Synthesis of Highly Substituted Oxetanes via [2+2] Cycloaddition Reactions of Allenoates Catalyzed by a Guanidine Lewis Base

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1. General Methods

All reactions were performed in HPLC grade acetonitrile. No vigorous exclusion of water or air was necessary, but as TBD readily reacts with atmospheric CO₂ the reactions were performed under argon atmosphere. Small amounts of H₂O introduced by weighing highly hygroscopic TBD in air proved to be unproblematic.

TLC was performed on glass plates (0.25 mm silica gel 60, F254) with detection by UV (254 nm) or KMnO₄ stain. Column chromatography was performed under medium pressure as flash chromatography on silica gel 60 (230-400 mesh) with the indicated solvents. Solvents for flash chromatography were distilled prior to use.

¹H and ¹³C NMR spectra were recorded on a Varian (Agilent) Mercury 300, VNMRS-400 or VNMRS-600 spectrometer at 25 °C. Spectra were calibrated to their respective solvent residue signals (CDCl₃: ¹H 7.26 ppm, ¹³C 77.0 ppm). Multiplicities of ¹³C NMR signals were determined by APT/DEPT and 2D HMQC experiments. Mass spectra were measured on a Finnigan SSQ7000 (EI, 70 eV), Thermo Finnigan LCQ Deca XP Plus (ESI) or ThermoFisher Scientific LTQ Orbitrap XL (ESI, HR-ESI) spectrometer. IR spectra were measured on a Perkin-Elmer FT-IR Spectrum 100 spectrometer as liquid film (film) or using an ATR unit (ATR). Melting points were measured on a Büchi B-540 melting point apparatus and are uncorrected.

2. Experimental Details

2.1 Synthesis of Starting Materials

All required trifluoromethylketones were commercially available and used without additional purification. TBD was purchased from Sigma Aldrich Inc. and used as received.

Allenoates 1a, 1b, 1c, 1d, 1e, 1f and 1g were synthesized using literature-known method.¹¹ The following allenoates were purified via column chromatography over silica gel instead of distillation under reduced pressure: 1a (pentane/Et₂O = 20/1), 1b (pentane/Et₂O = 20/1), 1f (pentane/Et₂O = 20/1), 1g (pentane/Et₂O = 50/1). The alkynoate 1h was synthesized using the reported procedure.²

2.2 **Standard Experimental Procedure**

Allenoates 1a-g or alkynoate 1h and the respective trifluoromethylketone 2 (1.0 equiv.) are dissolved in MeCN at r.t. in a Schlenk-flask. Catalyst (8 - 30 mol% TBD) is added all at once, and the reaction mixture is stirred at r.t. until TLC indicates complete conversion of the allenoate or alkynoate ester (typically 10-20 min). The reaction is quenched by the addition of solid NH₄Cl (excess), filtered and the NH₄Cl washed with CH₂Cl₂. After evaporation of the solvents, the residue is purified by flash column chromatography to give the product(s).

2.3 **Studies Concerning Catalyst Poisoning**

During the reactions between allenoate 1a and trifluoromethyl ketones containing electron withdrawing groups incomplete consumption of 1a was detected even after prolonged time after the addition of TBD (up to 1 h 20 min for 2g). To study the possibility of concurring reactions, TBD was mixed with 2g in a 1:1 molar ratio in CD₃CN and the reaction mixture was monitored by ¹³C NMR spectroscopy (See example ¹³C NMR spectra below). A complete disappearance of the characteristic signal of the carbonyl group [180.9 (qₓCF, ²J_CF = 35.6 Hz, COCF₃)] indicated that the starting material reacted to products which could not be further identified. This implies, indeed, that the reaction between TBD and 2g led to poisoning of the catalyst and resulted in the observed incomplete consumption of the starting materials.
Example \textit{\textsuperscript{13}C NMR spectrum}: trifluoromethyl ketone \textit{2g} in CD$_3$CN.

Example \textit{\textsuperscript{13}C NMR spectrum}: trifluoromethyl ketone \textit{2g} completely consumed after addition of TBD (1 eq.) in CD$_3$CN.
2.4 Determination of the Double Bond Configuration of 3ia

The double bond configuration of products 3aa-ah could be unambiguously determined by crystallographic methods and comparison of characteristic chemical shifts of the α-protons. Due to the fact that the oxetane 3ia does not bear an α-protons additional NMR experiments were performed in order to determine its double bond configuration. For this purpose 1D NOESY was measured (See Fig. S1 and 1D NOESY below). Upon selective excitation of the α-methyl protons (1.11 ppm, positive signal), the relaxation (negative signals) of three different groups was detected: γ-methyl group (1.81 ppm), ethylene protons of the ethyl carboxylate group (4.15 ppm) as well as phenyl group (7.45 ppm). The obtained spectra showed significantly stronger relaxation signals of the aromatic protons than of the γ-methyl group. This implied that the α-methyl group is closer to the phenyl groups than to the γ-methyl group and therefore the isolated compound has the (E)-configuration. In the case of an opposite double bond configuration, a stronger relaxation of the γ-methyl than of the phenyl group should be expected.

Fig. S1 Characteristic NOE signals of 3ia

\[ =\text{C(CH}_3\text{)}\text{CO}_2\text{Et} \]

\[ ^1\text{D NOESY spectrum of 3ia}. \] After selective excitation of the protons at 1.11 ppm (positive signal), relaxation of the protons at 1.81, 4.15 and 7.45 ppm (negative signals) was detected.
2.5 Determination of Diastereomeric Ratios of Products and Yields of (Z)-Oxetanes from $^1$H NMR Spectra of Crude Reaction Mixtures

Isolation of (Z)-configured oxetanes proved to be rather complicated in many cases due to presence of inseparable impurities. The relative ratios of the (E)- and (Z)-isomers were determined by $^1$H NMR integration in the crude product mixture prior to the isolation of the (E)-isomer. The respective yield of the (Z)-isomer was then calculated by multiplication of this (E)/(Z)-ratio with the yield of the isolated, pure (E)-isomer. The relative amounts of both configurational isomers were based on integration of the signals of corresponding α-protons which were well separated and enabled secure integration (See Fig. S2 and example $^1$H NMR spectra below).

Taking into account longer relaxation times needed for these olefinic protons, their intensity was only 80–90% of the expected value under a standard $^1$H NMR pulse sequence (relaxation delay 1.0 sec, 45° pulse, 16 scans, 400 MHz or relaxation delay 1.0 sec, 45° pulse, 4 scans, 600 MHz). In order to estimate the possible inaccuracy of the integration, a standard $^1$H NMR spectrum of the crude reaction mixture containing (E)-3aa and (Z)-3aa was recorded and the integrals were compared to those obtained after $^1$H NMR experiment with modified delay time and pulse angle (relaxation delay 25.0 sec, 90° pulse, 16 scans, 400 MHz). As can be seen below, both the relative integrals of the configurational isomers [(E)-3aa:(Z)-3aa = 89:11] and the diastereomeric ratios [17:83 for (E)-3aa and 34:66 for (Z)-3aa] remain the same under either conditions. Therefore, using a standard $^1$H NMR pulse sequence was sufficient for the chosen purpose.

![Fig. S2](image-url) All isomers of the product 3aa present in the crude mixture after the reaction between 1a and 2a.
Example $^1$H NMR spectrum: mixture of (E)- and (Z)-3aa. Standard pulse sequence (relaxation delay 1.0 sec, 45° pulse, 16 scans, 400 MHz).

Example $^1$H NMR spectrum: mixture of (E)- and (Z)-3aa. Modified pulse sequence (relaxation delay 25.0 sec, 90° pulse, 16 scans, 400 MHz).
2.6 Proposed Reaction Mechanisms

The formation of oxetanes can be explained by TBD-induced Morita-Baylis-Hillman and consecutive oxa-Michael reaction (Fig. S3). Addition of TBD to the allenoate ester 1 leads to the formation of dienolate A which reacts with trifluoromethyl ketone 2 to intermediate B. Subsequent intramolecular oxa-Michael reaction to C and elimination produce the oxetane product 3 and regenerate TBD catalyst which can now start a new catalytic cycle. An analogous reaction mechanism is expected for the PPh₃-catalyzed reaction between 1a and 2a producing the oxetane 3aa (See Scheme 2 in the main manuscript).

![Proposed catalytic cycle for the formation of oxetanes with TBD catalyst.](image)

In the case where tetrahydrofuran 4 was obtained (Fig. S4), the initial addition of PPh₃ catalyst to the allenoate 1i leads to the formation of the dienolate A' which isomerises to ylide B'. The ylide formation results in an Umpolung of the reactive intermediate which is now nucleophilic at the δ-carbon atom. Nucleophilic addition to the trifluoromethyl ketone 2 (to C'), double-bond isomerisation (to D'), Michael-cyclization (to E') and elimination of PPh₃ results in the formation of five membered ring 4.
Fig. S4 Proposed catalytic cycle for the formation of 4 with PPh₃ as catalyst.
3 Spectroscopic data
3.1 Spectroscopic Data Related to Table 1

*rac*-ethyl 2-[(3R,4R)-3-methyl-4-phenyl-4-(trifluoromethyl)oxetanylidene]acetate (3aa)

(Table 1, Entry 3)

Allenolate 1a (72 mg, 570 µmol) and ketone 1a (80 µL, 99 mg, 570 µmol, 1.0 equiv.) were reacted in MeCN (2.3 mL) with TBD (6.4 mg, 46 µmol, 8 mol%) using standard procedure (15 min, r. t.). Flash column chromatography (Si, 2.0×20 cm, pentane/EtOAc = 20/1) gave product (E)-3aa (133.7 mg, 445 µmol, 78%, 18:82 d.r.) as a colourless oil which solidified upon standing at 7 °C. An additional more polar fraction was isolated and purified by column chromatography (Si, 1.5×10 cm, pentane/EtOAc = 20/1) to afford minor product (Z)-3aa (14.9 mg, 50 µmol, 9%, 48:52 d.r.) as a colourless oil.

(E)-3aa:

\[ R_f = 0.39 \ (P/\text{EtOAc} = 96/4, \text{[UV, KMnO}_4]) \].
m.p. 59-62 °C (pentane)

\[ \text{H} \text{NMR (}600 \text{ MHz, CDCl}_3\text{) } \delta 7.46 - 7.36 (m, 5H, CH}_2\text{Ar, both diastereomers), 5.40 (d, } J = 1.8 \text{ Hz, 1H, CHCOOEt, major diastereomer), 5.37 (d, } J = 2.4 \text{ Hz, 1H, CHCOOEt, minor diastereomer), 4.20 (qd, } J = 7.2, 1.8 \text{ Hz, 1H, CHCH}_3, \text{ major diastereomer), 4.15 - 4.09 (m, 2H, CO}_2\text{CH}_2\text{CH}_3, \text{ both diastereomers and 1H, CHCH}_3, \text{ minor diastereomer), 1.75 (dd, } J = 7.8, 1.8 \text{ Hz, 3H, CHCH}_3, \text{ minor diastereomer), 1.25 (t, } J = 7.2 \text{ Hz, 3H, CO}_2\text{CH}_2\text{CH}_3, \text{ major diastereomer), 1.23 (t, } J = 6.6 \text{ Hz, 3H, CO}_2\text{CH}_2\text{CH}_3, \text{ minor diastereomer), 1.15 (d, } J = 7.2 \text{ Hz, 3H, CHCH}_3, \text{ major diastereomer).} \]

\[ \text{C NMR (major diastereomer, } 151 \text{ MHz, CDCl}_3\text{) } \delta 178.1 (s, \text{ COOEt), 166.6 (s, C=CHCOOEt), 135.1 (C}_2\text{Ar), 129.6 (C}_2\text{Ar), 128.75 (C}_2\text{Ar), 126.2 (C}_2\text{Ar) 124.5 (q}_C\text{CF, } ^1J_{CF} = 283.4 \text{ Hz, CF}_3), 93.29 (d, CHCOOEt), 89.5 (q}_C\text{CF, } ^2J_{CF} = 31.7 \text{ Hz, CCF}_3), 60.06 (t, CO}_2\text{CH}_2\text{CH}_3, \text{ 44.0 (d, CHCH}_3), 14.47 (q, CO}_2\text{CH}_2\text{CH}_3), 13.1 (q, CHCH}_3). \]

\[ \text{C NMR (minor diastereomer, } 151 \text{ MHz, CDCl}_3\text{) } \delta 177.6 (s, \text{ COOEt), 166.5 (d, CHCOOEt), 130.7 (C}_2\text{Ar), 128.70 (C}_2\text{Ar), 125.5 (C}_2\text{Ar) 123.7 (q}_C\text{CF, } ^1J_{CF} = 283.7 \text{ Hz, CF}_3), 93.32 (d, CHCOOEt), 88.7 (q}_C\text{CF, } ^2J_{CF} = 31.3 \text{ Hz, CCF}_3), 60.03 (t, CO}_2\text{CH}_2\text{CH}_3, \text{ 49.2 (d, CHCH}_3), 14.49 (q, CO}_2\text{CH}_2\text{CH}_3), 11.5 (q, CHCH}_3). \text{ One C}_2\text{Ar-signal was not included due to overlaps resulting from low resolution.} \]

\[ \text{F NMR (}282 \text{ MHz, CDCl}_3\text{) } \delta -74.9 \text{ (minor diastereomer), -79.9 (major diastereomer).} \]
IR (ATR) \( \tilde{\nu} = 2991 \text{ cm}^{-1} \) (w), 2095 (w), 1908 (w), 1705 (s, CO\(_2\)Et), 1705 (s), 1452 (m), 1374 (m), 1246 (m), 1170 (s), 1109 (s), 915 (m), 722 (s), 664 (m).

MS (EI, 70 eV) \( m/z \) (%) 300.1 (3) [M\(^+\)], 254.4 (4) [(M–OEt\(^+\)], 230.9 (8) [(M–Ph\(^+\)], 185.9 (100) [C\(_{10}\)H\(_9\)F\(_3\)\(^+\)], 121.0 (67), 116.9 [C\(_9\)H\(_9\)\(^+\)] (99), 77.1 (20) [Ph\(^+\)], 69.1 (74) [CF\(_3\)\(^+\)].

MS (ESI, Orbitrap) \( m/z \) 339.1 (M+K\(^+\)), 323.1 (M+Na\(^+\)), 301.1 (M+H\(^+\)).

HRMS (ESI, Orbitrap) calcd. for C\(_{15}\)H\(_{15}\)F\(_3\)NaO\(_3\)\(^+\) (M+Na\(^+\)): 323.08655; found: 323.08542

\((\text{Z})\)-3aa:

\( R_T = 0.18 \) (P/EtOAc = 96/4, [UV, KMnO\(_4\)]).

\(^1\text{H} \) NMR (600 MHz, CDCl\(_3\)) \( \delta \) 7.47 – 7.39 (m, 5H, CH\(_\text{Ar}\), both diastereomers), 4.88 (d, \( J = 1.2 \) Hz, 1H, CHCOOEt, major diastereomer), 4.87 (d, \( J = 1.8 \) Hz, 1H, CHCOOEt, minor diastereomer), 4.23 – 4.13 (m, 2H, CO\(_2\)C\(_\text{H}_2\)CH\(_3\), both diastereomers), 3.97 (qd, \( J = 7.2, 1.8 \) Hz, 1H, CHCH\(_3\), major diastereomer), 3.90 (qd, \( J = 7.2, 1.1 \) Hz, 1H, CHCH\(_3\), minor diastereomer).

