Organic & Biomolecular Chemistry

Cite this: *Org. Biomol. Chem.*, 2012, **10**, 7628

www.rsc.org/obc

PAPER

Phosphine-catalyzed domino reaction: an efficient method for the synthesis of highly functionalized spirooxazolines†

Lihua Yang, Peizhong Xie, Erqing Li, Xin Li, You Huang* and Ruyu Chen

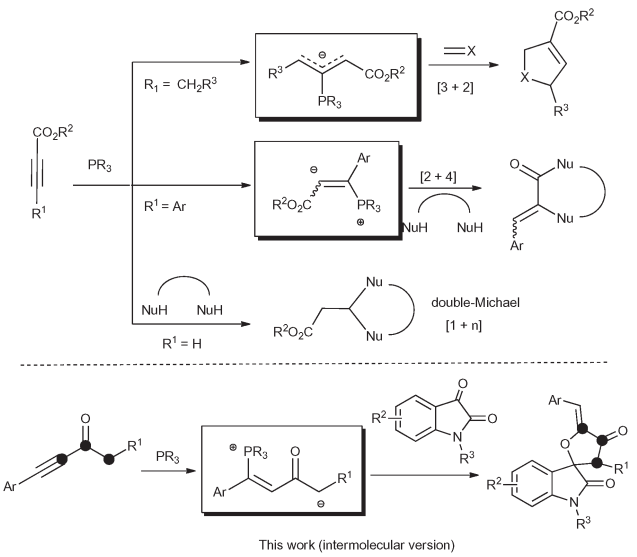
Received 25th March 2012, Accepted 1st August 2012
DOI: 10.1039/c2ob26338f

A novel phosphine-catalyzed intermolecular [3 + 2] cycloaddition of ynones and *N*-substituted isatins was developed. In this reaction, substituted ynones, serving as a C_3 synthon, were successfully applied in intermolecular annulation reactions. A number of functionalized spirooxazolines were obtained in high yields and stereoselectivity.

Introduction

Oxindole skeletons with a spirocyclic quaternary stereocenter occur widely in a large number of clinical pharmaceuticals and natural products.[1] Thus, methods for the synthesis of these compounds are highly important in organic chemistry. Although the stereoselective preparation of spirooxindoles has been addressed in elegant studies, such as organocatalyst promoted reactions,[2] and transition metal-catalyzed processes,[3] a straightforward and flexible method is still needed.

Recently, phosphine-catalyzed domino reaction has become a powerful tool in generating carbo- and heterocycles.[4] Compared with the well studied electron-deficient alkenes,[5] alkynes always have some special reactivity, such as in the [3 + 2],[6] [2 + 4][7] and [1 + *n*][8] cycloaddition (Scheme 1) and so on.[9] Relatively little attention has been focused on ynone derivatives; only recently Tomita and Fu successively exploited elegant intramolecular cycloaddition reactions.[10] Nevertheless, the unsatisfactory yields and restricted substrate scope were often problematic. The intermolecular version has also been little investigated.[11] Based upon this pioneering work and our studies on phosphine-catalyzed domino reactions,[12] now we report the novel phosphine-catalyzed intermolecular cycloaddition of ynones and *N*-substituted isatins. In this reaction, a variety of functionalized spirooxazolines were obtained in high yields and stereoselectivity.



Scheme 1 Phosphine-catalyzed formal cycloaddition reactions of electron-deficient alkynes.

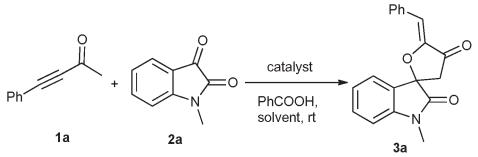
Results and discussion

We initiated our study by evaluating the reaction of **1a** and **2a** in $CHCl_3$ at room temperature with 10 mol% PPh_3 as catalyst (Table 1, entry 1). To our delight, compound **3a** was obtained in 58% yield. In order to improve the yield of **3a**, benzoic acid (30 mol%) was used as an additive, which was found to favor the reaction (entry 2). Decreasing the additive loading had an obviously adverse impact on the yield (entries 3, 6). Then, various phosphine catalysts were studied (entries 2–5) and PPh_2Et found to give the best result (entry 3) among these tests. What is more, the reaction time had little affect on the yield (entries 3, 7). Reducing the catalyst loading, a prolonged reaction time was required (entries 3, 8). Screening of other solvents, such as DMF, toluene and THF, allowed no better result to be obtained (entries 9–12). In addition, the structure and stereochemistry of **3a** were characterized by a combination of NMR, HRMS spectra and single-crystal X-ray analysis (Fig. 1).[13]

State Key Laboratory and Institute of Elemento-organic Chemistry Nankai University, Tianjin 300071, People's Republic of China. E-mail: hyou@nankai.edu.cn; Fax: (+86) 22-23503627; Tel: (+86) 22-23503159

†Electronic supplementary information (ESI) available. CCDC 862108 (**3a**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ob26338f

Table 1 Studies on the reaction of ynone **1a** with *N*-methyl isatin **2a** to generate spirooxazoline[a]



Entry	Solvent	Catalyst	Time/h	Yield[b] (%)
1[c]	$CHCl_3$	PPh_3	8	58
2	$CHCl_3$	PPh_3	9	86
3	$CHCl_3$	PPh_2Et	4	86
4	$CHCl_3$	$PPhEt_2$	36	43[f]
5	$CHCl_3$	PBu_3	24	0[f]
6[d]	$CHCl_3$	PPh_2Et	4	69
7	$CHCl_3$	PPh_2Et	6	87
8[e]	$CHCl_3$	PPh_2Et	16	90
9	Toluene	PPh_2Et	7	84
10	DMF	PPh_2Et	24	NR
11	CH_2Cl_2	PPh_2Et	5	87
12	THF	PPh_2Et	36	45[f]

[a] Unless otherwise noted, the reactions were carried out on 0.5 mmol scale in solvent (2.0 mL), 30% mol of PhCOOH and 10% mol PPh_2Et was used. The ratio of **1a** : **2a** was 2 : 1. [b] Isolated yields. [c] The reaction was carried out without PhCOOH. [d] 10 mol% PhCOOH was used. [e] 5 mol% PPh_2Et was used. [f] In the entry 4 23% starting material **2a** was recovered; in the entry 5 62% **2a** was recovered; in the entry 12 30% **2a** was recovered.

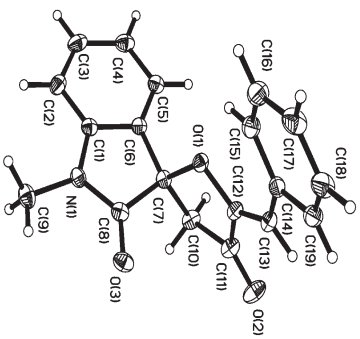
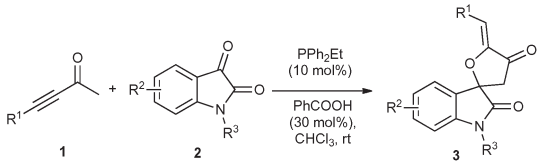


Fig. 1 X-ray crystal structure of **3a**.

