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Ruthenium-Catalyzed Oxidative Cross-Coupling Reaction of Activated Olefins with Vinyl Boronates for the Synthesis of (*E,E*)-1,3-Dienes

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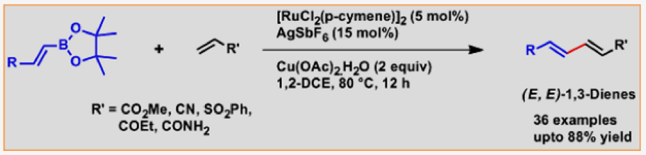
ABSTRACT: An oxidative cross-coupling reaction between activated olefins and vinyl boronate derivatives has been developed for the highly stereoselective construction of synthetically useful (*E,E*)-1,3-dienes. The highlight of this reaction is that exclusive stereoselectivity (only *E,E*-isomer) was achieved from a base-free, ligand-free, and mild catalytic condition with a less expensive $[RuCl_2(p\text{-cymene})]_2$ catalyst.



INTRODUCTION

Palladium-catalyzed arylation of olefins has been routinely used as powerful carbon−carbon bond forming reactions (Scheme 11:a) since its discovery in the early 1970s, which triggered the era of natural product synthesis and medicinal chemistry.[1−6] Substituted 1,3-dienes are valuable synthetic intermediates in organic chemistry, which also feature as structural motifs in numerous natural products and medicinally important molecules.[7] Indeed, these conjugated dienes serve as building blocks for fabricating the complexity in chemical transformations such as cross-coupling reactions, cycloadditions, ene-reaction, and metathesis, including recently developed asymmetric hydrofunctionalizations, difunctionalizations, etc. It is well-understood that the syntheses of stereo- and regiodefined conjugated dienes are often influenced by the geometry of olefins involved in the reaction.[8] Hence, innumerable synthetic strategies have been explored for the stereoselective construction of substituted 1,3-dienes.[9] Oxidative boron Heck reactions are known to be efficient, require mild reaction conditions, show good functional group tolerance, and are capable of coupling challenging substrates such as highly substituted or cyclic olefins, many of which are reluctant to undergo normal Heck coupling.[10] In this regard, many oxidative Heck reactions of phenyl boronates with activated olefins have been developed,[11−14] but there is only one report in the literature on oxidative Heck reaction using alkenyl boranes by Jung et al. (Scheme 11:b).[15] Although this protocol developed by Jung et al. provides access to dienes in very good yields, it gives poor stereoselectivity when acrylonitrile and styrenes are used as coupling partners. The major problem in oxidative Heck coupling is that poor stereoselectivity was observed for these reactions. To overcome these stereoselective problems, sterically hindered acrylates (activated olefins) such as tertiary butyl acrylate were used. This limits the substrate scope and its application in synthesis. Poor stereoselectivity of the oxidative Heck reaction coupled with skyrocketing prices of palladium has led to an increased need to develop more sustainable strategies for such kinds of carbon−carbon-bond formations. Herein, we report a new catalytic system for the cross-coupling reaction of organoboron compounds with activated olefins to afford conjugated 1,3-dienes in a highly stereoselective manner using the commercially available, less expensive $[RuCl_2(p\text{-cymene})]_2$ catalyst and $Cu(OAc)_2$ as a reoxidant for the ruthenium(0) species under base- and ligand-free conditions (Scheme 22:).

RESULTS AND DISCUSSION

An optimization study revealed that the couplings of organoborane derivatives with various acrylates were found to be beneficial in terms of functional group tolerance and yield. To begin with, the cross-coupling reaction was performed using *trans*-2-phenyl vinyl boronic ester **1a** and methyl acrylate **2a** in trifluoroethanol at 80 °C for 12 h with 5 mol % $[RuCl_2(p\text{-cymene})]_2$ as the catalyst, 2 equivalents of $Cu(OAc)_2$ as the oxidant, and 15 mol % $AgSbF_6$ as an additive. The desired 1,3-diene **3aa** was obtained in 28% yield as a single *E,E*-isomer (Table 1, entry 1). Change of the solvent to CH_3CN, t-AmOH, or NMP (entries 2−4) did not produce better results. Change of the solvent to dichloromethane afforded the coupling product in 35% at 40 °C (entry 5), whereas replacement with toluene generated the cross-coupled

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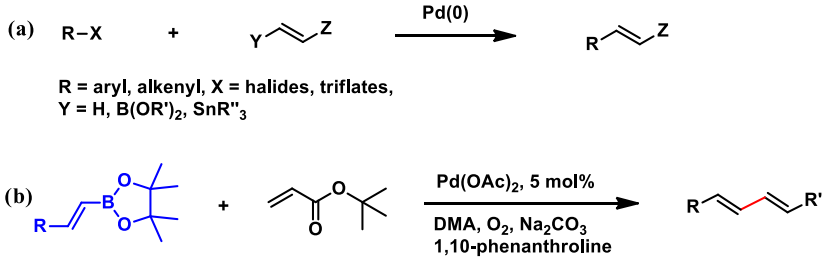
Scheme 1



Scheme 2. This Work

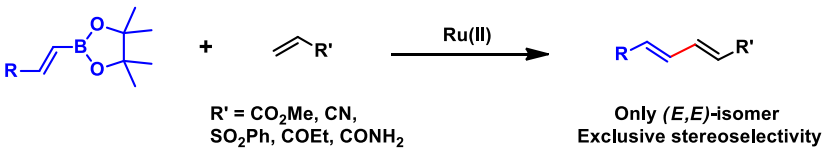
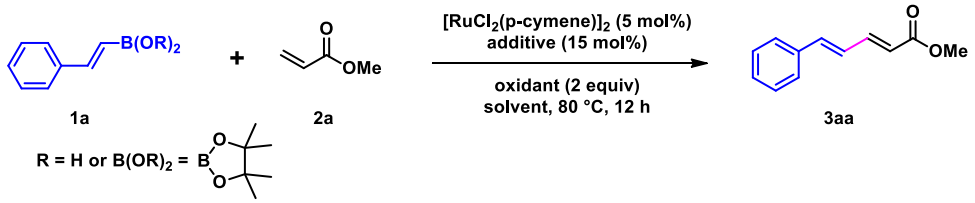


Table 1. Optimization of Reaction Conditions



entry	solvent	additive (15 mol %)	oxidant (2 equiv)	[e]yield [%]
1	TFE	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	28
2	CH_3CN	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	trace
3	t-AmOH	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	16
4	NMP	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	25
5	DCM	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	35
6	toluene	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	65
7[a]	toluene	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	42
8[b]	DCE	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	45
9	DCE	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	88
10	DCE	$AgSbF_6$	KOAc	12
11	DCE	NH_4PF_6	$Cu(OAc)_2{\cdot}H_2O$	75
12	toluene	NH_4PF_6	$Cu(OAc)_2{\cdot}H_2O$	48
13	DCE	AgOAc	$Cu(OAc)_2{\cdot}H_2O$	trace
14	DCE	Ag_2CO_3	$Cu(OAc)_2{\cdot}H_2O$	0
15	DCE		AgOAc	16
16[c]	DCE		$Cu(OAc)_2{\cdot}H_2O$	0
17[d]	DCE	$AgSbF_6$		0

[a]Reaction Conditions. Reaction at 110 °C. [b]Reaction at 60 °C. [c]The reaction was performed without $AgSbF_6$. [d]The reaction was performed without $Cu(OAc)_2{\cdot}H_2O$. [e]Isolated yield of **3aa**.

product in 65% yield at 80 °C (entry 6). An increase in the temperature to 110 °C resulted in a lower yield probably due to decomposition of the starting material (entry 7). Use of 1,2-dichloroethane as a solvent afforded 45% of the desired product at 60 °C (entry 8), and to our delight, when the temperature was increased to 80 °C, the yield increased to 88% (entry 9). When the reaction was conducted by replacing $AgSbF_6$ with a variety of additives, the reaction was found to be sluggish, but in the case of NH_4PF_6, diene **3** was obtained in 75% yield at 80 °C using 1,2-dichloroethane as a solvent (entry 11). Change of the solvent to toluene and using NH_4PF_6 as an additive at 80 °C afforded the desired coupling product in only 48% yield (entry 12). It was found that similar reactivity in terms of rate and yield was observed when boronate esters were replaced with corresponding boronic acids. It is noteworthy to mention that the reaction did not occur when carried out in the absence of either $AgSbF_6$ (entry 16) or $Cu(OAc)_2$ (entry 17), revealing that $Cu(OAc)_2$ as a reoxidant and $AgSbF_6$ as an additive were necessary for the reaction.

The scopes of the alkenyl boronates and the acrylates were subsequently examined. As shown in Scheme 3, phenyl and (4′-methyl) phenyl-substituted vinyl boronates **1a,b** reacted well with methyl (**2a**), butyl (**2b**), and cyclohexyl (**2c**) acrylates independently to afford the corresponding cross-coupled products **3aa**−**bc** in very good yields and excellent stereoselectivity. Notably, halogen-containing vinyl boronate derivatives such as **1c**−**e** showed their chemoselective reactivity for the coupling reaction under a reactive catalytic

