SUPPLEMENTARY INFORMATION

Direct Transfer of Tri- and di- fluoroethanol Units Enabled by Radical Activation of Organosilicon Reagents

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Supplementary Methods

General information

Chromatography: HaiLang Silica Flash P60 size 40–63 μm (200–300 mesh), TLC: HaiLang silica gel 60 (0.25mm). Visualization of the chromatogram was performed by UV, phosphomolybdic acid and K\text{MnO}_4 staining. Mass spectra were recorded on Bruker UltiMate3000 & Compact, Thermo ISQ LT, LTQ XL and VELOS pro & ORBITRAP mass spectrometers. \textsuperscript{1}H, \textsuperscript{13}C, \textsuperscript{19}F were recorded on Bruker 400, Bruker 600 and JNM–ECZ 400 using CDCl\textsubscript{3} or DMSO-d\textsubscript{6} as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard (CDCl\textsubscript{3}: \(\delta\) 7.26 for \textsuperscript{1}H, \(\delta\) 77.16 for \textsuperscript{13}C). Data are reported as follows: chemical shifts, multiplicity (s = singlet, bs = broad singlet, d = doublet, dd = doublet of doublets, t = triplet, td = triplet of doublets, m = multiplet), coupling constants (Hz), and integration. Infrared spectra were recorded on an Agilent Technologies Cary 630 FTIR and wavelengths are reported in cm\textsuperscript{-1}. Melting point was measured by INESA SGW X–4. All reagents were used as received and solvents were dried and degassed according to standard procedure. If no special description, all reactions were conducted under nitrogen. MnF\textsubscript{3}, MnPO\textsubscript{4} hydrate and Mn(OAc)\textsubscript{3}·\textsubscript{2}H\textsubscript{2}O was purchased from Alfa, Mn(OAc)\textsubscript{3}·\textsubscript{4}H\textsubscript{2}O was purchased from adamas, L(−)-menthol, Epiandrosterone, Cholesterol, Diosgenin for preparation of 7ai, 7aj, 7ak, 7am were purchased from energy-chemicals and Testosterone, Estrone, (8α)-Estradiol for preparation of 7al, 7ao, 7ap were purchased from adamas. Vitamin E for preparation of 7n was purchased from TCI. Other alcohols and ketones were purchased from Bidepharm and Meryer. Cinnamic acids 12a–12l were purchased from adamas and used without further purification.

Synthesis of \(\alpha\)-silyl trifluoroethanols

**Synthesis of 1-((dimethyl)(phenyl)silyl)-2,2,2-trifluoroethan-1-ol (1a)**

![Supplementary Figure. 1 Synthesis of 1-((dimethyl)(phenyl)silyl)-2,2,2-trifluoroethan-1-ol (1a)]

1-((Dimethyl)(phenyl)silyl)-2,2,2-trifluoroethan-1-ol was synthesized according to Welch’s protocol with slightly variation and modification.\textsuperscript{[1]} To a stirring solution of 2,2,2-trifluoroethanol (6.0 g, 60 mmol) and phenyldimethylchlorosilane (10.2 g, 60 mmol, 1.0 equiv.) and HMPA (6.0 mL) in dry THF (60 mL) in low temperature bath under −78 °C, was added LDA (prepared by Diisopropylamine with \(n\)-BuLi in THF, 3.5 equiv.) dropwise with syringe. The mixture was kept for 4 h under −78 °C and allowed to rt, after which the mixture was stirred for another 15 h. After addition of triethylchlorosilane (15 mL, 90 mmol, 1.5 equiv.) to the mixture at 0 °C, the mixture was stirred for 4 h, and then quenched by the addition of a saturated aqueous solution of NH\textsubscript{4}Cl (20 mL), 4 was isolated by silica gel column chromatography (siliga: 200–300 mesh) using PE as eluent (colorless oil, 16.5 g, 50.4 mmol, 84% yield).

To a solution of Selectfluor (5.4 g, 15 mmol, 1.5 equiv.) in 40 mL of MeCN was added a solution of compound 4 (3.3 g, 10 mmol) in 10 mL of DCM at 0 °C. The resulting mixture was stirred at room temperature for 24 h and quenched by the addition of 20 mL water, then extracted with DCM. The organic layer was dried over Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated. Product 5 was purified by either silica gel column chromatography (siliga: 200–300 mesh) using PE as eluent (slight yellow oil, 1.9 g, 8.2 mmol, 82% yield).
To a stirring solution of 5 (0.46 g, 2.0 mmol) in MeOH (0.05 M) at 0 °C was added NaBH₄ (0.074 g, 2.0 mmol, 1.0 equiv.) in portions, the resulting mixture was stirred for 0.5 h and quenched by water, then extracted with DCM. The organic layer was dried over Na₂SO₄, filtered, and concentrated. 1-((dimethyl)(phenyl)silyl)-2,2,2-trifluoroethan-1-ol (1a) was further purified by silica gel column chromatography (siliga: 200~300 mesh) using PE/EA (50/1, v/v) (colorless oil, 0.40 g, 1.72 mmol, 86% yield).

### I-(dimethyl(phenyl)silyl)-2,2,2-trifluoroethan-1-one (5) NMR spectroscopy

- [1]H NMR (400 MHz, CDCl₃) δ 7.56 (d, J = 6.7 Hz, 2H), 7.49~7.40 (m, 3H), 0.65 (s, 6H); [1]C NMR (100 MHz, CDCl₃) δ 222.4 (q, J = 36.4 Hz), 134.3, 131.2, 130.9, 128.5, 116.0 (q, J = 294.7 Hz), −5.0; [1]F NMR (375 MHz, CDCl₃) δ −79.4 (s, 3F). IR (ATR): 3075, 1682, 1537, 1457, 1356, 1285, 1271, 1188, 1085, 1044, 738, 701 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₀H₁₆F₆SiO⁺ (M⁺): 232.0533; Found: 232.0531; Found: 232.0533.

### I-(Diphenyl)(phenyl)silyl)-2,2,2-trifluoroethanol (1a) NMR spectroscopy

- [1]H NMR (400 MHz, CDCl₃) δ 7.61 (d, J = 6.1 Hz, 2H), 7.47~7.39 (m, 3H), 3.84 (q, J = 11.1 Hz, 1H), 0.49 (d, J = 3.1 Hz, 6H); [1]C NMR (100 MHz, CDCl₃) δ 134.4, 134.2, 130.3, 128.2, 127.1 (q, J = 278.4 Hz), 65.3 (q, J = 33.1 Hz), −4.7, −5.4; [1]F NMR (375 MHz, CDCl₃) δ −70.6 (d, J = 8.9 Hz, 3F). IR (ATR): 3441, 2963, 2919, 1428, 1253, 1148, 1085, 1044, 738, 701 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₀H₁₆F₆NaO⁺ (M+Na⁺): 257.0580; Found: 257.0570.

### Synthesis of 1-((methyl)(diphenyl)silyl)-2,2,2-trifluoroethan-1-ol (1b)

1-((Diphenyl)(methyl)silyl)-2,2,2-trifluoroethan-1-ol was synthesized according to Welch’s protocol with slightly variation and modification.[1] To a stirring solution of 2,2,2-trifluoroethanol (3.0 g, 30 mmol) and methyldiphenylchlorosilane (6.96 g, 30 mmol, 1.0 equiv.) and HMPA (3 mL) in dry THF (30 mL) in low temperature bath under −78 °C, was added LDA (2.0 M in THF, 3.5 equiv.) dropwise with syringe, the mixture was kept for 4 h under −78 °C and allowed to RT, after which the mixture was stirred for 15 h. After addition of triethylchlorosilane (7.5 mL, 45 mmol, 1.5 equiv.) to the mixture under 0 °C, the resulting mixture was stirred for 4 h and then quenched by the addition of a saturated aqueous solution of NH₄Cl (20 mL), compound 4b was coarsely isolated by silica gel column chromatography (siliga: 200~300 mesh) using PE as eluent (colorless oil, 7.9 g, 20.1 mmol, 67% yield).

To a solution of Selectfluor (5.4 g, 15 mmol, 1.5 equiv.) in 40 mL of MeCN was added a solution of compound 4b (3.9 g, 10 mmol) in 10 mL of DCM under 0 °C. The resulting mixture was stirred at room temperature for 24 h and quenched by the addition of 20 mL water, then extracted with DCM. The organic layer was dried over Na₂SO₄, filtered, and concentrated. Product 5b was purified by silica gel column chromatography (siliga: 200~300 mesh) using PE as eluent (slight yellow oil, 1.0 g, 3.3 mmol, 66% yield).

To a stirring solution of 5b (0.58 g, 2.0 mmol) in MeOH (0.05 M) under 0 °C was added NaBH₄ (0.074 g, 2.0 mmol, 1.0 equiv.) in portions, the resulting mixture was stirred for 0.5 h and quenched by water, then extracted with DCM. The organic layer was dried over Na₂SO₄, filtered, and concentrated. 1-((Diphenyl)(methyl)silyl)-2,2,2-trifluoroethan-1-ol (1b) was further purified by silica gel column chromatography (siliga: 200~300 mesh) using PE/EA (50/1, v/v) (colorless oil, 0.35 g, 1.2 mmol, 61% yield).
Trifluoroacetyldiphenylmethylsilane (5b) NMR spectroscopy: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64 (d, $J = 6.7$ Hz, 4H), 7.53 (t, $J = 7.2$ Hz, 2H), 7.46 (t, $J = 7.2$ Hz, 4H), 0.97 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 221.1 (q, $J = 34.8$ Hz), 135.2, 131.1, 129.9, 128.6, 115.9 (q, $J = 295.2$ Hz), $-5.5$; $^{19}$F NMR (375 MHz, CDCl$_3$) $\delta$ $-78.9$ (s, 3F). IR (ATR): 3075, 1685, 1431, 1267, 1193, 1137, 731, 697 cm$^{-1}$. HRMS (ESI, m/z): calcd for C$_{10}$H$_{15}$F$_{3}$NaOSi$^+$ (M+Na)$^+$: 317.0580; Found: 317.0570.

I-((methyl)(Diphenyl)silyl)-2,2,2-trifluoroethanol (1b) NMR spectroscopy: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.67–7.64 (m, 4H), 7.48–7.40 (m, 6H), 4.23 (q, $J = 11.1$ Hz, 1H), 0.78 (s, 3H), 2.00 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 135.5, 135.0, 132.8, 132.0, 130.5, 130.4, 128.3, 128.3, 126.8 (q, $J = 278.6$ Hz), 64.9 (q, $J = 32.8$ Hz), $-5.9$; $^{19}$F NMR (375 MHz, CDCl$_3$) $\delta$ $-69.8$ (d, $J = 11.9$ Hz, 3F). IR (ATR): 3429, 2919, 1428, 1256, 1152, 1085, 1044, 731, 697 cm$^{-1}$. HRMS (ESI, m/z): calcd for C$_{10}$H$_{15}$F$_{3}$NaOSi$^+$ (M+Na)$^+$: 319.0736; Found: 319.0739.

Synthesis of 2,2,2-trifluoro-1-((triethyl)silyl)ethan-1-ol (1c)

**Supplementary Figure. 3 Synthesis of 2,2,2-trifluoro-1-((triethyl)silyl)ethan-1-ol (1c)**

2,2,2-trifluoro-1-((triethyl)silyl)-ethan-1-ol was synthesized according to Welch’s protocol with slight variation and modification.$^{[1]}$ To a stirring solution of 2,2,2-trifluoroethanol (3.0 g, 30 mmol) and triethylchlorosilane (5.0 mL, 30 mmol, 1.0 equiv.) in dry THF (30 mL) in low temperature bath under $-78$ °C, was added LDA (2.0 M in THF, 3.5 equiv.) dropwise with syringe, the mixture was kept for 2 h under $-78$ °C and allowed to rt, after which the mixture was stirred for 3 h. After addition of triethylchlorosilane (7.5 mL, 45 mmol, 1.5 equiv.) to the mixture at 0 °C, the resulting mixture was stirred for 4 h and then quenched by the addition of a saturated aqueous solution of NH$_4$Cl (20 mL), compound 4c was coarsely isolated with 67% yield (colorless oil, 6.2 g, 20.1 mmol) by silica gel column chromatography using PE as eluent.

To a solution of Selectfluor (2.66 g, 7.5 mmol) in 50 mL of MeCN was added a solution of compound 4c (5 mmol) in 12.5 mL of DCM at 0 °C. The resulting mixture was stirred at room temperature for 12 h and quenched by the addition of 20 mL water, then extracted with DCM. The organic layer was dried over Na$_2$SO$_4$, filtered, and concentrated. Product 5c was purified by distillation under reduced pressure using cold trap (slight yellow oil, 0.5 g, 2.4 mmol, 48% yield).

To a stirring solution of 5c (0.42 g, 2.0 mmol) in MeOH (0.05 M) at 0 °C was added NaBH$_4$ (0.148 g, 4.0 mmol, 2.0 equiv.) in portions, the resulting mixture was stirred for 0.5 h and quenched by water, then extracted with DCM. The organic layer was dried over Na$_2$SO$_4$, filtered, and concentrated, 2,2,2-trifluoro-1-((triethyl)silyl)ethan-1-ol (1c) was further purified by silica gel column chromatography using PE/EA (10/1, v/v) (colorless oil, 0.32 g, 1.5 mmol, 75% yield).

I-((triethyl)silyl)-2,2,2-trifluoroethanol (1c) NMR spectroscopy: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.79 (q, $J = 11.5$ Hz, 1H), 1.01 (t, $J = 7.8$ Hz, 9H), 0.76–0.69 (m, 6H), 1.82 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 127.5 (q, $J = 278.4$ Hz), 64.1 (q, $J = 33.1$ Hz), 7.2, 1.9; $^{19}$F NMR (375 MHz, CDCl$_3$) $\delta$ $-71.0$ (d, $J = 8.9$ Hz, 3F). IR (ATR): 3429, 2960, 2881, 1461, 1264, 1152, 1085, 723, 686 cm$^{-1}$. HRMS (EI, m/z): calcd for C$_{10}$H$_{15}$F$_{3}$O$^+$ (M–Et)$^+$: 185.0610; Found: 185.0607.
Synthesis of 1-triphenylsilyl-2,2,2-trifluoroethanol (1d)

2,2,2-Trifluoro-1-(triphenylsilyl)-ethan-1-ol was synthesized according to Welch’s protocol with slightly variation and modification.[1] To a stirring solution of 2,2,2-trifluoroethanol (3.0 g, 30 mmol) and triphenylchlorosilane (8.82 g, 30 mmol, 1.0 equiv.) and HMPA (3 mL) in dry THF (30 mL) in low temperature bath under −78 °C, was added LDA (2.0 M in THF, 3.5 equiv.) dropwise with syringe. The mixture was kept for 4 h under −78 °C and allowed to rt, after which the mixture was stirred for 15 h. After addition of triethylchlorosilane (7.5 mL, 45 mmol, 1.5 equiv.) to the mixture at 0 °C, the mixture was stirred for 4 h, and then quenched by the addition of a saturated solution of NH₄Cl (20 mL), compound 4d was coarsely isolated by silica gel column chromatography (siliga: 200-300 mesh) using PE as eluent (colorless oil, 9.1 g, 20.1 mmol, 67% yield).

To a solution of Selectfluor (5.40 g, 15 mmol, 1.5 equiv.) in 40 mL of MeCN was added a solution of compound 4d (4.5 g, 10 mmol) in 10 mL of DCM at 0 °C. The resulting mixture was stirred at room temperature for 12 h and quenched by the addition of water, then extracted with DCM. The organic layer was dried over Na₂SO₄, filtered, and concentrated. Product 5d was purified by silica gel column chromatography (siliga: 200-300 mesh) using PE as eluent (white solid, 2.0 g, 5.6 mmol, 56% yield).

To a stirring solution of 5d (0.71 g, 2.0 mmol) in MeOH (0.05 M) at 0 °C was added NaBH₄ (0.074 g, 2.0 mmol, 1.0 equiv.) in portions, the resulting mixture was stirred for 0.5 h and quenched by water, then extracted with DCM. The organic layer was dried over Na₂SO₄, filtered, and concentrated. 2,2,2-trifluoro-1-(triphenylsilyl)ethan-1-ol (1d) was further purified by silica gel column chromatography (siliga: 200-300 mesh) using PE/EA (50/1, v/v) (white solid, 0.54 g, 1.5 mmol, 75% yield).

1-((Triphenylsilyl)-2,2,2-trifluoroethanol (1d), white solid, mp: 127 °C–130 °C, NMR spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 7.65 (dd, J = 7.9, 1.2 Hz, 6H), 7.52–7.47 (m, 3H), 7.44–7.40 (m, 6H), 4.55 (q, J = 11.1 Hz, 1H), 2.13 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 136.5, 130.9, 130.6, 130.6, 128.3, 126.7 (q, J = 278.4 Hz), 65.4 (q, J = 33.1 Hz); ¹⁹F NMR (375 MHz, CDCl₃) δ −68.4 (d, J = 11.9 Hz, 3F). IR (ATR): 3470, 2922, 1379, 1276 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₀H₁₅F₃O⁺ (M+H)⁺: 359.1074; Found: 359.1066.

Synthesis of 1-phenyldimethylsilyl-2,2-difluoroethanol (2a)

To a stirring solution of 4 (15.7 g, 48 mmol, 1.0 equiv.) in dry THF (10 mL) at 0 °C was added con. HCl (20 mL), the reaction medium was brought to room temperature and stirred for 3.0 h, then extracted with EA. The combined organic phase was washed with brine, dried over Na₂SO₄, filtered, and concentrated. Product 6 was purified by silica gel column chromatography (siliga: 200–300 mesh) using PE as eluent (light yellow oil, 8.1 g, 37.9 mmol, 79% yield).
To a stirring solution of 6 (0.43 g, 2.0 mmol) in MeOH (0.05 M) at 0 °C was added NaBH₄ (0.074 g, 2.0 mmol, 1.0 equiv.) in portions, the resulting mixture was stirred for 0.5 h and quenched by water, then extracted with DCM. The organic layer was dried over Na₂SO₄, filtered, and concentrated. 2,2-difluoro-1-(phenyldimethylsilyl)ethan-1-ol (2a) was further purified by silica gel column chromatography (siliga: 200~300 mesh) using PE/EA (50/1, v/v) (colorless oil, 0.38 g, 1.8 mmol, 88% yield).

Difluoroacetylyphenyldimethylsilanil (6) NMR spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, J = 6.4 Hz, 2H), 7.45~7.39 (m, 3H), 5.39 (t, J = 54.9 Hz, 1H), 0.62 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 233.0 (t, J = 32.0 Hz), 134.3 132.4, 130.5, 128.4, 112.2 (t, J = 249.9 Hz), −4.7; ¹⁹F NMR (375 MHz, CDCl₃) δ −125.3 (d, J = 53.6 Hz, 3F). IR (ATR): 3071, 2960, 1670, 1428, 1252, 1118, 1044, 828, 787, 697 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₀H₁₂F₂OSi⁺ (M+H)⁺: 215.0698; Found: 215.0693.

I-((Phenyl)(dimethyl)silyl)-2,2-difluoroethanol (2a) NMR spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 7.62~7.59 (m, 2H), 7.44~7.40 (m, 3H), 5.77 (td, J = 56.4, 4.1 Hz, 1H), 3.70 (ddd, J = 24.1 Hz), 66.2 (t, J = 4.1 Hz, 1H), 0.47 (d, J = 2.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 134.7, 134.3, 130.1, 128.3, 117.7 (t, J = 242.3 Hz), 66.2 (t, J = 24.1 Hz), -5.01, -5.14; ¹⁹F NMR (375 MHz, CDCl₃) δ −121.1~−123.1 (m, 2F). IR (ATR): 3567, 3422, 3071, 2960, 2915, 1457, 1428, 1379, 1252, 1110, 1059, 1014, 962, 820, 783, 701 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₀H₁₀F₂NaOSi⁺ (M+Na)⁺: 239.0674; Found: 239.0668.

Preparation of substituted allylic sulfone.

Synthesis of phenyl-2-acylallylic sulfone
Phenyl-2-acylalillic sulfones (7b~7i, 7k~7p, 7ah) were synthesized according to reported procedure.[²]

Synthesis of 2-((Phenylsulfonfonyl)methyl)acrylate
2-((Phenylsulfonfonyl)methyl)acryloyl chloride was prepared according to reported procedure.[³] 4-bromobut-2-en-1-ol was prepared by reduction of methyl 4-bromocrotonate with DIBAL.[⁴] Estradiol was protected with benzyl group before esterification.[⁵] Allylic sulfone (7j, 7r~7z, 7ae, 7ai~7ap) were prepared following the general esterification procedure shown below:

Supplementary Figure. 6 Synthesis of 2-((Phenylsulfonfonyl)methyl)acrylate

Under N₂ atmosphere, to a solution of corresponding alcohol (4.0 mmol) and triethylamine (505 mg, 5 mmol, 1.25 equiv.) in DCM (10 mL) was added acryl chloride (1220.0 mg, 5 mmol, 1.25 equiv.) in 5 mL DCM at 0 °C. Then the resulting mixture was stirred at room temperature overnight. The reaction was quenched by addition of water (10 mL), and the resulting mixture was extracted three times with DCM (3×30 mL) and the combined organic layer was dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified with column chromatography on silica gel (siliga: 200~300 mesh; PE/EA) to afford the desired product.

4-Bromo-but-2-en-1-yl 2-((phenyl)sulfonfonyl)methyl)acrylate (7j)

Rₜ = 0.14 (PE/EA = 4/1, v/v). Colorless oil, (1.0 g, 3.2 mmol, 46% yield). NMR spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 7.87~7.85 (m, 2H), 7.65 (t, J = 7.5 Hz, 1H), 7.65~7.53 (m, 2H), 6.54 (s, 1H), 5.95 (s, 1H), 5.88~5.72 (m, 2H), 4.49~4.48 (m, 2H), 4.16 (s, 2H), 4.06~4.04 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 164.5, 138.4, 134.1, 134.0, 130.2,
129.2, 128.9, 127.9, 64.7, 57.6, 43.9. IR (ATR): 2960, 2922, 2855, 1722, 1446, 1260, 1085, 1010, 790, 734 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₉H₂₃BrO₃NaS⁺ (M+Na)⁺: 380.9767; Found: 380.9767.

**Methoxyprop-2-yl 2-(((phenyl)sulfonyl)methyl)acrylate (7r)**

![Methoxyprop-2-yl 2-(((phenyl)sulfonyl)methyl)acrylate](image)

Rᵣ = 0.16 (PE/EA = 4:1, v/v). Colorless oil (1.0 g, 3.3 mmol, 83% yield). NMR spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, J = 7.4 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.55–7.51 (m, 2H), 6.50 (s, 1H), 5.91 (s, 1H), 5.03–4.82 (m, 1H), 4.23–4.08 (m, 2H), 3.43–3.28 (m, 5H), 1.11 (d, J = 6.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.4, 138.4, 134.0, 133.6, 129.2, 129.1, 128.9, 74.8, 70.8, 59.2, 57.4, 16.4. IR (ATR): 2982, 2937, 2885, 1718, 1446, 1308, 1148, 1085, 727 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₉H₂₃NaO₃S⁺ (M+Na)⁺: 321.0767; Found: 321.0776.

**2,3-Dihydro-1H-inden-1-yl 2-(((phenyl)sulfonyl)methyl)acrylate (7s)**

![2,3-Dihydro-1H-inden-1-yl 2-(((phenyl)sulfonyl)methyl)acrylate](image)

Rᵣ = 0.16 (PE/EA = 8:1, v/v). White solid, mp: 70 °C–72 °C, (1.0 g, 2.6 mmol, 87% yield). NMR spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 7.6 Hz, 2H), 7.64–7.48 (m, 3H), 7.32–7.19 (m, 4H), 6.49 (s, 1H), 6.08–6.05 (m, 1H), 5.91 (s, 1H), 4.17 (s, 2H), 3.10–3.03 (m, 1H), 2.90–2.82 (m, 1H), 2.48–2.39 (m, 1H), 1.99–1.91 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 164.9, 144.5, 140.5, 138.5, 133.9, 133.7, 129.2, 129.2, 128.9, 126.9, 125.7, 124.9, 79.8, 57.5, 32.2, 30.3. IR (ATR): 2989, 2937, 1703, 1446, 1293, 1148, 757, 690 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₉H₁₆NaO₃S⁺ (M+Na)⁺: 365.0818; Found: 365.0829.

**Benzod[1,3]dioxol-5-ylmethyl 2-(((phenyl)sulfonyl)methyl)acrylate (7t)**

![Benzod[1,3]dioxol-5-ylmethyl 2-(((phenyl)sulfonyl)methyl)acrylate](image)

Rᵣ = 0.19 (PE/EA = 4:1, v/v). White solid, mp: 87 °C–90 °C, (1.4 g, 3.9 mmol, 78% yield). NMR spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, J = 7.3 Hz, 2H), 7.62 (t, J = 7.5 Hz, 1H), 7.50 (t, J = 7.7 Hz, 2H), 6.81–6.71 (m, 3H), 6.53 (s, 1H), 5.98 (s, 2H), 5.95 (s, 1H), 4.89 (s, 2H), 4.16 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 164.7, 147.9, 138.3, 134.1, 134.0, 129.2, 129.1, 128.9, 128.9, 122.5, 109.2, 108.4, 101.4, 67.3, 57.5. IR (ATR): 2960, 2926, 1715, 1491, 1256, 1141, 1085, 1036, 798, 731 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₅H₁₂NaO₃S⁺ (M+Na)⁺: 383.0560; Found: 383.0570.

**2-Idobenzyl 2-(((phenyl)sulfonyl)methyl)acrylate (7u)**

![2-Idobenzyl 2-(((phenyl)sulfonyl)methyl)acrylate](image)

Rᵣ = 0.24 (PE/EA = 4:1, v/v). White solid, mp: 85 °C–86 °C, (1.1 g, 2.6 mmol, 88% yield). NMR spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 7.85 (t, J = 6.9 Hz, 3H), 7.60 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.5 Hz, 1H), 7.28 (d, J = 6.7 Hz, 1H), 7.04 (t, J = 7.0 Hz, 1H), 6.61 (s, 1H), 6.00 (s, 1H), 5.02 (s, 2H), 4.19 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 164.5, 139.7, 137.9, 134.4, 134.0, 130.2, 129.9, 129.2, 128.9, 128.8, 128.5, 98.6, 70.9, 57.5. IR (ATR): 2982, 2933, 1718, 1305, 1148, 1407, 760, 690 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₉H₁₅INaO₃S⁺ (M+Na)⁺: 464.9628; Found: 464.9646.

**4-Bromobenzyl 2-(((phenyl)sulfonyl)methyl)acrylate (7v)**
Rf = 0.47 (PE/EA = 2/1, v/v). White solid, mp: 64 °C–66 °C, (1.1 g, 2.7 mmol, 68% yield). NMR spectroscopy: 1H NMR (400 MHz, CDCl3) \( \delta \) 7.83 (d, \( J = 7.6 \) Hz, 2H), 7.61 (t, \( J = 7.5 \) Hz, 1H), 7.50–7.47 (m, 4H), 7.16 (d, \( J = 7.9 \) Hz, 2H), 6.54 (s, 1H), 5.94 (s, 1H), 4.97 (s, 2H), 4.16 (s, 2H); 13C NMR (100 MHz, CDCl3) \( \delta \) 164.7, 138.4, 134.4, 134.2, 134.0, 131.9, 130.1, 129.2, 128.9, 128.8, 122.6, 77.5, 77.2, 76.8, 66.6, 57.5. IR (ATR): 2933, 2930, 1715, 1446, 1293, 1337, 1085, 753, 686 cm\(^{-1}\). HRMS (ESI, m/z): calcd for C\(_{17}\)H\(_{18}\)BrNaO\(_2\)S\(_2\) (M+Na\(^+\)): 416.9767; Found: 416.9783.

