DOI: 10.1002/adsc.201100338

Efficient One-Pot Synthesis of Dibenzopyranones *via* a Decarboxylative Cross-Coupling and Lactonization Sequence

Jiaying Luo,[a] Youling Lu,[a] Saiwen Liu,[a] Jing Liu,[a] and Guo-Jun Deng[a,*]

[a] Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, People's Republic of China
Fax: (+86)-731-5829-2251; phone: (+86)-731-5829-8601; e-mail: gjdeng@xtu.edu.cn

Received: May 1, 2011; Revised: June 26, 2011; Published online: October 10, 2011

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adcs.201100338.

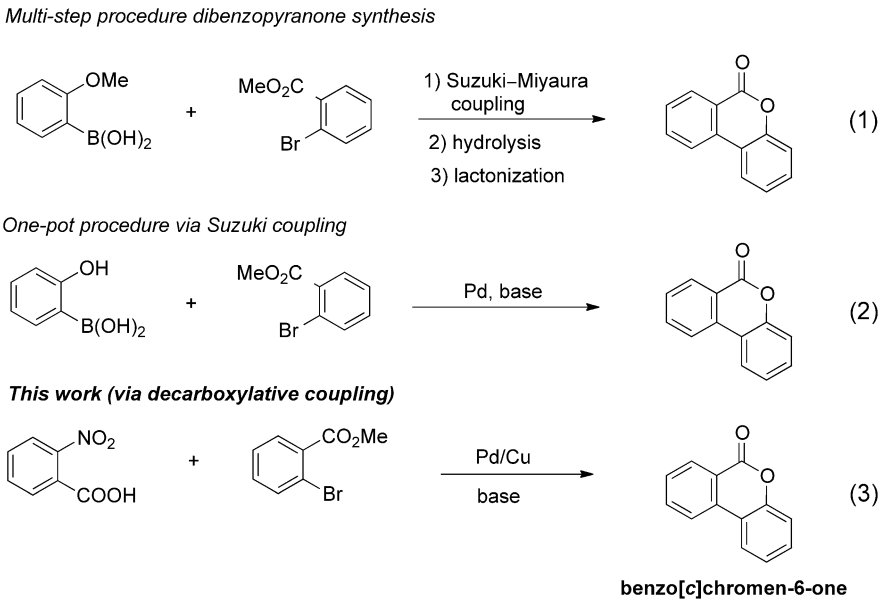
Abstract: A highly selective palladium bis(acetoacetonate)/copper(I) chloride [$Pd(acac)_2$/CuCl] catalytic system for the preparation of dibenzopyranones has been developed. Tandem decarboxylative coupling and lactonization can be realized in one pot using commercially available starting materials. The reaction proceeded well for a range of different substrates.

Keywords: copper; decarboxylation; dibenzopyranones; lactonization; palladium; tandem reactions

Dibenzopyranone motifs are present in many natural products and biologically active molecules.[1] Dibenzopyranones are of great importance as intermediates for the synthesis of various pharmaceutically interesting compounds such as glucocorticoids,[2] progesterone,[3] endothelial cell proliferation inhibitors[4] and androgen receptor ligands.[5] Common lactone synthesis mainly relies on lactonization from the corresponding carboxylic acids and alcohols.[6] There are several methods available for the synthesis of dibenzopyranones which usually require several steps.[7] The most used method involves Suzuki–Miyaura cross-coupling followed by Lewis acid-[8] or metal[9]-mediated lactonization of ester and methoxy groups [Scheme 1, Eq. (1)]. For the lactonization step, other alternative synthetic routes have also been developed, for example, the direct lactonization of carboxylic acid to an aromatic ring,[10] the displacement of a nitro group with carboxylic acid[11] and the displacement of a benzyl group.[12] However, these methods generally include several steps and require the purification of the intermediates. Also, relatively expensive reagents such as boronic acids and boron tribromide are needed. Thus, the search for a dibenzopyranone synthesis using widely available starting materials and fewer steps is highly desirable. Very recently, Visnumurthy and co-workers developed a microwave-promoted one-step parallel synthesis of dibenzopyranones *via* Suzuki–Miyaura cross-coupling from bromoarylcarboxylates and *o*-hydroxyarylboronic acids, followed by lactonization. Various dibenzopyranones can be prepared by this method in high yields [Scheme 1, Eq. (2)].[13] However, most of the starting materials used for this transformation are not commercially available.