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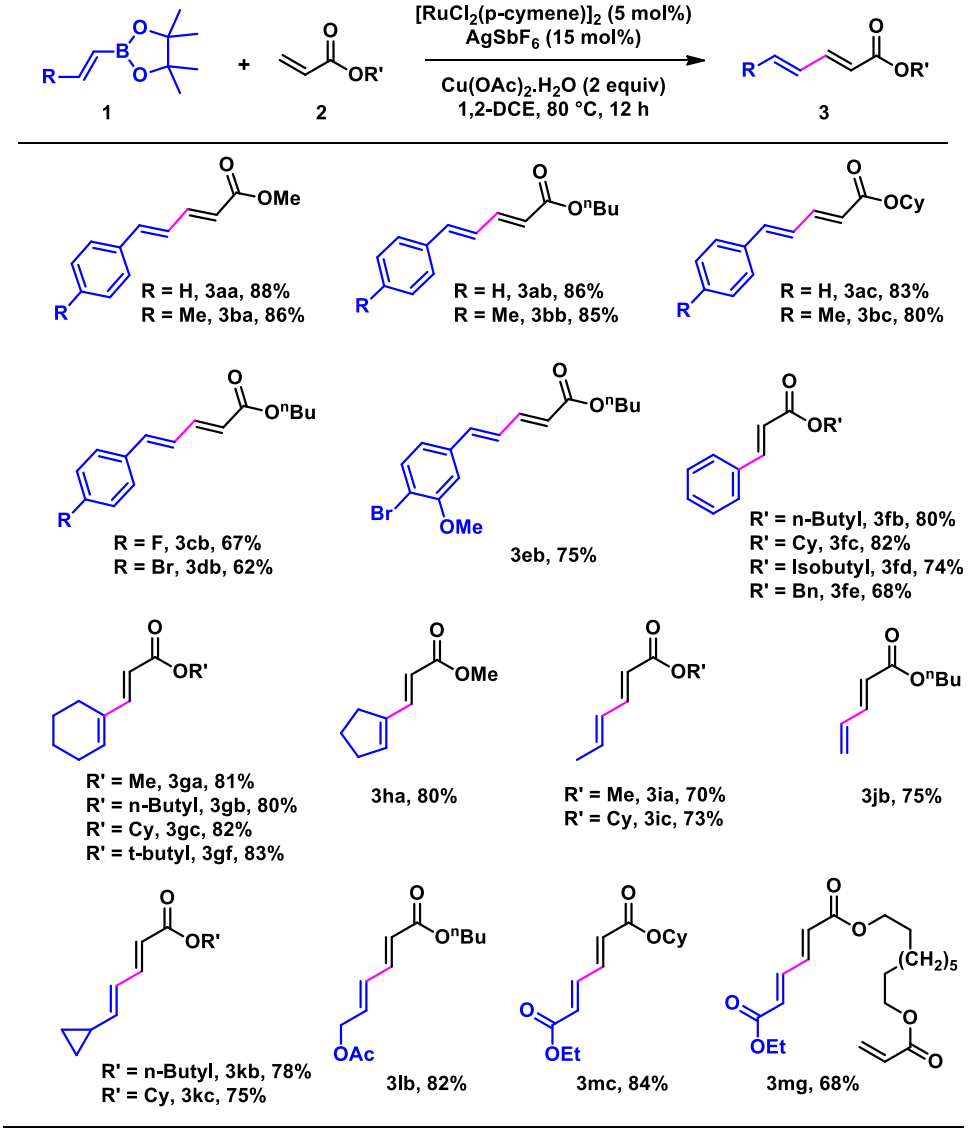
Scheme 3. Reaction of Various Acrylates with Different Organoboron Derivatives[a]



[a]Reaction conditions: **1** (1 equiv), **2** (1 equiv), $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol %), $AgSbF_6$ (15 mol %), and $Cu(OAc)_2 \cdot H_2O$ (2 equiv) at 80 °C in 1,2-DCE (3.0 mL), under argon for 12 h. Cy, cyclohexyl.

system to generate corresponding coupling products **3cb−eb** without affecting the labile carbon−halogen (C−Br) bond, which can be utilized for further functionalization. Phenylboronic acid **1f** on reaction with various acrylates **2b−e** generated the corresponding cross-coupled products **3fb−fe** in very good yields and excellent stereoselectivity. Sterically crowded cyclohexenyl boronate ester **1g** reacted smoothly with various acrylates **2a−c, f** to generate corresponding dienes **3ga−gc, gf**, respectively, in very good yields. Cyclopentenyl boronate ester **1h** underwent a coupling reaction with methyl acrylate **2a** to afford **3ha** in 80% yield. Allyl boronate ester **1i** underwent a coupling reaction with methyl (**2a**) and cyclohexyl acrylate (**2c**) individually to afford **3ia** and **3ic** in 70% and 73% yields, respectively. Vinyl boronate ester **1j** on reaction with *n*-butyl acrylate (**2b**) generated the single isomer **3jb** in 75% yield. Interestingly, cyclopropyl vinyl boronate ester **1k** furnished dienes **3kb** and **3kc** in 78 and 75% yields, respectively, without affecting its highly strained cyclopropyl ring. It is important to highlight that the coupling reaction of highly strained cyclopropane ring derivatives is likely to undergo ring cleavage under a palladium catalytic system.[16] Also, electron-withdrawing acetoxy-substituted vinyl boronate ester **1l** reacted with *n*-butyl acrylate (**2b**) to generate functionalized diene **3lb** in 82% yield. Highly activated vinyl boronate derivative **1m** underwent a coupling reaction with cyclohexyl acrylate (**2c**) to afford the coupled product **3mc** in 84% yield. Interestingly, the introduction of an ester side chain has no effect on product selectivity. Markedly, symmetric diacrylate **2g** reacted with vinyl boronate derivative **1m** to form the coupled product **3mg** in a somewhat moderate yield (68%). Also, these conjugate diesters (**3mc, mg**) represent the structure of an important class, called muconate derivatives.[17] This differentiable terminal functionality of conjugated muconates can be eventually transformed into versatile synthetic intermediates widely used in organic synthesis. To date, no catalytic method has been developed for the stereoselective construction of (*E,E*)-muconate derivatives.[18] It is noteworthy to mention that when the coupling reaction

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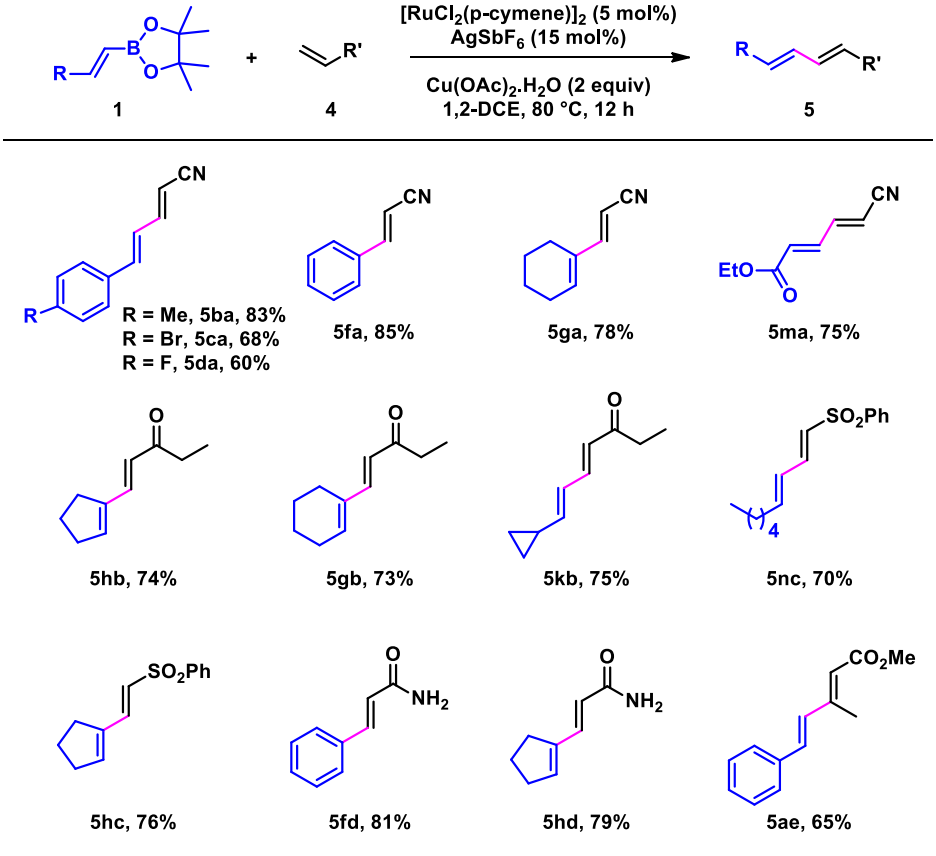
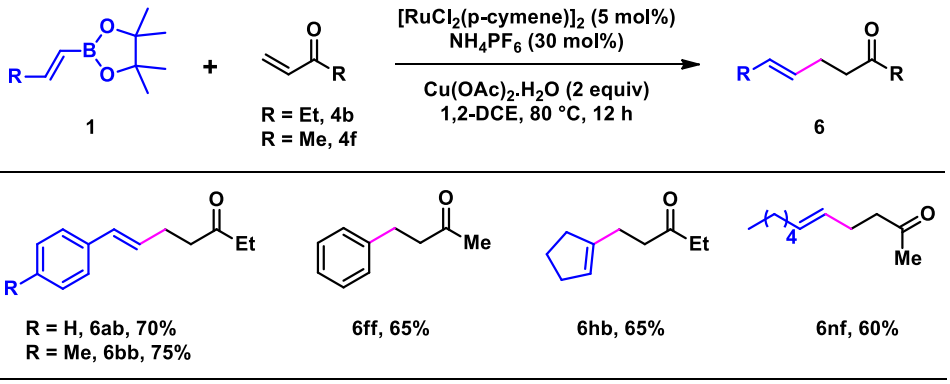
Scheme 4. Reaction of Various Activated Olefins with Different Organoboron Derivatives



Scheme 5. : Reaction of Organoboron Derivatives with Enones Using NH_4PF_6



was carried out on a gram scale, similar results were obtained without affecting productivity in terms of yield and stereoselectivity.

Moreover, this newly developed catalytic protocol is not limited only to acrylates but also applicable to various activated olefins such as acrylonitrile, vinyl ketones, vinyl sulfones, and acrylamides (Scheme 4). Series of vinyl boronates (**1b−d, 1f,g, and 1m**) were independently treated with acrylonitrile (**4a**) to afford the desired products (**5ba−da, 5fa, 5ga, and 5ma**) in good yields with excellent stereoselectivity. It is worth mentioning that palladium-catalyzed Heck oxidative coupling showed poor stereoselectivity especially with acrylonitriles.[15,19] It was interesting to observe that when ethyl vinyl ketone, **4b**, was used as a coupling partner, it generated 1,3-dienes embedded with an enone substituent in very good yields. Furthermore, phenyl vinyl sulfone, **4c**, was subjected to a coupling reaction to deliver a single (*E,E*)-isomer of desired dienes **5nc** and **5hc** in 76 and 70% yields, respectively. A similar reactivity was observed when acrylamide, **4d**, was reacted with phenylboronic acid and cyclopentenyl boronate ester to provide corresponding coupling products **5fd** and **5hd** in 81 and 79% yields, respectively. Additionally, the desired product (**5ae**) was obtained when (*E*)-methyl crotonate **4e** was subjected to a coupling reaction with boronate ester, albeit with a moderate yield (65%), highlighting the broad scope of an olefinic partner.

