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Halohydroxylation of 1-Cyclopropylallenes: An Efficient and Stereoselective Method for the Preparation of Multisubstituted Olefins

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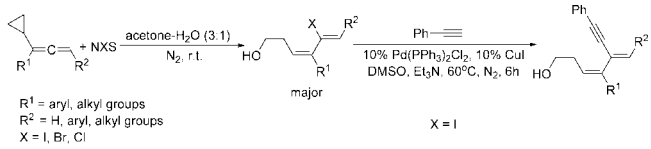

The halohydroxylation of 1-cyclopropylallenes would generate two multisubstituted C=C double bonds and at the same time stereoselectively gives 5-halohexa-3,5-dien-1-ols in moderate to good yields. The latter could be transformed into the corresponding alkynyl-substituted conjugated dienes through the further Sonogashira coupling.

Multisubstituted olefins are ubiquitous and essential structural constituents in organic molecules. Due to the discovery of many multisubstituted olefinic natural products and their broad applications,[1] the stereospecific synthesis of multisubstituted olefins has been one of the most challenging subjects in synthetic organic chemistry for a long time. During the past decade, a variety of novel methods have been developed to synthesize multisubstituted olefins.[2] 1-Cyclopropylallenes,[3] which contain both a cyclopropyl group and an allene structural unit, are a kind of high-activated small organic molecule. Our recent research[4] has found that the electrophilic addition to 1-cyclopropylallenes would provide a convenient and stereoselective method for the synthesis of 2,6-disubstituted-1,3-hexadienes, which contain at least one multisubstituted C=C double bond in their molecules.

Halohydroxylations of the C=C double bond are efficient methods for the preparation of β-halogen substituted alcohols,[5] since the two functional groups, i.e., −X and −OH, could be introduced into substrates at the same time. However, for allenes, the regio- and stereoselectivity would be a formidable challenge to make this methodology feasible. Previously, Ma has reported that introducing a heteroatom such as sulfur or selenium adjacent to allenes would be an effective solution and a series of corresponding 2-halogen-substituted allylic alcohols could be regio- and stereoselectively synthesized via the halohydroxylation of the modified allenes.[6] Encouraged by these works, we are interested in the halohydroxylation of activated olefins. Herein, we wish to report the halohydroxylations of allenes with an adjacent cyclopropyl group introduced as the factor to control the selectivity, which might provide a novel method for the stereoselective synthesis of multisubstituted olefins.

We initially examined the reaction of 1-phenyl-1-cyclopropylallene (**1a**) with I_2 in $CH_2Cl_2-H_2O$ (5:1) at room temperature under nitrogen atmosphere. After stirring for 0.5 h, the anticipated iodohydroxylation product **2a** could be isolated in very low yield while the iodine adduct **3a** was obtained in 56% yield as the major product (entry 1, Table 1). Further screening demonstrated that acetone−H_2O should be a better solvent (entry 3, Table 1). To enhance the yield of **2a**, we increased the ratio of water in solvent (entry 3−7, Table 1). However, the byproduct **3a** could not be totally eliminated, even when the reaction was carried out overnight (entry 6, Table 1). This was due to the existence of iodine anions, which could react with the intermediate homoallylic carbocation. Therefore, we tried to employ some other "I^+" donors, which did not contain iodine anion. When *N*-iodosuccinimide (NIS) was employed as the "I^+" donor, the yield of iodohydroxylation product **2a** was enhanced and the byproduct **3a** could be avoided (entry 8, Table 1).This reaction was highly selective and only *Z*-isomer was obtained. The configuration of **2a** was established by the NOESY spectrum studies (Scheme 1).

[†] Zhejiang University (Xixi Campus).

[‡] Chinese Academy of Sciences.

