Preparation of Functionalized Arylmagnesium Reagents Bearing an *o*-Chloromethyl Group

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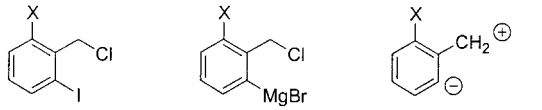
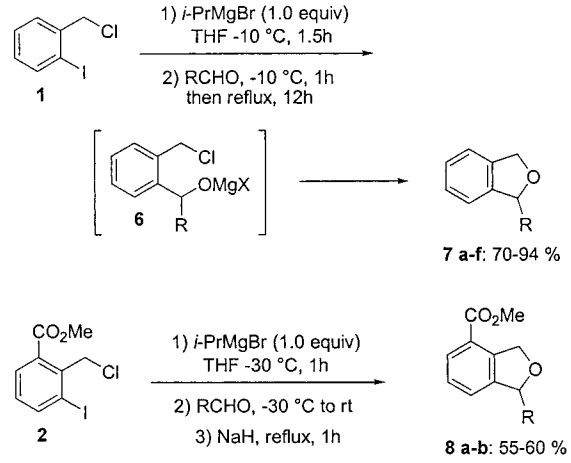
Received June 28, 2000

The iodine−magnesium exchange is a unique method for the preparation of polyfunctional organomagnesium reagents.[1,2] The efficient reaction of *i*-PrMgX with a wide range of functionalized aryl iodides proceeds under mild conditions so that various sensitive functional groups such as an ester, a nitrile, or an amide function are tolerated during the organomagnesium reagent formation. This method complements nicely the classical synthesis of Grignard reagents involving the direct insertion of magnesium metal.[3,4] Herein, we report the selective iodine−magnesium exchange of 2-chloromethyl-1-iodobenzenes such as **1** or **2**. The resulting organomagnesium reagents **3** and **4** are synthetic equivalents of the zwitterionic synthon **5** and prove to be well suited for the performance of cyclization reactions. Thus, the reaction of **1** with *i*-PrMgBr (1.0 equiv) in THF at −10 °C affords within 1.5 h the corresponding Grignard reagent **3** in >95% yield. Its reaction with various aliphatic, aromatic,

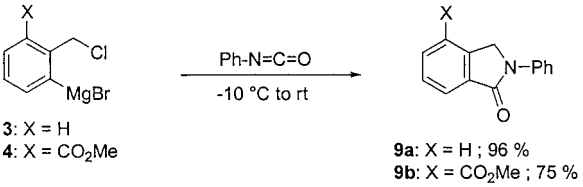


or unsaturated aldehydes furnishes the intermediate magnesium alcoholates of type **6**, which after 12 h of heating at reflux, afford the heterocycles **7a**−**f** in 70−91% yield (Scheme 1 and Table 1). Similarly, the ester substituted aryl iodide **2** undergoes a smooth iodine−magnesium exchange at −30 °C. The electron-withdrawing ester substituent facilitates the iodine-exchange reaction, and the aryl iodide **2** is converted to the organomagnesium species **4** within 1 h at −30 °C. Its

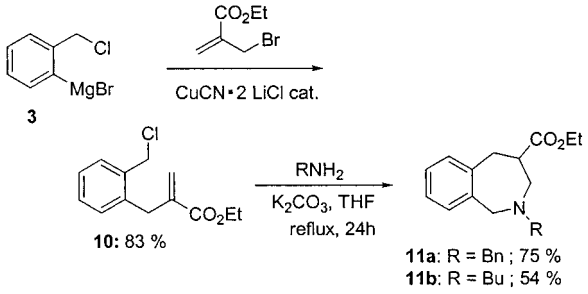
Scheme 1



Scheme 2



Scheme 3



reaction with aldehydes proceeds similarly, leading to the corresponding isobenzofurans **8a**,**b** in 55−60% yield (Scheme 1 and Table 1). The preparation conditions and the stability of the Grignard compounds **3** and **4** make these reagents convenient intermediates for synthetic applications. In strong contrast the corresponding unfunctionalized organolithium reagent (2-(chloromethyl)-phenyllithium) can only be prepared and handled at −100 °C.[5] Phenyl isocyanate reacts with **3** and **4** leading to the corresponding *N*-phenylphthalimidine derivative **9a**,**b** in excellent yield (75−96%, Scheme 2).

Finally, benzoazepine derivatives are readily obtained, starting from the functionalized organomagnesium **3**. Thus, the reaction of **3** with ethyl (2-bromomethyl)-acrylate[6] provides the allylated product **10**, which by treatment with an amine in the presence of K_2CO_3 in refluxing THF affords the benzoazepines **11a**,**b** in 54−75% yield (Scheme 3).

