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Tandem Michael Addition/Aldol Reaction of Allenic Ketones with Alkyl Vinyl Ketones: Versatile Synthesis of 2-Alkynyl 1,5-Diketones, 4-Alkynyl-3-hydroxycyclohexanones and 4-Alkynylcyclohexenones

Deepika Malhotra,[a] Le-Ping Liu,*[a] and Gerald B. Hammond*[a]

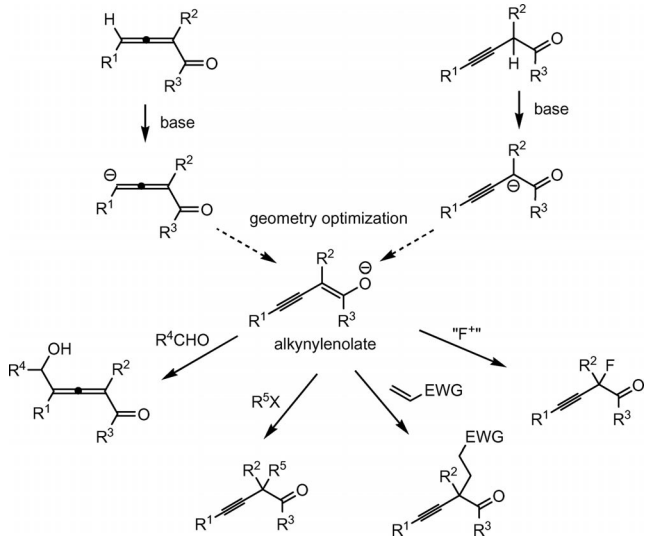
Keywords: Michael addition / Aldol reactions / Allenic ketones / Vinyl ketones / Alkynes

The reactivity of alkynylenolate was investigated in the reactions of allenic ketones and vinyl ketones. We found that different products could be obtained under different conditions. The tetrabutylammonium fluoride (TBAF)-mediated Michael addition of allenic ketones to vinyl ketones gave 2-alkynyl 1,5-diketones as the product. Under stronger basic conditions, a tandem Michael addition/aldol reaction of the two starting materials occurred in one pot, and 4-alkynyl-3-hydroxycyclohexanone could be isolated at low temperature, whereas 4-alkynylcyclohexenones was obtained at room temperature. It should be noted that only one diastereoisomer of 4-alkynyl-3-hydroxycyclohexanone was isolated from the reaction even when ethyl vinyl ketone was used as the Michael acceptor, as determined by ^{1}H and ^{13}C NMR spectroscopy. The configurations of the diastereoisomers were confirmed by NOESY spectroscopy.

Introduction

Michael additions and aldol reactions are important tools for the synthesis of complex organic molecules; their enolate chemistry continue to enrich the arsenal of organic synthetic chemistry.[1,2] Recently, we became interested in studying the reactivity of alkynylenolates – an alkynyl-substituted enolate generated from allenoates or propargylic esters under basic conditions – as potential nucleophile in reactions such as aldol condensation, Michael addition, alkylation and halogenation (Scheme 1).[3]

To probe further the reactivity of the alkynylenolate, we speculated that the Michael addition of allenic ketones to vinyl ketones could yield 2-alkynyl 1,5-diketones, triggering an intramolecular aldol reaction leading to hydroxycyclohexanones or cyclohexenones in tandem fashion.[4] Herein, we wish to report the tandem Michael addition/aldol reaction of allenic ketones with alkyl vinyl ketones and the versatile synthesis of 2-alkynyl 1,5-diketones, 4-alkynyl-3-hydroxycyclohexanones and 4-alkynylcyclohexenones. Although 1,5-diketones, hydroxycyclohexanones and cyclohexenones have often been employed in organic synthesis and found as substructures in bioactive molecules or natural products,[5] the synthetically more interesting 2-alkynyl-substituted analogs have been rarely reported in the literature.[6]



Scheme 1. Reactivity of alkynylenolates generated from allenoates or propargylic esters.

Results and Discussion

Using 2-methyl-1,4-diphenylbuta-2,3-dien-1-one (**1a**) and methyl vinyl ketone (**2a**, MVK) as model substrates, we investigated the formation of the products **3a**–**5a**; the results are outlined in Table 1. As expected, 2-alkynyl 1,5-diketone **3a** was obtained in good yield when tetrabutylammonium fluoride (TBAF) was used as the base, no product **4a** or **5a** was found (Table 1, entry 1).[7] When potassium carbonate was employed as the base, only trace amounts of **3a** was found, with most of the starting material remaining (Table 1, entry 1). Phase-transfer catalysis helped the reac-

[a] Department of Chemistry, University of Louisville, Louisville, Kentucky 40292, USA
Fax: +1-502-852-3899
E-mail: leping.liu@louisville.edu
gb.hammond@louisville.edu

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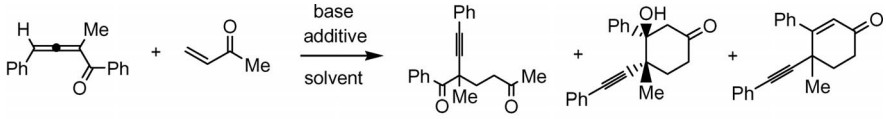
Table 1. Base-mediated reactions of allenic ketone 1a with methyl vinyl ketone.[a]



1a **2a** **3a** **4a** **5a**

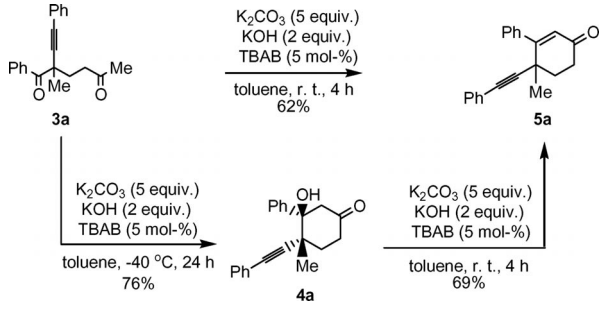
Entry	Base	Additive	Solvent	Temp.	Yield (%)[b]		
					3a	**4a**	**5a**
1	**TBAF**	**none**	**THF**	**r. t.**	**73**	**0**	**0**
2	K_2CO_3	none	toluene	r. t.	trace	0	0
3	K_2CO_3	TBAB	toluene	r. t.	48	0	0
4	K_2CO_3	TBAB	toluene	80 °C	22	0	16
5	KOH	none	toluene	r. t.	0	0	36
6	KOH	TBAB	toluene	r. t.	0	0	54
7	LiOH	TBAB	toluene	r. t.	0	16	32
8	NaOH	TBAB	toluene	r. t.	0	0	42
9	$CsOH·H_2O$	TBAB	toluene	r. t.	0	0	54
10	$Ca(OH)_2$	TBAB	toluene	r. t.	0	0	0
11	$Ca(OH)_2/K_2CO_3$	TBAB	toluene	r. t.	0	24	26
12	**KOH/K_2CO_3**	**TBAB**	**toluene**	**r. t.**	**0**	**0**	**71**
13[c]	**KOH/K_2CO_3**	**TBAB**	**toluene**	**-40 °C**	**trace**	**83**	**0**
14	KOH/K_2CO_3	$BnNEt_3Cl$	toluene	r. t.	0	0	55
15	KOH/K_2CO_3	Bu_4NHSO_4	toluene	r. t.	0	0	58
16	KOH/K_2CO_3	TBAB	CH_2Cl_2	r. t.	0	16	35
17	KOH/K_2CO_3	TBAB	DMF	r. t.	0	0	26
18	KOH/K_2CO_3	TBAB	THF	r. t.	0	0	49
19	KOH/K_2CO_3	TBAB	dioxane	r. t.	0	14	44
20	KOH/K_2CO_3	TBAB	Et_2O	r. t.	0	20	32
21	KOH/K_2CO_3	TBAB	CH_3CN	r. t.	0	17	25

