Asymmetric Synthesis of Polyfunctionalized Allenic Esters: Toward the Synthesis of an Iphionane Sesquiterpene

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Dedicated to Professor Guy Ourisson on the occasion of his 80th birthday

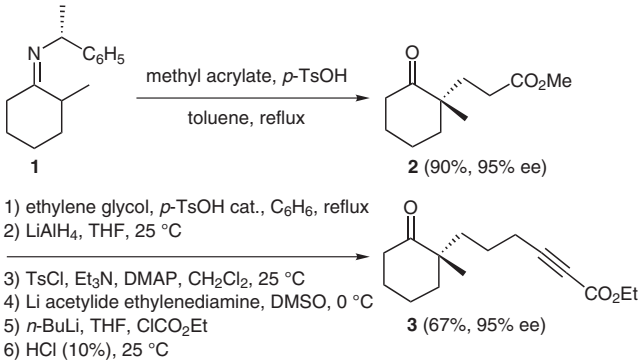
Abstract: Tetrabutylammonium fluoride (TBAF) reacts smoothly with optically active acetylenic ω-keto esters to afford optically active allenic esters (ee >95%) in high yield. After protection of the hydroxyl group, the addition of morpholine followed by an acidic hydrolysis, quantitatively led to optically active bicyclic α,β-unsaturated ketones (ee >95%). By using this methodology, the formal synthesis of an iphionane sesquiterpene was achieved.

Key words: alkynes, fluorine, domino reactions, nucleophilic addition, fused rings

Electrophilic optically active allenes (especially esters) are important building blocks for the total synthesis of bioactive compounds. However, synthetic routes for optically active allenic esters are rare.[1] Recently, we have developed a new cascade reaction that produces electrophilic allenic esters starting from acetylenic ω-keto esters.[2] To further extend the utility of our methodology, we present herein a new, multigram scale synthesis of optically active allenic esters so that the latter can be considered as appropriate synthons for further synthetic applications.

For that purpose, we had to develop a new reaction sequence because our former route was inefficient to get effectively optically active allenic esters. We started from the chiral imine **1** that was obtained by addition of (*R*)-(+)-methylbenzylamine to 2-methylcyclohexanone as previously described.[3] The Michael addition of methyl acrylate to **1** proceeded smoothly to afford compound **2**. Protection of the carbonyl group as a dioxolane, reduction with $LiAlH_4$, and subsequent addition of tosyl chloride afforded the tosyl derivative. Addition of the acetylide as an ethylenediamine complex led to the acetylenic derivative which was readily transformed into the desired acetylenic ω-keto ester **3** after addition of ethyl chloroformate to the corresponding acetylide and acidic deprotection of the dioxolane group (Scheme 1).

The next stage called for our TBAF reaction with the acetylenic ω-keto ester **3**. The reaction proceeded smoothly and the desired optically active allenic ester **4** was isolated

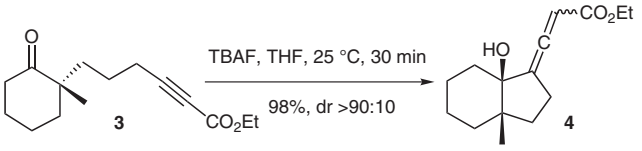


Scheme 1

in 98% yield (ee >95% for this determination, see below; dr = 90:10) (Scheme 2).

For further synthetic purposes, allene **4** had to be converted into the hydroxy ketone **6**. Indeed, the latter represents an important substructure of bioactive iphionane sesquiterpenes (Figure 1).[4]

Thus, an allenic ester can be transformed into the corresponding β-keto ester **5** by addition of an amine (for example morpholine) followed by hydrolysis of the corre-



