Supporting Information

For

Visible-Light-Mediated Allylation of Alkyl Radicals with Allylic Sulfones via Deaminative Strategy

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1. General remarks

$^1$H NMR spectra were recorded on 400 or 600 MHz (100 or 150 MHz for $^{13}$C NMR) agilent NMR spectrometer with CDCl$_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in parts per million (ppm, $\delta$ scale) downfield from TMS at 0.00 ppm and referenced to the CDCl$_3$ at 7.26 ppm (for $^1$H NMR) or 77.16 ppm (for $^{13}$C NMR). HRMS was recorded on a GCT Premier™ (CI) Mass Spectrometer. Infrared (FT-IR) spectra were recorded on a Varian 1000FT-IR, $\nu_{\text{max}}$ in cm$^{-1}$. All commercially available reagents and solvents were used as received unless otherwise specified. The substrates we are readily prepared according to known methods. (J. Am. Chem. Soc. 2017, 139, 5313; Org. Lett. 2018, 20, 3296; Chem. Commun. 2016, 52, 9052.)

2. Synthesis of pyridinium salts and allyl sulfones

2.1 Synthesis of pyridinium salts

![Synthesis of pyridinium salts](image)

Synthetic procedures:
To a solution of triphenylpyrylium tetrafluoroborate (1.0 equiv) and the corresponding primary amine (1.2 equiv) in ethanol (1.0 M). The reaction mixture was heated to 90 °C and after 4 h cooled to rt. If precipitation occurred during this step, the solid was collected by filtration and washed with ethanol and MTBE. In case no precipitation occurred, MTBE was added to the reaction mixture and the resulting suspension was stirred at rt for at least 1 h to complete the precipitation process. The solid was collected by filtration and washed with MTBE. The solid was then dried under reduced pressure to give the analytically pure pyridinium salts. All pyridinium salts used in this study were prepared following this procedure. (J. Am. Chem. Soc. 2017, 139, 5313.)

In case amine hydrochlorides were used as feedstock for the preparation of pyridinium salts, the amine hydrochloride (1.2 equiv.) and Et$_3$N (1.2 equiv.) were added in ethanol (1.0 M) stirred for 30 min at rt. Next, triphenylpyrylium tetrafluoroborate (1.0 equiv.) was added and the reaction mixture was heated to 90 °C for 4 h. To remove the water-soluble impurities, the collected solid was washed with water before washing with ethanol and/or MTBE.

2.2 Synthesis of allyl sulfones

Procedure for the synthesis of 2a-e.
**Typical synthetic procedures:**

To a solution of paraformaldehyde (3.98 g, 133.2 mmol) and ethylacrylate (10.8 mL, 100 mmol) in 80 mL dioxane-water (1:1, v/v) was added DABCO (14.96 g, 133.2 mmol) and the reaction progress was monitored by TLC. Upon completion, the reaction mixture was partitioned with EtOAc (200 mL) and water (100 mL). The organic layer was separated and washed with brine (100 mL), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give \( \text{B1} \) as a colorless oil (8.45 g, 65% yield).

To a solution of \( \text{B1} \) (8.45 g, 65 mmol) was added PBr₃ (2.15 ml, 22.6 mmol) in dry THF (65 mL) at -10 °C. The temperature was allowed to rise to rt and stirring was continued for 3 h. Water (20 mL) was then added and the mixture was extracted with petroleum ether (3 x 100 mL). The organic phase was washed with brine (100 mL), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give \( \text{B2} \) as a colorless oil (10.36 g, 83% yield).

To a solution of \( \text{B2} \) (10.36 g, 54.0 mmol) in dry methanol (100 mL) was added sodium phenylsulfinate (10.63 g, 64.8 mmol). After 2 h of reflux, the mixture was concentrated under reduced pressure, the obtained residue was dissolved in EtOAc and the mixture was washed with water, brine, dried with Na₂SO₄, filtered and the filtrate was evaporated and purified by chromatography to give \( \text{2a} \) as a viscous oil (11.11 g, 81% yield). (Org. Lett. 2018, 20, 3296.)

**Procedure for the synthesis of \( 2f-k \).**

A mixture of methyltriphenylphosphonium bromide (1.2 equiv) in dry THF (0.5 M) under argon atmosphere was cooled to 0 °C. Then, \( n \)-BuLi (2.5 M solution in hexane, 1.2 equiv) was added slowly under stirring. After, the resulting orange mixture was maintained at 0 °C for 1 h, a solution of the corresponding ketone (1.0 equiv) in dry THF was added dropwisely at 0 °C. The reaction was allowed to warm up to rt, stirred overnight, and finally quenched with a saturated aqueous solution of NaCl. The resulting mixture was extracted with DCM. The combined organic phases were washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography to give the corresponding propene \( \text{S1} \).

To a solution of NBS (1.05 equiv) and TSOH (0.1 equiv) in dry THF (0.5M) under...
argon atmosphere. Then, S1 (1.0 equiv) was added. The reaction solution was heated to 100 °C and stirred for 4 h, then cooled down to rt. Quenched with water, extracted with EtOAc. The combined organic layer was dried over Na2SO4, filtered and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography to afford the product S2. (Chem. Commun. 2016, 52, 9052.)

To a solution of S2 (1.0 equiv) in dry methanol (0.5 M) was added sodium phenylsulfinate (1.2 equiv). After 2 h of reflux, the mixture was concentrated under reduced pressure, the obtained residue was dissolved in EtOAc and the mixture was washed with water, brine, dried with Na2SO4, filtered and the filtrate was evaporated and purified by chromatography to give 2f-k.

3. Typical experimental procedure

\[
\begin{align*}
1a & + 2a \quad \text{(2 equiv)} \quad \text{Ir[(ppy)2(dtbbpy)]PF6 (2 mol%), i-Pr2NEt (8 equiv), DCE/DMA (1:1), blue LEDs, rt, 1 h} \\
& \quad \rightarrow 3a 
\end{align*}
\]

A 10 mL oven-dried Schlenk-tube was charged with 1a (115.6 mg, 0.2 mmol), Ir[(ppy)2(dtbbpy)]PF6 (4 mg, 2 mol%), DIPEA (265 μL, 1.6 mmol), 2a (101.6 mg, 0.4 mmol) and a magnetic stirring bar. The tube was evacuated and backfilled with argon (three times). 2 mL of DCE/DMA was injected into the tube by syringe. The resulting mixture was stirred at rt for 3 h upon irradiation with blue LEDs (22 W). The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to give 3a as a colorless oil (55 mg, 93 % yield).