(1) Selected examples: (a) Negishi, E.; Abramovitch, A. *Tetrahedron Lett.* **1977**, *18*, 411. (b) Onoda, T.; Shirai, R.; Koiso, Y.; Iwasaki, S. *Tetrahedron Lett.* **1995**, *36*, 5765. (c) Ohta, S.; Uno, M.; Yoshimura, M.; Hiraga, Y.; Ikegami, S. *Tetrahedron Lett.* **1996**, *37*, 2265. (d) Jordan, V. C. *Nat. Rev. Drug Discovery* **2003**, *2*, 205. (e) Robertson, D. W.; Katzenellenbogen, J. A. *J. Org. Chem.* **1982**, *47*, 2387. (f) Kido, J.; Shionoya, H.; Nagai, K. *Appl. Phys. Lett.* **1995**, *67*, 2281. (g) Kim, J.-H.; Noh, S.; Kim, K.; Lim, S.-T.; Shin, D.-M. *Synth. Met.* **2001**, *117*, 227.

(2) Selected recent articles: (a) McKinley, N. F.; O'Shea, D. F. *J. Org. Chem.* **2006**, *71*, 9552. (b) Ma, S.-M.; Negishi, E. *J. Org. Chem.* **1997**, *62*, 784. (c) Asao, N.; Yoshikawa, E.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 4874. (d) Konno, T.; Daitoh, T.; Noiri, A.; Chae, J.; Ishihara, T.; Yamanaka, H. *Org. Lett.* **2004**, *6*, 933. (e) Yamagami, T.; Shintani, R.; Shirakawa, E.; Hayashi, T. *Org. Lett.* **2007**, *9*, 1045. (f) Shindo, M.; Matsumoto, K.; Mori, S.; Shishido, K. *J. Am. Chem. Soc.* **2002**, *124*, 6840. (g) Yamago, S.; Fujita, K.; Miyoshi, M.; Kotani, M.; Yoshida, J. *Org. Lett.* **2005**, *7*, 909. (h) Itami, K.; Ushiogi, Y.; Nokami, T.; Ohashi, Y.; Yoshida, J. *Org. Lett.* **2004**, *6*, 3695. (i) Nishihara, Y.; Miyasaka, M.; Okamoto, M.; Takahashi, H.; Inoue, E.; Tanemura, K.; Takagi, K. *J. Am. Chem. Soc.* **2007**, *129*, 12634. (j) Itami, K.; Nokami, T.; Ishimura, Y.; Misudo, K.; Kamei, T.; Yoshida, J. *J. Am. Chem. Soc.* **2001**, *123*, 11577.

(3) 1-Cyclopropylallenes could be conveniently prepared by the classical reaction of cyclopropyl Grignard reagent with toluene-4-sulfonic acid prop-2-ynyl ester catalyzed by copper(I) bromide. For details see: Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumlenes*; Elsevier: Amsterdam, The Netherlands, 1981.

(4) (a) Yu, L.; Meng, B.; Huang, X. *Synlett* **2007**, 2919. (b) Yu, L.; Meng, B.; Huang, X. *Synlett* **2008**, 1331.

(5) (a) Cabanal-Duvillard, I.; Berrien, J.; Royer, J.; Husson, H. *Tetrahedron Lett.* **1998**, *39*, 5181. (b) Rossen, K.; Reamer, R. A.; Volante, R. P.; Reider, P. J. *Tetrahedron Lett.* **1996**, *37*, 6843. (c) Mevellec, L.; Evers, M.; Huet, F. *Tetrahedron* **1996**, *52*, 15103. (d) Sawyer, D. T.; Hage, J. P.; Sobkowiak, A. *J. Am. Chem. Soc.* **1995**, *117*, 106. (e) Fu, H.; Kondo, H.; Ichikawa, Y.; Look, G. C.; Wong, C. *J. Org. Chem.* **1992**, *57*, 7265. (f) Lai, J.; Wang, F.; Guo, G.; Dai, L. *J. Org. Chem.* **1993**, *58*, 6944. (g) Rodebaugh, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1994**, *116*, 3155. (h) Yamashita, M.; Iida, A.; Ikai, K.; Oshikawa, T.; Hanaya, T.; Yamamoto, H. *Chem. Lett.* **1992**, 407. (i) Kato, T.; Hirukawa, T.; Namiki, K. *Tetrahedron Lett.* **1992**, *33*, 1475.

