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Rhodium(III)-Catalyzed C-H Activation of Benzoylacetonitriles and Cyclization with Sulfoxonium Ylides to Naphthols

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Abstract. Rhodium(III)-Catalyzed C-H activation of benzoylacetonitriles in coupling with sulfoxonium ylides was developed to synthesize diversified substituted naphthols, in which aryl, heterocyclic and alkyl group in sulfoxonium ylides are tolerated. Intriguingly, we have further implemented transformation for 1-naphthols to give some intriguing fused tricyclic compounds and derivatives of propranolol, which demonstrate the practical utility of this methodology.

Keywords: C-H activation; Rhodium(III)-Catalyzed; Benzoylacetonitriles; Sulfoxonium ylides; Naphthol

Introduction

Naphthols are an important class of structural motifs in natural products and pharmaceuticals,[1] and have received a great deal of attention recently because of their unusual structures and interesting biological properties, such as anti-HIV (mollugin),[2] antiarrhythmic (propranolol),[3] antimalarial (dioncophylline A and korupensamine A)[4] and antitumor activities (gossypol)[5] (Figure 1). Consequently, general methods for the synthesis of such structural motifs have long been regarded as an important target in synthetic organic chemistry.[6] Although some well-established methodologies have been reported, it is attractive to employ the C-H activation strategy for straightforward access to these naphthol derivatives.

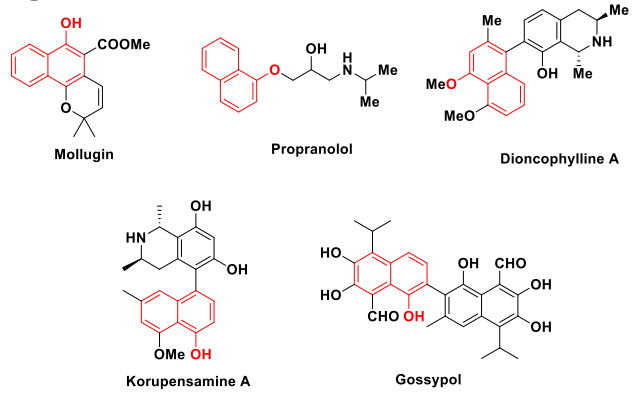
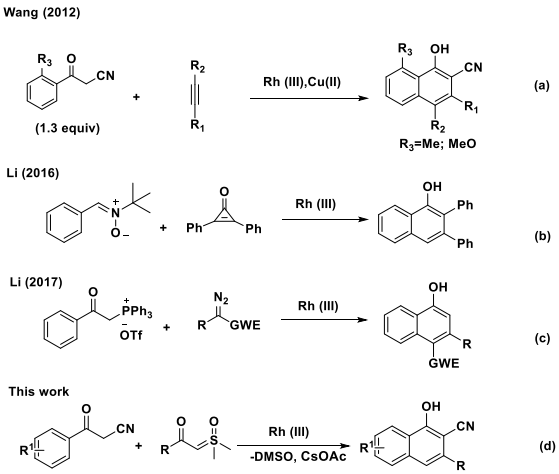


Figure 1. Representative bioactive compounds with naphthol skeletons.



Scheme 1. Rh (III) Catalyzed Synthesis of Naphthols.

In the past decades, Rh(III)-catalysts played increasingly important roles in the activation of C-H bonds to build heterocyclic scaffolds.[7] Wang and co-workers reported a pioneering Rh(III)-catalyzed oxidative annulation of *ortho*-substituted benzoylacetonitriles with diphenylacetylenes to synthesize 3,4-diphenyl-1-naphthols, but these naphthols could be obtained only when *ortho*-substituted benzoylacetonitriles were used (Scheme 1a)[8], other benzoylacetonitriles underwent a cascade annulation to give naphtho[1,8-bc]pyrans. These results indicated that alkynes seem to be an effective synthon to build 1-naphthols. Recently, Zhu's group

