

Supporting Information

Visible-light promoted three-component tandem reaction: one-pot synthesis of difluoromethylated oxazolidin-2-imine

Kun Bao^{a,b#}, *Jun Wei*^{a#}, *Huihui Yan*^{a,b}, *Rong Sheng*^{a*}

^a Zhejiang Province Key Laboratory of Anti-Cancer Drug Research, College of Pharmaceutical Sciences, Zhejiang University, Hangzhou, 310058, China

^b Collaborative Innovation Center of Yangtze River Delta Region Green Pharmaceuticals, Zhejiang University of Technology, Hangzhou, 310014, P. R. China

[#] These authors contributed equally to this paper.

Tel/Fax: 86-571-88208458;

Table of Contents

1. General information	S2
2. Typical procedure for the synthesis of 1a-1p	S2-S5
3. Characterization data of 1a-1p	S5-10
4. General procedure for the synthesis of 4aa-4pa , 4ab-4ak	S10
5. Characterization data of compound 4aa-4pa , 4ab-4ak	S10-S24
6. Luminescence quenching experiments	S24-S28
7. The energy level gaps coordinate data of intermediates B_{ai} and C_{ai}	S28-S33
8. X-ray crystal structure analysis of 4ai	S33
9. Reference	S34
10. Copies of NMR Spectra	S35-S86

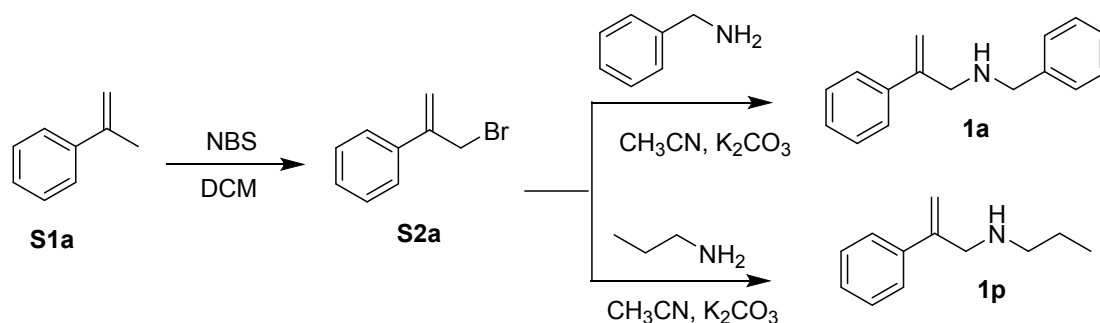
1. General information

Unless otherwise mentioned, all manipulations were conducted with a standard Schlenk tube under N₂ atmosphere, and reagents were purchased from commercial sources and used without further purification. Reactions were monitored by thin layer chromatography purchased from commercial suppliers. Subsequent to elution, spots were visualized using UV radiation (254 nm). Flash chromatography was performed using 200-300 mesh silica gel. NMR spectra were obtained on a BRUCKER AVANCE III 500 (500 MHz for ¹H NMR, 126 MHz for ¹³C NMR) or Zhongke-Niujin WNMR-I-400 (376 MHz for ¹⁹F NMR). ¹H NMR and ¹³C NMR chemical shifts were determined relative to internal (CH₃)₄Si (TMS) at δ 0.0. High Resolution MS (HRMS) were performed on an Agilent 6224 TOF LC/MS spectrometer.

Commercially available chemicals were obtained from Adamas, Energy-Chemical, Aladdin, Macklin, Bidepharm and used as received unless otherwise stated. Anhydrous *N,N*-Dimethylformamide (DMF) was purchased from Shanghai Energy-Chemical, and stored over molecular sieves under nitrogen unless otherwise stated. The Isocyanate were purchased from Aladdin, Macklin, Bidepharm and Adamas. DABCO and Ru(bpy)₃Cl₂·6H₂O were obtained from Energy-Chemical. Allylamines **1a-1o**, 2-(difluoromethylsulfonyl)benzo[*d*]thiazole **2**, were synthesized according to the literature procedure.

2. Typical procedure for the synthesis of 1a-1p

2.1 The procedure for the synthesis of 1a, 1p

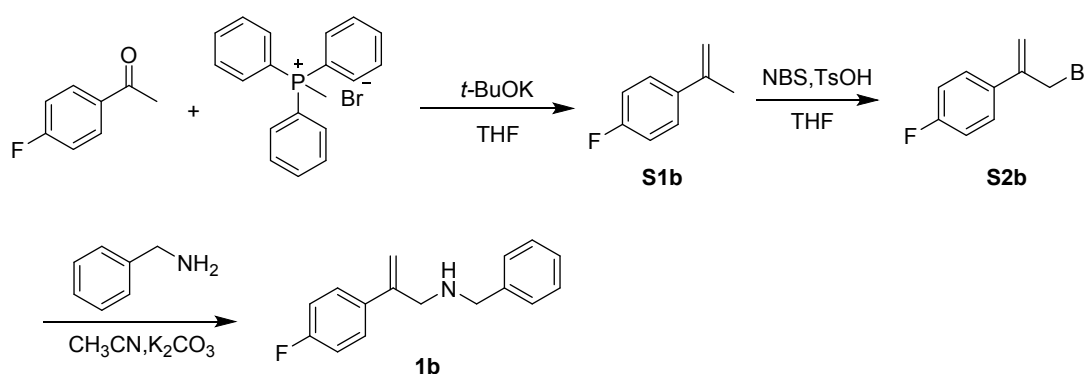


Compound **1a** and **1p** were prepared according to the reported procedures.^{1,2} Prop-1-en-2-yl-benzene **S1a** (30 mmol, 1.0 equiv.) was dissolved in a round bottomed flask containing 50 mL DCM. The NBS (60 mmol, 2.0 equiv.) was added to the solution

and the mixture was stirred at 45 °C for 18 h. After completion of reaction, the resulting system was quenched with aqueous NaHCO₃ solution (100 mL) and the mixture was extracted with DCM (80 mL × 3). The combined organic layer was washed with brine and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum and the resulting crude product **S2a** was used directly in the next step.¹

The mixture of (3-bromoprop-1-en-2-yl)-benzene **S2a** (3.0 mmol, 1.0 equiv.), benzyl amine or *n*-propyl amine (3.6 mmol, 1.2 equiv.), and K₂CO₃ (3.0 mmol, 1.0 equiv.) in 20 mL CH₃CN were refluxed overnight. After removing of CH₃CN under vacuum and the mixture was extracted with ethyl acetate (50 mL × 3). The combined organic layer was washed with brine and dried over Na₂SO₄. The solvent was removed under vacuum and the residue was purified by column chromatography over silica gel (200-300 mesh) using petroleum ether/ethyl acetate as eluent to afford **1a**, **1p** as yellow oil, respectively.²

2.2 General procedure for the synthesis of 1b-1n



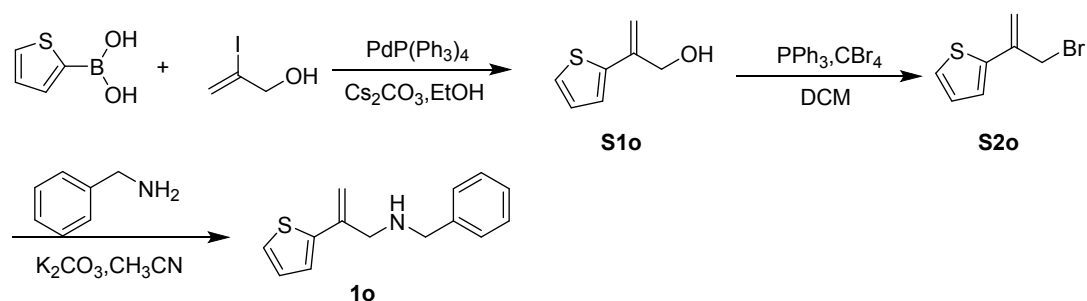
The *t*-BuOK (1.95 mmol, 1.5 equiv.) was added to a suspension of methyl triphenylphosphonium bromide (1.95 mmol, 1.5 equiv.) in 20 mL anhydrous THF at 0 °C, and the resulting mixture was stirred in ice bath for 45 minutes. Then, a solution of substituted 1-(4-fluorophenyl)ethan-1-one (1.3 mmol, 1.0 equiv.) in 2 mL THF was added dropwise to the mixture and stirred at room temperature for 16 h. The reaction mixture was filtered over Celite and the filtrate was concentrated under vacuum to yield **S1b** was used directly in the next step.³

The mixture of 1-fluoro-4-(prop-1-en-2-yl)benzene **S1b** (1.3 mmol, 1.0 equiv.), NBS (1.56 mmol, 1.2 equiv.), and TsOH (0.13 mmol, 0.1 equiv.) in 20 mL anhydrous THF were refluxed overnight. After removing of THF under vacuum and the mixture was extracted with petroleum ether (75 mL × 3). The combined organic layer was

dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum to obtain **S2b** was used directly in the next step.⁴

The mixture of the **S2b** (1.3 mmol, 1.0 equiv.), benzylamine (1.56 mmol, 1.2 equiv.), and K_2CO_3 (1.3 mmol, 1.0 equiv.) in 20 mL CH_3CN were refluxed overnight. After removing of CH_3CN under vacuum and the mixture was extracted with ethyl acetate (20 mL $\times$ 3). The organic layer was washed with brine and dried over anhydrous Na_2SO_4 . The solvent was removed under vacuum and purification by column chromatography over silica gel (200-300 mesh) using petroleum ether/ethyl acetate as eluent afforded **1b** as a yellow oil.² The **1c-1n** were prepared in similar manner.

2.3 The procedure for the synthesis of **1o**



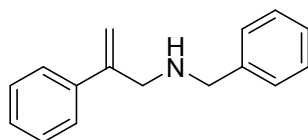
The mixture of the thiophen-2-ylboronic acid (5.0 mmol, 1.0 equiv.), 2-iodoprop-2-en-1-ol (6.0 mmol, 1.2 equiv.), $\text{Pd}(\text{PPh}_3)_4$ (0.025 mmol, 5% equiv.) and Cs_2CO_3 (10.0 mmol, 2.0 equiv.) in 20 mL EtOH was purged with nitrogen and then stirred at 70 °C for 12 h. After removing of EtOH under vacuum and extracted with ethyl acetate (60 mL $\times$ 3). The organic layer was washed with brine and dried over anhydrous Na_2SO_4 . The solvent was removed under vacuum and purification by column chromatography over silica gel (200-300 mesh) using petroleum ether/ethyl acetate as eluent afforded desired 2-(thiophen-2-yl)prop-2-en-1-ol **S1o** as a yellow oil.

