Palladium-Catalyzed Annulation of Internal Alkynes by Arene-Containing Vinylic Iodides and Triflates

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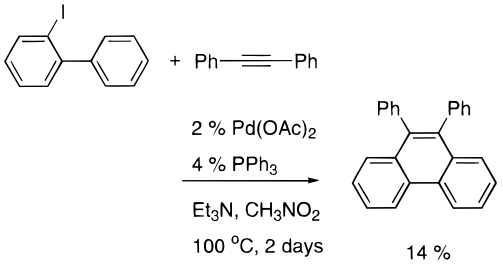
In the presence of a palladium catalyst, internal alkynes undergo carboannulation by cyclic and acyclic vinylic iodides and triflates bearing a neighboring aromatic ring to produce a variety of carbocycles. For example, a number of 9,10-disubstituted-1,2,3,4-tetrahydrophenanthrenes have been prepared in good yields through the palladium-catalyzed annulation of internal alkynes by 2-phenyl-1-cyclohexenyl triflate (**1**) or 1-iodo-2-phenylcyclohexene (**2**). This annulation process is fairly general and highly regioselective. The process appears to involve oxidative addition of the vinylic substrate to Pd(0) to produce a vinylic palladium intermediate, which adds the carbon moiety to the less hindered end and the palladium to the more hindered end of the alkyne, followed by intramolecular ring closure onto the neighboring aryl group. The scope and limitations of this methodology are discussed.

Introduction

The transition-metal mediated annulation of alkynes has proven useful for the synthesis of a variety of hetero- and carbocyclic ring systems.[1] Methodology based on palladium is of special value, since the palladium complexes are readily available, generally not oxygen or moisture sensitive, and accommodate a number of different functional groups.[2]

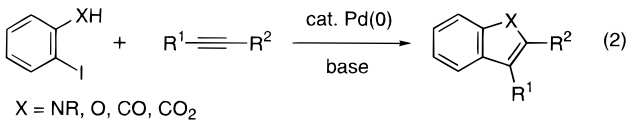
Heck first reported the synthesis of 9,10-diphenylphenanthrene from 2-iodobiphenyl and diphenylacetylene by a palladium-catalyzed annulation process; however, the yield was only 14% (eq 1).[3] We have recently optimized reaction conditions and extended this process to a wide variety of iodobiaryls and internal alkynes.[4] Merlic and McInnes simultaneously demonstrated that substituted indolocarbazoles can be formed by this same palladium-catalyzed cross-coupling of biindolyl iodides and internal alkynes.[5]



(1)

Polycyclic aromatic hydrocarbons have also been prepared by other palladium-catalyzed processes involving aryl halides and alkynes. For example, the synthesis of 9,10-disubstituted phenanthrenes has been achieved by the coupling of simple aryl iodides and diarylacetylenes.[6] Grigg has synthesized polycyclic aromatics by the intramolecular coupling of aryl halides bearing alkyne units.[7]

Recently, convenient palladium−alkyne annulation methodology has been developed in this group, which offers useful routes to indoles,[8] indenones,[9] benzofurans and isocoumarins (eq 2).[10]



(2)

All of this previous methodology utilizes aryl iodides to annulate internal alkynes to give the desired products. This methodology would be still more useful if it could be expanded to vinylic iodides and triflates.[11] In this paper, we report the regioselective annulation of internal alkynes by cyclic and acyclic vinylic iodides and triflates bearing neighboring aryl groups, which leads to the synthesis of derivatives of 1,2,3,4-tetrahydrophenanthrene,[12] 7*H*-benzo[*c*]fluoren-7-one,[13] 7*H*-benzo[*c*]xanthen-7-one,[14] and naphthalene.[15]

(1) (a) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (b) Ojima, I.; Tzamarioudaki, M.;Li, Z.; Donovan, R. T. *Chem. Rev.* **1996**, *96*, 635.
(2) (a) Pfeffer, M. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 567. (b) Pfeffer, M.; Spencer, J.; Decian, A.; Fisher, J. *J. Org. Chem.* **1995**, *60*, 1005.
(3) Wu, G.; Rheingold, A. L.; Geib, S. J.; Heck, R. F. *Organometallics* **1987**, *6*, 1941.
(4) (a) Larock, R. C.; Doty, M. J.; Tian, Q.; Zenner, J. M. *J. Org. Chem.* **1997**, *62*, 2, 7536. (b) Larock, R. C.; Zenner, J. M. Full paper to be published.
(5) Merlic, C. A.; McInnes, D. M. *Tetrahedron Lett.* **1997**, *38*, 7661.
(6) Dyker, G.; Kellner, A. *Tetrahedron Lett.* **1994**, *35*, 7633.
(7) (a) Grigg, R.; Loganathan, V.; Sridharan, V. *Tetrahedron Lett.* **1996**, *37*, 3399. (b) Brown, D.; Grigg, R.; Sridharan, V.; Tambyrajah, V. *Tetrahedron Lett.* **1995**, *36*, 8137. (c) Grigg, R.; Kennewell, P.; Teasdale, A.; Sridharan, V. *Tetrahedron Lett.* **1993**, *34*, 153.
(8) Larock, R. C.; Yum, E. K. *J. Am. Chem. Soc.* **1991**, *113*, 6689.
(9) Larock, R. C.; Doty, M. J.; Cacchi, S. *J. Org. Chem.* **1993**, *58*, 4579.
(10) Larock, R. C.; Yum, E. K.; Doty, M. J.; Sham, K. K. C. *J. Org. Chem.* **1995**, *60*, 3270.
(11) For a preliminary communication, see ref 4a.
(12) (a) Song, C.; Hanaoka, K.; Ono, T.; Nomura, M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3788. (b) Morin, F. G.; Horton, W. J.; Grant, D. M.; Pugmire, R. J.; Dalling, D. K. *J. Org. Chem.* **1985**, *50*, 3380.
(13) (a) Fu, J.; Zhao, B.; Sharp, M. J.; Snieckus, V. *J. Org. Chem.* **1991**, *56*, 1683. (b) Streitwieser, A., Jr.; Brown, S. M. *J. Org. Chem.* **1988**, *53*, 904.
(14) Kamat, S. P.; Paknikar, S. K. *Ind. J. Chem., Sec. B* **1988**, *27B*, 773.

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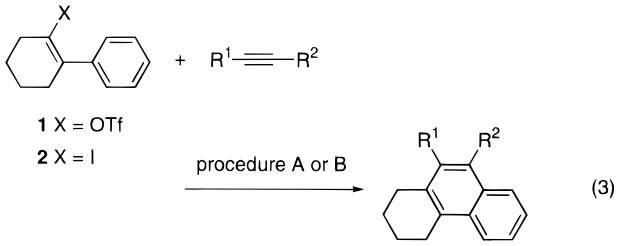
Results and Discussion

We initiated our studies on vinylic systems by employing compound **1** as the starting material (eq 3, X = OTf). Two procedures have been developed for the annulation



(3)

of internal alkynes by this triflate: procedure A, 5 mol % $Pd(OAc)_2$, 2 equiv of NaOAc, 3 equiv of n-Bu_4NCl in DMF at 100 °C; and procedure B, 5 mol % $Pd(OAc)_2$, 2 equiv of NaOAc, 1 equiv of LiCl in DMF at 100 °C. An excess of the alkyne (2 equiv) has generally been employed. Our results are summarized in Table 1.