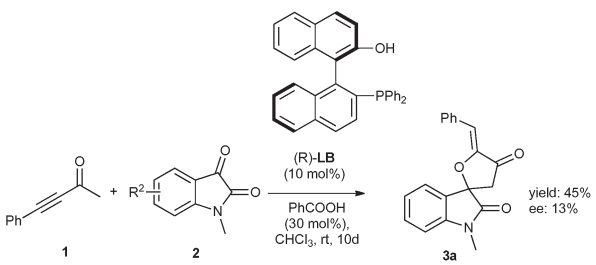
Having established the optimal reaction conditions, the tolerance of the reaction was then investigated. Various ynones and *N*-protected isatins were evaluated (Table 2). Basically, the reaction proceeded smoothly to give the desired products in high yields under the standard conditions. Substrates with different steric parameters were tolerated, affording the products in good to excellent yields (entries 1–5) except for the *N*-Ac isatin **1c** (entry 3); its lower yield may be on account of decomposition of the starting material during the reaction. The electronic property of compound **1** has little influence on the reaction. However, the yield was to some degree sensitive to the electronic property of the substituent on the phenyl ring of substrates **2** and benefited from electronic donating groups. Even with steric hindrance at the α-position of the ynone, the desired product **3f** could also be obtained in high yield, albeit a prolonged reaction time was needed (entry 6).

Table 2 Investigating the scope of ynones **1** and isatin derivatives **2** in the reaction[a]



Entry	R^1	R^2	R^3	*t*/h	Yield[b] (%)
1	C_6H_4	H	CH_3	3	86 (**3a**)
2	C_6H_4	H	Bn	4	90 (**3b**)
3	C_6H_4	H	Ac	2	51 (**3c**)
4	C_6H_4	H	Allyl	3	82 (**3d**)
5	C_6H_4	H	CH_2CO_2Et	4	78 (**3e**)
6[c]	C_6H_4	H	CH_3	24	73 (**3f**)
7	C_6H_4	*p*-CH_3	CH_3	4	90 (**3g**)
8	C_6H_4	*p*-Cl	CH_3	6	74 (**3h**)
9	C_6H_4	*o*-Cl	CH_3	6	75 (**3i**)
10	*p*-MeC_6H_4	H	CH_3	3.5	94 (**3j**)
11	*p*-MeC_6H_4	*p*-CH_3	CH_3	5	93 (**3k**)
12	*p*-MeC_6H_4	*p*-Cl	CH_3	5	74 (**3l**)
13	*p*-MeC_6H_4	*o*-Cl	CH_3	5.5	77 (**3m**)
14	*p*-FC_6H_4	H	CH_3	5	81 (**3n**)
15	*p*-FC_6H_4	*p*-CH_3	CH_3	5.5	87 (**3o**)
16	*p*-FC_6H_4	*p*-Cl	CH_3	5	72 (**3p**)
17	*p*-FC_6H_4	*o*-Cl	CH_3	5	85 (**3q**)

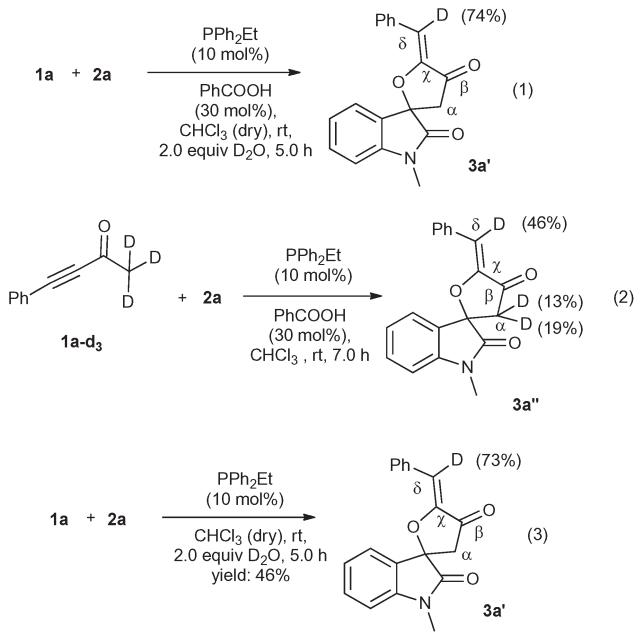
[a] Unless otherwise noted, the reactions were carried out in 0.5 mmol scale in solvent (2.0 mL). The ratio of the **1** : **2** is 2.0 : 1.0. [b] Isolated yields. [c] In entry 6 **1f** 4-methyl-1-phenylpent-1-yn-3-one was used.



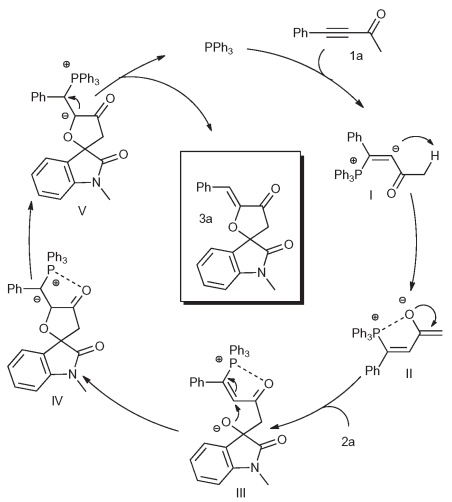
Scheme 2 Asymmetric annulation.

Preliminary studies on the asymmetric variant of this reaction was tested with the optically pure bifunctional catalyst **LB**, (*R*)-(2′-(diphenylphosphino)-[1,1′-binaphthalen]-2-ol). We obtained a promising 13% enantiomeric excess for **3a** in 45% yield with 29% yield of recovered **2** (Scheme 2).

In order to demonstrate the function of the additive and the proton migration process, control experiments were run. According to the experiment result of entry 1 in Table 1 as well as the great influence of additive on the reaction, we thought that the proton migration process might be accelerated by the proton of $PhCO_2H$. To explore this possibility, two equivalent of deuteroxide were added to the reaction system[14] and deuterated product **3a′** was obtained in 76% yield with 74% D incorporation at the δ carbon (Scheme 3 eq (1)). Furthermore, the reaction of **1a**-d_3 and **2a** in dry $CHCl_3$ was also carried out. However, **3a″** was isolated in 73% yield and only 13–46% D at α and δ carbons (Scheme 3 eq (2)). These results clearly indicated that H/D



Scheme 3 The control experiments.

