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Synthesis and rotational barriers of atropisomers of 1,2-bis[5-(11*H*-benzo[*b*]fluorenyl)]benzenes and related compounds

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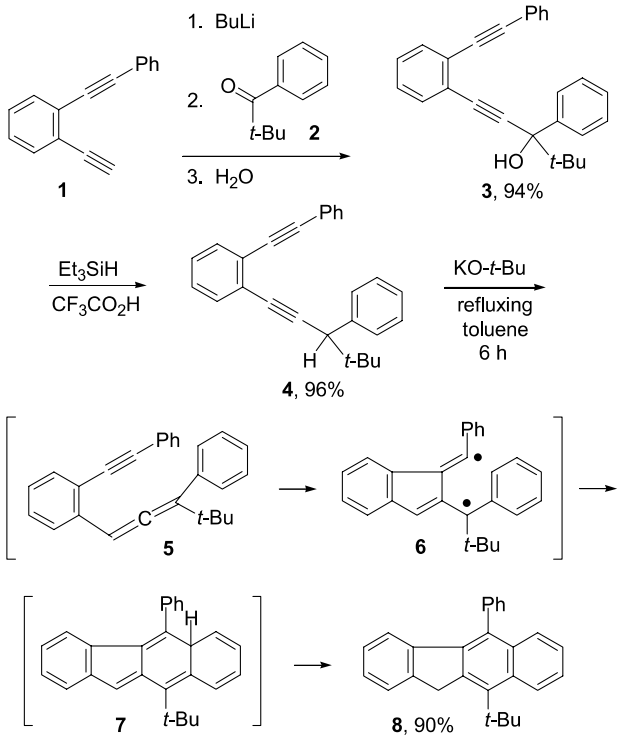
Abstract—Several 1,2-bis[5-(11*H*-benzo[*b*]fluorenyl)]benzenes and related compounds were synthesized via a cascade reaction sequence of the corresponding benzannulated enyne-allene precursors. The X-ray structures showed that the two benzo[*b*]fluorenyl moieties attached via the C5 carbons to the adjacent carbon atoms of the central benzene ring are oriented essentially perpendicular to the central benzene ring. The rates of rotation around the carbon–carbon single bonds attaching the benzo[*b*]fluorenyl moieties to the central benzene ring are relatively slow, allowing several *anti* and *syn* atropisomers to be separated at ambient temperature.

1. Introduction

Benzannulated enyne-allenes bearing an aryl substituent at the alkynyl terminus have been shown to undergo a cascade sequence of reactions, including a biradical-forming Schmittel cyclization reaction,[1–4] to produce 11*H*-benzo[*b*]fluorenes under mild thermal conditions.[5–13] For instance, we reported that condensation between **1** and **2** followed by reduction of the resulting propargylic alcohol **3** with triethylsilane in the presence of trifluoroacetic acid provided the benzannulated enediyne **4**, which on treatment with potassium *t*-butoxide in refluxing toluene produced 10-(1,1-dimethylethyl)-5-phenyl-11*H*-benzo[*b*]fluorene (**8**) in excellent yield (Scheme 1).[7] Presumably, the transformation involves an initial prototropic rearrangement of **4** to form in situ the benzannulated enyne-allene **5** followed by a Schmittel cyclization reaction[1–4] to generate biradical **6**. A subsequent intramolecular radical–radical coupling then gave **7**, which in turn underwent a prototropic rearrangement to regain aromaticity leading to **8**. It occurred to us that by starting from compounds bearing two enediynyl units for condensation with 2 equiv of **2** and related ketones, the synthetic sequence outlined in Scheme 1 could lead to compounds bearing two benzo[*b*]fluorenyl moieties. Bridged bis(benzofluorenyl) zirconium dichloride complexes and related compounds



Scheme 1.

Keywords: 1,2-Bis[5-(11*H*-benzo[*b*]fluorenyl)]benzenes; Atropisomers; Benzannulated enyne-allenes.
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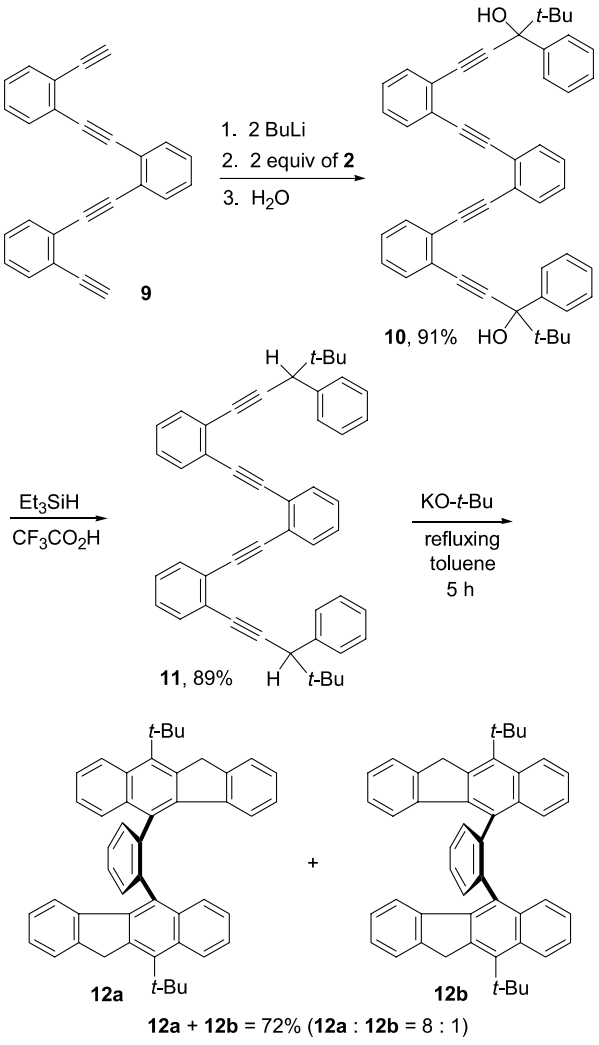
have been shown to exhibit high activities in catalytic ethylene and propylene polymerization.[14] The use of tetraacetylene **9** bearing two benzannulated enediynyl units (Scheme 2) to start the synthetic sequence could provide easy access to a variety of bis(benzofluorenyl)benzenes and related compounds as ligands with diverse structural features and a new bridging connectivity for metal complex formation.



