A facile solid-phase synthesis of Baylis–Hillman products from polymeric selenium reagents

Bin Huang, Shou-Ri Sheng[1]*, Yi-Xiang Huang, Qin Xin, Li-Yan Song and Nian-Hua Luo

College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang, 330027, P. R. China

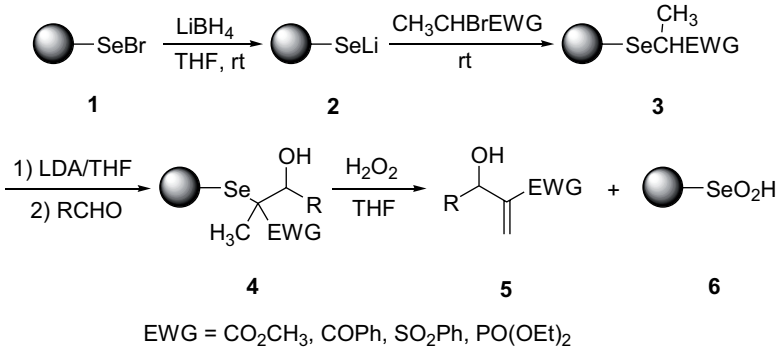
Treatment of lithio derivatives of polystyrene-supported methyl α-selenopropionate, 2-selenopropiophenone, 1-selenoethyl phenyl sulfone and diethyl 1-selenoethylphosphonate with aldehydes respectively, followed by cleavage from the polymer by oxidation-elimination with 30% hydrogen peroxide efficiently afforded Baylis–Hillman products in good yields and high purities.

Keywords: solid-phase organic synthesis, polymer-supported selenium reagents, Baylis–Hillman product, oxidation–elimination.

Polymer-supported reagents have attracted growing interest because they can provide attractive and practical methods for combinatorial chemistry and solid-phase synthesis.[1] Synthesis on a polymer support shows a number of advantages as compared to solution chemistry. The most salient one is the possibility to apply excesses of reagents and remove them without involving time-consuming separation techniques. The Baylis–Hillman reaction has become an important tool in organic synthesis, since it allows for the formation of carbon–carbon bonds under mild reaction conditions.[2] Although methods for the synthesis of Baylis–Hillman adducts are well documented,[2,3] efforts are continuing for the development of more efficient methods with experimental simplicity. It is well known that organoselenium reagents are now commonly used as a powerful tool for introducing new functional groups into organic substrates under extremely mild conditions.[4] For example, phenylseleno group is readily converted to a leaving group giving access to carbon–carbon double bond *via* oxidation followed by β-elimination. Katzenellenbogen *et al.* previously reported the synthetic method of Baylis–Hillman products from the α-phenylselenenyl esters and aldehydes.[5] However, organoselenium reagents always have a foul smell and are quite toxic, which is often problematic in organic synthesis. The use of the selenium reagents immobilised on polymer-resin has provided significant advantages, including decreased volatility and simplification of product work-up.[6] In connection with our interest in solid-phase organoselenium chemistry.[7] Herein, we report a convenient and efficient solid-phase synthetic approach to Baylis-Hillman products with traceless selenium linker based on polymer-supported selenium reagents (Scheme 1).

The resin **3a–d** was easily prepared in 90–92% yield by a few steps from cross-linked (1%) polystyrene by reaction of polystyrene-supported lithium selenide **2**[6a] with methyl 2-bromopropionate, 2-bromopropiophenone, 1-bromoethylphenyl sulfone and diethyl 1-bromoethylphosphonate, respectively. The formation of **3a–d** was monitored by FT-IR showing characteristic absorption at 1710 cm^{-1} (CO), 1690 cm^{-1} (Ph*CO*), 1145 cm^{-1} (SO_2) and 1245 cm^{-1} (P = O), respectively. Resin **3** can be stored at room temperature for long time without diminution of capacity or the liberation of disagreeable odours. As illustrated, reaction of the lithio derivative of resin **3** generated by treating resin **3** with lithium diisopropylamide with aldehyde furnished the resin **4,** which could not be reliably analysed with FT-IR. Hence next step of oxidation–elimination reaction was carried out directly with 30% hydrogen peroxide at 0°C and then at room temperature to afford the corresponding Baylis–Hillman products **5** in good yields and with a purity greater than 95% (Table 1). The residual resin **6**, polystyrene-supported phenylseleninic acid, was obtained as a by-product, whose IR data was identical to the previously reported data,[8] and showed no residual C=O, SO_2, P = O absorptions indicating the oxidation–elimination was complete. The polymer-supported phenylseleninic acid could be converted to resin **1** for recycle by treatment of it with $KI/Na_2S_2O_3$[7c,9] followed by bromine.[7a] For instance, methyl 3-hydroxy-2-methylene-3-phenylpropanoate (**5a**) was obtained in 86% yield under the same reaction condition using the recovered selenenyl bromide resin **1** (second run) (Table 1, entry 2), and in 83% yield after fourth recycle (*i.e.* fourth run) (Table 1, entry 3). It was shown that recycling 3-4 times led to a gradual decrease in yield but the purity remained almost same as when the selenium bromide resin was firstly used.

