Organic LETTERS

Letter

pubs.acs.org/OrgLett

Synthesis of Substituted Benzenes via $Bi(OTf)_3$-Mediated Intramolecular Carbonyl Allylation of α-Prenyl or α-Geranyl β-Arylketosulfones

Meng-Yang Chang,* Yu-Chieh Cheng, and Yi-Ju Lu

Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung 80708, Taiwan

Supporting Information

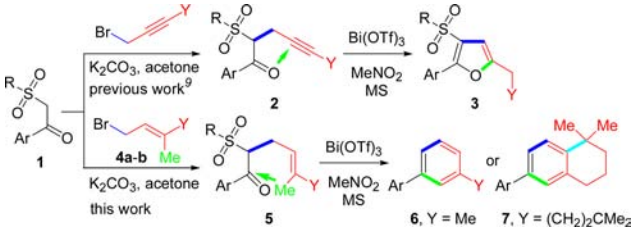
ABSTRACT: Intramolecular carbonyl allylation of α-prenyl or α-geranyl β-arylketosulfones **5** in the presence of molecule sieves (MS) affords substituted benzenes **6**–**7** in moderate to good yields. The facile transformation proceeds by a synthetic sequence starting with the α-prenylation or α-geranylation of **1** and the $Bi(OTf)_3$-mediated annulation of **5** followed by a sequential desulfonative aromatization or then an intramolecular Friedel–Crafts alkylation. A plausible mechanism has been studied and proposed.

$Bi(OTf)_3$ as a Lewis acid has been used in a growing number of synthetic applications,[1] including Mukaiyama-type reaction,[2] hydroamination,[3] alkylation,[4] benzannulation,[5] oxidation,[6] and other reactions.[7] For catalytic transformations, the low toxicity of $Bi(OTf)_3$ and its reasonably low cost make this bismuth salt attractive. However, new $Bi(OTf)_3$-mediated synthetic conversions that create a new C–C bond represent a continuing need in the organic field. In continuation of our investigations on the $Bi(OTf)_3$-mediated conversion of γ-alkynones **2** (derived from α-propargylation of β-ketosulfones **1**[8]) into 2-arylfurans **3**,[9a] the novel one-pot synthesis of substituted benzenes **6** and tetralins **7** has been studied here via the process of α-prenylation or α-geranylation of **1** with bromides **4a** or **4b**, $Bi(OTf)_3$-mediated intramolecular carbonyl allylation of **5** in $MeNO_2$, and sequential desulfonative aromatization or Friedel–Crafts alkylation (see Scheme 1).

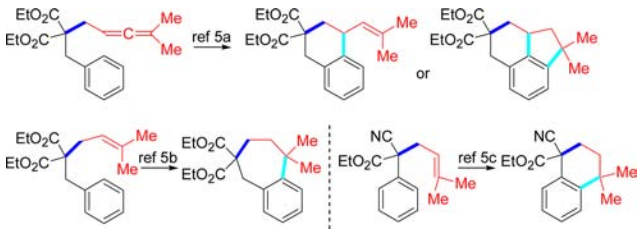
Recently, Dunach et al. reported atom-economic synthetic routes toward tetralins and benzosuberans via the $Bi(OTf)_3$-catalyzed intramolecular hydroarylation of 1,3-dicarbonyl synthons with an α-allenyl or α-prenyl motif (see Scheme 2).[5] A novel catalytic $Bi(OTf)_3$-mediated annulation route to substituted benzenes has been developed via metal triflate mediated reactions.[9] Similarly, Narender et al. have also reported a synthesis of biaryls via the Al(III)-catalyzed domino reaction of prenylated acetophenone.[10] The construction of substituted benzenes is of great interest because they constitute useful building blocks in organic and medicinal chemistry.[11] However, transition metal-mediated reactions are the most popular route to such compounds among the existing methods, especially Suzuki-Miyaura coupling[12] or Reppe alkyne cyclotrimerization.[13]

