**Borane-Catalyzed Cascade Friedel-Crafts Alkylation/[1,5]-Hydride Transfer/Mannich Cyclization to Afford Tetrahydroquinolines**

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1. General information

$^{1}$H and $^{13}$C NMR spectra were recorded on a Bruker (400 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform $\delta$ 7.26), carbon (chloroform $\delta$ 77.0) or tetramethylsilane (TMS $\delta$ 0.00) was used as a reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), bs (broad singlet). Coupling constants were reported in Hertz (Hz). All high resolution mass spectra (HRMS) were obtained on Agilent 1260-6224 LC-MS TOF using ESI (electrospray ionization). For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with I$_2$ and KMnO$_4$.

All reactions were carried out under nitrogen atmosphere. All commercially available reagents were used as received for the reactions without any purification. All solvents were dried on alumina columns using a solvent dispensing system. B(C$_6$F$_5$)$_3$ were purchased from TCI. Tertiary anilines 1 were synthesized following the reported procedure$^1$. Alkynones 2 and 5 were synthesized following the reported procedure$^{2,3}$.
2. General procedure for syntheses of functionalized 1,2,3,4-tetrahydroquinolines

To a Schlenk tube equipped with a dried stir bar was added B(C₆F₅)₃ (0.02 mmol), tertiary aniline 1 (0.24 mmol), alkynone 2 (0.20 mmol), TMSOTf (0.02 mmol) and toluene (1.0 mL) in the glovebox. The Schlenk tube was sealed with a Teflon screw cap. The reaction mixture was taken outside the glovebox and allowed to stir at 80 °C for 24 hours. The crude reaction mixture was concentrated under reduced pressure and directly purified by silica gel chromatography (ethyl acetate:hexanes = 1:10) to afford the desired functionalized 1,2,3,4-tetrahydroquinolines 3.

To a Schlenk tube equipped with a dried stir bar was added B(C₆F₅)₃ (0.02 mmol), N,N,4-trimethylaniline 1a (0.24 mmol), tris(trifluoromethyl)-α,β-ynones 5 (0.20 mmol), TMSOTf (0.02 mmol) and toluene (1.0 mL) in the glovebox. The Schlenk tube was sealed with a Teflon screw cap. The reaction mixture was taken outside the glovebox and allowed to stir at 80 °C for 24 hours. The crude reaction mixture was concentrated under reduced pressure and directly purified by silica gel chromatography (ethyl acetate:hexanes = 1:10) to afford the desired functionalized tetrahydroquinolines 6.
3. Analytical data for products

ethyl 2-(trans-1,6-dimethyl-4-phenyl-1,2,3,4-tetrahydroquinolin-3-yl)-2-oxo-acetate (3a):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3a as a yellow oil, 46.5 mg, 69% yield, >20:1 dr. Rf = 0.47 (1:5 EtOAc/Hexanes).

\[ \text{Rf} = 0.47 \text{ (1:5 EtOAc/Hexanes).} \]

**\( ^1\text{H NMR} \) (400 MHz, Chloroform-\( d \)) \( \delta \): 7.31 – 7.26 (m, 2H), 7.24 – 7.20 (m, 1H), 7.14 – 7.12 (m, 2H), 6.95 (dd, \( J = 8.3 \), 2.2 Hz, 1H), 6.64 – 6.61 (m, 2H), 4.50 (d, \( J = 6.5 \) Hz, 1H), 4.25 – 4.17 (m, 2H), 3.80 (td, \( J = 6.7 \), 3.4 Hz, 1H), 3.42 (dd, \( J = 11.3 \), 6.4 Hz, 1H), 3.33 (dd, \( J = 11.7 \), 3.4 Hz, 1H), 2.93 (s, 3H), 2.13 (s, 3H), 1.28 (t, \( J = 7.1 \) Hz, 3H).

**\( ^1\text{C NMR} \) (101 MHz, Chloroform-\( d \)) \( \delta \): 194.66, 161.26, 144.53, 143.93, 130.72, 129.11, 128.44, 128.28, 126.68, 123.29, 111.91, 62.30, 49.76, 44.59, 39.68, 20.24, 13.89.

**HRMS (ESI):** m/z Calcd. for \([\text{C}_{21}\text{H}_{24}\text{NO}_3], \text{M+H}\]^+: 338.1750; Found: 338.1750.

ethyl 2-(trans-6-ethyl-1-methyl-4-phenyl-1,2,3,4-tetrahydroquinolin-3-yl)-2-oxo-acetate (3b):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3b as a yellow solid, 46.3 mg, 66% yield, >20:1 dr. m.p.: 78–79 °C. Rf = 0.47 (1:5 EtOAc/Hexanes).

**\( ^1\text{H NMR} \) (400 MHz, Chloroform-\( d \)) \( \delta \): 7.31 – 7.26 (m, 2H), 7.24 – 7.20 (m, 1H), 7.15 – 7.11 (m, 2H), 6.98 (dd, \( J = 8.4 \), 2.8 Hz, 1H), 6.65 (d, \( J = 8.4 \) Hz, 1H), 6.62 (d, \( J = 2.2 \) Hz, 1H), 4.51 (d, \( J = 6.6 \) Hz, 1H), 4.24 – 4.16 (m, 2H), 3.82 (td, \( J = 6.8 \), 3.4 Hz, 1H), 3.43 (dd, \( J = 11.7 \), 7.0 Hz, 1H), 3.33 (dd, \( J = 11.7 \), 3.4 Hz, 1H), 2.93 (s, 3H), 2.43 (q, \( J = 7.6 \) Hz, 2H), 1.27 (t, \( J = 7.2 \) Hz, 3H), 1.09 (t, \( J = 7.6 \) Hz, 3H).
$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 194.74, 161.25, 144.46, 144.11, 133.27, 129.65, 129.13, 128.43, 126.98, 126.68, 123.31, 111.85, 62.30, 49.85, 49.77, 44.75, 39.67, 27.74, 15.78, 13.89.

HRMS (ESI): m/z Calcd. for [C$_{22}$H$_{26}$NO$_3$, M+H]$^+$:352.1907; Found: 352.1907.

ethyl 2-(trans-6-(tert-butyl)-1-methyl-4-phenyl-1,2,3,4-tetrahydroquinolin-3-yl)-2-oxoacetate (3c):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3c as a yellow solid, 52.2 mg, 69% yield, >20:1 dr. m.p.: 102–104 °C. Rf = 0.47 (1:5 EtOAc/Hexanes).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.28 – 7.24 (m, 2H), 7.22 – 7.17 (m, 1H), 7.16 – 7.09 (m, 3H), 6.77 (d, $J = 1.5$ Hz, 1H), 6.64 (d, $J = 8.6$ Hz, 1H), 4.50 (d, $J = 6.8$ Hz, 1H), 4.21 – 4.13 (m, 2H), 3.81 (td, $J = 7.0$, 3.3 Hz, 1H), 3.30 (dd, $J = 11.7$, 3.3 Hz, 1H), 2.92 (s, 3H), 1.25 (t, $J = 7.1$ Hz, 3H), 1.14 (s, 9H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 194.85, 161.28, 144.34, 143.79, 140.03, 129.11, 128.38, 127.27, 126.67, 124.39, 122.89, 111.31, 62.29, 49.89, 49.75, 45.06, 39.54, 33.70, 31.34, 13.90.

HRMS (ESI): m/z Calcd. for [C$_{24}$H$_{30}$NO$_3$, M+H]$^+$:380.2220; Found: 380.2222.

ethyl 2-(trans-6-benzyl-1-methyl-4-phenyl-1,2,3,4-tetrahydroquinolin-3-yl)-2-oxoacetate (3d):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3d as a yellow oil, 50.6 mg, 61% yield, > 20:1 dr. Rf = 0.47 (1:5 EtOAc/Hexanes).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.31 – 7.27 (m, 2H), 7.26 – 7.22 (m, 3H), 7.17 – 7.12 (m, 3H), 7.10 – 7.08 (m, 2H), 6.94 (dd, $J = 8.4$, 2.2 Hz, 1H), 6.68 (d, $J = 2.0$ Hz, 1H), 6.64 (d, $J = 8.4$ Hz, 1H), 4.52 (d, $J = 6.5$ Hz, 1H), 4.24 – 4.16 (m, 2H), 3.82 (td, $J = 6.7$, 3.4 Hz, 1H), 3.77 (s, 2H), 3.45 (dd, $J = 11.4$, 6.5 Hz, 1H), 3.34 (dd, $J = 11.8$, 3.4 Hz, 1H), 2.93 (s, 3H), 1.28 (t, 3H).
**Supporting information**

**13C NMR** (101 MHz, Chloroform-\(d\)) \(\delta\) 194.64, 161.22, 144.38, 141.84, 130.81, 129.83, 129.08, 128.63, 128.42, 128.20, 126.70, 125.67, 123.21, 111.91, 62.31, 49.66, 44.63, 40.81, 39.56, 13.88.

**HRMS (ESI):** m/z Calcd. for [C\(_{27}\)H\(_{28}\)NO\(_3\), M+H]\(^+\): 414.2063; Found: 414.2064.

**ethyl 2-(trans-1-methyl-4,6-diphenyl-1,2,3,4-tetrahydroquinolin-3-yl)-2-oxo-acetate (3e):**

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3e as a yellow oil, 48.0 mg, 60% yield, > 20:1 dr. Rf = 0.44 (1:5 EtOAc/Hexanes).

**1H NMR** (400 MHz, Chloroform-\(d\)) \(\delta\) 7.43 – 7.40 (m, 3H), 7.34 – 7.28 (m, 4H), 7.25 – 7.20 (m, 2H), 7.19 – 7.15 (m, 2H), 7.07 (d, \(J = 1.3\) Hz, 1H), 6.78 (d, \(J = 8.6\) Hz, 1H), 4.59 (d, \(J = 6.4\) Hz, 1H), 4.26 – 4.18 (m, 2H), 3.87 (td, \(J = 6.6, 3.5\) Hz, 1H), 3.52 (dd, \(J = 11.9, 6.8\) Hz, 1H), 3.41 (dd, \(J = 11.9, 3.5\) Hz, 1H), 3.01 (s, 3H), 1.29 (t, \(J = 7.1\) Hz, 3H).