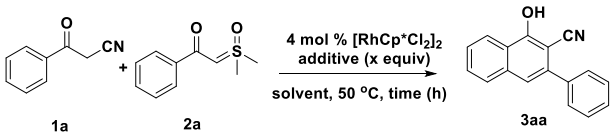
and Li's group reported two synthetic strategies to prepare 3,4-diaryl-substituted naphthalenes and 3,4-diaryl-substituted naphthols *via* rhodium-catalyzed C-H activation of enaminones and phenylglyoxal-derived nitrones with alkyne synthons, respectively.[9,10] However, alkyl-alkyl alkynes were not tolerated as the substrates in this transformation and failed to give desired products. Besides, Li's group reported the other two synthetic strategies to build more diversified naphthol derivatives by employing phenacyl triphenylphosphonium salts and nitrones as the starting materials *via* a Rh (III)-catalyzed C-H activation and annulation (Scheme 1b and 1c), respectively.[11,12] But these reaction systems are limited to the employment of unavailable starting materials.[13] Recently, sulfoxonium ylides were widely used as excellent synthetic materials.[14] On the basis of these challenges and our efforts in the construction of heterocyclic scaffolds *via* Rh/Ru-catalyzed transformations,[15] we herein report a novel Rh(III)-catalyzed cascade transformation with benzoylacetonitriles and sulfoxonium ylides compounds to prepare diversified 3-substituted naphthols, in which aryl, heterocyclic and alkyl group in sulfoxonium ylides are tolerated. More importantly, the intriguing naphthols could be converted into the derivatives of propranolol which is an antiarrhythmia drug in clinic (Scheme 1d). It is worth mentioning that during our submission Li's group also reported a very similar strategy to build the intriguing naphthol and naphtho[1,8-bc]pyran derivatives.[16]

Results and Discussion

We initiated our studies by exploring the coupling of benzoylacetonitrile **1a** (0.1 mmol) with sulfoxonium ylide **2a** (0.12 mmol) in the presence of $[Cp^*RhCl_2]_2$ (4.0 mol %) as the catalyst and CsOAc (2 equiv) as the additive in MeOH at 80 °C for 12 h, and the desired product **3aa** was achieved at 30% yield (Table 1, entry 1). Its structure was unambiguously confirmed by its ^1H and ^{13}C NMR spectra, mass spectrometry data, and X-ray crystallographic analysis,[17] respectively. Based on this result, we have further explored the reaction conditions. Through the change of solvent at 50 °C, the yields of **3aa** occurred disappointing decrease in most solvents, and DCE gave the best yield (entries 2-6). We noted that the starting materials disappeared completely and many impurities were observed using DCE as the solvent for 12 h. Therefore, we attempted to shorten the reaction time and the results displayed that a better yield (81%) was delivered for 6 h (entries 7-8). Further screening of the additives showed CsOAc proved to be the best choice for this transformation (entries 9-14). Reducing the additive loading to 1 equiv resulted in a lower yield, only 65% of desired product was obtained (entry 15). Further investigation showed that the target product could not be found in the absence of CsOAc (entry 16). Additionally, raising or lowering the reaction temperature was detrimental to the yield of this transformation (entries 17 and 18).

With the optimal reaction conditions in hand, we then sought to evaluate the scope and generality of benzoylacetonitriles in the coupling with sulfoxonium ylide **2a** in this catalytic system. Diversified

Table 1. Optimization of Reaction Conditions[a].



entry	solvent	Additive (x equiv)	time (h)	yield (%) **3aa**
1	MeOH	CsOAc (2)	12	30 [b]
2	H_2O	CsOAc (2)	12	N.R.
3	THF	CsOAc (2)	12	14
4	PhMe	CsOAc (2)	12	23
5	CH_3CN	CsOAc (2)	12	27
6	DCE	CsOAc (2)	12	46
7	DCE	CsOAc (2)	6	81
8	DCE	CsOAc (2)	3	57
9	DCE	CsOPiv(2)	6	75
10	DCE	NaOAc(2)	6	N.R.
11	DCE	AgOAc (2)	6	N.R.
12	DCE	PivOH(2)	6	N.R.
13	DCE	CsF(2)	6	45
14	DCE	Cs_2SO_4(2)	6	30
15	DCE	CsOAc(1)	6	65
16	DCE	-	6	N.R.
17	DCE	CsOAc (2)	6	12 [c]
18	DCE	CsOAc (2)	6	23 [b]