In summary, we have developed a convenient method for preparing arylmagnesium reagents bearing an ortho-

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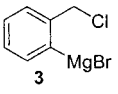
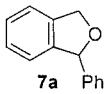
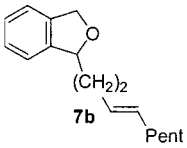
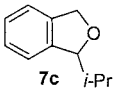
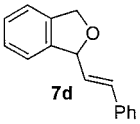
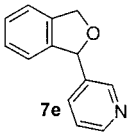
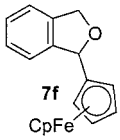
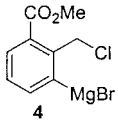
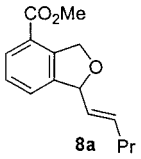
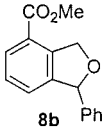
10.1021/jo000971x CCC: $19.00
Published on Web 10/21/2000

Table 1. Heterocycles 7a−f and 8a,b Obtained by the Reaction of Polyfunctional Organomagnesium Reagents 3 and 4 with Aldehydes

Grignard Reagent	Aldehyde RCHO (R)	Product of type 7 or 8	yield (%)[a]
 **3**	Ph	 **7a**	82
3	(*E*)-Pent-CH=CH-$(CH_2)_2$-	 **7b**	70
3	*i*-Pr	 **7c**	86
3	(*E*)-Ph-CH=CH-	 **7d**	91
3	3-pyridyl	 **7e**	78
3		 **7f**	81
 **4**	(*E*)-Pr-CH=CH-	 **8a**	60
4	Ph	 **8b**	55

[a] Yield of analytically pure products.

chloromethyl group. These reagents proved to be very useful for preparing various functionalized heterocycles.

Experimental Section

General Methods. Unless otherwise indicated, all reactions were carried out under an argon atmosphere. THF was distilled from sodium/benzophenone. Reactions were monitored by gas chromatography (GC) analysis of worked up reaction aliquots. Analytical thin-layer chromatography (TLC) was performed using Merck silica gel (60 F-254) plates (0.25 mm) precoated with a fluorescent indicator. Column chromatography was carried out on silica gel 60 (70−230 mesh). NMR data were recorded on a 200, 300, and 400 MHz NMR spectrometer. The ionization method used was electron impact ionization (EI, 70 eV). Melting points are uncorrected. Elemental analyses were performed by the Microanalytical Service Laboratory of Universität München.

Starting Materials. 2-(Chloromethyl)iodobenzene (**1**) was purchased from Aldrich.

Isopropylmagnesium Bromide. A dry three-necked flask was charged with magnesium (12.8 g, 0.53 mmol) covered with a small amount of THF. Isopropyl bromide (10 mL, 0.106 mmol) in THF (100 mL) was added dropwise. A water bath was used to keep the temperature below 35 °C. The reaction mixture was stirred overnight at room temperature, and excess magnesium was removed by filtration under argon.

Methyl 2-(Chloromethyl)-3-iodobenzoate (2). A THF solution of the known corresponding 2-(bromomethyl)benzoate[7] and LiCl (3 equiv) was heated at reflux for 4 h. After usual work up and filtration on silica, **2** was obtained as a colorless oil in a quantitative yield. IR (neat): 1713 (s), 1266 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.96 (d, J = 7.9 Hz, 1H), 7.79 (d, J = 7.9 Hz, 1H), 6.97 (t, J = 7.9 Hz, 1H), 5.08 (s, 2H), 3.85 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.9, 144.2, 140.5, 132.0, 131.5, 130.3, 130.8, 53.1, 48.6. MS *m*/*z* (EI-MS): 310 (6), 275 (100). HRMS: calcd for $C_9H_8ClIO_2$ 309.9258; found 309.9259.

Typical Procedure A (Table 1). Preparation of 1-Isopropyl-1,3-dihydro-2-benzofuran (7c).[8] A solution of *i*-PrMgBr (1.1 mmol) in THF (0.88 M, 1.25 mL) was added dropwise to a stirred solution of **1** (253 mg, 1.0 mmol) in THF (2 mL) at −10 °C under argon. The resulting solution was then stirred for 1.5 h, and isobutyraldehyde (108 mg, 1.5 mmol) was added. The reaction was slowly allowed to warm to room temperature, heated at reflux for 12 h, and quenched with brine. After usual work up and purification by column chromatography on silica (hexanes/ether 95:5) compound **7c** was obtained (140 mg, 86%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 7.18−7.07 (m, 4H), 5.05−4.99 (m, 3H), 1.99−1.96 (m, 1H), 0.98 (d, J = 7.7 Hz, 3H), 0.73 (d, J = 7.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.3, 140.3, 127.7, 127.4, 122.0, 121.2, 89.2, 73.6, 34.2, 19.4, 16.5. MS *m*/*z* (EI-MS): 161 (72), 135 (100).