Scheme 2.

2. Results and discussion

Tetraacetylene **9** bearing two benzannulated enediynyl units was prepared by the Sonogashira reactions between 1,2-diethynylbenzene and 2 equiv of 1-iodo-2-[(trimethylsilyl)-ethynyl]benzene followed by desilylation as reported previously.[15] Condensation between **9** and 2 equiv of **2** followed by the reduction of the resulting propargylic diol **10** then afforded **11**. Treatment of **11** with potassium *t*-butoxide in refluxing toluene for 5 h produced the *anti* atropisomer (racemic) **12a** and the *syn* atropisomer (*meso*) **12b** bearing two benzo[*b*]fluorenyl substituents attached via the C5 carbons to the adjacent carbon atoms of the central benzene ring.

The ^{1}H NMR spectrum of the reaction mixture of **12a** and **12b** exhibits two sets of AB quartets at δ 4.03/3.86 ($J=21$ Hz) and δ 3.92/3.80 ($J=21$ Hz) in an 8:1 ratio attributable to the diastereotopic hydrogens on the five-membered rings of **12a** and **12b**, respectively. A single crystal of **12a** suitable for X-ray structure analysis was obtained (Fig. 1). The X-ray structure showed that the two benzo[*b*]fluorenyl moieties are oriented essentially perpendicular to the central benzene ring, making the geminal hydrogens on the five membered rings chemically and magnetically nonequivalent. It is also worth noting that the AB quartet signals of the *anti* atropisomer **12a** appear to shift downfield from those of the *syn* atropisomer **12b**.

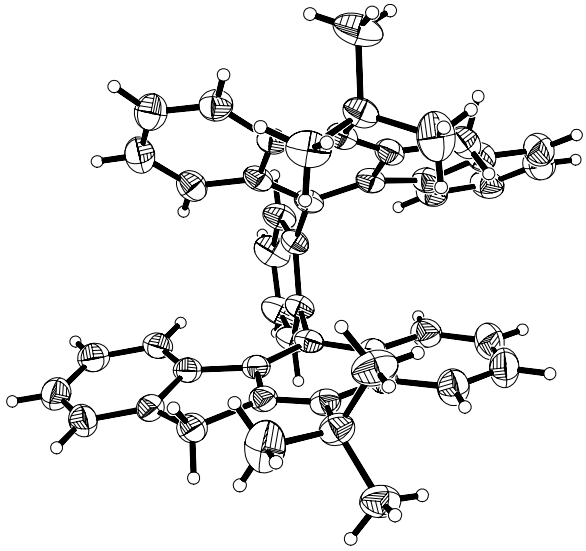
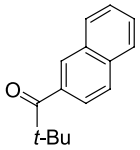
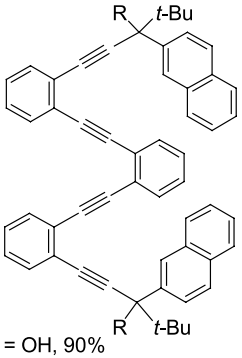
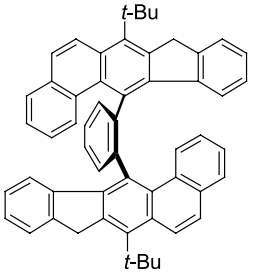
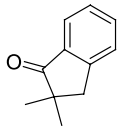
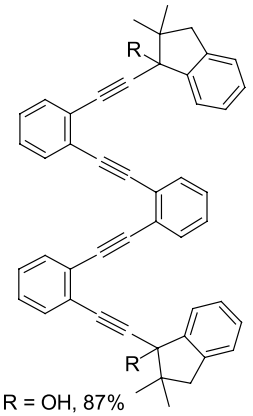
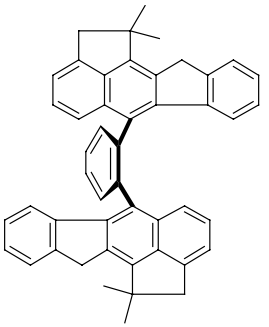
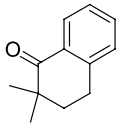
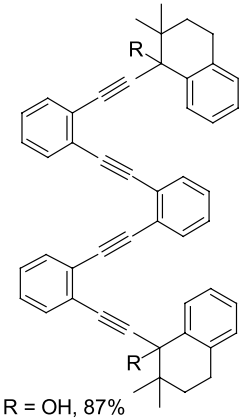
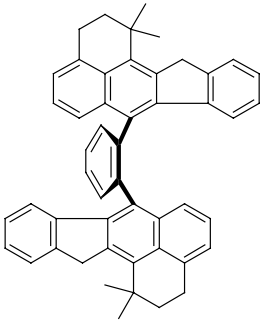
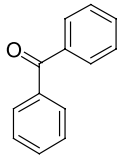
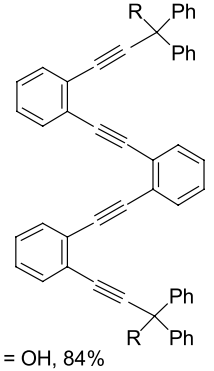
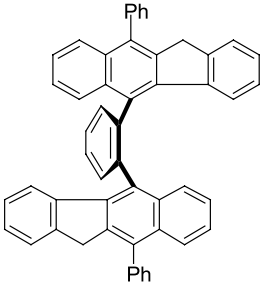