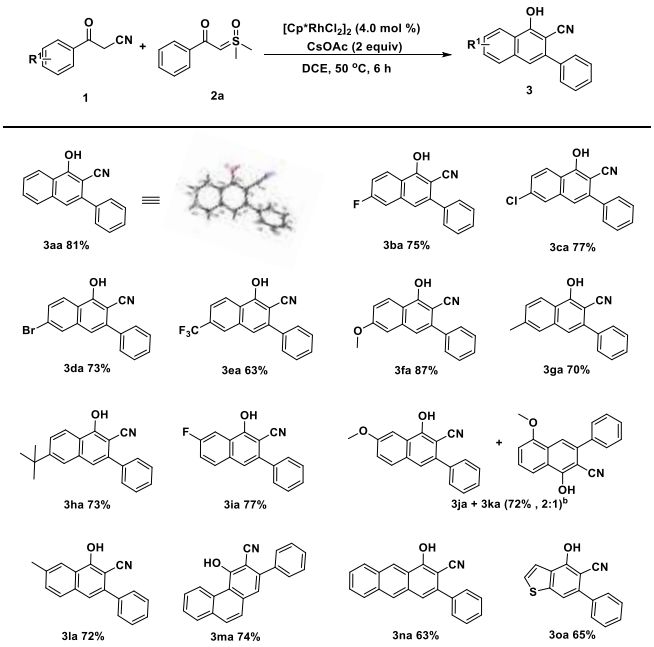
[a] Reaction condition: **1a** (0.1 mmol), **2a** (0.12 mmol), $[Cp^*RhCl_2]_2$(4.0 mol %), additive (x equiv) in the solvent (3 mL) at 50 °C for time (h). THF = tetrahydrofuran. DCE = 1,2-dichloroethane. N.R. = no reaction. [b] 80 °C. [c] Room temperature.

benzoylacetonitriles bearing various aryl moieties substituted by electron-donating groups, electron-withdrawing groups and halide groups were explored and the results demonstrated that a smooth coupling with sulfoxonium ylide **2a** could be detected and the desired products were obtained with moderate to good yields (Table 2, **3aa-3oa**, 63-87%). Among them, the benzoylacetonitrile substrates with the *para* position substituted by various electron-withdrawing groups and halides, such as $-CF_3$, -F, -Cl and -Br

10.1002/adsc.201800362

could be smoothly converted into the desired products with 63%-77% yields (Table 2, **3ba-3ea**). Introduction of the electron-donating groups (methoxyl, methyl and tert-butyl) to the *para* position of benzene ring of benzoylacetonitrile **1a** was also tolerated to the standard reaction conditions, and the reaction yields were maintained at a higher level (Table 2, **3fa-3ha**). We further introduced -F, -OCH_3 and -CH_3 groups into the 3-position of benzene ring of benzoylacetonitrile **1a** and good results were also obtained (**3ia-3la**, 72−77%). However, introduction

Table 2. Substrate Scope of Benzoylacetonitriles[a)]



[a)] Reaction condition: **1** (0.1 mmol), **2a** (0.12 mmol), $[Cp^*RhCl_2]_2$ (4.0 mol %), additive (2 equiv) in DCE (3 mL) at 50 °C for 6 h. [b)] Determined by ^1H NMR analysis of the crude reaction mixtures.

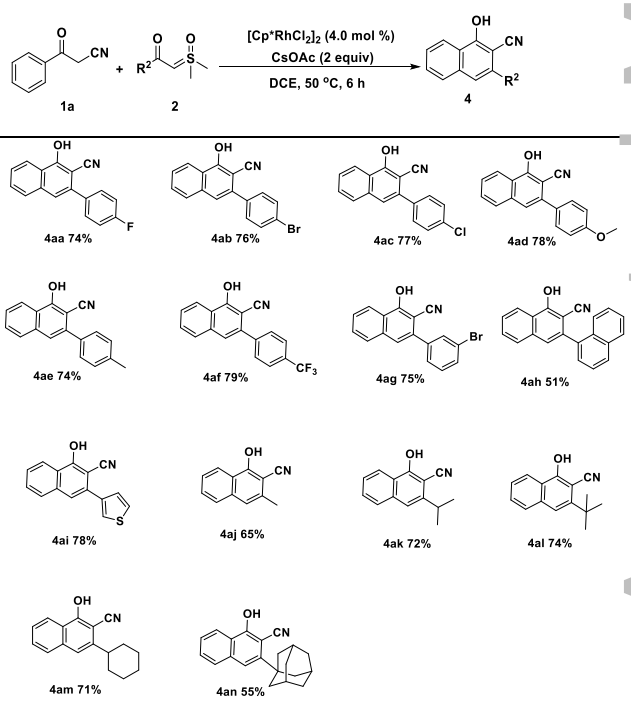
of -OCH_3 group brought a geometric isomer, a small amount of 1-hydroxy-5-methoxy-3-phenyl-2-naphthonitrile was detected (Table 2, **3ka**). In addition, the naphthalene ring and thiophene ring derivatives were also well tolerated in this reaction (Table 2, **3ma**, **3na**, **3oa**).

