One-Pot Method for Stereoselective Cyclopropanation of Electron-Deficient Olefins with Methyl Bromoacetate and Phenacyl Bromide in the Presence of Triphenylarsine

Zhongjiao Ren,*[a] Weiguo Cao,[a,b] Weiyu Ding,[a] Yu Wang[a]

[a] Department of Chemistry, Shanghai University, Shanghai, 200444, P. R. of China
Fax +86(21)66134856; E-mail: renrui198229@hotmail.com

[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, 200032, P. R. of China

Received 6 April 2005; revised 18 May 2005

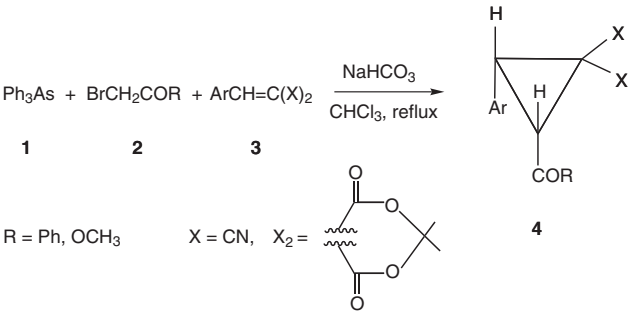
Abstract: A triphenylarsine-catalyzed one-pot procedure for the preparation of *cis*-cyclopropanes with acyclic electron-deficient olefins with carbonyl-stabilized arsonium ylides formed from methyl bromoacetate or phenacyl bromide in the presence of $NaHCO_3$ has been achieved. This method is simple, high-yielding and *cis*-selective. The success of this method depends on the choice of base, solvent and temperature.

Key words: one-pot, triphenylarsine, cyclopropanation, stereoselectivity, $NaHCO_3$

The search for efficient methods for the preparation of cyclopropane has been attracting organic chemists, because of the unique structure and reactivity of cyclopropanes. Cyclopropanes have been used as building blocks for the synthesis of natural and artificial products and are also found as a basic structural unit in a wide range of naturally occurring biologically active compounds in plants and microorganisms.[1] The reaction involving ylides and electron-deficient olefins, Michael-initiated ring closure (MIRC), is one of the most important methods for preparation of cyclopropane.[2] A highly stereoselective cyclopropanation via MIRC has been reported for cyclic olefins.[3] Although there have been a few examples of *cis*-selective cyclopropanation,[4] most of the reactions via MIRC with acyclic olefins as substrates yield a mixture of *cis* and *trans* isomers or thermodynamically stable *trans*-cyclopropanes.[2,5] The stereoselective preparation of *cis*-cyclopropane from acyclic olefin is still a real problem.

Huang and coworkers first reported a method for the stereoselective synthesis of cyclopropane with arsonium ylide and olefin.[6] Later, Ding and coworkers reported a process for the highly stereoselective synthesis of *cis*-1,2-cyclopropane with arsonium salt and olefin as the starting material.[7] Our group has investigated stereoselective cyclopropanation with arsonium salts and olefins.[8] Although these methods with acyclic olefin as the substrate are satisfactory for stereoselectivity, they involve a two- or three-step reaction. The total process consists of the following sequence: (1) the preparation of arsonium salt from triphenylarsine and halogen compound; (2) the conversion of arsonium salt to ylide in the presence of the base; and (3) the cyclopropanation of ylide and olefin. In this multistep operation, each step requires its own condition, reagent and solvent. After each reaction is completed, the solvent and waste are separated and the product is purified. The improvements of the efficiency of organic processes and the reduction of the amount of reagents and solvents have been major goals in synthetic chemistry. Up to now the development of a new one-step process for the stereoselective preparation of *cis*-cyclopropane using acyclic olefin as substrate has remained a challenge.