[a] General reaction conditions: allenic ketone **1a** (0.4 mmol), methyl vinyl ketone **2a** (0.6 mmol), strong base (2 equiv.), potassium carbonate (5 equiv.), additive (5 mol-%), solvent (2.0 mL), reaction was quenched in 4 h. For entry 1, 0.2 equiv. of TBAF was used. [b] Isolated yields. [c] Reaction time was prolonged to 24 h.

tion, as shown by the fact that **3a** was obtained in moderate yield when tetrabutylammonium bromide (TBAB) was employed (Table 1, entry 3).[8] Also, under this weakly basic conditions, the tandem Michael addition/aldol condensation product **5a** could be isolated at higher temperature (Table 1, entry 4). When a strong base such as potassium hydroxide, lithium hydroxide, sodium hydroxide or cesium hydroxide was used in the reaction, compound **5a** was obtained as the only product in most cases (Table 1, entries 5–9). Calcium hydroxide could not promote the reaction, possibly because of its poor solubility (Table 1, entry 10). Although potassium hydroxide could promote the reaction, its high hydrophilicity and lack of dispersion caused the reaction mixture to become dark quickly. Fortunately, when potassium carbonate was used as a co-promoter, the reaction became more gentle and higher yield of product **5a** was obtained (Table 1, entry 12). Product **5a** was thought to arise from the dehydration of **4a**, prompting us to postulate that the dehydration would not take place at low temperature. Indeed, **4a** was isolated as the major product in good yield when the reaction was conducted at –40 °C (Table 1, entry 13). Other phase-transfer catalysts such as benzyltriethylammonium chloride and tetrabutylammonium hydrogen sulfate were also investigated in the reaction, and similar results were obtained (Table 1, entries 14–15). The solvent effect was also studied, toluene being the best solvent for the generation of product **5a** (Table 1, entries 12 and 16–21).

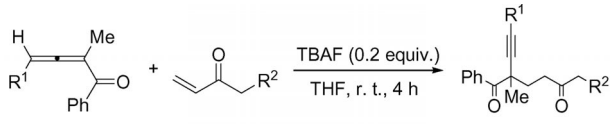
Control reactions were performed under the optimized conditions to demonstrate the transformations between **3a**, **4a** and **5a**; the results are shown in Scheme 2. It was found that **3a** could transform into **4a** under basic conditions at

low temperature, and both compounds could transform into **5a** under the same conditions at room temperature. With the optimum conditions in hand, we proceeded to study the scope and limitations of these reactions. First, we investigated the TBAF-mediated Michael addition of allenic ketones **1** with vinyl ketones **2** to obtain 2-alkynyl 1,5-diketones **3** (Table 2). These reactions proceeded smoothly for both aromatic and aliphatic substrates, furnishing **3** in moderate to good yields. Next, we carried out the tandem Michael addition/aldol reaction of allenic ketones **1** with vinyl ketones **2** at low temperature (–40 °C), with the corresponding products **4** obtained in moderate to good yields (Table 3). This reaction is slow under the conditions utilized, and prolonged reaction times were needed; higher yields were obtained for aromatic substrates, which may be due to the higher stability of the aromatic system. It should be noted that only one diastereoisomer of the product was obtained, even when ethyl vinyl ketone was used as the Michael acceptor, as determined by the ^{1}H and ^{13}C NMR spectroscopy.



Scheme 2. Control transformations between compounds **3a**, **4a** and **5a**.

Table 2. TBAF-mediated Michael addition of allenic ketones **1** to vinyl ketones **2**.[a]

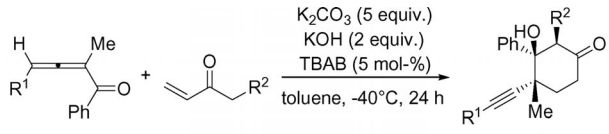


1 **2** **3**

Entry	R^1	R^2	Yield (%)[b]
1	C_6H_5 (**1a**)	H (**2a**)	**3a**, 73
2	*p*-$CH_3OC_6H_4$ (**1b**)	H (**2a**)	**3b**, 76
3	*p*-ClC_6H_4 (**1c**)	H (**2a**)	**3c**, 71
4	*n*-C_6H_{13} (**1d**)	H (**2a**)	**3d**, 37
5	*i*Pr (**1e**)	H (**2a**)	**3e**, 63
6	*t*Bu (**1f**)	H (**2a**)	**3f**, 65
7	Bn (**1g**)	H (**2a**)	**3g**, 72
8	$CypCH_2$ (**1h**)	H (**2a**)	**3h**, 41
9	CH_3 (**1i**)	H (**2a**)	**3i**, 69
10	C_6H_5 (**1a**)	CH_3 (**2b**)	**3j**, 73
11	*p*-$CH_3OC_6H_4$ (**1b**)	CH_3 (**2b**)	**3k**, 57
12	*p*-ClC_6H_4 (**1c**)	CH_3 (**2b**)	**3l**, 54

[a] General reaction conditions: allenic ketones **1** (0.4 mmol), vinyl ketones **2** (0.6 mmol), TBAF (0.2 equiv.), THF (2.0 mL). [b] Isolated yields.

Table 3. Tandem Michael addition/aldol reaction of allenic ketones **1** with vinyl ketones **2** at low temperature.[a]

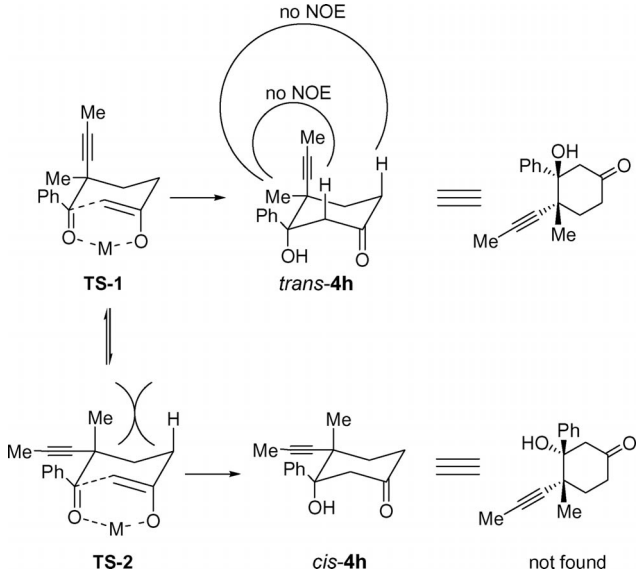


1 **2** **4**

Entry	R^1	R^2	Yield (%)[b]
1	C_6H_5 (**1a**)	H (**2a**)	**4a**, 83
2	*p*-$CH_3OC_6H_4$ (**1b**)	H (**2a**)	**4b**, 52
3	*p*-ClC_6H_4 (**1c**)	H (**2a**)	**4c**, 49
4	*n*-C_6H_{13} (**1d**)	H (**2a**)	**4d**, 32
5	*i*Pr (**1e**)	H (**2a**)	**4e**, 32
6	*t*Bu (**1f**)	H (**2a**)	**4f**, 39
7	$CypCH_2$ (**1h**)	H (**2a**)	**4g**, 28
8	CH_3 (**1i**)	H (**2a**)	**4h**, 53
9	C_6H_5 (**1a**)	CH_3 (**2b**)	**4i**, 59
10	*p*-$CH_3OC_6H_4$ (**1b**)	CH_3 (**2b**)	**4j**, 41
11	*n*-C_6H_{13} (**1d**)	CH_3 (**2b**)	**4k**, 35