**13C NMR** (101 MHz, Chloroform-\(d\)) \(\delta\) 194.58, 161.18, 145.35, 144.02, 140.93, 130.01, 129.07, 128.76, 128.55, 128.51, 126.84, 126.38, 126.20, 126.00, 123.28, 111.89, 62.39, 49.48, 49.39, 44.84, 39.45, 13.90.

**HRMS (ESI):** m/z Calcd. for [C\(_{26}\)H\(_{26}\)NO\(_3\), M+H]\(^+\): 400.1907; Found: 400.1908.

**ethyl 2-(trans-6-methoxy-1-methyl-4-phenyl-1,2,3,4-tetrahydroquinolin-3-yl)-2-oxoacetate (3f):**

Flash column chromatography (eluent: EtOAc/Hexanes = 1/8, v/v) to afford 3f as a yellow oil, 36.1 mg, 51% yield, > 20:1 dr. Rf = 0.32 (1:5 EtOAc/Hexanes).

**1H NMR** (400 MHz, Chloroform-\(d\)) \(\delta\) 7.28 – 7.25 (m, 2H), 7.22 – 7.17 (m, 1H), 7.12 – 7.10 (m, 2H), 6.73 (dd, \(J = 8.6, 3.3\) Hz, 1H),
6.65 (d, $J = 8.9$ Hz, 1H), 6.38 (d, $J = 3.8$ Hz, 1H), 4.50 (d, $J = 6.6$ Hz, 1H), 4.23 – 4.15 (m, 2H), 3.81 (td, $J = 6.8$, 3.4 Hz, 1H), 3.62 (s, 3H), 3.36 (dd, $J = 11.7$, 6.9 Hz, 1H), 3.30 (dd, $J = 11.7$, 3.4 Hz, 1H), 2.89 (s, 3H), 1.27 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 194.52, 161.16, 151.95, 144.26, 140.71, 129.11, 128.48, 126.76, 124.96, 115.89, 113.33, 113.16, 62.36, 55.55, 50.17, 49.89, 44.72, 40.15, 13.91.

HRMS (ESI): m/z Calcd. for [C$_{21}$H$_{24}$NO$_4$, M+H]$^+$:354.1699; Found: 354.1698.

ethyl 2-(trans-6-chloro-1-methyl-4-phenyl-1,2,3,4-tetrahydroquinolin-3-yl)-2-oxo acetate (3g):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/8, v/v) to afford 3g as a yellow oil, 40.3 mg, 56% yield, $> 20:1$ dr. Rf = 0.32 (1:5 EtOAc/Hexanes).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.32 – 7.28 (m, 2H), 7.25 – 7.21 (m, 1H), 7.10 – 7.06 (m, 3H), 6.75 (d, $J = 2.5$ Hz, 1H), 6.60 (d, $J = 8.8$ Hz, 1H), 4.45 (d, $J = 6.3$ Hz, 1H), 4.25 – 4.17 (m, 2H), 3.79 (td, $J = 6.4$, 3.5 Hz, 1H), 3.45 (dd, $J = 11.9$, 6.6 Hz, 1H), 3.35 (dd, $J = 12.0$, 3.5 Hz, 1H), 2.93 (s, 3H), 1.28 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 194.28, 161.07, 144.54, 143.53, 129.75, 129.04, 128.72, 127.66, 127.10, 124.64, 122.11, 112.76, 62.56, 49.37, 49.11, 44.52, 39.56, 13.97.

HRMS (ESI): m/z Calcd. for [C$_{20}$H$_{21}$ClNO$_3$, M+H]$^+$:358.1204; Found: 358.1205

ethyl 2-(trans-6-bromo-1-methyl-4-phenyl-1,2,3,4-tetrahydroquinolin-3-yl)-2-oxo acetate (3h):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/8, v/v) to afford 3h as a yellow solid, 28.1 mg, 35% yield, $> 20:1$ dr. m.p.: 91~92 °C. Rf = 0.32 (1:5 EtOAc/Hexanes).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.32 – 7.27 (m, 2H), 7.26 –
7.18 (m, 2H), 7.11 – 7.07 (m, 2H), 6.88 (dd, J = 2.4, 0.9 Hz, 1H), 6.55 (d, J = 8.8 Hz, 1H), 4.46 (d, J = 6.2 Hz, 1H), 4.25 – 4.17 (m, 2H), 3.78 (td, J = 6.4, 3.5 Hz, 1H), 3.45 (dd, J = 12.0, 6.5 Hz, 1H), 3.35 (dd, J = 12.0, 3.5 Hz, 1H), 2.93 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 194.17, 161.01, 144.85, 143.44, 132.45, 130.49, 128.95, 128.65, 127.04, 124.94, 113.12, 109.20, 62.49, 49.16, 48.97, 44.38, 39.41, 13.90.

HRMS (ESI): m/z Calcd. for [C$_{20}$H$_{21}$BrNO$_3$, M+H]$^+$: 402.0699; Found: 402.0699.

Ethyl 2-oxo-2-(trans-1,6,7-trimethyl-4-phenyl-1,2,3,4-tetrahydroquinolin-3-yl)acetate (3i):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3i as a yellow oil, 40.0mg, 57% yield, > 20:1 dr. Rf = 0.48 (1:5 EtOAc/Hexanes).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.29 – 7.25 (m, 2H), 7.23 – 7.18 (m, 1H), 7.14 – 7.10 (m, 2H), 6.52 (d, J = 6.7 Hz, 2H), 4.46 (d, J = 6.5 Hz, 1H), 4.23 – 4.14 (m, 2H), 3.78 (td, J = 6.7, 3.3 Hz, 1H), 3.39 (dd, J = 12.1, 7.3 Hz, 1H), 3.30 (dd, J = 11.7, 3.3 Hz, 1H), 2.91 (s, 3H), 2.21 (s, 3H), 2.03 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 194.75, 161.28, 144.65, 144.16, 135.72, 131.23, 129.09, 128.41, 126.63, 125.56, 120.81, 113.41, 62.28, 49.87, 49.84, 44.30, 39.75, 19.94, 18.57, 13.90.

HRMS (ESI): m/z Calcd. for [C$_{22}$H$_{26}$NO$_3$, M+H]$^+$: 352.1907; Found: 352.1907.

Ethyl 2-(trans-6,7-dimethoxy-1-methyl-4-phenyl-1,2,3,4-tetrahydroquinolin-3-yl)-2-oxoacetate (3j):
Flash column chromatography (eluent: EtOAc/Hexanes = 1/5, v/v) to afford 3j as a yellow oil, 56.8 mg, 74% yield, > 20:1 dr. Rf = 0.16 (1:5 EtOAc/Hexanes).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.30 – 7.26 (m, 2H), 7.23 – 7.19 (m, 1H), 7.13 – 7.10 (m, 2H), 6.34 (s, 1H), 6.32 (s, 1H), 4.48 (d, $J$ = 5.9 Hz, 1H), 4.26 – 4.18 (m, 2H), 3.88 (s, 3H), 3.73 (td, $J$ = 6.2, 3.1 Hz, 1H), 3.63 (s, 3H), 3.39 (dd, $J$ = 11.8, 6.5 Hz, 1H), 3.29 (dd, $J$ = 11.8, 3.1 Hz, 1H), 2.93 (s, 3H), 1.29 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 194.48, 161.24, 148.61, 144.75, 141.50, 140.77, 128.97, 128.41, 126.68, 114.61, 114.33, 97.53, 62.32, 56.42, 55.79, 49.93, 49.68, 43.92, 40.26, 13.90.

HRMS (ESI): m/z Calcd. for [C$_{22}$H$_{26}$NO$_5$, M+H]$^+$: 384.1805; Found: 384.1805.

**ethyl 2-(1,6-dimethyl-2,4-diphenyl-1,2,3,4-tetrahydroquinolin-3-yl)-2-oxoacetate (3k):**

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3k as a yellow solid, 45.2 mg, 55% yield. m.p.: 145~146 °C. Rf = 0.53 (1:5 EtOAc/Hexanes).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.32 – 7.21 (m, 10H), 7.01 (dd, $J$ = 8.2, 2.1 Hz, 1H), 6.74 (d, $J$ = 8.3 Hz, 1H), 6.39 (s, 1H), 4.55 – 4.45 (m, 2H), 4.40 (dd, $J$ = 10.5, 1.3 Hz, 1H), 3.79 – 3.72 (m, 2H), 2.72 (s, 3H), 2.13 (s, 3H), 0.97 (t, $J$ = 7.1 Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 196.09, 159.66, 144.43, 140.19, 139.78, 129.56, 128.84, 128.71, 128.59, 128.31, 128.04, 127.95, 127.17, 126.25, 126.09, 112.47, 66.56, 61.97, 56.05, 47.65, 37.00, 20.30, 13.61.

HRMS (ESI): m/z Calcd. for [C$_{27}$H$_{28}$NO$_3$, M+H]$^+$: 414.2063; Found: 414.2064.

**ethyl 2-(1,6-dimethyl-2,4-diphenyl-1,2,3,4-tetrahydroquinolin-3-yl)-2-oxoacetate (3k'):**
Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3k' as a yellow solid, 10.0 mg, 12% yield. m.p.: 140~141 °C. Rf = 0.44 (1:5 EtOAc/Hexanes).

**1H NMR** (400 MHz, Chloroform-d) δ 7.27 – 7.22 (m, 5H), 7.20 – 7.17 (m, 3H), 7.02 – 6.95 (m, 1H), 6.94 – 6.91 (m, 2H), 6.64 (d, J = 8.3 Hz, 1H), 6.41 (s, 1H), 5.74 (d, J = 4.5 Hz, 1H), 4.94 (d, J = 4.5 Hz, 1H), 4.57 (dd, J = 11.7, 4.5 Hz, 1H), 4.31 – 4.20 (m, 3H), 2.94 (s, 3H), 2.11 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H).

