Advanced Synthesis & Catalysis

DOI: 10.1002/adsc.201300728

Concise Synthesis of 1-Naphthols under Mild Conditions through a Copper-Catalyzed Arylation of Methyl Ketones

Zhenbang Lou,[a,b] Shu Zhang,[a,c] Chao Chen,[a,*] Xinlong Pang,[a,b] Ming Li,[b] and Lirong Wen[b]

[a] Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China
Fax: (+86)-10-6277-31149; phone: (+86)-10-6277-3684; e-mail: chenchao01@mails.tsinghua.edu.cn
[b] College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, People's Republic of China
[c] Department of Applied Chemistry, China Agricultural University, Beijing 100193, People's Republic of China

Received: August 12, 2013; Revised: October 16, 2013; Published online: January 10, 2014

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201300728.

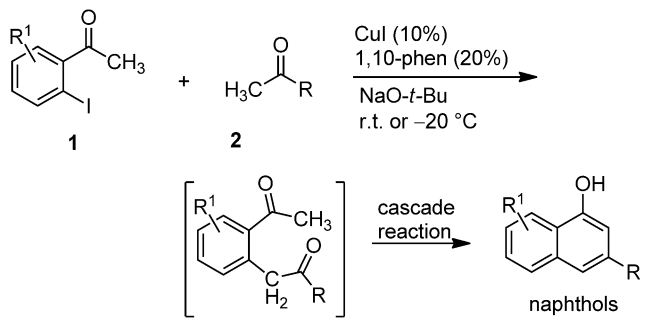
Abstract: A concise synthesis of 1-naphthols *via* cyclization of *o*-iodoacetophenones and methyl ketones has been realized under very mild conditions. The cyclization process is initiated by a rare copper-catalyzed arylation of simple methyl ketones with *ortho*-iodoacetophenones.

Keywords: arylation; copper-catalyzed reaction; *ortho*-iodoacetophenones; methyl ketones; 1-naphthols

1-Naphthols are important classes of organic compounds that are not only applied in organic synthesis, organic catalysts and as ligands for transition-metal catalysts, but they also occur in numerous natural products and pharmaceuticals as privileged scaffolds.[1] Therefore, synthetic chemists have made great efforts in the development of new and efficient methodologies for the synthesis of polysubstituted 1-naphthol derivatives.[2] Meanwhile, the synthesis of naphthalene derivatives has made much progress, especially aided by transition metals[3] and some of the syntheses are also applicable to 1-naphthols. Nevertheless, the present synthetic methods to 1-naphthols often require complicated starting materials (most of them are not readily available),[2a–d,f–g,i,j] precious catalysts,[2e,3i] high temperature and/or a prolonged reaction time.[2h,3h–i] To date, the facile construction of multisubstituted 1-naphthols from readily available starting materials under mild conditions still remains a big challenge.

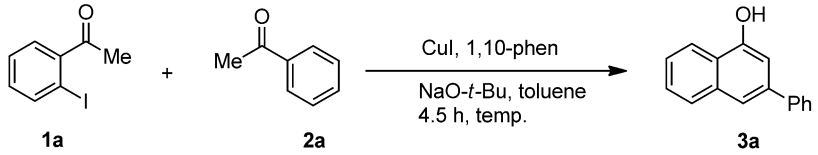
The Cu-catalyzed α-arylation of highly activated carbonyl compounds such as keto esters, malonic acid derivatives, or diketones is well known and more recently the Cu-catalyzed α-arylation of benzyl phenyl ketones has also been realized.[4] One-pot strategies for the synthesis of various useful cyclic compounds based on the Cu-catalyzed α-arylation of activated ketones have been investigated, but rarely applied to simple methyl ketones.[5,6] Herein, we would like to report a facile construction of 1-naphthols *via* cyclization from *ortho*-iodoacetophenones[7] and methyl ketones catalyzed by CuI. The reaction was realized under mild conditions initiated by a rare Cu-catalyzed arylation of simple methyl ketones (Scheme 1).

During our study on synthesizing cyclic compounds with copper catalysts,[8] we found the formation of naphthol **3a** in the reaction of *ortho*-iodoacetophenone **1a** with acetophenone **2a** under simple Cu-catalyzed conditions (Table 1). When 1.0 mmol of *ortho*-iodoacetophenone **1a** was treated with acetophenone **2a** (3 equiv.) in the presence of NaO-*t*-Bu (base, 4 equiv.), CuI (catalyst, 10 mol%) and 1,10-phen (1,10-phenanthroline, ligand, 20 mol%) in toluene at



Scheme 1. Concise synthesis of 1-naphthols *via* cyclization of *ortho*-iodoacetophenones and methyl ketones under mild conditions.

Table 1. Optimization of reaction conditions for the formation of **3a**.



