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The first example of 1,3-dipolar cycloaddition reactions of nitrones to vinylidenecyclopropanes

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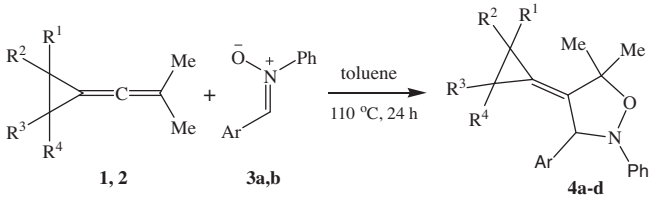
ABSTRACT

The first example of 1,3-dipolar cycloaddition reactions of nitrones to vinylidenecyclopropanes is described. The nitrones react with the C1′–C2′ double bond of vinylidenecyclopropanes to give the corresponding 4-cyclopropylidene-isoxazolidines in moderate yields.

The 1,3-dipolar cycloaddition reaction has long been recognized as an important strategy for the synthesis of heterocyclic rings.[1] Nitrones are remarkably versatile building blocks in organic synthesis, and are known to take part in 1,3-dipolar cycloaddition reactions with a wide range of dipolarophiles. Cycloadditions of nitrones to alkenes and allenes are well established reactions by which isoxazolidines are formed, often with a high degree of stereochemical control.[2] These cycloadducts attracted considerable attention due to the potential biological activities of isoxazolidines.[1a,b] Isoxazolidines have also been used as precursors to β-amino alcohols through reductive cleavage of the N–O bond, which are potential precursors for the synthesis of such natural products as alkaloids and β-lactam antibiotics.[2a]

The groups of Brandi, de Meijere, and Molchanov have studied the 1,3-dipolar cycloaddition of methylenecyclopropanes and cyclopropenes with nitrones.[3] Recently Shi reported the first example of $Yb(OTf)_3$-catalyzed formal [3+3] cycloaddition of vinylidenecyclopropane-dicarboxylates to nitrones with the formation of 2-benzylidenepiperidin-3-ones in good yields.[4] The 1,3-dipolar cycloaddition reactions of vinylidenecyclopropanes with aromatic diazomethanes generated in situ from the corresponding aromatic aldehydes and tosylhydrazines, and also with a 1,3-dipole intermediate derived from phthalazine-1,4-dione were described in the papers of Shi and co-workers.[5] The chemistry of vinylidenecyclopropanes has been explored extensively. Novel intramolecular rearrangements and cycloaddition reactions with compounds

Table 1
Reactions of vinylidenecyclopropanes **1** and **2** with nitrones **3a**,**b**



1, 2 **3a,b** **4a-d**

Entry	R^1	R^2	R^3	R^4	Ar	Yield of **4**[a] (%)
1	Me	Me	Me	Me (**1**)	Ph (**3a**)	29 (**4a**)[b]
2	Me	Me	Me	Me (**1**)	4-ClC_6H_4 (**3b**)	34 (**4b**)[c]
3	H	$-(CH_2)_4-$		H (**2**)	Ph (**3a**)	23 (**4c**)[d,e]
4	H	$-(CH_2)_4-$		H (**2**)	4-ClC_6H_4 (**3b**)	28 (**4d**)[f,g]

[a] Isolated yield.
[b] 17% of starting material **1** was recovered.
[c] 14% of starting material **1** was recovered.
[d] Chromatographically inseparable mixture of two diastereomers (7.3:1 by ^1H NMR data).
[e] 15% of starting material **2** was recovered.
[f] Chromatographically inseparable mixture of two diastereomers (7.0:1 by ^1H NMR data).
[g] 12% of starting material **2** was recovered.

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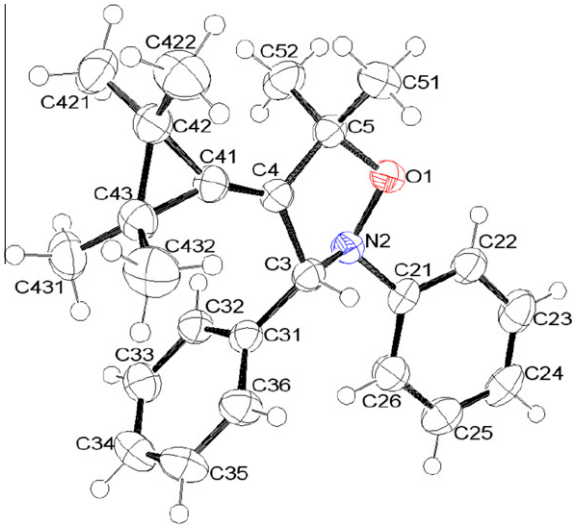


Figure 1. ORTEP representation of **4a**.