As seen from the Table 1, whether aliphatic, aromatic or hetero-aromatic aldehydes can give good results. For aromatic aldehydes, substitution of an electron-withdrawing group or an electron-donating group on the aromatic ring resulted in no obvious effect on the reaction yields. On the other hand, ketones in place of aldehydes were investigated under the same conditions. For example, the reaction of resin **3a** with acetone and acetophenone provided methyl 3-hydroxy-3-



Scheme 1

* Correspondent. E-mail: shengsr@jxnu.edu.cn

Table 1 The yields and purities of Baylis–Hillman products **5**[a]

Entry	R^1	EWG	Products	Yield (%)[b]
1	C_6H_5	CO_2CH_3	**5a**	89
2	C_6H_5	CO_2CH_3	**5a**[c]	86
3	C_6H_5	CO_2CH_3	**5a**[d]	83
4	*p*-$CH_3C_6H_4$	CO_2CH_3	**5b**	91
5	*p*-$CH_3OC_6H_4$	CO_2CH_3	**5c**	89
6	*p*-$NO_2C_6H_4$	CO_2CH_3	**5d**	90
7	*p*-ClC_6H_4	CO_2CH_3	**5e**	88
8	*p*-FC_6H_4	CO_2CH_3	**5f**	85
9	2,4-$Cl_2C_6H_3$	CO_2CH_3	**5g**	87
10	2-naphthyl	CO_2CH_3	**5h**	88
11	2-furyl	CO_2CH_3	**5i**	86
12	2-pyridyl	CO_2CH_3	**5j**	89
13	*n*-C_3H_7	CO_2CH_3	**5k**	85
14	C_6H_5	COC_6H_5	**5l**	90
15	*p*-$NO_2C_6H_4$	$SO_2C_6H_5$	**5m**	90
16	C_6H_5	$PO(OEt)_2$	**5n**	91

[a]Purity was determined by 1H NMR of crude cleavage product.
[b]Overall yields was based on polymer-supported selenium bromide **1** (1.18 mmol Br/g).
[c]With the second regenerated resin **1**.
[d]With the fourth regenerated resin **1**.

methyl-2-methylene butanoate (**5o**) and methyl 3-hydroxy-2-methylene-3-phenylbutanoate (**5p**) in lower yields (70% and 62%, respectively) than that of aldehydes, which might be ascribed to the larger steric restriction of ketones than that of aldehydes.

In summary, an efficient and convenient method for the solid-phase synthesis of Baylis–Hillman products in good yields and purities employing a selenium-based traceless linker strategy has been developed. Simple workup procedure replaces the time-consuming isolation and purification steps in the corresponding solution-phase synthesis. Moreover, the polymeric reagent can be regenerated and reused for several times as environmentally benign reagent.

Experimental

Melting points were uncorrected. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance (400 MHz) spectrometer, using $CDCl_3$ as the solvent and TMS as internal standard. Mass spectra (EI, 70eV) were recorded on a HP5989B mass spectrometer. FT-IR spectra were taken on a Perkin-Elmer SP One FT-IR spectrophotometer. Microanalyses were performed with a PE 2400 elemental analyser. Polystyrene (H 1000, 100–200 mesh, cross-linked with 1% divinylbenzene) for the preparation of polystyrene-supported selenium bromide and other starting materials were purchased from commercial suppliers and used without further purification. DMF was distilled from calcium hydride and THF was stilled from sodium-benzophenone immediately prior to use.