\(^{13}\text{C} \) NMR (major diastereomer, 151 MHz, CDCl\(_3\)) \( \delta \) 174.51 (s, COOEt), 164.82 (s, C=CHCOOEt), 135.0 (C\(_\text{Ar}\)), 129.71 (C\(_\text{Ar}\)), 128.8 (C\(_\text{Ar}\)), 126.4 (C\(_\text{Ar}\)), 124.0 (q, CF\(_3\)\(^+\)), 91.2 (d, CHCOOEt), 89.1 (q, \( J_{CF} = 32.5 \) Hz, CCF\(_3\)), 60.08 (t, CO\(_2\)C\(_\text{H}_2\)CH\(_3\)), 42.3 (d, CHCH\(_3\)), 14.57 (q, CO\(_2\)CH\(_2\)C\(_\text{H}_3\)), 14.0 (q, CHCH\(_3\)).

\(^{13}\text{C} \) NMR (minor diastereomer, 151 MHz, CDCl\(_3\)) \( \delta \) 174.50 (s, COOEt), 164.78 (d, CHCOOEt), 130.2 (C\(_\text{Ar}\)), 129.69 (C\(_\text{Ar}\)), 128.7 (C\(_\text{Ar}\)), 125.6 (C\(_\text{Ar}\)), 123.6 (q, CF\(_3\)\(^+\)), 90.3 (d, CHCOOEt), 88.9 (q, \( J_{CF} = 31.3 \) Hz, CCF\(_3\)), 60.05 (t, CO\(_2\)C\(_\text{H}_2\)CH\(_3\)), 47.5 (d, CHCH\(_3\)), 14.55 (q, CO\(_2\)CH\(_2\)C\(_\text{H}_3\)), 12.2 (q, CHCH\(_3\)).

\(^{19}\text{F} \) NMR (282 MHz, CDCl\(_3\)) \( \delta \) -74.8 (minor diastereomer), -79.6 (major diastereomer).

IR (film) \( \tilde{\nu} = 3434 \text{ cm}^{-1} \) (w), 2982 (m), 1962 (w), 1716 (s, CO\(_2\)Et), 1454 (m), 1378 (m), 1258 (m), 1183 (s), 1013 (s), 906 (m), 703 (m), 620 (w).

MS (EI, 70 eV) \( m/z \) (%) 300.1 (4) [M\(^+\)], 254.7 (12) [(M–OEt\(^+\)], 231.0 (12) [(M–Ph\(^+\)], 185.9 (100) [C\(_{10}\)H\(_9\)F\(_3\)\(^+\)], 117.0 [C\(_9\)H\(_9\)\(^+\)] (84), 115.0 (30), 77.1 (7) [Ph\(^+\)], 69.2 (42) [CF\(_3\)\(^+\)].

MS (ESI, Orbitrap) \( m/z \) 339.1 (M+K\(^+\)), 323.1 (M+Na\(^+\)), 301.1 (M+H\(^+\)).

HRMS (ESI, Orbitrap) calcd. for C\(_{15}\)H\(_{15}\)F\(_3\)NaO\(_3\)\(^+\) (M+Na\(^+\)): 323.08655; found: 323.08542
**Rac-benzyl 2-[(3R,4R)-3-methyl-4-phenyl-4-(trifluoromethyl)oxetanylidene]acetate (3ba)**

(Table 1, Entry 5)

Allenolate 1b (110 mg, 584 µmol) and ketone 2a (82 µL, 102 mg, 584 µmol, 1.0 equiv.) were reacted in MeCN (2.3 mL) with TBD (8.1 mg, 58 µmol, 10 mol%) using standard procedure (10 min, r.t.). Flash column chromatography (Si, 2.0×22 cm, pentane/EtOAc = 20/1→7/1) gave product (E)-3ba (149 mg, 411 µmol, 70%, 19:81 d.r.) as a colourless oil and a minor product (Z)-3ba (20 mg, 55 µmol, 9%, 43:57 d.r.) as a colourless oil.

**(E)-3ba:**

$$R_f = 0.54 \text{ (P/EtOAc = 14/1, [UV, KMnO}_4\text{]).}$$

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.51 – 7.40 (m, 5H, CH$_{Ar}$, both diastereomers), 7.40 – 7.31 (m, 5H, CH$_{Ar}$, both diastereomers), 5.52 (d, $J = 1.9$ Hz, 1H, CHCOOBn, major diastereomer), 5.49 (d, $J = 2.1$ Hz, 1H, CHCOOBn, minor diastereomer), 5.15 (2×d, $J = 12.4$ Hz, 2H, COOCH$_2$Ph, major diastereomer), 5.13 (2×d, $J = 12.3$ Hz, 2H, COOCH$_2$Ph, minor diastereomer), 4.25 (qd, $J = 7.4$, 1.9 Hz, 1H, CHCH$_3$, major diastereomer), 4.16 (qd, $J = 7.4$, 1.8 Hz, 1H, CHCH$_3$, minor diastereomer), 1.77 (dq, $J = 7.5$, 1.7 Hz, 3H, CHCH$_3$, minor diastereomer), 1.16 (d, $J = 7.4$ Hz, 3H, CHCH$_3$, major diastereomer).

$^{13}$C NMR (major diastereomer, 101 MHz, CDCl$_3$) δ 178.6 (s, COOBn), 166.3 (s, C=CHCOOBn), 136.2 (C$_{Ar}$), 129.6 (C$_{Ar}$), 128.7 (C$_{Ar}$), 128.34 (C$_{Ar}$), 126.1 (C$_{Ar}$) 124.2 (q$_{CF}$, $^1$J$_{CF} = 283.1$ Hz, CF$_3$), 92.9 (d, CHCOOBn), 89.6 (q$_{CF}$, $^2$J$_{CF} = 31.5$ Hz, CCF$_3$), 65.9 (t, COOCH$_2$Ph), 44.0 (d, CHCH$_3$), 12.9 (q, CHCH$_3$). Three C$_{Ar}$-signals were not included due to overlaps resulting from low resolution.

$^{13}$C NMR (minor diastereomer, 101 MHz, CDCl$_3$) δ 178.2 (s, COOBn), 166.2 (s, C=CHCOOBn), 136.7 (C$_{Ar}$), 134.9 (C$_{Ar}$), 130.6 (C$_{Ar}$), 128.6 (C$_{Ar}$), 128.29 (C$_{Ar}$), 125.4 (C$_{Ar}$) 123.6 (q$_{CF}$, $^1$J$_{CF} = 283.8$ Hz, CF$_3$), 88.7 (q$_{CF}$, $^2$J$_{CF} = 30.9$ Hz, CCF$_3$), 65.8 (t, COOCH$_2$Ph), 49.1 (d, CHCH$_3$), 11.4 (q, CHCH$_3$). Two C$_{Ar}$-signals and the CHCOOBn signal were not included due to overlaps resulting from low resolution.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -74.9 (minor diastereomer), -79.6 (major diastereomer).

IR (film) $\tilde{\nu} = 3443$ cm$^{-1}$ (w), 2946 (m), 1714 (s, CO$_2$Bn), 1455 (m), 1381 (m), 1258 (s), 1179 (s), 1107 (s), 1010 (s), 916 (m), 729 (s), 604 (w).
MS (EI, 70 eV) m/z (%) 362.1 [M⁺] (7), 255.1 (16) [(M–OBn)⁺], 185.9 (21) [C₁₀H₉F₃⁺], 117.1 [C₈H₅⁺] (27), 115.1 (6), 91.1 [Bn⁺] (100), 77.1 (5) [Ph⁺], 69.1 (17) [CF₃⁺].

MS (ESI, Orbitrap) m/z 363.2 (M+H⁺), 385.1 (M+Na⁺).

HRMS (ESI, Orbitrap) calcd. for C₂₀H₁₇F₃NaO₃⁺ (M+Na⁺): 385.10220; found: 385.10263.

(Z)-3ba:

Rᵣ = 0.5 (P/EtOAc = 14/1, [UV, KMnO₄]).

¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.29 (m, 10H, CH Ar, both diastereomers), 5.21 (2×d, J = 12.5 Hz, 2H, COOCH₂Ph, major diastereomer), 5.20 (s, 2H, COOCH₂Ph, minor diastereomer), 4.97 (d, J = 1.8 Hz, 1H, CHCOOBn, major diastereomer), 4.95 (d, J = 1.8 Hz, 1H, CHCOOBn, minor diastereomer), 4.01 (qd, J = 7.4 Hz, 1H, CHCH₃, major diastereomer), 3.94 (qd, J = 7.5, 1.5 Hz, 1H, CHCH₃, minor diastereomer), 1.58 (dq, J = 7.6, 1.5 Hz, 3H, CHCH₃, minor diastereomer), 1.01 (d, J = 7.4 Hz, 3H, CHCH₃, major diastereomer).

¹³C NMR (major diastereomer, 151 MHz, CDCl₃) δ 175.06 (s, COOBn), 164.45 (s, C=CHCOOBn), 136.51 (C Ar), 134.8 (C Ar), 130.1 (C Ar), 128.8 (C Ar), 128.61 (C Ar), 128.2 (C Ar), 128.12 (C Ar), 126.3 (C Ar), 123.9 (qCF, ¹JC₉F = 282.8 Hz, CF₃), 90.8 (d, CHCOOBn), 89.15 (qCF, ²JC₉F = 32.3 Hz, CCF₃), 65.75 (t, COOCH₂Ph), 42.3 (d, CHCH₃), 14.0 (q, CHCH₃).

¹³C NMR (minor diastereomer, 151 MHz, CDCl₃) δ 175.05 (s, COOBn), 164.43 (s, C=CHCOOBn), 136.53 (C Ar), 129.67 (C Ar), 128.7 (C Ar), 128.59 (C Ar), 128.10 (C Ar), 128.08 (C Ar), 125.5 (C Ar), 123.6 (qCF, ¹JC₉F = 284.1 Hz, CF₃), 90.0 (d, CHCOOBn), 89.03 (qCF, ²JC₉F = 30.9 Hz, CCF₃), 65.70 (t, COOCH₂Ph), 47.5 (d, CHCH₃), 12.1 (q, CHCH₃). One C Ar-signal was not included due to overlaps resulting from insufficient resolution.

¹⁹F NMR (376 MHz, CDCl₃) δ -74.8 (minor diastereomer), -79.7 (major diastereomer).

IR (film) ν = 3442 cm⁻¹ (w), 2938 (m), 1718 (s, CO₂Bn), 1453 (m), 1381 (m), 1259 (s), 1181 (s), 1002 (s), 912 (w), 730 (m), 606 (w).

MS (EI, 70 eV) m/z (%) 362.1 [M⁺] (1), 255.1 (22) [(M–OBn)⁺], 185.9 (19) [C₁₀H₉F₃⁺], 117.1 [C₈H₅⁺] (27), 115.1 (7), 91.1 [Bn⁺] (100), 77.2 (6) [Ph⁺], 69.1 (20) [CF₃⁺].

MS (ESI, Orbitrap) m/z 363.1 (M+H⁺), 385.1 (M+Na⁺), 401.1 (M+K⁺).

HRMS (ESI, Orbitrap) calcd. for C₂₀H₁₇F₃O₃⁺ (M+H⁺): 363.12026; found: 363.12073.
**rac-methyl 2-[(3R,4S)-3-methyl-4-phenyl-4-(trifluoromethyl)oxetanylidene]acetate (3ca)**

(Table 1, Entry 6)

Allenolate 1c (83 mg, 740 µmol) and ketone 2a (104 µL, 129 mg, 740 µmol, 1.0 equiv.) were reacted in MeCN (3 mL) with TBD (15.5 mg, 111 µmol, 15 mol%) using standard procedure (20 h, r.t., TLC showed incomplete conversion of 1c). Flash column chromatography (Si, 2.0×22 cm, pentane/EtOAc = 30/1→10/1) gave product (E)-3ca (108 mg, 377 µmol, 51%, 27:73 d.r.) as a colourless oil. The yield of the minor isomer (Z)-3ca (7%, 57:73 d.r.) was determined from the 1H-NMR spectrum of the crude reaction mixture based on isolated product (E)-3ca.

(E)-3ca:

R_t = 0.54 (P/EtOAc = 14/1, [UV, KMnO_4]).

1H NMR (600 MHz, CDCl_3) δ 7.48 – 7.39 (m, 5H, CH_Ar, both diastereomers), 5.44 (d, J = 1.9 Hz, 1H, CHCOOMe, major diastereomer), 5.40 (d, J = 2.2 Hz, 1H, CHCOOMe, minor diastereomer), 4.23 (qd, J = 7.4, 1.9 Hz, 1H, CHCH_3, major diastereomer), 4.13 (qd, J = 7.5, 2.1 Hz, 1H, CHCH_3, minor diastereomer), 3.68 (s, 3H, COOC_3H_7, major diastereomer), 3.66 (s, 3H, COOC_3H_7, minor diastereomer), 1.77 (dq, J = 7.6, 1.7 Hz, 3H, CHCH_3, minor diastereomer), 1.17 (d, J = 7.4 Hz, 3H, CHCH_3, major diastereomer).

13C NMR (major diastereomer, 151 MHz, CDCl_3) δ 178.3 (s, C_OOMe), 166.9 (s, C=CHCOOMe), 130.6 (C_Ar), 128.7 (C_Ar), 126.1 (C_Ar) 124.2 (q_CF, J_CF = 283.1 Hz, CF_3), 92.79 (d, CHCOOMe), 89.5 (q_CF, J_CF = 31.8 Hz, CCF_3), 51.2 (q, COOC_3H_7), 43.9 (d, CHCH_3), 13.0 (q, CHCH_3). One C_Ar-signal was not included due to overlaps resulting from low resolution.

13C NMR (minor diastereomer, 151 MHz, CDCl_3) δ 178.3 (s, C_OOMe), 166.9 (s, C=CHCOOMe), 135.0 (C_Ar), 129.6 (C_Ar), 128.64 (C_Ar), 125.4 (C_Ar) 123.6 (q_CF, J_CF = 283.6 Hz, CF_3), 92.80 (d, CHCOOMe), 88.7 (q_CF, J_CF = 31.1 Hz, CCF_3), 51.1 (q, COOC_3H_7), 49.1 (d, CHCH_3), 11.4 (q, CHCH_3).

19F NMR (376 MHz, CDCl_3) δ -74.9 (minor diastereomer), -79.7 (major diastereomer).

IR (film) v = 3439 cm^{-1} (w), 2953 (m), 1720 (s, CO_2Me), 1444 (s), 1356 (s), 1287 (s), 1180 (s), 1117 (s), 1011 (s), 923 (m), 719 (m), 665 (w).

