An Efficient Iodine-Catalyzed Benzylation Reaction of 1,3-Dicarbonyl Compounds

Zhongxian Li, Zheng Duan,* Huaiqiu Wang, Rongqiang Tian, Qianrui Zhu, Yangjie Wu*

Chemistry Department, The Key Lab of Chemical Biology and Organic Chemistry of Henan Province, The Key and Open Lab of Applied Chemistry of Henan Universities, Zhengzhou University, Zhengzhou 450052, P. R. of China
Fax +86(371)67979408; E-mail: duanzheng@zzu.edu.cn; E-mail: wyj@zzu.edu.cn

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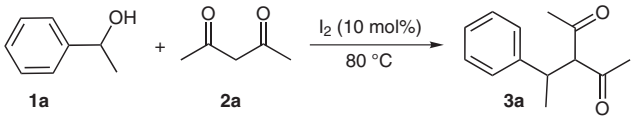
Abstract: Under mild conditions, iodine promotes the direct alkylation of 1,3-dicarbonyl compounds with benzylic alcohols or benzylic acetates.

Key words: iodine, catalysis, benzylation, Friedel–Crafts, C–H activation

Over the last few decades the quest for more economical ways to the C–C bond formation has become a matter of increasing importance among both industrial and academic research.[1] The alkylation of 1,3-dicarbonyl compounds plays an important role in modern organic synthesis.[2] However, the standard protocol usually requires stoichiometric amount of base, and a large amount of side products are generated.[3] Several atom-economical approaches via acid-catalyzed addition of 1,3-dicarbonyl derivatives to alkenes or alcohols were reported.[4] The direct reaction between 1,3-dicarbonyl derivatives and alcohols are noteworthy, since no organic halides are generated and water is the sole byproduct. Recently, several efficient methods of intermolecular benzylation and alkylation of active methylene compounds using alcohols as electrophiles have been reported. In these processes, transition metals, such as ruthenium,[5] palladium,[6] indium,[7] bismuth,[8] iron,[2] rare-earth metal,[9] and Brønsted acid,[10] were used as catalysts. However, the disposal of these metal salts or corrosive acids is troublesome and prevents their large-scale applications.

In recent years, molecular iodine as a simple, less expensive, less toxic reagent has attracted more attention in organic synthesis.[11] Herein, we wish to describe the first benzylation of activated methylene compounds catalyzed by I_2. Initially, we explored the iodine-catalyzed reaction of phenylethyl alcohol (**1a**) with active methylene **2a** under different reaction conditions (Table 1), such as catalyst loading, temperature, reaction time, substrate ratio, and solvent. The effect of solvents on this reaction was remarkable. Compared with the reactions using other solvents (DCE, MeCN, and H_2O) or in the absence of solvents, nitromethane could improve this I_2-catalyzed benzylation reaction efficiently (Table 1, entries 1–5). When the reaction was carried out at a lower temperature, the target compound **3a**[12,13] was obtained in a low yield (Table 1, entries 11 and 12). With 5 mol% of iodine catalyst, the product could be obtained in 97% yield (Table 1, entry 13), and no product could be isolated without the catalyst (Table 1, entry 14). On the other hand, both the reaction time and substrate ratio had a minor impact on this reaction (Table 1, entries 2, 6–10). Based on these results, the best conditions with respect to product yield were secured (5–10 mol% of iodine in $MeNO_2$ at 80 °C) (Table 1, entries 8 and 9). The reaction could proceed smoothly without exclusion of moisture and air from the reaction mixture.

Table 1 Reaction of 1-Phenylethanol with Acetylacetone[a]



1a 2a 3a

Entry	Solvent	1a/2a	Time (h)	Yield (%)[b]
1	–	1:4	2	97
2	$MeNO_2$	1:4	8	99
3	MeCN	1:4	8	41
4	H_2O	1:4	8	0
5	DCE	1:4	8	51
6	$MeNO_2$	1:2	8	92
7	$MeNO_2$	1:1	8	87
8	$MeNO_2$	1:4	2	99
9	$MeNO_2$	1:4	1	99
10	$MeNO_2$	1:4	0.5	92
11	$MeNO_2$	1:4	2	50[c]
12	$MeNO_2$	1:4	2	85[d]
13	$MeNO_2$	1:4	2	97[e]
14	$MeNO_2$	1:4	4	–[f]

[a] All reactions were carried out with 1-phenylethanol (0.5 mmol), I_2 (0.05 mmol), solvent (2 mL) at 80 °C.
[b] Isolated yield.
[c] Reaction at r.t.
[d] Reaction at 50 °C.
[e] I_2 (0.025 mmol) was used.
[f] Without catalyst.