To a solution of **S1o** (1.2 mmol, 1.0 equiv.) in 10 mL CH_2Cl_2 , PPh_3 (1.4 mmol, 1.2 equiv.) was added in ice bath. The mixture was stirred for 10 min, then CBr_4 (1.3 mmol, 1.1 equiv.) was added portionwise to the system and the mixture was stirred in ice bath for 3 h. After the completion of reaction, the resulting solution was extracted with DCM and dried over anhydrous Na_2SO_4 . The solvent was removed under vacuum to obtain **S2o**.⁵

The mixture of the 2-(3-bromoprop-1-en-2-yl)thiophene **S2o** (1.2 mmol, 1.0 equiv.), phenylmethanamine (1.4 mmol, 1.2 equiv.), and K₂CO₃ (2.3 mmol, 2.0 equiv.) in 15 mL CH₃CN was refluxed overnight. After removing of CH₃CN under vacuum and the mixture was extracted with ethyl acetate (20 mL × 3). The organic layer was washed with brine and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum and purification by column chromatography over silica gel (200-300 mesh) using petroleum ether/ethyl acetate as eluent to afforded **1o** as a yellow oil.²

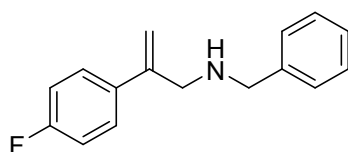
3. Characterization data of 1a-1o

N-benzyl-2-phenylprop-2-en-1-amine (1a)



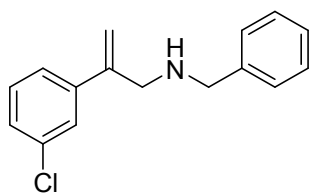
¹H NMR (500 MHz, DMSO-*d*₆) δ 7.49 – 7.47 (m, 2H), 7.36 – 7.32 (m, 4H), 7.31 – 7.28 (m, 3H), 7.24 – 7.22 (m, 1H), 5.45 (d, *J* = 1.5 Hz, 1H), 5.29 (d, *J* = 2.0 Hz, 1H), 3.72 (s, 2H), 3.55 (s, 2H), 3.32 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 144.30, 140.03, 139.20, 128.79, 128.37, 128.29, 128.21, 127.03, 126.66, 107.38, 53.01, 50.18. MS (ESI): *m/z* calcd. for C₁₆H₁₈N [M+H]⁺ 224.14, found: 224.15.

N-benzyl-2-(4-fluorophenyl)prop-2-en-1-amine (1b)



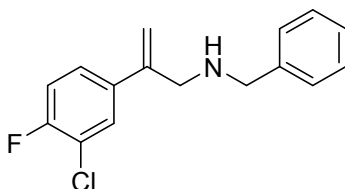
¹H NMR (500 MHz, CDCl₃) δ 7.41 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.34 – 7.27 (m, 5H), 7.04 (t, *J* = 9.0 Hz, 2H), 5.40 (s, 1H), 5.29 (s, 1H), 3.83 (s, 2H), 3.68 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 163.48 (d, *J* = 247.3 Hz), 144.42, 138.89, 135.56 (d, *J* = 3.3 Hz), 128.50, 128.48, 127.95, 127.88, 127.32, 115.43, 115.26, 114.37, 52.52, 52.22. MS (ESI): *m/z* calcd. for C₁₆H₁₇FN [M+H]⁺ 242.13, found: 242.15.

N-benzyl-2-(3-chlorophenyl)prop-2-en-1-amine (1c)



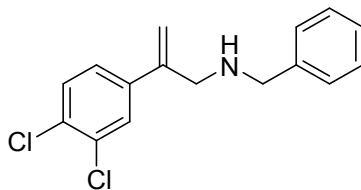
^1H NMR (500 MHz, CDCl_3) δ 7.43 – 7.42 (m, 1H), 7.33 – 7.29 (m, 5H), 7.26 – 7.24 (m, 3H), 5.44 (d, J = 1.0 Hz, 1H), 5.31 (d, J = 1.5 Hz, 1H), 3.81 (s, 2H), 3.64 (d, J = 1.5 Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 145.08, 141.74, 139.91, 134.34, 129.61, 128.41, 128.23, 127.67, 127.04, 126.47, 124.37, 114.79, 52.95, 52.50. HRMS (ESI): m/z calcd. for $\text{C}_{16}\text{H}_{17}\text{ClN}$ $[\text{M}+\text{H}]^+$ 258.1044, found: 258.1044.

N-benzyl-2-(3-chloro-4-fluorophenyl)prop-2-en-1-amine (1d)



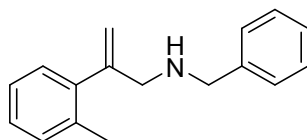
^1H NMR (500 MHz, CDCl_3) δ 7.50 (dd, J = 7.0, 2.5 Hz, 1H), 7.35 – 7.26 (m, 6H), 7.11 (t, J = 8.5 Hz, 1H), 5.39 (s, 1H), 5.29 (d, J = 1.5 Hz, 1H), 3.81 (s, 2H), 3.60 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 158.55 (d, J = 249.7 Hz), 144.27, 139.93, 137.12 (d, J = 3.9 Hz), 128.51, 128.43, 128.20, 127.07, 126.01 (d, J = 7.1 Hz), 120.91 (d, J = 17.9 Hz), 116.43 (d, J = 21.2 Hz), 114.68 (d, J = 1.5 Hz), 53.04, 52.68. HRMS (ESI): m/z calcd. for $\text{C}_{16}\text{H}_{16}\text{ClFN}$ $[\text{M}+\text{H}]^+$ 276.0950, found: 276.0949.

N-benzyl-2-(3,4-dichlorophenyl)prop-2-en-1-amine (1e)



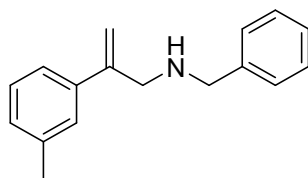
^1H NMR (500 MHz, CDCl_3) δ 7.53 (d, J = 2.0 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.36 – 7.27 (m, 6H), 5.46 (s, 1H), 5.34 (s, 1H), 3.83 (s, 2H), 3.63 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 143.79, 139.74, 139.28, 132.53, 131.61, 130.30, 128.52, 128.36, 128.28, 127.28, 125.61, 115.65, 52.83, 52.20. MS (ESI): m/z calcd. for $\text{C}_{16}\text{H}_{16}\text{Cl}_2\text{N}$ $[\text{M}+\text{H}]^+$ 292.07, found: 292.05.

N-benzyl-2-(o-tolyl)prop-2-en-1-amine (1f)



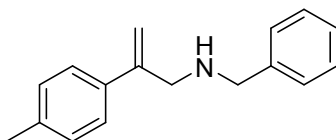
^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 7.31 – 7.27 (m, 4H), 7.22 – 7.19 (m, 1H), 7.17 – 7.12 (m, 3H), 7.07 (dd, $J = 6.5, 1.5$ Hz, 1H), 5.43 (q, $J = 2.0$ Hz, 1H), 4.94 – 4.93 (m, 1H), 3.72 (s, 2H), 3.31 (s, 2H), 2.22 (s, 3H). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 147.41, 141.01, 140.24, 134.04, 129.44, 127.64, 127.60, 127.42, 126.41, 126.04, 124.91, 113.18, 53.12, 51.60, 19.02. MS (ESI): m/z calcd. for $\text{C}_{17}\text{H}_{20}\text{N}$ $[\text{M}+\text{H}]^+$ 238.16, found: 238.20.

N-benzyl-2-(m-tolyl)prop-2-en-1-amine (1g)



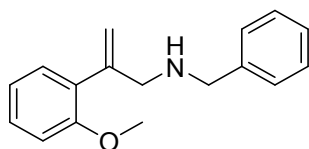
^1H NMR (500 MHz, CDCl_3) δ 7.35 – 7.31 (m, 4H), 7.27 – 7.23 (m, 4H), 7.13 – 7.10 (m, 1H), 5.42 (s, 1H), 5.27 (d, $J = 1.0$ Hz, 1H), 3.82 (s, 2H), 3.68 (s, 2H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 146.12, 139.87, 139.71, 138.03, 128.52, 128.41, 128.39, 128.36, 127.05, 126.99, 123.34, 113.63, 52.81, 52.53, 21.54. MS (ESI): m/z calcd. for $\text{C}_{17}\text{H}_{20}\text{N}$ $[\text{M}+\text{H}]^+$ 238.16, found: 238.20.

N-benzyl-2-(p-tolyl)prop-2-en-1-amine (1h)



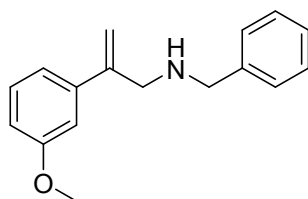
^1H NMR (500 MHz, CDCl_3) δ 7.34 – 7.33 (m, 1H), 7.32 – 7.30 (m, 5H), 7.27 – 7.23 (m, 1H), 7.16 (d, $J = 7.5$ Hz, 2H), 5.41 (d, $J = 1.5$ Hz, 1H), 5.24 (q, $J = 1.5$ Hz, 1H), 3.81 (s, 2H), 3.67 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 145.67, 139.74, 137.55, 136.75, 129.19, 128.41, 128.37, 127.06, 126.09, 113.12, 52.79, 52.50, 21.15. MS (ESI): m/z calcd. for $\text{C}_{17}\text{H}_{20}\text{N}$ $[\text{M}+\text{H}]^+$ 238.16, found: 238.20.

N-benzyl-2-(2-methoxyphenyl)prop-2-en-1-amine (1i)



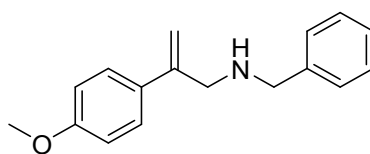
^1H NMR (500 MHz, CDCl_3) δ 7.22 – 7.12 (m, 7H), 6.87 (t, J = 7.5 Hz, 1H), 6.79 (d, J = 8.5 Hz, 1H), 5.24 (d, J = 1.5 Hz, 1H), 5.12 (d, J = 2.0 Hz, 1H), 3.68 (s, 3H), 3.66 (s, 2H), 3.58 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 156.66, 147.11, 140.49, 130.50, 130.26, 128.87, 128.32, 128.30, 126.84, 120.77, 115.36, 110.72, 55.39, 53.34, 52.65. HRMS (ESI): m/z calcd. for $\text{C}_{17}\text{H}_{20}\text{NO}$ $[\text{M}+\text{H}]^+$ 254.1539, found: 254.1541.

N-benzyl-2-(3-methoxyphenyl)prop-2-en-1-amine (1j)



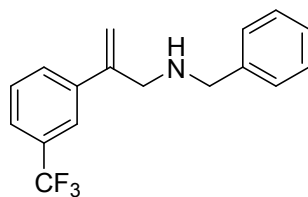
^1H NMR (500 MHz, CDCl_3) δ 7.29 – 7.25 (d, J = 5.0 Hz, 4H), 7.23 – 7.19 (m, 2H), 6.98 – 6.96 (m, 1H), 6.95 (dd, J = 2.5, 1.5 Hz, 1H), 6.81 – 6.78 (m, 1H), 5.39 (d, J = 1.5 Hz, 1H), 5.22 (d, J = 1.0 Hz, 1H), 3.76 (s, 5H), 3.62 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 159.69, 146.11, 141.38, 140.04, 129.46, 128.41, 128.30, 127.02, 118.74, 113.94, 113.05, 112.17, 55.25, 52.93, 52.72. MS (ESI): m/z calcd. for $\text{C}_{17}\text{H}_{20}\text{NO}$ $[\text{M}+\text{H}]^+$ 254.15, found: 254.20.

N-benzyl-2-(4-methoxyphenyl)prop-2-en-1-amine (1k)



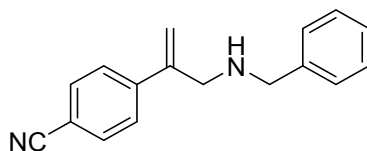
^1H NMR (500 MHz, CDCl_3) δ 7.39 – 7.36 (m, 2H), 7.31 – 7.29 (m, 4H), 7.25 – 7.24 (m, 1H), 6.88 – 6.85 (m, 2H), 5.35 (d, J = 1.5 Hz, 1H), 5.18 (d, J = 1.0 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 2H), 3.64 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 159.70, 145.95, 140.60, 132.69, 128.75, 128.65, 127.74, 127.34, 114.25, 112.49, 55.69, 53.39, 53.25. MS (ESI): m/z calcd. for $\text{C}_{17}\text{H}_{20}\text{NO}$ $[\text{M}+\text{H}]^+$ 254.15, found: 254.20.