Scheme 2

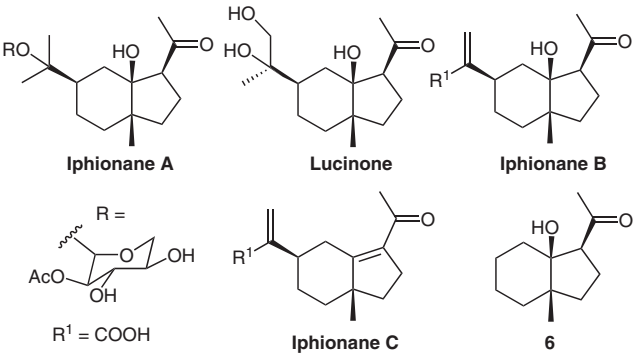


Figure 1 Bioactive iphionane sesquiterpenes

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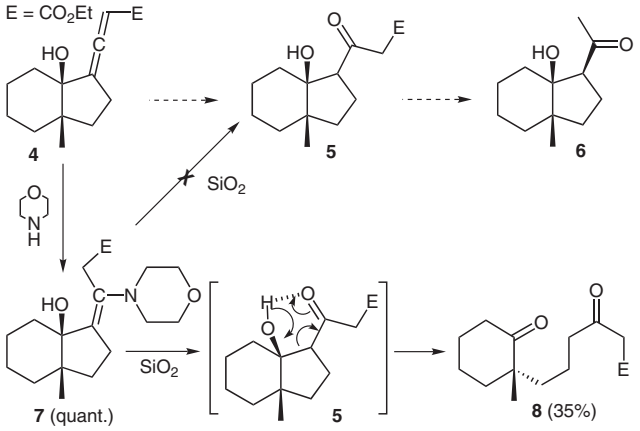
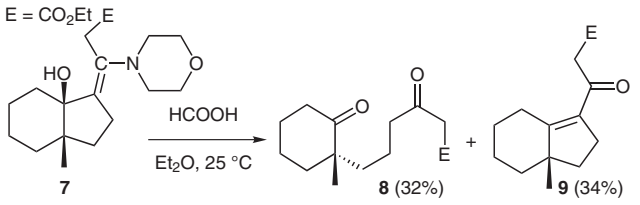
sponding enamine.[5] A saponification–decarboxylation reaction should then afford ketone **6**. When morpholine was added to **4**, the quantitative formation of enamine **7** was observed. Unfortunately, during the purification stage by silica gel column chromatography, the enamine **7** led to the corresponding 1,6-diketone **8**, which was isolated in 35% yield along with degradation products. The desired hydroxy β-keto ester **5** was not detected (Scheme 3).



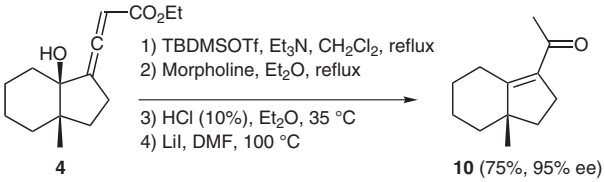
Scheme 3

On the other hand, treatment of the crude enamine **7** with formic acid afforded a mixture of two compounds: the 1,6-diketone **8** as above and the α,β-unsaturated β-keto ester **9** were isolated respectively in 34 and 32% yield. Once again, the formation of the hydroxy β-keto ester **5** was not observed (Scheme 4).



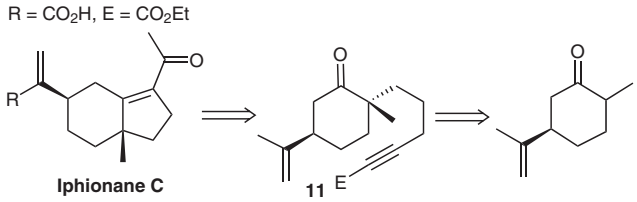
Scheme 4

Finally, after protection of the hydroxyl group as a *tert*-butyldimethylsilyl ether followed by addition of morpholine, acidic hydrolysis, and a saponification–decarboxylation sequence, the α,β-unsaturated ketone **10** was isolated in 75% overall yield with no trace of the hydroxy β-keto ester **5** (Scheme 5). The enantiomeric excess (ee) of ketone **10** was determined by chiral GC analysis and is in accord with the data recently reported in the literature.[6] Consequently, we can estimate that the ee of the allene derivative **4** is at least 95%. This is in good agreement not only with the value determined for ketone **10**, but also with the ee value (95% determined by chiral GC analysis) of the Michael adduct **2**. Thus, our new reaction sequence can readily afford optically active allenic esters in high yield and high ee. Moreover, it is possible to run our reaction sequence on a multigram scale.