1a **2a** **3a**

Entry	CuI (equiv.)	1,10-phen (equiv.)	NaO-*t*-Bu (equiv.)	Ratio of **1a**:**2a**	Temperature [°C]	Yield [%][a]
1	10%	20%	4	1:3	25	30
2	10%	20%	3	1:3	25	trace
3	10%	20%	5	1:3	25	74
4	**10%**	**20%**	**6**	**1:3**	**25**	**87 (85)**
5	10%	20%	6	1:3	0	62
6	10%	20%	6	1:3	40	85
7	10%	20%	6	1:3	60	37
8	10%	20%	6	1:1	25	24
9	10%	20%	6	1:2	25	75
10	5%	10%	6	1:3	25	37
11	10%	0	6	1:3	25	51
12	0	20%	6	1:3	25	trace
13[b]	10%	20%	6	1:3	0	0
14[b]	10%	20%	6	1:3	30	0
15[b]	10%	20%	6	1:3	60	0

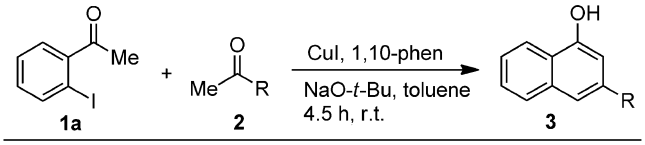
[a] GC yield with *n*-dodecane as internal standard (isolated yield in brackets).
[b] *ortho*-Bromoacetophenone was used instead of 2-iodoacetophenone.

room temperature for 4.5 h, 3-phenyl-1-naphthol **3a** was formed in 30% yield (entry 1). To date, there have been seven other methods reported for the synthesis of 3-phenyl-1-naphthol **2a** in multi-step procedures suffering from harsh conditions.[9] Considering the importance of this compound and the easy manipulation of our method, we were encouraged to perform an optimization study on bases, solvents, catalysts and ligands (see the Supporting Information for details). Gratifyingly, we found NaO-*t*-Bu was the best base for this reaction and the amount of NaO-*t*-Bu was crucial: **3a** was formed in 74% yield with 5 equiv. of NaO-*t*-Bu, and in 87% yield with 6 equiv. of NaO-*t*-Bu. The decreased loading of **2a** also affected the yield of **3a** (entries 8 and 9). Under otherwise the same conditions without CuI, no product was formed (entry 12). After lots of attempts, the optimal conditions were found as shown in entry 4 with the following parameters: CuI as a precatalyst (10%), 1,10-phen as a ligand (20%), NaO-*t*-Bu as a base (6 equiv.), toluene as a solvent at 25 °C, and a ratio of **1a**:**2a** = 1:3. We also investigated the reaction of *ortho*-bromoacetophenone with acetophenone, however, the reaction did not occur under our standard conditions even at 60 °C (entries 13–15).

Under these optimized conditions, a study on the substrate scope of methyl ketones **2** was carried out with **1a**, and the results are listed in Table 2. Generally, acetophenones **2** with a range of substitutents such as methyl, trifluoromethyl, cyano, fluoro, chloro, bromo and phenyl groups at *ortho*-, *meta*- or *para*-positions all worked well to give 3-substituted phenyl-1-naphthols. Substrates with electron-withdrawing groups and halo groups gave the products in higher yields than those with electron-donating groups. Besides those with substituted phenyl groups, substrates with 1- and 2-naphthyl, 1-furanyl and 1-thienyl groups also reacted well with **1a** to give 3-aryl-1-naphthols.[9] Excitingly, acetone **2r** could react with **1a** at −20 °C to give 3-methyl-1-naphthol **3r** in a synthetically useful yield. Interestingly, the reaction of 2-butanone **2s** with **1a** at −20 °C only afforded 3-ethyl-1-naphthol **3s** in 54% yield suggesting that the reactivity of a methyl group was higher than that of an ethyl group in 2-butanone (entry 19). Finally, the reaction of 1-phenyl-1-propanone **2t** with **1a** at room temperature produced 3-phenyl-4-methyl-1-naphthol **3t** in 48% yield (entry 20).

After the successful preparation of naphthol with substituents on the phenol ring, we turned to introduce more substituents by using substituted *ortho*-iodoacetophenones **1** with methyl ketones **2** (Table 3). 5-Bromo-2-iodoacetophenone **1b** was first reacted with acetophenone **2a** under standard conditions and 1-naphthol **4a** was obtained in 76% yield with the bromine atom intact. We examined more reactions of **1b** with other methyl ketones and 1-naphthols **4b**–**4e** were isolated in good yields with the bromine atom being retained in all cases (entries 1–5). Other *ortho*-iodoacetophenones with substituents such as phenyl, phenylethynyl, and dioxylyl groups also worked well

Table 2. Naphthols **3** formed from the reaction of *ortho*-iodoacetophenone **1a** with various methyl ketones **2**.



