Synthesis of Monosubstituted 1,1-Dicarbonyl Ester 1,3-Dienes

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Supporting Information

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1. General

**Solvents:** unless mentioned, all solvents (for reactions, extractions or purification by chromatography) were used without further purification.

**Reactants and reagents:** commercially available reagents were used as purchased.

**Thin layer chromatographies (TLCs):** TLCs were carried out on Merck Silica gel 60 F 254 aluminium backed plates using UV light, potassium permanganate or p-anisaldehyde solution as revelator.

**Flash chromatographies:** flash chromatographies were performed using Merck Silica gel 60Å (40-63 μm).

**Nuclear magnetic resonance (NMR) spectroscopy:** NMR spectra were recorded either on a 300 MHz Bruker avance II 300 or on a 500 MHz Bruker avance 500 spectrometer in the indicated solvent. Chemical shifts are given in ppm relative to the reference (TMS) and coupling constants are given in Hz. For some molecules, the $^1$H and $^{13}$C signals’ attributions required additional analysis (COSY, HMQC, HMBC, $^{13}$C DEPT-135).

**Mass spectrometry:** mass spectra and high resolution mass spectra were obtained on a Thermo Orbitrap Exactive device. The mass are given in Dalton.

**Infra-red spectroscopy:** Infra-red spectra were obtained on a Shimadzu FTIR-8400S device. Absorption frequencies are given in cm$^{-1}$. 
2. Experimental details and products characterization

2.1. Synthesis of 3-substituted dicarbonyl ester 1,3-dienes

2.1.1. Dimethyl (2-methylprop-2-en-1-ylidene)malonate (2a)

Procedure:

In a dry round bottom flask was added 12 mL of THF under inert atmosphere. A solution of TiCl₄ (6 mmol) in 1.5 mL of CCl₄ was then added, slowly, at 0 °C. After 10 min stirring at 0 °C, methacrolein (3 mmol) and dimethyl malonate (1.5 mmol) were added, slowly. After 20 min stirring at 0 °C, pyridine (12 mmol) was added, slowly, at 0 °C. After 16 h of stirring at room temperature, the reaction mixture was diluted with Et₂O (10 mL) and water (10 mL). The layers were separated and the aqueous layer was extracted twice with Et₂O (2*10 mL). The combined organic layers were washed with a NaHCO₃ sat solution (10 mL) and then brine (10 mL). The organic layer was dried over Na₂SO₄, filtered and concentrated under reduced pressure.

CAS Reg. No. 63646-70-8

Yield : 77%
Mol. formula: C₉H₁₂O₄
Mol. Wt. : 184.19 g·mol⁻¹
Aspect: colorless liquid

¹H NMR (300 MHz, CDCl₃): δ 7.34 (s, 1H, H=C), 5.38 (s, 1H, H₂C=C), 5.33 (s, 1H, H₂C=C), 3.76 (s, 3H, O-C₃H₃), 3.72 (s, 3H, O-C₃H₃), 1.80 (s, 3H, C=C₃H₃).

¹³C NMR (125 MHz, CDCl₃): δ 167.0, 164.8, 144.5, 139.3, 127.9, 124.6, 52.6, 52.5, 18.8.

2.1.2. Dimethyl (2-phenylprop-2-en-1-ylidene)malonate (2b)

**Procedure:**

In a dry round bottom flask was added 6 mL of THF under inert atmosphere. A solution of TiCl₄ (3 mmol) in 1 mL of CCl₄ was then added, slowly, at 0 °C. After 10 min stirring at 0 °C, atropaldehyde¹ (1.5 mmol) diluted in 0.2 mL THF and dimethyl malonate (0.8 mmol) were added, slowly, at -78 °C. After 40 min stirring at -78 °C, pyridine (7 mmol) was added, slowly, at -78 °C. The cooling bath was then removed. When the reaction mixture reached room temperature, it was refluxed for 2h. Then, after cooling, the reaction mixture was diluted with Et₂O (10 mL) and water (10 mL). The layers were separated and the aqueous layer was extracted twice with Et₂O (2*10 mL). The organic layers were combined, washed with a NaHCO₃sat solution (10 mL) and brine (10 mL). The organic layer was dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (05/95 EtOAc/cyclohexane).

\[ \text{Yield: } 34\% \]

Mol. formula: C₁₄H₁₄O₄

Mol. Wt.: 246.26 g.mol⁻¹

Aspect: colorless liquid

**¹H NMR (300 MHz, CDCl₃):** δ 7.63 (s, 1H, H=C), 7.38 – 7.27 (massif, 5H, Ar), 5.65 (s, 2H, H₂C=C), 3.82 (s, 3H, O-C₃H₃), 3.34 (s, 3H, O-CH₃).

**¹³C NMR (125 MHz, CDCl₃):** δ 165.8, 164.6, 144.2, 138.2, 128.5, 128.4, 127.8, 127.8, 127.5, 123.8, 52.8, 52.2 (one quaternary carbon is not observed).

**FT-IR (cm⁻¹):** 3028, 2951, 1728, 1620, 1603, 1495, 1435, 1364, 1315, 1300, 1244, 1184, 1067, 1005, 916, 843, 777, 752, 704.

**MS (APCI):** \( m/z = 247 [M + H]^+ \), 216 [M – CH₃O]⁺.

**HRMS (APCI):** \( m/z = 247.09680 [M + H]^+ \); calcd. for C₁₄H₁₄O₄: 247.09649.

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2.2. Synthesis of 2-Substituted dicarbonyl ester 1,3-Dienes

2.2.1. Knoevenagel Condensation

General procedure:
In a round bottom flask was added malonate (93 mmol) and aldehyde (110 mmol) in absolute ethanol (40 mL), then acetic acid (17 mmol) and piperidine (15 mmol). The reaction vessel was heated to reflux for 48 hours. Then by-product was distilled in a Kugelrohr apparatus under vacuum. The desired compound was obtained with an excellent yield.

diethyl benzylidenemalonate (4a)
CAS Reg. No. 5292-53-5

Yield: 88%
Mol. formula: C_{14}H_{16}O_{4}
Mol. Wt.: 248.27 g.mol^{-1}
Aspect: yellow oil

^{1}H NMR (300 MHz, CDCl_{3}): \delta 7.74 (s, 1H, HAr), 7.47 – 7.37 (massif, 5H, Ar), 4.32 (m, 4H, 2\*H_{2}C-CH_{3}), 1.34 (t, J = 7.2 Hz, 3H, H_{2}C-C\_H_{3}), 1.29 (t, J = 7.2 Hz, 3H, H_{2}C-C\_H_{3}).

