Polarity Matching of Radical Trapping: High Yielding 3-*exo* and 4-*exo* Cyclizations

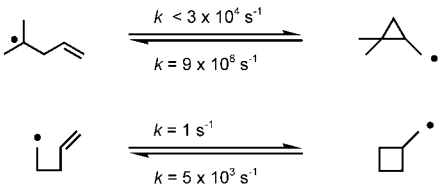
Andreas Gansäuer,* Thorsten Lauterbach, and Daniel Geich-Gimbel[a]

Abstract: A catalyzed synthesis of cyclopropanes and cyclobutanes via radical chemistry is described. The method that generally proceeds in high yields uses epoxides as radical precursors and titanocene(III) complexes as the electron transfer catalysts (see scheme). The key to the success of the transformation is constituted by the chemoselectivity of radical reduction. Electrophilic enol radicals generated through cyclization are reduced rapidly whereas their precursors, nucleophilic alkyl radicals, remain unaffected.

Keywords: cyclobutanes · cyclopropanes · epoxides · radical reactions · titanium

Introduction

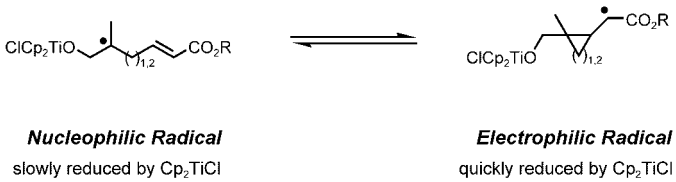
Radical cyclization reactions are amongst the most powerful and versatile methods for the construction of mono- and polycyclic systems.[1] However, the synthesis of small rings, that is, cyclopropanes, a highly interesting functional group under theoretical, preparative and structural aspects,[2] and cyclobutanes, is usually difficult. In the former case this is because ring openings of the intermediate cyclopropyl carbinyl radicals are amongst the fastest radical reactions known ($k \sim 10^8$–$10^9\ s^{-1}$)[3] and in the latter case, ring closure is one of the slowest radical reactions ($k \sim 1\ s^{-1}$) while ring opening of the cyclobutylcarbinyl radical is fast,[4] as shown in Scheme 1.



Scheme 1. Kinetics of the 3-*exo* and 4-*exo* cyclization.

In this publication we wish to report our first results on high yielding, catalytic, and tin free[5] radical syntheses of cyclopropanes and cyclobutanes circumventing these problems. The method is complementary to the concepts used in traditional free radical chemistry for the synthesis of small rings. In these cases the stabilization of the carbinyl radicals through conjugation and incorporation of some of the ring strain of the cyclopropanes into the starting materials have been utilized with good success.[6]

Our approach exploits the different and polarity controlled reactivity of alkyl radicals generated from epoxides[7,8] and enol radicals generated after cyclization towards [Cp_2TiCl], the electron transfer reagent used in this study. This allows both formation and trapping of the unstable carbinyl radicals as shown in Scheme 2.



Scheme 2. Polarity matching for radical trapping.

At first glance our approach may seem similar to the one employed by Fernández-Mateos in his elegant stoichiometric cyclization reactions of epoxide derived radicals to aldehydes and ketones[7e] or to nitriles.[7f] However, both reactions do not work under our catalytic conditions and must therefore be considered as conceptually different. While a detailed study on this discrepancy would have to be carried out to establish the differences, we suggest hydrogen atom abstraction from THF by the highly electrophilic and short-lived radicals generated under Fernández-Mateos' conditions as a plausible cause.[9] Catalyst regeneration would

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then become difficult. This is not the case under our conditions.

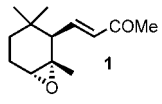
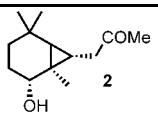
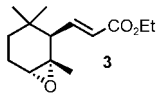
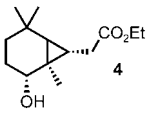
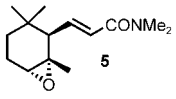
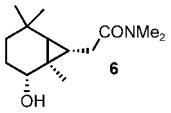
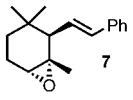
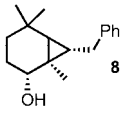
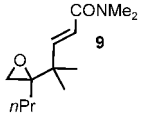
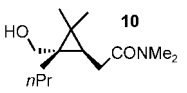
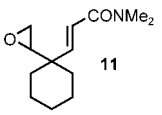
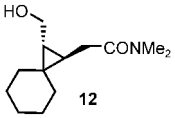
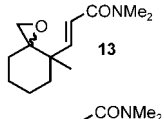
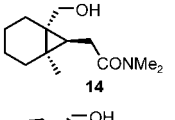
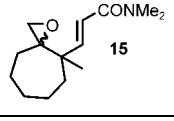
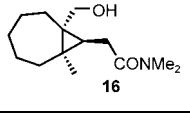
In free radical chain reactions polarity controlled transformations have been used with excellent success, for example, in Roberts' polarity reversed catalysis.[10]

Nucleophilic alkyl radicals generated through epoxide opening are only slowly reduced by [Cp_2TiCl]. Since no other radical pathway than cyclization is available under our reaction conditions they remain fairly stable. This results in increased longevity that is decisive for the very slow formation of the cyclobutyl carbinyl radicals in the 4-*exo* cyclization. The unfavorable equilibrium for the formation of both rings is therefore irrelevant if the radicals generated through cyclization are reduced efficiently. The swift and exothermic trapping of the electrophilic enol radical to yield titanium enolates provides this desired electronic differentiation and thus a driving force for irreversible termination of small ring formation.

Results and Discussion

We decided to check the validity of the concept for 3-*exo* cyclizations first to avoid anticipated problems of the very slow 4-*exo* cyclization. The results summarized in Table 1 amply demonstrate the validity of our approach.

Table 1. Titanocene catalyzed 3-*exo* cyclizations.[10] For reasons of clarity only the major isomer is shown.

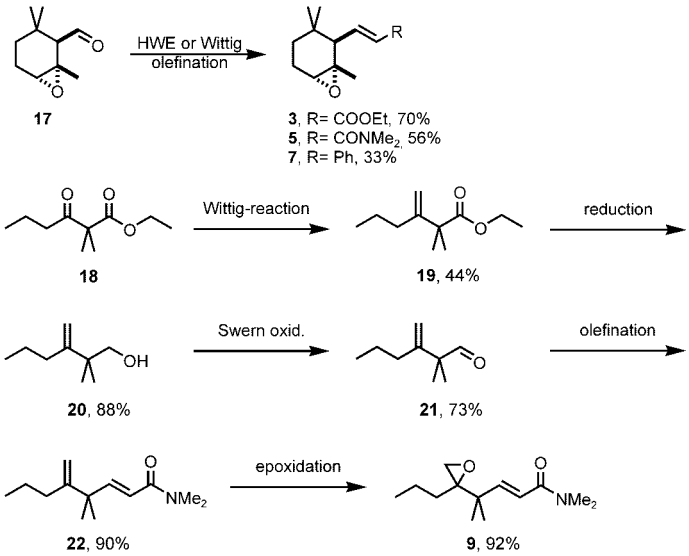
Entry	Substrate	Product	Yield [%]
1	 **1**	 **2**	72
2	 **3**	 **4**	92
3	 **5**	 **6**	96
4	 **7**	 **8**	<10
5	 **9**	 **10**	95, *dr* 63:37
6	 **11**	 **12**	88, *dr* 81:19
7	 **13**	 **14**	72, *dr* 75:25
8	 **15**	 **16**	84, *dr* 75:25

With the β-ionone derived epoxides **1**, **3**, and **5** good to excellent yields of the desired cyclopropanes were achieved through polarity controlled reduction (entries 1–3). Diastereoselectivities of the cyclizations were excellent. It is important to note the good yield of the reaction of **1** containing an enone.[11] As this sensitive functional group is reduced rapidly by other popular electron transfer reagents, for example, SmI_2,[12] the mildness of the radical generation from epoxides with [Cp_2TiCl] is impressively highlighted.

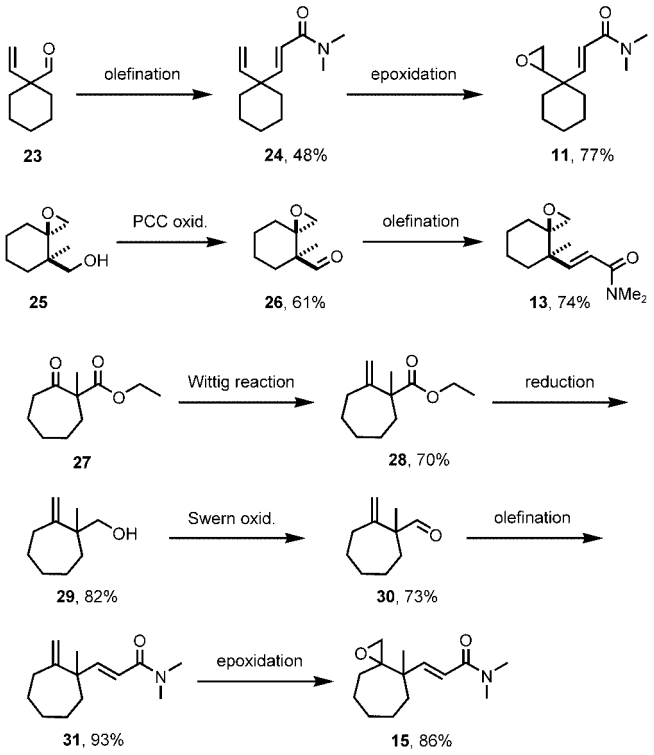
The alternative approach of a thermodynamic stabilization of the cyclopropyl carbinyl radical, that has been applied with success in traditional free radical chemistry together with incorporation of some of the cyclopropane's strain[6,13] in the starting material, was also investigated (entry 4). With epoxide **7** cyclization should lead to a highly stabilized benzyl radical. This intermediate is, however, reduced even more slowly by [Cp_2TiCl] than simple alkyl radicals.[8l] As none of the desired product could be isolated it is clear that the thermodynamic promotion of the 3-*exo* cyclization is not relevant for the other examples in table 1 also, since radical stabilization by ketone, ester, and amide groups (entries 1–3) is much smaller compared with arenes,[14] especially when a tertiary radical adds to the α,β-unsaturated carbonyl compounds (all entries except entry 6).