4. Investigation on the reaction mechanism

4.1 Radical trapping experiment

When 2.0 equiv of TEMPO was added to the reaction of 1a with 2a under the standard conditions, the product 3a was obtained in 21% yield. The crude product was also analyzed by HRMS (ESI) and the MS spectrum showed that an adduct of TEMPO with the cyclohexyl radical could be generated.
4.2 Stern-Volmer luminescence quenching studies

Emission intensities were recorded using LS55 Luminescence Spectrometer for all experiments. All Ir[(ppy)_2(dtbbpy)]PF_6 solutions were excited at 420 nm and the emission intensity was collected at 560 nm. In a typical experiment, the DMF solution of Ir[(ppy)_2(dtbbpy)]PF_6 (30 μM) was added the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette. After degassing with argon for 15 min, the emission spectra of the samples were collected. The results showed that DIPEA, Katritzky salts 1b and 1e quenched the photoexcited Ir[(ppy)_2(dtbbpy)]PF_6 effectively, while the allyl sulfone 2a was not effective.
Figure S2. a) Ir(ppy)₂(dtbbpy)PF₆ emission quenching by DIPEA. b) Ir(ppy)₂(dtbbpy)PF₆ emission quenching by Katritzky salt 1b. c) Ir(ppy)₂(dtbbpy)PF₆ emission quenching by Katritzky salt 1e. d) Ir(ppy)₂(dtbbpy)PF₆ emission quenching by allyl sulfone 2a.

5. Characterization of the substrates and products

![Diagram](Image)

1-(1-((tert-Butoxycarbonyl)piperidin-4-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1a): ¹H NMR (600 MHz, CDCl₃) δ 7.80 – 7.65 (m, 8H), 7.63 – 7.53 (m, 6H), 7.53 – 7.48 (m, 1H), 7.47 – 7.39 (m, 2H), 4.80 – 4.72 (m, 1H), 4.02 – 3.79 (m, 2H), 2.27 – 2.00 (m, 4H), 1.72 – 1.55 (m, 2H), 1.30 (s, 9H); ¹³C NMR (150 MHz, CDCl₃) δ 157.2, 155.5, 154.3, 134.1, 133.9, 132.1, 131.2, 129.7, 129.4, 129.1, 128.4, 80.2, 70.0, 44.7, 43.8, 32.8, 28.4; ¹⁹F NMR (564 MHz, CDCl₃) δ -152.96 (s), -153.01 (s).

![Diagram](Image)

1-Cyclohexyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1b): ¹H NMR (600 MHz, CDCl₃) δ 7.76 (s, 2H), 7.71 (t, J = 6.8 Hz, 6H), 7.63 – 7.52 (m, 6H), 7.49 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 4.64 – 4.55 (m, 1H), 2.15 – 2.05 (m, 2H), 1.61 – 1.52 (m, 2H), 1.52 – 1.40 (m, 2H), 1.37 – 1.30 (m, 1H), 0.78 – 0.67 (m, 2H), 0.65 – 0.54 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 157.2, 155.1, 134.12, 134.09, 131.9, 130.9, 129.6, 129.4, 128.4, 128.2, 128.0, 33.7, 26.6, 24.7; ¹⁹F NMR (564 MHz, CDCl₃) δ -153.30 (s), -153.36 (s).

![Diagram](Image)

1-(4-(Methoxycarbonylcyclohexyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1c): ¹H NMR (600 MHz, CDCl₃) δ 7.76 – 7.68 (m, 6H), 7.65 (d, J = 7.5 Hz, 2H), 7.62 – 7.50 (m, 6), 7.47 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 4.59 (t, J = 12.2 Hz, 1H), 3.51 (s, 3H), 2.21 (d, J = 12.1 Hz, 2H), 1.91 – 1.75 (m, 3H), 1.68 (t, 1H), 1.59 – 1.49 (m, 2H), 0.96 – 0.87 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ
174.5, 157.0, 155.0, 133.9, 133.8, 131.9, 131.0, 129.5, 129.3, 128.8, 128.2, 128.1, 70.5, 51.7, 41.5, 32.0, 28.7; ¹⁹F NMR (564 MHz, CDCl₃) δ -153.07 (s), -153.13 (s).

1-(4-(Methoxycarbonyl)benzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1d): ¹H NMR (400 MHz, CDCl₃) δ 7.92 (s, 2H), 7.83 – 7.64 (m, 8H), 7.60 – 7.38 (m, 9H), 6.57 (d, J = 7.9 Hz, 2H), 5.87 (s, 2H), 3.84 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 166.1, 157.48, 157.46, 156.5, 138.91, 138.87, 133.6, 132.54, 132.47, 131.1, 129.9, 129.8, 129.2, 129.1, 128.2, 126.5, 126.2, 58.0, 52.3; ¹⁹F NMR (564 MHz, CDCl₃) δ -152.67 – -152.88 (m).

1-(1-Methoxy-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1e): ¹H NMR (600 MHz, CDCl₃) δ 7.93 (s, 2H), 7.89 – 7.68 (m, 4H), 7.65 – 7.39 (m, 11H), 7.15 – 7.04 (m, 3H), 6.77 (d, J = 7.3 Hz, 2H), 5.64 (dd, J = 7.5, 3.7 Hz, 1H), 3.69 (s, 3H), 3.50 – 3.41 (m, 1H), 2.93 (dd, J = 14.4, 8.0 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 168.0, 157.1, 157.0, 136.4, 133.8, 132.5, 132.4, 131.7, 129.8, 129.6, 129.2, 129.1, 128.72, 128.66, 128.0, 127.3, 70.3, 53.9, 37.8; ¹⁹F NMR (564 MHz, CDCl₃) δ -152.80 (d, J = 4.5 Hz), -152.86 (d, J = 3.5 Hz).

1-(3-(4-Chlorophenyl)-1-methoxy-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1f): ¹H NMR (600 MHz, CDCl₃) δ 7.92 (s, 2H), 7.83 – 7.72 (m, 4H), 7.60 – 7.45 (m, 11H), 7.01 (d, J = 8.1 Hz, 2H), 6.74 (d, J = 8.1 Hz, 2H), 5.55 (d, J = 8.4 Hz, 1H), 3.67 (s, 3H), 3.49 (d, J = 14.3 Hz, 1H), 2.82 (dd, J = 14.3, 8.7 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 167.9, 157.2, 156.8, 135.4, 133.9, 133.1, 132.5, 132.4, 131.7, 130.6, 129.8, 129.5, 129.3, 128.7, 128.6, 128.0, 70.0, 53.9, 37.3; ¹⁹F NMR (564 MHz, CDCl₃) δ -152.57 (s), -152.62 (s).
1-(1-Methoxy-3-(4-methoxyphenyl)-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1g): $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.90 (s, 2H), 7.86 – 7.69 (m, 4H), 7.63 – 7.37 (m, 11H), 6.67 (d, $J = 8.2$ Hz, 2H), 6.60 (d, $J = 7.8$ Hz, 2H), 5.58 (dd, $J = 7.1$, 4.9 Hz, 1H), 3.69 (s, 3H), 3.67 (s, 3H), 3.31 (dd, $J = 14.5$, 4.3 Hz, 1H), 2.89 (dd, $J = 14.6$, 7.7 Hz, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 167.8, 158.7, 156.9, 133.6, 132.5, 132.2, 131.6, 130.1, 129.7, 129.5, 129.2, 128.6, 128.0, 127.8, 114.0, 70.4, 55.3, 53.8, 36.9; $^{19}$F NMR (564 MHz, CDCl$_3$) $\delta$ -152.75 – -152.80 (m), -152.80 – -152.85 (m).

