Palladium catalyzed allylation is under stereoelectronic control

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Abstract
Palladium catalyzed allylation of menthone and 4-*t*-butylcyclohexanone derivatives is shown to be under stereoelectronic control leading to the products of axial allylation. The stereochemical assignment is supported by ^{1}H NMR experiments and X-Ray crystallography of selected examples.

Keywords: Palladium, allylation, stereoelectronic

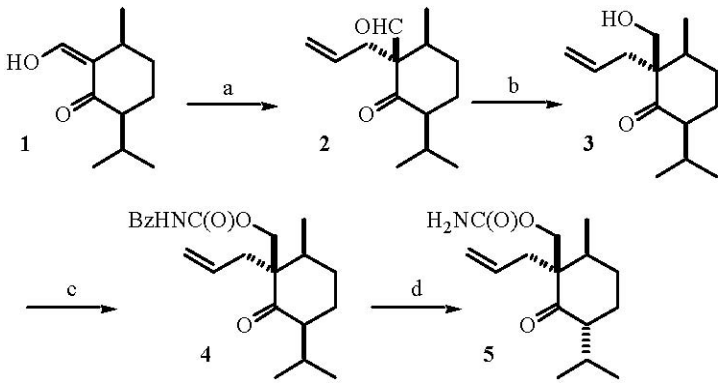
Introduction

The stereochemistry of palladium catalyzed allylation has been extensively studied in terms of the use of asymmetric ligands to induce chirality[1] and the stereochemistry of the allylic starting material.[2] We are not aware of previous studies concerning preexisting chirality in carbon nucleophiles in these reactions.[3]

Results and Discussion

Recently we had occasion to perform the allylation of formyl isomenthone **1**[4] and were pleased to find the expected[5] exclusive *C*-allylation product **2** was obtained as a single diastereoisomer (Scheme 1). Selective reduction of the aldehyde to alcohol **3** and the subsequent treatment with benzoyl isocyanate gave carbamate **4** which upon treatment with methanolic potassium carbonate yielded a carbamate derivative **5** that was amenable to X-Ray crystallography (Figure 1).[6] This unequivocally showed the *trans* relationship of the allyl and methyl groups, although they were now diequatorial, due to epimerization at the *iso*-propyl center during methanolysis. A small amount of the diastereomer was also obtained. Hence, it was concluded that the original

allylation was exclusively axial.



Scheme 1. Reagents (a) allyl acetate, K_2CO_3, $Pd(dba)_2$, PPh_3, THF; (b) $NaBH_4$, MeOH; (c) BzNCO (Bz = benzoyl), CH_2Cl_2; (d) K_2CO_3, MeOH.

This selectivity may be attributed to the steric hindrance of one face by the α−methyl group, but it could also be due to stereoelectronic effects which are known to favor axial alkylation and protonation.[7] We, therefore, turned to the 4-*t*-butylcyclohexanone system, which is sterically unbiased and has been widely used in stereoelectronic studies. The 2-formyl,[8] 2-carbethoxy[9] and 2-phenylsulfonyl[10] derivatives, **6**, **7** and **8** were prepared by literature methods. Allylation was carried out by treatment with allyl acetate in THF in the presence of a catalyst system consisting of $Pd(dba)_2$ and triphenyl phosphine (Scheme 2). For the formyl compounds, potassium carbonate was an effective base. For the ester and sulfone substrates, this base was ineffective, while tetramethyl guanidine resulted in a sluggish reaction. Potassium *t*-butoxide was found to be the base of choice.

