Supporting Information

Radical-mediated Intramolecular $\beta$-C(sp$^3$)–H Amidation of Alkylimidates: Facile Synthesis of 1,2-Amino Alcohols

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1. **Reagents:** All commercial materials were used as received unless otherwise noted. DCM were dried by distillation over CaH$_2$. THF and toluene were dried by distillation over sodium/benzophenone. TLC were performed on silica gel Huanghai HSGF254 plates and visualization of the developed chromatogram was performed by fluorescence quenching ($\lambda_{\text{max}} = 254$ nm). Flash chromatography was performed using Silica gel (200-300 mesh) purchased from Qingdao Haiyang Chemical Co., China. PhI(OAc)$_2$ (99%, Energy Chemical), NIS (99%, J&K Chemical), DCE (99.5%, TCI chemical) were used in the radical-mediated $\beta$-C(sp$^3$)-H amination reactions.

2. **Instruments:** NMR spectra were recorded on Bruker AVANCE AV 400 instruments and all NMR experiments were reported in units, parts per million (ppm), using residual solvent peaks as internal reference. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, br s = broad singlet, m = multiplet. High resolution ESI mass experiments were operated on Waters Xevo G2-Xs QT or Thermo-Fisher Scientific Q instrument. X-ray crystallography was recorded on SuperNova diffractometer.

Note: For most of the trichloroacetimidate s, we were unable to detect the molecular ion peaks for HRMS analysis, only the trichloroacetimidate cleaved fragments were observed.

3. **Preparation of imidate substrates**

3.1 **General procedure for preparation of trichloroacetimidate substrates**
To a stirred mixture of alcohol (10 mmol, 1 equiv) in 20 mL of dichloromethane, was added trichloroacetonitrile (1.5 mL, 15 mmol, 1.5 equiv) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.15 mL, 1 mmol, 0.1 equiv). The resulting reaction mixture was continuously stirred at room temperature. After 12 h, the reaction mixture was diluted with water, the aqueous phase was separated and extracted with dichloromethane. The combined organic layer was washed with brine, dried over Na₂SO₄, filtered and concentrated *in vacuo*. The residue was purified by column chromatography with triethylamine-treated silica gel using 3% of triethylamine in hexane as eluent to give the desired product.

**Compound 1** was prepared following the general procedure in 94% yield as colorless oil (Rᵣ = 0.4, Hexanes:EtOAc = 40:1). **¹H NMR** (400 MHz, CDCl₃) δ 8.21 (br s, 1H), 4.27 (t, J = 6.6 Hz, 2H), 1.82–1.72 (m, 2H), 1.48–1.38 (m, 2H), 1.35–1.25 (m, 8H), 0.87 (t, J = 6.9 Hz, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 163.1, 91.8, 69.7, 31.9, 29.3, 28.3, 25.9, 22.7, 14.2.

**Compound 4-1** was prepared following the general procedure in 93% yield as colorless oil (Rᵣ = 0.4, Hexanes:EtOAc = 40:1). **¹H NMR** (400 MHz, CDCl₃) δ 8.20 (br s, 1H), 4.28 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 163.1, 91.8, 69.7, 31.9, 29.3, 28.3, 25.9, 22.7, 14.2.

**Compound 5-1** was prepared following the general procedure in 77% yield as colorless oil (Rᵣ = 0.4, Hexanes:EtOAc = 40:1). **¹H NMR** (400 MHz, CDCl₃) δ 8.17 (br s, 1H), 5.15–4.97 (m, 1H), 1.28 (d, J = 6.3 Hz, 6H); **¹³C NMR** (101 MHz, CDCl₃) δ
162.0, 92.0, 72.7, 21.1. The spectra data are consistent with those reported in literature.

\[
\text{Cl}_3\text{C} = \text{NH} \\
7-1
\]

Compound 7-1 was prepared following the general procedure in 82\% yield as colorless oil (\(R_f = 0.4\), Hexanes:EtOAc = 40:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.20 (br s, 1H), 5.02–4.89 (m, 1H), 1.83–1.60 (m, 2H), 1.33 (d, \(J = 6.2\) Hz, 3H), 0.98 (t, \(J = 7.4\) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 162.5, 92.2, 77.6, 28.7, 18.6, 9.7.

\[
\text{Cl}_3\text{C} = \text{NH} \\
8-1
\]

Compound 8-1 was prepared following the general procedure in 90\% yield as colorless oil (\(R_f = 0.4\), Hexanes:EtOAc = 40:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.16 (br s, 1H), 4.15 (t, \(J = 6.5\) Hz, 2H), 1.77–1.61 (m, 2H), 0.92 (t, \(J = 7.4\) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 162.8, 91.6, 70.9, 21.6, 10.3.

\[
\text{Cl}_3\text{C} = \text{NH} \\
9-1
\]

Compound 9-1 was prepared following the general procedure in 91\% yield as colorless oil (\(R_f = 0.4\), Hexanes:EtOAc = 40:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.21 (br s, 1H), 4.28 (t, \(J = 6.5\) Hz, 2H), 1.81–1.70 (m, 2H), 1.54–1.40 (m, 2H), 0.96 (t, \(J = 7.4\) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 163.2, 91.8, 69.5, 30.4, 19.2, 13.8.

\[
\text{Cl}_3\text{C} = \text{NH} \\
10-1
\]

Compound 10-1 was prepared following the general procedure in 96\% yield as colorless oil (\(R_f = 0.4\), Hexanes:EtOAc = 40:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.20 (br s, 1H), 4.25 (t, \(J = 6.6\) Hz, 2H), 1.78–1.69 (m, 2H), 1.46–1.35 (m, 2H), 1.35–1.18 (m, 14H), 0.85 (t, \(J = 6.8\) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 163.0, 91.8, 69.7, 32.0, 29.69, 29.66, 29.61, 29.4, 29.3, 28.3, 25.9, 22.8, 14.2; \text{HRMS} (ESI) calcd for C\(_{11}\)H\(_{22}\) [M-C\(_2\)H\(_3\)Cl\(_3\)NO\(^+\): 154.1722, found: 154.1720.
Compound 11-1 was prepared following the general procedure in 84% yield as colorless oil ($R_f = 0.4$, Hexanes:EtOAc = 40:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.24 (br s, 1H), 7.32–7.18 (m, 5H), 5.30–5.19 (m, 1H), 3.10 (dd, $J = 13.8, 6.7$ Hz, 1H), 2.88 (dd, $J = 13.8, 6.2$ Hz, 1H), 1.34 (d, $J = 6.2$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.9, 137.4, 129.6, 128.3, 126.5, 91.9, 76.7, 41.7, 18.5; HRMS (ESI) calcd for C$_9$H$_{10}$ [M-C$_2$H$_2$Cl$_3$NO]$^+$: 118.0783, found: 118.0781.

Compound 12-1 was prepared following the general procedure in 89% yield as colorless oil ($R_f = 0.4$, Hexanes:EtOAc = 40:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.20 (br s, 1H), 4.05 (d, $J = 6.6$ Hz, 2H), 2.17–2.05 (m, 1H), 1.00 (d, $J = 6.7$ Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 163.2, 91.8, 75.6, 27.8, 19.1.

Compound 13-1 was prepared following the general procedure in 56% yield as white solid ($R_f = 0.3$, Hexanes:EtOAc = 40:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.42 (br s, 1H), 7.81 (d, $J = 7.5$ Hz, 2H), 7.76 (d, $J = 7.5$ Hz, 2H), 7.44 (t, $J = 7.5$ Hz, 2H), 7.35 (t, $J = 7.5$ Hz, 2H), 4.55 (d, $J = 7.6$ Hz, 2H), 4.43 (t, $J = 7.5$ Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.9, 143.7, 141.4, 128.0, 127.3, 125.6, 120.1, 91.5, 71.8, 46.7; HRMS (ESI) calcd for C$_{14}$H$_{10}$ [M-C$_2$H$_2$Cl$_3$NO]$^+$: 178.0783, found: 178.0780.
Compound 14-1 was prepared following the general procedure in 79% yield as colorless oil ($R_f$ = 0.3, Hexanes:EtOAc = 10:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.55 (d, $J$ = 4.7 Hz, 1H), 8.30 (br s, 1H), 7.61 (t, $J$ = 7.7 Hz, 1H), 7.26 (d, $J$ = 8.1 Hz, 1H), 7.17–7.11 (m, 1H), 4.68 (t, $J$ = 6.6 Hz, 2H), 3.27 (t, $J$ = 6.6 Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.5, 157.7, 149.4, 136.2, 123.6, 121.6, 91.3, 68.4, 36.9; HRMS (ESI) calcd for C$_7$H$_7$N [M-C$_2$H$_2$Cl$_3$NO]$: 105.0578, found: 105.0577.

Compound 15-1 was prepared following the general procedure in 87% yield as colorless oil ($R_f$ = 0.4, Hexanes:EtOAc = 40:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.34 (br s, 1H), 7.27–7.22 (m, 2H), 7.21–7.16 (m, 2H), 5.72–5.65 (m, 1H), 3.42 (dd, $J$ = 17.1, 6.7 Hz, 2H), 3.18 (dd, $J$ = 17.1, 3.3 Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.5, 140.3, 126.9, 124.7, 91.7, 80.0, 39.2; HRMS (ESI) calcd for C$_9$H$_8$ [M-C$_2$H$_2$Cl$_3$NO]$: 116.0626, found: 116.0621.

Compound 16-1 was prepared following the general procedure in 84% yield as colorless oil ($R_f$ = 0.5, Hexanes:EtOAc = 4:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.34 (br s, 1H), 6.10 (brs, 1H), 4.54 (t, $J$ = 6.1 Hz, 2H), 3.18 (dd, $J$ = 13.3, 6.9 Hz, 2H), 2.62 (t, $J$ = 6.1 Hz, 2H), 1.56–1.42 (m, 2H), 0.87 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 169.7, 162.2, 91.1, 65.6, 41.2, 35.4, 22.6, 11.3; HRMS (ESI) calcd for C$_6$H$_{11}$NO [M-C$_2$H$_2$Cl$_3$NO]$: 113.0841, found: 113.0840.