The scope of sulfoxonium ylides was further examined (Table 3). Sulfoxonium ylides bearing various electron-donating and electron-withdrawing substituents such as methyl, methoxy, halogen, and trifluoromethyl groups at the 4-position (or 3-position) of benzene ring all could couple smoothly with **1a** in excellent yields (Table 3, **4aa**−**4ag**). Introduction of naphthalene or thiophene ring was also tolerated and gave good results (Table 3, **4ah-4ai**). More importantly, replacing R^2 group with different alkyl and cycloalkyl groups could also react smoothly with **1a** to provide the 3-alkyl substituted 2-cyanonaphthols (Table 3, **4aj-4an**) with moderate to high yields (55%-74%).

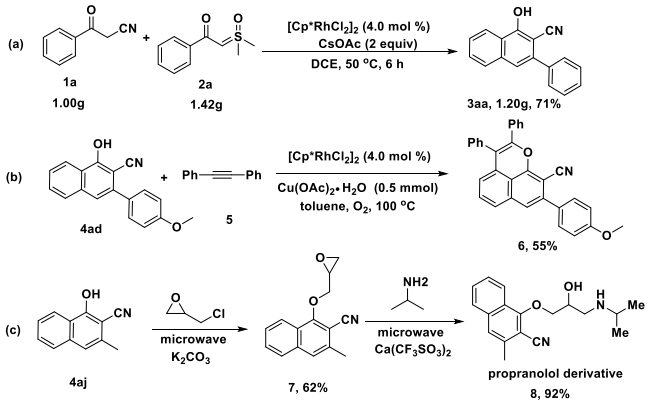
Some synthetic utilities of this protocol were explored. As shown in Scheme 2, a gram-scale preparation of product **3aa** was carried out with 71% isolated yield. Oxidative coupling of the naphthol product **4ad** with diphenylacetylene delivered the fused tricyclic compound **6** with 55% yield, and its analogues were widely used in solid-state fluorescence (Scheme 2b).[18] More intriguingly, the naphthol **4aj** could readily be converted to the derivative of propranolol **8**, which is a sympatholytic nonselective beta blocker and used to treat anti-arrhythmia,[19] with a simple two-step operations (Scheme 2c).

With the established substrate scope and utility of the product, we conducted a series of studies to elucidate the possible mechanism. Several H/D exchange experiments were carried out (Scheme 3). The C-H bond cleavage was likely involved in the turnover-limiting step, as evidenced by the rather large values of k_H/k_D = 2.3 (measured from the competition experiment) and k_H/k_D = 3.4 (measured from parallel reactions) as shown in Scheme 3a. To determine the reversibility of the C-H activation step, a hydrogen-deuterium exchange experiment of **1a** was carried out using D_2O under standard conditions. Both the methylene proton and *ortho* C-H were deuterated by 20% (Scheme 3b), indicating the reversibility of the C(methylene)-H and the C(aryl)-H bond cleavage.

Table 3. Substrate Scope of Sulfoxonium ylide Compouds[a)]

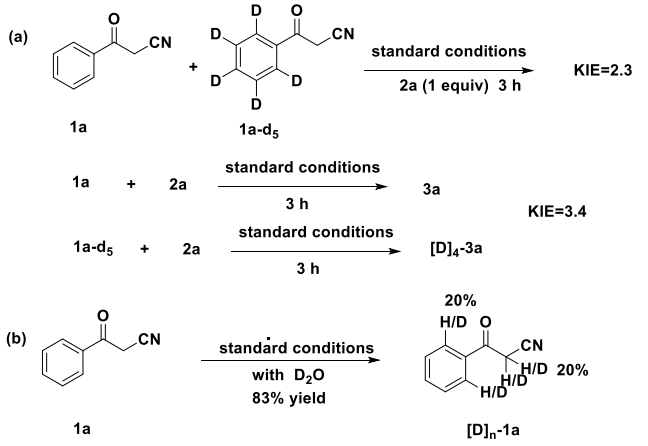


[a)] Reaction condition: **1a** (0.1 mmol), **2** (0.12 mmol), $[Cp^*RhCl_2]_2$ (4.0 mol %), additive (2 equiv) in DCE (3 mL) at 50 °C for 6 h.

