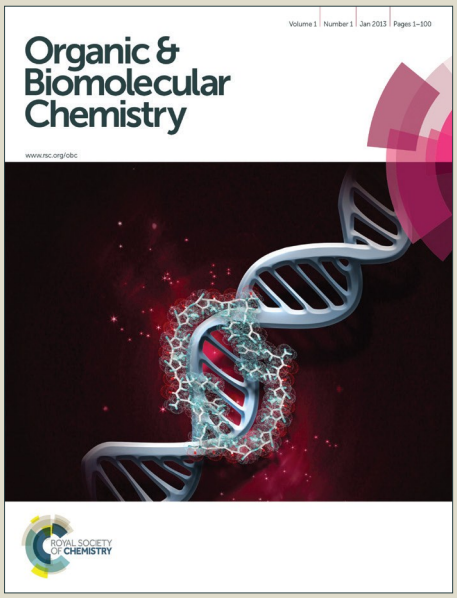
Organic & Biomolecular Chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: T. Chen and Y. Yeung, *Org. Biomol. Chem.*, 2016, DOI: 10.1039/C6OB00756B.



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/obc

DOI: 10.1039/C6OB00756B

Organic & Biomolecular Chemistry

COMMUNICATION

Trifluoroacetic Acid Catalyzed Highly Regioselective Bromocyclization of Styrene-Type Carboxylic Acid†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Tao Chen[b] and Ying-Yeung Yeung*[a,b]

A trifluoroacetic acid catalyzed highly 6-*endo* regioselective bromocyclization of styrene-type carboxylic acid has been developed. The resulting 3,4-dihydroisocoumarines are valuable building blocks in organic synthesis.

Isocoumarine is a class of heterocycle which exhibits various pharmacological activities such as immunomodulatory, antiallergic, antifungal and antiangiogenic effects.[1] In particular, 3,4-dihydroisocoumarine structures are ubiquitous in natural products such as Hydragenol, Phyllodulcin, macrophyllo and Thunberginol G (Figure 1). Significant efforts have been devoted to the synthesis of different isocoumarine.

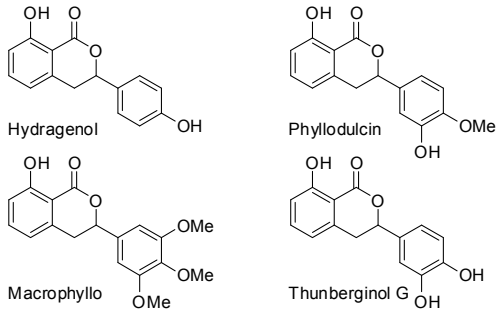
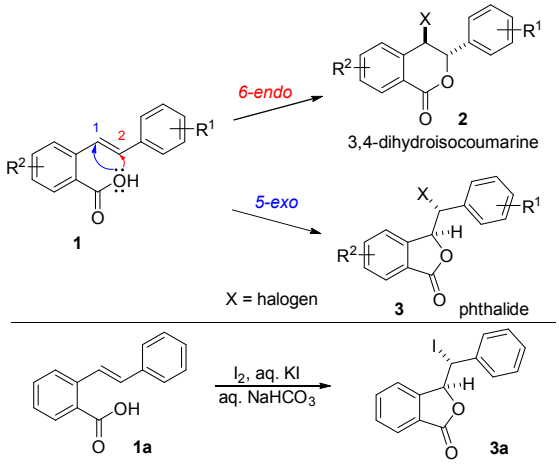


Figure 1 Examples of 3,4-Dihydroisocoumarine-Containing Natural Products.

scaffolds through transition metal-catalyzed reaction.[2] Nonetheless, a versatile and metal-free method to the synthesis of this kind of compounds is still highly desired.[3]

