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# Polycyclic Aromatic Compounds via Radical Cyclizations of Benzannulated Enyne-Allenes Derived from Ireland−Claisen Rearrangement

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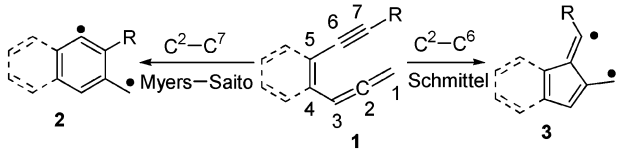
A new synthetic sequence involving the use of Ireland−Claisen rearrangement of propargylic acetates to form the corresponding benzannulated enyne-allenes followed by Schmittel cyclization to generate benzofulvene biradicals for radical cyclizations leading to polycyclic aromatic compounds was established. Treatment of 9-fluorenone (**8**) with the lithium acetylide **9** followed by acetic anhydride produced the propargylic acetate **10**. A sequence of reactions occurred after **10** was converted to the corresponding silyl ketene acetal **11**. An initial Ireland−Claisen rearrangement produced the benzannulated enyne-allene **12**, which then underwent a Schmittel cyclization reaction to generate the benzofulvene biradical **13**. A subsequent intramolecular radical−radical coupling then produced the formal Diels−Alder adduct **14**, which in turn underwent a prototropic rearrangement to give the silyl ester **15** and, after hydrolysis, the carboxylic acid **16** in 57% overall yield from **10** in a single operation. An intramolecular acylation reaction of **16** produced the ketone **17**. The carboxylic acids **24**−**26** were likewise prepared from the diaryl ketones **18**−**20**, respectively. However, the intramolecular [2 + 2] cycloaddition reaction of the benzannulated enyne-allene **33** having a *tert*-butyl group at the allenic terminus occurred preferentially, producing the 1*H*-cyclobut-[*a*]indenyl acetic acid **35** as the predominant product.

## Introduction

Biradicals generated from cyclization of (*Z*)-1,2,4-heptatrien-6-ynes (enyne-allenes) and the benzannulated analogues under mild thermal conditions provide many opportunities for subsequent synthetic applications.[1] Cyclization of the enyne-allene **1** could proceed either via the $C^2-C^7$ pathway (Myers−Saito cyclization) to form the α,3-didehydrotoluene/naphthalene biradical **2**[2] or via the $C^2-C^6$ pathway (Schmittel cyclization) to produce the fulvene/benzofulvene biradical **3** (Scheme 1).[3] The enyne-allenes bearing an aryl substituent or a sterically demanding group, such as the *tert*-butyl group or the trimethylsilyl group, at the alkynyl terminus favor the Schmittel cyclization pathway.

One of the synthetic methods that has been used to prepare in situ the benzannulated enyne-allenes for the subsequent Myers−Saito cyclization reaction involves producing the allenic moiety via thermolysis of propargyl vinyl ethers to promote the [3,3] sigmatropic Claisen rearrangement at 150 °C.[4] The corresponding Lewis acid catalyzed [3,3] sigmatropic Claisen rearrangement promoted by $AgBF_4$ was also successfully adopted for the preparation of the benzannulated enyne-allenes at 25 °C.[4]

**SCHEME 1**




The silyl ketene acetals of propargylic acetates have also been reported to undergo facile Ireland−Claisen rearrangement to produce, after hydrolysis, the corresponding allenyl acetic acids.[5] Specifically, the propargylic acetate **4** was treated with lithium diisopropylamide

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† To whom correspondence concerning the X-ray structures should be addressed. Phone: (304) 293-3435, ext 6423. Fax: (304) 293-4904. E-mail: jeffrey.petersen@mail.wvu.edu.

(1) For reviews, see: (a) Nicolaou, K. C.; Dai, W.-H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1387−1416. (b) Maier, M. E. *Synlett* **1995**, 13−26. (c) Wang, K. K. *Chem. Rev.* **1996**, *96*, 207−222. (d) Saito, I.; Nakatani, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 3007−3019. (e) Grissom, J. W.; Gunawardena, G. U.; Klingberg, D.; Huang. D. *Tetrahedron* **1996**, *52*, 6453−6518.