MS (EI, 70 eV) m/z (%) 286.1 (3) [M^+], 255.1 (11) [(M–OMe)^+], 217.1 (16) [(M–CF_3)^+], 186.1 (91) [C_{10}H_{9}F_3^+], 117.1 (100) [C_9H_9^+], 115.1 (25), 77.1 (8) [Ph^+], 69.1 (29) [CF_3^+].
MS (ESI, Orbitrap) m/z 287.1 (M+H\(^{+}\)), 309.1 (M+Na\(^{+}\)), 325.0 (M+K\(^{+}\)).
HRMS (ESI, Orbitrap) calcd. for C\(_{14}\)H\(_{14}\)F\(_{3}\)O\(_{3}\) \((M+H^{+})\): 287.08896; found: 287.08942

\((Z)-3\text{ca}\):
This isomer was not isolated in pure form. Therefore, the signals were assigned from the crude reaction mixture. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.93 (d, \(J\) = 1.6 Hz, 1H, CHCOOMe, minor diastereomer), 4.91 (d, \(J\) = 2.0 Hz, 1H, CHCOOMe, major diastereomer), 1.58 (dq, \(J\) = 7.2, 1.2 Hz, 3H, CHCH\(_3\), major diastereomer), 1.00 (d, \(J\) = 7.2 Hz, 3H, CHCH\(_3\), minor diastereomer).

\(\text{rac-isopropyl 2-[(3R,4S)-3-methyl-4-phenyl-4-trifluoromethyl]oxetanyliden]acetate (3da)}\) (Table 1, Entry 7)
Allenote 1d (103 mg, 735 \(\mu\)mol) and ketone 2a (103 \(\mu\)L, 128 mg, 735 \(\mu\)mol, 1.0 equiv.) were reacted in MeCN (3 mL) with TBD (10.3 mg, 73 \(\mu\)mol, 10 mol\%) using standard procedure (50 min, r.t.). Flash column chromatography (Si, 2.0×22 cm, pentane/EtOAc = 50/1→20/1) gave product \((E)-3\text{da}\) (132 mg, 420 \(\mu\)mol, 57%, 30:70 d.r.) as a colourless oil. The yield of the minor isomer \((Z)-3\text{da}\) (7%, 62:38 d.r.) was determined from the \(^1\)H-NMR spectrum of the crude reaction mixture based on isolated product \((E)-3\text{da}\).

\((E)-3\text{da}\):
\(R_t = 0.71\) (P/EtOAc = 14/1, [UV, KMnO\(_4\)]).
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.49 – 7.36 (m, 5H, CH\(_{Ar}\), both diastereomers), 5.40 (d, \(J\) = 1.9 Hz, 1H, CHCOO\(_{iPr}\), major diastereomer), 5.37 (d, \(J\) = 2.2 Hz, 1H, CHCOO\(_{iPr}\), minor diastereomer), 5.06 – 4.97 (m, 1H, CHMe\(_2\), both diastereomers), 4.21 (qd, \(J\) = 7.4, 1.9 Hz, 1H, CHCH\(_3\), major diastereomer), 4.13 (q, \(J\) = 7.2 Hz, 1H, CHCH\(_3\), minor diastereomer), 1.78 (qd, \(J\) = 7.5, 1.8 Hz, 3H, CHCH\(_3\), minor diastereomer), 1.26 – 1.21 (m, 6H, m, 1H, CHMe\(_2\) both diastereomers), 1.17 (d, \(J\) = 7.4 Hz, 3H, CHCH\(_3\), major diastereomer).
\(^13\)C NMR (major diastereomer, 151 MHz, CDCl\(_3\)) \(\delta\) 177.7 (s, COO\(_{iPr}\)), 166.0 (s, C=CHCOO\(_{iPr}\)), 130.7 (C\(_{Ar}\)), 128.66 (C\(_{Ar}\)), 126.1 (C\(_{Ar}\)) 124.2 (q\(_{CF}\), \(^1\)J\(_{CF} = 283.1\) Hz, CF\(_3\)), 93.70 (d, CHCOO\(_{iPr}\)), 89.38 (q\(_{CF}\), \(^2\)J\(_{CF} = 30.9\) Hz, CCF\(_3\)), 67.27 (d, CO\(_2\)CHMe\(_2\)), 43.9 (d,
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CHCH₃), 22.09 [q, CO₂CH(CH₃)₂], 13.0 (q, CHCH₃). One C₆Ar-signal was not included due to overlaps resulting from low resolution.

¹³C NMR (minor diastereomer, 151 MHz, CDCl₃) δ 177.2 (s, COOᵢPr), 165.9 (s, C=CHCOCOᵢPr), 135.2 (C₆Ar), 129.5 (C₆Ar), 128.61 (C₆Ar), 125.2 (C₆Ar) 123.6 (q, CF₃), 93.73 (d, CHCOCOᵢPr), 88.51 (q, CF₃, ²JCF = 30.9 Hz, CCF₃), 67.23 (d, CO₂CHMe₂), 49.1 (d, CHCH₃), 22.07 [q, CO₂CH(CH₃)₂], 11.5 (q, CHCH₃).

¹⁹F NMR (282 MHz, CDCl₃) δ -74.9 (minor diastereomer), -79.6 (major diastereomer).

IR (film) ν = 3437 cm⁻¹ (w), 2983 (m), 1715 (s, CO₂ᵢPr), 1454 (m), 1374 (s), 1267 (m), 1179 (s), 1107 (s), 1010 (s), 912 (m), 719 (m), 664 (w).

MS (EI, 70 eV) m/z (%) 315.2 (5), 255.1 (8) [(M-OᵢPr)+], 185.9 (100) [C₁₀H₉F₃⁺], 117.1 [C₈H₅⁺] (77), 115.1 (15), 77.1 (6) [Ph⁺], 69.1 (39) [CF₃⁺].

MS (ESI, Orbitrap) m/z 315.1 (M+H⁺), 337.1 (M+Na⁺), 353.1 (M+K⁺).

HRMS (ESI, Orbitrap) calcd. for C₁₆H₁₈F₃O₃⁺ (M+H⁺): 315.12026; found: 315.12088

(Z)-3da:
This isomer was not isolated in pure form. Therefore, the signals were assigned from the crude reaction mixture. ¹H NMR (400 MHz, CDCl₃) δ 4.90 (d, J = 1.6 Hz, 1H, CHCOCOᵢPr, minor diastereomer), 4.88 (d, J = 1.6 Hz, 1H, CHCOCOᵢPr, major diastereomer), 1.56 (dq, J = 7.6, 1.6 Hz, 3H, CHCH₃, major diastereomer), 1.00 (d, J = 7.6 Hz, 3H, CHCH₃, minor diastereomer).

rac-tert-butyl 2-[(3R,4S)-3-methyl-4-phenyl-4-(trifluoromethyl)oxetanyliden]acetate (3ea) (Table 1, Entry 8)
Allenolate 1e (107 mg, 694 µmol) and ketone 2a (97 µL, 121 mg, 694 µmol, 1.0 equiv.) were reacted in MeCN (2.8 mL) with TBD (14.5 mg, 104 µmol, 15 mol%) using standard procedure (50 min., r.t., TLC showed incomplete conversion of 1e). Flash column chromatography (Si, 2.0×22 cm, pentane/ETOAc = 20/1→15/1) gave product (E)-3ea (115 mg, 359 µmol, 50%, 43:57 d.r.) as a colourless oil. The yield of the minor isomer (Z)-3ea (6%, 79:21 d.r.) was determined from the ¹H-NMR spectrum of the crude reaction mixture based on isolated product (E)-3ea.
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(E)-3ea:

$R_t = 0.57$ (P/EtOAc = 14/1, [UV, KMnO$_4$]).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48 – 7.38 (m, 5H, CH$_2$Ar, both diastereomers), 5.34 (d, $J = 1.9$ Hz, 1H, CHCOO$t$Bu, minor diastereomer), 5.31 (d, $J = 2.2$ Hz, 1H, CHCOO$t$Bu, major diastereomer), 4.18 (qd, $J = 7.4$, 1.9 Hz, 1H, CH$_2$H$_3$, minor diastereomer), 4.11 (q, $J = 7.3$, 1.9 Hz, 1H, CH$_2$H$_3$, major diastereomer), 1.77 (dq, $J = 7.6$, 1.7 Hz, 3H, CHCH$_3$, major diastereomer), 1.47 [s, 9H, COOC(CH$_3$)$_3$, minor diastereomer], 1.16 (d, $J = 7.4$ Hz, 3H, CHCH$_3$, minor diastereomer).

$^{13}$C NMR (major diastereomer, 101 MHz, CDCl$_3$) $\delta$ 176.9 (s, C=CHCOO$t$Bu), 165.8 (s, C=CHCOO$t$Bu), 135.3 (C$_{Ar}$), 129.47 (C$_{Ar}$), 128.6 (C$_{Ar}$), 125.5 (C$_{Ar}$) 123.7 (q, CF$_3$, $^1$J$_{CF} = 283.4$ Hz, CF$_3$), 94.9 (d, CHCOO$t$Bu), 88.4 (qCF, $^2$J$_{CF} = 30.7$ Hz, CCF$_3$), 80.2 [s, COOC(CH$_3$)$_3$], 49.0 (d, CHCH$_3$), 28.38 [q, COOC(CH$_3$)$_3$], 11.5 (q, CHCH$_3$). One signal was not included due to overlaps resulting from low resolution.

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -74.9 (minor diastereomer), -79.6 (major diastereomer).

IR (film) $\tilde{\nu}$ = 3440 cm$^{-1}$ (w), 2978 (m), 1713 (s, CO$_2$Et), 1454 (m), 1363 (s), 1250 (m), 1179 (s), 1111 (s), 1009 (s), 912 (w), 707 (m), 664 (w).

**MS** (EI, 70 eV) $m/z$ (%) 272.7 [(M-tBu$^+$)] (19), 255.0 (6) [(M-OtBu$^+$)], 185.9 (100) [C$_{10}$H$_9$F$_3$$^+$], 117.1 [C$_9$H$_8$$^+$] (57), 115.0 (16), 77.1 (6) [Ph$^+$], 69.1 (40) [CF$_3$$^+$].

**MS** (ESI, Orbitrap) $m/z$ 351.1 (M+Na$^+$), 329.1 (M+H$^+$).

**HRMS** (ESI, Orbitrap) calcd. for C$_{17}$H$_{19}$F$_3$NaO$_3$$^+$ (M+Na$^+$): 351.11785; found: 351.11829.

(Z)-3ea:

*This isomer was not isolated in pure form. Therefore, the signals were assigned from the crude reaction mixture.* $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.84 (d, $J = 1.6$ Hz, 1H, CHCOO$t$Bu, minor diastereomer), 4.83 (d, $J = 1.6$ Hz, 1H, CHCOO$t$Bu, major diastereomer), 1.56 (dq, $J = 7.6$, 1.6 Hz, 3H, CHCH$_3$, major diastereomer), 1.00 (d, $J = 7.2$ Hz, 3H, CHCH$_3$, minor diastereomer).
**rac-ethyl 2-[(3R,4R)-3-isopropyl-4-phenyl-4-(trifluoromethyl)oxetanyliden]acetate (3fa)**

(Table 1, Entry 9)

Allenolate 1f (97 mg, 612 µmol) and ketone 2a (88 µL, 109 mg, 629 µmol, 1.0 equiv.) were reacted in MeCN (2.5 mL) with TBD (17.5 mg, 126 µmol, 20 mol%) using standard procedure (1 h 20 min, r. t.). Flash column chromatography (Si, 2.0 × 22 cm, pentane/EtOAc = 50/1 → 15/1) gave product (E)-3fa (55 mg, 167 µmol, 27%, 3:97 d.r.) as a colourless oil and a major product (Z)-3fa (94 mg, 287 µmol, 46%, 58:42 d.r.) as a colourless oil.

**E)-3fa:**

\[ R_t = 0.60 \text{ (P/EtOAc = 14/1, [UV, KMnO}_4]) \]

1H NMR (400 MHz, CDCl3) δ 7.57 – 7.48 (m, 2H, CHAr), 7.48 – 7.40 (m, 3H, CHAr), 5.55 (d, J = 1.9 Hz, 1H, CHCOOEt), 4.19 – 4.09 (m, 3H, CO2C2H5 and C2H3), 2.25 (heptd, J = 7.1, 4.0 Hz, 1H, CHMe2), 1.27 (t, J = 7.1 Hz, 3H, CO2CH2CH3), 0.84 [d, J = 7.1 Hz, 3H, CHCH3(CH3)], 0.79 [d, J = 7.0 Hz, 3H, CHCH3(CH3)].

13C NMR (101 MHz, CDCl3) δ 175.1 (s, COOEt), 166.5 (s, C=CHCOOEt), 130.1 (C6), 129.1 (C6), 128.5 (C6), 126.6 (C6) 124.5 (qCF, \( J_{CF} = 284.4 \text{ Hz} \), CF3), 94.8 (d, CHCOOEt), 89.3 (qCF, \( J_{CF} = 31.3 \text{ Hz} \), CCF3), 60.0 (t, CO2CH2CH3), 55.3 (d, CHiPr), 27.0 (d, CHMe2), 20.1 [q, CHCH3(CH3)], 18.9 [q, CHCH3(CH3)], 14.5 (q, CO2CH2CH3).

IR (film) \( ν = 3457 \text{ cm}^{-1} \) (m), 2973 (s), 1899 (w), 1716 (s, CO2Et), 1680 (s), 1459 (s), 1379 (s), 1260 (s), 1176 (s), 1110 (s), 825 (m), 719 (s).

MS (EI, 70 eV) \( m/z \) (%): 328.1 (12) [M]+, 383.0 (8) [(M–OEt)+], 214.1 (32) [C12H13F3]+, 199.0 \( [C_{11}H_{10}F_3]^+ \) (100), 145.0 \( [C_{11}H_{13}^+] \) (35), 115.0 (18), 77.1 (9) [Ph]+, 69.1 (31) [CF3]+.

MS (ESI, Orbitrap) \( m/z \) 329.1 (M+H+).

HRMS (ESI, Orbitrap) calcd. for \( C_{17}H_{26}F_5O_3^+ \) (M+H+): 329.13591; found: 329.13510

19F NMR (376 MHz, CDCl3) δ -79.1.
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(Z)-3fa:

\[ R_f = 0.40 \text{ (P/EtOAc = 14/1, [UV, KMnO₄]).} \]

\(^1\)H NMR (600 MHz, CDCl₃) \( \delta \) 7.60 – 7.54 (m, 2H, CH₃Ar, major diastereomer), 7.53 – 7.49 (m, 2H, CH₃Ar, minor diastereomer), 7.47 – 7.39 (m, 3H, CH₃Ar, both diastereomers), 5.03 (d, \( J = 1.8 \) Hz, 1H, CHCOOEt, minor diastereomer), 5.02 (d, \( J = 1.6 \) Hz, 1H, CHCOOEt, major diastereomer), 4.25 – 4.13 (m, 2H, CO₂CH₂CH₃ both diastereomers), 3.65 (dd, \( J = 7.9, 1.6 \) Hz, 1H, CHiPr, major diastereomer), 3.50 (dd, \( J = 11.1, 1.7 \) Hz, 1H, CHiPr, minor diastereomer), 2.58 – 2.49 (m, 1H, CHMe₂, minor diastereomer), 1.76 – 1.67 (m, 1H, CHMe₂, major diastereomer), 1.30 (t, \( J = 7.3 \) Hz, 3H, CO₂CH₂CH₃, major diastereomer), 1.28 (t, \( J = 7.0 \) Hz, 3H, CO₂CH₂CH₃, minor diastereomer), 1.23 [d, \( J = 6.5 \) Hz, 3H, CHCH₃(CH₃), minor diastereomer], 1.10 [d, \( J = 6.6 \) Hz, 3H, CHCH₃(CH₃), minor diastereomer], 0.79 [d, \( J = 6.7 \) Hz, 3H, CHCH₃(CH₃), major diastereomer], 0.74 (d, \( J = 6.7 \) Hz, 3H, CHCH₃(CH₃), major diastereomer).