Interesting results were observed when coupling reactions between vinyl boronates and α,β-unsaturated ketones were carried out by replacing $AgSbF_6$ with NH_4PF_6 (Scheme 5). An unanticipated double-bond reduced product, **6ab**, was formed

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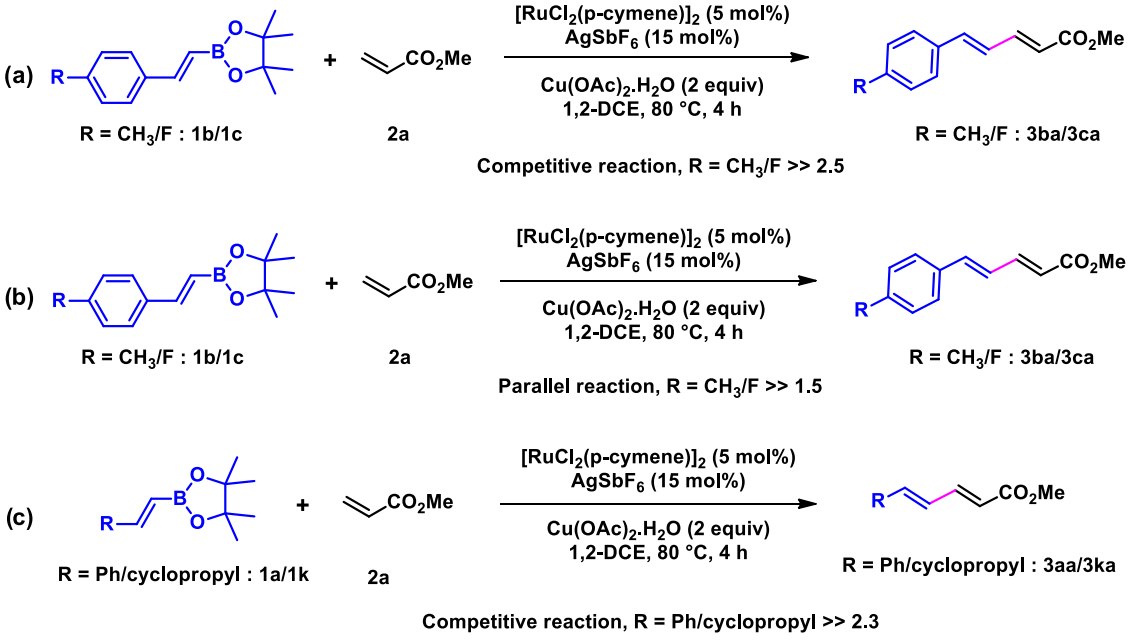
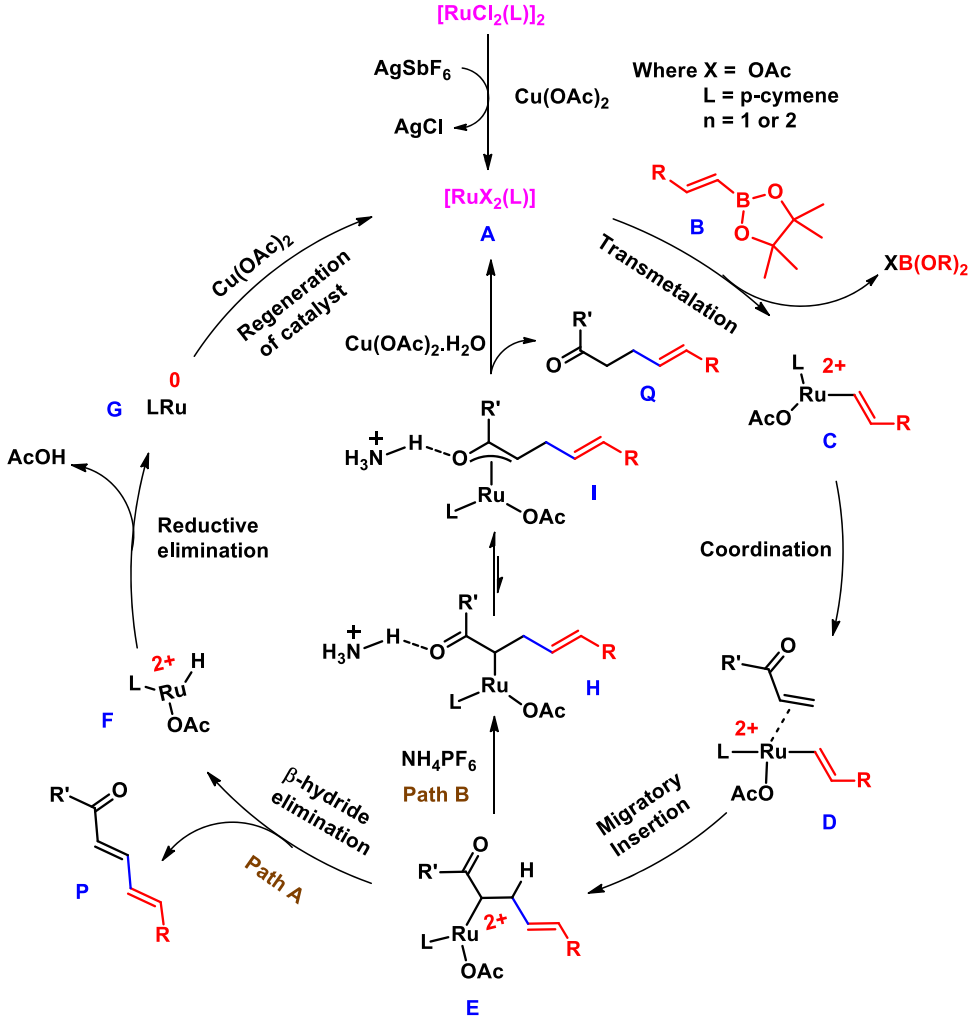
Scheme 6. Competitive Experiments



Scheme 7. Plausible Mechanism



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in 70% yield when boronate ester **1a** was reacted with ethyl vinyl ketone **4b**. This may be due to facile enol formation/protonation in the case of enones in the presence of the NH_4^+ ion, which restricts β-hydride elimination. To check the generality of this reaction, various vinyl boronate esters were subjected to a coupling reaction with ethyl/methyl vinyl ketone; similar results were obtained and afforded coupling products (**6bb, ff, hb, nf**) in moderate to good yields.

To determine the effect of substituents on the rate of the coupling reaction, we performed intermolecular competitive reactions between differently substituted vinyl boronates. When (4-methyl)-phenyl (**1b**) and (4-fluoro)-phenyl (**1c**) vinyl boronate and methyl acrylate were employed, the electron-rich substrate reacted more predominantly with a reactivity difference of almost 1:0.4 (Scheme 6a). Similarly, a mixture of compounds **3ba** and **3ca** in a 1:0.65 ratio was observed from parallel reactions (Scheme 6b). When a competitive reaction between alkyl and phenyl-substituted vinyl boronate esters was performed, phenyl-substituted vinyl boronate reacted preferentially with a reactivity difference of 1:0.45 (Scheme 6c).

Based on a previous report,[20] a plausible reaction mechanism for the cross-coupling reaction of vinyl boronate with activated olefins is depicted in Scheme 7. The catalytic cycle is initiated by in situ-generated reactive ruthenium(II) species **A**, which further undergoes transmetalation with vinyl boronate ester **B** to provide an intermediate **C**. Coordination followed by regioselective insertion of activated olefin to the ruthenium−carbon bond of intermediate **C** would generate the ruthenium(II) intermediate **E**. Subsequent β-hydride elimination of **E** leads to the formation of the stereoselective cross-coupled product **P**, followed by reductive elimination of the Ru(II) intermediate **F**, which results in the formation of the Ru(0) intermediate **G**. In the presence of $Cu(OAc)_2$, the reduced [Ru(0)] species could undergo oxidation to regenerate the ruthenium (II) cationic reactive complex **A** for the next catalytic cycle. In the presence of NH_4PF_6, the catalytic cycle follows path **B** to afford product **Q**. This unanticipated result may be due to facile enol formation/protonation in the case of enones in the presence of the NH_4^+ ion, which restricts β-hydride elimination.

CONCLUSIONS

In summary, ruthenium-catalyzed oxidative cross-coupling between vinyl boronates and activated olefins has been developed for efficient and direct access to synthetically useful (*E*,*E*)-1,3-dienes in a highly stereoselective manner. This reaction features a base-free, mild reaction condition, easily accessible starting materials, a broad substrate scope, and excellent stereoselectivity. The present simplified methodology for carbon−carbon bond formation is highly practical, holding great promise for wide use in organic and medicinal chemistry.

EXPERIMENTAL SECTION

General Aspects. Experiments involving moisture- and air-sensitive components were performed in oven-dried glassware. Commercial solvents and reagents were used without further purification unless otherwise noted. Yields refer to chromatographically pure compounds, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel plates (60F-254) using UV light as a visualizing agent and *p*-anisaldehyde and heat as developing agents. Merck silica gel (particle size 100−200 and 230−400 mesh) was used for flash column chromatography. Neat compounds were used to record IR spectra. NMR spectra were recorded on a Bruker Avance 400 (1H, 400 MHz; 13C, 100 MHz), Bruker Avance 500 (1H, 500 MHz; 13C, 125 MHz), or JEOL DELTA (ECX) 500 (1H, 500 MHz; 13C, 125 MHz). Mass spectrometric data were obtained using WATERS-Q-Tof-Premier-HAB213 and WATERS-QTof-Premier-ESI-MS instruments, and IR data were recorded from a PerkinElmer FTIR spectrometer. The following abbreviations were used to explain the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; spt, septet; dd, doublet of doublet; ddd, doublet of a doublet of a doublet; dt, doublet of a triplet; td, triplet of a doublet; m, multiplet; br, broad.

