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# A *n*BuLi-Mediated, Expeditious and Stereoselective Ring-Opening Rearrangement of (Arylmethylene)cyclopropane-1,1-dicarboxylates

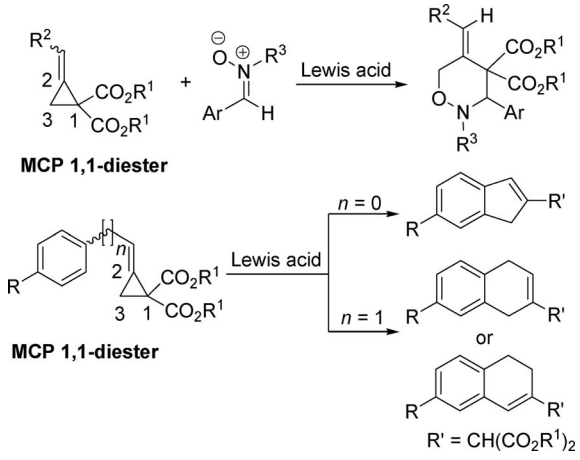
**Bao Hu,[a] Linan Jiang,[a] Jun Ren,[a] and Zhongwen Wang*[a]**

**Keywords:** Small ring systems / Strained molecules / Rearrangement / Ring opening / 1,3-Dienes / Methylenecyclopropane

We report herein an *n*BuLi-mediated, expeditious, ring-opening rearrangement of (arylmethylene)cyclopropane 1,1-diesters to prepare 1,3-diene derivatives with good stereoselectivity. The reaction mechanism has also been discussed.

## Introduction

Methylenecyclopropanes (MCPs), a group of highly strained molecules, have received much attention due to their ready availability[1] and good reactivity.[2] Recently, we reported a hetero [3+3] cycloaddition[3a] and a tandem ring-opening/intramolecular Friedel–Crafts reaction of MCP 1,1-diesters under the catalysis of Lewis acids (Scheme 1).[3b] It has been shown that being further activated by two geminal ester groups on the $sp^3$-hybridized carbon of the strained three-membered carbocycle, activated MCPs displayed different chemistry from that of non-activated MCPs. In order to continue our investigations, we needed C3-functionalized analogues of MCP 1,1-diesters.




Scheme 1. Hetero [3+3] cycloaddition and tandem ring-opening/intramolecular Friedel–Crafts reaction of MCP 1,1-diesters.

[a] State Key Laboratory of Elemento-Organic Chemistry, Institute of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P. R. China
E-mail: wzwrj@nankai.edu.cn

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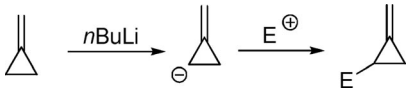
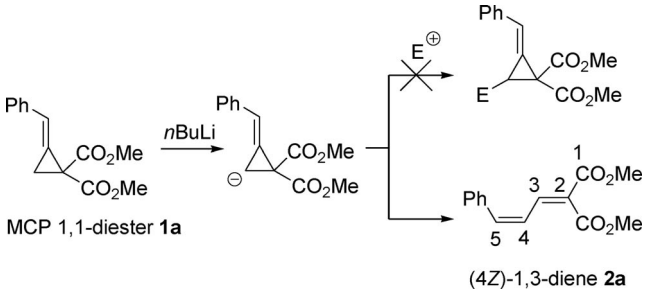
The most commonly used methods for functionalization of MCPs at C-3 are reactions of MCPs and various electrophiles with *n*BuLi as the base (Scheme 2).[4]




Scheme 2. Functionalization of the $sp^3$-hybridized MCP carbon atom by carbolithiation.

When we applied this method on phenyl MCP 1,1-diester **1a**, instead of the anticipated C3-functionalized product, we observed a ring-opening rearrangement leading to 1,3-diene **2a** (Scheme 3). In this paper, we wish to report our recent results.




Scheme 3. Ring-opening rearrangement of phenyl MCP 1,1-diester **1a** leading to 1,3-diene **2a**.

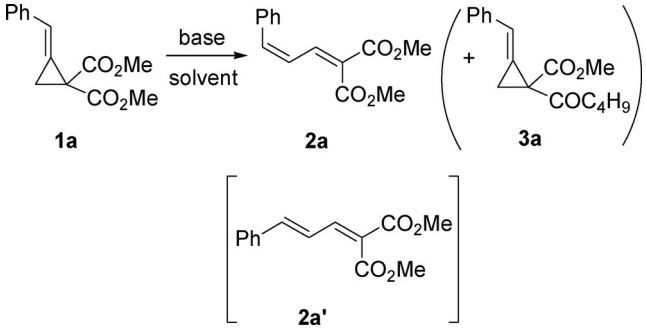
## Results and Discussion

Initially, we treated a solution of MCP **1a** in THF with *n*BuLi (0.5 equiv.) at –90 °C, and obtained the ring-opening product **2a** in 22% yield together with nucleophilic substitution product **3a** (12% yield, Table 1, Entry 1). We note that the stereoselectivity of the ring-opening rearrangement was excellent, and (4*Z*)-1,3-diene isomer **2a** formed exclusively. We established the structure of **2a** by $^1H$ and $^{13}C$ NMR