Scheme 5

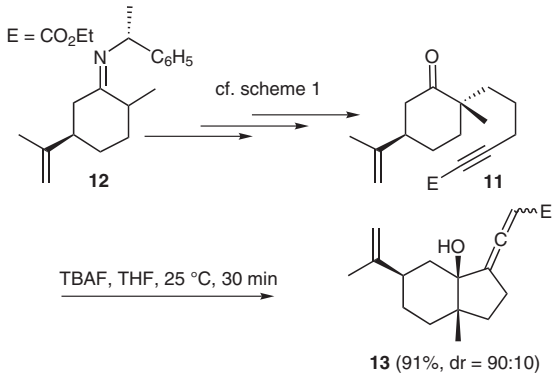
To further extend the utility of this methodology, we envisioned the enantioselective synthesis of iphionane C isolated from *Jasonia candicans*.[7] Based on our previous results, the latter could be prepared from the acetylenic ω-keto ester **11** which could result from (+)-dihydrocarvone, a readily available, optically active, starting material (Scheme 6).[8]



Scheme 6

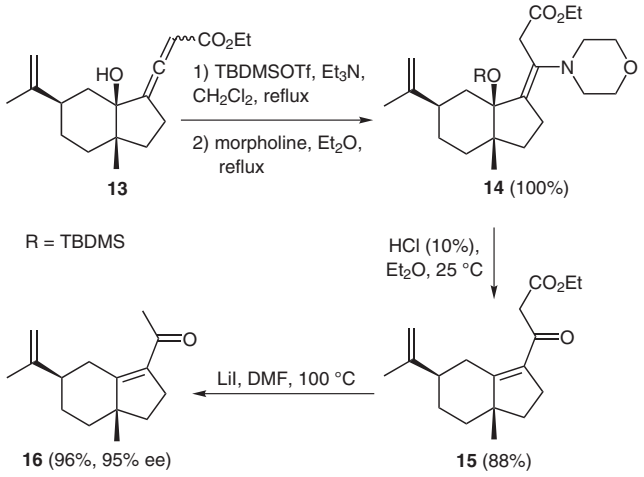
Indeed, the synthesis of the acetylenic ω-keto ester **11** was readily achieved starting from the chiral imine **12** which was prepared by reaction of (*R*)-(+)-methylbenzylamine with (+)-dihydrocarvone. The allenic ester **13** was obtained as a mixture of isomers (dr = 90:10) by using the route described in Scheme 1 (Scheme 7).

After protection of the hydroxyl group as a *tert*-butyldimethylsilyl ether, the addition of morpholine to the corresponding allenic ester led quantitatively to the enamine **14**. The latter was hydrolyzed under acidic conditions to give the β-keto ester **15** in 88% yield. This compound was readily transformed into the desired α,β-unsaturated ketone **15**, isolated in 96% yield; this compound being a potential precursor of iphionane C (Scheme 8). As before, we can estimate that compound **16** was obtained with 95%



Scheme 7

ee, since the reaction sequence is identical to that in described in Scheme 5.



Scheme 8

In summary, we presented here a new and efficient methodology for the synthesis of not only optically active polyfunctionalized allenic esters, but also of polyfunctionalized hexahydroindene fused rings. Further investigations of this chemistry are currently under way in our laboratory.

Melting points were measured on a Stuart Scientific melting point apparatus (SMP 3) and are uncorrected. Reactions were carried out under argon with magnetic stirring and degassed solvents. Et_2O and THF were distilled from Na/benzophenone. TLC was carried out on silica gel plates (Merck $60F_{254}$) and the spots were visualized under UV lamp (254 or 365 nm) and/or sprayed with a solution of vanillin (25 g) in EtOH–H_2SO_4 (98:2; 1 L) or with phosphomolybdic acid followed by heating on a hot plate. For column chromatography, silica gel (Merck, silica gel 60, 40–60 μm) was used. IR spectra were recorded in CCl_4 on a PerkinElmer IR-881 spectrophotometer. ^1H NMR spectra were recorded at 300 MHz (Bruker AC-300) and ^{13}C NMR spectra at 75 MHz (Bruker AC-300) using the signal of the residual nondeuterated solvent as internal reference. Microanalyses were performed at the Service Commun de Microanalyse, Institut de Chimie, Strasbourg. The optical rotations were measured on a PerkinElmer polarimeter Model 341. The enantiomeric excesses were measured on a GC-14B Shimadzu equipped with a BPN-β-cyclodextrin chiral column. The allene ratio was determined on a GC-Varian 3400 CX equipped with a Factor Four VF-5ms column (length: 60 m; internal diameter: 0.25 mm).

