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Synthesis and Structures of 9-Triptycylallene Derivatives

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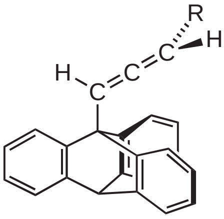
9-Triptycylallene (**1**) was synthesized by $LiAlH_4$ reduction of 1-(9-triptycyl)-2-propynyl methanesulfonate (**7**), and three 3-substituted derivatives of **1** were also obtained by reacting compound **7** with appropriate metal reagents. $LiAlH_4$ reduction of 1,3-di(9-triptycyl)-2-propynyl methanesulfonate (**10**) gave 1,3-di(9-triptycyl)propyne (**12**). The molecular structures of some of the allenes and of the propyne were determined by X-ray crystallography. As well, the allenes and some of the related compounds were characterized by NMR spectroscopy.

Unique stereochemical features of an allene moiety have been of interest for quite some time, and a vast amount of research has been reported on the synthesis, structures, and chiroptical properties of allene derivatives.[1] During the course of our studies on the static and dynamic stereochemistry of triptycene derivatives,[2] we have been interested in the stereochemical behavior of 9-triptycylallene derivatives. In this article, we report and discuss the synthesis of 9-triptycylallene (**1**) and several 3-substituted derivatives: 3-methyl (**2**), 3-phenyl (**3**), and 3-(9-triptycyl) (**4**). In addition, X-ray crystallography of compounds **1**, **3**, and **4**, and the NMR spectroscopy of compounds **1**–**4** are reported (Chart 1).

Compound **4** is an extended analog of bis(9-triptycyl)-X compounds (Tp_2X), which have been extensively studied by Iwamura's and Mislow's groups because they behave like tightly meshed molecular bevel gears.[3]

Results and Discussion

Synthesis. Various synthetic routes to allenes have been reported,[1] and it has been shown that treatments of $LiAlH_4$ and various organocuprate reagents with 2-propynyl sulfonates afford allenes by S_N2'-type reactions.[4] Therefore, 1-(9-triptycyl)-2-propynyl methanesulfonate (**7**) was used as the precursor for the target compounds **1**–**4**, and the synthetic route is shown in Scheme 1.



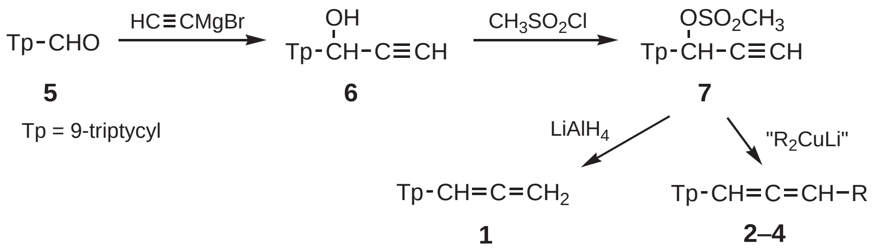
1: R = H
2: R = CH_3
3: R = C_6H_5
4: R = 9-Triptycyl (Tp)

Chart 1.

It had been reported[5] that triptycene-9-carbaldehyde (**5**) can not be obtained directly from the reaction of anthracene-9-carbaldehyde with benzyne generated by thermal decomposition of benzenediazonium-2-carboxylate and that the formyl group should be protected in advance, e.g., as an acetal. However, we found that the direct reaction of anthracene-9-carbaldehyde with benzyne gave compound **5** in a moderate yield (47%).

The reaction of compound **5** with ethynylmagnesium bromide afforded 1-(9-triptycyl)-2-propyn-1-ol (**6**), which was then converted to the methanesulfonate **7**. Compound **1** was obtained by $LiAlH_4$ reduction of the methanesulfonate **7**. Reactions of compound **7** with the cuprate reagents, prepared by reacting commercially available methyllithium and phenyllithium with copper(I) iodide, gave the allenes **2** and **3**, respectively, in moderate yields. The 9-triptycyl cuprate reagent could only be prepared when CuI was dried thoroughly under high vacuum at ca. 100 °C for 10 h. Compound **4** was produced in 98% yield.

As for the synthesis of 1,3-di(9-triptycyl)allene (**4**), we at first attempted the routes shown in Scheme 2 with the expectation that $LiAlH_4$ reduction of a 1,3-di(9-triptycyl)-2-propynyl derivative, i.e., compounds **8**, **9**, or **10**, would afford compound **4**. Reaction of triptycene-9-carbaldehyde (**5**) with 9-triptycyl-



Scheme 1.

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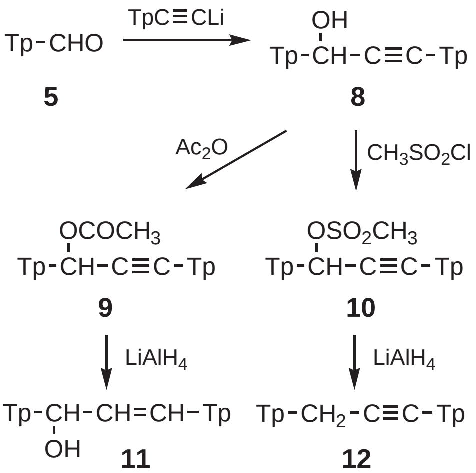
ethynyllithium gave the alcohol **8**, which was then converted to the acetate **9** and the methanesulfonate **10**. The reaction of compound **8** with $LiAlH_4$ did not proceed at all, and the treatment of the acetate **9** with $LiAlH_4$ resulted in the formation of what was speculated to be (*E*)-1,3-di(9-triptycyl)-2-propen-1-ol (**11**) by ^{1}H NMR spectral data. Reaction of compound **10** with $LiAlH_4$ gave 1,3-di(9-triptycyl)propyne (**12**) as the sole product via an S_N2-type displacement of the sulfonate group.

