

Photo flow protocol for bromoallylation of alkynes and alkenes

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Dedicated to Prof. Samir Z. Zard for his great contribution to organic chemistry

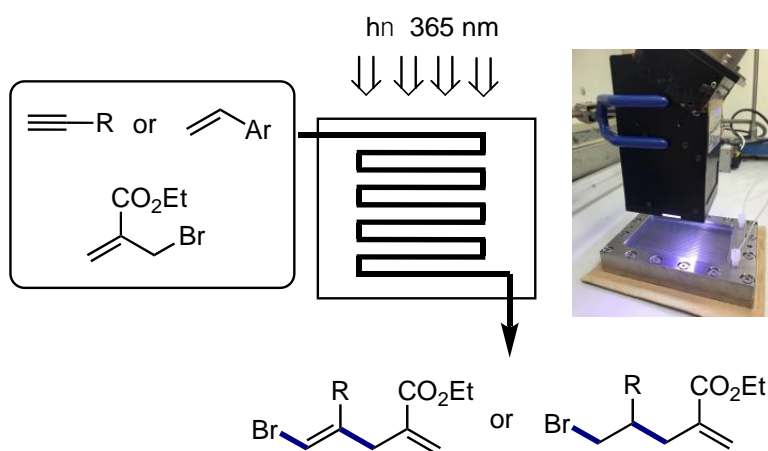
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Abstract

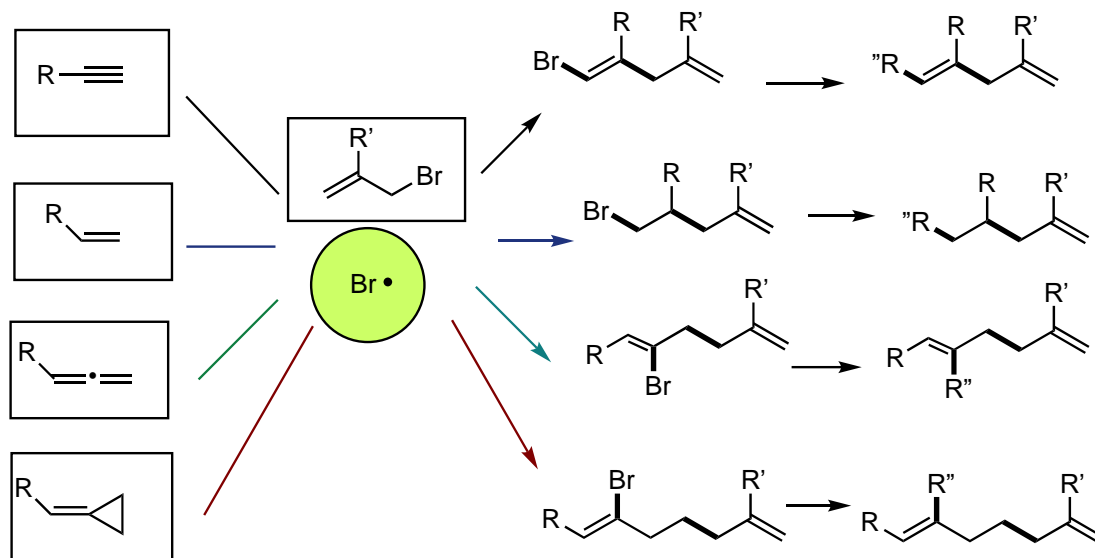
We investigated photo flow bromoallylation of alkynes and alkenes using a photo reactor MiChS L-1S and UV-LED (MiChS UV-LED-S). Flow bromoallylation of alkynes proceeded well with a residence time of 10 or 20 min, which considerably shortened the reaction time of the batch reaction (Xe irradiation for 12 h). Bromoallylation of alkenes was also successful using the same photo flow protocol.



Keywords: Photoreaction, flow reactor, LED, bromoallylation, allyl bromide,

Introduction

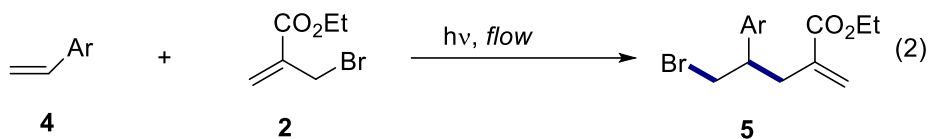
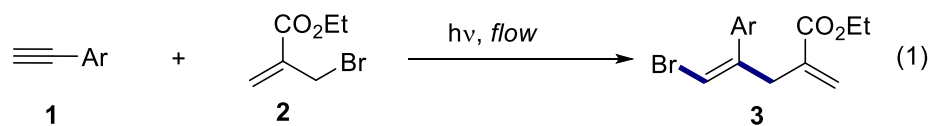
Allyl bromides act as a useful unimolecular chain transfer (UMCT) reagent in radical chemistry.^{1,2} We previously reported a series of radical bromoallylation of unsaturated compounds,³ such as alkynes,^{4,5} alkenes,⁶ allenes,^{7,8} methylenecyclopropanes,⁹ and vinylcyclopropanes,¹⁰ using allylic bromides (Scheme 1). This methodology provides convenient access to a wide variety of bromine-containing unsaturated compounds, ready for the subsequent derivatization of the carbon-bromine bond by radical and transition-metal catalyzed reactions.