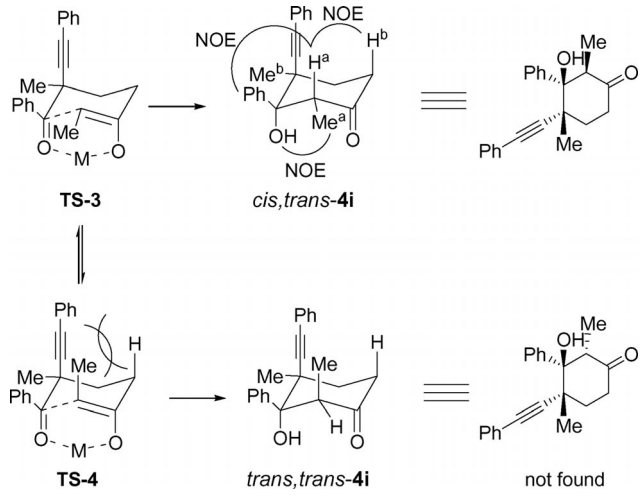
[a] General reaction conditions: allenic ketones **1** (0.4 mmol), vinyl ketones **2** (0.6 mmol), KOH (2 equiv.), K_2CO_3 (5 equiv.), TBAB (5 mol-%), toluene (2.0 mL). [b] Isolated yields.

The configuration of **4** was deduced by conformational analysis of the transition states and confirmed by NOESY studies of compounds **4h** and **4i** (Scheme 3 and Scheme 4). When methyl vinyl ketone was used in the reaction, transition state TS-1 is kinetically more favorable than TS-2 be-



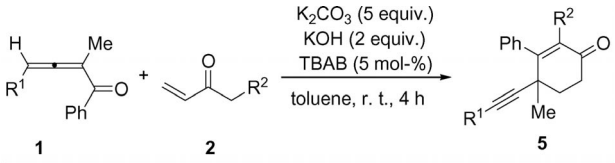
Scheme 3. Conformational analysis of transition states and NOESY effect of compound **4h**.

cause there is a 1,3-diaxial interaction between the methyl group and the axial proton in TS-2, whereas the interaction is diminished in TS-1, where the alkynyl moiety is axial. Thus, *trans*-**4h** was obtained as product through TS-1 instead of *cis*-**4h** through TS-2. This configuration was also supported by NOESY experiment on the product. Likewise, when ethyl vinyl ketone was used as the Michael acceptor in the reaction, the more favorable transition state is also the one in which the alkynyl group is axial and the methyl[(b)] group is equatorial. On the other hand, the *Z*-enolate in TS-3 is also less sterically hindered than the *E*-enolate in TS-4. Thus, TS-3 is more favorable than TS-4, and *cis,trans*-**4i** was hence obtained from the reaction instead of *trans,trans*-**4i**. The configuration of **4i** was also confirmed by its NOESY effect, where spatial proximity exists between the two axial protons, between the methyl[(a)] group and the hydroxy group, and between the proton[(a)] and the phenyl group.



Scheme 4. Conformational analysis of transition states and NOESY effect of compound **4i**.

Table 4. Tandem Michael addition/aldol condensation of allenic ketones **1** with vinyl ketones **2** at room temperature.[a]



1 **2** **5**

Entry	R^1	R^2	Yield(%)[b]
1	C_6H_5 (**1a**)	H (**2a**)	**5a**, 71
2	*p*-$CH_3OC_6H_4$ (**1b**)	H (**2a**)	**5b**, 53
3	*p*-ClC_6H_4 (**1c**)	H (**2a**)	**5c**, 51
4	*n*-C_6H_{13} (**1d**)	H (**2a**)	**5d**, 47
5	*i*Pr (**1e**)	H (**2a**)	**5e**, 33
6	*t*Bu (**1f**)	H (**2a**)	**5f**, 45
7	$CypCH_2$ (**1h**)	H (**2a**)	**5g**, 31
8	CH_3 (**1i**)	H (**2a**)	**5h**, 49
9	C_6H_5 (**1a**)	CH_3 (**2b**)	**5i**, 59
10	*p*-$CH_3OC_6H_4$ (**1b**)	CH_3 (**2b**)	**5j**, 51
11	*p*-ClC_6H_4 (**1c**)	CH_3 (**2b**)	**5k**, 42
12	*n*-C_6H_{13} (**1d**)	CH_3 (**2b**)	**5l**, 39

[a] General reaction conditions: allenic ketones **1** (0.4 mmol), vinyl ketones **2** (0.6 mmol), KOH (2 equiv.), K_2CO_3 (5 equiv.), TBAB (5 mol-%), toluene (2.0 mL). [b] Isolated yields.

The tandem Michael addition/aldol condensation of allenic ketones **1** with vinyl ketones **2** at room temperature was also performed and 4-alkynylcyclohexenones **5** were obtained as the products in moderate to good yields (Table 4). These reactions also proceeded smoothly and better results were obtained with aromatic substrates.

Conclusions

Using allenic ketones and vinyl ketones as substrates, we investigated the reactivity of alkynylenolate, and various alkynyl-substituted molecules were obtained. We found that TBAF could mediate the Michael addition furnishing 2-alkynyl 1,5-diketones. Under stronger basic conditions, a tandem Michael addition/aldol reaction of the two starting materials was developed, and 4-alkynyl-3-hydroxycyclohexanones were isolated at low temperature, whereas 4-alkynylcyclohexenones were obtained at room temperature. By analyzing the conformations of the reaction transition states, an explanation was provided for the formation of a single diastereoisomer of **4**.

Experimental Section

General Procedure for the Synthesis of 2-Alkynyl 1,5-Diketones: To a solution of allenic ketone **1a** (119 mg, 0.50 mmol) in THF (2.0 mL) was added methyl vinyl ketone (MVK) (44 mg, 0.60 mmol) and TBAF (0.1 mL, 1 M in THF, 0.10 mmol). The mixture was stirred for 4 h at room temperature; afterwards the reaction mixture was quenched with water and extracted with diethyl ether. The solvent of the organic layer was removed under reduced pressure and the residue was subjected to a flash column chromatography (eluent: ethyl acetate/*n*-hexane = 1:10) to give product **3a** (111 mg, 73%) as a colorless oil.

