Supporting Information For

**Electrochemical Semipinacol Rearrangements of Allylic Alcohols: Construction of All-Carbon Quaternary Stereocenters**

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Section 1. general information

All reactions were carried out in undivided electrochemical cells (30 mL) using pre-dried glassware. The electrochemical cells were fitted with a threaded Teflon cap with electrical feed-throughs. (Figure 1 left). Electrocatalysis was conducted using an DC-power supplier HY3005ET in constant current mode, CV studies were performed using a CHI660E workstation. All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on gel F254 plates. Silica gel (200~300 mesh), petroleum ether (bp. 60~90 °C), and ethyl acetate are used for product purification by flash column chromatography. $^1$H, $^{19}$F and $^{13}$C NMR spectra in CDCl$_3$ were acquired on a Bruker AM-500 MHz spectrometer. Chemical shifts (δ) are reported in ppm relative to residual solvent signals (CDCl$_3$: 7.26 ppm for $^1$H NMR, 77.0 ppm for $^{13}$C NMR. The following abbreviations are used to indicate the multiplicity in NMR spectra: s, singlet; d, doublet; t, triplet; m, multiplet. High-resolution mass spectral analysis (HRMS) data were determined on an APEXII 47e FT-ICR spectrometer by means of the ESI technique. The allylic alcohols and alkenyl bromides were prepared according to the related references.1-7

Figure S1.a) left, 0.4 mmol scale set-up b) right, gram scale experiment set-up

Section 2. Cyclic voltammetry studies

**General information:** Cyclic voltammetry (CV) experiments were conducted in a 30 mL electrochemical cells fitted with a threaded Teflon cap of a glassy carbon working electrode (3 mm in diameter), a Ag/AgNO$_3$ reference electrode, SCE reference electrode, and a platinum wire counter
electrode. The solution of interest was sparged with nitrogen for 3-5 minutes before data collection. The diagrams were made using OriginLab 8.0.

Figure S2. Cyclic voltammogram study of CF$_3$SO$_2$Na Conditions: LiClO$_4$ 0.05 M in 15 mL MeCN, using glass carbon as the working electrode, Pt wire, and SCE as the counter and reference electrode, respectively, at a scan rate of 100 mV/s with (a) background. (b) 10 mM CF$_3$SO$_2$Na. (c) 10 mM CF$_3$SO$_2$Na in MeCN + 100 uL H$_2$O. (d) 5 mM 1a, 10 mM CF$_3$SO$_2$Na in MeCN + 100 uL H$_2$O (e) 10 mM p-tolSO$_2$Na, in MeCN/H$_2$O=15:1
Figure S3. Cyclic voltammogram studies of sunstrate: LiClO$_4$ 0.1 M in 15 mL MeCN, using glass carbon as the working electrode, Pt wire, and Ag/AgNO$_3$ electrode, as the counter and reference electrode, respectively, at a scan rate of 100 mV/s. The potentials were reported in mV against the SCE. a) background b) 10mM 1a

Section 3. Synthesis of starting materials

All allylic alcohols were synthesized according to the literature,$^{1-7}$ and the spectra of $^1$H-NMR was in accordance with the literature.

General procedure for the substrates
Under argon atmosphere, a solution of P(OPh)$_3$ (5.76 mL, 22 mmol, 1.1 equiv) in dry DCM (60 mL) was slowly added Br$_2$ (1.23 mL, 24 mmol, 1.2 equiv) at -60 °C, after 10 minutes, Et$_3$N (3.61 mL, 26 mmol, 1.3 equiv) was added, after another 10 minutes, acetophenone (20 mmol) was added, the reaction mixture was stirred at this temperature for 16 h. The reaction was then placed in an oil bath and heated at reflux for 2 h. After it was cooled to room temperature, saturated sodium sulfite (20 mL) was added to quench the reaction. The aqueous phase was extracted with DCM (3 ×30 mL), and the combined organic phase was washed with brine and dried over Na$_2$SO$_4$, filtered and concentrated to give the crude compound. Purification of the residue by flash chromatography yielded pure the corresponding product (1-bromovinyl)arene.

In a heat gun dried two necked round bottomed flask equipped with a magnetic stir bar and a reflux condenser under argon atmosphere, addition of dry THF to a mixture of magnesium turnings (3.0 equiv) and iodine crystals (0.02 equiv) resulted in an intense brown reaction mixture. Brown colour disappeared after a few drops of (1-bromovinyl)arene was added to the reaction mixture at rt. A solution of (1-bromovinyl)arene (1.0 equiv) in THF (1 mmol/mL) was then added dropwise to the reaction mixture. The reaction mixture was allowed to stir at 65 °C for 1 h. A solution of ketone (1 mmol/mL, 1.4 equiv) in THF was added dropwise at 65 °C and the resulted reaction mixture was allowed to stir at 65 °C for another 8 h. The reaction mixture was quenched with satd. NH$_4$Cl solution. The organic phase was extracted with ethyl acetate and dried over MgSO$_4$. Solvents were removed under reduced pressure and the crude reaction mixture was purified by flash column chromatography through silica gel (eluent = pentane:ethyl acetate 19:1 to 9:1) to afford the pure product.

**Section 4. General procedure for the electrochemical tandem trifluoromethylation/semipinacol rearrangement**
General Method A: To an oven-dried, undivided electrochemical cell equipped with a magnetic stir bar, a carbon anode (10.0 mm * 20.0 mm), and a graphite plate cathode (10.0 mm * 10.0 mm) were added CF$_3$SO$_2$Na (2.0 equiv, 0.8 mmol), LiClO$_4$ (3.0 equiv, 1.2 mmol), allylic alcohol 1 (1.0 equiv, 0.4 mmol) and followed by the addition of 8 mL MeCN and 4 mL H$_2$O. The mixture was stirred for 1 min. The electrolysis was controlled at a constant current 15 mA and was terminated after 2 h, electricity = 2.8 F (12 mA, 2.2 h, electricity = 2.5 F for 2h-2j). DCM (10 mL) and water (10 mL) was added, the aqueous layer was separated and extracted with dichloromethane (3×5 mL), and the combined organic layers were washed with brine and dried over sodium sulfate. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product.

The detailed synthetic procedure for 5 mmol-scale of the substrate 1a:

General Method B: To an oven-dried flask equipped with a magnetic stir bar, a carbon anode (30.0 mm * 30.0 mm), and a graphite plate cathode (10.0 mm * 10.0 mm) were added CF$_3$SO$_2$Na (2.0 equiv, 10 mmol, 1.56 g), LiClO$_4$ (3.0 equiv, 15 mmol, 1.59 g), 1-(1-phenylvinyl)cyclobutane-1-ol (1a 1.0 equiv, 5 mmol, 870 mg) and followed by the addition of 100 mL MeCN and 50 mL H$_2$O. The mixture was stirred for 10 min. The electrolysis was controlled at a constant current 150 mA until the consumption of allylic alcohol. DCM and water were added, the aqueous layer was separated and extracted with dichloromethane three times, and the combined organic layers were washed with brine and dried over sodium sulfate. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product (786 mg, 65%).