General Procedure for Ruthenium-Catalyzed Oxidative Coupling Reaction between Activated Olefins and Vinyl Boronate Esters. An 8 mL screw-cap vial was charged with $[RuCl_2(p\text{-cymene})]_2$ (15.5 mg, 0.025 mmol, 5.0 mol %), $Cu(OAc)_2\cdot H_2O$ (200 mg, 1.0 mmol, 2.0 equiv), $AgSbF_6$ (25.7 mg, 0.075 mmol, 15 mol %), and 1,2-dichloroethane (3.0 mL). Then, boronic ester (0.5 mmol, 1.0 equiv) and activated olefins (0.5 mmol, 1.0 equiv) [2.0 equivalents of acrylonitrile and methyl crotonate were used] were added into the solution in sequence. The vial was sealed under N_2 and heated to 80 °C with stirring for 12 h (using an oil bath). After cooling down, the mixture was diluted with ethyl acetate, filtered, and concentrated to give the crude compound, which was directly purified by column chromatography. [Note: A general procedure was followed for the oxidative coupling reaction of boronic esters with vinyl ketone in the presence of 30 mol % NH_4PF_6 (25 mg) in the place of $AgSbF_6$.]

Gram-Scale Synthesis of 3ac. A 100 mL screw-cap vial was charged with $[RuCl_2(p\text{-cymene})]_2$ (134 mg, 0.22 mmol, 5.0 mol %), $AgSbF_6$ (180 mg, 0.52 mmol, 12 mol %), and $Cu(OAc)_2\cdot H_2O$ (1.8 g, 8.72 mmol, 2.0 equiv) in 1,2-dichloroethane (25 mL) and stirred for 5 minutes at room temperature under a nitrogen atmosphere. Then, phenyl-substituted vinyl boronate ester **1a** (1.0 g, 4.4 mmol, 1.0 equiv) and cyclohexyl acrylate **2c** (0.7 mL, 4.4 mmol, 1.0 equiv, density = 0.975 g/mL) were added into the solution in sequence and the vial was sealed under N_2 and heated to 80 °C with stirring for 12 h (using an oil bath). After cooling down, the mixture was diluted with ethyl acetate, filtered, and concentrated to give the crude compound, which was directly purified by column chromatography to obtain the pure product **3ac** (0.95 g, 3.7 mmol, 85%).

Competitive Reactions between 1b and 1c. An 8 mL screw-cap vial was charged with $[RuCl_2(p\text{-cymene})]_2$ (13 mg, 0.02 mmol, 5.0 mol %), $Cu(OAc)_2\cdot H_2O$ (160 mg, 0.8 mmol, 2.0 equiv), $AgSbF_6$ (21 mg, 0.06 mmol, 15 mol %), and 1,2-dichloroethane (2.5 mL). Then, boronic esters **1b** (50 mg, 0.2 mmol, 0.5 equiv) and **1c** (50 mg, 0.2 mmol, 0.5 equiv) followed by methyl acrylate (38 mg, 0.44 mmol, 1.1 equiv) were added into the solution in sequence. The vial was sealed under N_2 and heated to 80 °C with stirring for 4 h (using an oil bath). After cooling down, the mixture was diluted with ethyl acetate, filtered, and concentrated to give the crude compound, which was directly purified by column chromatography using 0−5% EtOAc in pet ether to afford a mixture of compounds **3ba** and **3ca** in a 1:0.4 ratio.

Parallel Reactions. Similarly, two parallel reactions were performed with 0.2 mmol each of **1b** and **1c** for 4 h at 80 °C. After cooling down, the reaction mixtures were mixed, diluted with ethyl acetate, filtered, and concentrated to give the crude compound, which was directly purified by column chromatography using 0−5% EtOAc in pet ether to afford a mixture of compounds **3ba** and **3ca** in a 1:0.65 ratio.

Competitive Reactions between 1a and 1k. An 8 mL screw-cap vial was charged with $[RuCl_2(p\text{-cymene})]_2$ (13 mg, 0.02 mmol, 5.0 mol %), $Cu(OAc)_2\cdot H_2O$ (160 mg, 0.8 mmol, 2.0 equiv), $AgSbF_6$ (21 mg, 0.06 mmol, 15 mol %), and 1,2-dichloroethane (2.5 mL). Then, boronic esters **1a** (55 mg, 0.24 mmol, 0.5 equiv) and **1k** (43 mg, 0.24 mmol, 0.5 equiv) followed by methyl acrylate (38 mg, 0.44 mmol, 1.1 equiv) were added into the solution in sequence. The vial was sealed under N_2 and heated to 80 °C with stirring for 4 h (using an oil bath). After cooling down, the mixture was diluted with ethyl acetate, filtered, and concentrated to give the crude compound, which

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was directly purified by column chromatography using 0−5% EtOAc in pet ether to afford a mixture of compounds **3aa** and **3ka** in a 1:0.45 ratio.

(2*E*,4*E*)-Methyl 5-Phenylpenta-2,4-dienoate (3aa). Following the general procedure, **3aa** was purified by silica column chromatography (hexane/EtOAc at a 20:1 ratio), obtained as a white solid (77 mg, 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49−7.42 (m, 3H), 7.38−7.28 (m, 3H), 6.93−6.83 (m, 2H), 5.99 (d, J = 15.3 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$) δ 167.6, 144.9, 140.7, 136.1, 129.2, 128.9 (2C), 127.3 (2C), 126.3, 120.9, 51.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{13}O_2$ 189.0916; found 189.0910. IR (neat): ν_{max}/cm^{-1} 2926, 1717, 1628, 1439, 1450, 1321, 1344, 1242, 1172, 1137, 995.

(2*E*,4*E*)-Methyl 5-*p*-Tolylpenta-2,4-dienoate (3ba). Following the general procedure, **3ba** was purified by silica column chromatography (hexane/EtOAc at a 20:1 ratio), obtained as a white solid (81 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, J = 9.8, 15.3 Hz, 1H), 7.37−7.33 (m, 2H), 7.17−7.13 (m, 2H), 6.90−6.77 (m, 2H), 5.96 (d, J = 15.3 Hz, 1H), 3.76 (s, 3H), 2.35 (s, 3H). ^{13}C NMR{^{1}H} (100 MHz, $CDCl_3$) δ 167.6, 145.1, 140.7, 139.4, 133.4, 129.6(2C), 127.2(2C), 125.3, 120.3, 51.6, 21.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{15}O_2$ 203.1072; found 203.1070. IR (neat): ν_{max}/cm^{-1} 2924, 1711, 1605, 1622, 1434, 1350, 1318, 1243, 1171, 1132, 1010, 840, 806.

(2*E*,4*E*)-Butyl 5-Phenylpenta-2,4-dienoate (3ab). Following the general procedure, **3ab** was purified by silica column chromatography (hexane/EtOAc at a 20:1 ratio), obtained as a white solid (100 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48−7.38 (m, 3 H), 7.37−7.26 (m, 3 H), 6.95−6.78 (m, 2 H), 5.98 (d, J = 15.3 Hz, 1 H), 4.16 (t, J = 6.7 Hz, 2 H), 1.70−1.61 (m, 2 H), 1.41 (qd, J = 7.4, 15.1 Hz, 2 H), 0.95 (t, J = 7.3 Hz, 3 H). ^{13}C NMR{^{1}H} (125 MHz, $CDCl_3$) δ 167.2, 144.6, 140.4, 136.1, 129.1, 128.9, 127.3, 126.3, 121.5, 64.4, 30.9, 19.3, 13.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{19}O_2$ 231.1385; found 231.1382. IR (neat): ν_{max}/cm^{-1} 3049, 3009, 2964, 2927, 2857, 1699, 1604, 1621, 1314, 1243, 1135, 1020.

(2*E*,4*E*)-Butyl 5-*p*-Tolylpenta-2,4-dienoate (3bb). Following the general procedure, **3bb** was purified by silica column chromatography (hexane/EtOAc at a 20:1 ratio), obtained as a white solid (115 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, J = 9.2, 15.3 Hz, 1H), 7.38−7.31 (m, J = 7.9 Hz, 2H), 7.20−7.11 (m, J = 7.9 Hz, 2H), 6.91−6.76 (m, 2H), 5.95 (d, J = 15.3 Hz, 1H), 4.16 (t, J = 6.7 Hz, 2H), 2.35 (s, 3H), 1.71−1.61 (m, 2H), 1.47−1.36 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 167.3, 144.8, 140.5, 139.3, 133.4, 129.6(2C), 127.2(2C), 125.4, 120.8, 64.3, 30.9, 21.4, 19.3, 13.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{21}O_2$ 245.1542; found 245.1544. IR (neat): ν_{max}/cm^{-1} 2958, 1709, 1626, 1343, 1449, 1240, 1174, 1133, 1064.

(2*E*,4*E*)-Cyclohexyl 5-Phenylpenta-2,4-dienoate (3ac). Following the general procedure, **3ac** was purified by silica column chromatography (hexane/EtOAc at a 30:1 ratio), obtained as a white solid (106 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49−7.38 (m, 3 H), 7.38−7.32 (m, 2 H), 7.32−7.26 (m, 1 H), 6.93−6.81 (m, 2 H), 5.98 (d, J = 15.5 Hz, 1 H), 4.90−4.79 (m, 1 H), 1.95−1.84 (m, 2 H), 1.81−1.69 (m, 2 H), 1.59−1.52 (m, 1 H), 1.52−1.34 (m, 4 H), 1.33−1.24 (m, 1 H). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 166.6, 144.3, 140.2, 136.2, 129.0, 128.9, 127.2, 126.4, 122.1, 72.6, 31.8, 25.5, 23.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{21}O_2$ 257.1542; found 257.1540. IR (neat): ν_{max}/cm^{-1} 2917, 2849, 1706, 1627, 1465, 1237, 1134, 740.