Carboxylic acids are easy to store, simple to handle, and when necessary, are accessible preparatively by means of a large number of well-established methods. The ready availability of carboxylic acids makes them extremely promising raw materials for chemical synthesis.[14] In the 1960s, Nilsson et al. observed that biaryls could be obtained from aryl iodides and aromatic carboxylic acids.[15] However, this reaction has not attracted much attention for a long time due to the low reaction yield, high reaction temperature and large amount of copper salt used. Recently, transition metal-catalyzed decarboxylative cross-couplings have received much attention and have evolved as an advantageous alternative for biaryls synthesis. Using catalytic amounts of metal catalysts, various biaryls can be prepared from aromatic carboxylic acids and aryl halides[16] or even C–H bonds.[17] Palladium and copper are the most used catalysts for decarboxylative coupling reactions. Electron-withdrawing groups such as nitro group at the *ortho*-position of the carboxylic acid can significantly increase the reactivity.

Based on this knowledge, we hypothesized that an alternative procedure using commercially available starting materials for dibenzopyranone preparation might be possible *via* a decarboxylative coupling reaction and lactonization sequence using 2-nitrobenzoic acid and methyl 2-bromobenzoate as starting materials. The decarboxylative coupling of these substrates



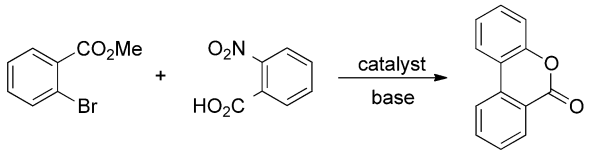
Scheme 1. Methods for the synthesis of dibenzopyranones.

will generate a methyl 2′-nitrobiphenyl-2-carboxylate intermediate, and hydrolysis of the methyl carboxylate will generate the corresponding carboxylic acid which will undergo a displacement reaction between the carboxylic acid and the nitro group.[11] To get the methyl 2′-nitrobiphenyl-2-carboxylate intermediate, we started our investigation by using similar reaction conditions to those developed by Goossen and coworkers for decarboxylative preparation of 2-nitrobiphenyl derivatives using a Pd/Cu catalytic system.[16a] To our surprise, we did not get the intermediate methyl 2′-nitrobiphenyl-2-carboxylate. Instead, the final product, dibenzopyranone, was observed as detemined by GC-MS and ^{1}H NMR methods in low yield. This unexpected reaction inspired us to re-optimize the reaction conditions to get a satisfying yield for substituted dibenzopyranones in one pot using commercially available starting materials. Herein we report a one pot synthesis of dibenzopyranones by palladium/copper-catalyzed decarboxylative coupling and lactonization of esters with a nitro group [Scheme 1, Eq. (3)].

To begin our study, the reaction of commercially available methyl 2-bromobenzoate (**1a**) and 2-nitrobenzoic acid (**2a**) was chosen as a model using Pd(OAc)$_2$ and CuI as catalysts. When methyl 2-bromobenzoate was reacted with 1.2 equivalents of 2-nitrobenzoic acid, the desired product was observed in 16% yield (Table 1, entry 1). The reaction showed very poor selectivity and homo-coupling by-products of **1a** and **2a** were obtained in 22% and 24% yields, respectively. To improve the reaction yield and selectivity, various palladium and copper salts were tested for this transformation (entries 2–9). Among the palladium salts tested, Pd(acac)$_2$ showed the best yield, and the desired product was obtained in 30% yield (entry 7). The combination of Pd(acac)$_2$ and CuCl gave the desired product in 40% yield (entry 9). The reaction was inefficient in the absence of a copper catalyst (entry 10). However, the desired product could be achieved in 21% yield when CuCl was used as the sole catalyst (entry 11). Various ligands were screened using Pd(acac)$_2$ and CuCl as catalysts (entries 12–19). Among the nitrogen-containing ligands investigated, bipyridine exhibited the best efficiency (entry 13). Various phosphines were also tested as ligands and were more efficient than nitrogen-containing ligands (entries 15–19). The desired product could be achieved in 88% yield when DPEphos {bis[(2-diphenylphosphino)phenyl] ether} was used as ligand (entry 19). The reactions in other solvents were also investigated (entries 20–22). DMSO (dimethyl sulfoxide) and DMA (*N*,*N*-dimethylacetamide) are good solvents for this reaction.