1-(1-Methoxy-1-oxo-4-phenylbutan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1h): $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.90 (s, 2H), 7.81 (d, $J = 7.5$ Hz, 2H), 7.73 (br, 2H), 7.59 – 7.39 (m, 11H), 7.16 – 7.06 (m, 3H), 6.92 (d, $J = 6.5$ Hz, 2H), 5.37 (dd, $J = 8.5$, 2.1 Hz, 1H), 3.71 (s, 3H), 2.48 – 2.35 (m, 3H), 2.02 – 1.96 (m, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 168.7, 157.1, 156.9, 138.7, 134.0, 132.6, 132.4, 131.5, 129.8, 129.2, 128.71, 128.65, 128.56, 128.1, 126.6, 68.1, 53.8, 33.5, 33.2; $^{19}$F NMR (564 MHz, CDCl$_3$) $\delta$ -152.86 (s), -152.92 (s).

1-(1-Methoxy-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1i): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 (s, 2H), 7.79 – 7.69 (m, 4H), 7.66 – 7.44 (m, 11H), 5.52 (q, $J = 7.0$ Hz, 1H), 3.66 (s, 3H), 1.47 (d, $J = 7.1$ Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 168.9, 157.0, 156.8, 134.0, 132.7, 132.3, 131.5, 129.7, 129.2, 128.5, 127.9, 64.6, 53.8, 17.3; $^{19}$F NMR (564 MHz, CDCl$_3$) $\delta$ -153.17 (s), -153.22 (s).

1-(1-Methoxy-4-methyl-1-oxopentan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1j): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.90 (s, 2H), 7.81 (d, $J = 7.3$ Hz, 2H), 7.76 – 7.44 (m, 13H), 5.47 (dd, $J = 7.8$, 2.8 Hz, 1H), 3.75 (s, 3H), 1.81 –
1.64 (m, 1H), 1.64 – 1.50 (m, 1H), 1.39 – 1.26 (m, 1H), 0.57 (d, $J = 6.5$ Hz, 3H), 0.42 (d, $J = 6.4$ Hz, 3H); $^{13}$C NMR (150 MHz, CDCl3) δ 168.7, 156.8, 156.7, 133.7, 132.5, 132.3, 131.6, 129.6, 129.4, 129.1, 128.5, 127.9, 67.4, 53.9, 40.4, 26.1, 22.3, 20.7; $^{19}$F NMR (564 MHz, CDCl3) δ -153.01 (s), -153.07 (s).

1-(1-Methoxy-3-methyl-1-oxopentan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1k): d.r. (1.1:1); $^1$H NMR (600 MHz, CDCl3) δ 7.99 (s, 2H), 7.88 (d, $J = 7.3$ Hz, 2H), 7.75 – 7.43 (m, 13H), 5.31 (d, $J = 10.2$ Hz, 0.48H)/ 5.16 (d, $J = 10.2$ Hz, 0.52H), 3.75 – 3.68 (m, 3H), 2.04 – 1.64 (m, 2H), 1.42 – 0.90 (m, 2H), 0.87 – 0.66 (m, 5H); $^{13}$C NMR (150 MHz, CDCl3) δ 167.0, 166.8, 157.10, 157.15, 133.1, 133.0, 131.9, 129.9, 129.8, 129.7, 129.4, 129.2 128.9, 128.8, 128.6, 127.8, 73.5, 71.3, 53.93, 53.87, 36.0, 35.6, 27.8, 25.4, 18.5, 15.2, 11.1, 9.5; $^{19}$F NMR (564 MHz, CDCl3) δ -153.28 (s), -153.34 (s).

1-(1-Methoxy-4-(methylthio)-1-oxobutan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1l): $^1$H NMR (400 MHz, CDCl3) δ 7.87 (s, 2H), 7.83 – 7.69 (m, 4H), 7.63 – 7.39 (m, 11H), 5.92 (d, $J = 7.7$ Hz, 1H), 3.73 (s, 3H), 2.37 – 2.16 (m, 3H), 1.94 – 1.85 (m, 1H), 1.83 (s, 3H); $^{13}$C NMR (150 MHz, CDCl3) δ 168.4, 156.9, 133.8, 132.5, 132.2, 131.5, 129.6, 129.1, 128.5, 66.7, 53.9, 31.4, 30.8, 14.7; $^{19}$F NMR (564 MHz, CDCl3) δ -152.74 (s), -152.79 (s).

1-(1,4-Dimethoxy-1,4-dioxobutan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1m): $^1$H NMR (400 MHz, CDCl3) δ 7.93 (br, 3H), 7.86 – 7.75 (m, 3H), 7.70 – 7.41 (m, 11H), 6.22 (d, $J = 9.4$ Hz, 1H), 3.63 (s, 3H), 3.53 (s, 3H), 3.38 (d, $J = 17.4$ Hz, 1H), 2.55 (dd, $J = 17.4$, 9.7 Hz, 1H); $^{13}$C NMR (150 MHz, CDCl3) δ 169.6, 167.74, 167.70, 157.4, 133.9, 132.5, 131.7, 129.8, 129.4, 128.6, 64.1, 54.1, 52.6, 36.0; $^{19}$F NMR (564 MHz, CDCl3) δ -152.78 (d, $J = 4.1$ Hz), -152.83 (s).
1-(1,5-Dimethoxy-1,5-dioxopentan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (1n): \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.93 (s, 2H), 7.86 – 7.71 (m, 4H), 7.69 – 7.44 (m, 11H), 5.60 (t, \(J = 6.2\) Hz, 1H), 3.71 (s, 3H), 3.46 (s, 3H), 2.26 (dt, \(J = 13.0, 6.3\) Hz, 1H), 2.23 – 2.13 (m, 2H), 2.07 (td, \(J = 14.1, 7.0\) Hz, 1H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 172.1, 168.2, 157.2, 133.7, 132.5, 132.4, 131.7, 129.8, 129.4, 128.6, 128.1, 67.6, 54.0, 51.8, 30.8, 27.0; \(^{19}\)F NMR (564 MHz, CDCl\(_3\)) \(\delta\) -153.06 (s), -153.11 (s).

Ethyl 2-((phenylsulfonyl)methyl)acrylate (2a): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.83 (d, \(J = 7.6\) Hz, 2H), 7.62 (t, \(J = 7.2\) Hz, 1H), 7.51 (t, \(J = 7.4\) Hz, 2H), 6.48 (s, 1H), 5.88 (s, 1H), 4.14 (s, 2H), 3.98 (q, \(J = 6.9\) Hz, 2H), 1.14 (t, \(J = 7.0\) Hz, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 164.8, 138.4, 133.9, 133.4, 129.2, 129.1, 128.8, 61.5, 57.6, 14.0.

((2-Methylallyl)sulfonyl)benzene (2b): \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.88 (d, \(J = 7.7\) Hz, 2H), 7.64 (t, \(J = 7.4\) Hz, 1H), 7.54 (t, \(J = 7.6\) Hz, 2H), 5.02 (s, 1H), 4.68 (s, 1H), 3.76 (s, 2H), 1.86 (s, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 138.4, 133.8, 133.5, 129.1, 128.6, 120.9, 64.6, 22.8.

