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Regio- and Stereoselective Nickel-Catalyzed Coupling of Boronic Acids with Allenoates

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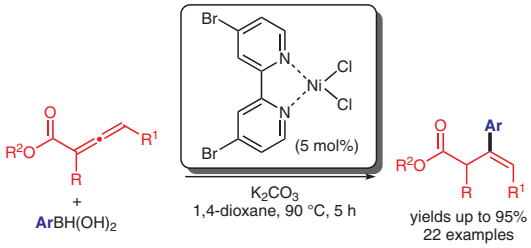

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Abstract The Ni(II)-catalyzed cross-coupling of arylboronic acids with allenoates is documented. The high regio- and stereoselectivity of the process enables a wide range of β-aryl β,γ-unsaturated esters to be prepared in good to excellent yields (up to 95%) and high *E*/*Z*-selectivity. Additionally, [3+2]-cascade sequence was observed when 2-formylphenylboronic acid was employed.

Key words allenoate, boronic acid, catalysis, cross-coupling, nickel, stereoselection

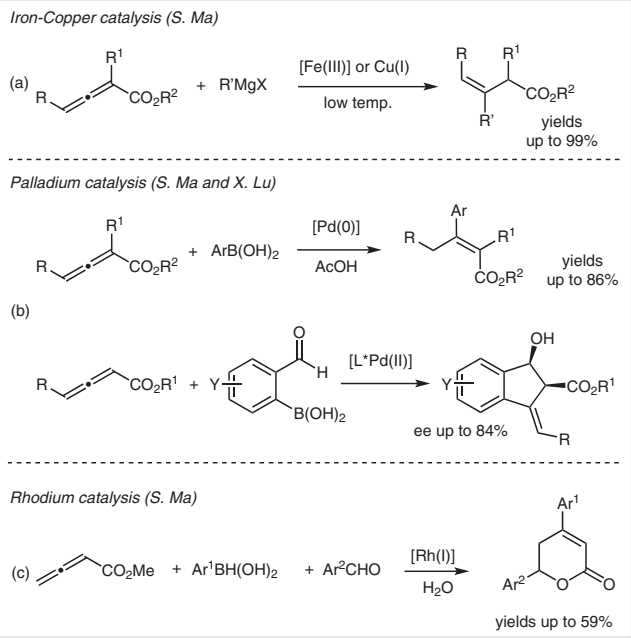
The impact of nickel catalysis in modern organic synthesis is flourishing with a plethora of applications in diversified research lines such as cross-coupling processes, synthesis of natural/bioactive compounds, asymmetric transformations, and photo-redox methodologies.[1] Low cost, earth abundance, mild reaction conditions, fine-tunability via ligand modulation, and wide range of easily accessible oxidation states are some of main features that are contributing to expand the applicability of nickel catalysis in organic synthesis.[2]

In this context, Ni-promoted nucleophilic type cross-coupling transformations deserve a prominent role.[1,3] [Ni(0)] species, mainly based on [Ni(COD)$_2$] precursor, have traced some landmarks in the field, however, the high sensitivity of these nickel-precatalysts prompted to envision the applicability of more stable [Ni(II)] precursors in redox-active as well as redox-neutral C–C and C–X cross-coupling processes.[4]

In conjunction with our interest in the transition-metal-catalyzed functionalization of cumulate π-systems,[5] we have recently documented on the site-selective condensation of boronic acids[6] to *N*-allenamides under [Ni(bpy)Cl$_2$] catalysis.[7] A wide range of configurationally defined enamides was obtained in high yields. Accordingly, we envisioned the possibility to extend our protocol to allenotates,[8] a well-known family of 'electronically modified' allenes that, to the best of our knowledge, have never been subjected to Ni-assisted condensation with boronic acids. Notably, the reverse electron perturbation with respect to allenamides (EWG are present instead of EDG) could impact on the chemo-, regio-, and stereoselectivity. Additionally, previous examples on transition-metal-catalyzed addition of organometallic species (i.e., Grignard reagents,[9] boronic acids[10]) to allenoates clearly emphasized that also the nature of the metal species substantially contributes to determine the formation of α,β- or β,γ-unsaturated β-arylated esters (Scheme 1, a–c).

In order to verify the extension of the Ni-catalysis to EWG-conjugated allenes, allenoate **1a** and phenylboronic acid (**2a**) were subjected to an extensive survey of reaction conditions regarding structure of the nickel catalyst, base, and temperature. A collection of results is documented in Table 1 from which some conclusions are drawn.

Interestingly, bis-pyridyl-based complexes **Cat1**–**6**/**8** (5 mol%) displayed moderate to very good selectivity (yield up to 95% with **Cat3**, Table 1, entry 3) towards the formation of the β-phenyl-β,γ-unsaturated ester **3aa** with high stereoselectivity and affording the *E*-isomer in major amount (up to 13:1). In contrast, keto-bridged catalyst **Cat7**, NHC, and phosphine-based [Ni(II)] complex analogues failed in promoting the cross-coupling reaction. Interestingly, [Ni(PPh$_3$)$_2$Cl$_2$] displayed a divergent chemical course delivering the isomeric conjugate diene isomer **3aa″** in 50% yield (entry 9). This finding can be seen as a preliminary indication that the presence of [Ni(0)] intermediate (more likely with P-based complexes with respect to pyridyl analogues) disfavors the cross-coupling process with boronic acids. The catalyst of election (**Cat3**) enabled lowering of the catalyst up to 2.5 mol% with only a slight erosion in chemical yield

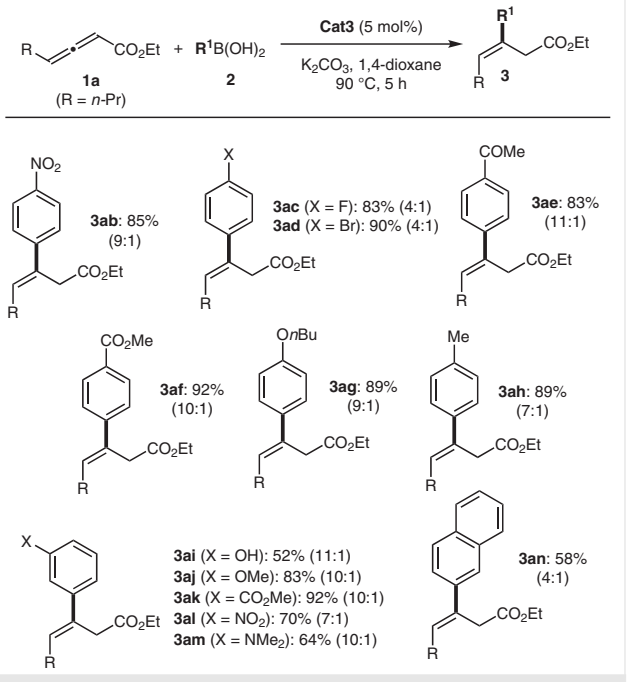


Scheme 1 Previous work on the metal-catalyzed condensation of boronic acids to allenoates

(84%, entry 13). Additionally, the possibility to carry out the reaction also with the in situ formed complex was verified (entry 14, 88% yield, 11:1 stereoisomeric ratio). A very brief survey of inorganic bases elected K_2CO_3 as the most efficient one. The use of [Cu(**L1**)Cl] furnished similar **3aa**/**3aa′** selectivity but in lower extent (53% yield, entry 11), while $[Pd(PPh_3)_4]$ under acidic conditions[10c] resulted in the isolation of the α,β-unsaturated compound **3aa′** (entry 12). Finally, the impact of the temperature on the kinetics and stereochemistry of the process was also examined (entries 15 and 16). Here, while at 60 °C the reaction did not proceed at all, at 110 °C a drop in *E*/*Z* ratio with respect to 90 °C was recorded (5:1 vs 11:1).