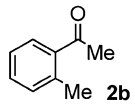
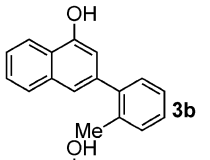
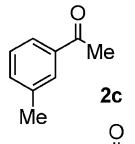
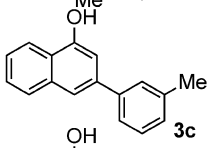
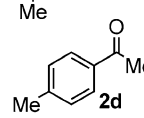
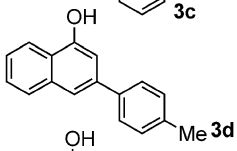
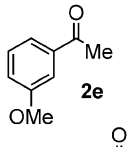
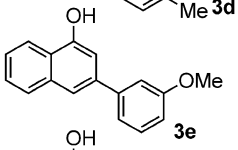
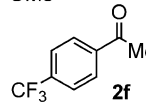
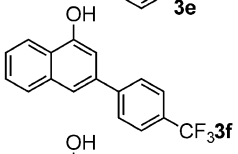
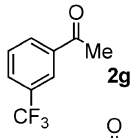
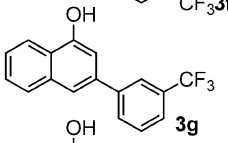
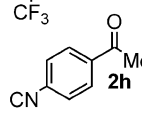
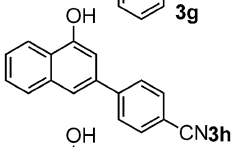
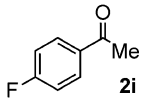
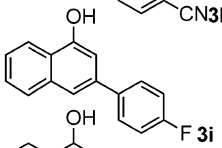
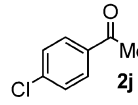
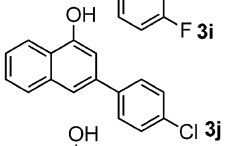
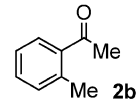
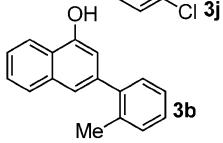
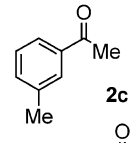
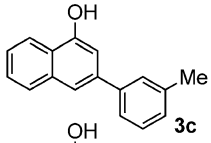
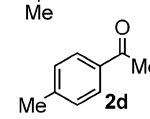
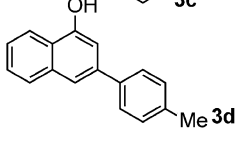
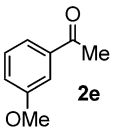
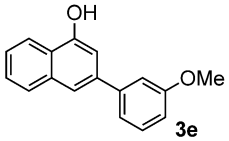
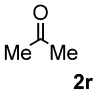
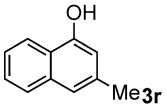
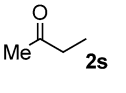
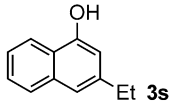
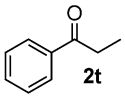
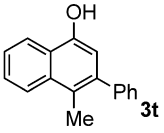
Entry	Methyl Ketone	Products	Yield[a]
1			58%
2			68%
3			70%
4			65%
5			98%
6			85%
7			71%
8			92%
9			95%
10			58%
11			68%
12			70%

Table 2. (Continued)

Entry	Methyl Ketone	Products	Yield[a]
13			65%
18			62%[b]
19			54%[b]
20			48%

[a] Isolated yields.
[b] Performed at −20 °C.

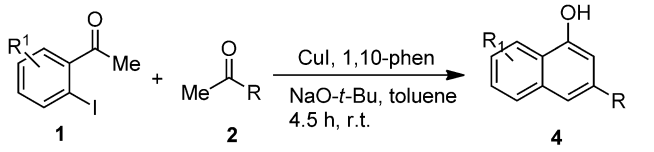
to produce the corresponding 1-naphthols in good yields (entries 6–11).