Evidence of ditrifluoromethylation product
\[ ^1\text{H NMR} \ (500 \text{ MHz, Chloroform-d}) \delta \ 7.65 \ (s, \ 1H), \ 7.61 \ (d, \ J = 7.8 \text{ Hz, } 1H), \ 7.56 \ (d, \ J = 7.9 \text{ Hz, } 1H), 7.52 – 7.46 \ (m, \ 1H), \ 2.96 \ (dd, \ J = 14.1, 6.1 \text{ Hz, } 1H), 2.83 \ (dq, \ J = 15.5, 11.0 \text{ Hz, } 1H), 2.51 – 2.43 \ (m, \ 1H), 2.38 – 2.30 \ (m, \ 2H), 2.29 – 2.22 \ (m, \ 1H), 2.19 – 2.11 \ (m, \ 1H), 2.11 – 1.99 \ (m, \ 1H), 1.87 – 1.75 \ (m, \ 1H). \]
2-phenyl-2-(2,2,2-trifluoroethyl)cyclopentan-1-one (2a): Followed General Method A using the allylic alcohol 1-(1-phenylvinyl)cyclobutan-1-ol (70.4 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 200:1) to give 86.4 mg (85% yield) of 2a as a colorless oil. Rf = 0.75 (petroleum ether/ethyl acetate, 10:1). $^1$H NMR (500 MHz, Chloroform-d) δ 7.41 – 7.33 (m, 3H), 7.31 – 7.26 (m, 1H), 2.92 (dd, $J = 13.9$, 6.1 Hz, 1H), 2.80 (dq, $J = 15.5$, 11.2 Hz, 1H), 2.49 (dq, $J = 15.5$, 11.1 Hz, 1H), 2.37 – 2.27 (m, 1H), 2.27 – 2.16 (m, 1H), 2.16 – 2.05 (m, 1H), 2.05 – 1.95 (m, 1H), 1.76-1.88 (m, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 216.16, 136.04, 128.95, 127.69, 126.81, 126.22 (q, $J = 278.2$ Hz), 53.34 (q, $J = 1.6$ Hz), 42.03 (q, $J = 27.4$ Hz), 35.51, 32.44, 18.31. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -60.38. HR-MS (ESI): m/z calculated for [C$_{20}$H$_{24}$NO$_3$S]$^+$ ([M+Na]$^+$): 265.0811, measured: 265.0817.
2-(o-tolyl)-2-(2,2,2-trifluoroethyl)cyclopentan-1-one (2b): Followed General Method A using the allylic alcohol 1-(1-(o-tolyl)vinyl)cyclobutan-1-ol (75.2 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 200:1) to give 57.1 mg (56% yield) of 2b as a colorless oil. Rf = 0.80 (petroleum ether/ethyl acetate, 10:1). \(^1\)H NMR (500 MHz, Chloroform-d) δ 7.23 – 7.17 (m, 2H), 7.13 – 7.08 (m, 1H), 7.02 (d, J = 7.9 Hz, 1H), 2.95 – 2.72 (m, 3H), 2.46 (s, 3H), 2.44 – 2.38 (m, 1H), 2.31 – 2.17 (m, 2H), 1.97 – 1.89 (m, 1H), 1.72 – 1.64 (m, 1H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 217.31, 136.58, 136.19, 133.55, 127.70, 127.18, 126.11 (q, J = 278.3 Hz), 126.05, 54.51 (q, J = 1.4 Hz), 38.57 (q, J = 27.2 Hz), 36.09, 33.20, 21.19, 18.09. \(^{19}\)F NMR (471 MHz, CDCl\(_3\)) δ -60.43. HR-MS (ESI): \(m/z\) calculated for [C\(_{14}\)H\(_{15}\)F\(_3\)ONa]\(^+\) ([M+Na\(^+\)]: 279.0967, measured: 279.0970.

2-(m-tolyl)-2-(2,2,2-trifluoroethyl)cyclopentan-1-one (2c): Followed General Method A using the corresponding allylic alcohol 1-(1-(m-tolyl)vinyl)cyclobutan-1-ol (75.2 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 200:1) to give 79.5 mg (78% yield) of 2c as a colorless oil. Rf = 0.75 (petroleum ether/ethyl acetate, 10:1). \(^1\)H NMR (500 MHz, Chloroform-d) δ 7.24 (t, J = 7.6 Hz, 1H), 7.20 – 7.15 (m, 2H), 7.09 (d, J = 7.4 Hz, 1H), 2.90 (dd, J = 13.9, 6.1 Hz, 1H), 2.77 (dq, J = 15.5, 11.2 Hz, 1H), 2.50 (dq, J = 15.6, 11.1 Hz, 1H), 2.34 (s, 3H), 2.32 – 2.28 (m, 1H), 2.25 – 2.15 (m, 1H), 2.13 – 2.05 (m, 1H), 2.03 – 1.94 (m, 1H), 1.87 – 1.72 (m, 1H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 216.26, 138.60, 136.04, 128.76, 128.42, 127.46, 126.21 (q, J = 278.3 Hz), 123.71, 53.29 (q, J = 1.5 Hz), 41.96 (q, J = 27.3 Hz), 35.50, 32.39, 21.56, 18.29. \(^{19}\)F NMR (471 MHz, CDCl\(_3\)) δ -60.36. HR-MS (ESI): \(m/z\) calculated for [C\(_{14}\)H\(_{15}\)F\(_3\)ONa]\(^+\) ([M+Na\(^+\)]: 279.0967, measured: 279.0973.

2-(3-chlorophenyl)-2-(2,2,2-trifluoroethyl)cyclopentan-1-one (2d): Followed General Method A using the allylic alcohol 1-(1-(3-chlorophenyl)vinyl)cyclobutan-1-ol (83.2 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 200:1) to give 80.3 mg (73% yield) of 2d as a colorless oil. Rf = 0.75 (petroleum ether/ethyl acetate, 10:1). \(^1\)H NMR (500 MHz, Chloroform-d) δ 7.38 (s, 1H), 7.33 – 7.26 (m, 3H), 2.88 (dd, J = 14.0, 6.1 Hz, 1H), 2.79 (dq, J = 15.5, 11.1 Hz, 1H), 2.46 (dq, J = 15.5, 10.9 Hz, 1H), 2.39 – 2.27 (m, 1H), 2.28 – 2.18 (m, 1H), 2.16 – 2.07 (m, 1H), 2.07 – 1.98 (m, 1H), 1.84 – 1.72 (m, 1H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 215.56, 138.19, 134.99, 130.16, 128.01, 127.11, 126.04 (q, J
= 278.2 Hz), 125.09, 53.10 (q, J = 1.5 Hz), 42.00 (q, J = 27.6 Hz), 35.53, 32.47, 18.35. 19F NMR (471 MHz, CDCl₃) δ -60.38. HR-MS (ESI): m/z calculated for [C₁₃H₁₂F₃ONa]+ ([M+Na]+): 299.0421, measured: 299.0423

2-(4-fluorophenyl)-2-(2,2,2-trifluoroethyl)cyclopentan-1-one (2e): Followed General Method A using the allylic alcohol 1-(1-(4-fluorophenyl)-vinyl)cyclobutan-1-ol (76.8 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 200:1) to give 82.1 mg (79% yield) of 2e as a colorless oil. Rf = 0.75 (petroleum ether/ethyl acetate, 10:1). ¹H NMR (500 MHz, Chloroform-d) δ 7.39 – 7.33 (m, 2H), 7.08 – 7.01 (m, 2H), 2.89 (dd, J = 13.9, 6.1 Hz, 1H), 2.79 (dq, J = 15.5, 11.1 Hz, 1H), 2.43 (dq, J = 15.4, 10.9 Hz, 1H), 2.36 – 2.27 (m, 1H), 2.27 – 2.16 (m, 1H), 2.16 – 2.07 (m, 1H), 2.07 – 1.98 (m, 1H), 1.84 – 1.72 (m, 1H). ¹³C NMR (126 MHz, Chloroform-d) δ 215.92, 162.22 (d, J = 247.6 Hz), 131.49 (d, J = 3.4 Hz), 128.67 (d, J = 8.2 Hz), 126.18 (q, J = 278.2 Hz), 115.87 (d, J = 21.4 Hz), 52.74 (q, J = 1.5 Hz), 42.11 (q, J = 27.4 Hz). 35.44, 32.75, 18.30. 19F NMR (471 MHz, CDCl₃) δ -60.40, -114.64. HR-MS (ESI): m/z calculated for [C₁₃H₁₂F₃ONa]+ ([M+Na]+): 283.0716, measured: 283.0734.