With the optimized conditions in hand, the scope of the reaction with respect to the substituted aryl esters (**1**) and 2-nitrobenzoic acid (**2a**) was investigated (Table 2). The desired product could be achieved in 76% yield when methyl 2-bromobenzoate (**1a**) was used (entry 1). The reaction yield decreased significantly when ethyl 2-bromobenzoate was used, and only 34% yield was obtained (entry 2). Methyl 2-chlorobenzoate (**1c**) and methyl 2-iodobenzoate (**1d**) also could be successfully coupled with **2a** and gave the desired products in 70% and 65% yields, respectively (entries 3 and 4). Electron-donating groups present on the aryl esters favored the reaction and good yields were obtained when **1e** and **1f** were used

Table 1. Optimization of reaction conditions.[a]

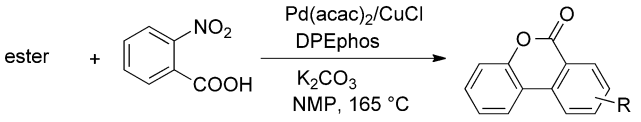


1a **2a** **3a**

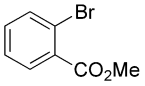
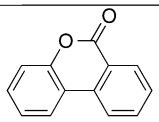
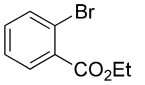
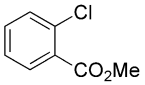
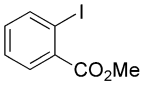
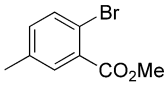
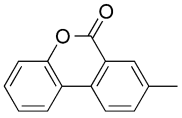
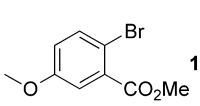
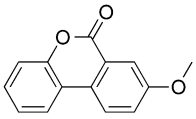
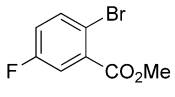
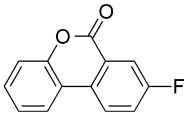
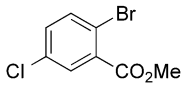
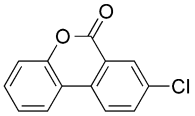
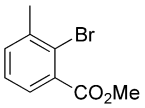
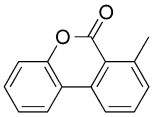
Entry	Pd	Cu	Ligand	Solvent	Yield [%][b]
1	$Pd(OAc)_2$	CuI	Phen	NMP	16
2	$Pd(OH)_2$	CuI	Phen	NMP	13
3	$Pd(TFA)_2$	CuI	Phen	NMP	15
4	$PdCl_2$	CuI	Phen	NMP	15
5	$Pd_2(dba)_3$	CuI	Phen	NMP	13
6	$PdBr_2$	CuI	Phen	NMP	20
7	$Pd(acac)_2$	CuI	Phen	NMP	30
8	$Pd(acac)_2$	CuBr	Phen	NMP	18
9	$Pd(acac)_2$	CuCl	Phen	NMP	40
10	$Pd(acac)_2$	----	Phen	NMP	0
11	----	CuCl	Phen	NMP	21
12	$Pd(acac)_2$	CuCl	DBU	NMP	45
13	$Pd(acac)_2$	CuCl	bipyridine	NMP	66
14	$Pd(acac)_2$	CuCl	DMAP	NMP	49
15	$Pd(acac)_2$	CuCl	PPh_3	NMP	72
16	$Pd(acac)_2$	CuCl	dppe	NMP	70
17	$Pd(acac)_2$	CuCl	dppp	NMP	73
18	$Pd(acac)_2$	CuCl	dppb	NMP	82
19	**$Pd(acac)_2$**	**CuCl**	**DPEphos**	**NMP**	**88**
20	$Pd(acac)_2$	CuCl	DPEphos	DMSO	84
21	$Pd(acac)_2$	CuCl	DPEphos	DMA	78
22	$Pd(acac)_2$	CuCl	DPEphos	diglyme	6

[a] *Conditions:* **1a** (0.2 mmol), **2a** (1.2 equiv.), Pd (2.5 mol%), Cu (25 mol%), ligand (10 mol%), K_2CO_3 (2.5 equiv.), solvent (0.5 mL), 4 Å molecular sieves (150 mg), 165 °C, 16 h under argon.
[b] GC-MS yield based on **1a**.