X-ray Crystallography. The molecular structures of the allenes **1**, **3**, and **4**, and of the propyne **12** were determined by X-ray crystallography. Single crystals suitable for the analysis were obtained by recrystallization from diethyl ether–methanol for **1** and **3**, and from ethyl acetate–hexane for **4**. Crystals of compound **4** contained ethyl acetate molecules in a 1:1 ratio: The molecular structure of **4** could be definitely determined, while that of ethyl acetate could not be refined, because the molecule seemed to turn around within a cavity formed by molecules of **4**. Crystallization of compound **12** from chloroform afforded crystals containing one chloroform molecule per one molecule of **12**. ORTEP drawings of compounds **1** and **3** are shown in Fig. 1, and those of compounds **4** and **12** are shown in Figs. 2 and 3, respectively. Selected bond lengths and angles of the allenes are listed in Table 1, and those of **12** are listed in Table 2.

The lengths of the C=C bonds of the allene moieties are 1.287–1.300 Å, except for the $C^2{=}C^3$ bond in compound **3**, which is somewhat longer, 1.318 Å, presumably because of conjugation with the phenyl group. The Tp–C bond lengths lie in a narrow range of 1.505–1.512 Å, while the Ph–C bond length in compound **3** is 1.471 Å. The difference in lengths is ascribed to sp^2–sp^3 and sp^2–sp^2 bond characters. The Tp–C=C bond angles are 126–132° and are significantly larger than the typical sp^2 bond angle of 120°. The C=C=C moiety is almost linear in compounds **1** and **3**, while slightly bent in compound **4**, due to the steric repulsion between the two Tp groups. The Tp–C and Ph–C bonds in compound **3** and the two Tp–C bonds in compound **4** have dihedral angles of 96.4 and 102.9°, respectively, that are considerably larger than the orthogonality. The large angles are also ascribed to the steric repulsion between the terminal groups.



Scheme 2.

In compounds **1** and **3**, the allene moiety does not bisect the dihedral angle between the planes of the two flanking benzene rings in the Tp group, but is twisted by ca. 15° to avoid eclipsing the allenic hydrogen with the peri-hydrogen of the third benzene ring (Fig. 1 and Table 1). One of the Tp groups in compound **4**—the one bonded to C1 in Fig. 2—adopts arrangement similar to those in compounds **1** and **3**, while the other Tp group, bonded to C3 in Fig. 2, is twisted differently

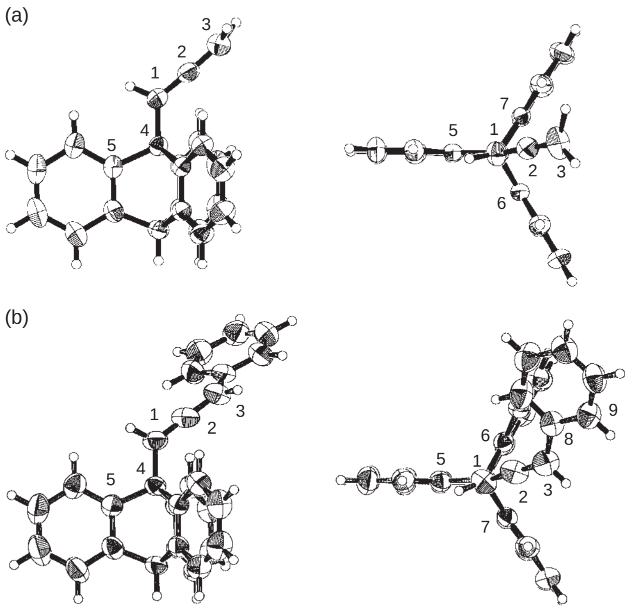


Fig. 1. ORTEP diagrams with 50% probability ellipsoids of (a) compound **1**, and (b) compound **3**.

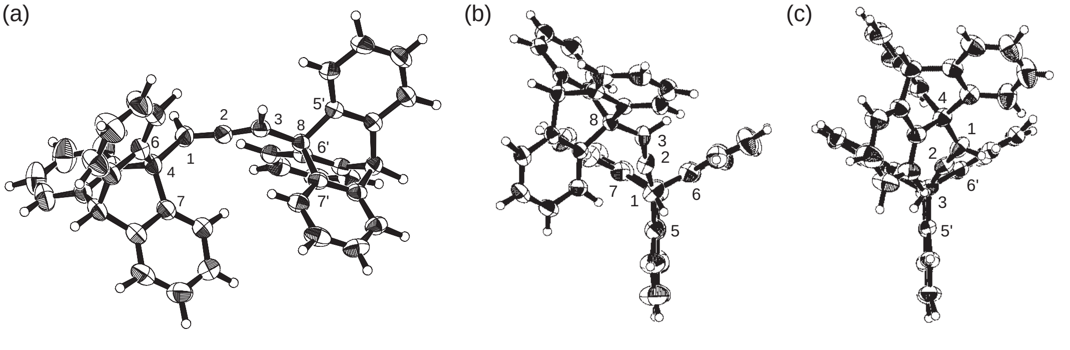


Fig. 2. ORTEP diagrams of compound **4** with 50% probability ellipsoids; (a) the side view, (b) looking down along the C1–C4 bond, and (c) looking down along the C3–C8 bond.

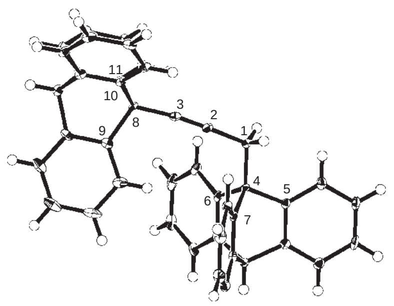


Fig. 3. ORTEP diagram of compound **12** with 50% probability ellipsoids.