2-(4-chlorophenyl)-2-(2,2,2-trifluoroethyl)cyclopentan-1-one (2f): Followed General Method A using the corresponding allylic alcohol 1-(1-(4-chlorophenyl)vinyl)cyclobutan-1-ol (83.2 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 200:1) to give 82.8 mg (75% yield) of 2f as a colorless oil. ¹H NMR (500 MHz, Chloroform-d) δ 7.33 (s, 4H), 2.89 (dd, J = 13.9, 6.1 Hz, 1H), 2.79 (dq, J = 15.5, 11.1 Hz, 1H), 2.43 (dq, J = 15.5, 11.1 Hz, 1H), 2.36 – 2.28 (m, 1H), 2.28 – 2.17 (m, 1H), 2.15 – 1.97 (m, 2H), 1.83 – 1.70 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 215.73, 134.36, 133.84, 129.10, 128.30, 126.10 (q, J = 278.3 Hz), 52.83 (q, J = 1.6 Hz), 42.00 (q, J = 27.5 Hz), 35.43, 32.52, 18.31. 19F NMR (471 MHz, CDCl₃) δ -60.37. HR-MS (ESI): m/z calculated for [C₁₃H₁₂F₃ONa]+ ([M+Na]+): 299.0421, measured: 299.0417
2-(p-tolyl)-2-(2,2,2-trifluoroethyl)cyclopentan-1-one (2g): Followed General Method A using the allylic alcohol 1-(1-(p-tolyl)vinyl)cyclobutan-1-ol (75.2 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 200:1) to give 78.1 mg (77% yield) of 2g as a colorless oil. R<sub>f</sub> = 0.75 (petroleum ether/ethyl acetate, 10:1). <sup>1</sup>H NMR (500 MHz, Chloroform-<d>) δ 7.27 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 2.90 (dd, J = 13.8, 6.1 Hz, 1H), 2.78 (dq, J = 15.5, 11.1 Hz, 1H), 2.47 (dq, J = 15.5, 11.1 Hz, 1H), 2.38 – 2.27 (m, 4H), 2.24 – 2.15 (m, 1H), 2.12 – 2.03 (m, 1H), 2.02 – 1.94 (m, 1H), 1.86 – 1.74 (m, 1H). <sup>13</sup>C NMR (126 MHz, Chloroform-<d>) δ 216.26, 137.48, 132.89, 129.66, 126.70, 126.28 (q, J = 278.3 Hz), 53.02 (q, J = 1.5 Hz), 41.97 (q, J = 27.2 Hz), 35.43, 32.44, 20.93, 18.29. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -60.38. HR-MS (ESI): m/z calculated for [C<sub>14</sub>H<sub>15</sub>F<sub>3</sub>ONa]<sup>+</sup> ([M+Na]<sup>+</sup>): 279.0967, measured: 279.0971.

2-(4-methoxyphenyl)-2-(2,2,2-trifluoroethyl)cyclopentan-1-one (2h):

Followed General Method A using the allylic alcohol 1-(1-(4-methoxyphenyl)vinyl)cyclobutan-1-ol (81.6 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 100:1) to give 73.1 mg (68% yield) of 2h as a colorless oil. R<sub>f</sub> = 0.65 (petroleum ether/ethyl acetate, 10:1). <sup>1</sup>H NMR (500 MHz, Chloroform-<d>) δ 7.32 – 7.28 (m, 2H), 6.91 – 6.85 (m, 2H), 3.79 (s, 3H), 2.88 (dd, J = 13.8, 6.1 Hz, 1H), 2.77 (dq, J = 15.5, 11.2 Hz, 1H), 2.43 (dq, J = 15.4, 11.0 Hz, 1H), 2.36 – 2.27 (m, 1H), 2.25 – 2.14 (m, 1H), 2.10 – 1.94 (m, 2H), 1.86-1.72 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 216.26, 137.48, 132.89, 129.66, 126.70, 126.28 (q, J = 278.5 Hz), 114.28, 55.21, 52.60 (q, J = 1.5 Hz), 41.97 (q, J = 27.4 Hz), 35.35, 32.59, 18.25. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -60.38. HR-MS (ESI): m/z calculated for [C<sub>14</sub>H<sub>15</sub>F<sub>3</sub>O<sub>2</sub>Na]<sup>+</sup> ([M+Na]<sup>+</sup>): 295.0967, measured: 295.0918.

2-((1,1'-biphenyl)-4-yl)-2-(2,2,2-trifluoroethyl)cyclopentan-1-one (2i):

Followed General Method A using the allylic alcohol 1-(1-(1,1'-biphenyl)-4-yl)vinyl)cyclobutan-1-ol (100.0 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 200:1) to give 78.1 mg (55% yield) of 2i as a colorless oil. R<sub>f</sub> = 0.80 (petroleum ether/ethyl acetate, 10:1). <sup>1</sup>H NMR (500 MHz, Chloroform-<d>) δ 7.61 – 7.56 (m, 4H), 7.48 – 7.41 (m, 4H), 7.39 – 7.32 (m, 1H), 2.96
(dd, J = 13.9, 6.1 Hz, 1H), 2.84 (dq, J = 15.5, 11.2 Hz, 1H), 2.53 (dq, J = 15.4, 11.0 Hz, 1H), 2.41 – 2.32 (m, 1H), 2.30 – 2.18 (m, 1H), 2.18 – 2.08 (m, 1H), 2.08 – 1.98 (m, 1H), 1.91 – 1.78 (m, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 216.10, 140.50, 140.18, 134.95, 128.79, 127.55, 127.51, 127.25, 127.01, 126.22 (q, J = 278.3 Hz), 53.12 (q, J = 1.4 Hz), 41.98 (q, J = 27.3 Hz), 35.54, 32.45, 18.37. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -60.28. HR-MS (ESI): m/z calculated for [C$_{19}$H$_{17}$F$_{3}$O$_2$Na]$^+$ ([M+Na]$^+$): 341.1124, measured: 341.1125.

$^{2}$-(benzo[d][1,3]dioxol-5-yl)-2-(2,2,2-trifluoroethyl)cyclopentan-1-one (2j):
Followed General Method A using the allylic alcohol 1-(1-(benzo[d][1,3]dioxol-5-yl)vinyl)cyclobutan-1-ol (87.2 mg, 0.40 mmol) and purified using silica gel chromatography (n-pentane/ethyl acetate = 150:1) to give 69.1 mg (61% yield) of 2j as a colorless oil. R$_f$ = 0.68 (petroleum ether/ethyl acetate, 10:1). $^1$H NMR (500 MHz, Chloroform-d) δ 6.88 (d, J = 2.0 Hz, 1H), 6.83 (dd, J = 8.2, 2.0 Hz, 1H), 6.77 (d, J = 8.2 Hz, 1H), 5.98 – 5.93 (m, 2H), 2.85 – 2.70 (m, 2H), 2.46 – 2.28 (m, 2H), 2.24 – 2.14 (m, 1H), 2.10 – 1.95 (m, 2H), 1.86 – 1.75 (m, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 215.89, 148.32, 147.11, 129.39, 126.22 (q, J = 278.3 Hz), 120.37, 108.42, 107.32, 101.28, 52.91 (q, J = 1.6 Hz), 42.04 (q, J = 27.2 Hz), 35.32, 32.83, 18.24. $^{19}$F NMR (471 MHz, CDCl$_3$) δ -60.43. HR-MS (ESI): m/z calculated for [C$_{14}$H$_{13}$F$_{3}$O$_3$Na]$^+$ ([M+Na]$^+$): 309.0710, measured: 309.0721.

$^{2}$-(4-chloro-3-methylphenyl)-2-(2,2,2-trifluoroethyl)cyclopentan-1-one (2k):
Followed General Method A using the allylic alcohol 1-(1-(4-chloro-3-methylphenyl)vinyl)cyclobutan-1-ol (88.9 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 150:1) to give 81.2 mg (70% yield) of 2k as a colorless oil. R$_f$ = 0.75 (petroleum ether/ethyl acetate, 10:1). $^1$H NMR (400 MHz, Chloroform-d) δ 7.31 (d, J = 8.4 Hz, 1H), 7.22 (d, J = 2.5 Hz, 1H), 7.15 (dd, J = 8.4, 2.5 Hz, 1H), 2.87 (dd, J = 13.5, 6.1 Hz, 1H), 2.77 (dq, J = 15.5, 11.1 Hz, 1H), 2.44 (dq, J = 15.5, 11.1 Hz, 1H), 2.36 (s, 3H), 2.33 – 2.27 (m, 1H), 2.26 – 2.15 (m, 1H), 2.12 – 1.96 (m, 2H), 1.86 – 1.69 (m, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 215.86, 136.64, 134.44, 133.97, 129.48, 129.43, 125.92 (d, J = 277.5 Hz), 125.51, 52.84 (q, J=1.5Hz), 41.97 (q, J=27.7Hz), 35.44, 32.48, 20.27, 18.31. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -60.35. HR-MS (ESI): m/z calculated for [C$_{14}$H$_{14}$ClF$_{3}$ONa]$^+$ ([M+Na]$^+$): 313.0577, measured: 313.0570.
2'-((trifluoromethyl)-3',4'-dihydro-2'H-spirocyclopentane-1,1'-naphthalen)-2-one (2l): Followed General Method using the allylic alcohol 1-(3,4-dihydronaphthalen-1-yl)cyclobutan-1-ol (80.0 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 150:1) to give 79.2 mg (73% yield) of 2l as a white solid.

