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Gold catalysed cyclisation reactions of 1,6-diynes triggered by the addition of methanol

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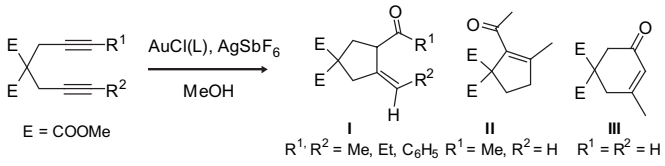
ABSTRACT

Further investigations on our recently discovered gold catalysed cyclisation reaction of 1,6-diynes are reported. By varying the steric and electronic nature of the alkyne substituents, the potentials and limitations of the new reaction have been identified.

1. Introduction

Gold catalysis of organic reactions has become a rapidly expanding field in very recent years.[1–3] Gold catalysts interact with π-systems to activate multiple carbon–carbon bonds for nucleophilic attack. Gold catalysed hydration reactions of alkynes are well known. Chabanas et al. reported the addition of alcohols to alkynes, catalysed by different gold(I)-catalysts in the presence of an acid as a cocatalyst.[4] Depending on the alkyne substrate acetals or enol ethers were formed. Tanaka et al. treated a number of alkynes in a methanol-water mixture with a $(PPh_3)AuCH_3/H^+$ catalytic system to form the respective ketones.[5] The application of NHC–gold catalysts for alkyne hydration reactions has recently been reported.[6] A gold catalysed cycloisomerisation–hydroalkoxylation reaction of homopropargylic alcohols has been demonstrated to form the respective cyclic acetals.[7] Alcohols have further been used in gold catalysed alkoxycyclisations of 1,6-enynes to trap cationic intermediates.[8,9]

We have previously reported a new gold catalysed cyclisation reaction of disubstituted 1,6-diynes[10], providing stereoselectively *Z*-cyclopentylidene derivatives (**I**) (Scheme 1). Mono- and di-terminal 1,6-diynes afforded α,β-unsaturated cyclopentene (**II**) and cyclohexenone (**III**) products. Plausible reaction mechanisms were proposed for the formation of the products, including initial alkyne activation by the gold complex, nucleophilic addition of methanol and subsequent cyclisation after final activation of the remaining alkyne-moiety.



Scheme 1. Cyclisation reactions of 1,6-diynes.

The previous study was carried out on Me-, Et- and phenyl-substituted diynes, as well as terminal alkynes. We hereby present the results from further studies on gold catalysed cyclisation reactions of 1,6-diynes, varying the steric and electronic nature of the alkyne substituents. Our results of the investigations in order to identify the potentials and limitations of the new reaction, including both gold–NHC and gold–phosphine catalysts, are discussed below.

2. Results and discussion

2.1. Preparation of 1,6-diyne substrates

The malonate based 1,6-diynes **3a**–**g** and **6a**–**b** were readily prepared by the procedures shown in Scheme 2. Unsymmetrically substituted diynes **3a**–**b** and **6a** were obtained by stepwise malonate alkylation with propargylbromides in 68–89% yield. The

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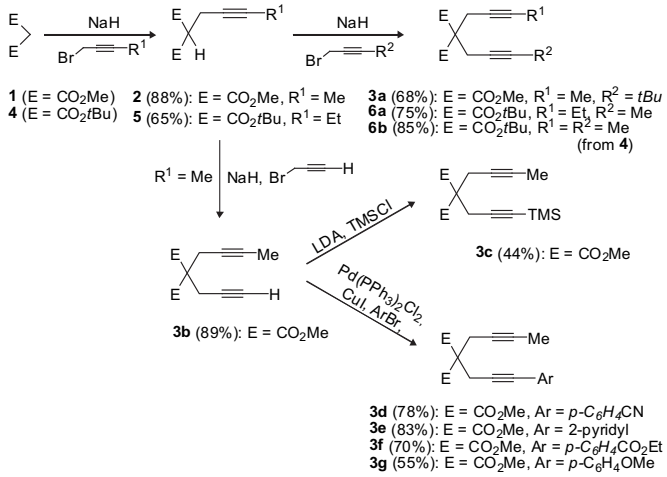
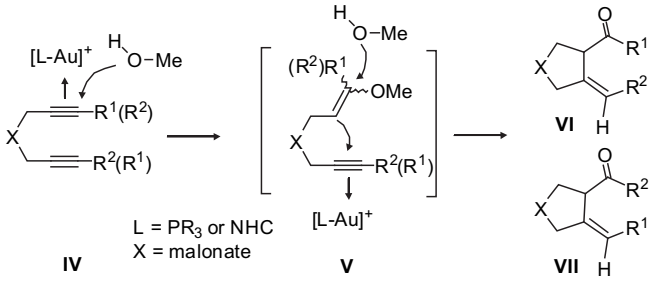
TMS–substituted diyne **3c** was prepared by silylation of the terminal alkyne **3b** via the corresponding lithium acetylide in 44% yield. Sonogashira cross-coupling of the terminal alkyne **3b** with the appropriate arylbromides gave access to the aryl substituted 1,6-diynes **3d**–**g** in 55–83% yield. The symmetrically substituted *t*-Bu-malonate **6b** was directly obtained by di-alkylation of **4** (85%).



Scheme 2. Preparation of malonate connected 1,6-diynes.

2.2. Gold catalysed cyclisation experiments

The present cyclisation reactions were performed in a similar manner to the previous studies.[10] The standard cyclisation experiments were carried out in methanol at room temperature in the presence of 5 mol % $AuCl(PEt_3)$ or AuCl(IMes). The counter ion exchange was achieved by the addition of 6 mol % $AgSbF_6$. The 5-*exo-dig* cyclisation of unsymmetrically disubstituted 1,6-diynes **IV** would give rise to two possible regioisomers, **VI** and **VII**, as shown in Scheme 3. The steric and electronic nature of the alkyne substituents R^1 and R^2 would affect the regioselectivity.



Scheme 3. Formation of two possible regioisomers.

