Palladium-Catalyzed Reductive Electrocarboxylation of Allyl Esters with Carbon Dioxide

(Supporting Information)

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1 General Information

All the electrochemical reduction were performed in an undivided cell equipped with one platinum electrode (1.0×1.0 cm$^2$) and a magnesium rod as sacrificial anode unless otherwise noted. Solvents and commercially available reagents were used without purification. Column chromatography was performed using either 100-200 Mesh or 300-400 Mesh silica gel. Visualization of spots on TLC plate was accomplished with UV light (254 nm) and staining over I$_2$ chamber. All the platinum electrodes were purchased from Ida Hengsheng Technology Co., Ltd, Tianjin, China. The potentiostat (E36105A, KEYSIGHT) was purchased from Shiqiang Telecom Co., Ltd, Shenzhen, China. The all commercial reagents were purchased from TCI, Sigma-Aldrich, Adamas-beta, 9-Ding chemistry and Energy Chemical of the highest purity grade. They were used without further purification unless specified. $^1$H NMR and $^{13}$C NMR spectra were recorded on Agilent AV 400, Varian Inova 400 (400 MHz and 100 MHz, respectively). $^{19}$F NMR spectra were recorded on Agilent AV 400, Varian Inova 400 (376 MHz) instrument and are reported relative to the CFCl$_3$ as the internal standard. The peaks were internally referenced to TMS (0.00 ppm) or residual undeuterated solvent signal. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. Infrared spectra were obtained on a Bio-Rad FTS-185 instrument. High resolution mass spectra were recorded at the Center for Mass Spectrometry, Shanghai Institute of Organic Chemistry. Analytical and spectral data of all those known compounds are exactly matching with the reported values.
2 Structures of Starting Materials

Cinnamyl ester (3a-3g)
3 Synthesis and Characterization of Starting Materials

General scheme 1 for the synthesis of 1a, 1c-1u

General Procedure A: Synthesis of α, β-Unsaturated Esters from Aldehydes:
To a stirred solution of the aldehyde (1.0 equiv) in CH₂Cl₂ (10 mL/g aldehyde) was added ethyl 2-(triphenylphosphoranylidene)acetate (1.05 equiv). The reaction was stirred overnight at rt, concentrated in vacuo, the residue triturated with PE / Et₂O (9:1), and the solids removed by filtration. The solvent was removed in vacuo and the crude residue purified by flash chromatography on silica gel to leave the pure α,β-unsaturated esters.

General Procedure B: Synthesis of α, β-Unsaturated Esters from Acids:
To a stirred solution of the α,β-unsaturated acid (1.0 equiv) in ethanol (10 mL / g acid) was added conc. H₂SO₄ (0.1 mL / g acid). The reaction was heated at reflux for 3 h, allowed to cool, and concentrated in vacuo. The residue was neutralised with NaHCO₃ (sat. aq.), extracted with EtOAc (3 equal volume) and the combined organics washed with brine (equal volume). The organic layer was dried over Na₂SO₄, filtered, and concentrated in vacuo to leave the pure α,β-unsaturated esters.

General Procedure C: Synthesis of allyl alcohol
To a stirred solution of the α, β-unsaturated ester (1.0 equiv) in anhydrous CH₂Cl₂ (0.2 M) at −78 °C under N₂ was added DIBAL-H (1.0-1.2 M in toluene or hexane, 2.2 equiv) dropwise. The reaction was stirred for 1.5 h at −78 °C, and quenched with NaOH (10% aq.) (equal volume). The resultant mixture was allowed to warm to rt and stirred for 1 h. The layers were separated and the aqueous layer extracted with CH₂Cl₂ (2 equal volume). The combined organics were washed with brine (equal volume), dried over Na₂SO₄, filtered, and concentrated in vacuo to leave the pure allylic alcohols.

General Procedure D: Synthesis of allyl acetate
To a stirred solution of allylic alcohol in CH₂Cl₂ (1.1M) was added Ac₂O (2.0 equiv) and DMAP (0.05 equiv). The reaction was stirred at room temperature for 1h, and then CH₃OH (8.0 equiv) was added and stirring continued for a further 1h. The reaction was mixture was taken up in hexanes (2.5 equal volume DCM), successively washed with H₂O and a sat. NaHCO₃ solution (2 x equal volume DCM), and dried over MgSO₄. The solution was removed under vacuum and the crude product was purified by
chromatography on SiO$_2$ with hexane/EtOAc to afford the product

**(E)-3-(4-Bromophenyl)allyl acetate (1a)**

![Structural formula of (E)-3-(4-Bromophenyl)allyl acetate](image)

**Route for 1a**

Following general procedure B, the reaction of (E)-3-(4-Bromophenyl)acrylic acid (S1) (5.0 g, 22.0 mmol, 1.0 equiv) with conc. H$_2$SO$_4$ (0.50 mL) in EtOH (50 mL) gave the title compound S2 (5.15 g, 20.2 mmol, 92%) as a colorless oil that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl 3-(4-Bromophenyl)acrylate (S2) (5.10 g, 20.0 mmol, 1.0 equiv) in anhydrous CH$_2$Cl$_2$ (100 mL) with DIBAL-H (1.2 M in toluene, 36.7 mL, 44.0 mmol, 2.2 equiv) gave the title compound S3 (4.81 g, 17.5 mmol, 88%) as a white solid that was used without further purification.

Following general procedure D, the reaction of (E)-3-(4-Bromophenyl)prop-2-en-1-ol (S3) (5.00 g, 22.0 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (20 mL) with Ac$_2$O (4.30 mL, 44.0 mmol, 2.0 equiv) and DMAP (133.6 mg, 1.1 mmol, 0.05 equiv) gave the title compound 1a (5.40 g, 21.2 mmol, 96%) as a colorless oil.

**$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.43 (d, $J = 6.8$ Hz, 2H), 7.23 (d, $J = 6.8$ Hz, 2H), 6.57 (d, $J = 16.0$ Hz, 1H), 6.34–6.13 (m, 1H), 4.69 (d, $J = 6.3$ Hz, 2H), 2.08 (s, 3H). **$^{13}$C NMR** (101 MHz, CDCl$_3$) $\delta$ 170.48, 135.10, 132.54, 131.64, 128.08, 124.09, 64.70, 20.89.

**(E)-3-(p-Tolyl)allyl acetate (1c)**

![Structural formula of (E)-3-(p-Tolyl)allyl acetate](image)

**Route for 1c**

Following general procedure B, the reaction of (E)-3-(p-Tolyl)acrylic acid (S4) (5.0 g, 30.8 mmol, 1.0 equiv) with conc. H$_2$SO$_4$ (0.50 mL) in EtOH (50 mL) gave the title compound S5 (5.74 g, 30.2 mmol, 98%) as a colorless oil that was used without further purification.
purification.

Following general procedure C, the reaction of (E)-ethyl 3-(p-Tolyl)acrylate (S5) (5.70 g, 30.0 mmol, 1.0 equiv) in anhydrous CH$_2$Cl$_2$ (150 mL) with DIBAL-H (1.0 M in toluene, 66.0 mL, 66.0 mmol, 2.2 equiv) gave the title compound S6 (4.36 g, 29.4 mmol, 98%) as a white solid that was used without further purification.

Following general procedure D, the reaction of (E)-3-(p-Tolyl)prop-2-en-1-ol (S6) (4.3 g, 29.0 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (25 mL) with Ac$_2$O (5.7 mL, 58.0 mmol, 2.0 equiv) and DMAP (177.1 mg, 1.45 mmol, 0.05 equiv) gave the title compound 1c (4.30 g, 22.6 mmol, 78%) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.29 (d, $J = 8.1$ Hz, 2H), 7.13 (d, $J = 8.0$ Hz, 2H), 6.62 (d, $J = 15.9$ Hz, 1H), 6.24 (dt, $J = 15.9$, 6.5 Hz, 1H), 4.72 (d, $J = 6.6$ Hz, 2H), 2.34 (s, 3H), 2.10 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.76, 137.91, 134.22, 129.32, 126.56, 122.08, 65.22, 21.22, 20.97.

(E)-(4-Methoxyphenyl)allyl acetate (1d)  

Route for 1d

Following general procedure B, the reaction of (E)-3-(4-Methoxyphenyl)acrylic acid (S7) (5.0 g, 28.1 mmol, 1.0 equiv) with conc. H$_2$SO$_4$ (0.50 mL) in EtOH (50 mL) gave the title compound S8 (5.03 g, 24.4 mmol, 87%) as a white solid that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl-3-(4-Methoxyphenyl)acrylate (S8) (3.3 g, 16.0 mmol, 1.0 equiv) in anhydrous CH$_2$Cl$_2$ (80 mL) with DIBAL-H (1.0 M in hexane, 35.2 mL, 35.2 mmol, 2.2 equiv) gave the title compound S9 (2.2 g, 14.8 mmol, 93%) as a white solid that was used without further purification.

Following general procedure D, the reaction of (E)-3-(4-Methoxyphenyl)prop-2-en-1-ol (S9) (2.0 g, 13.5 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (13 mL) with Ac$_2$O (2.60 mL, 27.0 mmol, 2.0 equiv) and DMAP (83.1 mg, 0.68 mmol, 0.05 equiv) gave the title compound 1d (1.8 g, 8.8 mmol, 65%) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.32 (d, $J = 8.7$ Hz, 2H), 6.85 (d, $J = 8.7$ Hz, 2H), 6.59 (d, $J = 15.8$ Hz, 1H), 6.14 (dt, $J = 15.8$, 6.6 Hz, 1H), 4.69 (d, $J = 6.6$ Hz, 2H), 3.79 (s, 3H), 2.08 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.84, 159.56, 133.98, 128.89,
127.84, 120.79, 113.98, 77.50, 77.18, 76.86, 65.33, 55.20, 20.99.

(E)-3-(4-(tert-Butyl)phenyl)allyl acetate (1e)

Following general procedure A, the reaction of 4-(tert-butyl)benzaldehyde (S10) (4.87 g, 30.0 mmol, 1.0 equiv) with the phosphorane (10.90 g, 31.5 mmol, 1.05 equiv) in CH$_2$Cl$_2$ (50 mL) gave the title compound S11 (6.06 g, 26.1 mmol, 87%) as a white solid that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl-3-(4-(tert-Butyl)phenyl)acrylate (S11) (4.00 g, 17.2 mmol, 1.0 equiv) in anhydrous CH$_2$Cl$_2$ (86 mL) with DIBAL-H (1.0 M in hexane, 37.9 mL, 37.9 mmol, 2.2 equiv) gave the title compound S12 (3.2 g, 16.8 mmol, 98%) as a white solid that was used without further purification.