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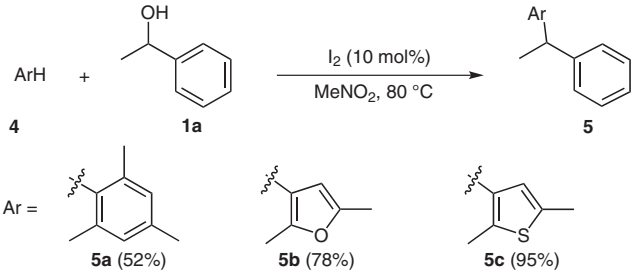
Under the optimized conditions, we investigated the I_2-catalyzed reactions of various benzylic alcohols and benzylic acetates with acetylacetone. Both electron-rich and moderately electron-poor aromatic substrates reacted smoothly with acetylacetone and the corresponding benzylation products were isolated in excellent yields (Table 2, entries 1–7). But when the reaction was carried out with the highly electron-deficient benzylic alcohol **1j**, only trace amount of the desired product was obtained (Table 2, entry 10). When 1,1′-diacetoxytoluene was used, a Knoevenagel condensation product was obtained in excellent yield (Table 2, entry 9).

Further investigations were concentrated on the scope and limitations of this reaction. Other 1,3-dicarbonyl compounds were reacted with 1-phenylethanol. Benzoylacetone and dibenzoylmethane were almost quantitatively converted into corresponding products under optimized conditions within one hour (Table 2, entries 11 and 12). When 2-acetylcyclohexanone and ethyl acetoactate were used (Table 2, entries 13 and 14), products **3m** and **3n** were obtained in 89% and 92% yields, respectively. 1,3-Cyclohexanedione provided the isomerized product **3o** in 56% yield (Table 2, entry 15). The reason for this moderate yield of **3o** might be the lower solubility of **2f** in nitromethane.

In order to expand the reaction scope of this I_2-catalyzed benzylation reaction, further research was carried out with other nucleophiles instead of activated methylene compounds. In this context, mesitylene was chosen as the nucleophile to react with 1-phenylethanol in the presence of I_2. Gratifyingly, the desired alkylation product **5a** could be obtained in 52% yield (Scheme 1). The corresponding alkylation products **5b** and **5c** could also obtained from 2,5-dimethylfuran and 2,5-dimethyl-thiophene, respectively, in good yields.[14]



Scheme 1 Iodine-Catalyzed benzylation of arenes and heteroarenes

In summary, we have developed a general and efficient I_2-catalyzed substitution reaction of benzylic alcohols or benzylic acetates with 1,3-dicarbonyl compounds, electron-rich arenes, and heterocyclic compounds. The mild and metal-free conditions made this method noteworthy. The scope, mechanism, and synthetic applications of this reaction are under further investigation in our group.

Table 2 Reaction of Various Benzylic Alcohols or Esters with Pentanediones[a]

