

Selective and CO-Retentive Addition Reactions of Acid Chlorides to Terminal Alkynes in Synthesis of β-Chloro-α,β-unsaturated Ketones Using ZnO

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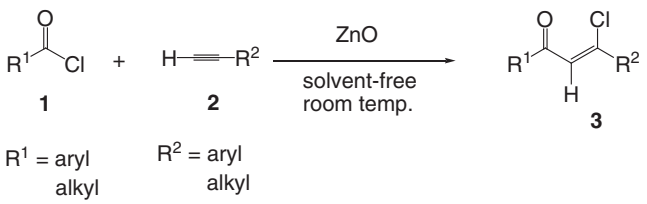
The addition reaction of acid chlorides with terminal alkynes to afford β-chloro-α,β-unsaturated ketones using ZnO as catalyst has been studied under solvent-free conditions. All the reactions were done at room temperature and β-chloro-α,β-unsaturated ketones were obtained with selectivity in high yields.

β-Chloro-α,β-unsaturated ketones have received considerable attention due to their utility as synthetic intermediates particularly for the synthesis of heterocyclic systems.[1] A useful reaction for the synthesis of β-chloro-α,β-unsaturated ketones involves the addition of acid chloride derivatives to terminal alkynes. However, the addition of acid chlorides to alkynes often proceeds with concomitant decarbonylation.[2] In 1996, Miura and co-workers[3] reported for the first time rhodium-catalyzed addition of acid chlorides to alkynes. This reaction proceeded with complete decarbonylation. Tanaka,[4] Chung,[5] and co-workers reported rhodium-catalyzed addition reactions of chloroformates,[4a,5] ethoxalyl chloride,[4b] perfluorinated acid chlorides,[4c] and chloroacetyl chlorides[4d] to terminal alkynes. The electronegative substituent bond to the carbonyl group appeared to play an important role to prevent possible decarbonylation in these reactions.

The addition reaction of acid chlorides to alkynes using a stoichiometric or catalytic amount of Lewis acids such as $AlCl_3$, $FeBr_2$, or $CeCl_3$ is known.[6] However, as is expected in using the Lewis acid catalysts, the major products are usually (*E*)-isomers or suffer from the lack of stereoselectivity. Recently Tsuji and co-workers[7] reported the addition of acid chlorides to alkynes proceeded without decarbonylation although this reaction suffered from one or more of the following disadvantages: long reaction times (20 h), use of expensive or unavailable reagents, high temperature (90 °C), toxic solvent (toluene), and not applicable for aliphatic acid chlorides. Therefore, a capable, efficient, low-cost, and commercially available catalyst must be developed for the reaction.

In recent years, inorganic solid oxides like SiO_2, Al_2O_3, ZnO, and others have received considerable interest because of their chemoselectivity and availability at low cost. Hence, according to our previous work on the application of metal oxides as catalyst,[8] herein we successfully report the addition of acid chlorides **1** to terminal alkynes **2**, catalyzed by ZnO, to afford (*Z*)-adducts selectively without decarbonylation at room temperature under solvent-free conditions (Scheme 1).



Scheme 1.

Results and Discussion

First, the reaction between benzoyl chloride (**1a**) and phenylacetylene (**2a**) in 1:1 molar ratio was optimized using different metal oxides such as TiO_2, MgO, CaO, etc. (Table 1). As is clear from Table 1, the synthesis of compound **3a** is completed after 70 min at room temperature in 90% isolated yields using 20 mol % of ZnO. Other inorganic solids as catalyst have also been examined on the yield of the compound **3a** (Entries 2–7). For comparison, when CaO, Al_2O_3, TiO_2, and $ZnCl_2$ were used in place of ZnO under the same conditions, reactions were ineffective. In fact, only 32% and 21% conversions were observed when MgO and SiO_2 were used, respectively. In the next instance, the effect of the amount of catalyst on promotion of the reaction was examined (Entries 8–11). It was observed that the variation for ZnO had an effective influence. The best amount of nano ZnO is 20 and 50 mol %, which afforded the desired product in 90% yields (Entries 1 and 10). We also examined the effect of solvents. Although the reaction proceeded smoothly in THF or dioxane, only 75% and 70% yields of the product were detected after long reaction times (Entries 14 and 15). Probably, ZnO surface contributes to the reaction so the solvents maybe deactivate the catalyst and decrease the reaction yields. In addition, the reaction did not proceed without any catalysts (Entry 17). As a result, ZnO was found the most effective catalyst, affording **3a** in 90% yield after 70 min at room temperature with high *Z*-selectivity (Table 1, Entry 1) showing regio- and stereoselectivity.

