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Synthesis of Cyclopentenones through Rhodium-Catalyzed C−H Annulation of Acrylic Acids with Formaldehyde and Malonates

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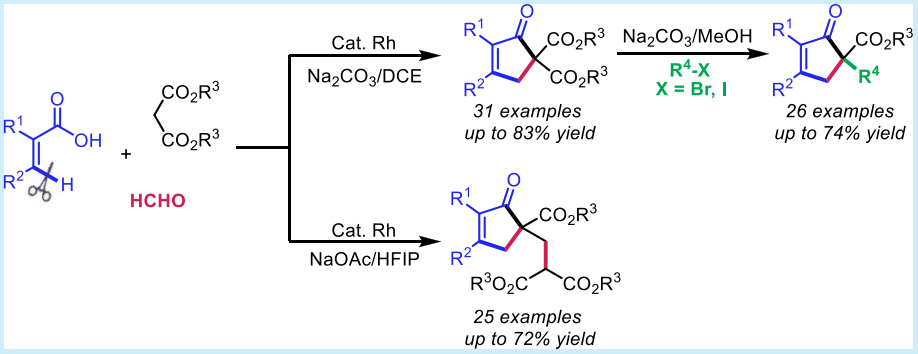

ABSTRACT: An efficient rhodium-catalyzed protocol for the synthesis of cyclopentenones based on a three-component reaction of acrylic acids, formaldehyde, and malonates via vinylic C−H activation is reported. Exploratory studies showed that 5-alkylation of as-prepared cyclopentenones could be realized smoothly by the treatment of a variety of alkyl halides with a Na_2CO_3/MeOH solution. Excess formaldehyde and malonate led to a multicomponent reaction that afforded the multisubstituted cyclopentenones through a Michael addition.

Cyclopentenones are important constituents of numerous natural products and biologically active drugs.[1] Their enone structure allows a broad diversity of chemical modifications.[2] Consequently, considerable effort has been devoted to the discovery and development of efficient approaches to these important compounds.[3] Nazarov intramolecular cyclization is a well-established method for accessing the cyclopentenones from divinyl ketone precursors (Scheme 1a).[4] This electrocyclic reaction is initiated by formation of an extended cationic π-system in the presence of Lewis or Brønsted acids and undergoes 4π-electrocyclization to give cyclopentenone. In general, the preparation of starting divinyl ketone substrates requires multistep syntheses and the formation of the byproducts from an oxyallyl cation intermediate is difficult to avoid.[5] The cobalt-mediated multicomponent cyclization from an alkyne, an alkene, and a carbon monoxide, known as Pauson−Khand reaction (PKR), provides a convergent and versatile method for the synthesis of cyclopentenones (Scheme 1b).[6] However, challenges, including the excess use of toxic carbon monoxide and low reactivity as well as poor selectivity of alkenes associated with the intermolecular PKR, make the development of a novel strategy for cyclopentenones highly attractive. In this respect, important advancements from the groups of Chung,[7] Montgomery,[8] Ogoshi,[9] Ready,[10] Morandi,[11] and others[12] have been documented (Scheme 1c). Notably, most of these works focused on the development of three-carbon components without alkene and carbon monoxide in the PKR. However, the straightforward disconnection by C−H cleavage, which is a concise and economical route, is not realized.

Chelation-assisted C−H functionalization represents one of the most straightforward and atom-economical reaction types,[13] which not only avoids prefunctionalization of the substrates but also provides novel disconnections in retrosynthetic analysis. Although this field has witnessed a renaissance in the past decades, the studies are mainly limited to aryl C(sp^2)−H activation.[14] A direct cross-coupling reaction of easily accessible acrylic acids via vinylic C−H cleavage is relatively difficult and challenging due to the lability of the alkenyl moiety and the lower rotational barriers of the carboxyl−vinyl bond.[15] On the contrary, multicomponent reactions involving three or more simple precursors have unique potential for the concise and clean one-step synthesis of complex molecules without the construction of sophisticated educts.[16] The strategy of combining positionally selective C−H activation and multicomponent reaction would lead to