^{13}C NMR (75 MHz, CDCl_{3}): \delta 166.2, 163.7, 141.6, 132.6, 130.2, 129.1, 128.5, 126.1, 61.3, 61.2, 13.8, 13.5.

^{1}H and ^{13}C NMR spectra were in accord with literature; see Meskini, I.; Toupet, L.; Daoudi, M.; Kerbal, A.; Akkurt, M.; Chohan, Z. H.; Ben Hadda, T. J. Chem. Crystallogr. 2010, 40, 812.

\footnote{For R = n-Bu (4h), the mixture was stirred 16h at room temperature and then concentrated under vacuum. The residue was diluted with AcOEt (50 mL), H_{2}O (20 mL) and HCl 1N (10 mL). The aqueous layer was extracted two more times with AcOEt (20 mL). The combined organic layers were washed with brine (20 mL), dried over MgSO_{4} and then concentrated under vacuum. The residue was purified by flash chromatography (4/96 => 10/90 AcOEt/cyclohexane) to give the desired compound in 43% yield.}
\textit{diethyl (4-chlorobenzylidene)malonate (4b)}

CAS Reg. No. 6827-40-3

Yield: 92%
Mol. formula: \( \text{C}_{14}\text{H}_{15}\text{ClO}_{4} \)
Mol. Wt.: 282.72 g.mol\(^{-1} \)
Aspect: yellow oil

\(^{1}\text{H NMR (300 MHz, CDCl}_3\)): \( \delta \) 7.67 (s, 1H, HCAr), 7.41 – 7.32 (massif, 4H, Ar), 4.32 (m, 4H, \( 2^\times\text{H}_2\text{C-CH}_3 \)), 1.33 (t, \( J = 7.2 \text{ Hz}, 3\text{H, H}_2\text{C-CH}_3 \)), 1.29 (t, \( J = 7.2 \text{ Hz}, 3\text{H, H}_2\text{C-CH}_3 \)).

\(^{13}\text{C NMR (75 MHz, CDCl}_3\)): \( \delta \) 166.6, 164.0, 140.8, 136.7, 131.5, 130.8, 129.2, 127.0, 62.0, 61.9, 14.3, 14.0.

\(^{1}\text{H and }^{13}\text{C NMR spectra were in accord with literature; see Meskini, I.; Toupet, L.; Daoudi, M.; Kerbal, A.; Ben Hadda, T. } \textit{J. Chem. Crystallogr.} \textbf{2011}, \textbf{41}, 891. \)

\textit{diethyl (4-fluorobenzylidene)malonate (4c)}

CAS Reg. No. 790-53-4

Yield: 99%
Mol. formula: \( \text{C}_{14}\text{H}_{15}\text{FO}_{4} \)
Mol. Wt.: 266.26 g.mol\(^{-1} \)
Aspect: yellow oil

\(^{1}\text{H NMR (300 MHz, CDCl}_3\)): \( \delta \) 7.69 (s, 1H, HCAr), 7.46 (m, 2H, Ar), 7.07 (dd, 2H, \( J = 8.7, 8.7 \text{ Hz, Ar} \)), 4.34 (q, 2H, \( J = 7.2 \text{ Hz, CH}_2\text{CH}_3 \)), 4.31 (q, 2H, \( J = 7.2 \text{ Hz, CH}_2\text{CH}_3 \)), 1.33 (t, 3H, \( J = 7.2 \text{ Hz, CH}_2\text{CH}_3 \)), 1.30 (t, 3H, \( J = 7.2 \text{ Hz, CH}_2\text{CH}_3 \)).

\(^{13}\text{C NMR (75 MHz, CDCl}_3\)): \( \delta \) 166.7, 164.0 (d, \( J = 251.2 \text{ Hz} \)), 164.1, 140.9, 131.7 (d, \( J = 8.6 \text{ Hz} \)), 129.2 (d, \( J = 3.2 \text{ Hz} \)), 126.2, 116.1 (d, \( J = 21.7 \text{ Hz} \)), 61.9, 61.8, 14.2, 14.0.

\( \text{FT-IR (cm}^{-1}\)): 1724, 1634, 160, 1510, 1259, 1238, 1223, 1213, 1196, 1163, 1065, 835.

\( \text{MS (APCI)}: m/z = 267 \text{ [M + H]}^+, 221 \text{ [M - C}_2\text{H}_5\text{O]}^+. \)

\( \text{HRMS (APCI)}: m/z = 267.10268 \text{ [M + H]}^+; \text{ calcd. for } \text{C}_{14}\text{H}_{16}\text{O}_4\text{F: 267.10271.} \)
**diethyl (4-fluorobenzylidene)malonate (4d)**

CAS Reg. No. 14111-33-2

![diethyl (4-fluorobenzylidene)malonate](image)

Yield: >99%

Mol. formula: C_{12}H_{18}O_3

Mol. Wt.: 262.30 g mol⁻¹

Aspect: yellow oil

**¹H NMR (300 MHz, CDCl₃):** δ 7.70 (s, 1H, HCAr), 7.35 (d, 2H, J = 8.1 Hz, Ar), 7.18 (d, 2H, J = 8.1 Hz, Ar), 4.34 (q, 2H, J = 7.2 Hz, CH₂CH₃), 4.30 (q, 2H, J = 7.2 Hz, CH₂CH₃), 2.36 (s, 3H, H₃CAr), 1.33 (t, 3H, J = 7.2 Hz, CH₂CH₃), 1.30 (t, 3H, J = 7.2 Hz, CH₂CH₃).

**¹³C NMR (75 MHz, CDCl₃):** δ 167.1, 164.4, 142.3, 141.3, 130.2, 129.7, 129.7, 125.3, 61.8, 61.7, 21.6, 14.3, 14.0.


**diethyl (4-methoxybenzylidene)malonate (4e)**

CAS Reg. No. 6768-23-6

![diethyl (4-methoxybenzylidene)malonate](image)

Yield: 90%

Mol. formula: C_{12}H_{18}O_3

Mol. Wt.: 278.30 g mol⁻¹

Aspect: yellow oil

**¹H NMR (300 MHz, CDCl₃):** δ 7.67 (s, 1H, HCAr), 7.42 (m, 2H, Ar), 6.88 (m, 2H, Ar), 4.35 (q, J = 7.1 Hz, 2H, CH₂CH₃), 4.29 (q, J = 7.1 Hz, 2H, CH₂CH₃), 3.83 (s, 3H, H₃C-O-Ar), 1.320 (t, J = 7.1 Hz, 3H, CH₂-C₃H₃), 1.316 (t, J = 7.1 Hz, 3H, CH₂-C₃H₃).