**Cyclohexylpropyl 2-(((phenyl)sulfonyl)methyl)acrylate (7x)**

Rf = 0.59 (DCM). White solid, mp: 57 °C–59 °C, (1.2 g, 3.5 mmol, 69% yield). NMR spectroscopy: 1H NMR (400 MHz, CDCl3) \( \delta \) 7.84 (d, \( J = 7.4 \) Hz, 2H), 7.63 (t, \( J = 7.4 \) Hz, 1H), 7.52 (t, \( J = 7.7 \) Hz, 2H), 6.49 (s, 1H), 5.90 (s, 1H), 4.15 (s, 2H), 3.90 (t, \( J = 6.8 \) Hz, 2H), 1.73–1.60 (m, 5H), 1.58–1.47 (m, 2H), 1.27–1.08 (m, 6H), 0.94–0.75 (m, 2H); 13C NMR (100 MHz, CDCl3) \( \delta \) 164.9, 138.4, 134.0, 133.4, 129.1, 128.8, 66.1, 57.6, 37.3, 33.5, 33.3, 26.7, 26.4, 25.8. IR (ATR): 2930, 2848, 1715, 1472, 1320, 1148, 1085 cm\(^{-1}\). HRMS (ESI, m/z): calcd for C\(_{20}\)H\(_{22}\)NaO\(_2\)S\(_2\) (M+Na\(^+\)): 373.1444; Found: 373.1450.

**Adamantan-2-yl 2-(((phenyl)sulfonyl)methyl)acrylate (7y)**

Rf = 0.46 (PE/EA = 4/1, v/v). White solid, mp: 75 °C–78 °C, (1.3 g, 3.5 mmol, 88% yield). NMR spectroscopy: 1H NMR (400 MHz, CDCl3) \( \delta \) 7.85 (d, \( J = 7.3 \) Hz, 2H), 7.62 (t, \( J = 7.4 \) Hz, 1H), 7.52 (t, \( J = 7.7 \) Hz, 2H), 6.55 (s, 1H), 5.95 (s, 1H), 4.79 (s, 1H), 4.19 (s, 2H), 1.98–1.48 (m, 14H); 13C NMR (100 MHz, CDCl3) \( \delta \) 164.1, 138.4, 133.9, 133.2, 129.6, 129.1, 128.9, 78.5, 57.4, 37.3, 36.3, 32.0, 31.7, 27.2, 26.9. IR (ATR): 2907, 2855, 1707, 1446, 1297, 1141, 984, 895, 757, 686 cm\(^{-1}\). HRMS (ESI, m/z): calcd for C\(_{20}\)H\(_{22}\)O\(_2\)S\(_2\) (M+Na\(^+\)): 383.1288; Found: 383.1303.

**N,N-diphenyl 2-(((phenyl)sulfonyl)methyl)acrylamide (7z)**

Rf = 0.28 (PE/EA = 2/1, v/v). White solid, mp: 154 °C–155 °C, (0.9 g, 2.4 mmol, 60% yield after recrystallization). NMR spectroscopy: 1H NMR (400 MHz, CDCl3) \( \delta \) 7.91 (d, \( J = 7.6 \) Hz, 2H), 7.64 (t, \( J = 7.3 \) Hz, 1H), 7.53 (t, \( J = 7.6 \) Hz, 2H), 7.37–7.33 (m, 4H), 7.27–7.24 (m, 6H), 5.69 (s, 1H), 5.33 (s, 1H), 3.84 (s, 2H); 13C NMR (100 MHz, CDCl3) \( \delta \) 167.7, 143.3, 138.5, 134.0, 133.7, 131.4, 129.5, 129.2, 128.7, 127.6, 127.0, 60.1. IR (ATR): 1651, 1625, 1364, 1305, 1148, 1081, 760, 690 cm\(^{-1}\). HRMS (ESI, m/z): calcd for C\(_{20}\)H\(_{19}\)NNaO\(_2\)S\(_2\) (M+Na\(^+\)): 400.0978; Found: 400.0991.

**Cyclobutyl 2-(((phenyl)sulfonyl)methyl)acrylate (7ae)**

Rf = 0.14 (PE/EA = 8:1, v/v). White solid, mp: 43 °C–45 °C, (0.5 g, 1.7 mmol, 57% yield). NMR spectroscopy: 1H NMR (400 MHz, CDCl3) \( \delta \) 7.84 (d, \( J = 7.5 \) Hz, 2H), 7.64 (t, \( J = 7.4 \) Hz, 1H), 7.53 (t, \( J = 7.7 \) Hz, 2H), 6.50 (s, 1H), 5.92 (s, 1H), 4.76 (p, \( J = 7.5 \) Hz, 1H), 4.14 (s, 2H), 2.30–2.16 (m, 2H), 2.01–1.84 (m, 2H), 1.81–1.68 (m, 1H), 1.63–1.50 (m, 1H); 13C NMR (100 MHz, CDCl3) \( \delta \) 164.1, 138.4, 134.0, 133.7, 129.2, 129.1, 128.9, 69.9, 57.5, 30.1, 13.5. IR (ATR): 2989, 2937,
1722, 1450, 1323, 1249, 1144, 1070, 753, 686 cm\(^{-1}\). HRMS (ESI, m/z): calcld for \(\text{C}_{13}\text{H}_{18}\text{NaO}_{4}\text{S}^+\) (M+Na\(^+\)): 303.0662; Found: 303.0668.

(1S,2R,5S)-2-Isopropyl-5-methylocyclohexyl 2-((phenylsulfonyl)methyl)acrylate (7ai)

\[
\begin{align*}
\text{Me} &\quad \text{Me} \\
\text{O} &\quad \text{SO}_2\text{Ph} \\
\end{align*}
\]

\(R_t = 0.50\) (PE/EA = 4:1, v/v). Colorless oil, (1.2 g, 3.2 mmol, 79% yield). NMR spectroscopy: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.85\) (dt, \(J = 8.2, 1.6\) Hz, 2H), 7.64–7.60 (m, 1H), 7.52 (t, \(J = 7.5\) Hz, 2H), 6.48 (d, \(J = 0.6\) Hz, 1H), 5.96 (d, \(J = 0.6\) Hz, 1H), 4.58–4.52 (m, 1H), 4.17 (s, 2H), 1.77–1.69 (m, 2H), 1.67–1.62 (m, 2H), 1.45–1.33 (m, 2H), 1.05–0.95 (m, 1H), 0.88–0.77 (m, 8H), 0.67 (d, \(J = 7.0\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 164.4, 138.5, 134.0, 133.1, 129.4, 129.2, 128.9, 75.8, 57.3, 47.0, 40.6, 34.2, 31.4, 26.5, 23.6, 22.1, 20.8, 16.6. IR (ATR): 2952, 2930, 2870, 1711, 1446, 1312, 1245, 1193, 1144, 1085, 794, 753 cm\(^{-1}\). HRMS (ESI, m/z): calcld for \(\text{C}_{20}\text{H}_{26}\text{NaO}_{5}\text{S}^+\) (M+Na\(^+\)): 387.1601; Found: 387.1599.

(3S,5S,9S,10R,13S,14S)-5,13-Dimethyl-17-oxohexadecahydro-1H-cyclopenta[alpha]phenanthren-3-yl 2-((phenylsulfonyl)methyl)acrylate (7aj)

\[
\begin{align*}
\text{O} &\quad \text{SO}_2\text{Ph} \\
\end{align*}
\]

\(R_t = 0.43\) (PE/EA = 2:1, v/v). White solid, mp: 147 °C–148 °C, (1.0 g, 2.0 mmol, 90% yield). NMR spectroscopy: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.87–7.84\) (m, 2H), 7.65–7.61 (m, 1H), 7.55–7.51 (m, 2H), 6.48 (d, \(J = 0.6\) Hz, 1H), 5.88 (d, \(J = 0.6\) Hz, 1H), 4.60–4.52 (m, 1H), 4.15 (s, 2H), 2.46–2.40 (m, 1H), 2.11–2.01 (m, 1H), 1.95–1.89 (m, 1H), 1.81–1.77 (m, 2H), 1.74–1.62 (m, 3H), 1.58–1.39 (m, 4H), 1.37–1.13 (m, 7H), 1.02–0.94 (m, 2H), 0.85 (s, 3H), 0.83 (s, 3H), 0.72–0.66 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 221.4, 164.4, 138.6, 134.0, 133.2, 129.5, 129.2, 128.9, 75.0, 57.6, 54.4, 51.5, 47.9, 44.7, 36.7, 36.0, 35.7, 35.1, 33.8, 31.6, 30.9, 28.4, 27.3, 21.9, 20.6, 13.9, 12.4. IR (ATR): 2933, 2851, 1733, 1715, 1305, 1241, 1189, 1141, 1085, 1014, 764, 705 cm\(^{-1}\). HRMS (ESI, m/z): calcld for \(\text{C}_{20}\text{H}_{26}\text{NaO}_{5}\text{S}^+\) (M+Na\(^+\)): 521.2332; Found: 521.2329.

(8R,9S,10R,13S,14S,17S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[alpha]phenanthren-17-yl 2-(((phenylsulfonyl)methyl)acrylate (7al)

\[
\begin{align*}
\text{O} &\quad \text{SO}_2\text{Ph} \\
\end{align*}
\]

\(R_t = 0.21\) (PE/EA = 2:1, v/v). White solid, mp: 133 °C–135 °C, (0.9 g, 2.6 mmol, 66% yield after recrystallization). NMR spectroscopy: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.85\) (d, \(J = 7.6\) Hz, 2H), 7.63 (t, \(J = 7.3\) Hz, 1H), 7.52 (t, \(J = 7.6\) Hz, 2H), 6.48 (s, 1H), 5.86 (s, 1H), 5.72 (s, 1H), 4.49 (t, \(J = 8.1\) Hz, 1H), 4.19–4.10 (m, 2H), 2.41–2.25 (m, 4H), 2.09–2.00 (m, 2H), 1.85–1.54 (m, 6H), 1.42–1.30 (m, 3H), 1.18 (s, 3H), 1.15–0.89 (m, 4H), 0.83 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 199.5, 170.9, 164.8, 138.5, 133.9, 133.2, 129.3, 129.2, 128.9, 124.1, 83.8, 57.5, 53.8, 50.3, 42.8, 38.7, 36.7, 35.8, 35.5, 34.0, 32.8, 31.6, 27.4, 23.6, 20.6, 17.5, 12.3. IR (ATR): 2956, 2930, 1726, 1659, 1305, 1193, 1156, 898, 708 cm\(^{-1}\). HRMS (ESI, m/z): calcld for \(\text{C}_{20}\text{H}_{26}\text{NaOsO}^+\) (M+Na\(^+\)): 519.2176; Found: 519.2195.

(4S,5'R,6aR,6bS,8aS,8bR,9S,10R,11aS,12aS,12bS)-5',6a,8a,9-Tetramethyl-1,3,3',4,4',5,5',6,6a,6b,6',7,8,8a,8b,9,9,11a,12,12a,12b-icosahydrospiro[naphtho[2',1':4,5]inden[2,1-b][furan-10,2'-pyran]-4-yl 2-(((phenylsulfonyl)methyl)acrylate (7am)
(R)-2,5,7,8-Tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl 2-((phenylsulfonyl)methyl)acrylate (7an)

R<sub>t</sub> = 0.50 (PE/EA = 4:1, v/v). White solid, mp: 43 °C–45 °C, (1.7 g, 2.6 mmol, 88% yield). NMR spectroscopy: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.92 (d, J = 7.6 Hz, 2H), 7.64 (t, J = 7.3 Hz, 1H), 7.54 (t, J = 7.6 Hz, 2H), 6.48 (s, 1H), 6.20 (s, 1H), 4.30 (s, 2H), 2.65 (m, 2H), 2.06 (s, 3H), 1.85 (s, 3H), 1.83 (s, 3H), 1.78–1.71 (m, 2H), 1.52–1.07 (m, 23H), 0.88–0.84 (m, 13H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.8, 149.7, 140.4, 138.6, 134.5, 134.1, 129.3, 128.8, 128.4, 126.8, 125.1, 123.3, 117.6, 57.2, 57.1, 39.5, 37.6, 37.4, 32.9, 28.1, 24.9, 24.6, 22.9, 22.8, 21.2, 20.7, 19.9, 19.8, 13.0, 12.1, 11.9. IR (ATR): 2922, 2863, 1733, 1446, 1320.0, 1152, 1023, 753 cm<sup>−1</sup>. HRMS (ESI, m/z): calcd for C<sub>30</sub>H<sub>36</sub>NaO<sub>3</sub>S<sup>+</sup> (M+Na)<sup>+</sup>: 661.3897; Found: 661.3906.

(8R,9S,13S,14S)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 2-((phenylsulfonyl)methyl)acrylate (7ao)

R<sub>t</sub> = 0.23 (PE/EA = 2:1, v/v). Slight yellow solid, mp: 203 °C–205 °C, (1.5 g, 3.2 mmol, 79% yield). NMR spectroscopy: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91 (d, J = 7.6 Hz, 2H), 7.67 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.6 Hz, 2H), 7.25 (d, J = 10.4 Hz, 1H), 6.72–6.63 (m, 3H), 6.08 (s, 1H), 4.26 (s, 2H), 2.88–2.86 (m, 2H), 2.54–2.47 (m, 1H), 2.41–2.38 (m, 1H), 2.29–2.27 (m, 1H), 2.17–1.95 (m, 4H), 1.66–1.41 (m, 6H), 0.91 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 220.8, 163.9, 148.4, 138.5, 138.2, 137.8, 135.0, 134.1, 129.3, 129.0, 128.8, 126.5, 121.4, 118.5, 57.7, 50.5, 48.1, 44.3, 38.1, 36.0, 31.7, 29.5, 26.4, 25.9, 21.7, 14.0. IR (ATR): 2933, 2881, 1722, 1495, 1301, 1245, 1133, 760, 686 cm<sup>−1</sup>. HRMS (ESI, m/z): calcd for C<sub>32</sub>H<sub>36</sub>NaO<sub>3</sub>S<sup>+</sup> (M+K)<sup>+</sup>: 517.1446; Found: 517.1462.

(8R,9S,13S,14S,17S)-3-(Benzyloxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-1-7-yl 2-((phenylsulfonyl)methyl)acrylate (7ap)

R<sub>t</sub> = 0.26 (PE/EA = 4:1, v/v). Slight yellow solid, mp: 127 °C–128 °C, (1.9 g, 3.3 mmol, 83% yield). NMR spectroscopy: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.88 (d, J = 7.9 Hz, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.7 Hz, 2H), 7.49–7.29 (m, 5H), 7.21 (d, J = 8.6 Hz, 1H), 6.80 (dd, J = 8.5, 2.3 Hz, 1H), 6.73 (bs, 1H), 6.53 (s, 1H), 5.93 (s, 1H), 5.04 (s, 2H), 4.67–4.50 (m, 1H), 4.19 (q, J = 13.8 Hz, 2H), 2.99–2.76 (m, 2H), 2.35–2.02 (m, 3H), 1.93–1.69 (m, 3H), 1.51–1.22 (m,
7H), 0.83 (s, 3H); 13C NMR (100 MHz, CDCl₃) δ 164.8, 156.8, 138.4, 138.0, 137.3, 133.9, 133.3, 132.7, 129.3, 129.2, 128.9, 128.7, 127.9, 127.5, 126.4, 114.9, 112.4, 84.0, 70.0, 57.4, 49.7, 43.8, 43.2, 38.6, 36.9, 29.8, 27.5, 27.3, 26.2, 23.3, 12.3.

IR (ATR): 2945, 2848, 1711, 1495, 1312, 1189, 1152, 1085, 727 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₃H₁₉NaO₅S⁺ (M+Na)⁺: 593.2332; Found: 593.2349.

3.3 Synthesis of phenyl-2-(tosylsulfonyl)allylic sulfone (7ab)

Phenyl-2-(tosylsulfonyl)allylic sulfone 7ab was synthesized according to reported protocol.⁶

Phenyl-2-(tosylsulfonyl)allylic sulfone

Rf = 0.30 (PE/EA = 2/1). White solid, mp: 125 °C–127 °C (8.4 mmol, 84% yield for 3 steps from phenyl propargyl sulfide). NMR spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 7.77–7.74 (m, 2H), 7.66 (tt, J = 7.5, 1.4 Hz, 1H), 7.60 (dt, J = 8.3, 1.8 Hz, 2H), 7.51 (t, J = 7.8 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 6.64 (d, J = 0.9 Hz, 1H), 6.50 (d, J = 1.2 Hz, 1H), 4.05 (s, 2H), 2.44 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 145.3, 139.8, 137.9, 134.8, 134.4, 130.8, 130.2, 129.4, 128.7, 54.3, 21.8. IR (ATR): 2956, 2922, 2855, 1595, 1446, 1312, 1141, 1081, 727 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₆H₁₆O₄NaS₂⁺ (M+Na⁺): 359.0382; Found: 359.0383.

Preparation of ((3-methyl-2-methylene-3-phenylbutyl)sulfonyl)benzene (7ad)

((3-Methyl-2-methylene-3-phenylbutyl)sulfonyl)benzene (7ad) was prepared according to reported methods.⁷,⁸ Synthetic routine is shown as below:

Preparation of ((3-methyl-2-methylene-3-phenylbutyl)sulfonyl)benzene (7ad)

To a solution of 2-methyl-2-phenylpropionic acid (4.92 g, 30 mmol) in diethyl ether at −30 °C was added a solution of methyl lithium (1.6 M, 56.0 mL, 3.0 equiv.) dropwise with syringe pump, after which the resulting mixture was allowed to RT and kept stirring for 1.5 h. The reaction was cooled to 0 °C and poured into iced hydrogen chloride solution, extracted with PE (3×100 mL), the organic phase was combined, concentrated under reduced pressure and purified with column chromatography on silica gel (siliga: 200~300 mesh) and PE as eluent to afford the colorless oil S₂ (3.0 g, 18.6 mmol, 62% yield).

To a 10 mL tube was added S₃ (0.7 g, 4.3 mmol), NBS (0.84 g, 4.73 mmol, 1.1 equiv.) and chloroform (2 M), then the tube was sealed, the resulting mixture was stirred at 100 °C till NBS was completely dissolved, then the mixture was moved to ambient temperature and filtered under reduced pressure, the filtrate was washed with brine, dried over Na₂SO₄, removed solvent and purified with column chromatography on silica gel (siliga: 200~300 mesh) and PE as eluent to afford the colorless oil S₃ (1.57 g, 9.84 mmol, 82% yield).

To a 10 mL tube was added S₃ (0.7 g, 4.3 mmol), NBS (0.84 g, 4.73 mmol, 1.1 equiv.) and chloroform (2 M), then the tube was sealed, the resulting mixture was stirred at 100 °C till NBS was completely dissolved, then the mixture was moved to ambient temperature and filtered under reduced pressure, the filtrate was washed with brine, dried over Na₂SO₄, removed solvent and purified with column chromatography on silica gel (siliga: 200~300 mesh) and PE as eluent to
afford the slight yellow oil S4 (0.72 g, 3.0 mmol, 70% yield).

To a 50 mL round bottom flask was added S4 (0.7g, 3.0 mmol) and phenylsulfinate (0.98 g, 6.0 mmol) and DMF (0.25 M), the resulting mixture was stirred at 60 °C for 12 h, then washed with water and brine, dried over Na2SO4, purified with column chromatography on silica gel (200~300 mesh) and PE/EA (20/1~5/1,v/v) as eluent to afford the white solid 7ad (0.45 g, 1.5 mmol, 50% yield).

((3-methyl-2-methylene-3-phenylbutyl)sulfonetyl)benzene (7ad) mp: 47 °C–49 °C. NMR spectroscopy: 1H NMR (400 MHz, CDCl3) δ 7.80 (d, J = 7.3 Hz, 2H), 7.62 (t, J = 7.3 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.26–7.13 (m, 5H), 5.70 (s, 1H), 5.53 (s, 1H), 5.30 (s, 2H), 1.34 (s, 6H); 13C NMR (100 MHz, CDCl3) δ 146.3, 143.2, 139.6, 133.7, 129.2, 128.6, 128.6, 126.4, 126.2, 116.7, 58.7, 44.7, 27.8. IR (ATR): 2937, 2867, 1646, 1446, 1308, 1144, 1085, 1017, 768, 723, 686 cm⁻¹. HRMS (ESI, m/z): calcd for C18H18NaO2S⁺ (M+Na)⁺: 323.1076; Found: 323.1085.

Preparation of 6-hydroxyhexyl 2-((phenyl)sulfonyl)methyl)acrylate (7af)

6-Hydroxyhexyl 2-((phenyl)sulfonyl)methyl)acrylate was prepared according to reported method.[9]

6-Hydroxyhexyl 2-((phenyl)sulfonyl)methyl)acrylate (7af)

Rf = 0.26 (PE/EA = 1/1, v/v). Colorless oil, (1.8 g, 5.7 mmol, 57% yield). NMR spectroscopy: 1H NMR (400 MHz, CDCl3) δ 7.83 (d, J = 7.6 Hz, 2H), 7.63 (t, J = 7.3 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 6.47 (s, 1H), 5.86 (s, 1H), 4.14 (s, 2H), 3.96 (t, J = 6.7 Hz, 2H), 3.61 (t, J = 6.6 Hz, 2H), 1.75 (s, 1H), 1.55 (t, J = 6.7 Hz, 4H), 1.34–1.31 (m, 4H); 13C NMR (100 MHz, CDCl3) δ 164.9, 138.4, 134.0, 129.2, 128.8, 65.6, 62.7, 57.6, 32.6, 28.4, 25.7, 25.4. IR (ATR): 3541, 3422, 2933, 2859, 1715, 1308, 1189, 1148, 1085, 913, 731 cm⁻¹. HRMS (ESI, m/z): calcd for C16H16NaO2S⁺ (M+Na)⁺: 349.1078. Found: 349.1078.

Preparation of 6-oxohexyl 2-((phenyl)sulfonyl)methyl)acrylate (7ag)

6-Oxohexyl 2-((phenyl)sulfonyl)methyl)acrylate was prepared via oxidation of 4ax with DMP (3.0 equiv.) in DCM at ambient temperature.

6-Oxohexyl 2-((phenyl)sulfonyl)methyl)acrylate (7ag)

Rf = 0.16 (PE/EA = 2/1, v/v). Colorless oil, (298 mg, 0.92 mmol, 46% yield). NMR spectroscopy: 1H NMR (400 MHz, CDCl3) δ 9.75 (t, J = 1.4 Hz, 1H), 7.84 (d, J = 8.6 Hz, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 6.47 (s, 1H), 5.86 (s, 1H), 4.14 (s, 2H), 3.97 (t, J = 6.6 Hz, 2H), 2.44 (td, J = 7.3, 1.4 Hz, 2H), 1.66–1.54 (m, 4H), 1.38–1.30 (m, 2H); 13C NMR (100 MHz, CDCl3) δ 202.3, 164.9, 138.5, 134.0, 133.4, 129.2, 128.8, 65.3, 57.6, 43.8, 28.3, 25.5, 21.7. IR (ATR): 2937, 2863, 1715, 1446, 1308, 1245, 1185, 1144, 1085, 757 cm⁻¹. HRMS (ESI, m/z): calcd for C16H16NaO2S⁺ (M+Na)⁺: 347.0922; Found: 347.0922.

synthesis of other starting materials

synthesis of acrylamides 10

Acrylamides 10a–10i was synthesized via condensation of corresponding amine and acyl chloride according to reported reference.[10]

Synthesis of dimethyl 4-(3-(3-methyl-4-hydroxyphenyl)propyl)phthalate 15

Dimethyl 4-(3-(3-methyl-4-hydroxyphenyl)propyl)phthalate 15 was synthesized according to reported reference[11].
Supplementary Figure 8 Synthesis of S6

Under N₂ atmosphere, to a stirring mixture of NaH (3.5 g, 87 mmol, 1.1 equiv.) in DMF (30 mL) was added a solution of 4-bromo-2-methylphenol S5 (14.8 g, 79 mmol) in DMF (100 mL) slowly, the resulting mixture was kept stirring for 0.5 h then ethoxymethyl chloride (EOMCl) (9.0 g, 95.7 mmol, 1.1 equiv.) was added slowly in 10 min, the reaction medium was stirred for another 5 h and quenched by addition of water, the mixture was extracted with EA (200 mL×3 times), the combined organic phase was washed with water, dried over Na₂SO₄, concentrated under reduced pressure, the residue was purified through a silica plug, a yellow oil was obtained (15.3 g, 60.0 mmol, 76% yield).

The product (7.4 g, 30.0 mmol) was dissolved in DMF (65 mL), to which was added allyltributyltin (14.3 mL, 45.0 mmol, 1.5 equiv.), then the mixture is degassed, then 900 mg of dichlorobis(triphenylphosphino)palladium was added, the resulting mixture was stirred at 120 °C for 10 h. The reaction was quenched by addition of water, and extracted with EA, the combined organic layer was dried over Na₂SO₄, and concentrated under reduced pressure, the residue was purified by chromatography on a 10% wt K₂CO₃-silica column with PE as an eluent. A yellow oil S6 is obtained (5.0 g, 24 mmol, 81% yield).

Supplementary Figure 9 Synthesis of S8

Under N₂ atmosphere, to a stirring solution of S7 (8.4 g, 40 mmol), NEt₃ (8.4 mL, 62 mmol, 1.55 equiv.) and DCM (200 mL) was added Tf₂O (11.8 g, 42 mmol, 1.05 equiv.) slowly in 10 min at 0 °C, the resulting mixture was brought to room temperature and stirred for 2 h, and then quenched by addition of water and extracted with DCM (100 mL×3 times), the organic phase was washed with dilute sodium bicarbonate and dried over Na₂SO₄, and concentrated under reduced pressure, the residue was purified by chromatography on a silica column with PE/EA (8/1, v/v) as an eluent. A yellow oil S8 is obtained (12.3 g, 36.0 mmol, 90% yield).

Supplementary Figure 10 Synthesis of S9

Under N₂ atmosphere, 3.5 g (16 mmol) of S6 was dissolved in 40 mL anhydrous THF, the resulting mixture was cooled to 0 °C, 40.8 mL 9-BBN (0.5 M, 1.3 equiv.) was added, and the medium was brought to room temperature and stirred for 12 h. A solution of S8 in 70 mL DMF was added, as well as 4.7 g (34 mmol, 2.1 equiv.) of potassium carbonate and Pd(dppf)Cl₂ (652.8 mg, 0.8 mmol, 5 mol%), the reaction mixture was degassed, heated to 50 °C for 3 h and quenched with ammonium chloride solution. The mixture was extracted with EA, the organic phase was washed with dilute sodium bicarbonate and dried over Na₂SO₄, and concentrated under reduced pressure, the residue was purified by chromatography on a silica column with PE/EA (8/1, v/v) as an eluent. A colorless oil S9 is obtained (4.1 g, 10.2 mmol, 64% yield).
Supplementary Figure 11 Synthesis of 15

Under air atmosphere, to a solution of S5 (2.9 g, 7.3 mmol) in MeOH (30 mL) was added con. HCl (30 mL) slowly at room temperature, the resulting mixture was stirred for 3 h and monitored by TLC, upon completion, extracted with EA, the organic phase was dried over Na₂SO₄, and concentrated under reduced pressure, the residue was purified by chromatography on a silica column with PE/EA (4/1, v/v) as an eluent. A colorless oil 15 is obtained (2.3 g, 6.9 mmol, 94% yield).

Investigation of reaction conditions

Investigation of metallic salts

Supplementary Table 1 Investigation of metallic salts

| entry | metallic salt                   | yield /% b,c | c.r. /%c |
|-------|---------------------------------|--------------|----------|
| 1     | Ce(NH₄)(NO₃)₆                   | 0            | 100      |
| 2     | Ce(SO₄)₂·4H₂O                   | 0            | 100      |
| 3     | Fe(NO₃)₃·9H₂O                   | 0            | 100      |
| 4     | Fe₂(SO₄)₃·9H₂O                  | 0            | 100      |
| 5     | Cu(OAc)₂                        | 0            | 5        |
| 6     | Co(acac)₃                       | 0            | 10       |
| 7     | Mn(OAc)₃·2H₂O                   | 0            | 2        |
| 8     | MnF₃                            | 0            | 12       |
| 9     | Mn[PO₄]₃                        | 0            | 0        |
| 10    | Mn(acac)₃                       | 8            | 12       |

a) reaction condition: 1a (0.1 mmol), 7a (1.2 equiv.), metallic salt (2.0 equiv.), DCM, 70 °C, N₂, 36 h; b) yield by ¹⁹F NMR with PhCF₃ as internal standard.