The triflate annulation process works best for alkynes containing hindered groups, such as phenyl, *tert*-butyl, and trialkylsilyl groups. Without these hindered groups, alkynes such as 1-phenyl-1-propyne, 1-phenyl-1-butyne, and 4-octyne gave inseparable mixtures containing several products. It was also noticed that alkynes bearing an electron-withdrawing group directly on the triple bond afforded poor results. For example, ethyl phenylpropiolate did not give the desired product.

The annulation of unsymmetrical alkynes has proven to be highly regioselective in most cases, providing only the regioisomers shown in Table 1. The regiochemistry has been assigned based on all of our previous work on these types of alkyne annulations in which the aryl or vinylic group has always added to the less hindered end of the alkyne.[8−10] The regiochemistry of the product shown in entry 4 of Table 1 has been confirmed by 2D NOESY.[16] The 2D NOESY spectrum of 9-*tert*-butyl-10-phenyl-1,2,3,4-tetrahydrophenanthrene (Figure 1 and entry 4, Table 1) showed a cross-peak between H-15 and H-8 and a cross-peak between H-15 and H-12, but none between H-15 and H-1. 2D NOESY cross-peaks were also observed between H-4 and H-5, and between H-1 and H-12. These 2D NOESY cross-peaks are totally consistent with the structure shown in Figure 1. The regiochemistry of this process thus follows the pattern established in our previous research in which the organic moiety of the organopalladium intermediate (see the later mechanistic discussion) adds to the less hindered end of the alkyne and the palladium moiety to the more hindered end.[8−10]

The silyl-substituted products produced by this process (entries 11−15, Table 1) have special synthetic value, since the silyl group can be easily converted to other functional groups.[17] It was noticed, however, that reactions of alkynes with trialkylsilyl groups did not offer particularly high yields. This may be due to desilylation of the starting alkyne or the product during the reaction. Fortunately, the yield can be improved by simply increasing the steric bulk of the silyl group. For example, 1-phenyl-2-(triethylsilyl)acetylene (entries 11 and 12, Table 1) afforded a significantly better yield than 1-phenyl-2-(trimethylsilyl)acetylene (entries 13−15, Table 1).

Compound **2**, the iodide corresponding to triflate **1**, has also been employed in this annulation process in order to compare the results using an iodide and a triflate under similar reaction conditions (eq 3, X = I). It was found that vinylic iodide **2** provided very similar yields and mixtures of regioisomers to compound **1**. Thus, cyclic vinylic iodides appear to be as reactive and versatile as cyclic vinylic triflates in the annulation process.

The yield for the annulation of 1-phenyl-2-(trimethylsilyl)acetylene (entries 13 and 14, Table 1) by **2** was improved by replacing n-Bu_4NCl (3 equiv) with LiCl (1 equiv). It may be that the ammonium salt facilitates desilylation, but note that less LiCl was necessary to get comparable yields.

This annulation reaction appears to proceed by the following mechanism: (1) reduction of $Pd(OAc)_2$ to the actual catalyst Pd(0), (2) oxidative addition of the vinylic triflate or iodide to Pd(0) to produce a vinylic palladium intermediate, (3) vinylpalladium coordination to the alkyne and subsequent insertion to form a new vinylpalladium intermediate, (4) either oxidative addition of the resulting vinylpalladium intermediate to the neighboring aryl C−H bond to form a palladium(IV) intermediate[18] (path 1) and subsequent HX (X = OTf or I) elimination by base, or electrophilic palladation[19] of the arene (path 2), and finally (5) reductive elimination of the product with concomitant regeneration of the Pd(0) catalyst (Scheme 1). All steps are well precedented in organopalladium chemistry.

To determine the scope and limitations of this process, this annulation methodology has been applied to a number of other interesting vinylic iodides and triflates. The reaction of 2-iodo-3-phenylcyclohex-2-enone (**3**) afforded 3-hydroxybiphenyl in high yield, regardless of the alkyne used (entries 18 and 19, Table 1). No annulation products were observed. However, the reaction of diphenylacetylene and 2-iodo-3-phenylcyclohex-2-enol, obtained by the reduction of **3**, afforded the desired annulation product, 1-hydroxy-9,10-diphenyl-1,2,3,4-tetrahydrophenanthrene, in 51% yield (entry 20, Table 1).

As shown in entry 21 of Table 1, 5,6-diphenyl-7*H*-benzo[*c*]fluoren-7-one was obtained in 54% yield from the reaction of 2-iodo-3-phenylindenone and diphenylacetylene. On the other hand, the reaction of 3-iodoflavone and diphenylacetylene afforded the desired product, 5,6-diphenyl-7*H*-benzo[*c*]xanthen-7-one, in only 25% yield. The major product was in fact 3-benzoyl-2-(2-hydroxyphenyl)-4,5-diphenylfuran isolated in 61% yield. This product apparently arises by alkyne insertion and subsequent electrophilic attack of the vinylpalladium intermediate on the carbonyl oxygen, followed by opening of the pyrone ring. Conjugation from the oxygen of the

(15) (a) Donaldson, N. *The Chemistry and Technology of Naphthalene Compounds*; Edward Arnold Ltd.: London, 1958. (b) Amer, I.; Blume, J.; Vollhardt, K. P. C. *J. Mol. Catal.* **1990**, *60*, 323.

(16) Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546.

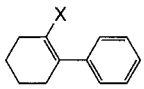
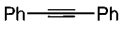
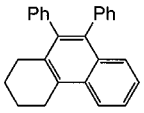
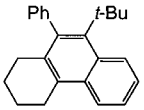
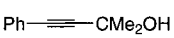
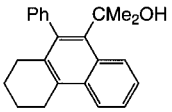
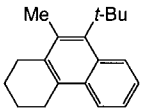
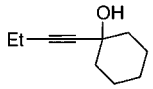
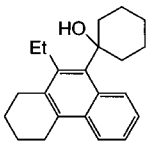
(17) (a) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. (b) Patai, S.; Rappoport, Z. *The Chemistry of Organic Silicon Compounds*; John Wiley & Sons: New York, 1989.

(18) (a) González, J. J.; García, N.; Gómez-Lor, B.; Echavarren, A. M. *J. Org. Chem.* **1997**, *62*, 1286. (b) Pogodin, S.; Biedermann, P. U.; Agranat, I. *J. Org. Chem.* **1997**, *62*, 2285. (c) Rice, J. E.; Cai, Z.-W. *J. Org. Chem.* **1993**, *58*, 1415. (d) Dyker, G. Chem. Ber./Recueil **1997**, *130*, 1567.

(19) (a) Ames, D. E.; Bull, D. *Tetrahedron* **1982**, *38*, 383. (b) Catellani, M.; Chiusoli, G. P. *J. Organomet. Chem.* **1992**, *425*, 151.

(20) Doty, M. J. Ph.D. Dissertation, Iowa State University, 1995.