Compound 17-1 was prepared following the general procedure in 65% yield as colorless oil ($R_f$ = 0.4, Hexanes:EtOAc = 10:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.33 (br s, 1H), 5.48–5.37 (m, 1H), 3.68 (s, 3H), 2.83 (dd, $J$ = 15.7, 7.6 Hz, 1H), 2.61 (dd, $J$ = 15.7, 5.7 Hz, 1H), 1.42 (d, $J$ = 6.3 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.5,
Compound 18-1 was prepared following the general procedure in 71% yield as colorless oil (Rf = 0.5, Hexanes:EtOAc = 4:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.37 (br s, 1H), 6.33 (d, $J = 8.3$ Hz, 1H), 4.65-4.55 (m, 3H), 3.71 (s, 3H), 2.70 (t, $J = 5.7$ Hz, 2H), 2.18–2.08 (m, 1H), 0.92 (d, $J = 6.9$ Hz, 3H), 0.89 (d, $J = 6.9$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.5, 169.7, 162.5, 91.2, 65.5, 57.2, 52.3, 35.8, 31.5, 19.0, 18.0.

Compound 19-1 was prepared following the general procedure in 74% yield as colorless oil (Rf = 0.3, Hexanes:EtOAc = 40:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.33 (br s, 1H), 7.15–7.02 (m, 4H), 5.39–5.27 (m, 1H), 3.20 (dd, $J = 16.7$, 5.1 Hz, 1H), 3.05–2.92 (m, 2H), 2.87–2.77 (m, 1H), 2.17–2.02 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.0, 135.5, 133.4, 129.3, 128.5, 126.04, 125.96, 91.8, 74.7, 33.8, 27.1, 26.4; HRMS (ESI) calcd for C$_{10}$H$_{10}$ [M-C$_2$H$_2$Cl$_3$NO]$: 130.0783, found: 130.0782.

Compound 20-1$^{[2]}$ was prepared following the general procedure in 76% yield as colorless oil (Rf = 0.3, Hexanes:EtOAc = 40:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.19 (br s, 1H), 5.16–5.01 (m, 1H), 2.47–2.38 (m, 2H), 2.23–2.11 (m, 2H), 1.90–1.80 (m, 1H), 1.71–1.59 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 161.9, 91.6, 73.4, 30.0, 13.5. The spectra data are consistent with those reported in literature.
Compound 21-1 was prepared following the general procedure in 84% yield as colorless oil (= 0.4, Hexanes:EtOAc = 40:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.18 (br s, 1H), 5.32–5.26 (m, 1H), 1.93–1.83 (m, 4H), 1.81–1.74 (m, 2H), 1.67–1.59 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.5, 92.1, 82.3, 32.3, 23.9; HRMS (ESI) calcd for C$_5$H$_8$ [M-C$_2$H$_2$Cl$_3$NO]$^+$: 68.0626, found: 68.0623.

![Compound 22-1](image)

Compound 22-1 was prepared following the general procedure in 81% yield as colorless oil (R$_f$ = 0.4, Hexanes:EtOAc = 40:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.20 (br s, 1H), 4.97–4.89 (m, 1H), 1.96–1.88 (m, 2H), 1.81–1.73 (m, 2H), 1.69–1.60 (m, 2H), 1.57–1.48 (m, 1H), 1.47–1.35 (m, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.2, 92.2, 77.4, 30.7, 25.6, 23.4; HRMS (ESI) calcd for C$_6$H$_{10}$ [M-C$_2$H$_2$Cl$_3$NO]$^+$: 82.0783, found: 82.0783.

![Compound 23-1](image)

Compound 23-1 was prepared following the general procedure in 81% yield as colorless oil (R$_f$ = 0.5, Hexanes:EtOAc = 40:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.16 (br s, 1H), 5.11–4.99 (m, 1H), 2.01–1.92 (m, 2H), 1.86–1.76 (m, 2H), 1.73–1.65 (m, 2H), 1.61–1.53 (m, 4H), 1.51–1.42 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.0, 92.2, 80.0, 32.9, 28.3, 22.8; HRMS (ESI) calcd for C$_7$H$_{12}$ [M-C$_2$H$_2$Cl$_3$NO]$^+$: 96.0939, found: 96.0939.

![Compound 24-1](image)

Compound 24-1 was prepared following the general procedure in 65% yield as white solid (R$_f$ = 0.5, Hexanes:EtOAc = 20:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.23 (br s, 1H), 5.41 (d, $J$ = 4.4 Hz, 1H), 4.81–4.71 (m, 1H), 2.52 (dd, $J$ = 12.7, 3.2 Hz, 1H), 2.43 (t, $J$
= 11.6 Hz, 1H), 2.07–1.94 (m, 3H), 1.93–1.87 (m, 1H), 1.87–1.77 (m, 1H), 1.76–1.65 (m, 1H), 1.61–1.44 (m, 7H), 1.38–1.09 (m, 11H), 1.05 (s, 3H), 1.01–0.95 (m, 2H), 0.91 (d, J = 6.5 Hz, 3H), 0.86 (d, J = 5.4 Hz, 6H), 0.68 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 162.1, 139.6, 123.0, 92.1, 79.0, 56.8, 56.3, 50.2, 42.4, 39.9, 39.7, 37.5, 37.1, 36.8, 36.3, 35.9, 32.1, 32.0, 28.4, 28.2, 27.2, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.0; HRMS (ESI) calcd for C27H44[M-C2H2Cl3NO]+: 368.3443, found: 368.3456.

Compound 25-1 was prepared following the general procedure in 81% yield as white solid (Rf = 0.4, Hexanes:EtOAc = 8:1). 1H NMR (400 MHz, CDCl3) δ 8.22 (d, J = 3.4 Hz, 2H), 8.20 (s, 1H), 7.64 (t, J = 7.3 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.35 (d, J = 8.5 Hz, 1H), 6.99 (d, J = 8.5 Hz, 1H), 6.95 (s, 1H), 4.85 (t, J = 8.2 Hz, 1H), 2.98–2.84 (m, 2H), 2.42–2.28 (m, 3H), 2.04 (d, J = 12.0 Hz, 1H), 1.97–1.89 (m, 1H), 1.85–1.77 (m, 1H), 1.72–1.65 (m, 1H), 1.64–1.30 (m, 6H), 0.97 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 165.5, 163.1, 148.8, 138.3, 138.0, 133.6, 130.3, 129.8, 128.6, 126.6, 121.8, 118.8, 92.1, 87.5, 49.8, 44.2, 43.6, 38.3, 37.1, 29.7, 27.2, 27.1, 26.2, 23.4, 12.2; HRMS (ESI) calcd for C25H26O2[M-C2H2Cl3NO]+: 358.1933, found: 358.1934.

Compound 37 was prepared following the general procedure in 83% yield as white solid (Rf = 0.4, Hexanes:EtOAc = 40:1). 1H NMR (400 MHz, CDCl3) δ 8.18 (br s, 1H), 5.05 (t, J = 3.1 Hz, 1H), 2.23–2.10 (m, 4H), 1.91–1.75 (m, 8H), 1.62–1.57 (m, 2H); 13C NMR (101 MHz, CDCl3) δ 162.2, 92.3, 82.1, 37.5, 36.4, 31.9, 31.3, 27.3, 27.2; HRMS (ESI) calcd for C10H14[M-C2H2Cl3NO]+: 134.1096, found: 134.1093.
3.2 Preparation of compound 39

To a suspension of 1,2-octanediol 39-4 (1.6 mL, 10 mmol, 1 equiv) and imidazole (0.82 g, 12 mmol, 1.2 equiv) in CH$_2$Cl$_2$ (50 mL) was added TBDPSCI (2.60 mL, 10 mmol, 1.0 equiv) dropwise over 10 min. The reaction mixture was stirred at room temperature for 4 hours and then half of the CH$_2$Cl$_2$ was removed at reduced pressure. The remaining suspension was diluted with 250 mL of hexanes and the resulting precipitate was removed by filtration. The filtrate was concentrated and the crude product was purified by chromatography (5% to 30% EtOAc-hexanes) to give 3.26 g (85% yield) of compound 39-3 as colorless oil (R$_f$ = 0.6, Hexanes:EtOAc = 4:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76–7.60 (m, 4H), 7.50–7.39 (m, 6H), 3.80–3.74 (m, 1H), 3.70 (dd, $J$ = 10.1, 3.1 Hz, 1H), 3.54 (dd, $J$ = 9.7, 7.7 Hz, 1H), 2.60 (br s, 1H), 1.54–1.39 (m, 3H), 1.35–1.23 (m, 7H), 1.12 (s, 9H), 0.91 (t, $J$ = 6.5 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 135.6, 133.3, 129.9, 127.9, 72.1, 68.2, 32.9, 31.9, 29.4, 27.0, 25.6, 22.7, 19.4, 14.2.
Triphenylphosphine (4.46 g, 17 mmol, 2 equiv), imidazole (1.16 g, 17 mmol, 2 equiv) and iodine (4.31 g, 17 mmol, 2 equiv) were dissolved in dichloromethane (40 mL), the resulting mixture was stirred at room temperature for 1 hour. Then a solution of compound 39-3 (3.26 g, 8.5 mmol, 1.0 equiv) in dichloromethane (10 mL) was added dropwise over 10 minutes. The resulting solution was continuously stirred at room temperature for 1 hour and then washed with 40 mL H₂O and 40 mL of a sodium hydrogen sulfite (NaHSO₃) solution. The organic phase was dried over MgSO₄, filtered and evaporated on a rotary evaporator. During this evaporation triphenylphosphine oxide crystallized as a white mass. The crude product was transferred into a 25 mL beaker, homogenized with 3 mL diethyl ether, and filtered. The filter cake was washed with diethyl ether (2 x 5 mL), leaving pure white triphenylphosphine oxide. The combined filtrate was concentrated in vacuo, the resulting residue was purified by column chromatography (1% to 5% EtOAc-hexanes) to give 3.68 g (87%) of compound 39-2 as colorless oil (Rf = 0.7, Hexanes:EtOAc = 20:1). ¹H NMR (400 MHz, CDCl₃) δ 7.68–7.61 (m, 4H), 7.40–7.30 (m, 6H), 4.11–4.01 (m, 1H), 3.86 (dd, J = 10.8, 5.4 Hz, 1H), 3.75 (dd, J = 10.7, 7.2 Hz, 1H), 1.90–1.79 (m, 1H), 1.79–1.68 (m, 1H), 1.52–1.41 (m, 1H), 1.34–1.19 (m, 7H), 1.05 (s, 9H), 0.85 (t, J = 6.6 Hz, 3H).