The other cases shown demonstrate that substitution patterns difficult to access with other methods[15] can be readily obtained in good to excellent yields. The epoxide precursors may be mono- (**11**, entry 6), di- (**9**, **13**, **15**, entries 5, 7, 8), and trisubstituted (**1**, **3**, **5**, entries 1, 2, 3). Thus tetra- (**2**, **4**, **6**, and **12**, entries 1–3, 6) and even pentasubstituted cyclopropanes (**10**, **14**, and **16**, entries 5, 7, and 8) can be easily prepared by our method. Diastereoselectivities are in the usual range for radical cyclizations.

The substrates for the cyclization were prepared according to standard procedures from known compounds as shown in Schemes 3 and 4.

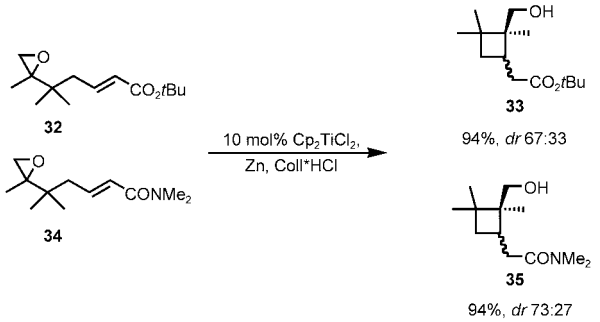


Scheme 3. Synthesis of 3-*exo* cyclization precursors. See Experimental Section for details.



Scheme 4. Synthesis of precursors for the 3-*exo* cyclization. See Experimental Section for details.

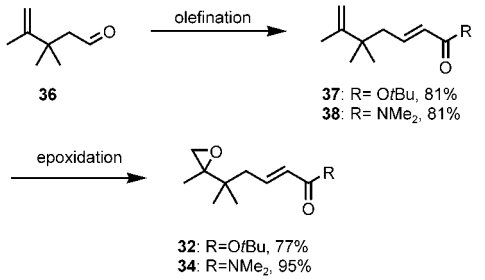
We then focussed our attention to 4-*exo* cyclizations. It turned out that under our conditions excellent results could be obtained as shown in Scheme 5.



Scheme 5. Titanocene catalyzed 4-*exo* cyclization.

The high yields indicate that the longevity of the alkyl radicals generated by electron transfer from titanocene(III) chloride is sufficient to enable the unusually slow 4-*exo* cyclization[16] without interference of competing radical pathways. This results in an almost quantitative trapping of the enol radicals obtained after cyclization to give the cyclobutanes in excellent yield. The starting materials were prepared as shown in Scheme 6.

Efficient 4-*exo* cyclizations via radical chain processes are rare and require special substrates or stabilization of the products.[16a,b] In SmI_2 chemistry only cyclization of ketyl radicals to enoates are known. However, at least in the case of ketones it has been unequivocally demonstrated that the enoate is reduced before the carbonyl group.[16d] To the best of our knowledge, our examples belong to the most efficient 4-*exo* cyclizations known as yet.



Scheme 6. Synthesis of precursors for the 4-*exo* cyclization. See Experimental Section for details.

In summary, the concept of polarity matching of radical trapping has provided a highly efficient and catalytic method for the preparation of cyclopropanes and cyclobutanes through radical chemistry. It also avoids the toxicity problems associated with tin reagents.

Experimental Section

General procedures: All reactions were performed in oven-dried (100 °C) glassware under Ar. THF was freshly distilled from K. Et_2O was freshly distilled from Na/K. CH_2Cl_2 was freshly distilled from CaH_2. The products were purified by flash chromatography on Merck silica gel 50 (eluents given in brackets, EE refers to ethyl acetate, CH to cyclohexane, PE to petrol ether 40–60 °C).[17] Yields refer to analytically pure samples. Isomer ratios were determined by suitable ^{1}H NMR integrals of cleanly separated signals. NMR: Bruker AMX 300, AM 400; ^{1}H NMR, [D_5]benzene (7.16 ppm) and $CHCl_3$ (7.26 ppm) in the indicated solvent as internal standard in the same solvent; ^{13}C NMR: $CDCl_3$ (77.16 ppm) and C_6D_6 (138.06 ppm) as internal standard in the same solvent; integrals in accord with assignments, coupling constants are measured in Hz and always constitutes *J*(H,H) coupling constants. An asterisk (*) indicates the signal of the minor diastereomer. Combustion analyses: Mr. Frank Hambloch, Institut für Organische Chemie der Georg-August-Universität Göttingen and Mrs. Annie Martens, Kekulé-Institut für Organische Chemie der Rheinischen Friedrich-Wilhelms-Universität Bonn. IR spectra: Perkin-Elmer 1600 series FT-IR as KBr-Pellets or neat films on KBr plates.

The following compounds were prepared according to literature procedures, or have already been described in the literature: The following compounds were synthesized according to literature procedures: **1**,[18] **17**,[19] **18**,[20] **23**,[21] **25**,[22] **27**,[23] **36**.[24]

General procedure 1 (GP 1)

Horner–Wadsworth–Emmons olefination: NaH (96.0 mg 4.00 mmol) was suspended in dry Et_2O (30 mL). The phosphonate (5.00 mmol) was added dropwise to the suspension. After the reaction mixture became clear (usually 5 min except 2 h for the *tert*-butyl) the aldehyde (3.00 mmol) was added. The solution was stirred at room temperature for the indicated time. The organic phase was washed with water (2 × 15 mL), the combined aqueous layers were extracted with CH_2Cl_2 (10 mL). The combined organic layers were washed with brine (5 mL) and dried ($MgSO_4$). The solvents were removed under reduced pressure and the crude product purified by silica gel chromatography.

General procedure 2 (GP 2)

Epoxidation of olefins by *m*CPBA: The olefin (2.00 mmol) was dissolved in dichloromethane (20 mL). At 0 °C *m*CPBA (518 mg, 3.00 mmol) was added. The reaction mixture was stirred at room temperature for the indicated time. After adding of Et_2O (50 mL) the organic phase was washed with 2 N NaOH (2 × 10 mL), the combined aqueous layers were

extracted with CH_2Cl_2 (10 mL). The combined organic layers were washed with brine (5 mL) and dried ($MgSO_4$). The solvents were removed under reduced pressure and the crude product purified by silica gel chromatography.

General procedure 3 (GP 3)

Radical cyclization: The epoxide (1.00 mmol) was added to a suspension of $[Cp_2TiCl_2]$(24.9 mg, 100μmol), collidine hydrochloride (394 mg, 2.50 mmol) and zinc dust (131 mg, 2.00 mmol), that were heated under vacuum until the collidine hydrochloride began to sublime slightly prior to use, in dry THF (10 mL) and the reaction mixture stirred at room temperature for the indicated time.

After adding of Et_2O (20 mL) the reaction mixture was washed with of 2N HCl (2×10 mL), in case of amides with water (2×10 mL), the combined aqueous layers were extracted with CH_2Cl_2 (10 mL). The combined organic layers were washed with brine (5 mL) and dried ($MgSO_4$). The solvents were removed under reduced pressure and the crude product purified by silica gel chromatography.

1-(2-Hydroxy-1,5,5-trimethyl-bicyclo[4.1.0]hept-7-yl)-propan-2-one (2): According to GP 3 **1** (417 mg, 2.00 mmol), $[Cp_2TiCl_2]$ (48.8 mg, 200 μg), collidine hydrochloride (788 mg, 5.00 mmol) and zinc dust (262 mg, 4.00 mmol) for 16 h. Silica gel chromatography (CH/EE 9:1) gave **2** (302 mg, 72%). R_f=0.4 (CH/EE 9:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ= 3.82 (t, ^3J=6.1 Hz, 1H), 3.99 (brs, 1H), 2.80 (dd, ^2J=18.9, ^3J=4.2 Hz, 1H), 2.13 (s, 3H), 2.12 (dd, ^2J=19.1, ^3J=10.3 Hz, 1H), 1.57 (dddd, ^2J= 14.1, ^3J=8.7, 5.4, 3.3 Hz, 1H), 1.25–1.04 (m, 2H), 1.01 (s, 3H), 1.00 (s, 3H), 0.99–0.88 (m, 2H), 0.87 (s, 3H), 0.40 ppm (d, ^3J=5, 8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=210.2, 72.2, 43.1, 39.8, 33.6, 31.6, 29.7, 28.6, 27.2, 19.9, 16.5 ppm; IR (film): $\tilde{\nu}$=3475, 2950, 1710, 1465, 1410, 1360, 1305, 1235, 1165, 1070, 1050, 985, 895 cm^{-1}; HRMS (EI, 70 eV): *m*/*z*: calcd for $C_{13}H_{22}O_2$: 210.1620; found: 210.1631 $[M]^+$.