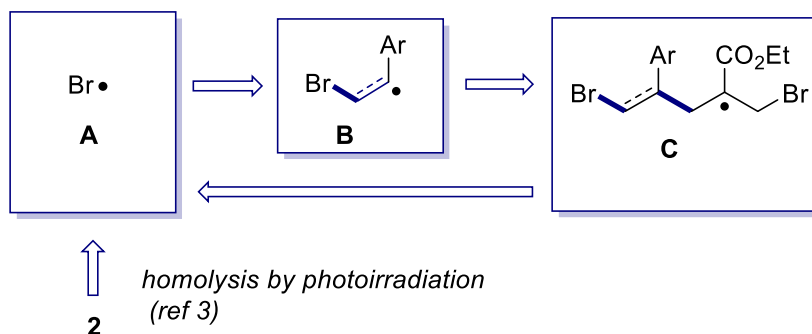
Scheme 1. Radical mediated bromoallylation.

These bromoallylation reactions generally require radical initiators such as AIBN and V-60 under thermal conditions. However, at a certain stage of the study, we noticed that simple photoirradiation (Pyrex, Xenon lamp) in the absence of a radical initiator or photocatalyst could initiate the bromoallylation of alkynes.^{4,5} In a separate experiment using 2-ethoxycarbonyl-substituted allyl bromide **2**, it was confirmed that photoirradiation caused homolysis of carbon-bromine bond in **2**, and thus generated bromine radical participates in the radical chain process for the cascade bond-forming reactions by way of **A**, **B**, and **C** (Scheme 2). Highly motivated by the progress of our ongoing project on photo flow reactions,¹¹⁻¹⁶ we decided to embark on flow bromoallylation under photoirradiation conditions. In this study, we report the results of the flow bromoallylation of arylalkynes **1** and arylalkenes **4** using allyl bromide **2**, for which we used our photo-flow setup consisting of a power-adjustable UV-LED (365 nm, up to 600W) and plate-curved micro reactors. Pleasingly, the photo flow system was successfully applicable to the efficient bromoallylation, which did not require any added radical initiator.

Flow Bromoallylation of Arylalkynes and Alkenes under Photoirradiation



Radical Relay



Scheme 2. This work: Flow photo bromoallylation of alkynes and alkenes.

Results and Discussion

The photoirradiation was carried out using a power variable UV-LED (MiChS UV-LED-S, 365 nm, 60-480 W)) and a photoflow reactor MiChS L-1S purchased from MiChS Co Ltd.(<http://www.michs.jp>) (Figure 1).

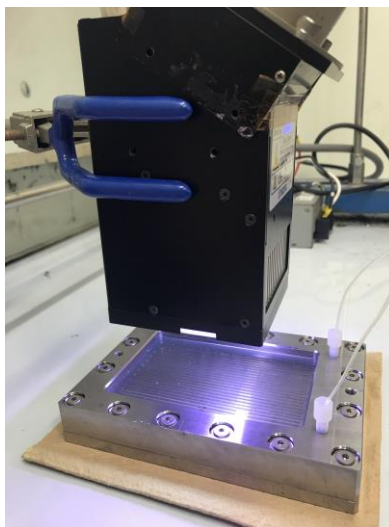
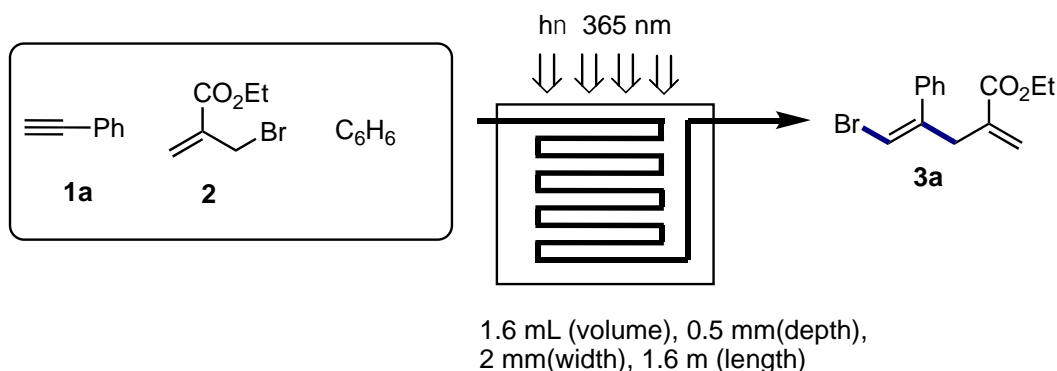


Figure 1. Setup of photo flow reaction.

We set out to study the flow bromoallylation of phenylacetylene **1a** using allyl bromide **2** (Table 1). The reaction with 5 min residence time under irradiation using a power-variable LED set to 60 W gave an 85% GC yield of **3a** with an *E/Z* ratio of 4/96 (entry 1). Prolonged residence time to 10 min gave **3a** in 99% GC yield (*E/Z* = 15/85) (entry 2). Higher irradiation power (120 and 240 W) gave **3a** rich in *E* isomer (entries 3-5).

