Extended Stereocontrol in Silyl Group-Transfer Cyclizations: Control of Four Contiguous Chiral Centers

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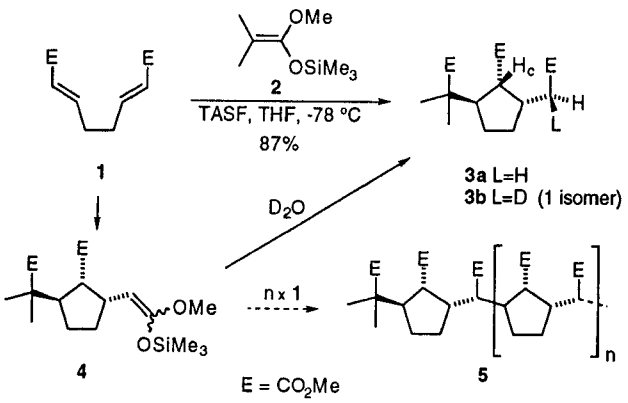
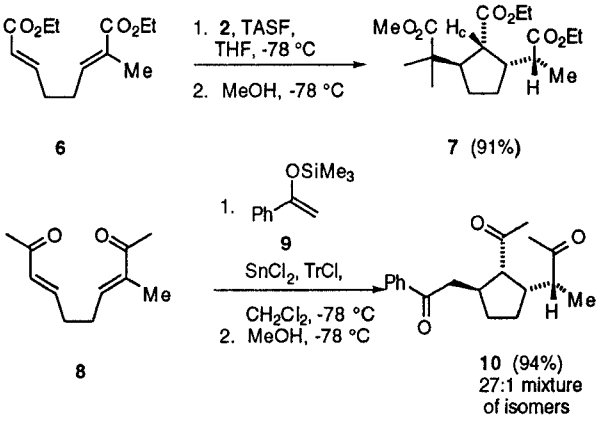
The potential for extended stereocontrol in silyl group-transfer cyclizations was explored in model studies which formed four contiguous chiral centers. The diastereofacial selectivity for the reaction of cyclized intermediates was outstanding for both fluoride and $SnCl_2$–trityl chloride mediated reactions. Good simple diastereoselectivity was observed in reactions initiated by prochiral silyl enolates.

We recently reported a series of methods for achieving ordered, multiple (serial) Michael reactions initiated by silyl enol ethers or silyl ketene acetals.[2,3] These "silyl group-transfer cyclizations", analogous to the silyl enolate initiated group-transfer polymerization of acrylates and related reactions,[4] afforded highly stereoselective entries into cyclopentanes and cyclohexanes with three contiguous chiral centers, as in the tris(dimethylamino)sulfonium trimethylsilyldifluoride (TASF) catalyzed conversion of diene **1** into cyclopentane **3a**. One of our goals in this area has been to develop methods for the synthesis of functionalized oligomers such as **5** with complete control of the relative stereochemistry throughout the chain. We report here the results of our model studies toward this end. Although we have had some difficulty in firmly establishing the stereochemistry of our products, our results indicate that good to complete control over the formation of four contiguous chiral centers[5] can be achieved, and that the prospects for the stereocontrolled production of extended systems are excellent.



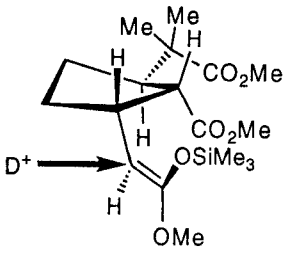
Our goals require success in two aspects of stereocontrol. The first requirement is diastereofacial selectivity[6] in the reaction of cyclized silyl enol ethers or silyl ketene acetals (e.g. **4**) with electrophiles. Secondly, the Michael reactions of these intermediates with prochiral acceptors must exhibit "simple diastereoselectivity." The feasibility of the first of these goals was initially suggested by the observation that deuteration of the intermediate silyl ketene acetal **4** afforded **3b** as a single diasteromer. This high diastereoselectivity occurs despite the fact that **4** is formed as a 2.5–5:1 mixture of geometrical isomers, as determined by ^{1}H NMR of a reaction carried out in DMSO-d_6.