The other shortcoming of cyclopropanation involving arsonium ylide is that triphenylarsine is expensive and toxic. One way to solve this problem is to use triphenylarsine as a catalyst in the process of preparing cyclopropane, but in the literature on cyclopropanation via MIRC, tellurium has been reported as the catalyst.[9] Here we report a new triphenylarsine-catalyzed one-pot procedure for cyclopropanation using bromides and acyclic olefins as the starting material in the presence of the $NaHCO_3$ with high yield and *cis*-selectivity (Scheme 1).



Scheme 1

For the preparation of cyclopropane from arsonium salt and olefin, the base is essential. The first base tested was K_2CO_3 which was used in our earlier method with arsonium salt and olefin.[7,8] In the initial model experiment, a mixture of triphenylarsine (0.5 equiv), phenacyl bromide (1.2 equiv), 4-methoxyphenylidenemalononitrile (1.0 equiv) and K_2CO_3 (3.0 equiv) in DME (5 mL) was stirred at room temperature. Unfortunately, the expected cyclopropane was not observed by TLC and the color of the so-

SYNTHESIS 2005, No. 16, pp 2718–2722
Advanced online publication: 23.09.2005
DOI: 10.1055/s-2005-916035; Art ID: F06505SS

lution became deep brown. Based on our previous experience, $NaHCO_3$ was employed instead of K_2CO_3. The reaction was carried out under the same conditions as in the model text above and the desired product was detected by TLC. After 170 hours, 1-benzoyl-2-(4-methoxyphenyl)-3,3-dicyanocyclopropane was obtained in 51% yield, but the cyclopropanation reaction was not completed, because there was residual 4-methoxyphenylidenemalononitrile in the solution. To our knowledge, this is the first report of the use of $NaHCO_3$ as a base in the production of arsonium ylide from arsonium salt.

For the above result, it is necessary to carry out the reaction at an increased temperature to achieve a satisfactory reaction rate and yield. Our studies began with the same model system using 0.5 equivalent of triphenylarsine with $NaHCO_3$ as base and DME as solvent. The results (Table 1, entries 1–3), show that the yield of the reaction increased and the time of the reaction decreased when the temperature was raised from room temperature to 50 °C, but the yield decreased when reaction was carried out at 60 °C (Table 1, entry 4). At 60 °C, some unknown side-products were generated. A further search for a suitable solvent was performed at 50 °C. The results in Table 1 demonstrated that chloroform was the best solvent among those tested (Table 1, entry 8). When the reaction was carried out in refluxing $CHCl_3$ (Table 1, entry 9), the yield reached 88% and the reaction took 18 hours.

Table 1 Results of the Optimization of Solvent and Temperature[a]

Entry	Solvent	Temp (°C)	Time (h)	Yield (%)[b]
1	DME	r.t.	170	51
2	DME	40	120	59
3	DME	50	84	70
4	DME	60	50	66
5	dioxane	50	72	58
6	THF	50	72	62
7	benzene	50	84	71
8	$CHCl_3$	50	64	86
9	$CHCl_3$	reflux	18	88
10	$CHCl_3$	40	110	83
11	$CHCl_3$	r.t.	240	63

[a] Unless otherwise specified, the reaction was carried out with Ph_3As (0.5 equiv), phenacyl bromide (1.2 equiv), 4-methoxyphenylidenemalononitrile (1.0 equiv), and $NaHCO_3$ (3.0 equiv).
[b] Yield of isolated product.

We investigated the relationship of the yield and the rate of the reaction to the amount of triphenylarsine used in refluxing $CHCl_3$. Various amounts of triphenylarsine as catalyst in refluxing $CHCl_3$ were tested. The results are shown in Table 2. When the amount of triphenylarsine is increased from 0.1 equivalent to 1 equivalent, the differences in the yield of cyclopropanation are not significant, but the differences in the rate of reaction are great. For example, a catalytic amount of triphenylarsine (0.1 equiv) showed good catalytic activity with 81% yield, but it took 68 hours to complete the reaction (Table 2, entry 1). The yield was 88% and time of reaction was 9 hours when 1 equivalent of triphenylarsine was used as catalyst (Table 2, entry 5). To achieve a satisfactory reaction rate, 0.5 equivalent of triphenylarsine was used in optimal condition.

