Supplementary Information

Radical Cascade Synthesis of Azoles via Tandem Hydrogen Atom Transfer

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I. General Information

All chemicals and reagents were purchased from Sigma-Aldrich, Alfa Aesar, Acros, TCI, or ChemImpex. DCE, MeCN and Et₃N were distilled over CaH₂ before use. PhMe, CH₂Cl₂, and Et₂O were dried using an Innovative Technology solvent system. Silicycle F60 (230-400 mesh) silica gel was used for flash column chromatography. Thin layer chromatography (TLC) analyses were performed using Merck silica gel 60 F254 plates and visualized under UV (254 nm) or KMnO₄ stain. ¹H, ¹⁹F, ¹³C NMR spectra were recorded using a Bruker AVIII 400 or AVIII 600 MHz NMR spectrometer. ¹H NMR and ¹³C NMR chemical shifts are reported in parts per million and referenced with respect to CDCl₃ (¹H: residual CHCl₃ at δ 7.26, ¹³C: CDCl₃ triplet at δ 77.16) or DMSO-d₆ (¹H: residual DMSO quintet at 2.50, ¹³C: DMSO-d₆ sept at 39.51). ¹H NMR data are reported as chemical shifts (δ ppm), multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, m = multiplet, app t = apparent triplet, app q = apparent quartet, app qd = apparent quartet of doublets), coupling constant (Hz), relative integral. ¹⁹F NMR data are reported as chemical shifts (δ ppm). High resolution mass spectra were obtained using Bruker MicrOTOF (ESI). IR spectra were recorded using a Thermo Fisher Nicolet iS10 FT-IR and are reported in terms of frequency of absorption (cm⁻¹). Melting points were determined using a Laboratory Devices MEL-TEMP II.

Photochemical reactions were performed by placing reaction vessels approximately 5 cm away from two 23W TCP Model EDXO-23 compact fluorescent lightbulbs (CFL, 0.380 A, 1450 lumens). Reaction temperature was maintained at approximately 23 °C by with two fans (Figure S1).

![Figure S1. Photochemistry reaction set-up with two 23W CFLs and fans](image-url)
II. General Procedures

General Procedure to Prepare Benzimidates (GP1)

To address challenges with benzimidate synthesis, a new method was developed (see Section III for further discussion).

To a 4-dram vial containing a stir bar was added alcohol (1 equiv.), nitrile (1.1 equiv.), PhMe (0.5 M), and triflic acid (1.2 equiv.). The solution was heated to 110 °C and stirred. After 24 h the solution was cooled to room temperature, and then stored at -15 °C until crystallization of the hydrotriflate salt was observed. The salt was then isolated via filtration and washed with cold hexanes and Et₂O; residual solvent was removed under vacuum. The salt was suspended in Et₂O (0.1 M), and NaHCO₃ (sat. aqueous) was added dropwise until the dissolution of the salt observed (typically ~5 minutes). The aqueous phase was extracted with CH₂Cl₂, and the combined organic phases were dried over Na₂SO₄, concentrated under vacuum, and then used as is, or purified via column chromatography (silica gel treated with 1% Et₃N/hexanes to avoid hydrolysis).

General Procedure for Transimidation (GP2)

Step 1: To a pressure tube equipped with a stir bar was added nitrile (1 equiv.), trifluoroethanol (12 equiv.), and acetyl chloride (8 equiv.). The solution was heated to 80 °C and stirred. After 48 h the reaction was cooled to room temperature and carefully vented (Note: HCl gas is formed as a by-product, see below for additional instructions on safe handling), which immediately induced precipitation of the benzimidate hydrochloride salt. The benzimidate salt was collected via filtration with cold hexanes.

Caution: The pressure tube reactions were vented by bubbling through a solution of saturated NaHCO₃ to neutralize the by-product HCl gas. Even at room temperature, venting may be violent.

Step 2: To a 2-dram vial equipped with a stir bar was added trifluoroethyl benzimidate hydrochloride salt (1 equiv.), alcohol (1 equiv.), and MeCN (0.16 M). The reaction was heated to 50 °C and stirred. Reaction progress was monitored by consumption of starting trifluoroethyl benzimidate via crude ¹H NMR. Upon completion, the solution was concentrated and the resulting crude solid was suspended in dry Et₂O and subjected to the free-base protocol from GP1. The crude reaction mixture was then purified via column chromatography (silica gel treated with 1% Et₃N in hexanes to avoid hydrolysis).

Note: Transimidation is time-sensitive. Prolonged reaction times lead to decomposition.
General Procedure for Tandem Oxidation (GP3)

To a 2-dram vial containing a stir bar were added: imidate (0.2 mmol, 1 equiv.), CsI (0.6 mmol, 3 equiv.), and PhI(OAc)$_2$ (0.6 mmol, 3 equiv.). This was followed by evacuation and backfilling of the headspace with N$_2$, three times. Degassed PhMe (0.1 M, degassing method described below) was then added, and the solution was stirred under visible irradiation (2 x 23W CFL bulbs) with two fans maintaining ambient temperature (23 °C vs. 35 °C without). Reaction progress was monitored by TLC. Upon completion, the crude reaction was quenched with 10% aq. Na$_2$S$_2$O$_3$ and extracted with CH$_2$Cl$_2$. The combined organic layers were dried over Na$_2$SO$_4$, concentrated, and then purified via column chromatography (silica gel with ethyl acetate and hexanes).

Note: Reaction solvents were degassed using three freeze-pump-thaw cycles prior to use. CsI and PhI(OAc)$_2$ were ground with a mortar and pestle and dried under high vacuum prior to usage. This both increased yields and improved reproducibility.
III. Imidate Synthesis Optimization

To improve the efficiency, handling, and safety of our benzimidate synthesis, we developed a triflic acid variant of the Pinner reaction.\(^1\) To activate benzonitrile (pK\(_a\) of conjugate acid = -10),\(^2\) we used triflic acid (pK\(_a\) = -14) as opposed to HCl (pK\(_a\) = -8). Triflic acid also has the significant advantage of being a liquid, preventing the need to use a sealed pressure tube or venting of gaseous species upon work-up.

2-phenylethanol was subjected to GP1 under modified conditions listed below. Upon completion, the crude mixture was concentrated and quantified via \(^1\)H NMR using 1 equiv of 1,2-dichloroethane or 1,2-dibromomethane as an internal standard.

Table S1. Optimization of Triflic Acid Pinner Reaction

| Solvent | T (°C) | Alcohol (eq) | PhCN (eq) | HOTf (eq) | Time (h) | Yield |
|---------|--------|--------------|-----------|-----------|----------|-------|
| CH\(_2\)Cl\(_2\) | 23 | 2 | 1 | 1 | 17 | 6% |
| CH\(_2\)Cl\(_2\) | 23 | 1 | 1 | 2 | 17 | 12% |
| CH\(_2\)Cl\(_2\) | 50 | 1 | 1 | 1 | 17 | 58% |
| DCE | 80 | 1 | 1 | 1 | 21 | 75% |
| DCE | 80 | 1 | 2 | 1.2 | 24 | 69%* |
| DCE | 80 | 2 | 1 | 1.2 | 24 | 73%* |
| PhMe | 110 | 1 | 1 | 1.2 | 24 | 70%* |

*indicates isolated yield of the hydrotriflate salt S2

The reaction efficiency was found to scale well, from 1.0 mmol (0.12 g) to 24.0 mmol (2.93 g, last entry of Table S1). A variety of Lewis acids were tried unsuccessfully in the place of HOTf: BF\(_3\)·Et\(_2\)O, CuBr\(_2\), CuCl\(_2\), Cu(OAc)\(_2\), Cu(acac)\(_2\), Cu(tfac)\(_2\), AlMe\(_3\), AlCl\(_3\), AlBr\(_3\), AuCl\(_3\), Hf(O Tf)\(_4\); all resulting in no formation of imidate.

Notes: The hydrotriflate salts typically precipitate out upon cooling to room temperature, which can be facilitated with the addition of diethyl ether and hexanes, and refrigeration. Isolation is carried out via filtration and, with sufficient solvent washes, the resulting hydrotriflate salt is more stable for storage compared to its free-based form.

The salt was suspended in Et\(_2\)O (0.1 M), and NaHCO\(_3\) (sat. aqueous) was added dropwise until the dissolution of the salt observed (typically ~5 minutes). If the initial salt was washed carefully during the prior filtration step, the resultant free-based imidate was often pure enough to use without additional purification (i.e. no column chromatography required).

When additional purification was needed, the silica gel was deactivated with 1% NEt\(_3\) in hexanes, as hydrolysis of the benzimidates to their corresponding esters was often observed. For particularly sensitive compounds, shorter lengths of silica and quicker elution times were necessary to prevent hydrolysis. The benzimidates were typically stored neat in a refrigerator.

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1 Roger, R.; Neilson, D. G. *Chem. Rev.* **1961**, *61*, 179–211.

2 Deno, C. N.; Gaugler, R. W.; Wisotsky, M. J. *J. Org. Chem.* **1966**, *31*, 1967–1968.
Decomposition of the free-based imidate to esters and amides was observed after a few months, while the salt was stable indefinitely.

In the course of substrate exploration, we observed that secondary or benzylic alcohols afforded amides via cationic rearrangement, but primary alcohols (including phenol) and thiols formed imidate salts with varying efficiency (Figure S2).

Figure S2. Summary of alcohol and thiol compatibilities under Triflic Acid Pinner conditions
IV. Substrate Synthesis

2,2,2-trifluoroethyl benzimidate hydrochloride salt (S1)

2,2,2-Trifluoroethanol (16.8 mL, 222 mmol) and benzonitrile (2 mL, 19.4 mmol) were subjected to **GP2 Step 1**. After filtration, the benzimidate hydrochloride salt S1 was isolated (3.4 g, 74%) as a white solid. Characterization data is consistent with reported literature data.  

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 13.48 - 11.96$ (bs, 2H), 8.42 – 8.35 (d, $J = 7.5$ Hz, 2H), 7.83 – 7.75 (t, $J = 7.5$ Hz, 1H), 7.67 – 7.58 (t, $J = 7.9$ Hz, 2H), 5.38 – 5.28 (q, $^3J_{HF} = 7.5$ Hz, 2H).

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = -73.3$.

Phenethyl benzimidate hydrotriflate salt (S2)

2-phenylethanol-1-ol (1.2 g, 9.7 mmol) was subjected to **GP1**, with the following modifications: dry DCE (20 mL) instead of PhMe, and a reaction temperature of 80 °C instead of 110 °C. After filtration, the benzimidate hydrotriflate salt S2 was isolated (2.0 g, 56%) as a white solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 10.69$ (bs, 1H), 10.33 (bs, 1H), 7.97 (d, $J = 8.4$ Hz, 2H), 7.73 (t, $J = 7.5$ Hz, 1H), 7.55 (t, $J = 7.3$ Hz, 2H), 7.40 – 7.28 (m, 5H), 4.92 (t, $J = 6.2$ Hz, 2H), 3.27 (t, $J = 6.2$ Hz, 2H).

$^{13}$C NMR (100 MHz, DMSO-d$_6$): $\delta = 171.3$, 136.6, 135.5, 129.3, 129.1, 128.8, 128.6, 128.2, 127.4, 126.9, 125.9, 73.2, 33.5.

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = -78.5$.

HRMS (ESI-TOF) $m/z$: calc’d for C$_{15}$H$_{16}$NO$^+$ [M+H]$^+$ 226.1226, found 226.1232.

IR (film) (cm$^{-1}$): 3065, 2360, 2341, 1653, 1602, 1574, 1506, 1455, 1437, 1369, 1241, 1224, 1163, 1106, 1027, 966, 936.

**MP**: 118 – 119 °C.

Phenethyl benzimidate (1)

Benzimidate hydrotriflate salt S2 (1.0 g, 2.7 mmol) was free-based according to **GP1**. Purification via column chromatography (silica gel, 1% ethyl acetate/hexanes with 1% Et$_3$N to 7.5% ethyl acetate/hexanes) yielded benzimidate 1 (0.59 g, 98%) as a clear oil. Characterization data is consistent with reported literature data.  

$R_t$: 0.46 (30% Ethyl acetate/hexanes)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.81$ (bs, 1H), 7.67 (bs, 2H), 7.49 – 7.37 (m, 3H), 7.35 – 7.29 (m, 4H), 7.25 – 7.20 (m, 1H), 4.53 (bs, 2H), 3.13 (t, $J = 6.9$ Hz, 2H).

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3 Wappes, E. A.; Nakafuku, K. M.; Nagib, D. A. *J. Am. Chem. Soc.*, 2017, 139, 10204 – 10207.
2-methylphenethyl benzimidate (S4)

2-(o-tolyl)ethan-1-ol (0.14 g, 1.0 mmol) was subjected to GP2, with acidification after transimidation to facilitate removal of unconsumed alcohol (see below). Upon completion, the free-based crude was concentrated, dissolved in dry Et₂O, and acidified with 2M HCl in Et₂O. Upon precipitation, the hydrochloride salt was isolated via filtration, and washed with cold hexanes and Et₂O, yielding the benzimidate salt (0.17 g, 63%) as a white solid. The benzimidate salt was free-based according to GP1; no purification was needed, yielding benzimidate S4 (0.14 g, 98%) as a clear oil.

Rf: 0.38 (30% Ethyl acetate/hexanes)

1H NMR (600 MHz, CDCl₃): δ = 7.76 (bs, 1H), 7.71 (d, J = 7.4 Hz, 2H), 7.47 – 7.44 (m, 1H), 7.42 – 7.39 (m, 2H), 7.28 – 7.26 (m, 1H), 7.19 – 7.14 (m, 3H), 4.49 (t, J = 7.0 Hz, 2H), 3.14 (t, J = 7.0 Hz, 2H), 2.40 (s, 3H).

13C NMR (150 MHz, CDCl₃): δ = 168.0, 136.7, 136.6, 133.0, 131.0, 130.4, 129.7, 128.6, 128.2, 126.7, 126.4, 65.8, 32.5, 19.6.

HRMS (ESI-TOF) m/z: calc’d for C₁₆H₁₈NO⁺ [M+H]⁺ 240.1383, found 240.1388.

IR (film) cm⁻¹: 3330, 3061, 3022, 2950, 2359, 2341, 1717, 1632, 1577, 1492, 1447, 1392, 1329, 1295, 1164, 1075, 1027, 1000, 973.

2-chlorophenethyl benzimidate (S5)

2-(2-chlorophenyl)ethan-1-ol (0.47 g, 3.0 mmol) was subjected to GP1 without isolation of the hydrotriflate salt, as no precipitation was observed. The crude reaction was free-based according to GP1. Purification via column chromatography (silica gel, 1% ethyl acetate/hexanes with 1% Et₃N to 20% ethyl acetate/hexanes), yielded benzimidate S5 (0.32 g, 41%) as a yellow oil.

Rf: 0.31 (30% Ethyl acetate/hexanes)

1H NMR (600 MHz, CDCl₃): δ = 7.80 (bs, 1H), 7.70 (d, J = 6.6 Hz, 2H), 7.45 – 7.34 (m, 5H), 7.24 – 7.16 (m, 2H), 4.44 (m, 2H), 3.28, (t, J = 6.8 Hz, 2H).

13C NMR (100 MHz, CDCl₃): δ = 168.1, 136.3, 134.4, 132.8, 131.3, 131.0, 129.7, 128.6, 128.1, 126.9, 126.8, 65.1, 33.0.

HRMS (ESI-TOF) m/z: calc’d for C₁₅H₁₃ClNO⁺ [M+H]⁺ 260.0837, found 260.0842.

IR (film) cm⁻¹: 3330, 3061, 2950, 2359, 2341, 1717, 1632, 1577, 1492, 1447, 1392, 1329, 1295, 1164, 1075, 1027, 1000, 973.

2-(pyridin-2-yl)ethyl benzimidate (S6)

2-(pyridin-2-yl)ethan-1-ol (0.79 mL, 7.0 mmol) was subjected to GP1, with the following modifications: additional triflic acid (1.4 mL, 15 mmol) was used, reaction temperature was 100 °C instead of 110 °C, and sufficient precipitation was achieved at 23 °C. After filtration, the
benzimidate bis hydrotriflate salt was isolated (3.7 g, 100%) as a brown solid. A portion of the benzimidate salt (1.5 g, 2.8 mmol) was free-based according to GP1; final purification was done via column chromatography (silica gel, 10% ethyl acetate/hexanes with 1% Et₃N to 50% ethyl acetate/hexanes with 1% Et₃N), yielding benzimidate S6 (0.30 g, 46%) as a yellow oil.

R₁: 0.1 (50% Ethyl acetate/hexanes)

**¹H NMR (600 MHz, CDCl₃):** δ = 8.57 (d, J = 4.7 Hz, 1H), 7.81 (m, 1H), 7.65 (bs, 1H), 7.61 (td, J = 7.6, 1.7 Hz, 2H), 7.46 – 7.42 (m, 1H), 7.39 – 7.37 (m, 2H), 7.27 (d, J = 2.7 Hz, 1H) 7.14 (ddd, J = 7.5, 4.9, 1.0 Hz, 1H), 4.67 (bs, 2H), 3.31 (t, J = 6.6 Hz, 2H).

**¹³C NMR (100 MHz, CDCl₃):** δ = 158.9, 149.6, 136.4, 132.9, 131.0, 128.6, 126.8, 123.6, 121.6, 65.3, 37.7.

**HRMS (ESI-TOF) m/z:** calc’d for C₁₄H₁₅N₂O [M+H]+ 227.1179, found 227.1178.

**IR (film) cm⁻¹:** 3283, 2922, 1633.

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3-methylphenethyl benzimidate (S7)

2-(m-tolyl)ethan-1-ol (0.55 g, 4.0 mmol) was subjected to GP1. After filtration, the benzimidate salt was isolated (0.40 g, 25%) as a white solid. A portion of the benzimidate salt (0.29 g, 0.8 mmol) was free-based according to GP1; no purification was needed, yielding benzimidate S7 (0.17 g, 100%) as an off-white solid.

R₁: 0.46 (30% Ethyl acetate/hexanes)

**¹H NMR (400 MHz, CDCl₃):** δ = 7.85 – 7.78 (m, 1H), 7.69 (bs, 2H), 7.49 – 7.37 (m, 3H), 7.21 (t, J = 7.5 Hz, 1H), 7.15 – 7.09 (m, 2H), 7.08 – 7.02 (m, 1H), 4.49 (bs, 2H), 3.09 (t, J = 7.1 Hz, 2H), 3.34 (s, 3H).

**¹³C NMR (100 MHz, CDCl₃):** δ = 169.0, 138.5, 138.1, 132.9, 132.2, 131.0, 130.0, 128.8, 128.6, 128.5, 127.5, 127.3, 126.8, 126.2, 66.8, 35.2, 21.5.

**HRMS (ESI-TOF) m/z:** calc’d for C₁₆H₁₈NO [+M+H]+ 240.1383, found 240.1388.

**IR (film) cm⁻¹:** 3325, 3025, 2950, 2359, 2341, 1670, 1632, 1577, 1489, 1447, 1392, 1329, 1295, 1164, 1078, 1027, 1000, 973.

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3-(trifluoromethyl)phenethyl benzimidate (S8)

2-(3-(trifluoromethyl)phenyl)ethan-1-ol (0.76 g, 4.0 mmol) and benzonitrile (0.45 mL, 4.4 mmol) were subjected to GP1. After filtration, the benzimidate salt was isolated (0.97 g, 55%) as a white solid. A portion of the benzimidate salt (0.50 g, 1.1 mmol) was free-based according to GP1; no purification was needed, yielding benzimidate S8 (0.31 g, 96%) as an off-white oil.

R₁: 0.46 (30% Ethyl acetate/hexanes)

**¹H NMR (400 MHz, CDCl₃):** δ = 7.83 (bs, 1H), 7.74 – 7.61 (m, 2H), 7.59 (s, 1H), 7.54 – 7.47 (m, 2H), 7.47 – 7.37 (m, 4H), 4.63 – 4.39 (m, 2H), 3.19 (t, J = 6.6 Hz, 2H).

**¹³C NMR (150 MHz, CDCl₃):** δ = 168.1, 139.7, 132.6, 132.5, 131.1, 129.0, 128.6, 126.7, 126.1, 123.5, 123.4, 66.2, 35.1.

**¹⁹F NMR (376 MHz, CDCl₃):** δ = –62.6.
HRMS (ESI-TOF) m/z: calc'd for C\textsubscript{16}H\textsubscript{15}F\textsubscript{3}NO\textsuperscript{+} [M+H]\textsuperscript{+} 294.1100, found 294.1093.

IR (film) (cm\textsuperscript{−1}): 3334, 3061, 2953, 2359, 1633, 1492, 1470, 1448, 1392, 1330, 1321, 1197, 1160, 1118, 1071, 1028, 1001, 781, 693.

3-methoxyphenethyl benzimidate (S9)

2-(3-methoxyphenyl)ethan-1-ol (0.15 g, 1.0 mmol) was subjected to GP\textsubscript{2}, with acidification after transimidation to facilitate removal of unconsumed alcohol (see below). Upon completion, the free-based crude was concentrated, dissolved in dry Et\textsubscript{2}O, and acidified with 2M HCl in Et\textsubscript{2}O. Upon precipitation, the hydrochloride salt was isolated via filtration, and washed with cold hexanes and Et\textsubscript{2}O, yielding the benzimidate salt (0.16 g, 66%) as a white solid. The benzimidate salt was free-based according to GP\textsubscript{1}; no purification was needed, yielding benzimidate S9 (0.14 g, 98%) as a clear oil.

R\textsubscript{f}: 0.46 (30% Ethyl acetate/hexanes)

\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}): δ = 7.76 (bs, 1H), 7.70 (d, J = 7.3 Hz, 2H), 7.47 – 7.44 (m, 1H), 7.42 – 7.39 (m, 2H), 7.24 (t, J = 7.9 Hz, 1H), 6.91 (d, J = 7.5 Hz, 1H), 6.87 – 6.86 (m, 1H), 6.79 (dd, J = 8.2, 2.5 Hz, 1H), 4.51 (t, J = 6.5 Hz, 2H), 3.80 (s, 3H), 3.11 (t, J = 6.9 Hz, 2H).

\textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}): δ = 167.8, 159.8, 140.3, 132.9, 131.0, 129.5, 128.6, 126.8, 121.5, 114.8, 112.1, 66.6, 55.3, 35.4.

HRMS (ESI-TOF) m/z: calc'd for C\textsubscript{16}H\textsubscript{15}F\textsubscript{3}NO\textsuperscript{+} [M+H]\textsuperscript{+} 256.1332, found 256.1329.

IR (film) (cm\textsuperscript{−1}): 3330, 2952, 2834, 2359, 2341, 1717, 1633, 1601, 1578, 1487, 1448, 1392, 1328, 1294, 1257, 1164, 1151, 1077, 1057, 1041, 995, 975, 925.

4-fluorophenethyl benzimidate (S10)

2-(4-fluorophenyl)ethan-1-ol (0.50 mL, 4.0 mmol) was subjected to GP\textsubscript{1}. After filtration, the benzimidate salt was isolated (1.4 g, 91%) as a white solid. A portion of the benzimidate salt (0.89 g, 2.3 mmol) was free-based according to GP\textsubscript{1}. Purification via column chromatography (silica gel, 10% ethyl acetate/hexanes with 1% Et\textsubscript{3}N to 30% ethyl acetate/hexanes) yielded benzimidate S10 (0.23 g, 41%) as a white solid.

R\textsubscript{f}: 0.23 (30% Ethyl acetate/hexanes)

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ = 7.81 (bs, 1H), 7.68 (d, J = 7.5 Hz, 2H), 7.48 – 7.39 (m, 3H), 7.29 – 7.24 (m, 2H), 7.03 – 6.97 (m, 2H), 4.19 (bs, 2H), 3.16 (t, J = 6.8 Hz, 1H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ = 167.9, 161.8 (d, J\textsubscript{C,F} = 243.9 Hz), 134.4 (d, J\textsubscript{C,F} = 2.7 Hz), 132.8, 131.0, 130.5 (d, J\textsubscript{C,F} = 8.0 Hz), 128.6, 126.7, 115.3 (d, J\textsubscript{C,F} = 21.5 Hz), 66.6, 34.5.

\textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}): δ = −118.1.

HRMS (ESI-TOF) m/z: calc'd for C\textsubscript{15}H\textsubscript{15}FNO\textsuperscript{+} [M+H]\textsuperscript{+} 244.1132, found 244.1137.

IR (film) cm\textsuperscript{−1}: 3335, 3066, 1629

MP: 53 – 54 °C.
4-chlorophenethyl benzimidate (S11)

2-(4-chlorophenyl)ethan-1-ol (0.62 g, 4.0 mmol) was subjected to GP1. After filtration, the benzimidate salt was isolated (1.4 g, 84%) as a white solid. A portion of the benzimidate salt (0.26 g, 0.6 mmol) was free-based according to GP1; no purification was needed, yielding benzimidate S11 (0.16 g, 100%) as an off-white solid.

\[ \text{S11} \]

\[ \text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 7.71 - 7.62 \text{ (m, 2H), 7.49 - 7.37 \text{ (m, 2H), 7.32 - 7.26 \text{ (m, 2H), 7.25 - 7.20 \text{ (m, 2H), 4.49 \text{ (t, } J = 6.7 \text{ Hz, 2H), 3.09 \text{ (t, } J = 5.0 \text{ Hz, 2H).}}}} 

\[ \text{C NMR (100 MHz, CDCl}_3\text{): } \delta = 167.9, 137.2, 132.7, 133.4, 131.1, 130.5, 128.7, 128.6, 126.7, 63.4, 34.7. \]

HRMS (ESI-TOF) m/z: calc’d for C_{15}H_{15}ClNO \[ \text{[M+H]} \] 260.0837, found 260.0842.

IR (film) (cm\(^{-1}\)): 3332, 2964, 2923, 2360, 2341, 1627, 1576, 1490, 1475, 1410, 1396, 1339, 1186, 1162, 1107, 1079, 1060, 1026, 1014, 974, 922.

4-bromophenethyl benzimidate (S12)

2-(4-bromophenyl)ethan-1-ol (2.4 g, 12.0 mmol) was subjected to GP1, with the following modifications: dry DCE (20 mL) instead of PhMe, and a reaction temperature of 80 °C instead of 110 °C. After filtration, the benzimidate salt was isolated (2.9 g, 53%) as a white solid. A portion of the benzimidate salt (2.2 g, 4.9 mmol) was free-based according to GP1; no purification was needed, yielding benzimidate S12 (1.3 g, 85%) as an off-white solid.

\[ \text{S12} \]

\[ \text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 7.82 \text{ (bs, 1H), 7.71 - 7.58 \text{ (m, 2H), 7.49 - 7.36 \text{ (m, 5H), 7.21 - 7.16 \text{ (m, 2H), 4.51 \text{ (t, } J = 6.3 \text{ Hz, 2H), 3.08 \text{ (t, } J = 6.7 \text{ Hz, 2H).}}}} 

\[ \text{C NMR (100 MHz, CDCl}_3\text{): } \delta = 168.2, 137.8, 132.7, 131.6, 131.1, 130.9, 128.6, 126.7, 120.4, 66.4, 34.7. \]

HRMS (ESI-TOF) m/z: calc’d for C_{15}H_{15}BrNO \[ \text{[M+H]} \] 304.0332, found 304.0326.

IR (film) (cm\(^{-1}\)): 3331, 3060, 2965, 2896, 2866, 2359, 2341, 1627, 1575, 1485, 1457, 1407, 1394, 1334, 1300, 1292, 1185, 1162, 1106, 1082, 1069, 1059, 1026, 1010, 1001, 973, 921.

MP: 83 – 84 °C.

4-iodophenethyl benzimidate (S13)

2-(4-iodophenyl)ethan-1-ol (0.99 g, 4.0 mmol) was subjected to GP1. After filtration, the benzimidate salt was isolated (1.4 g, 70%) as a white solid. A portion of the benzimidate salt (0.57 g, 1.1 mmol) was free-based according to GP1; no purification was needed, yielding benzimidate S13 (0.40 g, 100%) as an off-white solid.
1H NMR (400 MHz, CDCl3): δ = 7.82 (bs, 1H), 7.72 – 7.60 (m, 4H), 7.50 – 7.37 (m, 3H), 7.09 – 7.02 (m, 2H), 4.60 – 4.38 (m, 2H), 3.07 (t, J = 6.7 Hz, 2H).

13C NMR (150 MHz, CDCl3): δ = 168.1, 138.4, 137.6, 132.7, 131.2, 131.0, 128.6, 126.7, 91.8, 66.3, 34.8.

HRMS (ESI-TOF) m/z: calc’d for C15H15NO [M+H]+ 352.0193, found 352.0176.

IR (film) (cm−1): 3058, 2950, 2888, 2362, 2342, 1633, 1577, 1484, 1447, 1397, 1330, 1297, 1183, 1165, 1080, 1062, 1028, 1000, 976.

MP: 79 – 80 °C.

4-(trifluoromethyl)phenethyl benzimidate (S14)

2-(4-(trifluoromethyl)phenyl)ethan-1-ol (0.76 g, 4.0 mmol) was subjected to GP1. After filtration, the benzimidate salt was isolated (1.1 g, 62%) as a white solid. A portion of the benzimidate salt (0.72 g, 1.6 mmol) was free-based according to GP1; no purification was needed, yielding benzimidate S14 (0.47 g, 99%) as a white solid.

1H NMR (400 MHz, CDCl3): δ = 7.82 (bs, 1H), 7.72 – 7.56 (m, 2H), 7.50 – 7.36 (m, 5H), 7.22 – 7.15 (m, 2H), 4.51 (t, J = 6.3 Hz, 2H), 3.08 (t, J = 6.7 Hz, 2H).

13C NMR (100 MHz, CDCl3): δ = 168.0, 143.0, 132.6, 131.1, 129.4, 129.0 (q, JCF = 33.0 Hz), 128.7, 126.7, 125.5 (q, JCF = 3.7 Hz), 124.43 (q, JCF = 272.0 Hz), 66.1, 35.1.

19F NMR (376 MHz, CDCl3): δ = −62.4.

HRMS (ESI-TOF) m/z: calc’d for C16H15F3NO+ [M+H]+ 294.1100, found 294.1088.

IR (film) (cm−1): 3337, 2955, 2894, 2359, 2341, 1628, 1617, 1576, 1496, 1448, 1419, 1397, 1324, 1187, 1168, 1153, 1124, 1110, 1086, 1063, 1027, 1017, 1000, 974, 957, 924.

MP: 83 – 84 °C.

4-(trifluoromethoxy)phenethyl benzimidate (S15)

2-(4-(trifluoromethoxy)phenyl)ethan-1-ol (0.94 g, 4.5 mmol) was subjected to GP1. After filtration, the benzimidate salt was isolated (1.4 g, 68%) as a white solid. A portion of the benzimidate salt (0.76 g, 1.7 mmol) was free-based according to GP1; no purification was needed, yielding benzimidate S15 (0.52 g, 99%) as an off-white solid.

1H NMR (400 MHz, CDCl3): δ = 7.83 (bs, 1H), 7.73 – 7.57 (m, 2H), 7.50 – 7.37 (m, 3H), 7.37 – 7.29 (m, 2H), 7.16 (d, J = 7.9 Hz, 2H), 4.62 – 4.42 (m, 2H), 3.13 (t, J = 6.7 Hz, 2H).

13C NMR (150 MHz, CDCl3): δ = 168.2, 148.0, 137.6, 132.7, 131.1, 130.4, 128.6, 126.7, 121.1, 120.6 (q, JCF = 256.6 Hz), 66.4, 34.6.

19F NMR (376 MHz, CDCl3): δ = −57.9.

HRMS (ESI-TOF) m/z: calc’d for C16H15F3NO2+ [M+H]+ 310.1049, found 310.1044.

IR (film) (cm−1): 3332, 2966, 2896, 2359, 2342, 1627, 1577, 1507, 1474, 1448, 1399, 1339, 1259, 1211, 1195, 1152, 1108, 1080, 1058, 1027, 1018, 1001, 974, 957.

MP: 61 – 62 °C.
1,2,3,4-tetrahydronaphthalen-2-yl benzimidate (S16)

1,2,3,4-tetrahydronaphthalen-2-ol (0.30 g, 2.0 mmol) was subjected to GP2 Step 2, with the following modifications: a reaction temperature of 60 °C instead of 50 °C, and 2 equivalents of Trifluoroethanol benzimidate was used. Final purification was done via column chromatography (silica gel, 1% ethyl acetate/hexanes with 1% Et₃N to 20% ethyl acetate/hexanes with 1% Et₃N), yielding the imidate S16 (0.27 g, 52%) as a clear oil.

Note: The transimidation is temperature sensitive; at 50 °C the alcohol is not consumed, and at 80 °C, the imidate decomposes into benzamide. Multiple columns may be needed to obtain pure benzimidate.

Rf: 0.26 (20% Ethyl acetate/hexanes)

1H NMR (400 MHz, CDCl₃): δ = 7.83 (bs, 1H), 7.70 (d, J = 7.2 Hz, 2H), 7.46 – 7.38 (m, 3H), 7.15 – 7.09 (m, 4H), 5.48 (bs, 1H), 3.28 (dd, J = 16.8, 5.1 Hz, 1H), 3.16 – 3.00 (m, 2H), 2.91 (td, J = 16.7, 6.7 Hz, 1H), 2.25 – 2.09 (m, 2H).

13C NMR (100 MHz, CDCl₃): δ = 167.2, 136.0, 134.4, 134.3, 130.9, 129.6, 128.7, 128.6, 126.8, 126.0, 126.0, 70.6, 34.6, 27.8, 26.7.

HRMS (ESI-TOF) m/z: calc'd for C₁₇H₁₈NO [M+H]+ 252.1383, found 252.1378.

IR (film) cm⁻¹: 3328, 3018, 1630.

phenethyl 4-methoxybenzimidate (S17)

4-methoxybenzonitrile (1 g, 7.5 mmol) was subjected to GP1. After filtration, the crude benzimidate salt was isolated as a white solid. A portion of the benzimidate salt (1.0 g, 2.5 mmol) was free-based according to GP1. Purification via column chromatography (silica gel, 10% ethyl acetate/hexanes with 1% Et₃N to 25% ethyl acetate/hexanes) yielded benzimidate S17 (0.52 g, 82%) as a white solid.

Rf: 0.09 (20% Ethyl acetate/hexanes)

1H NMR (400 MHz, CDCl₃): δ = 7.67 (bs, 1H), 7.66 (d, J = 8.7 Hz, 2H), 7.35 – 7.30 (m, 4H), 7.26 – 7.22 (m, 1H), 6.92 – 6.88 (m, 2H), 4.49 (t, J = 6.8 Hz, 2H), 3.84 (s, 3H), 3.13 (t, J = 6.8 Hz, 2H).

13C NMR (100 MHz, CDCl₃): δ = 167.4, 161.8, 138.7, 129.1, 128.52, 128.46, 126.5, 125.3, 113.8, 66.5, 55.5, 35.3.

HRMS (ESI-TOF) m/z: calc'd for C₁₉H₁₈NO₂ [M+H]+ expected 256.1338, found 256.1319.

IR (film) cm⁻¹: 3276, 3096, 2996, 2955, 2922, 2835, 1624, 1604, 1509.
phenethyl 4-bromobenzimidate (S18)

4-bromobenzonitrile was subjected to GP2, yielding the corresponding TFE-benzimidate (1.43 g, 82%) as a white solid. A portion of the TFE-benzimidate salt (2 reactions at 0.2 g scale) was freebased according to GP2 Step 2. Purification via column chromatography (silica gel, 10% ethyl acetate/hexanes with 1% Et$_3$N) yielded benzimidate S18 (0.25 g, 65%) as a white solid.

R$_f$: 0.09 (20% Ethyl acetate/hexanes)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.80 (bs, 1H), 7.55 – 7.50 (m, 4H), 7.34 – 7.23 (m, 5H), 4.52 (t, $J$ = 6.8 Hz, 2H), 3.11 (t, $J$ = 6.8 Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 167.1, 138.5, 131.8, 129.1, 128.6, 128.4, 126.6, 125.6, 66.9, 35.2.

HRMS (ESI-TOF) m/z: calc'd for C$_{15}$H$_{15}$BrNO [M+H]$^+$ expected 304.0337, found 304.0315.

IR (film) cm$^{-1}$: 3336, 3085, 3032, 2969, 2951, 2931, 2891, 2861, 1639, 1586.

MP: 57 – 59 °C.

phenethyl 4-(trifluoromethyl)benzimidate (S19)

4-trifluoromethylbenzonitrile (0.5 mL, 0.64 mL, 3.7 mmol) was subjected to GP1. After filtration, the crude benzimidate salt was isolated. The benzimidate salt was free-based according to GP1. Purification via column chromatography (silica gel, 5% ethyl acetate/hexanes with 1% Et$_3$N), yielded benzimidate S19 (0.65 g, 59%) as a white solid.

R$_f$: 0.22 (20% Ethyl acetate/hexanes)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.94 (bs, 1H), 7.78 (bs, 2H), 7.66 (d, $J$ = 8.3 Hz, 2H), 7.36 – 7.29 (m, 4H), 7.27 – 7.23 (m, 1H), 4.54 (bs, 2H), 3.14 (t, $J$ = 6.7 Hz, 2H).

$^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 166.9, 138.5, 136.1, 132.7 ($^2$J = 32.8 Hz), 129.0, 128.5, 127.1, 126.6, 125.5, 122.9, 67.1, 35.1.

HRMS (ESI-TOF) m/z: calc’d for C$_{16}$H$_{15}$F$_3$NO [M+H]$^+$ expected 294.1106, found 294.1099.

IR (film) cm$^{-1}$: 3335, 3059, 3026, 2962, 2893, 1638, 1577, 1541.

MP: 62.5 – 63.5 °C.

phenethyl 3-chlorobenzimidate (S20)

3-chlorobenzonitrile was subjected to GP2, yielding the corresponding TFE-benzimidate (0.54 g, 54%) as a white solid. A portion of the TFE-benzimidate salt (0.2 g) was subjected to GP2 Step
Purification via column chromatography (silica gel, 10% ethyl acetate/hexanes with 1% Et₃N) yielded benzimidate S20 (0.18 g, 96%) as a white solid.

**Rₓ:** 0.15 (20% Ethyl acetate/hexanes)

**¹H NMR (400 MHz, CDCl₃):** δ = 7.83 (bs, 1H), 7.63 (bs, 1H), 7.53 – 7.51 (m, 1H), 7.43 (ddd, J = 8.0, 2.1, 1.1 Hz, 1H), 7.36 – 7.29 (m, 5H), 7.26 – 7.24 (m, 1H), 4.53 (t, J = 6.9 Hz, 2H), 3.12 (t, J = 6.8 Hz, 2H).

**¹³C NMR (100 MHz, CDCl₃):** δ = 166.7, 138.4, 134.7, 131.0, 129.8, 129.1, 128.6, 128.4, 127.2, 126.6, 124.9, 67.0, 35.2.

**HRMS (ESI-TOF) m/z:** calc'd for C₁₅H₁₅ClNO [M+H]⁺ expected 260.0842, found 260.0835.

**IR (film) cm⁻¹:** 3338, 3062, 3029, 2958, 2895, 2859, 1632, 1595, 1566.

**MP:** 35 – 36 °C.

**phenethyl 3-chloro-4,5-dimethoxybenzimidate (S21)**

3,4-dichloro-5-methoxybenzonitrile (2.0 g, 10.0 mmol) was subjected to **GP1**, with the following modifications: dry DCE (18 mL) instead of PhMe, and a reaction temperature of 80 °C instead of 110 °C. After filtration, the benzimidate salt was isolated (2.4 g, 57%) as a white solid. A portion of the benzimidate salt (0.52 g, 1.1 mmol) was free-based according to **GP1**; no purification was needed, yielding benzimidate S21 (590 mg, 98%) as a yellow oil.

**¹H NMR (400 MHz, CDCl₃):** δ = 7.81 – 7.62 (m, 1H), 7.41 – 7.27 (m, 5H), 7.25 – 7.20 (m, 1H), 7.14 – 6.94 (m, 1H), 4.67 – 4.32 (m, 2H), 3.89 (s, 3H), 3.86 (s, 3H), 3.16 – 3.07 (t, J = 6.8 Hz, 2H).

**¹³C NMR (100 MHz, CDCl₃):** δ = 153.6, 147.7, 138.5, 129.1, 128.6, 126.6, 120.9, 120.7, 110.9, 109.6, 66.8, 60.9, 56.3, 35.2.

**HRMS (ESI-TOF) m/z:** calc'd for C₁₇H₁₉ClNO₃ [M+H]⁺ 320.1048, found 320.1040.

**IR (film) cm⁻¹:** 3324, 2939, 2833, 2359, 2341, 1670, 1634, 1596, 1566, 1491, 1453, 1405, 1324, 1277, 1235, 1175, 1134, 1077, 1047, 996, 940.

**MP:** 33 – 34 °C.

**phenethyl 3-bromo-4-fluorobenzimidate (S22)**

3-bromo-4-fluorobenzonitrile (2 g, 14.5 mmol) was subjected to **GP2 Step 1**, yielding the corresponding TFE-benzimidate (1.63 g, 67%) as a white solid. A portion of the TFE-benzimidate salt (0.17 g) was subjected to **GP2 Step 2**. Purification via column chromatography (silica gel, 10% ethyl acetate/hexanes with 1% Et₃N), yielded benzimidate S22 (0.12 g, 87%) as a white solid.

**Rₓ:** 0.12 (20% Ethyl acetate/hexanes)
**1H NMR (400 MHz, CDCl₃):** δ = 7.89 (bs, 1H), 7.77 (bs, 1H), 7.59 (m, 1H), 7.35 – 7.23 (m, 5H), 7.13 (t, J = 8.4 Hz, 1H), 4.49 (bs, 2H), 3.12 (t, J = 6.9 Hz, 2H).

**13C NMR (100 MHz, CDCl₃):** δ = 162.0, 159.5, 138.3, 132.7, 130.5, 129.1, 128.7, 127.8, 126.7, 116.5 (d, J = 22.8 Hz), 109.4 (d, J = 22.1), 66.9, 35.2.

**19F NMR (376 MHz, CDCl₃):** δ = –103.5.

**HRMS (ESI-TOF) m/z:** calc'd for C₁₅H₁₄BrFNO [M+H]⁺ expected 322.0243, found 322.0215.

**IR (film) cm⁻¹:** 3362, 3057, 3026, 2956, 2942, 2883, 1900, 1641, 1597, 1584.

**MP:** 58 – 58.8 °C.

**phenethyl 1-naphthimidate (S23)**

1-naphthonitrile (0.5 g, 3.3 mmol) was subjected to GP1. After filtration, the crude benzimidate salt was isolated. The benzimidate salt was free-based according to GP1. Purification was done via column chromatography (silica gel, 10% ethyl acetate/hexanes with 1% Et₃N) yielding benzimidate S23 (0.12 g, 13%) as a clear oil.

**Rᶠ:** 0.34 (20% Ethyl acetate/hexanes)

**1H NMR (400 MHz, CDCl₃):** δ = 7.91 – 7.85 (m, 3H), 7.62 (bs, 1H), 7.54 – 7.42 (m, 4H), 7.33 – 7.31 (m, 4H), 7.28 – 7.24 (m, 1H), 4.66 (t, J = 6.8 Hz, 2H), 3.16 (t, J = 6.9 Hz, 2H).

**13C NMR (100 MHz, CDCl₃):** δ = 170.2, 138.7, 133.7, 130.3, 129.8, 129.2, 128.6, 128.5, 127.1, 126.6, 126.3, 125.7 (2C), 125.3. 125.0, 67.1, 35.3.

**HRMS (ESI-TOF) m/z:** calc'd for C₁₉H₁₇NONa [M+Na]⁺ expected 298.1208, found 298.1209.

**IR (film) cm⁻¹:** 3317, 3057, 3027, 2954, 2915, 2893, 1950, 1629.

**MP:** 66 – 68 °C.

**phenethyl 2-naphthimidate (S24)**

2-naphthonitrile (0.5 g, 3.3 mmol) was subjected to GP1. After filtration, the crude benzimidate salt was isolated. A portion of the benzimidate salt (0.75 g, 1.8 mmol) was free-based according to GP1. Purification via column chromatography (silica gel, 10% ethyl acetate/hexanes with 1% Et₃N) yielded benzimidate S24 (0.12 g, 25%) as a white solid with a minor ester impurity (ca. 10%).

**Rᶠ:** 0.11 (20% Ethyl acetate/hexanes)

**1H NMR (400 MHz, CDCl₃):** δ = 8.21 (bs, 1H), 7.91 – 7.85 (m, 3H), 7.76 (dd, J = 8.5, 1.6 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.37 – 7.32 (m, 4H), 7.29 – 7.24 (m, 1H), 4.57 (t, J = 6.8 Hz, 2H), 3.19 (t, J = 6.9 Hz, 2H).

**13C NMR (100 MHz, CDCl₃):** δ = 167.6, 138.7, 134.5, 132.9, 130.0, 129.2, 129.1, 128.6, 128.4, 127.8, 127.6, 127.3, 126.8, 126.6, 123.6, 66.8, 35.4.

**HRMS (ESI-TOF) m/z:** calc'd for C₁₉H₁₇NO [M+H]⁺ expected 276.1388, found 276.1374.

**IR (film) cm⁻¹:** 3335, 3060, 3031, 2951, 2915, 2893, 1950, 1638, 1599, 1552.

**MP:** 66 – 68 °C.
phenethyl [1,1'-biphenyl]-4-carbimidate (S25)

4-phenylbenzonitrile (1 g, 5.6 mmol) was subjected to GP1. After filtration, the crude benzimidate salt was isolated. A portion of the benzimidate salt (0.5 g, 1.1 mmol) was free-based according to GP1. Final purification via column chromatography (silica gel, 10% ethyl acetate/hexanes with 1% Et$_3$N), yielded benzimidate S25 (0.12 g, 36%) as a white solid.

Rf: 0.09 (20% Ethyl acetate/hexanes)
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.85 (bs, 1H), 7.75 – 7.73 (m, 2H), 7.64 – 7.60 (m, 4H), 7.48 – 7.44 (m, 2H), 7.40 – 7.36 (m, 1H), 7.33 (d, $J$ = 4.3 Hz, 4H), 7.27 – 7.23 (m, 1H) 4.56 (t, $J$ = 6.2 Hz, 2H), 3.15 (t, $J$ = 6.8 Hz, 2H).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 167.3, 143.8, 140.2, 138.7, 129.1, 129.0, 128.6, 128.0, 127.4, 127.31, 127.29, 127.26, 126.5, 66.7, 35.3.
HRMS (ESI-TOF) m/z: calc'd for C$_{21}$H$_{20}$NO [M+H]$^+$ expected 302.1545, found 302.1538.
IR (film) cm$^{-1}$: 3335, 3062, 3030, 2942, 1629, 1607, 1582.
MP: 116 – 118 °C.

2-chloroethyl benzimidate hydrotriflate salt (S26)

2-chloroethanol (1.2 g, 15 mmol) was subjected to GP1. After filtration, the benzimidate salt was isolated (3.1 g, 51%) as a white solid.