3-(1,3,3-Trimethyl-7-oxa-bicyclo[4.1.0]hept-2-yl)-acrylic ethyl ester (3): According to GP 1 **17** (1.68 g, 10.0 mmol), NaH (300 mg, 12.5 mmol), the phosphonate (3.36 g, 15.0 mmol) in THF (50 mL) for 16 h. Silica gel chromatography (CH/EE 9:1) to yield **3** (1.62 g, 70%). R_f=0.4 (CH/EE 17:3); ^{1}H NMR (400 MHz, C_6D_6): δ=7.26 (dd, ^3J=15.7, 10.4 Hz, 1H), 5.97 (dd, ^3J=15.7, ^5J=0.6 Hz, 1H), 4.03 (qd, ^3J=7.1, ^5J=1.5 Hz, 2H), 2.65 (dd, ^3J=2.5, 1.6 Hz, 1H), 1.76 (d, ^3J=10.4 Hz, 1H), 1.69 (dddd, ^2J= 15.2, ^3J=5.3, 3.9, 1.4 Hz, 1H), 1.43 (dddd, ^2J=15.2, ^3J=10.8, 5.9, 2.7 Hz, 1H), 1.25 (ddd, ^2J=13.5, ^3J=10.8, 5.3 Hz, 1H), 1.02 (s, 3H), 0.97 (t, ^3J= 7.1 Hz, 3H), 0.63 (s, 3H), 0.59 (s, 3H), 0.63–0.55 ppm (m, 1H); ^{13}C NMR (100 MHz, C_6D_6): δ=165.6, 147.0, 124.3, 60.1, 58.8, 58.1, 52.2, 31.1, 28.7, 27.7, 27.2, 23.9, 22.0, 14.3 ppm; IR (film): $\tilde{\nu}$=2960, 1720, 1650, 1450, 1365, 1340, 1305, 1260, 1215, 1160, 1115, 1095, 1045, 990, 960, 905 cm^{-1}; HRMS (EI, 70 eV): *m*/*z*: calcd for $C_{14}H_{22}O_3$: 238.1569; found: 238.1575 $[M]^+$.

(2-Hydroxy-1,5,5-trimethyl-bicyclo[4.1.0]hept-7-yl)-acetic ethyl ester (4): According to GP 3 **3** (238 mg, 1.00 mmol), $[Cp_2TiCl_2]$ (24.9 mg, 100 μg), collidine hydrochloride (394 mg, 2.50 mmol) and zinc dust (131 mg, 2.00 mmol) for 16 h. Silica gel chromatography (CH/EE 49:1) gave **4** (222 mg, 92%). R_f=0.1 (CH/EE 19:1); ^{1}H NMR (400 MHz, C_6D_6): δ= 3.93–3.88 (m, 1H), 3.91 (q, ^3J=7.1 Hz, 2H), 2.70 (dd, ^3J=9.8, 5.0 Hz, 1H), 2.34 (dd, ^2J=17.7, ^3J=5.1 Hz, 1H), 1.81 (dd, ^2J=17.6, ^3J=10.3 Hz, 1H), 1.55 (dddd, ^2J=14.1, ^3J=8.8, 5.5, 3.3 Hz, 1H), 1.29 (dddd, ^2J=13.9, ^3J=9.5, 6.7, 2.8 Hz, 1H), 1.11 (ddd, ^2J=13.7, ^3J=9.0, 2.8 Hz, 1H), 1.04 (s, 3H), 1.00 (ddd, ^2J=10.6, ^3J=9.5, 3.3 Hz, 1H), 0.95 (t, ^3J=7.2 Hz, 3H), 0.93 (s, 3H), 0.91–0.86 (m, 1H), 0.84 (s, 3H), 0.20 ppm (d, ^3J=5.8 Hz, 1H); ^{13}C NMR (100 MHz, C_6D_6): δ=174.0, 71.8, 60.5, 39.8, 33.6, 33.6, 31.4, 28.6, 28.2, 27.6, 27.4, 19.8, 17.6, 14.1 ppm; IR (film): $\tilde{\nu}$=3450, 2950, 1720, 1465, 1370, 1310, 1195, 1070, 1035, 930, 855 cm^{-1}; HRMS (EI, 70 eV): *m*/*z*: calcd for $C_{14}H_{24}O_3$: 240.1725; found: 240.1728 $[M]^+$.

***N,N*-Dimethyl-3-(1,3,3-trimethyl-7-oxa-bicyclo[4.1.0]hept-2-yl)-acrylamide (5)**: According to GP 1 **17** (466 mg, 2.77 mmol), NaH (72.0 mg, 3.00 mmol), the phosphonate (781 mg, 3.50 mmol) in THF (25 mL) for 16 h. Silica gel chromatography (CH/EE 1:1) to yield **5** (368 mg, 56%). R_f=0.4 (EE); ^{1}H NMR (400 MHz, C_6D_6): δ=7.12 (d, ^3J=14.5, 10.4 Hz, 1H), 6.15 (d, ^3J=15.7 Hz, 1H), 2.72 (brs, 3H), 2.71 (dd, ^3J=2.3, 1.1 Hz, 1H), 2.41 (brs, 3H), 1.85 (d, ^3J=10.0 Hz, 1H), 1.75 (dddd, ^2J=15.1, ^3J= 5.3, 4.1, 1.2 Hz, 1H), 1.50 (dddd, ^2J=15.1, ^3J=10.3, 5.7, 2.8 Hz, 1H), 1.33 (ddd, ^2J=13.3, ^3J=10.3, 5.3 Hz, 1H), 1.13 (s, 3H), 0.73 (s, 3H), 0.69 (s, 3H), 0.70–0.61 ppm (m, 1H); ^{13}C NMR (100 MHz, C_6D_6): δ=165.8, 142.9, 123.7, 58.7, 58.2, 52.3, 36.5, 35.1, 31.3, 29.1, 28.1, 27.2, 24.1, 22.1 ppm; IR (film): $\tilde{\nu}$=2930, 1660, 1610, 1415, 1390, 1305, 1260, 1150, 1110, 1045, 990, 895, 870, 805, 745, 715, 650, 620 cm^{-1}; HRMS (EI, 70 eV): *m*/*z*: calcd for $C_{14}H_{23}NO_2$: 237.1729; found: 137.1734 $[M]^+$.

2-(2-Hydroxy-1,5,5-trimethyl-bicyclo[4.1.0]hept-7-yl)-*N,N*-dimethylacetamide (6): According to GP 3 **5** (237 mg, 1.00 mmol), $[Cp_2TiCl_2]$ (24.9 mg, 100 μg), collidine hydrochloride (394 mg, 2.50 mmol) and zinc dust (131 mg, 2.00 mmol) for 16 h. Silica gel chromatography (CH/EE 17:5) gave **6** (229 mg, 96%). R_f=0.1 (CH/EE 17:5); ^{1}H NMR (400 MHz, C_6D_6): δ=4.78 (brs, 1H), 4.09 (dd, ^3J=5.8, 5.8 Hz, 1H), 2.56 (s, 3H), 2.20 (dd, ^2J=17.2, ^3J=4.2 Hz, 1H), 2.10 (s, 3H), 1.68 (dddd, ^2J=13.9, ^3J=9.6, 5.8, 3.6 Hz, 1H), 1.51 (dddd, ^2J=14.3, ^3J=8.4, 6.0, 2.8 Hz, 1H), 1.42 (dd, ^2J=17.2, ^3J=11.2 Hz, 1H), 1.26 (ddd, ^2J=13.6, ^3J=9.7, 3.0 Hz, 1H), 1.12 (ddd, ^3J=11.2, 6.4, 4.2 Hz, 1H), 1.09 (s, 3H), 1.03 (s, 3H), 0.96 (ddd, ^2J=13.9, ^3J=9.0, 3.4 Hz, 1H), 0.94 (s, 3H), 0.20 ppm (d, ^3J=5.9 Hz, 1H); ^{13}C NMR (100 MHz, C_6D_6): δ=172.6, 71.3, 39.4, 35.7, 34.9, 33.3, 32.2, 31.3, 29.0, 28.4, 28.0, 26.9, 20.1, 18.1 ppm; IR (film): $\tilde{\nu}$=3350, 2950, 2870, 1610, 1500, 1460, 1415, 1360, 1270, 1150, 1120, 1035, 1000, 920, 855, 795 cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{25}NO_2$ (239.35): C 70.25, H 10.53, N 5.85; found: C 69.96, H 10.46, N 5.79.

