A New Two-Step Synthesis of 2-Alkylated 1,4-Diketones and α-Alkylated γ-Keto Esters

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Abstract: 2-Alkylated 1,4-diketones and α-alkylated γ-keto esters can be easily prepared by a two-step procedure which involves first the conjugate addition of a nitroalkane to an enedione derivative in acetonitrile with DBU as base, followed by chemoselective hydrogenation of the C–C double bond (H_2, 10% Pd/C) of the Michael adduct, obtained after elimination of nitrous acid.

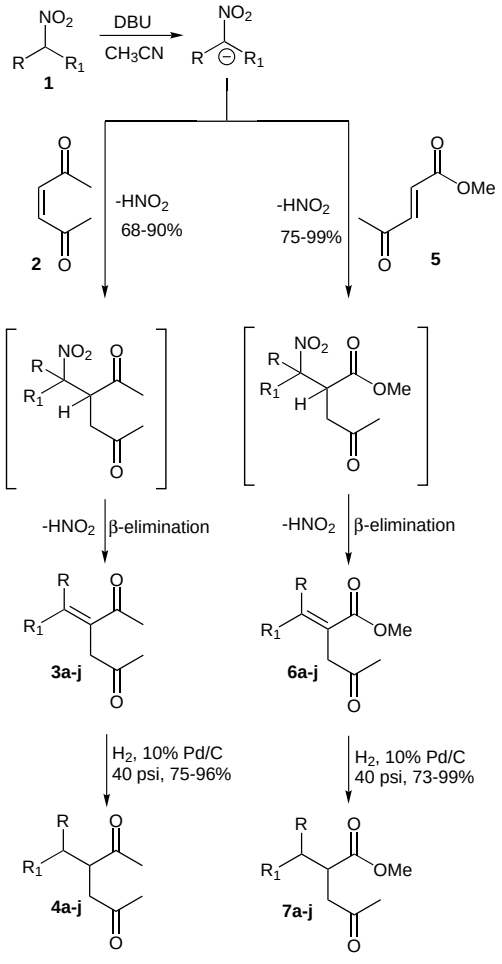
Key words: 2-Alkyl 1,4-diketones, α-alkyl γ-keto esters, nitroalkanes, conjugated addition, nitrous acid elimination

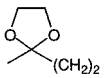
1,4-Diketones are important intermediates in the synthesis of cyclopentenones and heterocyclic compounds such as furans, pyrroles, thiophenes, and pyridazines.[1–6] γ-Keto esters represent a valuable class of compounds as intermediates for various heterocycles such as lactones, β-lactam antibiotics, isoquinolines and lactonic sex pheromones.[7]

Although several methods have been reported[4,5] for the synthesis of the above compounds, most of these suffer from drawbacks such as the use of harsh conditions, employment of expensive chemicals, low yields and/or tedious procedures.

Aliphatic nitro compounds can be considered as versatile building blocks in organic synthesis,[8] both the activating effect of the nitro group and its facile transformation into various functionalities have extended the importance of nitro compounds in the preparation of complex molecules. In the past the nitroalkanes have already been used to obtain 1,4-diketones[9] and γ-keto esters[10] through Michael addition to electron-deficient alkenes, followed by the Nef reaction.

In the course of our studies to explore the novel utilities of nitroalkanes in the Michael reaction,[11] we have disclosed



6,7	R	R1
a	H	$CH_3(CH_2)_2$
b	Me	Me
c	H	C_2H_5
d	-(CH2)5-	
e	H	$MeO_2C(CH_2)_2$
f	H	
g	H	$CH_3CH(OH)CH_2CH_2$
h	H	$PhCH_2$
i	H	$CH_3CO(CH_2)_2$
j	H	$MeO_2C(CH_2)_3$

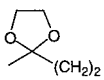
3,4	R	R1
a	H	$CH_3(CH_2)_2$
b	H	$MeO_2C(CH_2)_2$
c	-(CH2)5-	
d	H	$CH_3(CH_2)_4$
e	H	C_2H_5
f	H	$PhCH_2$
g	H	$MeO_2C(CH_2)_3$
h	H	$CH_3CO(CH_2)_2$
i	H	Me_2CHCH_2
j	H	