**MS (APCI):** m/z = 279 [M + H]⁺, 233 [M - C₂H₅O]⁺.

**HRMS (APCI):** m/z = 279.12278 [M + H]⁺; calcd. for C_{15}H_{19}O₅: 279.12270.

**diethyl (2-methylpropylidene)malonate (4f)**

CAS Reg. No. 5652-68-6

Yield: 92%
Mol. formula: C\textsubscript{11}H\textsubscript{18}O\textsubscript{4}
Mol. Wt.: 214.26 g.mol\textsuperscript{-1}
Aspect: yellow oil

\(^1\)H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) 6.77 (d, \(J = 10.6\) Hz, 1H, HC-(CO\textsubscript{2}Et)\textsubscript{2}), 4.29 (q, \(J = 7.1\) Hz, 2H, CH\textsubscript{2}-CH\textsubscript{3}), 4.22 (q, \(J = 7.1\) Hz, 2H, CH\textsubscript{2}-CH\textsubscript{3}), 2.68 (m, 1H, HC(CH\textsubscript{3})\textsubscript{2}), 1.32 (t, \(J = 7.1\) Hz, 3H, CH\textsubscript{2}-C\textsubscript{H}\textsubscript{3}), 1.28 (t, \(J = 7.1\) Hz, 3H, CH\textsubscript{2}-CH\textsubscript{3}), 1.06 (d, \(J = 6.6\) Hz, 6H, HC(CH\textsubscript{3})\textsubscript{2}).

MS (APCI): \(m/z = 215\) [M + H]\textsuperscript{+}, 169 [M – C\textsubscript{2}H\textsubscript{5}O]\textsuperscript{+}.

HRMS (APCI): \(m/z = 215.12783\) [M + H]\textsuperscript{+}; calcd. for C\textsubscript{11}H\textsubscript{19}O\textsubscript{4}: 215.12779.

\(^1\)H and mass spectra were in accord with literature; see Schuppan, J.; Minnaard, A. J.; Feringa, B. L. *Chem Commun* 2004, 40, 792.

**diethyl pentylidene malonate (4h)**

CAS Reg. No. 18795-86-3

Yield: 43%
Mol. formula: C\textsubscript{12}H\textsubscript{20}O\textsubscript{4}
Mol. Wt.: 228.28 g.mol\textsuperscript{-1}
Aspect: very pale yellow turbid liquid

\(^1\)H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) 6.99 (t, \(J = 7.9\) Hz, 1H, HC-(CO\textsubscript{2}Et)\textsubscript{2}), 4.30 (q, \(J = 7.1\) Hz, 2H, O-CH\textsubscript{2}-CH\textsubscript{3}), 4.23 (q, \(J = 7.1\) Hz, 2H, O-CH\textsubscript{2}-CH\textsubscript{3}), 2.29 (dt, \(J = 7.5, 7.5\) Hz, 2H, HC-CH\textsubscript{2}), 1.52 – 1.24 (massif, 4H, CH\textsubscript{3}-(CH\textsubscript{2})\textsubscript{2}), 1.32 (t, \(J = 7.1\) Hz, 3H, O-CH\textsubscript{2}-CH\textsubscript{3}), 1.29 (t, \(J = 7.1\) Hz, 3H, O-CH\textsubscript{2}-CH\textsubscript{3}), 0.90 (t, \(J = 7.2\) Hz, 3H, H\textsubscript{3}C-(CH\textsubscript{2})\textsubscript{3}).

MS (APCI): \(m/z = 229\) [M + H]\textsuperscript{+}, 183 [M – C\textsubscript{2}H\textsubscript{5}O]\textsuperscript{+}.

HRMS (APCI): \(m/z = 229.14424\) [M + H]\textsuperscript{+}; calcd. for C\textsubscript{12}H\textsubscript{21}O\textsubscript{4}: 229.14344.

The analyses’ results were in accord with literature; see Cahiez, G.; Alami, M. *Tetrahedron* 1989, 45, 4163.
2.2.2. Wittig olefination³

**Procedure³:**

In a round bottom flask was added diethyl malonate (4 mmol), (carbethoxymethylene)triphenylphosphorane (4 mmol) and 5 mL of toluene at 0 °C under inert atmosphere. The reaction mixture was stirred 3 h at room temperature. After concentration under reduced pressure, the residue was purified by flash chromatography (20/80 EtOAc/cyclohexane).

**Diethyl Ethoxycarbonylbutenidienoate (4g)**

CAS Reg. No. 13049-86-0

Yield: 98%

Mol. formula: C₁₁H₁₆O₆

Mol. Wt.: 244.24 g.mol⁻¹

Aspect: colorless liquid

¹H NMR (500 MHz, CDCl₃): δ 6.87 (s, 1H, HC-CO₂Et), 4.38 (q, J = 7.2 Hz, 2H, CH₂-CH₃), 4.30 (q, J = 7.2 Hz, 2H, CH₂-CH₃), 4.25 (q, J = 7.2 Hz, 2H, CH₂-CH₃), 1.36 (t, J = 7.0 Hz, 3H, CH₂-C₃H₇), 1.34 – 1.29 (m, 6H, 2*CH₂-CH₃).

¹³C NMR (75 MHz, CDCl₃): δ 164.4, 163.7, 162.4, 139.0, 130.2, 62.6, 62.2, 61.9, 14.12, 14.10, 14.06.

¹H and ¹³C NMR spectra were in accord with literature; see Okuro, K.; Alper, H. *J Org Chem* 2012, 77, 4420.

2.2.3. Bromination

**General procedure:**

In a round bottom flask was added compound 4 (7 mmol) and bromine (8 mmol) in CCl₄ (4 mL) at 0 °C. The reaction mixture was stirred at this temperature for 1 h and then warmed to room temperature for 3 h. The solution was diluted with dichloromethane (30 mL) then washed with a 10% NaOH solution (15 mL) and brine (10

mL). The organic layer was dried over MgSO₄, filtered and concentrated under reduced pressure. The desired compound was used in the next step without further purification.