spectroscopy and HRMS. We prepared (4*E*)-1,3-diene isomer **2a′** by the reported method[5] for further confirmation of the structure of **2a**. We then optimized the reaction conditions. The results in Table 1 show that the reaction proceeded rapidly to afford **2a** in 69% yield after being treated with 1.5 equiv. of 1.72 M *n*BuLi (Table 1, Entry 8). We further improved the yield to 72% when we used 2.1 M *n*BuLi (Table 1, Entry 9). We note that the concentration of the reaction had a dramatic effect on the yield of **2a** (Table 1, Entries 8, 11 and 12). When we submitted a 0.06 M solution of **1a** to identical conditions, we only obtained product **2a** in 22% yield together with **3a** (18%) and small amounts of several other unidentified side products (Table 1, Entry 11), which probably resulted from the increased ratio of contaminants in solvent to the reactants. A higher concentration of **1a** slightly decreased the yield of **2a** (59%, Table 1, Entry 12). Subsequently, we examined the effect of various strong bases (Table 1, Entries 2, 3 and 17–20) and found that, except lithium diisopropylamide (LDA, Table 1, Entry 19), other bases such as *t*BuOK, NaH, *s*BuLi, *t*BuLi and LiHMDS were ineffective. Further investigation indicated that other solvents gave inferior yields (Table 1, Entries 15 and 16). We conducted the reaction in hexane at room temperature due to the poor solubility of MCP **1a** in hexane below 25 °C (Table 1, Entry 16). Finally, we selected THF for further investigation.

With the optimized reaction conditions in hand, we next probed the scope of the ring-opening rearrangement using a variety of MCP 1,1-diesters (Table 2). All of the MCP 1,1-diesters were (*E*) isomers except **1c**, **1l** and **1m**. We observed no obvious relationship between the (*E*/*Z*) ratios of the starting material and the product (Table 2, Entry 3). The reactions of halogenated, phenyl-substituted MCP 1,1-diesters (Table 2, Entries 2–6) afforded **2** in moderate yields. The reaction of *p*-tolyl-substituted MCP 1,1-diester (Table 2, Entry 7) also succeeded; however, *p*-MeO-phenyl-substituted MCP 1,1-diester **1h** (Table 2, Entry 8) gave a complex result. We hypothesize that the reactivity was related to the regioselectivity of carbolithiation (Scheme 5). We note that the halogen-lithium exchange occurred in the reaction of MCP **1b** (13%, Table 2, Entry 2).[6] In all successful cases, the (4*Z*) selectivities for the formation of 1,3-

Table 1. Optimization of conditions for the ring-opening rearrangement of MCP 1,1-diester **1a**.[a]

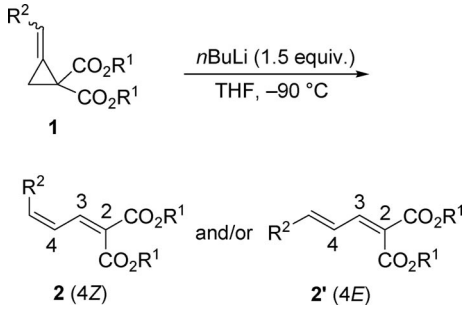



| Entry | Base | Solvent | *T* [°C] | Time [h] | Conversion [%][b] | Yield of **2a** [%][c,m] |
|---|---|---|---|---|---|---|
| 1 | *n*BuLi (0.5 equiv.) | THF | –90 | 1 | 61 | 22 |
| 2 | *t*BuOK (1.4 equiv.) | THF | 66 | 26 | 10 | 0 |
| 3 | NaH (1.0 equiv.) | THF | 66 | 2 | 0 | NR[d] |
| 4 | *n*BuLi (0.3 equiv.) | THF | –90 | 0.05 | 29 | 16 |
| 5 | *n*BuLi (0.8 equiv.) | THF | –90 | 0.25 | 100 | 28 |
| 6 | *n*BuLi (1.0 equiv.) | THF | –90 | 0.05 | 100 | 27 |
| 7 | *n*BuLi (1.2 equiv.) | THF | –90 | 0.05 | 100 | 36 |
| 8 | *n*BuLi (1.5 equiv.) | THF | –90 | 0.05 | 100 | 69 |
| 9[e] | *n*BuLi (1.5 equiv.) | THF | –90 | 0.05 | 100 | 72 |
| 10 | *n*BuLi (1.8 equiv.) | THF | –90 | 0.05 | 100 | 63 |
| 11[f] | *n*BuLi (1.5 equiv.) | THF | –90 | 0.05 | 100 | 22 |
| 12[g] | *n*BuLi (1.5 equiv.) | THF | –90 | 0.05 | 100 | 59 |
| 13[h] | *n*BuLi (1.5 equiv.) | THF | –90 | 0.05 | 100 | 68 |
| 14[i] | *n*BuLi (1.5 equiv.) | THF | –90 | 0.05 | 100 | 27 |
| 15 | *n*BuLi (1.5 equiv.) | $Et_2O$ | –90 | 0.25 | 100 | 24 |
| 16 | *n*BuLi (1.5 equiv.) | hexane | room temp. | 0.05 | 100 | trace |
| 17[j] | *s*BuLi (1.5 equiv.) | THF | –90 to room temp. | 12 | 84 | <10 |
| 18[k] | *t*BuLi (1.5 equiv.) | THF | –90 | 0.05 | 24 | 9 |
| 19[h] | LDA (1.5 equiv.) | THF | –90 | 0.10 | 100 | 61 |
| 20[l] | LiHMDS (1.5 equiv.) | THF | 0 | 4 | 30 | 0 |