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Table 1. Solvent Screening for the Reaction of Benzoyl Chloride (**1a**) with Phenylacetylene (**2a**) Using ZnO[a)]

Entry	Catalyst (mol %)	Solvent	Reaction time /h	Yield /%[b),c)]
1	ZnO (20)	none	1:10'	90
2	MgO (20)	none	15	32
3	SiO_2 (20)	none	15	21
4	CaO (20)	none	24	trace
5	Al_2O_3 (20)	none	24	0
6	TiO_2 (20)	none	24	trace
7	$ZnCl_2$ (20)	none	24	0
8	ZnO (5)	none	2	86
9	ZnO (10)	none	1.5	87
10	ZnO (50)	none	1:10'	90
11	ZnO (100)	none	2	75
12	ZnO (20)	CH_3CN	24	trace
13	ZnO (20)	CH_2Cl_2	24	0
14	ZnO (20)	THF	13	75
15	ZnO (20)	Dioxane	9.5	70
16	ZnO (20)	H_2O	24	0
17	none	none	24	0

a) Conditions: **1a** (1.0 mmol), **2a** (1.0 mmol), at rt. b) Isolated yields. c) The product was characterized by IR, ^{1}H NMR, and ^{13}C NMR.

After preliminary experiments, we found that the representative procedure could be successfully used to obtain various β-chloro-α,β-unsaturated ketones **3** with high regio- and stereoselectivity from **1** and **2**. The results are shown in Table 2.

The terminal alkynes and catalyst are air stable and the humidity is not high enough to hydrolyze the acid chloride. Therefore, an inert atmosphere is not required and all reactions were done at room temperature in an open vessel. To prove this, the addition reaction of **1a**, **1b**, and **1f** with **2a** in the presence of ZnO were completed under an inert atmosphere and gave the same results as those obtained under air (Table 2, Entries 1, 2, and 6).

As shown in Table 2, the addition reactions have taken place with regio- and stereoselectivity. Routine workup allowed isolation of *Z*- and *E*-isomers, which were fully characterized by comparing with the known ^{1}H NMR data reported previously.[7] Electron-withdrawing and electron-donating substituent acid chlorides were converted to the corresponding β-chloro-α,β-unsaturated ketones **3b** and **3c** in high yield and stereoselectivity without decarbonylation (Entries 2 and 3). The electronic effect of the *para*-substituents is not significant; the highly electronegative *p*-nitro-substituent decreases the reactivity (Entry 4). Heteroatom and aliphatic acid chloride such as 2-thienyl chloride (**1e**) and cyclohexanoyl chloride (**1f**) also conforms to the reaction (Entries 5 and 6). To understand the scope and the generality of this protocol, aliphatic alkynes were synthesized and reacted with benzoyl chloride in the presence of ZnO. As shown in Table 2, aliphatic alkynes reacted smoothly with benzoyl chloride and afforded the corresponding ketones **3g** and **3h** in high yield and stereoselectivity (Entries 7 and 8).

Reusability of the ZnO was studied through a condensation reaction of **1a** with **2a**. After completion of the reaction (monitored by TLC), ethyl acetate was added to the reaction mixture and centrifuged until the catalyst was deposited at the bottom of centrifuge tube. The deposited ZnO was washed with ethyl acetate 2–3 times to complete removal of organic residuals, dried in an oven at 100–120 °C for 5–6 h and then the catalyst was reused for the same reaction. It was shown that ZnO can be recovered and is reusable. The results of the reusability of ZnO are listed in Table 3.

