-yn-1-ol (1.34 ml, 17.91 mmol, 2.2 equivalents) was added dropwise over a 30 min period to sodium hydride (80% suspension in mineral oil, 534 mg, 17.80 mmol, 2.2 equivalents) in dry DMF (12 ml) under stirring while temperature was kept below 15 °C. The yellowish suspension was stirred at room temperature for 1.5 h. Dibromide **3** (ref.[12]) (3.0 g, 8.24 mmol) in dry DMF (10 ml) was added dropwise over a 10 min period and the resulting green solution was left at room temperature overnight. The reaction mixture was partitioned between ether and water. The ethereal layer was separated and the aqueous phase was extracted with ether (2×). The ethereal portions were combined, washed with water (2×), dried over Na_2SO_4 and evaporated *in vacuo*. Flash chromatography on silica gel (petroleum ether–ether 90 : 10) afforded rearranged dibromide **14** (191 mg, 5%) and more polar triyne **9** (1.97 g, 69%) as oils.

Method C. Butyllithium (1.6 M solution in hexanes, 420 μl, 0.672 mmol, 2.1 equivalents) was added dropwise to terminal alkyne **8** (100 mg, 0.318 mmol) in dry THF (2 ml) at –78 °C under argon. After stirring at –78 °C for 10 min, methyl iodide (60 μl, 0.964 mmol, 3.0 equivalents) was added and the mixture was stirred at –78 °C to room temperature overnight. The solvents were removed *in vacuo*. Flash chromatography on silica gel (petroleum ether–ether 98 : 2 to 95 : 5) afforded dimethylated triyne **9** (67 mg, 62%) as an oil. IR ($CHCl_3$): 3 070 w, 2 944 w, 2 922 m, 2 893 w, 2 856 m, 2 243 w, 2 225 w, 1 601 w, 1 572 w, 1 492 m, 1 452 m, 1 386 m, 1 356 m, 1 107 m (sh), 1 101 m, 1 074 vs, 1 021 m, 951 m.

^{1}H NMR (500 MHz, $CDCl_3$): 1.83 (t, 6 H, J = 2.3, $2 \times CH_3$); 4.24 (q, 4 H, J = 2.3, $2 \times CH_3C{\equiv}CC\mathbf{H}_2$); 4.85 (brs, 4 H, CH_2Ar, CH_2Ar'); 7.28 (dt, 2 H, J = 7.6, 7.6, 1.5, 4,5′-H); 7.36 (dt, 2 H, J = 7.6, 7.6, 1.5, 4′,5-H); 7.52 (brdd, 2 H, J = 7.8, 1.4, 3′,6-H); 7.55 (dd, 2 H, J = 7.6, 1.5, 3,6′-H). ^{13}C NMR ($CDCl_3$): 3.56 (q, $2 \times CH_3$), 58.35 (t, $2 \times CH_3C{\equiv}CCH_2$), 69.72 (t, CH_2Ar, CH_2Ar'), 75.14 (s, $2 \times CH_3C{\equiv}C$), 82.78 (s, $2 \times CH_3C{\equiv}C$), 91.47 (s, $ArC{\equiv}CAr'$), 121.97 (s, C-1′,2), 127.43 (d, C-4,5′), 127.87 (d, C-4′,5), 128.63 (d, C-3′,6), 132.13 (d, C-3,6′), 139.54 (s, C-1,2′). EI MS (*m/z*, rel.%): 342 ($M^{+\bullet}$, 28), 309 (8), 289 (22), 271 (11), 259 (17), 235 (48), 219 (79), 203 (48), 178 (57), 165 (35), 149 (30), 133 (46), 97 (46), 91 (22), 83 (48), 69 (100), 57 (90), 43 (57), 29 (11). FAB MS (*m/z*, dithiothreitol–dithioerythritol matrix): 343 ($(M + H)^+$), 289, 243, 228, 219, 191, 165, 115. HR EI MS: calculated for $C_{24}H_{22}O_2$ 342.1619, found 342.1567.

Bis[({[3-(trimethylsilyl)prop-2-yn-1-yl]oxy}methyl)phenyl]acetylene (**10**)

Butyllithium (1.6 M solution in hexanes, 420 μl, 0.672 mmol, 2.1 equivalents) was added dropwise to terminal alkyne **8** (100 mg, 0.318 mmol) in dry THF (2 ml) at –78 °C under argon. After stirring at –78 °C for 10 min, trimethylsilyl chloride (100 μl, 0.788 mmol, 2.5 equivalents) was added and the mixture was stirred at –78 °C to room temperature overnight. The solvents were removed *in vacuo*. Flash chromatography on silica gel (petroleum ether–ether 90 : 10) afforded disilylated triyne **10** (103 mg, 71%) as an oil. IR ($CHCl_3$): 3 068 vw, 2 960 m, 2 926 m, 2 901 w, 2 854 w, 2 173 w, 1 601 w, 1492 w, 1 453 w, 1 408 w, 1 351 w, 1 252 s, 1 113 w, 1 102 w, 1 079 s, 1 028 w, 949 vw, 847 vs, 654 w. ^{1}H NMR (500 MHz, $CDCl_3$): 0.16 (s, 18 H, $6 \times CH_3$); 4.28 (s, 4 H, $2 \times (CH_3)_3SiC{\equiv}CC\mathbf{H}_2$); 4.86 (brs, 4 H, CH_2Ar, CH_2Ar'); 7.29 (dt, 2 H, J = 7.4, 7.4, 1.5, 4,5′-H); 7.36 (dt, 2 H, J = 7.6, 7.6, 1.4, 4′,5-H); 7.52 (ddd, 2 H, J = 7.6, 1.4, 0.7, 3′,6-H); 7.55 (dd, 2 H, J = 7.7, 1.4, 3,6′-H). ^{13}C NMR ($CDCl_3$): –0.24 (q, $6 \times CH_3$), 58.61 (t, $2 \times (CH_3)_3SiC{\equiv}CCH_2$), 69.95 (t, CH_2Ar, CH_2Ar'), 91.49 (s, $ArC{\equiv}CAr'$), 96.69 (s, $2 \times (CH_3)_3SiC{\equiv}CCH_2$), 101.53 (s, $2 \times (CH_3)_3SiC{\equiv}CCH_2$), 121.99 (s, C-1′,2), 127.51 (d, C-4,5′), 127.98 (d, C-4′,5), 128.63 (d, C-3′,6), 139.36 (s, C-1,2′). EI MS (*m/z*, rel.%): 458 ($M^{+\bullet}$, 2), 419 (13), 347 (27), 317 (11), 219 (41), 204 (27), 191 (11), 111 (13), 83 (25), 73 (100), 43 (9). HR EI MS: calculated for $C_{25}H_{31}O_2Si_2$ ($M - C_3H_3$) 419.1863, found 419.1830.

(*Z*)-{2-[((1*H*,3*H*)-2-Benzofuran-1-ylidene)methyl]phenyl}methanol (**11**)

Dry THF (5 ml) was added to diol **2** (ref.[11]) (30 mg, 0.126 mmol) and sodium hydride (80% suspension in mineral oil, 10 mg, 0.333 mmol, 2.6 equivalents) under argon and the yellowish suspension was stirred at 50 °C for 1.5 h. The excess of sodium hydride was decomposed with water and the mixture was evaporated *in vacuo* to dryness. The residue was dissolved in acetone and quickly passed through a short pad of silica gel to get enol ether **11** (29 mg, 97%) as a white solid, m.p. 103–105 °C (petroleum ether–acetone). IR ($CHCl_3$): 3 606 w, 3 066 w, 2 942 w, 2 932 w, 2 877 m, 1 654 m, 1 612 w, 1 599 m, 1 488 m, 1 468 m, 1 460 m, 1 452 m, 1 376 m, 1 332 w, 1 297 m, 1 236 m, 1 183 m, 1 097 m, 1 062 m, 1 039 vs, 1 005 m (sh), 996 s, 946 w, 604 w, 584 w, 528 w, 462 w. ^{1}H NMR (500 MHz, acetone-d_6): 4.24 (t, 1 H, J = 3.6, OH); 4.86 (d, 2 H, J = 3.6, $HOC\mathbf{H}_2$); 5.62 (s, 2 H, 3′-H); 6.40 (s, 1 H, -CH=); 7.19 (dt, 1 H, J = 7.6, 7.6, 1.4, 5-H); 7.32 (dt, 1 H, J = 7.8, 7.8, 1.7, 4-H); 7.47–7.58 (m, 4 H, 4′,5′,6′,7′-H); 7.82 (brd, 1 H, J = 8.3, 3-H); 8.27 (dd, 1 H, J = 7.8, 1.4, 6-H). ^{13}C NMR (acetone-d_6): 63.33 (t, $HOCH_2$), 75.52 (t, C-3′), 92.52 (d, -CH=), 120.96 (d, C-3), 122.44 (d, C-6′), 125.92 (d, C-5), 127.64 (d, C-4), 128.31 (d, C-5′), 128.96 (d, C-4′), 129.12 (d, C-6), 129.84 (d, C-7′), 135.01 (s, C-2), 135.69 (s, C-7a′), 139.05 (s, C-3a′), 140.54 (s, C-1), 157.45 (s, C-1′). EI MS (*m/z*, rel.%): 238 ($M^{+\bullet}$, 30), 181 (10), 161 (10), 135 (24), 119 (27), 104 (100), 91 (16), 77 (15), 69 (35), 57 (27), 43 (20). HR EI MS: calculated for $C_{16}H_{14}O_2$ 238.0993, found 238.1003.

{2-[((1*H*,3*H*)-2-Benzofuran-1-yl)methyl]phenyl}methanol (**12**) and 1-(2-Methylbenzyl)-(1*H*,3*H*)-2-benzofuran (**13**)

Enol ether **11** (30 mg, 0.126 mmol) in ethanol (8 ml) was hydrogenated (1 atm) over palladium on charcoal (10% Pd/C, 5 mg) at room temperature for 22 h. The catalyst was filtered off and the filtrate was evaporated to dryness. Flash chromatography on silica gel (petroleum ether–ether–acetone–methanol 80 : 10 : 10 : 0 to 50 : 30 : 17 : 3) afforded the deoxygenated product **13** (9 mg, 33%) and the more polar alcohol **12** (9 mg, 31%) as oils. Compound **12**: ^{1}H NMR (200 MHz, $CDCl_3$): 3.12 (dd, 1 H, *J* = 14.0, 7.9, CH_2); 3.33 (dd, 1 H, *J* = 14.0, 3.7, CH_2); 3.85 (brs, 1 H, OH); 4.55 (dd, 1 H, *J* = 11.6, 3.2, 3′-H); 4.70 (d, 1 H, *J* = 11.6, 3′-H); 4.98 (s, 2 H, $C\mathbf{H}_2OH$); 5.48 (ddd, 1 H, *J* = 7.9, 3.7, 3.2, 1′-H); 7.12–7.40 (m, 8 H, 3,4,4′,5,5′,6,6′,7′-H). Compound **13**: IR ($CHCl_3$): 3 077 m, 1 604 w, 1 493 m, 1 480 m, 1 462 s, 1 380 w, 1 364 m, 1 289 w, 1 254 m, 1 156 w, 1 132 w, 1 110 m, 1 036 vs, 1 018 s (sh), 942 m, 864 w, 562 w, 557 w, 459 m. ^{1}H NMR (500 MHz, $CDCl_3$): 2.32 (s, 3 H, CH_3); 3.06 (dd, 1 H, *J* = 14.2, 7.6, CH_2); 3.10 (dd, 1 H, *J* = 14.2, 5.6, CH_2); 5.04 (brd, 1 H, *J* = 12.2, 3′-H); 5.12 (dd, 1 H, *J* = 12.2, 2.7, 3′-H); 5.49 (brddd, 1 H, *J* = 7.6, 5.6, 2.7, 1′-H); 7.14–7.29 (m, 8 H, 3,4,4′,5,5′,6,6′,7′-H). ^{13}C NMR ($CDCl_3$): 19.76 (q, CH_3), 39.94 (t, CH_2), 72.41 (t, C-3′), 83.87 (d, C-1′), 120.98 (d, C-3), 121.59 (d, C-6′), 125.84 (d, C-5), 126.53 (d, C-4′), 127.07 (d, C-5′), 127.54 (d, C-4), 130.10 (d, C-6), 130.25 (d, C-7′), 136.16 (s, C-3a′), 136.73 (s, C-1), 139.42 (s, C-7a′), 141.75 (s, C-2). EI MS (*m/z*, rel.%): 223 ($(M - 1)^+$, 13), 178 (7), 151 (10), 133 (63), 105 (100), 91 (17), 77 (35), 65 (9), 51 (19), 39 (10). FAB MS (*m/z*, thioglycerol–glycerol matrix): 223 ($(M - H)^+$), 221, 205, 193, 178, 165, 131, 115, 105, 91, 77, 65. HR EI MS: calculated for $C_{16}H_{15}O$ (M – H) 223.1123, found 223.1124.