A solution of compound 39-2 (3.68 g, 7.4 mmol, 1 equiv) in tetrahydrofuran (20 mL) was added to a mixture of tetrabutylammonium fluoride (TBAF) (2.88 g, 11 mmol, 1.5 equiv) and acetic acid in tetrahydrofuran (The pH value was adjusted to 5 by controlling the amount of acetic acid). The resulting reaction mixture was continuously stirred at room temperature. After 3 hours, the reaction mixture was diluted with water, the aqueous phase was separated and extracted with dichloromethane. The combined organic layer was washed with brine, dried over Na₂SO₄, filtered and concentrated in
The residue was purified by column chromatography (5% to 30% EtOAc-hexanes) to give compound 39-1 (1.72 g) in 91% yield as colorless oil ($R_f = 0.5$, Hexanes:EtOAc = 4:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.28–4.18 (m, 1H), 3.80–3.65 (m, 2H), 2.01 (t, $J = 6.8$ Hz, 1H), 1.93–1.81 (m, 1H), 1.81–1.71 (m, 1H), 1.58–1.47 (m, 1H), 1.42–1.26 (m, 7H), 0.88 (t, $J = 6.7$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 68.7, 42.3, 36.4, 31.7, 29.5, 28.6, 22.7, 14.2.

To a stirred mixture of compound 39-1 (1.72 g, 6.7 mmol, 1 equiv) in 20 mL of dichloromethane, was added trichloroacetonitrile (1.0 mL, 10 mmol, 1.5 equiv) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.1 mL, 0.67 mmol, 0.1 equiv). The resulting reaction mixture was continuously stirred at room temperature. After 12 hours, the reaction mixture was diluted with water, the aqueous phase was separated and extracted with dichloromethane. The combined organic layer was washed with brine, dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The residue was purified by column chromatography with triethylamine-treated silica gel using 3% of triethylamine in hexane as eluent to give compound 39 (2.35 g) in 88% yield as colorless oil ($R_f = 0.2$, Hexanes:EtOAc = 20:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.35 (br s, 1H), 4.59 (dd, $J = 11.3$, 5.7 Hz, 1H), 4.43 (dd, $J = 11.3$, 7.6 Hz, 1H), 4.36–4.28 (m, 1H), 1.90–1.79 (m, 2H), 1.60–1.47 (m, 1H), 1.43–1.36 (m, 1H), 1.34–1.24 (m, 6H), 0.86 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.0, 91.2, 73.6, 36.3, 31.6, 29.7, 29.0, 28.5, 22.6, 14.2.

3.3 Experimental procedure for preparation of benzimidates 28-1, 30-1, 31-1
Acetyl chloride (7.1 mL, 100 mmol, 10 equiv) was added dropwise to a stirred mixture of aromatic cyanide (10 mmol, 1 equiv) in the corresponding alcohol (20 mL) at 0 °C. The resulting solution was allowed to warm up to room temperature and continuously stirred for 24 hours. The reaction mixture was then concentrated in vacuo. The residue was dissolved in dichloromethane and washed with Sat. NaHCO₃ and brine. The organic layer was separated, dried with Na₂SO₄, filtered and concentrated in vacuo. The resulting residue was purified by chromatography on silica gel (10-30% EtOAc in hexanes) to give the desired product.

Compound 28-1 (3.5:1 mixture of inseparable isomers) was prepared in 45% yield as colorless oil (R₂F = 0.4, Hexanes:EtOAc = 20:1).<sup>1</sup>H NMR (400 MHz, DMSO-d₆) δ 9.58 (br s, 1H), 8.52–8.32 (m, 2H), 7.99 (s, 1H), 4.24 (q, J = 6.9 Hz, 1.51H), 4.11 (q, J = 6.6 Hz, 0.44H), 1.28 (t, J = 7.0 Hz, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-d₆) δ 161.4, 157.8, 136.4, 134.3, 130.7 (q, J_C:F = 33 Hz), 127.4, 123.6, 123.0 (q, J_C:F = 270 Hz), 61.4, 61.0, 13.6, 13.4; <sup>19</sup>F NMR (376 MHz, CDCl₃) δ -63.00 (s, 6F): HRMS (ESI) calcd for C₁₁H₁₀F₆NO [M+H⁺]: 286.0661, found: 286.0660.
Compound 30-1 was prepared in 58% yield as colorless oil (R_f = 0.3, Hexanes:EtOAc = 2:1). ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 6.5 Hz, 2H), 7.46–7.39 (m, 3H), 4.03 (d, J = 5.9 Hz, 2H), 2.19–2.06 (m, 1H), 1.05 (d, J = 6.7 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 168.3, 133.0, 130.8, 128.5, 126.7, 72.3, 27.9, 19.4.

Compound 31-1 was prepared in 61% yield as colorless oil (R_f = 0.6, Hexanes:EtOAc = 4:1). ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 4.37 (q, J = 7.0 Hz, 2H), 2.41 (s, 3H), 1.46 (t, J = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 167.6, 140.8, 130.0, 129.0, 126.5, 61.5, 21.2, 14.1.

3.4 Experimental procedure for preparation of benzimidates 29-1, 32-1, 33-1, 34-1, 35-1, 36-1

A mixture of corresponding alcohol (5 mmol, 1 equiv) and aromatic cyanide (5 mmol, 1 equiv) in 4 M HCl in dioxane (12.5 mL, 50 mmol, 10 equiv) were stirred at room temperature for 24 hours. The reaction mixture was then concentrated _in vacuo_. The residue was dissolved in dichloromethane, washed with Sat. NaHCO₃ and brine. The organic layer was separated, dried with Na₂SO₄, filtered and concentrated _in vacuo_. The
resulting residue was purified by chromatography on silica gel (10-30% EtOAc in hexanes) to give the desired product.

Compound 29-1 was prepared in 65% yield as colorless oil (R_f = 0.4, Hexanes:EtOAc = 20:1). ^1H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 7.0 Hz, 2H), 7.47–7.36 (m, 3H), 4.24 (t, J = 6.6 Hz, 2H), 1.84–1.75 (m, 2H), 1.52–1.42 (m, 2H), 1.39–1.24 (m, 8H), 0.88 (t, J = 6.8 Hz, 3H); ^13C NMR (101 MHz, CDCl₃) δ 167.9, 133.0, 130.8, 128.5, 126.7, 77.5, 77.2, 76.8, 66.2, 31.9, 29.4, 29.3, 28.7, 26.3, 22.7, 14.1; HRMS (ESI) calcd for C₁₅H₂₄NO [M+H⁺]: 234.1852, found: 234.1855.

Compound 32-1 was prepared in 72% yield as colorless oil (R_f = 0.3, Hexanes:EtOAc = 20:1). ^1H NMR (400 MHz, CDCl₃) δ 7.68 (s, 2H), 7.47–7.37 (m, 3H), 7.34–7.30 (m, 4H), 7.27–7.21 (m, 1H), 4.51 (br s, 2H), 3.13 (t, J = 6.9 Hz, 2H); ^13C NMR (101 MHz, CDCl₃) δ 168.2, 138.6, 132.7, 130.9, 129.1, 128.5, 126.6, 126.4, 66.7, 35.2; HRMS (ESI) calcd for C₁₅H₁₆NO [M+H⁺]: 226.1226, found: 226.1226.

Compound 33-1 was prepared in 67% yield as colorless oil (R_f = 0.3, Hexanes:EtOAc = 20:1). ^1H NMR (400 MHz, CDCl₃) δ 7.71 (d, J = 7.0 Hz, 2H), 7.42–7.32 (m, 3H), 4.03 (d, J = 5.8 Hz, 2H), 1.89–1.78 (m, 3H), 1.77–1.70 (m, 2H), 1.70–1.62 (m, 1H), 1.32–1.15 (m, 3H), 1.12–1.01 (m, 2H); ^13C NMR (101 MHz, CDCl₃) δ 167.7, 132.9, 130.7, 128.3, 126.6, 71.2, 37.2, 29.9, 26.4, 25.8; HRMS (ESI) calcd for C₁₄H₂₀NO [M+H⁺]: 218.1539, found: 218.1544.
Compound 34-1 was prepared in 41% yield as colorless oil ($R_f = 0.3$, Hexanes:EtOAc = 20:1). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.85 (br s, 1H), 7.82 (d, $J = 7.0$ Hz, 2H), 7.53–7.38 (m, 3H), 5.17–5.06 (m, 1H), 2.42–2.31 (m, 2H), 2.13–2.00 (m, 2H), 1.77 (q, $J = 10.1$ Hz, 1H), 1.69–1.55 (m, 1H); $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 163.9, 132.3, 130.5, 128.2, 126.8, 68.8, 30.2, 13.3; HRMS (ESI) calcd for C$_{11}$H$_{14}$NO [M+H$^+$]: 176.1070, found: 176.1074.

