Supplementary Information

Enantioselective radical C-H amination for the synthesis of β-amino alcohols

Kohki M. Nakafuku†, Zuxiao Zhang†, Ethan A. Wappes†
Leah M. Stateman, Andrew D. Chen, David A. Nagib*

The Ohio State University, Department of Chemistry and Biochemistry, Columbus, OH, USA
*Correspondence to: nagib.1@osu.edu; †Equal contributions
| Section | Page |
|---------|------|
| I. General Information | S3 |
| II. General Procedure | S4 |
| III. Optimization for Enantioselective, Radical C-H Amination | S6 |
| IV. Synthesis of Catalysts and Ligand | S7 |
| V. Synthesis of Oxime Imidates | S8 |
| VI. Enantioselective, Radical C-H Amination of Alcohols | S25 |
| VII. Post-Functionalization of Oxazolines | S61 |
| VIII. Mechanistic Experiments | S66 |
| a. Energy Transfer | S66 |
| b. Stern-Volmer Quenching Studies | S67 |
| c. Kinetic Isotope Effects (KIE) | S69 |
| d. Radical Clock Experiments | S70 |
| e. UV-vis Absorption Studies | S76 |
| IX. Computational Studies | S77 |
| X. References | S86 |
| XI. NMR Spectra | S88 |
I. General Information

All chemicals and reagents were purchased from Sigma-Aldrich, Alfa Aesar, Acros, TCI, or ChemImplex. Solvents were purified in the following manner. Acetonitrile and amine bases were distilled over calcium hydride. CH\textsubscript{2}Cl\textsubscript{2}, THF, Et\textsubscript{2}O, and DMF were degassed with N\textsubscript{2} and dried by passing through columns containing alumina, copper, or molecular sieves. Flash column chromatography, or preparative thin-layer chromatography, was performed with Silicycle F60 (230-400 mesh) silica gel. Thin layer chromatography (TLC) analyses were performed using EMD 60 F254 TLC plates and visualized by fluorescence quenching or KMnO\textsubscript{4} stain. All yields are averages of at least two experimental runs.

Nuclear magnetic resonance (NMR) spectra (\textsuperscript{1}H, \textsuperscript{13}C) were recorded using either a Bruker AVIII 400 or AVIII 600 MHz NMR spectrometer. \textsuperscript{1}H and \textsuperscript{13}C NMR chemical shifts are reported in parts per million and referenced to residual CHCl\textsubscript{3} signals in CDCl\textsubscript{3} (\textsuperscript{1}H: δ 7.26; \textsuperscript{13}C: δ 77.16), benzene in C\textsubscript{6}D\textsubscript{6} (\textsuperscript{1}H: δ 7.16; \textsuperscript{13}C: δ 128.06), or DMSO in DMSO-d\textsubscript{6} (\textsuperscript{1}H: δ 2.50); \textsuperscript{19}F chemical shifts are reported in ppm relative to CFCl\textsubscript{3} as the external standard. \textsuperscript{1}H NMR data are reported as follows: chemical shifts (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad, ap = apparent), coupling constant (Hz), relative integral. Data for \textsuperscript{13}C and \textsuperscript{19}F NMR are reported in terms of chemical shift and multiplicity where appropriate. High-resolution Mass Spectrometry (HRMS) data were obtained using Bruker MicrOTOF (ESI). Infrared (IR) spectra were recorded using a Thermo Fisher Nicolet iS10 FT-IR and are reported in terms of frequency of absorption (cm\textsuperscript{-1}).

High Pressure Liquid chromatography (HPLC) was performed on an Agilent InfinityLab LC Series 1260 Infinity II Quaternary System using a chiral column (25 cm) and guard column (5 cm) as noted for each compound. Optical rotations were recorded on a Perkin-Elmer Model 241 polarimeter at Mercury 578nm.

Photochemical reactions were performed by placing reaction vessels approximately 10 cm away from one 90 W blue LED lamp (Kessil A360WE tuna blue) or two 45 W blue LED lamps (Kessil A160WE tuna blue). The temperature of the reaction was maintained at approximately 25 °C with a fan. The reaction set-ups can be seen below. Photochemical reactions with UV light were performed using a Rayonet RPR-100 Photochemical Reactor with 300 nm bulbs.
II. General Procedure

General Procedure 1 (GP1)

To a flame-dried round bottom flask equipped with a stir bar was added alcohol (2 mmol, 1.0 equiv) and dry THF (20 mL). NaH (60% dispersion in mineral oil, 3.0 mmol, 1.5 equiv) was carefully added to the stirring dispersion. The mixture was allowed to stir for 1 hour at room temperature. Imidoyl chloride (2.2 mmol, 1.1 equiv) was added and the resulting solution was stirred until full consumption of alcohol. Upon completion, silica gel was added to quench the reaction, then the solvent was removed by vacuum. The residue was purified by column chromatography to afford the corresponding oxime in 80-99% yield.

General Procedure 2 (GP2)

To a flame-dried round bottom flask equipped with a stir bar was added alcohol (2 mmol, 1.0 equiv), PPh₃ (2.4 mmol, 1.2 equiv), and dry THF (20 mL). DIAD (2.4 mmol, 1.2 equiv) was carefully added, followed by portion-wise addition of amide (2.4 mmol, 1.2 equiv). The resulting solution was stirred until full consumption of alcohol. Upon completion, silica gel was added to quench the reaction and the solvent was removed by vacuum. The residue was purified by column chromatography to afford the corresponding oxime imidate in 50-99% yield.
General Procedure 3 (GP3)

To an oven-dried 2-dram vial equipped with a stir bar was added imidate (0.1 mmol) and (1R,3S)-(+-)camphoric acid (0.025 mmol, 0.25 equiv). After the vial was transferred into a glovebox, 1 mL of a 0.002M solution of L1•CuBArF4 (2 mol%) in Et2O and 1 mL of a 0.001M solution of Ir1 (1 mol%) in Et2O were added. After diluting with 4 mL of pentane, the vial was then sealed with parafilm and removed from the glovebox. The reaction was irradiated with a 455 nm blue LED for 1 hour. Two fans were employed to cool the reaction setup. Upon completion, the reaction was concentrated and the crude oxazoline was loaded directly onto silica gel and purified by column chromatography. Enantioselectivity was determined by HPLC analysis of the purified oxazoline product.

Catalyst solutions:

**L1•CuBArF4:** To an oven-dried 20 mL vial equipped with a stir bar was added L1 (0.08 mmol, 2.0 eq) and Cu(MeCN)4BArF4 (0.04 mmol, 1 equiv) in a glove box. Et2O (20 mL) was added and stirred at 23 °C for 1 hour to afford the title solution.

**Ir1:** To an oven-dried 20 mL vial was added [Ir(dF(CF3)ppy)2(dtbbpy)] BArF4 (0.02 mmol, 36 mg) in a glove box. Et2O (20 mL) was then added to afford the title solution.

Notes:

1. Both pentane and Et2O were purified by solvent system and then transferred in glovebox and stored with pre-activated 4Å molecular sieves.

2. L1•CuBArF4 can be generated outside of the glovebox using Schlenk technique and solvent degassed using a freeze-pump-thaw technique.

3. If the oxazoline product co-elutes with phenol byproduct, after column chromatography the material was dissolved in 20 mL EtOAc and then washed with 1 M NaOH, water, and brine sequentially. The organic phase was then dried over Na2SO4 and concentrated to afford the pure oxazoline.

4. Racemic samples were prepared from a 50:50 mixture of enantiopure catalysts, since smaller, achiral ligands are less efficient for this C-H amination.
III. Optimization of Enantioselective, Radical C-H Amination

Table 1. Reaction optimization.

| entry | CuX          | Ligand | co-catalyst | solvent          | results<sup>a</sup> |
|-------|--------------|--------|-------------|------------------|--------------------|
| 1     | Cu(OTf)<sub>2</sub> | L2     | AcOH        | benzene : DMac = 9:1 | 78%, 34%ee        |
| 2     | Cu(OTf)<sub>2</sub> | L2     | AcOH        | MeCN : DMac = 10.5 | 78%, 37%ee        |
| 3     | Cu(OTf)<sub>2</sub> | L2     | AcOH        | MeCN : DMac = 20:1 | 34%, 39%ee        |
| 4     | Cu(OTf)<sub>2</sub> | L2     | AcOH        | pentanes : EtO<sub>2</sub> = 2:1 | 42%, 61%ee        |
| 5     | Cu(OTf)<sub>2</sub> | L2     | (+)-CA      | pentanes : EtO<sub>2</sub> = 2:1 | 38%, 82%ee        |
| 6     | CuBar<sup>F</sup><sub>4</sub> | L2     | AcOH        | pentanes : EtO<sub>2</sub> = 2:1 | 68%, 56%ee        |
| 7     | CuBar<sup>F</sup><sub>4</sub> | L2     | (+)-CA      | pentanes : EtO<sub>2</sub> = 2:1 | 90%, 85%ee        |
| 8     | CuBar<sup>F</sup><sub>4</sub> | L1     | AcOH        | pentanes : EtO<sub>2</sub> = 2:1 | 75%, 83%ee        |
| 9     | CuBar<sup>F</sup><sub>4</sub> | L1     | (+)-CA      | pentanes : EtO<sub>2</sub> = 2:1 | 95%, 94%ee        |
| 10    | CuBar<sup>F</sup><sub>4</sub> | L1     | (+)-CA      | pentanes : EtO<sub>2</sub> = 2:1 | 94%, 92%ee        |
| 11    | Cu(OTf)<sub>2</sub> | L1     | (+)-CA      | pentanes : EtO<sub>2</sub> = 2:1 | 87%, 83%ee        |
| 12    | CuBar<sup>F</sup><sub>4</sub> | L1     | none        | pentanes : EtO<sub>2</sub> = 2:1 | 16%, 85%ee        |
| 13    | CuBar<sup>F</sup><sub>4</sub> | L1     | (+)-CA      | pentanes : EtO<sub>2</sub> = 2:1 | 20%, 0%ee         |
| 14<sup>c</sup> | CuBar<sup>F</sup><sub>4</sub> | L1     | (+)-CA      | pentanes : EtO<sub>2</sub> = 2:1 | 0%                |
| 15    | CuBar<sup>F</sup><sub>4</sub> | L1     | (-)-CA      | pentanes : EtO<sub>2</sub> = 2:1 | 93%, 93%ee        |
| 16    | CuBar<sup>F</sup><sub>4</sub> | L1     | adamantyl acid | pentanes : EtO<sub>2</sub> = 2:1 | 84%, 92%ee        |
| 17    | CuBar<sup>F</sup><sub>4</sub> | L1     | phosphoric acid | pentanes : EtO<sub>2</sub> = 2:1 | 15%, 36%ee        |
| 18    | CuBar<sup>F</sup><sub>4</sub> | L1     | trifluoroacetic acid | pentanes : EtO<sub>2</sub> = 2:1 | 41%, 18%ee        |

<sup>a</sup> Reactions were run with 0.05 mmol of 1a, <sup>1</sup>H NMR yield based on S1 using N,N-dimethyl-2,2,2-trifluoroacetamide as the internal standard. <sup>b</sup> Using Ir1•PF<sub>6</sub> instead of Ir1•Bar<sup>F</sup><sub>4</sub>. <sup>c</sup> without Ir photoredox catalyst.
IV. Synthesis of Catalysts and Ligand

Synthesis of Cu(MeCN)₂BArF₄
Cu(II)Cl (100 mg, 1.0 mmol, 1 equiv) and NaBArF₄ (985 mg, 1.1 mmol, 1.1 equiv) were dissolved in freshly distilled MeCN (50 mL) and stirred at room temperature for 1 h. The crude mixture was filtered through 0.45 µm nylon membrane Millipore filters. The resulting solution was concentrated under the flow of N₂ and dried under reduced pressure to give the titled compound as a white solid (1.09 g, quant.).

Synthesis of (Ir[dF(CF₃)ppy]₂(dtbbpy))BArF₄
In an oven dried 2 dram vial equipped with PTFE septa cap, [Ir(dF(CF₃)ppy)₂Cl]₂ (74 mg, 0.05 mmol, 1 equiv) and 4,4''-di-tert-butyl-2,2''-dipyridyl (34 mg, 0.125 mmol, 2.5 equiv) were added. The vial was then evacuated and refilled three times with N₂. Ethylene glycol (3 mL) was then added via syringe. The reaction mixture was then heated to 150 °C for 16 h. After this time the flask was allowed to return to room temperature. The mixture was diluted in water (10 mL) and hexane (10 mL). The aqueous phase was then separated and then re-extracted with hexane (2 x 10 mL). The aqueous phase was transferred to a flask that was heated at 80 °C for 1 hour to remove residual hexane. The flask was allowed to return to room temperature, and NaBArF₄ (266 mg, 0.3 mmol, 6 equiv) was added with stirring, and a vibrant yellow precipitate was formed. Ethyl acetate was added to dissolve the solid, and the organic phase was washed with water. Then, the organic layer was dried with MgSO₄, filtered, evaporated under reduced pressure. The crude material was loaded onto silica gel and purified (CH₂Cl₂ to 10% acetone in CH₂Cl₂) to yield the (Ir[dF(CF₃)ppy]₂(dtbbpy))BArF₄ as a bright yellow solid.

Synthesis of BOX-ligand (S,S)-L₁
Following reported procedure with slight modification:²³ Di-²Pr malononitrile (2.0 mmol, 1.0 equiv) was dissolved in PhMe (30 mL) and to the solution was added (S)-2-phenyl glycinol (5.0 mmol, 2.5 equiv), and Zn(OTf)₂ (5.0 mmol, 2.5 equiv). The reaction mixture was sealed and heated at 145 °C for 48 h. The reaction mixture was cooled to ambient temperature and quenched with sat. Na₂CO₃ (30 mL). After extraction with CH₂Cl₂ (100 mL x 1, 50 mL x 3), the combined organic layer was dried over Na₂SO₄, concentrated, and loaded onto silica gel and purified (hexane/ethyl acetate = 9:1) to afford the ligand (S,S)-L₁.

The enantiomer, (R,R)-L₁, was synthesized by the same protocol utilizing (R)-2-phenyl glycinol.

¹H NMR (600 MHz, CDCl₃) δ 7.35 – 7.31 (m, 4H), 7.29 – 7.24 (m, 6H), 5.24 (dd, J = 10.1, 8.1 Hz, 2H), 4.66 (dd, J = 10.2, 8.4 Hz, 2H), 4.11 (t, J = 8.2 Hz, 2H), 2.16 – 2.02 (m, 4H), 1.41 – 1.30 (m, 4H), 0.97 (t, J = 7.3 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 169.30 (s), 142.56 (s), 128.82 (s), 127.67 (s), 126.90 (s), 75.16 (s), 69.76 (s), 46.45 (s), 35.26 (s), 17.57 (s), 14.58 (s).

Absolute stereochemistry: The (S,S)-L₁ catalyst affords oxazoline (R)-1, which matches the HPLC trace of a sample independently synthesized from (R)-2-phenyl glycinol.
V. Synthesis of Oxime Imidates

**phenethyl N-phenoxybenzimidate (S1)**

![Chemical Structure]

Prepared following **GP1**. $^1$H NMR (600 MHz, C$_6$D$_6$) δ 7.78 – 7.70 (m, 2H), 7.43 (dt, $J = 9.1, 1.7$ Hz, 2H), 7.24 – 7.18 (m, 2H), 7.12 – 7.05 (m, 6H), 7.04 – 6.99 (m, 2H), 6.93 – 6.88 (m, 1H), 4.45 (t, $J = 6.9$ Hz, 2H), 2.81 (t, $J = 6.9$ Hz, 2H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 160.11 (s), 156.74 (s), 138.09 (s), 131.67 (s), 130.57 (s), 129.69 (s), 129.41 (s), 128.77 (s), 128.52 (s), 127.82 (s), 126.82 (s), 122.39 (s), 114.89 (s), 73.51 (s), 36.89 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 340.1308, found: 340.1303.

**4-fluorophenethyl N-phenoxybenzimidate (S2)**

![Chemical Structure]

Prepared following **GP1**. $^1$H NMR (600 MHz, C$_6$D$_6$) δ 7.73 (dd, $J = 7.9, 1.7$ Hz, 2H), 7.43 (dd, $J = 8.7, 1.0$ Hz, 2H), 7.25 – 7.18 (m, 2H), 7.12 – 7.04 (m, 3H), 6.97 – 6.89 (m, 1H), 6.82 – 6.67 (m, 4H), 4.34 (t, $J = 6.8$ Hz, 2H), 2.67 (t, $J = 6.8$ Hz, 2H). $^{19}$F NMR (565 MHz, C$_6$D$_6$) δ –116.43 (tt, $J = 8.3, 5.6$ Hz). $^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 162.25 (d, $J = 244.3$ Hz), 160.05 (s), 156.66 (s), 133.72 (d, $J = 3.2$ Hz), 131.54 (s), 130.85 (d, $J = 7.8$ Hz), 130.68 (s), 129.74 (s), 128.56 (s), 127.73 (s), 122.49 (s), 115.48 (d, $J = 21.2$ Hz), 114.85 (s), 73.29 (s), 35.92 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 358.1214, found: 358.1199.

**4-chlorophenethyl N-phenoxybenzimidate (S3)**

![Chemical Structure]

Prepared following **GP1**. $^1$H NMR (600 MHz, C$_6$D$_6$) δ 7.75 – 7.70 (m, 2H), 7.46 – 7.39 (m, 2H), 7.25 – 7.18 (m, 2H), 7.12 – 7.00 (m, 5H), 6.94 – 6.89 (m, 1H), 6.70 (d, $J = 8.2$ Hz, 2H), 4.31 (t, $J = 6.8$ Hz, 2H), 2.68 – 2.55 (m, 2H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 160.03 (s), 156.60 (s), 136.53 (s), 132.76 (s), 131.49 (s), 130.74 (s), 130.71 (s), 129.74 (s), 128.86 (s), 128.57 (s), 127.71 (s), 122.52 (s), 114.84 (s), 73.05 (s), 36.03 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 374.0918, found: 374.0912.

**4-bromophenethyl N-phenoxybenzimidate (S4)**

![Chemical Structure]

Prepared following **GP1**. $^1$H NMR (600 MHz, C$_6$D$_6$) δ 7.73 – 7.69 (m, 2H), 7.42 (dt, $J = 9.0, 1.7$ Hz, 2H), 7.25 – 7.18 (m, 4H), 7.12 – 7.05 (m, 3H), 6.95 – 6.89 (m, 1H), 6.63 (d, $J = 8.2$ Hz, 2H), 4.31 (t, $J = 6.8$ Hz, 2H), 2.59 (t, $J = 6.8$ Hz, 2H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 160.02 (s), 156.60 (s), 137.00 (s), 131.48 (s), 131.11 (s), 130.71 (s), 129.75 (s), 128.57 (s), 127.70 (s), 122.52 (s), 120.81 (s), 114.84 (s), 72.97 (s), 36.08 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 418.0413, found: 418.0410.
4-iodophenethyl N-phenoxybenzimidate (S5)

Prepared following GP1. $^1$H NMR (600 MHz, C$_6$D$_6$) $\delta$ 7.74 – 7.68 (m, 2H), 7.46 – 7.36 (m, 4H), 7.25 – 7.18 (m, 2H), 7.13 – 7.06 (m, 3H), 6.95 – 6.89 (m, 1H), 6.51 (d, $J = 8.0$ Hz, 2H), 4.30 (t, $J = 6.8$ Hz, 2H), 2.58 (t, $J = 6.8$ Hz, 2H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) $\delta$ 160.01 (s), 156.60 (s), 137.83 (s), 137.64 (s), 131.47 (s), 131.38 (s), 129.74 (s), 128.57 (s), 127.71 (s), 122.51 (s), 114.84 (s), 92.12 (s), 72.97 (s), 36.19 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 466.0274, found: 466.0265.

4-methylphenethyl N-phenoxybenzimidate (S6)

Prepared following GP1. $^1$H NMR (600 MHz, C$_6$D$_6$) $\delta$ 7.79 – 7.75 (m, 2H), 7.47 – 7.41 (m, 2H), 7.23 – 7.18 (m, 2H), 7.13 – 7.05 (m, 3H), 7.00 – 6.93 (m, 4H), 6.93 – 6.89 (m, 1H), 4.48 (t, $J = 6.9$ Hz, 2H), 2.84 (t, $J = 6.9$ Hz, 2H), 2.11 (s, 3H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) $\delta$ 160.14 (s), 156.78 (s), 136.12 (s), 135.00 (s), 131.74 (s), 130.55 (s), 129.69 (s), 129.48 (s), 128.50 (s), 127.85 (s), 122.36 (s), 114.90 (s), 73.74 (s), 36.53 (s), 21.03 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 354.1465, found: 354.1460.

4-methoxyphenethyl N-phenoxybenzimidate (S7)

Prepared following GP1. $^1$H NMR (600 MHz, C$_6$D$_6$) $\delta$ 7.82 – 7.76 (m, 2H), 7.47 – 7.42 (m, 2H), 7.23 – 7.18 (m, 2H), 7.13 – 7.05 (m, 3H), 6.99 – 6.94 (m, 2H), 6.91 (tt, $J = 7.4$, 1.1 Hz, 1H), 6.74 (d, $J = 8.7$ Hz, 2H), 4.46 (t, $J = 6.9$ Hz, 2H), 3.31 (s, 3H), 2.82 (t, $J = 6.9$ Hz, 2H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) $\delta$ 160.14 (s), 156.82 (s), 131.74 (s), 130.57 (s), 130.38 (s), 129.90 (s), 129.70 (s), 128.53 (s), 127.85 (s), 122.37 (s), 114.90 (s), 114.34 (s), 73.84 (s), 54.81 (s), 36.08 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 370.1414, found: 370.1404.

4-(trifluoromethyl)phenethyl N-phenoxybenzimidate (S8)

Prepared following GP1. $^1$H NMR (600 MHz, C$_6$D$_6$) $\delta$ 7.68 (dt, $J = 3.9$, 2.3 Hz, 2H), 7.45 – 7.39 (m, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.24 – 7.19 (m, 2H), 7.09 (qd, $J = 5.9$, 2.7, 1.7 Hz, 3H), 6.92 (tt, $J = 7.4$, 1.1 Hz, 1H), 6.81 (d, $J = 8.0$ Hz, 2H), 4.31 (t, $J = 6.7$ Hz, 2H), 2.63 (t, $J = 6.7$ Hz, 2H). $^{19}$F NMR (565 MHz, C$_6$D$_6$) $\delta$ –62.09 (s). $^{13}$C NMR (151 MHz, C$_6$D$_6$) $\delta$ 159.97 (s), 156.82 (s), 131.74 (s), 130.57 (s), 130.38 (s), 129.90 (s), 129.70 (s), 128.53 (s), 127.85 (s), 122.37 (s), 114.90 (s), 114.34 (s), 73.84 (s), 54.81 (s), 36.08 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 408.1182, found: 408.1176.
4-(trifluoromethoxy)phenethyl N-phenoxybenzimidate (S9)

Prepared following GP2. $^1$H NMR (600 MHz, C$_6$D$_6$) δ 7.71 – 7.67 (m, 2H), 7.44 – 7.40 (m, 2H), 7.24 – 7.19 (m, 2H), 7.11 – 7.05 (m, 3H), 6.92 (tt, $J = 7.4$, 1.0 Hz, 1H), 6.86 (d, $J = 7.9$ Hz, 2H), 6.77 – 6.72 (m, 2H), 4.31 (t, $J = 6.7$ Hz, 2H), 2.62 (t, $J = 6.7$ Hz, 2H). $^{19}$F NMR (565 MHz, C$_6$D$_6$) δ –57.74 (s). $^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 160.01 (s), 156.60 (s), 148.29 (s), 136.98 (s), 131.42 (s), 130.74 (s), 130.70 (s), 129.76 (s), 128.56 (s), 127.69 (s), 122.56 (s), 121.28 (q, $J = 256.5$ Hz), 121.26 (s), 114.83 (s), 72.93 (s), 35.94 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 424.1131, found: 402.1298.

2-methylphenethyl N-phenoxybenzimidate (S10)

Prepared following GP1. $^1$H NMR (600 MHz, C$_6$D$_6$) δ 7.77 – 7.72 (m, 2H), 7.46 – 7.41 (m, 2H), 7.23 – 7.17 (m, 2H), 7.12 – 7.05 (m, 3H), 7.06 – 6.99 (m, 3H), 6.99 – 6.95 (m, 1H), 6.91 (t, $J = 7.3$ Hz, 1H), 4.51 – 4.34 (m, 2H), 2.88 (t, $J = 7.2$ Hz, 2H), 2.04 (s, 3H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 160.15 (s), 156.89 (s), 136.66 (s), 136.01 (s), 131.62 (s), 130.62 (s), 130.58 (s), 130.07 (s), 129.69 (s), 128.56 (s), 127.86 (s), 127.07 (s), 126.47 (s), 122.40 (s), 114.91 (s), 72.49 (s), 34.04 (s), 19.35 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 354.1465, found: 354.1459.

2-(trifluoromethyl)phenethyl N-phenoxybenzimidate (S11)

Prepared following GP1. $^1$H NMR (600 MHz, C$_6$D$_6$) δ 7.76 – 7.72 (m, 2H), 7.45 – 7.40 (m, 2H), 7.39 (d, $J = 7.8$ Hz, 1H), 7.23 – 7.18 (m, 2H), 7.12 – 7.05 (m, 4H), 6.95 (t, $J = 7.6$ Hz, 1H), 6.91 (tt, $J = 7.4$, 1.0 Hz, 1H), 6.79 (t, $J = 7.6$ Hz, 1H), 4.42 (t, $J = 6.8$ Hz, 2H), 3.13 (t, $J = 6.7$ Hz, 2H). $^{19}$F NMR (565 MHz, C$_6$D$_6$) δ –59.25 (s). $^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 160.06 (s), 156.73 (s), 136.73 (s), 136.57 (s), 132.26 (s), 131.90 (s), 131.33 (s), 130.66 (s), 129.70 (s), 129.14 (q, $J = 29.6$ Hz), 128.60 (s), 127.74 (s), 126.91 (s), 126.56 (q, $J = 5.7$ Hz), 125.28 (d, $J = 273.9$ Hz), 122.47 (s), 114.88 (s), 72.36 (s), 33.50 (s), 19.35 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 408.1182, found: 408.1161.