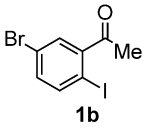
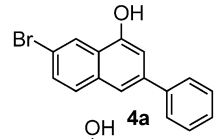
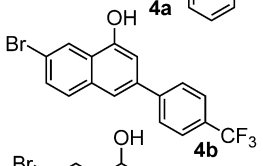
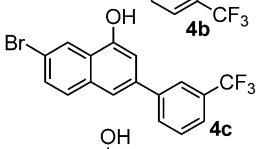
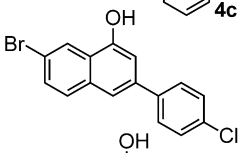
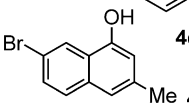
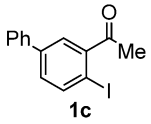
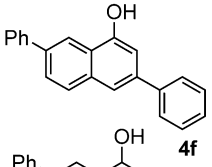
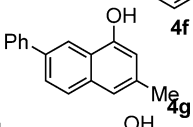
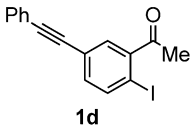
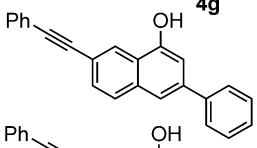
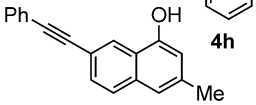
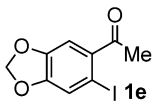
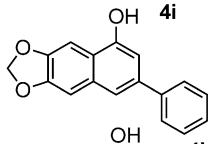
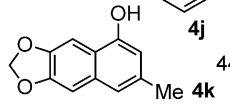
To get an insight of the mechanism, 2,5-diiodoacetophenone **1f** was prepared and reacted with acetophenone **2a** and acetone **2r**. Interestingly, only the 2-iodo atoms of **2a** and **2r** were substituted giving naphthols **4l** and **4m** while the 5-iodo atoms remained intact [Scheme 2, Eq. (1)]. This result implied that the 2-iodo atom was activated by an acetyl group in compound **1** during the Cu-catalyzed reaction. Additionally, the aldol condensation product **7** was separately prepared from **1a** and **3r** *via* classic Mukaiyama reaction followed by dehydration.[10] Treatment of **7** under the standard conditions for the formation of 1-naphthols failed to generate **3r**. This result suggested that the aldol condensation product **7** was not an intermediate for the formation of 1-naphthols.

Based on the results above, we proposed the following mechanism (Scheme 3): the reaction of **1** with CuI and 1,10-phen *via* oxidative addition provides Cu(III) species **I**, which is stabilized by the intramolecular coordination of a carbonyl group. Meanwhile, the methyl ketone is deprotonated by NaO-*t*-Bu to give enolate **II**. The reaction of **I** and enolate **II** *via* transmetallation affords **III**, and reductive elimination of **III** (C-arylation of methyl ketone) gives **IV**, regenerating the copper catalyst. The transformation of **IV** into naphthol *via* aldol reaction, dehydration and tautomerization was realized in the presence of NaO-*t*-Bu as reported in the previous study.[9,11]

As a convenient method to prepare 1-naphthols, the reaction was also performed in a scale of 10 mmol. To our delight, product **3a** was isolated in

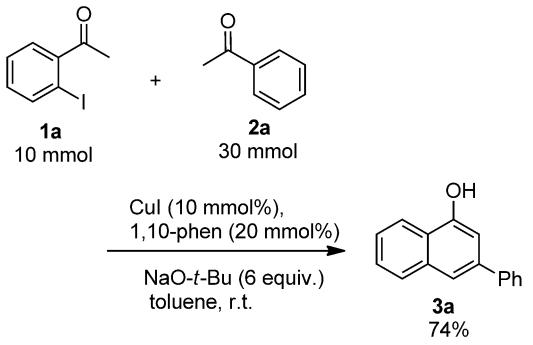
Table 3. Naphthols **4** formed from the reaction of various substituted *ortho*-iodoacetophenones **1** with methyl ketones **2**.



Entry	*ortho*-Iodo-acetophenones	Methyl ketones	Products	Yield[a]
1	 **1b**	**2a**	 **4a**	76%
2	**1b**	**2f**	 **4b**	95%
3	**1b**	**2g**	 **4c**	94%
4	**1b**	**2j**	 **4d**	68%
5	**1b**	**2r**	 **4e**	65%[b]
6	 **1c**	**2a**	 **4f**	83%
7	**1c**	**2r**	 **4g**	72%[b]
8	 **1d**	**2a**	 **4h**	80%
9	**1d**	**2r**	 **4i**	66%[b]
10	 **1e**	**2a**	 **4j**	41%
11	**1e**	**2r**	 **4k**	44%[b]

[a] Isolated yields.
[b] Performed at −20 °C.

74% yield [Eq. (2)]. Additionally, when the reaction was performed in a two-necked round-bottom flask under an N_2 atmosphere, product **3a** was isolated in 85% yield.



(2)

In conclusion, we have developed a cyclization reaction for the synthesis of 1-naphthols under mild conditions with readily available starting materials: *ortho*-iodoacetophenones **1** and simple methyl ketones **2.** The process was initiated by a rare Cu-catalyzed arylation of simple methyl ketones and could tolerate various functional groups in the substrates providing the opportunity for further transformations. Therefore, we believe this method will find many applications in organic chemistry and medicinal chemistry.