1,3,3-Trimethyl-2-styryl-7-oxa-bicyclo[4.1.0]heptane (7): Benzyltriphenylphosphonium bromide (3.47 g, 8.00 mmol) was suspended in THF (60 mL). At 0°C *n*-butyl lithium (384 mg (2.4M in hexane), 6.00 mmol) was added dropwise (5 min). After the reaction mixture was stirred for 30 min at 0°C, **17** (1.01 g, 6.00 mmol) was added dropwise (10 min). The solution was allowed to stir at rt for 16 h. After addition of water (30 mL) triphenylphosphine oxide was precipitated by dropwise addition of PE. The organic layer was filtered and dried ($MgSO_4$). The solvents were removed under reduced pressure and the crude product purified by silica gel chromatography (CH/EE 49:1) to yield **7** (480 mg, 33%, *dr* 10:1). R_f=0.4 (CH/EE 19:1); ^{1}H NMR (400 MHz, C_6D_6): δ=7.35–7.29 (m, 2H), 7.14–7.09 (m, 2H), 7.07–7.01 (m, 1H), 6.44 (dd, ^3J=15.9, 9.3 Hz, 1H), 6.36 (d, ^3J=15.8 Hz, 1H), 2.79 (dd, ^3J=2.8, 1.4 Hz, 1H), 1.89 (dd, ^3J=9.2, ^4J=0.8 Hz, 1H), 1.84 (dddd, ^2J=15.2, ^3J=5.3, 4.4, 1.1 Hz, 1H), 1.57 (dddd, ^2J=15.1, ^3J=10.2, 5.8, 3.0 Hz, 1H), 1.43 (ddd, ^2J=13.2, ^3J=10.1, 5.3 Hz, 1H), 1.18 (s, 3H), 0.79 (s, 3H), 0.78 (dddd, ^2J= 13.3, ^3J=5.6, 4.5, ^4J=1.0 Hz, 1H), 0.66 ppm (s, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ=138.0, 133.0, 129.0, 128.8, 127.3, 126.7, 59.2, 59.0, 53.3, 31.6, 29.8, 28.3, 27.2, 24.1, 22.4 ppm; IR (film): $\tilde{\nu}$=3025, 2955, 1600, 1940, 1450, 1380, 1305, 1180, 1145, 1095, 1045, 975, 895, 860, 800, 755, 725, 695 cm^{-1}; HRMS (EI, 70 eV): *m*/*z*: calcd for $C_{17}H_{22}O$: 242.1671; found: 242.1664 $[M]^+$.

2,2-Dimethyl-3-propyl-but-3-enoic ethyl ester (19): NaH (661 mg, 28.8 mmol) was suspended in dry DMSO (30 mL) and heated at 70°C for 1 h. Methyltriphenylphosphonium bromide (10.3 g, 28.8 mmol) in DMSO (30 mL) was added. After 1 h **18** (4.66 g, 25.0 mmol) was added and the reaction mixture was stirred at 55°C for 16 h. The Reaction was stopped by adding water (60 mL) and extracting with Et_2O (3×50 mL). The combined organic layer was washed with water/DMSO (1:1, 50 mL), brine (20 mL) and dried ($MgSO_4$). The solvents were removed under reduced pressure and the crude product purified by silica gel chromatography (PE/Et_2O 99:1) to yield **19** (2.02 g, 44%). R_f=0.4 (PE/Et_2O 19:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ=4.98 (s, 1H), 4.87 (s, 1H), 4.11 (q, ^3J= 7.1 Hz, 2H), 1.93 (t, ^3J=7.7 Hz, 2H), 1.48 (qt, ^3J=7.7, 7.6 Hz, 2H), 1.31 (s, 6H), 1.22 (t, ^3J=7.1 Hz, 3H), 0.91 ppm (t, ^3J=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=176.7, 152.0, 108.3, 60.5, 48.1, 34.3, 24.8, 21.6, 14.1, 14.0 ppm; IR (film): $\tilde{\nu}$=2960, 1730, 1640, 1465, 1380, 1255, 1135, 1030, 895 cm^{-1}; HRMS (EI, 70 eV): *m*/*z*: calcd for $C_{11}H_{20}O_2$: 184.1463; found: 184.1454 $[M]^+$.

2,2-Dimethyl-3-propyl-but-3-en-1-ol (20): Compound **19** (8.29 g, 45.0 mmol) was added dropwise to a suspension of $LiAlH_4$ (854 mg, 22.5 mmol) in dry THF at 0°C. The reaction mixture was stirred for 24 h at room temperature. Water (1.5 mL), NaOH (1.5 mL, 15% *w*/*v*) and water (4.5 mL) were added subsequently. The solid was filtered off and the solvents were removed under reduced pressure to yield **20** (5.62 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=4.94 (s, 2H), 4.38 (s, 2H), 1.97 (t, ^3J=7.8 Hz, 2H), 1.27 (qt, ^3J=7.6, 7.5 Hz, 2H), 1.05 (s, 6H), 0.94 ppm (t, ^3J=7.3 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ=153.4, 110.0, 69.9, 41.6, 33.5, 24.0, 22.0, 14.1 ppm; IR (film): $\tilde{\nu}$=3390, 2960, 1633, 1465, 1040, 895, 825, 640 cm^{-1}; HRMS (EI, 70 eV): *m*/*z*: calcd for $C_9H_{18}O$: 142.1356; found: 142.1356 $[M]^+$.

2,2-Dimethyl-3-propyl-but-3-enal (21): DMSO (6.56 g, 42.0 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a solution of oxalyl chloride (5.33 g, 42.0 mmol) in CH_2Cl_2 (150 mL) at −60 °C. After 30 min **20** (4.98 g, 35.0 mmol) was added. The reaction mixture was stirred for 16 h at −60 °C before NEt_3 (17.0 g, 168 mmol) was added. The reaction mixture was diluted with Et_2O (200 mL) and washed with water (2×100 mL) and brine (20 mL). After filtration through silica gel with Et_2O (500 mL) the solvents were removed under reduced pressure. Kugelrohr distillation (120 °C, 20 mbar) yielded **21** (3.56 g, 73 %). ^{1}H NMR (400 MHz, C_6D_6): δ = 9.17 (s, 1H), 4.86 (t, ^4J = 1.6 Hz, 1H), 4.81 (m, 1H), 1.75 (tdd, ^3J = 7.8, ^4J = 1.2, 1.1 Hz, 2H), 1.27 (qt, ^3J = 7.6, 7.5 Hz, 2H), 0.98 (s, 6H), 0.76 ppm (t, ^3J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ = 201.5, 149.5, 111.7, 52.1, 46.8, 34.5, 21.8, 20.9, 13.9 ppm; IR (film): $\tilde{\nu}$ = 2930, 1740, 1705, 1640, 1455, 1370, 1310, 1240, 1190, 1025 cm^{-1}; HRMS (EI, 70 eV): *m*/*z*: calcd for $C_9H_{16}O$: 140.1201; found: 140.1201 $[M]^+$.

4,4-Dimethyl-5-propyl-hexa-2,5-dienoic dimethylamide (22): According to GP 1 **21** (701 mg, 5.00 mmol), NaH (156 mg, 6.50 mmol) and the phosphonate (1.79 g, 8.00 mmol) in Et_2O (50 mL) for 16 h. Silica gel chromatography (CH:EE 3:1) gave **22** (946 mg, 90 %). R_f = 0.3 (CH/EE 3:1); ^{1}H NMR (300 MHz, C_6D_6): δ = 7.16 (d, ^3J = 15.4 Hz, 1H), 6.08 (d, ^3J = 15.4 Hz, 1H), 4.99 (dt, ^2J = 0.8, ^4J = 0.8 Hz, 1H), 4.84 (td, ^4J = 1.2, ^2J = 1.2 Hz, 1H), 2.73 (brs, 3H), 2.38 (brs, 3H), 1.72 (tdd, ^3J = 7.8, ^2J = 1.0, 1.1 Hz, 2H), 1.23 (qt, ^3J = 7.6, 7.5 Hz, 2H), 0.91 (s, 6H), 0.65 ppm (t, ^3J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6): δ = 166.0, 154.6, 153.5, 117.8, 108.7, 42.5, 36.3, 35.2, 34.3, 26.4, 22.4, 14.2 ppm; IR (film): $\tilde{\nu}$ = 2960, 1660, 1615, 1465, 1390, 1260, 1140, 990, 895, 715, 630 cm^{-1}; HRMS (EI, 70 eV): *m*/*z*: calcd for $C_{13}H_{23}NO$: 209.1780; found: 209.1786 $[M]^+$.