To explore the one-pot transformation from **5** to **6**–**7**, α-prenylation of **1a** (R = Tol, Ar = Ph) with prenyl bromide (**4a**,

Scheme 1. Synthetic Applications of 1



Scheme 2. $Bi(OTf)_3$-Mediated Hydroarylation by Dunach

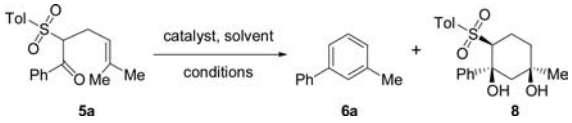


Received: May 19, 2015
Published: June 11, 2015

DOI: 10.1021/acs.orglett.5b01461
Org. Lett. 2015, 17, 3142–3145

Y = Me) was first examined. In the presence of K_2CO_3, a reaction of **1a** with **4a** afforded **5a** in a 90% yield in boiling acetone for 8 h. Furthermore, the use of various metal triflates was investigated in the presence of MS for the intramolecular annulation of **5a**. Among the screened catalysts, which included AgOTf, $Mg(OTf)_2$, $Ni(OTf)_2$, $Sn(OTf)_2$, $Zn(OTf)_2$, $Fe(OTf)_3$, $Yb(OTf)_3$, $Sm(OTf)_3$, $Ga(OTf)_3$, $La(OTf)_3$, $Sc(OTf)_3$, and $Bi(OTf)_3$, only $Bi(OTf)_3$ provided a 62% yield of *m*-phenyltoluene (**6a**) along with a 15% yield of **8** in $MeNO_2$ at 25 °C for 8 h (see Table 1, entry 1). Under these conditions,

Table 1. Reaction Conditions[a]



5a 6a 8

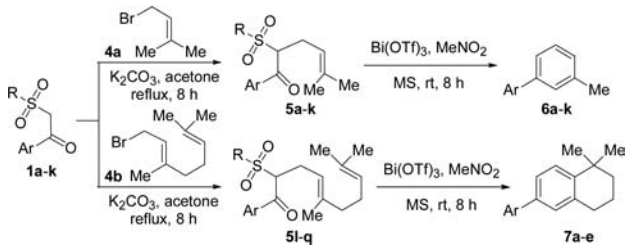
entry	catalyst (mol %), solvent (mL), temp (°C)	yield (%)[b] 6a/8
1	$Bi(OTf)_3$ (2), $MeNO_2$ (5), 25	62/15
2	$BiBr_3$ (2), $MeNO_2$ (5), 25	–/–[c]
3	Bi_2O_3 (2), $MeNO_2$ (5), 25	–/–[c]
4	$Bi(OAc)_3$ (2), $MeNO_2$ (5), 25	–/–[c]
5	$Bi(OTf)_3$ (5), $MeNO_2$ (5), 25	60/20
6	$Bi(OTf)_3$ (2), $MeNO_2$ (10), 25	50/28
7	$Bi(OTf)_3$ (2), $MeNO_2$ (5), 70	65/23
8	$Bi(OTf)_3$ (2), $MeNO_2$ (5), 25[d]	70/12
9	$Bi(OTf)_3$ (2), $(CH_2Cl)_2$ (5), 25	–/–[c]
10	$Bi(OTf)_3$ (2), benzene (5), 25	–/–[c]
11	$Bi(OTf)_3$ (2), dioxane (5), 25	–/–[c]
12	$Bi(OTf)_3$ (2), $MeNO_2$ (5, dry),[e] 25	86/–
13	$Bi(OTf)_3$ (2), $MeNO_2$ (5, wet),[f] 25	28/61

[a]The reactions were run on a 1.0 mmol scale with **5a** for 8 h. [b]Isolated yields. [c]**5a** was recovered. [d]40 h. [e]MS (4 Å, 100 mg) was added. [f]H_2O (0.1 mL) was added.