Note: The benzimidate salt was found to rapidly tautomerize to the corresponding amide under free-base conditions.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 10.68 (bs, 2H), 8.15 (d, $J$ = 7.4 Hz, 2H), 7.78 (t, $J$ = 7.5 Hz, 1H), 7.60 (t, $J$ = 8.0 Hz, 2H), 4.94 (t, $J$ = 4.8 Hz, 2H), 3.99 (t, $J$ = 4.8 Hz, 2H).
$^{13}$C NMR (150 MHz, DMSO-d$_6$): $\delta$ = 171.2, 135.7, 129.4, 129.0, 127.2, 72.5, 41.4.
$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ = –78.5.
HRMS (ESI-TOF) m/z: calc'd for C$_9$H$_{11}$ClNO [M+H]$^+$ expected 184.0524, found 184.0529.
IR (film) cm$^{-1}$: 1628, 1602, 1507, 1460, 1432, 1376, 1270, 1226, 1167, 1106, 1086, 1027, 1000, 962.
MP: 114 – 115 °C.

Phenethyl pivalimidate (S27)

2-phenylethan-1-ol (0.82 mL, 8.0 mmol) and pivalonitrile (0.97 mL, 8.8 mmol) were subjected to GP1. After filtration, the pivalimidate salt was isolated (680 g, 24%) as a white solid. A portion of the pivalimidate salt (420 mg, 1.2 mmol) was free-based according to GP1. Purification via column
chromatography (silica gel, 20% ethyl acetate/hexanes with 1% Et₃N), yielded pivalimidate S27 (100 mg, 44%) as a clear oil.

Note: The phenethyl pivalimidate hydrotriflate salt took over a week to precipitate out at -15 °C. Alkyl imidates are generally more hydrolytically unstable than their corresponding benzimidates. As such, column chromatography for this substrate was done quickly, in less than 3 minutes. The crude free-based material can be used without any observable difference in reactivity.

Rf: 0.42 (20% Ethyl acetate/hexanes)

¹H NMR (400 MHz, CDCl₃): δ = 7.30 – 7.20 (m, 5H), 6.90 (Bs, 1H), 4.29 (t, J = 6.7 Hz, 2H), 3.00 (t, J = 6.7 Hz, 2H), 1.14 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ = 179.2, 138.8, 129.1, 128.4, 126.4, 66.5, 37.9, 35.3, 27.8

HRMS (ESI-TOF) m/z: calc’d for C₁₃H₂₀NO [M+H]+ 206.1539, found 206.1543.

IR (film) cm⁻¹: 3028, 2958, 2871, 1726, 1639.

Phenethyl 2,2,2-trichloroacetimidate (S28)

Trichloroacetimidate S28 was prepared following a literature method.³

To a 250 mL round bottom flask containing a stirbar, 2-phenylethanol (2.2 g, 18 mmol) and CH₂Cl₂ (180 mL) were added trichloroacetonitrile (3.6 mL, 36 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.55 mL, 4.5 mmol). The solution was stirred at 23 °C and monitored by TLC until consumption of alcohol. Upon completion, the solution was concentrated and directly loaded onto silica gel (treated with 1% Et₃N in hexanes) and purified, yielding trichloroacetimidate S28 (4.2 g, 87%) as a light-yellow oil.

Characterization data is consistent with reported literature data.³

Rf: 0.66 (20% Ethyl acetate/hexanes)

¹H NMR (400 MHz, CDCl₃): δ = 8.28 (bs, 1H), 7.34 – 7.26 (m, 4H), 7.25 – 7.21 (m, 1H), 4.50 (t, J = 6.9 Hz, 2H), 3.09 (t, J = 6.9 Hz, 2H).

N-methyl-N-phenethyl-4-(trifluoromethyl)benzimidamide (S29)

Amidine S29 was prepared following a literature method.⁴

To a 2-dram vial equipped with stirbar and N-methyl phenethylamine (0.54 g, 4.0 mmol) and PhMe (4.5 mL) at 0 °C, was added AlMe₃ (25% w/w in hexanes, 2.7 mL, 6.2 mmol) dropwise. The reaction was stirred and warmed to room temperature for 15 minutes. 4-trifluorobenzonitrile (1.0 g, 6.0 mmol) in PhMe (1.0 mL) was added dropwise, and then brought to 110 °C for 24 h. The reaction was quenched with H₂O, extracted with ethyl acetate, and then purified via column

³ Chen, H.; Kaga, A.; Chiba, S. Org. Lett. 2014, 16, 6136–6139.
chromatography (silica gel with 1% Et₃N, 20% ethyl acetate/hexanes to 97% ethyl acetate/3% Et₃N) yielding amidine S29 (0.31 g, 25%) as a yellow oil.

Rf: 0.29 (97% Ethyl acetate/triethylamine)

¹H NMR (400 MHz, CDCl₃): δ = 7.56 (d, J = 8.0 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.25 – 7.20 (m, 2H), 7.16 (d, J = 7.9 Hz, 2H), 7.04 (d, J = 6.7 Hz, 2H), 3.42 (t, J = 7.0 Hz, 2H), 2.94 (s, 3H), 2.83 (t, J = 7.2 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃): δ = 168.1, 142.1, 140.1, 138.8, 130.9 (q, J_CF = 32.7 Hz), 129.0, 128.6, 128.0, 127.1, 126.6, 126.2, 125.6 (q, J_CF = 3.7 Hz), 123.9 (q, J_CF = 272.7 Hz), 53.2, 36.1, 34.3.

¹⁹F NMR (376 MHz, CDCl₃): δ = –62.8.

HRMS (ESI-TOF) m/z: calc’d for C₁₁₂H₁₈F₃N₂⁺ [M+H]+ 307.1417, found 307.1405.

IR (film) cm⁻¹: 3367, 3027, 2345, 2115, 1685, 1618, 1585, 1570, 1520, 1496, 1478, 1454, 1406, 1364, 1322, 1665, 1123, 1065, 1030.

2,2,2-trichloro-N-methyl-N-phenethylacetimidamide (S30)

Amidine S30 was prepared following a literature method.⁴

To a 250 mL round bottom flask containing a stirbar, N-methyl-phenethylamine (0.68 g, 5.0 mmol) and CH₂Cl₂ (50 mL) were added trichloroacetonitrile (1.0 mL, 10 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (1.5 mL, 1.0 mmol). The solution was stirred at 23 °C and monitored by TLC until consumption of amine. Upon completion, the solution was concentrated and directly loaded onto silica gel (treated with 1% Et₃N in hexanes) and purified, yielding amidine S30 (0.8 g, 56%) as a light yellow oil.

Rf: 0.21 (30% Ethyl acetate/hexanes)

¹H NMR (400 MHz, CDCl₃): δ = 7.68 (bs, 1H), 7.34 – 7.27 (m, 2H), 7.25 – 7.19 (m, 3H), 3.79 – 3.71 (m, 2H), 3.12 (s, 3H), 3.01 – 2.93 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ = 179.2, 138.8, 129.14, 129.10, 128.4, 66.5, 37.9, 35.3, 27.8.

HRMS (ESI-TOF) m/z: calc’d for C₁₁₂H₁₈F₃N₂⁺ [M+H]+ 279.0217, found 279.0215.

IR (film) cm⁻¹: 3315, 2922, 1709, 1685, 1573, 1522, 1488, 1449, 1426, 1373, 1328, 1310, 1258, 1168, 1071, 1029, 1008.

2-phenylbutyl benzimidate (34)

2-phenylbutan-1-ol (0.15 g, 1.0 mmol) was subjected to GP2. The crude reaction mixture was washed with NaHCO₃ and purification via column chromatography (silica gel treated with 1% Et₃N) yielded benzimidate 34 (0.034 g, 13%) as a clear oil.

Rf: 0.22 (20% Ethyl acetate/hexanes)

¹H NMR (600 MHz, CDCl₃): δ = 7.80 (bs, 1H), 7.47 – 7.44 (m, 1H), 7.42 – 7.23 (m, 10H), 4.53 – 4.40 (m, 2H), 3.10 – 3.01 (m, 1H), 2.04 – 1.90 (m, 1H), 1.83 – 1.71 (m, 1H) 0.92 (t, J = 7.4 Hz, 3H).
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 167.5, 141.4, 131.8, 129.8, 127.6, 127.0, 127.7, 126.7, 125.6, 66.3, 45.8, 24.5, 10.9\).

HRMS (ESI-TOF) \(m/z\): calc'd for C\(_{17}\)H\(_{20}\)NO\(^+\) [M+H]\(^+\) 254.1539, found 254.1416.

1-phenylpropan-2-yl benzimidate (38)

1-phenyl-2-propanol (0.273 g, 2.0 mmol) was combined with trifluoroethanol benzimidate (hydrochloride salt) (1.16 g, 4.8 mmol) in MeCN (8 mL) and stirred at 60 °C for 16h. The solvent was evaporated, and the residue was freebased according to GP1. The crude product was purified via column chromatography (silica gel, 5% ethyl acetate/hexanes with 1% Et\(_3\)N to yield benzimidate 38 (0.20 g, 0.84 mmol, 42%) as a clear oil.

Note: the transimidation is temperature sensitive; at 50 °C the alcohol is not consumed, and at 80 °C, the imidate decomposes into benzamide. Multiple columns may be needed to obtain pure benzimidate.

**R\(_f\):** 0.37 (20% Ethyl acetate/hexanes)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.75\) (bs, 1H), 7.68 (d, J = 7.2 Hz, 2H), 7.47 – 7.38 (m, 3H), 7.30 – 7.27 (m, 4H), 7.25 – 7.20 (m, 1H), 5.40 (bs, 1H), 3.14 (dd, J = 13.6, 6.4 Hz, 1H), 2.94 (dd, J = 13.7, 6.4 Hz, 1H), 1.37 (d, J = 6.2 Hz, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 167.3, 138.3, 133.5, 130.8, 129.7, 128.4, 126.8, 126.4, 72.4, 42.4, 19.3\).

HRMS (ESI-TOF) \(m/z\): calc'd for C\(_{16}\)H\(_{18}\)NO\(^+\) [M+H]\(^+\) 240.1383, found 240.1376.

IR (film) cm\(^{-1}\): 3026, 3018, 2926, 1630.
V. Tandem Oxidation Optimization

Solvent Effects with CsI

Benzimidate 3 (0.2 mmol) was subjected to GP3, with different solvents listed below. Upon completion, the crude mixture was quenched, concentrated, and quantified via $^1$H NMR using 1 equiv of 1,2-dichloroethane as an internal standard.

| Solvent          | ε   | Time (h) | Imidate | Oxazoline | Oxazole |
|------------------|-----|----------|---------|-----------|---------|
| Hexanes          | 1.88| 8        | 53%     | 28%       | 7%      |
| 1,4-Dioxane      | 2.25| 8        | 0%      | 63%       | 24%     |
| PhH              | 2.27| 8        | 0%      | 32%       | 25%     |
| PhMe             | 2.38| 8        | 0%      | 63%       | 36%     |
| PhMe             | 2.38| 24       | 0%      | 0%        | 88%     |
| p-Xylene         | 2.57| 8        | 0%      | 49%       | 29%     |
| Ethyl acetate    | 6.02| 8        | 31%     | 64%       | 0%      |
| THF              | 7.5 | 8        | 0%      | 91%       | 0%      |
| PhCF$_3$         | 9.04| 8        | 34%     | 50%       | 14%     |
| CH$_2$Cl$_2$     | 9.1 | 8        | 0%      | 50%       | 45%     |
| CH$_2$Cl$_2$     | 9.1 | 24       | 0%      | 10%       | 64%     |
| MeCN             | 37.5| 8        | 0%      | 100%      | 0%      |
| DMF              | 38  | 8        | 0%      | 90%       | 0%      |

Counter-Ion Effects

Benzimidate 3 (0.2 mmol) was subjected to GP3, with different iodide salts listed below. Upon completion, the crude mixture was quenched, concentrated, and quantified via $^1$H NMR using 1 equiv of 1,2-dichloroethane as an internal standard.

| MI          | $r_{ion}$ (pm)$^5$ | Imidate | Oxazoline | Oxazole |
|-------------|--------------------|---------|-----------|---------|
| LiI         | 90                 | 0%      | 28%       | 63%     |
| NaI         | 116                | 0%      | 10-30%    | 65-85%  |
| CuI         | 77                 | 90%     | 10%       | 0%      |
| KI          | 152                | 0%      | 5%        | 76%     |
| CsI         | 181                | 0%      | 0%        | 96%     |
| $^{t}$BuI   | 494$^6$            | 0%      | 25%       | 55%     |

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$^5$ Shannon, R.D. Acta Crystallogr. A. 1976, A32, 751 – 767.

$^6$ Poli, I.; Eslava, S.; Cameron, P. J. Mater. Chem. A, 2017, 5, 22325 – 22333.
**Conditions:** imidate (0.2 mmol), MI (3 equiv), PhI(OAc)$_2$ (3 equiv), solvent (2 mL), 23 W compact fluorescent light (CFL), 23 °C, 24 h. $^1$H NMR yields vs DCE standard.

Note: NaI affords a variable range of yields, while CsI affords both more consistent and higher yields.

![Chemical structure](image)

**Figure S3.** Summary of improved yields with CsI compared to NaI. $^1$H NMR yields with 1 equiv 1,2-dichloromethane as an internal standard

**Light, Thermal, and Oxygen Controls**

Benzimidate 3 was subjected to GP3, with different conditions listed below. Upon completion, the crude mixture was quenched, concentrated, and quantified via $^1$H NMR using 1 equiv of 1,2-dichloroethane as an internal standard.

**Table S4.** Light and oxygen controls

| MI  | Solvent | Variation                      | Imidate | Oxazoline | Oxazole |
|-----|---------|--------------------------------|---------|-----------|---------|
| NaI | PhMe    | No Degas                       | 0%      | 9%        | 75%     |
| NaI | PhMe    | Freeze-Pump-Thaw; N$_2$        | 0%      | 12%       | 74%     |
| NaI | PhMe    | Freeze-Pump-Thaw; O$_2$        | 0%      | 14%       | 58%     |
| CsI | PhMe    | No change                      | 0%      | 0%        | 98%     |
| CsI | PhMe    | Blue LED                       | 0%      | 0%        | 82%     |
| CsI | PhMe    | No light, r.t.                 | 15%     | 75%       | 12%     |
| CsI | PhMe    | No light, 50 °C                | 0%      | 50%       | 35%     |
| CsI | PhMe    | Ambient light, r.t.            | 0%      | 75%       | 22%     |
Oxidant Loading and Catalytic I$_2$ Studies

Benzimidate 3 was subjected to GP$_3$, with different loadings of CsI and PhI(OAc)$_2$ listed below. Upon completion, the resultant crude mixture was concentrated and quantified via $^1$H NMR using 1 equiv of 1,2-dichloroethane as an internal standard.

| Table S5. Oxidant loading studies |
|-----------------------------------|
| Csl (eq) | PhI(OAc)$_2$ (eq) | Imidate | Oxazoline | Oxazole |
|---------|------------------|---------|-----------|---------|
| 1       | 1                | 54%     | 6%        | 34%     |
| 2       | 2                | 15%     | 14%       | 59%     |
| 3       | 3                | 0%      | 0%        | 98%     |

Conditions: imidate (0.2 mmol), solvent (2 mL), 23 W compact fluorescent light (CFL), 23 °C. $^1$H NMR yields vs DCE standard.

Intermediate oxazoline 2 was subjected to oxidation conditions which have been reported in the literature for oxazoline to oxazole conversion.

Benzimidate 3 was subjected to conditions reported in the literature for PhI(OAc)$_2$ oxidation with catalytic amounts of I$_2$ listed below. Upon completion, the resultant crude mixture was concentrated and quantified via $^1$H NMR using 1 equiv of 1,2-dichloroethane as an internal standard.

| Table S6. Catalytic I$_2$ conditions |
|-------------------------------------|
| Solvent | PhI(OAc)$_2$ (eq) | Variation | Imidate | Oxazoline | Oxazole |
|---------|------------------|-----------|---------|-----------|---------|
| DMF     | 1.2              | 50 °C     | 0%      | 95%       | 0%      |
| DMF     | 2.2              | 50 °C     | 0%      | 84%       | 0%      |
| MeCN    | 2.2              | 50 °C     | 0%      | 90%       | 0%      |
| PhMe    | 2.2              | 50 °C     | 0%      | 78%       | 6%      |
| PhMe    | 2.2 (5%) PhI(OAc)$_2$ | 23 W CFL, 23 °C | 0% | 24% | 58% |
| PhMe    | 3.0              | 23 W CFL, 23 °C, 20% I$_2$ | 0% | 11% | 60% |

Conditions: imidate (0.2 mmol), solvent (1 mL), I$_2$ (5 mol%). $^1$H NMR yields vs DCE standard.

Time Studies

Benzimidate 3 was subjected to GP$_3$, and quenched at different times listed below. Upon completion, the resultant crude mixture was concentrated and quantified via $^1$H NMR using 1 equiv of 1,2-dichloroethane as an internal standard.

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7 Stateman, L. M.; Wappes, E. A.; Nakafuku, K. M.; Edwards, K. M.; Nagib, D. A. *Chem. Sci.* 2019, 10, 2693 – 2699.
Table S7. Time study of tandem oxidation

| Time (h) | Imidate | Oxazoline | Oxazole |
|----------|---------|-----------|---------|
| 1        | 76%     | 23%       | 5%      |
| 2        | 50%     | 34%       | 10%     |
| 4        | 50%     | 32%       | 13%     |
| 8        | 0%      | 34%       | 54%     |
| 10       | 0%      | 18%       | 83%     |
| 12       | 0%      | 6%        | 96% (97%)* |
| 14       | 0%      | 0%        | 94%     |

Conditions: imidate (0.2 mmol), CsI (3 equiv), PhI(OAc)$_2$ (3 equiv), solvent (2 mL), 23 W compact fluorescent light (CFL), 23 °C. $^1$H NMR yields vs DCE standard. *denotes isolated yield.

Longer runtimes did not result in a decreased yield of oxazole 3, indicating the stability of the product under reaction conditions.

Optimization of Trichloroacetimidate Tandem Oxidation

Trichloroacetimidate S28 was subjected to GP3, with modified conditions listed below. Upon completion, the crude mixture was quenched, concentrated, and quantified via $^1$H NMR using 1 equiv of 1,2-dichloroethane as an internal standard.

Table S8. Optimization of tandem oxidation for trichloroacetimidates

| MI    | Solvent          | Oxazoline | Oxazole |
|-------|------------------|-----------|---------|
| Nal   | MeCN             | 100%      | 0%      |
| Nal   | PhMe             | 76%       | 16%     |
| Nal   | PhMe/CHCl$_3$ (3:1) | 11%      | 52%     |
| Nal   | PhMe/CHCl$_3$ (1:1) | **10%**  | **58%** |
| Nal   | PhMe/CHCl$_3$ (1:3) | 19%      | 50%     |
| Nal   | CHCl$_3$         | 5%        | 40%     |
| CsI   | PhMe/CHCl$_3$ (50:50) | 19%     | 28%     |

Other oxidants were tried and found to unsuccessfullly promote the tandem oxidation, including: PhI(OTFA)$_2$, Dess–Martin periodinane, IBX, N-iodosuccinimide, 1-acetoxy-1,2-benziodoxol-3-(1H)-one, Koser’s reagent.
VI. Tandem Oxidation

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

Oxazoline 2 was prepared following a literature method. To a 10 mL round bottom flask and stir bar was added benzimidate 1 (0.4 g, 1.8 mmol), and PhI(OAc)$_2$ (0.7 g, 2.2 mmol). This vial was evacuated and backfilled with N$_2$ (3x). A degassed stock solution of I$_2$ (47 mg, 0.018 mmol) in dry DMF (4.5 mL) was added to the flask under N$_2$. The reaction was heated to 50°C (by placing vial in an aluminum heating block) and stirred for 2 hours. Upon completion, the reaction was quenched with 10% aq. Na$_2$S$_2$O$_3$, extracted with EtOAc, and washed with H$_2$O. The crude was then purified via column chromatography (silica gel treated with 1% Et$_3$N in hexanes), yielding oxazoline 2 (0.34 g, 85%) as a light yellow oil. Characterization data is consistent with reported literature data.

$^1$H NMR (400 MHz, CDCl$_3$): δ = 8.07 – 8.02 (m, 1H), 7.47 – 7.41 (m, 2H), 7.39 – 7.25 (m, 5H), 5.39 (dd, $J$ = 10.2, 8.2 Hz, 1H), 4.80 (dd, $J$ = 10.0, 8.4 Hz, 1H), 4.28 (app t, $J$ = 8.3 Hz, 1H).

2,4-diphenyloxazole (3)

Benzimidate 1 (45 mg, 0.2 mmol) was subjected to GP3. Purification via column chromatography, yielded oxazole 3 (43 mg, 97%) as an off-white solid.

R$_f$: 0.48 (10% Ethyl acetate/hexanes)

$^1$H NMR (400 MHz, CDCl$_3$): δ = 8.16 – 8.10 (m, 2H), 7.97 (s, 1H), 7.86 – 7.80 (m, 2H), 7.53 – 7.38 (m, 6H), 7.37 – 7.31 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ = 162.1, 142.2, 133.6, 131.3, 130.5, 128.9, 128.3, 127.7, 126.7, 125.80

HRMS (ESI-TOF) $m/z$: calc’d for C$_{15}$H$_{12}$NO$^+$ [M+H]$^+$ 222.0913, found 222.0920.

IR (film) (cm$^{-1}$): 2924, 2852, 2360, 2341, 1553, 1487, 1146, 1339, 1290, 1274, 1157, 1123, 1069, 1022, 942, 929.

MP: 94 – 96 °C

2-phenyl-4-(o-tolyl)oxazole (4)

Benzimidate S4 (48 mg, 0.2 mmol) was subjected to GP3. Purification via column chromatography yielded oxazole 4 (44 mg, 94%) as an off-white solid.
**4-(2-chlorophenyl)-2-phenyloxazole (5)**

Benzimidate **S5** (52 mg, 0.2 mmol) was subjected to **GP3**. Purification via column chromatography yielded oxazole **5** (33 mg, 63%) as a tan solid.

**M.P 65 – 66 °C.**

\[
\text{Rf: 0.45 (5% Ethyl acetate/hexanes)}
\]

**1H NMR (400 MHz, CDCl}_3\): δ = 8.21 – 8.08 (m, 2H), 7.98 – 7.88 (m, 1H), 7.82 (s, 1H), 7.56 – 7.40 (m, 3H), 7.34 – 7.26 (m, 3H), 2.51 (s, 3H).

**13C NMR (100 MHz, CDCl}_3\): δ = 161.1, 141.2, 135.8, 135.4, 131.0, 130.6, 130.5, 128.9, 128.1, 127.7, 126.7, 126.2, 21.9.

**HRMS (ESI-TOF) m/z**: calc'd for C\textsubscript{16}H\textsubscript{14}NO\textsuperscript{+} [M+H\textsuperscript{+}] 236.1070, found 236.1067.

**IR (film) cm\textsuperscript{-1}:** 3177, 3059, 2926, 2359, 2341, 1556, 1488, 1462, 1448, 1378, 1339, 1288, 1262, 1235, 1134, 1111, 1081, 1066, 1043, 1023, 934

**2 phenyl-4-(pyridin-2-yl)oxazole (6)**

Benzimidate **S6** (45 mg, 0.2 mmol) was subjected to **GP3**, with the following modifications: addition of K\textsubscript{2}HPO\textsubscript{4} (40 mg, 0.2 mmol). Purification via column chromatography yielded oxazole **6** (22 mg, 49%) as a tan solid.

**Rf: 0.25 (30% Ethyl acetate/hexanes)**

**1H NMR (400 MHz, CDCl}_3\): δ = 8.61 (dq, J = 4.8, 0.8 Hz, 1H), 8.31 (s, 1H), 8.01 (dt, J = 7.7, 1.0 Hz, 1H), 7.78 (td, J = 7.7, 1.8 Hz, 1H), 7.52 – 7.45 (m, 3H), 7.23 (ddd, J = 7.6, 4.8, 1.2 Hz, 1H).