Following general procedure D, the reaction of (E)-3-(4-(tert-Butyl)phenyl)prop-2-en-1-ol (S12) (3.20 g, 16.8 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (15 mL) with Ac$_2$O (3.20 mL, 33.6 mmol, 2.0 equiv) and DMAP (102.6 mg, 0.84 mmol, 0.05 equiv) gave the title compound 1e (3.79 g, 16.3 mmol, 97%) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) \(\delta\) 7.39–7.33 (m, 4H), 6.66 (d, \(J = 15.9\) Hz, 1H), 6.28 (dt, \(J = 15.9, 6.5\) Hz, 1H), 4.74 (d, \(J = 6.5\) Hz, 2H), 2.11 (s, 3H), 1.34 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) \(\delta\) 170.77, 151.17, 134.13, 133.45, 126.40, 125.53, 122.36, 65.23, 34.61, 31.30, 21.00.

(E)-3-(4-Fluorophenyl)allyl acetate (1f)

Following general procedure B, the reaction of (E)-3-(4-Fluorophenyl)acrylic acid (S13) (5.0 g, 30.1 mmol, 1.0 equiv) with conc. H$_2$SO$_4$ (0.50 mL) in EtOH (50 mL) gave the title compound S14 (4.97 g, 25.6 mmol, 85%) as a colorless oil that was used without further purification.
Following general procedure C, the reaction of (E)-ethyl-3-(4-Fluorophenyl)acrylate (S14) (4.90 g, 25.2 mmol, 1.0 equiv) in anhydrous CH₂Cl₂ (120 mL) with DIBAL-H (1.0 M in toluene, 56.0 mL, 55.4 mmol, 2.2 equiv) gave the title compound S15 (3.79 g, 24.9 mmol, 99%) as a white solid that was used without further purification.

Following general procedure D, the reaction of (E)-3-(4-Fluorophenyl)prop-2-en-1-ol (S15) (2.0 g, 13.1 mmol, 1.0 equiv) in CH₂Cl₂ (12 mL) with Ac₂O (2.5 mL, 26.2 mmol, 2.0 equiv) and DMAP (80.3 mg, 0.66 mmol, 0.05 equiv) gave the title compound 1f (2.02 g, 10.4 mmol, 79%) as a colorless oil.

1H NMR (400 MHz, CDCl₃) δ 7.36–7.26 (m, 2H), 6.99 (t, \( J = 8.6 \) Hz, 2H), 6.59 (d, \( J = 15.9 \) Hz, 1H), 6.18 (dt, \( J = 15.9, 6.5 \) Hz, 1H), 4.69 (d, \( J = 6.5 \) Hz, 2H), 2.08 (s, 3H).

13C NMR (101 MHz, CDCl₃) δ 170.71, 162.49 (d, \( J = 247.4 \) Hz), 132.87, 132.36 (d, \( J = 3.3 \) Hz), 128.13 (d, \( J = 8.1 \) Hz), 122.93 (d, \( J = 2.3 \) Hz), 115.46 (d, \( J = 21.6 \) Hz), 64.87, 20.81.

19F NMR (376 MHz, CDCl₃) δ -113.68.

(E)-3-(4-(Trifluoromethyl)phenyl)allyl acetate (1g) ¹

Following general procedure B, the reaction of (E)-3-(4-(Trifluoromethyl)phenyl)acrylic acid (S16) (2.0 g, 9.25 mmol, 1.0 equiv) with conc. H₂SO₄ (0.20 mL) in EtOH (20 mL) gave the title compound S17 (2.20 g, 9.01 mmol, 97%) as a white solid that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl 3-(4-(Trifluoromethyl)phenyl)acrylate (S17) (2.16 g, 8.84 mmol, 1.0 equiv) in anhydrous CH₂Cl₂ (45 mL) with DIBAL-H (1.2 M in toluene, 16.21 mL, 19.45 mmol, 2.2 equiv) gave the title compound S18 (1.70 g, 8.40 mmol, 95%) as a white solid that was used without further purification.

Following general procedure D, the reaction of (E)-3-(4-(Trifluoromethyl)phenyl)prop-2-en-1-ol (S18) (1.65 g, 8.16 mmol, 1.0 equiv) in CH₂Cl₂ (8 mL) with Ac₂O (1.53 mL, 16.32 mmol, 2.0 equiv) and DMAP (49.8 mg, 0.41 mmol, 0.05 equiv) gave the title compound 1g (1.91 g, 7.83 mmol, 96%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, \( J = 8.2 \) Hz, 2H), 7.46 (d, \( J = 8.1 \) Hz, 2H), 6.66 (d, \( J = 16.0 \) Hz, 1H), 6.36 (dt, \( J = 15.9, 6.2 \) Hz, 1H), 4.74 (d, \( J = 6.2 \) Hz, 2H), 2.10 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -62.64.

(E)-3-(4-Chlorophenyl)allyl acetate (1h) ¹
Route for 1h

Following general procedure A, the reaction of 4-Chlorobenzaldehyde (S19) (2.81 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv) in CH$_2$Cl$_2$ (30 mL) gave the title compound S20 (4.17 g, 19.8 mmol, 99%) as a colorless oil that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl 3-(4-Chlorophenyl)acrylate (S20) (4.10 g, 19.5 mmol, 1.0 equiv) in anhydrous CH$_2$Cl$_2$ (90 mL) with DIBAL-H (1.0 M in toluene, 43.0 mL, 42.9 mmol, 2.2 equiv) gave the title compound S21 (3.22 g, 19.1 mmol, 98%) as a colorless oil that was used without further purification.

Following general procedure D, the reaction of (E)-3-(4-Chlorophenyl)prop-2-en-1-ol (S21) (3.00 g, 17.8 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (16 mL) with Ac$_2$O (3.5 mL, 35.6 mmol, 2.0 equiv) and DMAP (108.7 mg, 0.89 mmol, 0.05 equiv) gave the title compound 1h (3.18 g, 15.1 mmol, 85%) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35–7.18 (m, 4H), 6.58 (d, $J = 15.9$ Hz, 1H), 6.24 (dt, $J = 15.9, 6.4$ Hz, 1H), 4.70 (d, $J = 6.4$ Hz, 2H), 2.09 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.69, 134.68, 133.63, 132.68, 128.73, 127.78, 123.90, 64.79, 20.92.

(E)-3-(2-Fluorophenyl)allyl acetate (1i)  

Route for 1i

Following general procedure A, the reaction of 2-Fluorobenzaldehyde (S22) (2.5 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv) in CH$_2$Cl$_2$ (25 mL) gave the title compound S23 (3.50 g, 18.0 mmol, 90%) as a colorless oil that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl 3-(2-Fluorophenyl)acrylate (S23) (3.50 g, 18.0 mmol, 1.0 equiv) in anhydrous CH$_2$Cl$_2$ (90 mL) with DIBAL-H (1.0
M in toluene, 39.6 mL, 39.6 mmol, 2.2 equiv) gave the title compound S24 (2.50 g, 16.4 mmol, 91%) as a colorless oil that was used without further purification.

Following general procedure D, the reaction of (E)-3-(2-Fluorophenyl)prop-2-en-1-ol (S24) (2.50 g, 16.4 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (15 mL) with Ac$_2$O (3.1 mL, 32.8 mmol, 2.0 equiv) and DMAP (100.1 mg, 0.82 mmol, 0.05 equiv) gave the title compound 1i (2.84 g, 14.6 mmol, 89%) as a colorless oil. mixture of cis and trans isomers

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.38 (t, $J = 7.6$ Hz, 1H), 7.20–7.11 (m, 1H), 7.06–6.93 (m, 2H), 6.74 (d, $J = 16.1$ Hz, 1H), 6.32 (dt, $J = 16.0$, 6.2 Hz, 1H), 4.68 (d, $J = 6.2$ Hz, 2H), 2.04 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.69, 160.26 (d, $J = 249.7$ Hz), 129.31 (d, $J = 8.5$ Hz), 127.54 (d, $J = 3.6$ Hz), 126.21 (d, $J = 3.5$ Hz), 125.84 (d, $J = 5.1$ Hz), 124.11 (d, $J = 3.6$ Hz), 123.95 (d, $J = 12.1$ Hz), 115.70 (d, $J = 22.1$ Hz), 65.00, 20.82. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -115.70 – -121.34 (m, 1F).

(E)-3-(2-Chlorophenyl)allyl acetate (1j) 3

Route for 1j

Following general procedure A, the reaction of 2-Chlorobenzaldehyde (S25) (2.81 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv) in CH$_2$Cl$_2$ (30 mL) gave the title compound S26 (3.79 g, 18.0 mmol, 90%) as a colorless oil that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl 3-(2-Chlorophenyl)acrylate (S26) (3.70 g, 17.6 mmol, 1.0 equiv) in anhydrous CH$_2$Cl$_2$ (80 mL) with DIBAL-H (1.0 M in toluene, 39.0 mL, 38.7 mmol, 2.2 equiv) gave the title compound S27 (2.82 g, 16.7 mmol, 95%) as a colorless oil that was used without further purification.

Following general procedure D, the reaction of (E)-3-(2-Chlorophenyl)prop-2-en-1-ol (S27) (2.70 g, 16.0 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (15 mL) with Ac$_2$O (3.2 mL, 32.0 mmol, 2.0 equiv) and DMAP (97.7 mg, 0.80 mmol, 0.05 equiv) gave the title compound 1j (3.03 g, 14.4 mmol, 90%) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.39 (dd, $J = 7.1$, 2.1 Hz, 1H), 7.26–7.18 (m, 1H), 7.13 – 7.01 (m, 2H), 6.93 (d, $J = 15.9$ Hz, 1H), 6.23–6.07 (m, 1H), 4.64 (d, $J = 4.5$, 1.6 Hz, 2H), 1.99 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.38, 134.24, 133.04, 129.59, 129.56, 128.94, 126.86, 126.83, 126.16, 64.64, 20.73.

(E)-3-(2-Bromophenyl)allyl acetate (1k) 3
Following general procedure B, the reaction of (E)-3-(2-Bromophenyl)acrylic acid (S28) (5.0 g, 22.0 mmol, 1.0 equiv) with conc. H$_2$SO$_4$ (0.50 mL) in EtOH (50 mL) gave the title compound S29 (5.0 g, 19.6 mmol, 89%) as a colorless oil that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl 3-(2-Bromophenyl)acrylate (S29) (4.80 g, 18.8 mmol, 1.0 equiv) in anhydrous CH$_2$Cl$_2$ (95 mL) with Dibal-H (1.0 M in hexane, 41.4 mL, 41.4 mmol, 2.2 equiv) gave the title compound S30 (4.70 g, 18.4 mmol, 98%) as a colorless oil that was used without further purification.

