Solvent-free Microwave-Assisted *Ortho*-Alkylation of Aromatic Ketimine with Acrylic Acid Derivatives by Rh(I) Catalyst[†]

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Microwave(MW)-assisted *ortho*-alkylation of aromatic imine with acrylic acid derivatives was performed in the presence of a $(PPh_3)_3RhCl$ catalyst, and corresponding *ortho*-alkylated ketones were obtained after hydrolysis of the resulting ketimines. This solventless MW-assisted *ortho*-alkylation was highly efficient compared with conventional heating, probably due to the specific MW effect.

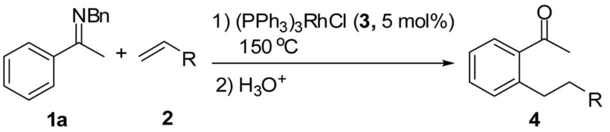
Key Words : *Ortho*-alkylation, Microwave, Rhodium, Homogeneous catalyst, Ketimine

Introduction

Catalytically selective activation of organic molecules by transition metal catalysts is a current interest in organic synthesis[1] because this strategy may allow the avoidance of environmental problems such as waste formation that can occur in industrial synthesis. An interesting example of selective C-H bond activation is Ru-catalyzed *ortho*-alkylation of aromatic ketone, known as Murai's reaction.[2] One drawback of this reaction is the limited usefulness of olefin substrates, due to the difficulty of applying olefins bearing a functional group. To overcome this limitation, a new procedure using a ketimine of aromatic ketone with Rh(I) catalyst was developed for *ortho*-alkylation and *ortho*-alkenylation.[3] Since this strategy using ketimine tolerates various functional groups of olefin substrates, functionalized olefins can be successfully applied to the *ortho*-alkylation of aromatic ketimine,[4] in which vigorous reaction conditions are required to initiate the reaction. Recently, much interest has been shown in microwave-assisted reactions to facilitate transition metal catalyzed reactions.[5] It is especially environmentally benign since the reaction can be carried out without solvent. Therefore, we are intrigued by the use of MW-assisted reactions under solvent-free conditions in *ortho*-alkylation reaction. Among many unsaturated substrates, acryl amide and acrylic ester exhibited high reactivity in MW-assisted *ortho*-alkylation compared to conventional heating. In this paper, we report on the solventless *ortho*-alkylation of aromatic ketimine with acrylic acid derivatives under microwave irradiation.

When the reaction of benzylimine **1a** and dimethyl acrylamide (**2a**) was carried out in the presence of $(PPh_3)_3RhCl$ (**3**) at 150 °C for 5 min under microwave irradiation (25 watt), *ortho*-alkylated acetophenone **4a** was obtained in a 90% isolated yield after hydrolysis of the resulting ketimine (Table 1, entry 1).

Table 1. Comparison between the reactivity of acryl amide and that of *t*-butylethylene toward *ortho*-alkylation under thermal and MW-irradiated conditions



Entry	Alkene (**2**, R)[a]	Heat[b]	Time	Product (**4**)	Isolated yield[c] (%) of **4**
1	**2a** ($CONMe_2$)	MW	5 min	**4a**	90(95)
2	**2a** ($CONMe_2$)	Δ	5 min	**4a**	6(12)
3	**2a** ($CONMe_2$)	Δ	1 h	**4a**	89(96)
4	**2b** (COOMe)	MW	5 min	**4b**	85(88)
5	**2b** (COOMe)	Δ	5 min	**4b**	49(53)
6	**2b** (COOMe)	Δ	1 h	**4b**	92(100)
7	**2c** (t-C_4H_9)	MW	5 min	**4c**	18(22)
8	**2c** (t-C_4H_9)	Δ	5 min	**4c**	20(25)
9	**2c** (t-C_4H_9)	Δ	3 h	**4c**	92(100)

[a]1.2 eq. of olefin was used. [b]Microwave (MW) or oil bath under similar conditions (Δ). [c]Isolated yields. GC yield of **4** given in the parentheses.