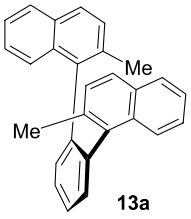
Figure 1. Perspective view of the molecular structure of **12a** with the thermal ellipsoids scaled to enclose 30% probability.

Apparently, at ambient temperature the rate of rotation around the carbon–carbon single bonds attaching the benzo[*b*]fluorenyl substituents to the central benzene ring is relative slow, allowing **12a** to be isolated. However, heating **12a** in refluxing toluene (110 °C) for 5 h resulted in equilibration between **12a** and **12b**, again producing an 8:1 mixture. In refluxing benzene (80 °C), the rate constant of this kinetic process leading to equilibrium (**12a**:**12b**=9.1:1) was determined to be 2.1×10^{-5} s^{-1}, corresponding to a free energy of activation of 28.3 kcal/mol to convert **12a** to **12b** and a half-life of 0.91 h to reach equilibrium.

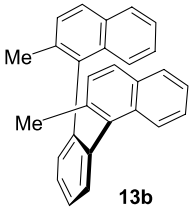
The preference for the *anti* atropisomer **12a** is in contrast to an earlier report showing essentially no preference for the *anti* atropisomer **13a** over the *syn* atropisomer **13b** (**13a/13b**=1.1:1) after the equilibrium is reached at 150 °C.[16] Unlike **13b**, the *syn* atropisomer **12b** appears to suffer from unfavorable nonbonded steric interactions between the two outer benzene rings on the same side of the five-membered rings, making it the less stable rotational isomer. Starting from **13b**, the rate constant for the transformation to **13a** was determined to be 4.7×10^{-5} s^{-1} at 130 °C, corresponding to a free energy of activation of 31.2 kcal/mol and a half-life of 2.0 h to reach equilibrium.[16] This rotational barrier is considerably higher than that of **12a**.

Table 1. Synthesis of 1,2-bis[5-(11*H*-benzo[*b*]fluorenyl)]benzenes and related compounds **26–29**

Aryl ketone	Propargylic alcohol and enediyne	Product	Aryl ketone	Propargylic alcohol and enediyne	Product
 **14**	 **18**: R = OH, 90% **22**: R = H, 87%	 **26**, 56% (*anti* : *syn* > 98 : 2)	 **16**	 **20**: R = OH, 87% **24**: R = H, 84%	 **28**, 40% (*anti* : *syn* = 1 : 1.7)
 **15**	 **19**: R = OH, 87% **23**: R = H, 90%	 **27**, 87% (*anti* : *syn* = 12 : 1)	 **17**	 **21**: R = OH, 84% **25**: R = H, 83%	 **29**, 42% (*anti* : *syn* = 14 : 1)



13a



13b

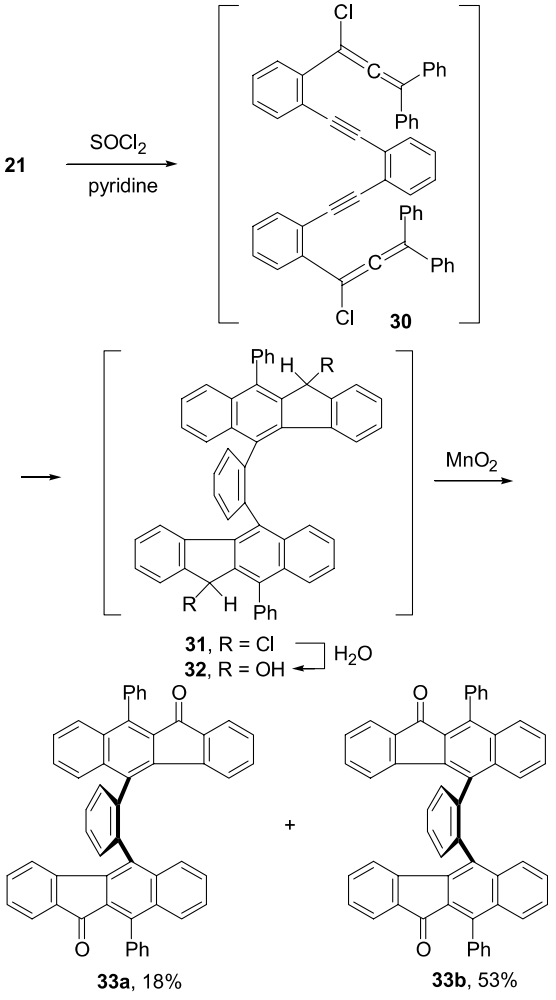
Similarly, condensation between **9** and aryl ketones **14–17** produced the corresponding propargylic alcohols **18–21** for subsequent reduction with triethylsilane in the presence of trifluoroacetic acid to form the benzannulated enediynes **22–25** (Table 1). Treatment of **22** with potassium *t*-butoxide in refluxing toluene for 4 h then furnished **26** bearing two indeno[2,1-*b*]phenanthryl moieties on the adjacent carbon atoms of the central benzene ring. Only the *anti* atropisomer was detected (*anti*:*syn*>98:2). The structure of the *anti* atropisomer was established by X-ray structure analysis. It showed that the two indeno[2,1-*b*]phenanthryl moieties are nonplanar, bending away from each other in order to minimize nonbonded steric interactions. Compared to **12a** and **12b**, the presence of two more fused benzene rings on the indeno[2,1-*b*]phenanthryl moieties appears to cause the *syn* atropisomer of **26** to suffer from even more severe nonbonded steric interactions.