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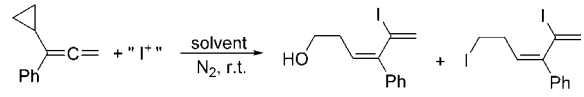
TABLE 1. Optimization of the Reaction Conditions of the Iodohydroxylation of 1-Phenyl-1-cyclopropylallene (1a)[a]

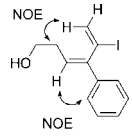


1a 2a 3a

entry	" I^+ "	solvent	time (h) [b]	yield of **2**[a] (%)[c]	yield of **3a** (%)[c]
1	I_2	$CH_2Cl_2-H_2O$ (5:1)	0.5	24	56
2	I_2	$CHCl_3-H_2O$ (5:1)	0.5	17	58
3	I_2	acetone$-H_2O$ (5:1)	1	34	41
4	I_2	acetone$-H_2O$ (4:1)	1	40	36
5	I_2	acetone$-H_2O$ (3:1)	2	51	34
6	I_2	acetone$-H_2O$ (3:1)	24	64	25
7	I_2	acetone$-H_2O$ (2:1)	3	41	18
8	NIS	acetone$-H_2O$ (3:1)	3	76	0
9	NIS	CH_3CN-H_2O (3:1)	5	trace[d]	0

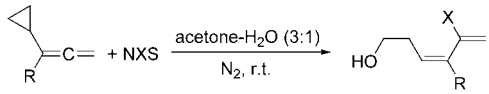
[a] 0.3 mmol of **1a** and 0.3 mmol of "I^+" reagent and 2 mL of solvent were employed. [b] The reaction was monitored by TLC (eluent: petroleum ether). [c] Isolated yields. [d] Only unidentified complex mixtures were obtained.

SCHEME 1. Configuration of *Z*-2a



Z-2a

TABLE 2. Halohydroxylations of 1-Cyclopropylallenes (1)



1 2

entry	R	X	time (h) [a]	yield of **2** (%)[b]
1	C_6H_5 (**1a**)	I	3	76 (**2a**)
2	*o*-$CH_3C_6H_4$ (**1b**)	I	3	70 (**2b**)
3	*m*-$CH_3C_6H_4$ (**1c**)	I	3	75 (2[c])
4	*p*-$CH_3C_6H_4$ (**1d**)	I	2	82 (**2d**)
5	*p*-ClC_6H_4 (**1e**)	I	4	67 (**2e**)
6	Bn (**1f**)	I	3	53 (**2f**) (*Z*/*E* = 82:18)[c]
7	C_6H_5 (**1a**)	Br	3	78 (**2g**)
8	*m*-$CH_3C_6H_4$ (**1c**)	Br	3	65 (**2h**)
9	C_6H_5 (**1a**)	Cl	4	46 (**2i**)

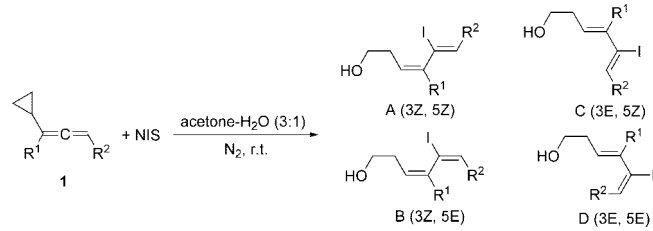
[a] The reaction was monitored by TLC (eluent: petroleum ether). [b] Isolated yields. [c] The ratio of *Z*/*E* was calculated from ^1H NMR spectrum.