Investigation of solvents
**Investigation of solvents**

**Supplementary Table 2**

| entry | solvent | yield (%)<sup>b</sup> | c.r. (%)<sup>c</sup> |
|-------|---------|------------------------|---------------------|
| 1     | DCM     | 70 (67)<sup>c</sup>    | 90 (98)<sup>c</sup> |
| 2     | Chloroform | 10                    | 82 |
| 3     | Hexane  | 47                     | 83 |
| 4     | Decalin | 56                     | 62 |
| 5     | DMAC    | 60                     | 84 |
| 6     | DMF     | 11                     | 59 |
| 7     | NMP     | 10                     | 47 |
| 8     | MeCN    | 38                     | 70 |
| 9     | CyHexane | 26                    | 48 |
| 10    | MCPE    | 28                     | 50 |
| 11    | EA      | 33                     | 65 |

<sup>a</sup> reaction condition: 1a (0.1 mmol), 7a (1.2 equiv.), Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O (2.0 equiv.), solvent (0.1 M), 70 °C, N<sub>2</sub>, 36 h; <sup>b</sup> yield by <sup>19</sup>F NMR with PhCF<sub>3</sub> as internal standard; <sup>c</sup> repeated reaction. MCPE = methyl cyclopentyl ether.

**Investigation of oxidant for catalytic reaction conditions**

**Supplementary Table 3**

| Entry | Oxidant | Yield (%) | c.r. (%) |
|-------|---------|-----------|----------|
| 1     | WO<sub>3</sub> | 12        | 11       |
| 2     | NCS     | 32        | 34       |
| 3     | TEAPC   | --        | --       |
| 4     | p-NPO   | 0         | 0        |
| 5     | TBPB    | 60        | 75       |
| 6<sup>c</sup> | DCP     | 0         | 0        |
| 7<sup>d</sup> | TBPB    | 0         | 0        |
| 8<sup>e</sup> | TBPB    | 39        | 41       |
| 9<sup>e</sup> | TBPB    | 59        | 60       |
| 10<sup>f</sup> | TBPB    | 64        | 81       |
| 11    | PIDA    | 8         | 100      |
| 12    | PIDTFA  | 0         | 100      |
| 13    | I<sub>2</sub> | 0         | 0        |
| 14    | NBS     | 16        | 100      |
| 15    | MnO<sub>2</sub> | 14       | 34       |
| 16    | NaBrO<sub>3</sub> | 20       | 55       |
| 17    | DQ      | 6         | 31       |
| 18    | DMP     | 0         | 100      |

<sup>a</sup> reaction condition: 1a (0.1 mmol), 7a (1.2 equiv.), Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O (2.0 equiv.), DCM (0.1 M), 70 °C, N<sub>2</sub>, 12 h; <sup>b</sup> yield by <sup>19</sup>F NMR with TMFB as internal standard; <sup>c</sup> absence of Mn<sup>II</sup>; <sup>d</sup> 1.0 equiv of TBPB was used; <sup>e</sup> 1.5 equiv of TBPB was used; <sup>f</sup> 2.5 equiv of TBPB was used; TEAPC = tetraethylammonium perchlorate, PIDTFA = [Bis(trifluoroacetoxy)iodo]benzene, p-NPO = 4-Nitropyridine N-oxide.
Radical inhibition experiments

Supplementary Figure 12 Radical inhibition experiments

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₃•2H₂O (16.1 mg, 0.06 mmol, 20 mol%), 7b (257.4 mg, 0.9 mmol, 3.0 equiv.) and TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) (45.7 mg, 0.3 mmol, 1.0 equiv.) or BHT (butylated hydroxytoluene) (66.1 mg, 0.3 mmol, 1.0 equiv.) was added DCM (3.0 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPB (146.0 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was stirred at 70 °C in heating block for 14 h. After the mixture was cooled to ambient temperature, yield of 20 and conversion ratio of 1a were determined via ¹⁹F NMR with PhCF₃ as an internal standard. Recovery of 7b was determined via ¹H NMR with 1,3,5-trimethoxylbenzene as an internal standard. We found reaction was totally inhibited when radical scavenger (TEMPO or BHT) was added to the mixture and compound 21 was detected by HRMS. HRMS (ESI, m/z): calcd for C₁₉H₃₁F₃NO₂Si⁺ (M+H)⁺ : 390.2071; Found:390.2059.

Proposed mechanism for allylation, alkylation and alkenylation via radical C-Si bond activation

Supplementary Figure 13 Proposed Mechanism for allylation via radical C-Si activation

The radical inhibition experiments indicate that a radical process might be involved. We found that Mn(OAc)₃•2H₂O is able to mediate the reaction without external oxidant, but Mn(OAc)₂•4H₂O can not mediate the reaction without TBPB (Table 1, entries 1 and 8 in the manuscript). The HRMS analysis of the reaction mixture of 1a and 7a suggests the generation of benzenesulfonyl benzoic anhydride, tert-butyl benzenesulfonate, benzesulfonic acid and benzenesulfinic acid as by-products. Based on these experimental results and literature about allylation from allyl sulfones,[13,14] we propose a possible mechanism (Fig. S2). Ligand exchange between Mn(III) species and alcohol 1a might generate intermediate I, which undergoes homolysis to produce alkoxyl radical II and Mn(II) intermediate. Carbon radical III would be generated through Brook rearrangement, and then undergo radical addition reaction to generate intermediate
IV. Compound V would be generated after β-elimination of sulfonyl radical. The alcohol product TM would be generated after the desilylation step. Mn(III) catalyst is likely to be regenerated by the oxidation of Mn(II) by TBPB. The sulfonyl radical is likely to be captured by TBPB, generating the side-product benzenesulfonyl benzoic anhydride. Meanwhile, sulfonyl radical could react with TBPB or tert-butoxy radical to form tert-butyl benzenesulfonate. Benzenesulfonyl benzoic anhydride and tert-butyloxyl benzenesulfonate could be hydrolyzed to generate benzenesulfonic acid. Moreover, the sulfonyl radical could be transformed to sulfonic acid via H atom abstraction reaction under the reaction condition.

Benzenesulfonyl benzoic anhydride: HRMS (ESI, m/z): calcd for C_{13}H_{10}NaO_{3}S^+ (M+Na)^+: 285.0192; Found: 285.0195.

tert-Butyl benzenesulfonate: HRMS (ESI, m/z): calcd for C_{10}H_{14}NaO_{3}S^+ (M+Na)^+: 237.0556; Found: 237.0561

Benzenesulfinic acid: HRMS (ESI, m/z): calcd for C_{6}H_{6}NaO_{2}S^+ (M+Na)^+: 164.9981; Found: 164.9975.

Benzenesulfonic acid: HRMS (ESI, m/z): calcd for C_{6}H_{7}O_{3}S^+ (M+H)^+: 159.0110; Found: 159.0115.

For the alkylation reaction, we propose that radical III would be generated following similar mechanism as that in the allylation reaction (Fig. S3.). When an acryl amide was used as the radical acceptor instead of an allylic sulfoxone, we propose that radical III could undergo addition reaction to generate intermediate IV', which undergo intramolecular addition to generate intermediate V'. Aromatization reaction via radical oxidation and deprotonation then would generate compound VI'. The alcohol product TM' would be generated after the desilylation step. Mn(III) catalyst is likely to be regenerated by the oxidation of Mn(II) by TBPB. Similar oxidative aromatization process was also proposed in the Fe and Ag catalyzed radical reactions of acryl amides. [15,16]
Supplementary Figure 15 Proposed Mechanism for alkenylation via radical C-Si activation

There are reports on radical decarboxylative alkenylation with α,β-unsaturated carboxylic acids.[17,18] Based on our experimental results and literature reports,[17,18] we propose a possible mechanism for our reaction as shown in Fig. S4. Ligand exchange between Mn(III) species and alcohol 1a might generate intermediate I, which undergoes homolysis to produce alkoxyl radical II and Mn(II) intermediate. Carbon radical III would be generated through Brook rearrangement, and then undergo radical addition reaction via two possible pathways to generate TM'.

Pathway a: addition of radical III to the α-position of the double bond in an α,β-unsaturated carboxylic acid would generate intermediate IV''. Intermediate IV'' was oxidized to cation intermediate V'' which then eliminated carbon dioxide and proton to generate the product VI''. Similar proposal was proposed in Ni-catalyzed radical alkenylation with α,β-unsaturated carboxylic acids.[17] The alcohol product TM'' would be generated after the desilylation step.

Pathway b: compound A could be transformed to compound B via ligand exchange process. Addition of radical III to the α-position of the double bond in compound B would generate intermediate IV''', which then eliminate carbon dioxide and Mn(II) to generate compound VI''. Similar proposal was proposed in Cu-catalyzed alkenylation with α,β-unsaturated carboxylic acids. The alcohol product TM''' would be generated after the desilylation step.

Mn(III) catalyst is likely to be regenerated by the oxidation of Mn(II) by TBPB.

Synthesis of α-CF₃ substituted homoallylic alcohols

Ethyl 5,5,5-trifluoro-4-(((dimethyl(phenyl)silyl)oxy)-2-methylenepentanoate (8a)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂·4H₂O (4.9 mg, 0.02 mmol, 20 mol%) was added DCM (1 mL, 0.1 M), 1a (23.4 mg, 0.1 mmol), 7a (50.8 mg, 0.2 mmol, 2.0 equiv.) and TBPB (48.6 mg, 0.25 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 18 h. The reaction mixture was quenched with water (2 mL), extracted with DCM.
3×10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with flash column chromatography on silica gel (200−300 mesh) and PE/EA (50/1−20/1, v/v) as eluent to afford 22.1 mg of the title compound as a colorless oil (64% yield).

Rᵣ = 0.60 (PE/EA = 20/1, v/v). NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, J = 6.4 Hz, 2H), 7.43−7.35 (m, 3H), 6.26 (s, 1H), 5.65 (s, 1H), 4.23−4.09 (m, 3H), 2.78−2.42 (m, 2H), 1.24 (t, J = 7.3 Hz, 3H), 0.38 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 166.4, 136.1, 134.9, 133.8, 130.1, 130.0, 128.0, 125.0 (q, J = 281.0 Hz), 70.1 (q, J = 30.7 Hz), 61.0, 34.6, 14.2, −1.27, −1.47; ¹⁹F NMR (375 MHz, CDCl₃) δ −78.5 (bs, 3F). IR (ATR): 2956, 2922, 2855, 1715, 1260, 1170, 1129, 1018, 790, 701 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₉H₂₃F₂O₃Si⁺ (M+H)⁺: 437.1289; Found: 437.1273.

4-((Dimethyl(phenyl)silyl)oxy)-5,5,5-trifluoro-2-methylene-1-phenylpentan-1-one (20)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂•2H₂O (26.8 mg, 0.1 mmol, 20 mol%), 7b (429.5 mg, 1.5 mmol, 3.0 equiv.) was added DCM (5 mL). 1a (117.1 mg, 0.5 mmol) and TBPB (242.7 mg, 1.25 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200−300 mesh) and PE/EA (20/1−10/1, v/v) as eluent to afford 149.4 mg of the title compound as a colorless oil (79% yield).

Rᵣ = 0.30 (PE/EA = 80/1, v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, J = 7.5 Hz, 2H), 7.45−7.41 (m, 3H), 7.32−7.23 (m, 5H), 5.88 (s, 1H), 5.64 (s, 1H), 4.30−4.22 (m, 1H), 2.88−2.53 (m, 2H), 0.29−0.28 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 197.4, 141.8, 137.5, 136.5, 133.7, 132.3, 131.4, 129.6, 128.3, 128.0, 127.8, 125.1 (q, J = 281.7 Hz), 70.0 (q, J = 30.7 Hz), 34.9, −1.2, −1.7; ¹⁹F NMR (375 MHz, CDCl₃) δ −77.6 (d, J = 6.0 Hz, 3F). IR(ATR): 3071, 2960, 1655, 1446, 1338, 1282, 1163, 1126, 1051, 790 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₀H₂₅F₂O₃Si⁺ (M+Na)⁺: 401.1155; Found: 401.1161.

Ethyl 5,5,5-trifluoro-4-hydroxy-2-methylenepentanoate (9a)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂•4H₂O (14.7 mg, 0.06 mmol, 20 mol%) was added DCM (3 mL, 0.1 M). 1a (70.2 mg, 0.3 mmol), 7a (152.4 mg, 0.6 mmol, 2.0 equiv.) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed and the resulting mixture was kept stirring at 70 °C in heating block for 18 h. The mixture was then cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the resulting mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200−300 mesh) and PE/EA (20/1−10/1, v/v) as eluent to afford 40.0 mg of the title compound as a colorless oil (62% yield).

Rᵣ = 0.23 (PE/EA = 8/1, v/v). NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 6.35 (s, 1H), 5.80 (s, 1H), 4.25 (q, J = 7.2 Hz, 2H), 4.16−4.08 (m, 1H), 3.63 (s, 1H), 2.78−2.57 (m, 2H), 1.32 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.1, 135.2, 129.8, 124.9 (q, J = 280.5 Hz), 70.0 (q, J = 30.7 Hz), 61.8, 33.5, 14.2; ¹⁹F NMR (375 MHz, CDCl₃) δ −79.6 (d, J = 6.0 Hz, 3F). IR (ATR): 3444, 2986, 2937, 1700, 1633, 1413, 1316, 1275, 1163, 1126, 1021, 712 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₀H₁₉F₂NaO₃⁺ (M+Na)⁺: 235.0552; Found: 235.0556.
5,5,5-Trifluoro-4-hydroxy-2-methylene-1-phenylpentan-1-one (9b)

Under N\textsubscript{2} atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)\textsubscript{3}·2H\textsubscript{2}O (16.1 mg, 0.06 mmol, 20 mol%) and 7b (257.4 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M). 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with brine, dried over Na\textsubscript{2}SO\textsubscript{4}, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1–10/1, v/v) as eluent to afford 1.25 g of the title compound as a white solid (71% yield).

\begin{align*}
\text{Rf} & = 0.40 \text{ (PE/EA = 5/1, v/v).} \\
\text{IR (ATR):} & 3418, 3060, 1750, 1640, 1339, 1279, 1163, 1036, 753 \text{ cm}^{-1}. \\
\text{HRMS (ESI, m/z):} & \text{calcd for C}_{12}\text{H}_{12}\text{F}_3\text{O}^+ (\text{M}+\text{H})^+: 245.0784; \text{Found: 245.0778.}
\end{align*}

1-(1,1'-Biphenyl)-4-yl)-5,5,5-trifluoro-4-hydroxy-2-methylenepentan-1-one (9c)

Under N\textsubscript{2} atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)\textsubscript{3}·2H\textsubscript{2}O (16.1 mg, 0.06 mmol, 20 mol%) and 7c (326.2 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M). 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with brine, dried over Na\textsubscript{2}SO\textsubscript{4}, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1–10/1, v/v) as eluent to afford 74.9 mg of the title compound as a white solid (78% yield).

\begin{align*}
\text{Rf} & = 0.50 \text{ (PE/EA = 5/1, v/v).} \\
\text{IR (ATR):} & 3418, 3060, 1750, 1640, 1339, 1279, 1163, 1036, 753 \text{ cm}^{-1}. \\
\text{HRMS (ESI, m/z):} & \text{calcd for C}_{12}\text{H}_{12}\text{F}_3\text{O}^+ (\text{M}+\text{H})^+: 245.0784; \text{Found: 245.0778.}
\end{align*}

Gram scale experiment

Under N\textsubscript{2} atmosphere, to a dried 100 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)\textsubscript{3}·2H\textsubscript{2}O (321.7 mg, 1.2 mmol, 20 mol%) and 7c (6.52 g, 18.0 mmol, 3.0 equiv.) was added DCM (50 mL). 1a (1.41 g, 6 mmol) and TBPB (2.91 g, 15 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in oil bath for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 7.2 mL, 7.2 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (20 mL) and extracted with DCM (3×100 mL). The organic phase was combined and washed with brine, dried over Na\textsubscript{2}SO\textsubscript{4}, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1–10/1, v/v) as eluent to afford 1.25 g of the title compound as a white solid (65% yield) and starting material 7c was 61% recovered (3.97 g, 11.0 mmol).
2H), 7.69 (d, J = 8.3 Hz, 2H), 7.63 (d, J = 7.3 Hz, 2H), 7.49 (t, J = 7.3 Hz, 2H), 7.42 (t, J = 7.2 Hz, 1H), 6.18 (s, 1H), 5.95 (s, 1H), 4.38 (d, J = 4.9 Hz, 1H), 4.18–4.17 (m, 1H), 2.92–2.74 (m, 2H); 13C NMR (100 MHz, CDCl3) δ 199.1, 146.1, 142.3, 139.8, 135.3, 131.5, 130.8, 129.1, 128.5, 127.4, 127.2, 125.0 (q, J = 280.8 Hz), 70.6 (q, J = 30.7 Hz), 33.9; 19F NMR (375 MHz, CDCl3) δ −79.3 (d, J = 6.0 Hz, 3F). IR (ATR): 339, 3060, 2926, 1640, 1599, 1409, 1344, 1275, 1163, 1129, 1029, 757 cm⁻¹. HRMS (ESI, m/z): calcd for C15H12F2O2⁺ (M+H)⁺: 263.0690; Found: 263.0684.

5,5,5-Trifluoro-1-(4-fluorophenyl)-4-hydroxy-2-methylenepentan-1-one (9d)

\[
1a + 7d \rightarrow 9d
\]

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₃•2H₂O (16.1 mg, 0.06 mmol, 20 mol%) and 7d (273.6 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was then washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) and PE/EA (20/1~10/1, v/v) as eluent to afford 49.0 mg of the title compound as a yellow oil (62% yield).

R₁ = 0.50 (PE/EA = 5/1, v/v). 1H NMR (400 MHz, CDCl₃) δ 7.84–7.81 (m, 2H), 7.17–7.12 (m, 2H), 6.14 (s, 1H), 5.86 (s, 1H), 4.15 (bs, 2H), 2.89–2.70 (m, 2H); 13C NMR (100 MHz, CDCl₃) δ 197.9, 165.9 (d, J = 255.3 Hz), 142.2, 132.9 (d, J = 2.9 Hz), 132.7 (d, J = 8.7 Hz), 131.4, 124.9 (q, J = 280.8 Hz), 115.8 (d, J = 22.2 Hz), 70.4 (q, J = 30.8 Hz), 33.8; 19F NMR (375 MHz, CDCl₃) δ −79.4 (d, J = 6.0 Hz, 3F), −104.6 (s, 1F). IR (ATR): 3439, 2930, 1644, 1416, 1338, 1275, 1156, 1129, 1029, 850 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₅H₁₂F₃O₂⁺ (M+H)⁺: 279.0389; Found: 279.0389.

1-(4-Chlorophenyl)-5,5,5-trifluoro-4-hydroxy-2-methylenepentan-1-one (9e)

\[
1a + 7e \rightarrow 9e
\]

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₃•2H₂O (16.1 mg, 0.06 mmol, 20 mol%) and 7e (288.0 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol), TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was then washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) and PE/EA (20/1~10/1, v/v) as eluent to afford 57.2 mg of the title compound as a yellow oil (69% yield).

R₁ = 0.40 (PE/EA = 5/1, v/v). 1H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 8.3 Hz, 2H), 6.16 (s, 1H), 5.87 (s, 1H), 4.15 (s, 1H), 3.96 (s, 1H), 2.90–2.71 (m, 2H); 13C NMR (100 MHz, CDCl₃) δ 198.1, 142.1, 139.7, 135.0, 131.7, 131.4, 128.9, 124.9 (q, J = 281.8 Hz), 70.4 (q, J = 30.7 Hz), 33.8; 19F NMR (375 MHz, CDCl₃) δ −79.4 (d, J = 8.9 Hz, 3F). IR (ATR): 3437, 2930, 1651, 1588, 1478, 1402, 1334, 1275, 1163, 1129, 1092, 790 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₅H₁₁ClF₂O₂⁺ (M+H)⁺: 279.0394; Found: 279.0389.
**I-(3-Chlorophenyl)-5,5,5-trifluoro-4-hydroxy-2-methylenepentan-1-one (9f)**

![Chemical Structure](image)

Under \( N_2 \) atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing \( \text{Mn(OAc)}_2 \cdot 2\text{H}_2\text{O} \) (16.1 mg, 0.06 mmol, 20 mol%) and 7f (288.0 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol), TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.12 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with brine, dried over \( \text{Na}_2\text{SO}_4 \), concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) and PE/EA (20/1~10/1, v/v) as eluent to afford 69.4 mg of the title compound as a yellow oil (78% yield).

**I-(2-Chlorophenyl)-5,5,5-trifluoro-4-hydroxy-2-methylenepentan-1-one (9g)**

![Chemical Structure](image)

Under \( N_2 \) atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing \( \text{Mn(OAc)}_2 \cdot 2\text{H}_2\text{O} \) (16.1 mg, 0.06 mmol, 20 mol%) and 7g (288.0 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.12 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with brine, dried over \( \text{Na}_2\text{SO}_4 \), concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) and PE/EA (20/1~10/1, v/v) as eluent to afford 69.4 mg of the title compound as a yellow oil (83% yield).

**I-(4-Bromophenyl)-5,5,5-trifluoro-4-hydroxy-2-methylenepentan-1-one (9h)**

![Chemical Structure](image)
Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₃•2H₂O (16.1 mg, 0.06 mmol, 20 mol%) and 7h (329.0 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) and PE/EA (20/1~10/1, v/v) as eluent to afford 78.9 mg of the title compound as a yellow oil (81% yield).

$$R_f = 0.50 \text{ (PE/EA = 5/1, v/v).}$$

1H NMR (400 MHz, CDCl₃) δ 7.66–7.60 (m, 4H), 6.17 (s, 1H), 5.87 (s, 1H), 4.15–4.14 (m, 1H), 3.92–3.91 (m, 1H), 2.90–2.71 (m, 2H); 13C NMR (100 MHz, CDCl₃) δ 198.3, 142.1, 135.5, 131.9, 131.8, 131.5, 128.4, 124.9 (q, J = 280.8 Hz), 70.4 (q, J = 30.9 Hz), 33.7; 19F NMR (375 MHz, CDCl₃) δ −79.4 (d, J = 6.0 Hz, 3F). IR (ATR): 3422, 2920, 2855, 1648, 1398, 1275, 1167, 1133, 1074, 790 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₂H₁₃BrF₂O₄⁺ (M+H)⁺: 322.9889; Found: 322.9888.

5,5,5-Trifluoro-4-hydroxy-1-(4-iodophenyl)-2-methylenepentan-1-one (9i)

![Chemical structure](image)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₃•2H₂O (16.1 mg, 0.06 mmol, 20 mol%), 7i (370.8 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) and PE/EA (20/1~10/1, v/v) as eluent to afford 72.0 mg of the title compound as a yellow oil (81% yield).

$$R_f = 0.50 \text{ (PE/EA = 5/1, v/v).}$$

1H NMR (400 MHz, CDCl₃) δ 7.83 (d, J = 8.3 Hz, 2H), 7.48 (d, J = 8.3 Hz, 2H), 6.16 (s, 1H), 5.86 (s, 1H), 4.14 (s, 1H), 3.95 (d, J = 4.6 Hz, 1H), 2.89–2.70 (m, 2H); 13C NMR (100 MHz, CDCl₃) δ 198.5, 142.1, 137.9, 136.0, 131.8, 131.4, 124.9 (q, J = 280.8 Hz), 101.0, 70.3 (q, J = 31.1 Hz), 33.8; 19F NMR (375 MHz, CDCl₃) δ −79.4 (d, J = 6.0 Hz, 3F). IR (ATR): 3429, 2926, 2855, 1648, 1480, 1390, 1275, 1163, 1126, 1100, 787 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₂H₁₃BrF₂O₄⁺ (M+Na)⁺: 392.9570; Found: 392.9560.

4-Bromobut-2-en-1-yl 5,5,5-trifluoro-4-hydroxy-2-methylenepentanoate (9j)

![Chemical structure](image)

Under N₂ atmosphere, to a dried Schlenk tube containing Mn(OAc)₃•2H₂O (168.0 mg, 0.6 mmol, 2.0 equiv.), 7j (323.1 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 6 h. After which the mixture was cooled to −10 °C with low temperature bath, TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at −10 °C for 0.5 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude
product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1–5/1, v/v) as eluent to afford 45.7 mg of the title compound as a colorless oil (48% yield).

$R_t = 0.57$ (PE/EA = 4/1, v/v). NMR Spectroscopy: $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 6.39 (s, 1H), 5.95–5.92 (m, 2H), 5.85 (s, 1H), 4.71 (d, J = 4.3 Hz, 2H), 4.18–4.07 (m, 3H), 3.28 (s, 1H), 2.80–2.58 (m, 2H); $^{13}C$ NMR (100 MHz, CDCl$_3$) $\delta$ 167.5, 134.9, 130.4, 130.3, 127.9, 124.9 (q, $J = 281.2$ Hz), 69.9 (q, $J = 31.2$ Hz), 64.7, 43.9, 33.5. $^{19}F$ NMR (375 MHz, CDCl$_3$) $\delta$ –79.6 (d, $J = 8.9$ Hz, 3F). IR (ATR): 3444, 3100, 2950, 1655, 1416, 1349, 1275, 1163, 1129, 1029, 794 cm$^{-1}$. HRMS (ESI, m/z): calcd for $C_{10}$H$_2$F$_3$O$_3$• ($M$+Na)$^+$: 237.0733; Found: 237.0726.

5,5,5-Trifluoro-4-hydroxy-1-(4-methoxyphenyl)-2-methylenepentan-1-one (9k)

Under N$_2$ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)$_3$•2H$_2$O (16.1 mg, 0.06 mmol, 20 mol%), 7k (284.4 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with brine, dried over Na$_2$SO$_4$, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1–10/1, v/v) as eluent to afford 56.0 mg of the title compound as a colorless oil (68% yield).

$R_t = 0.30$ (PE/EA = 5/1, v/v). $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 (d, $J = 8.8$ Hz, 2H), 6.95 (d, $J = 9.2$ Hz, 2H), 6.08 (s, 1H), 5.83 (s, 1H), 4.78 (d, $J = 3.4$ Hz, 1H), 4.11 (s, 1H), 3.88 (s, 3H), 2.85–2.58 (m, 2H); $^{13}C$ NMR (100 MHz, CDCl$_3$) $\delta$ 198.2, 164.1, 142.2, 132.7, 130.0, 129.0, 125.0 (q, $J = 280.5$ Hz), 113.9, 70.8 (q, $J = 30.9$ Hz), 55.7, 34.1; $^{19}F$ NMR (375 MHz, CDCl$_3$) $\delta$ –79.4 (d, $J = 6.0$ Hz, 3F). IR (ATR): 3414, 2937, 2844, 1636, 1595, 1429, 1242, 1260, 1163, 1129, 1029, 794 cm$^{-1}$. HRMS (ESI, m/z): calcd for $C_{13}$H$_7$F$_3$O$_3$• ($M$+H)$^+$: 275.0890; Found: 275.0880.

5,5,5-Trifluoro-4-hydroxy-2-methylene-1-(4-nitrophenyl)pentan-1-one (9l)

Under N$_2$ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)$_3$•2H$_2$O (16.1 mg, 0.06 mmol, 20 mol%), 7l (297.9 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with brine, dried over Na$_2$SO$_4$, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1~10/1, v/v) as eluent to afford 69.4 mg of the title compound as a yellow oil (80% yield).

$R_t = 0.30$ (PE/EA = 5/1, v/v). $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 8.31 (d, $J = 9.0$ Hz, 2H), 7.89 (d, $J = 9.0$ Hz, 2H), 6.27 (s, 1H), 5.88 (s, 1H), 4.21–4.20 (m, 1H), 3.37 (s, 1H), 2.96–2.76 (m, 2H); $^{13}C$ NMR (100 MHz, CDCl$_3$) $\delta$ 197.1, 150.1, 142.3, 142.2, 133.2, 130.6, 124.6 (q, $J = 281.0$ Hz), 123.7, 69.9 (q, $J = 31.1$ Hz), 33.2; $^{19}F$ NMR (375 MHz, CDCl$_3$) $\delta$ –79.4 (d, $J = 6.0$ Hz, 3F). IR (ATR): 3444, 3109, 2930, 1655, 1416, 1349, 1275, 1163, 1129, 1029, 753 cm$^{-1}$. HRMS (ESI, m/z): calcd for $C_{12}$H$_9$F$_3$NaNO$_3$• ($M$+Na)$^+$: 312.0454; Found: 312.0450.
4-(5,5,5-Trifluoro-4-hydroxy-2-methylenepentanoyl)benzonitrile (9m)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₃·2H₂O (16.1 mg, 0.06 mmol, 20 mol%), 7m (280.2 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) and PE/EA (20/1~10/1, v/v) as eluent to afford 65.0 mg of the title compound as a yellow oil (80% yield).

5,5,5-Trifluoro-1-(furan-2-yl)-4-hydroxy-2-methylenepentan-1-one (9n)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₃·2H₂O (16.1 mg, 0.06 mmol, 20 mol%), 7n (248.7 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) and PE/EA (20/1~10/1, v/v) as eluent to afford 65.0 mg of the title compound as a yellow oil (80% yield).