Preparation of polystyrene-supported methyl α-selenopropionate **3a**; *typical procedure*

Under a nitrogen atmosphere, to polystyrene-supported selenium bromide **1** (1.0 g, 1.18 mmol Br/g, the loading of functional Br was analysed by elementary analysis) swelled in THF (10 ml) for 30 min was added $LiBH_4$ (2.5 mmol). After 1 h with stirring at room temperature, methyl 2-bromopropionate (3 mmol) in 2 ml of THF was added slowly and the mixture was stirred for 10 h. The resin **3a** was collected by filtration and washed successively with H_2O (2 × 20 ml), THF (2 × 5 ml) and CH_2Cl_2 (2 × 5 ml) and then dried in a vacuum. **3a**: 1.05 mmol CO_2Me/g, IR ν (KBr): 3022, 2921, 1710, 1495, 1448, 1317, 1303, 1145, 1070, 810, 751, 696, 579, 526 cm^{-1}. Resins **3b**, **3c** and **3d** were obtained using similar synthetic method as above.

Preparation of Baylis–Hillman products **5***; general procedure*

Resin **3** (1.0 mmol) was swelled in THF (10 ml) at room temperature for 30 min. After cooling to –78°C, a solution of LDA (1.0 ml, 2.0 M) was added under nitrogen and the mixture was stirring at the same temperature for 30 min. the neat aldehyde (2.0 mmol in 5 ml THF) was added dropwise over ca. 15 min. Twenty minutes after addition of the aldehyde, the reaction mixture was warmed up gradually to room temperature and kept standing for 2 h. After neutralisation with 1% hydrochloric acid, the resin **4** was collected on a filter and washed successively with H_2O (3 × 15 ml), THF (3 × 5 ml) and Et_2O (3 × 5 ml) and then suspended in THF (10 ml) and treated with 1.0 ml (11.6 mmol) of 30% H_2O_2. After stirring for 30 min at 0°C, and then for 30 min at room temperature, the residual resin was collected by filtration and washed CH_2Cl_2 (4 × 5 ml). The filtrate was washed with water (2 × 30 ml), dried over magnesium sulfate and concentrated to afford target product **5**.

Methyl 3-hydroxy-2-methylene-3-phenylpropanoate (**5a**): Colourless oil. (Lit.[3a] Oil); ^{1}H NMR: δ = 7.43–7.41 (m, 2 H), 7.21–7.19 (m, 3 H), 6.31 (s, 1 H), 5.90 (s, 1 H), 5.51 (s, 1 H), 3.70 (s, 3 H), 2.83 (br., OH); IR (film): ν = 3468, 1720, 1630, 1394, 1250 cm^{-1}.

Methyl3-hydroxy-3-(p-methylphenyl)-2-methylenepropanoate(**5b**): Colourless solid. m.p.39–40 (Lit.[10] 39–42°C); ^{1}H NMR: δ = 7.28 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 6.34 (s, 1H), 6.30 (s, 1H), 5.10 (s, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 2.85 (br., OH). IR (KBr): ν = 3448, 1722, 1629, 1397, 1275 cm^{-1}.

Methyl 3-hydroxy-3-(p-methoxylphenyl)-2-methylenepropanoate (**5c**): Colourless oil. (Lit.[3a] Oil); ^{1}H NMR: δ = 7.27 (d, *J* = 8.8 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 2H), 6.35 (s, 1H), 6.31 (s, 1H), 5.10 (s, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 2.92 (br., OH); IR (film): ν = 3470, 1720, 1612, 1395, 1250 cm^{-1}.

Methyl 3-hydroxy-3-(p-nitrophenyl)-2-methylenepropanoate (**5d**): Yellow solid, m.p. 70–71°C (Lit.[10] 71–73°C); ^{1}H NMR: δ = 8.18 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 6.37 (1 s, 1H), 5.86 (s, 1H), 5.60 (s, 1H), 3.73 (s, 3H), 2.93 (br., OH); IR (KBr): ν = 3473, 1689, 1630, 1380, 1195 cm^{-1}.

Methyl 3-hydroxy-3-(p-chlorophenyl)-2-methylenepropanoate (**5e**): Pale yellow solid, m.p. 43–44°C (Lit.[10] 43–44°C); ^{1}H NMR: δ = 7.33 (d, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 6.32 (s, 1H), 5.80 (s, 1H), 5.49 (s, 1H), 3.74 (s, 3H), 2.59 (br., OH); IR (KBr): ν = 3448, 1716, 1630, 1406, 1284 cm^{-1}.

Methyl 3-hydroxy-3-(p-fulorophenyl)-2-methylenepropanoate (**5f**): Pale yellow oil. (Lit.[10] Oil); ^{1}H NMR: δ = 7.30–7.36 (m, 2H), 6.98–7.05 (m, 2H), 6.32 (s, 1H), 5.80 (s, 1H), 5.53 (s, 1H), 3.71 (s, 3H), 2.57 (br., OH); IR (film): ν = 3446, 1718, 1626, 1490, 1400, 1284 cm^{-1}.