XRD patterns of solid ZnO before and after using in the reaction are shown in Figure 1. The observed diffraction peaks in all the recorded XRD patterns are in agreement with those of the JCPDS card 89-7102 for hexagonal ZnO with wurtzite structure. No peaks of any other phase were detected. From the FWHM of diffraction lines, crystallite size is estimated employing Scherrer's formula. Average size is $>1\,\mu$m. The XRD pattern of the reused catalyst is shown in Figure 1b. Clearly, the ZnO structure of the catalyst remains intact. Thus, the catalyst is stable in the reaction condition.

Conclusion

In conclusion, a new strategy, ZnO-catalyzed addition of acid chlorides with alkynes is established as a tool of defunctionalization of terminal acetylenes for the regio- and stereoselective synthesis of highly functionalized olefins. Further studies on the reaction mechanism and the application of ZnO are under investigation. So, herein we have presented the first example of ZnO-catalyzed synthesis of β-chloro-α,β-unsaturated ketones under mild conditions. This new and efficient catalytic method provides a protocol that enables the synthesis of (*Z*)-β-chloro-α,β-unsaturated ketones in stereo- and regioselectively, while displaying good functional group tolerance. This protocol benefits from short reaction times, operational simplicity, neutral reaction conditions, reusability of the catalyst, avoidance of solvents, reduced environmental and economic impacts, and chemoselectivity. No toxic reagent or by product were involved and no laborious purifications were necessary.

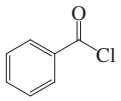
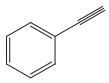
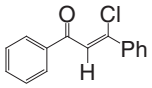
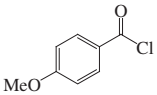
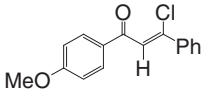
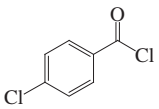
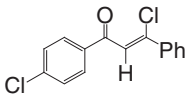
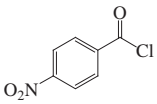
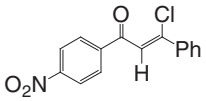
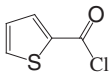
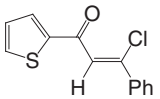
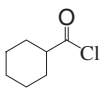
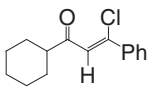
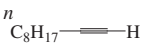
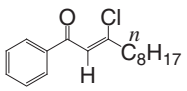
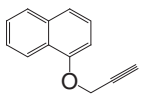
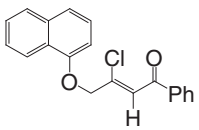
Experimental

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance DPX FT 250 and 62.9 MHz spectrometer with TMS as an internal reference. IR spectra were obtained on a Perkin-Elmer or FTIR-8300 instruments. Mass spectra were obtained on a Shimadzu GCMS0QP 1000EX at 20 and/or 70 eV. Elemental analyses were performed on a Thermo Finnigan, Flash EA 1112 series microanalyzer by the head of the CHN lab.

General Procedure for Synthesis of β-Chloro-α,β-unsaturated Ketones. The acid chlorides (1.0 mmol) were added to a mixture of ZnO (0.016 g, 20 mol %) and phenylacetylene (1.0 mmol) with stirring at room temperature. The reaction progress was monitored by TLC. After completion, the crude reaction mixture was extracted with water and EtOAc (3×15 mL). The organic layers were dried with $MgSO_4$ and evaporated. The resulting crude material was purified by column chromatography (hexan/EtOAc), affording pure (*Z*)-3-chloro-1,3-diphenyl-2-propen-1-one (**3a**).

