Synthesis of Geminal Enediynes with Saturated and Unsaturated Carbocyclic Backbones by Palladium-Catalyzed Alkynylation of Dibromoolefins

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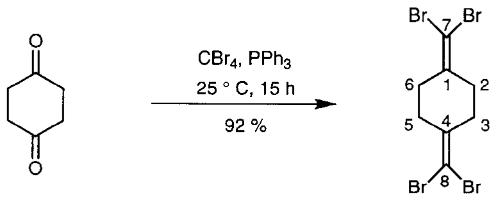
Abstract: The conversion of cyclic diketones **1** and **3** into the corresponding dibromoalkenes **2** and **4** via Corey–Fuchs procedure is described. Subsequent alkynylation of **2** and **4** as well as 9-(dibromomethylene)fluorene **(6)** yields the geminal enediynes **5a–e**, **7a–e**, and **8a–c**.The cyclohexane backbone of **5a,d** can be oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to the *p*-quinoid systems **9a,b**.

Key words: dibromoalkenes, alkynylation, geminal enediynes, oxidation

In our earlier work,[1, 2] we have explored the syntheses of peri-ethynyl substituted 1,6-methano[10]annulene derivatives and investigated the interactions between their acetylene fragments. Several multi-ethynyl substituted derivatives were synthesized and the properties of these and other isolated products were investigated; we have also synthesized some enediyne units as derivatives of 1,6-methano[10]annulenes using palladium-catalyzed cross coupling reactions.[1, 2]

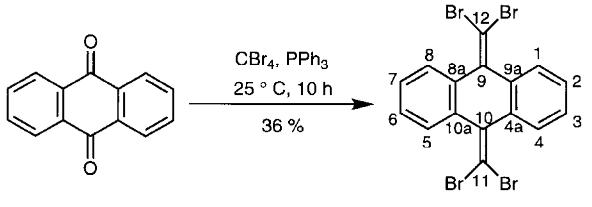
Enediyne units can also be substructures in molecules designed to serve as precursors to two-dimensional carbon networks.[3] Very often, substances of this type are made up of tetraethynylethene building blocks.[4] Carbon networks prepared from this type of molecules would have distinctive physical properties; selective substitution of the monomeric starting materials with cyclic aliphatic or aromatic saturated or polyunsaturated groups could probably significantly change the physical properties of the resulting polymeric carbon networks.

In order to prepare suitable precursors for such novel all carbon networks, we chose to transform cyclohexane-1,4-dione **(1)** and anthraquinone **(3)** into the corresponding dibromoalkenes (Schemes 1 and 2). These dibromoalkenes as well as the known fluorene derivative **6**[5] (Scheme 4) should represent suitable starting materials for catalytic alkynylation yielding novel cyclic geminal enediynes.



1 **2**

Scheme 1

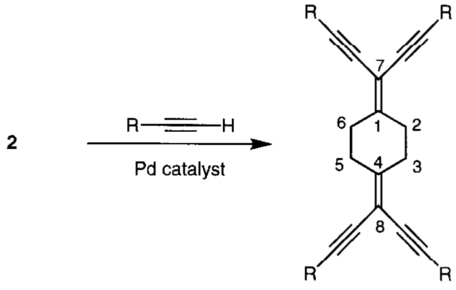


3 **4**

Scheme 2

According to known literature procedures,[6] the ketones **1** and **3** were reacted with CBr$_4$/PPh$_3$ mixtures in anhydrous benzene. After reaction at room temperature for 15 and 10 hours, respectively, the dibromoalkenes **2** and **4** could be isolated by filtration of the reaction mixtures, evaporation of the filtrates and column chromatography on silica gel in yields of 93% for **2** and 36% for **4**. Dibromoalkenes **2** and **4** are colorless solids that are stable to air at ambient temperature and melt at 140–145 °C (subl.) and 73 °C, respectively.

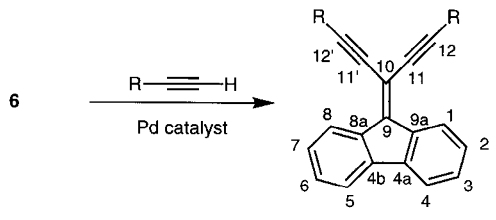
Besides these two dibromoalkenes, 9-(dibromomethylene)-9*H*-fluorene[5] **(6)** was chosen as an interesting starting material for alkynylations.[7] Substitution of bromine atoms in **2**, **4**, and **6** was achieved by using different palladium catalysts, namely, Pd(PPh$_3$)$_4$, Pd(PPh$_3$)$_2$Cl$_2$ and Pd(PhCN)$_2$Cl$_2$. No systematic relation between the structure of the dibromoalkenes or the type of alkyne and the best suited catalyst was observed; instead, the optimum catalyst for a given reaction was found by comparison between several runs under different conditions. Reactions were conducted in anhydrous benzene at temperatures between room temperature and 80 °C. For elimination of the HBr formed during the substitution reactions, various amines were employed. Pure alkynylation products were isolated by evaporation of the volatile portion of the reaction mixtures and column chromatography of the residue on silica gel. The resulting geminal enediynes **5a–e** (Scheme 3), **7a–e** (Scheme 4), and **8a–c** (Scheme 5) are



