Electronic Supplementary Information

Photocatalyst- and additive-free decarboxylative alkylation of N-aryl tetrahydroisoquinolines induced by visible light

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1. General Information

Glassware and stir bars were dried in an oven at 110 °C for at least 12 h and then cooled in a desiccator cabinet prior to use. Optimization and substrate screens were performed in 10-mL Schlenk Storage Tubes (with High Vacuum Valves, SYNTHWARE, Mfr. No. F580010). Photochemical reactions were performed under the irradiation of Cree® XLamp® XT-E Royal Blue LEDs (3W, $\lambda_{\text{max}}$=450 nm) using a self-designed device. The reaction temperature was measured to be between 25 °C and 30 °C using this setup. Reactions were carried out under a nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. All other reactions were performed in round-bottom flasks sealed with rubber septa. Plastic syringes or glass pipets were used to transfer liquid reagents and solvents. Reactions were stirred magnetically using Teflon-coated, magnetic stir bars. Analytical thin-layer chromatography (TLC) was performed using plates pre-coated with 0.25 mm of 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm) supplied. TLC plates were visualized by exposure to ultraviolet light and/or iodine stain. Organic solutions were concentrated under reduced pressure using a rotary evaporator. Flash-column chromatography was performed on silica gel (Qingdao Haiyang Chemical Co., Ltd., 200–300 meshes) under pressure.

Nuclear magnetic resonance spectra were recorded at ambient temperature (unless otherwise stated) on a Bruker Avance III 500 MHz or 600 MHz NMR spectrometer. All values for proton chemical shifts are reported in parts per million (δ) and are calibrated using residual undeuterated solvent as an internal reference (CDCl$_3$: δ = 7.26 ppm). All values for carbon chemical shifts are reported in parts per million (δ) and are calibrated against the deuterated solvent peak (CDCl$_3$: δ = 77.16 ppm). NMR data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintuplet, sext = sextet, sep = septet, dd = doublet of doublets, td = triplet of doublets, dq = doublet of quartets, m = multiplet, br = broad), coupling constant (Hz), and integration. High-resolution mass spectra were obtained using a liquid chromatography-electrospray ionization and Time-of-Flight mass spectrometer. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Solvents for chromatography were used as supplied by Adamas-beta®.
2. Experimental Substrates

2.1 Preparation of N-aryl tetrahydroisoquinolines

(1)

\[
\begin{align*}
\text{R}^1 & \begin{aligned} & \text{NH} \\
& \text{(1.5 equiv)} \end{aligned} + \begin{aligned} & \text{R}^2 \text{I} \\
& \text{(1.0 equiv)} \end{aligned} & \xrightarrow{\text{CuI (10 mol%), ethylene glycol (2.0 equiv), K_3PO_4 (2.0 equiv), 2-propanol (1.0 mL/mmol)}} \text{85-90 °C} & \text{N} \begin{aligned} & \text{R}^1 \\
& \text{(1.5 equiv)} \end{aligned} + \begin{aligned} & \text{R}^2 \text{+Br} \\
& \text{(1.0 equiv)} \end{aligned}
\end{align*}
\]

The THIQ substrates 1a-1j, 1o-1p, 1r-1t and 1v were synthesized according to literature procedures.\cite{1}

A typical procedure is described as following: In a 100 mL high pressure schlenk tube were placed copper(I) iodide (190.5 mg, 1.0 mmol) and potassium phosphate (4.25 g, 20.0 mmol). The tube was evacuated and back filled with argon. 2-Propanol (10.0 mL), ethylene glycol (1.11 mL, 20.0 mmol), 1,2,3,4-tetrahydroisoquinoline (1.90 mL, 15.0 mmol) and aryl iodides (10.0 mmol) were added successively via syringes at room temperature. The reaction mixture was heated at 85–90 °C and kept for 24 h and then allowed to cool to room temperature. Ethyl acetate (50 mL) and water (80 mL) were then added. The aqueous layer was extracted by ethyl acetate (2×50 mL). The combined organic phases were washed with brine and dried over sodium sulfate. The solvent was removed via rotary evaporation and the remaining residue was purified via flash column chromatography (PE/EA, 50:1-20:1) to give the desired product.

(2)

\[
\begin{align*}
\text{1} \begin{aligned} & \text{NH} \\
& \text{(1.5 equiv)} \end{aligned} + \begin{aligned} & \text{Br} \\
& \text{(1.0 equiv)} \end{aligned} & \xrightarrow{\text{Pd_2(dba)_2 (5 mol%), BINAP (10 mol%), t-BuONa (1.0 equiv), toluene, reflux, 20 h}} \text{2} \begin{aligned} & \text{N} \\
& \text{(1.5 equiv)} \end{aligned} + \begin{aligned} & \text{Br} \\
& \text{(1.0 equiv)} \end{aligned}
\end{align*}
\]

The substrates 1k and 1l were synthesized according to literature procedures.\cite{2}

A 50 mL round bottomed flask was charged with Pd_2(dba)_2 (228.9 mg, 0.25 mmol), BINAP (311.3 mg, 0.50 mmol), and 15.0 mL of toluene. The resulting solution was degassed by sparging with argon for 10 min before refluxing at 110 °C for 15 min. The reaction mixture was allowed to cool to room temperature and sodium tert-butoxide (480.5 mg, 5.0 mmol), 1-bromonaphthalene (0.70 mL, 5.0 mmol) or 2-bromonaphthalene (1.04 g, 5.0 mmol), and 1,2,3,4-tetrahydroisoquinoline (1.25 mL, 10.0 mmol) were added. The resulting mixture was heated to reflux for 20 h before being cooled to room temperature and filtered through a pad of celite. The solvent was removed via rotary
evaporation, and the residue was purified by chromatography on silica gel using PE/EA (50:1-20:1) as the eluent to afford the desired product.

\[(3)\]

\[
\begin{align*}
\text{Br} \quad \text{Br} & \quad + \quad R^1 \quad \text{NH}_2 \\
(1.5 \text{ equiv}) & \quad \quad (1.0 \text{ equiv}) \\
\text{K}_2\text{CO}_3 \quad (20.0 \text{ equiv}) \\
\text{EtOH, reflux, 8 h}
\end{align*}
\]

The substrates 1m and 1n were synthesized according to literature procedures.\[^3\]

A stirred absolute ethanol solution (50 mL) of compound 2-(2-bromoethyl)benzyl bromide (1.39 g, 5.0 mmol), aniline (5.0 mmol) and potassium carbonate (13.8 g, 100.0 mmol) was refluxed for 8 h. The solvent was evaporated and the resulting residue was hydrolysed with water (20 mL) and extracted with ethyl acetate (3×25 mL). The organic layer was dried over anhydrous sodium sulfate and evaporated. The residue was then purified by column chromatography (silica gel; PE/EA, 50:1-20:1) to yield pure product.

\[(4)\]

\[
\begin{align*}
\text{NH} & \quad \text{Cl} \\
\text{Cl} & \quad \text{triethylamine (2.5 equiv)} \\
\text{1-methyl-pyrrolidin-2-one, 150°C, 2 h}
\end{align*}
\]

The substrate 1q was synthesized according to literature procedures.\[^4\]

To 1,2,3,4-tetrahydroisoquinoline (0.63 mL, 5.0 mmol) and 4-chloropyridine hydrochloride (750.1 mg, 5.0 mmol) in 6.0 mL of 1-methyl-2-pyrrolidinone was added triethylamine (1.74 mL, 12.5 mmol). The reaction mixture was slowly heated to 150°C for 2 h. After cooling down, ethyl acetate was added and the mixture was washed with water. The organic layer was separated, dried over anhydrous sodium sulfate, and the solvent was evaporated. The residue was then purified by column chromatography (silica gel; PE/EA, 30:1-20:1) to yield pure product.

\[(5)\]

\[
\begin{align*}
\text{NH} & \quad \text{Cl} \\
\text{Cl} & \quad \text{K}_2\text{CO}_3 \quad (1.6 \text{ equiv}) \\
\text{DMSO, 80°C, 2 h}
\end{align*}
\]

The substrate 1u was synthesized according to a patented literature.\[^{5a}\]

To a stirred solution of 4-fluorobenzaldehyde (0.54 mL, 5.0 mmol) in dimethylsulfoxide (10.0 mL)
at room temperature was added potassium carbonate (1.12 g, 8.1 mmol) and 1,2,3,4-
tetrahydroisoquinoline (0.69 mL, 5.5 mmol). The reaction mixture was heated at 80 °C for 2 h. The
reaction mixture was poured into cold water after completion of reaction. The mixture was extracted
in ethyl acetate (2x30 mL). The combined organic layer was washed with water (30 mL) and brine
(25 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo.
The crude material was purified by flash chromatography using PE/EA (50:1-30:1) as an eluent to
afford the desired product.

(6)
The substrate 1w was synthesized according to literature procedures.[5b-d]

To a solution of 1,2,3,4-tetrahydro-9H-pyrido[3,4-b]indole (816.1 mg, 5.0 mmol) in CH₂Cl₂ (10
mL) was added slowly di-tert-butyl-dicarbonate (1.2 mL, 5.0 mmol) at 0 °C. After the addition was
completed, the reaction mixture was allowed to reach room temperature and stirred for 3 h. And
then the solvent was evaporated to get the crude product, which was crystallized from water to give
the desired product as a white solid.

tert-Butyl 3,4-dihydro-1H-pyrido[3,4-b]indole-2(9H)-carboxylate (817.1 mg, 3.0 mmol) in THF
was added to NaH (144.0 mg, 60 wt % mineral oil suspension, 3.6 mmol) in THF (0.25 M) at 0 °C.
The mixture was warmed to room temperature, and MeI (0.28 mL, 4.5 mmol) was added. After 30
min, water was added, and the mixture was extracted with Et₂O. The combined organic extracts
were washed with brine, dried over anhydrous sodium sulfate, filtered, and evaporated. Purification
by column chromatography on silica gel, eluting with petrol–EtOAc (90:10), gave tert-butyl 9-
methyl-1,3,4,9-tetrahydro-2H-pyrido[3,4-b]indole-2-carboxylate as an amorphous solid.

CF₃COOH (1.50 mL, 20.0 mmol) was added slowly to the solution of 9-methyl carbamate (572.8
mg, 2.0 mmol) in dichloromethane (0.25 M) at room temperature. The mixture was heated to
refluxing for 30 min. The reaction was diluted with H$_2$O and basified to pH 9−10 using NaOH (aq). The reaction extracted with dichloromethane. The combined organic phases were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification by column chromatography on silica gel, eluting with CH$_2$Cl$_2$−MeOH (90:10), gave the desired product as a solid.

9-Methyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (186.3 mg, 1.0 mmol), iodobenzene (0.23 mL, 2.0 mmol), Cul (39.0 mg, 0.2 mmol) and anhydrous K$_3$PO$_4$ (1.27 g, 5.0 mmol) were added into a mixed solvent of ethylene glycol (2.0 mL) and isopropyl alcohol (4.0 mL) in a dried schlenk tube. The mixture was stirred at 90 °C under the protection of N$_2$ for 12 h. Then water (10 mL) was added and the aqueous suspension was extracted with DCM (3 x 20 mL). The organic phase was dried over anhydrous anhydrous sodium sulfate and the product was purified by column chromatography on silica gel (PE/EA, from 20 : 1 to 5:1).

The N-Aryl tetrahydroisoquinoline substrates 1a-1l, 1o, and 1q-1w have been previously reported, and all spectra data were identical to the literature.

**Characterization data for N-aryl tetrahydroisoquinolines**

2-((1,1′-biphenyl)-2-yl)-1,2,3,4-tetrahydroisoquinoline (1m).

General procedure was followed using 2-aminodiphenyl (846.1 mg, 5.0 mmol, 1.0 equiv). Purification through column chromatography using PE/DCM (3/1) as an eluent, 1m was obtained in 46% yield (656.4 mg) as a white solid. 1H NMR (500 MHz, CDCl$_3$): δ 7.74−7.72 (m, 2H), 7.47−7.44 (m, 2H), 7.42−7.35 (m, 3H), 7.26−7.21 (m, 3H), 7.20−7.17 (m, 1H), 7.16−7.12 (m, 2H), 4.26 (s, 2H), 3.14 (t, $J$ = 5.8 Hz, 2H), 2.66 (t, $J$ = 5.8 Hz, 2H); 13C NMR (126 MHz, CDCl$_3$): δ 150.2, 141.6, 135.2, 135.1, 134.9, 131.9, 128.90, 128.89, 128.4, 128.3, 126.8, 126.5, 126.2, 125.7, 122.5, 118.3, 52.6, 50.6, 29.1; HRMS (ESI-TOF) m/z [M+H]$^+$ caleed for C$_{23}$H$_{20}$N 286.1590, found 286.1596.
2-(2,6-dimethoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (1n).

General procedure was followed using 2,6-dimethoxyaniline (765.9 mg, 5.0 mmol, 1.0 equiv). Purification through column chromatography using PE/DCM (1/1) as an eluent, 1n was obtained in 43% yield (579.1 mg) as a grey solid. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.19–7.14 (m, 3H), 7.09–7.05 (m, 2H), 6.61 (d, $J = 8.5$ Hz, 2H), 4.38 (s, 2H), 3.81 (s, 6H), 3.45 (t, $J = 5.5$ Hz, 2H), 2.97 (t, $J = 5.5$ Hz, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 157.5, 136.9, 135.4, 129.5, 129.1, 126.2, 125.5, 125.4, 124.9, 105.6, 56.1, 52.4, 48.9, 30.4; HRMS (ESI-TOF) m/z [M+H]$^+$ calcd for C$_{17}$H$_{20}$NO$_2$ 270.1489, found 270.1496.