General Procedure for the Synthesis of 4-Alkynyl-3-hydroxycyclohexanones: To a solution of allenic ketone **1a** (119 mg, 0.50 mmol) in toluene (2.0 mL) was added methyl vinyl ketone (MVK) (44 mg, 0.60 mmol) and TBAB (8 mg, 5 mol-%). The mixture was cooled to –40 °C followed by the addition of potassium carbonate (345 mg, 2.5 mmol) and potassium hydroxide (56 mg, 1 mmol). The mixture was stirred at –40 °C for 24 h; afterwards the reaction mixture was quenched with water and extracted with diethyl ether. The solvent of the organic layer was removed under reduced pressure and the residue was subjected to a flash column chromatography (eluent: ethyl acetate/*n*-hexane = 1:10) to give product **4a** (126 mg, 83%) as a colorless oil.

General Procedure for the Synthesis of 4-Alkynylcyclohexenones: To a solution of allenic ketone **1a** (119 mg, 0.50 mmol) in toluene (2.0 mL) was added methyl vinyl ketone (MVK) (44 mg, 0.60 mmol), TBAB (8 mg, 5 mol-%), potassium carbonate (345 mg, 2.5 mmol) and potassium hydroxide (56 mg, 1 mmol). The mixture

was stirred at room temperature for 4 h; afterwards the reaction mixture was quenched with water and extracted with diethyl ether. The solvent of the organic layer was removed under reduced pressure and the residue was subjected to a flash column chromatography (eluent: ethyl acetate/*n*-hexane = 1:10) to give product **5a** (101 mg, 71%) as a colorless oil.

Data for 3a: A colorless oil. IR (neat): $\tilde{\nu}$ = 2982, 1716, 1682, 1596, 1490, 1363, 1168, 965 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.58 (s, 3 H), 1.95–2.01 (m, 1 H), 2.08 (s, 3 H), 2.34–2.43 (m, 1 H), 2.52–2.58 (m, 1 H), 2.63–2.69 (m, 1 H), 7.18–7.27 (m, 5 H), 7.35–7.38 (t, J = 7.5 Hz, 2 H), 7.45–7.48 (t, J = 7.5 Hz, 1 H), 8.23–8.25 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 26.6, 30.0, 33.6, 39.7, 45.9, 86.7, 91.5, 122.8, 128.0, 128.3, 129.7, 131.3, 132.7, 135.3, 198.8, 208.0 ppm. $C_{21}H_{20}O_2$ (304.14): calcd. C 82.86, H 6.62, found C 82.75, H 6.62.

Data for 3b: Colorless oil. IR (neat): $\tilde{\nu}$ = 2959, 2933, 1716, 1681, 1606, 1509, 1446, 1289, 1172, 1031, 966, 690 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.65 (s, 3 H), 2.02–2.08 (m, 1 H), 2.17 (s, 3 H), 2.44–2.49 (m, 1 H), 2.61–2.66 (m, 1 H), 2.66–2.78 (m, 1 H), 3.79 (s, 3 H), 6.81–6.84 (m, 2 H), 7.27–7.30 (m, 2 H), 7.43–7.46 (m, 2 H), 7.52–7.55 (m, 1 H), 8.32–8.33 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 26.9, 30.3, 33.9, 40.0, 46.1, 55.5, 86.8, 90.2, 114.2, 115.2, 128.3, 130.0, 132.9, 133.0, 135.6, 159.8, 199.3, 208.3 ppm.

Data for 3c: A colorless oil. IR (neat): $\tilde{\nu}$ = 2932, 2870, 1717, 1683, 1489, 1239, 1090, 966, 715 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.64 (s, 3 H), 2.01–2.09 (m, 1 H), 2.08 (s, 3 H), 2.42–2.49 (m, 1 H), 2.54–2.61 (m, 1 H), 2.67–2.71 (m, 1 H), 7.24–7.25 (d, J = 2.8 Hz, 4 H), 7.43–7.45 (t, J = 6.8 Hz, 2 H), 7.51–7.55 (t, J = 6.5 Hz, 1 H), 8.25–8.28 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 26.5, 30.0, 33.6, 39.7, 45.9, 85.6, 92.5, 121.3, 128.1, 128.7, 129.6, 132.5, 132.8, 134.4, 135.2, 198.6, 207.9 ppm. $C_{21}H_{19}ClO_2$ (338.10): calcd. C 74.44, H 5.65, found C 74.36, H 5.68.

Data for 3d: Colorless oil. IR (neat): $\tilde{\nu}$ = 2931, 2858, 1717, 1681, 1441, 1240, 1176, 967, 714 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.86–0.89 (t, J = 7.0 Hz, 3 H), 1.26–1.47 (m, 9 H), 1.54 (s, 3 H), 1.91–1.95 (m, 1 H), 2.16–2.20 (m, 4 H), 2.31–2.37 (m, 1 H), 2.51–2.58 (m, 1 H), 2.65–2.72 (m, 1 H), 7.41–7.44 (t, J = 7.5 Hz, 2 H), 7.52–7.54 (t, J = 7.0 Hz, 1 H), 8.27–8.28 (d, J = 7.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 14.2, 19.1, 22.8, 27.1, 28.7, 30.2, 31.5, 34.0, 40.1, 45.6, 65.2, 82.4, 87.4, 128.1, 130.1, 132.7, 135.6, 200.1, 208.5 ppm.

Data for 3e: Colorless oil. IR (neat): $\tilde{\nu}$ = 2929, 2871, 1715, 1651, 1555, 1279, 1178, 965, 763, 694 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.11–1.12 (d, J = 7.0 Hz, 6 H), 1.52 (s, 3 H), 1.69–1.93 (m, 1 H), 2.16 (s, 3 H), 2.20–2.35 (m, 1 H), 2.51–2.56 (m, 2 H), 2.62–2.69 (m, 1 H), 7.34–7.43 (t, J = 8.0 Hz, 2 H), 7.50–7.51 (m, 1 H), 8.26–8.28 (dd, J = 7.5, 1.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 20.6, 22.7, 26.7, 29.9, 33.6, 39.7, 45.2, 81.5, 92.4, 127.7, 129.8, 132.4, 135.4, 199.6, 208.2 ppm. $C_{18}H_{22}O_2$ (270.16): calcd. C 79.96, H 8.20, found C 79.69, H 8.20.

Data for 3f: Colorless oil. IR (neat): $\tilde{\nu}$ = 2967, 2931, 1717, 1683, 1596, 1456, 1172, 966, 715 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.16 (s, 9 H), 1.51 (s, 3 H), 1.86–1.92 (m, 1 H), 2.15 (s, 3 H), 2.29–2.35 (m, 1 H), 2.47–2.55 (m, 1 H), 2.62–2.68 (m, 1 H), 7.39–7.42 (t, J = 7.5 Hz, 2 H), 7.49–7.52 (t, J = 7.5 Hz, 1 H), 8.26–8.27 (d, J = 7.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 26.8, 27.5, 29.9, 30.7, 33.6, 39.7, 45.1, 80.8, 95.2, 127.7, 129.8, 132.4, 135.4, 199.7, 208.2 ppm. $C_{19}H_{24}O_2$ (284.17): calcd. C 80.24, H 8.51, found C 79.95, H 8.41.