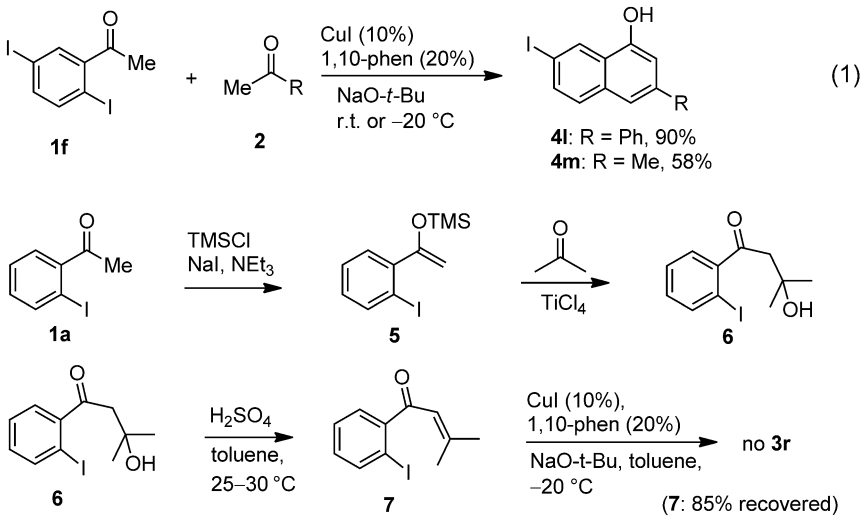
Experimental Section

Representative Procedure of the Synthesis of 3a

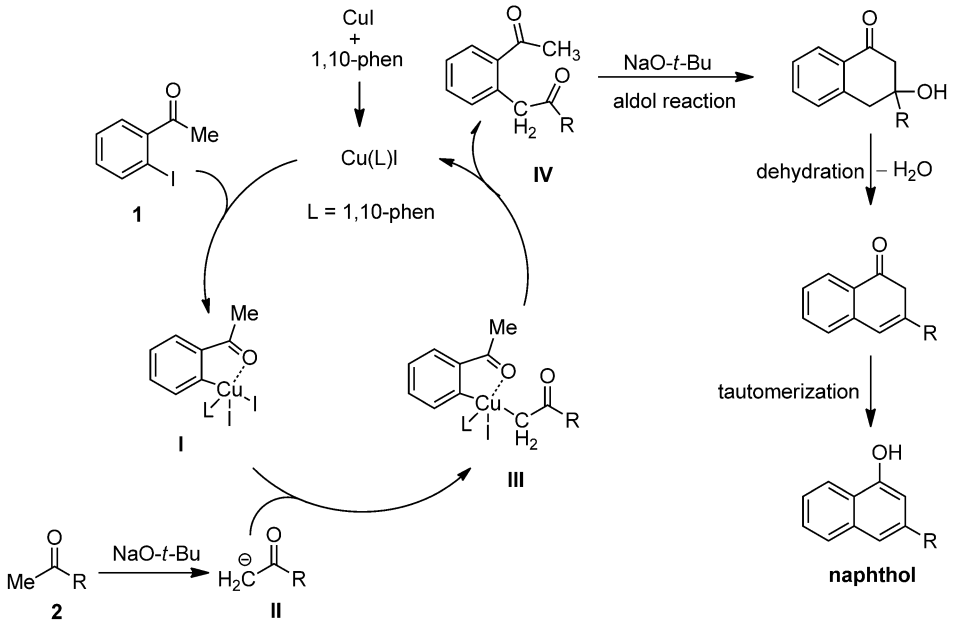
A sealed tube was charged with a mixture of CuI (0.1 mmol, 19.0 mg), 1,10-phen (0.2 mmol, 36.0 mg) and NaO-*t*-Bu (6 mmol, 0.576 g). After being evacuated and recharged with N_2 for 3 times, 2-iodoacetophenone **1a** (1.0 mmol) and acetophenone **2a** (3.0 mmol) were added into the tube. After toluene (2.0 mL) had been added, the tube was sealed and the mixture was allowed to stir at room temperature for 4.5 h. Afterwards, 2 N aqueous HCl was added and the mixture was extracted with Et_2O (5 mL × 3). The organic phase was combined and dried over anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel (petroleum ether/diethyl ether: 25/1 to 10/1) provided 3-phenyl-1-naphthol (**3a**) as a light yellow solid; yield: 191 mg (85%).[9] ^{1}H NMR (301 MHz, $CDCl_3$): $\delta = 8.23$ (d, $J = 7.7$ Hz, 1H), 7.89 (dd, $J = 6.8$, 2.1 Hz, 1H), 7.69–7.65 (m, 3H), 7.56–7.46 (m, 4H), 7.44–7.39 (m, 1H), 7.08 (d, $J = 1.5$ Hz, 1H), 5.65 (broad, 1H); ^{13}C NMR (76 MHz, $CDCl_3$): $\delta = 151.9$, 141.0, 139.0, 135.1, 129.0 (2×CH), 128.2, 127.6, 127.4(2×CH), 127.0, 125.5, 123.8, 121.6, 118.9, 108.6; GC-MS: $m/z = 220$ (M^+); ESI-HR-MS: $m/z = 219.0819$, calcd. for $C_{16}H_{12}O$ $[M-H]^-$: 219.0815.