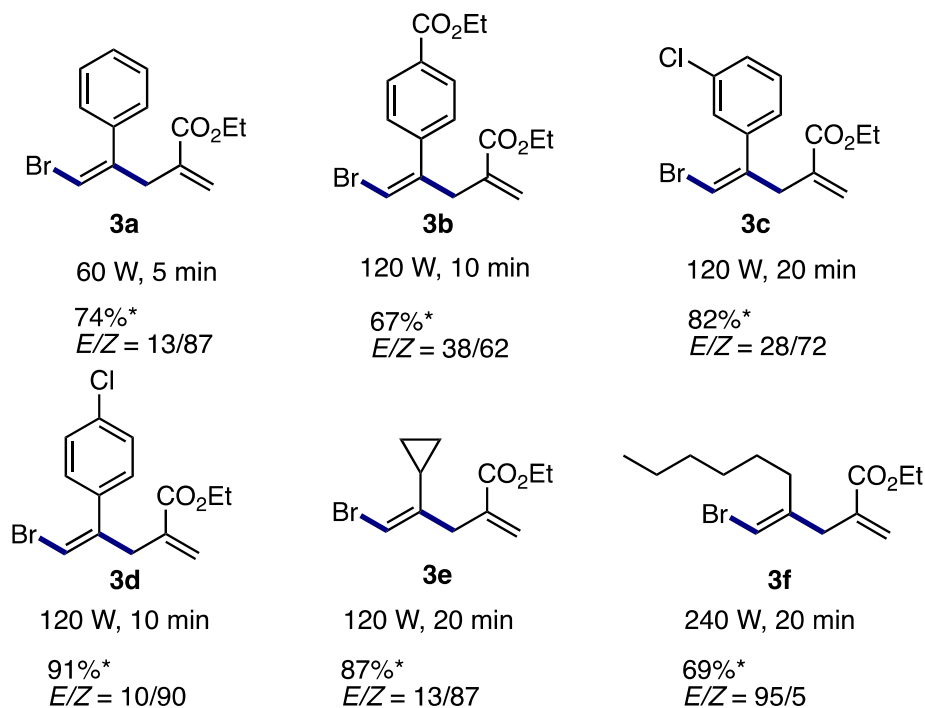
Table 1. Conditions search for **3a**^a



entry	power of LED (W)	residence time (min)	yield (%) ^b	<i>E/Z</i> ^b
1	60	5	85	4/96
2	60	10	99	15/85
3	120	10	99	29/71
4	240	10	91	61/39
5	240	20	91	70/30

a) A solution of **1a** (13 mmol), **2** (54 mmol), and tetradecane (900 mg, internal standard) in C₆H₆ (13 mL) was placed in a 25 mL gas-tight syringe and pumped to the reactor using a syringe pump. 0.5 mL of samples were collected for each condition. b) Both yields and *E/Z* ratios were determined by GC analysis.

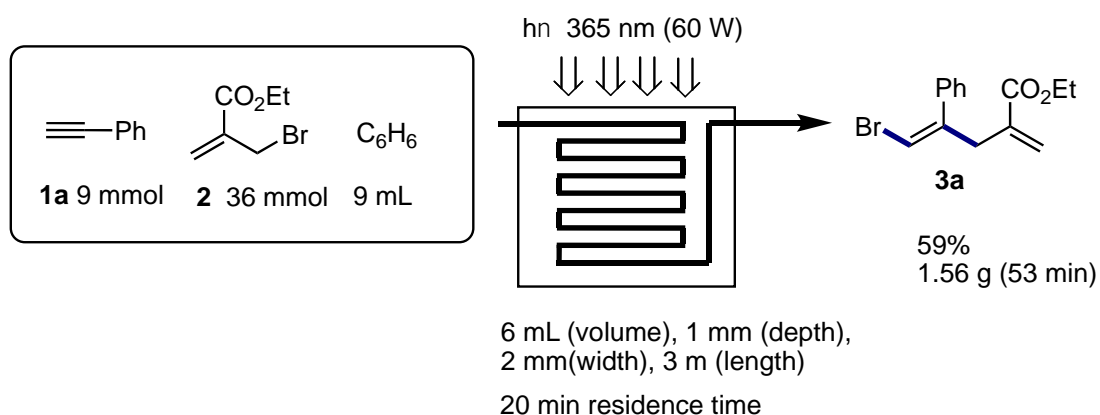
We then examined the generality of the photo flow bromoallylation of a variety of alkynes using the photo flow setup in a preparative manner. The results are summarized in Scheme 3. Phenyl alkyne **1b**, having an ester moiety, reacted with **2** to give **3b** in 67% isolated yield (*E/Z* = 38/62). The chlorine-substituted phenyl alkynes **1c** and **1d** gave **3c** and **3d** in 82% (*E/Z* = 28/72) and 91% (*E/Z* = 10/90) isolated yields, respectively. Alkyl-substituted acetylenes, such as ethynylcyclopropane and 1-octyne, also afforded **3e** and **3f** in 87% and 69% isolated yields, respectively. These cases required 20 min of residence time to complete.



*Isolated yield after purification by silica gel chromatography.