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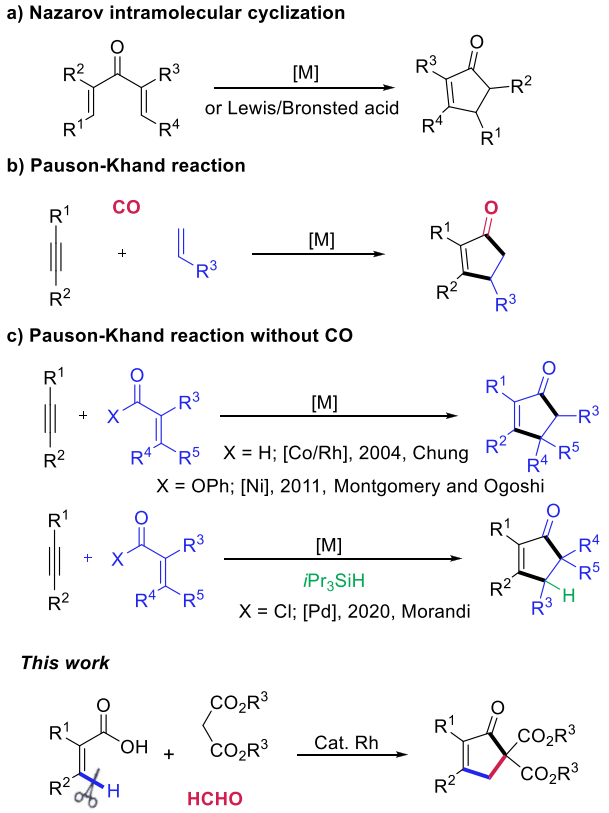
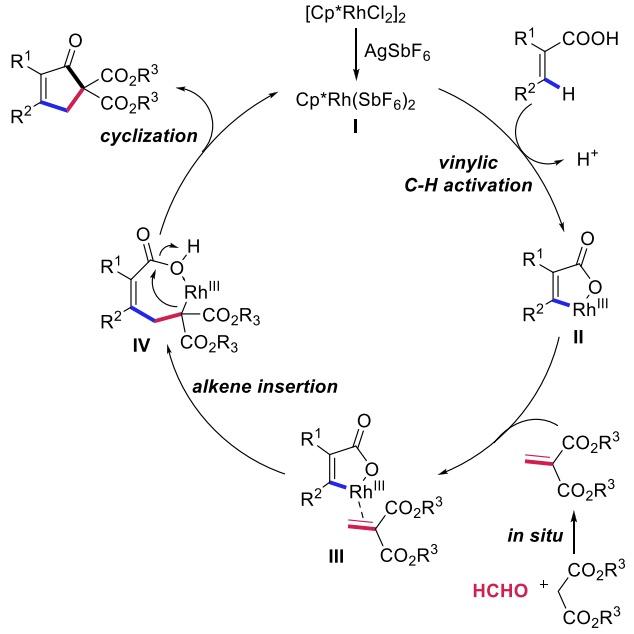
Scheme 1. Strategies for Cyclopentenones



Scheme 2. Proposed Reaction Pathway



simpler procedures for the useful molecules and bring us closer to the goal of more environmentally friendly processes. However, to date, examples of multicomponent reaction involving vinylic C−H activation have not been reported. Herein, we disclose the first example of the application of a vinylic C−H activation in multicomponent annulation of acrylic acids, formaldehyde, and malonates for the efficient synthesis of cyclopentenones. The reaction is initiated by the carboxyl-directed rhodium-catalyzed vinylic C−H activation and proceeds precisely with formaldehyde and malonate to give the cyclopentenone products. It should be noted that the carboxyl of acrylic acids participates in the annulation reaction by turning into one carbon of the cyclopentenone structural motif. Treatment of as-prepared cyclopentenones with alkyl halides in a Na_2CO_3/MeOH solution affords a variety of 5-alkylated cyclopentenones. Importantly, multicomponent reaction occurred with an adjustment of the reaction conditions, which allows the rapid and atom-economical formation of a variety of highly functionalized cyclopentenones.

We had recently shown that a three-component annulation of benzoic acids and formaldehyde as well as malonates gave indanones via aromatic C−H activation by rhodium catalysis.[17] We questioned if a proposed key intermediate **II** could be formed through the rhodium activation of the vinylic C−H bond of acrylic acids (Scheme 2). This was then thought to undergo an insertion into methylenemalonates, which could be formed in situ by formaldehyde and malonates under the reaction conditions, to generate intermediate **IV**. The subsequent cyclization could produce the desired cyclopentanones. Such a reaction pathway could open a useful route to cyclopentenones that would compare favorably with established methodologies in some features, including readily available starting materials, and be practical without the use of toxic carbon monoxide.

