Supporting Information

*N*-Hydroxyphthalimide-catalyzed chemoselective intermolecular benzylic C–H amination of unprotected arylalkanols
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1. Experimental data and possible reaction mechanism

### Table S1  Solvent screening using DEAD

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$T$ (°C)</th>
<th>Yield (%)</th>
<th>2c</th>
<th>1c (RSM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCE</td>
<td>80</td>
<td>40</td>
<td>17</td>
<td></td>
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<tr>
<td>AcOEt</td>
<td>60</td>
<td>17</td>
<td>31</td>
<td></td>
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<tr>
<td>MeCN</td>
<td>80</td>
<td>25</td>
<td>33</td>
<td></td>
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<tr>
<td>$t$BuOH</td>
<td>60</td>
<td>no reaction</td>
<td></td>
<td></td>
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<tr>
<td>AcOH</td>
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<td>6</td>
<td>10</td>
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<tr>
<td>TFE</td>
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<td>28</td>
<td>54</td>
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</tr>
<tr>
<td>HFIP</td>
<td>60</td>
<td>85</td>
<td>5</td>
<td></td>
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<tr>
<td>HFIP*</td>
<td>60</td>
<td>87</td>
<td>trace</td>
<td></td>
</tr>
</tbody>
</table>

a) 0.5 M

### Scheme S1  Examination for the cleavage of the N–N bond of 2c

### Figure S1  Possible reaction mechanism

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S1
Scheme S2  C–H amination of tertiary alkanol S3

\[
\begin{align*}
\text{S3} & \quad \text{OH} \\
\xrightarrow{10 \text{ mol}\% \text{ NHPI} \quad \text{TrocN=NTroc}} & \quad \text{HFIP, 60 °C, 5 h} \\
& \quad \text{S4 88\%}
\end{align*}
\]

Scheme S3  C–H amination of 1a in hexafluoroisopropyl methyl ether

\[
\begin{align*}
\text{1a} & \quad \text{OH} \\
\xrightarrow{10 \text{ mol}\% \text{ NHPI} \quad \text{TrocN=NTroc}} & \quad \text{HFIP, 60 °C, 24 h} \\
& \quad \text{2a <35\%}
\end{align*}
\]
Figure S2  Experimental data for C–H amination of benzoate 16

10 mol% NHPI  
TrocN≡NTroc  
(2.4 equiv)  
solvent: 60 °C, 3 h  

NMR charts of the crude materials  
solvent: HFIP, internal standard: trimethoxybenzene 13.4 mg (79.7 μmol)

solvent: DCE, internal standard: trimethoxybenzene 5.84 mg (34.7 μmol)
Figure S3  NMR charts of BTCEAD and BTCEAD+HFIP

The signals assigned to the carbonyl carbon and -CH$_2$- of BTCEAD were shifted downfield by the addition of HFIP.
2. Experimental procedures

2-1. General considerations

All reactions were carried out under an argon atmosphere. Solvents and other reagents were purchased from chemical suppliers and used as received. Reactions were monitored by thin-layer chromatography (TLC: Merck Silica Gel 60 F$_{254}$). Column chromatography was carried out using neutral silica gel (Cica silica gel 60N, particle size 0.040-0.050 mm, neutral, KANTO CHEMICAL CO., INC.). NMR spectra were measured by JEOL ECS-400 (400 MHz). $^1$H and $^{13}$C NMR chemical shifts are reported in parts per million (ppm, δ scale) relative to residual solvents or internal/external references ($^1$H NMR: CHCl$_3$ at 7.26 ppm or tetramethylsilane at 0.00 ppm as an internal reference in CDCl$_3$; $^{13}$C NMR: CDCl$_3$ at 77.00 ppm as an internal reference in CDCl$_3$). Coupling constants (J) are reported in Hz. Multiplicities are reported using the following abbreviations; s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet; br, broad. Because the rotamers were observed in the NMR charts at 25 °C, $^1$H and $^{13}$C NMR spectra of the C-H amination products were corrected at 50 °C in CDCl$_3$ or 100 °C in toluene-$d_8$.$^1$ Infrared (IR) spectra were recorded on a JASCO FT/IR-4200 at 4.0 cm$^{-1}$ resolution and reported in wavenumbers. Mass spectra were measured by JEOL JMS-T100LP using Electrospray Ionization (ESI) or Direct Analysis in Real Time (DART).

Preparations and Analytical data of arylalkanols

1a-1c, 1j and 9 were purchased from chemical suppliers. 1f, 1g, 1l-1n, 1p-1r, 11, were prepared from the corresponding aromatic aldehyde or ketone (for 11) by the three-step method consisting of HWE reaction using triethyl phosphonoacetate, hydrogenation (H$_2$, Pd/C), and LiAlH$_4$ or LiBH$_4$ (for 11) reduction. 1d, 1h, 1i, 1k, and 1o was prepared from the corresponding carboxylic acid by LiAlH$_4$ or BH$_3$·THF reduction. 7 was prepared from the corresponding methyl ester by LiAlH$_4$ reduction.$^2$ 13 was prepared by methylation of 3-phenylpropanal using MeMgBr.

Preparation of 1e

To a degassed solution methyl 10-undecenoate (980 μL, 4.4 mmol,) in THF (8.8 mL) was added 9-BBN (0.5 M solution in THF, 10 mL, 5.0 mmol) at 0 °C. The solution was stirred for 6 h at room temperature. Then, K$_2$CO$_3$ (1.12 g, 8.0 mmol) was added to the solution. After the resultant solution was degassed, a solution of Pd(dpdpf)Cl$_2$ (87.2 mg, 0.12 mmol) and PhBr (420 μL, 4.0 mmol) in degassed DMF (20 mL) was added. After the reaction mixture was stirred at 50 °C for 12 h, H$_2$O was added. The aqueous layer was extracted with E$_2$O and the combined organic layers were washed with brine, dried over MgSO$_4$, and
concentrated in vacuo. The crude product was purified by silica gel column chromatography (hexane/AcOEt 50:1) to afford methyl 11-phenyldecanoate (859 mg, 78%).

To a solution of LiAlH₄ (281 mg, 7.4 mmol) in THF (6 mL) was added a solution of methyl 11-phenyldecanoate (858 mg, 3.1 mmol) in THF (6 mL) at 0 °C. The reaction mixture was stirred for 25 min at room temperature. The reaction mixture was carefully quenched with H₂O (1.8 mL), 15% NaOH (1.8 mL), and H₂O (5.4 mL) at 0 °C, and filtered through a pad of Celite. The filtrate was extracted with AcOEt, washed with brine, dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/AcOEt 6:1) to afford phenylalkanol 1e (704 mg, 91%) as a colorless oil.

1H NMR (400 MHz, CDCl₃, 25 °C) δ 7.30–7.25 (m, 2H), 7.20–7.14 (m, 3H), 3.64 (td, J = 6.8, 5.6 Hz, 2H), 2.60 (t, J = 7.6 Hz, 2H), 1.65–1.52 (m, 4H), 1.38–1.20 (m, 14H), 1.20 (t, J = 5.6 Hz, 1H); 13C NMR (100 MHz, CDCl₃, 25 °C) δ 142.9, 128.3, 128.1, 125.5, 62.9, 35.9, 32.7, 31.5, 29.5, 29.4, 29.3, 25.7; IR (neat, cm⁻¹) 3332; HRMS (DART, m/z) Calcd. for C₁₇H₃₂NO ([M+ NH₄]+): 266.2484, found 266.2494.