the recovery of **5a** only was observed for other metal triflates. The use of other Bi(III) salts was examined for the synthesis of **6a**. When **5a** was treated with $BiBr_3$, Bi_2O_3 or $Bi(OAc)_3$, recovery of **5a** was observed (entries 2–4). In comparison with these Bi(III) salts, $Bi(OTf)_3$ is a better catalyst for the generation of **6a**. With the use of $Bi(OTf)_3$ as the catalyst, variation of the equivalents, reaction concentration, solvents and temperature was next studied. When 5 mol % of $Bi(OTf)_3$ was used (entry 5), the yield and ratio of **6a** and **8** were similar to when 2 mol % was used. After decreasing the reaction concentration (5 → 10, entry 6), the ratio of **6a** to **8** was 2:1. No obvious changes occurred at elevated temperature (25 → 70, entry 7). Elongating the reaction time (8 → 40, entry 8) increased the isolated ratio to 6:1. After changing the solvents (from $MeNO_2$ to $(CH_2Cl)_2$, benzene or dioxane), a sluggish conversion was achieved (entries 9–11). Entry 12 shows that the addition of molecular sieves increased the yield of **6a**. In contrast, the use of water generated **8** (61%) as the major product along with 28% of **6a** (entry 13). The structure of **8** was determined by single-crystal X-ray crystallography.[14]

The introduction of water caused a competition between hydration (for **8** with a cyclohexane-1,3-diol skeleton) and aromatization (for **6a** with a benzene skeleton) during the $Bi(OTf)_3$-mediated process. Overall, we envisioned that the system of $Bi(OTf)_3/MeNO_2/MS$ would provide an optimal combination for the formation of **6a** via C–H cycloallylation of **5a**. Among the methods for allylic C–H activation, the S_N2' electrophilic cross-coupling of allylpalladium species with electron-rich molecules is a major pathway and has been used for amination, oxidation, and alkylation.[15] To the best of our knowledge, no literature on Bi(III)-mediated intramolecular allylic C–H cycloannulation of *β*-ketosulfones with an *α*-prenyl or *α*-geranyl has been reported. With the optimized conditions (Table 1, entry 12), we further explored the substrate scope of the reaction, and the results are shown in Table 2.

Table 2. Synthesis of 6 and 7[a,b]



entry	1, Ar =, R = ; 4a or 4b	yield (%)[c] 5	6/7
1	**1a**, Ph, Tol; **4a**	**5a**, 90	**6a**, 86
2	**1b**, 4-FC_6H_4, Tol; **4a**	**5b**, 92	**6b**, 82
3	**1c**, 4-$MeOC_6H_4$, Tol; **4a**	**5c**, 89	**6c**, 80
4	**1d**, 4-MeC_6H_4, Tol; **4a**	**5d**, 88	**6d**, 82
5	**1e**, 3-$NO_2C_6H_4$, Tol; **4a**	**5e**, 84	**6e**, 78
6	**1f**, 4-$NO_2C_6H_4$, Tol; **4a**	**5f**, 83	**6f**, 76
7	**1g**, 4-$CF_3C_6H_4$, Tol; **4a**	**5g**, 86	**6g**, 80
8	**1h**, 4-PhC_6H_4, Tol; **4a**	**5h**, 86	**6h**, 85
9	**1i**, 2-naphthalene,Tol; **4a**	**5i**, 87	**6i**, 85
10	**1j**, 4-$MeOC_6H_4$, Ph; **4a**	**5j**, 84	**6c**, 82
11	**1k**, 4-$MeOC_6H_4$, Me; **4a**	**5k**, 89	**6c**, 82
12	**1a**, Ph, Tol; **4b**	**5l**, 82	**7a**, 78
13	**1b**, 4-FC_6H_4, Tol; **4b**	**5m**, 86	**7b**, 73
14	**1c**, 4-$MeOC_6H_4$, Tol; **4b**	**5n**, 87	**7c**, 75
15	**1l**, 4-PhC_6H_4, Me; **4b**	**5o**, 84	**7d**, 76
16	**1i**, 2-naphthalene,Tol; **4b**	**5p**, 86	**7e**, 77
17	**1k**, 4-$MeOC_6H_4$, Me; **4b**	**5q**, 82	**7c**, 73