But-2-yn-1-yl 2-{[2-(Dibromomethyl)phenyl]ethynyl}benzyl Ether (**14**)

For preparation, see **9** (Method *B*). IR ($CHCl_3$): 3 097 w, 3 071 m, 2 947 m, 2 922 s, 2 856 s, 2 294 w, 2 243 w, 2 215 m, 1 601 m, 1 567 m, 1 491 vs, 1 476 m, 1 450 s, 1 386 m, 1 356 s, 1 151 s, 1 138 s, 1 108 s, 1 074 vs, 1 021 m, 951 m, 867 m, 830 w, 633 s, 595 m, 570 vs (sh). ^{1}H NMR (500 MHz, $CDCl_3$): 1.83 (t, 3 H, *J* = 2.3, CH_3); 4.26 (q, 2 H, *J* = 2.3, $CH_3C{\equiv}CC\mathbf{H}_2$); 4.87 (s, 2 H, CH_2Ar); 7.31 (dt, 1 H, *J* = 7.5, 7.5, 1.2, 5′-H); 7.32 (dt, 1 H, *J* = 7.6, 7.6, 1.4, 5-H); 7.35 (s, 1 H, CHAr′); 7.39 (dt, 1 H, *J* = 7.7, 7.7, 1.5, 4-H); 7.44 (dt, 1 H, *J* = 7.8, 7.8, 1.3, 4′-H); 7.48 (dd, 1 H, *J* = 7.7, 1.3, 6′-H); 7.53 (brd, 1 H, *J* = 7.6, 3-H); 7.59 (dd, 1 H, *J* = 7.6, 1.4, 6-H); 7.98 (brdd, 1 H, *J* = 7.9, 1.2, 3′-H). ^{13}C NMR ($CDCl_3$): 3.38 (q, CH_3), 38.89 (d, CHAr′), 58.38 (t, $CH_3C{\equiv}CCH_2$), 69.80 (t, CH_2Ar), 75.06 (s, $CH_3C{\equiv}CCH_2$), 82.89 (s, $CH_3C{\equiv}CCH_2$), 89.45 (s, ArC≡CAr′), 94.16 (s, ArC≡CAr′), 119.15 (s, C-1′), 121.42 (s, C-2), 127.65 (d, C-6), 128.28 (d, C-4), 129.14 (d, C-5), 129.14 (d, C-3′), 129.44 (d, C-5′), 129.47 (d, C-4′), 132.34 (d, C-3), 139.70 (s, C-1), 142.55 (s, C-2′). EI MS (*m/z*, rel.%): 434 ($M^{+\bullet}$ with ^{81}Br, 0.7), 432 ($M^{+\bullet}$ with ^{81}Br/^{79}Br, 1.4), 430 ($M^{+\bullet}$ with ^{79}Br, 0.7), 323 (6), 299 (10), 272 (34), 257 (11), 242 (39), 219 (100), 204 (91), 189 (75), 165 (19), 101 (30), 69 (15), 63 (26).

Bis(2-{[(trimethylsilyl)oxy]methyl}phenyl)acetylene (**15**)

Diol **2** (ref.[11]) (80 mg, 0.336 mmol) in dry THF (4 ml) was added to sodium hydride (80% suspension in mineral oil, 23 mg, 0.800 mmol, 2.4 equivalents) in dry THF (2 ml) under argon at 0 °C and the mixture was stirred for 1 h. (3-Bromoprop-1-yn-1-yl)trimethylsilane (120 µl, 0.848 mmol, 2.5 equivalents) was added and the suspension was stirred at 0 °C to room temperature overnight. The reaction mixture was evaporated *in vacuo* to dryness and the crude product was purified by flash chromatography on silica gel (petroleum ether) to provide disilylated diol **15** (48 mg, 37%) as an oil. ^{1}H NMR (200 MHz, $CDCl_3$): 0.19 (s, 18 H, 6 × CH_3); 4.96 (s, 4 H, 2 × CH_2); 7.25 (ddd, 2 H, *J* = 7.6, 7.3, 1.5, 4′,5-H); 7.38 (dt, 2 H, *J* = 7.6, 7.6, 1.2, 4,5′-H); 7.50 (dd, 2 H, *J* = 7.3, 1.2, 3′,6-H); 7.58 (brdd, 2 H, *J* = 7.6, 1.5, 3,6′-H).

[2-(Bromomethyl)phenyl][2-(bromomethyl)-4-fluorophenyl]acetylene (**17**)

Triphenylphosphine (45 mg, 0.172 mmol, 2.1 equivalents) in dry acetonitrile (1 ml) and tetrabromomethane (62 mg, 0.187 mmol, 2.3 equivalents) in dry acetonitrile (1 ml) were subsequently added to a solution of diol **16** (ref.[10b]) (21 mg, 0.082 mmol) in dry acetonitrile (1 ml) under argon. The reaction mixture was strirred at room temperature overnight. After removal of the solvent *in vacuo*, the crude product was purified by flash chromatography (hexane–ether 90 : 10) to provide dibromide **17** (25 mg, 80%) as a white amorphous solid. IR ($CHCl_3$): 3 068 w, 1 609 m, 1 598 w, 1 582 m, 1 570 w, 1 497 vs, 148 3 w (sh), 1 451 w, 1 438 w, 1 419 w, 1 292 w, 1 277 s, 1 233 s, 1 159 m, 1 125 w, 1 039 vw, 951 w, 875 w, 825 s, 609 m, 583 w, 555 m, 416 w. ^{1}H NMR (500 MHz, $CDCl_3$): 4.76 (s, 2 H, CH_2Ar); 4.79 (s, 2 H, CH_2Ar′); 7.04 (dt, 1 H, *J* = 8.4, 8.4, 2.7, 5-H); 7.19 (dd, 1 H, *J* = 9.0, 2.7, 3-H); 7.33 (ddd, 1 H, *J* = 7.8, 7.5, 1.4, 5′-H); 7.35 (ddd, 1 H, *J* = 7.8, 7.5, 1.4, 4′-H); 7.46 (ddd, 1 H, *J* = 7.8, 1.4, 0.5, 3′-H); 7.59 (dd, 1 H, *J* = 8.6, 5.9, 6-H); 7.59 (ddd, 1 H, *J* = 7.8, 1.4, 0.5, 6′-H). ^{13}C NMR ($CDCl_3$): 31.17 (t, CH_2Ar′), 32.17 (t, CH_2Ar), 91.07 (s, ArC≡CAr′), 91.72 (s, ArC≡CAr′), 116.00 (dd, $J_{C\text{-}F}$ = 22.0, C-3), 116.91 (dd, $J_{C\text{-}F}$ = 22.9, C-5), 119.05 (d, $J_{C\text{-}F}$ = 2.9, C-1), 122.87 (s, C-1′), 128.62 (d, C-5′), 129.20 (d, C-4′), 129.83 (d, C-3′), 132.80 (d, C-6′), 134.65 (dd, $J_{C\text{-}F}$ = 9.2, C-6), 139.12 (s, C-2′), 141.57 (d, $J_{C\text{-}F}$ = 7.3, C-2), 162.44 (d, $J_{C\text{-}F}$ = 250.9, C-4). ^{19}F NMR ($CDCl_3$): –109.77 (dt, $J_{F\text{-}H}$ = 8.5, 8.5, 5.9). EI MS (*m/z*, rel.%): 384 ($M^{+\bullet}$ with ^{81}Br, 13), 382 ($M^{+\bullet}$ with ^{81}Br/^{79}Br, 26), 380 ($M^{+\bullet}$ with ^{79}Br, 14), 303 (36), 301 (35), 222 (100), 221 (99), 220 (77), 202 (5), 200 (4), 110 (24), 98 (14), 85 (6), 63 (5), 39 (5). HR EI MS: calculated for $C_{16}H_{11}F^{79}Br_2$ 379.9212, found 379.9189.

[4-Fluoro-2-({[(prop-2-yn-1-yl)oxy]methyl}phenyl)](2-{[(prop-2-yn-1-yl)oxy]methyl}phenyl)acetylene (**18**)

Prop-2-yn-1-ol (3.5 µl, 0.060 mmol, 2.4 equivalents) in dry DMF (0.5 ml) was added to sodium hydride (80% suspension in mineral oil, 1.6 mg, 0.053 mmol, 2.2 equivalents) in dry DMF (0.5 ml) under argon and the mixture was stirred at room temperature for 5 min. Dibromide **17** (9.4 mg, 0.025 mmol) in dry DMF (0.5 ml) was added. After stirring at room temperature for 10 min, the reaction mixture was partitioned between ether and water. The ethereal layer was separated and the aqueous phase was extracted with ether (2×). The ethereal portions were combined, washed with water (1×), dried over Na_2SO_4 and evaporated *in vacuo* to afford triyne **18** (6.4 mg, 78%). ^{1}H NMR (200 MHz, $CDCl_3$): 2.46 (t, 1 H, *J* = 2.4, HC≡C); 2.49 (t, 1 H, *J* = 2.4, HC≡C); 4.28 (d, 2 H, *J* = 2.4, HC≡CC**H**$_2$); 4.31 (d, 2 H, *J* = 2.4, HC≡CC**H**$_2$); 4.82 (s, 4 H, CH_2Ar, CH_2Ar′); 6.95–7.58 (m, 7 H, H-arom.).

tert-Butyl *N*-Prop-2-yn-1-yl-*N*-tosylcarbamate (**19**)

Diethyl diazenedicarboxylate (4.84 ml, 30.74 mmol, 2.5 equivalents) was added over a 30 min period to prop-2-yn-1-ol (720 µl, 12.37 mmol), *tert*-butyl *N*-tosylcarbamate[19] (5.0 g, 18.43 mmol, 1.5 equivalent), and triphenylphosphine (9.67 g, 30.87 mmol, 3.0 equivalents) in dry THF (30 ml) under argon at 10–15 °C. The mixture was stirred at room temperature overnight and then the solvent was removed *in vacuo*. Flash chromatography on silica gel (petroleum ether–ether–acetone 90 : 10 : 0 to 80 : 10 : 10) gave carbamate **19** (2.92 g, 76%) as a white solid. ^{1}H NMR (200 MHz, $CDCl_3$) in accord with the literature data[20].

tert-Butyl *N*-But-2-yn-1-yl-*N*-tosylcarbamate (**20**)

Diethyl diazenedicarboxylate (1.70 ml, 10.80 mmol, 2.4 equivalents) was added over a 15 min period to but-2-yn-1-ol (320 µl, 4.51 mmol), *tert*-butyl *N*-tosylcarbamate[19] (1.74 g, 6.41 mmol, 1.4 equivalent), and triphenylphosphine (3.37 g, 12.85 mmol, 2.9 equivalents) in dry THF (10 ml) under argon at 10–15 °C. The mixture was stirred at room temperature overnight and then the solvent was removed *in vacuo*. Flash chromatography on silica gel (petroleum ether–ether–acetone 100 : 0 : 0 to 90 : 10 : 0 to 80 : 10 : 10) gave carbamate **20** (1.14 g, 78%) as a white solid. ^{1}H NMR (200 MHz, $CDCl_3$): 1.34 (s, 9 H, $(CH_3)_3C$); 1.83 (t, 3 H, J = 2.4, $CH_3C{\equiv}C$); 2.44 (s, 3 H, $CH_3C_6H_4$); 4.57 (q, 2 H, CH_2); 7.30 (d, 2 H, J = 8.5, 3,5-H); 7.91 (d, 2 H, J = 8.5, 2,6-H).

4-Methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (**21**)

Trifluoroacetic acid (2.2 ml, 28.55 mmol, 3.0 equivalents) was added to *tert*-butyl *N*-tosyl-*N*-(prop-2-yn-1-yl)carbamate **19** (ref.[20]) (2.92 g, 9.44 mmol) in dry dichloromethane (5 ml) under nitrogen. After stirring at room temperature for 45 min, the mixture was partitioned between brine and dichloromethane. The organic layer was separated and the aqueous phase was extracted with dichloromethane (2×). The organic portions were combined, washed with aqueous $KHCO_3$ (2×), dried over Na_2SO_4 and evaporated *in vacuo* to afford sulfonamide **21** (1.72 g, 87%) as a white solid. ^{1}H NMR (200 MHz, $CDCl_3$) in accord with the literature data[17].

N-But-2-yn-1-yl-4-methylbenzenesulfonamide (**22**)

Trifluoroacetic acid (380 µl, 4.93 mmol, 3.3 equivalents) was added to *tert*-butyl *N*-but-2-yn-1-yl-*N*-tosylcarbamate **20** (480 mg, 1.48 mmol) in dry dichloromethane (3 ml) under nitrogen. After stirring at room temperature for 4 h, the mixture was partitioned between brine and dichloromethane. The organic layer was separated and the aqueous phase was extracted with dichloromethane (2×). The organic portions were combined, washed with aqueous $KHCO_3$ (2×), dried over Na_2SO_4 and evaporated *in vacuo* to afford sulfonamide **22** (292 mg, 88%) as a white solid. ^{1}H NMR (200 MHz, $CDCl_3$): 1.60 (t, 3 H, J = 2.4, $CH_3C{\equiv}C$); 2.43 (s, 3 H, $CH_3C_6H_4$); 3.77 (dq, 2 H, J = 5.5, 2.4, 2.4, 2.4, CH_2); 4.51 (t, 1 H, J = 5.5, NH); 7.32 (d, 2 H, J = 8.4, 3,5-H); 7.77 (d, 2 H, J = 8.4, 2,6-H).