1H NMR (400 MHz, CDCl₃, 25 °C) δ 7.32 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 3.69 (t, J = 6.4 Hz, 2H), 2.68 (t, J = 8.0 Hz, 2H), 1.94–1.85 (m, 2H), 1.31 (s, 9H), 1.26 (br s, 1H); 13C NMR (100 MHz, CDCl₃, 25 °C) δ 148.6, 138.7, 128.0, 125.2, 62.4, 34.3, 34.2, 31.5, 31.4; IR (neat, cm⁻¹) 3325; HRMS (ESI, m/z) Calcd. for C₁₃H₂₀NaO ([M+Na]+): 215.1407, found 215.1412.

1H NMR (400 MHz, CDCl₃, 25 °C) δ 7.58 (d, J = 7.2 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.33 (t, J = 7.6 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 3.72 (q, J = 5.6 Hz, 2H), 2.76 (t, J = 7.6 Hz, 2H), 1.98–1.90 (m, 2H), 1.27 (t, J = 5.6 Hz, 1H); 13C NMR (100 MHz, CDCl₃, 25 °C) δ 140.96, 140.89, 138.8, 128.8, 128.7, 127.1, 127.0, 126.9, 62.2, 34.1, 31.6; IR (neat, cm⁻¹) 3276; HRMS (ESI, m/z) Calcd. for C₁₅H₁₆NaO ([M+Na]+): 235.1099, found 235.1082.

1H NMR (400 MHz, CDCl₃, 25 °C) δ 7.17–7.12 (m, 2H), 7.00–6.92 (m, 2H), 3.67 (td, J = 6.4, 5.2 Hz, 2H), 2.69 (t, J = 8.0 Hz, 2H), 1.91–1.83 (m, 2H), 1.24 (t, J = 5.2 Hz, 1H); 13C NMR (100 MHz, CDCl₃, 25 °C) δ 161.2 (d, J = 242.1 Hz), 137.4, 129.7 (d, J = 7.6 Hz), 115.1 (d, J = 20.0 Hz), 62.0, 34.3, 31.2; IR (neat, cm⁻¹) 3335; HRMS (DART, m/z) Calcd. for C₉H₁₅FNO ([M+ NH₄]+): 172.1138, found 172.1109.
colorless oil; $^1$H NMR (400 MHz, CDCl$_3$, 25 °C) δ 7.25 (d, $J = 8.4$ Hz, 2H), 7.13 (d, $J = 8.4$ Hz, 2H), 3.67 (q, $J = 5.6$ Hz, 2H), 2.69 (t, $J = 7.6$ Hz, 2H), 1.91 – 1.83 (m, 2H), 1.26 (t, $J = 5.6$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C) δ 140.2, 131.5, 129.7, 128.4, 62.0, 34.0, 31.3; IR (neat, cm$^{-1}$) 3333; HRMS (DART, m/z) Calcd. for C$_9$H$_7$ClNO ([M+NH$_4$]$^+$): 188.0842, found 188.0828.

colorless oil; $^1$H NMR (400 MHz, CDCl$_3$, 25 °C) δ 7.54 (d, $J = 8.0$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 3.69 (td, $J = 6.4$, 5.2 Hz, 2H), 2.78 (t, $J = 7.6$ Hz, 2H), 1.94 – 1.87 (m, 2H), 1.29 (t, $J = 5.2$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C) δ 146.0, 128.7, 128.2 (q, $J = 32.4$ Hz), 125.3 (q, $J = 2.9$ Hz), 124.3 (q, $J = 271$ Hz), 61.9, 33.8, 31.9; IR (neat, cm$^{-1}$) 3334; HRMS (DART, m/z) Calcd. for C$_{10}$H$_{15}$F$_3$NO ([M+NH$_4$]$^+$): 222.1106, found 222.1130.

colorless oil; $^1$H NMR (400 MHz, CDCl$_3$, 25 °C) δ 7.96 (d, $J = 7.6$ Hz, 2H), 7.27 (d, $J = 7.6$ Hz, 2H), 3.90 (s, 3H), 3.68 (td, $J = 6.4$, 5.2 Hz, 2H), 2.77 (t, $J = 8.0$ Hz, 2H), 1.95 – 1.86 (m, 2H), 1.28 (t, $J = 5.2$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C) δ 167.1, 147.4, 129.7, 128.4, 127.9, 62.0, 52.0, 33.8, 32.1; IR (neat, cm$^{-1}$) 3420; HRMS (ESI, m/z) Calcd. for C$_{11}$H$_{14}$NaO$_3$ ([M+Na]$^+$): 217.0841, found 217.0822.

white solid; $^1$H NMR (400 MHz, CDCl$_3$, 25 °C) δ 7.82 – 7.76 (m, 3H), 7.64 (s, 1H), 7.48 – 7.39 (m, 2H), 7.35 (dd, $J = 8.0$, 2.0 Hz, 1H), 3.72 (dt, $J = 6.4$, 4.8 Hz, 2H), 2.89 (t, $J = 7.6$ Hz, 2H), 2.04 – 1.95 (m, 2H), 1.28 (t, $J = 4.8$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C) δ 139.3, 133.6, 132.0, 127.9, 127.6, 127.4, 127.2, 126.4, 125.9, 125.2, 62.2, 34.0, 32.2; IR (neat, cm$^{-1}$) 3269; HRMS (ESI, m/z) Calcd. for C$_{13}$H$_{14}$NaO ([M+Na]$^+$): 209.0942, found 209.0922.

colorless oil; $^1$H NMR (400 MHz, CDCl$_3$, 25 °C) δ 8.06 (d, $J = 8.0$ Hz, 1H), 7.88 – 7.84 (m, 1H), 7.72 (d, $J = 8.0$ Hz, 1H), 7.54 – 7.45 (m, 1H), 7.41 (t, $J = 7.6$ Hz, 1H), 7.35 (d, $J = 6.4$ Hz, 2H), 3.79 – 3.72 (m, 2H), 3.19 (t, $J = 8.0$ Hz, 2H), 2.08 – 2.00 (m, 2H), 1.33 (br s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C) δ 137.8, 133.8, 131.8, 128.7, 126.5, 125.9, 125.7, 125.4, 125.3, 123.7, 62.3, 33.3, 29.0; IR (neat, cm$^{-1}$) 3335; HRMS (ESI, m/z) Calcd. for C$_{13}$H$_{14}$NaO ([M+Na]$^+$): 209.0942, found 209.0930.

A colorless oil; $^1$H NMR (400 MHz, CDCl$_3$, 25 °C) δ 7.12 (d, $J = 8.0$ Hz, 2H), 6.84 (d, $J = 8.0$ Hz, 2H), 3.79 (s, 3H), 3.67 (q, $J = 6.0$ Hz, 2H), 2.66 (t, $J = 8.0$ Hz, 2H), 1.91 – 1.83 (m, 2H), 1.25 (t, $J = 6.0$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C) δ 157.8, 133.8, 129.3, 113.8, 62.3, 55.2, 34.4, 31.1; IR (neat, cm$^{-1}$) 3348; HRMS (ESI, m/z) Calcd. for C$_{10}$H$_{14}$NaO$_2$ ([M+Na]$^+$): 189.0892, found 189.0886.
A colorless oil; $^1$H NMR (400 MHz, CDCl$_3$, 25 °C) $\delta$ 7.19 (t, $J = 7.6$ Hz, 1H), 7.15 (d, $J = 7.6$ Hz, 1H), 6.90 (t, $J = 7.6$ Hz, 1H), 6.86 (d, $J = 7.6$ Hz, 1H), 3.84 (s, 3H), 3.60 (q, $J = 6.0$ Hz, 2H), 2.73 (t, $J = 7.2$ Hz, 2H), 1.90 – 1.81 (m, 2H), 1.75 (t, $J = 6.0$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C) $\delta$ 157.3, 130.1, 129.9, 127.1, 120.6, 110.2, 61.7, 55.3, 32.9, 25.8; IR (neat, cm$^{-1}$) 3348; HRMS (ESI, m/z) Calcd. for C$_{10}$H$_{18}$NaO$_2$ ([M+Na]$^+$): 189.0892, found 189.0862.