3-methoxyphenethyl N-phenoxybenzimidate (S12)

Prepared following GP1. $^1$H NMR (600 MHz, C$_6$D$_6$) δ 7.81 – 7.75 (m, 2H), 7.46 – 7.40 (m, 2H), 7.39 (d, $J = 7.8$ Hz, 1H), 7.23 – 7.17 (m, 2H), 7.12 – 7.03 (m, 4H), 6.91 (dd, $J = 10.8$, 3.9 Hz, 1H), 6.77 (d, $J = 1.7$ Hz, 1H), 6.70 (dd, $J = 7.9$, 2.0 Hz, 2H), 4.48 (t, $J = 6.9$ Hz, 2H), 3.30 (s, 3H), 2.83 (t, $J = 6.9$ Hz, 2H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 160.46 (s), 160.11 (s), 156.70 (s), 139.64 (s), 131.69 (s), 130.57 (s), 129.78 (s), 129.69 (s), 128.52 (s), 127.84 (s), 122.37 (s), 121.68 (s), 115.20 (s), 114.90 (s), 112.55 (s), 73.54 (s), 54.72 (s), 36.96 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 370.1414, found: 370.1401.
3-(trifluoromethyl)phenethyl (Z)-N-phenoxybenzimidate (S13)

Prepared following **GP1**. \(^1\)H NMR (600 MHz, C\(_6\)D\(_6\)) \(\delta\) 7.71 – 7.67 (m, 2H), 7.41 (dd, \(J = 8.7, 1.0\) Hz, 2H), 7.32 (s, 1H), 7.24 (d, \(J = 7.8\) Hz, 1H), 7.23 – 7.19 (m, 2H), 7.11 – 7.06 (m, 3H), 6.96 (d, \(J = 7.6\) Hz, 1H), 6.93 – 6.90 (m, 1H), 6.86 (t, \(J = 7.7\) Hz, 1H), 4.27 (t, \(J = 6.6\) Hz, 2H), 2.59 (t, \(J = 6.6\) Hz, 2H). \(^19\)F NMR (565 MHz, C\(_6\)D\(_6\)) \(\delta\) –62.21 (s).

**2,4-**dichlorophenethyl N-phenoxybenzimidate (S14)

Prepared following **GP1**. \(^1\)H NMR (600 MHz, C\(_6\)D\(_6\)) \(\delta\) 7.76 – 7.70 (m, 2H), 7.42 (dt, \(J = 9.1, 1.7\) Hz, 2H), 7.23 – 7.18 (m, 2H), 7.13 (d, \(J = 2.1\) Hz, 1H), 7.10 – 7.05 (m, 3H), 6.94 – 6.89 (m, 1H), 6.78 (dd, \(J = 8.2, 2.1\) Hz, 1H), 6.70 (d, \(J = 8.2\) Hz, 1H), 4.38 (t, \(J = 6.7\) Hz, 2H), 2.85 (t, \(J = 6.7\) Hz, 2H). \(^13\)C NMR (151 MHz, C\(_6\)D\(_6\)) \(\delta\) 160.01 (s), 156.55 (s), 139.99 (s), 156.42 (s), 139.28 (s), 132.72 (s), 131.39 (s), 130.97 (q, \(J = 31.9\) Hz), 130.73 (s), 129.74 (s), 129.14 (s), 128.57 (s), 127.64 (s), 126.17 (q, \(J = 3.7\) Hz), 124.98 (q, \(J = 272.3\) Hz), 123.65 (q, \(J = 3.8\) Hz), 122.55 (s), 114.82 (s), 72.72 (s), 36.34 (s). HRMS (ESI-TOF) \(m/z\) calcd for [M+Na]\(^+\) 408.1182, found: 408.1179.

**3,4-**dichlorophenethyl N-phenoxybenzimidate (S15)

Prepared following **GP1**. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.75 – 7.68 (m, 2H), 7.43 (dd, \(J = 8.8, 1.0\) Hz, 2H), 7.26 – 7.18 (m, 2H), 7.13 – 7.07 (m, 3H), 7.01 – 6.89 (m, 3H), 6.49 (dd, \(J = 8.2, 2.1\) Hz, 1H), 4.20 (t, \(J = 6.6\) Hz, 2H), 2.45 (t, \(J = 6.6\) Hz, 2H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 159.96 (s), 156.43 (s), 156.34 (s), 139.96 (s), 156.43 (s), 138.40 (s), 132.74 (s), 131.41 (s), 131.34 (s), 130.99 (s), 130.79 (s), 130.55 (s), 129.77 (s), 128.73 (s), 128.62 (s), 127.64 (s), 122.60 (s), 114.83 (s), 72.55 (s), 35.66 (s). HRMS (ESI-TOF) \(m/z\) calcd for [M+Na]\(^+\) 408.0529, found: 408.0516.
3-fluoro-4-methoxyphenethyl N-phenoxybenzimidate (S16)

Prepared following **GP1**. $^1$H NMR (600 MHz, C$_6$D$_6$) δ 7.81 – 7.74 (m, 2H), 7.45 (dd, $J = 8.7$, 1.0 Hz, 2H), 7.26 – 7.18 (m, 2H), 7.12 – 7.06 (m, 3H), 6.91 (tt, $J = 7.4$, 1.0 Hz, 1H), 6.78 (dd, $J = 12.0$, 2.1 Hz, 1H), 6.67 (d, $J = 8.3$ Hz, 1H), 6.45 (t, $J = 8.5$ Hz, 1H), 4.35 (t, $J = 6.8$ Hz, 2H), 3.28 (s, 3H), 2.67 (t, $J = 6.8$ Hz, 2H). $^{19}$F NMR (565 MHz, C$_6$D$_6$) δ –134.33 – –134.47 (m). $^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 160.08 (s), 156.68 (s), 153.03 (d, $J = 246.4$ Hz), 147.05 (d, $J = 10.7$ Hz), 131.59 (s), 130.98 (d, $J = 6.0$ Hz), 130.66 (s), 129.73 (s), 128.57 (s), 124.91 (d, $J = 3.5$ Hz), 122.46 (s), 117.17 (d, $J = 18.0$ Hz), 114.87 (s), 113.92 (d, $J = 2.1$ Hz), 73.29 (s), 55.84 (s), 35.83 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 388.1319, found: 388.1312.

3,5-bis(trifluoromethyl)phenethyl N-phenoxybenzimidate (S17)

Prepared following **GP2**. $^1$H NMR (600 MHz, C$_6$D$_6$) δ 7.70 – 7.65 (m, 2H), 7.64 (s, 1H), 7.40 (dd, $J = 8.7$, 0.9 Hz, 2H), 7.31 (s, 2H), 7.24 – 7.20 (m, 2H), 7.11 – 7.07 (m, 3H), 6.92 (t, $J = 6.9$ Hz, 1H), 4.13 (t, $J = 6.4$ Hz, 2H), 2.41 (t, $J = 6.4$ Hz, 2H). $^{19}$F NMR (565 MHz, C$_6$D$_6$) δ –62.53 (s). $^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 159.85 (s), 155.98 (s), 141.03 (s), 131.82 (q, $J = 33.1$ Hz), 131.17 (s), 130.86 (s), 129.78 (s), 129.60 (s), 128.63 (s), 127.45 (s), 123.92 (q, $J = 272.7$ Hz), 122.72 (s), 120.74 (dt, $J = 7.7$, 3.8 Hz), 114.78 (s), 71.97 (s), 35.93 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 476.1056, found: 476.1059.

2-(naphthalen-2-yl)ethyl N-phenoxybenzimidate (S18)

Prepared following **GP1**. $^1$H NMR (600 MHz, C$_6$D$_6$) δ 7.77 – 7.72 (m, 2H), 7.63 (d, $J = 7.7$ Hz, 1H), 7.59 (d, $J = 7.8$ Hz, 1H), 7.57 (d, $J = 8.4$ Hz, 1H), 7.45 (dd, $J = 11.9$, 11.0 Hz, 3H), 7.30 – 7.23 (m, 2H), 7.23 – 7.18 (m, 2H), 7.13 (dd, $J = 8.4$, 1.6 Hz, 1H), 7.08 – 7.04 (m, 1H), 7.01 (t, $J = 7.5$ Hz, 2H), 6.92 (t, $J = 7.3$ Hz, 1H), 4.53 (t, $J = 6.9$ Hz, 2H), 2.97 (t, $J = 6.9$ Hz, 2H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 160.12 (s), 155.98 (s), 141.03 (s), 131.82 (q, $J = 33.1$ Hz), 131.17 (s), 130.86 (s), 129.78 (s), 129.60 (s), 128.50 (s), 128.48 (s), 127.94 (s), 127.92 (s), 127.80 (s), 125.78 (s), 124.22 (s), 114.91 (s), 73.46 (s), 37.02 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 390.1465, found: 390.1450.
2-(naphthalen-1-yl)ethyl N-phenoxybenzimidate (S19)

\[
\text{Ph} \quad \text{NOPh} \quad \text{Ph}
\]

Prepared following GP1. \({}^1\)H NMR (600 MHz, CD\(_6\)D\(_6\)) \(\delta\) 7.83 – 7.79 (m, 1H), 7.77 – 7.72 (m, 2H), 7.66 – 7.62 (m, 1H), 7.55 (p, \(J = 3.2\) Hz, 1H), 7.44 – 7.40 (m, 2H), 7.28 – 7.17 (m, 6H), 7.11 – 7.03 (m, 3H), 6.91 (t, \(J = 7.4\) Hz, 1H), 4.59 (t, \(J = 7.3\) Hz, 2H), 3.34 (t, \(J = 7.3\) Hz, 2H).

\(13\)C NMR (151 MHz, CD\(_6\)D\(_6\)) \(\delta\) 160.12 (s), 156.71 (s), 134.47 (s), 133.81 (s), 132.62 (s), 131.59 (s), 130.56 (s), 129.68 (s), 129.18 (s), 128.54 (s), 127.84 (s), 127.80 (s), 127.68 (s), 126.38 (s), 125.80 (s), 123.87 (s), 122.40 (s), 114.95 (s), 72.65 (s), 33.85 (s). HRMS (ESI-TOF) \(m/z\) calcd for [M+Na]\(^{+}\) 390.1465, found: 390.1465.

2-(pyridin-3-yl)ethyl N-phenoxybenzimidate (S20)

\[
\text{Ph} \quad \text{NOPh} \quad \text{N}
\]

Prepared following GP1. \({}^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.56 (d, \(J = 1.8\) Hz, 1H), 8.51 (dd, \(J = 4.8, 1.6\) Hz, 1H), 7.72 – 7.66 (m, 2H), 7.63 (dd, \(J = 7.8, 2.2, 1.7\) Hz, 1H), 7.49 – 7.39 (m, 1H), 7.39 – 7.29 (m, 4H), 7.29 – 7.26 (m, 3H), 7.24 – 7.21 (m, 1H), 7.04 (dd, \(J = 7.2, 1.3\) Hz, 1H), 4.66 (t, \(J = 6.7\) Hz, 2H), 3.14 (t, \(J = 6.7\) Hz, 2H). \({}^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 159.35, 156.51, 150.61, 148.39, 136.73, 133.38, 130.78, 130.64, 129.48, 128.59, 127.49, 123.54, 122.33, 114.54, 77.37, 77.16, 76.95, 72.66, 34.04. HRMS (ESI-TOF) \(m/z\) calcd for [M+Na]\(^{+}\) 319.1447, found: 319.1561.

2-(thiophen-3-yl)ethyl N-phenoxybenzimidate (S21)

\[
\text{Ph} \quad \text{NOPh} \quad \text{S}
\]

Prepared following GP1. \({}^1\)H NMR (600 MHz, CD\(_6\)D\(_6\)) \(\delta\) 7.76 (dd, \(J = 7.5, 2.0\) Hz, 2H), 7.43 (d, \(J = 8.5\) Hz, 2H), 7.20 (dd, \(J = 13.6, 4.8\) Hz, 2H), 7.14 – 7.06 (m, 3H), 6.88 (ddd, \(J = 9.8, 7.8, 5.1\) Hz, 2H), 6.75 – 6.66 (m, 2H), 4.38 (t, \(J = 6.7\) Hz, 2H), 2.77 (t, \(J = 6.7\) Hz, 2H). \({}^{13}\)C NMR (151 MHz, CD\(_6\)D\(_6\)) \(\delta\) 160.08 (s), 156.70 (s), 140.87 (s), 139.33 (s), 132.27 (s), 131.49 (s), 130.64 (s), 138.21 (s), 131.63 (s), 130.61 (s), 129.71 (s), 128.55 (s), 128.54 (s), 127.79 (s), 125.73 (s), 122.42 (s), 122.15 (s), 114.86 (s), 72.90 (s), 31.25 (s). HRMS (ESI-TOF) \(m/z\) calcd for [M+Na]\(^{+}\) 346.0872, found: 346.0863.

2-(benzo[b]thiophen-3-yl)ethyl N-phenoxybenzimidate (S22)

\[
\text{Ph} \quad \text{NOPh} \quad \text{S}
\]

Prepared following GP1. \({}^1\)H NMR (600 MHz, CD\(_6\)D\(_6\)) \(\delta\) 7.76 (d, \(J = 6.7\) Hz, 2H), 7.57 (d, \(J = 8.0\) Hz, 1H), 7.44 (dd, \(J = 11.1, 8.4\) Hz, 3H), 7.20 (t, \(J = 8.0\) Hz, 2H), 7.13 (t, \(J = 7.4\) Hz, 1H), 7.11 – 7.03 (m, 4H), 6.92 (t, \(J = 7.3\) Hz, 1H), 6.81 (s, 1H), 4.48 (t, \(J = 6.9\) Hz, 2H), 2.98 (t, \(J = 6.8\) Hz, 2H). \({}^{13}\)C NMR (151 MHz, CD\(_6\)D\(_6\)) \(\delta\) 160.08 (s), 156.70 (s), 140.87 (s), 139.33 (s), 132.27 (s), 131.49 (s), 130.64 (s), 129.72 (s), 128.58
3-methylbut-3-en-1-yl N-phenoxycobenzimidate (S23)

Prepared following GP1. $^1$H NMR (600 MHz, C$_6$D$_6$) δ 7.98 – 7.91 (m, 2H), 7.45 (dd, $J = 8.7, 1.0$ Hz, 2H), 7.21 (td, $J = 7.4, 2.5$ Hz, 2H), 7.14 – 7.10 (m, 3H), 6.95 – 6.88 (m, 1H), 4.79 (d, $J = 9.1$ Hz, 2H), 4.41 (td, $J = 6.7, 1.4$ Hz, 2H), 2.28 (t, $J = 6.7$ Hz, 2H), 1.56 (s, 3H).

$^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 160.11 (s), 156.62 (s), 141.73 (s), 131.90 (s), 130.63 (s), 129.70 (s), 128.56 (s), 127.77 (s), 122.38 (s), 114.86 (s), 112.90 (s), 71.34 (s), 38.44 (s), 22.44 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 396.1029, found: 396.1020.

3-methylbut-3-en-1-yl N-phenoxycobenzimidate (S24)

Prepared following GP1. $^1$H NMR (600 MHz, C$_6$D$_6$) δ 7.95 – 7.90 (m, 2H), 7.46 – 7.42 (m, 2H), 7.24 – 7.18 (m, 2H), 7.14 – 7.09 (m, 3H), 6.95 – 6.88 (m, 1H), 5.68 (ddt, $J = 17.0, 10.2, 6.8$ Hz, 1H), 5.06 – 4.93 (m, 2H), 4.26 (t, $J = 6.6$ Hz, 2H), 2.26 (qt, $J = 6.6, 1.3$ Hz, 2H).

$^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 160.10 (s), 156.62 (s), 134.41 (s), 131.82 (s), 130.62 (s), 129.71 (d, $J = 8.5$ Hz), 128.56 (s), 127.77 (s), 122.38 (s), 117.45 (s), 114.87 (s), 72.30 (s), 34.91 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 304.1151, found: 304.1154.

but-3-en-1-yl N-phenoxycobenzimidate (S25)

Prepared following GP1. $^1$H NMR (600 MHz, C$_6$D$_6$) δ 8.01 – 7.93 (m, 2H), 7.41 – 7.35 (m, 2H), 7.23 – 7.17 (m, 2H), 7.15 – 7.10 (m, 3H), 6.91 (tt, $J = 7.6, 1.1$ Hz, 1H), 4.24 (t, $J = 6.6$ Hz, 2H), 2.24 (td, $J = 6.6, 2.7$ Hz, 2H), 1.71 (t, $J = 2.7$ Hz, 1H).

$^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 159.92 (s), 156.20 (s), 131.52 (s), 130.73 (s), 129.67 (s), 128.54 (s), 122.47 (s), 114.88 (s), 80.51 (s), 70.88 (s), 70.57 (s), 20.60 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 288.0995, found: 288.0999.

pent-3-yn-1-yl N-phenoxycobenzimidate (S26)

Prepared following GP1. $^1$H NMR (600 MHz, C$_6$D$_6$) δ 8.03 – 7.97 (m, 2H), 7.42 – 7.37 (m, 2H), 7.22 – 7.17 (m, 2H), 7.14 – 7.10 (m, 3H), 6.93 – 6.87 (m, 1H), 4.34 (t, $J = 6.7$ Hz, 2H), 2.43 – 2.33 (m, 2H), 1.47 (t, $J = 2.5$ Hz, 3H).

$^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 160.01 (s), 156.54 (s), 131.69 (s), 130.65 (s), 129.65 (s), 128.52 (s), 122.41 (s), 114.91 (s), 77.76 (s), 75.59 (s), 71.72 (s), 21.07 (s), 3.28 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 302.1151, found: 302.1147.
4-phenylbut-3-yne-1-yl N-phenoxybenzimidate (S27)

\[
\text{Ph} \begin{array}{c}
\text{NO} \text{Ph} \\
\end{array} \begin{array}{c}
\text{Ph} \\
\end{array}
\]

Prepared following GP2. $^1$H NMR (600 MHz, C$_6$D$_6$) $\delta$ 8.07 – 8.03 (m, 2H), 7.45 – 7.40 (m, 4H), 7.23 – 7.18 (m, 2H), 7.13 – 7.09 (m, 3H), 7.01 – 6.95 (m, 3H), 6.92 (ddd, $J$ = 7.4, 2.0, 1.0 Hz, 1H), 4.35 (t, $J$ = 6.4 Hz, 2H), 2.52 (t, $J$ = 6.4 Hz, 2H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) $\delta$ 159.99 (s), 156.50 (s), 132.01 (s), 131.60 (s), 130.73 (s), 129.68 (s), 128.59 (s), 128.57 (s), 128.13 (s), 124.16 (s), 122.48 (s), 114.94 (s), 86.74 (s), 82.91 (s), 71.16 (s), 21.65 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 364.1308, found: 364.1302.

2-((1R,3s)-adamantan-1-yl)ethyl N-phenoxybenzimidate (S28)

Prepared following GP1. $^1$H NMR (600 MHz, C$_6$D$_6$) $\delta$ 7.96 (dt, $J$ = 5.1, 3.8 Hz, 2H), 7.55 – 7.46 (m, 2H), 7.24 – 7.18 (m, 2H), 7.15 – 7.12 (m, 3H), 6.91 (tt, $J$ = 7.4, 1.0 Hz, 1H), 4.45 (t, $J$ = 7.4 Hz, 2H), 1.83 (s, 3H), 1.65 – 1.48 (m, 9H), 1.42 (d, $J$ = 2.4 Hz, 6H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) $\delta$ 160.25 (s), 157.06 (s), 131.91 (s), 130.57 (s), 129.69 (s), 128.61 (s), 127.84 (s), 122.32 (s), 114.89 (s), 69.60 (s), 44.28 (s), 42.68 (d, $J$ = 21.9 Hz), 37.23 (s), 31.89 (s), 29.00 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 398.2091, found: 398.2090.

3-methoxy-3-methylbutyl N-phenoxybenzimidate (S29)

Prepared following GP1. $^1$H NMR (600 MHz, C$_6$D$_6$) $\delta$ 7.94 – 7.90 (m, 2H), 7.48 (dt, $J$ = 9.1, 1.7 Hz, 2H), 7.23 – 7.18 (m, 2H), 7.14 – 7.10 (m, 3H), 6.90 (tt, $J$ = 7.4, 1.0 Hz, 1H), 4.60 – 4.48 (m, 2H), 2.91 (s, 3H), 1.96 – 1.86 (m, 2H), 0.98 (s, 6H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) $\delta$ 160.22 (s), 156.99 (s), 131.91 (s), 130.57 (s), 129.69 (s), 128.61 (s), 127.84 (s), 122.32 (s), 114.89 (s), 73.20 (s), 69.85 (s), 48.96 (s), 40.46 (s), 25.18 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 336.1570, found: 336.1572.

3,3-dimethylbutyl N-phenoxybenzimidate (S30)

Prepared following GP1. $^1$H NMR (600 MHz, C$_6$D$_6$) $\delta$ 7.98 – 7.90 (m, 2H), 7.52 – 7.44 (m, 2H), 7.24 – 7.19 (m, 2H), 7.15 – 7.11 (m, 3H), 6.91 (tt, $J$ = 7.4, 1.0 Hz, 1H), 4.52 – 4.28 (m, 2H), 1.70 – 1.52 (m, 2H), 0.81 (s, 9H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) $\delta$ 160.20 (s), 156.90 (s), 132.00 (s), 130.59 (s), 129.71 (s), 128.61 (s), 127.78 (s), 122.34 (s), 114.85 (s), 70.76 (s), 43.43 (s), 29.69 (s), 29.58 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 320.1621, found: 320.1623.
**isopentyl N-phenoxybenzimidate (S31)**

![Chemical Structure]

Prepared following **GP1**. $^1$H NMR (600 MHz, C$_6$D$_6$) $\delta$ 7.97 – 7.90 (m, 2H), 7.50 – 7.44 (m, 2H), 7.25 – 7.18 (m, 2H), 7.15 – 7.10 (m, 3H), 6.91 (tt, $J$ = 7.4, 1.1 Hz, 1H), 4.31 (t, $J$ = 6.7 Hz, 2H), 1.76 – 1.64 (m, 1H), 1.50 (q, $J$ = 6.8 Hz, 2H), 0.79 (d, $J$ = 6.7 Hz, 6H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) $\delta$ 160.19 (s), 156.96 (s), 131.96 (s), 130.59 (s), 129.70 (s), 128.59 (d, $J$ = 7.8 Hz), 127.73 (s), 122.34 (s), 114.87 (s), 71.67 (s), 39.14 (s), 25.04 (s), 22.57 (s). HRMS (ESI-TOF) $m/z$ calcd for [M+Na]$^+$ 306.1465, found: 306.1465.

**phenethyl N-phenoxyfuran-2-carbimidate (S32)**

![Chemical Structure]

Prepared following **GP1**. $^1$H NMR (600 MHz, C$_6$D$_6$) $\delta$ 7.49 – 7.43 (m, 2H), 7.19 – 7.16 (m, 3H), 7.15 (s, 1H), 7.12 – 7.08 (m, 2H), 7.07 – 7.01 (m, 3H), 6.96 (dd, $J$ = 1.7, 0.8 Hz, 1H), 6.90 – 6.85 (m, 1H), 4.39 (t, $J$ = 6.9 Hz, 2H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) $\delta$ 160.00 (s), 150.44 (s), 145.62 (s), 144.58 (s), 137.99 (s), 129.67 (s), 129.40 (s), 128.73 (s), 126.83 (s), 114.86 (s), 113.51 (s), 111.44 (s), 73.64 (s), 36.77 (s). HRMS (ESI-TOF) $m/z$ calcd for [M+Na]$^+$ 330.1101, found: 330.1099.

**phenethyl 4-methoxy-N-phenoxybenzimidate (S33)**

![Chemical Structure]

Prepared following **GP1**. $^1$H NMR (600 MHz, C$_6$D$_6$) $\delta$ 7.75 – 7.70 (m, 2H), 7.46 (dt, $J$ = 9.1, 1.7 Hz, 2H), 7.25 – 7.20 (m, 2H), 7.14 – 7.10 (m, 2H), 7.06 (dd, $J$ = 7.2, 5.2 Hz, 3H), 6.91 (tdd, $J$ = 7.1, 3.3, 2.3 Hz, 1H), 6.73 – 6.67 (m, 2H), 4.50 (t, $J$ = 6.9 Hz, 2H), 3.21 (s, 3H), 2.85 (t, $J$ = 6.9 Hz, 2H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) $\delta$ 162.03 (s), 160.24 (s), 156.98 (s), 156.98 (s), 138.23 (s), 129.69 (s), 129.43 (s), 128.77 (s), 128.80 (s), 123.90 (s), 122.23 (s), 114.89 (s), 114.06 (s), 73.46 (s), 54.81 (s), 36.92 (s). HRMS (ESI-TOF) $m/z$ calcd for [M+Na]$^+$ 370.1414, found: 370.1412.