Compound 35-1 was prepared in 36% yield as colorless oil ($R_f = 0.3$, Hexanes:EtOAc = 20:1). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.82 (br s, 1H), 7.83–7.77 (m, 2H), 7.53–7.40 (m, 3H), 5.36–5.30 (m, 1H), 1.99–1.83 (m, 2H), 1.82–1.68 (m, 4H), 1.65–1.54 (m, 2H); $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 164.5, 132.8, 130.6, 128.4, 126.8, 76.6, 32.3, 23.6; HRMS (ESI) calcd for C$_{12}$H$_{16}$NO [M+H$^+$]: 190.1226, found: 190.1226.

Compound 36-1 (4.8:1 mixture of inseparable isomers) was prepared in 30% yield as colorless oil ($R_f = 0.3$, Hexanes:EtOAc = 20:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.19 (s, 1H), 8.12 (d, $J = 7.8$ Hz, 0.34H), 8.02 (d, $J = 8.2$ Hz, 1.58H), 7.80 (d, $J = 8.3$ Hz, 2H), 5.04–4.93 (m, 0.81H), 4.70–4.61 (m, 0.17H), 1.98–1.81 (m, 2H), 1.71–1.65 (m, 2H), 1.57–1.45 (m, 3H), 1.42–1.24 (m, 3H); $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 162.9, 136.2, 130.6 (q, $J_{C,F} = 32.0$ Hz), 129.9,127.6, 125.4, 72.1, 30.8, 25.2, 23.2; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -62.86 (s, 3F); HRMS (ESI) calcd for C$_{14}$H$_{17}$F$_3$NO [M+H$^+$]: 272.1257, found: 272.1260.
4. Optimization of reaction conditions

Reactions were carried out in a 12 mL sealed vial at a 0.2 mmol scale on bench top. The vials were purged with Ar for 1 min if necessary. After 3 hours, the reactions mixture were cooled to room temperature and concentrated \textit{in vacuo}, the crude residue was dissolved in 1 mL of deuterated chloroform for $^1$H-NMR analysis. 1,1,2,2-tetrachloroethane (33.6 mg, 0.2 mmol, 1 equiv, a singlet peak around 5.97 ppm was set as 2.00) was added as internal standard. Yields of compounds 2 were determined based on the following method:

Yield of 2 = integration of peak (δ $4.62$) × 100%

Table S1. Evaluation of different oxidants and solvents$^a$

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<th>entry</th>
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<th>yield (%)$^b$</th>
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<td>Entry</td>
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<td>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</td>
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(a) All the reactions were run on a 0.2 mmol scale. (b) <sup>1</sup>H-NMR yield using 1,1,2,2-tetrachloroethane as internal standard. (c) ND: not detected.

**Table S2. Evaluation of more oxidants and reaction concentration**

![Chemical structure](image.png)

DCE, Ar, 110 °C, 3 h
(a) All the reactions were run on a 0.2 mmol scale. (b) $^1$H-NMR yield using 1,1,2,2-tetrachloroethane as internal standard. (c) ND: not detected.

### Table S3. Evaluation of different hydrolization conditions

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<td>13</td>
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1. NIS (3 equiv), DCE (0.5 mL), Ar, 110 °C, 3 h
2. aq. HCl (12 N), THF, rt

$\delta$ 4.27 (t, $J = 6.6$ Hz, 2H)

$\delta$ 3.78 (dd, $J = 11.7$, 3.4 Hz, 1H)

$\delta$ 3.56 (dd, $J = 11.6$, 6.7 Hz, 1H)
A mixture of octyl trichloroacetimidate 1 (55 mg, 0.2 mmol, 1.0 equiv), NIS (135 mg, 0.6 mmol, 3 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 °C for 3 hours. The mixture was then cooled to room temperature and diluted with THF (if necessary). Specific amount of aq. HCl (12 M) was added according to the Table S2, and the resulting mixture was continuously stirred at room temperature. Then the mixture was concentrated in vacuo, the crude residue was dissolved in 1 mL of deuterated chloroform for $^1$H-NMR analysis. 1,1,2,2-tetrachloroethane (33.6 mg, 0.2 mmol, 1 equiv, a singlet peak around 5.97 ppm was set as 2.00) was added as internal standard. Yields of compounds 3 were determined based on the following method:

Yield of 3 = integration of peak (δ 3.78) $\times$ 100%

5. Hydrolization of oxazoline 2 under different conditions

A mixture of octyl trichloroacetimidate 1 (55 mg, 0.2 mmol, 1.0 equiv), NIS (135 mg, 0.6 mmol, 3 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 °C for 3 hours. The mixture was then cooled to room temperature and concentrated in vacuo, the residue was purified by silica gel flash chromatography to give oxazoline 2 in 33% yield as colorless oil and 27 in 40% yield as white solid.
$$R_f = 0.4, \text{Hexanes:EtOAc} = 10:1$$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.62 (t, $J = 8.0$ Hz, 1H), 4.34–4.24 (m, 1H), 4.19 (t, $J = 8.0$ Hz, 1H), 1.77–1.66 (m, 1H), 1.59–1.48 (m, 1H), 1.42–1.34 (m, 1H), 1.32–1.21 (m, 7H), 0.83 (t, $J = 6.7$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.1, 86.7, 75.9, 67.1, 34.9, 31.7, 29.1, 25.4, 22.6, 14.1; HRMS (ESI) calcd for C$_{10}$H$_{17}$Cl$_3$NO [M+H$^+$]: 272.0370, found: 272.0376.

$$R_f = 0.5, \text{Hexanes:EtOAc} = 4:1$$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.85 (d, $J = 7.7$ Hz, 1H), 4.01–3.91 (m, 1H), 3.79 (dd, $J = 11.1$, 3.6 Hz, 1H), 3.72 (dd, $J = 11.0$, 4.3 Hz, 1H), 1.78 (br s, 1H), 1.67–1.58 (m, 3H), 1.39–1.32 (m, 3H), 1.32–1.26 (m, 4H), 0.88 (t, $J = 6.9$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.3, 92.8, 63.9, 53.5, 31.7, 30.9, 29.1, 25.9, 22.6, 14.1; HRMS (ESI) calcd for C$_{10}$H$_{19}$Cl$_3$NO$_2$ [M+H$^+$]: 290.0476, found: 290.0467.

Scheme S8
A mixture of octyl trichloroacetimidate 1 (55 mg, 0.2 mmol, 1.0 equiv), NIS (135 mg, 0.6 mmol, 3 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 °C for 3 hours. The mixture was then cooled to room temperature and diluted with THF (4 mL). aq. HCl (166 µL, 12 M, 10 equiv) was added, and the resulting mixture was continuously stirred for 5 h at room temperature. Then the mixture was concentrated in vacuo, the crude residue was purified by chromatography on silica gel (5%-10% methanol in dichloromethane) to give compound 3 in 74% yield as pale yellow oil (Rf = 0.4, CH2Cl2:MeOH = 8:1). 1H NMR (400 MHz, MeOD-d4) δ 3.78 (dd, J = 11.7, 3.4 Hz, 1H), 3.56 (dd, J = 11.6, 6.7 Hz, 1H), 3.24–3.16 (m, 1H), 1.73–1.56 (m, 2H), 1.36 (m, 8H), 0.94 (t, J = 6.7 Hz, 3H); 13C NMR (101 MHz, MeOD-d4) δ 63.0, 55.4, 33.3, 31.1, 30.8, 27.1, 24.2, 15.1.
(s, 1H), 1.92-1.81 (m, 1H), 1.78-1.65 (m, 1H), 1.44-1.21 (m, 8H), 0.88 (t, J = 5.8 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 61.4, 54.7, 31.7, 29.7, 29.2, 25.8, 22.7, 14.2.

![Chemical Structure](27)

A mixture of octyl trichloroacetimidate 1 (55 mg, 0.2 mmol, 1.0 equiv), NIS (135 mg, 0.6 mmol, 3 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 °C for 3 hours. The mixture was then cooled to room temperature and mixed with silica gel (500 mg) and concentrated. The resulting mixture was placed at room temperature overnight then purified by silica gel flash chromatography to give compound 27 in 80% yield.

6. Substrate scope of β-C(sp$^3$)-H amination of trichloroacetimidates

![Chemical Reaction](Scheme S8)

6.1 General experimental procedure A for preparation of 1,2-aminol alcohol hydrochlorides: A mixture of trichloroacetimidate (0.2 mmol, 1.0 equiv), NIS (135 mg, 0.6 mmol, 3 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 °C for 3 hours. The mixture was then cooled to room temperature and diluted with THF (4 mL). aq. HCl (166 µL, 12 M, 10 equiv) was added, and the resulting mixture was continuously stirred for 5 h at room temperature. Then the mixture was concentrated in vacuo, the crude residue was purified by chromatography on silica gel (5%-10% methanol in dichloromethane) to give the desired product.
Compound 4 was prepared following the general procedure A in 63% yield as pale yellow oil (Rf = 0.3, CH₂Cl₂:MeOH = 2:1). ¹H NMR (400 MHz, MeOD-d₄) δ 3.80 (t, J = 5.1 Hz, 2H), 3.08 (t, J = 5.1 Hz, 2H); ¹³C NMR (101 MHz, MeOD-d₄) δ 59.7, 43.7.

Compound 5 was prepared following the general procedure A in 69% yield as pale yellow oil (Rf = 0.3, CH₂Cl₂:MeOH = 4:1). ¹H NMR (400 MHz, MeOD-d₄) δ 4.04–3.94 (m, 1H), 3.03 (dd, J = 12.7, 2.9 Hz, 1H), 2.79 (dd, J = 12.6, 9.3 Hz, 1H), 1.26 (d, J = 6.3 Hz, 3H); ¹³C NMR (101 MHz, MeOD-d₄) δ 65.7, 48.0, 21.9.