Representative Procedure of the Synthesis of 3r

A sealed tube was charged with a mixture of CuI (0.1 mmol, 19.0 mg), 1,10-phen (0.2 mmol, 36.0 mg) and NaO-*t*-Bu (6 mmol, 0.576 g). After evacuated and recharged with N_2



Scheme 2. The mechanistic study of Cu-catalyzed synthesis of 1-naphthols.



Scheme 3. Proposed mechanism.

for 3 times, 2-iodoacetophenone **1a** (1.0 mmol) and acetone **2r** (3.0 mmol) were added into the tube. After toluene (2.0 mL) had been added, the tube was sealed and the mixture was allowed to stir at −20 °C for 4.5 h. Afterwards, 2 N aqueous HCl was added and the mixture was extracted with Et_2O (5 mL × 3). The organic phase was combined and dried over anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel (petroleum ether/diethyl ether: 25/1 to 10/1) provided 3-methyl-1-naphthol (**3r**) as a light yellow solid; yield: 98 mg (62%).[12] ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.12$ (dd, $J = 7.8$, 1.2 Hz, 1H), 7.74 (dd, $J = 7.4$, 1.8 Hz, 1H), 7.45 (ddd, $J = 7.5$, 2.7, 1.4 Hz, 2H), 7.24 (s, 1H), 6.65 (d, $J = 1.2$ Hz, 1H), 5.24 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 151.2$, 136.0, 135.0, 127.2, 126.6, 124.5, 122.7, 121.5, 119.9, 112.0, 21.9; GC-MS: $m/z = 158$ (M^+); ESI-HR-MS: $m/z = 157.0730$, calcd. for $C_{11}H_{10}O$ $[M-H]^-$: 157.0732.

Acknowledgements

This work was supported by National Natural Science Foundation of China (21102080, 21372138) and Tsinghua University Initiative Scientific Research Program (2011Z02150).

References

[1] a) P. Kilian, F. Knight, R. Fergus, J. D. Woollins, *Chem. Eur. J.* **2011**, *17*, 2302–2328; b) Y. S. Cai, Y. W. Guo, K. Krohn, *Nat. Prod. Rep.* **2010**, *27*, 1840–1870; c) J. Sperry, P. Bachu, M. A. Brimble, *Nat. Prod. Rep.* **2008**, *25*, 376–400; d) J. K. Son, S. J. Jung, J. H. Jung, Z. Fang, C. S. Lee, C. S. Seo, D. C. Moon, B. S. Min, M. R. Kim, M. H. Woo, *Chem. Pharm. Bull.* **2008**, *56*, 213–216; e) S. Boonsri, C. Karalai, C. Ponglimanont, S. Chantrapromma, A. Kanjana-opas, *J. Nat. Prod.* **2008**, *71*, 1173–1177; f) R. Irie, T. Katsuki, *Chem. Rec.* **2004**, *4*, 96–109; g) C. B. de Koning, A. L. Rousseau, W. A. L. van Otterlo, *Tetrahedron* **2003**, *59*, 7–36; h) A. Mulrooney, X. Li, E. S. DiVirgilio, M. C. Kozlowski, *J. Am. Chem. Soc.* **2003**, *125*, 6856–6857; i) G. Bringmann, K. Messer, K. Wolf, J. Mühlbacher, M. Grüne, R. Brun, A. M. Louis, *Phytochemistry* **2002**, *60*, 389–397; j) H. Itokawa, Z. Z. Ibraheim, Y. F. Qiao, K. Takeya, *Chem. Pharm. Bull.* **1993**, *41*, 1869–1872; k) H. Itokawa, K. Mihara, K. Takeya, *Chem. Pharm. Bull.* **1983**, *31*, 2353–2358; l) K. L. Rinehart Jr, *Acc. Chem. Res.* **1972**, *5*, 57–64.