Table 1 Enone Derivatives **3** Prepared

Product[a]	Yield (%)	IR (film) ν (cm^{-1})	^1H NMR ($CDCl_3$/TMS) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$) δ
3a	68	1719, 1665	0.95 (t, 3H, *J* = 7.3), 1.4–1.6 (m, 2H), 2.15–2.25 (m, 2H), 2.2 (s, 3H), 2.46 (s, 3H), 3.5 (s, 3H), 6.8 (t, 1H, *J* = 7.3)	14.0, 18.7, 23.3, 29.5, 33.4, 138.5, 141.3, 199.2, 204.1
3b	72	1730, 1666	2.2 (s, 3H), 2.3 (s, 3H), 2.5–2.6 (m, 2H), 3.5 (s, 3H), 3.7 (s, 3H), 6.8 (t, 1H, *J* = 7.4)	18.6, 23.8, 32.6, 33.0, 51.6, 137.0, 139.5, 173.2, 200.0, 203.5
3c	75	1715, 1681	1.5–1.7 (m, 6H), 2.1 (t, 2H, *J* = 6.4), 2.2 (s, 3H), 2.3 (s, 3H), 2.4 (t, 2H, *J* = 7.5), 3.5 (s, 2H)	18.6, 26.5, 27.2, 28.2, 33.0, 34.1, 36.4, 132.8, 150.8, 203.3, 204.5
3d	85	1720, 1665	0.9 (t, 3H, *J* = 6.7), 1.2-1.5 (m, 6H), 1.2–1.5 (m, 2H), 2.2 (s, 3H), 2.4 (s, 3H), 3.4 (s, 1H), 6.8 (t, 1H, *J* = 7.2)	14.0, 18.6, 22.8, 23.9, 26.5, 29.3, 30.9, 33.0, 138.5, 140.1, 200.0, 203.5
3e	77	1717, 1665	1.1 (t, 3H, *J* = 7.4), 2.1–2.3 (m, 2H), 2.2 (s, 3H), 2.4 (s, 3H), 3.4 (s, 2H), 6.8 (t, 1H, *J* = 7.4)	14.0, 18.6, 21.3, 24.4, 32.9, 139.7, 140.1, 199.2, 202.7
3f'	40	1712, 1666	2.06 (s, 3H), 2.19 (s, 3H), 3.16 (s, 2H), 3.96 (d, 2H, *J* = 7.9), 7.15-7.4 (m, 5H)	18.5, 23.9, 33.2, 39.8, 127.4, 128.3, 129.0, 137.9, 140.6, 141.8, 199.8, 203.5
3f"	33	1712	2.06 (s, 3H), 2.11 (s, 3H), 2.5–2.69 (m, 2H), 3.04–3.09 (m, 1H), 6.07–6.13 (dd, 1H, *J* = 9.2, 15.9), 6.6 (d, 1H, *J* = 15.9), 7.1–7.55 (m, 5H)	16.3, 29.3, 44.9, 56.7, 126.2, 127.6, 129.0, 132.4, 133.5, 136.4, 207.1, 210.4
3g	90	1733, 1665	1.4–1.8 (m, 2H), 2.15 (t, 2H, *J* = 7.0), 2.2–2.4 (m, 2H), 2.2 (s, 3H), 2.35 (s, 3H), 3.4 (s, 2H), 3.7 (s, 3H), 6.8 (t, 1H, *J* = 7.2)	18.6, 23.9, 28.11, 32.6, 33.0, 51.4, 139.0, 139.1, 173.7, 199.9, 203.5
3h	80	1706, 1661	2.3 (s, 3H), 2.3-2.6 (m, 4H), 2.4 (s, 3H), 3.4 (s, 2H), 7.1 (t, 1H, *J* = 7.2)	18.5, 23.8, 29.7, 33.0, 43.2, 137.6, 140.5, 199.9, 203.5, 207.7
3i	70	1720, 1666	0.9 (d, 6H, *J* = 6.6), 1.7-1.9 (m, 1H), 2.09 (t, 2H, *J* = 7.1), 2.15 (s, 3H), 2.3 (s, 3H), 3.4 (s, 2H), 6.8 (t, 1H, *J* = 7.3)	18.6, 22.5, 23.9, 27.2, 33.1, 33.6, 136.8, 139.6, 200.8, 203.5
3j	77	1717, 1665	1.3 (s, 3H), 1.7-1.9 (m, 2H), 2.2-2.4 (m, 2H), 2.2 (s, 3H), 2.3 (s, 3H), 3.4 (s, 2H), 3.8-4.0 (m, 2H), 6.8 (t, 1H, *J* = 7.3)	18.6, 22.4, 23.8, 33.0, 38.8, 64.6, 110.3, 139.1, 140.2, 199.9, 203.5

