116. α,α-Disubstituted Allyl Sulfones: An Approach to the Synthesis of Vinyl-Branched Pheromone Analogues

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The two-step alkylation of phenyl prop-2-enyl sulfone (**1**) with protected ω-bromoalkanols and 1-iodoalkanes (→ **3**; see *Scheme 1*) followed by a Pd-catalyzed desulfonylation with $LiBH_4$ affords a 96:4 mixture of vinyl-branched, protected alcohols and corresponding ethylidene-branched isomers (see *Scheme 2*; **4** and **5**, respectively). By utilizing the large difference in reactivity of mono- and trisubstituted C=C bonds towards singlet oxygen, the ethylidene derivatives are easily removed from the mixture by photo-oxygenation. The vinyl-branched compounds are inert to this reaction and can be conveniently isolated in highly pure form (99.5%) and *ca.* 45% overall yield.

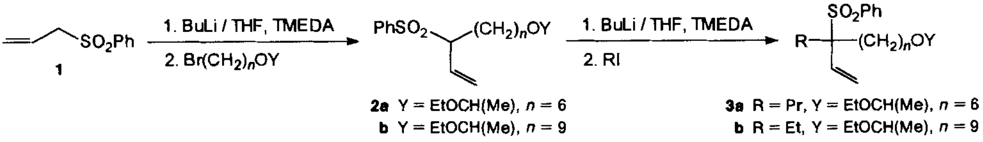
Racemic 7-propylnon-8-en-1-yl acetate (**8a**; *Scheme 2*) was recently found to effectively disrupt the pheromone-mediated attraction of the false codling moth *Cryptophlebia leucotreta* (Lepidoptera) to virgin females or to synthetic lures [1]. This compound was isolated by prep. GC as an impurity in the commercial synthesis of the actual pheromone, which is a blend [2] of (*E*)- and (*Z*)-dodec-8-enyl acetates in a 1:1 ratio. Note that both the total number of C-atoms (12) and the position of the C=C bond at C(8) are the same in analog **8a** as in the actual pheromone components. The mode of action of **8a** and its inhibitory threshold have not been determined so far. Further, it might be advisable to know if the vinyl-branched analogues of other lepidopteran pheromones could similarly act as inhibitors of the pheromone-mediated insect attraction.

Since it appeared that the access to vinyl-branched pheromone analogues might provide further insight into the structure-activity relationships within the insect chemoreception, we examined a new synthetic strategy that would potentially lead to a variety of different analogues. We sought for a general synthesis that would lead quantities on the gram scale required for extensive behavioral tests. Detailed herein is the synthesis of two vinyl-branched compounds **8a** and **8b**. While the former compound represents a branched analog of (*E*)/(*Z*)-dodec-8-enyl acetate (a pheromone component of *Cryptophlebia leucotreta* [2] and *Cydia molesta* [3]), the latter compound is derived from (*E*)/(*Z*)-tetradec-11-enyl acetate (a pheromone component [4] of *Ostrinia nubilalis* and many other pests).

Our strategy illustrated in *Schemes 1* and *2* was generally based on the chemistry of allyl sulfones. The key step was the generation of allyl sulfonyl carbanions [5] [6] from allyl phenyl sulfone (**1**) and their reactions with haloalkanes, leading to the formation of new C–C bonds. Sulfone **1** was conveniently prepared by the reaction of allyl bromide with sodium benzenesulfinate according to the procedure described in [7].

Thus, the α,α-dialkylated allyl sulfones **3** were generally synthesized by treating sulfone **1** with 1.1 equiv. of BuLi in THF/*N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) at −60 to 0°, followed by reaction with an appropriate alkylating agent (*Scheme 1*). Typically, **1** was first reacted with a protected bromoalcohol (6-bromohexan-1-ol or 9-bromononan-1-ol) and the obtained monoalkylated derivatives **2a**, **b** alkylated with 1-iodopropane or 1-iodoethane to produce the dialkylated sulfones **3a**, **b** in *ca.* 57% yield (with respect to **1**).