(2*E*,4*E*)-Cyclohexyl 5-*p*-Tolylpenta-2,4-dienoate (3bc). Following the general procedure, **3bc** was purified by silica column chromatography (hexane/EtOAc at a 30:1 ratio), obtained as a white solid (108 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (dd, J = 10.0, 15.2 Hz, 1 H), 7.37−7.32 (m, J = 8.0 Hz, 2 H), 7.18−7.13 (m, J = 8.0 Hz, 2 H), 6.90−6.74 (m, 2 H), 5.95 (d, J = 14.9 Hz, 1 H), 4.91−4.72 (m, 1 H), 2.35 (s, 3 H), 1.93−1.84 (m, 2 H), 1.75 (dd, J = 4.0, 9.2 Hz, 2 H), 1.63−1.52 (m, 2 H), 1.47−1.37 (m, 4 H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$) δ 166.7, 144.6, 140.3, 139.3, 133.5, 129.6, 127.2, 125.5, 121.5, 72.6, 31.8, 25.5, 23.9, 21.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{18}H_{22}O_2Na$ 293.1517; found 293.1520. IR (neat): ν_{max}/cm^{-1} 2937, 1708, 1448, 1234, 1132, 1009, 846, 808.

(2*E*,4*E*)-Butyl 5-(4-Fluorophenyl)penta-2,4-dienoate (3cb). Following the general procedure, **3cb** was purified by silica column chromatography (hexane/EtOAc at a 30:1 ratio), obtained as a white solid (83 mg, 67%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49−7.34 (m, 3 H), 7.03 (t, J = 8.6 Hz, 2 H), 6.93−6.69 (m, 2 H), 5.97 (d, J = 15.5 Hz, 1 H), 4.16 (t, J = 6.6 Hz, 2 H), 1.69−1.63 (m, 2 H), 1.46−1.37 (m, 2 H), 0.95 (t, J = 7.4 Hz, 3 H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$) δ 167.2, 144.4, 139.0, 128.9, 128.9, 126.1, 121.5, 116.0, 115.9, 64.4, 30.9, 19.3, 13.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{17}O_2FNa$ 271.1110; found 271.1119. IR (neat): ν_{max}/cm^{-1} 2978, 2865, 1712, 1676, 1614, 1628, 1598, 1235, 1029, 1012.

(2*E*,4*E*)-Butyl 5-(4-Bromophenyl)penta-2,4-dienoate (3db). Following the general procedure, **3db** was purified by silica column chromatography (hexane/ EtOAc at a 30:1 ratio), obtained as a white solid (95 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49−7.43 (m, J = 7.9 Hz, 2H), 7.43−7.35 (m, 1H), 7.33−7.27 (m, J = 8.5 Hz, 2H), 6.89−6.76 (m, 2H), 5.99 (d, J = 15.3 Hz, 1H), 4.16 (t, J = 6.7 Hz, 2H), 1.70−1.61 (m, 2H), 1.41 (qd, J = 7.4, 15.0 Hz, 2H), 0.94 (t, J = 7.3 Hz, 3H). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 167.1, 144.1, 138.9, 135.0, 132.1 (2C), 128.6 (2C), 127.0, 123.0, 122.1, 64.5, 30.8, 19.3, 13.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{15}H_{17}O_2BrNa$ 331.0310; found 331.0315. IR (neat): ν_{max}/cm^{-1} 3047, 3027, 3006, 2253, 1897, 1663, 1702, 1623, 1474, 1464, 1358, 1277, 1241, 1157, 1175, 1018, 1009.

(2*E*,4*E*)-Butyl 5-(4-Bromo-3-methoxyphenyl)penta-2,4-dienoate (3eb). Following the general procedure, **3eb** was purified by silica column chromatography (hexane/EtOAc at a 30:1 ratio), obtained as a white solid (127 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 1.8 Hz, 1 H), 7.43−7.31 (m, 2 H), 6.86 (d, J = 8.5 Hz, 1 H), 6.80−6.67 (m, 2 H), 5.95 (d, J = 15.3 Hz, 1 H), 4.15 (t, J = 6.7 Hz, 2 H), 3.90 (s, 3 H), 1.68−1.62 (m, 2 H), 1.44−1.37 (m, 2 H), 0.96−0.92 (m, 3 H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$) δ 167.2, 156.5, 144.4, 138.4, 131.7, 130.4, 127.9, 125.5, 121.2, 112.3, 112.0, 64.4, 56.4, 30.9, 19.3, 13.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{19}O_3BrNa$ 361.0415; found 361.0413. IR (neat): ν_{max}/cm^{-1} 2924, 2852,1713, 1625, 1593, 1496, 1461, 1378, 1338, 1280, 1262, 1174, 1131, 1054, 1019, 996, 871, 501, 458, 418.

(*E*)-Butyl Cinnamate (3fb). Following the general procedure, **3fb** was purified by silica column chromatography (hexane/EtOAc at a 40:1 ratio), obtained as a white solid (77 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 16.0 Hz, 1 H), 7.49 (br. s., 2 H), 7.34 (br. s., 3 H), 6.41 (d, J = 16.0 Hz, 1 H), 4.17 (s, 2 H), 1.68 (s, 2 H), 1.42 (s, 2 H), 0.92 (s, 3 H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$) δ 167.2, 144.6, 134.6, 130.3, 128.9, 128.1, 118.4, 64.5, 30.8, 19.3, 13.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{17}O_2$ 205.1229; found 205.1227. IR (neat): ν_{max}/cm^{-1} 2926, 1720, 1626, 1440, 1452, 1321, 1344, 1242, 1176, 1141.

(*E*)-Cyclohexylcinnamate (3fc). Following the general procedure, **3fc** was purified by silica column chromatography (hexane/EtOAc at a 40:1 ratio), obtained as a white solid (81 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 16.0 Hz, 1 H), 7.55−7.44 (m, 2 H), 7.42−7.29 (m, 3 H), 6.43 (d, J = 16.0 Hz, 1 H), 4.96−4.81 (m, 1 H), 1.92 (dd, J = 4.6, 12.6 Hz, 2 H), 1.82−1.70 (m, 2 H), 1.62−1.45 (m, 3 H), 1.45−1.35 (m, 2 H), 1.33−1.26 (m, 1 H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$) δ 166.5, 144.3, 134.7, 130.2, 128.9, 128.1, 119.0, 72.8, 31.8, 25.5, 23.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{19}O_2$ 231.1385; found 231.1389. IR (neat): ν_{max}/cm^{-1} 2924, 1717, 1615, 1622, 1434, 1350, 1316, 1243, 1171, 1135, 1010, 840, 806.

(*E*)-Isobutyl Cinnamate (3fd). Following the general procedure, **3fd** was purified by silica column chromatography (hexane/EtOAc at a 40:1 ratio), obtained as a white solid (100 mg, 74%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 16.0 Hz, 1 H), 7.57−7.48 (m, 2 H), 7.42−7.33 (m, 3 H), 6.45 (d, J = 16.0 Hz, 1 H), 3.99 (d, J = 6.9 Hz, 2 H), 2.01 (td, J = 6.8, 13.3 Hz, 1 H), 0.98 (d, J = 6.9 Hz, 6 H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$) δ 167.2, 144.6, 134.6, 130.3, 128.9, 128.1, 118.4, 70.8, 27.9, 19.2. HRMS (ESI-TOF) m/z: $[M + H]^+$

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calcd for $C_{13}H_{17}O_2$ 205.1229; found 205.1232. IR (neat): $\nu_{max/cm}{}^{-1}$ 2964, 2927, 2857, 1718, 1621, 1314, 1243, 1135, 1020.

(*E*)-Benzyl Cinnamate (3fe). Following the general procedure, **3fe** was purified by silica column chromatography (hexane/EtOAc at a 30:1 ratio), obtained as a white solid (115 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 15.9 Hz, 1 H), 7.58−7.49 (m, 2 H), 7.49−7.28 (m, 8 H), 6.50 (d, J = 15.9 Hz, 1 H), 5.26 (s, 2 H). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 166.9, 145.3, 136.2, 134.4, 130.5, 129.0, 128.7, 128.4, 128.2, 118.0, 66.5. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{16}H_{15}O_2$ 239.1072; found 239.1069. IR (neat): ν_{max}/cm^{-1} 2958, 1709, 1626, 1343, 1449, 1240, 1174, 1133, 1064.

(2*E*)-Methyl 3-Cyclohexenylacrylate (3ga). Following the general procedure, **3ga** was purified by silica column chromatography (hexane/EtOAc at a 10:1 ratio), obtained as a colorless oil (61 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, J = 15.9 Hz, 1H), 6.16 (t, J = 3.9 Hz, 1H), 5.76 (d, J = 15.8 Hz, 1H), 3.73 (s, 3H), 2.20 (d, J = 3.4 Hz, 2H), 2.15−2.11 (m, 2H), 1.71−1.66 (m, 2H), 1.64−1.59 (m, 2H). ^{13}C NMR {^{1}H}(100 MHz, $CDCl_3$) δ 168.2, 148.4, 139.0, 135.0, 114.2, 51.5, 26.5, 24.2, 22.1 (2C). HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{10}H_{15}O_2$ 167.1072; found 167.1080. IR (neat): ν_{max}/cm^{-1} 2928, 2856, 1721, 1628, 1435, 1378, 1309, 1269, 1167, 1136, 1073, 982.

(2*E*)-Butyl 3-Cyclohexenylacrylate (3gb). Following the general procedure, **3gb** was purified by silica column chromatography (hexane/EtOAc at a 10:1 ratio), obtained as a colorless oil (83 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 15.9 Hz, 1 H), 6.15 (t, J = 4.0 Hz, 1 H), 5.75 (d, J = 15.3 Hz, 1 H), 4.13 (t, J = 6.7 Hz, 2 H), 2.23−2.09 (m, 4 H), 1.70−1.59 (m, 6 H), 1.45−1.34 (m, 2 H), 0.93 (t, J = 7.3 Hz, 3 H). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 167.9, 148.1, 138.8, 135.0, 114.7, 64.1, 30.9, 26.5, 24.2, 22.1 (2C), 22.1, 19.3, 13.8. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{13}H_{21}O_2$ 209.1542; found 209.1538. IR (neat): ν_{max}/cm^{-1} 2957, 2931, 2863, 1716, 1630, 1458, 1286, 1164.