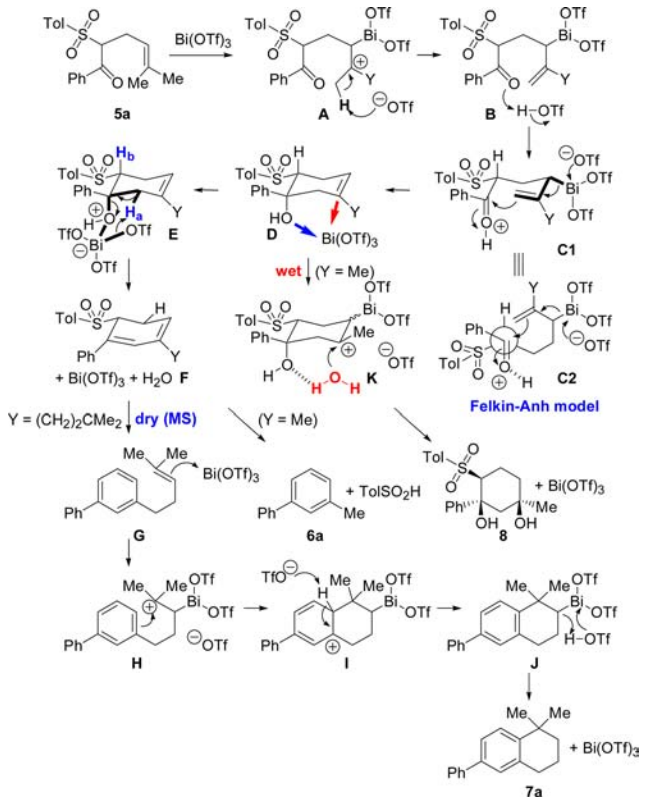
[a]The reactions were run on a 1.0 mmol scale with **1**, K_2CO_3 (2.9 mmol), **4a–b** (1.05 mmol), acetone (10 mL), reflux, 8 h. [b]The reactions were run on a 1.0 mmol scale with **5**, $Bi(OTf)_3$ (0.02 mmol), MS (4 Å, 100 mg), $MeNO_2$ (5 mL), 25 °C, 8 h. [c]Isolated yield.

For the Ar and R groups of **1** (Ar = Ph, 4-FC_6H_4, 4-$MeOC_6H_4$, 4-MeC_6H_4, 3-$NO_2C_6H_4$, 4-$NO_2C_6H_4$, 4-$CF_3C_6H_4$, 4-PhC_6H_4, 2-naphthalene; R = 4-MeC_6H_4, Ph, Me), the phenyl ring, with both electron-withdrawing and electron-donating substituents, was well tolerated, and provided the desired products **5** and **6**–**7** in moderate to good yields. When using 1.05 equiv of prenyl bromide (**4a**) or geranyl bromide (**4b**), **5a–q** were typically obtained in good yields (entries 1–17). The one-pot intramolecular carbonyl allylation of **5a–q** with the combination of $Bi(OTf)_3/MeNO_2/MS$ was also examined. All entries showed that **6a–i** and **7a–e** were isolated in 76%–86% and 73%–78% yields when Ar and R were aryl or alkyl groups. Different substituents did not affect the procedure, and the isolated yield was maintained. No obvious yield changes were exhibited for the generation of **6a–i** and **7a–e**. The structure of **7d** was determined by single-crystal X-ray crystallography.[14]

DOI: 10.1021/acs.orglett.5b01461
Org. Lett. 2015, 17, 3142–3145

On the basis of the results, a possible reaction mechanism is shown in Scheme 3. Mechanistically, the sequence initiates with