**Major diastereomer**: Rf = 0.75 (petroleum ether/ethyl acetate, 10:1). **m.p.** 95-97 °C ¹H NMR (500 MHz, Chloroform-d) δ 7.19 – 7.13 (m, 2H), 7.12 – 7.08 (m, 1H), 6.98 – 6.94 (m, 1H), 2.99 (ddd, J = 17.0, 8.2, 5.5 Hz, 1H), 2.81 (dt, J = 17.1, 6.4 Hz, 1H), 2.73 – 2.64 (m, 2H), 2.62 – 2.33 (m, 4H), 2.19 – 2.12 (m, 2H), 2.12 – 2.01 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 218.49, 138.74, 136.15, 128.95, 127.85, 127.05 (q, J = 282.2 Hz), 126.62, 126.56, 52.83, 46.34 (q, J = 25.2 Hz), 41.31, 38.09, 26.95, 19.96 (q, J = 3.1 Hz), 18.47. ¹⁹F NMR (471 MHz, CDCl₃) δ -63.37. HR-MS (ESI): m/z calculated for [C₁₅H₁₅F₃ONa]⁺ ([M+Na]⁺): 291.0967 measured: 291.0970.

6'-methoxy-2'-((trifluoromethyl)-3',4'-dihydro-2'H-spirocyclopentane-1,1'-naphthalen)-2-one (2m): Followed General Method A using the allylic alcohol 1-(6-methoxy-3,4-dihydronaphthalen-1-yl)cyclobutan-1-ol (92.0 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 150:1) to give 51.0 mg (43% yield) of 2m as a colorless oil. Rf = 0.75 (petroleum ether/ethyl acetate, 10:1). ¹H NMR (500 MHz, Chloroform-d) δ 6.87 (d, J = 8.8 Hz, 1H), 6.74 (dd, J = 8.8, 2.8 Hz, 1H), 6.61 (d, J = 2.8 Hz, 1H), 3.77 (s, 3H), 2.95 (dd, J = 8.3, 5.5 Hz, 1H), 2.83 – 2.76 (m, 1H), 2.72 – 2.62 (m, 2H), 2.55 – 2.27 (m, 4H), 2.17 – 2.10 (m, 2H), 2.09 – 2.01 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 218.79, 157.86, 137.54, 130.82, 128.93, 127.07 (q, J = 282.2 Hz), 113.29, 113.11, 55.18, 52.28, 46.32 (q, J = 25.5 Hz), 41.09, 37.97, 27.24, 19.95 (q, J = 3.4 Hz), 18.39. ¹⁹F NMR (471 MHz, CDCl₃) δ -63.35. HR-MS (ESI): m/z calculated for [C₁₆H₁₇F₃O₂Na]⁺ ([M+Na]⁺): 321.1073 measured: 321.1079.

2-phenyl-2-(2,2,2-trifluoroethyl)cyclohexan-1-one (2n): Followed General Method A using the allylic alcohol 1-(1-phenylvinyl)cyclopentan-1-ol (75.2 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 150:1) to
give 28.6 mg (28% yield) of 2n as a colorless oil. Rf = 0.83 (petroleum ether/ethyl acetate, 10:1). 

**1H NMR** (500 MHz, Chloroform-\(d\)) \(\delta\) 7.40 – 7.34 (m, 2H), 7.32 – 7.27 (m, 1H), 7.23 – 7.19 (m, 2H), 3.08 – 2.98 (m, 1H), 2.76 – 2.56 (m, 2H), 2.34 – 2.27 (m, 2H), 2.01 – 1.93 (m, 1H), 1.88 – 1.64 (m, 4H). 

**13C NMR** (126 MHz, CDCl\(_3\)) \(\delta\) 210.36, 138.26, 129.12, 127.47, 126.94, 126.56 (q, \(J = 278.3\) Hz), 54.46 (q, \(J = 1.4\) Hz), 42.98 (q, \(J = 26.8\) Hz), 39.19, 34.21, 27.99, 21.40. 

**19F NMR** (471 MHz, CDCl\(_3\)) \(\delta\) -58.74. 

**HR-MS (ESI):** \(m/z\) calculated for [\(\text{C}_{14}\text{H}_{15}\text{F}_3\text{ONa}\]^+ ([M+Na]^+): 279.0967 measured: 279.0960.

**10-phenyl-10-(2,2,2-trifluoroethyl)phenanthren-9(10H)-one (2o):** Followed General Method A using the allylic alcohol 9-(1-phenylvinyl)-9H-fluoren-9-ol (115.8 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 150:1) followed by recrystallized from hexane to give 95.1 mg (69% yield) of 2o as a white solid. Rf = 0.80 (petroleum ether/ethyl acetate, 10:1). m.p. = 250-252°C. 

**1H NMR** (500 MHz, Chloroform-\(d\)) \(\delta\) 8.19 (d, \(J = 7.3\) Hz, 1H), 8.16 – 8.08 (m, 2H), 7.76 – 7.67 (m, 1H), 7.53 – 7.47 (m, 1H), 7.45 – 7.38 (m, 2H), 7.30 (d, \(J = 7.9\) Hz, 1H), 7.26 – 7.19 (m, 3H), 7.11 – 7.05 (m, 2H), 4.20 (dq, \(J = 14.9, 10.6\) Hz, 1H), 3.24 (dq, \(J = 14.9, 9.7\) Hz, 1H). 

**13C NMR** (126 MHz, CDCl\(_3\)) \(\delta\) 196.61, 141.54, 138.36, 136.92, 134.94, 130.34, 130.12, 130.11, 128.87, 128.83, 128.73, 128.43, 128.11, 127.99, 127.60, 126.82, 125.58 (q, \(J = 279.3\) Hz), 123.83, 123.14, 55.03 (q, \(J = 1.9\) Hz), 42.06 (q, \(J = 27.4\) Hz). 

**19F NMR** (471 MHz, CDCl\(_3\)) \(\delta\) -58.04. 

**HR-MS (ESI):** \(m/z\) calculated for [\(\text{C}_{14}\text{H}_{15}\text{F}_3\text{ONa}\]^+ ([M+Na]^+): 375.0967 measured: 375.0964.

**4,4,4-trifluoro-1,2,2-triphenylbutan-1-one (2p):** Followed General Method A using the allylic alcohol 1,1,2-triphenylprop-2-en-1-ol (114.4 mg 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 150:1) to give 46.4mg (33% yield) of 2p as a white solid. Rf = 0.80 (petroleum ether/ethyl acetate, 10:1). m.p. > 300°C. 

**1H NMR** (500 MHz, Chloroform-\(d\)) \(\delta\) 7.58 (d, \(J = 7.5\) Hz, 2H), 7.41 (t, \(J = 7.4\) Hz, 1H), 7.27 – 7.24 (m, 2H), 7.22 – 7.19 (m, 2H), 7.19 – 7.14 (m, 2H), 7.13 – 7.08 (m, 1H), 7.08 – 6.97 (m, 3H), 3.01 (dq, \(J = 15.4, 10.0\) Hz, 1H), 2.24 (dq, \(J = 15.3, 10.3\) Hz, 1H). 

**13C NMR** (126 MHz, CDCl\(_3\)) \(\delta\) 198.36, 138.57, 136.41, 134.94, 130.34, 130.12, 128.87, 128.83, 128.73, 128.43, 128.11, 127.99, 127.60, 126.82, 125.58 (q, \(J = 279.3\) Hz), 122.83, 123.14, 55.03 (q, \(J = 1.9\) Hz), 42.06 (q, \(J = 27.4\) Hz). 

