A New Protocol for Baylis−Hillman Reactions: Chirality Transfer in a Lithium Phenylselenide Induced Tandem-Michael-Aldol−Retro-Michael Reaction

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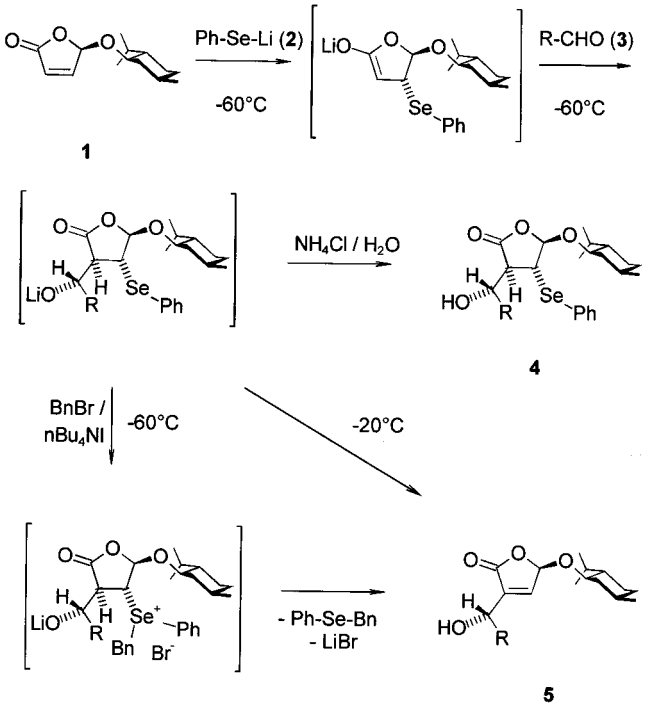
Tandem reactions[1] are versatile methods for constructing complex structures in one step. One of the huge number of tandem reactions known is the Baylis−Hillman reaction[2] which has drawn considerable attention over the past few years. Diastereoselective and enantioselective Baylis−Hillman reactions are of special interest, and numerous examples can be found in the recent literature dealing with these topics.[2] For this purpose, chiral activated olefins, chiral aldehydes, chiral catalysts, or chiral solvents have been used, but only with moderate success at atmospheric pressure. Herein we report a new and simple protocol for a highly diastereoselective and enantiospecific variant of the Baylis−Hillman reaction.

During the course of our efforts toward the total synthesis of polycyclic natural products, Feringa's excellent work on 4-menthyloxy-butenolide (**1**) came to our attention.[3] **1** is easily available in both enantiomeric forms in two steps from furfural and (+)- or (−)-menthol[4] and is an excellent Michael acceptor[3,5] which renders **1** an ideal candidate for enantiospecific and diastereoselective Baylis−Hillman reactions. Additionally, the butenolide moiety can be modified through hydrolysis or reductive ring opening and further subsequent transformations and is thus a suitable building block for the synthesis of complex molecules.[6]

Scheme 1. Lithium Phenylselenide Induced Baylis−Hillman Reaction



Our investigations started with the standard conditions for the Baylis−Hillman reaction, i.e., reaction of **1** with benzaldehyde in THF in the presence of catalytic amounts of DABCO at room temperature. Under these conditions no reaction occurred. Therefore, we changed to lithium phenylselenide[7] (**2**), a more powerful nucleophile than DABCO. When a solution of **2** was treated with a mixture of **1** and an aldehyde **3** at −60 °C, the Michael-aldol adduct **4** could be isolated[8] in high yield and excellent diastereoselectivity after quenching with saturated NH_4Cl solution (Scheme 1, Table 1). Treatment of **4** prior to quenching with either BnBr/^{n}Bu$_4$NI at −60 °C or simply warming the reaction mixture to −20 °C[9] led to the Baylis−Hillman product **5**, again in excellent

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(1) (a) Tietze, L. F.; Beifuss, U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 131−163. (b) Ho, T.-L. *Tandem Organic Reactions*; Wiley-Interscience: New York, 1992.

