DOI: 10.1002/ejoc.201201340

A Flexible Metal-Catalyzed Synthesis of Highly Substituted Aryl Phenanthrenyl Selenides

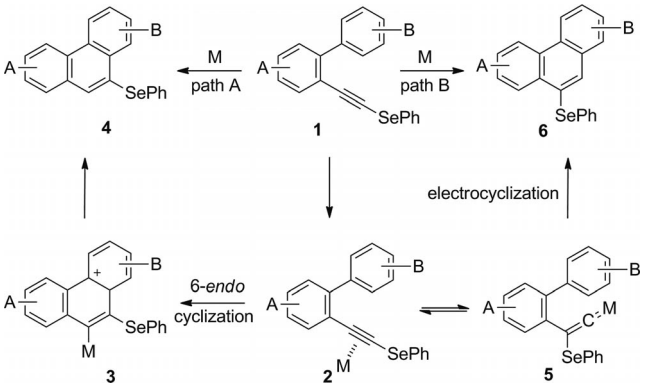
Wontaeck Lim[a] and Young Ho Rhee*[a]

Keywords: Homogeneous catalysis / Gold / Aromaticity / Synthetic methods / Selenium

An efficient method for the preparation of diaryl selenides, which are important in biology and materials science, is described. Specifically, the development of highly substituted phenanthrenyl phenyl selenides **4** and **6** by metal-catalyzed cyclization of *o*-phenylarylalkynes species **1** was successfully performed. The selectivity for 9- and 10-selenyl phenanthrenes was perfectly controlled by indium(III) and gold(I) catalysts, and the reactions proceed through different pathways. For the $In(OTf)_3$ catalyst system, 6-*endo* cyclization of alkyne **3** gives product **4** in which the selenium group is retained. In contrast, for the $AuCl(IPr)/AgSbF_6$ catalyst system, transformation of metal–alkyne complex **2** into vinylidene–gold intermediate **5** gives product **6** in which the selenium group is migrated. Various substrates, even electronically poor substrates, can be converted into phenanthrenes with high selectivity in high yield under very mild conditions.

Introduction

Diaryl selenides are an important class of compounds because of their utility in biologically related areas and materials science.[1] Thus, the development of new procedures to prepare diversely substituted diaryl selenides is an important task in organic synthesis.[2] Conventionally, these compounds are synthesized by the substitution reaction of aryl carbanions with selenium electrophiles or by the reaction of selenium anions with aryl halides. These traditional methods require the stoichiometric generation of the reactive intermediates under strongly basic conditions. Thus, the development of more efficient methods that can operate under mild conditions is highly desirable. In this context, we envisioned that diversely substituted aryl phenanthrenyl selenides could be accessed through transition-metal-catalyzed cycloisomerization of (*o*-phenylaryl)alkynes species **1** (Scheme 1). We were particularly interested in the possibility of a divergent pathway. In one path of this scenario, alkyne **1** can generate cycloisomerized product **4** in the presence of a suitable metal catalyst that can effectively activate alkynes towards nucleophilic attack of the phenyl group (Scheme 1, path A). In fact, generation of alkyl-substituted and halogen-substituted polyaromatic compounds by metal-catalyzed cycloisomerization of acyclic precursors has been studied.[3a,3b] However, the cycloisomerization of selenium-substituted alkynes is extremely rare.[4a] Moreover, the migration of the selenyl group from selenyl-substituted alkynes in the presence of a Ru complex to form metal–vinylidene complex **5** has been noted.[4b] However, catalytic reactions that utilize this interesting reactivity are still limited.[5] On the basis of these precedents, we reasoned that species **5** might undergo electrocyclization to give isomeric phenanthrene product **6** in an alternative course of the reaction (Scheme 1, path B).[6] Because it is well established that metal–alkyne complex **2** and corresponding metal–vinylidene species **5** are in equilibrium,[7] the key issue in this divergent pathway was to find metal catalysts that can render selectivity in the formation of the product. Herein, we wish to report our recent results, which indeed show that the product can be successfully controlled. Thus, the generation of cycloisomerized product **3** with retention of the selenyl group was optimized with the indium catalyst (path A). In contrast, alternative cycloisomerization with 1,2-migration of the selenyl group to generate isomeric



Scheme 1. Divergent pathways for the synthesis of diaryl selenides containing a phenanthrene moiety.