Benzyl 2-((phenylsulfonyl)methyl)acrylate (2c): \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.82 (d, \(J = 7.9\) Hz, 2H), 7.59 (t, \(J = 7.4\) Hz, 1H), 7.46 (t, \(J = 7.7\) Hz, 2H), 7.38 – 7.30 (m, 3H), 7.26 (d, \(J = 7.3\) Hz, 2H), 6.53 (s, 1H), 5.92 (s, 1H), 5.00 (s, 2H), 4.17 (s, 2H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 164.6, 138.2, 135.3, 133.9, 133.8, 129.0, 128.8, 128.6, 128.5, 128.4, 128.2, 67.1, 57.4.

tert-Butyl 2-((phenylsulfonyl)methyl)acrylate (2d): \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.84 (d, \(J = 7.4\) Hz, 2H), 7.61 (t, \(J = 7.4\) Hz, 1H), 7.51 (t, \(J = 7.7\) Hz, 2H), 6.42 (s, 1H),
5.87 (s, 1H), 4.12 (s, 2H), 1.31 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 163.8, 138.6, 133.9, 132.8, 130.4, 129.1, 128.9, 81.9, 57.5, 27.8.

2-((Phenylsulfonyl)methyl)acrylonitrile (2e): $^1$H NMR (600 MHz, CDCl$_3$) δ 7.93 (d, $J = 7.8$ Hz, 2H), 7.73 (t, $J = 7.5$ Hz, 1H), 7.62 (t, $J = 7.7$ Hz, 2H), 6.22 (s, 1H), 6.01 (s, 1H), 3.93 (s, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 139.6, 137.5, 134.9, 129.7, 128.9, 116.5, 111.6, 60.0.

((2-Phenylallyl)sulfonyl)benzene (2f): $^1$H NMR (600 MHz, CDCl$_3$) δ 7.77 (d, $J = 7.9$ Hz, 2H), 7.53 (t, $J = 7.4$ Hz, 1H), 7.41 (t, $J = 7.6$ Hz, 2H), 7.28 − 7.18 (m, 5H), 5.58 (s, 1H), 5.20 (s, 1H), 4.27 (s, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 138.7, 138.3, 136.4, 133.7, 128.9, 128.6, 128.0, 126.2, 121.9, 62.0.

1-Chloro-4-(3-(phenylsulfonyl)prop-1-en-2-yl)benzene (2g): $^1$H NMR (600 MHz, CDCl$_3$) δ 7.78 (d, $J = 7.8$ Hz, 2H), 7.59 (t, $J = 7.4$ Hz, 1H), 7.46 (t, $J = 7.7$ Hz, 2H), 7.21 (s, 4H), 5.58 (s, 1H), 5.21 (s, 1H), 4.23 (s, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 138.4, 137.3, 135.6, 134.2, 133.9, 129.1, 128.7, 128.7, 127.7, 122.5, 62.1.

1-Bromo-4-(3-(phenylsulfonyl)prop-1-en-2-yl)benzene (2h): $^1$H NMR (600 MHz, CDCl$_3$) δ 7.77 (d, $J = 7.3$ Hz, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.44 (t, $J = 7.7$ Hz, 2H), 7.35 (d, $J = 8.3$ Hz, 2H), 7.14 (d, $J = 8.3$ Hz, 2H), 5.57 (s, 1H), 5.20 (s, 1H), 4.22 (s, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 138.3, 137.7, 135.6, 133.8, 131.5, 129.1, 128.6, 127.9, 122.5, 122.2, 62.0.
1-Methyl-4-(3-(phenylsulfonyl)prop-1-en-2-yl)benzene (2i): $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.79 (d, $J = 7.9$ Hz, 2H), 7.55 (t, 1H), 7.43 (t, $J = 15.5$, 7.9 Hz, 2H), 7.17 (d, $J = 7.8$ Hz, 2H), 7.05 (d, $J = 7.8$ Hz, 2H), 5.55 (s, 1H), 5.13 (s, 1H), 4.26 (s, 2H), 2.31 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 138.5, 138.0, 136.4, 135.9, 133.7, 129.2, 129.0, 128.7, 126.2, 121.1, 62.2, 21.2.

1-Methoxy-4-(3-(phenylsulfonyl)prop-1-en-2-yl)benzene (2j): $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.78 (d, $J = 8.1$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.22 (d, $J = 8.6$ Hz, 2H), 6.77 (d, $J = 8.6$ Hz, 2H), 5.50 (s, 1H), 5.07 (s, 1H), 4.24 (s, 2H), 3.77 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 159.5, 138.4, 135.8, 133.7, 131.2, 128.9, 128.7, 127.5, 120.2, 113.8, 62.2, 55.4.

2-(3-(Phenylsulfonyl)prop-1-en-2-yl)naphthalene (2k) $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.80 (d, $J = 7.9$ Hz, 2H), 7.79 – 7.75 (m, 1H), 7.75 – 7.69 (m, 2H), 7.64 (s, 1H), 7.49 – 7.43 (m, 3H), 7.41 (d, $J = 8.2$ Hz, 1H), 7.36 (t, $J = 15.1$, 7.3 Hz, 2H), 5.74 (s, 1H), 5.33 (s, 1H), 4.39 (s, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 138.6, 136.5, 136.0, 133.7, 133.2, 133.0, 129.0, 128.8, 128.4, 128.3, 127.6, 126.5, 125.6, 124.2, 122.3, 62.3.

tert-Butyl 4-(2-(ethoxycarbonyl)allyl)piperidine-1-carboxylate (3a): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to give the colorless oil; 93% yield (55 mg); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.17 (s, 1H), 5.49 (s, 1H), 4.19 (q, $J = 7.1$ Hz, 2H), 4.14 – 3.95 (m, 2H), 2.73 – 2.54 (m, 2H), 2.23 (d, $J = 6.2$ Hz, 2H), 1.68 – 1.55 (m, 3H), 1.44 (s, 9H), 1.29 (t, $J = 7.1$ Hz, 3H), 1.12 – 1.00 (m, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 167.3, 155.0, 138.7, 126.3, 79.3, 60.8, 44.2, 39.3, 35.2, 32.1, 28.6, 14.4; FT-IR (thin film, KBr): $\nu$ (cm$^{-1}$): 2980, 2920, 2849, 1685, 1108; HRMS (CI) calcd C$_{16}$H$_{26}$NO$_4$ [M - H]$^+$: 296.1862, found: 296.1869.

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Ethyl 2-(cyclohexylmethyl)acrylate (3b): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 50:1) to give the colorless oil; 85% yield (33 mg); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 6.13 (d, $J = 1.7$ Hz, 1H), 5.45 (d, $J = 0.8$ Hz, 1H), 4.19 (q, $J = 7.1$ Hz, 2H), 2.18 (d, $J = 7.0$ Hz, 2H), 1.72 – 1.66 (m, 4H), 1.63 – 1.59 (m, 1H), 1.48 – 1.38 (m, 1H), 1.29 (t, $J = 7.1$ Hz, 3H), 1.26 – 1.08 (m, 5H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 167.7, 139.6, 125.6, 60.7, 40.0, 36.8, 33.2, 26.7, 26.4, 14.3; FT-IR (thin film, KBr): $\nu$ (cm$^{-1}$): 2923, 2852, 1715, 1150, 1111; HRMS (CI) calcd C$_{12}$H$_{21}$O$_2$ [M + H]$^+$: 197.1542, found: 197.1537.