Halocyclization of styrene-type olefinic acid **1** offer an efficient tool towards the synthesis of 3,4-dihydroisocoumarin **2**.[4] The halogen handle in **2** can easily be manipulated to yield various functional molecules. However, practically halocyclization of **1** suffered from an inherent challenge: the halocyclization (e.g. bromocyclization) can go through the 5-*exo* [by the attack of C(1)] and 6-*endo* [by the attack of C(2)] pathways to give a mixture of phthalide and 3,4-dihydroisocoumarin (Scheme 1). Since both C(1) and C(2) are benzylic carbons, poor regioselectivity was usually obtained. The two product isomers have similar solvent mobility on silica gel and are commonly difficulty to be separated by column chromatography. These roadblocks obstruct the utility of halocyclization of **1** in the synthesis of 3,4-dihydroisocoumarin. Indeed, it has been reported that treatment of **1a** with I_2/KI gave phthalide **3a** (X = I) (Scheme 1).[5] In order to develop an



Scheme 1 Bromocyclization of Styrene-type Carboxylic Acid.

electrophilic halocyclization that is practically useful in the synthesis of 3,4-dihydrocoumarin, a highly regioselective catalytic protocol is highly desired. To address this problem, herein we are pleased to report our recent success in using trifluoroacetic acid (TFA) as the catalyst in the highly 6-*endo* selective bromocyclization of **1** to give 3,4-dihyroisocoumarines **2**.

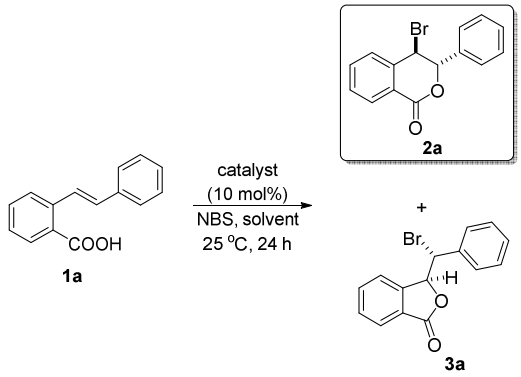
Bromocyclization of **1a** was performed using *N*-bromosuccinimide (NBS) and $CHCl_3$ as the electrophilic

[a] Department of Chemistry, The Chinese University of Hong Kong, Shatin, NT, Hong Kong, China, E-Mail: yyyeung@cuhk.edu.hk
[b] Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore†Electronic Supplementary Information (ESI) available. For ESI, see DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C6OB00756B

brominating reagent and the solvent, respectively. When no catalyst was applied, it was found that a mixture of isomers 3,4-dihydroisocoumarine **2a** and phthalide **3a** was obtained with low regioselectivity (**2a**/**3a** = 5:1) (Table 1, entry 1). To

Table 1 Reaction optimization[a]

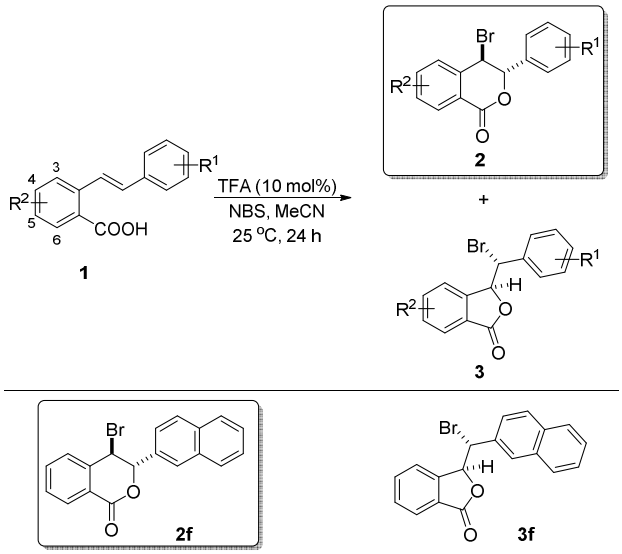


Entry	Catalyst	Solvent	Yield[b] (%)	**2a**:**3a**[c]
1	None	$CHCl_3$	98	5:1
2	DMAP	$CHCl_3$	90	1:1.4
3[d]	Na_2CO_3	$CHCl_3$	82	1:1.3
4	Ph_3PS	$CHCl_3$	80	30:1
5	Ph_3PSe	$CHCl_3$	82	24:1
6	CF_3COOH	$CHCl_3$	99	50:1
7	AcOH	$CHCl_3$	98	3.6:1
8	PhCOOH	$CHCl_3$	98	5:1
9	CF_3COOH	THF	80	30:1
10	CF_3COOH	EtOAc	36	>99:1
11	CF_3COOH	MeCN	99	88:1
12[e]	CF_3COOH	MeCN	99	>99:1
13	None	MeCN	99	3.8:1
14[e,f]	CF_3COOH	MeCN	99	>99:1
15[e,g]	CF_3COOH	MeCN	99	>99:1