**13C NMR** (101 MHz, Chloroform-d) δ 192.15, 160.75, 143.21, 143.00, 138.39, 130.58, 129.71, 128.42, 128.37, 127.96, 127.23, 126.59, 125.65, 124.22, 110.43, 63.79, 62.50, 54.04, 40.33, 38.56, 20.32, 13.89.

**HRMS (ESI)**: m/z Calcd. for [C_{27}H_{28}NO_{3}, M+H]^+: 414.2063; Found: 414.2063.

**ethyl 2-(1,6-dimethyl-4-phenyl-2-vinyl-1,2,3,4-tetrahydroquinolin-3-yl)-2-oxoacetate (3l):**

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3l as a mixture of diastereomers, yellow oil, 51.1 mg, 70% yield, 1:1:1 dr. Rf = 0.53 (1:5 EtOAc/Hexanes).

Major diastereomer **1H NMR** (400 MHz, Chloroform-d) δ 7.32 – 7.17 (m, 5H), 6.97 – 6.95 (m, 1H), 6.68 (d, J = 8.3 Hz, 1H), 6.38 (s, 1H), 5.74 – 5.64 (m, 1H), 5.21 – 5.15 (m, 2H), 4.30 (d, J = 10.9 Hz, 1H), 4.26 – 4.17 (m, 1H), 4.10 – 4.02 (m, 2H), 3.94 (t, J = 9.1 Hz, 1H), 2.90 (s, 3H), 2.10 (s, 3H), 1.16 (t, J = 7.1 Hz, 3H).

Major diastereomer **13C NMR** (101 MHz, Chloroform-d) δ 195.72, 160.67, 144.03, 142.39, 137.90, 130.77, 129.64, 128.69, 128.38, 127.21, 126.42, 125.72, 119.32, 112.45, 63.30, 62.35, 53.53, 40.90, 36.25, 20.35, 13.94.

Minor diastereomer **1H NMR** (400 MHz, Chloroform-d) δ 7.32 – 7.17 (m, 5H), 6.92 (dd, J = 8.6, 1.8 Hz, 1H), 6.59 (d, J = 8.3 Hz, 1H), 6.44 (s, 1H), 5.74 – 5.64 (m, 1H), 5.15 – 5.13 (m, 1H), 5.01 (dt, J = 17.0, 1.2 Hz, 1H), 4.48 (d, J = 11.9 Hz, 1H), 4.36 (dd, J = 11.9, 3.9 Hz, 1H), 4.26 – 4.17 (m, 3H), 2.94 (s, 3H), 2.08 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H).
Supporting information

Minor diastereomer \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 192.67, 160.44, 143.65, 140.71, 132.24, 129.56, 128.97, 128.48, 128.22, 126.66, 126.18, 124.76, 119.01, 111.70, 63.30, 62.35, 53.53, 40.90, 36.25, 20.35, 13.85.

HRMS (ESI): m/z Calcd. for \([C_{23}H_{26}NO_3], M+H\]^+: 364.1907; Found: 364.1910.

ethyl 2-(2-ethynyl-1,6-dimethyl-4-phenyl-1,2,3,4-tetrahydroquinolin-3-yl)-2-oxoacetate (3m):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3m as a yellow oil, 41.2 mg, 57% yield, 6:1 dr. Rf = 0.41 (1:5 EtOAc/Hexanes).

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.32 – 7.19 (m, 5H), 6.98 (dd, \(J = 8.3, 1.5\) Hz, 1H), 6.72 (d, \(J = 8.3\) Hz, 1H), 6.44 (s, 1H), 4.37 – 4.24 (m, 3H), 4.12 – 4.05 (m, 2H), 3.04 (s, 3H), 2.31 (d, \(J = 2.0\) Hz, 1H), 2.11 (s, 3H), 1.18 (t, \(J = 7.1\) Hz, 3H).

\(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 194.65, 160.37, 142.99, 140.38, 129.59, 128.98, 128.58, 128.36, 127.60, 127.31, 126.03, 113.46, 80.56, 74.41, 62.44, 54.35, 52.50, 46.50, 36.97, 20.36, 13.79.

HRMS (ESI): m/z Calcd. for \([C_{23}H_{24}NO_3], M+H\]^+: 362.1750; Found: 362.1755.

ethyl 2-(7-methyl-5-phenyl-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-2-oxoacetate (3n):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3n as a yellow solid, 37.9 mg, 52% yield, > 20:1 dr. m.p.: 108–110 °C. Rf = 0.54 (1:5 EtOAc/Hexanes).

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.31 – 7.21 (m, 3H), 7.19 – 7.16 (m, 2H), 6.96 – 6.90 (m, 1H), 6.46 (d, \(J = 8.1\) Hz, 1H), 6.35 (s, 1H), 4.22 (d, \(J = 11.3\) Hz, 1H), 4.07 – 4.00 (m, 2H), 3.74 (dd, \(J = 11.3, 9.9\) Hz, 1H), 3.66 (td, \(J = 9.8, 4.8\) Hz, 1H), 3.45 (td, \(J = 9.0, 2.3\) Hz, 1H), 3.32 (td, \(J = 8.9, 7.3\) Hz, 1H), 2.14 – 1.93 (m, 6H), 1.69 – 1.61 (m, 1H), 1.15 (t, \(J = 7.1\) Hz, 3H).
**Supporting information**

**13C NMR** (101 MHz, Chloroform-\(d\)) \(\delta\) 197.96, 160.74, 141.58, 141.07, 129.38, 129.24, 128.58, 128.24, 127.12, 124.40, 124.18, 110.63, 62.30, 60.06, 52.80, 48.99, 47.29, 30.93, 23.64, 20.34, 13.76.

**HRMS (ESI):** m/z Calcd. for [C\(_{23}\)H\(_{26}\)NO\(_3\), M+H]\(^{+}\): 364.1907; Found: 364.1906.

**ethyl 2-(8-methyl-6-phenyl-2,3,4,4a,5,6-hexahydro-1H-pyrido[1,2-a]quinolin-5-yl)-2-oxoacetate (3o):**

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3o as a yellow solid, 32.8 mg, 44% yield, > 20:1 dr. m.p.: 126–128 °C. Rf = 0.54 (1:5 EtOAc/Hexanes).

**1H NMR** (400 MHz, Chloroform-\(d\)) \(\delta\) 7.31 – 7.21 (m, 3H), 7.18 – 7.16 (m, 2H), 6.95 (dd, \(J = 8.6, 2.2\) Hz, 1H), 6.84 (d, \(J = 8.5\) Hz, 1H), 6.41 (s, 1H), 4.27 (d, \(J = 11.7\) Hz, 1H), 4.12 – 4.02 (m, 3H), 3.97 (dd, \(J = 12.1, 3.2\) Hz, 1H), 3.30 (td, \(J = 10.1, 2.8\) Hz, 1H), 2.74 (td, \(J = 12.2, 2.9\) Hz, 1H), 2.09 (s, 3H), 1.84 – 1.62 (m, 4H), 1.45 – 1.36 (m, 2H), 1.15 (t, \(J = 7.1\) Hz, 3H).

**13C NMR** (101 MHz, Chloroform-\(d\)) \(\delta\) 197.76, 160.67, 144.06, 141.41, 129.51, 129.33, 128.55, 128.16, 127.03, 126.97, 126.64, 113.42, 62.25, 58.84, 55.08, 48.53, 48.32, 30.77, 25.33, 23.51, 20.18, 13.73.

**HRMS (ESI):** m/z Calcd. for [C\(_{24}\)H\(_{27}\)NO\(_3\)Na, M+Na]\(^{+}\): 400.1883; Found: 400.1883.

**ethyl 2-(3-methyl-5-phenyl-5,6,6a,7,8,9,10,11-octahydroazepino[1,2-a]quinolin-6-yl)-2-oxoacetate (3p):**

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3p as a mixture of diastereomers, yellow solid, 52.5 mg, 67% yield, 3:1 dr. m.p.: 113–114 °C. Rf = 0.53 (1:5 EtOAc/Hexanes).

Major diastereomer **1H NMR** (400 MHz, Chloroform-\(d\)) \(\delta\) 7.30 – 7.15 (m, 5H), 6.88 (dd, \(J = 8.3, 2.2\) Hz, 1H), 6.56 (d, \(J = 8.4\) Hz, 1H), 6.42 (s, 1H), 4.52 (d, \(J = 12.1\) Hz, 1H), 4.26 – 4.18 (m, 3H), 4.03 – 3.97 (m, 1H), 3.84 (dt, \(J = 11.2, 6.9\) Hz, 1H), 3.44 (dd, \(J = 11.2, 2.1\) Hz, 1H).
3.9 Hz, 1H), 3.31 – 3.23 (m, 1H), 2.06 (s, 3H), 1.79 – 1.31 (m, 8H), 1.28 (t, $J = 7.2$ Hz, 3H).

Major diastereomer $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 193.90, 160.80, 144.50, 141.08, 131.01, 129.64, 128.31, 128.12, 126.46, 124.76, 122.95, 110.54, 62.41, 58.77, 53.93, 50.30, 40.59, 29.97, 27.05, 25.95, 25.83, 20.25, 13.86.

Minor diastereomer $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.30 – 7.15 (m, 5H), 6.92 (dd, $J = 7.7$, 1.9 Hz, 1H), 6.66 (d, $J = 8.3$ Hz, 1H), 6.39 (s, 1H), 4.60 – 4.18 (m, 1H), 4.10 – 4.14 (m, 2H), 3.95 – 3.93 (m, 1H), 3.80 – 3.76 m, 2H), 3.59 (ddd, $J = 14.9$, 6.3, 2.4 Hz, 1H), 3.35 (ddd, $J = 15.2$, 9.5, 2.5 Hz, 1H), 2.09 (s, 3H), 1.79 – 1.31 (m, 8H), 1.17 (t, $J = 7.2$ Hz, 3H).