Table 2. . Reaction of 2-nitrobenzoic acid **2a** with various esters[a]



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

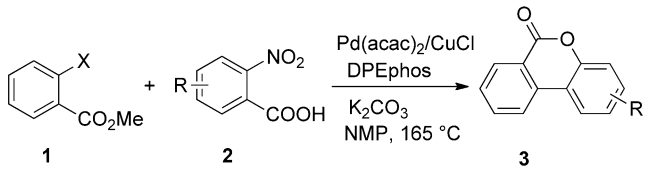
Entry	Ester		Product		Yield [%][b]
1		**1a**		**3a**	76
2		**1b**		**3a**	34
3		**1c**		**3a**	70
4		**1d**		**3a**	65
5		**1e**		**3b**	75
6		**1f**		**3c**	81
7		**1g**		**3d**	53
8[c]		**1h**		**3e**	46
9		**1i**		**3f**	60

[a] *Conditions:* **1** (0.2 mmol), **2a** (0.24 mmol), $Pd(acac)_2$ (2.5 mol%), CuCl (25 mol%), DPEphos (10 mol%), K_2CO_3 (2.5 equiv.), 4 Å molecular sieves (150 mg), NMP (0.5 mL), 165 °C, 16 h under argon.
[b] Isolated yield.
[c] Reaction was carried out at 145 °C.

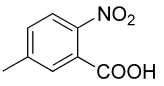
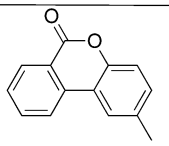
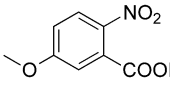
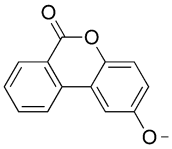
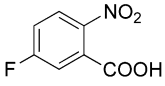
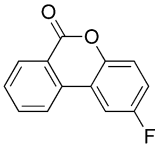
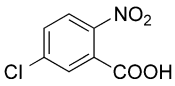
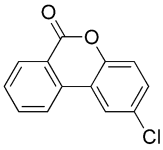
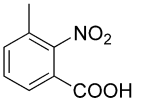
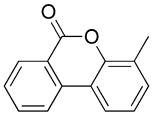
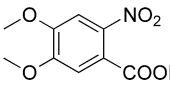
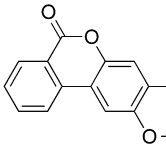
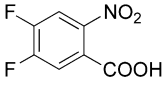
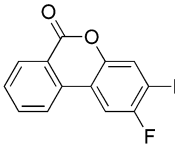
(entries 5 and 6). However, electron-withdrawing substituted groups resulted in lower yields (entries 7 and 8). Substrate with a methyl group *ortho* to the bromide also reacted smoothly with **2a** and gave the desired product in moderate yield (entry 9).

Other substituted 2-nitrobenzoic acids were also investigated under the same conditions. 5-Methyl-2-nitrobenzoic acid (**2b**) reacted with methyl 2-bromobenzoate, methyl 2-chlorobenzoate, methyl 2-iodobenzoate and gave the desired product **3g** in 76%, 65% and 63% yield, respectively (Table 3, entries 1–3). 5-Methoxy-2-nitrobenzoic acid (**2c**) also reacted with **1** and gave the desired product **3h** in 83%, 74% and 68% yield, respectively (entries 4–6). Electron-withdrawing substituent groups such as fluoride at the *para*-position of the nitro group resulted in lower yields (entries 7–9). Functional groups such as chlo-

Table 3. Reaction of **1** with various substituted 2-nitrobenzoic acids **2**.[a]



1 2 3

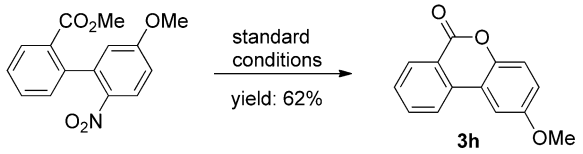
Entry	Carboxylic acid	Product	Yield (%)[b]
1			76 (X = Br)
2	**2b**	**3g**	65 (X = Cl)
3			63 (X = I)
4			83 (X = Br)
5	**2c**	**3h**	74 (X = Cl)
6			68 (X = I)
7			60 (X = Br)
8	**2d**	**3i**	52 (X = Cl)
9			62 (X = I)
10			52 (X = Br)
	2e	**3j**	
11			64 (X = Br)
	2f	**3k**	
12			80 (X = Br)
	2g	**3l**	
13[c]			6 (X = Br)
	2h	**3m**	

[a] *Conditions:* **1** (0.2 mmol), **2** (0.24 mmol), Pd (acac)$_2$ (2.5 mol%), CuCl (25 mol%), DPEphos (10 mol%), K_2CO_3 (2.5 equiv.), 4 Å molecular sieves (150 mg), NMP (0.5 mL), 165 °C, 16 h under argon.