A colorless oil; $^1$H NMR (400 MHz, CDCl$_3$, 25 °C) $\delta$ 6.80 (d, $J = 8.4$ Hz, 1H), 6.74 (d, $J = 8.4$ Hz, 1H), 6.73 (s, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.69 (td, $J = 6.4$, 5.2 Hz, 2H), 2.67 (t, $J = 8.0$ Hz, 2H), 1.93 – 1.84 (m, 2H), 1.25 (t, $J = 5.2$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C) $\delta$ 148.8, 147.2, 134.4, 120.1, 111.7, 111.2, 62.3, 55.9, 55.8, 34.4, 31.7; IR (neat, cm$^{-1}$) 3365; HRMS (ESI, m/z) Calcd. for C$_{11}$H$_{20}$NO$_3$ ([M+Na]$^+$): 214.1443, found 214.1456.

A white solid; $^1$H NMR (400 MHz, CDCl$_3$, 25 °C) $\delta$ 7.40 (d, $J = 8.4$ Hz, 2H), 7.15 (d, $J = 8.4$ Hz, 2H), 7.10 (br s, 1H), 3.67 (td, $J = 6.0$, 4.4 Hz, 2H), 2.68 (t, $J = 7.6$ Hz, 2H), 2.17 (s, 3H), 1.91 – 1.83 (m, 2H), 1.27 (br d, $J = 4.4$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C) $\delta$ 157.9; IR (neat, cm$^{-1}$) 3277; HRMS (ESI, m/z) Calcd. for C$_{11}$H$_{15}$NaO$_2$ ([M+Na]$^+$): 216.1001, found 216.0995.

The corresponding ester was prepared from ibuprofen according to the reported protocol.$^2$ A white solid; $^1$H NMR (400 MHz, CDCl$_3$, 25 °C) $\delta$ 7.28 (d, $J = 8.0$ Hz, 2H), 7.12 (d, $J = 8.0$ Hz, 2H), 3.60 (d, $J = 6.8$ Hz, 2H), 2.45 (d, $J = 7.2$ Hz, 2H), 1.91 – 1.79 (m, 1H), 1.33 (s, 6H), 1.19 (t, $J = 6.8$ Hz, 1H), 0.90 (d, $J = 6.8$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C) $\delta$ 143.4, 139.4, 129.1, 125.9, 73.1, 44.9, 39.7, 30.1, 25.3, 22.4; IR (neat, cm$^{-1}$) 3230; HRMS (ESI, m/z) Calcd. for C$_{15}$H$_{26}$NO ([M+NH$_4]^+$): 224.2038, found 224.2038.

A colorless oil; $^1$H NMR (400 MHz, CDCl$_3$, 25 °C) $\delta$ 7.40 – 7.20 (m, 5H), 3.69 – 3.54 (m, 2H), 2.99 – 2.88 (m, 1H), 1.91 (q, $J = 6.8$ Hz, 2H), 1.32 (d, $J = 6.8$ Hz, 3H), 1.20 – 1.14 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C) $\delta$ 146.8, 128.4, 126.9, 126.0, 61.0, 40.9, 36.4, 22.3; IR (neat, cm$^{-1}$) 3335; HRMS (ESI, m/z) Calcd. for C$_{10}$H$_{18}$NO ([M+NH$_4]^+$): 168.1388, found 168.1359.
A colorless oil; $^1$H NMR (400 MHz, CDCl$_3$, 25 °C) δ 7.32 – 7.26 (m, 2H), 7.23 – 7.16 (m, 3H), 3.90 – 3.78 (m, 1H), 2.81 – 2.63 (m, 2H), 1.85 – 1.70 (m, 2H), 1.34 (br s, 1H), 1.23 (d, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C) δ 142.0, 128.3, 128.3, 125.7, 67.4, 40.8, 32.1, 23.5; IR (neat, cm$^{-1}$) 3357; HRMS (ESI, $m/z$) Calcd. for C$_{10}$H$_{18}$NO ([M+NH$_4^+$]): 168.1388, found 168.1361.

2-2. Representative procedures for chemoselective benzylic C–H amination of arylalkanols and analytical data of the products

Representative procedure A: To a solution of 1a (40.9 mg, 0.3 mmol) and NHPI (4.9 mg, 0.03 mmol) in HFIP (0.6 mL) was added TrocN=NTroc (BTCEAD, 274 mg, 0.72 mmol) at ambient temperature. The solution was degassed. The reaction mixture was stirred at 60 °C for 5 h. The reaction progress was monitored by TLC analysis. The solvent was removed in vacuo, and the crude product was purified by silica gel column chromatography (hexane/AcOEt 5:2) to afford 2a (138 mg, 89%) as an amorphous colorless solid.

$^1$H NMR (400 MHz, CDCl$_3$, 50 °C) δ 7.45 – 7.30 (m, 5H), 6.68 (br s, 1H), 5.59 (br s, 1H), 5.00 – 4.60 (m, 4H), 4.04 – 3.86 (m, 1H), 3.85 – 3.70 (m, 1H), 2.50 – 2.30 (m, 1H), 2.25 – 2.03 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 50 °C) δ 154.5, 154.5, 137.8, 128.8, 128.5, 128.1, 94.9, 94.8, 75.9, 75.2, 59.7, 59.7, 33.2; IR (neat, cm$^{-1}$) 3291, 1726; HRMS (ESI, $m/z$) Calcd. for C$_{15}$H$_{16}$Cl$_5$Cl$_3$N$_2$O$_5$ ([M+Na$^+$]): 538.9059, found 538.9037.

Analytical data of byproducts obtained from the reaction in DCE

An amorphous blue green solid; $^1$H NMR (400 MHz, CDCl$_3$, 50 °C) δ 7.41 – 7.24 (m, 5H), 6.07 (br d, $J$ = 4.4 Hz, 1H), 5.58 (t, $J$ = 7.6 Hz, 1H), 4.91 (d, $J$ = 12.0 Hz, 1H), 4.81 (s, 2H), 4.80 (d, $J$ = 12.0 Hz, 1H), 2.91 (br s, 1H), 2.74 (ddd, $J$ = 14.0, 7.6, 1.2 Hz, 1H), 2.41 – 2.32 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 50 °C) δ 155.9, 152.9, 139.8, 128.8, 128.5, 128.1, 94.9, 94.8, 75.9, 75.2, 59.7, 59.7, 33.2; IR (neat, cm$^{-1}$) 3437, 1727; HRMS (DART, $m/z$) Calcd. for C$_{15}$H$_{16}$Cl$_5$Cl$_3$N$_2$O$_5$ ([M+NH$_4^+$]): 531.9348, found 531.9334
An amorphous colorless solid; $^1$H NMR (400 MHz, CDCl$_3$, 50 °C) δ 7.44-7.30 (m, 5H), 6.45 (br s, 1H), 5.66-5.52 (m, 1H), 5.00-4.60 (m, 6H), 4.60-4.45 (m, 1H), 4.44-4.26 (m, 1H), 2.65-2.45 (m, 1H), 2.44-2.26 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 50 °C) δ 154.0, 153.8, 153.8, 136.9, 129.0, 128.8, 128.0, 94.7, 94.7, 94.3, 75.9, 75.7, 75.1, 66.0, 58.8, 29.6; IR (neat, cm$^{-1}$) 3304, 1759; HRMS (ESI, m/z) Calcd. for C$_{18}$H$_{17}$Cl$_7$Cl$_2$N$_2$NaO$_7$ ([M+Na]$^+$): 714.8071, found 714.8063.