Scheme 3 **5 a - e**

Table 1. Alkynylation Products **5a–e** Prepared

Compound	R	Catalyst	Time	Temp. (°C)	Yield (%)
5a	Ph	$Pd(PPh_3)_2Cl_2$	4 d	25	12
5b	*t*-Bu	$Pd(PPh_3)_2Cl_2$	30 h	60	31
5c	$(CH_2)_5CH_3$	$Pd(PhCN)_2Cl_2$	6 h	70	45
5d	$SiMe_3$	$Pd(PPh_3)_2Cl_2$	48 h	25	78
5e	$Si(^iPr)_3$	$Pd(PPh_3)_2Cl_2$	24 h	60	51

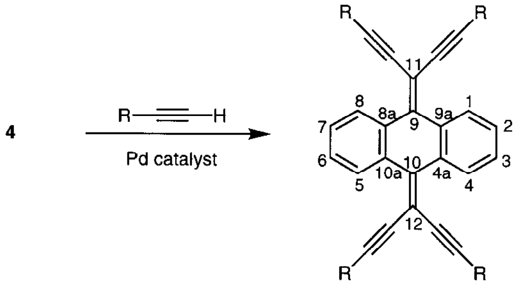


Scheme 4

7 a - e

Table 2. Alkynylation Products **7a–e** Prepared

Compound	R	Catalyst	Time	Temp. (°C)	Yield (%)
7a	Ph	$Pd(PPh_3)_4$	7 d	25	12
7b	*t*-Bu	$Pd(PPh_3)_2Cl_2$	3.5 h	70	47
7c	$(CH_2)_5CH_3$	$Pd(PPh_3)_2Cl_2$	5 h	80	16
7d	$SiMe_3$	$Pd(PPh_3)_2Cl_2$	24 h	25	54
7e	$Si(^iPr)_3$	$Pd(PPh_3)_2Cl_2$	3 h	80	71



Scheme 5

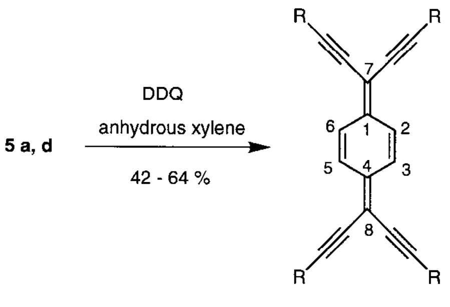
8 a - c

Table 3. Alkynylation Products **8a–c** Prepared

Compound	R	Catalyst	Time	Temp. (°C)	Yield (%)
8a	Ph	$Pd(PPh_3)_2Cl_2$	48h	25	29
8b	*t*-Bu	$Pd(PPh_3)_2Cl_2$	8 h	80	32
8c	$SiMe_3$	$Pd(PhCN)_2Cl_2$	6 h	80	26

yellowish to red solids, very soluble in hexane and can be stored for extended periods of time at ambient temperature. Solutions of the above mentioned compounds decompose slowly.

The cyclohexane backbone of **5a** and **5d** is an interesting target for attempts to transform it into a *p*-quinoid system. Oxidation was brought about by reaction of **5a** and **5d** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in anhydrous xylene at reflux. The resulting *p*-quinoid, alkynyl-substituted systems **9a** and **9b** are intensively orange colored, stable solids.



Scheme 6

9 a, b

In conclusion, it can be said that the transformation of ketones **1** and **3** to dibromoalkenes **2** and **4** is easily achieved by using reaction conditions analogous to those published by Corey and Fuchs.[3d] Alkynylation of dibromoalkenes **2**, **4**, and **6** yields geminal enediynes with cyclohexane-1,4-diyl, anthracene and fluorene backbones and various substituents on the alkynyl groups. These geminal enediynes could possibly serve as interesting precursors to two-dimensional carbon networks. Geminal enediynes **5a** and **5d** were oxidized to *p*-quinoid molecules bearing substituted alkynyl groups.

All reactions were performed under N_2 using standard Schlenk techniques. Et_2O and benzene were dried by distillation from sodium/benzophenone, amines were distilled from CaH_2. Reagents of commercial quality were used unless otherwise stated. Analytical TLC: Macherey–Nagel Polygram Sil G/UV_{254} (0.2 mm silica with fluorescence indicator); column chromatography: silica gel (60–200 mesh), ICN Biomedicals. IR spectra were recorded on a Perkin–Elmer FT-1600 IR spectrophotometer, mps were determined on a Reichert melting point microscope and are uncorrected. UV-vis spectra were recorded on a Hewlett–Packard HP 8452 A spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on NMR spectrometers Bruker AM 360 (360.12 MHz ^1H and 90.56 MHz ^{13}C), Bruker WM 250 (250.13 MHz ^1H and 62.89 MHz ^{13}C) and Varian XL 300 (299.95 MHz ^1H and 75.43 MHz ^{13}C). The degree of substitution was determined by *J* modulated spin-echo experiments. Chemical shifts are given as δ in ppm rel. to TMS. MS were performed on a Varian MAT 311 A mass spectrometer (ionization energy 70 eV).

Elemental analyses were obtained on a Foss–Heraeus Vario EL; all compounds gave satisfactory microanalyses (C, H ± 0.3).

1,4-Bis(dibromomethylene)cyclohexane (2):

To a solution of PPh_3 (13.64 g, 52 mmol) in anhyd benzene (100 mL) was added CBr_4 (8.62 g, 26 mmol). After stirring at r.t. for 30 min, cyclohexane-1,4-dione **(1)** (1.12 g, 10 mmol) was added and the mixture was subsequently stirred for 15 h at r.t. The green precipitate was removed from the solution by filtration, the filtrate was evaporated under reduced pressure and the residue absorbed on Celite. Chromatography (silica gel, 15 × 3 cm, hexane) yielded **2** (3.92 g, 92%) as colorless crystals; mp 140–145 °C (subl.).