Motivated by this valuable synthetic opportunity, we began to explore the catalytic system even though the strategy for the aryl C−H functionalization is difficult to implement simply into the analogous vinylic C−H cleavage.[18] Cyclohex-1-ene-1-carboxylic acid **1a** was chosen as a model substrate to perform the multicomponent reaction with formaldehyde **2** and malonate **3a**. The failure to produce the desired cyclopentenone product was not unexpected when the catalytic system we used previously for aryl carboxylic acids was employed (see the Supporting Information).[17] To improve the reactivity of the rhodium catalyst, a variety of additives were screened. To our delight, the desired cyclopentenone **4aa** was obtained in 44% isolated yield when 20 mol % $AgSbF_6$ was employed (see the Supporting Information). Encouraged by this result, we examined a range of silver salts, including $AgBF_4$, AgOTf, and $AgNTf_2$, but no better results were observed (see the Supporting Information). In subsequent studies, we found that the base has a significant impact on the catalytic reactivity (see the Supporting Information), and Na_2CO_3 was proven to be the best choice to give a 73% yield. Other transition metal catalysts, such as $[IrCp^*Cl_2]_2/AgSbF_6$, $[Ru(p\text{-cymene})Cl_2]_2/AgSbF_6$, and $Cp^*Co(CO)I_2/AgSbF_6$, gave inferior reactivity. Among the solvents tested, dichloroethane (DCE) gave the best outcome. The yield of **4aa** could be improved to 82% when the reaction temperature was increased (see the Supporting Information).

With the optimal reaction conditions identified, we first investigated the scope of α-substituted acrylic acids as revealed in Scheme 3. A range of alkyl groups, such as ethyl, propyl, isopropyl, *n*-butyl, ethylphenyl, cyclopentyl, and cyclohexyl, were well tolerated, generating the multicomponent products smoothly with formaldehyde and dimethyl malonate in moderate yields (Scheme 3, **4a**−**4g**). α-Benzyl acrylic acid took part in this multicomponent reaction well to give the corresponding cyclopentenone in 73% yield (Scheme 3, **4h**). The alkyl group of dialkyl melonates influenced the reaction,

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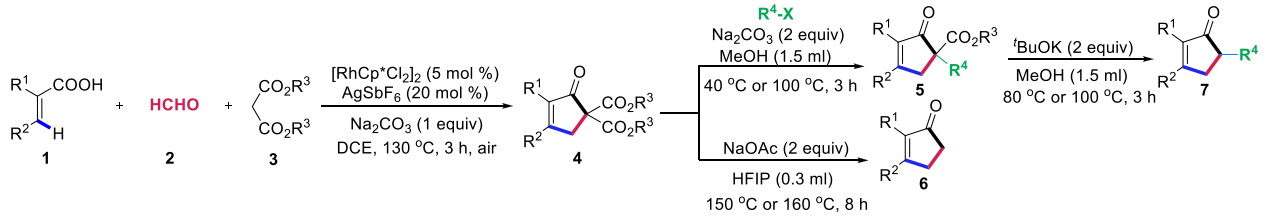
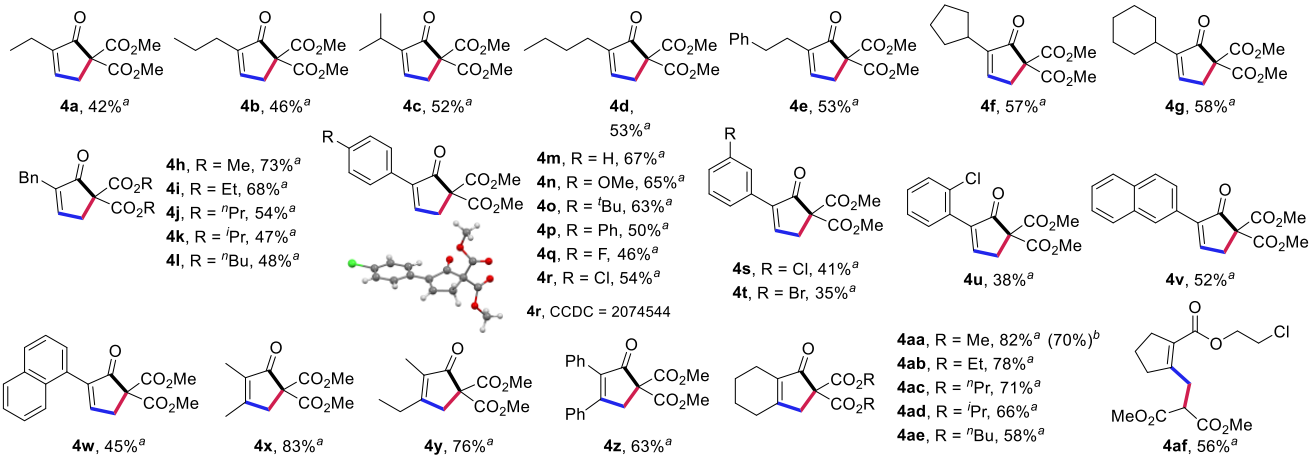
Org. Lett. 2021, 23, 5054−5059