**diethyl bromo[bromo(phenyl)methyl]malonate (5a)**

CAS Reg. No. 77752-84-2

\[
\begin{array}{c}
\text{O} \\
\text{Br}
\end{array}
\]

Yield: 97%
Mol. formula: C₁₄H₁₄Br₂O₄
Mol. Wt.: 408.08 g mol⁻¹
Aspect: yellow oil

\(^1\)H NMR (300 MHz, CDCl₃): δ 7.58 (m, 2H, Ar), 7.34 – 7.25 (massif, 3H, Ar), 5.77 (s, 1H, HCAr), 4.36 (m, 2H, H₂C-CH₃), 4.16 (q, J = 7.2 Hz, 2H, H₂C-CH₃), 1.34 (t, J = 7.2 Hz, 3H, H₂C-C₃H₃), 1.19 (t, J = 7.2 Hz, 3H, H₂C-C₃H₃).

\(^1\)C NMR (75 MHz, CDCl₃): δ 164.5, 164.5, 136.4, 130.0, 129.4, 128.1, 68.7, 63.9, 63.8, 53.3, 14.0, 13.8.

FT-IR (cm⁻¹): 2992, 1743, 1465, 1451, 1367, 1237, 1190, 1095, 992, 861, 756, 698, 671.


**diethyl bromo[bromo(4-chlorophenyl)methyl]malonate (5b)**

CAS Reg. No. 77752-87-5

\[
\begin{array}{c}
\text{O} \\
\text{Br}
\end{array}
\]

Yield: 97%
Mol. formula: C₁₄H₁₅Br₂ClO₄
Mol. Wt.: 442.53 g mol⁻¹
Aspect: yellow oil

\(^1\)H NMR (300 MHz, CDCl₃): δ 7.54 (d, J = 8.7 Hz, 2H, Ar), 7.29 (d, J = 8.7 Hz, 2H, Ar), 5.73 (s, 1H, HCAr), 4.36 (m, 2H, H₂C-CH₃), 4.18 (q, J = 7.2 Hz, 2H, H₂C-CH₃), 1.34 (t, J = 7.2 Hz, 3H, H₂C-CH₃), 1.21 (t, J = 7.2 Hz, 3H, H₂C-CH₃).

\(^1\)C NMR (75 MHz, CDCl₃): δ 164.3, 164.2, 135.2, 134.9, 131.4, 128.1, 68.3, 63.9, 63.8, 52.3, 13.9, 13.8.

FT-IR (cm⁻¹): 2983, 1741, 1592, 1482, 1457, 1399, 1377, 1242, 1197, 1096, 1019, 862, 826, 730, 678.
**diethyl bromo[bromo(4-fluorophenyl)methyl]malonate (5c)**

Yield: 87%
Mol. formula: C_{14}H_{16}Br_{2}O_{4}
Mol. Wt.: 426.07 g mol\(^{-1}\)
Aspect: orange oil

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.58 (m, 2H, Ar), 7.00 (dd, \(J = 8.6, 8.6\) Hz, 2H, Ar), 5.75 (s, 1H, HCAr), 4.36 (m, 2H, \(CH_{2}CH_{3}\)), 4.17 (q, \(J = 7.1\) Hz, 2H, \(CH_{2}CH_{3}\)), 1.3 (t, \(J = 7.1\) Hz, 3H, \(CH_{2}CH_{3}\)), 1.2 (t, \(J = 7.1\) Hz, 3H, \(CH_{2}CH_{3}\)).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 164.4, 164.3, 163.0 (d, \(J = 248.2\) Hz), 132.3 (d, \(J = 3.2\) Hz), 132.0 (d, \(J = 8.3\) Hz), 114.9 (d, \(J = 21.7\) Hz), 68.6, 63.9, 63.7, 52.3, 13.9, 13.7.

FT-IR (cm\(^{-1}\)): 1743, 1605, 1514, 1464, 1298, 1240, 1199, 1030, 1020.

**diethyl bromo[bromo(4-methylphenyl)methyl]malonate (5d)**

Yield: 95%
Mol. formula: C_{15}H_{18}Br_{2}O_{4}
Mol. Wt.: 422.11 g mol\(^{-1}\)
Aspect: orange oil

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.46 (d, \(J = 8.2\) Hz, 2H, Ar), 7.11 (d, \(J = 8.0\) Hz, 2H, Ar), 5.75 (s, 1H, HCAr), 4.35 (m, 2H, \(CH_{2}CH_{3}\)), 4.17 (q, \(J = 7.1\) Hz, 2H, \(CH_{2}CH_{3}\)), 2.33 (s, 3H, H_{3}CAr), 1.34 (t, \(J = 7.1\) Hz, 3H, \(CH_{2}CH_{3}\)), 1.20 (t, \(J = 7.1\) Hz, 3H, \(CH_{2}CH_{3}\)).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 164.6, 164.6, 139.5, 133.5, 129.8, 128.8, 68.9, 63.8, 63.7, 53.3, 21.3, 14.0, 13.8.

FT-IR (cm\(^{-1}\)): 1747, 1514, 1464, 1298, 1240, 1199, 1030, 1020.
MS (APCI): $m/z = 423 \ [M(^{81}\text{Br}) + \text{H}]^+$, 263 $[\text{M} - \text{Br}_2 + \text{H}]^+$, 217 $[\text{M} - \text{Br}_2 - \text{C}_2\text{H}_5\text{O}]^+$.

HRMS (APCI): $m/z = 420.96445 \ [\text{M} + \text{H}]^+$; calcd. for $C_{15}H_{19}O_4^{79}\text{Br}_2$: 420.96446.

diethyl bromo(1-bromo-2-methylpropyl)malonate (5f)

1H NMR (500 MHz, CDCl$_3$): $\delta$ 4.70 (d, $J = 3.0$ Hz, 1H, HC-Br), 4.30 (q, $J = 7.1$ Hz, 4H, 2*CH$_2$-CH$_3$), 2.32 (dqq, $J = 6.6, 6.6, 3.0$ Hz, 1H, HC-(CH$_3$)$_2$), 1.32 (t, $J = 7.1$ Hz, 3H, CH$_2$-C(CH$_3$)$_2$), 1.31 (t, $J = 7.1$ Hz, 3H, CH$_2$-C(CH$_3$)$_2$), 1.07 (d, $J = 6.7$ Hz, 3H, HC(CH$_3$)$_2$), 1.06 (d, $J = 6.4$ Hz, 3H, HC(CH$_3$)$_2$).

13C NMR (125 MHz, CDCl$_3$): $\delta$ 165.5, 164.5, 68.5, 63.9, 63.6, 62.7, 32.0, 23.3, 19.9, 14.0, 13.9.

FT-IR (cm$^{-1}$): 2980, 2937, 2908, 2878, 1740, 1464, 1445, 1389, 1367, 1337, 1327, 1298, 1238, 1192, 1121, 1096, 1068, 1020, 991, 858.