[a] Department of Chemistry, POSTECH,
Pohang University of Science and Technology.
San 31, Hyoja-dong, Pohang, Kyungbuk 790-784, Korea
Fax: +82-54-279-3399
E-mail: yhrhee@postech.ac.kr
Homepage: http://yhrhee.postech.ac.kr

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201201340.

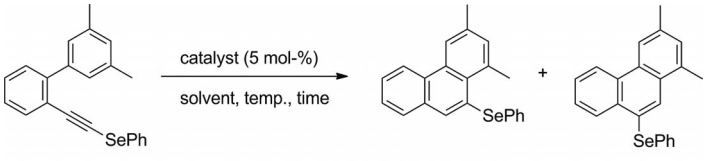
product **5** was optimized with Au catalysts (path B). From a synthetic viewpoint, this flexible route should provide powerful access to diversely substituted phenanthrene ring systems.[8]

Results and Discussion

At the initial stage of the study, a number of metal catalysts (5 mol-%) were screened for the cycloisomerization reaction with **7** as the substrate. On the basis of the precedents discussed above, we first investigated various Rh[9] and Ru[10] complexes. As shown in Table 1, Wilkinson's catalyst was found to be completely unreactive even at elevated temperature (Table 1, entry 1). Using $RhCl_3$, the reaction suffered from poor reactivity, even though a small amount of the migrated product[11] was obtained (Table 1, entry 2). Other Ru and Rh catalysts also showed poor reactivity (Table 1, entries 3–7). In contrast, the use of indium(III) chloride gave cycloisomerized product **8a** with retention of phenylselenyl group in 65% yield (Table 1, entry 8). In this case, migratory cycloisomerization product **8b** was obtained in a trace amount (ca. 9%). Thus, the competition between the two pathways seems to be operating. Switching to indium triflate improved the yield of **8a** to 93% with no apparent involvement of the migratory cycloisomerization (Table 1, entry 9). Lowering the temperature decreased the reactivity of the catalyst (Table 1, entry 10). Then, we looked into the alternative migratory cycloisomerization pathway. When a phosphane-ligated platinum complex was used, the reaction was completely unreactive (Table 1, entry 11). Switching to $PtCl_2$ (Table 1, entry 12), however, a mixture of products was obtained. When $AuCl_3$ was employed, desired compound **8b** was obtained in 93% yield with complete selectivity towards the migratory cycloisomerization (Table 1, entry 13). The use of AuCl maintained the reactivity and the yield of the cycloisomerization (Table 1, entry 14). Again, the competing cycloisomerization reaction was not observed. Lowering the temperature also selectively gave the migratory product in very high yield (Table 1, entry 15). Next, we looked into cationic gold(I) complexes. Even though the electrophilic complexes were inefficient in this case (Table 1, entry 16), the use of a more electron-donating complex gave the desired compound in excellent yield (Table 1, entry 17). The optimal result was obtained when the AuCl(IPr)/$AgSbF_6$ complex was used (Table 1, entry 18). Under these conditions, the desired cycloisomerization product was obtained in 97% isolated yield at room temperature within a relatively shorter reaction time than AuCl. Thus, we decided to use AuCl(IPr)/$AgSbF_6$ as the optimal catalyst.

With the use of the conditions described in entries 9 and 18 in Table 1, the divergent pathways for the synthesis of the phenanthrenyl selenides were explored (Tables 2 and Table 3). We first investigated the retentive cycloisomerization by using the indium catalyst (Table 2). The substituent on the aryl ring that attacks the metal-bound alkyne had a significant effect on the reaction outcome. For example, the reaction with a substrate bearing an electron-donating

Table 1. Screening of the metal catalyst for the divergent synthesis of selenyl-substituted phenanthrene.