Data for 3g: A colorless oil. IR (neat): $\tilde{\nu}$ = 2979, 2936, 1716, 1682, 1596, 1446, 1178, 966, 716 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.52–1.54 (d, J = 9.0 Hz, 3 H), 1.82–1.83 (d, J = 9.0 Hz, 3 H), 1.88–2.15 (m, 1 H), 2.15–2.17 (d, J = 8.5 Hz, 3 H), 2.30–2.38 (m, 1 H), 2.51–2.59 (m, 1 H), 2.63–2.2.71 (m, 1 H), 7.40–7.43 (q, J = 8.0 Hz, 2 H), 7.50–7.53 (t, J = 8.0 Hz, 1 H), 8.24–8.27 (t, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 3.7, 26.7, 29.9, 33.7, 39.8, 45.3, 81.2, 82.5, 127.9, 129.7, 132.5, 135.4, 199.5, 208.2 ppm. $C_{16}H_{18}O_2$ (242.13): calcd. C 79.31, H 7.49, found C 78.85, H 7.59.

Data for 3h: A colorless oil. IR (neat): $\tilde{\nu}$ = 2982, 2938, 1714, 1682, 1597, 1449, 1243, 1175, 967, 702 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.60 (s, 3 H), 1.96–2.02 (m, 1 H), 2.14 (s, 3 H), 2.37–2.43 (m, 1 H), 2.54–2.61 (m, 1 H), 2.67–2.74 (m, 1 H), 3.63 (s, 2 H), 7.23–7.26 (m, 5 H), 7.37–7.40 (m, 2 H), 7.51–7.54 (m, 1 H), 8.24–8.26 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 25.2, 26.7, 29.9, 33.7, 39.7, 45.4, 84.3, 84.5, 126.5, 127.8, 127.9, 128.4, 129.7, 132.5, 135.3, 136.4, 199.3, 208.1 ppm. HRMS (ESI): Calcd. for $C_{22}H_{23}O_2$ [M + H^+] calcd. 319.1693, found 319.1694.

Data for 3i: A colorless oil. IR (neat): $\tilde{\nu}$ = 2951, 2867, 1717, 1682, 1447, 1241, 1176, 965, 715 cm^{-1}. ^1H NMR (CDCl3, 500 MHz): δ = 1.16–1.22 (m, 2 H), 1.47–1.58 (m, 7 H), 1.67–1.72 (m, 2 H), 1.74–2.01 (m, 2 H), 2.14 (s, 3 H), 2.17–2.19 (d, J = 6.5 Hz, 2 H), 2.31–2.36 (m, 1 H), 2.52–2.58 (m, 1 H), 2.64–2.71 (m, 1 H), 7.39–7.42 (t, J = 7.5 Hz, 2 H), 7.49–7.52 (t, J = 7.5 Hz, 1 H), 8.25–8.27 (d, J = 7.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 24.6, 25.2, 26.8, 29.9, 31.9, 33.7, 38.9, 39.7, 45.3, 82.1, 86.6, 127.8, 129.7, 132.4, 135.3, 199.5, 208.1 ppm.

Data for 3j:[9] A colorless oil. IR (neat): $\tilde{\nu}$ = 2976, 2937, 1714, 1682, 1596, 1445, 1237, 1112, 972, 757, 691 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.01–1.04 (t, J = 7.6 Hz, 3 H), 1.64 (s, 3 H), 2.02–2.09 (m, 1 H), 2.40–2.51 (m, 3 H), 2.54–2.62 (m, 1 H), 2.66–2.73 (m, 1 H), 7.24–7.33 (m, 5 H), 7.40–7.44 (t, J = 7.6 Hz, 2 H), 7.50–7.54 (t, J = 7.2 Hz, 1 H), 8.29–8.31 (d, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 7.8, 26.6, 33.7, 36.0, 38.3, 45.9, 86.7, 91.5, 122.8, 128.1, 128.3, 129.7, 131.3, 132.7, 135.3, 198.9, 210.6 ppm. HRMS (ESI): Calcd. for $C_{22}H_{22}O_2Na$ [M + Na^+] calcd. 341.1512, found 341.1513.

Data for 3k:[9] A colorless oil. IR (neat): $\tilde{\nu}$ = 2975, 2936, 1714, 1683, 1606, 1510, 1457, 1249, 1109, 973, 716 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.93–0.97 (t, J = 7.2 Hz, 3 H), 1.55 (s, 3 H), 1.92–1.99 (m, 1 H), 2.34–2.46 (m, 3 H), 2.46–2.54 (m, 1 H), 2.58–2.67 (m, 1 H), 3.694 (s, 3 H), 6.71–6.73 (d, J = 8.8 Hz, 2 H), 7.17–7.20 (d, J = 8.8 Hz, 2 H), 7.33–7.37 (t, J = 7.2 Hz, 2 H), 7.42–7.46 (t, J = 7.2 Hz, 1 H), 8.22–8.24 (d, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 7.8, 26.6, 33.7, 36.0, 38.4, 45.9, 55.2, 86.5, 90.0, 113.9, 114.9, 128.0, 129.7, 132.6, 132.7, 135.4, 159.6, 199.1, 210.7 ppm. HRMS (ESI): Calcd. for $C_{23}H_{24}O_3Na$ [M + Na^+] 371.1618, found 371.1624.

Data for 3l:[9] A colorless oil. IR (neat): $\tilde{\nu}$ = 2976, 2836, 1715, 1684, 1490, 1237, 1091, 972, 715 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.98–1.04 (t, J = 7.6 Hz, 3 H), 1.62 (s, 3 H), 2.00–2.07 (m, 1 H), 2.38–2.50 (m, 3 H), 2.53–2.57 (m, 1 H), 2.62–2.67 (m, 1 H), 7.22 (s, 4 H), 7.39–7.43 (t, J = 7.6 Hz, 2 H), 7.49–7.53 (t, J = 7.2 Hz, 1 H), 8.24–8.25 (d, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 7.8, 26.4, 33.6, 36.0, 38.3, 45.9, 85.5, 92.6, 121.3, 128.1, 128.6, 129.6, 132.5, 132.8, 134.3, 135.3, 198.6, 210.5 ppm. HRMS (ESI): Calcd. for $C_{22}H_{21}ClO_2Na$ [M + Na^+] 375.1122, found 375.1126.

Data for 4a: A colorless oil. IR (neat): $\tilde{\nu}$ = 3423, 2960, 2934, 1716, 1685, 1491, 1217, 1060, 758, 715 cm^{-1}. ^1H NMR ($CDCl_3$,

500 MHz): δ = 1.19 (s, 3 H), 2.04–2.10 (m, 1 H), 2.38–2.51 (m, 3 H), 2.55–2.56 (d, J = 1.6 Hz, 1 H), 2.94–3.02 (m, 1 H), 3.80–3.83 (d, J = 14.0 Hz, 1 H), 7.31–7.34 (m, 4 H), 7.36–7.41 (m, 4 H), 7.63–7.64 (d, J = 7.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 22.3, 35.9, 39.0, 41.3, 52.2, 80.3, 84.4, 93.2, 123.1, 126.5, 127.6, 128.2, 128.4, 131.4, 143.2, 210.6 ppm. HRMS (ESI): Calcd. for $C_{21}H_{20}O_2Na$ [M + Na$^+$] 327.1356, found 327.1360.