Table 1. Selected Bond Lengths (Å) and Angles (°)[a)]

	1	3	4
1–2	1.287(2)	1.289(3)	1.299(3)
2–3	1.295(2)	1.318(4)	1.300(3)
1–4	1.510(2)	1.505(3)	1.512(3)
3–8	—	1.471(4)	1.508(2)
4–5	1.547(2)	1.547(3)	1.536(3), 1.542(2)[b)]
4–6	1.545(2)	1.553(3)	1.540(3), 1.550(2)[b)]
4–7	1.547(2)	1.542(3)	1.543(3), 1.539(2)[b)]
1–2–3	177.8(2)	179.0(3)	172.6(2)
2–3–8	—	125.7(3)	131.5(2)
2–1–4	128.4(2)	125.8(2)	126.2(2)
1–4–5	113.1(2)	114.7(2)	114.2(2), 111.3(2)[b)]
1–4–6	113.5(2)	111.1(2)	110.2(2), 118.1(2)[b)]
1–4–7	115.7(2)	116.6(2)	116.7(2), 112.5(2)[b)]
4–1–3–8	—	96.4	102.9
2–1–4–5	−168.7	−163.6(3)	−165.8(2), 144.3(2)[b)]
2–1–4–6	72.2	77.4(3)	77.1(3), 23.4(2)[b)]
2–1–4–7	−48.0	−42.6(4)	−43.3(3), −98.5(2)[b)]
2–3–8–9	—	−170.0(3)	

a) The numbering is shown in Figs. 1 and 2. b) The atom numbers 1, 4, 5, 6, and 7 should be read as 3, 8, 5′, 6′, and 7′, respectively.

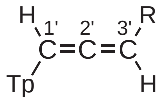
Table 2. Selected Bond Lengths (Å) and Angles (°) of Compound **12**[a)]

1–2	1.478(4)	1–2–3	175.3(3)	2–1–4–5	177.3
2–3	1.186(4)	2–3–8	170.9(3)	2–1–4–6	58.3
3–8	1.466(4)	2–1–4	112.7(2)	2–1–4–7	−65.5
1–4	1.540(4)	1–4–5	112.7(2)	4–1–8–9	10.4
4–5	1.536(4)	1–4–6	113.9(2)	4–1–8–10	−104.0
4–6	1.544(4)	1–4–7	114.3(2)	4–1–8–11	133.4
4–7	1.535(4)	3–8–9	112.2(2)		
8–9	1.532(4)	3–8–10	115.9(2)		
8–10	1.541(4)	3–8–11	112.9(2)		
8–11	1.540(4)				

a) The numbering is shown in Fig. 3.

(Fig. 2 and Table 1). Therefore, the torsion angles between the Tp and allene moieties are determined not only by the steric repulsions between the Tp and allene moieties but also by the repulsion between the two Tp moieties. The two Tp skeletons in compound **4** are well meshed with each other, like bevel gears.

Table 3. ^{1}H and ^{13}C NMR Data of the Allene Moieties of Compounds **1**–**4**[a)]



	1	2	3	4
R =	H	CH_3	C_6H_5	Tp
1′-H	6.474 (t, 7.1)	6.402 (dq, 7.2, 3.6)	6.896 (d, 6.9)	7.016 (s)
3′-H	5.193 (d, 7.1)	5.547 (quint, 7.2)	6.667 (d, 6.9)	7.016 (s)
1′-C	85.61	85.47	91.20	90.14
2′-C	211.65	208.50	207.69	209.43
3′-C	78.09	88.39	97.25	90.14

a) In parentheses are multiplicities and coupling constants in Hz.

In the propyne **12**, the two C≡C–C angles are 170.9 and 175.3° and the triple bond moiety is slightly bent so that the two Tp groups are closer to each other: Attractive van der Waals forces may occur between the two Tp moieties. The Tp–CH_2 bond is almost staggered, while the C1–C4 and C8–C9 bonds are nearly eclipsed with a dihedral angle of ca. 10° (Fig. 3 and Table 2).

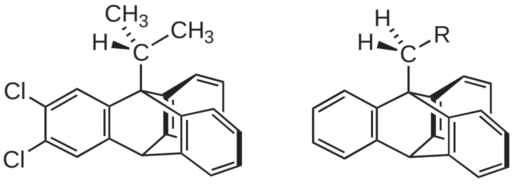
NMR Spectra. ^{1}H and ^{13}C NMR data of the allene moieties of compounds **1**–**4** are compiled in Table 3. Assignments of the proton chemical shifts, if not obvious, were made by use of NOE experiments. In compound **3**, irradiation of the signal at δ 7.71, assignable to the peri-protons (1-, 8-, and 13-H) of the Tp moiety, enhanced the doublet signal at δ 6.90, which was, therefore, assigned to 1′-H. The large coupling constants across the allene moiety ($^4J \approx 7$ Hz and $^5J \approx 4$ Hz) have been reported for other compounds.[6]

The carbon chemical shifts were assigned by CH-COSY experiments, when ambiguous. It has been well documented that the sp^2 carbons of alkyl- or aryl-substituted allenes appear at a significantly high field (δ 80–100) and the sp carbon appears at a very low field (δ 200–210).[7]

Stereodynamics. In any of the allenes **1**–**4**, the three benzene rings of the Tp moiety are equivalent in the NMR spectra at room temperature, indicating that rotation around the Tp–C bond is very fast on the NMR timescale. This is not surprising because rotation about a C(sp^3)–C(sp^2) bond has a low energy barrier except in special cases.[8]

Compound **4** showed a single sharp ABCD-pattern spectrum for the aromatic protons in CD_2Cl_2 at −107 °C. This shows that the rotations of the Tp–C bonds are fast even at this low temperature, although it is not yet clear whether rotation of the two Tp–C bonds take place independently or in a correlated fashion as dynamic molecular bevel gears.

