ORGANIC LETTERS

2012
Vol. 14, No. 22
5636–5639

Synthesis of Naphthalenes via Platinum-Catalyzed Hydroarylation of Aryl Enynes†

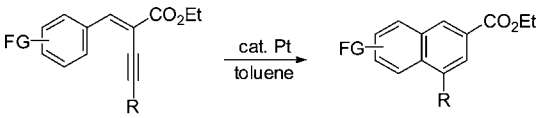
Dongjin Kang, Jinsik Kim, Susung Oh, and Phil Ho Lee*

Department of Chemistry, Kangwon National University, Chuncheon 200-701, Republic of Korea

phlee@kangwon.ac.kr

Received September 2, 2012

ABSTRACT



FG = H, AcO, MeO, $(MeO)_2$, OCH_2O, Cl, Br, I, CO_2Me, Furyl
R = H, alkyl, alkenyl, aryl, heteroaryl

An efficient synthetic method of functionalized naphthalenes having hydrogen, alkyl, alkenyl, aryl, or heteroaryl groups on the 4-position and ethoxycarbonyl group on the 2-position was developed through selective Pt-catalyzed 6-*endo* intramolecular hydroarylation of ethyl (*E*)-2-ethynyl/alkynyl cinnamates.

Transition-metal-catalyzed hydroarylation of alkynes has quite recently emerged as an efficient and atom-economic methodology for the construction of functionalized aromatic compounds and styrene derivatives.[1] Moreover, the importance of its intramolecular reaction has been widely recognized as a possible approach to cyclic vinylarene frameworks.[2] Since Fujiwara et al. first reported transition-matal-catalyzed intramolecular hydroarylation of alkynes in 2000,[3] a large number of transition-metal catalysts have been developed to date for this transformation.[1,4] Research efforts have been focused on catalytic efficiency and regioselectivity, whereas little attention has been paid to the scope and types of performable substrates. Accordingly, the development of new substrates in hydroarylation is as important as the transition-metal catalyst and ligand for the synthesis of valuable organic compounds such as annulated arene carbocycles and heterocycles.

† Dedicated to Prof. Kwan Soo Kim, Yonsei University, on the occasion of his honorable retirement.

(1) (a) Kitamura, T. *Eur. J. Org. Chem.* **2009**, 1111. (b) Biffis, A.; Tubaro, C.; Buscemi, G.; Basato, M. *Adv. Synth. Catal.* **2008**, *350*, 189. (c) Yeh, M. P.; Tsao, W. C.; Cheng, S. T. *J. Org. Chem.* **2008**, *73*, 2902. (d) Tarselli, M. A.; Gagné, M. R. *J. Org. Chem.* **2008**, *73*, 2439. (e) Saito, A.; Kanno, A.; Hanzawa, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 3931. (f) Ferrer, C.; Amijs, C. H. M.; Echavarren, A. M. *Chem.—Eur. J.* **2007**, *13*, 1359. (g) Otani, T.; Kunimatsu, S.; Nihei, H.; Abe, Y.; Saito, T. *Org. Lett.* **2007**, *9*, 5513. (h) Yamamoto, H.; Sasaki, I.; Imagawa, H.; Nishizawa, M. *Org. Lett.* **2007**, *9*, 1399. (i) Choi, D. S.; Kim, J. H.; Shin, U. S.; Deshmukh, R. R.; Song, C. E. *Chem. Commun.* **2007**, 3482. (j) Jimenez-Nunez, E.; Echavarren, A. M. *Chem. Commun.* **2007**, 333. (k) Oyamada, J.; Kitamura, T. *Tetrahedron* **2007**, *63*, 12754. (l) Ferrer, C.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 1105. (m) Bandini, M.; Emer, E.; Tommasi, S.; Umani-Ronchi, A. *Eur. J. Org. Chem.* **2006**, 3527. (n) Bajracharya, G. B.; Pahadi, N. K.; Gridnev, I. D.; Yamamoto, Y. *J. Org. Chem.* **2006**, *71*, 6204. (o) Nakamura, I.; Mizushima, Y.; Yamamoto, Y. *J. Am. Chem. Soc.* **2005**, *127*, 15022. (p) Nevado, C.; Echavarren, A. M. *Synthesis* **2005**, 167. (q) Kakiuchi, F.; Chatani, N. *Adv. Synth. Catal.* **2003**, *345*, 1077. (r) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633.