The generality of the methodology in term of boronic acids was then addressed by condensing **1a** with a series of differently substituted compounds **2** (optimal reaction conditions: **1a**, **2**, **Cat3**, K_2CO_3, 5 h, 90 °C, reagent grade 1,4-dioxane, Scheme 2). Remarkably, the protocol did not show any perturbation by varying position and electronic properties of the substituent on the aromatic ring. EWGs (i.e., NO_2, Br, COMe, CO_2Me, and F) and EDGs (i.e., OH, Me, O*n*-Bu, NMe_2, and OMe) were adequately supported providing the corresponding β,γ-unsaturated ethyl esters **3** in very high yields (up to 92%) and from moderate to very high *E*/*Z* ratio. Analogously, the 2-naphthylboronic acid (**2n**) performed satisfyingly in Ni-catalyzed process (58% yield, *E*/*Z* = 4:1). In contrast, aliphatic *c*-Hex$B(OH)_2$ proved ineffective in the catalytic process.

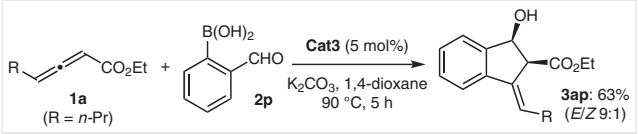
The generality of the protocol was further investigated by subjecting a range of diversely substituted allenoates **1b–i** to condensation with **2a** (Table 2). Structural variations on the allenoates were realized on the allenyl unit (both α- and γ-position with respect to ester group) and at the alkyloxy group (R^2). Substituted (R = alkyl, aryl) and unsubstituted (R = H) allenoates at the γ-position reacted satisfyingly under optimal conditions, delivering the corresponding cross adduct in synthetically useful yields. However, the stereochemical outcome proved to be dependent on R. As a matter of fact, with R = linear alkyl chain (i.e., *n*-C_3H_7 and *n*-C_9H_{19}) the corresponding β,γ-unsaturated esters were isolated with good *E*-predominance (up to 6:1) regardless the nature of R^2 [i.e., BnO, EtO, 3,5-$Me_2C_6H_3O$] (90 °C). Interestingly, the employment of mono-substituted allenes **1b** and **1e** at the same temperature resulted in a drop of β,γ/α,β ratio. However, by lowering the reaction temperature to 40 °C 80:20 chemoselectivity in favor of the unconjugated compound **3** was observed. Additionally, the γ-phenyl-substituted allenoate **1i** still delivered the β,γ-unsaturated adduct **3ia** in very high yield (85%) but a significant erosion in C=C stereoselection was recorded (Table 2, entry 8). A limitation of the methodology appeared when the α,γ-disubstituted allene **1h** was utilized. Here, the reaction became particular sluggish and the corresponding cross-coupling compounds was obtained only in traces (entry 7). Finally, the methodology proved competent also for



Scheme 2 Examining the reaction scope with respect to the phenylboronic acids

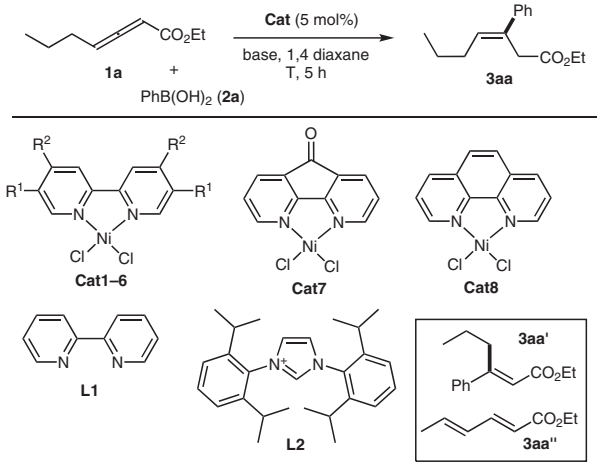
the keto-allenyl compound **1f** that provided the thermodynamically more stable enone (*E*)-**3fa** in 84% as a single stereoisomer (entry 5).

Interestingly, the use of 2-formylphenylboronic acid (**2p**) led to the isolation of the [3+2]-annulated compound **3ap** in 63% yield as a single diastereoisomer. Once again, absolute stereospecificity towards the formation of the *trans*-C=C bond was observed (Scheme 3).[11,12]



Scheme 3 Formal [3+2] cycloaddition between the 2-formylphenylboronic acid (**2p**) and allenoate **1a**

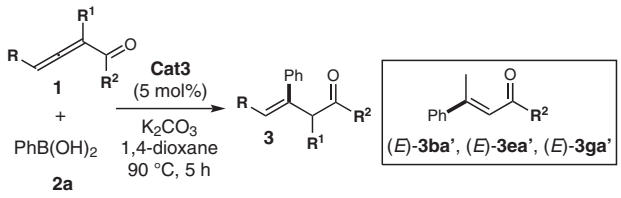
Table 1 Optimization of the Reaction Conditions[a]



Entry	Cat (5 mol%)	Base	Temp (°C)	Yield of **3aa** (%)[b]	*E*/*Z*[c]
1	**Cat1** (R^1 = R^2 = H)	K_2CO_3	90	52	13:1
2	**Cat2** (R^1 = H, R^2 = *t*-Bu)	K_2CO_3	90	82	10:1
3	**Cat3** (R^1 = H, R^2 = Br)	K_2CO_3	90	95	11:1
4	**Cat4** (R^1 = H, R^2 = OMe)	K_2CO_3	90	65	9:1
5	**Cat5** (R^1 = H, R^2 = CO_2Me)	K_2CO_3	90	90	7:1
6	**Cat6** (R^1 = Me, R^2 = H)	K_2CO_3	90	82	13:1
7	**Cat7**	K_2CO_3	90	traces	–
8	**Cat8**	K_2CO_3	90	73	11:1
9	[$Ni(PPh_3)_2Cl_2$]	K_2CO_3	90	(50, **3aa**'')	–
10	**L2**/$NiCl_2$(DME)	K_2CO_3	90	traces	–
11	**L1**/CuCl	K_2CO_3	90	53	11:1
12[d]	[$Pd(PPh_3)_4$]	–	r.t.	(34, **3aa**')	–
13	**Cat3** (2.5 mol%)	K_2CO_3	90	84	11:1
14[e]	**Cat3** (*in situ*)	K_2CO_3	90	88	11:1
15[f]	**Cat3**	K_2CO_3	60	traces	–
16	**Cat3**	K_2CO_3	110	85	5:1
17	**Cat3**	Na_2CO_3	90	82	10:1
18	**Cat3**	Cs_2CO_3	90	traces	–

[a] All the reactions were carried out under N_2 in reagent grade 1,4-dioxane, unless otherwise specified.
[b] Isolated yield after flash chromatography.
[c] Determined by ^{1}H NMR analysis and/or GC-MS on the reaction crude.
[d] In the presence of AcOH (100 mol%).
[e] Complex made in situ from 4,4′-Br_2-bpy and $NiCl_2$(DME).
[f] Reaction time: 16 h.