**phenethyl 3-chloro-N-phenoxybenzimidate (S34)**

![Chemical Structure]

Prepared following **GP1**. $^1$H NMR (600 MHz, C$_6$D$_6$) $\delta$ 7.87 (t, $J$ = 1.8 Hz, 1H), 7.60 (ddd, $J$ = 7.9, 1.6, 1.1 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.31 – 7.27 (m, 2H), 7.22 (tt, $J$ = 8.1, 1.6 Hz, 2H), 7.19 – 7.14 (m, 2H), 7.12 – 7.08 (m, 2H), 7.01 (tt, $J$ = 7.4, 1.1 Hz, 1H), 6.84 (t, $J$ = 7.9 Hz, 1H), 4.53 (t, $J$ = 6.8 Hz, 2H), 2.84 (t, $J$ = 6.8 Hz, 2H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) $\delta$ 159.84 (s), 155.13 (s), 137.91 (s), 134.71 (s), 133.64 (s), 130.59 (s), 129.74 (s), 129.34 (s), 128.84 (s), 127.98 (s), 127.74 (s), 126.98 (s), 125.67 (s), 122.63 (s), 114.84 (s), 73.79 (s), 36.75 (s). HRMS (ESI-TOF) $m/z$ calcd for [M+Na]$^+$ 374.0918, found: 374.0913.
phenethyl 2-chloro-N-phenoxybenzimidate (S35)

Prepared following GP1. $^1$H NMR (600 MHz, C$_6$D$_6$) δ 7.53 (d, J = 8.5 Hz, 2H), 7.19 – 7.12 (m, 2H), 7.09 – 7.04 (m, 2H), 7.04 – 6.97 (m, 4H), 6.96 (dd, J = 7.1, 2.1 Hz, 1H), 6.86 (t, J = 7.3 Hz, 1H), 6.75 – 6.66 (m, 2H), 3.97 (t, J = 6.9 Hz, 2H), 2.76 (t, J = 6.9 Hz, 2H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 160.47 (s), 156.33 (s), 137.75 (s), 134.23 (s), 132.24 (s), 131.37 (s), 129.99 (s), 129.64 (s), 129.51 (s), 128.75 (s), 126.90 (s), 126.84 (s), 122.12 (s), 114.87 (s), 71.46 (s), 36.70 (s). HRMS (ESI-TOF) m/z calcd for [M+H]$^+$ 352.1099, found: 352.1089.

phenethyl N-phenoxy-2-naphthimidate (S36)

Prepared following GP1. $^1$H NMR (600 MHz, C$_6$D$_6$) δ 8.09 (s, 1H), 8.02 (dd, J = 8.6, 1.6 Hz, 1H), 7.63 – 7.53 (m, 3H), 7.49 (dd, J = 8.6, 0.8 Hz, 2H), 7.26 – 7.19 (m, 4H), 7.14 – 7.02 (m, 5H), 6.94 (t, J = 7.3 Hz, 1H), 4.53 (t, J = 6.7 Hz, 2H), 2.87 (t, J = 6.7 Hz, 2H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 160.14 (s), 156.90 (s), 138.30 (s), 134.81 (s), 133.45 (s), 129.75 (s), 129.51 (s), 129.11 (s), 129.04 (s), 128.82 (s), 128.17 (s), 128.14 (s), 127.98 (s), 127.33 (s), 126.88 (s), 126.61 (s), 124.64 (s), 122.50 (s), 114.98 (s), 73.58 (s), 36.90 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 390.1465, found: 390.1453.

phenethyl N-phenoxy-1-naphthimidate (S37)

Prepared following GP1. $^1$H NMR (600 MHz, C$_6$D$_6$) δ 8.07 (dq, J = 6.9, 3.4 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.55 – 7.51 (m, 2H), 7.27 (dd, J = 7.0, 1.2 Hz, 1H), 7.22 – 7.17 (m, 4H), 7.09 – 6.99 (m, 5H), 6.98 – 6.94 (m, 2H), 6.88 (tt, J = 7.4, 1.0 Hz, 1H), 3.75 (t, J = 6.6 Hz, 2H), 2.66 (t, J = 6.6 Hz, 2H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 161.00 – 160.08 (m), 158.26 – 157.13 (m), 137.85 (s), 133.72 (s), 132.12 – 131.95 (m), 130.81 (s), 129.70 (s), 129.55 (s), 129.17 (s), 128.68 (s), 128.67 (s), 127.75 – 127.72 (m), 127.70 (s), 126.84 (s), 126.65 (s), 125.42 (s), 125.23 (s), 121.98 (s), 114.85 (s), 71.16 (s), 36.82 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 390.1465, found: 390.1466.
2,4-dichlorophenethyl N-phenoxy-1-naphthimidate (S38)

Prepared following GP2. $^1$H NMR (600 MHz, CDCl$_3$) δ 8.03 – 7.95 (m, 2H), 7.94 – 7.86 (m, 1H), 7.58 – 7.53 (m, 2H), 7.52 – 7.47 (m, 2H), 7.31 (ddd, $J = 8.9, 5.5, 1.9$ Hz, 2H), 7.29 – 7.26 (m, 3H), 7.22 (d, $J = 8.2$ Hz, 1H), 7.12 (dd, $J = 8.2, 2.1$ Hz, 1H), 7.01 (tt, $J = 7.2, 1.2$ Hz, 1H), 4.05 (t, $J = 6.7$ Hz, 2H), 3.14 – 2.97 (m, 2H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 159.71 (s), 157.99 (s), 134.95 (s), 133.51 (s), 133.50 (s), 133.47 (s), 132.80 (s), 131.61 (s), 131.22 (s), 129.39 (s), 129.38 (s), 129.05 (s), 128.72 (s), 127.74 (s), 127.24 (s), 126.75 (s), 126.46 (s), 125.25 (s), 124.77 (s), 122.03 (s), 114.68 (s), 68.95 (s), 34.04 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 458.0685, found: 458.0688.

2-(benzo[bl]thiophen-3-yl)ethyl N-phenoxy-1-naphthimidate (S39)

Prepared following GP2. $^1$H NMR (600 MHz, C$_6$D$_6$) δ 8.08 – 8.02 (m, 1H), 7.64 – 7.59 (m, 2H), 7.52 (ddd, $J = 5.2, 2.7, 1.1$ Hz, 3H), 7.25 (dd, $J = 7.0, 1.2$ Hz, 1H), 7.23 – 7.18 (m, 2H), 7.16 (dd, $J = 2.9, 1.2$ Hz, 3H), 7.15 – 7.14 (m, 1H), 7.07 – 6.98 (m, 3H), 6.92 – 6.85 (m, 1H), 3.78 (t, $J = 6.7$ Hz, 2H), 2.82 (dt, $J = 6.8, 3.3$ Hz, 2H).

$^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 160.68 (s), 157.88 (s), 140.75 (s), 139.21 (s), 133.69 (s), 132.05 (s), 131.95 (s), 130.83 (s), 129.73 (s), 129.19 (s), 128.69 (s), 127.73 (s), 127.47 (s), 126.71 (s), 125.27 (s), 125.23 (s), 124.45 (s), 124.13 (s), 123.91 (s), 123.00 (s), 122.06 (s), 121.81 (s), 114.86 (s), 69.47 (s), 29.47 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 446.1185, found: 446.1183.

4-(trifluoromethoxy)phenethyl N-phenoxy-1-naphthimidate (S40)

Prepared following GP2. $^1$H NMR (600 MHz, C$_6$D$_6$) δ 8.02 – 7.98 (m, 1H), 7.59 – 7.50 (m, 4H), 7.28 (dd, $J = 7.0, 1.2$ Hz, 1H), 7.22 – 7.17 (m, 4H), 7.09 (dd, $J = 8.2, 7.1$ Hz, 1H), 6.88 (tt, $J = 7.4, 1.1$ Hz, 1H), 6.82 (d, $J = 7.9$ Hz, 2H), 6.73 – 6.66 (m, 2H), 3.63 (t, $J = 6.4$ Hz, 2H), 2.47 (t, $J = 6.4$ Hz, 2H).

$^{19}$F NMR (565 MHz, CDCl$_3$) δ −57.62 (s).

$^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 160.58 (s), 157.85 (s), 148.30 (d, $J = 1.6$ Hz), 136.74 (s), 133.74 (s), 131.99 (s), 130.99 (s), 130.87 (s), 129.75 (s), 129.11 (s), 128.76 (s), 127.73 (s), 127.49 (s), 126.76 (s), 125.24 (s), 125.22 (s), 122.14 (s), 121.26 (q, $J = 256.5$ Hz), 121.14 (s), 114.77 (s), 70.68 (s), 35.85 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 474.1287, found: 474.1291.
4-methoxyphenethyl N-phenoxy-1-naphthimidate (S41)

![Structure of 4-methoxyphenethyl N-phenoxy-1-naphthimidate (S41)]

Prepared following **GP2**. $^1$H NMR (600 MHz, C$_6$D$_6$) δ 8.11 – 8.06 (m, 1H), 7.64 – 7.60 (m, 2H), 7.56 – 7.51 (m, 2H), 7.32 (dd, $J = 7.0, 1.2$ Hz, 1H), 7.21 – 7.17 (m, 4H), 7.08 (dd, $J = 8.3, 7.0$ Hz, 1H), 6.92 – 6.84 (m, 3H), 6.71 – 6.64 (m, 2H), 3.77 (t, $J = 6.7$ Hz, 2H), 3.28 (s, 3H), 2.67 (t, $J = 6.6$ Hz, 2H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 160.75 (s), 159.09 (s), 158.12 (s), 133.73 (s), 132.12 (s), 130.81 (s), 130.52 (s), 129.70 (s), 129.18 (s), 128.67 (s), 127.80 (s), 127.69 (s), 126.66 (s), 125.45 (s), 125.25 (s), 121.97 (s), 114.86 (s), 114.25 (s), 71.51 (s), 54.78 (s), 36.01 (s). HRMS (ESI-TOF) $m/z$ calcld for [M+H]$^+$ 398.1751, found: 398.1736.

3,5-bis(trifluoromethyl)phenethyl N-phenoxy-1-naphthimidate (S42)

![Structure of 3,5-bis(trifluoromethyl)phenethyl N-phenoxy-1-naphthimidate (S42)]

Prepared following **GP2**. $^1$H NMR (600 MHz, C$_6$D$_6$) δ 7.93 – 7.89 (m, 1H), 7.64 (s, 1H), 7.60 (dd, $J = 8.8, 1.0$ Hz, 2H), 7.56 – 7.51 (m, 2H), 7.33 (s, 2H), 7.24 (dd, $J = 7.0, 1.2$ Hz, 1H), 7.22 – 7.17 (m, 4H), 7.09 (dd, $J = 8.2, 7.0$ Hz, 1H), 6.90 – 6.86 (m, 1H), 3.44 (t, $J = 6.0$ Hz, 2H), 2.23 (t, $J = 6.0$ Hz, 2H). $^{19}$F NMR (377 MHz, C$_6$D$_6$) δ -62.46 (s). $^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 160.48 (s), 157.16 (s), 140.91 (s), 133.76 (s), 131.90 (s), 131.75 (q, $J = 33.0$ Hz), 131.07 (s), 129.79 (s), 129.78 (s), 129.72 (s), 129.00 (s), 128.82 (s), 127.81 (s), 127.30 (s), 126.84 (s), 125.24 (s), 125.00 (s), 123.94 (q, $J = 272.8$ Hz), 122.28 (s), 120.78 (dt, $J = 7.7, 3.8$ Hz), 114.75 (s), 69.66 (s), 35.71 (s). HRMS (ESI-TOF) $m/z$ calcld for [M+Na]$^+$ 526.1212, found: 526.1218.
2-(thiophen-3-yl)ethyl N-phenoxy-1-naphthimidate (S43)

Prepared following GP2. $^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 8.12 – 8.03 (m, 1H), 7.63 – 7.57 (m, 2H), 7.57 – 7.50 (m, 2H), 7.32 (dd, $J$ = 7.0, 1.2 Hz, 1H), 7.24 – 7.13 (m, 4H), 7.09 (dd, $J$ = 8.3, 7.0 Hz, 1H), 6.91 – 6.84 (m, 1H), 6.83 (dd, $J$ = 4.9, 2.9 Hz, 1H), 6.74 (dd, $J$ = 4.9, 1.3 Hz, 1H), 6.68 (ddt, $J$ = 2.9, 1.4, 0.8 Hz, 1H), 3.68 (t, $J$ = 6.4 Hz, 2H), 2.61 (t, $J$ = 6.4 Hz, 2H). $^{13}$C NMR (101 MHz, C$_6$D$_6$) $\delta$ 160.43 (d, $J$ = 50.8 Hz), 157.75 (d, $J$ = 45.5 Hz), 137.83 (d, $J$ = 33.4 Hz), 133.65 (d, $J$ = 16.8 Hz), 132.02 (d, $J$ = 13.0 Hz), 130.73 (d, $J$ = 21.8 Hz), 129.72 (s), 129.14 (s), 128.93 (s), 128.69 (s), 127.74 (s), 127.69 (s), 126.69 (s), 125.56 (s), 125.36 (s), 125.27 (s), 122.33 (s), 122.03 (s), 114.84 (s), 70.57 (s), 31.07 (d, $J$ = 7.1 Hz). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 396.1029, found: 396.1022.

3-methylbut-3-en-1-yl N-phenoxy-1-naphthimidate (S44)

Prepared following GP2. $^1$H NMR (600 MHz, C$_6$D$_6$) $\delta$ 8.22 – 8.17 (m, 1H), 7.61 – 7.58 (m, 2H), 7.51 (dd, $J$ = 7.0, 1.2 Hz, 1H), 7.24 – 7.15 (m, 5H), 7.12 (dd, $J$ = 8.2, 7.0 Hz, 1H), 4.74 – 4.61 (m, 2H), 3.70 (t, $J$ = 6.7 Hz, 2H), 2.14 (t, $J$ = 6.6 Hz, 2H), 1.45 (s, 3H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) $\delta$ 160.72 (s), 157.97 (s), 141.52 (s), 133.79 (s), 132.18 (s), 130.85 (s), 129.68 (s), 129.11 (s), 128.72 (s), 127.94 (s), 127.70 (s), 126.72 (s), 125.50 (s), 125.26 (s), 121.96 (s), 114.82 (s), 112.99 (s), 69.28 (s), 38.17 (s), 22.64 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 354.1465, found: 354.1468.

but-3-en-1-yl N-phenoxy-1-naphthimidate (S45)

Prepared following GP2. $^1$H NMR (600 MHz, C$_6$D$_6$) $\delta$ 8.18 (d, $J$ = 8.4 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.55 (dd, $J$ = 13.3, 4.9 Hz, 2H), 7.49 (dd, $J$ = 7.0, 1.1 Hz, 1H), 7.25 – 7.17 (m, 4H), 7.14 – 7.09 (m, 1H), 6.90 – 6.84 (m, 1H), 5.63 – 5.54 (m, 1H), 4.93 – 4.90 (m, 1H), 4.89 (t, $J$ = 1.2 Hz, 1H), 3.59 (t, $J$ = 6.6 Hz, 2H), 2.17 – 2.09 (m, 2H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) $\delta$ 160.71 (s), 157.93 (s), 133.85 (s), 133.81 (s), 132.16 (s), 130.84 (s), 129.68 (s), 129.11 (s), 128.71 (s), 127.97 (s), 127.70 (s), 126.72 (s), 125.53 (s), 125.26 (s), 121.99 (s), 117.55 (s), 114.85 (s), 69.85 (s), 34.54 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 340.1308, found: 340.1304.
but-3-yn-1-yl N-phenoxy-1-naphthimidate (S46)

Prepared following GP2. $^1$H NMR (600 MHz, C$_6$D$_6$) δ 8.18 (dd, $J$ = 8.2, 0.9 Hz, 1H), 7.60 – 7.51 (m, 4H), 7.48 (dd, $J$ = 7.0, 1.2 Hz, 1H), 7.25 – 7.17 (m, 4H), 7.10 (dd, $J$ = 8.3, 7.0 Hz, 1H), 6.86 (tt, $J$ = 7.4, 1.1 Hz, 1H), 3.60 (t, $J$ = 6.7 Hz, 2H), 2.15 (td, $J$ = 6.7, 2.7 Hz, 2H), 1.62 (t, $J$ = 2.7 Hz, 1H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 160.60 (s), 157.31 (s), 133.81 (s), 132.08 (s), 130.98 (s), 129.67 (s), 129.24 (s), 128.71 (s), 127.77 (s), 127.56 (s), 126.72 (s), 125.49 (s), 125.23 (s), 122.07 (s), 114.85 (s), 79.77 (s), 70.68 (s), 68.23 (s), 20.27 (s). HRMS (ESI-TOF) $m/z$ calcd for [M+H]$^+$ 316.1332, found: 316.1324.

pent-3-yn-1-yl N-phenoxy-1-naphthimidate (S47)

Prepared following GP2. $^1$H NMR (600 MHz, C$_6$D$_6$) δ 8.20 (d, $J$ = 8.3 Hz, 1H), 7.59 – 7.48 (m, 5H), 7.24 – 7.14 (m, 5H), 7.10 (dd, $J$ = 8.2, 7.1 Hz, 1H), 3.72 (t, $J$ = 6.9 Hz, 2H), 2.37 – 2.21 (m, 2H), 1.38 (t, $J$ = 2.5 Hz, 3H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 160.66 (s), 157.58 (s), 133.81 (s), 132.12 (s), 130.94 (s), 129.66 (s), 129.21 (s), 128.72 (s), 127.72 (s), 126.70 (s), 125.50 (s), 125.24 (s), 122.01 (s), 114.87 (s), 77.85 (s), 74.73 (s), 69.01 (s), 20.78 (s), 3.25 (s). HRMS (ESI-TOF) $m/z$ calcd for [M+H]$^+$ 352.1308, found: 352.1308.

4-phenylbut-3-yn-1-yl N-phenoxy-1-naphthimidate (S48)

Prepared following GP2. $^1$H NMR (600 MHz, C$_6$D$_6$) δ 8.25 (d, $J$ = 8.4 Hz, 1H), 7.61 – 7.50 (m, 5H), 7.39 – 7.34 (m, 2H), 7.23 – 7.17 (m, 2H), 7.17 (s, 1H), 7.15 (t, $J$ = 2.1 Hz, 1H), 7.10 (dd, $J$ = 8.2, 7.0 Hz, 1H), 6.98 – 6.91 (m, 3H), 6.86 (tt, $J$ = 7.4, 1.0 Hz, 1H), 3.73 (t, $J$ = 6.7 Hz, 2H), 2.45 (t, $J$ = 6.7 Hz, 2H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) δ 160.64 (s), 157.57 (s), 133.83 (s), 132.09 (s), 132.05 (s), 131.01 (s), 129.68 (s), 129.34 (s), 128.73 (s), 128.53 (s), 128.11 (d, $J$ = 1.8 Hz), 127.80 (s), 127.62 (s), 126.72 (s), 125.50 (s), 125.29 (s), 124.06 (s), 122.07 (s), 114.89 (s), 85.89 (s), 82.99 (s), 68.50 (s), 21.40 (s). HRMS (ESI-TOF) $m/z$ calcd for [M+H]$^+$ 414.1465, found: 414.1456.
3,3-dimethylbutyl N-phenoxy-1-naphthimidate (S49)

![Chemical structure of 3,3-dimethylbutyl N-phenoxy-1-naphthimidate (S49)](image)

Prepared following **GP2**. $^1$H NMR (600 MHz, C$_6$D$_6$) $\delta$ 8.21 (d, $J = 8.4$ Hz, 1H), 7.66 – 7.60 (m, 2H), 7.59 – 7.50 (m, 3H), 7.28 – 7.21 (m, 1H), 7.19 (ddd, $J = 6.6$, 3.6, 1.7 Hz, 3H), 7.16 – 7.10 (m, 1H), 6.91 – 6.84 (m, 1H), 3.75 (td, $J = 7.2$, 1.8 Hz, 2H), 1.52 – 1.43 (m, 2H), 0.66 (s, 9H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) $\delta$ 160.78 (s), 158.20 (s), 133.77 (s), 132.24 (s), 130.82 (s), 129.69 (s), 129.04 (s), 128.73 (s), 127.98 (s), 127.68 (s), 126.74 (s), 125.50 (s), 125.27 (s), 121.91 (s), 114.80 (s), 68.19 (s), 43.30 (s), 29.51 (s), 21.14 (s). HRMS (ESI-TOF) $m/z$ calcd for [M+H]$^+$ 348.1958, found: 348.1951.

2,3-dihydro-1H-inden-2-yl N-phenoxy-1-naphthimidate (S50)

![Chemical structure of 2,3-dihydro-1H-inden-2-yl N-phenoxy-1-naphthimidate (S50)](image)

Prepared following **GP2**. $^1$H NMR (600 MHz, C$_6$D$_6$) $\delta$ 8.33 (d, $J = 8.4$ Hz, 1H), 7.57 (t, $J = 7.0$ Hz, 3H), 7.49 (ddd, $J = 4.3$, 3.2, 1.7 Hz, 2H), 7.30 – 7.18 (m, 2H), 7.15 – 7.11 (m, 3H), 7.03 – 6.99 (m, 2H), 6.93 – 6.89 (m, 2H), 6.85 (tt, $J = 7.4$, 1.0 Hz, 1H), 4.90 – 4.75 (m, 1H), 3.16 (dd, $J = 16.5$, 3.8 Hz, 2H), 2.69 (dd, $J = 16.6$, 6.7 Hz, 2H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) $\delta$ 160.53 (s), 157.09 (s), 140.30 (s), 133.94 (s), 132.21 (s), 130.94 (s), 129.64 (s), 129.20 (s), 128.76 (s), 128.52 (s), 127.63 (s), 127.06 (s), 126.66 (s), 125.70 (s), 125.26 (s), 124.85 (s), 122.04 (s), 114.82 (s), 81.64 (s), 40.43 (s). HRMS (ESI-TOF) $m/z$ calcd for [M+Na]$^+$ 402.1465, found: 402.1463.

(±)-2-phenylethyl-2-d-N-phenoxybenzimidate (S51)

![Chemical structure of (±)-2-phenylethyl-2-d-N-phenoxybenzimidate (S51)](image)

Prepared following **GP1**. $^1$H NMR (600 MHz, C$_6$D$_6$) $\delta$ 7.77 – 7.73 (m, 2H), 7.46 – 7.41 (m, 2H), 7.22 – 7.18 (m, 3H), 7.13 – 7.00 (m, 7H), 6.91 (tt, $J = 7.4$, 1.0 Hz, 1H), 4.44 (d, $J = 6.8$ Hz, 2H), 2.86 – 2.68 (m, 1H). $^{13}$C NMR (151 MHz, C$_6$D$_6$) $\delta$ 160.12 (s), 156.74 (s), 138.05 (s), 131.67 (s), 130.56 (s), 129.69 (s), 129.40 (s), 128.77 (s), 128.52 (s), 128.35 (s), 127.82 (s), 126.83 (s), 122.39 (s), 114.89 (s), 36.86 – 36.14 (m). HRMS (ESI-TOF) $m/z$ calcd for [M+Na]$^+$ 341.1376 found: 341.1762.
(S)-2-(6-methoxynaphthalen-2-yl)propyl N-phenoxybenzimidate (S52)

Prepared following GP2. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.74 – 7.70 (m, 2H), 7.57 (d, $J = 8.4$ Hz, 1H), 7.52 – 7.45 (m, 4H), 7.24 – 7.18 (m, 4H), 7.07 – 6.98 (m, 3H), 6.96 (d, $J = 2.5$ Hz, 1H), 6.91 (tt, $J = 7.4$, 1.1 Hz, 1H), 4.51 (ddd, $J = 6.9$, 2.2 Hz, 2H), 3.41 (s, 3H), 3.25 (dd, $J = 13.9$, 6.9 Hz, 1H), 1.32 (d, $J = 7.0$ Hz, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 160.16 (s), 158.11 (s), 156.85 (s), 138.54 (s), 134.29 (s), 131.61 (s), 130.52 (s), 129.72 (s), 129.71 (s), 129.65 (s), 128.48 (s), 127.82 (s), 127.45 (s), 126.62 (s), 126.58 (s), 122.39 (s), 119.35 (s), 114.91 (s), 105.94 (s), 78.13 (s), 54.82 (s), 40.84 (s), 18.10 (s). HRMS (ESI-TOF) $m/z$ calcd for [M+Na]$^+$ 434.1727, found: 434.1726.

methyl (R)-2-((phenoxyimino)(phenyl)methoxy)-3-phenylpropanoate (S53)

Prepared following GP2. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.79 – 7.67 (m, 2H), 7.48 – 7.37 (m, 2H), 7.36 – 7.27 (m, 8H), 7.26 – 7.12 (m, 2H), 7.10 – 6.93 (m, 1H), 5.73 (dd, $J = 8.2$, 4.6 Hz, 1H), 3.64 (s, 3H), 3.31 (ddd, $J = 22.5$, 14.2, 6.4 Hz, 2H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 170.54 (s), 159.04 (s), 154.35 (s), 136.00 (s), 130.94 (s), 130.67 (s), 129.67 (s), 128.70 (s), 128.31 (s), 127.67 (s), 122.39 (s), 114.47 (s), 81.09 (s), 52.30 (s), 39.62 (s). HRMS (ESI-TOF) $m/z$ calcd for [M+Na]$^+$ 398.1368, found: 398.1394.

hexadecyl N-phenoxybenzimidate (S54)

Prepared following GP2. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 – 7.81 (m, 1H), 7.50 – 7.38 (m, 2H), 7.36 – 7.27 (m, 2H), 7.05 – 6.97 (m, 1H), 4.41 (t, $J = 6.7$ Hz, 1H), 1.80 (dt, $J = 14.6$, 6.7 Hz, 1H), 1.51 – 1.39 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.56 (s), 157.18 (s), 131.17 (s), 130.60 (s), 129.76 (s), 128.54 (s), 127.60 (s), 122.08 (s), 114.58 (s), 73.27 (s), 32.08 (s), 32.96 (3C, s), 29.86 (3C, s), 29.83 (s), 29.81 (s), 29.80 (s), 29.72 (s), 29.68 (s), 29.52 (s), 29.44 (s), 25.89 (s), 22.85 (s), 14.27 (s). HRMS (ESI-TOF) $m/z$ calcd for [M+H]$^+$ 438.3367, found: 438.3343.