Typical Procedure B. Preparation of Methyl 1-Oxo-2-phenylisoindoline-4-carboxylate (9b). A solution of *i*-PrMgBr (1.1 mol) in THF (0.88 M, 1.25 mL) was added dropwise to a stirred solution of **2** (310 mg, 1.0 mmol) in THF (4 mL) at −30 °C under argon. The resulting solution was then stirred for 1 h, and phenyl isocyanate (179 mg, 1.5 mmol) was added. The reaction was allowed to warm to room temperature, stirred for 2 h, and quenched with brine. After usual work up the crude residue was recrystallized (EtOAc) to give **9b** as colorless crystals (200 mg, 75%), mp 155 °C. IR (KBr): 1709 (s), 1697 (s), 1492 (m), 1380 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.15 (d, J = 7.6 Hz, 1H), 8.03 (d, J = 7.6 Hz, 1H), 7.84 (d, J = 7.9 Hz, 2H), 7.53 (t, J = 7.6 Hz, 1H), 7.35 (t, J = 7.9 Hz, 2H), 7.12 (t, J = 7.9 Hz, 1H), 5.08 (s, 2H), 3.91 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7, 166.2, 142.4, 139.6, 135.0, 133.8, 129.6, 129.1, 128.9, 125.5, 125.1, 120.0, 52.7. MS *m*/*z* (EI-MS): 266 (87), 252 (100). Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.40; H, 4.86; N, 5.25.

Typical Procedure C. Preparation of Ethyl 2-Benzyl-2,3,4,5-tetrahydro-1*H*-2-benzazepine-4-carboxylate (11a). To a solution of **10** (173 mg, 0.72 mmol) in THF (3 mL) was added benzylamine (93 mg, 0.87 mmol) and K_2CO_3 (152 mg, 1.1 mmol). The reaction was refluxed for 24 h and quenched with brine. After usual work up and purification by column chromatography on silica (hexanes/AcOEt 92:8) compound **11a** was obtained (167 mg, 75%) as a colorless oil. IR (neat): 1728 (s), 1454 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.24−7.02 (m, 8H), 6.80 (d, J = 7.2 Hz, 1H), 4.04 (q, J = 7.2 Hz, 2H), 3.98 (d, J_{AB} = 14.7 Hz, 1H), 3.65 (d, J_{AB} = 14.7 Hz, 1H), 3.47−2.76 (m, 7H), 1.15 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.7, 140.3, 139.4, 139.2, 130.4, 129.9, 129.3, 128.7, 127.8, 127.5, 126.8, 61.3, 60.9, 58.4, 57.1, 40.9, 38.5, 14.6. MS *m*/*z* (EI-MS): 308 (13), 218 (100). HRMS: calcd for $C_{20}H_{22}NO_2$ ($M - H^+$) 308.1650; found 308.1618.

Products of Table 1. 1-Phenyl-1,3-dihydro-2-benzofuran (7a).[9] The reaction was carried out according to typical procedure A affording **7a** (161 mg, 82%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 7.25−7.17 (m, 8H), 6.94 (d, J = 8.0 Hz, 1H), 6.07 (s, 1H), 5.24 (d, J_{AB} = 13.7 Hz, 1H), 5.13 (d, J_{AB} = 13.7 Hz,

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1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.6, 142.5, 139.6, 129.0, 128.5, 128.0, 127.9, 127.4, 122.7, 121.3, 86.7, 73.7.

1-[(3*E*)-Non-3-enyl]-1,3-dihydro-2-benzofuran (7b). The reaction was carried out according to typical procedure A affording **7b** (171 mg, 70%) as a colorless oil. IR (neat): 2955 (vs), 2853 (s), 1460 (w) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.18−7.07 (m, 4H), 5.36 (m, 2H), 5.16 (m, 1H), 5.02−4.98 (m, 2H), 2.08 (m, 2H), 1.89 (m, 3H), 1.74 (m, 1H), 1.21 (m, 6H), 0.80 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.6, 139.9, 131.4, 129.8, 127.7, 127.6, 121.5, 121.3, 83.8, 72.9, 36.7, 33.0, 31.9, 29.8, 28.6, 22.9, 14.5. MS *m*/*z* (EI-MS): 244 (15), 145 (55), 119 (100). HRMS: calcd for $C_{17}H_{24}O$ 244.1827; found 244.1837.