[a] Reactions were carried out with **1a** (0.3 mmol), NBS (0.33 mmol), and catalyst (0.03 mmol, 10 mol%)) in solvent (2 mL) at 25 °C in the absence of light. [b] The yields were determined by ^{1}H NMR analysis of the mixture with hexamethylbenzene as the internal standard. [c] The ratio was determined by ^{1}H NMR analysis of the mixture. [d] 1 equivalent of Na_2CO_3 was used. [e] Anhydrous MeCN was used. [f] 5 mol% CF_3COOH was used. [g] 100 mol% CF_3COOH was used.

efficiently obtain the 3,4-dihydroisocoumarine **2a**, a series of catalysts were subjected to the investigation. Although *N,N*-dimethylaminopyridine (DMAP) and Na_2CO_3 are well-known to facilitate halolactonization,[6] almost no regioselectivity was observed when these two bases were employed (Table 1, entries 2 and 3). Triphenylphosphine sulfide and triphenylphospine selenide, which are effective Lewis bases for electrophilic bromocyclization reactions,[7] offered good 6-*endo* selectivity in the bromocyclization of **1a** (Table 1, entries 4 and 5). To our delight, the 6-*endo* selectivity (**2a**/**3a** = 50:1) was dramatically improved when 10 mol% TFA was applied (Table 1, entry 6). On the other hand, other weaker acids such as acetic acid or benzoic acid gave much lower selectivity (Table 1, entries 7 and 8). Next, a brief survey on solvent was conducted (Table 1, entries 9–11) and acetonitrile was found to be the suitable reaction media in which 3,4-dihydroisocoumarine **2a** was obtained in exceedingly high 6-*endo* selectivity (**2a**/**3a** = 88:1) (Table 1, entry 11). Ethyl acetate was found to be a suitable solvent to give high regioselectivity but the reaction was sluggish (Table 1, entry 10). A control experiment was performed using acetonitrile as the solvent in the absence of catalyst, revealed the crucial role of TFA in controlling the regioselectivity (Table 1, entry 13). After extensive experimentation, it was realized that **2a** could be accomplished as the exclusive product when anhydrous acetonitrile was used (Table 1, entry 12). When the TFA loading was decreased to 5 mol% or increased to 100 mol%, the excellent 6-*endo* selectivity preserved (Table 1, entries 14 and 15). It is noteworthy that TFA can easily be removed *in vacuo*, which simplifies the purification process.

Table 2 TFA-Catalyzed Bromocyclization of **1**[a]



Entry	Substrate	R^1	R^2	Yield[b] (%)	**2**:**3**[c]
1	**1a**	H	H	99	>99:1 (3.8:1)
2	**1b**	4-F	H	98	>99:1 (4.6:1)
3	**1c**	4-Cl	H	99	>99:1 (1.1:1)
4	**1d**	4-Me	H	98	>99:1 (5:1)
5	**1e**	4-MeO	H	99	>99:1 (9:1)
6	**1f**	-	H	99	>99:1 (8.3:1)
7	**1g**	2-Me	H	95	>99:1 (2.5:1)
8	**1h**	3-Me	H	99	>99:1 (1.6:1)
9	**1i**	H	4-F	99	>99:1 (8.3:1)
10	**1j**	H	5-F	99	>99:1 (4.8:1)

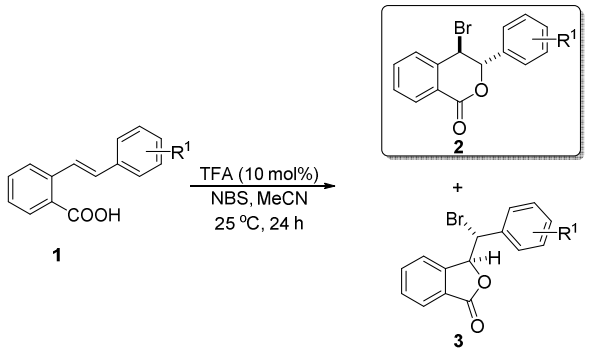
[a] Reactions were carried out with **1** (0.15 mmol), NBS (0.165 mmol), and TFA (0.015 mmol, 10 mol%) in MeCN (1 mL) at 25 °C in the absence of light. [b] Isolated yield. [c] The ratio was determined by ^{1}H NMR analysis of the mixture. The ratio of **2**:**3** in the absence of TFA is indicated in the parentheses.