2-(3,4-dichlorophenyl)-1,2,3,4-tetrahydroisoquinoline (1p).

General procedure was followed using 3,4-dichloriodobenzene (2.73 g, 10.0 mmol, 1.0 equiv). Purification through column chromatography using PE/DCM (3/1) as an eluent, 1p was obtained in 83% yield (2.31 g) as a white solid. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.30 (d, $J = 9.0$ Hz, 1H), 7.25–7.17 (m, 4H), 7.00 (d, $J = 3.0$ Hz, 1H), 6.77 (dd, $J = 9.0$, 3.0 Hz, 1H), 4.38 (s, 2H), 3.53 (t, $J = 6.0$ Hz, 2H), 2.99 (t, $J = 6.0$ Hz, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 149.7, 134.7, 133.7, 132.9, 130.5, 128.5, 126.7, 126.6, 126.4, 120.7, 115.8, 114.0; HRMS (ESI-TOF) m/z [M+H]$^+$ calcd for C$_{15}$H$_{14}$Cl$_2$N 278.0498, found 278.0500.

2.2 Preparation of redox-active tetrachloro-N-hydroxyphthalimide esters

Redox-active esters were prepared according to the previously reported procedure$^6$. In short, a flame-dried round-bottom flask was charged with (if solid) carboxylic acid (5.0 mmol, 1.0 equiv), tetrachloro-N-hydroxyphthalimide (5.0 mmol, 1.50 g, 1.0 equiv) and DMAP (0.5 mmol, 61.1 mg, 0.1 equiv). CH$_2$Cl$_2$ was added (0.1 M), and the mixture was stirred vigorously. Carboxylic acid (5.0 mmol, 1.0 equiv) was added via syringe (if liquid). DIC (5.5 mmol, 0.85 mL, 1.1 equiv) was then
added dropwise via syringe, and the mixture was allowed to stir until the acid was consumed (determined by TLC). Typical reaction times were between 0.5 h and 12 h. The mixture was filtered (over Celite®, through a fritted funnel) and rinsed with additional CH₂Cl₂. The solvent was removed under reduced pressure, and purification by column chromatography afforded the desired TCNHPI redox-active ester. (Notes: Unless stated, no precautions were taken throughout the syntheses of the TCNHPI esters. No attempts were made to optimize for yield.)

The redox-active ester substrates 2d, 2i-2j, 2l-2m, 2q-2s, and 2v-2x have been previously reported, and all spectra data were identical to the literature.

**Characterization data for redox-active esters**

![Chemical Structure](image)

4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl butyrate (2a).

General procedure was followed using butyric acid (0.46 mL, 5.0 mmol, 1.0 equiv). Purification through column chromatography using PE/DCM (1/1) as an eluent, 2a was obtained in 50% yield (0.93 g) as a white solid. ¹H NMR (600 MHz, CDCl₃): δ 2.63 (t, J = 7.2 Hz, 2H), 1.84–1.78 (m, 2H), 1.06 (t, J = 7.5 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃): δ 169.1, 157.6, 141.0, 130.5, 124.8, 32.8, 18.4, 13.5; HRMS (ESI-TOF) m/z [M+H]⁺ calcd for C₁₂H₈Cl₄NO₄ 369.9202, found 369.9198.

![Chemical Structure](image)

4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl octanoate (2b).

General procedure was followed using octanoic acid (0.79 mL, 5.0 mmol, 1.0 equiv). Purification through column chromatography using PE/DCM (1/1) as an eluent, 2b was obtained in 70% yield (1.49 g) as a white solid. ¹H NMR (600 MHz, CDCl₃): δ 2.65 (t, J = 7.5 Hz, 2H), 1.79–1.74 (m, 2H), 1.45–1.40 (m, 2H), 1.36–1.25 (m, 6H), 0.88 (t, J = 6.9 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃): δ 169.3, 157.6, 141.0, 130.5, 124.8, 31.6, 31.0, 28.9, 28.8, 24.8, 22.7, 14.2; HRMS (ESI-TOF) m/z [M+H]⁺ calcd for C₁₆H₁₆Cl₄NO₄ 425.9828, found 425.9833.
4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl dodecanoate (2c).

General procedure was followed using lauric acid (1.00 g, 5.0 mmol, 1.0 equiv). Purification through column chromatography using PE/DCM (1/1) as an eluent, 2c was obtained in 64% yield (1.55 g) as a white solid. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 2.65 (t, $J = 9.0$ Hz, 2H), 1.80–1.74 (m, 2H), 1.46–1.40 (m, 2H), 1.34–1.26 (m, 14H), 0.87 (t, $J = 8.4$ Hz, 3H); $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 169.3, 157.7, 141.0, 130.5, 124.9, 32.0, 30.9, 29.71, 29.69, 29.462, 29.458, 29.2, 28.9, 24.8, 22.8, 14.2; HRMS (ESI-TOF) m/z [M+H]$^+$ calcd for C$_{20}$H$_{24}$Cl$_4$NO$_4$ 482.0454, found 482.0457.

4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl 2-cyclohexylacetate (2e).

General procedure was followed using cyclohexylacetic acid (0.71 mL, 5.0 mmol, 1.0 equiv). Purification through column chromatography using PE/DCM (1/1) as an eluent, 2e was obtained in 58% yield (1.23 g) as a white solid. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.53 (d, $J = 6.5$ Hz, 2H), 1.96–1.86 (m, 3H), 1.75 (dt, $J = 13.5, 3.5$ Hz, 2H), 1.70–1.65 (m, 1H), 1.35–1.27 (m, 2H), 1.19 (tt, $J = 12.5, 3.5$ Hz, 1H), 1.13–1.05 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 168.5, 157.7, 141.1, 130.6, 124.9, 38.7, 35.2, 32.9, 26.1, 26.0; HRMS (ESI-TOF) m/z [M+H]$^+$ calcd for C$_{16}$H$_{14}$Cl$_4$NO$_4$ 423.9671, found 423.9679.

4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl 2-phenylacetate (2f).

General procedure was followed using phenylacetic acid (0.68 g, 5.0 mmol, 1.0 equiv). Purification through column chromatography using PE/DCM (1/1) as an eluent, 2f was obtained in 74% yield (1.55 g) as a white solid. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.40–7.35 (m, 4H), 7.34–7.31 (m, 1H), 3.99 (s, 2H); $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 167.3, 157.5, 141.2, 131.3, 130.6, 129.3, 129.1, 128.0, 124.8, 37.7; HRMS (ESI-TOF) m/z [M+H]$^+$ calcd for C$_{16}$H$_{18}$Cl$_4$NO$_4$ 417.9202, found 417.9197.
4,5,6,7-tetrachloro-1,3-dioxoisindolin-2-yl 2-(4-methoxyphenyl)acetate (2g).

General procedure was followed using 4-methoxyphenylacetic acid (0.83 g, 5.0 mmol, 1.0 equiv). Purification through column chromatography using DCM/EA (30/1) as an eluent, 2g was obtained in 76% yield (1.71 g) as a white solid. \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.28–7.26 (m, 2H), 6.90–6.87 (m, 2H), 3.92 (s, 2H), 3.79 (s, 3H); \(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \(\delta\) 167.5, 159.3, 157.5, 141.1, 130.5, 130.4, 124.8, 123.2, 114.4, 55.4, 36.9; HRMS (ESI-TOF) m/z [M+H]\(^+\) calcd for C\(_{17}\)H\(_{10}\)Cl\(_{4}\)NO\(_{5}\) 447.9308, found 447.9302.

4,5,6,7-tetrachloro-1,3-dioxoisindolin-2-yl (tert-butoxycarbonyl)glycinate (2h).

General procedure was followed using \(N\)-Boc glycine (0.88 g, 5.0 mmol, 1.0 equiv). Purification through column chromatography using DCM/EA (20/1) as an eluent, 2h was obtained in 51% yield (1.17 g) as a white solid. \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 5.10 (s, 1H), 4.35–4.21 (m, 2H), 1.50–1.46 (m, 9H); \(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \(\delta\) 166.9, 157.2, 155.4, 141.3, 130.7, 124.7, 81.0, 40.4, 28.4; HRMS (ESI-TOF) m/z [M+Na]\(^+\) calcd for C\(_{15}\)H\(_{12}\)Cl\(_{4}\)N\(_2\)O\(_6\)Na 478.9342, found 478.9346.

4,5,6,7-tetrachloro-1,3-dioxoisindolin-2-yl cyclobutanecarboxylate (2k).

General procedure was followed using cyclobutane carboxylic acid (0.48 mL, 5.0 mmol, 1.0 equiv). Purification through column chromatography using PE/DCM (1/1) as an eluent, 2k was obtained in 79% yield (1.51 g) as a white solid. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 3.54–3.47 (m, 1H), 2.54–2.46 (m, 2H), 2.45–2.38 (m, 2H), 2.16–2.00 (m, 2H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) 171.1, 157.8, 141.1, 130.6, 124.9, 35.0, 25.5, 18.9; HRMS (ESI-TOF) m/z [M+H]\(^+\) calcd for C\(_{13}\)H\(_{7}\)Cl\(_{4}\)NO\(_{4}\)Na 403.9021, found 403.9018.
4,5,6,7-tetrachloro-1,3-dioxoisindolin-2-yl cycloheptanecarboxylate (2n).

General procedure was followed using cycloheptane carboxylic acid (0.71 g, 5.0 mmol, 1.0 equiv).
Purification through column chromatography using PE/DCM (1/1) as an eluent, 2n was obtained in 60% yield (1.28 g) as a white solid. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.92–2.86 (m, 1H), 2.14–2.08 (m, 2H), 1.90–1.77 (m, 4H), 1.64–1.53 (m, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 172.5, 157.9, 141.0, 130.5, 124.9, 42.1, 30.8, 28.3, 26.3; HRMS (ESI-TOF) m/z [M+H]$^+$ calcd for C$_{16}$H$_{14}$Cl$_4$NO$_4$ 423.9671, found 423.9663.

4,5,6,7-tetrachloro-1,3-dioxoisindolin-2-yl cyclohex-3-ene-1-carboxylate (2o).

General procedure was followed using cyclohexene carboxylic acid (0.58 mL, 5.0 mmol, 1.0 equiv).
Purification through column chromatography using PE/DCM (1/1) as an eluent, 2o was obtained in 74% yield (1.51 g) as a white solid. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 5.76–5.74 (m, 1H), 5.72–5.69 (m, 1H), 3.02–2.97 (m, 1H), 2.47–2.38 (m, 2H), 2.26–2.13 (m, 3H), 1.93–1.86 (m, 1H); $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 171.4, 157.8, 141.1, 130.5, 126.9, 124.9, 124.3, 36.9, 27.2, 25.0, 23.9; HRMS (ESI-TOF) m/z [M+H]$^+$ calcd for C$_{15}$H$_{10}$Cl$_4$NO$_4$ 407.9358, found 407.9365.

4,5,6,7-tetrachloro-1,3-dioxoisindolin-2-yl 4-oxocyclohexane-1-carboxylate (2p).

General procedure was followed using 4-oxocyclohexane carboxylic acid (0.71 g, 5.0 mmol, 1.0 equiv). Purification through column chromatography using DCM/EA (30/1) as an eluent, 2p was obtained in 72% yield (1.53 g) as a white solid. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.23–3.18 (m, 1H), 2.61 (dt, $J$ = 15.0, 6.3 Hz, 2H), 2.47–2.41 (m, 2H), 2.39–2.33 (m, 2H), 2.31–2.23 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 208.7, 170.2, 157.7, 141.4, 130.7, 124.8, 39.2, 38.0, 28.3; HRMS (ESI-TOF) m/z [M+H]$^+$ calcd for C$_{15}$H$_{10}$Cl$_4$NO$_5$ 423.9308, found 423,9307.
4,5,6,7-tetrachloro-1,3-dioxoisindolin-2-yl pivalate (2t).

General procedure was followed using pivalic acid (0.57 mL, 5.0 mmol, 1.0 equiv). Purification through column chromatography using PE/DCM (1/1) as an eluent, 2t was obtained in 78% yield (1.50 g) as a white solid. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.42 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 174.0, 157.8, 141.1, 130.5, 124.9, 38.6, 27.1; HRMS (ESI-TOF) m/z [M+H]$^+$ calcd for C$_{13}$H$_{10}$Cl$_4$NO$_4$ 383.9358, found 383.9354.

4,5,6,7-tetrachloro-1,3-dioxoisindolin-2-yl 2,2-dimethylbutanoate (2u).