Yield: 91%
Mol. formula: $C_{15}H_{19}Br_2O_4$
Mol. Wt.: 374.07 g.mol$^{-1}$
Aspect: yellow oil

triethyl 1,2-dibromoethane-1,1,2-tricarboxylate (5g)

1H NMR (300 MHz, CDCl$_3$): $\delta$ 5.14 (s, 1H, HC-CO$_2$Et), 4.41 – 4.24 (massif, 6H, 3*CH$_2$-CH$_3$), 1.38 – 1.30 (massif, 9H, 3*CH$_2$-CH$_3$).

13C NMR (75 MHz, CDCl$_3$): $\delta$ 165.8, 164.5, 163.5, 64.0, 63.9, 62.9, 62.0, 46.4, 13.8, 13.8, 13.7.

Yield: 93%
Mol. formula: $C_{15}H_{19}Br_2O_6$
Mol. Wt.: 404.05 g.mol$^{-1}$
Aspect: colorless liquid
FT-IR (cm\(^{-1}\)): 2984, 2939, 2907, 1740, 1466, 1445; 1393, 1367, 1327, 1296, 1244, 1192, 1155, 1111, 1096, 1020, 914, 856, 731.

MS (APCI): \(m/z = 405 \quad [M \quad (^{79}\text{Br}^{81}\text{Br}) + \text{H}]^+\).

HRMS (APCI): \(m/z = 402.93892 \quad [M \quad (^{79}\text{Br}_2) + \text{H}]^+\); calcd. for \(C_{11}H_{17}O_6^{79}\text{Br}_2\): 402.93864.

### 2.2.4. Elimination/Suzuki-Miyaura cross coupling

![Reagents and conditions for elimination/Suzuki-Miyaura cross coupling](image)

**General procedure:**

In a dry round bottom flask was added the compound 5a-d (2.4 mmol) and 20 mL CH\(_2\)Cl\(_2\). Then DBU (3.5 mmol) was added, slowly, at 0 °C. After 20 min stirring at room temperature, the solution was diluted with H\(_2\)O (10 mL), and then washed with HCl 1M solution (10 mL). The organic layer was dried over MgSO\(_4\), filtered and concentrated under reduced pressure.

The residue (compound 6a-d) was then diluted with 20 mL EtOH, and potassium vinyltrifluoroborate (430 mg, 3.2 mmol), PdCl\(_2\)dpdpf (90 mg, 0.12 mmol) and triethylamine (0.53 mL, 3.8 mmol) were added under inert atmosphere. The reaction mixture was heated at 40°C for 16 h and then concentrated under vacuum. The residue was diluted with EtOAc (40 mL), washed with H\(_2\)O (20 mL), NH\(_4\)Cl\(_{\text{sat}}\) solution (20 mL), and brine (20 mL). The organic layer was dried over MgSO\(_4\) and then concentrated under reduced pressure. The residue was purified by flash chromatography with the appropriate mixture of cyclohexane and EtOAc.

**diethyl (1-phenylprop-2-en-1-ylidene)malonate (7a)**

Yield: 44%

Mol. formula: \(C_{16}H_{18}O_4\)

Mol. Wt.: 274.31 g/mol

Aspect: yellow oil

\(^1\text{H NMR (500 MHz, CDCI}_3\): \(\delta 7.48 \quad (dd, \ J = 17.2, 10.8 \text{ Hz, 1H, H}_2\text{C=CH}_2), \quad 7.36 – 7.27 \quad \text{(massif, 3H, Ar), 7.16 (m, 2H, Ar), 5.60 (dd, \ J = 10.5, 1.5 \text{ Hz, 1H, HCH}), 5.13 (dd, \ J = 17.3, 1.3 \text{ Hz, 1H, HCH}), 4.28 (q, \ J = 7.2 \text{ Hz, 2H, H}_2\text{C-CH}_3), 3.89 (q, \ J = 7.2 \text{ Hz, 2H, H}_2\text{C-CH}_3), 1.29 (t, \ J = 7.0 \text{ Hz, 3H, H}_2\text{C-CH}_3), 0.89 (t, \ J = 7.0 \text{ Hz, 3H, H}_2\text{C-CH}_3).}
$^{13}$C NMR (125 MHz, CDCl$_3$): δ 165.7, 164.2, 153.0, 136.4, 134.8, 128.9, 128.4, 127.9, 127.6, 125.7, 61.3, 61.0, 14.1, 13.6.

FT-IR (cm$^{-1}$): 1728, 1252, 1224, 1095, 1065, 1023, 701.

MS (APCI): $m/z$ = 229 [M – C$_2$H$_5$O]$^+$.  

HRMS (APCI): $m/z$ = 275.12773 [M + H]$^+$; calcd. for C$_{16}$H$_{19}$O$_4$: 275.12779.

diethyl [1-(4-chlorophenyl)prop-2-en-1-ylidene]malonate (7b)

Yield : 36%
Mol. formula: C$_{16}$H$_{17}$ClO$_4$
Mol. Wt. : 308.76 g.mol$^{-1}$
Aspect: yellow oil

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.43 (dd, $J$ = 17.5, 10.5 Hz, 1H, H$_2$C=CH), 7.33 (massif, 2H, Ar), 7.12 (massif, 2H, Ar), 5.63 (dd, $J$ = 10.5, 1.0 Hz, 1H, HCH), 5.14 (dd, $J$ = 17.5, 1.0 Hz, 1H, HCH), 4.31 (q, $J$ = 7.2 Hz, 2H, H$_2$C-CH$_3$), 3.96 (q, $J$ = 7.2 Hz, 2H, H$_2$C-CH$_3$), 1.33 (t, $J$ = 7.0 Hz, 3H, H$_2$C-C$_3$H$_3$), 1.00 (t, $J$ = 7.0 Hz, 3H, H$_2$C-C$_3$H$_3$).

$^{13}$C NMR (125 MHz, CDCl$_3$): δ 165.4, 164.3, 151.7, 134.8, 134.8, 134.6, 130.4, 128.3, 127.7, 126.2, 61.6, 61.3, 14.2, 13.8.

FT-IR (cm$^{-1}$): 1732, 1715, 1614, 1582, 1487, 1464, 1445, 1393, 1367, 1325, 1300, 1215, 1178, 1124, 1088, 1061, 1028, 1014, 937, 833, 741.

MS (APCI): $m/z$ = 309 [M$^{35}$Cl + H]$^+$, 263 [M$^{35}$Cl – C$_2$H$_5$O]$^+$.  