Minor diastereomer $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 197.54, 161.07, 144.10, 141.50, 129.39, 129.20, 128.57, 128.23, 126.98, 125.30, 112.68, 62.28, 60.07, 53.11, 49.27, 47.93, 33.13, 28.91, 28.86, 24.22, 13.80.

HRMS (ESI): m/z Calcd. for [C$_{25}$H$_{30}$NO$_3$, M+H]$^+$: 392.2220; Found: 392.2220.

ethyl 2-(trans-1,6-dimethyl-4-(o-tolyl)-1,2,3,4-tetrahydroquinolin-3-yl)-2-oxo-acetate (3q):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3q as a yellow oil, 43.4 mg, 62% yield, > 20:1 dr. Rf = 0.55 (1:5 EtOAc/Hexanes).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.19 – 7.07 (m, 3H), 6.94 (dd, $J = 8.4$, 2.1 Hz, 2H), 6.89 (dd, $J = 7.4$, 1.7 Hz, 1H), 6.62 (d, $J = 8.3$ Hz, 1H), 6.52 (s, 1H), 4.70 (d, $J = 6.4$ Hz, 1H), 4.23 – 4.15 (m, 2H), 3.77 (td, $J = 6.6$, 3.4 Hz, 1H), 3.45 (dd, $J = 11.8$, 6.9 Hz, 1H), 3.36 (dd, $J = 11.7$, 3.4 Hz, 1H), 2.93 (s, 3H), 2.38 (s, 3H), 2.12 (s, 3H), 1.27 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 194.96, 161.35, 143.99, 142.33, 136.04, 130.48, 130.27, 129.93, 128.11, 126.81, 126.59, 126.05, 123.74, 111.80, 62.28, 49.90, 47.88, 40.95, 39.66, 20.25, 19.51, 13.88.

HRMS (ESI): m/z Calcd. for [C$_{22}$H$_{26}$NO$_3$, M+H]$^+$: 352.1907; Found: 352.1906.
ethyl \(2-(\text{trans}-4-(2\text{-methoxyphenyl})-1,6\text{-dimethyl}-1,2,3,4\text{-tetrahydroquinolin}-3\text{-yl})\)
\(-2\text{-oxoacetate} \ (3r):\)

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3r as a yellow solid, 42.8 mg, 58% yield, > 20:1 dr. m.p.: 103–104 °C. Rf = 0.40 (1:5 EtOAc/Hexanes).

\(^1\text{H NMR} \ (400 \text{ MHz, Chloroform-}d) \ \delta \ 7.23 - 7.19 \ (m, 1\text{H}), 6.94 \ (d, J = 8.4 \text{ Hz, 1H}), 6.89 - 6.82 \ (m, 2\text{H}), 6.75 \ (d, J = 7.5 \text{ Hz, 1H}), 6.68 \ (s, 1\text{H}), 6.62 \ (d, J = 8.4 \text{ Hz, 1H}), 4.90 \ (d, J = 4.1 \text{ Hz, 1H}), 4.29 - 4.21 \ (m, 2\text{H}), 3.84 \ (s, 3\text{H}), 3.67 \ (q, J = 4.3, 3.7 \text{ Hz, 1H}), 3.47 \ (dd, J = 12.0, 5.3 \text{ Hz, 1H}), 3.27 \ (dd, J = 11.9, 3.0 \text{ Hz, 1H}), 2.88 \ (s, 3\text{H}), 2.16 \ (s, 3\text{H}), 1.31 \ (t, J = 7.2 \text{ Hz, 3H}).

\(^{13}\text{C NMR} \ (101 \text{ MHz, Chloroform-}d) \ \delta \ 194.62, 161.76, 156.50, 144.39, 133.34, 131.12, 130.76, 128.01, 127.62, 126.82, 122.72, 120.24, 111.80, 110.08, 62.05, 55.28, 49.10, 47.56, 39.61, 37.57, 20.25, 13.94.

\text{HRMS (ESI)}: \text{m/z Calcd. for [C}_{22}\text{H}_{26}\text{NO}_{4}, \text{M+H}]:368.1856; \text{Found: 368.1859.}

ethyl \(2-(\text{trans}-4-(2\text{-chlorophenyl})-1,6\text{-dimethyl}-1,2,3,4\text{-tetrahydroquinolin}-3\text{-yl})\)-2-oxoacetate \ (3s):\)

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3s as a yellow oil, 53.4 mg, 72% yield, > 20:1 dr. Rf = 0.52 (1:5 EtOAc/Hexanes).

\(^1\text{H NMR} \ (400 \text{ MHz, Chloroform-}d) \ \delta \ 7.40 - 7.38 \ (m, 1\text{H}), 7.19 - 7.11 \ (m, 2\text{H}), 6.96 \ (dd, J = 8.4, 2.3 \text{ Hz, 1H}), 6.85 \ (dd, J = 7.3, 2.2 \text{ Hz, 1H}), 6.65 - 6.62 \ (m, 2\text{H}), 5.00 \ (d, J = 3.7 \text{ Hz, 1H}), 4.32 - 4.24 \ (m, 2\text{H}), 3.68 \ (q, J = 3.5 \text{ Hz, 1H}), 3.51 \ (ddd, J = 12.1, 4.9, 1.3 \text{ Hz, 1H}), 3.28 \ (dd, J = 12.1, 3.1 \text{ Hz, 1H}), 2.89 \ (s, 3\text{H}), 2.16 \ (s, 3\text{H}), 1.33 \ (t, J = 7.1 \text{ Hz, 3H}).

\(^{13}\text{C NMR} \ (101 \text{ MHz, Chloroform-}d) \ \delta \ 193.64, 161.45, 144.17, 142.56, 133.42, 131.96, 130.85, 129.52, 128.49, 127.87, 127.19, 126.65, 121.65, 112.04, 62.27, 48.57, 47.52, 40.31, 39.59, 20.23, 13.95.

\text{HRMS (ESI)}: \text{m/z Calcd. for [C}_{21}\text{H}_{22}\text{ClNO}_{3}\text{Na, M+Na}]:394.1180; \text{Found: 394.1180.}
ethyl 2-(trans-1,6-dimethyl-4-(m-tolyl)-1,2,3,4-tetrahydroquinolin-3-yl)-2-oxoacetate (3t):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford **3t** as a yellow oil, 46.6 mg, 66% yield, > 20:1 dr. Rf = 0.55 (1:5 EtOAc/Hexanes).

**1H NMR** (400 MHz, Chloroform-d) δ 7.17 (t, J = 7.6 Hz, 1H), 7.04 (d, J = 7.6 Hz, 1H), 6.96 – 6.93 (m, 2H), 6.90 (d, J = 7.7 Hz, 1H), 6.63 (d, J = 8.4 Hz, 2H), 4.45 (d, J = 6.5 Hz, 1H), 4.25 – 4.17 (m, 2H), 3.80 (td, J = 6.6, 3.4 Hz, 1H), 3.41 (dd, J = 11.7, 6.8 Hz, 1H), 3.33 (dd, J = 11.7, 3.4 Hz, 1H), 2.92 (s, 3H), 2.31 (s, 3H), 2.14 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H).

**13C NMR** (101 MHz, Chloroform-d) δ 194.74, 161.27, 144.48, 143.92, 138.02, 130.74, 129.73, 128.30, 128.21, 127.45, 126.67, 126.27, 123.43, 111.85, 62.28, 49.83, 49.78, 44.54, 39.70, 21.39, 20.26, 13.89.

**HRMS (ESI):** m/z Calcd. for [C_{22}H_{26}NO_3, M+H]^+: 352.1907; Found: 352.1907.

ethyl 2-(trans-4-(3-bromophenyl)-1,6-dimethyl-1,2,3,4-tetrahydroquinolin-3-yl)-2-oxoacetate (3u):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford **3u** as a yellow oil, 57.2 mg, 69% yield, > 20:1 dr. Rf = 0.51 (1:5 EtOAc/Hexanes).

**1H NMR** (400 MHz, Chloroform-d) δ 7.36 (ddd, J = 7.9, 2.0, 1.1 Hz, 1H), 7.29 (t, J = 1.9 Hz, 1H), 7.15 (t, J = 7.8 Hz, 1H), 7.04 (dt, J = 7.8, 1.5 Hz, 1H), 6.95 (dd, J = 8.4, 2.2 Hz, 1H), 6.62 (d, J = 8.4 Hz, 1H), 6.57 (s, 1H), 4.48 (d, J = 6.4 Hz, 1H), 4.28 – 4.20 (m, 2H), 3.76 (td, J = 6.6, 3.4 Hz, 1H), 3.39 (dd, J = 11.8, 6.7 Hz, 1H), 3.32 (dd, J = 11.8, 3.5 Hz, 1H), 2.91 (s, 3H), 2.14 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H).

**13C NMR** (101 MHz, Chloroform-d) δ 194.09, 161.11, 147.10, 143.87, 131.95, 130.69, 130.03, 129.90, 128.57, 127.89, 126.94, 122.59, 122.45, 112.10, 62.48, 49.75, 49.71, 44.08, 39.68, 20.26, 13.91.

**HRMS (ESI):** m/z Calcd. for [C_{23}H_{26}BrNO_3, M+H]^+: 416.0855; Found: 416.0855.
ethyl 2-\((trans\)-1,6-dimethyl-4-(p-tolyl)-1,2,3,4-tetrahydroquinolin-3-yl\)-2-oxo-acetate (3v):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3v as a yellow oil, 42.9 mg, 61% yield, > 20:1 dr. Rf = 0.54 (1:5 EtOAc/Hexanes).

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) δ 7.09 (d, \(J = 7.9\) Hz, 2H), 7.00 (d, \(J = 8.1\) Hz, 2H), 6.94 (dd, \(J = 8.3, 2.1\) Hz, 1H), 6.62 – 6.60 (m, 2H), 4.45 (d, \(J = 6.4\) Hz, 1H), 4.24 – 4.16 (m, 2H), 3.77 (td, \(J = 6.6, 3.3\) Hz, 1H), 3.41 (dd, \(J = 11.7, 6.8\) Hz, 1H), 3.32 (dd, \(J = 11.7, 3.4\) Hz, 1H), 2.91 (s, 3H), 2.32 (s, 3H), 2.12 (s, 3H), 1.27 (t, \(J = 7.1\) Hz, 3H).