Table 1. Palladium-catalyzed Annulation of Internal Alkynes by Arene-containing Vinylic Iodides and Triflates

entry	iodide/ triflate	alkyne	product(s)	procedure,[a] rxn time	isolated % yield
1				X = I, A, 10 h	86
2				X = OTf, A, 6 h	78
3				X = I, A, 10 h	73
4				X = OTf, A, 10 h	81
5				X = I, A, 7 h	71
6				X = OTf, A, 7 h	67
7				X = I, A, 24 h	54
8				X = OTf, A, 24 h	53
9				X = I, A, 72 h	54
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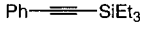
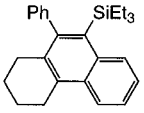
11				X = I, A, 10 h	55
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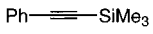
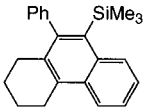
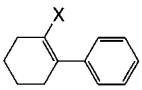
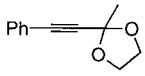
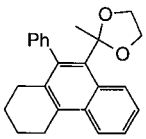
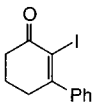
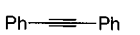
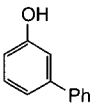
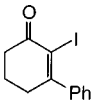
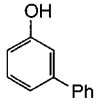
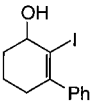
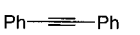
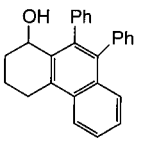
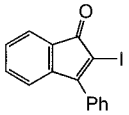
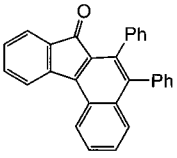
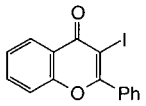
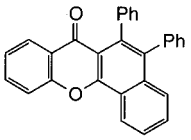
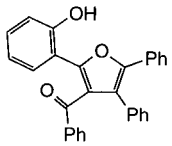
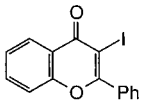
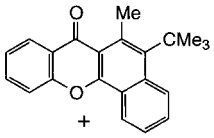
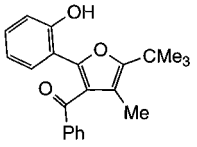
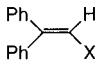
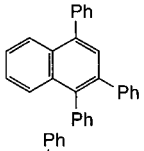
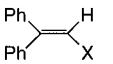
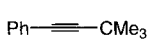
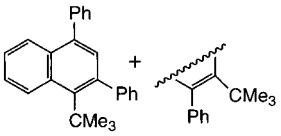
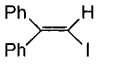
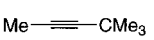
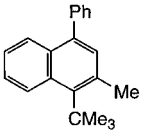
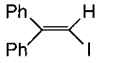
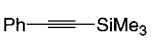
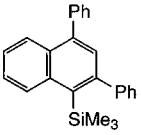
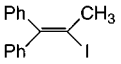
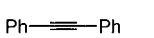
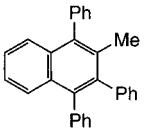
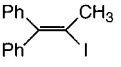
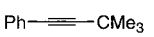
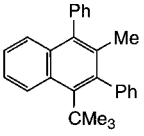
13				X = I, A, 10 h	33
14				B, 10 h	44
15				X = OTf, A, 10 h	35
16				X = I, A, 48 h	51
17				X = OTf, A, 48 h	52
18				B, 24 h	89
19				B, 24 h	83
20				B, 72 h	51
21				B, 48 h	54

Table 1 (Continued)

entry	iodide/ triflate	alkyne	product(s)	procedure,[a] rxn time	isolated % yield
22			 + 	B, 72 h	25 61
23			 + 	B, 72 h	10 69
24 25				X = I, B, 48 h X = OTf, A, 22h,	49 36
26 27				X = I, B, 48 h X = OTf, A, 22h,	62 (3:1) 45 (2:1)
28				B, 120 h	52
29				B, 26 h	19
30				B, 148 h	65
31				B, 48 h	46

[a] See the text for these procedures.

flavone ring is expected to enhance the nucleophilicity of the carbonyl oxygen. A similar furan-containing product was obtained from 4,4-dimethyl-2-pentyne (entry 23, Table 1).

Acyclic vinylic iodides and triflates have also been examined as annulating agents. No annulation products were obtained from (*Z*)-1-iodo-2-phenylethylene, perhaps due to β-hydrogen elimination from the vinylic palladium intermediate. On the other hand, 2-iodo-1,1-diphenylethylene, which has no β-hydrogen, afforded the expected products (entries 24, 26, 28, and 29, Table 1). Although the regioselectivity for 4,4-dimethyl-2-pentyne was quite good, a mixture of regioisomers was obtained when 3,3-dimethyl-1-phenyl-1-butyne was employed (compare entries 26 and 28). For 2-iodo-1,1-diphenylethylene, the group in the α-position of the vinylic palladium is

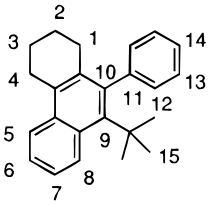


Figure 1. The structure of 9-*tert*-butyl-10-phenyl-1,2,3,4-tetrahydrophenanthrene.

hydrogen, which may be too small to control the regioselectivity of the addition of the vinylic palladium intermediate to the internal alkyne. Thus, it was expected that the regioselectivity might be improved were the size of the α-group to be increased. This was confirmed by experiment. Only one regioisomer was obtained from the reaction of 3,3-dimethyl-1-phenyl-1-butyne and 2-iodo-1,1-diphenylpropene, which has a larger α-substituent (CH_3) (entry 31, Table 1).

Acyclic iodides and triflates (entries 24−31, Table 1), which are generally not as reactive as cyclic vinylic iodides and triflates, required longer reaction times and generally afforded lower yields. While the acyclic triflates appear to be more reactive than the corresponding iodides, the yields of the annulation products are lower and different procedures have been employed (compare entries 24 and 25, and 26 and 27, Table 1). This is in contrast to the situation for the cyclic systems, where cyclic triflates afforded the same yields as the corresponding iodides under identical reaction conditions.

Conclusion

The palladium-catalyzed annulation of internal alkynes by arene-containing vinylic iodides and triflates has been achieved. The generality of this process has been demonstrated by the use of a variety of cyclic and acyclic iodides and triflates, and internal alkynes. This generality, combined with the high regioselectivity, make this annulation process an attractive synthetic route to a range of polycyclic aromatic hydrocarbons.

Experimental Section

General. All ^1H and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz, respectively. 2D COSY and NOESY NMR spectra were recorded at 400 MHz. Thin-layer chromatography (TLC) was performed using commercially prepared 60 mesh silica gel plates (Whatman K6F), and visualization was effected with short wavelength UV light (254 nm), or basic $KMnO_4$ solution (3 g $KMnO_4$ + 20 g K_2CO_3 + 5 mL NaOH (5%) + 300 mL H_2O).

Reagents. All reagents were used directly as obtained commercially unless otherwise noted. Anhydrous forms of NaOAc, LiCl, DMF, CH_2Cl_2, hexanes, and ethyl acetate were purchased from Fisher-Scientific. $Pd(OAc)_2$ was donated by Johnson Mathey, Inc. and Kawaken Fine Chemicals Co., Ltd. Diphenylacetylene, 1-phenyl-2-(trimethylsilyl)acetylene, and *N*-phenyltrifluoromethanesulfonimide were obtained from Aldrich Chemical Co., Inc. 4-Phenyl-2-methyl-3-butyn-2-ol and 1-(1-butynyl)cyclohexanol were purchased from Farchan Scientific Co. 4,4-Dimethyl-2-pentyne was purchased from Lancaster Synthesis Inc. 3,3-Dimethyl-1-phenyl-1-butyne,[9] 1-phenyl-2-(triethylsilyl)acetylene,[20] and 2-(2-phenylethynyl)-2-methyl-1,3-dioxolane,[21] (*Z*)-1-iodo-2-phenylethylene,[22] 2-iodo-1,1-diphenylethylene,[23] and 3-iodoflavone[24] were prepared according to previous literature procedures. The following starting materials were prepared.