Even more satisfying selectivity was observed in the cyclizations of the unsymmetrical addends **6** and **8**. The fluoride-catalyzed reaction of **6** with **2** afforded **7** as a single diastereomer in 91% yield, and the $SnCl_2$–trityl chloride mediated reaction of **8** with **9** afforded **10** in 94% yield as a 27:1 mixture of isomers. In each example, the least-substituted enoate or enone reacts first, and there is high selectivity for a single product out of 12 possible! It is also notable that the one-step formation of four contiguous chiral centers in **3b**, **7**, and **10** from C_s symmetric starting materials is distinct from the similar accomplishments of Diels–Alder reactions and cationic polyene cyclizations, in that no aspect of the relative stereochemistry is predetermined by stereospecificity.



The relative stereochemistries of the *endocyclic* stereocenters of **7** and **10** were assigned from analogy with the firmly established[2] demethyl analogs (e.g. **3** in the case of **7**). There is also a similarity of coupling constants for the central methine proton H_c for **7** and **3**: in **7** H_c appeared as a doublet of doublets at $\delta = 2.75$ with $J = 4.5$ and 8.4 Hz while in **3** H_c appeared as a doublet of doublets at $\delta = 2.87$ with $J = 6.2$ and 9.2 Hz. The analogous stereochemistry of **7** and **10** with the demethyl analogs is expected based on a bicyclic transition state model which correctly rationalized the stereochemistry in the simpler systems.[2]

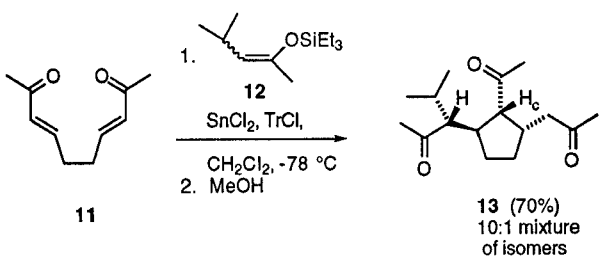
The exocyclic stereocenters of **3b**, **7**, and **10** are the result of diastereofacially selective protonations of cyclized intermediates like **4**. The stereochemistry of **3b** is unchanged in reactions performed in DMSO versus THF, suggesting that the diastereofacial selectivity arises from a simple steric effect as opposed to some kind of intramolecular proton delivery. If this is the case, then the stereochemistry assigned in **3b** would be the result of protonation of **4** from the least hindered side in its most stable conformation. Since it is unlikely that the extra methyl groups in **7** and **10** would result in a complete reversal of protonation stereochemistry, the exocyclic ste-



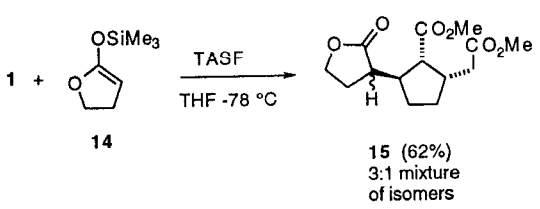
reocenters of **7** and **10** were assigned analogously. It should be noted that the isomers of **10** slowly equilibrated on acidic silica gel to a mixture containing larger amounts of the kinetically minor isomer indicating that the stereoselectivity is not the result of thermodynamic control. Unfortunately, all attempts to chemically or spectroscopically establish the exocyclic stereocenters of **3b, 7** and **10**, or more solidly establish the endocyclic stereocenters of **10**, have so far been fruitless, and the assignments must be considered highly tentative.

However, the high diastereofacial selectivity of the cyclized intermediates was secure, and we turned our attention to models for obtaining simple diastereoselectivity in the Michael addition of cyclized intermediates in their reactions with prochiral Michael acceptors. Although a number of highly diastereoselective Michael reactions are known,[6] many of the methods have proven unsuitable for serial reactions. Also, the Michael reactions of silyl enolates have sometimes been notably unselective.[4c] Our reactions face the additional complication that mixtures of isomers (e.g. **4**) of cyclized intermediates are generally formed. However, based on observations of Heathcock,[7] there was some hope that stereoselectivity could be obtained even with a mixture of silyl enolate isomers.

As a model for these complications, we choose to react **12**, as a 2:1 mixture of *Z* and *E* isomers, with **11**. We were pleased to find that the $SnCl_2$–trityl chloride mediated addition of **12** to **11** at −78 °C afforded a 70% yield of **13** as a 10:1 mixture of two diastereomers.