Our previous results[10] showed that almost complete regioselectivity was obtained from a Me-/phenyl-substituted diyne **3h** (Table 1, entries 13 and 14), while an approximately 2:1 ratio was formed from the Me-/Et-diyne **3j** in the presence of $AuCl(PEt_3)$ (Table 1, entry 21). The presently studied Me-/*t*-Bu-diyne **3a** would potentially afford an improved regioselectivity as an initial activation of the less sterical hindered triple bond was expected. However, the cyclisation of **3a** failed, indicating that the bulky *t*-Bu-substituent prevents the cyclisation reaction (Table 1, entries 1 and 2). Thus, only the monohydration product **9a** was formed in 79% and 95% yield by applying the gold–phosphine or the gold–NHC catalyst, respectively. Such monohydration products were also identified in our previous studies.[10]

A possible cyclisation of the alternative sterically demanding TMS–alkyne substrate **3c** was attempted, as the Si–C bond length is in general larger than the equivalent C–C bond.[11] However, by gold–phosphine catalysis, desilylation took place and the terminal alkyne **3b** was formed, together with the monohydration product **9c** (Table 1, entry 3). In order to avoid desilylation, which is known to occur under hydrolytic conditions, the reaction was repeated at −20 °C. However, no conversion of **3c** took place after 1 h and rapid desilylation was observed upon warming to 0 °C. Correspondingly, no reaction took place in the presence of AuCl(IMes) at 0 °C, but when heated to room temperature, instant desilylation occurred (Table 1, entry 4). According to the literature[12], it is also conceivable, that the silver additive may catalyse the TMS-cleavage.

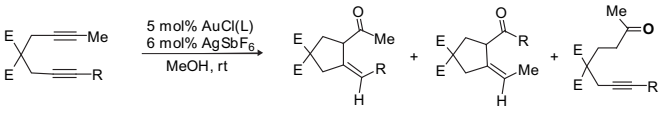
Modification of diyne substrates to include electron-withdrawing substituents was afforded by introducing the *p*-cyanophenyl-(**3d**) and 2-pyridyl-substituent (**3e**). However, no conversion of these 1,6-diyne substrates **3d** and **3e** was observed, even upon heating to 50 °C for several hours (Table 1, entries 5–8). The electron-withdrawing properties of such substituents might explain the missing ability of the electrophilic gold species to coordinate to the respective triple bond. However, this does not explain the lack of hydration of the methyl substituted alkyne-moiety to provide the expected ketone products **9d**–**e**.

To study whether a potential coordination of the nitrile or the pyridyl groups would deactivate the gold catalyst, supplementary cyclisation experiments with the dimethyl-substituted diyne **3i**, $AuCl(PEt_3)$ and $AgSbF_6$ were performed in the presence of one equivalent of benzonitrile or pyridine, respectively. According to GC, the reaction was not hampered by the addition of benzonitrile and full conversion of **3i** was observed within 3 h at room temperature. Further more, the commercial available, bulky gold–phosphine catalyst **13** (Scheme 4) shows high catalytic activity although acetonitrile is coordinated to the metal centre. On the other hand, the alkyne-moiety in **3d** may act as an electron donor, increasing the electron density of the aryl group and hence the ability of the nitrile group to coordinate to the gold species. On the contrary, the addition of 1 equiv of pyridine completely blocked any reaction and no conversion of **3i** was observed after 3 h. Thus, the presence of pyridine and pyridyl groups deactivates the gold catalytic system.

In order to avoid the unwanted deactivating effect of the cyano- and pyridyl-moieties on the gold catalyst, the electron-withdrawing alkyne substituent was replaced by a *p*-benzoate group (**3f**). The gold catalysed cyclisation of 1,6-diyne **3f** took place with total regioselectivity, since only the cyclic product **7f** was formed (Table 1, entries 9 and 10). Independent on the catalytic system, the monohydration product **9f** was isolated in 31% yield. This indicates a selective initial gold activation of the methyl substituted alkyne-moiety, which is supposed to have the highest electron density. The gold–NHC catalyst afforded stronger activation of the substrate **3f** towards cyclisation and increased the yield of product **7f** fourfold relative to the gold–phosphine catalysed reaction from 15% to 61% (Table 1, entries 9 and 10). No cyclisation reaction was observed when the monohydrated compound **9f** was treated under standard conditions with either $AuCl(PEt_3)$ or AuCl(IMes) in separate experiments.

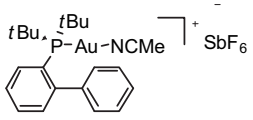
As expected, the opposite effect was observed by cyclisation of a diyne with an electron-donating *p*-anisole substituent (**3g**), since the formation of the other cyclic regioisomer **8g** was favoured in the presence of the phosphine gold complex (Table 1, entry 11; **7g**/**8g** 27:73). This indicates initial gold activation and subsequent attack of methanol at the anisole substituted triple bond, which is supposed to have a higher electron density. The gold–NHC catalyst was inactive towards the electron rich substrate **3g** and no reaction occurred in the presence of AuCl(IMes) and $AgSbF_6$ (Table 1, entry 12).

Table 1
Gold catalysed cyclisations of 1,6-diynes[a]



Entry	Substrate	R	(L)	*T* [h]	Temp.	Yield[b] [%]			Ratio[c]
						7a–g **10a–b**	**8a–g** **11a–b**	**9a–g** **12a–b**	7:8 10:11
1	**3a**	*t*-Bu	PEt_3	22	rt	—	—	95	—
2	**3a**	*t*-Bu	IMes	6.5	rt	—	—	79	—
3	**3c**	TMS	PEt_3	7.5	rt	—	—	24[d]	—
4	**3c**	TMS	IMes	2.5	0 °C to rt	—	—	[e]	—
5	**3d**	*p*-C_6H_4CN	PEt_3	22	rt to 50 °C	No reaction			—
6	**3d**	*p*-C_6H_4CN	IMes	15	rt to 50 °C	No reaction			—
7	**3e**	2-pyridyl	PEt_3	15	rt to 50 °C	No reaction			—
8	**3e**	2-pyridyl	IMes	15	rt to 50 °C	No reaction			—
9	**3f**	*p*-$C_6H_4CO_2Et$	PEt_3	23	rt	15	—	31	
10	**3f**	*p*-$C_6H_4CO_2Et$	IMes	24	rt	61	—	31	
11	**3g**	*p*-C_6H_4OMe	PEt_3	22	rt	57		—	27:73
12	**3g**	*p*-C_6H_4OMe	IMes	22	rt	No reaction			—
13	**3h**[f]	C_6H_5	PEt_3	3	rt	49		—	95:5
14	**3h**[f]	C_6H_5	IMes	3	rt	56		—	97:3
15	**6b**	Me	PEt_3	20	rt	54	—	—	—
16	**6b**	Me	IMes	6	rt	72	—	—	—
17	**3i**[f]	Me	PEt_3	3	rt	60	—	—	—
18	**3i**[f]	Me	IMes	3	rt	60	—	—	—
19	**6a**	Et	PEt_3	6	rt	53		—	62:38
20	**6a**	Et	IMes	22	rt	42		—	58:42
21	**3j**[f]	Et	PEt_3	5	rt	60		22	69:31
22	**3j**[f]	Et	IMes	3	rt	83		—	48:52

[a] Reactions were run at 250 mM in MeOH at room temperature with 5 mol % AuCl(L) and 6 mol % $AgSbF_6$.
[b] Isolated yield.
[c] Ratio of isolated cyclic products.
[d] Together with 27% of desilylated product **3b**.
[e] Not isolated.
[f] See Ref. 10.