2-Phenyl-1-cyclohexenyl Triflate. 2-Phenyl-1-cyclohexenyl triflate was prepared according to a literature procedure.[25] To a suspension of NaH (60% in mineral oil, 0.92 g, 22.9 mmol) in 30 mL of DMF at room temperature was added dropwise 2-phenylcyclohexanone (2.0 g, 12 mmol) in 10 mL of DMF. After stirring for 2 h under N_2, *N*-phenyltrifluoromethanesulfonimide (4.97 g, 13.8 mmol) was added in one portion and the mixture was stirred overnight, diluted with ether, washed with satd NH_4Cl, water, and brine, dried ($MgSO_4$), and concentrated. Chromatography (200:1 hexanes/ethyl acetate) gave a colorless liquid (2.18 g, 60%): ^1H NMR ($CDCl_3$) δ 1.80 (m, 2 H), 1.88 (m, 2 H), 2.50 (m, 4 H), 7.25−7.38 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 22.1, 23.0, 28.1, 31.3, 118.0, 127.9, 128.1, 128.3, 131.1, 136.9, 143.8; IR (CH_2Cl_2) 3026, 2942, 1414, 1207 (S=O) cm^{-1}; HRMS *m/z* 306.0543 (calcd for $C_{13}H_{13}F_3O_3S$, 306.0538).

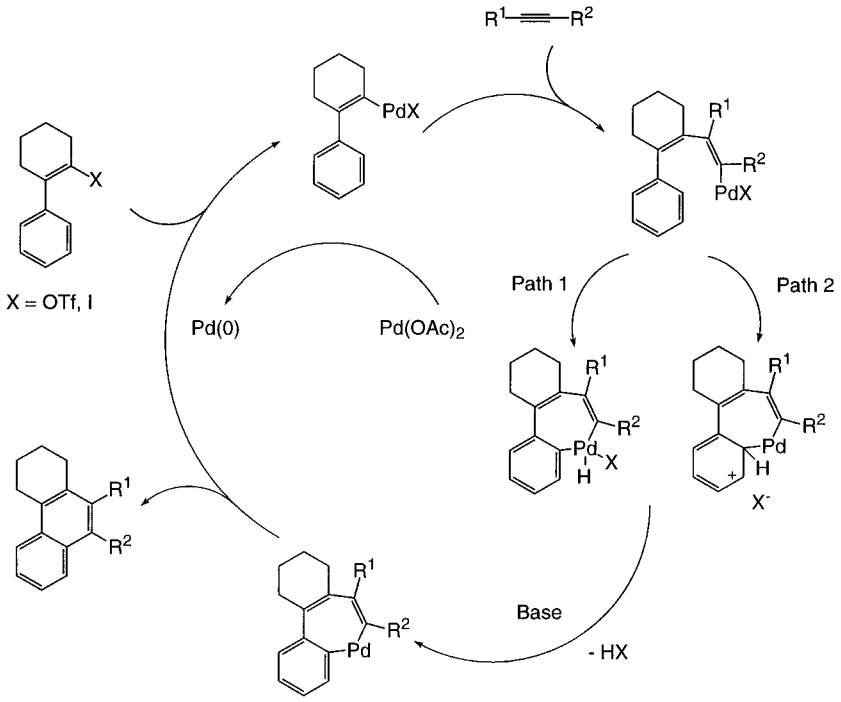
1-Iodo-2-phenylcyclohexene. 1-Iodo-2-phenylcyclohexene was prepared according to a literature procedure.[26] 2-Phenyl-1-cyclohexenyl triflate (1.0 g, 3.3 mmol), MgI_2 (2.7 g, 9.8 mmol), and Et_3N (0.4 g, 3.9 mmol) were placed in 40 mL of cyclohexane. The solution was refluxed at 95 °C for 20 h. After the reaction mixture was allowed to cool, it was diluted with ether, washed with satd $NaHSO_3$ and water, dried ($MgSO_4$), filtered, and concentrated. Chromatography (hexanes) gave a colorless oil (0.71 g, 77%): ^1H NMR ($CDCl_3$) δ 1.75 (m, 2 H), 1.86 (m, 2 H), 2.44 (m, 2 H), 2.79 (m, 2 H), 7.15 (m, 2 H), 7.33 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 22.9, 25.5, 34.0, 41.5, 98.7, 127.0, 127.8, 128.2, 144.2, 146.9; IR (CH_2Cl_2) 3019, 2931, 1498 cm^{-1}; HRMS *m/z* 284.0062 (calcd for $C_{12}H_{13}I$, 284.0062).

2-Iodo-3-phenylcyclohex-2-enone. 2-Iodo-phenylcyclohex-2-enone was prepared according to a literature procedure.[27] To a solution of 3-phenylcyclohex-2-enone[28] (2.0 g, 11.6 mmol) in CH_2Cl_2 (20 mL) was added trimethylsilyl azide (3.8 mL, 28.8 mmol) at 0 °C. After the mixture was stirred at 0 °C for 2 h, a solution of I_2 (11.8 g, 46.4 mmol) in CH_2Cl_2 (30 mL) and pyridine (30 mL) was added slowly at 0 °C. The mixture was allowed to warm to room temperature and stirred for 4 days. The resulting mixture was then diluted with diethyl ether (250 mL). The organic layer was washed with water (200 mL), HCl (10%, 200 mL), satd $NaHCO_3$ (200 mL), $Na_2S_2O_3$ (10%, 200 mL) and brine, and dried ($MgSO_4$). Filtration, concentration, and recrystallization from ethanol gave a light orange solid (1.2 g, 3.9 mmol, 33%): mp 129−131 °C (ethanol); ^1H NMR ($CDCl_3$) δ 2.14 (quintet, J = 6.0 Hz, 2 H), 2.73 (t, J = 6.0 Hz, 2 H), 2.80 (t, J = 6.0 Hz, 2 H), 7.24 (m, 2 H), 7.41 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 27.3, 40.0, 41.0, 111.4, 131.1, 133.0, 133.3, 148.8, 172.2, 197.3; IR (CH_2Cl_2) 3054, 2960, 1674 (C=O) cm^{-1}; HRMS *m/z* 297.9859 (calcd for $C_{12}H_{11}IO$, 297.9855).

2-Iodo-3-phenylcyclohex-2-enol. 2-Iodo-3-phenylcyclohexenol was prepared according to a literature procedure.[29] To a solution of 2-iodo-3-phenylcyclohex-2-enone (0.2 g, 0.67 mmol) and $CeCl_3 \cdot 7H_2O$ (0.26 g, 0.68 mmol) in MeOH (5 mL) was added $NaBH_4$ (0.026 g, 0.69 mmol) in one portion with stirring under Ar. After 10 min, gas evolution ceased and the reaction was quenched with satd NH_4Cl, followed by 5% HCl, extracted with Et_2O, dried over $MgSO_4$, filtered, concentrated, and purified by chromatography (5:1 hexanes/ethyl acetate). A white solid (0.19 g, 0.63 mmol, 95%) was obtained: mp 74−75 °C (CH_2Cl_2/MeOH); ^1H NMR ($CDCl_3$) δ 1.82 (m, 1 H), 1.98 (m, 3 H), 2.27 (d, J = 4.2 Hz, 1 H), 2.45 (m, 2 H), 4.45 (m, 1

(20) Zenner, J. M. Ph.D. Dissertation, Iowa State University, 1996.
(22) Dieck, H. A.; Heck, R. F. *J. Org. Chem.* **1975**, *40*, 1083.
(23) Curtin, D. Y.; Flynn, E. W. *J. Am. Chem. Soc.* **1959**, *81*, 4714.
(24) Costa, A. M. B. S. R. C. S.; Dean, F. M.; Jones, M. A.; Varma, R. S. *J. Chem. Soc., Perkin Trans. 1* **1985**, 799.
(25) Keenan, R. M.; Weinstock, J.; Franz, R. G.; Gaitanopoulos, D. E.; Girad, G. R.; Gill, D. T.; Morgan, T. M.; Samanen, J. M.; Hempel, J.; Eggleston, D. S.; Aiyar, N.; Grittin, E.; Ohlstein, E. H.; Stack, E. J.; Weidley, E. F.; Edwards, R. *J. Med. Chem.* **1992**, *35*, 3870.
(26) Martínez, A. G.; Alvarez, R. M.; Fraile, A. G. *Synthesis* **1986**, 222.
(27) Sha, C.; Huang, S. *Tetrahedron Lett.* **1995**, *36*, 6927.
(28) Farnum, D. G.; Mostashari, A.; Hagedorn, A. A., III. *J. Org. Chem.* **1971**, *36*, 698.
(29) Gemal, A. L.; Luche, J. L. *J. Org. Chem.* **1979**, *44*, 4187.