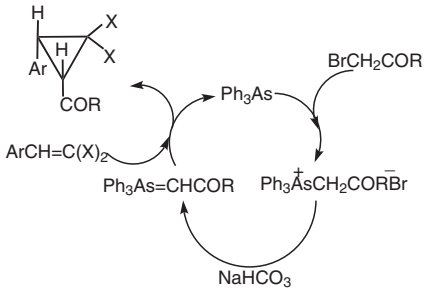
Table 2 Yields of Cyclopropanes and Rates of Reaction with Various Amounts of Triphenylarsine[a]

Entry	Triphenylarsine (equiv)	Time (h)	Yield (%)[b]
1	0.1	68	81
2	0.25	30	85
3	0.5	18	88
4	0.75	12	88
5	1.0	9	88

[a] Unless otherwise specified, the reaction was carried out with phenacyl bromide (1.2 equiv), 4-methoxyphenylidenemalononitrile (1.0 equiv), and $NaHCO_3$ (3.0 equiv) in refluxing $CHCl_3$.
[b] Yield of isolated product.

The scope of the triphenylarsine-catalyzed cyclopropanation with other bromide and electron-deficient olefin was further explored. In each case, high yields of *cis*-cyclopropanes were obtained under the aforementioned optimal condition (Table 3).

In our experiments, the arsonium salts were observed by TLC. The *cis*-cyclopropane **4e** was produced in a yield of 84% when a mixture of arsonium salt (1 mmol), 4-methoxyphenylidenemalononitrile (1 mmol) and $NaHCO_3$ (3 mmol) was refluxed in $CHCl_3$ for seven hours. On the basis of experimental observation and the literature, the mechanism of this reaction is likely to proceed via a cyclic process involving the formation of arsonium salt from triphenylarsine and bromide followed by the production of ylide in the presence of $NaHCO_3$, and the MIRC of ylide and olefin generating the *cis*-cyclopropane and triphenylarsine. This cyclic process is depicted in Scheme 2.



Scheme 2

Table 3 Triphenylarsine-Catalyzed Cyclopropanation with Bromides and Olefins[a]

Entry	Product	Ar	R	X	Time (h)	Yield (%)[b]
1	**4a**	4-$NO_2C_6H_4$	Ph	CN	16	82
2	**4b**	4-FC_6H_4	Ph	CN	16	83
3	**4c**	4-ClC_6H_4	Ph	CN	18	88
4	**4d**	4-MeC_6H_4	Ph	CN	18	90
5	**4e**	4-$MeOC_6H_4$	Ph	CN	18	88
6	**4f**	Ph	Ph	CN	18	88
7	**4g**	2-ClC_6H_4	Ph	CN	18	87
8	**4h**	2,4-$Cl_2C_6H_3$	Ph	CN	18	89
9	**4i**	3,4-$(OCH_2O)C_6H_3$	Ph	CN	22	82
10	**4j**	2,4-$(MeO)_2C_6H_3$	Ph	CN	30	84
11	**4k**	4-ClC_6H_4	OMe	CN	120	80
12	**4l**	4-MeC_6H_4	OMe	CN	120	83
13	**4m**	Ph	Ph	Meldrum's acid	45	76
14	**4n**	Ph	OMe	Meldrum's acid	60	74

[a] Unless otherwise specified, the reaction was carried out with Ph_3As (0.5 equiv), phenacyl bromide (1.2 equiv), arylidenemalononitrile (1.0 equiv), and $NaHCO_3$ (3.0 equiv) in refluxing $CHCl_3$.
[b] Yield of isolated product.