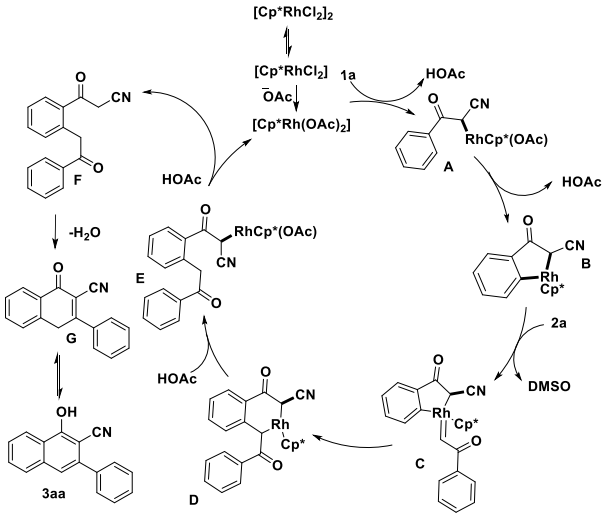


Scheme 2. Gram-Scale Preparation of **3aa** and Conversion of the Products

Based on the preliminary mechanistic experiments and literature precedents, a plausible mechanism is proposed (Scheme 4). Firstly, benzoylacetonitrile was activated by Rh(III) catalyst to give intermediate **A**, followed by the concerted metalation-deprotonation (CMD) pathway to obtain a five membered rhodacycle **B**, which is trapped by the ylide compound **2a** to form the rhodium-carbene **C** upon extrusion of DMSO. Then, migratory insertion of the carbene into the Rh-aryl bond furnishes the six-membered rhodacyclic intermediate **D**, and protonolysis of the Rh-alkyl bond by HOAc leads to intermediate **E**. The catalytic cycle is completed through the ralease of Rh catalysis to give the key intermediate **F**, which underwent a sequential aldol condensation and intramolecular double bond shift to form the desired product **3aa**.



Scheme 3. Preliminary Mechanistic Studies



Scheme 4. Proposed Mechanism

Conclusion

In summary, we developed an efficient Rh(III)-catalyzed annulation of benzoylacetonitriles with sulfoxonium ylides to provide a concise synthetic strategy for 3-substituted naphthols, in which aryl, heterocyclic and alkyl groups in sulfoxonium ylides are tolerated. More importantly, we further implemented derivatization of 1-naphthols to synthesize fused tricyclic scaffolds naphtho[1,8-bc]pyrans and propranolol derivatives *via* some simple operations.

Experimental Section

General precedure for the Synthesis of the Target Naphthols 3 and 4 (3aa as an example)

A pressure tube was charged with $[Cp^*RhCl_2]_2$ (4 mol %, 2.5 mg), CsOAc (0.2 mmol, 19.2 mg), benzoylacetonitrile**1a** (0.1 mmol, 14.5 mg), sulfoxonium ylide **2a** (0.12 mmol, 23.6 mg) and DCE (3 mL). The reaction mixture was stirred at 50 °C for 6 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using DCM/MeOH to afford the product **3aa**, white solid, 19.8 mg, yield 81%. ^{1}HNMR (400 MHz, DMSO-d_6) δ 11.59 (s, 1H), 8.40 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.75-7.71 (t, 1H), 7.68-7.62 (m, 3H), 7.58-7.53 (m, 3H), 7.51 (dd, J = 10.6, 3.8 Hz, 1H). ^{13}CNMR (125 MHz, DMSO-d6) δ 93.5, 116.4, 119.7, 122.0, 122.6, 125.9, 127.6 127.7, 127.8, 128.2, 129.0, 134.8, 137.9, 138.5, 159.1. HRMS (ESI) m/z: calculated for $C_{17}H_{10}NO$ $[M-H]^-$: 244.0768, found: 244.0765.

Synthesis of 8-(4-methoxyphenyl)-2,3-diphenyl-benzo[de]chromene-9-carbonitrile (6)