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Scheme 4. Acetonitrile coordinated gold complex.

As both alkyne groups of diyne **3g** have sufficient reactivity to be activated by the gold catalyst and further involved in reactions, cyclisation was preferred. A single monohydration did not take place and no ketone hydration product **9g** was observed. Thus, ketone products were only formed from diynes with one bulky (**3a**, **3c**, **3j**) or one electron-withdrawing (**3f**) substituent.

To study the potential influence of the malonate ester moiety on both, reactivity and regioselectivity, gold catalysed cyclisation reactions of the di-*t*-Bu malonates **6a** and **6b** were carried out. The reaction of the symmetrically substituted di-*t*-Bu malonate **6b** provided comparable yields of the cyclopentylidene derivative **10b** compared to previous reactions[10] of the dimethyl malonate **3i** (Table 1, entries 15–18). The unsymmetrically substituted di-*t*-Bu malonate **6a** afforded lower yields than the analogous methyl malonate **3j**, indicating some lower reactivity of the sterically hindered *t*-Bu-malonate **6a** (Table 1, entries 19–22). However, the regioselectivity seemed to be controlled by the applied gold catalyst, since no explicit changes in the regioselectivity were observed for the sterically demanding substrate **6a** compared to the respective dimethyl malonate substrate **3j**. In both cases better regiocontrol was observed with the gold–phosphine complex, favouring the formation of cyclopentylidene derivatives **10a** and **7j**, respectively. In contrast, the more bulky gold–NHC catalyst afforded an approximately 1:1 mixture. The observed regioselectivity obtained with $AuCl(PEt_3)$ is still remarkable, since the sterical differences between a methyl and an ethyl group is small (Table 1, entries 19 and 21).

3. Conclusion

Further investigations on our recently discovered gold catalysed cyclisation reaction of 1,6-diynes are reported. By varying the steric and electronic nature of the alkyne substituents, some features of the new reaction have been identified. An electron-withdrawing *p*-benzoate diyne substituent (**3f**) afforded cyclisation with 100% regioselectivity (**7f**/**8f** 100:0) while an electron-donating *p*-anisole diyne substituent (**3g**) gave the opposite regioselectivity (**7g**/**8g** 27:73). Ketone hydration products were only formed from diynes with one bulky (**3a**, **3c**, **3j**) or one electron-withdrawing (**3f**) substituent. Some limitations of the reaction were observed, as the presence of a bulky *t*-Bu-substituent (**3a**) prevented the cyclisation reaction. Pyridine and pyridyl groups (**3e**) as well as the *p*-cyanophenyl-substituent (**3d**) totally deactivated the gold catalytic system, while TMS–alkyne substrates (**3c**) underwent desilylation.

4. Experimental

4.1. General

[AuCl(IMes)][13] was prepared according to literature. All reactions were monitored by GC and thin-layer chromatography

(TLC) using E. Merck silica gel 60 F_{254} (0.25-mm thickness). Flash chromatography was carried out using Merck silica gel 60 (0.040–0.063 mm). ^1H and ^{13}C NMR spectra were recorded using a Bruker Avance DPX 300 or 400 MHz spectrometer. Chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane (TMS) as internal standard. Coupling constants (J) are reported in hertz (Hz). The attributions of the chemical shifts were determined by means of COSY, HMQC and NOESY experiments. High resolution mass spectra (HRMS) were determined with an Agilent 6520 QTOF MS instrument equipped with a dual electrospray ion source. IR spectra were obtained with a Nicolet 20SXC FT-IR spectrometer by using a Smart Endurance reflexion cell.

4.1.1. 1-Bromo-4,4-dimethylpent-2-yne. To a solution of 3,3-dimethyl-1-butyne (1.07 g, 13.0 mmol) in dry diethyl ether (13 mL), *n*-BuLi (7.7 mL, 12.4 mmol, 1.6 M in hexane) was added dropwise over 15 min at −78 °C. The reaction mixture was kept at −78 °C for 15 min. The reaction was heated to −45 °C and stirring was continued for additional 45 min. After cooling to −78 °C, paraformaldehyde (469 mg, 15.6 mmol) was added as a solid. The cooling bath was removed and the mixture was stirred at room temperature for 3 h. Work-up was performed by the addition of a ammonium chloride solution (25 mL, satd aq) and subsequent extraction with EtOAc (3×25 mL). The combined organic layers were washed with brine (25 mL), dried (Na_2SO_4) and the solvent was removed under reduced pressure. Distillation afforded 4,4-dimethylpent-2-yn-1-ol (974 mg, 67%) as a colourless liquid (bp 51–52 °C/8 mbar). The obtained ^1H NMR spectrum was in accordance with the literature.[14] To a solution of the alcohol (203 mg, 1.81 mmol) in dry ether (1.25 mL) was added pyridine (12.5 mL) at −30 °C followed by the addition of PBr_3 (60 μL, 168 mg, 0.62 mmol) over 15 min. The solution was slowly heated to room temperature over 3 h and finally refluxed for 1 h. The reaction mixture was added dropwise to brine (10 mL) at 0 °C and the aqueous layer was extracted with diethyl ether (3×10 mL). The combined organic layers were washed with brine (10 mL), dried (Na_2SO_4) and evaporated to dryness to yield 1-bromo-4,4-dimethyl-2-pentyne as a colourless liquid (317 mg, 80%). The product was pure according to ^1H NMR spectroscopy and was used in the next step without further purification. δ_H (300 MHz, $CDCl_3$) 3.93 (2H, s, CH_2), 1.22 (9H, s, $C(CH_3)_3$).