The structures of products **4a–n** were determined by IR, ^{1}H NMR spectroscopy. The *cis* configurations of the compounds **4a–n** were confirmed by comparison of the coupling constant of two protons situated at adjacent carbon atoms in the cyclopropane ring. It has been reported that the cyclopropyl protons with a *cis* relationship have larger coupling constants (~ 7–10 Hz), while those with a *trans* relationship have smaller coupling constants (~ 3–7 Hz).[10] The coupling constants of cyclopropanes **4a–n** (Table 3) were 8.0–9.6 Hz.

We have achieved a triphenylarsine-catalyzed one-step procedure for the preparation of *cis*-cyclopropane with acyclic electron deficient olefins and methyl bromoacetate and phenacyl bromide in the presence of $NaHCO_3$. This method is simple, high-yielding and *cis*-selective. The success of this method depends on the choice of base, solvent and temperature. Further exploration of the scope of the triphenylarsine-catalyzed process is in progress.

All reagents and solvents were obtained from commercial source and used without purification. Melting points were determined on WRS-1 digital melting point apparatus made by Shanghai physical instrument factory (SPOIF), China and are uncorrected. IR spectra were measured in KBr on a PE-580B spectrometer. ^{1}H NMR spectra were recorded at a Bruker AM-300, using $CDCl_3$ as solvent and TMS as internal reference.

***cis*-1-Acyl-2-arylcyclopropanes 4a–n; General Procedure**
A mixture of Ph_3As (**1**; 0.145 g, 0.5 mmol), bromide **2** (1.2 mmol), olefin **3** (1 mmol) and $NaHCO_3$ (0.240 g, 3 mmol) was stirred in refluxing $CHCl_3$. The completion of the reaction was determined by TLC. The $CHCl_3$ was removed under reduced pressure and the residue was eluted on a silica gel chromatographic column. Ph_3As can be recovered and the desired products **4** obtained, respectively.

***cis*-1-Benzoyl-3,3-dicyano-2-(4-nitrophenyl)cyclopropane (4a)**
Colorless solid; mp 185–186 °C (hexane–EtOAc) (Lit.[8c] mp 188–189 °C).

IR (KBr): 3073, 2254, 1674, 1595 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.02 (d, *J* = 8.0 Hz, 1 H), 4.11 (d, *J* = 8.0 Hz, 1 H), 7.59–7.66 (m, 3 H), 7.75–7.78 (t, *J* = 7.8 Hz, 2 H), 8.12 (d, *J* = 8.0 Hz, 2 H), 8.34 (d, *J* = 8.4 Hz, 2 H).

***cis*-1-Benzoyl-3,3-dicyano-2-(4-fluorophenyl)cyclopropane (4b)**
Colorless solid; mp 158–159 °C (hexane–EtOAc) (Lit.[8c] mp 156–157 °C).

IR (KBr): 3065, 2251, 1662, 1596 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.91 (d, *J* = 8.0 Hz, 1 H), 4.01 (d, *J* = 8.0 Hz, 1 H), 7.14–7.20 (t, *J* = 8.1 Hz, 2 H), 7.37–7.41 (q, *J* = 7.1 Hz, 2 H), 7.59–7.64 (t, *J* = 8.5 Hz, 2 H), 7.72–7.78 (t, *J* = 8.1 Hz, 1 H), 8.09–8.13 (d, *J* = 8.2 Hz, 2 H).

***cis*-1-Benzoyl-2-(4-chlorophenyl)-3,3-dicyanocyclopropane (4c)**
Colorless solid; mp 179–180 °C (hexane–EtOAc) (Lit.[8c] mp 181–182 °C).

IR (KBr): 3036, 2247, 1675, 1595 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.89 (d, *J* = 8.0 Hz, 1 H), 4.00 (d, *J* = 8.0 Hz, 1 H), 7.34 (d, *J* = 8.5 Hz, 2 H), 7.45 (d, *J* = 8.7 Hz, 2 H), 7.58–7.64 (t, *J* = 8.0 Hz, 2 H), 7.72–7.77 (t, *J* = 7.0 Hz, 1 H), 8.08–8.11 (d, *J* = 7.4 Hz, 2 H).