**19F NMR** (471 MHz, CDCl\(_3\)) \(\delta\) -60.61. 

**HR-MS (ESI):** \(m/z\) calculated for [\(\text{C}_{22}\text{H}_{17}\text{F}_3\text{ONa}\]^+ ([M+Na]^+): 377.1124 measured: 377.1128.
2,2,3-triphenyl-3-(2,2,2-trifluoroethyl)oxirane (4pa): Obtained as a white solid 79.1 mg (56% yield). Rf = 0.70 (petroleum ether/ethyl acetate, 10:1). m.p. > 300ºC. 

$^1$H NMR (500 MHz, Chloroform-d) δ 7.58 – 7.49 (m, 2H), 7.48 – 7.42 (m, 4H), 7.38 – 7.27 (m, 7H), 7.23 – 7.14 (m, 2H), 3.39 (q, J = 10.5 Hz, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 138.33, 137.57, 136.22, 128.71, 128.02, 127.72, 127.59, 127.55, 127.45, 127.09, 127.03, 126.79, 125.78 (q, J = 279.1 Hz), 71.82, 66.67 (q, J = 2.5 Hz), 38.79 (q, J = 27.8 Hz).

$^{19}$F NMR (471 MHz, CDCl$_3$) δ -57.23.

HR-MS (ESI): m/z calculated for [C$_{22}$H$_{17}$F$_{3}$ONa]$^+$ ([M+Na]$^+$): 377.1124 measured: 377.1111.

4,4,4-trifluoro-2-methyl-1,2-diphenylbutan-1-one (2q): Followed General Method A using the allylic alcohol 2-methyl-1,1-diphenylprop-2-en-1-ol (89.6 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 150:1) to give 95.1 mg (56% yield) of 2q as a colorless oil. Rf = 0.80 (petroleum ether/ethyl acetate, 10:1). $^1$H NMR (400 MHz, Chloroform-d) δ 7.45 – 7.31 (m, 8H), 7.26 – 7.19 (m, 2H), 3.15 – 2.97 (m, 1H), 2.83 (dq, J = 15.5, 11.2 Hz, 1H), 1.83 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 201.40, 140.80, 136.03, 131.82, 129.32, 129.24, 128.07, 127.75, 126.41 (q, J = 278.5 Hz), 126.28, 51.87 (q, J = 1.4 Hz), 43.39 (q, J = 26.8 Hz), 21.99. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -58.58. HR-MS (ESI): m/z calculated for [C$_{17}$H$_{15}$F$_{3}$ONa]$^+$ ([M+Na]$^+$): 315.0967 measured: 315.0651

Section 5. General procedure for the electrochemical tandem sulfonylation/semipinacol rearrangement

General Method C: To an oven-dried undivided electrochemical cell equipped with a magnetic stir bar, a carbon anode (10.0 mm * 20.0 mm), and a graphite plate cathode (10.0 mm * 10.0 mm) were added ArSO$_2$Na (3.0 equiv, 1.2 mmol), LiClO$_4$ (3.0 equiv, 1.2 mmol), allylic alcohol 1 (1.0 equiv, 0.4 mmol), and followed by the addition of 6 mL MeCN and 6 mL H$_2$O. The mixture was stirred for 1 min. The electrolysis was controlled at a constant current 10 mA, and the reaction was terminated after 3 h, electricity = 2.8F. DCM (10 mL) and water (10 mL) was added, the aqueous layer was separated and
extracted with dichloromethane (3×5 mL), and the combined organic layers were washed with brine and dried over sodium sulfate. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product.

*2-phenyl-2-(tosylmethyl)cyclopentan-1-one (3a):* Followed General Method C using the allylic alcohol 1-(1-phenylvinyl)cyclobutan-1-ol (70.4 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 10:1) to give 95.7 mg (78% yield) of 3a as a white solid. Rf = 0.50 (petroleum ether/ethyl acetate, 4:1). m.p. 98-101 °C. $^1$H NMR (500 MHz, Chloroform-d) δ 7.57 (d, $J = 8.1$ Hz, 2H), 7.31 – 7.27 (m, 2H), 7.25 – 7.16 (m, 5H), 3.71 (d, $J = 14.5$ Hz, 1H), 3.61 (d, $J = 14.5$ Hz, 1H), 3.03 (dd, $J = 13.9, 6.2$ Hz, 1H), 2.67 (m, 1H), 2.49-2.18 (m, 5H), 2.10 – 2.03 (m, 1H), 1.82 – 1.71 (m, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 215.91, 144.30, 137.94, 135.61, 129.67, 128.91, 127.68, 127.57, 127.04, 63.99, 54.70, 35.91, 32.50, 21.57, 18.64. HR-MS (ESI): m/z calculated for [C$_{19}$H$_{24}$NO$_3$S]$^+$ ([M+NH$_4$]$^+$): 346.1471, measured: 346.1473

*2-(o-tolyl)-2-(tosylmethyl)cyclopentan-1-one (3b):* Followed General Method C using the allylic alcohol 1-(1-(o-tolyl)vinyl)cyclobutan-1-ol (75.2 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 10:1) to give 85.5 mg (63% yield) of 3b as a white solid. Rf = 0.55 (petroleum ether/ethyl acetate, 4:1). m.p. 110-115 °C. $^1$H NMR (500 MHz, Chloroform-d) δ 7.72 (d, $J = 8.1$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.21 – 7.09 (m, 1H), 7.08 – 7.00 (m, 2H), 6.93 (d, $J = 7.9$ Hz, 1H), 3.87 (d, $J = 14.5$ Hz, 1H), 3.69 (d, $J = 14.5$ Hz, 1H), 3.03 – 2.96 (m, 1H), 2.85 – 2.78 (m, 1H), 2.53 – 2.42 (m, 5H), 2.40 (s, 3H), 2.12 – 2.03 (m, 1H), 1.70 – 1.61 (m, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 217.61, 144.30, 137.94, 135.61, 129.67, 127.85, 127.68, 127.04, 125.92, 60.62, 55.84, 36.66, 33.42, 21.54, 21.09, 18.67. HR-MS (ESI): m/z calculated for [C$_{20}$H$_{26}$NO$_3$S]$^+$ ([M+NH$_4$]$^+$): 360.1628, measured: 360.1630

*2-(m-tolyl)-2-(tosylmethyl)cyclopentan-1-one (3c):* Followed General Method C using the allylic alcohol 1-(1-(m-tolyl)vinyl)cyclobutan-1-ol (75.2 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 10:1) to give 110.0 mg (81% yield) of 3c as a white solid. Rf = 0.50 (petroleum ether/ethyl acetate,
4:1). **m.p.** 115-118 °C; **^1H NMR** (500 MHz, Chloroform-\(d\)) \(\delta\) 7.55 (d, \(J = 8.2\) Hz, 2H), 7.18 (d, \(J = 8.0\) Hz, 2H), 7.15 – 7.08 (m, 2H), 7.01 (s, 1H), 6.98 (d, \(J = 6.5\) Hz, 1H), 3.73 (d, \(J = 14.6\) Hz, 1H), 3.59 (d, \(J = 14.6\) Hz, 1H), 3.03 (dd, \(J = 13.9, 6.2\) Hz, 1H), 2.68 – 2.60 (m, 1H), 2.42 – 2.30 (m, 5H), 2.21 (s, 3H), 2.10 – 2.02 (m, 1H), 1.84 – 1.71 (m, 1H). **^13C NMR** (126 MHz, CDCl\(_3\)) \(\delta\) 215.89, 144.10, 138.47, 137.86, 135.26, 129.48, 128.71, 128.36, 127.75, 127.49, 123.93, 63.92, 54.57, 35.83, 32.49, 21.47, 21.36, 18.57. **HR-MS (ESI):** \(m/z\) calculated for [\(\text{C}_{20}\text{H}_{26}\text{NO}_{3}\text{S}\)]\(^+\) ([M+NH\(_4\)]\(^+\)): 360.1628, measured: 360.1632

![Image](image)