Following general procedure D, the reaction of (E)-3-(2-Bromophenyl)prop-2-en-1-ol (S30) (1.6 g, 7.0 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (7 mL) with Ac$_2$O (1.3 mL, 14.0 mmol, 2.0 equiv) and DMAP (43.0 mg, 0.35 mmol, 0.05 equiv) gave the title compound 1k (1.7 g, 6.7 mmol, 95%) as a colourless oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.54–7.46, (m, 2H), 7.24 (t, $J = 7.6$ Hz, 1H), 7.08 (t, $J = 7.6$ Hz, 1H), 6.98 (d, $J = 15.9$ Hz, 1H), 6.21 (dt, $J = 15.8$, 6.2 Hz, 1H), 4.74 (d, $J = 6.2$ Hz, 2H), 2.09 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.60, 136.03, 132.92, 132.34, 129.26, 127.51, 127.13, 126.26, 123.69, 64.68, 20.93.

(E)-3-(2-(Trifluoromethyl)phenyl)allyl acetate (1l)

Following general procedure A, the reaction of 2-Trifluoromethylbenzaldehyde (S31) (3.48 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv) in CH$_2$Cl$_2$ (35 mL) gave the title compound S32 (4.20 g, 17.2 mmol, 86%) as a white solid that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl-3-(2-(Trifluoromethyl)phenyl)acryl-
yl)acrylate (S32) (4.00 g, 16.4 mmol, 1.0 equiv) in anhydrous CH₂Cl₂ (80 mL) with DIBAL-H (1.0 M in toluene, 33.0 mL, 32.8 mmol, 2.2 equiv) gave the title compound S33 (2.95 g, 14.6 mmol, 89%) as a white solid that was used without further purification.

Following general procedure D, the reaction of (E)-3-(2-(Trifluoromethyl)phenyl)prop-2-en-1-ol (S33) (2.90 g, 14.3 mmol, 1.0 equiv) in CH₂Cl₂ (13 mL) with Ac₂O (2.80 mL, 28.6 mmol, 2.0 equiv) and DMAP (88.0 mg, 0.72 mmol, 0.05 equiv) gave the title compound 1l (3.00 g, 13.4 mmol, 94%) as a colorless oil. mixture of cis and trans isomers

¹H NMR (400 MHz, CDCl₃) δ 7.67–7.60 (m, 2H), 7.50 (t, J = 7.5 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.02 (d, J = 15.9 Hz, 1H), 6.34–6.03 (m, 1H), 4.76 (d, J = 5.9 Hz, 2H), 2.12 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -59.54. HRMS (ESI-TOF) calcd for C₁₂H₁₅F₃NO₂ [M+NH₄]⁺: 262.1049, found: 262.105.

(E)-3-(3-Bromophenyl)allyl acetate (1m) ⁴

Route for 1m

Following general procedure A, the reaction of 3-Bromobenzaldehyde (S34) (3.7 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv) in CH₂Cl₂ (40 mL) gave the title compound S35 (4.80 g, 18.8 mmol, 94%) as a colorless oil that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl-3-(3-Bromophenyl)acrylate (S35) (4.80 g, 18.8 mmol, 1.0 equiv) in anhydrous CH₂Cl₂ (100 mL) with DIBAL-H (1.0 M in toluene, 41.4 mL, 41.4 mmol, 2.2 equiv) gave the title compound S36 (3.2 g, 15.0 mmol, 80%) as a colorless oil that was used without further purification.

Following general procedure D, the reaction of (E)-3-(3-Bromophenyl)prop-2-en-1-ol (S36) (3.20 g, 15.0 mmol, 1.0 equiv) in CH₂Cl₂ (30 mL) with Ac₂O (2.80 mL, 30.0 mmol, 2.0 equiv) and DMAP (84.0 mg, 0.75 mmol, 0.05 equiv) gave the title compound 1m (3.67 g, 14.4 mmol, 96%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.44 (s, 1H), 7.29 (d, J = 7.8 Hz, 1H), 7.19 (d, J = 7.6 Hz, 1H), 7.08 (t, J = 7.8 Hz, 1H), 6.46 (d, J = 15.9 Hz, 1H), 6.19 (dt, J = 12.8, 6.1 Hz, 1H), 4.64 (d, J = 6.2 Hz, 2H), 2.03 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.70, 138.32, 132.28, 130.84, 130.10, 129.40, 125.23, 124.84, 122.74, 64.64, 20.95.

(E)-3-(3-Fluoro-4-methoxyphenyl)allyl acetate (1n)
Following general procedure A, the reaction of 3-Fluoro-4-methoxybenzaldehyde (S37) (3.1 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv) in CH₂Cl₂ (30 mL) gave the title compound S38 (4.00 g, 17.83 mmol, 89%) as a white solid that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl-3-(3-Fluoro-4-methoxyphenyl)acrylate (S38) (3.95 g, 17.6 mmol, 1.0 equiv) in anhydrous CH₂Cl₂ (90 mL) with DIBAL-H (1.2 M in toluene, 32.3 mL, 38.72 mmol, 2.2 equiv) gave the title compound S39 (3.06 g, 16.8 mmol, 95%) as a colorless oil that was used without further purification.

Following general procedure D, the reaction of (E)-3-(3-Fluoro-4-methoxyphenyl)prop-2-en-1-ol (S39) (3.06 g, 16.8 mmol, 1.0 equiv) in CH₂Cl₂ (30 mL) with Ac₂O (3.2 mL, 33.6 mmol, 2.0 equiv) and DMAP (94.2 mg, 0.84 mmol, 0.05 equiv) gave the title compound 1n (3.27 g, 14.6 mmol, 87%) as a colorless oil.

**1H NMR** (400 MHz, CDCl₃) δ 7.13 (d, J = 12.4 Hz, 1H), 7.05 (d, J = 8.4 Hz, 1H), 6.88 (t, J = 8.5 Hz, 1H), 6.53 (d, J = 15.9 Hz, 1H), 6.19–6.05 (m, 1H), 4.68 (d, J = 6.4 Hz, 2H), 3.86 (s, 3H), 2.08 (s, 3H).

**13C NMR** (101 MHz, CDCl₃) δ 170.68, 152.26 (d, J = 245.5 Hz), 147.44 (d, J = 10.9 Hz), 132.64 (d, J = 2.2 Hz), 129.55 (d, J = 6.5 Hz), 123.00 (d, J = 3.3 Hz), 122.27, 113.44 (d, J = 18.7 Hz), 113.05 (d, J = 2.2 Hz), 64.83, 55.98, 20.79.

**19F NMR** (376 MHz, CDCl₃) δ -135.24.

**HRMS** (EI) calcd for C₁₂H₁O₃F: 224.0849, found: 224.0852.

(E)-3-(2-Bromo-4-methylphenyl)allyl acetate (1o)

Following general procedure A, the reaction of 2-Bromo-4-methylbenzaldehyde (S40) (3.98 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv)
in CH$_2$Cl$_2$ (40 mL) gave the title compound S41 (5.22 g, 19.4 mmol, 97%) as a white solid that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl-3-(2-Bromo-4-methylphenyl)acrylate (S41) (5.00 g, 18.6 mmol, 1.0 equiv) in anhydrous CH$_2$Cl$_2$ (90 mL) with DIBAL-H (1.0 M in toluene, 41.0 mL, 40.9 mmol, 2.2 equiv) gave the title compound S42 (4.14 g, 18.2 mmol, 98%) as a colorless oil that was used without further purification.

Following general procedure D, the reaction of (E)-3-(2-Bromo-4-methoxyphenyl)prop-2-en-1-ol (S42) (4.10 g, 18.1 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (16 mL) with Ac$_2$O (3.5 mL, 36.2 mmol, 2.0 equiv) and DMAP (110.5 mg, 0.91 mmol, 0.05 equiv) gave the title compound 1o (3.88 g, 14.4 mmol, 80%) as a colorless oil. mixture of cis and trans isomers

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 (d, $J$ = 8.1 Hz, 1H), 7.37 (s, 1H), 7.11–7.04 (m, 1H), 6.95 (d, $J$ = 15.7 Hz, 1H), 6.18 (dt, $J$ = 15.8, 6.4 Hz, 1H), 4.74 (d, $J$ = 6.3 Hz, 2H), 2.30 (s, 3H), 2.10 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.67, 139.58, 133.28, 133.07, 132.39, 128.41, 126.76, 125.13, 123.51, 64.86, 20.95, 20.75. HRMS (ESI-TOF) calcd for C$_{12}$H$_{17}$BrNO$_2$ [M+NH$_4$]$^+$: 286.0437, found: 284.0436.

(E)-3-(2-Bromo-4-fluorophenyl)allyl acetate (1p)

Route for 1p

Following general procedure A, the reaction of 2-Bromo-4-fluorobenzaldehyde (S43) (4.06 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv) in CH$_2$Cl$_2$ (40 mL) gave the title compound S44 (5.30 g, 19.4 mmol, 97%) as a white solid that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl-3-(2-Bromo-4-fluorophenyl)acrylate (S44) (5.00 g, 18.3 mmol, 1.0 equiv) in anhydrous CH$_2$Cl$_2$ (90 mL) with DIBAL-H (1.0 M in toluene, 41.0 mL, 40.3 mmol, 2.2 equiv) gave the title compound S45 (2.80 g, 12.1 mmol, 66%) as a colorless oil that was used without further purification.

Following general procedure D, the reaction of (E)-3-(2-Bromo-4-fluorophenyl)prop-2-en-1-ol (S45) (2.70 g, 11.7 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (11 mL) with Ac$_2$O (2.3 mL, 23.4 mmol, 2.0 equiv) and DMAP (71.5 mg, 0.59 mmol, 0.05 equiv) gave the title
compound 1p (2.70 g, 9.9 mmol, 85%) as a white solid.

^1^H NMR (400 MHz, CDCl₃) δ 7.53–7.43 (m, 1H), 7.30 (d, J = 8.2 Hz, 1H), 7.01 (t, J = 8.3 Hz, 1H), 6.92 (d, J = 15.8 Hz, 1H), 6.25–6.10 (m, 1H), 4.75 (d, J = 6.2 Hz, 2H), 2.12 (s, 3H). ^1^C NMR (101 MHz, CDCl₃) δ 170.74, 161.85 (d, J = 251.9 Hz), 132.43, 131.46, 128.10 (d, J = 8.4 Hz), 126.05, 123.60 (d, J = 9.3 Hz), 120.00 (d, J = 24.4 Hz), 114.94 (d, J = 21.3 Hz), 64.64, 20.96. ^1^F NMR (376 MHz, CDCl₃) δ -112.02. HRMS (EI) calcd for C₁₁H₁₀O₂FBr: 271.9848, found: 271.9853.