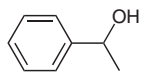
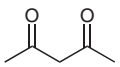
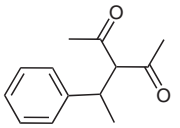
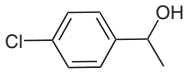
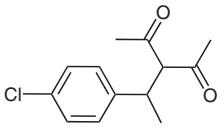
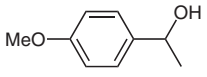
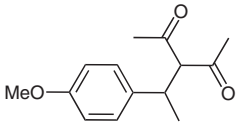
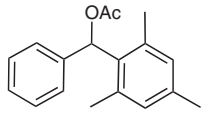
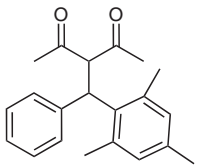
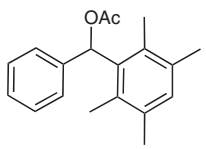
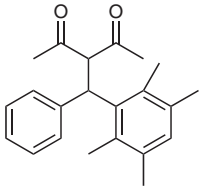
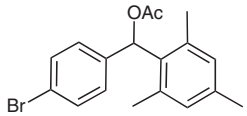
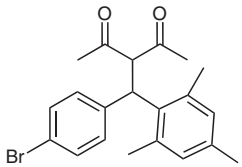
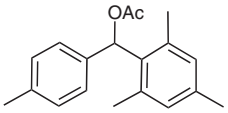
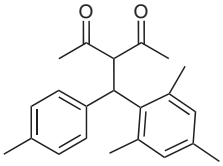
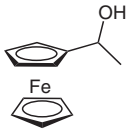
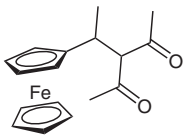
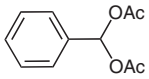
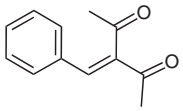
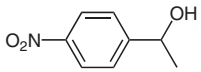
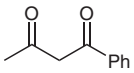
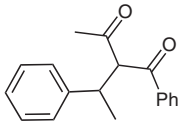
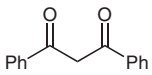
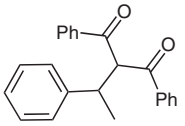
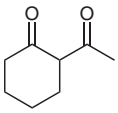
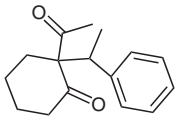
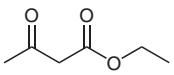
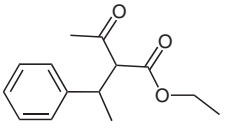
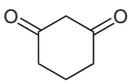
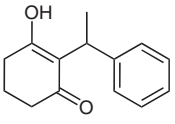
Entry	1	2	Time (h)	Product		Yield (%)[b]
1	 **1a**	 **2a**	1		**3a**	99[c] (98)[d]
2	 **1b**	**2a**	2		**3b**	97[c]
3	 **1c**	**2a**	1		**3c**	99[c]
4	 **1d**	**2a**	1		**3d**	99[c]
5	 **1e**	**2a**	1		**3e**	95[c]

Table 2 Reaction of Various Benzylic Alcohols or Esters with Pentanediones[a] (continued)

Entry	1	2	Time (h)	Product		Yield (%)[b]
6	 **1f**	**2a**	1		**3f**	99[c]
7	 **1g**	**2a**	1		**3g**	95[c]
8	 **1h**	**2a**	2		**3h**	85[c]
9	 **1i**	**2a**	4		**3i**	91[c]
10	 **1j**	**2a**	20	–	**3j**	–[c]
11	**1a**	 **2b**	1		**3k**	98 (5:4)[e]
12	**1a**	 **2c**	1		**3l**	99
13	**1a**	 **2d**	4		**3m**	89 (3:2)[f]
14	**1a**	 **2e**	2		**3n**	92 (1:1)[e,g]
15	**1a**	 **2f**	4		**3o**	56