Treatment of **23** with potassium *t*-butoxide in refluxing toluene for 6 h produced **27** as a mixture of the *anti* and *syn* atropisomers (*anti*:*syn*=12:1) similar to what was observed in **12a** and **12b**. The assignment of the *anti* atropisomer as the major isomer is based on the observation that a major set of the AB quartet signals occurred at δ 4.01/3.75, downfield from a minor set of the AB quartet signals at δ 3.86/3.58, in good correlation with those of **12a** and **12b**.

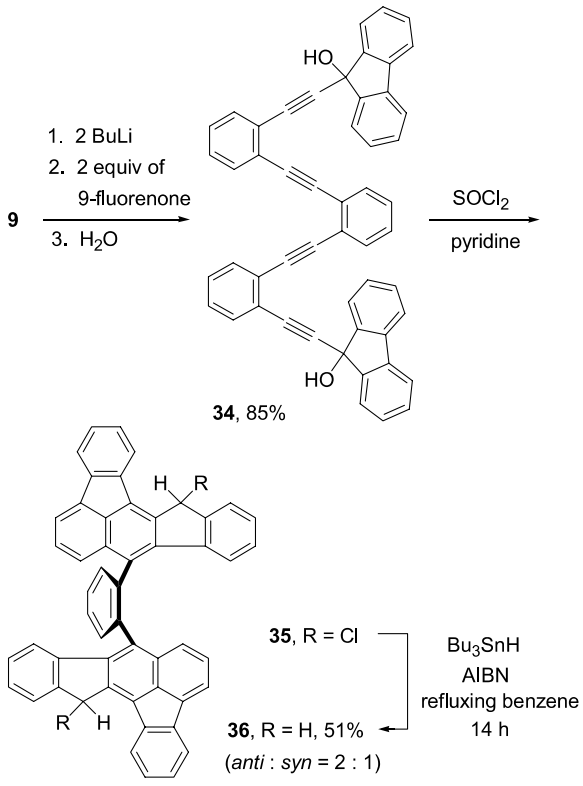
Interestingly, treatment of **24** with potassium *t*-butoxide in refluxing benzene (80 °C) for 5 h furnished **28** in favor of the *syn* atropisomer (*anti*:*syn*=1:1.7) with the isomeric assignment also based on the chemical shift correlations of the AB quartet signals at δ 3.92/3.70 and 3.66/3.33. However, after 20 h in refluxing benzene the equilibrium was reached, and the *anti* atropisomer became the predominant rotational isomer (*anti*:*syn*=5:1). Clearly, the majority of the *syn* atropisomer was formed as the kinetic product initially, which was then converted to the thermodynamically more stable *anti* atropisomer after prolonged heating. The *anti*:*syn* ratio of **28** became 4.8:1 after it had been heated in refluxing toluene for 24 h.

Similar results were obtained when **25** was treated with potassium *t*-butoxide in refluxing toluene for 4 h to give **29** as a mixture of the *anti* and *syn* atropisomers (*anti*:*syn*=14:1). The isomeric assignment is again based on the chemical shift correlations of the AB quartet signals at δ 3.58/3.30 and 3.44/3.04. Compared to **12a** and **12b**, replacing the two *t*-butyl substituents with two phenyl substituents in **29** showed no significant effect on the ratio of the rotational isomers.