Scheme 1

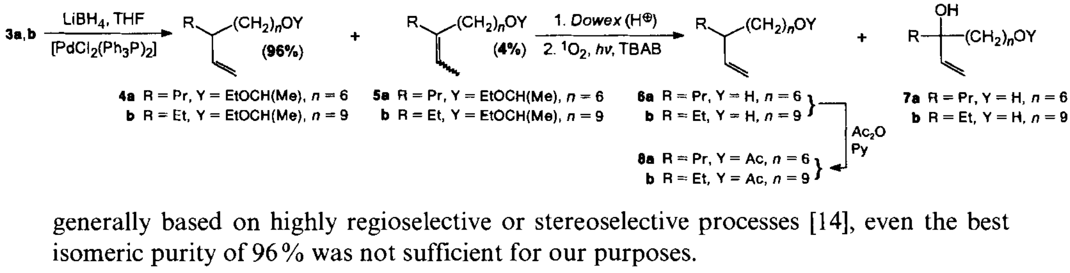


2a Y = EtOCH(Me), n = 6
b Y = EtOCH(Me), n = 9

3a R = Pr, Y = EtOCH(Me), n = 6
b R = Et, Y = EtOCH(Me), n = 9

For the reductive removal of the PhSO$_2$ group, a large variety of reagents are available [8]. Sodium amalgam either in alcohol or buffered with anhydrous Na$_2$HPO$_4$ is most frequently employed, among other electron-transfer reagents such as aluminium amalgam in aqueous THF, *Grignard* reagents with Ni or Pd catalysts, Li in aliphatic amines [9], and Na or Mg in alcohols [10]. The excellent ability of low-valent Pd complexes to facilitate the displacement of the PhSO$_2$ group at an allylic position by a hydride ion as nucleophile is also well documented [11] [12]. This reaction may proceed *via* a π-allyl intermediate and, as a consequence, the hydride transfer may occur either at the α- or the γ-position yielding a regioisomer mixture. However, by this method, for the generation of terminal olefins, having the C=C bond either stabilized by conjugation with a Ph group or disubstituted with Me groups or else for β-tosyl homoallylic alcohols, desulfonylation occurred without any migration of the C=C bond [12] [13]. In our hands, attempts to prepare isomerically pure terminal olefins from the dialkylated sulfones **3a**, **b** by this way failed. Depending on the reaction conditions examined (reducing agents: NaBH$_4$, LiBH$_4$, LiBHEt$_3$, HCO$_2$NH$_4$; catalyst: [Pd(PPh$_3$)$_4$] or [PdCl$_2$(PPh$_3$)$_2$]), terminal olefins were obtained in only *ca.* 60–96% selectivity. The combination [PdCl$_2$(PPh$_3$)$_2$]/LiBH$_4$ at −60° proved to be the best one, affording an unseparable 96:4 mixture of vinyl- and ethylidene-branched compounds **4** and **5** (*Scheme 2*). However, as the mode of pheromonal action is generally based on highly regioselective or stereoselective processes [14], even the best isomeric purity of 96% was not sufficient for our purposes.

Scheme 2



4a R = Pr, Y = EtOCH(Me), n = 6
b R = Et, Y = EtOCH(Me), n = 9

5a R = Pr, Y = EtOCH(Me), n = 6
b R = Et, Y = EtOCH(Me), n = 9

6a R = Pr, Y = H, n = 6
b R = Et, Y = H, n = 9

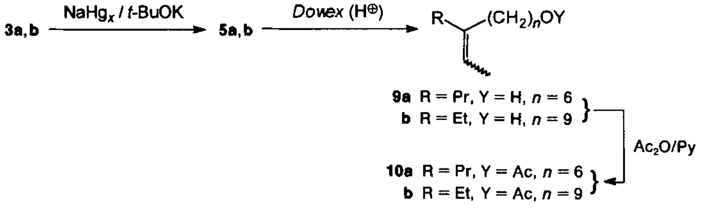
8a R = Pr, Y = Ac, n = 6
b R = Et, Y = Ac, n = 9