Compound 7 (1.8:1 mixture of inseparable isomers) was prepared following the general procedure A in 39% yield as pale yellow oil (Rf = 0.3, CH₂Cl₂:MeOH = 4:1). ¹H NMR (400 MHz, MeOD-d₄) δ 3.99–3.92 (m, 0.37H), 3.71–3.61 (m, 0.69H), 3.31–3.22 (m, 0.48H), 3.10–3.01 (m, 0.66H), 1.31–1.20 (m, 6H); ¹³C NMR (101 MHz, MeOD-d₄) δ 70.3, 68.4, 55.7, 54.2, 21.2, 19.5, 16.6, 13.3.

Compound 8 was prepared following the general procedure A in 74% yield as pale yellow oil (Rf = 0.3, CH₂Cl₂:MeOH = 4:1). ¹H NMR (400 MHz, MeOD-d₄) δ 3.75 (dd, J = 11.6, 3.9 Hz, 1H), 3.53 (dd, J = 11.6, 7.1 Hz, 1H), 3.42–3.34 (m, 1H), 1.30 (d, J = 6.7 Hz, 3H); ¹³C NMR (101 MHz, MeOD-d₄) δ 64.8, 51.4, 16.0.
Compound 9\(^{[8]}\) was prepared following the general procedure A in 76% yield as pale yellow oil (R\(_f\) = 0.4, CH\(_2\)Cl\(_2\):MeOH = 4:1). \(^1\)H NMR (400 MHz, MeOD-\(d_4\)) \(\delta\) 3.80 (dd, \(J = 11.7, 3.7\) Hz, 1H), 3.60 (dd, \(J = 11.8, 6.7\) Hz, 1H), 3.21–3.13 (m, 1H), 1.78–1.65 (m, 2H), 1.06 (t, \(J = 7.5\) Hz, 3H); \(^13\)C NMR (101 MHz, MeOD-\(d_4\)) \(\delta\) 62.4, 56.6, 24.0, 11.0.

![Compound 9](image)

Compound 10 was prepared following the general procedure A in 77% yield as pale yellow oil (R\(_f\) = 0.5, CH\(_2\)Cl\(_2\):MeOH = 8:1). \(^1\)H NMR (400 MHz, MeOD-\(d_4\)) \(\delta\) 3.78 (dd, \(J = 11.7, 3.6\) Hz, 1H), 3.56 (dd, \(J = 11.7, 6.8\) Hz, 1H), 3.25–3.14 (m, 1H), 1.73–1.55 (m, 2H), 1.49–1.28 (m, 14H), 0.93 (t, \(J = 6.8\) Hz, 3H); \(^13\)C NMR (101 MHz, MeOD-\(d_4\)) \(\delta\) 63.0, 55.5, 33.7, 31.3, 31.24, 31.21, 31.17, 31.1, 27.2, 24.4, 15.2; HRMS (ESI) calcd for C\(_{11}\)H\(_{26}\)NO [M+H\(^+\)]: 188.2009, found: 188.2013.

![Compound 10](image)

Compound 11\(^{[9]}\) (1.1:1 mixture of inseparable isomers) was prepared following the general procedure A in 63% yield as pale yellow oil (R\(_f\) = 0.4, CH\(_2\)Cl\(_2\):MeOH = 8:1). \(^1\)H NMR (400 MHz, MeOD-\(d_4\)) \(\delta\) 7.57–7.42 (m, 5H), 4.29–4.21 (m, 1H), 4.14–4.04 (m, 0.58H), 4.00 (d, \(J = 9.2\) Hz, 0.52H), 1.08 (d, \(J = 6.2\) Hz, 1.6H), 1.08 (d, \(J = 6.3\) Hz, 1.4H); \(^13\)C NMR (101 MHz, MeOD-\(d_4\)) \(\delta\) 137.2, 135.7, 131.4, 131.2, 130.9, 130.6, 130.5, 129.8, 70.4, 68.8, 64.3, 61.9, 21.5, 20.5.

![Compound 11](image)

Compound 12\(^{[10]}\) was prepared following the general procedure A in 38% yield as pale yellow oil (R\(_f\) = 0.5, CH\(_2\)Cl\(_2\):MeOH = 4:1). \(^1\)H NMR (400 MHz, MeOD-\(d_4\)) \(\delta\) 3.51 (s, 2H), 1.32 (s, 6H); \(^13\)C NMR (101 MHz, MeOD-\(d_4\)) \(\delta\) 68.8, 57.0, 23.5.
Compound 13-1 was aminated following the general procedure A to give compound 13 in 83% yield as white solid ($R_f = 0.5$, CH$_2$Cl$_2$:MeOH = 4:1). For easy characterization analysis by NMR, compound 13 was dissolved in dichloromethane, washed with Sat. NaHCO$_3$ and brine. The organic phase was dried with Na$_2$SO$_4$, filtered and concentrated in vacuo to afford compound 13'. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.67 (d, $J = 7.5$ Hz, 2H), 7.60 (d, $J = 7.4$ Hz, 2H), 7.38 (t, $J = 7.4$ Hz, 2H), 7.30 (t, $J = 7.4$ Hz, 2H), 3.71 (s, 2H), 2.75 (br s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 148.3, 139.7, 128.8, 127.9, 124.0, 120.2, 69.1, 65.9; HRMS (ESI) calcd for C$_{14}$H$_{14}$NO [M+H$^+$]: 212.1070, found: 212.1068.

Compound 14$^{[1]}$ was prepared following the general procedure A in 63% yield as pale yellow oil ($R_f = 0.5$, CH$_2$Cl$_2$:MeOH = 4:1). $^1$H NMR (400 MHz, MeOD-$d_4$) $\delta$ 8.83 (d, $J = 4.8$ Hz, 1H), 8.33 (t, $J = 7.7$ Hz, 1H), 7.91 (d, $J = 7.9$ Hz, 1H), 7.80 (t, $J = 6.3$ Hz, 1H), 4.78–4.73 (m, 1H), 4.08 (dd, $J = 11.6, 4.2$ Hz, 1H), 3.96 (dd, $J = 11.6, 6.2$ Hz, 1H); $^{13}$C NMR (101 MHz, MeOD-$d_4$) $\delta$ 153.2, 147.7, 145.2, 128.1, 126.6, 63.9, 57.0.

Compound 15 was prepared following the general procedure A in 77% yield as pale yellow oil ($R_f = 0.3$, CH$_2$Cl$_2$:MeOH = 4:1). $^1$H NMR (400 MHz, MeOD-$d_4$) $\delta$ 7.53 (d, $J = 7.3$ Hz, 1H), 7.45–7.29 (m, 3H), 4.76 (dd, $J = 11.0, 5.5$ Hz, 1H), 4.63 (d, $J = 5.2$ Hz,
1H), 3.27 (dd, J = 16.3, 6.2 Hz, 1H), 3.06 (dd, J = 16.3, 4.9 Hz, 1H); $^{13}$C NMR (101 MHz, MeOD-$d_4$) δ 143.4, 138.3, 131.6, 129.1, 127.4, 127.1, 72.4, 59.2, 40.9; HRMS (ESI) calcd for C$_9$H$_{12}$NO [M+H$^+$]: 150.0913, found: 150.0912.

Compound 15 was dissolved in ethyl acetate and washed with Sat. NaHCO$_3$ and brine. The organic phase was dried over anhydrous Na$_2$SO$_4$, filtered and concentrated in vacuo to give compound 15'. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.30 (d, J = 5.1 Hz, 1H), 7.25 (m, 3H), 4.42–4.36 (m, 1H), 4.32 (d, J = 5.2 Hz, 1H), 3.10 (dd, J = 16.4, 5.5 Hz, 1H), 2.95 (dd, J = 16.4, 2.4 Hz, 1H), 2.38 (br s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 144.1, 141.0, 128.1, 127.1, 125.6, 124.0, 72.9, 58.6, 39.5. The spectra data are consistent with those of cis-1-amino-2-indanol reported in literature.$^{[12]}$

$\text{NH}_2$\text{-HCl}

Compound 16 was prepared following the general procedure A in 76% yield as pale yellow oil (R$_f$ = 0.3, CH$_2$Cl$_2$:MeOH = 4:1). $^1$H NMR (400 MHz, MeOD-$d_4$) δ 4.13–4.07 (m, 1H), 4.02 (dd, J = 11.7, 4.0 Hz, 1H), 3.91 (dd, J = 11.6, 6.2 Hz, 1H), 3.24 (t, J = 7.0 Hz, 2H), 1.66–1.52 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H); $^{13}$C NMR (101 MHz, MeOD-$d_4$) δ 169.0, 62.6, 57.0, 43.2, 24.2, 12.6; HRMS (ESI) calcd for C$_6$H$_{15}$N$_2$O$_2$ [M+H$^+$]: 147.1128, found: 147.1129.

$\text{NH}_2$\text{-HCl}

Compound 17$^{[13]}$ (mixture of 1.6:1 inseparable isomers) was prepared following the general procedure A in 62% yield as pale yellow oil (R$_f$ = 0.3, CH$_2$Cl$_2$:MeOH = 4:1). $^1$H NMR (400 MHz, MeOD-$d_4$) δ 4.35–4.23 (m, 1H), 4.11 (d, J = 2.5 Hz, 0.57H), 3.96 (d, J = 3.4 Hz, 0.40H), 3.88 (s, 3H), 1.35 (d, J = 6.5 Hz, 1.23H), 1.29 (d, J = 6.5 Hz, 1.72H);
\[^{13}\text{C NMR}\] (101 MHz, MeOD-\(d_4\)) δ 170.2, 169.4, 67.2, 67.1, 60.6, 60.2, 54.9, 54.7, 21.4, 19.6.