As reported earlier,[6,7,9,12] the use of thionyl chloride to induce two S_Ni' reactions of propargylic diol **21** at ambient or sub-ambient temperatures presumably furnished in situ **30** bearing two units of the chlorinated enyne-allene moiety (Scheme 3). The subsequent cyclization reactions also occurred at ambient or sub-ambient temperatures leading to **31**, which was readily hydrolyzed to yield diol **32** as a mixture of the rotational isomers and the configurational isomers due to the presence of two chiral centers on the five-membered rings. Because the relative reaction rates of the steps of the S_Ni' reactions and the subsequent cyclization reactions have not been determined, it is also possible that the first unit of the benzannulated enediynyl propargylic alcohol moiety could undergo an S_Ni' reaction followed by a Schmittel cyclization reaction, a radical–radical coupling reaction, and a prototropic rearrangement before the second unit would begin its cyclization sequence. Oxidation of **32** with manganese dioxide at ambient temperature then afforded the *anti* atropisomer **33a** in 18% yield and the *syn* atropisomer **33b** in 53% yield. The structures of **33a** and **33b** were established by X-ray structure analyses. As observed in the case of **28**, the *syn* atropisomer **33b** is the kinetic product. On heating **33b** in refluxing benzene for 186 h, the equilibrium between **33a** and **33b** was essentially established, producing the *anti* atropisomer **33a** predominantly (*anti*:*syn*=2.2:1). The rate constant for the transformation of **33b** to **33a** was determined to be 2.3×10^{-6} s^{-1}, corresponding to a free energy of activation of 29.9 kcal/mol and a half-life of 58 h to reach equilibrium.

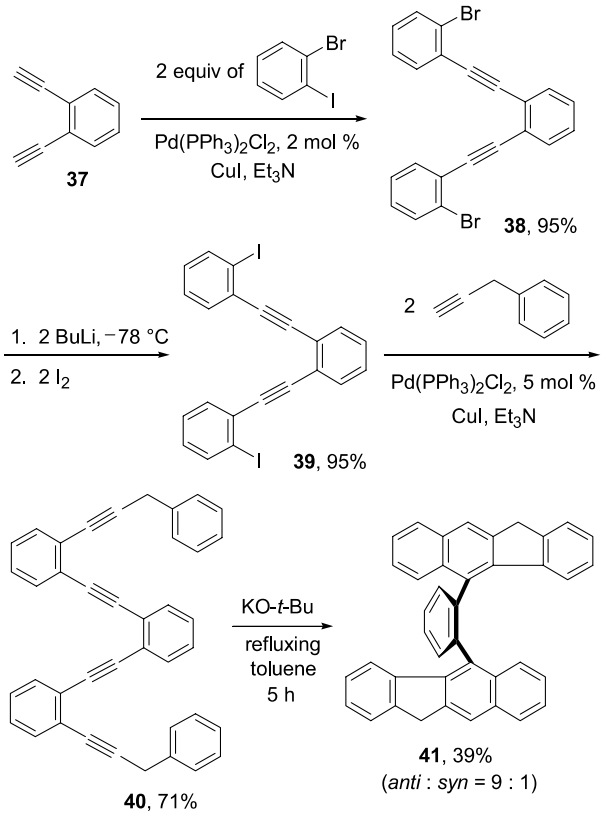


Scheme 3.



Scheme 4.

Similarly, the use of 9-fluorenone for condensation with **9** produced **34**, which was then treated with thionyl chloride to furnish in situ dichloride **35** (Scheme 4). Reduction of **35** with tributyltin hydride in refluxing benzene for 14 h then gave **36** as a mixture of the *anti* and *syn* atropisomers (*anti*:*syn*=2:1). The isomeric assignment is again based on the chemical shift correlations of the AB quartet signals at δ 4.25/4.12 and 4.00/3.85.



Scheme 5.

A synthetic sequence leading to **41** without additional substituents on the two benzo[*b*]fluorenyl units was also developed (Scheme 5). Coupling between **37** and 2 equiv of 1-bromo-2-iodobenzene produced **38**, which was converted to **39** by bromo to iodo exchange. Two Sonogashira reactions between **39** and 3-phenylpropyne then produced tetraacetylene **40**. Treatment of **40** with potassium *t*-butoxide in refluxing toluene for 5 h furnished **41** as a mixture of the *anti* and *syn* atropisomers (*anti*:*syn*=9:1) with the isomeric assignment again based on the chemical shift correlations of the AB quartet signals at δ 3.90/3.71 and 3.65/3.46.

3. Conclusion

New synthetic pathways to 1,2-bis[5-(11*H*-benzo[*b*]-fluorenyl)]benzenes and related compounds were developed. These compounds could exist either as the *anti* atropisomers or the *syn* atropisomers at ambient temperature because of relatively high rotational barriers. The *anti* atropisomers are the thermodynamically more stable rotational isomers, whereas in a few cases the thermodynamically less stable *syn* atropisomers could be produced as the kinetic products predominantly. The X-ray structures of several representative examples showed that the two benzo[*b*]fluorenyl moieties are oriented essentially perpendicular to the central benzene ring.

4. Experimental

4.1. General

All reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere. Diethyl ether and tetrahydrofuran (THF) were distilled from benzophenone ketyl prior to use. *n*-Butyllithium (2.5 M) in hexanes, *t*-butyllithium (1.7 M) in pentane, $Pd(PPh_3)_2Cl_2$, copper(I) iodide, $CuBr\cdot SMe_2$, pivalophenone (**2**), triethylsilane, trifluoroacetic acid, potassium *t*-butoxide (1.0 M) in 2-methyl-2-propanol, 2-naphthoyl chloride, α-tetralone, 1-indanone, benzophenone, 9-fluorenone, and 3-phenylpropyne were purchased from chemical suppliers and were used as received. 1,2-Bis[(2-ethynylphenyl)ethynyl]benzene (**9**) was prepared as reported previously.[15] *t*-Butyl 2-naphthyl ketone (**14**) was prepared by treatment of 2-naphthoyl chloride with *t*-butylcopper, prepared from *t*-butyllithium and $CuBr\cdot SMe_2$, in quantitative yield as described previously for a similar aryl *t*-butyl ketone.[8] 1-Oxo-2,2-dimethyl-1,2,3,4-tetrahydronaphthalene (**15**)[7] and 2,2-dimethyl-1-indanone (**16**)[7] were prepared as reported previously. The kinetic studies of the rates of rotations of **12a** and **33b** were conducted by following the progress of the equilibration processes with the integrations of pertinent ^{1}H NMR signals. The rate constants were obtained by regarding the equilibration processes as reversible first-order reactions. The temperatures of

