Electronic Supplementary Information

Silver-Catalyzed Three-Component Reaction via Stabilized Cation:
Synthesis of Polysubstituted Tetrahydronaphthols and Tetrahydronaphthylamines

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1. Experimental procedures and spectroscopic data

1.1 General information

All reactions were carried out under an inert atmosphere of dry N\textsubscript{2} in Schlenk tube, solvents were purified by standard method. \textsuperscript{1}H, \textsuperscript{13}C, \textsuperscript{19}F NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz for \textsuperscript{1}H; 100 MHz for \textsuperscript{13}C; 376 MHz for \textsuperscript{19}F), \textsuperscript{1}H NMR and \textsuperscript{13}C NMR chemical shifts were determined relative to internal standard TMS at \( \delta \) 0.0 and \textsuperscript{19}F NMR chemical shifts were determined relative to CFCl\textsubscript{3} as external standard. Chemical shifts (\( \delta \)) are reported in ppm, and coupling constants (\( J \)) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared (IR) spectra are recorded on a Nicolet 210 spectrophotometer and were recorded in potassium bromide (KBr) pellet. Mass spectra (MS) were obtained using EI mass spectrometer. Melting points were determined using a hot stage apparatus. All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature.

1.2 General procedure for the synthesis of enynals

1.2.1 Enynals were prepared according to the literature procedures \textsuperscript{1-4}:

\[
\text{R}^1\text{BR} \quad \text{CHO} + \quad \equiv \equiv \quad \text{Pd}(\text{PPh}_3)_2\text{Cl}_2 \quad \text{CuI, NEt}_3, 50^\circ \text{C} \quad \text{R}^1\text{R}^2\text{C} = \equiv \text{CHO}
\]

To a solution of the corresponding 2-bromobenzaldehyde (1.0 equiv.), Pd(Ph\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} (2.0 mol %), and CuI (1.0 mol %) in NEt\textsubscript{3} (0.25 M) was added the appropriate acetylene (1.2 equiv.). The resulting mixture was stirred under nitrogen atmosphere at 50 °C overnight. After the reaction was finished, the mixture was filtered by short silica, then the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the desired product 1. Spectral data of product 1 was consistent with data reported in the literature \textsuperscript{1}.

1.3 Preparation of 2-alkynylarylaldimines

2-Alkynylarylaldimines were prepared according to the literature procedures \textsuperscript{5}:

\[
\text{R}^1\text{CHO} + \quad \text{R}^3\text{NH}_2 \quad \text{MgSO}_4 \quad \text{DCM, rt} \quad \text{R}^1\text{R}^2\text{N} \equiv \text{R}^3
\]

A solution of aryl amines S1 (5 mmol) and enynals 1 (5.0 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (20 mL) was added MgSO\textsubscript{4} (2.0 g), the reaction mixture was stirred at room temperature overnight. After the reaction was finished, the mixture was filtered through short pad of celite and the filtrate was concentrated under reduced pressure to afford 2-Alkynylarylaldimines 4 which were used as such without further purification.
2-(Phenylethynyl)benzaldehyde (1a)

\[ \text{H NMR (400 MHz, CDCl}_3\] \( \delta \) 10.63 (s, 1H), 7.92 (dd, \( J = 7.8, 0.9 \text{ Hz, 1H} \)), 7.63 – 7.59 (m, 1H), 7.54 (dd, \( J = 8.9, 5.0, 1.5 \text{ Hz, 3H} \)), 7.41 (t, \( J = 7.6 \text{ Hz, 1H} \)), 7.38 – 7.34 (m, 3H). \[ \text{C NMR (100 MHz, CDCl}_3\] \( \delta \) 191.7, 135.9, 133.8, 133.3, 131.7, 129.1, 128.6, 128.6, 127.3, 126.9, 122.4, 96.4, 85.9.

2-((4-Methoxyphenylethynyl)benzaldehyde (1b)

\[ \text{H NMR (400 MHz, CDCl}_3\] \( \delta \) 10.64 (s, 1H), 7.93 (d, \( J = 7.8 \text{ Hz, 1H} \)), 7.61 (d, \( J = 7.7 \text{ Hz, 1H} \)), 7.55 (s, 1H), 7.50 (d, \( J = 8.7 \text{ Hz, 2H} \)), 7.41 (t, \( J = 7.5 \text{ Hz, 1H} \)), 6.90 (d, \( J = 8.7 \text{ Hz, 2H} \)), 3.83 (d, \( J = 1.1 \text{ Hz, 3H} \)). \[ \text{C NMR (100MHz, CDCl}_3\] \( \delta \) 191.8, 160.3, 135.7, 133.8, 133.2, 131.8, 128.2, 127.4, 127.3, 114.4, 114.3, 96.6, 83.8, 55.4.

2-((p-Tolyethynyl)benzaldehyde (1c)

\[ \text{H NMR (400 MHz, CDCl}_3\] \( \delta \) 10.65 (d, \( J = 0.6 \text{ Hz, 1H} \)), 7.94 (dd, \( J = 7.8, 0.9 \text{ Hz, 1H} \)), 7.62 (dd, \( J = 7.7, 0.8 \text{ Hz, 1H} \)), 7.56 (td, \( J = 7.5, 1.4 \text{ Hz, 1H} \)), 7.44 (dd, \( J = 14.4, 7.8 \text{ Hz, 3H} \)), 7.18 (d, \( J = 7.9 \text{ Hz, 2H} \)), 2.38 (s, 3H). \[ \text{C NMR (100 MHz, CDCl}_3\] \( \delta \) 191.8, 139.4, 135.8, 133.7, 133.2, 131.6, 129.3, 128.4, 127.2, 127.2, 119.3, 96.7, 84.4, 21.6.

2-((4-Chlorophenylethynyl)benzaldehyde (1d)

\[ \text{H NMR (400 MHz, CDCl}_3\] \( \delta \) 10.61 (s, 1H), 7.95 (dd, \( J = 7.8, 0.6 \text{ Hz, 1H} \)), 7.64 (dd, \( J = 7.7, 0.8 \text{ Hz, 1H} \)), 7.60 (dd, \( J = 7.3, 1.1 \text{ Hz, 1H} \)), 7.50 (d, \( J = 1.8 \text{ Hz, 1H} \)), 7.49 – 7.46 (m, 2H), 7.39 – 7.34 (m, 2H). \[ \text{C NMR (100 MHz, CDCl}_3\] \( \delta \) 191.4, 135.9, 135.2, 133.8, 133.3, 132.9, 128.9, 127.5, 126.4, 120.9, 95.1, 85.9.

2-(m-Tolyethynyl)benzaldehyde (1e)

\[ \text{H NMR (400 MHz, CDCl}_3\] \( \delta \) 10.65 (d, \( J = 0.6 \text{ Hz, 1H} \)), 7.94 (dd, \( J = 7.8, 0.9 \text{ Hz, 1H} \)), 7.62 (dd, \( J = 7.7, 0.8 \text{ Hz, 1H} \)), 7.56 (td, \( J = 7.6, 1.3 \text{ Hz, 1H} \)), 7.43 (t, \( J = 7.5 \text{ Hz, 1H} \)), 7.40 – 7.33 (m, 2H), 7.26 (dd, \( J = 10.2, 4.9 \text{ Hz, 1H} \)), 7.19 (d, \( J = 7.6 \text{ Hz, 1H} \)), 2.36 (s, 3H). \[ \text{C NMR (100 MHz, CDCl}_3\] \( \delta \) 191.7, 138.3, 135.9, 133.8, 133.2, 132.3, 130.0, 128.8, 128.5, 128.5, 127.3, 127.0, 122.2, 96.7, 84.6, 21.24.

2-((2-Chlorophenylethynyl)benzaldehyde (1f)

\[ \text{H NMR (400 MHz, CDCl}_3\] \( \delta \) 10.72 (d, \( J = 0.8 \text{ Hz, 1H} \)), 7.96 (dd, \( J = 7.8, 0.9 \text{ Hz, 1H} \)), 7.67 (dd, \( J = 7.7, 0.7 \text{ Hz, 1H} \)), 7.61 – 7.56 (m, 2H), 7.49 – 7.43 (m, 2H), 7.33 – 7.24 (m, 2H). \[ \text{C NMR (100 MHz, CDCl}_3\] \( \delta \) 191.8, 136.3, 136.1, 133.8, 133.4, 130.1, 129.5, 129.0, 127.2, 126.7, 126.4, 122.4, 93.0, 80.0.

5-Fluoro-2-(phenylethynyl)benzaldehyde (1g)

\[ \text{H NMR (400 MHz, CDCl}_3\] \( \delta \) 10.58 (d, \( J = 3.2 \text{ Hz, 1H} \)), 7.65 – 7.58 (m, 2H), 7.57 – 7.51 (m, 2H), 7.40 – 7.35 (m, 3H), 7.27 (td, \( J = 8.1, 2.6 \text{ Hz, 1H} \)). \[ \text{C NMR (100 MHz, CDCl}_3\] \( \delta \) 190.4, 162.4 (d, \( J = 251.0 \text{ Hz} \)), 137.8 (d, \( J = 6.6 \text{ Hz} \)), 135.3 (d, \( J = 7.6 \text{ Hz} \)), 83.8, 55.4.
Hz), 131.7, 129.2, 128.6, 123.0, 123.0, 122.1, 121.5, 121.2, 113.8, 113.6, 96.1, 83.9. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -108.9.

5-Methoxy-2-(phenylethynyl)benzaldehyde (1h)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.60 (s, 1H), 7.56 – 7.52 (m, 3H), 7.42 (d, $J$ = 2.8 Hz, 1H), 7.35 (dd, $J$ = 6.6, 3.8 Hz, 3H), 7.12 (dd, $J$ = 8.6, 2.8 Hz, 1H), 3.86 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 191.5, 159.8, 137.2, 134.6, 131.5, 128.8, 128.5, 122.7, 121.7, 119.6, 109.9, 94.9, 84.9, 55.6.