1-Isopropyl-1,3-dihydro-2-benzofuran (7c). See typical procedure A.

1-[(*E*)-2-Phenylethenyl]-1,3-dihydro-2-benzofuran (7d). The reaction was carried out according to typical procedure A affording **7d** (202 mg, 91%) as a yellow oil. IR (neat): 3029 (m), 2855 (m), 1766 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31−7.08 (m, 9H), 6.63 (d, J = 15.7 Hz, 1H), 6.18 (dd, J = 15.7 Hz, J = 7.6 Hz, 1H), 5.65 (d, J = 7.6 Hz, 1H), 5.12 (d, J_{AB} = 12.2 Hz, 1H), 5.01 (d, J_{AB} = 12.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.3, 139.9, 135.4, 130.9, 128.0, 127.5, 126.8, 126.7, 126.4, 120.9, 120.0, 84.2, 71.7. MS *m*/*z* (EI-MS): 222 (100), 118 (56). Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.09; H, 6.42.

3-(1,3-Dihydro-2-benzofuran-1-yl)pyridine (7e). The reaction was carried out according to typical procedure A affording **7e** (154 mg, 78%) as a colorless oil. IR (neat): 1770 (s), 1286 (s), 1026 (vs) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.54 (s, 1H), 8.45 (dd, J = 4.9 Hz, J = 1.7 Hz, 1H), 7.51 (d, J = 7.2 Hz, 1H), 7.21−7.11 (m, 4H), 6.92 (d, J = 7.2 Hz, 1H), 6.09 (s, 1H), 5.24 (d, J_{AB} = 12.3 Hz, 1H), 5.12 (d, J_{AB} = 12.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.8, 148.9, 141.4, 139.4, 138.1, 135.0, 128.4, 128.1, 124.0, 122.5, 121.5, 84.2, 73.8. MS *m*/*z* (EI-MS): 197 (10), 196 (49), 168 (98), 119 (82), 106 (100). HRMS: calcd for $C_{13}H_{11}NO$ 197.0840; found 197.0834.

1-Ferrocenyl-1,3-dihydro-2-benzofuran (7f). The reaction was carried out according to typical procedure A affording **7f** (246 mg, 81%) as an orange solid, mp 107 °C. IR (KBr): 2852 (m), 1458 (w) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25−7.13 (m, 4H), 5.99 (s, 1H), 5.12 (d, J_{AB} = 12.1 Hz, 1H), 5.01 (d, J_{AB} = 12.1 Hz, 1H), 4.20−3.99 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.8, 139.9, 128.0, 127.5, 122.5, 121.4, 89.9, 82.8, 72.9, 69.1, 68.9, 68.0, 67.0, 66.9. MS *m*/*z* (EI-MS): 304 (100), 208 (15). Anal. Calcd for $C_{18}H_{16}FeO$: C, 71.08; H, 5.30. Found: C, 71.25; H, 5.41.

Methyl 1-[(1*E*)-Pent-1-enyl]-1,3-dihydro-2-benzofuran-4-carboxylate (8a). The reaction was carried out according to typical procedure A. The crude residue was dissolved in THF (2 mL). NaH (24 mg, 1.0 mmol, 1.0 equiv) was added, and the reaction mixture was heated at reflux for 1 h. After usual work up and purification by column chromatography on silica (hexanes/AcOEt 9:1), compound **8a** was obtained (167 mg, 60%) as a colorless oil. IR (neat): 2959 (w), 2931 (w), 1767 (w), 1723 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86 (d, J = 7.5 Hz, 1H), 7.29−7.19 (m, 2H), 5.85−5.70 (m, 1H), 5.60−5.52 (m, 2H), 5.46 (d, J_{AB} = 14.6 Hz, 1H), 5.31 (d, J_{AB} = 14.6 Hz, 1H), 3.83 (s, 3H), 2.02−1.99 (m, 2H), 1.41−1.34 (m, 2H), 0.85 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.4, 142.0, 140.8, 133.8, 128.6, 128.1, 126.7, 125.4, 123.4, 83.9, 72.8, 51.0, 33.2, 21.2, 12.6. MS *m*/*z* (EI-MS): 246 (4), 203 (100), 171 (20). HRMS: calcd for $C_{15}H_{18}O_3$ 246.1256; found 246.1246.