the refluxing benzene and toluene solutions were determined by inserting a thermometer into the solutions and were found to be 80 ± 0.5 and 110 ± 0.5 °C, respectively. Melting points were uncorrected. ^{1}H (270 MHz) and ^{13}C (67.9 MHz) NMR spectra were recorded in $CDCl_3$ using $CHCl_3$ (^{1}H δ 7.26) and $CDCl_3$ (^{13}C δ 77.0) as internal standards unless otherwise indicated for those recorded on a 600-MHz NMR spectrometer.

4.1.1. Propargylic alcohol 10. To 0.471 g (1.44 mmol) of **9** in 40 mL of anhydrous diethyl ether under a nitrogen atmosphere at 0 °C was added 1.15 mL of a 2.5 M solution of *n*-butyllithium (2.88 mmol) in hexanes. After 30 min of stirring, a solution of 0.470 g of pivalophenone (**2**, 2.90 mmol) in 20 mL of diethyl ether was introduced via cannula, and the reaction mixture was allowed to warm to room temperature. After an additional 2 h, 50 mL of water was introduced, and the reaction mixture was extracted with diethyl ether. The combined organic extracts were washed with brine and water, dried over sodium sulfate, and concentrated. The residue was purified by flash column chromatography (silica gel/20% diethyl ether in hexanes) to provide 0.854 g (1.31 mmol, 91%, 1:1 mixture of two diastereomers) of **10** as a yellow liquid: IR 3436, 2085, 1637 cm^{-1}; ^{1}H (1:1 mixture) δ 7.78–7.72 (4H, m), 7.58–7.49 (4H, m), 7.42–7.38 (2H, m), 7.32–7.20 (12H, m), 2.50 and 2.47 (2H, two singlets, 1:1 ratio), 1.09 (18H, s); ^{13}C (1:1 mixture) δ 142.0, 132.4, 132.1, 131.7, 128.1, 128.0, 127.8, 127.2, 127.0, 125.7, 125.0, 96.3, 92.5, 92.0, 84.4, 79.5, 39.7, 25.5.

4.1.2. Benzannulated enediyne 11. To a mixture of **10** (0.379 g, 0.583 mmol) and triethylsilane (0.203 g, 1.75 mmol) in 15 mL of methylene chloride was added 0.35 mL of trifluoroacetic acid (0.54 g, 4.7 mmol). After 5 min of stirring at room temperature, 0.48 g of sodium carbonate (4.6 mmol) was added followed by 10 mL of water and 40 mL of diethyl ether. The organic layer was separated, dried over sodium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/10% CH_2Cl_2 in hexanes) provided 0.321 g (0.519 mmol, 89%, 1:1 mixture of two diastereomers) of **11** as a yellow solid: mp 56–58 °C; IR 2226, 1490, 756 cm^{-1}; ^{1}H δ 7.56–7.52 (2H, m), 7.48–7.38 (6H, m), 7.36–7.31 (2H, m), 7.25–7.14 (12H, m), 3.659 and 3.655 (2H, two singlets), 1.032 and 1.029 (18H, two singlets); ^{13}C δ 139.2, 132.4, 132.0, 131.8, 129.8, 127.9, 127.8, 127.5, 127.3, 126.6, 126.2, 125.9, 125.7, 95.7, 92.8, 91.7, 82.4, 50.6, 35.5, 27.8.

4.1.3. *anti* and *syn* Atropisomers of 1,2-bis[5-[10-(1,1-dimethylethyl)-11*H*-benzo[*b*]fluorenyl]]benzene (12a and 12b). To 0.389 g of **11** (0.629 mmol) in 15 mL of anhydrous toluene under a nitrogen atmosphere was added 1.26 mL of a 1.0 M solution of potassium *t*-butoxide (1.26 mmol) in 2-methyl-2-propanol. The reaction mixture was then heated under reflux for 5 h. After the reaction mixture was allowed to cool to room temperature, 10 mL of water and 40 mL of methylene chloride were introduced, and the organic layer was separated, dried over sodium sulfate, and concentrated. The residue was purified by flash column chromatography (silica gel/10% methylene chloride in hexanes) to provide 0.279 g of **12a** and **12b** (0.451 mmol, 72%, **12a**:**12b**=8:1) as a pale yellow solid. **12a**: ^{1}H (600 MHz) δ 8.06 (2H, d, J=9.0 Hz), 7.90–7.82 (4H, m), 7.43 (2H, d, J=8.4 Hz), 7.30 (2H, d, J=7.8 Hz), 7.20 (2H, t, J=7.2 Hz), 7.11 (2H, t, J=7.2 Hz), 6.91 (2H, t, J=7.5 Hz), 6.82 (2H, d, J=7.2 Hz), 6.20 (2H, t, J=7.5 Hz), 4.03 (2H, d, J=21 Hz), 3.86 (2H, d, J=20.4 Hz), 1.57 (18H, s); ^{13}C δ 143.9, 140.8, 140.2, 139.5, 138.3, 136.5, 133.2, 132.7, 131.6, 130.0, 128.7, 128.1, 126.4, 126.3, 125.7, 124.3, 123.5, 122.4, 121.6, 39.3, 38.2, 34.0; MS *m*/*z* 618 (M^+), 561, 547; HRMS calcd for $C_{48}H_{42}$ 618.3287, found 618.3299. Recrystallization from a mixture of hexanes and methylene chloride produced a crystal suitable for X-ray structure analysis.