*4.1.2. Dimethyl 2-(but-2-ynyl)malonate (**2**).* To an ice cooled suspension of NaH (407 mg, 17.0 mmol) in THF (35 mL), dimethyl malonate **19** (4.53 g, 34.3 mmol) was added dropwise over a period of 20 min. The mixture was stirred at 0 °C for 20 min and 1-bromo-2-butyne (1.47 g, 11.1 mmol) in THF (2 mL) was added dropwise over a period of 5 min. After removal of the ice bath, the mixture was stirred at room temperature for an additional 3 h. Water (50 mL) was added, the phases were separated and the aqueous layer was extracted with diethyl ether (3×50 mL). The combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (6% EtOAc/*n*-pentane) to yield **2** as a colourless oil (1.30 g, 63%). ^1H NMR spectrum was in accordance with the literature.[15]

*4.1.3. Dimethyl 2-(but-2-ynyl)-2-(4,4-dimethyl-pent-2-ynyl)malonate (**3a**)*[16]. Malonate **2** (195 mg, 1.06 mmol) was added dropwise to an ice cooled suspension of NaH (28.1 mg, 1.17 mmol) in THF (5 mL) followed by the addition of 1-bromo-4,4-dimethylpent-2-yne (195 mg, 1.11 mmol). The ice bath was removed, and the mixture was stirred at room temperature for 4 h. Water (10 mL) was added, and the aqueous layer was extracted with diethyl ether (3×20 mL). The combined organic layers were washed with brine (20 mL), dried (Na_2SO_4) and concentrated in vacuo. After column chromatography (6% EtOAc/*n*-pentane) **3a** was obtained as a white solid (197 mg, 68%). Mp 53–55 °C; R_f (6% EtOAc/*n*-pentane) 0.24; ν_{max} (neat) 2966, 1733, 1434 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 3.74 (6H, s, 2×O*Me*), 2.89 (4H, m, 2×CH_2), 1.75 (3H, t, *J* 2.6 Hz, CH_3), 1.17 (9H, s, *t-Bu*); δ_C (100 MHz, $CDCl_3$) 169.7 (2×*C*O), 92.3 (C_{alkyne}), 78.8 (C_{alkyne}), 73.2 (C_{alkyne}), 72.7 (C_{alkyne}), 57.4 ($C(CO_2Me)_2$), 52.7 (2×O*Me*), 31.1 ($C(CH_3)_3$), 27.3 (C$(CH_3)_3$), 22.9 (2×CH_2), 3.5 (CH_3); *m*/*z* (ESI) 279 (MH^+); HRMS (ESI): MNa^+, found 301.1410. $C_{16}H_{22}NaO_4$ requires 301.1410.

*4.1.4. 2-(But-2-ynyl)-2-(prop-2-ynyl)malonate (**3b**).* The title compound **3b** was prepared from **2** (1.21 g, 6.57 mmol), NaH (174 mg, 7.25 mmol) in THF (35 mL) and 3-bromo-1-propyne (1.09 g, 7.33 mmol, 80% in toluene) as described above for **3a**. Purification by column chromatography (9% EtOAc/*n*-pentane) yielded **3b** (1.30 g, 89%) as a white solid. Mp 65–66 °C (lit.[17] 63–64 °C).

*4.1.5. Dimethyl (2-but-2-ynyl)-2-(3-trimethylsilanyl-prop-2-ynyl) malonate (**3c**).* To an ice cold solution of *i*-Pr_2NH (142 mg, 198 μL, 1.41 mmol) in THF (4.5 mL) was added *n*-BuLi (879 μL, 1.41 mmol, 1.6 M in hexane). After 30 min, the reaction mixture was cooled to −78 °C and a solution of **3b** (252 mg, 1.13 mmol) was added. The orange solution was stirred for 1 h at −78 °C and TMSCl (183 mg, 132 μL, 1.69 mmol,) was added. After stirring for additional 4 h, H_2O (20 mL) was added and the aqueous layer was extracted with diethyl ether (3×40 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed under reduced pressure. The residue was purified by column chromatography (4.5% EtOAc/*n*-pentane to 6% EtOAc/*n*-pentane) to provide **3c** (147 mg, 44%) as a colourless oil. The ^1H NMR data were in accordance with the literature.[18]

*4.1.6. Dimethyl 2-(but-2-ynyl)-2-(3-(4-cyanophenyl)prop-2-ynyl) malonate (**3d**).* CuI (17 mg, 0.090 mmol), $Pd(PPh_3)_2Cl_2$ (32 mg, 0.045 mmol) and 4-bromobenzonitrile (213 mg, 1.17 mmol) were dissolved in a mixture of THF (1.25 mL) and *i*-Pr_2NH (2.5 mL). After stirring for 15 min, **3b** (200 mg, 0.90 mmol) in THF (1.25 mL) was added and the reaction mixture was stirred for additional 4 h at room temperature. The mixture was diluted with EtOAc (50 mL), filtered and the solvent was removed under reduced pressure. Purification by column chromatography (14% EtOAc/*n*-pentane) yielded **3d** (225 mg, 78%) as an orange solid. Mp 92–93 °C; R_f (50% EtOAc/*n*-pentane) 0.55; ν_{max} (neat) 2228, 1736, 1604 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.57 (2H, d, *J* 8.7 Hz, $H_{arom.}$), 7.44 (2H, d, *J* 8.7 Hz, $H_{arom.}$), 3.78 (6H, s, 2×O*Me*), 3.22 (2H, s, CH_2), 2.96 (2H, q, *J* 2.6 Hz, CH_2), 1.77 (3H, t, *J* 2.6 Hz, CH_3); δ_C (100 MHz, $CDCl_3$) 169.3 (2×*C*O), 132.2 ($C_{arom.}$), 131.9 (2×$CH_{arom.}$), 128.0 (2×$CH_{arom.}$), 118.4 (*C*N), 111.4 ($C_{arom.}$), 89.2 (C_{alkyne}), 82.2 (C_{alkyne}), 79.5 (C_{alkyne}), 72.7 (C_{alkyne}), 56.9 ($C(CO_2Me)_2$), 53.1 (2×O*Me*), 23.7 (CH_2), 23.3 (CH_2), 3.5 (CH_3); *m*/*z* (ESI) 324 (MH^+); HRMS (ESI): MH^+, found 324.1231. $C_{19}H_{18}NO_4$ requires 324.1230.