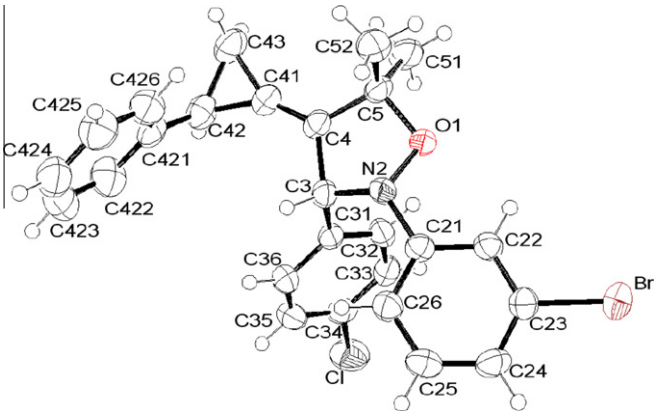


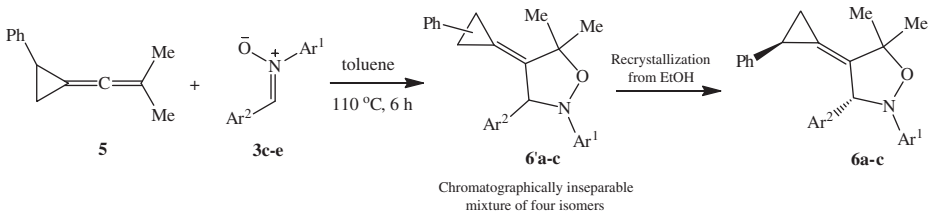
Figure 2. ORTEP representation of **6c**.

containing carbon–carbon or carbon–heteroatom multiple bonds, such as imines, aldehydes, nitriles, and α,β-unsaturated ketones have been studied.[6,7] However, 1,3-dipolar cycloaddition reactions of vinylidenecyclopropanes with nitrones have not been studied as yet. In continuation of our earlier work,[8] we have studied the reaction of non-activated vinylidenecyclopropanes with nitrones. In the present work we show for the first time that nitrones react with the C1′–C2′ double bond of vinylidenecyclopropanes to give the corresponding 4-cyclopropylidene-isoxazolidines in moderate yields.

As a model study, we investigated the cycloaddition of *C*,*N*-diarylnitrones with 1,1,2,2-tetramethyl-3-(2-methylprop-1-enylidene)cyclopropane (**1**). Heating vinylidenecyclopropane **1** and nitrones **3a,b** in toluene (110 °C, 24 h) led to the formation of 4-cyclopropylidene-isoxazolidines **4a,b** in 29% and 34% yields (Table 1, entries 1 and 2). Running the reaction in benzene at 80 °C for 36 h gave the corresponding isoxazolidines in yields less than 10%. The reaction products were isolated by preparative thin layer chromatography on silica. The compositions and structures of the products were established by elemental and spectral analyses.[9] The structure of compound **4a** was confirmed additionally by X-ray diffraction analysis (Fig. 1).[10] A similar reaction occurred on treatment of vinylidenecyclopropane **2** with nitrones **3a,b** giving isoxazolidines **4c,d** as inseparable mixtures of two diastereomers (Table 1, entries 3 and 4, the diastereomeric ratio were determined from ^{1}H NMR spectra by integration of the C3–*H* signal). Increasing the nitrone concentration in the reaction mixture and the reaction time (36–48 h) did not lead to a significant increase in the yield of the isoxazolidines. At the same time increased amounts of unidentified products were observed in these cases, which made product separation difficult. Regioisomeric products and products of nitrone addition to the C1–C1′ double bond were not observed in the reaction mixtures.

The 1,3-dipolar cycloaddition of nitrones **3c–e** with 1-phenyl-2-(2-methylprop-1-enylidene)cyclopropane (**5**) was then attempted (toluene, 110 °C, 6 h). The reaction gave inseparable mixtures of four diastereomers **6′a–c**. Separation of the crude mixtures on silica gel and subsequent crystallization from methanol gave pure samples of isoxazolidines **6a–c** as single diastereomers in 11–16% yields (Table 2). The other diastereomers were not isolated in pure form (the ^{1}H NMR spectra mixture of isomers **6′a–c** were too complicated and it was impossible to identify the single diastereomers). The compositions and structures of products **6a–c** were established by elemental and spectral analyses.[11] The structure of compound **6c** was confirmed additionally by X-ray diffraction analysis (Fig. 2).[12]

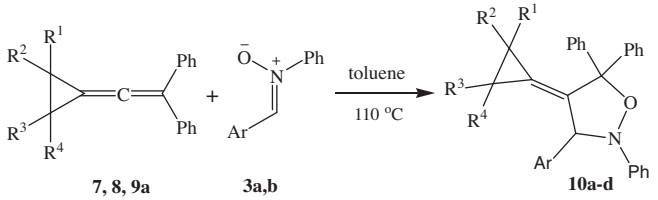
Table 2
Reactions of vinylidenecyclopropane **5** with nitrones **3c–e**