7a R = Pr, Y = H, n = 6
b R = Et, Y = H, n = 9

Since a large difference in reactivity towards singlet oxygen should exist [15] between compounds **4** (monosubstituted C=C bond) and **5** (trisubstituted C=C bond), we employed the singlet photo-oxygenation to achieve their separation. Thus, the alcohol mixture, obtained by deprotection with *Dowex* (H^+ form) from **4a**/**5a** 96:4, was photo-oxygenated by the method of simultaneous oxidation and reduction [16], *i.e.* in the presence of $(Bu_4N)BH_4$ (TBAH), using Bu_4N-solubilized *Rose Bengal* as sensitizer and $CHCl_3$ as solvent. In a clean reaction and under total conversion (GC) of the ethylidene-branched alcohol derived from **5a**, diol **7a** was obtained and identified by ^1H- and ^{13}C-NMR. The formation of this tertiary alcohol was anticipated, as it is known [17] that $^1O_2$ prefers to react with trisubstituted olefins on the more crowded side (*syn*-addition). In contrast, the vinyl-branched alcohol **6a** derived from **4a** remained intact and could be conveniently isolated in highly pure form ($>$ 99.5 by cap. GC). The loss of material associated with this procedure only amounted to some 5–10%. No attempt was made to isolate **7b** from the mixture **6b**/**7b** obtained similarly from **4b**/**5b**. The overall yields of the desired vinyl-branched alcohols **6a** and **6b** were 42 and 45%, respectively. Subsequent acetylation of **6a** and **6b** yielded the target compounds **8a** and **8b**, respectively.

Another, synthetically also interesting transformation of the disubstituted allyl sulfones **3** consists in the desulfonylation to produce pure ethylidene isomers. It is known [18] that α-monoalkylated β,γ-unsaturated phenyl sulfones are easily isomerized to α,β-unsaturated derivatives with a catalytic amount of *t*-BuOK. This suggests a possible control of regioselective product formation *via* tandem desulfonylation/isomerization of the sulfones **3**. Indeed, exposure of **3a,b** to $NaHg_x$ and *t*-BuOK in dry MeOH at 0° resulted in a smooth one-pot conversion to the isomers **5a,b** in generally high yield (*ca.* 85%) and a purity exceeding 99% (*Scheme 3*). Subsequent deprotection with *Dowex* (H^+ form) and acetylation led *via* **9a,b** to **10a,b**, the double-bond isomers of **8a,b**.

Scheme 3



In conclusion, the α,α-disubstituted allyl sulfones are intermediates in the synthesis of racemic vinyl-branched alkanols. The two-step transformation includes a Pd-catalyzed reductive desulfonylation leading to a mixture of terminal and non-terminal olefins, and the removal of the latter from the mixture by photo-oxygenation; the method makes the difficult separation of vinyl and ethylidene isomers unnecessary. One of the attractive features of the α,α-disubstituted allyl sulfones is that they may alternatively provide pure ethylidene isomers when using sodium amalgam/*t*-BuOK in the desulfonylation step.

Although this approach is primarily connected with pheromone research, its scope is by no means restricted only to this area.

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Experimental Part

General. GLC: *Hewlett-Packard-HP-5880A* chromatograph, FID detector; 25-m capillary column (internal diameter 0.3 mm, *HP5*-5% phenyl methylsilicone, cross-linked). Prep. medium-pressure liquid chromatography (MPLC): *Merck 60* silica gel (0.040–0.063 mm); *Büchi-B-680-Prep-LC* system with stepwise gradient of Et_2O in light petroleum ether. ^1H- and ^{13}C-NMR Spectra: $CDCl_3$ solns.; *Varian Unity-500* spectrometer, operating at 499.5 MHz; chemical shifts δ in ppm rel. to TMS; data in *Tables 1–3*.

9-(1-Ethoxyethoxy)-3-(phenylsulfonyl)non-1-ene (**2a**). To a stirred soln. of dry THF (240 ml), TMEDA (10.5 g, 90 mmol), and phenyl prop-2-enyl sulfone (**1**; 16.4 g, 90 mmol) under Ar, BuLi (2.5M in hexanes; 38 ml, 96 mmol) was added over 15 min at –60°. After 1 h, 1-bromo-6-(1-ethoxyethoxy)hexane (23.0 g, 90 mmol) was added and stirring continued at –60° for 3 h. The temp. was raised to 0° and the mixture poured into ice-water and extracted with Et_2O (3 × 150 ml). After washing with brine, drying (K_2CO_3), and evaporating, **2a** was isolated by prep. MPLC: 23.3 g (73%). Anal. calc. for $C_{19}H_{30}O_4S$ (354.5): C 64.4, H 8.5, S 9.0; found: C 64.2, H 8.3, S 8.9.