Data for 4b: A colorless oil. IR (neat): $\tilde{\nu}$ = 3460, 2960, 2936, 1708, 1606, 1509, 1248, 1165, 1032, 732, 701 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.18 (s, 3 H), 1.65–1.66 (m, 1 H), 2.07–2.09 (m, 1 H), 2.39–2.50 (m, 3 H), 2.97–3.03 (m, 1 H), 3.83 (s, 3 H), 3.83–3.85 (d, J = 11.0 Hz, 1 H), 6.84–6.85 (d, J = 9.0 Hz, 2 H), 7.31–7.39 (m, 5 H), 7.62–7.63 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 22.4, 36.0, 39.1, 41.2, 52.3, 55.3, 80.4, 84.3, 91.6, 114.0, 115.2, 126.5, 127.6, 132.8, 143.2, 159.5, 210.4 ppm. HRMS (ESI): Calcd. for $C_{22}H_{23}O_3$ [M + H$^+$] 335.1642, found 335.1646.

Data for 4c: A colorless oil. IR (neat): $\tilde{\nu}$ = 3428, 2958, 2934, 1707, 1489, 1091, 909, 828, 701 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.20 (s, 3 H), 2.06–2.09 (m, 1 H), 2.41–2.51 (m, 3 H), 2.60–2.66 (m, 1 H), 2.92–2.98 (m, 1 H), 3.77–3.81 (d, J = 14.5 Hz, 1 H), 7.28–7.41 (m, 7 H), 7.61–7.63 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 22.6, 36.2, 39.2, 41.6, 52.4, 80.4, 83.7, 94.5, 121.8, 126.7, 127.8, 127.9, 128.9, 132.9, 134.5, 143.3, 210.7 ppm. HRMS (ESI): Calcd. for $C_{21}H_{19}ClO_2Na$ [M + Na$^+$] 361.0966, found 361.0968.

Data for 4d: A colorless oil. IR (neat): $\tilde{\nu}$ = 3433, 2955, 2929, 2858, 1715, 1447, 701 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.89–0.90 (m, 3 H), 1.07 (s, 3 H), 1.28–1.39 (m, 7 H), 1.50–1.54 (m, 2 H), 1.90–1.96 (m, 1 H), 2.20–2.27 (t, J = 6.5 Hz, 2 H), 2.33–2.40 (m, 3 H), 2.89–2.93 (m, 1 H), 3.74–3.76 (d, J = 14.0 Hz, 1 H), 7.27–7.35 (m, 3 H), 7.57–7.58 (d, J = 7.0 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 14.3, 18.9, 22.8, 22.9, 28.9, 29.1, 31.5, 36.5, 39.2, 40.9, 52.5, 80.5, 83.8, 84.8, 126.8, 127.6, 127.7, 143.6, 211.2 ppm. HRMS (ESI): Calcd. for $C_{21}H_{28}O_2Na$ [M + Na$^+$] 335.1982, found 335.1985.

Data for 4e: A colorless oil. IR (neat): $\tilde{\nu}$ = 3419, 2967, 2933, 1714, 1656, 1321, 967, 701 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.03 (s, 3 H), 1.15–1.17 (t, J = 6.4 Hz, 6 H), 1.87–1.93 (m, 1 H), 2.07–2.11 (m, 1 H), 2.29–2.39 (m, 3 H), 2.51–2.59 (m, 1 H), 2.51–2.85–2.93 (m, 1 H), 3.72–3.75 (d, J = 14.0 Hz, 1 H), 7.24–7.34 (m, 3 H), 7.54–7.56 (d, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 20.5, 22.5, 23.1, 23.2, 36.1, 38.9, 40.4, 52.2, 80.3, 82.9, 89.9, 126.5, 127.3, 127.4, 143.3, 210.8 ppm. HRMS (ESI): Calcd. for $C_{18}H_{22}O_2Na$ [M + Na$^+$] 293.1512, found 293.1516.

Data for 4f: A colorless oil. IR (neat): $\tilde{\nu}$ = 3386, 2963, 2929, 2866, 1703, 1636, 1360, 915, 701 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.04 (s, 3 H), 1.24 (s, 9 H), 1.88–1.92 (m, 1 H), 2.32–2.39 (m, 4 H), 2.86–2.92 (m, 1 H), 3.73–3.76 (d, J = 15.0 Hz, 1 H), 7.29–7.36 (m, 3 H), 7.58–7.60 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 22.5, 27.4, 30.4, 36.2, 38.9, 40.3, 52.2, 80.3, 82.2, 92.7, 126.6, 126.9, 127.3, 127.4, 143.3, 210.9 ppm. HRMS (ESI): Calcd. for $C_{19}H_{24}O_2Na$ [M + Na$^+$] 307.1669, found 307.1671.

Data for 4g: A colorless oil. IR (neat): $\tilde{\nu}$ = 3446, 2951, 2867, 1707, 1447, 1373, 1053, 970, 701 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.06 (s, 3 H), 1.54–1.62 (m, 5 H), 1.76–1.79 (m, 2 H), 1.90–1.96 (m, 1 H), 2.01–2.08 (m, 1 H), 2.14 (s, 1 H), 2.20–2.22 (d, J = 6.0 Hz, 2 H), 2.32–2.42 (m, 3 H), 2.87–2.96 (m, 1 H), 3.73–3.77 (d, J = 14.4 Hz, 1 H), 7.28–7.37 (m, 3 H), 7.56–7.58 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 22.6, 24.7, 31.5, 32.1, 36.3, 39.0, 39.2, 40.6, 47.6, 52.4, 80.3, 83.6, 84.0, 126.4, 127.0, 127.4, 127.5, 143.3, 210.7 ppm. HRMS (ESI): Calcd. for $C_{21}H_{26}O_2Na$ [M + Na$^+$] 333.1825, found 333.1827.

Data for 4h: A colorless oil. IR (neat): $\tilde{\nu}$ = 3372, 2974, 2936, 1715, 1558, 1338, 1069, 970, 766, 703 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.97 (s, 3 H), 1.76 (s, 3 H), 1.81–1.85 (m, 1 H), 2.23–2.31 (m, 3 H), 2.41 (s, 1 H), 2.46–2.85 (m, 1 H), 3.63–3.66 (d, J = 14.4 Hz, 1 H), 7.18–7.29 (m, 3 H), 7.46–7.49 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 3.5, 22.5, 36.1, 39.0, 40.6, 52.2, 79.7, 80.2, 82.7, 126.5, 127.4, 127.5, 143.4, 211.1 ppm. HRMS (ESI): Calcd. for $C_{16}H_{18}O_2Na$ [M + Na$^+$] 265.1199, found 265.1202.

Data for 4i: A colorless oil. IR (neat): $\tilde{\nu}$ = 3501, 2976, 2937, 1711, 1489, 1262, 1099, 994, 757, 692 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.73–0.75 (d, J = 6.8 Hz, 3 H), 1.05 (s, 3 H), 1.97–2.03 (m, 2 H), 2.33–2.46 (m, 2 H), 2.95–3.03 (td, J = 14, 6.0 Hz, 1 H), 3.67–3.73 (q, J = 6.8 Hz, 1 H), 7.17–7.35 (m, 7 H), 7.45–7.55 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 8.3, 23.0, 36.1, 39.1, 42.3, 50.2, 83.6, 84.7, 93.6, 123.2, 127.3, 128.1, 128.3, 131.4, 141.6, 211.2 ppm. HRMS (ESI): Calcd. for $C_{22}H_{23}O_2$ [M + H$^+$] 319.1693, found 319.1695.