A dried schlenk tube equipped with a stir bar was loaded with the naphthol **4ad** (59.2 mg, 0.2 mmol), 1,2-diphenylethyne (17.8 mg, 0.1 mmol), [Cp*RhCl2]2 (2.5 mg, 0.004 mmol), $Cu(OAc)_2{\cdot}H_2O$(1.8 mg, 0.01 mmol) and toluene (3 mL) under the atmosphere of O_2 (1 atm). The tube was then stirred at 100 °C for 12 h. After cooling down to room temperature, the solvent was evaporated in vacuum, the residue was purified through flash column chromatography on silica gel to afford the pure product 6,

yellow solid, 16.7 mg, yield: 55%. ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.7 Hz, 2H), 7.48-7.35 (m, 7H), 7.29-7.25 (m, 4H), 7.24-7.21 (m, 2H), 7.08-7.02 (m, 2H), 6.65 (d, *J* = 6.6 Hz, 1H), 3.88 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 160.0, 157.8, 149.4, 141.4, 135.9, 134.6, 132.7, 132.1, 131.2, 130.9, 130.7, 130.1, 129.5, 129.0, 128.9, 128.2, 128.0, 124.0, 120.4, 119.6, 118.4, 117.4, 116.1, 114.1, 90.8, 55.4. HRMS (ESI) m/z: calculated for $C_{32}H_{22}NO_2$ $[M+H]^+$: 452.0334, found: 452.0335.

Synthesis of 1-(2-hydroxy-3-(isopropylamino) propoxy)-3-methyl-2-naphthonitrile (8)

The naphthol **4aj** (1 equiv, 50.0 mg) was dissolved in acetone (3 mL), and potassium carbonate (2 equiv, 75.4 mg) was added in a microwave tube. After epichlorohydrin (2 equiv, 50.5 mg) was added, the tube was sealed and irradiated in a microwave reactor for 20 min at 100 ºC with 100 W. After TLC control, purification with flash chromatography was performed (40.5 mg, yield: 62%).The oxirane **7** (1 equiv, 20.0 mg) and isopropylamine (10 equiv, 50 mg) and calcium trifluoromethanesulfonate (0.5 equiv, 14.1 mg) were added in a microwave tube with seal. The mixtures were irradiated in a microwave reactor for 25 min (100 W, 100 ºC) with the sealed tube. After TLC control, the reaction mixture was purified by flash chromatography to afford oil product **8**: colorless oil, 23.0 mg, yield 92%. ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.3 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.45-7.39 (m, 1H), 7.34 (s, 1H), 4.82-4.72 (m, 1H), 4.32 (d, *J* = 4.0 Hz, 2H), 3.62-3.42 (m, 3H), 2.50 (s, 3H), 1.57-1.43 (m, 6H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 159.9, 136.2, 135.4, 129.5, 127.4, 126.8, 125.2, 124.3, 122.7, 116.3, 103.1, 66.2, 51.9, 48.1, 20.6, 19.1, 18.9. HRMS (ESI) m/z: calculated for $C_{18}H_{23}N_2O_2$ $[M+H]^+$: 299.1754, found: 299.1755.

Acknowledgements

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References

[1] a) M. Granda, C. Blanco, P. Alvarez, J. W. Patrick, R. Menendez, *Chem. Rev.* **2014**, *114*, 1608-1636; b) X. Cai, K. Ng, H. Panesar, S. J. Moon, M. Paredes, K. Ishida, C. Hertweck, T. G. Minehan, *Org. Lett.* **2014**, *16*, 2962-2965; c) E. M. O'Brien, B. J. Morgan, C. A. Mulrooney, P. J. Carroll, M. C. Kozlowski, *J. Org. Chem.* **2010**, *75*, 57-68; d) M. Medarde, A. B. S. Maya, C. Pérez-Melero, *J. Enzyme Inhib. Med. Chem.* **2008**, *19*, 521-540; e) T. Kometani, Y. Takeuchi, E. Yoshii, *J. Org. Chem.* **1983**, *48*, 2630-2632.

[2] a) L.-K. Ho, M.-J. Don, H.-C. Chen, S.-F. Yeh, J.-M. Chen, *J. Nat. Prod.* **1996**, *59*, 330-333; b) M.-I. Chung, S.-J. Jou, T.-H. Cheng, C.-N. Lin, F.-N. Ko, C.-M. Teng, *J. Nat. Prod.* **1994**, *57*, 313-316; c) Y. Kawasaki, Y. Goda, K. Yoshihira, *Chem. Pharm. Bull.* **1992**, *40*, 1504-1509; d) H. Itokawa, K. Mihara, K. Takeya, *Chem. Pharm. Bull.* **1983**, *31*, 2353-2358.

[3] a) S. Chinnadurai, C. Fonnesbeck, K. M. Snyder, N. A. Sathe, A. Morad, F. E. Likis, M. L. McPheeters, *Pediatrics* **2016**, *137*, e20153896; b) J. Hampton, *J. R. Soc. Med.* **2015**, *108*, 418-420; c) J. K. Baker, D. O. Rauls, R. F. Borne, *J. Med. Chem.* **1979**, *22*, 1301-1306.