\(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) δ 194.76, 161.28, 143.91, 141.50, 136.23, 130.67, 129.12, 128.98, 128.19, 126.64, 124.38, 111.84, 62.26, 49.81, 49.75, 44.18, 39.68, 20.96, 20.24, 13.87.

HRMS (ESI): m/z Calcd. for \([\text{C}_{22}\text{H}_{26}\text{NO}_3, \text{M}+\text{H}]^+\):352.1907; Found: 352.1907.

ethyl 2-\((trans\)-4-(4-(tert-butyl)phenyl)-1,6-dimethyl-1,2,3,4-tetrahydroquinolin-3-yl\)-2-oxoacetate (3w):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3w as a yellow oil, 47.3 mg, 60% yield, > 20:1 dr. Rf = 0.59 (1:5 EtOAc/Hexanes).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.31 – 7.27 (m, 2H), 7.04 – 7.02 (m, 2H), 6.94 (dd, \(J = 8.4, 2.1\) Hz, 1H), 6.65 (s, 1H), 6.62 (d, \(J = 8.3\) Hz, 1H), 4.46 (d, \(J = 5.9\) Hz, 1H), 4.23 – 4.15 (m, 2H), 3.75 (td, \(J = 6.2, 3.3\) Hz, 1H), 3.43 (dd, \(J = 11.3, 6.0\) Hz, 1H), 3.32 (dd, \(J = 11.8, 3.3\) Hz, 1H), 2.91 (s, 3H), 2.14 (s, 3H), 1.30 (s, 9H), 1.28 (t, \(J = 7.1\) Hz, 3H).

\(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) δ 194.84, 161.33, 149.38, 143.90, 141.46, 130.75, 128.66, 128.21, 126.62, 125.29, 123.25, 111.81, 62.23, 49.70, 49.51, 44.01, 39.67, 34.37, 31.32, 20.27, 13.93.

HRMS (ESI): m/z Calcd. for \([\text{C}_{25}\text{H}_{32}\text{NO}_3, \text{M}+\text{H}]^+\):394.2376; Found: 394.2376.

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ethyl 2-(trans-4-((1,1'-biphenyl)-4-yl)-1,6-dimethyl-1,2,3,4-tetrahydroquinolin-3-yl)-2-oxoacetate (3x):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3x as a yellow oil, 50.5 mg, 61% yield, > 20:1 dr. Rf = 0.49 (1:5 EtOAc/Hexanes).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.61 – 7.58 (m, 2H), 7.56 – 7.52 (m, 2H), 7.46 – 7.43 m, 2H), 7.38 – 7.33 (m, 1H), 7.22 (d, $J$ = 8.2 Hz, 2H), 6.98 (dd, $J$ = 8.4, 2.2 Hz, 1H), 6.70 – 6.64 (m, 2H), 4.57 (d, $J$ = 6.4 Hz, 1H), 4.27 – 4.19 (m, 2H), 3.86 (td, $J$ = 6.6, 3.4 Hz, 1H), 3.46 (dd, $J$ = 11.7, 6.7 Hz, 1H), 3.39 (dd, $J$ = 11.7, 3.4 Hz, 1H), 2.95 (s, 3H), 2.17 (s, 3H), 1.29 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 194.61, 161.26, 143.93, 143.64, 140.66, 139.53, 130.73, 129.52, 128.73, 128.34, 127.20, 127.12, 126.93, 126.75, 123.18, 111.95, 62.33, 49.76, 44.22, 39.68, 20.26, 13.89.

HRMS (ESI): m/z Calcd. for [C_{27}H_{28}NO_{3}, M+H]^+:414.2063; Found: 414.2062.

ethyl 2-(trans-4-(4-methoxyphenyl)-1,6-dimethyl-1,2,3,4-tetrahydroquinolin-3-yl)-2-oxoacetate (3y):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3y as a yellow oil, 41.0 mg, 56% yield, > 20:1 dr. Rf = 0.46 (1:5 EtOAc/Hexanes).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.06 – 7.02 (m, 2H), 6.93 (dd, $J$ = 8.4, 2.1 Hz, 1H), 6.84 – 6.80 (m, 2H), 6.63 – 6.58 (m, 2H), 4.42 (d, $J$ = 6.9 Hz, 1H), 4.23 – 4.15 (m, 2H), 3.81 – 3.77 (m, 4H), 3.40 (dd, $J$ = 11.7, 7.1 Hz, 1H), 3.32 (dd, $J$ = 11.7, 3.4 Hz, 1H), 2.92 (s, 3H), 2.13 (s, 3H), 1.27 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 194.92, 161.22, 158.32, 143.86, 136.33, 130.59, 130.09, 128.19, 126.61, 123.78, 113.80, 111.85, 62.31, 55.19, 49.99, 49.78, 44.01, 39.69, 20.27, 13.90.

HRMS (ESI): m/z Calcd. for [C_{22}H_{26}NO_{4}, M+H]^+:368.1856; Found: 368.1857
ethyl 2-(trans-4-(4-fluorophenyl)-1,6-dimethyl-1,2,3,4-tetrahydroquinolin-3-yl)-2-oxoacetate (3z):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3z as a yellow oil, 46.2 mg, 65% yield, > 20:1 dr. Rf = 0.50 (1:5 EtOAc/Hexanes).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.11 – 7.07 (m, 2H), 7.00 – 6.93 (m, 3H), 6.62 (d, $J$ = 8.3 Hz, 1H), 6.55 (s, 1H), 4.47 (d, $J$ = 6.9 Hz, 1H), 4.26 – 4.18 (m, 2H), 3.79 (td, $J$ = 7.0, 3.4 Hz, 1H), 3.39 (dd, $J$ = 11.7, 7.0 Hz, 1H), 3.32 (dd, $J$ = 11.7, 3.5 Hz, 1H), 2.92 (s, 3H), 2.13 (s, 3H), 1.29 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 194.49, 161.64 (d, $J$ = 245.9 Hz), 161.14, 143.85, 140.13 (d, $J$ = 3.0 Hz), 130.59, 130.58 (d, $J$ = 7.9 Hz), 128.41, 126.77, 123.25, 115.3 (d, $J$ = 21.6 Hz), 112.00, 62.43, 49.94, 49.80, 43.93, 39.70, 20.25, 13.90.

$^{19}$F NMR (377 MHz, Chloroform-d) $\delta$ -116.11.

HRMS (ESI): m/z Calcd. for [C$_{21}$H$_{23}$FNO$_3$, M+H]$^+$:356.1656; Found: 356.1652.

ethyl 2-(trans-4-(4-chlorophenyl)-1,6-dimethyl-1,2,3,4-tetrahydroquinolin-3-yl)-2-oxoacetate (3aa):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3aa as a yellow oil, 54.3 mg, 73% yield, > 20:1 dr. Rf = 0.47 (1:5 EtOAc/Hexanes).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.27 – 7.24 (m, 2H), 7.08 – 7.05 (m, 2H), 6.95 (dd, $J$ = 8.4, 2.1 Hz, 1H), 6.63 (d, $J$ = 8.3 Hz, 1H), 6.56 (s, 1H), 4.48 (d, $J$ = 6.8 Hz, 1H), 4.27 – 4.19 (m, 2H), 3.78 (td, $J$ = 6.9, 3.5 Hz, 1H), 3.42 – 3.36 (m, 1H), 3.32 (dd, $J$ = 11.7, 3.5 Hz, 1H), 2.92 (s, 3H), 2.13 (s, 3H), 1.30 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 194.25, 161.07, 143.85, 143.03, 132.49, 130.58, 130.45, 128.60, 128.46, 126.81, 122.86, 112.02, 62.46, 49.85, 49.70, 43.91, 39.67, 20.23, 13.88.

HRMS (ESI): m/z Calcd. for [C$_{21}$H$_{23}$ClNO$_3$, M+H]$^+$:372.1361; Found: 372.1361.
ethyl 2-(trans-4-(4-bromophenyl)-1,6-dimethyl-1,2,3,4-tetrahydroquinolin-3-yl)-
2-oxoacetate (3ab):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3ab as a yellow oil, 57.1 mg, 68% yield, > 20:1 dr. Rf = 0.47 (1:5 EtOAc/Hexanes).

\[ ^1H \text{NMR} (400 \text{ MHz, Chloroform-}d) \delta 7.42 - 7.39 (m, 2H), 7.02 - 6.99 (m, 2H), 6.95 (dd, \ J = 8.3, 2.1 \text{ Hz, 1H}), 6.62 (d, \ J = 8.4 \text{ Hz, 1H}), 6.55 (s, 1H), 4.46 (d, \ J = 6.8 \text{ Hz, 1H}), 4.27 - 4.19 (m, 2H), 3.77 (td, \ J = 6.8, 3.4 \text{ Hz, 1H}), 3.38 (dd, \ J = 11.7, 7.3 \text{ Hz, 1H}), 3.31 (dd, \ J = 11.7, 3.4 \text{ Hz, 1H}), 2.91 (s, 3H), 2.13 (s, 3H), 1.29 (t, \ J = 7.2 \text{ Hz, 3H}). \]

\[ ^{13}C \text{NMR} (101 \text{ MHz, Chloroform-}d) \delta 194.22, 161.07, 143.86, 143.59, 131.56, 130.85, 130.60, 128.48, 126.85, 122.78, 120.63, 112.04, 62.48, 49.86, 49.67, 43.97, 39.69, 20.25, 13.90. \]

HRMS (ESI): m/z Calcd. for [C_{21}H_{23}BrNO_{3}, M+H]^+: 416.0855; Found: 416.0856.

ethyl 2-(trans-1,6-dimethyl-4-(naphthalen-2-yl)-1,2,3,4-tetrahydroquinolin-3-yl)-
2-oxoacetate (3ac):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3ac as a yellow oil, 54.1 mg, 70% yield, > 20:1 dr. Rf = 0.43 (1:5 EtOAc/Hexanes).