(2) (a) Menon, R. S.; Findlay, A. D.; Bissember, A. C.; Banwell, M. G. *J. Org. Chem.* **2009**, *74*, 8901. (b) Nakao, Y.; Kashihara, N.; Kanyiva, K. S.; Hiyama, T. *J. Am. Chem. Soc.* **2008**, *130*, 16170. (c) Kanyiva, K. S.; Nakao, Y.; Hiyama, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 8872. (d) Watanabe, T.; Oishi, S.; Fujii, N.; Ohno, H. *Org. Lett.* **2007**, *9*, 4821. (e) Liu, X.-Y.; Ding, P.; Huang, J.-S.; Che, C.-M. *Org. Lett.* **2007**, *9*, 2645. (f) Ahlquist, M.; Fabrizi, G.; Cacchi, S.; Norrby, P.-O. *J. Am. Chem. Soc.* **2006**, *128*, 12785. (g) Yadav, J. S.; Reddy, B. V. S.; Padmavani, B.; Gupta, M. K. *Tetrahedron Lett.* **2004**, *45*, 7577. (h) Reetz, M. T.; Sommer, K. *Eur. J. Org. Chem.* **2003**, 3485. (i) Tsuchimoto, T.; Maeda, T.; Shirakawa., E.; Kawakami, Y. *Chem. Commun.* **2000**, 1573. (j) Jia, C.; Piao, D.; Kitamura, T.; Fujiwara, Y. *J. Org. Chem.* **2000**, *65*, 7516. (k) Kido, Y.; Yamaguchi, M. *J. Org. Chem.* **1998**, *63*, 8086.

(3) (a) Jia, C.; Lu, W.; Oyamada, J.; Kitamura, T.; Matsuda, K.; Irie, M.; Fujiwara, Y. *J. Am. Chem. Soc.* **2000**, *122*, 7252. (b) Jia, C.; Piao, D.; Oyamada, J.; Lu, W.; Kitamura, T.; Fujiwara, Y. *Science* **2000**, *287*, 1992.

(4) (a) Mamane, V.; Hannen, P.; Fürstner, A. *Chem.—Eur. J.* **2004**, *10*, 4556. (b) Nevado, C.; Echavarren, A. M. *Chem.—Eur. J.* **2005**, *11*, 3155. (c) Mo, J.; Eom, D.; Lee, E.; Lee, P. H. *Org. Lett.* **2012**, *14*, 3684.

(5) (a) Zotto, C. D.; Wehbe, J.; Virieux, D.; Campagne, J.-M. *Synlett* **2008**, 2033. (b) Zhang, L.; Kozmin, S. A. *J. Am. Chem. Soc.* **2004**, *126*, 10204. (c) Nishizawa, M.; Takao, H.; Yadav, V. K.; Imagawa, H.; Sugihara, T. *Org. Lett.* **2003**, *5*, 4563. (d) Barluenga, J.; González, J. M.; Campos, P. J.; Asensio, G. *Angew. Chem., Int. Ed.* **1988**, *27*, 1546.

(6) (a) Kitamura, T; Otsubo, K. *J. Org. Chem.* **2012**, *77*, 2978. (b) Li, R.; Wang, S. R.; Lu, W. *Org. Lett.* **2007**, *9*, 2219. (c) Shi, Z.; He, C. *J. Org. Chem.* **2004**, *69*, 3669. (d) Jia, C.; Piao, D.; Kitamura, T.; Fujiwara, Y. *J. Org. Chem.* **2000**, *65*, 7516.

10.1021/ol302437v
Published on Web 10/25/2012

Until now, a variety of substrates having linkers such as ethylene ($-CH_2CH_2-$),[5] ester,[6] *N*-tosyl,[7] amide,[8] ether,[9] diethyl malonate,[10] ynamide,[11] and arene[12] between the arene and alkyne have been used in hydroarylation reactions (Figure 1).

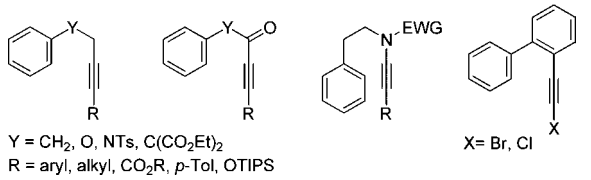
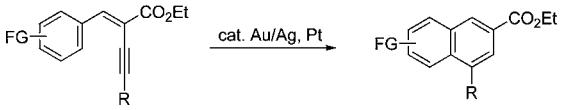


Figure 1. Substrates for intramolecular hydroarylation.