[b] Isolated yield based on **1**.

[c] GC-MS yield.

ride could survive under the optimized reaction conditions and a moderate reaction yield was obtained when 5-chloro-2-nitrobenzoic acid was used (entry 10). A methyl group at the *ortho*-position of the nitro group did not significantly affect the reaction yield (entry 11). An excellent yield was obtained when 4,5-dimethoxy-2-nitrobenzoic acid (**2g**) was used whereas only 6% yield was obtained when 4,5-difluoro-2-nitrobenzoic acid (**2h**) was used (entries 12 and 13).



Scheme 2. Lactonization of 5′-methoxy-2′-nitrobiphenyl-2-carboxylate.

When methyl 5′-methoxy-2′-nitrobiphenyl-2-carboxylate was treated with palladium/copper catalysts under the standard reaction conditions, the desired product **3h** was obtained in 62% yield (Scheme 2). When the amount of molecular sieves was increased to 500 mg, the desired product was obtained in a similar yield. This means the displacement occurred directly between the ester group and the nitro group without hydrolysis. The mechanism for the direct displacement reaction is not clear at this stage.[18]

In summary, we have developed a highly selective palladium/copper-catalyzed tandem reaction for the formation of substituted dibenzopyranones. The decarboxylative cross-coupling and cyclization were realized in one pot. The reaction proceeded well for a range of different substrates. This research affords a short cut for the preparation of substituted dibenzopyranones. Further investigations including studies on the scope and mechanism are in progress in our laboratory.

Experimental Section

Typical Procedure

A 10-mL oven-dried reaction vessel was charged with $Pd(acac)_2$ (1.53 mg, 0.005 mmol), DPEphos (10.76 mg, 0.02 mmol), CuCl (4.95 mg, 0.05 mmol), K_2CO_3 (69.0 mg, 0.5 mmol), 4 Å molecular sieves (150 mg), 2-nitrobenzoic acid (**2a**, 40.1 mg, 0.24 mmol) and purged with argon three times. Methyl 2-bromobenzoate (**1a**, 28.7 μL, 0.2 mmol) and NMP (0.5 mL) were added by syringe. The resulting solution was stirred at 165 °C for 16 h. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **3a** as white solid; yield: 29.8 mg (76%).

Acknowledgements

This work was supported by the National Natural Science Foundation of China (20902076, 21172185), the Hunan Provincial Natural Science Foundation of China (11JJ1003) and the One Hundred Talent Project of Hunan Province (11QDZ28).

References

[1] a) K. Koch, J. Podlech, E. Pfeiffer, M. Metzler, *J. Org. Chem.* **2005**, *70*, 3275; b) H. Abe, K. Nishioka, S. Takeda, M. Arai, Y. Takeuchi, T. Harayama, *Tetrahedron Lett.* **2005**, *46*, 3197; c) C. Garino, F. Bihel, N. Pietrancosta, Y. Laras, G. Quelever, I. Woo, P. Klein, J. Bain, J. L. Boucher, J. L. Kraus, *Bioorg. Med. Chem. Lett.* **2005**, *15*, 135; d) W. Sun, L. D. Cama, E. T. Birzin, S. Warrier, L. Locco, R. Mosley, M. L. Hammond, S. P. Rohrer, *Bioorg. Med. Chem. Lett.* **2006**, *16*, 1468; e) R. W. Pero, D. Harvan, *Tetrahedron Lett.* **1973**, 945; f) W. T. L. Sidwell, H. Fritz, C. Tamm, *Helv. Chim. Acta* **1971**, *54*, 207; g) H. Raistrick, C. E. Stilkings, R. Thomas, *Biochemistry* **1953**, *55*, 421.

[2] a) M. J. Coghlan, P. R. Kym, S. W. Elmore, A. X. Wang, J. R. Luly, D. Wilcox, M. Stshko, C. W. Lin, J. Miner, C. Tyree, M. Nakane, P. Jacobsen, B. C. Lane, *J. Med. Chem.* **2001**, *44*, 2879; b) Y. Y. Ku, T. Grieme, P. Raje, P. Sharma, S. A. King, H. E. Morton, *J. Am. Chem. Soc.* **2002**, *124*, 4282.