4-Fluoro-2-(phenylethynyl)benzaldehyde (1i)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.55 (s, 1H), 7.96 (dd, $J$ = 8.7, 5.9 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.44 – 7.37 (m, 3H), 7.30 (dd, $J$ = 9.0, 2.2 Hz, 1H), 7.13 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 190.0, 165.7 (d, $J$ = 255.0 Hz), 164.4, 132.6 (d, $J$ = 2.9 Hz), 131.8, 130.1 (d, $J$ = 10.3 Hz), 129.5, 129.4, 129.3, 128.6, 121.8, 119.8, 119.6, 116.6, 116.4, 97.4, 83.8 (d, $J$ = 3.0 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -103.27.

2-(Oct-1-yn-1-yl)benzaldehyde (1j)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.54 (d, $J$ = 0.7 Hz, 1H), 7.90 – 7.86 (m, 1H), 7.52 – 7.47 (m, 2H), 7.40 – 7.35 (m, 1H), 2.48 (t, $J$ = 7.1 Hz, 2H), 1.64 (dd, $J$ = 9.5, 5.3 Hz, 2H), 1.47 (dq, $J$ = 9.7, 7.0 Hz, 2H), 1.32 (td, $J$ = 7.1, 3.4 Hz, 4H), 0.93 – 0.89 (m, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 192.2, 136.0, 133.6, 133.2, 127.9, 127.8, 126.9, 98.2, 76.3, 31.3, 28.6, 28.5, 22.5, 19.6, 14.0.
1.4 Optimization of the reaction conditions for Synthesis of 3a

Table S1 Optimization of the Reaction Conditions for Synthesis of 3a

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<tr>
<th>Entry</th>
<th>cat. (5 mol %)</th>
<th>additive</th>
<th>H₂O (equiv.)</th>
<th>Yield (%)</th>
<th>dr</th>
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</table>

Unless otherwise noted, the reaction was performed in DCE at rt for 12 h using 5 mol % catalyst, 1.0 equiv. of additive and 2.0 equiv. of H₂O under N₂. The molar ratio of 1a:2a = 1:5. [1a] = 0.2M. NPO: 4-nitropyridine N-oxide; PNO: pyridine N-oxide; TEA: triethyl amine; DMAP: N,N-dimethylamino-pyridine; NB: nitrobenzene; o-DNB: 1,2-dinitrobenzene; Imine: (E)-N,1-diphenylmethanimine. The yields were determined by ¹H NMR. Isolated yield. ⁰0.5 equivalent NPO. ⁴0.1 equiv. of NPO.

1.5 General procedure for the synthesis of 3a-3z

To a dichloroethane (DCE, 1.0 mL) suspension of AgSbF₆ (5 mol %) in Schlenk tube with a magnetic
bar under a nitrogen atmosphere, was added 4-Nitropyridine N-oxide (NPO, 0.20 mmol), olefin (2, 1.0 mmol), H₂O (0.4 mmol) and enynals (1, 0.2 mmol), the reaction was stirred at room temperature unless being noted. The reaction was monitored by TLC. The reaction mixture was purified by chromatography with petroleum / ethyl acetate, 4:1, 3 was obtained. Spectral data of product 3 was consistent with data reported in the literature.

Tetrahydronaphthol (3a)⁶

Yield: 89%; dr (E:Z) = 9:1. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 7.8 Hz, 2H), 7.46 (d, J = 8.1 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.29 – 7.23 (m, 1H), 7.21 – 7.11 (m, 6H), 6.92 (d, J = 7.7 Hz, 1H), 4.94 (d, J = 9.3 Hz, 1H), 4.87 (s, 1H), 3.93 – 3.83 (m, 1H), 3.07 (br, 1H), 2.38 – 2.29 (m, 1H), 2.27 – 2.17 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 203.4, 143.5, 138.2, 137.4, 135.2, 133.2, 130.1, 129.0, 128.7, 128.6, 128.5, 128.4, 127.5, 127.5, 126.8, 67.8, 54.9, 39.4, 37.9.

Tetrahydronaphthol (3b)⁶

Yield: 92%; dr (E:Z) = 10:1. ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 7.6 Hz, 2H), 7.50 – 7.42 (m, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.24 (d, J = 9.5 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 7.02 (q, J = 7.8 Hz, 3H), 6.97 – 6.88 (m, 2H), 4.91 (t, J = 9.7 Hz, 1H), 4.85 (s, 1H), 3.89 – 3.80 (m, 1H), 3.14 (br, 1H), 2.34 – 2.26 (m, 1H), 2.23 (d, J = 10.1 Hz, 3H), 2.17 (d, J = 15.7 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 203.4, 140.5, 138.2, 137.4, 136.3, 135.3, 133.1, 130.1, 129.3, 1291, 129.0, 128.6, 128.4, 127.4, 127.4, 67.8, 55.1, 38.9, 38.1, 21.0.

Tetrahydronaphthol (3c)⁶

Yield: 80%; dr (E:Z) = 9:1. ¹H NMR (400 MHz, CDCl₃) δ 7.75 – 7.67 (m, 2H), 7.49 – 7.43 (m, 2H), 7.31 (t, J = 7.8 Hz, 2H), 7.22 (d, J = 15.7, 8.6 Hz, 3H), 7.15 (d, J = 7.6, 1.3 Hz, 1H), 7.09 – 7.06 (m, 2H), 6.91 (d, J = 7.7 Hz, 1H), 4.92 (d, J = 9.0 Hz, 1H), 4.84 (t, J = 3.5 Hz, 1H), 3.83 (m, 1H), 2.97 (br, 1H), 2.33 (m, 1H), 2.27 – 2.18 (m, 1H), 1.24 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 203.8, 149.6, 140.4, 138.4, 137.5, 135.3, 133.0, 130.0, 129.0, 129.6, 128.5, 127.4, 127.1, 125.5, 67.7, 54.9, 39.0, 37.8, 34.4, 31.34.

Tetrahydronaphthol (3d)⁶

Yield: 93%, dr (E:Z) = 10:1. ¹H NMR (400 MHz, CDCl₃) δ 7.78 – 7.69 (m, 2H), 7.53 – 7.43 (m, 2H), 7.35 (t, J = 7.8 Hz, 2H), 7.25 (s, 1H), 7.16 (td, J = 7.6, 1.3 Hz, 1H), 7.14 – 7.07 (m, 2H), 6.95 – 6.83 (m, 3H), 4.88 (t, J = 7.1 Hz, 2H), 3.94 – 3.84 (m, 1H), 3.03 (br, 1H), 2.36 – 2.27 (m, 1H), 2.25 – 2.15 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 203.3, 161.6 (d, J = 243 Hz), 139.2, 139.1, 137.9, 137.4, 135.2, 133.3, 130.2, 129.1, 129.0, 128.9, 128.7, 128.3, 127.6, 115.5, 115.3, 67.7, 55.2, 38.6, 38.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -116.0.

Tetrahydronaphthol (3e)⁶

Yield: 70%, dr (E:Z) = 4:1. ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, J = 7.8 Hz, 2H), 7.54 – 7.43 (m, 2H), 7.36 (t, J = 7.7 Hz, 2H), 7.26 (d, J = 8.4 Hz, 1H), 7.16 (d, J = 8.4 Hz, 3H), 7.08 (d, J = 8.4 Hz, 2H), 6.91 (d, J = 7.7 Hz, 1H), 4.87 (d, J = 9.3 Hz, 1H).
Tetrahydronaphthol (3f)\(^6\)

Yield: 83%, \(dr (E:Z) = 5:1\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.78 – 7.70\) (m, 2H), 7.51 (t, \(J = 7.4\) Hz, 1H), 7.45 (d, \(J = 7.5\) Hz, 1H), 7.37 (t, \(J = 7.8\) Hz, 2H), 7.30 (dd, \(J = 15.2, 7.9\) Hz, 3H), 7.17 (t, \(J = 7.5\) Hz, 1H), 7.03 (d, \(J = 8.4\) Hz, 2H), 6.91 (d, \(J = 7.7\) Hz, 1H), 4.87 (d, \(J = 9.7\) Hz, 2H), 3.92 – 3.83 (m, 1H), 3.01 (br, 1H), 2.35 – 2.26 (m, 1H), 2.23 – 2.12 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 203.0, 142.0, 137.9, 137.3, 135.0, 133.4, 132.5, 130.1, 129.0, 129.0, 128.8, 128.8, 128.7, 128.3, 127.6, 67.6, 54.9, 38.7, 37.8.

Tetrahydronaphthol (3g)\(^6\)

Yield: 68%, \(dr (E:Z) = 4:1\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.80 – 7.74\) (m, 2H), 7.56 – 7.48 (m, 4H), 7.39 (t, \(J = 7.8\) Hz, 2H), 7.33 – 7.28 (m, 3H), 7.22 (td, \(J = 7.6, 1.2\) Hz, 1H), 6.98 – 6.92 (m, 1H), 4.95 (dd, \(J = 7.9, 4.9\) Hz, 4H), 4.06 – 3.98 (m, 1H), 3.03 (br, 1H), 2.37 (dt, \(J = 13.5, 3.4\) Hz, 1H), 2.32 – 2.22 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 202.8, 147.6, 137.8, 137.2, 134.8, 133.4, 130.2, 129.06 – 128.63, 128.3 (d, \(J = 4.3\) Hz), 128.0, 127.7, 125.6 (q, \(J = 3.7\) Hz), 67.5, 54.7, 39.2, 37.7. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta -62.5\).

Tetrahydronaphthol (3h)\(^6\)

Yield: 46%, \(dr (E:Z) = 2:1\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.07\) (d, \(J = 8.7\) Hz, 2H), 7.76 (dd, \(J = 13.4, 6.0\) Hz, 2H), 7.56 (dd, \(J = 13.1, 6.2\) Hz, 1H), 7.47 (d, \(J = 7.2\) Hz, 1H), 7.40 – 7.32 (m, 5H), 7.18 (dd, \(J = 7.6, 1.2\) Hz, 1H), 6.91 (d, \(J = 8.2\) Hz, 1H), 4.94 (dd, \(J = 10.9, 6.8\) Hz, 2H), 4.13 – 4.03 (m, 1H), 2.38 – 2.31 (m, 1H), 2.30 – 2.21 (m, 1H). \(^{13}\)C NMR (100MHz, CDCl\(_3\)) \(\delta 202.3, 151.1, 146.9, 137.5, 137.1, 134.6, 133.6, 130.2, 129.0, 128.9, 128.7, 128.5, 127.8, 123.9, 67.4, 54.5, 39.2, 37.5.