General procedure was followed using 2,2-dimethylbutyric acid (0.63 mL, 5.0 mmol, 1.0 equiv). Purification through column chromatography using PE/DCM (1/1) as an eluent, 2u was obtained in 74% yield (1.48 g) as a white solid. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.77 (q, $J$ = 7.5 Hz, 2H), 1.37 (s, 6H), 1.03 (t, $J$ = 7.5 Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 173.5, 157.9, 141.1, 130.5, 124.9, 42.8, 33.6, 24.8, 9.3; HRMS (ESI-TOF) m/z [M+H]$^+$ calcd for C$_{14}$H$_{12}$Cl$_4$NO$_4$ 397.9515, found 397.9513.
3. Additional Experimental Optimization Experiments

3.1 Screening of additional esters

$\text{Reaction conditions: 1 (0.20 mmol), 2q (0.24 mmol) in anhydrous DMF (2.0 mL) under N}_2 \text{ at room temperature for 24 hours under irradiation of blue LEDs (3 W). Yields of 3 were determined based on } ^1\text{H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. Isolated yield after silica gel chromatography.}$

3.2 Screening of other solvents

$\text{Reaction conditions: 1a (0.20 mmol), 2q (0.24 mmol) in anhydrous solvent (2.0 mL) under N}_2 \text{ at room temperature for 24 hours under irradiation of blue LEDs (3 W). Isolated yield after silica gel chromatography. THF = tetrahydrofuran, TBME = } \text{tert}-\text{butyl methyl ether, DME = 1,2-dimethoxyethane, NMP = N-methyl-2-pyrrolidinone.}$

3.3 Screening of reaction time
3.4 Screening of reaction concentration

3.5 Screening of mole ratio between 1 and 2

4. General Procedure for Visible-Light-Driven Decarboxylative alkylation
A 10-mL Schlenk Storage Tube equipped with magnetic stir bar was charged with $N$-aryl tetrahydroisoquinoline 1 (0.20 mmol, 1.0 equiv), redox-active tetrachloro-$N$-hydroxyphthalimide ester 2 (0.24 mmol, 1.2 equiv) under air. The tube was evacuated and backfilled with $N_2$ for 3 times (3 × 5 min). Degassed DMF (2.0 mL) was added by syringe under $N_2$. The resulting mixture was degassed by using a “freeze–pump–thaw” procedure for 3 times. The mixture was then irradiated by 3 W blue LEDs and stirred at room temperature for 24 hours. Upon completion, the reaction mixture was transferred to a separate funnel using 20.0 mL ethyl acetate and 5.0 mL water. The organic layer was separated and the aqueous layer extracted with 10.0 mL ethyl acetate. The combined organic extracts were successively washed with aqueous sodium hydroxide (0.10 M), water, brine, dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (PE/DCM or DCM/EA) to give the desired product 3 or 4.
A 100-mL Schlenk Storage Tube equipped with magnetic stir bar was charged with *N*-aryl tetrahydroisoquinoline 1a (1.05g, 5.0 mmol), redox-active tetrachloro-*N*-hydroxyphthalimide ester 2q (2.21g, 5.35 mmol) under air. The tube was evacuated and backfilled with N\textsubscript{2} for 3 times (3 × 5 min). Degassed DMF (30.0 mL) was added by syringe under N\textsubscript{2}. The resulting mixture was degassed by using a “freeze–pump–thaw” procedure for 3 times. The mixture was then irradiated by 3 W blue LEDs and stirred at room temperature for 24 hours. Upon completion, the reaction mixture was transferred to a separate funnel using 100.0 mL ethyl acetate and 20.0 mL water. The organic layer was separated and the aqueous layer extracted with 50.0 mL ethyl acetate. The combined organic extracts were successively washed with aqueous sodium hydroxide (0.10 M), water, brine, dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (DCM/EA=30:1) to give the desired product 3q (1.28g, 87% yield) as a colorless oil.
2-phenyl-1-propyl-1,2,3,4-tetrahydroisoquinoline (3a). 3a was prepared according to the general procedure, using 1a (41.9 mg, 0.20 mmol) and 2a (89.0 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (PE/DCM=3:1) afforded 3a (23.1 mg, 46% yield) as a colorless oil. 1H NMR (500 MHz, CDCl₃): δ 7.25–7.22 (m, 2H), 7.18–7.10 (m, 4H), 6.88 (d, J = 8.0 Hz, 2H), 6.72 (t, J = 7.3 Hz, 1H), 4.66 (t, J = 7.3 Hz, 1H), 3.63 (ddd, J = 12.8, 8.0, 4.8 Hz, 1H), 3.59 (dt, J = 12.5, 5.5 Hz, 1H), 3.02 (ddd, J = 15.8, 8.3, 5.5 Hz, 1H), 2.86 (dt, J = 16.0, 5.5 Hz, 1H), 1.95 (dddd, J = 13.5, 10.5, 7.5, 5.0 Hz, 1H), 1.69 (ddddd, J = 13.8, 10.3, 7.0, 6.0 Hz, 1H), 1.54–1.37 (m, 2H), 0.95 (t, J = 7.5 Hz, 3H); 13C NMR (126 MHz, CDCl₃): δ 149.8, 139.3, 135.1, 129.4, 128.6, 127.4, 126.5, 125.8, 117.0, 113.8, 59.1, 42.0, 39.2, 27.3, 20.2, 14.3.

Spectra data were identical to the literature.[7]

1-heptyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3b). 3b was prepared according to the general procedure, using 1a (41.9 mg, 0.20 mmol) and 2b (102.5 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (PE/DCM=3:1) afforded 3b (18.4 mg, 30% yield) as a colorless oil. 1H NMR (500 MHz, CDCl₃): δ 7.26–7.21 (m, 2H), 7.18–7.09 (m, 4H), 6.87 (d, J = 8.5 Hz, 2H), 6.71 (t, J = 7.3 Hz, 1H), 4.64 (t, J = 7.0 Hz, 1H), 3.63 (ddd, J = 12.8, 8.3, 5.0 Hz, 1H), 3.59 (dt, J = 13.0, 5.8 Hz, 1H), 3.02 (ddd, J = 16.0, 8.0, 5.5 Hz, 1H), 2.85 (dt, J = 16.0, 5.5 Hz, 1H), 2.00–1.92 (m, 1H), 1.73–1.66 (m, 1H), 1.52–1.44 (m, 1H), 1.42–1.34 (m, 2H), 1.32–1.21 (m, 7H), 0.87 (t, J = 7.0 Hz, 3H); 13C NMR (126 MHz, CDCl₃): δ 149.8, 139.4, 135.1, 129.4, 128.6, 127.5, 126.5, 125.8, 117.0, 113.8, 59.4, 41.9, 37.0, 32.0, 29.8, 29.4, 27.2, 27.1, 22.8, 14.2.

Spectra data were identical to the literature.[8]

2-phenyl-1-undecyl-1,2,3,4-tetrahydroisoquinoline (3c). 3c was prepared according to the general procedure, using 1a (41.9 mg, 0.20 mmol) and 2c (116.0 mg, 0.24 mmol) as starting materials.
Purification using silica gel column chromatography (PE/DCM=3:1) afforded 3c (30.5 mg, 42% yield) as a colorless oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.25–7.22 (m, 2H), 7.17–7.09 (m, 4H), 6.87 (d, $J = 8.0$ Hz, 2H), 6.71 (t, $J = 7.3$ Hz, 1H), 4.64 (t, $J = 7.0$ Hz, 1H), 3.63 (ddd, $J = 12.5$, 8.0, 5.0 Hz, 1H), 3.59 (dt, $J = 12.5$, 5.5 Hz, 1H), 3.02 (ddd, $J = 16.0$, 8.0, 5.5 Hz, 1H), 2.85 (dt, $J = 16.0$, 5.5 Hz, 1H), 1.99–1.92 (m, 1H), 1.73–1.66 (m, 1H), 1.52–1.44 (m, 1H), 1.42–1.36 (m, 1H), 1.32–1.22 (m, 16H), 0.89 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 149.8, 139.4, 135.1, 129.4, 128.6, 127.5, 126.5, 125.8, 117.0, 113.8, 59.4, 41.9, 37.0, 32.08, 32.07, 29.80, 29.78, 29.77, 29.52, 29.49, 27.2, 27.0, 22.8, 14.3.

Spectra data were identical to the literature.$^{[8]}$

![Chemical structure of 2-phenyl-1-(4-phenylbutyl)-1,2,3,4-tetrahydroisoquinoline (3d).](image)

2-phenyl-1-(4-phenylbutyl)-1,2,3,4-tetrahydroisoquinoline (3d). 3d was prepared according to the general procedure, using 1a (41.9 mg, 0.20 mmol) and 2d (110.7 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (PE/DCM=3:1) afforded 3d (26.6 mg, 39% yield) as a colorless oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.29–7.22 (m, 4H), 7.20–7.12 (m, 6H), 7.10–7.06 (m, 1H), 6.87 (d, $J = 8.0$ Hz, 2H), 6.73 (d, $J = 7.3$ Hz, 1H), 4.64 (t, $J = 7.0$ Hz, 1H), 3.63 (ddd, $J = 12.8$, 8.3, 5.0 Hz, 1H), 3.59 (dt, $J = 13.0$, 5.8 Hz, 1H), 3.02 (ddd, $J = 15.8$, 8.0, 5.8 Hz, 1H), 2.85 (dt, $J = 15.5$, 5.5 Hz, 1H), 2.64–2.56 (m, 2H), 2.04–1.97 (m, 1H), 1.78–1.70 (m, 1H), 1.69–1.63 (m, 2H), 1.59–1.51 (m, 1H), 1.50–1.42 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 149.8, 142.7, 139.2, 135.1, 129.4, 128.6, 128.5, 128.4, 127.4, 126.5, 125.9, 125.8, 117.1, 113.9, 59.3, 42.0, 36.7, 36.0, 31.7, 27.2, 26.7; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for C$_{25}$H$_{28}$N 342.2216, found 342.2226.

![Chemical structure of 1-(cyclohexylmethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3e).](image)

1-(cyclohexylmethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3e). 3e was prepared according to the general procedure, using 1a (41.9 mg, 0.20 mmol) and 2e (102.0 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (PE/DCM=3:1) afforded 3e (34.2 mg, 56% yield) as a colorless syrup. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.25–7.21 (m, 2H), 7.18–7.13
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(m, 2H), 7.11–7.08 (m, 2H), 6.89 (d, \( J = 8.0 \) Hz, 2H), 6.72 (t, \( J = 7.3 \) Hz, 1H), 4.80 (t, \( J = 7.3 \) Hz, 1H), 3.63 (dd, \( J = 7.0, 5.0 \) Hz, 2H), 3.02 (dt, \( J = 16.0, 7.5 \) Hz, 1H), 2.80 (dt, \( J = 16.0, 5.0 \) Hz, 1H), 1.94–1.87 (m, 2H), 1.77–1.71 (m, 2H), 1.69–1.64 (m, 2H), 1.56–1.50 (m, 1H), 1.47–1.37 (m, 1H), 1.33–1.14 (m, 3H), 1.10–0.95 (m, 2H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta \) 150.0, 139.7, 135.0, 129.4, 128.8, 127.4, 126.4, 125.8, 117.2, 56.4, 44.6, 41.7, 34.6, 33.80, 33.76, 26.8, 26.6, 26.4, 26.3. Spectra data were identical to the literature.\[^9\]

1-benzyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3f). 3f was prepared according to the general procedure, using 1a (41.9 mg, 0.20 mmol) and 2f (100.6 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (PE/DCM=3:1) afforded 3f (27.5 mg, 46% yield) as a white syrup. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.25–7.21 (m, 4H), 7.19–7.13 (m, 3H), 7.07–7.02 (m, 2H), 6.85 (d, \( J = 8.0 \) Hz, 2H), 6.76–6.72 (m, 2H), 4.91 (t, \( J = 6.8 \) Hz, 1H), 3.66 (ddd, \( J = 12.3, 7.8, 5.0 \) Hz, 1H), 3.56 (ddd, \( J = 12.0, 6.5, 5.5 \) Hz, 1H), 3.27 (dd, \( J = 13.5, 6.0 \) Hz, 1H), 3.01 (dd, \( J = 13.5, 7.5 \) Hz, 1H), 2.76 (dt, \( J = 16.0, 5.9 \) Hz, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta \) 149.5, 139.0, 137.8, 135.2, 129.9, 129.4, 128.4, 128.3, 127.8, 126.7, 126.4, 125.6, 117.3, 113.8, 61.6, 42.6, 42.3, 27.6. Spectra data were identical to the literature.\[^{7, 9 and 10}\]

1-(4-methoxybenzyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3g). 3g was prepared according to the general procedure, using 1a (41.9 mg, 0.20 mmol) and 2g (107.8 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=50:1) afforded 3g (64.6 mg, 98% yield) as a colorless oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.28–7.25 (m, 2H), 7.19–7.14 (m, 2H), 7.12–7.06 (m, 1H), 6.94 (d, \( J = 8.5 \) Hz, 2H), 6.88 (d, \( J = 8.0 \) Hz, 2H), 6.80–6.78 (m, 3H), 6.76 (t, \( J = 7.3 \) Hz, 1H), 4.89 (t, \( J = 6.5 \) Hz, 1H), 3.80 (s, 3H), 3.65 (ddd, \( J = 12.0, 7.5, 5.0 \) Hz, 1H), 3.55 (dt, \( J = 12.5, 5.8 \) Hz, 1H), 3.21 (ddd, \( J = 13.5, 5.5 \) Hz, 1H), 3.03–2.96 (m, 2H), 2.75 (dt, \( J = 15.5, 6.0 \) Hz, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta \) 158.3, 149.5, 137.8, 135.2, 131.0, 130.8, 129.4, 128.3,
127.8, 126.7, 125.6, 117.2, 113.69, 113.67, 61.7, 55.3, 42.3, 41.6, 27.7.