Recently, we developed a stereoselective synthetic method for securing ethyl (*E*)-2-ethynyl/alkynyl cinnamates via DABCO-catalyzed elimination, or a sequential Sonogashira cross-coupling with allenyl acetates.[13] Because polysubstituted naphthalenes have played an important role in the chemical and pharmaceutical industries,[14] the development of new and efficient methodologies for the regioselective synthesis of polysubstituted naphthalenes has attracted much attention.[15] In this regard, we envisioned that treatment of ethyl (*E*)-2-alkynyl cinnamates with a variety of catalysts would give naphthalenes. Moreover, because there are two nucleophilic centers in ethyl (*E*)-2-alkynyl cinnamates, we envisaged that a sharp reversal of the selectivity or reaction pathway would be achieved by varing the catalysts. Rossi et al. reported that 3-[l-(aryl)methylidene]- and 3-(1-alkylidene)-3*H*-furan-2-ones have been synthesized by cyclization of the corresponding (*E*)-2-(1-alkynyl)-3-aryl/alkylpropenoic acids in the presence of Ag- or Pd-catalysts.[16] Although Burton et al. described a synthetic method for synthesizing naphthalenes via Sonogashira reaction of α-bromocinnamates followed by electrocyclization of *in situ* generated allene intermediates, catalyzed by DBU, the reaction conditions are very harsh (NMP, 200 °C).[17] Also, because isomerization of enynes to allenes is necessary to obtain hydroarylated products, *tert*-butyl- or phenyl-substituted aryl enynes did not produce naphthalenes. To overcome the inherent problems of the previously reported method, and develop a new reaction pathway to naphthalenes that depended on variation of the catalyst, we describe herein our results on the selective hydroarylation reaction of a number of aryl enynes with Au- and Pt-catalysts (Scheme 1).

Scheme 1. Transition-Metal-Catalyzed Intramolecular Hydroarylation of Aryl Enynes



We initiated our investigation using ethyl (*E*)-2-ethynyl cinnamate **1a**[13] (Table 1). Although **1a** did not react with $AuCl_3$ (5 mol %) and AgOTf (15 mol %), the hydroarylated product **2a** was obtained in 20% yield in 6-*endo* mode with $AuCl_3$/AgOTf or $Ph_3PAuCl/AgBF_4$ (5 mol % each) in the presence of trifluoromethanesulfonic acid (TfOH, 5 mol %) (entries 1−3). To check the possibility of cyclization by a protic acid, we attempted the cyclization in the presence of TfOH (1 equiv) and found that **2a** was not produced (entry 4). $Pt(PPh_4)_4$ (5 mol %) and $PtCl_2(PPh_3)_2$ (5 mol %) also did not give the cyclized product (entries 5 and 6), while $PtCl_2$ (5 mol %) provided **2a** in 70% yield (entry 7). Of the hydroarylation reactions screened, the best results were obtained with $PtCl_4$ (5 mol %) in toluene at 110 °C for 10 min, which selectively produced **2a** (87%) (entry 8). Toluene was the best solvent among the several examined (toluene, DCM, acetonitrile, and DCE) (enties 8−11).

To demonstrate the efficiency and scope of the present method, we applied this catalytic system to a wide range of ethyl (*E*)-2-ethynyl cinnamate derivatives **1**, and the results

(7) (a) Komeyama, K.; Igawa, R.; Takaki, K. *Chem. Commun.* **2010**, *46*, 1748. (b) Huang, W.; Shen, Q.-S.; Wang, J.-L.; Zhou, X.-G. *J. Org. Chem.* **2008**, *73*, 1586. (c) Nieto-Oberhuber, C.; Muñoz, M. P.; Buñuel, E.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2402. (d) Ishikawa, T.; Manabe, S.; Aikawa, T.; Kudo, T.; Saito, S. *Org. Lett.* **2004**, *6*, 2361. (e) Martín-Matute, B.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *J. Am. Chem. Soc.* **2003**, *125*, 5757.