HRMS (APCI): $m/z$ = 309.08856 [M$^{35}$Cl + H]$^+$; calcd. for C$_{16}$H$_{17}$O$_4^{35}$Cl: 309.08881.

diethyl [1-(4-fluorophenyl)prop-2-en-1-ylidene]malonate (7c)

Yield : 32%
Mol. formula: C$_{16}$H$_{17}$FO$_4$
Mol. Wt. : 292.30 g.mol$^{-1}$
Aspect: yellow oil
\(^{1}\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.44 (dd, \(J = 17.2, 10.6 \text{ Hz}, 1H, H_2C=CH-C\)), 7.16 – 7.11 (massif, 2H, Ar), 7.04 – 6.98 (massif, 2H, Ar), 5.59 (dd, \(J = 10.5, 1.2 \text{ Hz}, 1H, HCH\)), 5.10 (dd, \(J = 17.1, 1.2 \text{ Hz}, 1H, HCH\)), 4.26 (q, \(J = 7.1 \text{ Hz}, 2H, H_3C-CH_3\)), 3.92 (q, \(J = 7.1 \text{ Hz}, 2H, H_3C-CH_3\)), 1.28 (t, \(J = 7.2 \text{ Hz}, 3H, H_3C-CH_3\)), 0.95 (t, \(J = 7.0 \text{ Hz}, 3H, H_3C-CH_3\)).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 165.6, 164.2, 162.8 (d, \(J = 246.4 \text{ Hz}\)), 151.9, 134.9, 132.3 (d, \(J = 3.2 \text{ Hz}\)), 130.8 (d, \(J = 8.1 \text{ Hz}\)), 127.6, 126.2, 115.1 (d, \(J = 21.5 \text{ Hz}\)), 61.5, 61.1, 14.1, 13.7.

FT-IR (cm\(^{-1}\)): 1716, 1614, 1603, 1576, 1504, 1466, 1446, 1367, 1323, 1250, 1228, 1200, 1159, 1122, 1095, 1059, 1030, 1014, 937, 864, 839, 820, 791.

MS (APCI): \(m/z = 293\) [M + H]\(^{+}\), 247 [M – C\(_2\)H\(_5\)O]\(^{+}\).

HRMS (APCI): \(m/z = 293.11832\) [M + H]\(^{+}\); calcd. for C\(_{16}\)H\(_{18}\)O\(_4\)F: 293.11836.

diethyl [1-(4-methylphenyl)prop-2-en-1-ylidene]malonate (7d)

Yield : 16%
Mol. formula: C\(_{17}\)H\(_{20}\)O\(_4\)
Mol. Wt. : 288.34 g.mol\(^{-1}\)
Aspect: colorless oil

\(^{1}\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.47 (dd, \(J = 17.2, 10.6 \text{ Hz}, 1H, H_2C=CH=C\)), 7.14 (d, \(J = 8.1 \text{ Hz}, 2H, Ar\)), 7.06 (d, \(J = 8.1 \text{ Hz}, 2H, Ar\)), 5.60 (dd, \(J = 10.6, 1.0 \text{ Hz}, 1H, HCH\)), 5.17 (dd, \(J = 17.1, 0.9 \text{ Hz}, 1H, HCH\)), 4.28 (q, \(J = 7.1 \text{ Hz}, 2H, H_3C-CH_3\)), 3.93 (q, \(J = 7.1 \text{ Hz}, 2H, H_3C-CH_3\)), 2.34 (s, 3H, H\(_3\)C-Ar), 1.30 (t, \(J = 7.2 \text{ Hz}, 3H, H_3C-CH_3\)), 0.95 (t, \(J = 7.0 \text{ Hz}, 3H, H_3C-CH_3\)).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 166.0, 164.5, 153.4, 138.4, 135.1, 133.6, 129.0, 128.7, 127.6, 125.6, 61.4, 61.1, 21.4, 14.2, 13.8.

FT-IR (cm\(^{-1}\)): 2986, 2913, 1614, 1578, 1510, 1464, 1446, 1367, 1325, 1227, 1184, 1122, 1096, 1063, 1032, 820.

MS (ESI): \(m/z = 327\) [M + K]\(^{+}\), 311 [M + Na]\(^{+}\), 289 [M + H]\(^{+}\), 243 [M – C\(_2\)H\(_5\)O]\(^{+}\).

HRMS (ESI): \(m/z = 289.14376\) [M + H]\(^{+}\); calcd. for C\(_{17}\)H\(_{21}\)O\(_4\): 289.14344.
triethyl buta-1,3-diene-1,1,2-tricarboxylate (7g)

Yield: 47%
Mol. formula: C_{13}H_{18}O_{6}
Mol. Wt.: 270.28 g mol^{-1}
Aspect: colorless liquid

^1H NMR (500 MHz, CDCl_3): δ 6.65 (dd, J = 17.5, 11.0 Hz, 1H, CH=C=CH), 5.68 (d, J = 11.0 Hz, 1H, CH=C=CH), 5.65 (d, J = 17.5 Hz, 1H, CH=C=CH), 4.36 (q, J = 7.0 Hz, 2H, CH2-CH3), 4.33 (q, J = 7.0 Hz, 2H, CH2-CH3), 4.24 (q, J = 7.0 Hz, 2H, CH2-CH3), 1.35 (t, J = 7.0 Hz, CH2-CH3), 1.33 (t, J = 7.0 Hz, CH2-CH3), 1.28 (t, J = 7.0 Hz, CH2-CH3).

^13C NMR (125 MHz, CDCl_3): δ 166.1, 164.4, 163.1, 145.1, 129.7, 126.8, 125.4, 62.11, 62.06, 62.04, 14.19, 14.11, 14.09.

FT-IR (cm^{-1}): 2984, 2962, 2926, 2905, 2872, 2853, 1724, 1620, 1595, 1466, 1447, 1391, 1367, 1319, 1298, 1244, 1182, 1163, 1096, 1068, 1024, 943, 862, 800, 779, 719.


HRMS (APCI): m/z = 271.11734 [M + H]^+; calcd. for C_{13}H_{18}O_6: 271.11761.