The crude was purified by flash column chromatography on silica gel (hexane/AcOEt = 9:2) afford 2b (123.6 mg, 83%) as an amorphous colorless solid; $^1$H NMR (400 MHz, CDCl$_3$, 100 °C) δ 7.42 - 7.28 (m, 5H), 6.67 (br s, 1H), 5.64 - 5.50 (m, 1H), 4.90 - 4.60 (m, 7H), 4.54 - 4.40 (m, 1H), 4.37 - 4.26 (m, 1H), 2.60 - 2.40 (m, 1H), 2.37 - 2.20 (m, 1H); IR (neat, cm$^{-1}$) 3460, 3196, 1732; HRMS (ESI, m/z) Calcd. for C$_{14}$H$_{19}$Cl$_7$Cl$_2$N$_2$NaO$_5$ ([M+Na]$^+$): 772.8238, found 772.8242.

The crude was purified by flash column chromatography on silica gel (hexane/AcOEt = 5:2) afford 2c (140.5 mg, 89%) as an amorphous colorless solid; $^1$H NMR (400 MHz, CDCl$_3$, 50 °C) δ 7.41 - 7.30 (m, 5H), 6.55 (br s, 1H), 5.48 - 5.34 (m, 1H), 5.00 - 4.60 (m, 4H), 3.78 - 3.64 (m, 2H), 2.30 - 2.27 (m, 1H), 2.10 - 1.95 (m, 1H), 1.95 - 1.77 (m, 1H), 1.77 - 1.60 (m, 1H), 1.56 - 1.36 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 50 °C) δ 154.6, 154.2, 138.0, 128.8, 128.5, 128.2, 95.0, 94.9, 75.9, 75.2, 62.4, 29.6, 26.9; IR (neat, cm$^{-1}$) 3290, 1724; HRMS (ESI, m/z) Calcd. for C$_{16}$H$_{18}$Cl$_6$Cl$_2$N$_2$NaO$_5$ ([M+Na]$^+$): 552.9215, found 552.9211.

The crude was purified by flash column chromatography on silica gel (hexane/AcOEt = 5:2) afford 2d (149.2 mg, 91%) as an amorphous colorless solid; $^1$H NMR (400 MHz, CDCl$_3$, 50 °C) δ 7.42 - 7.28 (m, 5H), 6.52 (br s, 1H), 5.44 - 5.30 (m, 1H), 5.0 - 4.66 (m, 4H), 3.68 - 3.57 (m, 2H), 2.24 - 2.08 (m, 1H), 2.01 - 1.86 (m, 1H), 1.78 - 1.38 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$, 50 °C) δ 154.6, 154.2, 138.0, 128.8, 128.4, 128.2, 95.0, 94.9, 75.9, 75.2, 62.3, 62.3, 32.2, 30.1, 22.6; IR (neat, cm$^{-1}$) 3288, 1725; HRMS (ESI, m/z) Calcd. for C$_{17}$H$_{20}$Cl$_6$Cl$_2$N$_2$NaO$_5$ ([M+Na]$^+$): 566.9372, found 566.9372.
The crude was purified by flash column chromatography on silica gel (hexane/AcOEt = 4:1) to afford 2e (166.3 mg, 88%) as an amorphous colorless solid; \(^1\)H NMR (400 MHz, CDCl\(_3\), 50 °C) \(\delta\) 7.40 – 7.30 (m, 5H), 6.45 (br s, 1H), 5.40 – 5.30 (m, 1H), 4.94 – 4.66 (m, 4H), 3.63 (t, \(J = 6.8\) Hz, 2H), 2.18 – 2.01 (m, 1H), 2.00 – 1.88 (m, 1H), 1.60 – 1.50 (m, 2H), 1.40 – 1.20 (m, 14H); \(^13\)C NMR (100 MHz, CDCl\(_3\), 50 °C) \(\delta\) 154.4, 154.1, 138.2, 128.6, 128.2, 95.0, 95.0, 75.8, 75.0, 63.0, 62.2, 32.7, 30.5, 29.34, 29.31, 26.3, 25.7; IR (neat, cm\(^{-1}\)) 3289, 1728; HRMS (ESI, \(m/z\)) Calcd. for \(\text{C}_{23}\text{H}_{32}\text{Cl}_{5}\text{N}_{2}\text{NaO}_{5}\) ([M+Na\(^+\)]): 651.0311, found 651.0317.

The crude was purified by flash column chromatography on silica gel (hexane/AcOEt = 5:2) to afford 2f (163.1 mg, 95%) as an amorphous colorless solid; \(^1\)H NMR (400 MHz, CDCl\(_3\), 50 °C) \(\delta\) 7.39 (br d, \(J = 8.0\) Hz, 2H), 7.31 (br d, \(J = 8.0\) Hz, 2H), 6.57 (br s, 1H), 5.70 – 5.50 (s, 1H), 5.00 – 4.60 (m, 4H), 4.01 – 3.74 (m, 2H), 2.50 – 2.00 (m, 2H), 1.33 (s, 9H); \(^13\)C NMR (100 MHz, CDCl\(_3\), 50 °C) \(\delta\) 154.5, 154.5, 151.6, 134.7, 127.8, 125.8, 95.0, 94.8, 75.9, 75.2, 59.8, 34.6, 33.4, 31.3; IR (neat, cm\(^{-1}\)) 3289, 1726; HRMS (ESI, \(m/z\)) Calcd. for \(\text{C}_{19}\text{H}_{24}\text{Cl}_{5}\text{N}_{2}\text{NaO}_{5}\) ([M+Na\(^+\)]): 594.9685, found 594.9658.

The crude was purified by flash column chromatography on silica gel (hexane/AcOEt = 5:2) to afford 2g (162.9 mg, 92%) as an amorphous colorless solid; \(^1\)H NMR (400 MHz, CDCl\(_3\), 50 °C) \(\delta\) 7.62 – 7.54 (m, 4H), 7.48 – 7.42 (m, 4H), 7.36 (t, \(J = 7.8\) Hz, 1H), 6.67 (br s, 1H), 5.70 – 5.58 (m, 1H), 5.00 – 4.65 (m, 4H), 4.05 – 3.93 (m, 1H), 3.89 – 3.79 (m, 1H), 2.50 – 2.36 (m, 1H), 2.23 – 2.10 (m, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\), 50 °C) \(\delta\) 154.6, 154.4, 141.3, 140.3, 136.7, 128.8, 128.7, 127.4, 127.1, 126.9, 94.9, 94.9, 75.8, 75.1, 59.6, 33.3; IR (neat, cm\(^{-1}\)) 3291, 1726; HRMS (ESI, \(m/z\)) Calcd. for \(\text{C}_{15}\text{H}_{15}\text{Cl}_{5}\text{N}_{2}\text{NaO}_{5}\) ([M+Na\(^+\)]): 614.9372, found 614.9351.