Scheme 1



H), 7.15 (m, 2 H), 7.34 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 18.8, 31.5, 34.7, 73.7, 105.5, 127.4, 127.5, 128.4, 145.8, 148.2; IR ($CDCl_3$) 3380 (OH), 3020, 2937, 1409 cm^{-1};HRMS *m/z* 300.0006 (calcd for $C_{12}H_{13}IO$, 300.0011).

2-Iodo-3-phenylindenone. 2-Iodo-3-phenylindenone was prepared according to a literature procedure.[30] An ICl solution in CH_2Cl_2 (1 M, 1.62 mL, 1.62 mmol) was slowly added to a solution of 3-phenyl-2-(trimethylsilyl)indenone[9] in CH_2Cl_2 (1.5 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 2 h. Then, the mixture was quenched by adding excess ether, washed with $Na_2S_2O_3$ solution, water, and brine, dried ($MgSO_4$) and filtered. The mixture was concentrated, followed by recrystallization from CH_2Cl_2/MeOH. Orange crystals (0.4 g, 1.20 mmol, 89%) were obtained: mp 120−121 °C (CH_2Cl_2/MeOH); ^{1}H NMR ($CDCl_3$) δ 7.09 (d, J = 7.5 Hz, 1 H), 7.30 (m, 2 H), 7.6 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 96.5, 121.1, 123.8, 128.1, 128.8, 130.2, 130.5, 132.8, 133.6, 146.5, 163.5, 191.6 (one sp^2 C missing due to overlap); IR ($CDCl_3$) 3063, 3027, 1715 (C=O) cm^{-1};HRMS *m/z* 331.9705 (calcd for $C_{15}H_9IO$, 331.9698).

1,1-Diphenyl-2-propen-2-yl Triflate. 1,1-Diphenyl-2-propen-2-yl triflate was prepared according to a literature procedure.[25] To a suspension of NaH (60% in mineral oil, 0.92 g, 22.9 mmol) in 30 mL of DMF at room temperature was added dropwise 1,1-diphenylacetone (2.52 g, 12 mmol) in 10 mL of DMF. After stirring for 2 h under N_2, *N*-phenyltrifluoromethanesulfonimide (4.97 g, 13.8 mmol) was added in one portion and the mixture was stirred overnight, diluted with ether, washed with satd NH_4Cl, water, and brine, dried ($MgSO_4$), and concentrated. Chromatography (hexanes) gave a light yellow oil (1.4 g, 45%): ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 3 H), 7.20−7.40 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 19.1, 118.1, 128.1, 128.2, 128.5, 129.6, 129.7, 135.6, 137.1, 138.3, 143.1 (one sp^2 C missing due to overlap); IR (CH_2Cl_2) 3058, 2926, 1494, 1209 (S=O) cm^{-1}; HRMS *m/z* 342.0538 (calcd for $C_{16}H_{13}F_3O_3S$, 342.0538).

2-Iodo-1,1-diphenyl-1-propene. 2-Iodo-1,1-diphenyl-1-propene was prepared according to a literature procedure.[26] 1,1-Diphenyl-2-propen-2-yl triflate (0.5 g, 1.5 mmol), MgI_2 (1.2 g, 4.4 mmol), and Et_3N (0.4 mL, 2.6 mmol) were placed in 20 mL of cyclohexane. The solution was refluxed at 95 °C for 10 h. After the reaction mixture was allowed to cool, it was diluted with ether, washed with satd $NaHSO_3$ and water, dried ($MgSO_4$), filtered and concentrated. Chromatography (hexanes) gave a light yellow oil (0.39 g, 83%): ^{1}H NMR ($CDCl_3$) δ 2.68 (s, 3 H), 7.00−7.15 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 32.6, 100.2, 126.7, 127.2, 127.8, 128.0, 128.7, 130.1, 141.0, 144.6, 144.7; IR (CH_2Cl_2) 3027, 2922, 1492 cm^{-1}; HRMS *m/z* 320.0059 (calcd for $C_{15}H_{13}I$, 320.0062).

General Procedure for the Palladium-Catalyzed Annulation of Alkynes by Vinylic Iodides or Triflates. $Pd(OAc)_2$ (2.8 mg, 0.0125 mmol), NaOAc (42 mg, 0.5 mmol), n-Bu_4NCl (208 mg, 0.75 mmol, procedure A) or LiCl (11 mg, 0.25 mmol, procedure B), vinylic iodide or triflate (0.25 mmol), the alkyne (0.5 mmol, except 0.75 mmol for 4,4-dimethyl-2-pentyne), and 5 mL of DMF were placed in a 4 dram vial, which was heated in an oil bath at 100 °C for the period of time indicated in Table 1. The reaction mixture was allowed to cool, diluted with ether, washed with saturated NH_4Cl, dried over anhydrous $MgSO_4$, and filtered. The solvent was evaporated under reduced pressure and the product was isolated by chromatography or preparative TLC.

The following compounds were prepared by the above procedure.

9,10-Diphenyl-1,2,3,4-tetrahydrophenanthrene (entries 1 and 2, Table 1). Obtained as a white solid from the reaction of compound **1** or **2** and diphenylacetylene using procedure A after purification by column chromatography (hexanes): mp 190−192 °C (hexanes); ^{1}H NMR ($CDCl_3$) δ 1.80 (m, 2 H), 1.97 (m, 2 H), 2.57 (t, J = 6.3 Hz, 2 H), 3.16 (t, J = 6.3 Hz, 2 H), 7.00−7.65 (m, 13 H), 8.12 (d, J = 8.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.0, 23.3, 26.6, 30.1, 122.7, 127.5, 125.0, 125.7, 126.2, 126.5, 127.4, 127.5, 130.2, 131.1, 131.2, 131.5, 131.8, 133.2, 136.7, 139.7, 139.8, 140.8; IR (CH_2Cl_2) 3054, 1491 cm^{-1}; HRMS *m/z* 334.1719 (calcd for $C_{26}H_{22}$, 334.1721).

9-*tert*-Butyl-10-phenyl-1,2,3,4-tetrahydrophenanthrene (entries 3 and 4, Table 1). Obtained as a white solid from the reaction of compound **1** or **2** and 3,3-dimethyl-1-phenyl-1-butyne using procedure A after purification by column chromatography (hexanes): mp 150−152 °C (hexanes); ^{1}H NMR ($CDCl_3$) δ 1.37 (s, 9 H), 1.61 (m, 2 H), 1.84 (m, 2 H), 2.17 (t, J = 5.7 Hz, 2 H), 3.14 (t, J = 6.0 Hz, 2 H), 7.18−7.48 (m, 7 H), 8.06 (d, J = 8.1 Hz, 1 H), 8.53 (d, J = 8.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.8, 23.6, 27.1, 30.6, 35.3, 38.3, 122.8, 123.3, 124.6, 126.4, 127.3, 128.9, 130.4, 130.9, 131.0, 133.4,

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134.1, 139.7, 140.6, 143.9; IR (CH_2Cl_2) 3074, 1429 cm^{-1};HRMS *m/z* 314.2042 (calcd for $C_{24}H_{26}$, 314.2034).