Spectra data were identical to the literature.[9a, 10e and 11]

\[
\text{BocHN} \quad \text{tert-butyl ((2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)methyl)carbamate (3h).} \quad \text{3h was prepared according to the general procedure, using 1a (41.9 mg, 0.20 mmol) and 2h (109.9 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=30:1) afforded 3h (62.3 mg, 92% yield) as a white syrup.} \\
\begin{align*}
\delta & \text{7.29–7.13 (m, 6H), 7.00 (d, } J = 8.0 \text{ Hz, 2H), 6.81 (t, } J = 7.3 \text{ Hz, 1H), 4.93–4.56 (m, 2H), 3.70–3.32 (m, 4H), 3.08–3.02 (m, 1H), 2.86–2.74 (m, 1H), 1.49 (s, 9H); } \\
\delta & \text{156.2, 150.1, 135.7, 135.4, 129.4, 128.8, 127.7, 127.0, 126.2, 118.3, 114.9, 59.1, 45.0, 41.6, 28.5, 26.4; HRMS (ESI-TOF) m/z [M + H] }^+ \text{calcd for C}_{21}H_{27}N_2O_2 339.2067, \text{ found 339.2069.} \\
\end{align*}
\]

1-isopropyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3i). 3i was prepared according to the general procedure, using 1a (41.9 mg, 0.20 mmol) and 2i (89.0 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (PE/DCM=3:1) afforded 3i (47.8 mg, 95% yield) as a colorless oil. \(1^H \text{NMR (500 MHz, CDCl}_3\): } \delta 7.27–7.22 (m, 2H), 7.20–7.12 (m, 4H), 6.89 (d, \( J = 8.0 \text{ Hz, 2H}), 6.71 (t, \( J = 7.3 \text{ Hz, 1H}), 4.41 (d, \( J = 8.0 \text{ Hz, 1H}), 3.76 (d, \( J = 12.0, 6.0 \text{ Hz, 1H}), 3.49 (dt, \( J = 12.0, 7.0 \text{ Hz, 1H}), 3.07–2.97 (m, 2H), 2.21–2.11 (m, 1H), 1.10 (d, \( J = 7.0 \text{ Hz, 3H}), 0.97 (d, \( J = 7.0 \text{ Hz, 3H}); \quad 1^C \text{NMR (126 MHz, CDCl}_3\): } \delta 150.2, 137.9, 135.5, 129.2, 128.4, 128.3, 126.7, 125.4, 116.6, 113.3, 64.7, 43.1, 34.5, 27.5, 20.8, 20.2.

Spectra data were identical to the literature.[9b, 10a, 10e and 12]

1-(heptan-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3j). 3j was prepared according to the general procedure, using 1a (41.9 mg, 0.20 mmol) and 2j (102.5 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (PE/DCM=3:1) afforded 3j (51.7 mg, 84% yield, dr = 1:1) as a colorless oil (two pairs of diastereomers, which can not be separated
by silica gel column chromatography). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.23–7.19 (m, 2H), 7.18–7.09 (m, 4H), 6.87 (d, \(J = 8.5\) Hz, 2H), 6.69 (t, \(J = 7.0\) Hz, 1H), 4.62 (d, \(J = 8.5, 1H\)), 4.61 (d, \(J = 9.0, 1H\)), 3.72 (dt, \(J = 12.0, 6.5\) Hz, 1H), 3.53 (dt, \(J = 12.5, 6.8\) Hz, 1H), 3.03–2.94 (m, 2H), 1.84–1.75 (m, 1H), 1.64–1.40 (m, 3H), 1.37–1.16 (m, 5H), 0.91–0.84 (m, 6H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) 150.5, 150.4, 138.71, 138.70, 135.44, 135.43, 129.20, 129.18, 128.49, 128.47, 128.09, 128.08, 126.6, 125.39, 125.38, 116.81, 116.77, 113.9, 113.8, 60.82, 60.76, 45.3, 44.8, 43.2, 31.7, 29.44, 29.43, 29.2, 28.7, 27.1, 23.3, 23.2, 22.9, 22.6, 14.3, 14.2, 11.7, 10.7; HRMS (ESI-TOF) m/z [M + H]\(^+\) calcd for C\(_{22}\)H\(_{30}\)N 308.2373, found 308.2375.

![](image1.png)

1-cyclobutyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3k). 3k was prepared according to the general procedure, using 1a (41.9 mg, 0.20 mmol) and 2k (91.9 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (PE/DCM=3:1) afforded 3k (51.1 mg, 97% yield) as a colorless syrup. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.24 (t, \(J = 8.0\) Hz, 2H), 7.19–7.10 (m, 4H), 6.95 (d, \(J = 8.0\) Hz, 2H), 6.74 (t, \(J = 7.3\) Hz, 1H), 4.62 (d, \(J = 8.0\) Hz, 1H), 3.66–3.58 (m, 2H), 3.02 (dt, \(J = 16.0, 7.5\) Hz, 1H), 2.90–2.82 (m, 1H), 2.77 (dt, \(J = 16.0, 4.8\) Hz, 1H), 1.99–1.86 (m, 4H), 1.82–1.68 (m, 2H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) 150.4, 137.7, 134.9, 129.3, 128.8, 127.3, 126.6, 125.7, 117.4, 114.6, 63.4, 42.1, 41.8, 27.6, 27.1, 26.8, 18.2.

Spectra data were identical to the literature.\(^[8, 9b and 12]\)

![](image2.png)

1-cyclopentyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3l). 3l was prepared according to the general procedure, using 1a (41.9 mg, 0.20 mmol) and 2l (95.3 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (PE/DCM=3:1) afforded 3l (52.7 mg, 95% yield) as a white syrup. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.25–7.20 (m, 2H), 7.18–7.11 (m, 4H), 6.91 (d, \(J = 8.0\) Hz, 2H), 6.70 (t, \(J = 7.3\) Hz, 1H), 4.56 (d, \(J = 9.0\) Hz, 1H), 3.75 (ddd, \(J = 13.0, 8.5, 5.5\) Hz, 1H), 3.66 (dt, \(J = 13.0, 5.8\) Hz, 1H), 3.05 (ddd, \(J = 16.3, 8.4, 6.5\) Hz, 1H), 2.90 (dt, \(J = 16.5, 5.5\) Hz, 1H), 2.39–2.30 (m, 1H), 1.90–1.84 (m, 1H), 1.76–1.61 (m, 3H), 1.59–1.37 (m, 4H); \(^{13}\)C NMR
(126 MHz, CDCl$_3$): $\delta$ 150.1, 139.0, 135.0, 129.3, 128.7, 127.8, 126.6, 125.5, 116.9, 114.0, 62.9, 47.3, 42.1, 31.2, 30.8, 26.9, 25.3, 24.6.

Spectra data were identical to the literature.$^{[8 \text{ and } 9b]}$

1-cyclohexyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline ($3m$). $3m$ was prepared according to the general procedure, using $1a$ (41.9 mg, 0.20 mmol) and $2m$ (98.7 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (PE/DCM=3:1) afforded $3m$ (57.1 mg, 98% yield) as a white syrup. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.26–7.22 (m, 2H), 7.20–7.13 (m, 3H), 7.09 (d, $J = 7.5$ Hz, 1H), 6.88 (d, $J = 8.5$ Hz, 2H), 6.70 (t, $J = 7.3$ Hz, 1H), 4.45 (d, $J = 8.0$ Hz, 1H), 3.75 (dt, $J = 12.0$, 6.0 Hz, 1H), 3.49 (ddd, $J = 12.0$, 7.5, 6.5 Hz, 1H), 3.05 (ddd, $J = 17.0$, 8.5, 7.0 Hz, 1H), 3.01 (dt, $J = 16.0$, 6.5 Hz, 1H), 2.00 (dd, $J = 11.5$, 1.5 Hz, 1H), 1.81–1.61 (m, 5H), 1.24–1.03 (m, 5H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 150.1, 138.0, 135.4, 129.2, 128.5, 128.3, 126.7, 125.3, 116.4, 113.1, 63.9, 44.2, 43.1, 31.1, 30.8, 27.5, 26.8, 26.6, 26.5.

Spectra data were identical to the literature.$^{[8, 9, 10c \text{ and } 12]}$

1-cycloheptyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline ($3n$). $3n$ was prepared according to the general procedure, using $1a$ (41.9 mg, 0.20 mmol) and $2n$ (102.0 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (PE/DCM=3:1) afforded $3n$ (58.0 mg, 95% yield) as a colorless syrup. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.25–7.22 (m, 2H), 7.20–7.12 (m, 4H), 6.86 (d, $J = 8.5$ Hz, 2H), 6.70 (t, $J = 7.3$ Hz, 1H), 4.48 (d, $J = 8.5$ Hz, 1H), 3.74 (dt, $J = 12.0$, 5.8 Hz, 1H), 3.46 (ddd, $J = 12.0$, 8.5, 6.0 Hz, 1H), 3.07 (ddd, $J = 16.0$, 8.0, 6.0 Hz, 1H), 3.00 (dt, $J = 16.0$, 6.0 Hz, 1H), 2.00–1.89 (m, 2H), 1.78–1.72 (m, 2H), 1.68–1.57 (m, 2H), 1.55–1.45 (m, 3H), 1.44–1.30 (m, 4H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 150.2, 138.7, 135.5, 129.2, 128.3, 128.2, 126.6, 125.4, 116.5, 113.1, 64.0, 46.4, 43.5, 32.5, 31.2, 28.9, 27.9, 27.7, 27.1, 26.5.

Spectra data were identical to the literature.$^{[9b]}$
1-(cyclohex-3-en-1-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3o). 3o was prepared according to the general procedure, using 1a (41.9 mg, 0.20 mmol) and 2o (98.2 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (PE/DCM=3:1) afforded 3o (55.6 mg, 96% yield, dr = 1:1) as a colorless oil (two pairs of diastereomers, which can not be separated by silica gel column chromatography). ^1H NMR (500 MHz, CDCl₃): δ 7.27–7.23 (m, 2H), 7.22–7.11 (m, 4H), 6.90 (d, J = 9.0 Hz, 2H), 6.71 (dd, J = 13.5, 7.0 Hz, 1H), 5.72–5.63 (m, 2H), 4.55 (d, J = 8.0 Hz, 0.54H), 4.52 (d, J = 8.5 Hz, 0.46H), 3.80–3.74 (m, 1H), 3.59–3.49 (m, 1H), 3.09–2.99 (m, 2H), 2.33–1.87 (m, 6H), 1.50–1.36 (m, 1H); ^13C NMR (126 MHz, CDCl₃): δ 150.2, 150.1, 137.9, 137.7, 135.5, 135.3, 129.3, 129.2, 128.6, 128.5, 128.4, 128.1, 127.3, 126.9, 126.84, 126.79, 126.7, 126.4, 125.5, 125.3, 116.73, 116.65, 113.4, 113.2, 63.3, 62.9, 43.2, 42.7, 40.5, 39.9, 30.0, 29.6, 27.4, 27.2, 26.7, 26.3, 26.0, 25.4; HRMS (ESI-TOF) m/z [M + H]^+ calcd for C₂₁H₂₄N₂ 290.1903, found 290.1911.

4-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)cyclohexan-1-one (3p). 3p was prepared according to the general procedure, using 1a (41.9 mg, 0.20 mmol) and 2p (102.0 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=30:1) afforded 3p (53.1 mg, 87% yield) as a white syrup. ^1H NMR (500 MHz, CDCl₃): δ 7.26–7.15 (m, 5H), 7.09 (d, J = 7.5 Hz, 1H), 6.87 (d, J = 8.0 Hz, 2H), 6.73 (t, J = 7.3 Hz, 1H), 4.54 (d, J = 8.5 Hz, 1H), 3.79 (dt, J = 12.0, 6.3 Hz, 1H), 3.52 (dt, J = 12.0, 7.0 Hz, 1H), 3.04 (t, J = 6.5 Hz, 2H), 2.44–2.29 (m, 4H), 2.28–2.20 (m, 2H), 2.10–2.04 (m, 1H), 1.70–1.53 (m, 2H); ^13C NMR (126 MHz, CDCl₃): δ 211.8, 149.8, 137.0, 135.3, 129.4, 128.6, 128.2, 127.2, 125.7, 117.3, 113.6, 62.6, 43.3, 42.7, 41.2, 40.8, 30.6, 30.2, 27.4.
Spectra data were identical to the literature.^[12]
2-phenyl-1-(tetrahydro-2H-pyran-4-yl)-1,2,3,4-tetrahydroisoquinoline (3q). 3q was prepared according to the general procedure, using 1a (41.9 mg, 0.20 mmol) and 2q (99.1 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=30:1) afforded 3q (55.2 mg, 94% yield) as a colorless syrup. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.25–7.21 (m, 2H), 7.20–7.13 (m, 3H), 7.08 (d, \(J = 7.5\) Hz, 1H), 6.88 (d, \(J = 8.0\) Hz, 2H), 6.72 (t, \(J = 7.0\) Hz, 1H), 4.45 (d, \(J = 8.5\) Hz, 1H), 4.02–3.96 (m, 2H), 3.74 (dt, \(J = 12.0, 6.5\) Hz, 1H), 3.54 (dt, \(J = 13.0, 6.5\) Hz, 1H), 3.33 (td, \(J = 12.0, 2.0\) Hz, 1H), 3.25 (td, \(J = 11.8, 2.5\) Hz, 1H), 3.07–2.95 (m, 2H), 2.03–1.95 (m, 1H), 1.88–1.84 (m, 1H), 1.59–1.44 (m, 3H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) 150.0, 136.9, 135.3, 129.3, 128.6, 128.4, 127.0, 125.5, 117.0, 113.5, 68.5, 68.0, 63.3, 42.9, 41.6, 31.1, 31.0, 27.2.