(E)-3-(2-Bromo-4-methoxyphenyl)allyl acetate (1q)

Following general procedure A, the reaction of 2-Bromo-4-methoxybenzaldehyde (S₄₆) (4.30 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv) in CH₂Cl₂ (45 mL) gave the title compound S₄₇ (4.73 g, 16.6 mmol, 83%) as a white solid that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl-3-(4-Bromo-2-methoxyphenyl)acrylate (S₄₇) (4.70 g, 16.5 mmol, 1.0 equiv) in anhydrous CH₂Cl₂ (80 mL) with DIBAL-H (1.0 M in toluene, 36.3 mL, 36.3 mmol, 2.2 equiv) gave the title compound S₄₈ (3.93 g, 16.2 mmol, 98%) as a colorless oil that was used without further purification.

Following general procedure D, the reaction of (E)-3-(2-Bromo-4-methoxyphenyl)prop-2-en-1-ol (S₄₈) (3.90 g, 16.0 mmol, 1.0 equiv) in CH₂Cl₂ (15 mL) with Ac₂O (3.1 mL, 32.0 mmol, 2.0 equiv) and DMAP (97.7 mg, 0.80 mmol, 0.05 equiv) gave the title compound 1q (3.97 g, 13.9 mmol, 87%) as a colorless oil. mixture of cis and trans isomers

^1^H NMR (400 MHz, CDCl₃) δ 7.43 (d, J = 8.7 Hz, 1H), 7.07 (s, 1H), 6.91 (d, J = 15.7 Hz, 1H), 6.82 (d, J = 8.7 Hz, 1H), 6.11 (dt, J = 15.5, 6.5 Hz, 1H), 4.72 (d, J = 6.4 Hz, 1H), 3.78 (s, 3H), 2.09 (s, 3H). ^1^C NMR (101 MHz, CDCl₃) δ 170.59, 159.65, 132.05, 128.38, 127.54, 124.08, 123.94, 117.57, 114.03, 64.91, 55.40, 20.88. HRMS (EI) calcd for C₁₂H₁₄O₂Br: 284.0048, found: 284.0045.

(E)-3-(4-Bromo-2-methoxyphenyl)allyl acetate (1r)

S15
Route for 1r

Following general procedure A, the reaction of 4-Bromo-2-methoxybenzaldehyde (S49) (4.3 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv) in CH₂Cl₂ (45 mL) gave the title compound S50 (5.53 g, 19.4 mmol, 97%) as a white solid that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl-3-(4-Bromo-2-methoxyphenyl)acrylate (S50) (5.40 g, 18.9 mmol, 1.0 equiv) in anhydrous CH₂Cl₂ (95 mL) with DIBAL-H (1.0 M in toluene, 41.6 mL, 41.6 mmol, 2.2 equiv) gave the title compound S51 (3.08 g, 12.7 mmol, 67%) as a colorless oil that was used without further purification.

Following general procedure D, the reaction of (E)-3-(4-Bromo-2-methoxyphenyl)prop-2-en-1-ol (S51) (3.00 g, 12.3 mmol, 1.0 equiv) in CH₂Cl₂ (12 mL) with Ac₂O (2.3 mL, 24.6 mmol, 2.0 equiv) and DMAP (75.1 mg, 0.62 mmol, 0.05 equiv) gave the title compound 1r (3.25 g, 11.4 mmol, 93%) as a white solid. mixture of cis and trans isomers

¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, J = 8.1 Hz, 1H), 6.90 (s, 1H), 6.86 (d, J = 8.1 Hz, 1H), 6.59 (d, J = 15.8 Hz, 1H), 6.39–6.18 (m, 1H), 4.72 (d, J = 6.2 Hz, 2H), 3.91 (s, 3H), 2.11 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.80, 155.88, 136.90, 133.30, 133.18, 124.08, 120.18, 111.30, 109.69, 64.79, 56.14, 20.99. HRMS (EI) calcd for C₁₂H₁₃O₃Br: 284.0048, found: 284.0056.

(E)-3-(Naphthalen-2-yl)allyl acetate (1s) ⁵

Route for 1s

Following general procedure A, the reaction of 2-Naphthaldehyde (S52) (3.12 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv) in CH₂Cl₂ (30 mL) gave the title compound S53 (4.16 g, 18.4 mmol, 92%) as a white solid that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl-3-(Naphthalen-2-yl)acrylate
(S53) (4.00 g, 17.7 mmol, 1.0 equiv) in anhydrous CH₂Cl₂ (90 mL) with DIBAL-H (1.0 M in toluene, 40.0 mL, 38.9 mmol, 2.2 equiv) gave the title compound S54 (2.90 g, 15.8 mmol, 89%) as a white solid that was used without further purification.

Following general procedure D, the reaction of (E)-3-(Naphthalen-2-yl)prop-2-en-1-ol (S54) (2.80 g, 15.2 mmol, 1.0 equiv) in CH₂Cl₂ (15 mL) with Ac₂O (3.0 mL, 30.4 mmol, 2.0 equiv) and DMAP (92.8 mg, 0.76 mmol, 0.05 equiv) gave the title compound 1s (2.92 g, 12.9 mmol, 85%) as a white solid.

$^1$H NMR (400 MHz, CDCl₃) δ 7.85–7.77 (m, 3H), 7.75 (s, 1H), 7.59 (d, J = 8.5 Hz, 1H), 7.50–7.40 (m, 2H), 6.81 (d, J = 15.9 Hz, 1H), 6.49–6.31 (m, 1H), 4.78 (d, J = 6.5 Hz, 2H), 2.12 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl₃) δ 170.89, 134.28, 133.64, 133.48, 133.18, 128.30, 128.06, 127.68, 126.88, 126.36, 126.12, 123.49, 123.46, 65.17, 21.06.

(E)-3-(Naphthalen-1-yl)allyl acetate (1t)

Route for 1t

Following general procedure A, the reaction of 2-Naphthaldehyde (S55) (3.12 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv) in CH₂Cl₂ (30 mL) gave the title compound S56 (4.07 g, 18.0 mmol, 90%) as a colorless oil that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl-3-(Naphthalen-2-yl)acrylate (S56) (4.00 g, 17.7 mmol, 1.0 equiv) in anhydrous CH₂Cl₂ (90 mL) with DIBAL-H (1.0 M in toluene, 40.0 mL, 38.9 mmol, 2.2 equiv) gave the title compound S57 (3.10 g, 16.8 mmol, 95%) as a colorless oil that was used without further purification.

Following general procedure D, the reaction of (E)-3-(Naphthalen-2-yl)prop-2-en-1-ol (S57) (3.00 g, 16.3 mmol, 1.0 equiv) in CH₂Cl₂ (15 mL) with Ac₂O (3.2 mL, 32.6 mmol, 2.0 equiv) and DMAP (99.5 mg, 0.82 mmol, 0.05 equiv) gave the title compound 1t (3.53 g, 16.8 mmol, 96%) as a colorless oil.

$^1$H NMR (400 MHz, CDCl₃) δ 8.11 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.61 (d, J = 7.1 Hz, 1H), 7.56–7.48 (m, 2H), 7.48–7.38 (m, 2H), 6.33 (dt, J = 15.5, 6.4 Hz, 1H), 4.85 (d, J = 6.3 Hz, 2H), 2.15 (s, 3H). $^{13}$C NMR (101 MHz, CDCl₃) δ 170.75, 133.97, 133.68, 131.25, 131.19, 128.65, 128.47, 126.46, 126.27, 125.93, 125.66, 124.14, 123.73, 65.23, 21.02.
(E)-3-(Phenanthren-9-yl)allyl acetate (1u)

Route for 1u

Following general procedure A, the reaction of Phenanthrene-9-carbaldehyde (S58) (4.12 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv) in CH₂Cl₂ (40 mL) gave the title compound S59 (3.98 g, 14.4 mmol, 72%) as a yellow solid that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl-3-(Phenanthren-9-yl)acrylate (S59) (3.80 g, 13.7 mmol, 1.0 equiv) in anhydrous CH₂Cl₂ (70 mL) with DIBAL-H (1.0 M in toluene, 31.0 mL, 30.1 mmol, 2.2 equiv) gave the title compound S60 (2.47 g, 10.5 mmol, 77%) as a yellow solid that was used without further purification.

Following general procedure D, the reaction of (E)-3-(Phenanthren-9-yl)prop-2-en-1-ol (S60) (2.40 g, 10.2 mmol, 1.0 equiv) in CH₂Cl₂ (10 mL) with Ac₂O (2.0 mL, 20.4 mmol, 2.0 equiv) and DMAP (62.3 mg, 0.51 mmol, 0.05 equiv) gave the title compound 1u (2.21 g, 8.0 mmol, 78%) as a yellow solid.

**1H NMR** (400 MHz, CDCl₃) δ 8.71 (d, J = 7.6 Hz, 1H), 8.64 (d, J = 8.1 Hz, 1H), 8.14 (d, J = 7.4 Hz, 1H), 7.89 (d, J = 7.5 Hz, 1H), 7.83 (s, 1H), 7.72–7.56 (m, 4H), 7.40 (d, J = 15.5 Hz, 1H), 6.40 (dt, J = 15.5, 6.3 Hz, 1H), 4.89 (d, J = 6.3 Hz, 1H), 2.19 (s, 3H).

**13C NMR** (101 MHz, CDCl₃) δ 170.92, 132.97, 131.87, 131.65, 130.41, 130.33, 128.73, 126.83, 126.73, 126.61, 125.18, 124.56, 123.12, 122.55, 65.19, 21.13. **HRMS** (EI) calcd for C₁₉H₁₆O₂: 276.1150, found: 276.1156.

**General scheme 2 for the synthesis of 3a-3e**

**General procedure E:**
To a stirred solution of cinnamyl alcohol (1.0 equiv) in anhydrous CH₂Cl₂ (3 mL/mmoll) was added triethylamine (3.0 equiv) and acetyl chloride derivative (1.1 equiv) at 0 °C. The mixture was stirred for 30 min and then allowed to warm to room temperature and stirred overnight. The mixture was quenched with NH₄Cl (aq) and extracted with CH₂Cl₂ (3 equal volume). The combine organic layers was washed with brine, dried
over MgSO₄, and the solution was removed under vacuum and the crude residue was purified by chromatography on SiO₂ with hexane/EtOAc to afford corresponding product 3a⁷, 3b⁶, 3c⁸, 3d⁹, 3e¹⁰.