However, when the identical reaction was applied by conventional thermal heating at 150 °C for 5 min, only 6% yield of **4a** was isolated, and extended reaction time to 1h afforded **4a** in a 89% yield (entries 2 and 3). This dramatic difference between the reactivity under MW and that of conventional heating reveals an important specific microwave effect. In the reaction of **1a** and acrylic ester (**2b**) under identical reaction conditions, corresponding *ortho*-alkylated ketone **4b** was isolated in a 85% yield under MW irradiation and a 49% yield for thermal heating, respectively (entries 4 and 5). Although the yield difference was not marginal between MW and thermal heating compared with the reaction of **2a**, a certain difference could still be observed in this reaction. For comparison with these functionalized olefins, the reaction of *t*-butylethylene (**2c**) with **1a** was performed at 150°C for 5 min under MW irradiation to afford only 18% isolated yield of **4c**, while the reaction with conventional heating produced a 20% isolated yield of **4c**, and the reaction was completed in 3h (entries 7-9). Among

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[†]This paper is dedicated to Professor Sang Chul Shim on the occasion of his honorable retirement.

Table 2. Rh(I)-Catalyzed *ortho*-Alkylation of Aromatic Ketimine **1a** with acryl amide **2a**[a]

$$\mathbf{1a} + \mathbf{2a} \xrightarrow[\text{2) } H_3O^+]{\text{1) } (PPh_3)_3RhCl\ (\mathbf{3},\ 5\ mol\%)\ \ MW,\ 130^{\circ}C,\ 10min} \mathbf{4a}$$

Entry	Microwave (MW) or thermal heating (Δ)[b]	Isolated yield (%) of **4a**[c]
1	MW (27 W)	46(49)
2	MW (55 W)	67(72)
3	MW (74 W)	93(100)
4	Δ	0(2)

[a]Reaction conditions: **3** (0.015 mmol), **1a** (0.3 mmol), 1.2 equiv. of **2a** mixture at 130 °C for 10 min. [b]The power (watts) of MW can be controlled by adjusting the pressure of air blowing. [c]Isolated yields. GC yield of **4** given in the parentheses.

the olefins tested, acryl amide **2a** and ester **2b** showed much higher reactivity than *t*-butylethylene (**2c**). The MW reaction of acrylamide **2a** especially showed a fairly high enhancement of reactivity compared with the thermal reaction.

From these results, we can infer an important specific MW effect with **2a**, which leads to the increased yield of the product as MW power increases.[6] When the reaction of **1a** and **2a** was carried out at 130 °C for 10 min with moderate MW power (27 watt), 46% isolated yield of **4a** was obtained. In comparison, isolation yields of 67% and 93% for **4a** were obtained with high powered MW of 55 and 74 watts respectively, under the same reaction temperature and time in the presence of same catalyst (Table 2, entries 2 and 3). These high powered MWs could be obtained by blowing an air with a certain amount of pressure to the reaction vessel to maintain the temperature (130 °C) of the reaction mixture (Figure 1).

The reaction mechanism is shown in Scheme 1. The Rh(I) complex **3** reacts with the *ortho*-C-H bond in the phenyl group of **1a** to generate a 5-membered ring metallacycle intermediate **5a**. Subsequent hydride-insertion into **2a** affords **6a**. Reductive elimination of **6a** leads to the *ortho*-alkylated ketimine **8a**, which is hydrolyzed by acidic water to give **4a**.

A. Loupy emphasized that specific MW effect can be observed for polar mechanism when the polarity is increased during the reaction, from the ground state (GS) towards the transition state (TS).[6,7] Therefore it may be explained by the possibility that the observed high specific MW-effect in the reaction of **1a** and **2a** is due to the development of a pronounced dipole-polarized intermediate **7a**, near to the transition state, generated from **6a**. Since the dipole of the **7a** is more pronounced than the ground state in the reaction, it results in a decreasing effect of activation enthalpy due to the enhanced dipole-dipole interactions with the electric field generated from the MW reactor when the reaction has progressed. Contrary to this result, the MW-assisted *ortho*-alkylation of **1a** with *t*-butylethylene (**2c**) did not show any dramatic rate-accelerating effect (Table 1, entry 7), probably due to the formation of non-polarized intermediate **7b**.