We next examined the application scope of this reaction under the optimized conditions. When R = aryl groups, the iodohydroxylation reaction proceeded smoothly and the corresponding *Z*-5-iodo-hexa-3,5-dien-1-ols (**2**) could be synthesized in moderate to good yields (entries 1−5, Table 2). When R = Bn, the yield of **2f** was obliviously decreased and the reaction selectivity was a little poorer (entry 6, Table 2). Similarly, NBS and NCS could also be employed as the halogen cation donor to give the corresponding 5-bromo- or 5-chlorohexa-3,5-dien-1-ols (entries 7−9, Table 2).

Accordingly, the halohydroxylation of 1-cyclopropylallenes would create a multisubstituted C=C double bond in product

(6) (a) Ma, S.-M.; Hao, X.-S.; Huang, X. *Chem. Commun.* **2003**, 1082. (b) Ma, S.-M.; Hao, X.-S.; Huang, X. *Org. Lett.* **2003**, *5*, 1217. (c) Ma, S.-M.; Ren, H.-J.; Wei, Q. *J. Am. Chem. Soc.* **2003**, *125*, 4817. (d) Ma, S.-M.; Wei, Q.; Wang, H. *Org. Lett.* **2000**, *2*, 3893.

TABLE 3. Iodohydroxylations of 1,3-Disubstituted-1-cyclopropylallenes

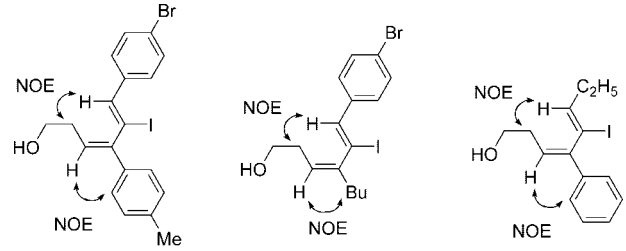


1 isomers of **2**

entry	R^1, R^2	time (h) [a]	yield of **2** (%)[b] (A/B/C/D)[c]
1	C_6H_5, *p*-BrC_6H_4 (**1g**)	2	78 (86:7:5:2) (**2j**)
2	*o*-$CH_3C_6H_4$, *p*-BrC_6H_4 (**1h**)	3	63 (99:0:1:0) (**2k**)
3	*m*-$CH_3C_6H_4$, *p*-BrC_6H_4 (**1i**)	3	60 (99:0:1:0) (**2l**)
4	*p*-$CH_3C_6H_4$, *p*-BrC_6H_4 (**1j**)	2	85 (83:10:7:0) (**2m**)
5	*p*-ClC_6H_4, *p*-BrC_6H_4 (**1k**)	4	72 (82:11:7:0) (**2n**)
6	*n*-C_4H_9, *p*-BrC_6H_4 (**1l**)	4	19 (42:16:32:10) (**2o**)
7	C_6H_5, C_6H_5 (**1m**)	3	80 (78:11:10:1) (**2p**)
8	C_6H_5, *p*-$CH_3C_6H_4$ (**1n**)	2	75 (86:6:6:2) (**2q**)
9	C_6H_5, *p*-ClC_6H_4 (**1o**)	3	71 (91:0:9:0) (**2r**)
10	C_6H_5, C_2H_5 (**1p**)	3	86 (56:44:0:0) (**2s**)

[a] The reaction was monitored by TLC (eluent: petroleum ether). [b] Isolated yields. [c] The ratio of the isomers was calculated from ^1H NMR spectrum.

SCHEME 2. Configurations of 3*Z*,5*Z*-2m, 2o, and 2s



3*Z*, 5*Z* - **2m** 3*Z*, 5*Z* - **2o** 3*Z*, 5*Z* - **2s**

2 stereoselectively. It is obvious that if the distally substituted substrate **1** were employed, the possible halohydroxylation products **2** would contain two multisubstituted C=C double bonds. The stereospecific synthesis of two multisubstituted C=C double bonds at the same time is a much more challenging subject. Hence, we tried to examine the iodohydroxylation of the distally substituted substrate **1**.