[3] a) J. P. Edwards, S. J. West, K. B. Marschke, D. E. Mais, M. M. Gottardis, T. K. Jones, *J. Med. Chem.* **1998**, *41*, 303; b) L. Zhi, C. M. Tegly, K. B. Marschke, D. E. Mais, T. K. Jones, *J. Med. Chem.* **1999**, *42*, 1466.

[4] J. M. Schmidt, G. B. Tremblay, M. Page, J. Mercure, M. Feher, R. Dunn-Dufault, M. G. Peter, P. R. Redden, *J. Med. Chem.* **2003**, *46*, 1289.

[5] a) L. G. Hamann, R. I. Higuchi, L. Zhi, J. P. Edwards, X. N. Wang, K. B. Marchke, J. W. Kong, L. J. Farmer, T. K. Jones, *J. Med. Chem.* **1998**, *41*, 623.

[6] For a review on lactonization in total synthesis of natural products, see: A. Parenty, X. Moreau, J. M. Campagne, *Chem. Rev.* **2006**, *106*, 911.

[7] a) M. E. Jung, D. A. Allen, *Org. Lett.* **2009**, *11*, 757; b) R. Sanz, Y. Fernandez, M. P. Castroviejo, A. Perez, F. J. Fananas, *Eur. J. Org. Chem.* **2007**, *1*, 62; c) J. A. Teske, A. Deiters, *Org. Lett.* **2008**, *10*, 2195; d) Y. Y. Ku, T. Grieme, P. Raje, H. E. Morton, M. Rozema, S. A. King, *J. Org. Chem.* **2003**, *68*, 3238; e) T. Pundt, M. Lau, I. Hussain, M. A. Yawer, H. Reinke, P. Langer, *Tetrahedron Lett.* **2007**, *48*, 2745; f) I. Hussain, M. A. Yawer, M. Lau, T. Pundt, C. Fischer, H. Goerls, P. Langer, *Eur. J. Org. Chem.* **2008**, 503; g) H. Palencia, F. Garcia-jiminez, J. Takcs, *Tetrahedron Lett.* **2004**, *45*, 3849; h) V. Nguyen, P. Langer, *Tetrahedron Lett.* **2005**, *46*, 1013; i) S. Qi, K. Kawagoe, S. Miyano, *Chem. Lett.* **1993**, 79; j) O. Boye, Y. Itoh, A. Brossi, *Helv. Chim. Acta* **1989**, *72*, 1690; k) A. D. Khanolkar, D. Liu, M. Ibrahim, R. Duclos Jr, G. A. Thakur, T. P. Malan Jr, F. Porreca, V. Veerappan, X. Tian, C. George, D. A. Parrish, D. P. Papahatjis, A. Markriyannis, *J. Med. Chem.* **2007**, *50*, 6493.

[8] a) I. Hussain, V. T. H. Nguyen, T. T. Yawer, C. Fiscer, H. Reinke, P. Langer, *J. Org. Chem.* **2007**, *72*, 6255; b) G. J. Kemperman, B. Ter Horst, D. Van de Goor, T. Roeters, J. Bergwerff, R. Van der Eem, J. Basten, *Eur. J. Org. Chem.* **2006**, *14*, 3169; c) Q. J. Zhou, K. Worm, R. E. Dolle, *J. Org. Chem.* **2004**, *69*, 5147; d) P. R. Kym, M. E. Kort, M. J. Coghlan, J. L. Moore, R. Tang, J. D. Ratajczyk, D. P. Larson, S. W. Elmore, J. K. Pratt, M. A. Stashko, H. Douglass Falls, C. W. Lin, M. Nakane, L. Miller, C. M. Tyree, J. N. Miner, P. B. Jacobson, D. M. Wilcox, P. Nguyen, B. C. Lane, *J. Med. Chem.* **2003**, *46*, 1016; e) B. I. Alo, P. A. Patil, M. J. Sharp, M. A. Siddiqui, V. Snieckus, *J. Org. Chem.* **1991**, *56*, 3763.

[9] N. Thasana, R. Worayuthakarn, P. Kradanrat, E. Hohn, L. Young, S. Ruchirawat, *J. Org. Chem.* **2007**, *72*, 9379.

