JOC*Note*

An Easy, Efficient, and Completely Stereoselective Synthesis of (*E*)-α,*β*-Unsaturated Esters via Sequential Aldol-Type/Elimination Reactions Promoted by Samarium Diiodide or Chromium Dichloride

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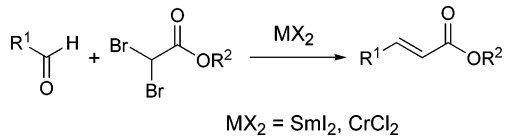
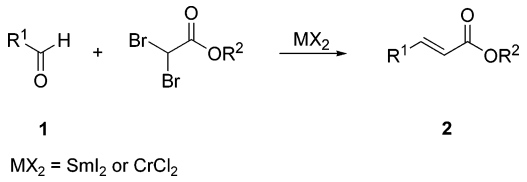


(*E*)-α,*β*-Unsaturated esters can be obtained with complete stereoselectivity by reaction of different aldehydes and ethyl dibromoacetate promoted by SmI_2 or $CrCl_2$. The transformation takes place as two sequential reactions: an aldol-type reaction and a *β*-elimination reaction.

Sequential reactions constitute very attractive methods due to their enormous simplicity. In recent years, samarium diiodide has become among the most important reagents for sequential or cascade reactions performed under reducing conditions.[1] Chromium dichloride has been also used to perform highly selective sequential reactions.[2] However, to the best of our knowledge, no cascade reactions from 2,2-dihaloesters to obtain α,*β*-unsaturated esters by using SmI_2 or $CrCl_2$ have been described.[3]

Moreover, α,*β*-unsaturated esters are attractive starting materials in organic synthesis, and for this reason, an important number of papers have described their synthesis.[4] However, in most of these methods, complete control of the stereoselectivity of the carbon−carbon double-bond formation remained unresolved,[5] and in other cases, tedious multipot procedures or starting materials that are not readily available are necessary.

SCHEME 1. Synthesis of α,*β*-Unsaturated Esters 2



Previously, we have described the highly stereoselective preparation of (*E*)-α,*β*-unsaturated esters by treatment of 2-halo-3-hydroxyesters with samarium diiodide[6] or chromium dichloride.[7] The starting 2-halo-3-hydroxyesters were obtained by successive generation of the corresponding enolate derived from α-haloesters and condensation with different aldehydes at low temperature. For this, a synthesis of α,*β*-unsaturated esters from commercially available compounds would be necessary.

Our objective in this work is to describe an improved method of the SmI_2-promoted synthesis of (*E*)-α,*β*-unsaturated esters with total stereoselectivity by using more readily available starting compounds such as commercial ethyl dibromoacetate and a variety of aldehydes. This transformation takes place as a sequential process, with the first step being an aldol-type reaction, followed by a *β*-elimination reaction as the second step. Moreover, we have developed another alternative method of this sequential process by using $CrCl_2$.

Treatment of a mixture of different aldehydes and ethyl dibromoacetate with a solution of SmI_2 (5 equiv) in THF[8] for 60 min at room temperature afforded, after hydrolysis, the corresponding (*E*)-α,*β*-unsaturated esters **2** with total stereoselectivity and in high yield (Scheme 1).

(1) To see the pioneering paper on synthetic application of SmI_2: (a) Namy, J. L.; Girard, P.; Kagan, H. B. *Nouv. J. Chim.* **1977**, *1*, 5−7. (b) Namy, J. L.; Girard, P.; Kagan, H. B.; Caro, P. E. *Nouv. J. Chim.* **1981**, *5*, 479−484. For recent reviews of sequencing reactions with SmI_2, see: (c) Molander, G. A.; Harris, C. R. *Tetrahedron* **1998**, 54, 3321−3354. (d) Molander, G. A.; Harris, C. R. *Chem. Rev.* **1996**, *92*, 307−338. For recent reviews of synthetic applications of SmI_2, see: (e) Krief, A.; Laval, A. M. *Chem. Rev.* **1999**, *99*, 745−777. (f) Steel, P. G. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2727−2751. (g) Kagan H. B. *Tetrahedron* **2003**, *59*, 10351−10372. (h) Concellón J. M.; Rodríguez-Solla, H. *Chem. Soc. Rev.* **2005**, *33*, 599−609. (i) Dahlén A.; Hilmerson, G. *Eur. J. Inorg. Chem.* **2004**, 3393−3403.