(2) For recent reviews, see (a) Ciganek, E. *Org. React.* **1997**, *51*, 201−350. (b) Basavaiah, D.; Rao, P. D.; Hyma, R. S. *Tetrahedron* **1996**, *52*, 8001−8062. (c) Drewes, S. E.; Roos, G. H. P. *Tetrahedron* **1988**, *44*, 4653−4670. For related methods, see: (d) Kataoka, T.; Iwama, T.; Tsujiyama, S. *J. Chem. Soc. Chem. Commun.* **1998**, 197−198. (e) Kataoka, T.; Iwama, T.; Tsujiyama, S.; Iwamura, T.; Watanabe, S. *Tetrahedron* **1998**, *54*, 11813−11824. (f) Kataoka, T.; Iwama, T.; Kinoshita, H.; Tsujiyama, S.; Tsurukami, Y.; Iwamura, T.; Watanabe, S. *Synlett* **1999**, 197−198. (g) Kamimura, A.; Mitsudera, H.; Asano, S.; Kakehi, A.; Noguchi, M. *J. Chem. Soc., Chem. Commun.* **1998**, 1095−1096. (h) Li, G.; Wei, H. X.; Willis, S. *Tetrahedron Lett.* **1998**, *39*, 4607−4610. (i) See also Barrett, A. G. M.; Kamimura, A. *J. Chem. Soc., Chem. Commun.* **1995**, 1755−1756. (j) An enantiospecific Baylis−Hillman reaction has been reported by Brzezinski, L. J.; Rafael, S.; Leahy, J. W. *Tetrahedron* **1997**, *53*, 16423−16434. (k) For a recent review on asymmetric Baylis−Hillman reactions, see Langer, P. *Angew. Chem.* **2000**, *39*, 3049−3052.

(3) For a comprehensive review on Feringa's work, see: Feringa, B. L.; de Jong, J. C. *Bull. Soc. Chim. Belg.* **1992**, *101*, 627−640, and references therein.

(4) (a) de Jong, J. C.; van Bolhuis, F.; Feringa, B. L. *Tetrahedron: Asymmetry* **1991**, *2*, 1247−1262. (b) Feringa, B. L.; de Lange, B. *Tetrahedron* **1988**, *44*, 7213−7222. (c) Lee, N.; Kim, Y.-W.; Chang, K.; Kim, K. H.; Jew, S.-S.; Kim, D.-K. *Tetrahedron Lett.* **1996**, *37*, 2429−2432.

(5) For Michael additions of unsubstituted 2-buten-4-olide, see: Watanabe, M.; Shirai, K.;Kumamoto, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3318−3320.

(6) For recent examples using Feringa's butenolide in syntheses of complex molecules, see (a) van Oeveren, A.; Jansen, J. F. G. A.; Feringa, B. L. *J. Org. Chem.* **1994**, *59*, 5999−6007. (b) Pelter, A.; Ward, R. S.; Jones, D. M.; Maddocks, P. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2621−2629. (c) van Speybroeck, R.; Guo, H.; van der Eycken, J.; Vandewalle, M. *Tetrahedron* **1991**, *47*, 4675−4682. (d) Bush, E. J.; Jones, D. W. *J Chem. Soc., Perkin Trans. 1* **1996**, 151−155.

(7) Lithium phenylselenide was prepared according to Ley's method for sodium phenylselenide: (a) Ley, S. V.; O'Neil, I. A.; Low, C. M. R. *Tetrahedron* **1986**, *42*, 5363−5368. (b) For the solution structure of lithium phenylselenide see: Reich, H. J.; Dykstra, R. R. *Organometallics* **1994**, *13*, 4578−4585. (c) In some experiments we also successfully used sodium phenylselenide, but we did not obtain the desired product using potassium phenylselenide, probably due to very poor solubility of the latter in THF at low temperatures.

(8) The plausible mechanism of the DABCO induced Baylis−Hillman reaction is based on kinetic studies, and intermediates never have been isolated. Thus, the isolation of **4** gives additional experimental evidence for the postulated mechanism of Baylis−Hillman reactions.

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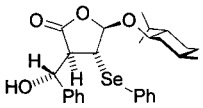
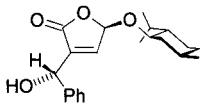
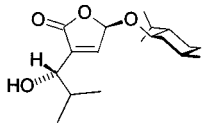
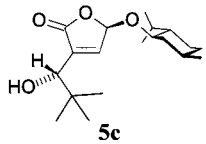
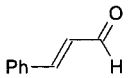
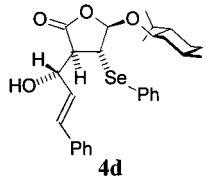
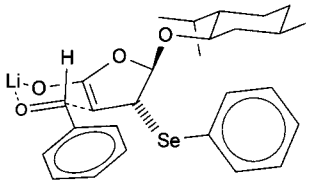
Table 1

aldehyde	conditions[a]	4/5	yield[b] of 4/5 (%)	de of 4/5 (%)
Ph-CHO	A		65.0	>99
3a		**4a**		
3a	B		82.5	>99
		5a		
3a	C	**5a**	84.5	>99
	B		89.0	>99
3b		**5b**		
	B		67.3	>99
3c		**5c**		
	A		79.8	>99
3d		**4d**		