[a] Reaction conditions: **1a** (0.10 M solution in the indicated solvent, 0.50 mmol) was added to *n*BuLi (1.72 M in hexane) in 2.0 mL of the same solvent over 15 min under a $N_2$ atmosphere. [b] Determined by $^1H$ NMR after purification. [c] Isolated yield. [d] No reaction occurred. [e] *n*BuLi (2.10 M in hexane). [f] 0.06 M solution of **1a** in THF. [g] 0.25 M solution of **1a** in THF. [h] **1a** was added to the indicated base. [i] 100 mg of molecular sieves (3 Å) were added. [j] *s*BuLi (1.3 M in hexane). [k] *t*BuLi (1.7 M in pentane). [l] LiHMDS (1.0 M in hexane). [m] When *n*BuLi was used as the base, **3a** was also observed as a byproduct in most cases.

Table 2. *n*BuLi-mediated, ring-opening rearrangement of MCP 1,1-diesters **1**.[a]

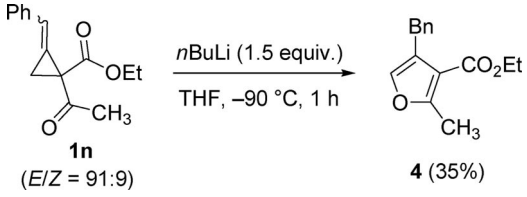



| Entry | MCP **1** | $R^1$ | $R^2$ | (*E*/*Z*) ratio of **1**[c] | Product **2** | Yield [%][b] | (*Z*/*E*) ratio of **2**[c] |
|---|---|---|---|---|---|---|---|
| 1 | **1a** | Me | $C_6H_5$ | 100:0 | **2a** | 72 | >20:1 |
| 2[d,e] | **1b** | Me | 4-Br$C_6H_4$ | 100:0 | **2b** | 44 | >20:1 |
| 3[d] | **1c** | Me | 2-Br$C_6H_4$ | 65:35 | **2c/2c′** | 35[f] | 77:23 |
| 4[d] | **1d** | Me | 4-Cl$C_6H_4$ | 100:0 | **2d** | 58 | >20:1 |
| 5[d] | **1e** | Me | 3-Cl$C_6H_4$ | 100:0 | **2e/2e′** | 44[f] | 81:19 |
| 6[d] | **1f** | Me | 4-F$C_6H_4$ | 100:0 | **2f** | 59[f] | 93:7 |
| 7 | **1g** | Me | 4-Me$C_6H_4$ | 100:0 | **2g/2g′** | 46[f] | 88:12 |
| 8 | **1h** | Me | 4-MeO$C_6H_4$ | 100:0 | **2h** | complex | – |
| 9 | **1i** | Et | $C_6H_5$ | 100:0 | **2i/2i′** | 29[f] | 87:13 |
| 10 | **1j** | *i*Pr | $C_6H_5$ | 100:0 | **2j** | 60[f] | 88:12 |
| 11 | **1k** | Bn | $C_6H_5$ | 100:0 | **2k** | 53 | >20:1 |
| 12 | **1l** | Me | Bn | 67:33 | **2l** | <5 | – |
| 13 | **1m** | Me | *n*-$C_7H_{15}$ | 70:30 | **2m** | 0 | – |

[a] Reaction conditions: **1a** (0.10 M solution in THF, 0.50 mmol) was added to *n*BuLi (2.10 M in hexane) in 2.0 mL of THF under a $N_2$ atmosphere. [b] Isolated yield after silica gel chromatography. [c] The (*E*/*Z*) [or (*Z*/*E*)] ratio was determined on the basis of the $^1$H NMR spectroscopic data. [d] 0.30 mmol scale. [e] **2a** was also obtained in 13% yield. [f] The total yield is given for a mixture of two diastereomers.

dienes were good to excellent [(*Z*/*E*) = 77:23 to >20:1]. The reactions of alkyl-substituted MCP 1,1-diesters **1l** and **1m** failed (Table 2, Entries 12 and 13).

In contrast to the MCP 1,1-diesters, when we treated MCP 1,1-keto ester **1n** with *n*BuLi for 1 h under the above conditions, instead of the rearrangement process, a ring-opening cycloisomerization happened, from which we obtained furan **4** in 35% yield (Scheme 4).