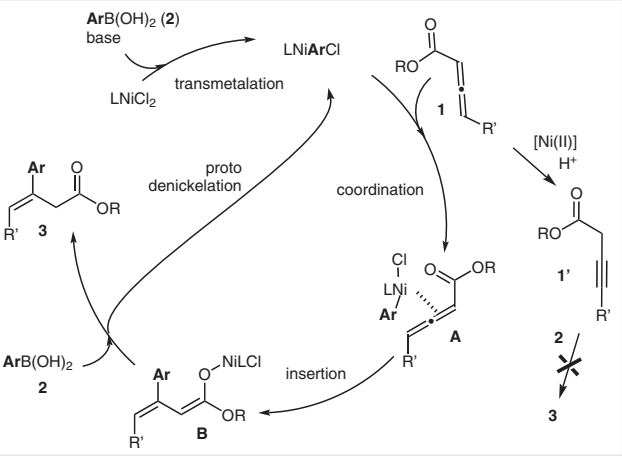
Table 2 Reaction Scope of Allenoates **1**[a]



Entry	R/R^1/R^2 (**1**)	Yield of **3** (%)[b]	*E*/*Z*[c]
1	H/H/OBn (**1b**)	82 (**3ba**)	4:1[d]
2	*n*-Pr/H/OBn (**1c**)	89 (**3ca**)	6:1
3	*n*-Pr/H/3,5-$Me_2C_6H_3O$ (**1d**)	81 (**3da**)	9:1
4	H/H/3,5-$Me_2C_6H_3O$ (**1e**)	90 (**3ea**)	2:1[e]
5	*n*-C_8H_{17}/H/OEt (**1f**)	84 (**3fa**)	6:1
6	H/H/Ph (**1g**)	84 (**3ga′**)	>95:5[f]
7	*n*-Pr/Me/OEt (**1h**)	traces (**3ha**)	–
8	Ph/H/OEt (**1i**)	85 (**3ia**)	1:1

[a] All the reactions were carried out under N_2 in reagent grade 1,4-dioxane.
[b] Isolated yield after flash chromatography.
[c] Determined by ^{1}H NMR analysis and/or GC-MS on the reaction crude.
[d] The β,γ-/α,β-conjugated compound is represented, reaction at 40 °C.
[e] The β,γ-/α,β-conjugated compound is represented.
[f] The (*E*)-α,β-unsaturated isomer was obtained exclusively (reaction at 40 °C).

As a speculative mechanism, the reaction process depicted in the Scheme 4 is presented. Initially, base-assisted transmetalation between the arylboronic acid **2** and the preformed [Ni(II)] complex could lead to the organonickel intermediate [LNiArCl] that engages the allenoate **1** in a coordinating event (**A**). Transfer of the aryl group to the central carbon of the allenyl unit, *anti* with respect to R′, would result in the formal nickel-enolate **B**. A second molecule of $ArB(OH)_2$ finally delivers the compound **3** by selective proto-denickelation. The possible allene → alkyne isomerization and consequent cross-coupling event is unlikely. As a matter of fact, when a mixture of allene/alkyne (~1:1)[13] was employed as the starting material, the reaction rate dropped significantly and a mixture of inseparable compounds was recorded with most of the alkyne unreacted.



Scheme 4 Tentative mechanistic picture

In conclusion, the [Ni(II)]-catalyzed synthesis of β,γ-unsaturated esters via condensation of boronic acids to allenoates is presented. Excellent isolated yields were accompanied by high levels of chemo-, regio-, and stereoselectivity. The robustness of the chemistry, ready availability of the nickel precatalyst, and relatively mild reaction conditions predict the present cross-coupling type methodology as a valuable synthetic protocol for the synthesis of added value organic compounds.

^{1}H NMR spectra were recorded on Varian 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard ($CDCl_3$: 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (standard abbreviations), coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard ($CDCl_3$: 77.0 ppm). GC-MS spectra were taken by EI ionization at 70 eV on a Hewlett-Packard 5971 with GC injection. LC-electrospray ionization mass spectra were obtained with Agilent Technologies MSD1100 single-quadrupole mass spectrometer. Chromatographic purification was done with 240–400 mesh silica gel. Elemental analyses were carried out by using a EACE 1110 CHNOS analyzer. All anhydrous solvents were supplied by Sigma Aldrich in Sureseal® bottles and used without any further purification. Commercially available chemicals were purchased from Sigma Aldrich, and used without any further purification. IR spectra were recorded on a Bruker-alpha spectrophotometer. Melting points were measured using open glass capillaries in a Bibby Stuart Scientific Melting Point Apparatus SMP 3 and are calibrated by comparison with literature values (Aldrich). Allenoate **1a** was obtained following a known procedure.

Allenoates 1b–f,h,i;[14] 3,5-Dimethylphenyl Buta-2,3-dienoate (1e); Typical Procedure

A dry two-necked flask was charged with a stirring bar, 3,5-dimethylphenol (1.22 g, 10 mmol), CH_2Cl_2 (30 mL), and pyridine (1.77 mL, 22 mmol). The mixture was cooled to 0 °C, and bromoacetyl bromide (0.86 mL, 10 mmol) was added to the mixture slowly. The mixture was warmed to r.t. and stirred overnight. After the completion of the reaction (TLC monitoring), the mixture was washed with H_2O (2 × 20 mL) and the organic phase was dried (Na_2SO_4). The solvent was removed and the residue was purified by flash chromatography on silica gel (*c*-Hex/EtOAc 10:1) to give 3,5-dimethylphenyl 2-bromoacetate (2.1 g, 86%) as a colorless oil.

A dry two-neck flask was charged with PPh_3 (786 mg, 3.0 mmol) and $CHCl_3$ (10 mL). The solution was cooled to 0 °C and the above prepared 3,5-dimethylphenyl 2-bromoacetate (729 mg, 3.0 mmol) was added. The reaction was warmed to r.t. and stirred overnight. The mixture was washed with aq 2 N NaOH (2 × 20 mL) and the collected organic phase was dried (Na_2SO_4). After removal of solvent under vacuum, the intermediate pure ylide was obtained as a white solid (1.20 g, 95%) and used in the next step without further purification.

A dry Schlenk tube was charged with a stirring bar, CH_2Cl_2 (6 mL), the above prepared ylide (2.0 mmol), and Et_3N (305 µL, 2.2 mmol). The mixture was cooled to 0 °C in ice bath. A solution of acetyl chloride (2.2 mmol) in CH_2Cl_2 (2 mL) was added dropwise to the reaction mixture. The mixture was warmed to r.t. and stirred overnight. After the completion of the reaction (TLC monitoring), most of solvent was removed under vacuum, and Et_2O (50 mL) was added to the flask, and the mixture was stirred for 0.5 h (***Caution***: longer reaction time may promote the isomerization of allenoate to the corresponding alkyl ester). The mixture was filtered and the organic phase was concentrated under vacuum. The residue was purified by flash chromatography on silica gel (*c*-Hex/EtOAc 20:1) to give the allenoate **1e**; yield: 147 mg (78%); colorless oil; R_f = 0.65 (*c*-Hex/EtOAc 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.87 (s, 1 H), 6.75 (s, 2 H), 5.84–5.79 (m, 1 H), 5.34–5.29 (m, 2 H), 2.35–2.30 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 216.69, 164.49, 150.84, 139.39, 127.76, 119.26, 87.94, 79.81, 21.38.

MS (70 eV): *m*/*z* (%) = 188 (100).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.41; H, 6.61.

Benzyl Buta-2,3-dienoate (1b)

Yield: 296 mg (85%); colorless oil; R_f = 0.65 (*c*-Hex/EtOAc 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.32 (m, 5 H), 5.69 (t, *J* = 6.5 Hz, 1 H), 5.24 (d, *J* = 6.5 Hz, 2 H), 5.20 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 216.14, 165.66, 136.02, 128.67, 128.34, 128.26, 88.00, 79.54, 66.76.

MS (70 eV): *m*/*z* (%) = 174 (100).

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.71; H, 5.61.

Benzyl Hepta-2,3-dienoate (1c)

Yield: 302 mg (70%); colorless oil; R_f = 0.70 (*c*-Hex/EtOAc 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (m, *J* = 4.3 Hz, 4 H), 7.35–7.31 (m, 1 H), 5.63 (m, *J* = 7.5, 3.9 Hz, 2 H), 5.18 (d, *J* = 4.7 Hz, 2 H), 2.15–2.09 (m, 2 H), 1.55–1.44 (m, 2 H), 0.94 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.84, 166.23, 136.22, 128.62, 128.24, 128.21, 95.47, 88.11, 66.55, 29.64, 22.14, 13.62.