12-(1-Ethoxyethoxy)-3-(phenylsulfonyl)dodec-1-ene (**2b**) was synthesized analogously from **1** (25.2 g, 138 mmol), BuLi (2.5M; 58 ml, 145 mmol), and 1-bromo-9-(1-ethoxyethoxy)nonane (40.8 g, 138 mmol): 41.3 g (74%). Anal. calc. for $C_{22}H_{36}O_4S$ (396.6): C 66.6, H 9.2, S 8.1; found: C 66.8, H 9.3, S 8.0.

9-(1-Ethoxyethoxy)-3-(phenylsulfonyl)-3-propylnon-3-ene (**3a**). BuLi (2.5M in hexanes; 8.8 ml, 22 mmol) was added dropwise (15 min), under Ar, to a stirred and cooled (–60°) soln. of **2a** (7.14 g, 20 mmol) and TMEDA (2.3 g, 20 mmol) in dry THF (70 ml). After 1 h, PrI (3.7 g, 22 mmol) was added and stirring continued at –60° for 3 h. Then, the reaction mixture was quenched with ice-cold H_2O (500 ml) and extracted with Et_2O (3 × 100 ml). The combined Et_2O extract was washed with H_2O and brine, dried (K_2CO_3), and evaporated and the residue purified by prep. MPLC: 6.3 g (79%) of **3a**. Anal. calc. for $C_{22}H_{36}O_4S$ (396.6): C 66.6, H 9.2, S 8.1; found: C 66.3, H 9.1, S 7.9.

12-(1-Ethoxyethoxy)-3-ethyl-3-(phenylsulfonyl)dodec-1-ene (**3b**). In the same manner as described above, **2b** (7.93 g, 20 mmol) was alkylated with EtI (3.4 g, 22 mmol): 6.5 g (76%) of **3b**. Anal. calc. for $C_{24}H_{40}O_4S$ (424.6): C 67.9, H 9.5, S 7.6; found: C 68.1, H 9.4, S 7.4.

7-Propylnon-8-en-1-ol (**6a**) *and 7-Propylnon-8-ene-1,7-diol* (**7a**). A soln. of $[PdCl_2(PPh_3)_2]$ (175 mg, 0.25 mmol) in dry THF (10 ml) was added dropwise, under Ar, to a stirred and cooled (–60°) soln. of **3a** (2.00 g, 5.04 mmol) and $LiBH_4$ (540 mg, 25.0 mmol) in dry THF (25 ml). The mixture was stirred for 8 h at r.t. Then, the reaction mixture was quenched with ice-cold H_2O (100 ml) and extracted with Et_2O (3 × 50 ml). The combined Et_2O extract was washed with H_2O and brine, dried (K_2CO_3), and evaporated and the residue purified by prep. MPLC: 1.15 g (90%) of **4a**/**5a** 96:4 (GLC and ^1H-NMR). This mixture was dissolved in MeOH (50 ml) and stirred with *Dowex 50W* (H^+ form; 1 g) for 24 h. The ion exchanger was filtered off, the solvent evaporated, and the residue mixed with a stock soln. of Bu_4N-solubilized *Rose Bengal* in $CHCl_3$ (250 ml) and irradiated with a constant flow of O_2 bubbling through the soln. using a *Hanau* 150-W high-pressure Hg lamp in a commercial quartz-glass photoreactor (*Normag*). At 0, 15, and 45 min of irradiation, 1.42 g (5.8 mmol) of $(Bu_4N)BH_4$ was added in 3 portions. After 60 min of irradiation, the $CHCl_3$ was evaporated. Et_2O (50 ml) and KI (1 g) dissolved in a minimum amount of H_2O were added with stirring to precipitate Bu_4NI. After 30 min, the solids were filtered and washed with Et_2O. The Et_2O layer was dried ($MgSO_4$) and evaporated and the residue separated by prep. MPLC: 758 mg (82%) of **6a** and 32 mg of **7a**. **6a**: Anal. calc. for $C_{12}H_{24}O$ (184.3): C 78.2, H 13.1; found: C 78.0, H 13.3. **7a**: Anal. calc. for $C_{12}H_{24}O_2$ (200.3): C 72.0, H 12.1; found: C 72.1, H 12.2.

10-Ethyldodec-11-en-1-ol (**6b**) was synthesized analogously from **3b** (2.0 g, 4.7 mmol), $LiBH_4$ (510 mg, 23.5 mmol), and $[PdCl_2(PPh_3)_2]$ (175 mg, 0.25 mmol): 907 mg (80%). Anal. calc. for $C_{14}H_{28}O$ (212.4): C 79.2, H 13.3; found: C 79.0, H 13.2.