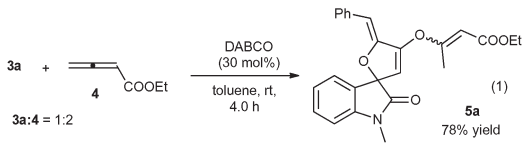


Scheme 4 Plausible mechanism.

exchange is easy in the reaction system and the proton in solvent accelerated the proton migration. In order to further clarify whether D incorporation at the δ carbon in the last step went through deprotonation/protonation or 1,2 migration, the reaction was carried out only with 2.0 equiv of deuteroxide and without acid additive. Deuterated product **3a′** was obtained in 46% yield with 73% D incorporation at the δ carbon (Scheme 3 eq (3)), which indicated that the δ-D incorporations in the last step went through deprotonation/protonation rather than 1,2 migration.

According to the experimental results and previous studies,[10,11] we proposed the mechanism as follows (Scheme 4). The reaction is initiated by the conjugate addition of the phosphine to **1a**, producing the intermediate I. Then an intramolecular proton migration occurred to give another enolate intermediate II.[10a] A nucleophilic attack of the resulting enolate on the carbonyl group at the 3-position of **2a** produces intermediate III. Next, a second conjugate addition happens to generate IV. Tautomerization and elimination[10b] of the phosphine affords the spirooxazoline **3a**.

The high level of functionalization presented in the final products **3** promotes us to investigate the primary transformations. **5a** was obtained in 78% yield by a β-addition of allenoates[15] in the presence of DABCO (eq (1)):



(1)

Conclusions

In summary, we have developed an efficient method for the synthesis of a new class of spirocyclic oxindole derivative in high yields and stereoselectivity. Ynones served as the first C_3 synthons successfully used in intermolecular annulation. The utility of ynones was expanded in this reaction and they might be applied extensively to other phosphine-catalyzed systems. More mechanistic details and further work on the application of the present reaction is currently being investigated in our group.

Experimental

General information

All the solvents were used without further purification. The ^{1}H NMR and spectra was recorded at 400 MHz, ^{13}C NMR was recorded at 100 MHz. ^{1}H and ^{13}C NMR Chemical shifts were calibrated to tetramethylsilane as an external reference. Coupling constants are given in Hz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet: t, triplet; q, quartet; m, multiplet; HRMS were obtained on an IonSpec FT-ICR mass spectrometer with ESI resource. Melting points were measured on a RY-I apparatus and are reported uncorrected. Ynones[16] and *N*-methyl isatin[17] compounds were prepared according to the known methods.

General procedure for the synthesis of spirooxazolines

Ynones **1** (2.00 eq), *N*-methyl isatins **2** (0.50 mmol) and benzoic acid (30 mol%) were dissolved in $CHCl_3$ (2.0 mL), and then, PPh_2Et (10 mol%) was added to this solution. The reaction was stirred at room temperature. As indicated by TLC, after complete conversion, all volatiles were removed *in vacuo* and the residue was purified *via* column chromatography (petroleum ether (60–90)–ethyl acetate = 6 : 1).

(*E*)-5-Benzylidene-1′-methyl-3*H*-spiro[furan-2,3′-indoline]-2′,4-(5*H*)-dione (3a). The product is a white solid with **mp**: 181–183 °C. 13% ee, $[\alpha]_D^{25}$ = +130.5 (c = 0.4 in $CHCl_3$); **IR (KBr)** 1741, 1728, 1645, 1618, 1494, 1469 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.2 Hz, 2H), 7.44 (t, J = 7.8 Hz, 1H), 7.39 (d, J = 7.4 Hz, 1H), 7.34–7.20 (m, 3H), 7.15 (t, J = 7.6 Hz, 1H), 6.93 (d, J = 7.8 Hz, 1H), 6.49 (s, 1H), 3.25

(s, 3H), 3.10 (d, J = 18.2 Hz, 1H), 2.93 (d, J = 18.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.51, 173.83, 146.05, 144.15, 133.09, 131.33, 130.54, 128.58, 128.50, 127.14, 124.27, 123.78, 109.06, 106.99, 80.97, 42.45, 26.56. HRMS (**ESI/[M + Na]$^+$**) Cacld for: $C_{19}H_{15}NO_3Na$ 328.0950, found 328.0949.

(*E*)-1′-Benzyl-5-benzylidene-3*H*-spiro[furan-2,3′-indoline]-2′,4-(5*H*)-dione (3b). The product is a red solid with **mp**: 179–182 °C. **IR (KBr)** 1735, 1720, 1635, 1616, 1490, 1469 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.1 Hz, 2H), 7.44–7.20 (m, 10H), 7.10 (dd, J = 11.1, 4.0 Hz, 1H), 6.81 (d, J = 7.9 Hz, 1H), 6.51 (s, 1H), 5.04–4.65 (m, 2H), 3.14 (d, J = 18.2 Hz, 1H), 2.98 (d, J = 18.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.40, 174.04, 146.03, 143.36, 135.04, 133.14, 131.26, 130.54, 129.01, 128.60, 128.53, 128.02, 127.41, 127.01, 124.43, 123.78, 110.09, 107.08, 81.00, 44.07, 42.35. ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.40, 174.04, 146.03, 143.36, 135.04, 133.14, 131.26, 130.54, 129.01, 128.60, 128.53, 128.02, 127.41, 127.01, 124.43, 123.78, 110.09, 107.08, 81.00, 44.07, 42.35. **HRMS (ESI/[M + Na]$^+$)** Cacld for: $C_{25}H_{19}NO_3Na$ 404.1263, found 404.1259.

(*E*)-1′-Acetyl-5-benzylidene-3*H*-spiro[furan-2,3′-indoline]-2′,4-(5*H*)-dione (3c). The product is a white solid with **mp:** 188–190 °C. **IR (KBr)** 1755, 1739, 1722, 1645, 1610, 1533, 1467 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.2 Hz, 1H), 7.67 (d, J = 7.4 Hz, 2H), 7.58–7.40 (m, 2H), 7.38–7.18 (m, 4H), 6.52 (s, 1H), 3.12 (d, J = 18.3 Hz, 1H), 2.99 (d, J = 18.2 Hz, 1H), 2.69 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.42, 174.70, 170.33, 145.55, 140.84, 132.78, 131.82, 130.59, 128.87, 128.60, 126.34, 125.95, 124.20, 117.36, 107.57, 80.91, 43.05, 26.50. **HRMS (ESI/[M + Na]$^+$)** Cacld for: $C_{20}H_{15}NO_4Na$ 356.0899, found 356.0895.