Entry	Ar^1	Ar^2	Yield of **6′**[a] (%)	Yield of **6**[a] (%)
1	Ph	4-FC_6H_4 (**3c**)	49 (**6′a**)[b,c]	14 (**6a**)
2	Ph	4-MeC_6H_4 (**3d**)	41 (**6′b**)[d,e]	11 (**6b**)
3	3-BrC_6H_4	4-ClC_6H_4 (**3e**)	57 (**6′c**)[f,g]	16 (**6c**)

[a] Isolated yield.
[b] Chromatographically inseparable mixture of four isomers (0.6:0.5:0.2:1.0 by ^{1}H NMR data).
[c] 12% of starting material **5** was recovered.
[d] Chromatographically inseparable mixture of four isomers (0.6:0.4:0.2:1.0 by ^{1}H NMR data).
[e] 13% of starting material **5** was recovered.
[f] Chromatographically inseparable mixture of four isomers (0.6:0.5:0.1:1.0 by ^{1}H NMR data).
[g] 9% of starting material **5** was recovered.

Table 3
Reactions of vinylidenecyclopropanes **7**,**8,** and **9a** with nitrones **3a**,**b**



Entry	R^1	R^2	R^3	R^4	Ar	Time (h)	Yield of **10**[a] (%)
1	Me	Me	Me	Me (**7**)	Ph (**3a**)	24	41 (**10a**)[b]
2	Me	Me	Me	Me (**7**)	4-ClC_6H_4 (**3b**)	24	36 (**10b**)[c]
3	Ph	Ph	H	H (**8**)	Ph (**3a**)	48	0 [d]
4	H	–$(CH_2)_4$–		H (**9a**)	Ph (**3a**)	24	48 (**10c**)[e,f]
5	H	–$(CH_2)_4$–		H (**9a**)	4-ClC_6H_4 (**3b**)	24	43 (**10d**)[g,h]

[a] Isolated yield.
[b] 0% of starting material **7** was recovered.
[c] 9% of starting material **7** was recovered.
[d] 73% of starting material **8** was recovered. Product **10** was not present in the reaction mixture.
[e] Chromatographically inseparable mixture of two diastereomers (2.7:1 by ^1H NMR data).
[f] 12% of starting material **9a** was recovered.
[g] Chromatographically inseparable mixture of two diastereomers (3.2:1 by ^1H NMR data).
[h] 14% of starting material **9a** was recovered.

Next, the reactions of vinylidenecyclopropanes **7, 8,** and **9a**, containing aryl groups on the double bond, with nitrones were investigated. The reaction of vinylidenecyclopropane **7** with nitrones **3a,b** at 110 °C for 24 h gave 5,5-diphenyl-4-(tetramethylcyclopropylidene)isoxazolidines **10a,b** in 41% and 36% isolated yields (Table 3, entries 1 and 2). The products of the reactions were isolated by preparative thin layer chromatography on silica gel. The structures of isoxazolidines **10a,b** were assigned on the basis of their spectral

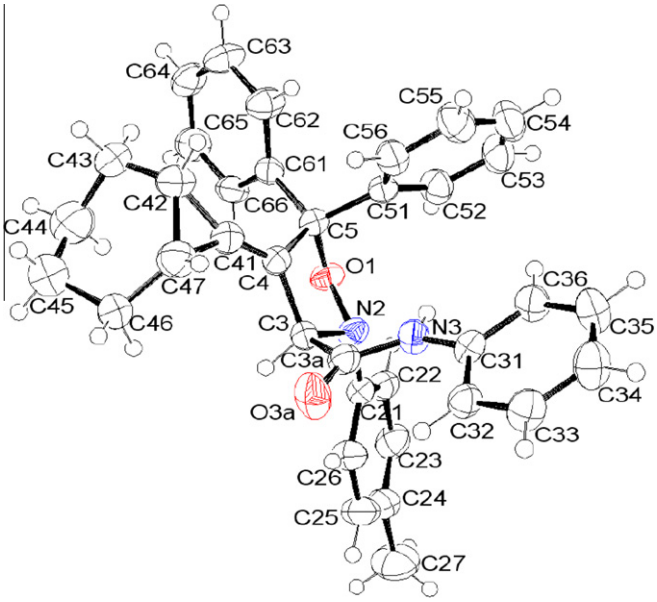
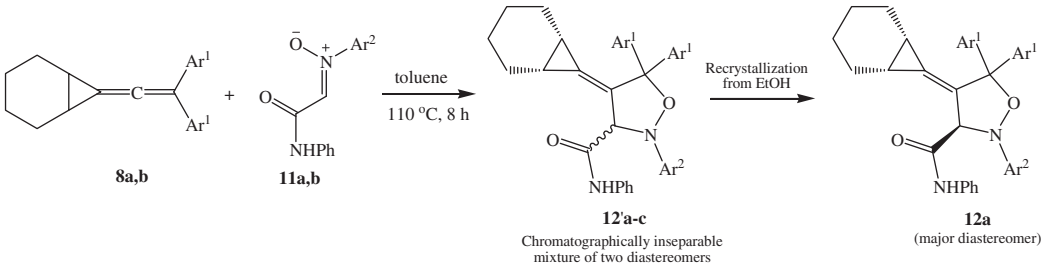