7-Propylnon-7-en-1-ol (**9a**). Sodium amalgam (2.5%; 22 g) and *t*-BuOK (150 mg) were added to a cooled (0°) soln. of **3a** (2.2 g, 5.57 mmol) and anh. NaH_2PO_4 (2.64 g, 22 mmol) in dry MeOH (70 ml). After stirring for 2 h, the mixture was decomposed by H_2O (250 ml) and extracted with Et_2O (3 × 80 ml). The combined extract was washed with H_2O and brine, dried (K_2CO_3), and evaporated: 1.5 g of **5a**. The yellow oil was dissolved in MeOH (50 ml) and treated with *Dowex 50W* (H^+ form; 1.5 g) for 24 h. The ion exchanger was filtered off and MeOH evaporated. Purification of the residue by prep. MPLC gave 0.87 g (85%) of **9a**. Anal. calc. for $C_{12}H_{24}O$ (184.3): C 78.2, H 13.1; found: C 78.3, H 13.0.

10-Ethyldodec-10-en-1-ol (**9b**) was synthesized analogously from **3b** (1.5 g, 3.5 mmol), sodium amalgam (2.5%; 15 g), and *t*-BuOK (100 mg): 650 mg (87.5%). Anal. calc. for $C_{14}H_{28}O$ (212.21): C 79.2, H 13.3; found: C 79.4, H 13.5.

7-Propylnon-8-en-1-yl Acetate (**8a**), *10-Ethyldodec-11-en-1-yl Acetate* (**8b**), *7-Propylnon-7-en-1-yl Acetate* (**10a**), *and 10-Ethyldodec-10-en-1-yl Acetate* (**10b**). A typical procedure was as follows: alcohol **6a** (500 mg, 2.71

Table 1. *^{1}H-NMR Parameters of Compounds* **2a–10a**[a]). For convenience, **3a–10a** are all numbered as **2a**: $CH_2(1)=CHCH(PhSO_2)(CH_2)_5CH_2(9)OY$ (**2a**).

	2a[b])	**3a**[c])	**4a**[d])	**5a**[e])	**6a**	**7a**	**8a**[f])	**9a**	**10a**[g])
$CH_2(9)$	3.30–3.70 (*m*)	3.40 (*dt*, J = 9.3, 6.6) 3.56 (*dt*, J = 9.3, 6.7)	3.46 (*dt*, J = 9.3, 7.1) 3.56 (*dt*, J = 9.3, 7.1)	3.41 (*dt*, J = 9.3, 6.6) 3.56 (*dt*, J = 9.3, 6.6)	3.64 (*dt*, J = 6.7)	3.64 (*dt*, J = 6.6)	4.05 (*t*, J = 6.8)	3.64 (*dt*, J = 6.6)	4.05 (*t*, J = 7.0)[h])
$CH_2(5)$ to $CH_2(8)$	1.20–1.53 (*m*)	1.30–1.73 (*m*)	1.16–1.70 (*m*)	1.10–1.60 (*m*)	1.16–1.56 (*m*)	1.18–1.66 (*m*)	1.15–1.75 (*m*)	1.19–1.78 (*m*)	1.20–1.75 (*m*)
$CH_2(4)$	1.20–1.53 (*m*)	1.30–1.73 (*m*)	1.16–1.70 (*m*)	1.97 (*m*)	1.16–1.56 (*m*)	1.18–1.66 (*m*)	1.15–1.75 (*m*)	1.94 (*m*)	1.98 (*m*)
$CH_2(3)$	3.30–3.70 (*m*)	–	1.95 (*m*)	–	1.94 (*m*)	–	2.05 (*m*)	–	–
$CH_2(2)$	5.61 (*ddd*, J = 9.2, 10.2, 17.1)	5.77 (*dd*, J = 11.0, 17.6)	5.51 (*ddd*, J = 8.8, 11.0, 16.3)	5.19 (br. *q*, J = 6.6)[h])	5.51 (*ddd*, J = 8.8, 10.2, 16.8)	5.79 (*dd*, J = 11.0, 17.8)	5.52 (*ddd*, J = 8.8, 10.2, 17.1)	5.19 (br. *q*, J = 6.6)	5.20 (br. *q*, J = 6.6)[h])
2 H–C(1) or Me(1)	5.02 (*ddd*, J = 0.7, 1.2, 17.1) 5.28 (*dd*, J = 1.2, 10.2)	4.98 (*d*, J = 17.6) 5.31 (*d*, J = 11.0)	4.91 (*dd*, J = 0.7, 16.3) 4.91 (*dd*, J = 2.1, 11.0)	1.57 (br. *q*, J = 6.6)	4.92 (*ddd*, J = 0.8, 2.2, 16.8) 4.94 (*dd*, J = 2.2, 10.2)	5.19 (*dd*, J = 1.2, 17.8) 5.24 (*dd*, J = 1.2, 11.0)	4.90 (*ddd*, J = 0.8, 2.3, 17.4) 4.97 (*dd*, J = 2.3, 11.0)	–	–
$MeCH_2C\mathit{H}_2–C(3)$	–	1.30–1.73 (*m*)	1.16–1.70 (*m*)	1.97 (*m*)	1.16–1.56 (*m*)	1.18–1.66 (*m*)	1.15–1.75 (*m*)	1.98 (*m*)	1.98 (*m*)
$MeC\mathit{H}_2CH_2–C(3)$	–	1.30–1.73 (*m*)	1.16–1.70 (*m*)	1.10–1.60 (*m*)	1.16–1.56 (*m*)	1.18–1.66 (*m*)	1.15–1.75 (*m*)	1.19–1.78 (*m*)	1.20–1.75 (*m*)
$\mathit{Me}CH_2CH_2–C(3)$	–	0.93 (*t*, J = 7.3)	0.87 (*t*, J = 6.5)	0.86 (*t*, J = 7.1) 0.89 (*t*, J = 7.1)	0.87 (*t*, J = 6.3)	0.92 (*t*, J = 7.3)	0.87 (*t*, J = 6.8)	0.87 (*t*, J = 7.4) 0.88 (*t*, J = 7.4)	0.87 (*t*, J = 7.3) 0.89 (*t*, J = 7.3)