The acetylenic ω-keto esters **3** and **11** were prepared by the reactions outlined in Schemes 1 and 7.

Acetylenic ω-Keto Ester 3

Compound **3** was prepared according to literature procedures.[2a,2c]

Colorless oil; $[\alpha]_D^{20}$ –40.3 (c = 1.01, $CHCl_3$).

IR (CCl_4): 1712, 2239 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.05 (s, 3 H), 1.29 (t, J = 7.1 Hz, 3 H), 1.35–1.65 (m, 4 H), 1.66–1.90 (m, 6 H), 2.31 (t, J = 6.7 Hz, 2 H), 2.36 (t, J = 6.4 Hz, 2 H), 4.20 (q, J = 7.1 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.0, 19.2, 21.0, 22.2, 22.5, 27.4, 36.7, 38.7, 39.1, 48.3, 61.7, 73.5, 88.7, 153.7, 215.5.

Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 72.20; H, 9.09.

Acetylenic ω-Keto Ester 11

Compound **11** was prepared according to literature procedures.[2a,2c]

Colorless oil; $[\alpha]_D^{20}$ +37.1 (c = 0.98, $CHCl_3$).

IR (CCl_4): 1644, 1715, 2239 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.12 (s, 3 H), 1.28 (t, J = 7.1 Hz, 3 H), 1.45–1.70 (m, 6 H), 1.72 (s, 3 H), 1.73–1.90 (m, 2 H), 2.25–2.40 (m, 4 H), 2.49 (dd, J = 12.8, 14.8 Hz, 1 H), 4.19 (q, J = 7.1 Hz, 2 H), 4.73 (d, J = 16.8 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.0, 13.4, 20.7, 22.4, 23.1, 26.0, 36.4, 37.2, 43.2, 45.7, 47.3, 61.7, 73.3, 89.0, 110.0, 147.3, 153.8, 214.8.

Anal. Calcd for $C_{18}H_{26}O_3$: C, 74.45; H, 9.02. Found: C, 74.35; H, 9.19.

Allene 4

At 20 °C, to a solution of acetylenic ω-keto ester **3** (3.90 g, 15.6 mmol) in THF (75 mL) was added TBAF as a 1.0 M solution in THF (18.70 mL). After 30 min of gentle stirring at 20 °C, the mixture was quenched with a sat. aq NH_4Cl solution (20 mL), H_2O (3 × 20 mL) and then extracted with Et_2O (3 × 10 mL). The combined organic layers were washed with brine, dried ($MgSO_4$) and filtered before solvents were removed under reduced pressure (15 mm Hg/30 °C). The crude product was purified on a silica gel column (75 g SiO_2, EtOAc–hexane, 5:95) to afford compound **4** as a 9:1 mixture of isomers; yield: 3.824 g (98%). By additional chromatography on a silica gel column, it was not possible to get an analytical sample of each isomer. Nevertheless, we obtained an $[\alpha]_D^{20}$ value, but this value corresponded to a mixture of the two isomers. The IR and microanalysis were also performed on the mixture of the two isomers. The mixture of the two isomers was a white powder; mp 57–58 °C.

Allene 4a

$[\alpha]_D^{20}$ –112.3 (mixture of isomers, c = 1.01, $CHCl_3$).

IR (mixture of isomers, CCl_4): 1717, 1961, 3400, 3602 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.06 (s, 3 H), 1.26 (t, J = 7.1 Hz, 3 H), 1.30–1.90 (m, 11 H), 2.50–2.85 (m, 2 H), 4.17 (ABX_3, J_{AB} = 10.8, J_{BX} = 7.1, J_{AX} = 7.1 Hz, Δδ = 0.085 ppm, δ_A = 4.21, δ_B = 4.13, 2 H), 5.66 (t, J = 4.2 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.1, 18.1, 21.5, 23.2, 25.0, 32.4, 34.9, 36.0, 45.8, 60.6, 84.2, 90.9, 113.5, 166.1, 207.2.