Spectral Data. (*Z*)-3-Chloro-1,3-diphenyl-2-propen-1-one (3a): Pale yellow oil; IR (neat): ν 1666.4, 1600.8, 1573.8, 1490.9, 1236.3 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.02–7.98

Table 2. Addition of Acid Chlorides **1** to Terminal Alkynes **2** Using ZnO at Room Temperature under Solvent-Free Conditions[a)]

Entry	Acid chloride	Alkyne	Product **3**	Time /min	Yield /%[b)]	Z/E[c)]
1	 **1a**	 **2a**	 **3a**	70	90 (87)[d)]	95/5
2	 **1b**	**2a**	 **3b**	40	85 (83)[d)]	90/10
3	 **1c**	**2a**	 **3c**	180	70	95/5
4	 **1d**	**2a**	 **3d**	240	0	0
5	 **1e**	**2a**	 **3e**	20	90	90/10
6	 **1f**	**2a**	 **3f**	10	95 (91)[d)]	100/0
7	**1a**	 **2b**	 **3g**	60	90	90/10
8	**1a**	 **2c**	 **3h**	10	95	100/0

a) Conditions: **1** (1.0 mmol), **2** (1.0 mmol), ZnO (0.016 g, 20 mol %) were mixed at rt, under solvent-free condition. b) Isolated yields. c) Determined by ^{1}H NMR and GC analysis. d) The reaction was performed under nitrogen atmosphere.

(m, 2H, Ar–H), 7.78–7.74 (m, 2H, Ar–H), 7.61–7.54 (m, 1H, Ar–H), 7.50–7.42 (m, 5H, Ar–H), 7.36 (s, 1H, –COC*H*=C(Cl)–); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ 189.6, 143.1, 137.6, 137.1, 133.3, 130.6, 128.7, 128.6, 128.1, 127.1, 121.5; EI-MS: m/z 244 (16.8% $[M+2]^+$), 243 (36.2 $[M+1]^+$), 242 (57.3, $[M]^+$), 241 (100 $[M-1]^+$), 165 (29.0), 105 (61.7), 77 (83.4); Anal. Calcd for $C_{15}H_{11}ClO$: C, 74.23; H, 4.57%. Found: C, 74.14; H, 4.66%.

(*Z*)-3-Chloro-1-(4-methoxyphenyl)-3-phenyl-2-propen-1-one (3b): Pale yellow solids; mp: 86–88 °C (Lit.[1] 88–89 °C); IR (KBr): ν 1651.0, 1602.7, 1585.4, 1573.8, 1238.2 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.99 (d, $J = 8.97$ Hz, 2H, Ar–H), 7.75–7.72 (m, 2H, Ar–H), 7.44–7.41 (m, 3H, Ar–H), 7.28 (s, 1H, –COC*H*=C(Cl)–), 6.95 (d, $J = 8.95$ Hz, 2H, Ar–H), 3.89 (s, 3H, –OMe); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ 188.7, 163.8, 141.9, 137.2, 131.1, 130.5, 130.3, 128.6, 127.0, 122.0, 113.8, 55.5; EI-MS: m/z 274 (13.1% $[M+2]^+$), 273 (26.5 $[M+1]^+$), 272 (36.6 $[M]^+$), 165 (27.2), 135 (100), 77 (55.6); Anal. Calcd for $C_{16}H_{13}ClO_2$: C, 70.46; H, 4.80%. Found: C, 70.34; H, 4.76%.

(*Z*)-3-Chloro-1-(4-chlorophenyl)-3-phenyl-2-propen-1-one (3c): Pale yellow solids: mp: 64–66 °C (Lit.[1] 66–67 °C); IR (KBr): ν 1658.7, 1591.2, 1573.8, 1203.5, 759.9 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.94 (d, $J = 8.6$ Hz, 2H, Ar–H), 7.78–7.73 (m, 2H, Ar–H), 7.49–7.44 (m, 5H, Ar–H), 7.28 (s, 1H, –COC*H*=C(Cl)–); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ

Table 3. Reusability of the ZnO Catalysts in Synthesis of **3a**

Entry	Catalytic runs	**1a**/mmol	Catalyst/g	Yield/%[a)]
1	Fresh	5	0.2	90
2	1	4	0.16	90
3	2	3	0.12	87
4	3	2	0.08	85

a) Isolated yields.