The crude was purified by flash column chromatography on silica gel (hexane/AcOEt = 5:2) to afford 2h (131.0 mg, 80%) as an amorphous colorless solid; \(^1\)H NMR (400 MHz, CDCl\(_3\), 50 °C) \(\delta\) 7.42 – 7.34 (m, 2H), 7.08 – 6.98 (m, 2H), 6.68 (br s, 1H), 5.62 – 5.52 (m, 1H), 4.94 – 4.60 (m, 4H), 4.00 – 3.86 (m, 1H), 3.85 – 3.74 (m, 1H), 2.46 – 2.30 (m, 1H), 2.26 – 2.00 (m, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\), 50 °C) \(\delta\) 162.7 (d, \(J = 247\) Hz), 154.5, 154.4, 133.8, 129.8 (d, \(J = 6.7\) Hz), 115.7 (d, \(J = 20.0\) Hz), 94.9, 94.8, 75.9, 75.2, 59.7, 59.7, 33.4; IR (neat, cm\(^{-1}\)) 3291, 1726; HRMS (ESI, \(m/z\)) Calcd. for \(\text{C}_{15}\text{H}_{15}\text{Cl}_{5}\text{N}_{2}\text{NaO}_{5}\) ([M+Na\(^+\)]): 556.8964, found 556.8966.
The crude was purified by flash column chromatography on silica gel (hexane/AcOEt = 5:2) to afford 2i (141.9 mg, 85%) as an amorphous colorless solid; \(^1\)H NMR (400 MHz, CDCl\(_3\), 50 °C) \(\delta 7.38 - 7.30 (m, 4H), 6.70 (br s, 1H), 5.62 - 5.50 (m, 1H), 4.90 - 4.60 (m, 4H), 4.00 - 3.90 (m, 1H), 3.85 - 3.75 (m, 1H), 2.37 - 1.70 (m, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), 50 °C) \(\delta 154.5, 154.5, 136.4, 134.5, 129.5, 129.0, 94.9, 94.8, 75.9, 75.3, 59.7, 33.2; IR (neat, cm\(^{-1}\)) 3290, 1727; HRMS (ESI, m/z) Calcd. for C\(_{15}\)H\(_{15}\)Cl\(_6\)N\(_3\)O\(_5\) ([M+Na]+): 572.8668, found 572.8678.

The crude was purified by flash column chromatography on silica gel (hexane/AcOEt = 5:2) to afford 2j (152.6 mg, 85%) as an amorphous colorless solid; \(^1\)H NMR (400 MHz, CDCl\(_3\), 50 °C) \(\delta 7.50 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 8.8 Hz, 2H), 6.71 (br s, 1H), 5.60 - 5.50 (m, 1H), 4.96 - 4.64 (m, 4H), 4.00 - 3.90 (m, 1H), 3.85 - 3.74 (m, 1H), 2.45 - 2.31 (m, 1H), 2.14 - 2.02 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), 50 °C) \(\delta 154.6, 154.3, 136.9, 131.9, 129.9, 94.8, 75.8, 75.1, 59.5, 59.5, 33.1; IR (neat, cm\(^{-1}\)) 3391, 1726; HRMS (ESI, m/z) Calcd. for C\(_{15}\)H\(_{15}\)Br\(_3\)Cl\(_5\)N\(_2\)O\(_5\) ([M+Na]+): 616.8164, found 616.8183.

The crude was purified by flash column chromatography on silica gel (hexane/AcOEt = 5:2) to afford 2k (115.3 mg, 66%) as an amorphous colorless solid; \(^1\)H NMR (400 MHz, CDCl\(_3\), 50 °C) \(\delta 7.63 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 6.83 (br s, 1H), 5.67 - 5.58 (m, 1H), 4.98 - 4.60 (m, 4H), 4.01 - 3.91 (m, 1H), 3.84 - 3.74 (m, 1H), 2.52 - 2.35 (m, 1H), 2.20 - 2.04 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), 50 °C) \(\delta 154.5, 154.5, 141.8 (q, J = 20.0 Hz), 130.6 (q, J = 32.4 Hz), 128.5, 125.7, 123.8 (q, J = 271 Hz), 94.7, 94.7, 75.7, 75.0, 59.7, 32.7; IR (neat, cm\(^{-1}\)) 3290, 1731; HRMS (ESI, m/z) Calcd. for C\(_{16}\)H\(_{15}\)Br\(_3\)Cl\(_5\)N\(_2\)Na\(_5\) ([M+Na]+): 606.8932, found 606.8921.

An amorphous colorless solid, 11.2 mg (6%); \(^1\)H NMR (400 MHz, CDCl\(_3\), 50 °C) \(\delta 7.60 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 6.09 (d, J = 5.2 Hz, 1H), 5.61 (d, J = 7.6 Hz, 1H), 4.94 (d, J = 12.0 Hz, 1H), 4.86 - 4.70 (m, 3H), 3.03 (br s, 1H), 2.80 (ddd, J = 13.2, 7.6, 1.6 Hz, 1H), 2.27 (ddd, J = 13.2, 7.6, 5.2 Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), 50 °C) \(\delta 155.9, 152.9, 144.0, 130.2, 126.3, 125.9, 124.0 (q, J = 271 Hz), 94.8, 83.3, 75.8, 75.7, 62.7, 43.1; IR (neat, cm\(^{-1}\)) 3437, 1731; HRMS (DART, m/z) Calcd. for C\(_{16}\)H\(_{17}\)Cl\(_5\)F\(_3\)N\(_2\)O\(_5\) ([M+NH\(_4\)]+): 599.9222, found 599.9246.

The amount of this compound is too small to obtain \(^{13}\)C NMR spectra.
The crude was first purified by flash column chromatography on silica gel (AcOEt), and then by PTLC separation to afford 2l (112.0 mg, 65%) as an amorphous colorless solid; \( ^1 \)H NMR (400 MHz, CDCl\(_3\), 50 °C) \( \delta \) 8.03 (d, \( J = 8.0 \) Hz, 2H), 7.48 (d, \( J = 8.0 \) Hz, 2H), 6.73 (br s, 1H), 5.67 – 5.57 (m, 1H), 4.90 – 4.64 (m, 4H), 4.01 – 3.90 (m, 1H), 3.92 (s, 3H), 3.85 – 3.75 (m, 1H), 2.50 – 2.32 (m, 1H), 2.18 – 2.05 (m, 1H); \( ^{13} \)C NMR (100 MHz, CDCl\(_3\), 50 °C) \( \delta \) 166.6, 154.6, 154.4, 142.9, 130.2, 130.0, 128.1, 94.8, 94.8, 75.9, 75.2, 59.6, 59.6, 52.1, 33.0; IR (neat, cm\(^{-1}\)) 3280, 1719; HRMS (ESI, m/z) Calcd. for C\(_{17}\)H\(_{18}\)Cl\(_5\)N\(_2\)O\(_7\) (\([M+Na]^+\)): 596.9113, found 596.9123.

An amorphous light brown solid, 17.2 mg (10%); \(^1\)H NMR (400 MHz, CDCl\(_3\), 25 °C) \( \delta \) 8.01 (d, \( J = 8.4 \) Hz, 2H), 7.48 (d, \( J = 8.4 \) Hz, 2H), 6.09 – 6.06 (m, 1H), 5.61 (t, \( J = 7.6 \) Hz, 1H), 4.93 (d, \( J = 11.2 \) Hz, 1H), 4.85 – 4.77 (m, 2H), 4.79 (d, \( J = 11.2 \) Hz, 1H), 3.91 (s, 3H), 2.88 – 2.83 (m, 1H), 2.79 (ddd, \( J = 13.2, 8.0, 1.6 \) Hz, 1H), 2.33 – 2.24 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), 25 °C) \( \delta \) 166.6, 155.9, 152.9, 145.0, 130.2, 129.9, 125.9, 94.84, 94.80, 83.2, 75.72, 75.66, 62.9, 52.1, 43.1; IR (neat, cm\(^{-1}\)) 3430, 3305, 1722; HRMS (DART, m/z) Calcd. for C\(_{17}\)H\(_{20}\)Cl\(_6\)N\(_2\)O\(_7\) (\([M+NH_4]^+\)): 589.9403, found 589.9387.