(2) (a) Myers, A. G.; Kuo, E. Y.; Finney, N. S. *J. Am. Chem. Soc.* **1989**, *111*, 8057−8059. (b) Myers, A. G.; Dragovich, P. S. *J. Am. Chem. Soc.* **1989**, *111*, 9130−9132. (c) Nagata, R.; Yamanaka, H.; Okazaki, E.; Saito, I. *Tetrahedron Lett.* **1989**, *30*, 4995−4998. (d) Nagata, R.; Yamanaka, H.; Murahashi, E.; Saito, I. *Tetrahedron Lett.* **1990**, *31*, 2907−2910.

(3) (a) Schmittel, M.; Strittmatter, M.; Kiau, S. *Tetrahedron Lett.* **1995**, *36*, 4975−4978. (b) Schmittel, M.; Strittmatter, M.; Vollmann, K.; Kiau, S. *Tetrahedron Lett.* **1996**, *37*, 999−1002. (c) Schmittel, M.; Strittmatter, M.; Kiau, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1843−1845. (d) Schmittel, M.; Kiau, S.; Siebert, T.; Strittmatter, M. *Tetrahedron Lett.* **1996**, *37*, 7691−7694. (e) Schmittel, M.; Keller, M.; Kiau, S.; Strittmatter, M. *Chem.−Eur. J.* **1997**, *3*, 807−816. (f) Schmittel, M.; Steffen, J.-P.; Maywald, M.; Engels, B.; Helten, H.; Musch, P. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1331−1339.

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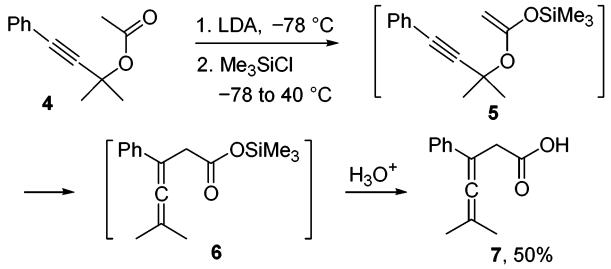
**SCHEME 2**