N-benzyl-2-(3-(trifluoromethyl)phenyl)prop-2-en-1-amine (1l)



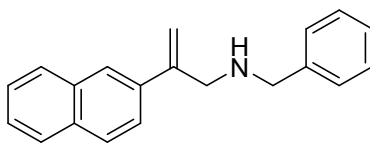
^1H NMR (500 MHz, CDCl_3) δ 7.63 (s, 1H), 7.55 (d, $J = 7.5$ Hz, 1H), 7.47 (d, $J = 7.5$ Hz, 1H), 7.39 (t, $J = 7.5$ Hz, 1H), 7.27 – 7.23 (m, 4H), 7.20 – 7.17 (m, 1H), 5.42 (d, $J = 1.0$ Hz, 1H), 5.30 (d, $J = 1.0$ Hz, 1H), 3.76 (s, 2H), 3.60 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 144.00, 139.62, 138.72, 129.86 (d, $J = 32.1$ Hz), 128.50, 127.80, 127.42, 127.22, 126.09, 123.34 (q, $J = 3.5$ Hz), 122.11 (q, $J = 3.8$ Hz), 114.31, 52.00, 51.52. HRMS (ESI): m/z calcd. for $\text{C}_{17}\text{H}_{17}\text{F}_3\text{N}$ $[\text{M}+\text{H}]^+$ 292.1308, found: 292.1315.

4-(3-(benzylamino)prop-1-en-2-yl)benzonitrile (1m)



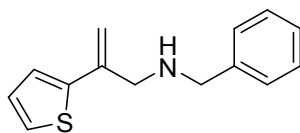
^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 7.80 – 7.78 (m, 2H), 7.69 – 7.67 (m, 2H), 7.29 (d, $J = 4.5$ Hz, 4H), 7.22 (dd, $J = 8.5, 4.0$ Hz, 1H), 5.63 (s, $J = 1.0$ Hz, 1H), 5.42 (d, $J = 1.5$ Hz, 1H), 3.68 (s, 2H), 3.55 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 143.80, 143.41, 138.68, 131.15, 127.42, 127.19, 126.13, 125.89, 117.87, 115.63, 110.09, 52.01, 51.32. MS (ESI): m/z calcd. for $\text{C}_{17}\text{H}_{17}\text{N}_2$ $[\text{M}+\text{H}]^+$ 249.14, found: 249.15.

N-benzyl-2-(naphthalen-2-yl)prop-2-en-1-amine (1n)



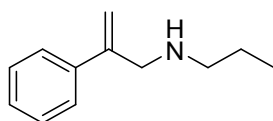
^1H NMR (500 MHz, CDCl_3) δ 7.84 – 7.81 (m, 4H), 7.61 (d, $J = 8.5$ Hz, 1H), 7.51 – 7.45 (m, 2H), 7.34 – 7.27 (m, 5H), 5.62 (s, 1H), 5.42 (s, 1H), 3.88 (s, 2H), 3.83 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 145.25, 139.10, 136.67, 133.39, 133.00, 128.54, 128.50, 128.25, 128.15, 127.58, 127.28, 126.25, 126.05, 124.95, 124.57, 114.93, 52.63, 52.18. MS (ESI): m/z calcd. for $\text{C}_{20}\text{H}_{20}\text{N}$ $[\text{M}+\text{H}]^+$ 274.16, found: 274.10.

N-benzyl-2-(thiophen-2-yl)prop-2-en-1-amine (1o)



^1H NMR (500 MHz, CDCl_3) δ 7.29 – 7.24 (m, 4H), 7.20 – 7.17 (m, 1H), 7.12 (dd, J = 5.5, 1.5 Hz, 1H), 7.02 (dd, J = 4.0, 1.5 Hz, 1H), 6.92 – 6.90 (m, 1H), 5.46 (s, 1H), 5.13 (s, 1H), 3.78 (s, 2H), 3.58 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 142.40, 138.39, 138.05, 127.42, 127.36, 126.34, 126.14, 123.54, 122.62, 111.58, 51.71, 51.58. MS (ESI): m/z calcd. for $\text{C}_{14}\text{H}_{16}\text{NS}$ $[\text{M}+\text{H}]^+$ 230.10, found: 230.15.

2-phenyl-N-propylprop-2-en-1-amine (1p)



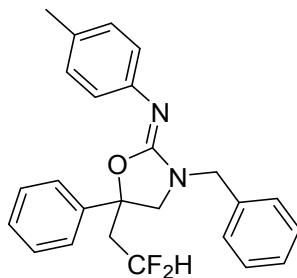
^1H NMR (500 MHz, CDCl_3) δ 7.44 – 7.42 (m, 2H), 7.36 – 7.32 (m, 2H), 7.30 – 7.26 (m, 1H), 5.39 (m, 1H), 5.24 (q, J = 1.5 Hz, 1H), 3.66 (dd, J = 1.5, 1.0 Hz, 2H), 2.60 (t, J = 7.0 Hz, 2H), 1.53 (h, J = 7.5 Hz, 2H), 0.90 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 146.53, 140.04, 128.55, 127.76, 126.28, 113.35, 53.48, 51.19, 23.15, 11.88. MS (ESI): m/z calcd. for $\text{C}_{12}\text{H}_{18}\text{N}$ $[\text{M}+\text{H}]^+$ 176.14, found: 176.25.

4. General procedure for the synthesis of compound 4aa-4pa, 4ab-4ak

A mixture of aryl allylamine substrate **1** (0.50 mmol, 1.0 equiv.), difluoromethyl sulfone **2** (0.6 mmol, 1.2 equiv.) $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (0.025 mmol, 5% equiv.), DABCO (1.0 mmol, 2.0 equiv.) were added in a Schlenk tube. The tube was evacuated and backfilled with pure N_2 for 3 times, then DMF (2 mL) and the isocyanates **3** was added to the mixture. The mixture was irradiated by a 6 W blue LED for 16 h at 8~10 °C. After the reaction was complete, H_2O (20 mL) was added. The aqueous layer was extracted with ethyl acetate (15 mL $\times$ 3) and the organic phase was combined and dried over anhydrous Na_2SO_4 . The solvent was removed under vacuum and the resulting residue was purified by column chromatography over silica gel (200-300 mesh) using petroleum ether/ethyl acetate as eluent to provide products **4aa-4pa**, **4ab-4ak**.

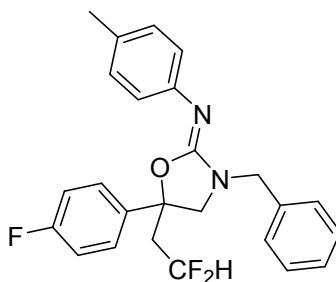
5. Characterization data of compound 4aa-4pa, 4ab-4ak.

3-benzyl-5-(2,2-difluoroethyl)-5-phenyl-N-(p-tolyl)oxazolidin-2-imine (4aa)



White solid, 75% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.39 – 7.36 (m, 2H), 7.35 – 7.31 (m, 2H), 7.30 – 7.26 (m, 6H), 7.12 (s, 4H), 5.81 (tt, $J = 55.5, 4.5$ Hz, 1H), 4.68 (d, $J = 15.0$ Hz, 1H), 4.54 (d, $J = 15.0$ Hz, 1H), 3.64 (d, $J = 9.0$ Hz, 1H), 3.52 (d, $J = 9.0$ Hz, 1H), 2.59 – 2.50 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 150.93, 144.46, 141.09, 136.38, 131.53, 129.29, 128.94, 128.73, 128.42, 128.23, 127.73, 124.29, 123.37, 116.59 (t, $J = 240.0$ Hz), 81.55 (t, $J = 5.9$ Hz), 56.32, 49.18, 44.93 (t, $J = 21.8$ Hz), 20.94. ^{19}F NMR (376 MHz, CDCl_3) δ -113.52 (dt, $J = 55.6, 15.4$ Hz). HRMS (ESI): m/z calcd. for $\text{C}_{25}\text{H}_{25}\text{F}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 407.1929, found: 407.1941.

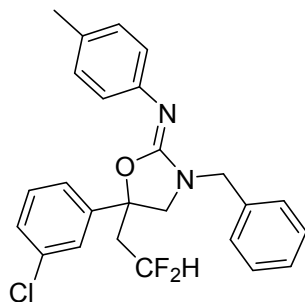
3-benzyl-5-(2,2-difluoroethyl)-5-(4-fluorophenyl)-N-(p-tolyl)oxazolidin-2-imine (4ba)



Light yellow oil, 68% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.34 – 7.32 (m, 1H), 7.31 – 7.27 (m, 4H), 7.25 – 7.22 (m, 2H), 7.13 – 7.03 (m, 6H), 5.82 (tt, $J = 55.5, 4.5$ Hz, 1H), 4.66 (d, $J = 15.0$ Hz, 1H), 4.57 (d, $J = 15.0$ Hz, 1H), 3.63 (d, $J = 8.5$ Hz, 1H), 3.48 (d, $J = 9.0$ Hz, 1H), 2.57 – 2.48 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 163.74 (d, $J = 248.3$ Hz), 150.95, 144.68, 137.25 (d, $J = 3.8$ Hz), 136.60, 131.93, 129.63, 129.06, 128.51, 128.09, 126.58, 126.51, 123.60, 116.76 (t, $J = 240.5$ Hz), 116.26, 116.09, 81.47 (t, $J = 6.3$ Hz), 56.71, 49.45, 45.16 (t, $J = 22.1$ Hz), 21.22.

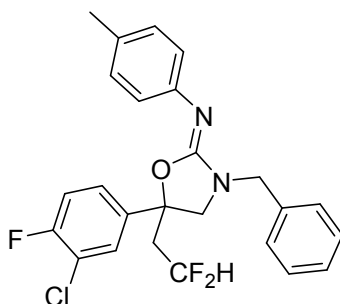
^{19}F NMR (376 MHz, CDCl_3) δ -113.13(s), -113.60 (dt, J = 55.6, 15.8 Hz). HRMS (ESI): m/z calcd. for $\text{C}_{25}\text{H}_{24}\text{F}_3\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 425.1835, found: 425.1830.

3-benzyl-5-(3-chlorophenyl)-5-(2,2-difluoroethyl)-N-(p-tolyl)oxazolidin-2-imine (4ca)



Light yellow solid, 75% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.34 – 7.32 (m, 1H), 7.30 – 7.29 (m, 3H), 7.28 – 7.26 (m, 2H), 7.25 – 7.24 (m, 2H), 7.16 – 7.11 (m, 3H), 7.10 – 7.07 (m, 2H), 5.84 (tt, J = 55.5, 5.0 Hz, 1H), 4.64 (d, J = 15.0 Hz, 1H), 4.52 (d, J = 15.0 Hz, 1H), 3.61 (d, J = 9.0 Hz, 1H), 3.45 (d, J = 9.0 Hz, 1H), 2.58 – 2.43 (m, 2H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 150.47, 144.07, 143.14, 136.11, 135.00, 131.78, 130.28, 129.33, 128.77, 128.67, 128.25, 127.84, 124.67, 123.21, 122.52, 116.26 (t, J = 240.7 Hz), 81.03 (t, J = 5.0 Hz), 56.20, 49.20, 44.66 (t, J = 21.4 Hz), 20.91. ^{19}F NMR (376 MHz, CDCl_3) δ -114.00 – -114.26 (m). HRMS (ESI): m/z calcd. for $\text{C}_{25}\text{H}_{24}\text{ClF}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 441.1540, found: 441.1542.