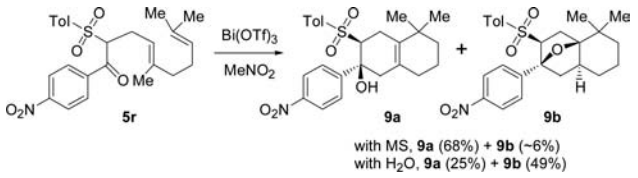
Scheme 3. Possible Mechanism



the formation of tertiary carbocation **A** by complexation of an alkenyl motif of **5a** with $Bi(OTf)_3$. Participation of a triflate anion leads to a Hofmann intermediate **B** with an allylic bismuth motif via abstraction of a less sterically hindered proton (E_2 elimination). Protonation of **B** with *in situ* generated HOTf gives **C1**. On the basis of the Felkin-Anh model,[16] an intramolecular nucleophilic addition of **C2** by the methylene group leads to an alternative tertiary alcohol intermediate via a six-membered ring closure. Following debismuthation by the triflate anion, **D** is obtained. After the $Bi(OTf)_3$-mediated chelation of **D** (see blue symbols), a regioselective *syn*-dehydration (deprotonated H_a, not H_b) of the generated **E** forms the diene **F** via a six-membered chair conformation. The addition of MS absorbs the resulting H_2O. Then, desulfonative aromatization of **F** (removal of $TolSO_2H$) yields **6a** (Y = Me). When Y is a prenyl group, tertiary carbocation **H** can arise via the $Bi(OTf)_3$-mediated attack in **G**. Next, an intramolecular Friedel–Crafts alkylation of **H** generates **I**.[17] Finally, after dehydrogenative aromatization of **I** by the triflate anion, the resulting HOTf continues the debismuthation from **J** to **7a**. In contrast (see red symbols), the isolation of **8** demonstrates that wet $MeNO_2$ promotes the conversion from **D** to **K** via $Bi(OTf)_3$-mediated stereoselective hydration.[5b] According to the above experimental conditions and results (Tables 1 and 2), the intramolecular carbonyl allylation of **1a** demonstrates the proposed mechanism.

When **5r** was treated with the combination of $Bi(OTf)_3$/$MeNO_2$/MS with a 4-nitrophenyl group, a decalin skeleton **9a** and a bridged skeleton **9b** were obtained in 68% and 6% yields, respectively, via the intramolecular Friedel–Crafts C-alkylation of **D** and the O-alkylation of **K** (Scheme 4). Through the addition of H_2O (0.1 mL), the isolated yield of **9b** was

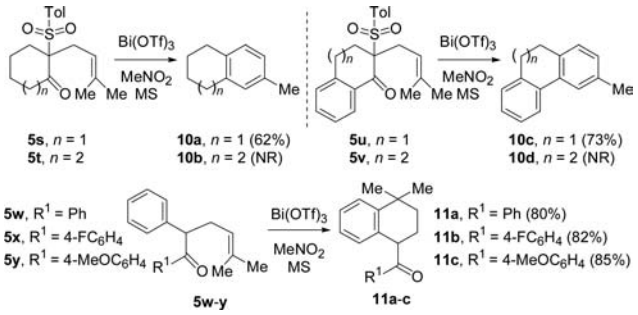
Scheme 4. $Bi(OTf)_3$-Mediated Reaction of 5r



increased to 49% under wet conditions. However, attempts to increase the reaction time (8 → 40 h) failed to afford **7**. On the basis of the isolation of **9a–b**, we envision that the present mechanism is reasonable to demonstrate $Bi(OTf)_3$-mediated intramolecular carbonyl allylation of **5**.