MS (70 eV): *m*/*z* (%) = 216 (100).

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.61; H, 7.31.

3,5-Dimethylphenyl Hepta-2,3-dienoate (1d)

Yield: 336 mg (73%); colorless oil; R_f = 0.70 (*c*-Hex/EtOAc 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.86 (s, 1 H), 6.75 (s, 2 H), 5.75 (m, 1 H), 5.70 (m, 1 H), 2.32 (s, 6 H), 2.17 (ddd, *J* = 14.4, 7.1, 3.0 Hz, 2 H), 1.57–1.51 (m, 2 H), 1.00 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.43, 165.02, 150.96, 139.28, 127.57, 119.28, 119.06, 95.66, 87.98, 29.61, 22.12, 21.34, 13.62.

MS (70 eV): *m*/*z* (%) = 230 (100).

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.09; H, 7.71.

Ethyl Dodeca-2,3-dienoate (1f)

Yield: 181 mg (81%); colorless oil; R_f = 0.75 (*c*-Hex/EtOAc 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.00–5.90 (m, 2 H), 4.55 (m, 2 H), 2.48 (qd, *J* = 7.1, 3.2 Hz, 2 H), 1.80 (dd, *J* = 14.8, 7.4 Hz, 2 H), 1.68 (m, 2 H), 1.63 (m, 11 H), 1.24 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.44, 166.45, 95.53, 88.37, 60.85, 32.00, 29.47, 29.38, 29.08, 28.88, 27.65, 22.80, 14.40, 14.23.

MS (70 eV): *m*/*z* (%) = 244 (100).

Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 8.45. Found: C, 74.77; H, 8.35.

Ethyl 2-Methylhepta-2,3-dienoate (1h)

Yield: 84 mg (50%); colorless oil; R_f = 0.65 (*c*-Hex/EtOAc 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.47–5.38 (m, 1 H), 4.22–4.13 (m, 2 H), 2.07 (q, *J* = 7.0 Hz, 2 H), 1.85 (d, *J* = 2.9 Hz, 3 H), 1.54–1.38 (m, 2 H), 1.26 (t, *J* = 7.1 Hz, 3 H), 0.95 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 210.25, 168.22, 95.69, 93.67, 60.87, 30.16, 22.21, 15.37, 14.41, 13.60.

MS (70 eV): *m*/*z* (%) = 168 (100).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.30; H, 9.71.

Ethyl 4-Phenylbuta-2,3-dienoate (1i)

Yield: 248 mg (66%); colorless oil; R_f = 0.55 (*c*-Hex/EtOAc 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.27 (m, 5 H), 6.62 (d, *J* = 6.4 Hz, 1 H), 6.02 (d, *J* = 6.4 Hz, 1 H), 4.28–4.19 (m, 2 H), 1.29 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 214.75, 165.24, 131.33, 128.99, 128.24, 127.65, 98.81, 92.09, 61.28, 14.39.

MS (70 eV): *m*/*z* (%) = 188 (100).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.41; H, 6.38.

1-Phenylbuta-2,3-dien-1-one (1g)

A dry two-necked flask was charged with DMF/Et_2O (6 mL, 1:1), benzaldehyde (530 mg, 5 mmol), and Zn dust (630 mg, 10 mmol). The reaction mixture was cooled to 0 °C and propargyl bromide (1.08 mL, 10 mmol, 80% in toluene) was added dropwise. The mixture was warmed to r.t. and stirred for 24 h when TLC showed the completion of the reaction. The mixture was filtered, the organic phase concentrated under vacuum, and the residue was purified by flash chromatography on silica gel (*c*-Hex/EtOAc 5:1) to give propargyl 1-phenylbut-3-yn-1-ol (613 mg, 84%) as a colorless oil.

A dry single-necked flask was charged with CH_2Cl_2 (6 mL), propargyl 1-phenylbut-3-yn-1-ol (292 mg, 2.0 mmol), followed by 2-iodoxybenzoic acid (IBX; 1.68 g, 6.0 mmol). The reaction mixture was stirred for 20 h at r.t. The mixture was filtered and the organic phase concentrated under vacuum. The residue was purified by flash chromatography on silica gel (*c*-Hex/EtOAc 20:1) to give **1g**, yield: 225 mg (78%); colorless oil; R_f = 0.80 (*c*-Hex/EtOAc 10:1)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93–7.86 (m, 2 H), 7.58–7.53 (m, 1 H), 7.48–7.42 (m, 2 H), 6.44 (t, *J* = 6.5 Hz, 1 H), 5.28–5.23 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 217.20, 191.07, 137.59, 132.90, 128.79, 128.48, 93.37, 79.33.

MS (70 eV): *m*/*z* (%) = 144 (100).

Anal. Calcd for $C_{10}H_8O$: C, 83.31; H, 5.59. Found: C, 83.18; H, 5.40.

Nickel-Catalyzed Coupling of Boronic Acids with Allenoates; Ethyl (*E*)-3-Phenylhept-3-enoate (3aa); Typical Procedure

A flame-dried Schlenk tube, filled with N_2, was charged sequentially with reagent grade 1,4-dioxane (1 mL), [4,4′-dibromobpy-$NiCl_2$] (4.0 mg, 5 mol%), phenylboronic acid (**2a**; 37 mg, 0.3 mmol, 1.5 equiv), allenoate **1a** (30.8 mg, 0.2 mmol, 1.0 equiv), and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv). The reaction mixture was then heated at 90 °C for 5 h (complete consumption of the allenoate was monitired by TLC). Then the solvent was removed under vacuum and the residue purified via flash chromatography.

Ethyl (*E*)-3-Phenylhept-3-enoate (3aa)

Yield: 44 mg (95%); colorless oil; R_f = 0.45 (*c*-Hex/EtOAc 100:1 → 30:1); *E*/*Z* = 11:1.

IR (neat): 2961, 2934, 2874, 1960, 1713, 1463, 1249, 1154, 1039, 796 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.37 (m, 2 H), 7.33–7.28 (m, 2 H), 7.23–7,21 (m, 1 H), 5.95 (t, *J* = 7.3 Hz, 1 H), 4.10 (q, *J* = 7.1 Hz, 1 H), 3.52 (s, 1 H), 2.26–2.17 (m, 1 H), 1.57–1.45 (m, 1 H), 1.19 (t, *J* = 7.1 Hz, 2 H), 0.97 (t, *J* = 7.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.61, 142.57, 132.76, 132.60, 128.38, 126.91, 126.09, 60.79, 36.22, 31.21, 22.75, 14.24, 14.04.

MS (70 eV): *m*/*z* (%) = 232 (100).

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.51; H, 8.45.

Ethyl (*E*)-3-(4-Nitrophenyl)hept-3-enoate (3ab)

Yield: 47 mg (85%); colorless oil; R_f = 0.45 (*c*-Hex/EtOAc 20:1); *E*/*Z* = 9:1.

IR (neat): 2960, 2932, 2872, 1731, 1526, 1347, 1154, 1157, 736, 683 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.18–8.14 (m, 2 H), 7.54–7.50 (m, 2 H), 6.11 (t, *J* = 7.3 Hz, 1 H), 4.11 (q, *J* = 7.1 Hz, 2 H), 3.53 (s, 2 H), 2.25 (q, *J* = 7.4 Hz, 2 H), 1.58–1.48 (m, 2 H), 1.20 (t, *J* = 7.1 Hz, 3 H), 0.98 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.92, 149.10, 136.69, 131.45, 129.65, 126.76, 123.79, 61.12, 35.86, 31.38, 22.53, 14.25, 14.01.

MS (70 eV): *m*/*z* (%) = 277 (100).