*4.1.7. Dimethyl 2-(but-2-ynyl)-2-(3-(pyridin-2-yl)prop-2-ynyl)malonate (**3e**).* The title compound **3e** was prepared from **3b** (300 mg, 1.35 mmol) and 2-bromopyridine (277 mg, 1.75 mmol), as described above for **3d**. Purification by column chromatography (50% EtOAc/*n*-pentane) yielded **3e** (337 mg, 83%) as a dark orange oil. R_f (50% EtOAc/*n*-pentane) 0.38; ν_{max} (neat) 1736, 1581, 1464 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.54 (1H, ddd, *J* 4.9, 1.7, 1.0 Hz, $H_{pyr.}$), 7.61 (1H, td, *J* 7.7, 1.7 Hz, $H_{pyr.}$), 7.35 (1H, dt, *J* 7.7, 1.0 Hz, $H_{pyr.}$), 7.20 (1H, ddd, *J* 7.7, 4.9, 1.0 Hz, H_{pyr}), 3.78 (6H, s, 2×O*Me*), 3.24 (2H, s, CH_2), 3.00 (2H, q, *J* 2.6 Hz, CH_2), 1.76 (3H, t, *J* 2.6 Hz, CH_3); δ_C (100 MHz, $CDCl_3$) 169.3 (2×*C*O), 149.8 ($CH_{pyr.}$), 143.1 ($C_{pyr.}$), 135.9 ($CH_{pyr.}$), 127.2 ($CH_{pyr.}$), 122.6 (CH_{pyr}), 84.5 (C_{alkyne}), 83.1 (C_{alkyne}), 79.4 (C_{alkyne}), 72.8 (C_{alkyne}), 56.9 ($C(CO_2Me)_2$), 53.0 (2×O*Me*), 23.4 (CH_2), 23.2 (CH_2), 3.4

(CH_3); *m*/*z* (ESI) 322 (MNa^+), 300 (MH^+); HRMS (ESI): MH^+, found 300.1237. $C_{17}H_{18}NO_4$ requires 300.1230.

*4.1.8. Dimethyl 2-(but-2-ynyl)-2-(3-(4-(ethoxycarbonyl)-phenyl) prop-2-ynyl) malonate (**3f**).* The title compound **3f** was prepared from **3b** (300 mg, 1.35 mmol) and ethyl 4-bromobenzoate (401 mg, 1.75 mmol) as described above for **3d**, except that *i*-Pr_2NH was replaced by NEt_3 (3.7 mL). The crude product was purified by column chromatography (20% EtOAc/*n*-pentane) to give the desired product **3f** (349 mg, 70%) as an orange solid. Mp 90–91 °C; R_f (20% EtOAc/*n*-pentane) 0.35; ν_{max} (neat) 1735, 1716, 1607 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.95 (2H, d, *J* 8.2 Hz, H_{arom}), 7.41 (2H, d, *J* 8.2 Hz, $H_{arom.}$), 4.37 (2H, q, *J* 7.2 Hz, CH_2CH_3), 3.78 (6H, s, 2×O*Me*), 3.21 (2H, s, CH_2), 2.98 (2H, q, *J* 2.5 Hz, CH_2), 1.77 (3H, t, *J* 2.5 Hz, CH_3), 1.39 (3H, t, *J* 7.2 Hz, CH_2CH_3); δ_C (100 MHz, $CDCl_3$) 169.4 (2×*C*O), 166.0 (*C*O), 131.5 (2×$CH_{arom.}$), 129.7 ($C_{arom.}$), 129.3 (2×$CH_{arom.}$), 127.6 ($CH_{arom.}$), 87.3 (C_{alkyne}), 83.0 (C_{alkyne}), 79.3 (C_{alkyne}), 72.8 (C_{alkyne}), 61.0 (OCH_2CH_3), 57.0 ($C(CO_2Me)_2$), 53.0 (2×O*Me*), 23.7 (CH_2), 23.2 (CH_2), 14.2 (OCH_2CH_3), 3.5 (CH_3); *m*/*z* (ESI) 393 (MNa^+), 371 (MH^+); HRMS (ESI): MH^+, found 371.1491. $C_{21}H_{23}O_6$ requires 371.1489.

*4.1.9. Dimethyl 2-(but-2-ynyl)-2- (3-(4-methoxyphenyl)prop-2-ynyl) malonate (**3g**).* The title compound **3g** was prepared from **3b** (250 mg, 1.13 mmol) and 1-bromo-4-methoxybenzene (274 mg, 1.46 mmol) as described above for **3d**. In this reaction DMF (3 mL) and NEt_3 (3 mL) were used as solvent and co-solvent, respectively, and the reaction mixture was stirred at 80 °C for 17 h. After purification by column chromatography (14% EtOAc/*n*-pentane) **3g** (203 mg, 55%) was obtained as a red-orange oil. R_f (20% EtOAc/*n*-hexane) 0.27; ν_{max} (neat) 2954, 1737, 1606 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.29 (2H, d, *J* 8.8 Hz, $H_{arom.}$), 6.79 (2H, d, *J* 8.8 Hz, $H_{arom.}$), 3.78 (3H, s, O*Me*), 3.76 (6H, s, 2×CO_2Me), 3.16 (2H, s, CH_2), 2.98 (2H, q, *J* 2.6 Hz, CH_2), 1.76 (3H, t, *J* 2.6 Hz, CH_3); δ_C (100 MHz, $CDCl_3$) 169.6 (2×*C*O), 159.3 ($C_{arom.}$), 133.0 (2×$CH_{arom.}$), 115.2 ($C_{arom.}$), 113.8 (2×$CH_{arom.}$), 83.4 (C_{alkyne}), 82.4 (C_{alkyne}), 79.1 (C_{alkyne}), 73.0 (C_{alkyne}), 57.2 ($C(CO_2Me)_2$), 55.2 (O*Me*), 52.9 (2×CO_2CH_3), 23.6 (CH_2), 23.1 (CH_2), 3.5 (CH_3); HRMS (ESI): MH^+, found 329.1388. $C_{19}H_{21}O_5$ requires 329.1384.