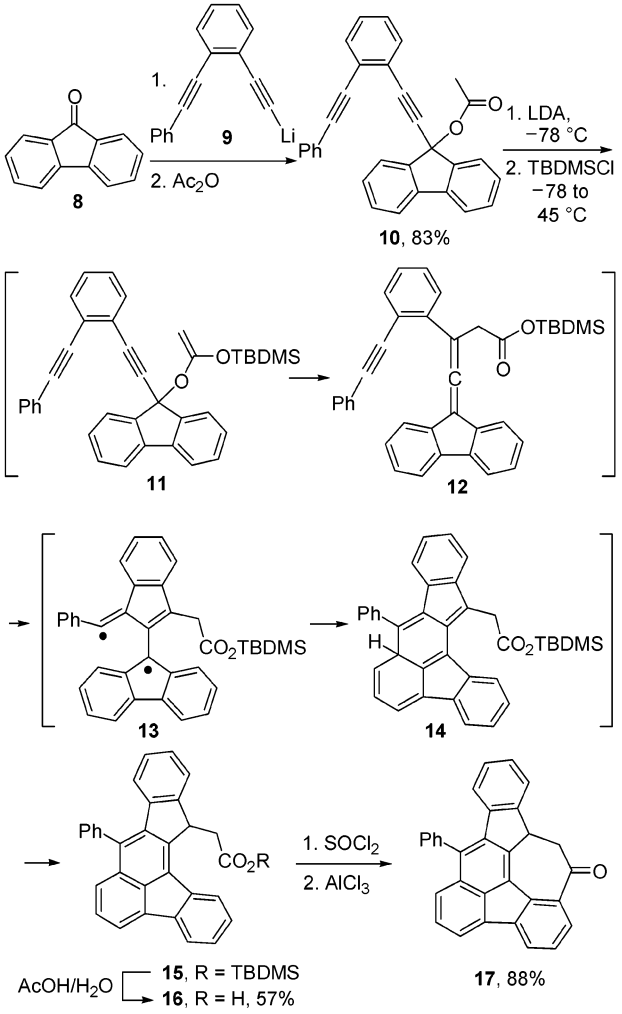

(LDA) followed by trapping the resulting enolate with trimethylsilyl chloride to form the silyl ketene acetal **5** at −78 °C (Scheme 2). When the reaction mixture warmed to 40 °C, the Ireland−Claisen rearrangement occurred to produce the silyl ester **6**, which after hydrolysis furnished the allenyl acetic acid **7** in 50% overall yield. However, this reaction sequence did not appear to have been adopted for the synthesis of enyne-allenes. The mildness of the reaction conditions and the ready availability of a variety of silyl ketene acetals make the transformation well suited for the preparation of thermally labile enyne-allenes and the benzannulated analogues. We now report our findings in using this synthetic strategy to produce in situ the benzannulated enyne-allenes for radical cyclizations leading to polycyclic aromatic compounds.

## Results and Discussion

Condensation between 9-fluorenone (**8**) and the lithium acetylide **9**[6] as reported previously furnished the corresponding alkoxide,[7] which was captured by acetic anhydride to afford the propargylic acetate **10** (Scheme 3). Treatment of **10** with LDA at −78 °C followed by trapping the resulting enolate with *tert*-butyldimethylsilyl chloride (TBDMSCl) then gave the silyl ketene acetal **11**.[8] A series of reactions then occurred upon warming the reaction mixture to 45 °C, including an Ireland−Claisen rearrangement to form the benzannulated enyne-allene **12** followed by a Schmittel cyclization to generate the benzofulvene biradical **13**. An intramolecular radical−radical coupling then produced the formal Diels−Alder adduct **14**, which in turn underwent a prototropic rearrangement to give the silyl ester **15** and, after hydrolysis, the carboxylic acid **16** in 57% overall yield from **10** in a single operation. The cascade transformation from **12** to **15** is reminiscent of what was observed previously in a chlorinated enyne-allene system derived from condensation between **8** and **9** to form the corresponding propargylic alcohol followed by treatment of the propargylic alcohol with thionyl chloride.[7]

The pendent carboxylic acid group in **16** also provided the opportunity for an intramolecular acylation reaction. Conversion of **16** to the corresponding acid chloride with thionyl chloride followed by an aluminum chloride promoted intramolecular acylation reaction then produced the polycyclic aromatic ketone **17** in 88% yield. The structure of **17** was established by X-ray structure analysis (see Supporting Information).

**SCHEME 3**




The diaryl ketone **18**,[9] readily obtained by oxidation of the corresponding hydrocarbon, 4*H*-cyclopenta[*def*]-phenanthrene,[10] was also selected for condensation with **9** leading to the propargylic acetate **21** in 81% yield (Table 1). The acetate **21** was converted to the carboxylic acid **24**[11] via the tandem sequence of Ireland−Claisen rearrangement and Schmittel cyclization. Similarly, the use of the diaryl ketone **19**[12a,b] and benzophenone (**20**) led to the carboxylic acids **25** and **26**, respectively. It is worth noting that the structures of **24** and **25** contain a benzo[*ghi*]fluoranthene unit and a dihydrobenzo[*ghi*]-fluoranthene unit, respectively. Several synthetic methods for benzo[*ghi*]fluoranthene and related derivatives