7 **8a** **8b**

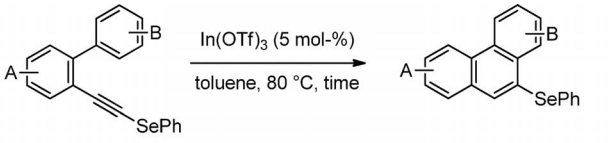
Entry	Catalyst (5 mol-%)	Solvent	*T* [°C]	Time [h]	Conversion [%]	**8a/8b** Yield[a] [%]
1	$[RhCl(PPh_3)_3]$	toluene	80	20	0	–
2	$RhCl_3$	toluene	80	19	25	0:23
3	$RuCl_3$	toluene	80	20	0	–
4	$[RuCl_2(PPh_3)_3]$	toluene	80	20	0	–
5	$Rh_2(OAc)_2$	toluene	80	14	0	–
6	$[Cp^*Ru(MeCN)_3]PF_6$	toluene	80	16	0	–
7	$[RhClcod]_2$	toluene	80	16	0	–
8	$InCl_3$	toluene	80	20	100	65:9
9	$In(OTf)_3$	toluene	80	14	100	93:0
10	$In(OTf)_3$	toluene	r.t	20	0	–
11	$[PtCl_2(PPh_3)_2]$	toluene	80	19	0	–
12	$PtCl_2$	toluene	80	4	100	4:64
13	$AuCl_3$	toluene	80	19	100	0:93
14	AuCl	toluene	80	2	100	0:94
15	AuCl	CH_2Cl_2	r.t.	14	100	0:99
16	$[AuClP(C_6F_5)_3]/AgSbF_6$	CH_2Cl_2	r.t.	1	15	0:13
17	$[Au\{(t\text{Bu})_2P(o\text{-biPh})\}](CH_3CN)SbF_6$	CH_2Cl_2	r.t.	5.5	100	0:99
18	[AuCl(IPr)]/$AgSbF_6$	CH_2Cl_2	r.t.	0.25	100	0:98 (97[b])

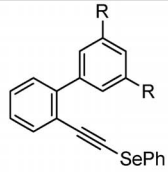
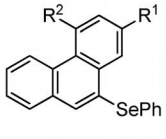
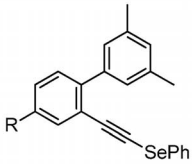
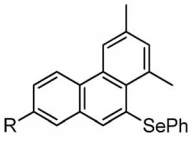
[a] Determined by analysis of the crude material by ^1H NMR spectroscopy by using 1,3,5-trimethoxybenzene as an internal standard. [b] Isolated yield.

methoxy group was complete within a short time (Table 2, entry 2), whereas the same reaction performed with a substrate bearing the electron-withdrawing fluorine group drastically slowed the reaction (Table 2, entry 3). In the latter case, only about 50% conversion was observed, even if 10 mol-% catalyst was used. This result well addresses the carbocationic nature of intermediate **3** generated in the retentive pathway (Scheme 1). Substrate **13** possessing an unsubstituted aryl ring (Table 2, entry 4) maintained the catalytic activity. Introducing a methoxy or methyl group at other positions of the phenyl ring also gave the cycloisomerized products in good yields (Table 2, entries 5–8). The effect of the substituents on the connecting aryl ring was then studied. As can be seen from Table 2, the substrate possessing a methoxy group increased the rate of the reaction (Table 2, entry 9), whereas a chloride group slowed the reaction (Table 2, entry 10). This result is again consistent with the mechanistic rationale shown in Scheme 1.

Next, we investigated the scope of the migratory cycloisomerization by using the gold catalyst. As shown in Table 3, this pathway proved more sensitive to the substituents than the retentive cycloisomerization. For example, the reaction of substrate **9** was significantly slower than that of substrate **7** and produced only retentive cycloisomerized product **10a** in low yield (Table 3, entry 2). However, substrate **11** produced only migratory cycloisomerization product **12b** in 86% yield (Table 3, entry 3). Interestingly, introduction of methoxy or methyl substituents at other positions of the attacking aryl ring had a less significant effect, and the migratory cycloisomerization products were constantly produced in good yield (Table 3, entries 5–8). Substrates **23** and **25** also generated the migratory cycloisomerization products in good yield. As with the retentive cyclo-