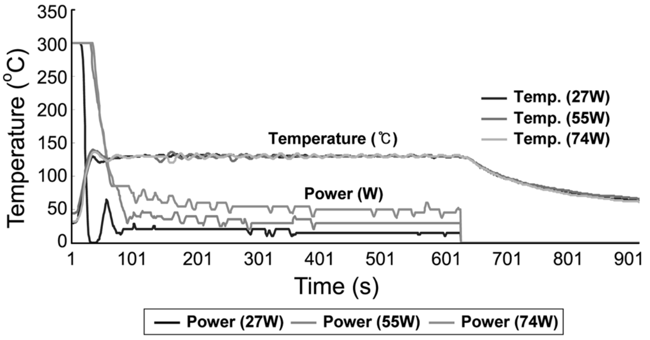
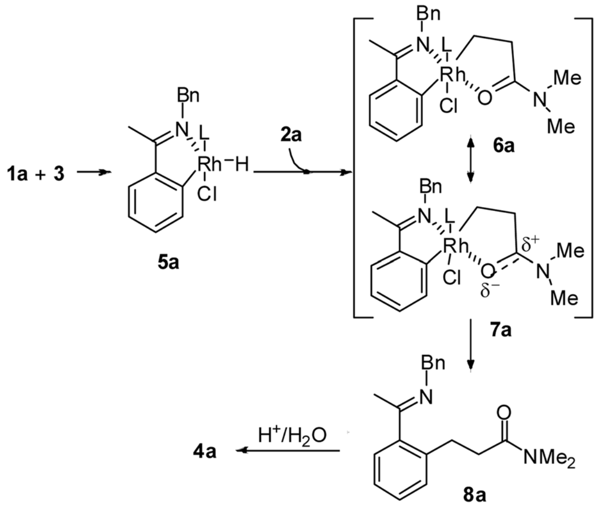
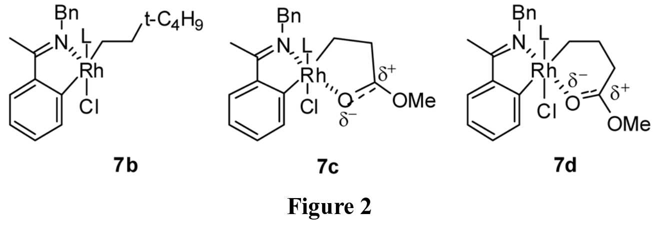


Figure 1. Reaction **1a** and **2a** with **3** at 130 °C under different power of MW irradiation (normal and air cooling).



Scheme 1. Proposed Mechanism for *ortho*-Alkylation of Ketimine **1a** with **2a** under catalyst **3**.

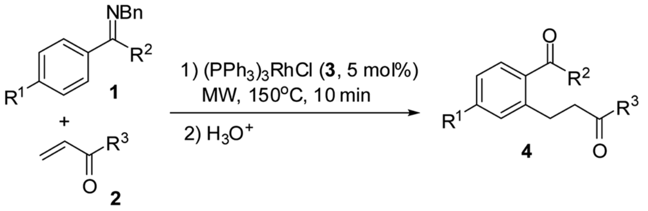
Other functionalized olefins were applied in this reaction and representative examples were indicated in Table 3. When the reactivity of the aromatic ketimines having different alkyl substituents (R^1) were compared, the electron-donating group, such as the methoxy group on the phenyl ring, showed a better result than the electron-withdrawing group such as the trifluoromethyl group (entries 1 and 2). The reactivity of **1d** is low compared with that of **1a** (entry 3). The cyclic tertiary amine functionality in the amide of **2d** also resulted in a good yield of corresponding *ortho*-alkylated product **4g**. In particular, acrylamide **2e** bearing a secondary amine functionality showed a large acceleration rate in producing *ortho*-alkylated product **4h** since the MW reaction was completed in 2 min, determined by GC, while thermal conventional heating resulted in only a 9% GC yield of product.

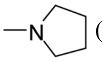
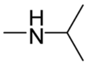


7b **7c** **7d**

Figure 2

Table 3. Rh(I)-Catalyzed *ortho*-Alkylation of Aromatic Ketimine **1** with Functionalized Olefins **2**

