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Supporting Information

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SUPPORTING INFORMATION FOR:

Divergent Titanium-Mediated Allylations via Modulation by Nickel or Palladium

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General: For the reactions employing titanocene all solvents and additives were rigorously deoxygenated prior to use. The following known compounds were isolated as pure samples and showed NMR spectra identical to reported data: **3**[1], **4**[1], **5**[2], **6**[3], **10**[4], **11**[4], **12**[5], **13**[6], **14**[7], **15**[8], ***Z*-22**[9], **24**[10], **25**[10], **26**[11], and **32**.[12]

General procedure for Pd^0-Ti^{III} allylation of carbonyl compounds with allyl carbonates.

Protocol A. Rigorously deoxygenated THF (20 mL) was added to a mixture of Cp_2TiCl_2 (2.0 mmol), $PdCl_2$ (0.2 mmol), PPh_3 (0.4 mmol) and Mn dust (8.0 mmol) under Ar atmosphere, and the suspension was stirred at room temperature until it turned dark green (about 15 min). A solution of carbonyl compound (1.0 mmol) and allyl carbonate (4.0 mmol) in THF (2 mL) was then added. The mixture was stirred for 6 h and then diluted with AcOEt, washed with brine, dried over anhydrous $MgSO_4$ and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane mixtures) to give the corresponding products.

Protocol B. Rigorously deoxygenated THF (20 mL) was added to a mixture of Cp_2TiCl_2 (0.4 mmol), $PdCl_2$ (0.2 mmol), PPh_3 (0.4 mmol) and Mn dust (8.0 mmol) under Ar atmosphere, and the suspension was stirred at room temperature until it turned dark green (about 15 min). A solution of carbonyl compound (1.0 mmol), allyl carbonate (4.0 mmol), 2,4,6-collidine (7.0 mmol) and Me_3SiCl (4.0 mmol) in THF (2 mL) was then added. The mixture was stirred for 16 h and then diluted with AcOEt, washed with 10% aqueous HCl solution and washed with brine, dried over anhydrous $MgSO_4$ and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane mixtures) to give the corresponding products.

General procedure for Ni^0-Ti^{III}-promoted allylation of alkenes with allyl carbonates. Rigorously deoxygenated THF (20 mL) was added to a mixture of Cp_2TiCl_2 (2.0 mmol), $NiCl_2(PPh_3)_2$ (0.2 mmol) and Mn dust (8.0 mmol) under Ar atmosphere, and the suspension was stirred at room temperature until it turned dark brownish (about 15 min). A solution of allyl carbonate (1.0 mmol) in THF (2 mL) was then added. The mixture was stirred for 16 h and then diluted with EtOAc, washed with brine, dried over anhydrous $MgSO_4$ and the solvent was removed. The residue was submitted to flash chromatography (EtOAc/Hexane mixtures) to give the corresponding products.

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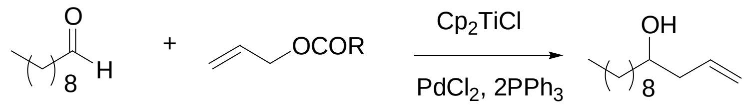
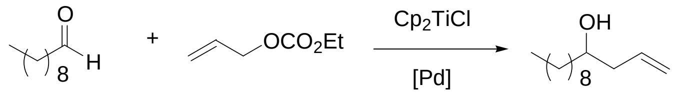
Influence of the allylic derivative in the Pd^0-Ti^{III}-promoted allylation of carbonyl compounds



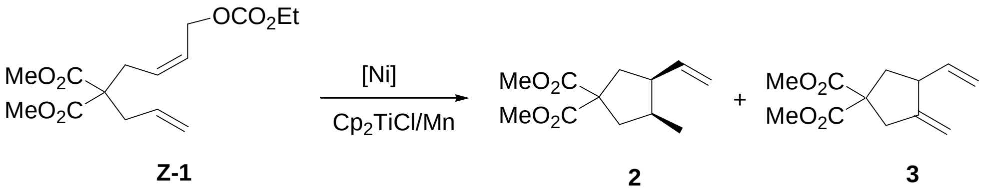
R	Yield
CH_3	30 %
Ph	40 %
OEt	77 %
OCH_2CCl_3	10 %

Influence of the palladium complex in the Pd^0-Ti^{III}-promoted allylation of carbonyl compounds



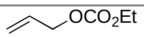
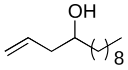
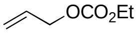
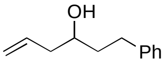
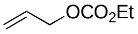
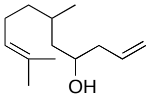
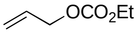
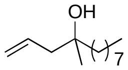
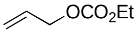
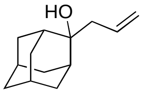
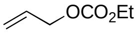
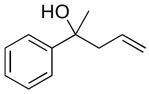
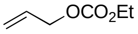
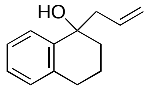
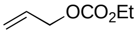
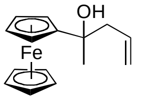
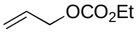
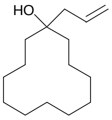
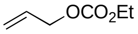
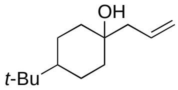
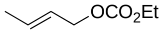
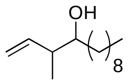
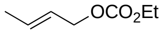
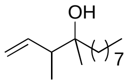
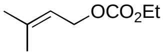
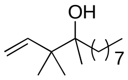
[Pd]	Yield
$PdCl_2$	22 %
Na_2PdCl_4	20 %
$PdCl_2/2PPh_3$	77 %
$Pd(PPh_3)_2Cl_2$	54 %
$Pd(PPh_3)_4$	56 %
$Pd_2(dba)_3.dba$	26 %
$Pd(OAc)_2$	-
$Pd(OAc)_2$ + 2 PPh_3	48 %
$Pd(MeCN)_2Cl_2$	-
$Pd(MeCN)_2Cl_2$ + 2 PPh_3	46 %

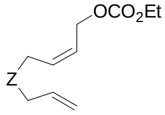
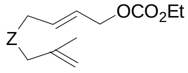
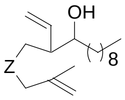
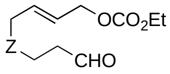
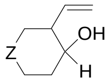
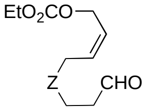
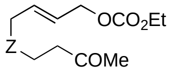
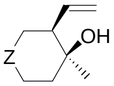
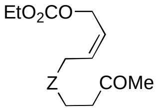
Influence of the nickel complex and the titanium:nickel molar relationship in the Ni^0-Ti^{III}-promoted allylation of alkenes.



Cp_2TiCl_2 (mol %)	Ni complex	(mol %)	3:4	Yield
400	$Ni(PPh_3)_2Cl_2$	10	(97:3)	75
400	$Ni(PPh_3)_2Cl_2$	20	(85:15)	72
200	$Ni(PPh_3)_2Cl_2$	20	(80:20)	98
100	$Ni(PPh_3)_2Cl_2$	20	(65:35)	86
40	$Ni(PPh_3)_2Cl_2$	20	(60:40)	56
10	$Ni(PPh_3)_2Cl_2$	20	(30:70)	60
200	$Ni(dppe)Cl_2$	20	-	-
200	$NiCl_2.7H_2O$	20	-	-
200	$NiCl_2.7H_2O/2PPh_3$	20	(80:20)	59
200	$Ni(acac)_2$	20	-	-
200	$NiCl_2/2PPh_3$	20	(80:20)	45
200	$NiBr_2/2PPh_3$	20	(80:20)	51

Complete experimental data for the Pd^0-Ti^{III}-promoted allylation of carbonyl compounds

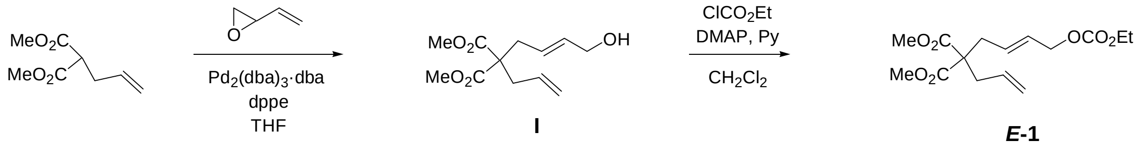
Entry	Allyl carbonate	Carbonyl compound	Product (Protocol, Yield, %)
1		decanal	 **5** A, 77; B, 75
2		3-phenyl propanal	 **6** A, 57; B, 54
3		citronelal	 **7** A ,64; B, 73[b]
4		2-decanone	 **8** A, 85; B, 59
5		adamantanone	 **9** A, 72; B, 79
6		acetophenone	 **10** A, 87; B, 74
7		tetralone	 **11** A, 77; B, 74
8		acetyl ferrocene	 **12** A, 99
9		cyclododecanone	 **13** A, 54; B, 78
10		*t*-Butyl-cyclohexanone	 **14** A 61; B, 65[c]
11		decanal	 **15** A 65; B, 58[d]
12		2-decanone	 **16** A, 65; B, 75[e]
13		2-decanone	 **17** A, 61; B, 55

14	 **Z-1** Z = $C(CO_2Me)_2$	decanal	**2** A, 59; B 52
15	 **18** Z = $C(CO_2Me)_2$	decanal	 **19** A, 63[f]
16	 **_E_-20** Z = $C(CO_2Me)_2$	-	 **21** A, 73[b]
17	 **_Z_-20** Z = $C(CO_2Me)_2$	-	**21** A, 74[b]
18	 **_E_-22** Z = $C(CO_2Me)_2$	-	 **23** A, 98; B 95
19	 **_E_-22** Z = $C(CO_2Me)_2$		**23** A, 70; B 92

Synthesis of starting materials (*E*-1, *Z*-1, 18, *E*-20, *Z*-20, *E*-22, 27, 29, 31, 33, 35, 37, 39)

General procedure for the synthesis of allyl carbonates from alcohols. Ethylchloroformiate (1.0 mmol) was slowly added to a mixture of DMAP (0.2 mmol), pyridine (2.0 mmol) and allyl alcohol (1 mmol) in CH_2Cl_2 (25-30 mL). The reaction was stirred for 4 h and then subsequently washed with 10% aqueous HCl, 10% aqueous NaOH and brine, dried over anhydrous $MgSO_4$ and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane mixtures) to give the corresponding allyl carbonate.