UV-vis (*hexane*): λ (log ε) = 206 (4.03), 218 nm (3.96).

IR (KBr): ν = 2911 (C–H), 1713, 1463, 1377, 1252, 1195 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.50 (s, 8 H).

^{13}C NMR (75.43 MHz, CDCl$_3$): δ = 32.3 (C-2,3,5,6); 84.3 (C-7,8); 141.4 (C-1,4).
MS (EI): *m/z* (%) = 428 (4) [^{81}Br$_4$ M]$^+$, 426 (16) [^{81}Br$_3$^{79}Br M]$^+$, 424 (26) [^{81}Br$_2$^{79}Br$_2$ M]$^+$, 422 (19) [^{81}Br^{79}Br$_3$ M]$^+$, 420 (6) [^{79}Br$_4$ M]$^+$, 347 (4), 345 (13), 343 (11) [M – ^{81}Br]$^+$, 341 (5), 266 (47), 265 (11), 264 (100) [M – ^{81}Br^{79}Br]$^+$, 263 (12), 262 (50), 225 (4), 199 (4), 197 (3), 185 (10), 184 (14), 183 (13) [M – ^{81}Br$_2$^{79}Br]$^+$.
HRMS: *m/z* calcd for C$_8$H$_8$^{81}Br$_2$^{79}Br$_2$: 423.7318; found: 423.7317.

9,10-Bis(dibromomethylene)-9,10-dihydroanthracene (4):
To a solution of PPh$_3$ (2.73 g, 10.4 mmol) in anhyd benzene (30 mL) was added CBr$_4$ (1.72 g, 5.2 mmol). After stirring at r.t. for 30 min, anthraquinone **(3)** (0.42 g, 2 mmol) was added and the mixture was stirred at r.t. for 10 h. The precipitate was removed from the solution by filtration and washed with benzene. Removal of the solvent under reduced pressure and absorption of the residue on Celite, followed by chromatography (silica gel, 5 × 25 cm, hexane) yielded **4** (0.37 g, 36%) as a colorless solid; mp 73 °C.
UV-vis (CH$_2$Cl$_2$): λ (log ε) = 301 (4.09), 264 (4.08), 251 nm (4.20).
IR (KBr): ν = 3060 (w, C–H), 1718 (w), 1583 (m, arom. C=C), 1564 (m, arom. C=C), 1181 (m), 1162 cm^{-1} (m).
^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.25–7.88 (m, 8 H).
^{13}C NMR (75.43 MHz, CDCl$_3$): δ = 90.2 (C-11,12); 126.8, 127.4, 135.6 (arom. C); 139.3 (C-9,10).
MS (EI): *m/z* (%) = 524 (10) [^{81}Br$_4$ M]$^+$, 522 (34) [^{81}Br$_3$^{79}Br M]$^+$, 520 (51) [^{81}Br$_2$^{79}Br$_2$ M]$^+$, 518 (36) [^{81}Br^{79}Br$_3$ M]$^+$, 516 (11) [^{79}Br$_4$ M]$^+$, 362 (23), 361 (8), 360 (46) [M – ^{81}Br^{79}Br]$^+$, 359 (4), 358 (24), 260 (4), 259 (3), 201 (16), 200 (100) [M – ^{81}Br$_2$^{79}Br$_2$]$^+$.
HRMS: *m/z* = calcd for C$_{16}$H$_8$^{79}Br$_2$^{81}Br$_2$: 519.7319; found: 519.7319.

***gem*-Enediynes 5a–e, 7a–e, 8a–c; General Procedure:**
To a solution of amine, dibromoalkene and alkyne in anhyd benzene (30 mL) were added the palladium catalyst (5 mol%) and CuI (10 mol%). The mixture was stirred at temperatures between 25 and 80 °C (Tables 1–3), concentrated in vacuo, and the residue was absorbed on Celite. Column chromatography (silica gel, hexane) yielded the alkynylation products as colorless to yellow solids. Crude products were recrystallized from mixtures of hexane and Et$_2$O.

1,4-Bis[bis(phenylethynyl)methylene]cyclohexane (5a):
From **2** (0.40 g, 0.94 mmol) and phenylacetylene (1 mL, 9.1 mmol); yield: 60 mg (12%); red needles; mp 218 °C.
UV-vis (*hexane):* λ (log ε) = 226 (5.06), 308 (4.05), 430 nm (4.04).
IR (KBr): ν = 3051 (w, arom. C–H), 3048 (w, arom. C–H), 2963 (s, aliphat. C–H), 2105 (w, C≡C), 1489 (m), 1419 (w), 1261 (s), 1094 (s), 1022 cm^{-1} (s).
^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.96 (s, 8 H, C*H*$_2$); 7.17–7.56 (m, 20 H, arom. H).
^{13}C NMR (75.43 MHz, CDCl$_3$): δ = 32.3 (C-2,3,5,6); 75.4 (C-7,8); 89.7, 99.1 (*C*≡C–Ph, C≡*C*–Ph); 121.7, 122.8, 125.6, 131.2 (arom. C); 143.7 (C-1,4).
MS (EI): *m/z* (%) = 507 (10) [M – H]$^+$, 506 (24), 395 (17), 394 (9), 393 (53), 392 (3), 379 (6), 378 (4), 377 (20), 365 (5), 364 (7), 362 (4), 351 (8), 350 (4), 349 (16), 333 (8), 214 (6), 213 (4).
HRMS: *m/z* = calcd for C$_{40}$H$_{28}$: 508.2191; found: 508.2191.