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(3) Previously, only one example of the synthesis of the corresponding α,*β*-unsaturated ester by reaction of 4-*tert*-butylcyclohexanone with ethyl dibromoacetate (no mixture of *Z*/*E* isomers can be obtained) by using a mixture of SmI_2, Sm, and $CrCl_3$ has been described: Matsubara, S.; Horiuchi, M.; Takai, K.; Utimoto, K. *Chem. Lett.* **1995**, 259−260.

(4) For recent reviews for the synthesis of α,*β*-unsaturated esters, see: (a) Franklin, A. S. *J. Chem Soc., Perkin Trans. 1* **1998**, 2451−2465. (b) Shen, Y. *Acc. Chem. Res.* **1998**, *31*, 584−592. By using the Wittig reaction: (c) Patil, V. J.; Mävers, U. *Tetrahedron Lett.* **1996**, *37*, 1281−1284. (d) Suzuki, K.; Matsukura, H.; Matsuo, G.; Koshino, H.; Nakata, T. *Tetrahedron Lett.* **2002**, *43*, 8653−8655. (e) Beji, F.; Lebreton, J.; Villieras, J.; Amri, H. *Synth. Commun.* **2002**, *32*, 3273−3278. (f) Huang, Z.; Sun, R. J. *Chinese J. Org. Chem.* **2002**, *20*, 1460−1462. (g) Shen, Y.; Zhang, Y. *Heteroatom Chem.* **2003**, *14*, 276−279. By using the Horner−Emmons reaction: (h) Ando, K. *J. Org. Chem.* **1999**, *64*, 6815−6821. (i) Ando, K. *J. Org. Chem.* **1997**, *62*, 1934−1939. (j) Ando, K. *Tetrahedron Lett.* **1995**, *36*, 4105−4108. By using Heck reaction: (k) Moreno-Mañas, M.; Pérez, M.; Pleixants, R. *Tetrahedron Lett.* **1996**, *37*, 7449−7452. (l) Beller, M.; Riermeier, T. H. *Tetrahedron Lett.* **1996**, *37*, 635−638.

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(8) A solution of SmI_2 in THF was very rapidly generated by reaction of diiodomethane with samarium powder in the presence of sonic waves: Concellón, J. M.; Rodríguez-Solla, H.; Bardales, E.; Huerta, M. *Eur. J. Org. Chem.* **2003**, 1775−1778.

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TABLE 1. Synthesis of (*E*)-α,*β*-Unsaturated Esters

entry	**2**	MX_2 [a]	R^1	R^2	*T* [a] (°C)	yield (%)[b]
1	**2a**	SmI_2	*n*-C_7H_{15}	Et	rt	66
2	**2a**	$CrCl_2$	*n*-C_7H_{15}	Et	reflux	75
3	**2b**	SmI_2	Cy	Et	rt	76
4	**2b**	$CrCl_2$	Cy	Et	reflux	84
5[c]	**2c**	SmI_2	Cy	Me	rt	60
6	**2d**	$CrCl_2$	PhCH=CH	Et	reflux	79[d]
7	**2e**	SmI_2	$CH_3CH(Ph)$	Et	rt	69
8	**2e**	$CrCl_2$	$CH_3CH(Ph)$	Et	reflux	88
9	**2f**	SmI_2	Ph_2CH	Et	rt	68
10	**2f**	$CrCl_2$	Ph_2CH	Et	reflux	74
11	**2g**	SmI_2	*p*-$MeOC_6H_4$	Et	rt	70
12	**2g**	$CrCl_2$	*p*-$MeOC_6H_4$	Et	reflux	72
13	**2h**	SmI_2	Ph	Et	rt	81
14	**2h**	$CrCl_2$	Ph	Et	reflux	95

[a] In all cases, 3 equiv of SmI_2 was used. Reactions with $CrCl_2$ were performed with 6 equiv. [b] Isolated yield after column chromatography based on the starting aldehyde **1**. [c] By using methyl dichloroacetate. [d] De = 91%.

The results are compiled in Table 1, showing that the sequential reaction using aldehydes seems to be general: aliphatic (linear, branched, or cyclic) and aromatic (*E*)-α,*β*-unsaturated esters can be obtained. It is notheworthy that when aldehydes with high proclivity to enolize are used (Table 1, entry 7 and 9), the reaction takes place in good yield.[9]

Interestingly, no byproducts were detected from reactions involving aromatic aldehydes known to undergo pinacol coupling.

The synthesis of α,*β*-unsaturated esters can be also carried out by using methyl dichloroacetate. In this case, the reaction was carried out at reflux and by using a greater amount of SmI_2 (6 equiv) to drive the reaction to completion, furnishing the α,*β*-unsaturated esters in lower yield. For these reasons, it was found to be advantageous to use dibromo- instead of dichloroacetate.