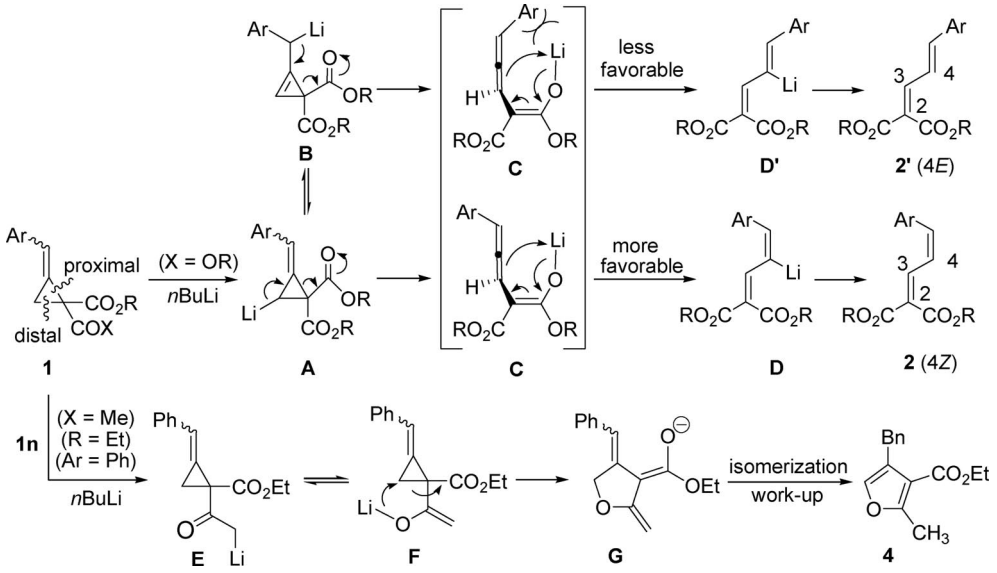

Scheme 4. *n*BuLi-promoted, ring-opening/cycloisomerization of MCP 1,1-keto ester **1n**.

A plausible mechanism for the formation of 1,3-diene **2**, **2′** and furan **4** is illustrated in Scheme 5. Initially, cyclopropyl carbanion **A** was generated upon deprotonation of MCP **1** with *n*BuLi. Due to the electron-withdrawing activation of the two germinal ester groups, proximal bond cleavage of the three-membered ring via an allylic anion (**A** or **B**) afforded allenoate anion **C**. Shi and coworkers reported a similar result on vinylidenecyclopropane.[7] A 1,5-shift of lithium afforded a vinyl anion existing as (*Z*)-**D** or (*E*)-**D′**. The selective formation of (4*Z*) isomer **2** could be explained by the more favorable electrophilic attack of lithium from the direction of less steric hindrance. This stereochemistry is also well in accordance with the results from allenes reported by Xu and coworkers[8a] and Ma and coworkers.[8b] Attempts to trap the anionic intermediates (**A**, **B**, **C**, **D** or **D′**) with aldehydes[9a] or deuterated reagents (DCl, $CF_3CO_2D$ or $D_2O$)[9b] failed, probably due to the rapidity of the reaction,[9b] to afford the active vinyl anion, which was then protonated either by the intermolecular shift of the allylic hydrogen in MCP **1** or by other proton sources in the reaction mixture (e.g. contaminants in the solvent and reagent) prior to the addition of the electrophiles. At present, we do not have enough experimental evidence to prove if the reaction proceeds in a catalytic manner or not. The treatment of MCP 1,1-keto ester **1n** with *n*BuLi afforded enolate **F**, which then cycloisomerized to intermediate **G**. We obtained furan **4** after isomerization and protonation. A similar process promoted by $PdCl_2$/NaI was reported by Ma and coworkers.[10] Further investigations on the mechanism are still needed.

## Conclusions

In conclusion, we have disclosed an *n*BuLi-mediated, expeditious and stereoselective reaction of aryl-MCP 1,1-diesters. This provides a protocol for the synthesis of 1,3-dienes, although the yields are moderate.




Scheme 5. A plausible mechanism for the formation of 1,3-dienes **2** and **2′** and furan **4**.

## Experimental Section

**General Remarks:** MCPs **1** were prepared according to the literature procedure.[3,11] All NMR spectra were recorded with a spectrometer at 400 MHz ($^1$H NMR) and 100 MHz ($^{13}$C NMR) in $CDCl_3$. The chemical shifts are reported in ppm referenced to $CDCl_3$ ($\delta$ = 7.26 ppm) for $^1$H NMR and relative to the central $CDCl_3$ resonance ($\delta$ = 77.0 ppm) for $^{13}$C NMR spectroscopy. Column chromatography was performed on silica gel (100–200 or 200–300 mesh) using petroleum ether and EtOAc as eluent. Thin layer chromatography (TLC) was performed on Merck silica gel GF254 plates and visualized by UV light (254 nm). Melting points were uncorrected. All solvents were purified and dried using standard procedures.