With the optimized conditions in hand, a series of carboxylic acids **1** were investigated. As shown in Table 2, when the reactions were performed in the absence of TFA, the respective regioselectivity was poor with the **2**/**3** ratio ranging from 1:1 to 9:1. In a stark contrast, the reactions gave the

View Article Online
DOI: 10.1039/C6OB00756B

desired 3,4-dihydroisocoumarines **2** exclusively and quantitatively regardless of the electronic property of the substituent. For instance, electron-deficient (**1b–c**) and electron-rich aryls (**1d–e**) substrates worked well to give the desired 6-*endo* cyclization products **2b–e** (Table 2, entries 2–5). Sterically hindered substituents such as 2-naphthyl (**1f**), 2-methylphenyl (**1g**) and 3-methylphenyl (**1h**) substrates were also examined and **2f–h** were obtained smoothly as the exclusive products (Table 2, entries 6–8). In addition, substrates such as **1i** and **1j** with the substituent on benzoic acid moiety, the corresponding 6-*endo* selective products were also obtained as the sole products in quantitative yield (Table 2, entries 9 and 10). A group of substrates **1k–1n** were also studied (Table 3). These substrates contain electron-withdrawing R^1 groups, which lead to the 5-*exo* selective products predominately in the uncatalyzed electrophilic bromocyclization reaction. Nonetheless, the inherent preference of 5-*exo* was overridden in the presence of 10 mol% of TFA, furnishing **2k–2n** in high 6-*endo* selectivity and reaction yields (Table 3, entries 1–5). For the case using substrate **1n**, the **2n**/**3n** selectivity could be further enhanced when 1 equivalent of TFA was used (Table 3, entry 5).

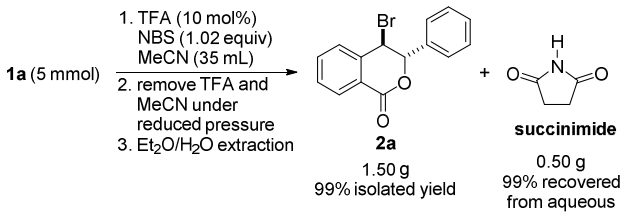
Table 3 Studies on Highly Electron-Deficient Substrates **1k–1n**[a]



Entry	Substrate	R^1	Yield[b] (%)	**2**:**3** with TFA[c]	**2**:**3** without TFA[c]
1	**1k**	2-Cl	98	11:1	1:3
2	**1l**	3-NO_2	91	2:1	1:12
3	**1m**	4-Br	99	>99:1	1:2
4	**1n**	4-CF_3	98	4:1	1:3.3
5	**1n**	4-CF_3	99	5:1[d]	1:3.3

[a] Reactions were carried out with **1a** (0.3 mmol), NBS (0.33 mmol), and catalyst (0.03 mmol, 10 mol%)) in solvent (2 mL) at 25 °C in the absence of light. [b] The yields were determined by ^{1}H NMR analysis of the mixture with hexamethylbenzene as the internal standard. [c] The ratio was determined by ^{1}H NMR analysis of the mixture. [d] 1 equivalent of Na_2CO_3 was used. [e] Anhydrous MeCN was used.