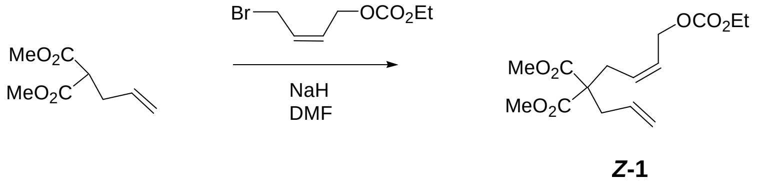
Synthesis of carbonate *E*-1.



Synthesis of alcohol I. 1,3-butadiene monoxide (81 mg, 1.1 mmol) was added to a solution of dimethyl allylmalonate (200 mg, 1.1 mmol), $Pd_2(dba)_3$·dba (10 mg, 0.05 mmol) and dppe (23 mg, 0.05 mmol) in THF (10 mL). The resulting mixture was stirred at room temperature for 3 h and then reduced in volume to 0.5 mL. The residue was submitted to flash chromatography (EtOAc/Hexane,2/3) to give **I** (275 mg, 98 %) as a colourless oil. Its spectroscopic data were identical to the reported compound.[11]

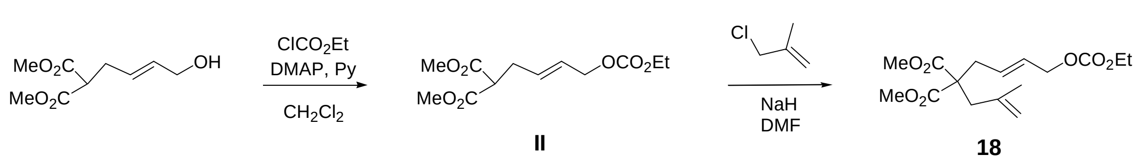
Carbonate *E*-1. It was prepared from **I** according to previously described general procedure. The compound was purified by flash chromatography (EtOAc/Hexane, 15/85) to give ***E*-1** in a 84 % yield as a colourless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 5.69-5.57 (m, 3H), 5.11-5.08 (m, 2H), 4.53 (d, *J* = 4.5 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.71 (s, 6H), 2.64-2.61 (m, 4H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$; DEPT) δ (ppm): 171.5 (C), 155.5 (C), 132.6 (CH), 130.5 (CH), 128.6 (CH), 120.0 (CH_2), 68.2 (CH_2), 64.5 (CH_2), 58.1 (C), 52.9 (CH_3), 37.7 (CH_2), 36.0 (CH_2), 14.8 (CH_3); ESHRMS calcd. for $C_{15}H_{22}O_7Na$ *m/z* 337.1257, found *m/z* 337.1258.

Synthesis of carbonate *Z*-1.



A sample of (*Z*)-$BrCH_2CH=CHCH_2OCO_2Et$[13] (777 mg, 3.4 mmol) was added to a mixture of NaH (84 mg, 3.4 mmol) and dimethyl allylmalonate (300 mg, 1.7 mmol) in DMF (25 mL). The resulting solution was stirred at room temperature for 4 h and then diluted with Et_2O, washed with 10% aqueous HCl and dried with anhydrous Na_2SO_4, and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane,15/85) to give **Z-1** (530 mg, 97 %) as a colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 5.75-5.09 (m, 3H), 5.14 (dd, *J* = 13.7, 1.8 Hz, 2H), 4.69 (d, *J* = 6.6 Hz, 2H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.75 (s, 6H), 2.73 (d, *J* = 7.7 Hz, 2H), 2.67 (d, *J* = 7.5 Hz, 2H), 1.33 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (755 MHz, $CDCl_3$; DEPT) δ (ppm): 171.2 (C), 155.3 (C), 132.2 (CH), 128.5 (CH), 127.1 (CH), 119.7 (CH_2), 64.2 (CH_2), 63.4 (CH_2), 57.6 (C), 52.8 (CH_3), 37.4 (CH_2), 30.8 (CH_2), 14.5 (CH_3); ESHRMS calcd. for $C_{15}H_{22}O_7Na$ *m/z* 337.1257, found *m/z* 337.1258.

Synthesis of allyl carbonate 18.



Synthesis of carbonate II. It was prepared from dimethyl (*E*)-2-(4-hydroxy-2-butenyl)malonate[14] according to previously described general procedure. The compound was isolated by flash chromatography (EtOAc/Hexane,15/85) to give **II** in a 85 % yield as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.76-5.61 (m, 2H), 4.54 (d, *J* = 5.6 Hz, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.73 (s, 6H), 3.44 (t, *J* = 7.6 Hz, 1H), 2.65 (t, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$;

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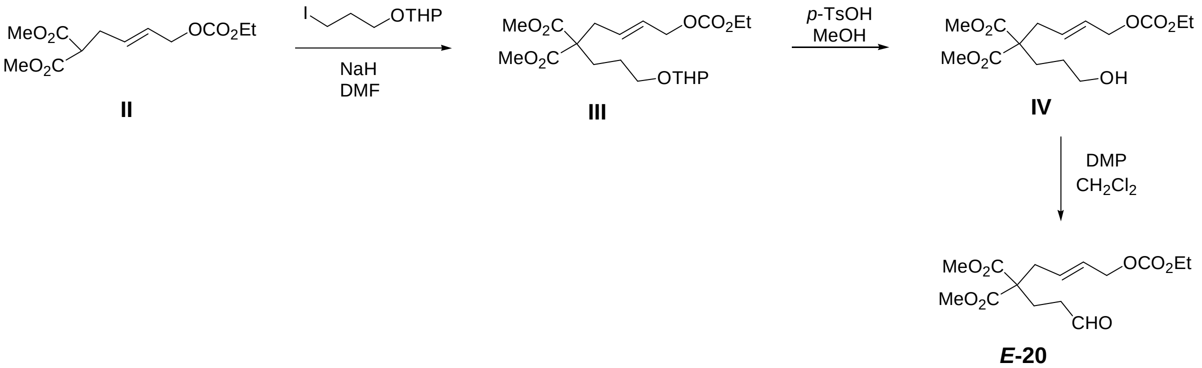
[13] W. Oppolzer, A. Fürstner. *Helv. Chim. Acta.* **1993**, *76*, 2369-2337.

[14] C. Fernández-Rivas, M. Méndez, C. Nieto-Oberhuber, A. M. Echavarren. *J. Org. Chem.* **2002**, *67*, 5197-5201.

DEPT) δ (ppm): 166.6 (C), 152.5 (C), 129.0 (CH), 124.4 (CH), 65.2 (CH_2), 61.6 (CH_2), 50.2 (CH_3), 48.8 (CH), 29.0 (CH_2), 11.8 (CH_3); ESHRMS calcd. for $C_{12}H_{18}O_7Na$ *m/z* 297.0944, found *m/z* 297.0949.

Carbonate 18. A sample of 3-chloro-2-methylpropene (600 mg, 6.6 mmol) was added to a mixture of NaH (159 mg, 6.6 mmol) and compound **II** (908 mg, 3.3 mmol) in DMF (30nmL). This solution was stirred at room temperature for 4 h and then diluted with Et_2O, washed with 10% aqueous HCl and dried with anhydrous Na_2SO_4, and the solvent was removed. The residue was submitted to flash chromatography (EtOAc/Hexane,3/7) to give **18** (902 mg, 83 %) as a colourless oil; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.67 (m, 2H), 4.87 (s, 1H), 4.73 (s, 1H), 4.53 (d, *J* = 4.4 Hz, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.71 (s, 6H), 2.71-2.66 (m, 4H), 1.64 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ (ppm): 169.0 (C), 152.6 (C), 137.9 (C), 128.1 (CH), 125.6 (C), 113.6 (CH_2), 65.3 (CH_2), 61.6 (CH_2), 54.8 (C), 50.0 (CH_3), 38.2 (CH_2), 33.2 (CH_2), 20.7 (CH_3), 11.9 (CH_3); ESHRMS calcd. for $C_{16}H_{24}O_7Na$ *m/z* 351.1414, found *m/z* 351.1389.

Synthesis of aldehyde *E*-20.



Synthesis of compound III. A sample of $I(CH_2)_3OTHP$[15] (271 mg, 1.0 mmol) was added to a mixture of NaH (33 mg, 1.4 mmol) and compound **II** (250 mg, 1.0 mmol) in DMF (25 mL). The resulting solution was stirred at room temperature for 4 h and then diluted with Et_2O, washed with 10% aqueous HCl and dried with anhydrous Na_2SO_4, and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane,1/4) to give **III** (315 mg, 83 %) as a colourless oil; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 5.66-5.64 (m, 2H), 4.54 (d, *J* = 2.8, 1H), 4.55-4.50 (m, 3H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.82 (t, *J* = 10.4 Hz, 1H), 3.72-3.68 (m, 1H), 3.70 (s, 6H), 3.48 (dt, *J* = 11.1, 4.6 Hz, 1H), 3.35-3.32 (m, 1H), 2.64 (d, *J* = 5.4 Hz, 2H), 1.90-1.89 (m, 2H), 1.82-1.72 (m, 1H), 1.71-1.66 (m, 1H), 1.56-1.44 (m, 6H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$; DEPT) δ (ppm): 173.9 (C), 157.4 (C), 132.6 (CH), 130.4 (CH), 101.3 (CH), 70.2 (CH_2), 69.6 (CH_2), 66.5 (CH_2), 64.8 (CH_2), 59.9 (C), 55.0 (CH_3), 38.2 (CH_2), 33.2 (CH_2), 31.9 (CH_2), 28.0 (CH_2), 27.1 (CH_2), 22.1 (CH_2), 16.8 (CH_3); ESHRMS calcd. for $C_{20}H_{32}O_9Na$ *m/z* 439.1938, found *m/z* 439.1931.