Methyl 3-hydroxy-3-(2,4-dichlorophenyl)-2-methylenepropanoate (**5g**): Pale yellow oil. (Lit.[10] Oil); ^{1}H NMR: δ = 7.49 (s, 1H), 7.24–7.36 (m, 2H), 6.30 (s, 1H), 5.90 (s, 1H), 5.55 (s, 1H), 3.76 (s, 3H), 2.97 (br., OH); IR (film): ν = 3450, 1721, 1628, 1405, 1285 cm^{-1}.

Methyl 3-hydroxy-2-methylene-3-(2-naphthyl)propanoate (**5h**): Colourless oil. (Lit.[3a] Oil); ^{1}H NMR: δ = 7.91–7.30 (m, 7H), 6.36 (s, 1H), 6.31 (s, 1H), 5.18–5.19 (m, 1H), 3.75 (s, 3H), 2.58 (br., OH); IR (film): ν = 3445, 1718, 1634, 1387, 1285 cm^{-1}.

Methyl 3-hydroxy-3-(2-furyl)-2-methylenepropanoate (**5i**): Pale yellow oil. (Lit.[10] Oil); ^{1}H NMR: δ = 7.35 (s, 1H), 6.36 (s, 1H), 6.24–6.35 (m, 2H), 5.92 (s, 1H), 5.57 (s, 1H), 3.74 (s, 3H), 2.87 (br., OH); IR (neat): ν = 3440, 1721, 1633, 1385, 1284 cm^{-1}.

Methyl 3-hydroxy-2-methylene-3-(3-pyridyl)propanoate (**5j**): Colourless oil. (Lit.[3a] Oil); ^{1}H NMR: δ = 8.35 (s, 1H), 8.25 (d, *J* = 3.6 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.17 (dd, *J* = 4.8, 8.1 Hz, 1H), 6.31 (s, 1H), 5.98 (s, 1H), 5.20 (s, 1H), 5.17 (br s, 1H), 3.60 (s, 3H); IR (film): ν = 3450, 1718, 1626, 1380, 1280 cm^{-1}.

Methyl 3-hydroxy-2-methylenehexanoate (**5k**): Colourless oil. (Lit.[11] Oil); ^{1}H NMR: δ = 6.24 (s, 1 H), 5.85 (s, 1 H), 4.41 (t, *J* = 6.5 Hz, 1 H), 3.78 (s, 3 H), 2.72 (br., 1 H), 1.71–1.62 (m, 2 H), 1.39–1.25 (m, 2 H), 0.92 (t, *J* = 7 Hz, 3 H); IR (film): ν = 3498, 1715, 1620, 1285, 1061 cm^{-1}.

3-Hydroxy-3-phenyl-2-methylenepropiophenone (**5l**): Colourless oil; ^{1}H NMR: δ = 7.44–7.41 (m, 2H), 7.25–7.19 (m, 8H), 6.28 (s, 1H), 6.01 (s, 1H), 5.55 (s, 1H), 2.92 (br, OH); ^{13}C NMR: δ = 196.1, 140.1, 137.4, 132.8, 130.2, 129.0, 128.6, 128.4, 127.5, 127.1, 123.3, 71.0; IR (film): ν = 3480, 1653, 1624, 1500, 1042, 961 cm^{-1}; EIMS: *m/z* (%) = 238 (M^+); Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.61; H, 5.96.

1-(4-Nitrophenyl)-2-phenylsulfonyl-2-propen-l-o1 (**5m**): Light yellow solid, m.p. 116–118°C; ^{1}H NMR: δ = 8.08 (t, *J* = 8.5 Hz, 2 H); 7.75 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.47 (t, *J* = 8 Hz, 1 H), 7.35 (t, *J* = 8.5 Hz, 2 H), 6.56 (s, 1 H), 5.91 (s, 1 H), 5.66 (d, J = 3.9 Hz, 1 H), 3.32 (d, *J* = 3.9 Hz, 1H); ^{13}C NMR: δ = 152.1, 147.6, 146.0, 138.7, 133.9, 129.2, 128.0, 127.8, 127.5, 123.5, 70.5; IR (KBr): ν = 3490, 1726, 1630, 1520, 1345, 1285, 1151 cm^{-1}; EIMS: *m/z* (%) = 319 (M^+); Anal. Calcd for $C_{15}H_{13}NO_5S$: C, 56.42; H, 4.10; N, 4.39. Found: C, 56.46; H, 4.16; N, 4.13.