[a]) In $CDCl_3$, TMS as internal standard, chemical shifts δ in ppm, coupling constants J in Hz.

[b]) EtOC*H*(Me): 4.66 (*q*, J = 5.4); 3.30–3.70 (*m*); 1.20 (*t*, J = 7.1); 1.30 (*d*, J = 5.4). SO_2Ph: 7.48–7.69 (*m*); 7.80–7.88 (*m*).

[c]) EtOCH(Me): 4.68 (*q*, J = 5.4); 3.48 (*dq*, J = 9.3, 7.1); 3.65 (*dq*, J = 9.3, 7.1); 3.65 (*dq*, J = 9.3, 7.1); 1.21 (*t*, J = 7.1); 1.31 (*d*, J = 5.4). SO_2Ph: 7.50–7.77 (*m*).

[d]) EtOCH(Me): 4.68 (*q*, J = 5.4); 3.48 (*dq*, J = 9.3, 7.1); 3.63 (*dq*, J = 9.3, 7.1); 1.21 (*t*, J = 7.1); 1.31 (*d*, J = 5.4).

[e]) EtOCH(Me): 4.68 (*q*, J = 5.4); 3.48 (*dq*, J = 9.3, 7.1); 3.65 (*dq*, J = 9.3, 7.1); 1.21 (*t*, J = 7.1); 1.31 (*d*, J = 5.4).

[f]) Ac: 2.04 (*s*).

[g]) Ac: 2.05 (*s*).

[h]) Observed signals were doubled.

Table 2. *^{1}H-NMR Parameters of Compounds* **2a–10b**[a]). For convenience, **3b–6b** and **8b–10b** are all numbered as **2b**: $CH_2(1){=}CHCH(PhSO_2)(CH_2)_8CH_2(12)OY$ (**2b**).