Synthesis of compound IV. *p*-Toluenesulfonic acid (16 mg, 0.09 mmol) was added to a solution of THP-derivative **III** (359 mg, 0.9 mmol) in MeOH (20 mL). The resulting mixture was stirred for 14 h and then diluted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4 and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane:1/1) to give **IV** (267 mg, 93 %) as a colourless oil; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.67-5.64 (m, 2H), 4.54 (d, *J* = 7.0 Hz), 4.17 (q, *J* = 7.2 Hz, 2H), 3.71 (s, 6H), 3.61 (t, *J* = 6.4 Hz, 2H), 2. 65 (d, *J* = 5.2 Hz, 2H), 1.97-1.83 (m, 2H), 1.49-1.42 (m, 2H), 1. 29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ (ppm): 171.7 (C), 155.2 (C), 130.2 (CH), 128.2 (CH), 69.3 (CH_2), 67.7 (CH_2), 62.8 (CH_2), 57.5 (C), 52.8 (CH_3), 39.3 (CH_2), 36.1 (CH_2), 29.3 (CH_2), 14.5 (CH_3); ESHRMS calcd. for $C_{15}H_{24}O_8Na$ *m/z* 355.1363, found *m/z* 355.1368.

Aldehyde *E*-20. Dess-Martin Periodinane (DMP) (607 mg, 1.4 mmol) was added to a solution of **IV** (238 mg, 0.7 mmol) in CH_2Cl_2 (30 mL). The resulting mixture was stirring for 2 h at room temperature and then washed with saturated aqueous solution of Na_2SO_3 and $NaHCO_3$ in 1:1 proportion, dried over anhydrous Na_2SO_4 and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane,3/7) to give ***E*-20** (185 mg, 78 %) as a colourless oil; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.70 (s, 1H), 5.71-5.60 (m, 2H), 4.52 (d, *J* = 4.7 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.70 (s, 6H), 2.63 (d, *J* = 5.8 Hz, 2H), 2.46 (t, *J* = 7.5 Hz, 2H), 2.19-2.14 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$; DEPT) δ (ppm): 200.0 (CH), 170.9 (C), 154.8 (C), 129.4 (CH), 128.3 (CH), 67.4 (CH_2), 64.0 (CH_2), 56.4 (C), 52.6 (CH_3), 39.0 (CH_2), 36.6 (CH_2), 25.2 (CH_2), 14.2 (CH_3); Compound **E-20** is an air-sensitive compound and only a good quality HRMS was obtained for the closely related acid derivative, ESHRMS calcd. for $C_{15}H_{22}O_9Na$ *m/z* 369.1156, found *m/z* 369.1152.

Synthesis of aldehyde *Z*-20.

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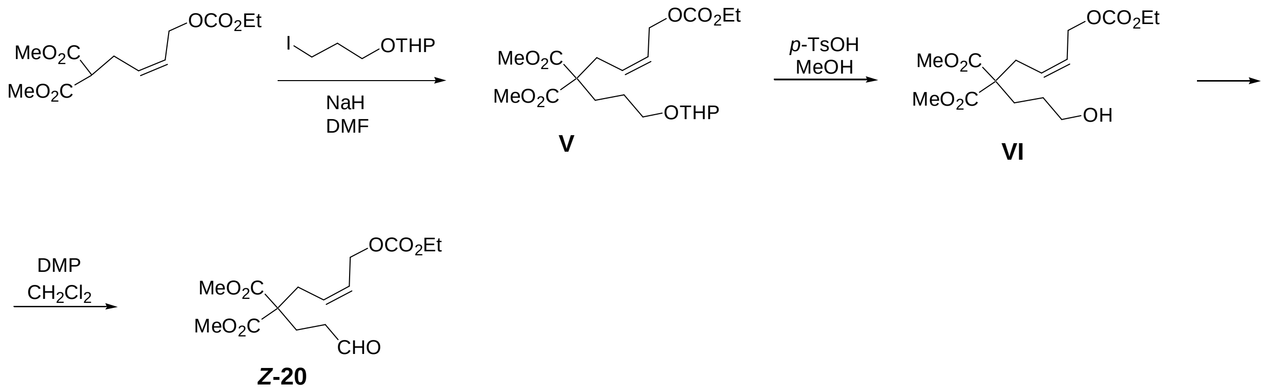
[15] It was prepared from $OH(CH_2)_3OTHP$ according to known procedure: J. Garegg, B. Samuelsson. *J. Chem. Soc. Perkin I.* **1980**, 2866-2869. $I(CH_2)_3OTHP$ was isolated as pure sample and showed NMR spectra identical to those reported: G. G. Cox, C. Moody. J. *Tetrahedron*. **1993**, *49*, 5109-5126.

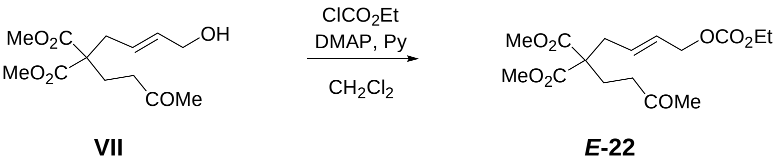


Synthesis of compound V. A sample of $I(CH_2)_3OTHP$[15] (271 mg, 1.0 mmol) was added to a mixture of NaH (33 mg, 1.4 mmol) and dimethyl (*Z*)-2-(4-ethoxycarbonyloxy-2-butenyl)malonate[9] (250 mg, 0.9 mmol) in DMF (25 mL). This solution was stirred at room temperature for 4 h and then diluted with Et_2O, washed with 10% aqueous HCl and dried with anhydrous Na_2SO_4, and the solvent was removed. The residue was submitted to flash chromatography (EtOAc/Hexane,1/4) to give **V** (262 mg, 69 %) as a colourless oil; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 5.76-5.68 (m, 1H), 5.61-5.52 (m, 1H), 4.70 (d, *J* = 6.6 Hz, 2H), 4.59 (t, *J* = 4.2 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.84 (t, *J* = 12.8 Hz, 1H), 3.75-3.73 (m, 1H), 3.74 (s, 6H), 3.52 (dt, *J* = 12.0, 6.0 Hz, 1H), 3.39 (dt, *J* = 9.6, 6.0 Hz, 1H), 2.75 (d, *J* = 7.5 Hz, 2H), 2.03-1.96 (m, 2H), 1.81 (t, *J* = 16.0 Hz, 1H), 1.68 (t, *J* = 16.0 Hz, 1H), 1.61-1.49 (m, 6H), 1.33 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ (ppm): 171.6 (C), 155.2 (C), 128.7 (CH), 127.1 (CH), 98.9 (CH), 67.25 (CH_2), 64.24 (CH_2), 63.34 (CH_2), 62.46 (CH_2), 57.47 (C), 55.9 (CH_3), 31.0 (CH_2), 30.8 (CH_2), 29.7 (CH_2), 25.6 (CH_2), 24.8 (CH_2), 19.7 (CH_2), 14.5 (CH_3); ESHRMS calcd. for $C_{20}H_{32}O_9Na$ *m/z* 439.1938, found *m/z* 439.1925.

Synthesis of compound VI. *p*-Toluenesulfonic acid (7 mg, 0.03 mmol) was added to a solution of ether **V** (152 mg, 0.3 mmol) in MeOH (15 mL). The resulting mixture was stirred for 14 h and then diluted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4 and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane,1/1) to give **VI** (687 mg, 96 %) as a colourless oil; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.71-5.64 (m, 1H), 5.52-5.46 (m, 1H), 4.66 (d, *J* = 6.8 Hz, 2H), 4.17 (q, *J* = 6.8 Hz, 2H), 3.71 (s, 6H), 3.61 (t, *J* = 6.0 Hz, 2H), 2.71 (d, *J* = 7.6 Hz, 2H), 1.96-1.91 (m, 2H), 1.49–1.43 (m, 2H), 1.28 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ (ppm): 172.0 (C), 157.9 (C), 129.1 (CH), 127.5 (CH), 64.7 (CH_2), 63.7 (CH_2), 63.2 (CH_2), 57.7 (C), 53.1 (CH_3), 31.6 (CH_2), 29.7 (CH_2), 28.1 (CH_2), 14.8 (CH_3); ESHRMS calcd. for $C_{15}H_{24}O_8Na$ *m/z* 355.1363, found *m/z* 355.1347.