Figure 3. ORTEP representation of **12a**.

data.[13] The formation of a cycloaddition product was not observed in the reaction of nitrone **3a** with vinylidenecyclopropane **8** (Table 3, entry 3). This is possibly the result of steric hindrance in the transition state. Heating nitrones **3a,b** and vinylidenecyclopropane **9a** in boiling toluene led to the formation of isoxazolidines **10c,d** as mixtures of two diastereomers which could not be separated by silica gel chromatography (Table 3, entries 4 and 5). Compound **10d**, in a diastereomeric ratio of 12:1, was isolated by recrystallization from MeOH.

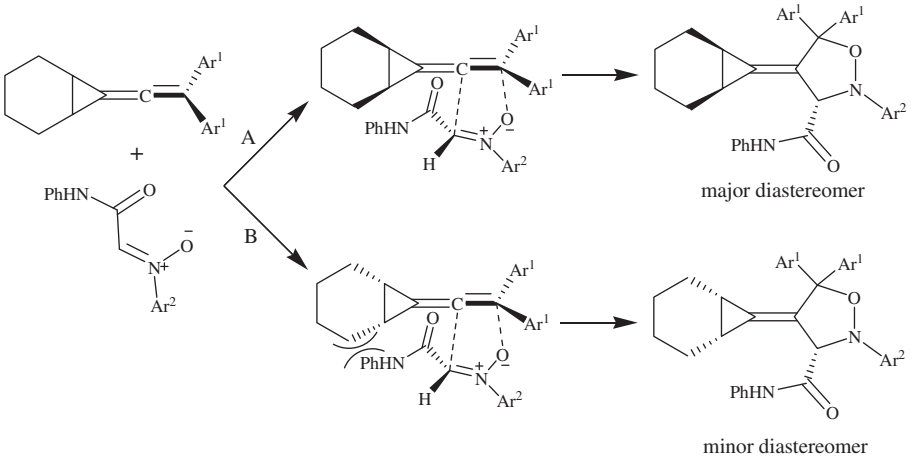
We also examined the reaction of amidonitrones **11a,b** with vinylidenecyclopropanes **8a,b**. In this case chromatographically inseparable mixtures of two diastereomers **12′a–c** were produced. The products of the reactions were isolated by preparative thin layer chromatography on silica gel. Crystallization of the mixture of **12′a** from ethanol resulted in pure **12a** in 21% yield (Table 4,

Table 4
Reactions of vinylidenecyclopropanes **8a**,**b** with nitrones **11a**,**b**



Entry	Ar^1	Ar^2	Yield of **12′**[a] (%)	Yield of **12**[a] (%)
1	Ph (**8a**)	4-MeC_6H_4 (**11a**)	63 (**12′a**)[b,c]	21 (**12a**)
2	4-MeC_6H_4 (**8b**)	4-MeC_6H_4 (**11a**)	60 (**12′b**)[d,e]	—
3	4-MeC_6H_4 (**8b**)	Ph (**11b**)	56 (**12′c**)[f,g]	—

[a] Isolated yield.
[b] Chromatographically inseparable mixture of two diastereomers (1.6:1 by ^1H NMR data).
[c] 7% of starting material **8a** was recovered.
[d] Chromatographically inseparable mixture of two diastereomers (1.5:1 by ^1H NMR data).
[e] 9% of starting material **8b** was recovered.
[f] Chromatographically inseparable mixture of two diastereomers (1.7:1 by ^1H NMR data).
[g] 12% of starting material **8b** was recovered.



Scheme 1. Possible pathways for the reaction of nitrones **11a**,**b** with vinylidenecyclopropanes **8a**,**b**.

entry 1).[14] It was not possible to isolate the major diastereomers from the mixtures of **12′b,c**. The structure of **12a** was established unequivocally by X-ray diffraction analysis (Fig. 3).[15] The stereochemical outcome of the reaction between **8a,b** and **11a,b** is outlined in Scheme 1. Formation of the major diastereomer occurs by approach of the nitrone dipole from the least hindered side of the cyclopropane ring (Scheme 1, path A).