Data for 4j: A colorless oil. IR (neat): $\tilde{\nu}$ = 3502, 2972, 2936, 1715, 1653, 1606, 1457, 1247, 1031, 832, 737, 702 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.72–0.74 (d, J = 6.8 Hz, 3 H), 1.03 (s, 3 H), 1.96–2.00 (m, 1 H), 2.05 (s, 1 H), 2.31–2.46 (m, 2 H), 2.95–3.03 (td, J = 13.6, 6.4 Hz, 1 H), 3.67–3.71 (q, J = 6.8 Hz, 1 H), 3.74 (s, 3 H), 6.77–6.79 (d, J = 8.4 Hz, 2 H), 7.18–7.30 (m, 5 H), 7.49–7.55 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 101 Hz): δ = 8.3, 23.1, 36.2, 39.2, 42.3, 50.1, 55.3, 83.7, 84.5, 92.0, 114.0, 115.3, 127.2, 132.8, 141.7, 159.5, 211.3 ppm. HRMS (ESI): Calcd. for $C_{23}H_{25}O_3$ [M + H$^+$] 349.1798, found 349.1801.

Data for 4k: A colorless oil. IR (neat): $\tilde{\nu}$ = 3488, 2932, 2858, 1711, 1652, 1456, 1340, 1159, 936, 701 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.70–0.72 (d, J = 7.2 Hz, 3 H), 0.80–0.83 (t, J = 7.2 Hz, 3 H), 0.92 (s, 3 H), 1.15–1.35 (m, 7 H), 1.43–1.50 (m, 2 H), 1.82–1.87 (m, 2 H), 2.14–2.17 (t, J = 7.2 Hz, 2 H), 2.23–2.31 (td, J = 13.2, 4.0 Hz, 1 H), 2.35–2.40 (m, 1 H), 2.87–2.96 (td, J = 13.6, 6.4 Hz, 1 H), 3.61–3.66 (q, J = 6.8 Hz, 1 H), 7.19–7.28 (m, 3 H), 7.46 (br. s, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 8.3, 14.0, 18.8, 22.5, 23.3, 28.6, 28.8, 31.3, 36.4, 39.1, 41.7, 50.0, 83.6, 83.9, 84.8, 125.9, 127.1, 127.9, 141.7, 211.6 ppm. HRMS (ESI): Calcd. for $C_{22}H_{31}O_2$ [M + H$^+$] 327.2319, found 327.2323.

Data for 5a: A colorless oil. IR (neat): $\tilde{\nu}$ = 3058, 2931, 1714, 1681, 1490, 1330, 1265, 1056, 756 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.44 (s, 3 H), 2.19–2.25 (m, 1 H), 2.38–2.42 (m, 1 H), 2.56–2.61 (m, 1 H), 2.99–3.06 (m, 1 H), 6.06 (s, 1 H), 7.32–7.33 (m, 3 H), 7.38–7.39 (m, 3 H), 7.43–7.45 (m, 2 H), 7.62–7.63 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 28.1, 35.2, 35.3, 38.9, 83.1, 91.6, 122.9, 127.4, 127.6, 128.2, 128.3, 128.8, 131.6, 138.7, 163.6, 198.8 ppm. HRMS (ESI): Calcd. for $C_{21}H_{19}O$ [M + H$^+$] 287.1430, found 287.1434.

Data for 5b: A colorless oil. IR (neat): $\tilde{\nu}$ = 2930, 2837, 1673, 1606, 1456, 1248, 1172, 1032, 731 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.43 (s, 3 H), 2.19–2.26 (m, 1 H), 2.38–2.42 (m, 1 H), 2.56–2.60 (m, 1 H), 3.01–3.09 (m, 1 H), 3.82 (s, 3 H), 6.06 (s, 1 H), 6.86–6.87 (d, J = 9.0 Hz, 2 H), 7.38–7.40 (m, 5 H), 7.63–7.64 (d, J = 3.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 28.4, 35.5, 35.6, 39.3, 55.6, 83.2, 90.3, 114.2, 115.3, 127.7, 127.8, 128.5, 129.1, 133.3, 139.1, 159.9, 164.4, 199.2 ppm. HRMS (ESI): Calcd. for $C_{22}H_{21}O_2$ [M + H$^+$] 317.1536, found 317.1538.

Data for 5c: A colorless oil. IR (neat): $\tilde{\nu}$ = 2955, 2928, 1676, 1597, 1489, 1264, 1091, 828, 766, 701 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.45 (s, 3 H), 2.21–2.27 (m, 1 H), 2.40–2.43 (m, 1 H), 2.58–2.61 (m, 1 H), 2.97–3.04 (m, 1 H), 6.07 (s, 1 H), 7.30–7.41 (m, 7 H), 7.60–7.61 (d, J = 3.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz):

δ = 28.3, 35.4, 35.6, 39.2, 82.3, 92.9, 121.6, 127.6, 128.0, 128.5, 128.9, 129.2, 133.1, 134.6, 138.9, 163.6, 198.9 ppm. HRMS (ESI): Calcd. for $C_{21}H_{18}ClO$ [M + H$^+$] 321.1041, found 321.1045.

Data for 5d: A colorless oil. IR (neat): $\tilde{\nu}$ = 2930, 2858, 1683, 1456, 1264, 701 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.87–0.89 (t, J = 7.0 Hz, 3 H), 1.25–1.32 (m, 7 H), 1.35–1.42 (m, 2 H), 1.49–1.55 (m, 2 H), 2.06–2.13 (m, 1 H), 2.21–2.24 (m, 3 H), 2.47–2.52 (m, 1 H), 2.91–2.98 (m, 1 H), 5.97 (s, 1 H), 7.35–7.37 (m, 3 H), 7.56–7.58 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 14.0, 18.7, 22.5, 28.4, 28.5, 28.7, 31.2, 34.7, 35.2, 39.3, 82.3, 83.4, 127.2, 127.4, 128.1, 128.7, 138.9, 164.4, 199.2 ppm. HRMS (ESI): Calcd. for $C_{21}H_{27}O$ [M + H$^+$] 295.2056, found 295.2059.

Data for 5e: A colorless oil. IR (neat): $\tilde{\nu}$ = 2968, 2930, 2870, 1675, 1653, 1558, 1320, 1150, 701 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.10 (s, 6 H), 1.22 (s, 3 H), 1.98–2.05 (m, 1 H), 2.14–2.16 (m, 1 H), 2.40–2.45 (m, 1 H), 2.51–2.54 (m, 1 H), 2.83–2.90 (m, 1 H), 5.89 (s, 1 H), 7.29 (**s,** 3 H), 7.50 (**s,** 2 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 20.6, 23.0, 28.3, 34.6, 35.2, 39.2, 81.5, 88.8, 127.2, 127.4, 128.1, 128.7, 138.9, 164.6, 199.3 ppm. HRMS (ESI): Calcd. for $C_{18}H_{21}O$ [M + H$^+$] 253.1587, found 253.1589.