Anal. Calcd for $C_{15}H_{19}NO_4$: C, 64.97; H, 6.91. Found: C, 64.81; H, 6.77.

(*Z*)-3ab

^1H NMR (400 MHz, $CDCl_3$): δ (diagnostic signals) = 5.74 (t, *J* = 7.5 Hz, 1 H), 3.37 (d, *J* = 0.8 Hz, 2 H), 1.96 (dd, *J* = 14.8, 7.4 Hz, 2 H), 1.15 (t, *J* = 7.1 Hz, 3 H), 0.85 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (diagnostic signals) = 146.74, 134.68, 123.55.

Ethyl (*E*)-3-(4-Fluorophenyl)hept-3-enoate (3ac)

Yield: 42 mg (83%); colorless oil; R_f = 0.70 (*c*-Hex/EtOAc 10:1), *E*/*Z* = 4:1.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.33 (m, 2 H), 6.99 (m, 2 H), 5.87 (t, *J* = 7.3 Hz, 1 H), 4.10 (q, *J* = 7.1 Hz, 2 H), 3.48 (s, 2 H), 2.19 (q, *J* = 7.3 Hz, 2 H), 1.51 (dt, *J* = 14.8, 7.4 Hz, 2 H), 1.18 (t, *J* = 7.1 Hz, 3 H), 0.97 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.42, 162.05 (d, *J* = 244.0 Hz), 138.72 (d, *J* = 3.0 Hz), 132.72, 131.80, 127.70 (d, *J* = 8.0 Hz), 115.12 (d, *J* = 22.0 Hz), 60.83, 36.35, 31.17, 22.73, 14.23, 14.00.

MS (70 eV): *m*/*z* (%) = 250 (100).

Anal. Calcd for $C_{15}H_{19}FO_2$: C, 71.98; H, 7.65. Found: C, 71.69; H, 7.40.

(*Z*)-3ac

^1H NMR (400 MHz, $CDCl_3$): δ (diagnostic signals) = 5.62 (t, *J* = 7.5 Hz, 1 H), 4.05 (q, *J* = 7.1 Hz, 2 H), 3.31 (s, 2 H), 1.95 (q, *J* = 7.4 Hz, 2 H), 1.36 (dt, *J* = 10.6, 5.4 Hz, 2 H), 1.17–1.13 (m, 3 H), 0.84 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (diagnostic signals) = 171.66, 163.06, 132.25 (d, *J* = 9.0 Hz), 130.24 (d, *J* = 8.0 Hz), 115.16, 114.95.

Ethyl (*E*)-3-(4-Bromophenyl)hept-3-enoate (3ad)

Yield: 56 mg (90%); colorless oil; R_f = 0.75 (*c*-Hex/EtOAc 10:1); *E*/*Z* = 4:1.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.39 (m, 2 H), 7.26–7.22 (m, 2 H), 5.93 (t, *J* = 7.3 Hz, 1 H), 4.09 (q, *J* = 7.1 Hz, 2 H), 3.47 (s, 2 H), 2.19 (q, *J* = 7.4 Hz, 2 H), 1.55–1.45 (m, 2 H), 1.18 (t, *J* = 7.1 Hz, 3 H), 0.96 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.33, 141.53, 133.40, 131.45, 131.36, 130.41, 127.81, 120.84, 60.90, 44.57, 36.07, 31.22, 22.67, 14.26, 14.02.

MS (70 eV): *m*/*z* (%) = 310 (100).

Anal. Calcd for $C_{15}H_{19}BrO_2$: C, 57.89; H, 6.15. Found: C, 57.55; H, 6.00.

(*Z*)-3ad

^1H NMR (400 MHz, $CDCl_3$): δ (diagnostic signals) = 5.63 (t, *J* = 7.4 Hz, 1 H), 4.08–4.02 (q, *J* = 7.1 Hz, 2 H), 3.31 (s, 2 H), 1.95 (q, *J* = 7.4 Hz, 2 H), 1.36 (dq, *J* = 14.6, 7.4 Hz, 2 H), 1.17–1.13 (m, 3 H), 0.84 (t, *J* = 7.4 Hz, 3 H).

Ethyl (*E*)-3-(4-Acetylphenyl)hept-3-enoate (3ae)

Yield: 45 mg (83%); colorless oil; R_f = 0.35 (*c*-Hex/EtOAc 10:1); *E*/*Z* =11:1.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.91–7.87 (m, 2 H), 7.48–7.43 (m, 2 H), 6.06 (t, *J* = 7.3 Hz, 1 H), 4.09 (q, *J* = 7.1 Hz, 2 H), 3.52 (s, 2 H), 2.58 (s, 3 H), 2.23 (q, *J* = 7.4 Hz, 2 H), 1.57–1.46 (m, 2 H), 1.18 (t, *J* = 7.1 Hz, 3 H), 0.97 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.73, 171.21, 147.22, 135.63, 135.01, 132.04, 128.61, 126.14, 60.94, 35.90, 31.30, 26.68, 22.62, 14.24, 14.01.

MS (70 eV): *m*/*z* (%) = 274 (100).

Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.25; H, 7.97.

(*Z*)-3ae

^1H NMR (400 MHz, $CDCl_3$): δ (diagnostic signals) = 5.68 (t, *J* = 7.4 Hz, 1 H), 4.07–4.00 (m, 2 H), 3.35 (s, 2 H), 2.59 (s, 3 H), 1.96 (dd, *J* = 14.8, 7.4 Hz, 2 H), 1.37 (dd, *J* = 14.8, 7.4 Hz, 2 H), 1.14 (t, *J* = 7.1 Hz, 3 H), 0.84 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (diagnostic signals) = 128.92, 128.33.

Methyl (*E*)-4-(1-Ethoxy-1-oxohept-3-en-3-yl)benzoate (3af)

Yield: 53 mg (92%); colorless oil; R_f = 0.45 (*c*-Hex/EtOAc 10:1); *E*/*Z* =10:1.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.99–7.95 (m, 2 H), 7.43 (d, *J* = 8.6 Hz, 2 H), 6.05 (t, *J* = 7.3 Hz, 1 H), 4.09 (q, *J* = 7.1 Hz, 2 H), 3.90 (s, 3 H), 3.52 (s, 2 H), 2.22 (q, *J* = 7.4 Hz, 2 H), 1.57–1.46 (m, 2 H), 1.17 (t, *J* = 7.1 Hz, 3 H), 1.13 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.23, 167.08, 147.06, 134.79, 132.10, 129.77, 128.53, 125.97, 60.91, 52.11, 35.95, 31.28, 22.62, 14.22, 14.01.

MS (70 eV): *m*/*z* (%) = 290 (100).

Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.21; H, 7.51.

(*Z*)-3af

^1H NMR (400 MHz, $CDCl_3$): δ (diagnostic signals) = 5.67 (t, *J* = 7.4 Hz, 1 H), 4.07–4.00 (m, 2 H), 3.90 (s, 3 H), 3.34 (s, 1 H), 1.95 (dd, *J* = 14.8, 7.4 Hz, 2 H), 1.36 (dd, *J* = 14.7, 7.4 Hz, 2 H), 0.83 (t, *J* = 7.4 Hz, 3 H).

Ethyl (*E*)-3-(4-Butoxyphenyl)hept-3-enoate (3ag)

Yield: 54 mg (89%); colorless oil; R_f = 0.70 (*c*-Hex/EtOAc 10:1); *E*/*Z* = 9:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.8 Hz, 2 H), 6.83 (d, *J* = 8.8 Hz, 2 H), 5.86 (t, *J* = 7.3 Hz, 1 H), 4.10 (q, *J* = 7.1 Hz, 2 H), 3.95 (t, *J* = 6.5 Hz, 2 H), 3.48 (s, 2 H), 2.19 (q, *J* = 7.3 Hz, 2 H), 1.76 (m, 2 H), 1.56–1.42 (m, 4 H), 1.19 (t, *J* = 7.1 Hz, 3 H), 0.99–0.95 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.70, 158.32, 134.95, 132.06, 131.05, 127.11, 114.36, 67.82, 60.73, 36.29, 31.49, 31.18, 22.85, 19.39, 14.26, 14.03, 13.98.