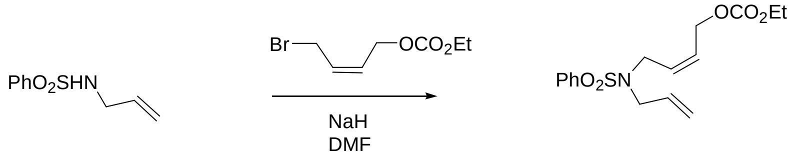
Aldehyde *Z*-20. Dess-Martin Periodinane (DMP) (1.7 g, 4.1 mmol) was added to a solution of **IV** (687 mg, 2.1 mmol) in CH_2Cl_2 (30 mL). The resulting mixture was stirring for 2 h at room temperature and then washed with saturated aqueous solution of Na_2SO_3 and $NaHCO_3$ in 1:1 proportion, dried over anhydrous Na_2SO_4 and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane,3/7) to give **Z-20** (505 mg, 74 %) as a colourless oil; ^1H NMR (400mHz, $CDCl_3$) δ(ppm): 9.75 (s, 1H), 5.79-5.70(m, 1H), 5.59-5.50(m, 1H), 4.66(d, *J* = 6.8Hz, 2H), 4.19(q, *J* = 6.8Hz, 2H), 3.73(s, 6H), 2.72(d, *J* = 7.6Hz, 2H), 2.50(t, *J* = 7.6 Hz, 2H), 2.20(t, *J* = 8Hz, 2H), 1.30(t, *J* = 6.8Hz, 3H); ^{13}C NMR (125MHz, $CDCl_3$; DEPT) δ(ppm): 200.5(C), 171.0(C), 155.1(C), 128.2(CH), 127.3(CH), 64.1(CH_2), 63.0(CH_2), 56.6(C), 52.7(CH_3), 39.2(CH_2), 31.7(CH_2), 25.3(CH_2), 14.3(CH_3); Compound **Z-20** is an air-sensitive compound and only a good quality HRMS was obtained for the closely related acid derivative ESHRMS calcd. for $C_{15}H_{22}O_9Na$ *m/z* 369.1156, found *m/z* 369.1156.

Synthesis of ketone *E*-22.



It was prepared from compound **VII**[9] according to previously described general procedure. The compound was isolated by flash chromatography (EtOAc/Hexane,3/7) to give ***E*-22** in a 95 % yield as a colourless oil; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.66 (m, 2H), 4.53 (d, *J* = 4.0 Hz, 2H), 4.18 (q, *J* = 6.4 Hz, 3H), 3.71 (s, 6H), 2.63 (d, *J* = 5.2 Hz, 2H), 2.45 (t, *J* = 7.2 Hz, 2H), 2.16-2.10 (m, 2H), 2.12 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ (ppm): 207.1 (C), 171.3 (C), 155.1 (C), 129.9 (CH), 128.5 (CH), 67.7 (CH_2), 64.2 (CH_2), 57.0 (C), 52.8 (CH_3), 38.7 (CH_2), 37.0 (CH_2), 30.1 (CH_2), 26.9 (CH_3), 14.4 (CH_3); ESHRMS calcd. for $C_{16}H_{24}O_8Na$ *m/z* 367.1363, found *m/z* 367.1356.

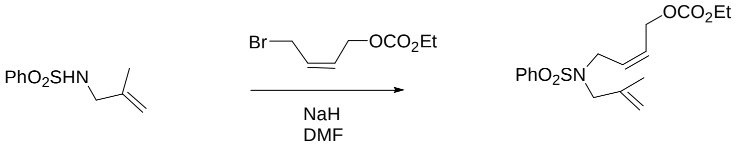
Synthesis of carbonate 27.



27

A sample of (*Z*)-$BrCH_2CH{=}CHCH_2OCO_2Et$[13] (81 mg, 0.3 mmol) was added to a mixture of NaH (11 mg, 0.4 mmol) and *N*-allylbenzenesulfonamide[16] (48 mg, 0.2 mmol) in DMF (8 mL). The resulting solution was stirred at room temperature for 4 h and then diluted with Et_2O, washed with 10% aqueous HCl and dried with anhydrous Na_2SO_4, and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane,2/8) to give **27** (65 mg, 79 %) as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.82 (d, *J* = 8.4 Hz, 2H), 7.60-7.49 (m, 3H), 5.71-5.48 (m, 3H), 5.19-5.14 (m, 2H), 4.61 (d, *J* = 6.8 Hz, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.90 (d, *J* = 6.8 Hz, 2H), 3.81 (d, *J* = 6.0 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 155.2, 140.4, 132.9, 132.8, 129.8, 129.3, 127.3, 127.1, 119.4, 64.3, 62.9, 50.2, 43.8, 14.4; ESHRMS calcd. for $C_{16}H_{21}NO_5S$ *m/z* 339.1140, found *m/z* 340.1211.

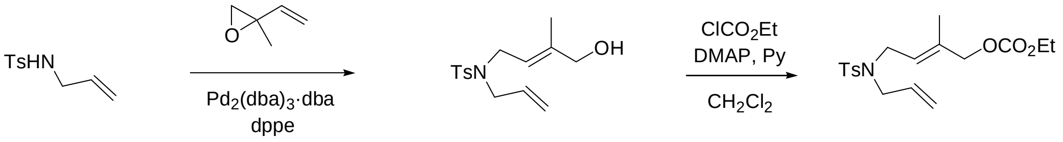
Synthesis of carbonate 29.



29

A sample of (*Z*)-$BrCH_2CH{=}CHCH_2OCO_2Et$[13] (158 mg, 0.7 mmol) was added to a mixture of NaH (22 mg, 0.9 mmol) and *N*-(2-methyl-allyl)-benzenesulfonamide[16] (100 mg, 0.4 mmol) in DMF (15 mL). The resulting solution was stirred at room temperature for 4 h and then diluted with Et_2O, washed with 10% aqueous HCl and dried with anhydrous Na_2SO_4, and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane,2/8) to give **29** (80 mg, 48 %) as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.82 (d, *J* = 7.8 Hz, 2H), 7.59-7.49 (m, 3H), 5.65-5.59 (m, 1H), 5.46-5.40 (m, 1H), 4.92 (s, 1H), 4.85 (s, 1H), 4.59 (d, *J* = 6.8 Hz, 2H), 4.18 (q, 6.8 Hz, 2H), 3.87 (d, *J* = 6.8 Hz, 2H), 3.71 (s, 2H), 1.70 (s, 3H), 1.29 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$; DEPT) δ (ppm): 155.1 (C), 140.4 (C), 140.3 (C), 132.8 (CH), 129.5 (CH), 129.3 (CH), 127.4 (CH), 127.0 (CH), 114.9 (CH_2), 62.8 (CH_2), 53.8 (CH_2), 43.8 (CH_2), 29.9 (CH_2), 19.9 (CH_3), 14.4 (CH_3); ESHRMS calcd. for $C_{17}H_{23}NO_5SNa$ *m/z* 376.1189, found *m/z* 376.1186.

Synthesis of allyl carbonate 31.



VIII **31**

Synthesis of alcohol VIII. Isoprene monoxide (40 mg, 0.4 mmol) was added to a solution of N-allyl-*p*-toluenesulfonamide[17] (100 mg, 0.4 mmol), $Pd_2(dba)_3{\cdot}dba$ (4 mg, 0.05 mmol) and dppe (9 mg, 0.05 mmol) in THF (15 mL). The resulting mixture was stirred at room temperature for 24 h and then reduced in volume to 0.5 mL. The residue was submitted to flash chromatography (EtOAc/Hexane,3/7) to give **VIII** (60 mg, 43 %) as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.68 (d, *J* = 8.0Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.70-5.60 (m, 2H), 5.29-5.11 (m, 2H), 4.08 (s, 2H), 3.83-3.77 (m, 4H), 2.42 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ (ppm): 142.9 (C), 138.9 (C), 136.9 (C), 132.8 (CH), 129.3 (CH), 126.9 (CH), 121.8 (CH), 118.4 (CH_2), 60.8 (CH_2), 49.8 (CH_2), 43.5 (CH_2), 21.2 (CH_3), 21.1 (CH_3); ESHRMS calcd. for $C_{15}H_{22}NO_3S$ *m/z* 296.1314, found *m/z* 296.1312.

Carbonate 31. Ethyl carbonate **31** was prepared from allyl alcohol **VIII** according to previously described general procedure. The compound was isolated by flash chromatography (EtOAc/Hexane, 1/4) to give **31** in a 79 % yield as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.72 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 5.70-5.58 (m, 1H), 5.35-5.29 (m, 1H), 5.16 (d, *J* = 16.3 Hz, 1H), 5.15 (d, *J* = 10.5 Hz, 1H), 4.58 (s, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.88 (d, *J* = 7.0 Hz, 2H), 3.81 (d, *J* = 6.0 Hz, 2H), 2.45 (s, 3H), 1.78 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ (ppm): 152.7 (C),

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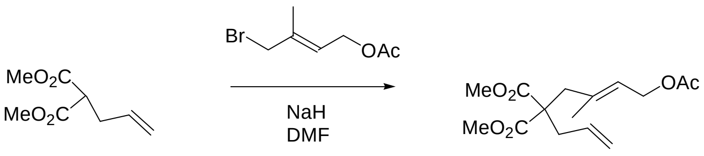
[16] A. Padwa, H. Nimmesgern, G. S. K. Wong. *J. Org. Chem.* **1985**, *50*, 5620-5627.

[17] A. Lei, X. Lu. *Org. Lett.* **2000**, *2*, 2357-2360.

140.9 (C), 136.7 (C), 134.9 (C), 130.7 (CH), 127.3 (CH), 124.8 (CH), 123.3 (CH), 116.4 (CH_2), 63.2 (CH_2), 61.8 (CH_2), 47.5 (CH_2), 41.6 (CH_2), 19.1 (CH_3), 18.9 (CH_3), 11.9 (CH_3); ESHRMS calcd. for $C_{18}H_{26}NO_5S$ *m/z* 368.1526, found *m/z* 368.1543.

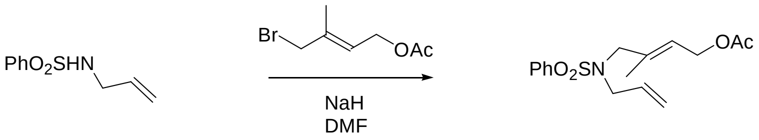
Synthesis of acetate 33.