In conclusion, the first examples of 1,3-dipolar cycloaddition reactions of nitrones to non-activated vinylidenecyclopropanes have been described. The nitrones react with the C1′–C2′ double bond of the vinylidenecyclopropanes to give the corresponding 4-cyclopropylidene-isoxazolidines in moderate yields. Regioisomeric products and products of nitrone addition to the C1–C1′ double bond were not observed. It is clear from the data that the cycloaddition occurs with high regioselectivity. The high regioselectivity observed in these 1,3-dipolar cycloadditions can be explained from two point of views: (1) steric interactions between the substituents on the reactants, and (2) atomic orbital coefficients of the HOMO (nitrone)–LUMO (vinylidenecyclopropane) favour the expected interaction for this type of cycloaddition, which is in accordance with previous literature on cycloadditions of nitrones to allenes.[2]

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Supplementary data

Supplementary data associated with this Letter can be found, in the online version, at doi:10.1016/j.tetlet.2011.08.116.

References and notes

1. (a) Tufariello, J. J. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, NY, 1984; Vol. 2, pp 83–168; (b) Jones, R. C. F.; Martin, J. N. In *Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry Toward Heterocycles and Natural Products*; Padwa, A., Pearson, W. H., Eds.; Wiley: New York, NY, 2002; pp 1–81; (c) Gothelf, K. V.; Jørgensen, K. A. *Chem. Rev.* **1998**, *98*, 863; (d) Gothelf, K. V.; Kanemasa, S. In *Cycloaddition Reactions in Organic Synthesis*; Kobayashi, S., Jørgensen, K. A., Eds.; Wiley: Weinheim (Germany), 2002; pp 211–280; (e) Gothelf, K. V.; Jørgensen, K. A. *Chem. Commun.* **2000**, 1449; (f) Kanemasa, S. *Synlett* **2002**, 1371; (g) Maas, G. In *The Chemistry of Heterocyclic Compounds*; Padwa, A., Pearson, W., Eds.; Wiley: New York, NY, 2002; Vol. 59, pp 539–621.
2. (a) Torsell, K. B. G. *Nitrile Oxides, Nitrones, and Nitronates in Organic Synthesis*; VCH: Weinheim, Germany, 1988; (b) Brandi, A.; Cicchi, S.; Cordero, F. M.; Goti, A. *Chem. Rev.* **2003**, *103*, 1213; (c) Dugovič, B.; Fišera, L.; Reißig, H. *Eur. J. Org. Chem.* **2008**, 277; (d) Piperno, A.; Rescifina, A.; Corsaro, A.; Chiacchio, M.; Procopio, A.; Romeo, R. *Eur. J. Org. Chem.* **2007**, 1517; (e) Chiacchio, U.; Corsaro, A.; Iannazzo, D.; Piperno, A.; Romeo, G.; Romeo, A.; Saita, M. G.; Rescifina, A. *Eur. J. Org. Chem.* **2007**, 4758; (f) Dolbier, W. G., Jr.; Burkholder, K. G.; Wicks, G. E.; Palenik, G. J.; Gawron, M. *J. Am. Chem. Soc.* **1985**, *107*, 7183; (g) Dolbier, W. R.; Wicks, G. E.; Burkholder, G. R. *J. Org. Chem.* **1987**, *52*, 2196; (h) Padwa, A.; Kline, D. N.; Koehler, K. F.; Matzinger, M.; Venkatramanan, M. K. *J. Org. Chem.* **1987**, *52*, 3909; (i) Padwa, A.; Matzinger, M.; Tomioka, Y.; Venkatramanan, M. K. *J. Org. Chem.* **1988**, *53*, 955; (j) Padwa, A.; Bullock, W. H.; Kline, D. N.; Perumattam, J. *J. Org. Chem.* **1989**, *54*, 2862; (k) Padwa, A.; Kline, D. N.; Norman, B. H. *J. Org. Chem.* **1989**, *54*, 810; (l) Tufariello, J. J.; Ali, Sk. A.; Klingele, H. O. *J. Org. Chem.* **1989**, *44*, 4213; (m) Kawai, T.; Kodama, K.; Ooi, T.; Kusumi, T. *Tetrahedron Lett.* **2004**, *45*, 4097; (n) Padwa, A.; Carter, S. P.; Chiacchio, U.; Kline, D. N. *Tetrahedron Lett.* **1986**, *27*, 2683; (o) Sasaki, T.; Eguchi, S.; Hirako, Y. *Tetrahedron Lett.* **1976**, *7*, 541; (p) Padwa, A.; Meske, M.; Ni, Z. *Tetrahedron Lett.* **1993**, *34*, 5047; (q) Wilkens, J.; Kühling, A.; Blechert, S. *Tetrahedron* **1987**, *43*, 3237; (r) Padwa, A.; Meske, M.; Ni, Z. *Tetrahedron* **1995**, *51*, 89; (s) Zhao, B.-X.; Eguchi, S. *Tetrahedron* **1997**, *53*, 9575; (t) Pellissier, H. *Tetrahedron* **2010**, *66*, 8341.