\[ ^1H \text{NMR} (400 \text{ MHz, Chloroform-}d) \delta 7.84 (dt, \ J = 13.8, 5.1 \text{ Hz, 3H}), 7.59 (s, 1H), 7.50-7.45 (m, 2H), 7.31 (dd, \ J = 8.5, 1.7 \text{ Hz, 1H}), 7.00 (ddd, \ J = 8.4, 2.1, 0.9 \text{ Hz, 1H}), 6.69 (d, \ J = 8.3 \text{ Hz, 1H}), 6.64 (s, 1H), 4.67 (d, \ J = 7.3 \text{ Hz, 1H}), 4.14- 3.98 (m, 3H), 3.49 - 3.38 (m, 2H), 2.98 (s, 3H), 2.12 (s, 3H), 1.16 (t, \ J = 7.1 \text{ Hz, 3H}). \]

\[ ^{13}C \text{NMR} (101 \text{ MHz, Chloroform-}d) \delta 194.76, 161.07, 144.02, 143.86, 143.59, 133.20, 132.37, 130.76, 128.36, 128.34, 128.30, 127.75, 127.53, 126.79, 126.70, 126.07, 125.74, 123.46, 111.96, 62.28, 50.24, 49.48, 45.15, 39.73, 20.22, 13.68. \]

HRMS (ESI): m/z Calcd. for [C_{25}H_{26}NO_{3}, M+H]^+: 388.1907; Found: 388.1907.
ethyl 2-(trans-1,6-dimethyl-4-(thiophen-2-yl)-1,2,3,4-tetrahydroquinolin-3-yl)-2-oxoacetate (3ad):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3ad as a yellow oil, 40.4 mg, 59% yield, > 20:1 dr. Rf = 0.53 (1:5 EtOAc/Hexanes).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.19 (dd, $J = 5.2$, 1.3 Hz, 1H), 6.96 (d, $J = 8.3$ Hz, 1H), 6.92 (ddd, $J = 5.1$, 3.4, 1.6 Hz, 1H), 6.83 (s, 1H), 6.76 (d, $J = 2.4$ Hz, 1H), 6.60 (d, $J = 8.4$ Hz, 1H), 4.79 (d, $J = 5.1$ Hz, 1H), 4.32 – 4.24 (m, 2H), 3.80 – 3.76 m, 1H), 3.49 (dd, $J = 11.9$, 5.8 Hz, 1H), 3.45 – 3.38 (m, 1H), 2.89 (s, 3H), 2.18 (s, 3H), 1.33 (t, $J = 7.1$, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 193.79, 161.23, 148.70, 143.22, 130.77, 128.63, 126.79, 126.56, 126.23, 124.43, 122.68, 112.06, 62.37, 50.37, 49.52, 39.58, 39.08, 20.28, 13.95.

HRMS (ESI): m/z Calcd. for [C_{19}H_{22}NO_{3}S, M+H]^+:344.1314; Found: 344.1314.

methyl 2-(trans-1,6-dimethyl-4-phenyl-1,2,3,4-tetrahydroquinolin-3-yl)-2-oxoacetate (3ae):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 3ae as a yellow oil, 45.3 mg, 70% yield, > 20:1 dr. Rf = 0.42 (1:5 EtOAc/Hexanes).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.32 – 7.27 (m, 2H), 7.25 – 7.20 (m, 1H), 7.15 – 7.10 (m, 2H), 6.95 (dd, $J = 8.4$, 2.1 Hz, 1H), 6.66 – 6.59 (m, 2H), 4.50 (d, $J = 6.4$ Hz, 1H), 3.81 (td, $J = 6.6$, 3.4 Hz, 1H), 3.76 (s, 3H), 3.41 (dd, $J = 11.7$, 6.7 Hz, 1H), 3.34 (dd, $J = 11.7$, 3.4 Hz, 1H), 2.93 (s, 3H), 2.14 (s, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 194.16, 161.55, 144.55, 143.93, 130.73, 129.11, 128.44, 128.29, 126.77, 126.69, 123.25, 111.95, 52.80, 49.87, 49.73, 44.45, 39.72, 20.25.

HRMS (ESI): m/z Calcd. for [C_{20}H_{22}NO_{3}, M+H]^+:324.1594; Found: 324.1594.
Synthesis of 4a

To a Schlenk tube equipped with a dried stir bar was added B(C₆F₅)₃ (0.02 mmol), tertiary aniline 1a (0.24 mmol), alkynone 2a (0.20 mmol), TMSOTf (0.02 mmol) and toluene (1.0 mL) in the glovebox. The Schlenk tube was sealed with a Teflon screw cap. The reaction mixture was taken outside the glovebox and allowed to stir at 60 °C for 24 hours. The crude reaction mixture was concentrated under reduced pressure and directly purified by silica gel chromatography (ethyl acetate:hexanes = 1:10) to afford 4a in 28% yield.

ethyl 4-(2-(dimethylamino)-5-methylphenyl)-2-oxo-4-phenylbut-3-enoate (4a):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 4a as a red solid. m.p.: 132~133 °C. Rf = 0.52 (1:5 EtOAc/Hexanes).

1H NMR (400 MHz, Chloroform-d) δ 7.42 – 7.32 (m, 5H), 7.11 (dd, J = 7.5, 2.2 Hz, 1H), 6.88 (d, J = 8.2 Hz, 1H), 6.83 – 6.77 (m, 2H), 4.01 (q, J = 7.2 Hz, 2H), 2.53 (s, 6H), 2.24 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H).

13C NMR (101 MHz, CDCl₃) δ 183.57, 162.74, 156.06, 149.12, 140.35, 132.65, 130.69, 130.08, 129.72, 128.34, 128.16, 121.94, 118.28, 61.81, 42.85, 20.44, 13.88.

HRMS (ESI): m/z Calcd. for [C₂₁H₂₄NO₃, M+H]⁺: 338.1750; Found: 338.1750.

1-(trans-1,6-dimethyl-4-phenyl-1,2,3,4-tetrahydroquinolin-3-yl)-2,2,2-trifluoroethan-1-one (6a):
Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford **6a** as a yellow oil, 53.5 mg, 80% yield, > 20:1 dr. Rf = 0.47 (1:1:20 triethylamine/aceton/Hexanes).

**\(^1\)H NMR** (400 MHz, Chloroform-\(d\)) \(\delta\) 7.34 – 7.23 (m, 3H), 7.13 – 7.10 (m, 2H), 6.98 (dd, \(J = 8.6, 2.1\) Hz, 1H), 6.66 (d, \(J = 8.3\) Hz, 1H), 6.61 (s, 1H), 4.53 (d, \(J = 7.2\) Hz, 1H), 3.60 (td, \(J = 7.1, 3.7\) Hz, 1H), 3.43 – 3.36 (m, 2H), 2.96 (s, 3H), 2.15 (s, 3H).

**\(^{13}\)C NMR** (101 MHz, Chloroform-\(d\)) \(\delta\) 191.38 (q, \(J = 34.9\) Hz), 143.80, 143.66, 130.72, 128.96, 128.62, 128.43, 127.03, 126.98, 123.11, 115.49 (q, \(J = 293.8\) Hz), 112.00, 50.38, 49.18, 44.62, 39.67, 20.26.

**\(^{19}\)F NMR** (377 MHz, Chloroform-\(d\)) \(\delta\) -77.90.

**HRMS (ESI):** m/z Calcd. for [C\(_{19}\)H\(_{19}\)F\(_3\)NO, M+H]\(^+\):334.1413; Found: 334.1413.

1-**(trans-1,6-dimethyl-4-(m-tolyl)-1,2,3,4-tetrahydroquinolin-3-yl)-2,2,2-trifluoroethane-1-one** (**6b**):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford **6b** as a yellow oil, 43.8 mg, 63% yield, > 20:1 dr. Rf = 0.47 (1:1:20 triethylamine/aceton/Hexanes).

**\(^1\)H NMR** (400 MHz, Chloroform-\(d\)) \(\delta\) 7.19 (t, \(J = 7.6\) Hz, 1H), 7.07 (d, \(J = 7.4\) Hz, 1H), 6.98 (dd, \(J = 8.4, 2.1\) Hz, 1H), 6.94 (s, 1H), 6.89 (d, \(J = 7.7\) Hz, 1H), 6.66 (d, \(J = 8.4\) Hz, 1H), 6.62 (s, 1H), 4.49 (d, \(J = 7.1\) Hz, 1H), 3.59 (td, \(J = 7.0, 3.6\) Hz, 1H), 3.43 – 3.34 (m, 2H), 2.96 (s, 3H), 2.33 (s, 3H), 2.15 (s, 3H).

**\(^{13}\)C NMR** (101 MHz, Chloroform-\(d\)) \(\delta\) 191.43 (q, \(J = 34.9\) Hz), 143.78, 143.63, 138.25, 130.75, 129.54, 128.46, 128.36, 126.97, 127.78, 126.10, 123.21, 115.48 (q, \(J = 294.0\) Hz), 111.94, 50.35, 49.15, 44.49, 39.68, 21.38, 20.28.

**\(^{19}\)F NMR** (377 MHz, Chloroform-\(d\)) \(\delta\) -77.81.

**HRMS (ESI):** m/z Calcd. for [C\(_{20}\)H\(_{21}\)F\(_3\)NO, M+H]\(^+\):348.1570; Found: 348.1570.
1-(trans-4-(4-(tert-butyl)phenyl)-1,6-dimethyl-1,2,3,4-tetrahydroquinolin-3-yl)-2,2,2-trifluoroethan-1-one (6c):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 6c as a yellow oil, 60.1 mg, 77% yield, > 20:1 dr.
Rf = 0.45 (1:1:20 triethylamine/acetone/Hexanes).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.31 (dd, $J = 8.4$, 1.8 Hz, 2H), 7.01 (dd, $J = 8.4$, 1.9 Hz, 2H), 6.97 (d, $J = 8.5$ Hz, 1H), 6.68 – 6.64 (m, 2H), 4.51 (d, $J = 6.1$ Hz, 1H), 3.55 – 3.51 (m, 1H), 3.41 – 3.37 (m, 2H), 2.95 (d, $J = 1.4$ Hz, 3H), 2.16 (s, 3H), 1.32 (d, $J = 1.8$ Hz, 9H).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 191.36 (q, $J = 34.7$ Hz), 149.79, 143.66, 140.97, 130.82, 128.50, 128.38, 126.92, 125.45, 122.89, 115.57 (q, $J = 294.0$ Hz), 111.89, 49.76, 49.15, 43.77, 39.60, 34.41, 31.30, 20.28.