**13C NMR (100 MHz, CDCl}_3\): δ = 162.2, 151.0, 149.7, 142.4, 137.0, 130.7, 128.9, 127.5, 126.7, 122.9, 120.5.

**HRMS (ESI-TOF) m/z**: calc'd for C\textsubscript{15}H\textsubscript{11}NO\textsuperscript{+} [M+H\textsuperscript{+}] 223.0866, found 223.0871.

**IR (film) cm\textsuperscript{-1}:** 3121, 3058, 1607, 1576.

**M.P 94 – 95 °C.**
2-phenyl-4-(m-tolyl)oxazole (7)

Benzimidate S7 (48 mg, 0.2 mmol) was subjected to GP3. Purification via column chromatography yielded oxazole 7 (44 mg, 94%) as a white solid.

**Rf:** 0.45 (10% Ethyl acetate in hexanes)

**1H NMR (400 MHz, CDCl3):** δ = 8.19 – 8.07 (m, 2H), 7.96 (s, 1H), 7.70 – 7.65 (m, 1H), 7.64 – 7.58 (m, 1H), 7.53 – 7.42 (m, 3H), 7.35 – 7.29 (t, H = 7.7 Hz, 1 H), 7.18 – 7.12 (m, 1H), 2.42 (s, 3H).

**13C NMR (150 MHz, CDCl3):** δ = 162.4, 142.3, 138.6, 133.6, 131.2, 130.5, 129.1, 128.9, 128.8, 127.7, 126.7, 126.5, 122.9, 21.6.

**HRMS (ESI-TOF) m/z:** calc’d for C16H14NO+ [M+H]+ 236.1070, found 236.1067.

**IR (film) (cm⁻¹):** 3058, 2920, 2857, 2359, 2341, 1616, 1598, 1555, 1488, 1448, 1337, 1275, 1113, 1081, 1060, 1023, 960, 932.

**MP:** 50 – 51 °C.

2-phenyl-4-(3-(trifluoromethyl)phenyl)oxazole (8)

Benzimidate S8 (59 mg, 0.2 mmol) was subjected to GP3. Purification via column chromatography yielded oxazole 8 (43 mg, 77%) as a white solid.

**Rf:** 0.38 (10% Ethyl acetate in hexanes)

**1H NMR (400 MHz, CDCl3):** δ = 8.17 – 8.09 (m, 3H), 8.03 (s, 1H), 8.03 – 7.98 (m, 1H), 7.62 – 7.52 (m, 2H), 7.52 – 7.46 (m, 3H).

**13C NMR (150 MHz, CDCl3):** δ = 162.4, 141.0, 134.2, 132.2, 131.4 (q, 2JC_F = 32.3 Hz), 130.8, 129.4, 129.0, 126.7, 124.8 (q, 3JC_F = 3.8 Hz), 124.22 (q, 1JC_F = 272.3 Hz), 122.6 (q, 3JC_F = 4.0 Hz).

**19F NMR (376 MHz, CDCl3):** δ = –62.8.

**HRMS (ESI-TOF) m/z:** calc’d for C16H11F3NO+ [M+H]+ 290.0787, found 290.0789.

**IR (film) (cm⁻¹):** 2359, 2341, 1620, 1558, 1491, 1479, 1448, 1341, 1317, 1284, 1277, 123, 1169, 1157, 1107, 1094, 1060, 1022, 956, 931

**MP:** 70 – 72 °C.
4-(3-methoxyphenyl)-2-phenyloxazole (9)

Benzimidate S9 (51 mg, 0.2 mmol) was subjected to GP3. Purification via column chromatography yielded oxazole 9 (50 mg, 100%) as a white solid.

Rf: 0.28 (10% Ethyl acetate in hexanes)

$^1$H NMR (600 MHz, CDCl$_3$): δ = 8.14 – 8.12 (m, 2H), 7.98 (s, 1H), 7.50 – 7.47 (m, 3H), 7.42 (dd, J = 2.5, 1.4 Hz, 1H), 7.39 (dt, J = 7.6, 1.2 Hz, 1H), 7.34 (t, J = 7.9 Hz, 1H), 6.89 (ddd, J = 8.1, 2.6, 1.0 Hz, 1H), 3.89 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$): δ = 162.0, 160.2, 142.1, 133.8, 132.6, 130.6, 129.9, 128.9, 127.6, 126.7, 118.2, 114.2, 111.1, 55.5.

HRMS (ESI-TOF) m/z: calc'd for C$_{16}$H$_{14}$NO$_2$ [M+H]$^+$ 252.1019, found 252.1021.

IR (film) cm$^{-1}$: 3061, 2999, 2935, 2833, 2360, 2341, 1609, 1591, 1571, 1555, 1489, 1465, 1447, 1431, 1337, 1320, 1303, 1280, 1245, 1212, 1177, 1079, 1043, 1023, 960, 932.

M.P: 67 – 68 °C.

4-(4-fluorophenyl)-2-phenyloxazole (10)

Benzimidate S10 (49 mg, 0.2 mmol) was subjected to GP3. Purification via column chromatography yielded oxazole 10 (41 mg, 85%) as an off-white solid.

Rf: 0.35 (5% Ethyl acetate/hexanes)

$^1$H NMR (400 MHz, CDCl$_3$): δ = 8.12 (m, 2H), 7.92 (s, 1H), 7.80 (dd, J = 8.9, 5.4 Hz, 2H), 7.48 (m, 3H), 7.13 (t, J = 8.8 Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ = 162.8 (q, $^3$J$_{C-F}$ = 247.2 Hz), 162.1, 141.3, 133.2 (q, $^3$J$_{C-F}$ = 1.1 Hz), 130.6, 128.9, 127.6, 127.5 (q, $^3$J$_{C-F}$ = 8.0 Hz), 126.6, 115.9 (q, $^2$J$_{C-F}$ = 21.8 Hz).

$^{19}$F NMR (376 MHz, CDCl$_3$): δ = –114.68.

HRMS (ESI-TOF) m/z: calc'd for C$_{15}$H$_{11}$FNO [M+H]$^+$ 240.0819, found 240.0830.

IR (film) cm$^{-1}$: 3132, 3059, 1718, 1610, 1556.

M.P 104 – 105 °C.
4-(4-chlorophenyl)-2-phenyloxazole (11)

Benzimidate S11 (42 mg, 0.2 mmol) was subjected to GP3. Purification via column chromatography yielded oxazole 11 (39 mg, 94%) as a white solid.

Rf: 0.50 (5% Ethyl acetate/hexanes)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.14 – 8.09$ (m, 2H), 7.96 (s, 1H), 7.86 – 7.75 (m, 2H), 7.52 – 7.46 (m, 3H), 7.42 – 7.39 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 162.2, 141.2, 133.9, 133.7, 130.7, 129.4, 128.9, 128.9, 127.7, 127.1, 126.7$

HRMS (ESI-TOF) $m/z$: calc'd for C$_{15}$H$_{11}$NaO$_3$ $[M+Na]^+$ 378.0343, found 378.0374

IR (film) (cm$^{-1}$): 3364, 3120, 3057, 2959, 2923, 2852, 1657, 1609, 1565, 1555, 1486, 1449, 1404, 1340, 1312, 1292, 1271, 1121, 1103, 1068, 191, 1059, 1024, 1013, 942, 932, 829

MP: 129 ºC.

4-(4-bromophenyl)-2-phenyloxazole (12)

Benzimidate S12 (61 mg, 0.2 mmol) was subjected to GP3. Purification via column chromatography yielded oxazole 12 (59 mg, 98%) as a white solid.

Rf: 0.53 (5% Ethyl acetate/hexanes)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.14 – 8.09$ (m, 2H), 7.97 (s, 1H), 7.73 – 7.68 (m, 2H), 7.59 – 7.53 (m, 2H), 7.52 – 7.45 (m, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 162.26, 141.25, 133.72, 132.03, 130.69, 130.28, 128.94, 127.47, 127.34, 126.69, 122.08.$

HRMS (ESI-TOF) $m/z$: calc'd for C$_{15}$H$_{11}$BrNO$_3$ $[M+H]^+$ 300.0019, found 300.0022.

IR (film) (cm$^{-1}$): 3369, 3181, 3055, 2952, 2853, 1726, 1659, 1606, 1589, 1577

MP: 137 – 138 ºC.
4-(4-iodophenyl)-2-phenyloxazole (13)

Benzimidate S13 (70 mg, 0.2 mmol) was subjected to GP3. Purification via column chromatography yielded oxazole 13 (64 mg, 93%) as a white solid.

Rf: 0.45 (10% Ethyl acetate in hexanes)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.12 – 8.10 (m, 2H), 7.98 (s, 1H), 7.78 – 7.75 (m, 2H), 7.59 – 7.56 (m, 2H), 7.50 – 7.46 (m, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 162.1, 141.2, 137.8, 133.7, 130.7, 128.8, 127.4, 127.3, 126.6, 93.4.

HRMS (ESI-TOF) m/z: calc'd for C$_{15}$H$_{11}$INO $^+ \text{[M+H]}^+$ 347.9880, found 347.9869.

IR (film) (cm$^{-1}$): 2360, 2342, 1157, 1473, 1447, 1396, 1338, 1267, 1120, 1100, 1063, 1022, 1005, 940, 932.

MP: 156 °C.

2-phenyl-4-(4-(trifluoromethyl)phenyl)oxazole (14)

Benzimidate S14 (59 mg, 0.2 mmol) was subjected to GP3. Purification via column chromatography yielded oxazole 14 (49 mg, 84%) as a white solid.

Rf: 0.43 (5% Ethyl acetate/hexanes)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.16 – 8.10 (m, 2H), 8.05 (s, 1H), 7.98 – 7.92 (d, $J = 8.0$ Hz, 2H), 7.66-7.72 (d, $J = 8.3$ Hz, 2H), 7.53 – 7.47 (m, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 162.5, 141.0, 134.8, 134.6, 130.8, 130.1 (q, $^2J_{CF} = 32.4$ Hz), 129.0, 127.4, 126.7, 125.9, 125.9 (q, $^3J_{CF} = 3.8$ Hz), 124.3 (q, $^1J_{CF} = 272.0$ Hz).

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ = –12.56.

HRMS (ESI-TOF) m/z: calc'd for C$_{16}$H$_{11}$F$_3$NO $^+ \text{[M+H]}^+$ 290.0787, found 290.0789.

IR (film) (cm$^{-1}$): 2359, 2342, 1620, 1558, 1450, 1415, 1335, 1166, 1156, 1110, 1076, 1065, 943, 930.

MP: 145 – 146 °C.
2-phenyl-4-(4-(trifluoromethoxy)phenyl)oxazole (15)

Benzimidate S15 (62 mg, 0.2 mmol) was subjected to GP3. Purification via column chromatography yielded oxazole 15 (57 mg, 94%) as a white solid.

Rf: 0.53 (5% Ethyl acetate/hexanes)
1H NMR (400 MHz, CDCl3): δ = 8.15 – 8.10 (m, 2H), 7.97 (s, 1H), 7.89 – 7.83 (m, 2H), 7.51 – 7.46 (m, 3H), 7.32 – 7.27 (m, 2H).
13C NMR (150 MHz, CDCl3): δ = 162.3, 149.1, 141.0, 133.7, 130.7, 130.1, 129.0, 127.5, 127.2, 126.7, 121.4, 120.7 (q, 1JCF = 257.4 Hz).
19F NMR (376 MHz, CDCl3): δ = –57.8.
HRMS (ESI-TOF) m/z: calc’d for C16H11F3NO2 [M+H]+ 306.0736, found 306.0737.
IR (film) cm⁻¹: 3054, 2983, 2928, 2111, 2029, 2008, 1963, 1574, 1499, 1450
MP: 96 °C.

2-phenynaphtho[1,2-d]oxazole (16)

Benzimidate S16 (50 mg, 0.2 mmol) was subjected to GP3, with the following modifications: additional CsI (208 mg, 0.8 mmol), Phl(OAc)2 (258 mg, 0.8 mmol), and PhMe (3 mL). Purification via column chromatography yielded oxazole 16 (37 mg, 75%) as an off-white solid.

Rf: 0.35 (5% Ethyl acetate/hexanes)
1H NMR (400 MHz, CDCl3): δ = 8.62 (d, J = 8.2 Hz, 1H), 8.35 (m, 2H), 7.97 (d, J = 8.2 Hz, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.70 – 7.67 (m, 1H), 7.57 – 7.51 (m, 4H).
13C NMR (100 MHz, CDCl3): δ = 162.4, 148.2, 137.8, 131.4, 131.2, 129.0, 128.7, 127.7, 127.5, 127.1, 126.1, 125.5, 122.4, 110.9
HRMS (ESI-TOF) m/z: calc’d for C17H12NO [M+H]+ 264.0913, found 264.0917.
IR (film) cm⁻¹: 3068, 2924, 1639, 1551.
M.P 133 – 134 °C.

2-(4-methoxyphenyl)-4-phenyloxazole (17)

Benzimidate S17 (51 mg, 0.2 mmol) was subjected to GP3. Purification via column chromatography yielded oxazole 17 (38 mg, 76%) as a white solid.
**Rt:** 0.50 (20% Ethyl acetate/hexanes)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.08 – 8.04\) (m, 2H), 7.92 (s, 1H), 7.83 – 7.80 (m, 2H), 7.45 – 7.41 (m, 2H), 7.35 – 7.31 (m, 1H), 7.01 – 6.98 (m, 2H), 3.88 (s, 3H).

\(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 162.1, 161.5, 141.9, 133.0, 131.4, 128.8, 128.3, 128.1, 125.7, 120.5, 114.3, 55.5\).

HRMS (ESI-TOF) m/z: calc'd for C\(_{16}\)H\(_{14}\)NO\(_2\)\(^+\) [M+H]\(^+\) expected 252.1025, found 252.1019.

IR (film) cm\(^{-1}\): 3042, 2969, 2920, 2843, 1613, 1592.

MP: 95 – 96 °C.

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2-(4-bromophenyl)-4-phenyloxazole (18)

Benzimidate S\(_{18}\) (61 mg, 0.2 mmol) was subjected to GP3. Purification via column chromatography yielded oxazole 18 (55 mg, 92%) as a white solid.

**Rt:** 0.65 (20% Ethyl acetate/hexanes)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.01 – 7.97\) (m, 3H), 7.82 – 7.80 (m, 2H), 7.64 – 7.60 (m, 2H), 7.46 – 7.41 (m, 2H), 7.37 – 7.32 (m, 1H).

\(^13\)C NMR (150 MHz, CDCl\(_3\)): \(\delta 161.2, 142.4, 133.8, 132.2, 131.1, 128.9, 128.4, 128.1, 126.6, 125.8, 125.0\).

HRMS (ESI-TOF) m/z: calc'd for C\(_{15}\)H\(_{11}\)BrNO\(^+\) [M+H]\(^+\) expected 300.0024, found 299.9998.

IR (film) cm\(^{-1}\): 3120, 3078, 3058, 3026, 2981, 1600, 1551.

MP: 143 – 145 °C.

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4-phenyl-2-(4-(trifluoromethyl)phenyl)oxazole (19)

Benzimidate S\(_{19}\) (59 mg, 0.2 mmol) was subjected to GP3. Purification via column chromatography yielded oxazole 19 (45 mg, 77%) as a white solid.

**Rt:** 0.40 (20% Ethyl acetate/hexanes)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.25 – 8.23\) (m, 2H), 8.02 (s, 1H), 7.84 – 7.82 (m, 2H), 7.76 – 7.73 (m, 2H), 7.47 – 7.43 (m, 2H), 7.38 – 7.34 (m, 1H).

\(^13\)C NMR (150 MHz, CDCl\(_3\)): \(\delta 160.7, 142.7, 134.3, 132.2 (\delta J = 32.0 Hz), 130.9, 130.8, 129.0, 128.6, 126.9, 126.0, 125.6, 125.6 (\delta J = 32.0 Hz), 123.1\).

HRMS (ESI-TOF) m/z: calc'd for C\(_{16}\)H\(_{11}\)F\(_3\)NO\(^+\) [M+H]\(^+\) expected 290.0793, found 290.0822.

IR (film) cm\(^{-1}\): 2981, 2923, 2890, 1659, 1620, 1587, 1563.

MP: 143 – 144 °C.
2-(3-chlorophenyl)-4-phenyloxazole (20)

Benzimidate S20 (52 mg, 0.2 mmol) was subjected to GP3. Purification via column chromatography yielded oxazole 20 (59 mg, 89%) as a low-melting yellow solid.

Rf: 0.69 (20% Ethyl acetate/hexanes)
1H NMR (400 MHz, CDCl3): δ = 8.13 – 8.12 (m, 1H), 8.02 – 7.99 (m, 1H), 7.98 (s, 1H), 7.83 – 7.81 (m, 2H), 7.46 – 7.42 (m, 4H), 7.37 – 7.33 (m, 1H).
13C NMR (100 MHz, CDCl3): δ = 160.7, 142.4, 135.0, 133.9, 131.0, 130.5, 130.2, 129.3, 128.9, 128.4. 126.7, 125.8, 124.7.
HRMS (ESI-TOF) m/z: calc’d for C15H11ClNO+ [M+H]+ expected 256.0529, found 256.0526.
IR (film) cm⁻¹: 3123, 3062, 2981, 2881, 1587, 1549.

2-(3-chloro-4,5-dimethoxyphenyl)-4-phenyloxazole (21)

Benzimidate S21 (64 mg, 0.2 mmol) was subjected to GP3. Purification via column chromatography yielded oxazole 21 (41 mg, 70%) as a white solid.

Rf: 0.24 (5% Ethyl acetate/hexanes)
1H NMR (400 MHz, CDCl3): δ = 7.96 (s, 1H), 7.85-7.78 (m, 2H), 7.78 – 7.73 (m, 1H), 7.62 – 7.56 (m, 1H), 7.48 – 7.40 (m, 2H), 7.38 – 7.31 (m, 1H), 3.99 (s, 3H), 3.93 (s, 3H).
13C NMR (150 MHz, CDCl3): δ = 160.8, 154.2, 147.5, 142.4, 133.8, 131.0, 129.0, 128.9, 128.4, 125.8, 123.9, 120.5, 109.1, 61.0, 56.5.
HRMS (ESI-TOF) m/z: calc’d for C17H15ClNO3+ [M+H]+ 316.0735, found 316.0735.
IR (film) cm⁻¹: 3055, 2939, 2833, 1549, 1487, 1464, 1447, 1429, 1410.
MP: 96 °C.

2-(3-bromo-4-fluorophenyl)-4-phenyloxazole (22)

Benzimidate S22 (64 mg, 0.2 mmol) was subjected to GP3. Purification via column chromatography yielded oxazole 22 (51 mg, 81%) as a white solid.

Rf: 0.65 (20% Ethyl acetate/hexanes)
$^1$H NMR (600 MHz, CDCl$_3$): $\delta = 8.34$ (dd, $J = 6.5$, 2.1 Hz, 1H), 8.04 (ddd, $J = 8.6$, 4.7, 2.1 Hz, 1H), 7.96 (s, 1H), 7.82 – 7.80 (m, 2H), 7.45 – 7.43 (m, 2H), 7.37 – 7.34 (m, 1H), 7.22 (app t, $J = 8.3$ Hz, 1H).

$^{13}$C NMR (150 MHz, CDCl$_3$): $\delta = 161.3$, 159.8 ($^1$J$_{CF} = 35$ Hz), 142.5, 133.9, 132.0, 130.9, 128.9, 128.5, 127.4 ($^2$J$_{CF} = 7.7$ Hz), 125.8, 125.3 ($^4$J$_{CF} = 4.2$ Hz), 117.1 ($^2$J$_{CF} = 23.1$ Hz), 109.9 ($^4$J$_{CF} = 21.8$ Hz).

HRMS (ESI-TOF) m/z: calc'd for C$_{15}$H$_{10}$BrFNO [$\text{M+H}^+$] expected 317.9930, found 317.9915.

IR (film) cm$^{-1}$: 3145, 3092, 3034, 2981, 1603, 1585.

MP: 101 – 102 °C.

2-(naphthalen-1-yl)-4-phenyloxazole (23)

Benzimidate S23 (55 mg, 0.2 mmol) was subjected to GP3. Purification via column chromatography yielded oxazole 23 (44 mg, 86%) as a yellow solid.

R$_f$: 0.55 (20% Ethyl acetate/hexanes)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.47 – 9.44$ (m, 1H), 8.27 (dd, $J = 7.3$, 1.2 Hz, 1H), 8.08 (s, 1H), 8.00 – 7.98 (m, 1H), 7.95 – 7.92 (m, 3H), 7.71 – 7.67 (m, 1H), 7.61 – 7.56 (m, 2H), 7.50 – 7.46 (m, 2H), 7.40 – 7.35 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 161.9$, 142.1, 134.1, 133.3, 131.42, 131.39, 130.4, 128.9, 128.7, 128.3, 128.0, 127.7, 126.5, 126.4, 125.9, 125.1, 124.1.

HRMS (ESI-TOF) m/z: calc'd for C$_{19}$H$_{14}$NO [$\text{M+H}^+$] expected 272.1075, found 272.1103.

IR (film) cm$^{-1}$: 3145, 3048, 2979, 2923, 1587, 1542.

MP: 70 – 72 °C.

2-(naphthalen-2-yl)-4-phenyloxazole (24)

Benzimidate S24 (61 mg, 0.2 mmol) was subjected to GP3. Purification via column chromatography yielded oxazole 24 (43 mg, 67%; corrected yield, contains ca. 10% inseparable iodinated oxazole) as a white solid.

R$_f$: 0.61 (20% Ethyl acetate/hexanes)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.62$ (s, 1H), 8.23 (dd, $J = 8.5$, 1.7 Hz, 1H), 8.02 (s, 1H), 7.98 – 7.94 (m, 2H), 7.89 – 7.86 (m, 3H), 7.57 – 7.54 (m, 2H), 7.48 – 7.44 (m, 2H), 7.38 – 7.34 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 162.2$, 142.4, 134.3, 133.7, 133.2, 131.3, 128.91, 128.89, 128.7, 128.3, 128.0, 127.4, 126.9, 126.6, 125.8, 125.0, 123.7.

HRMS (ESI-TOF) m/z: calc'd for C$_{19}$H$_{14}$NO [$\text{M+H}^+$] expected 272.1075, found 272.1049.

IR (film) cm$^{-1}$: 3059, 2980, 2887, 1609, 1586, 1549.
2-((1,1′-biphenyl)-4-yl)-4-phenyloxazole (25)

Benzimidate S25 (60 mg, 0.2 mmol) was subjected to GP3. Purification via column chromatography yielded oxazole 25 (40 mg, 67%) as a white solid.

Rf: 0.66 (20% Ethyl acetate/hexanes)

1H NMR (600 MHz, CDCl3): δ = 8.21 – 8.19 (m, 2H), 7.99 (s, 1H), 7.86 – 7.84 (m, 2H), 7.73 – 7.71 (m, 2H), 7.67 – 7.65 (m, 2H), 7.49 – 7.44 (m, 4H), 7.41 – 7.38 (m, 1H), 7.37 – 7.34 (m, 1H).

13C NMR (150 MHz, CDCl3): δ = 162.0, 143.2, 142.3, 140.4, 133.6, 131.3, 129.1, 128.9, 128.3, 128.0, 127.6, 127.3, 127.1, 126.5, 125.8.

HRMS (ESI-TOF) m/z: calc’d for C21H16NO [M+H]+ expected 298.1232, found 298.1247.

IR (film) cm⁻¹: 3056, 3038, 2981, 2919, 2850, 1610, 1576.

MP: 161 – 163 °C.

4-chloro-2-phenyloxazole (26)

Benzimidate hydrotriflate S26 (67 mg, 0.2 mmol) was subjected to GP3, with the following modifications: addition of NaOAc (33 mg, 0.4 mmol) to effect the freebase in situ. Analysis of the crude by 1H NMR with 1 equiv of 1,2-dichloroethane as an internal standard gave 60% yield. Purification via column chromatography yielded oxazole 26 (4.9 mg, 27%) as a white solid.