N,*N*′-Di(prop-2-yn-1-yl)-*N*,*N*′-{ethynediylbis[(2,1-phenylene)methylene]}-dibenzenesulfonamide (**23**)

4-Methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **21** (115 mg, 0.550 mmol, 2.0 equivalents) in dry DMF (5 ml) was added at 0 °C to sodium hydride (80% suspension in mineral oil, 17 mg, 0.567 mmol, 2.1 equivalents) in dry DMF (1 ml) under argon. After stirring at 0 °C for 1 h, dibromide **3** (ref.[12]) (100 mg, 0.275 mmol) in dry DMF (2 ml) was added and the mixture was stirred at room temperature overnight. The resulting brown solution was partitioned between ether and water. The ethereal layer was separated and the aqueous phase was extracted with ether (2×). The ethereal portions were combined, washed with water (1×), dried over Na_2SO_4 and evaporated *in vacuo*. The crude product was purified by flash chromatography on silica gel (petroleum ether–ether–acetone 70 : 20 : 10 to 70 : 0 : 30 to 50 : 0 : 50) and then by preparative HPLC on silica gel (hexane–acetone 80 : 20) to get triyne **23** (45 mg, 27%) as a white solid, m.p. 169.5–170.5 °C (hexane–acetone). IR ($CHCl_3$): 3 307 m, 3 066 w, 3 031 m, 3 012 w, 2 926 w, 2 868 w, 2 122 vw, 1 599 m, 1 571 vw, 1 495 m, 1 452 m, 1 430 m, 1 401 w, 1 349 s, 1 335 s (sh), 1 306 m, 1 290 w, 1 185 w, 1 162 vs, 1 119 m, 1 092 s, 1 062 m, 1 041 w, 1 019 w, 959 w, 928 w, 902 s, 864 w, 814 m, 660 s, 636 m, 590 m, 567 m, 543 m, 504 w. ^1H NMR (500 MHz, $CDCl_3$): 1.88 (t, 2 H, *J* = 2.4, 2 × HC≡C); 2.44 (brs, 6 H, 2 × CH_3); 3.99 (d, 4 H, *J* = 2.4, 2 × HC≡CC**H**$_2$); 4.65 (s, 4 H, CH_2Ar, CH_2Ar'); 7.26 (dt, 2 H, *J* = 7.6, 7.6, 1.5, 4,5′-H); 7.30–7.32 (m, 4 H, 2 × 3,5-H (Ts)); 7.34 (dt, 2 H, *J* = 7.6, 7.6, 1.5, 4′,5-H); 7.51 (dd, 2 H, *J* = 7.6, 1.5, 3,6′-H); 7.54 (brd, 2 H, *J* = 7.8, 3′,6-H); 7.80–7.82 (m, 4 H, 2 × 2,6-H (Ts)). ^{13}C NMR ($CDCl_3$): 21.55 (q, 2 × CH_3), 36.34 (t, 2 × $HC{\equiv}CCH_2$), 48.32 (t, CH_2Ar, CH_2Ar'), 73.99 (d, 2 × HC≡C), 91.71 (s, ArC≡CAr′), 122.95 (s, C-1′,2), 127.75 (d, C-4,5′), 127.96 (d, 2 × C-2,6 (Ts)), 128.92 (d, C-4′,5), 128.95 (d, C-3′,6), 129.52 (d, 2 × C-3,5 (Ts)), 132.63 (d, C-3,6′), 136.04 (s, 2 × C-4 (Ts)), 136.79 (s, C-1,2′), 143.66 (2 × C-1 (Ts)); signal of $HC{\equiv}CCH_2$ overlapped with $CDCl_3$ signals. EI MS (*m/z*, rel.%): 465 ($(M - C_7H_7SO_2)^+$, 14), 309 (61), 271 (42), 256 (100), 217 (26), 155 (19), 91 (72), 57 (27). FAB MS (*m/z*, thioglycerol–glycerol matrix): 621 ($(M + H)^+$), 568, 520, 467, 429, 391, 307, 293, 279, 257, 232. HR FAB MS: calculated for $C_{36}H_{33}N_2O_4S_2$ (M + H) 621.1882, found 621.1959.

N,*N*′-Di(but-2-yn-1-yl)-*N*,*N*′-{ethynediylbis[(2,1-phenylene)methylene]}-dibenzenesulfonamide (**24**)

Method A. *N*-(But-2-yn-1-yl)-4-methylbenzenesulfonamide **22** (300 mg, 1.35 mmol, 2.0 equivalents) in dry THF (15 ml) was added at 0 °C to sodium hydride (80% suspension in mineral oil, 52 mg, 1.73 mmol, 2.6 equivalents) in dry THF (5 ml) under argon. After stirring at 0 °C for 30 min, dibromide **3** (ref.[12]) (245 mg, 0.673 mmol) in dry THF (10 ml) and dry DMF (5 ml) was added and the mixture was stirred at 65 °C for 20 min. The resulting greenish suspension was cooled to room temperature and the fine precipitate was filtered off. The filtrate was concentrated *in vacuo* and the residue was partitioned between ether and water. The ethereal layer was separated and the aqueous phase was extracted with ether (2×). The ethereal portions were combined, washed with water (2×), dried over Na_2SO_4 and evaporated *in vacuo*. The crude product was purified by flash chromatography on silica gel (petroleum ether–ether–acetone 80 : 10 : 10 to 70 : 20 : 10) to get triyne **24** (275 mg, 63%) as a white solid.

Method B. Diethyl diazenedicarboxylate (170 μl, 1.08 mmol, 2.6 equivalents) was added to diol **2** (ref.[11]) (100 mg, 0.420 mmol), *N*-(but-2-yn-1-yl)-4-methylbenzenesulfonamide **22** (188 mg, 0.842 mmol, 2.0 equivalents), triphenylphosphine (329 mg, 1.25 mmol, 3.0 equivalents) in dry THF (4 ml) under argon. The mixture was stirred at room temperature for 1 h and then the solvent was removed *in vacuo*. Flash chromatography on silica gel (petroleum ether–ether–acetone 80 : 10 : 10) gave triyne **24** (196 mg, 72%) as a white solid, m.p. 146–147.5 °C ($CHCl_3$). IR ($CHCl_3$): 3 068 w, 2 922 m, 2 855 m, 2 222 vw, 1 559 m, 1 495 m, 1 452 m, 1 434 m, 1 399 w (sh), 1 348 s, 1 336 s (sh), 1 306 m, 1 293 w, 1 185 w, 1 161 vs, 1 147 m (sh), 1 118 m, 1 091 m, 1 087 m (sh), 1 040 w, 1 019 w, 909 m, 848 w, 814 m, 702 w, 658 s, 635 vw, 588 w (sh), 566 m, 547 m, 538 m. ^{1}H NMR (500 MHz, $CDCl_3$): 1.32 (t, 6 H, *J* = 2.4, 2 × $CH_3C{\equiv}C$); 2.44 (s, 6 H, 2 × $C\mathbf{H}_3C_6H_4$); 3.92 (brq, 4 H, *J* = 2.4, 2 × $CH_3C{\equiv}CC\mathbf{H}_2$); 4.61 (s, 4 H, CH_2Ar, CH_2Ar'); 7.24 (dt, 2 H, *J* = 7.5, 7.5, 1.4, 4,5′-H); 7.30–7.32 (m, 4 H, 2 × 3,5-H (Ts)); 7.34 (dt, 2 H, *J* = 7.6, 7.6, 1.5, 4′,5-H); 7.48 (dd, 2 H, *J* = 7.9, 1.5, 3,6′-H); 7.58 (brdd, 2 H, *J* = 7.8, 1.4, 3′,6-H); 7.81–7.83 (m, 4 H, 2 × 2,6-H (Ts)). ^{13}C NMR ($CDCl_3$): 3.04 (q, 2 × $CH_3C{\equiv}C$), 21.50 (q, 2 × $CH_3C_6H_4$), 36.93 (t, 2 × $CH_3C{\equiv}CCH_2$), 48.20 (t, CH_2Ar, CH_2Ar'), 71.76 (s, 2 × $CH_3C{\equiv}C$), 81.92 (s, 2 × $CH_3C{\equiv}C$), 91.54 (s, $ArC{\equiv}CAr'$), 122.88 (s, C-1′,2), 127.57 (d, C-4,5′), 128.07 (d, 2 × C-2,6 (Ts)), 128.92 (d, C-4′,5), 129.07 (d, C-3′,6), 129.27 (d, 2 × C-3,5 (Ts)), 132.35 (d, C-3,6′), 136.19 (s, 2 × C-4 (Ts)), 137.32 (s, C-1,2′). EI MS (*m/z*, rel.%): 648 ($M^{+\bullet}$, 1), 493 (20), 338 (31), 323 (18), 309 (13), 285 (32), 270 (100), 256 (43), 242 (16), 218 (37), 155 (10), 91 (53), 65 (11), 53 (16). FAB MS (*m/z*, 2-hydroxyethyldisulfide matrix): 673 ($(M + Na)^+$), 649 ($(M + H)^+$), 493, 426, 339, 270, 256, 243, 228, 218, 203, 115, 91. HR FAB MS: calculated for $C_{38}H_{37}N_2O_4S_2$ (M + H) 649.2195, found 649.2204.

Trimethyl[3-({2-[(2-{4-(trimethylsilyl)-1-[(trimethylsilyl)oxy]-3-butynyl}phenyl)ethynyl]benzyl}oxy)-1-propynyl]silane (**25**)

Butyllithium (1.6 M solution in hexanes, 2.0 ml, 3.20 mmol, 2.4 equivalents) was added dropwise to triyne **8** (420 mg, 1.34 mmol) in dry THF (5 ml) at –78 °C under argon. After stirring at –78 °C for 40 min, trimethylsilyl chloride (440 μl, 3.47 mmol, 2.6 equivalents) was added and the mixture was stirred at –78 °C to room temperature overnight. The precipitate was filtered off, washed with ether and filtrate was evaporated *in vacuo* to dryness. Flash chromatography on silica gel (petroleum ether–ether 90 : 10) provided the rearranged silylated triyne **25** (156 mg, 22%), the silylated triyne **10** (295 mg, 48%), and the recovered triyne **8** (22%) as oils. Compound **25**: IR ($CHCl_3$): 2 961 m, 2 900 w, 2 175 m, 1 410 w, 1 252 s, 1 113 m, 1 079 s, 847 vs, 699 w, 648 w. ^{1}H NMR (500 MHz, $CDCl_3$): 0.12 (s, 9 H, $(CH_3)_3SiO$); 0.13 (s, 9 H, $(C\mathbf{H}_3)_3SiC{\equiv}CCH_2CH$); 0.16 (s, 9 H, $(C\mathbf{H}_3)_3SiC{\equiv}CCH_2O$); 2.55 (dd, 1 H, *J* = 16.8, 8.7, $C{\equiv}CC\mathbf{H}HCH$); 2.78 (dd, 1 H, *J* = 16.8, 3.6, $C{\equiv}CCH\mathbf{H}CH$); 4.29 (s, 2 H, $C{\equiv}CC\mathbf{H}_2O$); 4.88 (s, 2 H, CH_2Ar); 5.40 (dd, 1 H, *J* = 8.6, 3.6, $(CH_3)_3SiOC\mathbf{H}$); 7.24 (dt, 1 H, *J* = 7.5, 7.5, 1.4, 5′-H); 7.30 (dt, 1 H, *J* = 7.5, 7.5, 1.4, 4-H); 7.35 (brdt, 1 H, *J* = 7.6, 7.6, 1.3, 5-H); 7.37 (dt, 1 H, *J* = 7.4, 7.4, 1.4, 4′-H); 7.49 (ddd, 1 H, *J* = 7.7, 1.4, 0.5, 6-H); 7.54 (brdd, 1 H, *J* = 7.8, 1.5, 0.7, 3-H); 7.59 (brdd, 1 H, *J* = 7.9, 1.4, 3′-H); 7.60 (brdd, 1 H, *J* = 7.8, 1.4, 6′-H). ^{13}C NMR ($CDCl_3$): –0.22 (q, $(CH_3)_3SiC{\equiv}CCH_2O$), 0.02 (q, $(CH_3)_3SiC{\equiv}CCH_2CH$), 0.08 (q, $(CH_3)_3SiO$), 31.13 (t, $C{\equiv}CCH_2CH$), 58.57 (t, $C{\equiv}CCH_2O$), 69.95 (t, CH_2Ar), 69.95 (d, $(CH_3)_3SiOCH$), 85.90 (s, $C{\equiv}CCH_2CH$), 91.50 (s, $ArC{\equiv}CAr'$), 91.62 (s, $ArC{\equiv}CAr'$), 92.30 (s, $C{\equiv}CCH_2O$), 101.53 (s, $C{\equiv}CCH_2O$), 104.67 (s, $C{\equiv}CCH_2CH$), 120.20 (s, C-2), 121.99 (s, C-1′), 125.80 (d, C-5′), 127.10 (d, C-3′), 127.54 (d, C-6), 128.00 (d, C-4), 128.63 (d, C-5), 128.71 (d, C-4′), 131.85 (d, C-6′), 132.38 (d, C-3), 139.22 (s, C-1), 145.79 (s, C-2′). EI MS (*m/z*, rel.%): 530 ($M^{+\bullet}$, 0.6), 457 (1), 419 (61), 329 (12), 219 (10), 97 (12), 73 (100), 57 (17), 43 (16). FAB MS (*m/z*, thioglycerol–glycerol matrix): 419 ($(M - C_6H_{11}Si)^+$), 403, 329, 241, 215, 169, 155, 147, 133, 111, 97. HR EI MS: calculated for $C_{25}H_{31}O_2Si_2$ (M – $C_6H_{11}Si$) 419.1863, found 419.1875.

4-(Trimethylsilyl)-1-(2-{[2-({[3-(trimethylsilyl)-2-propynyl]oxy}methyl)phenyl]ethynyl}phenyl)-3-butyn-1-ol (**26**)

Butyllithium (1.6 M solution in hexanes, 1.2 ml, 1.92 mmol, 4.9 equivalents) was added dropwise to triyne **8** (122 mg, 0.388 mmol) in dry THF (3 ml) at –78 °C under argon. After stirring at –78 °C for 1.5 h, trimethylsilyl chloride (250 μl, 1.97 mmol, 5.1 equivalents) was added and the mixture was stirred at –78 °C to room temperature overnight. The precipitate was filtered off, washed with ether and filtrate was evaporated *in vacuo* to dryness. Flash chromatography on silica gel (petroleum ether–ether 90 : 10) provided the rearranged silylated triyne **26** (41 mg, 23%) as an oil. ^{1}H NMR (200 MHz, $CDCl_3$): 0.15 (s, 9 H, $(C\mathbf{H}_3)_3SiC{\equiv}CCH_2CH$); 0.16 (s, 9 H, $(C\mathbf{H}_3)_3SiC{\equiv}CCH_2O$); 2.68 (dd, 1 H, *J* = 16.9, 7.8, $C{\equiv}CC\mathbf{H}HCH$); 2.83 (brs, 1 H, OH); 2.95 (dd, 1 H, *J* = 16.9, 4.4, $C{\equiv}CCH\mathbf{H}CH$); 4.27 (s, 2 H, $C{\equiv}CCH_2O$); 4.84 (s, 2 H, CH_2Ar'); 5.39 (dd, 1 H, *J* = 7.8, 4.4, $C{\equiv}CCH_2C\mathbf{H}$); 7.23–7.63 (m, 8 H, H-arom.).