3. (a) Goti, A.; Cordero, F. M.; Brandi, A. *Top. Curr. Chem.* **1996**, *178*, 1; (b) de Meijere, A.; Kozhushkov, S. I.; Khlebnikov, A. F. *Top. Curr. Chem.* **2000**, *207*, 89; (c) de Meijere, A.; Kozhushkov, S. I.; Hadjiarapoglou, L. P. *Top. Curr. Chem.* **2000**, *207*, 149; (d) de Meijere, A.; Kozhushkov, S. I. *Eur. J. Org. Chem.* **2000**, 3809; (e) de Meijere, A.; Kozhushkov, S. I.; Spath, T.; von Seebach, M.; Lohr, S.; Nuske, H.; Pohlmann, T.; Es-Sayed, M.; Brase, S. *Pure Appl. Chem.* **2000**, *72*, 1745; (f) Revuelta, J.; Cicchi, S.; de Meijere, A.; Brandi, A. *Eur. J. Org. Chem.* **2008**, 1085; (g) Brandi, A.; Goti, A. *Chem. Rev.* **1998**, *98*, 589; (h) Cardona, F.; Goti, A.; Brandi, A. *Eur. J. Org. Chem.* **2007**, 1551; (i) Marradi, M.; Brandi, A.; Magull, J.; Schill, H.; de Meijere, A. *Eur. J. Org. Chem.* **2006**, 5485; (j) Brandi, A.; Cardona, F.; Cicchi, S.; Cordero, F. M.; Goti, A. *Chem. Eur. J.* **2009**, *15*, 7808; (k) Revuelta, J.; Cicchi, S.; Goti, A.; Brandi, A. *Synthesis* **2007**, 485; (l) Marradi, M.; Brandi, A.; de Meijere, A. *Synlett* **2006**, 1125; (m) Tran, T. Q.; Diev, V. V.; Molchanov, A. P. *Tetrahedron* **2011**, *67*, 2391; (n) Diev, V. V.; Stetsenko, O. N.; Tran, T. Q.; Kopf, J.; Kostikov, R. R.; Molchanov, A. P. *J. Org. Chem.* **2008**, *73*, 2396; (o) Diev, V. V.; Tran, T. Q.; Molchanov, A. P. *Eur. J. Org. Chem.* **2009**, 525.
4. Wu, L.; Shi, M. *Chem. Eur. J.* **2010**, *16*, 1149.
5. (a) Wu, L.; Shi, M. *J. Org. Chem.* **2010**, *75*, 2296; (b) Liu, L.-P.; Lu, J.-M.; Shi, M. *Org. Lett.* **2007**, *9*, 1303.
6. (a) Shi, M.; Shao, L.-X.; Lu, J.-M.; Wei, Y.; Mizuno, K.; Maeda, H. *Chem. Rev.* **2010**, *110*, 5883; (b) Su, C.; Huang, X. *Adv. Synth. Catal.* **2009**, *351*, 135; (c) Yao, L.-F.; Shi, M. *Chem. Eur. J.* **2009**, *15*, 3875; (d) Wu, L.; Shi, M. *Eur. J. Org. Chem.* **2011**, 1099; (e) Lu, J.-M.; Shi, M. *Chem. Eur. J.* **2009**, *15*, 6065; (f) Yao, L.-F.; Shi, M. *Eur. J. Org. Chem.* **2009**, 4036; (g) Su, C.; Huang, X.; Liu, Q.; Huang, X. *J. Org. Chem.* **2009**, *74*, 8272; (h) Li, W.; Shi, M. *J. Org. Chem.* **2009**, *74*, 856; (i) Jiang, M.; Shi, M. *Tetrahedron* **2009**, *65*, 5222; (j) Li, W.; Shi, M. *Tetrahedron* **2009**, *65*, 6815; (k) Lu, B.-L.; Lu, J.-M.; Shi, M. *Tetrahedron* **2009**, *65*, 9328; (l) Lu, B.-L.; Lu, J.-M.; Shi, M. *Tetrahedron Lett.* **2010**, *51*, 321; (m) Lu, J.-M.; Shi, M. *J. Org. Chem.* **2008**, *73*, 2206; (n) Li, W.; Shi, M. *J. Org. Chem.* **2008**, *73*, 4151; (o) Li, W.; Shi, M. *J. Org. Chem.* **2008**, *73*, 6698; (p) Shi, M.; Wu, L.; Lu, J.-M. *J. Org. Chem.* **2008**, *73*, 8344; (q) Lu, J.-M.; Shi, M. *Org. Lett.* **2008**, *10*, 1943; (r) Campbell, M. J.; Pohlhaus, P. D.; Min, G.; Ohmatsu, K.; Johnson, J. S. *J. Am. Chem. Soc.* **2008**, *130*, 9180; (s) Shi, M.; Yao, L.-F. *Chem. Eur. J.* **2008**, *14*, 8725; (t) Xu, G.-C.; Liu, L.-P.; Lu, J.-M.; Shi, M. *J. Am. Chem. Soc.* **2005**, *127*, 14552; (u) Maeda, H.; Hirai, T.; Sugimoto, A.; Mizuno, K. *J. Org. Chem.* **2003**, *68*, 7700; (v) Shi, M.; Lu, J.-M. *J. Org. Chem.* **2006**, *71*, 1920.
7. (a) Zhang, Y.-P.; Lu, J.-M.; Xu, G.-C.; Shi, M. *J. Org. Chem.* **2007**, *72*, 509; (b) Mizuno, K.; Maeda, H.; Sugita, H.; Nishioka, S.; Hirai, T.; Sugimoto, A. *Org. Lett.* **2001**, *3*, 581; (c) Li, Q.; Shi, M.; Timmons, C.; Li, G. *Org. Lett.* **2006**, *8*, 625; (d) Shao, L.-X.; Yun-Peng Zhang, Y.-P.; Qi, M.-X.; Shi, M. *Org. Lett.* **2007**, *9*, 117; (e) Lu, J.-M.; Shi, M. *Org. Lett.* **2007**, *9*, 1805; (f) Xu, G.-C.; Ma, M.; Liu, L.-P.; Shi, M.