(8) (a) Shibuya, T.; Shibata, Y.; Noguchi, K.; Tanaka, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 3963. (b) Jiang, T.-S.; Tang, R.-Y.; Zhang, X.-G.; Li, X.-H.; Li, J.-H. *J. Org. Chem.* **2009**, *74*, 6749. (c) Yoon, M. Y.; Kim, J. H.; Choi, D. S.; Shin, U. S.; Lee, J. Y.; Song, C. E. *Adv. Synth. Catal.* **2007**, *349*, 1725. (d) Song, C. E.; Jung, D.-u.; Choung, S. Y.; Roh, E. J.; Lee, S.-g. *Angew. Chem., Int. Ed.* **2004**, *43*, 6183.

(9) (a) Barluenga, J.; Trincado, M.; Marco-Arias, M.; Ballesteros, A.; Rubio, E.; González, J. M. *Chem. Commun.* **2005**, 2008. (b) Pastine, S. J.; Youn, S. W.; Sames, D. *Org. Lett.* **2003**, *5*, 1055. (c) Pastine, S. J.; Youn, S. W.; Sames, D. *Tetrahedron* **2003**, *59*, 8859.

(10) (a) Huang, W.; Zheng, P.; Zhang, Z.; Liu, R.; Chen, Z.; Zhou, X. *J. Org. Chem.* **2008**, *73*, 6845. (b) Inoue, H.; Chatani, N.; Muari, S. *J. Org. Chem.* **2002**, *67*, 1414. (c) Chatani, N.; Inoue, H.; Ikeda, T.; Murai, S. *J. Org. Chem.* **2000**, *65*, 4913.

(11) Zhang, Y.; Hsung, R. P.; Zhang, X.; Huang, J.; Slafer, B. W.; Davis, A. *Org. Lett.* **2005**, *7*, 1047.

(12) (a) Chernyak, N.; Gevorgyan, V. *J. Am. Chem. Soc.* **2008**, *130*, 5636. (b) Yao, T.; Campo, M. A.; Larock, R. C. *Org. Lett.* **2004**, *6*, 2677. (c) Fürstner, A.; Mamane, V. *Chem. Commun.* **2003**, 2112. (d) Fürstner, A.; Mamane, V. *J. Org. Chem.* **2002**, *67*, 6264. (e) Yamaguchi, S.; Swager, T. M. *J. Am. Chem. Soc.* **2001**, *123*, 12087.

(13) (a) Choe, Y.; Lee, P. H. *Org. Lett.* **2009**, *11*, 1445. (b) Kim, H.; Shin, D.; Lee, K.; Lee, S.; Kim, S.; Lee, P. H. *Bull. Korean Chem. Soc.* **2010**, *31*, 742.

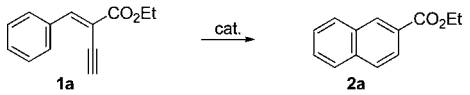
(14) (a) Xie, X.; Kozlowski, M. C. *Org. Lett.* **2001**, *3*, 2661. (b) Terao, Y.; Satoh, T.; Miura, M.; Nomura, M. *Tetrahedron* **2000**, *56*, 1315. (c) Ukita, T.; Nakamura, Y.; Kubo, A.; Yamamoto, Y.; Takahashi, M.; Kotera, J.; Ikeo, T. *J. Med. Chem.* **1999**, *42*, 1293. (d) Zhao, H.; Neamati, N.; Mazumder, A.; Sunder, S.; Pommier, Y.; Burke, T. R., Jr. *J. Med. Chem.* **1997**, *40*, 1186. (e) Eich, E.; Pertz, H.; Kaloga, M.; Schulz, J.; Fesen, M. R.; Mazumder, A.; Pommier, Y. *J. Med. Chem.* **1996**, *39*, 86. (f) Padwa, A.; Chiacchio, U.; Fairfax, D. J.; Kassir, J. M.; Litrico, A.; Semones, M. A.; Xu, S. L. *J. Org. Chem.* **1993**, *58*, 6429. (g) Batt, D. G.; Maynard, G. D.; Petraitis, J. J.; Shaw, J. E.; Galbraith, W.; Harris, R. R. *J. Med. Chem.* **1990**, *33*, 360. (h) Whiting, D. A. *Nat. Prod. Rep.* **1985**, *2*, 191.