To examine the limitations of this $Bi(OTf)_3$-mediated route (Scheme 5), **5s–y** were investigated. Bicyclic **10a** (62%) and

Scheme 5. $Bi(OTf)_3$-Mediated Reactions of 5s–y



tricyclic **10c** (73%) were isolated, but no formation of **10b** and **10d** with the seven-membered ring was observed. A change of the substituent from a sulfonyl to an aryl group gave none of the desired skeleton via the intramolecular carbonyl allylation of **5w–y**. Only Friedel–Crafts cycloadducts **11a–c** were produced in 80%–85% yields. The results are consistent with the Dunach reports.[5] The structures of **9a–b** and **11b** were determined by single-crystal X-ray crystallography.[14] In summary, we have developed a $Bi(OTf)_3$/$MeNO_2$/MS-mediated intramolecular carbonyl allylation of **5** to generate substituted benzenes **6–7** and **10–11** at 25 °C for 8 h. Skeleton **5** was also provided in good yields via *α*-prenylation and *α*-genarylation of **1**. A plausible mechanism has been proposed for these cyclization reactions. The structures of the key products were confirmed by X-ray crystallography. Further investigations regarding the synthetic application of *β*-ketosulfones will be conducted and published.

■ ASSOCIATED CONTENT

Supporting Information

Experimental data and scanned photocopies of ^1H and ^{13}C NMR spectral data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01461.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: mychang@kmu.edu.tw

DOI: 10.1021/acs.orglett.5b01461
Org. Lett. 2015, 17, 3142–3145

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the Ministry of Science and Technology of the Republic of China for financial support.

■ REFERENCES

(1) (a) Le Roux, C.; Dubac, J. *Synlett* **2002**, 181. (b) Leonard, N. M.; Wieland, L. C.; Mohan, R. S. *Tetrahedron* **2002**, *58*, 8373. (c) Gaspard-Iloughmane, H.; Le Roux, C. *Eur. J. Org. Chem.* **2004**, 2517. (d) Gaspard-Iloughmane, H.; Le Roux, C. *Eur. J. Org. Chem.* **2004**, 2517. (e) Gaspard-Iloughmane, H.; Le Roux, C. *Trends Org. Chem.* **2006**, *11*, 65. (f) Hua, R. *Curr. Org. Synth.* **2008**, *5*, 1. (g) Salvador, J. A. R.; Pinto, R. M. A.; Silvestre, S. M. *Curr. Org. Synth.* **2009**, *6*, 426. (h) Salvador, J. A. R.; Pinto, R. M. A.; Silvestre, S. M. *Mini-Rev. Org. Chem.* **2009**, *6*, 241. (i) Bothwell, J. M.; Krabbez, S. W.; Mohan, R. S. *Chem. Soc. Rev.* **2011**, *40*, 4649. (j) Ollevier, T. *Org. Biomol. Chem.* **2013**, *11*, 2740.

(2) (a) Ollevier, T.; Bouchard, J.-E.; Desyroy, V. *J. Org. Chem.* **2008**, *73*, 331. (b) Attanasi, O. A.; Favi, G.; Giorgi, G.; Mantellini, F.; Karapetyan, V.; Langer, P. *Tetrahedron* **2009**, *65*, 5456.

(3) (a) Qin, H.; Yamagiwa, N.; Matsunaga, S.; Shibasaki, M. *Chem.—Asian J.* **2007**, *2*, 150. (b) Mathia, F.; Szolcsanyi, P. *Org. Biomol. Chem.* **2012**, *10*, 2830. (c) Komeyama, K.; Kouya, Y.; Ohama, Y.; Takaki, K. *Chem. Commun.* **2011**, *47*, 5031.

(4) (a) Anzalone, P. W.; Baru, A. R.; Danielson, E. R.; Hayes, P. D.; Nguyen, M.-P.; Panico, A. F.; Smith, R. C.; Mohan, R. S. *J. Org. Chem.* **2005**, *70*, 2091. (b) Rubenbauer, P.; Herdtweck, E.; Strassner, T.; Bach, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 10106. (c) Rueping, M.; Nachtsheim, B. J.; Kuenkel, A. *Org. Lett.* **2007**, *9*, 825.