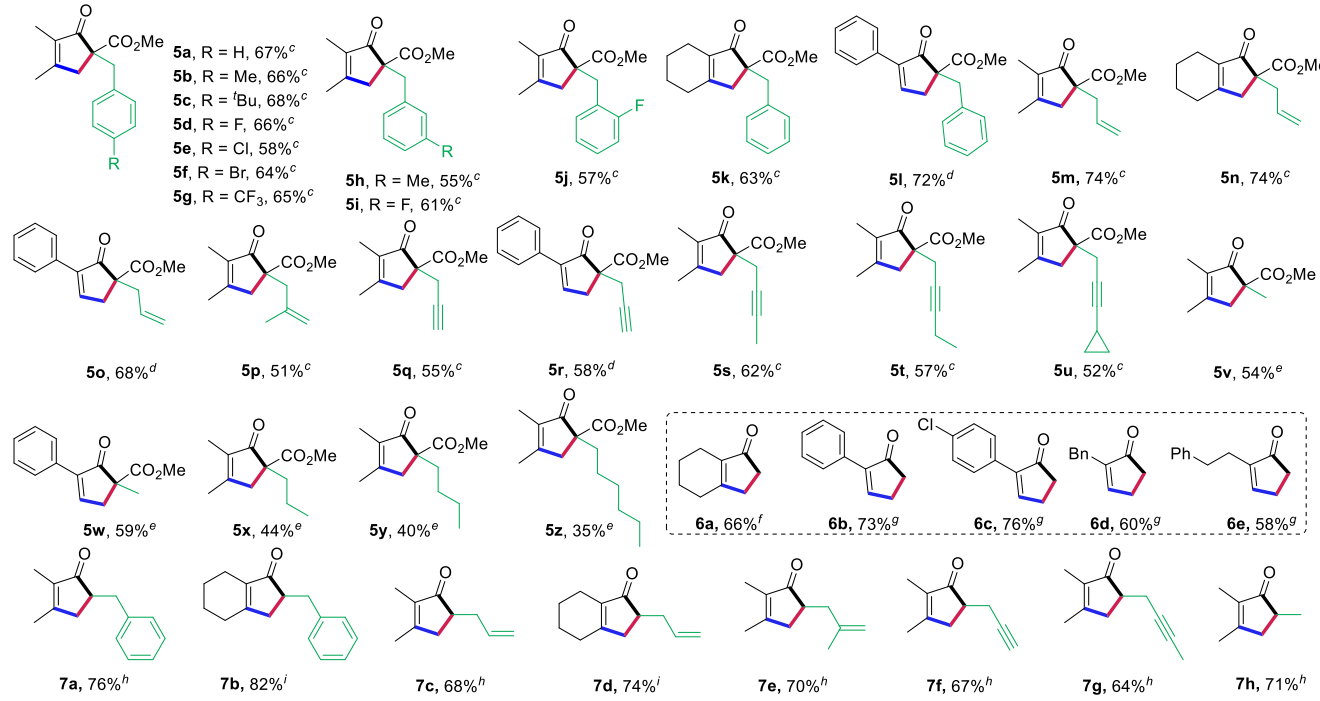
Scheme 3. Synthesis of Cyclopentenones and 5-Alkylated Cyclopentenones[a]



(a) Scope of Polysubstituted Cyclopentenones[a,b]



(b) Variation of the 5-Alkylated Cyclopentenones[c,d,e,f,g,h,i]