4-Methyl-4-(2-propyl-oxiranyl)-pent-2-enoic dimethylamide (9): According to GP 2 **22** (250 mg, 1.19 mmol) and *m*CPBA (77 %, 535 mg, 2.39 mmol) in CH_2Cl_2 (29 mL) for 16 h. Silica gel chromatography (CH/EE 7:3) gave **9** (246 mg, 92 %). R_f = 0.1 (CH/EE 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.84 (d, ^3J = 15.4 Hz, 1H), 6.20 (d, ^3J = 15.4 Hz, 1H), 3.05 (s, 3H), 3.29 (s, 3H), 2.67 (d, ^2J = 4.3 Hz, 1H), 2.56 (d, ^2J = 4.3 Hz, 1H), 1.72 (ddd, ^2J = 14.6, ^3J = 10.7, 5.9 Hz, 1H), 1.58 (ddd, ^2J = 14.7, ^3J = 10.7, 5.2 Hz, 1H), 1.25–1.11 (m, 2H), 1.09 (s, 3H), 1.04 (s, 3H), 0.83 ppm (t, ^3J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ = 165.9, 151.3, 118.9, 62.2, 47.3, 40.2, 36.4, 35.2, 32.6, 23.6, 22.8, 17.8, 14.5 ppm; IR (film): $\tilde{\nu}$ = 2965, 2875, 1660, 1620, 1470, 1395, 1280, 1145, 990, 945, 850, 820, 715, 630 cm^{-1}; HRMS (EI, 70 eV): *m*/*z*: calcd for $C_{13}H_{23}NO_2$: 225.1729; found: 225.1731 $[M]^+$.

2-(2-Hydroxymethyl-3,3-dimethyl-2-propyl-cyclopropyl)-*N*,*N*-dimethyl-acetamide (10): According to GP 3 **9** (169 mg, 0.75 mmol), $[Cp_2TiCl_2]$ (28.0 mg, 113 μmol), collidine hydrochloride (296 mg, 1.88 mmol) and zinc dust (98.0 mg, 1.50 mmol) for 72 h. Silica gel chromatography (CH/EE 1:1) gave **10** (162 mg, 95 %, *dr* 63:37). R_f = 0.4 (EE); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.83 (d, ^2J = 10.7 Hz, 1H), 3.69* (d, ^2J = 11.7 Hz, 1H), 3.48* (dd, ^2J = 12.1, ^3J = 1.1 Hz, 1H), 3.31 (dd, ^2J = 10.6, ^3J = 1.3 Hz, 1H), 3.31* (s, 3H), 3.27 (s, 3H), 2.94* (s, 3H), 2.93 (s, 3H), 2.81* (dd, ^2J = 15.4, ^3J = 3.5 Hz, 1H), 2.56 (dd, ^2J = 17.3, ^3J = 4.2 Hz, 1H), 2.11* (ddd, ^2J = 14.1, ^3J = 11.6, 4.9 Hz, 3H), 2.02* (d, ^3J = 10.9, 1H), 1.98 (dd, ^2J = 15.3, ^3J = 11.2 Hz, 1H), 1.68 (ddd, ^2J = 13.9, ^3J = 11.5, 4.7 Hz, 1H), 1.60–1.46* (m, 1H), 1.60–1.46* (m, 1H), 1.35–1.15* (m, 1H), 1.35–1.15 (m, 1H), 1.11 (s, 3H), 1.10* (s, 3H), 1.01 (s, 3H), 0.97* (s, 3H), 0.94 (dddd, ^2J = 14.1, ^3J = 11.7, 4.8, 1.0 Hz, 1H), 0.86 (t, ^3J = 7.3 Hz, 3H), 0.86* (t, ^3J = 7.3 Hz, 3H), 0.83 (dddd, ^2J = 14.0, ^3J = 11.5, 4.8, 1.7 Hz, 1H), 0.72 (dd, ^3J = 10.9, 4.2 Hz, 1H), 0.41* ppm (dd, ^3J = 11.6, 3.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.6*, 173.3, 65.6, 60.3*, 37.9*, 36.9, 35.8*, 35.6, 34.5, 32.1, 31.9*, 30.4*, 29.1*, 28.8, 28.1*, 27.7, 23.8*, 23.7, 22.9, 21.9*, 19.9*, 19.5, 17.8, 16.8*, 14.6, 14.5* ppm; IR (film): $\tilde{\nu}$ = 3395, 2950, 1625, 1400, 1260, 1130, 1015, 795 cm^{-1}; HRMS (EI, 70 eV): *m*/*z*: calcd for $C_{13}H_{25}NO_2$: 227.1885; found: 227.1877 $[M]^+$.

***N*,*N*-Dimethyl-3-(1-vinyl-cyclohexyl)-acrylamide (24)**: According to GP 1 the phosphonate (2.43 g, 10.9 mmol), NaH (0.23 g, 9.10 mmol) and **23** (1.00 g, 7.25 mmol) in Et_2O (40 mL) for 15 h. Silica gel chromatography (CH/EE 98:2) gave **24** (1.08 g, 48 %). R_f = 0.2 (CH/EE 96:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.7 (dd, ^3J = 15.4, ^4J = 2.8 Hz, 1H), 6.11 (dd, ^3J = 15.4, ^5J = 2.3 Hz, 1H), 5.64 (ddd, ^3J = 17.6, ^3J = 10.8, ^4J = 2.8, ^5J = 2.3 Hz, 1H), 5.05 (dddd, ^3J = 10.8, ^5J = 1.2 Hz, 1H), 4.95 (dddd, ^3J = 17.7, ^5J = 1.3 Hz, 1H), 3.00 (s, 3H), 2.94 (s, 3H), 2.20–2.0 (m, 2H), 1.67–1.31 ppm (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 152.7, 144.4, 118.2, 113.8, 43.2, 37.4, 35.8, 35.4, 26.1, 22.2 ppm; IR (neat): $\tilde{\nu}$ = 3485, 2930, 2855, 1650, 1450, 1390, 1264 cm^{-1}; HRMS (EI, 70 eV): *m*/*z*: calcd for $C_{13}H_{21}NO$: 207.1623, found 207.1620 $[M]^+$.

***N*,*N*-Dimethyl-3-(1-oxiranyl-cyclohexyl)-acrylamide (11)**: According GP 2 **24** (1.00 g, 4.80 mmol) and *m*CPBA (1.25 g (77 %), 7.24 mmol) in CH_2Cl_2 (40 mL) for 16 h. Silica gel chromatography (CH/EE 60:40) yield to **11** (0.72 g, 67 %). R_f = 0.2 (CH/EE 60:40); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.62 (d, ^3J = 15.8 Hz, 1H), 6.26 (d, ^3J = 15.8 Hz, 1H), 3.04 (s, 3H), 2.96 (s, 3H), 2.76 (dd, ^3J = 3.9, ^3J = 2.9 Hz, 1H), 2.76 (dd, ^2J = 4.7, ^3J = 3.9 Hz, 1H), 2.55 (dd, ^4J = 4.7, ^3J = 3.9 Hz, 1H), 1.71–1.65 (m, 1H), 1.65–1.50 (m, 5H), 1.48–1.30 (m, 3H), 1.27–1.15 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7, 147.8, 121.4, 58.5, 39.9, 37.5, 35.8, 33.3, 31.7, 26.0, 22.0, 21.9 ppm; IR (film): 3445, 2925, 1655, 1610, 1395, 1150 cm^{-1}; HRMS (EI, 70 eV): *m*/*z*: calcd for $C_{13}H_{21}NO_2$: 223.1572, found 223.1575 $[M]^+$.

2-Hydroxymethyl-spiro[2.5]octane-1-carboxylic dimethylamide (12): According to GP 3 **11** (223 mg, 1.00 mmol), $[Cp_2TiCl_2]$ (25 mg, 0.10 mmol), collidine hydrochloride (394 mg, 2.50 mmol) and zinc dust (131 mg, 2.00 mmol) for 16 h. Silica gel chromatography (CH/EE 90:10→50:50) gave **12** (202 mg, 90 %). R_f = 0.1 (CH/EE 90:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.62 (d, ^3J = 15.8 Hz, 1H), 6.26 (d, ^3J = 15.8 Hz, 1H), 3.04 (s, 3H), 2.96 (s, 3H), 2.76 (dd, ^3J = 3.9, ^3J = 2.9 Hz, 1H), 2.76 (dd, ^2J = 4.7, ^3J = 3.9 Hz, 1H), 2.55 (dd, ^4J = 4.7, ^3J = 3.9 Hz, 1H), 1.71–1.65 (m, 1H), 1.65–1.50 (m, 5H), 1.48–1.30 (m, 5H), 1.27–1.15 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.6*, 173.6, 63.9*, 62.5, 58.8, 58.6, 39.7*, 39.3*, 37.9*, 36.9, 35.9*, 35.8, 33.2, 31.9, 28.8*, 28.0, 26.9*, 26.7, 26.3*, 26.2, 26.0, 25.7*, 25.5, 23.6* ppm; IR (film): $\tilde{\nu}$ = 3400, 2925, 1725, 1635, 1400, 1265, 1025 cm^{-1}; HRMS (EI, 70 eV): *m*/*z*: calcd for $C_{13}H_{23}NO_2$: 225.1729, found 225.1723 $[M]^+$.