**Cinnamyl isobutyrate (3a)**

![Structure of Cinnamyl isobutyrate]

**¹H NMR** (400 MHz, CDCl₃) δ 7.39 (d, J = 7.1 Hz, 2H), 7.32 (t, J = 7.4 Hz, 2H), 7.25 (t, J = 7.2 Hz, 1H), 6.64 (d, J = 15.9 Hz, 1H), 6.29 (dt, J = 15.9, 6.4 Hz, 1H), 4.73 (d, J = 7.6 Hz, 2H), 2.78–2.34 (m, 1H), 1.22 (d, J = 7.0 Hz, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 176.78, 136.28, 133.88, 128.60, 128.02, 126.61, 123.43, 64.86, 34.03, 19.03.

**Cinnamyl pivalate (3b)**

![Structure of Cinnamyl pivalate]

**¹H NMR** (400 MHz, CDCl₃) δ 7.38 (d, J = 7.0 Hz, 2H), 7.33–7.27 (m, 2H), 7.26–7.20 (m, 1H), 6.63 (d, J = 15.9 Hz, 1H), 6.39–6.17 (m, 1H), 4.72 (d, J = 6.2 Hz, 2H), 1.27 (s, 9H). **¹³C NMR** (101 MHz, CDCl₃) δ 178.00, 136.33, 133.6 (s), 128.60, 127.99, 126.62, 123.55, 64.89, 38.78, 27.26.

**Cinnamyl 2-methoxyacetate (3c)**

![Structure of Cinnamyl 2-methoxyacetate]

**¹H NMR** (400 MHz, CDCl₃) δ 7.27 (d, J = 7.1 Hz, 2H), 7.20 (t, J = 6.7 Hz, 2H), 7.16–7.11 (m, 1H), 6.53 (d, J = 15.8 Hz, 1H), 6.25–6.10 (m, 1H), 4.68 (d, J = 6.1 Hz, 2H), 3.93 (s, 2H), 3.31 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 169.97, 135.98, 134.54, 128.56, 128.11, 126.59, 122.61, 69.56, 65.19, 59.11.

**Cinnamyl 4-methoxybenzoate (3d)**

![Structure of Cinnamyl 4-methoxybenzoate]

**¹H NMR** (400 MHz, CDCl₃) δ 8.07 (d, J = 8.7 Hz, 2H), 7.43 (d, J = 7.1 Hz, 2H), 7.34 (t, J = 7.4 Hz, 2H), 7.27 (t, J = 6.6 Hz, 1H), 7.02–6.88 (m, 2H), 6.74 (d, J = 15.9 Hz, 1H), 6.42 (dt, J = 15.9, 6.3 Hz, 1H), 4.97 (d, J = 6.3 Hz, 2H), 3.84 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 166.12, 163.42, 136.30, 134.00, 131.72, 128.64, 128.06, 126.66, 123.56, 122.60, 113.65, 65.27, 55.41.

**Cinnamyl benzoate (3e)**
\[ \text{General scheme 3 for the synthesis of 3f, 3g} \]

**General procedure F:**
To a stirred solution of benzoic acid derivative (1.0 equiv) in anhydrous \( \text{CH}_2\text{Cl}_2 \) (3 mL/mmol) was added dropwise oxalyl chloride (1.5 equiv) and drops of DMF at 0 °C for 30 min. Then the mixture was stirred at room temperature until no gas releasing and evaporated to afford the crude product without further purification.
To a stirred solution of acetyl chloride derivative (1.0 equiv) in anhydrous \( \text{CH}_2\text{Cl}_2 \) (3 mL/mmol) was added triethylamine (3.0 equiv) cinnamyl alcohol (0.9 equiv) at 0 °C. The mixture was stirred for 30 min and then allowed to warm to room temperature and stirred overnight. The mixture was quenched with \( \text{NH}_4\text{Cl} \) (aq) and extracted with \( \text{CH}_2\text{Cl}_2 \) (3 equal volume). The combine organic layers was washed with brine, dried over \( \text{MgSO}_4 \), and the solution was removed under vacuum and the crude residue was purified by chromatography on SiO\(_2\) with hexane/EtOAc to afford corresponding product 3f-3g.

**Cinnamyl [1,1'-biphenyl]-4-carboxylate (3f)**

\[ \text{1H NMR (400 MHz, CDCl}_3\) \delta 8.17 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 7.3 Hz, 2H), 7.52 - 7.38 (m, 5H), 7.35 (t, J = 7.4 Hz, 2H), 7.31 - 7.25 (m, 1H), 6.77 (d, J = 15.9 Hz, 1H), 6.44 (dt, J = 15.9, 6.4 Hz, 1H), 5.02 (d, J = 6.4 Hz, 2H). \]

\[ \text{13C NMR (101 MHz, CDCl}_3\) \delta 166.29, 145.72, 139.98, 136.22, 134.29, 133.05, 130.24, 129.71, 128.67, 128.43, 128.14, 126.70, 123.29, 65.58. \]

**Cinnamyl 4-(methylsulfonyl)benzoate (3g)**
$^1\text{H NMR}$ (400 MHz, CDCl$_3$) $\delta$ 8.25 (d, $J = 8.3$ Hz, 2H), 8.02 (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 7.3$ Hz, 2H), 7.33 (t, $J = 7.4$ Hz, 2H), 7.26 (t, $J = 7.2$ Hz, 1H), 6.75 (d, $J = 15.9$ Hz, 1H), 6.39 (dt, $J = 15.8$, 6.5 Hz, 1H), 5.01 (d, $J = 6.4$ Hz, 2H), 3.07 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl$_3$) $\delta$ 164.73, 144.31, 135.94, 135.11, 134.95, 130.60, 128.67, 128.31, 127.50, 126.69, 122.45, 66.36, 44.28.
## 4 Conditions Screening of the Reaction

![Chemical Reaction Diagram]

**Catalysts**

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**Other**

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*a* Reaction conditions: 1b (0.3 mmol), Pd(OAc)₂ (5.0 mol%), DPPPh (5.3 mol%), Et₄NNO₃ (0.15 g) and EtOH (1.0 equiv). DMF (6 mL) in an undivided cell with a palladium electrode and magnesium electrode as sacrificial anode. *b* The yield was determined by H¹-NMR with CH₃Br₂ as the internal standard. *c* The ratio of BL products was determined by H¹-NMR. *d* Isolated yield.

Note: 1) The reason for choosing alcohol as additive is that the alcohol may be useful for the activation of CO₂. When the additive was ethanol, the crude ¹H NMR was...
much cleaner and the yield was significantly increased.

2) When no ligand or simple PPh₃ was employed as the ligand, after the electrolysis, the platinum cathode was covered by a black precipitation. This may arise from the palladium catalyst deactivation.
5 Photographic Guide for Electrochemical Carboxylation

1 Easily hand-made electrochemical cell

Step 0. Overview of materials used.
From left to right: 1) The magnesium rod attached to a copper wire. 2) The platinum cathode 3) The rubber stopper pierced with two hypodermic needles. 4) A 10 mL hydrogenation tube.

Step 1. Preparation of the sacrificial magnesium rod anode
Cut a magnesium rod about 3 cm with a scissors.
Strip the protective skin of the copper wire with a tweezer.
Wrap the magnesium with copper wire.

Step 2. Assembly of the cell
Pierce the rubber stopper with the platinum cathode.
The magnesium rod and stopper were fitted into the tube.
Note: the copper wire is not supposed to be immersed the reaction. (the black line on the tube, 6 mL)
2 Graphical Guide for Electrochemical carboxylation

Left materials used in the reaction. Right the electrolyte weighted in glovebox was dissolved in DMF (SuperDry) and injected into the tube charged with a stir bar with a 10.0mL disposable syringe.
Left Bubbling CO\textsubscript{2} for 30 mins. Right injected the catalysts, EtOH, SM.

Attached to electrode (the red (+) to the magnesium, the black (-) to the platinum). Conducted constant current electrolysis (I = 8.0 mA) using an potentiostat.(E36105A, KEYSIGHT) under continuous bubbling CO\textsubscript{2}. (green line)
6 General Procedure for the Electrolysis

A 10 mL hydrogenation tube charged with a stir bar was installed a platinum electrode (1.0 x 1.0 cm$^2$) as cathode and magnesium rod as sacrificial anode. The electrolyte was dissolved in DMF (6.0 mL, superDry) and was injected into the tube with a 10 mL syringe. After bubbling of CO$_2$ gas (dried over conc. H$_2$SO$_4$) into the electrolytes for 30 min, Pd(OAc)$_2$ (0.015 mmol, 3.4 mg, 5 mol%), DPPPh (0.016 mmol, 7.2 mg, 5.3 mol%), allyl eater (0.3 mmol, 1.0 equiv), and EtOAc (0.3 mmol, 1.0 equiv) were added to the tube. Under continuous bubbling of CO$_2$ gas, the reaction mixture was electrolyzed under a constant current of 8 mA until the complete consumption of the starting materials as judged by TLC (about 3 hours). After that, the reaction mixture was transferred to a 50 mL erlenmeyer flask and acidized with HCl (1 N). The aqueous layer extracted with EtOAc (3 x equal volume) and the combined organics were washed with sat. NH$_4$Cl (4 x equal volume), dried over MgSO$_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography to furnish the desired product.

Characterization Data for the Products

2-(4-Bromophenyl)but-3-enoic acid (2a) $^{14}$

According to the procedure, (E)-3-(4-Bromophenyl)allyl acetate (1a) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford 2a (58.6 mg, 81% yield) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 6.25–6.07 (m, 1H), 5.28 (t, J = 7.9 Hz, 1H), 5.19 (d, J = 17.1 Hz, 1H), 4.29 (d, J = 7.8 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 178.17, 136.22, 134.31, 131.89, 129.87, 121.73, 118.61, 54.84. HRMS (EI) calcd for C$_{10}$H$_9$O$_2$Br: 239.9786, found: 239.9794.