9-(1-Hydroxy-1-methylethyl)-10-phenyl-1,2,3,4-tetrahydrophenanthrene (entries 5 and 6, Table 1). Obtained as a white solid from the reaction of compound **1** or **2** and 2-methyl-4-phenyl-3-butyn-2-ol using procedure A after purification by column chromatography (hexanes): mp 154−156 °C (hexanes); ^1H NMR ($CDCl_3$) δ 1.63 (s, 6 H), 1.66 (m, 2 H), 1.86 (m, 2 H), 2.19 (t, J = 6.0 Hz, 2 H), 3.16 (t, J = 5.7 Hz, 2 H), 7.18−7.52 (m, 7 H), 8.06 (d, J = 8.1 Hz, 1 H), 8.75 (d, J = 9.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) d 22.8, 23.4, 27.1, 30.4, 34.0, 76.0, 123.14, 123.8, 125.1, 126.7, 127.9, 128.8, 129.8, 131.6, 133.4, 133.7, 138.2, 139.3, 143.3 (one sp^2 C missing due to overlap); IR (CH_2Cl_2) 3589 (OH), 3054, 1422 cm^{-1}; HRMS *m/z* 316.1826 (calcd for $C_{23}H_{23}O$, 316.1827).

9-*tert*-Butyl-10-methyl-1,2,3,4-tetrahydrophenanthrene (entries 7 and 8, Table 1). Obtained as a white solid from the reaction of compound **1** or **2** and 4,4-dimethyl-2-pentyne using procedure A after purification by column chromatography (hexanes): mp 84−86 °C (hexanes); ^1H NMR ($CDCl_3$) δ 1.70 (s, 9 H), 2.43 (s, 3 H), 1.90 (m, 4 H), 2.75 (t, J = 6.0 Hz, 2 H), 3.10 (t, J = 6.0 Hz, 2 H), 7.33 (m, 2 H), 7.95 (dd, J = 3.0, 9.0 Hz, 1 H), 8.31 (dd, J = 3.0, 9.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.0, 22.9, 23.6, 26.4, 28.2, 34.2, 38.4, 121.9, 122.9, 123.6, 126.9, 129.3, 131.5, 131.9, 134.2, 135.0, 142.2; IR (CH_2Cl_2) 3051, 1506 cm^{-1}; HRMS *m/z* 252.1882 (calcd for $C_{19}H_{24}$, 252.1878).

10-Ethyl-9-(1-hydroxycyclohexyl)-1,2,3,4-tetrahydrophenanthrene (entries 9 and 10, Table 1). Obtained as a white solid from the reaction of compound **1** or **2** and 1-(1-butynyl)cyclohexanol using procedure A after purification by column chromatography (hexanes): mp 88−90 °C (hexanes); ^1H NMR ($CDCl_3$) δ 1.27 (t, J = 4.0 Hz, 3 H), 1.50−1.98 (m, 14 H), 2.75 (dt, J = 4.5, 10 Hz, 2 H), 2.92 (t, J = 6.0 Hz, 2 H), 3.13 (t, J = 6.0 Hz, 2 H), 3.23 (br s, 1 H), 7.29−7.40 (m, 2 H), 7.96 (dd, J = 3.0, 9.0 Hz, 1 H), 8.56 (d, J = 9.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 16.4, 22.3, 22.9, 23.6, 24.2, 25.1, 27.0, 27.1, 38.3, 77.4, 122.5, 122.8, 123.9, 127.3, 129.9, 131.2, 132.2, 135.0, 139.9, 140.0; IR (CH_2Cl_2) 3587 (OH), 3072, 1449 cm^{-1}; HRMS *m/z* 308.2146 (calcd for $C_{22}H_{28}O$, 308.2140).

10-Phenyl-9-(triethylsilyl)-1,2,3,4-tetrahydrophenanthrene (entries 11 and 12, Table 1). Obtained as a white solid from the reaction of compound **1** or **2** and 1-phenyl-2-(triethylsilyl)acetylene using procedure A or B after purification by column chromatography (hexanes): mp 124−125 °C (hexanes); ^1H NMR ($CDCl_3$) δ 0.52 (q, J = 7.5 Hz, 6 H), 0.80 (t, J = 7.5 Hz, 9 H), 1.68 (m, 2 H), 1.89 (m, 2 H), 2.27 (t, J = 6.0 Hz, 2 H), 3.20 (t, J = 6.0 Hz, 2 H), 7.19−7.22 (m, 2 H), 7.37 (m, 3 H), 7.48 (m, 2 H), 8.07 (dd, J = 3.0, 7.5 Hz, 1 H), 8.30 (dd, J = 3.0, 7.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 5.6, 8.3, 22.8, 23.3, 26.9, 30.1, 123.3, 123.9, 124.9, 126.9, 127.6, 128.7, 130.6, 130.7, 131.9, 133.1, 133.4, 135.9, 143.7, 150.1; IR (CH_2Cl_2) 3055, 1456 cm^{-1}; HRMS *m/z* 372.2278 (calcd for $C_{26}H_{32}Si$, 372.2273).

10-Phenyl-9-(trimethylsilyl)-1,2,3,4-tetrahydrophenanthrene (entries 13−15, Table 1). Obtained as a white solid from the reaction of compound **1** or **2** and 1-phenyl-2-(trimethylsilyl)acetylene using procedure A or B after purification by column chromatography (hexanes): mp 144−145 °C (hexanes); ^1H NMR ($CDCl_3$) δ 0.04 (s, 9 H), 1.68 (m, 2 H), 1.90 (m, 2 H), 2.33 (t, J = 6.0 Hz, 2 H), 3.20 (t, J = 6.0 Hz, 2 H), 7.22 (m, 2 H), 7.38 (m, 3 H), 7.49 (m, 2 H), 8.08 (dd, J = 3.0, 9.0 Hz, 1 H), 8.25 (dd, J = 3.0, 9.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 2.8, 22.8, 23.3, 26.9, 30.1, 123.4, 124.2, 125.1, 127.0, 127.9, 129.3, 130.5, 132.1, 133.1, 133.2, 133.5, 135.4, 143.6, 148.8; IR (CH_2Cl_2) 3054, 1457 cm^{-1}; HRMS *m/z* 330.1806 (calcd for $C_{23}H_{26}Si$, 330.1804).

9-(2-Methyl-2-(1,3-dioxolanyl))-10-phenyl-1,2,3,4-tetrahydrophenanthrene (entries 16 and 17, Table 1). Obtained as a white solid from the reaction of compound **1** or **2** and 2-(2-phenyl-1-ethynyl)-2-methyl-1,3-dioxolane using procedure A after purification by column chromatography (hexanes): mp 175−176 °C (hexanes); ^1H NMR ($CDCl_3$) δ 1.67 (m, 2 H), 1.86 (m, 2 H), 1.96 (s, 3 H), 2.22 (t, J = 6.0 Hz, 2 H), 3.17 (t, J = 6.0 Hz, 2 H), 3.53 (m, 2 H), 3.70 (m, 2 H), 7.16 (m, 2 H), 7.38 (m, 3 H), 7.51 (m, 2 H), 8.05 (m, 1 H), 8.82 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.7, 23.3, 27.1, 29.7, 30.3, 63.32, 110.5, 122.8, 124.5, 125.4, 126.0, 127.5, 127.6, 128.2, 129.4, 132.6, 132.9, 133.8, 133.9, 138.9, 143.7; IR (CH_2Cl_2) 3054, 1599, 1191 (C−O) cm^{-1}; HRMS *m/z* 344.1778 (calcd for $C_{24}H_{24}O_2$, 344.1776).