5,5,5-Trifluoro-4-hydroxy-2-methylene-1-(thiophen-2-yl)pentan-1-one (9o)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₃·2H₂O (16.1 mg, 0.06 mmol, 20 mol%), 7o (261.0 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mg, 0.3 mmol) and TBPPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) and PE/EA (20/1~10/1, v/v) as eluent to afford 65.0 mg of the title compound as a yellow oil (80% yield).
mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1–10/1, v/v) as eluent to afford 61.4 mg of the title compound as a yellow solid (82% yield).

Rᵣ = 0.40 (PE/EA = 5/1, v/v). mp: 42 °C–44 °C (from PE and EA). ¹H NMR (400 MHz, CDCl₃) δ 7.77–7.72 (m, 2H), 7.18–7.16 (m, 1H), 6.10 (s, 1H), 6.05 (s, 1H), 4.46 (s, 1H), 4.14–4.11 (m, 1H), 2.85–2.66 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 190.6, 142.4, 142.2, 135.8, 135.6, 129.3, 128.4, 124.9 (q, J = 280.8 Hz), 70.7 (q, J = 30.7 Hz), 34.1; ¹⁹F NMR (375 MHz, CDCl₃) δ −79.3 (d, J = 6.0 Hz, 3F). IR (ATR): 3418, 3101, 2930, 2850, 1610, 1513, 1413, 1357, 1275, 1163, 1129, 1055, 727 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₀H₁₀F₃O₅⁺ (M+H)⁺: 251.0348; Found: 251.0341.

**5,5,5-Trifluoro-4-hydroxy-2-methylene-1-(naphthalen-2-yl)pentan-1-one (9p)**

![](image)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₃·2H₂O (16.1 mg, 0.06 mmol, 20 mol%), 7p (302.4 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1–10/1, v/v) as eluent to afford 63.0 mg of the title compound as a white solid (72% yield).

Rᵣ = 0.40 (PE/EA = 5/1, v/v). mp: 42 °C–44 °C (from PE and EA). ¹H NMR (400 MHz, CDCl₃) δ 8.30 (s, 1H), 7.95–7.85 (m, 4H), 7.65–7.55 (m, 2H), 6.21 (s, 1H), 5.97 (s, 1H), 4.42 (d, J = 5.2 Hz, 1H), 4.25–4.15 (m, 1H), 2.96–2.77 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 199.5, 142.4, 135.7, 133.9, 132.2, 132.1, 131.7, 129.6, 128.8, 128.7, 128.0, 127.1, 125.5, 125.0 (q, J = 280.7 Hz), 70.6 (q, J = 30.9 Hz), 34.0; ¹⁹F NMR (375 MHz, CDCl₃) δ −79.3 (d, J = 6.0 Hz, 3F). IR (ATR): 3411, 3060, 2933, 1644, 1469, 1357, 1275, 1167, 1126, 1033, 746 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₆H₁₄F₅O₅⁺ (M+H)⁺: 295.0940; Found: 295.0932.

**N,N-diphenyl 5,5,5-trifluoro-4-hydroxy-2-methylenepentanamide (9q)**

![](image)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₃·4H₂O (14.7 mg, 0.06 mmol, 20 mol%), 7q (279.0 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 18 h. After which the mixture was cooled to 5 °C with ice bath, TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (8/1, v/v) as eluent to afford 46.0 mg of the title compound as
a colorless oil (57% yield). 

Rt = 0.24 (PE/EA = 4/1, v/v). NMR Spectroscopy: 1H NMR (400 MHz, CDCl3) δ 6.39 (s, 1H), 5.80 (s, 1H), 4.31–4.09 (m, 4H), 3.92–3.78 (m, 2H), 2.78–2.61 (m, 2H), 2.08–1.92 (m, 3H), 1.69–1.62 (m, 1H); 13C NMR (100 MHz, CDCl3) δ 167.6, 135.1, 130.2, 125.0 (q, J = 281.0 Hz), 76.5, 76.4 (C'), 70.1 (q, J = 30.7 Hz, C), 70.1 (q, J = 30.7 Hz, C'), 68.6, 68.6 (C'), 67.4, 67.3 (C'), 33.6, 28.0, 25.8; 19F NMR (375 MHz, CDCl3) δ −79.6 (d, J = 6.0 Hz, 3F), −79.7 (d, J = 6.0 Hz, 3F'). IR (ATR): 3384, 2950, 1715, 1633, 1413, 1316, 1275, 1167, 1126, 1021, 712 cm⁻¹. HRMS (ESI, m/z): calcd for C11H13F3NaO4⁺ (M+Na)+: 290.0815; Found: 290.0810.

1-Methoxypropan-2-yl 5,5,5-trifluoro-4-hydroxy-2-methylenepentanoate (9r)

Under N2 atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)2•4H2O (24.5 mg, 0.1 mmol, 20 mol%), 7r (298.4 mg, 1.5 mmol, 3.0 equiv.) was added DCM (5 mL, 0.1 M), 1a (117.1 mg, 0.5 mmol) and TBPP (242.7 mg, 1.5 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 18 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.60 mL, 0.60 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with brine, dried over Na2SO4, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1~10/1, v/v) as eluent to afford 93.0 mg of the title compound as a colorless oil (73% yield).

Rt = 0.40 (PE/EA = 5/1, v/v). 1H NMR (400 MHz, CDCl3) δ 6.35–6.34 (m, 1H), 5.77–5.74 (m, 1H), 5.19–5.10 (m, 1H), 4.20–4.00 (m, 1H), 3.52–3.36 (m, 6H), 2.88–2.81 (m, 2H), 1.28 (d, J = 6.4 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 167.3, 167.2 (C'), 135.8, 135.3 (C'), 130.0, 129.4 (C'), 125.0 (q, J = 281.5 Hz), 75.0, 75.0 (C'), 70.8, 70.7, 70.6 (q, J = 28.7 Hz), 69.7 (q, J = 29.2 Hz, C'), 59.2, 59.1 (C'), 33.6, 33.3 (C'), 16.5, 16.5 (C'); 19F NMR (375 MHz, CDCl3) δ −77.0 (d, J = 8.9 Hz, 3F'), −77.4 (d, J = 8.9 Hz, 3F'). IR (ATR): 3422, 2986, 2937, 2889, 1711, 1633, 1454, 1275, 1170, 1126, 1033, 708 cm⁻¹. HRMS (ESI, m/z): calcd for C10H15F3NaO4⁺ (M+Na)+: 279.0814; Found: 279.0808.

2,3-Dihydro-1H-inden-1-yl 5,5,5-trifluoro-4-hydroxy-2-methylenepentanoate (9s)

Under N2 atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)2•4H2O (14.7 mg, 0.06 mmol, 20 mol%), 7s (205.2 mg, 0.6 mmol, 2.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPP (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 18 h. After which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na2SO4, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1, v/v) as eluent to afford 66.0 mg of the title compound as a colorless oil (73% yield).

Rt = 0.30 (PE/EA = 8/1, v/v). NMR Spectroscopy: 1H NMR (400 MHz, CDCl3) δ 7.43 (d, J = 7.3 Hz, 1H), 7.35–7.31 (m, 2H), 7.25 (t, J = 6.3 Hz, 1H), 6.32–6.28 (m, 2H), 5.79 (s, 1H), 4.14–4.12 (m, 1H), 3.67 (s, 1H), 3.18–3.11 (m, 1H), 2.96–2.89 (m, 1H), 2.80–2.76 (m, 1H), 2.66–2.52 (m, 2H), 2.20–2.13 (m, 1H); 13C NMR (100 MHz, CDCl3) δ 168.1, 144.6, 140.6, 135.3, 130.1, 130.0 (C'), 129.4, 127.0, 125.8, 125.7 (C'), 125.0, 124.9 (q, J = 280.8 Hz), 79.9, 71.2 (q, J = 30.9 Hz, C), 70.1 (q, J = 31.2 Hz, C'), 33.6, 32.4, 30.3; 19F NMR (375 MHz, CDCl3) δ −79.5–−79.5 (m, 3F, 3F'). IR
Benzo[d][1,3]dioxol-5-ylmethy 5,5,5-trifluoro-4-hydroxy-2-methylenepentanoate (9t)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂•4H₂O (14.7 mg, 0.06 mmol, 20 mol%), 7t (216 mg, 0.6 mmol, 2.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 18 h. After which the mixture was cooled to 5 °C with ice bath, TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and was dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) and PE/EA (8/1, v/v) as eluent to afford 61.0 mg of the title compound as a colorless oil (64% yield).

IR (ATR): 3422, 2900, 1707, 1633, 1491, 1446, 1327, 1252, 1167, 1122, 1036, 712 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₅H₁₅F₃NaO₃⁺ (M+Na)⁺: 323.0866; Found: 323.0867.

2-Iodobenzyl 5,5,5-trifluoro-4-hydroxy-2-methylenepentanoate (9u)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂•4H₂O (14.7 mg, 0.06 mmol, 20 mol%), 7u (406.8 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 18 h. After which the mixture was cooled to 5 °C with ice bath, TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and was dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) and PE/EA (12/1, v/v) as eluent to afford 83.0 mg of the title compound as a colorless oil (68 % yield).

IR (ATR): 3291, 2919, 2848, 1707, 1633, 1439, 1327, 1275, 1167, 1122, 1036, 712 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₃H₁₂F₃NaO₅⁺ (M+Na)⁺: 422.9675; Found: 422.9664.
(4-Bromophenyl)methyl 5,5,5-trifluoro-4-hydroxy-2-methylenepentanoate (9v)

\[
\begin{align*}
1a & \quad 7v & \quad 9v \\
\text{O} & \quad \text{OH} & \quad \text{Br}\text{Ph}_2 & \quad \text{SO}_2\text{Ph} & \quad \text{Mn(OAc)}_2\cdot 4\text{H}_2\text{O} (20 \text{ mol}) & \quad \text{TPBP} (2.5 \text{ equiv}) \\
\text{F}_3\text{C} & \quad \text{SiPh}_2\text{Me}_2 & \quad \text{O} & \quad \text{O} & \quad \text{DCM} (0.1 \text{ M}, \text{N}_2, 18 \text{ h}) & \quad \text{then TBAF (1.2 equiv.)} \\
\end{align*}
\]

Under N\(_2\) atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)\(_2\)•4H\(_2\)O (14.7 mg, 0.06 mmol, 20 mol%), 7v (355.5 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 18 h. After which the mixture was cooled to 5 °C with ice bath, TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na\(_2\)SO\(_4\), concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (8/1, v/v) as eluent to afford 60.0 mg of the title compound as a colorless oil (56% yield).

R\(_t\) = 0.23 (PE/EA = 4/1, v/v). NMR Spectroscopy: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.51 (d, \(J = 8.3\) Hz, 2H), 7.25 (d, \(J = 8.4\) Hz, 2H), 6.39 (s, 1H), 5.85 (s, 1H), 5.17 (s, 2H), 4.17–4.09 (m, 1H), 2.81–2.59 (m, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.6, 134.8, 134.5, 132.0, 130.4, 130.1, 124.9 (q, \(J = 279.8\) Hz), 122.7, 69.9 (q, \(J = 31.1\) Hz), 66.6, 33.4; \(^19\)F NMR (375 MHz, CDCl\(_3\)) \(\delta\) –79.6 (d, \(J = 6.0\) Hz, 3F), IR (ATR): 3422, 3528, 2498, 1715, 1633, 1439, 1331, 1275, 1170, 1126, 1014, 712 cm\(^{-1}\). HRMS (ESI, m/z): calcd for C\(_{29}\)H\(_{29}\)BrF\(_3\)NaO\(_3\)\(^+\) (M+Na\(^+\)): 374.9814; Found:374.9807.

Naphthalen-1-ylmethyl 5,5,5-trifluoro-4-hydroxy-2-methylenepentanoate (9w)

\[
\begin{align*}
1a & \quad 7w & \quad 9w \\
\text{O} & \quad \text{OH} & \quad \text{Br}\text{Ph}_2 & \quad \text{SO}_2\text{Ph} & \quad \text{Mn(OAc)}_2\cdot 4\text{H}_2\text{O} (20 \text{ mol}) & \quad \text{TPBP} (2.5 \text{ equiv}) \\
\text{F}_3\text{C} & \quad \text{SiPh}_2\text{Me}_2 & \quad \text{O} & \quad \text{O} & \quad \text{DCM} (0.1 \text{ M}, \text{N}_2, 18 \text{ h}) & \quad \text{then TBAF (1.2 equiv.)} \\
\end{align*}
\]

Under N\(_2\) atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)\(_2\)•4H\(_2\)O (14.7 mg, 0.06 mmol, 20 mol%), 7w (329.8 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with brine, dried over Na\(_2\)SO\(_4\), concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1–10/1, v/v) as eluent to afford 70.0 mg of the title compound as a colorless oil (72% yield).

R\(_t\) = 0.3 (PE/EA = 10/1, v/v). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.03 (d, \(J = 7.9\) Hz, 1H), 7.89 (t, \(J = 8.9\) Hz, 2H), 7.60–7.52 (m, 3H), 7.47 (t, \(J = 7.5\) Hz, 1H), 6.35 (s, 1H), 5.80 (s, 1H), 5.70 (s, 2H), 4.17–4.09 (m, 1H), 3.31 (s, 1H), 2.81–2.59 (m, 2H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.8, 134.9, 133.9, 131.8, 131.0, 130.5, 129.7, 128.95, 127.87, 126.86, 126.19, 125.40, 124.9 (q, \(J = 280.8\) Hz), 123.5, 69.9 (q, \(J = 30.7\) Hz), 65.8, 33.5; \(^19\)F NMR (375 MHz, CDCl\(_3\)) \(\delta\) –79.6 (d, \(J = 6.0\) Hz, 3F), IR(ATR): 3444, 3049, 2937, 1707, 1633, 1413, 1320, 1271, 1167, 1126, 1029, 775 cm\(^{-1}\). HRMS (ESI, m/z): calcd for C\(_{29}\)H\(_{29}\)BrF\(_3\)NaO\(_3\)\(^+\) (M+Na\(^+\)): 347.0866; Found: 347.0875.
Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂•4H₂O (14.7 mg, 0.06 mmol, 20 mol%), 7x (210.0 mg, 0.6 mmol, 2.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 18 h. After which the mixture was cooled to 5 °C with ice bath, TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (15/1, v/v) as eluent to afford 61.0 mg of the title compound as a colorless oil (66% yield).

Rᵣ = 0.54 (PE/EA = 4/1, v/v). NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 6.34 (s, 1H), 5.80 (s, 1H), 4.18−4.08 (m, 3H), 2.79−2.58 (m, 3H), 1.71−1.64 (m, 7H), 1.26−1.12 (m, 6H), 0.92−0.87 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 168.2, 135.3, 129.8, 124.9 (q, J = 280.5 Hz), 70.1 (q, J = 31.1 Hz), 66.3, 37.4, 33.7, 33.6, 33.4, 26.7, 26.4, 26.0; ¹⁹F NMR (375 MHz, CDCl₃) δ −79.6 (d, J = 6.0 Hz, 3F). IR (ATR): 3422, 2922, 2851, 1711, 1633, 1413, 1320, 1275, 1174, 1129, 1033, 712 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₅H₂₄F₃O₃⁺ (M+H)⁺: 309.1672; Found: 309.1665.

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂•4H₂O (14.7 mg, 0.06 mmol, 20 mol%), 7y (216.0 mg, 0.6 mmol, 2.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 18 h. After which the mixture was cooled to 5 °C with ice bath, TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (15/1, v/v) as eluent to afford 78.0 mg of the title compound as a colorless oil (82 % yield).

Rᵣ = 0.43 (PE/EA = 8/1, v/v). NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 6.40 (s, 1H), 5.81 (s, 1H), 5.03 (s, 1H), 4.15−4.12 (m, 1H), 3.66 (s, 1H), 2.81−2.60 (m, 2H), 2.06−2.00 (m, 4H), 1.90−1.76 (m, 8H), 1.63−1.60 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 167.5, 135.9, 129.5, 125.0 (q, J = 280.8 Hz), 78.7, 70.2 (q, J = 30.7 Hz), 37.4, 36.4, 33.6, 32.1, 32.0, 27.3, 31.1; ¹⁹F NMR (375 MHz, CDCl₃) δ −79.5 (d, J = 6.0 Hz, 3F). IR (ATR): 3444, 2907, 2855, 1696, 1633, 1413, 1316, 1275, 1174, 1129, 1044, 712 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₆H₂₁F₃NaO₃⁺ (M+Na)⁺: 341.1335; Found: 341.1330.

N,N-diphenyl 5,5,5-trifluoro-4-hydroxy-2-methylenepentanamide (9z)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂•4H₂O (14.7 mg, 0.06 mmol, 20 mol%), 7z (216.0 mg, 0.6 mmol, 2.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 18 h. After which the mixture was cooled to 5 °C with ice bath, TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1, v/v) as eluent to afford 78.0 mg of the title compound as a colorless oil (82 % yield).

Rᵣ = 0.43 (PE/EA = 8/1, v/v). NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 6.40 (s, 1H), 5.81 (s, 1H), 5.03 (s, 1H), 4.15−4.12 (m, 1H), 3.66 (s, 1H), 2.81−2.60 (m, 2H), 2.06−2.00 (m, 4H), 1.90−1.76 (m, 8H), 1.63−1.60 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 167.5, 135.9, 129.5, 125.0 (q, J = 280.8 Hz), 78.7, 70.2 (q, J = 30.7 Hz), 37.4, 36.4, 33.6, 32.1, 32.0, 27.3, 31.1; ¹⁹F NMR (375 MHz, CDCl₃) δ −79.5 (d, J = 6.0 Hz, 3F). IR (ATR): 3444, 2907, 2855, 1696, 1633, 1413, 1316, 1275, 1174, 1129, 1044, 712 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₆H₂₁F₃NaO₃⁺ (M+Na)⁺: 341.1335; Found: 341.1330.
Under N\(_2\) atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)\(_2\)•4H\(_2\)O (14.7 mg, 0.06 mmol, 20 mol%), 7a (33.9 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 18 h. After which the mixture was cooled to 5 °C with ice bath, TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na\(_2\)SO\(_4\), concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) and PE/EA (8/1, v/v) as eluent to afford 54.0 mg of the title compound as a colorless oil (54% yield).

\( R_1 = 0.27 \) (PE/EA = 4/1, v/v). NMR Spectroscopy: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.37 (t, \( J = 7.8 \) Hz, 4H), 7.29–7.25 (m, 2H), 7.19–7.17 (m, 4H), 5.45 (s, 1H), 5.32 (s, 1H), 4.15–4.07 (m, 1H), 2.64–2.50 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 172.4, 143.2, 138.6, 129.5, 127.3, 127.2, 125.8, 125.0 (q, \( J = 280.3 \) Hz), 71.1 (q, \( J = 30.7 \) Hz), 34.8; \(^{19}\)F NMR (375 MHz, CDCl\(_3\)) \( \delta \) –79.5 (d, \( J = 6.0 \) Hz, 3F). IR (ATR): 3288, 2963, 2930, 1644, 1592, 1491, 1364, 1275, 1163, 1126, 1029, 693 cm\(^{-1}\). HRMS (ESI, m/z): calcd for C\(_{33}\)H\(_{39}\)F\(_3\)NO\(_2\)\(_4\) (M+H\(^+\)): 336.1206; Found: 336.1197.

### 5,5,5-Trifluoro-4-hydroxy-N,N-dimethyl-2-methylenepentanamide (9aa)

[Diagram of 5,5,5-Trifluoro-4-hydroxy-N,N-dimethyl-2-methylenepentanamide (9aa)]

Under N\(_2\) atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)\(_2\)•4H\(_2\)O (14.7 mg, 0.06 mmol, 20 mol%), 7aa (227.9 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with brine, dried over Na\(_2\)SO\(_4\), concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) and PE/EA (8/1, v/v) as eluent to afford 40.0 mg of the title compound as a colorless oil (63% yield).

\( R_1 = 0.30 \) (PE/EA = 2/1, v/v). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 5.58 (s, 1H), 5.37 (s, 1H), 4.10–4.02 (m, 1H), 3.14 (s, 3H), 3.03 (s, 3H), 2.64–2.41 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 172.4, 137.6, 125.1 (q, \( J = 280.3 \) Hz), 121.8, 71.1 (q, \( J = 30.7 \) Hz), 39.8, 35.5, 34.8; \(^{19}\)F NMR (375 MHz, CDCl\(_3\)) \( \delta \) –79.4 (d, \( J = 6.0 \) Hz, 3F). IR (ATR): 3329, 2930, 1610, 1454, 1264, 1167, 1118, 1029, 734 cm\(^{-1}\). HRMS (ESI, m/z): calcd for C\(_{33}\)H\(_{39}\)F\(_3\)NO\(_2\)\(_4\) (M+Na\(^+\)): 234.0712; Found: 234.0707.

### 1,1,1-Trifluoro-4-tosylpent-4-en-2-ol (9ab)

[Diagram of 1,1,1-Trifluoro-4-tosylpent-4-en-2-ol (9ab)]

Under N\(_2\) atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)\(_2\)•2H\(_2\)O (16.1 mg, 0.06 mmol, 20 mol%), 7ab (302.7 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with brine, dried over Na\(_2\)SO\(_4\), concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) and PE/EA (8/1, v/v) as eluent to afford 0.40 mg of the title compound as a colorless oil.
chromatography on silica gel (200–300 mesh) and PE/EA (20/1–10/1, v/v) as eluent to afford 63.5 mg of the title compound as a colorless oil (72% yield).

\[ \text{R}_2 = 0.30 \text{ (PE/EA = 5/1, v/v)} \]

\[ ^1\text{H NMR (400 MHz, CDCl}_3\text{):} \delta 7.76 \text{ (d, } J = 8.4 \text{ Hz, 2H), 7.37 \text{ (d, } J = 8.0 \text{ Hz, 2H), 6.47 \text{ (s, } 1\text{H), 5.96 \text{ (s, } 1\text{H), 4.30–4.22 \text{ (m, } 1\text{H), 2.63–2.46 \text{ (m, } 5\text{H); } ^1\text{C NMR (100 MHz, CDCl}_3\text{):} \delta 145.5, 145.0, 134.7, 130.3, 128.6, 128.3, 124.6 \text{ (q, } J = 277.9 \text{ Hz), 69.1 \text{ (q, } J = 31.4 \text{ Hz), 31.2, 21.8; } ^1\text{H NMR (375 MHz, CDCl}_3\text{):} \delta −79.7 \text{ (d, } J = 6.0 \text{ Hz, 3F). IR (ATR):} 3474, 2930, 2855, 1595, 1431, 1279, 1137, 1081, 734 \text{ cm}^{-1}. \text{HRMS (ESI, m/z):} \text{calcd for } C_{12}H_{13}F_3NaO}_2^+: 317.0430; \text{Found:} 317.0432. \]

1,1,1-Trifluoro-4-phenylpent-4-en-2-ol (9ac)

Under \( N_2 \) atmosphere, to a dried 25 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)_2·4H_2O (29.4 mg, 0.12 mmol, 20 mol%) and 7ac (465.0 mg, 1.8 mmol, 3.0 equiv.) was added DCM (6 mL, 0.1 M), 1a (140.4 mg, 0.6 mmol), and TBPB (291.3 mg, 1.5 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70°C in a heating block for 18 h, after which the mixture was cooled to 5°C with ice bath. TBAF (1.0 M in THF, 0.72 mL, 0.72 mmol, 1.2 equiv.) was added and the mixture was stirred at 5°C for 0.5 h. The reaction mixture was quenched with water (10 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (30/1–20/1, v/v) as eluent to afford 56.0 mg of the title compound as a colorless oil (43% yield).

\[ \text{R}_2 = 0.47 \text{ (PE/EA = 8/1, v/v)} \]

\[ ^1\text{H NMR (400 MHz, CDCl}_3\text{):} \delta 7.42–7.31 \text{ (m, } 5\text{H), 5.49 \text{ (s, } 1\text{H), 5.28 \text{ (s, } 1\text{H), 4.00 \text{ (bs, } 1\text{H), 3.11–2.67 \text{ (m, } 2\text{H), 2.21 \text{ (s, } 1\text{H); } ^1\text{C NMR (100 MHz, CDCl}_3\text{):} \delta 142.7, 139.4, 128.8, 128.3, 126.3, 125.2 \text{ (q, } J = 279.8 \text{ Hz), 121.1, 117.0, 68.7 \text{ (q, } J = 30.9 \text{ Hz), 36.3; } ^1\text{H NMR (375 MHz, CDCl}_3\text{):} \delta −79.5 \text{ (d, } J = 6.0 \text{ Hz, 3F). IR (ATR):} 3444, 2974, 2873, 1446, 1390, 701 \text{ cm}^{-1}. \text{HRMS (ESI, m/z):} \text{calcd for } C_{13}H_{13}F_3O^+ (M+H)^+: 217.0835; \text{Found:} 217.0828. \]

1,1,1-Trifluoro-5-methyl-5-phenylhex-4-en-2-ol (9ad)

Under \( N_2 \) atmosphere, to a dried 25 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)_2·4H_2O (29.4 mg, 0.12 mmol, 20 mol%) and 7ad (540.0 mg, 1.8 mmol, 3.0 equiv.) was added DCM (6 mL, 0.1 M), 1a (140.4 mg, 0.6 mmol), and TBPB (291.3 mg, 1.5 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70°C in a heating block for 14 h, after which the mixture was cooled to 5°C with ice bath. TBAF (1.0 M in THF, 0.72 mL, 0.72 mmol, 1.2 equiv.) was added and the mixture was stirred at 5°C for 0.5 h. The reaction mixture was quenched with water (10 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (30/1–20/1, v/v) as eluent to afford 62.0 mg of the title compound as a colorless oil (40% yield).

\[ \text{R}_2 = 0.42 \text{ (PE/EA = 8/1, v/v)} \]

\[ ^1\text{H NMR (400 MHz, CDCl}_3\text{):} \delta 7.32–7.31 \text{ (m, } 4\text{H), 7.24–7.19 \text{ (m, } 1\text{H), 5.37 \text{ (s, } 1\text{H), 5.15 \text{ (s, } 1\text{H), 3.81–3.73 \text{ (m, } 1\text{H), 2.28–2.00 \text{ (m, } 2\text{H), 1.79 \text{ (s, } 1\text{H), 1.48–1.47 \text{ (m, } 6\text{H); } ^1\text{C NMR (100 MHz, CDCl}_3\text{):} \delta 150.8, 146.9, 128.6, 126.5, 126.2, 125.0 \text{ (q, } J = 280.3 \text{ Hz), 111.5, 69.4 \text{ (q, } J = 30.7 \text{ Hz), 44.4, 32.9, 28.3; } ^1\text{H NMR (375 MHz, CDCl}_3\text{):} \delta −80.0 \text{ (d, } J = 6.0 \text{ Hz, 3F). IR (ATR):} 3444, 2974, 2878, 1640, 1446, 1383, 1275, 1167, 1126, 1029, 701 \text{ cm}^{-1}. \text{HRMS (ESI, m/z):} \text{calcd for } C_{14}H_{14}F_3NaO^+ (M+Na)^+: 281.1124; \text{Found:} 281.1121. \]
Cyclobutyl 5,5,5-trifluoro-4-hydroxy-2-methylenepentanoate (9ae)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂•4H₂O (14.7 mg, 0.06 mmol, 20 mol%), 4ae (252.0 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 3a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 18 h. After which the mixture was cooled to 5 °C with ice bath, TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (15/1–8/1, v/v) as eluent to afford 50.0 mg of the title compound as a colorless oil (70% yield).

R₁ = 0.36 (PE/EA = 8/1, v/v). NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 6.35 (s, 1H), 5.80 (s, 1H), 5.09–5.02 (m, 1H), 4.15–4.07 (m, 1H), 2.77–2.56 (m, 2H), 2.42–2.35 (m, 2H), 2.18–2.07 (m, 2H), 1.87–1.60 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 167.5, 135.4, 129.8, 124.9 (q, J = 283.4 Hz), 70.1 (q, J = 30.9 Hz), 70.1, 33.48, 30.34, 13.6; ¹⁹F NMR (375 MHz, CDCl₃) δ -79.6 (bs, 3F). IR (ATR): 3344, 2993, 2952, 1700, 1633, 1435, 1320, 1275, 1163, 1126, 1029, 712 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₀H₁₂F₂O₄ (M+Na)+: 239.0890; Found: 239.0889.