(*E*)-1′-Allyl-5-benzylidene-3*H*-spiro[furan-2,3′-indoline]-2′,4-(5*H*)-dione (3d). The product is an orange yellow solid with **mp**: 175–177 °C. **IR (KBr)** 1737, 1716, 1639, 1616, 1489, 1467 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.2 Hz, 2H), 7.43–7.36 (m, 2H), 7.34–7.19 (m, 3H), 7.13 (t, J = 7.5 Hz, 1H), 6.92 (d, J = 7.9 Hz, 1H), 6.49 (s, 1H), 5.95–5.76 (m, 1H), 5.31 (d, J = 9.6 Hz, 1H), 5.28 (s, 1H), 4.49–4.12 (m, 1H), 3.10 (d, J = 18.1 Hz, 1H), 2.95 (d, J = 18.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.40, 173.60, 146.07, 143.41, 133.12, 131.23, 130.76, 130.52, 128.56, 128.50, 127.06, 124.37, 123.72, 118.32, 109.98, 106.95, 80.92, 42.65, 42.44. **HRMS (ESI/[M + Na]$^+$)** Cacld for: $C_{21}H_{17}NO_3Na$ 354.1106, found 354.1107.

(*E*)-Ethyl-2-(5-benzylidene-2′,4-dioxo-4,5-dihydro-3*H*-spiro-[furan-2,3′-indolin]-1′-yl) acetate (3e). The product is a white solid with **mp**: 171–173 °C. **IR (KBr)** 1735, 1728, 1720, 1645, 1616, 1492, 1467 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.2 Hz, 2H), 7.41 (t, J = 7.2 Hz, 2H), 7.33–7.21 (m, 3H), 7.16 (t, J = 7.5 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.49 (s, 1H), 4.59 (d, J = 17.6 Hz, 1H), 4.36 (d, J = 17.6 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 3.13 (d, J = 18.3 Hz, 1H), 2.97 (d, J = 18.3 Hz, 1H), 1.28 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.23, 173.93, 166.99, 145.99, 142.87, 133.05, 131.30, 130.54, 128.61, 128.51, 126.84, 124.52, 124.12, 109.13, 107.12, 80.87, 62.06, 42.57, 41.52, 14.12. **HRMS (ESI/[M + Na]$^+$)** Cacld for: $C_{22}H_{19}NO_5Na$ 400.1161, found 400.1153.

(*E*)-5-Benzylidene-1′,3,3-trimethyl-3*H*-spiro[furan-2,3′-indoline]-2′,4(5*H*)-dione (3f). The product is a yellow solid with **mp**: 199–201 °C. **IR (KBr)** 1741, 1716, 1643, 1612, 1492, 1465 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.5 Hz, 2H), 7.49 (dd, J = 10.7, 7.7 Hz, 2H), 7.34–7.12 (m, 4H), 6.93 (d, J = 7.8 Hz, 1H), 6.51 (s, 1H), 3.18 (s, 3H), 1.33 (s, 3H), 1.07 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.47, 174.23, 145.55, 145.31, 133.50, 131.27, 130.37, 128.41, 128.17, 127.16, 123.06, 122.93, 108.92, 106.77, 87.99, 49.19, 26.21, 22.26, 16.94. **HRMS (ESI/[M + Na]$^+$)** Cacld for: $C_{21}H_{19}NO_3Na$ 356.1263, found 356.1249.

(*E*)-5-Benzylidene-1′,5′-dimethyl-3*H*-spiro[furan-2,3′-indoline]-2′,4(5*H*)-dione (3g). The product is a white solid with **mp**: 206–208 °C. **IR (KBr)** 1735, 1716, 1625, 1604, 1500, 1471 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.3 Hz, 2H), 7.35–7.13 (m, 5H), 6.81 (d, J = 7.9 Hz, 1H), 6.48 (s, 1H), 3.23 (s, 3H), 3.09 (d, J = 18.2 Hz, 1H), 2.91 (d, J = 18.2 Hz, 1H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.64, 173.77, 146.13, 141.68, 133.56, 133.14, 131.48, 130.53, 128.52, 128.48, 127.14, 124.99, 108.79, 106.83, 81.13, 42.50, 26.56, 21.03. **HRMS (ESI/[M + Na]$^+$)** Cacld for: $C_{20}H_{17}NO_3Na$ 342.1106, found 342.1108.

(*E*)-5-Benzylidene-5′-chloro-1′-methyl-3*H*-spiro[furan-2,3′-indoline]-2′,4(5*H*)-dione (3h). The product is a white solid with **mp**: 212–214 °C. **IR (KBr)** 1745, 1724, 1647, 1618, 1492, 1463 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.2 Hz, 2H), 7.41 (d, J = 8.3 Hz, 1H), 7.37 (s, 1H), 7.34–7.20 (m, 3H), 6.85 (d, J = 8.3 Hz, 1H), 6.50 (s, 1H), 3.24 (s, 3H), 3.09 (d, J = 18.2 Hz, 1H), 2.91 (d, J = 18.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.74, 173.42, 145.65, 142.63, 132.88, 131.19, 130.57, 129.18, 128.75, 128.67, 128.53, 124.80, 110.08, 107.47, 80.68, 42.32, 26.67. **HRMS (ESI/[M + Na]$^+$)** Cacld for: $C_{19}H_{14}ClNO_3Na$ 362.0560, found 362.0551.

(*E*)-5-Benzylidene-7′-chloro-1′-methyl-3*H*-spiro[furan-2,3′-indoline]-2′,4(5*H*)-dione (3i). The product is a white solid with **mp**: 195–197 °C. **IR (KBr)** 1737, 1724, 1647, 1612, 1587, 1463 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.2 Hz, 1H), 7.41 (d, J = 8.3 Hz, 1H), 7.37 (s, 1H), 7.34–7.20 (m, 2H), 6.85 (d, J = 8.3 Hz, 1H), 6.50 (s, 1H), 3.24 (s, 2H), 3.09 (d, J = 18.2 Hz, 1H), 2.91 (d, J = 18.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.78, 170.29, 145.84, 134.72, 134.33, 133.03, 132.10, 130.63, 129.68, 129.17, 128.88, 128.76, 127.86, 127.38, 127.07, 107.41, 84.22, 53.55, 44.28. **HRMS (ESI/[M + Na]$^+$)** Cacld for: $C_{19}H_{14}ClNO_3Na$ 362.0560, found 362.0561.

(*E*)-1′-Methyl-5-(4-methylbenzylidene)-3*H*-spiro[furan-2,3′-indoline]-2′,4(5*H*)-dione (3j). The product is a light yellow solid with **mp**: 198–200 °C. **IR (KBr)** 1746, 1720, 1635, 1620, 1494, 1473 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.1 Hz, 1H), 7.49–7.32 (m, 1H), 7.12 (dd, J = 15.7, 7.8 Hz, 1H), 6.92 (d, J = 7.8 Hz, 1H), 6.47 (s, 1H), 3.24 (s, 1H), 3.09 (d, J = 18.2 Hz, 1H), 2.91 (d, J = 18.2 Hz, 1H), 2.31 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.46, 173.90, 145.58, 144.11, 138.83, 131.25, 130.53, 130.27, 129.26, 127.30, 124.23, 123.74, 109.02, 107.21, 80.87, 42.53, 26.53, 21.52. **HRMS (ESI/[M + Na]$^+$)** Cacld for: $C_{20}H_{17}NO_3Na$ 342.1106, found 342.1103.