**A Typical Experimental Procedure for the Formation of (4*Z*)-1,3-Diene (2a):** Under a $N_2$ atmosphere, to MCP **1a** (123 mg, 0.50 mmol) in THF (5.0 mL) was slowly added *n*BuLi (0.36 mL, 0.75 mmol, 2.1 M in hexane) in THF (2.0 mL) at –90 °C over approximately 15 min, and the mixture was stirred at the same temperature for a further 3 min. The reaction was then quenched by the addition of aqueous ammonium chloride and warmed to room temperature. The solution was extracted with $Et_2O$ (3 × 10 mL), and the combined organic layers were washed with water and dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (EtOAc/petroleum ether, 1:20) to give **2a** [89 mg, 72% yield, single (*Z*) isomer] as a yellow liquid. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.83 (d, *J* = 12.0 Hz, 1 H, PhCH=CHC*H*), 7.45–7.28 (m, 5 H, Ar), 7.03 (d, *J* = 11.2 Hz, 1 H, PhC*H*=CH), 6.65 (t, *J* = 12.0 Hz, 1 H, PhCH=C*H*CH), 3.89 (s, 3 H, $OCH_3$), 3.79 (s, 3 H, $OCH_3$) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 165.8, 165.0, 141.9, 140.8, 135.7, 129.6, 128.8, 128.6, 126.6, 124.0, 52.5, 52.4 ppm. IR (thin film): $\tilde{\nu}$ = 2953, 1720, 1618, 1436, 1251, 1220, 1104, 1057 cm$^{-1}$. HRMS (ESI): calcd. for $C_{14}H_{14}O_4Na$ [M + Na]$^+$ 269.0784; found 269.0791.

**Dimethyl 2-(2-Bromobenzylidene)cyclopropane-1,1-dicarboxylate (1c):** Yield 1.97 g, 40%, a mixture of stereoisomers, (*E*/*Z*) = 65:35, pale yellow solid, m.p. 58–60 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.76–7.66 (m, 1 H, Ar), 7.59–7.53 (m, 1 H, Ar), 7.38–7.33 (m, 0.62 H, Ar), 7.31–7.27 (m, 1.38 H, Ar), 7.15–7.09 (m, 1 H, ArC*H*=C), 3.77 (s, 3.89 H, $OCH_3$), 3.73 (s, 2.11 H $OCH_3$), 2.51 (d, *J* = 2.8 Hz, 1.30 H, C$H_2$, cyclopropane), 2.29 (t, *J* = 2.8 Hz, 0.70 H, C$H_2$, cyclopropane) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 168.0, 167.6, 134.9, 134.2, 133.2, 133.0, 129.5, 127.9, 127.8, 127.7, 127.4, 125.0, 124.2, 123.9, 119.1, 119.0, 53.0, 41.1, 32.7, 31.2, 19.1, 16.7 ppm. IR (KBr): $\tilde{\nu}$ = 2953, 2927, 1732, 1436, 1310, 1282, 1257, 1107, 1024, 756 cm$^{-1}$. HRMS (ESI): calcd. for $C_{14}H_{13}BrO_4Na$ [M + Na]$^+$ 346.9889; found 346.9889.

**(*E*)-Dimethyl 2-(3-Chlorobenzylidene)cyclopropane-1,1-dicarboxylate (1e):** Yield 2.69 g, 48%, a single (*E*) isomer, pale yellow solid, m.p. 43–45 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.49 (s, 1 H, Ar), 7.36 (d, *J* = 7.2 Hz, 1 H, Ar), 7.32–7.23 (m, 2 H, Ar), 6.88 (t, *J* = 2.4 Hz, 1 H, ArC*H*=C), 3.76 (s, 6 H, 2 $OCH_3$), 2.51 (d, *J* = 2.4 Hz, 2 H, C$H_2$, cyclopropane) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 167.9, 137.4, 134.6, 129.9, 128.1, 127.1, 125.7, 124.0, 119.1, 52.9, 30.1, 19.2 ppm. IR (KBr): $\tilde{\nu}$ = 3062, 3003, 2954, 2846, 1735, 1435, 1311, 1265, 1107, 888, 786, 683 cm$^{-1}$. HRMS (ESI): calcd. for $C_{14}H_{13}ClO_4Na$ [M + Na]$^+$ 303.0395; found 303.0394.

**(*E*)-Dibenzyl 2-Benzylidenecyclopropane-1,1-dicarboxylate (1k):** Yield 2.07 g, 26%, a single (*E*) isomer, yellow liquid. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.53 (d, *J* = 7.0 Hz, 2 H, Ar), 7.36–7.32 (m, 13 H, Ar), 6.99 (t, *J* = 2.4 Hz, 1 H, PhC*H*=C), 5.22 (s, 2 H, OC$H_2$Ph), 5.21 (s, 2 H, OC$H_2$Ph), 2.57 (d, *J* = 2.4 Hz, 2 H, C$H_2$, cyclopropane) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 167.6, 135.5, 128.7, 128.5, 128.4, 128.3, 128.0, 127.5, 126.2, 122.5, 120.6, 67.4, 30.5, 19.4 ppm. IR (thin film): $\tilde{\nu}$ = 3064, 3033, 2956, 1732, 1455, 1294, 1266, 1101, 750, 696 cm$^{-1}$. HRMS (ESI): calcd. for $C_{26}H_{22}O_4Na$ [M + Na]$^+$ 421.1410; found 421.1416.