*4.1.10. Di-tert-butyl 2-(pent-2-ynyl)malonate (**5**).* To an ice cold suspension of NaH (147 mg, 6.12 mmol) in THF (10 mL) was added di-*tert*-butylmalonate (1.32 g, 1.37 mL, 6.12 mmol). After 1 h 1-bromo-2-pentyne (300 mg, 209 μL, 2.04 mmol) in THF (2 mL) was added. The cooling bath was removed and the resulting suspension was stirred for 23 h at room temperature. After the addition of H_2O (40 mL), the aqueous layer was extracted with EtOAc (3×50 mL). The combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and evaporated to dryness. The residue was purified by column chromatography (50% EtOAc/*n*-hexane) and subsequent kugelrohr distillation (0.3 mbar; 65 °C) to yield **5** (376 mg, 65%) as a colourless oil. R_f (20% EtOAc/*n*-hexane) 0.55; ν_{max} (neat) 2978, 1727, 1136 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 3.30 (1H, t, *J* 7.8 Hz, C*H*), 2.62 (2H, d, *J* 7.8 Hz, CH_2), 2.12 (2H, q, *J* 7.5 Hz, CH_2CH_3), 1.46 (18H, s, *t-Bu*), 1.08 (3H, t, *J* 7.5 Hz, CH_3); δ_C (100 MHz, $CDCl_3$) 167.6 (2×*C*O), 83.4 (2×$C(CH_3)_3$), 81.6 (C_{alkyne}), 75.3 (C_{alkyne}), 53.5 (*C*H), 27.8 (2×C$(CH_3)_3$), 22.7 (CH_2), 18.6 (CH_2), 14.0 (CH_2CH_3), 12.3 (CH_2CH_3); HRMS (ESI): MNa^+, found 305.1723. $C_{16}H_{26}NaO_4$ requires 305.1727.

*4.1.11. Di-tert-butyl 2-(but-2-ynyl)-2-(pent-2-ynyl)malonate (**6a**).* To an ice cold suspension of NaH (30.4 mg, 1.27 mmol) in THF (7 mL) was added **5** (300 mg, 1.06 mmol) in THF (2 mL). After 10 min 1-bromo-2-butyne (155.4 mg, 102 μL, 1.17 mmol) was added and stirring was continued for 4 h. After the addition of H_2O (10 mL) the aqueous layer was extracted with EtOAc (3×25 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (6.5% EtOAc/*n*-hexane) to yield **6a** (269 mg, 75%) as a colourless solid. Mp 66 °C; R_f (6.5% EtOAc/*n*-hexane) 0.30; ν_{max} (neat) 2976, 2932, 1729 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 2.76–2.83 (4H, m, CH_2), 2.12 (2H, qt, *J* 7.5, 2.4 Hz, CH_2CH_3), 1.74 (3H, t, *J* 2.6 Hz, CH_3), 1.45 (18H, s, *t-Bu*), 1.07 (3H, t, *J* 7.5 Hz, CH_2CH_3); δ_C (100 MHz, $CDCl_3$) 168.4 (2×*C*O), 84.5 (C_{alkyne}), 81.4 (2×$C(CH_3)_3$), 78.3 (C_{alkyne}), 74.0 (C_{alkyne}), 73.8 (C_{alkyne}), 57.7 ($C(CO_2t$-$Bu)_2$), 27.7 (2×$C(CH_3)_3$), 22.8 (CH_2), 22.6 (CH_2), 14.0 (CH_2CH_3), 12.3 (CH_2CH_3), 3.6 (CH_3); HRMS (ESI): MNa^+, found 357.2036. $C_{20}H_{30}NaO_4$ requires 357.2036.

*4.1.12. Di-tert-butyl 2,2-di(but-2-ynyl)malonate (**6b**).* To an ice cold suspension of NaH (48.8 mg, 2.03 mmol) in dry THF (4.5 mL) was subsequently added di-*tert*-butylmalonate (200 mg, 207 μL, 0.92 mmol) and 1-bromo-2-butyne (271 mg, 178 μL, 2.03 mmol) in THF (4.5 mL). After the cooling bath was removed the reaction mixture was stirred for 3 h at room temperature. H_2O (25 mL) was added and the aqueous layer was extracted with EtOAc (3×10 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed under reduced pressure. The residue was purified by column chromatography (9% EtOAc/*n*-hexane) to yield **6b** (252 mg, 85%) as a colourless solid. Mp 82 °C; R_f (20% EtOAc/*n*-hexane) 0.61; ν_{max} (neat) 2980, 1750, 1722 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 2.78 (4H, q, *J* 2.4 Hz, CH_2), 1.73 (6H, t, *J* 2.4 Hz, CH_3), 1.45 (18H, s, *t-Bu*); δ_C (100 MHz, $CDCl_3$) 168.5 (2×*C*O), 81.6 (2×$C(CH_3)_3$), 78.4 (2×C_{alkyne}), 73.8 (2×C_{alkyne}), 57.8 ($C(CO_2t$-$Bu)_2$), 27.8 (2×$C(CH_3)_3$), 22.7 (CH_2), 3.44 (CH_3); HRMS (ESI): MNa^+, found 343.1876. $C_{19}H_{28}NaO_4$ requires 343.1880.

4.2. General procedure for cyclisation reactions

In a typical experiment AuCl(L) (5 mol %), AgX (6 mol %) and the 1,6-diyne substrate (50 mg) were suspended in methanol (*c*=250 mM) and stirred at room temperature. The reaction was carefully monitored by GC, and work-up was performed when full conversion was achieved or after 24 h. The reaction mixture was added dropwise to HCl (5 mL, 1 M) and the aqueous layer was extracted with EtOAc (3×20 mL). The combined organic layers were washed with brine (15 mL), dried (Na_2SO_4) and concentrated in vacuo. The crude mixture was purified by column chromatography.

*4.2.1. Dimethyl 2-(4,4-dimethylpent-2-ynyl)-2-(3-oxobutyl)malonate (**9a**).* The reaction of **3a** was performed as described in the general procedure above with AuCl(PEt_3) and $AgSbF_6$ for 22 h. Purification (14% EtOAc/*n*-heptane) yielded **9a** (95%) as a colourless oil. R_f (50% EtOAc/*n*-pentane) 0.45; ν_{max} (neat) 2967, 1733, 1436 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 3.69 (6H, s, O*Me*), 2.71 (2H, s, CH_2), 2.46 (2H, t, *J* 7.1 Hz, CH_2), 2.26 (2H, t, *J* 7.1 Hz, CH_2), 2.12 (3H, s, CH_3), 1.13 (9H, s, *t-Bu*); δ_C (100 MHz, $CDCl_3$) 207.1 (*C*O), 170.6 (2×COOMe), 92.6 (C_{alkyne}), 72.5 (C_{alkyne}), 56.6 ($C(CO_2R)_2$), 52.5 (2×O*Me*), 38.6 (CH_2), 31.0 ($C(CH_3)_3$), 29.7 (CH_3), 27.3 (C$(CH_3)_3$), 26.5 (CH_2), 24.0 (CH_2); *m*/*z* (ESI) 319 (MNa^+), 297 (MH^+); HRMS (ESI): MH^+, found 297.1696. $C_{16}H_{25}O_5$ requires 297.1697.