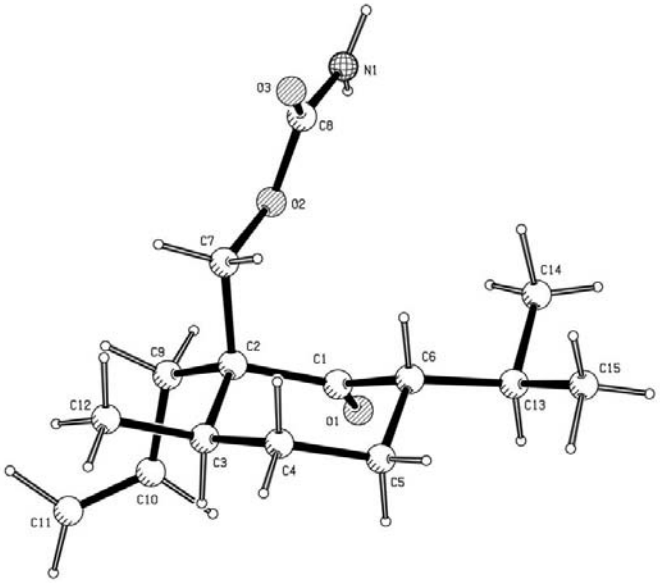
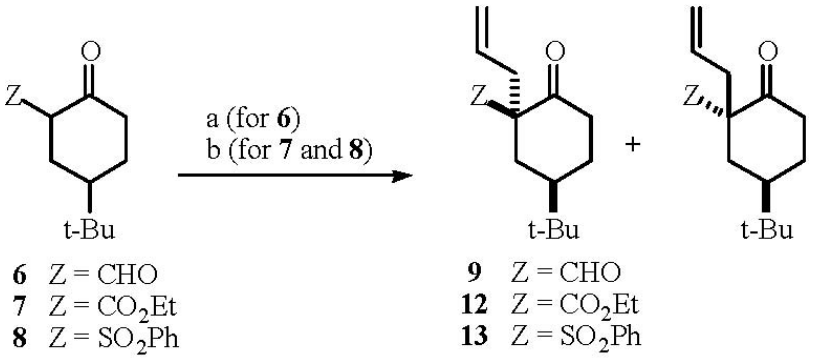
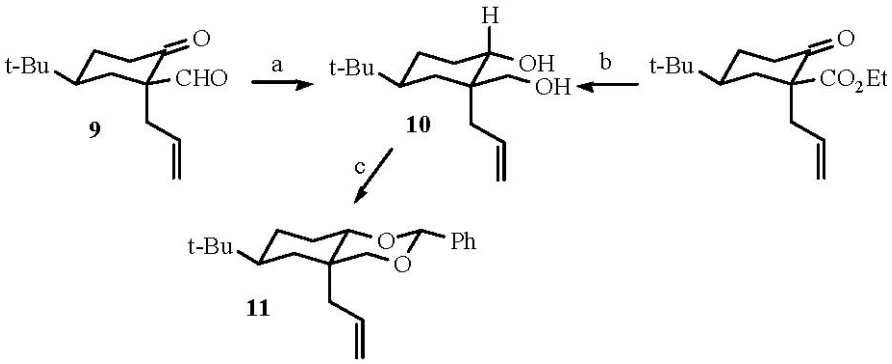


Figure 1. X-Ray structure of carbamate **5**



Scheme 2. Reagents: (a) allyl acetate, K_2CO_3, $Pd(dba)_2$, PPh_3, THF; (b) allyl acetate, KO*t* -Bu, $Pd(dba)_2$, PPh_3, THF.

In each case, two isomers were formed, but in unequal amounts (Table). For the 2-formyl substrate **6**, the stereochemistry was unequivocally demonstrated by reduction of the major isomer **9** to the diol **10** with sodium borohydride (Scheme 3). The coupling constants of the methyne proton confirmed that the product was the expected equatorial secondary alcohol.[11] Conversion of diol **10** to 1,3-dioxane **11** by exchange with benzaldehyde dimethyl acetal, allowed the proof of the stereochemistry through NOESY interactions. In particular the correlation between the three axial protons of the dioxolane ring (δ 3.35, 3.60, 5.55) is consistent only with the structure shown. The same diol was obtained by $LiAlH_4$ reduction of the major isomer of the allylated β-ketoester **12**, thus also providing the stereochemical assignment in this case.



Scheme 3. (a) $NaBH_4$, MeOH. (b) $LiAlH_4$, THF. (c) $PhCH(OMe)_2$, ppts.

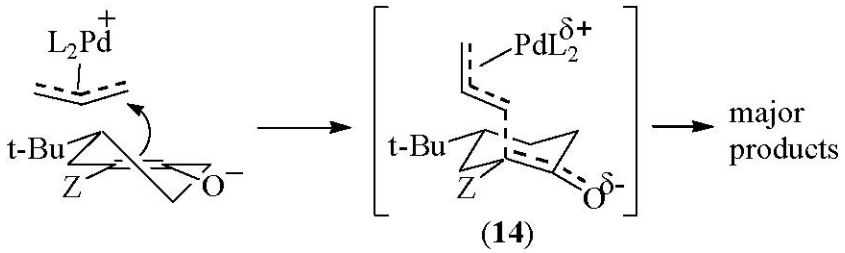
Recrystallization from hexane of the major isomer of the allylated ketosulfone **13** yielded crystals, which permitted X-ray determination of their structure.[12] This showed that the major allylation product **13** was formed with the same sense of diastereoselectivity, i.e. *trans* to the *t*-Bu group. In this case however, the allylation product **13** adopted a distorted boat conformation.