[a] All reactions were carried out with **1** (0.5 mmol), 1,3-dicarbonyl compounds **2** (1 mmol), and I_2 (0.05 mmol) at 80 °C in $MeNO_2$ (2 mL).
[b] Isolated yield.
[c] The amount of 2 mmol of **2a** was used.
[d] The amount of 5 mmol of **1a** was used.
[e] The ratio of two diastereomers was determined by ^1H NMR spectroscopy.
[f] Two diastereomers were isolated, respectively, from the mixture by preparative TLC.
[g] The amount of 2 mmol of **2e** was used.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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(12) **General Procedure**
All procedures were carried out under air. To a 10 mL flask, benzylic alcohols or benzylic acetates (0.5 mmol), 1,3-dicarbonyl compounds, $MeNO_2$ (2 mL), and molecular iodine (13 mg, 0.05 mmol) were added successively. The mixture was magnetically stirred at 80 °C. After completion of the reaction (by GC), the solvent was concentrated under reduced pressure by an aspirator, and the residue was purified by preparative TLC using PE–EtOAc (10:1) as an eluent to afford products.
(13) **Selected Spectroscopic Data**
All prepared compounds were known and identified by ^{1}H NMR, ^{13}C NMR, and MS.
Compound **3a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.27 (m, 2 H), 7.22–7.18 (m, 3 H), 4.04 (d, *J* = 11.3 Hz, 1 H), 3.63–3.55 (m, 1 H), 2.56 (s, 3 H), 1.83 (s, 3 H), 1.21 (d, *J* = 6.9 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.5, 203.4, 143.0, 128.8, 127.3, 127.0, 76.7, 40.4, 29.8, 29.7, 20.8. ESI-MS: *m/z* = 227.0 [M + Na^+].
Compound **3b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.25 (m, 2 H), 7.15–7.12 (m, 2 H), 4.00 (d, *J* = 11.3 Hz, 1 H), 3.61–3.57 (m, 1 H), 2.26 (s, 3 H), 1.87 (s, 3 H), 1.19 (d, *J* = 6.9 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.0, 202.9, 141.5, 132.6, 128.9, 128.6, 76.5, 39.6, 29.8, 29.6, 20.7. ESI-MS: *m/z* = 261.1 [M + Na^+].
Compound **3c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.12–7.08 (m, 2 H), 6.84–6.82 (m, 2 H), 3.98 (d, *J* = 11.3 Hz, 1 H), 3.78 (s, 3 H), 3.57–3.53 (m, 1 H), 2.26 (s, 3 H), 1.84 (s, 3 H), 1.18 (d, *J* = 6.9 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.6, 203.5, 158.4, 134.9, 128.2, 114.1, 76.9, 55.1, 39.7, 29.8, 29.6, 20.9. ESI-MS: *m/z* = 257.0 [M + Na^+].
Compound **3d**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22–7.18 (m, 2 H), 7.14–7.12 (m, 1 H), 6.97 (d, *J* = 7.8 Hz, 2 H), 6.88 (s, 1 H), 6.69 (s, 1 H), 5.48 (d, *J* = 11.7 Hz, 1 H), 4.94 (d, *J* = 11.7 Hz, 1 H), 2.55 (s, 3 H), 2.29 (s, 3 H), 2.20 (s, 3 H), 1.99 (s, 3 H), 1.83 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.7, 203.0, 141.1, 137.3, 136.7, 136.7, 134.9, 131.3, 129.6, 128.4, 126.9, 126.1, 70.5, 43.0, 30.3, 28.9, 21.7, 20.9, 20.7. Anal. Calcd for: C, 81.78; H, 7.84. Found: C, 81.74; H, 7.93.