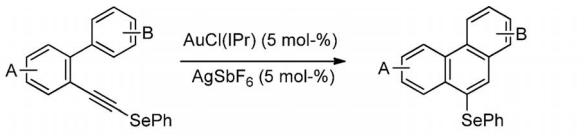
Table 2. Scope of the indium(III)-catalyzed cycloisomerization reaction.[a]

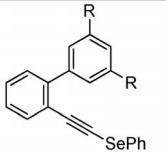
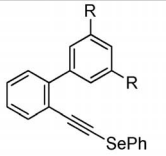
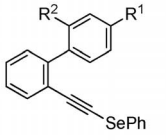
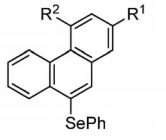
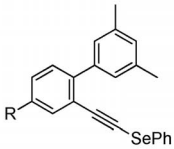
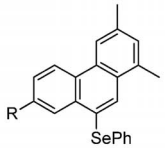


Entry	Substrate	Time [h]	Product	Yield[b] [%]
				
1	**7** (R = Me)	4	**8a** (R = Me)	93
2	**9** (R = OMe)	1	**10a** (R = OMe)	99
3	**11** (R = F)	46	**12a** (R = F)	49[c,d]
				
4	**13** (R^1 = H, R^2 = H)	2	**14** (R^1 = H, R^2 = H)	93
5	**15** (R^1 = Me, R^2 = H)	1	**16a** (R^1 = Me, R^2 = H)	99
6[e]	**17** (R^1 = OMe, R^2 = H)	4	**18a** (R^1 = OMe, R^2 = H)	86
7	**19** (R^1 = H, R^2 = Me)	1.5	**20a** (R^1 = H, R^2 = Me)	91
8	**21** (R^1 = H, R^2 = OMe)	2	**22a** (R^1 = H, R^2 = OMe)	82
				
9	**23** (R = MeO)	1	**24a** (R = OMe)	82
10	**25** (R = Cl)	5	**26a** (R = Cl)	85

[a] General procedure: A mixture of the substrate and $In(OTf)_3$ (5 mol-%) was stirred at 80 °C. [b] Isolated yield. [c] 10 mol-% of indium-catalyst was used. [d] The substrate was recovered in 49% yield. [e] When AuCl (5 mol-%) was used at 80 °C, the product was formed in 40% yield.

Table 3. Scope of the gold-catalyzed cycloisomerization reaction.[a]

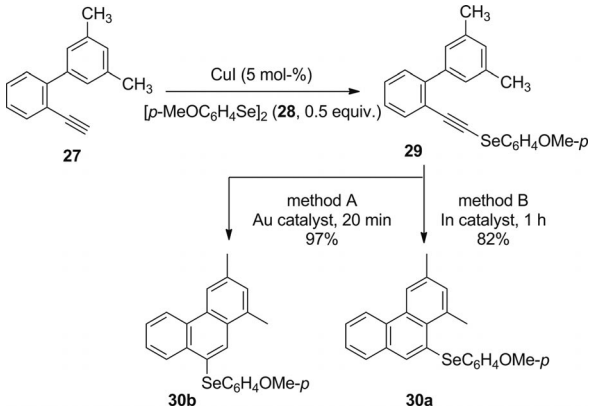


Entry	Substrate	Method	Time [h]	Product	Yield[b] [%]
					
1	**7** (R = Me)	A	0.25	**8b** (R = Me)	97
2	**9** (R = OMe)	A	2	**10a** (R = OMe)	36
3	**11** (R = F)	B	10	**12b** (R = F)	86
					
4	**13** (R^1 = H, R^2 = H)	B	0.33	**14** (R^1 = H, R^2 = H)	95
5	**15** (R^1 = Me, R^2 = H)	B	0.25	**16b** (R^1 = Me, R^2 = H)	86
6	**17** (R^1 = OMe, R^2 = H)	B	1.5	**18b** (R^1 = OMe, R^2 = H)	86
7	**19** (R^1 = H, R^2 = Me)	B	0.33	**20b** (R^1 = H, R^2 = Me)	92
8	**21** (R^1 = H, R^2 = OMe)	B	1	**22b** (R^1 = H, R^2 = OMe)	88
					
9	**23** (R = MeO)	A	0.33	**24b** (R = OMe)	93
10	**25** (R = Cl)	A	2	**26b** (R = Cl)	91

[a] Method A: The reaction was performed at room temperature with the catalyst (5 mol-%). Method B: The reaction was performed at 80 °C with the catalyst (5 mol-%). [b] Isolated yield.

isomerization, effects of the substituents on the connecting aryl ring were observed.