1-[2-({2-[(2-Propynyloxy)methyl]phenyl}ethynyl)phenyl]-3-butyn-1-ol (**27**)

Butyllithium (1.6 M solution in hexanes, 810 μl, 1.30 mmol, 5.0 equivalents) was added dropwise to triyne **8** (81 mg, 0.258 mmol) in dry THF (2 ml) at –78 °C under argon. After stirring at –78 °C for 30 min, methyl iodide (90 μl, 1.45 mmol, 5.6 equivalents) was added and the mixture was stirred at –78 °C to room temperature for 3 h. The solvents were removed *in vacuo*. Flash chromatography on silica gel (petroleum ether–ether–acetone–methanol 80 : 10 : 10 : 0 to 50 : 30 : 17 : 3) provided the rearranged triyne **27** (25 mg, 31%) as an oil. ^{1}H NMR (200 MHz, $CDCl_3$): 2.11 (t, 1 H, *J* = 2.6, $\mathbf{H}C{\equiv}CCH_2CH$); 2.48 (t, 1 H, *J* = 2.3, $\mathbf{H}C{\equiv}CCH_2O$); 2.67 (ddd, 1 H, *J* = 16.9, 7.8, 2.6, $HC{\equiv}CC\mathbf{H}HCH$); 2.82 (d, 1 H, *J* = 4.1, OH); 2.91 (ddd, 1 H, *J* = 16.9, 4.5, 2.6, $HC{\equiv}CCH\mathbf{H}CH$); 4.28 (d, 2 H, *J* = 2.3, $HC{\equiv}CC\mathbf{H}_2O$); 4.87 (s, 2 H, CH_2Ar'); 5.43 (ddd, 1 H, *J* = 7.8, 4.5, 4.1, $C{\equiv}CCH_2C\mathbf{H}$); 7.25–7.64 (m, 8 H, H-arom.).

1-[2-({2-[(2-Butynyloxy)methyl]phenyl}ethynyl)phenyl]-2-methyl-2,3-butadien-1-ol (**28**)

Butyllithium (1.6 M solution in hexanes, 300 μl, 0.480 mmol, 2.6 equivalents) was added dropwise to triyne **9** (64 mg, 0.187 mmol) in dry THF (2 ml) at –78 °C under argon. After stirring at –78 °C for 30 min, methyl iodide (40 μl, 0.642 mmol, 3.4 equivalents) was added and the mixture was stirred at –78 °C to room temperature for 3 h. The solvents were removed *in vacuo* and products were separated by flash chromatography on silica gel (petroleum ether–ether–acetone–methanol 80 : 10 : 10 : 0 to 50 : 30 : 17 : 3) to provide monoallene **28** (9 mg, 14%) and the more polar diallene **29** (18 mg, 28%; a 1 : 1 mixture of the (*R**,*R**) and (*R**,*S**) diastereoisomers according to ^{1}H NMR) as oils. Compound **28**: ^{1}H NMR (200 MHz, $CDCl_3$): 1.68 (t, 3 H, *J* = 3.1, $CH_2{=}C{=}C(C\mathbf{H}_3)$); 1.84 (t, 3 H, *J* = 2.3, $CH_3C{\equiv}C$); 2.57 (d, 1 H, *J* = 5.2, OH); 4.23 (q, 2 H, *J* = 2.3, $CH_3C{\equiv}CC\mathbf{H}_2$); 4.82–4.88 (m, 2 H, $CH_2{=}C{=}C$); 4.84 (s, 2 H, CH_2Ar'); 5.68–5.70 (m, 1 H, $C\mathbf{H}(OH)$); 7.25–7.59 (m, 8 H, H-arom.).

1-(2-{[2-(1-Hydroxy-2-methyl-2,3-butadienyl)phenyl]ethynyl}phenyl)-2-methyl-2,3-butadien-1-ol (**29**)

Method A. For preparation, see **28**.

Method B. *tert*-Butyllithium (1.7 M solution in pentane, 300 μl, 0.510 mmol, 2.5 equivalents) was added dropwise to triyne **9** (69 mg, 0.201 mmol) in dry THF (2 ml) at –78 °C under argon. After stirring at –78 °C for 2 h, distilled water (300 μl, 16.70 mmol, 83 equivalents) was added and the mixture was stirred at –78 °C to room temperature overnight. The solvents were removed *in vacuo* and the crude product was purified by flash chromatography on silica gel (petroleum ether–ether–acetone 70 : 20 : 10) to give diallene **29** (21 mg, 31%; a 1 : 1 mixture of (*R**,*R**) and (*R**,*S**) diastereoisomers according to ^{1}H NMR) as an oil. IR ($CHCl_3$): 3 601 m, 3 559 m, 3 466 w, 3 070 w, 2 987 m, 1 959 s, 1 706 w, 1 442 m, 1 376 s, 1 043 s, 1 016 s, 909 vs, 957 m, 856 s, 620 m. ^{1}H NMR (500 MHz, $CDCl_3$): 1.65 (dt, 3 H, *J* = 3.2, 3.2, 0.6, 2 × CH_3 of one diastereoisomer); 1.66 (dt, 3 H, *J* = 3.2, 3.2, 0.6, 2 × CH_3 of one d.); 2.51 (brs, 2 H, 2 × OH of both d.); 4.82–4.85 (m, 4 H, 2 × CH_2 of both d.); 5.65 (t, 2 H, *J* = 2.8, 2 × C**H**(OH) of one d.); 5.67 (t, 2 H, *J* = 2.8, 2 × C**H**(OH) of one d.); 7.28 (dt, 2 H, *J* = 7.5, 7.5, 1.3, 4,5′-H of both d.); 7.37 (dt, 2 H, *J* = 7.4, 7.4, 1.5, 4′,5-H of both d.); 7.51–7.54 (m, 4-H, 3,3′,6,6′-H of both d.). ^{13}C NMR ($CDCl_3$): 15.08 (q, 2 × CH_3 of one diastereoisomer), 15.17 (q, 2 × CH_3 of one d.), 72.39 (d, 2 × CH(OH) of one d.), 72.41 (d, 2 × CH(OH) of one d.), 78.02 (t, 2 × CH_2=C=C of one d.), 78.18 (t, 2 × CH_2=C=C of one d.), 92.08 (s, 2 × CH_2=C=C of one d.), 92.13 (s, 2 × CH_2=C=C of one d.), 102.29 (s, ArC≡CAr′ of one d.), 102.41 (s, ArC≡CAr′ of one d.), 121.82 (s, C-1′,2 of one d.), 121.83 (s, C-1′,2 of one d.), 126.59 (d, C-4,5′ of one d.), 126.61 (d, C-4,5′ of one d.), 127.57 (d, C-4′,5 of both d.), 128.74 (d, C-3′,6 of one d.), 128.76 (d, C-3′,6 of one d.), 132.39 (d, C-3,6′ of both d.), 143.43 (s, C-1,2′ of one d.), 143.45 (s, C-1,2′ of one d.), 204.99 (s, 2 × CH_2=C=C of one d.), 205.12 (s, 2 × CH_2=C=C of one d.). EI MS (*m/z*, rel.%): 324 ($(M - H_2O)^+$, 10), 309 (24), 295 (22), 281 (16), 266 (18), 228 (55), 215 (20), 202 (16), 171 (31), 129 (18), 115 (18), 83 (100), 69 (16), 57 (25), 43 (34). HR EI MS: calculated for $C_{24}H_{20}O$ ($M - H_2O$) 324.1515, found 324.1446.

Bis[2-(but-3-yn-1-yl)phenyl]acetylene (**30**)

Butyllithium (1.6 M solution in hexanes, 11.0 ml, 17.60 mmol, 2.1 equivalents) was added dropwise over a 10 min period to a solution of trimethyl(prop-1-yn-1-yl)silane (2.60 ml, 17.56 mmol, 2.1 equivalents) in THF (50 ml) at –78 °C under argon. After stirring at –78 °C for 2 h, dibromide **3** (ref.[12]) (3.03 g, 8.31 mmol) in THF (30 ml) was added dropwise over a 10 min period. The mixture was stirred at –78 °C for 1 h and then warmed to room temperature. Tetrabutylammonium fluoride (1.3 M solution in THF, 51 ml, 66.30 mmol, 8.0 equivalents) was added and the mixture was stirred at room temperature for 16 h. The solution was evaporated *in vacuo* to dryness and the residue was passed through a pad of silica gel (petroleum ether–ether 95 : 5 to 0 : 100). The crude product was purified by flash chromatography on silica gel (petroleum ether–ether 99 : 1) to get triyne **30** (1.58 g, 67%) as an amorphous solid. IR ($CHCl_3$): 3 309 vs, 3 097 w, 3 070 w, 2 958 m, 2 935 m, 2 864 w, 2 842 w, 2 211 vw, 2 118 w, 1 600 w, 1 569 vw, 1 492 s, 1 452 s, 1 432 m, 1 340 w, 1 160 w, 1 127 vw, 1 104 w, 640 vs, 597 w, 523 w, 495 m, 489 m. ^{1}H NMR (500 MHz, $CDCl_3$): 1.99 (t, 2 H, *J* = 2.6, 2 × HC≡C); 2.61 (dt, 4 H, *J* = 7.5, 7.5, 2.6, 2 × HC≡CC$\mathbf{H_2}$); 3.11 (t, 4 H, *J* = 7.5, CH_2Ar, CH_2Ar′); 7.22–7.55 (m, 8 H, 3,3′,4,4′,5,5′,6,6′-H). ^{13}C NMR ($CDCl_3$): 19.60 (t, 2 × HC≡CCH_2); 33.84 (t, CH_2Ar, CH_2Ar′); 69.01 (d, 2 × HC≡C); 83.70 (s, 2 × HC≡C); 91.69 (s, ArC≡CAr′); 122.81 (s, C-1′,2), 126.51 (d, C-4,5′), 128.49 (d, C-4′,5), 129.10 (d, C-3′,6), 132.52

(d, C-3,6′), 142.02 (s, C-1,2′). EI MS (*m/z*, rel.%): 282 ($M^{+\bullet}$, 99), 281 (100), 265 (93), 253 (54), 239 (67), 228 (58), 215 (39), 202 (54), 189 (16), 165 (23), 141 (25), 115 (34), 101 (17), 91 (15), 69 (26), 55 (12). HR EI MS: calculated for $C_{22}H_{18}$ 282.1409, found 282.1552.

Bis[2-(pent-3-yn-1-yl)phenyl]acetylene (**31**)

Butyllithium (1.6 M solution in hexanes, 1.20 ml, 1.92 mmol, 2.2 equivalents) was added dropwise over a 3 min period to triyne **30** (249 mg, 0.882 mmol) in dry THF (5 ml) at –78 °C under argon. After stirring at –78 °C for 10 min, methyl iodide (120 μl, 1.93 mmol, 2.2 equivalents) was added and the mixture was stirred at –78 °C for 15 min. The solvent was evaporated *in vacuo* and the crude product was purified by flash chromatography on silica gel (petroleum ether–ether 99 : 1) to afford dimethylated triyne **31** (248 mg, 91%) as an oil. IR (CCl_4): 3 097 w, 3 069 m, 3 026 w, 2 956 m, 2 920 vs, 2 859 m, 2 845 w, 2 232 vvw, 2 211 vvw, 1 601 w, 1 570 vw, 1 491 vs, 1 479 m, 1 452 s, 1 434 m, 1 378 w, 1 160 w, 1 102 w. ^{1}H NMR (500 MHz, $CDCl_3$): 1.77 (t, 6 H, *J* = 2.5, 2 × CH_3); 2.53 (tq, 4 H, *J* = 7.5, 7.5, 2.5, 2.5, 2.5, 2 × $C{\equiv}CCH_2$); 3.06 (t, 4 H, *J* = 7.5, CH_2Ar, CH_2Ar′); 7.21 (ddd, 2 H, *J* = 7.6, 6.4, 2.5, 4,5′-H); 7.27 (ddd, 2 H, *J* = 7.7, 6.4, 1.3, 4′,5-H); 7.29 (ddd, 2 H, *J* = 7.7, 2.5, 0.6, 3′,6-H); 7.53 (ddd, 2 H, *J* = 7.6, 1.3, 0.6, 3,6′-H). ^{13}C NMR ($CDCl_3$): 3.49 (q, 2 × CH_3), 19.98 (t, 2 × $C{\equiv}CCH_2$), 34.44 (t, CH_2Ar, CH_2Ar′), 76.28 (s, 2 × $C{\equiv}CCH_2$), 78.52 (s, 2 × $C{\equiv}CCH_2$), 91.57 (s, ArC≡CAr′), 122.82 (s, C-1′,2), 126.24 (d, C-4,5′), 128.31 (d, C-4′,5), 129.03 (d, C-3′,6), 132.39 (d, C-3,6′), 142.60 (s, C-1,2′). EI MS (*m/z*, rel.%): 310 ($M^{+\bullet}$, 8), 295 (56), 280 (100), 265 (48), 252 (20), 239 (40), 228 (29), 215 (35), 202 (54), 189 (10), 165 (22), 129 (26), 115 (34), 97 (15), 83 (18), 69 (37), 57 (39), 43 (41). HR EI MS: calculated for $C_{24}H_{22}$ 310.1722, found 310.1699.

Bis{2-[4-(trimethylsilyl)but-3-yn-1-yl]phenyl}acetylene (**32**)

Butyllithium (1.6 M solution in hexanes, 490 μl, 0.784 mmol, 2.1 equivalents) was added dropwise over a 3 min period to triyne **30** (104 mg, 0.368 mmol) in dry THF (2 ml) at –78 °C under argon. After stirring at –78 °C for 10 min, trimethylsilyl chloride (100 μl, 0.788 mmol, 2.1 equivalents) was added and the mixture was stirred at –78 °C for 15 min. The solvent was evaporated *in vacuo* and the crude product was purified by flash chromatography on silica gel (petroleum ether–ether 100 : 0 to 99 : 1) to furnish disilylated triyne **32** (154 mg, 98%) as an oil. IR (CCl_4): 3 096 vw, 3 070 w, 3 027 w, 2 961 m, 2 935 w, 2 901 w, 2 863 vw, 2 175 m, 1 600 vw, 1 492 w, 1 452 w, 1 427 w, 1 407 vw, 1 338 w, 1 250 s, 1 160 vw, 1 103 w, 843 vs, 698 w, 645 w, 638 w. ^{1}H NMR (500 MHz, $CDCl_3$): 0.13 (s, 18 H, 6 × CH_3); 2.63 (t, 4 H, *J* = 7.5, 2 × $C{\equiv}CCH_2$); 3.09 (t, 4 H, *J* = 7.5, CH_2Ar, CH_2Ar′); 7.21 (ddd, 2 H, *J* = 7.5, 7.0, 1.9, 4,5′-H); 7.27 (ddd, 2 H, *J* = 7.5, 7.0, 1.5, 4′,5-H); 7.30 (ddd, 2 H, *J* = 7.5, 1.9, 0.6, 3′,6-H); 7.53 (ddd, 2 H, *J* = 7.5, 1.5, 0.7, 3,6′-H). ^{13}C NMR ($CDCl_3$): 0.08 (q, 6 × CH_3), 21.19 (t, 2 × $C{\equiv}CCH_2$), 34.05 (t, CH_2Ar, CH_2Ar′), 85.41 (s, 2 × $C{\equiv}CCH_2$), 91.67 (s, ArC≡CAr′), 106.50 (s, 2 × $C{\equiv}CCH_2$), 122.78 (s, C-1′,2), 126.39 (d, C-4,5′), 128.29 (d, C-4′,5), 129.33 (d, C-3′,6), 132.39 (d, C-3,6′), 142.16 (s, C-1,2′). EI MS (*m/z*, rel.%): 426 ($M^{+\bullet}$, 14), 411 (6), 395 (13), 354 (32), 337 (18), 323 (100), 295 (8), 279 (75), 265 (12), 253 (18), 239 (16), 228 (11), 215 (15), 205 (22), 185 (10), 149 (16), 137 (22), 109 (16), 97 (37), 73 (67), 41 (8). HR EI MS: calculated for $C_{28}H_{34}Si_2$ 426.2199, found 426.2209.