***cis*-1-Benzoyl-3,3-dicyano-2-(4-methylphenyl)cyclopropane (4d)**
Colorless solid; mp 156–157 °C (hexane–EtOAc) (Lit.[8c] mp 157–158 °C).

IR (KBr): 3035, 2247, 1677, 1595 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.38 (s, 3 H), 3.86 (d, *J* = 8.0 Hz, 1 H), 4.03 (d, *J* = 8.0 Hz, 1 H), 7.26 (s, 4 H), 7.56–7.62 (t, *J* = 8.0 Hz, 2 H), 7.70–7.72 (t, *J* = 7.5 Hz, 1 H), 8.08–8.11 (d, *J* = 7.4 Hz, 2 H).

***cis*-1-Benzoyl-3,3-dicyano-2-(4-methoxyphenyl)cyclopropane (4e)**
Colorless solid; mp 163–164 °C (hexane–EtOAc) (Lit.[8c] mp 161–162 °C).

IR (KBr): 3065, 2246, 1675, 1595 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.83 (s, 3 H), 3.86 (d, *J* = 8.0 Hz, 1 H), 4.00 (d, 1 H, *J* = 8.0 Hz, 1 H), 6.97 (d, *J* = 8.8 Hz, 2 H), 7.30 (d, *J* = 8.6 Hz, 2 H), 7.58–7.63 (t, *J* = 8.0 Hz, 2 H), 7.71–7.74 (t, *J* = 7.4 Hz, 1 H), 8.09–8.12 (d, *J* = 7.4 Hz, 2 H).

***cis*-1-Benzoyl-3,3-dicyano-2-phenylcyclopropane (4f)**
Colorless solid; mp 134–135 °C (hexane–EtOAc) (Lit.[8c] mp 132–133 °C).

IR (KBr): 3043, 2243, 1681, 1596 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.91 (d, *J* = 8.0 Hz, 1 H), 4.06 (d, *J* = 8.0 Hz, 1 H), 7.38–7.45 (m, 5 H), 7.5–7.60 (t, *J* = 7.7 Hz, 2 H), 7.69–7.74 (t, *J* = 7.4 Hz, 1 H), 8.08–8.11 (d, *J* = 7.1 Hz, 2 H).

***cis*-1-Benzoyl-2-(2-chlorophenyl)-3,3-dicyanocyclopropane (4g)**
Colorless solid; mp 156–157 °C (hexane–EtOAc) (Lit.[8c] mp 154–155 °C).

IR (KBr): 3060, 2249, 1674, 1597 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.97 (d, *J* = 8.2 Hz, 1 H), 4.03 (d, *J* = 8.2 Hz, 1 H), 7.26–7.39 (m, 3 H), 7.44–7.78 (m, 4 H), 8.12–8.15 (d, *J* = 7.4 Hz, 2 H).

***cis*-1-Benzoyl-3,3-dicyano-2-(2,4-dichlorophenyl)cyclopropane (4h)**
Colorless solid; mp 142–143 °C (hexane–EtOAc) (Lit.[8c] mp 141–142 °C).

IR (KBr): 3072, 2247, 1681, 1597 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.92 (d, *J* = 8.2 Hz, 1 H), 3.99 (d, *J* = 8.2 Hz, 1 H), 7.21–7.27 (t, *J* = 8.4 Hz, 2 H), 7.34–7.37 (d, *J* = 8.5 Hz, 1 H), 7.60–7.67 (m, 2 H), 7.75–7.80 (t, *J* = 7.7 Hz, 1 H), 8.12–8.15 (d, *J* = 7.4 Hz, 2 H).

***cis*-1-Benzoyl-3,3-dicyano-2-(3,4-methylenedioxyphenyl)cyclopropane (4i)**
Colorless solid; mp 187–188 °C (hexane–EtOAc) (Lit.[8c] mp 188–189 °C).