[4] a) Y. Hemberger, G. Zhang, R. Brun, M. Kaiser, G. Bringmann, *Chem. Eur. J.* **2015**, *21*, 14507-14518; b) V. Kumar, A. Mahajan, K. Chibale, *Biorg. Med. Chem.* **2009**, *17*, 2236-2275; c) G. Bringmann, M. Ochse, R. Götz, *J. Org. Chem.* **2000**, *65*, 2069-2077; d) Y. F. Hallock, K. P. Manfredi, J.-R. Dai, J. H. Cardellina, R. J. Gulakowski, J. B. McMahon, M. Schäffer, M. Stahl, K.-P. Gulden, G. Bringmann, G. François, M. R. Boyd, *J. Nat. Prod.* **1997**, *60*, 677-683; e) G. Bringmann, J. Holenz, B. Wiesen, B. W. Nugroho, P. Proksch, *J. Nat. Prod.* **1997**, *60*, 342-347; f) Y. F. Hallock, K. P. Manfredi, J. W. Blunt, J. H. Cardellina, M. Schaeffer, K.-P. Gulden, G. Bringmann, A. Y. Lee, J. Clardy, *J. Org. Chem.* **1994**, *59*, 6349-6355.

[5] a) L. Lan, C. Appelman, A. R. Smith, J. Yu, S. Larsen, R. T. Marquez, H. Liu, X. Wu, P. Gao, A. Roy, A. Anbanandam, R. Gowthaman, J. Karanicolas, R. N. De Guzman, S. Rogers, J. Aubé, M. Ji, R. S. Cohen, K. L. Neufeld, L. Xu, *Mol. Oncol.* **2015**, *9*, 1406-1420; b) C. Van Poznak, A. D. Seidman, M. M. Reidenberg, M. M. Moasser, N. Sklarin, K. Van Zee, P. Borgen, M. Gollub, D. Bacotti, T. J. Yao, R. Bloch, M. Ligueros, M. Sonenberg, L. Norton, C. Hudis, *Breast Cancer Res. Treat.* **2001**, *66*, 239-248; c) M. D. Shelley, L. Hartley, P. W. Groundwater, R. G. Fish, *Anticancer. Drugs* **2000**, *11*, 209-216; d) T. S. Lin, R. Schinazi, B. P. Griffith, E. M. August, B. F. Eriksson, D. K. Zheng, L. A. Huang, W. H. Prusoff, *Antimicrob. Agents Chemother.* **1989**, *33*, 2149-2151.

[6] a) R.-Q. Xu, Q. Gu, S.-L. You, *Angew. Chem. Int. Ed.* **2017**, *56*, 7252-7256; b) L. Pu, *Acc. Chem. Res.* **2014**, *47*, 1523-1535; c) T. Dohi, N. Takenaga, T. Nakae, Y. Toyoda, M. Yamasaki, M. Shiro, H. Fujioka, A. Maruyama, Y. Kita, *J. Am. Chem. Soc.* **2013**, *135*, 4558-4566; d) S. Brandes, M. Bella, A. Kjærsgaard, K. A. Jørgensen, *Angew. Chem. Int. Ed.* **2006**, *45*, 1147-1151; e) C. B. de Koning, A. L. Rousseau, W. A. L. van Otterlo, *Tetrahedron* **2003**, *59*, 7-36; f) C. A. Mulrooney, X. Li, E. S. DiVirgilio, M. C. Kozlowski, *J. Am. Chem. Soc.* **2003**, *125*, 6856-6857; g) Z. Luo, Q. Liu, L. Gong, X. Cui, A. Mi, Y. Jiang, *Angew. Chem. Int. Ed.* **2002**, *41*, 4532-4535.