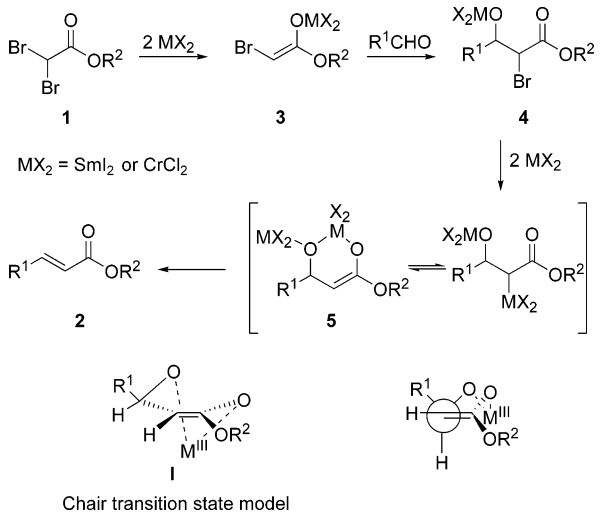
The presence of a single stereoisomer was shown in the crude reaction products by GC-MS and by ^{1}H NMR spectroscopy.

The *E* stereochemistry in the C=C double bond of α,*β*-unsaturated esters **2** was assigned on the basis of the value of the ^{1}H NMR coupling constant between the olefinic protons of compounds **2**[10] and, in other cases, by NOE experiments.

This method constitutes an important improvement on our previous synthesis of (*E*)-α,*β*-unsaturated esters[6] due to increased simplicity, total stereoselectivity, a shorter reaction time, and commercially available starting compounds. In addition, the yield of the sequential process is better than the total yield of the two-pot process (synthesis of starting 2-halo-3-hydroxyesters and SmI_2-promoted elimination reaction).

To the best of our knowledge, this sequential C−C bond formation/elimination reaction constitutes the first method described in the literature to perform the olefination of aldehydes using SmI_2 with total stereoselectivity.

SCHEME 2. Proposed Mechanism



Using $CrCl_2$ can also accomplish the same transformation. Thus, treatment of a mixture of ethyl dibromoacetate and various aldehydes with 6 equiv of $CrCl_2$ at 65 °C afforded, after hydrolysis, the corresponding (*E*)-α,*β*-unsaturated esters in high yield and with total stereoselectivity (Scheme 1 and Table 1). When the reaction was carried out at room temperature, the reaction did not achieve completion and starting aldehyde was recovered after 2 h.

Results in Table 1 show that α,*β*-unsturated esters can be prepared from cinnamaldehyde by using $CrCl_2$ (Table 1, entry 6) with very high stereoselectivity (de = 92%, GC-MS). The reaction of cinnamaldehyde with SmI_2, afforded a complex mixture of products. In the other cases, marginally higher yields were obtained by using $CrCl_2$ instead of SmI_2, the stereoselectivity being complete in both cases. Given these facts, the two proposed methods can be complementary and represent valuable methods for the preparation α,*β*-unsaturated esters. Using SmI_2 allows the reaction to be carried out at room temperature, whereas heating at 65 °C is necessary to perform this process with $CrCl_2$.

In a manner similar to the SmI_2-promoted reaction, the total stereoselectivity of the sequential reaction using $CrCl_2$ was established by GC-MS and by ^{1}H and ^{13}C NMR spectroscopy of crude products, and the relative configuration of the C=C bond was assigned on the basis of the coupling constant between the olefinic protons of compounds **2**.

Formation of products **2** using SmI_2 or $CrCl_2$ can be explained by assuming a sequential process in both cases (Scheme 2).

Thus, reaction of 2 equiv of SmI_2 or $CrCl_2$ with ethyl dibromoacetate generates a samarium or chromium enolate **3**, which reacts with the carbonyl compound to afford the corresponding 2-bromoester **4**. A metalation of **4** with 2 equiv of samarium diiodide or chromium dichloride gives the enolate intermediate **5**. Chelation of the Sm^{III} or Cr^{III} centers with the oxygen atom of the alcohol group produces a six-membered ring. Tentatively, we propose a half-chair transition state model **I**[11] with the bulkier group R^1 in the equatorial orientation (to avoid 1,3-diaxial interactions). Elimination from **I** affords (*E*)-α,*β*-unsaturated esters.

(9) When the Wittig reactions are carried out with enolizable carbonyl compounds, alkenes are obtained in very low yield (see ref 5).