[a] Satisfactory microanalyses obtained: C ± 0.18, H ± 0.14.

that the nitro group may, contemporaneously, behave both as an electron-withdrawing and as a leaving group.[12] The latter result suggested us a new convenient, two-step way to prepare the title compounds. Our procedure involves first the conjugate addition of the nitronate derived from the nitro compound **1** to the enedione derivatives **2** and **5** (with this substrate a regiospecific addition occurs) in acetonitrile and with DBU (1 equiv) as base (Scheme 1), then chemoselective hydrogenation (10% Pd/C as catalyst) of the C–C double bond of the enones **3** and **6** obtained by the elimination of nitrous acid from the Michael adducts, completes the conversion to the title compounds **4** and **7**. The *E*-isomers were highly predominant (up to 93%, determined by NMR analysis of the crude reaction mixture) in the intermediates **3** and **6**. In fact, it is well documented that a β-alkyl substituent *syn* to a carbonyl moiety in α,β-conjugated enones resonates downfield relative to the *anti* alkyl substituent in the NMR spectrum.[13] Consequently, the NMR chemical shift of the β-methylene, or γ-methylene protons, β-methylene, or γ-methine protons of β-secondary alkyl substituents provides a reliable guide for the assignment of the olefin configuration.

When 2-phenylnitroethane is used as starting material, the conjugate addition to **2** or **5** produces (Scheme 2) a mixture of isomers **3f'**/**3f"** (5.5:4.5), and **6h'**/**6h"** (7.3:3.7), respectively. However, the hydrogenation of these mixtures converts both the isomers to the saturated products **4f** and **7h**, respectively. By this procedure high yields (Tables 1–4) are observed for each step (68–90% **1** to **3**; 75–96% **3** to **4**; 75–99% **1** to **6**; and 75–99% **6** to **7**) and several other fuctionalities, such as ester, carbonyl, hydroxyl, and ketal can be preserved, so that, our method allows the formation of functionalized 2-alkylated 1,4-diketones and α-alkylated γ-keto esters, both difficult to prepare by other ways.

It is important to point out that while in the previous approach to obtain 1,4-diketones and γ-keto esters from nitroalkanes [(i) conjugate addition, (ii) Nef reaction],[9,10]