(2*E*)-Cyclohexyl 3-Cyclohexenylacrylate (3gc). Following the general procedure, **3gc** was purified by silica column chromatography (hexane/EtOAc at a 10:1 ratio), obtained as a colorless oil (96 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ7.23 (s, 1 H), 6.14 (br. s., 1 H), 5.74 (d, J = 15.9 Hz, 1 H), 4.87−4.75 (m, 1 H), 2.24−2.08 (m, 4 H), 1.87 (dd, J = 4.0, 10.1 Hz, 2 H), 1.78−1.66 (m, 4 H), 1.66−1.56 (m, 3 H), 1.49−1.26 (m, 5 H). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 167.2, 147.8, 138.6, 135.0, 115.3, 72.4, 31.9 (2C), 26.5, 25.5, 24.2, 23.9 (2C), 22.2 (2C). HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{15}H_{22}O_2Na$ 257.1517; found 257.1512. IR (neat): ν_{max}/cm^{-1} 3025, 2934, 2859, 2661, 1712, 1629, 1450, 1435, 1350, 1318, 1301, 1286, 1167, 1039, 1018, 925.

(2*E*)-*tert*-Butyl 3-Cyclohexenylacrylate (3gf). Following the general procedure, **3gf** was purified by silica column chromatography (hexane/EtOAc at a 10:1 ratio), obtained as a colorless oil (86 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, J = 15.9 Hz, 1H), 6.11 (t, J = 4.3 Hz, 1H), 5.68 (d, J = 15.9 Hz, 1H), 2.21−2.15 (m, 2H), 2.11 (t, J = 6.1 Hz, 2H), 1.71−1.63 (m, 2H), 1.63−1.57 (m, 2H), 1.48 (s, 9H). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 167.2, 147.2, 138.1, 135.0, 116.5, 80.0, 28.3 (3C), 26.5, 24.3, 22.2 (2C). HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{13}H_{20}O_2Na$ 231.1361; found 231.1360. IR (neat): ν_{max}/cm^{-1} 2976, 2931, 2861, 1705, 1631, 1619, 1455, 1435, 1367, 1316, 1287, 1268, 1149, 1098, 982.

(2*E*)-Methyl 3-Cyclopentenylacrylate (3ha). Following the general procedure, **3ha** was purified by silica column chromatography (hexane/EtOAc at a 10:1 ratio), obtained as a colorless oil (55 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 15.9 Hz, 1H), 6.16 (s, 1H), 5.72 (d, J = 15.9 Hz, 1H), 3.74 (s, 3H), 2.51−2.40 (m, 4H), 2.00−1.91 (m, 2H). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 168.0, 141.5, 141.2, 140.8, 117.8, 51.6, 33.6, 30.8, 23.1. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_9H_{13}O_2$ 153.0916; found 153.0916. IR (neat): ν_{max}/cm^{-1} 2924, 2849, 1720, 1630, 1434, 1308, 1272, 1221, 1191, 1166, 1038, 980.

(2*E*,4*E*)-Methyl Hexa-2,4-dienoate (3ia). Following the general procedure, **3ia** was purified by silica column chromatography (hexane/EtOAc at a 20:1 ratio), obtained as a colorless oil (44 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27−7.20 (m, 1H), 6.22−6.08 (m, 2H), 5.76 (d, J = 15.5 Hz, 1H), 3.72 (s, 3H), 1.83 (d, J = 6.3 Hz, 3H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$) δ 167.8, 145.2, 139.5, 129.8, 118.6, 51.5, 18.7. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_7H_{11}O_2$ 127.0759; found 127.0760. IR (neat): ν_{max}/cm^{-1} 3483, 2955, 2925, 2853, 1724, 1650, 1437, 1309, 1271, 1172, 1200, 1029, 982, 858, 813, 633, 723, 541.

(2*E*,4*E*)-Cyclohexyl Hexa-2,4-dienoate (3ic). Following the general procedure, **3ic** was purified by silica column chromatography (hexane/EtOAc at a 20:1 ratio), obtained as a colorless oil (71 mg, 73%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (dd, J = 10.3, 15.3 Hz, 1H), 6.28−6.07 (m, 2H), 5.76 (d, J = 15.3 Hz, 1H), 4.92−4.77 (m, 1H), 1.90−1.82 (m, 5H), 1.72 (dd, J = 5.2, 7.7 Hz, 2H), 1.62−1.35 (m, 6H). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 166.9, 144.7, 139.0, 129.9, 119.8, 72.4, 31.8 (2C), 25.5, 23.9 (2C), 18.7. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{12}H_{19}O_2$ 195.1385; found 195.1389. IR (neat): ν_{max}/cm^{-1} 3025, 2934, 2661, 1712, 1629, 1450, 1435, 1350, 1318, 1286, 1167, 1039, 1018.

(*E*)-Butyl Penta-2,4-dienoate (3jb). Following the general procedure, **3jb** was purified by silica column chromatography (hexane/EtOAc at a 20:1 ratio), obtained as a colorless oil (54 mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29−7.22 (m, 1H), 6.50−6.40 (m, 1H), 5.90 (d, J = 15.5 Hz, 1H), 5.60 (d, J = 17.0 Hz, 1H), 5.48 (d, J = 10.5 Hz, 1H), 4.15 (t, J = 6.7 Hz, 2H), 1.67−1.61 (m, 2H), 1.40 (m, J = 7.5 Hz, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 167.0, 144.6, 134.8, 125.5, 122.3, 64.4, 30.8, 19.2, 13.8. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_9H_{15}O_2$ 155.1072; found 155.1075. IR (neat): ν_{max}/cm^{-1} 2960, 2928, 2854, 1713, 1601, 1643, 1445, 1267, 1144.

(2*E*,4*E*)-Butyl 5-Cyclopropylpenta-2,4-dienoate (3kb). Following the general procedure, **3kb** was purified by silica column chromatography (hexane/EtOAc at a 20:1 ratio), obtained as a colorless oil (76 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, J = 11.6, 15.3 Hz, 1 H), 6.24 (dd, J = 11.0, 15.3 Hz, 1 H), 5.73 (d, J = 15.3 Hz, 1 H), 5.59 (dd, J = 9.5, 15.0 Hz, 1 H), 4.11 (t, J = 6.7 Hz, 2 H), 1.65−1.59 (m, 2 H), 1.53−1.44 (m, 1 H), 1.42−1.33 (m, 2 H), 0.95−0.83 (m, 5 H), 0.56−0.45 (m, 2 H). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 167.6, 148.8, 144.8, 125.8, 118.0, 64.1, 30.8, 19.2, 15.0, 13.8, 8.4(2C). HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{12}H_{19}O_2$ 195.1385; found 195.1386. IR (neat): ν_{max}/cm^{-1} 3084, 3006, 1934, 2960, 2873, 1712, 1637, 1456, 1388, 1302, 1243, 1126, 1150.

(2*E*,4*E*)-Cyclohexyl 5-Cyclopropylpenta-2,4-dienoate (3kc). Following the general procedure, **3kc** was purified by silica column chromatography (hexane/EtOAc at a 20:1 ratio), obtained as a colorless oil (83 mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (dd, J = 11.2, 15.2 Hz, 1 H), 6.24 (dd, J = 10.9, 14.9 Hz, 1 H), 5.73 (d, J = 15.5 Hz, 1 H), 5.59 (dd, J = 9.5, 15.2 Hz, 1 H), 4.85−4.75 (m, 1 H), 1.91−1.79 (m, 2 H), 1.72 (dd, J = 3.4, 9.2 Hz, 2 H), 1.55−1.47 (m, 2 H), 1.45−1.32 (m, 4 H), 1.30−1.24 (m, 1 H), 0.89−0.84 (m, 2 H), 0.54−0.49 (m, 2 H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$) δ 167.0, 148.5, 144.6, 125.9, 118.7, 72.3, 31.8, 25.5, 23.9, 14.9, 8.4. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{14}H_{20}O_2Na$ 243.1361; found 243.1366. IR (neat): ν_{max}/cm^{-1} 3085, 3008, 2918, 2850, 2252, 1701, 1636, 1453, 1382, 1257, 1300, 1242, 1151.

(2*E*,4*E*)-Butyl 6-Acetoxyhexa-2,4-dienoate (3lb). Following the general procedure, **3lb** was purified by silica column chromatography (hexane/EtOAc at a 7:1 ratio), obtained as a colorless oil (93 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, J = 11.0, 15.9 Hz, 1H), 6.37 (dd, J = 11.6, 15.3 Hz, 1H), 6.11 (td, J = 5.8, 15.3 Hz, 1H), 5.90 (d, J = 15.9 Hz, 1H), 4.66 (d, J = 6.1 Hz, 2H), 4.14 (t, J = 6.7 Hz, 2H), 2.08 (s, 3H), 1.70−1.61 (m, 2H), 1.39 (m, J = 7.5, 2H), 0.95−0.90 (m, 3H). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 170.7, 166.9, 143.1, 135.2, 130.8, 122.7, 64.5, 63.9, 30.8, 20.9, 19.2, 13.8. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{12}H_{19}O_4$ 227.1283; found 227.1285. IR (neat): ν_{max}/cm^{-1} 2959, 2927, 2874, 1746, 1715, 1621, 1650, 1455, 1364, 1382, 1234, 1182, 1139, 1077, 1026, 1001.

(2*E*,4*E*)-Cyclohexyl Ethyl Hexa-2,4-dienedioate (3mc). Following the general procedure, **3mc** was purified by silica column chromatography (hexane/EtOAc at a 5:1 ratio), obtained as a colorless oil (106 mg, 84%). ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.36−

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7.19 (m, 2H), 6.28−6.09 (m, 2H), 4.90−4.73 (m, 1H), 4.22 (q, J = 6.9 Hz, 2H), 1.86 (dd, J = 4.3, 9.2 Hz, 2H), 1.73 (dd, J = 3.7, 9.2 Hz, 2H), 1.60−1.32 (m, 6H), 1.29 (t, J = 7.3 Hz, 3H). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 166.0, 165.4, 141.0, 140.5, 131.7 (2C), 128.3, 73.3, 60.9, 31.7, 25.4, 23.8 (2C), 14.3. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{14}H_{20}O_4Na$ 275.1259; found 275.1252. IR (neat): ν_{max}/cm^{-1} 3400, 3066, 2938, 2861, 1699, 1611, 1456, 1446, 1310, 1251, 1167, 1027, 1015, 935.