4-Methyl-1-oxa-spiro[2.5]octane-4-carbaldehyde (26): Compound **25** (4.69 g, 30.0 mmol) was added to a solution of Celite (11.0 g), 4 Å molecular sieves (1.78 g) and PCC (7.54 g, 35 mmol) in CH_2Cl_2 (125 mL) and stirred for 5 h at room temperature. After filtration through Florisil the solvent was removed under reduced pressure and the crude product purified by silica gel chromatography (CH/EE 47:3) to yield **26** (2.83 g, 61 %). R_f = 0.3 (CH/EE 9:1); ^{1}H NMR (400 MHz, C_6D_6): δ = 9.50 (s, 1H), 2.27 (dd, ^2J = 4.2, ^4J = 0.6 Hz, 1H), 1.94 (d, ^2J = 4.2 Hz, 1H), 1.90 (ddd, ^2J = 13.2, ^3J = 8.7, 4.5 Hz, 1H), 1.52–1.42 (m, 1H), 1.34–1.26 (m, 2H), 1.25–1.14 (m, 3H), 0.94 (ddd, ^2J = 13.6, ^3J = 7.7, 4.1 Hz, 1H), 0.74 ppm (s, 3H); ^{13}C NMR (75 MHz, C_6D_6): δ = 203.9, 60.2, 49.1, 48.5, 32.2, 31.9, 24.5, 21.2, 16.9 ppm; IR (film): $\tilde{\nu}$ = 2930, 1725, 1450, 1040, 775 cm^{-1}; HRMS (EI, 70 eV): *m*/*z*: calcd for $C_9H_{14}O_2$: 154.0994; found: 154.1001 $[M]^+$.

***N*,*N*-Dimethyl-3-(4-methyl-1-oxa-spiro[2.5]oct-4-yl)-acrylamide (13)**: According to GP 1 **26** (540 mg, 3.50 mmol), NaH (96.0 mg, 4.00 mmol) and the phosphonate (1.00 g, 4.50 mmol) in THF (35 mL) for 2 h. Kugelrohr distillation (230 °C, 1 mbar) and silica gel chromatography (CH/EE 63:37) gave **13** (580 mg, 74 %). R_f = 0.4 (EE); ^{1}H NMR (400 MHz, C_6D_6): δ = 7.17 (d, ^2J = 15.7 Hz, 1H), 6.43 (d, ^2J = 15.7 Hz, 1H), 2.72 (brs, 3H), 2.44 (dd, ^2J = 4.7, ^4J = 1.2 Hz, 1H), 2.39 (brs, 3H), 1.99 (d, ^2J = 4.8 Hz, 1H), AB signal (δ_{A1} = 1.68, δ_{B1} = 1.65, J_{AB} = 13.3 Hz, additionally split by ^3J = 6.7, 3.9, ^4J = 1.2 Hz, 2H), 1.63–1.51 (m, 1H), 1.40–1.19 (m, 4H), 1.12 (ddd, ^2J = 13.4, ^3J = 9.4, 4.0 Hz, 1H), 0.83 ppm (s, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ = 166.1, 150.2, 120.9, 62.0, 49.4, 40.3, 38.4, 36.4, 35.1, 32.0, 25.5, 22.5, 22.3 ppm; IR (film): $\tilde{\nu}$ = 2935, 2860, 1660, 1620, 1495, 1395, 1265, 1145, 1035, 990, 925, 900, 835, 800, 765, 710, 620 cm^{-1}; HRMS (EI, 70 eV): *m*/*z*: calcd for $C_{13}H_{21}NO_2$: 223.1572; found: 223.1570 $[M]^+$.

2-(1-Hydroxymethyl-6-methyl-bicyclo[4.1.0]hept-7-yl)-*N*,*N*-dimethylacetamide (14): According to GP 3 **13** (223 mg, 1.00 mmol), $[Cp_2TiCl_2]$ (24.9 mg, 100 μmol), collidine hydrochloride (394 mg, 2.50 mmol) and zinc dust (131 mg, 2.00 mmol) for 16 h. Silica gel chromatography (CH/EE 1:1) gave **14** (162 mg, 72 %). R_f = 0.2 (EE); ^{1}H NMR (300 MHz, C_6D_6): δ = 4.27* (brs, 1H), 4.06 (brs, 1H), 3.90* (d, ^2J = 10.2 Hz, 1H), 3.76 (s, 2H), 3.61* (d, ^2J = 12.2 Hz, 1H), 2.58* (s, 3H), 2.56 (s, 3H), 2.36 (dd, ^2J = 15.4, ^3J = 3.6 Hz, 1H), 2.24–2.10* (m, 1H), 2.19 (s, 3H), 2.18–2.12* (dm, ^3J = 4.3 Hz, 1H), 2.16* (s, 3H), 2.01 (ddd, ^2J = 14.2, ^3J = 9.3 Hz, 5.2 Hz, 1H), 1.84* (dd, ^2J = 16.9, ^3J = 11.0 Hz, 1H), 1.83 (dd, ^2J = 15.3, ^3J = 11.5 Hz, 1H), 1.64 (dddd, ^2J = 13.4, ^3J = 4.8, 4.8, 1.5 Hz, 1H), 1.47–0.92 (m, 6H), 1.47–0.92* (m, 7H), 1.06* (s, 3H), 0.89 (s, 3H), 0.76* (dd, ^3J = 10.8, 4.2 Hz, 1H), 0.69 ppm (dd, ^3J = 11.5, 3.6 Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6): δ = 174.0, 172.3*, 70.0*, 64.2, 36.8, 35.2*, 35.2, 35.0*,

33.7*, 29.7, 29.4*, 29.9, 28.8*, 28.6*, 28.4, 28.4, 27.3, 24.3*, 24.2*, 22.7*, 22.6*, 22.3, 21.8, 21.8*, 21.6, 17.2 ppm; IR (film): $\tilde{\nu}$ = 3390, 2925, 1720, 1635, 1400, 1260, 1145, 1010, 615 cm^{-1}; HRMS (EI, 70 eV): *m/z*: calcd for $C_{13}H_{23}NO_2$: 225.1729; found: 225.1725 $[M]^+$.

1-Methyl-2-methylene-cycloheptanecarboxylic ethyl ester (28): NaH (1.78 g, 70.5 mmol) and DMSO (40 mL) were heated for 1 h at 70 °C. To the stirred solution methyltriphenylphosphonium bromide (25.5 g, 70.5 mmol) in DMSO (80 mL) was added. After 1 h **27** (13.3 g, 67.2 mmol) was added and the reaction mixture stirred for 16 h at 55 °C. The reaction was interrupted by adding water (80 mL) and extracting with cyclohexane (3 × 50 mL). The combined organic layers were washed with water/DMSO (1:1, 80 mL), with brine (50 mL) and dried ($MgSO_4$). The solvents were removed under reduced pressure and the crude product purified by silica gel chromatography (CH/EE 95:5) to yield **28** (9.30 g, 70 %). R_f = 0.2 (CH/EE 95:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.94 (s, 1H), 4.85 (s, 1H), 4.10 (t, ^3J = 7.1 Hz, 2H), 2.26 (m, 2H), 2.15 (d, ^3J = 9.2 Hz, 1H), 2.12 (d, ^3J = 9.3 Hz, 1H), 1.75–1.63 (m, 3H), 1.61–1.50 (m, 2H), 1.49–1.32 (m, 3H), 1.31 (s, 1H), 1.20 ppm (t, ^3J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.9, 113.0, 60.6, 50.9, 38.4, 35.1, 31.4, 30.5, 25.0, 24.5, 14.2 ppm; IR (film): $\tilde{\nu}$ = 2925, 1725, 1630, 1445, 1235, 1155, 1105 cm^{-1}; HRMS (EI, 70 eV): *m/z*: calcd for $C_{17}H_{20}O_2$: 196.1463; found 196.1471 $[M]^+$.

(1-Methyl-2-methylene-cycloheptyl)-methanol (29): Compound **28** (9.81 g, 50.0 mmol) was added dropwise to a suspension of $LiAlH_4$ (0.95 g, 25.0 mmol) in dry diethyl ether (100 mL) at 0 °C. The reaction mixture was stirred for 10 h at room temperature. Water (1.0 mL), NaOH (1.0 mL, 15 % *w/v*) and water (3.0 mL) were added subsequently. The solid was filtered off and the solvents were removed under reduced pressure. Distillation (b.p. 4.8 mbar/130–135 °C) of the crude product lead to **29** (6.32 g, 41 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.94 (s, 1H), 4.78 (s, 1H), 3.22 (dd, ^2J = 10.6, ^3J = 3.6 Hz, 1H), 3.18 (dd, ^2J = 10.4, ^3J = 9.4 Hz, 1H), 2.16 (dd, ^2J = 13.1, ^3J = 7.6 Hz, 1H), 1.98 (dd, ^2J = 13.0, ^3J = 13.0 Hz, 1H), 1.83–1.77 (m, 1H), 1.70–1.53 (m, 3H), 1.42–1.37 (m, 2H), 1.29–1.18 (m, 4H), 1.03 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.1, 113.0, 70.2, 45.1, 37.3, 34.5, 32.2, 31.0, 23.7, 23.2 ppm; IR (film): $\tilde{\nu}$ = 3385, 2920, 1725, 1630, 1445, 1045 cm^{-1}; HRMS (EI, 70 eV): *m/z*: calcd for $C_{10}H_{18}O$: 154.1358; found 154.1352 $[M]^+$.