Table: Allylation Diastereoselectivity

Entry	Substrate	Z	Base	Combined yield	Ratio
1	**6**	CHO	K_2CO_3	81%[a]	7:1
2	**7**	CO_2Et	KO*t*-Bu	52%[b]	1.6:1
3	**8**	SO_2Ph	KO*t*-Bu	77%[a]	2.9:1

[a] Separable by flash chromatography. [b] Incomplete separation by flash chromatography

All of the major products of the allylation reactions are consistent with the approach of the π-allyl palladium intermediate towards the face of the enolate so that a chair like transition state **14** results, rather than the alternative boat (Scheme 4).



Scheme 4. The stereoelectronic effect.

Conclusions

Palladium catalyzed allylation of cyclohexanone derivatives has been shown to favor the formation of the axial isomer. This is consistent with previous observations made on simple alkylation and protonation reactions, and shows that the same stereoelectronic principles apply. The selectivity was found to be highly dependant on the activating group - with the formyl group giving the highest stereoselectivity. We anticipate that these results will be useful in synthesis.

Experimental Section

General Procedures. Flash chromatography was carried out on silica gel (230-400 mesh, Merck). Melting points were determined on a Büchi 535. NMR spectra were recorded on a Varian Gemini 2000 or Bruker BZH 200 at 200 MHz (^{1}H) with $CDCl_3$ as the solvent and residual $CHCl_3$ or Me_4Si as the internal reference. IR spectra were recorded on a PE 1760X instrument, either neat or as nujol mulls. MS were recorded on a Finigan GCQ insturment and HRMS on a Finigan Mat 90 instrument. Optical rotation data was recorded on a Jasco P-1020 polarimeter. Elemental analysis was performed at the Instrument Centre of Chulalongkorn

University.

Materials. $Pd(dba)_2$ was prepared by a literature method.[13] All other materials were commercial, unless otherwise stated. THF was distilled from Na/benzophenone, methanol from magnesium and dichloromethane from CaH_2.

(2*R*,3S,6*S*)-2-Formyl-3-methyl-2-(3'-propenyl)-6-isopropylcyclohexanone (2). A mixture of formyl isomenthone **1**[3] (2.03 g, 11.09 mmol), anhydrous potassium carbonate (1.53 g, 11.09 mmole), triphenylphosphine (0.15 g, 0.55 mmol), $Pd(dba)_2$ (0.16 g, 0.28 mmol) and allyl acetate (2.39 mL, 22.18 mmole) in THF (40 mL) was stirred at room temperature under N_2 overnight. The mixture was filtered through celite and the volatiles were evaporated. The residue was purified by flash chromatography on silica gel, eluting with 4% EtOAc/hexane to give the aldehyde **2** as an oil (2.09 g, 85%). ^{1}H NMR δ 0.82 (3H, d, *J* = 7, CH_3), 0.84 (3H, d, *J* = 7, CH_3), 0.93 (3H, d, *J* = 7, CH_3), 1.45-1.80 (2H, m,), 1.80-2.30 (5H, m), 2.60 (1H, dd, *J* = 8,13 C<u>H</u>CH=CH_2), 2.72 (1H, ddt, *J* = 13,6,1, C<u>H</u>CH=CH_2), 4.95 (1H, d, *J* = 10, =CH_2), 5.00 (1H, d, *J* = 18, =CH_2), 5.40 (1H, m, CH=), 10.00 (1H, s, CHO); ^{13}C NMR ˜ 15.7, 16.0, 19.0, 22.0, 26.5, 28.0, 37.5, 39.0, 54.0, 65.5, 119.0, 132.5, 205.5, 213.5; ν/cm-1: 2953, 1724, 1720, 1629; m/z (EI) 223 (1.4) (M+), 139 (43), 111 (60), 69 (100), 55 (89); HRMS calcd for $C_{14}H_{22}O_2$ 223.1698,.Found 223.1693; $[\alpha]_D^{28}$ = + 25.3° (c = 0.133, CH_2Cl_2).