Anal. Calcd for $C_{15}H_{22}O_3$ (mixture of isomers): C, 71.97; H, 8.86. Found: C, 72.00; H, 8.87.

Allene 4b

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.06 (s, 3 H), 1.26 (t, J = 7.1 Hz, 3 H), 1.30–1.90 (m, 11 H), 2.50–2.85 (m, 2 H), 4.17 (ABX_3, J_{AB} = 10.8, J_{BX} = 7.1, J_{AX} = 7.1 Hz, Δδ = 0.085 ppm, δ_A = 4.21, δ_B = 4.13, 2 H), 5.68 (t, J = 4.2 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.1, 19.2, 22.6, 23.6, 24.8, 31.9, 34.6, 35.5, 45.4, 60.8, 83.6, 91.0, 113.5, 166.1, 207.2.

Allene 13

Allene **13** was prepared starting from acetylenic ω-keto ester **11** (4.96 g, 17.2 mmol) and TBAF (1.0 M THF solution, 13.80 mL) by using the same procedure as for allene **4**. This reaction afforded allene **13** as a mixture of isomers in the ratio 9:1; yield: 4.535 g (91%). Even by additional chromatography on a silica gel column, it was not possible to obtain an analytical sample of each isomer. Nevertheless, we observed an $[\alpha]_D^{20}$ value, but this value corresponds to a

mixture of the two isomers. The IR and microanalysis was also performed on the mixture of the two isomers. The mixture of the two isomers was a white powder; mp 53–54 °C.

Allene 13a

$[\alpha]_D^{20}$ –152.2 (mixture of isomers, *c* = 1.00, $CHCl_3$).

IR (mixture of isomers, CCl_4): 1646, 1717, 1961, 3400, 3602 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.06 (t, *J* = 7.1 Hz, 3 H), 1.18 (s, 3 H), 1.30–1.70 (m, 7 H), 1.84 (s, 3 H), 1.95–2.10 (m, 2 H), 2.40–2.85 (m, 2 H), 3.55 (s, 1 H), 4.09 (qd, *J* = 0.9, 7.1 Hz, 2 H), 4.90–5.05 (m, 2 H), 5.85 (t, *J* = 4.2 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.8, 17.9, 20.5, 25.0, 26.7, 34.8, 36.5, 36.8, 41.9, 45.1, 60.2, 84.2, 90.6, 108.5, 113.5, 149.3, 165.1, 207.5.

Anal. Calcd for $C_{18}H_{26}O_3$ (mixture of isomers): C, 74.45; H, 9.02. Found: C, 74.35; H, 9.25.

Allene 13b

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.01 (t, *J* = 7.1 Hz, 3 H), 1.25 (s, 3 H), 1.30–1.70 (m, 7 H), 1.74 (s, 3 H), 2.10–2.25 (m, 2 H), 2.40–2.85 (m, 2 H), 3.55 (s, 1 H), 4.02 (qd, *J* = 0.9, 7.1 Hz, 2 H), 4.80–4.90 (m, 2 H), 5.83 (t, *J* = 4.2 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.7, 17.9, 20.5, 25.0, 26.7, 34.9, 36.7, 36.8, 43.1, 45.1, 60.7, 83.6, 90.2, 108.6, 114.9, 148.8, 166.9, 207.5.

Enamine 7

At 40 °C, to a solution of allene **4** (300 mg, 1.20 mmol) in Et_2O (50 mL), was added morpholine (418 mg, 4.80 mmol). After stirring for 3 d at 40 °C, the mixture was quenched with H_2O (20 mL) and then extracted with Et_2O (3 × 10 mL). The combined organic layers were washed with brine, dried ($MgSO_4$) and filtered before solvents were removed under reduced pressure (15 mm Hg/30 °C) leading to the crude enamine **7**, which was not purified further; yield: 405 mg (ca. 100%).