\(^{13}\)C NMR (major diastereomer, 151 MHz, CDCl₃) \( \delta \) 172.0 (s, COOEt), 164.6 (s, C=CHCOOEt), 130.6 (C₆Ar), 129.7 (C₆Ar), 128.6 (C₆Ar), 126.6 (C₆Ar) 124.2 (qCF, \( J_{CF} = 283.3 \) Hz, CF₃), 92.8 (d, CHCOOEt), 88.8 (qCF, \( J_{CF} = 31.9 \) Hz, CCF₃), 60.0 (t, CO₂CH₂CH₃), 54.6 (d, CHiPr), 26.5 (d, CHMe₂), 21.35 [q, CHCH₃(CH₃)], 18.6 [q, CHCH₃(CH₃)], 14.47 (q, CO₂CH₂CH₃).

\(^{13}\)C NMR (minor diastereomer, 151 MHz, CDCl₃) \( \delta \) 172.7 (s, COOEt), 164.7 (d, CHCOOEt), 134.9 (C₆Ar), 129.5 (C₆Ar), 126.0 (C₆Ar) 123.8 (qCF, \( J_{CF} = 283.9 \) Hz, CF₃), 92.0 (d, CHCOOEt), 89.2 (qCF, \( J_{CF} = 31.4 \) Hz, CCF₃), 60.07 (t, CO₂CH₂CH₃), 59.9 (d, CHiPr), 26.9 (d, CHMe₂), 22.35 [q, CHCH₃(CH₃)], 21.32 [q, CHCH₃(CH₃)], 14.45 (q, CO₂CH₂CH₃). One C₆Ar-signal was not included due to overlaps resulting from low resolution.

\(^{19}\)F NMR (564 MHz, CDCl₃) \( \delta \) -74.2 (minor diastereomer), -78.3 (major diastereomer).

IR (film) \( \tilde{\nu} \) = 3437 cm\(^{-1}\) (w), 2976 (s), 1712 (s, CO₂Et), 1461 (s), 1374 (s), 1262 (s), 1180 (s), 1004 (s), 806 (m), 713 (s).

MS (EI, 70 eV) \( m/z \) (%): 328.1 (6) [M⁺], 383.1 (13) [(M-OEt)⁺], 214.1 (34) [C₁₂H₁₃F₃⁺], 199.0 [C₁₁H₁₀F₅⁺] (94), 145.0 [C₁₁H₉⁺] (45), 115.0 (100), 77.1 (6) [Ph⁺], 69.1 (32) [CF₃⁺].

MS (ESI, Orbitrap) \( m/z \): 367.1 (M⁺), 351.1 (M⁺Na⁺), 329.1 (M⁺H⁺).

HRMS (ESI, Orbitrap) calcd. for C₁₁H₂₀F₅O₅⁺ (M⁺H⁺): 329.13591; found: 329.13556
**rac-benzyl 2-[(3R,4R)-3-isopropyl-4-phenyl-4-(trifluoromethyl)oxetanyliden]acetate (3ga)** (Table 1, Entry 10)

Allenolate 1g (106 mg, 490 µmol) and ketone 2a (85 mg, 490 µmol, 1.0 equiv.) were reacted in MeCN (2.0 mL) with TBD (13.7 mg, 98 µmol, 20 mol%) using standard procedure (1 h, r. t.). Flash column chromatography (Si, 2.0×22 cm, pentane/EtOAc = 50/1→15/1) gave product (E)-3ga (43 mg, 111 µmol, 23%, 3:97 d.r.) as a colourless oil and a major product (Z)-3ga (92 mg, 236 µmol, 48%, 68:32 d.r.) as a colourless oil.

(E)-3ga:

\[ R_f = 0.58 \text{ (P/EtOAc = 14/1, [UV, KMnO}_4\text{]).} \]

1H NMR (400 MHz, CDCl₃) δ 7.56 – 7.49 (m, 2H, CH₆Ar), 7.47 – 7.43 (m, 3H, CH₂Ar), 7.39 – 7.31 (m, 5H, CH₆Ar), 5.63 (d, J = 1.9 Hz, 1H, CHCOOBn), 5.15 (s, 2H, COOC₂H₅Ph), 4.13 (dd, J = 4.0, 1.9 Hz, 1H, CHiPr), 2.25 (heptd, J = 7.1, 4.0 Hz, 1H, CMe₂), 0.81 [d, J = 7.1 Hz, 3H, CHC(H)₃(CH₃)], 0.78 [d, J = 7.1 Hz, 3H, CHCH₃(C(H)₃)]. One C₆Ar signal was not included due to overlaps resulting from insufficient resolution.

13C NMR (151 MHz, CDCl₃) δ 175.7 (s, COOBn), 166.3 (s, C=CHCOOBn), 136.2 (C₆Ar), 130.8 (C₆Ar), 129.6 (C₆Ar), 128.7 (C₆Ar), 128.5 (C₆Ar), 128.3 (C₆Ar), 126.6 (C₆Ar), 124.5 (q, JₐCF = 284.3 Hz, CF₃), 94.5 (d, CHCOOBn), 65.9 (t, CO₂C₂H₂Ph), 55.4 (d, CHiPr), 27.0 (d, CHMe₂), 20.5 [q, CHCH₃(CH₃)], 18.8 [q, CHCH₃(CH₃)].

19F NMR (564 MHz, CDCl₃) δ -79.0.

IR (film) ν = 3439 cm⁻¹ (w), 2966 (m), 1890 (w), 1717 (s, CO₂Et), 1678 (s), 1455 (m), 1382 (m), 1263 (s), 1176 (s), 1109 (s), 826 (m), 723 (s).

MS (EI, 70 eV) m/z (%) 390.1 (16) [M⁺], 283.1 (6) [(M–OBn)⁺], 214.1 (13) [C₁₂H₁₃F₃⁺], 199.1 [C₁₁H₁₀F₃⁺] (49), 145.1 [C₁₁H₁₅⁺] (15), 91.1 (100) [Bn⁺], 69.1 (23) [CF₃⁺].

MS (ESI, Orbitrap) m/z 429.1 (M+K⁺), 413.1 (M+Na⁺), 391.1 (M+H⁺).

HRMS (ESI, Orbitrap) calcd. for C₂₂H₂₂F₃O₅⁺ (M+H⁺): 391.15156; found: 391.15115.
(Z)-3ga:

$R_t = 0.35$ (P/EtOAc = 14/1, [UV, KMnO$_4$]).

$^1$H NMR (400 MHz, CDCl$_3$) 7.61 – 7.56 (m, 2H, CH$_{Ar}$, major diastereomer), 7.55 – 7.51 (m, 2H, CH$_{Ar}$, minor diastereomer), 7.48 – 7.29 (m, 8H, CH$_{Ar}$, both diastereomers), 5.27 – 5.18 (m, 2H, COOCH$_2$Ph, both diastereomers), 5.10 (d, $J = 1.8$ Hz, 1H, CHCOOBn, minor diastereomer), 5.09 (d, $J = 1.6$ Hz, 1H, CHCOOBn, major diastereomer), 3.68 (dd, $J = 7.9$, 1.6 Hz, 1H, CH$i$Pr, major diastereomer), 3.53 (dd, $J = 11.2$, 1.7 Hz, 1H, CH$i$Pr, minor diastereomer), 2.56 (hept, $J = 5.3$ Hz, 1H, CHMe$_2$, minor diastereomer), 1.73 (virt dp, $J = 7.9$, 6.6 Hz, 1H, CHMe$_2$, major diastereomer), 1.24 [d, $J = 6.5$ Hz, 3H, CH$i$Pr, minor diastereomer], 1.10 [d, $J = 6.6$ Hz, 3H, CHCH$_3$(CH$_3$), minor diastereomer], 0.81 [d, $J = 6.6$ Hz, 3H, CHCH$_3$(CH$_3$), major diastereomer], 0.75 [d, $J = 6.7$ Hz, 1H, 3H, CHCH$_3$(CH$_3$), major diastereomer].

$^{13}$C NMR (major diastereomer, 151 MHz, CDCl$_3$) $\delta$ 172.6 (s, COOBn), 164.3 (s, C=CHCOOBn), 136.48 (C$_{Ar}$), 129.7 (C$_{Ar}$), 128.7 (C$_{Ar}$), 128.60 (C$_{Ar}$), 128.2 (C$_{Ar}$), 128.11 (C$_{Ar}$), 126.6 (C$_{Ar}$), 124.2 (q$_{CF}$, $^1$J$_{CF} = 283.3$ Hz, CF$_3$), 92.6 (d, CHCOOBn), 88.9 (q$_{CF}$, $^2$J$_{CF} = 31.8$ Hz, CCF$_3$), 65.75 (t, COOCH$_2$Ph), 54.7 (d, CH$i$Pr), 26.5 (d, CHMe$_2$), 21.35 [q, CHCH$_3$(CH$_3$)], 18.6 [q, CHCH$_3$(CH$_3$)]. One C$_{Ar}$-signal was not included due to overlaps resulting from insufficient resolution.

$^{13}$C NMR (minor diastereomer, 151 MHz, CDCl$_3$) $\delta$ 173.3 (s, COOBn), 164.4 (s, C=CHCOOBn), 136.52 (C$_{Ar}$), 134.8 (C$_{Ar}$), 130.5 (C$_{Ar}$), 129.5 (C$_{Ar}$), 128.57 (C$_{Ar}$), 128.07 (C$_{Ar}$), 126.0 (C$_{Ar}$), 123.7 (q$_{CF}$, $^1$J$_{CF} = 284.0$ Hz, CF$_3$), 91.8 (d, CHCOOBn), 89.3 (q$_{CF}$, $^2$J$_{CF} = 31.8$ Hz, CCF$_3$), 65.67 (t, COOCH$_2$Ph), 60.5 (d, CH$i$Pr), 26.9 (d, CHMe$_2$), 22.3 [q, CHCH$_3$(CH$_3$)], 21.31 [q, CHCH$_3$(CH$_3$)]. One C$_{Ar}$-signal was not included due to overlaps resulting from insufficient resolution.

$^{19}$F NMR (564 MHz, CDCl$_3$) $\delta$ -74.2 (minor diastereomer), -78.3 (major diastereomer).

IR (film) $\tilde{\nu} = 3396$ cm$^{-1}$ (w), 2968 (s), 1716 (s, CO$_2$Et), 1455 (s), 1380 (m), 1263 (s), 1176 (s), 1006 (s), 815 (m), 701 (s).

MS (EI, 70 eV) m/z (%) 390.1 (13) [M$^+$], 284.1 (35), 241.1 (45), 214.1 (16) [C$_{12}$H$_{13}$F$_3^+$], 199.1 [C$_{11}$H$_{10}$F$_3^+$] (64), 145.1 [C$_{11}$H$_{15}^+$] (23), 91.1 (100) [Bn$^+$], 69.1 (28) [CF$_3^+$].

MS (ESI, Orbitrap) m/z 429.1 (M+K$^+$), 413.1 (M+Na$^+$), 391.1 (M+H$^+$).

HRMS (ESI, Orbitrap) calcd. for C$_{22}$H$_{22}$F$_3$O$_3^+$ (M+H$^+$): 391.15156; found: 391.15054.
**rac-ethyl 2-[(3R,4R)-3-butyl-4-phenyl-4-(trifluoromethyl)oxetanyliden]acetate (3ha)**

(Table 1, Entry 11)

Alkynoate 1h (103 mg, 612 µmol) and ketone 2a (86 µL, 107 mg, 612 µmol, 1.0 equiv.) were reacted in MeCN (2.4 mL) with TBD (8.5 mg, 61 µmol, 10 mol%) using standard procedure (10 min, r. t.). Flash column chromatography (Si, 2.0×22 cm, pentane/EtOAc = 50/1→20/1) gave product (E)-3ha (137 mg, 400 µmol, 65%, 14:86 d.r.) as a colourless oil and a minor product (Z)-3ha (35 mg, 102 µmol, 17%, 65:35 d.r.) as a colourless oil.

**(E)-3ha:**  
R<sub>t</sub> = 0.50 (P/EtOAc = 14/1, [UV, KMnO<sub>4</sub>]).

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 7.52 – 7.48 (m, 2H, CH<sub>Ar</sub>, both diastereomers), 7.48 – 7.40 (m, 3H, CH<sub>Ar</sub>, both diastereomers), 5.46 (d, J = 2.0 Hz, 1H, CHCOOEt, major diastereomer), 5.39 (d, J = 2.2 Hz, 1H, CHCOOEt, minor diastereomer), 4.19 – 4.08 (m, 3H, COOC<sub>2</sub>H<sub>4</sub>CH<sub>3</sub> and C<sub>4</sub>H<sub>9</sub>, both diastereomers), 4.00 (dt, J = 11.5, 2.6 Hz, 1H, C<sub>4</sub>H<sub>9</sub>, minor diastereomer), 2.55 – 2.48 (m, 1H, H<sub>alkyl</sub>, minor diastereomer), 2.13 – 2.05 (m, 1H, H<sub>alkyl</sub>, minor diastereomer), 1.93 – 1.84 (m, 1H, H<sub>alkyl</sub>, major diastereomer), 1.71 – 1.63 (m, 1H, H<sub>alkyl</sub>, minor diastereomer), 1.56 – 1.49 (m, 1H, H<sub>alkyl</sub>, major diastereomer), 1.49 – 1.38 (m, 1H, H<sub>alkyl</sub>, major diastereomer), 1.26 (t, J = 7.2 Hz, 3H, COOCH<sub>2</sub>CH<sub>3</sub>, major diastereomer), 1.24 (t, J = 7.1 Hz, 3H, COOCH<sub>2</sub>CH<sub>3</sub>, minor diastereomer), 1.12 – 1.04 (m, 2H, H<sub>alkyl</sub>, major diastereomer), 1.04 – 0.97 (m, 2H, H<sub>alkyl</sub>, major diastereomer), 0.99 (t, J = 7.3 Hz, 3H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, minor diastereomer), 0.65 (t, J = 6.9 Hz, 3H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, major diastereomer). Signals of two alkyl protons of the minor diastereomer were not included due to overlaps resulting from low resolution.