Tetrahydronaphthol (3i)\(^6\)

Yield: 85%, \(dr (E:Z) = 6:1\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.87 – 7.82\) (m, 2H), 7.57 – 7.49 (m, 2H), 7.39 (t, \(J = 7.7\) Hz, 2H), 7.34 – 7.28 (m, 3H), 7.20 (dd, \(J = 9.0, 7.6, 1.4\) Hz, 2H), 7.12 (td, \(J = 7.6, 1.7\) Hz, 1H), 7.02 – 6.97 (m, 1H), 5.13 (d, \(J = 8.5\) Hz, 1H), 4.89 (t, \(J = 3.6\) Hz, 1H), 4.51 – 4.40 (m, 1H), 3.33 (br, 1H), 2.35 (dt, \(J = 13.6, 4.3\) Hz, 1H), 2.32 – 2.24 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 202.7, 140.8, 138.5, 136.8, 134.7, 133.8, 133.3, 132.9, 130.1, 129.8, 129.0, 128.7, 128.6, 128.0, 127.6, 67.7, 53.0, 36.8, 36.2.

Tetrahydronaphthol (3j)\(^6\)

Yield: 79%, \(dr (E:Z) = 5:1\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.81 – 7.70\) (m, 2H), 7.49 (t, \(J = 7.4\) Hz, 1H), 7.44 (d, \(J = 6.9\) Hz, 1H), 7.39 – 7.29 (m, 3H), 7.29 – 7.22 (m, 2H), 7.15 (td, \(J = 7.6, 1.3\) Hz, 1H), 7.10 – 7.00 (m, 2H), 6.90 (t, \(J = 9.3\) Hz, 1H), 4.87 (dd, \(J = 9.9, 6.5\) Hz, 2H), 3.96 – 3.77 (m, 1H), 3.31 (br, 1H), 2.29 (dt, \(J =

57
= 13.6, 3.4 Hz, 1H), 2.23 – 2.10 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 203.1, 145.9, 137.8, 137.3, 134.9, 133.4, 130.7, 130.2, 130.0, 129.0, 128.8, 128.7, 128.4, 128.4, 127.6, 126.3, 122.7, 67.5, 54.8, 39.1, 37.7.

Tetrahydronaphthol (3k)$^6$

Yield: 81%, dr (E:Z) = 13:1. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.77 – 7.71 (m, 2H), 7.46 (m, 2H), 7.32 (dd, J = 10.7, 4.8 Hz, 2H), 7.27 (t, J = 7.5 Hz, 1H), 7.17 (td, J = 7.6, 1.3 Hz, 1H), 7.08 (s, 1H), 6.95 (d, J = 7.7 Hz, 1H), 6.89 (d, J = 7.7 Hz, 1H), 6.84 (t, J = 6.4 Hz, 1H), 5.04 (d, J = 9.3 Hz, 1H), 4.85 (t, J = 3.1 Hz, 1H), 4.13 (m, 1H), 3.30 (br, 1H), 2.22 (s, 3H), 2.07 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 203.9, 141.6, 138.3, 137.4, 135.6, 135.5, 133.2, 132.7, 130.5, 130.1, 128.9, 128.7, 128.6, 128.5, 127.5, 127.2, 127.1, 68.0, 54.2, 38.4, 34.3, 21.2, 19.0.

Tetrahydronaphthol (3l)$^6$

Yield: 84%, dr (E:Z) = 10:1. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.76 (dd, J = 10.9, 7.8 Hz, 4H), 7.71 – 7.66 (m, 1H), 7.61 (s, 1H), 7.51 (d, J = 6.9 Hz, 1H), 7.49 – 7.39 (m, 3H), 7.38 – 7.28 (m, 4H), 7.21 (td, J = 7.6, 1.4 Hz, 1H), 6.99 (d, J = 7.7 Hz, 1H), 5.10 (d, J = 9.2 Hz, 1H), 4.94 (t, J = 3.2 Hz, 1H), 4.16 – 4.06 (m, 1H), 3.18 (br, 1H), 2.43 (dt, J = 13.7, 3.8 Hz, 1H), 2.33 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 203.3, 141.0, 138.2, 137.3, 135.1, 133.5, 133.2, 132.5, 130.1, 129.0, 128.7, 128.6, 128.5, 127.7, 127.6, 126.3, 126.1, 125.6, 67.8, 54.7, 39.4, 38.1.

Tetrahydronaphthol (3m)$^6$

Yield: 81%, dr (E:Z) > 20:1. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.68 – 7.58 (m, 3H), 7.39 – 7.30 (m, 1H), 7.25 – 7.19 (m, 3H), 7.17 – 7.09 (m, 6H), 7.07 (d, J = 7.3 Hz, 3H), 6.94 (dd, J = 10.4, 4.8 Hz, 2H), 6.84 (dd, J = 8.2, 6.4 Hz, 1H), 5.79 (s, 1H), 4.13 (dd, J = 10.6, 5.8 Hz, 1H), 3.49 (dd, J = 12.1, 10.9 Hz, 1H), 2.75 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 201.7, 146.7, 145.9, 140.5, 138.6, 134.8, 132.4, 128.4, 128.2, 128.1, 127.8, 127.8, 127.8, 127.5, 127.4, 126.4, 126.2, 67.6, 53.1, 49.8, 38.9.

Tetrahydronaphthol (3n)$^6$

Yield: 89%, dr (E:Z) = 2:1. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.16 – 8.13 (m, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.65 – 7.58 (m, 3H), 7.52 (t, J = 7.6 Hz, 2H), 7.42 – 7.32 (m, 5H), 7.26 (dt, J = 7.5, 1.5 Hz, 4H), 7.22 – 7.11 (m, 3H), 7.11 – 7.04 (m, 3H), 7.00 – 6.94 (m, 3H), 5.54 (s, 1H), 5.08 (s, 1H), 4.99 (dd, J = 9.3, 7.0 Hz, 1H), 4.35 (t, J = 8.2 Hz, 1H), 3.12 – 3.02 (m, 1H), 2.84 (br, 1H), 2.62 (d, J = 8.3 Hz, 1H), 2.41 (m, 1H), 1.43 (s, 3H), 1.29 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 202.1, 201.9, 146.5, 145.5, 140.2, 139.3, 138.8, 138.5, 134.7, 134.1, 133.5, 132.4, 129.0, 128.9, 128.8, 128.5, 128.3, 128.2, 128.1, 128.0, 127.6, 127.5, 127.5, 126.5, 126.3, 126.0, 125.74, 67.7, 67.1, 56.3, 52.3, 42.6, 41.8, 41.2, 38.1, 30.5, 27.2.

Tetrahydronaphthol (3o)$^6$

Yield: 77%, dr (E:Z) > 20:1. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.73 – 7.65 (m, 2H), 7.48 (t, J = 7.4 Hz, 1H), 7.43 (dd, J = 7.5, 0.9 Hz, 1H), 7.32 (t, J = 7.8 Hz, 2H), 7.26 (dd, J
Tetrahydronaphthol (3p)

Yield: 86%, dr (E:Z) = 20:1. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.09 (d, \(J = 7.4\) Hz, 2H), 7.63 (t, \(J = 7.4\) Hz, 1H), 7.55 – 7.47 (m, 3H), 7.23 (dd, \(J = 9.2, 5.2\) Hz, 1H), 7.14 (d, \(J = 5.2\) Hz, 4H), 7.11 – 7.06 (m, 1H), 6.88 (d, \(J = 7.5\) Hz, 1H), 4.86 (d, \(J = 5.2\) Hz, 1H), 4.68 (d, \(J = 5.7\) Hz, 1H), 4.17 (br, 1H), 4.13 (dd, \(J = 8.6, 5.2\) Hz, 1H), 3.21 – 3.05 (m, 2H), 2.79 (dd, \(J = 15.0, 5.4\) Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 204.0, 143.6, 139.7, 137.0, 134.6, 133.4, 130.0, 129.2, 128.8, 128.7, 128.6, 128.4, 128.2, 127.5, 126.8, 73.0, 56.0, 45.7, 39.8, 16.2.

Tetrahydronaphthol (3q)

Yield: 31%, dr (E:Z) = 6:1. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.03 – 7.97 (m, 2H), 7.58 (td, \(J = 7.3, 5.4\) Hz, 2H), 7.49 (dd, \(J = 11.9, 7.9\) Hz, 2H), 7.31 – 7.25 (m, 1H), 7.08 (t, \(J = 7.5\) Hz, 1H), 6.76 (d, \(J = 7.6\) Hz, 1H), 4.50 (d, \(J = 9.6\) Hz, 1H), 4.28 (d, \(J = 10.8\) Hz, 1H), 2.57 (d, \(J = 3.5\) Hz, 1H), 2.40 (t, \(J = 10.1\) Hz, 1H), 1.96 (d, \(J = 3.5\) Hz, 1H), 1.69 (d, \(J = 10.4\) Hz, 1H), 1.66 – 1.58 (m, 2H), 1.57 – 1.50 (m, 1H), 1.33 (d, \(J = 8.0\) Hz, 1H), 1.27 (d, \(J = 9.7\) Hz, 2H), 1.17 (d, \(J = 10.4\) Hz, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 202.8, 140.7, 138.3, 135.8, 133.5, 128.9, 128.5, 126.9, 126.8, 125.5, 122.7, 70.7, 52.2, 48.2, 45.6, 41.8, 40.1, 33.7, 29.6, 29.4.