*4.2.2. Dimethyl 2-(but-2-ynyl)-2-(prop-2-ynyl)malonate (**3b**) and dimethyl 2-(but-2-ynyl)-2-(2-oxopropyl)malonate (**9c**).* The reaction was performed according to the general procedure above from **3c** with AuCl(PEt_3) and $AgSbF_6$ for 7.5 h. Column chromatography (20% EtOAc/*n*-hexane) provided **3b** (27%) and **9c** (24%) both as colourless oils. The ^1H NMR spectra of **3b** are reported previously[4] and the ^1H NMR spectra of **9c** were in accordance with the literature.[10]

*4.2.3. (Z)-Dimethyl 3-acetyl-4-(1-(4-(ethoxycarbonyl)-phenyl)ethylidene)cyclopentane-1,1-dicarboxylate (**7f**) and dimethyl 2-(3-(4-(ethoxycarbonyl)phenyl)prop-2-ynyl)-2-(3-oxobutyl)malonate*

(***9f***). The reaction was performed according to the general procedure above from **3f** with AuCl(IMes) and $AgSbF_6$ for 24 h. Column chromatography (16% EtOAc/*n*-hexane) yielded **7f** (61%) and **9f** (31%), both as colourless oils. **7f**: R_f (50% EtOAc/*n*-hexane) 0.42; ν_{max} (neat) 2955, 1733, 1712, 1606 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.97 (2H, d, *J* 8.5 Hz, $H_{arom.}$), 7.21 (2H, d, *J* 8.5 Hz, $H_{arom.}$), 6.60 (1H, s, =C*H*), 4.36 (2H, q, *J* 7.2 Hz, OCH_2CH_3), 3.97–4.02 (1H, m, (CO)C*H*), 3.76 (3H, s, O*Me*), 3.75 (3H, s, O*Me*), 3.29 (1H, dt, *J* 16.6, 2.5 Hz, =CCH_aH_b), 3.13 (1H, d, *J* 16.6 Hz, =CCH_aH_b), 2.80 (1H, dd, *J* 13.5, 2.0 Hz, CHCH_aH_b), 2.45 (1H, dd, *J* 13.5, 6.8 Hz, CHCH_aH_b), 2.00 (3H, s, (CO)CH_3), 1.38 (3H, t, *J* 7.2 Hz, OCH_2CH_3); δ_C (100 MHz, $CDCl_3$) 206.9 (*C*O), 171.4 (*C*OOMe), 171.1 (*C*OOMe), 166.2 (*C*OOEt), 141.4 (*C*=CH and $C_{arom.}$), 129.8 (2×$CH_{arom.}$), 128.9 ($C_{arom.}$), 127.8 (2×$CH_{arom.}$), 125.5 (C=CH), 61.0 (OCH_2CH_3), 58.2 (*C*$(CO_2Me)_2$), 54.1 ((CO)CH), 53.1 (2×O*Me*), 43.4 (=*C*CH_2), 37.5 (CH*C*H_2), 27.8 ((CO)*C*H_3), 14.3 (OCH_2CH_3); HRMS (ESI): MH^+, found 389.1598. $C_{21}H_{25}O_7$ requires 389.1595. **9f**: R_f (50% EtOAc/*n*-hexane) 0.35; ν_{max} (neat) 2962, 1715, 1606 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.95 (2H, d, *J* 8.6 Hz, $H_{arom.}$), 7.40 (2H, d, *J* 8.6 Hz, $H_{arom.}$), 4.37 (2H, q, *J* 7.1 Hz, OCH_2CH_3), 3.76 (6H, s, 2×O*Me*), 3.06 (2H, s, alkyne-CH_2), 2.55 (2H, t, *J* 8.1 Hz, (CO)CH_2), 2.39 (2H, t, *J* 8.1 Hz, (CO)CH_2CH_2), 2.15 (3H, s, (CO)CH_3), 1.39 (3H, t, *J* 7.1 Hz, OCH_2CH_3); δ_C (100 MHz, $CDCl_3$) 206.9 (*C*O), 170.5 (2×*C*OOMe), 166.0 (*C*OOEt), 131.5 (2×$CH_{arom.}$), 129.8 ($C_{arom.}$), 129.4 (2×$CH_{arom.}$), 127.5 ($C_{arom.}$), 87.0 (C_{alkyne}), 83.3 (C_{alkyne}), 61.1 (OCH_2CH_3), 56.4 (*C*$(CO_2Me)_2$), 52.9 (2×O*Me*), 38.6 (CH_2), 29.9 (*C*H_3), 26.7 (*C*H_2), 24.9 (CH_2), 14.3 (OCH_2CH_3); *m*/*z* (ESI) 411 (MNa^+), 389 (MH^+); HRMS (ESI): MH^+, found 389.1603. $C_{21}H_{25}O_7$ requires 389.1595.