Initially, we employed 1-phenyl-3-(*p*-bromophenyl)-1-cyclopropylallene (**1g**) as substrate and the expected product **2j** could be obtained in 78% yield smoothly (entry 1, Table 3). Further experimental results showed that when R^1 and R^2 are both aryl groups, the selectivity of this reaction was generally good and the 3*Z*,5 *Z* isomers were obtained as the overwhelming major product in moderate to good yields (entries 1−5 and 7−9, Table 3). When R^1 = *n*-C_4H_9, both the yield of **2** and the reaction stereoselectivity clearly declined (entry 6, Table 3). When R^2 = C_2H_5, the stereoselectivity on the 5-position C=C double bond declined and both of the 3*Z*,5*Z* and 3*Z*,5*E* isomers were obtained (entry 10, Table 3). The configurations of the 3*Z*,5*Z* isomers of **2m**, **2o**, and **2s** were established by the NOESY spectrum studies (Scheme 2).

A possible mechanism of this reaction was shown in Scheme 3. Electrophilic addition of halogen cation to **1** would give the intermediate allylic carbon cation **4**, which could

SCHEME 3. Possible Mechanism of the Halohydroxylation

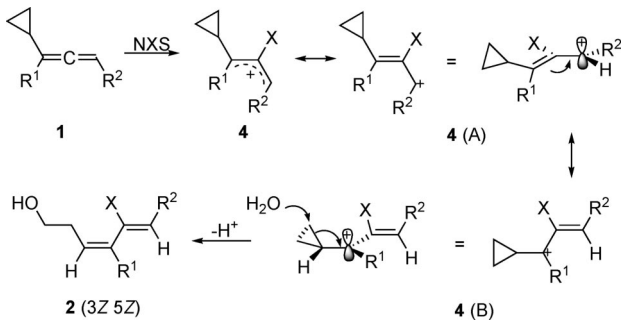
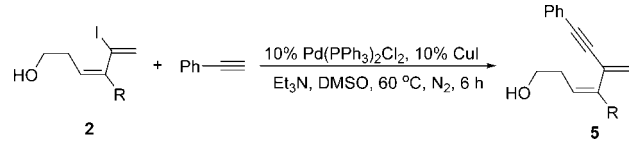


TABLE 4. Sonogashira Coupling of 2



entry	R	yield of **5** (%)[a]
1	C_6H_5 (**2a**)	94(**5a**)
2	*m*-$CH_3C_6H_4$ (**2c**)	85(**5b**)
3	*p*-$CH_3C_6H_4$ (**2d**)	90(**5c**)
4	*p*-ClC_6H_4 (**2e**)	81(**5d**)
5	Bn (**2f**)	87(**5e**)

[a] Isolated yields.

be **4**(A) and **4**(B) in resonance.[4] In **4**(A), R^2 was inclined to be at the same side as X due to the steric hindrance factor while in **4**(B), R^1 was inclined to be at the same side as the hydrogen atom. These determined the configuration of the 3-position and 5-position C=C double bonds in product **2**.[7] Further reaction of **4**(B) with water would give the final product **2** in 3*Z*,5*Z* configuration as the overwhelming major product (Scheme 3). When R^1 = alkyl group, the carbon cation in **4**(B) could not be well stabilized. Thus, the yield of **2** declined (entry 6, Table 3). Meanwhile, when R^1 or R^2 were lower steric hindrance groups, the selectivity on the 3-position and 5-position C=C double bonds declined respectively (entry 6, Table 2 and entries 6 and 10, Table 3).

Containing both a conjugated diene structural unit and a homoallylic structural unit, **2** might be of potential value in organic synthesis.[8,9] Moreover, the Sonogashira coupling[10] of **2** with alkyne could give alkynyl-substituted conjugated dienes in good to excellent yields (Table 4).