Tetrahydronaphthol (3r)

Yield: 88%, dr (E:Z) > 20:1. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.74 (d, \(J = 7.8\) Hz, 2H), 7.50 (t, \(J = 7.3\) Hz, 1H), 7.35 (t, \(J = 7.7\) Hz, 2H), 7.25 – 7.17 (m, 3H), 7.17 – 7.11 (m, 3H), 6.88 (d, \(J = 6.5\) Hz, 2H), 4.92 (d, \(J = 8.5\) Hz, 1H), 4.80 (s, 1H), 3.86 – 3.78 (m, 1H), 3.05 (br, 1H), 2.37 – 2.17 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 203.1, 161.8 ((d, \(J = 245\) Hz), 143.2, 140.7, 140.6, 137.1, 133.3, 130.7, 130.2, 130.1, 128.9, 128.7, 127.4, 126.9, 116.2, 116.0, 115.9, 115.7, 67.4, 53.7, 39.5, 37.6. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -114.6.

Tetrahydronaphthol (3s)

Yield: 83%, dr (E:Z) = 4:1. \(^1\)H NMR (400 MHz, DMSO) \(\delta\) 7.84 (d, \(J = 7.5\) Hz, 2H), 7.57 (t, \(J = 7.4\) Hz, 1H), 7.43 (t, \(J = 7.7\) Hz, 2H), 7.20 (t, \(J = 7.1\) Hz, 4H), 7.09 (d, \(J = 7.8\) Hz, 1H), 7.01 (d, \(J = 2.7\) Hz, 1H), 6.75 (dd, \(J = 8.5, 2.7\) Hz, 1H), 6.66 (d, \(J = 8.5\) Hz, 1H), 5.40 (d, \(J = 4.2\) Hz, 1H), 4.99 (d, \(J = 10.3\) Hz, 1H), 4.76 – 4.66 (m, 1H), 3.82 – 3.76 (m, 1H), 3.74 (s, 3H), 2.27 (td, \(J = 13.1, 3.7\) Hz, 1H), 2.01 (dt, \(J = 13.3, 3.2\) Hz, 1H). \(^{13}\)C NMR (100 MHz, DMSO) \(\delta\) 202.7, 158.2, 144.3, 140.6, 137.8, 133.5, 129.1, 129.0, 128.7, 128.7, 127.4, 126.9, 115.0, 114.4, 66.1, 55.5, 53.5, 39.38, 38.5.

Tetrahydronaphthol (3t)

Yield: 83%, dr (E:Z) > 20:1. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.73 (d, \(J = 7.9\) Hz, 2H), 7.49 (t, \(J = 7.4\) Hz, 1H), 7.44 (dd, \(J = 8.4, 6.0\) Hz, 1H), 7.34 (t, \(J = 7.7\) Hz, 2H), 7.23 – 7.17 (m, 2H), 7.17 – 7.11 (m, 3H), 6.96 (m, 1H), 6.61 (dd, \(J = 9.6, 2.0\) Hz, 1H), 4.91
(d, J = 9.2 Hz, 1H), 4.85 (s, 1H), 3.90 – 3.80 (m, 1H), 3.11 (br, 1H), 2.37 – 2.18 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 202.8, 161.4 (d, J = 246 Hz) 143.1, 137.4, 137.3, 137.2, 134.3, 131.8, 131.7, 128.9, 128.7, 127.5, 127.0, 114.9, 114.8, 114.7, 114.6, 67.1, 54.6, 39.2, 37.9. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -112.81.

**Tetrahydronaphthol (3u)$^6$**

Yield: 77%, dr (E:Z) = 20:1. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.79 – 7.73 (m, 2H), 7.44 (d, J = 6.9 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.21 (d, J = 9.0 Hz, 1H), 7.19 – 7.14 (m, 4H), 7.14 – 7.10 (m, 1H), 6.91 (d, J = 7.7 Hz, 1H), 6.83 – 6.78 (m, 2H), 4.89 (d, J = 9.2 Hz, 1H), 4.85 (s, 1H), 3.87 (m, 1H), 3.78 (s, 3H), 2.34 (m, 1H), 2.20 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 201.8, 163.7 143.8, 138.3, 135.5, 131.5, 130.3, 130.0, 128.6, , 128.4, 127.5, 127.4, 126.8, 113.8, 67.8, 55.5, 54.4, 39.4, 38.0.

**Tetrahydronaphthol (3v)$^6$**

Yield: 83%, dr (E:Z) = 10:1. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.66 (d, J = 8.3 Hz, 2H), 7.44 (m, 1H), 7.28 – 7.23 (m, 1H), 7.21 – 7.17 (m, 3H), 7.17 – 7.10 (m, 5H), 6.91 (d, J = 7.7 Hz, 1H), 4.92 (d, J = 9.2 Hz, 1H), 4.86 (t, J = 3.3 Hz, 1H), 3.88 (m, 1H), 3.23 (br, 1H), 2.36 – 2.30 (m, 4H), 2.20 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 203.0, 144.1, 143.7, 138.2, 135.4, 134.9, 130.0, 129.4, 129.2, 128.6, 128.4, 127.6, 127.4, 126.8, 67.8, 54.6, 39.3, 37.9, 21.6.

**Tetrahydronaphthol (3w)$^6$**

Yield: 85%, dr (E:Z) = 10:1. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.65 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 7.5 Hz, 1H), 7.31 – 7.24 (m, 3H), 7.23 – 7.17 (m, 2H), 7.15 (dd, J = 10.0, 5.1 Hz, 4H), 6.88 (d, J = 7.7 Hz, 1H), 4.88 (t, J = 3.2 Hz, 1H), 4.84 (d, J = 9.8 Hz, 1H), 3.90 – 3.82 (m, 1H), 3.11 (br, 1H), 2.32 (m, 1H), 2.27 – 2.18 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 202.2, 143.2, 139.7, 137.9, 135.6, 135.0, 130.4, 130.3, 128.9, 128.7, 128.3, 127.6, 127.5, 127.0, 67.7, 55.5, 39.4, 37.8.

**Tetrahydronaphthol (3x)$^6$**

Yield: 76%, dr (E:Z) > 20:1. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.56 – 7.50 (m, 2H), 7.46 – 7.42 (m, 1H), 7.30 – 7.20 (m, 3H), 7.20 – 7.09 (m, 6H), 6.90 (d, J = 7.7 Hz, 1H), 4.94 (d, J = 9.3 Hz, 1H), 4.84 (t, J = 3.0 Hz, 1H), 3.88 (m, 1H), 3.27 (br, 1H), 2.33 (m, 1H), 2.28 (s, 3H), 2.25 – 2.16 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 203.7, 143.7, 138.4, 138.3, 137.5, 135.4, 134.0, 130.1, 129.5, 128.6, 128.5, 128.4, 127.6, 127.4, 126.8, 126.2, 67.8, 54.8, 39.4, 37.9, 21.3.

**Tetrahydronaphthol (3y)$^6$**

Yield: 71%, dr (E:Z) > 20:1. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.44 (dd, J = 7.5, 1.1 Hz, 1H), 7.30 – 7.23 (m, 3H), 7.22 – 7.15 (m, 2H), 7.15 – 7.03 (m, 6H), 6.99 (d, J = 1.5 Hz, 1H), 4.97 (d, J = 8.8 Hz, 1H), 4.76 (t, J = 3.5 Hz, 1H), 3.83 – 3.72 (m, 1H), 3.08 (br, 1H), 2.29 (m, 1H), 2.15 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 205.3, 143.4, 139.1, 138.6, 134.2, 131.9, 131.5, 130.6, 130.0, 129.8, 129.0, 128.7, 128.5, 127.7, 127.6, 126.8, 126.6, 67.5, 57.8, 39.5.
Tetrahydronaphthol (3z)\textsuperscript{6}

Yield: 79\%, dr (E:Z) > 20:1. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.42 (d, \(J = 7.5\) Hz, 1H), 7.34 – 7.28 (m, 3H), 7.24 (dd, \(J = 11.3, 5.8\) Hz, 4H), 6.97 (d, \(J = 7.2\) Hz, 1H), 4.84 (s, 1H), 4.12 (d, \(J = 10.0\) Hz, 1H), 3.67 – 3.58 (m, 1H), 2.73 (s, 1H), 2.43 – 2.34 (m, 1H), 2.30 – 2.17 (m, 2H), 2.08 (td, \(J = 13.3, 3.1\) Hz, 1H), 1.47 – 1.35 (m, 2H), 1.25 – 1.18 (m, 2H), 1.12 (dd, \(J = 11.0, 7.7\) Hz, 4H), 0.83 (t, \(J = 7.1\) Hz, 3H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 213.0, 143.5, 137.9, 134.1, 130.2, 128.8, 128.6, 128.1, 127.5, 127.5, 126.9, 67.7, 59.9, 42.5, 38.3, 31.4, 28.6, 23.2, 22.4, 14.0.

phenyl-2-phenyl-1,2-dihydronaphthalen-1-yl)methanone (4a)

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.87 (d, \(J = 7.8\) Hz, 2H), 7.51 (t, \(J = 7.2\) Hz, 1H), 7.40 (t, \(J = 7.6\) Hz, 2H), 7.21 (d, \(J = 4.1\) Hz, 5H), 7.16 (d, \(J = 6.0\) Hz, 2H), 7.05 (t, \(J = 7.3\) Hz, 1H), 6.84 (d, \(J = 7.5\) Hz, 1H), 6.62 (d, \(J = 9.6\) Hz, 1H), 5.97 (dd, \(J = 9.6, 4.1\) Hz, 1H), 5.01 (d, \(J = 7.9\) Hz, 1H), 4.21 – 4.16 (m, 1H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 201.1, 142.9, 137.2, 133.7, 133.0, 131.9, 130.3, 128.7, 128.7, 128.6, 128.0, 127.9, 127.8, 127.7, 127.4, 127.0, 126.6, 53.5, 44.0.

1.6 Optimization of the reaction conditions for Synthesis of 6a

Table S2. Optimization of the Reaction Conditions for Synthesis of 6a\textsuperscript{4}

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<th>Entry</th>
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\textsuperscript{6} Unless otherwise noted, the reaction was performed in DCE for 12 h using 5 mol % catalyst, 1.0 equiv.
of additive and 2.0 equiv. of H₂O under N₂. The molar ratio of 4a:2a or 5a = 1:5. [1a] = 0.2M. NPO: 4-nitopyridine N-oxide; The yields and dr value were determined by ¹H NMR. Isolated yield.