**<sup>13</sup>C NMR (major diastereomer, 151 MHz, CDCl<sub>3</sub>)** δ 176.9 (s, C=O), 130.7 (C<sub>Ar</sub>), 129.7 (C<sub>Ar</sub>), 128.6 (C<sub>Ar</sub>), 126.3 (C<sub>Ar</sub>), 124.40 (q<sub>CF</sub>, <sup>1</sup>J<sub>CF</sub> = 283.3 Hz, CF<sub>3</sub>), 93.6 (d, CHCOOEt), 89.9 (q<sub>CF</sub>, <sup>2</sup>J<sub>CF</sub> = 31.7 Hz, CCF<sub>3</sub>), 60.0 (t, COOCH<sub>2</sub>CH<sub>3</sub>), 49.6 (d, CHC<sub>4</sub>H<sub>9</sub>), 28.5 (C<sub>alkyl</sub>), 25.5 (C<sub>alkyl</sub>), 22.3 (C<sub>alkyl</sub>), 14.43 (q, CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 13.6 (C<sub>alkyl</sub>).

**<sup>13</sup>C NMR (minor diastereomer, 151 MHz, CDCl<sub>3</sub>)** δ 176.8 (s, C=O), 166.4 (s, C=CHCOOEt), 135.0 (C<sub>Ar</sub>), 129.4 (C<sub>Ar</sub>), 125.9 (C<sub>Ar</sub>), 123.73 (d q<sub>CF</sub>, <sup>1</sup>J<sub>CF</sub> = 283.6 Hz, CF<sub>3</sub>), 93.4 (d, CHCOOEt), 89.6 (q<sub>CF</sub>, <sup>2</sup>J<sub>CF</sub> = 31.7 Hz, CCF<sub>3</sub>), 59.9 (t, COOCH<sub>2</sub>CH<sub>3</sub>), 55.1 (d,
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CHC\textsubscript{4}H\textsubscript{3}), 30.4 (C\textsubscript{alkyl}), 25.3 (C\textsubscript{alkyl}), 22.8 (C\textsubscript{alkyl}), 14.41 (q, CO\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 14.0 (C\textsubscript{alkyl}). One C\textsubscript{Ar}-signal was not included due to overlaps resulting from low resolution.

\textsuperscript{19}F NMR (282 MHz, CDCl\textsubscript{3}) \(\delta\) 74.7 (minor diastereomer), -78.7 (major diastereomer).

IR (film) \(\tilde{\nu} = 3434\) cm\(^{-1}\) (w), 2958 (s), 1715 (s, CO\textsubscript{2}Et), 1457 (m), 1375 (m), 1252 (s), 1177 (s), 1002 (s), 912 (w), 726 (m), 606 (w).

MS (EI, 70 eV) \(m/z\) (%) 277.1 (35) \([\text{M}^+]\), 227.8 (12) \([\text{C}_{13}\text{H}_{18}\text{F}_{5}^+]\), 171.9 (100), 114.9 (12), 77.1 (5) \([\text{Ph}^+]\), 69.0 (30) \([\text{CF}_{3}^+]\).

HRMS (ESI, Orbitrap) calcd. for C\textsubscript{18}H\textsubscript{22}F\textsubscript{3}O\textsubscript{5} \((\text{M}^+): 343.15156\); found: 343.15149.

(Z)-3ha:

\(R_t = 0.23\) (P/EtOAc = 14/1, [UV, KMnO\textsubscript{4}]).

\(^{1}\text{H} \text{NMR} (400 \text{ MHz, CDCl}_3) \delta \ 7.53 - 7.39\) (m, 5H, CH\textsubscript{Ar}, both diastereomers), 4.96 (d, \(J = 1.6\) Hz, 1H, CHCOOEt, minor diastereomer), 4.94 (d, \(J = 1.8\) Hz, 1H, CHCOOEt, major diastereomer), 4.28 - 4.11 (m, 2H, COOCH\textsubscript{2}CH\textsubscript{3}, both diastereomers), 3.85 - 3.80 (m, 1H, CH\textsubscript{4}H\textsubscript{2}, minor diastereomer), 3.79 - 3.75 (m, 1H, CH\textsubscript{4}H\textsubscript{2}, major diastereomer), 2.09 - 1.92 (m, 2H, H\textsubscript{alkyl}, major diastereomer), 1.53 - 1.36 (m, 3H, H\textsubscript{alkyl}, both diastereomers), 1.31 (t, \(J = 7.2\) Hz, 3H, COOCH\textsubscript{2}CH\textsubscript{3}, minor diastereomer), 1.29 (t, \(J = 7.2\) Hz, 3H, COOCH\textsubscript{2}CH\textsubscript{3}, major diastereomer), 1.25 - 1.12 (m, 2H, H\textsubscript{alkyl}, minor diastereomer), 0.96 (t, \(J = 7.1\) Hz, 3H, CH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}, major diastereomer), 0.79 (t, \(J = 7.2\) Hz, 3H, CH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}, minor diastereomer). One H\textsubscript{alkyl}-signal of the minor diastereomer and one H\textsubscript{alkyl}-signal of the major diastereomer were not included due to overlaps resulting from low resolution.

\(^{13}\text{C} \text{NMR} (\text{major diastereomer}, 101 \text{ MHz, CDCl}_3) \delta \ 174.1\) (s, COOEt), 164.71 (s, C=CHCOOEt), 129.5 (C\textsubscript{Ar}), 128.6 (C\textsubscript{Ar}), 126.2 (C\textsubscript{Ar}), 125.7 (C\textsubscript{Ar}), 123.69 (q\textsubscript{CF}, \(^{1}J_{CF} = 284.1\) Hz, CF\textsubscript{3}), 90.7 (d, CHCOOEt), 89.0 (q\textsubscript{CF}, \(^{2}J_{CF} = 31.4\) Hz, CCF\textsubscript{3}), 59.9 (t, COOCH\textsubscript{2}CH\textsubscript{3}), 53.0 (d, CH\textsubscript{3}CH\textsubscript{2}H\textsubscript{2}), 30.3 (C\textsubscript{alkyl}), 27.3 (C\textsubscript{alkyl}), 22.7 (C\textsubscript{alkyl}), 14.48 (q, CO\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 13.9 (C\textsubscript{alkyl}).

\(^{13}\text{C} \text{NMR} (\text{minor diastereomer}, 101 \text{ MHz, CDCl}_3) \delta \ 173.7\) (s, COOEt), 164.73 (s, C=CHCOOEt), 135.0 (C\textsubscript{Ar}), 130.4 (C\textsubscript{Ar}), 129.6 (C\textsubscript{Ar}), 128.7 (C\textsubscript{Ar}), 91.8 (d, CHCOOEt), 60.0 (t, COOCH\textsubscript{2}CH\textsubscript{3}), 47.4 (d, CH\textsubscript{3}CH\textsubscript{2}H\textsubscript{2}), 28.7 (C\textsubscript{alkyl}), 28.4 (C\textsubscript{alkyl}), 22.4 (C\textsubscript{alkyl}), 14.50 (q, CO\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 13.8 (C\textsubscript{alkyl}). Two signals (CCF\textsubscript{3} and CF\textsubscript{3}) were not included due to low signal to noise ratio.
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$^{19}$F NMR (282 MHz, CDCl$_3$) δ -74.8 (major diastereomer), -79.0 (minor diastereomer).

IR (film) $\tilde{\nu}$ = 3435 cm$^{-1}$ (w), 2961 (m), 1716 (s, CO$_2$Et), 1456 (m), 1373 (w), 1260 (m), 1179 (s), 1040 (m), 998 (s), 714 (m), 661 (w).

MS (EI, 70 eV) $m/z$ (%) 342.2 (1) [M$^+$], 297.1 (7) [(M–OEt)$^+$], 228.2 (20) [C$_{13}$H$_5$F$_3$$^+$], 172.1 (100), 115.1 (42), 77.2 (4) [Ph$^+$], 69.2 (25) [CF$_3$$^+$].

MS (ESI, Orbitrap) $m/z$ 343.1 (M+H$^+$), 365.1 (M+Na$^+$), 381.1 (M+K$^+$).

HRMS (ESI, Orbitrap) calcd. for C$_{18}$H$_{22}$F$_3$O$_3$ (M+H$^+$): 343.15156; found: 343.15091.

3.2 Spectroscopic Data Related to Table 2

**rac-ethyl 2-[(3R,4R)-4-(4-methoxyphenyl)-3-methyl-4-(trifluoromethyl)oxetanyliden] acetate (3ab)** (Table 2, Entry 1)

Allenolate 1a (113 mg, 553 µmol) and ketone 2b (70 mg, 553 µmol, 1.0 equiv.) were reacted in MeCN (2.2 mL) with TBD (7.7 mg, 55 µmol, 10 mol%) using standard procedure (10 min, r. t.). The main product ($E$)-3ab (138 mg, 418 µmol, 76%, 17:83 d.r.) was obtained as a colourless oil after purification of the crude reaction mixture by flash column chromatography (Si, 2.0×20 cm, pentane/EtOAc = 20/1). The yield of the minor isomer ($Z$)-3ab (9%, 34:66 d.r.) was determined from the $^1$H NMR spectrum of the crude reaction mixture based on isolated product ($E$)-3ab.

($E$)-3ab:

$R_f$ = 0.45 (P/EtOAc = 14/1, [UV, KMnO$_4$]).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.32 (d, $J$ = 8.6 Hz, 2H, CH$_{Ar}$, both diastereomers), 6.97 (d, $J$ = 9.1 Hz, 2H, CH$_{Ar}$, major diastereomer), 6.94 (d, $J$ = 8.9 Hz, 2H, CH$_{Ar}$, minor diastereomer), 5.40 (d, $J$ = 1.9 Hz, 1H, CHCOOEt, major diastereomer), 5.37 (d, $J$ = 2.2 Hz, 1H, CHCOOEt, minor diastereomer), 4.17 (qd, $J$ = 7.4, 1.9 Hz, 1H, CHMe, major diastereomer), 4.17 − 4.06 (m, 2H, CO$_2$CH$_2$CH$_3$ both diastereomers and 1H, CHMe minor diastereomer), 3.82 (s, 3H, OCH$_3$, major diastereomer), 3.81 (s, 3H, OCH$_3$, minor diastereomer), 1.74 (dq, $J$ = 7.6, 1.7 Hz, 3H, CHCH$_3$, minor diastereomer), 1.26 (t, $J$ = 7.1 Hz, 3H, CO$_2$CH$_2$CH$_3$, major diastereomer), 1.25 (t, $J$ = 7.1 Hz, 3H, CO$_2$CH$_2$CH$_3$, minor diastereomer), 1.16 (d, $J$ = 7.3 Hz, 3H, CHCH$_3$, major diastereomer).
$^{13}$C NMR (major diastereomer, 101 MHz, CDCl$_3$) δ 178.2 (s, COOEt), 166.5 (s, C=CHCOOEt), 160.46 (s, C$_A$OMe), 132.8 (C$_A$), 127.5 (C$_A$), 124.3 (q$_{CF}$, $^1J_{CF}$ = 283.1 Hz, CF$_3$), 114.1 (C$_A$), 93.1 (d, CHCOOEt), 89.4 (q$_{CF}$, $^2J_{CF}$ = 31.8 Hz, CCF$_3$), 59.94 (t, CO$_2$CH$_2$CH$_3$), 55.36 (q, OCH$_3$), 43.9 (d, CHCH$_3$), 14.39 (q, CO$_2$CH$_2$CH$_3$), 7.2 (q, CHCH$_3$).

$^{13}$C NMR (minor diastereomer, 101 MHz, CDCl$_3$) δ 177.8 (s, COOEt), 166.4 (s, C=CHCOOEt), 126.9 (C$_A$), 123.7 (q$_{CF}$, $^1J_{CF}$ = 283.5 Hz, CF$_3$), 122.5 (C$_A$), 59.91 (t, CO$_2$CH$_2$CH$_3$), 55.42 (q, OCH$_3$), 49.0 (d, CHCH$_3$), 14.40 (q, CO$_2$CH$_2$CH$_3$), 11.4 (q, CHCH$_3$). Two signals of the minor diastereomer CHCOOEt and CCF$_3$ were not included due to overlaps resulting from low signal to noise ratio and low resolution.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -75.2 (minor diastereomer), -80.0 (major diastereomer).

IR (film) $\tilde{\nu}$ = 3435 cm$^{-1}$ (w), 2980 (m), 2055 (w), 1898 (w), 1716 (s, CO$_2$Et), 1613 (m), 1458 (m), 1380 (m), 1254 (s), 1178 (s), 1110 (s), 918 (m), 720 (w), 590 (w).

MS (EI, 70 eV) m/z (%) 330.1 (8) [M$^+$], 285.1 (3) [(M–OEt)$^+$], 257.1 (16) [(M–COOEt)$^+$], 216.1 (100) [C$_{11}$H$_{11}$F$_3$O$^+$], 147.1 (37), 115.0 (10), 69.1 (16) [CF$_3$$^+$].

MS (ESI, Orbitrap) m/z 311.1 (M+H$^+$).

HRMS (ESI, Orbitrap) calcd. for C$_{16}$H$_{18}$F$_3$O$_4$ (M+H$^+$): 331.11517; found: 331.11475.

(Z)-3ab:

This isomer was not isolated in pure form. Therefore, the signals were assigned from the crude reaction mixture. $^1$H NMR (400 MHz, CDCl$_3$) δ 4.90 (d, $J$ = 1.5 Hz, 1H, CHCOOEt, major diastereomer), 4.89 (d, $J$ = 1.8 Hz, 1H, CHCOOEt, minor diastereomer), 3.90 (s, 3H, OCH$_3$, major diastereomer), 1.55 (dq, $J$ = 7.5, 1.5 Hz, 3H, CHCH$_3$, minor diastereomer), 1.00 (d, $J$ = 7.4 Hz, 3H, CHCH$_3$, major diastereomer).
rac-ethyl 2-[(3S,4R)-4-(2-methoxyphenyl)-3-methyl-4-(trifluoromethyl)oxetanyliden] acetate (3ac) (Table 2, Entry 2)

Allenolate 1a (61 mg, 483 µmol) and ketone 2c (101 mg, 494 µmol, 1.0 equiv.) were reacted in MeCN (1.9 mL) with TBD (10.1 mg, 72 µmol, 15 mol%) using standard procedure (1 h, r.t.). The main product (E)-3ac (64 mg, 195 µmol, 40%, 81:19 d.r.) was obtained as a colourless oil after purification of the crude reaction mixture by flash column chromatography (Si, 2.0×20 cm, pentane/EtOAc = 20/1). The yield of the minor isomer (Z)-3ac (10%, 89:11 d.r.) was determined from the 1H NMR spectrum of the crude reaction mixture based on isolated product (E)-3ac.

(E)-3ac:

\[ R_t = 0.41 \ (P/\text{EtOAc} = 14/1, [\text{UV}, \text{KMnO}_4]). \]

1H NMR (600 MHz, CDCl3) 7.46 (dd, J = 7.7, 1.7 Hz, 1H, CHAr, minor diastereomer), 7.44 – 7.37 (m, 2H, CHAr, major diastereomer and 1H, CHAr, minor diastereomer), 7.06 (t, J = 7.6 Hz, 1H, CHAr, minor diastereomer), 7.03 (t, J = 7.5 Hz, 1H, CHAr, major diastereomer), 6.953 (d, J = 8.2 Hz, 1H, CHAr, minor diastereomer), 6.946 (d, J = 8.3 Hz, 1H, CHAr, major diastereomer), 5.33 (d, J = 2.2 Hz, 1H, COEt, major diastereomer), 4.22 – 4.09 (m, 2H, CO2C2H5 and 1H, CHMe, both diastereomers), 3.86 (s, 3H, OCH3, major diastereomer), 3.81 (s, 3H, OCH3, minor diastereomer), 1.74 (dd, J = 7.5, 1.7 Hz, 3H, CHCH3, major diastereomer), 1.35 (d, J = 7.3 Hz, 3H, CHCH3, minor diastereomer), 1.28 (t, J = 7.2 Hz, 3H, CO2CH2CH3, minor diastereomer), 1.25 (t, J = 7.1 Hz, 3H, CO2CH2CH3, major diastereomer). One CHCOOEt (minor diastereomer) was not included due to overlaps resulting from insufficient resolution.