33

A sample of *trans*-4-acetoxy-1-bromo-2-methyl-2-butene[18] (541 mg, 2.6 mmol) was added to a mixture of NaH (60 mg, 2.6 mmol) and dimethyl allylmalonate (300 mg, 1.7 mmol) in DMF (20 mL). This solution was stirred at room temperature for 4 h and then diluted with Et_2O, washed with 10% aqueous HCl and dried with anhydrous Na_2SO_4, and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane,2/8) to give **33** (453 mg, 90 %) as a colourless oil; ^1H NMR (200 MHz, $CDCl_3$) δ (ppm): 5.70 (m, 1H), 5.42 (t, *J* = 6.9 Hz, 1H). 5.10 (m. 2H), 4.56 (d, *J* = 7.0 Hz, 2H), 3.71 (s, 6H), 2.72 (s, 2H), 2.63 (d, *J* = 7.1 Hz, 2H), 2.05 (s, 3H), 1.63 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 170.87, 170.80, 136.01, 132.19, 124.09, 118.63, 60.35, 57.17, 51.77, 41.73, 36.76, 20.31, 16.61. Elemental analysis calcd for $C_{15}H_{22}O_6$: C, 60.39, H, 7.43. Found: C, 60.46; H, 7.70.

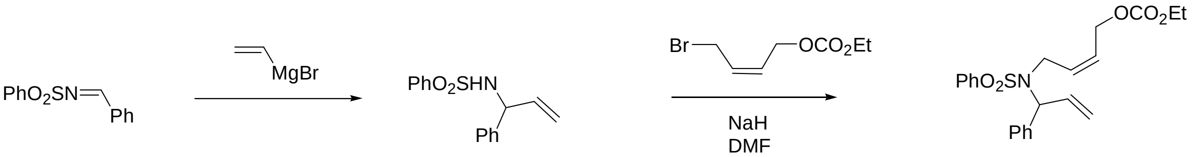
Synthesis of acetate 35.



35

A sample of *trans*-4-acetoxy-1-bromo-2-methyl-2-butene[18] (92 mg, 0.4 mmol) was added to a mixture of NaH (13 mg, 0.5 mmol) and *N*-allylbenzenesulfonamide[16] (54 mg, 0.3 mmol) in DMF (10 mL). The resulting solution was stirred at room temperature for 4 h and then diluted with Et_2O, washed with 10% aqueous HCl and dried with anhydrous Na_2SO_4, and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane,3/7) to give **35** (55 mg, 62 %) as a colourless oil. Compound **35** was obtained as a 5.4:1 mixture of *E*:*Z* diastereoisomers; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.82 (d, *J* = 8.4 Hz, 2H), 7.59-7.48 (m, 3H), 5.55-5.43 (m, 2H), 5.08 (d, *J* = 9.6 Hz, 1H), 5.06 (d, *J* = 16.8 Hz, 1H), 4.58 (d, *J* = 6.8 Hz, 2H), 3.75 (d, *J* = 6.8 Hz, 2H), 3.72 (s, 2H), 2.03 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ (ppm): 168.5 (C), 137.9 (C), 133.5 (C), 130.3 (CH), 129.8 (CH), 126.7 (CH), 124.8 (CH), 122.8 (CH), 117.0 (CH_2), 58.4 (CH_2), 51.7 (CH_2), 47.4 (CH_2), 18.5 (CH_3), 12.0 (CH_3); ESHRMS calcd. for $C_{16}H_{21}NO_4SNa$ *m/z* 346.1083, found *m/z* 346.1098.

Synthesis of allyl carbonate 37.



IX **37**

Synthesis of sulfonamide IX. Vinylmagnesium chloride (2.65 mL, 1.0 M in THF) was slowly added to a solution of *N*-benzylidenbenzenesulfonamide (500 mg, 2.0 mmol) in 1:1 mixture of THF:Et_2O (20 mL) at rt and continued stirring for 15 h. The reaction mixture was quenched with saturated NH_4Cl and extracted with ether. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4 and concentrated to give the crude product. Purification by column chromatography (EtOAc/Hexane,15/8) gave the pure product **IX** (395 mg, 72%) as a colourless oil; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.75 (d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.23-7.20 (m, 3H), 7.10-7.08 (m, 2H), 5.87 (ddd, *J* = 16.4, 10.4, 6.2 Hz, 1H), 5.14 (d, *J* = 8.8 Hz, 1H), 5.12 (d, *J* = 18.0 Hz, 1H), 4.97 (t, *J* = 6.8 Hz, 1H), 4.84 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$; DEPT) δ (ppm): 140.9 (C), 139.4 (C), 137.2 (CH), 132.6 (CH), 129.0 (CH), 128.8 (CH), 128.0 (CH), 127.9 (CH), 127.3 (CH), 117.1 (CH_2), 60.1 (CH); ESHRMS calcd. for $C_{15}H_{15}NO_2NaS$ *m/z* 296.0715, found *m/z* 296.0711.

Carbonate 37. A sample of (*Z*)-$BrCH_2CH{=}CHCH_2OCO_2Et$[13] (183 mg, 0.8 mmol) was added to a mixture of NaH (25 mg, 1.1 mmol) and sulfonamide **IX** (149 mg, 0.5 mmol) in DMF (10 mL). The resulting solution was stirred at room temperature for 4 h and then diluted with Et_2O, washed with 10% aqueous HCl and dried with anhydrous Na_2SO_4, and the solvent removed. The

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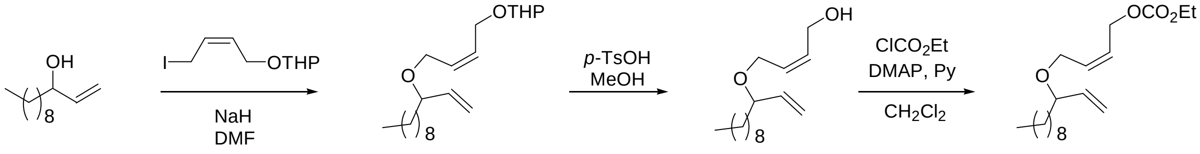
[18] K. Sato, S. Inoue, S. Ota, Y. Fujita, *J. Org. Chem.* **1972**, *37*, 462-466.

residue was submitted to flash chromatography (EtOAc/Hexane:2/8) to give **37** (145 mg, 64 %) as a colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.85 (d, *J* = 6.9 Hz, 2H), 7.59-7.48 (m, 3H), 7.32-7.24 (m, 5H), 6.04 (ddd, *J* = 17.2, 10.3, 6.7 Hz, 1H), 5.72 (d, *J* = 6.7 Hz, 1H), 5.43-5.40 (m, 2H), 5.31 (dd, *J* = 9.2, 1.2 Hz, 1H), 5.15 (dd, *J* = 17.2, 1.2 Hz, 1H), 4.37 (d, *J* = 3.7 Hz, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.81 (d, *J* = 3.4 Hz, 2H), 1.33 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$; DEPT) δ (ppm): 155.1 (C), 141.1 (C), 138.3 (C), 134.4 (CH), 132.6 (CH), 131.9 (CH), 129.0 (CH), 128.7 (CH), 128.5 (CH), 128.2 (CH), 127.7 (CH), 126.6 (CH), 119.5 (CH_2), 67.2 (CH_2), 64.2 (CH_2), 63.5 (CH), 46.6 (CH_2), 14.5 (CH_3); ESHRMS calcd. for $C_{22}H_{25}NO_5SNa$ *m/z* 438.4924, found *m/z* 438.1354.

Synthesis of carbonate 39.



X **XI** **39**

Synthesis of compound X. A sample of (*Z*)-$ICH_2CH=CHCH_2OTHP$[19] (356 mg, 1.2 mmol) was added to a mixture of NaH (33 mg, 1.4 mmol) and dodec-1-en-3-ol[20] (250 mg, 1.2 mmol) in DMF (15 mL). The resulting solution was stirred at room temperature for 4 h and then diluted with Et_2O, washed with 10% aqueous HCl, dried over anhydrous Na_2SO_4 and the solvent removed. The residue was submitted to flash chromatography (5:95, EtOAc/Hexane,1/9) to give **X** (275 mg, 65 %) as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.85-5.81 (m, 2H), 5.66 (ddd, *J* = 16.4, 10.8, 7.6, 1H), 5.16 (d, *J* = 10.8 Hz, 1H), 5.15 (d, *J* = 16.4 Hz, 1H), 4.64 (t, *J* = 3.6 Hz, 1H), 4.24 (bd, *J* = 11.2 Hz, 1H), 4.05-3.96 (m, 2H), 3.89-3.81 (m, 2H), 3.65 (q, *J* = 6.8 Hz, 1H), 3.51-3.48 (m, 1H), 1.87-1.81 (m, 1H), 1.74-1.69 (m, 1H), 1.61-1.24 (m, 20H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$; DEPT) δ (ppm): 139.4 (CH), 129.9 (CH), 129.0 (CH), 98.1 (CH_2), 81.2 (CH), 81.1 (CH), 68.4 (CH_2), 67.3 (CH_2), 62.3 (CH_2), 35.6 (CH_2), 32.1 (CH_2), 30.8 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.5 (CH_2), 25.7 (CH_2), 25.5 (CH_2), 22.9 (CH_2), 19.6 (CH_2), 14.3 (CH_3), (one carbon signal was not observed); ESHRMS calcd. for $C_{21}H_{38}O_3Na$ *m/z* 361.2713, found *m/z* 361.2707.