Methyl 4-(2-(ethoxycarbonyl)allyl)cyclohexane-1-carboxylate (3c): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to give the colorless oil; 76% yield (39 mg); d.r. (1.5:1); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 6.15 (s, 0.4H)/6.14 (s, 0.6H), 5.46 (s, 1H), 4.23 – 4.14 (m, 2H), 3.67 (s, 1.8H)/3.64(s, 1.2H), 2.56 – 2.48 (m, 0.6H), 2.27 – 2.16 (m, 2.4H), 2.03 – 1.90 (m, 2H), 1.79 (d, $J = 12.4$ Hz, 1H), 1.64 – 1.49 (m, 3H), 1.48 – 1.34 (m, 1H), 1.29 (t, $J = 7.1$ Hz, 3H), 1.26 – 1.15 (m, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 176.7/176.0, 167.5, 139.4/139.2, 125.9, 60.8/60.7, 51.63/51.61, 43.4/39.7, 40.5/38.1, 36.1/34.7, 32.1/29.2, 29.0/26.2, 14.3; FT-IR (thin film, KBr): $\nu$ (cm$^{-1}$): 2929, 1730, 1180, 1147, 1115; HRMS (CI) calcd C$_{14}$H$_{23}$O$_4$ [M + H]$^+$: 255.1596, found: 255.1603.

Methyl 4-(3-(ethoxycarbonyl)but-3-en-1-yl)benzoate (3d): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to give the colorless oil; 68% yield (36 mg); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.95 (d, $J = 8.0$ Hz, 2H), 7.24 (d, 2H), 6.15 (s, 1H), 5.47 (s, 1H), 4.22 (q, $J = 7.1$ Hz, 2H), 3.90 (s, 3H), 2.85 (t, 2H), 2.63 (t, $J = 7.8$ Hz, 2H), 1.31 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 167.2, 167.1, 147.0, 139.8, 129.8, 128.7, 128.1, 125.6, 60.9, 52.1, 35.1, 33.7, 14.4; FT-IR (thin film, KBr): $\nu$ (cm$^{-1}$): 2956, 1709, 1275, 1177, 1102; HRMS (CI) calcd C$_{15}$H$_{19}$O$_4$ [M + H]$^+$: 263.1283, found: 263.1285.

5-Ethyl 1-methyl 2-benzyl-4-methylenepentanedioate (3e): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to give the colorless oil; 69% yield (38 mg); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.27 (t, $J = 6.9$ Hz, 2H), 7.23 – 7.11 (m, 3H), 6.18 (s, 1H), 5.57 (s, 1H), 4.19 (q, $J = 6.8$ Hz, 2H), 3.54
(s, 3H), 3.07 – 2.89 (m, 2H), 2.88 – 2.72 (m, 1H), 2.58 (d, J = 6.5 Hz, 2H), 1.28 (t, J = 7.0 Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 175.3, 166.7, 138.9, 138.1, 129.0, 128.5, 126.9, 126.6, 60.9, 51.5, 46.7, 38.6, 34.8, 14.3; FT-IR (thin film, KBr): v (cm$^{-1}$): 2962, 2920, 1719, 1185, 698; HRMS (CI) calcd C$_{18}$H$_{21}$O$_4$ [M + H]$^+$: 277.1440, found: 277.1441.

5-Ethyl 1-methyl 2-(4-chlorobenzyl)-4-methylenepentanedioate (3f): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to give the colorless oil; 73% yield (45 mg); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.23 (d, J = 8.2 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 6.18 (s, 1H), 5.57 (s, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.54 (s, 3H), 2.97 (ddd, J = 14.6, 8.3, 6.5 Hz, 1H), 2.90 (dd, J = 13.6, 8.9 Hz, 1H), 2.75 (dd, J = 13.6, 6.1 Hz, 1H), 2.58 – 2.54 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 175.0, 166.6, 137.9, 137.4, 132.4, 130.3, 128.6, 127.1, 60.9, 51.6, 46.6, 37.8, 35.0, 14.3; FT-IR (thin film, KBr): v (cm$^{-1}$): 2985, 2950, 1712, 1165, 1132; HRMS (CI) calcd C$_{16}$H$_{20}$O$_4$Cl$^+$: 311.1050, found: 311.1056.

1-Ethyl 5-methyl 4-(4-methoxybenzyl)-2-methylenepentanedioate (3g): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to give the colorless oil; 88% yield (54 mg); $^1$H NMR (600 MHz, CDCl$_3$) δ 7.07 (d, J = 8.3 Hz, 2H), 6.80 (d, J = 8.3 Hz, 2H), 6.17 (s, 1H), 5.56 (s, 1H), 4.25 – 4.12 (m, 2H), 3.77 (s, 3H), 3.54 (s, 3H), 3.00 – 2.92 (m, 1H), 2.92 – 2.85 (m, 1H), 2.77 – 2.69 (m, 1H), 2.55 (d, J = 7.0 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 175.4, 166.7, 158.3, 138.1, 130.9, 129.9, 126.8, 113.9, 60.9, 55.3, 51.5, 47.0, 37.8, 34.8, 14.3; FT-IR (thin film, KBr): v (cm$^{-1}$): 2950, 1715, 1510, 997; HRMS (CI) calcd C$_{17}$H$_{23}$O$_5$ [M + H]$^+$: 307.1545, found: 307.1548.

Ethyl 5-methyl 2-methylene-4-phenethylpentanedioate (3h): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to give the colorless oil; 76% yield (44 mg); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32 – 7.23 (m, 2H), 7.22 – 7.13 (m, 3H), 6.17 (s, 1H), 5.54 (s, 1H), 4.19 (q, J = 6.9 Hz, 2H), 3.65 (s, 3H), 2.78 – 2.68 (m, 1H), 2.66 – 2.49 (m, 4H), 2.06 – 1.88 (m, 1H), 1.87 – 1.72 (m, 1H), 1.27 (t, J = 7.0 Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 175.8, 166.8, 141.5,
138.1, 128.5, 128.5, 126.8, 126.1, 60.9, 51.6, 44.4, 35.0, 34.1, 33.7, 14.3; FT-IR (thin film, KBr): ν (cm\(^{-1}\)): 2950, 1730, 1156, 1132, 695; HRMS (CI) calcd C\(_{17}\)H\(_{23}\)O\(_4\) [M + H\(^+\)]: 291.1596, found: 291.1607.