MS (70 eV): *m*/*z* (%) = 304 (100).

Anal. Calcd for $C_{19}H_{28}O_3$: C, 74.96; H, 9.27. Found: C, 74.77; H, 9.15.

(*Z*)-3ag

^{1}H NMR (400 MHz, $CDCl_3$): δ (diagnostic signals) = 5.60–5.54 (m, 1 H), 4.05 (dd, *J* = 14.3, 7.1 Hz, 2 H), 3.31 (s, 2 H), 2.00 (dd, *J* = 14.7, 7.3 Hz, 2 H), 0.85 (t, *J* = 7.4 Hz, 3 H).

Ethyl (*E*)-3-(*p*-Tolyl)hept-3-enoate (3ah)

Yield: 44 mg (89%); colorless oil; R_f = 0.70 (*c*-Hex/EtOAc 10:1); *E*/*Z* = 7:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (t, *J* = 5.5 Hz, 2 H), 7.11 (d, *J* = 8.0 Hz, 2 H), 5.92 (t, *J* = 7.3 Hz, 1 H), 4.10 (q, *J* = 7.1 Hz, 2 H), 3.50 (s, 2 H), 3.32 (s, 2 H), 2.33 (s, 3 H), 2.20 (q, *J* = 7.3 Hz, 2 H), 1.55–1.45 (m, 2 H), 1.19 (t, *J* = 7.1 Hz, 3 H), 0.97 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.65, 139.72, 136.56, 132.44, 131.92, 129.07, 125.96, 60.74, 36.23, 31.18, 22.80, 21.15, 14.26, 14.03.

MS (70 eV): *m*/*z* (%) = 246 (100).

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.87; H, 8.45.

(*Z*)-3ah

^{1}H NMR (400 MHz, $CDCl_3$): δ (diagnostic signals) = 5.59 (t, *J* = 7.3 Hz, 1 H), 4.08–4.03 (m, 2 H), 3.32 (s, 2 H), 2.34 (s, 2 H), 1.99 (dd, *J* = 14.7, 7.4 Hz, 2 H), 1.40–1.35 (m, 3 H), 0.85 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (diagnostic signals) = 128.85, 128.48.

Ethyl (*E*)-3-(3-Hydroxyphenyl)hept-3-enoate (3ai)

Yield: 26 mg (52%); colorless oil; R_f = 0.40 (*c*-Hex/EtOAc 10:1); *E*/*Z* = 11:1.

IR (neat): 3392, 2960, 2932, 2872, 1701, 1581, 1446, 1295, 1196, 1157, 1026, 783, 695 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15 (t, *J* = 7.9 Hz, 1 H), 6.93 (dd, *J* = 7.8, 0.6 Hz, 1 H), 6.87–6.84 (m, 1 H), 6.73–6.66 (m, 1 H), 5.94 (t, *J* = 7.3 Hz, 1 H), 5.34 (s, 1 H), 4.11 (q, *J* = 7.1 Hz, 2 H), 3.49 (s, 2 H), 2.19 (q, *J* = 7.3 Hz, 2 H), 1.55–1.44 (m, 2 H), 1.19 (t, *J* = 7.1 Hz, 3 H), 0.96 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.95, 155.78, 144.27, 133.01, 132.20, 129.55, 118.55, 113.99, 113.22, 60.99, 36.25, 31.17, 22.71, 14.23, 14.02.

MS (70 eV): *m*/*z* (%) = 248 (100).

Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 77.55; H, 8.12.

(*Z*)-3ai

^{1}H NMR (400 MHz, $CDCl_3$): δ (diagnostic signals) = 5.59 (t, *J* = 7.4 Hz, 1 H), 4.08–4.03 (q, *J* = 7.1 Hz, 2 H), 3.32 (s, 2 H), 1.98 (dd, *J* = 14.7, 7.4 Hz, 2 H), 1.39–1.32 (m, 2 H), 1.15 (t, *J* = 7.1 Hz, 3 H), 0.84 (t, *J* = 7.4 Hz, 3 H).

Ethyl (*E*)-3-(3-Methoxyphenyl)hept-3-enoate (3aj)

Yield: 44 mg (83%); colorless oil; R_f = 0.65 (*c*-Hex/EtOAc 10:1); *E*/*Z* = 11:1.

IR (neat): 2958, 2932, 2871, 2835, 1731, 1598, 1149, 1034, 778, 695 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (t, *J* = 7.9 Hz, 1 H), 6.99–6.95 (m, 1 H), 6.95–6.92 (m, 1 H), 6.78 (ddd, *J* = 8.1, 2.5, 0.7 Hz, 1 H), 5.96 (t, *J* = 7.3 Hz, 1 H), 4.11 (q, *J* = 7.1 Hz, 2 H), 3.81 (s, 3 H), 3.50 (s, 2 H), 2.20 (q, *J* = 7.3 Hz, 2 H), 1.56–1.45 (m, 2 H), 1.19 (t, *J* = 7.1 Hz, 3 H), 0.97 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.54, 159.69, 144.19, 132.92, 132.55, 129.31, 118.68, 112.33, 112.05, 60.79, 55.33, 36.32, 31.19, 22.73, 14.26, 14.02.

MS (70 eV): *m*/*z* (%) = 262 (100).

Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.02; H, 8.21.

(*Z*)-3aj

^{1}H NMR (400 MHz, $CDCl_3$): δ (diagnostic signals) = 5.60 (t, *J* = 7.3 Hz, 1 H), 4.06 (dd, *J* = 14.3, 7.2 Hz, 2 H), 3.80 (s, 3 H), 3.32 (d, *J* = 0.7 Hz, 2 H), 2.00 (dd, *J* = 14.7, 7.4 Hz, 2 H), 1.37 (dt, *J* = 14.0, 7.1 Hz, 2 H), 1.16 (t, *J* = 7.1 Hz, 3 H), 0.86 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (diagnostic signals) = 132.31, 129.14, 121.09, 114.34.

Methyl (*E*)-3-(1-Ethoxy-1-oxohept-3-en-3-yl)benzoate (3ak)

Yield: 54 mg (93%); colorless oil; R_f = 0.70 (*c*-Hex/EtOAc 10:1); *E*/*Z* = 10:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 1.5 Hz, 1 H), 7.89 (dd, *J* = 7.7, 1.1 Hz, 1 H), 7.59–7.54 (m, 1 H), 7.37 (t, *J* = 7.7 Hz, 1 H), 5.99 (t, *J* = 7.3 Hz, 1 H), 4.09 (q, *J* = 7.1 Hz, 2 H), 3.52 (s, 2 H), 2.22 (q, *J* = 7.4 Hz, 2 H), 1.57–1.45 (m, 2 H), 1.18 (t, *J* = 7.1 Hz, 3 H), 0.97 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.28, 167.26, 142.91, 133.86, 131.97, 130.66, 130.28, 128.46, 128.04, 127.31, 60.87, 52.21, 36.11, 31.23, 22.67, 14.22, 14.02.

MS (70 eV): *m*/*z* (%) = 290 (100).

Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 77.45; H, 7.80.

(*Z*)-3ak

^{1}H NMR (400 MHz, $CDCl_3$): δ (diagnostic signals) = 5.66 (t, *J* = 7.3 Hz, 1 H), 4.06–4.00 (m, 2 H), 3.35 (s, 2 H), 1.94 (dd, *J* = 14.7, 7.4 Hz, 2 H), 1.37 (td, *J* = 14.8, 7.4 Hz, 2 H), 1.14 (t, *J* = 7.2 Hz, 3 H), 0.84 (t, *J* = 7.4 Hz, 3 H).