(5) (a) Lemiere, G.; Cacciuttolo, B.; Belhassen, E.; Dunach, E. *Org. Lett.* **2012**, *14*, 2750. (b) Cacciuttolo, B.; Poulain-Martini, S.; Fontaine-Vive, F.; Abdo, M. A. H.; El-Kashef, H.; Dunach, E. *Eur. J. Org. Chem.* **2014**, 7458. (c) Cacciuttolo, B.; Poulain-Martini, S.; Dunach, E. *Eur. J. Org. Chem.* **2011**, 3710. (d) Cacciuttolo, B.; Ondet, P.; Poulain-Martini, S.; Lemiere, G.; Dunach, E. *Org. Chem. Front.* **2014**, *1*, 765.

(6) (a) Bonvin, Y.; Callens, E.; Larrosa, I.; Henderson, D. A.; Oldham, J.; Burton, A. J.; Barrett, A. G. M. *Org. Lett.* **2005**, *7*, 4549. (b) Vatele, J.-M. *Synlett* **2008**, 1785. (c) Barnych, B.; Vatèle, J.-M. *Synlett* **2011**, 2048.

(7) (a) Godeau, J.; Olivero, S.; Antoniotti, S.; Dunach, E. *Org. Lett.* **2011**, *13*, 3320. (b) Kelly, B. D.; Allen, J. M.; Tundel, R. E.; Lambert, T. H. *Org. Lett.* **2009**, *11*, 1381. (c) Komeyama, K.; Takahashi, K.; Takaki, K. *Org. Lett.* **2008**, *10*, 5119. (d) Murai, M.; Hosokawa, N.; Roy, D.; Takai, K. *Org. Lett.* **2014**, *16*, 4134. (e) Murai, M.; Origuchi, K.; Takai, K. *Org. Lett.* **2014**, *16*, 3828. (f) Jaratjaroonphong, J.; Tuengpanya, S.; Ruengsangtongkul, S. *J. Org. Chem.* **2015**, *80*, 559. (g) Yun, J.; Park, J.; Kim, J.; Lee, K. *Tetrahedron Lett.* **2015**, *56*, 1045. (h) Ono, F.; Ishikura, Y.; Tada, Y.; Endo, M.; Sato, T. *Synlett* **2008**, 2365. (i) Diaf, I.; Lemiere, G.; Dunach, E. *Angew. Chem., Int. Ed.* **2014**, *53*, 4177. (j) Ondet, P.; Joffrin, A.; Diaf, I.; Lemiere, G.; Dunach, E. *Org. Lett.* **2015**, *17*, 1002.

(8) (a) Pospisil, J.; Sato, H. *J. Org. Chem.* **2011**, *76*, 2269. (b) Tsui, G. C.; Glenadel, Q.; Lau, C.; Lautens, M. *Org. Lett.* **2011**, *13*, 208. (c) Sreedhar, B.; Rawat, V. S. *Synlett* **2012**, *23*, 413. (d) Lu, Q.; Zhang, J.; Zhao, G.; Qi, Y.; Wang, H.; Lei, W. *J. Am. Chem. Soc.* **2013**, *135*, 11481. (e) Tang, X.; Huang, L.; Xu, Y.; Yang, J.; Wu, W.; Jiang, H. *Angew. Chem., Int. Ed.* **2014**, *53*, 4205. (f) Chawla, R.; Singh, A. K.; Yadav, L. D. S. *Eur. J. Org. Chem.* **2014**, *10*, 2032. (g) Singh, A. K.; Chawla, R.; Yadav, L. D. S. *Tetrahedron Lett.* **2014**, *55*, 4742. (h) Shi, X.; Ren, X.; Ren, Z.; Li, J.; Wang, Y.; Yang, S.; Gu, J.; Gao, Q.; Huang, G. *Eur. J. Org. Chem.* **2014**, *10*, 5083. (i) Xuan, J.; Feng, Z.-J.; Chen, J.-R.; Lu, L.-Q.; Xiao, W.-J. *Chem.—Eur. J.* **2014**, *20*, 3045.