**2-(p-tolyl)-2-(tosylmethyl)cyclopentan-1-one (3d):** Followed General Method C using the allylic alcohol 1-(1-(p-tolyl)vinyl)cyclobutan-1-ol (75.2 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 10:1) to give 120.0 mg (88% yield) of 3d as a white solid. \(R_f\) = 0.50 (petroleum ether/ethyl acetate, 4:1). **m.p.** 120-124 °C; **^1H NMR** (500 MHz, Chloroform-\(d\)) \(\delta\) 7.57 (d, \(J = 8.3\) Hz, 2H), 7.23 – 7.16 (m, 4H), 7.04 (d, \(J = 8.1\) Hz, 2H), 3.75 (d, \(J = 14.5\) Hz, 1H), 3.59 (d, \(J = 14.5\) Hz, 1H), 3.05 (dd, \(J = 13.9, 6.3\) Hz, 1H), 2.72 – 2.57 (m, 1H), 2.41 (s, 3H), 2.39 – 2.31 (m, 2H), 2.29 (s, 3H), 2.12 – 2.03 (m, 1H), 1.86 – 1.75 (m, 1H). **^13C NMR** (126 MHz, CDCl\(_3\)) \(\delta\) 215.82, 144.08, 137.92, 137.48, 132.19, 129.48, 127.50, 126.88, 63.97, 54.26, 35.71, 32.43, 21.49, 20.82, 18.53. **HR-MS (ESI):** \(m/z\) calculated for [\(\text{C}_{20}\text{H}_{26}\text{NO}_{3}\text{S}\)]\(^+\) ([M+NH\(_4\)]\(^+\)): 360.1628, measured: 360.1631.

![Image](image)

**2-(4-fluorophenyl)-2-(tosylmethyl)cyclopentan-1-one (3e):** Followed General Method C using the allylic alcohol 1-1-(4-fluorophenyl)vinyl)cyclobutan-1-ol (76.8 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 10:1) to give 110.0 mg (80% yield) of 3e as a white solid. \(R_f\) = 0.50 (petroleum ether/ethyl acetate, 4:1). **m.p.** 112-115 °C; **^1H NMR** (500 MHz, Chloroform-\(d\)) \(\delta\) 7.53 (d, \(J = 8.3\) Hz, 2H), 7.29 – 7.25 (m, 2H), 7.21 (d, \(J = 8.0\) Hz, 2H), 6.98 – 6.83 (m, 2H), 3.74 (d, \(J = 14.7\) Hz, 1H), 3.52 (d, \(J = 14.7\) Hz, 1H), 3.05 (dd, \(J = 14.1, 6.2\) Hz, 1H), 2.67 – 2.51 (m, 1H), 2.39 (s, 3H), 2.35 – 2.28 (m, 1H), 2.13 – 2.02 (m, 1H), 1.83 – 1.68 (m, 1H). **^13C NMR** (126 MHz, CDCl\(_3\)) \(\delta\) 215.63, 162.17 (d, \(J = 248.0\) Hz), 144.39, 137.75, 130.70 (d, \(J = 3.4\) Hz), 129.62, 128.96 (d, \(J = 8.1\) Hz), 127.50, 115.69 (d, \(J = 21.5\) Hz), 64.02, 53.95, 35.72, 32.70, 21.52, 18.56. **HR-MS (ESI):** \(m/z\) calculated for [\(\text{C}_{20}\text{H}_{26}\text{NO}_{3}\text{S}\)]\(^+\) ([M+NH\(_4\)]\(^+\)): 364.1377, measured: 364.1381.
2-(4-chlorophenyl)-2-(tosylmethyl)cyclopentan-1-one (3f): Followed General Method C using the allylic alcohol 1-(1-(4-chlorophenyl)vinyl)cyclobutan-1-ol (83.2 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 10:1) to give 93.1 mg (65% yield) of 3f as a white solid. R_t = 0.50 (petroleum ether/ethyl acetate, 4:1). m.p. 117-120 °C; ^1H NMR (500 MHz, Chloroform-d) δ 7.49 (d, J = 8.0 Hz, 2H), 7.24 - 7.17 (m, 4H), 7.14 (d, J = 8.6 Hz, 2H), 3.77 (d, J = 14.8 Hz, 1H), 3.48 (d, J = 14.7 Hz, 1H), 3.06 (dd, J = 14.2, 6.2 Hz, 1H), 2.60 – 2.51 (m, 1H), 2.40 (s, 3H), 2.37 – 2.27 (m, 2H), 2.13 – 2.02 (m, 1H), 1.84 – 1.69 (m, 1H). ^13C NMR (126 MHz, CDCl_3) δ 215.38, 144.41, 137.61, 133.94, 133.36, 129.60, 128.86, 127.47, 63.93, 54.00, 35.70, 32.54, 21.52, 18.55. HR-MS (ESI): m/z calculated for [C_{19}H_{23}ClNO_3]^+ ([M+NH_4]^+): 380.1082, measured: 380.1085.

2-(4-methoxyphenyl)-2-(tosylmethyl)cyclopentan-1-one (3g): Followed General Method C using the allylic alcohol 1-(1-(4-methoxyphenyl)vinyl)cyclobutan-1-ol (81.6 mg, 0.40 mmol) and purified using silica gel chromatography (n-pentane/ethyl acetate = 10:1) to give 130.0 mg (92% yield) of 3g as a white solid. R_t = 0.40 (petroleum ether/ethyl acetate, 4:1). m.p. 115-120 °C; ^1H NMR (500 MHz, Chloroform-d) δ 6.72 – 6.68 (m, 2H), 3.75 – 3.69 (m, 4H), 3.52 (d, J = 14.6 Hz, 1H), 3.00 (dd, J = 14.0, 6.0 Hz, 1H), 2.63-2.52 (m, 1H), 2.35 (s, 3H), 1.79 – 1.68 (m, 1H), 2.33 – 2.24 (m, 2H), 2.07 – 1.97 (m, 1H) ^13C NMR (126 MHz, CDCl_3) δ 215.38, 158.89, 143.92, 137.80, 129.40, 128.15, 127.37, 126.52, 114.02, 63.89, 55.03, 53.70, 35.50, 32.43, 21.35, 18.39. HR-MS (ESI): m/z calculated for [C_{20}H_{26}NO_4]^+ ([M+NH_4]^+): 376.1577, measured: 376.1581.

2-([1,1'-biphenyl]-4-yl)-2-(tosylmethyl)cyclopentan-1-one (3h): Followed General Method C using the allylic alcohol 1-(1-([1,1'-biphenyl]-4-yl)vinyl)cyclobutan-1-ol (100.0 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 10:1) to give 135.0 mg (82% yield) of 3h as a white solid. R_t = 0.60 (petroleum ether/ethyl acetate, 4:1). m.p. 124-128 °C; ^1H NMR (500 MHz, Chloroform-d) δ 7.52 (dd, J = 13.6, 7.9 Hz, 4H), 7.46 – 7.39 (m, 4H), 7.37 – 7.32 (m, 3H), 7.15
(d, \(J = 8.1\) Hz, 2H), 3.84 (d, \(J = 14.8\) Hz, 1H), 3.60 (d, \(J = 14.8\) Hz, 1H), 3.14 (dd, \(J = 14.0, 6.2\) Hz, 1H), 2.69 – 2.58 (m, 1H), 2.41 – 2.33 (m, 2H), 2.32 (s, 3H), 2.16 – 2.06 (m, 1H), 1.91 – 1.77 (m, 1H). 13C NMR (126 MHz, CDCl₃) δ 215.77, 144.15, 140.56, 140.07, 137.82, 133.94, 129.56, 128.80, 127.58, 127.55, 127.38, 126.92, 64.10, 54.38, 35.85, 32.57, 21.50, 18.66. HR-MS (ESI): \(m/\zeta\) calculated for [C25H28NO3S]+ ([M+NH4]+): 422.1784, measured: 422.1787.