1,4-Bis[bis(*tert*-butylethynyl)methylene]cyclohexane (5b):
From **2** (0.20 g, 0.47 mmol) and *tert*-butylacetylene (0.6 mL, 0.40 g, 4.8 mmol); yield: 63 mg (31%); yellow solid; mp 209 °C.
UV-vis (CH$_2$Cl$_2$): λ (log ε) = 274 (4.34), 385 (3.53), 408 nm (3.49).
IR (KBr): ν = 2966 (vs., C–H), 2865 (s, C–H), 2211 (w, C≡C), 1457 (m), 1359 (m), 1324 (m), 1204 (m), 1096 cm–^{1} (m).
^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.27 [s, 36 H, C(C*H*$_3$)$_3$]; 2.55 (s, 8 H, C*H*$_2$).
^{13}C NMR (75.43 MHz, CDCl$_3$): δ = 28.1 [*C*(CH$_3$)$_3$]; 31.1 [C(*C*H$_3$)$_3$]; 31.2 (C-2,3,5,6); 76.1 (C-7,8); 99.6, 100.1 (*C*≡C–*t*-Bu, C≡*C*–*t*-Bu); 154.2 (C-1,4).
MS (EI): *m/z* (%) = 430 (6), 429 (31) [M]$^+$, 428 (100), 427 (5), 426 (14), 414 (3), 413 (9), 385 (7), 372 (15), 371 (44), [M – *t-Bu*]$^+$, 358 (5), 357 (16), 356 (5), 341 (7), 327 (3), 316 (5), 315 (18) [M – 2 t-Bu]$^+$, 313 (5), 306 (7), 305 (28), 301 (7), 300 (6), 299 (8), 285 (7), 271 (6), 259 (6), 257 (5), 253 (9), 245 (5), 214 (5), 207 (4).
HRMS: *m/z* = calcd for C$_{32}$H$_{44}$: 428.3443; found: 428.3443.

1,4-Bis[bis(oct-1-ynyl)methylene]cyclohexane (5c):
From **2** (0.21 g, 0.5 mmol) and oct-1-yne (0.55 g; 5.0 mmol); yield: 121 mg (45%); orange solid; mp 88 °C.
UV-vis (*hexane):* λ (log ε) = 235 (3.50), 283 (4.21), 411 nm (3.96).
IR (KBr): ν = 2955 (s, C–H), 2933 (s, C–H), 2888 (m), 2855 (m), 2211 (w, C≡C), 1711 (s), 1616 (w), 1461 (w), 1433 (m), 1372 (w), 1344 (w), 1250 (s), 1194 (m), 1100 (w), 1022 cm^{-1} (w).
^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.8–1.6 (br. m, 52 H, Alkyl-H); 2.50 (s, 8H, H-2,3,5,6).
^{13}C NMR (62.89 MHz, CDCl$_3$): δ = 14.0 (-*C*H$_3$); 19.2, 22.5, 28.6, 29.7, 31.3, 32.3 (*C*H$_2$); 65.3 (C-7,8); 77.6, 84.3 (*C*≡C–^{n}Hexyl, C≡*C*–^{n}Hexyl); 141.6 (C-1,4).
MS (EI): *m/z* (%) = 541 (100) [M]$^+$, 512 (36), 504 (28), 500 (33), 468 (12), 416 (10), 386 (10), 385 (14), 353 (12), 352 (11), 324 (40), 302 (32), 298 (14), 232 (45).
HRMS: *m/z* = calcd for C$_{40}$H$_{60}$: 540.4695; found: 540.4695.

1,4-Bis[bis(trimethylsilylethynyl)methylene]cyclohexane (5d):
From **2** (0.20 g, 0.47 mmol) and trimethylsilylacetylene (0.36 g, 3.6 mmol); yield: 0.18 g (78%); yellow crystals; mp 93 °C.
UV-vis (*hexane):* λ (log ε) = 234 (3.60), 280 nm (4.10).
IR (KBr): ν = 2960 (s, C–H), 2900 (m, C–H), 2844 (w, C–H), 2144 (m, C≡C), 1433 (m), 1295 (w), 1260 (w), 1249 (s), 1197 (m), 1104 (w), 1066 (w), 1020 cm^{-1} (w).
^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.17–0.19 [m, 36 H, Si(C*H*$_3$)$_3$]; 2.48 (s, 8 H, C*H*$_2$).
^{13}C NMR (75.43 MHz, CDCl$_3$): δ = –0.75 [Si(*C*H$_3$)$_3$]; 32.02 (*C*H$_2$); 84.27 (C-7,8); 87.9, 100.63 (*C*≡C–SiMe$_3$, C≡*C*–SiMe$_3$); 159.25 (C-1,4).
MS (EI): *m/z* (%) = 493 (6) [M]$^+$, 492 (18), 491 (25), 490 (52), 393 (4), 377 (4), 349 (4), 230 (1), 73 (100) [SiMe$_3$]$^+$.
HRMS: *m/z* = calcd for C$_{28}$H$_{44}$Si$_4$: 492.2520; found: 492.2522.