**Representative procedure B:** To a solution of 1m (55.4 mg, 0.3 mmol) and NHPI (5.0 mg, 0.03 mmol) in HFIP (0.3 mL) and DCE (0.3 mL) was added TrocN=NTroc (BTCEAD, 275 mg, 0.72 mmol) at ambient temperature. The solution was degassed. The reaction mixture was stirred at 60 °C for 6 h. The reaction progress was monitored by TLC analysis. The solvent was removed in vacuo, and the crude product was purified by silica gel column chromatography (hexane/AcOEt 5:2) to afford 2m (117 mg, 70%) as an amorphous colorless solid and the purification by silica gel column chromatography (hexane/AcOEt 2:1) afforded 6 (4.7 mg, 3%) as an amorphous colorless solid.

\(^1\)H NMR (400 MHz, CDCl\(_3\), 50 °C) \( \delta \) 8.30 – 7.80 (m, 3H), 7.60 – 7.40 (m, 4H), 6.48 – 6.40 (m, 1H), 6.15 (br s, 1H), 5.10 – 4.60 (m, 4H), 4.16 – 3.80 (m, 2H), 2.76 – 2.44 (m, 1H), 2.30 – 2.10 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), 50 °C) \( \delta \) 154.9, 154.6, 133.9, 132.5, 131.4, 131.6, 129.4, 129.0, 127.1, 126.2, 125.1, 122.8, 94.8, 94.7, 75.6, 75.0, 59.0, 53.8, 33.4; IR (neat, cm\(^{-1}\)) 3294, 1720; HRMS (ESI, m/z) Calcd. for C\(_{19}\)H\(_{18}\)Cl\(_5\)N\(_2\)O\(_5\) (\([M+Na]^+\)): 588.9215, found 588.9226.
An amorphous colorless solid; $^1$H NMR (400 MHz, CDCl$_3$, 50 °C) $\delta$ 8.17 – 8.09 (m, 1H), 8.08 – 7.95 (m, 1H), 7.78 – 7.68 (m, 1H), 7.62 – 7.50 (m, 2H), 7.42 – 7.33 (m, 1H), 5.00 – 4.60 (m, 4H), 3.80 – 3.70 (m, 2H), 3.26 – 3.14 (m, 2H), 2.08 – 1.97 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$, 50 °C) $\delta$ 154.3, 154.3, 140.2, 135.3, 133.5, 132.8, 130.2, 126.8, 126.4, 125.8, 125.8, 124.5, 122.9, 94.7, 94.7, 75.9, 75.4, 62.3, 33.4, 29.2; IR (neat, cm$^{-1}$) 3292, 2954, 1734; HRMS (DART, m/z) Calcd. for C$_{19}$H$_{22}$Cl$_3$N$_3$O$_5$ ([M+NH$_4$]$^+$): 583.9661, found 583.9681.

The crude was purified by flash column chromatography on silica gel (hexane/AcOEt = 5:2) to afford 2n (147.4 mg, 87%) as an amorphous colorless solid; $^1$H NMR (400 MHz, CDCl$_3$, 50 °C) $\delta$ 7.88 – 7.80 (m, 4H), 7.54 – 7.48 (m, 3H), 6.64 (br s, 1H), 5.82 – 5.71 (m, 1H), 5.00 – 4.64 (m, 4H), 4.07 – 3.94 (m, 1H), 3.92 – 3.82 (m, 1H), 2.58 – 2.40 (m, 1H), 2.30 – 2.20 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 50 °C) $\delta$ 154.5, 154.5, 135.1, 133.3, 133.2, 128.7, 128.1, 127.7, 127.1, 126.5, 126.4, 126.0, 94.9, 94.8, 75.9, 75.1, 59.8, 59.8, 33.2; IR (neat, cm$^{-1}$) 3291, 1726; HRMS (ESI, m/z) Calcd. for C$_{19}$H$_{18}$Cl$_3$N$_2$NaO$_6$ ([M+Na]$^+$): 588.9215, found 588.9191.

The crude was first purified by flash column chromatography on silica gel (hexane/AcOEt = 2:1) to afford 2o (145.9 mg, 89%) as an amorphous colorless solid; $^1$H NMR (400 MHz, CDCl$_3$, 50 °C) $\delta$ 7.30 (d, $J$ = 8.4 Hz, 2H), 6.89 (d, $J$ = 8.4 Hz, 2H), 6.64 (br s, 1H), 5.61-5.49 (m, 1H), 5.00 – 4.60 (m, 4H), 4.07 – 3.94 (m, 1H), 3.82 – 3.82 (m, 1H), 2.58 – 2.40 (m, 1H), 2.30 – 2.20 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 50 °C) $\delta$ 159.8, 154.4, 154.4, 129.9, 129.4, 114.2, 95.0, 94.8, 75.8, 75.2, 59.8, 59.8, 55.3, 33.5; IR (neat, cm$^{-1}$) 3287, 1726; HRMS (ESI, m/z) Calcd. for C$_{16}$H$_{18}$Cl$_5$N$_3$O$_6$ ([M+Na]$^+$): 568.9164, found 568.9143.

The crude was first purified by flash column chromatography on silica gel (hexane/AcOEt = 5:2) to afford 2p (153.7 mg, 93%) as an amorphous colorless solid; $^1$H NMR (400 MHz, CDCl$_3$, 50 °C) $\delta$ 7.37 – 7.27 (m, 2H), 7.00 – 6.93 (m, 1H), 6.92 (d, $J$ = 8.4 Hz, 1H), 6.52 (br s, 1H), 5.96 – 5.80 (m, 1H), 4.90 – 4.60 (m, 4H), 4.05 – 3.92 (m, 1H), 3.90 – 3.76 (m, 1H), 3.84 (s, 3H), 2.43 – 2.25 (m, 1H), 2.14 – 2.00 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 50 °C) $\delta$ 157.5, 154.6, 154.6, 128.9, 125.8, 120.6, 110.9, 95.0, 94.9, 75.9, 75.1, 59.6, 55.6, 54.2, 33.3; IR (neat, cm$^{-1}$) 3286, 1725; HRMS (ESI, m/z) Calcd. for C$_{16}$H$_{22}$Cl$_6$N$_3$O$_6$ ([M+Na]$^+$): 563.9610, found 563.9639.
The crude was first purified by flash column chromatography on silica gel (hexane/AcOEt = 2:1) to afford 2q (110.3 mg, 64%) as an amorphous colorless solid; $^1$H NMR (400 MHz, CDCl$_3$, 50 °C) δ 6.92 (d, $J = 8.0$ Hz, 1H), 6.91 (s, 1H), 6.84 (d, $J = 8.0$ Hz, 1H), 6.58 (br s, 1H), 5.57–5.48 (br s, 1H), 4.90–4.60 (m, 4H), 4.00–3.75 (m, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 2.40–2.25 (m, 1H), 2.15–2.03 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 50 °C) δ 154.4, 154.4, 149.4, 149.4, 130.4, 120.4, 112.0, 111.5, 95.0, 94.9, 75.8, 75.1, 59.7, 59.7, 56.1, 56.0, 33.5; IR (neat, cm$^{-1}$) 3289, 1730; HRMS (ESI, m/z) Calcd. for C$_{17}$H$_{20}$Cl$_3$N$_2$NaO$_7$ ([M+Na]$^+$): 598.9270, found 598.9269.

The crude was first purified by flash column chromatography on silica gel (hexane/AcOEt = 3:5) to afford 2r (108.8 mg, 63%) as an amorphous colorless solid; $^1$H NMR (400 MHz, CDCl$_3$, 50 °C) δ 7.47 (br d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.19 (br s, 1H), 6.77 (br s, 1H), 5.62–5.48 (m, 1H), 4.96–4.54 (m, 4H), 4.00–3.86 (m, 1H), 3.84–3.74 (m, 1H), 2.44–2.28 (m, 1H), 2.16 (s, 3H), 2.16–2.12 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 50 °C) δ 168.7, 154.8, 154.4, 138.0, 133.8, 128.8, 120.3, 94.9, 94.9, 75.8, 75.1, 59.7, 59.7, 33.3, 24.4; IR (neat, cm$^{-1}$) 3305, 1719; HRMS (ESI, m/z) Calcd. for C$_{17}$H$_{19}$Cl$_3$N$_2$NaO$_6$ ([M+Na]$^+$): 595.9273, found 595.9280.