Synlett **2005**, 1869; (g) Shi, M.; Lu, J.-M. *Synlett* **2005**, 2352; (h) Lu, J.-M.; Shi, M. *Tetrahedron* **2007**, *63*, 7545; (i) Shi, M.; Wu, L.; Lu, J.-M. *Tetrahedron* **2008**, *64*, 3315; (j) Mizuno, K.; Sugita, H.; Hirai, T.; Maeda, H.; Otsuji, Y.; Yasuda, M.; Hashiguchi, M.; Shima, K. *Tetrahedron Lett.* **2001**, *42*, 3363.

8. (a) Stepakov, A. V.; Larina, A. G.; Molchanov, A. P.; Stepakova, L. V.; Starova, G. L.; Kostikov, R. R. *Russ. J. Org. Chem.* **2007**, *43*, 41; (b) Stepakov, A. V.; Larina, A. G.; Radina, O. V.; Boitsov, V. M.; Molchanov, A. P. *Chem. Heterocycl. Compd.* **2008**, *44*, 430; (c) Stepakov, A. V.; Larina, A. G.; Radina, O. V.; Molchanov, A. P.; Kostikov, R. R. *Vestnik SPbGU* **2009**, *1*(4), 110.
9. *^{1}H NMR data for* ***4a***: δ_H (300 MHz, $CDCl_3$) 0.17 (s, 3H, Me), 0.99 (s, 3H, Me), 1.11 (s, 3H, Me), 1.15 (s, 3H, Me), 1.46 (s, 3H, Me), 1.65 (s, 3H, Me), 4.89 (s, 1H, CH), 6.91 (t, 1H, Ph, *J* = 7.3 Hz), 7.00 (d, 2H, Ph, *J* = 8.1 Hz), 7.17 (t, 2H, Ph, *J* = 7.3 Hz), 7.28 (t, 1H, Ph, *J* = 7.3 Hz), 7.36 (t, 2H, *J* = 8.1 Hz), 7.48 (d, 2H, Ph, *J* = 7.3). *^{13}C NMR data for* ***4a***: δ_c (75 MHz, $CDCl_3$) 19.5 (Me), 21.0 (Me), 21.4 ($C_{cycloprop}$), 21.7 ($C_{cycloprop}$), 21.8 (Me), 22.4 (Me), 26.8 (Me), 27.8 (Me), 74.1 (C3), 82.2 (C5), 116.8 (2C_{Ar}H), 122.3 (C_{Ar}H), 128.0 (C_{Ar}H), 128.8 (2C_{Ar}H), 129.0 (4C_{Ar}H), 134.3 (=$C_{cycloprop}$), 141.5 (=C4), 141.9 (C_{Ar}), 151.3 (C_{Ar}).
10. Crystallographic data for the structure **4a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 825728. Copies of these data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (email: deposit@ccdc.cam.ac.uk).
11. *^{1}H NMR data for* ***6c***: δ_H (300 MHz, $CDCl_3$) 1.21–1.29 (m, 1H, CH_2), 1.64 (s, 3H, Me), 1.65 (s, 3H, Me), 1.63–1.72 (m, 1H, CH_2, overlapped with the Me group signal), 2.07–2.11 (m, 1H, CH), 4.90 (s, 1H, CH), 6.68 (d, 1H, Ar, *J* = 8.1 Hz), 6.93–7.02 (m, 4H, Ar), 7.15–7.29 (m, 8H, Ar). *^{13}C NMR data for* ***6c***: δ_c (75 MHz, $CDCl_3$) 13.3 (CH_2), 18.2 (CH), 26.5 (Me), 26.7 (Me), 72.1 (C3), 82.9 (C5), 114.7 (C_{Ar}H), 118.3 (C_{Ar}), 119.4 (C_{Ar}H), 123.0 (C_{Ar}), 125.1 (C_{Ar}H), 126.2 (2C_{Ar}H), 126.5 (C_{Ar}H), 129.0 (4C_{Ar}H), 129.1 (2C_{Ar}H), 129.4 (C_{Ar}H), 133.6 (=$C_{cycloprop}$), 139.0 (C_{Ar}), 141.0 (C_{Ar}), 141.4 (=C4), 151.6 (C_{Ar}).