A minor set of ^{1}H NMR signals attributable to **12b** were also observed at δ (partial, 600 MHz) 7.96 (2H, dd, J=5.4, 3.6 Hz), 7.40 (2H, d, J=8.4 Hz), 7.15 (2H, d, J=7.8 Hz), 7.08 (2H, d, J=7.2 Hz), 7.02 (2H, t, J=7.5 Hz), 6.86 (2H, t, J=7.2 Hz), 6.77 (2H, t, J=7.5 Hz), 6.55 (2H, t, J=7.8 Hz), 3.92 (2H, d, J=21.0 Hz), 3.80 (2H, d, J=21.0 Hz), and 1.58 (18H, s).

4.1.4. Rotational barrier of the transformation from 12a to 12b. A solution of 0.016 g of **12a** in 10 mL of benzene was heated under reflux. At the intervals of 10, 20, 30, 80, 140, 200 min, 8, and 30 h, 1-mL aliquot of the reaction mixture was withdrawn and cooled to room temperature immediately. Benzene was removed under reduced pressure, and the residue was dissolved in 0.75 mL of $CDCl_3$. The progress of the equilibration process was determined by integrations of the well separated ^{1}H NMR signals (600 MHz) of **12a** at δ 6.20 and **12b** at δ 6.55. After 8 h, the equilibrium was reached, and the equilibrium constant ([**12b**]/[**12a**]) was determined to be 0.11. A linear plot of $\ln([\mathbf{12a}]_{eq}-[\mathbf{12a}]_0/[\mathbf{12a}]_{eq}-[\mathbf{12a}])$ versus time for the first five data points of this reversible first-order reaction was obtained, and the sum of the rate constants (k_1+k_2) was determined from the slope of the plot to be 2.1×10^{-4} s^{-1}. From the equilibrium constant K ($k_1/k_2=0.11$) and the sum of the rate constants, the rate constant k_1 for the transformation from **12a** to **12b** was calculated to be 2.1×10^{-5} s^{-1}.

From the rate constant k_1, the free energy of activation ($\Delta G^{\ddagger}$) was calculated to be 28.3 kcal/mol using the Erying equation of $\Delta G^{\ddagger}=4.57\ (T)\ (10.32+\log T/k)$. The half-life of 0.91 h to reach equilibrium was calculated from the equation $t_{1/2}=0.693/(k_1+k_2)$.

4.1.5. *anti* Atropisomer 33a and *syn* atropisomer 33b. To **21** (0.083 g, 0.12 mmol) in 5 mL of THF at 0 °C was added via cannula a solution of thionyl chloride (0.06 mL, 0.8 mmol) and anhydrous pyridine (0.14 mL) in 3 mL of THF. The reaction mixture then was allowed to warm to room temperature. After an additional 12 h, 10 mL of water was introduced, and the reaction mixture was extracted with 30 mL of diethyl ether. The combined organic extracts were washed with water, dried over magnesium sulfate, and concentrated to furnish the crude dichloride **31**. The crude dichloride was stirred with silica gel in methylene chloride for 2 h at ambient temperature. Silica gel was filtered and methylene chloride was evaporated to produce the crude diol **32**. To **32** dissolved in 4 mL of toluene was added 0.2 g

of manganese dioxide. The reaction mixture was stirred for 48 h before manganese dioxide was filtered. Toluene was evaporated, and the residue was purified by flash column chromatography (silica gel/50% CH_2Cl_2 in hexanes) to provide 0.015 g (0.022 mmol, 18%) of **33a** and 0.043 g (0.063 mmol, 53%) of **33b** as yellow solids. Compound **33a**. IR 1739, 1366, 731 cm^{-1}; ^1H δ 8.01–7.92 (4H, m), 7.54 (2H, d, $J=6.7$ Hz), 7.48–7.37 (10H, m), 7.31–7.20 (6H, m), 6.97–6.91 (4H, m), 6.83–6.79 (2H, m), 6.39 (2H, ddd, $J=8.2$, 6.9, 1.2 Hz); ^{13}C δ 191.8, 144.8, 140.2, 138.3, 136.5, 136.3, 135.5, 135.4, 134.1, 132.7, 132.4, 129.3, 129.2, 129.0, 128.7, 128.05, 127.96, 127.92, 127.8, 126.8, 126.6, 124.1, 123.9. Recrystallization from a mixture of methylene chloride and ethanol produced a crystal suitable for X-ray structure analysis. Compound **33b**. IR 1739, 1366, 1217 cm^{-1}; ^1H δ 8.09–8.04 (2H, m), 7.97–7.93 (2H, m), 7.47–7.40 (6H, m), 7.36 (2H, d, $J=8.4$ Hz), 7.28–7.17 (6H, m), 7.08–7.02 (4H, m), 6.94–6.85 (4H, m), 6.81–6.76 (4H, m); ^{13}C δ 191.5, 144.1, 140.1, 138.1, 136.1, 135.73, 135.69, 135.6, 133.4, 132.9, 132.7, 131.7, 129.2, 129.1, 128.6, 128.5, 128.2, 127.7, 127.6, 127.13, 127.06, 126.0, 124.8, 123.4. Recrystallization from a mixture of methylene chloride and ethanol produced a crystal suitable for X-ray structure analysis.