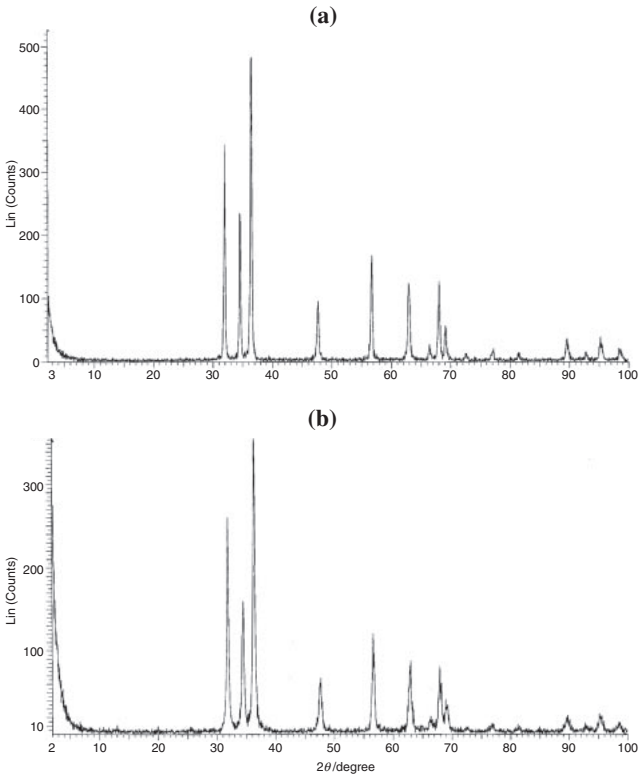


Figure 1. The XRD patterns of ZnO; (a) before reaction, (b) after reaction.

188.6, 143.9, 139.8, 137.1, 136.0, 130.7, 130.0, 129.0, 128.7, 127.2, 120.9; EI-MS: m/z 278 (34.9% $[M+2]^+$), 277 (69.8 $[M+1]^+$), 276 (56.3 $[M]^+$), 275 (100 $[M-1]^+$), 165 (34.9), 139 (65.6), 102 (71.4), 75 (59.4); Anal. Calcd for $C_{15}H_{10}Cl_2O$: C, 65.01; H, 3.64%. Found: C, 64.91; H, 3.50%.

(*Z*)-3-Chloro-3-phenyl-1-(2-thienyl)-2-propen-1-one (3e): Pale yellow-brown oil; IR (neat): ν 1643, 1585.4, 1573.8, 1446.5, 1245.9 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ 7.78–7.73 (m, 3H, Ar–H), 7.69–7.66 (m, 1H), 7.47–7.45 (m, 2H, Ar–H), 7.44–7.43 (m, 1H), 7.34 (s, 1H, –COC*H*=C(Cl)), 7.15–7.13 (m, 1H, Ar–H); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ 181.0, 145.5, 144.4, 137.3, 134.3, 132.1, 130.7, 128.7, 128.3, 127.3, 120.3; EI-MS: m/z 250 (18.5% $[M+2]^+$), 249 (42.6 $[M+1]^+$), 248 (53.7 $[M]^+$), 247 (100 $[M-1]^+$), 184 (30.6), 165 (14.8), 111 (95.5), 102 (53.7); Anal. Calcd for $C_{13}H_9ClOS$: C, 62.77; H, 3.65%. Found: C, 62.61; H, 3.55%.