12. Crystallographic data for the structure **6c** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 825729. Copies of these data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (email: deposit@ccdc.cam.ac.uk).
13. *^{1}H NMR data for* ***10a***: δ_H (300 MHz, $CDCl_3$) 0.18 (s, 3H, Me), 0.32 (s, 3H, Me), 0.82 (s, 3H, Me), 1.05 (s, 3H, Me), 5.14 (s, 1H, CH), 6.90 (t, 1H, Ph, *J* = 7.3 Hz), 7.03 (d, 2H, Ph, *J* = 8.0 Hz), 7.16 (t, 2H, Ph, *J* = 7.3 Hz), 7.22–7.34 (m, Ph, 10H), 7.38–7.43 (m, 3H, Ph), 7.6 (d, 2H, Ph, *J* = 7.3 Hz). *^{13}C NMR data for* ***10a***: δ_c (75 MHz, $CDCl_3$) 19.8 (Me), 19.9 (Me), 20.6 (Me), 20.7 (Me), 21.7 ($C_{cycloprop}$), 23.3 ($C_{cycloprop}$), 74.6 (C3), 89.9 (C5), 116.7 (2C_{Ar}H), 122.3 (C_{Ar}H), 127.9 (2C_{Ar}H), 128.0 (2C_{Ar}H), 128.2 (2C_{Ar}H), 128.3 (2C_{Ar}H), 128.7 (2C_{Ar}H), 128.9 (4C_{Ar}H), 129.1 (2C_{Ar}H), 129.2 (2C_{Ar}H), 138.8 (=$C_{cycloprop}$), 139.6 (C_{Ar}), 141.5 (=C4), 143.3 (C_{Ar}), 156.7 (C_{Ar}).
14. *^{1}H NMR data for* ***12a***: δ_H (300 MHz, $CDCl_3$) −0.14 to −0.12 (m, 1H, CH), 0.68–0.77 (m, 1H, CH), 0.95–1.23 (m, 4H, 2CH_2), 1.47–1.80 (m, 4H, 2CH_2), 2.30 (s, 3H, Me), 4.76 (s, 1H, CH), 6.94–7.22 (m, 15H, Ar), 7.36–7.39 (m, 3H, Ar), 7.62 (m, 1H, Ar), 7.67 (s, 1H, NH). *^{13}C NMR data for* ***12a***: δ_c (75 MHz, $CDCl_3$) 13.3 (CH), 14.9 (CH), 20.8 (CH_2), 21.0 (Me), 21.3 (CH_2), 21.5 (CH_2), 21.8 (CH_2), 72.8 (C3), 89.7 (C5), 116.1 (2C_{Ar}H), 119.7 (2C_{Ar}H), 124.3 (C_{Ar}H), 127.9 (C_{Ar}H), 128.2 (2C_{Ar}H), 128.3 (2C_{Ar}H), 128.4 (C_{Ar}H), 128.5 (2C_{Ar}H), 128.8 (2C_{Ar}H), 129.0 (2C_{Ar}H), 129.9 (2C_{Ar}H), 130.8 (C_{Ar}), 132.6 (C_{Ar}), 132.8 (=$C_{cycloprop}$), 137.7 (C_{Ar}), 141.4 (=C4), 142.6 (C_{Ar}), 146.8 (C_{Ar}), 166.7 (C=O).
15. Crystallographic data for the structure **12a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 825730. Copies of these data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (email: deposit@ccdc.cam.ac.uk).