The result shown above indeed illustrate that various substituents can be installed in the phenanthrene ring by exploiting the flexible nature of the cycloisomerization reaction. A higher degree of substituent diversity in the product could be introduced by varying the phenyl group. Thus, our final task was to establish a general method that would allow introduction of a substituted phenyl group. For this purpose, we pursued the synthesis of compound **30** (Scheme 2). Substrate **29** was prepared uneventfully from dehydrogenative coupling of terminal alkyne **27** with diaryl diselenide **28**.[12] Reaction of this substrate by using $In(OTf)_3$ gave retentive cycloisomerization product **30a** in 82% yield, whereas the use of the Au catalyst generated isomeric **30b** in 97% yield.



Scheme 2. Synthesis of compounds **30a** and **30b**.

Conclusions

We optimized reaction conditions to synthesize multisubstituted phenanthrene derivatives, including derivatives containing an electron-deficient substituent. The AuClIPr/$AgSbF_6$ complex can be used as a good catalyst under mild conditions to afford the desired products in short reaction times. This reaction proceeds via a gold–vinylidene intermediate, which has a low transition energy. An electron-rich N-heterocyclic carbene ligand allowed easier formation of the metal–vinylidene intermediate. Further investigation of this reaction for the synthesis of polyaromatic hydrocarbons is in progress.

Experimental Section

(6,8-Dimethylphenanthren-9-yl)(phenyl)selane (8a): To a solution of [(3′,5′-dimethylbiphenyl-2-yl)ethynyl](phenyl)selane (**7**) (36.2 mg, 0.10 mmol) in toluene (1 mL) was added a solution of indium(III) trifluoromethanesulfonate (2.8 mg, 0.005 mmol) in toluene (1 mL), and the resulting mixture was stirred for 1 h. After the reaction was complete, the solvent was removed under reduced pressure, and the resulting yellow solid was purified by flash column chromatography on silica gel to give the product as a pale yellow solid. This solid was further purified by recrystallization from diethyl ether/MeOH to give the product (33.9 mg, 0.093 mmol) as a white powder in 93% yield, m.p. 100.2–101.3 °C. R_f = 0.49 (hexane/diethyl ether = 95:5). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.64 (d, J = 8.1 Hz, 1 H), 8.47 (s, 1 H), 7.78 (s, 1 H), 7.63–7.49 (m, 5 H), 7.34–7.32 (m, 4 H), 3.15 (s, 3 H), 2.59 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.44, 135.97, 134.05, 133.52, 133.43, 133.16, 132.62, 131.89, 130.25, 130.01, 129.76, 128.32, 127.77, 127.66, 126.81, 126.76, 123.18, 121.77, 25.75, 21.72 ppm. IR (NaCl): $\tilde{\nu}$ = 2920, 1577, 1476, 1437, 1022, 850, 756, 734, 689 cm^{-1}. HRMS (EI): calcd. for $C_{22}H_{18}Se$ $[M]^+$ 362.0574; found 362.0572.