Alkynyl-substituted conjugated dienes are very important organic compounds, in part because of their applications in Diels–Alder reactions and exploration of materials for electronic and photonic applications,[11] and in part because of their existence in many chromophores as a substructure.[12] Recently, the synthesis of alkynyl-substituted conjugated dienes has been widely reported.[13] Here, we developed a novel and convenient method for the synthesis of these analogues.

In conclusion, we reported the halohydroxylation of 1-cyclopropylallenes. The selectivity of this reaction was good and two multisubstituted C=C double bonds could be generated at the same time stereoselectively to give 5-halohexa-3,5-dien-1-ols. Further Sonogashira coupling of 5-iodohexa-3,5-dien-1-ols would give the corresponding alkynyl-substituted conjugated dienes in high yield. All of these analogues are useful in organic synthesis.

Experimental Section

General Procedure for the Halohydroxylation of 1-Cyclopropylallenes. In a Schlenk tube, 0.3 mmol of **1** was dissolved in 2 mL of acetone–H_2O (3:1) under nitrogen atmosphere. Then, 0.3 mmol of NXS was added slowly. The mixture was stirred at room temperature and the reaction was monitored by TLC (eluent: petroleum ether). When the reaction terminated, the solvent was evaporated under vacuum and the residue was isolated by preparative TLC (eluent: petroleum:EtOAc 4:1) to give the corresponding product **2**. Compound **2a**: Yellow oil. IR (film): 3352, 2924, 2876, 1603, 1444, 1088, 1047, 907, 763, 697 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.30–7.44 (m, 5H), 6.22 (s, 1H), 6.20 (s, 1H), 5.93 (t, J = 7.6 Hz, 1H), 3.78 (t, J = 6.8 Hz, 2H), 2.54–2.59 (m, 2H), 1.64 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 33.3, 61.7, 103.0, 125.3, 126.5, 127.9, 128.4, 130.6, 137.5, 146.1. MS (EI, 70 eV): *m*/*z* (%) 300 (10) [M^+], 173 (44), 141 (100). HRMS (EI): *m*/*z* calcd for $C_{12}H_{13}OI$ 300.0011, found 300.0019.

General Procedure for the Sonogashira Coupling. Under nitrogen atmosphere, 0.2 mmol of **2**, 0.4 mmol of alkyne, 0.5 mL of DMSO, and 0.5 mL of newly distilled Et_3N were added to a Schlenk tube. Then, 0.02 mmol of $Pd(PPh_3)_2Cl_2$ and 0.02 mmol of CuI were added. The mixture was stirred at 60 °C. After 6 h, the reaction liquid was cooled to room temperature and quenched with 5 mL of water. The mixture was extracted with EtOAc (3 × 5 mL) and the combined organic layer was washed two times with 5 mL of saturated NaCl solution. After drying with $MgSO_4$, the solvent was evaporated under vacuum and the residue was purified with TLC (eluent: petroleum ether: EtOAc 4:1) to give the corresponding product **5**. Compound **5a**: Yellow oil. IR (film): 3384, 3057, 2926, 1724, 1598, 1490, 1443, 1099, 1047, 913, 875 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.26–7.49 (m, 10H), 5.99 (t, J = 7.6 Hz, 1H), 5.91 (s, 1H), 5.47 (s, 1H), 3.80 (t, J = 6.4 Hz, 2H), 2.66–2.71 (m, 2H), 1.60 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 33.2, 62.4, 89.5, 89.6,

(7) Siriwardana, A. I.; Nakamura, I.; Yamamoto, I. *Tetrahedron Lett.* **2003**, *44*, 985.