(2*R*,3S,6*S*)-2-Hydroxymethyl-3-methyl-2-(3'-propenyl)-6-isopropyl cyclohexanone (3). Sodium borohydride (320 mg, 8.72 mmol) was added to a solution of the β-ketoaldehyde **2** (3.89 g, 17.44 mmol) in methanol under N_2 at -78 °C. The mixture was stirred for ten minutes, then allowed to warm slowly to room temperature. Aqueous ammonium chloride was added and the mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried (Na_2SO_4) and evaporated. Purification of the residue by flash chromatography on silica gel (90 g) eluting with 3% EtOAc/hexane gave the alcohol **3** (2.54 g, 65%) as a colorless solid, mp 72-75 °C. ^{1}H NMR: δ 0.65-0.95 (9H, m, CH_3), 1.35-1.60 (3H, m), 1.70-2.65 (7H, m,), 3.35 (1H, d, *J* = 12, C<u>H</u>HOH), 3.83 (1H, d, *J* = 12, C<u>H</u>HOH), 4.95-5.15 (2H, m, =CH_2), 5.65 (1H, m, CH=); ^{13}C NMR: δ 13.3, 15.0, 18.0, 20.8, 23.3, 25.4, 27.4, 35.3, 36.7, 51.7, 55.7, 62.8, 118.1, 132.8; ν/cm-1: 3299, 2919, 1690, 1464, 1370; m/z (EI) 225 (18), 224 (M+) (12), 191 (10), 153 (21), 107 (76, 81 (100); found C 74.98, H 10.70 %, $C_{14}H_{24}O_2$ requires C 74.95, H 10.78 %; $[\alpha]_D^{28}$ = + 85.5° (c = 0.033, CH_2Cl_2).

(2*R*,3*S*,6S)-2-*N*-Benzoyl-carbamoyloxymethyl-3-methyl-2-(3'-propenyl)-6-isopropyl cyclohexanone (4). Benzoyl isocyanate (88 μL of a 5M solution in CH_2Cl_2, 0.44 mmole) was added to a solution of the alcohol **3** (100 mg, 0.44 mmol) in CH_2Cl_2 (4 mL) under N_2 at -78 °C. After thirty minutes, the mixture was allowed to warm to room temperature and evaporated. Purification by flash chromatography on silica gel (3 g) eluting with 15% EtOAc/hexane gave the N-acyl carbamate **4** (150 mg, 91%) as a colourless solid mp 58-62 °C. ^{1}H NMR: δ 0.80-1.00 (9H, m, CH_3), 1.45-1.70 (2H, m2), 1.95-2.60 (6H, m), 2.80 (1H, m), 4.34 (1H, d, *J* = 11, C<u>H</u>HO), 4.47 (1H, d, *J* = 11, C<u>H</u>HO), 5.00-5.15 (2H, m, =CH_2), 5.40-5.70 (1H, m, CH=), 7.35-7.60 (3H, m, Ph), 7.85 (2H, d, *J* = 7, Ph), 9.00 (1H, brs, NH); ^{13}C NMR: δ 15.2, 18.6, 21.3, 25.0, 26.1, 27.9,

36.6, 37.5, 52.5, 55.2, 65.6, 118.9, 127.8, 128.6, 132.1, 152.3, 165.0, 213.9; IR ν/cm^{-1}: 3428, 3278, 3186, 3073, 2966, 2873, 1762, 1609, 1527; MS m/z (EI) 371 (0.5), 225 (35), 106 (100), 77 (93); found C 71.19, H 7.82, N 3.75 %, $C_{22}H_{25}O_4N$ requires C 71.13, H 7.87, N 3.77 %; $[\alpha]_D^{28}$ = + 27.8° (c = 0.044, CH_2Cl_2).