1,4-Bis[bis(triisopropylsilylethynyl)methylene]cyclohexane (5e):
From **2** (0.40 g, 0.93 mmol) and triisopropylsilylacetylene (1.02 g, 5.6 mmol); yield: 0.39 g (51%); yellow needles; mp 96–98 °C.
UV-vis (*hexane):* λ (log ε) = 251 (4.06), 265 (3.22), 281 nm (3.01).
IR (KBr): ν = 2945 (s, C–H), 2866 (s, C–H), 2062 (m, C≡C), 1465 (m), 1252 (w), 1073 (w), 1018 (m), 993 (m), 919 (w), 882 (m), 679 (s), 663 (s), 631 (m), 529 (w), 477 cm^{-1} (m).
^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.09 [s, 84 H, Si(^{i}Pr)$_3$]; 2.50 (s, 8 H, C*H*$_2$).
^{13}C NMR (75.43 MHz, CDCl$_3$): δ = 11.3 [Si(*C*H(CH$_3$)$_2$)$_3$]; 18.5 [Si(CH(*C*H$_3$)$_2$)$_3$]; 32.2 (C-2,3,5,6); 81.5, 90.1 [*C*≡C–Si(^{i}Pr)$_3$, C≡*C*–Si(^{i}Pr)$_3$]; 84.2 (C-7,8); 141.4 (C-1,4).
MS (EI): *m/z* (%) = 829 (9), 828 (100) [M]$^+$, 827 (19), 727 (12), 724 (13), 626 (4), 363 (6), 362 (16), 321 (10), 320 (31), 291 (9), 277 (10), 263 (6), 250 (4), 249 (12), 235 (4).
HRMS: *m/z* = calcd for C$_{52}$H$_{92}$Si$_4$: 828.6276; found: 828.6276.

9-[Bis(phenylethynyl)methylene]-9*H*-fluorene (7a):
From **6** (197 mg, 0.58 mmol) and phenylacetylene (0.14 g, 1.4 mmol); yield: 27 mg (12%); red solid; mp 95–97 °C.
UV-vis (*hexane):* λ (log ε) = 240 (4.11), 256 (4.00), 272 (4.04), 298 (3.70), 386 nm (3.92).
IR (KBr): ν = 3052 (w, arom. C–H), 3033 (w, arom. C–H), 2177 (w, C≡C), 1700 (m), 1653 (m, aliphat. C=C), 1576 (m, arom. C=C), 1570 (m, arom. C=C), 1560 (w, arom. C=C), 1540 (m), 1533 (m), 1521 (m), 1507 (m), 1490 (s), 1457 (m), 1441 (vs.), 1354 (m), 1261 (s), 1092 (m), 1023 cm^{-1} (s).
^{1}H NMR (300 MHz, CDCl$_3$): δ = 6.4–7.8 (m, 18 H, arom. H).

^{13}C NMR (75.43 MHz, $CDCl_3$): δ = 88.9, 97.8 (C-11,11',12,12'); 101.2 (C-10); 119.5 (C-1,8); 122.8, 125.4, 127.4, 128.5, 129.0, 129.4, 131.7, 137.4, 140.1, (arom. C); 145.0 (C-9).
MS (EI): *m/z* (%) = 380 (5), 379 (30), 378 (100) $[M]^+$, 377 (29), 376 (32), 375 (11), 374 (15), 350 (4), 348 (2), 301 (3), 300 (9) $[M – Ph]^+$, 299 (2), 298 (3), 252 (2), 190 (3), 189 (8), 188 (13), 187 (16), 186 (3), 180 (4), 175 (5), 174 (4), 162 (2), 150 (2), 105(1).
HRMS: *m/z* = calcd for $C_{30}H_{18}$: 378.1409; found: 378.1408.

9-[Bis(*tert*-butylethynyl)methylene]-9*H*-fluorene (7b):

From **6** (0.34 g, 1 mmol) and *tert*-butylacetylene (0.62 mL, 0.41 g, 5 mmol); yield: 0.15 g (47%); yellow solid; mp 99 °C.
UV-vis (*hexane):* λ (log ε) = 366 (4.32), 348 (4.22), 332 (3.86), 272 (4.20), 262 (4.14), 240 nm (4.25).
IR (KBr): ν = 3054 (m, arom. C–H), 3031 (w, arom. C–H), 2968 (vs., aliphat. C–H), 2930 (s), 2866 (s), 2144 (m, C≡C), 1734 (w), 1718 (w), 1685 (w), 1653 (w), 1475 (s), 1444 (s), 1391 (w), 1362 (s), 1324 (w), 1285 (m), 1243 (vs.), 1201 (s), 1085 (m), 1035 cm^{-1} (w).
^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 [s, 18 H, $C(CH_3)_3$]; 7.19–7.32 (m, 4 H, arom. H); 7.59 (d, ^3J = 8 Hz, 2 H, arom. H); 8.68 (d, ^3J = 8 Hz, 2 H, arom. H).
^{13}C NMR (75.43 MHz, $CDCl_3$): δ = 30.6 [$C(CH_3)_3$]; 63.6 [$C(CH_3)_3$]; 79.8 (C-10); 86.1, 106.8 (C-11,11',12,12'); 119.1, 124.8, 126.7, 128.5 137.6, 139.5 (arom. C); 142.7 (C-9).
MS (EI): *m/z* (%) = 340 (4), 339 (29), 338 (100) $[M]^+$, 323 (4) $[M – CH_3]^+$, 308 (3) $[M – 2\ CH_3]^+$, 307 (2), 295 (2), 294 (3), 293 (8) $[M – 3\ CH_3]^+$, 292 (2), 291 (3), 289 (2), 281 (4) $[M – {}^tBu]^+$, 280 (4), 279 (5), 278 (6), 277 (10), 276 (7), 268 (2), 267 (8), 266 (13), 265 (9), 264 (3), 263 (5), 254 (5), 253 (12), 252 (14), 250 (2), 240 (3), 239 (9), 229 (3), 228 (2), 227 (2), 226 (4), 215 (4), 203 (2), 202 (4).
HRMS: *m/z* = calcd for $C_{26}H_{26}$: 338.2036; found: 338.2036.