[10] a) H. Togo, T. Muraki, M. Yokoyama, *Tetrahedron Lett.* **1995**, *36*, 7089; b) T. Muraki, H. Togo, M. Yokoyama, *J. Chem. Soc. Perkin Trans. 1* **1999**, 1713.

[11] a) D. H. Hey, J. A. Leonard, C. W. Rees, *J. Chem. Soc.* **1962**, 4579; b) G. A. Val′kova, T. V. Sakhno, D. N. Shigovin, A. M. Andriecskii, A. Nn. Poplavskii, *Russ. J. Phys. Chem.* **1981**, *55*, 459; c) C. Finzi, V. Bellavita, *Gazz. Chim. Ital.* **1936**, *66*, 421.

[12] W. J. Zhang, B. I. Wilke, J. X. Zhan, K. Watanable, C. N. Boddy, Y. Tang, *J. Am. Chem. Soc.* **2007**, *129*, 9304.

[13] K. Visnumurthy, A. Makriyannis, *J. Comb. Chem.* **2010**, *12*, 664.

[14] L. J. Goossen, N. Rodríguez, K. Goossen, *Angew. Chem.* **2008**, *120*, 3144; *Angew. Chem. Int. Ed.* **2008**, *47*, 3100.

[15] a) M. Nilsson, *Acta Chem. Scand.* **1966**, *20*, 423; b) M. Nilsson, C. Ullenius, *Acta Chem. Scand.* **1968**, *22*, 1998.

[16] For selected decarboxylative biaryl synthesis, see: a) L. J. Goossen, G. J. Deng, L. M. Levy, *Science* **2006**, *313*, 662; b) P. Forgione, M. St-Onge, K. H. Thesen, M. D. Bailey, F. Bilofeu, *J. Am. Chem. Soc.* **2006**, *128*, 11350; c) L. J. Goossen, N. Rodríguez, B. Melzer, C. Linder, G. J. Deng, L. M. Levy, *J. Am. Chem. Soc.* **2007**, *129*, 4824; d) L. J. Goossen, B. Zimmermann, T. Knauber, *Angew. Chem.* **2008**, *120*, 7211; *Angew. Chem. Int. Ed.* **2008**, *47*, 7103; e) L. J. Goossen, N. Rodríguez, C. Linder, *J. Am. Chem. Soc.* **2008**, *130*, 15248; f) L. J. Goossen, F. Rudolphi, C. Oppel, N. Rodríguez, *J. Am. Chem. Soc.* **2008**, *130*, 15240; g) J. Cornella, P. F. Lu, I. Larrosa, *Org. Lett.* **2009**, *11*, 5506; h) R. Shang, Q. Xu, Y. Y. Jiang, Y. Wang, L. Liu, *Org. Lett.* **2010**, *12*, 1000; i) J. M. Becht, C. Catala, C. Drian, A. Wagner, *Org. Lett.* **2007**, *9*, 1781; j) M. Miyasaka, A. Fukushima, T. Satoh, K. Hirano, M. Miura, *Chem. Eur. J.* **2009**, *15*, 3674; k) P. P. Lange, L. J. Goossen, P. Podmore, T. Underwood, N. Sciammetta, *Chem. Commun.* **2011**, *47*, 3628; l) L. J. Goossen, B. Melzer, *J. Org. Chem.* **2007**, *72*, 7473.

[17] a) C. Y. Wang, I. Piel, F. Glorius, *J. Am. Chem. Soc.* **2009**, *131*, 4194; b) A. Voutchkova, A. Coplin, N. E. Leadbeater, R. H. Crabtree, *Chem. Commun.* **2008**, 6312; c) H. Q. Zhao, Y. Wei, J. Xu, J. Kan, W. P. Su, M. C. Hong, *J. Org. Chem.* **2011**, *76*, 882; d) K. Xie, Z. Yong, X. L. Zhou, X. J. Li, S. Z. Wang, Z. Tan, C. C. Guo, *Org. Lett.* **2010**, *12*, 1564; e) W. Y. Yu, N. Sit, Z. Y. Zhou, A. S. C. Chan, *Org. Lett.* **2009**, *11*, 3174.

[18] When 2-nitrobenzoic acid (**2a**) was replaced by 2-fluorobenzoic acid, the desired product **3a** was obtained in 56% yield.