1-Ethyl 5-methyl 4-methyl-2-methylenepentanedioate (3i): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to give the colorless oil; 74% yield (30 mg); \(^1\)H NMR (600 MHz, CDCl\(_3\)) δ 6.19 (s, 1H), 5.56 (s, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.65 (s, 3H), 2.79 – 2.71 (m, 1H), 2.67 (dd, J = 13.9, 8.0 Hz, 1H), 2.40 (dd, J = 13.9, 6.6 Hz, 1H), 1.30 (t, J = 7.1 Hz, 3H), 1.16 (d, J = 7.0 Hz, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) δ 176.6, 166.9, 138.3, 126.9, 60.9, 51.7, 38.7, 36.3, 17.2, 14.3; FT-IR (thin film, KBr): ν (cm\(^{-1}\)): 2977, 2953, 1736, 1712, 1145; HRMS (CI) calcd C\(_{10}\)H\(_{17}\)O\(_4\) [M + H\(^+\)]: 201.1127, found: 201.1127.

1-Ethyl 5-methyl 4-isobutyl-2-methylenepentanedioate (3j): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to give the colorless oil; 75% yield (36 mg); \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 6.16 (s, 1H), 5.55 (s, 1H), 4.21 (q, J = 6.9 Hz, 2H), 3.62 (s, 3H), 2.82 – 2.69 (m, 1H), 2.50 (d, J = 7.3 Hz, 2H), 1.59 – 1.49 (m, 2H), 1.35 – 1.22 (m, 4H), 0.89 (d, J = 5.6 Hz, 6H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) δ 176.4, 166.8, 138.3, 126.7, 60.9, 51.5, 43.0, 41.8, 35.5, 26.2, 23.0, 22.2, 14.3; FT-IR (thin film, KBr): ν (cm\(^{-1}\)): 2959, 2869, 1733, 1712, 1147; HRMS (CI) calcd C\(_{13}\)H\(_{23}\)O\(_4\) [M + H\(^+\)]: 243.1596, found: 243.1600.

5-Ethyl 1-methyl 2-(sec-butyl)-4-methylenepentanedioate (3k): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to give the colorless oil; 67% yield (33 mg); d.r. (1.2:1); \(^1\)H NMR (600 MHz, CDCl\(_3\)) δ 6.14 (s, 1H), 5.56 (s, 0.54H)/5.55 (s, 0.46H), 4.25 – 4.15 (m, 2H), 3.61 (s, 3H), 2.63 – 2.56 (m, 2H), 2.54 – 2.44 (m, 1H), 1.74 – 1.64 (m, 1H), 1.54 – 1.39 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H), 1.26 – 1.15 (m, 1H), 0.96 – 0.87 (m, 6H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) δ 175.6/175.3, 166.93/166.91, 138.8/138.7, 126.6, 60.9, 51.3/51.2, 50.1/49.6, 37.3/37.2, 32.6/31.2, 27.4/26.9, 16.5/16.2, 14.3, 11.7/11.2; FT-IR (thin film, KBr): ν (cm\(^{-1}\)): 2959, 1730, 1712, 1144, 1025; HRMS (CI) calcd C\(_{13}\)H\(_{23}\)O\(_4\) [M + H\(^+\)]: 243.1596, found: 243.1602.
1-Ethyl 5-methyl 2-methylene-4-(2-(methylthio)ethyl)pentanedioate (3l): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to give the colorless oil; 59% yield (31 mg); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.18 (s, 1H), 5.56 (s, 1H), 4.20 (q, $J$ = 7.1 Hz, 2H), 3.64 (s, 3H), 2.87 – 2.76 (m, 1H), 2.64 – 2.42 (m, 4H), 2.07 (s, 3H), 2.01 – 1.86 (m, 1H), 1.82 – 1.68 (m, 1H), 1.30 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 175.4, 166.7, 137.9, 127.0, 61.0, 51.7, 43.8, 34.9, 31.9, 31.6, 15.5, 14.3; FT-IR (thin film, KBr): $\nu$ (cm$^{-1}$): 2950, 2914, 1717, 1439, 1153; HRMS (CI) calcd C$_{12}$H$_{21}$O$_4$S [M + H]$^+$: 261.1161, found: 261.1156.

4-Ethyl 1,2-dimethyl pent-4-ene-1,2,4-tricarboxylate (3m): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 30:1 to 10:1) to give the colorless oil; 57% yield (30 mg); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 6.22 (s, 1H), 5.57 (s, 1H), 4.21 (q, $J$ = 7.1 Hz, 2H), 3.67 (s, 3H), 3.66 (s, 3H), 3.17 – 3.08 (m, 1H), 2.74 – 2.65 (m, 2H), 2.54 – 2.44 (m, 2H), 1.30 (t, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 174.7, 172.2, 166.5, 137.5, 127.6, 61.1, 52.0, 51.9, 40.4, 35.5, 34.5, 14.3; FT-IR (thin film, KBr): $\nu$ (cm$^{-1}$): 2956, 1736, 1709, 1438, 1165; HRMS (CI) calcd C$_{12}$H$_{19}$O$_6$ [M + H]$^+$: 259.1182, found: 259.1190.

4-Ethyl 1,3-dimethyl hex-5-ene-1,3,5-tricarboxylate (3n): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 30:1 to 10:1) to give the colorless oil; 63% yield (34 mg); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 6.18 (s, 1H), 5.57 (s, 1H), 4.20 (q, $J$ = 7.1 Hz, 2H), 3.65 (s, 3H), 3.63 (s, 3H), 2.75 – 2.66 (m, 1H), 2.59 (dd, $J$ = 14.0, 8.8 Hz, 1H), 2.49 (dd, $J$ = 14.0, 5.9 Hz, 1H), 2.38 – 2.26 (m, 2H), 1.95 – 1.81 (m, 2H), 1.28 (t, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 175.2, 173.3, 166.7, 137.8, 127.1, 60.9, 51.8, 51.7, 43.9, 34.8, 31.8, 27.1, 14.3; FT-IR (thin film, KBr): $\nu$ (cm$^{-1}$): 2956, 1712, 1435, 1159, 1138; HRMS (CI) calcd C$_{13}$H$_{21}$O$_6$ [M + H]$^+$: 273.1338, found: 273.1343.

Dimethyl 2-(2-methylallyl)pentanedioate (4a): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 40:1 to 20:1) to give the colorless oil; 43% yield (19 mg); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.76 (s, 1H), 4.70 (s, 1H), 3.66 (s, 6H), 2.71 – 2.55 (m, 1H), 2.47 – 2.22 (m, 3H), 2.15 (dd, $J$ = 14.1, 6.7 Hz, 1H), 1.86 (dd, $J$ = 14.7, 7.4 Hz, 2H), 1.71 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 175.7, 173.5, 142.6, 112.7, 51.8, 51.7, 43.1, 40.7, 31.8, 27.0, 22.2; FT-IR (thin film,
KBr): \( \nu \) (cm\(^{-1}\)): 2950, 1720, 1435, 1159, 891; HRMS (CI) calcd C\(_{11}\)H\(_{10}\)O\(_4\) [M + H]\(^+\): 215.1283, found: 215.1286.