1.7 General procedure for the synthesis of 6a-6u

To a dichloromethane (DCE, 1.0 mL) suspension of AgSbF₆ (5 mol %) in Schlenk tube with a magnetic bar under a nitrogen atmosphere, was added olefin (5, 1.0 mmol), enynimines (4, 0.2 mmol) and H₂O (0.4 mmol), the reaction was stirred at room temperature unless being noted. The reaction was monitored by TLC. The reaction mixture was purified by chromatography with petroleum / ethyl acetate, 20/1, 6 was obtained.

Tetrahydronaphthalamines (6a)

Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 86%, 63.8 mg, dr = 13:1; ¹H NMR (400 MHz, CDCl₃) δ 8.14 – 8.09 (m, 2H), 7.62 (dd, J = 8.3, 6.4 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.42 (d, J = 7.5 Hz, 1H), 7.24 – 7.19 (m, 3H), 7.16 – 7.12 (m, 1H), 6.88 (d, J = 7.7 Hz, 1H), 6.75 – 6.69 (m, 3H), 4.98 (d, J = 6.9 Hz, 1H), 4.84 (t, J = 4.9 Hz, 1H), 4.26 – 4.20 (m, 1H), 3.58 – 3.51 (m, 1H), 3.35 (m, 1H), 2.42 (m, 1H), 2.09 – 2.02 (m, 1H), 1.03 (t, J = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 202.7, 147.3, 138.2, 138.1, 134.7, 133.5, 129.5, 129.0, 128.9, 128.7, 127.9, 127.3, 117.5, 113.0, 75.1, 64.7, 53.2, 50.6, 32.4, 15.4. IR (KBr, cm⁻¹) 3398, 3057, 2973, 2927, 2865, 1680, 1598, 1500, 1442, 1322, 1212, 1171, 1093, 989, 748, 695, 508. HRMS (ESI) Calcd for C₂₃H₂₆NO₂ (M+H)⁺ 372.1958, found 372.1962.

Tetrahydronaphthalamines (6b)

Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 78%, 62.2 mg, dr = 13:1; ¹H NMR (400 MHz, CDCl₃) δ 8.14 – 8.07 (m, 2H), 7.62 (dd, J = 6.6, 3.9, 1.2 Hz, 1H), 7.53 (dd, J = 10.5, 4.7 Hz, 2H), 7.42 (d, J = 7.4 Hz, 1H), 7.26 – 7.18 (m, 4H), 7.14 (dd, J = 7.5, 1.4 Hz, 1H), 6.88 (d, J = 7.6 Hz, 1H), 6.73 (dd, J = 7.8, 6.6 Hz, 3H), 4.98 (d, J = 6.9 Hz, 1H), 4.85 (t, J = 4.8 Hz, 1H), 4.24 – 4.18 (m, 1H), 3.50 (dt, J = 9.2, 6.4 Hz, 1H), 3.27 (dt, J = 9.2, 6.6 Hz, 1H), 2.42 (m, 1H), 2.04 (m, 1H), 1.38 (m, 2H), 1.18 (dd, J = 15.1, 7.4 Hz, 2H), 0.77 (t, J = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 202.8, 147.3 138.2, 138.1, 134.7, 133.4, 129.5, 128.9, 128.9, 128.8, 128.7, 127.9, 127.3, 117.4, 113.0, 75.4, 69.1, 53.1, 50.6, 32.2, 31.9, 19.2, 13.8. IR (KBr, cm⁻¹) 3397, 3057, 3019, 2969, 2924, 2863, 1680, 1597, 1502, 1439, 1365, 1321, 1212, 1171, 1125, 1090, 989, 943, 869, 747, 694, 628, 507, 472. HRMS (ESI) Calcd for C₂₇H₂₆NO₂ (M+H)⁺ 400.2271, found 400.2273.

Tetrahydronaphthalamines (6c)

Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 52%, 38.4mg, dr = 20:1; ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, J = 7.3 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H),
7.49 (t, $J = 7.6$ Hz, 2H), 7.35 (s, 1H), 7.20 (t, $J = 7.8$ Hz, 3H), 7.13 (t, $J = 7.0$ Hz, 1H), 6.93 (s, 1H), 6.74 (t, $J = 7.3$ Hz, 1H), 6.68 (d, $J = 7.8$ Hz, 2H), 4.81 (d, $J = 7.5$ Hz, 1H), 4.75 – 4.68 (m, 1H), 4.37 (d, $J = 9.2$ Hz, 1H), 4.21 (s, 1H), 4.05 – 3.95 (m, 1H), 3.70 (td, $J = 8.8$, 6.3 Hz, 1H), 2.57 – 2.43 (m, 1H), 2.31 – 2.20 (m, 1H), 1.93 – 1.84 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 200.9, 147.7, 139.7, 137.8, 134.3, 133.6, 129.5, 128.8, 127.4, 127.3, 127.2, 125.6, 117.7, 113.0, 79.1, 67.8, 56.7, 51.56, 49.1, 31.5. IR (KBr, cm$^{-1}$) 3377, 3057, 2975, 2913, 2866, 1921, 1673, 1594, 1509, 1440, 1363, 1319, 1273, 1210, 1171, 1066, 991, 946, 865, 807, 742, 692, 644, 578, 507, 459. HRMS (ESI) Calcd for C$_{28}$H$_{32}$NO$_2$ (M+H)$^+$ 370.1802, found 370.1800.

**Tetrahydronaphthylaminess (6d)**

Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 56%, 45.0 mg, $dr > 20$: $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.14 – 8.09 (m, 2H), 7.65 (t, $J = 7.4$ Hz, 1H), 7.53 (t, $J = 7.6$ Hz, 2H), 7.43 (d, $J = 7.5$ Hz, 1H), 7.20 (t, $J = 7.4$ Hz, 1H), 7.13 (td, $J = 7.5$, 1.2 Hz, 1H), 6.88 (d, $J = 7.7$ Hz, 1H), 6.86 – 6.78 (m, 2H), 6.72 – 6.67 (m, 2H), 4.96 (d, $J = 7.0$ Hz, 1H), 4.75 (t, $J = 4.8$ Hz, 1H), 4.27 – 4.20 (m, 1H), 3.76 (s, 3H), 3.58 – 3.50 (m, 1H), 3.40 – 3.30 (m, 1H), 2.41 (m, 1H), 2.02 (m, 1H), 1.03 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (100MHz, CDCl$_3$) $\delta$ 202.8, 152.2, 141.5, 138.3, 138.3, 134.6, 133.4, 128.9, 128.9, 128.7, 127.8, 127.3, 115.1, 114.6, 75.0, 64.7, 55.8, 53.3, 51.7, 32.4, 15.4. IR (KBr, cm$^{-1}$) 3399, 3062, 2973, 2929, 2866, 2832, 1680, 1587, 1511,1447, 1336, 1285, 1238, 1173, 1126, 1089, 1035, 988, 822, 749, 696, 623. HRMS (ESI) Calcd for C$_{28}$H$_{32}$NO$_2$ (M+H)$^+$ 402.2064, found 402.2067.

**Tetrahydronaphthylaminess (6e)**

Yellow solid, m.p = 107-108 °C, purified by chromatography (PE/EA = 20/1), yield = 86%, 66.2 mg, $dr > 20$: $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.11 (d, $J = 7.5$ Hz, 2H), 7.62 (t, $J = 7.3$ Hz, 1H), 7.52 (t, $J = 7.6$ Hz, 2H), 7.42 (d, $J = 7.6$ Hz, 1H), 7.20 (dd, $J = 12.8$, 5.3 Hz, 1H), 7.13 (t, $J = 7.4$ Hz, 1H), 7.03 (d, $J = 7.8$ Hz, 2H), 6.87 (d, $J = 7.6$ Hz, 1H), 6.65 (d, $J = 8.0$ Hz, 2H), 4.96 (d, $J = 6.8$ Hz, 1H), 4.80 (s, 1H), 4.23 (t, $J = 7.6$ Hz, 1H), 3.96 (br, 1H), 3.59 – 3.50 (m, 1H), 3.39 – 3.29 (m, 1H), 2.46 – 2.37 (m, 1H), 2.26 (s, 3H), 2.04 (dd, $J = 15.7$, 6.5 Hz, 1H), 1.03 (td, $J = 7.0$, 1.3 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 202.7, 145.1, 138.3, 138.3, 134.7, 133.4, 130.0, 129.0, 128.9, 128.9, 128.7, 127.9, 127.3, 126.7, 113.2, 75.1, 64.7, 53.2, 51.0, 32.4, 20.5, 15.4. IR (KBr, cm$^{-1}$) 3398, 3061, 3022, 2974, 2923, 2865, 1860, 1612, 1518, 1445, 1366, 1331, 1289, 1212, 1173, 1127, 1090, 989, 946, 905, 809, 750, 696, 625, 580, 508, 465. HRMS (ESI) Calcd for C$_{28}$H$_{32}$NO$_2$ (M+H)$^+$ 386.2115, found 386.2118.

**Tetrahydronaphthylaminess (6f)**

Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 60%, 46.7 mg, $dr > 20$: $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15 – 8.09 (m, 2H), 7.62 (t, $J = 7.3$ Hz, 1H), 7.53 (t, $J = 7.7$ Hz, 2H), 7.41 (d, $J = 7.6$ Hz, 1H), 7.20 (t, $J = 7.4$ Hz, 1H), 7.13 (t, $J = 7.5$ Hz, 1H), 6.90 (dd, $J = 16.6$, 7.7 Hz, 3H), 6.69 – 6.59 (m, 2H), 5.02 – 4.95 (m, 1H), 4.76 (s, 1H), 4.26 – 4.18 (m, 1H), 3.54 (m, 1H), 3.42 – 3.29 (m, 1H), 2.39 (m, 1H), 2.07 – 1.99 (m, 1H), 1.04 (td, $J = 7.0$, 1.6 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 202.7, 155.8 (d, $J = 233$Hz), 143.6, 138.1, 138.0, 134.6, 133.5, 128.9, 128.8, 127.9, 127.3, 115.9, 115.7, 114.0, 75.0, 64.7, 53.1, 51.3, 32.1, 15.3. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -127.8. IR (KBr, cm$^{-1}$) 3401, 3063, 2975,
2929, 2867, 1680, 1606, 1589, 1510, 1445, 1326, 1281, 1216, 1125, 1092, 989, 907, 822, 753, 696, 623, 508. HRMS (ESI) Calcd for C_{23}H_{25}FNO_2 (M+H)^+ 390.1864, found 390.1861.