(2*R*,3S,6*R*)-2-Carbamoyloxymethyl-3-methyl-2-(3'-propenyl)-6-isopropyl cyclohexanone (5). Anhydrous potassium carbonate (220 mg, 1.71 mmol) was added to a solution of the N-acyl carbamate **4** (640 mg, 1.71 mmol) in methanol (3.5 mL) at room temperature. The mixture was stirred for four hours, then treated with aqueous ammonium chloride and extracted with dichloromethane. The organic layer was washed with brine, dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography on silica gel (20 g), eluting with 15 and 20% EtOAc/ hexane to give the carbamate **5** (320 mg, 70%) as a colorless solid, mp 125-127 °C. ^{1}H NMR: δ 0.70-1.00 (9H, m, CH_3), 1.15-1.40 (1H, m), 1.65-2.15 (6H, m), 2.28 (1H, m, C$\underline{H}_2$CH=), 2.80 (1H, dd, *J* = 5,14 C$\underline{H}$2CH=), 4.00 (1H, d, *J* = 11, C$\underline{H}$HO), 4.55-4.80 (3H, m, C$\underline{H}$HO, NH_2), 4.95-5.10 (2H, m, =CH_2), 5.70-5.95 (1H, m, CH=); ^{13}C NMR: δ 15.6, 19.1, 21.6, 26.6, 29.1, 30.5, 37.2, 39.0, 53.6, 55.7, 67.9, 117.3, 135.6, 156.8, 212.7; IR ν/cm^{-1}: 3432, 3334, 3286, 3201, 2925, 2853, 1737, 1706, 1609, 1460, 1388, 1321; MS (*m/z*) (EI): 268 (25) (M+H+), 206 (22), 191 (51), 163 (20), 135 (19) 93 (100); found C 67.39, H 9.44, N 5.31 %, $C_{15}H_{25}O_3N$ requires C 67.38, H 9.42, N 5.24 %; $[\alpha]_D^{28}$ = + 49.1° (c = 0.013, CH_2Cl_2).

4-*t*-Butyl-2-(3'-propenyl)-cyclohexanone-2-carboxaldehyde (9). The same method was used as for compound **2**: major isomer: ^{1}H NMR: δ 0.85 (9H, s, t-Bu), 1.35-1.90 (4H, mH), 2.05 (1H, m), 2.40 (2H, m), 2.55 (1H, dd, *J* = 6, 14), 2.69 (1H, dd, *J* = 6,14), 5.06 (1H, d, J = 10 =CH_2), 5.10 (d, *J* = 16, =CH_2), 5.60 (1H, m, CH=), 9.75 (1H, s, CHO); ^{13}C NMR: δ 25.5, 26.9, 27.6, 30.7, 32.4, 36.3, 39.1, 40.9, 62.0, 67.9, 119.2, 131.4, 202.0, 211.8; IR ν/cm^{-1}: 3068, 2960, 2863, 1716, 1634; MS (*m/z*) 223 (2) (M+H+), 195 (5), 139 (43), 111 (56), 69 (100); HRMS Calcd for $C_{13}H_{22}O$ (M+ - CO) 194.1671, found 194.1665.

4-*t*-Butyl-2-hydroxymethyl-2-(3'-propenyl)-cyclohexanol (10). Sodium borohydride (140 mg, 3.68 mmol) was added to a solution of the ketoaldehyde **9** (550 mg, 2.45 mmol) in methanol (8.5 mL). The solution was stirred until TLC showed disappearance of the starting material. The mixture was quenched with aqueous ammonium chloride and extracted with dichloromethane. The organic layer was washed with brine, dried (Na_2SO_4) and evaporated. Purification by flash chromatography on silica gel eluting with 10% and 50% EtOAc/Hexane gave the diol **10** (0.35 g, 62%) as a colourless solid, mp 64-67 °C; ^{1}H NMR: δ 0.49 (1H, t, *J* = 13), 0.85 (9H, s, t-Bu), 0.90-1.80 (6H, m), 2.20 (1H, dd, *J* = 16,8, C$\underline{H}_2$CH=CH_2), 2.54 (1H, dd, *J* = 16,8, C$\underline{H}_2$CH=CH_2), 2.82 (1H, brs, OH), 3.08 (1H, brs, OH), 3.38 (1H, d, *J* = 10, C$\underline{H}$HOH), 3.60 (1H, d, *J* = 10, C$\underline{H}$HOH), 3.67 (1H, dd, *J* = 11,4 C$\underline{H}$OH), 5.11 (1H d, *J* = 10, =CH_2), 5.13 (1H d, *J* = 17, =CH_2), 5.83 (1H, ddt, *J* = 17,10,8, CH=); ^{13}C NMR: δ 28.9, 31.1, 32.8, 33.6, 35.9, 44.2, 44.5, 65.3, 75.1, 82.2, 122.5, 138.0; IR ν/cm^{-1}: 3306, 2958, 1638, 1367, 1064, 1010, 919; MS (*m/z*) (EI) 225 (2), 191 (15), 109 (19), 107 (20), 95 (24); HRMS calcd for $C_{14}H_{26}O_2$: 227.2011, found 227.2010.