**(*E*)-Dimethyl 2-(3-Phenylallylidene)malonate (2a′):**[5,12] Yield 1.28 g, 52%, yellow solid, m.p. 63–64 (lit. 66–68 °C). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.57 (d, *J* = 11.6 Hz, 1 H, PhCH=CHC*H*), 7.54–7.47 (m, 2 H, Ar), 7.42–7.32 (m, 3 H, Ar), 7.27 (dd, *J* = 11.6, 15.2 Hz, 1 H, PhCH=C*H*CH), 7.06 (d, *J* = 15.2 Hz, 1 H, PhC*H*=CH), 3.09 (s, 3 H, $OCH_3$), 3.82 (s, 3 H, $OCH_3$) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 165.7, 165.2, 146.2, 145.2, 135.5, 130.0, 128.9, 127.9, 124.0, 123.3, 52.4, 52.4 ppm. IR (KBr): $\tilde{\nu}$ = 2951, 1716, 1613, 1435, 1309, 1284, 1242, 1213, 1151, 1063, 752 cm$^{-1}$. HRMS (ESI): calcd. for $C_{14}H_{14}O_4Na$ [M + Na]$^+$ 269.0784; found 269.0788.

**(*Z*)-Dimethyl 2-[3-(4-Bromophenyl)allylidene]malonate (2b):** Yield 44 mg, 44%, colorless oil. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.72 (d, $J$ = 12.0 Hz, 1 H, PhCH=CHC*H*), 7.53 (d, $J$ = 8.4 Hz, 2 H, Ar), 7.18 (d, $J$ = 8.4 Hz, 2 H, Ar), 6.93 (d, $J$ = 11.2 Hz, 1 H, PhC*H*=CH), 6.66 (t, $J$ = 11.6 Hz, 1 H, PhCH=C*H*CH), 3.88 (s, 3 H, $OCH_3$), 3.79 (s, 3 H, $OCH_3$) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 165.6, 164.9, 140.3, 140.1, 134.5, 131.9, 131.0, 127.1, 124.6, 123.1, 52.6, 52.5 ppm. IR (thin film): $\tilde{\nu}$ = 2953, 1731, 1619, 1436, 1255, 1221, 1072, 1056 cm$^{-1}$. HRMS (ESI): calcd. for $C_{14}H_{13}BrO_4Na$ [M + Na]$^+$ 346.9889; Found: 346.9896.

**Dimethyl 2-[3-(2-Bromophenyl)allylidene]malonate (2c, 2c′):** Yield 34 mg, 35%, yellow liquid, a mixture of isomers [(*Z*/*E*) = 77:23]; data for the major isomer: $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.83 (dd, $J$ = 12.0, 0.8 Hz, 1 H, PhCH=CHC*H*), 7.41–7.30 (m, 4 H, Ar), 7.03 (d, $J$ = 10.8 Hz, 1 H, PhC*H*=CH), 6.65 (t, $J$ = 12.0 Hz, 1 H, PhCH=C*H*CH), 3.89 (s, 3 H, $OCH_3$), 3.79 (s, 3 H, $OCH_3$) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 165.8, 165.0, 141.9, 140.8, 135.7, 129.6, 128.9, 128.8, 128.6, 127.9, 124.0, 52.5, 52.4 ppm. IR (thin film): $\tilde{\nu}$ = 2953, 1720, 1618, 1436, 1251, 1221, 1058 cm$^{-1}$. HRMS (ESI): calcd. for $C_{14}H_{13}BrO_4Na$ [M + Na]$^+$ 346.9889; found 346.9886.

**(*Z*)-Dimethyl 2-[3-(4-Chlorophenyl)allylidene]malonate (2d):** Yield 49 mg, 58%, yellow liquid. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.73 (d, $J$ = 12.0 Hz, 1 H, PhCH=CHC*H*), 7.37 (d, $J$ = 8.4 Hz, 2 H, Ar), 7.24 (d, $J$ = 8.4 Hz, 2 H, Ar), 6.95 (d, $J$ = 11.6 Hz, 1 H, PhC*H*=CH), 6.65 (t, $J$ = 11.6 Hz, 1 H, PhCH=C*H*CH), 3.88 (s, 3 H, $OCH_3$), 3.79 (s, 3 H, $OCH_3$) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 165.6, 164.9, 140.3, 140.1, 134.8, 134.1, 130.8, 128.9, 127.1, 124.5, 52.5, 52.5 ppm. IR (thin film): $\tilde{\nu}$ = 2953, 1720, 1619, 1437, 1254, 1220, 1091, 1055 cm$^{-1}$. HRMS (ESI): calcd. for $C_{14}H_{13}ClO_4Na$ [M + Na]$^+$ 303.0395; found 303.0303.

**Dimethyl 2-[3-(3-Chlorophenyl)allylidene]malonate (2e, 2e′):** Yield 37 mg, 44%, yellow liquid, a mixture of isomers [(*Z*/*E*) = 81:19]; data for the major isomer: $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.73 (d, $J$ = 12.4 Hz, 1 H, PhCH=CHC*H*), 7.35–7.28 (m, 3 H, Ar), 7.22–7.16 (m, 1 H, Ar), 6.94 (d, $J$ = 11.2 Hz, 1 H, PhC*H*=CH), 6.68 (t, $J$ = 11.6 Hz, 1 H, PhCH=C*H*CH), 3.89 (s, 3 H, $OCH_3$), 3.80 (s, 3 H, $OCH_3$) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 165.6, 164.8, 139.9, 139.8, 137.3, 134.6, 129.9, 129.3, 128.8, 127.6, 125.1, 52.6, 52.5 ppm. IR (thin film): $\tilde{\nu}$ = 2953, 1724, 1620, 1436, 1253, 1221, 1057 cm$^{-1}$. HRMS (ESI): calcd. for $C_{14}H_{13}ClO_4Na$ [M + Na]$^+$ 303.0395; found 303.0395.