[a] Conditions A: reaction temperature −60 °C for 4 h and subsequent quenching with saturated NH_4Cl at −60 °C. Conditions B: reaction temperature −60 °C for 4 h with subsequent addition of $^nBu_4NI$/BnBr in THF at −60 °C and stirring overnight at this temperature. Conditions C: Sodium phenylselenide instead of lithium phenylselenide; reaction temperature −60 °C for 4 h with subsequent quenching with saturated NH_4Cl. [b] Isolated yield of pure compounds.

yield and diastereoselectivity (Scheme 1, Table 1). The absolute configuration[10] of the new stereocenter in **5a** was determined through X-ray analysis of suitable crystals obtained by crystallization of **5a** from pentane.[11] Thus, the new chiral center in **5a** has *R* configuration (ORTEP in Supporting Information). This can be rationalized through the Zimmermann−Traxler model[12] of the transition state in the aldol addition step (Scheme 2). In summary, we have successfully developed a new protocol for the diastereoselective and enantioselective Baylis−Hillman reaction under very mild conditions with excellent yields and selectivity, which finds application in the synthesis of complex natural products.[13,14]

Scheme 2. Zimmermann-Traxler Transition State for the Aldol Addition Step



Experimental Section

General. All reactions were carried out under nitrogen in oven-dried flasks using syringe techniques. THF was distilled from potassium/benzophenone. Diphenyl diselenide was purchased from Acros Organics, Geel, Belgium. Aldehydes were freshly distilled under nitrogen before use. Benzyl bromide and tetra-*n*-butylammonium iodide were purchased from Aldrich, Steinheim, Germany and were used as received.

Lithium phenylselenide (2): 10 mg of lithium powder (1.44 mmol) and some crystals of benzophenone are suspended in 3.5 mL of freshly distilled THF under argon. The suspension is sonicated and after appearance of the blue color of benzophenone ketyl, a solution of 190 mg of diphenyl diselenide (0.61 mmol) in 3 mL of THF is added dropwise via syringe. Sonication is continued until all diphenyl diselenide has been added (30 min). The yellow solution is used in the following procedures.

Analogously, a solution of sodium phenylselenide in THF is prepared from 28.1 mg of sodium (1.22 mmol) and 190 mg of diphenyl diselenide (0.61 mmol).

Alternatively, a solution of lithium phenylselenide is prepared from a solution of 190 mg of diphenyl diselenide, dissolved in 3 mL of THF under argon, by adding 0.4 mL of a 1.5 M solution of ^{n}BuLi in hexanes (0.6 mmol) at −20 °C. The mixture is stirred for 10 min and used immediately.

2(*R*)-(1′(*R*)-Hydroxybenzyl)-3(*R*)-phenylselenyl-4(*R*)-(1″(*R*), 2″(*S*), 5″(*R*)-menthyl)-oxy-butanolide (4a). Procedure A (see Table 1). A solution of lithium phenylselenide, prepared as described above is cooled to −60 °C and a mixture of 238.3 mg of (4*R*,1′*R*,2′*S*,5′*R*)-(+)-4-menthyloxy-2-butenolide (**1**) (1.00 mmol) and 159.1 mg of benzaldehyde (**3a**) (1.50 mmol) in 3.5 mL of THF is added dropwise during 30 min. Stirring is continued for 8 h. Quenching with saturated ammonium chloride solution (30 mL), extraction with ether (3 × 20 mL), and drying of the combined organic phases with $MgSO_4$ gives the crude product after evaporation of the solvent in a vacuum. Purification by flash chromatography with pentane/diethyl ether 3:1 (v/v) gives a clear oil, which solidifies upon standing. Yield: 325.0 mg (65.0%). $[\alpha]^{20}_D = +75.1$ ($c = 10.7$; $CHCl_3$). ^{1}H NMR (360 MHz, $CDCl_3$, δ in ppm): 7.37−7.29 and 7.24−7.19 (m, 10H), 5.58 (d, 2.6 Hz, 1H), 4.93 (dd, 8.6 Hz, 2.2 Hz, 1H), 3.75 (d. 2.2 Hz, 1H), 3.45 (td, 10.6 Hz, 4.2 Hz, 1H), 3.25 (dd, 5.3 Hz, 2.6 Hz, 1H), 2.85 (dd, 8.6 Hz, 5.3 Hz, 1H), 2.06 (septd, 7.1 Hz, 2.6 Hz, 1H), 1.77 (dm, 12.8 Hz, 1H), 1.66−1.60 (m, 2 H), 1.31−1.15 (m, 2 H), 0.88 (d, 7.3 Hz, 3H), 0.86 (d, 7.1 Hz, 3H), 0.76 (d, 7.1 Hz), 0.97−0.62 (m, 3H). ^{13}C NMR (90.5 MHz, $CDCl_3$) δ 175.9, 139.4, 135.2, 129.4, 128.6, 128.5, 126.9, 126.3, 105.4, 78.5, 74.4, 53.5, 47.5, 41.7, 39.5, 34.1, 31.2, 25.5, 22.8, 22.1, 20.9, 15.4. EI-MS *m/z*