(9) (a) Chang, M.-Y.; Cheng, Y.-J.; Lu, Y.-R. *Org. Lett.* **2015**, *17*, 1264. (b) Chang, M.-Y.; Chen, Y.-C.; Chan, C.-K.; Huang, G. G. *Tetrahedron* **2015**, *71*, 2095.

(10) Narender, T.; Sarkar, S.; Rajendar, K.; Tiwari, S. *Org. Lett.* **2011**, *13*, 6140.

(11) (a) Saito, S.; Yamamoto, Y. *Chem. Rev.* **2000**, *100*, 2901. (b) Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359. (c) Liu, J.-K. *Chem. Rev.* **2006**, *106*, 2209.

(12) (a) Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359. (b) Schroter, S.; Stock, C.; Bach, T. *Tetrahedron* **2005**, *61*, 2245. (c) Schnurch, M.; Flasik, R.; Khan, A. F.; Spina, M.; Mihovilovic, M. D.; Stanetty, P. *Eur. J. Org. Chem.* **2006**, 3283. (d) Wang, R.; Manabe, K. *Synthesis* **2009**, 1405.

(13) (a) Varela, J. A.; Saa, C. *Chem. Rev.* **2003**, *103*, 3787. (b) Grotjahn, D. B. Transition Metal Alkyne Complexes: Transition Metal-Catalyzed Cyclotrimerization. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Hegedus, L. S., Eds.; Pergamon: Oxford, U.K., 1995; Vol. *12*, p 741. (c) Hilt, G.; Vogler, T.; Hess, W.; Galbiati, F. *Chem. Commun.* **2005**, 1474. (d) Xu, L.; Yu, R.; Wang, Y.; Chen, J.; Yang, Z. *J. Org. Chem.* **2013**, *78*, 5744. (e) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. (f) Kotha, S.; Brahmachary, E.; Lahiri, K. *Eur. J. Org. Chem.* **2005**, 4741. (g) Gandon, V.; Aubert, C.; Malacria, M. *Chem. Commun.* **2006**, 2209.

(14) CCDC 1057389 (**7d**), 1055718 (**8**), 1055717 (**9a**), 1401723 (**9b**), and 1062664 (**11b**), contain the supplementary crystallographic data for this paper. This data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

(15) (a) Lin, S.; Song, C.-X.; Cai, G.-X.; Wang, W.-H.; Shi, Z.-J. *J. Am. Chem. Soc.* **2008**, *130*, 12901. (b) Reed, S. A.; White, M. C. *J. Am. Chem. Soc.* **2008**, *130*, 3316. (c) Delcamp, J. H.; White, M. C. *J. Am. Chem. Soc.* **2006**, *128*, 15076. (d) Chen, M. S.; Prabagaran, N.; Labenz, N. A.; White, M. C. *J. Am. Chem. Soc.* **2005**, *127*, 6970. (e) Chen, M. S.; White, M. C. *J. Am. Chem. Soc.* **2004**, *126*, 1346.

(16) (a) Mengel, A.; Reser, O. *Chem. Rev.* **1999**, *99*, 1191. (b) Gung, B. W. *Tetrahedron* **1996**, *52*, 5263. (c) Ager, D. J.; East, M. B. *Tetrahedron* **1992**, *48*, 2803.

(17) For $Bi(OTf)_3$, see: (a) Nammalwar, B.; Bunce, R. A. *Tetrahedron Lett.* **2013**, *54*, 4330. For AgOTf, see: (b) Youn, S. W.; Pastine, S. J.; Sames, D. *Org. Lett.* **2004**, *6*, 581. For $In(OTf)_3$, see: (c) Xie, K.; Wang, S.; Li, P.; Li, X.; Yang, Z.; An, X.; Guo, C.-C.; Tan, Z. *Tetrahedron Lett.* **2010**, *51*, 4466.

DOI: 10.1021/acs.orglett.5b01461
Org. Lett. 2015, 17, 3142−3145