[a]Reactions were performed on a 0.2 mmol scale. See the Supporting Information for experimental details. Isolated yields. [b]On a 1 mmol scale. [c]Alkyl bromides (0.4 mmol), **4** (0.2 mmol), and Na_2CO_3 (2 equiv) in MeOH (1.5 mL) at 40 °C for 3 h. [d]Alkyl bromides and **4** at 100 °C. [e]Alkyl iodides and **4** at 100 °C. [f]**4** (0.2 mmol) and NaOAc (2 equiv) in HFIP (0.3 mL) at 160 °C for 8 h. [g]**4** in HFIP at 150 °C. [h]**5** (0.2 mmol) and ^{t}BuOK (2 equiv) in MeOH (1.5 mL) at 80 °C for 3 h. [i]**5** in MeOH at 100 °C.

and larger alkyl groups gave lower yields (Scheme 3, **4i**−**4l**). Acrylic acids of α-aromatic substitution with different substitution patterns on the aryl ring were converted successfully to the desired cyclopentenone products (**4m**−**4w**). Aryl substitution with electron-donating groups (Scheme 3, **4m**−**4p**) presented reactivities higher than that with withdrawing groups to give the cyclopentenones in higher yields (Scheme 3, **4q** and **4r**). *meta*- and *ortho* substitution in the aryl ring delivered lower yields, which might be attributed to the steric effect (Scheme 3, **4s**−**4u**). α-Naphthyl-substituted acrylic acids were amenable to participation in this multicomponent reaction to give the corresponding cyclopente-

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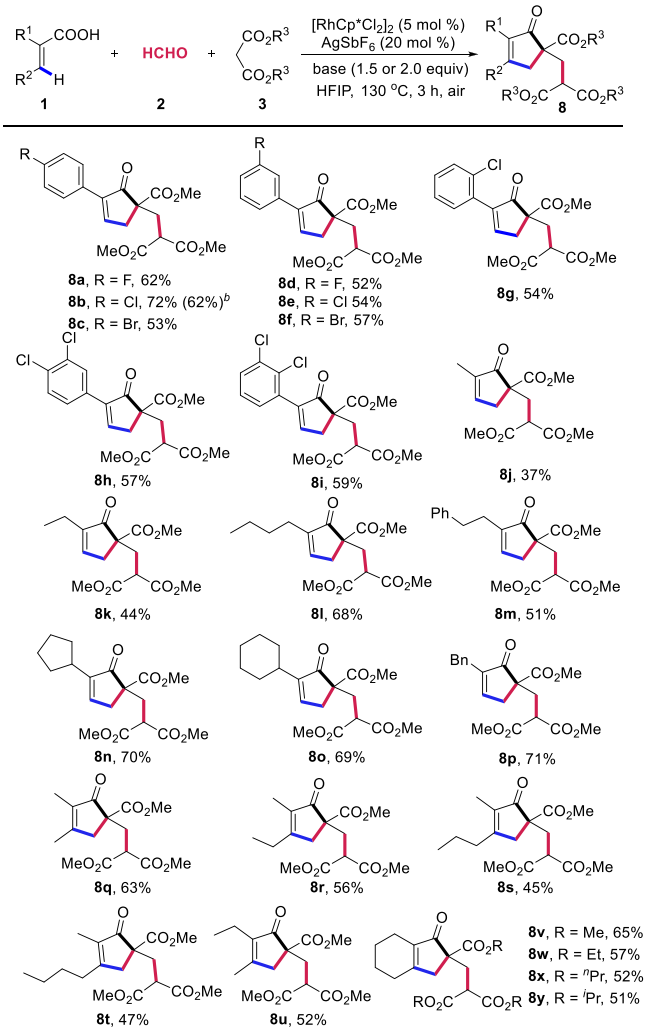
nones in moderate yields (**4v** and **4w**). α,β-Disubstituted acrylic acids, typically more reactive compared to their *mono*-α-substituted counterparts, were found to successfully engage in this transformation to provide the corresponding cyclopentenones (Scheme 3, **4x**–**4z**). Cyclopentene-1-carboxylic acid failed to produce the desired cyclopentenone but delivered the alkylated product, presumably due to the high ring strain (Scheme 3, **4af**).[19] In contrast, cyclohexene-1-carboxylic acid was active to generate hexahydro-1*H*-inden-1-one products with different malonates (Scheme 3, **4aa**–**4ae**). Cinnamic acid is inactive under reaction conditions, and the experiment with other aromatic or aliphatic aldehydes failed. This transformation could be carried out on a larger scale (1 mmol) to give **4aa** in 70% yield. The structure of cyclopentenone **4r** was explicitly characterized by single-crystal X-ray diffraction.