Table 2 2-Alkylated 1,4-Diketones **4** Prepared

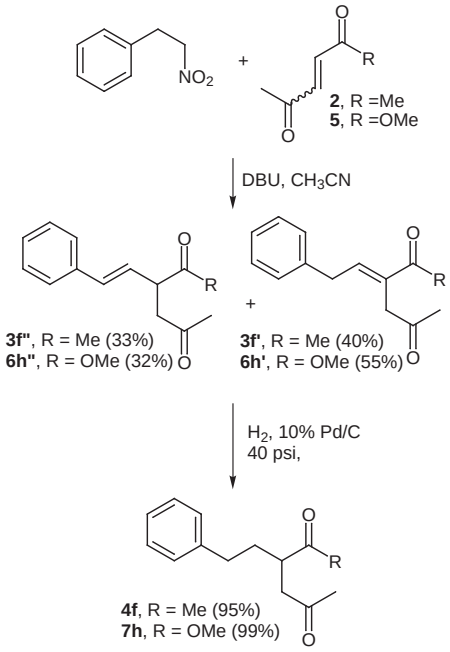
Product	Yield (%)	IR (film) ν (cm^{-1})	^1H NMR ($CDCl_3$/TMS) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$) δ
4a	90	1710	0.9 (t, 3H, *J* = 6.2), 1.1–1.7 (m, 6H), 2.15 (s, 3H), 2.21 (s, 3H), 2.4 (d, 1H, *J* = 14.1), 2.9 (d, 1H, *J* = 9.8), 2.9-3.1 (m, 1H)	14.0, 22.3, 27.0, 29.8, 30.3, 31.1, 43.5, 53.1, 208.7, 210.9
4b	95	1709	1.2–1.7 (m, 4H), 2.12 (s, 3H), 2.25 (s, 3H), 2.3 (t, 2H, *J* = 3.3), 2.45 (d, 1H, *J* = 9.8), 3.0–3.1 (m, 1H), 3.68 (s, 3H)	21.2, 23.2, 27.6, 29.7, 29.9, 43.2, 50.9, 51.3, 172.4, 208.1, 211.6
4c	95	1712	1.1–1.8 (m, 11H), 2.15 (s, 3H), 2.25 (s, 3H), 2.4 (d, 1H, *J* = 14.3), 2.9 (d, 1H, *J* = 9.6), 2.9–3.1 (m, 1H)	26.2, 26.5, 27.9, 28.9, 29.6, 29.9, 37.9, 42.3, 53.5, 207.1, 211.7
4d	95	1711	0.85 (t, 3H, *J* = 6.3 Hz), 1.2–1.6 (m, 10H), 2.15 (s, 3H), 2.25 (s, 3H), 2.4 (d, 1H, *J* = 14.3), 2.9 (d, 1H, *J* = 9.7), 2.9–3.1 (m, 1H)	14.1, 21.7, 22.7, 29.5, 27.6, 29.7, 30.3, 31.9, 43.2, 53.1, 208.1, 211.6
4e	90	1709	0.85–0.9 (t, 3H, *J* = 6.9), 1.2-1.4 (m, 4H), 2.1 (s, 3H), 2.2 (s, 3H), 2.4 (d, 1H, *J* = 14.2), 2.87 (d, 1H, *J* = 10.0 Hz), 2.95–3.1 (m, 1H)	15.8, 22.7, 27.1, 29.1, 31.7, 43.8, 51.0, 207.3, 211.1
4f	95	1710	1.5–1.8 (m, 4H), 2.15 (s, 3H), 2.25 (s, 3H), 2.4 (d, 1H, *J* = 14.0), 2.9 (d, 1H, *J* = 9.9), 3.0–3.2 (m, 1H), 7.0–7.4 (m, 5H)	27.6, 29.7, 30.6, 33.8, 43.3, 53.2, 125.7, 127.6, 128.2, 142.7, 208.1, 211.4
4g	95	1710	1.2–1.8 (m, 6H), 2.15 (s, 3H), 2.22 (s, 3H), 2.3 (t, 2H, *J* = 4.2), 2.4 (d, 1H, *J* = 14.6), 2.9 (d, 1H , *J* = 10.1), 2.9–3.1 (m, 1H), 3.7 (s, 3H)	24.5, 26.6, 27.6, 29.7, 29.8, 32.8, 43.2, 51.3, 52.2, 174.1, 208.1, 211.6
4h	96	1705	1.2–1.4 (m, 4H), 2.1 (s, 3H), 2.2 (s, 3H), 2.4 (s, 3H), 2.4 (d, 1H, *J* = 14.7), 2.5 (t, 2H, *J* = 3.2), 2.9 (d, 1H, *J* = 9.9 Hz), 3.0–3.1 (m, 1H)	21.1, 27.6, 29.7, 30.0, 43.2, 43.7, 50.5, 208.1, 209.2, 211.6
4i	75	1712	0.9 (d, 6H, *J* = 6.6), 1.1–1.3 (m, 4H), 1.3–1.6 (m, 1H), 2.15 (s, 3H), 2.22 (s, 3H), 2.4 (d, 1H, *J* = 14.2), 2.95 (d, 1H, *J* = 12.8), 2.9–3.0 (m, 1H)	22.7, 26.5, 27.3, 27.6, 29.7, 32.8, 43.3, 51.0, 208.1, 212.5
4j	94	1709	1.3 (s, 3H), 1.31-1.7 (m, 6H), 2.12 (s, 3H), 2.21 (s, 3H), 2.45 (d, 1H, *J* = 13.9), 2.45 (d, 1H, *J* = 9.2), 2.91-3.1 (m, 1H), 3.8–4.0 (m, 4H)	24.0, 25.4, 27.6, 29.7, 31.3, 37.6, 43.2, 52.2, 64.5, 110.0, 208.1, 211.6

[a] Satisfactory microanalysis obtained: C ± 0.13, H ± 0.16.