Benzylidene acetal (11). A solution of benzaldehyde dimethylacetal (66 mL, 0.44 mmole) and the diol **10** (0.10 g, 0.44 mmol) in dichloromethane (2 mL) was stirred overnight with a catalytic

amount of ppts. Aqueous sodium bicarbonate was added and the mixture was extracted with dichloromethane. The organic layer was dried (Na_2SO_4) and evaporated to give the acetal **11** as an oil (0.11 g, 79%) containing a trace of benzaldehyde. ^{1}H NMR: δ 0.80 (9H, s, t-Bu), 1.15 (1H, m), 1.4 (2H, m), 1.8 (3H, m), 2.35 (1H, dd, *J* = 8,14), 2.84 (1H, dd, *J* = 8, 14), 3.35 (1H, d, *J* = 11, CHHO); 3.60 (1H, dd, *J* = 11, 6, CHO), 4.02 (1H, d, *J* = 11, CHHO), 5.15 (1H, d, *J* = 19, $=CH_2$), 5.20 (1H, d, *J* = 10, $=CH_2$), 5.55 (1H, s, CHPh), 5.85 (1H, m, C<u>H</u>$=CH_2$), 7.20-7.60 (5H, m, Ph).

4-*t*-Butyl-2-carbethoxy-2-(3'-propenyl)-cyclohexanone (12). The same method as for compound **2** was used, except that KOt-Bu was employed as the base. ^{1}H NMR: δ0.90 (9H, s, t-Bu), 1.27 (3H, t, *J* = 7, CH_3), 1.450 (2H, m, CH_2), 2.00 (3H, m), 2.43 (2H, m), 2.55 (1H, dd, *J* = 6,10, C<u>H</u>$_2$CH$=CH_2$), 2.75 (1H, dd, *J* = 5,10, C<u>H</u>$_2$CH$=CH_2$), 4.25 (2H, q, *J* = 7, OCH_2), 5.12 (1H, d, *J* =10, $=CH_2$), 5.14 (1H, d, *J* = 16, $=CH_2$), 5.70 (1H, m, C<u>H</u>$=CH_2$); ^{13}C NMR: δ 23.9, 27.0, 29.4, 33.0, 38.1, 39.0, 41.5, 74.8, 120.1, 128.5, 130.7, 131.0, 134.0, 135.3, 206.5; IR (ν/cm^{-1}): 1751, 1713, 1640, 1221; MS (*m/z)* (EI): 267 (100) (M+H+), 266 (4) (M+), 193 (3), 191 (4), 154 (2); HRMS calcd 266.1882, found 266.1884.

4-*t*-Butyl-2-phenylsulfonyl-2-(3'-propenyl)-cyclohexanone (13). The same method as for compound **2** was used, except that KOt-Bu was employed as the base. major (more polar) isomer: mp 91-92 °C: ^{1}H NMR: δ 1.00 (9H, s, *t*-Bu), 1.40 (1H, m), 1.60-2.00 (2H, m), 2.25 (1H, dt, *J* = 16,3),2.3-2.7 (4H, m, CH) 2.85 (1H, ddd, *J* = 5, 8, 17), 5.12 (1H, d, *J* = 16, $=CH_2$), 5.14 (1H, d, *J* = 11, $=CH_2$), 5.70 (1H, m, CH=), 7.50-8.00 (5H, m, Ph); ^{13}C NMR: δ 23.9, 27.0, 29.4, 33.0, 38.1, 39.0, 41.5, 74.8, 120.1, 128.5, 130.7, 131.0, 134.0, 135.3, 206.5; IR ν/cm^{-1}: 1709, 1648, 1319, 1291; MS (*m/z*) (EI) 335 (140 (M+H+), 193 (89), 192 (100), 119 (61); HRMS calcd for $C_{19}H_{26}SO_3$: 335.1681, found 365.1685.

Minor (less polar) isomer: mp 92-94 °C; ^{1}H NMR δ 1.00 (9H, s, t-Bu), 1.37 (1H, dq, *J* = 4,13), 1.84 (1H, dd, *J* = 15,13), 2.1 (2H, m), 2.37 (1H, tt, *J* = 12,3), 2.65 (2H, m), 3.11 (1H, ddd, *J* = 16, 14, 6), 5.03 (1H, d, *J* = 16, $=CH_2$), 5.12 (1H, d, *J* = 10, $=CH_2$), 5.4 (1H, m, CH=),7.5=7.8 (5H, m, Ph); ^{13}C NMR :δ 26.2, 27.2, 31.1, 32.6, 41.6, 74.8, 120.5, 128.7, 130.2, 131.6, 134.2, 135.2, 205.0.

Acknowledgements

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