(8) Selected recent articles about conjugated dienes: (a) Zhou, C.; Fu, C.-L.; Ma, S.-M. *Tetrahedron* **2007**, *63*, 7612. (b) Shi, M.; Wang, B.-Y.; Huang, J.-W. *J. Org. Chem.* **2005**, *70*, 5606. (c) Wong, K.; Hung, Y. *Tetrahedron Lett.* **2003**, *44*, 8033. (d) Taylor, D. K.; Avery, T. D.; Greatrex, B. W.; Tiekink, E. R. T.; Macreadie, I. G.; Macreadie, P. I.; Humphries, A. D.; Kalkanidis, M.; Fox, E. N.; Klonis, N.; Tilley, L. *J. Med. Chem.* **2004**, *47*, 1833.

(9) Selected recent articles about homoallylic compounds: (a) Shi, M.; Xu, B. *Org. Lett.* **2002**, *4*, 2145. (b) Xu, B.; Shi, M. *Org. Lett.* **2003**, *5*, 1415. (c) Liu, L.-P.; Shi, M. *J. Org. Chem.* **2004**, *69*, 2805. (d) Huang, J.-W.; Shi, M. *Tetrahedron* **2004**, *60*, 2057. (e) Huang, X.; Yu, L. *Synlett* **2005**, 2953. (f) Chen, Y.; Shi, M. *J. Org. Chem.* **2004**, *69*, 426. (g) Huang, J.-W.; Shi, M. *Tetrahedron Lett.* **2003**, *44*, 9343. (h) Shao, L.-X.; Huang, J.-W.; Shi, M. *Tetrahedron* **2004**, *60*, 11895. (i) Zhou, H.-W.; Huang, X.; Chen, W.-L. *Synlett* **2003**, 2080.

(10) Negishi, E.; de Meijere, A. ; et al. *Organopalladium Chemistry for Organic Synthesis*; Wiley: New York, 2002; pp 493–529, and references cited therein.

(11) (a) Hopf, H.; Jager, H.; Ernst, L. *Liebigs Ann.* **1996**, 815. (b) Kros, A.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. *Adv. Mater.* **2002**, *14*, 1779. (c) Carroll, R. L.; Gorman, C. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 4378. (d) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537. (e) Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791. (f) Liphardt, M.; Goonesekera, A.; Jones, B. E.; Ducharme, S.; Takacs, J. M.; Zhang, L. *Science* **1994**, *263*, 367. (g) Miller, J. S. *Adv. Mater.* **1993**, *5*, 671. (h) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628. (i) Nalwa, H. S. *Adv. Mater.* **1993**, *5*, 341. (j) Buckley, A. *Adv. Mater.* **1992**, *4*, 153.

(12) (a) Michinobu, T.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Frank, B.; Moonen, N. N. P.; Gross, M.; Diederich, F. *Chem.-Eur. J.* **2006**, *12*, 1889. (b) Pahadi, N. K.; Camacho, D. H.; Nakamura, I.; Yamamoto, Y. *J. Org. Chem.* **2006**, *71*, 1152. (c) Michinobu, T.; May, J. C.; Lim, J. H.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Gross, M.; Biaggio, I.; Diederich, F. *Chem. Commun.* **2005**, 737.

(13) (a) Shao, L.-X.; Shi, M. *J. Org. Chem.* **2005**, *70*, 8635. (b) Kim, M.; Miller, R. L.; Lee, D. *J. Am. Chem. Soc.* **2005**, *127*, 12818. (c) Sim, S. O.; Park, H.-J.; Lee, S. I.; Chung, Y. K. *Org. Lett.* **2008**, *10*, 433.

122.9, 126.1, 126.6, 126.9, 127.3, 128.1, 128.2 (d), 128.8, 131.5, 140.0, 142.0. MS (EI, 70 eV): *m*/*z* (%) 274 (90) [M^+], 259 (66), 228 (100). HRMS (EI): *m*/*z* calcd for $C_{20}H_{18}O$ 274.1358, found 274.1370.

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Supporting Information Available: General experimental procedures and spectroscopic data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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