(*Z*)-3-Chloro-1-cyclohexyl-3-phenyl-2-propen-1-one (3f): Pale yellow oil; IR (neat): ν 2931.6, 2852.5, 1693.4, 1593.09, 1446.5, 1228.8 cm^1; ^1H NMR (250 MHz, $CDCl_3$): δ 7.64 (d, $J=7.68$ Hz, 2H, Ar–H), 7.38–7.34 (m, 3H, Ar–H), 6.84 (s, 1H, –COC*H*=C(Cl)–), 2.58–2.55 (m, 1H, cyclohexyl), 1.93–1.66 (m, 5H, cyclohexyl), 1.42–1.21 (m, 5H, cyclohexyl); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ 201.1, 142.3, 137.3, 130.4, 128.5, 127.1, 122.6, 51.4, 28.2, 28.0, 26.09, 25.8; EI-MS: m/z 250 (2.4% $[M+2]^+$), 249 (2.5 $[M+1]^+$), 248 (6.7 $[M]^+$), 213 (11.3), 165 (100), 137 (10), 102 (27.1); Anal. Calcd for $C_{15}H_{17}ClO$: C, 72.43; H, 6.89%. Found: C, 72.31; H, 6.77%.

(*Z*)-3-Chloro-1-phenyl-2-undecen-1-one (3g): Pale yellow oil; IR (neat): ν 2925.8, 2856.4, 1695.3, 1598.9, 1448.4, 1218.9 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ 7.93 (d, $J=8.0$ Hz, 2H, Ar–H), 7.59–7.42 (m, 3H, Ar–H), 6.81 (s, 1H, –COC*H*=C(Cl)–), 2.53 (t, $J=7.2$ Hz, 2H, –CH=C(Cl)–CH_2–), 1.72–1.59 (m, 2H, –CH=C(Cl)–CH$_2$–CH_2–), 1.33–1.25 (m, 10H, –CH=C(Cl)–C_2H_4–C_5H_{10}–CH_3), 0.90 (t, $J=6.59$ Hz, 3H, –CH_3); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ 189.6, 147.7, 137.6, 133.1, 128.56, 128.45, 121.1, 41.16, 31.8, 29.2, 29.1, 28.6, 27.3, 22.6, 14.0; EI-MS: m/z 279 (2.7% $[M+1]^+$), 278 (4.4 $[M]^+$), 243 (1.4 $[M-Cl]^+$), 105 (100), 77 (47); Anal. Calcd for $C_{17}H_{23}ClO$: C, 73.23; H, 8.31%. Found: C, 73.08; H, 8.23%.

(*Z*)-3-Chloro-4-(1-naphthalenyloxy)-1-phenyl-2-buten-1-one (3h): Pale brown solids; mp: 130 °C; IR (KBr): ν 1647.1, 1616.2, 1573.8, 1508.2, 1228.6 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ 8.40–8.31 (m, 2H, Ar–H), 7.85 (d, $J=8.5$ Hz, 2H, Ar–H), 7.61–7.45 (m, 7H, Ar–H, COC*H*=C(Cl)–), 6.94 (d, 2H, $J=8.08$ Hz, Ar–H), 4.95 (s, 2H, –OCH_2–); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ 197.28, 155.98, 139.18, 132.68, 132.63, 130.6, 130.3, 129.1, 129.07, 128.3, 126.0, 125.8, 125.7, 122.3, 103.5, 76.2; EI-MS: m/z 323 (0.3% $[M+1]^+$), 322 (0.4 $[M]^+$), 286 (49), 247 (91.7), 191 (68.7), 105 (100), 77 (60.4); Anal. Calcd for $C_{20}H_{15}ClO_2$: C, 74.42; H, 4.68%. Found: C, 74.37; H, 4.56%.

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References

1 a) A. E. Pohland, W. R. Benson, *Chem. Rev.* **1966**, *66*, 161. b) N. G. Prodanchuk, I. V. Megera, V. K. Patratii, *Pharm. Chem. J.* **1984**, *18*, 108. c) A. N. Mirskova, G. G. Levkovskaya, I. D. Kalikhman, M. G. Voronkov, *Zh. Org. Khim.* **1979**, *15*, 2301. d) G. G. Levkovskaya, G. V. Bozhenkov, R. N. Malyushenko, A. N. Mirskova, *Russ. J. Org. Chem.* **2001**, *37*, 1795. e) G. G. Levkovskaya, G. V. Bozhenkov, L. I. Larina, A. N. Mirskova, *Russ. J. Org. Chem.* **2002**, *38*, 1501. f) R. Arnaud, A. Bensadat, A. Ghobsi, A. Laurent, I. Le Dréan, S. Lesniak, A. Selmi, *Bull. Soc. Chim. Fr.* **1994**, *131*, 844. g) A. G. Aliev, *Russ. J. Org. Chem.* **2005**, *41*, 1192. h) N. K. Kochetkov, A. N. Nesmeanov, N. A. Semenov, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1952**, 87. i) A. Alberola, J. M. Andres, A. Gonzalez, R. Pedrosa, P. Pradanos, *Synth. Commun.* **1990**, *20*, 2537. j) J. Diab, A. Laurent, I. Le Dréan, *J. Fluorine Chem.* **1997**, *84*, 145.