Rf: 0.40 (3% Ethyl acetate/hexanes)

1H NMR (400 MHz, CDCl3): δ = 8.05 – 7.99 (m, 2H), 7.66 (s, 1H), 7.51 – 7.44 (m, 3H).

13C NMR (100 MHz, CDCl3): δ = 134.6, 133.7, 131.2, 130.8, 129.0, 129.0, 126.8, 126.6.

HRMS (ESI-TOF) m/z: calc’d for C9H7ClNO [M+H]⁺ expected 180.0211, found 180.0224.

IR (film) cm⁻¹: 2922, 2851, 2360, 2125, 1758, 1724, 1517, 1451, 1236, 1177, 1066, 1041, 1023, 999.

2-(tert-butyl)-4-phenyloxazole (27)

Pivalimidate S27 (41 mg, 0.2 mmol) was subjected to GP3. Purification via column chromatography yielded oxazole 27 (31 mg, 77%) as a clear yellow oil.

Rf: 0.29 (5% Ethyl acetate/hexanes)

1H NMR (400 MHz, CDCl3): δ = 7.80 (s, 1H), 7.75 – 7.71 (m, 2H), 7.41 – 7.36 (m, 2H), 7.30 – 7.26 (m, 1H), 1.43 (s, 9H).

13C NMR (100 MHz, CDCl3): δ = 171.7, 140.4, 132.9, 131.7, 128.8, 127.9, 125.7, 34.0, 28.7.

HRMS (ESI-TOF) m/z: calc’d for C13H16NO [M+H]⁺ 202.1226, found 202.1238.
IR (film) cm\(^{-1}\): 3033, 2970, 1724, 1564.

4-phenyl-2-(trichloromethyl)oxazole (28)

Trichloroacetimidate S\textsuperscript{28} (53 mg, 0.2 mmol) was subjected to GP\textsuperscript{3}, with the following modifications: NaI instead of CsI as the source of iodide, and a 50:50 mixture of PhMe/CHCl\(_3\) instead of PhMe as solvent. Purification via column chromatography yielded oxazole 28 (33 mg, 63%) as a yellow solid.

Characterization data is consistent with reported literature data.\textsuperscript{3}

R\textsubscript{f}: 0.43 (10% Ethyl acetate in hexanes)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.01\) (s, 1H), 7.80 – 7.74 (m, 2H), 7.47 – 7.40 (m, 2H), 7.40 – 7.37 (m, 1H).

5-iodo-1-methyl-4-phenyl-2-(4-(trifluoromethyl)phenyl)-1H-imidazole (29)

Amidine S\textsuperscript{29} (61 mg, 0.2 mmol) was subjected to GP\textsuperscript{3}, with the following modifications: additional CsI (2 mg, 0.8 mmol) and PhI(OAc)\(_2\) (258 mg, 0.8 mmol). Purification via column chromatography yielded imidazole 29 (59 mg, 68%) as a white solid.

R\textsubscript{f}: 0.35 (10% Ethyl acetate in hexanes)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.99 – 7.92\) (m, 2H), 7.77 (q, \(J = 8.5\) Hz, 4H), 7.47 – 7.40 (m, 2H), 7.37 – 7.30 (m, 1H), 7.37 (s, 3H).

\(^13\)C NMR (150 MHz, CDCl\(_3\)): \(\delta = 149.6, 144.9, 134.3, 133.8, 131.2\) (q, \(2^J_{CF} = 32.7\) Hz), 129.4, 128.4, 127.8, 127.7, 125.8 (q, \(2^J_{CF} = 3.8\) Hz), 124.0 (q, \(1^J_{CF} = 273.5\) Hz), 72.4, 36.5.

HRMS (ESI): m/z calculated for C\textsubscript{17}H\textsubscript{13}F\textsubscript{3}IN\textsubscript{2} [M+H]\textsuperscript{+}: 429.0070, found 429.0063.

IR (film): 2981, 2361, 2342, 2160, 1977, 1616, 1528, 1481, 1459, 1444, 1378, 1325, 1165, 1120, 1106, 1073, 1013, 955, 850.

MP: 157 °C.

5-iodo-1-methyl-4-phenyl-2-(trichloromethyl)-1H-imidazole (30)

Amidine S\textsuperscript{30} (61 mg, 0.2 mmol) was subjected to GP\textsuperscript{3}, with the following modifications: additional CsI (2 mg, 0.8 mmol) and PhI(OAc)\(_2\) (258 mg, 0.8 mmol). Purification via column chromatography yielded imidazole 30 (25 mg, 32%) as an orange solid.
Rf: 0.28 (10% Ethyl acetate in hexanes)
1H NMR (400 MHz, CDCl₃): δ = 8.56 – 8.49 (m, 2H), 7.59 – 7.52 (m, 1H), 7.52 – 7.45 (m, 2H), 3.58 (s, 3H).
13C NMR (150 MHz, CDCl₃): δ = 164.5, 158.3, 145.5, 132.8, 129.9, 129.3, 129.0, 111.6, 30.1.
HRMS (ESI): The molecule was not amenable to HRMS analysis and fragmented into a number of species.
IR (film): 3315, 2922, 1709, 1619, 1572, 1522, 1488, 1448, 1426, 1373, 1328, 1310, 1258, 1168, 1071, 1029, 1008.
MP: 99 – 100 °C.

4-ethyl-2,4-diphenyl-4,5-dihydrooxazole (35)

Benzimidate 34 (19 mg, 0.08 mmol) was subjected to GP3. Analysis of the crude by 1H NMR with 1 equiv of 1,2-dichloroethane as an internal standard gave 84% yield of oxazoline 35.

Rf: 0.3 (5% Ethyl acetate/hexanes)
1H NMR (600 MHz, CDCl₃): δ = 8.07 – 8.03 (m, 2H), 7.52 – 7.32 (m, 7H), 7.21 – 7.21 (m, 1H), 4.55(d, J = 8.5 Hz, 1H), 4.41(d, J = 8.5 Hz, 1H), 2.08 – 1.92 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H).
13C NMR (100 MHz, CDCl₃): δ = 162.6, 146.8, 131.3, 128.4, 128.4, 128.3, 128.0, 126.7, 125.7, 77.8, 35.5, 8.4.
HRMS (ESI-TOF) m/z: calc’d for C₁₇H₂₀NO+ [M+H]+ 252.1383, found 252.1468.

5-methyl-2,4-diphenyloxazole (40)

The two-step protocol outlined in IX. Mechanistic Studies: Steric Effects of Benzimidates was used to obtain oxazole 40 in 58% via 1H NMR with 1,2-dichloromethane as internal standard. The crude material was worked up according to GP3. Purification via column chromatography yielded oxazole 40 as a white solid.

Rf: 0.28 (5% Ethyl acetate/hexanes)
1H NMR (400 MHz, CDCl₃): δ = 8.10 – 8.07 (m, 2H), 7.76 – 7.74 (m, 2H), 7.49 – 7.43 (m, 2H), 7.35 – 7.31 (m, 1H), 2.62 (s, 3H).
13C NMR (100 MHz, CDCl₃): δ = 159.5, 144.1, 136.1, 132.6, 130.1, 128.8, 128.7, 127.8, 127.4, 127.0, 126.3, 12.1.
HRMS (ESI-TOF) m/z: calc’d for C₁₆H₁₄NO [M+H]+ 236.1070, found 236.1065.
IR (film) cm⁻¹: 3089, 2915, 1615, 1597, 1555.
M.P 71 – 73 °C.
VII. One-Pot Optimization

Tandem Oxidation from Benzimidate Hydrotriflate Salt

In the development of a one-pot procedure, we explored the efficiency of the tandem oxidation from the benzimidate hydrotriflate salt. Benzimidate hydrotriflate salt S2 was subjected to GP3 with the addition of base described in Table S9.

Table S9. Investigation of bases for tandem oxidation

| Base       | Eq | Yield |
|------------|----|-------|
| None       | -  | 53%   |
| KOAc       | 1.1| 53%   |
| CsOAc      | 1.1| 51%   |
| NaHCO₃     | 1.1| 33%   |
| K₂HPO₄     | 1.1| 50%   |
| DBU        | 1.1| 37%   |
| Lutidine   | 1.1| 34%   |
| DTBP       | 1.1| 38%   |
| NaOAc      | 0.5| 67%   |
| NaOAc      | 1.1| 65%   |
| **NaOAc**  | 1.5| 74% (77%) |
| NaOAc      | 2.0| 71%   |

DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene, DTBP = 2,6-Di-tert-butylpyridine; quantification via ¹H NMR with 1 equiv of 1,2-dichloroethane as internal standard, parentheses denotes isolated yield.

One-pot Conversion of Alcohol to 2-Trichloromethyl Oxazole

To a 2-dram vial containing a stir bar, 2-phenylethan-1-ol (24.0 μL, 0.2 mmol), CH₂Cl₂ (1 mL), and trichloroacetonitrile (30.0 μL, 0.3 mmol) was added 1,8-diazabicyclo[5.4.0]undec-7-ene (3.0 μL, 0.02 mmol). The reaction was stirred and monitored by TLC. Upon consumption of alcohol, the crude mixture was concentrated and immediately subjected to GP3 with the following modifications: NaI instead of CsI as the iodide source, and a 50:50 mixture of PhMe/CHCl₃ instead of PhMe for solvent. After the tandem oxidation was complete, purification via column chromatography yielded oxazole 28 (32 mg, 62%) as a yellow solid.
One-pot Conversion of Alcohol to 2-Phenyl Oxazole

![Chemical Reaction](image)

2-phenylethan-1-ol (24.0 μL, 0.2 mmol) was subjected to GP1 for 24 hours. The crude was reduced under vacuum and immediately subjected to GP3 with the following modification: addition of NaOAc (33 mg, 0.4 mmol) to effect the freebase in situ. After the tandem oxidation was complete, analysis of the crude by $^1$H NMR with 1 equiv of 1,2-dichloroethane as an internal standard gave 45% yield. Purification via column chromatography yielded oxazole 3 (17.6 mg, 40%) as a white solid.

Modified Procedure 1: The crude imidate hydrotriflate salt from (i) was first filtered and residual solvent removed under vacuum. The washed salt was then subjected to GP3 with the following modification: addition of NaOAc (33 mg, 0.4 mmol) to effect the freebase in situ. After the tandem oxidation was complete, purification via column chromatography yielded oxazole 3 (27.3 mg, 62%) as a white solid.

Modified Procedure 2: The crude imidate hydrotriflate salt from (i) was first filtered and residual solvent removed under vacuum. The washed salt was then free-based according to GP1. The resulting imidate was then subjected to GP3. After the tandem oxidation was complete, purification via column chromatography yielded oxazole 3 (35 mg, 78%) as a white solid.
VIII. Post-Synthetic Functionalization

General Procedure for Derivatization of Trichloromethyl Oxazoles (GP4)

To a 2-dram vial equipped with a stir bar was added oxazole 28 (0.2 mmol, 1 equiv.), NaH₂PO₄·H₂O (0.6 mmol, 3 equiv.), amine (0.8 mmol, 4 equiv.), and MeCN (0.1 M). The reaction was stirred at 80 °C and progress was monitored by TLC. Upon completion, the reaction was quenched with water and extracted with ethyl acetate. The combined organic layers were dried over Na₂SO₄, concentrated, and then purified via column chromatography (silica gel with ethyl acetate and hexanes).

N-benzyl-4-phenyloxazole-2-carboxamide (31)

Oxazole 28 (44 mg, 0.2 mmol) and benzylamine (44 μL, 0.8 mmol) were subjected to GP4. Purification via column chromatography (silica gel, hexanes to 20% ethyl acetate/hexanes) yielded oxazole 31 (30 mg, 53%) as a white solid.

Rᵣ: 0.26 (20% Ethyl acetate in hexanes)
¹H NMR (400 MHz, CDCl₃) δ: 8.04 (s, 1H), 7.74 – 7.71 (m, 2H), 7.44 – 7.31 (m, 9H), 4.67 (d, J = 6.1 Hz, 2H).
¹³C NMR (100 MHz, CDCl₃) δ: 155.2, 142.0, 137.3, 136.1, 130.0, 129.04, 129.02, 128.9, 128.2, 128.0, 125.8, 43.8.
HRMS (ESI): m/z calculated for C₁₇H₁₄N₂O₂Na [M+Na]⁺: 301.0953, found 301.0933.
IR (neat): 3272, 3136, 3110, 3058, 3031, 2917, 1667, 1579, 1526, 1346, 1262, 1204, 1185, 938, 763, 722.
MP: 137 – 139 °C.

Morpholino(4-phenyloxazol-2-yl)methanone (32)

Oxazole 28 (44 mg, 0.2 mmol) and morpholine (68 μL, 0.8 mmol) were subjected to GP4. Purification via column chromatography (silica gel, hexanes to 20% ethyl acetate/hexanes) yielded oxazole 32 (37 mg, 71%) as a brown solid.

Rᵣ: 0.15 (20% Ethyl acetate in hexanes)
¹H NMR (400 MHz, CDCl₃) δ: 8.02 (s, 1H), 7.75 – 7.73 (m, 2H), 7.45 – 7.41 (m, 2H), 7.38 – 7.34 (m, 1H), 4.38 – 4.35 (m, 2H), 3.85 – 3.79 (m, 6H).
\[ ^{13}\text{C NMR (100 MHz, CDCl}_3 \] \( \delta \): 155.4, 154.5, 141.5, 135.0, 130.2, 129.0, 128.9, 125.8, 67.2, 66.9, 47.7, 43.4.

**HRMS (ESI):** m/z calculated for C\(_{14}\)H\(_{14}\)N\(_2\)O\(_3\)Na [M+Na]\(^+\): 281.0902, found 281.0897.

**IR (neat):** 3140, 3115, 3026, 3018, 2963, 2922, 2853, 1635, 1533, 1430, 1271, 1171, 1110, 1021, 947.

**MP:** 82 – 84 °C.

(4-phenyloxazol-2-yl)(pyrrolidin-1-yl)methanone (33)

Oxazole 28 (44 mg, 0.2 mmol) and pyrrolidine (66 \( \mu \)L, 0.8 mmol) were subjected to GP4. Purification via column chromatography (silica gel, 100% hexanes to 20% ethyl acetate/hexanes) yielded oxazole 33 (41 mg, 85%) as a yellow solid.

\( R_f \): 0.15 (20% Ethyl acetate in hexanes)

\( ^1\text{H NMR (400 MHz, CDCl}_3 \] \( \delta \): 8.01 (s, 1H), 7.78 – 7.76 (m, 2H), 7.45 – 7.41 (m, 2H), 7.37 – 7.32 (m, 1H), 4.15 (t, \( J = 6.8 \) Hz, 2H), 3.72 (t, \( J = 6.9 \) Hz, 2H), 2.08 – 2.01 (m, 2H), 1.99 – 1.92 (m, 2H).

\[ ^{13}\text{C NMR (100 MHz, CDCl}_3 \] \( \delta \): 155.6, 154.8, 141.7, 134.9, 130.5, 129.0, 128.7, 125.8, 49.3, 47.4, 26.7, 24.0.

**HRMS (ESI):** m/z calculated for C\(_{14}\)H\(_{14}\)N\(_2\)O\(_2\)Na [M+Na]\(^+\): 269.0953, found 265.0955.

**IR (neat):** 3133, 3105, 3043, 2977, 2923, 2876, 1654, 1540, 1431, 1340, 1305, 1295, 1165, 1115, 1071, 943, 819, 759, 694, 679.

**MP:** 116 – 119 °C.
IX. Mechanistic Studies

Intermediacy of Oxazoline

Oxazoline 2 (45 mg, 0.2 mmol) was subjected to GP3. Upon completion, the crude mixture was quenched, concentrated, and quantified via $^1$H NMR using 1 equiv of 1,2-dichloroethane as an internal standard.

Additionally, the appearance and disappearance of oxazoline 2 under short time points (Table S7) and quantitative yield of oxazole 3 from 2 under our normal tandem reaction conditions strongly support oxazolines as an intermediate product en route to oxazoles.

Intermediacy of Di-iodide

2,2-diiodooctyl 2,2,2-trichloroacetimidate 36 (21 mg, 0.04 mmol) was subjected to GP3, with the following modifications: NaI instead of CsI, and 1:1 PhMe/CHCl$_3$ instead of PhMe. Upon completion, the crude mixture was quenched, concentrated, and quantified via $^1$H NMR using 1 equiv of 1,2-dichloroethane as an internal standard.

Analysis by $^1$H NMR showed consumption of starting material but did not show a clear oxazole major product, and TLC confirms a complex mixture. Coupled with the absence of observed di-iodide in previous reactions, a mechanism invoking di-iodination followed by substitution and elimination to the oxazole is unlikely.

Intemolecular HAT Studies

Benzimidate 1 (45 mg, 0.2 mmol) was subjected to GP3 with the following modifications, NaI was used instead of CsI, and 2,2,2-trifluoroethyl benzimidate (16.2 mg, 0.08 mmol) was added. Upon completion, the crude mixture was quenched, concentrated, and quantified via $^1$H NMR using 1 equiv of 1,2-dichloroethane as an internal standard.

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8 Wappes, E. A.; Vanitcha, A.; Nagib, D. A. Chem. Sci., 2018, 9, 4500 – 4504.
To probe if the second HAT event was mediated by residual imidate starting material, the TFE benzimidate was added in sub-stoichiometric quantities to the reaction mixture to observe if it had an effect on the efficiency of the oxazoline to oxazole transformation. The yields obtained are comparable to reactions without additional TFE benzimidate and thus does not support the hypothesis that the second HAT event is mediated by intermolecular imidate HAT.

**Trapping of Non-aromatizable Oxazoline via HAT**

Benzimidate 34 (19 mg, 0.08 mmol) was subjected to GP3. Purification via column chromatography yielded oxazoline 35 (84% via $^1$H NMR with DCE as internal standard) as a clear oil.

This substrate afforded only oxazoline 35, with no additional functionalization at the α-oxygen position, indicating that HAT is not efficient at this position.

**Deuterated Solvent Experiments**

Oxazoline 2 (23 mg, 0.1 mmol) was subjected to GP3 with the following modifications, PhMe-d8 was used instead of PhMe. Upon completion, the crude mixture was quenched, concentrated, and quantified via $^1$H NMR using 1 equiv of 1,2-dichloroethane as an internal standard.

Oxazoline 2 (23 mg, 0.1 mmol) was subjected to GP3 with the following modifications, MeCN-d3 was used instead of PhMe. Upon completion, the crude mixture was quenched, concentrated, and quantified via $^1$H NMR using 1 equiv of 1,2-dichloroethane as an internal standard.

To explore the role of solvent as a hydrogen atom source, and therefore quenching any radical intermediates generated under our reaction conditions and suppressing the second HAT, we employed PhMe-d8 and MeCN-d3 to observe any possible deuterium trapping. No deuterium incorporation was observed in either reaction suggesting that solvent C-H bonds are not serving as a hydrogen atom source.
Benzylc Hydrogen Atom Transfer via Other Oxidants

Oxazoline 2 (23 mg, 0.1 mmol) and chloranil (49 mg, 0.2 mmol) were added to an 8 mL vial with stir bar. The vial was degassed and DCE (1 mL) was added. The reaction was then stirred for 15 h at 80 °C. The crude mixture was quenched with 1M NaOH and extracted with CH$_2$Cl$_2$, dried over MgSO$_4$ and concentrated. The reaction mixture was quantified via $^1$H NMR using 1 equiv of 1,2-dichloroethane as an internal standard.

![Reaction Scheme]

To probe whether the conversion of the intermediate oxazolines to oxazoles occurs via an intermolecular HAT, we subjected oxazoline 2 to oxidants known to perform HAT at benzylic positions. Chloranil has been shown to oxidize benzylic C-H bonds, and it performs well in the aromatization of the intermediate oxazoline.

Additionally, DDQ at 50 °C in CH$_2$Cl$_2$ was found to decompose the oxazoline.

**Steric Effects of Secondary Benzimidate**

Benzimidate 38 (48 mg, 0.2 mmol) was added to an 8 mL vial and heated at 50 °C for 3 h with Phl(OAc)$_2$ (77 mg, 0.24 mmol) in 1 mL of an I$_2$ solution (0.01 M in DMF). The solvent was removed and residue was purified by column chromatography to yield a diastereomeric mixture of syn/anti oxazoline 39 (34 mg, 72%, dr = 1.4:1, syn:anti) as a clear oil. The mixture of syn/anti oxazoline 39 (31 mg, 0.13 mmol) was subjected to GP3. The reaction crude was quantified via $^1$H NMR using 1,2-dichloroethane as an internal standard, yielding 58% oxazole 40 and 30% of anti oxazoline 39.
Figure S4. Top spectra is of the mixture of syn/anti 39 prior to subjection to GP3. Middle spectra is of the crude reaction after subjection to GP3. Bottom spectra is of independently synthesized oxazole 40.
X. Substrate Limitations

In the course of substrate exploration, the following substrates afforded oxazolines, but not oxazoles.

![Figure S5. Examples of incomplete cascade reactions](image)
Figure S6. Commercial availability of feedstock chemicals

The above data were collected from Reaxys for the indicated structural motifs on 14 Mar 2019 with the following options: As Drawn, Stereo, Additional Ring Closures, Related Markush, Salts, Charges. The results were filtered by “product for purchase” and “SigmaAldrich”.
XII. Computational Studies

Computational Methods

All calculations were performed using the Gaussian 16 (revision A.03) suite of programs. Geometry optimizations and frequency calculations were performed using the ωB97X-D functional\(^9\) with the 6-311++G(d,p) basis set\(^1\) (Def2-TZVPP for iodine),\(^12\) and the default PCM solvation model for PhMe,\(^13\) and an integration grid of "UltraFine" to help minimize uncertainty in computed free energies. All stationary points were confirmed to have no imaginary frequencies. Transition states were confirmed as first order saddle points with the presence of a single imaginary frequency, and scanned in both directions along their intrinsic reaction coordinate. Reported Gibbs free energies and enthalpies in solution include thermal corrections computed at 298.15 K and 1 atm. Visualization carried out with CYLview.\(^14\)

Oxidation Potentials

The oxidation potentials of oxazole and imidazole were calculated according to the method described in the literature\(^15\) using the B3LYP functional\(^16\) with the 6-311++g(d,p) basis set, and the CPCM solvation model for MeCN.\(^17\)

All calculated \(\Delta E^0_{1/2}\) are reported versus SCE in MeCN and are summarized in Table S10.

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\(^9\) Gaussian 16, Revision A.03, 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, G. B.; 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, J. A., Jr.; 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, Inc., Wallingford CT, 2016.

\(^10\) ωB97X-D Functional: Chai, J-D., Head-Gordon, M. Phys. Chem. Chem. Phys., 2008, 10, 6615 – 6620.

\(^11\) 6-311G Basis Set: Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. J. Chem. Phys. 1980, 72, 650 – 654.

\(^12\) Def2-TZVPP Basis Set for Iodine: (a) Weigend, F.; Ahlrichs, R. Phys. Chem. Chem. Phys., 2005, 7, 3297 – 3305; (b) Schäfer, A.; Horn, H.; Ahlrichs, R. J. Chem. Phys., 1992, 97, 2571 – 2577; (c) Schäfer, A.; Huber, C.; Ahlrichs, R. J. Chem. Phys., 1994, 100, 5829 – 5835 (d) Eichhorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, R. Theor. Chem. Acc., 1997, 97, 119 – 124; (e) Weigend, F.; Furfaro, F.; Ahlrichs, R. J. Chem. Phys. 2003, 119, 12753 – 12762; (f) Peterson, K. A.; Figgen, D.; Goll, E.; Stoll, H.; Dolg, M. J. Chem. Phys. 2003, 119, 11113 – 11123.