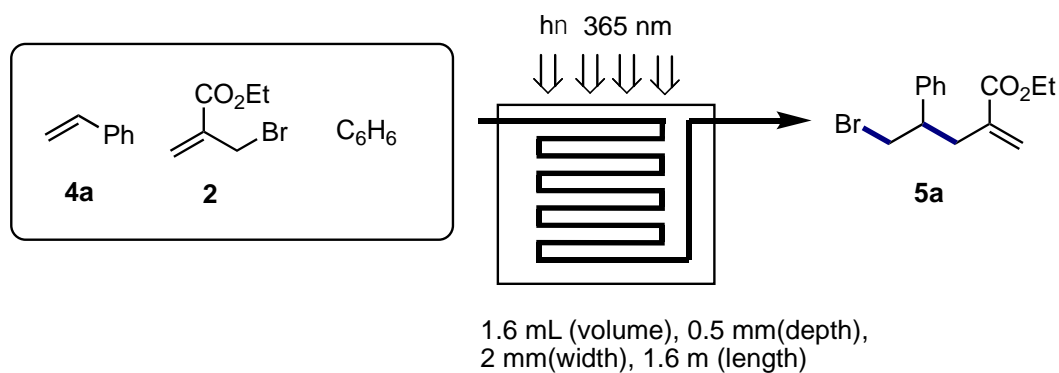
Scheme 3. Photo flow bromoallylation of alkynes.

Using a photoreactor having a larger inner volume (MiChS L-1L, 6 mL, 1 mm depth, 2 mm width, 3 m length), we then examined scalable synthesis of **3a**. As a result, 1.56 g of **3a** was obtained over 53 min operation (59% isolated yield).



Scheme 4. Scalable synthesis of **3a**.

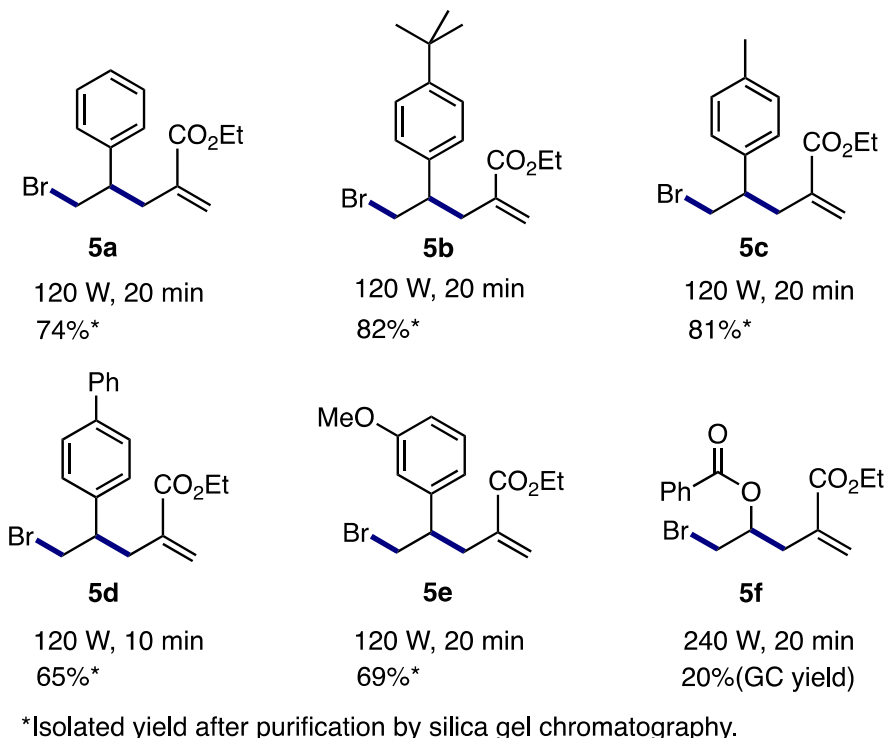
We then moved on to photo flow bromoallylation of styrene **4a** using allyl bromide **2** leading to **5a** (Table 2). The reaction with 60 W of the power of LED and 10 min residence time gave a 46% GC yield of **5a** (entry 1). Higher power (120 W) increased the yield of **5a** to 62% (entry 2). Consequently, the residence time was extended to 20 min, which gave 94% of **5a** (entry 3).

Table 2. Conditions Search for **5a**

entry	power of LED (W)	residence time (min)	yield (%) ^b
1	60	10	47
2	120	10	62
3	120	20	94

a) A solution of **4a** (6 mmol), **2** (24 mmol), and tetradecane (600 mg, internal standard) in C₆H₆ (6 mL) was placed in a 10 mL gas-tight syringe and pumped by a syringe pump. 0.5 mL of samples were collected for each condition. b) Yields were determined by GC analysis.

We examined the reaction of styrene derivatives and vinyl benzoate in a preparative manner. These results are shown in Scheme 5. Bromoallylated product **5a** was obtained in 74% isolated yield. *p*-*t*-Butylstyrene and *p*-methylstyrene gave the corresponding bromoallylated products **5b** and **5c** in 82% and 81% isolated yields, respectively. Similarly, *p*-phenyl styrene and *m*-methoxy styrene gave **5d** (65%) and **5e** (69%), respectively. On the other hand, the reaction of vinyl benzoate was sluggish, with only 20% yield of **5f** despite using higher power (240 W) of LED during irradiation.