(9) When sodium phenylselenide is used instead of lithium phenylselenide, the final elimination of phenylselenide anion takes place at −60 °C without warming the reaction mixture to −20 °C.

(10) Our first efforts focused on the determination of the absolute configuration via ^{1}H NMR spectroscopy of the corresponding Mosher esters of **5a**. For some examples using this method, see (a) Velten, R.; Steglich, W.; Anke, T. *Tetrahedron: Asymmetry* **1994**, *5*, 1229−1232. (b) Preite, M. D.; Zinczuk, J.; Colombo, M. I.; Bacigaluppo, J. A.; Gonzales-Sierra, M.; Ruveda, E. A. *Tetrahedron: Asymmetry* **1993**, *4*, 17−20. (c) Ohtani, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H. *J. Am. Chem. Soc.* **1991**, *113*, 4092−4096. The preparation of the Mosher esters of **5a** showed that it is extremely base sensitive. Subsequent NMR experiments revealed that this method is not applicable in this case, probably because the anisotropic effect of the two phenyl rings present in **5a** influence each other and therefore lead to chemical shifts of the other protons in an unpredictable way.

(11) Compound **5a** crystallizes in space group *P*212121 with a = 6.8555(1) Å, b = 11.8140(2) Å c = 24.379(2) Å, $\alpha = \beta = \gamma = 90°$, V = 1973.6(3) Å^3, D_{calcd} = 1.156 g/cm^3 for $Z = 4$. Least-squares refinement based on 3150 reflections ($I > 2.0\,\sigma(I)$) converged to a final $R_1 = 3.83\%$ and $wR_2 = 10.61\%$.

(12) Heathcock, C. H. in *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: Orlando, 1984; pp 111−212.

(13) Jauch, J. *Synlett* **1999**, 1325−1327.

(14) Jauch, J. *Angew. Chem.* **2000**, *112*, 2874−2875; *Angew. Chem., Int. Ed.* **2000**, *39*, 2764−2765.

(relative intensity): 502 (34%); 290 (46%); 239 (15%); 139 (100%); 133 (72%); 107 (46%); 105 (47%); 83 (92%); 69 (44%); 57 (33%); 55 (65%). HRMS: calculated for $C_{27}H_{34}O_4Se$: 502.16219; found: 502.16739. IR (cm^{-1}; $CHCl_3$): 3523; 3064; 2956; 1761; 1456; 1101; 908.

2-(1′(*R*)-Hydroxybenzyl)-4(*R*)-(1″(*R*), 2″(*S*), 5″(*R*)-menthyl)-oxy-2-butenolide (5a). Procedure B (see Table 1). A solution of lithium phenylselenide is cooled to −60 °C and a mixture of 238.3 mg of 4-menthyloxy-2-butenolide (**1**) (1.00 mmol) and 159.1 mg of benzaldehyde (**3a**) (1.50 mmol) in 3.5 mL of THF is added dropwise during 30 min. Stirring is continued for 4 h, and then the reaction mixture is warmed to −20 °C within 4 h. Quenching with saturated aqueous NH_4Cl (30 mL), extraction with diethyl ether (3 × 30 mL), drying of the combined extracts with $MgSO_4$, and evaporating the solvent in a vacuum leads to the crude product which is purified by flash chromatography with pentane/diethyl ether 5:1 (v/v). Yield: 284.0 mg (82.5%) of a clear oil which can be crystallized from pentane. mp 84.5−85.5 °C. $[\alpha]^{20}_D = -65.1$ ($c = 0.315$; $CHCl_3$).