	2b[b])	**3b**[c])	**4b**[d])	**5b**[e])	**6b**	**8b**[f])	**9b**	**10b**[g])
$CH_2(12)$	3.40 (*dt*, $J = 9.3, 6.6$) 3.54 (*dt*, $J = 9.3, 6.6$)	3.41 (*dt*, $J = 9.3, 6.6$) 3.56 (*dt*, $J = 9.3, 6.6$)	3.44 (*dt*, $J = 9.3, 6.6$) 3.55 (*dt*, $J = 9.3, 6.6$)	3.43 (*dt*, $J = 9.3, 6.6$) 3.56 (*dt*, $J = 9.3, 6.6$)	3.64 (*dt*, $J = 6.6$)	4.05 (*t*, $J = 6.6$)	3.64 (*dt*, $J = 6.6$)	4.05 (*t*, $J = 6.8$)[h])
$CH_2(5)$ to $CH_2(11)$	1.12–1.81 (*m*)	1.17–1.81 (*m*)	1.13–1.58 (*m*)	1.12–1.64 (*m*)	1.13–1.62 (*m*)	1.16–1.48 (*m*)	1.18–1.39 (*m*)	1.22–1.40 (*m*)
$CH_2(4)$	1.12–1.81 (*m*)	1.98 (*m*)	1.13–1.58 (*m*)	1.98 (*m*)	1.13–1.62 (*m*)	1.16–1.48 (*m*)	1.97 (*m*)	1.97 (*m*)
$CH_2(3)$	3.30–3.45 (*m*)	–	1.82 (*m*)	–	1.83 (*m*)	1.83 (*m*)	–	–
$CH_2(2)$	5.61 (*ddd*, $J = 9.1, 10.1, 16.9$)	5.76 (*dd*, $J = 10.7, 17.6$)	5.52 (*ddd*, $J = 8.5, 10.7, 16.8$)	5.17 (br. *q*, $J = 6.6$)[h])	5.52 (*ddd*, $J = 8.8, 10.8, 16.4$)	5.51 (*ddd*, $J = 8.8, 10.2, 17.1$)	5.15 (br. *q*, $J = 6.6$) 5.18 (br. *q*, $J = 6.6$)	5.15 (br. *q*, $J = 6.6$) 5.19 (br. *q*, $J = 6.6$)
2 H–C(1) or Me(1)	5.02 (*ddd*, $J = 0.8, 1.2, 16.9$) 5.28 (*dd*, $J = 1.2, 10.1$)	4.99 (*d*, $J = 17.6$) 5.32 (*d*, $J = 10.7$)	4.76 (*ddd*, $J = 0.9, 2.1, 16.8$) 4.96 (*dd*, $J = 2.1, 10.7$)	1.57 (br. *q*, $J = 6.6$)	4.93 (*ddd*, $J = 0.8, 2.1, 16.4$) 4.96 (*dd*, $J = 2.1, 10.8$)	4.93 (*ddd*, $J = 0.8, 2.1, 17.1$) 4.96 (*dd*, $J = 2.1, 10.1$)	1.58 (br. *q*, $J = 6.6$)[h]) –	1.58 (*dt*, $J = 6.6, 1.2$) –
$MeCH_2$–C(3)	–	1.77 (*dq*, $J = 12.5, 7.5$) 2.00 (*dq*, $J = 12.5, 7.5$)	2.00 (*m*, $J = 7.4$)	2.00 (*m*, $J = 7.4$)	1.83 (*m*)	1.16–1.48 (*m*)	2.02 (br. *q*, $J = 7.5$)	2.02 (br. *q*, $J = 7.5$)
$MeCH_2$–C(3)	–	1.02 (*t*, $J = 7.5$)	0.84 (*t*, $J = 7.4$)	0.95 (*t*, $J = 7.4$) 0.97 (*t*, $J = 7.4$)	0.84 (*t*, $J = 7.3$)	0.84 (*t*, $J = 7.4$)	0.95 (*t*, $J = 7.5$) 0.97 (*t*, $J = 7.5$)	0.95 (*t*, $J = 7.5$) 0.97 (*t*, $J = 7.5$)

[a]) In $CDCl_3$, TMS as internal standard, chemical shifts δ in ppm, coupling constants J in Hz.

[b]) EtOC*H*(Me): 4.68 (*q*, $J = 5.3$); 3.47 (*dq*, $J = 9.4, 7.1$); 3.65 (*dq*, $J = 9.4, 7.1$); 1.20 (*t*, $J = 7.1$); 1.30 (*d*, $J = 5.3$). SO_2Ph: 7.48–7.69 (*m*); 7.80–7.88 (*m*).