**(*Z*)-Dimethyl 2-[3-(4-Fluorophenyl)allylidene]malonate (2f):** Yield 53 mg, 59%, yellow liquid. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.75 (d, $J$ = 12.0 Hz, 1 H, PhCH=CHC*H*), 7.35–7.23 (m, 2 H, Ar), 7.08 (t, $J$ = 8.4 Hz, 2 H, Ar), 6.96 (d, $J$ = 11.2 Hz, 1 H, PhC*H*=CH), 6.63 (t, $J$ = 11.6 Hz, 1 H, PhCH=C*H*CH), 3.88 (s, 3 H, $OCH_3$), 3.78 (s, 3 H, $OCH_3$) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 165.7, 164.9, 164.2, 161.7, 140.5, 140.3, 131.8, 131.8, 131.4, 131.3, 126.8, 123.9, 115.9, 115.6, 52.5, 52.4 ppm. IR (thin film): $\tilde{\nu}$ = 2955, 1731, 1619, 1594, 1508, 1437, 1251, 1158, 1106, 1058 cm$^{-1}$. HRMS (ESI): calcd. for $C_{14}H_{13}FO_4Na$ [M + Na]$^+$ 287.0690; found 287.0698.

**Dimethyl 2-(3-*p*-Tolylallylidene)malonate (2g, 2g′):** Yield 60 mg, 46%, slightly yellow liquid, a mixture of isomers [(*Z*/*E*) = 88:12]; data for the major isomer: $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.84 (d, $J$ = 12.0 Hz, 1 H, PhCH=CHC*H*), 7.26–7.16 (m, 4 H, Ar), 6.98 (d, $J$ = 11.6 Hz, 1 H, PhC*H*=CH), 6.59 (t, $J$ = 11.6 Hz, 1 H, PhCH=C*H*CH), 3.87 (s, 3 H, $OCH_3$), 3.77 (s, 3 H, $OCH_3$), 2.36 (s, 3 H, Ph$CH_3$) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 165.8, 165.1, 142.0, 141.2, 139.0, 132.9, 129.6, 129.4, 127.9, 126.1, 123.3, 52.4, 52.4, 21.3 ppm. IR (thin film): $\tilde{\nu}$ = 2953, 1720, 1617, 1436, 1251, 1220, 1102, 1057 cm$^{-1}$. HRMS (ESI): calcd. for $C_{15}H_{16}O_4Na$ [M + Na]$^+$ 283.0941; found 283.0947.

**Diethyl 2-(3-Phenylallylidene)malonate (2i, 2i′):** Yield 40 mg, 29%, slightly yellow liquid, a mixture of isomers [(*Z*/*E*) = 87:13]; data for the major isomer: $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.81 (d, $J$ = 12.4 Hz, 1 H, PhCH=CHC*H*), 7.44–7.30 (m, 5 H, Ar), 7.00 (d, $J$ = 11.2 Hz, 1 H, PhC*H*=CH), 6.65 (t, $J$ = 11.6 Hz, 1 H, PhCH=C*H*CH), 4.36 (q, $J$ = 7.2 Hz, 2 H, O$CH_2$$CH_3$), 4.24 (q, $J$ = 7.2 Hz, 2 H, O$CH_2$$CH_3$), 1.36 (t, $J$ = 7.2 Hz, 3 H, $OCH_2CH_3$), 1.28 (t, $J$ = 7.2 Hz, 3 H, $OCH_2CH_3$) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 165.4, 164.6, 141.4, 139.9, 135.7, 129.6, 128.7, 128.6, 127.5, 124.0, 61.4, 61.3, 14.2, 14.1 ppm. IR (thin film): $\tilde{\nu}$ = 2982, 1716, 1619, 1373, 1245, 1152, 1098, 1056, 1024 cm$^{-1}$. HRMS (ESI): calcd. for $C_{16}H_{18}O_4Na$ [M + Na]$^+$ 297.1097; found 297.1103.

**Diisopropyl 2-(3-Phenylallylidene)malonate (2j, 2j′):** Yield 109 mg, 60%, slightly yellow liquid, a mixture of isomers [(*Z*/*E*) = 88:12]; data for the major isomer: $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.75 (d, $J$ = 12.0 Hz, 1 H, PhCH=CHC*H*), 7.38–7.27 (m, 5 H, Ar), 6.95 (d, $J$ = 11.6 Hz, 1 H, PhC*H*=CH), 6.61 (t, $J$ = 11.6 Hz, 1 H, PhCH=C*H*CH), 5.27–5.17 (m, 1 H, $CH_3CHCH_3$), 5.13–5.02 (m, 1 H, $CH_3CHCH_3$), 1.32 (d, $J$ = 6.0 Hz, 6 H, $CH_3CHCH_3$), 1.24 (d, $J$ = 6.4 Hz, 6 H, $CH_3CHCH_3$) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 164.0, 163.1, 139.9, 138.1, 134.7, 128.5, 127.6, 127.5, 122.9, 67.9, 67.8, 20.7 ppm. IR (thin film): $\tilde{\nu}$ = 2981, 1716, 1621, 1374, 1258, 1218, 1182, 1145, 1108, 1045 cm$^{-1}$. HRMS (ESI): calcd. for $C_{18}H_{22}O_4Na$ [M + Na]$^+$ 325.1415; found 325.1410.