13C NMR (major diastereomer, 151 MHz, CDCl3) δ 179.1 (s, COOEt), 166.67 (s, C=CHCOOEt), 156.5 (s, CAr,OMe), 131.1 (CAr), 128.2 (CAr), 123.8 (qCF, JCF = 284.6 Hz, CF3), 122.8 (CAr), 120.6 (CAr), 111.3 (CAr), 92.4 (d, CHCOOEt), 88.5 (qCF, JCF = 31.8 Hz, CCF3), 59.8 (t, CO2CH2CH3), 55.6 (q, OCH3), 47.9 (d, CHCH3), 14.47 (q, CO2CH2CH3), 11.0 (q, CHCH3).

13C NMR (minor diastereomer, 151 MHz, CDCl3) δ 179.6 (s, COOEt), 166.69 (s, C=CHCOOEt), 156.2 (s, CAr,OMe), 131.2 (CAr), 128.6 (CAr), 124.4 (qCF, JCF = 285.1 Hz, CF3), 121.0 (CAr), 119.5 (CAr), 111.4 (CAr), 92.1 (d, CHCOOEt), 90.7 (qCF, JCF = 32.3 Hz,
CCF₃, 59.9 (t, CO₂CH₂CH₃), 55.3 (q, OCH₃), 44.4 (d, CHCH₃), 14.44 (q, CO₂CH₂CH₃), 12.0 (q, CHCH₃).

¹⁹F NMR (282 MHz, CDCl₃) δ -75.4 (minor diastereomer), -79.0 (major diastereomer).

IR (film) ν = 3434 cm⁻¹ (w), 2980 (s), 1716 (s, CO₂Et), 1677 (s), 1464 (s), 1376 (s), 1259 (s), 1179 (s), 1113 (s), 918 (m), 714 (s), 655 (m).

MS (EI, 70 eV) m/z (%) 330.1 (12) [M⁺], 285.0 (7) [(M-OEt)⁺], 216.1 (79) [C₁₁H₁₁F₃O⁺], 196.0 (100), 115.0 (17), 69.1 (18) [CF₃⁺].

MS (ESI, Orbitrap) m/z 369.1 (M+K⁺), 353.1 (M+Na⁺), 331.1 (M+H⁺).

HRMS (ESI, Orbitrap) calcd. for C₁₆H₁₈F₃O₄⁺ (M+H⁺): 331.11517; found: 331.11484.

This isomer was not isolated in pure form. Therefore, the signals were assigned from the crude reaction mixture. ¹H NMR (400 MHz, DMSO-d6) δ 5.08 (d, J = 1.4 Hz, 1H, CHCOOEt, minor diastereomer), 5.04 (d, J = 1.8 Hz, 1H, CHCOOEt, major diastereomer), 1.49 (dq, J = 7.5, 1.5 Hz, 3H, CHCH₃, major diastereomer).

**rac-ethyl 2-[(3R,4S)-3-methyl-4-(2-thienyl)-4-(trifluoromethyl)oxetanylid]acetate (3ad)** (Table 2, Entry 3)

Allenoate 3ad (65 mg, 515 µmol) and ketone 3ad (92 mg, 515 µmol, 1.0 equiv.) were reacted in MeCN (2.1 mL) with TBD (7.2 mg, 51 µmol, 10 mol%) using standard procedure (1 h, r.t.). The main product (E)-3ad (113 mg, 368 µmol, 71%, 11:89 d.r.) was obtained after purification of the crude reaction mixture by flash column chromatography (Si, 2.0×20 cm, pentane/EtOAc = 20/1) as a colourless oil which solidified upon standing at -20 °C. The yield of the minor isomer (Z)-3ad (7%, 35:65 d.r.) was determined from the ¹H NMR spectrum of the crude reaction mixture based on isolated product (E)-3ad.

(E)-3ad:

Rᵣ = 0.53 (P/EtOAc = 14/1, [UV, KMnO₄]).

m.p. 52-55 °C (CHCl₃)

¹H NMR (400 MHz, CDCl₃) δ 7.45 (dd, J = 4.9, 1.4 Hz, 1H, CH₃Ar, major diastereomer), 7.43 (dd, J = 5.1, 1.2 Hz, 1H, CH₃Ar, minor
diastereomer), 7.20 (d, J = 3.7 Hz, 1H, CHAr, minor diastereomer), 7.15 – 7.10 (m, 2H, CHAr, major diastereomer), 7.06 (dd, J = 5.1, 3.7 Hz, 1H, CHAr, minor diastereomer), 5.44 (d, J = 1.9 Hz, 1H, CHCOOEt, major diastereomer), 5.41 (d, J = 2.2 Hz, 1H, CHCOOEt, minor diastereomer), 4.20 (qd, J = 7.4, 1.9 Hz, 1H, CHMe, major diastereomer), 4.19 – 4.08 (m, 2H, CO₂CH₂CH₃ both diastereomers and 1H, CHMe minor diastereomer), 1.70 (dq, J = 7.5, 1.8 Hz, 3H, CHCH₃, minor diastereomer), 1.265 (t, J = 7.1 Hz, 3H, CO₂CH₂CH₃, major diastereomer), 1.257 (t, J = 7.1 Hz, 3H, CO₂CH₂CH₃, minor diastereomer), 1.21 (d, J = 7.4 Hz, 3H, CHCH₃, major diastereomer).

$^{13}$C NMR (major diastereomer, 101 MHz, CDCl₃) δ 177.3 (s, COOEt), 166.29 (s, C=CHCOOEt), 132.8 (C₆Ar), 127.8 (C₆Ar), 127.49 (C₆Ar), 126.8 (qCF, $^1J_{CF}$ = 1.4 Hz, C₆Ar), 123.7 (qCF, $^1J_{CF}$ = 282.7 Hz, CF₃), 94.0 (d, CHCOOEt), 88.8 (qCF, $^2J_{CF}$ = 33.7 Hz, CCF₃), 60.1 (t, CO₂CH₂CH₃), 44.8 (d, CHCH₃), 14.39 (q, CO₂CH₂CH₃), 12.4 (q, CHCH₃).

$^{13}$C NMR (minor diastereomer, 101 MHz, CDCl₃) δ 177.0 (s, COOEt), 166.28 (s, C=CHCOOEt), 136.6 (C₆Ar), 127.9 (C₆Ar), 127.53 (C₆Ar), 127.4 (C₆Ar), 123.3 (qCF, $^1J_{CF}$ = 283.7 Hz, CF₃), 93.8 (d, CHCOOEt), 60.0 (t, CO₂CH₂CH₃), 50.7 (d, CHCH₃), 14.41 (q, CO₂CH₂CH₃), 11.0 (q, CHCH₃). Two signals of the minor diastereomer CHCOOEt and CCF₃ were not included due to overlaps resulting from low signal to noise ratio and low resolution.

$^{19}$F NMR (282 MHz, CDCl₃) δ -74.8 (minor diastereomer), -80.7 (major diastereomer).

IR (film) $\tilde{\nu}$ = 3385 cm$^{-1}$ (w), 3104 (w), 2984 (s), 1718 (s, CO₂Et), 1681 (s), 1447 (m), 1376 (s), 1236 (s), 1177 (s), 1109 (s), 714 (s), 607 (w)

MS (EI, 70 eV) m/z (%) 306.1 (14) [M$^+$], 261.0 (5) [(M–OEt)$^+$], 192.0 (100) [C₈H₂F₃S$^+$], 123.0 (52) [C₇H₇S$^+$], 115.1 (34), 69.1 (9) [CF₃$^+$].

MS (ESI, Orbitrap) m/z 329.0 (M+Na$^+$), 307.1 (M+H$^+$).

HRMS (ESI, Orbitrap) calcd. for C$_{13}$H$_{13}$F$_{3}$NaO$_{3}$S$^+$ (M+Na$^+$): 329.04297; found: 329.04251.

(Z)-3ad:

This isomer was not isolated in pure form. Therefore, the signals were assigned from the crude reaction mixture. $^1$H NMR (400 MHz, CDCl₃) δ 4.90 (d, J = 1.6 Hz, 1H, CHCOOEt, major diastereomer), 4.89 (d, J = 1.8 Hz, 1H, CHCOOEt, minor diastereomer), 1.46 (d, J = 7.5 Hz, 3H, CHCH₃, minor diastereomer), 0.99 (d, J = 7.5 Hz, 3H, CHCH₃, major diastereomer).
**rac-ethyl 2-[(3R,4R)-4-(4-isopropylphenyl)-3-methyl-4-(trifluoromethyl)oxetanyliden] acetate (3ae)** (Table 2, Entry 4)

Allenolate 1a (47 mg, 372 µmol) and ketone 2e (83 mg, 384 µmol, 1.0 equiv.) were reacted in MeCN (2.2 mL) with TBD (5.2 mg, 37 µmol, 10 mol%) using standard procedure (10 min, r. t.). The main product (E)-3ae (94 mg, 274 µmol, 74%, 21:79 d.r.) was obtained as a colourless oil after purification of the crude reaction mixture by flash column chromatography (Si, 2.0×20 cm, pentane/EtOAc = 20/1). The yield of the minor isomer (Z)-3ae (14%, 45:55 d.r.) was determined from the $^1$H NMR spectrum of the crude reaction mixture based on isolated product (E)-3ae.

*(E)-3ae:

$R_t = 0.68$ (P/EtOAc = 14/1, [UV, KMnO$_4$]).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.34 – 7.27 (m, 4H, CH$_{Ar}$, both diastereomers), 5.41 (d, $J = 1.9$ Hz, 1H, CHCOOEt, major diastereomer), 5.37 (d, $J = 2.2$ Hz, 1H, CHCOOEt, minor diastereomer), 4.20 (dq, $J = 7.4$, 1.9 Hz, 1H, CHMe, major diastereomer), 4.18 – 4.10 (m, 2H, CO$_2$CH$_2$CH$_3$ both diastereomers and 1H, CHMe minor diastereomer), 2.94 (hept, $J = 6.9$ Hz, 1H, CHMe$_2$, major diastereomer), 2.93 (hept, $J = 6.8$ Hz, 1H, CHMe$_2$, minor diastereomer), 1.76 (dq, $J = 7.7$, 1.8 Hz, 3H, CHCH$_3$, minor diastereomer), 1.30 – 1.23 [m, 3H, CO$_2$CH$_2$CH$_3$ and 6H, CH(CH$_3$)$_2$ both diastereomers], 1.17 (d, $J = 7.5$ Hz, 3H, CHCH$_3$, major diastereomer).

$^{13}$C NMR (major diastereomer, 151 MHz, CDCl$_3$) $\delta$ 178.3 (s, COOEt), 166.6 (s, C=CHCOOEt), 150.3 (s, C$_{Ar'd}$Pr), 132.4 (C$_{Ar}$), 126.75 (C$_{Ar}$), 126.08 (C$_{Ar}$), 124.3 (q$_{CF}$, $^1$J$_{CF} = 283.1$ Hz, CF$_3$), 93.11 (d, CHCOOEt), 89.6 (q$_{CF}$, $^2$J$_{CF} = 31.6$ Hz, CCF$_3$), 60.0 (t, CO$_2$CH$_2$CH$_3$), 43.9 (d, CHCH$_3$), 34.0 (d, CHMe$_2$), 23.94 [q, CH(CH$_3$)$_2$], 14.43 (q, CO$_2$CH$_2$CH$_3$), 13.0 (q, CHCH$_3$).

$^{13}$C NMR (minor diastereomer, 151 MHz, CDCl$_3$) $\delta$ 177.8 (s, COOEt), 166.4 (s, C=CHCOOEt), 150.4 (s, C$_{Ar'd}$Pr), 127.9 (C$_{Ar}$), 126.71 (C$_{Ar}$), 125.5 (C$_{Ar}$), 123.7 (q$_{CF}$, $^1$J$_{CF} = 283.6$ Hz, CF$_3$), 93.07 (d, CHCOOEt), 88.7 (q$_{CF}$, $^2$J$_{CF} = 31.0$ Hz, CCF$_3$), 59.9 (t, CO$_2$CH$_2$CH$_3$), 49.1 (d, CHCH$_3$), 34.1 (d, CHMe$_2$), 23.91 [q, CH(CH$_3$)$_2$], 14.44 (q, CO$_2$CH$_2$CH$_3$), 11.4 (q, CHCH$_3$).

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -75.0 (minor diastereomer), -79.8 (major diastereomer).
IR (film) $\tilde{\nu} = 3430$ cm$^{-1}$ (w), 2966 (s), 1915 (w), 1718 (s, CO$_2$Et), 1679 (s), 1461 (m), 1375 (s), 1264 (s), 1176 (s), 1109 (s), 920 (m), 715 (m).

MS (EI, 70 eV) m/z (%) 342.1 (1) [M$^+$], 297.1 (4) [(M-OEt)$^+$], 228.1 (48) [C$_{13}$H$_{15}$F$_3^+$], 213.1 (100), 115.0 (9), 69.1 (13) [CF$_3^+$].

MS (ESI, Orbitrap) m/z 365.1 (M+Na$^+$), 343.1 (M+H$^+$).

HRMS (ESI, Orbitrap) calcd. for C$_{18}$H$_{21}$F$_3$NaO$_3^+$ (M+Na$^+$): 365.13350; found: 365.13391.

(Z)-3ae:

This isomer was not isolated in pure form. Therefore, the signals were assigned from the crude reaction mixture. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 4.89 (d, $J = 1.5$ Hz, 1H, CHCOOEt, major diastereomer), 4.87 (d, $J = 1.7$ Hz, 1H, CHCOOEt, minor diastereomer), 1.56 (dq, $J = 7.6$, 1.4 Hz, 3H, CHC$_3$H$_3$, minor diastereomer), 1.00 (d, $J = 7.4$ Hz, 3H, CHC$_3$H$_3$, major diastereomer).

Rac-ethyl 2-[(3R,4R)-4-(4-chlorophenyl)-3-methyl-4-(trifluoromethyl)oxetanyliden] acetate (3af) (Table 2, Entry 5)

Allenoate 1a (73 mg, 579 µmol) and ketone 2f (121 mg, 579 µmol, 1.0 equiv.) were reacted in MeCN (2.3 mL) with TBD (8.1 mg, 58 µmol, 10 mol%) using standard procedure (25 min, r. t., TLC showed incomplete conversion of 1a). The main product (E)-3af (104 mg, 312 µmol, 54%, 25:75 d.r.) was obtained as a colourless oil after purification of the crude reaction mixture by flash column chromatography (Si, 2.0×20 cm, pentane/EtOAc = 25/1). The yield of the minor isomer (Z)-3af (6%, 48:52 d.r.) was determined from the $^1$H NMR spectrum of the crude reaction mixture based on isolated product (E)-3af.