6-Hydroxyhexyl 5,5,5-trifluoro-4-hydroxy-2-methylenepentanoate (9af)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂•4H₂O (14.7 mg, 0.06 mmol, 20 mol%), 7af (302.4 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 18 h. After which the mixture was cooled to 5 °C with ice bath, TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1–2/1, v/v) as eluent to afford 40.0 mg of the title compound as a colorless oil (45 % yield).

R₁ = 0.45 (PE/EA = 1/1, v/v). NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 6.33 (s, 1H), 5.79 (s, 1H), 4.22–4.09 (m, 3H), 3.65 (t, J = 6.4 Hz, 2H), 2.79–2.56 (m, 2H), 2.30 (s, 2H), 1.73–1.70 (m, 2H), 1.59–1.56 (m, 2H), 1.42–1.40 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 168.0, 135.2, 129.7, 125.0 (q, J = 280.8 Hz), 69.8 (q, J = 30.9 Hz), 65.6, 62.9, 33.5, 32.6, 28.5, 25.8, 25.4; ¹⁹F NMR (375 MHz, CDCl₃) δ -79.5 (d, J = 6.0 Hz, 3F). IR (ATR): 3384, 2937, 2863, 1707, 1633, 1435, 1316, 1275, 1167, 1126, 1033, 708 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₂H₁₂F₂NaO₄ (M+Na)+: 307.1128; Found: 307.1117.

6-Oxoheptyl 5,5,5-trifluoro-4-hydroxy-2-methylenepentanoate (9ag)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂•4H₂O
(14.7 mg, 0.06 mmol, 20 mol%), 7ag (291.6 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 18 h. After which the mixture was cooled to 5 °C with ice bath, TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) and PE/EA (20/1~2/1, v/v) as eluent to afford 39.0 mg of the title compound as a colorless oil (46 % yield).

Rₚ = 0.61 (PE/EA = 2/1, v/v), NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 9.77 (t, J = 1.5 Hz, 1H), 6.33 (s, 1H), 5.80 (s, 1H), 4.22~4.09 (m, 3H), 2.79~2.57 (m, 2H), 2.47 (td, J = 7.2, 1.3 Hz, 2H), 1.76~1.64 (m, 4H), 1.46~1.38 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 202.5, 167.9, 135.2, 129.8, 124.9 (q, J = 281.1 Hz), 69.9 (q, J = 30.7 Hz), 65.3, 43.8, 33.5, 28.4, 25.6, 21.7; ¹⁹F NMR (375 MHz, CDCl₃) δ −79.6 (d, J = 6.0 Hz, 3F). IR (ATR): 3425, 2922, 2855, 1651, 1440, 1360, 1340, 1294 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₂H₂₃SO₄F²⁺ (M+Na)⁺: 305.0971; Found: 305.0970.

I-Cyclopropyl-5,5,5-trifluoro-4-hydroxy-2-methylenepentan-1-one (9ah)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂•2H₂O (16.1 mg, 0.06 mmol, 20 mol%) was added DCM (3 mL), 1a (70.2 mg, 0.3 mmol), 7ah (225.0 mg, 0.9 mmol, 3.0 equiv.) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) and PE/EA (20/1~10/1, v/v) as eluent to afford 38.7 mg of the title compound as a yellow oil (62% yield).

Rₚ = 0.50 (PE/EA = 5/1, v/v). ¹H NMR (400 MHz, CDCl₃) δ 6.38 (s, 1H), 6.04 (s, 1H), 4.27 (s, 1H), 4.00 (s, 1H), 2.71~2.57 (m, 2H), 2.49~2.43 (m, 1H), 1.16~1.00 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 204.5, 144.3, 129.3, 125.0 (q, J = 280.8 Hz), 70.5 (q, J = 30.7 Hz), 33.4, 16.8, 12.7, 12.3; ¹⁹F NMR (375 MHz, CDCl₃) δ −79.5 (d, J = 6.0 Hz, 3F). IR(ATR): 3437, 3012, 2922, 2855, 1651, 1443, 1398, 1275, 1163, 1129, 1062, 746 cm⁻¹. HRMS (ESI, m/z): calcd for C₅H₇F₃O₂⁺ (M+H)⁺: 209.0784; Found: 209.0784.

(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl 5,5,5-trifluoro-4-hydroxy-2-methylenepentanoate (9ai)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂•4H₂O (14.7 mg, 0.06 mmol, 20 mol%), 7ai (218.4 mg, 0.6 mmol, 2.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 18 h. After which the mixture was cooled to 5 °C with ice bath, TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column
chromatography on silica gel (200–300 mesh) and PE/EA (15/1–8/1, v/v) as eluent to afford 63.0 mg of the title compound as a colorless oil (65% yield).

Rt = 0.50 (PE/EA = 10/1, v/v). NMR Spectroscopy: 

\( ^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.31 (s, 1H), 5.78 (s, 1H), 4.81–4.75 (m, 1H), 4.11–4.10 (m, 1H), 3.72–3.66 (m, 1H), 2.78–2.59 (m, 2H), 2.04–2.01 (m, 1H), 1.87–1.81 (m, 1H), 1.72–1.69 (m, 2H), 1.53–1.43 (m, 2H), 1.13–0.99 (m, 2H), 0.93–0.89 (m, 7H), 0.77–0.76 (m, 3H); 

\( ^3C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.9, 135.7, 129.4, 129.4 (C'), 124.9 (q, \(J = 272.4\) Hz), 76.0, 70.2 (q, \(J = 30.7\) Hz), 47.2, 40.8, 34.3, 33.7, 33.6 (C'), 31.6, 26.6, 23.7, 23.6 (C'), 22.1, 20.8, 20.8 (C'), 16.6, 16.5 (C'); 

\( ^19F\) NMR (375 MHz, CDCl\(_3\)) \(\delta\) –79.5 (d, \(J = 6.0\) Hz, 3F), –79.5 (d, \(J = 6.0\) Hz, 3F).

HRMS (ESI, m/z): calcd for \(\text{C}_{3}\text{H}_{2}\text{F}_{3}\text{NaO}_{2}\)\(^{+}\) (M+Na\(^{+}\)): 345.1648; Found: 345.1643.

(3S,5S,8R,9S,10S,13S,14S)-10,13-Dimethyl-17-oxohenadecahydro-1H-cyclopenta[a]pennanthren-3-yl 5,5,5-trifluoro-4-hydroxy-2-methylenepentanoate (9aj)

Under N\(_2\) atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)\(_2\)•4H\(_2\)O (14.7 mg, 0.06 mmol, 20 mol%), 7aj (298.8 mg, 0.6 mmol, 2.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 18 h. After which the mixture was cooled to 5 °C with ice bath, TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na\(_2\)SO\(_4\), concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (5/1, v/v) as eluent to afford 81.0 mg of the title compound as a white solid (59% yield).

Rt = 0.24 (PE/EA = 2/1, v/v); mp: 95 °C–97 °C. NMR Spectroscopy:

\( ^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.31 (s, 1H), 5.77 (s, 1H), 4.81–4.73 (m, 1H), 4.11–4.08 (m, 1H), 3.82 (s, 1H), 2.76–2.55 (m, 2H), 2.46–2.39 (m, 1H), 2.11–2.01 (m, 1H), 1.95–1.75 (m, 5H), 1.67–1.19 (m, 12H), 1.09–0.96 (m, 2H), 0.86 (s, 3H), 0.85 (s, 3H), 0.75–0.69 (m, 1H); 

\( ^3C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 221.7, 167.5, 135.5, 129.5, 124.9 (q, \(J = 280.8\) Hz), 75.1, 70.0 (q, \(J = 30.9\) Hz), 54.3, 54.1, 47.9, 44.7, 36.7, 36.0, 35.7, 35.1, 33.9, 33.5, 31.6, 30.9, 28.3, 27.4, 21.9, 20.6, 13.9, 12.3; 

\( ^19F\) NMR (375 MHz, CDCl\(_3\)) \(\delta\) –79.5––79.5 (m, 3F, 3F).

IR (ATR): 3370, 2933, 2855, 1718, 1633, 1405, 1457, 1316, 1275, 1178, 1129, 1036, 712 cm\(^{-1}\).

HRMS (ESI, m/z): calcd for \(\text{C}_{25}\text{H}_{33}\text{F}_{3}\text{NaO}_{4}\)\(^{+}\) (M+Na\(^{+}\)): 479.2380; Found: 479.2370.

(3S,8S,9S,10R,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetrad ecahydro-1H-cyclopenta[a]pennanthren-3-yl 5,5,5-trifluoro-4-hydroxy-2-methylenepentanoate (9ak)

Under N\(_2\) atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)\(_2\)•4H\(_2\)O (14.7 mg, 0.06 mmol, 20 mol%). 4ak (357.6 mg, 0.6 mmol, 2.0 equiv.) was added DCM (3 mL, 0.1 M), 3a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 18 h. After which the mixture was cooled to 5 °C with ice bath, TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with...
brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (5/1, v/v) as eluent to afford 99.5 mg of the title compound as a white solid (60 % yield).

Rₙ = 0.48 (PE/EA = 8/1, v/v). mp: 83 °C–85 °C. NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 6.33 (s, 1H), 5.78 (s, 1H), 5.40 (d, J = 4.3 Hz, 1H), 4.73–4.65 (m, 1H), 4.12–4.09 (m, 1H), 3.75 (s, 1H), 2.77–2.57 (m, 2H), 2.37 (d, J = 7.6 Hz, 2H), 2.03–1.95 (m, 2H), 1.92–1.79 (m, 3H), 1.70–1.43 (m, 7H), 1.40–1.25 (m, 4H), 1.20–1.08 (m, 7H), 1.03–0.95 (m, 6H), 0.91 (d, J = 6.4 Hz, 3H), 0.86 (dd, J = 6.7, 1.8 Hz, 6H), 0.68 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.6, 139.4, 135.6, 129.6, 124.9 (q, J = 280.8 Hz), 123.2, 75.64, 70.1 (q, J = 30.7 Hz), 56.8, 56.2, 50.1, 42.4, 39.8, 39.6, 38.1, 37.0, 36.7, 36.3, 35.9, 33.6, 32.0, 31.9, 28.4, 28.1, 27.8, 24.4, 24.0, 23.0, 22.7, 21.9, 18.8, 12.0; ¹⁹F NMR (375 MHz, CDCl₃) δ −79.5 (bs, 3F). IR (ATR): 3422, 2937, 2870, 1711, 1633, 1465, 1331, 1275, 1170, 1129, 1036, 730 cm⁻¹. HRMS (ESI, m/z): calcd for C₃₅H₅₃F₃NaO₃(M+Na)⁺: 575.3683; Found: 575.3671.

(8R,9S,10R,13S,14S,17S)-10,13-dimethyl-3-oxo–2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[α]phenanthrene-17-yl 5,5,5-trifluoro-4-hydroxy-2-methylenepentanoate (9α)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂•4H₂O (14.7 mg, 0.06 mmol, 20 mol%), 7α (297.6 mg, 0.6 mmol, 2.0 equiv.) was added DCM (3 mL, 0.1 M), 1α (70.2 g, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 18 h. After which the mixture was cooled to 5 °C with ice bath, TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3x10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (8/1, v/v) as eluent to afford 86.0 mg of the title compound as a white solid (63% yield).

Rₙ = 0.43 (PE/EA = 2/1, v/v). mp: 105 °C–107 °C. NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 6.34 (s, 1H), 5.79 (s, 1H), 5.73 (s, 1H), 4.68 (t, J = 7.3 Hz, 1H), 4.14–4.10 (m, 1H), 3.56 (s, 1H), 2.79–2.58 (m, 2H), 2.47–2.19 (m, 5H), 2.05–2.01 (m, 1H), 1.88–1.79 (m, 2H), 1.74–1.57 (m, 7H), 1.44–1.37 (m, 2H), 1.19 (s, 3H), 1.14–1.04 (m, 2H), 0.99–0.93 (m, 1H), 0.89 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 199.7, 171.0, 167.9, 135.4, 129.7, 129.6 (C'), 125.0 (q, J = 276.5 Hz) 124.1, 83.9, 83.9 (C'), 70.1 (q, J = 32.4 Hz, C), 70.0 (q, J = 32.1 Hz, C'), 53.8, 50.3, 43.0, 38.7, 36.8, 35.8, 35.5, 34.0, 33.6, 33.5 (C'), 32.9, 31.6, 27.6, 23.7, 20.7, 17.5, 12.3; ¹⁹F NMR (375 MHz, CDCl₃) δ −79.6 (d, J = 6.0 Hz, 3F). IR (ATR): 3355, 2937, 2855, 1711, 1659, 1435, 1376, 1275, 1170, 1126, 1036, 730 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₅H₃₃F₃O₃(M+H)⁺: 455.2404; Found: 455.2394.

(4S,5'R,6aR,6bS,8aS,8bR,9S,10R,11aS,12aS,12bS)-5',6a,8a,9-tetramethyl-1,3,3',4,4',5,5',6,6a,6b,6',7,8,8a,8b,9,11a,12,12a,12b-icosahydrospiro[naphtho[2',1':4,5]indenofuran-10,2'-pyran]-4-yl

5,5,5-trifluoro-4-hydroxy-2-methylenepentanoate (9α)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂•4H₂O (14.7 mg, 0.06 mmol, 20 mol%), 7αm (373.5 mg, 0.6 mmol, 2.0 equiv.) was added DCM (3 mL, 0.1 M), 1α (70.2 mg,
0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 18 h. After which the mixture was cooled to 5 °C with ice bath, TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) and PE/EA (12/1, v/v) as eluent to afford 108.0 mg of the title compound as a white solid (62 % yield).

Rf = 0.29 (PE/EA = 10/1, v/v). mp: 163 °C–165 °C (from EA and PE).

NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 6.33 (s, 1H), 5.79 (s, 1H), 5.40 (d, J = 4.0 Hz, 1H), 4.73–4.65 (m, 1H), 4.41 (q, J = 7.4 Hz, 1H), 4.12–4.09 (m, 1H), 3.64 (s, 1H), 3.49–3.34 (m, 2H), 2.77–2.58 (m, 2H), 2.38 (d, J = 7.6 Hz, 2H), 2.03–1.96 (m, 2H), 1.90–1.84 (m, 3H), 1.80–1.42 (m, 12H), 1.33–1.12 (m, 4H), 1.05 (s, 3H), 0.98–0.96 (m, 4H), 0.79–0.78 (m, 6H);

¹³C NMR (100 MHz, CDCl₃) δ 167.5, 139.5, 135.6, 129.5, 125.0 (q, J = 280.0 Hz), 122.9, 109.4, 81.0, 75.6, 70.2 (q, J = 30.1 Hz), 67.0, 62.2, 56.6, 50.1, 41.8, 40.4, 39.9, 38.1, 37.0, 36.9, 33.6, 33.6, 32.2, 32.0, 31.6, 30.4, 29.0, 27.8, 21.0, 19.5, 17.3, 16.4, 14.7; ¹⁹F NMR (375 MHz, CDCl₃) δ −79.5 (d, J = 6.0 Hz, 3F). IR (ATR): 3422, 2948, 2904, 1711, 1633, 1454, 1331, 1275, 1170, 1129, 1051, 734 cm⁻¹. HRMS (ESI, m/z): calcd for C₃₃H₄₈F₃O₅+ (M+H)+: 581.3448; Found: 581.3435.

(R)-2,5,7,8-tetramethyl-2-(((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl
5,5,5-trifluoro-4-hydroxy-2-methylenepentanoate (9an)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂•4H₂O (14.7 mg, 0.06 mmol, 20 mol%), 7an (297.6 mg, 0.6 mmol, 2.0 equiv.) was added DCM (3 mL, 0.1 M), 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 18 h. After which the mixture was cooled to 5 °C with ice bath, TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) and PE/EA (15/1 ~ 10/1, v/v) as eluent to afford 131.0 mg of the title compound as a colorless oil (73% yield).

Rf = 0.41 (PE/EA = 8/1, v/v). NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 6.68 (s, 1H), 6.01 (s, 1H), 4.23–4.20 (m, 1H), 2.91–2.72 (m, 3H), 2.62–2.59 (m, 2H), 2.11 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H), 1.87–1.77 (m, 2H), 1.56–1.06 (m, 23H), 0.88–0.84 (m, 13H); ¹³C NMR (100 MHz, CDCl₃) δ 167.0, 149.8, 140.4, 134.8, 131.1, 126.7, 125.0, 124.9 (q, J = 280.0 Hz), 123.4, 117.7, 75.3, 70.1 (q, J = 30.8 Hz), 39.5, 37.6, 37.4, 33.8, 32.9, 31.2 (q, J = 27.5 Hz), 28.1, 24.9, 24.6, 22.9, 22.8, 21.1, 20.7, 19.9, 19.8, 13.0, 12.2, 12.0; ¹⁹F NMR (375 MHz, CDCl₃) δ −79.3 (bs, 3F). IR (ATR): 3265, 2930, 2866, 1730, 1636, 1461, 1342, 1275, 1167, 1133, 1051, 731 cm⁻¹. HRMS (ESI, m/z): calcd for C₃₅H₅₅F₃NaO₄⁺ (M+Na)⁺: 619.3945; Found: 619.3960.
(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[α]phenanthrene-3-yl 5,5,5-trifluoro-4-((dimethyl(phenyl)silyl)oxy)-2-methylenepentanoate (9a)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂·4H₂O (14.7 mg, 0.06 mmol, 20 mol%). 7a (286.8 mg, 0.6 mmol, 2.0 equiv.) was added DCM (3 mL, 0.1 M). 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 18 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with flash column chromatography on silica gel (200–300 mesh) and PE/EA (6/1, v/v) as eluent to afford 80.0 mg of the title compound as a white solid (46% yield).

Rt = 0.32 (PE/EA = 4/1, v/v); mp: 106–108 °C. NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, J = 6.4 Hz, 2H), 7.42–7.36 (m, 3H), 7.30 (d, J = 8.6 Hz, 1H), 6.79 (d, J = 8.6 Hz, 1H), 6.74 (s, 1H), 6.49 (s, 1H), 5.85 (s, 1H), 4.31–4.25 (m, 1H), 2.93–2.85 (m, 3H), 2.59–2.49 (m, 2H), 2.44–2.41 (m, 1H), 2.33–2.29 (m, 1H), 2.21–1.97 (m, 4H), 1.70–1.44 (m, 6H), 0.93 (s, 3H), 0.42–0.42 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 221.0, 165.2, 148.5, 138.3, 137.7, 136.2, 134.3, 133.8, 131.8, 130.2, 128.0, 126.6, 124.9 (q, J = 275.5 Hz), 121.6, 118.7, 70.0 (q, J = 30.8 Hz), 50.5, 48.1, 44.3, 38.1, 36.0, 34.7, 31.7, 29.5, 25.6, 25.9, 21.7, 14.0, –1.2, –1.4; ¹⁹F NMR (375 MHz, CDCl₃) δ –78.4 (m, 3F). IR (ATR): 3425, 2922, 2851, 1707, 1610, 1453, 1312, 1275, 1170, 1129, 1025, 731 cm⁻¹. HRMS (ESI, m/z): calcld for C₃₂H₃₇F₃NaO₃Si⁺ (M+Na)⁺: 593.2305; Found: 593.2305.

(8R,9S,13S,14S,17S)-3-(benzyloxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[α]phenanthrene-1-yl 5,5,5-trifluoro-4-hydroxy-2-methylenepentanoate (9ap)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂·4H₂O (14.7 mg, 0.06 mmol, 20 mol%). 7ap (342.0 mg, 0.6 mmol, 2.0 equiv.) was added DCM (3 mL, 0.1 M). 1a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 18 h. After which the mixture was cooled to 5 °C with ice bath, TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (15/1–8/1, v/v) as eluent to afford 112.0 mg of the title compound as a white solid (71% yield).

Rt = 0.20 (PE/EA = 8/1, v/v); mp: 106–108 °C. NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 7.46–7.37 (m, 4H), 7.35–7.31 (m, 1H), 7.21 (d, J = 8.6 Hz, 1H), 6.80 (dd, J = 8.6, 2.8 Hz, 1H), 6.74 (d, J = 2.8 Hz, 1H), 6.37 (s, 1H), 5.81 (s, 1H), 5.04 (s, 2H), 4.81–4.76 (m, 1H), 4.19–4.11 (m, 1H), 2.90–2.60 (m, 4H), 2.34–2.21 (m, 3H), 1.93–1.89 (m, 2H), 1.84–1.76 (m, 1H), 1.67–1.58 (m, 1H), 1.55–1.27 (m, 6H), 0.90 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.1, 168.0 (C'), 156.9, 138.0, 137.4, 135.4, 132.7, 129.7, 129.6 (C'), 128.67, 127.98, 127.57, 126.48, 124.9 (q, J = 280.8 Hz), 114.9, 112.4, 84.2, 84.2 (C'), 70.1 (q, J = 30.9 Hz, C), 70.1 (q, J = 30.9 Hz, C'), 70.1, 69.6, 49.8, 43.9, 43.4, 38.6, 37.1, 37.1 (C'), 33.5, 27.7, 27.3, 26.3, 23.4, 12.4 12.3 (C'); ¹⁹F NMR (375 MHz, CDCl₃) δ –79.4 (d, J = 6.0 Hz, 3F), –79.5 (d, J = 6.0 Hz, 3F). IR (ATR): 3422, 2922, 2851, 1707, 1610, 1453, 1312, 1275, 1170, 1129, 1025, 731 cm⁻¹. HRMS (ESI, m/z): calcld for C₃₀H₂₆F₃NaO₃ (M+Na)⁺: 551.2380; Found: 551.2389.
Synthesis of α-trifluoromethylated alkyl alcohols

3-Methyl-1-phenyl-3-(3,3,3-trifluoro-2-hydroxypropyl)indolin-2-one (11a)

![Chemical structure of 11a]

Under N₂ atmosphere, to a dried 25 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂·4H₂O (29.4 mg, 0.12 mmol, 20 mol%), 10a (170.7 mg, 0.72 mmol, 1.2 equiv.) was added DCM (6 mL, 0.1 M), 1a (140.4 mg, 0.6 mmol) and TBPB (291.5 mg, 1.5 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 14 h. Then, the reaction was moved to 5 °C, and TBAF (188.3 mg, 0.72 mmol, 1.2 equiv.) was added, and the resulting mixture was stirred for 30 min. Then, the reaction mixture was quenched with water (8 mL), extracted with DCM (3×20 mL) and organic phase was combined and washed with saturated sodium carbonate solution and brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) and PE/EA (10/1–5/1, v/v) as eluent to afford 183.0 mg of the title compound as a white solid (91% yield, the yield of two diastereomers).

More polar diastereomer: Rₐ = 0.32 (PE/EA = 5/1 v/v). mp: 116 °C–118 °C. NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 7.54–7.49 (m, 2H), 7.43–7.39 (m, 3H), 7.26–7.22 (m, 2H), 7.16–7.12 (m, 1H), 6.85–6.82 (m, 1H), 3.66–3.57 (m, 1H), 2.53–2.22 (m, 2H), 1.91 (s, 1H), 1.54 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 184.0, 143.8, 134.6, 131.6, 129.8, 128.6, 128.3, 126.8, 124.8 (q, J = 280.3 Hz), 123.4, 122.9, 110.0, 68.7 (q, J = 31.2 Hz), 46.1, 37.8, 25.8; ¹⁹F NMR NMR (375 MHz, CDCl₃) δ −80.0 (d, J = 7.2 Hz, 3F). IR (ATR): 3377, 3056, 2967, 2926, 2913, 1703, 1610, 1506, 1379, 1282, 1163, 1126, 1028, 854, 760 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₃H₁₆F₃NO₃Na⁺ (M+Na)⁺: 358.1025; Found: 358.1012.

1,3-Dimethyl-3-(3,3,3-trifluoro-2-hydroxypropyl)indolin-2-one (11b)

![Chemical structure of 11b]

Under N₂ atmosphere, to a dried 25 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂·4H₂O (29.4 mg, 0.12 mmol, 20 mol%), 10b (126.1 mg, 0.72 mmol, 1.2 equiv.) was added DCM (6 mL, 0.1 M), 1a (140.4 mg, 0.6 mmol) and TBPB (291.5 mg, 1.5 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 14 h. Then, the reaction was moved to 5 °C, and TBAF (188.3 mg, 0.72 mmol, 1.2 equiv.) was added, and the resulting mixture was stirred for 30 min. Then, the reaction mixture was quenched with water (8 mL), extracted with DCM (3×20 mL) and organic phase was combined and washed with saturated sodium carbonate solution and brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) and PE/EA (5/1–2/1, v/v) as eluent to afford 124.6 mg of the title compound as a light yellow solid (76% yield, the yield of two diastereomers).

More polar diastereomer: Rₐ = 0.34 (PE/EA = 2/1 v/v). mp: 99 °C–100 °C. NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 7.32 (td, J = 7.7, 1.4 Hz, 1H), 7.19-7.16 (m, 1H), 7.10 (td, J = 7.5, 1.0 Hz, 1H), 6.89 (d, J = 7.8 Hz, 1H), 3.58–3.49 (m, 1H), 3.21 (s, 3H), 2.43–2.13 (m, 3H), 1.42 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 180.9, 143.6, 132.1, 128.7, 124.8 (q, J = 280.2 Hz), 123.0, 122.6, 108.8, 68.4 (q, J = 31.3 Hz), 46.0, 37.4, 26.6, 25.4; ¹⁹F NMR (375 MHz, CDCl₃) δ −80.2 (d, J = 7.5 Hz, 3F). IR (ATR): 3377, 3056, 2967, 2930, 1696, 1614, 1495, 1379, 1353, 1308, 1279, 1167, 1122, 1028, 954, 757 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₃H₁₅F₃NO₃ (M+H)⁺: 274.1049; Found: 274.1041.
Under N$_2$ atmosphere, to a dried 25 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)$_2$·4H$_2$O (29.4 mg, 0.12 mmol, 20 mol%) was added DCM (6 mL, 0.1 M), 1a (140.4 mg, 0.6 mmol), 10c (180.7 mg, 0.72 mmol, 1.2 equiv.) and TBPB (291.5 mg, 1.5 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 14 h. Then, the reaction was moved to 5 °C, and TBAF (188.3 mg, 0.72 mmol, 1.2 equiv.) was added, and the resulting mixture was stirred for 30 min. Then, the reaction mixture was quenched with water (8 mL), extracted with DCM (3×20 mL) and organic phase was combined and washed with saturated sodium carbonate solution and brine, dried over Na$_2$SO$_4$ concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) and PE/EA (10/1~5/1, v/v) as eluent to afford 11c (350.1362; Found: 350.1357).

More polar diastereomer: R$_f$ = 0.36 (PE/EA = 5/1 v/v). mp: 110 °C–112 °C. NMR Spectroscopy: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34–7.30 (m, 4H), 7.23 (m, 2H), 7.00 (m, 2H), 6.92 (m, 1H), 4.91 (d, $J$ = 1.3 Hz, 2H), 3.66–3.56 (m, 1H), 2.50–2.18 (m, 3H), 1.47 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 180.9, 142.7, 135.9, 132.1, 128.9, 128.5, 127.8, 127.5, 124.8 (q, $J$ = 280.4 Hz), 123.0, 122.7, 109.8, 68.4 (q, $J$ = 31.0 Hz), 46.1, 44.1, 37.1, 26.0; $^{19}$F NMR (375 MHz, CDCl$_3$) δ −80.0 (d, $J$ = 7.4 Hz, 3F). IR (ATR): 3384, 3064, 2930, 1691, 1491, 1383, 1308, 1275, 1163, 1126, 1029, 999, 954, 790 cm$^{-1}$. HRMS (ESI, m/z): calcd for C$_{19}$H$_{10}$F$_3$NO$_2^+$ (M+H)$^+$: 350.1362; Found: 350.1357.