Compound 18\(^{[14]}\) (mixture of 1:1 inseparable isomers) was prepared following the general procedure A in 70\% yield as pale yellow oil (\(R_f = 0.2\), CH\(_2\)Cl\(_2\):MeOH = 4:1).

\[^{1}\text{H NMR}\] (400 MHz, MeOD-\(d_4\)) δ 4.43 (t, \(J = 5.9\) Hz, 1H), 4.09 (s, 1H), 4.05–3.96 (m, 1H), 3.91–3.80 (m, 1H), 3.75 (s, 3H), 2.30–2.16 (m, 1H), 0.99 (d, \(J = 6.9\) Hz, 6H); \[^{13}\text{C NMR}\] (101 MHz, MeOD-\(d_4\)) δ 173.1, 173.0, 168.5, 168.4, 67.4, 28.6, 27.6.

\[^{1}\text{H NMR}\] (400 MHz, MeOD-\(d_4\)) δ 7.43 (d, \(J = 7.3\) Hz, 1H), 7.38–7.23 (m, 3H), 4.43 (d, \(J = 3.8\) Hz, 1H), 4.28–4.17 (m, 1H), 3.11–3.01 (m, 1H), 2.97–2.85 (m, 1H), 2.11–2.00 (m, 1H), 1.99–1.86 (m, 1H); \[^{13}\text{C NMR}\] (101 MHz, MeOD-\(d_4\)) δ 138.8, 132.0, 131.5, 131.0, 130.9, 128.4, 67.4, 54.8, 28.6, 27.6;

HRMS (ESI) calcd for C\(_{10}\)H\(_{14}\)NO [M+H\(^+\)]: 164.1070, found: 164.1069.

Compound 19 was dissolved in ethyl acetate and washed with Sat. NaHCO\(_3\) and brine. The organic phase was dried over anhydrous Na\(_2\)SO\(_4\), filtered and concentrated \textit{in vacuo} to give compound 19'. \[^{1}\text{H NMR}\] (400 MHz, CDCl\(_3\)) δ 7.34–7.26 (m, 1H), 7.24–7.15 (m, 2H), 7.11 (d, \(J = 6.4\) Hz, 1H), 3.97–3.86 (m, 2H), 2.97–2.86 (m, 1H), 2.85–2.72 (m, 1H), 2.28 (br s, 3H), 1.98–1.88 (m, 1H), 1.87–1.74 (m, 1H); \[^{13}\text{C NMR}\] (101 MHz, CDCl\(_3\)) δ 139.6, 135.8, 129.6, 128.9, 127.3, 126.4, 68.6, 52.5, 27.6, 26.8. The spectra
data are consistent with those of cis-1-amino-2-hydroxy-1,2,3,4-tetrahydronaphthalene reported in literature.\textsuperscript{15}

\begin{center}
\includegraphics[width=0.4\textwidth]{compound_24.png}
\end{center}

Compound 24 was prepared following the general procedure A in 62% yield on 0.2 mmol scale (84% yield was obtained on 2 mmol scale) as white solid ($R_f = 0.6$, CH$_2$Cl$_2$:MeOH = 8:1). $^1$H NMR (400 MHz, MeOD-$d_4$) $\delta$ 5.90 (d, $J = 2.0$ Hz, 1H), 3.79 (t, $J = 4.5$ Hz, 1H), 3.74 (dd, $J = 10.0, 4.5$ Hz, 1H), 2.23–2.14 (m, 1H), 2.11–2.04 (m, 1H), 1.93–1.85 (m, 2H), 1.82–1.75 (m, 2H), 1.72–1.58 (m, 3H), 1.57–1.48 (m, 3H), 1.46–1.29 (m, 5H), 1.26–1.12 (m, 7H), 1.09 (s, 3H), 1.07–0.99 (m, 3H), 0.95 (d, $J = 6.5$ Hz, 3H), 0.89 (dd, $J = 6.6, 1.3$ Hz, 6H), 0.74 (s, 3H); $^{13}$C NMR (101 MHz, MeOD-$d_4$) $\delta$ 139.4, 135.3, 70.2, 63.6, 61.4, 58.9, 58.1, 52.1, 44.2, 41.6, 41.4, 38.1, 37.8, 37.5, 34.0, 33.5, 30.9, 29.8, 26.7, 25.9, 25.7, 24.0, 23.7, 22.3, 21.6, 20.1, 13.1; HRMS (ESI) calcd for C$_{27}$H$_{48}$NO [M+H$^+$]: 402.3730, found: 402.3732.

6.2 General experimental procedure B for preparation of 1,2-aminol alcohol hydrochlorides: A mixture of trichloroacetimidate (0.2 mmol, 1.0 equiv), NIS (135 mg, 0.6 mmol, 3 equiv) and Ag$_2$O (69 mg, 0.3 mmol, 1.5 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 ℃ for 3 hours. The mixture was then cooled to room temperature, diluted with THF (4 mL) and filtered through a pad of Celite. aq. HCl (166 µL, 12 M, 10 equiv) was added, and the resulting mixture was continuously stirred for 5 h at 80 ℃. Then the mixture was concentrated in vacuo, the residue was purified by chromatography on silica gel (5%-10% methanol in dichloromethane) to give the desired product.
Compound 21 was prepared following the general procedure B in 68% yield (45% yield was obtained when the general procedure A was applied) as pale yellow oil ($R_f$ = 0.4, CH$_2$Cl$_2$:MeOH = 4:1). $^1$H NMR (400 MHz, MeOD-$d_4$) $\delta$ 4.25 (d, $J = 3.6$ Hz, 1H), 3.44 (dd, $J = 12.8$, 7.6 Hz, 1H), 2.15–2.03 (m, 1H), 2.01–1.89 (m, 2H), 1.84–1.72 (m, 2H), 1.71–1.61 (m, 1H); $^{13}$C NMR (101 MHz, MeOD-$d_4$) $\delta$ 72.7, 56.5, 34.6, 29.4, 22.2. The spectra data are consistent with those reported in literature.$^{[16]}$

Compound 22 was prepared following the general procedure B in 48% yield as pale yellow oil ($R_f$ = 0.4, CH$_2$Cl$_2$:MeOH = 8:1). $^1$H NMR (400 MHz, MeOD-$d_4$) $\delta$ 4.02 (d, $J = 2.3$ Hz, 1H), 3.25–3.18 (m, 1H), 1.88–1.82 (m, 1H), 1.81–1.71 (m, 3H), 1.70–1.56 (m, 2H), 1.50–1.39 (m, 2H); $^{13}$C NMR (101 MHz, MeOD-$d_4$) $\delta$ 67.3, 54.8, 33.1, 26.9, 25.0, 20.9. The spectra data are consistent with those reported in literature.$^{[17]}$

Compound 23 (3:1 mixture of inseparable isomers) was prepared following the general procedure B in 61% yield as pale yellow oil ($R_f$ = 0.4, CH$_2$Cl$_2$:MeOH = 8:1). $^1$H NMR (400 MHz, MeOD-$d_4$) $\delta$ 4.07 (s, 1H), 3.60–3.51 (m, 0.32H), 3.30 (m, 1H), 2.98 (t, $J = 8.7$ Hz, 0.31H), 1.98–1.66 (m, 8H), 1.66–1.38 (m, 5H); $^{13}$C NMR (101 MHz, MeOD-$d_4$) $\delta$ 75.4, 70.6, 60.8, 57.9, 36.2, 34.7, 30.0, 29.7, 28.4, 28.3, 25.7, 25.0, 23.6, 22.8. The spectra data are consistent with those reported in literature.$^{[18]}$

6.3 Experimental procedure for preparation of compound 6 and 20
Scheme S9

A mixture of commercial available tert-butyl trichloroacetimidate 6-1 (43.4 mg, 0.2 mmol, 1.0 equiv), NIS (135.0 mg, 0.6 mmol, 3 equiv) and Ag₂O (69 mg, 0.3 mmol, 1.5 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 60 °C for 1 h. After been cooled to room temperature, the reaction mixture was filtered through a pad of Celite and the filtrate was mixed with silica gel (500 mg) and concentrated. The resulting mixture was placed at room temperature overnight then purified by silica gel flash chromatography to give compound 6 in 40% yield as white solid (Rf = 0.4, Hexanes:EtOAc = 2:1). ¹H NMR (400 MHz, CDCl₃) δ 7.15 (br s, 1H), 3.37 (d, J = 5.9 Hz, 2H), 1.78 (br s, 1H), 1.29 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 162.6, 92.9, 70.9, 51.5, 27.5; HRMS (ESI) calcd for C₆H₁₁Cl₃NO₂ [M+H⁺]: 233.9850, found: 233.9846.

Scheme S10

A mixture of cyclobutyl trichloroacetimidate 20-1 (43 mg, 0.2 mmol, 1.0 equiv), NIS (135 mg, 0.6 mmol, 3 equiv) and Ag₂O (69 mg, 0.3 mmol, 1.5 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 °C for 3 h. After been cooled to room temperature, the reaction mixture was filtered through a pad of Celite and the filtrate was mixed with silica gel (500 mg) and concentrated. The resulting mixture was placed at room temperature overnight then purified by silica gel flash chromatography to give compound 20 in 38% yield as colorless oil that solidifies at low temperature (Rf = 0.3, Hexanes:EtOAc = 4:1).
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.53 (br s, 1H), 4.69–4.55 (m, 1H), 4.39–4.25 (m, 1H), 2.47 (br s, 1H), 2.32–2.21 (m, 2H), 2.14–2.04 (m, 1H), 2.04–1.93 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 161.8, 92.6, 68.6, 50.5, 28.0, 25.0; HRMS (ESI) calcd for C$_6$H$_9$Cl$_3$NO$_2$ [M+H$^+$]: 231.9693, found: 231.9688.