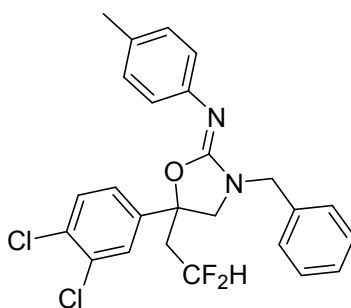
3-benzyl-5-(3-chloro-4-fluorophenyl)-5-(2,2-difluoroethyl)-N-(p-tolyl)oxazolidin-2-imine (4da).



Light yellow oil, 80% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.35 – 7.33 (m, 1H), 7.32 – 7.26 (m, 5H), 7.14 – 7.12 (m, 4H), 7.09 (d, J = 8.0 Hz, 2H), 5.85 (tt, J = 55.5, 5.0 Hz, 1H), 4.66 (d, J = 14.5 Hz, 1H), 4.58 (d, J = 14.5 Hz, 1H), 3.63 (d, J = 9.0 Hz, 1H),

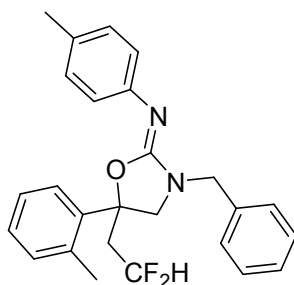
3.46 (d, $J = 9.0$ Hz, 1H), 2.60 – 2.44 (m, 2H), 2.34(s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 158.83 (d, $J = 251.2$ Hz), 150.31, 144.09, 138.29 (d, $J = 3.8$ Hz), 136.08, 131.87, 129.41, 128.82, 128.26, 127.92, 126.98, 124.41 (d, $J = 7.4$ Hz), 123.20, 121.82 (d, $J = 18.1$ Hz), 117.20 (d, $J = 21.4$ Hz), 116.22 (t, $J = 240.4$ Hz), 80.70 (t, $J = 5.9$ Hz), 56.30, 49.18, 44.60 (t, $J = 21.9$ Hz), 20.94. ^{19}F NMR (376 MHz, CDCl_3) δ -113.57 – -113.85 (m), -115.04 (s). HRMS (ESI): m/z calcd. for $\text{C}_{25}\text{H}_{23}\text{ClF}_3\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 459.1446, found: 459.1463.

3-benzyl-5-(3,4-dichlorophenyl)-5-(2,2-difluoroethyl)-N-(p-tolyl)oxazolidin-2-imine (4ea)



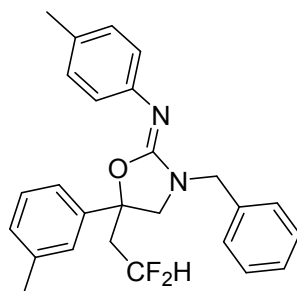
Light yellow solid, 65% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.45 (d, $J = 8.5$ Hz, 1H), 7.35 – 7.27 (m, 6H), 7.14 – 7.06 (m, 5H), 5.85 (tt, $J = 55.5, 4.5$ Hz, 1H), 4.64 (d, $J = 15.0$ Hz, 1H), 4.56 (d, $J = 15.0$ Hz, 1H), 3.62 (d, $J = 9.0$ Hz, 1H), 3.45 (d, $J = 9.0$ Hz, 1H), 2.59 – 2.43 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 150.23, 144.19, 141.45, 136.11, 133.32, 132.80, 131.90, 131.01, 129.45, 128.86, 128.31, 127.97, 126.68, 123.90, 123.23, 116.21 (t, $J = 240.7$ Hz), 80.65 (t, $J = 5.8$ Hz), 56.24, 49.24, 44.51 (t, $J = 22.1$ Hz), 20.98. ^{19}F NMR (376 MHz, CDCl_3) δ -113.52 – -113.83 (m). HRMS (ESI): m/z calcd. for $\text{C}_{25}\text{H}_{23}\text{Cl}_2\text{F}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 475.1150, found: 475.1148.

3-benzyl-5-(2,2-difluoroethyl)-5-(o-tolyl)-N-(p-tolyl)oxazolidin-2-imine (4fa)



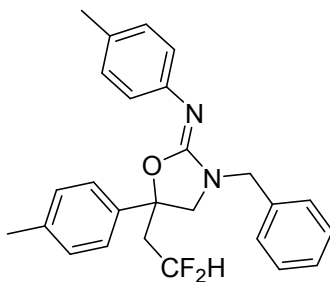
Light yellow oil, 48% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.40 – 7.33 (m, 5H), 7.33 – 7.29 (m, 1H), 7.25 – 7.20 (m, 2H), 7.19 – 7.11 (m, 5H), 5.89 (tt, $J = 55.5$, 4.5 Hz, 1H), 4.77 (d, $J = 15.0$ Hz, 1H), 4.50 (d, $J = 15.0$ Hz, 1H), 3.79 (d, $J = 9.0$ Hz, 1H), 3.56 (d, $J = 9.0$ Hz, 1H), 2.67 – 2.48 (m, 2H), 2.36 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 150.53, 144.51, 138.92, 136.36, 133.12, 132.37, 131.48, 129.25, 128.77, 128.45, 128.24, 127.77, 126.40, 125.20, 123.29, 116.61 (t, $J = 239.4$ Hz), 82.19 (t, $J = 6.3$ Hz), 55.88, 49.18, 43.70 (t, $J = 21.4$ Hz), 21.02, 20.92. ^{19}F NMR (376 MHz, CDCl_3) δ -113.36 (dt, $J = 55.6$, 15.8 Hz). HRMS (ESI): m/z calcd. for $\text{C}_{26}\text{H}_{27}\text{F}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 421.2086, found: 421.2082.

3-benzyl-5-(2,2-difluoroethyl)-5-(m-tolyl)-N-(p-tolyl)oxazolidin-2-imine (4ga)



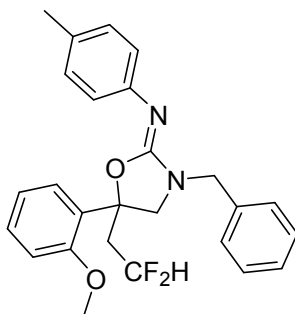
Light yellow solid, 85% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.34 – 7.32 (m, 1H), 7.31 – 7.30 (m, 1H), 7.29 – 7.27 (m, 3H), 7.25 (d, $J = 7.5$ Hz, 1H), 7.14 – 7.11 (m, 5H), 7.08 – 7.05 (m, 2H), 5.81 (tt, $J = 55.5$, 4.5 Hz, 1H), 4.67 (d, $J = 15.0$ Hz, 1H), 4.52 (d, $J = 15.0$ Hz, 1H), 3.62 (d, $J = 8.5$ Hz, 1H), 3.50 (d, $J = 9.0$ Hz, 1H), 2.60 – 2.45 (m, 2H), 2.34 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 151.15, 144.37, 138.28, 138.02, 136.39, 131.55, 129.59, 129.29, 128.74, 128.27, 127.74, 124.26, 123.41, 116.69 (t, $J = 240.0$ Hz), 81.71 (t, $J = 6.0$ Hz), 56.35, 49.21, 44.95 (t, $J = 21.8$ Hz), 21.10, 20.95. ^{19}F NMR (376 MHz, CDCl_3) δ -113.53 (dt, $J = 55.6$, 15.4 Hz). HRMS (ESI): m/z calcd. for $\text{C}_{26}\text{H}_{27}\text{F}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 421.2086, found: 421.2103.

3-benzyl-5-(2,2-difluoroethyl)-N,5-di-p-tolylloxazolidin-2-imine (4ha)



White solid, 62% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.32 – 7.27 (m, 5H), 7.18 – 7.14 (m, 4H), 7.11 (s, 4H), 5.80 (tt, $J = 56.0, 5.0$ Hz, 1H), 4.66 (d, $J = 15.0$ Hz, 1H), 4.53 (d, $J = 15.0$ Hz, 1H), 3.61 (d, $J = 9.0$ Hz, 1H), 3.50 (d, $J = 9.0$ Hz, 1H), 2.56 – 2.48 (m, 2H), 2.34 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 151.05, 144.45, 141.02, 138.70, 136.40, 131.52, 129.29, 129.17, 128.84, 128.73, 128.27, 127.74, 124.91, 123.37, 121.40, 116.65 (t, $J = 240.0$ Hz), 81.65 (t, $J = 6.0$ Hz), 56.25, 49.20, 44.94 (t, $J = 21.8$ Hz), 21.61, 20.94. ^{19}F NMR (376 MHz, CDCl_3) δ -113.59 (dt, $J = 55.3, 15.8$ Hz). HRMS (ESI): m/z calcd. for $\text{C}_{26}\text{H}_{27}\text{F}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 421.2086, found: 421.2096.

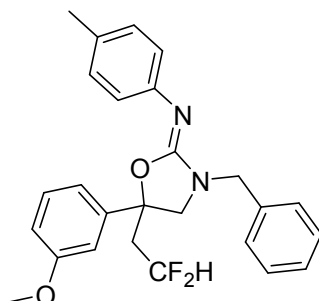
3-benzyl-5-(2,2-difluoroethyl)-5-(2-methoxyphenyl)-N-(p-tolyl)oxazolidin-2-imine (4ia)



Light yellow oil, 40% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.46 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.35 – 7.27 (m, 6H), 7.16 – 7.12 (m, 4H), 6.99 (td, $J = 7.5, 1.0$ Hz, 1H), 6.88 (dd, $J = 8.0, 1.0$ Hz, 1H), 5.89 (tt, $J = 55.5, 4.5$ Hz, 1H), 4.76 (d, $J = 15.0$ Hz, 1H), 4.45 (d, $J = 15.0$ Hz, 1H), 3.78 (s, 3H), 3.74 (d, $J = 9.5$ Hz, 1H), 3.46 (d, $J = 9.5$ Hz, 1H), 2.73 – 2.56 (m, 2H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 154.64, 150.79, 144.61, 136.70, 131.31, 129.62, 129.24, 129.10, 128.65, 128.08, 127.55, 125.74, 123.34, 120.98, 116.94 (t, $J = 239.5$ Hz), 110.89, 80.84 (t, $J = 6.2$ Hz), 56.27, 55.28, 48.97, 42.79 (t, $J = 21.8$ Hz), 20.91. ^{19}F NMR (376 MHz, CDCl_3) δ -113.32 (dt, $J = 55.6,$

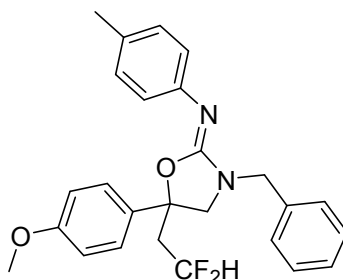
15.4 Hz). HRMS (ESI): m/z calcd. for $C_{26}H_{27}F_2N_2O_2$ $[M+H]^+$ 437.2035, found: 437.2024.

3-benzyl-5-(2,2-difluoroethyl)-5-(3-methoxyphenyl)-N-(p-tolyl)oxazolidin-2-imine (4ja)



Light yellow oil, 69% yield. 1H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.30 – 7.27 (m, 4H), 7.14 – 7.10 (m, 4H), 6.87 – 6.80 (m, 3H), 5.82 (tt, J = 55.5, 4.5 Hz, 1H), 4.69 (d, J = 15.0 Hz, 1H), 4.55 (d, J = 15.0 Hz, 1H), 3.78 (s, 3H), 3.63 (d, J = 9.0 Hz, 1H), 3.52 (d, J = 9.0 Hz, 1H), 2.56 – 2.48 (m, 2H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.95, 150.92, 144.53, 142.76, 136.38, 131.52, 130.11, 129.55, 129.28, 128.74, 128.24, 127.74, 123.34, 116.60 (t, J = 240.0 Hz), 116.47, 113.51, 110.45, 81.44 (t, J = 6.0 Hz), 56.28, 55.29, 49.16, 44.84 (t, J = 21.9 Hz), 20.95. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.63 (dt, J = 55.6, 15.8 Hz). HRMS (ESI): m/z calcd. for $C_{26}H_{27}F_2N_2O_2$ $[M+H]^+$ 437.2035, found: 437.2064.