(15) (a) de Koning, C. B.; Rousseau, A.; van Otterlo, W. A. L. *Tetrahedron* **2003**, *59*, 7. (b) *Modern Arene Chemistry*; Astruc, D., Ed.; Wiley-VCH: Weinheim, 2002. (c) Katritzky, A. R.; Li, J.; Xie, L. *Tetrahedron* **1999**, *55*, 8263.

(16) Rossi, R.; Bellina, F.; Bechini, C.; Mannina, L.; Vergamin, P. *Tetrahedron* **1998**, *54*, 135.

(17) (a) Wang, Y.; Burton, D. J. *Org. Lett.* **2006**, *8*, 5295. (b) Wang, Y.; Xu, J.; Burton, D. J. *J. Org. Chem.* **2006**, *71*, 7780.

Table 1. Optimization of Intramolecular Hydroarylation



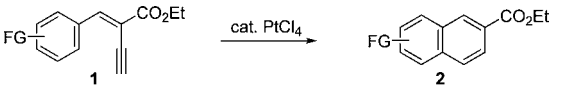
entry	cat.[a] (mol %)	additive (mol %)	solvent	temp (°C)	time (h)	yield (%)[b]
1	$AuCl_3$/AgOTf		DCE	80	5	0
2	$AuCl_3$/AgOTf	TfOH	DCE	50	5	20[c]
3	$Ph_3PAuCl/AgBF_4$	TfOH	DCE	25	24	20[c]
4		TfOH	DCE	25	0.3	0[d]
5	$Pt(PPh_4)_4$		toluene	110	12	0
6	$PtCl_2(PPh_3)_2$		toluene	110	12	0
7	$PtCl_2$		toluene	110	2	70
8	$PtCl_4$		toluene	110	0.2	87
9	$PtCl_4$		CH_2Cl_2	40	4.5	80
10	$PtCl_4$		CH_3CN	80	14	64
11	PtCl		DCE	80	0.2	68

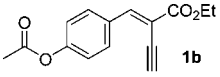
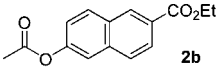
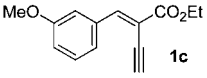
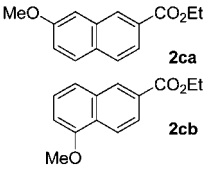
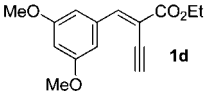
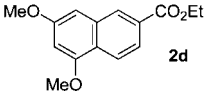
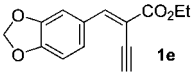
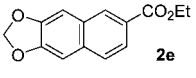
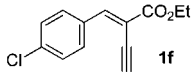
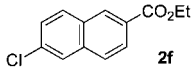
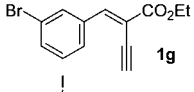
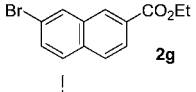
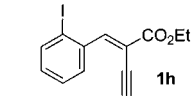
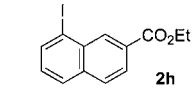
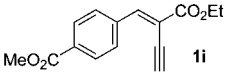
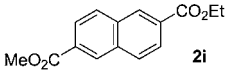
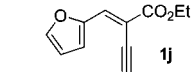
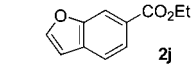
[a] Au and Pt (5 mol % each) were used. AgOTf (15 mol %) and $AgBF_4$ (5 mol %) were used. [b] Isolated yields. [c] TfOH (10 mol %) was used. [d] TfOH (1 equiv) was used.

are summarized in Table 2. Varying the electron demand of the substituents on the phenyl ring did not diminish the efficiency of cyclization. Treatment of enyne **1b** having an acetoxy group on the phenyl ring with $PtCl_4$ (5 mol %) selectively gave the 6-*endo* hydroarylated product **2b** in 74% yield after heating in toluene at 110 °C for 20 min (entry 1). When aryl enyne **1c**, having a 3-methoxy group, was employed as the substrate, theoretically, there could have been two possible products from two different cyclization directions of the corresponding enyne. It was not surprising therefore that ethyl 7-methoxy-2-naphthoate **2ca** and 5-methoxy-2-naphthoate **2cb** were obtained in 71% and 10% yields, respectively (entry 2). Under the optimized reaction conditions, enyne **1d** smoothly cyclized to produce ethyl 5,7-dimethoxy-2-naphthoate **2d** in 70% yield (entry 3). In contrast, enyne **1e** having a 3,4-methylenedioxy group underwent cyclization to produce 6,7-(methylenedioxy)naphthoate **2e** in 75% yield as the sole product, even though two products were possible (entry 4). Moreover, cyclization proceeded smoothly counter-intuitively with enynes having an electron-withdrawing group on the phenyl ring. Aryl enynes **1f**–**h** having a chloride, bromide, and iodide group gave the desired naphthalenes **2f**–**h** in 6-*endo* mode in good yields, without loss of halogen functionality (entries 5–7). Electron-poor arenes possessing a 4-methoxycarbonyl group (**1i**) took part in the hydroarylation reaction, giving rise to the desired product **2i** in 75% yield (entry 8). When enyne **1j** having a 2-furyl group was subjected to the reaction conditions, 5-ethoxycarbonylbenzofuran **2j** was obtained in 67% yield (entry 9).