Scheme 5. Photo flow bromoallylation of alkenes.

Conclusions

Flow bromoallylation of alkynes and alkenes was studied under photoirradiation conditions using a setup consisting of a power-adjustable UV-LED (MiChS UV-LED-s, 365 nm, 60 to 240 W) and a plate-type photo flow reactor (MiChS, L-1 series). Consequently, we established flow protocols, which are free of radical initiator, for the synthesis of 1-bromo-1,4-dienes **3** and 4-alkenyl bromides **5**. Reactions were fast, as the residence time of 10-20 min was sufficient. We also confirmed that gram order synthesis of **5a** is possible over ca. 1 h with the use of a larger size of flow reactor having an inner volume of 6 mL.

Experimental Section

General. The photo reactors MiChS L-1S (inner volume: 1.6 mL, 0.5 mm x 2.0 mm x 1.6 m) and MiChS L-1L (inner volume 6.0 mL, 1.0 mm x 2.0 mm x 6 m) and a UV-LED (MiChS UV-LED-S, 365 nm, 60-480 W) were provided by MiChS Co. Ltd. (<http://www.michs.jp>). Products were purified by flash chromatography on silica gel (Kanto Chem. Co. Silica Gel 60N (spherical, neutral, 40-50 μ m)) and, if necessary, were further purified by preparative HPLC (Japan Analytical Industry Co., Ltd., LC-908, LC-918) equipped with GPC columns (JAIGEL-1H + JAIGEL-2H columns) using CHCl_3 as eluent. ^1H NMR spectra were recorded on a JEOL ECS-400 (400 MHz) and referenced to the solvent peak at 7.26 ppm. ^{13}C NMR spectra were recorded on a JEOL ECS-400 (100MHz) and referenced to the solvent peak at 77.0 ppm. Splitting patterns are indicated as follows: s: singlet, d: doublet, dd: doublet of doublet, t: triplet, q: quartet, m: multiplet.

Typical procedure for the bromoallylation of alkynes. A mixture of **1c** (4 mmol, 544 mg) and **2** (16 mmol, 3.08 g) in C₆H₆ (4 mL) (total 7 mL) was placed in a 10 mL gas-tight syringe. The mixture was pumped through a photoreactor MiChS L-1S having a channel of 0.5 mm depth, 2.0 mm width, and 1.6 m length by a syringe pump with a flow rate of 0.08 mL/min. The photo reactor was irradiated from UV-LED (MiChS UV-LED-S) with a power of 120 W. The reaction mixture (2.4 mL) from the first 30 min operation was discarded, and the subsequent 1.75 mL portion was collected, in which 1 mmol of **1c** had been contained. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on SiO₂ and preparative HPLC (chloroform) to give **3c** in 82% yield (270 mg).

Scalable flow synthesis of 3a. A mixture of **1a** (18 mmol, 1.84 g) and **2** (72 mmol, 13.9 g) in C₆H₆ (18 mL) (total 31.5 mL) was placed in a 50 mL gas-tight syringe. The mixture was pumped through a photoreactor MiChS L-1L having a channel of 1.0 mm depth, 2.0 mm width, and 3 m length by a syringe pump with a flow rate of 0.3 mL/min. The photo reactor was irradiated from UV-LED (MiChS UV-LED-S) with a power of 60 W. The reaction mixture (9 mL) from the first 30 min operation was discarded, and the subsequent 15.8 mL portion was collected, in which 9 mmol of **1a** had been contained. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on SiO₂ and preparative HPLC (chloroform) to give **3a** in 59% yield (1.56 g).

Typical procedure for the bromoallylation of alkenes. A mixture of **4a** (4 mmol, 416 mg) and **2** (16 mmol, 3.09 g) in C₆H₆ (4 mL) (total 7 mL) was placed in a 10 mL gas-tight syringe. The mixture was pumped through a photoreactor MiChS L-1S having a channel of 0.5 mm depth, 2.0 mm width, and 1.6 m length by a syringe pump with a flow rate of 0.08 mL/min. The photo reactor was irradiated from UV-LED (MiChS UV-LED-S) with a power of 120 W. The reaction mixture (2.4 mL) from the first 30 min operation was discarded, and the subsequent 1.75 mL portion was collected, in which 1 mmol of **4a** had been contained. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on SiO₂ and preparative HPLC (chloroform) to give **5a** in 74% yield (220 mg).

Spectral data. All products were known compounds, and their ¹H and ¹³C NMR spectra were consistent with those reported in the literature.^{5,6}

Ethyl 5-bromo-2-methylene-4-phenyl-4-pentenoate (3a).⁵ Z isomer: ¹H NMR (400 MHz, CDCl₃) δ 1.29 (t, *J* = 6.8 Hz, 3H), 3.44 (s, 2H), 4.19 (q, *J* = 6.8 Hz, 2H), 5.50 (m, 1H), 6.21 (s, 1H), 6.32 (s, 1H), 7.23-7.32 (m, 3H), 7.35-7.38 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 40.4, 60.8, 104.7, 127.2, 127.6, 128.07, 128.12, 136.8, 138.8, 142.9, 166.3. E isomer: ¹H NMR (400 MHz, CDCl₃) δ 1.31 (t, *J* = 6.8 Hz, 3H), 3.71 (s, 2H), 4.21 (q, *J* = 6.8 Hz, 2H), 5.52 (s, 1H), 6.21 (s, 1H), 6.67 (s, 1H), 7.26-7.32 (m, 3H), 7.35-7.38 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 34.8, 60.8, 108.2, 125.4, 126.2, 127.9, 128.5, 135.7, 139.3, 142.4, 166.6.