^{1}H NMR spectra of the propynyl compounds **6**, **7**, **8**, **9**, and **10** at room temperature showed that the three benzene rings of the 1-Tp group are not equivalent because of slow rotation around the Tp–C(sp^3) bond on the NMR timescale, while the benzene rings of the 3-Tp group in compounds **8**–**10** are equivalent reflecting fast rotation about the Tp–C(sp) bond. For example, the peri-proton (1-, 8-, and 13-H) signals of 1-Tp group of **6** in toluene-d_8 appeared as three sharp doublets at the low-



13

14a: R = C_6H_5
14b: R = Cl

Chart 2.

est field of the aromatic region. The signals broadened upon elevation of the temperature, but did not coalesce even at 117 °C. Lineshape analysis afforded a rate constant k of $20\,s^{-1}$ at 117 °C, with a corresponding free energy of activation, $\Delta G^{\ddagger}$, of $86.7\,kJ\,mol^{-1}$ at this temperature. This is comparable with $\Delta G^{\ddagger} = 86.2\,kJ\,mol^{-1}$ at 100 °C for the rotation of the Tp–^{i}Pr bond in 2,3-dichloro-9-isopropyltriptycene (**13**), a prototype of triptycene derivatives carrying a secondary alkyl group at the bridgehead (Chart 2).[9]

In the ^{1}H NMR spectrum of the propyne **12**, the peri-protons (1-, 8-, and 13-H) of the Tp group bonded to the methylene carbon had a very broad single peak at room temperature, which split into two signals with the intensity ratio of 2:1 upon lowering the temperature, indicating the slow-down of the Tp–CH_2 bond rotation. Lineshape analysis at four temperatures in the range of −28 to 21 °C gave the following kinetic parameters: $\Delta H^{\ddagger} = 49.4 \pm 0.3\,kJ\,mol^{-1}$, $\Delta S^{\ddagger} = -15.9 \pm 1.4\,J\,mol^{-1}\,K^{-1}$, $\Delta G^{\ddagger}$ (0 °C) $= 53.7\,kJ\,mol^{-1}$. For comparison, $\Delta G^{\ddagger}$ (0 °C) for 9-benzyltriptycene (**14a**)[10] and 9-chloromethyltriptycene (**14b**),[11] which have a primary alkyl group at the bridgehead, are 45.8 and $58.5\,kJ\,mol^{-1}$, respectively, for the Tp–CH_2 bond rotation (Chart 2). The barrier height for compound **12** lies between those for compounds **14a** and **14b**.

Conclusion

Four 9-triptycylallenes have been synthesized and characterized. Especially, 1,3-di(9-triptycyl)allene (**4**) was shown to be static molecular bevel gears. We are trying to determine whether **4** behaves as dynamic molecular gears. In order to do this, we are synthesizing a derivative with labels on the Tp moieties and studying whether it shows phase isomerism.[3] Since compounds **1–4** are chiral, resolution and chiroptical studies of these compounds are also underway.

Experimental

General. Melting points are not corrected. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker ARX-300 spectrometer operating at 300.1 MHz for ^{1}H and 75.4 MHz for ^{13}C, respectively. Chemical shifts are referenced to internal tetramethylsilane (δ_H 0.00) and $CDCl_3$ (δ_C 77.00). The letters p, s, t, and q written beside the ^{13}C chemical shifts denote primary, secondary, tertiary, and quaternary, respectively. In the variable-temperature experiments, temperatures were calibrated using a methanol or an ethylene glycol sample and are reliable to ±1 °C. Preparative gel permeation chromatography (GPC) was performed on an LC-908 Liquid Chromatograph (Japan Analytical Industry Co., Ltd.) using a series of JAIGEL 1H and 2H columns and chloroform as the eluent.

Triptycene-9-carbaldehyde (5). To a boiling solution of 2.06 g (10.0 mmol) of anthracene-9-carbaldehyde in 60 mL of butanone was slowly added a slurry of benzenediazonium-2-carboxylate,[12] prepared from 5.49 g (40.0 mmol) of anthranilic acid, in 60 mL of butanone over the course of 50 min, and the mixture was heated under reflux for another 30 min. After evaporation of the solvent, the residue was subjected to column chromatography through silica gel with dichloromethane–hexane (1:1) as the eluent. Recrystallization of the eluate from dichloromethane–hexane gave 1.33 g (4.71 mmol, 47%) of compound **5**, mp 243–247 °C (lit.[5] 235–238 °C). ^{1}H NMR ($CDCl_3$) δ 5.401 (1H, s), 7.01–7.08 (6H, m), 7.429 (3H, m), 7.619 (3H, m), 11.217 (1H, s). ^{13}C NMR ($CDCl_3$) δ 54.15 (1C, t), 60.83 (1C, q), 122.41 (3C, t), 124.06 (3C, t), 125.19 (3C, t), 125.81 (3C, t), 142.59 (3C, q), 145.78 (3C, q), 200.98 (1C, t).