6.4 Experimental procedure for preparation of compound 25

A mixture of compound 25-1 (104 mg, 0.2 mmol, 1.0 equiv), NIS (135 mg, 0.6 mmol, 3 equiv) and Ag$_2$O (69 mg, 0.3 mmol, 1.5 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 °C for 3 hours. After been cooled to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a pad of Celite. The filtrate was washed with Sat. Na$_2$SO$_3$ and brine. The organic phase was dried over anhydrous Na$_2$SO$_4$, filtered and concentrated in vacuo. The residue was purified by silica gel flash chromatography to give compound 25 in 52% yield as white solid ($R_f$ = 0.4, Hexanes:EtOAc = 10:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.20 (d, $J$ = 7.6 Hz, 2H), 7.63 (t, $J$ = 7.4 Hz, 1H), 7.51 (t, $J$ = 7.7 Hz, 2H), 7.33 (d, $J$ = 8.5 Hz, 1H), 6.99 (d, $J$ = 10.3 Hz, 1H), 6.94 (s, 1H), 4.77 (d, $J$ = 9.9 Hz, 1H), 4.66 (dd, $J$ = 17.3, 8.6 Hz, 1H), 2.95–2.88 (m, 2H), 2.49–2.36 (m, 2H), 2.35–2.27 (m, 1H), 2.19 (d, $J$ = 11.8 Hz, 1H), 2.02–1.92 (m, 1H), 1.67–1.50 (m, 5H), 1.49–1.42 (m, 1H), 0.88 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 165.5, 161.8, 148.9, 138.1, 137.3, 133.6, 130.2, 129.6, 128.6, 126.5, 121.8, 118.9, 94.5, 87.0, 71.0, 49.2, 45.5, 43.9, 37.7, 37.4, 32.2, 29.5, 27.7, 26.1, 12.2; HRMS (ESI) calcd for C$_{27}$H$_{27}$Cl$_3$NO$_3$ [M+H$^+$]: 518.1051, found: 518.1044.
6.5 Experimental procedure for gram scale reaction

A mixture of 1-octanol (1.04 g, 8 mmol, 1.0 equiv), trichloroacetonitrile (1.2 mL, 12 mmol, 1.5 equiv) and DBU (119 µL, 0.8 mmol, 0.1 equiv) in 1,2-dichloroethane (30 mL) in a 100 mL sealed tube was stirred at room temperature. After 12 hours, NIS (5.4 g, 24 mmol, 3 equiv) was added to the above reaction mixture, the resulting suspension was heated to 110 °C and continuously stirred under an atmosphere of Argon. After 12 hours, the reaction mixture was cooled to room temperature and concentrated in vacuo. The resulting residue was dissolve in tetrahydrofuran (20 mL) and aq. HCl (6.7 mL, 12 M, 10 equiv) were added. The mixture was continuously stirred for 12 hours before concentrated in vacuo and the resulting residue was purified by silica gel flash chromatography to give compound 3 in 70% yield (1.01 g).

7. Substrate scope of β-C(sp³)-H amination of benzimidates

7.1 General experimental C procedure H for β C-H amination of benzimidates.
A mixture of benzimidates (0.2 mmol, 1.0 equiv) and NIS (135 mg, 0.6 mmol, 3 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 °C for 3 hours. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate and washed with Sat. Na₂SO₃ and brine. The organic phase was dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. The residue was purified by silica gel flash chromatography to give the desired product.

Compound 28 was prepared following the general procedure C in 60% yield as colorless oil. (Rf = 0.4, Hexanes:EtOAc = 10:1). ¹H NMR (400 MHz, CDCl₃) δ 8.40 (s, 2H), 7.96 (s, 1H), 4.51 (t, J = 9.6 Hz, 2H), 4.12 (t, J = 9.6 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 162.4, 132.1 (q, J_C-F = 34 Hz), 130.0, 128.5, 124.8, 123.1 (q, J_C-F = 271 Hz), 68.4, 55.2; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.94 (s, 6F); HRMS (ESI) calcd for C₁₁H₈F₆NO [M+H⁺]: 284.0505, found: 284.0506.
Compound 29\textsuperscript{[19]} was prepared following the general procedure C in 85% yield as colorless oil ($R_f = 0.4$, Hexanes:EtOAc = 10:1). \textsuperscript{1}H NMR (400 MHz, CDCl$_3$) $\delta$ 8.02–7.92 (m, 2H), 7.51–7.45 (m, 1H), 7.44–7.37 (m, 2H), 4.49 (dd, $J = 9.3$, 8.2 Hz, 1H), 4.34–4.24 (m, 1H), 4.04 (t, $J = 7.9$ Hz, 1H), 1.85–1.71 (m, 1H), 1.61–1.52 (m, 1H), 1.51–1.43 (m, 1H), 1.43–1.26 (m, 7H), 0.90 (t, $J = 6.8$ Hz, 3H); \textsuperscript{13}C NMR (101 MHz, CDCl$_3$) $\delta$ 163.4, 131.3, 128.4, 128.3, 128.0, 72.7, 66.9, 36.1, 31.8, 29.4, 26.0, 22.7, 14.2.

Compound 30\textsuperscript{[20]} was prepared following the general procedure C in 71% yield as colorless oil ($R_f = 0.4$, Hexanes:EtOAc = 10:1). \textsuperscript{1}H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96–7.91 (m, 2H), 7.48–7.43 (m, 1H), 7.39 (t, $J = 7.4$ Hz, 2H), 4.10 (s, 2H), 1.38 (s, 6H); \textsuperscript{13}C NMR (101 MHz, CDCl$_3$) $\delta$ 162.2, 131.3, 128.4, 128.3, 128.2, 79.2, 67.7, 28.5.

Compound 31 was prepared following the general procedure C in 35% yield as colorless oil ($R_f = 0.4$, Hexanes:EtOAc = 4:1). \textsuperscript{1}H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 (d, $J = 8.2$ Hz, 2H), 7.21 (d, $J = 8.0$ Hz, 2H), 4.42 (t, $J = 9.5$ Hz, 2H), 4.05 (t, $J = 9.5$ Hz, 2H), 2.39 (s, 3H); \textsuperscript{13}C NMR (101 MHz, CDCl$_3$) $\delta$ 164.8, 141.7, 129.1, 128.1, 124.9, 67.6, 54.8, 21.6. The spectra data are consistent with those reported in literature.\textsuperscript{[21]}

Compound 33 was prepared following the general procedure C in 67% yield as colorless oil ($R_f = 0.4$, Hexanes:EtOAc = 10:1). \textsuperscript{1}H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97–7.90 (m, 2H), 7.48–7.43 (m, 1H), 7.42–7.35 (m, 2H), 4.15 (s, 2H), 1.87–1.73 (m, 4H), 1.66–1.58.
(m, 3H), 1.38–1.26 (m, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 161.6, 131.0, 128.2, 128.1, 77.0, 71.2, 37.5, 25.2, 23.0; HRMS (ESI) calcd for C$_{16}$H$_{18}$NO [M+H$^+$]: 216.1383, found: 216.1383.

7.2 General experimental D procedure H for β C-H amination of benzimidates.

Scheme S14

A mixture of benzimidates (0.2 mmol, 1.0 equiv), NIS (135 mg, 0.6 mmol, 3 equiv) and Ag$_2$O (69 mg, 0.3 mmol, 1.5 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 °C for 3 hours. After been cooled to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a pad of Celite. The filtrate was washed with Sat. Na$_2$SO$_3$ and brine. The organic phase was dried over anhydrous Na$_2$SO$_4$, filtered and concentrated in vacuo. The residue was purified by silica gel flash chromatography to give the desired product.
Compound 28 was prepared following the general procedure D in 72% yield as colorless oil.

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

Compound 31 was prepared following the general procedure D in 60% yield.

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

Compound 34 was prepared following the general procedure D in 64% yield as colorless oil ($R_f = 0.4$, Hexanes:EtOAc = 10:1). $^1\text{H NMR}$ (400 MHz, CDCl$_3$) $\delta$ 8.02–7.96 (m, 2H), 7.51–7.45 (m, 1H), 7.41 (dd, $J = 11.4$, 4.4 Hz, 2H), 5.06 (dd, $J = 6.7$, 3.9 Hz, 1H), 4.67 (dd, $J = 5.6$, 2.7 Hz, 1H), 2.58–2.48 (m, 2H), 2.35–2.25 (m, 1H), 2.22–2.12 (m, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl$_3$) $\delta$ 165.5, 131.5, 128.48, 128.45, 128.2, 79.0, 68.1, 30.2, 28.8; HRMS (ESI) calcd for C$_{11}$H$_{12}$NO [M+H$^+$]: 174.0913, found: 174.0916.

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

Compound 35$^{[19]}$ was prepared following the general procedure D in 66% yield as colorless oil ($R_f = 0.4$, Hexanes:EtOAc = 10:1). $^1\text{H NMR}$ (400 MHz, CDCl$_3$) $\delta$ 7.91 (d, $J = 7.9$ Hz, 2H), 7.46 (t, $J = 7.0$ Hz, 1H), 7.39 (t, $J = 7.6$ Hz, 2H), 5.11 (t, $J = 6.4$ Hz, 1H), 4.73 (t, $J = 7.3$ Hz, 1H), 2.08 (dd, $J = 13.1$, 6.0 Hz, 1H), 1.99 (dd, $J = 13.0$, 6.0 Hz, 1H), 1.80–1.71 (m, 1H), 1.70–1.62 (m, 2H), 1.56–1.42 (m, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl$_3$) $\delta$ 163.9, 131.3, 128.4, 128.3, 127.9, 84.9, 71.9, 34.9, 34.1, 22.4.