Spectra data were identical to the literature.\(^{[9b and 12]}\)

tert-butyl 4-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)piperidine-1-carboxylate (3r). 3r was prepared according to the general procedure, using 1a (41.9 mg, 0.20 mmol) and 2r (122.9 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=30:1) afforded 3r (73.0 mg, 93% yield) as a white syrup. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.25–7.20 (m, 2H), 7.19–7.13 (m, 3H), 7.06 (d, \(J = 7.5\) Hz, 1H), 6.86 (d, \(J = 8.5\) Hz, 2H), 6.71 (t, \(J = 7.3\) Hz, 1H), 4.45 (d, \(J = 8.5\) Hz, 1H), 4.15–4.11 (m, 2H), 3.74 (dt, \(J = 12.0, 6.5\) Hz, 1H), 3.51 (dt, \(J = 12.0, 7.0\) Hz, 1H), 3.06–2.96 (m, 2H), 2.61 (t, \(J = 12.3\) Hz, 1H), 2.53 (t, \(J = 10.5\) Hz, 1H), 1.94–1.85 (m, 2H), 1.68–1.63 (m, 2H), 1.45 (s, 9H), 1.38–1.30 (m, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) 154.9, 149.9, 137.0, 135.3, 129.3, 128.6, 128.4, 127.0, 125.5, 117.0, 113.4, 79.4, 63.1, 43.0, 42.7, 30.1, 29.9, 28.6, 27.3, 21.2, 14.3.

Spectra data were identical to the literature.\(^{[9b and 12]}\)
2-phenyl-1-(1-phenylethyl)-1,2,3,4-tetrahydroisoquinoline (3s). 3s was prepared according to the general procedure, using 1a (41.9 mg, 0.20 mmol) and 2s (103.9 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (PE/DCM=3:1) afforded 3s′ (13.8 mg, 22% yield) as a colorless oil and 3s″ (13.2 mg, 21% yield) as a colorless oil. (3s′): 1H NMR (500 MHz, CDCl₃): δ 7.31–7.26 (m, 2H), 7.21–7.14 (m, 3H), 7.12 (td, J = 7.5, 1.0 Hz, 1H), 7.00–6.91 (m, 4H), 6.86 (d, J = 7.0 Hz, 2H), 6.75 (t, J = 7.3 Hz, 1H), 6.61 (d, J = 8.0 Hz, 1H), 4.79 (d, J = 7.0 Hz, 1H), 3.61 (dt, J = 11.5, 5.5 Hz, 1H), 3.41–3.31 (m, 2H), 2.66 (dt, J = 16.0, 5.5 Hz, 1H), 2.02 (ddd, J = 15.5, 9.0, 6.5 Hz, 1H), 1.44 (d, J = 7.5 Hz, 3H); 13C NMR (126 MHz, CDCl₃): δ 149.6, 143.8, 136.1, 136.0, 129.4, 129.0, 128.5, 128.0, 127.9, 126.8, 126.7, 125.0, 116.7, 112.8, 65.1, 45.7, 43.2, 27.2, 18.7. (3s''): 1H NMR (500 MHz, CDCl₃): δ 7.24–7.20 (m, 2H), 7.18–7.12 (m, 7H), 7.10–7.07 (m, 1H), 6.91 (d, J = 7.5 Hz, 1H), 6.80 (d, J = 8.0 Hz, 2H), 6.66 (t, J = 7.3 Hz, 1H), 4.86 (d, J = 7.0 Hz, 1H), 3.58 (ddd, J = 12.5, 6.5, 6.0 Hz, 1H), 3.46–3.37 (m, 2H), 3.00–2.89 (m, 2H), 1.32 (d, J = 7.5 Hz, 3H); 13C NMR (126 MHz, CDCl₃): δ 150.1, 144.3, 136.8, 135.6, 129.1, 128.8, 128.5, 128.12, 128.10, 126.8, 126.4, 125.3, 117.2, 114.1, 65.0, 45.0, 42.9, 27.2, 18.6. Spectra data were identical to the literature.[10b and 10d]

1-(tert-butyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3t). 3t was prepared according to the general procedure, using 1a (41.9 mg, 0.20 mmol) and 2t (92.4 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (PE/DCM=5:1) afforded 3t (30.3 mg, 57% yield) as a colorless syrup. 1H NMR (500 MHz, CDCl₃): δ 7.23–7.21 (m, 2H), 7.20–7.16 (m, 2H), 7.14–7.10 (m, 2H), 6.93 (d, J = 8.0 Hz, 2H), 6.68 (t, J = 7.0 Hz, 1H), 4.68 (s, 1H), 3.88 (dt, J = 12.5, 6.5 Hz, 1H), 3.55 (dt, J = 12.5, 7.0 Hz, 1H), 3.07 (dt, J = 16.0, 7.0 Hz, 1H), 2.99 (dt, J = 16.5, 6.8 Hz, 1H), 1.03 (s, 9H); 13C NMR (126 MHz, CDCl₃): δ 151.3, 137.2, 135.6, 129.1, 128.9, 128.5, 126.7, 125.2, 116.8, 114.3, 66.2, 44.1, 39.3, 29.4, 27.4. Spectra data were identical to the literature.[9b and 12]

1-(tert-pentyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3u). 3u was prepared according to the
general procedure, using 1a (41.9 mg, 0.20 mmol) and 2u (95.8 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (PE/DCM=5:1) afforded 3u (24.6 mg, 44% yield) as a colorless syrup. 1H NMR (500 MHz, CDCl3): δ 7.22–7.15 (m, 4H), 7.12 (t, J = 6.8 Hz, 2H), 6.92 (d, J = 8.5 Hz, 2H), 6.68 (t, J = 7.3 Hz, 1H), 4.71 (s, 1H), 3.88 (dt, J = 12.5, 7.0 Hz, 1H), 3.61 (dt, J = 13.0, 6.5 Hz, 1H), 3.05–2.96 (m, 2H), 1.49 (q, J = 7.5 Hz, 2H), 0.95 (s, 3H), 0.94 (s, 3H), 0.90 (t, J = 7.3 Hz, 3H); 13C NMR (126 MHz, CDCl3): δ 151.6, 137.2, 135.7, 129.1, 128.8, 128.6, 126.6, 125.1, 117.0, 114.7, 65.1, 44.1, 41.8, 33.4, 27.1, 26.1, 24.8, 8.9.

Spectra data were identical to the literature.\[9b\]

\begin{center}
\includegraphics[width=0.2\textwidth]{image1.png}
\end{center}

1-(1-methylcyclohexyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3v). 3v was prepared according to the general procedure, using 1a (41.9 mg, 0.20 mmol) and 2v (102.0 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (PE/DCM=5:1) afforded 3v (44.0 mg, 72% yield) as a colorless syrup. 1H NMR (500 MHz, CDCl3): δ 7.23–7.16 (m, 4H), 7.14–7.11 (m, 2H), 6.95 (d, J = 8.0 Hz, 2H), 6.69 (t, J = 7.3 Hz, 1H), 4.67 (s, 1H), 3.89 (dt, J = 13.0, 6.5 Hz, 1H), 3.60 (dt, J = 12.5, 7.0 Hz, 1H), 3.05 (dt, J = 16.5, 7.0 Hz, 1H), 2.99 (dt, J = 16.5, 7.0 Hz, 1H), 1.55–1.36 (m, 9H), 1.18–1.08 (m, 1H), 0.96 (s, 3H); 13C NMR (126 MHz, CDCl3): δ 151.6, 137.0, 135.7, 129.1, 129.0, 128.5, 126.6, 125.1, 116.9, 114.7, 67.0, 44.5, 41.9, 36.9, 36.1, 27.2, 26.2, 22.5, 22.1, 21.5.

Spectra data were identical to the literature.\[9b and 12\]

\begin{center}
\includegraphics[width=0.2\textwidth]{image2.png}
\end{center}

1-(adamantan-1-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3w). 3w was prepared according to the general procedure, using 1a (41.9 mg, 0.20 mmol) and 2w (111.2 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (PE/DCM=5:1) afforded 3w (66.0 mg, 96% yield) as a white syrup. 1H NMR (500 MHz, CDCl3): δ 7.23 (t, J = 8.0 Hz, 2H), 7.20–7.11 (m, 4H), 6.96 (d, J = 8.5 Hz, 2H), 6.69 (t, J = 7.0 Hz, 1H), 4.57 (s, 1H), 3.93 (ddd, J = 11.8, 6.8, 5.0 Hz, 1H), 3.48 (dt, J = 11.5, 8.0 Hz, 1H), 3.18 (dt, J = 16.0, 8.0 Hz, 1H), 2.97 (ddd, J = 16.0, 6.5, 5.0 Hz, 1H).
Hz, 1H), 1.95 (s, 3H), 1.76 (d, J = 11.5 Hz, 3H), 1.66–1.57 (m, 9H); \(^{13}\text{C}\) NMR (126 MHz, CDCl\(_3\)): \(\delta\) 151.4, 136.3, 135.7, 129.2, 129.0, 128.2, 126.7, 125.1, 116.4, 113.9, 67.1, 45.3, 41.5, 41.0, 37.0, 29.0, 27.9.

Spectra data were identical to the literature.\(^{[9b]}\)

\[\text{Et} \]

2-(4-ethylphenyl)-1-(tetrahydro-2H-pyran-4-yl)-1,2,3,4-tetrahydroisoquinoline (4b). 4b was prepared according to the general procedure, using 1b (47.5 mg, 0.20 mmol) and 2q (99.1 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=30:1) afforded 4b (57.2 mg, 89% yield) as a colorless oil. \(^1\text{H}\) NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.20–7.12 (m, 3H), 7.07 (d, \(J\) = 8.5 Hz, 3H), 6.83 (d, \(J\) = 9.0 Hz, 2H), 4.39 (d, \(J\) = 8.5 Hz, 1H), 4.03–3.96 (m, 2H), 3.73 (ddd, \(J\) = 12.5, 7.0, 6.0 Hz, 1H), 3.53 (dt, \(J\) = 12.5, 6.3 Hz, 1H), 3.34 (td, \(J\) = 12.0, 2.0 Hz, 1H), 3.25 (td, \(J\) = 11.5, 2.5 Hz, 1H), 3.03 (dt, \(J\) = 16.5, 6.8 Hz, 1H), 2.94 (dt, \(J\) = 16.0, 6.5 Hz, 1H), 2.56 (q, \(J\) = 7.5 Hz, 2H), 2.02–1.96 (m, 1H), 1.91–1.87 (m, 1H), 1.60–1.47 (m, 3H), 1.20 (t, \(J\) = 7.5 Hz, 3H); \(^{13}\text{C}\) NMR (126 MHz, CDCl\(_3\)): \(\delta\) 148.2, 137.0, 135.3, 132.9, 128.7, 128.6, 128.4, 126.9, 125.4, 113.9, 68.5, 68.1, 63.6, 43.0, 41.6, 31.1, 31.0, 27.8, 27.0, 16.0; HRMS (ESI-TOF) m/z [M + H]\(^+\) calcd for C\(_{22}\)H\(_{28}\)NO 322.2165, found 322.2170.

\[\text{Ph} \]

2-([1,1′-biphenyl]-4-yl)-1-(tetrahydro-2H-pyran-4-yl)-1,2,3,4-tetrahydroisoquinoline (4c). 4c was prepared according to the general procedure, using 1c (57.1 mg, 0.20 mmol) and 2q (99.1 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=30:1) afforded 4c (59.1 mg, 80% yield) as a white syrup. \(^1\text{H}\) NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.56 (d, \(J\) = 7.5 Hz, 2H), 7.51 (d, \(J\) = 8.5 Hz, 2H), 7.41 (t, \(J\) = 7.5 Hz, 2H), 7.28 (d, \(J\) = 7.5 Hz, 1H), 7.23–7.16 (m, 3H), 7.11 (d, \(J\) = 7.0 Hz, 1H), 6.96 (d, \(J\) = 8.5 Hz, 2H), 4.52 (d, \(J\) = 8.5 Hz, 1H), 4.05–3.98 (m, 2H), 3.79 (dt, \(J\) = 12.0, 6.5 Hz, 1H), 3.59 (d, \(J\) = 12.5, 6.8 Hz, 1H), 3.35 (t, \(J\) = 11.5 Hz, 1H), 3.26 (td, \(J\) = 11.5, 2.5 Hz, 1H), 3.11–3.00 (m, 2H), 2.09–1.98 (m, 1H), 1.89 (d, \(J\) = 13.5 Hz, 1H), 1.64–1.49 (m, 3H); \(^{13}\text{C}\) NMR (126 MHz, CDCl\(_3\)): \(\delta\) 149.3, 141.1, 136.8, 135.2, 129.7, 128.8, 128.6, 128.4,
127.9, 127.1, 126.4, 126.2, 125.5, 113.6, 68.4, 68.0, 63.4, 43.0, 41.6, 31.05, 31.01, 27.3; HRMS (ESI-TOF) m/z [M + H]+ calcd for C_{26}H_{28}NO 370.2165, found 370.2166.