Ethyl 5-bromo-4-(4-ethoxycarbonylphenyl)-2-methylene-4-pentenoate (3b).⁵ Z isomer: ¹H NMR (400 MHz, CDCl₃) δ 1.29 (t, *J* = 6.8 Hz, 3H), 1.39 (t, *J* = 6.8 Hz, 3H), 3.45 (s, 2H), 4.19 (q, *J* = 6.8 Hz, 2H), 4.37 (q, *J* = 6.8 Hz, 2H), 5.48 (s, 1H), 6.19 (s, 1H), 6.38 (s, 1H), 7.33-7.35 (m, 2H), 8.04-8.06 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 14.2, 14.3, 40.3, 60.5, 60.9, 105.7, 127.5, 128.3, 129.4, 129.7, 136.6, 142.3, 143.5, 166.0, 166.1. E isomer: ¹H NMR (400 MHz, CDCl₃) δ 1.30 (t, *J* = 7.2 Hz, 3H), 1.39 (t, *J* = 7.2 Hz, 3H), 3.73 (s, 2H), 4.22 (q, *J* = 7.2 Hz, 2H), 4.37 (q, *J* = 7.2 Hz, 2H), 5.48 (s, 1H), 6.2 (s, 1H), 6.78 (s, 1H), 7.36-7.38 (m, 2H), 7.98-8.00 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 14.2, 34.7, 60.5, 60.9, 110.0, 125.7, 126.2, 129.7, 135.8, 141.8, 143.5, 166.1, 166.5.

Ethyl 5-bromo-4-(4-chlorophenyl)-2-methylene-4-pentenoate (3c)⁵ Z isomer: ¹H NMR (400 MHz, CDCl₃) δ 1.28 (t, *J* = 6.8 Hz, 3H), 3.42 (s, 2H), 4.19 (q, *J* = 6.8 Hz, 2H), 5.48-5.49 (m, 1H), 6.20-6.21 (m, 1H), 6.33-6.34 (m, 1H), 7.20-7.23 (m, 2H), 7.32-7.35 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 40.4, 60.9, 105.4, 127.5, 128.4, 129.6, 133.6, 136.6, 137.1, 141.9, 166.2. E isomer: ¹H NMR (400 MHz, CDCl₃) δ 1.32 (t, *J* = 7.2 Hz, 3H), 3.67-3.68 (m,

2H), 4.21 (q, $J = 7.2$ Hz, 2H), 5.48-5.49 (m, 1H), 6.20-6.21 (m, 1H), 6.67 (s, 1H), 7.20-7.24 (m, 2H), 7.29-7.35 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 34.8, 61.7, 108.6, 125.8, 127.6, 128.7, 133.7, 135.6, 137.5, 141.0, 166.3.

Ethyl 5-bromo-4-(3-chlorophenyl)-2-methylene-4-pentenoate (3d)⁵ Z isomer: ^1H NMR (400 MHz, CDCl_3) δ 1.28 (t, $J = 6.8$ Hz, 3H), 3.42 (s, 2H), 4.20 (q, $J = 6.8$ Hz, 2H), 5.49 (d, $J = 1.6$ Hz, 1H), 6.22 (s, 1H), 6.34 (s, 1H), 7.11-7.22 (m, 2H), 7.24-7.32 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.2, 40.4, 60.9, 105.8, 126.5, 127.6, 127.82, 128.23, 129.5, 133.9, 136.6, 140.6, 141.8, 166.2. E isomer: ^1H NMR (400 MHz, CDCl_3) δ 1.30 (t, $J = 7.2$ Hz, 3H), 3.69 (s, 2H), 4.22 (q, $J = 7.2$ Hz, 2H), 5.49 (2, 1H), 6.22 (s, 1H), 6.70 (s, 1H), 7.11-7.22 (m, 1H), 7.24-7.32 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.2, 34.9, 61.0, 109.5, 124.4, 125.7, 126.4, 128.1, 129.8, 134.4, 135.4, 141.1, 141.4, 166.6.

Ethyl 5-bromo-4-cyclopropyl-2-methylene-4-pentenoate (3e)⁵ Z isomer: ^1H NMR (400 MHz, CDCl_3) δ 0.57-0.60 (m, 2H), 0.74-0.80 (m, 2H), 1.30 (t, $J = 6.8$ Hz, 3H), 1.93-1.99 (m, 1H), 2.73 (s, 2H), 4.20 (q, $J = 6.8$ Hz, 2H), 5.58 (s, 1H), 5.95 (s, 1H), 6.26 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 5.4, 14.1, 14.4, 33.3, 60.9, 104.3, 126.7, 137.7, 141.8, 166.5. E isomer: ^1H NMR (400 MHz, CDCl_3) δ 0.43-0.47 (m, 2H), 0.62-0.67 (m, 2H), 1.32 (t, $J = 6.8$ Hz, 3H), 1.37-1.48 (m, 1H), 3.19 (s, 2H), 4.23 (q, $J = 6.8$ Hz, 2H), 5.58 (s, 1H), 6.09 (s, 1H), 6.25 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 5.4, 14.1, 16.5, 34.2, 60.9, 103.3, 125.4, 136.2, 143.4, 166.5.