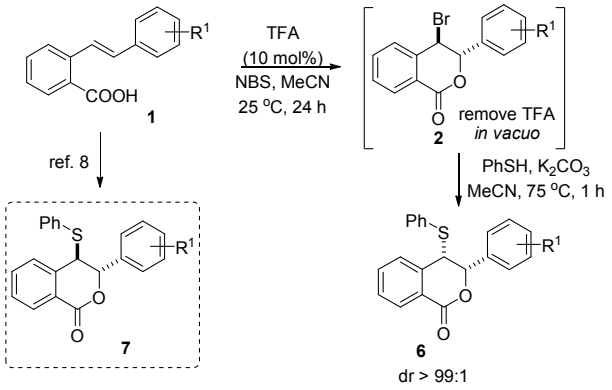
The reaction was found to be readily scalable without loss of reaction yield and regioselectivity. Since TFA has a relatively low boiling point, it could be removed under reduced pressure. To this end, we conducted a gram-scale reaction and purified the product without using column chromatography[8] with the following sequence: (1) 1.12 g of **1a** was subjected to the bromocyclization under the optimized conditions; (2) the solvent MeCN and the catalyst TFA were removed under reduced pressure; (3) the residue was extracted with Et_2O/H_2O. Pure product **2a** (analyzed by NMR) was obtained (1.50 g, 99% yield) from the Et_2O fraction. Succinimide, the Br carrier, was recovered quantitatively from the aqueous extract.



chromatography-free condition

Scheme 2 Chromatography-Free Synthesis of **2a** in Gram-Scale.

We applied this type of catalysis to the one-pot synthesis of *cis*-3-aryl-4-(phenylthio)dihydroisocoumarines (Scheme 3). After the bromocyclization of **1**, TFA was removed under reduced pressure. Thiophenol and potassium carbonate were then added and the resultant solution was heated to 75 °C for 1 h. The desired *cis*-3-aryl-4-(phenylthio)dihydroisocoumarines **6** were obtained in high yields with excellent diastereoselectivities. This transformation is complementary to the electrophilic cyclization towards the construction of *trans*-3-aryl-4-(phenylthio)dihydroisocoumarines **7** using the diaryl disulfide as the reagent.[9]



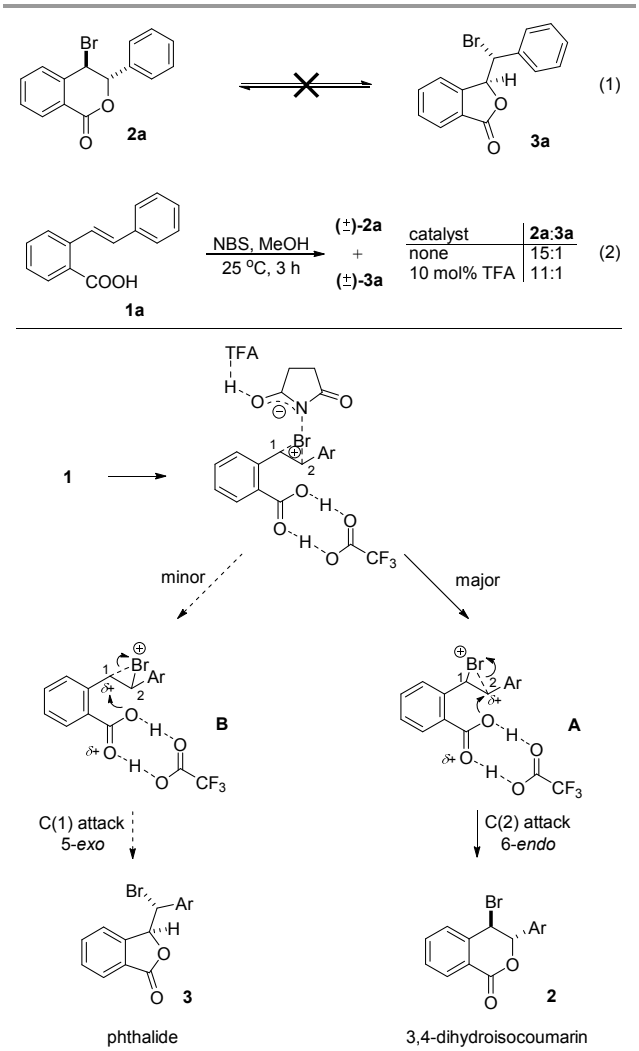
substrate	product **6**	yield (%)
1a	**6a**	80
1c	**6c**	74
1d	**6d**	81
1f	**6f**	75

Scheme 3 One-pot Synthesis of **6**.