1-Methyl-2-methylene-cycloheptanecarbaldehyd (30): DMSO (9.38 g, 120 mmol) in CH_2Cl_2 (10 mL) was added to a solution of oxalyl chloride (7.62 g, 60.0 mmol) in CH_2Cl_2 (150 mL) at −60 °C. After 15 min **29** (7.70 g, 50.0 mmol) was added. The reaction stirred overnight before NEt_3 (34.7 mL, 250 mmol) was added. The reaction mixture was diluted with Et_2O (100 mL) and washed with water (2 × 100 mL) and brine (50 mL). Drying ($MgSO_4$), evaporation and purifying of the crude product by silica gel chromatography (CH/EE 99:1) yield to **30** (5.16 g, 68 %). R_f = 0.2 (CH/EE 98:2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.40 (s, 1H), 5.09 (s, 1H), 4.81 (s, 1H), 2.26 (dd, ^2J = 13.1, ^3J = 1.6 Hz, 1H), 2.24 (dd, ^2J = 13.1, ^3J = 1.6 Hz, 1H), 2.15–2.08 (m, 2H), 2.04 (d, ^2J = 15.1 Hz, 1H), 1.99 (d, ^2J = 14.7 Hz, 1H), 1.80–1.36 ppm (m, 6H), 1.20 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.6, 151.6, 115.3, 55.2, 35.1, 34.4, 31.6, 24.0, 22.4 ppm; IR (film): $\tilde{\nu}$ = 2925, 2855, 2695, 1725, 1630, 1445, 1370 cm^{-1}; HRMS (EI, 70 eV): *m/z*: calcd for $C_{10}H_{16}O$: 152.1201; found 152.1198 $[M]^+$.

***N,N*-Dimethyl-3-(1-methyl-2-methylen-cycloheptyl)-acryl amide (31)**: According to GP 1 the phosphonate (3.71 g, 15.0 mmol), NaH (0.33 g, 12.5 mmol) and **30** (1.52 mmol, 10.0 mmol) in Et_2O (40 mL) for 16 h. Silica gel chromatography (CH/EE 50:50) yield to **31** (1.94 g, 93 %). R_f = 0.2 (CH/EE 50:50); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.86 (d, ^3J = 15.4 Hz, 1H), 6.09 (d, ^3J = 15.4 Hz, 1H), 4.86 (s, 1H), 4.73 (s,1H), 3.00 (s, 3H), 2.95 (s, 3H), 2.20–2.04 (m, 2H), 1.68–1.30 (m, 8H), 1.14 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 156.3, 153.8, 116.2, 112.9, 45.4, 37.3, 35.7, 34.1, 31.8, 30.7, 29.0, 26.9, 25.4, 23.8 ppm; IR (film): $\tilde{\nu}$ = 2930, 2860, 1710, 1650, 1460, 1370, 1160 cm^{-1}; HRMS (EI, 70 eV): *m/z*: calcd for $C_{13}H_{21}NO$: 221.1780; found 221.1776 $[M]^+$.

***N,N*-Dimethyl-3-(4-methyl-1-oxa-spiro[2.6]-non-4-yl)-acrylamide (15)**: According GP 2 **31** (1.60 g, 7.70 mmol) and *m*CPBA (1.98 g (77 %), 11.5 mmol) in CH_2Cl_2 (40 mL) for 8 h. Silica gel chromatography (CH/EE 50:50) yield to **15** (1.56 g, 86 %). R_f = 0.15 (CH/EE 50:50); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.79* (d, ^3J = 15.6 Hz, 1H), 6.75 (d, ^3J = 15.4 Hz, 1H), 6.14* (d, ^3J = 15.6 Hz, 1H), 6.07 (d, ^3J = 15.4 Hz, 1H), 3.01 (s, 6H), 2.93 (s, 6H), 2.59 (dd, ^2J = 4.9, ^4J = 0.8 Hz, 1H), 2.58* (dd, ^2J = 5.2, ^4J = 0.8 Hz, 1H), 2.38 (d, ^3J = 4.8 Hz, 1H), 2.35* (d, ^2J = 5.2 Hz, 1H), 1.74–1.40 (m, 20H), 0.94 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.5*, 166.9, 150.9, 150.0*, 118.1*, 117.0, 63.8, 63.0, 52.6, 51.1*, 42.6*, 42.6, 40.0*, 39.8, 37.5*, 37.3, 37.7, 35.6*, 32.7, 32.5*, 30.5, 30.0*, 25.6, 25.2*, 23.7*, 23.1, 23.0*, 21.5 ppm; IR (film): $\tilde{\nu}$ = 2925, 1660, 1615, 1460, 1390, 1270, 1140 cm^{-1}; HRMS (EI, 70 eV): *m/z*: calcd for $C_{14}H_{23}NO_2$: 237.1729, found: 237.1725 $[M]^+$; elemental analysis calcd (%) for $C_{14}H_{23}NO_2$: C 70.85, H 9.77, N 5.90; found: C 70.16, H 9.42, N 5.86.

2-(1-Hydroxymethyl-7-methyl-bicyclo[5.1.0]oct-8-yl)-*N,N*-dimethylacetamide (16): According to GP 3 **15** (223 mg, 0.94 mmol), $[Cp_2TiCl_2]$ (24 mg, 0.1 mmol), collidine hydrochloride (370 mg, 2.35 mmol) and zinc dust (123 mg, 1.88 mmol) for 16 h. Silica gel chromatography (CH/EE 85:15→0:100) yield to **16** (200 mg, 88 %). R_f = 0.05 (CH/EE 85:15). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.87* (d, ^2J = 10.6 Hz, 1H), 3.74 (d, ^2J = 12.1 Hz, 1H), 3.46 (dd, ^2J = 12.2, ^4J = 1.4 Hz, 1H), 3.28* (dd, ^2J = 10.5, ^4J = 1.8 Hz, 1H), 3.06* (s, 3H), 2.98* (s, 3H), 2.96 (s, 3H), 2.92 (s, 3H), 2.90* (dd, ^3J = 15.3, ^5J = 3.0 Hz, 2H), 2.65 (m, 2H), 2.19–1.55 (m, 11H), 2.19–1.55* (m, 11H), 1.13* (s, 3H), 0.97 (s, 3H), 0.95–0.73 (m, 1H), 0.63* ppm (dd, ^3J = 12.1, ^5J = 2.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.9, 173.5*, 66.4*, 60.5, 41.2*, 38.0, 37.0*, 36.0, 35.8*, 34.7, 34.3*, 33.5*, 33.4, 32.0, 29.8*, 28.8, 26.7, 26.5*, 26.3*, 22.1*, 15.0 ppm; IR (film): $\tilde{\nu}$ = 3340, 2920, 1620, 1465, 1400, 1020 cm^{-1}; HRMS (EI, 70 eV): *m/z*: calcd for $C_{14}H_{25}NO_2$: 239.1885, found: 239.1889 $[M]^+$; elemental analysis calcd (%) for $C_{14}H_{25}NO_2$: C 70.25, H 10.53, N 5.85; found: C 70.09, H 10.34, N 5.68.

5,5,6-Trimethyl-hepta-2,6-dienoic *tert*-butyl ester (37): According to GP 1 the phosphonate (379 mg, 3.00 mmol), NaH (96.0 mg, 4.00 mmol) and **36** (1.26 g, 5.00 mmol) in Et_2O (50 mL) for 16 h. Silica gel chromatography (CH/EE 97:3) gave **37** (542 mg, 81 %). R_f = 0.4 (CH/EE 19:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.67 (dt, ^3J = 15.3, ^3J = 7.6 Hz, 1H), 5.61 (dt, ^3J = 15.5, ^4J = 1.4 Hz, 1H), 4.67 (dq, ^3J = 1.4, ^4J = 1.4 Hz, 1H), 4.62 (dd, ^3J = 1.3, ^4J = 0.5 Hz, 1H), 2.12 (dd, ^3J = 7.6, ^4J = 1.4 Hz, 2H), 1.63 (dd, ^4J = 1.3, ^4J = 0.5 Hz, 3H), 1.37 (s, 9H), 0.96 ppm (s, 6H); ^{13}C NMR: δ = 165.9, 150.9, 145.2, 124.7, 110.2, 80.0, 43.3, 39.0, 28.2, 27.0, 19.4 ppm; IR (film): $\tilde{\nu}$ = 2970, 1715, 1650, 1455, 1367, 1335, 1160, 985, 895 cm^{-1}; HRMS: *m/z*: calcd for $C_{10}H_{16}O_2$: 168.1150; found: 168.1148 $[M-C_4H_8]^+$.

5-Methyl-5-(2-methyl-oxiranyl)-hex-2-enoic *tert*-butylester (32): According to GP 2 **37** (449 mg, 2.00 mmol) and *m*-CPBA (672 mg (77 %), 3.00 mmol) in CH_2Cl_2 (25 mL) for 1 h. Silica gel chromatography (CH/EE 9:1) gave **32** (387 mg, 81 %). R_f = 0.2; ^{1}H NMR (400 MHz, C_6D_6): δ = 7.06 (dt, ^3J = 15.5, ^3J = 7, 7 Hz, 1H), 5.84 (dt, ^3J = 15.5, ^4J = 1.4 Hz, 1H), 2.39 (dq, ^3J = 4.6, ^4J = 0.8 Hz, 1H), 1.99 (d, ^3J = 4.5 Hz, 1H), 1.92, 1.88, AB signal, ^2J = 14.1 Hz, additionally split by ^3J = 7.7 Hz and ^4J = 1.4 Hz, 2H), 1.43 (s, 9H), 0.99 (d. ^4J = 0.8 Hz, 3H), 0.74 (s, 3H), 0.66 ppm (s, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ = 165.4, 144.6, 125.8, 79.6, 60.3, 50.7, 41.8, 36.8, 28.2, 23.5, 22.8, 18.4 ppm; IR (film): $\tilde{\nu}$ = 2975, 1715, 1650, 1455, 1370, 1340, 1285, 1165, 1075, 985, 890, 855, 825, 780 cm^{-1}; HRMS: *m/z*: calcd for $C_{14}H_{24}O_3$: 240.1725; found: 240.1730 $[M]^+$.