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(6) Li, H.; Petersen, J. L.; Wang, K. K. *J. Org. Chem.* **2001**, *66*, 7804−7810.
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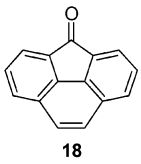
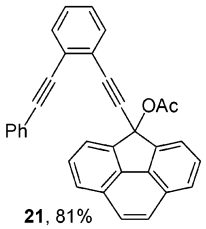
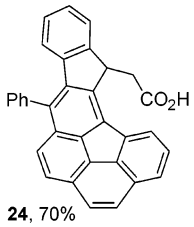
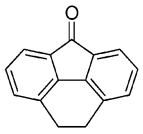
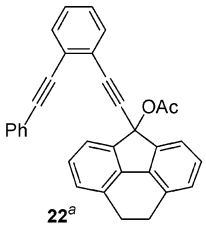
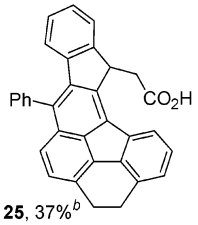
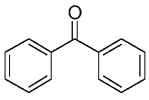
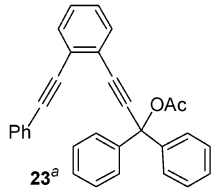
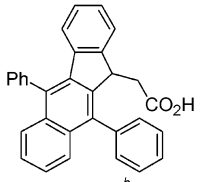
(9) (a) Harvey, R. G.; Abu-shqara, E.; Yang, C. *J. Org. Chem.* **1992**, *57*, 6313−6317. (b) Muzart, J. *Tetrahedron Lett.* **1987**, *28*, 2131−2132.
(10) (a) Yang, C. X.; Harvey, R. G. *Polycyclic Aromat. Compd.* **1992**, *2*, 229−233. (b) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons*; Wiley: New York, 1997; pp 336−337.
(11) The structure was established by X-ray structure analysis (see Supporting Information).
(12) (a) Yoshida, M.; Kadokura, A.; Minabe, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1179−1180. (b) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 1730−1745. (c) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 380−381.

**TABLE 1. Synthesis of Polycyclic Aromatic Carboxylic Acids from Diaryl Ketones**

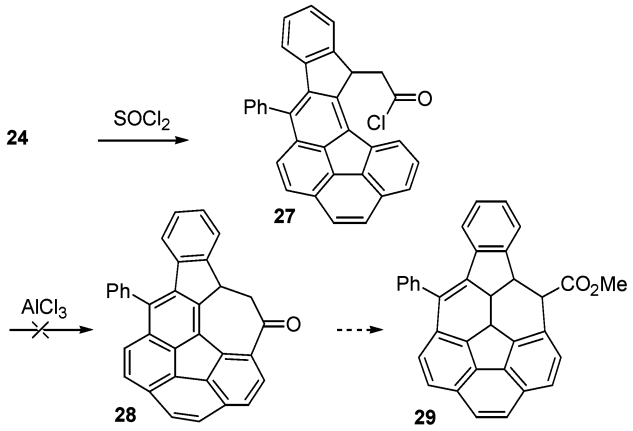
| diaryl ketone | propargylic acetate | carboxylic acid |
|---|---|---|
|  **18** |  **21**, 81% |  **24**, 70% |
|  **19** |  **22**[a] |  **25**, 37%[b] |
|  **20** |  **23**[a] |  **26**, 53%[b] |

[a] The crude product was used for the next step without isolation. [b] Overall yield from the diaryl ketone.

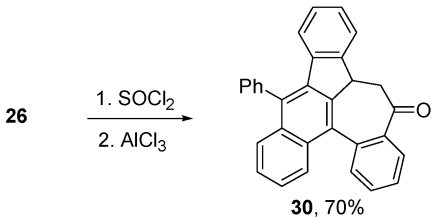
have been reported.[12b,c,13] One of these derivatives was used in the first synthesis of the bowl-shaped corannulene.[12b,c] Development of new synthetic methods for corannulene and related compounds has attracted renewed interest and considerable attention in recent years.[14]

The acid **24** was also readily converted to the acid chloride **27** with thionyl chloride (Scheme 4). However, attempts to promote the intramolecular acylation reaction of **27** using aluminum chloride as the catalyst to form **28** were unsuccessful. The $^1$H NMR spectrum of the crude

**SCHEME 4**




reaction mixture showed only very broad peaks in the aromatic region, indicating that intermolecular acylation occurred to give polymerized adducts. It was envisioned that **28** could serve as a precursor for ring contraction[15] to form **29** having an indeno-fused dihydrocorannulene moiety. The acid chloride of **25** was also used for the acylation reaction in the hope that the intermolecular reaction could be avoided. Unfortunately, such an attempt was also unsuccessful. Treatment of **25** with concentrated sulfuric acid at room temperature for 12 h resulted in the recovery of unreacted **25**. On the other hand, the aryl ketone **30**[11] was readily obtained from **26** in 70% yield (eq 1).