Synthesis of alcohol XI. *p*-Toluenesulfonic acid (8 mg, 0.04 mmol) was added to a solution of ether **X** (139 mg, 0.4 mmol) in MeOH (25 mL). The resulting mixture was stirred for 14 h and then diluted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4 and the solvent removed. The residue was submitted to flash chromatography (EtOAc/Hexane:2/8) to give **XI** (88 mg, 84 %) as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.86 (dt, *J* = 15.6, 4.8 Hz, 1H), 5.70 (dt, *J* = 15.6, 4.8 Hz, 1H), 5.65 (ddd, *J* = 17.2, 10.0, 7.6 Hz, 1H), 5.16 (d, *J* = 10.0 Hz, 1H), 5.15 (d, *J* = 17.6 Hz, 1H), 4.13 (d, *J* = 4.8 Hz, 2H), 4.02 (dd, *J* = 12.8, 5.2 Hz, 1H), 3.82 (dd, *J* = 12.8, 5.6 Hz, 1H), 3.65 (q, *J* = 6.8 Hz, 1H), 1.25 (m, 16H), 0.86 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$; DEPT) δ (ppm): 139.3 (CH), 131.9 (CH), 128.6 (CH), 117.0 (CH_2), 81.3 (CH), 68.3 (CH_2), 63.3 (CH_2), 35.6 (CH_2), 32.1 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.5 (CH_2), 25.5 (CH_2), 22.9 (CH_2), 14.3 (CH_3), (one carbon signal was not observed); ESHRMS calcd. for $C_{16}H_{30}O_2Na$ *m/z* 277.2143, found *m/z* 277.2134.

Carbonate 39. It was prepared from allyl alcohol **XI** according to previously described general procedure. The compound was isolated by flash chromatography (EtOAc/Hexane,) to give **39** in a 96 % yield as a colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.90-5.76 (m, 2H), 5.64 (ddd, *J* = 17.6, 10.8, 7.6 Hz, 1H), 5.15 (d, *J* = 9.2 Hz, 1H), 5.14 (d, *J* = 18.0 Hz, 1H), 4.61 (d, *J* = 5.2 Hz, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 4.03 (dd, *J* = 12.8, 4.4 Hz, 1H), 3.83 (dd, *J* = 12.8, 4.5 Hz, 1H), 3.64 (q, *J* = 6.8 Hz, 1H), 1.31-1.25 (m, 19H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$; DEPT) δ (ppm): 153.9 (C), 138.0 (CH), 131.3 (CH), 124.3 (CH), 115.8 (CH_2), 80.0 (CH), 66.6 (CH_2), 62.9 (CH_2), 62.7 (CH_2), 34.4 (CH_2), 30.8 (CH_2), 28.5 (CH_2), 28.3 (CH_2), 24.3 (CH_2), 21.6 (CH_2), 13.2 (CH_3), 13.0 (CH_3), (two carbon signals were not observed); ESHRMS calcd. for $C_{19}H_{34}O_4Na$ *m/z* 349.2349, found *m/z* 349.2322.

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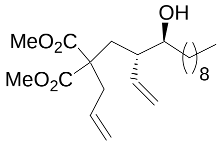
[19] It was prepared from (*Z*)-$OHCH_2CH=CHCH_2OTHP$ according to known procedure: J. Garegg, B. Samuelsson. *J. Chem. Soc. Perkin I.* **1980**, 2866-2869. (*Z*)-$ICH_2CH=CHCH_2OTHP$ was isolated as a pure sample and showed NMR spectra identical to those reported: R. A. Holton, J. R. Zoeller. *J. Am. Chem. Soc.* **1985**, *107*, 2124-2126.

[20] J. H. Babler, B. J. Invergo, S. J. Sarussi. *J. Org. Chem.* **1980**, *45*, 4241-4243.

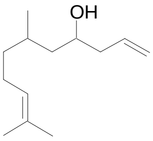
Allylation Products

Compound 2.



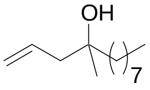
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.65-5.50 (m, 2H), 5.10 (d, *J* = 10.2 Hz, 1H), 5.08 (d, *J* = 17.0 Hz, 1H), 5.07 (d, *J* = 10.5 Hz, 1H), 5.01 (d, *J* = 17.2 Hz, 1H), 3.67 (s, 3H), 3.63 (s, 3H), 3.42-3.39 (m, 1H), 2.71 (dd, *J* = 14.2, 7.0 Hz, 1H), 2.62 (dd, *J* = 14.2, 7.2 Hz, 1H), 2.16-2.09 (m, 2H), 2.03-1.97 (m, 1H), 1.42-1.37 (m, 2H), 1.34-1.19 (m, 14H), 0.86 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; DEPT) δ (ppm): 171.8 (C), 171.7 (C), 138.0 (CH), 132.6 (CH), 119.3 (CH_2), 118.2 (CH_2), 74.6 (CH), 57.0 (C), 52.5 (CH_3), 52.2 (CH_3), 45.8 (CH_2), 37.8 (CH), 34.4 (CH_2), 33.8 (CH_2), 32.0 (CH_2), 29.9 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 26.1 (CH_2), 22.8 (CH_2), 14.3 (CH_3); ESHRMS calcd. for $C_{22}H_{38}O_5Na$ *m/z* 405.2611, found *m/z* 405.2596.

Compound 7.



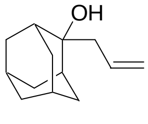
Compound **7** was obtained as a 1:1 mixture of diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.79 (ddt, *J* = 16.5, 10.7, 7.4 Hz, 1H), 5.13 (bd, *J* = 16.5 Hz, 1H), 5.06 (bd, *J* = 10.7 Hz, 1H), 5.06 (bt, *J* = 6.5 Hz, 1H), 3.75-3.70 (m, 1H), 2.30-1.94(m, 4H), 1.66 (s, 3H), 1.58 (s, 3H), 1.50-1.17 (m, 5H), 0.88 (d, *J* = 6.2 Hz, 3H, one diastereoisomer), 0.84 (d, *J* = 6.2 Hz, 3H, other diastereoisomer); ^{13}C NMR (100 MHz, $CDCl_3$; DEPT) δ (ppm): 134.9 (CH), 131.5 (C), 124.8 (CH), 118.1 (CH_2), 68.7 (CH), 44.3 (CH_2), 42.2 (CH_2), 37.9 (CH_2), 28.9 (CH), 25.7 (CH_3), 25.4 (CH_2), 20.2 (CH_3), 17.7 (CH_3); FABHRMS calcd. for $C_{13}H_{24}ONa$ *m/z* 219.1724, found *m/z* 219.1718.

Compound 8.



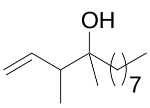
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.85 (ddt, *J* = 17.2, 10.0, 7.2 Hz, 1H), 5.14 (d, *J* = 7.6 Hz, 1H), 5.11 (d, *J* = 16.0 Hz, 1H), 2.22 (d, *J* = 7.6 Hz, 2H), 1.45-1.26 (m, 14H), 1.16 (s, 3H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; DEPT) δ (ppm): 134.1 (CH), 118.4 (CH_2), 72.1 (C), 46.2 (CH_2), 41.8 (CH_2), 31.8 (CH_2), 30.1 (CH_2), 29.5 (CH_2), 29.2 (CH_2), 26.6 (CH_3), 23.8 (CH_2), 22.6 (CH_2), 14.0 (CH_3); ESHRMS calcd. for $C_{13}H_{26}ONa$ *m/z* 221.1875, found *m/z* 221.1867.

Compound 9.



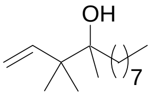
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.85 (ddt, *J* = 17.1, 10.2, 7.5 Hz, 1H), 5.12 (dd, *J* = 10.2, 2.4 Hz, 1H), 5.10 (dd, *J* = 17.1, 2.4 Hz, 1H), 2.40 (d, *J* = 7.5 Hz, 2H), 2.15 (bd, *J*= 12.4 Hz, 2H), 1.85-1.49 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$; DEPT) δ (ppm): 133.8 (CH), 118.9 (CH_2), 74.5 (C), 42.8 (CH_2), 38.4 (CH_2), 37.1 (CH), 34.5 (CH_2), 33.0 (CH_2), 27.5 (CH), 27.4 (CH), (some carbon signals were not observed); ESHRMS calcd. for $C_{13}H_{20}ONa$ *m/z* 215.1406, found *m/z* 215.1415.

Compound 16.



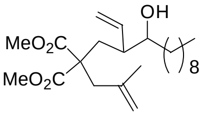
Compound **16** was obtained as a 3:2 mixture of diastereomers; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.82 (ddt, *J* = 16.9, 10.6, 6.9 Hz, 1H), 5.10 (dd, *J* = 10.6, 1.7 Hz, 1H), 5.07 (dd, *J* = 16.9, 1.7 Hz, 1H), 2.24 (quint, *J* = 6.9 Hz, 1H), 1.49-1.27 (m, 14H), 1.11 (s, 3H, minor stereoisomer), 1.09 (s, 3H, major stereoisomer), 1.03 (d, *J* = 6.9 Hz, 3H, minor stereoisomer), 1.00 (d, *J* = 6.9 Hz, 3H, major stereoisomer), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; DEPT) δ (ppm): 140.7 (CH), 140.5 (CH), 116.4 (CH_2), 115.9 (CH_2), 73.8 (C), 47.9 (CH), 47.2 (CH), 40.1 (CH_2), 39.6 (CH_2), 31.9 (CH_2), 30.4 (CH_2), 29.7 (CH_2), 29.4 (CH_2), 24.2 (CH_3), 23.7 (CH_3), 23.4 (CH_2), 23.3 (CH_2), 22.8 (CH_2), 14.6 (CH_3),14.2 (CH_3), (some carbon signals were not observed); FABHRMS calcd. for $C_{14}H_{28}O$ - H_2O *m/z* 194.2034, found *m/z* 194.2032.

Compound 17.