2-(4-fluorophenyl)-1-(tetrahydro-2H-pyran-4-yl)-1,2,3,4-tetrahydroisoquinoline (4d). 4d was prepared according to the general procedure, using 1d (45.5 mg, 0.20 mmol) and 2q (99.1 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=30:1) afforded 4d (54.2 mg, 87% yield) as a colorless oil. $^1$H NMR (500 MHz, CDCl$_3$): δ 7.21–7.14 (m, 3H), 7.09–7.07 (m, 1H), 6.94–6.89 (m, 2H), 6.82–6.78 (m, 2H), 4.28 (d, $J$ = 9.0 Hz, 1H), 4.03–3.96 (m, 2H), 3.71 (ddd, $J$ = 12.8, 7.3, 6.0 Hz, 1H), 3.50 (dt, $J$ = 13.0, 6.0 Hz, 1H), 3.34 (td, $J$ = 11.8, 2.0 Hz, 1H), 3.25 (td, $J$ = 11.8, 2.5 Hz, 1H), 3.00 (dt, $J$ = 16.5, 6.8 Hz, 1H), 2.91 (dt, $J$ = 16.5, 6.0 Hz, 1H), 2.00–1.92 (m, 1H), 1.89–1.85 (m, 1H), 1.59–1.43 (m, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 155.7 (d, $J$ = 236.6 Hz), 146.9 (d, $J$ = 1.9 Hz), 136.7, 135.1, 128.8, 128.4, 127.0, 125.7, 115.6 (d, $J$ = 22.1 Hz), 115.4 (d, $J$ = 7.3 Hz), 68.4, 68.0, 64.0, 43.4, 41.5, 31.1, 31.0, 26.7; HRMS (ESI-TOF) m/z [M + H]+ calcd for C$_{20}$H$_{23}$FNO 312.1758, found 312.1764.

2-(4-chlorophenyl)-1-(tetrahydro-2H-pyran-4-yl)-1,2,3,4-tetrahydroisoquinoline (4e). 4e was prepared according to the general procedure, using 1e (48.7 mg, 0.20 mmol) and 2q (99.1 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=30:1) afforded 4e (45.9 mg, 70% yield) as a colorless oil. $^1$H NMR (500 MHz, CDCl$_3$): δ 7.22–7.14 (m, 5H), 7.09–7.06 (m, 1H), 6.80–6.77 (m, 2H), 4.37 (d, $J$ = 9.0 Hz, 1H), 4.02–3.95 (m, 2H), 3.71 (dt, $J$ = 12.0, 6.3 Hz, 1H), 3.48 (dt, $J$ = 12.0, 7.0 Hz, 1H), 3.32 (td, $J$ = 12.0, 2.0 Hz, 1H), 3.23 (td, $J$ = 11.5, 2.5 Hz, 1H), 3.05–2.95 (m, 2H), 2.00–1.92 (m, 1H), 1.83–1.80 (m, 1H), 1.57–1.47 (m, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 148.6, 136.6, 135.0, 129.0, 128.7, 128.3, 127.2, 125.6, 121.7, 114.7, 68.4, 68.0, 63.5, 43.1, 41.6, 31.03, 30.99, 27.1; HRMS (ESI-TOF) m/z [M + H]+ calcd for C$_{20}$H$_{23}$ClNO 328.1463, found 328.1468.
2-(4-bromophenyl)-1-(tetrahydro-2H-pyran-4-yl)-1,2,3,4-tetrahydroisoquinoline (4f). 4f was prepared according to the general procedure, using 1f (57.6 mg, 0.20 mmol) and 2q (99.1 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=30:1) afforded 4f (59.6 mg, 80% yield) as a colorless syrup. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.30–7.27 (m, 2H), 7.22–7.14 (m, 3H), 7.07 (dd, $J = 7.0, 2.0$ Hz, 1H), 6.75–6.72 (m, 2H), 4.37 (d, $J = 8.5$ Hz, 1H), 4.01–3.95 (m, 2H), 3.70 (dt, $J = 12.5, 6.0$ Hz, 1H), 3.47 (dt, $J = 12.5, 6.8$ Hz, 1H), 3.31 (td, $J = 11.8, 2.0$ Hz, 1H), 3.23 (td, $J = 11.5, 2.5$ Hz, 1H), 3.05–2.96 (m, 2H), 1.99–1.91 (m, 1H), 1.83–1.78 (m, 1H), 1.56–1.43 (m, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 149.0, 136.6, 135.0, 131.9, 128.6, 128.3, 127.2, 125.6, 115.1, 108.8, 68.4, 68.0, 63.4, 43.1, 41.6, 31.02, 30.99, 27.1; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for C$_{20}$H$_{23}$BrNO 372.0958, found 372.0955.

2-(4-methoxyphenyl)-1-(tetrahydro-2H-pyran-4-yl)-1,2,3,4-tetrahydroisoquinoline (4g). 4g was prepared according to the general procedure, using 1g (47.9 mg, 0.20 mmol) and 2q (99.1 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=20:1) afforded 4g (34.9 mg, 54% yield) as a colorless oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.18–7.11 (m, 3H), 7.09–7.06 (m, 1H), 6.83–6.77 (m, 4H), 4.23 (d, $J = 8.5$ Hz, 1H), 4.02–3.95 (m, 2H), 3.73 (s, 3H), 3.69 (ddd, $J = 12.5, 8.0, 5.5$ Hz, 1H), 3.50 (dt, $J = 13.0, 6.0$ Hz, 1H), 3.33 (td, $J = 11.5, 1.5$ Hz, 1H), 3.24 (td, $J = 11.8, 2.5$ Hz, 1H), 2.97 (ddd, $J = 16.5, 7.5, 6.5$ Hz, 1H), 2.84 (dt, $J = 16.5, 6.0$ Hz, 1H), 1.99–1.89 (m, 2H), 1.55–1.42 (m, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 152.1, 145.0, 136.9, 135.3, 128.9, 128.5, 126.8, 125.3, 116.3, 114.8, 68.5, 68.1, 64.2, 55.9, 43.6, 41.5, 31.2, 31.1, 26.6; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for C$_{21}$H$_{26}$NO$_2$ 324.1958, found 324.1963.
as starting materials. Purification using silica gel column chromatography (DCM/EA=30:1) afforded 4h (52.3 mg, 85% yield) as a colorless oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.20–7.07 (m, 5H), 6.70–6.69 (m, 2H), 6.55 (d, $J$ = 7.5 Hz, 1H), 4.44 (d, $J$ = 8.5 Hz, 1H), 4.02–3.96 (m, 2H), 3.72 (dt, $J$ = 12.5, 6.5 Hz, 1H), 3.54 (dt, $J$ = 12.5, 6.5 Hz, 1H), 3.33 (td, $J$ = 12.0, 2.0 Hz, 1H), 3.24 (td, $J$ = 11.5, 2.5 Hz, 1H), 3.04 (dt, $J$ = 16.0, 6.5 Hz, 1H), 2.97 (td, $J$ = 16.0, 6.5 Hz, 1H), 2.32 (s, 3H), 2.01–1.94 (m, 1H), 1.88–1.84 (m, 1H), 1.59–1.47 (m, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 150.1, 139.0, 137.0, 135.3, 129.2, 128.6, 128.4, 127.0, 125.4, 118.0, 114.3, 110.7, 68.5, 68.0, 63.3, 41.6, 31.1, 31.0, 27.2, 22.1; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for C$_{21}$H$_{26}$NO 308.2009, found 308.2017.

![Diagram](image)

2-(3-chlorophenyl)-1-(tetrahydro-2H-pyran-4-yl)-1,2,3,4-tetrahydroisoquinoline (4i). 4i was prepared according to the general procedure, using 1i (48.7 mg, 0.20 mmol) and 2q (99.1 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=30:1) afforded 4i (59.0 mg, 90% yield) as a colorless oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.22–7.15 (m, 3H), 7.08–7.05 (m, 2H), 6.98 (t, $J$ = 1.8 Hz, 1H), 6.81 (dd, $J$ = 7.5, 1.0 Hz, 1H), 6.78 (dd, $J$ = 8.5, 2.5 Hz, 1H), 4.41 (d, $J$ = 9.0 Hz, 1H), 4.02–3.96 (m, 2H), 3.70 (dt, $J$ = 12.0, 6.3 Hz, 1H), 3.47 (dt, $J$ = 12.5, 7.0 Hz, 1H), 3.32 (td, $J$ = 11.8, 2.0 Hz, 1H), 3.23 (td, $J$ = 11.5, 3.0 Hz, 1H), 3.03 (t, $J$ = 6.8 Hz, 2H), 2.00–1.92 (m, 1H), 1.81–1.78 (m, 1H), 1.57–1.46 (m, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 151.1, 136.6, 134.9, 130.5, 128.6, 128.3, 127.3, 125.7, 123.6, 119.6, 116.0, 111.8, 68.3, 67.9, 63.3, 43.0, 41.6, 31.0, 30.9, 27.2; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for C$_{20}$H$_{23}$ClNO 328.1463, found 328.1466.

![Diagram](image)

2-(3-bromophenyl)-1-(tetrahydro-2H-pyran-4-yl)-1,2,3,4-tetrahydroisoquinoline (4j). 4j was prepared according to the general procedure, using 1j (57.6 mg, 0.20 mmol) and 2q (99.1 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=30:1) afforded 4j (52.9 mg, 71% yield) as a colorless syrup. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.23–7.15...
(m, 3H), 7.12 (t, J = 8.3 Hz, 1H), 7.08 (d, J = 7.5 Hz, 1H), 6.82 (t, J = 7.0 Hz, 1H), 6.74 (dd, J = 8.5, 2.5 Hz, 1H), 6.67 (dd, J = 7.0, 2.0 Hz, 1H), 4.41 (d, J = 9.0 Hz, 1H), 4.02–3.96 (m, 2H), 3.71 (dt, J = 12.0, 6.0 Hz, 1H), 3.48 (dt, J = 12.0, 7.0 Hz, 1H), 3.32 (td, J = 12.0, 2.0 Hz, 1H), 3.23 (td, J = 11.5, 3.0 Hz, 1H), 3.03 (t, J = 6.8 Hz, 2H), 2.00–1.92 (m, 1H), 1.82–1.78 (m, 1H), 1.57–1.45 (m, 3H); 13C NMR (126 MHz, CDCl3): δ 151.0, 136.6, 135.2, 134.9, 130.2, 128.6, 128.3, 127.3, 125.7, 116.7, 113.1, 111.4, 68.4, 68.0, 63.4, 43.1, 41.6, 31.0, 30.9, 27.2; HRMS (ESI-TOF) m/z [M + H]+ calcd for C20H23BrNO 372.0958, found 372.0952.

2-(naphthalen-1-yl)-1-(tetrahydro-2H-pyran-4-yl)-1,2,3,4-tetrahydroisoquinoline (4k). 4k was prepared according to the general procedure, using 1k (51.9 mg, 0.20 mmol) and 2q (99.1 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=30:1) afforded 4k (56.3 mg, 82% yield) as a white syrup. 1H NMR (500 MHz, CDCl3): δ 8.31 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.54–7.47 (m, 3H), 7.25–7.20 (m, 4H), 7.14–7.12 (m, 1H), 6.87 (d, J = 7.0 Hz, 1H), 4.17 (d, J = 7.5 Hz, 1H), 4.05 (dd, J = 11.0, 4.0 Hz, 1H), 3.98 (dt, J = 11.0, 2.5 Hz, 1H), 3.78 (ddd, J = 13.8, 10.8, 4.5 Hz, 1H), 3.55 (ddd, J = 13.8, 6.3, 2.5 Hz, 1H), 3.42–3.37 (m, 1H), 3.34–3.29 (m, 1H), 2.75 (ddd, J = 16.5, 10.5, 6.0 Hz, 1H), 2.61 (dt, J = 16.0, 3.0 Hz, 1H), 2.12–2.05 (m, 2H), 1.66–1.51 (m, 3H); 13C NMR (126 MHz, CDCl3): δ 149.5, 137.2, 135.7, 135.1, 129.6, 129.4, 128.6, 128.3, 126.4, 125.91, 125.85, 125.54, 124.54, 124.2, 123.4, 118.5, 68.7, 68.3, 66.0, 46.4, 42.2, 31.5, 31.0, 25.8; HRMS (ESI-TOF) m/z [M + H]+ calcd for C23H29NO 344.2009, found 344.2014.

2-(naphthalen-2-yl)-1-(tetrahydro-2H-pyran-4-yl)-1,2,3,4-tetrahydroisoquinoline (4l). 4l was prepared according to the general procedure, using 1l (51.9 mg, 0.20 mmol) and 2q (99.1 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=30:1) afforded 4l (52.9 mg, 77% yield) as a colorless oil. 1H NMR (500 MHz, CDCl3): δ 7.71 (d, J = 9.0 Hz, 1H), 7.68 (d, J = 8.5 Hz, 1H), 7.38–7.35 (m, 1H), 7.31 (dd, J = 9.0, 2.5 Hz, 1H), 7.23–7.14 (m,
5H), 7.06 (d, J = 2.5 Hz, 1H), 4.60 (d, J = 9.0 Hz, 1H), 4.02–3.99 (m, 2H), 3.84 (dt, J = 13.0, 6.5 Hz, 1H), 3.73 (dt, J = 13.0, 6.5 Hz, 1H), 3.35 (td, J = 11.8, 2.0 Hz, 1H), 3.27 (td, J = 11.5, 3.0 Hz, 1H), 3.10 (dt, J = 16.5, 6.5 Hz, 1H), 3.02 (dt, J = 16.5, 6.5 Hz, 1H), 2.08–2.00 (m, 1H), 1.91–1.87 (m, 1H), 1.62–1.53 (m, 3H); 13C NMR (126 MHz, CDCl3): δ 147.8, 136.9, 135.1, 128.9, 128.8, 128.4, 127.4, 127.14, 127.08, 126.4, 126.3, 125.5, 122.4, 117.2, 107.7, 68.4, 68.0, 63.4, 42.9, 41.5, 31.2, 31.1, 27.1; HRMS (ESI-TOF) m/z [M + H]+ calcd for C24H26NO 344.2009, found 344.2013.