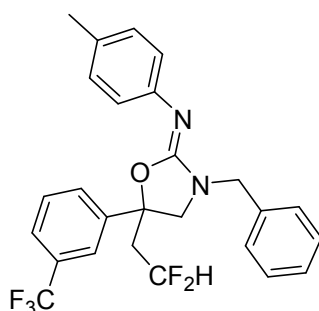
3-benzyl-5-(2,2-difluoroethyl)-5-(4-methoxyphenyl)-N-(p-tolyl)oxazolidin-2-imine (4ka)



Light yellow oil, 66% yield. 1H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.30 – 7.27 (m, 3H), 7.20 – 7.17 (m, 2H), 7.12 – 7.08 (m, 4H), 6.90 – 6.87 (m, 2H), 5.79 (tt, J = 56.0, 5.0 Hz, 1H), 4.65 (d, J = 15.0 Hz, 1H), 4.54 (d, J = 15.0 Hz, 1H), 3.80 (s, 3H), 3.60 (d, J = 9.0 Hz, 1H), 3.49 (d, J = 9.0 Hz, 1H), 2.56 – 2.47 (m, 2H), 2.33 (s,

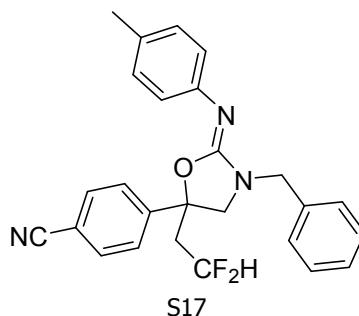
3H). ^{13}C NMR (126 MHz, CDCl_3) δ 159.49, 151.05, 144.48, 136.42, 132.92, 131.47, 129.27, 128.72, 128.22, 127.72, 125.67, 123.36, 116.70 (t, $J = 240.0$ Hz), 114.22, 81.47 (t, $J = 5.9$ Hz), 56.32, 55.35, 49.17, 44.97 (t, $J = 21.9$ Hz), 20.94. ^{19}F NMR (376 MHz, CDCl_3) δ -113.69 (dt, $J = 55.3, 15.8$ Hz). HRMS (ESI): m/z calcd. for $\text{C}_{26}\text{H}_{27}\text{F}_2\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 437.2035, found: 437.2054.

3-benzyl-5-(2,2-difluoroethyl)-N-(p-tolyl)-5-(3-(trifluoromethyl)phenyl)oxazolidin-2-imine (4la)



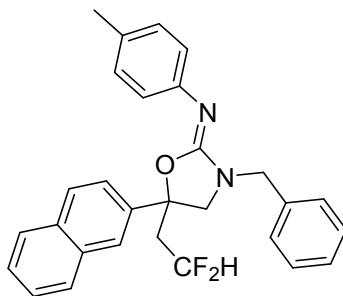
Light yellow oil, 55% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.61 – 7.59 (m, 1H), 7.52 – 7.47 (m, 3H), 7.33 – 7.26 (m, 4H), 7.25 – 7.24 (m, 1H), 7.14 – 7.06 (m, 4H), 5.86 (tt, $J = 55.0, 4.5$ Hz, 1H), 4.63 (d, $J = 15.0$ Hz, 1H), 4.54 (d, $J = 15.0$ Hz, 1H), 3.67 (d, $J = 9.0$ Hz, 1H), 3.49 (d, $J = 9.0$ Hz, 1H), 2.61 – 2.49 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 150.32, 144.33, 142.42, 136.13, 131.81, 131.50 (d, $J = 32.8$ Hz), 129.60, 129.39, 128.79, 128.21, 127.87, 127.85, 125.42 (q, $J = 3.7$ Hz), 124.87 (d, $J = 273.0$ Hz), 123.15, 121.29 (q, $J = 4.0$ Hz), 116.21 (t, $J = 240.4$ Hz), 81.01 (t, $J = 5.8$ Hz), 56.18, 49.15, 44.58 (t, $J = 22.1$ Hz), 20.92. ^{19}F NMR (376 MHz, CDCl_3) δ -62.68(s), -113.62 – -113.91 (m). HRMS (ESI): m/z calcd. for $\text{C}_{26}\text{H}_{24}\text{F}_5\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 475.1803, found: 475.1809.

4-(3-benzyl-5-(2,2-difluoroethyl)-2-(p-tolylimino)oxazolidin-5-yl)benzonitrile (4ma)



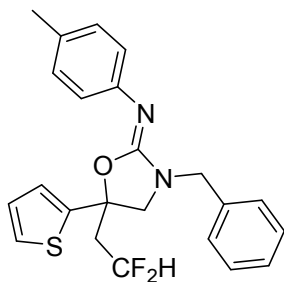
Light yellow oil, 61% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.38 – 7.30 (m, 8H), 7.24 – 7.13 (m, 4H), 6.99 (t, J = 7.5 Hz, 1H), 5.81 (tt, J = 55.5, 5.0 Hz, 1H), 4.69 (d, J = 14.5 Hz, 1H), 4.57 (d, J = 14.5 Hz, 1H), 3.70 (d, J = 9.0 Hz, 1H), 3.56 (d, J = 8.5 Hz, 1H), 2.56 (tt, J = 16.0, 5.0 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 150.11, 146.26, 143.93, 135.96, 132.75, 131.96, 129.40, 128.81, 128.22, 127.94, 125.26, 123.17, 118.14, 116.04 (t, J = 240.7 Hz), 112.52, 80.99 (t, J = 5.0 Hz), 56.28, 49.19, 44.40 (t, J = 21.4 Hz), 20.92. ^{19}F NMR (376 MHz, CDCl_3) δ -113.88 – -114.26 (m). HRMS (ESI): m/z calcd. for $\text{C}_{26}\text{H}_{24}\text{F}_2\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 432.1882, found: 475.1876.

3-benzyl-5-(2,2-difluoroethyl)-5-(naphthalen-2-yl)-N-(p-tolyl)oxazolidin-2-imine (4na)



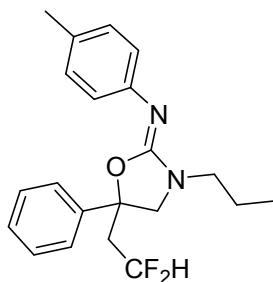
Light yellow oil, 62% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.85 – 7.79 (m, 3H), 7.75 (d, J = 2.0 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.33 – 7.30 (m, 1H), 7.29 – 7.27 (m, 4H), 7.26 – 7.23 (m, 1H), 7.15 (s, 4H), 5.84 (tt, J = 55.5, 4.5 Hz, 1H), 4.65 (d, J = 15.0 Hz, 1H), 4.53 (d, J = 15.0 Hz, 1H), 3.69 (d, J = 8.5 Hz, 1H), 3.60 (d, J = 8.5 Hz, 1H), 2.67 – 2.58 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 150.92, 144.53, 138.15, 136.34, 132.91 (d, J = 3.6 Hz), 131.57, 129.52, 129.33, 129.08, 128.72, 128.30, 128.23, 127.73, 127.69, 126.83, 126.76, 123.46, 123.36, 122.03, 116.59 (t, J = 240.1 Hz), 81.67 (t, J = 6.0 Hz), 56.19, 49.21, 44.80 (t, J = 21.9 Hz), 20.96. ^{19}F NMR (376 MHz, CDCl_3) δ -113.94 (dt, J = 55.6, 15.4 Hz). HRMS (ESI): m/z calcd. for $\text{C}_{29}\text{H}_{27}\text{F}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 457.2086, found: 457.2069.

3-benzyl-5-(2,2-difluoroethyl)-5-(thiophen-2-yl)-N-(p-tolyl)oxazolidin-2-imine (4oa)



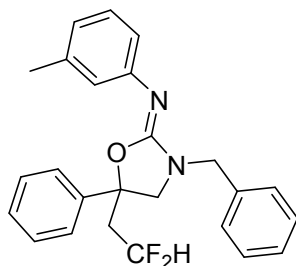
White solid, 42% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.35 – 7.29 (m, 6H), 7.09 (s, 4H), 6.99 (dd, $J = 5.0, 3.5$ Hz, 1H), 6.94 (dd, $J = 3.5, 1.0$ Hz, 1H), 5.85 (tt, $J = 55.5, 4.5$ Hz, 1H), 4.68 (d, $J = 30.5$ Hz, 2H), 3.63 (s, 2H), 2.67 – 2.59 (m, 2H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 150.37, 144.53, 144.20, 136.26, 131.59, 129.23, 128.74, 128.26, 127.78, 127.20, 125.96, 124.23, 123.34, 116.51 (t, $J = 240.0$ Hz), 79.92 (t, $J = 6.3$ Hz), 56.74, 49.21, 44.83 (t, $J = 22.4$ Hz), 20.93. ^{19}F NMR (376 MHz, CDCl_3) δ -114.15 (tt, $J = 55.6, 14.7$ Hz). HRMS (ESI): m/z calcd. for $\text{C}_{23}\text{H}_{23}\text{F}_2\text{N}_2\text{OS}$ $[\text{M}+\text{H}]^+$ 413.1494, found: 413.1486.

5-(2,2-difluoroethyl)-5-phenyl-3-propyl-N-(p-tolyl)oxazolidin-2-imine (4pa)



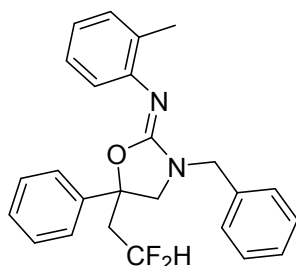
Light yellow oil, 56% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.41 – 7.38 (m, 2H), 7.36 – 7.33 (m, 1H), 7.32 – 7.30 (m, 2H), 7.10 – 7.05 (m, 4H), 5.85 (tt, $J = 55.5, 5.0$ Hz, 1H), 3.85 (d, $J = 8.5$ Hz, 1H), 3.67 (d, $J = 9.0$ Hz, 1H), 3.43 – 3.32 (m, 2H), 2.62 – 2.54 (m, 2H), 2.32 (s, 3H), 1.63 (q, $J = 7.0$ Hz, 2H), 0.94 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 151.02, 144.72, 141.40, 131.27, 129.18, 128.93, 128.36, 124.24, 123.27, 116.64 (t, $J = 240.0$ Hz), 81.19 (t, $J = 5.9$ Hz), 56.86, 46.72, 45.02 (t, $J = 21.8$ Hz), 20.89, 20.49, 11.23. ^{19}F NMR (376 MHz, CDCl_3) δ -113.49 (dt, $J = 55.6, 15.8$ Hz). HRMS (ESI): m/z calcd. for $\text{C}_{21}\text{H}_{25}\text{F}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 359.1929, found: 359.1918.