2,2′-Di(prop-2-yn-1-yl)-2,2′-{ethynediylbis[(2,1-phenylene)methylene]}dimalonate (**33**)

Dimethyl 2-(prop-2-yn-1-yl)malonate[22] (96 mg, 0.564 mmol, 2.1 equivalents) in dry THF (3 ml) was added to sodium hydride (80% suspension in mineral oil, 18 mg, 0.587 mmol, 2.1 equivalents) in dry THF (3 ml) at room temperature under argon. The mixture was stirred at room temperature for 15 min and then dibromide **3** (ref.[12]) (100 mg, 0.274 mmol) in dry THF (3 ml) was added. After stirring at room temperature for 30 h, the precipitate was filtered off and the filtrate was evaporated *in vacuo* to dryness. The crude product was purified by flash chromatography on silica gel (petroleum ether–ether–acetone 80 : 10 : 10 to 80 : 0 : 20 to 50 : 0 : 50) to get triyne **33** (147 mg, 99%) as an amorphous solid. IR (CCl_4): 3 313 w, 3 070 vw, 3 028 vw, 3 002 vw, 2 953 w, 2 928 w, 2 122 vvw, 1 758 m, 1 740 s, 1 600 vvw, 1 495 w, 1 450 w, 1 437 w, 1 329 w, 1 282 m, 1 243 w, 1 182 m, 1 104 w, 1 068 w, 1 039 w, 853 w, 649 w, 635 w. ^{1}H NMR (500 MHz, $CDCl_3$): 2.07 (t, 2 H, J = 2.7, 2 × HC≡C); 2.79 (d, 4 H, J = 2.7, 2 × HC≡CC**H**$_2$); 3.69 (s, 12 H, 4 × CH_3); 3.73 (s, 4 H, CH_2Ar, CH_2Ar′); 7.23 (ddd, 2 H, J = 7.7, 7.4, 1.3, 4,5′-H); 7.25 (ddd, 2 H, J = 7.9, 7.4, 1.4, 4′,5-H); 7.38 (ddd, 2 H, J = 7.9, 1.3, 0.3, 3′,6-H); 7.57 (ddd, 2 H, J = 7.7, 1.4, 0.3, 3,6′-H). ^{13}C NMR ($CDCl_3$): 23.15 (t, 2 × HC≡CCH_2), 35.55 (t, CH_2Ar, CH_2Ar′), 52.83 (q, 4 × CH_3), 58.08 (s, 2 × $C(CO_2CH_3)_2$), 72.07 (d, 2 × HC≡C), 79.62 (s, 2 × HC≡C), 91.68 (s, ArC≡CAr′), 124.43 (s, C-1′,2), 127.17 (d, C-4,5′), 128.31 (d, C-4′,5), 130.42 (d, C-3′,6), 132.81 (d, C-3,6′), 137.27 (s, C-1,2′), 170.24 (s, 4 × CO). EI MS (*m/z*, rel.%): 541 ($(M - H)^+$, 15), 511 (12), 483 (6), 451 (13), 423 (62), 391 (36), 363 (86), 331 (30), 303 (53), 279 (41), 253 (100), 215 (51), 169 (14), 137 (20), 113 (16), 59 (32). HR EI MS: calculated for $C_{32}H_{30}O_8$ 542.1941, found 542.1911.

2,2′-Di(but-2-yn-1-yl)-2,2′-{ethynediylbis[(2,1-phenylene)methylene]}dimalonate (**34**)

Dimethyl 2-(but-2-yn-1-yl)malonate[23] (278 mg, 1.0 mmol, 2.2 equivalents) in dry THF (2 ml) was added to sodium hydride (80% suspension in mineral oil, 44 mg, 1.45 mmol, 3.1 equivalents) in dry THF (2 ml) at room temperature under argon. The mixture was stirred at room temperature for 30 min and then dibromide **3** (ref.[12]) (86 mg, 0.230 mmol) in dry THF (3 ml) was added. After stirring at room temperature for 1 h, the precipitate was filtered off and the filtrate was evaporated *in vacuo* to dryness. The crude product was purified by flash chromatography on silica gel (petroleum ether–acetone 85 : 15) to furnish triyne **34** (115 mg, 86%) as an oil. IR (CCl_4): 3 000 w, 2 953 m, 2 235 vw, 1 756 m, 1 739 vs, 1 601 vw, 1 495 w, 1 450 w, 1 438 m, 1 282 m, 1 244 m, 1 210 s, 1 200 s (sh), 1 182 m, 1 104 w, 1 067 m, 1 050 w, 1 038 w, 952 w, 859 w, 591 vw. ^{1}H NMR (500 MHz, $CDCl_3$): 1.73 (t, 6 H, J = 2.5, 2 × CH_3C≡C); 2.74 (q, 4 H, J = 2.5, 2 × CH_3C≡CC**H**$_2$); 3.67 (s, 12 H, 4 × CH_3O_2C); 3.69 (brs, 4 H, CH_2Ar, CH_2Ar′); 7.24 (dt, 2 H, J = 7.3, 7.3, 1.7, 4′,5-H); 7.27 (dt, 2 H, J = 7.6, 7.6, 2.0, 4,5′-H); 7.39 (dd, 2 H, J = 7.5, 1.9 , 3′,6-H); 7.56 (dd, 2 H, J = 7.5, 1.9, 3,6′-H). ^{13}C NMR ($CDCl_3$): 3.49 (q, 2 × CH_3C≡C), 23.42 (t, 2 × CH_3C≡CCH_2), 35.42 (t, CH_2Ar, CH_2Ar′), 52.69 (q, 4 × CH_3O_2C), 58.31 (s, 2 × $C(CO_2CH_3)_2$), 74.12 (s, 2 × CH_3C≡C), 79.56 (s, 2 × CH_3C≡C), 91.54 (s, ArC≡CAr′), 124.42 (s, C-1′,2), 127.04 (d, C-4,5′), 128.18 (d, C-4′,5), 130.52 (d, C-3′,6), 132.75 (d, C-3,6′), 137.61 (s, C-1,2′), 170.63 (s, 4 × CO). EI MS (*m/z*, rel.%): 569 ($M^{+\bullet}$, 65), 495 (41), 451 (80), 391 (87), 331 (55), 253 (100), 215 (98), 183 (27), 151 (68), 113 (25), 83 (30), 59 (57). HR EI MS: calculated for $C_{34}H_{34}O_8$ 570.2254, found 570.2197.

(1-{2-[2-(Hydroxymethyl)phenyl]ethyn-1-yl}-2-naphthyl)methanol (**36**)

$Na[AlH_2(OCH_2CH_2OCH_3)_2]$ (Red-Al®, 3.5 M solution in toluene, 400 μl, 1.40 mmol, 5.0 equivalents) was added to diester **35** (ref.[11]) (95 mg, 0.276 mmol) in toluene (2 ml) at 0 °C under argon and the mixture was stirred at 0 °C for 1 h. Anhydrous Na_2SO_4 was added and the excess of hydride was decomposed by adding saturated aqueous solution of Na_2SO_4. The mixture was passed through a pad of silica gel using toluene to get diol **36** (65 mg, 82%) as a white solid, m.p. 138–140 °C (petroleum ether–acetone). IR ($CHCl_3$): 3 606 m, 3 460 m, 3 061 m, 2 940 m, 2 882 m, 2 210 vw, 1 600 w, 1 593 w, (sh), 1 568 w, 1 508 w, 1 486 m, 1 450 m, 1 026 m, 1 014 s, 868 w, 822 s, 610 w. ^{1}H NMR (500 MHz, $CDCl_3$): 4.92 (brs, 2 H, CH_2Ph); 5.04 (s, 2 H, CH_2Nph); 7.36 (dt, 1 H, *J* = 7.7, 7.7, 1.7, 5-H (Ph)); 7.36 (dt, 1 H, *J* = 7.6, 7.6, 1.7, 4-H (Ph)); 7.47 (dd, 1 H, *J* = 7.1, 1.8, 3-H (Ph)); 7.53 (ddd, 1 H, *J* = 8.1, 6.8, 1.2, 6-H (Nph)); 7.58 (d, 1 H, *J* = 8.3, 3-H (Nph)); 7.61 (ddd, 1 H, *J* = 8.3, 6.8, 1.2, 7-H); 7.71 (dd, 1 H, *J* = 8.1, 1.8, 6-H (Ph)); 7.84 (brd, 1 H, *J* = 8.3, 4-H (Nph)); 7.85 (brd, 1 H, *J* = 8.2, 5-H (Nph)); 8.46 (ddt, 1 H, *J* = 8.4, 1.2, 0.8, 0.8, 8-H). ^{13}C NMR ($CDCl_3$): 64.14 (t, CH_2Ph), 64.39 (t, CH_2Nph), 89.62 (s, PhC≡CNph), 97.18 (s, PhC≡CNph), 119.07 (s, C-1 (Nph)), 122.14 (s, C-1 (Ph)), 125.92 (d, C-3 (Nph)), 126.08 (d, C-8), 126.40 (d, C-6 (Nph)), 127.10 (d, C-7), 127.80 (d, C-5 (Ph)), 128.15 (q, C-3 (Ph)), 128.22 (d, C-5 (Nph)), 128.91 (d, C-4 (Nph)), 128.91 (d, C-4 (Ph)), 132.48 (d, C-6 (Ph)), 132.67 (s, C-4a), 133.35 (s, C-8a), 141.35 (s, C-2 (Nph)), 142.29 (s, C-2 (Ph)). EI MS (*m/z*, rel.%): 288 ($M^{+•}$, 12), 270 (100), 253 (10), 241 (60), 226 (17), 215 (13), 202 (6), 169 (8), 141 (12), 119 (19), 91 (6), 77 (5). HR EI MS: calculated for $C_{20}H_{16}O_2$ 288.1150, found 288.1162.

2-(Bromomethyl)-1-{2-[2-(bromomethyl)phenyl]ethyn-1-yl}naphthalene (**37**)

Phosphorus tribromide (400 μl, 4.21 mmol, 1.4 equivalent) was added to diol **36** (847 mg, 2.94 mmol) in dry THF (20 ml) at 0 °C under nitrogen. After stirring at 0 °C for 2 h, the solvent was removed *in vacuo*. Flash chromatography on silica gel (petroleum ether–ether–-acetone 80 : 10 : 10 to 70 : 0 : 30) gave the crude product (1.61 g) that was recrystallized from acetone to afford dibromide **37** (797 mg, 65%) as a white solid, m.p. 155–157 °C (petroleum ether–acetone). IR (CCl_4): 3 060 m, 3 030 w (sh), 2 973 m, 2 855 w, 1 599 w, 1 593 w, 1 568 w, 1 509 m, 1 488 s, 1 450 s, 1 228 m, 1 086 w, 1 027 w, 949 w, 867 m, 820 vs, 607 s, 592 m. ^{1}H NMR (500 MHz, $CDCl_3$): 4.89 (s, 2 H, CH_2Ph); 5.04 (s, 2 H, CH_2Nph); 7.37–7.42 (m, 2 H, 4,5-H (Ph)); 7.50–7.52 (m, 1 H, 3-H (Ph)); 7.56 (d, 1 H, *J* = 8.3, 3-H (Nph)); 7.56 (ddd, 1 H, *J* = 8.1, 6.9, 1.2, 6-H (Nph)); 7.64 (ddd, 1 H, *J* = 8.3, 6.8, 1.2, 7-H); 7.74–7.76 (m, 1 H, 6-H (Ph)); 7.85 (brd, 1 H, *J* = 8.3, 4-H (Nph)); 7.86 (brd, 1 H, *J* = 8.1, 5-H (Nph)); 8.53 (brd, 1 H, *J* = 8.3, 8-H). ^{13}C NMR ($CDCl_3$): 32.17 (t, CH_2Ph), 32.93 (t, CH_2Nph), 90.25 (s, PhC≡CNph), 97.56 (s, PhC≡CNph), 120.42 (s, C-1 (Nph)), 123.18 (s, C-1 (Ph)), 126.72 (d, C-3 (Nph)), 126.94 (d, C-8), 127.08 (d, C-6 (Nph)), 127.51 (d, C-7), 128.24 (d, C-5 (Ph)), 128.70 (d, C-3 (Ph)), 129.33 (d, C-5 (Nph)), 129.43 (d, C-4 (Nph)), 129.98 (d, C-4 (Ph)), 132.90 (s, C-4a), 133.09 (d, C-6 (Ph)), 133.43 (s, C-8a), 138.04 (s, C-2 (Nph)), 139.18 (s, C-2 (Ph)). EI MS (*m/z*, rel.%): 416 ($M^{+•}$, with ^{81}Br, 7), 414 ($M^{+•}$ with ^{81}Br/^{79}Br, 14), 412 ($M^{+•}$ with ^{79}Br, 8), 335 (33), 333 (29), 273 (10), 271 (10), 254 (59), 253 (52), 252 (48), 137 (71), 135 (68), 97 (11), 83 (29), 55 (100), 41 (27). HR EI MS: calculated for $C_{20}H_{14}{}^{79}Br^{81}Br$ 413.9442, found 413.9540.