Ethyl (*E*)-3-(3-Nitrophenyl)hept-3-enoate (3al)

Yield: 39 mg (70%); colorless oil; R_f = 0.40 (*c*-Hex/EtOAc 10:1); *E*/*Z* = 7:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (t, *J* = 1.9 Hz, 1 H), 8.10–8.05 (m, 1 H), 7.70 (ddd, *J* = 7.8, 1.7, 1.0 Hz, 1 H), 7.47 (t, *J* = 8.0 Hz, 1 H), 6.05 (t, *J* = 7.3 Hz, 1 H), 4.11 (q, *J* = 7.1 Hz, 2 H), 3.54 (s, 2 H), 2.24 (q, *J* = 7.4 Hz, 2 H), 1.58–1.47 (m, 2 H), 1.23–1.18 (m, 3 H), 1.15 (t, *J* = 7.1 Hz, 1 H), 0.98 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.95, 148.50, 144.30, 135.52, 132.15, 131.05, 129.29, 121.73, 121.06, 61.10, 35.96, 31.27, 22.56, 14.23, 14.01.

MS (70 eV): *m*/*z* (%) = 277 (100).

Anal. Calcd for $C_{15}H_{19}NO_4$: C, 64.97; H, 6.91. Found: C, 64.85; H, 6.75.

(*Z*)-3al

^{1}H NMR (400 MHz, $CDCl_3$): δ (diagnostic signals) = 5.74 (t, *J* = 7.4 Hz, 1 H), 4.06 (dd, *J* = 15.2, 8.0 Hz, 2 H), 3.37 (s, 2 H), 1.95 (dd, *J* = 14.7, 7.4 Hz, 2 H), 1.39 (dd, *J* = 15.5, 8.1 Hz, 3 H), 0.85 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (diagnostic signals) = 135.05, 134.54, 123.65, 122.03.

Ethyl (*E*)-3-[3-(Dimethylamino)phenyl]hept-3-enoate (3am)

Yield: 18 mg (64%); colorless oil; R_f = 0.30 (*c*-Hex/EtOAc 10:1); *E*/*Z* = 10:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17 (t, *J* = 7.9 Hz, 1 H), 6.79–6.74 (m, 2 H), 6.64 (dd, *J* = 8.3, 2.4 Hz, 1 H), 5.95 (t, *J* = 7.3 Hz, 1 H), 4.11 (q, *J* = 7.1 Hz, 2 H), 3.51 (s, 2 H), 2.95 (s, 6 H), 2.21 (q, *J* = 7.3 Hz, 2 H), 1.56–1.46 (m, 2 H), 1.20 (t, *J* = 7.1 Hz, 3 H), 0.97 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.76, 150.80, 143.65, 133.34, 132.27, 128.97, 114.94, 111.58, 110.78, 60.72, 40.85, 36.59, 31.22, 22.79, 14.29, 14.05.

MS (70 eV): *m*/*z* (%) = 275 (100).

Anal. Calcd for $C_{17}H_{25}NO_2$: C, 72.84; H, 8.56. Found: C, 72.32; H, 8.32.

(*Z*)-3am

^{1}H NMR (400 MHz, $CDCl_3$): δ (diagnostic signals) = 3.33 (s, 2 H), 2.94 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (diagnostic signals) = 131.63, 128.79, 117.10, 113.04, 111.29.

Ethyl (*E*)-3-(Naphthalen-2-yl)hept-3-enoate (3an)

Yield: 18 mg (64%); colorless oil; R_f = 0.45 (*c*-Hex/EtOAc 10:1); *E*/*Z* = 4:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82–7.77 (m, 3 H), 7.72–7.64 (m, 1 H), 7.60–7.53 (m, 1 H), 7.50–7.40 (m, 2 H), 6.11 (t, *J* = 7.3 Hz, 1 H), 4.11 (q, *J* = 7.1 Hz, 2 H), 3.63 (s, 2 H), 2.28 (q, *J* = 7.3 Hz, 2 H), 1.56 (dd, *J* = 14.8, 7.4 Hz, 2 H), 1.19 (t, *J* = 7.1 Hz, 3 H), 1.05–0.97 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.60, 139.84, 133.37, 132.62, 128.69, 128.57, 128.22, 127.92, 127.61, 126.16, 125.70, 124.76, 124.59, 60.83, 36.27, 31.36, 22.81, 14.28, 14.08.

MS (70 eV): *m*/*z* (%) = 282 (100).

Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.82; H, 7.85. Found: C, 80.59; H, 7.61.

(*Z*)-3an

^{1}H NMR (400 MHz, $CDCl_3$): δ (diagnostic signals) = 5.71 (t, *J* = 7.3 Hz, 1 H), 4.05 (q, *J* = 7.1 Hz, 2 H), 3.44 (s, 2 H), 2.03 (dd, *J* = 14.7, 7.4 Hz, 2 H), 1.40 (m, *J* = 14.8, 7.4 Hz, 2 H), 1.13 (t, *J* = 7.1 Hz, 3 H), 0.85 (t, *J* = 7.4 Hz, 3 H).

Benzyl 3-Phenylbut-3-enoate (3ba)

Yield: 41 mg (82%); colorless oil; R_f = 0.55 (*c*-Hex/EtOAc 10:1); *E*/*Z* = 4:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.41 (m, 2 H), 7.40–7.37 (m, 1 H), 7.36–7.29 (m, 5 H), 7.23 (m, 2 H), 5.56 (s, 1 H), 5.25 (s, 1 H), 5.10 (s, 2 H), 3.59 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.67, 156.47, 140.89, 135.87, 128.59, 128.54, 128.25, 128.17, 127.93, 125.96, 116.55, 66.67, 41.42.

MS (70 eV): *m*/*z* (%) = 252 (100).

(*E*)-3ba′

^{1}H NMR (400 MHz, $CDCl_3$): δ (diagnostic signals) = 6.22 (d, *J* = 1.2 Hz, 1 H), 5.22 (s, 2 H), 2.62 (d, *J* = 1.1 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (diagnostic signals) = 171.24, 166.69, 142.21, 139.81, 136.41, 129.21, 128.69, 128.63, 128.36, 126.43, 116.87, 65.89, 27.04.

Benzyl (*E*)-3-Phenylhept-3-enoate (3ca)

Yield: 52 mg (89%); colorless oil; R_f = 0.60 (*c*-Hex/EtOAc 10:1); *E*/*Z* = 6:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.37 (m, 2 H), 7.32 (m, 5 H), 7.24 (m, 3 H), 5.97 (t, *J* = 7.3 Hz, 1 H), 5.10 (s, 2 H), 3.60 (s, 2 H), 2.21 (q, *J* = 7.4 Hz, 2 H), 1.56–1.45 (m, 2 H), 0.96 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.37, 142.46, 136.04, 132.93, 132.48, 128.57, 128.43, 128.19, 128.13, 126.97, 126.15, 66.57, 36.18, 31.23, 22.74, 14.01.

MS (70 eV): *m*/*z* (%) = 294 (100).

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.38; H, 7.39.

(*Z*)-3ca

^{1}H NMR (400 MHz, $CDCl_3$): δ (diagnostic signals) = 5.64 (t, *J* = 7.3 Hz, 1 H), 5.05 (s, 2 H), 3.42 (d, *J* = 0.7 Hz, 2 H), 1.99 (q, *J* = 7.4 Hz, 2 H), 1.37 (m, 2 H), 0.85 (t, *J* = 7.4 Hz, 3 H).