Diethyl l-[hydroxy(phenyl)methyl]vinylphosphonate (**5n**): Colourless oil; ^{1}H NMR: δ = 7.43–7.40 (m, 2H), 7.27–7.22 (m, 3H), 6.31 (s, 1H), 6.05 (s, 1H), 5.58 (s, 1H), 4.10 (dq, J_{HH} = 7.1 Hz, J_{PH} = 11.0 Hz, 4H), 2.94 (br, OH), 1.33 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR: δ = 140.3, 130.2, 128.7, 127.3, 127.0, 122.8, 71.3, 61.4, 16.5; IR (neat): ν = 3478, 1632, 1495, 1450, 1240, 1045 cm^{-1}; EIMS: *m/z* (%) = 270 (M^+); Anal. Calcd for $C_{13}H_{19}O_4P$: C, 57.78; H, 7.09. Found: C, 57.83; H, 7.16.

Methyl 3-hydroxy-3-methyl-2-methylenebutanoate (**5o**): Colourless oil. (Lit.[12] Oil); ^{1}H NMR: δ = 6.22 (s, 1 H), 5.85 (s, 1 H), 3.76 (s, 3 H), 2.32 (br., 1 H), 1.25 (s, 6 H); IR (film): ν = 3500, 1717, 1628, 1380, 1060 cm^{-1}.

Methyl 3-hydroxy-2-methylene-3-phenylbutanoate (**5p**): Colourless oil; ^{1}H NMR: δ = 7.45–7.41 (m, 2 H), 7.20–7.15 (m, 3 H), 6.25 (s, 1 H), 6.04 (s, 1 H), 4.94 (br., OH), 3.70 (s, 3 H), 1.28 (s, 3 H); ^{13}C NMR: δ = 165.3, 141.9, 140.8, 128.7, 127.5, 127.3, 124.5, 70.3, 51.8, 31.5; IR (film): ν = 3489, 1717, 1629, 1378, 1150 cm^{-1}; EIMS: *m/z* (%) = 206 (M^+); Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 69.93; H, 6.90.

We gratefully acknowledge financial support from the National Natural Science Foundation of China (No.20562005) and NSF of Jiangxi Province (No.0420017).

Received 13 April 2006; accepted 5 July 2006
Paper 06/3901

References

1 Recent reviews on SPOS. (a) F. Guillier, D. Orain and M. Bradley, *Chem. Rev.,* 2000, **100**, 2091; (b) R.E. Sammelson and M.J. Kurth, *Chem. Rev.,* 2001, **101**, 137; (c) A.W. Czarnik, *Solid-phase organic synthesis*; Wiley: New York, 2001; Vol. 1; (d) K.C. Nicolaou, R. Hanko and H. Hartwig, *Handbook of Combinatorial Chemistry*; Wiley-VCH: Weinheim, Germany, 2002; (e) R.E. Dolle, *J. Comb. Chem*., 2002, **4**, 369; (f) W. Bannwarth, In *Combinatorial Chemistry: A Practical Approach*; W. Bannwarth and E. Felder, Ed.; Wiley-VCH: Weinheim, 2000; pp. 47-95 and references cited therein.

2 For review, see: (a) S.E. Drewes and G.H.P. Roos, *Tetrahedron,* 1988, **44**, 4653; (b) D. Basavaiah, P.D. Rao and R.S. Hyma, *Tetrahedron,* 1996, **52**, 8001; (c) E. Ciganek, *Org. React.,* 1997, **51**, 201; (d) I.E. Marko, G.P. Giles and N.J. Hindley, *Tetrahedron,* 1997, **53**, 1015; (e) P. Langer, *Angew. Chew., Int. Ed.,* 2000, **39**, 3049; (f) D. Basavaiah, A.J. Rao and T. Satyanarayana, *Chem. Rev.,* 2003, **103**, 811.