Unfortunately, we have only observed lower diastereoselectivity in the fluoride-catalyzed reactions of prochiral silyl ketene acetals. Addition of silyl ketene acetal **14** to **1** afforded **15** in 62% yield as a 3:1 mixture of two diastereomers.



The relative stereochemistries of the endocyclic stereocenters of **13** were assigned from the observation that the central methine proton H_c appeared as a triplet at $\delta = 2.84$ with $J = 8$ Hz while the same proton in three products of similar cyclizations of **11** all appeared as triplets around $\delta = 3$ with $J = 8$ Hz.[2] The endocyclic stereocenters of **15** were assigned by analogy with **3**. We have had no success in spectroscopically assigning the exocyclic stereocenters in **13** and **15**, but the stereochemistry of **13** is likely to be that shown, based on many examples of a preference for formation of the anti product in similar Mukaiyama–Michael reactions.[7] The equilibration of the isomers of **13** on acidic silica gel indicates that this mixture is not the result of thermodynamic control.

In conclusion, the very high diastereofacial selectivity in reactions of the cyclized products and reasonable simple diastereoselectivity in the Michael reactions establishes the intriguing possibility of extended stereocontrol in oligomers from silyl group-transfer cyclizations.

The general experimental methods and procedures were as outlined in reference 2. The standard workup procedure involved extraction with Et_2O (3 × 40 mL), drying of the combined organic layers ($MgSO_4$), filtration, and concentration on a rotary evaporator. Medium performance liquid chromatography (MPLC) was carried out using a 17.5 in × 57 mm or a 12 in × 26 mm Michael–Miller MPLC silica gel column using a Fluid Metering, Inc. lab pump (model RP-SY). Compounds **7, 10, 13** and **15** gave C, H ± 0.4%.

Diethyl (2*E*,6*E*)-2-Methylocta-2,6-diene-1,8-dioate (6):[8]

To a mixture of 20.0 g (232 mmol) of succinaldehyde in 200 mL of CH_2Cl_2 was added dropwise a mixture of 18.8 g (54.0 mmol) of ethyl (triphenylphosphoranylidene)acetate and 100 mL of CH_2Cl_2. After stirring for 1 d, the solvent was removed on a rotary evaporator, and the residue was chromatographed (8 in × 56 mm silica gel column; 20% EtOAc/petroleum ether) to afford 7.3 g (87%) of ethyl (2*E*)-6-oxohex-2-enoate [^{1}H NMR ($CDCl_3$): $\delta = 9.77$ (t, $J = 2$ Hz, 1 H), 6.91 (dt, $J = 6.6$, 15.6 Hz, 1 H), 5.82 (dt, $J = 1.4$, 15.6 Hz, 1 H), 4.15 (q, $J = 7.1$ Hz, 2 H), 3.30 (s, 3 H), 2.68–2.42 (m, 4 H), 1.25 (t, $J = 7.1$ Hz, 3 H)].

NaH (2.40 g of a 60% by weight dispersion in mineral oil, 60.0 mmol) was rinsed with 3 × 40 mL portions of pentane under a stream of N_2. THF (75 mL) was added, and the mixture was cooled to 0 °C. A mixture of 12.4 g (52.0 mmol) of ethyl 2-(diethylphosphono)propionate and 25 mL of THF was added dropwise. After H_2 evolution ceased, a mixture of 7.3 g (47 mmol) of ethyl (2*E*)-6-oxohex-2-enoate and 20 mL of THF was added dropwise. The reaction mixture was stirred for 30 min at 0 °C, warmed to r. t. over 3 h, and quenched by the addition of 75 mL of 0.5 N aq HCl. The mixture was extracted with Et_2O (3 × 100 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated on a rotary evaporator. The residue was chromatographed (7 in × 56 mm silica gel column; 5% EtOAc/petroleum ether) to afford 6.3 g (53%) of a 5:1 mixture (GC analysis) of **6** and its 2*Z* isomer. The isomers were separated on MPLC (5% EtOAc/petroleum ether). The spectral properties of **6** were as follows.