Although the role of TFA in inducing high regioselectivity of the cyclization of **1** remains unclear, it is interesting to see that the regioselectivity of the cyclization can be overridden particularly for the electron-deficient substrates (Table 3). Several experiments were conducted in order to shed light on the mechanistic picture. We had suspected that **2** and **3** might be interchangeable in the presence of TFA.[10] However, there was no observable change in the constitution when either **2a** or **3a** was stirred in acetonitrile and 10 mol% of TFA,

View Article Online
DOI: 10.1039/C6OB00756B

suggesting that **2** and **3** were formed independently from **1** (Scheme 4, eq. 1). We have also conducted the cyclization using anhydrous MeOH as the solvent and it was realized that the effect of TFA on the regioselectivity was negligible (Scheme 4, eq. 2). Together with the observation that the moisture has a deteriorated effect on the regioselectivity (Table 1, entries 11 and 12), one of the possible explanations is that water (or MeOH) might interrupt the hydrogen-bond interaction between the substrate and TFA.



Scheme 4 A Plausible Reaction Mechanism.

A plausible mechanism is illustrated in Scheme 4. While TFA could interact with NBS, we speculated that TFA could also hydrogen-bond to the carboxylic moiety in **1**. Since both C(1) and C(2) are benzylic carbons, the partial positive charge in the bromiranium ion species could be stabilized on both carbons (i.e. species **A** or **B**); this could explain why a mixture of **2** and **3** is usually obtained in the bromocyclization of **1**. However, protonation of the carboxylic acid in **1** by TFA would lead to the destabilization of the partial positive charge on C(1) (through conjugation), which would disfavor the formation of species **B** and result in the selective formation of 3,4-dihydroisocoumarin **2** through species **A**. We also suspected that water or MeOH might interrupt the hydrogen-bond interaction between **1** and TFA, resulting in a lower regioselectivity. Even though the formation of phthalide **3** through 5-*exo*-cyclization was favored when the aryl group is highly electron-deficient [which can destabilize the partial carbocation on C(2)], the effect of TFA appears to be strong which can override the inherent preference (see Table 3).

In summary, we have developed an efficient methodology to synthesize 3,4-dihydroisocoumarine derivatives through highly 6-*endo* selective bromocyclization of styrene-type carboxylic acids by simply using TFA as the catalyst. Catalytic amount of TFA could improve the ratios of 6-*endo*/5-*exo* products to > 99:1 in most cases. The reaction could be well carried out in gram-scale synthesis without loss of the selectivity. The bromocyclized product could be obtained without using of chromatography and succinimide could be easily recovered. This methodology has been applied to the one-pot synthesis of *cis*-3-aryl-4-(phenylthio)dihydroisocoumarine. A detailed mechanistic study is underway.

We thank the financial supports from The Chinese University of Hong Kong Direct Grant (project code: 4053157) and Tier 1 funding from National University of Singapore (grant no. 143-000-605-112).

Notes and references

1 (*a*) H. Matsuda, H. Shimoda, J. Yamahara, M. Yoshikawa, *Bioorg*. *Med*. *Chem*. *Lett*., 1998, **8**, 215–220; (*b*) H. Matsuda, H. Shimoda, M. Yoshikawa, *Bioorg*. *Med*. *Chem*., 1999, **7**, 1445–1450; (*c*) K. Nozawa, M. Yamada, Y. Tsuda, K. Kawai, S. Nakajima, *Chem*. *Pharm*. *Bull*., 1981, **29**, 2491–2495; (*d*) K. Nozawa, M. Yamada, Y. Tsuda, K. Kawai, S. Nakajima, *Chem*. *Pharm*. *Bull*., 1981, **29**, 2689–2691; (*e*) J. H. Lee, Y. J. Park, H. S. Kim, Y. S. Hong, K.-W. Kim, J. J. Lee, *J*. *Antibiot*., 2001, **54**, 463–466.