(1)

With the propargylic acetate **32**, derived from 2,2-dimethylpropiophenone (**31**), the 1*H*-cyclobut[*a*]indenyl acetic acid **35** was obtained as the predominant product along with ca. 1% of the 11*H*-benzo[*b*]fluorenyl acetic acid **36** (Scheme 5). Conceivably, the initially formed benzannulated enyne-allene **33** underwent a [2 + 2] cycloaddition reaction preferentially, perhaps also via the biradical **34**, to produce **35**. The low propensity for **34** to undergo the radical−radical coupling reaction involving a double bond of the phenyl substituent to produce the formal Diels−Alder adduct leading to **36** may be attributed to the emergence of the nonbonded steric interactions between the silyl ester group and the *tert*-butyl group depicted in **34** along the pathway toward **36**. Such a change of the reaction pathway was also observed previously in the chlorinated enyne-allene system.[7]

As in the case of the chlorinated enyne-allene system, the use of the ketone **37**[16] having the keto group incor-

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(15) (a) Nongrum, F. M.; Myrboh, B. *Synthesis* **1987**, 845−846. (b) Taylor, E. C.; Chiang, C.-S.; McKillop, A.; White, J. F. *J. Am. Chem. Soc.* **1976**, *98*, 6750−6752. (c) Wiberg, K. B.; Furtek, B. L.; Olli, L. K. *J. Am. Chem. Soc.* **1979**, *101*, 7675−7679.

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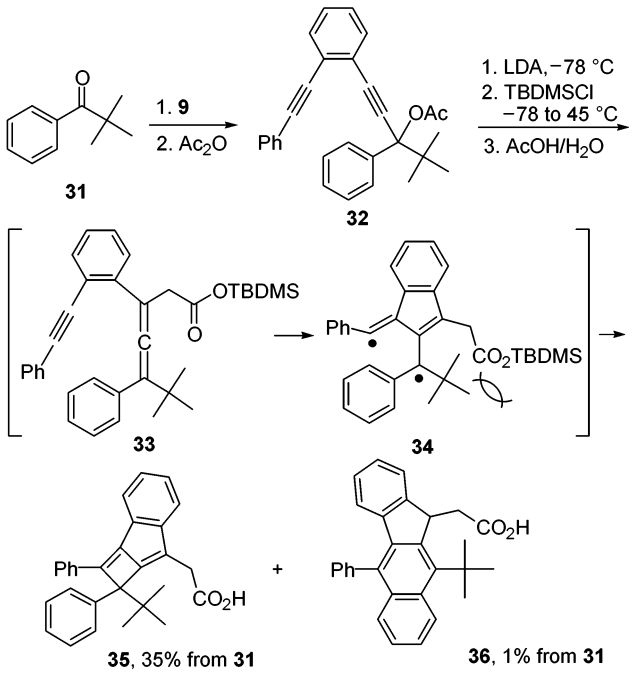
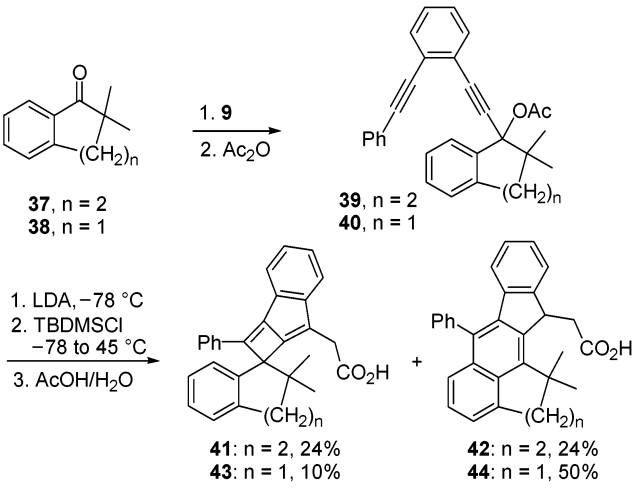
**SCHEME 5**




**SCHEME 6**




porated in the six-membered ring to prepare the propargylic acetate **39** for the cascade transformation appears to reduce the nonbonded steric interactions along the pathway leading to the Diels−Alder adduct (Scheme 6). As a result, the [2 + 2] cycloaddition adduct **41** and the Diels−Alder adduct **42** were produced in essentially equal amounts. In the case of **40**, prepared from **38**[17] having a five-membered ring, the effect was particularly dramatic and resulted in the formation of the Diels−Alder adduct **44** predominantly.