^{1}H NMR ($CDCl_3$): $\delta = 7.00$–6.83 (m, 1 H), 6.74–6.64 (m, 1 H), 5.83 (d, $J = 15.6$ Hz, 1 H), 4.17 (q, $J = 7.3$ Hz, 4 H), 2.34–2.30 (m, 4 H), 1.81 (d, $J = 1.2$ Hz, 3 H), 1.32–1.22 (m, 6 H).

^{13}C NMR ($CDCl_3$): $\delta = 167.87$ (C), 166.38 (C), 147.34 (CH), 139.78 (CH), 128.95 (C), 122.09 (CH), 60.48 (CH_2), 60.21 (CH_2), 30.98 (CH_2), 27.07 (CH_2), 14.22 (CH_3), 12.42 (CH_3).

Methyl (1α,2β,3β)-2-(Ethoxycarbonyl)-3-[1-(ethoxycarbonyl)ethyl]-α,α-dimethylcyclopentaneacetate (7):

To a mixture of 162 mg (0.675 mmol) of **6** and 415 mg (2.30 mmol) of **2** in 10 mL of THF at −78 °C was added 36 mg (0.13 mmol) of

TASF as a solution in 1 mL of dry MeCN. The mixture was stirred for 90 min, and 5 mL of MeOH was then added. After stirring for an additional 30 min at −78 °C, the mixture was warmed to r.t., and 20 mL of water was added. The residue after the standard workup procedure was a single diasteromer of pure **7**, as evidenced by GC and ^{1}H NMR analyses; yield 209 mg (91%). The spectral properties of **7** were as follows.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.20–4.05 (m, 4H), 3.61 (s, 3H), 2.75 (dd, J = 4.5, 8.5 Hz, 1H), 2.66–2.59 (m, 1H), 2.31 (dq, J = 6.8, 11.2 Hz, 1H), 2.02–1.92 (m, 1H), 1.84–1.75 (m, 1H), 1.68–1.55 (m, 2H), 1.40–1.30 (m, 1H), 1.23 (t, J = 8.3 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H), 1.15 (d, J = 6.8 Hz, 3H), 1.11 (s, 6H).

^{13}C NMR ($CDCl_3$): δ = 177.45 (C), 176.07 (C), 175.72 (C), 60.13 (CH_2), 51.60 (CH), 51.50 (CH_3), 48.60 (CH), 47.16 (CH), 44.87 (C), 41.35 (CH), 30.41 (CH_2), 27.36 (CH_2), 23.41 (CH_3), 21.94 (CH_3), 16.75 (CH_3), 14.15 (CH_3).

IR (neat): ν = 3020, 1750, 1210 cm^{-1}.

Preparation of 7 Uusing Benzoate Catalysis:

To a mixture of 195 mg (0.812 mmol) of **6**, 195 mg (0.490 mmol) of tetrabutylammonium *m*-chlorobenzoate, and 25 mL of THF was added 585 mg (3.36 mmol) of **2**. The mixture was stirred for 1 h, and then 5 mL of MeOH was added. After stirring for an additional 5 min, the mixture was poured into 25 mL of water. After the normal workup procedure, the residue was chromatographed (8 in × 26 mm silica gel column; 20% EtOAc/petroleum ether) to afford 175 mg (63%) of **7** as a single diastereomer.

(3*E*,7*E*)-3-Methyldeca-3,7-diene-2,9-dione (8):

To 6.25 g (33.5 mmol) of 2-triethylsiloxy-2-butene (prepared in 60% yield by the hydrosilylation of methyl vinyl ketone)[9] in 150 mL of dry MeCN was added 6.50 g (36.5 mmol) of *N*-bromosuccinimide. After stirring for 2.5 h, 11.0 g (41.9 mmol) of PPh_3 (purchased from Fluka Chemical Company, 97% pure) was added, and the reaction was heated at 60–65 °C overnight. The mixture was then cooled, 10 mg of phenolphthalein was added, and 4 N aq NaOH was added with swirling until a pink color persisted. CH_2Cl_2 (100 mL) was added, the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and the filtrate was concentrated on a rotary evaportor to afford 9.0 g (81%) of 3-triphenylphosphoranylidene-2-butanone as an amorphous solid [^{1}H NMR ($CDCl_3$): δ = 7.50–7.20 (m, 15H), 2.14 (s, 3H), 1.66 (d, J = 17 Hz, 3H)].