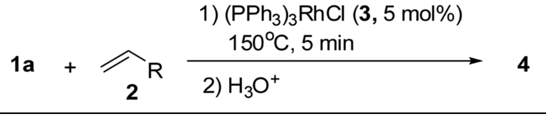


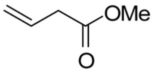
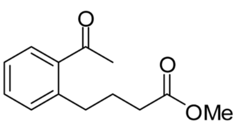
Entry	**1** (R^1, R^2)	R^3 (**2**)^a	**4**	MW or Δ^b	Time (min)	Isolated yield (%) of **4**^{c}
1	**1b** (OMe, Me)	NMe_2 (**2a**)	**4d**	MW Δ	5	90 (100) (0)
2	**1c** (CF_3, Me)	(**2a**)	**4e**	MW Δ	10	63(77) 6(14)
3	**1d** (H, *n*-Hexyl)	(**2a**)	**4f**	MW Δ	10	22(27) 0(4)
4	**1a** (H, Me)	 (**2d**)	**4g**	MW Δ	10	86(100) 0(7)
5	**1a** (H, Me)	 (**2e**)	**4h**	MW Δ	2	74(100) 5(9)
6	**1a** (H, Me)	OEt (**2f**)	**4i**	MW Δ	10	82(86) 40(45)
7	**1a** (H, Me)	O^{t}Bu (**2g**)	**4j**	MW Δ	3	95(100) 54(59)

^{a}1.2 equiv. of olefin was used. ^{b}Microwave (MW) or oil bath under similar conditions (Δ). ^{c}Isolated yields GC yield of **4** given in the parentheses.

Like *α,β*-unsaturated amides, *α,β*-unsaturated esters also exhibited rate enhancement under MW irradiation compared with conventional heating. For example, when the reaction was performed with ethyl acrylate (**2f**) under MW irradiation for 10 min, corresponding *ortho*-alkylated acetophenone **4i** was isolated in 82% yield, while only 40% isolated yield of product was obtained with conventional heating (entry 6). In particular, with *t*-butyl acrylate (**2g**) the reaction was completed to give **4j** in 95% isolated yield within 3 min under MW conditions whereas the reaction with conventional heating afforded a 54% isolated yield of the product (entry 7).

Table 4. Rh(I)-catalyzed *ortho*-alkylation of aromatic ketimine **1a** with unsaturated esters, **2a** and **2h**



Entry	Alkene (**2**, R)^a	Product (**4**)	Isolated yield^b (%) of **4**
1	**2a** (COOMe)	**4a**	92(98)
2	 (**2h**)	 (**4k**)	33 (37)

^{a}1.2 equiv. of olefin was used. ^{b}Isolated yields. GC yield of **4** given in the parentheses.

As already stated, the enhanced reactivity of acrylic ester with MW reaction can be also explained by the pronounced dipole-polarized transition state of **7c** due to the formation of a stable 5-membered metallacyclic complex through the carbonyl coordination to the rhodium metal. To confirm this hypothesis, one carbon elongated olefin, **2h**, was applied for MW-assisted orthoalkylation of **1a**, and only a 33% isolated yield of corresponding orthoalkylated product **4k** was obtained, differently from 92% yield of **4a** with **2a** under the identical reaction conditions (Table 4, entries 1 and 2). This result implies that methyl 3-butenoate (**2h**) acts as a common non-functionalized olefin such as *t*-butylethylene (**2c**) since a dipole-polarized intermediate **7d** is hardly formed because of its unstable nature of six-membered metallacyclic intermediate.

In conclusion, MW-assisted *ortho*-alkylation of aromatic benzylimine has been successfully achieved with olefins bearing carboxylic acid derivatives. The *ortho*-alkylation of aromatic ketimine with these olefins showed enhanced rate acceleration effect compared with the conventional thermal reaction, probably due to the specific MW effect. The reason for this effect must come from the involvement of C-O dipole-polarized intermediate of a stable 5-membered metallacycle through the coordination of the carbonyl group to the metal center. The reaction is environmentally benign since it can be carried out with dramatically short reaction time with very high yields and solventless conditions. Further applications of these *ortho*-alkylation reactions with functionalized olefins are under study.

Experimental Section

General. Microwave reaction was performed using a single-mode microwave reactor (CEM Discover). The microwave power can be modulated from 15 to 300 W (2,450 MHz) and the high powered microwave can be obtained by blowing air to the reaction vessel to maintain the temperature. The reaction temperature, pressure, and microwave power were monitored using a computer controlled CEM-Discover focused synthesis system. The thick-walled 10-mL Pyrex reaction vessel with Teflon septa was used as a reaction vessel. In order to compare microwave irradiation with conventional heating, the reactions were performed in the same reaction vessel under similar experimental conditions (weight of reactants and temperature) using a thermostated oil bath with similar profiles of increasing temperature. The ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Advance/DPX 250 (250 MHz ^1H, 62.9 MHz ^{13}C NMR) spectrometers with chemical shifts reported relative to residual deuterated solvent peaks. ^1H NMR spectra were referenced to tetramethylsilane (0.00 ppm) as an internal standard. ^{13}C NMR spectra were referenced to the residual $CDCl_3$ (77.26 ppm). Gas chromatographic analyses were performed on a Donam DS 6200 instrument with FID detector and a Hewlett Packard HP-5 capillary column. Low- resolution mass spectra were measured on a