(*E*)-1′,5′-Dimethyl-5-(4-methylbenzylidene)-3*H*-spiro[furan-2,3′-indoline]-2′,4(5*H*)-dione (3k). The product is a white solid with **mp**: 212–214 °C. **IR (KBr)** 1743, 1718, 1647, 1604, 1500, 1469 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.1 Hz, 1H), 7.18 (s, 1H), 7.10 (d, J = 8.1 Hz, 2H), 6.81 (d, J = 7.9 Hz, 1H), 6.47 (s, 1H), 3.23 (s, 3H), 3.08 (d, J = 18.1 Hz, 1H), 2.89 (d, J = 18.1 Hz, 1H), 2.33 (s, 3H), 2.31 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.60, 173.84, 145.64, 141.63, 138.79, 133.52, 131.39, 130.54, 130.31, 129.25, 127.36, 124.94, 108.74, 107.12, 81.02, 42.61, 26.55, 21.51, 21.02. **HRMS (ESI/[M + Na]$^+$)** Cacld for: $C_{21}H_{19}NO_3Na$ 356.1263, found 356.1264.

(*E*)-5′-Chloro-1′-methyl-5-(4-methylbenzy-lidene)-3*H*-spiro-[furan-2,3′-indoline]-2′,4(5*H*)-dione (3l). The product is a white solid with **mp**: 221–223 °C. **IR (KBr)** 1743, 1726, 1645, 1612, 1492, 1663 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.1 Hz, 2H), 7.40 (dd, J = 8.3, 2.0 Hz, 1H), 7.36 (d, J = 1.9 Hz, 1H), 7.11 (d, J = 8.0 Hz, 2H), 6.85 (d, J = 8.3 Hz, 1H), 6.49 (s, 1H), 3.23 (s, 3H), 3.09 (d, J = 18.1 Hz, 1H), 2.89 (d, J = 18.1 Hz, 1H), 2.32 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.64, 173.49, 145.17, 142.59, 139.06, 131.10, 130.58, 130.08, 129.30, 129.17, 128.91, 124.75, 110.01, 107.76, 80.58, 42.43, 26.65, 21.51. **HRMS (ESI/[M + Na]$^+$)** Cacld for: $C_{20}H_{16}ClNO_3Na$ 376.0716, found 376.0715.

(*E*)-7′-Chloro-1′-methyl-5-(4-methylbenzylidene)-3*H*-spiro-[furan-2,3′-indoline]-2′,4(5*H*)-dione (3m). The product is a white solid with **mp**: 197–199 °C. **IR (KBr)** 1747, 1720, 1647, 1612, 1512, 1463 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.2 Hz, 1H), 7.26 (d, J = 6.6 Hz, 1H), 7.10 (d, J = 8.0 Hz, 2H), 7.04 (t, J = 7.8 Hz, 1H), 6.47 (s, 1H), 3.60 (s, 3H), 3.08 (d, J = 18.2 Hz, 1H), 2.87 (d, J = 18.1 Hz, 1H), 2.31 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.86, 174.19, 145.25, 139.97, 139.02, 133.41, 130.56, 130.16, 130.10, 129.30, 124.57, 122.76, 116.46, 107.59, 80.16, 42.76, 29.98, 29.62, 21.53. **HRMS (ESI/[M + Na]$^+$)** Cacld for: $C_{20}H_{16}ClNO_3Na$ 376.0716, found 376.0716.

(*E*)-5-(4-Fluorobenzylidene)-1′-methyl-3*H*-spiro[furan-2,3′-indoline]-2′,4(5*H*)-dione (3n). The product is a white solid with **mp:** 208–210 °C. **IR (KBr)** 1743, 1724, 1651, 1618 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (dd, J = 8.5, 5.7 Hz, 2H), 7.48 (t, J = 7.8 Hz, 1H), 7.42 (d, J = 7.3 Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 7.06–6.91 (m, 3H), 6.48 (s, 1H), 3.28 (s, 3H), 3.12 (d, J = 18.2 Hz, 1H), 2.96 (d, J = 18.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.31, 173.82, 163.81, 161.32, 145.70, 144.17, 132.35 (d, J = 8.2 Hz), 131.40, 129.35(d, J = 3.3 Hz), 127.02, 124.27, 123.81, 115.71, 115.49, 109.10, 105.83, 81.01, 42.41, 26.55. **HRMS (ESI/[M + Na]$^+$)** Cacld for: $C_{19}H_{14}FNO_3Na$ 346.0855, found 346.0857.

(*E*)-5-(4-Fluorobenzylidene)-1′,5′-dimethyl-3*H*-spiro[furan-2,3′-indoline]-2′,4(5*H*)-dione (3o). The product is a white solid with **mp**: 219–221 °C. **IR (KBr)** 1743, 1722, 1651, 1627, 1500, 1463 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (dd, J = 8.6, 5.7 Hz, 2H), 7.24 (t, J = 7.8 Hz, 1H), 7.20 (s, 1H), 6.98 (t, J = 8.7 Hz, 2H), 6.82 (d, J = 7.9 Hz, 1H), 6.44 (s, 1H), 3.23 (s, 3H), 3.09 (d, J = 18.2 Hz, 1H), 2.91 (d, J = 18.2 Hz, 1H), 2.35 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.45, 173.76, 163.78, 161.30, 145.77, 145.74, 141.70, 133.61, 132.35 (d, J = 8.2 Hz), 131.55, 129.40 (d, J = 3.4 Hz), 127.01, 124.98, 115.68, 115.47, 108.84, 105.68, 81.17, 42.46, 26.55, 21.02. **HRMS (ESI/[M + Na]$^+$)** Cacld for: $C_{20}H_{16}FNO_3Na$ 360.1012, found 360.1013.

(*E*)-5′-Chloro-5-(4-fluorobenzylidene)-1′-methyl-3*H*-spiro[furan-2,3′-indoline]-2′,4(5*H*)-dione (3p). The product is a white solid with **mp**: 207–209 °C. **IR (KBr)** 1743, 1724, 1651, 1620, 1508, 1457 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (dd, J = 8.7, 5.6 Hz, 2H), 7.42 (dd, J = 8.3, 2.0 Hz, 1H), 7.37 (d, J = 1.9 Hz, 1H), 7.00 (t, J = 8.7 Hz, 2H), 6.87 (d, J = 8.3 Hz, 1H), 6.47 (s, 1H), 3.25 (s, 3H), 3.09 (d, J = 18.2 Hz, 1H), 2.91 (d, J = 18.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.53, 173.40, 163.92, 161.43, 145.26, 142.63, 132.43 (d, J = 8.2 Hz), 131.25, 129.24, 129.14 (d, J = 3.3 Hz), 128.58, 124.80, 115.77, 115.55, 110.11, 106.35, 80.70, 42.31, 26.68. **HRMS (ESI/[M + Na]$^+$)** Cacld for: $C_{19}H_{13}ClFNO_3Na$ 380.0466, found 380.0469.