Under N$_2$ atmosphere, to a dried 25 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)$_2$·4H$_2$O (29.4 mg, 0.12 mmol, 20 mol%) was added DCM (6 mL, 0.1 M), 1a (140.4 mg, 0.6 mmol), 10d (138.9 mg, 0.72 mmol, 1.2 equiv.) and TBPB (291.5 mg, 1.5 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 14 h. Then, the reaction was moved to 5 °C, and TBAF (188.3 mg, 0.72 mmol, 1.2 equiv.) was added, and the resulting mixture was stirred for 30 min. Then, the reaction mixture was quenched with water (8 mL), extracted with DCM (3×20 mL) and organic phase was combined and washed with saturated sodium carbonate solution and brine, dried over Na$_2$SO$_4$ concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) and PE/EA (10/1~5/1, v/v) as eluent to afford 11d (350.1362; Found: 350.1357).
Under N₂ atmosphere, to a dried 25 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂·4H₂O (29.4 mg, 0.12 mmol, 20 mol%) was added DCM (6 mL, 0.1 M), 1a (140.4 mg, 0.6 mmol), 10e (138.9 mg, 0.72 mmol, 1.2 equiv.) and TBPB (291.5 mg, 1.5 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was stirred for 30 min. Then, the reaction mixture was quenched with water (8 mL), extracted with DCM (3×20 mL) and organic phase was combined and washed with saturated sodium carbonate solution and brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) and PE/EA (10/1–2/1, v/v) as eluent to afford 147.4 mg of the title compound as a light yellow solid (84% yield, the yield of two diastereomers).

More polar diastereomer: R₁ = 0.21 (PE/EA = 2/1 v/v). mp: 164 °C–166 °C. NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 7.05–7.00 (m, 1H), 6.94 (dd, J = 7.7, 2.6 Hz, 1H), 6.81 (dd, J = 8.5, 4.1 Hz, 1H), 3.65–3.50 (m, 1H), 3.20 (s, 3H), 2.47 (d, J = 8.4 Hz, 1H), 2.43–2.10 (m, 2H), 1.42 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 180.5, 159.6 (d, J = 240.2 Hz), 139.5 (d, J = 2.0 Hz), 133.8 (d, J = 7.7 Hz), 124.7 (q, J = 280.4 Hz), 114.9 (d, J = 23.3 Hz), 110.9 (d, J = 24.4 Hz), 109.3 (d, J = 8.0 Hz), 68.3 (q, J = 31.2 Hz), 46.5 (d, J = 1.8 Hz), 37.3, 26.7, 25.2; ¹⁹F NMR (375 MHz, CDCl₃) δ -80.1 (d, J = 8.2 Hz, 3F), -119.8–119.9 (m, 1F). IR (ATR): 3396, 2922, 2855, 1692, 1621, 1498, 1375, 1312, 1275, 1234, 1170, 1126, 1029, 898, 812, 701 cm⁻¹. HRMS (ESI, m/z): calced for C₁₃H₁₃F₄N₂O⁺ (M+Na)⁺: 314.0775; Found: 314.0765.

Under N₂ atmosphere, to a dried 25 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂·4H₂O (29.4 mg, 0.12 mmol, 20 mol%), 10f (216.7 mg, 0.72 mmol, 1.2 equiv.) was added DCM (6 mL, 0.1 M), 1a (140.4 mg, 0.6 mmol) and TBPB (291.5 mg, 1.5 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was stirred for 30 min. Then, the reaction mixture was quenched with water (8 mL), extracted with DCM (3×20 mL) and organic phase was combined and washed with saturated sodium carbonate solution and brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) and PE/EA (10/1–2/1, v/v) as eluent to afford 172.6 mg of the title compound as a white solid (72% yield, the yield of two diastereomers).

More polar diastereomer: R₁ = 0.26 (PE/EA = 2/1 v/v). mp: 176 °C–178 °C. NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 7.64 (dd, J = 8.1, 1.7 Hz, 1H), 7.46 (d, J = 1.7 Hz, 1H), 6.67 (d, J = 8.2 Hz, 1H), 3.65–3.54 (m, 1H), 3.18 (s, 3H), 2.42–2.10 (m, 3H), 1.41 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 180.1, 143.3, 137.6, 134.6, 131.5, 124.7 (q, J = 280.1 Hz), 110.8, 85.4, 68.3 (q, J = 31.2 Hz), 46.0, 37.1, 26.6, 25.3; ¹⁹F NMR (375 MHz, CDCl₃) δ -80.0 (d, J = 7.3 Hz, 3F). IR (ATR): 3332, 2967, 2926, 1700, 1603, 1491, 1454, 1416, 1349, 1275, 1174, 1126, 1021, 880, 809, 734 cm⁻¹. HRMS (ESI, m/z): calced for C₁₃H₁₃F₃NO₂⁺ (M+Na)⁺: 421.9835; Found: 421.9829.
**5-Methoxy-1,3-dimethyl-3-(3,3,3-trifluoro-2-hydroxypropyl)indolin-2-one (11g)**

![Chemical structure of 11g]

Under N$_2$ atmosphere, to a dried 25 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)$_2$·4H$_2$O (29.4 mg, 0.12 mmol, 20 mol%) was added DCM (6 mL, 0.1 M), 1a (140.4 mg, 0.6 mmol), 10g (147.7 mg, 0.72 mmol, 1.2 equiv.) and TBPB (291.5 mg, 1.5 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 14 h. Then, the reaction was moved to 5 °C, and TBAF (188.3 mg, 0.72 mmol, 1.2 equiv.) was added, and the resulting mixture was stirred for 30 min. Then, the reaction mixture was quenched with water (8 mL), extracted with DCM (3×20 mL) and organic phase was combined and washed with saturated sodium carbonate solution and brine, dried over Na$_2$SO$_4$, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) and PE/EA (10/1~2/1, v/v) as eluent to afford 129.4 mg of the title compound as a white solid (71% yield, the yield of two diastereomers).

More polar diastereomer: $R_t = 0.17$ (PE/EA = 2/1 v/v), mp: 145 °C–147 °C. NMR Spectroscopy: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.84–6.82 (m, 1H), 6.80–6.78 (m, 2H), 3.81 (s, 3H), 3.62–3.53 (m, 1H), 3.19 (s, 3H), 2.57 (d, $J = 8.4$ Hz, 1H), 2.41–2.10 (m, 2H), 1.41 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 180.6, 156.4, 137.0, 133.6, 124.8 (q, $J = 280.3$ Hz), 112.4, 110.4, 109.1, 68.4 (q, $J = 31.2$ Hz), 56.0, 46.5, 37.4, 26.7, 25.4; $^{19}$F NMR (375 MHz, CDCl$_3$) $\delta$ -80.1 (d, $J = 6.4$ Hz, 3F).

IR (ATR): 3377, 2930, 2874, 1692, 1435, 1372, 1282, 1167, 1126, 1040, 805, 698 cm$^{-1}$. HRMS (ESI, m/z): calcd for C$_{13}$H$_{17}$F$_3$NO$_3$ (M+H)$^+$: 304.1155; Found: 304.1143.

**1-Methyl-1-(3,3,3-trifluoro-2-hydroxypropyl)-5,6-dihydro-1H-pyrrolo[3,2,1-ij]quinolin-2(4H)-one (11h)**

![Chemical structure of 11h]

Under N$_2$ atmosphere, to a dried 25 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)$_2$·4H$_2$O (29.4 mg, 0.12 mmol, 20 mol%), 10h (144.8 mg, 0.72 mmol, 1.2 equiv.) was added DCM (6 mL, 0.1 M), 1a (140.4 mg, 0.6 mmol) and TBPB (291.5 mg, 1.5 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 14 h. Then, the reaction was moved to 5 °C, and TBAF (188.3 mg, 0.72 mmol, 1.2 equiv.) was added, and the resulting mixture was stirred for 30 min. Then, the reaction mixture was quenched with water (8 mL), extracted with DCM (3×20 mL) and organic phase was combined and washed with saturated sodium carbonate solution and brine, dried over Na$_2$SO$_4$, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) and PE/EA (10/1~1.5/1, v/v) as eluent to afford 138.1 mg of the title compound as a light yellow solid (77% yield, the yield of two diastereomers).

More polar diastereomer: $R_t = 0.48$ (PE/EA = 1.5/1 v/v), mp: 69 °C–72 °C. NMR Spectroscopy: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.07–6.96 (m, 3H), 3.76–3.64 (m, 2H), 3.61–3.53 (m, 1H), 2.81–2.78 (m, 2H), 2.41–2.12 (m, 2H), 2.05–1.98 (m, 2H), 1.42 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 179.8, 139.3, 130.6, 127.4, 124.9 (q, $J = 280.3$ Hz), 122.4, 120.9, 120.4, 68.4 (q, $J = 31.0$ Hz), 47.4, 39.1, 37.3, 25.1, 24.7, 21.2; $^{19}$F NMR (375 MHz, CDCl$_3$) $\delta$ -80.1 (d, $J = 6.2$ Hz, 3F).

IR (ATR): 3377, 2963, 2930, 2874, 1692, 1638, 1484, 1394, 1361, 1279, 1163, 1126, 958, 783, 697 cm$^{-1}$. HRMS (ESI, m/z): calcd for C$_{13}$H$_{17}$F$_3$NO$_3$ (M+H)$^+$: 300.1206; Found: 300.1201.
Methyl 1,3-dimethyl-2-oxo-3-(3,3-trifluoro-2-hydroxypropyl)indoline-5-carboxylate (11i)

Under N₂ atmosphere, to a dried 25 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₃•4H₂O (29.4 mg, 0.12 mmol, 20 mol%), 10i (167.8 mg, 0.72 mmol, 1.2 equiv.) was added DCM (6 mL, 0.1 M), 1a (140.4 mg, 0.6 mmol) and TBPB (291.5 mg, 1.5 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 14 h. Then, the reaction was moved to 5 °C, and TBAF (188.3 mg, 0.72 mmol, 1.2 equiv.) was added, and the resulting mixture was stirred for 30 min. Then, the reaction mixture was quenched with water (8 mL), extracted with DCM (3×20 mL) and organic phase was combined and washed with saturated sodium carbonate solution and brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300 400 mesh) and PE/EA (10/1~1.5/1, v/v) as eluent to afford 63.8 mg of the title compound as a light yellow solid (63% yield, the yield of two diastereomers).

More polar diastereomer: R₁ = 0.39 (PE/EA = 1.5/1, v/v). mp: 118 °C–120 °C. NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 8.05 (dd, J = 8.2, 1.7 Hz, 1H), 7.85 (dd, J = 1.7, 0.5 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 3.91 (s, 3H), 3.59–3.49 (m, 1H), 3.23 (s, 3H), 2.67 (d, J = 8.3 Hz, 1H), 2.45–2.16 (m, 2H), 1.43 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 181.2, 166.9, 147.8, 132.1, 131.4, 124.8, 124.7 (q, J = 280.4 Hz), 124.0, 108.2, 68.3 (q, J = 31.2 Hz), 52.3, 45.8, 37.2, 26.8, 25.1; ¹⁹F NMR (375 MHz, CDCl₃) δ −79.9 (d, J = 7.5 Hz, 3F). IR (ATR): 3422, 2956, 1707, 1618, 1498, 1457, 1375, 1286, 1256, 1167, 1126, 1025, 917, 835, 775, 738 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₆H₁₇F₂NO₄⁺ (M+H)⁺: 332.1104; Found: 332.1099.

Synthesis of α-trifluoromethylated allylic alcohols

(E)-1,1,1-trifluoro-4-(2-fluorophenyl)but-3-en-2-ol (13a)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₃•2H₂O (21.4 mg, 0.08 mmol, 20 mol%) and 12a (132.8 mg, 0.8 mmol, 2.0 equiv.) was added hexane (1 mL, 0.4 M), TBPB (194.3 mg, 1.0 mmol, 2.5 equiv.) and 1a (93.6 mg, 0.4 mmol) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 14 h. The mixture was then cooled to −10 °C with low temperature bath, TBAF (1.0 M in THF, 0.48 mL, 0.48 mmol, 1.2 equiv.) was added and the resulting mixture was stirred at −10 °C for 1.0 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) and PE/EA (20/1~10/1, v/v) as eluent to afford 63.8 mg of the title compound as a colorless oil (73% yield).

R₁ = 0.56 (PE/EA = 4/1, v/v). NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 7.47 (t, J = 7.2 Hz, 1H), 7.31–7.26 (m, 1H), 7.15–7.00 (m, 3n), 6.31 (dd, J = 16.2, 6.4 Hz, 1H), 4.69–4.63 (m, 1H), 2.44 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 160.7 (d, J = 250.5 Hz), 130.3 (d, J = 8.7 Hz), 129.0 (d, J = 2.9 Hz), 128.1 (d, J = 2.9 Hz), 124.4 (q, J = 273.4 Hz), 124.4 (d, J = 3.9 Hz), 123.4, 123.4 (d, J = 6.7 Hz), 116.1 (d, J = 22.2 Hz), 71.9 (q, J = 32.1 Hz); ¹⁹F NMR (375 MHz, CDCl₃) δ −78.9 (d, J = 6.0 Hz, 3F), −117.0–117.0 (m, 1F). IR (ATR): 3396, 2922, 1659, 1491, 1457, 1267, 1174, 1125, 969, 883, 753 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₀H₁₄F₂O⁻ (M–H)⁻: 219.0439; Found: 219.0441.
(E)-1,1,1-Trifluoro-4-(3-fluorophenyl)but-3-en-2-ol (13b)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₃·2H₂O (21.4 mg, 0.08 mmol, 20 mol%) and 12b (132.8 mg, 0.8 mmol, 2.0 equiv.) was added hexane (1 mL, 0.4 M), TBPB (194.3 mg, 1.0 mmol, 2.5 equiv.) and 1a (93.6 mg, 0.4 mmol) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 14 h. The mixture was then cooled to −10 °C with low temperature bath, TBAF (1.0 M in THF, 0.48 mL, 0.48 mmol, 1.2 equiv.) was added and the resulting mixture was stirred at −10 °C for 1.0 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) and PE/EA (20/1~10/1, v/v) as eluent to afford 56.3 mg of the title compound as a colorless oil (60% yield).

R₁ = 0.64 (PE/EA = 4/1, v/v). NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 7.33–7.28 (m, 1H), 7.18 (d, J = 7.6 Hz, 1H), 7.11 (d, J = 9.8 Hz, 1H), 6.99 (t, J = 8.3 Hz, 1H), 6.83 (d, J = 15.9 Hz, 1H), 6.20 (dd, J = 15.9, 6.1 Hz, 1H), 4.66–4.63 (m, 1H), 2.39 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 163.20 (d, J = 246.3 Hz), 137.8 (d, J = 8.0 Hz), 135.1 (d, J = 2.6 Hz), 130.4 (d, J = 8.5 Hz), 123.0 (d, J = 2.8 Hz), 124.3 (q, J = 280.4 Hz), 122.2, 115.7 (d, J = 21.5 Hz), 113.5 (d, J = 21.9 Hz), 71.5 (q, J = 32.5 Hz); ¹⁹F NMR (375 MHz, CDCl₃) δ −79.0 (d, J = 6.0 Hz, 3F), −112.9−−113.0 (m, 1F). IR (ATR): 3418, 2904, 1588, 1491, 1267, 1178, 1129, 969, 783 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₀H₇F₄O⁻ (M−H)⁻: 219.0439; Found: 219.0441.

(E)-1,1,1-Trifluoro-4-(4-fluorophenyl)but-3-en-2-ol (13c)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₃·2H₂O (21.4 mg, 0.08 mmol, 20 mol%) and 12c (132.8 mg, 0.8 mmol, 2.0 equiv.) was added hexane (1 mL, 0.4 M), TBPB (194.3 mg, 1.0 mmol, 2.5 equiv.) and 1a (93.6 mg, 0.4 mmol) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 14 h. The mixture was then cooled to −10 °C with low temperature bath, TBAF (1.0 M in THF, 0.48 mL, 0.48 mmol, 1.2 equiv.) was added and the resulting mixture was stirred at −10 °C for 1.0 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) and PE/EA (20/1~10/1, v/v) as eluent to afford 56.3 mg of the title compound as a colorless oil (64% yield).

R₁ = 0.56 (PE/EA = 4/1, v/v). NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 7.38 (dd, J = 7.6, 5.8 Hz, 2H), 7.04 (t, J = 8.7 Hz, 2H), 6.81 (d, J = 15.9 Hz, 1H), 6.12 (dd, J = 15.9, 6.6 Hz, 1H), 4.66–4.59 (m, 1H), 2.78 (bs, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 163.1 (d, J = 248.5 Hz), 135.2, 131.7, 128.7 (d, J = 8.7 Hz), 124.4 (d, J = 280.8 Hz), 120.5, 115.9 (d, J = 21.2 Hz), 71.7 (q, J = 32.4 Hz); ¹⁹F NMR (375 MHz, CDCl₃) δ −78.9 (d, J = 6.0 Hz, 3F), −112.5−−112.5 (m, 1F). IR (ATR): 3377, 2049, 2919, 1662, 1603, 1510, 1264, 1174, 1126, 969, 839, 693 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₀H₇F₄O⁻ (M−H)⁻: 219.0439; Found: 219.0441.
(E)-1,1,1-Trifluoro-4-(2,6-difluorophenyl)but-3-en-2-ol (13d)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₃·2H₂O (21.4 mg, 0.08 mmol, 20 mol%) and 12d (147.2 mg, 0.8 mmol, 2.0 equiv.) was added hexane (1 mL, 0.4 M), TBPB (194.3 mg, 1.0 mmol, 2.5 equiv.) and 1a (93.6 mg, 0.4 mmol) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 14 h. The mixture was then cooled to −10 °C with low temperature bath, TBAF (1.0 M in THF, 0.48 mL, 0.48 mmol, 1.2 equiv.) was added and the resulting mixture was stirred at −10 °C for 1.0 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1–10/1, v/v) as eluent to afford 69.3 mg of the title compound as a colorless oil (67% yield).

Rₜ = 0.38 (PE/EA = 4/1, v/v), NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 7.26–7.18 (m, 1H), 6.95–6.88 (m, 3H), 6.56 (dd, J = 16.2, 6.1 Hz, 1H), 4.66 (d, J = 5.8 Hz, 1H), 2.58 (d, J = 5.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 161.2 (dd, J = 252.9, 7.2 Hz), 129.6 (t, J = 11.1 Hz), 127.5 (t, J = 7.2 Hz), 124.3 (d, J = 280.8 Hz), 122.6, 113.0 (t, J = 14.9 Hz), 111.8 (dd, J = 19.7, 6.3 Hz), 72.15 (q, J = 32.4 Hz); ¹⁹F NMR (375 MHz, CDCl₃) δ −78.9 (d, J = 6.0 Hz, 3F), −112.6 (t, J = 7.5 Hz, 2F). IR (ATR): 3358, 2915, 1659, 1614, 1502, 1431, 1274, 1267, 1112, 995, 876, 782 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₀H₁₃F₆O⁺ (M+H)⁺: 239.0490; Found: 239.0481.

(E)-1,1,1-Trifluoro-4-(2,4-difluorophenyl)but-3-en-2-ol (13e)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₃·2H₂O (21.4 mg, 0.08 mmol, 20 mol%) and 12e (147.2 mg, 0.8 mmol, 2.0 equiv.) was added DCM (1 mL, 0.4 M), TBPB (194.3 mg, 1.0 mmol, 2.5 equiv.) and 1a (93.6 mg, 0.4 mmol) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 14 h. The mixture was then cooled to −10 °C with low temperature bath, TBAF (1.0 M in THF, 0.48 mL, 0.48 mmol, 1.2 equiv.) was added and the resulting mixture was stirred at −10 °C for 1.0 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1–10/1, v/v) as eluent to afford 60.1 mg of the title compound as a white solid (63% yield).

Rₜ = 0.68 (PE/EA = 4/1, v/v), mp: 47 °C–49 °C NMR Spectroscopy: ¹H NMR (600 MHz, CDCl₃) δ 7.45 (td, J = 8.6, 6.3 Hz, 2H), 6.95 (d, J = 16.2 Hz, 1H), 6.91–6.85 (m, 2H), 6.85–6.79 (m, 2H), 6.24 (dd, J = 16.1, 6.3 Hz, 2H), 4.68–4.62 (m, 2H), 2.44 (d, J = 5.3 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 163.1 (dd, J = 249.6, 12.0 Hz), 160.8 (dd, J = 251.8, 11.7 Hz), 129.0 (dd, J = 9.6, 5.0 Hz), 128.1–128.1 (m), 124.3 (q, J = 282.1 Hz), 123.0–122.9 (m), 119.8 (dd, J = 12.1, 4.1 Hz), 111.9 (dd, J = 21.3, 3.7 Hz), 104.5 (t, J = 25.4 Hz), 71.8 (q, J = 32.0 Hz); ¹⁹F NMR (375 MHz, CDCl₃) δ −79.0 (d, J = 6.0 Hz, 3F), −108.9−108.8 (m, 1F), −112.7−112.6 (m, 1F). IR (ATR): 3358, 2915, 1659, 1614, 1502, 1431, 1274, 1174, 1126, 969, 854, 731 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₀H₉F₄O⁺ (M+H)⁺: 237.0344; Found: 237.0346.
(E)-1,1,1-trifluoro-4-(3,5-difluorophenyl)but-3-en-2-ol (13f)

Under N_{2} atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc){sub 3}•2H_{2}O (21.4 mg, 0.08 mmol, 20 mol%) and 12f (147.2 mg, 0.8 mmol, 2.0 equiv.) was added DCM (1 mL, 0.4 M), TBPB (194.3 mg, 1.0 mmol, 2.5 equiv.) and 1a (93.6 mg, 0.4 mmol) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 14 h. The mixture was then cooled to −10 °C with low temperature bath, TBAF (1.0 M in THF, 0.48 mL, 0.48 mmol, 1.2 equiv.) was added and the resulting mixture was stirred at −10 °C for 1.0 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na_{2}SO_{4}, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1–10/1, v/v) as eluent to afford 71.5 mg of the title compound as a colorless oil (75% yield).

R_{f} = 0.25 (PE/EA = 10/1, v/v). NMR Spectroscopy: \(^{1}H\) NMR (600 MHz, CDCl_{3}) \(\delta\) 6.94–6.92 (m, 2H), 6.80 (d, \(J = 16.0\) Hz, 1H), 6.75 (tt, \(J = 8.8, 2.3\) Hz, 1H), 6.22 (dd, \(J = 15.9, 5.9\) Hz, 1H), 4.72–4.61 (m, 1H), 2.55 (s, 1H); \(^{13}C\) NMR (150 MHz, CDCl_{3}) \(\delta\) 163.4 (dd, \(J = 248.5, 13.0\) Hz), 138.8 (t, \(J = 9.5\) Hz), 134.0 (t, \(J = 2.8\) Hz), 124.2 (q, \(J = 32.4\) Hz), 123.5, 109.8 (dd, \(J = 20.4, 5.2\) Hz), 104.1 (t, \(J = 25.5\) Hz), 71.2 (q, \(J = 32.4\) Hz); \(^{19}F\) NMR (375 MHz, CDCl_{3}) \(\delta\) −78.9 (d, \(J = 6.0\) Hz, 3F), −109.6 (t, \(J = 8.9\) Hz, 1F). IR (ATR): 3384, 3094, 2904, 1621, 1595, 1439, 1267, 1118, 969, 854, 667 cm\(^{-1}\). HRMS (ESI, m/z): calcd for C_{10}H_{6}F_{10}O− (M−H)\(^{−}\): 237.0344; Found: 237.0335.

(E)-1,1,1-trifluoro-4-(4-chlorophenyl)but-3-en-2-ol (13g)

Under N_{2} atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc){sub 3}•2H_{2}O (21.4 mg, 0.08 mmol, 20 mol%) and 12g (145.6 mg, 0.8 mmol, 2.0 equiv.) was added hexane (1 mL, 0.4 M), TBPB (194.3 mg, 1.0 mmol, 2.5 equiv.) and 1a (93.6 mg, 0.4 mmol) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 14 h. The mixture was then cooled to −10 °C with low temperature bath, TBAF (1.0 M in THF, 0.48 mL, 0.48 mmol, 1.2 equiv.) was added and the resulting mixture was stirred at −10 °C for 1.0 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na_{2}SO_{4}, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1–10/1, v/v) as eluent to afford 63.2 mg of the title compound as a white solid (67% yield).

R_{f} = 0.22 (PE/EA = 10/1, v/v). mp: 41 °C–42 °C. NMR Spectroscopy: \(^{1}H\) NMR (400 MHz, CDCl_{3}) \(\delta\) 7.36–7.31 (m, 4H), 6.82 (d, \(J = 15.9\) Hz, 1H), 6.18 (dd, \(J = 15.9, 6.1\) Hz, 1H), 4.65–4.63 (m, 1H), 2.44 (d, \(J = 4.0\) Hz, 1H); \(^{13}C\) NMR (100 MHz, CDCl_{3}) \(\delta\) 135.1, 134.7, 134.0, 129.1, 128.3, 124.3 (q, \(J = 279.4\) Hz), 121.4, 71.6 (q, \(J = 32.1\) Hz); \(^{19}F\) NMR (375 MHz, CDCl_{3}) \(\delta\) −79.0 (d, \(J = 6.0\) Hz, 3F). IR (ATR): 3399, 2911, 1491, 1267, 1129, 1092, 969, 831 cm\(^{-1}\). HRMS (ESI, m/z): calcd for C_{10}H_{6}F_{10}O− (M−H)\(^{−}\): 235.0143; Found: 237.0146.

(E)-1,1,1-trifluoro-4-(4-bromophenyl)but-3-en-2-ol (13h)

Under N_{2} atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc){sub 3}•2H_{2}O

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(21.4 mg, 0.08 mmol, 20 mol%) and 5e (181.6 mg, 0.8 mmol, 2.0 equiv.) was added hexane (1 mL, 0.4 M), TBPB (194.3 mg, 1.0 mmol, 2.5 equiv.) and 3a (93.6 mg, 0.4 mmol) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 14 h. The mixture was then cooled to −10 °C with low temperature bath, TBAF (1.0 M in THF, 0.48 mL, 0.48 mmol, 1.2 equiv.) was added and the resulting mixture was stirred at −10 °C for 1.0 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na2SO4, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1~10/1, v/v) as eluent to afford 68.6 mg of the title compound as a white solid (61% yield).

Rf = 0.23 (PE/EA = 10/1, v/v), mp: 55 °C–57 °C. NMR Spectroscopy: 1H NMR (400 MHz, CDCl3) δ 7.48 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 6.81 (d, J = 16.2 Hz, 1H), 6.19 (dd, J = 16.0, 6.3 Hz, 1H), 4.63 (bs, 1H), 2.46 (s, 1H); 13C NMR (100 MHz, CDCl3) δ 135.1, 134.5, 132.1, 128.5, 124.3 (q, J = 280.8 Hz), 122.8, 121.6, 71.6 (q, J = 32.4 Hz); 19F NMR (375 MHz, CDCl3) δ −78.9 (d, J = 6.0 Hz, 3F). IR (ATR): 3340, 2926, 1655, 1487, 1267, 1178, 1126, 1033, 969, 835, 693 cm−1. HRMS (ESI, m/z): calcd for C10H7BrF2O (M–H)+: 278.9638; Found: 278.9640.

(E)-1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-en-2-ol (13i)

Under N2 atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)2•2H2O (21.4 mg, 0.08 mmol, 20 mol%) and 12i (142.4 mg, 0.8 mmol, 2.0 equiv.) was added hexane (1 mL, 0.4 M), TBPB (194.3 mg, 1.0 mmol, 2.5 equiv.) and 1a (93.6 mg, 0.4 mmol) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 14 h. The mixture was then cooled to −10 °C with low temperature bath, TBAF (1.0 M in THF, 0.48 mL, 0.48 mmol, 1.2 equiv.) was added and the resulting mixture was stirred at −10 °C for 1.0 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na2SO4, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1~10/1, v/v) as eluent to afford 50.1 mg of the title compound as a white solid (54% yield).

Rf = 0.38 (PE/EA = 4/1, v/v), mp: 47 °C–49 °C. NMR Spectroscopy: 1H NMR (400 MHz, CDCl3) δ 7.36 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.79 (d, J = 15.9 Hz, 1H), 6.06 (dd, J = 15.9, 6.7 Hz, 1H), 4.63–4.57 (m, 1H), 3.82 (s, 3H), 2.42 (s, 1H); 13C NMR (100 MHz, CDCl3) δ 160.2, 136.1, 128.4, 128.3, 124.5 (q, J = 280.8 Hz), 118.5, 114.3, 72.0 (q, J = 32.4 Hz, 03), 55.5; 19F NMR (375 MHz, CDCl3) δ −79.0 (d, J = 6.0 Hz, 3F). IR (ATR): 3407, 3008, 2960, 2840, 1606, 1513, 1252, 1170, 1126, 1033, 969, 835, 693 cm−1. HRMS (ESI, m/z): calcd for C11H12F2O2+ (M+H)+: 233.0784; Found: 233.0783.