To 3.4 g (25 mmol) of (3*E*)-7-oxo-3-hepten-2-one (prepared in 75% yield from succinaldehyde by the method of House[10]) in 75 mL of CH_2Cl_2 was added a mixture of 5.7 g (16.4 mmol) of 3-triphenylphosphoranylidene-2-butanone and 25 mL of CH_2Cl_2. The reaction was stirred for 14 h, the solvent was removed with a rotary evaporator, the solid residue was washed with Et_2O (40 mL) and filtered, and the filtrate was concentrated on a rotary evaporator. The residue was chromatographed on a 6 in × 56 mm silica gel column to afford 1.8 g (61%, based on the phosphorane) of **8** as a yellow liquid.

^{1}H NMR ($CDCl_3$): δ = 6.82–6.68 (m, 1H), 6.58–6.50 (m, 1H), 6.10 (d, J = 15.9 Hz, 1H), 2.42–2.32 (m, 4H), 2.28 (s, 3H), 2.23 (s, 3H), 1.76 (d, J = 1.1 Hz, 3H).

^{13}C NMR ($CDCl_3$): δ = 199.43 (C), 198.19 (C), 146.02 (CH), 140.82 (CH), 138.56 (C), 131.79 (CH), 31.19 (CH_2), 27.43 (CH_2), 26.98 (CH_2), 25.42 (CH_3), 11.24 (CH_3).

IR (neat): ν = 2932, 1734, 1718, 1697, 1668, 1641, 1628, 1255 cm^{-1}.

(1α,2β,3β)-2-Acetyl-3-(1-methyl-2-oxopropyl-(β-oxophenethyl)-cyclopentane (10):

To a mixture of 226 mg (1.19 mmol) of $SnCl_2$, 263 mg (0.94 mmol) of trityl chloride, 200 mg (1.11 mmol) of **8**, and 20 mL of CH_2Cl_2 at −78 °C was added 898 mg (4.67 mmol) of 1-phenyl-1-trimethylsiloxyethene. The reaction was stirred for 2 h, and 10 mL of MeOH was added. The mixture was stirred for 20 min, and was then poured into 20 mL of water. Gas chromatographic and ^{1}H NMR analysis of the residue after the normal workup showed a 27:1 mixture of 2 diastereomers. This residue was chromatographed (20% EtOAc/petroleum ether; 6 in × 19 mm silica gel column, pre-washed with 150 mL of a 75:20:5 mixture of petroleum ether/EtOAc/NEt_3). Gas chromatographic analysis of the purified product (314 mg, 94%) indicated a 13:1 mixture of 2 diastereomers of **9**, which were separated on MPLC (20% EtOAc/petroleum ether). The spectral properties of the major diastereomer were as follows.

^{1}H NMR ($CDCl_3$): δ = 7.90 (dd, J = 1.8, 8.9 Hz, 2H), 7.60–7.36 (m, 3H), 3.09–3.02 (m, 2H), 2.87–2.60 (m, 3H), 2.25 (s, 3H), 2.22–1.95 (m, 2H), 2.10 (s, 3H), 1.80–1.50 (m, 2H), 1.40–1.20 (m, 1H), 0.95 (d, J = 6.6 Hz, 3H).

^{13}C NMR ($CDCl_3$): δ = 212.73 (C), 211.65 (C), 199.03 (C), 136.69 (C), 133.20 (CH), 128.62 (CH), 127.89 (CH), 57.50 (CH), 47.10 (CH), 45.44 (CH), 45.19 (CH_2), 38.24 (CH), 31.43 (CH_3), 31.09 (CH_2), 30.03 (CH_3), 29.65 (CH_2), 16.93 (CH_3).

IR (neat): ν = 2966, 2872, 2254, 1701, 1596, 1355 cm^{-1}.

2-Triethylsiloxy-4-methyl-2-pentene (12):

This compound was prepared as a 2:1 mixture of *Z*:*E* olefin isomers in 69% yield by the hydrosilylation of mesityl oxide.[11] The NMR data given is for the major isomer.

^{1}H NMR ($CDCl_3$): δ = 4.20 (d, J = 9.5 Hz, 1H), 2.70–2.60 (m, 1H), 1.75–1.73 (m, 3H), 1.05–0.80 (m, 15H), 0.72–0.47 (m, 6H).