4,4,4-trifluorobutyl N-phenoxybenzimidate (S55)

Prepared following GP1. $^1$H NMR (600 MHz, C$_6$D$_6$) $\delta$ 7.82 – 7.77 (m, 2H), 7.44 – 7.40 (m, 2H), 7.26 – 7.18 (m, 2H), 7.14 – 7.08 (m, 3H), 6.92 (tt, $J = 7.4$, 1.1 Hz, 1H), 3.89 (t, $J = 6.2$ Hz, 2H), 1.90 – 1.74 (m, 2H), 1.55 (ddd, $J = 13.9$, 10.1, 6.1 Hz, 2H). $^{19}$F NMR (565 MHz, C$_6$D$_6$) $\delta$ –66.21 (t, $J = 11.0$ Hz). $^{13}$C NMR (151 MHz, C$_6$D$_6$) $\delta$ 159.94 (s), 156.46 (s), 131.29 (s), 130.81 (s), 129.76 (s), 127.87 (s), 127.45 (q, $J = 276.1$ Hz), 127.54 (s), 122.61 (s), 114.80 (s), 70.97 (s), 30.42 (q, $J = 29.0$ Hz), 23.15 (q, $J = 3.0$ Hz). HRMS (ESI-TOF) $m/z$ calcd for [M+Na]$^+$ 346.1025, found: 346.1013.
3-phenylpropyl N-phenoxybenzimidate (S56)

Prepared following GP2. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.89 – 7.79 (m, 2H), 7.50 – 7.39 (m, 3H), 7.35 – 7.27 (m, 6H) 7.23 – 7.18 (m, 3H), 7.02 (tt, $J$ = 7.3, 1.2 Hz, 1H), 4.44 (t, $J$ = 6.4 Hz, 2H), 2.90 – 2.77 (m, 2H), 2.25 – 2.05 (m, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 159.50, 157.05, 141.39, 131.02, 130.67, 129.42, 128.65, 128.62, 128.58, 127.58, 126.18, 122.15, 114.57, 77.37, 77.16, 76.95, 72.22, 32.14, 32.01.

HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 354.1470, found: 354.1585.

(Z)-hex-3-en-1-yl-N-phenoxybenzimidate (S57)

Prepared following GP1. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.94 (ddd, $J$ = 4.5, 2.5, 1.5 Hz, 2H), 7.47 – 7.42 (m, 2H), 7.22 – 7.19 (m, 2H), 7.14 – 7.10 (m, 3H), 6.91 (tt, $J$ = 7.4, 1.1 Hz, 1H), 5.48 – 5.41 (m, 1H), 5.39 – 5.25 (m, 1H), 4.29 (t, $J$ = 6.8 Hz, 2H), 2.44 – 2.28 (m, 2H), 1.99 – 1.85 (m, 2H), 0.84 (t, $J$ = 7.5 Hz, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 160.14, 156.72, 134.64, 131.88, 130.60, 129.68, 128.56, 127.82, 124.34, 122.36, 114.88, 72.64, 28.61, 20.96, 14.34. HRMS (ESI-TOF) calcd For [M+H]$^+$ 202.1232, found: 202.1220.

(E)-hex-3-en-1-yl-N-phenoxybenzimidate (S58)

Prepared following GP1. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.95 (ddd, $J$ = 4.4, 2.4, 1.5 Hz, 2H), 7.51 – 7.40 (m, 2H), 7.24 – 7.18 (m, 2H), 7.14 – 7.10 (m, 3H), 6.94 – 6.87 (m, 1H), 5.45 (dtt, $J$ = 15.2, 6.3, 1.2 Hz, 1H), 5.32 (dtt, $J$ = 15.1, 6.8, 1.5 Hz, 1H), 4.31 (t, $J$ = 6.7 Hz, 3H), 2.30 (qd, $J$ = 6.7, 1.1 Hz, 2H), 1.94 – 1.83 (m, 1H), 0.88 (t, $J$ = 7.5 Hz, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 160.15 (s), 156.77 (s), 135.34 (s), 131.93 (s), 130.58 (s), 129.68 (s), 128.53 (s), 127.83 (s), 124.71 (s), 122.34 (s), 114.89 (s), 72.91 (s), 33.93 (s), 26.01 (s), 13.81 (s). HRMS (ESI-TOF) calcd For [M+H]$^+$ 202.1232, found: 202.1236.

(±)-cis-2-phenylcyclopropyl)ethyl-N-phenoxybenzimidate (S59)

Prepared following GP1. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.83 – 7.75 (m, 2H), 7.50 – 7.45 (m, 3H), 7.45 – 7.37 (m, 2H), 7.37 – 7.31 (m, 3H), 7.28 – 7.16 (m, 4H), 7.04 (t, $J$ = 7.2 Hz, 1H), 4.35 (tdd, $J$ = 13.2, 8.3, 5.0 Hz, 2H), 2.34 – 2.13 (m, 1H), 1.66 (dt, $J$ = 13.2, 6.7 Hz, 1H), 1.50 – 1.41 (m, 1H), 1.34 (dd, $J$ = 14.6, 6.4 Hz, 1H), 1.07 (td, $J$ = 8.5, 5.2 Hz, 1H), 0.83 – 0.75 (m, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 159.51 (s), 157.17 (s), 138.91 (s), 130.57 (s), 129.38 (s), 129.11 (s), 128.51 (s), 128.17 (s), 127.62 (s), 126.03 (s), 122.08 (s), 114.58 (s), 72.80 (s), 29.50 (s), 20.89 (s), 15.54 (s), 9.48 (s). HRMS (ESI-TOF) calcd for [M+Na]$^+$ 380.1626, found: 380.1632.
VI. Enantioselective, Radical C-H Amination of Alcohols

(R)-2,4-diphenyl-4,5-dihydrooxazole (1)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 1 as colorless oil (17.8 mg, 80% yield, 94% e.e.). $[\alpha]^{20}_D = +30.2$ (c = 0.63, CHCl$_3$). R$_f$ = 0.45 (hexane : EtOAc = 5:1). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.08 – 8.03 (m, 2H), 7.54 – 7.49 (m, 1H), 7.47 – 7.41 (m, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.27 (m, 3H), 5.40 (dd, $J$ = 10.1, 8.2 Hz, 1H), 4.80 (dd, $J$ = 10.1, 8.4 Hz, 1H), 4.29 (t, $J$ = 8.3 Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 164.89 (s), 142.53 (s), 131.68 (s), 128.90 (s), 128.62 (s), 127.76 (s), 127.72 (s), 126.90 (s), 75.03 (s), 70.28 (s). HRMS (ESI-TOF) m/z calcd for [M+H]$^+$ 224.1070, found: 224.1065. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 6.4 min (major) and 17.2 min (minor).

(R)-4-(4-fluorophenyl)-2-phenyl-4,5-dihydrooxazole (2)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 2 as white solid (23.7 mg, 98% yield, 93% e.e.); $[\alpha]^{20}_D = +31.0$ (c = 0.98, CHCl$_3$). R$_f$ = 0.45 (hexane : EtOAc = 5:1). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.07 – 8.01 (m, 2H), 7.52 (dd, $J$ = 8.6, 2.4, 1.2 Hz, 1H), 7.48 – 7.39 (m, 2H), 7.33 – 7.27 (m, 2H), 7.09 – 7.00 (m, 2H), 5.38 (dd, $J$ = 10.0, 8.2 Hz, 1H), 4.79 (dd, $J$ = 10.1, 8.4 Hz, 1H), 4.23 (t, $J$ = 8.3 Hz, 1H). $^{19}$F NMR (565 MHz, CDCl$_3$) δ -114.95 – -115.14 (m). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 165.00 (s), 163.25 (s), 161.62 (s), 138.33 (d, $J$ = 3.2 Hz), 131.78 (s), 128.58 (d, $J$ = 9.2 Hz), 128.51 (d, $J$ = 8.3 Hz), 127.57 (s), 115.72 (d, $J$ = 21.5 Hz), 74.99 (s), 69.60 (s). HRMS (ESI-TOF) m/z calcd for [M+H]$^+$ 242.0976, found: 242.0978. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 6.1 min (major) and 20.3 min (minor).
The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 3 as white solid (22.3 mg, 87% yield, 94% e.e.). $[\alpha]_{20}^{26} = +26.4$ (c = 1.0, CHCl$_3$). R$_f$ = 0.5 (hexane : EtOAc = 5:1). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.08 – 8.00 (m, 2H), 7.55 – 7.49 (m, 1H), 7.48 – 7.42 (m, 2H), 7.36 – 7.30 (m, 2H), 7.27 – 7.22 (m, 2H), 5.37 (dd, J = 10.1, 8.2 Hz, 1H), 4.79 (dd, J = 10.1, 8.4 Hz, 1H), 4.22 (t, J = 8.3 Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 165.18 (s), 141.06 (s), 133.54 (s), 131.82 (s), 129.02 (s), 128.62 (s), 128.56 (s), 128.25 (s), 127.49 (s), 74.84 (s), 69.60 (s). HRMS (ESI-TOF) m/z calcd for [M+H]$^+$ 258.0680, found: 258.0675. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 6.6 min (major) and 23.6 min (minor).
(R)-4-(4-bromophenyl)-2-phenyl-4,5-dihydrooxazole (4)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 4 as white solid (26.9 mg, 89% yield, 95% e.e.). \( \alpha = +21.5 \) (c = 1.0, CHCl3). \( R = 0.5 \) (hexane : EtOAc = 5:1). \(^1\)H NMR (600 MHz, CDCl3) \( \delta \) 8.03 (dd, \( J = 8.3, 1.3 \) Hz, 2H), 7.54 – 7.50 (m, 1H), 7.50 – 7.47 (m, 2H), 7.46 – 7.41 (m, 2H), 7.21 – 7.17 (m, 2H), 5.35 (dd, \( J = 10.1, 8.2 \) Hz, 1H), 4.79 (dd, \( J = 10.1, 8.4 \) Hz, 1H), 4.22 (t, \( J = 8.3 \) Hz, 1H). \(^{13}\)C NMR (151 MHz, CDCl3) \( \delta \) 165.22 (s), 141.59 (s), 131.98 (s), 131.83 (s), 128.62 (s), 128.61 (s), 128.56 (s), 127.48 (s), 121.65 (s), 74.78 (s), 69.65 (s). HRMS (ESI-TOF) \( m/z \) calcd for [M+H]\(^+\) 302.0175, found: 302.0170. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5\( \mu \)m, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 6.6 min (major) and 23.6 min (minor).

(R)-4-(4-iodophenyl)-2-phenyl-4,5-dihydrooxazole (5)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 5 as off white solid (27.6 mg, 79% yield, 93% e.e.). \( \alpha = +16.2 \) (c = 1.2, CHCl3). \( R = 0.5 \) (hexane : EtOAc = 5:1). \(^1\)H NMR (600 MHz, CDCl3) \( \delta \) 8.05 – 8.00 (m, 2H), 7.68 (d, \( J = 8.3 \) Hz, 2H), 7.65 (t, \( J = 7.7 \) Hz, 2H), 7.06 (d, \( J = 8.3 \) Hz, 2H), 5.34 (dd, \( J = 10.0, 8.3 \) Hz, 1H), 4.79 (dd, \( J = 10.1, 8.5 \) Hz, 1H), 4.21 (t, \( J = 8.3 \) Hz, 1H). \(^{13}\)C NMR (151 MHz, CDCl3) \( \delta \) 165.22 (s), 142.26 (s), 131.83 (s), 128.86 (s), 128.62 (s), 128.56 (s), 127.47 (s), 93.19 (s), 74.75 (s), 69.72 (s). HRMS (ESI-TOF) \( m/z \) calcd for [M+H]\(^+\) 350.0036, found: 350.0022. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5\( \mu \)m, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 6.8 min (major) and 28.0 min (minor).
The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 6 as colorless oil (21.2 mg, 89% yield, 91% e.e.), $[\alpha]^{20}_{D} = +31.3$ (c = 0.9, CHCl$_3$). R$_f$ = 0.5 (hexane : EtOAc = 5:1). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.05 (d, $J$ = 7.6 Hz, 2H), 7.51 (t, $J$ = 7.4 Hz, 1H), 7.44 (t, $J$ = 7.5 Hz, 2H), 7.21 (d, $J$ = 8.1 Hz, 2H), 7.17 (d, $J$ = 7.9 Hz, 2H), 5.37 (t, $J$ = 8.9 Hz, 1H), 4.78 (dd, $J$ = 9.9, 8.4 Hz, 1H), 4.27 (t, $J$ = 8.2 Hz, 1H), 2.35 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 164.70 (s), 139.54 (s), 137.40 (s), 131.61 (s), 129.54 (s), 128.60 (s), 128.49 (s), 127.77 (s), 126.79 (s), 75.07 (s), 70.02 (s), 21.23 (s). HRMS (ESI-TOF) m/z calcd for [M+H]$^+$ 238.1226, found: 238.1228. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 6.1 min (major) and 17.3 min (minor).
(R)-4-(4-methoxyphenyl)-2-phenyl-4,5-dihydrooxazole (7)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 7 as colorless oil (21.3 mg, 80% yield, 84% e.e.). \([\alpha]^{20}_D = +42.1 \) (c = 1.1, CHCl3). \( R_t = 0.35 \) (hexane : EtOAc = 5:1). \(^1\)H NMR (600 MHz, CDCl3) \( \delta \) 8.08 – 8.01 (m, 2H), 7.51 (t, \( J = 7.4 \) Hz, 1H), 7.44 (t, \( J = 7.6 \) Hz, 2H), 7.25 – 7.21 (m, 2H), 6.93 – 6.86 (m, 2H), 5.35 (dd, \( J = 9.9, 8.2 \) Hz, 1H), 4.77 (dd, \( J = 10.0, 8.4 \) Hz, 1H), 4.26 (t, \( J = 8.2 \) Hz, 1H), 3.80 (s, 3H). \(^13\)C NMR (151 MHz, CDCl3) \( \delta \) 164.63 (s), 159.26 (s), 134.64 (s), 131.65 (s), 128.57 (d, \( J = 10.4 \) Hz), 128.49 (s), 128.03 (s), 127.71 (s), 114.28 (s), 69.68 (s), 55.43 (s). HRMS (ESI-TOF) \( m/z \) calcd for [M+H] \(^+\) 254.1176, found: 254.1180. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5\( \mu \)m, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 7.1 min (major) and 21.5 min (minor).

(R)-2-phenyl-4-(4-(trifluoromethyl)phenyl)-4,5-dihydrooxazole (8)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 8 as white solid (20.4 mg, 70% yield, 95% e.e.). \([\alpha]^{20}_D = +11.6 \) (c = 0.7, CHCl3). \( R_t = 0.5 \) (hexane : EtOAc = 5:1). \(^1\)H NMR (600 MHz, CDCl3) \( \delta \) 8.07 – 8.02 (m, 2H), 7.62 (d, \( J = 8.1 \) Hz, 2H), 7.56 – 7.50 (m, 1H), 7.49 – 7.41 (m, 4H), 5.46 (dd, \( J = 10.0, 8.4 \) Hz, 1H), 4.84 (dd, \( J = 10.2, 8.5 \) Hz, 1H), 4.25 (t, \( J = 8.3 \) Hz, 1H). \(^19\)F NMR (565 MHz, CDCl3) \( \delta \) -62.50 (s). \(^13\)C NMR (151 MHz, CDCl3) \( \delta \) 165.50 (s), 146.53 (s), 131.94 (s), 130.07 (q, \( J = 32.4 \) Hz), 128.66 (s), 128.41 (s), 127.41 (s), 127.25 (s), 125.88 (q, \( J = 3.7 \) Hz), 124.26 (q, \( J = 272.0 \) Hz), 74.67 (s), 59.81 (s). HRMS (ESI-TOF) \( m/z \) calcd for [M+H] \(^+\) 292.0944, found: 292.0942. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5\( \mu \)m, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 7.1 min (major) and 22.7 min (minor).
The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 9 as white solid (29.0 mg, 94% yield, 92% e.e.). $[\alpha]_{20}^2 = +23.0$ (c = 1.1, CHCl$_3$). R$_f$ = 0.5 (hexane : EtOAc = 5:1). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.04 (dd, $J = 8.3, 1.2$ Hz, 2H), 7.52 (ddd, $J = 6.9, 2.5, 1.2$ Hz, 1H), 7.48–7.42 (m, 2H), 7.34 (dd, $J = 9.0, 2.3$ Hz, 2H), 7.21 (d, $J = 8.0$ Hz, 2H), 5.41 (dd, $J = 10.0, 8.2$ Hz, 1H), 4.81 (dd, $J = 10.1, 8.5$ Hz, 1H), 4.25 (t, $J = 8.3$ Hz, 1H). $^{19}$F NMR (565 MHz, CDCl$_3$) δ -57.90 (s). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 165.25 (s), 148.81 (d, $J = 1.7$ Hz), 141.29 (s), 131.87 (s), 128.64 (s), 128.58 (s), 128.34 (s), 127.47 (s), 121.46 (s), 120.61 (q, $J = 257.1$ Hz), 74.84 (s), 69.57 (s). HRMS (ESI-TOF) m/z calcd for [M+H]$^+$ 308.0893, found: 308.0889. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 5.7 min (major) and 20.0 min (minor).
(R)-2-phenyl-4-(o-tolyl)-4,5-dihydrooxazole (10)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 10 as light-yellow oil (22.6 mg, 95% yield, 91% e.e.). $[\alpha]^{20} = -40.2$ (c = 0.8, CHCl$_3$). $R_f = 0.5$ (hexane : EtOAc = 5:1). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.10 – 8.05 (m, 2H), 7.52 (dd, $J = 10.6$, 4.2 Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 2H), 7.36 – 7.30 (m, 1H), 7.24 – 7.16 (m, 3H), 5.61 (dd, $J = 9.8$, 8.8 Hz, 1H), 4.85 (dd, $J = 10.2$, 8.1 Hz, 1H), 4.15 (t, $J = 8.3$ Hz, 1H), 2.37 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 164.96 (s), 140.96 (s), 134.73 (s), 131.64 (s), 130.39 (s), 128.57 (s), 128.53 (s), 127.80 (s), 127.45 (s), 126.63 (s), 126.25 (s), 74.33 (s), 67.11 (s), 19.66 (s). HRMS (ESI-TOF) $m/z$ calcd for [M+H]$^+$ 238.1226, found: 238.1230. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 7.2 min (major) and 13.8min (minor).

(R)-2-phenyl-4-(2-(trifluoromethyl)phenyl)-4,5-dihydrooxazole (11)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 11 as colorless oil (22.6 mg, 81% yield, 97% e.e.). $[\alpha]^{20} = -72.5$ (c = 0.8, CHCl$_3$). $R_f = 0.5$ (hexane : EtOAc = 5:1). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.07 (dd, $J = 5.1$, 3.3 Hz, 1H), 7.68 (d, $J = 7.8$ Hz, 1H), 7.58 – 7.52 (m, 1H), 7.51 (d, $J = 7.7$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 1H), 7.39 (t, $J = 7.6$ Hz, 1H), 5.83 (t, $J = 9.2$ Hz, 1H), 4.83 (t, $J = 9.2$ Hz, 1H), 4.11 (t, $J = 8.4$ Hz, 1H). $^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ -58.96 (s). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 166.00 (s), 141.23 (s), 131.91 (s), 128.65 (s), 128.62 (s), 128.07 (s), 127.60 (s), 127.47 (s), 127.42 (s), 125.82 (q, $J = 5.7$ Hz), 124.52 (q, $J = 272.9$ Hz), 75.32 (d, $J = 1.6$ Hz), 66.13 (d, $J = 1.7$ Hz). HRMS (ESI-TOF) $m/z$ calcd for [M+H]$^+$ 292.0944, found: 292.0943. HPLC (CHIRALCEL IC, 0.46*25 cm, 5μm, hexane / isopropanol = 97.5/2.5, flow 0.5 mL/min, detection at 254 nm) retention time = 7.0 min (major) and 6.5min (minor).
The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline \(12\) as light-yellow oil (20.1 mg, 79\% yield, 93\% e.e.). \([\alpha]_D = +13.9 \ (c = 0.8, \text{CHCl}_3)\). \(R_f = 0.4 \ (\text{hexane} : \text{EtOAc} = 5:1)\).

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta 8.07 \ (\text{dd, } J = 5.2, 3.3 \text{ Hz, 2H}), 7.56 – 7.52 \ (\text{m, 1H}), 7.49 – 7.44 \ (\text{m, 2H}), 7.32 – 7.27 \ (\text{m, 1H}), 6.93 \ (\text{d, } J = 7.6 \text{ Hz, 1H}), 6.91 – 6.88 \ (\text{m, 1H}), 6.86 \ (\text{ddd, } J = 8.2, 2.6, 0.8 \text{ Hz, 1H}), 5.40 \ (\text{dd, } J = 10.1, 8.2 \text{ Hz, 1H}), 4.82 \ (\text{dd, } J = 10.1, 8.4 \text{ Hz, 1H}), 4.30 \ (\text{t, } J = 8.3 \text{ Hz, 1H}), 3.82 \ (\text{s, 3H})\).

\(^13\)C NMR (151 MHz, CDCl\(_3\)) \(\delta 164.95 \ (\text{s}), 160.11 \ (\text{s}), 144.15 \ (\text{s}), 131.68 \ (\text{s}), 129.94 \ (\text{s}), 128.62 \ (\text{s}), 128.50 \ (\text{s}), 127.69 \ (\text{s}), 119.18 \ (\text{s}), 113.14 \ (\text{s}), 112.53 \ (\text{s}), 74.91 \ (\text{s}), 70.17 \ (\text{s}), 55.38 \ (\text{s})\).

HRMS (ESI-TOF) \(m/z\) calc for \([M+H]^+\) 254.1176, found: 254.1178. HPLC (CHIRALCEL OD-H, 0.46\*25 cm, 5\(\mu\)m, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 7.0 min (major) and 19.5min (minor).
(R)-2-phenyl-4-(3-(trifluoromethyl)phenyl)-4,5-dihydrooxazole (13)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 13 as colorless oil (24.8 mg, 85% yield, 91% e.e.). $[\alpha]^{20}_{D} = +10.8$ (c = 0.6, CHCl$_3$); Rf = 0.5 (hexane : EtOAc = 5:1). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.09 – 8.01 (m, 2H), 7.62 – 7.42 (m, 7H), 5.46 (dd, $J = 10.1$, 8.4 Hz, 1H), 4.85 (dd, $J = 10.2$, 8.5 Hz, 1H), 4.25 (t, $J = 8.4$ Hz, 1H). $^{19}$F NMR (565 MHz, CDCl$_3$) $\delta$ -62.58 (s). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 165.54 (s), 143.54 (s), 131.94 (s), 131.25 (q, $J = 32.3$ Hz), 130.32 (s), 129.42 (s), 128.69 (s), 128.61 (s), 127.40 (s), 124.67 (q, $J = 3.8$ Hz), 124.20 (q, $J = 272.3$ Hz), 123.78 (q, $J = 3.7$ Hz), 74.74 (s), 69.86 (s). HRMS (ESI-TOF) m/z calcld for [M+H]$^+$ 292.0944, found: 292.0939. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 5.9 min (major) and 18.4 min (minor).

(R)-4-(2,4-dichlorophenyl)-2-phenyl-4,5-dihydrooxazole (14)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 14 as colorless oil (25.7 mg, 88% yield, 98% e.e.). $[\alpha]^{20}_{D} = -142.2$ (c = 0.9, CHCl$_3$). Rf = 0.5 (hexane : EtOAc = 5:1). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.06 (dd, $J = 8.2$, 1.1 Hz, 2H), 7.57 – 7.50 (m, 1H), 7.49 – 7.43 (m, 2H), 7.43 – 7.37 (m, 2H), 7.28 – 7.22 (m, 1H), 5.68 (dt, $J = 12.0$, 6.1 Hz, 1H), 4.98 – 4.90 (m, 1H), 4.14 – 4.05 (m, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 165.88 (s), 139.47 (s), 133.88 (s), 132.99 (s), 131.93 (s), 129.18 (s), 128.92 (s), 128.61 (s), 128.60 (s), 127.54 (s), 127.48 (s), 74.09 (s), 66.91 (s). HRMS (ESI-TOF) m/z calcld for [M+H]$^+$ 292.0290, found: 292.0288. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 5.7 min (major) and 7.5 min (minor).
(R)-4-(3,4-dichlorophenyl)-2-phenyl-4,5-dihydrooxazole (15)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 15 as colorless oil (25.4 mg, 87% yield, 93% e.e.). $[\alpha]_20 = +10.3$ (c = 1.2, CHCl$_3$). $R_f = 0.5$ (hexane : EtOAc = 5:1). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.06 – 8.00 (m, 2H), 7.55 – 7.50 (m, 1H), 7.49 – 7.43 (m, 2H), 7.43 (s, 1H), 7.42 – 7.40 (m, 1H), 7.15 (dd, $J$ = 8.3, 2.1 Hz, 1H), 5.35 (dd, $J$ = 10.1, 8.2 Hz, 1H), 4.80 (dd, $J$ = 10.2, 8.5 Hz, 1H), 4.21 (t, $J$ = 8.3 Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 165.57 (s), 142.80 (s), 132.99 (s), 131.98 (s), 131.77 (s), 130.84 (s), 128.90 (s), 128.67 (s), 128.61 (s), 127.28 (s), 126.24 (s), 74.59 (s), 69.17 (s). HRMS (ESI-TOF) $m/z$ calcld for [M+H]$^+$ 292.0290, found: 292.0293. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5$\mu$m, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 7.0 min (major) and 27.8 min (minor).
(R)-4-(3-fluoro-4-methoxyphenyl)-2-phenyl-4,5-dihydrooxazole (16)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 16 as white solid (24.5 mg, 90% yield, 89% e.e.). [α]$^\text{D}_{20}$ = +32.2 (c = 1.0, CHCl$_3$). R$_f$ = 0.35 (hexane : EtOAc = 5:1). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.06 – 8.00 (m, 2H), 7.55 – 7.49 (m, 1H), 7.47 – 7.41 (m, 2H), 7.09 – 7.00 (m, 2H), 6.93 (dd, $J = 10.5, 6.3$ Hz, 1H), 5.32 (dt, $J = 17.6, 8.8$ Hz, 1H), 4.76 (dd, $J = 10.1, 8.4$ Hz, 1H), 4.22 (t, $J = 8.2$ Hz, 1H), 3.87 (s, 3H). $^{19}$F NMR (565 MHz, CDCl$_3$) δ -134.42 (dd, $J = 11.6, 8.7$ Hz). $^{13}$C NMR (151 MHz, CDCl$_3$) δ -134.42 (dd, $J = 11.6, 8.7$ Hz). HRMS (ESI-TOF) m/z calcd for [M+H]$^+$ 272.1081, found: 272.1086. HPLC (CHIRALCEL OD-H, 0.46x25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 7.4 min (major) and 24.6 min (minor).