Compound **3e**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22–7.18 (m, 2 H), 7.14–7.11 (m, 1 H), 6.94 (d, *J* = 7.9 Hz, 2 H), 6.88 (s, 1 H), 5.67 (d, *J* = 11.3 Hz, 1 H), 4.94 (d, *J* = 11.3 Hz, 1 H), 2.46 (s, 3 H), 2.34 (s, 3 H), 2.28 (s, 3 H), 2.08 (s, 3 H), 1.88 (s, 3 H), 1.72 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.8, 202.8, 142.0, 137.9, 135.3, 134.1, 133.8, 133.1, 131.3, 128.5, 126.8, 126.0, 71.9, 43.3, 29.8, 29.2, 21.5, 20.4, 17.1, 16.8. Anal. Calcd for: C, 81.95; H, 8.13. Found: C, 81.64; H, 8.37.
Compound **3f**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 8.4 Hz, 2 H), 6.88 (s, 1 H), 6.84 (d, *J* = 8.3 Hz, 2 H), 6.71 (s, 1 H), 5.40 (d, *J* = 11.6 Hz, 1 H), 4.89 (d, *J* = 11.6 Hz, 1 H), 2.53 (s, 3 H), 2.29 (s, 3 H), 2.21 (s, 3 H), 1.98 (s, 3 H), 1.83 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.3, 202.6, 140.4, 137.3, 137.0, 136.6, 134.4, 131.5 (2C), 129.8, 128.8, 120.0, 70.4, 42.5, 30.3, 29.0, 21.7, 21.0, 20.7. Anal. Calcd for: C, 65.12; H, 5.99. Found: C, 65.03; H, 6.04.
Compound **3g**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.01 (d, *J* = 8.0 Hz, 2 H), 6.87–6.85 (m, 3 H), 6.69 (s, 1 H), 5.42 (d, *J* = 11.7 Hz, 1 H), 4.92 (d, *J* = 11.7 Hz, 1 H), 2.55 (s, 3 H), 2.29 (s, 3 H), 2.26 (s, 3 H), 2.21 (s, 3 H), 2.01 (s, 3 H), 1.82 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.0, 203.2, 138.1, 137.3, 136.8, 136.7, 135.7, 135.1, 131.4, 129.7, 129.1, 126.9, 70.8, 42.9, 30.2, 28.9, 21.8, 21.0, 20.9, 20.8. ESI-MS: *m/z* = 345.2 [M + Na^+].
Compound **3h**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.19 (s, 5 H), 4.16–4.05 (m, 4 H), 3.59 (d, *J* = 9.7 Hz, 1 H), 3.29–3.25 (m, 1 H), 2.15 (s, 3 H), 1.87 (s, 3 H), 1.26 (d, *J* = 6.5 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.5, 203.4, 91.7, 77.3, 68.8, 68.7, 67.8, 67.6, 65.4, 34.6, 32.0, 29.4, 18.3. Anal. Calcd for: C, 65.40; H, 6.46. Found: C, 65.40; H, 6.54.
Compound **3i**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (s, 1 H), 7.40 (s, 5 H), 2.43 (s, 3 H), 2.29 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.7, 196.6, 142.7, 139.9, 132.8, 130.7, 129.7, 129.0, 31.7, 26.5. ESI-MS: *m/z* = 211.0 [M + Na^+].
Compound **3k**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10–8.08 (m, 1 H), 7.49–7.04 (m, 9 H), 4.94 (d, *J* = 10.9 Hz, 1 H), 3.90–3.86 (m, 1 H), 1.90 (s, 3 H), 1.21 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.1, 195.2, 143.2, 137.2, 133.9, 128.9, 128.8, 128.5, 127.5, 127.0, 70.8, 41.0, 28.0, 21.6.
Another diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.78 (m, 1 H), 7.49–7.04 (m, 9 H), 4.50 (d, *J* = 11.0 Hz, 1 H), 3.90–3.86 (m, 1 H), 2.23 (s, 3 H), 1.30 (d, *J* = 7.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.6, 195.2, 143.5, 137.0, 133.4, 128.9, 128.6, 128.5, 127.4, 126.6, 71.4, 40.4, 27.6, 20.3.
Compound **3l**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05–8.02 (m, 2 H), 7.74 (d, *J* = 7.4 Hz, 2 H), 7.57–7.53 (m, 1 H), 7.46–7.39 (m, 3 H), 7.29–7.25 (m, 4 H), 7.19–7.15 (m, 2 H), 7.09–7.05 (m, 1 H), 5.61 (d, *J* = 10.1 Hz, 1 H), 4.10–4.06 (m, 1 H),