*4.2.4. (Z)-Dimethyl 3-acetyl-4-(4-methoxybenzylidene)-cyclopentane-1,1-dicarboxylate (**7g**) and (Z)-dimethyl 3-ethylidene-4-(4-methoxyphenyl)cyclopentane-1,1-dicarboxylate (**8g**).* The reaction was performed according to the general procedure above from **3g** with AuCl(PEt_3) and $AgSbF_6$ for 22 h. Column chromatography (14% EtOAc/*n*-hexane) yielded a mixture of **7g** and **8g** (57%, **7g**/**8g**=27:73) as a colourless oil. Compound **7g**: R_f (50% EtOAc/*n*-pentane) 0.35; δ_H (300 MHz, $CDCl_3$) 7.09 (2H, d, *J* 8.7 Hz, $H_{arom.}$), 6.84 (2H, d, *J* 8.7 Hz, $H_{arom.}$), 6.51 (1H, s, =C*H*), 3.92–3.98 (1H, m, (CO)C*H*), 3.79 (3H, s, O*Me*), 3.76 (3H, s, COO*Me*), 3.74 (3H, s, COO*Me*), 3.26 (1H, dt, *J* 16.1, 2.5 Hz, =CCH_aH_b), 3.09 (1H, d, *J* 16.1 Hz, =CCH_aH_b), 2.80 (1H, ddd, *J* 13.6, 9.0, 1.3 Hz, CHCH_aH_b), 2.40 (1H, dd, *J* 13.6, 7.2 Hz, CHCH_aH_b), 2.01 (3H, s, (CO)CH_3). **8g**: R_f (% EtOAc/*n*-pentane) 0.33; δ_H (300 MHz, $CDCl_3$) 8.00 (2H, d, *J* 8.9 Hz, $H_{arom.}$), 6.96 (2H, d, *J* 8.9 Hz, $H_{arom.}$), 5.57 (1H, q, *J* 6.7 Hz, =C*H*), 4.52 (1H, dm, *J* 8.6 Hz, (CO)C*H*), 3.88 (3H, s, O*Me*), 3.76 (3H, s, COO*Me*), 3.70 (3H, s, COO*Me*), 3.18 (1H, dq, *J* 15.5, 2.8 Hz, =CCH_aH_b), 3.00–2.89 (2H, m, CHCH_aH_b and =CCH_aH_b), 2.22 (1H, dd, *J* 13.6, 8.6 Hz, CHCH_aH_b), 1.39 (3H, dm, *J* 6.7 Hz, CH_3); HRMS (ESI): MH^+, found 347.1485. $C_{19}H_{23}O_6$ requires 347.1489.

*4.2.5. (Z)-Di-tert-butyl-3-acetyl-4-propylidenecyclopentane-1,1-dicarboxylate (**10a**) and (Z)-di-tert-butyl-3-ethylidene-4-propionylcyclopentane-1,1-dicarboxylate (**11a**).* The reaction of **6a** was performed as described in the general procedure above with AuCl(PEt_3) and $AgSbF_6$ for 6 h. Column chromatography (2.5% EtOAc/toluene) provided a mixture of **10a** and **11a** (53%, **10a**/**11a**=62:38) as a colourless oil. Compound **10a**: R_f (20% EtOAc/*n*-pentane) 0.48; δ_H (300 MHz, $CDCl_3$) 5.43 (1H, t, *J* 7.6H, =C*H*), 3.59 (1H, dd, *J* 9.0, 7.6 Hz, (CO)C*H*), 2.91 (1H, dm, *J* 15.4 Hz, =CCH_aH_b), 2.72 (1H, d, *J* 15.4 Hz, =CCH_aH_b), 2.65 (1H, ddd, *J* 13.4, 9.0, 1.8 Hz, CHCH_aH_b), 2.17 (1H, dd, *J* 13.4, 7.6 Hz, CHCH_aH_b), 2.15 (3H, s, (CO)CH_3), 1.91 (2H, m, CH_2CH_3), 1.44 (9H, s, *t-Bu*), 1.42 (9H, s, *t-Bu*), 0.92 (3H, t, *J* 7.6 Hz, CH_3). Compound **11a**: R_f (20% EtOAc/*n*-pentane) 0.48; δ_H (300 MHz, $CDCl_3$) 5.52 (1H, q, *J* 6.9 Hz, =C*H*), 3.63 (1H, dd, *J* 8.8, 7.6 Hz, (CO)C*H*), 2.92 (1H, dq, *J* 15.5, 2.2 Hz, =CCH_aH_b), 2.73 (1H, d, *J* 15.5 Hz, =CCH_aH_b), 2.65 (1H, ddd, *J* 13.3, 8.8, 1.5 Hz, CHCH_aH_b), 2.50 (2H, q, *J* 7.3 Hz, CH_2CH_3), 2.20 (1H, dd, *J* 13.3, 7.6 Hz, CHCH_aH_b), 1.54 (3H, dm, *J* 6.9 Hz, =CCH_3), 1.45 (9H, s, *t-Bu*), 1.43 (9H, s, *t-Bu*), 1.05 (3H, t, *J* 7.3 Hz, CH_2CH_3); HRMS (ESI) (mixture): MNa^+, found 375.2145. $C_{20}H_{32}NaO_5$ requires 375.2142.

*4.2.6. (Z)-Di-tert-butyl 3-acetyl-4-ethylidenecyclopentane-1,1-dicarboxylate (**10b**).* The reaction of **6b** was performed as described in the general procedure above with AuCl(IMes) and $AgSbF_6$ for 6 h. Purification by column chromatography (6% EtOAc/*n*-pentane) provided **10b** (72%) as a colourless oil. R_f (20% EtOAc/*n*-pentane) 0.46; ν_{max} (neat) 2978, 1723 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 5.55 (1H, q, *J* 7.0 Hz, C*H*), 3.60 (1H, dd, *J* 8.8, 7.6 Hz, (CO)C*H*), 2.91 (1H, dq, *J* 15.5, 2.5, CH_2), 2.74 (1H, d, *J* 15.5 Hz, CH_2), 2.65 (1H, ddd, *J* 13.4, 8.8, 1.6, CH_2), 2.22 (1H, dd, *J* 13.4, 7.6 Hz, CH_2), 2.16 (3H, s, CH_3), 1.56 (3H, dm, *J* 7.0 Hz, CH_3), 1.45 (9H, s, *t-B*u), 1.43 (9H, s, *t-Bu*); δ_C (100 MHz, $CDCl_3$) 208.1 (*C*O), 170.4 (*C*O*t*-Bu), 170.1 (*C*O*t*-Bu), 137.9 (*C*=CH), 120.5 (C=*C*H), 81.5 (*C*$(CH_3)_3$), 81.3 (*C*$(CH_3)_3$), 60.2 (*C*$(CO_2t\text{-}Bu)_2$), 53.3 ((CO)CH), 41.8 (CH_2), 36.3 (CH_2), 27.8 (2×C$(CH_3)_3$), 27.2 ((CO)*C*H_3), 14.7 (*C*H_3); *m*/*z* (ESI) 361 (MNa^+); HRMS (ESI): MNa^+, found 361.1984. $C_{19}H_{30}NaO_5$ requires 361.1985.

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