4-Methyl-*N*-(prop-2-en-1-yl)-*N*-({1-[2-(2-{[*N*-(prop-2-yn-1-yl)-*N*-tosylamino]methyl} phenyl)ethyn-1-yl]-2-naphthyl}methyl)benzenesulfonamide (**38**)

4-Methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide **21** (ref.[17]) (130 mg, 0.621 mmol, 2.6 equivalents) in dry DMF (2 ml) was added at 0 °C to sodium hydride (80% suspension in mineral oil, 20 mg, 0.667 mmol, 2.8 equivalents) in dry DMF (4 ml) under argon. After stirring at 0 °C for 1 h, dibromide **37** (100 mg, 0.241 mmol) in dry DMF (2 ml) was added and the mixture was stirred at room temperature overnight. The resulting clear solution was partitioned between ether and water. The ethereal layer was separated and the aqueous phase was extracted with ether (2×). The ethereal portions were combined, washed with water (1×), dried over Na_2SO_4 and evaporated *in vacuo*. The crude product was purified successively by flash chromatography on silica gel (petroleum ether–acetone 70 : 30) and preparative HPLC on silica gel (hexane–acetone 80 : 20) to afford triyne **38** (160 mg, 99%) as a white solid, m.p. 156–158 °C (petroleum ether–acetone). IR ($CHCl_3$): 3 307 m, 3 061 w, 3 032 w, 2 957 w, 2 926 w, 2 856 w, 2 123 vw, 1 599 w, 1 570 vw, 1 508 w, 1 495 w, 1 488 w, 1 450 w, 1 431 w, 1 400 w, 1 378 w, 1 349 s, 1 336 m (sh), 1 307 w, 1 291 w, 1 261 vw, 1 186 w, 1 162 vs, 1 119 w, 1 093 m, 1 072 w, 1 050 w, 1 025 vw, 1 019 w, 960 w, 929 w, 903 m, 869 w, 823 w (sh), 814 m, 661 m, 637 w, 590 w (sh), 573 m, 543 m, 521 w, 510 w. ^1H NMR (500 MHz, $CDCl_3$): 1.77 (t, 1 H, *J* = 2.4, $HC{\equiv}C^\frown$Nph); 1.84 (t, 1 H, *J* = 2.4, $HC{\equiv}C^\frown$Ph); 2.40 (brs, 3 H, $C\mathbf{H}_3C_6H_4SO_2N^\frown$Nph); 2.45 (brs, 3 H, $C\mathbf{H}_3C_6H_4SO_2N^\frown$Ph); 3.99 (d, 2 H, *J* = 2.4, $HC{\equiv}CC\mathbf{H}_2N^\frown$Ph); 4.06 (d, 2 H, *J* = 2.4, $HC{\equiv}CC\mathbf{H}_2N^\frown$Nph); 4.78 (s, 2 H, CH_2Ph); 4.86 (s, 2 H, CH_2Nph); 7.23–7.25 (m, 2 H, 3,5-H ($\mathbf{Ts}^\frown$Nph)); 7.28 (dt, 1 H, *J* = 7.6, 7.6, 1.3, 5-H (Ph)); 7.31–7.33 (m, 2 H, 3,5-H ($\mathbf{Ts}^\frown$Ph)); 7.37 (ddd, 1 H, *J* = 8.3, 6.9, 1.4, 7-H); 7.40 (dt, 1 H, *J* = 7.6, 7.6, 1.3, 4-H (Ph)); 7.51 (ddd, 1 H, *J* = 8.0, 6.9, 1.2, 6-H (Nph)); 7.53 (dd, 1 H, *J* = 7.7, 1.3, 3-H (Ph)); 7.63 (brd, 1 H, *J* = 8.0, 6-H (Ph)); 7.72 (d, 1 H, *J* = 8.5, 3-H (Nph)); 7.78–7.80 (m, 2 H, 2,6-H ($\mathbf{Ts}^\frown$Ph)); 7.83–7.85 (m, 2 H, 2,6-H ($\mathbf{Ts}^\frown$Nph); 7.86 (brd, 1 H, *J* = 8.5, 4-H (Nph)); 7.86 (brd, 1 H, *J* = 8.0, 5-H (Nph)); 8.28 (dq, 1 H, *J* = 8.5, 1.0, 1.0, 1.0, 8-H). ^{13}C NMR ($CDCl_3$): 21.51 (q, $CH_3C_6H_4SO_2N^\frown$Nph), 21.57 (q, $CH_3C_6H_4SO_2N^\frown$Ph), 36.38 (t, $HC{\equiv}CCH_2N^\frown$Ph), 36.59 (t, $HC{\equiv}CCH_2N^\frown$Nph), 48.46 (t, CH_2Ph), 48.85 (t, CH_2Nph), 74.00 (d, $HC{\equiv}CCH_2N^\frown$Ph), 74.29 (d, $HC{\equiv}CCH_2N^\frown$Nph), 76.50 (s, $HC{\equiv}CCH_2N^\frown$Nph), 89.97 (s, PhC≡CNph), 96.82 (s, PhC≡CNph), 120.25 (s, C-1 (Nph)), 122.59 (s, C-1 (Ph)), 126.17 (d, C-3 (Nph)), 126.54 (d, C-8), 126.57 (d, C-7), 126.99 (d, C-6 (Nph)), 127.58 (d, C-5 (Ph)), 127.86 (d, C-2,6 ($\mathbf{Ts}^\frown$Ph)), 128.00 (d, C-2,6 ($\mathbf{Ts}^\frown$Nph)), 128.14 (d, C-5 (Nph)), 128.26 (d, C-4 (Nph)), 129.23 (d, C-3 (Ph)), 129.23 (d, C-4 (Ph)), 129.57 (d, C-3 ($\mathbf{Ts}^\frown$Ph)), 129.60 (d, C-3,5 ($\mathbf{Ts}^\frown$Nph)), 132.66 (d, C-6 (Ph)), 132.71 (s, C-4a), 133.12 (s, C-8a), 136.02 (s, C-2 (Ph)), 136.04 (s, C-5 ($\mathbf{Ts}^\frown$Ph)), 136.07 (s, C-4 ($\mathbf{Ts}^\frown$Nph)), 137.07 (s, C-2 (Nph)), 143.69 (s, C-1 ($\mathbf{Ts}^\frown$Ph)), 143.74 (s, C-1 ($\mathbf{Ts}^\frown$Nph)); signal of $HC{\equiv}CCH_2N^\frown$Ph overlapped with $CDCl_3$ signals. EI MS (*m/z*, rel.%): 604 (7), 515 (24), 359 (40), 332 (20), 321 (28), 306 (64), 268 (25), 239 (13), 155 (13), 139 (14), 111 (25), 83 (52), 69 (64), 57 (100), 43 (82). FAB MS (*m/z*, dithiothreitol–dithioerythritol matrix): 671 ($(M + H)^+$), 633, 616, 515, 462, 424, 361, 307, 268, 155, 85. HR FAB MS (thioglycerol–glycerol matrix): calculated for $C_{40}H_{35}N_2O_4S_2$ (M + H) 671.2038, found 671.2161.

2-[(But-2-yn-1-yloxy)methyl]-1-(2-{2-[(but-2-yn-1-yloxy)methyl]phenyl}ethyn-1-yl) naphthalene (**39**)

But-2-yn-1-ol (320 μl, 4.23 mmol, 2.2 equivalents) in dry DMF (1 ml) was added to sodium hydride (80% suspension in mineral oil, 157 mg, 5.23 mmol, 2.7 equivalents) in dry DMF

(2 ml) under argon and the mixture was stirred at room temperature for 20 min. Then dibromide **37** (794 mg, 1.92 mmol) in dry DMF (15 ml) was added. After stirring at room temperature for 2 h, the reaction mixture was partitioned between ether and water. The ethereal layer was separated and the aqueous phase was extracted with ether (3×). The ethereal portions were combined, washed with water (1×), dried over Na_2SO_4 and evaporated *in vacuo*. Flash chromatography on silica gel (petroleum ether–ether 90 : 10) afforded triyne **39** (514 mg, 68%) as an oil. IR (CCl_4): 3 061 m, 3 020 w (sh), 2 944 m, 2 922 s, 2 855 s, 2 294 w, 2 249 w, 2 225 w, 1 621 w, 1599 w, 1 593 vw, 1 570 w, 1 509 m, 1 486 m, 1 467 m, 1 450 s, 1 387 m, 1 355 s, 1 081 vs, 866 m, 819 s. ^1H NMR (500 MHz, $CDCl_3$): 1.78 (t, 3 H, *J* = 2.3, CH_3⁀Nph); 1.82 (t, 3 H, *J* = 2.5, CH_3⁀Ph); 4.26 (q, 2 H, *J* = 2.3, C≡CCH_2O⁀Nph); 4.27 (q, 2 H, *J* = 2.5, C≡CCH_2O⁀Ph); 4.96 (s, 2 H, CH_2Nph); 5.08 (s, 2 H, CH_2Ph); 7.34 (dt, 1 H, *J* = 7.6, 7.6, 1.5, 5-H (Ph)); 7.40 (dt, 1 H, *J* = 7.6, 7.6, 1.5, 4-H (Ph)); 7.52 (ddd, 1 H, *J* = 8.1, 6.9, 1.2, 6-H (Nph)); 7.57 (brd, 1 H, *J* = 7.6, 3-H (Ph)); 7.60 (ddd, 1 H, *J* = 8.3, 6.9, 1.2, 7-H); 7.67 (d, 1 H, *J* = 8.6, 3-H (Nph)); 7.69 (dd, 1 H, *J* = 7.6, 1.4, 6-H (Ph)); 7.85 (brd, 1 H, *J* = 8.1, 5-H (Nph)); 7.86 (brd, 1 H, *J* = 8.5, 4-H (Nph)); 8.48 (dq, 1 H, *J* = 8.3, 0.9, 0.9, 0.9, 8-H). ^{13}C NMR ($CDCl_3$): 3.51 (q, CH_3⁀Nph), 3.54 (q, CH_3⁀Ph), 58.29 (t, CH_2O⁀Nph), 58.39 (t, CH_2O⁀Ph), 69.91 (t, CH_2Nph), 70.10 (t, CH_2Ph), 75.06 (s, C≡CCH_2⁀Nph), 75.21 (s, C≡CCH_2⁀Ph), 82.79 (s, C≡CCH_2⁀Nph), 82.87 (s, C≡CCH_2⁀Ph), 89.55 (s, NphC≡CPh), 97.08 (s, NphC≡CPh), 119.15 (s, C-1 (Nph)), 122.12 (s, C-1 (Ph)), 125.53 (d, C-3 (Nph)), 126.33 (d, C-3 (Ph)), 126.33 (d, C-8), 126.99 (d, C-6 (Nph)), 127.51 (d, C-7), 127.96 (d, C-5 (Ph)), 128.17 (d, C-5 (Nph)), 128.74 (d, C-4 (Nph)), 128.74 (d, C-4 (Ph)), 132.31 (d, C-6 (Ph)), 132.63 (s, C-4a), 133.26 (s, C-8a), 138.55 (s, C-2 (Ph)), 139.49 (s, C-2 (Nph)). EI MS (*m/z*, rel.%): 392 ($M^{+\bullet}$, 8), 339 (22), 321 (7), 309 (13), 293 (16), 269 (92), 254 (48), 239 (100), 228 (46), 202 (16), 165 (17), 119 (15), 84 (38), 53 (53). HR EI MS: calculated for $C_{28}H_{24}O_2$ 392.1776, found 392.1899.

2-[4-(Triisopropylsilyl)but-3-yn-1-yl]-1-(2-{2-[4-(triisopropylsilyl)but-3-yn-1-yl]phenyl} ethyn-1-yl)naphthalene (**40**)

Butyllithium (1.6 M solution in hexanes, 340 µl, 0.544 mmol, 2.3 equivalents) was added dropwise over a 10 min period to a solution of triisopropyl(prop-1-yn-1-yl)silane (130 µl, 0.543 mmol, 2.3 equivalents) in THF (2 ml) at –78 °C under argon. After stirring at –78 °C for 2 h, dibromide **37** (100 mg, 0.241 mmol) in THF (5 ml) was added dropwise over a 10 min period. The mixture was stirred at –78 °C for 1 h then warmed to room temperature and evaporated *in vacuo* to dryness. Flash chromatography on silica gel (petroleum ether–ether 90 : 10) gave triyne **40** (115 mg, 74%) as an amorphous solid. IR (CCl_4): 3 059 w, 2 958 s, 2 944 s, 2 925 s (sh), 2 891 s, 2 866 vs, 2 171 m, 1 621 vw, 1 599 vw, 1 569 vw, 1 509 w, 1 487 w, 1 463 w, 1 452 w, 1 429 w, 1 383 w, 1 366 w, 1 324 w, 1 290 w, 1 252 w, 1 146 vw, 1 102 vw, 1 073 w, 1 024 m, 996 m, 884 s, 865 w, 678 s, 661 s, 617 m, 523 w. ^1H NMR (500 MHz, $CDCl_3$): 1.01–1.04 (m, 42 H, 6 × $(C\mathbf{H}_3)_2C\mathbf{H}$); 2.76 (t, 4 H, *J* = 7.3, 2 × C≡CCH_2); 3.21 (t, 2 H, *J* = 7.3, CH_2Ph); 3.32 (t, 2 H, *J* = 7.3, CH_2Nph); 7.25 (dt, 1 H, *J* = 7.4, 7.4, 1.4, 5-H (Ph)); 7.29 (dt, 1 H, *J* = 7.4, 7.4, 1.5, 4-H (Ph)); 7.39 (brdd, 1 H, *J* = 7.4, 1.4, 3-H (Ph)); 7.48 (d, 1 H, *J* = 8.4, 3-H (Nph)); 7.48 (ddd, 1 H, *J* = 8.1, 6.8, 1.2, 6-H (Nph)); 7.58 (ddd, 1 H, *J* = 8.3, 6.9, 1.3, 7-H); 7.67 (brdd, 1 H, *J* = 7.4, 1.5, 6-H (Ph)); 7.76 (brd, 1 H, *J* = 8.4, 4-H (Nph)); 7.83 (brd, 1 H, *J* = 8.1, 5-H (Nph)); 8.43 (dq, 1 H, *J* = 8.3, 1.0, 1.0, 1.0, 8-H). ^{13}C NMR ($CDCl_3$): 11.31 (d, 6 × $(CH_3)_2CH$), 18.59 (q, 6 × $(CH_3)_2CH$), 21.24 (t, C≡CCH_2⁀Nph), 21.32 (t, C≡CCH_2⁀Ph), 34.36 (t, CH_2Nph), 35.02 (t, CH_2Ph), 81.20 (s, C≡CCH_2⁀Nph), 81.22 (s, C≡CCH_2⁀Ph), 89.75 (s, PhC≡CNph), 97.35 (s, PhC≡CNph), 107.84