^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.04 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.08 (d, *J* = 10.9 Hz, 1H), 5.05 (d, *J* = 17.5 Hz, 1H), 1.47-1.41 (m, 2H), 1.32-1.20 (m, 12H), 1.11 (s, 6H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; DEPT) δ (ppm): 145.6 (CH), 113.4 (CH_2), 75.7 (C), 44.6 (C), 36.6 (CH_2), 31.9 (CH_2), 30.6 (CH_2), 29.8 (CH_2), 23.9 (CH_2), 22.8 (CH_2), 22.3 (CH_3), 22.2 (CH_3), 21.1 (CH_3), 14.2 (CH_3), (one carbon signal was not observed); FABHRMS calcd. for $C_{15}H_{30}ONa$ *m/z* 249.2194, found *m/z* 249.2200.

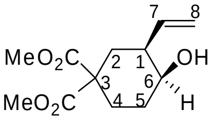
Compound 19.



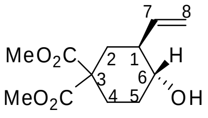
^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.54 (ddd, *J* = 17.4, 10.3, 9.1 Hz, 1H), 5.10 (dd, *J* = 10.3, 1.9 Hz, 1H), 5.00 (dd, *J* = 17.2, 1.9 Hz, 1H), 4.85 (s, 1H), 4.73 (s, 1H), 3.67 (s, 3H), 3.64 (s, 3H), 3.45-3.43 (m, 1H), 2.74 (s, 2H), 2.20-2.14 (m, 2H), 2.07-2.01 (m, 1H), 1.63 (s, 3H), 1.42-1.32 (m, 2H), 1.30-1.24 (m, 14H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; DEPT) δ (ppm): 172.1 (C), 171.8 (C), 140.7 (C), 137.6 (CH), 117.8 (CH_2), 115.7 (CH_2), 74.7 (CH), 56.1 (C), 52.2 (CH_3), 52.0 (CH_3), 45.5 (CH), 41.4 (CH_2), 34.3 (CH_2), 34.1 (CH_2), 31.9 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 25.9 (CH_2), 23.0 (CH_3), 22.6 (CH_2), 14.1 (CH_3); ESHRMS calcd. for $C_{23}H_{40}O_5Na$ *m/z* 419.2767, found *m/z* 419.2745.

Compound 21.

Compound **21** was obtained as a 1:1 mixture of diastereomers.

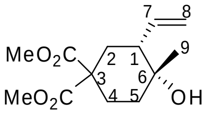


Diastereomer **21a**: ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.87 (ddd, *J* = 16.8, 10.8, 5.6 Hz, 1H), 5.19 (dd, *J* = 16.8, 1.2 Hz, 1H), 5.16 (dd, *J* = 10.8, 1.2 Hz, 1H), 3.89 (bs, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 2.36-2.32 (m, 1H), 2.19-2.02 (m, 4H), 1.91 (dq, *J* = 14.4, 3.0 Hz, 1H), 1.70-1.61 (m, 1H), 1.25 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$; DEPT) δ (ppm): 172.5 (C), 171.6 (C), 139.4 (CH), 116.3 (CH_2), 67.0 (CH), 54.8 (C), 52.8 (CH_3), 52.6 (CH_3), 41.4 (CH), 29.0 (CH_2), 28.6 (CH_2), 24.5 (CH_2); ESHRMS calcd. for $C_{12}H_{18}O_5Na$ *m/z* 265.1046, found *m/z* 265.1049.

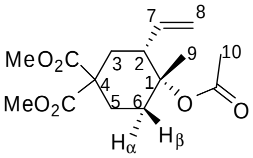


Diastereomer **21b**: ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.74 (ddd, *J* = 17.2, 10.0, 8.4Hz, 1H), 5.24-5.17 (m, 2H), 3.76 (s, 3H), 3.69 (s, 3H), 3.29 (td, *J* = 10.4, 4.4 Hz, 1H), 2.45-2.37 (m, 2H), 2.13-1.98 (m, 2H), 1.77 (td, *J* = 13.6, 3.6 Hz, 1H), 1.62 (t, *J* = 13.2 Hz, 1H), 1.39 (qd, *J* = 14.0, 3.6 Hz, 1H); NOE-diff. experiment: proton irradiated, (NOEs observed): H-6, (H-7), H-7, (H-6); ^{13}C NMR (125 MHz, $CDCl_3$; DEPT) δ (ppm): 172.3 (C), 171.1 (C), 139.0 (CH), 118.1 (CH_2), 71.8 (CH), 54.5 (C), 52.8 (CH_3), 52.7 (CH_3), 47.2 (CH), 35.5 (CH_2), 30.3 (CH_2), 29.9 (CH_2); ESHRMS calcd. for $C_{12}H_{18}O_5Na$ *m/z* 265.1046, found *m/z* 265.1049.

Compound 23.



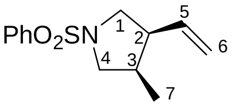
^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 5.91 (ddd, *J* = 17.1, 10.2, 7.2 Hz, 1H), 5.21 (dd, *J* = 10.2, 0.9 Hz, 1H), 5.15 (dd, *J* = 17.1, 0.9 Hz, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 2.40-1.98 (m, 5H), 1.73 (dt, *J* = 14.1, 3.3 Hz, 1H), 1.54 (td, *J* = 14.1, 4.5 Hz, 1H), 1.20 (s, 3H); NOE-diff. experiment: proton irradiated, (nOes observed): H-7, (H$_2$-8, H$_3$-9); ^{13}C NMR (75 MHz, CDCl$_3$; DEPT) δ (ppm): 172.7 (C), 171.8 (C) , 137.9 (CH), 117.6 (CH$_2$), 69.4 (C), 54.9 (C), 52.9 (CH$_3$), 52.7 (CH$_3$), 46.7 (CH), 36.3 (CH$_2$), 31.8 (CH$_2$), 29.4 (CH$_3$), 26.6 (CH$_2$); ESHRMS calcd. for $C_{13}H_{20}O_5Na$ *m/z* 279.1202, found *m/z* 279.1192.
The stereochemistry of **23** was confirmed based on NOE-diff. experiments of closely related acetylated derivative **23ac**:



^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 5.83-5.68 (m, 1H), 5.22-5.10 (m, 2H), 3.77 (s, 3H), 3.70 (s, 3H), 3.02 (dt, *J* = 14.8, 3.2 Hz, 1H), 2.29 (s, 3H), 2.26-2.19 (m, 2H), 2.15 (dt, *J* = 11.2, 3.2 Hz, 1H), 2.03-1.93 (m, 1H), 1.86-1.77 (m, 1H), 1.54 (s, 3H), 1.41 (td, *J* = 14.8, 3.6 Hz, 1H); NOE-diff. experiment: proton irradiated, (NOEs observed): H-6β, (H$_3$-9, H-2, H-6α), H$_3$-9, (H-2, H-6α, H-6β) , H-6α, (H-6β, H$_3$-9); ^{13}C NMR (125 MHz, CDCl$_3$; DEPT) δ (ppm): 172.3 (C), 171.6 (C) , 167.3 (C), 137.0 (CH),118.1 (CH$_2$), 83.2 (C), 54.4 (C), 52.9 (CH$_3$), 52.9 (CH$_3$), 49.2 (CH), 32.7 (CH$_2$), 31.3 (CH$_2$), 26.7 (CH$_2$), 25.6(CH$_3$), 24.2(CH$_3$).

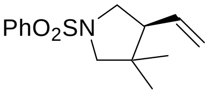
Cyclization Products

Compound 28.



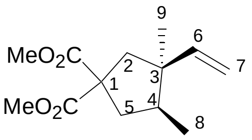
^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.80 (d, *J* = 7.8 Hz, 2H), 7.61-7.65 (m, 3H), 5.50-5.43 (m, 1H), 5.02-4.95 (m, 2H), 3.45-3.41 (m, 2H), 3.20 (dd, *J* = 10.0, 6.1 Hz, 1H), 2.98 (dd, *J* = 10.0, 6.1 Hz, 1H), 2.66 (quint., *J* = 7.1 Hz, 1H), 2.21 (sext., *J* = 6.7 Hz, 1H), 0.75 (d, *J* = 7 Hz, 3H); NOE-diff. experiment: proton irradiated, (NOEs observed): H-3, (H-2, H$_3$-7), H-5, (H-2, H$_3$-7); H$_3$-7 (H-3, H-5); ^{13}C NMR (125 MHz, CDCl$_3$; DEPT) δ (ppm): 137.5 (C), 135.0 (CH), 132.6 (CH), 129.1 (CH), 127.4 (CH), 117.2 (CH$_2$), 54.1 (CH$_2$), 51.4 (CH$_2$), 46.3 (CH), 36.7 (CH), 13.6 (CH$_3$); ESHRMS calcd. for $C_{13}H_{18}NO_2S$ *m/z* 252.1052, found *m/z* 252.1056.

Compound 30.



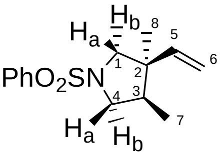
^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.84 (d, *J* = 8.0 Hz, 2H), 7.61-7.51 (m, 3H), 5.50 (ddd, *J* = 18.6, 10.3, 8.2 Hz, 1H), 5.07 (dd, *J* = 10.4, 1.6 Hz, 1H), 5.00 (dd, *J* = 17.1, 1.6 Hz, 1H), 3.50 (dd, *J* = 9.9, 7.9 Hz, 1H), 3.21-3.15 (m, 2H), 2.99 (d, *J* = 9.6 Hz, 1H), 2.25 (q, *J* = 8.4 Hz, 1H), 0.92 (s, 3H), 0.68 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$; DEPT) δ (ppm): 139.9 (C), 136.5 (CH), 135.2 (CH), 131.6 (CH), 129.9 (CH), 120.7 (CH$_2$), 63.5 (CH$_2$), 55.2 (CH), 53.6 (CH$_2$), 43.9 (C), 27.2 (CH$_3$), 23.4 (CH$_3$); ESHRMS calcd. for $C_{14}H_{19}NO_2SNa$ *m/z* 288.1028, found *m/z* 288.1015.