With this new protocol developed, we subsequently examined a variety of aryl enynes with internal alkynyl groups instead of terminal ones for the Pt-catalyzed intramolecular hydroarylation, because arylnaphthalene lignans occur widely in nature and exhibit various biological

Table 2. Pt-Catalyzed Intramolecular Hydroarylation[a]



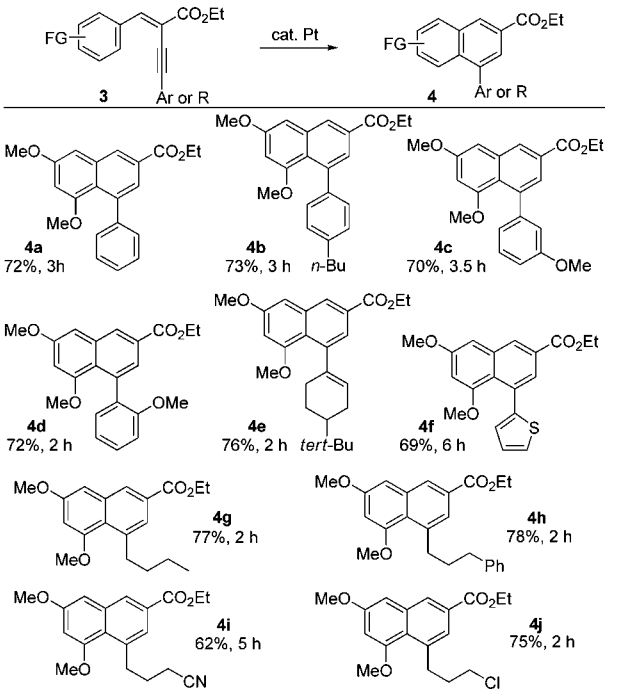
entry	substrate	product	yield (%)[b]
1	 1b	 2b	74
2	 1c	 2ca / 2cb	71 / 10
3	 1d	 2d	70
4	 1e	 2e	75
5	 1f	 2f	71
6	 1g	 2g	80
7	 1h	 2h	74
8	 1i	 2i	75
9	 1j	 2j	67

[a] Reactions were carried out with 5 mol % $PtCl_4$ in toluene at 110 °C within 30 min. [b] Isolated yields.

activities (Scheme 2).[18] Under the optimum reaction conditions, phenyl enyne having a 4-*n*-butylphenyl group on the distal alkynyl carbon gave the cyclized product in 10% yield. In addition, 3,5-dimethoxyphenyl enyne having a 4-ethoxycarbonylphenyl group provided a 23% yield in toluene at 110 °C after 18 h. These results indicate that the reactivity of hydroarylation of aryl enynes having an aryl group on the distal alkynyl carbon is lower than that of aryl enynes **1** having a terminal alkynyl group. On the basis of these results, we next turned our attention to the hydroarylation of 3,5-dimethoxyphenyl enynes bearing a phenyl, aryl with electron-donating substituents, alkyl, or alkenyl group on the distal alkynyl carbon. Gratifyingly, an aryl enyne having a phenyl group underwent cyclization to selectively produce the desired product **4a** in 72% yield in toluene at 110 °C after 3 h. The presence of the 4-*n*-butyl

(18) (a) Foley, P.; Eghbali, N.; Anastas, P. T. *J. Nat. Prod.* **2010**, *73*, 811. (b) Ward, R. S. *Nat. Prod. Rep.* **1999**, *16*, 75. (c) Ward, R. S. *Nat. Prod. Rep.* **1995**, *12*, 183.