**Tetrahydronaphthylaminess (6g)**

Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 65%, 50.2 mg, dt > 201; ^1H NMR (400 MHz, CDCl_3) δ 8.14 – 8.09 (m, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.43 (d, J = 7.5 Hz, 1H), 7.21 (t, J = 5.6 Hz, 1H), 7.14 (dd, J = 11.8, 4.4 Hz, 2H), 7.09 (d, J = 7.2 Hz, 1H), 6.90 (d, J = 7.6 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.68 (t, J = 7.3 Hz, 1H), 4.98 (d, J = 6.6 Hz, 1H), 4.91 (t, J = 4.8 Hz, 1H), 4.28 – 4.20 (m, 1H), 3.54 (dq, J = 9.2, 7.0 Hz, 1H), 3.35 (dq, J = 9.2, 7.0 Hz, 1H), 2.44 (m, 1H), 2.15 (s, 3H), 2.07 (m, 1H), 1.04 (t, J = 7.0 Hz, 3H). ^13C NMR (100 MHz, CDCl_3) δ 202.5, 145.3, 138.4, 138.1, 134.7, 133.4, 130.5, 128.9, 128.9, 128.8, 128.7, 127.9, 127.4, 127.2, 122.2, 117.0, 109.8, 75.1, 64.7, 53.3, 50.4, 32.3, 17.8, 15.4. IR (KBr, cm\(^{-1}\)) 3429, 3060, 2975, 2924, 2856, 1683, 1667, 1593, 1509, 1444, 1313, 1250, 1210, 1171, 1085, 1040, 987, 914, 802, 746, 697, 628, 574, 477. HRMS (ESI) Calcd for C_{28}H_{28}NO (M+H)^+ 386.2115, found 386.2113.

**Tetrahydronaphthylaminess (6h)**

Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 73%, 56.4 mg, dt > 201; ^1H NMR (400 MHz, CDCl_3) δ 8.15 – 8.08 (m, 2H), 7.62 (m, 1H), 7.53 (dd, J = 10.5, 4.7 Hz, 2H), 7.42 (d, J = 7.5 Hz, 1H), 7.20 (t, J = 7.3 Hz, 1H), 7.16 – 7.08 (m, 2H), 6.88 (d, J = 7.6 Hz, 1H), 6.59 – 6.52 (m, 3H), 4.97 (d, J = 7.0 Hz, 1H), 4.84 (t, J = 4.8 Hz, 1H), 4.27 – 4.20 (m, 1H), 3.55 (dq, J = 9.2, 7.0 Hz, 1H), 3.35 (dq, J = 9.3, 7.0 Hz, 1H), 2.47 – 2.37 (m, 1H), 2.30 (s, 3H), 2.04 (m, 1H), 1.04 (t, J = 7.0 Hz, 3H). ^13C NMR (100 MHz, CDCl_3) δ 202.7, 147.3, 139.2, 138.2, 138.2, 133.4, 129.3, 128.9, 128.9, 128.8, 128.7, 127.8, 127.3, 118.3, 113.7, 110.0, 75.1, 64.7, 53.2, 50.6, 32.4, 21.7, 15.3. IR (KBr, cm\(^{-1}\)) 3396, 3057, 3025, 2973, 2924, 2863, 1680, 1597, 1486, 1444, 1327, 1289, 1213, 1172, 1091, 990, 909, 849, 762, 695, 590, 476. HRMS (ESI) Calcd for C_{29}H_{32}NO_2 (M+H)^+ 386.2115, found 386.2113.

**Tetrahydronaphthylaminess (6j)**

Yellow solid, m. p. = 83-84 °C, purified by chromatography (PE/EA = 15/1), yield = 75%, 60.3 mg, dt = 15:1; ^1H NMR (400 MHz, CDCl_3) δ 8.14 – 8.08 (m, 2H), 7.41 (d, J = 7.5 Hz, 1H), 7.24 – 7.17 (m, 3H), 7.12 (dd, J = 7.5, 1.4 Hz, 1H), 7.02 – 6.98 (m, 2H), 6.88 (d, J = 7.6 Hz, 1H), 6.75 – 6.69 (m, 3H), 4.93 (d, J = 6.8 Hz, 1H), 4.83 (t, J = 4.8 Hz, 1H), 4.25 – 4.20 (m, 1H), 3.88 (s, 3H), 3.57 – 3.50 (m, 1H), 3.35 (dq, J = 9.3, 7.0 Hz, 1H), 2.43 (m, 1H), 2.07 – 2.00 (m, 1H), 1.04 (t, J = 7.0 Hz, 3H). ^13C NMR (100 MHz, CDCl_3) δ 200.9, 163.9, 147.3, 138.1, 134.9, 131.3, 131.2, 129.4, 128.9, 128.7, 127.8, 127.2, 117.3, 114.0, 113.0, 75.1, 64.7, 55.5, 52.7, 50.6, 32.4, 15.4. IR (KBr, cm\(^{-1}\)) 3396, 3057, 2973, 2928, 2872, 2843, 1732, 1670, 1600, 1504, 1451, 1424, 1366,1320, 1259, 1216, 1170, 1089, 1079, 1026, 984, 950, 907, 837, 745, 691, 622, 586, 510, 468. HRMS (ESI) Calcd for C_{28}H_{28}NO_2 (M+H)^+ 402.2064, found 402.2060.

**Tetrahydronaphthylaminess (6k)**

Brown solid, m. p. = 131-132 °C, purified by chromatography (PE/EA = 20/1), yield = 80%, 61.8mg, dt = 19:1; ^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, J = 8.1 Hz, 2H), 7.42
(d, J = 7.7 Hz, 1H), 7.33 (d, J = 8.2 Hz, 2H), 7.23 (s, 1H), 7.23 – 7.16 (m, 3H), 7.13 (dd, J = 10.6, 4.2 Hz, 1H), 6.88 (d, J = 7.7 Hz, 1H), 6.75 – 6.70 (m, 3H), 4.95 (d, J = 6.8 Hz, 1H), 4.84 (s, 1H), 4.27 – 4.20 (m, 1H), 3.58 – 3.50 (m, 1H), 3.36 (dq, J = 9.1, 7.0 Hz, 1H), 2.45 (s, 3H), 2.34 – 2.16 (m, 1H), 2.09 – 2.01 (m, 1H), 1.04 (t, J = 7.0 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 202.1, 147.3, 144.4, 138.1, 135.7, 134.8, 129.5, 129.4, 129.0, 128.9, 128.7, 127.8, 127.2, 117.4, 112.9, 75.0, 64.7, 52.9, 50.6, 53.2, 21.7, 15.4. IR (KBr, cm$^{-1}$) 3396, 3056, 3021, 2974, 2926, 2862, 1677, 1602, 1502, 1440, 1371, 1324, 1284, 1177, 1124, 1092, 988, 949, 908, 822, 745, 691, 625, 589, 510, 472. HRMS (ESI) Caled for C$_{29}$H$_{28}$NO$_2$ (M+H)$^+$ 436.2115, found 436.2118.

Tetrahydrophosphorylaminines (6l)

Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 78%, 63.2mg, dr = 17:1. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.07 – 8.04 (m, 2H), 7.52 – 7.48 (m, 2H), 7.41 (d, J = 7.5 Hz, 1H), 7.24 – 7.19 (m, 3H), 7.16 – 7.12 (m, 1H), 6.84 (d, J = 7.6 Hz, 1H), 6.76 – 6.69 (m, 3H), 4.90 (d, J = 7.2 Hz, 1H), 4.83 (t, J = 4.6 Hz, 1H), 4.24 – 4.17 (m, 1H), 3.58 – 3.52 (m, 1H), 3.31 (dq, J = 9.3, 7.0 Hz, 1H), 2.44 (m, 1H), 2.05 – 1.98 (m, 1H), 1.02 (t, J = 7.0 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 201.7, 147.1, 140.0, 138.0, 136.6, 134.5, 130.3, 129.4, 129.1, 128.5, 128.0, 127.4, 117.5, 112.9, 75.1, 64.7, 53.2, 50.7, 32.3, 15.3. IR (KBr, cm$^{-1}$) 3396, 3057, 2972, 2926, 2865, 1682, 1596, 1497, 1439, 1321, 1280, 1211, 1170, 1092, 998, 907, 828, 748, 691, 630, 543, 470. HRMS (ESI) Caled for C$_{29}$H$_{28}$ClNO$_2$ (M+H)$^+$ 406.1568, found 406.1569.

Tetrahydrophosphorylaminines (6m)

Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 68%, 55.1mg, dr > 20:1. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.59 (dd, J = 7.6, 1.7 Hz, 1H), 7.46 (dt, J = 9.4, 4.8 Hz, 2H), 7.41 (td, J = 7.6, 1.8 Hz, 1H), 7.34 (td, J = 7.4, 1.3 Hz, 1H), 7.25 – 7.17 (m, 4H), 7.07 (dd, J = 7.0, 1.7 Hz, 1H), 6.75 – 6.67 (m, 3H), 4.83 (t, J = 5.2 Hz, 2H), 4.22 – 4.15 (m, 1H), 3.96 (br, 1H), 3.53 (dq, J = 9.1, 7.0 Hz, 1H), 3.34 (dq, J = 9.2, 7.0 Hz, 1H), 2.36 (m, 1H), 2.08 (m, 1H), 1.05 (t, J = 7.0 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 204.2, 147.3, 139.8, 138.2, 133.3, 132.0, 131.3, 130.8, 129.7, 129.5, 129.3, 128.8, 127.8, 127.6, 126.9, 117.4, 112.9, 74.8, 64.4, 57.0, 50.1, 32.1, 15.3. IR (KBr, cm$^{-1}$) 3399, 3058, 2973, 2927, 2869, 1696, 1597, 1502, 1424, 1371, 1318, 1253, 1208, 1094, 1073, 988, 950, 871, 748, 695, 640, 509, 466. HRMS (ESI) Caled for C$_{29}$H$_{28}$ClNO$_2$ (M+H)$^+$ 406.1568, found 406.1571.