## Conclusions

The Ireland−Claisen rearrangement of the propargylic acetates was successfully adopted for the synthesis of the benzannulated enyne-allenes in situ for the subsequent Schmittel cyclization to generate benzofulvene biradicals for a cascade sequence of reactions. Several polycyclic aromatic derivatives of benzo[*ghi*]fluoranthene and 11*H*-benzo[*b*]fluorene were thus produced. In several cases, the [2 + 2] cycloaddition reaction of the benzannulated enyne-allenes also occurred, leading to the corresponding 1*H*-cyclobut[*a*]indenyl acetic acids.

## Experimental Section

**Propargylic Acetate 10.** The following procedure is representative for the preparation of the propargylic acetates. To a solution of 1.63 g (8.07 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne in 50 mL of diethyl ether under a nitrogen atmosphere at 0 °C was added 3.00 mL of a 2.5 M solution of *n*-butyllithium (7.50 mmol) in hexanes. The reaction mixture was then allowed to warm to room temperature. After 30 min at room temperature, a solution of 1.13 g (6.27 mmol) of 9-fluorenone (**8**) in 50 mL of diethyl ether was introduced dropwise via cannula. After an additional 2 h at room temperature, a solution of 0.78 g (7.64 mmol) of acetic anhydride in 50 mL of diethyl ether was introduced, and the reaction mixture was stirred for 4 h before 20 mL of water was added. The organic layer was separated, and the aqueous layer was back-extracted with diethyl ether. The combined organic extracts were washed with brine and water, dried over magnesium sulfate, and concentrated. A mixture of hexanes and diethyl ether (3:1, 10 mL) was added to the residue, and the solution was cooled to 0 °C. A solid precipitate appeared after ca. 15 min. The solid precipitate was collected by filtration and then washed with hexanes to furnish 2.20 g of **10** (5.19 mmol, 83%) as a light brown solid: mp 120−122 °C; IR 2219, 1749, 1229, 757 $cm^{-1}$; $^1H$ NMR $\delta$ 7.91 (2 H, d, $J$ = 7.7 Hz), 7.65 (2 H, d, $J$ = 7.7 Hz), 7.50 (2 H, tm, $J$ = 7.4, 2 Hz), 7.40 (2 H, td, $J$ = 7.4, 0.7 Hz), 7.35−7.20 (9 H, m), 2.02 (3 H, s); $^{13}C$ NMR $\delta$ 169.1, 144.1, 139.9, 132.5, 131.75, 131.70, 129.8, 128.41, 128.35, 128.25, 128.18, 127.8, 126.1, 126.0, 124.7, 123.1, 120.0, 93.2, 89.7, 87.8, 84.1, 79.6, 21.8; MS *m*/*z* 424 ($M^+$), 380, 366. HRMS: calcd for $C_{31}H_{20}O_2$, 424.1463; found, 424.1466.