Hewlett-Packard HP G1800A GCD system equipped with a Hewlett Packard HP-5 capillary column. Infrared spectra were obtained on a Nicolet Impact 400 spectrometer. High-resolution mass spectrometry was performed by the National Center for Inter-University Facilities, Seoul National University (Seoul 151-742, Korea). Flash column chromatography was performed using E. Merck 230-400 mesh silica gel. Column chromatography was monitored by analytical thin layer chromatography (TLC) that was performed on precoated silica gel plates with fluorescent indicator UV254 (layer thickness: 0.25 mm, silica gel 60, F-254, Merck).

Materials. Ketones and olefins used in the experiments were purchased from Aldrich Chemical Company and used as received without further purification unless otherwise stated. (PPh$_3$)$_3$RhCl (Wilkinson's complex) was prepared as described in the literature.[8] All aromatic ketimines are known compounds and, data extracted from them were consistent with that reported in the literature.[4,9] All products were previously characterized and known compounds in the literature[4] except **4d**, **4e**, **4f**, **4g**, and **4h**.

Experimental procedure for *ortho*-alkylation. A typical procedure (Table 1): A thick-wall Pyrex tube (10 mL) was charged with aromatic ketimine (**1**, 0.3 mmol), olefin (**2**, 0.36 mmol), and (PPh$_3$)$_3$RhCl (**3**, 0.015 mmol). The reaction vessel was capped with Teflon septa and installed in a CEM-Discover Microwave reactor. The reaction was carried out with an internal magnetic stirring bar for 10 min to ensure homogeneous conditions at 150 °C under microwave irradiation. For the conventional heating, the vessel was placed into the 150 °C-preheated oil bath. The reaction time was 10 min with an additional ramp time (60 sec). After cooling to room temperature, the reaction mixture was hydrolyzed with 1 N HCl for 12 h. The organic layer was neutralized with aqueous NaHCO$_3$, and the solution extracted with CH$_2$Cl$_2$ and EtOAc, and dried over anhydrous MgSO$_4$, filtered, and concentrated. The product **4** was purified by column chromatography (*n*-hexane:EtOAc = 2:5) on silica gel.

3-(2-Acetyl-5-methoxyphenyl)-*N,N*-dimethyl propionamide (4d). ^{1}H NMR (250 MHz; CDCl$_3$) δ 7.78 (d, J = 8.6, 1H), 6.87-6.78 (m, 2H), 3.84 (s, 3H), 3.18 (t, J = 7.5, 2H), 3.01 (s, 3H), 2.94 (s, 3H), 2.66 (t, J = 7.9, 2H), 2.56 (s, 3H); ^{13}C NMR (62.9 MHz; CDCl$_3$) δ 199.7 (CO), 172.8 (CON), 162.3, 145.6, 132.9, 129.8, 117.1, 111.8, 55.5, 37.4, 35.6, 35.5, 31.4, 29.3. IR (neat) $\nu_{\max}$/cm^{-1} 2939, 1673, 1644, 1602, 1567, 1495, 1455, 1416, 1356, 1321, 1293, 1248, 1142, 1068, 1033, 965, 813, 724. HR-MS (EI) calcd. for C$_{14}$H$_{19}$NO$_3$ (M$^+$) 249.1365, found 249.1367. MS (EI, 70 eV) *m/z* 249 (M$^+$, 18), 231 (11), 207 (35), 177 (33), 163 (78), 135 (13), 91 (11), 77 (10), 72 (25).

3-(2-Acetyl-5-trifluoromethyl-phenyl)-*N,N*-dimethyl propionamide (4e). ^{1}H NMR (250 MHz; CDCl$_3$) δ 7.74 (d, J = 8.0, 1H), 7.60-7.53 (m, 2H), 3.13 (t, J = 7.2, 2H), 2.97 (s, 3H), 2.94 (s, 3H), 2.67 (t, J = 7.4, 2H), 2.62 (s, 3H); ^{13}C NMR (62.9 MHz, CDCl$_3$) δ 201.5 (CO), 171.7 (CON), 142.0, 141.3, 128.8, 128.3, 128.2, 123.1, 123.0, 37.1, 35.3, 35.1, 29.9, 29.8; IR (neat) $\nu_{\max}$/cm^{-1} 2928, 2097, 1694, 1646, 1499, 1458, 1412, 1330, 1251, 1164, 1152, 1090, 833. HR-MS (EI) calcd. for C$_{14}$H$_{16}$F$_3$NO$_2$ (M$^+$) 287.1133, found 287.1132. MS (EI, 70 eV) *m/z* 287 (M$^+$, 31), 244 (100), 215 (28), 199 (37), 177 (14), 156 (10), 151 (16), 87 (82), 72 (49).