(1,3-Dimethylphenanthren-9-yl)(phenyl)selane (8b): To a solution of AuCl(IPr) (6.4 mg, 0.01 mmol) in dichloromethane (1.5 mL) was added a solution of $AgSbF_6$ (3.7 mg, 0.01 mmol) in dichloromethane (1.5 mL), and the resulting mixture was stirred for 10 min at room temperature. The precipitate was filtered through a pad of Celite, and the solvent was removed under reduced pressure. The residual oil was dried under reduced pressure for 2 h. To this residue was added a solution of [(3′,5′-dimethylbiphenyl-2-yl)ethynyl](phenyl)selane (**7**) (72.2 mg, 0.2 mmol) in dichloromethane (4 mL), and the resulting mixture was stirred for 15 min. When the reaction was complete, the solvent was removed under reduced pressure, and the resulting yellow solid was purified by flash column chromatography on silica gel to give the product as a pale yellow solid. This solid was further purified by recrystallization from diethyl ether/MeOH to give the product (71.2 mg, 0.19 mmol) as a white powder in 97% yield, m.p. 69.7–71.2 °C. R_f = 0.51 (hexane/diethyl ether = 95:5). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.72 (d, J = 8.1 Hz, 1 H), 8.42 (dd, J = 8.1, 0.6 Hz, 1 H), 8.37 (m, 2 H), 7.65 (ddd, J = 7.7, 7.8, 1.5 Hz, 1 H), 7.57 (ddd, J = 7.7, 7.8, 1.5 Hz, 1 H), 7.36–7.31 (m, 2 H), 7.30 (m, 3 H), 7.19–7.16 (m, 3 H), 2.65 (s, 3 H), 2.59 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.01, 134.90, 132.52, 132.28, 131.30, 131.12, 130.97, 130.18, 129.44, 128.90, 127.20, 126.96, 126.65, 126.33, 123.41, 120.75, 22.33, 19.79 ppm. IR (NaCl): $\tilde{\nu}$ = 2924, 1577, 1476, 1437, 1022, 849, 784, 742, 690 cm^{-1}. HRMS (EI): calcd. for $C_{22}H_{18}Se$ $[M]^+$ 362.0574; found 362.0569.

Supporting Information (see footnote on the first page of this article): Analytical data for all compounds, general procedure for the preparation of the substrates, determination of structures **8a** and **8b**, ^{1}H NMR and ^{13}C NMR spectra.

Acknowledgments

This work was supported by the Korean Government, National Research Foundation (grant numbers 2010-0009458 and 2008-0061957).

[1] a) L. C. Clark, G. F. Combs, B. W. Turnbull, E. H. Slate, D. K. Chalker, J. Chow, L. S. Davis, R. A. Glover, G. F. Graham, E. G. Gross, A. Krongrad, J. L. Lesher, H. K. Park, B. B. Sanders, C. L. Smith, J. R. Taylor, *J. Am. Med. Assoc.* **1996**, *276*, 1957–1963; b) G. Mugesh, W.-W. du Mont, H. Sies, *Chem. Rev.* **2001**, *101*, 2125–2180; c) A. J. Mukherjee, S. S. Zade, H. B. Singh, R. B. Sunoj, *Chem. Rev.* **2010**, *110*, 4357–4416; d) F. Yu, P. Li, G. Li, G. Zhao, T. Chu, K. Han, *J. Am. Chem. Soc.* **2011**, *133*, 11030–11033.

[2] For selected examples, see inter alia: a) S. Bhadra, A. Saha, B. C. Ranu, *J. Org. Chem.* **2010**, *75*, 4864–4867; b) L. Wang, M. Wang, K. Ren, *Adv. Synth. Catal.* **2009**, *351*, 1586–1594; c) S. N. Murthy, B. Madhav, V. P. Reddy, Y. V. D. Nageswar, *Eur. J. Org. Chem.* **2009**, 5902–5905; d) N. Taniguchi, T. Onami, *J. Org. Chem.* **2004**, *69*, 915–920; e) Y. Nishiyama, K. Tokunaga, N. Sonoda, *Org. Lett.* **1999**, *1*, 1725–1727; f) X. Zhao, Z. Yu,

S. Yan, S. Wu, R. Liu, W. He, L. Wang, *J. Org. Chem.* **2005**, *70*, 7338–7341; g) S. Narayanaperumal, E. E. Alberto, K. Gul, O. E. D. Rodrigues, A. L. Braga, *J. Org. Chem.* **2010**, *75*, 3886–3889; h) V. P. Reddy, A. V. Kumar, K. R. Rao, *J. Org. Chem.* **2010**, *75*, 8720–8723.