(R)-4-(3,5-bis(trifluoromethyl)phenyl)-2-phenyl-4,5-dihydrooxazole (17)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 17 as colorless oil (28.4 mg, 79% yield, 80% e.e.). [α]$^\text{D}_{20}$ = -3.3 (c = 0.9, CHCl$_3$). R$_f$ = 0.35 (hexane : EtOAc = 5:1). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.08 – 8.03 (m, 2H), 7.83 (s, 1H), 7.79 (s, 2H), 7.58 – 7.53 (m, 1H), 7.49 – 7.44 (m, 2H), 5.54 (dd, $J = 10.2, 8.6$ Hz, 1H), 4.90 (dd, $J = 10.3, 8.6$ Hz, 1H), 4.25 (t, $J = 8.6$ Hz, 1H). $^{19}$F NMR (565 MHz, CDCl$_3$) δ -62.83 (s). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 166.17 (s), 145.13 (s), 132.25 (q, $J = 33.3$ Hz), 132.20 (s), 128.77 (s), 128.69 (s), 127.23 (d, $J = 2.6$ Hz), 127.08 (s), 126.35 – 120.29 (m), 121.86 (q, $J = 3.8$ Hz), 121.83 (q, $J = 3.8$ Hz), 74.39 (s), 69.48 (s). HRMS (ESI-TOF) m/z calcd for [M+H]$^+$ 360.0818, found: 360.0816. HPLC (CHIRALCEL OD-H, 0.46x25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 5.6 min (major) and 10.1 min (minor).
(R)-4-(naphthalen-2-yl)-2-phenyl-4,5-dihydrooxazole (18)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 18 as yellow oil (25.2 mg in 92% yield, 93% e.e.). \([\alpha]^{20}= +36.3\) (c = 0.9, CHCl₃). R⁺ = 0.5 (hexane : EtOAc = 5:1). \(^1\)H NMR (600 MHz, CDCl₃) \(\delta\) 8.10 (dd, \(J = 8.3, 1.2\) Hz, 2H), 7.88 – 7.78 (m, 4H), 7.56 – 7.51 (m, 1H), 7.50 – 7.45 (m, 4H), 7.41 (dd, \(J = 8.5, 1.7\) Hz, 1H), 5.58 (dd, \(J = 10.0, 8.3\) Hz, 1H), 4.87 (dd, \(J = 10.1, 8.4\) Hz, 1H), 4.36 (t, \(J = 8.3\) Hz, 1H). \(^13\)C NMR (151 MHz, CDCl₃) \(\delta\) 165.05 (s), 139.79 (s), 131.74 (s), 128.88 (s), 128.68 (s), 128.56 (s), 128.06 (s), 127.72 (s), 127.82 (s), 127.72 (s), 126.35 (s), 126.02 (s), 125.70 (s), 124.77 (s), 74.90 (s), 70.40 (s). HRMS (ESI-TOF) \(m/z\) calcd for [M+H]^+ 274.1226, found: 274.1224. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 11.3 min (major) and 24.9 min (minor).
**(R)-4-(naphthalen-1-yl)-2-phenyl-4,5-dihydrooxazole (19)**

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 19 as yellow oil (27.1 mg, 99% yield, 94% e.e.). $[\alpha]_D^{20} = -251.5$ (c = 0.9, CHCl$_3$). R$_f$ = 0.5 (hexane : EtOAc = 5:1). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.13 (dd, $J = 8.2$, 1.1 Hz, 2H), 7.92 (d, $J = 7.9$ Hz, 1H), 7.87 (d, $J = 8.2$ Hz, 1H), 7.81 (d, $J = 8.2$ Hz, 1H), 7.61 (d, $J = 7.1$ Hz, 1H), 7.59 – 7.51 (m, 3H), 7.48 (dt, $J = 7.8$, 6.8 Hz, 3H), 6.14 (dd, $J = 10.1$, 8.5 Hz, 1H), 5.07 (d, $J = 10.4$, 8.2 Hz, 1H), 4.23 (t, $J = 8.3$ Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 165.12 (s), 138.75 (s), 134.02 (s), 131.73 (s), 130.77 (s), 129.21 (s), 128.64 (s), 128.58 (s), 128.01 (s), 127.84 (s), 126.44 (s), 125.91 (s), 125.76 (s), 123.61 (s), 122.91 (s), 74.65 (s), 66.83 (s). HRMS (ESI-TOF) m/z calcd for [M+H]$^+$ 274.1226, found: 274.1229. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 9.4 min (major) and 25.4 min (minor).

**HPLC Chromatogram**

---

**((R)-2-phenyl-4-(pyridin-3-yl)-4,5-dihydrooxazole (20)**

The reaction was conducted on a 0.05 mmol scale according to the GP3 and yielding 65% by $^1$HNMR using 1,2-dichloroethane as an internal standard. The crude mixture was purified by column chromatography affording oxazoline 20 as an off-white solid (12 mg, 82% e.e.). R$_f$ = 0.4 (dichloromethane : isopropanol = 9:1). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.64 – 8.54 (m, 1H), 8.10 – 8.00 (m, 1H), 7.65 (d, $J = 7.9$ Hz, 1H), 7.53 (t, $J = 7.4$ Hz, 1H), 7.45 (t, $J = 7.7$ Hz, 1H), 7.31 (dd, $J = 7.7$, 4.8 Hz, 1H), 5.44 (dd, $J = 10.0$, 8.2 Hz, 1H), 4.85 (dd, $J = 10.1$, 8.6 Hz, 1H), 4.27 (t, $J = 8.3$ Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 165.51 (s), 149.00 (s), 148.40 (s), 148.40 (s), 131.86 (s), 128.54 (s), 128.49 (s), 127.36 (s), 127.15 (s), 123.83 (s), 74.50 (s), 67.77 (s). HRMS (ESI) calcd. For C$_{14}$H$_{13}$N$_2$O [M+H]$^+$ 255.1016, found: 255.1028. HPLC (CHIRALCEL IC, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 18.2 min (minor) and 20.4 min (major).
(R)-2-phenyl-4-(thiophen-3-yl)-4,5-dihydrooxazole (21)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 21 as yellow solid (19.1 mg, 83% yield, 90% e.e.). $[\alpha]_{20}^\circ = +56.0 \ (c = 0.7, \text{CHCl}_3)$. Rf = 0.5 (hexane : EtOAc = 5:1). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.06 – 7.99 (m, 2H), 7.54 – 7.48 (m, 1H), 7.43 (t, $J = 7.6$ Hz, 2H), 7.33 (dd, $J = 5.0, 3.0$ Hz, 1H), 7.23 (d, $J = 2.4$ Hz, 1H), 7.04 (dd, $J = 5.0, 1.1$ Hz, 1H), 5.47 (dd, $J = 9.7, 8.2$ Hz, 1H), 4.74 (dd, $J = 9.9, 8.3$ Hz, 1H), 4.32 (t, $J = 8.1$ Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 164.71 (s), 143.32 (s), 131.68 (s), 128.58 (s), 128.50 (s), 127.64 (s), 126.14 (s), 121.59 (s), 74.15 (s), 66.12 (s). HRMS (ESI-TOF) m/z calcd for [M+H]$^+$ 230.0634, found: 230.0640. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 6.7 min (major) and 20.1 min (minor).
(R)-4-(benzo[b]thiophen-3-yl)-2-phenyl-4,5-dihydrooxazole (22)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 22 as yellow oil (25.8 mg in 92% yield, 95% e.e.). [α]$_D$ = -95.4 (c = 0.9, CHCl$_3$). R$_f$ = 0.5 (hexane : EtOAc = 5:1). Prepared following general procedure 3. $^1$H NMR (600 MHz, CDCl$_3$) δ 8.09 (dt, $J$ = 8.4, 1.6 Hz, 2H), 7.91 – 7.86 (m, 1H), 7.72 – 7.68 (m, 1H), 7.55 – 7.51 (m, 1H), 7.49 – 7.44 (m, 2H), 7.42 – 7.35 (m, 3H), 5.75 (ddd, $J$ = 10.1, 8.1, 0.8 Hz, 1H), 4.89 (dd, $J$ = 10.2, 8.3 Hz, 1H), 4.40 (t, $J$ = 8.2 Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 165.18 (s), 141.35 (s), 137.35 (s), 137.03 (s), 131.80 (s), 128.65 (s), 128.56 (s), 127.61 (s), 124.59 (s), 124.33 (s), 123.30 (s), 121.58 (s), 73.09 (s), 65.48 (s). HRMS (ESI-TOF) m/z calcd for [M+H]$^+$ 280.0791, found: 280.0787. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 8.7 min (major) and 27.4 min (minor).

(R)-2-phenyl-4-(prop-1-en-2-yl)-4,5-dihydrooxazole (23)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 23 as yellow oil (15.4 mg, 82% yield, 94% e.e.). [α]$_D$ = +56.8 (c = 0.4, CHCl$_3$). R$_f$ = 0.5 (hexane : EtOAc = 5:1). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.01 – 7.96 (m, 2H), 7.52 – 7.46 (m, 1H), 7.44 – 7.39 (m, 2H), 5.06 – 4.99 (m, 1H), 4.94 – 4.87 (m, 1H), 4.82 (dd, $J$ = 9.9, 8.0 Hz, 1H), 4.53 (dd, $J$ = 10.1, 8.3 Hz, 1H), 4.18 (t, $J$ = 8.1 Hz, 1H), 1.76 – 1.72 (m, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 164.49 (s), 144.59 (s), 131.57 (s), 128.52 (s), 128.48 (s), 127.77 (s), 112.56 (s), 71.89 (s), 71.65 (s), 18.53 (s). HRMS (ESI-TOF) m/z calcd for [M+H]$^+$ 188.1070, found: 188.1068. Note: The titled compound has a low boiling point. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 5.1 min (major) and 8.6 min (minor).
(R)-2-phenyl-4-vinyl-4,5-dihydrooxazole (24)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 24 as yellow oil (13.9 mg, 80% yield, 83% e.e.). $[\alpha]_{20}^E = +49.7$ (c = 0.4, CHCl₃). $R_f = 0.5$ (hexane : EtOAc = 5:1). $^1$H NMR (600 MHz, CDCl₃) $\delta$ 8.00 – 7.95 (m, 2H), 7.51 – 7.46 (m, 1H), 7.44 – 7.37 (m, 2H), 5.91 (ddd, $J = 17.2, 10.2, 7.2$ Hz, 1H), 5.33 (dt, $J = 17.1, 1.2$ Hz, 1H), 5.24 – 5.18 (m, 1H), 4.81 (dt, $J = 8.2, 7.3$ Hz, 1H), 4.57 (dd, $J = 9.8, 8.3$ Hz, 1H), 4.14 (t, $J = 8.2$ Hz, 1H). $^{13}$C NMR (151 MHz, CDCl₃) $\delta$ 164.57 (s), 138.10 (s), 131.60 (s), 128.50 (s), 128.46 (s), 127.71 (s), 116.91 (s), 72.48 (s), 69.00 (s). HRMS (ESI-TOF) $m/z$ calcd for [M+H]$^+$ 174.0913, found: 174.0937. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 5.6 min (major) and 9.1 min (minor).

(R)-4-ethynyl-2-phenyl-4,5-dihydrooxazole (25)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 25 as yellow solid (16.9 mg, 99% yield, 89% e.e.). $[\alpha]_{20}^E = +5.5$ (c = 0.6, CHCl₃). $R_f = 0.5$ (hexane : EtOAc = 5:1). $^1$H NMR (600 MHz, CDCl₃) $\delta$ 7.98 (ddd, $J = 8.5, 7.2, 1.3$ Hz, 2H), 7.52 – 7.47 (m, 1H), 7.44 – 7.37 (m, 2H), 5.00 (ddd, $J = 10.4, 8.4, 2.3$ Hz, 1H), 4.63 (dd, $J = 10.1, 8.1$ Hz, 1H), 4.40 (t, $J = 8.3$ Hz, 1H), 2.45 (d, $J = 2.3$ Hz, 1H). $^{13}$C NMR (151 MHz, CDCl₃) $\delta$ 165.91 (s), 131.96 (s), 128.66 (s), 128.49 (s), 127.16 (s), 82.73 (s), 73.04 (s), 72.74 (s), 57.21 (s). HRMS (ESI-TOF) $m/z$ calcd for [M+H]$^+$ 172.0757, found: 172.0775.
HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 6.6 min (major) and 9.0 min (minor).

(R)-2-phenyl-4-(prop-1-yn-1-yl)-4,5-dihydrooxazole (26)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 26 as colorless oil (17.9 mg, 96% yield, 83% e.e.). [α]$_{20}^{20}$ = +24.3 (c = 0.1, CHCl$_3$). $R_f$ = 0.5 (hexane : EtOAc = 5:1). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.00 – 7.95 (m, 2H), 7.48 (t, $J$ = 7.4 Hz, 1H), 7.40 (t, $J$ = 7.7 Hz, 2H), 5.00 – 4.93 (m, 1H), 4.59 (dd, $J$ = 9.9, 8.0 Hz, 1H), 4.31 (t, $J$ = 8.3 Hz, 1H), 1.85 (d, $J$ = 2.3 Hz, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 165.34 (s), 131.79 (s), 128.61 (s), 128.43 (s), 127.38 (s), 80.86 (s), 78.00 (s), 73.40 (s), 57.55 (s), 3.84 (s). HRMS (ESI-TOF) $m/z$ calcd for [M+H]$^+$ 186.0913, found: 186.0915.

Note: this compound is unstable under room temperature when exposed with air. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 6.0 min (major) and 8.3 min (minor).
The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 27 as yellow oil (22.1 mg, 89% yield, 83% e.e.). \([\alpha]_{D}^{20} = +45.8 \text{ (c = 0.2, CHCl}_3\)].  

\(\text{IR } {\mu}_c\text{m}^{-1}\) (film): 3336, 1664, 1616, 1465, 1420, 1264, 1213, 1148, 1038, 1019, 705, 614.  

\(\text{HRMS (ESI-TOF) } m/z\) calcd for [M+H]+ 248.1070, found: 248.1081.  

HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 10.8 min (minor) and 12.7 min (major).  

\(\text{(R)-2-phenyl-4-(phenylethynyl)-4,5-dihydrooxazole (27)}\)

\(\text{1H NMR (600 MHz, CDCl}_3\) \(\delta\) 8.01 (ddd, \(J\) = 8.5, 6.9, 5.0 Hz, 2H), 7.54 – 7.48 (m, 1H), 7.48 – 7.40 (m, 4H), 7.34 – 7.27 (m, 3H), 5.29 – 5.19 (m, 1H), 4.70 (dt, \(J\) = 18.0, 9.0 Hz, 1H), 4.48 (t, \(J\) = 8.3 Hz, 1H).  

\(\text{13C NMR (151 MHz, CDCl}_3\) \(\delta\) 165.70 (s), 131.96 (s), 131.91 (s), 128.68 (s), 128.55 (s), 128.51 (s), 128.37 (s), 127.39 (s), 122.79 (s), 87.91 (s), 84.56 (s), 73.33 (s), 58.08 (s).  

\(\text{HRMS (ESI-TOF) } m/z\) calcd for [M+H]+ 248.1070, found: 248.1081.  

HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 10.8 min (minor) and 12.7 min (major).

\[\text{The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 28 as white solid (10.2 mg, 36% yield, 89% e.e.). [}\alpha]^{20}_{D} = +78.1 \text{ (c = 0.5, CHCl}_3\].  

\(\text{IR } {\mu}_c\text{m}^{-1}\) (film): 3323, 1669, 1616, 1466, 1420, 1264, 1212, 1148, 1038, 1019, 705, 614.  

\(\text{HRMS (ESI-TOF) } m/z\) calcd for [M+H]+ 282.1852, found: 282.1852.  

HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 80/20, flow 0.7 mL/min, detection at 254 nm) retention time = 5.1 min (major) and 7.5 min (minor).  

\(\text{(R)-4-((3r,5r,7r)-adamantan-1-yl)-2-phenyl-4,5-dihydrooxazole (28)}\)
The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 29 as colorless oil (10.3 mg, 47% yield, 94% e.e.). \([\alpha]^{20} = +56.1 \text{ (c = 0.3, CHCl}_3\)]. R\(_f\) = 0.45 (hexane : EtOAc = 5:1). \(1^H\) NMR (600 MHz, CDCl\(_3\)) \(\delta 7.99 – 7.93 \text{ (m, 2H), 7.50 – 7.45 \text{ (m, 1H), 7.42 – 7.36 \text{ (m, 2H), 4.44 (dd, } J = 8.6, 7.7 \text{ Hz, 1H), 4.38 (dd, } J = 9.9, 8.6 \text{ Hz, 1H), 4.31 (dd, } J = 9.9, 7.6 \text{ Hz, 1H), 3.26 (s, 3H), 1.34 (s, 3H), 1.10 (s, 3H).}\) \(^{13}C\) NMR (151 MHz, CDCl\(_3\)) \(\delta 164.55 \text{ (s), 131.40 \text{ (s), 128.46 \text{ (s), 128.39 \text{ (s), 128.04 (s), 76.68 (s), 74.55 (s), 68.98 (s), 49.76 (s), 22.98 (s), 19.50 (s).} \) HRMS (ESI-TOF) m/z calcd for [M+H\(^+\)] 220.1332, found: 220.1348. HPLC (CHIRALCEL OD-H, 0.46\(\times\)25 cm, 5\(\mu\)m, hexane / isopropanol = 80/20, flow 0.7 mL/min, detection at 254 nm) retention time = 5.2 min (major) and 7.2 min (minor).

\((R)\)-4-(2-methoxypropan-2-yl)-2-phenyl-4,5-dihydrooxazole (29)

\((R)\)-4-(tert-butyl)-2-phenyl-4,5-dihydrooxazole (30)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 30 as colorless oil (10.2 mg, 86% yield, 89% e.e.). \([\alpha]^{20} = +79.1 \text{ (c = 0.2, CHCl}_3\)]. R\(_f\) = 0.65 (hexane : EtOAc = 5:1). \(^1H\) NMR (600 MHz, CDCl\(_3\)) \(\delta 7.99 – 7.92 \text{ (m, 2H), 7.49 – 7.44 \text{ (m, 1H), 7.43 – 7.37 \text{ (m, 2H), 4.34 (dd, } J = 10.1, 8.6 \text{ Hz, 1H), 4.26 – 4.21 \text{ (m, 1H), 4.05 (dd, } J = 10.1, 1.7 \text{ Hz, 1H), 0.96 (s, 9H).}\) \(^{13}C\) NMR (151
MHz, CDCl₃) δ 163.38 (s), 131.24 (s), 128.40 (s), 128.37 (s), 128.16 (s), 76.35 (s), 68.86 (s), 34.19 (s), 26.02 (s). HRMS (ESI-TOF) m/z calcld for [M+H]+ 204.1383, found: 204.1383. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 4.8 min (major) and 6.1 min (minor).

(R)-4-isopropyl-2-phenyl-4,5-dihydrooxazole (31)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 31 as colorless oil (9.5 mg, 50% yield, 79% e.e.). [α]²⁰ = +16.0 (c = 0.03, CHCl₃). R₉ = 0.65 (hexane : EtOAc = 5:1). ¹H NMR (600 MHz, CDCl₃) δ 7.97 – 7.93 (m, 2H), 7.48 – 7.44 (m, 1H), 7.42 – 7.37 (m, 2H), 4.43 – 4.38 (m, 1H), 4.17 – 4.08 (m, 2H), 1.87 (dq, J = 13.4, 6.7 Hz, 1H), 1.03 (d, J = 6.8 Hz, 3H), 0.93 (d, J = 6.8 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 163.50 (s), 131.30 (s), 128.41 (s), 128.39 (s), 128.12 (s), 72.76 (s), 70.22 (s), 32.98 (s), 19.10 (s), 18.21 (s). HRMS (ESI-TOF) m/z calcld for [M+H]+ 190.1226, found: 190.1231. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 80/20, flow 0.7 mL/min, detection at 254 nm) retention time = 5.3 min (major) and 10.6 min (minor).
(R)-2-(furan-2-yl)-4-phenyl-4,5-dihydrooxazole (32)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 32 as brown oil (11.9 mg, 56% yield, 97% e.e.). [α]$^20$ = -6.7 ($c = 0.5$, CHCl$_3$). $R_t = 0.50$ (hexane : EtOAc = 5:1). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.60 – 7.55 (m, 1H), 7.38 – 7.33 (m, 2H), 7.32 – 7.03 (m, 1H), 6.52 (dd, $J = 3.5$, 1.8 Hz, 1H), 5.39 (dd, $J = 9.9$, 8.4 Hz, 1H), 4.78 (dd, $J = 10.0$, 8.4 Hz, 1H), 4.27 (t, $J = 8.3$ Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 157.12 (s), 145.54 (s), 142.94 (s), 141.96 (s), 128.88 (s), 127.82 (s), 126.87 (s), 115.00 (s), 111.77 (s), 74.92 (s), 70.16 (s). HRMS (ESI-TOF) $m/z$ calcld for [M+H]$^+$ 214.0863, found: 214.0875. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 7.3 min (major) and 10.6 min (minor).

(R)-2-(4-methoxyphenyl)-4-phenyl-4,5-dihydrooxazole (33)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 33 as white solid (20.0 mg, 75% yield, 94% e.e.). [α]$^20$ = +14.7 ($c = 0.8$, CHCl$_3$). $R_t = 0.45$ (hexane : EtOAc = 5:1). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.02 – 7.97 (m, 2H), 7.35 (dd, $J = 10.2$, 4.7 Hz, 2H), 7.33 – 7.26 (m, 3H), 6.96 – 6.92 (m, 2H), 5.36 (dd, $J = 9.9$, 8.1 Hz, 1H), 4.77 (dd, $J = 10.0$, 8.3 Hz, 1H), 4.25 (t, $J = 8.2$ Hz, 1H), 3.86 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 164.66 (s), 162.39 (s), 142.77 (s), 130.34 (s), 128.85 (s), 127.68 (s), 126.89 (s), 120.19 (s), 113.87 (s), 74.93 (s), 70.22 (s), 55.50 (s). HRMS (ESI-TOF) $m/z$ calcld for [M+H]$^+$ 254.1176, found: 254.1178. HPLC (CHIRALCEL AD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 80/20, flow 0.7 mL/min, detection at 254 nm) retention time = 10.9 min (minor) and 13.1 min (major).
(R)-2-(3-chlorophenyl)-4-phenyl-4,5-dihydrooxazole (34)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 34 as colorless oil (25.4 mg, 99% yield, 93% e.e.). [α]$_D^{20}$ = +29.4 (c = 0.6, CHCl$_3$). R$_f$ = 0.50 (hexane : EtOAc = 5:1). $^1$H NMR (600 MHz, CDCl$_3$) δ 8.13 – 7.99 (m, 1H), 7.93 (d, $J$ = 7.8 Hz, 1H), 7.54 – 7.43 (m, 1H), 7.41 – 7.33 (m, 3H), 7.32 – 7.27 (m, 3H), 5.40 (dd, $J$ = 9.9, 8.5 Hz, 1H), 4.81 (dd, $J$ = 10.1, 8.5 Hz, 1H), 4.30 (t, $J$ = 8.3 Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 163.78 (s), 142.12 (s), 134.64 (s), 131.75 (s), 129.85 (s), 129.41 (s), 128.97 (s), 128.76 (s), 127.91 (s), 126.86 (s), 126.72 (s), 75.21 (s), 70.26 (s). HRMS (ESI-TOF) m/z calcld for [M+H]$_+$ 258.0680, found: 258.0687. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 6.6 min (major) and 8.7 min (minor).
(R)-2-(2-chlorophenyl)-4-phenyl-4,5-dihydrooxazole (35)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 35 as white solid (12.6 mg, 49% yield, 98% e.e.). \([\alpha]^{20}_D = -356.7 \text{ (c = 0.2, CHCl}_3\)). \(R_f = 0.50\) (hexane : EtOAc = 5:1). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta 7.75\) (dd, \(J = 7.7, 1.6 \text{ Hz, 1H}\)), 7.39 (dd, \(J = 8.0, 1.1 \text{ Hz, 1H}\)), 7.33 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 7.16 (s, 1H), 5.36 (dd, \(J = 10.2, 8.3 \text{ Hz, 1H}\)), 4.73 (dd, \(J = 10.2, 8.4 \text{ Hz, 1H}\)), 4.20 (t, \(J = 8.3 \text{ Hz, 1H}\)). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta 163.74\) (s), 142.23 (s), 133.76 (s), 131.91 (s), 131.67 (s), 130.90 (s), 128.93 (s), 127.82 (s), 127.55 (s), 126.87 (s), 126.73 (s), 75.07 (s), 70.55 (s). HRMS (ESI-TOF) \(m/z\) calcd for \([M+H]\)^+ 258.0680, found: 258.0676. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 90/10, flow 0.7 mL/min, detection at 254 nm) retention time = 12.3 min (minor) and 14.7 min (major).