2 a) Y. Obora, Y. Tsuji, T. Kawamura, *J. Am. Chem. Soc.* **1995**, *117*, 9814. b) T. Sugihara, T. Satoh, M. Miura, M. Nomura, *Angew. Chem., Int. Ed.* **2003**, *42*, 4672. c) X. Zhao, Z. Yu, *J. Am. Chem. Soc.* **2008**, *130*, 8136.

3 K. Kokubo, K. Matsumasa, M. Miura, M. Nomura, *J. Org. Chem.* **1996**, *61*, 6941.

4 a) R. Hua, S. Shimada, M. Tanaka, *J. Am. Chem. Soc.* **1998**,

120, 12365. b) R. Hua, S.-Y. Onozawa, M. Tanaka, *Chem.—Eur. J.* **2005**, *11*, 3621. c) T. Kashiwabara, K. Kataoka, R. Hua, S. Shimada, M. Tanaka, *Org. Lett.* **2005**, *7*, 2241. d) T. Kashiwabara, K. Fuse, R. Hua, M. Tanaka, *Org. Lett.* **2008**, *10*, 5469.

5 J. Y. Beak, S. I. Lee, S. H. Sim, Y. K. Chung, *Synlett* **2008**, 551.

6 a) C. C. Price, J. A. Pappalardo, *J. Am. Chem. Soc.* **1950**, *72*, 2613. b) H. Martens, F. Janssens, G. Hoornaert, *Tetrahedron* **1975**, *31*, 177. c) D. Manoiu, M. Manoiu, I. G. Dinulescu, M. Avram, *Rev. Roum. Chim.* **1985**, *30*, 223. d) H. Zhou, C. Zeng, L. Ren, W. Liao, X. Huang, *Synlett* **2006**, 3504. e) D. Manoiu, M. Manoiu, I. G. Dinulescu, M. Avram, *Rev. Roum. Chim.* **1984**, *29*, 201. f) R. A. Haack, K. R. Beck, *Tetrahedron Lett.* **1989**, *30*, 1605. g) D. Manoiu, M. Manoiu, I. G. Dinulescu, M. Avram, *Rev. Roum. Chim.* **1984**, *29*, 671. h) W. R. Benson, A. E. Pohland, *J. Org. Chem.* **1964**, *29*, 385. i) J. P. Clayton, A. W. Guest, A. W. Taylor, *J. Chem. Soc., Chem. Commun.* **1979**, 500. j) B. Wang, S. Wang, P. Li, L. Wang, *Chem. Commun.* **2010**, *46*, 5891.

7 T. Iwai, T. Fujihara, J. Terao, Y. Tsuji, *J. Am. Chem. Soc.* **2009**, *131*, 6668.

8 a) M. Hosseini-Sarvari, H. Sharghi, *J. Org. Chem.* **2006**, *71*, 6652. b) M. Hosseini Sarvari, H. Sharghi, *J. Org. Chem.* **2004**, *69*, 6953. c) M. Hosseini Sarvari, *Synthesis* **2005**, 787. d) M. Hosseini Sarvari, H. Sharghi, *Tetrahedron* **2005**, *61*, 10903. e) M. Hosseini Sarvari, S. Etemad, *Tetrahedron* **2008**, *64*, 5519. f) M. Hosseini-Sarvari, *Tetrahedron* **2008**, *64*, 5459.