2-[(1,1′-biphenyl)-2-yl]-1-(tetrahydro-2H-pyran-4-yl)-1,2,3,4-tetrahydroisoquinoline (4m). 4m was prepared according to the general procedure, using 1m (57.1 mg, 0.20 mmol) and 2q (99.1 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=30:1) afforded 4m (6.7 mg, 9% yield) as a colorless oil. 1H NMR (500 MHz, CDCl3): δ 7.49 (d, J = 7.0 Hz, 2H), 7.37 (t, J = 7.5 Hz, 2H), 7.29 (t, J = 7.3 Hz, 1H), 7.18 (dd, J = 7.5, 1.5 Hz, 1H), 7.16–7.11 (m, 2H), 7.08 (td, J = 7.8, 1.3 Hz, 1H), 7.03–6.96 (m, 3H), 6.86 (d, J = 8.0 Hz, 1H), 4.00 (dd, J = 11.3, 4.3 Hz, 1H), 3.94–3.90 (m, 2H), 3.30–3.25 (m, 1H), 3.22–3.15 (m, 2H), 3.13–3.09 (m, 1H), 2.65 (ddd, J = 16.8, 10.3, 7.0 Hz, 1H), 2.48 (ddd, J = 16.8, 5.3, 2.5 Hz, 1H), 1.89–1.81 (m, 2H), 1.54–1.51 (m, 1H), 1.44–1.34 (m, 3H); 13C NMR (126 MHz, CDCl3): δ 149.9, 142.3, 137.3, 135.7, 135.3, 132.0, 129.2, 129.1, 128.5, 128.4, 128.2, 126.7, 126.5, 125.2, 122.0, 121.0, 68.4, 68.1, 64.8, 43.7, 41.0, 31.3, 31.2, 25.9; HRMS (ESI-TOF) m/z [M + H]+ calcd for C26H28NO 370.2165, found 370.2170.

2-(2,6-dimethoxyphenyl)-1-(tetrahydro-2H-pyran-4-yl)-1,2,3,4-tetrahydroisoquinoline (4n). 4n was prepared according to the general procedure, using 1n (53.9 mg, 0.20 mmol) and 2q (99.1 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=20:1) afforded 4n (50.2 mg, 71% yield) as a colorless oil. 1H NMR (500 MHz, CDCl3): δ 7.17–7.12 (m, 3H), 7.08–7.02 (m, 2H), 6.55 (d, J = 8.5 Hz, 2H), 4.09 (d, J = 6.5 Hz, 1H), 3.93 (dd, J = 11.0, 4.0 Hz, 1H), 3.88 (dd, J = 11.0, 4.0 Hz, 1H), 3.71 (s, 6H), 3.41 (dt, J = 11.0, 5.0 Hz,
1H), 3.32–3.26 (m, 1H), 3.25–3.20 (m, 1H), 3.07 (ddd, \(J = 10.8, 9.3, 4.0\) Hz, 1H), 2.96 (ddd, \(J = 15.0, 9.0, 4.5\) Hz, 1H), 2.69 (dt, \(J = 15.0, 4.8\) Hz, 1H), 1.83 (d, \(J = 13.5\) Hz, 1H), 1.80–1.73 (m, 1H), 1.50–1.39 (m, 2H), 1.29–1.20 (m, 1H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) 157.7, 139.0, 137.2, 130.3, 128.1, 127.9, 125.6, 125.0, 124.7, 105.1, 68.8, 68.6, 66.2, 55.7, 47.6, 43.8, 30.5, 30.4, 30.1; HRMS (ESI-TOF) m/z [M + H]\(^{+}\) calcd for C\(_{22}\)H\(_{28}\)NO\(_3\) 354.2064, found 354.2067.

2-(3,4-dimethylphenyl)-1-(tetrahydro-2H-pyran-4-yl)-1,2,3,4-tetrahydroisoquinoline (4o). 4o was prepared according to the general procedure, using 1o (47.5 mg, 0.20 mmol) and 2q (99.1 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=30:1) afforded 4o (47.6 mg, 74% yield) as a colorless syrup. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.19–7.12 (m, 3H), 7.09–7.08 (m, 1H), 6.98 (d, \(J = 8.5\) Hz, 1H), 6.71 (d, \(J = 2.5\) Hz, 1H), 6.64 (dd, \(J = 8.5, 2.5\) Hz, 1H), 4.38 (d, \(J = 9.0\) Hz, 1H), 4.03–3.97 (m, 2H), 3.72 (ddd, \(J = 12.5, 7.0, 6.5\) Hz, 1H), 3.55 (dt, \(J = 12.5, 6.3\) Hz, 1H), 3.34 (td, \(J = 12.0, 2.0\) Hz, 1H), 3.25 (td, \(J = 11.8, 2.5\) Hz, 1H), 3.03 (dt, \(J = 16.0, 6.8\) Hz, 1H), 2.92 (dt, \(J = 16.0, 6.5\) Hz, 1H), 2.24 (s, 3H), 2.17 (s, 3H), 2.01–1.93 (m, 1H), 1.89 (d, \(J = 13.5\) Hz, 1H), 1.60–1.47 (m, 3H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) 148.4, 137.2, 137.0, 135.3, 130.3, 128.7, 128.4, 126.8, 125.3, 125.2, 115.6, 111.4, 68.5, 68.1, 63.4, 42.9, 41.5, 31.1, 31.0, 27.0, 20.6, 18.7; HRMS (ESI-TOF) m/z [M + H]\(^{+}\) calcd for C\(_{22}\)H\(_{28}\)NO 322.2165, found 322.2171.

2-(3,4-dichlorophenyl)-1-(tetrahydro-2H-pyran-4-yl)-1,2,3,4-tetrahydroisoquinoline (4p). 4p was prepared according to the general procedure, using 1p (55.6 mg, 0.20 mmol) and 2q (99.1 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=30:1) afforded 4p (33.3 mg, 46% yield) as a colorless syrup. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.24–7.20 (m, 2H), 7.18–7.14 (m, 2H), 7.08 (dd, \(J = 7.0, 2.0\) Hz, 1H), 6.90 (d, \(J = 3.0\) Hz, 1H), 6.69 (dd, \(J = 9.0, 3.0\) Hz, 1H), 4.36 (d, \(J = 9.0\) Hz, 1H), 4.01–3.95 (m, 2H), 3.69 (dt, \(J = 12.0, 6.0\) Hz, 1H), 3.44 (dt, \(J = 12.0, 7.0\) Hz, 1H), 3.31 (td, \(J = 11.8, 2.0\) Hz, 1H), 3.22 (td, \(J = 11.5, 3.0\) Hz, 1H), 3.07–2.98 (m, 2H), 1.98–1.90 (m, 1H), 1.78–1.75 (m, 1H), 1.55–1.46 (m, 3H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)):
δ 149.4, 136.3, 134.7, 132.9, 130.5, 128.6, 128.3, 127.4, 125.8, 119.4, 114.6, 112.8, 68.3, 67.9, 43.3, 41.6, 31.00, 30.98, 27.1; HRMS (ESI-TOF) m/z [M + H]+ calcd for C_{20}H_{22}Cl_{2}NO 362.1073, found 362.1076.

2-(pyridin-4-yl)-1-(tetrahydro-2H-pyran-4-yl)-1,2,3,4-tetrahydroisoquinoline (4q). 4q was prepared according to the general procedure, using 1q (42.1 mg, 0.20 mmol) and 2q (99.1 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=20:1) afforded 4q (35.3 mg, 60% yield) as a white syrup. 1H NMR (500 MHz, CDCl₃): δ 7.47–7.43 (m, 2H), 7.22–7.14 (m, 3H), 7.07–7.05 (m, 1H), 6.66–6.63 (m, 2H), 4.38 (d, J = 9.0 Hz, 1H), 4.01–3.94 (m, 2H), 3.69 (dt, J = 12.0, 6.0 Hz, 1H), 3.46 (dt, J = 12.0, 7.0 Hz, 1H), 3.31 (td, J = 11.8, 2.0 Hz, 1H), 3.22 (td, J = 11.5, 3.0 Hz, 1H), 3.01 (t, J = 6.5 Hz, 2H), 1.99–1.91 (m, 1H), 1.81–1.77 (m, 1H), 1.56–1.45 (m, 3H); 13C NMR (126 MHz, CDCl₃): δ 149.5, 137.8, 136.6, 135.0, 128.6, 128.3, 127.2, 125.7, 115.6, 68.4, 68.0, 63.3, 43.0, 41.6, 31.02, 30.98, 27.2; HRMS (ESI-TOF) m/z [M + H]+ calcd for C_{19}H_{23}N_{2}O 295.1805, found 295.1807.

6,7-dimethoxy-2-phenyl-1-(tetrahydro-2H-pyran-4-yl)-1,2,3,4-tetrahydroisoquinoline (4r). 4r was prepared according to the general procedure, using 1r (53.9 mg, 0.20 mmol) and 2q (99.1 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=20:1) afforded 4r (50.2 mg, 71% yield) as a colorless oil. 1H NMR (500 MHz, CDCl₃): δ 7.24–7.20 (m, 2H), 6.88 (d, J = 8.5 Hz, 2H), 6.71 (t, J = 7.3 Hz, 1H), 6.65 (s, 1H), 6.59 (s, 1H), 4.34 (d, J = 8.5 Hz, 1H), 4.02–3.97 (m, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 3.69 (ddd, J = 12.8, 7.8, 6.0 Hz, 1H), 3.56 (dt, J = 12.5, 6.5 Hz, 1H), 3.34 (td, J = 12.0, 2.0 Hz, 1H), 3.27 (td, J = 11.8, 2.0 Hz, 1H), 2.96 (dt, J = 16.0, 6.8 Hz, 1H), 2.84 (dt, J = 16.5, 6.3 Hz, 1H), 1.98 (ddt, J = 20.0, 12.0, 3.9 Hz, 1H), 1.87 (ddd, J = 13.5, 3.0, 1.5 Hz, 1H), 1.64–1.60 (m, 1H), 1.57–1.47 (m, 2H); 13C NMR (126 MHz, CDCl₃): δ 150.1, 148.0, 146.6, 129.3, 128.9, 127.3, 117.2, 113.9, 112.0, 111.7, 68.5, 68.0, 63.1, 56.3, 56.0, 42.6, 41.6, 31.2, 31.1, 26.5; HRMS (ESI-TOF) m/z [M + H]+ calcd for C_{22}H_{24}NO₃
2-(4-fluorophenyl)-6,7-dimethoxy-1-(tetrahydro-2H-pyran-4-yl)-1,2,3,4-tetrahydroisoquinoline (4s). 4s was prepared according to the general procedure, using 1s (57.5 mg, 0.20 mmol) and 2q (99.1 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=20:1) afforded 4s (40.1 mg, 54% yield) as a colorless oil. $^1$H NMR (500 MHz, CDCl$_3$): δ 6.92–6.87 (m, 2H), 6.81–6.77 (m, 2H), 6.62 (s, 1H), 6.58 (s, 1H), 4.16 (d, $J = 8.5$ Hz, 1H), 3.99 (td, $J = 11.5$, 3.5 Hz, 2H), 3.87 (s, 3H), 3.84 (s, 3H), 3.66 (ddd, $J = 13.0$, 8.5, 5.5 Hz, 1H), 3.52 (dt, $J = 13.0$, 6.0 Hz, 1H), 3.33 (td, $J = 11.8$, 2.0 Hz, 1H), 3.26 (td, $J = 12.0$, 2.5 Hz, 1H), 2.90 (ddd, $J = 16.5$, 8.8, 6.3 Hz, 1H), 2.75 (dt, $J = 16.5$, 5.5 Hz, 1H), 1.99–1.91 (m, 1H), 1.90–1.86 (m, 1H), 1.63–1.59 (m, 1H), 1.54–1.43 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 155.8 (d, $J = 237.0$ Hz), 148.0, 147.0 (d, $J = 1.9$ Hz), 146.6, 128.5, 127.1, 116.0 (d, $J = 7.3$ Hz), 115.6 (d, $J = 21.9$ Hz), 111.9, 111.8, 68.5, 68.0, 63.8, 56.3, 56.0, 43.3, 41.5, 31.3, 31.1, 25.9; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for C$_{22}$H$_{27}$FNO$_3$ 372.1969, found 372.1973.