5-Substituted cyclopentenones are key prevalent motifs of natural products and biologically active drugs. In general, the 5-alkylation of cyclopentenones can be achieved only by using a kinetic base such as LDA. During our studies, we detected the formation of trace 5-monoester-substituted cyclopentenones, which should be produced from a cyclopentenone **4**.

We envisioned that the subsequent alkylation of 5-monoester-substituted cyclopentenones might drive the reaction to formation of a 5-alkylated product. To our delight, 5-alkylated cyclopentenones were successfully obtained directly when a variety of alkyl halides were treated with 5,5-diester cyclopentenone **4** with 1 equiv of Na_2CO_3 in MeOH (Scheme 3, **5a**–**5z**). Benzyl bromides were active in reacting with as-prepared 5,5-diester cyclopentenones smoothly to give the diverse 5-benzyl-substituted cyclopentanones (Scheme 3, **5a**–**5l**). Benzyl bromides with both electron-donating and -withdrawing groups in the aryl ring carried out the reaction fast, and the steric hindrance had little effect on the alkylation. Allylic and propargyl bromides showed equal reactivity (Scheme 3, **5m**–**5u**). Alkyl bromides showed poor reactivity. However, a variety of alkyl iodides were compatible with the method to give the 5-alkylated cyclopentenones in moderate yields (Scheme 3, **5v**–**5z**). The ester group in cyclopentenone **4** and cyclopentenone **5** could be easily removed by decarboxylation (Scheme 3, **6a**–**6e** and **7a**–**7h**).

On the basis of this efficient three-component cyclization, the reaction to the multicomponent reaction was extended by the addition of excess formaldehyde and malonates to afford 5-alkylated cyclopentenones as shown in Scheme 4. With the optimal reaction conditions, cyclopentenone **8v** was isolated in 65% yield using NaOAc as a base in hexafluoroisopropanol (HFIP) (Scheme 4, **8v**). This reaction exhibited a broad substrate scope. α-Aryl-substituted acrylic acids participated in the reaction very well to give the desired cyclopentenones smoothly (Scheme 4, **8a**–**8i**). Electronic and steric effects of the aryl ring almost did not influence the reaction, and fluoro, chloro, and bromo groups were tolerated. A range of α-alkyl-substituted acrylic acids, including methyl, ethyl, butyl, phenylethyl, cyclopentyl, cyclohexyl, and benzyl, were compatible, producing the expected 5-alkylated cyclopentenones in good yields (Scheme 4, **8j**–**8p**). α,β-Disubstituted acrylic acids presented good reactivity, furnishing the polysubstituted cyclopentenones fast (Scheme 4, **8q**–**8u**). Cyclohexene-1-carboxylic acid reacted well with various malonates to afford hexahydro-1*H*-inden-1-one products (Scheme 4, **8v**–**8y**).

Scheme 4. Synthesis of 5-Alkyated Cyclopentenones[a]



[a]Reactions were performed on a 0.2 mmol scale. See the Supporting Information for experimental details. Isolated yields. [b]On a 1 mmol scale.

To elucidate the pathway of this multicomponent reaction, several control experiments were conducted (see the Supporting Information for experimental details).

In conclusion, a novel protocol for the rapid synthesis of cyclopentenones from a Rh-catalyzed three-component cyclization involving vinylic C–H cleavage has been developed. The readily available starting materials (acrylic acids, formaldehyde, and malonates) are precisely assembled in order to afford the cyclopentenones in one reaction vessel. It should be emphasized that the carboxyl directing group subsequently participates in the reaction, supplying one carbon to cyclopentenone products. A variety of 5-alkylated cyclopentenones were smoothly obtained by the exposure of a mixture of as-prepared cyclopentenones to various alkyl halides in a Na_2CO_3/MeOH solution. A multicomponent reaction occurred after the modification of the reaction conditions to give the multisubstituted cyclopentenones in one pot with excessive formaldehyde and malonates. This protocol provides a highly efficient synthesis of cyclopentenones from abundant starting materials without the use of toxic carbon monoxide and therefore complements the existing synthetic methods. Addi-

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tional work on the multicomponent reaction involving vinylic C−H cleavage is currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01569.

General experimental procedures, characterization data, NMR spectra, details of the mechanistic investigation, and crystallographic data for compound **4r** (PDF)

Accession Codes

CCDC 2074544 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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