9-[Bis(oct-1-ynyl)methylene]-9*H*-fluorene (7c):

From **6** (0.15 g, 0.45 mmol) and oct-1-yne (0.20 g; 1.79 mmol); yield: 28 mg (16%); colorless solid; mp 68 °C.
UV-vis (*hexane):* λ (log ε) = 230 (4.70), 256 (4.40), 266 (4.33), 346 (3.96), 364 nm (3.96).
IR (film): ν = 3059 (m, arom. C–H), 2955 (s, aliphat. C–H), 2928 (vs., aliphat. C–H), 2857 (m, aliphat. C–H), 2204 (m, C≡C), 1943 (w), 1911 (w), 1876 (w), 1723 (w), 1609 (w, arom. C=C), 1580 (w, arom. C=C), 1563 (w, arom. C=C), 1466 (m), 1446 (m), 1377 (w), 1352 (w), 1305 (w), 1222 (w), 1154 (w), 1108 (w), 1037 (w), 1007 cm^{-1} (w).
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.75–1.72 (br. m, 26 H, aliphat. H); 7.20–8.65 (m, 8 H, arom. H).
^{13}C NMR (75.43 MHz, $CDCl_3$): δ = 15.8 (C-18,18'); 22.4, 23.7, 28.7, 29.4, 32.6 (CH_2); 71.5, 97.4 (C-11,11',12,12'); 102.1 (C-10); 118.6, 125.9, 126.8, 129.0, 136.2, 142.7 (arom. C); 147.2 (C-9).
MS (EI): *m/z* (%) = 396 (5), 395 (32), 394 (100) $[M]^+$, 323 (11), 281 (2), 279 (2), 267 (6), 266 (3), 265 (4), 255 (6), 254 (4), 253 (13), 252 (9), 242 (3), 241 (14), 240 (5), 239 (6), 229 (3), 216 (3), 215 (9).
HRMS: *m/z* = calcd for $C_{30}H_{34}$: 394.2661; found: 394.2661.

9-[Bis(trimethylsilylethynyl)methylene]-9*H*-fluorene (7d):

From **6** (0.20 g, 0.60 mmol) and trimethylsilylacetylene (0.5 mL, 0.35 g, 3.6 mmol); yield: 0.22 g (54%); yellow needles; mp 132–133 °C.
UV-vis (*hexane):* λ (log ε) = 230 (4.50), 238 (4.50), 262 (4.46), 272 (4.53), 294 (3.70), 306 (3.72), 336 (4.21), 354 (4.54), 374 nm (4.64).
IR (KBr): ν = 3057 (w, arom. C–H), 2955 (m, aliphat. C–H), 2344 (w), 2124 (m, C≡C), 1792 (w), 1772 (w), 1751 (w), 1734 (w), 1718 (w), 1700 (w), 1696 (w), 1684 (w), 1653 (m), 1599 (m, arom. C=C), 1576 (m, arom. C=C), 1570 (w, arom. C=C), 1507 (m), 1448 (m), 1405 (w), 1362 (w), 1249 (s), 1225 (m), 1178 cm^{-1} (w).
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.36 [s, 18 H, $Si(CH_3)_3$]; 7.26 (dt, ^3J = 7.6 Hz, ^4J = 1.2 Hz, 2 H, arom. H); 7.36 (dt, ^3J = 7.4 Hz, ^4J = 1.1 Hz, 2 H, arom. H); 7.64 (d, ^3J = 7.6 Hz, 2 H, arom. H); 8.68 (d, ^3J = 7.9 Hz, 2 H, arom. H).
^{13}C NMR (75.43 MHz, $CDCl_3$): δ = 29.8 [$Si(CH_3)_3$]; 100.8 (C-10); 103.3, 104.5 (C-11,11',12,12'); 119.4, 125.8, 127.1, 129.6, 137.2, 140.1 (arom. C); 146.7 (C-9).
MS (EI): *m/z* (%) = 373 (2), 372 (15), 371 (34), 370 (100) $[M]^+$, 357 (3), 356 (6), 355 (18) $[M – CH_3]^+$, 340 (3), 339 (8), 325 (3), 323 (2), 309 (3), 298 (2), 297 (5), 296 (2), 295 (4), 293 (4), 283 (4), 282 (4), 281 (9), 280 (3), 279 (7), 269 (5), 268 (3), 267 (8), 266 (4), 265 (5), 257 (4), 256 (3), 255 (4), 253 (4), 252 (2), 243 (3), 242 (3), 241 (4), 239 (6), 229 (3).
HRMS: *m/z* = calcd for $C_{24}H_{26}Si_2$: 370.1573; found: 370.1572.