^1H NMR ($CDCl_3$, 300 MHz): δ = 0.88 (s, 3 H), 1.25 (t, *J* = 7.1 Hz, 3 H), 1.30–2.35 (m, 13 H), 2.57 (dt, *J* = 4.0, 3.3 Hz, 1 H), 3.40 (AB, J_{AB} = 15.5 Hz, δ_A = 3.77, δ_B = 3.03, 2 H), 3.66 (t, *J* = 4.5 Hz, 4 H), 4.13 (q, *J* = 7.1 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.0, 21.4, 21.6, 23.7, 24.9, 29.4, 31.2, 32.2, 33.6, 44.0, 49.6, 61.2, 67.4, 67.4, 79.7, 134.5, 143.9, 174.5.

Enamine 14

Enamine **14** was prepared starting from allene **13** (2.0, 4.97 mmol) and morpholine (1.730 g, 19.90 mmol) by using the same procedure as for enamine **7**; yield: 2.444 g (ca. 100%).

^1H NMR ($CDCl_3$, 300 MHz): δ = 0.00 (s, 3 H), 0.03 (s, 3 H), 0.83 (s, 9 H), 0.98 (s, 3 H), 1.15–1.23 (m, 3 H), 1.24 (t, *J* = 7.1 Hz, 3 H), 1.40–1.65 (m, 2 H), 1.67 (s, 3 H), 1.70–1.70 (m, 2 H), 1.95–2.15 (m, 2 H), 2.30–2.60 (m, 2 H), 2.79 (dt, *J* = 7.1, 4.6, 4 H), 3.34 (AB, J_{AB} = 17.1 Hz, δ_A = 3.51, δ_B = 3.17, 2 H), 3.65 (t, *J* = 4.8 Hz, 4 H), 4.10 (ABX_3, J_{AB} = 10.8, J_{AX} = 7.1, J_{BX} = 7.1 Hz, Δδ = 0.03, δ_A = 4.12, δ_B = 4.08, 2 H), 4.64 (d, *J* = 0.9 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = –2.1, –2.6, 14.1, 18.7, 19.0, 20.7, 25.9, 27.2, 27.8, 33.9, 35.6, 35.0, 37.6, 41.8, 48.2, 49.5, 60.6, 67.8, 85.2, 108.3, 135.5, 139.5, 149.7, 171.1.

Hydrolysis of Enamine 7 to 1,6-Diketone 8 and β-Keto Ester 9

At 20 °C, to a solution of enamine **7** (285 mg, 0.85 mmol), was added formic acid (3 mL). After 2 h gentle stirring at 20 °C, the mixture was hydrolyzed with a sat. aq Na_2CO_3 solution (20 mL), H_2O (3 × 20 mL) and then extracted with Et_2O (3 × 10 mL). The combined organic layers were washed with brine, dried ($MgSO_4$) and filtered before solvents were removed under reduced pressure (15 mm Hg/30 °C). The crude product was purified on a silica gel column (35 g SiO_2, EtOAc–hexane, 5:95) to afford compound **8** (73 mg, 32% yield) and compound **9** (72 mg, 34% yield).

1,6-Diketone 8

Colorless oil; $[\alpha]_D^{20}$ –27.9 (*c* = 0.98, $CHCl_3$).

IR (CCl_4): 1712, 1716 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.06 (s, 3 H), 1.27 (t, *J* = 7.1 Hz, 3 H), 1.35–1.90 (m, 10 H), 2.37 (t, *J* = 5.8 Hz, 2 H), 2.54 (t, *J* = 6.4 Hz, 2 H), 3.42 (s, 2 H), 4.19 (q, *J* = 7.1 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.1, 17.8, 21.0, 22.5, 27.4, 36.7, 38.7, 39.0, 43.1, 48.4, 49.3, 61.4, 167.2, 202.5, 215.8.

Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.14; H, 9.01. Found: C, 66.95; H, 9.12.

β-Keto Ester 9

Colorless oil; $[\alpha]_D^{20}$ +71.1 (*c* = 1.02, $CHCl_3$).

IR (CCl_4): 1644, 1682, 1746 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.06 (s, 3 H), 1.27 (t, *J* = 7.1 Hz, 3 H), 1.30–1.45 (m, 2 H), 1.50–1.65 (m, 4 H), 1.70–2.10 (m, 4 H), 2.30–2.70 (m, 2 H), 3.54 (AB, J_{AB} = 15.7 Hz, δ_A = 3.57, δ_B = 3.51, 2 H), 4.19 (q, *J* = 7.1 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.1, 21.9, 22.9, 25.3, 27.0, 30.2, 39.0, 41.5, 48.8, 49.3, 59.9, 130.9, 165.4, 171.7, 192.9.