[7] a) M. Barday, C. Janot, N. R. Halcovitch, J. Muir, C. Aïssa, *Angew. Chem. Int. Ed.* **2017**, *56*, 13117-13121; b) J. Zheng, S. B. Wang, C. Zheng, S. L. You, *Angew. Chem. Int. Ed.* **2017**, *56*, 4540-4544; c) J. Q. Wu, S. S. Zhang, H. Gao, Z. Qi, C. J. Zhou, W. W. Ji, Y. Liu, Y. Chen, Q. Li, X. Li, H. Wang, *J. Am. Chem. Soc.* **2017**, *139*, 3537-3545; d) J.-R. Huang, C. Bolm, *Angew Chem. Int. Ed.* **2017**, *56*, 15921-15925; e) S. Y. Hong, J. Jeong, S. Chang, *Angew. Chem. Int. Ed.* **2017**, *56*, 2408-2412; f) X. Chen, S. Yang, H. Li, B. Wang, G. Song, *ACS Catal.* **2017**, *7*, 2392-2396; g) Y. Yang, K. Li, Y. Cheng, D. Wan, M. Li, J. You, *Chem. Commun.* **2016**, *52*, 2872-2884; h) G. Song, X. Li, *Acc. Chem. Res.* **2015**, *48*, 1007-1020; i) N. Kuhl, N. Schröder, F. Glorius, *Adv. Synth. Catal.* **2014**, *356*, 1443-1460; j) L. Ackermann, *Acc. Chem. Res.* **2014**, *47*, 281-295; k) G. Song, F. Wang, X. Li, *Chem. Soc. Rev.* **2012**, *41*, 3651-3678; l) T. Satoh, M. Miura, *Chem. Eur. J.* **2010**, *16*,

11212-11222; m) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624-655.

[8]X. Tan, B. X. Liu, X. Y. Li, B. Li, S. S. Xu, H. B. Song, B. Q. Wang, *J. Am. Chem. Soc.* **2012**, *134*, 16163-16166.

[9] S. Zhou, J. Wang, L. Wang, C. Song, K. Chen, J. Zhu, *Angew. Chem. Int. Ed.* **2016**, *55*, 9384–9388.

[10]Q. Wang, Y. Xu, X. Yang, Y. Li, X. Li, *Chem. Commun.* **2017**, *53*, 9640-9643.

[11]F. Xie, S. J. Yu, Z. S. Qi, X. W. Li, *Angew. Chem. Int. Ed*. **2016**, *55*, 15351-15355.

[12]Y. Y. Li, Q. A. Wang, X. F. Yang, F. Xie, X. W. Li, *Org. Lett.* **2017**, *19*, 3410-3413.

[13]Y. W. Xu, X. F. Yang, X. K. Zhou, L. H. Kong, X. W. Li, *Org. Lett.* **2017**, *19*, 4307-4310.

[14] a) Y. Xu, G. Zheng, X. Yang, X. Li, *Chem. Commun.* **2018**, *54*, 670-673; b) X. Wu, H. Xiong, S. Sun, J. Cheng, *Org. Lett.* **2018**, *20*, 1396-1399; c) K. S. Halskov, M. R. Witten, G. L. Hoang, B. Q. Mercado, J. A. Ellman, *Org. Lett.* **2018**; d) J. Vaitla, A. Bayer, K. H. Hopmann, *Angew. Chem. Int. Ed.* **2017**, *56*, 4277-4281.

[15]a) Y. Xie, X. Wu, C. Li, J. Wang, J. Li, H. Liu, *J. Org. Chem.* **2017**, *82*, 5263-5273; b) X. Wu, B. Wang, Y. Zhou, H. Liu, *Org. Lett.* **2017**, *19*, 1294-1297; c) X. Wu, B. Wang, S. Zhou, Y. Zhou, H. Liu, *ACS Catal.* **2017**, *7*, 2494-2499; d) B. Wang, C. Li, H. Liu, *Adv. Synth. Catal.* **2017**, *359*, 3029-3034; e) Y. Li, J. Li, X. Wu, Y. Zhou, H. Liu, *J. Org. Chem.* **2017**, *82*, 8984-8994; f) F. Fang, C. Zhang, C. Zhou, Y. Zhou, H. Liu, *Org. Lett.* **2018**, *20*, 1720-1724.

[16] P. Hu, Y. Zhang, Y. Xu, S. Yang, B. Liu, X. Li, *Org. Lett.* **2018**, DOI: 10.1021/acs.orglett.8b00420.

[17]These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC 1830538).

[18]S. Mochida, M. Shimizu, K. Hirano, T. Satoh, M. Miura, *Chem. Asian J.* **2010**, *5*, 847-851.

[19]N. Huynh, G. J. Lavigne, P. A. Lanfranchi, J. Y. Montplaisir, J. de Champlain, *Sleep* **2006**, *29*, 307-316.

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FULL PAPER

Rh(III)-Catalyzed C-H Activation of Benzoylacetonitriles and Cyclization with Sulfoxonium Ylides to Naphthols

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