1-(9-Triptycyl)-2-propyn-1-ol (6). To an ice-cold solution of 3.00 g (10.6 mmol) of triptycene-9-carbaldehyde (**5**) in 30 mL of anhydrous tetrahydrofuran (THF) was added 50.8 mL (25.4 mmol) of a 0.5 M solution of ethynylmagnesium bromide in THF, and the mixture was stirred for 2 h, during which time the temperature was allowed to increase to room temperature. The reaction mixture was quenched with water and extracted with diethyl ether. The extracts were washed with brine, dried over $MgSO_4$, and evaporated. Column chromatography of the residue through silica gel with hexane–dichloromethane (5:1) as the eluent gave 2.69 g (8.72 mmol, 82%) of compound **6**, mp 257–259 °C (dec). Found: C, 89.64; H, 5.25%. Calcd for $C_{23}H_{16}O$: C, 89.58; H, 5.23%. ^{1}H NMR ($CDCl_3$) δ 2.696 (1H, d, $J = 4.6$ Hz, OH), 2.807 (1H, d, $J = 2.3$ Hz, CCH), 5.351 (1H, s), 6.125 (1H, dd, $J = 4.6$, 2.3 Hz), 6.93–7.12 (6H, m), 7.32–7.38 (2H, m), 7.44 (1H, m), 7.63–7.71 (2H, m), 8.18 (1H, m). ^{13}C NMR ($CDCl_3$) δ 54.50 (1C, t), 58.08 (1C, q), 62.02 (1C, t), 77.80 (1C, t), 83.13 (1C, q), 122.72 (1C, t), 123.02 (1C, t), 123.39 (1C, t), 123.50 (1C, t), 123.84 (1C, t), 124.59 (1C, t), 124.65 (1C, t), 124.68 (1C, t), 125.00 (1C, t), 125.19 (1C, t), 125.21 (1C, t), 125.46 (1C, t), 141.07 (1C, q), 143.77 (1C, q), 144.01 (1C, q), 146.15 (1C, q), 147.02 (1C, q), 147.04 (1C, q).

1-(9-Triptycyl)-2-propynyl Methanesulfonate (7). To an ice-cold solution of 1.54 g (5.00 mmol) of compound **6** in 50 mL of anhydrous THF was added 4.50 mL (7.0 mmol) of a 1.54 M solution of butyllithium in hexane, and the mixture was stirred for 1 h at 0 °C. To this solution was added 0.54 mL (7.0 mmol) of methanesulfonyl chloride, and the mixture was stirred for 24 h at room temperature. The mixture was poured onto ice-water and extracted with diethyl ether. The extracts were washed with brine, dried over $MgSO_4$, and evaporated. Column chromatography of the residue through silica gel with dichloromethane as the eluent followed by recrystallization from dichloromethane–hexane gave 0.516 g (1.34 mmol, 27%) of compound **7**, mp 132–134 °C. Found: C, 74.58; H, 4.78%. Calcd for $C_{24}H_{18}O_3S$: C, 74.59; H, 4.69%. ^{1}H NMR ($CDCl_3$) δ 3.057 (1H, d, $J = 2.3$ Hz), 3.419 (3H, s), 5.360 (1H, s), 6.854 (1H, d, $J = 2.3$ Hz), 6.96–7.12 (6H, m), 7.34–7.40 (2H, m), 7.45 (1H, m), 7.54 (1H, m), 7.61 (1H, m), 8.00 (1H, m). ^{13}C NMR ($CDCl_3$) δ 40.42 (1C, p), 54.41 (1C, t), 57.15 (1C, q), 69.64 (1C, t), 78.32 (1C, q), 81.80 (1C, t), 121.94 (1C, t), 122.51 (1C, t), 123.64 (1C, t), 123.66 (1C, t), 123.72 (1C, t), 124.58 (1C, t), 124.68 (1C, t), 124.78 (1C, t), 125.28 (1C, t), 125.43 (1C, t), 125.55 (1C, t), 125.78 (1C, t), 140.39 (1C, q), 142.48 (1C, q), 142.73 (1C, q), 145.37 (1C, q), 146.53 (1C, q), 146.81 (1C, q).

1-(9-Triptycyl)propadiene (1). To a solution of 100 mg (0.26 mmol) of compound **7** in 10 mL of anhydrous THF was added 30 mg (0.78 mmol) of $LiAlH_4$ and the mixture was heated under reflux for 24 h. The reaction mixture was treated with aq

NH_4Cl and extracted with diethyl ether. The ether layer was washed with water and dried over $MgSO_4$, and the solvent was evaporated. Recrystallization of the residue from dichloromethane–hexane afforded 48 mg (0.164 mmol, 63%) of **1**, mp 201–202 °C. Found: C, 94.25; H, 5.56%. Calcd for $C_{23}H_{16}$: C, 94.48; H, 5.52%. ^{1}H NMR ($CDCl_3$) δ 5.193 (2H, d, $J = 7.1$ Hz, 3′-H), 5.382 (1H, s, 10-H), 6.474 (1H, t, $J = 7.1$ Hz, 1′-H), 7.03–7.13 (6H, m), 7.373 (3H, m), 7.618 (3H, m). ^{13}C NMR ($CDCl_3$) δ 53.29 (1C, q), 54.16 (1C, t), 78.09 (1C, s), 85.61 (1C, t), 122.23 (3C, t), 123.53 (3C, t), 124.78 (3C, t), 125.23 (3C, t), 145.79 (6C, q), 211.65 (1C, q).

1-(9-Triptycyl)-1,2-butadiene (2). To a suspension of 380 mg (2.0 mmol) of copper(I) iodide in 30 mL of diethyl ether at −20 °C was added 3.50 mL (4.0 mmol) of a 1.14 M solution of methyllithium in diethyl ether, and the mixture was stirred for 0.5 h at this temperature. To this mixture was added 230 mg (0.59 mmol) of the methanesulfonate **7**, and the mixture was stirred for 2 h. The mixture was poured into water, and the organic layer was washed with aq NH_4Cl and dried over $MgSO_4$. Column chromatography through silica gel with dichloromethane as the eluent followed by preparative GPC afforded 90.0 mg (0.29 mmol, 49%) of compound **2**, mp 122–123 °C (from dichloromethane–hexane). Found: C, 93.87; H, 6.01%. Calcd for $C_{24}H_{18}$: C, 94.08; H, 5.92%. ^{1}H NMR ($CDCl_3$) δ 1.913 (3H, dd, $J = 7.2$, 3.6 Hz, CH_3), 5.384 (1H, s, 10-H), 5.547 (1H, quint, $J = 7.2$ Hz, 3′-H), 6.402 (1H, dq, $J = 7.2$, 3.6 Hz, 1′-H), 6.95–7.05 (6H, m), 7.37 (3H, m), 7.61 (3H, m). ^{13}C NMR ($CDCl_3$) δ 14.20 (1C, p), 53.76 (1C, q), 54.22 (1C, t), 85.47 (1C, t), 88.39 (1C, t), 122.29 (3C, t), 123.49 (3C, t), 124.75 (3C, t), 125.15 (3C, t), 145.90 (3C, q), 146.01 (3C, q), 208.50 (1C, q).