[c]) EtOC*H*(Me): 4.68 (*q*, $J = 5.3$); 3.48 (*dq*, $J = 9.3, 7.1$); 3.65 (*dq*, $J = 9.3, 7.1$); 1.21 (*t*, $J = 7.1$); 1.31 (*d*, $J = 5.3$). SO_2Ph: 7.47–7.52 (*m*); 7.59–7.63 (*m*); 7.76–7.80 (*m*).

[d]) EtOC*H*(Me): 4.68 (*q*, $J = 5.4$); 3.48 (*dq*, $J = 9.3, 7.1$); 3.63 (*dq*, $J = 9.3, 7.1$); 1.20 (*t*, $J = 7.1$); 1.31 (*d*, $J = 5.4$).

[e]) EtOC*H*(Me): 4.68 (*q*, $J = 5.3$); 3.48 (*dq*, $J = 9.3, 7.1$); 3.65 (*dq*, $J = 9.3, 7.1$); 1.21 (*t*, $J = 7.1$); 1.30 (*d*, $J = 5.3$).

[f]) Ac: 2.04 (*s*).

[g]) Ac: 2.05 (*s*).

[h]) Observed signals were doubled.

Table 3. *^{13}C-NMR Chemical Shifts* [ppm] *of Compounds* **8a**, **10a**, **8b**, *and* **10b**. For numbering, see *Tables 1* and *2*.

	8a	**10a**	**8b**	**10b**
C(12)	–	–	64.66 (*t*)	64.69 (*t*)
C(11)	–	–	28.60 (*t*)	29.49 (*t*)
C(10)	–	–	25.89 (*t*)	28.13 (*t*)
C(9)	64.65 (*t*)	64.64 (*t*)	29.73 (*t*)	29.73 (*t*)
C(8)	28.59 (*t*)	29.50 (*t*)	29.52 (*t*)	29.51 (*t*)
C(7)	25.88 (*t*)	29.31 (*t*)	29.50 (*t*)	29.62 (*t*)
C(6)	29.35 (*t*)	25.83 (*t*); 25.88 (*t*)	29.24 (*t*)	29.26 (*t*)
C(5)	27.02 (*t*)	28.03 (*t*); 28.08 (*t*)	27.16 (*t*)	28.61 (*t*)
C(4)	34.90 (*t*)	36.83 (*t*)	34.63 (*t*)	36.67 (*t*)
C(3)	43.80 (*d*)	140.16 (*s*)	45.79 (*d*)	142.13 (*s*)
C(2)	143.54 (*d*)	118.36 (*d*); 118.44 (*d*)	143.37 (*d*)	116.92 (*d*); 117.48 (*d*)
C(1)	113.86 (*t*)	13.16 (*q*); 13.17 (*q*)	113.99 (*t*)	12.85 (*q*); 12.88 (*q*)
Pr–C(3)	37.29 (*t*); 20.23 (*t*); 14.15 (*q*)	39.15 (*t*); 21.28 (*t*); 21.28 (*t*); 13.91 (*q*); 14.12 (*q*)	–	–
Et–C(3)	–	–	27.67 (*t*); 11.62 (*q*)	29.82 (*t*); 13.00 (*q*); 13.16 (*q*)
AcO	171.24 (*s*); 21.02 (*q*)	171.24 (*s*); 20.99 (*q*)	171.25 (*s*); 21.02 (*q*)	171.28 (*s*); 21.03 (*q*)

mmol) was added to Ac_2O (1.33 g, 13 mmol), pyridine (2.04 g, 23 mmol), and 4-(dimethylamino)pyridine (25 mg) at −10° and left in the refrigerator overnight. The mixture was then poured into ice-cold H_2O, extracted with Et_2O, and chromatographed (prep. MPLC): almost quant. yield of pure (99.5% by GLC) **8a**. Anal. calc. for $C_{14}H_{26}O_2$ (**1a**; 226.4): C 74.3, H 11.6; found: C 74.4, H 11.6. **8b**: Anal. calc. for $C_{16}H_{30}O_2$ (254.4): C 75.5, H 11.9; found: C 75.7, H12.0. **10a**: Anal. calc. for $C_{14}H_{26}O_2$ (226.4): C 74.3, H 11.6; found: C 74.1, H 11.4. **10b**: Anal. calc. for $C_{16}H_{30}O_2$ (254.4): C 75.5, H 11.9; found: C 75.3, H 11.8.

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