\(^13\) CPCM Solvation Model: Tomasi, J.; Mennucci, B.; Cammi, R. Chem. Rev., 2005, 105, 2999 – 3094.

\(^14\) CYLview: C. Y. Legault, CYLview, 1.0b. (Université de Sherbrooke, 2009); www.cylview.org.

\(^15\) Calculation of Electrochemical Potentials: Roth, H. G.; Romero, N. A.; Nicewicz, D. A. Synlett. 2016, 27, 714 – 723.

\(^16\) (a) Vosko, S. H.; Wilk, L.; Nusair, M. Can. J. Phys. 1980, 58, 1200 – 1211; (b) Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. B, 1988, 37, 785 – 789 (c) Becke, A. D. J. Chem. Phys. 1993, 98, 5648 – 5652; (d) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. J. Phys. Chem. 1994, 98, 11623 – 11627.

\(^17\) CPCM Solvation Model: (a) Klamt, A.; Schüürmann, G. J. Chem. Soc., Perkin Trans. 2, 1993, 0, 799 – 805 (b) Barone, V.; Cossi, M. J. Phys. Chem. A, 1998, 102, 1995 – 2001.
Notes: EE = sum of electronic energies, conversion factor: 1 hartree = 627.509 kcal/mol = 27.2114 eV

Table S10. Oxidation potentials of oxazole and imidazole

| Structure | $\Delta G^\circ_{\text{Neutral}}$ (hartree) | $\Delta G^\circ_{\text{Oxidized}}$ (hartree) | $\Delta G^\circ_{1/2}$ (kcal/mol) | $\Delta E^\circ_{1/2}$ Calc. (V) | HOMO (hartree) | HOMO (eV) | LUMO (hartree) | LUMO (eV) |
|-----------|------------------------------------------|------------------------------------------|---------------------------------|------------------------------|----------------|------------|----------------|------------|
| Oxazole   | -246.114858                              | -245.855263                             | -162.8981989                   |                              |                |            |                |            |
| Imidazole | -226.249238                              | -226.013029                             | -148.2237234                   |                              |                |            |                |            |

Reaction Modeling

Activation energies ($\Delta G^\dagger$) were calculated as the difference in free energies between the optimized transition state and its preceding ground state. Reaction energies ($\Delta G^\circ$) were calculated as the difference between the free energies of the product(s) and reactant(s). In the case of the bimolecular 2nd HAT reactions, the products and reactants were treated separately to properly account for entropy. These are summarized in Table S11 and all relevant energies for these calculations are contained in Table S12.

Table S11. Activation ($\Delta G^\dagger$) and Reaction ($\Delta G^\circ$) Energies for Hydrogen Atom Transfers (in kcal/mol)

| Reaction      | Scheme | $\Delta G^\dagger$ | $\Delta G^\circ$ |
|---------------|--------|--------------------|------------------|
| 1,4 HAT       | ![Scheme](image1) | 19.4               | 0.1              |
| 1,5 HAT       | ![Scheme](image2) | 14.3               | -6.2             |
| 2nd HAT (+OAc)| ![Scheme](image3) | 8.3                | -33.9            |
| 2nd HAT (+Me) | ![Scheme](image4) | 11.9               | -30.0            |
| 2nd HAT (+I)  | ![Scheme](image5) | 6.0                | -5.0             |
| 2\textsuperscript{nd} HAT (+lm) | ![Chemical Structure] | ![Chemical Structure] | ![Chemical Structure] | 15.9 | -22.0 |
|--------------------------------|----------------------|----------------------|----------------------|------|-------|
| 2\textsuperscript{nd} HAT at C-5 | ![Chemical Structure] | ![Chemical Structure] | ![Chemical Structure] | 12.4 | -12.3 |
### Table S12. Computed Free Energies of Reaction Intermediates and Transition States

| Entry                | Species | $\Delta G^\circ$ (hartree) | $\Delta G^\circ$ (kcal/mol) |
|----------------------|---------|----------------------------|----------------------------|
| Intermediate I       | ![Structure](image1) | -710.322025                | -445733.4636               |
| Intermediate II      | ![Structure](image2) | -1007.490338              | -632209.2545               |
| Intermediate III     | ![Structure](image3) | -709.670713                | -455324.7594               |
| Transition State IV-TS(1,5) | ![Structure](image4) | -709.647874                | -44531.4278                |
| Intermediate IV      | ![Structure](image5) | -709.680539                | -445330.9253               |
| Intermediate V       | ![Structure](image6) | -1007.518019              | -632226.6246               |
| Intermediate VI      | ![Structure](image7) | -709.131391                | -444986.3300               |
| Transition State VII-TS(OAc) | ![Structure](image8) | -937.502842                | -588291.4709               |
| Intermediate VII     | ![Structure](image9) | -708.514596                | -444599.2856               |
| Intermediate VIII    | ![Structure](image10) | -1006.329815              | -631481.0159               |
| Intermediate IX      | ![Structure](image11) | -707.945636                | -444242.2581               |

#### Intermediates and Transition States for Alternate Pathways

| Entry                | Species | $\Delta G^\circ$ (hartree) | $\Delta G^\circ$ (kcal/mol) |
|----------------------|---------|----------------------------|----------------------------|
| Transition State IV-TS(1,4) | ![Structure](image12) | -709.639839                | -445305.3857               |
| Intermediate IV(1,4) | ![Structure](image13) | -709.670556                | -445324.6609               |
| Transition State VII-TS(Me) | ![Structure](image14) | -748.93616                 | -469964.1808               |
Bond dissociation free energies were calculated as the difference in free energies between the sum of radical products resulting from hemolytic cleavage of the indicated bond and the non-cleaved starting material. Multiple combinations of common functionals and solvent models were used to provide a range of bond dissociation free energies (Table S13).

| Transition State VII-TS(I) | -1006.899787 | -631838.6784 |
|---------------------------|--------------|--------------|
| Transition State VII-TS(Im) | -1148.533376 | -720715.0302 |
| Transition State VII-TS(α-O) | -937.496431 | -588287.4479 |
| Intermediate VII(α-O) | -708.480227 | -444577.7188 |

Table S13. Computed Bond Dissociation Free Energies

| Functional | Solvent     | BDFE (kcal/mol) | BDFE (kcal/mol) | BDFE (kcal/mol) | BDFE (kcal/mol) |
|------------|-------------|-----------------|-----------------|-----------------|-----------------|
| B3LYP      | PCM-PhMe    | 60.3            | 94.8            | 17.7            | 85.1            |
| ωB97X-D    | PCM-PhMe    | 64.8            | 98.7            | 23.0            | 86.8            |
| M06-2x     | SMD-PhMe    | 65.4            | 103.8           | 28.3            | 88.8            |

Global and Local Radical Philicities

The global and local radical electrophilicities were calculated according to the method described in the literature.  

Geometries for each of the radical species were first optimized using the ωB97X-D functional, 6-311++g(d,p) basis set, and the PCM solvation model for PhMe. From these optimized geometries, electronic energies were then determined at N, N+1, and N-1 electron counts without additional geometry optimization, which are summarized in Table S15. The global and local radical electrophilicities, along with the electronic properties from which they are derived, are summarized in Table S14.

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18 Calculation of Radical Philicities: De Vleeschouwer, F.; Van Speybroeck, V.; Waroquier, M.; Geerlings, P.; De Proft, F. *Org. Lett.* 2007, 9, 2721 – 2724.
Table S14. Computed global and local electrophilicities; electron densities $\rho$ refer to highlighted atom; **key:** $I$ = Ionization Energy, $EA$ = Electron Affinity, $\chi$ = Electronegativity, $\mu$ = Electronic Chemical Potential, $\eta$ = Chemical Hardness, $\omega$ = Global Electrophilicity, $\rho_{N+1}$ = Electron Population of N+1 Electron Species, $\rho_N$ = Electron Population of N-Electron Species, $f^*$ = Fukui Index, $\omega_{rc}^*$ = Local Electrophilicity

| Radical | $I$ (eV) | $EA$ (eV) | $\chi$ (eV) | $\mu$ (eV) | $\eta$ (eV) | $\omega$ (eV) | $\rho_{N+1}$ | $\rho_N$ | $f^*$ | $\omega_{rc}^*$ (eV) |
|---------|----------|-----------|-------------|------------|-------------|---------------|--------------|---------|------|------------------|
| $\cdot$ | 10.30 | 4.71 | 7.51 | -7.51 | 5.59 | **5.04** | 54 | 53 | 1 | **5.04** |
| $\cdot$ | 8.86 | 2.49 | 5.67 | -5.67 | 6.37 | **2.53** | 7.914 | 7.306 | 0.608 | **1.54** |
| $\cdot$ | 11.24 | 4.15 | 7.70 | -7.70 | 7.09 | **4.18** | 8.836 | 8.402 | 0.434 | **1.81** |
| $\cdot$ | 7.91 | 1.53 | 4.72 | -4.72 | 6.38 | **1.75** | 7.471 | 6.477 | 0.994 | **1.73** |
| $\cdot$ | 5.05 | 1.96 | 3.51 | -3.51 | 3.09 | **1.99** | 6.044 | 5.807 | 0.237 | **0.47** |

Table S15. Calculated electronic energies of N, N+1, and N-1 electron count species from previously optimized molecular geometries

| Radical | N Electrons | N+1 Electrons | N-1 Electrons |
|---------|-------------|---------------|---------------|
| $\cdot$ | -297.760405 | -297.933519 | -297.381876 |
| $\cdot$ | -439.535245 | -439.626818 | -439.209753 |
| $\cdot$ | -228.404778 | -228.557343 | -227.991619 |
| $\cdot$ | -39.835237 | -39.891477 | -39.544668 |
| $\cdot$ | -708.957361 | -709.003249 | -708.738938 |
Optimized Cartesian Coordinates

Note: Oxazole (N electrons), Oxazole (N-1 electrons), Imidazole (N electrons), and Imidazole (N-1 electrons) molecular geometries were all optimized at the B3LYP/6-311++g(d,p)/CPCM(MeCN) level of theory. All other molecular geometries optimized at the ωB97X-D/6-311++g(d,p)/Def2-TZVPP (for I and Cs)/CPCM(PhMe) level of theory, except for PhI(OAc)$_2$, PhI, CsOAc, and CsI which were calculated in the gas phase.

Oxazole (N electrons)

| Total EE (hartree) | -246.146950 |
|--------------------|-------------|
| EE + Zero-Point Energy Correction (hartree) | -246.088689 |
| EE + Thermal Enthalpy Correction (hartree) | -246.084189 |
| EE + Thermal Free Energy Correction (hartree) | -246.114858 |

| Cartesian Coordinates |
|-----------------------|
| C | 1.10535000 | 0.05493300 | 0.00000000 |
| C | -0.91874300 | 0.70670400 | -0.00000100 |
| C | -0.93600700 | -0.64514800 | 0.00000100 |
| O | 0.36574700 | -1.07915300 | 0.00000100 |
| H | 2.17743100 | -0.05921500 | 0.00000000 |
| H | -1.74846900 | 1.39439600 | 0.00000000 |
| H | -1.70227200 | -1.39997300 | -0.00000050 |
| N | 0.40624800 | 1.14272600 | 0.00000000 |

Oxazole (N-1 electrons)

| Total EE (hartree) | -245.885348 |
|--------------------|-------------|
| EE + Zero-Point Energy Correction (hartree) | -245.828347 |
| EE + Thermal Enthalpy Correction (hartree) | -245.823674 |
| EE + Thermal Free Energy Correction (hartree) | -245.855263 |

| Imaginary Frequencies (cm$^{-1}$) |
|-----------------------------------|
| 0 |

| $\langle S^2 \rangle$ |
|-----------------------|
| 0.7501 |

| Cartesian Coordinates |
|-----------------------|
| C | 1.08999800 | 0.15561600 | 0.00000000 |
| C | -0.95469400 | 0.66680400 | 0.00000000 |
| C | -0.84021900 | -0.76710000 | 0.00000000 |
| O | 0.44549800 | -1.05895800 | 0.00000000 |
| H | 2.16974100 | 0.13769800 | -0.00000100 |
| H | -1.86412400 | 1.24924300 | 0.00000000 |
| H | -1.56159500 | -1.57133000 | -0.00000010 |
| N | 0.27449700 | 1.18916100 | 0.00000000 |
### Imidazole (N electrons)

| Total EE (hartree)          | -226.294102 |
|----------------------------|-------------|
| EE + Zero-Point Energy Correction (hartree) | -226.222991 |
| EE + Thermal Enthalpy Correction (hartree)   | -226.218329 |
| EE + Thermal Free Energy Correction (hartree) | -226.249238 |
| Imaginary Frequencies (cm\(^{-1}\)) | 0           |
| Cartesian Coordinates       |             |
| C                          | 0.99430800  -0.53387200  0.00000000 |
| C                          | -1.14006400 0.28537000   0.00000000 |
| C                          | -0.61370400 0.98075400   0.00000000 |
| H                          | 1.99355000  -0.94094600  0.00000000 |
| H                          | -2.18035700 0.57161000   0.00000200 |
| H                          | -1.06697300 1.95751900  -0.00002000 |
| N                          | -0.12864200 -1.22601400  0.00000000 |
| N                          | 0.75186800  0.80462200   0.00000000 |
| H                          | 1.44796200  1.53570300   0.00000100 |

### Imidazole (N-1 electrons)

| Total EE (hartree)          | -226.056427 |
|----------------------------|-------------|
| EE + Zero-Point Energy Correction (hartree) | -225.986070 |
| EE + Thermal Enthalpy Correction (hartree)   | -225.982261 |
| EE + Thermal Free Energy Correction (hartree) | -226.013029 |
| Imaginary Frequencies (cm\(^{-1}\)) | 0           |
| <S\(^2\)>                  | 0.7501      |
| Cartesian Coordinates       |             |
| C                          | 0.29413900  -1.07980000  0.00000000 |
| C                          | -1.02436700 0.58785200   0.00000000 |
| C                          | 0.33486700  1.11034000   0.00000000 |
| H                          | 0.68751000  -2.08531000  0.00000000 |
| H                          | -1.93214400 1.17268500   0.00000000 |
| H                          | 0.70627800  2.12358500   0.00000000 |
| N                          | -1.00152600 -0.73922100  0.00000000 |
| N                          | 1.11323000  0.03292600   0.00000000 |
| H                          | 2.12859400  0.02275200  -0.00000100 |
**Intermediate I**

![Chemical Structure Image]

| Description                                                                 | Value               |
|-----------------------------------------------------------------------------|---------------------|
| Total EE (hartree)                                                          | -710.544074         |
| EE + Zero-Point Energy Correction (hartree)                                 | -710.276987         |
| EE + Thermal Enthalpy Correction (hartree)                                  | -710.261489         |
| EE + Thermal Free Energy Correction (hartree)                               | -710.322025         |
| Imaginary Frequencies (cm$^{-1}$)                                          | 0                   |
| Cartesian Coordinates                                                       |                     |
| C 1                           | 1.59941400 0.87674900 0.02713600 |
| N 1                           | -1.44212200 2.13625900 0.05752200 |
| H 1                           | -0.46690700 2.41897100 0.06519600 |
| O 1                           | -0.63434200 -0.06775300 0.00735200 |
| C 2                           | 0.72624800 0.34735400 0.01707800 |
| H 2                           | 0.93134400 0.97269100 -0.85986800 |
| H 3                           | 0.93116300 0.92676000 -0.85986800 |
| C 3                           | 1.59303000 -0.90262900 0.86025400 |
| H 4                           | 1.35385400 -1.51818900 0.86025400 |
| H 5                           | 1.35385400 -1.51818900 0.86025400 |
| C 6                           | -2.95886100 0.26753900 0.00852000 |
| C 7                           | -4.07805800 1.10108800 -0.02350000 |
| C 8                           | -3.13437900 -1.11620500 0.02310600 |
| C 9                           | -5.35410100 0.55733900 -0.04002600 |
| H 10                          | -3.92920800 2.17372700 -0.03589500 |
| C 11                          | -4.41448300 -1.65795100 0.00772400 |
| H 12                          | -2.26939800 -1.76617400 0.04724100 |
| C 13                          | -5.52577800 -0.82406400 -0.02396800 |
| H 14                          | -6.21787100 1.21199000 -0.06560400 |
| H 15                          | -4.54239700 -2.73445900 0.02033900 |
| H 16                          | -6.52365500 -1.24821200 -0.03650000 |
| C 17                          | 3.05602800 -0.53339400 -0.01033000 |
| C 18                          | 3.74371700 -0.35263000 1.18974400 |
| C 19                          | 3.73583100 -0.31976600 -1.20947200 |
| C 20                          | 5.07987200 0.03141100 1.19296600 |
| H 21                          | 3.22841200 -0.51940000 2.13097300 |
| C 22                          | 5.07198900 0.06434200 -1.21098300 |
| H 23                          | 3.21424500 -0.46069200 -2.15146000 |
| C 24                          | 5.74769900 0.24150400 -0.00858500 |
| H 25                          | 5.60081300 0.16335500 2.13478500 |
| H 26                          | 5.58670100 0.22205100 -2.15227200 |
| H 27                          | 6.79038700 0.53842500 -0.00794900 |
Intermediate II

| Total EE (hartree)                  | -1007.697171 |
|-------------------------------------|--------------|
| EE + Zero-Point Energy Correction   | -1007.441082 |
| (hartree)                           |              |
| EE + Thermal Enthalpy Correction    | -1007.423996 |
| (hartree)                           |              |
| EE + Thermal Free Energy Correction | -1007.490338 |
| (hartree)                           |              |
| Imaginary Frequencies (cm\(^{-1}\))| 0            |

Cartesian Coordinates

|   |       |       |            |
|---|-------|-------|------------|
| C | 1.37743000 | -0.36656300 | 0.27645400 |
| N | 2.13575300 | 0.40860600  | -0.38997700|
| O | 0.49875300 | 0.01899400  | 1.23626100 |
| C | -0.81509500| 0.40433000  | 0.78984100 |
| H | -1.21701400| 1.01298000  | -0.38997700|
| H | -0.72995600| 1.03778300  | -0.09869500|
| C | -1.72288500| -0.79060400 | 0.51002300 |
| H | -1.29307500| -1.40430000 | -0.28592200|
| H | -1.78301100| -1.41304900 | 1.40663500 |
| C | 1.50148500 | -1.83603600 | 0.06736000 |
| C | 2.09416500 | -2.39963300 | -1.09282700|
| C | 1.03192600 | -2.71853600 | 1.04058400 |
| C | 2.20532200 | -3.70965700 | -1.27768200|
| H | 2.45849900 | -1.64885200 | -1.84305200|
| C | 1.15475800 | -4.08986900 | 0.85562600 |
| H | 0.57784500 | -2.32623600 | 1.94157900 |
| C | 1.73756300 | -4.58772800 | -0.30375800|
| H | 2.65790600 | -4.09481300 | -2.18421900|
| H | 0.79398400 | -4.76975600 | 1.61888200 |
| H | 1.82748300 | -5.65825600 | -0.44986200|
| C | -3.09478800| -0.30880600 | 0.10884500 |
| C | -3.39312000| -0.04885100 | -1.22879600|
| C | -4.07395000| -0.06543400 | 1.07208300 |
| C | -4.64160700| 0.43930900  | -1.59698000|
| H | -2.64142000| -0.23590900 | -1.98983400|
| C | -5.32393200| 0.42223200  | 0.70822700 |
| H | -3.85654800| -0.26516000 | 2.11712000 |
| C | -5.61085400| 0.67650900  | -0.62846500|
| H | -4.85848300| 0.63173600  | 2.64185000 |
| H | -6.07546400| 0.60112700  | 1.46918600 |
| H | -6.58591600| 1.05460700  | -0.91426600|
| I | 2.02313900 | 2.41475700  | -0.05112200|
Intermediate III

![Chemical Structure](image)

| Description                                              | Value             |
|-----------------------------------------------------------|-------------------|
| Total EE (hartree)                                        | -709.877971       |
| EE + Zero-Point Energy Correction (hartree)               | -709.624149       |
| EE + Thermal Enthalpy Correction (hartree)                | -709.608567       |
| EE + Thermal Free Energy Correction (hartree)             | -709.670713       |
| Imaginary Frequencies (cm⁻¹)                             | 0                |
| <S²>                                                     | 0.7501           |

**Cartesian Coordinates**

|        |        |        |        |
|--------|--------|--------|--------|
| C      | -1.58825000 | 0.79078200 | 0.18730100 |
| N      | -1.32717300 | 1.98030200 | 0.53164600 |
| O      | -0.64012300 | -0.12099500 | -0.08856800 |
| C      | 0.72042900  | 0.31060400 | 0.05365400  |
| H      | 0.90543300  | 1.15116700 | -0.62275200 |
| H      | 0.88537700  | 0.65243300 | 1.08038300  |
| H      | 1.61103000  | -0.87333300 | -0.28344400 |
| C      | 1.37135900  | -1.70041800 | 0.39033500  |
| H      | 1.39185500  | -1.20366200 | -1.30227800 |
| C      | -2.97782500 | 0.27160300 | 0.06621100  |
| C      | -4.05096900 | 1.16284600 | 0.02107500  |
| C      | -3.21072100 | -1.10157100 | 0.00896200  |
| C      | -5.34799900 | 0.68030600 | -0.07564200 |
| H      | -3.86458900 | 2.22994000 | 0.05590200  |
| C      | -4.51221200 | -1.57870100 | -0.08802500 |
| H      | -2.37510800 | -1.78909400 | 0.04069200  |
| C      | -5.58090600 | -0.69082100 | -0.12967800 |
| H      | -6.17889200 | 1.37523200 | -0.11311300 |
| H      | -4.69045200 | -2.64702200 | -0.13119400 |
| C      | -6.59519800 | -1.06584400 | -0.20685300 |
| C      | 3.06691100  | -0.49719700 | -0.15511800 |
| C      | 3.72911700  | -0.62445000 | 1.06587300  |
| C      | 3.76500400  | 0.02642400 | -1.24311100 |
| C      | 5.05864100  | -0.24036800 | 1.19739700  |
| H      | 3.19885500  | -1.03259800 | 1.92111900  |
| C      | 5.09467400  | 0.41191900 | -1.11612500 |
| H      | 3.26297200  | 0.12910100 | -2.20047000 |
| C      | 5.74530900  | 0.27950800 | 0.10562800  |
| H      | 5.55952200  | -0.34975500 | 2.15289700  |
| H      | 5.62380100  | 0.81357700 | -1.97318300 |
| H      | 6.78287400  | 0.57747900 | 0.20578600  |
Transition State IV-TS(1,5)

Total EE (hartree) | -709.853471
EE + Zero-Point Energy Correction (hartree) | -709.604410
EE + Thermal Enthalpy Correction (hartree) | -709.589756
EE + Thermal Free Energy Correction (hartree) | -709.647874
Imaginary Frequencies (cm⁻¹) | 1, -1695.14