(2*E*,4*E*)-9-(Acryloyloxy)nonyl Ethyl Hexa-2,4-dienedioate (3mg). Following the general procedure, **3mg** was purified by silica column chromatography (hexane/EtOAc at a 6:1 ratio), obtained as a colorless oil (124 mg, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (s, 1H), 7.31 (s, 1H), 6.38 (d, J = 17.1 Hz, 1H), 6.24−5.97 (m, 3H), 5.79 (d, J = 10.4 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 4.14 (q, J = 7.3 Hz, 4H), 1.71−1.62 (m, 4H), 1.35−1.27 (m, 13H). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 166.4, 166.1, 166.0, 140.9 (2C), 130.6, 128.7, 128.5 (2C), 65.1, 64.7, 61.0, 29.5, 29.4, 29.3, 29.2, 28.7, 26.0 (2C), 14.3. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{20}H_{31}O_6$ 367.2121; found 367.2128. IR (neat): ν_{max}/cm^{-1} 3070, 2928, 2855, 1721, 1703, 1613, 1473, 1313, 1295, 1260, 1240, 1021.

(2*E*,4*E*)-5-*p*-Tolylpenta-2,4-dienenitrile (5ba). Following the general procedure, **5ba** was purified by silica column chromatography (hexane/EtOAc at a 30:1 ratio), obtained as a white solid (70 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 7.9 Hz, 2H), 7.18−7.09 (m, 3H), 6.87−6.76 (m, 2H), 5.39 (d, J = 15.9 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 150.6, 141.5, 140.1, 132.6, 129.8 (2C), 127.5 (2C), 124.6, 118.6, 97.6, 21.5. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{12}H_{12}N$ 170.0970; found 170.0971. IR (neat): ν_{max}/cm^{-1} 3028, 3049,2924, 2856,2254, 2209, 1732, 1605, 1623, 1593, 1454, 1310, 1286, 1153, 968, 995, 980.

(2*E*,4*E*)-5-(4-Bromophenyl)penta-2,4-dienenitrile (5ca). Following the general procedure, **5ca** was purified by silica column chromatography (hexane/EtOAc at a 30:1 ratio), obtained as a white solid (80 mg, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, J = 8.6 Hz, 2H), 7.31 (d, J = 8.6 Hz, 2H), 7.12 (ddd, J = 2.6, 7.3, 16 Hz, 1H), 6.85−6.74 (m, 2H), 5.45 (d, J = 16.0 Hz, 1H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$) δ 150.0, 140.0, 134.3, 132.2 (2C), 128.8 (2C), 126.1, 123.9, 118.2, 99.1. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{11}H_9NBr$ 233.9918; found 233.9925. IR (neat): ν_{max}/cm^{-1} 3051, 3019, 2923, 2853, 2253, 2211, 1911, 1737, 1620, 1597, 1579, 1486, 1467, 1402, 1274, 1150, 1099, 1007, 1071, 983, 948.

(2*E*,4*E*)-5-(4-Fluorophenyl)penta-2,4-dienenitrile (5da). Following the general procedure, **5da** was purified by silica column chromatography (hexane/EtOAc at a 30:1 ratio), obtained as a white solid (86 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, J = 5.4, 8.4 Hz, 2H), 7.13 (dd, J = 10.7, 15.9 Hz, 1H), 7.06 (t, J = 8.6 Hz, 2H), 6.84 (d, J = 15.6 Hz, 1H), 6.73 (dd, J = 10.8, 15.5 Hz, 1H), 5.43 (d, J = 15.9 Hz, 1H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$) δ 164.5, 162.6 (d, $^1J_{CF}$ = 262.5 Hz), 150.2, 140.1, 131.6, 129.2 (2C, d, $^3J_{CF}$ = 8.75 Hz) 125.3, 118.3, 116.3, 116.1 (2C, d, $^2J_{CF}$ = 21.2 Hz), 98.4. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{11}H_9NF$ 174.0719; found 174.0720. IR (neat): ν_{max}/cm^{-1} 2911, 2883, 2212, 1726, 1671, 1616, 1402,1288, 1219, 1151, 1172, 1047, 983.

Cinnamonitrile (5fa). Following the general procedure, **5fa** was purified by silica column chromatography (hexane/EtOAc at a 30:1 ratio), obtained as a white solid (77 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47−7.35 (m, 6 H), 5.87 (d, J = 17.2 Hz, 1 H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$) δ 150.7, 133.6, 131.3, 129.2, 127.4, 118.2, 96.4. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_9H_{10}N$ 132.0813; found 132.0818. IR(neat): ν_{max}/cm^{-1} 2929, 2856, 1628, 1439, 1450, 1324, 1342, 1240, 1172, 1137, 1031.

(2*E*)-3-Cyclohexenylacrylonitrile (5ga). Following the general procedure, **5ga** was purified by silica column chromatography (hexane/EtOAc at a 30:1 ratio), obtained as a colorless oil (62 mg, 78%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (d, J = 16.4 Hz, 1 H), 6.14 (t, J = 4.2 Hz, 1 H), 5.17 (d, J = 16.3 Hz, 1 H), 2.24−2.19 (m, 2 H), 2.09−2.04 (m, 2 H), 1.71−1.66 (m, 2 H), 1.61 (td, J = 2.6, 8.4 Hz, 2 H). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 153.8, 140.0, 134.7, 92.4, 26.4, 23.5, 21.8, 21.8. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_9H_{12}N$ 134.0970; found 134.0970. IR (neat): ν_{max}/cm^{-1} 3058, 2927, 2857, 2215, 1738, 1626, 1598, 1448, 1434, 1378, 965.

(2*E*,4*E*)-Ethyl 5-Cyanopenta-2,4-dienoate (5ma). Following the general procedure, **5ma** was purified by silica column chromatography (hexane/EtOAc at a 10:1 ratio), obtained as a colorless oil (66 mg, 75%). ^{1}H NMR (500 MHz,$CDCl_3$) δ 7.24 (dd, J = 11.5, 15.5 Hz, 1H), 7.07 (dd, J = 11.2, 15.8 Hz, 1H), 6.19 (d, J = 14.3 Hz, 1H), 5.70 (d, J = 15.5 Hz, 1H), 4.24 (q, J = 6.9 Hz, 2H), 1.30 (t, J = 7.2 Hz, 3H). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 165.4, 147.1, 139.5, 129.6, 116.9, 106.1, 61.3, 14.3. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_8H_{10}NO_2$ 152.0712; found 152.0715. IR (neat): ν_{max}/cm^{-1} 3404, 3028, 3054, 2987, 2960, 2926, 2855, 2255, 2217, 1710, 1670, 1636, 1263, 1183, 1001, 910.

(1*E*)-1-Cyclohexenylpent-1-en-3-one (5gb). Following the general procedure, **5gb** was purified by silica column chromatography (hexane/EtOAc at a 20:1 ratio), obtained as a colorless oil (60 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, J = 15.9 Hz, 1H), 6.19 (t, J = 4.3 Hz, 1H), 6.06 (d, J = 16.5 Hz, 1H), 2.58 (q, J = 7.3 Hz, 2H), 2.24−2.17 (m, 2H), 2.16−2.11 (m, 2H), 1.72−1.65 (m, 2H), 1.64−1.59 (m, 2H), 1.10 (t, J = 7.3 Hz, 3H). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 201.7, 146.0, 139.7, 135.3, 123.1, 33.7, 26.7, 24.3, 22.1(2C), 8.5. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{11}H_{16}ONa$ 187.1099; found 187.1096. IR (neat): ν_{max}/cm^{-1} 2931, 2860, 1688, 1664, 1625, 1598, 1434, 1458, 1375, 1278, 1194, 1120, 1049, 1035.

(1*E*)-1-Cyclopentenylpent-1-en-3-one (5hb). Following the general procedure, **5hb** was purified by silica column chromatography (hexane/EtOAc at a 20:1 ratio), obtained as a colorless oil (56 mg, 74%). ^{1}H NMR (500 MHz, $CDCl_3$) δ7.37 (d, J = 16.0 Hz, 1 H), 6.21 (br. s., 1 H), 6.01 (d, J = 16.0 Hz, 1 H), 2.59 (q, J = 7.4 Hz, 2 H), 2.51−2.41 (m, 4 H), 2.02−1.88 (m, 2 H), 1.11 (t, J = 7.4 Hz, 3 H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$) δ 201.8, 141.9, 141.5, 138.6, 126.6, 33.7, 33.6, 30.9, 23.2, 8.4. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{10}H_{15}O$ 151.1123; found 151.1122. IR (neat): ν_{max}/cm^{-1} 3372, 3039, 2924, 2954, 2851, 1690, 1668, 1612, 1590, 1460, 1411, 1375, 1189, 1119, 1037.

(4*E*,6*E*)-7-Cyclopropylhepta-4,6-dien-3-one (5kb). Following the general procedure, **5kb** was purified by silica column chromatography (hexane/EtOAc at a 20:1 ratio), obtained as a colorless oil (56 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (dd, J = 11.3, 15.4 Hz, 1H), 6.25 (dd, J = 10.9, 15.0 Hz, 1H), 6.04 (d, J = 15.4 Hz, 1H), 5.64 (dd, J = 9.5, 15.0 Hz, 1H), 2.54 (q, J = 7.4 Hz, 2H), 1.54−1.46 (m, 1H), 1.09 (t, J = 7.2 Hz, 3H), 0.91−0.86 (m, 2H), 0.56−0.51 (m, 2H). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 201.5, 149.8, 142.7, 126.6, 126.4, 33.7, 15.2, 8.6, 8.4(2C). HRMS (ESI-TOF) m/z: [M + Li]$^+$ calcd for $C_{10}H_{14}OLi$ 157.1205; found 157.1208. IR (neat): ν_{max}/cm^{-1} 3085, 3007, 2975, 2927, 2855, 1897, 1715, 1688, 1662, 1632, 1595, 1455, 1377, 1281, 1201, 1033, 1049, 997, 950, 861.