(1α,2β,3β)-2-Acetyl-1-(1-acetyl-2-methyl)propyl-3-(2-oxopropyl)-cyclopentane (13):

To a mixture of 225 mg (1.19 mmol) of $SnCl_2$, 292 mg (1.05 mmol) of trityl chloride, and 188 mg (1.13 mmol) of **11**[2] in 30 mL of CH_2Cl_2 at −78 °C was added 463 mg (2.15 mmol) of **12** as a 2:1 mixture of *Z*:*E* double-bond isomers. After 1 h, 10 mL of MeOH was added, the mixture was stirred at −78 °C for 20 min, and was then poured into 30 mL of sat. brine. Gas chromatographic and ^{1}H NMR analysis of the residue following the normal workup indicated a 10:1 mixture of 2 diastereomers. This residue was chromatographed (40% EtOAc/petroleum ether, 6 in × 19 mm silica gel column, pre-washed with 150 mL of a 75:20:5 mixture of petroleum ether/EtOAc/NEt_3). Gas chromatographic analysis of the purified product (212 mg, 70%) indicated a 10:1 mixture of 2 diastereomers, which were separated on MPLC (30% EtOAc/petroleum ether). Also recovered from the column was 19 mg of **11** (79% yield of **13** based on recovered **11**). The major diastereomer was a white solid when pure, mp 68–69 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.84 (t, J = 8.44 Hz, 1H), 2.70 sep, J = 7 Hz, 1H), 2.59 (sep, J = 8.0 Hz, 1H), 2.45 (dd, J = 7.6, 18.2 Hz, 1H), 2.36–2.28 (m, 2H), 2.14 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H), 1.84–1.78 (m, 3H), 1.50–1.30 (m, 2H), 0.96 (d, J = 6.8 Hz, 3H), 0.81 (d, J = 6.8 Hz, 3H).

^{13}C NMR ($CDCl_3$): δ = 212.57 (C), 211.33 (C), 207.77 (C), 61.75 (CH), 57.65 (CH), 44.93 (CH_2), 41.40 (CH), 37.44 (CH), 33.53 (CH_3), 31.97 (CH_3), 31.83 (CH_2), 30.32 (CH_3), 29.51 (CH), 27.12 (CH_2), 21.46 (CH_3), 19.68 (CH_3).

IR ($CDCl_3$): ν = 2963, 1707, 1701, 1686, 1356 cm^{-1}.

Methyl (1α,2β,3β)-3-(Methoxycarbonylmethyl)1-(2-oxotetrahydrofuran-3-yl)cyclopentane-2-carboxylate (15):

To a mixture of 248 mg (1.25 mmol) of **1**, 640 mg (4.02 mmol) of **14**, and 25 mL of THF at −78 °C was added 30 mg (0.11 mmol) of TASF as a solution in 1.5 mL of dry MeCN. The reaction was stirred for 90 min, 10 mL of MeOH was added, and the mixture was warmed to r.t.and poured into 25 mL of water. After the normal workup, the residue was analyzed by GC, which showed a 3:1 mixture of 2 diastereomers of **15**. The residue was chromatographed (7 in × 19 mm silica gel column, 40% EtOAc/hexanes) to afford 220 mg (62%) of **15** as a 3:1 mixture of 2 diastereomers, which were separated on MPLC (30% EtOAc/petroleum ether). The spectral properties of the major diastereomer of **15** formed in the reaction were as follows.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.35–4.27 (m, 1H), 4.18–4.07 (m, 1H), 3.64 (s, 6H), 3.04 (dd, J = 7.4, 8.9 Hz, 1H), 2.75–2.62 (m, 3H), 2.37–2.22 (m, 3H), 2.15–2.07 (m, 1H), 2.02–1.87 (m, 2H), 1.53–1.37 (m, 2H).

^{13}C NMR ($CDCl_3$): δ = 177.67 (C), 174.83 (C), 172.80 (C), 66.20 (CH_2), 51.62 (CH_3), 51.56 (CH_3), 49.73 (CH), 42.37 (CH), 42.22

(CH), 38.97 (CH), 35.64 (CH_2), 31.77 (CH_2), 28.78 (CH_2), 27.58 (CH_2).

IR (neat): ν = 2920, 1760, 1750, 1720, 1430, 1370 cm^{-1}.

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