5-Benzyl 1,3-dimethyl hex-5-ene-1,3,5-tricarboxylate (4b): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 20:1 to 5:1) to give the colorless oil; 57% yield (38 mg); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.46 – 7.27 (m, 5H), 6.25 (s, 1H), 5.62 (s, 1H), 5.20 (s, 2H), 3.65 (s, 3H), 3.62 (s, 3H), 2.79 – 2.68 (m, 1H), 2.67 – 2.58 (m, 1H), 2.57 – 2.47 (m, 1H), 2.40 – 2.24 (m, 2H), 1.97 – 1.79 (m, 2H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \( \delta \) 175.2, 173.3, 166.5, 137.6, 136.0, 128.7, 128.3, 128.2, 127.6, 66.7, 51.8, 51.7, 43.9, 34.9, 31.8, 27.1; FT-IR (thin film, KBr): \( \nu \) (cm\(^{-1}\)): 2953, 1714, 1432, 1156, 695; HRMS (CI) calcd C\(_{18}\)H\(_{23}\)O\(_6\) [M + H]\(^+\): 335.1495, found: 335.1500.

5-(\textit{tert}-Butyl) 1,3-dimethyl hex-5-ene-1,3,5-tricarboxylate (4c): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 20:1 to 5:1) to give the colorless oil; 57% yield (34 mg); \(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 6.09 (s, 1H), 5.49 (s, 1H), 3.65 (s, 3H), 3.64 (s, 3H), 2.75 – 2.66 (m, 1H), 2.55 (dd, \( J = 13.9, 8.6 \) Hz, 1H), 2.45 (dd, \( J = 13.9, 6.0 \) Hz, 1H), 2.39 – 2.26 (m, 2H), 1.95 – 1.80 (m, 2H), 1.48 (s, 9H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \( \delta \) 175.3, 173.4, 165.9, 139.2, 126.2, 81.0, 51.8, 51.7, 44.0, 35.0, 31.8, 28.2, 27.1; FT-IR (thin film, KBr): \( \nu \) (cm\(^{-1}\)): 2947, 1736, 1706, 1156, 846; HRMS (CI) calcd C\(_{15}\)H\(_{25}\)O\(_6\) [M + H]\(^+\): 301.1651, found: 301.1639.

Dimethyl 2-(2-cyanoallyl)pentanedioate (4d): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 20:1 to 5:1) to give the colorless oil; 64% yield (29 mg); \(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 5.92 (s, 1H), 5.79 (s, 1H), 3.70 (s, 3H), 3.68 (s, 3H), 2.79 – 2.72 (m, 1H), 2.68 – 2.60 (m, 1H), 2.42 – 2.31 (m, 3H), 1.97 – 1.88 (m, 2H); \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \( \delta \) 174.1, 173.0, 132.9, 120.3, 118.1, 52.1, 51.9, 43.1, 37.0, 31.0, 26.7; FT-IR (thin film, KBr): \( \nu \) (cm\(^{-1}\)): 2950, 1727, 1438, 1203, 1162; HRMS (CI) calcd C\(_{11}\)H\(_{16}\)NO\(_4\) [M + H]\(^+\): 226.1079, found: 226.1080.
Dimethyl 2-(2-phenylallyl)pentanedioate (4e): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 30:1 to 10:1) to give the colorless oil; 67% yield (37 mg); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.42 – 7.22 (m, 5H), 5.30 (s, 1H), 5.10 (s, 1H), 3.62 (s, 3H), 3.60 (s, 3H), 2.91 (dd, \(J = 14.2, 7.8\) Hz, 1H), 2.64 (dd, \(J = 14.2, 6.8\) Hz, 1H), 2.60 – 2.49 (m, 1H), 1.96 – 1.81 (m, 2H); \(^1\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 175.5, 173.4, 145.7, 140.4, 128.5, 127.8, 126.4, 115.0, 51.7, 51.7, 43.5, 38.2, 31.8, 26.8; FT-IR (thin film, KBr): \(\nu\) (cm\(^{-1}\)): 2953, 1726, 1203, 1162, 778; HRMS (CI) calcd C\(_{16}\)H\(_{21}\)O\(_4\) [M + H]\(^+\): 277.1440, found: 277.1440.

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\text{Br} \\
\text{CO}_2\text{Me} \\
\text{CO}_2\text{Me}
\end{array}
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Dimethyl 2-(2-(4-chlorophenyl)allyl)pentanedioate (4f): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 30:1 to 10:1) to give the colorless oil; 62% yield (39 mg); \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.36 – 7.26 (m, 4H), 5.27 (s, 1H), 5.10 (s, 1H), 3.62 (s, 3H), 3.59 (s, 3H), 2.85 (dd, \(J = 14.4, 8.0\) Hz, 1H), 2.61 (dd, \(J = 14.4, 6.7\) Hz, 1H), 2.54 – 2.47 (m, 1H), 2.37 – 2.28 (m, 1H), 2.27 – 2.19 (m, 1H), 1.94 – 1.80 (m, 2H); \(^1\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 175.3, 173.3, 144.6, 138.9, 133.6, 128.7, 127.7, 115.5, 51.8, 51.7, 43.5, 38.2, 31.7, 26.8; FT-IR (thin film, KBr): \(\nu\) (cm\(^{-1}\)): 2950, 1730, 1435, 1162, 831; HRMS (CI) calcd C\(_{16}\)H\(_{20}\)O\(_4\)\(^{35}\)Cl [M + H]\(^+\): 311.1050, found: 311.1054.

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\text{Cl} \\
\text{CO}_2\text{Me} \\
\text{CO}_2\text{Me}
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Dimethyl 2-(2-(4-bromophenyl)allyl)pentanedioate (4g): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 30:1 to 10:1) to give the colorless oil; 66% yield (47 mg); \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.45 (d, \(J = 8.3\) Hz, 2H), 7.23 (d, \(J = 8.3\) Hz, 2H), 5.28 (s, 1H), 5.11 (s, 1H), 3.62 (s, 3H), 3.59 (s, 3H), 2.85 (dd, \(J = 14.4, 8.0\) Hz, 1H), 2.60 (dd, \(J = 14.4, 6.7\) Hz, 1H), 2.55 – 2.45 (m, 1H), 2.36 – 2.28 (m, 1H), 2.28 – 2.18 (m, 1H), 1.93 – 1.82 (m, 2H); \(^1\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 175.1, 173.1, 144.5, 139.2, 131.5, 127.9, 121.6, 115.4, 51.6, 51.5, 43.3, 38.0, 31.6, 26.7; FT-IR (thin film, KBr): \(\nu\) (cm\(^{-1}\)): 2947, 1726, 1432, 1162, 831; HRMS (CI) calcd C\(_{16}\)H\(_{20}\)O\(_4\)\(^{79}\)Br [M + H]\(^+\): 355.0545, found: 355.0554.
Dimethyl 2-(2-(p-tolyl)allyl)pentanedioate (4h): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 30:1 to 10:1) to give the colorless oil; 63% yield (37 mg); ¹H NMR (600 MHz, CDCl₃) δ 7.26 (d, J = 7.9 Hz, 2H), 7.13 (d, J = 7.9 Hz, 2H), 5.26 (s, 1H), 5.05 (s, 1H), 3.62 (s, 3H), 3.60 (s, 3H), 2.88 (dd, J = 14.3, 7.7 Hz, 1H), 2.62 (dd, J = 14.3, 7.0 Hz, 1H), 2.57 – 2.50 (m, 1H), 2.35 (s, 3H), 2.32 – 2.28 (m, 1H), 2.28 – 2.19 (m, 1H), 1.92 – 1.84 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 175.5, 173.4, 145.4, 137.5, 137.4, 129.2, 126.2, 114.1, 51.7, 51.6, 43.5, 38.2, 31.7, 26.8, 21.2; FT-IR (thin film, KBr): ν (cm⁻¹): 2953, 1726, 1432, 1159, 828; HRMS (CI) calcd C₁₇H₂₃O₄ [M + H]⁺: 291.1596, found: 291.1599.