2-Phenylbut-3-enoic acid (2b) $^{15}$

According to the procedure, cinnamyl acetate (1b) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford 2b (28.2 mg, 58% yield) as a pale-yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.45–7.27 (m, 5H), 6.38–6.17 (m, 1H), 5.28 (d, J = 10.2 Hz, 1H), 5.23 (d, J = 17.1 Hz, 1H), 4.37 (d, J = 8.0 Hz, 1H). $^{13}$C NMR (101 MHz,
CDCl₃ δ 178.80, 137.37, 134.97, 128.83, 128.12, 127.65, 118.13, 55.59. HRMS (ESI-TOF) calcd for C₁₀H₁₃O₂ [M+H]⁺: 163.0754, found: 163.0754.

2-(p-Tolyl)but-3-enoic acid (2c) ¹⁴

According to the procedure, (E)-3-(p-Tolyl)allyl acetate (1c) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford 2c (35.0 mg, 65% yield) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 7.21 (d, J = 8.0 Hz, 1H), 7.15 (d, J = 7.9 Hz, 1H), 6.28 –6.12 (m, 1H), 5.23 (d, J = 10.2 Hz, 1H), 5.17 (d, J = 17.7 Hz, 1H), 4.29 (d, J = 8.0 Hz, 1H), 2.33 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 178.79, 137.33, 135.10, 134.38, 129.47, 127.92, 117.85, 55.11, 21.05. HRMS (ESI-TOF) calcd for C₁₁H₁₁O₂ [M+H]⁺: 177.0910, found: 177.0910.

2-(4-Methoxyphenyl)but-3-enoic acid (2d) ¹⁴

According to the procedure, (E)-3-(4-Methoxyphenyl)allyl acetate (1d) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford 2d (36.0 mg, 62% yield) as a pale-yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.24 (d, J = 8.7 Hz, 1H), 6.88 (d, J = 8.6 Hz, 1H), 6.31 –6.09 (m, 1H), 5.23 (d, J = 10.2 Hz, 1H), 5.17 (d, J = 17.1 Hz, 1H), 4.28 (d, J = 7.9 Hz, 1H), 3.80 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 178.79, 137.33, 135.10, 134.38, 129.47, 127.92, 117.85, 55.28, 54.63. HRMS (ESI-TOF) calcd for C₁₁H₁₃O₃ [M+H]⁺: 193.0859, found: 193.0860.

2-(4-(tert-Butyl)phenyl)but-3-enoic acid (2e)

According to the procedure, (E)-3-(4-Methoxyphenyl)allyl acetate (1d) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford 2d (52.4 mg, 80% yield) as a yellowish solid.

¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 6.31 –6.15 (m, 1H), 5.31 –5.18 (m, 2H), 4.33 (d, J = 8.2 Hz, 1H), 1.34 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 179.00, 150.51, 135.10, 134.32, 127.67, 125.75, 117.88, 55.18,
According to the procedure, (E)-3-(4-Fluorophenyl)allyl acetate (1f) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford 2f (42.8 mg, 78% yield) as a yellow oil.

**1H NMR** (400 MHz, CDCl₃) δ 7.31–7.28 (m, 2H), 7.04 (t, J = 8.6 Hz, 2H), 6.30–6.09 (m, 1H), 5.27 (d, J = 10.1 Hz, 1H), 5.19 (d, J = 17.1 Hz, 1H), 4.32 (d, J = 7.8 Hz, 1H).

**13C NMR** (101 MHz, CDCl₃) δ 178.56, 162.21 (d, J = 246.4 Hz), 134.69, 132.98 (d, J = 3.3 Hz), 129.76 (d, J = 8.1 Hz), 118.31, 115.66 (d, J = 21.5 Hz), 54.65.

**19F NMR** (376 MHz, CDCl₃) δ -114.77.

**HRMS (EI) calcd for C₁₁H₉O₂F: 180.0587, found: 180.0588.**

**IR (neat):** 3084, 2963, 2929, 2869, 1698, 1639, 1287, 929, 822, 711 cm⁻¹.

2-(4-Fluorophenyl)but-3-enoic acid (2f)

According to the procedure, (E)-3-(4-Fluorophenyl)allyl acetate (1g) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford 2g (43.0 mg, 62% yield) as a yellowish oil.

**1H NMR** (400 MHz, CDCl₃) δ 7.61 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 6.24–6.14 (m, 1H), 5.31 (d, J = 10.2 Hz, 1H), 5.21 (d, J = 17.1 Hz, 1H), 4.40 (d, J = 7.9 Hz, 1H).

**13C NMR** (101 MHz, CDCl₃) δ 177.75, 141.09, 134.01, 129.95 (q, J = 32.5 Hz), 128.56, 125.70 (q, J = 7.3, 3.6 Hz), 123.95 (q, J = 272.7 Hz), 118.95, 55.17.

**19F NMR** (376 MHz, CDCl₃) δ -62.67.

**HRMS (EI) calcd for C₁₁H₉O₂F₃: 230.0555, found: 230.0557.**

**IR (neat):** 3088, 3021, 2925, 1708, 1640, 1322, 1164, 1121, 1067, 834 cm⁻¹.

2-(4-(Trifluoromethyl)phenyl)but-3-enoic acid (2g)

According to the procedure, (E)-3-(4-(Trifluoromethyl)phenyl)allyl acetate (1h) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford 2h (51.0 mg, 87% yield) as a white solid.

**1H NMR** (400 MHz, CDCl₃) δ 7.33 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 6.23–6.12 (m, 1H), 5.28 (d, J = 10.2 Hz, 1H), 5.19 (d, J = 17.1 Hz, 1H), 4.31 (d, J = 7.9 Hz).

**13C NMR** (101 MHz, CDCl₃) δ 177.75, 141.09, 133.01, 129.95 (q, J = 32.5 Hz), 128.56, 125.70 (q, J = 7.3, 3.6 Hz), 123.95 (q, J = 272.7 Hz), 118.95, 55.17.

**19F NMR** (376 MHz, CDCl₃) δ -62.67.

**HRMS (EI) calcd for C₁₁H₉O₂F₃: 230.0555, found: 230.0557.**

**IR (neat):** 3088, 3021, 2925, 1708, 1640, 1322, 1164, 1121, 1067, 834 cm⁻¹.

2-(4-Chlorophenyl)but-3-enoic acid (2h)

According to the procedure, (E)-3-(4-Chlorophenyl)allyl acetate (1i) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford 2h (51.0 mg, 87% yield) as a white solid.

**1H NMR** (400 MHz, CDCl₃) δ 7.33 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 6.23–6.12 (m, 1H), 5.28 (d, J = 10.2 Hz, 1H), 5.19 (d, J = 17.1 Hz, 1H), 4.31 (d, J = 7.9 Hz).
2-(2-Fluorophenyl)but-3-enoic acid (2i)

According to the procedure, (E)-3-(2-Fluorophenyl)allyl acetate (1i) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford 2i (49.0 mg, 91% yield) as a yellow oil.

\[ \text{IR (neat): 3086, 3024, 2987, 2907, 1705, 1490, 1407, 1284, 1229, 925, 751 \text{ cm}^{-1}.} \]

2-(2-Chlorophenyl)but-3-enoic acid (2j)

According to the procedure, (E)-3-(2-Chlorophenyl)allyl acetate (1h) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford 2h (52.0 mg, 87% yield) as a yellow solid.

\[ \text{IR (neat): 3067, 2961, 2919, 2853, 1693, 1293, 928, 747, 648 \text{ cm}^{-1}.} \]

2-(2-Bromophenyl)but-3-enoic acid (2k)

According to the procedure, with DPPE as the ligand, (E)-3-(2-Bromophenyl)allyl acetate (1k) was electrolyzed for 4h. The product was purified by flash column chromatography on silica to afford 2k (61.5 mg, 85% yield) as a colorless oil.

\[ \text{IR (neat): 3067, 2919, 2853, 1693, 1293, 928, 747, 648 \text{ cm}^{-1}.} \]
1H), 5.18 (d, J = 7.1 Hz, 1H), 4.89 (d, J = 7.1 Hz, 1H). 13C NMR (101 MHz, CDCl3) δ 177.72, 136.81, 133.36, 133.11, 129.82, 129.06, 127.74, 124.63, 118.82, 54.19. HRMS (EI) calcd for C10H9O2Br: 239.9786, found: 239.9792.

IR (neat): 3061, 3001, 2983, 2826, 1692, 1636, 1422, 1292, 1024, 926, 744, 643 cm⁻¹

2-(2-(Trifluoromethyl)phenyl)but-3-enoic acid (2l)

According to the procedure, (E)-3-(2-(Trifluoromethyl)phenyl)allyl acetate (1l) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford 2l (50.0 mg, 72% yield) as a yellow oil.

1H NMR (400 MHz, CDCl3) δ 7.66 (d, J = 8.0 Hz, 1H), 7.59–7.49 (m, 2H), 7.37 (t, J = 7.1 Hz, 1H), 6.19–6.10 (m, 1H), 5.26 (d, J = 10.2 Hz, 1H), 5.14 (d, J = 17.1 Hz, 1H), 4.79 (d, J = 7.1 Hz, 1H). 13C NMR (101 MHz, CDCl3) δ 177.81, 135.81, 134.36, 132.07, 130.26, 128.51 (q, J = 59.8, 29.9 Hz), 127.57, 126.05 (q, J = 5.7 Hz), 124.15 (q, J = 273 Hz), 118.74, 50.40. 19F NMR (376 MHz, CDCl3) δ -58.60. HRMS (EI) calcd for C11H9O2F3: 230.0555, found: 230.0566.

IR (neat): 3088, 3023, 2989, 2920, 1709, 1310, 1114, 1035, 926, 766 cm⁻¹.

2-(3-Bromophenyl)but-3-enoic acid (2m)

According to the procedure, (E)-3-(3-Bromophenyl)allyl acetate (1m) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford 2m (58.0 mg, 80% yield) as a yellow oil.

1H NMR (400 MHz, CDCl3) δ 7.47 (s, 1H), 7.42 (d, J = 7.7 Hz, 1H), 7.25 (d, J = 7.6 Hz, 1H), 7.20 (t, J = 7.7 Hz, 1H), 6.24–6.08 (m, 1H), 5.27 (d, J = 10.2 Hz, 1H), 5.19 (d, J = 17.1 Hz, 1H), 4.28 (d, J = 8.0 Hz, 1H). 13C NMR (101 MHz, CDCl3) δ 178.18, 139.34, 134.15, 131.21, 130.79, 130.29, 126.80, 122.75, 118.82, 55.02. HRMS (EI) calcd for C10H9O2Br: 239.9786, found: 239.9782.