Hydrolysis of Enamine 14 to β-Keto Ester 15

At 20 °C, to a solution of enamine **14** (845 mg, 1.72 mmol) in Et_2O (30 mL), was added 10% HCl (10 mL). After 2 h gentle stirring at 20 °C, the mixture was quenched with a sat. aq Na_2CO_3 solution (20 mL), H_2O (3 × 20 mL) and then extracted with Et_2O (3 × 10 mL). The combined organic layers were washed with brine, dried ($MgSO_4$) and filtered before solvents were removed under reduced pressure (15 mm Hg/30 °C). The crude product was purified on a silica gel column (65 g SiO_2, EtOAc–hexane, 5:95) to afford β-keto ester **15**; yield: 440 mg (88%); colorless oil; $[\alpha]_D^{20}$ +25.22 (*c* = 1.03, $CHCl_3$).

IR (CCl_4): 1645, 1644, 1683, 1746 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.08 (s, 3 H), 1.27 (t, *J* = 7.1 Hz, 3 H), 1.35–1.70 (m, 5 H), 1.73 (s, 3 H), 1.75–1.90 (m, 2 H), 1.91–2.05 (m, 2 H), 2.35–2.75 (m, 2 H), 3.54 (AB, J_{AB} = 16.0 Hz, δ_A = 3.57; δ_B = 3.52, 2 H), 4.19 (q, *J* = 7.1 Hz, 2 H), 4.70–4.80 (m, 2 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 14.1, 20.7, 22.9, 27.4, 30.2, 31.1, 38.7, 40.8, 46.1, 48.5, 49.3, 61.1, 109.1, 130.9, 149.0, 164.7, 171.5, 192.9.

Anal. Calcd for $C_{18}H_{26}O_3$: C, 74.45; H, 9.02. Found: C, 74.54; H, 9.20.

α,β-Unsaturated Ketone 16

To a solution of β-keto ester **15** (740 mg, 1.62 mmol) in DMF (20 mL), was added LiI (867 mg, 6.48 mmol). The mixture was stirred during 2 h at 100 °C. At 25 °C, the mixture was quenched with H_2O (5 mL) and then extracted with Et_2O (4 × 20 mL). The combined organic layers were washed with brine, dried ($MgSO_4$) and filtered before solvents were removed under reduced pressure (15 mm Hg/30 °C). The crude product was purified on a silica gel column (65 g SiO_2, EtOAc–hexane, 5:95) to afford **16**; yield: 340 mg (96%); colorless oil; $[\alpha]_D^{20}$ +29.35 (*c* = 0.59, $CHCl_3$,).

IR (CCl_4): 1657, 1682 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.08 (s, 3 H), 1.30–1.70 (m, 4 H), 1.75 (t, *J* = 0.93 Hz, 3 H), 1.76–2.00 (m, 4 H), 2.23 (s, 3 H), 2.50–2.75 (m, 2 H), 3.30–3.45 (m, 1 H), 4.70–4.80 (m, 2 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 20.7, 22.9, 27.5, 30.2, 30.6, 31.4, 38.6, 40.9, 46.2, 48.3, 109.0, 132.3, 149.3, 161.5, 199.2.

Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.33; H, 10.47.

α,β-Unsaturated Ketone 10

Same procedure for α,β-unsaturated ketone **10** was used starting from β-keto ester **9** (210 mg, 0.84 mmol) and LiI (450 mg, 3.36 mmol); yield: 138 mg (92%); colorless oil; $[\alpha]_D^{20}$ +81.6 (*c* = 3.10, hexane).

IR (CCl_4):1657, 1679 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.05 (s, 3 H), 1.15–1.45 (m, 3 H), 1.46–1.65 (m, 2 H), 1.66–1.90 (m, 3 H), 1.91–2.10 (m, 1 H), 2.21 (s, 3 H), 2.45–2.70 (m, 2 H), 3.30 (dt, *J* = 14.3, 3.01 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 22.0, 22.8, 25.2, 27.1, 30.5, 30.9, 38.9, 41.5, 48.6, 131.9, 162.2, 199.2.

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 81.01; H, 9.95.

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