(E)-3af:

$R_f = 0.63$ (P/EtOAc = 14/1, [UV, KMnO$_4$]).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44 (d, $J = 8.9$ Hz, 2H, CH$_2$Ar, major diastereomer), 7.41 (d, $J = 8.8$, Hz, 2H, CH$_2$Ar, minor diastereomer), 7.28 (d, $J = 8.2$ Hz, 2H, CH$_2$Ar both diastereomers), 5.42 (d, $J = 1.9$ Hz, 1H, CHCOOEt, major diastereomer), 5.39 (d, $J = 2.2$ Hz, 1H, CHCOOEt, minor diastereomer), 4.20 (qd, $J = 7.4$, 1.9 Hz, 1H, CHMe, major
diastereomer), 4.18 – 4.06 (m, 2H, CO₂CH₂CH₃ both diastereomers and 1H, CHMe minor diastereomer), 1.75 (dq, J = 7.5, 1.7 Hz, 3H, CHCH₃, minor diastereomer), 1.26 (t, J = 7.2 Hz, 3H, CO₂CH₂CH₃, major diastereomer), 1.25 (t, J = 7.1 Hz, 3H, CO₂CH₂CH₃, minor diastereomer), 1.16 (d, J = 7.4 Hz, 3H, CHCH₃, major diastereomer).

13C NMR (major diastereomer, 101 MHz, CDCl₃) δ 177.5 (s, COOEt), 166.4 (s, C=CHCOOEt), 135.94 (C₆), 129.1 (C₆), 127.62 (C₆), 126.96 (C₆), 124.0 (q, JCF = 283.2 Hz, CF₃), 93.59 (d, CHCOOEt), 89.1 (q, JCF = 32.4 Hz, CCF₃), 60.09 (t, CO₂CH₂CH₃), 43.9 (d, C₆H₃), 14.43 (q, CO₂CH₂CH₃), 13.04 (q, CH₃C₆H₃).

13C NMR (minor diastereomer, 101 MHz, CDCl₃) δ 177.0 (s, COOEt), 166.3 (s, C=CHCOOEt), 135.86 (C₆), 129.3 (C₆), 129.0 (C₆), 93.60 (d, CHCOOEt), 60.06 (t, CO₂CH₂CH₃), 49.1 (d, CHCH₃), 14.45 (q, CO₂CH₂CH₃), 11.41 (q, CH₃C₆H₃). Only the most characteristic 13C-signals were given.

19F NMR (282 MHz, CDCl₃) δ -75.0 (minor diastereomer), -79.7 (major diastereomer).

IR (film) ν = 2985 cm⁻¹ (s), 2108 (w), 1910 (w), 1719 (s, CO₂Et), 1681 (s), 1493 (s), 1376 (s), 1263 (s), 1179 (s), 1103 (s), 919 (m), 742 (m), 611 (w).

MS (EI, 70 eV) m/z (%) 334.1 (2) [M⁺], 289.1 (5) [(M–OEt)⁺], 223.1 (4) [(M–Ar)⁺], 220.1 (100) [C₁₀H₈ClF₃⁺], 185.1 (37), 165.1 (21), 111.1 (4) [Ar⁺], 69.2 (30) [CF₃⁺].

MS (ESI, Orbitrap) m/z 357.0 (M+Na⁺), 335.1 (M+H⁺).

HRMS (ESI, Orbitrap) calcd. for C₁₅H₁₄ClF₃O₃⁺ (M+H⁺): 335.06563; found: 335.06546.

(Z)-3af: This isomer was not isolated in pure form. Therefore, the signals were assigned from the crude reaction mixture. 1H NMR (400 MHz, CDCl₃) δ 4.92 (d, J = 1.6 Hz, 1H, CHCOOEt, minor diastereomer), 4.91 (d, J = 1.8 Hz, 1H, CHCOOEt, major diastereomer), 1.55 (dq, J = 7.5, 1.5 Hz, 3H, CHCH₃, minor diastereomer), 1.00 (d, J = 7.3 Hz, 3H, CHCH₃, major diastereomer).
**rac-ethyl 2-[(3R,4R)-3-methyl-4-(trifluoromethyl)-4-[4-(trifluoromethyl)phenyl]oxetanyliden]acetate (3ag)** (Table 2, Entry 6)

Allenolate 1a (62 mg, 491 µmol) and ketone 2g (125 mg, 516 µmol, 1.0 equiv.) were reacted in MeCN (2 mL) with TBD (13.7 mg, 98 µmol, 20 mol%) using standard procedure (1 h 40 min, r. t., TLC showed incomplete conversion of 1a). The main product (E)-3ag (66 mg, 179 µmol, 36%, 22:78 d.r.) was obtained as a colourless oil after purification of the crude reaction mixture by flash column chromatography (Si, 2.0×20 cm, pentane/EtOAc = 30/1→20/1) three times. The yield of the minor isomer (Z)-3ag (4%, 48:52 d.r.) was determined from the 1H-NMR spectrum of the crude reaction mixture based on isolated product (E)-3ag.

(E)-3ag:

\[ R_f = 0.41 \text{(P/EtOAc = 14/1, [UV, KMnO}_4\text{])}. \]

(E)-3ag: major diastereomer

\[ \text{^1H NMR (400 MHz, CDCl}_3 \text{) } \delta \text{ 7.72 (d, } J = 8.3 \text{ Hz, 2H, CH}_2\text{Ar, both diastereomers), 7.54 (d, } J = 8.1 \text{ Hz, 2H, CH}_2\text{Ar, both diastereomers), 5.43 (d, } J = 1.9 \text{ Hz, CHCOOEt, major diastereomer), 5.40 (d, } J = 2.2 \text{ Hz, CHCOOEt, minor diastereomer), 4.24 (qd, } J = 7.4, 1.9 \text{ Hz, 1H, CHMe, major diastereomer), 4.20 – 4.04 (m, 2H, CO}_2\text{CH}_2\text{CH}_3 \text{ both diastereomers and 1H, CHMe minor diastereomer), 1.77 (dq, } J = 7.5, 1.6 \text{ Hz, 3H, CHCH}_3 \text{, minor diastereomer), 1.26 (t, } J = 7.1 \text{ Hz, 3H, CO}_2\text{CH}_2\text{CH}_3 \text{, major diastereomer), 1.22 (t, } J = 7.0 \text{ Hz, 3H, CO}_2\text{CH}_2\text{CH}_3 \text{, minor diastereomer), 1.16 (d, } J = 7.4 \text{ Hz, 3H, CHCH}_3 \text{, major diastereomer).} \]

(E)-3ag: minor diastereomer

\[ \text{^13C NMR (major diastereomer, 101 MHz, CDCl}_3 \text{) } \delta \text{ 177.1 (s, COOEt), 166.3 (s, C=CHCOOEt), 134.7 (C}_2\text{Ar}, 131.94 (q}_{CF}, 2J_{CF} = 32.8 \text{ Hz, C}_2\text{ArCF}_3 \text{), 126.8 (C}_2\text{Ar), 125.79 (q}_{CF}, 3J_{CF} = 3.6 \text{ Hz, CH}_2\text{Ar), 123.9 (q}_{CF}, 1J_{CF} = 283.6 \text{ Hz, CF}_3 \text{), 123.8 (q}_{CF}, 1J_{CF} = 272.3 \text{ Hz, CF}_3 \text{), 93.81 (d, CHCOOEt), 89.04 (q}_{CF}, 2J_{CF} = 32.4 \text{ Hz, C}_2\text{CF}_3 \text{), 60.16 (t, CO}_2\text{CH}_2\text{CH}_3 \text{), 44.1 (d, CHCH}_3 \text{), 14.4 (q, CO}_2\text{CH}_2\text{CH}_3 \text{), 13.1 (q, CHCH}_3 \text{).} \]

(E)-3ag: minor diastereomer

\[ \text{^13C NMR (minor diastereomer, 101 MHz, CDCl}_3 \text{) } \delta \text{ 176.6 (s, COOEt), 166.2 (s, C=CHCOOEt), 126.1 (C}_2\text{Ar), 93.84 (d, CHCOOEt), 60.13 (t, CO}_2\text{CH}_2\text{CH}_3 \text{), 48.2 (d, CHCH}_3 \text{), 11.4 (q, CHCH}_3 \text{). Only the most characteristic ^13C-signals were given.} \]

\[ \text{^19F NMR (376 MHz, CDCl}_3 \text{) } \delta \text{ -63.0 (C}_2\text{ArCF}_3 \text{, both diastereomers), -74.7 [C(Ar)CF}_3 \text{ minor diastereomer], -79.5 [C(Ar)CF}_3 \text{ major diastereomer].} \]
IR (film) $\tilde{\nu} = 3444$ cm$^{-1}$ (m), 2984 (s), 1718 (s, CO$_2$Et), 1459 (s), 1380 (s), 1328 (s), 1177 (s), 1119 (s), 921 (m), 721 (m), 608 (m).

MS (EI, 70 eV) $m/z$ (%) 368.1 (5) [M$^+$], 323.0 (13) [(M–OEt)$^+$], 254.0 (100) [C$_{11}$H$_5$F$_6^+$], 185.0 [C$_{10}$H$_8$F$_3^+$] (79), 145.0 [Ar$^+$] (8), 115.0 (22), 69.1 (34) [CF$_3^+$].

MS (ESI, Orbitrap) $m/z$ 391.1 (M+Na$^+$), 369.1 (M+H$^+$).

HRMS (ESI, Orbitrap) calcd. for C$_{16}$H$_{15}$F$_6$O$_3^+$ (M+H$^+$): 369.09199; found: 369.09167.

$(Z)$-3ag:
This isomer was not isolated in pure form. Therefore, the signals were assigned from the crude reaction mixture. $^1$H NMR (400 MHz, CDCl$_3$) δ 4.93 (d, $J = 1.6$ Hz, 1H, CHCOOEt, minor diastereomer), 4.91 (d, $J = 1.8$ Hz, 1H, CHCOOEt, major diastereomer), 1.56 (dq, $J = 7.5$, 1.5 Hz, 3H, CHCH$_3$, major diastereomer).

rac-ethyl 2-[(3R,4R)-4-(bromophenyl)-3-methyl-4-(trifluoromethyl)oxetanylidene acetate (3ah) (Table 2, Entry 7)

Allenolate 1a (27 mg, 214 µmol) and ketone 2h (54 mg, 214 µmol, 1.0 equiv.) were reacted in MeCN (0.8 mL) with TBD (3 mg, 21 µmol, 10 mol%) using standard procedure (20 min, r. t., TLC showed incomplete conversion of 1a). The main product (E)-3ah (49 mg, 129 µmol, 60%, 19:81 d.r.) was obtained as a colourless oil after purification of the crude reaction mixture by flash column chromatography (Si, 2.0×20 cm, pentane/EtOAc = 24/1). The yield of the minor isomer (Z)-3ah (7%, 43:57 d.r.) was determined from the $^1$H NMR spectrum of the crude reaction mixture based on isolated product (E)-3ah.

(E)-3ah:
$R_t = 0.58$ (P/EtOAc = 14/1, [UV, KMnO$_4$]).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.60 (d, $J = 8.8$ Hz, 2H, CH$_{Ar}$, major diastereomer), 7.57 (d, $J = 8.7$, Hz, 2H, CH$_{Ar}$, minor diastereomer), 7.28 (d, $J = 8.3$ Hz, 2H, CH$_{Ar}$, both diastereomers), 5.42 (d, $J = 1.9$ Hz, 1H, CHCOOEt, major diastereomer), 5.39 (d, $J = 2.2$ Hz, 1H, CHCOOEt, minor diastereomer), 4.20 (qd, $J = 7.4$, 1.9 Hz, 1H, CHMe, major diastereomer), 4.18 − 4.06 (m, 2H, CO$_2$CH$_3$CH$_3$ both...
Supporting information

diastereomers and 1H, CHMe minor diastereomer), 1.75 (dq, J = 7.5, 1.7 Hz, 3H, CHCH₃, minor diastereomer), 1.25 (t, J = 7.1 Hz, 3H, CO₂CH₂CH₃, major diastereomer), 1.22 (t, J = 7.0 Hz, 3H, CO₂CH₂CH₃, minor diastereomer), 1.16 (d, J = 7.4 Hz, 3H, CHCH₃, major diastereomer).

¹³C NMR (major diastereomer, 101 MHz, CDCl₃) δ 177.5 (s, COOEt), 166.35 (s, C=CHCOOEt), 132.04 (C₆), 129.79 (C₆), 127.86 (C₆), 124.17 (C₆), 123.9 (q, CF₃, ¹JCF = 283.1 Hz, CF₃), 93.60 (d, CHCOOEt), 89.1 (q, CF₃, ²JCF = 31.9 Hz, CCF₃), 60.10 (t, CO₂CH₂CH₃), 43.8 (d, CH₃), 14.43 (q, CH₂), 13.0 (q, CH₂).

¹³C NMR (minor diastereomer, 101 MHz, CDCl₃) δ 176.9 (s, COOEt), 166.29 (s, C=CHCOOEt), 134.1 (C₆), 131.96 (C₆), 127.2 (C₆), 124.03 (C₆), 93.61 (d, CHCOOEt), 60.06 (t, CO₂CH₂CH₃), 49.1 (d, CHCH₃), 14.44 (q, CH₂), 11.4 (q, CH₂). Two signals (CCF₃ and CF₃) were not included due to low signal to noise ratio.

IR (film) ʋ = 3433 cm⁻¹ (w), 2984 (m), 2105 (w), 1911 (w), 1718 (s, CO₂Et), 1681 (s), 1461 (m), 1379 (m), 1252 (m), 1180 (s), 1109 (s), 918 (m), 737 (m), 562 (w).

MS (EI, 70 eV) m/z (%) 378.1 (2) [M⁺], 333.0 (6) [(M-OEt)⁺], 305.0 (7) [(M-COOEt)⁺], 264.0 (100) [C₁₀H₈BrF₃⁺], 185.1 (31), 165.1 (40), 115.1 (40), 69.2 (39) [CF₃⁺].

MS (ESI, Orbitrap) m/z 417.2 (M+K⁺), 400.1 (M+Na⁺), 379.0 (M+H⁺).

HRMS (ESI, Orbitrap) calcd. for C₁₅H₁₅BrF₃O₃⁺ (M+H⁺): 379.01512; found: 379.01425.

(Z)-3ah:
This isomer was not isolated in pure form. Therefore, the signals were assigned from the crude reaction mixture. ¹H NMR (400 MHz, CDCl₃) δ 4.93 (d, J = 1.5 Hz, 1H, CHCOOEt, minor diastereomer), 4.91 (d, J = 1.8 Hz, 1H, CHCOOEt, major diastereomer), 1.56 (dq, J = 7.5, 1.5 Hz, 3H, CHCH₃, minor diastereomer).
3.3 Spectroscopic Data Related to Scheme 1

*rac*-ethyl 2-[(3R,4R)-3-butyl-4-phenyl-4-(trifluoromethyl)oxetanyliden]propanoate (3ia)
(Scheme 1, Left)

Allenolate 1i (82 mg, 585 µmol) and ketone 2a (82 µL, 102 mg, 585 µmol, 1.0 equiv.) were reacted in MeCN (2.3 mL) with TBD (24.4 mg, 176 µmol, 30 mol%) using standard procedure (21 h, r.t.). Flash column chromatography (Si, 2.0×22 cm, pentane/EtOAc = 50/1→20/1) gave product (E)-3ia (132 mg, 421 µmol, 72%, 15:85 d.r.) as a colourless oil.