[2] a) K. Okuma, R. Itoyama, A. Sou, N. Nagahora, K. Shioj, *Chem. Commun.* **2012**, *48*, 11145–11147; b) D. Mal, A. K. Jana, P. Mitra, K. Ghosh, *J. Org. Chem.* **2011**, *76*, 3392–3398; c) H. Xu, S. Li, H. Liu, H. Fu, Y. Jiang, *Chem. Commun.* **2010**, *46*, 7617–7619; d) G. Chai, Z. Lu, C. Fu, S. Ma, *Chem. Eur. J.* **2009**, *15*, 11083–11086; e) A. G. Sergeev, T. Schulz, C. Torborg, A. Spannenberg, H. Neumann, M. Beller, *Angew. Chem.* **2009**, *121*, 7731–7735; *Angew. Chem. Int. Ed.* **2009**, *48*, 7595–7599; f) S. Akai, T. Ikawa, S. Takayanagi, Y. Morikawa, S. Mohri, M. Tsubakiyama, M. Egi, Y. Wada, Y. Kita, *Angew. Chem.* **2008**, *120*, 7787–7790; *Angew. Chem. Int. Ed.* **2008**, *47*, 7673–7676; g) X. Huang, J. Xue, *J. Org. Chem.* **2007**, *72*, 3965–3968; h) H. Tsukamoto, Y. Kondo, *Org. Lett.* **2007**, *9*, 4227–4230; i) T. Hamura, T. Suzuki, T. Matsumoto, K. Suzuki, *Angew. Chem.* **2006**, *118*, 6442–6444; j) X. Zhang, S. Sarkar, R. C. Larock, *J. Org. Chem.* **2006**, *71*, 236–243.

[3] For transition metal-catalyzed naphthalene synthesis; for Cu, see: a) R. S. Reddy, P. K. Prasad, B. B. Ahuja, A. Sudalai, *J. Org. Chem.* **2013**, *78*, 5045–5050; b) C. C. Malakar, K. Sudheendran, H. G. Imrich, S. Mika, U. Beifuss, *Org. Biomol. Chem.* **2012**, *10*, 3899–3905; c) C. C. Malakar, D. Schmidt, J. Conrad, U. Beifuss, *Org. Lett.* **2011**, *13*, 1972–1975; d) Y. Isogai, Menggenbateer, F. N. Khan, N. Asao, *Tetrahedron* **2009**, *65*, 9575–9582; for Pd, see: e) R. M. Patel, N. P. Argade, *Org. Lett.* **2013**, *15*, 14–17; f) M. Shimizu, Y. Tomioka, I. Nagao, T. Kadowaki, T. Hiyama, *Chem. Asian J.* **2012**, *7*, 1644–1651; g) R. C. Larock, M. J. Doty, Q. Tian, J. M. Zenner, *J. Org. Chem.* **1997**, *62*, 7536–7537; h) J. A. Nieman, M. D. Ennis, *J. Org. Chem.* **2001**, *66*, 2175–2177; i) M. Y. Chang, C. K. Chan, S. Y. Lin, *Tetrahedron* **2013**, *69*, 1532–1538; for Rh, see: j) W. W. Chan, S. F. Lo, Z. Y. Zhou, W. Y. Yu, *J. Am. Chem. Soc.* **2012**, *134*, 13565–13568; k) Y. Xia, Z. X. Liu, Q. Xiao, P. Y. Qu, R. Ge, Y. Zhang, J. B. Wang, *Angew. Chem.* **2012**, *124*, 5812–5815; *Angew. Chem. Int. Ed.* **2012**, *51*, 5714–5717; for Au, see: l) N. Asao, K. Sato, Menggenbateer, Y. Yamamoto, *J. Org. Chem.* **2005**, *70*, 3682–3685; m) N. Asao, H. Aikawa, Y. Yamamoto, *J. Am. Chem. Soc.* **2004**, *126*, 7458–7459; for Fe, see: n) L. Llies, A. Matsumoto, M. Kobayashi, N. Yoshikai, E. Nakamura, *Synlett* **2012**, 2381–2384; o) X. L. Bu, L. C. Hong, R. T. Liu, J. Q. Hong, Z. X. Zhang, X. G. Zhou, *Tetrahedron* **2012**, *68*, 7960–7965; p) L. Adak, N. Yoshikai, *Tetrahedron* **2012**, *68*, 5167–5171; for gold, see: q) V. Gudla, R. Balamurugan, *Chem. Asian J.* **2013**, *8*, 414–428; r) V. Gudla, R. Balamurugan, *J. Org. Chem.* **2011**, *76*, 9919–9933; s) A. S. Dudnik, T. Schwier, V. Gevorgyan, *Tetrahedron* **2009**, *65*, 1859–1870; t) A. S. Dudnik, T. Schwier, V. Gevorgyan, *Org. Lett.* **2008**, *10*, 1465–1468; for Re, see: u) R. Umeda, S. Nishi, A. Kojima, K. Kaiba, Y. Nishiyama, *Tetrahedron Lett.* **2013**, *54*, 179–182; for Zr, see: v) X. Zhou, Z. P. Li, H. Wang, M. Kitamura, K. Kanno, K. Najajima, T. Takahashi, *J. Org. Chem.* **2004**, *69*, 4559–4562; w) Z. Duan, K. Nakajima, T. Takahashi, *Chem. Commun.* **2001**, 1672–1673; x) T. Takahashi, R. Hara, Y. Nishihara, M. Kotora, *J. Am. Chem. Soc.* **1996**, *118*, 5154–5155.