1-Phenyl-3-(9-triptycyl)propadiene (3). To a suspension of 500 mg (2.60 mmol) of copper(I) iodide in 30 mL of diethyl ether at −20 °C was added 5.00 mL (5.20 mmol) of a 1.04 M solution of phenyllithium in cyclohexane–diethyl ether, and the mixture was stirred for 1 h at this temperature. To this mixture was added 250 mg (0.65 mmol) of the methanesulfonate **7**, and the mixture was stirred for 2 h. The mixture was poured into water, and the organic layer was washed with aq NH_4Cl and dried over $MgSO_4$. Column chromatography through silica gel with dichloromethane–hexane (3:1) as the eluent afforded 110 mg (0.30 mmol, 46%) of compound **3**, mp 144–146 °C. Found: C, 94.48; H, 5.72%. Calcd for $C_{29}H_{20}$: C, 94.53; H, 5.47%. ^{1}H NMR ($CDCl_3$) δ 5.407 (1H, s, 10-H), 6.667 (1H, d, $J = 6.9$ Hz, 3′-H), 6.896 (1H, d, $J = 6.9$ Hz, 1′-H), 6.95–7.03 (6H, m), 7.27 (1H, m, *p*-H), 7.35–7.43 (5H, m, 4/5/16-H, *m*-H), 7.53 (2H, m, *o*-H), 7.71 (3H, m, 1/8/13-H). ^{13}C NMR ($CDCl_3$) δ 54.19 (1C, t), 54.29 (1C, q), 91.20 (1C, t), 97.25 (1C, t), 122.36 (3C, t), 123.51 (3C, t), 124.94 (3C, t), 125.30 (3C, t), 127.24 (2C, t), 127.36 (1C, t), 128.85 (2C, t), 133.99 (1C, q), 145.81 (3C, q), 145.84 (3C, q), 207.69 (1C, q).

1,3-Di(9-triptycyl)propadiene (4). To a suspension of 1.00 g (3.00 mmol) of 9-bromotriptycene in 25 mL of dry diethyl ether was added at room temperature 3.44 mL (5.30 mmol) of a 1.54 M solution of butyllithium in hexane and the mixture was stirred for 4 h. The supernatant diethyl ether was decanted off, and 120 mL of freshly distilled benzene was added to afford a solution of 9-triptycyllithium. The solution was added to a suspension of 300 mg (1.56 mmol) of well-dried copper(I) iodide in 18 mL of diethyl ether, and the mixture was stirred at room temperature for 1 h. To the mixture was added a solution of 150 mg (0.390 mmol) of compound **7** in 6 mL of diethyl ether and the mixture was stirred for 2 h. The mixture was poured into ice-water, and the organic layer was washed with aq NH_4Cl and dried over $MgSO_4$. Column chromatography through silica gel with dichloromethane–hexane (1:1) as the eluent gave 207 mg (0.380 mmol, 98%) of compound **4**, mp 311–312 °C (from diethyl ether–methanol). Found: C, 94.85; H, 5.22%. Calcd for $C_{43}H_{28}$: C, 94.82; H, 5.18%. ^{1}H NMR ($CDCl_3$) δ 5.441 (2H, s, 10-H), 6.878 (6H, td, $J = 7.5$, 1.2 Hz, 2/7/14-H), 6.996 (6H, td, $J = 7.5$, 1.2 Hz, 3/6/15-H), 7.016 (2H, s), 7.418 (6H, dd, $J = 7.2$, 1.2 Hz, 4/5/16-H), 7.815 (6H, d, $J = 7.5$ Hz, 1/8/13-H). ^{13}C NMR ($CDCl_3$) δ 53.73 (2C, q), 54.22 (2C, t), 90.14 (2C, t), 122.70 (6C, t), 123.53 (6C, t), 124.89 (6C, t), 125.27 (6C, t), 145.62 (6C, q), 145.84 (6C, q), 209.43 (1C, q).

1,3-Di(9-triptycyl)-2-propyn-1-ol (8). To a solution of 1.17 g (4.20 mmol) of 9-ethynyltriptycene[13] in 10 mL of dry diethyl ether was added at 0 °C under argon 2.5 mL (4.00 mmol) of 1.59 M butyllithium in hexane and the solution was stirred for 30 min at room temperature. To the solution was added 1.20 g (4.25 mmol) of **5** in 10 mL of diethyl ether, and the mixture was stirred for 3 h. The mixture was quenched with ice-water and extracted with diethyl ether. The ether layer was washed with brine and dried over $MgSO_4$, and the ether was then evaporated. Column chromatography through silica gel with hexane–ethyl acetate (2:1) as the eluent afforded 1.83 g (3.26 mmol, 77%) of compound **8**, mp 302–304 °C (dec). Found: C, 92.29; H, 5.04%. Calcd for $C_{43}H_{28}O$: C, 92.11; H, 5.03%. ^{1}H NMR ($CDCl_3$) δ 3.023 (1H, d, $J = 4.8$ Hz, OH), 5.381 (1H, s), 5.443 (1H, s), 6.685 (1H, d, $J = 4.8$ Hz), 6.89–7.13 (12H, m), 7.350 (3H, dd, $J = 7.2$, 1.2 Hz), 7.423 (2H, m), 7.504 (1H, m), 7.652 (3H, dd, $J = 7.1$, 1.2 Hz), 7.866 (1H, d, $J = 7.1$ Hz), 8.053 (1H, m), 8.581 (1H, m). ^{13}C NMR ($CDCl_3$) δ 53.23 (1C, t), 53.33 (1C, q), 54.60 (1C, t), 58.51 (1C, q), 62.91 (1C, t), 84.35 (1C, q), 92.12 (1C, q), 122.62 (3C, t), 123.09 (1C, t), 123.16 (1C, t), 123.39 (3C, t), 123.52 (1C, t), 123.63 (1C, t), 123.96 (1C, t), 124.60 (1C, t), 124.68 (1C, t), 125.09 (3C, t), 125.10 (1C, t), 125.15 (1C, t), 125.27 (1C, t), 125.32 (1C, t), 125.59 (1C, t), 125.66 (3C, t), 141.20 (1C, q), 143.97 (1C, q), 144.22 (3C, q), 144.27 (3C, q), 144.32 (1C, q), 146.29 (1C, q), 147.19 (1C, q), 147.32 (1C, q).