$^{19}$F NMR (377 MHz, Chloroform-d) δ -77.41.

HRMS (ESI): m/z Calcd. for [C$_{23}$H$_{27}$F$_3$NO, M+H]$^+$ :390.2039; Found: 390.2039.

1-(trans-4-((1,1'-biphenyl)-4-yl)-1,6-dimethyl-1,2,3,4-tetrahydroquinolin-3-yl)-2,2,2-trifluoroethan-1-one (6d):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 6d as a yellow oil, 64.8 mg, 79% yield, > 20:1 dr.
Rf = 0.37 (1:1:20 triethylamine/acetone/Hexanes).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.63 – 7.61 (m, 2H), 7.56 (d, $J = 8.3$ Hz, 2H), 7.46 (t, $J = 7.6$ Hz, 2H), 7.39 – 7.35 (m, 1H), 7.20 (d, $J = 6.3$ Hz, 2H), 7.01 (dd, $J = 8.4$, 2.1 Hz, 1H), 6.71 – 6.68 (m, 2H), 4.61 (d, $J = 7.0$ Hz, 1H), 3.64 (td, $J = 7.0$, 3.5 Hz, 1H), 3.45 – 3.40 (m, 2H), 2.99 (s, 3H), 2.18 (s, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 191.31 (q, $J = 34.8$ Hz), 143.67, 142.96, 140.56, 139.85, 130.76, 129.35, 128.75, 128.50, 127.29, 127.04, 126.98, 122.93, 120.27 – 115.53 (q, $J = 294.0$ Hz), 112.03, 50.22, 49.15, 44.14, 39.65, 20.27.

$^{19}$F NMR (377 MHz, Chloroform-d) δ -77.61.
HRMS (ESI): m/z Calcd. for [C_{25}H_{23}F_3NO, M+H]^+ :410.1726; Found: 410.1726.

2,2,2-trifluoro-1-(trans-4-(4-methoxyphenyl)-1,6-dimethyl-1,2,3,4-tetrahydroquinolin-3-yl)ethan-1-one (6e):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 6e as a yellow oil, 48mg, 66% yield, > 20:1 dr. Rf = 0.35 (1:1:20 triethylamine/acetone/Hexanes).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.04 (d, $J = 8.7$ Hz, 2H), 6.97 (d, $J = 8.3$ Hz, 1H), 6.85 (d, $J = 8.8$ Hz, 2H), 6.66 (d, $J = 8.4$ Hz, 1H), 6.62 (s, 1H), 4.48 (d, $J = 7.5$ Hz, 1H), 3.81 (s, 3H), 3.59 (td, $J = 7.4, 3.7$ Hz, 1H), 3.43 – 3.34 (m, 2H), 2.96 (s, 3H), 2.15 (s, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 191.55 (q, $J = 34.8$ Hz), 158.54, 143.58, 135.63, 130.62, 129.92, 128.33, 126.90, 123.57, 115.47 (q, $J = 294.0$ Hz), 113.96, 111.96, 55.15, 50.61, 49.21, 43.99, 39.66, 20.25.

$^{19}$F NMR (377 MHz, Chloroform-d) δ -77.99.

HRMS (ESI): m/z Calcd. for [C_{20}H_{21}F_3NO_2, M+H]^+ :364.1519; Found: 364.1519.

1-(trans-1,6-dimethyl-4-(thiophen-2-yl)-1,2,3,4-tetrahydroquinolin-3-yl)-2,2,2-trifluoroethan-1-one (6f):

Flash column chromatography (eluent: EtOAc/Hexanes = 1/10, v/v) to afford 6f as a yellow oil, 33.7mg, 50% yield, > 20:1 dr. Rf = 0.40 (1:1:20 triethylamine/acetone/Hexanes).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.23 (d, $J = 5.2$ Hz, 1H), 7.00 (d, $J = 8.3$ Hz, 1H), 6.96 – 6.94 (m, 1H), 6.86 (s, 1H), 6.81 (d, $J = 3.8$ Hz, 1H), 6.65 (d, $J = 8.4$ Hz, 1H), 4.83 (d, $J = 5.5$ Hz, 1H), 3.64 – 3.60 (m, 1H), 3.52 – 3.42 (m, 2H), 2.95 (s, 3H), 2.21 (s, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 190.74 (q, $J = 34.7$ Hz), 147.70, 143.03, 130.70, 128.81, 127.01, 126.64, 125.75, 122.43, 121.07 – 115.57 (q, $J = 294.0$ Hz), 112.09, 49.79, 49.75, 39.49, 39.19, 20.28.

$^{19}$F NMR (377 MHz, Chloroform-d) δ -77.08.

HRMS (ESI): m/z Calcd. for [C_{17}H_{17}F_3NOS, M+H]^+ :340.0977; Found: 340.0977.
4. Mechanistic studies

4.1 Deuterium-labelling experiment

To a Schlenk tube equipped with a dried stir bar was added B(C₆F₅)₃ (0.02 mmol), 1a-[D6] (0.24 mmol), alkynone 2a (0.20 mmol), TMSOTf (0.02 mmol) and toluene (1.0 mL) in the glovebox. The Schlenk tube was sealed with a Teflon screw cap. The reaction mixture was taken outside the glovebox and allowed to stir at 80 °C for 24 hours. The crude reaction mixture was concentrated under reduced pressure and directly purified by silica gel chromatography (ethyl acetate:hexanes = 1:10) to afford 3a-[D6] in 56% yield.
$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.31 – 7.27 (m, 2H), 7.24 – 7.20 (m, 1H), 7.14 – 7.12 (m, 2H), 6.95 (dd, $J = 8.2$, 2.0 Hz, 1H), 6.62 (d, $J = 8.4$ Hz, 2H), 4.24 – 4.17 (m, 2H), 3.77 (s, 1H), 2.13 (s, 3H), 1.28 (t, $J = 7.1$ Hz, 3H).

4.2 Crossover experiment

To a Schlenk tube equipped with a dried stir bar was added $\text{B(C}_6\text{F}_5)_3$ (0.02 mmol), 1a-[D6] (0.12 mmol), 1e (0.12 mmol), alkynone 2a (0.20 mmol), TMSOTf (0.02 mmol) and toluene (1.0 mL) in the glovebox. The Schlenk tube was sealed with a Teflon screw cap. The reaction mixture was taken outside the glovebox and allowed to stir at 80 °C for 24 hours. The crude reaction mixture was concentrated under reduced pressure and directly purified by silica gel chromatography (ethyl acetate:hexanes = 1:10) to afford 3a-[D6] and 3e in 63 and 62% yields, respectively.
4.3 Kinetic isotope effect

To a Schlenk tube equipped with a dried stir bar was added B(C₆F₅)₃ (0.02 mmol), 4a (0.10 mmol), 4a-[D₆] (0.10 mmol), TMSOTf (0.02 mmol) and toluene (1.0 mL) in the glovebox. The Schlenk tube was sealed with a Teflon screw cap. The reaction mixture was taken outside the glovebox and allowed to stir at 80 °C for 0.5 hours. The crude reaction mixture was concentrated under reduced pressure. The conversion of 4a and 4a-[D₆] were determined by ¹H NMR using 1,3,5-trimethoxybenzene as the internal standard. Then the mixture was purified by silica gel chromatography (ethyl acetate:hexanes = 1:10) to afford 3a in 13% yield. For the hydrogen on the α carbon
of amino moiety and the hydrogen on the benzyl carbon, the ratio of H to D were 75:25.

4.4 Role of TMSOTf

Additive TMSOTf was found to be able to improve the reaction efficiency. We have tried to use other acid as catalyst or additive, such as Lambert salt or Brookhart’s acid. However, they produced no desired product when used alone. When they were used in combination with B(C₆F₅)₃, diminished yields of 3a and 4a were observed.

| Catalyst                          | yield of 3a (%) | yield of 4a (%) |
|-----------------------------------|----------------|----------------|
| 10 mol% [Et₂Si(toluene)B(C₆F₅)₃]  | ND             | ND             |
| 10 mol% B(C₆F₅)₃ + 10 mol% [Et₂Si(toluene)B(C₆F₅)₃] | 45             | 22             |
| 10 mol% [H(OEt₂)₂][[(3,5-(CF₃)₂C₆H₃)B]⁻] | ND             | 3              |
| 10 mol% B(C₆F₅)₃ + 10 mol% [H(OEt₂)₂][[(3,5-(CF₃)₂C₆H₃)B]⁻] | 6              | 26             |
We surmised that TMSOTf could coordinate with B(C₆F₅)₃ to increase the Lewis acidity (Int S1). However, ¹⁹F NMR measurement of 1:1 ratio of TMSOTf and B(C₆F₅)₃ showed no obvious change in chemical shift and implied this hypothesis is likely not operative. Alternatively, we hypothesized that TMSOTf may coordinate with substrate 2a (e.g., through the ester moiety) to further increase its electrophilicity (Int S2).

a) ¹⁹F NMR of TMSOTf, B(C₆F₅)₃ and both

b) Two hypothesis of the effect of TMSOTf (Lewis acid activation of Lewis acid or substrate)
5. X-Ray crystallography data

Thermal ellipsoids are drawn on 50% probability level

The single-crystal diffraction data were collected on a Rigaku XtaLAB synergy four-circle diffractometer with Cu-Kα radiation (λ=1.54184 Å), with the CrysAlisPro software (version 1.171.39.34b) for data reduction and analysis. The crystal was kept at 100 K during data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were generated geometrically.