[3] a) V. Mamane, P. Hannen, A. Fürstner, *Chem. Eur. J.* **2004**, *10*, 4556–4575; b) R. S. Liu, H. C. Shen, J. M. Tang, H. K. Chang, C. W. Yang, *J. Org. Chem.* **2005**, *70*, 10113–10116.

[4] a) H. Kim, C. Lee, *J. Am. Chem. Soc.* **2005**, *127*, 10180–10181; b) A. F. Hill, A. G. Hulkes, A. J. P. White, D. J. Williams, *Organometallics* **2000**, *19*, 371–373.

[5] For vinylidene formation from internal alkynes, see: a) I. V. Seregin, V. Gevorgyan, *J. Am. Chem. Soc.* **2006**, *128*, 12050–12051; b) J. W. Dankwardt, *Tetrahedron Lett.* **2001**, *42*, 5809–5812; c) T. Miura, N. Iwasawa, *J. Am. Chem. Soc.* **2002**, *124*, 518–519; d) E. Shirakawa, R. Morita, T. Tsuchimoto, Y. Kawakami, *J. Am. Chem. Soc.* **2004**, *126*, 13614–13615; e) G. B. Bajracharya, N. K. Pahadi, I. D. Gridnev, Y. Yamamoto, *J. Org. Chem.* **2006**, *71*, 6204–6210; f) M. Movassaghi, M. D. Hill, *J. Am. Chem. Soc.* **2006**, *128*, 4592–4593.

[6] E. Soriano, J. Marco-Contelles, *Organometallics* **2006**, *25*, 4542–4553.

[7] Reviews: a) B. M. Trost, A. McClory, *Chem. Asian. J.* **2008**, *3*, 164–194; b) Y. Wakatsuki, *J. Organomet. Chem.* **2004**, *689*, 4092–4109.

[8] For other methods for the synthesis of phenanthrenes, see: a) A. Matsumoto, L. Ilies, E. Nakamura, *J. Am. Chem. Soc.* **2011**, *133*, 6557–6559; b) Y. Chen, G. Li, Y. Liu, *Adv. Synth. Catal.* **2011**, *353*, 392–400; c) H. K. Young, H. Lee, J. K. Yeong, T. K. Bum, J. N. Heo, *J. Org. Chem.* **2008**, *73*, 495–501; d) G. A. Kraus, K. Hoover, N. Zhang, *Tetrahedron Lett.* **2002**, *43*, 5319–5321; e) E. Yoshikawa, Y. Yamamoto, *Angew. Chem.* **2000**, *112*, 185; *Angew. Chem. Int. Ed.* **2000**, *39*, 173–175.

[9] For the use of rhodium catalysts in the formation of vinylidenes, see: a) B. M. Trost, A. McClory, *Angew. Chem.* **2007**, *119*, 2120; *Angew. Chem. Int. Ed.* **2007**, *46*, 2074–2077; b) C. Lee, H. Kim, *J. Am. Chem. Soc.* **2006**, *128*, 6336–6337; c) B. M. Trost, Y. H. Rhee, *J. Am. Chem. Soc.* **2003**, *125*, 7482–7483.

[10] For the use of ruthenium catalysts in the formation of vinylidenes, see: a) B. M. Trost, Y. H. Rhee, *Org. Lett.* **2004**, *6*, 4311–4313; b) J. J. Lian, A. Odedra, C. J. Wu, R. S. Liu, *J. Am. Chem. Soc.* **2005**, *127*, 4186–4187; c) B. M. Trost, Y. H. Rhee, *J. Am. Chem. Soc.* **2002**, *124*, 2528–2533; d) B. M. Trost, Y. H. Rhee, *J. Am. Chem. Soc.* **1999**, *121*, 11680–11683; e) C. A. Merlic, M. E. Pauly, *J. Am. Chem. Soc.* **1996**, *118*, 11319–11320.

[11] See the Supporting Information for how the structure was confirmed.

[12] D. Singh, A. M. Deobald, L. R. S. Camargo, G. Tabarelli, O. E. D. Rodrigues, A. L. Braga, *Org. Lett.* **2010**, *12*, 3288–3291.

Received: October 10, 2012
Published Online: December 10, 2012