1-Hydroxy-9,10-diphenyl-1,2,3,4-tetrahydrophenanthrene (entry 20, Table 1). Obtained as a white solid in 51% yield from the reaction of 2-iodo-3-phenylcyclohex-2-enol and diphenylacetylene using procedure B after purification by column chromatography (5:1 hexanes/ethyl acetate): mp 178−180 °C (CH_2Cl_2/MeOH); ^1H NMR ($CDCl_3$) δ 1.72 (dd, J = 0.6, 3.6 Hz, 1 H), 1.87 (m, 1 H), 2.04 (m, 2 H), 2.21 (m, 1H), 3.10 (m, 1 H), 3.50 (m, 1 H), 4.81 (m, 1 H), 7.00 (m, 1 H), 7.11−7.25 (m, 9 H), 7.39 (m, 1 H), 7.48−7.56 (m, 2 H), 8.14 (d, J = 8.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 17.0, 26.3, 30.6, 64.5, 123.4, 126.1, 126.4, 126.7, 127.4, 127.5, 127.6, 127.7, 127.8, 130.3, 130.8, 131.1, 131.2, 132.2, 132.6, 133.8, 138.1, 139.3, 139.4, 139.7; IR ($CDCl_3$) 3418 (OH), 3069, 2935, 1491 cm^{-1}; HRMS *m/z* 350.1671 (calcd for $C_{26}H_{22}O$, 350.1670).

5,6-Diphenyl-7*H*-benzo[*c*]fluoren-7-one (entry 21, Table 1). Obtained as an orange solid in 54% yield from the reaction of 2-iodo-3-phenylindenone and diphenylacetylene using procedure B after purification by column chromatography (10:1 hexanes/ethyl acetate): mp 238−240 °C (CH_2Cl_2/MeOH); ^1H NMR ($CDCl_3$) δ 7.11 (m, 4 H), 7.19−7.33 (m, 7 H), 7.46−7.67 (m, 5 H), 8.15 (d, J = 7.5 Hz, 1 H), 8.65 (d, J = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 123.4, 123.9, 124.8, 126.7, 127.0, 127.2, 127.4, 127.7, 128.5, 128.6, 128.7, 128.8, 128.9, 129.9, 131.1, 134.3, 134.7, 136.2, 136.8, 137.2, 138.1, 141.3, 143.0, 144.0, 193.9; IR ($CDCl_3$) 3073, 3022, 1710 (C═O), 1602 cm^{-1}; HRMS *m/z* 382.1360 (calcd for $C_{29}H_{18}O$, 382.1358).

5,6-Diphenyl-7*H*-benzo[*c*]xanthen-7-one (entry 22, Table 1). Obtained as a red solid in 25% yield from the reaction of 2-iodoflavone and diphenylacetylene using procedure B after purification by column chromatography (10:1 hexanes/ethyl acetate): mp 190−192 °C (hexanes); ^1H NMR ($CDCl_3$) δ 6.64 (d, J = 8.4 Hz, 1 H), 7.15 (t, J = 7.5 Hz, 1 H), 7.21−7.37 (m, 13 H), 7.49 (t, J = 8.4 Hz, 1 H), 7.77 (d, J = 7.8 Hz, 1 H), 9.34 (d, J = 7.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 112.5, 121.4, 121.9, 123.3, 124.5, 126.7, 127.0, 127.4, 127.9, 128.1, 129.4, 129.5, 130.3, 130.9, 133.8, 134.2, 136.6, 137.0, 137.8, 143.0, 146.4, 148.5, 164.4, 184.8 (one sp^2 C missing due to overlap); IR ($CDCl_3$) 3102, 3057, 1685 (C═O), 1599 cm^{-1}; HRMS *m/z* 398.1310 (calcd for $C_{29}H_{18}O_2$, 398.1307).

3-Benzoyl-2-(2-hydroxyphenyl)-4,5-diphenylfuran (entry 22, Table 1). Obtained as an orange solid in 61% yield from the reaction of 3-iodoflavone and diphenylacetylene using procedure B after purification by column chromatography (10:1 hexanes/ethyl acetate): mp 184−186 °C (hexanes); ^1H NMR (CD_2Cl_2) δ 7.0 (m, 2 H), 7.17−7.48 (m, 12 H), 7.52 (m, 3 H), 7.70 (m, 2 H), 8.24 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 118.1, 118.6, 121.0, 123.7, 125.4, 126.5, 127.9, 128.3, 128.6, 128.8, 128.9, 130.1, 130.2, 130.3, 130.7, 131.6, 132.4, 133.6, 137.5, 149.4, 151.1, 154.8, 195.2; IR ($CDCl_3$) 3305 (OH), 3060, 3031, 1656 (C═O) cm^{-1}; HRMS *m/z* 416.1411 (calcd for $C_{29}H_{20}O_3$, 416.1412).

5-*tert*-Butyl-6-methyl-7*H*-benzo[*c*]xanthen-7-one (entry 23, Table 1). Obtained as an orange solid in 10% yield from the reaction of 3-iodoflavone and 4,4-dimethyl-2-pentyne using procedure B after purification by column chromatography (10:1 hexanes/ethyl acetate): mp 125−127 °C (hexanes); ^1H NMR ($CDCl_3$) δ 1.65 (s, 9 H), 2.83 (s, 3 H), 7.40 (t, J = 8.5 Hz, 1 H), 7.62 (m, 2 H), 7.72 (m, 2 H), 8.05 (d, J = 8.5 Hz, 1 H), 8.20 (dd, J = 1.5, 7.8 Hz, 1 H), 8.61 (dd, J = 1.5, 8.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 19.7, 32.0, 39.2, 103.3, 117.0, 122.7, 123.2, 123.9, 124.1, 124.9, 125.9, 126.4, 129.6, 130.5, 133.4, 136.4, 145.2, 152.6, 154.2, 180.2; IR ($CDCl_3$) 3106, 3060, 1685 (C═O), 1610 cm^{-1}; HRMS *m/z* 316.1460 (calcd for $C_{22}H_{20}O_2$, 316.1463).

2-*tert*-Butyl-4-benzoyl-5-(2-hydroxyphenyl)-1-methylfuran (entry 23, Table 1). Obtained as an orange solid in 69% yield from the reaction of 3-iodoflavone and 4,4-dimethyl-2-pentyne using procedure B after purification by column chromatography (10:1 hexanes/ethyl acetate): mp 170−172 °C (hexanes); ^1H NMR (CD_2Cl_2) δ 1.42 (s, 9 H), 1.97 (s, 3 H), 6.76 (dt, J = 0.9, 7.5 Hz, 1 H), 6.93 (dd, J = 1.2, 8.7 Hz, 1 H), 7.16 (m, 2 H), 7.37 (t, J = 7.5 Hz, 2 H), 7.48 (m, 1 H), 7.80 (d, J = 6.0 Hz, 2 H), 8.10 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.7, 29.4, 34.0,

113.7, 117.6, 118.0, 120.3, 124.6, 128.4, 129.9, 130.0, 130.5, 133.4, 137.8, 148.7, 154.1, 157.8, 195.2; IR ($CDCl_3$) 3340 (OH), 3060, 2970, 1652 cm^{-1}; HRMS *m/z* 334.1570 (calcd for $C_{22}H_{22}O_3$, 334.1569).