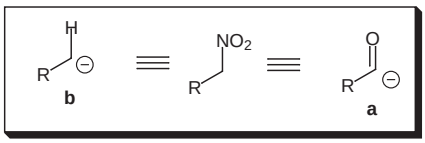
the latter compounds are employed as acyl anion equivalents **a**, this new procedure, here reported, utilises the nitroalkanes as alkyl anion synthons **b** (Scheme 3).

In conclusion, the principal advantages of the methodology presented here are high yields, high purity and the simple procedure using inexpensive chemicals.

All the reactions were monitored by TLC and gas chromatographic analyses, performed on a Carlo Erba Fractovap 4160 using a capillary column of duran glass (0.32 mm × 25 mt), stationary phase OV1 (film thickness 0.4–0.45 nm). All ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ at 200 and 75 MHz, respectively, on a Varian Gemini 200. Chemical shifts are expressed in ppm downfield from TMS. IR spectra were recorded with a Perkin-Elmer 257 spectrophotometer. All the products were purified by flash chromatography on Merck silica gel using EtOAc/cyclohexane as eluent. Elementary analyses were performed using a C, H, N, S Analyzer Model 185 from Hewlett-Packard.



Scheme 2



Scheme 3

Conjugate Addition of Nitroalkanes 1 to 2-Ene-1,4-dione Derivatives 2 and 5; General Procedure for the Synthesis of 3 and 6
DBU (3.04 g, 20 mmol) was added at r.t. to a solution of nitroalkane **1** (20 mmol) and enedione **2** or **5** (20 mmol) in MeCN (100 mL) . The solution was stirred for 7 h at r.t., then silica gel (Merck 0.04–0.063 mm, 5–6 g) was added and the solution was evaporated. The residue, consisting of crude silica gel, was flash chromatographed, using a suitable ratio of EtOAc/cyclohexane as eluent, affording the pure compound **3** or **6**.

Hydrogenation of the C–C Double Bond of the Enone Derivatives 3 and 6; General Procedure for the Synthesis of 4 and 7
The substrate **3** or **6** (11 mmol) was dissolved in EtOAc (120 mL) and 10% Pd/C (0.2 g) was added. The suspension was hydrogenated (40 psi) at r.t. for 5 h. The catalyst was removed by filtration through a Celite pad and was washed with EtOAc (10 × 3 mL). After evaporation of the solvent the crude product was purified by flash chromatography (EtOAc/cyclohexane) giving the pure product **4** or **7**.

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Table 3 Enone Derivatives **6** Prepared