Tetrahydrophosphorylaminines (6n)

Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 72%, 55.4mg, dr > 20:1. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.96 – 7.87 (m, 2H), 7.47 – 7.40 (m, 3H), 7.24 – 7.18 (m, 3H), 7.14 (td, J = 7.5, 1.3 Hz, 1H), 6.88 (d, J = 7.6 Hz, 1H), 6.73 (dd, J = 7.5, 5.2 Hz, 3H), 4.97 (d, J = 6.9 Hz, 1H), 4.85 (t, J = 4.5 Hz, 1H), 4.27 – 4.20 (m, 1H), 4.07 (br, 1H), 3.55 (dq, J = 9.2, 7.0 Hz, 1H), 3.36 (dq, J = 9.3, 7.0 Hz, 1H), 2.48 – 2.38 (m, 4H), 2.05 (m, 1H), 1.05 (t, J = 7.0 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 202.8, 147.2, 138.7, 138.2, 134.7, 134.2, 129.4, 129.3, 128.9, 128.7, 128.7, 127.8, 127.2, 126.1, 117.4, 112.9, 75.0, 64.7, 53.1, 50.6, 32.3, 21.4, 15.3. IR (KBr, cm$^{-1}$) 3396, 3054, 2970, 2922, 2868, 1678, 1597, 1500, 1426, 1366, 1318, 1243, 1165, 1091, 990, 954, 750, 693, 631, 587, 466. HRMS (ESI) Caled for C$_{29}$H$_{28}$NO$_2$ (M+H)$^+$ 386.2115, found 386.2115.
Tetrahydronaphthylamines (6o)

Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 81%, 61.4mg, 

\[ \text{dr > 20:1; } ^1H NMR \ (400 MHz, CDCl}_3 \delta 7.42 – 7.36 \ (m, 1H), 7.21 \ (dt, J = 10.2, 5.9 Hz, 4H), 6.97 – 6.90 \ (m, 1H), 6.76 – 6.65 \ (m, 3H), 4.78 \ (t, J = 4.9 Hz, 1H), 4.05 – 3.99 \ (m, 2H), 3.58 \ (m, 1H), 3.37 \ (dq, J = 9.2, 7.0 Hz, 1H), 2.76 – 2.58 \ (m, 2H), 2.39 – 2.31 \ (m, 1H), 1.94 \ (m, 1H), 1.69 – 1.59 \ (m, 2H), 1.32 \ (dt, J = 11.6, 6.0 Hz, 6H), 1.14 \ (t, J = 7.0 Hz, 3H), 0.89 \ (t, J = 6.7 Hz, 3H). \]

\[ ^{13}C \text{NMR (100 MHz, CDCl}_3 \delta 212.3, 147.2, 137.7, 133.7, 129.4, 129.1, 128.4, 127.9, 127.45, 117.5, 112.9, 74.6, 64.2, 58.4, 50.6, 44.5, 32.1, 31.6, 28.9, 23.4, 22.5, 15.4, 14.0. \]

\[ \text{IR (KBr, cm}^{-1} \text{): 3396, 3056, 2966, 2925, 2859, 1711, 1600, 1502, 1440, 1368, 1314, 1248, 1171, 1126, 1096, 956, 869, 749, 693, 628, 507, 465. } \]

HRMS (ESI) Calcd for C_{25}H_{32}NO_2 (M+H)^+ 380.2584, 

found 380.2586.

Tetrahydronaphthylamines (6p)

Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 46%, 35.5mg, 

\[ \text{dr > 20:1; } ^1H NMR \ (400 MHz, CDCl}_3 \delta 8.10 \ (d, J = 7.9 Hz, 2H), 7.63 \ (t, J = 7.4 Hz, 1H), 7.53 \ (t, J = 7.7 Hz, 2H), 7.24 – 7.18 \ (m, 3H), 6.85 \ (d, J = 6.8 Hz, 2H), 6.73 \ (dd, J = 12.4, 7.8 Hz, 3H), 4.96 \ (d, J = 5.4 Hz, 1H), 4.82 \ (s, 1H), 4.21 – 4.12 \ (m, 1H), 4.04 \ (br, 1H), 3.57 \ (dt, J = 7.1, 6.5 Hz, 1H), 3.46 – 3.37 \ (m, 1H), 2.24 \ (m, 1H), 2.19 – 2.10 \ (m, 1H), 1.09 \ (td, J = 7.0, 1.5 Hz, 3H). \]

\[ ^{13}C \text{NMR (100 MHz, CDCl}_3 \delta 201.7, 161.9 \ (d, J = 244.0 Hz), 147.1, 141.0, 140.9, 137.6, 133.6, 130.6, 130.5, 129.8, 129.8, 129.5, 128.9, 128.8, 117.7, 115.7, 114.9, 114.7, 113.1, 74.8, 64.7, 52.2, 49.8, 31.7, 15.4. \]

\[ ^{19}F \text{NMR (376 MHz, CDCl}_3 \delta -114.7, -114.7. } \]

\[ \text{IR (KBr, cm}^{-1} \text{): 3396, 3351, 3056, 2974, 2927, 2863, 1681, 1603, 1500, 1445, 1369, 1322, 1248, 1212, 1176, 1091, 993, 963, 914, 878, 809, 748, 695, 566, 512, 467. } \]

HRMS (ESI) Calcd for C_{26}H_{33}FNO_2 (M+H)^+ 390.1864, 

found 390.1869.

Tetrahydronaphthylamines (6q)

White solid, m. p. = 108-109 °C, purified by chromatography (PE/EA = 15/1), yield = 52%, 41.8mg, 

\[ \text{dr > 18:1; } ^1H NMR \ (400 MHz, CDCl}_3 \delta 8.10 \ (d, J = 7.4 Hz, 2H), 7.61 \ (t, J = 7.4 Hz, 1H), 7.52 \ (t, J = 7.6 Hz, 2H), 7.22 \ (dd, J = 10.7, 4.9 Hz, 2H), 6.97 \ (d, J = 2.6 Hz, 1H), 6.79 \ (d, J = 8.6 Hz, 1H), 6.75 – 6.69 \ (m, 4H), 4.91 \ (d, J = 6.6 Hz, 1H), 4.81 \ (t, J = 5.0 Hz, 1H), 4.24 – 4.17 \ (m, 1H), 3.70 \ (s, 3H), 3.58 – 3.50 \ (m, 1H), 3.40 – 3.30 \ (m, 1H), 2.37 \ (m, 1H), 2.05 \ (m, 1H), 1.04 \ (t, J = 7.0 Hz, 3H). \]

\[ ^{13}C \text{NMR (100 MHz, CDCl}_3 \delta 202.7, 158.7, 147.2, 139.4, 138.1, 133.4, 129.7, 129.4, 128.8, 126.6, 117.5, 114.7, 113.0, 75.1, 64.7, 55.3, 52.5, 50.71, 32.1, 15.4. } \]

\[ \text{IR (KBr, cm}^{-1} \text{): 3395, 3055, 2970, 2927, 2867, 2839, 1680, 1603, 1501, 1438, 1368, 1323, 1250, 1181, 1035, 992, 874, 809, 750, 695, 572, 512, 473. } \]

HRMS (ESI) Calcd for C_{26}H_{33}NO_3 (M+H)^+ 402.2064, 

found 402.2069.

Tetrahydronaphthylamines (6r)

Brown solid, m. p. = 82-83 °C, purified by chromatography (PE/EA = 20/1), yield = 50%, 40.3mg, 

\[ \text{dr > 20:1; } ^1H NMR \ (400 MHz, CDCl}_3 \delta 7.77 – 7.71 \ (m, 2H), 7.50 \ (t, J = 7.4 Hz, 1H), 7.44 \ (d, J = 7.1 Hz, 1H), 7.36 \ (t, J = 7.7 Hz, 2H), 7.25 \ (s, 1H), 7.21 – 7.14 \ (m, 7H), 7.13 – 7.08 \ (m, 1H), 6.91 \ (d, J = 7.7 Hz, 1H), 6.75 – 6.66 \ (m, 3H), 5.07 \ (d, J = 9.2 Hz, 1H), 4.76 \ (t, J = 3.4 Hz, 1H), 4.36 \ (br, 1H), 3.72 \ (m, 1H), 2.47 \ (dt, J = 13.3, 3.4 Hz, 1H), \]
2.28 – 2.19 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 203.6, 147.1, 143.5, 138.2, 137.8, 136.1, 133.2, 130.3, 129.5, 128.7, 128.7, 128.6, 128.5, 128.2, 127.6, 127.4, 126.8, 117.4, 113.0, 53.6, 50.9, 40.2, 34.0. IR (KBr, cm⁻¹) 3407, 3337, 3058, 3021, 2944, 2919, 2857, 1678, 1595, 1499, 1441, 1326, 1256, 1211, 1169, 1111, 1068, 994, 909, 865, 758, 696, 589, 541, 505, 473. HRMS (ESI) Caled for C₂₅H₂₅N₂O (M+H)⁺ 404.2009, found 404.2014.