1.34 (d, *J* = 7.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.0, 194.6, 143.8, 137.2, 136.9, 133.6, 133.0, 128.9, 128.8, 128.5, 128.5, 128.4, 127.7, 126.6, 64.9, 41.2, 20.2. ESI-MS: *m/z* = 351.3 [M + Na^+].

Compound **3m**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.20 (m, 3 H), 7.14–7.12 (m, 2 H), 3.79 (q, *J* = 7.0 Hz, 1 H), 2.53–2.46 (m, 2 H), 2.19–2.10 (m, 1 H), 1.97–1.92 (m, 1 H), 1.86 (s, 3 H), 1.84–1.79 (m, 2 H), 1.67–1.55 (m, 2 H), 1.30 (d, *J* = 7.1 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.6, 205.9, 141.4, 128.7, 128.3, 127.0, 72.1, 42.7, 42.4, 28.2, 26.7, 25.9, 22.2, 17.4. ESI-MS: *m/z* = 267.1 [M + Na^+].

Another diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.24 (m, 4 H), 7.21–7.19 (m, 1 H), 3.89 (q, *J* = 7.4 Hz, 1 H), 2.38–2.34 (m, 2 H), 2.16–2.07 (m, 1 H), 2.12 (s, 3 H), 1.67–1.65 (m, 1 H), 1.63–1.60 (m, 1 H), 1.47–1.43 (m, 1 H), 1.42–1.40 (m, 2 H), 1.16 (d, *J* = 7.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.2, 205.4, 141.9, 129.9, 127.8, 126.7, 72.1, 42.3, 41.5, 29.4, 27.1, 25.5, 21.9, 16.2. ESI-MS: *m/z* = 267.1 [M + Na^+].

Compound **3n**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.26 (m, 2 H), 7.23–7.7.19 (m, 3 H), 3.87 (q, *J* = 7.1 Hz, 2 H), 3.81–3.73 (m, 1 H), 3.57–3.52 (m, 1 H), 1.93 (s, 3 H), 1.23 (d, *J* = 6.9 Hz, 3 H), 0.94 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.4, 168.6, 143.1, 128.7, 127.4, 126.9, 67.0, 61.5, 40.1, 29.9, 20.6, 14.1. ESI-MS: *m/z* = 257.1 [M + Na^+].

Another diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.26 (m, 2 H), 7.23–7.7.19 (m, 3 H), 4.23 (q, *J* = 7.1 Hz, 2 H), 3.81–3.73 (m, 1 H), 3.57–3.52 (m, 1 H), 2.30 (s, 3 H), 1.30 (d, *J* = 6.9 Hz, 3 H), 1.29 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.4, 168.2, 143.3, 128.4, 127.5, 126.8, 67.6, 61.1, 39.8, 29.5, 20.4, 13.7. ESI-MS: *m/z* = 257.1 [M + Na^+].

Compound **3o**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.32 (m, 2 H), 7.28–7.25 (m, 3 H), 5.27 (s, 1 H), 5.22–5.18 (q, *J* = 6.4 Hz, 1 H), 2.47–2.43 (m, 2 H), 2.30–2.26 (m, 2 H), 1.98–1.90 (m, 2 H), 1.57 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.7, 176.5, 141.3, 128.8, 128.0, 125.3, 104.6, 76.6, 36.6, 29.3, 23.6, 21.1.

Compound **5a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.21 (m, 2 H), 7.17–7.12 (m, 3 H), 6.81 (s, 2 H), 4.63 (q, *J* = 7.3 Hz, 1 H), 2.25 (s, 3 H), 2.10 (s, 6 H), 1.64 (d, *J* = 7.3 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.5, 140.1, 136.6, 135.4, 130.0, 128.2, 126.9, 125.3, 37.9, 21.1, 20.8, 16.9.

Compound **5b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.21 (m, 4 H), 7.17–7.14 (m, 1 H), 5.83 (s, 1 H), 3.89 (q, *J* = 7.2 Hz, 1 H), 2.20 (s, 3 H), 2.14 (s, 3 H), 1.50 (d, *J* = 7.3 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.2, 146.6, 144.7, 128.4, 127.1, 125.9, 124.1, 106.0, 35.6, 22.1, 13.6, 11.7.

Compound **5c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.23 (m, 2 H), 7.19–7.12 (m, 3 H), 6.50 (s, 1 H), 4.08 (q, *J* = 7.2 Hz, 1 H), 2.35 (s, 3 H), 2.25 (s, 3 H), 1.54 (d, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.3, 141.5, 135.1, 130.2, 128.4, 127.3, 125.9, 125.3, 38.3, 22.1, 15.4, 13.0. ESI-MS: *m/z* = 239.4 [M + Na^+].

(14) During the preparation of this manuscript, a similar result was reported, see: Srihari, P.; Bhunia, D. C.; Sreedhar, P.; Yadav, J. S. *Synlett* **2008**, 1045.