Scheme 2. Pt-Catalyzed Intramolecular Hydroarylation of Aryl Enynes[a]

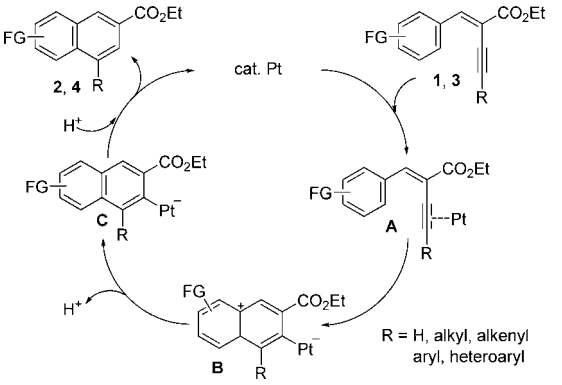


[a] Reactions were carried out with 5 mol % $PtCl_4$ in toluene at 110 °C.

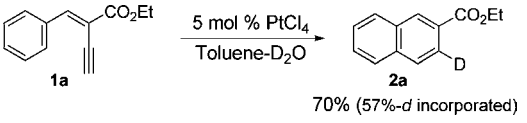
group had little effect on either the reaction rate (3 h) or the product yield (**4b**, 73%). Likewise, aryl enynes having a methoxyphenyl group on the distal alkynyl carbon efficiently cyclized with 5 mol % $PtCl_4$ to afford **4c** and **4d** in 70% and 72% yields, respectively. We were pleased to find that a 3,5-dimethoxy enyne possessing a 4-*tert*-butyl-1-cyclohexenyl group successfully engaged in the hydroarylation reaction. When a cyclization reaction was carried out with an aryl enyne with a 2-thienyl in the presence of 5 mol % $PtCl_4$, the desired naphthalene **4f** was obtained in 69% yield. Under the optimum reaction conditions, 3,5-dimethoxy enynes having an *n*-butyl or 3-phenylpropyl group on the distal alkynyl carbon were smoothly converted to the corresponding naphthalenes **4g** and **4h**. Chloride and nitrile groups are tolerable in the Pt-catalyzed hydroarylation reaction. However, ethyl (*E*)-2-(1-hexyn-1-yl)cinnamate was not cyclized even in the presence of TfOH.

Although the mechanism of the present reaction has not been fully established, a possible pathway for intramolecular Pt-catalyzed hydroarylation is shown in Scheme 3. Because aryl enynes **1** and **3** cannot be isomerized to an allene, the mechanism of the present reaction is different from that of hydroarylation via isomerization of enynes to allenes.[17] Thus, the reaction would be initiated by activation of the alkynyl group by the Pt-catalyst and followed by 6-*endo* cyclization to afford zwitterionic intermediate arylplatinum **B**. Aromatization to arylplatinum **C** and subsequent protonation would provide naphthalene **2** and **4**.

Scheme 3. Plausible Reaction Mechanism



Scheme 4. Deuterium Incorporation in Pt-Catalyzed Hydroarylation



Addition of 10 mol % D_2O to toluene provided **2a** in 70% yield with 57% *d*-incorporation, indicating that the present reaction might proceed through activation of the alkyne by the Pt-catalyst and that **C** might be formed (Scheme 4).

In summary, we have developed an efficient synthetic method for securing functionalized naphthalenes with hydrogen, alkyl, alkenyl, aryl, or heteroaryl groups on the 4-position and an ethoxycarbonyl group on the 2-position through Pt-catalyzed selective 6-*endo* hydroarylation of ethyl (*E*)-2-ethynyl/alkynyl cinnamates. Of special importance, because aryl enynes having a nonisomerizable group on the distal alkynyl carbon were smoothly converted to naphthalenes via Pt-catalyzed hydroarylation incorporated deuterium, the present reaction likely proceeds via arylplatinum intermediates. This method could pave the way to synthetically valuable processes for synthesizing a wide range of naphthalene derivatives.

Acknowledgment. This work was supported by the NCRL (2012-0001245) and BRL program (2009-0087013) funded by the National Research Foundation of Korea. We thank Dr. Sung Hong Kim at the KBSI (Daegu) for obtaining the HRMS data. P.H. thanks Profs. S. Chang (KAIST) and E. J. Yoo (KNU) for helpful discussions.

Supporting Information Available. ^1H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.