(s, C≡CCH$_2{}^\frown$Nph), 107.96 (s, C≡CCH$_2$Ph), 113.41 (s, C-1 (Nph)), 122.90 (s, C-1 (Ph)), 125.75 (d, C-8), 126.02 (d, C-3 (Nph)), 126.41 (d, C-5 (Ph)), 126.87 (d, C-6 (Nph)), 127.53 (d, C-7), 128.10 (d, C-5 (Nph)), 128.28 (d, C-4 (Ph)), 128.41 (d, C-4 (Nph)), 129.53 (d, C-3 (Ph)), 132.03 (s, C-4a), 132.62 (d, C-6 (Ph)), 133.56 (s, C-8a), 141.53 (s, C-2 (Nph)), 141.98 (s, C-2 (Ph)). EI MS (*m/z*, rel.%): 644 ($M^{+\bullet}$, 7), 601 (18), 486 (5), 443 (11), 329 (5), 291 (9), 157 (83), 129 (19), 115 (100), 101 (15), 87 (46), 73 (49), 59 (63), 43 (17). HR EI MS: calculated for $C_{44}H_{60}Si_2$ 644.4234, found 644.4183.

2-(But-3-yn-1-yl)-1-{2-[2-(but-3-yn-1-yl)phenyl]ethyn-1-yl}naphthalene (**41**)

Tetrabutylammonium fluoride (1.0 M solution in THF, 7.0 ml, 7.00 mmol, 4.9 equivalents) was added to silylated triyne **40** (930 mg, 1.44 mmol) in dry THF (15 ml) and the mixture was stirred under argon at room temperature for 1 h. The solution was evaporated *in vacuo* to dryness and the crude product was purified by flash chromatography on alumina (petroleum ether–ether 100 : 0 to 99 : 1) to get triyne **41** (466 mg, 97%) as an amorphous solid. IR ($CHCl_3$): 3 308 vs, 3 060 w, 2205 vw, 2 118 w, 1 620 w, 1597 w, 1 594 w, 1 567 w, 1 507 m, 1487 m, 1 451 m, 1 431 w, 1 259 w, 1 102 w, 1 041 vw, 1 025 w, 867 w, 820 m, 640 vs, 495 w. ^{1}H NMR (500 MHz, $CDCl_3$): 2.01 (t, 1 H, *J* = 2.6, HC≡C$^\frown$Ph); 2.03 (t, 1 H, *J* = 2.7, HC≡C$^\frown$Nph); 2.68 (dt, 2 H, *J* = 7.6, 7.6, 2.7, HC≡CC$\mathbf{H}_2{}^\frown$Ph); 2.69 (dt, 2 H, *J* = 7.6, 7.6, 2.7, HC≡CC$\mathbf{H}_2{}^\frown$Nph); 3.23 (t, 2 H, *J* = 7.6, CH$_2$Ph); 3.33 (t, 2 H, *J* = 7.6, CH$_2$Nph); 7.29 (dt, 1 H, *J* = 7.3, 7.3, 1.9, 5-H (Ph)); 7.33 (dt, 1 H, *J* = 7.6, 7.6, 1.5, 4-H (Ph)); 7.36 (dd, 1 H, *J* = 7.2, 1.9, 3-H (Ph)); 7.45 (d, 1 H, *J* = 8.4, 3-H (Nph)); 7.50 (ddd, 1 H, *J* = 8.1, 6.8, 1.3, 6-H (Nph)); 7.60 (ddd, 1 H, *J* = 8.3, 6.7, 1.3, 7-H); 7.68 (dd, 1 H, *J* = 7.3, 1.5, 6-H (Ph)); 7.80 (brd, 1 H, *J* = 8.4, 4-H (Nph)); 7.84 (brd, 1 H, *J* = 8.1, 5-H (Nph)); 8.45 (dq, 1 H, *J* = 8.3, 1.0, 1.0, 1.0, 8-H). ^{13}C NMR ($CDCl_3$): 19.81 (t, HC≡CCH$_2{}^\frown$Nph), 19.86 (t, HC≡CCH$_2{}^\frown$Ph), 34.07 (t, CH$_2$Nph), 34.55 (t, CH$_2$Ph), 69.12 (d, HC≡CCH$_2{}^\frown$Nph), 69.15 (d, HC≡CCH$_2{}^\frown$Ph), 83.66 (s, PhC≡CNph), 83.69 (s, PhC≡CNph), 89.69 (s, HC≡CCH$_2{}^\frown$Nph), 97.15 (s, HC≡CCH$_2{}^\frown$Ph), 119.44 (s, C-1 (Nph)), 122.94 (s, C-1 (Ph)), 125.91 (d, C-8), 126.10 (d, C-3 (Nph)), 126.61 (d, C-5 (Ph)), 127.01 (d, C-6 (Nph)), 127.28 (d, C-7), 128.16 (d, C-5 (Nph)), 128.49 (d, C-4 (Ph)), 128.61 (d, C-4 (Nph)), 129.19 (d, C-3 (Ph)), 132.03 (s, C-4a), 132.68 (d, C-6 (Ph)), 133.56 (s, C-8a), 141.22 (s, C-2 (Nph)), 141.84 (s, C-2 (Ph)). EI MS (*m/z*, rel.%): 332 ($M^{+\bullet}$, 37), 315 (30), 303 (20), 289 (22), 276 (29), 265 (12), 252 (27), 239 (12), 202 (12), 191 (100), 165 (16), 141 (15), 138 (14), 126 (13), 115 (12), 91 (12). HR EI MS: calculated for $C_{26}H_{20}$ 332.1565, found 332.1580.

2-(Pent-3-yn-1-yl)-1-{2-[2-(pent-3-yn-1-yl)phenyl]ethyn-1-yl}naphthalene (**42**)

Butyllithium (1.6 M solution in hexanes, 1.60 ml, 2.56 mmol, 2.2 equivalents) was added dropwise over a 5 min period to triyne **41** (385 mg, 1.16 mmol) in dry THF (12 ml) at –78 °C under argon. After stirring at –78 °C for 10 min, methyl iodide (180 μl, 2.89 mmol, 2.5 equivalents) was added and the mixture was stirred at –78 °C for 20 min. The solvents were removed *in vacuo* and the crude product was purified by flash chromatography on silica gel (petroleum ether–ether 96 : 4) to furnish dimethylated triyne **42** (387 mg, 93%) as an oil. IR (CCl_4): 3 094 vw, 3 059 m, 3 032 w, 2 956 m, 2 931 m, 2 920 s, 2 859 w, 2 845 w, 2 235 vvw, 2 198 vvw, 1 621 vw, 1 599 w, 1 569 w, 1 508 m, 1 487 m, 1 451 m, 1 434 m, 1 341 w, 1 326 w, 1 259 vw, 1 163 w, 1 102 w, 1 025 w, 865 w. ^{1}H NMR (500 MHz, $CDCl_3$): 1.77 (t, 3 H, *J* = 2.6, CH$_3{}^\frown$Ph); 1.79 (t, 3 H, *J* = 2.6, CH$_3{}^\frown$Nph); 2.61 (tq, 4 H, *J* = 7.6, 7.6, 2.6, 2.6, 2.6,

$C{\equiv}CCH_2{}^{\frown}Ph$, $C{\equiv}CCH_2{}^{\frown}Nph$); 3.18 (t, 2 H, *J* = 7.6, CH_2Nph); 3.28 (t, 2 H, *J* = 7.6, CH_2Ph); 7.26–7.31 (m, 2 H, 4,5-H (Ph)); 7.33 (dd, 1 H, *J* = 6.8, 1.6, 3-H (Ph)); 7.44 (d, 1 H, *J* = 8.4, 3-H (Nph)); 7.49 (ddd, 1 H, *J* = 8.1, 6.8, 1.2, 6-H (Nph)); 7.58 (ddd, 1 H, *J* = 8.3, 6.8, 1.3, 7-H); 7.68 (ddd, 1 H, *J* = 7.5, 1.5, 0.8, 6-H (Ph)); 7.78 (dt, 1 H, *J* = 8.4, 0.6, 0.6, 4-H (Nph)); 7.83 (ddt, 1 H, *J* = 8.1, 1.3, 0.7, 0.7, 5-H (Nph)); 8.46 (ddt, 1 H, *J* = 8.3, 1.2, 0.8, 0.8, 8-H)). ^{13}C NMR ($CDCl_3$): 3.50 (q, $CH_3{}^{\frown}Ph$), 3.53 (q, $CH_3{}^{\frown}Nph$), 20.18 (t, $C{\equiv}CCH_2{}^{\frown}Nph$), 20.25 (t, $C{\equiv}CCH_2{}^{\frown}Ph$), 34.69 (t, CH_2Nph), 35.17 (t, CH_2Ph), 76.35 (s, $C{\equiv}CCH_2{}^{\frown}Nph$), 76.42 (s, $C{\equiv}CCH_2{}^{\frown}Ph$), 78.49 (s, $C{\equiv}CCH_2{}^{\frown}Nph$), 78.54 (s, $C{\equiv}CCH_2{}^{\frown}Ph$), 89.64 (s, PhC≡CNph), 97.11 (s, PhC≡CNph), 119.47 (s, C-1 (Nph)), 123.06 (s, C-1 (Ph)), 125.76 (d, C-8), 126.21 (d, C-3 (Nph)), 126.36 (d, C-5 (Ph)), 126.86 (d, C-6 (Nph)), 127.40 (d, C-7), 128.09 (d, C-5 (Nph)), 128.27 (d, C-4 (Ph)), 128.45 (d, C-4 (Nph)), 129.13 (d, C-3 (Ph)), 131.97 (s, C-4a), 132.61 (d, C-6 (Ph)), 133.61 (s, C-8a), 141.88 (s, C-2 (Nph)), 142.50 (s, C-2 (Ph)). EI MS (*m*/*z*, rel.%): 360 ($M^{+\bullet}$, 46), 345 (40), 330 (88), 315 (53), 303 (25), 291 (52), 289 (69), 265 (41), 252 (100), 239 (29), 216 (22), 202 (21), 189 (18), 165 (33), 141 (20), 126 (15), 115 (24), 91 (33), 69 (43), 57 (40), 43 (34). HR EI MS: calculated for $C_{28}H_{24}$ 360.1878, found 360.1862.

2-[4-(Trimethylsilyl)but-3-yn-1-yl]-1-(2-{2-[4-(trimethylsilyl)but-3-yn-1yl]phenyl}ethyn-1-yl)-naphthalene (**43**)

Butyllithium (1.6 M solution in hexanes, 400 µl, 0.640 mmol, 2.2 equivalents) was added dropwise over a 3 min period to triyne **41** (97 mg, 0.292 mmol) in dry THF (3 ml) at –78 °C under argon. After stirring at –78 °C for 10 min, trimethylsilyl chloride (100 µl, 0.788 mmol, 2.7 equivalents) was added and the mixture was stirred at –78 °C for 20 min. The solvents were removed *in vacuo* and the crude product was purified by flash chromatography on silica gel (petroleum ether–ether 98 : 2) to furnish disilylated triyne **43** (129 mg, 93%) as an oil. IR (CCl_4): 3 059 w, 2 960 w, 2 935 w, 2 902 w, 2 864 w, 2 175 w, 1 599 vw, 1 508 w, 1 487 w, 1 451 w, 1 428 vw, 1 407 vw, 1 338 vw, 1 324 vw, 1 250 m, 1 162 vw, 1 102 vw, 1 027 vw (sh), 844 s, 698 w, 639 w. ^{1}H NMR (500 MHz, $CDCl_3$): 0.128 (s, 9 H $(CH_3)_3Si{}^{\frown}Ph$); 0.132 (s, 9 H $(CH_3)_3Si{}^{\frown}Nph$); 2.70 (t, 2 H, *J* = 7.6, $C{\equiv}CCH_2{}^{\frown}Nph$); 2.71 (t, 2 H, *J* = 7.6, $C{\equiv}CCH_2Ph$); 3.20 (t, 2 H, *J* = 7.6, CH_2Nph); 3.31 (t, 2 H, *J* = 7.6, CH_2Ph); 7.28 (dt, 1 H, *J* = 7.5, 7.5, 1.6, 5-H (Ph)); 7.32 (dt, 1 H, *J* = 7.5, 7.5, 1.7, 4-H (Ph)); 7.35 (ddd, 1 H, *J* = 7.4, 1.6, 0.8, 3-H (Ph)); 7.45 (d, 1 H, *J* = 8.4, 3-H (Nph)); 7.50 (ddd, 1 H, *J* = 8.1, 6.8, 1.2, 6-H (Nph)); 7.60 (ddd, 1 H, *J* = 8.3, 6.8, 1.4, 7-H); 7.68 (ddd, 1 H, *J* = 7.3, 1.7, 0.7, 6-H (Ph)); 7.78 (dt, 1 H, *J* = 8.4, 0.6, 0.6, 4-H (Nph)); 7.84 (ddt, 1 H, *J* = 8.1, 1.4, 0.7, 0.7, 5-H (Nph)); 8.44 (dq, 1 H, *J* = 8.4, 0.9, 0.9, 0.9, 8-H). ^{13}C NMR ($CDCl_3$): 0.06 (q, $(CH_3)_3Si{}^{\frown}Nph$), 0.09 (q, $(CH_3)_3Si{}^{\frown}Ph$), 21.37 (t, 2 × $C{\equiv}CCH_2$), 34.23 (t, CH_2Nph), 34.76 (t, CH_2Ph), 85.47 (s, $C{\equiv}CCH_2{}^{\frown}Nph$), 85.54 (s, $C{\equiv}CCH_2{}^{\frown}Ph$), 89.68 (s, PhC≡CNph), 97.20 (s, PhC≡CNph), 106.38 (s, $C{\equiv}CCH_2{}^{\frown}Nph$), 106.47 (s, $C{\equiv}CCH_2{}^{\frown}Ph$), 119.46 (s, C-1 (Nph)), 122.97 (s, C-1 (Ph)), 125.81 (d, C-8), 126.10 (d, C-3 (Nph)), 126.49 (d, C-5 (Ph)), 126.93 (d, C-6 (Nph)), 127.57 (d, C-7), 128.12 (d, C-5 (Nph)), 128.25 (d, C-4 (Ph)), 128.43 (d, C-4 (Nph)), 129.42 (d, C-3 (Ph)), 132.01 (s, C-4a), 132.61 (d, C-6 (Ph)), 133.53 (s, C-8a), 141.46 (s, C-2 (Nph)), 142.01 (s, C-2 (Ph)). EI MS (*m*/*z*, rel.%): 476 ($M^{+\bullet}$, 2), 404 (7), 387 (5), 373 (6), 329 (23), 289 (5), 267 (6), 252 (9), 96 (3), 73 (100), 59 (8), 45 (5), 28 (4). HR EI MS: calculated for $C_{32}H_{36}Si_2$ 476.2356, found 476.2351.