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

Compound 36$^{[22]}$ was prepared following the general procedure D in 52% yield as colorless oil ($R_f = 0.4$, Hexanes:EtOAc = 10:1). $^1\text{H NMR}$ (400 MHz, CDCl$_3$) $\delta$ 8.07 (d, $J = 8.1$ Hz, 2H), 7.66 (d, $J = 8.2$ Hz, 2H), 4.75–4.69 (m, 1H), 4.20–4.12 (m, 1H), 1.96–1.85 (m, 3H), 1.68–1.60 (m, 1H), 1.59–1.50 (m, 2H), 1.48–1.37 (m, 2H); $^{13}\text{C NMR}$
(101 MHz, CDCl$_3$) $\delta$ 163.2, 132.9 (q, $J_{C,F}=33$ Hz), 131.8, 128.6, 125.4 (q, $J_{C,F}=4$ Hz), 122.6, 79.4, 63.9, 27.7, 26.3, 19.9, 19.1; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -62.86 (s, 3F).

7.3 Experimental procedure for preparation of compound 32

A mixture of benzimidates 32-1 (45 mg, 0.2 mmol, 1.0 equiv), NIS (54 mg, 0.24 mmol, 1.2 equiv) and Ag$_2$O (28 mg, 0.12 mmol, 0.6 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 °C for 3 hours. After been cooled to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a pad of Celite. The filtrate was washed with Sat. Na$_2$SO$_3$ and brine. The organic phase was dried over anhydrous Na$_2$SO$_4$, filtered and concentrated in vacuo. The residue was purified by silica gel flash chromatography to give compound 32 in 82% yield as colorless oil ($R_f = 0.4$, Hexanes:EtOAc = 10:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.11–8.05 (m, 2H), 7.56–7.49 (m, 1H), 7.48–7.43 (m, 2H), 7.41–7.28 (m, 5H), 5.40 (dd, $J = 10.0$, 8.2 Hz, 1H), 4.80 (dd, $J = 10.1$, 8.4 Hz, 1H), 4.29 (t, $J = 8.3$ Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 164.8, 142.5, 131.6, 128.8, 128.55, 128.47, 127.71, 127.65, 126.9, 75.0, 70.2.

8. Mechanistic studies

8.1 Reaction of 2-adamantanol substrate 37
Scheme S16

A mixture of compound 37 (59.3 mg, 0.2 mmol, 1.0 equiv), NIS (135.0 mg, 0.6 mmol, 0.1 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 °C for 3 hours. After being cooled to room temperature, the mixture was washed with Sat. Na$_2$SO$_3$ and brine. The organic phase was dried over anhydrous Na$_2$SO$_4$, filtered and concentrated in vacuo. The residue was purified by silica gel flash chromatography to give compound 38 in 83% yield as white solid ($R_f = 0.2$, Hexanes:EtOAc = 20:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.70 (s, 1H), 5.94 (s, 1H), 2.97 (d, $J = 12.6$ Hz, 2H), 2.77 (s, 4H), 2.43 (d, $J = 11.6$ Hz, 2H), 1.87 (t, $J = 19.0$ Hz, 4H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 161.0, 92.0, 87.4, 51.7, 44.8, 43.4, 36.1, 35.7, 33.9; HRMS (ESI) calcd for C$_{12}$H$_{15}$Cl$_3$I$_2$NO [M+H$^+$]: 547.8303, found: 547.8292.

8.2 Observation of the iodinated intermediate 39

Scheme S17

A mixture of octyl trichloroacetimidate 1 (55 mg, 0.2 mmol, 1.0 equiv), NIS (135 mg, 0.6 mmol, 3 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 50 °C for 30 minutes. The mixture was then cooled...
to room temperature and concentrated *in vacuo*, the crude residue was dissolved in 1 mL of deuterated chloroform for $^1$H-NMR analysis. 1,1,2,2-tetrachloroethane (33.6 mg, 0.2 mmol, 1 equiv, a singlet peak around 5.97 ppm was set as 2.00) was added as internal standard. Yields of compounds 2 and 39 were determined based on the following method:

Yield of 2 = integration of peak (δ 4.62) × 100%

Yield of 39 = integration of peak (δ 4.59) × 100%

A mixture of compound 39 (80 mg, 0.2 mmol, 1.0 equiv) in 1,2-dichloroethane (1 mL) in a 12 mL glass vial (purged with Ar, sealed with PTFE cap) was heated at 110 °C for 10 minutes. The mixture was then cooled to room temperature and concentrated *in vacuo*, the crude residue was dissolved in 1 mL of deuterated chloroform for $^1$H-NMR analysis. 1,1,2,2-tetrachloroethane (33.6 mg, 0.2 mmol, 1 equiv, a singlet peak around 5.97 ppm was set as 2.00) was added as internal standard. Yields of compounds 2 were determined based on the following method:

Yield of 2 = integration of peak (δ 4.62) × 100%

9. X-ray crystallographic data

9.1 X-ray crystallographic data for compound 24
Compound 24 (219 mg, 0.5 mmol, 1 equiv) was dissolved in dichloromethane (5 mL) and cooled to 0 °C. To this solution was added triethylamine (346 µL, 2.5 mmol, 5 equiv) followed by dropwise addition of benzoyl chloride (144 µL, 1.25 mmol, 2.5 equiv). The resulting mixture was continuously stirred for 5 h at room temperature, then diluted with dichloromethane and sat. NH₄Cl. The organic layer was washed with sat. NaHCO₃ and brine, dried over Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography to give compound 24’ in 65% yield (198.3 mg) as white solid (Rf = 0.6, Hexanes:EtOAc = 10:1). 

**Scheme S19**

\[ \text{Scheme S19} \]

1H NMR (400 MHz, CDCl₃) δ 7.93 (d, \( J = 7.1 \) Hz, 2H), 7.73 (d, \( J = 6.8 \) Hz, 2H), 7.53–7.42 (m, 4H), 7.38–7.31 (m, 2H), 6.48 (d, \( J = 5.5 \) Hz, 1H), 5.97 (s, 1H), 5.15–5.05 (m, 2H), 2.21–2.12 (m, 1H), 2.08–1.90 (m, 5H), 1.88–1.80 (m, 1H), 1.55–1.45 (m, 4H), 1.39–1.27 (m, 7H), 1.20 (s, 3H), 1.15–1.07 (m, 4H), 1.06–0.96 (m, 4H), 0.91 (d, \( J = 3.8 \) Hz, 3H), 0.87 (d, \( J = 1.1 \) Hz, 3H), 0.86 (d, \( J = 2.0 \) Hz, 3H), 0.67 (s, 3H); 13C NMR (101 MHz, CDCl₃) δ 167.0, 165.8, 139.0, 135.5, 133.0, 131.5, 130.6, 130.5, 129.8, 128.8, 128.4, 126.9, 73.4, 57.0, 56.2, 55.8, 50.4, 42.3, 39.7, 36.5, 36.3, 35.9, 32.3, 31.9, 29.9, 28.3, 28.2, 27.4, 24.4, 24.0, 23.4, 23.0, 22.7, 21.6, 20.6, 18.9, 12.0. HRMS (ESI) calcd for C₄₁H₅₆NO₃ [M+H⁺]: 610.4255, found: 610.4255.
Figure S1.

Single crystals for X-ray studies were grown by slow evaporation of a solution of compound 24’ in a mixture of dichloromethane and hexane at room temperature. The X-ray crystal structure is deposited in the Cambridge Crystallographic Data Centre with a number of CCDC 1561816.

9.2 X-ray crystallographic data for compound 38

![Figure S2. X-ray crystallographic data for compound 38](image)

Single crystals for X-ray studies were grown by slow evaporation of a solution of compound 38 in a mixture of dichloromethane and hexane at room temperature. The X-ray crystal structure is deposited in the Cambridge Crystallographic Data Centre with a number of CCDC 1561818.

Table S4. Parameters of crystallography structures

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<thead>
<tr>
<th>Compounds</th>
<th>24’</th>
<th>38</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C₄₁H₅₅N O₃</td>
<td>C₁₂H₁₄Cl₂I₂NO</td>
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<tr>
<td><strong>Mol. wt.</strong></td>
<td>609.86</td>
<td>548.39</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
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<td>monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
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<td>P 1 21/c 1</td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
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<td>12.7496 (5)</td>
</tr>
<tr>
<td><strong>b (Å)</strong></td>
<td>11.3225 (6)</td>
<td>10.1118 (3)</td>
</tr>
<tr>
<td><strong>c (Å)</strong></td>
<td>22.7080 (11)</td>
<td>12.9485 (4)</td>
</tr>
<tr>
<td><strong>α (deg)</strong></td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td><strong>β (deg)</strong></td>
<td>106.085 (6)</td>
<td>96.469 (3)</td>
</tr>
<tr>
<td>Parameter</td>
<td>Value</td>
<td>Value</td>
</tr>
<tr>
<td>----------------------------</td>
<td>----------------</td>
<td>----------------</td>
</tr>
<tr>
<td>$\gamma$ (deg)</td>
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<td>90</td>
</tr>
<tr>
<td>$V$ ($\text{Å}^3$)</td>
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<td>1658.71 (9)</td>
</tr>
<tr>
<td>$Z$</td>
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<td>4</td>
</tr>
<tr>
<td>$T$ (K)</td>
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<td>298 (10)</td>
</tr>
<tr>
<td>$\rho_{\text{calc}}$ (Mg/m$^3$)</td>
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</tr>
<tr>
<td>$\mu$ (mm$^{-1}$)</td>
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<td>4.267</td>
</tr>
<tr>
<td>Final $R$ indices [I $&gt; 2\sigma(I)$]</td>
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<td>$R = 0.0363$</td>
</tr>
<tr>
<td></td>
<td>$wR^2 = 0.1492$</td>
<td>$wR^2 = 0.0870$</td>
</tr>
<tr>
<td>$S$</td>
<td>1.027</td>
<td>1.054</td>
</tr>
</tbody>
</table>
10. References


11. NMR Spectra

\[ \text{Diagram of NMR spectra for compound 1} \]

\[ \text{Diagram of NMR spectra for compound 2} \]
11-1

\[ \text{Cl}_2\text{C} - \text{NH} - \text{O} - \text{Ph} \]

11-1

\[ \text{CH}_3\text{C} - \text{NH} - \text{O} - \text{Ph} \]