IR (KBr): 3050, 2248, 1672, 1595 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.84 (d, *J* = 8.0 Hz, 1 H), 3.98 (d, *J* = 8.0 Hz, 1 H), 6.02 (s, 2 H), 6.83–6.84 (d, *J* = 6.3 Hz, 3 H), 7.59–7.62 (t, *J* = 8.8 Hz, 2 H), 7.70–7.73 (t, *J* = 7.0 Hz, 1 H), 8.07–8.11 (m, 2 H).

***cis*-1-Benzoyl-3,3-dicyano-2-(2,4-dimethoxyphenyl)cyclopropane (4j)**
Colorless solid; mp 149-151 °C (hexane–EtOAc) (Lit.[8c] mp 150–151 °C).

IR (KBr): 3030, 2243, 1677, 1609 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.60 (d, *J* = 8.2 Hz, 1 H), 3.82 (s, 3 H), 3.91 (s, 3 H), 3.97 (d, *J* = 8.2 Hz, 1 H), 6.47–6.53 (m, 2 H), 7.04–7.07 (d, *J* = 8.2 Hz, 1 H), 7.59–7.61 (t, *J* = 6.8 Hz, 2 H), 7.69–7.74 (t, *J* = 6.9 Hz, 1 H), 8.08–8.11 (d, *J* = 7.9 Hz, 2 H).

***cis*-2-(4-Chlorophenyl)-3,3-dicyano-1-methoxycarbonylcyclopropane (4k)**
Colorless solid; mp 124–125 °C (hexane–EtOAc) (Lit.[8b] mp 128–130 °C).

IR (KBr): 3051, 2250, 1737, 1597 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.12 (d, *J* = 8.2 Hz, 1 H), 3.66 (d, *J* = 8.0 Hz, 1 H), 3.92 (s, 3 H), 7.26 (d, *J* = 8.5 Hz, 2 H), 7.43 (d, *J* = 8.5 Hz, 2 H).

***cis*-3,3-Dicyano-1-methoxycarbonyl-2-(4-methylphenyl)cyclopropane (4l)**
Colorless solid; mp 90–91 °C (hexane–EtOAc) (Lit.[8b] mp 84–86 °C).

IR (KBr): 3053, 2247, 1738, 1610 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.37 (s, 3 H), 3.13 (d, *J* = 8.2 Hz, 1 H), 3.66 (d, *J* = 8.2 Hz, 1 H), 3.91 (s, 3 H), 7.17 (d, *J* = 8.2 Hz, 2 H), 7.23 (d, *J* = 8.2 Hz, 2 H).

***cis*-1-Benzoyl-6,6-dimethyl-2-phenyl-5,7-dioxaspiro[2,5]octane-4,8-dione (4m)**
Colorless solid; mp 182–183 °C (hexane–EtOAc) (Lit.[8a] mp 184–185 °C).

IR (KBr): 3003, 1744, 1693, 1594 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.71 (s, 3 H), 1.74 (s, 3 H), 4.11 (d, *J* = 9.6 Hz, 1 H), 4.44 (d, *J* = 9.6 Hz, 1 H), 7.37–7.42 (m, 5 H), 7.47–7.52 (t, *J* = 6.6 Hz, 2 H), 7.58–7.64 (t, *J* = 6.3 Hz, 1 H), 8.00–8.03 (d, *J* = 7.2 Hz, 2 H).

***cis*-1-Methoxycarbonyl-6,6-dimethyl-2-phenyl-5,7-dioxaspiro[2,5]octane-4,8-dione (4n)**
Colorless solid; mp 146–147 °C (hexane–EtOAc) (Lit.[7] mp 149–150 °C).

IR (KBr): 3010, 1743 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.71 (s, 3 H), 1.76 (s, 3 H), 3.82 (s, 3 H), 3.85 (d, *J* = 9.3 Hz, 1 H), 3.94 (d, *J* = 9.3 Hz, 1 H), 7.30–7.37 (m, 5 H).