2-(benzo[d][1,3]dioxol-5-yl)-2-(tosylmethyl)cyclopentan-1-one (3i) : Followed General Method C using the allylic alcohol 1-(1-(benzo[d][1,3]dioxol-5-yl)vinyl)cyclobutan-1-ol (87.2 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 10:1) to give 124.5 mg (84% yield) of 3i as a white solid. \(R_f = 0.40\) (petroleum ether/ethyl acetate, 4:1). m.p. 129-133 °C; 1H NMR (500 MHz, Chloroform-d) δ 7.54 (d, \(J = 8.0\) Hz, 2H), 7.20 (d, \(J = 8.0\) Hz, 2H), 6.75 (dd, \(J = 8.4, 1.6\) Hz, 1H), 6.72 – 6.70 (m, 1H), 6.66 – 6.59 (m, 1H), 5.90 – 5.84 (m, 3H), 3.73 (d, \(J = 14.6\) Hz, 1H), 3.48 (d, \(J = 14.6\) Hz, 1H), 2.98 (dd, \(J = 14.0, 6.1\) Hz, 1H), 2.65-2.47 (m, 1H), 2.38 (s, 3H), 2.35 – 2.26 (m, 2H), 2.10 – 1.97 (m, 1H), 1.84 – 1.73 (m, 1H). 13C NMR (126 MHz, CDCl₃) δ 215.45, 148.06, 147.08, 144.09, 137.79, 129.45, 128.47, 127.51, 120.64, 108.22, 107.59, 101.20, 64.01, 54.08, 35.56, 32.78, 21.47, 18.47. HR-MS (ESI): \(m/\zeta\) calculated for [C20H20NO5S]+ ([M+NH4]+): 390.1370, measured: 390.1374

2-(4-chloro-3-methylphenyl)-2-(tosylmethyl)cyclopentan-1-one (3j) : Followed General Method C using the allylic alcohol 1-(1-(4-chloro-3-methylphenyl)vinyl)cyclobutan-1-ol (88.9 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 10:1) to give 103.1 mg (69% yield) of 3j as a white solid. \(R_f = 0.50\) (petroleum ether/ethyl acetate, 4:1). m.p. 120-123 °C; 1H NMR (500 MHz, Chloroform-d) δ 7.51 – 7.45 (m, 2H), 7.16 (dd, \(J = 8.3, 6.3\) Hz, 3H), 7.06 (dd, \(J = 8.4, 2.5\) Hz, 1H), 7.04 – 7.00 (m, 1H), 3.82 (d, \(J = 14.8\) Hz, 1H), 3.47 (d, \(J = 14.9\) Hz, 1H), 3.08 (dd, \(J = 14.1, 6.2\) Hz, 1H), 2.63 – 2.46 (m, 1H), 2.39 (s, 3H), 2.34 – 2.28 (m, 2H), 2.20 (s, 3H), 2.12 – 2.04 (m, 1H), 1.86 – 1.72 (m, 1H). 13C NMR (126 MHz, CDCl₃) δ 215.45, 148.06, 147.08, 144.09, 137.61, 129.45, 128.47, 127.51, 120.64, 108.22, 107.59, 101.20, 64.01, 54.08, 35.56, 32.78, 21.47, 18.47. HR-MS (ESI): \(m/\zeta\) calculated for [C20H25ClNO3S]+ ([M+NH4]+): 394.1370, measured: 394.1243
2-(3,4-dichlorophenyl)-2-(tosylmethyl)cyclopentan-1-one (3k): Followed General Method C using the allylic alcohol 1-(1-(3,4-dichlorophenyl)-vinyl)cyclobutan-1-ol (97.2 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 10:1) to give 121.1 mg (73% yield) of 3k as a white solid. R_f = 0.50 (petroleum ether/ethyl acetate, 4:1). m.p. 121-125 °C; ^1H NMR (500 MHz, Chloroform-d) δ 7.44 (d, J = 8.0 Hz, 2H), 7.25 – 7.21 (m, 2H), 7.18 – 7.12 (m, 3H), 3.83 (d, J = 14.9 Hz, 1H), 3.41 (d, J = 14.9 Hz, 1H), 3.06 (dd, J = 14.4, 6.2 Hz, 1H), 2.55 – 2.44 (m, 1H), 2.39 (s, 3H), 2.37 – 2.25 (m, 2H), 2.15 – 2.04 (m, 1H), 1.86 – 1.71 (m, 1H). ^13C NMR (126 MHz, CDCl3) δ 214.78, 144.62, 137.19, 134.60, 132.89, 132.23, 130.45, 129.53, 127.35, 126.57, 63.68, 53.67, 35.68, 32.51, 21.53, 18.55. HR-MS (ESI): m/z calculated for [C19H22Cl2NO3S]+ ([M+NH4]4+): 414.0692, measured: 414.0696

2-(naphthalen-2-yl)-2-(tosylmethyl)cyclopentan-1-one (3l): Followed General Method C using the allylic alcohol 1-(1-(naphthalen-2-yl)vinyl)cyclobutan-1-ol (89.6 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 10:1) to give 122.1 mg (81% yield) of 3l as a white solid. R_f = 0.60 (petroleum ether/ethyl acetate, 4:1). m.p. 125-130 °C; ^1H NMR (500 MHz, Chloroform-d) δ 7.80 – 7.63 (m, 5H), 7.51 – 7.44 (m, 4H), 7.43 (dd, J = 28.3, 8.7 Hz, 1H), 6.98 (d, J = 7.8 Hz, 2H), 3.95 (d, J = 14.8 Hz, 1H), 3.64 (d, J = 14.8 Hz, 1H), 3.26 (dd, J = 14.3, 6.0 Hz, 1H), 2.76-2.66 (m, 1H), 2.48 – 2.29 (m, 2H), 2.22 (s, 3H), 2.18 – 2.10 (m, 1H), 2.00 – 1.77 (m, 1H). ^13C NMR (126 MHz, CDCl3) δ 215.71, 144.10, 137.56, 133.00, 132.48, 131.98, 129.30, 128.76, 128.04, 127.40, 127.27, 126.70, 126.52, 126.34, 124.35, 63.85, 54.71, 35.81, 32.64, 21.34, 18.64. HR-MS (ESI): m/z calculated for [C19H22Cl2NO3S]+ ([M+NH4]4+): 396.1628, measured: 396.1621

2'-tosyl-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2-one (3m): Followed General Method C using the allylic alcohol 1-(1H-inden-3-yl)cyclobutan-1-ol (75.2 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 10:1) to give 3m as a white solid. m.p. 103-105 °C. R_f = 0.60 (petroleum ether/ethyl acetate, 4:1). ^1H NMR (400 MHz, Chloroform-d) δ 7.79 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 9.0 Hz, 2H), 7.21 – 7.04 (m, 4H), 4.03 (dd, J = 10.5, 8.2 Hz, 1H), 3.60 (dd, J = 15.2, 10.5 Hz, 1H), 2.95 – 2.79 (m, 3H), 2.55 – 2.38 (m, 6H), 2.26 – 2.07 (m, 1H). ^13C NMR (126 MHz, CDCl3) δ 215.60, 144.84, 144.77, 139.85, 136.60, 129.74, 128.48, 127.88, 127.61, 124.69, 122.15, 75.05, 61.92,
2-phenyl-2-((phenylsulfonyl)methyl)cyclopentan-1-one (3aa): Followed General Method C using the allylic alcohol 1-(1-phenylvinyl)cyclobutan-1-ol (70.4 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 10:1) to give 92.7 mg (73% yield) of 3aa as a white solid. R_f = 0.50 (petroleum ether/ethyl acetate, 4:1). m.p. 93-97 °C; 1H NMR (500 MHz, Chloroform-d) δ 7.72 – 7.66 (m, 2H), 7.55 – 7.50 (m, 1H), 7.43 – 7.38 (m, 2H), 7.31 – 7.27 (m, 2H), 7.25 – 7.15 (m, 3H), 3.76 (d, J = 14.6 Hz, 1H), 3.62 (d, J = 14.6 Hz, 1H), 3.07 (dd, J = 13.9, 6.2 Hz, 1H), 2.71-2.60 (m, 1H), 2.40 – 2.28 (m, 2H), 2.13 – 2.02 (m, 1H), 1.84 – 1.72 (m, 1H). 13C NMR (126 MHz, CDCl3) δ 215.78, 215.78, 140.72, 135.25, 133.26, 133.26, 129.00, 128.87, 128.85, 127.75, 127.45, 127.42, 126.99, 126.94, 63.86, 54.62, 35.79, 32.50, 32.49, 18.57, 18.56. HR-MS (ESI): m/z calculated for [C18H21FNO3S]+ ([M+NH4]+): 332.1315, measured: 332.1318