<\text{S}^2> | 0.7503

Cartesian Coordinates

| C     | -1.23359400 | -0.06225500 | -0.15321000 |
| N     | -0.51019200 | -1.10269000 | -0.09668000 |
| O     | -0.77673700 | 1.20318000  | -0.39243000 |
| C     | 0.62338300  | 1.40644700  | -0.12792200 |
| H     | 0.83408700  | 2.38792500  | -0.55653100 |
| H     | 0.79972600  | 1.44996000  | 0.95105600  |
| C     | 1.44114600  | 0.31260800  | -0.77149600 |
| H     | 0.69651200  | -0.66205700 | -0.43347700 |
| H     | 1.36834600  | 0.32736000  | -1.86029100 |
| C     | -2.71673200 | -0.11713300 | -0.02745600 |
| C     | -3.37116300 | -1.34558800 | -0.13379600 |
| C     | -3.45552600 | 1.04256500  | 0.20439300  |
| C     | -4.75060300 | -1.41148300 | -0.00422900 |
| H     | -2.79005500 | -2.24090100 | -0.31972500 |
| C     | -4.83752000 | 0.97141000  | 0.33342000  |
| H     | -2.94613300 | 1.99431100  | 0.30916000  |
| H     | -5.48660300 | -0.25324800 | 0.22980800  |
| H     | -5.25402400 | -2.36762000 | -0.08947900 |
| H     | -5.40740000 | 1.87544600  | 0.51598000  |
| H     | -6.56496700 | -0.30642400 | 0.32944800  |
| C     | 2.81797900  | 0.07914900  | -0.28364100 |
| C     | 3.11675300  | 0.01420300  | 1.08383600  |
| C     | 3.85759100  | -0.12484200 | -1.19871400 |
| C     | 4.41270600  | -0.22864800 | 1.51712500  |
| H     | 2.32719800  | 0.13298200  | 1.81786900  |
| C     | 5.15426700  | -0.36724600 | -0.76594000 |
| H     | 3.64390000  | -0.08700500 | -2.26205400 |
| C     | 5.43809700  | -0.41720000 | 0.59541900  |
| H     | 4.62231900  | -0.27847900 | 2.57979800  |
| H     | 5.94510700  | -0.51705600 | -1.49163400 |
| H     | 6.44953100  | -0.60744200 | 0.93952100  |
Intermediate IV

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

| Total EE (hartree)                  | -709.888354 |
|-------------------------------------|-------------|
| EE + Zero-Point Energy Correction   | -709.635504 |
| EE + Thermal Enthalpy Correction    | -709.620023 |
| EE + Thermal Free Energy Correction | -709.680539 |
| Imaginary Frequencies (cm\(^{-1}\)) | 0           |
| <S\(^2\)>                           | 0.7512      |

Cartesian Coordinates

|       |          |          |          |
|-------|----------|----------|----------|
|       | C        | O        | C        |
| C     | -1.67952200 | -0.96649600 | 0.03037400 |
| O     | -0.63277200 | -0.11215900 | 0.05898500 |
| C     | 0.68211400 | -0.64847800 | 0.07800900 |
| H     | 0.80746400 | -1.29039200 | 0.96374300 |
| H     | 0.83764100 | -1.27682800 | -0.81157900 |
| C     | 1.63829200 | 0.49084000  | 0.10418900 |
| H     | 1.21187300 | 1.48376000  | 0.19131200 |
| C     | -2.97599000 | -0.23390400 | -0.00053000 |
| C     | -4.16826500 | -0.95942500 | 0.01906100 |
| C     | -3.02129000 | 1.15939000  | -0.05019600 |
| C     | -5.38803400 | -0.29958800 | -0.01049300 |
| H     | -4.12093500 | -2.04059500 | 0.05715800 |
| C     | -4.24524300 | 1.81745700  | -0.08096000 |
| H     | -2.09945800 | 1.72603400  | -0.06592400 |
| C     | -5.42973100 | 1.09093600  | -0.06078000 |
| H     | -6.30932200 | -0.87076100 | 0.00574400 |
| H     | -4.27198800 | 2.90050400  | -0.12063900 |
| H     | -6.38378600 | 1.60572800  | -0.08413000 |
| C     | 3.03780600  | 0.33369700  | 0.03984800 |
| C     | 3.65753900  | -0.93857400 | -0.06519900 |
| C     | 3.88409900  | 1.47240900  | 0.08056200 |
| C     | 5.03459800  | -1.05466500 | -0.12541100 |
| H     | 3.04961700  | -1.83623800 | -0.09821400 |
| C     | 5.25744000  | 1.34322400  | 0.01922700 |
| H     | 3.43382700  | 2.45634500  | 0.16111000 |
| C     | 5.84489000  | 0.08002900  | -0.08425700 |
| H     | 5.48596200  | -2.03740500 | -0.20533100 |
| H     | 5.88244300  | 2.22870200  | 0.05174000 |
| H     | 6.92312300  | -0.01801600 | -0.13209200 |
| H     | -0.69385200 | -2.60846000 | 0.05424800 |
| N     | -1.63752200 | -2.23517400 | 0.02861500 |

S61
Transition State IV-TS(1,4)

\[
\begin{array}{c}
\text{Total EE (hartree)} \\
\text{EE + Zero-Point Energy Correction (hartree)} \\
\text{EE + Thermal Enthalpy Correction (hartree)} \\
\text{EE + Thermal Free Energy Correction (hartree)} \\
\text{Imaginary Frequencies (cm}^{-1}) \\
\text{<S^2>}
\end{array}
\]

\[
\begin{array}{c}
-709.853471 \\
-709.604410 \\
-709.589756 \\
-709.647874 \\
1, -1695.14 \\
0.7617
\end{array}
\]

\[
\text{Cartesian Coordinates}
\]

|   |   |   |   |
|---|---|---|---|
| C | -1.37871600 | 0.24434400 | 0.34905100 |
| N | -0.73164900 | 1.33108400 | 0.51886600 |
| O | -0.69224000 | -0.92460500 | 0.36309200 |
| C | 0.66707100 | -0.55824500 | 0.57031900 |
| H | 0.39956000 | 0.75478800 | 0.64640300 |
| H | 1.02253100 | -0.88080200 | 1.54906300 |
| C | 1.55223900 | -0.86795800 | -0.60394700 |
| H | 1.55980200 | -1.95281800 | -0.76622600 |
| H | 1.11882800 | -0.41447700 | -1.50108600 |
| C | -2.83367300 | 0.13375000 | 0.12974400 |
| C | -3.61493000 | 1.29053000 | -0.10443100 |
| C | -3.43166100 | -1.11315400 | -0.05164100 |
| C | -4.98302600 | 1.19801900 | -0.10197200 |
| H | -3.14064600 | 2.25436300 | 0.24704600 |
| C | -4.80302800 | -1.20010800 | -0.25762200 |
| H | -2.82291200 | -2.00831900 | -0.03077900 |
| C | -5.57909400 | -0.04721200 | -0.28314700 |
| H | -5.58697400 | 2.09780600 | -0.12128700 |
| H | -5.26528800 | -2.17038600 | -0.39809400 |
| H | -6.64902700 | -0.11737300 | -0.44391000 |
| C | 2.95573800 | -0.36129700 | -0.37424600 |
| C | 3.97551100 | -1.22473200 | 0.02077900 |
| C | 3.24201500 | 0.99681700 | -0.51876800 |
| C | 5.25825500 | -0.74380800 | 0.26316300 |
| H | 3.76596200 | -2.28378000 | 0.13605000 |
| C | 4.52183500 | 1.48043700 | -0.27735300 |
| H | 2.45503600 | 1.67949900 | -0.82490400 |
| C | 5.53427400 | 0.61016600 | 0.11454200 |
| H | 6.04230500 | -1.42878100 | 0.56630800 |
| H | 4.72968300 | 2.53788900 | -0.39678500 |
| H | 6.53375300 | 0.98635500 | 0.30141400 |
Intermediate IV (1,4)

| Description                                                                 | Value             |
|----------------------------------------------------------------------------|-------------------|
| Total EE (hartree)                                                         | -709.876951       |
| EE + Zero-Point Energy Correction (hartree)                                | -709.624155       |
| EE + Thermal Enthalpy Correction (hartree)                                 | -709.608552       |
| EE + Thermal Free Energy Correction (hartree)                              | -709.670556       |
| Imaginary Frequencies (cm^{-1})                                            | 0                |
| \(<S^2>\)                                                                  | 0.7544            |
| **Cartesian Coordinates**                                                  |                   |
| C                            | -1.55706600       |
| O                            | -0.62546400       |
| C                            | 0.68948700        |
| H                            | 0.90520000        |
| C                            | -2.93708400       |
| C                            | -4.01656200       |
| C                            | -3.17527800       |
| C                            | -5.31567800       |
| H                            | -3.81995100       |
| C                            | -4.47882400       |
| H                            | -2.34148900       |
| C                            | -5.55012700       |
| H                            | -6.14862300       |
| H                            | -6.56643600       |
| C                            | 3.07013700        |
| C                            | 3.86069400        |
| C                            | 3.61805500        |
| C                            | 5.17404700        |
| H                            | 3.44675200        |
| C                            | 4.92867700        |
| H                            | 3.01044200        |
| C                            | 5.71112200        |
| H                            | 5.77697900        |
| H                            | 5.34136100        |
| H                            | 6.73452900        |
| H                            | -0.31845400       |
| N                            | -1.31298000       |
| C                            | 1.63495000        |
| H                            | 1.43298800        |
| H                            | 1.45823100        |
**Intermediate V**

![Intermediate V molecular structure](image)

| Description                                                                 | Value                          |
|------------------------------------------------------------------------------|--------------------------------|
| Total EE (hartree)                                                           | -1007.730364                   |
| EE + Zero-Point Energy Correction (hartree)                                  | -1007.473415                   |
| EE + Thermal Enthalpy Correction (hartree)                                   | -1007.456462                   |
| EE + Thermal Free Energy Correction (hartree)                                | -1007.521880                   |
| Imaginary Frequencies (cm$^{-1}$)                                            | 0                              |
| $\langle S^2 \rangle$                                                         | N/A                            |

**Cartesian Coordinates**

| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| C       | -2.05500800 | 1.43120500 | 0.35402200 |
| O       | -1.04004600 | 0.75779200 | -0.21332600 |
| C       | 0.27836200  | 1.16831000 | 0.11455800  |
| H       | 0.46860300  | 2.16366600 | -0.30123500 |
| H       | 0.39092000  | 1.23080500 | 1.19924800  |
| C       | 1.24312400  | 0.18291600 | -0.51713800 |
| H       | 0.99383400  | 0.06409900 | 1.57043100  |
| C       | -3.36538400 | 0.80215600 | 0.02762800  |
| C       | -4.52919000 | 1.57088000 | 0.01049100  |
| C       | -3.44001900 | -0.56397100| -0.24733100 |
| C       | -5.75437100 | 0.98033400 | -0.26783300 |
| H       | -4.48008400 | 2.63902500 | 0.19358800  |
| C       | -4.66833200 | -1.15379600| -0.51623400 |
| H       | -2.53465500 | -1.15876500| -0.24110300 |
| C       | -5.82647500 | -0.38421500| -0.52741000 |
| H       | -6.65226600 | 1.58708200 | -0.28799900 |
| H       | -4.72029800 | -2.21740700| -0.71875700 |
| H       | -6.78367900 | -0.84558800| -0.74251900 |
| C       | 2.67878900  | 0.59985800 | -0.36908600 |
| C       | 3.22020800  | 0.93252000 | 0.87466000  |
| C       | 3.48724400  | 0.68772900 | 1.50147800  |
| C       | 4.53925500  | 1.35062700 | 0.97907600  |
| H       | 2.61504200  | 0.84928100 | 1.77112000  |
| C       | 4.80995800  | 1.10332700 | -1.39734700 |
| H       | 3.07918600  | 0.42804600 | -2.47297200 |
| C       | 5.33859700  | 1.43739600 | -0.15692600 |
| H       | 4.94649100  | 1.60520900 | 1.95093600  |
| H       | 5.42598300  | 1.16545100 | -2.28723000 |
| H       | 6.36971700  | 1.76130900 | -0.07325600 |
| I       | 0.92453400  | -1.81525800| 0.28628200  |
| N       | -1.83418200 | 2.45471500 | 1.07152200  |
| H       | -2.69998300 | 2.81944700 | 1.45571400  |
**Intermediate VI**

|                                |                  |
|--------------------------------|------------------|
| **Total EE (hartree)**         | -709.333851      |
| **EE + Zero-Point Energy Correction (hartree)** | -709.088294 |
| **EE + Thermal Enthalpy Correction (hartree)** | -709.074122 |
| **EE + Thermal Free Energy Correction (hartree)** | -709.131391 |
| **Imaginary Frequencies (cm⁻¹)** | 0                |
| **Cartesian Coordinates**      |                  |
| C                              | -0.95745000      |
| N                              | -0.01901400      |
| O                              | -0.68908300      |
| C                              | 0.72141300       |
| H                              | 1.19964400       |
| H                              | 0.86791000       |
| C                              | -2.33597000      |
| C                              | -3.27872200      |
| C                              | -2.69632800      |
| C                              | -4.57369000      |
| H                              | -2.99526100      |
| C                              | -3.98955600      |
| H                              | -1.95363000      |
| C                              | -4.93035300      |
| H                              | -5.30433000      |
| H                              | -4.26639500      |
| H                              | -5.94111000      |
| C                              | 2.40065600       |
| C                              | 3.65640100       |
| C                              | 2.31227700       |
| C                              | 4.80816500       |
| H                              | 3.73526200       |
| C                              | 3.46100100       |
| H                              | 1.33651600       |
| C                              | 4.71275400       |
| H                              | 5.77899500       |
| H                              | 3.37907100       |
| H                              | 5.60846300       |
| C                              | 1.16259000       |
| H                              | 1.36150000       |

**Diagram:**

- **Ph**
- **N**
- **H**
- **Ph**
Transition State VII-TS(OAc)

| Total EE (hartree)          | -937.743622 |
|----------------------------|-------------|
| EE + Zero-Point Energy Correction (hartree) | -937.451002 |
| EE + Thermal Enthalpy Correction (hartree)   | -937.431477 |
| EE + Thermal Free Energy Correction (hartree) | -937.502842 |
| Imaginary Frequencies (cm⁻¹)        | 1, -283.41  |
| <S²>                                 | 0.7501      |

Cartesian Coordinates

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -1.44176100 | -0.30622700 | 0.53007300 |
| N    | -0.40797000 | -0.15181300 | -0.20778700 |
| O    | -1.24410900 | -0.53619500 | 1.84250500 |
| C    | 0.17467600  | -0.68957300 | 2.01218400 |
| H    | 0.38950700  | -0.10261700 | 2.87408300 |
| C    | -0.83554100 | -0.25102200 | 0.07302100 |
| C    | -3.88553600 | -0.49833900 | 0.95788000 |
| C    | -3.10497600 | 0.05200100  | -1.26341200 |
| C    | -5.19744800 | -0.44267600 | 0.50574400 |
| H    | -3.67179900 | -0.73188800 | 1.99336000 |
| C    | -4.41657900 | 0.10512900  | -1.70973000 |
| H    | -2.27942900 | 0.24373900  | -1.93799000 |
| C    | -5.46399000 | -0.14201400 | -0.82530900 |
| H    | -6.01245700 | -0.63414700 | 1.19390500 |
| H    | -4.62472100 | 0.34112200  | -2.74605200 |
| H    | -6.48909400 | -0.09877200 | -1.17563600 |
| C    | 1.93074500  | -0.94012700 | 0.13786100 |
| C    | 3.15019900  | -0.83649000 | 0.80984300 |
| C    | 1.84734800  | -1.72410700 | -1.01007500 |
| C    | 4.26754400  | -1.51807800 | 0.34720900 |
| H    | 3.22733400  | -0.20579600 | 1.69031100 |
| C    | 2.96827100  | -2.40425800 | -1.47419900 |
| H    | 0.90268400  | -1.79135500 | -1.53645300 |
| C    | 4.17861300  | -2.30435200 | -0.79802800 |
| H    | 5.21036500  | -1.42955800 | 0.87493100 |
| H    | 2.89509200  | -3.01263500 | -2.36876600 |
| H    | 5.05173800  | -2.83311000 | -1.16325800 |
| C    | 0.73740300  | -0.19637600 | 0.66640700 |
| H    | 1.07923300  | 0.88220400  | 0.81450900 |
| O    | 2.28617800  | 4.13193600  | -0.09460000 |
| C    | 1.92324400  | 2.96944700  | -0.16874700 |
| O    | 1.58482700  | 2.42495100  | 0.96739300 |
|      |          |          |          |
|------|----------|----------|----------|
| C    | 1.85681500 | 2.15645800 | -1.42249900 |
| H    | 2.60820900 | 1.36330300 | -1.37819500 |
| H    | 0.87860500 | 1.67884700 | -1.51796900 |
| H    | 2.05397200 | 2.79977600 | -2.27875400 |

**Transition State VII-TS(Me)**

![Transition State VII-TS(Me)](image)

| Total EE (hartree) | -749.162259 |
|--------------------|-------------|
| EE + Zero-Point Energy Correction (hartree) | -748.888537 |
| EE + Thermal Enthalpy Correction (hartree) | -748.871311 |
| EE + Thermal Free Energy Correction (hartree) | -748.936160 |
| Imaginary Frequencies (cm⁻¹) | 1, -1231.83 |
| <S²> | 0.7627 |

**Cartesian Coordinates**

|      |          |          |          |
|------|----------|----------|----------|
| C    | -1.09929600 | -0.3792000 | -0.15469200 |
| N    | -0.11752600 | 0.17767200 | 0.43779500 |
| O    | -0.83774100 | -1.47816400 | -0.90421800 |
| C    | 0.59344400 | -1.61119900 | -0.92159000 |
| H    | 0.95912400 | -1.32706700 | -1.91356600 |
| H    | 0.84357400 | -2.65343300 | -0.72058700 |
| C    | -2.50213800 | 0.05328200 | -0.09730900 |
| C    | -3.47950700 | -0.59107200 | -0.85560800 |
| C    | -2.85566200 | 1.12483400 | 0.72578800 |
| C    | -4.80029900 | -0.16506800 | -0.79156200 |
| H    | -3.20207400 | -1.42262100 | -1.49213700 |
| C    | -4.17497600 | 1.54683900 | 0.78512900 |
| H    | -2.08712100 | 1.61419300 | 1.31178200 |
| C    | -5.14959500 | 0.90296000 | 0.02676000 |
| H    | -5.55729800 | -0.66790700 | -1.38234700 |
| H    | -4.44621300 | 2.37889900 | 1.42471200 |
| H    | -6.18029000 | 1.23429600 | 0.07537600 |
| C    | 1.04184200 | -0.6333400 | 0.17284200 |
| H    | -1.21697000 | -1.3055900 | 1.18045900 |
| C    | 2.32698600 | 0.09171800 | -0.04711800 |
| C    | 3.45960500 | -0.62206100 | -0.44921600 |
| C    | 2.43870500 | 1.46377700 | 0.17632300 |
| C    | 4.67518100 | 0.02364300 | -0.63347100 |
| H    | 3.39330000 | -1.69325000 | -0.61618000 |
| C    | 3.65686100 | 2.10866000 | -0.00641000 |
| H    | 1.56210200 | 2.01846500 | 0.48789600 |
| C    | 4.77817100 | 1.39345100 | -0.41184400 |
| H    | 5.54427500 | -0.54317000 | -0.94826400 |
| H    | 3.72888700 | 3.17689100 | 0.16674900 |
| H    | 5.72659200 | 1.89895800 | -0.55467400 |
|     |     |     |     |
|-----|-----|-----|-----|
| C   | 1.38804800 | -2.21977800 | 2.38931100 |
| H   | 2.27653900 | -2.78864900 | 2.13174900 |
| H   | 1.50999400 | -1.48249600 | 3.17642000 |
| H   | 0.45325100 | -2.77230300 | 2.39784300 |

**Transition State VII-TS(i)**

| Total EE (hartree) | -1007.090383 |
|--------------------|--------------|
| EE + Zero-Point Energy Correction (hartree) | -1006.852084 |
| EE + Thermal Enthalpy Correction (hartree) | -1006.835884 |
| EE + Thermal Free Energy Correction (hartree) | -1006.899787 |
| Imaginary Frequencies (cm⁻¹) | 1, -707.20 |
| <S²> | 0.7723 |

**Cartesian Coordinates**

|     |     |     |     |
|-----|-----|-----|-----|
| C   | -1.57504800 | -0.58862100 | 0.51416500 |
| N   | -0.58101200 | -0.92489400 | -0.24252200 |
| O   | -1.27653900 | -0.22613700 | 1.77311100 |
| C   | 0.13508300 | -0.42735500 | 1.92832700 |
| H   | 0.29700300 | -1.28650800 | 2.58869200 |
| H   | 0.56864100 | 0.46841800 | 2.37473100 |
| C   | -2.98031300 | -0.56707800 | 0.12027200 |
| C   | -3.97502500 | -0.25060000 | 1.04832800 |
| C   | -3.32480800 | -0.86581400 | -1.20112500 |
| C   | -5.30564100 | -0.23617900 | 0.65435300 |
| H   | -3.70312800 | -0.01688900 | 2.07005300 |
| C   | -4.65581700 | -0.84986600 | -1.58656600 |
| H   | -2.54211900 | -1.10365300 | -1.91090000 |
| C   | -5.64708200 | -0.53574500 | -0.66033400 |
| H   | -6.07745100 | 0.01013900 | 1.37401600 |
| H   | -4.92614400 | -1.08000100 | -2.61133600 |
| H   | -6.68735900 | -0.52264900 | -0.96528800 |
| C   | 0.57160500 | -0.71592700 | 0.50364000 |
| H   | 0.95675700 | 0.65947300 | 0.05280400 |
| C   | 1.81872600 | -1.40270500 | 0.17549100 |
| C   | 2.90735700 | -1.34347200 | 1.05518700 |
| C   | 1.95806200 | -2.08163700 | -1.04132300 |
| C   | 4.10322000 | -1.96677300 | 0.73170000 |
| H   | 2.82342800 | -0.80129500 | 1.99135500 |
| C   | 3.15654800 | -2.70141400 | -1.35886000 |
| H   | 1.11726500 | -2.11785400 | -1.72293100 |
| C   | 4.23160200 | -2.64778900 | -0.47523700 |
| H   | 4.93911400 | -1.91724200 | 1.41990100 |
| H   | 3.25501200 | -3.22925700 | -2.30056400 |
Transition State VII-TS(Im)

| Total EE (hartree)          | -1148.860556 |
|-----------------------------|--------------|
| EE + Zero-Point Energy Correction (hartree) | -1148.475489 |
| EE + Thermal Enthalpy Correction (hartree)   | -1148.451388 |
| EE + Thermal Free Energy Correction (hartree) | -1148.533376 |
| Imaginary Frequencies (cm⁻¹) | 1, -1760.98  |
| \(<S²>\)                     | 0.7661       |

**Cartesian Coordinates**

|       |        |        |        |
|-------|--------|--------|--------|
| C     | -2.18120300 | -0.58036200 | -0.51925100 |
| N     | -1.69496600  | 0.33505900   | 0.23012800   |
| O     | -1.89851400  | -0.52239100  | -1.183655400 |
| C     | -1.55658800  | 0.69330800   | -2.03575300  |
| H     | -1.78345700  | 1.39748600   | -2.59076300  |
| H     | -0.25549000  | 0.45808400   | -2.60384200  |
| C     | -3.02354700  | -1.69768200  | -0.07461800  |
| C     | -3.54511000  | -2.60672600  | -0.99545700  |
| C     | -3.30243100  | -1.84720100  | 1.28562700   |
| C     | -4.34149700  | -3.65684500  | -0.55650300  |
| H     | -3.32510600  | -2.48243000  | -2.04904000  |
| C     | -4.09846000  | -2.89669400  | 1.71795900   |
| H     | -2.88846900  | -1.13551000  | 1.98958100   |
| C     | -4.61908300  | -3.80316000  | 0.79784100   |
| H     | -4.74520800  | -4.36209000  | -1.27373000  |
| H     | -4.31303900  | -3.01101900  | 2.77423300   |
| H     | -5.24033500  | -4.62401200  | 1.13813100   |
| C     | -0.86705100  | 1.15258200   | -0.60382000  |
| H     | 0.30903800   | 0.76475100   | -0.44222500  |
| C     | 2.28429400   | -0.14614200  | 0.33202200   |
| N     | 1.56067200   | 0.16862400   | -0.66122900  |
| C     | 3.51770700   | -0.96423000  | 0.11362500   |
| C     | 3.62423500   | -1.76487900  | -1.02406700  |
| C     | 4.56774600   | -0.92443300  | 1.03049800   |
| C     | 4.77150000   | -2.51416400  | -1.24359500  |
| H     | 2.80068100   | -1.79653400  | -1.72698600  |
Intermediate VII