(E)-1,1,1-trifluoro-4-(4-benzyloxyphenyl)but-3-en-2-ol (13j)

Under N2 atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)2•2H2O (21.4 mg, 0.08 mmol, 20 mol%) and 12j (203.2 mg, 0.8 mmol, 2.0 equiv.) was added hexane (1 mL, 0.4 M), TBPB (194.3 mg, 1.0 mmol, 2.5 equiv.) and 1a (93.6 mg, 0.4 mmol) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 14 h. The mixture was then cooled to −10 °C with low temperature bath, TBAF (1.0 M in THF, 0.48 mL, 0.48 mmol, 1.2 equiv.) was added and the resulting mixture was stirred at −10 °C for 1.0 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was
combined and washed with brine, dried over Na$_2$SO$_4$, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1–10/1, v/v) as eluent to afford 62.9 mg of the title compound as a colorless oil (72% yield).

$R_t = 0.40$ (PE/EA = 4/1, v/v), mp: 89°C–91°C. NMR Spectroscopy: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45–7.34 (m, 7H), 6.96 (d, $J = 8.6$ Hz, 2H), 6.79 (d, $J = 15.9$ Hz, 1H), 6.07 (dd, $J = 16.0$, 6.9 Hz, 1H), 5.09 (s, 2H), 4.64–4.56 (m, 1H), 2.33 (d, $J = 5.5$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.4, 136.8, 136.1, 128.8, 128.5, 128.4, 128.2, 127.6, 124.5 (d, $J = 279.9$ Hz), 118.6, 115.2, 71.9 (q, $J = 32.1$ Hz), 70.2; $^{19}$F NMR (375 MHz, CDCl$_3$) $\delta$ –79.0 (d, $J = 6.0$ Hz, 3F). IR (ATR): 3373, 3037, 2922, 2855, 1610, 1513, 1454, 1264, 1170, 1125, 1036, 977, 738, 697 cm$^{-1}$. HRMS (ESI, m/z): calcd for C$_{11}$H$_{16}$F$_3$O$_2$ $^+$(M+H)$^+$: 309.1097; Found: 309.1089.

(E)-1,1,1-trifluoro-4-((3-trifluoromethyl)phenyl)but-3-en-2-ol (13k)

Under N$_2$ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)$_3$·2H$_2$O (21.4 mg, 0.08 mmol, 20 mol%) and 12k (172.8 mg, 0.8 mmol, 2.0 equiv.) was added hexane (1 mL, 0.4 M), TBPB (194.3 mg, 1.0 mmol, 2.5 equiv.) and 1a (93.6 mg, 0.4 mmol) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70°C in heating block for 14 h. The reaction mixture was then cooled to –10°C with low temperature bath, TBAF (1.0 M in THF, 0.48 mL, 0.48 mmol, 1.2 equiv.) was added and the resulting mixture was stirred at –10°C for 1.0 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na$_2$SO$_4$, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1–10/1, v/v) as eluent to afford 70.6 mg of the title compound as a colorless oil (65% yield).

$R_t = 0.46$ (PE/EA = 4/1, v/v). NMR Spectroscopy: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.66–7.46 (m, 4H), 6.92 (d, $J = 16.2$ Hz, 1H), 6.28 (dd, $J = 16.0$, 6.0 Hz, 1H), 4.68 (d, $J = 5.8$ Hz, 1H), 2.48 (d, $J = 4.9$ Hz, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 136.3, 134.7, 131.4 (q, $J = 32.1$ Hz), 130.1, 129.4, 125.4 (q, $J = 3.7$ Hz), 124.3 (q, $J = 280.4$ Hz), 124.1 (q, $J = 270.8$ Hz), 123.7 (q, $J = 3.8$ Hz), 122.7, 71.4 (q, $J = 32.1$ Hz); $^{19}$F NMR (375 MHz, CDCl$_3$) $\delta$ –62.8 (s, 3F), –78.9 (d, $J = 6.0$ Hz, 3F). IR (ATR): 3370, 3053, 2922, 1331, 1267, 1167, 1122, 1074, 794, 693 cm$^{-1}$. HRMS (ESI, m/z): calcd for C$_{11}$H$_{16}$F$_3$O$^-$ (M–H)$^-$: 269.0407; Found: 269.0409.

(E)-1,1,1-trifluoro-4-((4-trifluoromethyl)phenyl)but-3-en-2-ol (13l)

Under N$_2$ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)$_3$·2H$_2$O (21.4 mg, 0.08 mmol, 20 mol%) and 12l (172.8 mg, 0.8 mmol, 2.0 equiv.) was added hexane (1 mL, 0.4 M), TBPB (194.3 mg, 1.0 mmol, 2.5 equiv.) and 1a (93.6 mg, 0.4 mmol) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70°C in heating block for 14 h. The mixture was then cooled to –10°C with low temperature bath, TBAF (1.0 M in THF, 0.48 mL, 0.48 mmol, 1.2 equiv.) was added and the resulting mixture was stirred at –10°C for 1.0 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na$_2$SO$_4$, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1–10/1, v/v) as eluent to afford 77.8 mg of the title compound as a colorless oil (72% yield).

$R_t = 0.43$ (PE/EA = 4/1, v/v). NMR Spectroscopy: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60 (d, $J = 7.9$ Hz, 2H), 7.51 (d, $J =$
7.6 Hz, 2H), 6.91 (d, J = 15.9 Hz, 1H), 6.30 (dd, J = 15.9, 5.8 Hz, 1H), 4.70–4.67 (m, 1H), 2.66 (bs, 1H); 13C NMR (100 MHz, CDCl3) δ 139.0, 134.7, 130.6 (q, J = 32.4 Hz), 127.2, 125.9 (q, J = 3.9 Hz), 124.3 (q, J = 280.5 Hz), 124.2 (q, J = 270.7 Hz), 123.4, 71.4 (q, J = 32.4 Hz); 19F NMR (375 MHz, CDCl3) δ −62.6 (s, 3F), −78.9 (d, J = 6.0 Hz, 3F). IR (ATR): 3377, 2922, 1618, 1416, 1323, 1167, 1122, 969, 835, 697 cm⁻¹. HRMS (ESI, m/z): calcd for C11H8F2O− (M−H): 269.047; Found: 269.0407.

Synthesis of α-difluoromethylated alcohols

5,5-Difluoro-1-phenyl-4-hydroxy-2-methylenepentan-1-one (14a)

\[ \begin{align*}
\text{2a} & \quad + \quad \text{7b} & \quad \text{Mn(OAc)₂} \cdot 2\text{H₂O} \quad (20 \text{ mol\%}) \\
\text{DCM} \quad (0.1 \text{ M}) \quad 70 ^\circ \text{C}, \text{N₂, 14 h;} & \quad \text{then TBAF (1.2 equiv.),} \quad 5 ^\circ \text{C, 0.5 h}
\end{align*} \]

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂·2H₂O (16.1 mg, 0.06 mmol, 20 mol%) and 7b (257.4 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 2a (64.8 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1 v/v) as eluent to afford 54.3 mg of the title compound as a colorless oil (80% yield).

R₁ = 0.25 (PE/EA = 10/1, v/v). NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, J = 7.3 Hz, 2H), 7.58 (t, J = 7.3 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 6.11 (s, 1H), 5.86–5.58 (m, 2H), 3.98–3.91 (m, 1H), 3.83 (s, 1H), 2.84–2.63 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 199.5, 143.1, 137.0, 133.0, 130.9, 128.5, 116.1 (t, J = 24.2 Hz), 70.9 (t, J = 24.1 Hz), 33.7; ¹⁹F NMR (375 MHz, CDCl₃) δ −128.5–−131.2 (m, 2F). IR (ATR): 3452, 3064, 2941, 2292, 2251, 1655, 1446, 1409, 1375, 1330, 1219, 1174, 1140, 1059, 947, 757 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₂H₁₀F₂O⁺ (M+H)⁺: 227.0878; Found: 227.0871.

5,5-Difluoro-1-(4-fluorophenyl)-4-hydroxy-2-methylenepentan-1-one (14b)

\[ \begin{align*}
\text{2a} & \quad + \quad \text{7d} & \quad \text{Mn(OAc)₂} \cdot 2\text{H₂O} \quad (20 \text{ mol\%}) \\
\text{DCM} \quad (0.1 \text{ M}) \quad 70 ^\circ \text{C}, \text{N₂, 14 h;} & \quad \text{then TBAF (1.2 equiv.),} \quad 5 ^\circ \text{C, 0.5 h}
\end{align*} \]

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂·2H₂O (16.1 mg, 0.06 mmol, 20 mol%) and 7d (273.6 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 2a (64.8 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1 v/v) as eluent to afford 48.3 mg of the title compound as a colorless oil (66% yield).

R₁ = 0.32 (PE/EA = 5/1, v/v). NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 7.86–7.79 (m, 2H), 7.18–7.09 (m, 2H), 6.09 (s, 1H), 5.87–5.56 (m, 2H), 4.02–3.85 (m, 1H), 3.65 (m, 1H), 2.86–2.59 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 197.8, 165.8 (d, J = 252.3 Hz), 143.1, 133.2 (d, J = 3.2 Hz), 132.7 (d, J = 9.1 Hz), 130.2, 116.1 (t, J = 242.0 Hz), 115.7 (d, J = 21.9 Hz), 70.9 (t, J = 23.7 Hz), 33.7 (t, J = 4.1 Hz); ¹⁹F NMR (375 MHz, CDCl₃) δ −104.9 (m, 1F), −126.2–−132.7 (m, 2F). IR (ATR): 3422, 2926, 1648, 1595, 1506, 1413, 1156, 1059, 939, 794 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₂H₁₂F₂O⁺ (M+H)⁺: 267.0603; Found: 267.0604.
5,5-Difluoro-4-hydroxy-2-methylene-N,N-diphenylpentanamide (14c)

\[
\text{OH} \quad \overset{\text{HF}_2\text{C} \quad \text{SiPhMe}_2}{\longrightarrow} \quad \text{Ph} \quad \overset{\text{N}}{\longrightarrow} \quad \text{O} \quad \overset{\text{SO}_2\text{Ph}}{\longrightarrow}
\]

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂•4H₂O (14.7 mg, 0.06 mmol, 20 mol%), 7z (393.9 mg, 0.9 mmol, 3.0 equiv.) was added DCM (3 mL, 0.1 M), 2a (64.8 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 18 h. After which the mixture was cooled to 5 °C with ice bath, TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (3/1, v/v) as eluent to afford 63.3 mg of the title compound as a white solid (83% yield).

Rₜ = 0.55 (PE/EA = 3/1, v/v). NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 7.40–7.33 (m, 4H), 7.29–7.23 (m, 2H), 7.21–7.16 (m, 4H), 5.71 (td, J = 56.0, 4.0 Hz, 1H), 5.40 (s, 1H), 5.29 (s, 1H), 4.01–3.85 (m, 1H), 2.60–2.42 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 172.6, 143.3, 129.5, 127.3, 125.0, 116.1 (t, J = 241.8 Hz), 71.5 (t, J = 24.1 Hz), 34.7 (t, J = 4.3 Hz); ¹⁹F NMR (375 MHz, CDCl₃) δ −127.5–−132.3 (m, 2F). IR (ATR): 3366, 2970, 1648, 1588, 1491, 1361, 1252, 1137, 760, 697 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₅H₁₉F₂NO₄⁺ (M+H)⁺: 318.1300; Found: 318.1298.

(8R,9S,10R,13S,14S,17S)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 5,5-difluoro-4-hydroxy-2-methylenepentanoate (14d)

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂•4H₂O (14.7 mg, 0.06 mmol, 20 mol%), 7al (297.6 mg, 0.6 mmol, 2.0 equiv.) was added DCM (3 mL, 0.1 M), 2a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 18 h. After which the mixture was cooled to 5 °C with ice bath, TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (8/1, v/v) as eluent to afford 109.0 mg of the title compound as a white solid (83% yield).

Rₜ = 0.37 (PE/EA = 2/1, v/v). mp: 87.3 °C–88.9 °C. NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 6.31 (s, 1H), 5.86–5.52 (m, 3H), 4.72–4.62 (m, 1H), 3.92 (q, J = 12.8, 11.4 Hz, 1H), 2.70 (dd, J = 13.3, 2.9 Hz, 1H), 2.51 (dd, J = 14.2, 8.6 Hz, 1H), 2.46–2.17 (m, 5H), 2.05–1.98 (m, 1H), 1.90–1.76 (m, 2H), 1.75–1.64 (m, 2H), 1.64–1.52 (m, 3H), 1.47–1.33 (m, 2H), 1.30–1.22 (m, 1H), 1.18 (s, 3H), 1.14–0.90 (m, 3H), 0.88 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 199.7, 171.1, 167.8, 136.1, 129.0, 124.1, 116.0 (t, J = 241.8 Hz), 83.7, 70.4 (td, J = 23.7, 4.4 Hz), 53.8, 50.3, 42.9 (d, J = 3.0 Hz), 38.7, 36.8 (d, J = 2.8 Hz), 35.8, 35.5, 34.0, 33.3 (q, J = 3.5 Hz), 32.8, 31.6, 27.6, 23.6, 20.6, 17.5, 12.3; ¹⁹F NMR (375 MHz, CDCl₃) δ −128.5–−131.6 (m, 2F). IR (ATR): 3422, 2945, 1715, 1435, 1312, 1200, 1156, 1058, 943, 731 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₃H₂₆F₂O₄Na⁺ (M+Na)⁺: 459.2317; Found: 459.2315.
Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₂•4H₂O (14.7 mg, 0.06 mmol, 20 mol%), 7am (373.5 mg, 0.6 mmol, 2.0 equiv.) was added DCM (3 mL, 0.1 M), 2a (70.2 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 18 h. After which the mixture was cooled to 5 °C with ice bath, TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (200–300 mesh) and PE/EA (12/1, v/v) as eluent to afford 112.9 mg of the title compound as a white solid (67% yield).

Rₙ = 0.42 (PE/EA = 5/1, v/v), mp: 126.1 °C–127.4 °C. NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 6.29 (d, J = 1.3 Hz, 1H), 5.84–5.52 (m, 2H), 5.39 (d, J = 5.1 Hz, 1H), 4.74–4.61 (m, 1H), 4.40 (dd, J = 14.3, 8.1 Hz, 1H), 3.98–3.84 (m, 1H), 3.50–3.43 (m, 1H), 3.36 (t, J = 10.9 Hz, 1H), 2.69 (dd, J = 14.4, 3.3 Hz, 1H), 2.51 (dd, J = 14.4, 9.0 Hz, 1H), 2.37 (d, J = 7.9 Hz, 2H), 2.06–1.40 (m, 18H), 1.02 (s, 3H), 0.96 (d, J = 7.0 Hz, 3H), 0.78 (d, J = 4.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 167.4, 139.5, 136.3, 122.8, 116.0 (t, J = 244.3 Hz), 109.4, 80.9, 75.3, 70.6 (t, J = 23.8 Hz), 67.0, 62.2, 56.6, 41.7, 40.4, 39.8, 38.1, 37.0, 36.9, 33.4 (t, J = 4.0 Hz), 32.2, 32.0, 31.5, 28.9, 27.8, 20.9, 19.5, 17.2, 16.4, 14.6; ¹⁹F NMR (375 MHz, CDCl₃) δ –128.7––131.6 (m, 2F). IR (ATR): 3418, 2945, 1710, 1454, 1375, 1327, 1245, 1051, 980, 83 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₃H₂₈F₂O₅⁺ (M+H)⁺: 563.3543; Found: 563.3533.

- **3-(3,3-Difluoro-2-hydroxypropyl)-3-methyl-1-phenylindolin-2-one (14f)**

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₃•2H₂O (16.1 mg, 0.06 mmol, 20 mol%) and 10a (85.3 mg, 0.36 mmol, 1.2 equiv.) was added DCM (3 mL, 0.1 M), 2a (64.8 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath, TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with saturated Na₂CO₃ and brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (200–300 mesh) and PE/EA (20/1–10/1, v/v) as eluent to afford 76.5 mg of the title compound 14f (81% yield, 14f-a; 14f-b = 48:52).

Rₙ (14f-a) = 0.29 (PE/EA = 5/1, v/v), (37.0 mg, 39% yield, pale yellow oil). NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 7.58–7.52 (m, 2H), 7.47–7.40 (m, 3H), 7.30–7.28 (m, 1H), 7.24 (td, J = 7.7, 1.4 Hz, 1H), 7.18–7.14 (m, 1H), 6.86–6.84 (m, 1H), 5.83–5.54 (m, 1H), 4.51 (s, 1H), 4.26–4.16 (m, 1H), 2.29–1.93 (m, 2H), 1.60 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 181.7, 142.4, 134.5, 134.0, 129.8, 128.6, 128.4, 126.6, 123.9, 122.9, 116.1 (dd, J = 242.7, 240.6 Hz), 110.1, 68.7 (dd, J = 25.0, 23.4 Hz), 46.8, 36.7–36.0 (m), 23.1; ¹⁹F NMR (375 MHz, CDCl₃) δ –126.5––130.8 (m, 2F). IR (ATR): 3399, 2967, 1707, 1610, 1502, 1379, 1204, 1055, 757, 697 cm⁻¹. HRMS (ESI, m/z): calcd for C₁₆H₁₆F₂NO₂Na⁺ (M+Na)⁺: 340.1120; Found: 340.1116.
R(t (14f-b) = 0.23 (PE/EA = 5/1, v/v), (39.5 mg, 42% yield, white solid, mp: 136.1 °C–137.4 °C). NMR Spectroscopy: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.54–7.48 (m, 2H), 7.43–7.38 (m, 3H), 7.25–7.19 (m, 2H), 7.17–7.08 (m, 1H), 6.83 (dt, \(J = 7.5, 0.8\) Hz, 1H), 5.55 (td, \(J = 56.2, 3.9\) Hz, 1H), 3.53–3.30 (m, 1H), 2.43–2.13 (m, 2H), 1.53 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 180.8, 143.7, 134.8, 132.2, 129.7, 128.3, 128.2, 126.8, 123.2, 123.0, 116.0 (t, \(J = 242.5\) Hz), 109.8, 69.1 (t, \(J = 23.9\) Hz), 46.2, 37.8, 25.7; \(^{19}\)F NMR (375 MHz, CDCl\(_3\)) \(\delta\) –126.5––132.5 (m, 2F). IR (ATR): 3399, 2926, 1707, 1454, 1379, 1297, 1208, 1137, 1059, 760 cm\(^{-1}\). HRMS (ESI, m/z): calcd for C\(_{18}\)H\(_{16}\)F\(_2\)NO\(_3\)H\(^+\) (M+H\(^+\))\(^*\): 318.1300; Found: 318.1298.

**1-Benzyl-3-(3,3-difluoro-2-hydroxypropyl)-3-methylindolin-2-one (14g)**

\[
\text{HNOC} \quad \begin{array}{c}
\text{Me} \\
\text{O}
\end{array} \quad \text{N} \quad \begin{array}{c}
\text{Me} \\
\text{O}
\end{array} \quad \text{Me}
\]

Under N\(_2\) atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)\(_2\)2H\(_2\)O (16.1 mg, 0.06 mmol, 20 mol%) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with saturated Na\(_2\)CO\(_3\) and brine, dried over Na\(_2\)SO\(_4\), concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1–10/1, v/v) as eluent to afford 77.6 mg of the title compound 14g (78% yield, 14g-a:14g-b = 50:50).

R(t (14g-a) = 0.24 (PE/EA = 5/1, v/v), (39.0 mg, 39% yield, pale yellow oil). NMR Spectroscopy: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.37–7.26 (m, 5H), 7.23–7.16 (m, 2H), 7.08 (td, \(J = 7.5, 1.1\) Hz, 1H), 6.78 (dt, \(J = 7.8, 0.9\) Hz, 1H), 5.86–5.56 (m, 1H), 5.00–4.87 (m, 2H), 4.79 (s, 1H), 4.26–4.17 (m, 1H), 2.22–1.82 (m, 2H), 1.55 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 182.4, 141.4, 135.5, 134.8, 129.1, 128.4, 128.0, 127.3, 123.6, 122.7, 116.2 (t, \(J = 236.9\) Hz), 109.9, 68.9 (t, \(J = 24.2\) Hz), 46.7, 44.1, 36.1, 22.7; \(^{19}\)F NMR (375 MHz, CDCl\(_3\)) \(\delta\) –126.7––132.9 (m, 2F). IR (ATR): 3358, 2967, 1681, 1491, 1383, 1182, 1055, 943, 805, 753 cm\(^{-1}\). HRMS (ESI, m/z): calcd for C\(_{18}\)H\(_{16}\)F\(_2\)NO\(_3\)H\(^+\) (M+H\(^+\))\(^*\): 332.1457; Found: 332.1456.

**Methyl 3-(3,3-difluoro-2-hydroxypropyl)-3-methyl-2-oxo-1-phenylindoline-6-carboxylate (14h)**

\[
\text{HNOC} \quad \begin{array}{c}
\text{Me} \\
\text{O}
\end{array} \quad \text{N} \quad \begin{array}{c}
\text{Me} \\
\text{O}
\end{array} \quad \text{Me}
\]

Under N\(_2\) atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)\(_2\)2H\(_2\)O (16.1 mg, 0.06 mmol, 20 mol%) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF
(1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with saturated Na2CO3 and brine, dried over Na2SO4, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1–10/1, v/v) as eluent to afford 71.3 mg of the title compound 14h (76% yield, 14a-h: 14h-b = 51:49).

Rf (14a-h) = 0.28 (PE/EA = 2/1, v/v). (36.8 mg, 39% yield, white solid, mp: 107.2–108.9 °C. NMR Spectroscopy:1H NMR (400 MHz, CDCl3) δ 8.05 (dd, J = 8.1, 1.7 Hz, 1H), 7.88 (s, 1H), 6.92 (d, J = 8.2 Hz, 1H), 5.81–5.52 (m, 1H), 4.44 (s, 1H), 4.19–4.01 (m, 1H), 3.91 (s, 3H), 3.28 (s, 3H), 1.5–1.2 (m, 2H).) 

13C NMR (100 MHz, CDCl3) δ 182.4, 166.8, 146.4, 134.8, 131.2, 125.5, 123.9, 116.0 (t, J = 240.6 Hz), 108.4, 68.6 (t, J = 24.1 Hz), 52.3, 46.5, 36.0, 26.9, 22.6; 19F NMR (375 MHz, CDCl3) δ −124.8–−133.7 (m, 2F). IR (ATR): 3414, 2926, 1703, 1498, 1457, 1286, 1103, 1051, 797, 772 cm−1. HRMS (ESI, m/z): calcd for C15H16F3NO4+ (M+H)+: 314.1198; Found: 314.1198.

Rf (14b-h) = 0.17 (PE/EA = 2/1, v/v). (34.5 mg, 37% yield, white solid, mp: 128.4 °C–129.8 °C. NMR Spectroscopy:1H NMR (400 MHz, CDCl3) δ 8.05 (dd, J = 8.1, 1.7 Hz, 1H), 6.92 (d, J = 8.2 Hz, 1H), 5.81–5.52 (m, 1H), 4.43 (s, 1H), 4.21–4.07 (m, 1H), 3.91 (s, 3H), 3.27 (s, 3H), 2.23–1.76 (m, 1H).) 

13C NMR (100 MHz, CDCl3) δ 118.1, 167.0, 147.8, 132.5, 131.2, 124.7, 124.0, 115.8 (t, J = 242.5 Hz), 108.1, 68.8 (t, J = 23.8 Hz), 52.2, 45.9, 37.2, 26.7, 25.2; 19F NMR (375 MHz, CDCl3) δ −126.5–−133.0 (m, 2F). IR (ATR): 3422, 2922, 1707, 1498, 1457, 1372, 1286, 1055, 977, 772 cm−1. HRMS (ESI, m/z): calcd for C15H13F2NO4+ (M+H)+: 314.1198; Found: 314.1197.

3-(3,3-Difluoro-2-hydroxypropyl)-6-methoxy-1,3-dimethylindolin-2-one (14i)

Under N2 atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)2•2H2O (16.1 mg, 0.06 mmol, 20 mol%) and 10j (73.8 mg, 0.36 mmol, 1.2 equiv.) was added DCM (3 mL, 0.1 M), 2a (64.8 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with saturated Na2CO3 and brine, dried over Na2SO4, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1–10/1, v/v) as eluent to afford 69.5 mg of the title compound 14i (82% yield, 14i-a: 14i-b = 51:49).

Rf (14i-a) = 0.33 (PE/EA = 2/1, v/v). (35.5 mg, 42% yield, pale yellow oil). NMR Spectroscopy:1H NMR (400 MHz, CDCl3) δ 6.86–6.73 (m, 3H), 5.86–5.51 (m, 1H), 5.12 (s, 1H), 4.25–4.09 (m, 1H), 3.80 (s, 3H), 3.22 (s, 3H), 2.10–1.76 (m, 2H).) 

13C NMR (100 MHz, CDCl3) δ 181.9, 156.8, 136.2, 135.6, 116.2 (t, J = 239.6 Hz), 112.6, 110.1, 109.2, 68.5 (t, J = 24.1 Hz), 56.0, 47.1, 35.9, 26.7, 22.3; 19F NMR (375 MHz, CDCl3) δ −126.3–−133.4 (m, 2F). IR (ATR): 3384, 2920, 1674, 1498, 1435, 1383, 1286, 1047, 873, 741 cm−1. HRMS (ESI, m/z): calcd for C15H15F2NO4+ (M+H)+: 286.1249; Found: 286.1249.

Rf (14i-b) = 0.19 (PE/EA = 2/1, v/v). (34.0 mg, 40% yield, white solid, mp: 134.5 °C–136.1 °C. NMR Spectroscopy:1H NMR (400 MHz, CDCl3) δ 6.86–6.74 (m, 3H), 5.52 (td, J = 56.2, 3.8 Hz, 1H), 3.81 (s, 3H), 3.43–3.31 (m, 1H), 3.18 (s, 3H), 2.30–2.04 (m, 2H), 1.40 (s, 3H).) 

13C NMR (100 MHz, CDCl3) δ 180.9, 156.3, 137.1, 134.0, 115.9 (t, J = 242.2 Hz), 112.3, 110.5, 108.9, 68.9 (t, J = 23.8 Hz), 56.0, 46.6, 37.3, 26.6, 25.5; 19F NMR (375 MHz, CDCl3) δ −127.7–−132.3 (m, 2F). IR (ATR): 3392, 2930, 1685, 1498, 1290, 1238, 1126, 1036, 883, 701 cm−1. HRMS (ESI, m/z): calcd for C14H13F2NO4+ (M+H)+: 286.1249; Found: 286.1249.
Under \( \text{N}_2 \) atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)\(_2\)·2H\(_2\)O (16.1 mg, 0.06 mmol, 20 mol%) and 12d (110.4 mg, 0.6 mmol, 2.0 equiv.) was added Hexane (0.75 mL, 0.4 M), 2a (64.8 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with saturated Na\(_2\)CO\(_3\) and brine, dried over Na\(_2\)SO\(_4\), concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) and PE/EA (20/1~10/1, v/v) as eluent to afford 39.6 mg of the title compound as a pale yellow oil (60% yield).

R\(_f\) = 0.40 (PE/EA = 5/1, v/v). NMR Spectroscopy: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.24–7.16 (m, 1H), 6.94–6.84 (m, 3H), 6.59–6.53 (m, 1H), 5.89–5.69 (m, 1H), 4.48 (dq, \( J = 10.3, 5.2 \) Hz, 1H), 2.23 (s, 1H); \(^1\)C NMR (150 MHz, CDCl\(_3\)) \( \delta \) 161.2 (dd, \( J = 250.3, 7.3 \) Hz), 129.7–129.4 (m, 129.2 (t, \( J = 10.8 \) Hz), 121.2, 115.5 (t, \( J = 243.8 \) Hz), 113.4 (t, \( J = 15.1 \) Hz), 111.7 (dd, \( J = 21.5, 4.8 \) Hz), 72.8 (t, \( J = 24.4 \) Hz); \(^19\)F NMR (375 MHz, CDCl\(_3\)) \( \delta \) −112.7 (s, 2F), −126.3–−130.0 (m, 2F). IR (ATR): 3396, 2926, 1703, 1621, 1584, 1464, 1267, 1118, 1062, 999, 909 cm\(^{-1}\). HRMS (ESI, m/z): calcd for C\(_{10}\)H\(_{14}\)F\(_{3}\)O\(_4\)- (M+Na): 243.0404; Found: 243.0412.

\[ 5.5\text{-Difluoro-1-(4-fluorophenyl)-4-hydroxy-2-methylenepentan-1-one} (14k) \]

Under \( \text{N}_2 \) atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)\(_2\)·2H\(_2\)O (16.1 mg, 0.06 mmol, 20 mol%) and 12c (99.6 mg, 0.6 mmol, 2.0 equiv.) was added Hexane (0.75 mL, 0.4 M), 2a (64.8 mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was combined and washed with saturated Na\(_2\)CO\(_3\) and brine, dried over Na\(_2\)SO\(_4\), concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) and PE/EA (20/1~10/1, v/v) as eluent to afford 35.4 mg of the title compound as a colorless oil (58% yield).