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Dimethyl 2-(2-(4-methoxyphenyl)allyl)pentanedioate (4i): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 30:1 to 10:1) to give the colorless oil; 60% yield (37 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.31 (d, J = 8.1 Hz, 2H), 6.86 (d, J = 8.2 Hz, 2H), 5.22 (s, 1H), 4.99 (d, J = 15.6 Hz, 1H), 3.81 (s, 3H), 3.62 (s, 3H), 3.60 (s, 3H), 2.87 (dd, J = 13.8, 7.4 Hz, 1H), 2.69 – 2.45 (m, 2H), 2.39 – 2.14 (m, 2H), 1.95 – 1.79 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 175.5, 173.4, 159.3, 132.8, 130.1, 127.5, 113.9, 113.5, 55.4, 51.74, 51.68, 43.5, 38.3, 31.8, 26.8; FT-IR (thin film, KBr): ν (cm⁻¹): 2950, 1729, 1510, 1242, 831; HRMS (CI) calcd C₁₇H₂₃O₅ [M + H]⁺: 307.1545, found: 307.1546.

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Dimethyl 2-(2-(naphthalen-2-yl)allyl)pentanedioate (4j): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 30:1 to 10:1) to give the colorless oil; 57% yield (37 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.88 – 7.76 (m, 4H), 7.57 – 7.42 (m, 3H), 5.45 (s, 1H), 5.21 (s, 1H), 3.60 (s, 6H), 3.03 (dd, J = 14.1, 7.8 Hz, 1H), 2.76 (dd, J = 14.2, 6.7 Hz, 1H), 2.65 – 2.54 (m, 1H), 2.40 – 2.19 (m, 2H), 2.00 – 1.88 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 175.5, 173.4, 145.5, 145.5, 137.7, 133.5, 133.0, 128.3, 128.1, 127.7, 126.3, 126.1, 125.0, 124.8, 115.5, 51.70, 51.67, 43.6, 38.2, 31.8, 26.9; FT-IR (thin film, KBr): ν (cm⁻¹): 2917, 1727, 1438, 1159, 748; HRMS (CI) calcd C₂₀H₂₃O₄ [M + H]⁺: 327.1596, found: 327.1603.

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6. NMR Spectra for the substrates and products

$^1$H NMR of 1a

$^{13}$C NMR of 1a
$^{19}$F NMR of 1a

$^1$H NMR of 1b
$^{13}$C NMR of 1b

$^{19}$F NMR of 1b
$^1$H NMR of 1c

$^{13}$C NMR of 1c
$^{13}$C NMR of 1d

$^{19}$F NMR of 1d
$^1$H NMR of 1e

$^{13}$C NMR of 1e
$^{19}$F NMR of 1e

$^1$H NMR of 1f
$^{13}$C NMR of 1f

$^{19}$F NMR of 1f
$^1$H NMR of 1g

$^{13}$C NMR of 1g

S30
$^{19}$F NMR of 1g

$^1$H NMR of 1h
$^{13}$C NMR of $1h$

$^{19}$F NMR of $1h$
$^1$H NMR of 1i

$^{13}$C NMR of 1i
\(^{19}\text{F} \text{NMR of } 1i\)

\[\text{Diagram showing } \text{F NMR spectrum of } 1i\]

\(^1\text{H} \text{NMR of } 1j\)

\[\text{Diagram showing } \text{H NMR spectrum of } 1j\]
$^{13}$C NMR of Ij

$^{19}$F NMR of Ij
$^1$H NMR of 1k

$^{13}$C NMR of 1k
$^{19}$F NMR of 1k

$^1$H NMR of 1l
$^{13}$C NMR of II

$^{19}$F NMR of II
$^1$H NMR of Im

$^{13}$C NMR of Im
$^{19}$F NMR of 1m

$^1$H NMR of 1n
$^{13}$C NMR of $\text{In}$

$^{19}$F NMR of $\text{In}$
\(^1\)H NMR of 2a

\[ \text{CO}_2\text{Et} \quad \text{SO}_2\text{Ph} \]

\(^{13}\)C NMR of 2a

\[ \text{CO}_2\text{Et} \quad \text{SO}_2\text{Ph} \]
$^1$H NMR of 2b

\[
\text{SO}_2\text{Ph}
\]

$^{13}$C NMR of 2b

\[
\text{SO}_2\text{Ph}
\]
$^{1}H$ NMR of 2c

$^{13}C$ NMR of 2c
$^1$H NMR of 2d

$^{13}$C NMR of 2d
$^1$H NMR of 2e

$^13$C NMR of 2e
$^{1}H$ NMR of 2g

$^{13}C$ NMR of 2g
$^1$H NMR of $2h$

$^13$C NMR of $2h$
$^1$H NMR of 2i

$^{13}$C NMR of 2i
$^1$H NMR of 2j

$^{13}$C NMR of 2j
$^1$H NMR of 2k

$^{13}$C NMR of 2k
$^1$H NMR of 3a

$^{13}$C NMR of 3a
$^1$H NMR of 3b

$^{13}$C NMR of 3b
$^{1}H\text{ NMR of } 3c$

$^{13}C\text{ NMR of } 3c$
$^1$H NMR of 3d

$^{13}$C NMR of 3d
$^1$H NMR of 3e

$^{13}$C NMR of 3e
$^1$H NMR of 3f

$^{13}$C NMR of 3f
$^1$H NMR of 3g

$^{13}$C NMR of 3g
$^1$H NMR of 3h

$^{13}$C NMR of 3h
$^1$H NMR of 3i

$^{13}$C NMR of 3i
$^1$H NMR of 3j

$^{13}$C NMR of 3j
$^1$H NMR of 3k

$^{13}$C NMR of 3k
$^{1}$H NMR of 3l

$^{13}$C NMR of 3l
$^1$H NMR of 3m

$^{13}$C NMR of 3m
$^1$H NMR of 3n

$^{13}$C NMR of 3n
$^1$H NMR of 4a

$^{13}$C NMR of 4a
$^1$H NMR of 4b

$^{13}$C NMR of 4b
$^1$H NMR of 4c

$^{13}$C NMR of 4c
$^{1}H$ NMR of $4d$

$^{13}C$ NMR of $4d$
$^1$H NMR of 4e

$^{13}$C NMR of 4e
$^1$H NMR of 4f

$^{13}$C NMR of 4f
$^1$H NMR of 4g

$^{13}$C NMR of 4g
$^1\text{H NMR of 4h}$

$^{13}\text{C NMR of 4h}$
$^{1}H$ NMR of 4i

$^{13}C$ NMR of 4i
$^1$H NMR of 4j

$^{13}$C NMR of 4j