2-(2-Hydroxymethyl-2,3,3-trimethyl-cyclobutyl)-acetic *tert*-butyl ester (33): According to GP 3 **32** (240 mg, 1.00 mmol), $[Cp_2TiCl_2]$ (24.9 mg, 100 μg), collidine hydrochloride (394 mg, 2.50 mmol) and zinc dust (131 mg, 2.00 mmol) for 16 h. Silica gel chromatography (CH/EE 86:14) gave **33** (228 mg, 94 %, *dr* 63:37). R_f = 0.3 (CH/EE 3:1); ^{1}H NMR (400 MHz, C_6D_6): δ = 3.65* (d, ^2J = 10.9 Hz, 1H), 3.60 (d, ^2J = 10.7 Hz, 1H), 3.41* (d, ^2J = 11.0 Hz, 1H), 3.40 (d, ^2J = 10.6 Hz, 1H), 2.47–2.38 (m, 1H), 2.47–2.38* (m, 1H), 2.33 (brs, 1H), 2.21 (dd, ^2J = 16.3, ^3J = 9.9 Hz, 1H), 2.18* (dd, ^2J = 17.5, ^3J = 7.8 Hz, 1H), 2.02 (dd, ^2J = 16.5, ^3J = 5.4 Hz, 1H), 1.79* (brs, 1H), 1.63* (dd, ^2J = 10.8, ^3J = 8.0 Hz, 1H), 1.52 (dd, ^2J = 10.4, ^3J = 8.4 Hz, 1H), 1.42–1.36* (m, 1H), 1.36* (s, 9H), 1.32 (s, 9H), 1.20 (dd, ^2J = 10.5, ^3J = 10.4 Hz, 1H), 1.22–1.15* (m, 1H), 1.04* (s, 3H), 1.02 (s, 3H), 0.96 (s, 3H), 0.94* (s, 3H), 0.81 (s, 3H), 0.78* ppm (s, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ = 173.7, 173.0*,80.1, 79.8*, 68.8, 65.2*, 45.5, 45.3*, 38.3*, 37.5*, 37.4, 37.1*, 36.6, 36.5, 36.4*, 33.6, 28.1*, 28.0, 25.7*, 24.9, 24.2, 23.7*, 19.0*, 14.8 ppm; IR (film): $\tilde{\nu}$ = 3445, 2970, 1730, 1455, 1370, 1260, 1150, 1030, 950, 850, 765 cm^{-1}; HRMS (EI, 70 eV): *m/z*: calcd for $C_{14}H_{26}O_3$: 186.1256; found: 186.1252 $[M-C_4H_8]^+$.

5,5,6-Trimethyl-hepta-2,6-dienoic dimethylamide (38): According to GP 1 **36** (505 mg, 4.00 mmol), NaH (120 mg, 5.00 mmol) and **36** (1.34 g, 6.00 mmol) in Et_2O (50 mL) for 16 h. Silica gel chromatography (CH/EE

4:1) gave **38** (631 mg, 81%). R_f=0.4 (CH/EE 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ=6.67 (dt, ^3J=15.0, ^3J=7, 5 Hz, 1H), 6.16 (dt, ^3J=15.1, ^4J=1.4 Hz, 1H), 4.70 (dq, ^3J=1.4, ^4J=1.4 Hz, 1H), 4.69 (dd, ^3J=1.5, ^4J=0.7 Hz, 1H), 3.02 (brs, 3H), 2.95 (brs, 3H), 2.20 (dd, ^3J=7.6, ^4J=1.3 Hz, 2H), 1.71 (dd, ^4J=1.4, ^4J=0.56 Hz, 3H), 1.04 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=166.7, 151.0, 142.9, 122.2, 110.1, 43.8, 39.0, 37.3, 35.5, 27.0, 19.5 ppm; IR (film): $\tilde{\nu}$=2965, 1660, 1620, 1450, 1395, 1265, 1145, 1065, 980, 890, 825, 740, 620 cm^{-1}; HRMS (EI, 70 eV): *m*/*z*: calcd for $C_{12}H_{21}NO_2$: 195.1623; found: 195.1622 $[M]^+$.

5-Methyl-5-(2-methyl-oxiranyl)-hex-2-enoic dimethylamide (34): According to GP 2 **38** (391 mg, 2.00 mmol) and *m*CPBA (77%, 672 mg, 3.00 mmol) in CH_2Cl_2 (25 mL) for 16 h. Silica gel chromatography (CH/EE 1:1→0:1) gave **34** (402 mg, 95%). R_f=0.1 (CH/EE 1:1); ^{1}H NMR (400 MHz, C_6D_6): δ=7.11 (dt, ^3J=14.9, ^3J=7, 6 Hz, 1H), 6.03 (dt, ^3J=14.9, ^4J=1.5 Hz, 1H), 2.71 (brs, 3H), 2.49 (dq, ^3J=4.7, ^4J=0.6 Hz, 1H), 2.36 (brs, 3H), 2.06 (s, 3H), 1.99 (AB signal, ^2J=13.9 Hz, additionally split by ^3J=7.7 and ^4J=1.4 Hz, 2H), 1.07 (d, ^4J=0.6 Hz, 1H), 0.83 (s, 3H), 0.76 ppm (s, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ=165.8, 142.1, 123.3, 60.5, 51.0, 42.2, 36.8, 36.4, 35.2, 23.6, 22.8, 18.5 ppm; IR (film): $\tilde{\nu}$=2970, 1660, 1615, 1495, 1395, 1265, 1150, 1060, 980, 890, 815, 775 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{12}H_{20}NO_2$: 210.1494; found: 210.1496 $[M-H]^+$.

2-(2-Hydroxymethyl-2,3,3-trimethyl-cyclobutyl)-*N*,*N*-dimethylacetamide (35): According to GP 3 **34** (211 mg, 1.00 mmol), $[Cp_2TiCl_2]$ (24.9 mg, 100 μg), collidine hydrochloride (394 mg, 2.50 mmol) and zinc dust (131 mg, 2.00 mmol) for 72 h. Silica gel chromatography (EE) gave **35** (200 mg, 94%, *dr* 72:28). R_f=0.3 (EE); ^{1}H NMR (400 MHz, C_6D_6): δ=4.63 (dd, ^3J=10.0, 2.7 Hz, 1H), 4.45* (d, ^3J=6.8 Hz, 1H), 4.05* (d, ^2J=11.0 Hz, 1H), 4.01 (dd, ^2J=11.0, ^3J=1.8 Hz, 1H), 3.56* (dd, ^2J=10.7, ^3J=7.2 Hz, 1H), 3.43 (dd, ^2J=10.7, ^3J=10.2 Hz, 1H), 2.71 (dddd, ^3J=11.1, 10.7, 8.4, 3.0 Hz, 1H), 2.55* (s, 3H), 2.50 (s, 3H), 2.37* (dd, ^2J=14.5, ^3J=10.5 Hz, 1H), 2.26* (dddd, ^3J=9.9, 9.9, 8.4, 4.1 Hz, 1H), 2.22* (s, 3H), 2.15 (s, 3H), 2.11* (dd, ^2J=14.5, ^3J=4.0 Hz, 1H), 2.03 (dd, ^2J=17.3, ^3J=11.1 Hz, 1H), 1.77 (dd, ^2J=17.5, ^3J=2.9 Hz, 1H), 1.67* (dd, ^2J=0.8, ^3J=8.3 Hz, 1H), 1.57 (dd, ^2J=10.4, ^3J=8.4 Hz, 1H), 1.41* (dd, ^2J=10.2, ^3J=10.2 Hz, 1H), 1.28 (dd, ^2J=10.6, ^3J=10.6 Hz, 1H), 1.25* (s, 3H), 1.07 (s, 3H), 1.01 (s, 3H), 1.00* (s, 3H), 0.84 (s, 3H), 0.82* ppm (s, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ=173.4*, 173.1, 68.8, 64.7*, 46.1*, 45.7, 38.6*,37.6*,37.5, 36.8*, 36.6*, 36.4, 36.1, 35.0*, 34.9*, 34.3, 34.1, 25.9*, 24.5, 24.0, 23.3*, 19.3*, 14.8 ppm; IR (film): $\tilde{\nu}$=3265, 2935, 1610, 1505, 1560, 1410, 1260, 1160, 1045, 800, 770, 710, 690 cm^{-1}; HRMS (EI, 70 eV): *m*/*z*: calcd for $C_{12}H_{23}NO_2$: 213.1729; found: 213.1729 $[M]^+$.

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