2-(Bromomethyl)-1-iodonaphthalene (**45**)

Phosphorus tribromide (180 μl, 1.90 mmol, 0.5 equivalent) was added to (1-iodo-2-naphthyl)methanol **44** (ref.[11]) (989 mg, 3.48 mmol) in dry THF (10 ml) at 0 °C under nitrogen. After stirring at 0 °C for 1 h, the solvent was removed *in vacuo*. Flash chromatography on silica gel (petroleum ether–ether 95 : 5 to 85 : 15) gave bromide **45** (1.14 g, 94%) as an amorphous solid. IR (CCl_4): 3 057 w, 3 037 w (sh), 3 007 vw, 2 974 w, 2 859 vw, 1 607 vw, 1 596 vw, 1 552 m, 1 503 s, 1 462 w, 1 438 m, 1 350 w, 1 322 s, 1 260 m, 1 210 s, 1 032 w, 861 m, 589 m, 523 m. ^{1}H NMR (500 MHz, $CDCl_3$): 4.91 (s, 2 H, CH_2); 7.53 (ddd, 1 H, *J* = 8.1, 6.9, 1.2, 6-H); 7.55 (d, 1 H, *J* = 8.4, 3-H); 7.60 (ddd, 1 H, *J* = 8.5, 6.9, 1.4, 7-H); 7.77 (ddt, 1 H, *J* = 8.1, 1.4, 0.6, 0.6, 5-H); 7.80 (dt, 1 H, *J* = 8.4, 0.7, 0.7, 4-H); 8.25 (ddt, 1 H, *J* = 8.5, 1.3, 0.7, 0.7, 8-H). ^{13}C NMR ($CDCl_3$): 43.03 (t, CH_2), 106.27 (s, C-1), 127.13 (d, C-5), 127.20 (d, C-4), 128.23 (d, C-6), 128.28 (d, C-7), 129.43 (d, C-3), 133.16 (d, C-8), 133.52 (s, C-4a), 135.21 (s, C-8a), 139.36 (s, C-2). EI MS (*m/z*, rel.%): 348 ($M^{+\bullet}$ with ^{81}Br, 17), 346 ($M^{+\bullet}$ with ^{79}Br, 18), 267 (100), 140 (96), 127 (7), 113 (8), 79 (8), 63 (10). HR EI MS: calculated for $C_{11}H_8{}^{79}BrI$ 345.8854, found 345.8850.

1-Iodo-2-[4-(triisopropylsilyl)but-3-yn-1-yl]naphthalene (**46**)

Butyllithium (1.6 M solution in hexanes, 220 μl, 0.352 mmol, 1.2 equivalent) was added dropwise to a solution of triisopropyl(prop-1-yn-1-yl)silane (85 μl, 0.355 mmol, 1.2 equivalent) in dry THF (2 ml) at –78 °C under argon. After stirring at –78 °C for 2.5 h, bromide **45** (103 mg, 0.297 mmol) in dry THF (1 ml) was added dropwise. The mixture was stirred at –78 °C for 2.5 h and then warmed to room temperature. The solvents were removed *in vacuo*. Flash chromatography on silica gel (petroleum ether–ether 98 : 2) gave alkyne **46** (95 mg, 69%) as an oil. IR (CCl_4): 3 055 w, 2 866 vs, 2 171 m, 1 621 vw, 1 597 vw, 1 551 w, 1 501 m, 1 463 m, 1 451 m (sh), 1 428 w, 1 383 w, 1 366 w, 1 323 w, 1 256 w, 1 073 w, 1 030 m, 996 m, 884 m, 860 w, 678 s, 660 m. ^{1}H NMR (500 MHz, $CDCl_3$): 1.03 (m, 21 H, 3 × $(C\mathbf{H}_3)_2C\mathbf{H}$); 2.66 (t, 2 H, *J* = 7.3, $C\equiv CCH_2$); 3.26 (t, 2 H, *J* = 7.3, CH_2Nph); 7.45 (d, 1 H, *J* = 8.4, 3-H); 7.47 (ddd, 1 H, *J* = 8.1, 6.8, 1.2, 6-H); 7.55 (ddd, 1 H, *J* = 8.4, 6.8, 1.4, 7-H); 7.72 (brd, 1 H, *J* = 8.4, 4-H); 7.75 (ddq, 1 H, *J* = 8.1, 1.4, 0.7, 0.7, 0.7, 5-H); 8.23 (brdd, 1 H, *J* = 8.4, 1.2, 8-H). ^{13}C NMR ($CDCl_3$): 11.28 (d, 3 × $(CH_3)_2CH$), 18.60 (q, 3 × $(CH_3)_2CH$), 20.68 (t, $C\equiv CCH_2$), 42.02 (t, CH_2Nph), 81.49 (s, $C\equiv CCH_2$), 94.78 (s, $C\equiv CCH_2$), 107.41 (s, C-1), 125.99 (d, C-3), 127.62 (d, C-5), 127.90 (d, C-4), 128.13 (d, C-6), 128.51 (d, C-7), 132.70 (d, C-8), 132.93 (s, C-4a), 135.07 (s, C-8a), 142.51 (s, C-2). EI MS (*m/z*, rel.%): 462 ($M^{+\bullet}$, 7), 419 (100), 391 (10), 377 (11), 349 (5), 293 (10), 267 (10), 249 (17), 235 (5), 221 (24), 207 (22), 179 (8), 140 (11), 59 (5). HR EI MS: calculated for $C_{23}H_{31}ISi$ 462.1240, found 462.1235.

Bis{2-[4-(triisopropyl)but-3-yn-1-yl]-1-naphthyl}acetylene (**47**)

A mixture of naphthyl iodide **46** (5.60 g, 12.11 mmol), $Pd(PPh_3)_4$ (771 mg, 0.667 mmol, 6 mole %), and CuI (237 mg, 1.24 mmol, 10 mole %) in deoxygenated piperidine (40 ml) was stirred under 1 atm pressure of acetylene at 80 °C for 2 h (a rubber balloon filled with acetylene was attached to the Schlenk flask). The precipitated solid was removed by suction, washed with petroleum ether, and the filtrate was evaporated *in vacuo* to dryness. Flash chromatography on silica gel (petroleum ether–ether 100 : 0 to 96 : 4) furnished triyne **47** (3.25 g, 77%) as an oil. IR (CCl_4): 3 058 w, 3 012 vw, 2 958 s, 2 944 vs, 2 922 s (sh), 2 891 m, 2 866 vs, 2 171 m, 1 621 vw, 1 593 vw, 1 570 vw, 1 509 w, 1 463 m, 1 451 w (sh), 1 428 w, 1 388 w, 1 382 w, 1 366 w, 1 342 vw, 1 324 w, 1 252 vw, 1 242 w, 1 146 vw, 1 073 w, 1 026 w, 996 w, 883 m, 865 w, 818 m, 678 s, 660 m, 617 w, 596 w (sh). ^{1}H NMR (500 MHz, $CDCl_3$): 0.99–1.01 (m, 42 H, 6 × $(C\mathbf{H}_3)_2C\mathbf{H}$); 2.82 (t, 4 H, *J* = 7.3, 2 × $C≡CCH_2$); 3.43 (t, 4 H, *J* = 7.3, 2 × CH_2Nph); 7.50 (ddd, 2 H, *J* = 8.3, 6.9, 1.2, 2 × 6-H); 7.55 (d, 2 H, *J* = 8.3, 2 × 3-H); 7.63 (ddd, 2 H, *J* = 8.3, 6.9, 1.2, 2 × 7-H); 7.80 (brd, 2 H, *J* = 8.3, 2 × 4-H); 7.86 (brd, 2 H, *J* = 8.1, 2 × 5-H); 8.61 (ddt, 2 H, *J* = 8.4, 1.2, 0.8, 0.8, 2 × 8-H). ^{13}C NMR ($CDCl_3$): 11.32 (d, 6 × $(CH_3)_2CH$), 18.59 (q, 6 × $(CH_3)_2CH$), 21.49 (t, 2 × $C≡CCH_2$), 34.97 (t, 2 × CH_2Nph), 81.44 (s, 2 × $C≡CCH_2$), 95.11 (s, NphC≡CNph), 107.82 (s, 2 × $C≡CCH_2$), 119.61 (s, 2 × C-1), 125.79 (d, 2 × C-3), 126.20 (d, 2 × C-8), 127.01 (d, 2 × C-6), 127.68 (d, 2 × C-7), 128.19 (d, 2 × C-4), 128.41 (d, 2 × C-5), 132.14 (s, 2 × C-4a), 133.76 (s, 2 × C-8a), 141.61 (s, 2 × C-2). EI MS (*m/z*, rel.%): 694 ($M^{+\bullet}$, 7), 651 (11), 537 (5), 493 (5), 379 (5), 339 (5), 191 (6), 157 (57), 129 (16), 115 (100), 101 (13), 87 (51), 73 (50), 59 (63). HR EI MS: calculated for $C_{48}H_{62}Si_2$ 694.4390, found 694.4406.

Bis[2-(but-3-yn-1-yl)-1-naphthyl]acetylene (**48**)

Tetrabutylammonium fluoride (1.0 M solution in THF, 600 μl, 0.600 mmol, 4.3 equivalents) was added to silylated triyne **47** (98 mg, 0.141 mmol) in dry THF (2 ml) and the mixture was stirred under argon at room temperature for 1 h. The solution was evaporated *in vacuo* to dryness and the crude product was purified by flash chromatography on alumina (petroleum ether–ether 97 : 3 to 94 : 6) to get triyne **48** (38 mg, 70%) as an amorphous solid. IR (CCl_4): 3 314 vs, 3 293 w, 2 958 w, 2 936 w, 2 914 w, 2 865 w, 2 814 vw, 2 121 w, 1 622 vw, 1 593 w, 1 570 w, 1 508 w, 1 430 w, 1 398 w, 1 343 w, 1 326 w, 1 253 w, 1 146 w, 1 025 w, 864 w, 818 s, 636 vs. ^{1}H NMR (500 MHz, $CDCl_3$): 2.04 (t, 2 H, *J* = 2.7, 2 × HC≡C); 2.75 (dt, 4 H, *J* = 7.7, 7.7, 2.7, 2 × $C≡CCH_2$); 3.46 (t, 4 H, *J* = 7.7, 2 × CH_2Nph); 7.51 (d, 2 H, *J* = 8.3, 2 × 3-H); 7.53 (ddd, 2 H, *J* = 8.3, 6.8, 1.4, 2 × 7-H); 7.65 (ddd, 2 H, *J* = 8.2, 6.8, 1.3, 2 × 6-H); 7.85 (brd, 2 H, *J* = 8.3, 2 × 4-H); 7.88 (brd, 2 H, *J* = 8.2, 2 × 5-H); 8.60 (ddt, 2 H, *J* = 8.3, 1.3, 0.9, 0.9, 2 × 8-H). ^{13}C NMR ($CDCl_3$): 20.09 (t, 2 × $C≡CCH_2$), 34.76 (t, 2 × CH_2Nph), 69.25 (d, 2 × HC≡C), 83.65 (s, 2 × HC≡C), 95.02 (s, NphC≡CNph), 119.66 (s, 2 × C-1), 125.98 (d, 2 × C-3), 126.22 (d, 2 × C-6), 127.19 (d, 2 × C-8), 127.33 (d, 2 × C-7), 128.26 (d, 2 × C-4), 128.67 (d, 2 × C-5), 132.11 (s, 2 × C-4a), 133.72 (s, 2 × C-8a), 141.28 (s, 2 × C-2). EI MS (*m/z*, rel.%): 382 ($M^{+\bullet}$, 100), 366 (20), 353 (24), 339 (29), 326 (45), 313 (22), 302 (37), 289 (15), 276 (7), 239 (7), 215 (14), 202 (10), 189 (12), 176 (8), 163 (24), 151 (41), 141 (33), 57 (5), 43 (4). HR EI MS: calculated for $C_{30}H_{22}$ 382.1722, found 382.1717.

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9. Diester **1** and diol **2** were easily prepared in one step from methyl 2-iodobenzoate[10] or 2-iodobenzyl alcohol[11], respectively, and dibromide **3** in two steps from 2-iodo-4-methylbenzene[11,12]. In addition, diester **1** was reduced to diol **2** with $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ leaving the triple bond untouched in contrast to $LiAlH_4$ (Scheme 2). Dibromide **3** was routinely prepared from diol **2** on treatment with phosphorus tribromide (Scheme 2).
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