2-(3-Fluoro-4-methoxyphenyl)but-3-enoic acid (2n)

According to the procedure, (E)-3-(3-Fluoro-4-methoxyphenyl)allyl acetate (1n) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford 2n (53.0 mg, 83% yield) as a colorless oil.

1H NMR (400 MHz, CDCl3) δ 7.08 (dd, J = 12.1, 2.0 Hz, 1H), 7.02 (d, J = 8.6 Hz, 1H),
6.92 (t, J = 8.5 Hz, 1H), 6.28–6.06 (m, 1H), 5.26 (d, J = 10.2 Hz, 1H), 5.18 (d, J = 17.1 Hz, 1H), 4.26 (d, J = 7.9 Hz, 1H), 3.87 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 178.32, 152.25 (d, J = 264.4 Hz), 147.08 (d, J = 10.7 Hz), 134.5, 130.06 (d, J = 6.3 Hz), 123.89 (d, J = 3.6 Hz), 118.3, 115.93 (d, J = 19.2 Hz), 113.44 (d, J = 2.1 Hz), 56.25, 54.40. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -134.35. HRMS (EI) calcd for C$_{11}$H$_{11}$O$_3$: 210.0692, found: 210.0687.

IR (neat): 3083, 3010, 2936, 2841, 1704, 1513, 1270, 1150, 1026, 925, 759, 731, 638 cm$^{-1}$.

2-(2-Bromo-4-methylphenyl)but-3-enoic acid (2o)

According to the procedure, (E)-3-(2-Bromo-4-methylphenyl)allyl acetate (1o) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford 2o (73.3 mg, 95% yield) as a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.44 (s, 1H), 7.26 (d, J = 7.9 Hz, 1H), 7.13 (d, J = 7.8 Hz, 1H), 6.26–6.06 (m, 1H), 5.30 (d, J = 10.2 Hz, 1H), 5.20 (d, J = 17.2 Hz, 1H), 4.87 (d, J = 7.2 Hz, 1H), 2.32 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 178.28, 139.32, 133.78, 133.75, 133.54, 129.47, 128.62, 124.37, 118.64, 53.85, 20.70. HRMS (EI) calcd for C$_{11}$H$_{11}$O$_2$Br: 253.9942, found: 253.9953.

IR (neat): 3084, 3022, 2983, 2921, 1703, 1406, 1283, 1214, 1037, 922, 742, 673 cm$^{-1}$.

2-(2-Bromo-4-fluorophenyl)but-3-enoic acid (2p)

According to the procedure, (E)-3-(2-Bromo-4-fluorophenyl)allyl acetate (1p) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford 2p (73.0 mg, 93% yield) as a yellowish oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.39–7.31 (m, 2H), 7.05 (td, J = 8.2, 2.6 Hz, 1H), 6.21–6.05 (m, 1H), 5.32 (d, J = 10.2 Hz, 1H), 5.19 (d, J = 17.2 Hz, 1H), 4.86 (d, J = 7.1 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 177.74, 161.53 (d, J = 251.3 Hz), 133.42, 132.78 (d, J = 3.6 Hz), 130.80 (d, J = 8.5 Hz), 124.63 (d, J = 9.4 Hz), 120.26 (d, J = 24.5 Hz), 119.02, 114.98 (d, J = 21.1 Hz), 53.42. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -112.40. HRMS (EI) calcd for C$_{10}$H$_{8}$O$_2$FBr: 257.9692, found: 257.9700.

IR (neat): 3085, 3017, 2985, 2919, 1705, 1596, 1484, 1221, 1167, 875, 673 cm$^{-1}$.

2-(2-Bromo-4-methoxyphenyl)but-3-enoic acid (2q)
According to the procedure, (E)-3-(2-Bromo-4-methoxyphenyl)allyl acetate (1q) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford 2q (59.0 mg, 72% yield) as a colorless oil.

**1H NMR** (400 MHz, CDCl₃) δ 7.26 (d, J = 8.7 Hz, 1H), 7.12 (s, 1H), 6.85 (d, J = 8.6, 1H), 6.21–6.00 (m, 1H), 5.26 (d, J = 10.2 Hz, 1H), 5.15 (d, J = 17.2 Hz, 1H), 4.81 (d, J = 7.0 Hz, 1H), 3.77 (s, 1H).

**13C NMR** (101 MHz, CDCl₃) δ 177.88, 159.26, 133.91, 130.19, 128.80, 124.82, 118.44, 118.16, 113.93, 55.53, 53.33.

**HRMS** (EI) calcd for C₁₁H₁₁O₃Br: 269.9892, found: 269.9902.

**IR** (neat): 3084, 3005, 2939, 1907, 2836, 1703, 1601, 1490, 1283, 1228, 1180, 1026, 923, 862, 741, 676 cm⁻¹.

2-(4-Bromo-2-methoxyphenyl)but-3-enoic acid (2r)

According to the procedure, (E)-3-(4-Bromo-2-methoxyphenyl)allyl acetate (1r) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford 2r (61.0 mg, 75% yield) as a yellow oil.

**1H NMR** (400 MHz, CDCl₃) δ 7.49 (d, J = 8.1 Hz, 1H), 6.85 (s, 1H), 6.81 (d, J = 8.1 Hz, 1H), 6.23–6.11 (m, 1H), 5.27 (d, J = 10.2 Hz, 1H), 5.20 (d, J = 17.1 Hz, 1H), 4.29 (d, J = 7.8 Hz, 1H), 3.89 (s, 3H).

**13C NMR** (101 MHz, CDCl₃) δ 177.90, 156.00, 138.00, 134.32, 133.44, 121.47, 118.60, 111.85, 111.03, 56.22, 55.19.

**HRMS** (EI) calcd for C₁₁H₁₁O₃Br: 269.9891, found: 269.9901.

**IR** (neat): 3082, 3007, 2939, 1703, 1581, 1484, 1403, 1280, 1164, 1045, 1024, 725, 670 cm⁻¹.

2-(Naphthalen-2-yl)but-3-enoic acid (2s)

According to the procedure, with DPPE as the ligand, (E)-3-(Naphthalen-2-yl)allyl acetate (1s) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford 2s (52.5 mg, 82% yield) as a white solid.

**1H NMR** (400 MHz, CDCl₃) δ 7.89–7.77 (m, 4H), 7.54–7.44 (m, 3H), 6.42–6.26 (m, 1H), 5.31 (d, J = 10.2 Hz, 1H), 5.25 (d, J = 17.2 Hz, 1H), 4.53 (d, J = 7.7 Hz, 1H).

**13C NMR** (101 MHz, CDCl₃) δ 178.70, 134.86, 134.73, 133.44, 132.74, 128.54, 127.89, 127.65, 127.08, 126.30, 126.12, 126.00, 118.36, 55.60. **HRMS** (ESI-TOF) calcd for C₁₄H₁₆NO₂ [M+NH₄]^+: 230.1176, found: 230.1176

**IR** (neat): 3067, 2985, 2923, 2853, 1693, 1405, 1201, 929, 825, 748 cm⁻¹.

2-(Naphthalen-1-yl)but-3-enoic acid (2t)
According to the procedure, with DPPE as the ligand, (E)-3-(Naphthalen-1-yl)allyl acetate (1t) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford 2t (51.5 mg, 81% yield) as a white solid.

1H NMR (400 MHz, CDCl$_3$) $\delta$ 8.08 (d, $J = 8.2$ Hz, 1H), 7.90 (d, $J = 8.0$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.60–7.40 (m, 4H), 6.50–6.30 (m, 1H), 5.33 (d, $J = 10.3$ Hz, 1H), 5.23 (d, $J = 17.2$ Hz, 1H), 5.12 (d, $J = 7.1$ Hz, 1H). 13C NMR (101 MHz, CDCl$_3$) $\delta$ 178.99, 134.44, 134.06, 133.51, 131.29, 129.02, 128.43, 126.56, 126.32, 125.82, 125.53, 123.34, 118.60, 51.61. HRMS (ESI-TOF) calcd for C$_{14}$H$_{16}$NO$_2$ [M+NH$_4$]$^+$: 230.1176, found: 230.1176.

IR (neat): 3042, 2890, 2822, 2659, 2565, 1689, 1596, 1417, 1289, 775 cm$^{-1}$.

2-(Phenanthen-9-yl)but-3-enoic acid (2u)

According to the procedure, (E)-3-(Phenanthen-9-yl)allyl acetate (1u) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford 2u (72.4 mg, 92% yield) as a white solid.

1H NMR (400 MHz, CDCl$_3$) $\delta$ 8.76 (d, $J = 8.0$ Hz, 1H), 8.67 (d, $J = 8.2$ Hz, 1H), 8.09 (d, $J = 8.0$ Hz, 1H), 7.87 (d, $J = 7.8$ Hz, 1H), 7.77 (s, 1H), 7.72–7.54 (m, 4H), 6.46 (ddd, $J = 17.2$, 10.3, 7.0 Hz, 1H), 5.37 (d, $J = 10.3$ Hz, 1H), 5.27 (d, $J = 17.3$ Hz, 1H), 5.10 (d, $J = 6.9$ Hz, 1H). 13C NMR (101 MHz, CDCl$_3$) $\delta$ 178.45, 134.13, 131.85, 131.33, 130.95, 130.17, 130.14, 128.75, 127.57, 126.97, 126.93, 126.83, 126.55, 124.14, 123.40, 122.46, 118.97, 51.99. HRMS (ESI-TOF) calcd for C$_{18}$H$_{18}$NO$_2$ [M+NH$_4$]$^+$: 280.1332, found: 280.1333.

IR (neat): 2952, 2919, 2852, 1689, 1635, 1404, 1200, 926, 764, 742, 615 cm$^{-1}$.
7 Enantioselective Carboxylation

Ligands results

\[
\text{CO}_2\text{H} \quad \text{(R)-Ligand} \quad \text{Pd(OAc)}_2 (7.5 \text{ mol%}) \quad \text{Ligand (8.0 mol%)} \\
\text{Et}_4\text{NOTs (0.07 M)} \quad \text{EtOH (1.0 equiv)} \quad \text{DMF, Pt-Mg, CO}_2 \\
30 \degree \text{C}, 8 \text{ mA}, 3\text{h} \quad \text{(S)-Product}
\]

\[
\text{PPh}_2 \quad \text{PPh}_2 \\
\text{PPh}_2 \quad \text{PPh}_2 \\
\text{PPh}_2 \quad \text{PPh}_2
\]

\[
\text{(R)-BINAP} \quad 56.3\% \text{ ee} \\
\text{(S)-SegPHOS} \quad 60.9\% \text{ ee} \\
\text{(R)-MeO-BIPHEP} \quad 66.9\% \text{ ee}
\]

\[
\text{CO}_2\text{H} \quad \text{2b} \quad (\pm)-2\text{-phenylbut-3-enoic acid (2b)}
\]

**HPLC**: Chiralpak AD-H (10% IPA:hexane, flow rate 0.7 ml min\(^{-1}\), 214 nm, 40 °C) \(t_R\) minor: 8.4 min, \(t_R\) major: 9.2 min, 0\% ee
(R)-BINAP as the ligand. $t_R$ minor: 8.6 min, $t_R$ major: 9.4 min, 56% ee

(S)-SegPhos as the ligand. $t_R$ minor: 8.6 min, $t_R$ major: 9.4 min, 60% ee
(R)-MeO-BIPHE as the ligand. $t_R$ minor: 8.6 min, $t_R$ major: 9.4 min, 67% ee

Absolute Configuration of the Product

![HPLC graph](image)

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The (R)-2-phenylbutanoic acid was purchased for a contrast.