3-(2-Heptanoyl-phenyl)-*N,N*-dimethyl propionamide (4f). ^{1}H NMR (250 MHz, CDCl$_3$) δ 7.62 (d, J = 7.6, 1H), 7.40-7.27 (m, 3H), 3.08 (t, J = 7.3, 2H), 2.95 (s, 3H), 2.93 (s, 3H), 2.69 (t, J = 7.8, 2H), 1.71-1.66 (m, 2H), 1.38-1.32 (m, 6H), 0.91-0.86 (m, 3H); ^{13}C NMR (62.9 MHz, CDCl$_3$) δ 205.2 (CO), 172.6 (CON), 141.2, 138.7, 131.7, 131.3, 128.3, 126.2, 41.9, 37.2, 35.9, 35.5, 31.7, 30.3, 29.0, 24.4, 22.6, 14.1. IR (neat) $\nu_{\max}$/cm^{-1} 2924, 2851, 1683, 1651, 1482, 1392, 1270, 1135, 753. HR-MS (EI) calcd. for C$_{18}$H$_{27}$NO$_2$ (M$^+$) 289.2042, found 289.2042. MS (EI, 70 eV) *m/z* 289 (M$^+$, 24), 232 (49), 219 (33), 202 (61), 176 (91), 149 (27), 131 (69), 117 (15), 103 (25), 87 (13), 72 (42).

3-(2-Acetyl-phenyl)-1-pyrrolidinyl propanone (4g). ^{1}H NMR (250 MHz, CDCl$_3$) δ 7.70-7.29 (m, 4H), 3.45 (t, J = 6.6, 2H), 3.36 (t, J = 6.5, 2H), 3.15 (t, J = 7.8, 2H), 2.62 (t, J = 8.3, 2H), 2.59 (s, 3H), 1.93-1.78 (m, 4H). ^{13}C NMR (62.9 MHz, CDCl$_3$) δ 202.4 (CO), 171.4 (CON), 142.2, 138.0, 131.9, 129.5, 128.8, 126.3, 46.8, 45.8, 37.1, 30.3, 29.9, 26.3, 24.6. IR (neat) $\nu_{\max}$/cm^{-1} 2973, 2868, 1681, 1635, 1436, 1250, 1118, 759. HR-MS (EI) calcd. for C$_{15}$H$_{19}$NO$_2$ (M$^+$) 245.1416, found 245.1416. MS (EI, 70 eV) *m/z* 245 (M$^+$, 54), 202 (100), 133 (40), 113 (42), 98 (29), 77 (21), 70 (50), 55 (16).

3-(2-Acetyl-phenyl)-*N*-isopropyl propionamide (4h). ^{1}H NMR (250 MHz, CDCl$_3$) δ 7.75 (d, J = 8.5, 1H), 7.44-7.29 (m, 3H), 5.90-5.88 (br s, 1H), 3.11 (t, J = 7.8, 2H), 2.61 (s, 3H), 2.48 (t, J = 8.0, 2H), 1.19 (d, J = 6.6, 3H), 1.11 (d, J = 6.6, 3H). ^{13}C NMR (62.9 MHz, CDCl$_3$) δ 202.2 (CO), 171.9 (CON), 141.9, 137.1, 132.2, 131.7, 130.1, 126.6, 41.4, 39.3, 31.4, 29.8, 23.0, 22.4. IR (neat) $\nu_{\max}$/cm^{-1} 3298, 2930, 2097, 1732, 1678, 1641, 1546, 1450, 1413, 1251, 1071 and 767. HR-MS (EI) calcd. for C$_{14}$H$_{19}$NO$_2$ (M$^+$) 233.1416, found 233.1414. MS (EI, 70 eV) *m/z* 233 (M$^+$, 20), 190 (23), 175 (16), 146 (21), 131 (31), 103 (14), 77 (9).

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