Reaction of the Alcohol 8 with $LiAlH_4$. A mixture of 50.0 mg (0.089 mmol) of compound **8** and 38 mg (1.0 mmol) of $LiAlH_4$ in 10 mL of THF was heated under reflux for 24 h. After removal of the solvent, the residue was partitioned with water and dichloromethane. The organic layer was washed with water and dried over $MgSO_4$, and the solvent was evaporated. ^{1}H NMR spectrum of the residue showed mostly the signals of the unreacted **8** together with signals ascribable to a trace amount of 1,3-di(9-triptycyl)-2-propen-1-ol (**11**) (see below).

1,3-Di(9-triptycyl)-2-propynyl Acetate (9). A mixture of 50.0 mg (0.089 mmol) of compound **8**, 3.0 mL (32 mmol) of acetic anhydride, and 1.0 mL (12 mmol) of pyridine was stirred for 24 h at room temperature. The mixture was poured onto ice-water and extracted with dichloromethane. The extracts were washed with water and dried over $MgSO_4$, and the solvent was evaporated. Recrystallization of the residue from dichloromethane–hexane gave 39.2 mg (0.065 mmol, 73%) of compound **9**, mp 189–191 °C. Found: C, 89.97; H, 5.31%. Calcd for $C_{45}H_{30}O_2$: C, 89.67; H, 5.02%. ^{1}H NMR ($CDCl_3$) δ 2.367 (3H, s), 5.363 (1H, s), 5.455 (1H, s), 6.93–7.19 (13H, m), 7.339 (3H, m), 7.40–7.47 (2H, m), 7.499 (1H, s), 7.518 (1H, m), 7.662 (3H, m), 8.156 (1H, m), 8.524 (1H, m). ^{13}C NMR ($CDCl_3$) δ 21.39 (1C, p), 53.26 (1C, t), 53.30 (1C, q), 54.54 (1C, t), 57.10 (1C, q), 63.84 (1C, t), 84.86 (1C, q), 88.68 (1C, q), 121.34 (1C, t), 122.77 (3C, t), 123.33 (3C, t), 123.40 (1C, t), 123.66 (1C, t), 123.71 (1C, t), 123.82 (1C, t), 124.51 (1C, t), 124.65 (1C, t), 125.10 (4C, t), 125.29 (1C, t), 125.57 (1C, t), 125.65 (3C, t), 125.74 (1C, t), 125.80 (1C, t), 141.41 (1C, q), 143.27 (1C, q), 144.02 (1C, q), 144.16

(3C, q), 144.22 (3C, q), 145.65 (1C, q), 146.94 (1C, q), 147.18 (1C, q), 170.53 (1C, q).

Reaction of the Acetate 9 with $LiAlH_4$. A mixture of 100 mg (0.166 mmol) of compound **9** and 57 mg (1.5 mmol) of $LiAlH_4$ in 10 mL of THF was heated under reflux for 24 h. After removal of the solvent, the residue was partitioned by water and dichloromethane. The organic layer was washed with water and dried over $MgSO_4$, and the solvent was evaporated. Recrystallization of the residue from dichloromethane–hexane gave 54 mg (0.096 mmol, 58%) of a solid, which was guessed by ^{1}H NMR to be (*E*)-1,3-di(9-triptycyl)-2-propen-1-ol (**11**), mp 335–336 °C. ^{1}H NMR ($CDCl_3$) δ 2.859 (1H, d, $J = 4.1$ Hz, OH), 5.422 (1H, s), 5.436 (1H, s), 6.496 (1H, ddd, $J = 6.6, 4.1, 1.1$ Hz), 6.93–7.09 (10H, m), 7.136 (1H, td, $J = 7.5, 1.4$ Hz), 7.356 (1H, dd, $J = 16.7, 6.6$ Hz), 7.38–7.45 (6H, m), 7.491 (1H, dd, $J = 7.1, 1.4$ Hz), 7.709 (3H, m), 7.776 (1H, dd, $J = 16.7, 1.1$ Hz), 7.795 (1H, m), 7.958 (1H, d, $J = 7.4$ Hz), 8.116 (1H, d, $J = 7.2$ Hz).