Table S1. Crystal data and structure refinement for 3c (CCDC 2114097)

| Property                  | Value                  |
|---------------------------|------------------------|
| Empirical formula         | C_{24}H_{29}NO_{3}     |
| Formula weight            | 379.48                 |
| Temperature / K           | 100.01(10)             |
| Crystal system            | Monoclinic             |
| Space group               | C2/c                   |
| a / Å                     | 32.9756(4)             |
| b / Å                     | 9.21260(10)            |
| c / Å                     | 13.7861(2)             |
| α / °                     | 90                     |
| β / °                     | 101.2320(10)           |
| γ / °                     | 90                     |
| V / Å³                    | 4107.88(9)             |
| Z                         | 8                      |
| F(000)                    | 1632.0                 |
| D_{c} / g cm\(^{-3}\)     | 1.227                  |
| μ / mm\(^{-1}\)          | 0.635                  |
Thermal ellipsoids are drawn on 50% probability level

The single-crystal diffraction data were collected on a Rigaku XtaLAB synergy four-circle diffractometer with Cu-Kα radiation (λ=1.54184Å), with the CrysAlisPro software (version 1.171.39.34b) for data reduction and analysis. The crystal was kept at 100 K during data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were generated geometrically.

Table S2. Crystal data and structure refinement for 3k (CCDC 2114110)
| Parameter          | Value                  |
|--------------------|------------------------|
| $\beta$ /°         | 91.8450(10)            |
| $\gamma$ /°        | 90                     |
| $V$ / Å$^3$        | 4516.98(12)            |
| $Z$                | 8                      |
| $F$(000)           | 1760.0                 |
| $D_c$ / g cm$^{-3}$| 1.216                  |
| $\mu$ / mm$^{-1}$  | 0.625                  |
| Reflns coll.       | 52460                  |
| Independent reflections | 8780                  |
| $R_{int}$          | 0.0630                 |
| $^aR_f [I\geq2\sigma(I)]$ | 0.0460                |
| $^b\omega R_2$ (all data) | 0.1271                |
| GOF                | 1.034                  |
6. References

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7. NMR spectra of products

$^1$H-NMR of 3a (400 MHz, CDCl$_3$)

$^{13}$C-NMR of 3a (101 MHz, CDCl$_3$)
$^1$H-NMR of 3b (400 MHz, CDCl$_3$)

$^{13}$C-NMR of 3b (101 MHz, CDCl$_3$)
$^1$H-NMR of 3c (400 MHz, CDCl$_3$)

![1H-NMR spectrum of 3c](image)

$^{13}$C-NMR of 3c (101 MHz, CDCl$_3$)

![13C-NMR spectrum of 3c](image)
$^1$H-NMR of 3d (400 MHz, CDCl$_3$)

$^{13}$C-NMR of 3d (101 MHz, CDCl$_3$)

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$^1$H-NMR of 3e (400 MHz, CDCl$_3$)

$^{13}$C-NMR of 3e (101 MHz, CDCl$_3$)
$^1$H-NMR of 3f (400 MHz, CDCl$_3$)

$^{13}$C-NMR of 3f (101 MHz, CDCl$_3$)
$^1$H-NMR of 3g (400 MHz, CDCl$_3$)

$^{13}$C-NMR of 3g (101 MHz, CDCl$_3$)
$^1$H-NMR of 3h (400 MHz, CDCl$_3$)

$^{13}$C-NMR of 3h (101 MHz, CDCl$_3$)
$^1$H-NMR of 3i (400 MHz, CDCl$_3$)

$^{13}$C-NMR of 3i (101 MHz, CDCl$_3$)
$^1$H-NMR of $3j$ (400 MHz, CDCl$_3$)

$^{13}$C-NMR of $3j$ (101 MHz, CDCl$_3$)
$^1$H-NMR of 3k (400 MHz, CDCl$_3$)

$^{13}$C-NMR of 3k (101 MHz, CDCl$_3$)
$^1$H-NMR of 3k' (400 MHz, CDCl$_3$)

$^{13}$C-NMR of 3k' (101 MHz, CDCl$_3$)
$^1$H-NMR of 3l (400 MHz, CDCl$_3$)

$^{13}$C-NMR of 3l (101 MHz, CDCl$_3$)
$^{1}$H-NMR of 3m (400 MHz, CDCl$_3$)

$^{13}$C-NMR of 3m (101 MHz, CDCl$_3$)
Supporting information

$^1$H-NMR of 3n (400 MHz, CDCl₃)

$^{13}$C-NMR of 3n (101 MHz, CDCl₃)
$^1$H, $^1$H-NOESY of 3n (400 MHz, CDCl$_3$)

$^1$H-NMR of 3o (400 MHz, CDCl$_3$)
$^{13}\text{C-NMR}$ of 3o (101 MHz, CDCl$_3$)

$^1\text{H-NMR}$ of 3p (400 MHz, CDCl$_3$)
$^{13}$C-NMR of 3p (101 MHz, CDCl$_3$)

$^1$H-NMR of 3q (400 MHz, CDCl$_3$)
$^{13}$C-NMR of $3q$ (101 MHz, CDCl$_3$)

$^1$H-NMR of $3r$ (400 MHz, CDCl$_3$)
**Supporting information**

**$^{13}$C-NMR of 3r (101 MHz, CDCl$_3$)**

![$^{13}$C-NMR spectrum of 3r](image)

**$^1$H-NMR of 3s (400 MHz, CDCl$_3$)**

![$^1$H-NMR spectrum of 3s](image)
**Supporting information**

$^{13}$C-NMR of 3s (101 MHz, CDCl$_3$)

![NMR spectrum of 3s](image)

$^1$H-NMR of 3t (400 MHz, CDCl$_3$)

![NMR spectrum of 3t](image)
$^{13}$C-NMR of 3t (101 MHz, CDCl$_3$)

$^1$H-NMR of 3u (400 MHz, CDCl$_3$)
**Supporting information**

$^{13}$C-NMR of 3u (101 MHz, CDCl$_3$)

$^1$H-NMR of 3v (400 MHz, CDCl$_3$)
Supporting information

$^{13}$C-NMR of 3v (101 MHz, CDCl$_3$)

$^1$H-NMR of 3w (400 MHz, CDCl$_3$)
$^{13}$C-NMR of 3w (101 MHz, CDCl$_3$)

$^1$H-NMR of 3x (400 MHz, CDCl$_3$)
$^{13}$C-NMR of 3x (101 MHz, CDCl$_3$)

1H-NMR of 3y (400 MHz, CDCl$_3$)
**Supporting information**

\[ ^{13}\text{C-NMR of 3y (101 MHz, CDCl}_3\text{)} \]

\[ ^1\text{H-NMR of 3z (400 MHz, CDCl}_3\text{)} \]
Supporting information

$^{13}$C-NMR of 3z (101 MHz, CDCl$_3$)

\[
\begin{array}{c}
\text{Me} \\
\text{N} \\
\text{CO}_2\text{Et} \\
\text{O} \\
\text{F} \\
\end{array}
\]

3z

$^{19}$F-NMR of 3z (377 MHz, CDCl$_3$)

\[
\begin{array}{c}
\text{Me} \\
\text{N} \\
\text{CO}_2\text{Et} \\
\text{O} \\
\text{F} \\
\end{array}
\]

3z
$^1$H-NMR of 3aa (400 MHz, CDCl$_3$)

$^{13}$C-NMR of 3aa (101 MHz, CDCl$_3$)
Supporting information

\(^1\text{H-NMR of 3ab (400 MHz, CDCl}_3\)\)

\(\text{3ab}\)

\(^{13}\text{C-NMR of 3ab (101 MHz, CDCl}_3\)\)

\(\text{3ab}\)

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$^1$H-NMR of 3ac (400 MHz, CDCl$_3$)

$^{13}$C-NMR of 3ac (101 MHz, CDCl$_3$)
$^1$H-NMR of 3ad (400 MHz, CDCl$_3$)

$^{13}$C-NMR of 3ad (101 MHz, CDCl$_3$)
$^1$H-NMR of 3ae (400 MHz, CDCl$_3$)

13C-NMR of 3ae (101 MHz, CDCl$_3$)
$^1$H-NMR of 4a (400 MHz, CDCl$_3$)

$^{13}$C-NMR of 4a (101 MHz, CDCl$_3$)
Supporting information

$^1$H-NMR of 6a (400 MHz, CDCl$_3$)

$^{13}$C-NMR of 6a (101 MHz, CDCl$_3$)
$^{19}$F-NMR of 6a (377 MHz, CDCl$_3$)

$^1$H-NMR of 6b (400 MHz, CDCl$_3$)
$^{13}$C-NMR of 6b (101 MHz, CDCl$_3$)

\[
\text{6b}
\]

$^{19}$F-NMR of 6b (377 MHz, CDCl$_3$)

\[
\text{6b}
\]
$^1$H-NMR of 6c (400 MHz, CDCl$_3$)

13C-NMR of 6c (101 MHz, CDCl$_3$)
**Supporting information**

\[ ^19 \text{F-NMR of 6c} \ (377 \text{ MHz, CDCl}_3) \]

![Image of 6c NMR spectrum]

\[ ^1 \text{H-NMR of 6d} \ (400 \text{ MHz, CDCl}_3) \]

![Image of 6d NMR spectrum]
$^{13}$C-NMR of 6d (101 MHz, CDCl$_3$)

$^{19}$F-NMR of 6d (377 MHz, CDCl$_3$)
$^1$H-NMR of 6e (400 MHz, CDCl$_3$)

$^{13}$C-NMR of 6e (101 MHz, CDCl$_3$)
**Supporting information**

**$^{19}$F-NMR of 6e (377 MHz, CDCl$_3$)**

![$^{19}$F-NMR spectrum of 6e](Image)

**$^1$H-NMR of 6f (400 MHz, CDCl$_3$)**

![$^1$H-NMR spectrum of 6f](Image)
$^{13}$C-NMR of 6f (101 MHz, CDCl$_3$)

$^{19}$F-NMR of 6f (377 MHz, CDCl$_3$)