(*E*)-7′-Chloro-5-(4-fluorobenzylidene)-1′-methyl-3*H*-spiro[furan-2,3′-indoline]-2′,4(5*H*)-dione (3q). The product is a white solid with **mp**: 192–194 °C. **IR (KBr)** 1745, 1718, 1651, 1627, 1500, 1463 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (dd, J = 8.5, 5.6 Hz, 2H), 7.36 (d, J = 8.2 Hz, 1H), 7.27 (d, J = 7.6 Hz, 1H), 7.06 (t, J = 7.8 Hz, 1H), 6.99 (t, J = 8.7 Hz, 2H), 6.45 (s, 1H), 3.61 (s, 3H), 3.09 (d, J = 18.2 Hz, 1H), 2.89 (d, J = 18.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.68, 174.11, 163.90, 161.41, 145.35, 140.05, 133.55, 132.40 (d, J = 8.2 Hz), 129.89, 129.20 (d, J = 3.1 Hz), 124.61, 122.77, 116.57, 115.75, 115.54, 106.17, 80.29, 42.64, 29.99. **HRMS (ESI/[M + Na]$^+$)** Cacld for: $C_{19}H_{13}ClFNO_3Na$ 380.0466, found 380.0463.

Procedure for the synthesis of 1a-d_3

To phenylacetylene (2.04 g, 20.0 mmol) in THF (30 mL) was injected *n*-butyllithium (10.0 mL, 25.0 mmol; 2.5 M) dropwise at −78 °C, after which the solution was allowed to warm up to room temperature with stirring. The freshly generated phenylacetylide lithium reagent was then injected dropwise into a solution of deuterated acetyl chloride (6.48 g, 80.0 mmol) in THF (30.0 mL) at −78 °C. After stirring at −78 °C for 2 h, the reaction was quenched slowly with water (20.0 mL). The aqueous fraction was extracted with diethylether (3 × 20.0 mL). The combined ethereal fraction was then washed with saturated aqueous brine (3 × 20.0 mL) and dried with magnesium sulfate for 30 min. After the solvent was removed *in vacuo*, the dark yellow oil was purified by flash column chromatography (petroleum ether (60–90)–ethyl acetate = 30 : 1) to yield a yellow liquid[16b] (yield 65%).

Procedure for the control experiments and asymmetric version

The same procedure as the general procedure for the synthesis of spirooxazolines was used. The control experiments were carried out as follows: (1) Two equivalent deuteroxide was added into the reaction system. (2) We used **1a**-d_3 as the starting material instead of **1a**. (3) Two equivalent deuteroxide was added into the reaction system. For the asymmetric version, **LB** (*R*)-(2′-(diphenylphosphino)-[1,1′-binaphthalen]-2-ol) 10 mol% was used as the catalyst.

Procedure for the synthesis of 5a

To a mixture of **3a** (152 mg, 0.5 mmol) and **4** (112 mg, 1.0 mmol) in toluene (3 ml) was added DABCO (16.8 mg, 0.15 mmol), and the mixture was stirred at room temperature for 4 h then concentrated *in vacuo*. Finally the residue was purified *via* column chromatography (petroleum ether (60–90)–ethyl acetate = 8 : 1) to give **5a** 162 mg (yield 78%) as a light yellow oil. **IR (KBr)** 1732, 1716, 1651, 1614, 1494, 1471 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.6 Hz, 2H), 7.40 (td, J = 7.8, 0.7 Hz, 1H), 7.30 (d, J = 7.0 Hz, 1H), 7.23 (t, J = 7.7 Hz, 2H), 7.10 (t, J = 7.5 Hz, 2H), 6.89 (d, J = 7.8 Hz, 1H), 5.72 (s, 1H), 5.61 (s, 1H), 5.56 (s, 1H), 4.15 (q, J = 7.1 Hz, 2H), 3.24 (s, 3H), 2.52 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.25, 168.70, 166.98, 150.58, 150.16, 143.94, 134.69, 131.31, 128.56, 128.27, 126.25, 125.91, 125.41, 123.54, 111.56, 108.88, 100.46, 98.10, 88.64, 60.04, 26.77, 17.61, 14.33. **HRMS (ESI/[M + Na]$^+$)** Cacld for: $C_{25}H_{23}NO_5Na$ 440.1474, found 440.1472.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (20972076, 21172115) and the Natural Science Foundation of Tianjin (10JCYBJC04000). Xin. Li thanks the support of the Fundamental Research Funds for the Central Universities.

Notes and references

1 (*a*) C. Marti and E. M. Carreira, *Eur. J. Org. Chem.*, 2003, 2209; (*b*) H. Lin and S. J. Danishefsky, *Angew. Chem., Int. Ed.*, 2003, **42**, 36; (*c*) M. M. C. Lo, C. S. Neumann, S. Nagayama, E. O. Perlstein and S. L. Schreiber, *J. Am. Chem. Soc.*, 2004, **126**, 16077; (*d*) C. Chen, X. Li, C. S. Neumann, M. M. C. Lo and S. L. Schreiber, *Angew. Chem., Int. Ed.*, 2005, **44**, 2249; (*e*) K. Ding, *J. Am. Chem. Soc.*, 2005, **127**, 10130; (*f*) A. K. Franz, P. D. Dreyfuss and S. L. Schreiber, *J. Am. Chem. Soc.*, 2007, **129**, 1020; (*g*) C. V. Galliford and K. A. Scheidt, *Angew. Chem., Int. Ed.*, 2007, **46**, 8748; (*h*) V. Schulz, M. Davoust, M. Lemarie, J.-F. Lohier, J. S. O. Santos, P. Metzner and J.-F. Briere, *Org. Lett.*, 2007, **9**, 1745; (*i*) S. Shangary, *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**, 3933; (*j*) S. Ma, X. Q. Han, S. Krishnan, S. C. Virgil and B. M. Stoltz, *Angew. Chem., Int. Ed.*, 2009, **48**, 8037.