An amorphous light-brown solid, 1.72 mg (5%, as small amounts of inseparable impurities were contained, the yield was determined by $^1$H NMR spectroscopy with mesitylene as internal standard); $^1$H NMR (400 MHz, CDCl$_3$, 50 °C) δ 7.60–7.42 (m, 2H), 7.36–7.28 (m, 2H), 7.20 (br s, 1H), 6.61 (br s, 1H), 5.60–5.55 (m, 1H), 5.00–4.60 (m, 6H), 4.57–4.44 (m, 1H), 4.40–4.30 (m, 1H), 2.58–2.44 (m, 1H), 2.38–2.25 (m, 1H), 2.17 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, 50 °C) δ 168.5, 153.9, 153.9, 153.8, 138.2, 132.0, 128.7, 120.1, 94.7, 94.7, 94.3, 75.7, 75.3, 75.1, 66.0, 57.4, 24.6; IR (neat, cm$^{-1}$) 3306, 2959, 1760; HRMS (ESI, m/z) Calcd. for C$_{20}$H$_{20}$Cl$_3$N$_2$NaO$_5$ ([M+Na]$^+$): 771.8286, found 771.8279.

The crude was first purified by flash column chromatography on silica gel (hexane/AcOEt = 4:1) to afford 8 (156.8 mg, 89%) as an amorphous colorless solid; $^1$H NMR (400 MHz, CDCl$_3$, 50 °C) δ 7.38–7.27 (m, 4H), 6.46 (br s, 1H), 4.98–4.60 (m, 5H), 3.61 (s, 2H), 2.48–2.34 (m, 1H), 1.33 (s, 6H), 1.25 (br s, 3H), 0.80 (br d, $J = 6.0$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, 50 °C) δ 154.3, 154.3, 146.7, 134.7, 129.0, 126.5, 95.0, 95.0, 75.8, 75.1, 72.9, 69.2, 40.0, 28.3, 25.3, 20.4, 20.2; IR (neat, cm$^{-1}$) 3279, 1725; HRMS (ESI, m/z) Calcd. for C$_{20}$H$_{26}$Cl$_3$N$_2$NaO$_5$ ([M+Na]$^+$): 608.9841, found 608.9847.
The crude was first purified by flash column chromatography on silica gel (hexane/AcOEt = 2:1), and then purified by PTLC to afford 10 (123.8 mg, 77%) as an amorphous colorless solid; $^1$H NMR (400 MHz, CDCl$_3$, 50 ºC) δ 7.26 (d, $J = 8.4$ Hz, 2H), 6.91 (d, $J = 8.4$ Hz, 2H), 6.81 (br s, 1H), 4.95 – 4.65 (m, 6H), 4.09 (t, $J = 4.4$ Hz, 2H), 3.96 (br t, $J = 4.4$ Hz, 2H), 1.94 (br s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 50 ºC) δ 158.8, 154.2, 153.6, 130.3, 127.8, 115.0, 94.9, 94.8, 75.9, 75.1, 69.4, 61.4, 53.4; IR (neat, cm$^{-1}$) 3295, 1731; HRMS (DART, m/z) Calcd. for C$_{15}$H$_{20}$Cl$_3$IN$_3$O$_6$ ([M+NH$_4^+$]): 549.9454, found 549.9458.

The crude was purified by flash column chromatography on silica gel (hexane/AcOEt = 3:1) afford 12 (66.2 mg, <42%) with unidentified byproducts; $^1$H NMR (400 MHz, CDCl$_3$, 50 ºC) δ 7.67 – 7.19 (m, 6H), 4.95 – 4.56 (m, 4H), 4.05 – 3.96 (m, 2H), 2.90 – 2.82 (m, 1H), 2.20 – 2.10 (m, 1H), 1.61 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, 50 ºC) δ 155.2, 147.2, 128.6, 128.4, 126.7, 124.8, 95.1, 94.9, 75.5, 75.1, 66.0, 59.0, 37.3, 27.2; IR (neat, cm$^{-1}$) 3309, 2956, 1733; HRMS (ESI, m/z) Calcd. for C$_{16}$H$_{18}$Cl$_3$N$_2$NaO$_5$ ([M+Na$^+$]): 552.9210, found 552.9215.

The crude was purified by flash column chromatography on silica gel (hexane/AcOEt = 3:1) afford 14 (117.6 mg, 74%, an 5:4 inseparable mixture of diastereomers) as an amorphous colorless solid: major diastereomer; $^1$H NMR (400 MHz, toluene-$d_8$, 100 ºC) δ 7.35 – 7.27 (m, 2H), 7.17 – 6.94 (m, 3H), 6.14 (s, 1H), 5.56 – 5.46 (m, 1H), 4.70 – 4.30 (m, 4H), 3.70 – 3.58 (m, 1H), 2.30 – 1.60 (m, 2H), 1.00 – 0.91 (m, 3H); minor diastereomer; $^1$H NMR (400 MHz, toluene-$d_8$, 100 ºC) δ 7.28 – 7.20 (m, 2H), 7.17 – 6.94 (m, 3H), 6.47 (s, 1H), 5.67 – 5.57 (m, 1H), 4.70 – 4.30 (m, 4H), 4.15 – 4.00 (m, 1H), 2.30 – 1.60 (m, 2H), 1.20 – 1.10 (m, 3H); major and minor diastereomers $^{13}$C NMR (100 MHz, toluene-$d_8$, 100 ºC) δ 154.9, 154.9, 154.8, 154.5, 139.4, 139.4, 129.1, 129.0, 128.8, 128.7, 128.53, 128.47, 96.0, 95.9, 95.9, 95.8, 76.3, 76.3, 75.7, 75.7, 66.4, 64.8, 61.4, 60.4, 40.9, 40.5, 24.7, 23.6; IR (neat, cm$^{-1}$) 3290, 1726; HRMS (ESI, m/z) Calcd. for C$_{16}$H$_{18}$Cl$_3$N$_2$NaO$_5$ ([M+Na$^+$]): 552.9215, found 552.9215.

An amorphous colorless solid (8.0 mg, 5%). The following data were collected using the material obtained from the reaction in DCE; $^1$H NMR (400 MHz, CDCl$_3$, 50 ºC) δ 7.41 – 7.30 (m, 5H), 6.66 (br, 1H), 5.94 – 5.82 (m, 1H), 4.90 – 4.68 (m, 4H), 3.40 – 3.28 (m, 1H), 3.12 – 2.98 (m, 1H), 2.20 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, 50 ºC) δ 204.9, 154.7, 153.7, 137.5, 128.8, 128.5, 127.7, 94.8, 94.8, 75.9, 75.2, 58.0, 44.7, 30.1; IR (neat, cm$^{-1}$) 3285, 1728; HRMS (ESI, m/z) Calcd. for C$_{16}$H$_{18}$Cl$_3$N$_2$NaO$_5$ ([M+Na$^+$]): 550.9059, found 550.9059.
The crude was purified by flash column chromatography on silica gel (hexane/AcOEt = 8:1) afford S4 (143.5 mg, 88%) as an amorphous colorless solid; \(^1\)H NMR (400 MHz, CDCl\(_3\), 50 °C) \(\delta 7.46 - 7.24\) (m, 5H), 6.94 (br s, 1H), 5.68 (s, 1H), 5.10 – 4.50 (m, 4H), 3.98 – 3.85 (m, 0.25H), 2.70 – 2.54 (m, 0.25H), 2.54 – 2.48 (m, 0.75H), 1.94 – 1.82 (m, 0.75H), 1.80 – 1.68 (m, 0.25H), 1.70 – 1.52 (m, 0.75H), 1.33 (s, 6H); \(^{13}\)C NMR (100 MHz, toluene-d\(_8\), 100 °C) \(\delta 155.1, 153.9, 139.3, 128.7, 128.2, 127.8, 94.5, 94.9, 75.8, 75.2, 70.1, 57.9, 42.2, 32.4, 28.0\); IR (neat, cm\(^{-1}\)) 3292, 1727; HRMS (ESI, \(m/z\)) Calcd. for C\(_{17}\)H\(_{20}\)Cl\(_3\)ClN\(_2\)NaO\(_5\) ([M+Na]\(^+\)): 566.9372, found 566.9354.