(10) Coupling constants between the olefinic protons of compounds **2** ranging between *J* = 15.7 and 16.3 Hz were in accordance with the average literature values. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; John Wiley and Sons: New York, 1991; Chapter 4, Appendix F, p 221.

In conclusion, in this paper we have presented two easy, rapid, straightforward, general methods for the preparation of α,β-unsaturated esters in high yield and with total stereoselectivity starting from dibromoacetate and aldehydes (both commercially available), promoted by samarium diiodide or chromium dichloride. This transformation takes place through a sequential process: an aldol-type reaction, as the first step, followed by a totally *E*-stereoselective β-elimination reaction, as the second step. A mechanism to explain the high stereoselectivity has been proposed on the basis of the chelation of the Sm^{III} or Cr^{III} centers with both oxygen atoms.

Experimental Section

Synthesis of α,β-Unsaturated Esters (2) Using SmI_2. Under nitrogen, a solution of SmI_2 (3 mmol) was added to a stirred suspension of ethyl dibromoacetate (0.5 mmol) and the corresponding aldehyde (0.5 mmol) in THF. After stirring at room temperature for 2 h, the reaction was quenched with aqueous 0.1 M HCl. The organic layer was then extracted with dichloromethane. The combined extracts were dried over Na_2SO_4, and the solvent was removed in vacuo. Purification by flash chromatography on silica gel (hexane/EtOAc 10:1) afforded products **2**.

Synthesis of SmI_2 by Sonication. Samarium powder (3 mmol) was placed in a Schlenk tube at room temperature, and dry THF (30 mL) was added. The Schlenk tube was then partially submerged to the solvent level in a conventional cleaner sonicator (ultrasound laboratory cleaner 230 V, 150 W, 50 Hz), and diiodomethane (3 mmol) was added. After 5 min, a deep blue solution of SmI_2 was obtained.

Synthesis of α,β-Unsaturated Esters (2) Using $CrCl_2$. To a stirred suspension of $CrCl_2$ (6 mmol) in THF (10 mL) was added a solution of ethyl dibromoacetate (1 mmol) and the corresponding aldehyde (1 mmol), at 65 °C. After stirring at this temperature for 2 h, the reaction was quenched with 0.1 M HCl and extracted with hexane (3 × 10 mL). The combined extracts were dried over Na_2SO_4 and concentrated. The organic layer was then filtered through a pad of Celite, and the solvents were removed in vacuo. Purification by column chromatography on silica gel (hexane/EtOAc 10:1) afforded the α,β-unsaturated esters **2**.

Ethyl (*E*)-Dec-2-enoate (2a): orange oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.97 (dt, J = 7.5, 15.9 Hz, 1 H), 5.81 (d, J = 15.9 Hz, 1 H), 4.18 (q, J = 6.9 Hz, 2 H), 2.20 (apparent q, J = 7.0 Hz, 2 H), 1.70−0.89 (m, 13 H), 1.29 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 149.3, 121.1, 59.9, 32.1, 31.6, 29.0, 28.8, 27.9, 22.5, 14.1, 13.9; MS (70 eV, EI) *m/z* (%) 198 [M^+, 4], 169 (10), 141 (23), 123 (100); HRMS (70 eV) calcd for $C_{12}H_{22}O_2$ [M^+] 198.1620, found 198.1605; IR (neat) 2927, 1724, 1466 cm^{-1}; R_f = 0.4 (hexane/EtOAc 10:1). Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.91; H, 11.07.

Ethyl (*E*)-3-Cyclohexylprop-2-enoate (2b): white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.89 (dd, J = 6.7, 15.8 Hz, 1 H), 5.74 (d, J = 15.8 Hz, 1 H), 4.16 (q, J = 6.9 Hz, 2 H), 2.12−0.81 (m, 11 H), 1.26 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.9, 154.0, 118.6, 59.9, 40.2, 31.5, 25.7, 25.5, 14.0; MS (70 eV, EI) *m/z* (%) 182 [M^+, 34], 153 (3), 137 (65), 109 (22); HRMS (70 eV) calcd for $C_{11}H_{18}O_2$ [M^+] 182.1307, found 182.1319; IR (neat) 2926, 1723 cm^{-1}; R_f = 0.5 (hexane/EtOAc 3:1). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.71; H, 10.07.