1,3-Di(9-triptycyl)-2-propynyl Methanesulfonate (10). To a solution of 2.00 g (3.57 mmol) of compound **8** in 40 mL of dry THF was added at 0 °C under argon 2.70 mL (4.20 mmol) of 1.59 M butyllithium in hexane, and the mixture was stirred for 1 h. To the mixture was added 0.53 mL (6.85 mmol) of methanesulfonyl chloride, and the mixture was stirred for 24 h at room temperature. The reaction mixture was poured onto ice-water and extracted with dichloromethane. The extracts were washed with brine and dried over $MgSO_4$, and the solvent was evaporated. Recrystallization of the residue from dichloromethane–hexane afforded 1.76 g (2.76 mmol, 77%) of compound **10**, mp 290–291 °C (dec). Found: C, 82.83; H, 5.18%. Calcd for $C_{44}H_{30}O_3S$: C, 82.73; H, 4.73%. ^{1}H NMR ($CDCl_3$) δ 3.458 (3H, s), 5.375 (1H, s), 5.451 (1H, s), 6.91–7.17 (12H, m), 7.354 (3H, dd, $J = 6.9, 1.5$ Hz), 7.40–7.48 (2H, m), 7.432 (1H, s), 7.510 (1H, m), 7.656 (3H, dd, $J = 7.1, 1.5$ Hz), 7.704 (1H, d, $J = 7.2$ Hz), 8.015 (1H, m), 8.454 (1H, m). ^{13}C NMR ($CDCl_3$) δ 40.70 (1C, p), 53.22 (1C, t), 53.40 (1C, q), 54.48 (1C, t), 57.51 (1C, q), 70.25 (1C, t), 86.84 (1C, q), 88.79 (1C, q), 121.94 (1C, t), 122.46 (3C, t), 123.14 (1C, t), 123.54 (3C, t), 123.78 (1C, t), 123.81 (1C, t), 123.85 (1C, t), 124.57 (1C, t), 124.66 (1C, t), 125.21 (4C, t), 125.34 (1C, t), 125.45 (1C, t), 125.74 (1C, t), 125.88 (3C, t), 125.93 (1C, t), 140.52 (1C, q), 142.64 (1C, q), 143.09 (1C, q), 143.84 (3C, q), 144.14 (3C, q), 145.50 (1C, q), 146.88 (1C, q), 146.97 (1C, q).

1,3-Di(9-triptycyl)propyne (12). To a solution of 200 mg (0.313 mmol) of compound **10** in 15 mL of anhydrous THF was added 114 mg (3.0 mmol) of $LiAlH_4$, and the mixture was heated under reflux for 24 h. The reaction mixture was poured onto ice-water and extracted with dichloromethane. The extracts were washed with brine and dried over $MgSO_4$, and the solvent was evaporated. Recrystallization of the residue from dichloromethane–hexane gave 130 mg (0.239 mmol, 76%) of **12**, mp 299–300 °C. Found: C, 95.20; H, 5.15%. Calcd for $C_{43}H_{28}$: C, 94.82; H, 5.18%. ^{1}H NMR ($CDCl_3$) δ 4.366 (2H, s), 5.367 (1H, s), 5.474 (1H, s), 6.91–7.10 (12H, m), 7.339 (3H, m), 7.447 (3H, m), 7.692 (3H, m), 7.93 (3H, br s). ^{13}C NMR ($CDCl_3$) δ 19.42 (1C, s), 52.66 (1C, q), 53.24 (1C, t), 53.52 (1C, q), 54.25 (1C, t), 79.66 (1C, q), 89.85 (1C, q), 122.21 (3C, br t), 122.78 (3C, t), 123.25 (3C, t), 123.56 (3C, t), 124.83 (3C, t), 125.01 (3C, t), 125.31 (3C, t), 125.49 (3C, t), 144.37 (3C, q), 144.78 (3C, q), 144.9 (3C, br q), 146.60 (3C, q).

X-ray Crystallography. Crystals of compounds **1** and **3** were grown from diethyl ether–hexane, those of compound **4** were grown from ethyl acetate–hexane, and those of compound **12** were grown from chloroform. The crystal data and the parameters for data collection, structure determination, and refinement are summarized in Table 4. Diffraction data were collected on a Rigaku AFC7R or a Rigaku/MSC Mercury CCD diffractometer, and calculations were performed using the SHELXL97 program.[14] The structures were solved by direct methods followed by full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and all hydrogen atoms isotropic. Reflection data with $|I| > 2.0\sigma(I)$ were used.

Table 4. Crystal Data and Parameters for Data Collection, Structure Determination, and Refinement

Compound	**1**	**3**	**4**	**12**
Empirical formula	$C_{23}H_{16}$	$C_{29}H_{20}$	$C_{43}H_{28} \cdot C_4H_8O_2$	$C_{43}H_{28} \cdot CHCl_3$
Formula weight	292.38	368.48	632.80	664.07
Crystal system	triclinic	monoclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P2_1/a$	$P\bar{1}$	$P\bar{1}$
a/Å	8.278(1)	9.263(1)	8.716(2)	8.465(3)
b/Å	13.187(1)	13.059(2)	11.749(3)	12.658(3)
c/Å	8.162(1)	16.959(1)	17.803(4)	17.149(4)
α/°	94.45(1)	90.00	87.05(1)	65.07(1)
β/°	113.91(1)	97.05(1)	76.91(1)	77.73(1)
γ/°	73.91(1)	90.00	89.50(1)	88.22(1)
V/Å^3	782.1(1)	2036.0(4)	1773.4(7)	1624.7(8)
Z	2	4	2	2
D_{calcd}/g cm^{-3}	1.242	1.202	1.185	1.355
μ(Mo Kα)/cm^{-1}	0.070	0.068	0.071	0.314
Temp/K	293(2)	293(2)	100(2)	100(2)
$2\theta_{\mathrm{max}}$/°	55.0	55.0	55.0	54.5
No. of reflections measured				
Total	3601	4665	6619	6909
Unique	2946	2278	4960	5409
No. of refinement variables	208	262	554	424
Final R_1;[a] wR_2[b]	0.0450; 0.1187	0.0479; 0.1191	0.0665; 0.1921	0.0784; 0.1348
GOF	1.058	1.112	1.080	1.357

a) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. b) $wR_2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-604410 to CCDC-604413 for compounds **1**, **3**, **4**, and **12**, respectively. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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