Data for 5f: A colorless oil. IR (neat): $\tilde{\nu}$ = 2967, 2929, 2867, 1677, 1599, 1270, 1150, 701 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.24 (s, 9 H), 1.29 (s, 3 H), 2.06–2.13 (td, J = 13.0, 4.0 Hz, 1 H), 2.20–2.24 (dt, J = 13.0, 4.5 Hz, 1 H), 2.48–2.53 (dt, J = 16.5, 4.0 Hz, 1 H), 2.89–2.96 (m, 1 H), 5.97 (s, 1 H), 7.36–7.38 (t, J = 3.5 Hz, 3 H), 7.57–7.59 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 27.2, 28.1, 30.7, 34.3, 34.9, 38.9, 80.5, 91.4, 126.8, 127.2, 127.7, 128.4, 138.7, 164.4, 198.9 ppm. HRMS (ESI): Calcd. for $C_{19}H_{23}O$ [M + H$^+$] 289.1563, found 289.1566.

Data for 5g: A colorless oil. IR (neat): $\tilde{\nu}$ = 2949, 2865, 1677, 1558, 1264, 1151, 766, 701 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.25–1.29 (m, 2 H), 1.31 (s, 3 H), 1.54–1.66 (m, 4 H), 1.76–1.82 (m, 2 H), 2.04–2.15 (m, 2 H), 2.23–2.27 (m, 3 H), 2.49–2.54 (m, 1 H), 2.94–3.05 (m, 1 H), 5.99 (s, 1 H), 7.37–7.38 (t, J = 3.5 Hz, 3 H), 7.59–7.61 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 24.6, 25.3, 28.4, 32.0, 34.7, 35.2, 39.1, 39.4, 82.3, 82.8, 127.2, 127.4, 128.1, 128.7, 138.9, 164.4, 199.2 ppm. HRMS (ESI): Calcd. for $C_{21}H_{25}O$ [M + H$^+$] 293.1900, found 293.1906.

Data for 5h: A colorless oil. IR (neat): $\tilde{\nu}$ = 2951, 2922, 1674, 1616, 1558, 1456, 1264, 1151, 766, 701 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.29 (s, 3 H), 1.89 (s, 3 H), 2.07–2.13 (m, 1 H), 2.22–2.26 (m, 1 H), 2.48–2.53 (m, 1 H), 2.93–2.99 (m, 1 H), 5.98 (s, 1 H), 7.37–7.39 (m, 3 H), 7.57–7.58 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 3.6, 28.3, 34.6, 35.2, 39.2, 78.6, 81.3, 127.2, 127.4, 128.1, 128.7, 138.9, 164.2, 199.1 ppm. HRMS (ESI): Calcd. for $C_{16}H_{17}O$ [M + H$^+$] 225.1274, found 225.1278.

Data for 5i: A colorless oil. IR (neat): $\tilde{\nu}$ = 2928, 2864, 1675, 1597, 1443, 1306, 1013, 892, 756, 704 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.18 (s, 3 H), 1.48 (s, 3 H), 2.07–2.14 (td, J = 13.2, 4.0 Hz, 1 H), 2.26–2.31 (dt, J = 12.8, 4.8 Hz, 1 H), 2.52–2.58 (dt, J = 13.2, 4.4 Hz, 1 H), 2.89–2.98 (m, 1 H), 7.16–7.32 (m, 10 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 13.4, 28.3, 35.3, 36.8, 37.8, 82.7, 92.0, 123.2, 127.5, 127.7, 128.0, 128.3, 131.6, 132.1, 138.5, 158.2, 198.9 ppm. HRMS (ESI): Calcd. for $C_{22}H_{21}O$ [M + H$^+$] 301.1587, found 301.1590.

Data for 5j: A colorless oil. IR (neat): $\tilde{\nu}$ = 2961, 2929, 1674, 1606, 1456, 1291, 1172, 1032, 892, 731 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.17 (s, 3 H), 1.48 (s, 3 H), 2.06–2.14 (td, J = 13.2, 4.0 Hz, 1 H), 2.25–2.31 (dt, J = 13.2, 4.8 Hz, 1 H), 2.51–2.57 (dt, J = 16.8, 4.0 Hz, 1 H), 2.90–2.99 (m, 1 H), 3.72 (s, 3 H), 6.76–6.74 (d, J = 8.4 Hz, 2 H), 7.14–7.17 (m, 2 H), 7.24–7.27 (m, 3 H), 7.29–7.33 (t, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 13.4, 28.4, 35.4, 36.8, 37.8, 55.3, 82.5, 90.4, 113.9, 115.3, 127.5, 127.7, 128.0, 131.9, 132.9, 138.6, 158.4, 159.4, 199.1 ppm. HRMS (ESI): Calcd. for $C_{23}H_{22}O_2Na$ [M + Na$^+$] 353.1512, found 353.1515.

Data for 5k: A colorless oil. IR (neat): $\tilde{\nu}$ = 2966, 2928, 1674, 1606, 1456, 1306, 1089, 1013, 828, 762 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.20 (s, 3 H), 1.48 (s, 3 H), 2.08–2.16 (td, J = 12.8, 4.0 Hz, 1 H), 2.27–2.33 (dt, J = 13.2, 4.8 Hz, 1 H), 2.53–2.59 (td, J = 17.2, 4.4 Hz, 1 H), 2.87–2.96 (m, 1 H), 7.12–7.17 (m, 2 H), 7.18–7.23 (m, 4 H), 7.24–7.27 (m, 1 H), 7.30–7.34 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 13.4, 28.2, 35.2, 36.9, 37.7, 81.7, 93.1, 121.6, 127.6, 128.1, 128.6, 132.2, 132.8, 134.1, 138.4, 157.9, 198.8 ppm. HRMS (ESI): Calcd. for $C_{22}H_{20}ClO$ [M + H$^+$] 335.1197, found 335.1200.

Data for 5l: A colorless oil. IR (neat): $\tilde{\nu}$ = 2929, 2858, 1676, 1617, 1456, 1306, 1098, 896, 766 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.79–0.83 (t, J = 6.8 Hz, 3 H), 1.06 (s, 3 H), 1.20–1.32 (m, 6 H), 1.38–1.45 (m, 5 H), 1.97–2.05 (td, J = 12.8, 4.0 Hz, 1 H), 2.10–2.16 (m, 3 H), 2.46–2.52 (dt, J = 16.8, 4.0 Hz, 1 H), 2.84–2.93 (m, 1 H), 7.13 (br. s, 2 H), 7.22–7.32 (m, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 13.3, 14.0, 18.7, 22.5, 28.5, 28.6, 28.8, 31.3, 35.4, 36.2, 38.2, 82.4, 82.8, 127.3, 127.6, 127.8, 131.4, 138.7, 159.1, 199.4 ppm. HRMS (ESI): Calcd. for $C_{22}H_{29}O$ [M + H$^+$] 309.2213, found 309.2216.

Supporting Information (see also the footnote on the first page of this article): Copies of the NMR spetra (^{1}H, ^{13}C and NOESY) of the new compounds shown in Tables 1, 2, 3, and 4.

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[9] The ^{1}H NMR spectra of compounds **3j**, **3k**, and **3l** contain traces of olefinic impurity which might derive from ethyl vinyl ketone.

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