2 For these kind of examples, see: (*a*) B. Tan, N. R. Candeias and C. F. Barbas III, *Nat. Chem.*, 2011, **3**, 473; (*b*) B. Tan, N. R. Candeias and C. F. Barbas III, *J. Am. Chem. Soc.*, 2011, **133**, 4672; (*c*) B. Tan, G. Hernandez-Torres and C. F. Barbas III, *J. Am. Chem. Soc.*, 2011, **133**, 12354; (*d*) Y. Cao, X. Jiang, L. Liu, F. Shen, F. Zhang and R. Wang, *Angew. Chem., Int. Ed.*, 2011, **50**, 9124; (*e*) X. Jiang, Y. Cao, Y. Wang, L. Liu, F. Shen and R. Wang, *J. Am. Chem. Soc.*, 2010, **132**, 15328; (*f*) Q. Wei and L.-Z. Gong, *Org. Lett.*, 2010, **12**, 1008; (*g*) L.-L. Wang, L. Peng, J.-F. Bai, Q.-C. Huang, X.-Y. Xu and L.-X. Wang, *Chem. Commun.*, 2010, **46**, 8064; (*h*) L.-L. Wang, L. Peng, J.-F. Bai, L.-N. Jia, X.-Y. Luo, Q.-C. Huang, X.-Y. Xu and L.-X. Wang, *Chem. Commun.*, 2011, **47**, 5593; (*i*) Y.-B. Lan, H. Zhao, Z.-M. Liu, G.-G. Liu, J.-C. Tao and X.-W. Wang, *Org. Lett.*, 2011, **13**, 4866; (*j*) K. Jiang, Z.-J. Jia, X. Yin, L. Wu and Y.-C. Chen, *Org. Lett.*, 2010, **12**, 2766; (*k*) G. Bencivenni, L.-Y. Wu, A. Mazzanti, B. Giannichi, F. Pesciaioli, M.-P. Song, G. Bartoli and P. Melchiorre, *Angew. Chem., Int. Ed.*, 2009, **48**, 7200; (*l*) F. Zhong, X. Han, Y. Wang and Y. Lu, *Angew. Chem., Int. Ed.*, 2011, **50**, 7837; (*m*) A. Voituriez, N. Pinto, M. Neel, P. Retailleau and A. Marinetti, *Chem.–Eur. J.*, 2010, **16**, 12541; (*n*) X.-H. Chen, Q. Wei, S.-W. Luo, H. Xiao and L.-Z. Gong, *J. Am. Chem. Soc.*, 2009, **131**, 13819; (*o*) X.-N. Wang, Y.-Y. Zhang and S. Ye, *Adv. Synth. Catal.*, 2010, **352**, 1892; (*p*) V. Nair, S. Vellalath, M. Poonoth, R. Mohan and E. Suresh, *Org. Lett.*, 2006, **8**, 507.

3 For these kind of examples, see: (*a*) D. Hojo, K. Noguchi and K. Tanaka, *Angew. Chem., Int. Ed.*, 2009, **48**, 8129; (*b*) B. M. Trost, N. Cramer and S. M. Silverman, *J. Am. Chem. Soc.*, 2007, **129**, 12396; (*c*) D. Basavaiah and K. R. Reddy, *Org. Lett.*, 2007, **9**, 57; (*d*) J. J. Badillo, G. E. Arevalo, J. C. Fettinger and A. K. Franz, *Org. Lett.*, 2011, **13**, 418; (*e*) R. Shintani, S. Hayashi, M. Murakami, M. Takeda and T. Hayashi, *Org. Lett.*, 2009, **11**, 3754; (*f*) K. Tanaka, Y. Otake, H. Sagae, K. Noguchi and M. Hirano, *Angew. Chem., Int. Ed.*, 2008, **47**, 1312; (*g*) N. V. Hanhan, N. R. Ball-Jones, N. T. Tran and A. K. Franz, *Angew. Chem., Int. Ed.*, 2011, **50**, 1.

4 For reviews, see: (*a*) X. Lu, C. Zhang and Z. Xu, *Acc. Chem. Res.*, 2001, **34**, 535; (*b*) J. L. Methot and W. R. Roush, *Adv. Synth. Catal.*, 2004, **346**, 1035; (*c*) X. Lu, Y. Du and C. Lu, *Pure Appl. Chem.*, 2005, **77**, 1985; (*d*) V. Nair, R. S. Menon, A. R. Sreekanth, N. Abhilash and A. T. Biju, *Acc. Chem. Res.*, 2006, **39**, 520; (*e*) L.-W. Ye, J. Zhou and Y. Tang, *Chem. Soc. Rev.*, 2008, **37**, 1140.

5 For the examples about phosphine-catalyzed reactions of activated alkenes: (*a*) J. E. Wilson and G. C. Fu, *Angew. Chem., Int. Ed.*, 2006, **45**, 1426; (*b*) S. A. Frank, D. J. Mergott and W. R. Roush, *J. Am. Chem. Soc.*, 2002, **124**, 2404; (*c*) X.-F. Zhu, J. Lan and O. Kwon, *J. Am. Chem. Soc.*, 2003, **125**, 4716; (*d*) B. J. Cowen and S. J. Miller, *J. Am. Chem. Soc.*, 2007, **129**, 10988; (*e*) H. Guo, Q. Xu and O. Kwon, *J. Am. Chem. Soc.*, 2009, **131**, 6318; (*f*) Y. Du, X. Lu and Y. Yu, *J. Org. Chem.*, 2002, **67**, 8901; (*g*) Z. Lu, S. Zheng, X. Zhang and X. Lu, *Org. Lett.*, 2008, **10**, 3267; (*h*) K. Kumar, A. Kapur and M. P. S. Ishar, *Org. Lett.*, 2000, **2**, 787; (*i*) Y. Du, J. Feng and X. Lu, *Org. Lett.*, 2005, **7**, 1987; (*j*) V. Nair, A. T. Biju, K. Mohanan and E. Suresh, *Org. Lett.*, 2006, **8**, 2213; (*k*) C. E. Henry and O. Kwon, *Org. Lett.*, 2007, **9**, 3069; (*l*) Z. Lu, S. Zheng, X. Zhang and X. Lu, *Org. Lett.*, 2008, **10**, 3267; (*m*) S. Zheng and X. Lu, *Org. Lett.*, 2009, **11**, 3978.

6 (*a*) Z. Xu and X. Lu, *J. Org. Chem.*, 1998, **63**, 5031; (*b*) L.-G. Meng, P. Cai, Q. Guo and S. Xue, *J. Org. Chem.*, 2008, **73**, 8491.

7 (*a*) S. Gabillet, D. Lecerclé, O. Loreau, M. Carboni, S. Dezard, J.-M. Gomis and F. Taran, *Org. Lett.*, 2007, **9**, 3925; (*b*) S. Gabillet, D. Lecerclé, O. Loreau, S. Dezard, J.-M. Gomis and F. Taran, *Synthesis*, 2007, 515; (*c*) M. Carboni, J.-M. Gomis, O. Loreau and F. Taran, *Synthesis*, 2008, 417.