With sodium phenylselenide, the same procedure results in 291.0 mg of **5a** (84.5%) without warming to −20 °C (procedure C, see Table 1).

^{1}H NMR (360 MHz, $CDCl_3$) δ 7.45−7.30 (m, 5H), 6.70 (s, 1H), 5.98 (s, 1H), 5.58 (s, 1H), 3.59 (td, J = 10.6 Hz, 4.0 Hz, 1H), 3.36 (br. s, 1H), 2.09−2.05 (m, 2H), 1.68−1.62 (m, 2H), 1.39−1.33 (m, 1H), 1.26−1.18 (m, 2H), 1.06−0.77 (m, 2H), 0.92 (d, J = 6.5 Hz, 3H), 0.86 (d, J = 6.5 Hz, 3H), 0,77 (d, J = 7.1 Hz, 3H). ^{13}C NMR (90.5 MHz, $CDCl_3$) δ 170.4, 144.1, 139.7, 139.6, 128.7, 128.5, 126.6, 99.3, 79.3, 69.1, 47.7, 40.4, 34.1, 31.4, 25.3, 23.1, 22.1, 20.8, 15.8. EI-MS *m*/*z* (relative intensity): 344 (6%); 206 (96%); 188 (72%); 178 (100%); 115 (37%); 112 (34%); 95 (42%); 83 (61%); 81 (65%); 69 (55%); 55 (64%);. HRMS: calculated for $C_{21}H_{28}O_4$: 344.19874; found: 344.20575. IR (cm^{-1}; $CHCl_3$): 3530; 3022; 2957; 1761; 1336; 1184; 1015.

2-(1′(*S*)-Hydroxy-2′-methylpropyl)-4(*R*)-(1″(*R*), 2″(*S*),5″(*R*)-menthyl)-oxy-2-butenolide (5b). Procedure B. 238.3 mg of **1** (1.00 mmol) and 108.0 mg of isobutyraldehyde (**3b**) (1.50 mmol). Reaction temperature −55 °C. Solvent for flash chromatography: pentane/diethyl ether 2:1 (v/v). Yield: 276.2 mg of **5b** (89.0%) as a colorless oil. $[\alpha]^{20}_D = +141.0$ ($c = 5.66$; $CHCl_3$). ^{1}H NMR (360 MHz, $CDCl_3$) δ 6.91 (s, 1H), 5.99 (s, 1H), 4.29 (d, J = 5.3 Hz, 1H), 3.61 (td, J = 10.6 Hz, 4.0 Hz, 1H), 3.01 (br. s, 1H), 2.15−2.02 (m, 3H), 1.67−1.61 (m, 2H), 1.41−1.33 (m, 1H), 1.29−1.17 (m, 2H), 1.08−0.82 (m, 2H), 0.94 (d, J = 7.1 Hz, 3H), 0.91 (d, J = 5.8 Hz, 3H), 0.90 (d, J = 7.1 Hz, 3H), 0.83 (d, J = 7.1 Hz, 3H), 0.76 (d, J = 7.1 Hz, 3H). ^{13}C NMR (90.5 MHz, $CDCl_3$) δ 170.6, 144.1, 138.9, 99.1, 79.0, 71.8, 47.6, 40.3, 34.2, 32.3, 31.4, 25.4, 23.3, 22.1, 20.7, 18.9, 16.4, 15.9. EI-MS *m*/*z* (relative intensity): 292 (1%); 139 (86%); 138 (100%); 130 (31%); 113 (46%); 95 (50%); 83 (94%); 81 (83%); 55 (74%). HRMS calculated for $C_{18}H_{28}O_3$ ($[M - H_2O]^+$): 292.20383; found: 292.20691. IR (cm^{-1}; $CHCl_3$): 3513; 3032; 2958; 1763; 1466; 1397; 1340; 1127; 1021.