Acknowledgment

We gratefully acknowledge the help of Dr. Anthony G. Netting and Dr. Nancy Lynn Netting for polishing the manuscript. Thanks are due to the National Natural Science Foundation of China for financial support.

References

(1) (a) Tsuji, T.; Nishida, S. In *The Chemistry of the Cyclopropyl Group*; Patai, S., Ed.; Wiley: New York, **1987**. (b) Wong, H. N. C.; Hon, M.-Y.; Tse, C.-W.; Yip, Y.-C.; Tanko, J.; Hudlicky, T. *Chem. Rev.* **1989**, *89*, 165. (c) *Carbocyclic Three- and Four-Membered Ring Compounds,* In *Houben–Weyl - Methods of Organic Chemistry*, Vol. E17a,b; de Meijere, A., Ed.; Thieme: Stuttgart, **1997**. (d) *Small Ring Compounds in Organic Synthesis VI,* In *Topics in Current Chemistry*, Vol. 207; de Meijere, A., Ed.; Springer: New York, **2000**.
(2) Lebel, H.; Marcoux, J.-F.; Molinaro, C.; Charette, A. B. *Chem. Rev.* **2003**, *103*, 977.

(3) (a) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1962**, *84*, 867. (b) Gustafsson, J.; Sterner, O. *Tetrahedron* **1995**, *51*, 3865. (c) Haly, B.; Bharadwaj, R.; Sanghv, Y. S. *Synlett* **1996**, 687.
(4) (a) Doyle, M. P.; Zhou, Q.-L.; Simonsen, S. H.; Lynch, V. *Synlett* **1996**, 697. (b) Krysiak, J.; Kato, T.; Gornitzka, H.; Baceiredo, A.; Mikolajczyk, M.; Bertrand, G. *J. Org. Chem.* **2001**, *66*, 8240. (c) Hu, W.-H.; Timmons, J.; Doyle, M. P. *Org. Lett.* **2002**, *4*, 901.
(5) (a) Brunel, J. M.; Legrand, O.; Reymond, S.; Buono, G. *J. Am. Chem. Soc.* **1999**, *121*, 5807. (b) Calò, V.; Nacci, A.; Lopez, L.; Lerario, L. V. *Tetrahedron Lett.* **2000**, *41*, 8977. (c) Iwasa, S.; Takezawa, F.; Tuchiya, Y.; Nishiyama, H. *Chem. Commun.* **2001**, 59. (d) Huang, L.-Y.; Chen, Y.; Gao, G.-Y.; Zhang, X. P. *J. Org. Chem.* **2003**, *68*, 8179.
(6) Huang, Y.-Z.; Shen, Y. *Adv. Organomet. Chem.* **1982**, *20*, 115.
(7) Ding, W.-Y.; Han, Z.-H.; Chen, Y.-L.; Zou, Y.-J.; Liu, X. *Chem. Res. Chin. Univ.* **1996**, *12*, 50; *Chem. Abstr.* **1996**, *125*, 142141.
(8) (a) Pu, J.-Q.; Jiang, H.-Z.; Chen, X.; Qio, M.-Y.; Ding, W.-Y. *Hecheng Huaxue* **2000**, *8*, 356; *Chem. Abstr.* **2001**, *134*, 178514. (b) Ren, Z.-J.; Ding, W.-Y.; Cao, W.-G.; Wang, S.-H.; Huang, Z.-j. *Synth. Commun.* **2002**, *32*, 3143. (c) Ren, Z.-J.; Cao, W.-G.; Ding, W.-Y.; Wang, Y.; Wang, L.-L. *Synth. Commun.* **2004**, *34*, 3785.
(9) Huang, Y.-Z.; Tang, Y.; Zhou, Z.-L.; Xia, W.; Shi, L.-P. *J. Chem. Soc., Perkin Trans. 1* **1994**, 893.
(10) (a) Gunther, H. *NMR Spectroscopy*; Wiley: New York, **1980**, 108. (b) Gunther, H. *NMR Spectroscopy*; Wiley: New York, **1980**, 384.