2.2.5. Michael addition

General Procedure

In a dry round bottom flask was added Cul (2.8 mmol) and 20 mL of THF under inert atmosphere. A 0.5829 M solution of vinylmagnesiumbromide in THF (10.1 mL; 5.9 mmol) was next added dropwise at 0 °C; the reaction mixture was stirred 45 min at this temperature. A solution of compound 4 (2.3 mmol) in 20 mL of THF was next added dropwise at -78 °C. The reaction mixture was stirred overnight (the cooling bath recovering slowly to room temperature). The reaction was then quenched with a NH4Cl sat solution (5 mL), then diluted with water (10 mL) and Et2O (50 mL). After layer separation, the aqueous layer was extracted with Et2O (2x 30 mL). The combined organic layers was washed with brine, dried over MgSO4, and finally concentrated under vacuum. The residue was purified by flash chromatography (10/90 EtOAc/cyclohexane) to give the desired product.
**diethyl [1-(4-methoxyphenyl)prop-2-en-1-yl]malonate (8e)**

CAS Reg. No. 1127889-64-8

![Structural formula of 8e]

Yield: 48%

Mol. formula: C_{17}H_{23}O_{5}

Mol. Wt.: 306.35 g.mol⁻¹

Aspect: pale yellow liquid

**¹H NMR (500 MHz, CDCl₃):** δ 7.15 (m, 2H, Ar), 6.83 (m, 2H, Ar), 5.97 (ddd, J = 17.1, 10.2, 8.0 Hz, 1H, CH₂=CH₃), 5.09 (dd, J = 17.1, 1.2 Hz, 1H, CH₂=CH), 5.05 (dd, J = 10.2, 1.0 Hz, 1H, CH₂=CH), 4.20 (q, J = 7.1 Hz, 2H, CH₂-CH₃), 4.06 (dd, J = 11.1, 8.1 Hz, 1H, HC-Ar), 3.95 (m, 2H, CH₂-CH₃), 3.78 (d, J = 11.1 Hz, 1H, HC(O₂Et)₂), 3.77 (s, 3H, O-CH₃), 1.27 (t, J = 7.1 Hz, 3H, CH₂-C(H₃)), 1.02 (t, J = 7.1 Hz, 3H, CH₂-CH₃).

**¹³C NMR (125 MHz, CDCl₃):** δ 168.0, 167.7, 158.7, 138.4, 132.2, 129.2, 116.2, 114.1, 61.6, 61.4, 57.7, 55.4, 49.0, 14.2, 14.0.

**FT-IR (cm⁻¹):** 2982, 2935, 2907, 2361, 2338, 1753, 1730, 1637, 1610, 1583, 1512, 1464, 1445, 1391, 1367, 1246, 1176, 1157, 1144, 1124, 1095, 1034, 993, 922, 829, 658.

**MS (APCI):** m/z = 307 [M + H]⁺, 147 [M – C₇H₁₁O₄]⁺.

**HRMS (APCI):** m/z = 307.15391 [M + H]⁺; calcd. for C₁₇H₂₃O₅: 307.15400.

**diethyl (1-isopropylprop-2-en-1-yl)malonate (8f)**

CAS Reg. No. 908102-65-8

![Structural formula of 8f]

Yield: 65%

Mol. formula: C_{13}H_{22}O₄

Mol. Wt.: 242.31 g.mol⁻¹

Aspect: pale yellow liquid

**¹H NMR (500 MHz, CDCl₃):** δ 5.69 (ddd, J = 17.0, 10.1, 10.1 Hz, 1H, CH₂=CH), 5.10 (dd, J = 10.3, 2.0 Hz, 1H, CH₂=CH), 5.06 (dd, J = 17.0, 1.9 Hz, 1H, CH₂=CH), 4.22 – 4.12 (massif, 4H, 2*CH₂=CH₃, 9 and 12), 3.53 (d, J = 9.7 Hz, 1H, CH₃(CO₂Et)₂), 2.65 (ddd, J = 9.7, 9.7, 4.9 Hz, CH-(i-Pr), 3), 1.75 (m, 1H, CH-(CH₃)₂), 1.26 (t, J = 7.2 Hz, CH₂-CH₃, 10 or 13), 1.24 (t, J = 7.2 Hz, CH₂-CH₃, 13 or 10), 0.91 (d, J = 6.8 Hz, 3H, CH-(CH₃)₂), 0.84 (d, J = 6.9 Hz, 3H, CH-(CH₃)₂, 6 or 5).
$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 168.8 ; 168.5 (8,11), 135.0 (2), 118.8 (1), 61.5 ; 61.3 (9,12), 55.1 (7), 50.4 (3), 29.1 (4), 21.4 ; 17.7 (5,6), 14.2 (10,13).

FT-IR (cm$^{-1}$): 2974, 2961, 2934, 2905, 1755 (C=O), 1732 (C=O), 1639 (C=C), 1466, 1447, 1389, 1369, 1323, 1300, 1259, 1242, 1227, 1178, 1144, 1132, 1096, 1034, 1003, 920.

MS (APCI): $m/z = 243$ [M + H]$^+$, 197 [M – C$_2$H$_5$O]$^+$.

HRMS (APCI): $m/z = 243.15893$ [M + H]$^+$; calcd. for C$_{13}$H$_{23}$O$_4$: 243.15909.

diethyl (1-butylprop-2-en-1-yl)malonate (8h)
CAS Reg. No. 117749-06-1

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 5.64 (ddd, $J = 17.0$, 10.2, 9.4 Hz, 1H, CH$_2$=CH), 5.10 – 5.04 (massif, 2H, CH=CH), 4.19 (q, $J = 7.1$ Hz, 2H, O-CH$_2$-CH$_3$), 4.14 (q, $J = 7.1$ Hz, 2H, O-CH$_2$-CH$_3$), 3.33 (d, $J = 8.9$ Hz, 1H, HC(CO$_2$Et)$_2$), 2.75 (ddt, 9.1, 9.1, 3.4 Hz, 1H, HC-(n-Bu)$_2$), 1.37 – 1.14 (massif, 6H, (CH$_2$_n-But)$_2$-CH$_3$), 1.26 (t, $J = 7.1$ Hz, 3H, O-CH$_2$-CH$_2$), 1.24 (t, $J = 7.1$ Hz, 3H, O-CH$_2$-CH$_2$).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 168.6, 168.4, 138.4, 117.4, 61.4, 61.3, 57.2, 44.2, 32.1, 29.3, 22.6, 14.3, 14.1.

FT-IR (cm$^{-1}$): 2982, 2957, 2934, 2907, 2874, 2860, 2365, 2341, 2316, 1751, 1732, 1641, 1466, 1447, 1391, 1369, 1300, 1263, 1242, 1223, 1176, 1144, 1095, 1034, 918.

MS (APCI): $m/z = 257$ [M + H]$^+$, 211 [M – C$_2$H$_5$O]$^+$.

HRMS (APCI): $m/z = 257.17464$ [M + H]$^+$; calcd. for C$_{14}$H$_{25}$O$_4$: 257.17474.