2-(1′(*S*)-Hydroxy-2′,2′-dimethylpropyl)-4(*R*)-(1″(*R*),2″(*S*),5″-(*R*)-menthyl)-oxy-2-butenolide (5c). Procedure B. 238.3 mg of **1** (1.00 mmol) and 129.2 mg of pivalinaldehyde (1.50 mmol). Reaction temperature −50 °C. Solvent for flash chromatography: pentane/diethyl ether 2:1 (v/v). Yield 218.3 mg (67.3%) as a clear oil. $[\alpha]^{20}_D = +101.2$ ($c = 1.95$; $CHCl_3$). ^{1}H NMR (360 MHz, $CDCl_3$) δ 6.94 (s, 1H), 6.02 (s, 1H), 4.25 (br. s, 1H), 3.65 (td, J = 11.0 Hz, 4.5 Hz, 1H), 2.79 (br. s, 1H), 2.16−2.02 (m, 2H), 1.69−1.63 (m, 2H), 1.46−1.34 (m, 1H), 1.32−1.18 (m, 2H), 1.12−0.85 (m, 2H), 0.95 (d, J = 6.5 Hz, 3H), 0.95 (s, 9H), 0.86 (d, J = 7.2 Hz, 3H), 0.79 (d, J = 7.2 Hz, 3H). ^{13}C NMR (90.5 MHz, $CDCl_3$) δ 171.1, 145.4, 137.8, 98.8, 79.0, 74.5, 47.7, 40.3, 35.8, 34.2, 31.4, 25.6, 15.4, 23.4, 22.2, 20.7, 16.0. EI-MS *m*/*z* (relative intensity): 268 (1%); 152 (21%); 139 (43%); 130 (100%); 112 (42%); 95 (29%); 83 (75%); 81 (40%); 57 (66%);. HRMS: calculated for $C_{15}H_{24}O_4$ ($[M - C_4H_8]^+$): 268.16744; found: 268.16969. IR (cm^{-1}; $CHCl_3$): 3513; 3021; 2958; 1759; 1455; 1368; 1341; 1019.

2(*S*)-(1′(*S*)-Hydroxy-1′-(*E*)-styrylmethyl)-3(*R*)-phenylselenyl-4(*R*)-(1″(*R*),2″(*S*),5″(*R*)-menthyl)-oxy-butanolide (4d). Procedure A. 238.3 mg of **1** (1.00 mmol) and 198.3 mg of cinnamic aldehyde (1.5 mmol). Reaction temperature −50 °C to −30 °C. Solvent for flash chromatography: pentane/diethyl ether 3:1 (v/v). Yield: 421.0 mg of **4d** (79.8%) as colorless oil. $[\alpha]^{20}_D = +96.8$ ($c = 2.2$; $CHCl_3$). ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.60−7.50 (m, 2H), 7.39−7.20 (m, 8H), 6.65 (d, J = 16.2 Hz, 1H), 6.26 (dd, J = 7.1 Hz, 16.2 Hz, 1H), 5.62 (d, J = 3.9 Hz, 1H), 4.59 (t, J = 7.1 Hz, 1H), 3.51 (dd, J = 3.9 Hz, 7.1 Hz, 1H), 3.47 (td, J = 3.9 Hz, 10.4 Hz, 1H), 3.34 (br. s, 1H), 2.76 (t, J = 7.1 Hz, 1H), 215−2.06 (m, 1H), 1.85 (m, 1H), 1.65−1.59 (m, 2H), 1.39−1.25 (m, 1H), 1.25−1.18 (m, 1H), 1.02−0.68 (m, 3H), 0.89 (d, J = 6.5 Hz, 3H), 0.85 (d, J = 7.1 Hz, 3H), 0.76 (d, J = 6.5 Hz, 3H). ^{13}C NMR (90.5 MHz, $CDCl_3$) δ 174.8, 136.0, 135.6, 133.2, 129.4, 128.8, 128.5, 128.0, 127.5, 126.8, 126.3, 105.5, 78.9, 72.7, 52.3, 47.5, 41.9, 39.7, 34.1, 31.2, 25.3, 22.8, 22.1, 20.8, 15.5. EI-MS *m*/*z* (relative intensity): 528 (3%); 215 (28%); 158 (24%); 139 (51%); 133 (100%); 131 (73%); 83 (94%); 55 (78%); HRMS calculated for $C_{29}H_{36}O_4Se$: 528.17784; found: 528.18305. IR (cm^{-1}; $CHCl_3$): 3510; 2957; 1759; 1339; 1103; 968; 939.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for all new compounds; ORTEP of **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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