[4] For reviews on the catalytic Ullmann reaction, see: a) F. Monnier, M. Taillefer, *Angew. Chem.* **2009**, *121*, 7088–7105; *Angew. Chem. Int. Ed.* **2009**, *48*, 6954–6971; b) G. Evano, N. Blanchard, M. Toumi, *Chem. Rev.* **2008**, *108*, 3054–3131; c) A. W. Thomas, S. V. Ley, *Angew. Chem.* **2003**, *115*, 5558–5607; *Angew. Chem. Int. Ed.* **2003**, *42*, 5400–5449; for Cu-catalyzed α-arylation of benzyl phenyl ketones, see: d) G. Danoun, A. Tlili, F. Monnier, M. Taillefer, *Angew. Chem.* **2012**, *124*, 12987–12991; *Angew. Chem. Int. Ed.* **2012**, *51*, 12815–12819.

[5] Selected papers for copper-catalyzed synthesis of cyclic compounds, see: a) V. Kavala, C.-C. Wang, D. K. Barange, C.-W. Kuo, P.-M. Lei, C.-F. Yao, *J. Org. Chem.* **2012**, *77*, 5022–5029; b) S. Cai, F. Wang, C. Xi, *Synthesis* **2012**, *44*, 1892–1897; c) S. Cai, F. Wang, C. Xi, *J. Org. Chem.* **2012**, ***77***, 2331–2336; d) Z.-Y. Ge, X.-D. Fei, T. Tang, Y.-M. Zhu, J.-K. Shen, *J. Org. Chem.* **2012**, *77*, 5736–5743; e) X. Fan, Y. He, L. Cui, S. Guo, J. Wang, *Eur. J. Org. Chem.* **2012**, 673–677; f) X. Zhang, Y. Wang, Z. Sun, D. Ma, *Org. Lett.* **2008**, *10*, 625–628; g) Y. Chen, X. Xie, D. Ma, *J. Org. Chem.* **2007**, *72*, 9329–9334; h) Y. Fang, C. Li, *J. Org. Chem.* **2006**, *71*, 6427–6431; i) B. Lu, D. Ma, *Org. Lett.* **2006**, *8*, 6115–6118.

[6] R. Xie, Y. Ling, H. Fu, *Chem. Commun.* **2012**, *48*, 12210–12212.

[7] Naphthylene synthesis with *o*-iodoacetophenones under Pd-catalyzed conditions has been reported: X. Chen, J. Jin, N. Wang, P. Lu, Ya. Wang, *Eur. J. Org. Chem.* **2012**, 824–830.

[8] a) Y. Wang, C. Chen, J. Peng, M. Li, *Angew. Chem. Int. Ed.* **2013**, *52*, 5323–5327; b) X. Su, C. Chen, Y. Wang, J. Peng, Z. Lou, M. Li, *Chem. Commun.* **2013**, *49*, 6752–6754; c) F. Wang, C. Chen, G. Deng, C. Xi, *J. Org. Chem.* **2012**, *77*, 4148–4151.

[9] a) J. F. Hooper, A. B. Chaplin, C. González-Rodríguez, A. L. Weller, A. S. Thompson, M. C. Willis, *J. Am. Chem. Soc.* **2012**, *134*, 2906–2909; b) Z. Ding, S. Xue,

W. D. Wulff, *Chem. Asian J.* **2011**, *6*, 2130–2146, and references cited therein.
[10] a) M. Yamashita, K. Yamada, K. Tomioka, *J. Am. Chem. Soc.* **2004**, *126*, 1954–1955; b) M. Teruaki, N. Koichi, *Org. Syn.* **1986**, *65*, 6–11; c) H. Hata, T. Kobayashi, H. Amii, K. Uneyama, J. T. Welch, *Tetrahedron Lett.* **2002**, *43*, 6099–6102.
[11] R. Beugelmans, M. Bois-Choussy, Q. Tang, *J. Org. Chem.* **1987**, *52*, 3880–3883.
[12] E. Hasegawa, Y. Ogawa, K. Kakinuma, H. Tsuchida, E. Tosaka, S. Takizawa, H. Muraoka, T. Saikawa, *Tetrahedron* **2008**, *64*, 7724–7728.