Preparation of free amino alcohol 18 from 2c

To a solution of 2c (48.9 mg, 0.092 mmol) in glacial acetic acid (1.3 mL) was added zinc dust (477 mg, 7.3 mmol) at room temperature. After the solution was stirred for 30 min, acetone (66.9 \(\mu\)L, 0.9 mmol) was added. The reaction mixture was stirred at room temperature for 30 min. Then, CH\(_2\)Cl\(_2\) (6 ml) was added and the resultant mixture was sonicated for 1 min. The mixture was filtered through a pad of Celite. Sat. aqueous Na\(_2\)CO\(_3\) was added to the filtrate, and the mixture was extracted with CH\(_2\)Cl\(_2\). The combined organic layer was washed with brine and dried over MgSO\(_4\). and concentrated in vacuo. The crude product was purified by silica gel column chromatography (CHCl\(_3\)/MeOH 5:1) to afford (11.7 mg, 78%) as a white solid. Analytical data were identical with those of an authentic sample which was prepared from benzoate 17.

Authentic sample: A white solid; Mp 72.2 – 73.7 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\), 25 °C) \(\delta 7.27 - 7.22\) (m, 5H), 3.95 – 3.88 (m, 1H), 3.72 – 3.57 (m, 2H), 3.40 – 3.15 (m, 3H), 1.79 – 1.64 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), 25 °C) \(\delta 146.5, 128.6, 127.1, 125.8, 62.8, 56.2, 37.4, 30.7\); IR (neat, cm\(^{-1}\)) 3344, 3277, 2935; HRMS (DART, \(m/z\)) Calcd. for C\(_{10}\)H\(_{16}\)NO ([M+H]\(^+\)): 166.1205, found 166.1232.

3. References


4. NMR Charts

$^1$H NMR (400 MHz, CDCl$_3$, 50 °C)

$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 50 °C)
$^1H$ NMR (400 MHz, CDCl$_3$, 50 °C)

$^{13}C$($^1H$) NMR (100 MHz, toluene-$d_8$, 100 °C)
$^1$H NMR (400 MHz, CDCl$_3$, 50 °C)

$^{13}$C{${^1}$H} NMR (100 MHz, CDCl$_3$, 50 °C)
\[^1\text{H NMR (400 MHz, CDCl}_3\text{, 50 °C)}\]

\[\text{Troc}^-N-\text{Troc}^+\]

\[\text{OH}\]

\[2d\]

\[\text{^13C\{^1\text{H}\} NMR (100 MHz, CDCl}_3\text{, 50 °C)}\]

\[\text{X : parts per Million : Proton}\]

\[\text{9.0 8.0 7.0 6.0 ... 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0.0}\]

\[\text{X : parts per Million : Carbon13}\]

\[\text{170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0}\]
$^1$H NMR (400 MHz, CDCl$_3$, 50 °C)

$^{13}$C{${^1}$H} NMR (100 MHz, CDCl$_3$, 50 °C)
$^1$H NMR (400 MHz, CDCl$_3$, 50 °C)

$^13$C{$^1$H} NMR (100 MHz, CDCl$_3$, 50 °C)
$^1$H NMR (400 MHz, CDCl$_3$, 50 °C)

$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 50 °C)
$^1$H NMR (400 MHz, CDCl$_3$, 50 °C)

$^{13}$C$[^1]$H NMR (100 MHz, CDCl$_3$, 50 °C)
$^1$H NMR (400 MHz, CDCl$_3$, 50 °C)

$^{13}$C$[^1]$H NMR (100 MHz, CDCl$_3$, 50 °C)
$\text{H NMR (400 MHz, CDCl}_3$, 50 °C$}\$

$\text{NMR (100 MHz, CDCl}_3$, 50 °C$]\$

$\text{C}^{13}$H NMR (100 MHz, CDCl$_3$, 50 °C$)$
$^1$H NMR (400 MHz, CDCl$_3$, 50 °C)

$^{13}$C$^1$H NMR (100 MHz, CDCl$_3$, 50 °C)
$^1$H NMR (400 MHz, CDCl$_3$, 50 °C)

$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 50 °C)
$^1$H NMR (400 MHz, CDCl$_3$, 50 °C)

$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 50 °C)
$^1$H NMR (400 MHz, CDCl$_3$, 50 °C)

$^{13}$C$[^1]$H NMR (100 MHz, CDCl$_3$, 50 °C)
\[ \text{^1H NMR (400 MHz, CDCl}_3, \ 50^\circ \text{C)} \]

\[ \text{^13C\(^{\text{1H}}\) NMR (100 MHz, CDCl}_3, \ 50^\circ \text{C)} \]
\(^1\text{H NMR (400 MHz, CDCl}_3\text{, 50 °C)}\)

\(^{13}\text{C\(^1\text{H) NMR (100 MHz, CDCl}_3\text{, 50 °C)}\)

S33
1H NMR (400 MHz, CDCl₃, 50 °C)

13C{1H} NMR (100 MHz, CDCl₃, 50 °C)
**Page S35**

**1^H NMR (400 MHz, CDCl₃, 50 °C)**

**13C{^1H} NMR (100 MHz, CDCl₃, 50 °C)**
\[ ^1\text{H NMR (400 MHz, CDCl}_3, 50 \degree \text{C)} \]

\[ \text{Troc} \quad \text{N} \quad \text{Troc} \]

\[ \text{MeO} \quad \text{N} \quad \text{OH} \quad \text{MeO} \]

\[ 2q \]

\[ ^{13}\text{C}[^1\text{H}] \text{ NMR (100 MHz, CDCl}_3, 50 \degree \text{C)} \]
$^1$H NMR (400 MHz, CDCl$_3$, 50 °C)

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$, 50 °C)
**1H NMR (400 MHz, CDCl₃, 50 °C)**

![1H NMR spectrum](image)

**13C{¹H} NMR (100 MHz, CDCl₃, 50 °C)**

![13C{¹H} NMR spectrum](image)
$^1$H NMR (400 MHz, CDCl$_3$, 50 °C)

$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 50 °C)
$^1$H NMR (400 MHz, CDCl$_3$, 50 °C)

$^{13}$C$[^1]$H NMR (100 MHz, CDCl$_3$, 50 °C)
$^1$H NMR (400 MHz, CDCl$_3$, 50 °C)

$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 50 °C)
$^1$H NMR (400 MHz, CDCl$_3$, 50 °C)

$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 50 °C)
$^1$H NMR (400 MHz, CDCl$_3$, 50 °C)

$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$, 50 °C)
obtained from 2c as shown in Scheme 2

\[ 1^H \text{ NMR (400 MHz, CDCl}_3, 50 \, ^\circ\text{C)} \]

18

\[
\text{obtained from } 2\text{c as shown in Scheme 2}
\]