1-((1*E*,3*E*)-Nona-1,3-dienylsulfonyl)benzene (5nc). Following the general procedure, **5nc** was purified by silica column chromatography (hexane/EtOAc at a 3:1 ratio), obtained as a white solid (92 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, J = 0.9, 8.2 Hz, 2H), 7.62−7.56 (m, 1H), 7.56−7.47 (m, 2H), 7.24 (dd, J = 10.9, 14.7 Hz, 1H), 6.29−6.20 (m, 2H), 6.09 (dd, J = 10.9, 15.2 Hz, 1H), 2.16 (q, J = 7.1 Hz, 2H), 1.41 (q, J = 7.3 Hz, 2H), 1.30−1.25 (m, 4H), 0.87 (t, J = 6.9 Hz, 3H). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$) δ 148.1, 143.1, 141.2, 133.2, 129.3 (2C), 127.6 (2C), 127.5, 126.1, 33.1, 31.4, 28.2, 22.5, 14.1. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{15}H_{21}SO_2$ 265.1262; found 265.1260. IR (neat): ν_{max}/cm^{-1} 3404, 3028, 3054, 2987, 2960, 2926, 2855, 2255, 2217, 1710, 1670, 1636, 1263, 1183, 1001, 910.

1-((1*E*)-2-Cyclopentenylvinylsulfonyl)benzene (5hc). Following the general procedure, **5hc** was purified by silica column chromatography (hexane/EtOAc at a 3:1 ratio), obtained as a white solid (89 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91−7.85 (m, 2H), 7.62−7.56 (m, 1H), 7.56−7.45 (m, 3H), 6.33−6.26 (m, 1H), 6.16 (dd, J = 0.8, 15.0 Hz, 1H), 2.53−2.44 (m, 2H), 2.38−2.32 (m, 2H), 1.94 (m, 2H). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 143.8, 141.2, 139.5, 138.9, 133.2, 129.3 (2C), 127.6 (2C), 126.9, 33.8, 30.9,

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23.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{15}SO_2$ 235.0793; found 235.0787. IR (neat): ν_{max}/cm^{-1} 3028, 3054, 2987, 2960, 2926, 2217, 1710, 1670, 1636, 1263.

(*E*)-Cinnamamide (5fd). Following the general procedure, **5fd** was purified by silica column chromatography (hexane/EtOAc at a 1:4 ratio), obtained as a white solid (77 mg, 81%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 15.6 Hz, 1 H), 7.57−7.45 (m, 2 H), 7.38 (br. s., 3 H), 6.45 (d, J = 15.8 Hz, 1 H), 5.58 (br. s., 2 H). ^{13}C NMR $\{^1H\}$ (125 MHz, $CDCl_3$) δ 166.7, 141.7, 133.6, 129.1, 127.9, 127.0, 118.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for C_9H_9NONa 170.0582; found 170.0586. IR (neat): ν_{max}/cm^{-1} 2926, 1665, 1594, 1439, 1450, 1321, 1344, 1241, 1173, 1139, 1035.

(2*E*)-3-Cyclopentenylacrylamide (5hd). Following the general procedure, **5hd** was purified by silica column chromatography (hexane/EtOAc at a 1:4 ratio), obtained as a sticky solid (54 mg, 79%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 15.9 Hz, 1H), 6.13 (s, 1H), 5.73 (d, J = 15.3 Hz, 1H), 5.58 (br. s., 2H), 2.51−2.36 (m, 4H), 1.96 (m, J = 7.6 Hz, 2H). ^{13}C NMR $\{^1H\}$ (100 MHz, $CDCl_3$) δ168.7, 141.2, 140.1, 138.8, 119.5, 33.5, 31.0, 23.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_8H_{12}ON$ 138.0919; found 138.0914. IR (neat): ν_{max}/cm^{-1} 3355, 3169, 2954, 2852, 2923, 1662, 1592, 1397, 1462, 1439, 1243, 1103, 1037.

(2*E*,4*E*)-Methyl 3-Methyl-5-phenylpenta-2,4-dienoate (5ae). Following the general procedure, **5ae** was purified by silica column chromatography (hexane/EtOAc at a 20:1 ratio), obtained as a white solid (66 mg, 65%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.48−7.41 (m, 2H), 7.37−7.31 (m, 2H), 7.31−7.25 (m, 1H), 6.94 (d, J = 16.5 Hz, 1H), 6.80 (d, J = 15.9 Hz, 1H), 5.90 (s, 1H), 3.72 (s, 3H), 2.40 (s, 3H). ^{13}C NMR $\{^1H\}$ (100 MHz, $CDCl_3$) δ 167.5, 152.5, 136.4, 134.3, 131.9, 128.9 (2C), 128.7, 127.1 (2C), 119.4, 51.2, 13.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{15}O_2$ 203.1072; found 203.1075. IR (neat): ν_{max}/cm^{-1} 1712, 1609, 1433, 1357,1238, 1154, 960, 690.

(*E*)-7-Phenylhept-6-en-3-one (6ab). Following the general procedure, **6ab** was purified by silica column chromatography (hexane/EtOAc at a 20:1 ratio), obtained as a white solid (68 mg, 70%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.33−7.25 (m, 4H), 7.22−7.15 (m, 1H), 6.39 (d, J = 15.9 Hz, 1H), 6.18 (td, J = 6.7, 15.9 Hz, 1H), 2.61−2.54 (m, 2H), 2.52−2.39 (m, 4H), 1.06 (t, J = 7.3 Hz, 3H). ^{13}C NMR $\{^1H\}$ (100 MHz, $CDCl_3$) δ 210.8, 137.5, 130.8, 129.1, 128.6 (2C), 127.2, 126.1 (2C), 41.9, 36.2, 27.3, 7.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{17}O$ 189.1279; found 189.1282. IR (neat): ν_{max}/cm^{-1} 3059, 3025, 2974, 2934, 2852, 1714, 1597, 1448, 1260, 1114, 1027.

(*E*)-7-*p*-Tolylhept-6-en-3-one (6bb). Following the general procedure, **6bb** was purified by silica column chromatography (hexane/EtOAc at a 20:1 ratio), obtained as a white solid (76 mg, 75%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.23−7.18 (m, J = 8.5 Hz, 2H), 7.11−7.05 (m, J = 7.9 Hz, 2H), 6.36 (d, J = 15.9 Hz, 1H), 6.13 (td, J = 6.7, 15.9 Hz, 1H), 2.56 (d, J = 7.3 Hz, 2H), 2.50−2.40 (m, 4H), 2.31 (s, 3H), 1.05 (t, J = 7.3 Hz, 3H). ^{13}C NMR $\{^1H\}$ (100 MHz, $CDCl_3$) δ 210.9, 136.9, 134.7, 130.6, 129.3 (2C), 128.0, 126.0 (2C), 42.0, 36.1, 27.3, 21.2, 7.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{19}O$ 203.1436; found 203.1432. IR (neat): ν_{max}/cm^{-1} 3413, 3022, 2922, 2853, 1899, 1714, 1612, 1581, 1512, 1458, 1411, 1375, 1306, 1260, 1208, 1181, 1112, 1067, 1019.

4-Phenylbutan-2-one (6ff). Following the general procedure, **6ff** was purified by silica column chromatography (hexane/EtOAc at a 20:1 ratio), obtained as a colorless oil (60 mg, 65%). ^1H NMR (500 MHz,$CDCl_3$) δ 7.32−7.22 (m, 2 H), 7.22−7.11 (m, 3 H), 2.89 (t, J = 7.7 Hz, 2 H), 2.76 (t, J = 7.7 Hz, 2 H), 2.14 (s, 3 H). ^{13}C NMR $\{^1H\}$ (125 MHz, $CDCl_3$) δ 207.0, 140.1, 127.6, 127.4, 125.2, 44.3, 29.2, 28.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{10}H_{13}O$ 149.0966; found 149.0969. IR (neat): ν_{max}/cm^{-1} 2931, 2860, 1720, 1664, 1625, 1588, 1458, 1375, 1278, 1194, 1120, 1049, 1035.

1-Cyclopentenylpentan-3-one (6hb). Following the general procedure, **6hb** was purified by silica column chromatography (hexane/EtOAc at a 20:1 ratio), obtained as a colorless oil (50 mg, 65%). ^1H NMR (500 MHz, $CDCl_3$) δ 5.41−5.21 (m, 1H), 2.58−2.53 (m, 2H), 2.46−2.40 (m, 2H), 2.33 (t, J = 8.0 Hz, 2H), 2.27 (ddd, J = 2.3, 4.7, 9.6 Hz, 2H), 2.22 (t, J = 8.6 Hz, 2H), 1.87−1.80 (m, 2H), 1.05 (t, J = 7.4 Hz, 3H). ^{13}C NMR $\{^1H\}$ (100 MHz, $CDCl_3$) δ 211.4, 143.4, 123.7, 40.8, 35.9, 35.3, 32.5, 25.4, 23.4, 7.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{10}H_{17}O$ 153.1279; found 153.1280. IR (neat): ν_{max}/cm^{-1} 3045, 2925, 2850, 1717, 1651, 1614, 1460, 1413, 1376, 1111, 978.

(E)-Undec-5-en-2-one (6nf). Following the general procedure, **6nf** was purified by silica column chromatography (hexane/EtOAc at a 20:1 ratio), obtained as a colorless oil (50 mg, 60%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.49−5.27 (m, 2H), 2.49−2.42 (m, 2H), 2.23 (q, J = 6.7 Hz, 2H), 2.11 (s, 3H), 1.97−1.87 (m, 2H), 1.35−1.25 (m, 6H), 0.85 (t, J = 6.7 Hz, 3H). ^{13}C NMR $\{^1H\}$ (100 MHz, $CDCl_3$) δ 208.6, 131.7, 128.2, 43.7, 32.5, 31.4, 30.0, 29.2, 26.9, 22.6, 14.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{21}O$ 169.1592; found 169.1593. IR (neat): ν_{max}/cm^{-1} 2957, 2925, 2855, 1718, 1440, 1359, 1160, 969.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02823.

Copies of 1H and 13C spectra for all products and table of results from kinetics NMR experiments (PDF)

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Notes

The authors declare no competing financial interest.

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