**Tetrahydronaphthylamininess (6s)**

Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 33%. 27.8mg, dr > 20:1; ¹H NMR (400 MHz, CDCl₃) δ 7.77 – 7.72 (m, 2H), 7.50 (dd, J = 10.6, 4.2 Hz, 1H), 7.42 (d, J = 6.9 Hz, 1H), 7.37 (t, J = 7.7 Hz, 2H), 7.22 (t, J = 7.1 Hz, 2H), 7.18 – 7.15 (m, 2H), 7.11 (ddd, J = 8.7, 4.6, 1.6 Hz, 2H), 6.91 – 6.80 (m, 3H), 6.73 – 6.67 (m, 3H), 5.00 (d, J = 9.5 Hz, 1H), 4.76 (s, 1H), 4.31 (br, 1H), 3.72 (m, 1H), 2.44 (dt, J = 13.3, 3.3 Hz, 1H), 2.18 (d, J = 3.1 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 203.4, 161.6 (d, J = 244.0 Hz), 146.9, 146.7, 139.2, 139.1, 138.1, 137.5, 136.0, 133.3, 130.4, 129.4, 129.1, 129.0, 128.7, 128.6, 128.4, 128.2, 127.4, 117.4, 115.5, 115.2, 112.9, 53.8, 51.0, 39.4, 34.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -115.92. IR (KBr, cm⁻¹) 3402, 3055, 3016, 2951, 2920, 2856, 1677, 1597, 1503, 1437, 1322, 1303, 1211, 1166, 1108, 1068, 996, 905, 828, 748, 696, 543, 504. HRMS (ESI) Caled for C₂₅H₂₂FNO (M+H)⁺ 422.1915, found 422.1919.

**Tetrahydronaphthylamininess (6i)**

Yellow oil, purified by chromatography (PE/EA = 20/1), yield = 70%. 50.0mg, dr > 20:1; ¹H NMR (400 MHz, CDCl₃) δ 7.74 (dd, J = 10.0, 4.2 Hz, 2H), 7.46 (m, 2H), 7.37 – 7.31 (m, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.15 (dd, J = 15.9, 7.7 Hz, 3H), 6.95 (m, 5H), 6.71 – 6.65 (m, 3H), 5.05 (dd, J = 9.1, 4.4 Hz, 1H), 4.73 (d, J = 3.3 Hz, 1H), 4.32 (br, 1H), 3.73 – 3.64 (m, 1H), 2.44 (m, 1H), 2.24 – 2.14 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 203.7, 203.5, 147.1, 143.4, 140.4, 138.2, 138.1, 138.1, 137.91, 137.8, 136.3, 136.2, 136.1, 133.1, 130.3, 130.2, 129.4, 129.3, 128.7, 128.6, 128.5, 128.5, 128.4, 128.1, 127.5, 127.4, 127.3, 124.4, 117.3, 131.0, 53.6, 50.9, 40.0, 39.6, 34.2, 34.1, 21.4, 21.0. IR (KBr, cm⁻¹) 3041, 3055, 3017, 2951, 2919, 2858, 1727, 1678, 1598, 1502, 1438, 1321, 1253, 1212, 1173, 1111, 1070, 993, 905, 864, 818, 746, 696, 544, 506. HRMS (ESI) Caled for C₂₅H₂₅NO (M+H)⁺ 418.2165, found 418.2171.

**Tetrahydronaphthylamininess (6u)**

Yellow oil, purified by chromatography (PE/EA = 15/1), yield = 77%. 66.7mg, dr > 20:1; ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 7.6 Hz, 2H), 7.49 – 7.38 (m, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.22 – 7.11 (m, 4H), 7.05 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 7.5 Hz, 1H), 6.67 (t, J = 8.2 Hz, 5H), 5.02 (d, J = 9.1 Hz, 1H), 4.73 (s, 1H), 4.32 (br, 1H), 3.73 – 3.57 (m, 4H), 2.41 (d, J = 13.3 Hz, 1H), 2.16 (td, J = 13.1, 3.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 203.6, 158.3, 147.1, 138.2, 137.8, 136.2, 135.6, 133.2, 130.3, 129.5, 128.7, 128.5, 128.1, 127.3, 117.4, 114.0, 113.0, 55.2, 53.8, 51.0, 39.3, 34.3. IR (KBr, cm⁻¹) 3403, 3056, 3014, 2948, 2919, 2838, 1677, 1602, 1505, 1435, 1307, 1250, 1212, 1179, 1110, 1033, 993, 904, 824, 743, 696, 547. HRMS (ESI) Caled for C₂₅H₂₅N₂O₂ (M+H)⁺ 434.2115, found 434.2115.

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1.8 Chemical transformation of 6d

To a solution of compound 6d (41.2 mg, 0.2 mmol) in MeCN/H₂O (4:1, 1 mL) was added ceric ammonium nitrate (548.2 mg, 0.8 mmol) at 0 °C, and the reaction mixture was stirred for 1 hour. The reaction was quenched with 10% aqueous NaOH and adjusted to pH = 9 to give a mass. The mass was filtered through a pad of celite, washed with DCM. The solution was extracted with DCM. The organic phase was washed with brine and dried over anhydrous Na₂SO₄. The solvent was removed and the residue was purified on PE: EA=10:1 to give a brown oil.

(4-Amino-2-ethoxy-1,2,3,4-tetrahydronaphthalen-1-yl)(phenyl)methanone (7)

Brown solid, m. p. = 104-105 °C, purified by chromatography (PE/EA = 10:1), yield = 75%, 44.3 mg, dr > 20:1; ¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.83 (m, 2H), 7.46 – 7.39 (m, 3H), 7.35 (m, 2H), 7.24 (qd, J = 4.7, 1.7 Hz, 2H), 5.64 (dd, J = 3.2, 1.9 Hz, 1H), 5.13 (d, J = 3.3 Hz, 1H), 3.81 (dt, J = 8.6, 3.0 Hz, 1H), 3.66 (dq, J = 9.2, 7.0 Hz, 1H), 3.43 (dq, J = 9.2, 7.0 Hz, 1H), 2.30 – 2.20 (m, 1H), 1.37 – 1.32 (m, 1H), 1.09 (t, J = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 173.8, 140.7, 136.2, 134.4, 130.6, 128.6, 126.6, 126.3, 126.3, 125.5, 122.8, 73.6, 63.9, 62.1, 47.2, 34.4, 15.2. IR (KBr, cm⁻¹) 3650, 3072, 2968, 2925, 2857, 1731, 1679, 1603, 1568, 1448, 1347, 1164, 1096, 1049, 968, 874, 759, 692, 580, 523. HRMS (ESI) Calcd for C₁₉H₂₉NO₂ (M+H)⁺ 296.1642, found 296.1639.

1.9 Procedure for the preparation of the O¹⁸-3a

To a dichloroethane (DCE, 1.0 mL) suspension of AgSbF₆ (5 mol %) in Schlenk tube with a magnetic bar under a nitrogen atmosphere, was added 4-Nitropyridine N-oxide (NPO, 0.20 mmol), olefin (2a, 1.0 mmol), H₂O¹⁸ (0.4 mmol) and enynals (1a, 0.2 mmol), the reaction was stirred at room temperature. The reaction was monitored by TLC. The reaction mixture was purified by chromatography with petroleum / ethyl acetate, 4:1. O¹⁸-3a was obtained. The labeled O¹⁸ was on the carbonyl group as the ¹³C NMR illustrated (Figure S1).
$^{18}$O-3a

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 203.4, 143.5, 138.1, 137.3, 135.2, 133.2, 130.0, 128.9, 128.6, 128.6, 128.4, 127.5, 126.8, 67.8, 54.8, 39.3, 37.8. HRMS (ESI) Calcd for (M+Na)$^+$ 353.13930, found 353.13980.

Figure S1. Comparison and assignment of the carbonyl carbon signal in $^{13}$C NMR spectra of $^{18}$O-3a and 3a

2. References

3. X-Ray diffraction analysis

3.1 Crystal data and structure refinement for 3d

CCDC number 1589273
Identification code 3d
Empirical formula C₂₃H₁₉FO₂
Formula weight 346.38
Temperature/K 100.00(10)
Crystal system triclinic
Space group P-1
a/Å 8.9683(5)
b/Å 9.8217(5)
c/Å 11.3530(7)
α/° 75.074(5)
β/° 77.458(5)
γ/° 63.345(5)
Volume/Å³ 857.58(9)
Z 2
ρ calc g/cm³ 1.341
μ/mm⁻¹ 0.092
F(000) 364.0
Crystal size/mm³ 0.14 × 0.12 × 0.11
Radiation MoKα (λ = 0.71073)
2θ range for data collection/° 4.72 to 59.058
Index ranges -12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -15 ≤ l ≤ 15
Reflections collected 14359
Independent reflections 4222 [Rint = 0.0439, Rsigma = 0.0516]
Data/restraints/parameters 4222/0/236
Goodness-of-fit on F² 1.034
Final R indexes [I>2σ (I)] R₁ = 0.0489, wR₂ = 0.1073
Final R indexes [all data] R₁ = 0.0681, wR₂ = 0.1198
Largest diff. peak/hole / e Å⁻³ 0.28/ -0.30
3.2 Crystal data and structure refinement for 6q

CCDC number 1524750
Identification code 6q
Empirical formula C_{26}H_{27}NO_{3}
Formula weight 401.48
Temperature/K 100.00(10)
Crystal system triclinic
Space group P-1
a/Å 9.2089(3)
b/Å 10.5763(4)
c/Å 10.9769(4)
α/° 100.503(3)
β/° 95.221(3)
γ/° 91.160(3)
Volume/Å³ 1046.09(7)
Z 2
ρ_{calc}g/cm³ 1.275
μ/mm⁻¹ 0.658
F(000) 428.0
Crystal size/mm³ 0.25 × 0.21 × 0.18
Radiation Cu Kα (λ = 1.54184)
2θ range for data collection" 8.23 to 147.28
Index ranges -9 ≤ h ≤ 11, -10 ≤ k ≤ 13, -13 ≤ l ≤ 13
Reflections collected 6974
Independent reflections 4070 [R_{int} = 0.0153, R_{sigma} = 0.0185]
Data/restraints/parameters 4070/0/273
Goodness-of-fit on F² 1.044
Final R indexes [I>2σ (I)] R_1 = 0.0398, wR_2 = 0.1020
Final R indexes [all data] R_1 = 0.0418, wR_2 = 0.1039
Largest diff. peak/hole / e Å⁻³ 0.34/-0.35
4. Copies of NMR spectra
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\[ \text{Diagram of molecule} \]

\[ \text{Diagram of molecule} \]