HPLC: Chiralpak AD-H (10% IPA:hexane, flow rate 0.7 ml min$^{-1}$, 214 nm, 40 °C) $t_R$ minor: 8.3 min, $t_R$ major: 9.7 min, 99% ee
The product of (R)-MeO-BIPHME as ligand hydrogenated according to ref. 10
HPLC: Chiralpak AD-H (10% IPA:hexane, flow rate 0.7 ml min⁻¹, 214 nm, 40 °C) tᵣ minor: 8.3 min, tᵣ major: 9.7 min, 65% ee
A mixture of \((R)\)-2-phenylbutanoic acid and the hydrogenated product.

**HPLC:** Chiralpak AD-H (10% IPA:hexane, flow rate 0.7 ml min\(^{-1}\), 214 nm, 40 °C) \(t_R\) minor: 8.3 min, \(t_R\) major: 9.7 min, 0.7% ee
8 Electrochemical Set-up and Cyclic Voltammetry

1) Preparation of \([/(R)-\text{BINAP}]\text{Pd(OAc)}_2\)\(^{17}\)

![Chemical structure]

Procedure: A 25 mL Schlenk tube charged with stir bar was added Pd(OAc)\(_2\) (0.45 mmol Pd, 100 mg) and \((R)-\text{BINAP}\) (0.45 mmol, 280 mg). Capped vial and evacuated / backfilled with nitrogen three times. To the vial added 2 mL anhydrous toluene and stirred at room temperature for 5 – 10 minutes resulting in a red homogeneous solution. Added 5 mL pentane to reaction in air over 5 minutes resulting in a thick yellow slurry. The suspension was filtered, washed with 2x 5 mL pentane and dried under vacuum at room temperature for 1 hour. Collected 350 mg yellow solids for 92% yield.

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 7.89 (br, 5H), 7.80–7.66, (m, 5H), 7.55 (d, \(J = 8.3\) Hz, 5H), 7.49 (br, 7H), 7.34 (t, \(J = 7.4\) Hz, 2H), 7.24 (t, 2H), 7.19–7.11 (m, 2H), 7.01 (t, \(J = 7.7\) Hz, 2H), 6.80–6.72 (m, 3H), 6.68 (br, 3H), 6.53 (d, \(J = 8.6\) Hz, 2H). 2.34 (s, 3H), 1.34 (s, 6H).

\(^{31}\text{P NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\): 25.4 ppm. (The signal of \(\delta\) 2.34(s, 3H) belongs to toluene)

2) Cyclic Voltammetry

Cyclic voltammograms were recorded with a CHI660E potentiostat at room temperature in DMF. Bu\(_4\)NPF\(_6\) (0.07 M) was used as the supporting electrolyte, and a Pt electrode (0.03 cm\(^2\)) was used as the working electrode. The auxiliary electrode was a platinum sheet. All potentials are referenced against the Ag/AgI redox couple.

![Photograph of setup used for cyclic voltammetry.](image-url)
Figure 2. Cyclic voltammograms recorded on a Pt electrode (area = 0.031 cm²), A: (a) DMF containing 0.07 M Bu₄NPF₆; (b) solution (a) after addition of 2 mM [(R)-BINAP]Pd(OAc)₂ (v = 100 mV·s⁻¹); B: CVs of [(R)-BINAP]Pd(OAc)₂ (2 mM) eletroreduction at different scanning speed, (a) 0.01 V·s⁻¹ (b) 0.02 V·s⁻¹ (c) 0.05 V·s⁻¹ (d) 0.1 V·s⁻¹ (e) 0.2 V·s⁻¹ (f) 0.3 V·s⁻¹.

Figure 3. Cyclic voltammograms recorded on a Pt electrode (area = 0.031 cm²) at 100 mV·s⁻¹, A: (a) DMF containing 0.07 M Bu₄NPF₆; (b) solution (a) after addition of 2 mM [(R)-BINAP]Pd(OAc)₂; (c) solution (b) after addition of 20 mM 1b; B: DMF containing 0.07 M Bu₄NPF₆; (b) solution (a) after addition of 20 mM 1b.
Figure 4. Cyclic voltammograms recorded on a Pt electrode (area = 0.031 cm$^2$) at 100 mVs$^{-1}$ in: (a) DMF containing 0.07 M Bu$_4$NPF$_6$; (b) solution (a) after addition of 2 mM [(R)-BINAP]Pd(OAc)$_2$; (c) solution (b) after addition of 20 mM 1b; (d) solution (c) saturated with CO$_2$. 
9 Reference

10 Spectra of Compounds

$^1$H NMR Spectrum of 1l (CDCl$_3$)

$^{13}$C NMR Spectrum of 1l (CDCl$_3$)
$^{19}$F NMR Spectrum of 1l (CDCl$_3$)

$^1$H NMR Spectrum of 1n (CDCl$_3$)
$^{13}$C NMR Spectrum of 1n (CDCl$_3$)

$^{19}$F NMR Spectrum of 1n (CDCl$_3$)
$^1$H NMR Spectrum of 1o (CDCl$_3$)

$^{13}$C NMR Spectrum of 1o (CDCl$_3$)
$\text{H NMR Spectrum of 1p (CDCl}_3\text{)}$

![H NMR spectrum of 1p (CDCl3)](image)

$\text{C NMR Spectrum of 1p (CDCl}_3\text{)}$

![C NMR spectrum of 1p (CDCl3)](image)
\[ ^{19}F \text{ NMR Spectrum of } 1p \text{ (CDCl}_3\text{)} \]

\[ ^1H \text{ NMR Spectrum of } 1q \text{ (CDCl}_3\text{)} \]
$^{13}$C NMR Spectrum of 1r (CDCl$_3$)

\[ \text{OMe} \]
\[ \text{Br} \]
\[ 1r \]

$^1$H NMR Spectrum of 1u (CDCl$_3$)

\[ \text{OAc} \]
\[ 1u \]
$^{13}$C NMR Spectrum of 1u (CDCl$_3$)
$^1$H NMR Spectrum of 2a (CDCl$_3$)

$^{13}$C NMR Spectrum of 2a (CDCl$_3$)
$^1$H NMR Spectrum of 2b (CDCl$_3$)

$^{13}$C NMR Spectrum of 2b (CDCl$_3$)
$^1$H NMR Spectrum of 2c (CDCl$_3$)

$^{13}$C NMR Spectrum of 2c (CDCl$_3$)
$^1$H NMR Spectrum of 2d (CDCl$_3$)

$^{13}$C NMR Spectrum of 2d (CDCl$_3$)
\(^1\)H NMR Spectrum of 2f (CDCl\(_3\))

\(^{13}\)C NMR Spectrum of 2f (CDCl\(_3\))
$^{19}\text{F NMR Spectrum of 2f (CDCl}_3\text{)}$

$\text{CO}_2\text{H}$

2f

$^{1}\text{H NMR Spectrum of 2g (CDCl}_3\text{)}$

$\text{CO}_2\text{H}$

F$_3$C

2g

S59
\textbf{\textsuperscript{13}C NMR Spectrum of 2g (CDCl\textsubscript{3})}

\textbf{\textsuperscript{19}F NMR Spectrum of 2g (CDCl\textsubscript{3})}
$^1$H NMR Spectrum of 2h (CDCl$_3$)

$^{13}$C NMR Spectrum of 2h (CDCl$_3$)
$^1$H NMR Spectrum of 2i (CDCl$_3$)

$^{13}$C NMR Spectrum of 2i (CDCl$_3$)
\[ ^{19}F \text{ NMR Spectrum of } 2i \text{ (CDCl}_3) \]

\[ ^{1}H \text{ NMR Spectrum of } 2j \text{ (CDCl}_3) \]
$^{13}$C NMR Spectrum of 2j (CDCl$_3$)

1H NMR Spectrum of 2k (CDCl$_3$)
$^{13}$C NMR Spectrum of $2k$ (CDCl$_3$)

$^1$H NMR Spectrum of $2l$ (CDCl$_3$)
$^{13}$C NMR Spectrum of 2l (CDCl$_3$)

$^{19}$F NMR Spectrum of 2l (CDCl$_3$)
$^1$H NMR Spectrum of 2m (CDCl$_3$)

$^{13}$C NMR Spectrum of 2m (CDCl$_3$)
$^{19}$F NMR Spectrum of 2n (CDCl$_3$)

![19F NMR Spectrum of 2n](image)

$^1$H NMR Spectrum of 2o (CDCl$_3$)

![1H NMR Spectrum of 2o](image)
\textbf{\textit{\textsuperscript{13}C} NMR Spectrum of 2o (CDCl\textsubscript{3})}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{13C_NMR_Spectrum_of_2o}\end{figure}

\textbf{\textit{\textsuperscript{1}H} NMR Spectrum of 2p (CDCl\textsubscript{3})}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{1H_NMR_Spectrum_of_2p}\end{figure}
$^{13}$C NMR Spectrum of 2p (CDCl$_3$)

$^{19}$F NMR Spectrum of 2p (CDCl$_3$)
$^{1}$H NMR Spectrum of 2q (CDCl$_3$)

$^{13}$C NMR Spectrum of 2q (CDCl$_3$)
$^1$H NMR Spectrum of 2r (CDCl$_3$)

$^{13}$C NMR Spectrum of 2r (CDCl$_3$)
$^1$H NMR Spectrum of 2s (CDCl$_3$)

$^{13}$C NMR Spectrum of 2s (CDCl$_3$)
$^1$H NMR Spectrum of 2t (CDCl$_3$)

2t

$^{13}$C NMR Spectrum of 2t (CDCl$_3$)

2t