Methyl 1-Phenyl-1,3-dihydro-2-benzofuran-4-carboxylate (8b). The reaction was carried out according to typical procedure A. The crude residue was dissolved in THF (2 mL). NaH (24 mg, 1.0 mmol, 1.0 equiv) was added, and the reaction mixture was heated at reflux for 1 h. After usual work up and purification by column chromography on silica (hexanes/AcOEt 95:5), **8b** was obtained (140 mg, 55%) as a colorless oil. IR (neat): 1721 (vs), 1278 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 (d, J = 7.6 Hz, 1H), 7.32−7.06 (m, 7H), 6.05 (s, 1H), 5.54 (d, J_{AB} = 14.6 Hz, 1H), 5.35 (d, J_{AB} = 14.6 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.4, 142.5, 141.0, 140.5, 128.2, 127.6, 127.2, 126.9, 125.8, 125.7, 123.4, 84.6, 73.6, 51.0. MS *m*/*z* (EI-MS): 254 (64), 222 (75), 165 (100). HRMS: calcd for $C_{16}H_{14}O_3$ 254.0933; found 254.0928.

2-Phenylisoindolin-1-one (9a). The reaction was carried out according to typical procedure B affording **9a** (239 mg, 96%) as a colorless solid, mp 160 °C-161 °C. IR (KBr): 1688 (s), 1502 (w), 1391 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79−7.72 (m, 3H), 7.44−7.23 (m, 5H), 7.06−7.01 (m, 1H), 4.65 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.9, 140.6, 139.9, 134.2, 133.6, 129.7, 128.9, 124.8, 124.4, 123.0, 119.8, 51.1. MS *m*/*z* (EI-MS): 209 (100), 180 (40). HRMS: calcd for $C_{14}H_{11}NO$ 209.0841; found 209.0838.

Methyl 1-Oxo-2-phenylisoindoline-4-carboxylate (9b). See typical procedure B.

Ethyl 2-[2-(Chloromethyl)benzyl]acrylate (10). A solution of *i*-PrMgBr (3.25 mmol) in THF (0.88 M, 3.70 mL) was added dropwise to a stirred solution of **1** (780 mg, 3.1 mmol) in THF (4 mL) at −10 °C under argon. After 1.5 h, CuCN·2 LiCl (3.25 mL, 3.25 mmol, 1 M in THF) and ethyl (2-bromomethyl)acrylate (888 mg, 4.6 mmol) were added. The reaction was stirred 1 h at −10 °C and quenched with brine. After usual work up and purification by column chromatography (hexanes/AcOEt 98:2) compound **10** (610 mg, 83%) was obtained as a colorless oil. IR (neat): 2982 (s), 1715 (s), 1137 (w) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30−7.08 (m, 4H), 6.18 (s, 1H), 5.22 (s, 1H), 4.53 (s, 2H), 4.13 (q, J = 6.9 Hz, 2H), 3.69 (s, 2H), 1.20 (t, J = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.1, 140.1, 137.8, 136.2, 130.9, 130.7, 129.4, 127.6, 126.6, 61.3, 44.6, 34.8, 14.5. MS *m*/*z* (EI-MS): 238 (0.1), 129 (100). HRMS: calcd for $C_{13}H_{15}ClO_2$ 238.0753; found 238.0761.

Ethyl 2-Benzyl-2,3,4,5-tetrahydro-1*H*-2-benzazepine-4-carboxylate (11a). See typical procedure C.

Ethyl 2-Butyl-2,3,4,5-tetrahydro-1*H*-2-benzazepine-4-carboxylate (11b). The reaction was carried out according to typical procedure C affording **11b** (149 mg, 54%) as a colorless oil. IR (neat): 2956 (m), 2931 (m), 1729 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.08−7.01 (m, 4H), 4.06 (q, J = 7.3 Hz, 2H), 3.99 (d, J_{AB} = 14.7 Hz, 1H), 3.73 (d, J_{AB} = 14.7 Hz, 1H), 3.44−2.61 (m, 5H), 2.31−213 (m, 2H), 1.44−1.31 (m, 2H), 1.25−1.14 (m, 5H), 0.80 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 173.3, 138.7, 137.9, 128.6, 128.5, 126.3, 125.3, 59.8, 59.5, 57.4, 50.6, 39.0, 37.1, 28.5, 19.4, 13.2, 13.0. MS *m*/*z* (EI-MS): 275 (7), 232 (100). HRMS: calcd for $C_{17}H_{25}NO_2$ 275.1885; found 275.1879.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (Leibniz program) and the BASF AG for the generous financial support.

Supporting Information Available: Spectra of new compounds of Table 1 and Schemes 1−3. This material is available free of charge via Internet at http://pubs.acs.org.

JO000971X