(R)-2-(naphthalen-2-yl)-4-phenyl-4,5-dihydrooxazole (36)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 36 as white solid (17.5 mg, 64% yield, 94% e.e.). \([\alpha]^{20}_D = -13.2 \text{ (c = 0.7, CHCl}_3\)). \(R_f = 0.55\) (hexane : EtOAc = 5:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.55\) (d, \(J = 0.7 \text{ Hz, 1H}\)), 8.14 (dd, \(J = 8.6, 1.7 \text{ Hz, 1H}\)), 7.97 – 7.85 (m, 3H), 7.60 – 7.50 (m, 2H), 7.41 – 7.35 (m, 4H), 7.33 – 7.27 (m, 1H), 5.45 (dd, \(J = 10.1, 8.2 \text{ Hz, 1H}\)), 4.87 (dd, \(J = 10.1, 8.3 \text{ Hz, 1H}\)), 4.35 (t, \(J = 8.3 \text{ Hz, 1H}\)). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta 165.02\) (s), 142.51 (s), 134.99 (s), 132.85 (s), 129.21 (s), 129.08 (s), 128.94 (s), 128.29 (s), 127.93 (s), 127.81 (s), 127.75 (s), 126.94 (s), 126.71 (s), 125.14 (s), 124.99 (s), 75.11 (s), 70.40 (s). HRMS (ESI-TOF) \(m/z\) calcd for \([M+H]\)^+ 274.1226, found: 274.1225. HPLC (CHIRALCEL AD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 80/20, flow 0.7 mL/min, detection at 254 nm) retention time = 9.9 min (minor) and 21.8 min (major).
The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 37 as white solid (21.8 mg, 80% yield, 97% e.e.). \([\alpha]^{20}_D = -55.8\) (c = 1.0, CHCl3). \(R_f = 0.45\) (hexane : EtOAc = 5:1). \(1^H\) NMR (600 MHz, CDCl3) δ 9.27 (d, \(J = 8.7\) Hz, 1H), 8.21 (dd, \(J = 7.2, 1.2\) Hz, 1H), 8.00 (d, \(J = 8.2\) Hz, 1H), 7.90 (d, \(J = 8.1\) Hz, 1H), 7.61 (ddd, \(J = 8.5, 6.8, 1.4\) Hz, 1H), 7.57 – 7.51 (m, 2H), 7.44 – 7.38 (m, 4H), 7.35 – 7.30 (m, 1H), 5.58 (dd, \(J = 10.1, 8.3\) Hz, 1H), 4.84 (dd, \(J = 10.2, 8.3\) Hz, 1H), 4.31 (t, \(J = 8.2\) Hz, 1H). \(13^C\) NMR (151 MHz, CDCl3) δ 164.81 (s), 142.70 (s), 133.92 (s), 132.31 (s), 131.44 (s), 129.42 (s), 128.93 (s), 128.60 (s), 127.75 (s), 127.60 (s), 126.90 (s), 126.73 (s), 126.27 (s), 124.79 (s), 124.42 (s), 73.96 (s), 71.10 (s). HRMS (ESI-TOF) m/z calcd for [M+H]+ 274.1226, found: 274.1226. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 10.0 min (minor) and 13.1 min (major).
The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline \( \text{38} \) as colorless oil (22.5 mg, 64% yield, 99% e.e.). \([\alpha]^{20}_{D} = -230\) (c = 0.8, CHCl\(_3\)). \( R_f = 0.45 \) (hexane : EtOAc = 5:1). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 9.31 (d, \( J = 8.6 \) Hz, 1H), 8.21 (d, \( J = 7.2 \) Hz, 1H), 8.02 (d, \( J = 8.1 \) Hz, 1H), 7.92 (dd, \( J = 8.1, 0.5 \) Hz, 1H), 7.67 – 7.62 (m, 1H), 7.59 – 7.49 (m, 3H), 7.45 (d, \( J = 2.1 \) Hz, 1H), 7.27 (dd, \( J = 8.8, 2.4 \) Hz, 1H), 5.86 (dd, \( J = 10.3, 8.5 \) Hz, 1H), 5.04 – 4.90 (m, 1H), 4.13 (t, \( J = 8.4 \) Hz, 1H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \( \delta \) 165.80 (s), 139.48 (s), 133.95 (s), 133.93 (s), 133.06 (s), 132.64 (s), 131.39 (s), 129.68 (s), 129.24 (s), 128.75 (s), 127.74 (s), 127.62 (s), 126.58 (s), 126.36 (s), 124.82 (s), 124.03 (s), 72.90 (s), 67.93 (s). HRMS (ESI-TOF) \( m/z \) calcd for \([M+H]^+ \) 342.0447, found: 342.0438. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5\( \mu \)m, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 8.0 min (minor) and 8.6 min (major).

\((R)-4-(2,4\text{-dichlorophenyl})-2-(naphthalen-1-yl)-4,5\text{-dihydrooxazole (38)}\)

\((R)-4-(benzo[b]thiophen-3-yl)-2-(naphthalen-1-yl)-4,5\text{-dihydrooxazole (39)}\)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline \( \text{39} \) as light yellow solid (28.0 mg, 85% yield, 99% e.e.). \([\alpha]^{20}_{D} = -67.6\) (c = 1.1, CHCl\(_3\)). \( R_f = 0.45 \) (hexane : EtOAc = 5:1). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 9.31 (d, \( J = 8.6 \) Hz, 1H), 8.23 (dd, \( J = 7.2, 1.1 \) Hz, 1H), 8.02 (d, \( J = 8.2 \) Hz, 1H), 7.91 (dd, \( J = 7.4, 1.0 \) Hz, 2H), 7.84 – 7.74 (m, 1H), 7.63 (dd, \( J = 8.5, 6.8, 1.3 \) Hz, 1H), 7.59 – 7.52 (m, 2H), 7.49 (s, 1H), 7.45 – 7.34 (m, 2H), 5.99 – 5.85 (m, 1H), 4.93 (dd, \( J = 10.2, 8.1 \) Hz, 1H), 4.42 (t, \( J = 8.1 \) Hz, 1H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \( \delta \) 165.05 (s), 141.38 (s), 137.45 (s), 137.19 (s), 133.94 (s), 132.47 (s), 131.42 (s), 129.58 (s), 128.67 (s), 127.00 (s), 126.66 (s), 126.33 (s), 124.82 (s), 124.03 (s), 72.70 (s), 67.03 (s).
124.63 (s), 124.38 (s), 124.30 (s), 123.34 (s), 123.15 (s), 121.67 (s), 72.02 (s), 66.41 (s). HRMS (ESI-TOF) \( m/z \) calcd for \([M+H]^+\) 330.0947, found: 330.0942. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5\( \mu \)m, hexane / isopropanol = 80/20, flow 0.7 mL/min, detection at 254 nm) retention time = 26.6 min (minor) and 28.3 min (major).

\((R)-2\)-(naphthalen-1-yl)-4-(4-(trifluoromethoxy)phenyl)-4,5-dihydrooxazole (40)

\[\text{The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 40 as light yellow solid (27.6 mg, 77\% yield, 97\% e.e.). } [\alpha]_{20}^{\text{D}} = -66.2 \text{ (c = 0.15, CHCl}_3). \text{ Rf} = 0.45 \text{ (hexane : EtOAc = 5:1).} \]

\(^1\text{H} \text{NMR (600 MHz, CDCl}_3) \delta 9.29 – 9.18 \text{ (m, 1H), 8.20 (dd, } J = 7.2, 1.2 \text{ Hz, 1H), 8.00 (t, } J = 9.8 \text{ Hz, 1H), 7.91 (t, } J = 9.9 \text{ Hz, 1H), 7.65 – 7.58 \text{ (m, 1H), 7.56} – 7.50 \text{ (m, 2H), 7.46} – 7.36 \text{ (m, 2H), 7.24 (d, } J = 8.0 \text{ Hz, 2H), 5.58 (dd, } J = 10.1, 8.3 \text{ Hz, 1H), 4.83 (dt, } J = 17.9, 9.0 \text{ Hz, 1H), 4.27 (t, } J = 8.3 \text{ Hz, 1H).} \]

\(^1^3\text{C} \text{NMR (151 MHz, CDCl}_3) \delta 165.16 \text{ (s), 148.80 (d, } J = 1.7 \text{ Hz), 141.42 \text{ (s), 133.95 \text{ (s), 132.54 \text{ (s), 131.41 \text{ (s), 129.61 \text{ (s), 128.69 \text{ (s), 128.33 \text{ (s), 127.71 \text{ (s), 126.61 \text{ (s), 126.34 \text{ (s), 124.80 \text{ (s), 124.11 \text{ (s), 121.49 \text{ (s), 120.64 (q, } J = 257.0 \text{ Hz), 73.72 \text{ (s), 70.41 \text{ (s).}}}

HRMS (ESI-TOF) \( m/z \) calcd for \([M+H]^+\) 358.1049, found: 358.1048. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5\( \mu \)m, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 9.9 min (minor) and 11.4 min (major).
(R)-4-(4-methoxyphenyl)-2-(naphthalen-1-yl)-4,5-dihydrooxazole (41)

The reaction was conducted on a 0.1 mmol scale according to the **GP3** and afforded product 41 as off white solid (24.8 mg, 82% yield, 88% e.e.). \([\alpha]_{20} = -70.0 \) (c = 0.8, CHCl₃). Rᵣ = 0.35 (hexane : EtOAc = 5:1). ¹H NMR (600 MHz, CDCl₃) 8 9.25 (d, J = 8.6 Hz, 1H), 8.19 (dd, J = 7.2, 1.1 Hz, 1H), 7.99 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.60 (ddd, J = 8.5, 6.8, 1.3 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.36 – 7.29 (m, 2H), 6.99 – 6.85 (m, 2H), 5.52 (dd, J = 10.0, 8.3 Hz, 1H), 4.80 (dd, J = 10.1, 8.3 Hz, 1H), 4.28 (t, J = 8.2 Hz, 1H), 3.82 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) 8 164.53 (s), 159.26 (s), 135.03 – 134.92 (m), 133.92 (s), 132.26 (s), 131.44 (s), 129.43 (s), 128.59 (s), 128.04 (s), 127.57 (s), 126.75 (s), 126.26 (s), 124.80 (s), 124.50 (s), 114.31 (s), 74.06 (s), 70.58 (s), 55.46 (s). HRMS (ESI-TOF) m/z calcd for [M+H]⁺ 304.1332, found: 304.1327. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 10.4 min (minor) and 23.1 min (major).

(R)-4-(3,5-bis(trifluoromethyl)phenyl)-2-(naphthalen-1-yl)-4,5-dihydrooxazole (42)

The reaction was conducted on a 0.1 mmol scale according to the **GP3** and afforded product 42 as colorless oil (26.6 mg, 65% yield, 97% e.e.). \([\alpha]_{20} = -145.5 \) (c = 0.6, CHCl₃). Rᵣ = 0.45 (hexane : EtOAc = 5:1). ¹H NMR (600 MHz, CDCl₃) 8 9.23 (d, J = 8.6 Hz, 1H), 8.22 (dd, J = 7.2, 1.0 Hz, 1H), 8.04 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 9.9 Hz, 3H), 7.64 (ddd, J = 8.5, 6.8, 1.3 Hz, 1H), 7.59 – 7.52 (m,
2H), 5.71 (dd, J = 10.0, 8.8 Hz, 1H), 4.92 (dd, J = 10.3, 8.5 Hz, 1H), 4.28 (t, J = 8.5 Hz, 1H). $^{19}$F NMR (565 MHz, CDCl$_3$) δ -62.78 – -62.83 (m). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 166.06 (s), 145.22 (s), 133.97 (s), 132.89 (s), 132.29 (q, J = 33.4 Hz), 131.37 (s), 129.84 (s), 128.80 (s), 127.84 (s), 127.25 (d, J = 2.7 Hz), 126.46 (s), 126.41 (s), 124.82 (s), 123.67 (s), 123.40 (q, J = 272.7 Hz), 121.87 (q, J = 3.8 Hz), 121.84 (q, J = 3.8 Hz), 73.25 (s), 70.32 (s). HRMS (ESI-TOF) m/z calcd for [M+H]$^+$ 410.0974, found 410.0971.

HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 6.6 min (minor) and 10.8 min (major).

(R)-2-(naphthalen-1-yl)-4-(thiophen-3-yl)-4,5-dihydrooxazole (43)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 43 as white solid (24.8 mg, 83% yield, 93% e.e.). $^{[a]20\pi}$ = -38.9 (c = 0.9, CHCl$_3$). $R_f$ = 0.45 (hexane : EtOAc = 5:1). $^1$H NMR (600 MHz, CDCl$_3$) δ 9.23 (d, J = 8.7 Hz, 1H), 8.19 (dd, J = 7.2, 1.2 Hz, 1H), 7.99 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.61 (ddd, J = 8.5, 6.8, 1.4 Hz, 1H), 7.57 – 7.47 (m, 2H), 7.36 (dd, J = 5.0, 3.0 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.13 (dd, J = 5.0, 1.2 Hz, 1H), 5.70 – 5.60 (m, 1H), 4.78 (dd, J = 10.0, 8.2 Hz, 1H), 4.35 (t, J = 8.0 Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 164.65 (s), 143.48 (s), 133.89 (s), 132.34 (s), 131.38 (s), 129.47 (s), 128.61 (s), 126.70 (s), 126.64 (s), 126.28 (s), 126.21 (s), 124.78 (s), 124.36 (s), 121.52 (s), 73.14 (s), 66.94 (s). HRMS (ESI-TOF) m/z calcd for [M+H]$^+$ 280.0791, found: 280.0783. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 12.3 min (minor) and 13.5 min (major).
(R)-2-(naphthalen-1-yl)-4-(prop-1-en-2-yl)-4,5-dihydrooxazole (44)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 44 as yellow oil (19.2 mg, 82% yield, 94% e.e.). [α]$_{20}^2$ = +32.2 (c = 0.7, CHCl$_3$). R$_f$ = 0.45 (hexane : EtOAc = 5:1). $^1$H NMR (600 MHz, CDCl$_3$) δ 9.18 (d, J = 8.6 Hz, 1H), 8.13 (d, J = 7.2 Hz, 1H), 7.97 (d, J = 8.1 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.68 – 7.58 (m, 1H), 7.52 (dt, J = 18.9, 7.6 Hz, 2H), 5.12 (s, 1H), 5.03 – 4.92 (m, 2H), 4.57 (dd, J = 10.0, 8.4 Hz, 1H), 4.22 (dd, J = 11.7, 4.4 Hz, 1H), 1.84 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 164.37 (s), 144.71 (s), 133.87 (s), 132.14 (s), 131.36 (s), 129.27 (s), 128.56 (s), 128.50 (s), 127.50 (s), 126.63 (s), 126.23 (s), 124.77 (s), 124.56 (s), 112.45 (s), 72.69 (s), 70.67 (s), 18.77 (s). HRMS (ESI-TOF) m/z calc for [M+H]+ 238.1226, found: 238.1223. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 6.6 min (minor) and 8.4 min (major).

(R)-2-(naphthalen-1-yl)-4-vinyl-4,5-dihydrooxazole (45)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 45 as off white solid (21.6 mg, 91% yield, 87% e.e.). [α]$_{20}^2$ = +68.0 (c = 0.7, CHCl$_3$). R$_f$ = 0.45 (hexane : EtOAc = 5:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 9.22 – 9.13 (m, 1H), 8.12 (dd, J = 7.3, 1.2 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.91 – 7.83 (m, 1H), 7.61 (ddd, J = 8.5, 6.8, 1.4 Hz, 1H), 7.57 – 7.44 (m, 2H), 6.03 (ddd, J = 17.1, 10.2, 6.9 Hz, 1H), 5.41 (dt, J = 17.1, 1.3 Hz, 1H), 5.26 (dt, J = 10.2, 1.1 Hz, 1H), 5.00 (ddd, J = 9.6, 8.1, 7.0 Hz, 1H), 4.60 (dd, J = 9.8, 3.8 Hz, 1H), 4.18 (t, J = 8.2 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 164.45 (s), 138.22 (d, J = 5.8 Hz, 133.86 (s), 132.21 (s), 131.32 (s), 129.34 (s), 128.55 (s), 127.51 (s), 126.62 (s), 126.23 (s), 124.74 (s), 124.46 (s), 116.75 (s), 71.52 (s), 69.67 (s). HRMS (ESI-TOF) m/z calc for [M+H]+ 224.1070, found: 224.1081. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 7.8 min (minor) and 8.9 min (major).
(R)-4-ethynyl-2-(naphthalen-1-yl)-4,5-dihydrooxazole (46)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 46 as yellow oil (19.2 mg, 87% yield, 91% e.e.). [α]$_D$ = -28.3 (c = 0.7, CHCl$_3$). R$_f$ = 0.45 (hexane : EtOAc = 5:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 9.20 – 9.10 (m, 1H), 8.12 (dd, $J$ = 7.3, 1.3 Hz, 1H), 7.98 (d, $J$ = 8.2 Hz, 1H), 7.91 – 7.84 (m, 1H), 7.62 (ddd, $J$ = 8.5, 6.8, 1.4 Hz, 1H), 7.58 – 7.44 (m, 2H), 6.47 (dd, $J$ = 10.3, 8.3, 2.3 Hz, 1H), 4.66 (dd, $J$ = 10.1, 8.1 Hz, 1H), 4.44 (t, $J$ = 8.2 Hz, 1H), 2.49 (d, $J$ = 2.3 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 165.79 (s), 133.83 (s), 132.61 (s), 131.25 (s), 129.61 (s), 128.57 (s), 127.65 (s), 126.58 (s), 126.32 (s), 124.67 (s), 123.84 (s), 82.92 (s), 72.81 (s), 72.01 (s), 57.95 (s). HRMS (ESI-TOF) $m$/z calc for [M+H]$^+$ 222.0913, found: 222.0924. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 8.2 min (minor) and 11.6 min (major).
(R)-2-(naphthalen-1-yl)-4-(prop-1-yn-1-yl)-4,5-dihydrooxazole (47)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 47 as yellow oil (21.6 mg, 92% yield, 84% e.e.). [α]$^{20}$ = -48.4 (c = 0.7, CHCl₃). Rₜ = 0.45 (hexane : EtOAc = 5:1). ¹H NMR (400 MHz, CDCl₃) δ 9.14 (dd, J = 8.8, 0.7 Hz, 1H), 8.12 (dd, J = 7.3, 1.3 Hz, 1H), 7.96 (dd, J = 8.2 Hz, 1H), 7.91 – 7.80 (m, 1H), 7.60 (dd, J = 8.5, 6.8, 1.4 Hz, 1H), 7.56 – 7.43 (m, 2H), 5.14 (ddd, J = 10.0, 8.5, 2.3 Hz, 1H), 4.62 (dd, J = 10.0, 8.0 Hz, 1H), 4.36 (dd, J = 8.5, 8.0 Hz, 1H), 1.88 (d, J = 2.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.23 (s), 133.82 (s), 132.43 (s), 131.28 (s), 129.53 (s), 128.52 (s), 127.56 (s), 126.69 (s), 126.26 (s), 124.68 (s), 124.11 (s), 80.91 (s), 78.20 (s), 72.43 (s), 58.31 (s), 3.88 (s). HRMS (ESI-TOF) m/z calcld for [M+H]$^+$ 236.1070, found: 236.1077. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 8.4 min (minor) and 11.8 min (major).

(R)-2-(naphthalen-1-yl)-4-(phenylethynyl)-4,5-dihydrooxazole (48)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 48 as yellow oil (28.5 mg, 96% yield, 90% e.e.). [α]$^{20}$ = -204.7 (c = 0.15, CHCl₃). Rₜ = 0.45 (hexane : EtOAc = 5:1). ¹H NMR (600 MHz, CDCl₃) δ 9.18 (d, J = 8.7 Hz, 1H), 8.15 (dd, J = 7.3, 1.2 Hz, 1H), 7.99 (dd, J = 8.2 Hz, 1H), 7.88 (dd, J = 8.2, 0.6 Hz, 1H), 7.62 (dd, J = 8.5, 6.8, 1.4 Hz, 1H), 7.57 – 7.46 (m, 4H), 7.35 – 7.28 (m, 3H), 5.42 (dd, J = 10.0, 8.4 Hz, 1H), 4.74 (dd, J = 10.1, 8.0 Hz, 1H), 4.53 (t, J = 8.2 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 165.60 (s), 133.87 (s), 132.54 (s), 131.96 (s), 131.31 (s), 129.59 (s), 128.58 (s), 128.55 (s), 128.39 (s), 127.65 (s), 126.66 (s), 126.33 (s), 124.72 (s), 124.10 (s), 122.85 (s), 88.12 (s), 84.61 (s), 72.32 (s), 58.82 (s). HRMS (ESI-TOF) m/z calcld for [M+H]$^+$ 298.1226, found: 298.1226. HPLC
(CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 13.6 min (minor) and 15.6 min (major).

(R)-4-(tert-butyl)-2-(naphthalen-1-yl)-4,5-dihydrooxazole (49)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 49 as colorless oil (7.6 mg, 30% yield, 91% e.e.). [α]$_{20}$$^0$ = +74.6 (c = 0.13, CHCl$_3$). R$_f$ = 0.55 (hexane : EtOAc = 5:1). $^1$H NMR (600 MHz, CDCl$_3$) δ 9.14 (d, J = 8.6 Hz, 1H), 8.07 (d, J = 7.2 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.60 (ddd, J = 8.5, 6.8, 1.3 Hz, 1H), 7.55 – 7.45 (m, 2H), 4.40 (dd, J = 9.8, 8.5 Hz, 1H), 4.28 (t, J = 8.1 Hz, 1H), 4.22 (dd, J = 9.9, 7.9 Hz, 1H), 1.05 (s, 9H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 163.35 (s), 133.90 (s), 131.88 (s), 131.44 (s), 129.07 (s), 128.56 (s), 127.42 (s), 126.62 (s), 126.18 (s), 124.94 (s), 124.82 (s), 67.97 (s), 34.28 (s), 29.85 (s), 26.20 (s). HRMS (ESI-TOF) m/z calcd for [M+H]$^+$ 254.1539, found: 254.1540. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 85/15, flow 0.7 mL/min, detection at 254 nm) retention time = 5.8 min (minor) and 6.2 min (major).
(3aR,8aS)-2-(naphthalen-1-yl)-3a,8a-dihydro-8H-Indeno[1,2-d]oxazole (50)

![structure](image_url)

The reaction was conducted on a 0.1 mmol scale according to the GP3. The yield of oxazoline 50 (12% yield, >20:1 d.r., 67% e.e.) was determined by $^1$H NMR using N,N-dimethyl-2,2,2-trifluoroacetamide as internal standard. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.03 (d, $J = 8.5$ Hz, 1H), 8.07 – 8.01 (m, 1H), 7.92 (d, $J = 8.2$ Hz, 1H), 7.84 (dd, $J = 8.1, 1.4$ Hz, 1H), 7.64 (s, 1H), 7.60 – 7.53 (m, 1H), 7.52 – 7.42 (m, 2H), 7.32 – 7.28 (m, 3H), 5.90 (d, $J = 7.9$ Hz, 1H), 5.53 (ddd, $J = 8.1, 6.7, 1.7$ Hz, 1H), 3.57 (dd, $J = 17.9, 6.7$ Hz, 1H), 3.45 (d, $J = 17.9$ Hz, 1H). HRMS (ESI-TOF) m/z calcd for [M+H]$^+$ 286.1226, found: 286.1220. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 80/20, flow 0.7 mL/min, detection at 254 nm) retention time = 10.3 min (minor) and 13.6 min (major).

(R)-2,4-diphenyl-4,5-dihydrooxazole (51)

See Mechanistic section (VIII) for characterization of deuterated product 51

(R)-4-(6-methoxynaphthalen-2-yl)-4-methyl-2-phenyl-4,5-dihydrooxazole (52)

![structure](image_url)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 52 as white solid. R$_f$ = 0.55 (hexane : EtOAc = 5:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.15 – 8.06 (m, 2H), 7.85 (d, $J = 1.9$ Hz, 1H), 7.77 – 7.70 (m, 2H), 7.58 – 7.41 (m, 4H), 7.14 (dt, $J = 5.5, 2.5$ Hz, 2H), 4.57 – 4.46 (m, 2H), 3.92 (s, 3H), 1.82 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 163.27 (s), 157.82 (s), 141.93 (s), 133.69 (s), 131.69 (s), 129.76 (s), 128.86 (s), 128.70 (s), 128.5 (s), 127.94 (s), 127.39 (s), 124.59 (s), 119.09 (s), 105.69 (s), 80.5 (s), 73.18 (s), 55.44 (s), 29.24 (s). HRMS (ESI-TOF) m/z calcd for [M+H]$^+$ 318.1489, found: 318.1485. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 80/20, flow 0.7 mL/min, detection at 254 nm)
1) For racemic 6.2 min (major) and 8.7 min (minor), 25% e.e.
2) For (S,S) 6.2 min (minor) and 8.7 min (major), 49% e.e., \([\alpha]^{20}_D = +36.7 \ (c = 0.40, \text{CHCl}_3)\);
3) For (R,R) 6.2 min (major) and 8.7 min (minor), 69% e.e., \([\alpha]^{20}_D = -38.8 \ (c = 0.49, \text{CHCl}_3)\).

methyl (4R,5R)-2,4-diphenyl-4,5-dihydrooxazole-5-carboxylate (53)

The reaction was conducted on a 0.05 mmol scale according to the GP3 and afforded oxazoline 53 as a mixture of diastereomers by \(^1\)H NMR analysis using 1,2-dichloroethane as an internal standard (R-catalyst 8:1 cis:trans, 90%; S-catalyst 2:1 cis:trans, 87%). \(R_f = 0.33\) (hexane : EtOAc = 4:1). Major diastereomer: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.11 (dd, \(J = 8.4, 1.3 \text{ Hz}, 2\text{H})\), 7.63 – 7.52 (m, 1H), 7.52 – 7.43 (m, 2H), 7.43 – 7.29 (m, 4H), 7.25 – 7.18 (m, 1H), 5.75 (d, \(J = 10.8 \text{ Hz}, 1\text{H})\), 5.39 (d, \(J = 10.8 \text{ Hz}, 1\text{H})\), 3.21 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 170.82 (s), 164.16 (s), 137.11 (s), 132.09 (s), 129.03 (s), 128.90 (s), 128.63 (s), 128.28 (s), 127.94 (s), 126.64 (s), 81.29 (s), 74.83 (s), 51.74 (s). Minor diastereomer: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.11 (dd, \(J = 8.4, 1.3 \text{ Hz}, 2\text{H})\), 7.63 – 7.52 (m, 1H), 7.52 – 7.43 (m, 2H), 7.43 – 7.29 (m, 4H), 7.25 – 7.18 (m, 1H), 5.46 (d, \(J = 6.5 \text{ Hz}, 1\text{H})\), 4.93 (d, \(J = 6.5 \text{ Hz}, 1\text{H})\), 3.88 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 168.67 (s), 153.34 (s), 141.29 (s), 132.11 (s), 129.54 (s), 128.53 (s), 128.21 (s), 127.76 (s), 126.97 (s), 83.32 (s), 73.72 (s), 52.91 (s). HRMS (ESI-TOF) \(m/z\) calcd for [M+H]\(^+\) 282.1130, found: 282.1205.
(R)-2-phenyl-4-tetradecyl-4,5-dihydrooxazole (54)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 54 as colorless oil (66% yield, 55% e.e.). *Rf* = 0.61 (hexane : EtOAc = 4:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.10 – 7.86 (m, 1H), 7.59 – 7.33 (m, 2H), 4.48 (dd, J = 9.4, 8.1 Hz, 1H), 4.37 – 4.18 (m, 1H), 4.03 (t, J = 8.0 Hz, 1H), 1.86 – 1.63 (m, 1H), 1.53 – 1.21 (m, 13H), 0.88 (t, J = 6.9 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 159.56 (s), 157.18 (s), 131.17 (s), 130.60 (s), 129.40 (s), 128.54 (s), 127.56 (s), 122.08 (s), 114.58 (s), 73.27 (s), 32.08 (s), 30.36 (s), 29.86 (s), 29.84 – 29.84 (s), 29.83 (s), 29.83 (s), 29.81 (s), 29.80 (s), 29.72 (s), 29.68 (s), 29.52 (s), 29.44 (s), 25.89 (s), 22.85 (s), 14.27 (s). HRMS (ESI-TOF) *m/z* calcd for [M+H]+ 344.2948, found: 344.3071.

HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 4.7 min (major) and 6.5 min (minor).

(R)-2-phenyl-4-(2,2,2-trifluoroethyl)-4,5-dihydrooxazole (55)

The reaction was conducted on a 0.1 mmol scale according to the GP3 and afforded oxazoline 55 as colorless oil (10.1 mg, 44% yield, 74% e.e.). [α]$^20$ = +11.2 (c = 0.5, CHCl$_3$). *Rf* = 0.65 (hexane : EtOAc = 5:1). $^1$H NMR (600 MHz, CDCl$_3$) δ 7.96 – 7.91 (m, 2H), 7.50 (dd, J = 8.7, 2.6, 1.3 Hz, 1H), 7.45 – 7.39 (m, 2H), 4.64 – 4.53 (m, 2H), 4.20 (t, J = 7.7 Hz, 1H), 2.79 (qd, J = 14.9, 11.4, 3.6 Hz, 1H), 2.36 – 2.17 (m, 1H). $^{19}$F NMR (565 MHz, CDCl$_3$) δ -64.31 (t, J = 10.9 Hz). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 165.11 (s), 131.91 (s), 128.58 (s), 128.51 (s), 127.26 (s), 126.08 (q, J = 277.1 Hz), 72.56 (s), 61.32 (q, J = 2.9 Hz), 39.88 (q, J = 27.2 Hz). HRMS (ESI-TOF) *m/z* calcd for [M+H]⁺ 230.0787, found: 230.0790. Note: the titled compound has a low boiling point. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm) retention time = 5.4 min (major) and 6.5 min (minor).
The reaction was conducted on a 0.05 mmol scale according to the GP3 and afforded oxazoline 56 which matched literature precedent\(^4\) (59% yield, 63% e.e.). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 8.01 – 7.87 (m, 2H), 7.53 – 7.47 (m, 4H), 7.41 (t, \(J = 7.6\) Hz, 3H), 7.31 (t, \(J = 7.4\) Hz, 1H), 7.25 – 7.19 (m, 1H), 4.67 – 4.51 (m, 1H), 4.43 – 4.25 (m, 1H), 4.15 (dd, \(J = 8.3, 7.5\) Hz, 1H), 3.25 (dd, \(J = 13.8, 5.1\) Hz, 1H), 2.74 (dd, \(J = 13.8, 8.9\) Hz, 1H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 163.13 (s), 137.17 (s), 130.48 (s), 128.42 (s), 127.71 (s), 127.47 (s), 127.41 (s), 126.96 (s), 125.66 (s), 71.03 (s), 67.06 (s), 41.01 (s). Matches previously reported characterization.

\((R,Z)-4\)-benzyl-2-phenyl-4,5-dihydrooxazole (56)

See Mechanistic section (VIII) for characterization of radical clock 57

\((R,E)-4\)-(but-1-en-1-yl)-2-phenyl-4,5-dihydrooxazole (58, major)

See Mechanistic section (VIII) for characterization of radical clock 58

\((R,E)-5\)-phenylpent-2-en-1-yl benzimdate (59)

See Mechanistic section (VIII) for characterization of radical clock 59
VII. Post-Functionalization of Oxazolines

(R)-2-amino-2-phenylethanol (60)

![Chemical Structure Image]

To a vial containing oxazoline 1 (22.3 mg, 0.1 mmol) was added 4 M aq. HCl (0.5 mL), according to the literature. The suspension was heated to 100 °C for 16 hrs. The reaction was allowed to cool to room temperature and quenched with 4M aq. NaOH (0.5 mL). The aqueous solution was extracted with Et2O (5 x 10 mL), and dried over Na2SO4. The solvent was removed in vacuo to afford the amino alcohol 60 as a white solid (10.6 mg, 77%). [α]20 = −32.0 (c = 0.125, CHCl3) 1H NMR (600 MHz, CDCl3) δ 7.38 – 7.30 (m, 4H), 7.30 – 7.26 (m, 1H), 4.05 (dd, J = 8.2, 4.4 Hz, 1H), 3.75 (dd, J = 10.7, 4.4 Hz, 1H), 3.56 (dd, J = 10.7, 8.3 Hz, 1H), 2.06 (s, 1H). 13C NMR (151 MHz, CDCl3) δ 142.95 (s), 128.88 (s), 127.75 (s), 126.65 (s), 68.24 (s), 57.54 (s). HRMS (ESI-TOF) calcd. for [M+H]+ 138.0919, found: 138.0935.

(R)-tert-butyl-(2-hydroxy-1-phenylethyl)carbamate (60Boc)

![Chemical Structure Image]

Amino alcohol 60 (9 mg, 0.065 mmol, 1 equiv) and trimethylamine (10.8 µL, 0.078 mmol, 1.2 equiv) were dissolved in dry THF (2 mL) and cooled to 0°C. Di-tert-butyl dicarbonate (14.2 mg, 0.065 mmol, 1 equiv) was added to the solution and the mixture was allowed to stir at room temperature overnight. The reaction was concentrated, dissolved in CH2Cl2, and washed with 1M HCl extracting with CH2Cl2. The solution was dried and concentrated to dryness to afford the pure product 60Boc (9.4 mg, 61%, 98% e.s.) and was utilized to determine e.s. % of 60. 1H NMR (600 MHz, CDCl3) δ 7.39 – 7.33 (m, 2H), 7.29 (m, 3H), 5.20 (s, 1H), 4.79 (s, 1H), 3.85 (s, 2H), 2.28 (s, 1H), 1.44 (s, 9H). 13C NMR (151 MHz, CDCl3) δ 156.72 – 155.83 (m), 128.99 (s), 127.95 (s), 126.72 (s), 80.16 (s), 67.18 (s), 57.07 (s), 29.85 (s), 28.49 (s). HRMS (ESI-TOF) calcd. for [M+H]+ 238.1438, found: 238.1461.

(R)-N-(2-hydroxy-1-phenylethyl)benzamide (61)

![Chemical Structure Image]

The hydrolysis of oxazoline 1 was prepared from a modified literature procedure. Oxazoline 1 (48.2 mg, 0.1 mmol) 2M HCl (0.2 mL) was dissolved in THF (2 mL) and stirred at room temperature for 12 hrs. The reaction was quenched with 6M NaOH (0.8 mL) and extracted with EtOAc. The solvent was concentrated and loaded onto a silica gel column (hexanes to 50% EtOAc-Hexanes) to afford the pure product 61 as a
white solid (44 mg, 91%, 99% e.s. from 99% e.e. 1). \([\alpha]^20\) = 9.2 (c = 0.12, CHCl\(_3\)) \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.85 – 7.79 (m, 2H), 7.56 – 7.48 (m, 1H), 7.45 (t, \(J = 7.6\) Hz, 2H), 7.42 – 7.37 (m, 4H), 7.35 – 7.30 (m, 1H), 6.80 (s, 1H), 5.29 (dd, \(J = 11.1, 5.5, 3.9\) Hz, 1H), 4.03 (qd, \(J = 11.3, 4.7\) Hz, 2H), 2.51 (s, 1H). \(^1^\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 167.97 (s), 139.07 (s), 134.25 (s), 131.95 (s), 129.19 (s), 129.19 (s), 128.81 (s), 128.20 (s), 127.22 (s), 126.87 (s), 66.94 (s), 56.45 (s). HRMS (ESI-TOF) calcd. \([M+Na]^+\) 264.1000, found: 264.1010. HPLC (CHIRALCEL IC, 0.46*25 cm, 5\(\mu\)m, hexane / isopropanol = 90/10, flow 0.7 mL/min, detection at 254 nm)

\((R)\)-2-benzamido-2-phenylacetic acid (62)

\[
\begin{align*}
\text{NH}_2
\end{align*}
\]

The oxidation of benzamide 61 was afforded from a literature procedure\(^7\). Amido alcohol 61 (48.2 mg, 0.2 mmol), RuCl\(_3\)•H\(_2\)O (16.6 mg, 0.08 mmol, 0.04 equiv), and NaIO\(_4\) (85.6 mg, 0.8 mmol, 4 equiv) was dissolved in acetonitrile (0.6 mL) and water (0.4 mL) and stirred at room temperature for 2.5 hrs. The reaction was diluted with water and extracted with EtOAc. The solvent was concentrated and analyzed by \(^1\)HNMR with 1,2-dichloroethane as an internal standard resulting in 47% of product 62. The crude mixture was triturated with cold diethylether to afford the pure product 62 as an off-white solid (12 mg, 30%, 99% e.s. from 99% e.e. 1). \(^1\)H NMR (600 MHz, DMSO-d\(_6\)) \(\delta\) 8.67 (s, 1H), 7.86 (d, \(J = 7.5\) Hz, 2H), 7.54 (t, \(J = 7.3\) Hz, 1H), 7.47 (t, \(J = 7.5\) Hz, 2H), 7.42 (d, \(J = 7.5\) Hz, 2H), 7.29 (t, \(J = 7.5\) Hz, 2H), 7.22 (t, \(J = 7.2\) Hz, 1H), 5.20 (s, 1H). HRMS (ESI) calcd. For C\(_{14}\)H\(_{13}\)N\(_2\)O \([M+H]^+\) 278.0818, found: 278.0181. HPLC (CHIRALCEL IC, 0.46*25 cm, 5\(\mu\)m, hexane / isopropanol = 60/40, flow 0.7 mL/min, detection at 254 nm)
(R)-2-(benzylamino)-2-phenylethan-1-ol (63)

The reduction of oxazoline 1 was performed with the following literature procedure. Oxazoline 1 (22.3 mg, 0.1 mmol) was dissolved in dry THF (0.5 mL) under nitrogen and cooled to 0°C. DIBAL (0.3 mL, 3 equiv, 1.0 M in hexanes) was added dropwise and the mixture gradually warmed to room temperature. The solution was cooled to 0°C and slowly quenched with 1 M HCl. The organic layer was separated and the aqueous layer was basified with 5 M NaOH until pH 14. The solution was extracted with Et₂O, washed with water, and dried over Na₂SO₄. The solvent was removed in vacuo to afford the pure product 63 as a white solid (17.9 mg, 79%, 98% e.s. from 94% e.e. 1). [α]²⁰ = −33.2 (c = 0.25, CHCl₃) ¹H NMR (600 MHz, CDCl₃) δ 7.40 – 7.35 (m, 2H), 7.35 – 7.28 (m, 7H), 7.28 – 7.23 (m, 1H), 3.83 (dd, J = 8.6, 4.5 Hz, 1H), 3.77 (d, J = 13.0 Hz, 1H), 3.72 (dd, J = 10.8, 4.5 Hz, 1H), 3.61 (d, J = 10.7, 8.7 Hz, 1H), 2.19 (s, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 140.60 (s), 140.16 (s), 128.87 (s), 128.60 (s), 128.37 (s), 127.86 (s), 127.42 (s), 127.25 (s), 66.90 (s), 63.89 (s), 51.31 (s). HRMS (ESI) calcd. for [M+Na]⁺ 250.1208, found: 250.1223.

(R)-N-(2-chloro-1-phenylethyl)benzamide (64)

The nucleophilic ring opening of oxazoline 1 was conducted following a modified literature procedure. To a solution of oxazoline 1 (22.3 mg, 0.1 mmol) in anhydrous CH₂Cl₂, was added Me₃SiCl (50.8 µL, 0.4 mmol, 4 equiv, portion-wise, 2 equiv added after 16 hrs). The mixture stirred at room temperature until the reaction reached completion. The reaction was concentrated and analyzed by crude ¹H NMR using 1,2-dichloroethane as an internal standard, which provide a yield of 88% of compound 64. The reaction was then loaded onto a silica gel column (hexanes – 20% ethyl acetate/hexanes) to afford the desired chloride 60 as an off-white solid (17.2 mg, 69%, 98% e.s. from 94% e.e. 1). [α]²⁰ = 9.1 (c = 0.175, CHCl₃) ¹H NMR (600 MHz, CDCl₃) δ 7.83 (d, J = 7.2 Hz, 2H), 7.83 (d, J = 7.2 Hz, 1H), 7.53 (t, J = 7.4 Hz, 1H), 7.42 – 7.37 (m, 4H), 7.37 – 7.30 (m, 1H), 6.74 (s, 1H), 5.58 (dt, J = 7.8, 5.1 Hz, 1H), 4.04 – 3.97 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 167.09 (s), 138.56 (s), 134.16 (s), 132.03 (s), 129.02 (s), 128.86 (s), 128.36 (s), 127.20 (s), 126.86 (s), 53.98 (s), 47.90 (s). HRMS (ESI-TOF) calcd. for [M+Na]⁺ 282.0662, found: 282.0669. HPLC (CHIRALCEL IC, 0.46*25 cm, 5µm, hexane / isopropanol = 50/50, flow 0.7 mL/min, detection at 254 nm)
(R)-N-(2-bromo-1-phenylethyl)benzamide (65)

The nucleophilic ring opening of oxazoline 1 was conducted following a modified literature procedure\(^6\). To a solution of oxazoline 1 (22.3 mg, 0.1 mmol) in anhydrous CH\(_2\)Cl\(_2\), was added Me\(_3\)SiBr (52.8 µL, 0.4 mmol, 2 equiv portion wise, 2 equiv added after 16 hrs). The mixture stirred at room temperature until the reaction reached completion. The reaction was concentrated and analyzed by crude \(^1\)H NMR using 1,2-dichloroethane as an internal standard, which provide a yield of 89% of compound 65. The mixture was then loaded onto a silica gel column (hexanes – 20% ethyl acetate/hexanes) to afford the desired bromide 61 as an off-white solid (17.1 mg, 66%, 99% e.e., from 94% e.e. 1). \([\alpha]^{20}_{D} = -66.7 (c = 0.03, \text{CHCl}_3)\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.87 – 7.78 (m, 2H), 7.58 – 7.51 (m, 1H), 7.51 – 7.43 (m, 2H), 7.43 – 7.38 (m, 4H), 7.38 – 7.29 (m, 1H), 6.68 (s, 1H), 5.56 (dt, \(J = 7.7, 5.2\) Hz, 1H), 4.05 – 3.75 (m, 2H). \(^1\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 166.98 (s), 138.95 (s), 134.14 (s), 132.05 (s), 129.03 (s), 128.88 (s), 128.72 (s), 127.20 (s), 126.72 (s), 53.53 (s), 37.13 (s). HRMS (ESI-TOF) calcd. for [M+Na]\(^+\) 326.0156, found: 326.0163. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5µm, hexane / isopropanol = 85/15, flow 0.7 mL/min, detection at 254 nm).

(R)-N-(2-iodo-1-phenylethyl)benzamide (66)

The nucleophilic ring opening of oxazoline 1 was conducted following a modified literature procedure\(^6\). To a 2-dram vial equipped with PTFE septa cap and magnetic stir bar, was added hexamethyldisilane (0.2 mmol) and I\(_2\) (0.2 mmol) under N\(_2\). The reaction was refluxed for 2 hours. After cooling to room temperature, this \textit{in situ} generated Me\(_3\)SiI was added to a solution of oxazoline 1 (22.3 mg, 0.1 mmol) in
CH₂Cl₂ (0.5 mL), stirred for 12 hours, and analyzed by crude ¹H NMR using 1,2-dichloroethane as an internal standard, which provide a yield of 66% of compound. The reaction was concentrated, and loaded directly onto alumina to afford the target iodide 66 with reverted oxazoline 1. ¹H NMR (400 MHz, CDCl₃) δ 7.86 – 7.79 (m, 2H), 7.57 – 7.50 (m, 1H), 7.50 – 7.43 (m, 2H), 7.41 – 7.30 (m, 5H), 6.59 (s, 1H), 5.33 – 5.25 (m, 1H), 3.69 (ddd, J = 20.9, 10.3, 5.7 Hz, 2H).

Note: Aluminium oxide, acidic (Brockmann I, 50 – 200 m, LOT: A0303504, CAS: 1344-28-1) was used to isolate the desired product, which is prone to reverting to starting material, oxazoline 1, by cyclization on itself.

1,3-phenylenebis(ethane-2,1-diyl)-bis(N-phenoxybenzimidate) (67)

Prepared following GP1 using 2.2 equivalents of imidoyl chloride. ¹H NMR (600 MHz, CDCl₃) δ 7.77 – 7.72 (m, 4H), 7.44 – 7.41 (m, 4H), 7.22 – 7.18 (m, 4H), 7.10 – 7.02 (m, 7H), 6.91 (ddd, J = 7.4, 5.4, 1.3 Hz, 5H), 4.45 (t, J = 6.9 Hz, 4H), 2.80 (t, J = 6.9 Hz, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 160.08 (s), 156.70 (s), 138.33 (s), 131.64 (s), 130.61 (s), 130.36 (s), 129.71 (s), 128.95 (s), 128.53 (s), 127.79 (s), 127.64 (s), 122.42 (s), 114.89 (s), 73.52 (s), 36.79 (s). HRMS (ESI) calcd for [M+Na]+ 579.2260, found: 579.2257.

1,3-bis((R)-2-phenyl-4,5-dihydrooxazol-4-yl)benzene (68)

The reaction was conducted on a 0.1 mmol scale according to the GP3. Bis-oxazoline 68 was isolated as a white solid following column chromatography on silica gel (24.3 mg, 66% yield, 98% e.e., 15:1 d.r. determined by ¹H NMR of crude reaction mixture). ¹H NMR (400 MHz, CDCl₃) δ 8.07 – 7.98 (m, 4H), 7.54 – 7.47 (m, 2H), 7.47 – 7.39 (m, 4H), 7.39 – 7.32 (m, 1H), 7.28 – 7.22 (m, 3H), 5.40 (dd, J = 10.1, 8.2 Hz, 2H), 4.79 (dd, J = 10.1, 8.4 Hz, 2H), 4.27 (t, J = 8.3 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 164.98 (s), 143.03 (s), 131.67 (s), 129.48 (s), 128.63 (s), 128.56 (d, J = 11.9 Hz), 127.68 (s), 126.09 (s), 125.42 (s), 74.93 (s), 70.17 (s). HRMS (ESI-TOF) m/z calcd for [M+H]+ 369.1603, found: 369.1610. HPLC (CHIRALCEL AD-H, 0.46*25 cm, 5μm, hexane / isopropanol = 70/30, flow 0.7 mL/min, detection at 254 nm) retention time = 13.2 min (major) and 30.2 min (minor).
VIII. Mechanistic Experiments

a. Energy Transfer

The CV and DFT experimental data used to compare the ‘energy transfer’ vs ‘electron transfer’ mechanisms can be found in the following sources:

**imidate:**
- $E_{\text{red}}$: see reference
- $E_T$: see calculations below (section IX)

**photocatalysts:**
- $E_{\text{red}}$ and $\tau$: see reference
- $E_T$: see reference

**Table 2. Triplet energy sensitizer experiments.**

| entry | photosensitizer | $E_T$ (kcal/mol) | 1 | reduced | S1 |
|-------|----------------|-----------------|---|---------|----|
| 1     | none           | -               | 24% | 37%     | 23% |
| 2     | naphthalene    | 61.0            | 37% | 33%     | 12% |
| 3     | xanthone       | 74.1            | 45% | 27%     | 17% |

To probe the role of the Ir photocatalyst as a triplet sensitizer (versus single electron reductant), additional triplet energy sensitizer experiments were conducted. According to the proposed mechanism, the N-centered radical should also be accessible via direct UV irradiation of the oxime imidate. To test this, oxime imidate S1 was irradiated with 300 nm light, both in the presence and absence of known UV-absorbing photosensitizers. Oxazoline 1 was formed in all cases, along with the reduction side-product, which is consistent with the proposed triplet energy transfer mechanism to access N-centered radicals via N-O homolysis. Most notably, reactivity with only direct irradiation is inconsistent with an SET based activation.

![Imidate structure](imidate.png)

![Photocatalyst Ir2 structure](photocatalyst_ir2.png)

![Photocatalyst Ir1 structure](photocatalyst_ir1.png)
b. Stern-Volmer Quenching Studies

A Stern-Volmer quenching study was conducted to probe the rate of excited state photocatalyst decay in the presence of each reactant or reactant combination. Fluorescence quenching experiments were performed on Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer. A stock solution was prepared of Ir1·BArF4 in dry, degassed Et2O in a glovebox. In a typical experiment, a 0.005 mM solution of Ir1·BArF4 was added to varying amount of quencher in 1.0 cm quartz cuvette under N2. The solution was diluted with Et2O to a 3 mL total volume and the emission spectrum was collected. All solutions were excited at λ = 455 nm and emission intensity at λ = 498 nm was analyzed. Three separate quenching studies were performed, using imidate S1, with or without camphoric acid and CuBArF4 For the combination studies, to account for background imidate quenching, imidate S1 was held constant (0.0005 mM for Cu; 0.025 mM for camphoric acid) and increasing concentrations of the other component was varied.

![Stern-Volmer Quenching](image)

**Fig. 1.** Excited state photocatalyst quenching is observed for imidate S1 alone (blue line). Yet, no quenching is observed for camphoric acid and imidate (red line) – suggesting against proton-coupled electron transfer. Significantly increased quenching is observed for Cu and imidate (green line), as indicated by a nearly doubled slope – suggesting Cu is coordinated to imidate during radical initiation.

| Cu + Imidate | Imidate | Acid + Imidate |
|--------------|---------|----------------|
| conc. (mM)   | I       | Io/I           | conc. (mM)   | I       | Io/I           | conc. (mM)   | I       | Io/I           |
| 0            | 571     | 1              | 0            | 994     | 1              | 0            | 122     | 1              |
| 0.0005       | 419     | 1.36           | 0.0025       | 526     | 1.89           | 0.025        | 124     | 0.98           |
| 0.0010       | 366     | 1.56           | 0.0050       | 283     | 3.51           | 0.050        | 127     | 0.96           |
| 0.0015       | 243     | 2.35           | 0.0075       | 231     | 4.30           |              |         |                |
| 0.0020       | 207     | 2.76           | 0.0100       | 198     | 5.02           |              |         |                |
|              |         |                | 0.0125       | 147     | 6.76           |              |         |                |
|              |         |                | 0.0250       | 85      | 11.69          |              |         |                |
c. Kinetic Isotope Effects (KIE)

To determine if the hydrogen atom transfer (HAT) step is involved in the product determining step, an intramolecular KIE study was performed. Upon subjecting β-d1 phenylethanol imidate S51 to GP3, the deuterium incorporation was analyzed by $^1$H NMR of the isolated oxazoline. Imidate S51 (15.9 mg, 0.05 mmol) was subjected to GP3. The product was isolated following chromatography on silica gel eluting with 10% EtOAc-Hexanes to give a white solid (9 mg, 81%). $^1$H NMR (600 MHz, C$_6$D$_6$) δ 7.77 – 7.73 (m, 2H), 7.46 – 7.41 (m, 1H), 7.22 – 7.18 (m, 1H), 7.13 – 7.00 (m, 5H), 6.91 (tt, $J$ = 7.4, 1.0 Hz, 1H), 4.44 (d, $J$ = 6.8 Hz, 1H), 2.86 – 2.68 (m, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 164.90 (s), 142.55 (s), 142.50 (s), 131.68 (s), 128.91 (s), 128.63 (s), 128.52 (s), 127.78 (s), 127.74 (s), 126.90 (s), 75.04 (s), 74.95 (s), 70.30 (s), 70.08 – 69.67 (m), 29.85 (s). HRMS (ESI-TOF) m/z calcd for [M+Na]$^+$ 260.1263, found: 206.1236.

To calculate KIE, the ratio of protio- to deuterio-oxazoline formed was determined. The observed 7:1 methylene:methine ratio corresponds to 6/7 (or 86%) D- incorporation. An 86:14 D:H ratio in the product indicates a KIE of 6.1.

$^1$H NMR of the isolated oxazoline
d. Radical Clock Experiments

To probe radical character, a series of radical clocks was investigated.