3-benzyl-5-(2,2-difluoroethyl)-5-phenyl-N-(m-tolyl)oxazolidin-2-imine (4ab)



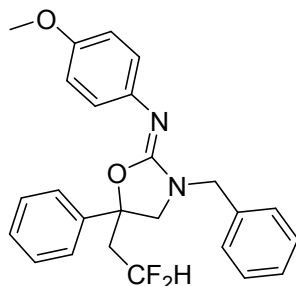
Light yellow oil, 72% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.40 – 7.37 (m, 2H), 7.36 – 7.32 (m, 3H), 7.31 – 7.28 (m, 5H), 7.24 (t, $J = 7.5$ Hz, 1H), 7.07 – 7.04 (m, 2H), 6.89 (d, $J = 7.5$ Hz, 1H), 5.83 (tt, $J = 55.5, 4.5$ Hz, 1H), 4.67 (d, $J = 15.0$ Hz, 1H), 4.54 (d, $J = 15.0$ Hz, 1H), 3.65 (d, $J = 8.5$ Hz, 1H), 3.53 (d, $J = 9.0$ Hz, 1H), 2.62 – 2.48 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 151.01, 146.98, 141.00, 138.26, 136.30, 128.94, 128.74, 128.44, 128.22, 127.75, 124.50, 124.30, 123.13, 120.39, 116.57 (t, $J = 240.2$ Hz), 81.59 (t, $J = 6.0$ Hz), 56.30, 49.14, 44.94 (t, $J = 21.8$ Hz), 21.55. ^{19}F NMR (376 MHz, CDCl_3) δ -113.56 (dt, $J = 55.6, 15.8$ Hz). HRMS (ESI): m/z calcd. for $\text{C}_{25}\text{H}_{25}\text{F}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 407.1929, found: 407.1936.

3-benzyl-5-(2,2-difluoroethyl)-5-phenyl-N-(o-tolyl)oxazolidin-2-imine (4ac)



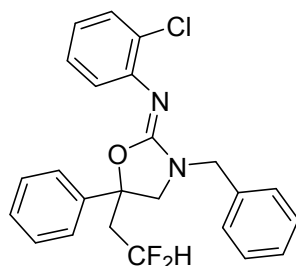
Light yellow oil, 30% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.39 – 7.30 (m, 8H), 7.24 – 7.13 (m, 5H), 6.99 (t, $J = 7.5$ Hz, 1H), 5.81 (tt, $J = 55.5, 5.0$ Hz, 1H), 4.69 (d, $J = 15.0$ Hz, 1H), 4.57 (d, $J = 15.0$ Hz, 1H), 3.70 (d, $J = 9.0$ Hz, 1H), 3.56 (d, $J = 9.0$ Hz, 1H), 2.56 – 2.48 (m, 2H), 2.28 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 150.06, 146.22, 143.89, 135.92, 132.71, 131.92, 129.36, 128.77, 128.18, 127.90, 125.22, 123.13, 118.09, 116.00 (t, $J = 240.7$ Hz), 112.49, 80.95 (t, $J = 5.0$ Hz), 56.24, 49.15, 44.37 (t, $J = 22.7$ Hz), 20.87. ^{19}F NMR (376 MHz, CDCl_3) δ -114.03 (dt, $J = 53.8, 13.9$ Hz). HRMS (ESI): m/z calcd. for $\text{C}_{25}\text{H}_{25}\text{F}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 407.1929, found: 407.1932.

**3-benzyl-5-(2,2-difluoroethyl)-N-(4-methoxyphenyl)-5-phenyloxazolidin-2-imine
(4ad)**



Light yellow oil, 61% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.39 – 7.36 (m, 2H), 7.35 – 7.29 (m, 4H), 7.28 – 7.26 (m, 4H), 7.19 – 7.16 (m, 2H), 6.89 – 6.86 (m, 2H), 5.82 (tt, $J = 55.5, 4.5$ Hz, 1H), 4.66 (d, $J = 15.0$ Hz, 1H), 4.51 (d, $J = 15.0$ Hz, 1H), 3.82 (s, 3H), 3.63 (d, $J = 8.5$ Hz, 1H), 3.50 (d, $J = 9.0$ Hz, 1H), 2.59 – 2.50 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 153.96, 149.69, 139.96, 139.23, 135.33, 127.85, 127.63, 127.32, 127.11, 126.62, 123.24, 123.19, 115.51 (t, $J = 240.2$ Hz), 112.87, 80.43 (t, $J = 5.9$ Hz), 55.27, 54.37, 48.08, 43.82 (t, $J = 21.8$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -113.48 (dt, $J = 55.6, 15.4$ Hz). HRMS (ESI): m/z calcd. for $\text{C}_{25}\text{H}_{25}\text{F}_2\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 423.1879, found: 423.1896.

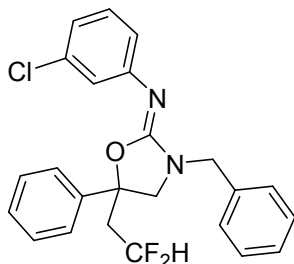
**3-benzyl-N-(2-chlorophenyl)-5-(2,2-difluoroethyl)-5-phenyloxazolidin-2-imine
(4ae)**



Light yellow oil, 25% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.42 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.38 – 7.29 (m, 8H), 7.24 – 7.18 (m, 4H), 7.00 (td, $J = 7.5, 1.5$ Hz, 1H), 5.86 (tt, $J = 55.5, 4.5$ Hz, 1H), 4.72 (d, $J = 14.5$ Hz, 1H), 4.56 (d, $J = 15.0$ Hz, 1H), 3.71 (d, $J = 9.0$ Hz, 1H), 3.55 (d, $J = 8.5$ Hz, 1H), 2.61 – 2.45 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 151.40, 145.10, 140.98, 136.02, 129.49, 128.88, 128.76, 128.41, 128.33, 127.92, 127.84, 127.02, 124.49, 124.16, 123.24, 116.50 (t, $J = 240.66$ Hz), 81.75 (t, J

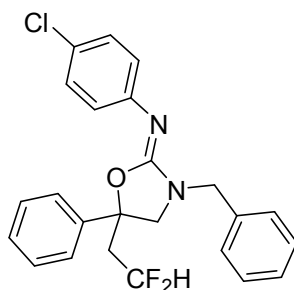
= 6.3 Hz), 56.50, 49.03, 44.87 (t, $J = 21.4$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -114.10 – -114.36 (m). HRMS (ESI): m/z calcd. for $\text{C}_{24}\text{H}_{22}\text{ClF}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 427.1383, found: 427.1378.

3-benzyl-N-(3-chlorophenyl)-5-(2,2-difluoroethyl)-5-phenyloxazolidin-2-imine (4af)



Light yellow oil, 50% yield ^1H NMR (500 MHz, CDCl_3) δ 7.41 – 7.37 (m, 2H), 7.36 – 7.29 (m, 4H), 7.28 – 7.26 (m, 2H), 7.26 – 7.24 (m, 2H), 7.23 – 7.20 (m, 2H), 7.10 – 6.99 (m, 2H), 5.79 (tt, $J = 55.5, 5.0$ Hz, 1H), 4.65 (d, $J = 15.0$ Hz, 1H), 4.52 (d, $J = 15.0$ Hz, 1H), 3.67 (d, $J = 9.0$ Hz, 1H), 3.56 (d, $J = 9.0$ Hz, 1H), 2.63 – 2.48 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 151.53, 148.77, 140.71, 136.08, 134.00, 129.60, 129.08, 128.85, 128.62, 128.21, 127.91, 124.26, 123.93, 122.23, 121.99, 116.52 (t, $J = 240.2$ Hz), 82.00 (t, $J = 6.2$ Hz), 56.27, 49.03, 44.94 (t, $J = 22.2$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -113.61 (dt, $J = 55.3, 15.4$ Hz). HRMS (ESI): m/z calcd. for $\text{C}_{24}\text{H}_{22}\text{ClF}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 427.1383, found: 427.1394.

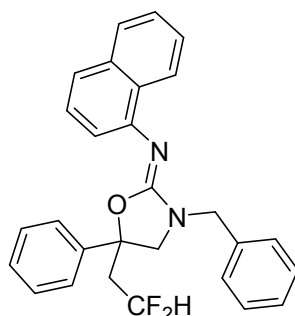
3-benzyl-N-(4-chlorophenyl)-5-(2,2-difluoroethyl)-5-phenyloxazolidin-2-imine (4ag)



Light yellow solid, 71% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.40 – 7.36 (m, 2H), 7.36 – 7.32 (m, 2H), 7.31 – 7.29 (m, 2H), 7.28 – 7.27 (m, 2H), 7.26 – 7.24 (m, 3H), 7.24 – 7.23 (m, 1H), 7.16 – 7.13 (m, 2H), 5.78 (tt, $J = 55.5, 5.0$ Hz, 1H), 4.66 (d, $J =$

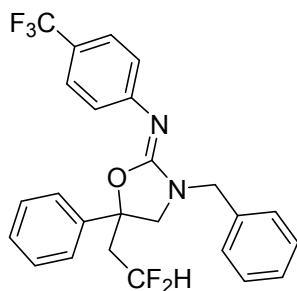
15.0 Hz, 1H), 4.52 (d, $J = 15.0$ Hz, 1H), 3.66 (d, $J = 9.0$ Hz, 1H), 3.54 (d, $J = 8.5$ Hz, 1H), 2.62 – 2.47 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 156.72, 151.27, 145.79, 140.67, 136.03, 128.99, 128.75, 128.57, 128.53, 128.13, 127.81, 127.19, 124.82, 124.16, 116.42 (t, $J = 240.2$ Hz), 81.80 (t, $J = 5.8$ Hz), 56.24, 49.03, 44.91 (t, $J = 21.8$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -114.06 (dt, $J = 55.6, 15.4$ Hz). HRMS (ESI): m/z calcd. for $\text{C}_{24}\text{H}_{22}\text{ClF}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 427.1383, found: 427.1392

3-benzyl-5-(2,2-difluoroethyl)-N-(naphthalen-1-yl)-5-phenyloxazolidin-2-imine (4ah)



Light yellow oil, 45% yield. ^1H NMR (500 MHz, CDCl_3) δ 8.22 – 8.20 (m, 1H), 7.76 – 7.74 (m, 1H), 7.49 – 7.47 (m, 1H), 7.40 – 7.34 (m, 3H), 7.28 – 7.27 (m, 4H), 7.26 – 7.24 (m, 2H), 7.23 – 7.16 (m, 3H), 7.13 – 7.11 (m, 2H), 5.69 (tt, $J = 55.5, 5.0$ Hz, 1H), 4.73 (d, $J = 15.0$ Hz, 1H), 4.61 (d, $J = 14.5$ Hz, 1H), 3.51 (d, $J = 9.0$ Hz, 1H), 3.64 (d, $J = 9.0$ Hz, 1H), 2.51 – 2.35 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 150.01, 142.58, 140.01, 135.27, 133.32, 128.55, 127.81, 127.74, 127.32, 127.11, 126.73, 126.68, 125.00, 124.58, 123.77, 123.24, 123.16, 121.13, 116.52, 115.44 (t, $J = 240.0$ Hz), 80.53 (t, $J = 5.8$ Hz), 55.41, 48.17, 43.79 (t, $J = 21.8$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -114.26 – -114.51 (m). HRMS (ESI): m/z calcd. for $\text{C}_{28}\text{H}_{25}\text{F}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 443.1929, found: 443.1932.