R\(_f\) = 0.32 (PE/EA = 5/1, v/v). NMR Spectroscopy: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.42–7.35 (m, 2H), 7.08–6.98 (m, 2H), 7.68 (dd, \( J = 16.0, 1.4 \) Hz, 1H), 6.16–6.10 (m, 1H), 5.88–5.56 (m, 1H), 4.49–4.20 (m, 1H), 2.29 (s, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 162.9 (d, \( J = 245.5 \) Hz), 133.8, 132.1 (d, \( J = 3.2 \) Hz), 128.5 (d, \( J = 8.0 \) Hz), 122.4, 115.8 (d, \( J = 21.5 \) Hz), 115.6 (d, \( J = 242.3 \) Hz), 72.3 (t, \( J = 24.4 \) Hz); \(^19\)F NMR (375 MHz, CDCl\(_3\)) \( \delta \) −113.0 (td, \( J = 9.9, 4.9 \) Hz), −126.5–−133.0 (m, 2F). IR (ATR): 3411, 2971, 1703, 1603, 1510, 1230, 1051, 969, 854, 746 cm\(^{-1}\). HRMS (ESI, m/z): calcd for C\(_{10}\)H\(_{10}\)F\(_4\)O\(_5\) (M+Na): 203.0678; Found: 203.0686.

\[ (E)-1,1\text{-Difluoro-4-(4-methoxyphenyl)but-3-en-2-ol} (14l) \]

Under \( \text{N}_2 \) atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)\(_2\)·2H\(_2\)O (16.1 mg, 0.06 mmol, 20 mol%) and 12l (106.8 mg, 0.6 mmol, 2.0 equiv.) was added Hexane (0.75 mL, 0.4 M), 2a (64.8
mg, 0.3 mmol) and TBPB (145.7 mg, 0.75 mmol, 2.5 equiv.) sequentially. The tube was then sealed, and the resulting mixture was stirred at 70 °C in a heating block for 14 h, after which the mixture was cooled to 5 °C with ice bath. TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv.) was added and the mixture was stirred at 5 °C for 0.5 h. The reaction mixture was quenched with water (2 mL) and extracted with DCM (3×10 mL). The organic phase was dried over Na2SO4 and brine, dried over Na2SO4, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1–10/1, v/v) as eluent to afford 34.7 mg of the title compound as a pale yellow solid (54% yield).

Rf = 0.31 (PE/EA = 5/1, v/v); mp: 51.3°C–52.8 °C. NMR Spectroscopy: 1H NMR (400 MHz, CDCl3) δ 7.39–7.29 (m, 1H), 6.93–6.83 (m, 2H), 6.74 (dd, J = 15.9, 1.4 Hz, 1H), 6.08–6.02 (m, Hz, 1H), 5.71 (td, J = 56.1, 4.1 Hz, 1H), 4.49–4.37 (m, 1H), 2.29 (d, J = 4.7 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ 160.0, 134.7, 128.7, 128.2, 120.3 (t, J = 4.1 Hz), 115.7 (t, J = 242.7 Hz), 114.2, 72.5 (t, J = 24.3 Hz), 55.4; 19F NMR (375 MHz, CDCl3) δ −119.5–−135.0 (m, 2F). IR (ATR): 3273, 2956, 1603, 1510, 1469, 1460, 1297, 1254, 1144, 809, 701 cm−1. HRMS (ESI, m/z): calcd for C11H13F2O2+ (M+H)+: 215.0878; Found: 215.0870.

**Application of radical C-Si bond activation in the synthesis of antitumor agent Z and its difluoro analog Z′.**

Under N2 atmosphere, to a solution of 15 (2.3 g, 6.8 mmol) and NEt3 (1.4 mL, 9.5 mmol, 1.4 equiv.) in DCM (35 mL) at −78 °C was added Tf2O (1.3 mL, 7.5 mmol, 1.1 equiv.) slowly in 15 min, the reaction medium was brought to room temperature and stirred for another 2 h, upon completion, a sodium bicarbonate solution was added to quench the reaction, the resulting mixture was extracted with EA (50 mL×3 times), the combined organic phase was dried over Na2SO4, and concentrated under reduced pressure, the residue was purified by chromatography on a silica column with PE/EA (4/1, v/v) as an eluent. A colorless oil 16 is obtained (3.1 g, 6.6 mmol, 97% yield).

Under N2 atmosphere, to a stirring solution of 16 (3.03 g, 6.4 mmol), Pd(OAc)2 (144.0 mg, 0.64 mmol, 10 mol%), dpdp (287.9 mg, 0.704 mmol, 11 mol%) and DMF (10 mL) was added NEt3 (2.9 mL, 19.2 mmol, 3.0 equiv.) and tertbutyl acrylate (4.1 g, 32.0 mmol, 5.0 equiv.). The resulting mixture was stirred at 110 °C for 15 h, quenched by addition of water, extracted with EA (50 mL×3 times), the combined organic phase was dried over Na2SO4, and concentrated under reduced pressure, the residue was used as a silica plug and used for next step without further purification. To the solution of tertbutyl substituted acrylate in DCM (6 mL) was added TFA (30 mL) slowly, the resulting mixture was open to air and stirred for 12 h. The solvent and excess TFA were removed under reduced pressure, the residue was extracted with EA, the combined organic phase was dried over Na2SO4, and concentrated under reduced pressure, the residue was purified by chromatography on a silica column with DCM/MeOH (10/1, v/v) as an eluent. A pale solid 17 is obtained (1.9 g, 76% yield for two steps).

Rf = 0.5 (DCM/MeOH = 10/1, v/v); mp: 80 °C–82 °C. 1H NMR (600 MHz, DMSO-d6 (treated with anhydrous Na2SO4)) δ 7.78 (d, J = 15.8 Hz, 1H), 7.66 (d, J = 7.8 Hz, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.53–7.44 (m, 2H), 7.04 (d, J = 9.7 Hz, 2H), 6.36 (d, J = 15.9 Hz, 1H), 3.79 (s, 3H), 3.79 (s, 3H), 2.66 (t, J = 7.7 Hz, 2H), 2.54 (t, J = 6.9 Hz, 2H), 2.32 (s, 3H), 1.86 (p, J = 7.8 Hz, 2H); 13C NMR (150 MHz, DMSO-d6) δ 167.9, 167.9, 167.3, 146.5, 144.1, 141.3, 137.4, 132.3, 131.4, 130.9, 130.6, 129.2, 128.6, 128.5, 126.7, 126.6, 119.2, 52.7, 52.7, 34.6, 34.5, 31.9, 19.4. IR (ATR): 2997, 2941, 2855, 1469, 1460, 1297, 1254, 1144, 809, 701 cm−1. HRMS (ESI, m/z): calcd for C23H25O6+ (M+H)+: 397.1646; Found: 397.1635.
Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₃·2H₂O (5.3 mg, 0.02 mmol, 20 mol%) and 17 (79.2 mg, 0.2 mmol, 2.0 equiv.) was added DCM (0.5 mL, 0.2 M), TBPB (48.5 mg, 0.25 mmol, 2.5 equiv.) and 3a (23.4 mg, 0.1 mmol) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 14 h. The mixture was then cooled to −10 °C with low temperature bath, TBAF (1.0 M in THF, 0.12 mL, 0.12 mmol, 1.2 equiv.) was added and the resulting mixture was stirred at −10 °C for 1.0 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1~10/1, v/v) as eluent to afford 27.0 mg of the title compound as a colorless oil (71% yield). The reaction conducted on 0.4 mmol scale afford 123 mg of the title compound (68% yield).

IR (ATR): 3459, 2948, 1722, 1607, 1435, 1286, 1126, 1070, 969, 790, 738 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₃H₂₆F₂O₅ Na⁺ (M+Na)⁺: 455.1641; Found: 455.1617.

Under N₂ atmosphere, to a dried 10 mL Schlenk tube equipped with a magnetic stir bar containing Mn(OAc)₃·2H₂O (10.6 mg, 0.04 mmol, 20 mol%) and 17 (158.4 mg, 0.4 mmol, 2.0 equiv.) was added DCM (1.0 mL, 0.2 M), TBPB (97.0 mg, 0.50 mmol, 2.5 equiv.) and 2a (43.2 mg, 0.2 mmol) sequentially. The tube was sealed, and the resulting mixture was kept stirring at 70 °C in heating block for 14 h. The mixture was then cooled to −10 °C with low temperature bath, TBAF (1.0 M in THF, 0.24 mL, 0.24 mmol, 1.2 equiv.) was added and the resulting mixture was stirred at −10 °C for 1.0 h. The reaction mixture was quenched with water (2 mL), extracted with DCM (3×10 mL) and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) and PE/EA (20/1~10/1, v/v) as eluent to afford 59.2 mg of the title compound as a colorless oil (69% yield).

IR (ATR): 3448, 3004, 2952, 2863, 1722, 1610, 1498, 1435, 1286, 1167, 1126, 969, 790, 738 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₃H₂₆F₂O₅ Na⁺ (M+Na)⁺: 455.1641; Found: 455.1625.
(E)-(4-(3-(methyl-4-(4,4-trifluoro-3-hydroxybut-1-en-1-yl)phenyl)propyl)-1,2-phenylene)dimethanol  (antitumor agent Z)

Under N₂ atmosphere, to a dried 10 mL round bottom flask equipped with a magnetic stir bar containing 18 (58.5 mg, 0.13 mmol) and DCM (1.5 mL) was added DIBAL-H (1.0 mL, 1.0 M in hexane, 1.0 mmol, 8.0 equiv.) slowly in 10 min, the reaction medium was brought to 0 °C gradually. The reaction was quenched with 1.0 M HCl, then the resulting mixture was extracted with EA, and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) and PE/EA (1/2, v/v) as eluent to afford 48.1 mg of the title compound as a white solid (94% yield). Rᵣ = 0.22 (PE/EA = 1/1, v/v); mp: 79 °C−81 °C. NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, J = 7.6 Hz, 1H), 7.45 (d, J = 9.2 Hz, 1H), 7.36–7.32 (m, 2H), 7.22–7.18 (m, 3H), 6.25 (dd, J = 15.9, 6.7 Hz, 1H), 4.90 (s, 4H), 4.82 (s, 1H), 3.28 (s, 2H), 3.10 (s, 1H), 2.86–2.79 (m, 4H), 2.53 (s, 3H), 2.17–2.10 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) 143.0, 142.8, 139.5, 136.9, 136.1, 134.1, 132.3, 130.7, 130.2, 130.1, 128.6, 126.5, 126.1, 124.5 (q, J = 280.1 Hz), 121.5, 71.9 (q, J = 31.9 Hz), 64.5, 64.2, 35.2, 35.2, 32.8, 19.9; ¹⁹F NMR (375 MHz, CDCl₃) −7.8 (d, J = 8.9 Hz, 3F). IR (ATR): 3340, 2922, 2855, 1610, 1454, 1267, 1170, 1126, 1010, 969, 831, 734 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₄H₂₅F₃O₃Na⁺ (M+Na)⁺: 417.1648; Found: 417.1648.

(E)-(4-(3-(4,4-difluoro-3-hydroxybut-1-en-1-yl)-3-methylphenyl)propyl)-1,2-phenylene)dimethanol  (difluoro analog Z’ of antitumor agent Z)

Under N₂ atmosphere, to a dried 10 mL round bottom flask equipped with a magnetic stir bar containing 19 (43.2 mg, 0.1 mmol) and DCM (1.5 mL) was added DIBAL-H (0.8 mL, 1.0 M in hexane, 0.8 mmol, 8.0 equiv.) slowly in 10 min, the reaction medium was brought to 0 °C gradually. The reaction was quenched with 1.0 M HCl, then the resulting mixture was extracted with EA, and organic phase was combined and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) and PE/EA (1/2, v/v) as eluent to afford 33.5 mg of the title compound as a white solid (89% yield). Rᵣ = 0.33 (PE/EA = 1/2, v/v); mp: 79 °C−80 °C. NMR Spectroscopy: ¹H NMR (600 MHz, CDCl₃) δ 7.38 (d, J = 7.8 Hz, 1H), 7.27–7.24 (m, 2H), 7.17 (s, 1H), 7.13 (d, J = 7.5 Hz, 1H), 7.03–6.93 (m, 3H), 6.06 (dd, J = 15.9, 6.4 Hz, 1H), 5.71 (td, J = 56.1, 4.2 Hz, 1H), 4.71 (s, 4H), 4.51–4.40 (m, 1H), 2.64 (t, 2H), 2.60 (t, J = 7.7 Hz, 2H), 2.45 (bs, 3H), 2.33 (s, 3H), 1.97–1.88 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) 143.0, 142.5, 139.6, 136.9, 135.9, 132.7, 132.7, 130.7, 130.1, 130.0, 128.6, 126.5, 126.0, 123.3 (t, J = 3.9 Hz), 115.7 (t, J = 243.7 Hz), 72.6 (t, J = 24.3 Hz), 64.6, 64.2, 35.2, 35.2, 32.8, 19.9; ¹⁹F NMR (375 MHz, CDCl₃) −127.3–129.6 (m, 2F). IR (ATR): 3355, 3213, 2922, 2855, 1610, 1454, 1267, 1170, 1126, 1010, 969, 831, 734 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₄H₂₆F₂O₃Na⁺ (M+Na)⁺: 399.1742; Found: 399.1730.
NMR spectra for new compounds

$^1$H NMR of 5 \((\text{CDCl}_3, 400 \text{ MHz}, 25 ^\circ \text{C})\)
$^{13}$C NMR of 5 (CDCl$_3$, 100 MHz, 25 ºC)
$^{19}$F NMR of 5 (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 1a (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 1a (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 1a (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 5b (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 5b (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 5b (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 1b (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 1b (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 1b (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 1c (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 1c (CDCl$_3$, 100 MHz, 25 ºC)
$^{19}$F NMR of 1c (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 1d (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 1d (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 1d (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 6 (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 6 (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 6 (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 2a (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 2a (CDCl$_3$, 100 MHz, 25 ºC)
$^{19}$F NMR of 2a (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 7j (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 7j (CDCl$_3$, 100 MHz, 25 °C)
$^1$H NMR of 7r (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 7r (CDCl$_3$, 100 MHz, 25 ºC)
$^1$H NMR of 7s (CDCl₃, 400 MHz, 25 ºC)
$^{13}$C NMR of 7s (CDCl$_3$, 100 MHz, 25 ºC)
$^1$H NMR of 7t (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 7t (CDCl$_3$, 100 MHz, 25 °C)
$^1$H NMR of 7u (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 7u (CDCl$_3$, 100 MHz, 25 °C)
$^1$H NMR of 7v (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 7v (CDCl$_3$, 100 MHz, 25 ºC)
$^1$H NMR of 7x (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 7x (CDCl$_3$, 100 MHz, 25 °C)
$^1$H NMR of 7y (CDCl₃, 400 MHz, 25 °C)
$^{13}$C NMR of $7_y$ (CDCl$_3$, 100 MHz, 25 °C)
$^1$H NMR of 7z(CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 7z(CDCl$_3$, 100 MHz, 25 °C)
$^1$H NMR of 7ae (CDCl$_3$, 400 MHz, 25 ºC)
\textsuperscript{13}C NMR of 7ae (CDCl\textsubscript{3}, 100 MHz, 25 ºC)
$^1$H NMR of 7ai (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 7ai (CDCl$_3$, 100 MHz, 25 °C)
$^1$H NMR of 7aj (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 7aj (CDCl$_3$, 100 MHz, 25 °C)
$^1$H NMR of 7al (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 7al (CDCl$_3$, 100 MHz, 25 °C)
$^1$H NMR of 7an (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 7an (CDCl$_3$, 100 MHz, 25 °C)
$^1$H NMR of 7ao (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 7ao (CDCl₃, 100 MHz, 25 °C)

[Chemical structure image]

[Graphical spectrum image]
$^1$H NMR of 7ab (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 7ab (CDCl$_3$, 100 MHz, 25 ºC)
$^1$H NMR of 7ad (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 7ad (CDCl$_3$, 100 MHz, 25 °C)
$^1$H NMR of 7af (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 7af (CDCl$_3$, 100 MHz, 25 ºC)
$^1$H NMR of 7ag (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 7ag (CDCl$_3$, 100 MHz, 25 ºC)
$^1$H NMR of 8a (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 8a (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 8a (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 9b* (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 9b' (CDCl$_3$, 100 MHz, 25 °C)
\[ ^{19}\text{F NMR of 9b}^* \text{ (CDCl}_3, 100 \text{ MHz, 25 }^\circ\text{C}) \]

\[
\begin{array}{c}
\text{O} \\
\text{CF}_3 \\
\text{OSiMe}_2\text{Ph} \\
\text{C} \\
\end{array}
\]
$^1$H NMR of 9a (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 9a (CDCl$_3$, 100 MHz, 25 ºC)
$^{19}$F NMR of 9a (CDCl$_3$, 375 MHz, 25 $^\circ$C)
$^1$H NMR of 9b (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 9b (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 9b (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 9c (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 9c (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 9e (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 9d (CDCl$_3$, 400 MHz, 25 °C)
$^{13}\text{C}$ NMR of 9d (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 9d (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 9e (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 9e (CDCl$_3$, 100 MHz, 25 ºC)
$^{19}$F NMR of 9e (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 9f (CDCl₃, 400 MHz, 25 ºC)
$^{13}$C NMR of 9f (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 9f (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 9g (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 9g (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 9g (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 9h (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 9h (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of $9h$ (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 91 (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 9i (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 91 (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 9j (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 9j (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 9j (CDCl$_3$, 375 MHz, 25 ºC)
$^1$H NMR of $9k$ (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 9k (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 9k (CDCl$_3$, 375 MHz, 25 ºC)
$^1$H NMR of 91 (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of $91$ (CDCl$_3$, 100 MHz, 25 ºC)
$^{19}$F NMR of 91 (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 9m (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 9m (CDCl$_3$, 100 MHz, 25 ºC)
$^{19}\text{F NMR of 9m (CDCl}_3,\ 375\text{ MHz, 25}\ ^\circ\text{C}}$
$^1$H NMR of $9n$ (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 9n (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 9n (CDCl$_3$, 375 MHz, 25 ºC)
$^1$H NMR of 9o (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 9o (CDCl$_3$, 100 MHz, 25 ºC)
\(^{19}\text{F NMR of 9o (CDCl}_3, 375 \text{ MHz, 25 } ^\circ \text{C}}\)
$^1$H NMR of 9p (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 9p (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 9p (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 9q (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 9q (CDCl$_3$, 100 MHz, 25 ºC)

![Chemical Structure](image)
$^{19}$F NMR of 9q (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 9r (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 9r (CDCl$_3$, 100 MHz, 25 ºC)
$^{19}$F NMR of 9r (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 9s (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 9s (CDCl$_3$, 100 MHz, 25 ºC)
$^{19}$F NMR of 9s (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 9t (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 9t (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 9t (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 9u (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 9u (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 9u (CDCl$_3$, 375 MHz, 25 ºC)
$^1$H NMR of 9v (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 9v (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 9v (CDCl$_3$, 375 MHz, 25 ºC)
$^1$H NMR of 9w (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 9w (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 9w (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 9x (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 9x (CDCl$_3$, 100 MHz, 25 ºC)
$^{19}$F NMR of 9x (CDCl$_3$, 375 MHz, 25 ºC)
$^1$H NMR of 9y (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 9y (CDCl$_3$, 100 MHz, 25 ºC)
$^{19}$F NMR of 9y (CDCl$_3$, 375 MHz, 25 ºC)
$^1$H NMR of 9z (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 9z (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 9z (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 9aa (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 9aa (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 9aa (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 9ab (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of $9_{ab}$ (CDCl$_3$, 100 MHz, 25 ºC)
$^{19}$F NMR of 9ab (CDCl$_3$, 375 MHz, 25 ºC)
$^1$H NMR of 9ac (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 9ac (CDCl₃, 100 MHz, 25 °C)
$^{19}$F NMR of 9ac (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 9ad (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 9ad (CDCl$_3$, 100 MHz, 25 °C)
$^1$H NMR of 9ad (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 9ae (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of $9\text{ae}$ (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 9ae (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 9af (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 9af (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 9af (CDCl$_3$, 375 MHz, 25 ºC)
$^1$H NMR of 9ag (CDCl$_3$, 400 MHz, 25 ºC)
$^1$C NMR of 9ag (CDCl$_3$, 100 MHz, 25 ºC)
$^{19}$F NMR of 9ag (CDCl$_3$, 375 MHz, 25 ºC)
$^1$H NMR of 9ah (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 9ah (CDCl$_3$, 100 MHz, 25 °C)

![NMR Spectrum Diagram]
$^{19}$F NMR of 9ah (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 9ai (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 9ai (CDCl₃, 100 MHz, 25 °C)
$^{19}$F NMR of 9ai (CDCl$_3$, 375 MHz, 25 ºC)
$^1$H NMR of 9aj (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 9aj (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 9aj (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 9ak (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 9ak (CDCl$_3$, 100 MHz, 25 ºC)
$^{19}$F NMR of 9ak (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 9al (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 9al (CDCl$_3$, 100 MHz, 25 ºC)
$^{19}$F NMR of 9al (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 9am (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 9am (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 9am (CDCl$_3$, 375 MHz, 25 ºC)
$^1$H NMR of 9an (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 9an (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 9an (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 9ao (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 9ao (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 9ao (CDCl$_3$, 375 MHz, 25 ºC)
$^1$H NMR of 9ap (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 9ap (CDCl$_3$, 100 MHz, 25 ºC)
$^{19}$F NMR of 9ap (CDCl₃, 375 MHz, 25 °C)
$^1$H NMR of 11a (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 11a (CDCl$_3$, 150 MHz, 25 °C)
$^{19}$F NMR of 11a (CDCl$_3$, 375 MHz, 25 ºC)
$^1$H NMR of 11b (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 11b (CDCl$_3$, 150 MHz, 25 ºC)
$^{19}$F NMR of 11b (CDCl$_3$, 375 MHz, 25 ºC)
$^1$H NMR of 11c (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of IIC (CDCl$_3$, 150 MHz, 25 °C)
$^{19}$F NMR of 11c (CDCl$_3$, 375 MHz, 25 ºC)
$^1$H NMR of 11d (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 11d (CDCl$_3$, 150 MHz, 25 °C)
$^{19}$F NMR of 11d (CDCl$_3$, 375 MHz, 25 °C)
$^{1}H$ NMR of $\text{He(CDC}_{3}$, 400 MHz, 25 ºC)
$^{13}$C NMR of 11e (CDCl₃, 150 MHz, 25 °C)
$^{19}$F NMR of 11e (CDCl$_3$, 375 MHz, 25 ºC)
$^1$H NMR of II (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of II (CDCl$_3$, 150 MHz, 25 °C)
$^{19}$F NMR of 11f (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 11g (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 11g (CDCl$_3$, 150 MHz, 25 °C)
$^{19}$F NMR of 11g (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 11h (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 11h (CDCl$_3$, 150 MHz, 25 °C)
$^{19}$F NMR of 11h (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of III (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of III (CDCl$_3$, 150 MHz, 25 °C)
\(^{19}\)F NMR of II (CDCl\(_3\), 375 MHz, 25 °C)
$^1$H NMR of 13a (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 13a (CDCl₃, 100 MHz, 25 °C)
$^{19}$F NMR of 13a (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 13b (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 13b (CDCl$_3$, 150 MHz, 25 ºC)
$^{19}F$ NMR of 13b (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 13c (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 13c (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 13c (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 13d (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 13d (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 13d (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 13e (CDCl$_3$, 600 MHz, 25 °C)
$^{13}$C NMR of 13e (CDCl$_3$, 150 MHz, 25 °C)
$^{19}$F NMR of 13e (CDCl$_3$, 375 MHz, 25 ºC)
$^{1}\text{H NMR of 13f (CDCl}_3$, 600 MHz, 25 °C)
$^{13}$C NMR of 13f (CDCl$_3$, 150 MHz, 25 °C)
$^{19}\text{F} \text{ NMR of 13f (CDCl}_3$, 375 MHz, 25 °C)
$^1$H NMR of 13g (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 13g (CDCl$_3$, 100 MHz, 25 ºC)
$^{19}$F NMR of 13g (CDCl$_3$, 375 MHz, 25 ºC)
$^1\text{H NMR of 13h (CDCl}_3, 400 \text{ MHz, 25} \, ^\circ\text{C}$}
$^{13}$C NMR of 13h (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 13h (CDCl₃, 375 MHz, 25 °C)
$^1$H NMR of 13i (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 13i (CDCl$_3$, 100 MHz, 25 °C)
$^{19F}$ NMR of **13i** (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 13j (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 13j (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 13j (CDCl$_3$, 375 MHz, 25 °C)
$^1\text{H NMR of 13k (CDCl}_3\text{, 400 MHz, 25 ºC)}$
$^{13}$C NMR of 13k (CDCl$_3$, 150 MHz, 25 ºC)
$^{19}$F NMR of 13k (CDCl$_3$, 375 MHz, 25 ºC)
$^1$H NMR of 13I (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 13I (CDCl$_3$, 100 MHz, 25 ºC)
$^{19}$F NMR of 13l (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 14a (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 14a (CDCl₃, 100 MHz, 25 °C)
$^{19}$F NMR of 14a (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 1b (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 14b (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 14b (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 14c (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 14c (CDCl$_3$, 100 MHz, 25 ºC)
$^{19}$F NMR of 14c (CDCl$_3$, 375 MHz, 25 ºC)
$^1$H NMR of 14d (CDCl₃, 400 MHz, 25 °C)
$^{13}$C NMR of 14d (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 14d (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 14e (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 14e (CDCl$_3$, 100 MHz, 25 °C)
$^1$H NMR of 14e (CDCl$_3$, 375 MHz, 25 ºC)
$^1$H NMR of 14f-a (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 14f-a (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 14f-a (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 14f-b (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 14f-b (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 14f-b (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 14g-a (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 14g-a (CDCl$_3$, 100 MHz, 25 ºC)
$^{19}$F NMR of 14g-a (CDCl$_3$, 375 MHz, 25 ºC)
$^1$H NMR of 14g-b (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 14g-b (CDCl$_3$, 100 MHz, 25 °C)
\(^{19}\)F NMR of 14g-b (CDCl\(_3\), 375 MHz, 25 °C)
$^1$H NMR of 14h-a (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 14h-a (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 14h-a (CDCl$_3$, 375 MHz, 25 ºC)
$^1$H NMR of 14h-b (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 14h-b (CDCl$_3$, 100 MHz, 25 ºC)
$^{19}$F NMR of 14h-b (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 14i-a (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 14i-a (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 14i-a (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 14i-b (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 14i-b (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 14i-b (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 14j (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of 14j (CDCl$_3$, 150 MHz, 25 °C)
$^{19}$F NMR of 14j (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 14k (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of $14k$ (CDCl$_3$, 100 MHz, 25 ºC)
$^{19}$F NMR of 14k (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 14I (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 14I (CDCl$_3$, 100 MHz, 25 ºC)
$^{19}$F NMR of 14l (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 17 (DMSO-d$_6$, 600 MHz, 25 °C)
$^{13}$C NMR of 17 (DMSO-d6, 150 MHz, 25 °C)
$^1$H NMR of 18 (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 18 (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of 18 (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of 19 (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of 19(CDCl$_3$, 150 MHz, 25 °C)
$^{19}$F NMR of 19 (CDCl$_3$, 375 MHz, 25 °C)
$^1$H NMR of antitumor agent Z (CDCl$_3$, 400 MHz, 25 ºC)
$^{13}$C NMR of antitumor agent Z (CDCl$_3$, 150 MHz, 25 °C)
$^{19}$F NMR of antitumor agent Z (CDCl$_3$, 375 MHz, 25 ºC)
$^1$H NMR of difluoro analog Z' of antitumor agent Z (CDCl$_3$, 400 MHz, 25 °C)
$^{13}$C NMR of difluoro analog Z' of antitumor agent Z (CDCl$_3$, 100 MHz, 25 °C)
$^{19}$F NMR of difluoro analog Z' of antitumor agent Z (CDCl$_3$, 375 MHz, 25 ºC)
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