**Z-alkene radical clock (57)**

Imidate S57 (14.8 mg, 0.05 mmol) was subjected to GP3. Upon crude \(^1\)H NMR analysis, a mixture of oxazolines were observed with the major isomer as the Z-alkene and the minor as E in a 10:1 ratio. The product was isolated following chromatography on silica eluting with 10% EtOAc-Hexanes to give an off-white solid (8.7 mg, 87%, 80% e.e.). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta 7.97 (d, J = 7.6 \text{ Hz}, 2H), 7.48 (t, J = 7.4 \text{ Hz}, 1H), 7.40 (t, J = 7.7 \text{ Hz}, 2H), 5.66 - 5.56 (m, 1H), 5.40 (dd, J = 10.6, 9.1 \text{ Hz}, 1H), 5.11 (dd, J = 18.1, 9.2 \text{ Hz}, 1H), 4.65 - 4.55 (m, 1H), 4.02 (t, J = 8.4 \text{ Hz}, 1H), 2.28 - 2.11 (m, 2H), 1.04 (t, J = 7.5 \text{ Hz}, 3H). ^{13}C\ NMR (151 MHz, CDCl\(_3\)) \(\delta 164.54, 134.85, 131.50, 129.44, 128.48, 128.44, 127.88, 127.88, 77.37, 77.16, 76.95, 73.29, 63.63, 21.31, 14.45.\) HRMS (ESI-TOF) \(m/z\) calcd for [M+H]\(^+\) 202.1232, found: 202.1220. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5\(\mu\)m, hexane / isopropanol = 80/20, flow 0.7 mL/min, detection at 254 nm) retention time = 6.1 min (major) and 6.6 min (minor).

**Crude \(^1\)H NMR of 57**

![Crude \(^1\)H NMR of 57](image-url)
Imidate **S58** (14.8 mg, 0.05 mmol) was subjected to **GP3**. Upon crude $^1$H NMR analysis, the major oxazoline retained the $E$-alkene geometry, while the minor $Z$-alkene was observed in a 20:1 ratio. The product was isolated following chromatography on silica eluting with 10% EtOAc-Hexanes to give an off-white solid (8.6 mg, 85%, 86% e.e.). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.97 (dd, $J = 8.4$, 1.3 Hz, 2H), 7.54 – 7.45 (m, 1H), 7.45 – 7.36 (m, 2H), 5.81 (ddd, $J = 12.5$, 6.2, 5.6 Hz, 1H), 5.48 (ddt, $J = 15.3$, 7.8, 1.6 Hz, 1H), 4.77 (dd, $J = 8.4$, 1.3 Hz, 1H), 4.55 (dd, $J = 9.7$, 8.3 Hz, 1H), 4.08 (t, $J = 8.3$ Hz, 1H), 2.16 – 2.03 (m, 2H), 1.02 (t, $J = 7.5$ Hz, 3H). $^{13}$C NMR (151 MHz, Chloroform-$d$) δ 164.20, 135.48, 131.50, 128.84, 128.49, 128.44, 72.94, 68.78, 29.86, 25.47, 13.40. HRMS (ESI-TOF) $m/z$ calcd for [M+H]$^+$ 202.1232, found: 202.1236. HPLC (CHIRALCEL OD-H, 0.46*25 cm, 5μm, hexane/isopropanol = 80/20, flow 0.7 mL/min, detection at 254 nm) retention time = 5.4 min (major) and 9.9 min (minor).
Crude $^1$H NMR of 58

HPLC trace for major (E-alkene) 58
**Cis-cyclopropyl radical isomerization (59)**

Imidate S59 was subjected to GP3 (17.8 mg, 0.05 mmol). Upon crude 1H NMR analysis, the oxazoline was observed in 10% by 1H NMR analysis. In addition, the ring-opened alkene was observed as a side product, which supports a radical intermediate. The large remainder of the mass balance (50%) is the reduced imidate, which may suggest the β methylene is too sterically encumbered for amination. The mixture was purified by preparatory TLC. No 13C NMR data is included due to very limited quantity of product obtained.

**Crude 1H NMR of 59**
Oxazoline 59 (with minor 59B alkene impurity)

Ring-Opened Alkene 59B
e. UV-vis Absorption Studies

UV-vis absorption studies were conducted to probe the role of the copper, ligand, and (+)-camphoric acid on the activation of the oxime imidates under photolytic conditions.

Absorption experiments were performed on Agilent Technologies Cary 5000 UV-Vis-NIR Spectrophotometer.

All experiments were prepared according to GP3, with the following modifications: 1.0 cm quartz cuvette sealed under N₂ instead of 2-dram vial, and scaled down to 3 mL of total volume. Three separate absorption studies were carried out: imidate S₁, imidate S₁ with L•CuBARF₄ and (+)-camphoric acid, and L₁•CuBARF₄ with (+)-camphoric acid. All solutions were scanned from 800 to 200 nm.

Fig. 2. Minimal absorption of all three experiments at λ > 400 nm is observed. Imidate S₁ alone (green line) displays a negligible peak at λ₄₁₇ with an ε of 5 M⁻¹·cm⁻¹. L•CuBARF₄ and (+)-camphoric acid (red line) shows no spectra features > 400 nm, but when combined with Imidate S₁ (purple line), shows a similarly negligible peak at λ₄₂₃ with an ε of 6 M⁻¹·cm⁻¹.

Fig. 3. Emission spectrum of Kessil A160WE tuna blue LED used as irradiation source (data provided by manufacturer). The onset of the major emission peak is > 400 nm.
IX. Computational Studies

Computational Details

All calculations were performed using density functional theory as implemented within the Gaussian 16 (revision A.03) suite of programs. Geometry optimizations and vibrational frequency calculations were performed using the ωB97X-D functional with the 6-311++G(d,p) basis set to calculate triplet energies, and the M06-2X functional with D3 empirical dispersion correction and the 6-311++G(d,p) basis set to calculate homolytic bond dissociation energies (BDEs). All stationary points were confirmed to have no imaginary frequencies. Total spin squared for all doublets and triplets were confirmed to be within 2% of 0.75 and 2.00, respectively. Reported Gibbs free energies and enthalpies include thermal corrections computed at 298.15 K and 1 atm, and are reported in kcal/mol using the conversion of 1 hartree = 627.509 kcal/mol.

Calculation of Triplet Energies

The gas phase triplet energies were calculated as follows:

$$E_T = \Delta G^\circ(\text{triplet}) - \Delta G^\circ(\text{singlet})$$

To ensure that the results of our triplet energy ($E_T$) calculations are appropriate, benchmark calculations with a variety of functionals and basis sets were carried out and compared against experimentally measured and reported values for quinoline. As shown in Table 3, the combination of the ωB97X-D functional with the 6-311++G(d,p) basis set shows agreement between calculated and experimental results. This combination was then applied to a variety of substrates with known triplet energies, as shown in Table 4. Finally, this approach was applied to provide the triplet energy for a representative oxime imidate, also in Table 4.

Table 3. Benchmarking of functional and basis set combinations for the determination of quinoline’s triplet energy

| Functional          | Basis Set            | $E_T$ (calc.) |
|---------------------|----------------------|---------------|
| M06-2X              | 6-311++G(d,p)        | 65.5          |
| B3LYP               | AUG-cc-PVTZ          | 59.7          |
| B3LYP               | cc-PVTZ              | 59.9          |
| B3LYP               | 6-311G(d,p)          | 59.8          |
| B3LYP               | 6-311+G (d,p)        | 59.5          |
| B3LYP               | 6-311++G(d,p)        | 59.4          |
| ωB97X-D             | 6-311++G(d,p)        | 61.7          |
| N/A                 | N/A                  | 62.4 (exp.)   |

![Diagram of quinoline triplet energy](image)
Table 4. Comparison of calculated and experimental triplet energies for a range of substrate classes with the ωB97X-D functional and 6-311++G(d,p) basis set

| Substrate | $E_T$ (calc.) | $E_T$ (exp.)$^\text{10}$ |
|-----------|---------------|--------------------------|
| ![Substrate Image] | 66.9          | 70.3                     |
| ![Substrate Image] | 70.1          | 71.3                     |
| ![Substrate Image] | 69.9          | 70.8                     |
| ![Substrate Image] | 70.8          | 72.0                     |
| ![Substrate Image] | 69.0          | 65.5                     |
| ![Substrate Image] | 76.2          | 76.8                     |
| ![Substrate Image] | **47.2**      | N/A                      |

Calculation of Homolytic Bond Dissociation Energies

The gas phase BDEs were calculated as follows:

$$\text{N-O BDE} = \Sigma \Delta H^\circ(\text{products}) - \Sigma \Delta H^\circ(\text{starting materials})$$

To ensure that the results of our BDE calculations are appropriate, benchmark calculations with a variety of functionals and basis sets were carried out and compared against experimentally measured and reported BDEs for N,O-dimethylhydroxylamine. As shown in Table 5, the combination of the M06-2X-D3 functional with the 6-311++G(d,p) basis set shows agreement between calculated and experimental results. This combination was then applied to a variety of additional hydroxylamine with known BDEs, as shown in Table 6.
Table 5. Benchmarking of functional and basis set combinations for the determination of N,O-dimethylhydroxylamine’s N-O BDE

| Functional   | Basis Set       | N-O BDE |
|--------------|-----------------|---------|
| B3LYP        | 6-311G(d,p)     | 47.6    |
| B3LYP        | 6-311+G(d,p)    | 45.0    |
| B3LYP        | 6-311++G(d,p)   | 45.0    |
| B3LYP-D3     | 6-311++G(d,p)   | 46.9    |
| B3P86        | 6-311+G(d,p)    | 49.6    |
| ωB97X-D      | 6-311+G(d,p)    | 50.1    |
| M05-2X       | 6-311++G(d,p)   | 52.4    |
| M06-2X       | 6-311+G(d,p)    | 54.1    |
| M06-2X       | 6-311++G(d,p)   | 54.1    |
| M06-2X-D3    | 6-311++G(d,p)   | 54.2    |
| N/A          | N/A             | 57.5 (exp.)^{16} |

Table 6. Comparison of calculated and experimental N-O BDEs for hydroxylamines with the M06-2X-D3 functional and 6-311++G(d,p) basis set

| Substrate | N-O BDE (calc.) | N-O BDE (exp.)^{16} |
|-----------|-----------------|---------------------|
| H$_2$N$^+$OH | 64.2          | 63.0                |
| HN$^+$OH   | 63.2          | 64.9                |
| H$_3$N$^+$O$^-$Me | 60.3        | 54.6                |

This combination was then used to calculate the N-O BDE for a representative oxime imidate from both its singlet and triplet states. As shown in Table 7, the N-O BDE from the triplet state is not only weaker than from the singlet state, but are also negative, which suggests spontaneous homolytic cleavage from the triplet state.

Table 7. Representative imidate oxime N-O BDEs from the singlet and triplet state with the M06-2X-D3 functional and 6-311++G(d,p) basis set

| Homolytic Cleavage | N-O BDE |
|--------------------|---------|
|                    | From Singlet | From Triplet |
| Ph$_2$N$^+$O$^-$Ph | 35.3     | -17.5        |
| Ph$_2$N$^+$O$^-$Ph | 35.3     | -17.5        |
Optimized Cartesian Coordinates

Geometry optimizations and frequency calculations for the determination of triplet energies were carried out using the ωB97X-D functional with the 6-311++G(d,p) basis set. Visualization carried out with CYLview\textsuperscript{17}. EE = Electronic Energy

**E_T: Methyl (Z)-N-phenoxbenzimidate (singlet state)**

| Total EE (hartree)                        | -746.379313 |
|------------------------------------------|-------------|
| EE + Zero-Point Energy Correction (hartree) | -746.137816 |
| EE + Thermal Enthalpy Correction (hartree)  | -746.122322 |
| EE + Thermal Free Energy Correction (hartree) | -746.181884 |
| Imaginary Frequencies (cm\(^{-1}\))     | None        |

| Cartesian Coordinates                  |
|----------------------------------------|
| C           | -3.43649100  | 0.67240300  | 0.27511800 |
| C           | -2.27885600  | -0.01328600 | -0.09103800|
| C           | -2.35623600  | -1.37055300 | -0.41265100|
| C           | -3.57295600  | -2.03198800 | -0.34914200|
| C           | -4.72523600  | -1.34654100 | 0.02473900 |
| C           | -4.65412800  | 0.00573300  | 0.33391800 |
| H           | -3.37788200  | 1.72734400  | 0.51058500 |
| H           | -1.45778100  | -1.89405200 | -0.71449100|
| H           | -3.62512800  | -3.08517400 | -0.60074500|
| H           | -5.54894300  | 0.54617300  | 0.62103100 |
| H           | -5.67619100  | -1.86552400 | 0.06895500 |
| C           | -0.97866900  | 0.69893500  | -0.13375200|
| N           | 0.08573700   | -0.01283600 | -0.16250900|
| O           | -1.09120700  | 2.03255600  | -0.16754100|
| C           | -0.13926300  | 2.86895900  | 0.49780200 |
| H           | -0.68213700  | 3.78234700  | 0.73905200 |
| H           | 0.21686800   | 2.39594900  | 1.41479300 |
| H           | 0.70615200   | 3.08934200  | -0.15085300|
| O           | 1.23480700   | 0.74545600  | -0.36392000|
| C           | 2.39200600   | 0.04961000  | -0.14335700|
| C           | 3.55444800   | 0.70345900  | -0.54266900|
| C           | 2.44562700   | -1.20280400 | 0.45523400 |
E_T: Methyl (Z)-N-phenoxybenzimidate (triplet state)

|    |                  |                  |                  |
|----|------------------|------------------|------------------|
| C  | 4.78311000      | 0.09434400       | -0.33834900      |
| H  | 3.47903400      | 1.67690100       | -1.01283500      |
| C  | 3.68779000      | -1.80002800      | 0.64691100       |
| H  | 1.53228100      | -1.69391500      | 0.75886000       |
| C  | 4.85775900      | -1.16189600      | 0.25662300       |
| H  | 5.68789200      | 0.60367900       | -0.65069200      |
| H  | 3.73416300      | -2.77849800      | 1.11219000       |
| H  | 5.81904200      | -1.63689000      | 0.41285500       |

Total EE (hartree)                           -746.298501
EE + Zero-Point Energy Correction (hartree)  -746.060362
EE + Thermal Enthalpy Correction (hartree)   -746.044330
EE + Thermal Free Energy Correction (hartree) -746.106604
Imaginary Frequencies (cm⁻¹)                 None
<S²>                                          2.0008

Cartesian Coordinates

|    |                  |                  |                  |
|----|------------------|------------------|------------------|
| C  | -3.50008600      | 0.47710400       | -0.19967100      |
| C  | -2.19402000      | 0.03115000       | 0.10886100       |
| C  | -1.98652600      | -1.35441300      | 0.30548100       |
| C  | -3.03878600      | -2.24342700      | 0.19347900       |
| C  | -4.32268800      | -1.79205700      | -0.11532100      |
| C  | -4.53979300      | -0.42830300      | -0.30904000      |
| H  | -3.67404900      | 1.53485600       | -0.35069200      |
| H  | -0.99433100      | -1.71730300      | 0.54758100       |
| H  | -2.86066300      | -3.30198700      | 0.34812300       |
| H  | -5.53496700      | -0.06938600      | -0.54842400      |
| H  | -5.14261300      | -2.49486400      | -0.20301900      |
| C  | -1.11811000      | 0.94764000       | 0.21527300       |
| N  | 0.15761600       | 0.55321800       | 0.64005400       |
| O  | -1.37536400      | 2.27029400       | 0.10174800       |
| C  | -0.27230300      | 3.14768200       | -0.08423900      |
| H  | -0.69981900      | 4.14506100       | -0.16747000      |
| H  | 0.41104700       | 3.11027100       | 0.76833000       |
| H  | 0.27245400       | 2.90025200       | -0.99951300      |
Geometry optimizations and frequency calculations for the determination of BDEs were carried out using the M06-2X functional with D3 empirical dispersion correction, and the 6-311++G(d,p) basis set.

### BDE: Methyl (Z)-N-phenoxybenzimidate (singlet state)

| Total EE (hartree) | -746.334486 |
|-------------------|-------------|
| EE + Zero-Point Energy Correction (hartree) | -746.092706 |
| EE + Thermal Enthalpy Correction (hartree) | -746.077263 |
| EE + Thermal Free Energy Correction (hartree) | -746.136665 |
| Imaginary Frequencies (cm⁻¹) | None |

**Cartesian Coordinates**

| Atom | X           | Y           | Z           |
|------|-------------|-------------|-------------|
| O    | 0.91216800  | 0.28831800  | -0.46558700 |
| C    | 2.21467900  | -0.10309900 | -0.20027600 |
| C    | 2.74333600  | -0.19090700 | 1.07970500  |
| C    | 2.96986600  | -0.40494000 | -1.32601000 |
| C    | 4.06708900  | -0.59291900 | 1.22048200  |
| H    | 2.13099400  | 0.04703900  | 1.93776500  |
| C    | 4.28901200  | -0.80319300 | -1.16457200 |
| H    | 2.51585000  | -0.32714000 | -2.30619000 |
| C    | 4.84252300  | -0.89854600 | 0.10836400  |
| H    | 4.49265800  | -0.66683600 | 2.21477100  |
| H    | 4.88523300  | -1.04138900 | -2.03782000 |
| H    | 5.87278200  | -1.21062500 | 0.23212200  |
BDE: Methyl (Z)-N-phenoxybenzimidate (triplet state)

Total EE (hartree)  
EE + Zero-Point Energy Correction (hartree)  
EE + Thermal Enthalpy Correction (hartree)  
EE + Thermal Free Energy Correction (hartree)  
Imaginary Frequencies (cm$^{-1}$)  
$\langle S^2 \rangle$  
Cartesian Coordinates

|  |   |   |   |
|---|---|---|---|
| H | 0.68541100 | 3.73833500 | -0.81602800 |
| H | -0.22147300 | 2.32800700 | -1.43025600 |
| H | -0.70877500 | 3.09438000 | 0.10038300 |
| O | -1.22565300 | 0.74560200 | 0.34446000 |
| C | -2.39288000 | 0.05172700 | 0.13977300 |
| C | -3.54988100 | 0.71690200 | 0.53891600 |
| C | -2.45424900 | -1.20827800 | -0.44347500 |
| C | -4.78321000 | 0.11100100 | 0.34949200 |
| H | -3.46246100 | 1.69475900 | 0.99667700 |
| C | -3.70174900 | -1.80163200 | -0.62055800 |
| H | -1.54519300 | -1.70635200 | -0.74692700 |
| C | -4.86939300 | -1.15289400 | -0.23057600 |
| H | -5.68322000 | 0.62775300 | 0.66093400 |
| H | -3.75613000 | -2.78462600 | -1.07363800 |
| H | -5.83056000 | -1.62502600 | -0.37518800 |

Cartesian Coordinates

|  |   |   |   |
|---|---|---|---|
| C | 3.50632200 | 0.48346500 | 0.16938200 |
| C | 2.19643100 | 0.02840600 | -0.10584800 |
| C | 1.98140700 | -1.36084500 | -0.26102700 |
| C | 3.03519600 | -2.24836700 | -0.14087200 |
| C | 4.32460500 | -1.78987100 | 0.13492800 |
| C | 4.54727200 | -0.42071100 | 0.28710600 |
| H | 3.67964000 | 1.54526600 | 0.28654000 |
| H | 0.98368000 | -1.72520000 | -0.47556900 |
| H | 2.85391500 | -3.30936700 | -0.26247000 |
| H | 5.54610300 | -0.05733300 | 0.49970500 |
| H | 5.14481000 | -2.49071200 | 0.22903200 |
| C | 1.11901100 | 0.94483300 | -0.21655700 |
| N | -0.15931700 | 0.53884300 | -0.64313100 |
| O | 1.37771600 | 2.26914400 | -0.16054600 |
**BDE: Methyl benzimidate radical**

| Cartesian Coordinates |  |
|-----------------------|------------------|
| C                    | -0.70224300 1.15104000 -0.00004000 |
| C                    | -0.21610100 -0.15492700 -0.00001700 |
| C                    | -1.10332500 -1.23309700 0.00002700 |
| C                    | -2.47105000 -1.00177800 0.00004000 |
| C                    | -2.95928000 0.30314700 0.00001000 |
| C                    | -2.07501200 1.37581300 -0.00002300 |
| H                    | -0.00614800 1.97953400 -0.00006600 |
| H                    | -0.71412500 -2.24442300 0.00004800 |
| H                    | -3.15835800 -1.83905000 0.00007100 |
| H                    | -2.45248700 2.39127300 -0.00003900 |
| H                    | -4.02804800 0.48147400 0.00002100 |
| C                    | 1.25022300 -0.40941600 -0.00002300 |
| N                    | 1.75079900 -1.57066200 -0.00007900 |
| O                    | 2.00130200 0.71096300 0.00004300 |
| C                    | 3.41169000 0.49754900 0.00003800 |
| H                    | 3.86267800 1.48623900 0.00019500 |
**BDE: Phenoxy radical**

| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| O    | 2.28954700 | 0.00000000 | 0.00000100 |
| C    | 1.04591300 | 0.00000000 | 0.00000000 |
| C    | 0.28894200 | 1.23815300 | 0.00000000 |
| C    | 0.28894200 | -1.23815300 | 0.00000000 |
| C    | -1.08192400 | 1.22342800 | 0.00000000 |
| H    | 0.85926200 | 2.15973900 | -0.00000100 |
| C    | -1.08192400 | -1.22342800 | 0.00000000 |
| H    | 0.85926200 | -2.15973900 | -0.00000100 |
| C    | -1.77584800 | 0.00000000 | 0.00000000 |
| H    | -1.63995800 | 2.15250200 | 0.00000000 |
| H    | -1.63995800 | -2.15250200 | 0.00000000 |
| H    | -2.85959600 | 0.00000000 | 0.00000000 |

| Total EE (hartree) | -306.772895 |
| EE + Zero-Point Energy Correction (hartree) | -306.681151 |
| EE + Thermal Enthalpy Correction (hartree) | -306.674896 |
| EE + Thermal Free Energy Correction (hartree) | -306.71072 |
| Imaginary Frequencies (cm$^{-1}$) | None |
| $\langle S^2 \rangle$ | 0.7511 |
X. References

1. Nakafuku, K. M., Fosu, S. C. & Nagib, D. A. Catalytic Alkene Difunctionalization via Imidate Radicals. *J. Am. Chem. Soc.* **140**, 11202–11205 (2018).

2. Evans, W. J., Zucchi G. & Ziller, J. W. Dinitrogen Reduction by Tm(II), Dy(II), and Nd(II) with Simple Amide and Aryloxide Ligands. *J. Am. Chem. Soc.* **125**, 10–11 (2003).

3. Silva, A. R., Carneiro, L., Carvalho, A. P. & Pires, J. Asymmetric benzylation of hydrobenzoin by copper(II) bis(oxazoline) anchored onto ordered mesoporous silicas and their carbon replicas. *Catal. Sci. Technol.* **3**, 2415–2424 (2013).

4. Stateman, L. M., Wappes, E. A., Nakafuku, K. M., Edwards K. M. & Nagib, D. A. Catalytic β C–H amination *via* an imidate radical relay. *Chem. Sci.* **10**, 2019, 2693–2699 (2019).

5. Umezawa, J., Takahashi, O., Furuhashi, K. & Nohira, H. Synthesis of optically active oxazolines from optically active epoxides. *Tetrahedron Asymmetry* **5**, 491–498 (1994).

6. Wappes, E. A., Nakafuku, K. M. & Nagib, D. A. Directed β C–H Amination of Alcohols via Radical Relay Chaperones. *J. Am. Chem. Soc.* **139**, 10204–10207 (2017).

7. Tayama, E. & Kimura, H. Asymmetric Sommelet–Hauser Rearrangement of N-Benzyl Ammonium Salts. *Angew. Chem. Int. Ed.* **46**, 8896–8871 (2007).

8. Meyers, A. I., Himmelsbach, R. J. & Reuman, M. Reductive cleavage of aryl oxazolines to benzaldehydes and substituted tolenes. *J. Org. Chem.* **48**, 4053–4058 (1983).

9. Teegardin, K., Day, J. I., Chan, J. & Weaver, J. Advances in Photocatalysis: A Microreview of Visible Light Mediated Ruthenium and Iridium Catalyzed Organic Transformations. *Org. Process Res. Dev.* **20**, 1156–1163 (2016).

10. Striet-Kalthoff, F., James, M. J., Teders, M., Pitzer, L. & Glorius, F. Energy transfer catalysis mediated by visible light: principles, applications, directions. *Chem. Soc. Rev.* **47**, 7190–7202 (2018).

11. Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Petersson, G. A., Nakatsuji, H., Li, X., Caricato, M., Marenich, A. V., Bloino, J., Janesko, B. G., Gomperts, R., Mennucci, B., Hratchian, H. P., Ortiz, J. V., Izmaylov, A. F., Sonnenberg, J. L., Williams-Young, D., Ding, F., Lipparini, F., Egidi, F., Goings, J., Peng, B., Petrone, A., Henderson, T., Ranasinghe, D., Zakrzewski, V. G., Gao, J., Rega, N., Zheng, G., Liang, W., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Throssell, K., Montgomery Jr., J. A., Peralta, J. E., Ogliaro, F., Bearpark, M. J., Heyd, J. J., Brothers, E. N., Kudin, K. N., Staroverov, V. N., Keith, T. A., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A. P., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Millam, J. M., Klene, M., Adamo, C., Cammi, R., Ochterski, J. W., Martin, R. L., Morokuma, K., Farkas, O., Foresman, J. B. & Fox, D. J. Gaussian 16, rev A.03 (Gaussian, Inc., 2016).

12. Chai, J-D. & Head-Gordon, M. Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. *Phys. Chem. Chem. Phys.* **10**, 6615–6620 (2008).
13. Krishnan, R., Binkley, J. S., Seeger, R. & Pople, J. A. Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. *J. Chem. Phys.* **72**, 650–654 (1980).

14. Zhao, Y. & Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **120**, 215–241 (2008).

15. Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. A consistent and accurate ab initio parameterization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **132**, 154104 (2010).

16. Luo, Y.-R. *Comprehensive Handbook of Chemical Bond Energies* (CRC Press, Boca Raton, FL, ed. 1, 2007).

17. Legault, C. Y. CYLview, 1.0b. (Université de Sherbrooke, 2009); www.cylview.org.
XI. NMR Spectra
Ph \xrightarrow{\text{O}} \text{Me}

27