3-benzyl-5-(2,2-difluoroethyl)-5-phenyl-N-(4-(trifluoromethyl)phenyl)oxazolidin-2-imine (4ai)



Light yellow solid, 58% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.56 (d, J = 8.0 Hz, 2H), 7.41 – 7.37 (m, 2H), 7.37 – 7.34 (m, 1H), 7.34 – 7.30 (m, 3H), 7.29 – 7.26 (m, 4H), 7.25 – 7.23 (m, 2H), 5.78 (tt, J = 55.5, 5.0 Hz, 1H), 4.69 (d, J = 14.5 Hz, 1H), 4.56 (d, J = 15.0 Hz, 1H), 3.69 (d, J = 9.0 Hz, 1H), 3.59 (d, J = 9.0 Hz, 1H), 2.63 – 2.48 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 151.63, 150.73 (d, J = 1.8 Hz), 140.59, 135.94, 129.08, 128.84, 128.65, 128.18, 127.93, 125.86 (q, J = 4.0 Hz), 124.19, 123.66, 116.42 (t, J = 240.2 Hz), 82.08 (t, J = 6.3 Hz), 56.24, 49.04, 44.96 (t, J = 22.3 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -61.50 (s), -113.61 (dt, J = 55.6, 15.8 Hz). HRMS (ESI): m/z calcd. for $\text{C}_{25}\text{H}_{22}\text{F}_5\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 461.1647, found: 461.1655.

6. Luminescence Quenching Experiments

Instrument

Model: Agilent Cary Eclipse FL Spectrophotometer

Instrument parameters

Measurement type: Wavelength scan

Scan mode: Emission Data mode: Fluorescence

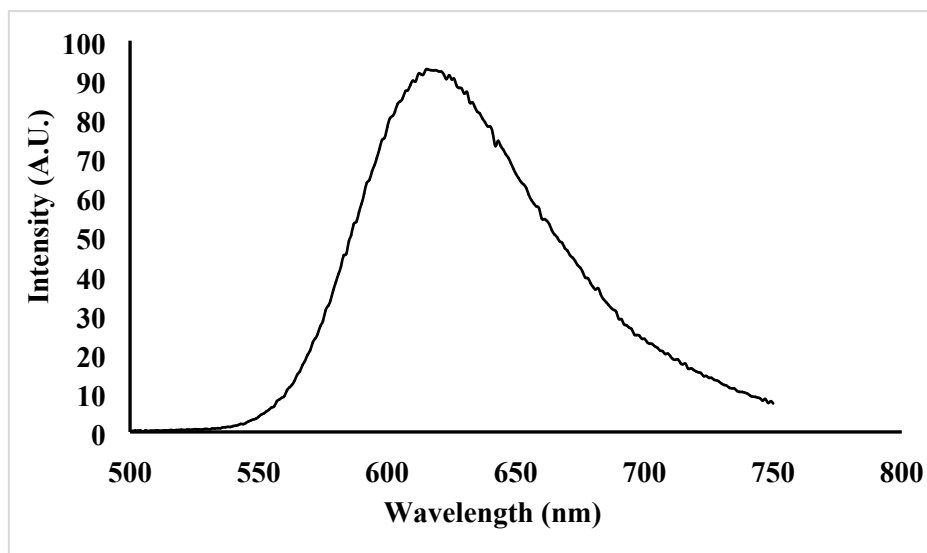
EX WL: 455.0 nm

EM Start WL: 500.0 nm

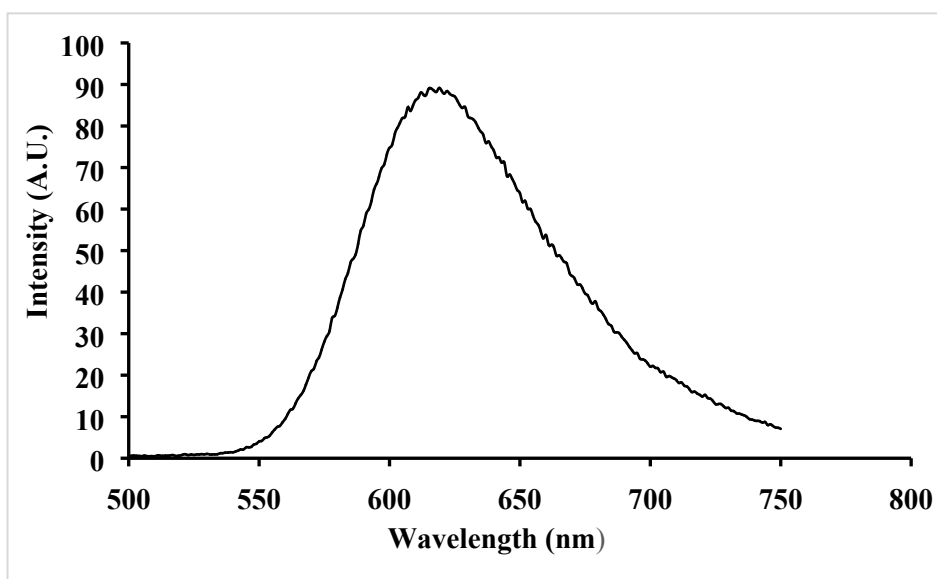
EM End WL: 750.0 nm

I_0 is the luminescence intensity without the quencher, I is the intensity with the quencher.

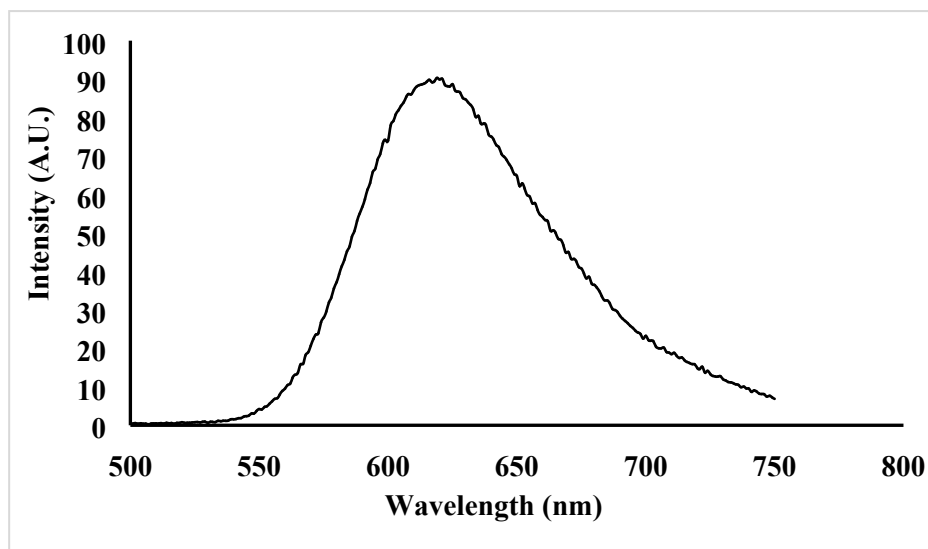
According to our group's previous work, we choose 5.0×10^{-5} mol/L catalyst to perform all the fluorescence quenching experiment.⁷



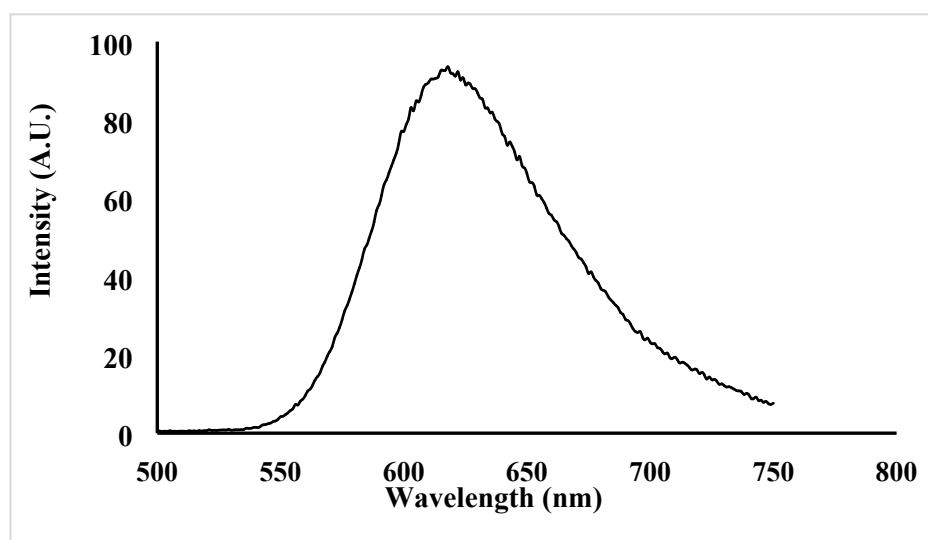
Fluorescence-emission of a 5.0×10^{-5} M solution of $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (without the quencher) in DMF, $I_0 = 92.6$



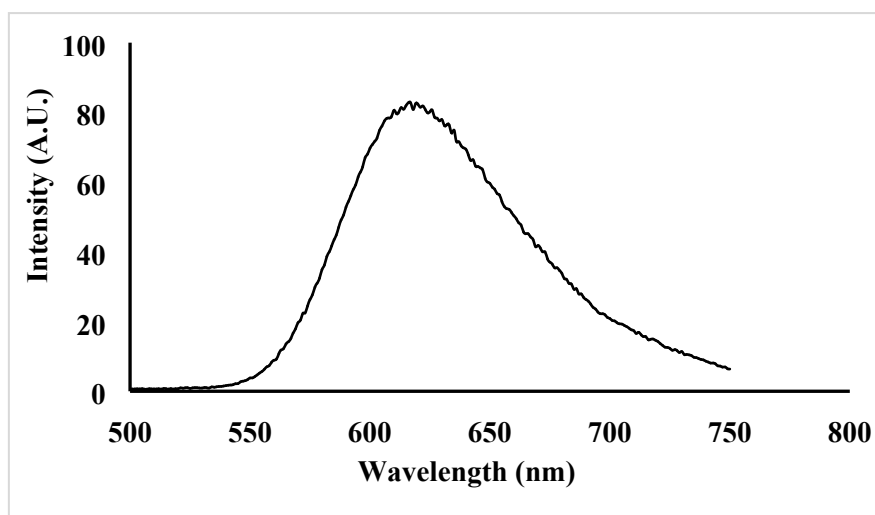
Fluorescence-emission of a solution of $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (5.0×10^{-5} M) with **1a** (1.0×10^{-3} M) in DMF, $I = 89.0$



Fluorescence-emission of a solution of $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (5.0×10^{-5} M) with difluoromethyl sulfone **2** (1.2×10^{-3} M) in DMF, I = 90.3



Fluorescence-emission of a solution of $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (5.0×10^{-5} M) with 1-isocyanato-4-methylbenzene **3a** (2.5×10^{-3} M) in DMF, I = 93.6



Fluorescence-emission of a solution of $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (5.0×10^{-5} M) with DABCO (2.0×10^{-3} M) in DMF, $I = 82.8$

Table S1. Luminescence Quenching Experiment Results

Entry	Sample	Relative luminescence intensity
1	$\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (5×10^{-5} M)	$I_0 = 1$
2	$\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (5×10^{-5} M) + 1a (1×10^{-3} M)	$I_0/I = 1.04$
3	$\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (5×10^{-5} M) + 2 (1.2×10^{-3} M)	$I_0/I = 1.03$
4	$\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (5×10^{-5} M) + 3a (2.5×10^{-3} M)	$I_0/I = 1.00$
5	$\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (5×10^{-5} M) + DABCO (2×10^{-3} M)	$I_0/I = 1.12$