(E)-3ia:

\[ \text{R} = 0.51 \text{ (P/EtOAc = 14/1, [UV, KMnO}_4\text{])}. \]

**1H NMR** (600 MHz, CDCl\textsubscript{3}) \(\delta\) 7.48 – 7.37 (m, 5H, CH\textsubscript{Ar}, both diastereomers), 4.21 – 4.21 (m, 2H, COOC\textsubscript{2}H\textsubscript{5}CH\textsubscript{3}, both diastereomers), 4.15 (qd, \(J = 7.3, 1.3\) Hz, 1H, CHCH\textsubscript{3}, major diastereomer), 4.07 (qd, \(J = 7.5, 1.7\) Hz, 1H, CHCH\textsubscript{3}, minor diastereomer), 1.81 (d, \(J = 1.3\) Hz, 3H, C=C(CH\textsubscript{3})COOEt, major diastereomer), 1.81 (d, \(J = 1.3\) Hz, 3H, C=C(CH\textsubscript{3})COOEt, minor diastereomer), 1.72 (dq, \(J = 7.5, 1.7\) Hz, 3H, CHCH\textsubscript{3}, minor diastereomer), 1.28 (t, \(J = 7.1\) Hz, 3H, COOCH\textsubscript{2}CH\textsubscript{3}, major diastereomer), 1.26 (t, \(J = 7.1\) Hz, 3H, COOCH\textsubscript{2}CH\textsubscript{3}, minor diastereomer), 1.11 (d, \(J = 7.3\) Hz, 3H, CHCH\textsubscript{3}, major diastereomer).

**13C NMR** (major diastereomer, 151 MHz, CDCl\textsubscript{3}) \(\delta\) 171.5 (s, COOEt), 167.53 (s, C\textsubscript{=C}(CH\textsubscript{3})COOEt), 135.7 (C\textsubscript{Ar}), 129.4 (C\textsubscript{Ar}), 128.58 (C\textsubscript{Ar}), 126.2 (C\textsubscript{Ar}) 124.4 (q\textsubscript{CF}, \(J_{CF} = 283.3\) Hz, CF\textsubscript{3}), 100.8 (s, C(CH\textsubscript{3})COOEt), 87.8 (q\textsubscript{CF}, \(J_{CF} = 31.5\) Hz, CCF\textsubscript{3}), 60.13 (t, COOCH\textsubscript{2}CH\textsubscript{3}), 43.8 (d, CHCH\textsubscript{3}), 14.40 (q, COOCH\textsubscript{2}CH\textsubscript{3}), 13.4 (q, CHCH\textsubscript{3}), 8.8 (q, C(CH\textsubscript{3})COOEt).

**13C NMR** (minor diastereomer, 151 MHz, CDCl\textsubscript{3}) \(\delta\) 171.0 (s, COOEt), 167.46 (s, C\textsubscript{=C}(CH\textsubscript{3})COOEt), 131.2 (C\textsubscript{Ar}), 128.54 (C\textsubscript{Ar}), 125.5 (C\textsubscript{Ar}) 123.8 (q\textsubscript{CF}, \(J_{CF} = 283.5\) Hz, CF\textsubscript{3}), 100.9 (s, C(CH\textsubscript{3})COOEt), 86.9 (q\textsubscript{CF}, \(J_{CF} = 30.7\) Hz, CCF\textsubscript{3}), 60.09 (t, COOCH\textsubscript{2}CH\textsubscript{3}), 49.0 (d, CHCH\textsubscript{3}), 14.43 (q, COOCH\textsubscript{2}CH\textsubscript{3}), 11.8 (q, CHCH\textsubscript{3}), 8.9 (q, C(CH\textsubscript{3})COOEt). One C\textsubscript{Ar}-signal was not included due to overlaps resulting from low resolution.

**19F NMR** (564 MHz, CDCl\textsubscript{3}) \(\delta\) -74.9 (minor diastereomer), -79.7 (major diastereomer).

IR (film) \(\tilde{\nu} = 3390\) cm\textsuperscript{-1} (w), 2984 (m), 1711 (s, CO\textsubscript{2}Et), 1453 (m), 1374 (m), 1302 (s), 1180 (s), 1100 (s), 1006 (s), 914 (m), 726 (m), 645 (w).
**Supporting information**

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MS (EI, 70 eV) \(m/z\) (%): 314.1 (13) [M⁺], 269.1 (7) [(M–OEt)⁺], 241.1 (41) [(M–COOEt)⁺], 186.1 (95) [C₁₀H₉F₃]⁺, 117.1 [C₉H₅⁺] (100), 115.1 (24), 77.1 (9) [Ph⁺], 69.2 (2) [CF₃⁺].

MS (ESI, Orbitrap) \(m/z\) 315.1 (M+H⁺), 337.1 (M+Na⁺).

HRMS (ESI, Orbitrap) calcd. for C₁₆H₁₈F₃O₃⁺ (M+H⁺): 315.12026; found: 315.11961.

**ethyl 2-[5-phenyl-5-(trifluoromethyl)dihydro-2(3H)-furanylidene]propanoate (4)**

(Scheme 1, Right)

Allenolate 1i (67 mg, 478 µmol) and ketone 2a (67 µL, 83 mg, 478 µmol, 1.0 equiv.) were dissolved in MeCN (2.0 mL) at room temperature in a Schlenk-flask under argon atmosphere. Triphenylphosphine (25.1 mg, 96 µmol, 20 mol%) was added all at once, and the reaction mixture was stirred at r.t. for 24 h (complete conversion of 1i according to TLC). The reaction mixture was concentrated in vacuo. Flash column chromatography (Si, 2.0 × 22 cm, pentane/EtOAc = 20/1→15/1) gave product (E)-4 (51 mg, 163 µmol, 34%) as a colourless oil. The double bond configuration of the product was determined by 2D NOESY.

**(E)-4:**

\[ \begin{align*}
\text{EtO}_2\text{C} & \quad \text{CF}_3 \\
\text{Ph} & \quad \text{O} \\
\text{H} & \quad \text{NMR} (400 MHz, CDCl}_3 \delta 7.53 - 7.49 (m, 2H, CH\text{Ar}), 7.43 - 7.39 (m, 3H, CH\text{Ar}), 4.17 (q, J = 7.1 Hz, 2H, COOCH}_2\text{CH}_3), 3.32 - 3.25 (m, 1H, CHH), 3.11 - 3.03 (m, 1H, CHH), 2.84 (ddd, J = 13.2, 9.7, 6.1 Hz, 1H, CHH), 2.48 (ddd, J = 13.2, 9.7, 6.7, 1.1 Hz, 1H, CHH), 2.00 (t, J = 1.7 Hz, 3H, =C(CH₃)COOEt), 1.28 (t, J = 7.2 Hz, 3H, COOCH₂CH₃).
\end{align*} \]

\[ \begin{align*}
\text{C} \quad & \quad \text{NMR} (151 MHz, CDCl}_3 \delta 168.8 (s, COOEt), 167.5 (s, C=\text{C(Me)COOEt}), 136.0 (C\text{Ar}), 129.3 (C\text{Ar}), 128.6 (C\text{Ar}), 126.5 (C\text{Ar}), 124.7 (q\text{CF}, J_{\text{CF}} = 284.4 Hz, CF₃), 100.6 (s, C(\text{Me})COOEt), 88.1 (q\text{CF}, J_{\text{CF}} = 30.1 Hz, CCF₃), 60.0 (t, CO₂CH₂CH₃), 32.3 (t, CH₂), 30.6 (t, CH₂), 14.5 (q, COOCH₂CH₃), 11.6 (q, C(CH₃)COOEt).
\end{align*} \]

\[ \begin{align*}
\text{F} \quad & \quad \text{NMR} (564 MHz, CDCl}_3 \delta -79.0.
\end{align*} \]

IR (film) \(\tilde{\nu} = 3439 \text{ cm}^{-1}\) (w), 2966 (m), 1890 (w), 1717 (s, CO₂Et), 1678 (s), 1455 (m), 1382 (m), 1263 (s), 1176 (s), 1109 (s), 826 (m), 723 (s).

MS (EI, 70 eV) \(m/z\) (%): 390.1 (16) [M⁺], 283.1 (6) [(M–OBn)⁺], 214.1 (13) [C₁₂H₁₃F₃⁺], 199.1 [C₁₁H₁₀F₃⁺] (49), 145.1 [C₁₁H₁₅⁺] (15), 91.1 (100) [Bn⁺], 69.1 (23) [CF₃⁺].

MS (ESI, Orbitrap) \(m/z\) 429.1 (M+K⁺), 413.1 (M+Na⁺), 391.1 (M+H⁺).

HRMS (ESI, Orbitrap) calcd. for C₂₂H₂₂F₃O₅⁺ (M+H⁺): 391.15156; found: 391.15115.
3.4 Details of the reaction leading to cis-3aa with PPh₃ as catalyst
(Scheme 2, Right)

Allenolate 1a (80 mg, 634 µmol) and ketone 2a (89 µL, 110 mg, 634 µmol, 1.0 equiv.) were dissolved in MeCN (2.5 mL) at room temperature in a Schlenk-flask under argon atmosphere. Triphenylphosphine (33.5 mg, 127 µmol, 20 mol%) was added all at once, and the reaction mixture was stirred at r.t. for 1.5 h (complete conversion of 1a according to TLC). The reaction mixture was concentrated in vacuo. Flash column chromatography (Si, 2.0×22 cm, pentane/EtOAc = 35/1→20/1→15/1→5/1) gave product (E)-3aa (109 mg, 362 µmol, 57%, cis/trans = 75/25) as colourless oil. The yield of the minor isomer (Z)-3aa (13%, cis/trans 71:29) was determined from the ¹H NMR spectrum of the crude reaction mixture based on isolated product (E)-3aa.

In addition to (E)-3aa a more polar fraction was isolated which consisted of a mixture of several compounds and contained traces of tetrahydrofuran byproduct (E)-4aa among other things (See example ¹H NMR spectrum below). This suggestion was based on the comparison of characteristic ¹H NMR signals with those of (E)-4 and reported compounds with similar structure.¹

(E)-4aa:

This isomer was not isolated in pure form. Only characteristic signals are listed. ¹H NMR (600 MHz, CDCl₃) δ 5.57 (t, J = 1.9 Hz, 1H, CHCO₂Et), 3.34 – 3.27 (m, 1H, CHH), 3.14 – 3.06 (m, 1H, CHH), 2.83 (ddd, J = 13.3, 9.7, 6.1 Hz, 1H, CHH), 2.47 (dddd, J = 13.3, 9.6, 6.6, 1.1 Hz, 1H, CHH).

Example ¹H NMR spectrum: characteristic signals were assigned to (E)-4aa.

Due to the fact that the isomers of 3aa and 4aa have α-protons with characteristic chemical shifts in $^1$H NMR, their relative amounts could be determined from the crude $^1$H NMR spectrum based on isolated (E)-3aa (See Fig. S5 and example $^1$H NMR spectrum below).

**Fig. S5** All isomers of the products 3aa and 4aa present in the crude mixture after the reaction between 1a and 2a with PPh$_3$ catalyst.

**Example $^1$H NMR spectrum:** crude reaction mixture containing isomers of 3aa and 4aa. Characteristic signals of α-protons are shown.
4. X-Ray Crystallographic Data

Crystal Structure Determination of (E)-3aa and (E)-3ad

(E)-3aa:
Crystal data from pentane: monoclinic space group $P 21/c$, $Z = 4$, $a = 9.8832(11)$ Å, $b = 7.3687(8)$ Å, $c = 19.706(2)$ Å, $\alpha = 90$, $\beta = 100.199(2)$, $\gamma = 90$, $V = 1412.4(3)$ Å$^3$, 16404 reflections, 2948 unique, $R_{int} = 0.0349$, absorption correction via observation of multiple reflections (Bruker AXS, SAINT, Program for Reduction of Data collected on Bruker, CCD Area Detector Diffractometer V. 6.02, Bruker AXS Inc.: Madison, WI, USA, 1999), $wR_2 = 0.0888$, $R_1 = 0.0360$, $S = 1.032$.

(E)-3ad:
Crystal data from chloroform: monoclinic space group $Cc$, $Z = 4$, $a = 12.4906(15)$ Å, $b = 12.0630(14)$ Å, $c = 9.5353(12)$ Å, $\alpha = 90$, $\beta = 103.731(2)$, $\gamma = 90$, $V = 1395.7(3)$ Å$^3$, 8352 reflections, 3852 unique, $R_{int} = 0.0306$, absorption correction via observation of multiple reflections (Bruker AXS, SAINT, Program for Reduction of Data collected on Bruker, CCD Area Detector Diffractometer V. 6.02, Bruker AXS Inc.: Madison, WI, USA, 1999), $wR_2 = 0.1088$, $R_1 = 0.0433$, $S = 1.093$.

Intensity data were collected with a Bruker APEX area detector equipped with an Incoatec microsource (Mo-K$_\alpha$ radiation, $\lambda = 0.71073$ Å, multilayer optics) at 100 K (Oxford Cryostream 700 instrument). Data were integrated with SAINT(Bruker AXS, SAINT, Program for Reduction of Data collected on Bruker, CCD Area Detector Diffractometer V. 6.02, Bruker AXS Inc.: Madison, WI, USA, 1999) and corrected for absorption by multi-scan methods (SADABS: Program for Empirical Absorption Correction of Area Detector Data V 2004/1, Bruker AXS Inc.: Madison, WI, USA, 2004.) The structure was solved by Patterson method (SHELXS-97), and were refined by full matrix least squares procedures based on $F^2$ as implemented in SHELXL-97 (G. M. Sheldrick, Acta Crystallogr., 2008, A64, 112–122). Non-hydrogen atoms were assigned anisotropic displacement parameters and hydrogen atoms were found, yet not anisotropic refined. Despite the modest quality of the structure model, the absolute structure based on anomalous dispersion can be unambiguously established. None solvate-molecules have been found in the lattices.
**Figure 1:** Displacement ellipsoid plots of the independent target molecule in the crystal structure of \((E)-\text{trans-3aa}\). Ellipsoids are drawn at 50 % probability.

**Figure 2:** Displacement ellipsoid plots of the independent target molecule in the crystal structure of \((E)-\text{trans-3ad}\). Ellipsoids are drawn at 50 % probability.
5. Copies of $^1$H and $^{13}$C NMR Spectra

(E)-3aa

major diastereomer
Supporting information

(E)-3ba

major
diastereomer
(E)-3ea major diastereomer
(Z)-3fa
major diastereomer
Supporting information

(E)-3ga
major
diastereomer

COOBn
F₃C
Ph
(Z)-3ha
major diastereomer
(E)-3ab

major
diastereomer
(E)-3ac
major
diastereomer
(E)-3af
major diastereomer