**Carboxylic Acid 16.** The following procedure is representative for the preparation of the carboxylic acids. To a flask containing 1.60 mL of a 2.5 M solution of *n*-butyllithium (4.00 mmol) in hexanes under a nitrogen atmosphere at 0 °C were added 0.56 mL (4.00 mmol) of diisopropylamine and then 5 mL of THF. After 30 min at 0 °C, the reaction mixture was cooled to −78 °C. A solution of 0.85 g (2.00 mmol) of **10** in 15 mL of THF was introduced dropwise via cannula. After 30 min at −78 °C, 1 mL of HMPA and 4 mL of a 1.0 M solution of TBDMSCl (4.00 mmol) in THF were introduced. The reaction mixture was allowed to warm to room temperature slowly and then heated to 45 °C. After an additional 12 h at 45 °C, the reaction mixture was allowed to cool to room temperature and a mixture of 10 mL of acetic acid and 3.3 mL of water was introduced. After 12 h, 20 mL of diethyl ether was added and the organic layer was separated. The aqueous layer was back-extracted with diethyl ether. The combined organic layers were washed with water (5 × 30 mL), dried over magnesium sulfate, and concentrated. Flash column chromatography (silica gel/25% acetone in hexanes) provided 0.487 g of **16** (1.15 mmol, 57%) as a yellow solid: mp 258−260 °C; IR 3500−2600 (br), 1708, 756 $cm^{-1}$; $^1H$ NMR $\delta$ 8.05 (1 H, d, $J$ = 7.7 Hz), 8.02 (1 H, d, $J$ = 7.7 Hz), 7.97 (1 H, d, $J$ = 6.2 Hz), 7.68 (1 H, d, $J$ = 7.7 Hz), 7.64−7.44 (9 H, m), 7.29 (1 H, t, $J$ = 6.9 Hz), 7.10 (1 H, t, $J$ = 7.4 Hz), 6.67 (1 H, d, $J$ = 7.7 Hz), 5.18 (1 H, dd, $J$ = 10.5, 1.4 Hz), 3.76 (1 H, dd, $J$ = 16.6, 2.2 Hz), 2.55 (1 H, dd, $J$ = 16.6, 10.9 Hz); $^{13}C$ NMR $\delta$ 177.5, 147.3, 141.6, 140.3, 140.2, 138.6, 137.83, 137.80, 136.4, 134.2, 131.8, 130.8, 130.2, 128.83, 128.75, 128.0, 127.80, 127.77, 127.58, 127.51, 125.9, 124.6, 123.9, 123.7, 121.8, 119.8, 41.9, 38.5; MS *m*/*z* 424 ($M^+$), 378, 365. HRMS: calcd for $C_{31}H_{20}O_2$, 424.1463; found, 424.1466.

**Ketone 17.** The following procedure is representative for the intramolecular acylation reaction. To a flask containing 0.25 g (0.59 mmol) of **16** under a nitrogen atmosphere was

(17) Lemmen, P.; Lenoir, D. *Chem. Ber.* **1984**, *117*, 2300−2313.

added 5.0 mL (68.5 mmol) of thionyl chloride. After 3 h at room temperature, the excess thionyl chloride was removed in vacuo to yield the crude acid chloride (IR 1794 $cm^{-1}$) as a brown-yellow oil. To the solution of the crude acid chloride in 130 mL of methylene chloride at 0 °C was added 0.21 g (1.57 mmol) of anhydrous aluminum chloride. The reaction mixture was allowed to warm to room temperature slowly. After 12 h, 10 mL of a 2 M solution of hydrochloric acid was added and the organic layer was separated. The aqueous layer was back-extracted with methylene chloride. The combined organic layers were washed with saturated aqueous sodium bicarbonate (3 × 50 mL) and water, dried over magnesium sulfate, and concentrated. Flash column chromatography (silica gel/50% methylene chloride in hexanes) furnished 0.21 g of **17** (0.52 mmol, 88%) as orange crystals: mp 323−325 °C; IR 1662, 774, 708 $cm^{-1}$; $^1$H NMR $\delta$ 8.08 (1 H, d, $J$ = 7.4 Hz), 7.97 (1 H, dd, $J$ = 7.7, 1.5 Hz), 7.94 (1 H, d, $J$ = 7.7 Hz), 7.63−7.43 (9 H, m), 7.33 (1 H, t, $J$ = 7.2 Hz), 7.14 (1 H, t, $J$ = 7.7 Hz), 6.85 (1 H, d, $J$ = 7.7 Hz), 4.51 (1 H, d, $J$ = 13.6 Hz), 3.64 (1 H, dd, $J$ = 12.9, 2.5 Hz), 3.24 (1 H, dd, $J$ = 13.6, 12.9 Hz); $^{13}$C NMR $\delta$ 199.2, 145.9, 144.0, 141.6, 139.9, 137.9, 137.2, 135.9, 134.7, 133.4, 130.7, 130.4, 130.1, 129.9, 128.9, 128.8, 128.7, 128.1, 128.0, 127.8, 127.6, 127.5, 126.9, 126.4, 126.1, 124.4, 123.8, 121.3, 44.4, 41.8; MS $m/z$ 406 ($M^+$), 389, 378. HRMS: calcd for $C_{31}H_{18}O$, 406.1358; found, 406.1347. Recrystallization of **17** from $CH_2Cl_2$/2-propanol produced a crystal suitable for X-ray structure analysis (see Supporting Information).