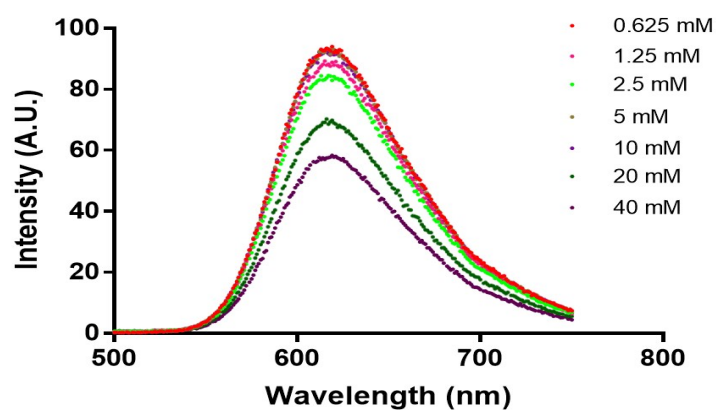


Figure S1 Quenching effect of DABCO with different concentration on photocatalysts

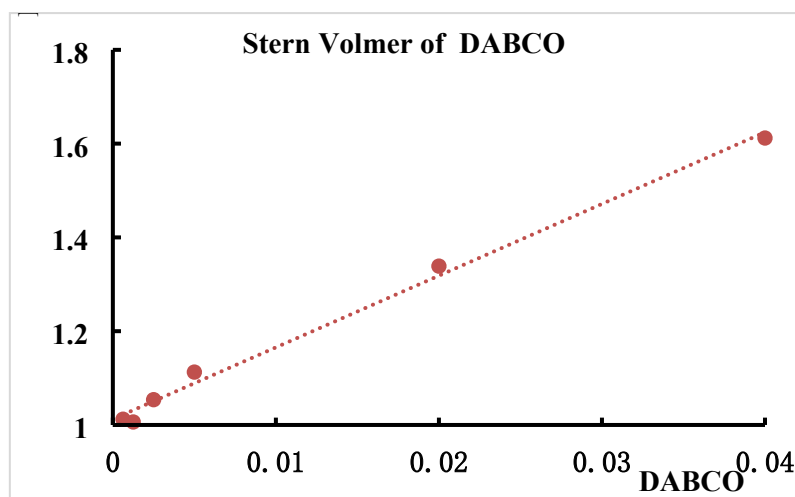


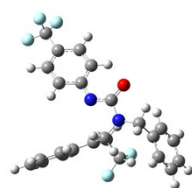
Figure S2 Stern Volmer of DABCO

As shown in Table S1, there was no obvious change in luminescence intensity when N-benzyl-2-phenylprop-2-en-1-amine **1a**, difluoromethyl sulfone **2** and 1-isocyanato-4-methylbenzene **3a** was used as a quencher to $[\text{Ru}]^*$ (Table S1, entries 2–4). And emission quenching of $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ should proceed with DBACO (entry 5) prior to substrate **1a**. In addition, fluorescence quenching effect is positively correlated with the concentration of DABCO (Figure S1 and Figure S2). Thus, we preferred that the single-electron transfer between $[\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}]^*$ and DABCO was the key initial step.

7. The energy level gaps coordinate data of intermediates B_{ai} and C_{ai}

Table S2 the energy level gaps of intermediate of B_{ai} and C_{ai}

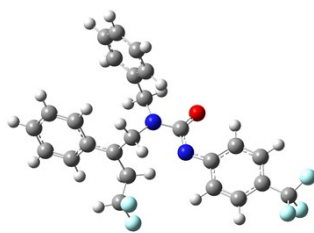
intermediate	Energy level gaps(eV)		
	HOMO-LUMO	HOMO-LUMO+1	HOMO-LUMO+2
B_{ai}	4.079	4.109	4.197
C_{ai}	4.235	4.279	4.415



B_{ai}

atom	x	y	z
C	-2.23018	-1.58702	-0.21844
C	-2.15166	-2.98008	-0.08776
C	-3.31693	-3.75626	-0.14787
C	-4.5607	-3.13938	-0.33875
C	-4.63921	-1.7463	-0.46954
C	-3.47394	-0.97012	-0.40933
H	-1.202	-3.45107	0.0579
H	-3.25701	-4.8199	-0.04803
H	-5.58883	-1.27529	-0.61536
H	-3.53386	0.09355	-0.50907
C	-5.84122	-3.99234	-0.40477
N	-1.00795	-0.77274	-0.15526
C	0.14031	-1.34161	0.02187
O	0.22121	-2.76306	0.15566
N	1.362	-0.52655	0.08573
C	2.50004	-1.30849	-0.41849
H	2.35082	-1.89103	0.46655
H	2.86144	-0.33449	-0.67464
C	4.0015	-1.52646	-0.15476
C	4.50315	-1.43911	1.15084
C	4.86611	-1.81206	-1.22002
C	5.86941	-1.63741	1.39127
H	3.84295	-1.22099	1.96414
C	6.23244	-2.01028	-0.97958
H	4.48308	-1.87877	-2.21689
C	6.73408	-1.92294	0.32607
H	6.25238	-1.57079	2.38816
H	6.89267	-2.2283	-1.79288

H	7.77729	-2.07428	0.50965
C	1.19109	0.67789	-0.73948
H	2.08022	1.27136	-0.69282
H	1.00595	0.39201	-1.75382
C	-0.00122	1.49697	-0.21123
C	-1.1809	0.78431	0.47583
H	-0.82877	-0.10245	0.96018
H	-1.91529	0.52274	-0.25708
C	-1.81043	1.7244	1.52059
H	-1.07606	1.98591	2.25353
F	-2.84468	1.09973	2.12278
F	-2.2546	2.84324	0.90951
C	-0.01402	3.02868	-0.37
C	0.53527	3.84149	0.63078
C	-0.57498	3.6097	-1.51525
C	0.52347	5.23535	0.48636
H	0.96364	3.39782	1.50515
C	-0.58673	5.00358	-1.65972
H	-0.99433	2.98905	-2.27935
C	-0.03754	5.81639	-0.65888
H	0.94282	5.85596	1.25051
H	-1.015	5.44723	-2.53418
H	-0.04656	6.88064	-0.76912
F	-5.68425	-5.09906	0.35222
F	-6.88517	-3.27357	0.06002
F	-6.07676	-4.35212	-1.68445



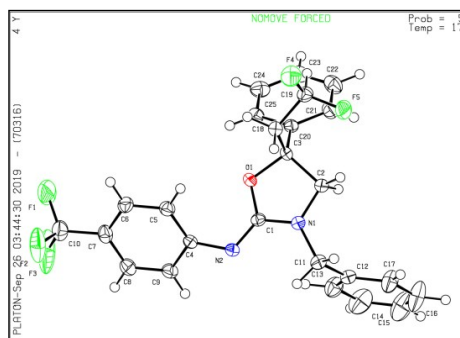
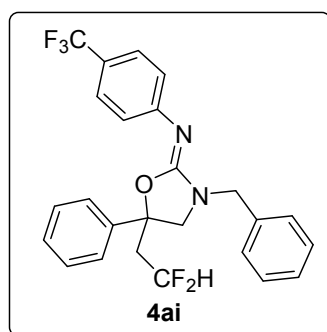
C_{ai}

atom	x	y	z
C	-2.45624	-1.32227	-0.28423
C	-3.84251	-1.29888	-0.08186
C	-4.56718	-2.48843	0.02617
C	-3.9167	-3.71748	-0.0903
C	-2.5162	-3.75813	-0.22209
C	-1.77851	-2.55643	-0.30636
H	-4.35127	-0.36099	-0.01113
H	-5.62348	-2.45755	0.19377
H	-2.01174	-4.70195	-0.2627
H	-0.7128	-2.58723	-0.39735
C	-4.75479	-5.01249	-0.07839
N	-1.77129	-0.02629	-0.48526
C	-1.62776	0.96795	0.59813
O	-2.65435	1.60571	0.94429
N	-0.36197	1.27842	1.28805
C	-0.49314	2.69642	1.70366
C	0.80927	1.00639	0.42193
C	1.79835	-0.1768	0.24234
C	1.21763	-1.59855	0.19194
C	2.1662	-2.52083	-0.59597
F	2.01796	-3.47212	0.35016
F	2.99713	-3.32858	-1.28754

H	2.94552	-1.77072	-0.52457
H	1.11207	-1.97597	1.18305
H	0.25619	-1.57272	-0.28482
H	1.40102	1.26145	1.27901
H	0.14961	0.24859	0.06232
H	-1.22429	2.74592	2.48256
H	0.44677	3.05643	2.0655
C	3.33764	-0.04725	0.13636
C	3.95395	0.16409	-1.10425
C	4.12914	-0.17286	1.29379
C	5.35527	0.18402	-1.19994
H	3.35719	0.30481	-1.97902
C	5.52917	-0.16052	1.19565
H	3.66396	-0.28697	2.25049
C	6.14144	0.00553	-0.05354
H	5.82398	0.33349	-2.15049
H	6.12914	-0.28067	2.0732
H	7.20856	-0.0034	-0.13154
C	-0.99757	3.58958	0.54035
C	-2.38636	3.66051	0.33053
C	-0.13462	4.32939	-0.28382
C	-2.91671	4.48416	-0.66836
H	-3.04482	3.07966	0.94202
C	-0.67186	5.17018	-1.27946
H	0.9239	4.26236	-0.15376
C	-2.06142	5.24901	-1.46652
H	-3.976	4.52918	-0.81983
H	-0.02088	5.75395	-1.89617
H	-2.46796	5.89368	-2.21966

F	-4.14883	-5.94947	-0.83824
F	-4.87345	-5.46628	1.18751
F	-5.9812	-4.75316	-0.57955

8. X-ray crystal structure analysis of 4ai:



Crystal data and structure refinement for 190925_bk_4_94a_0m.

Bond precision: C-C = 0.0040 Å

Wavelength=0.71073

Cell: α =8.6898(10)

β =11.1725(11)

γ =12.0639(13)

α =76.082(4)

β =73.273(4)

γ =77.314(4)

Temperature: 170 K

Table S3 Datablock for 190925_bk_4_94a_0m

	Calculated	Reported
Volume	1074.4(2)	1074.4(2)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C25 H21 F5 N2 O	C25 H21 F5 N2 O
Sum formula	C25 H21 F5 N2 O	C25 H21 F5 N2 O
Mr	460.44	460.44
Dx, g cm ⁻³	1.423	1.423
Z	2	2
Mu (mm ⁻¹)	0.117	0.117
F000	476.0	476.0
F000'	476.31	
h,k,lmax	10,13,15	10,13,15
Nref	4403	4333
Tmin, Tmax	0.966, 0.973	0.570, 0.745
Tmin'	0.966	

9. Reference

- [1] N. Scalacci, G. W. Black, G. Mattedi, N. L. Brown, N. J. Turner and D. Castagnolo, *ACS. Catal.*, 2017, **7**, 1295-1300.
- [2] J. Barluenga, F. J. Fananas, R. Sanz, C. Marcos and J. M. Ignacio, *Chem. Commun.*, 2005, 933-935.
- [3] A. Cabre, G. Sciortino, G. Ujaque, X. Verdaguer, A. Lledos and A. Riera, *Org. Lett.*, 2018, **20**, 5747-5751.
- [4] C. B. Tripathi and S. Mukherjee, *Angew. Chem., Int. Ed.*, 2013, **52**, 8450-8453.
- [5] J. Nan, Z. Zuo, L. Luo, L. Bai, H. Zheng, Y. Yuan, J. Liu, X. Luan and Y. Wang, *J. Am. Chem. Soc.*, 2013, **135**, 17306-17309.
- [6] J. Rong, L. Deng, P. Tan, C. Ni, Y. Gu and J. Hu, *Angew. Chem., Int. Ed.*, 2016, **55**, 2743-2747.
- [7] J. Wei, D. Gu, S. Wang, J. Hu, X. Dong and R. Sheng, *Org. Chem. Front.*, 2018, **5**, 2568-2572.

10. Copies of NMR spectra.