9-[Bis(triisopropylsilylethynyl)methylene]-9*H*-fluorene (7e):

From **6** (0.34 g, 1 mmol) and triisopropylsilylacetylene (1.1 mL, 0.9 g, 5 mmol); yield: 0.39 g (71%); yellow crystals; mp 112–113 °C.
UV-vis (*hexane):* λ (log ε) = 238 (4.49), 272 (4.51), 356 (4.54), 376 nm (4.66).
IR (KBr): ν = 3058 (m, arom. C–H), 2940 (s, aliphat, C–H), 2863 (s), 2122 (w, C≡C), 1701 (w), 1685 (w), 1654 (w), 1601 (m, arom. C=C), 1560 (m, arom. C=C), 1460 (s), 1448 (s), 1382 (m), 1355 (m), 1223 (s), 1192 (m), 1070 (m), 1012 cm^{-1} (m).
^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18 [br. s, 42 H, $Si(^iPr)_3$-H]; 7.22 (dt, ^3J = 7.6 Hz, ^4J = 1.1 Hz, 2 H, H-3,6); 7.34 (dt, ^3J = 7.5 Hz, ^4J = 1.0 Hz, 2 H, H-2,7); 7.63 (d, ^3J = 7.5 Hz, 2 H, H-1,8); 8.83 (d, ^3J = 7.8 Hz, 2 H, H-4,5).
^{13}C NMR (75.43 MHz, $CDCl_3$): δ = 11.4 [$Si–CH(CH_3)_2$]; 18.7 [$Si–CH(CH_3)_2$]; 101.2 (C-10); 102.0, 105.4 (C-11,11',12,12'); 119.2, 125.8, 127.0, 129.3, 137.2, 139,9 (arom. C); 145.1 (C-9).
MS (EI): *m/z* (%) = 540 (19), 539 (51), 538 (100) $[M]^+$, 495 (13), 454 (13), 453 (33), 439 (3), 425 (7), 412 (3), 411 (7), 383 (3), 369 (5), 355 (3), 341 (6), 339 (4), 327 (9), 326 (3), 325 (7), 313 (8), 199 (6), 297 (5), 295 (8), 283 (6), 281 (5), 269 (10), 257 (4), 255 (3), 226 (4).
HRMS: *m/z* = calcd for $C_{36}H_{50}Si_2$: 538.3451; found: 538.3453.

9,10-Bis[bis(phenylethynyl)methylene]-9,10-dihydroanthracene (8a):

From **4** (0.26 g, 0.5 mmol) and phenylacetylene (0.36 g, 3.5 mmol); yield: 88 mg (29%); yellow solid; mp 103 °C.
UV-vis (*hexane):* λ (log ε) = 285 (4.13), 340 (3.60), 362 nm (3.90).
IR (KBr): ν = 3048 (w, C–H), 2133 (w, C≡C), 1653 (m), 1595 (m, arom. C=C), 1507 (w), 1486 (w), 1449 (s), 1395 (w), 1316 (w), 1240 (m), 1204 (s), 1175 (s), 1068 (w), 1018 cm^{-1} (w).
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.17–7.97 (m, 28 H, arom. H).
^{13}C NMR (75.43 MHz, $CDCl_3$): δ = 82.1, 102.6 (*C*≡C–Ph, C≡*C*–Ph); 98.7 (C-11,12); 122.8, 127.6, 129.3, 130.2, 132.8, 121.5, 133.4 (arom. C); 153.0 (C-9,10).
MS (EI): *m/z* (%) = 604 (20) $[M]^+$, 569 (30), 568 (15), 526 (6), 525 (10), 403 (16), 402 (22), 401 (11), 393 (9), 392 (25), 351 (13), 350 (34), 281 (8), 265 (6), 239 (9), 237 (6), 227 (10), 223 (8), 221 (5), 211 (8), 209 (9), 507 (6).
HRMS: *m/z* = calcd for $C_{48}H_{28}$: 604.2191; found: 604.2191.

9,10-Bis[bis(*tert*-butylethynyl)methylene]-9,10-dihydroanthracene (8b):

From **4** (0.5 g, 0.96 mmol) and *tert*-butylacetylene (0.8 g, 9.6 mmol); yield: 0.16 g (32%); yellow needles; mp 118 °C.
UV-vis (*hexane):* λ (log ε) = 235 (4.69), 276 nm (3.45).
IR (film): ν = 3032 (w, arom. C–H), 2966 (s, aliphat. C–H), 2871 (s, aliphat. C–H), 2216 (m, C≡C), 1947 (m), 1755 (m), 1737 (m), 1713 (m), 1626 (m), 1674 (m), 1556 (w, arom. C=C), 1479 (m), 1462 (m), 1393 (w), 1365 (w), 1202 (m), 1100 cm^{-1} (w).
^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.2–1.4 [m, 36 H, $C(CH_3)_3$]; 7.15–8.45 (m, 8 H, arom. H).
^{13}C NMR (75.43 MHz, $CDCl_3$): δ = 27.5 [$C(CH_3)_3$]; 31.9 [$C(CH_3)_3$]; 83.4, 107.4 [$C≡C–C(CH_3)_3$, $C≡C–C(CH_3)_3$]; 102.4 (C-11,12); 123.6, 132.9, 134.2 (arom. C); 153.6 (C-9,10).

MS (EI): *m/z* (%) = 524 (100) [M]$^+$, 523 (11), 522 (28), 455 (3), 444 (5), 341 (3), 329 (3), 327 (3).
HRMS: *m/z* = calcd for $C_{40}H_{44}$: 524.3443; found: 524.3442.