2-(((4-fluorophenyl)sulfonyl)methyl)-2-phenylcyclopentan-1-one (3ab): Followed General Method C using the allylic alcohol 1-(1-phenylvinyl)cyclobutan-1-ol (70.4 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 10:1) to give 81.8 mg (61% yield) of 3ab as a white oil. R_f = 0.60 (petroleum ether/ethyl acetate, 4:1). 1H NMR (500 MHz, Chloroform-d) δ 7.68 – 7.63 (m, 2H), 7.30 – 7.26 (m, 2H), 7.25 – 7.18 (m, 3H), 7.08 – 7.03 (m, 2H), 3.80 (d, J = 14.8 Hz, 1H), 3.59 (d, J = 14.8 Hz, 1H), 3.14 – 3.06 (m, 1H), 2.65 – 2.54 (m, 1H), 2.41 – 2.26 (m, 2H), 2.12 – 2.03 (m, 1H), 1.86 – 1.73 (m, 1H). 13C NMR (126 MHz, CDCl3) δ 215.70, 165.42 (d, J = 256.0 Hz), 136.81 (d, J = 3.5 Hz), 134.94, 130.39 (d, J = 9.8 Hz), 128.93, 127.85, 127.07, 116.24 (d, J = 22.8 Hz), 64.19, 54.63, 35.74, 32.58, 18.54. HR-MS (ESI): m/z calculated for [C18H21FNO3S]+ ([M+NH4]+): 350.1221, measured: 350.1224
2-(((4-chlorophenyl)sulfonyl)methyl)-2-phenylcyclopentan-1-one (3ac):

Followed General Method C using the allylic alcohol 1-(1-phenylvinyl)cyclobutan-1-ol (70.4 mg, 0.40 mmol) and purified by silica gel chromatography (n-pentane/ethyl acetate = 10:1) to give 100.1 mg (75% yield) of 3ac as a colorless oil. 

Rf = 0.50 (petroleum ether/ethyl acetate, 4:1). 

\(^1\)H NMR (500 MHz, Chloroform-d) \(\delta\) 7.59 – 7.54 (m, 2H), 7.38 – 7.32 (m, 2H), 7.29 – 7.26 (m, 2H), 7.24 – 7.17 (m, 3H), 3.81 (d, \(J = 14.8\) Hz, 1H), 3.58 (d, \(J = 14.8\) Hz, 1H), 3.14 – 3.06 (m, 1H), 2.63 – 2.53 (m, 1H), 2.42 – 2.25 (m, 2H), 2.15 – 1.99 (m, 1H), 1.86 – 1.74 (m, 1H). 

\(^{13}\)C NMR (126 MHz, CDCl3) \(\delta\) 215.60, 139.96, 139.13, 134.81, 129.25, 128.99, 128.93, 127.83, 127.07, 64.13, 54.57, 35.70, 32.56, 18.53. 

HR-MS (ESI): \(m/z\) calculated for [C\(_{18}\)H\(_{21}\)ClNO\(_3\)S]\(^+\) ([M+NH\(_4\)]\(^+\)): 366.0925, measured: 366.0927
Section 6. X-ray Crystallography

Table 1. Crystal data and structure refinement for 2l.

| Property                      | Value                          |
|-------------------------------|--------------------------------|
| Identification code           | 2l                             |
| Empirical formula             | C15 H15 F3 O                   |
| Formula weight                | 268.27                         |
| Temperature                   | 296(2) K                       |
| Wavelength                    | 1.54178 Å                      |
| Crystal system, space group   | Monoclinic, P2(1)/c            |
| Unit cell dimensions          | a = 15.1470(8) Å, alpha = 90 deg. |
|                               | b = 12.1527(7) Å, beta = 114.703(2) deg. |
|                               | c = 15.3091(9) Å, gamma = 90 deg. |
|                              |                              |
|------------------------------|------------------------------|
| **Volume**                   | 2560.2(3) Å³               |
| **Z, Calculated density**    | 8, 1.392 Mg/m³             |
| **Absorption coefficient**   | 0.986 mm⁻¹                 |
| **F(000)**                   | 1120                        |
| **Crystal size**             | 0.220 x 0.200 x 0.160 mm   |
| **Theta range for data collection** | 3.211 to 68.365 deg.    |
| **Limiting indices**         | -18≤h≤14, -14≤k≤14, -18≤l≤18 |
| **Reflections collected / unique** | 24402 / 4667 [R(int) = 0.0707] |
| **Completeness to theta**    | 67.679 99.2 %              |
| **Refinement method**        | Full-matrix least-squares on F² |
| **Data / restraints / parameters** | 4667 / 0 / 344            |
| **Goodness-of-fit on F²**    | 1.052                       |
| **Final R indices [I>2sigma(I)]** | R₁ = 0.0599, wR₂ = 0.1624 |
| **R indices (all data)**     | R₁ = 0.1007, wR₂ = 0.2068 |
| **Extinction coefficient**   | 0.0047(6)                  |
| **Largest diff. peak and hole** | 0.250 and -0.219 eÅ⁻³      |
Table 2. Crystal data and structure refinement for 3m.

| Identification code | 3m    |
|---------------------|-------|
| Empirical formula   | C20 H20 O3 S |
| Formula weight      | 340.42 |
| Temperature         | 296(2) K |
| Wavelength          | 1.54178 Å |
| Crystal system, space group | Monoclinic, P2(1)/c |
| Unit cell dimensions| a = 12.4233(5) Å  alpha = 90 deg. |
|                     | b = 16.0092(6) Å beta = 96.142(2) deg. |
|                     | c = 8.7500(3) Å gamma = 90 deg. |
Volume 1730.27(11) Å³
Z, Calculated density 4, 1.307 Mg/m³
Absorption coefficient 1.778 mm⁻¹
F(000) 720
Crystal size 0.220 x 0.200 x 0.180 mm
Theta range for data collection 4.521 to 65.066 deg.
Limiting indices -14≤h≤14, -17≤k≤18, -10≤l≤10
Reflections collected / unique 18600 / 2868 [R(int) = 0.0757]
Completeness to theta = 65.066 97.2 %
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 2868 / 0 / 218
Goodness-of-fit on F² 1.145
Final R indices [I>2sigma(I)] R1 = 0.0727, wR2 = 0.1903
R indices (all data) R1 = 0.0980, wR2 = 0.2091
Extinction coefficient n/a
Largest diff. peak and hole 0.402 and -0.414 e.Å⁻³
Section 7 Reference

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2-(m-tolyl)-2-(2.2.2-trifluoroethyl)cyclopentan-1-one
(2c)
2-(3-chlorophenyl)-2-(2,2,2-trifluoroethyl)cyclopentan-1-one

2-(3-chlorophenyl)-2-(2,2,2-trifluoroethyl)cyclopentan-1-one
2-(4-methoxyphenyl)-2-(2,2,2-trifluoroethyl)cyclopentan-1-one (2h)
$2'-(\text{trifluoromethyl})-3',4'-\text{dihydro}-2'H$-
spiro[cyclopentane-1,1'-naphthalen]-2-one (28)

$2'-\text{(trifluoromethyl)}-3',4'-\text{dihydro}-2'H$-
spiro[cyclopentane-1,1'-naphthalen]-2-one (31)
2-phenyl-2-(2,2,2-trifluoroethyl)cyclohexan-1-one (2m)

2-phenyl-2-(2,2,2-trifluoroethyl)cyclohexan-1-one (2n)
2,2,3-triphenyl-1-(2,2,2-trifluoroethyl)oxirane (4pa)
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2-(4-chlorophenyl)-2-(tosylmethyl)cyclopentan-1-one (3h)

2-(4-methoxyphenyl)-2-(tosylmethyl)cyclopentan-1-one (3g)
2-phenyl-2-[[phenylsulfonyl]methy]cyclopentan-1-one (32a)

2-[[4-Fluorophenyl]sulfonyl]methy]cyclopentan-1-one (31b)
2-[[4-fluorophenyl]sulfonylmethyl]-2-phenylcyclopentan-1-one (3ab)

2-[[4-chlorophenyl]sulfonylmethyl]-2-phenoxy/cyclopentan-1-one (3ac)