2.2.6. Double bond reformation
General Procedure

In a dry round bottom flask was added compound 8 (1 mmol) in 5 mL of DMF under inert atmosphere. NaH (60% dispersion in mineral oil; 1.2 mmol) was then added at 0°C. The mixture was stirred for 1h at room temperature (= solution A).

In another dry round bottom flask was added PhSeCl (2 mmol) in 5 mL of DMF. This solution was cooled to -10°C, and then added, very slowly (over 2h), to solution A. This mixture was stirred for two more hours at -10°C and then for 2h at 0°C. Finally H2O2 (30% sol. in water; 15 mmol) was added, at 0 °C. The solution was stirred for 30 min at this temperature. The reaction was then quenched with a NaHCO3 sat solution (5 mL), diluted with water (20 mL) and extracted with EtOAc (2*20 mL). The combined organic layers were washed with water (10 mL), brine (10 mL), dried over MgSO4, and then concentrated under reduced pressure. The residue was purified by flash chromatography (05/95 => 10/90 EtOAc/cyclohexane) to give the desired product.

diethyl [1-(4-methoxyphenyl)prop-2-en-1-ylidene]malonate (7e)

![Structure of diethyl [1-(4-methoxyphenyl)prop-2-en-1-ylidene]malonate (7e)]

Yield: 47%
Mol. formula: C17H20O5
Mol. Wt.: 304.34 g.mol⁻¹
Aspect: pale yellow liquid

1H NMR (300 MHz, CDCl3): δ 7.47 (dd, J = 17.2, 10.5 Hz, 1H, CH₂=CH), 7.17 – 7.08 (m, 2H, Ar), 6.92 – 6.83 (m, 2H, Ar), 5.62 (dd, J = 10.5, 1.4 Hz, 1H, CH₂=CH), 5.21 (dd, J = 17.2, 1.4 Hz, CH₂=CH), 4.29 (q, J = 7.1 Hz, 2H, CH₂-CH₃), 3.96 (q, J = 7.1 Hz, 2H, CH₂-CH₃), 3.81 (s, 3H, O-CH₃), 1.31 (t, J = 7.1 Hz, 3H, CH₂-CH₃), 0.99 (t, J = 7.1 Hz, 3H, CH₂-CH₃).

13C NMR (75 MHz, CDCl₃): δ 166.2, 164.5, 159.9, 153.2, 135.4, 130.5, 128.8, 127.5, 125.5, 113.5, 61.4, 61.1, 55.4, 14.2, 13.8.

FT-IR (cm⁻¹): 2980, 2964, 2937, 2907, 2837, 1717, 1609, 1578, 1510, 1464, 1445, 1404, 1391, 1367, 1327, 1306, 1292, 1248, 1215, 1176, 1124, 1113, 1095, 1063, 1030, 939, 862, 835, 812, 797, 783.


HRMS (APCI): m/z = 305.13827 [M + H]+; calcd. for C₁₇H₂₀O₅: 305.13835.
**diethyl (1-isopropylprop-2-en-1-ylidene)malonate (7f)**

![Chemical structure](image)

Yield: 36%

Mol. formula: C₁₃H₂₀O₄

Mol. Wt.: 240.30 g mol⁻¹

Aspect: pale yellow liquid

**¹H NMR (300 MHz, CDCl₃)**: δ 6.42 (dd, J = 17.7, 11.7 Hz, 1H, CH₂=CH), 5.31 (dd, J = 17.7, 1.5 Hz, 1H, CH₂=CH), 5.27 (dd, J = 11.7, 1.5 Hz, 1H, CH₂=CH), 4.17 (q, J = 7.2 Hz, 2H, CH₂-CH₃), 4.12 (q, J = 7.2 Hz, 2H, CH₂-CH₃), 3.32 (sep, J = 6.9 Hz, 1H, CH-(CH₃)₂), 1.22 (t, J = 7.3 Hz, 3H, CH₂-C₃H₃), 1.20 (t, J = 7.3 Hz, 3H, CH₂-C₃H₃), 1.03 (d, J = 6.9 Hz, 6H, CH-(C₂H₃)₂).

**¹³C NMR (75 MHz, CDCl₃)**: δ 166.2, 165.0, 161.3, 132.6, 124.2, 120.9, 61.1, 30.9, 20.9, 14.1, 14.0.

**FT-IR (cm⁻¹)**: 2980, 2936, 2907, 2874, 1721, 1615, 1580, 1466, 1447, 1418, 1387, 1366, 1337, 1298, 1285, 1269, 1219, 1204, 1160, 1096, 1061, 1025, 934, 868, 791, 733.

**MS (APCI)**: m/z = 241 [M + H]⁺, 195 [M – C₂H₅O]⁺.

**HRMS (APCI)**: m/z = 241.14322 [M + H]⁺; calcd. for C₁₃H₂₁O₄: 241.14344.

**diethyl (1-butylprop-2-en-1-ylidene)malonate (7h)**

![Chemical structure](image)

Yield: 35%

Mol. formula: C₁₄H₂₂O₄

Mol. Wt.: 254.32 g mol⁻¹

Aspect: yellow liquid

**¹H NMR (300 MHz, CDCl₃)**: δ 6.93 (dd, J = 17.4, 11.0 Hz, 1H, CH₂=CH), 5.70 (d, J = 17.4 Hz, 1H, CH₂=CH), 5.50 (d, J = 11.0 Hz, 1H, CH₂=CH), 4.23 (q, J = 7.1 Hz, 4H, 2*CH₂-CH₃), 2.55 (m, 2H, CH₂-(n-prop)), 1.53 – 1.20 (massif, 4H, (CH₂)₂-CH₃), 1.28 (t, J = 7.1 Hz, 6H, 2*O-CH₂-CH₃), 0.90 (t, J = 7.1 Hz, 3H, CH₂-(CH₂)₃-C).

**¹³C NMR (75 MHz, CDCl₃)**: δ 165.6, 165.5, 153.7, 133.8, 125.3, 122.2, 61.3, 61.1, 31.9, 29.2, 23.2, 14.2, 13.9.

**FT-IR (cm⁻¹)**: 2978, 2959, 2933, 2907, 2872, 1717, 1620, 1583, 1464, 1447, 1389, 1366, 1300, 1279, 1223, 1198, 1115, 1096, 1061, 1030, 932, 868, 791, 733.
MS (APCI): \( m/z = 255 \ [M + H]^+, \ 209 \ [M - C_2H_5O]^+ \).

HRMS (APCI): \( m/z = 255.15882 \ [M + H]^+; \) caled. for \( C_{14}H_{23}O_4 \): 255.15909.