**Carboxylic Acids 35 and 36.** To a solution of 0.227 g (1.12 mmol) of 1-(2-ethynylphenyl)-2-phenylethyne in 20 mL of diethyl ether under a nitrogen atmosphere at 0 °C was added 0.44 mL of a 2.5 M solution of *n*-butyllithium (1.10 mmol) in hexanes. The reaction mixture was then allowed to warm to room temperature. After 30 min at room temperature, a solution of 0.162 g (1.00 mmol) of **31** in 20 mL of diethyl ether was introduced slowly via cannula. After an additional 2 h at room temperature, a solution of 0.112 g (1.10 mmol) of acetic anhydride in 10 mL of diethyl ether was introduced. After an additional 4 h, 20 mL of water was introduced. The organic layer was separated, and the aqueous layer was back-extracted with diethyl ether. The combined organic extracts were washed with brine and water, dried over magnesium sulfate, and concentrated in vacuo. The crude propargylic acetate **32** was used for the next step without further purification.

To a flask containing 0.80 mL of a 2.5 M solution of *n*-butyllithium (2.00 mmol) in hexanes under a nitrogen atmosphere at 0 °C were added 0.28 mL (2.00 mmol) of diisopropylamine and then 2 mL of THF. After 30 min at 0 °C, the reaction mixture was cooled to −78 °C. A solution of the crude propargylic acetate **32** in 15 mL of THF was introduced slowly via cannula. After 30 min at −78 °C, 1.2 mL of HMPA and 2.0 mL of a 1.0 M solution of TBDMSCl (2.0 mmol) in THF were introduced. The reaction mixture was allowed to warm to room temperature slowly and then heated at 45 °C. After an additional 12 h at 45 °C, the reaction mixture was allowed to cool to room temperature. A mixture of 7 mL of acetic acid and 3 mL of water was introduced. After 12 h, 20 mL of diethyl ether was introduced, and the organic layer was separated. The aqueous layer was back-extracted with diethyl ether. The combined organic layers were washed with water (5 × 30 mL), dried over magnesium sulfate, and concentrated. Flash column chromatography (silica gel/25% acetone in hexanes) provided 0.142 g of **35** (0.35 mmol, 35% from **31**) as an orange solid: mp 204−206 °C; IR 3500−2600 (br), 1707, 751, 693 $cm^{-1}$; $^1$H NMR $\delta$ 7.96 (2 H, d, $J$ = 7.2 Hz), 7.67 (1 H, d, $J$ = 7.4 Hz), 7.55−7.10 (11 H, m), 3.85 (2 H, s), 1.22 (9 H, s); $^{13}$C NMR $\delta$ 176.5, 153.7, 151.7, 148.4, 147.5, 142.8, 135.5, 129.3, 129.2, 129.0, 128.9, 128.8, 128.6, 127.6, 126.2, 124.0, 123.6, 120.1, 114.8, 77.2, 36.8, 33.2, 29.0; MS $m/z$ 406 ($M^+$), 360, 349. HRMS: calcd for $C_{29}H_{26}O_2$, 406.1933; found, 406.1915. The formation of **36** was detected in the crude reaction products with $^1$H NMR signals (partial) at $\delta$ 8.57 (1 H, d, $J$ = 8.9 Hz), 6.96 (1 H, t, $J$ = 6.7 Hz), 6.23 (1 H, d, $J$ = 7.7 Hz), 5.41 (1 H, d, $J$ = 11 Hz), 3.23 (1 H, d, $J$ = 16 Hz), 2.30 (1 H, dd, $J$ = 16, 11 Hz).

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**Supporting Information Available:** Experimental procedures and spectroscopic data for **21**, **22**, **24**−**26**, **30**, and **41**−**44**;$^1$H and $^{13}$C NMR spectra of compounds **10**, **16**, **17**, **21**, **22**, **24**−**26**, **30**, **35**, and **41**−**44**; and ORTEP drawings and tables of crystallographic data for the X-ray diffraction analysis of **17**, **24**, and **30** in PDF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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