Ethyl 4-bromomethylene-2-methylenedecanoate (3f)⁵ Z isomer: ^1H NMR (400 MHz, CDCl_3) δ 0.84-0.92 (m, 3H), 1.38-1.41 (m, 11H), 2.05-2.08 (m, 2H), 3.23 (s, 2H), 4.23 (q, $J = 6.8$ Hz, 2H), 5.55 (s, 1H), 5.94 (s, 1H), 6.25 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.1, 26.9, 27.6, 28.8, 34.4, 35.9, 60.9, 103.8, 125.8, 136.0, 140.3, 166.7. E isomer: ^1H NMR (400 MHz, CDCl_3) δ 0.82-0.90 (m, 3H), 1.25-1.33 (m, 11H), 2.16-2.20 (m, 2H), 3.10 (s, 2H), 4.20 (q, $J = 6.4$ Hz, 2H), 5.55 (s, 1H), 5.94 (s, 1H), 6.25 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.1, 22.6, 26.9, 29.1, 31.6, 32.5, 37.7, 60.8, 103.7, 126.7, 137.6, 142.7, 166.56.

Ethyl 5-bromo-2-methylene-4-phenylpentanoate (5a)⁶ ^1H NMR (400 MHz, CDCl_3) δ 1.28 (t, $J = 6.8$ Hz, 3H), 2.65 (dd, $J = 14.0, 6.8$ Hz, 1H), 2.94 (dd, $J = 14.0, 6.2$ Hz, 1H), 3.23-3.32 (m, 1H), 3.56-3.66 (m, 2H), 4.17 (q, $J = 6.8$ Hz, 2H), 5.41 (s, 1H), 6.12 (s, 1H), 7.16-7.33 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.1, 36.7, 37.9, 46.5, 60.8, 127.1, 127.3, 127.7, 128.5, 137.8, 141.4, 166.8.

Ethyl 5-bromo-4-(4-(tert-butyl)phenyl)-2-methylenepentanoate (5b)⁶ ^1H NMR (400 MHz, CDCl_3) δ 1.27 (t, $J = 6.8$ Hz, 3H), 1.30 (s, 9H), 2.67 (dd, $J = 14.0, 8.2$ Hz, 1H), 2.91 (dd, $J = 14.0, 6.4$ Hz, 1H), 3.20-3.28 (m, 1H), 3.59 (d, $J = 6.8$ Hz, 2H), 4.15 (q, $J = 6.8$ Hz, 2H), 5.44 (s, 1H), 6.14 (s, 1H), 7.09-7.11 (m, 2H), 7.30-7.33 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.2, 31.3, 34.4, 36.4, 38.2, 45.9, 60.7, 125.0, 125.3, 127.2, 127.3, 137.9, 138.2, 149.8, 166.8.

Ethyl 5-bromo-2-methylene-4-(p-tolyl)pentanoate (5c)⁶ ^1H NMR (400 MHz, CDCl_3) δ 1.28 (t, $J = 6.8$ Hz, 3H), 2.32 (s, 3H), 2.62 (dd, $J = 14.0, 8.2$ Hz, 1H), 2.93 (dd, $J = 14.0, 6.4$ Hz, 1H), 3.20-3.28 (m, 1H), 3.54-3.63 (m, 2H), 4.17 (q, $J = 6.8$ Hz, 2H), 5.40 (s, 1H), 6.11 (s, 1H), 7.05 (d, $J = 8.2$ Hz, 2H), 7.12 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.2, 21.1, 36.7, 38.2, 46.0, 60.7, 127.2, 127.5, 129.2, 136.7, 137.9, 138.3, 166.8.

Ethyl 4-([1,1'-biphenyl]-4-yl)-5-bromo-2-methylenepentanoate (5d)⁶ ^1H NMR (400 MHz, CDCl_3) δ 1.27 (t, $J = 7.2$ Hz, 3H), 2.70 (dd, $J = 14.0, 8.8$ Hz, 1H), 2.96 (dd, $J = 14.0, 6.4$ Hz, 1H), 3.30-3.37 (m, 1H), 3.60-3.69 (m, 2H), 4.19 (q, $J = 7.2$ Hz, 2H), 5.46 (s, 1H), 6.15 (d, $J = 1.2$ Hz, 1H), 7.24-7.27 (m, 2H), 7.32-7.35 (m, 1H), 7.41-7.45 (m, 2H), 7.54-7.60 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.1, 36.7, 37.8, 46.0, 60.7, 126.9, 127.1, 127.2, 127.4, 128.1, 128.6, 137.7, 139.8, 140.3, 140.6, 166.7.