2 Selected examples for tranisition metal catalyzed reactions in the synthesis of isocoumarines, see: (*a*) A.-Y. Peng, Y.-X. Ding, *J*. *Am*. *Chem*. *Soc*., 2003, **125**, 15006–15007; (*b*) H.-Y. Liao, C.-H. Cheng, *J*. *Org*. *Chem*., 1995, **60**, 3711–3716; (*c*) V. Subramanian, V. R. Batchu, D. Barange, M. Pal. *J*. *Org*. *Chem*., 2005, **70**, 4778–4783; (*d*) S. Roy, B. Neuenswander, D. Hill, R. C. Larock, *J*. *Comb*. *Chem*., 2009, **11**, 1128–1135; (*e*) R. Prakash, K. Shekarrao, S. Gogoi, R. C. Boruah, *Chem*. *Commun*., 2015, **51**, 9972–9974; (*f*) R. K. Chinnagolla, M. Jeganmohan, *Chem*. *Commun*., 2012, **48**, 2030–2032; (*g*) A. C. Tadd, M. R. Fielding, M. C. Willis, *Chem*. *Commun*., 2009, 6744–6746; (*h*) S. J. Cai, F. Wang, C. J. Xi, *J*. *Org*. *Chem*., 2012, **77**, 2331–2336; (*i*) K. Ueura, T. Satoh, M. Miura, *Org*. *Lett*., 2007, **9**, 1407–1409; (*j*) K. Ueura, T. Satoh, M. Miura, *J*. *Org*. *Chem*., 2007, **72**, 5362–5367; (*k*) B. Chen, S. M. Ma, *Org*. *Lett*., 2013, **15**, 3884–3887; (*l*) W.-J. Yoo, T. V. Q. Nguyen, S. Kobayashi, *Angew*. *Chem*. *Int*. *Ed*., 2014, **53**, 10213–10217; (*m*) S. Warratz, C. Kornhaaß, A. Cajaraville, B. NiepÖtter, D. Stalke, L. Ackermann, *Angew*. *Chem*. *Int*. *Ed*., 2015, **54**, 5513–5517.

3 (*a*) S. K. Gadakh, A. Sudalai, *RSC Adv*., 2014, **4**, 57658–57661; (*b*) W. E. Bauta, D. P. Lovett, Jr. W. R. Cantrell, B. D. Burke, *J*. *Org*. *Chem*., 2003, **68**, 5967–5973; (*c*) R. S. Mali, K. N. Babu, *J*. *Org*. *Chem*., 1998, **63**, 2488–2492; (*d*) M. Uchiyama, H. Ozawa, K. Takuma, Y. Matsumoto, M. Yonehara, K. Hiroya, T.

View Article Online
DOI: 10.1039/C6OB00756B

Sakamoto, *Org*. *Lett*., 2006, **8**, 5517–5520; (*e*) G.-H. Ma, B. Jiang, X.-J. Tu, Y. Ning, S.-J. Tu, G. Li, G. *Org*. *Lett*., 2014, **16**, 4504–4507; (*f*) G. C. A. Bellinger, W. E. Campbell, R. G. F. Giles, J. D. Tobias, *J. Chem*. *Soc*. *Perkin Trans*. *1*, 1982, 2819–2825; (*g*) M. E. Botha, R. G. F. Giles, C. M. Moorhoff, L. M. Engelhardt, A. H. White, A. Jardine, S. C. Yorkea, *J. Chem*. *Soc*. *Perkin Trans*. *1*, 1991, 89–95; (*h*) M. Brasholz, H.-U. Reissig, *Synlett,* 2004, 2736–2738; (*i*) G. L. Bras, A. Hamze, S. Messaoudi, O. Provot, P.-B. L. Calvez, J. D. Brion, M. Alami, *Synthesis,* 2008, 1607–1611; (*j*) K. Sudarshan, M. K. Manna, I. S. Aidhen, *Eur*. *J*. *Org*. *Chem*., 2015, 1797–1803.

4 (*a*) A. K. Verma, V. Rustagi, T. Aggarwal, A. P. Singh. *J. Org*. *Chem*., 2010, **75**, 7691–7703; (*b*) J. Chen, L. Zhou, C. K. Tan, Y.-Y. Yeung, *J*. *Org*. *Chem*., 2012, **77**, 999–1009.