3 For some recent examples for preparation of Baylis–Hillman adducts, see: (a) R.O.M.A. de Souza, B.A. Meireles, L.C.S. Aguiar and M.L.A.A. Vasconcellos, *Synthesis,* 2004, 1595; (b) P.R. Krishna, E.R. Sekhar and S.V. Kannan, *Synthesis,* 2004, 857; (c) L.-J. Zhao, H.S. He, M. Shi and P.H. Toy, *J. Comb. Chem.,* 2004, **6**, 680; (d) S.Z. Luo, P.G. Wang and J.-P. Cheng, *J. Org. Chem.,* 2004, **69**, 555; (d) P.R. Krishna, K.R. Lopinti and V. Kannan, *Tetrahedron Lett*., 2004, **45**, 7847; (e) P.R. Krishna, A. Manjuvani, V. Kannan and G.V.M. Sharma, *Tetrahedron Lett*., 2004, **45**, 1183; (f) X.L. Mi, S.Z. Luo and J.-P. Cheng, *J. Org. Chem.,* 2005, **70**, 2338; (g) P. Caumul and H.C. Hailes, *Tetrahedron Lett*., 2005, **46**, 8125; (h) S.I. Pereira, J. Adrio, A.M.S. Silva and J.C. Carretero, *J. Org. Chem.,* 2005, **70**, 10175; (i) S. Xue, L. He, K.-Z. Han, Y.-K. Liu and Q.-X. Guo, *Synlett,* 2005, 1247; (j) P.R. Krishna, A. Manjuvani, and E.P. Sekhar, *Arkivoc,* 2005, 99; (k) Y.-S. Lin, C.-Y. Lin, C.-E. Liu and T.Y. R. Tsai, *Tetrahedron,* 2006, **62**, 872.

4 (a) H.J. Reich, *Acc. Chem. Res*., 1979, **12**, 22; (b) D. Liotta, *Acc. Chem. Res*., 1984, **17**, 28; (c) K.C. Nicolaou and N.A. Petasis, *Selenium in Natural Product Synthesis*, CIS: Philadelphia, 1984; (d) C. Paulmier, Ed. *Selenium Reagents and Intermediates in Organic Synthesis*, Pergamon Press: Oxford, 1986; (e) D. Liotta, Ed. *Organoselenium Chemistry*, Wiley: New York, 1987; (f) A. Krief, *Comprehensive Organic Synthesis*, Pergamon: Oxford, 1991; (g) T.G. Back, *Organoselenium Chemistry*, Oxford University Press: Oxford, 1999; pp 173-191; (h) T. Wirth, *Organoselenium Chemistry*, Springer: Berlin, 2000.

5 S.W. Rollinson, R.A. Amos and J.A. Katzenellenbogen, *J. Am. Chem. Soc.,* 1981, **103**, 4114.

6 (a) K.C. Nicolaou, J. Pastor, S. Barluenga and N. Winssinger, *Chem. Commun*., 1998, 1947; (b) T. Ruhland, K. Andersen and H. Pedersen, *J. Org. Chem.,* 1998, **63**, 9204; (c) L. Uehlin and T. Wirth, *Org. Lett.,* 2001, **3**, 2931; (d) K.-I. Fujita, S. Hashimoto, A. Oishi and Y. Taguchi, *Tetrahedron Lett*., 2003, **44**, 3793; (e) S. Berlin, C. Ericsson and L. Engman, *J. Org. Chem.,* 2003, **68**, 8386; (f) R.J. Cohen, D.L. Fox and R.N. Salvatore, *J. Org. Chem.,* 2004, **69**, 4265.

7 (a) X. Huang and S.-R. Sheng, *Tetrahedron Lett*., 2001, **42**, 9035; (b) X. Huang and S.-R. Sheng, *J. Comb. Chem*., 2003, **5**, 273; (c) X. Huang and W.-M. Xu, *Tetrahedron Lett*., 2002, **43**, 5495; (d) S.-R. Sheng, X.-L. Liu, X.-C. Wang, Q. Xin and C.-S. Song, *Synthesis,* 2004, 2833; (e) X.-L. Liu, S.-R. Sheng, Q.-Y, Wang, W.-K. Sun, Q. Xin and H.-Y. Ao, *J. Chem. Res*. 2006**,** 118.

8 G. Zundel, *Angew. Chem., Int. Ed. Engl*., 1969, **8**, 499.

9 F. Ferranti and D.D. Filippo, *J. Chem. Soc. (B)*., 1971, 1925.

10 J.X. Cai, Z.H. Zhou, G.F. Zhao and C.C. Tang, *Org. Lett.,* 2002, **4**, 4723.

11 H. Martin, R. Hoffmann and J. Rabe, *J. Org. Chem.,* 1985, **50**, 3849.

12 J.S. Hill and N.S. Isaacs, *Tetrahedron Lett*., 1986, **27**, 5007.