Product[a]	Yield (%)	IR (film) ν (cm^{-1})	^{1}H NMR ($CDCl_3$/TMS) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$) δ
6a	75	1713, 1670	0.92 (t, 3H, *J* = 7.3), 1.38–1.59 (m, 2H), 2.02-2.2 (m, 2H), 2.18 (s, 3H), 3.41 (s, 3H), 3.71 (s, 3H), 6.98 (t, 1H, *J* = 7.5)	14.0, 19.4, 24.0, 30.6, 37.0, 51.9, 127.5, 147.0, 167.0, 207.0
6b	88	1718, 1656	1.8 (s, 3H), 2.12 (s, 3H), 2.15 (s, 3H), 3.45 (s, 2H), 3.7 (s, 3H)	20.6, 20.9, 24.4, 34.5, 52.3, 125.2, 144.3, 173.2, 205.9
6c	93	1713, 1650	1.05 (t, 3H, *J* = 7.5), 2.0–2.15 (m, 2H), 2.2 (s, 3H), 3.4 (s, 2H), 3.7 (s, 3H), 6.95 (t, 1H, *J* = 7.5)	13.6, 19.4, 21.2, 36.6, 51.9, 127.1, 136.6, 167.0, 205.6
6d	92	1710, 1630	1.52–1.65 (m, 6H), 2.14–2.16 (m, 2H), 2.18 (s, 3H), 2.6–2.7 (m, 2H), 3.45 (s, 2H), 3.69 (s, 3H)	20.6, 26.5, 29.1, 32.6, 35.5, 36.1, 52.3, 123.8, 151.9, 172.9, 205.9
6e	99	1717, 1640	2.2 (s, 3H), 2.4–2.5 (m, 4H), 3.4 (s, 2H), 3.67 (s, 3H), 3.71 (s, 3H), 6.97 (t, 1H, *J* = 7.2)	19.3, 23.6, 33.5, 36.6, 51.6, 51.9, 128.2, 143.0, 167.7, 173.2, 206.4
6f	98	1712, 1649	1.3 (s, 3H), 1.8–1.9 (m, 2H), 2.2 (s, 3H), 2.21–2.26 (m, 2H), 3.44 (s, 2H), 3.72 (s, 3H), 3.86–3.98 (m, 4H), 7.0 (t, 1H, *J* = 7.5)	19.4, 22.1, 23.8, 39.7, 51.9, 64.6, 110.3, 127.8, 146.1, 167.7, 206.4
6g	85	1712, 1649	1.18 (d, 3H, *J* = 6.2), 1.5–1.6 (m, 2H), 2.2 (s, 3H), 2.18–2.3 (m, 2H), 3.45 (s, 3H), 3.7 (s, 3H), 3.71–3.8 (m, 1H), 6.95 (t, 1H, *J* = 7.6)	19.4, 23.4, 24.5, 36.7, 37.0, 51.9, 66.3, 127.8, 145.9, 167.7, 206.4
6h'	55	1716, 1640	2.2 (s, 3H), 3.16 (s, 2H), 3.7 (s, 3H), 3.75 (d, 2H, *J* = 2.9), 6.3 (t, 1H, *J* = 7.8), 7.15–7.4 (m, 5H)	19.4, 36.8, 39.5, 51.9, 127.4, 128.3, 128.8, 129.2, 138.4, 141.2, 167.5, 206.4
6h"	32	1710	2.2 (s, 3H), 2.65–2.75 (m, 2H), 3.05–3.2 (m, 2H), 3.7 (s, 3H), 6.1 (dd, 1H, *J* = 8.4, 15.9), 6.55 (d, 1H, *J* = 15.9), 7.1–7.4 (m, 5H)	27.9, 45.5, 51.6, 51.9, 127.0, 127.6, 128.9, 131.6, 136.8, 174.1, 206.9
6i	82	1712, 1651	2.15 (s, 3H), 2.2 (s, 3H), 2.3–2.5 (m, 2H), 2.6 (t, 3H, *J* = 7.2), 3.5 (s, 2H), 3.7 (s, 3H), 6.9 (t, 1H, *J* = 7.6)	19.4, 23.3, 29.7, 36.7, 44.1, 51.9, 129.2, 143.4, 167.7, 206.4, 207.7
6j	98	1720, 1654	1.4–1.8 (m, 2H), 2.15 (t, 2H, *J* = 7.0), 2.2 (s, 3H), 3.4 (s, 2H), 3.65 (s, 3H), 3.7 (s, 3H), 6.95 (t, 1H, *J* = 7.5)	19.4, 23.2, 28.1, 29.8, 36.7, 42.9, 51.9, 127.8, 142.8, 167.7, 206.4, 208.2

[a] Satisfactory microanalyses obtained: C ± 0.13, H ± 0.10.