5 R. S. Mali, A. P. Massey, M. I. Talele, *J. Chem. Research (S),* 1998, 68–69.

6 (*a*) J. L. Huang, H. Y. Wang, A.-Y. Peng, *Eur*. *J*. *Org*. *Chem*., 2014, 8126–8132; (*b*) W. Zhang, H. D. Xu, H. Xu, W. P. Tang, *J*. *Am*. *Chem*. *Soc*., 2009, **131**, 3832–3833; (*c*) R. Antonioletti, S. Malancona, P. Bovicelli, *Tetrahedron*, 2002, **58**, 8825–8831; (*d*) R. Antonioletti, S. Malancona, F. Cattaruzza, P. Bovicelli, *Tetrahedron*, 2003, **59**, 1673–1678.

7 (*a*) Y. Kawato, A. Kubota, H. Ono, H. Egami, Y. Hamashima, *Org. Lett.,* 2015, **17**, 1244; (*b*) Y.-C. Wong, Z. Ke, Y.-Y. Yeung, *Org. Lett.,* 2015, **17**, 4944; (*c*) Z. Ke, C. K. Tan, F. Chen, Y.-Y. Yeung, *J. Am. Chem. Soc*., 2014, **136**, 562; (*d*) Y. Sawamura, H. Nakatsuji, A. Sakakura, K. Ishihara, *Chem. Sci*., 2013, **4**, 4181; (*e*) F. Chen, C. K. Tan, Y.-Y. Yeung, *J. Am. Chem*. *Soc.,* 2013, **135**, 1232; (*f*) S. J. Balkrishna, C. D. Prasad, P. Panini, M. R. Detty, D. Chopra, S. Kumar, *J. Org. Chem*., 2012, **77**, 9541; (*g*) X. Jiang, C. K. Tan, L. Zhou, Y.-Y. Yeung, *Angew. Chem. Int. Ed.,* 2012, **51**, 7771; (*h*) C. K. Tan, C. Le, Y.-Y. Yeung, *Chem. Commun.,* 2012, **48**, 5793; (*i*) L. Zhou, J. Chen, C. K. Tan, Y.-Y. Yeung, *J. Am. Chem. Soc.,* 2011, **133**, 9164; (*j*) C. K. Tan, L. Zhou, Y.-Y. Yeung, *Org. Lett.,* 2011, **13**, 2738; (*k*) S. Snyder, A. D. S. Treitler, A. P. Brucks, *J. Am. Chem. Soc*., 2010, **132**, 14303; (*l*) S. E. Denmark, M. T. Burk, *Proc. Natl. Acad. Sci. U.S.A*., 2010, **107**, 20655; (*m*) S. A. Snyder, D. S. Treitler, *Angew. Chem. Int. Ed*., 2009, **48**, 7899; (*n*) S. R. Mellegaard, J. A. Tunge, *J. Org. Chem*., 2004, **69**, 8979.

8 (*a*) G. An, C. Seifert, G. Li, *Org. Biomol. Chem.*, 2015, **13**, 1600–1617; (*b*) C. W. Seifert, S. Pindi, G. Li, *J. Org. Chem.*, 2015, **80**, 447−452; (*c*) B. Yang, M. Shen, X. Ji, Z. Xu, H. Sun, B. Jiang, G. Li, *J. Org. Chem.*, 2016, **81**, 2488–2493.

9 S. A. Shahzad, C. Venin, T. Wirth, *Eur*. *J*. *Org*. *Chem*., 2010, 3465–3472.

10 (*a*) W. P. Jackson, S .V. Ley, J. A. Morton, *Chem*. *Commun*., 1980, 1028–1029; (*b*) W. P. Jackson, S. V. Ley, J. A. Morton, *Chem*. *Commun*., 1980, 1173–1174; (*c*) W. P. Jackson, S. V. Ley, J. A. Morton, *Tetrahedron Lett*., 1981, **22**, 2601–2604; (*d*) S. V. Ley, B. Lygo, H. Molines, J. A. Morton, *Chem*. *Commun*., 1982, 1251–1252; (*e*) A. C. Cunat, D. Diez-Martin, S. V. Ley, F. J. Montgomery, *J. Chem*. *Soc*. *Perkin Trans*. *1*, 1996, 611–620; (*f*) M. Tiecco, L. Testaferri, M. Tingoli, F. Marini, *Chem*. *Commun*., 1994, 221–222.