4.1.6. Rotational barrier of the transformation from 33b to 33a. A solution of 0.014 g of **33b** in 10 mL of benzene was heated under reflux. At the intervals of 17, 40, 57, 74, 87, 128, 146, and 168 h, 1 mL aliquot of the reaction mixture was withdrawn and cooled to room temperature immediately. Benzene was removed under reduced pressure, and the residue was dissolved in 0.75 mL of $CDCl_3$. The progress of the equilibration process was determined by integrations of the ^1H NMR signals (270 MHz) of **33a** at δ 6.39 and the overlapping signals of **33a** and **33b** at δ 8.09–7.92. After 186 h, the equilibrium was essentially reached, and the equilibrium constant ([**33a**]/[**33b**]) was determined to be 2.2. A linear plot of $\ln([\mathbf{33b}]_{eq}-[\mathbf{33b}]_0/[\mathbf{33b}]_{eq}-[\mathbf{33b}])$ versus time for the first four data points of this reversible first-order reaction was obtained, and the sum of the rate constants was determined from the slope of the plot to be 3.3×10^{-6} s^{-1}. From the equilibrium constant K and the sum of the rate constants, the rate constant for the transformation from **33b** to **33a** was calculated to be 2.3×10^{-6} s^{-1}.

From the rate constant, the free energy of activation ($\Delta G^{\ddagger}$) of the rotational barrier to transform **33b** to **33a** was calculated to be 29.9 kcal/mol, corresponding to a half-life of 58 h to reach equilibrium.

4.1.7. *anti* and *syn* Atropisomers of 36. To **34** (0.088 g, 0.13 mmol) in 5 mL of THF at 0 °C was added via cannula a solution of thionyl chloride (0.035 mL, 0.48 mmol) and anhydrous pyridine (0.08 mL) in 4 mL of THF. The reaction mixture then was allowed to warm to room temperature. After an additional 12 h, 15 mL of water was introduced, and the reaction mixture was extracted with 30 mL of diethyl ether. The combined organic extracts were washed with water, dried over magnesium sulfate, and concentrated to furnish the crude dichloride **35**. To a flask containing AIBN (0.008 g) were added a solution of the crude **35** in 5 mL of benzene and tributyltin hydride (0.1 mL). The reaction mixture was heated under reflux for 14 h. After the reaction mixture was allowed to cool to room temperature, 5 mL of a 10% aqueous potassium fluoride solution was introduced. The reaction mixture was stirred for an additional 2 h and then filtered. The organic layer was separated, washed with water, dried over sodium sulfate, and concentrated to give a brown solid residue. The residue was purified by flash column chromatography (silica gel/10% methylene chloride in hexanes) to afford **36** (0.043 g, 0.066 mmol, 51%, *anti*:*syn*=2:1) as a yellow solid: IR 3056, 2923, 1444 cm^{-1}; ^1H δ 8.00–7.83 (4H, m), 7.76–7.48 (8H, m), 7.46–7.02 (12H, m), 6.67 (*syn*, 0.6H, t, $J=7.5$ Hz), 6.53 (*anti*, 1.4H, dd, $J=8.4$, 6.9 Hz), 4.25 (*anti*, 1.4H, d, $J=22.5$ Hz), 4.12 (*anti*, 1.4H, d, $J=22.3$ Hz), 4.00 (*syn*, 0.6H, d, $J=22.3$ Hz), 3.85 (*syn*, 0.6H, d, $J=21.8$ Hz); ^{13}C δ 143.9, 143.0, 141.7, 140.8, 139.9, 138.6, 138.5, 137.7, 137.5, 135.5, 133.4, 133.2, 133.0, 130.7, 130.5, 128.8, 128.6, 127.9, 127.1, 126.9, 126.7, 126.5, 125.8, 125.7, 125.20, 125.14, 124.5, 124.3, 122.7, 121.15, 121.07, 119.3, 119.1, 35.0, 34.7; MS *m/z* 654 (M^+), 538; HRMS calcd for $C_{52}H_{30}$ 654.2348, found 654.2354.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2005.10.062. Experimental procedures and spectroscopic data for **18–29**, **34**, **38**, **39**, **40**, and **41**; ^1H and ^{13}C NMR spectra of compounds **10**, **11**, **12a**, **18–29**, **33a**,**b**, **34**, **36**, and **38–41**; ORTEP drawings of the crystal structures of **12a**, **26**, **33a**, and **33b**; Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre. The CCDC nos. 281747, 281748, 281749, and 281750 have been assigned for the compounds **12a**, **26**, **33a**, and **33b**, respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

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