9,10-Bis[bis(trimethylsilylsilylethynyl)methylene]-9,10-dihydroanthracene (8c):
From **4** (0.25 g, 0.48 mmol) and trimethylsilylacetylene (0.47 g, 4.8 mmol); yield: 74 mg (26%); yellow crystals; mp 129 °C.
UV-vis (*hexane): λ* (log ε) = 246 (3.42), 279 nm (4.09).
IR (KBr): ν = 3061 (w, arom. C–H), 2957 (m, aliphat. C–H), 2919 (m, aliphat. C–H), 2849 (m), 2143 (m, C≡C), 1460 (w), 1449 (m), 1407 (w), 1247 (s), 1206 (s), 1123 (w), 1064 cm^{-1} (w).
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.23 [s, 36 H, Si(C*H*$_3$)$_3$]; 7.25–8.30 (m, 8 H, arom. H).
^{13}C NMR (75.43 MHz, $CDCl_3$): δ = –0.43 [Si(*C*H$_3$)$_3$]; 65.8 (C-11,12); 100.3, 103.6 (*C*≡C–SiMe$_3$, C≡*C*–SiMe$_3$); 126.7, 127.0, 134.0 (arom. C); 147.3 (C-9,10).
MS (EI): *m/z* (%) = 591 (4), 590 (14), 589 (26) [M]$^+$, 588 (48), 572 (3), 493 (3), 492 (5) [M – C≡C–SiMe$_3$]$^+$, 427 (1), 397 (2), 155 (1), 97 (2), 73 (100) [SiMe$_3$]$^+$, 59 (2), 45 (6).
HRMS: *m/z* = calcd for $C_{36}H_{44}Si_2$: 588.2520; found: 588.2519.

1,4-Bis[bis(phenylethynyl)methylene]cyclohexa-2,5-diene (9a):
DDQ (0.24 g, 1.06 mmol) was added to a solution of **5a** (0.1 g, 0.26 mmol) in anhyd xylene (30 mL). The mixture was heated to reflux for 24 h and filtered after cooling; the solvent was evaporated in vacuo and the residue absorbed on Celite. Column chromatography (silica gel, hexane/EtOAc 10:1) gave an orange zone, evaporation of the solvent in vacuo and recrystallization from Et_2O yielded **9a** (85 mg, 64%); light orange needles; mp 105 °C.
UV-vis (*hexane): λ* (log ε) = 273 (4.392), 334 (3.467), 582 nm (4.073).
IR (KBr): ν = 3057 (w, C–H), 3050 (w, C–H), 3046 (w, C–H), 2092 (m, C≡C), 1704 (w), 1630 (w), 1596 (m, arom. C=C), 1578 (w, arom. C=C), 1566 (m, arom. C=C), 1489 (m), 1441 (m), 1333 (s), 1258 (w), 1205 (w), 1168 cm^{-1} (m).
^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.53 (s, 4 H, H-2,3,5,6); 7.30–7.39 (m, 20 H, arom. H).
^{13}C NMR (75.43 MHz, $CDCl_3$): δ = 82.6 (C-7,8); 105.8, 111.4 (*C*≡C–Ph, C≡*C*–Ph); 120.9, 129.8, 130.0, 131.6, 137.1 (arom. C); 149.5 (C-1,4).
MS (EI): *m/z* (%) = 504 (100) [M]$^+$, 503 (20), 502 (9), 428 (12), 427 (23), 424 (20), 393 (10), 377 (6), 306 (14), 305 (12), 291 (26), 229 (20), 228 (18), 202 (32).
HRMS: *m/z* = calcd for $C_{40}H_{24}$: 504.1878; found: 504.1877.

1,4-Bis[bis(trimethylsilylethynyl)methylene]cyclohexa-2,5-diene (9b):
DDQ (60 mg, 0.27 mmol) was added to a solution of **5d** (0.1 g, 0.19 mmol) in anhyd xylene (25 mL). The mixture was heated to reflux for 24 h and filtered after cooling; the solvent was evaporated in vacuo and the residue absorbed on Celite. Column chromatography (silica gel, hexane) gave a yellow zone, evaporation of the solvent in vacuo and recrystallization from Et_2O/hexane yielded **9b** (39 mg, 42%); orange needles; mp 97 °C.
UV-vis (*hexane): λ* (log ε) = 270 (4.32), 326 (3.67), 565 nm (3.84).
IR (film): ν = 3067 (w, C–H), 3055 (w), 2110 (m, C≡C), 1689 (m), 1593 (m, arom. C=C), 1542 (w), 1464 (m), 1377 (w), 1342 (w), 1292 (w), 1248 (w), 1225 (w), 1135 (m), 1075 (m), 1024 (w).
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.03 [s, 36 H, Si(C*H*$_3$)$_3$]; 6.91 (s, 4 H, H-2,3,5,6).
^{13}C NMR (75.43 MHz, $CDCl_3$): δ = –0.01 [Si(*C*H$_3$)$_3$]; 102.8, 104.7 (*C*≡C–SiMe$_3$, C≡*C*–SiMe$_3$); 116.3 (C-7,8); 141.2 (C-2,3,5,6); 157.6 (C-1,4).
MS (EI): *m/z* (%) = 488 (100) [M]$^+$, 422 (6), 420 (5), 398 (17), 397 (13), 396 (4), 352 (10), 351 (8), 323 (16), 305 (25), 298 (17), 230 (3).
HRMS: *m/z* = calcd for $C_{28}H_{40}Si_4$: 488.2207; found: 488.2206.

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