Table 4 α-Alkylated γ-Ketoesters **7** Prepared

Product[a]	Yield	IR (film) ν (cm^{-1})	^1H NMR ($CDCl_3$/TMS) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$) δ
7a	78	1732	0.9 (t, 3H, *J* = 6.7 Hz), 1.2–1.7 (m, 6H), 2.11 (s, 3H), 2.4 (d, 1H, *J* = 12.9), 2.9 (d, 1H, *J* = 17.3), 2.81-2.9 (m, 1H), 3.65 (s, 3H)	13.9, 22.8, 28.7, 29.0, 30.1, 43.6, 45.1, 51.4, 174.2, 205.8
7b	75	1719	0.9 (d, 3H, *J* = 6.8), 0.95 (d, 3H, *J* = 6.9), 1.8–2.0 (m, 1H), 2.2 (s, 3H), 2.4 (d, 1H, *J* = 12.3 Hz), 2.7–2.8 (m, 1H), 2.9 (d, 1H, *J* = 17.1), 3.68 (s, 3H)	18.2, 20.2, 30.8, 30.9, 41.9, 46.9, 52.2, 175.1, 207.8
7c	73	1735	0.9 (t, 3H, *J* = 7.1), 1.2–1.6 (m, 4H), 2.15 (s, 3H), 2.45 (d, 1H, *J* = 12.3), 2.9 (d, 1H, *J* = 17.3), 2.8–2.9 (m, 1H), 3.69 (s, 3H)	14.1, 20.0, 28.2, 34.8, 43.4, 45.3, 50.9, 174.5, 204.3
7d	99	1732	1.5–1.8 (m, 11H), 2.15 (s, 3H), 2.5 (d, 1H, *J* = 12.1), 2.9 (d, 1H, *J* = 17.3 Hz), 2.91–3.1 (m, 1H), 3.4 (s, 3H)	26.8, 27.3, 30.0, 31.7, 33.7, 37.3, 42.5, 44.8, 51.1, 176.9, 207.5
7e	99	1735	1.5–1.7 (m, 4H), 2.18 (s, 3H), 2.3 (t, 2H, *J* = 6.7), 2.5 (d, 1H, *J* = 12.4), 2.9 (d, 1H, *J* = 15.2), 2.8–2.91 (m, 1H), 3.6 (s, 3H), 3.7 (s, 3H)	22.1, 22.4, 28.8, 30.4, 41.9, 44.7, 51.4, 51.5, 172.4, 174.9, 205.1
7f	99	1718	1.3 (s, 3H), 2.15 (s, 3H), 2.5 (d, 1H, *J* = 12.3), 2.9 (d, 1H, *J* = 15.3), 3.68 (s, 3H), 3.85–4.0 (m, 4H)	24.0, 25.1, 28.8, 31.9, 38.5, 42.8, 44.7, 51.5, 64.5, 110.0, 174.9, 205.1
7g	99	3400, 1715	1.18 (d, 3H, *J* = 6.0), 1.3–1.7 (m, 6H), 2.18 (s, 3H), 2.55 (d, 1H, *J* = 12.3), 2.9 (d, 1H, *J* = 17.1), 2.8–2.9 (m, 1H), 3.7–3.8 (m, 1H)	22.7, 23.5, 28.8, 30.3, 40.2, 42.8, 44.7, 51.5, 67.9, 174.9, 205.1
7h	99	1717, 1603	1.7–2.0 (m, 4H), 2.15 (s, 3H), 2.6 (d, 1H, *J* = 12.5), 2.9 (d, 1H, *J* = 17.3), 2.9–3.1 (m, 1H), 3.7 (s, 3H), 7.1–7.3 (m, 5H)	28.8, 31.4, 34.2, 43.7, 44.9, 51.5, 125.7, 128.0, 129.1, 142.6, 174.8, 205.1
7i	95	1710	1.5–1.6 (m, 4H), 2.12 (s, 3H), 2.15 (s, 3H), 2.5 (t, 2H, *J* = 6.7), 2.6 (d, 1H, *J* = 12.6), 2.9 (d, 1H, *J* = 15.3 Hz), 2.8–2.9 (m, 1H), 3.63 (s, 3H)	21.3, 28.9, 29.4, 30.0, 41.0, 44.3, 44.7, 51.5, 174.9, 205.1, 209.1
7j	99	1732	1.2–1.7 (m, 6H), 2.2 (s, 3H), 2.3 (t, 2H, *J* = 6.7), 2.5 (d, 1H, *J* = 12.5), 2.9 (d, 1H, *J* = 15.2), 2.8–2.9 (m, 1H), 3.69 (s, 3H), 3.71 (s, 3H)	22.9, 26.6, 28.5, 28.76, 29.8, 43.87, 44.7, 51.5, 175.0, 205.1, 207.7

[a] Satisfactory microanalyses obtained: C ± 0.15, H ± 0.14.

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