Ethyl 5-bromo-4-(3-methoxyphenyl)-2-methylenepentanoate (5e)⁶ ^1H NMR (400 MHz, CDCl_3) δ 1.28 (t, $J = 7.2$ Hz, 3H), 2.63 (dd, $J = 14.4, 8$ Hz, 1H), 2.93 (dd, $J = 14.4, 6$ Hz, 1H), 3.22-3.29 (m, 1H), 3.58-3.60 (m, 2H), 3.80 (s, 3H), 4.18 (q, $J = 7.2$ Hz, 2H), 5.42 (s, 1H), 6.12 (s, 1H), 6.70-6.72 (m, 1H), 6.76-6.79 (m, 2H), 7.21-7.25 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.3, 36.7, 46.4, 55.2, 60.8, 112.1, 113.8, 120.0, 127.3, 129.5, 137.7, 143.0, 159.6, 166.8.

1-Bromo-4-(ethoxycarbonyl)pent-4-en-2-yl benzoate (5f). ^1H NMR (400 MHz, CDCl_3) δ 1.28 (t, $J = 7.2$ Hz, 3H), 2.80 (dd, $J = 14.4, 7.6$ Hz, 1H), 2.94 (dd, $J = 14.4, 4.8$ Hz, 1H), 3.60 (dd, $J = 11.2, 4.8$ Hz, 1H), 3.69 (d, $J = 11.2, 4.8$ Hz, 1H), 4.17-4.23 (m, 2H), 5.46 (dq, $J = 7.6, 4.8$ Hz, 1H), 5.73 (s, 1H), 6.27 (s, 1H), 7.40-7.48 (m, 2H), 7.54-7.59 (m, 1H), 8.01-8.06 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.09, 33.92, 35.35, 61.02, 71.13, 128.36, 128.56, 129.44, 129.68, 133.17, 135.58, 165.53, 166.43.

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References

1. Curran, D. P.; Xu, J.; Lazzarini, E. *J. Am. Chem. Soc.* **1995**, *117*, 6603-6604.
<https://doi.org/10.1021/ja00129a029>
2. Curran, D. P.; Xu, J.; Lazzarini, E. *J. Chem. Soc., Perkin Trans. 1* **1995**, 3049-3059.
<https://doi.org/10.1039/P19950003049>
3. For a review on bromoallylation, see: Sumino, H.; Ryu, I. *Synlett* **2023**, *34*, 1001-1011.
<https://doi.org/10.1055/a-1998-7007>
4. Kippo, T.; Fukuyama, T.; Ryu, I. *Org. Lett.* **2010**, *12*, 4006-4009.
<https://doi.org/10.1021/ol1016096>
5. Kippo, T.; Hamaoka, K.; Ueda, M.; Fukuyama, T.; Ryu, I. *Tetrahedron* **2016**, *72*, 7866-7874.
<https://doi.org/10.1016/j.tet.2016.05.084>
6. Kippo, T.; Hamaoka, K.; Ueda, M.; Fukuyama, T.; Ryu, I. *Org. Lett.* **2017**, *19*, 5198-5200.
<https://doi.org/10.1021/acs.orglett.7b02471>
7. Kippo, T.; Fukuyama, T.; Ryu, I. *Org. Lett.* **2011**, *13*, 3864-3867.
<https://doi.org/10.1021/ol201395p>
8. Kippo, T.; Hamaoka, K.; Ryu, I. *J. Am. Chem. Soc.* **2013**, *135*, 632-635.
<https://doi.org/10.1021/ja311821h>
9. Kippo, T.; Ryu, I. *Chem. Commun.* **2014**, *50*, 5993-5996.
<https://doi.org/10.1039/C4CC01597E>
10. Fukuyama, T.; Kippo, T.; Hamaoka, K.; Ryu, I. *Sci. China Chem.* **2019**, *62*, 1525-1529.
<https://doi.org/10.1007/s11426-019-9595-0>
11. For a perspective, see: Fukuyama, T.; Kasakado, T.; Hyodo, M.; Ryu, I. *Photochem. Photobiol. Sci.* **2022**, *21*, 761-775.
<https://doi.org/10.1007/s43630-021-00151-6>
12. Hyodo, M.; Iwano, H.; Kasakado, T.; Fukuyama, T.; Ryu, I. *Micromachines*, **2021**, *12*, 1307-1315.
<https://doi.org/10.3390/mi12111307>
13. Kasakado, T.; Fukuyama, T.; Nakagawa, T.; Taguchi, S.; Ryu, I. *Beilstein J. Org. Chem.* **2022**, *18*, 152-158.
<https://doi.org/10.3762/bjoc.18.16>

14. Watanabe, H.; Takemoto, M.; Adachi, K.; Okuda, Y.; Dakegata, A.; Fukuyama, T.; Ryu, I.; Wakamatsu, K.; Orita, A.; *Chem. Lett.* **2020**, *49*, 409-412.
<https://dx.doi.org/10.1246/cl.200046>
15. Uno, M.; Sumino, S.; Fukuyama, T.; Matsuura, M.; Kuroki, Y.; Kishikawa, Y.; Ryu, I. *J. Org. Chem.* **2019**, *84*, 9330-9338.
<https://doi.org/10.1021/acs.joc.9b00901>
16. Ueda, M.; Imai, N.; Yoshida, S.; Yasuda, H.; Fukuyama, T.; Ryu, I. *Eur. J. Org. Chem.* **2017**, *2017*, 6483-6485.
<https://doi.org/10.1002/ejoc.201700745>

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