8 (*a*) V. Sriramurthy, G. A. Barcan and O. Kwon, *J. Am. Chem. Soc.*, 2007, **129**, 12928; (*b*) V. Sriramurthy and O. Kwon, *Org. Lett.*, 2010, **12**, 1084.

9 The acyclic reactions: (*a*) B. M. Trost and U. Kazmaier, *J. Am. Chem. Soc.*, 1992, **114**, 7933; (*b*) B. M. Trost and C.-J. Li, *J. Am. Chem. Soc.*, 1994, **116**, 3167; (*c*) B. M. Trost and G. R. Dake, *J. Am. Chem. Soc.*, 1997, **119**, 7595; (*d*) S. D. Rychnovsky and J. Kim, *J. Org. Chem.*, 1994, **59**, 2659; (*e*) B. M. Trost and G. R. Dake, *J. Org. Chem.*, 1997, **62**, 5670; (*f*) C. Alvarez-Ibarra, A. G. Csaky and C. Gomez de la Oliva, *J. Org. Chem.*, 2000, **65**, 3544; (*g*) D. Lecercle, M. Sawicki and F. Taran, *Org. Lett.*, 2006, **8**, 4283; (*h*) C. K.-W. Kwong, M. Y. Fu, C. S.-L. Lam and P. H. Toy, *Synthesis*, 2008, 2307; (*i*) L.-G. Meng, B. Hu, Q.-P. Wu, M. Liang and S. Xue, *Chem. Commun.*, 2009 (40), 6089. The cycloaddition reactions: (*j*) B. M. Trost and C.-J. Li, *J. Am. Chem. Soc.*, 1994, **116**, 10816; (*k*) H. Waldmann, V. Khedkar, H. Duckert, M. Schurmann, I. M. Oppel and K. Kumar, *Angew. Chem., Int. Ed.*, 2008, **47**, 6869; (*l*) H. Liu, Q. Zhang, L. Wang and X. Tong, *Chem. Commun.*, 2010, **46**, 312; (*m*) M. Sampath and T.-P. Loh, *Chem. Sci.*, 2010, **1**, 739; (*n*) C.-K. Jung, J.-C. Wang and M. J. Krisce, *J. Am. Chem. Soc.*, 2004, **126**, 4118; (*o*) S. Kamijo, C. Kanazawa and Y. Yamamoto, *J. Am. Chem. Soc.*, 2005, **127**, 9260; (*p*) B. Liu, R. Davis, B. Joshi and D. W. Reynolds, *J. Org. Chem.*, 2002, **67**, 4595; (*q*) C. Francois-Endelmond, T. Carlin, P. Thuery, O. Loreau and F. Taran, *Org. Lett.*, 2010, **12**, 40.

10 (*a*) H. Kuroda, I. Tomita and T. Endo, *Org. Lett.*, 2003, **5**, 129; (*b*) J. E. Wilson, J. Sun and G. C. Fu, *Angew. Chem., Int. Ed.*, 2010, **49**, 161.

11 (*a*) A. Siby, O. Loreau and F. Taran, *Synthesis*, 2009, 2365; (*b*) During the preparation of this manuscript, Shi reported a similar cycloaddition: Z. Lian and M. Shi, *Eur. J. Org. Chem.*, 2012, 581.

12 (*a*) X. Meng, Y. Huang and R. Chen, *Chem.–Eur. J.*, 2008, **14**, 6852; (*b*) X. Meng, Y. Huang and R. Chen, *Org. Lett.*, 2009, **11**, 137; (*c*) X. Meng, Y. Huang, H. Zhao, P. Xie, J. Ma and R. Chen, *Org. Lett.*, 2009, **11**, 991; (*d*) P. Xie, Y. Huang and R. Chen, *Org. Lett.*, 2010, **12**, 3768; (*e*) J. Ma, P. Xie, C. Hu, Y. Huang and R. Chen, *Chem.–Eur. J.*, 2011, **17**, 7418; (*f*) P. Xie, Y. Huang, W. Lai, X. Meng and R. Chen, *Org. Biomol. Chem.*, 2011, **9**, 6707; (*g*) P. Xie, Y. Huang and R. Chen, *Chem.–Eur. J.*, 2012, **18**, 7362; (*h*) P. Xie, W. Lai, Z. Geng, Y. Huang and R. Chen, *Chem.–Asian J.*, 2012, **7**, 1533.

13 CCDC-862108 (**3a**), contains the supplementary crystallographic data† for this paper.
14 (*a*) C. Hu, Z. Geng, J. Ma, Y. Huang and R. Chen, *Chem.–Asian J.*, 2012, **7**, 2032; (*b*) Y. Z. Xia, Y. Liang, Y. Y. Chen, M. Wang, L. Jiao, F. Huang, S. Liu, Y. H. Li and Z. X. Yu, *J. Am. Chem. Soc.*, 2007, **129**, 3470.
15 For examples of the β-addition of allenoates, see: (*a*) T. Sugita, M. Eida, H. Ito, N. Komatsu, K. Abe and M. Suama, *J. Org. Chem.*, 1987, **52**, 3789; (*b*) N. Chinkov, N. Morlender-Vais and I. Marek, *Tetrahedron Lett.*, 2002, **43**, 6009; (*c*) P. Elsner, L. Bernardi, G. D. Salla, J. Overgaard and K. A. Jørgensen, *J. Am. Chem. Soc.*, 2008, **130**, 4897; (*d*) M. A. Silvestri, D. C. Bromfield and S. D. Lepore, *J. Org. Chem.*, 2005, **70**, 8239.
16 (*a*) M. Schuler, F. Silva, C. Bobbio, A. Tessier and V. Gouverneur, *Angew. Chem., Int. Ed.*, 2008, **47**, 7927; (*b*) K. H. Chan, W. K. Leong, G. Jaouen, L. Leclerq, S. Top and A. Vessieres, *J. Organomet. Chem.*, 2006, **691**, 9; (*c*) L. Cao, J. Ding, M. Gao, Z. Wang, J. Li and A. Wu, *Org. Lett.*, 2009, **11**, 3810.
17 (*a*) *Organic Syntheses*, ed. C. S. Marvel and G. S. Hiers, John Wiley and Sons, New York, 1925, vol. 5, pp. 71–74; (*b*) X. Jiang, Y. Cao, Y. Wang, L. Liu, F. Shen and R. Wang, *J. Am. Chem. Soc.*, 2010, **132**, 15328; (*c*) D. J. Vyas, R. Frohlich and M. Oestreich, *J. Org. Chem.*, 2010, **75**, 6720; (*d*) *Organic Syntheses*, ed. T. L. Jacobs, S. Winstein, G. B. Linden, J. H. Robson, E. F. Levy and D. Seymour, John Wiley and Sons, New York, 1948, vol. 28, pp. 70–72.