Compound 34.



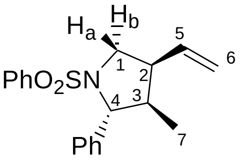
^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 5.75 (dd, *J* = 17.4, 10.8 Hz, 1H), 4.99 (d, *J* = 10.8 Hz, 1H), 4.94 (dd, *J* = 17.4, 0.7 Hz, 1H), 3.71 (s, 6H), 2.51 (d, *J* = 14.3 Hz, 1H), 2.35 (dd, *J* = 13.5, 6.5 Hz, 1H), 2.19 (d, *J* = 14.3 Hz, 1H), 1.99 (t, *J* = 13.3 Hz, 1H), 1.81 (sext, *J* = 6.6 Hz), 1.09 (s, 3H), 0.83 (d, *J* = 6.5 Hz, 3H); NOE-diff. experiment: proton irradiated, (NOEs observed): H-4, (H$_3$-8, H$_3$-9), H-6, (H$_3$-8, H$_3$-9); H$_3$-8 (H-4, H-6, H$_3$-9); H$_3$-9 (H-4, H-6, H$_3$-8); ^{13}C NMR (125 MHz, CDCl$_3$; DEPT) δ (ppm): 174.2 (C), 173.6 (C), 142.5 (CH), 113.3 (CH$_2$), 58.2 (C), 53.3 (CH$_3$), 53.2 (CH$_3$), 47.8 (C), 46.5 (CH$_2$), 45.0 (CH), 41.7 (CH$_2$), 24.7 (CH$_3$), 14.0 (CH$_3$); ESHRMS calcd. for $C_{13}H_{21}O_4$ *m/z* 241.1434, found *m/z* 241.1443.

Compound 36.



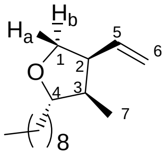
^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.85 (d, *J* = 6.8 Hz, 2H), 7.61-7.51 (m, 3H), 5.51 (dd, *J* = 17.6, 10.8 Hz, 1H), 4.98 (d, *J* = 10.8 Hz, 1H), 4.87 (d, *J* = 17.6 Hz, 1H), 3.52 (dd, *J* = 9.6, 7.6 Hz, 1H), 3.41 (d, *J* = 10.0 Hz, 1H), 3.04 (d, *J* = 10.0 Hz, 1H), 2.93 (t, *J* = 9.6 Hz, 1H), 1.80 (sext., *J* = 6.8 Hz, 1H), 1.01 (s, 3H), 0.75 (d, *J* = 7.2 Hz, 3H); NOE-diff. experiment: proton irradiated, (NOEs observed): H_a-1 (H-5, H_3-8), H_b-1 (H-3, H_3-8), H-3 (H_b-1, H_b-4, H_3-7, H_3-8), H_a-4, (H-3, H-5, H_3-7), H_b-4, (H-3, H_3-7, H_3-8), H-5 (H_3-7, H_3-8), H_3-7 (H_a-1, H_a-4, H_b-4, H-3, H-5, H_3-8), H_3-8 (H_a-1, H_b-1, H_b-4, H-3, H-5, H_3-7); ^{13}C NMR (125 MHz, $CDCl_3$; DEPT) δ (ppm): 137.6 (CH), 135.9 (C), 131.0 (CH), 127.5 (CH), 125.7 (CH), 112.6 (CH_2), 56.7 (CH_2), 51.9 (CH_2), 44.7 (C), 41.5 (CH), 24.7 (CH_3), 14.0 (CH_3); ESHRMS calcd. for $C_{14}H_{19}NO_2SNa$ *m/z* 288.1028, found *m/z* 288.1030.

Compound 38.



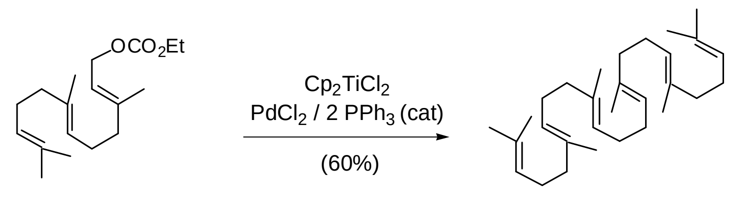
Mayor diastereomer **38** was obtained as a 9:1 mixture of epimers at C-2. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.75 (d, *J* = 8.4 Hz, 2H), 7.57-7.44 (m, 3H), 7.30-7.22 (m, 5H), 5.42 (ddd, *J* = 17.2, 11.2, 8.4 Hz, 1H). 5.01 (d, *J* = 11.0 Hz, 1H), 5.00 (d, *J* = 17.2 Hz, 1H), 4.38 (d, *J* = 4.4 Hz, 1H), 3.74 (dd, *J* = 10.0, 6.8 Hz, 1H), 3.43 (dd, *J* = 10.0, 7.2 Hz, 1H), 2.86 (quint, *J* = 6.8 Hz, 1H), 2.18 (sext., *J* = 6.0 Hz, 1H), 0.64 (d, *J* = 7.2 Hz, 3H); NOE-diff. experiment: proton irradiated, (NOEs observed): H-2 (H_a-1, H_b-1, H-3, H-5, H_3-7), H-3 (H_b-1, H-2, H-4, H_3-7), H-4 (H-3, H-5, H_3-7), H-5 (H_a-1, H-2, H-4, H_3-7), H_3-7 (H_a-1, H-3, H-4, H-5); ^{13}C NMR (125 MHz, $CDCl_3$; DEPT) δ (ppm): 142.1 (C), 134.6 (CH), 132.5 (CH), 128.8 (CH), 128.3 (CH), 127.4 (CH), 127.2 (CH), 126.3 (CH), 117.4 (CH_2), 70.2 (CH), 51.9 (CH_2), 47.2 (CH), 44.3 (CH), 13.5 (CH_3). (One carbon signal was not observed). Minor diastereomer: ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.11-4.19 (m, 1H), 3.98-3.95 (m, 1H), 3.35 (t, *J* = 11.6 Hz, 1H), 0.86 (d, *J* = 6.4, 3H); NOE-dif. experiment: proton irradiated, (NOEs observed): H_3-7 (H-2, H-4); ESHRMS calcd. for $C_{19}H_{22}NO_2S$ *m/z* 328.1365, found *m/z* 328.1371.

Compound 40.



^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 5.69 (dt, *J* = 17.0, 10.0 Hz, 1H), 4.99 (d, *J* = 10.0 Hz, 1H), 4.97 (d, *J* = 17.0 Hz, 1H), 3.90 (dd, *J* = 8.5, 7.0 Hz, 1H), 3.53 (dd, *J* = 8.5, 5.6 Hz, 1H), 3.37 (dt, *J* = 7.4, 3.6 Hz, 1H), 2.74 (quint, *J* = 6.9 Hz, 1H), 1.85 (sext., *J* = 7.2 Hz, 1H), 1.45-1.36 (m, 2H), 1.21-1.19 (m, 14H), 0.84 (d, *J* = 7.0 Hz, 3H), 0.81 (t, *J* = 6.9 Hz, 3H); NOE-diff. experiment: proton irradiated, (NOEs observed): H_b-1 (H-2, H-3), H-2 (H_a-1, H_b-1, H-3, H_3-7, H-5), H-3 (H_b-1, H-2, H-4, H_3-7), H-4 (H_a-1, H-3, H-5, H_3-7), H-5 (H_a-1, H-2, H-4, H_3-7), H_2-6 (H_a-1, H_b-1, H-2, H_3-7); ^{13}C NMR (125 MHz, $CDCl_3$; DEPT) δ (ppm): 135.8 (CH), 115.1 (CH_2), 84.4 (CH), 70.6 (CH_2), 46.7 (CH), 41.2 (CH), 33.8 (CH_2), 30.8 (CH_2), 28.8 (CH_2), 28.6 (CH_2), 28.5 (CH_2), 28.3 (CH_2), 25.4 (CH_2), 21.6 (CH_2), 13.0 (CH_3), 12.5 (CH_3); ESHRMS calcd. for $C_{16}H_{31}O$ *m/z* 239.2369, found *m/z* 239.2369.

Wurtz-type coupling of farnesyl ethyl carbonate



Farnesyl ethyl carbonate

squalene

Synthesis of farnesyl ethyl carbonate. It was prepared from farnesyl alcohol according to previously described general procedure. The compound was isolated by flash chromatography (EtOAc/Hexane, 5/95) to give farnesyl ethyl carbonate in a 92 % yield as colourless oil and the spectroscopic data were identical to the reported compound.[21]

Synthesis of squalene. Rigorously deoxygenated THF (20 mL) was added to a mixture of Cp_2TiCl_2 (11 mg, 0.04 mmol), $PdCl_2$ (15 mg, 0.08 mmol), PPh_3 (44 mg, 0.17 mmol) and Mn dust (186 mg, 3.3 mmol) under Ar atmosphere, and the suspension was stirred at room temperature until it turned dark green (about 15 min). A solution of farnesyl ethyl carbonate (125 mg, 0.4 mmol), 2,4,6-collidine (358 mg, 2.9 mmol) and Me_3SiCl (184 mg, 1.6 mmol) in THF (2 mL) was then added. The mixture was stirred for 16 h and then diluted with AcOEt, washed with brine, dried over anhydrous $MgSO_4$ and the solvent removed. The residue was submitted to flash chromatography (Hexane) to give squalene (53 mg, 60 %) as colourless oil. Its spectroscopic data were identical to the reported compound.[22]

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[21] E. Bemochi, S. Cacchi, E. Morera, G. Ortar. *Synlett* **1992**, 161-164.

[22] Pure samples of squalene for comparison were obtained from a commercial source.