1,2,4-Triphenylnaphthalene (entries 24 and 25, Table 1). Obtained as a white solid in 49% yield from the reaction of 2-iodo-1,1-diphenylethylene and diphenylacetylene using procedure B after purification by column chromatography (hexanes): mp 159−161 °C (hexanes); ^1H NMR ($CDCl_3$) δ 7.16−7.21 (m, 5 H), 7.25−7.34 (m, 5 H), 7.43−7.63 (m, 8 H), 7.77 (m, 1 H), 8.01 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 125.8, 126.0, 126.1, 126.3, 126.8, 127.2, 127.4, 127.6, 127.9, 128.4, 129.4, 130.1, 130.2, 131.0, 131.6, 133.1, 137.2, 137.9, 139.1, 139.8, 140.7, 141.9; IR ($CDCl_3$) 3059, 3026, 1600 cm^{-1}; HRMS *m/z* 356.1560 (calcd for $C_{28}H_{20}$, 356.1565).

1-*tert*-Butyl-2,4-diphenylnaphthalene and 2-*tert*-Butyl-1,4-diphenylnaphthalene (entry 26, Table 1). Obtained as a 3:1 mixture of regioisomers in 62% yield from the reaction of 2-iodo-1,1-diphenylethylene and 3,3-dimethyl-1-phenyl-1-butyne after purification by column chromatography. The mixture was partially separated through preparative TLC and both pure isomers were isolated. 1-*tert*-Butyl-2,4-diphenylnaphthalene: mp 139−140 °C (hexanes); ^1H NMR ($CDCl_3$) δ 1.26 (s, 9 H), 7.15−7.38 (m, 5 H), 7.45−7.60 (m, 8 H), 7.71 (s, 1 H), 7.89 (d, J = 8.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 33.2, 37.2, 125.1, 125.4, 127.0, 127.1, 127.2, 127.3, 127.6, 128.3, 129.8, 130.3, 131.7, 134.9, 137.0, 139.3, 141.4, 141.8, 144.2 (one sp^2 C missing due to overlap); IR ($CDCl_3$) 3074, 2962, 1492 cm^{-1};HRMS *m/z* 336.1887 (calcd for $C_{26}H_{24}$, 336.1878). 2-*tert*-Butyl-1,4-diphenylnaphthalene: mp 138−140 °C (hexanes); ^1H NMR ($CDCl_3$) δ 1.50 (s, 9 H), 7.15 (s, 1 H), 7.33−7.54 (m, 12 H), 7.96 (m, 1 H), 8.63 (d, J = 8.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 35.0, 38.2, 123.9, 124.6, 126.4, 127.1, 127.2, 127.5, 128.2, 128.4, 129.6, 130.2, 132.1, 132.3, 133.4, 137.5, 139.1, 140.6, 142.4, 147.1; IR (CH_2Cl_2) 3069, 2926, 1596 cm^{-1}; HRMS *m/z* 336.1880 (calcd for $C_{26}H_{24}$, 336.1878).

1-*tert*-Butyl-2-methyl-4-phenylnaphthalene (entry 28, Table 1). Obtained as a white solid in 52% yield from the reaction of 2-iodo-1,1-diphenylethylene and 4,4-dimethyl-2-pentyne using procedure B after purification by column chromatography (hexanes): mp 139−140 °C (hexanes); ^1H NMR ($CDCl_3$) δ 1.56 (s, 9 H), 2.93 (s, 3 H), 7.36−7.56 (m, 8 H), 7.86 (d, J = 8.7 Hz, 1 H), 8.18 (d, J = 8.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 18.2, 31.9, 36.0, 124.2, 125.0, 125.7, 126.2, 126.3, 127.0, 128.2, 130.0, 130.3, 131.1, 134.4, 137.8, 141.6, 144.4; IR ($CDCl_3$) 3058, 2956, 1591 cm^{-1}; HRMS *m/z* 274.1719 (calcd for $C_{21}H_{22}$, 274.1722).

1-(Trimethylsilyl)-2,4-diphenylnaphthalene (entry 29, Table 1). Obtained as a white solid in 19% yield from the reaction of 2-iodo-1,1-diphenylethylene and 1-phenyl-2-(trimethylsilyl)acetylene using procedure B after purification by column chromatography (hexanes): mp 146−148 °C (hexanes); ^1H NMR ($CDCl_3$) δ 0.16 (s, 9 H), 7.36−7.53 (m, 13 H), 7.97 (d, J = 8.7 Hz, 1 H), 8.30 (d, J = 8.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 2.8, 125.1, 125.2, 126.8, 127.3, 127.4, 128.0, 128.3, 129.3, 129.6, 130.0, 130.1, 130.6, 134.9, 138.4, 140.5, 140.8, 145.5, 148.3; IR ($CDCl_3$) 3058, 2847, 1486 cm^{-1}; HRMS *m/z* 352.1647 (calcd for $C_{25}H_{24}Si$, 352.1647).

2-Methyl-1,3,4-triphenylnaphthalene (entry 30, Table 1). Obtained as a white solid in 65% yield from the reaction of 2-iodo-1,1-diphenylpropene and diphenylacetylene using procedure B after purification by column chromatography (hexanes): mp 160−163 °C (hexanes); ^1H NMR ($CDCl_3$) δ 2.56 (s, 3 H), 6.78−6.86 (m, 5 H), 7.05−7.25 (m, 10 H), 7.43 (t, J = 8.1 Hz, 1 H), 7.62 (m, 2 H), 8.19 (d, J = 8.5 Hz, ^1H); ^{13}C NMR ($CDCl_3$) δ 17.2, 124.5, 125.2, 125.8, 126.0, 126.3, 127.3, 127.4, 127.6, 130.6, 131.2, 131.3, 131.4, 132.0, 132.1, 136.9, 139.0, 139.3, 139.7, 140.8, 141.4 (two sp2 C's missing due to overlap); IR ($CDCl_3$) 3058, 2923, 1602 cm^{-1}; HRMS *m/z* 370.1720 (calcd for $C_{29}H_{22}$, 370.1722).

1-*tert*-Butyl-3-methyl-2,4-diphenylnaphthalene (entry 31, Table 1). Obtained as a white solid in 46% yield from the reaction of 2-iodo-1,1-diphenylethylene and 3,3-dimethyl-1-phenyl-1-butyne using procedure B after purification by column chromatography (hexanes): mp 171−173 °C (hexanes); ^1H NMR ($CDCl_3$) δ 1.41 (s, 9 H), 2.34 (s, 3 H), 6.81−7.08 (m, 10 H), 7.52 (m, 2 H), 8.14 (m, 1 H), 8.63 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 17.4, 35.2, 38.4, 123.5, 124.8, 125.2, 125.5, 125.6, 126.2, 127.1, 129.0, 129.9, 130.0, 131.8, 132.2, 133.2, 139.1, 140.8, 141.1, 142.2, 143.9; IR ($CDCl_3$) 3064, 2927, 1599 cm^{-1}; HRMS *m/z* 350.2032 (calcd for $C_{27}H_{26}$, 350.2034).

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Supporting Information Available: ^1H and ^{13}C NMR spectra for all compounds in Table 1 (42 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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