**(*Z*)-Dibenzyl 2-(3-Phenylallylidene)malonate (2k):** Yield 91 mg, 53%, yellow liquid, $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.87 (d, $J$ = 12.0 Hz, 1 H, PhCH=CHC*H*), 7.40–7.23 (m, 15 H, Ar), 6.95 (d, $J$ = 11.6 Hz, 1 H, PhC*H*=CH), 6.65 (t, $J$ = 11.6 Hz, 1 H, PhCH=C*H*CH), 5.27 (s, 2 H, O$CH_2$Ph), 5.17 (s, 2 H, O$CH_2$Ph) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 165.1, 164.4, 142.2, 141.6, 135.7, 135.5, 129.7, 128.9, 128.7, 128.6, 128.4, 128.2, 128.0, 126.5, 124.0, 67.3, 67.0 ppm. IR (thin film): $\tilde{\nu}$ = 3064, 3033, 2957, 1716, 1616, 1455, 1236, 1105, 1050, 747, 697 cm$^{-1}$. HRMS (ESI): calcd. for $C_{26}H_{22}O_4Na$ [M + Na]$^+$ 421.1410; found 421.1408.

**(*E*)-Methyl 2-Benzylidene-1-pentanoylcyclopropanecarboxylate (3a):** Yield 16 mg, 12%, colorless liquid. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.50 (d, $J$ = 8.0 Hz, 2 H, Ar), 7.36 (t, $J$ = 7.6 Hz, 2 H, Ar), 7.28 (d, $J$ = 7.6 Hz, 1 H, Ar), 6.84 (s, 1 H, PhC*H*=C), 3.74 (s, 3 H, $OCH_3$), 2.86–2.74 (m, 1 H, $COCH_2CH_2CH_3$), 2.70–2.58 (m, 1 H, $COCH_2CH_2CH_3$), 2.54 (d, $J$ = 9.6 Hz, 1 H, $CH_2$, cyclopropane), 2.45 (d, $J$ = 9.6 Hz, 1 H, $CH_2$, cyclopropane), 1.65–1.56 (m, 2 H, $COCH_2CH_2CH_3$), 1.38–1.28 (m, 2 H, $COCH_2CH_2CH_3$), 0.91 (t, $J$ = 7.2 Hz, 3 H, $COCH_2CH_2CH_3$) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 202.2, 169.5, 135.6, 128.7, 128.2, 127.4, 123.8, 119.3, 52.6, 40.3, 37.4, 26.1, 22.2, 18.5, 13.9 ppm. IR (thin film): $\tilde{\nu}$ = 2957, 2933, 2873, 1728, 1454, 1436, 1290, 1263, 1201, 1129, 1109, 753, 694 cm$^{-1}$. HRMS (ESI): calcd. for $C_{17}H_{20}O_3Na$ [M + Na]$^+$ 295.1310; found 295.1304.

**Ethyl 4-Benzyl-2-methylfuran-3-carboxylate (4):** Yield 28 mg, 35%, yellow liquid. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.31 (t, $J$ = 7.2 Hz, 2 H, Ar), 7.23 (t, $J$ = 7.2 Hz, 3 H, Ar), 6.24 (s, 1 H, C*H*-furan), 4.25 (q, $J$ = 7.2 Hz, 2 H, O$CH_2$$CH_3$), 3.89 (s, 2 H, Ph$CH_2$C), 2.52 (s, 3 H, $CCH_3$), 1.31 (t, $J$ = 7.2 Hz, 3 H, $OCH_2CH_3$) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 164.3, 158.3, 152.4, 137.5, 128.7, 128.6, 126.7, 114.0, 107.0, 60.0, 34.2, 14.4, 13.8 ppm. IR (thin film): $\tilde{\nu}$ = 2980, 2959, 2929, 1716, 1583, 1286, 1217, 1081, 778, 700 cm$^{-1}$. HRMS (ESI): calcd. for $C_{15}H_{16}O_3Na$ [M + Na]$^+$ 267.0992; found 267.0996.

**Supporting Information** (see also the footnote on the first page of this article): Copies of $^1$H NMR and $^{13}$C NMR spectra of all compounds and NOESY of **2a**.

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[9] a) We treated MCP 1,1-diester **1a** with LDA or *n*BuLi in THF at –90 °C, and the reaction was subsequently quenched with *p*-anisaldehyde (or *p*-chlorobenzaldehyde). However, the result was complex, and no desired products were detected; b) MCP **1a** (0.10 M solution in THF, 0.10 mmol) was added to LDA (in 4.0 mL of THF, 0.15 or 0.20 mmol) over 2–3 min at –90 °C, and the reaction was immediately quenched with either DCl, $CF_3CO_2D$ or $D_2O$. However, no deuterated product was detected, and the recovered starting material **1a** was not deuterated either. Similar results were obtained when *n*BuLi was used.
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