Intermediate VII

| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| C       | 5.71634400 | -1.67359100 | 0.80490000 |
| H       | 4.48245400 | -0.30712300 | 1.91569100 |
| C       | 5.82062800 | -2.46906100 | -0.33051000 |
| H       | 4.84563200 | -3.13850800 | -2.12673300 |
| H       | 6.53095400 | -1.63592100 | 1.51929100 |
| C       | 6.71632600 | -3.05539800 | -2.12673300 |
| H       | 2.12680400 | 0.17023300 | 1.62829400 |
| C       | 1.10069400 | 1.09104200 | 1.99290000 |
| H       | 1.18793600 | 2.01196700 | 1.41136700 |
| H       | 1.12623700 | 1.30314900 | 3.04786300 |
| O       | 2.12680400 | 0.17023300 | 1.62829400 |
| C       | 1.10069400 | 1.09104200 | 1.99290000 |
| H       | 1.18793600 | 2.01196700 | 1.41136700 |
| H       | 1.12623700 | 1.30314900 | 3.04786300 |
| C       | 0.90873540 | 3.46034800 | -1.3117800 |
| C       | -1.54954100 | 3.15478700 | 0.75711800 |
| C       | -0.02787800 | 4.82194700 | 0.86747300 |
| H       | 0.47661500 | 3.04793600 | -1.96173100 |
| C       | -1.48630500 | 4.51824100 | 1.02086600 |
| C       | -2.14096500 | 2.49717600 | 1.38284100 |
| C       | -0.72674900 | 5.35580600 | 0.21148400 |
| H       | 0.56920100 | 5.46763500 | -1.50173100 |
| H       | -2.03557900 | 4.92837400 | 1.86126100 |
| H       | -0.67902800 | 6.41888900 | 0.41885000 |

Total EE (hartree) | -708.704268
EE + Zero-Point Energy Correction (hartree) | -708.472777
EE + Thermal Enthalpy Correction (hartree) | -708.458723
EE + Thermal Free Energy Correction (hartree) | -708.514596
Imaginary Frequencies (cm⁻¹) | 0
<\(S^2\)> | 0.7519

Cartesian Coordinates
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| C       | -1.05350400 | -0.46101800 | -0.00002300 |
| N       | 0.00314800 | 0.30912300 | 0.00004200 |
| O       | -0.79751500 | 1.09104200 | -0.00004200 |
| C       | 0.62891800 | -1.93017400 | -0.00001500 |
| H       | 0.93255500 | -2.49231400 | -0.89067800 |
| H       | 0.93252400 | -2.49223300 | 0.89070100 |
| C       | -2.43759400 | -0.02820200 | -0.00003500 |
| C       | -3.47882100 | -0.96366200 | 0.00002300 |
| C       | -2.73854500 | 1.34037800 | -0.00025200 |
Transition State VII-TS(α-O)

Total EE (hartree) | -937.736061
EE + Zero-Point Energy Correction (hartree) | -937.444965
EE + Thermal Enthalpy Correction (hartree) | -937.425681
EE + Thermal Free Energy Correction (hartree) | -937.496431
Imaginary Frequencies (cm⁻¹) | 1, -777.88
<S²> | 0.7582

Cartesian Coordinates

| C     | -0.69067500 -0.44969100 0.01106300 |
| N     | 0.15705300 -0.37467600 -0.93043700 |
| O     | -0.39770800 0.23513100 1.16310500 |
| C     | 0.73701400 0.99953400 0.87875300 |
| H     | 1.40920800 1.03079400 1.73608900 |
| H     | 0.40456400 2.12616200 0.71001800 |
| C     | -1.96022600 -1.18431400 0.00291300 |
| C     | -2.82841000 -1.12155000 1.09308700 |
| C     | -2.29885300 -1.94378800 -1.11902200 |
| C     | -4.03095000 -1.81604500 1.05828200 |
Intermediate VII(α-O)

| Total EE (hartree) | -708.669136 |
|--------------------|-------------|
| EE + Zero-Point Energy Correction (hartree) | -708.437530 |
| EE + Thermal Enthalpy Correction (hartree) | -708.423471 |
| EE + Thermal Free Energy Correction (hartree) | -708.480227 |
| Imaginary Frequencies (cm\(^{-1}\)) | 0 |
| \(<S^2>\) | 0.7550 |
| Cartesian Coordinates |
| C | -0.90703100 -0.62909300 0.22722100 |
| N | -0.01207700 -0.24173700 1.04092700 |
| O | -0.56044200 -1.63688700 -0.63488500 |
| C | 0.71402300 -2.00509100 -0.27640500 |
| H | 1.29192500 -2.49430100 -1.04719600 |
| C | -2.27414300 -0.10838600 0.10166600 |
Intermediate VIII

Total EE (hartree) | -1006.519329
---|---
EE + Zero-Point Energy Correction (hartree) | -1006.284573
EE + Thermal Enthalpy Correction (hartree) | -1006.268886
EE + Thermal Free Energy Correction (hartree) | -1006.329815
Imaginary Frequencies (cm\(^{-1}\)) | 0

Cartesian Coordinates

|   |   |   |   |   |
|---|---|---|---|---|
| C | -3.17079400 | -0.66487000 | -0.81053300 |
| C | -2.67207900 | 0.96088200 | 0.90683100 |
| C | -4.45833300 | -0.15347100 | -0.81053300 |
| H | -2.85984100 | -1.49439500 | -1.43323000 |
| C | -3.95839300 | 1.46679100 | 0.79804600 |
| H | -1.96478700 | 1.38302300 | 1.61047100 |
| C | -4.85329100 | 0.91089300 | -0.11256000 |
| H | -5.15358900 | -0.58787600 | -1.62362100 |
| H | -4.26526000 | 2.29673000 | 1.42399700 |
| H | -5.85859100 | 1.30832900 | -0.19571600 |
| C | 2.37200400 | -0.19314700 | 0.31387600 |
| C | 3.66499800 | -0.55016500 | 0.68707100 |
| C | 2.18456600 | 0.90622900 | -0.52185200 |
| C | 4.75901400 | 0.17526000 | 0.22681200 |
| H | 3.81917600 | -1.39983000 | 1.34533000 |
| C | 3.27561000 | 1.63536400 | -0.97762200 |
| H | 1.17974300 | 1.19982100 | -0.80605800 |
| C | 4.56632200 | 1.27039400 | -0.60920000 |
| H | 5.76093200 | -0.11162700 | 0.52624000 |
| H | 3.11811100 | 2.49309700 | -1.62210700 |
| H | 5.41695400 | 1.84079700 | -0.96262000 |
| C | 1.19040000 | -1.03713200 | 0.77268300 |
| H | 1.48611400 | -1.55324200 | 1.69528800 |
Intermediate IX

| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| C       | 1.040546   | -0.448202  | 0.000069   |
| N       | -0.011331  | 0.304241   | -0.000008  |
| O       | 0.756709   | -1.767012  | 0.000205   |
| C       | -0.601363  | -1.836077  | 0.000230   |
| H       | -1.034933  | -2.820644  | 0.000485   |
| C       | 2.444557   | -0.038000  | -0.000120  |
| C       | 3.470140   | -0.984909  | 0.000144   |
| C       | 2.757252   | 1.323208   | -0.000237  |
| C       | 4.795707   | -0.571021  | 0.000080   |
| H       | 3.229591   | -2.041096  | 0.000323   |
| C       | 4.083337   | 1.729522   | -0.000299  |
| H       | 1.954093   | 2.050231   | -0.000357  |
| C       | 5.105404   | 0.784552   | -0.000141  |
| H       | 5.588661   | -1.310012  | 0.000207   |
| H       | 4.321041   | 2.787076   | -0.000470  |
| H       | 6.141058   | 1.104979   | -0.000192  |

Intermediate IX

Total EE (hartree) | -708.125650
EE + Zero-Point Energy Correction (hartree) | -707.903549
EE + Thermal Enthalpy Correction (hartree) | -707.889932
EE + Thermal Free Energy Correction (hartree) | -707.945636
Imaginary Frequencies (cm⁻¹) | 0
### Acetoxy Radical

| C     | -2.47898100  | -0.09693500  | 0.00002400 |
| C     | -3.54904000  | -0.99630900  | -0.00044800 |
| C     | -2.74772600  | 1.27270900   | 0.000438500 |
| C     | -4.85761100  | -0.53492200  | -0.00048000 |
| H     | -3.36290800  | -2.06492500  | -0.00081400 |
| C     | -4.05891800  | 1.73243700   | 0.000385000 |
| H     | -1.91946000  | 1.97075500   | 0.000791000 |
| C     | -5.11807500  | 0.83225000   | -0.00006700 |
| H     | -5.67730400  | -1.24613000  | -0.00085000 |
| H     | -6.14080900  | 1.19185200   | -0.00010900 |
| C     | -1.08864000  | -0.57103800  | 0.000102000 |

**Cartesian Coordinates**

#### Acetoxy Radical

**Total EE (hartree)**: \(-228.404778\)

**EE + Zero-Point Energy Correction (hartree)**: \(-228.356997\)

**EE + Thermal Enthalpy Correction (hartree)**: \(-228.351583\)

**EE + Thermal Free Energy Correction (hartree)**: \(-228.384751\)

**Imaginary Frequencies (cm\(^{-1}\))**: 0

\(<S^2>\): 0.7576

### Acetic Acid

| C     | 0.09718700  | -0.00013900  | -0.00821600 |
| C     | 0.81155500  | -1.02892900  | 0.001468000 |
| C     | -1.38736100 | 0.00052800   | -0.00315800 |
| H     | -1.76229900 | 0.89450700   | -0.50167000 |
| H     | -1.76358700 | -0.89993400  | -0.48967500 |
| H     | -1.72752500 | 0.00733000   | 1.03565700  |
| O     | 0.81275200  | 1.02839900   | 0.001549000 |

**Cartesian Coordinates**

#### Acetic Acid

**Total EE (hartree)**: \(-229.090480\)

**EE + Zero-Point Energy Correction (hartree)**: \(-229.028308\)

**EE + Thermal Enthalpy Correction (hartree)**: \(-229.022806\)

**EE + Thermal Free Energy Correction (hartree)**: \(-229.055544\)

**Imaginary Frequencies (cm\(^{-1}\))**: 0
| | | | |
|---|---|---|---|
| H | 1.72408000 | -0.80523600 | -0.00076700 |
| C | -1.38962400 | -0.11933300 | 0.00002600 |
| H | -1.91690600 | 0.83147500 | 0.00325800 |
| H | -1.66648100 | -0.69847000 | -0.88319300 |
| H | -1.66653600 | -0.70514400 | 0.8782600 |
| O | 0.63042900 | 1.19883300 | -0.00002600 |

**Methyl Radical**

| Total EE (hartree) | -39.835237 |
|---|---|
| EE + Zero-Point Energy Correction (hartree) | -39.805568 |
| EE + Thermal Enthalpy Correction (hartree) | -39.801571 |
| EE + Thermal Free Energy Correction (hartree) | -39.823665 |
| Imaginary Frequencies (cm$^{-1}$) | 0 |
| $<S^2>$ | 0.7538 |

| Cartesian Coordinates | |
|---|---|
| C | 0.00000000 | 0.00000000 | 0.00000000 |
| H | 0.00000000 | 1.08165900 | 0.00000000 |
| H | 0.93674400 | -0.54083000 | 0.00000000 |
| H | -0.93674400 | -0.54083000 | 0.00000000 |

**Methane**

| Total EE (hartree) | -40.515661 |
|---|---|
| EE + Zero-Point Energy Correction (hartree) | -40.470949 |
| EE + Thermal Enthalpy Correction (hartree) | -40.467135 |
| EE + Thermal Free Energy Correction (hartree) | -40.488266 |
| Imaginary Frequencies (cm$^{-1}$) | 0 |

| Cartesian Coordinates | |
|---|---|
| C | 0.00000000 | 0.00000000 | 0.00000000 |
| H | 0.62966300 | 0.62966300 | 0.62966300 |
| H | -0.62966300 | -0.62966300 | 0.62966300 |
| H | -0.62966300 | 0.62966300 | -0.62966300 |
| H | 0.62966300 | -0.62966300 | -0.62966300 |

**Iodine Atom Radical**

| Total EE (hartree) | -297.760405 |
|---|---|
| EE + Zero-Point Energy Correction (hartree) | -297.760405 |
| EE + Thermal Enthalpy Correction (hartree) | -297.758045 |
| EE + Thermal Free Energy Correction (hartree) | -297.777908 |
| Imaginary Frequencies (cm$^{-1}$) | 0 |
| $<S^2>$ | 0.7525 |
### Hydrogen Iodide

|                            | Value          |
|---------------------------|----------------|
| Total EE (hartree)        | -298.387899    |
| EE + Zero-Point Energy Correction (hartree) | -298.382594 |
| EE + Thermal Enthalpy Correction (hartree) | -298.379289 |
| EE + Thermal Free Energy Correction (hartree) | -298.402721 |

#### Cartesian Coordinates

|       |     |     |
|-------|-----|-----|
| I     | 0.00000000 | 0.00000000 | 0.00000000 |
| H     | 0.00000000 | -1.57946500 | 0.00000000 |

### Hydrogen Atom Radical

|                            | Value          |
|---------------------------|----------------|
| Total EE (hartree)        | -0.502818      |
| EE + Zero-Point Energy Correction (hartree) | -0.502818 |
| EE + Thermal Enthalpy Correction (hartree) | -0.500458 |
| EE + Thermal Free Energy Correction (hartree) | -0.513472 |

#### Cartesian Coordinates

|       |     |     |
|-------|-----|-----|
| H     | 0.00000000 | 0.00000000 | 0.00000000 |

### Methyl Benzoimidate N-Centered Radical

|                            | Value          |
|---------------------------|----------------|
| Total EE (hartree)        | -439.535245    |
| EE + Zero-Point Energy Correction (hartree) | -439.391794 |
| EE + Thermal Enthalpy Correction (hartree) | -439.381994 |
| EE + Thermal Free Energy Correction (hartree) | -439.427262 |

#### Imaginary Frequencies (cm⁻¹)

|       |     |
|-------|-----|
|       | 0.7501 |

#### Cartesian Coordinates

|       |     |     |     |     |
|-------|-----|-----|-----|-----|
| C     | 1.25109800 | 0.40703100 | 0.05636000 | 0.05636000 |
| C     | -0.21460200 | 0.15471600 | 0.01788000 | 0.01788000 |
| C     | -1.09958200 | 1.22718600 | -0.10330800 | -0.10330800 |
| C     | -0.70646500 | -1.14609700 | 0.11430200 | 0.11430200 |
| C     | -2.46756600 | 0.99747800 | -0.12182600 | -0.12182600 |
| H     | -0.71239600 | 2.23587800 | -0.18862700 | -0.18862700 |
|    |        |        |        |
|----|--------|--------|--------|
|    | X      | Y      | Z      |
| C  | -2.07780700 | -1.36957000 | 0.09489700 |
| H  | -0.01674500 | -1.97562000 | 0.20483000 |
| C  | -2.95896100 | -0.30081000 | -0.02226400 |
| H  | -3.15178600 | 1.83241600 | -0.21880600 |
| H  | -2.45762900 | -2.38189900 | 0.17132000 |
| H  | -4.02829200 | -0.47865400 | -0.03876500 |
| N  | 1.74501600 | 1.54860500 | 0.29063500 |
| O  | 2.00031500 | -0.68655800 | -0.16574500 |
| C  | 3.41529900 | -0.49955000 | -0.09935500 |
| H  | 3.74173400 | 1.83241600 | -0.21880600 |
| H  | 3.70703100 | -0.14174700 | 0.89085300 |
| H  | 3.85196700 | -1.47664000 | -0.29188800 |

**N-Iodo Methyl Benzimidate**

![Chemical Structure](image)

|                        |        |
|------------------------|--------|
| Total EE (hartree)     | -450.955047 |
| EE + Zero-Point Energy Correction (hartree) | -450.809797 |
| EE + Thermal Enthalpy Correction (hartree) | -450.798172 |
| EE + Thermal Free Energy Correction (hartree) | -450.849184 |
| Imaginary Frequencies (cm⁻¹) | 0 |

**Cartesian Coordinates**

|    |        |        |        |
|----|--------|--------|--------|
| C  | 0.29691300 | 0.24770600 | 0.01038400 |
| C  | 1.75253000 | -0.07789000 | -0.03796800 |
| C  | 2.28642500 | -0.97750200 | 0.86093400 |
| C  | 2.57371400 | 0.52161200 | -0.99305500 |
| C  | 3.64128500 | -1.30324900 | 0.81601700 |
| H  | 1.63741600 | -1.47048300 | 1.58822800 |
| C  | 3.92436100 | 0.20510200 | -1.04090000 |
| H  | 2.15377700 | 1.22067600 | -1.70808900 |
| C  | 4.46070000 | -0.70241500 | -0.13249400 |
| H  | 4.05518100 | -2.01585700 | 1.51995600 |
| H  | 4.55826100 | 0.66373600 | -1.79091400 |
| H  | 5.51646800 | -0.94546100 | -0.16935500 |
| N  | -0.50325200 | -0.72214500 | -0.18947800 |
| I  | -2.55107200 | -0.27764900 | -0.08318900 |
| O  | -0.09219300 | 1.50932000 | 0.22257900 |
| C  | 0.81234500 | 2.45912200 | 0.79707800 |
| H  | 0.18405900 | 3.27912300 | 1.13766900 |
| H  | 1.34897200 | 2.02679800 | 1.64296800 |
| H  | 1.52337000 | 2.82239700 | 0.05428600 |
Methyl Benzimidate

| Total EE (hartree) | -440.201248 |
|--------------------|-------------|
| EE + Zero-Point Energy Correction (hartree) | -440.044572 |
| EE + Thermal Enthalpy Correction (hartree) | -440.034863 |
| EE + Thermal Free Energy Correction (hartree) | -440.079113 |
| Imaginary Frequencies (cm⁻¹) | 0 |

| Cartesian Coordinates |
|-----------------------|
| C 1.22808400 0.41352100 0.00002600 |
| C -0.23699000 0.14494600 0.00007000 |
| C -1.12610100 1.22104400 -0.00004900 |
| C -0.73662100 -1.15743100 0.00004100 |
| C -2.49496500 0.99663400 -0.00005900 |
| H -0.72701400 2.22777900 -0.00007600 |
| C -2.10896700 -1.37893900 0.00004500 |
| H -0.05096200 -1.99472000 0.00007600 |
| C -2.99020800 -0.30438600 -0.00007000 |
| H -3.17829500 1.83829000 -0.00010600 |
| H -2.48906800 -2.39426100 0.00008600 |
| H -4.06043200 -0.47888400 -0.00010000 |
| N 1.68168600 1.59924100 -0.00010800 |
| O 1.94166200 -0.73342500 0.00003500 |
| C 3.35670000 -0.64229300 -0.00005700 |
| H 3.71851500 -0.12840300 -0.89593500 |
| H 3.71853800 -0.12857000 0.89589900 |
| H 3.72169600 -1.66684500 -0.00019800 |
| H 2.69633400 1.63976000 0.00010400 |

PhI(OAc)₂

| Total EE (hartree) | -986.296037 |
|--------------------|-------------|
| EE + Zero-Point Energy Correction (hartree) | -986.102248 |
| EE + Thermal Enthalpy Correction (hartree) | -986.084323 |
| EE + Thermal Free Energy Correction (hartree) | -986.151250 |
### Imaginary Frequencies (cm⁻¹)

|   |       |
|---|-------|
|   | 0     |

### Cartesian Coordinates

| Element | Cartesian Coordinates |
|---------|-----------------------|
| Cs      | 0.00000000 0.00000000 1.66485600 |
| I       | 0.00000000 0.00000000 -1.72768100 |

---

### CsI

![Cs—I bond](image)

| Total EE (hartree) | -318.052659 |
|--------------------|-------------|
| EE + Zero-Point Energy Correction (hartree) | -318.052393 |
| EE + Thermal Enthalpy Correction (hartree) | -318.048385 |
| EE + Thermal Free Energy Correction (hartree) | -318.079668 |

### Imaginary Frequencies (cm⁻¹)

|   |       |
|---|-------|
|   | 0     |
### Phl

| Total EE (hartree) | -529.403162 |
|--------------------|-------------|
| EE + Zero-Point Energy Correction (hartree) | -529.312450 |
| EE + Thermal Enthalpy Correction (hartree) | -529.305693 |
| EE + Thermal Free Energy Correction (hartree) | -529.344118 |

#### Imaginary Frequencies (cm\(^{-1}\))

| 0 |

#### Cartesian Coordinates

| Atom | X | Y | Z |
|------|---|---|---|
| C    | 0.00000000 | 3.32604900 | 0.00000000 |
| C    | 0.00000000 | 2.62861400 | 1.20206000 |
| C    | 0.00000000 | 1.23812700 | 1.20908300 |
| C    | 0.00000000 | 0.55019800 | 0.00000000 |
| C    | 0.00000000 | 1.23812700 | -1.20908300 |
| H    | 0.00000000 | 4.40989000 | 0.00000000 |
| H    | 0.00000000 | 3.16544600 | 2.14398300 |
| H    | 0.00000000 | 0.69826700 | 2.14811600 |
| H    | 0.00000000 | 3.16544600 | -2.14398300 |
| I    | 0.00000000 | -1.54331500 | 0.00000000 |

### CsOAc

| Total EE (hartree) | -248.730424 |
|--------------------|-------------|
| EE + Zero-Point Energy Correction (hartree) | -248.680425 |
| EE + Thermal Enthalpy Correction (hartree) | -248.673038 |
| EE + Thermal Free Energy Correction (hartree) | -248.714013 |

#### Imaginary Frequencies (cm\(^{-1}\))

| 0 |

#### Cartesian Coordinates

| Atom | X | Y | Z |
|------|---|---|---|
| C    | 1.95700100 | 0.00058100 | -0.01383400 |
| O    | 1.36662300 | 1.11504200 | -0.00843000 |
| O    | 1.36649900 | -1.11390400 | -0.00845900 |
AcOI

|       | C                  | H                  | H                  | H                  | Cs                  |
|-------|--------------------|--------------------|--------------------|--------------------|---------------------|
|       | 3.47759300         | 3.80836800         | 3.86805300         | 3.87007400         | -1.20034600         |
|       | -0.00038000        | -0.02154600        | -0.00008700        | 0.90613100         | -0.00008700         |
|       | 0.00547800         | 1.04839300         | -0.48976900        | -0.45629700        | 0.00150800          |

Total EE (hartree)          | -526.231050
EE + Zero-Point Energy Correction (hartree) | -526.180063
EE + Thermal Enthalpy Correction (hartree) | -526.173117
EE + Thermal Free Energy Correction (hartree) | -526.212701
Imaginary Frequencies (cm⁻¹) | 0

Cartesian Coordinates

|       | C                  | H                  | H                  | H                  | Cs                  |
|-------|--------------------|--------------------|--------------------|--------------------|---------------------|
|       | 1.77126300         | 3.09923000         | 3.17642400         | 3.17577700         | -1.10369200         |
|       | 0.18576400         | -0.52672200        | -1.16388000        | -1.16591700        | -0.71892700         |
|       | -0.00026400        | -0.00007900        | 0.88239600         | 0.88111900         | 0.00016600          |
|       | -0.00026400        | -0.00007900        | 0.88239600         | 0.88111900         | 0.00016600          |
|       | -0.00026400        | -0.00007900        | 0.88239600         | 0.88111900         | 0.00016600          |

|       | O                  | O                  | I                  |
|-------|--------------------|--------------------|--------------------|
|       | 1.60807600         | 0.76984100         | -1.10369200        |
|       | 1.37190000         | 1.37190000         | -0.02001400        |
|       | -0.00115300        | -0.00016600        | 0.00008600         |
|       | -0.00115300        | -0.00016600        | 0.00008600         |

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