3,5-Dimethylphenyl (*E*)-3-Phenylhept-3-enoate (3da)

Yield: 50 mg (81%); colorless oil; R_f = 0.60 (*c*-Hex/EtOAc 10:1); *E*/*Z* = 9:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.46 (m, 2 H), 7.36–7.34 (m, 2 H), 7.29–7.25 (m, 1 H), 6.83 (s, 1 H), 6.57 (s, 2 H), 6.03 (t, *J* = 7.3 Hz, 1 H), 3.76 (s, 2 H), 2.35–2.32 (m, 2 H), 2.29 (s, 6 H), 1.63–1.52 (m, 2 H), 1.02 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.19, 150.85, 142.47, 139.26, 133.15, 132.43, 128.49, 127.57, 127.08, 126.29, 119.10, 36.45, 31.31, 22.78, 21.29, 14.04.

MS (70 eV): *m*/*z* (%) = 308 (100).

Anal. Calcd for $C_{21}H_{24}O_2$: C, 81.78; H, 7.84. Found: C, 81.66; H, 7.65.

(*Z*)-3da

Colorless oil; R_f = 0.55 (*c*-Hex/EtOAc 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ (diagnostic signals) = 5.04 (t, *J* = 7.7 Hz, 1 H), 3.53 (s, 2 H).

3,5-Dimethylphenyl 3-Phenylbut-3-enoate (3ea)

Yield: 48 mg (90%); colorless oil; R_f = 0.55 *c*-Hex/EtOAc 10:1); **3ea**/**3ea′** = 2:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (m, 1 H), 7.44–7.31 (m, 3 H), 6.84 (d, *J* = 0.6 Hz, 1 H), 6.79 (s, 1 H), 6.57 (s, 2 H), 5.62 (s, 1 H), 5.37 (d, *J* = 0.8 Hz, 1 H), 3.75 (d, *J* = 0.9 Hz, 2 H), 2.28 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.05, 150.75, 142.14, 139.30, 128.72, 128.61, 128.03, 127.66, 126.08, 119.06, 116.67, 41.58, 21.38.

MS (70 eV): *m*/*z* (%) = 266 (100).

(*E*)-3ea′

^{1}H NMR (400 MHz, $CDCl_3$): δ (diagnostic signals) = 6.89 (d, *J* = 0.5 Hz, 1 H), 6.38 (d, *J* = 1.2 Hz, 1 H), 2.66 (d, *J* = 1.2 Hz, 3 H), 2.35 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (diagnostic signals) = 165.47, 158.32, 150.72, 140.88, 139.92, 139.32, 129.46, 127.52, 126.52, 119.47, 116.36, 21.30, 18.33.

Ethyl (*E*)-3-Phenyldodec-3-enoate (3fa)

Yield: 51 mg (84%); colorless oil; R_f = 0.75 (*c*-Hex/EtOAc 10:1); *E*/Z = 7:1.

IR (neat): 3023, 2956, 2853, 1734, 1463, 1151, 1033, 757, 696 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.36 (m, 2 H), 7.31 (t, *J* = 7.7 Hz, 2 H), 7.24–7.20 (m, 1 H), 5.95 (t, *J* = 7.3 Hz, 1 H), 4.11 (q, *J* = 7.1 Hz, 2 H), 3.51 (s, 2 H), 2.23 (q, *J* = 7.3 Hz, 2 H), 1.53–1.44 (m, 2 H), 1.40–1.29 (m, 10 H), 1.21–1.15 (t, *J* = 7.1 Hz, 3 H), 0.90 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.58, 142.62, 132.99, 132.45, 128.37, 126.89, 126.11, 60.77, 36.25, 32.03, 29.66 (2C), 29.57, 29.56, 29.43, 29.21, 22.81, 14.24.

MS (70 eV): *m*/*z* (%) = 302 (100).

Anal. Calcd for $C_{20}H_{20}O_2$: C, 79.42; H, 10.00. Found: C, 79.21; H, 9.78.

(*Z*)-3fa

^{1}H NMR (400 MHz, $CDCl_3$): δ (diagnostic signals) = 5.62 (t, *J* = 7.3 Hz, 1 H), 4.05 (q, *J* = 7.1 Hz, 2 H), 3.34 (s, 2 H), 2.00 (q, *J* = 7.3 Hz, 2 H).

(*E*)-1,3-Diphenylbut-2-en-1-one (3ga)

Yield: 37 mg (84%); colorless oil; R_f = 0.75 (*c*-Hex/EtOAc 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03–7.97 (m, 2 H), 7.60–7.53 (m, 3 H), 7.48 (dd, *J* = 8.1, 6.7 Hz, 2 H), 7.43–7.40 (m, 2 H), 7.18–7.16 (m, 1 H), 2.60 (d, *J* = 1.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) : δ = 192.01, 155.20, 142.95, 139.53, 132.67, 129.26, 128.75, 128.69, 128.42, 126.64, 122.28, 19.04.

MS (70 eV): *m*/*z* (%) = 222 (100).

Anal. Calcd for $C_{16}H_{14}O_2$: C, 86.45; H, 6.35. Found: C, 86.29; H, 6.22.

Ehyl (*E*)-3,4-Diphenylbut-3-enoate (3ia)

Yield: 45 mg (85%); colorless oil; R_f = 0.75 (*c*-Hex/EtOAc 10:1); *E*/*Z* = 1:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.49 (m, 1 H), 7.40–7.21 (m, 9 H), 7.03 (s, 1 H), 4.09 (q, *J* = 7.1 Hz, 2 H), 3.71 (s, 2 H), 1.15 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ [(*E*)- + (*Z*)-**3ia**] = 171.61, 171.26, 141.88, 140.16, 137.59, 136.83, 135.42, 134.86, 131.34, 130.49, 129.29, 128.89, 128.81, 128.65, 128.58, 128.55, 128.01, 127.70, 127.45, 127.32, 126.88, 126.41, 60.91, 60.81, 45.99, 36.86, 14.24, 14.21.

MS (70 eV): *m*/*z* (%) = 266 (100).

(*Z*)-3ia

^{1}H NMR (400 MHz, $CDCl_3$): δ (diagnostic signals) = 6.59 (s, 1 H), 3.50 (d, *J* = 0.9 Hz, 2 H).

Ethyl (*E*)-1-Butylidene-3-hydroxy-2,3-dihydro-1*H*-indene-2-carboxylate (3ap)

Yield: 29 mg (63%); colorless oil; R_f = 0.36 (*c*-Hex/EtOAc 10:1); *E*/*Z* = 6:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (dd, *J* = 5.0, 3.8 Hz, 1 H), 7.44–7.40 (m, 1 H), 7.30–7.26 (m, 2 H), 6.08 (td, *J* = 7.6, 1.8 Hz, 1 H), 5.42 (dd, *J* = 11.3, 7.5 Hz, 1 H), 4.23–4.20 (m, 1 H), 4.17 (dd, *J* = 14.3, 7.1 Hz, 2 H), 3.05 (d, *J* = 11.4 Hz, 1 H), 2.29–2.20 (m, 2 H), 1.53–1.43 (m, 2 H), 1.26 (t, *J* = 7.1 Hz, 3 H), 0.97 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.77, 144.98, 139.85, 136.54, 128.93, 128.49, 124.72, 124.56, 120.08, 74.93, 61.18, 53.03, 31.74, 22.73, 14.31, 14.06.

MS (70 eV): *m*/*z* (%) = 260 (100).

Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.65; H, 7.55.

(*Z*)-3ap

^{1}H NMR (400 MHz, $CDCl_3$): δ (diagnostic signals) = 5.79 (t, *J* = 6.6 Hz, 1 H), 5.34 (dd, *J* = 10.8, 7.0 Hz, 1 H), 3.97 (dd, *J* = 7.0, 1.2 Hz, 1 H), 3.52 (d, *J* = 10.8 Hz, 1 H), 2.44 (dd, *J* = 14.7, 7.4 Hz, 2 H).

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1610023.

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