Methyl (*E*)-3-Cyclohexylprop-2-enoate (2c): orange oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.91 (dd, J = 6.8, 15.9 Hz, 1 H), 5.76 (dd, J = 2.8, 15.9 Hz, 1 H), 3.72 (s, 3 H), 2.15−0.87 (m, 11 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 154.3, 118.2, 51.1, 40.1, 31.4, 25.6, 25.4; MS (70 eV, EI) *m/z* (%) 168 [M^+, 58], 136 (50), 95 (50), 87 (96), 59 (17); IR (neat) 2926, 1726, 1653, 1275 cm^{-1}; R_f = 0.54 (hexane/EtOAc 3:1). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C,70.99; H, 9.51.

Ethyl (2*E*,4*E*)-5-Phenyl-pent-2,4-dienoate (2d): yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38−7.30 (m, 7 H), 6.87 (d, J = 4.8 Hz, 1 H), 5.99 (d, J = 15.2 Hz, 1 H), 4.23 (q, J = 7.1 Hz, 2 H), 1.32 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 144.4, 140.2, 135.9, 128.9, 128.7, 127.1, 126.1, 121.2, 60.2, 14.2; MS (70 eV, EI) *m/z* (%) 202 [M^+, 20], 157 (22), 129 (100), 77 (12); IR (neat) 2982, 1708, 1626 cm^{-1}; R_f = 0.41 (hexane/EtOAc 5:1). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.91; H, 6.86.

Ethyl (*E*)-4-Phenylpent-2-enoate (2e): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37−7.21 (m, 5 H), 7.14 (dd, J = 6.9, 16.0 Hz, 1 H), 5.83 (dd, J = 1.35, 15.6 Hz, 1 H), 4.20 (q, J = 7.1 Hz, 2 H), 3.64 (q, J = 6.7 Hz, 1 H), 1.46 (d, J = 6.9 Hz, 3 H), 1.30 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 152.4, 143.0, 128.8, 127.1, 126.5, 119.9, 60.0, 41.8, 19.9, 14.0; MS (70 eV, EI) *m/z* (%)204 [M^+, 28], 159 (38), 131 (100), 115 (76), 91 (54), 77 (29); IR (neat) 2977, 1717, 1650 cm^{-1}; R_f = 0.4 (hexane/EtOAc 3:1). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.68; H, 7.78.

Ethyl (*E*)-4,4-Diphenylbut-2-enoate (2f): pale orange oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45−7.20 (m, 11 H), 5.78 (d, J = 15.6 Hz, 1 H), 4.90 (d, J = 7.3 Hz, 1 H), 4.22 (q, J = 7.1 Hz, 2 H), 1.30 (d, J = 7.1 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.3, 149.7, 141.4, 129.0, 128.9, 128.5, 128.4, 126.8, 122.8, 60.3, 53.3, 14.1; MS (70 eV, EI) *m/z* (%) 266 [M^+, 12], 237 (10), 221 (20), 193 (100), 165 (34), 115 (94), 91 (23), 77 (10); IR (neat) 2982, 1720 cm^{-1}; R_f = 0.5 (hexane/EtOAc 5:1). Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.26; H, 6.75.

Ethyl (*E*)-3-(4-Methoxyphenyl)prop-2-enoate (2g): colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.63 (d, J = 15.9 Hz, 1 H), 7.48−7.43 (m, 2 H), 6.91−6.85 (m, 2 H), 6.29 (d, J = 15.9 Hz, 1 H), 4.24 (q, J = 7.2 Hz, 2 H), 3.80 (s, 3 H), 1.32 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.3, 161.2, 144.2, 129.6, 126.9, 115.6, 114.2, 60.3, 55.3, 14.3; MS (70 eV, EI) *m/z* (%) 206 [M^+, <62], 161 (100), 89 (10); HRMS (70 eV) calcd for $C_{12}H_{14}O_3$ [M^+] 206.0943, found 206.0927; IR (neat) 2980, 1708, 1605, 1171 cm^{-1}; R_f = 0.2 (hexane/EtOAc 3:1). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.90; H, 6.90.

Ethyl (*E*)-3-Phenylprop-2-enoate (2h): yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.69 (d, J = 16.0 Hz, 1 H), 7.53−7.35 (m, 5 H), 6.44 (d, J = 16.0, 1 H), 4.26 (q, J = 7.1 Hz, 2 H), 1.33 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.7, 144.3, 134.1, 129.9, 128.1, 127.7, 117.9, 60.1, 14.0; MS (70 eV, EI) *m/z* (%) 176 [M^+, <30], 147 (17), 131 (100), 103 (56), 77 (45); IR (neat) 2980, 1712, 1637 cm^{-1}; R_f = 0.5 (hexane/EtOAc 3:1). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.69; H 6.74.

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Supporting Information Available: ^{13}C NMR spectra of compounds **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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