2-(4-chlorophenyl)-6,7-dimethoxy-1-(tetrahydro-2H-pyran-4-yl)-1,2,3,4-tetrahydroisoquinoline (4t). 4t was prepared according to the general procedure, using 1t (60.8 mg, 0.20 mmol) and 2q (99.1 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=20:1) afforded 4t (52.0 mg, 67% yield) as a colorless oil. $^1$H NMR (500 MHz, CDCl$_3$): δ 7.15–7.12 (m, 2H), 6.79–6.76 (m, 2H), 6.64 (s, 1H), 6.58 (s, 1H), 4.25 (d, $J = 8.5$ Hz, 1H), 4.01–3.96 (m, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 3.66 (ddd, $J = 12.5$, 7.3, 5.8 Hz, 1H), 3.50 (dt, $J = 12.5$, 6.5 Hz, 1H), 3.32 (td, $J = 11.8$, 2.0 Hz, 1H), 3.25 (td, $J = 11.8$, 2.0 Hz, 1H), 2.93 (dt, $J = 16.0$, 7.0 Hz, 1H), 2.84 (dt, $J = 16.0$, 6.0 Hz, 1H), 1.99–1.91 (m, 1H), 1.84–1.80 (m, 1H), 1.60–1.57 (m, 1H), 1.53–1.44 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 148.8, 148.1, 146.7, 129.0, 128.5, 127.0, 121.9, 115.1, 111.9, 111.7, 68.4, 68.0, 63.3, 56.3, 56.0, 42.9, 41.6, 31.2, 31.1, 26.3; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for C$_{22}$H$_{27}$ClNO$_3$ 388.1674, found 388.1673.
4-(1-isopropyl-3,4-dihydroisoquinolin-2(1H)-yl)benzaldehyde (4u). 4u was prepared according to the general procedure, using 1u (47.5 mg, 0.20 mmol) and 2q (99.1 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=40:1) afforded 4u (24.0 mg, 43% yield) as a colorless oil. ¹H NMR (500 MHz, CDCl₃): δ 9.73 (s, 1H), 7.75–7.72 (m, 2H), 7.23–7.18 (m, 3H), 7.14–7.12 (m, 1H), 6.89 (d, J = 9.0 Hz, 2H), 4.59 (d, J = 8.5 Hz, 1H), 3.81 (ddd, J = 11.5, 6.5, 4.5 Hz, 1H), 3.52 (ddd, J = 12.0, 10.0, 6.0 Hz, 1H), 3.18 (ddd, J = 16.0, 9.5, 6.5 Hz, 1H), 3.03 (ddd, J = 15.5, 6.0, 5.0 Hz, 1H), 2.18–2.09 (m, 1H), 1.05 (d, J = 7.0 Hz, 3H), 0.96 (d, J = 7.0 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 190.3, 154.2, 137.3, 134.7, 132.1, 128.2, 128.2, 127.4, 126.0, 125.4, 111.7, 64.5, 43.7, 34.6, 27.8, 20.7, 20.3; HRMS (ESI-TOF) m/z [M + H]+ calcd for C₁₉H₂₂NO 280.1696, found 280.1703.

1-(4-(1-isopropyl-3,4-dihydroisoquinolin-2(1H)-yl)phenyl)ethan-1-one (4v). 4v was prepared according to the general procedure, using 1v (50.3 mg, 0.20 mmol) and 2q (99.1 mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=40:1) afforded 4v (21.7 mg, 37% yield) as a colorless oil. ¹H NMR (500 MHz, CDCl₃): δ 7.88–7.86 (m, 2H), 7.23–7.16 (m, 3H), 7.13–7.12 (m, 1H), 6.85–6.82 (m, 2H), 4.56 (d, J = 8.5 Hz, 1H), 3.79 (ddd, J = 11.5, 6.5, 5.0 Hz, 1H), 3.51 (ddd, J = 11.5, 9.5, 6.0 Hz, 1H), 3.16 (ddd, J = 16.0, 9.5, 6.5 Hz, 1H), 3.02 (dt, J = 16.0, 5.0 Hz, 1H), 2.50 (s, 3H), 2.18–2.09 (m, 1H), 1.05 (d, J = 7.0 Hz, 3H), 0.96 (d, J = 7.0 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 196.3, 153.1, 137.4, 134.8, 130.7, 128.2, 127.2, 125.8, 125.5, 111.3, 64.3, 43.5, 34.6, 27.7, 26.1, 20.7, 20.2; HRMS (ESI-TOF) m/z [M + H]+ calcd for C₂₀H₂₄NO 294.1852, found 294.1857.

9-methyl-2-phenyl-1-(tetrahydro-2H-pyran-4-yl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (4w). 4w was prepared according to the general procedure, using 1w (52.5 mg, 0.20 mmol) and 2q (99.1
mg, 0.24 mmol) as starting materials. Purification using silica gel column chromatography (DCM/EA=50:1) afforded 4w (47.2 mg, 68% yield) as a colorless oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.47 (d, $J$ = 8.0 Hz, 1H), 7.28 (d, $J$ = 8.0 Hz, 1H), 7.22–7.16 (m, 3H), 7.09 (t, $J$ = 7.3 Hz, 1H), 6.93 (d, $J$ = 8.0 Hz, 2H), 6.75 (t, $J$ = 7.0 Hz, 1H), 4.49 (d, $J$ = 9.0 Hz, 1H), 4.08–4.02 (m, 2H), 3.96 (dd, $J$ = 14.5, 6.3 Hz, 1H), 3.78 (ddd, $J$ = 14.5, 11.5, 5.0 Hz, 1H), 3.70 (s, 3H), 3.43–3.37 (m, 1H), 3.32 (td, $J$ = 11.8, 1.5 Hz, 1H), 3.11–3.04 (m, 1H), 2.72 (dd, $J$ = 16.0, 5.5 Hz, 1H), 2.27–2.20 (m, 1H), 2.01 (d, $J$ = 13.5 Hz, 1H), 1.75 (qd, $J$ = 12.0, 4.5 Hz, 1H), 1.65–1.59 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 151.2, 137.8, 136.2, 129.3, 127.2, 121.6, 119.3, 118.9, 118.2, 116.5, 109.2, 108.2, 68.6, 68.2, 59.3, 41.9, 41.4, 31.5, 31.3, 31.1, 19.3; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for C$_{23}$H$_{27}$N$_2$O 347.2118, found 347.2122.

7. Unsuccessful Substrates

8. Mechanistic Studies

8.1 Radical trapping experiments
A 10-mL Schlenk Storage Tube equipped with magnetic stir bar was charged with N-aryl tetrahydroisoquinoline 1a (41.9 mg, 0.20 mmol), redox-active tetrachloro-N-hydroxyphthalimide ester 2q (99.1 mg, 0.24 mmol) and TEMPO (78.1 mg, 0.50 mmol) under air. The tube was evacuated and backfilled with N₂ for 3 times (3 × 5 min). Degassed DMF (2.0 mL) was added by syringe under N₂. The resulting mixture was degassed by using a “freeze–pump–thaw” procedure for 3 times. The mixture was then irradiated by 3 W blue LEDs and stirred at room temperature for 24 hours. Upon completion, the reaction mixture was transferred to a separate funnel using 20.0 mL ethyl acetate and 5.0 mL water. The organic layer was separated and the aqueous layer extracted with 10.0 mL ethyl acetate. The combined organic extracts were successively washed with aqueous sodium hydroxide (0.10 M), water, brine, dried over anhydrous sodium sulfate and concentrated under vacuum. No desired alkylation product 3q was observed by ¹H NMR spectroscopy of crude reaction mixture.

A 10-mL Schlenk Storage Tube equipped with magnetic stir bar was charged with N-aryl tetrahydroisoquinoline 1a (41.9 mg, 0.20 mmol), redox-active tetrachloro-N-hydroxyphthalimide ester 2q (99.1 mg, 0.24 mmol) and BHT (110.2 mg, 0.50 mmol) under air. The tube was evacuated and backfilled with N₂ for 3 times (3 × 5 min). Degassed DMF (2.0 mL) was added by syringe under N₂. The resulting mixture was degassed by using a “freeze–pump–thaw” procedure for 3 times. The mixture was then irradiated by 3 W blue LEDs and stirred at room temperature for 24 hours. Upon completion, the reaction mixture was transferred to a separate funnel using 20.0 mL ethyl acetate and 5.0 mL water. The organic layer was separated and the aqueous layer extracted with 10.0 mL ethyl acetate. The combined organic extracts were successively washed with aqueous sodium hydroxide (0.10 M), water, brine, dried over anhydrous sodium sulfate and concentrated under vacuum. No desired alkylation product 3q was observed by ¹H NMR spectroscopy of crude reaction mixture.
hydroxide (0.10 M), water, brine, dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (DCM/EA=30:1) to give 44.6 mg (76%) of 3q as a colorless oil.

A 10-mL Schlenk Storage Tube equipped with magnetic stir bar was charged with N-aryl tetrahydroisoquinoline 1a (41.9 mg, 0.20 mmol), redox-active tetrachloro-N-hydroxyphthalimide ester 2q (99.1 mg, 0.24 mmol) and 1,1-diphenylethylene (89.0 μL, 0.50 mmol) under air. The tube was evacuated and backfilled with N₂ for 3 times (3 × 5 min). Degassed DMF (2.0 mL) was added by syringe under N₂. The resulting mixture was degassed by using a “freeze–pump–thaw” procedure for 3 times. The mixture was then irradiated by 3 W blue LEDs and stirred at room temperature for 24 hours. Upon completion, the reaction mixture was transferred to a separate funnel using 20.0 mL ethyl acetate and 5.0 mL water. The organic layer was separated and the aqueous layer extracted with 10.0 mL ethyl acetate. The combined organic extracts were successively washed with aqueous sodium hydroxide (0.10 M), water, brine, dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (DCM/EA=30:1) to give 64.4 mg (68%) of 5 as a colorless oil and 11.7 mg (20%) of 3q as a white syrup.

1-(1,1-diphenyl-2-(tetrahydro-2H-pyran-4-yl)ethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (5).

\(^1\)H NMR (500 MHz, CDCl₃): δ 7.54 (s, 2H), 7.32 (t, \(J = 7.8\) Hz, 2H), 7.28–7.20 (m, 3H), 7.11 (t, \(J = 7.8\) Hz, 2H), 7.07–7.03 (m, 4H), 6.87–6.77 (m, 5H), 6.05 (s, 1H), 3.77 (dd, \(J = 11.8, 3.3\) Hz, 1H), 3.45 (dt, \(J = 11.0, 2.8\) Hz, 1H), 3.28 (ddd, \(J = 13.0, 7.0, 4.5\) Hz, 1H), 3.18 (dt, \(J = 11.3, 2.3\) Hz, 1H), 3.01 (ddd, \(J = 13.5, 9.0, 6.0\) Hz, 1H), 2.79 (td, \(J = 11.8, 2.0\) Hz, 1H), 2.70 (dd, \(J = 14.8, 1.3\) Hz, 1H),
2.55–2.49 (m, 1H), 1.96 (dd, J = 14.8, 1.3 Hz), 1.50 (dt, J = 11.5, 5.0 Hz, 1H), 1.43–1.39 (m, 1H), 1.37–1.26 (m, 3H), 0.79–0.71 (m, 1H), -0.11 (d, J = 13.0 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃): δ 152.4, 145.7, 141.7, 136.9, 131.4, 130.0, 129.4, 128.7, 128.1, 127.9, 127.0, 126.8, 126.6, 126.5, 125.0, 118.4, 116.6, 68.3, 68.1, 66.2, 60.5, 46.5, 43.4, 35.3, 34.5, 32.2, 25.5; HRMS (ESI-TOF) m/z [M + H]+ calcd for C₃₄H₃₆NO 474.2791, found 474.2795.

### 8.2 Radical clock experiment

![Reaction Scheme](image)

A 10-mL Schlenk Storage Tube equipped with magnetic stir bar was charged with N-aryl tetrahydroisoquinoline 1a (41.9 mg, 0.20 mmol), redox-active tetrachloro-N-hydroxyphthalimide ester 2x (91.9 mg, 0.24 mmol) under air. The tube was evacuated and backfilled with N₂ for 3 times (3 × 5 min). Degassed DMF (2.0 mL) was added by syringe under N₂. The resulting mixture was degassed by using a “freeze–pump–thaw” procedure for 3 times. The mixture was then irradiated by 3 W blue LEDs and stirred at room temperature for 24 hours. Upon completion, the reaction mixture was transferred to a separate funnel using 20.0 mL ethyl acetate and 5.0 mL water. The organic layer was separated and the aqueous layer extracted with 10.0 mL ethyl acetate. The combined organic extracts were successively washed with aqueous sodium hydroxide (0.10 M), water, brine, dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (PE/DCM=3:1) to give 22.7 mg (43%) of homoallylation product 3x as a colorless oil.

1-(but-3-en-1-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3x). ¹H NMR (500 MHz, CDCl₃): δ 7.26–7.22 (m, 2H), 7.19–7.12 (m, 4H), 6.89 (d, J = 8.5 Hz, 2H), 6.73 (t, J = 7.3 Hz, 1H), 5.92–5.84 (m, 1H), 5.08–5.00 (m, 2H), 4.70 (t, J = 7.0 Hz, 1H), 3.67–3.59 (m, 2H), 3.04 (dt, J = 16.0, 7.0 Hz, 1H), 2.84 (dt, J = 16.0, 5.0 Hz, 1H), 2.28–2.15 (m, 2H), 2.12–2.04 (m, 1H), 1.86–1.79 (m, 1H); ¹³C NMR (126 MHz, CDCl₃): δ 149.8, 139.0, 138.5, 135.2, 129.4, 128.7, 127.5, 126.6, 125.9, 117.3, 115.1, 114.1, 58.6, 41.9, 35.9, 31.0, 27.0.
8.3 UV-visible spectroscopic measurements

UV-visible absorption spectra of N-phenyl tetrahydroisoquinoline 1a (0.10 M), redox-active tetrachloro-N-hydroxyphthalimide ester 2q (0.10 M), and equimolar mixture of 1a and 2q (0.10 M) in DMF were recorded using UV/vis spectrometer.

9. Byproduct Analysis

A 10-mL Schlenk Storage Tube equipped with magnetic stir bar was charged with N-aryl tetrahydroisoquinoline 1a (41.9 mg, 0.20 mmol), redox-active tetrachloro-N-hydroxyphthalimide ester 2t (192.5 mg, 0.50 mmol) under air. The tube was evacuated and backfilled with N₂ for 3 times (3 × 5 min). Degassed DMF (3.0 mL) was added by syringe under N₂. The resulting mixture was degassed by using a “freeze–pump–thaw” procedure for 3 times. The mixture was then irradiated by 3 W blue LEDs and stirred at room temperature for 24 hours. Upon completion, the reaction mixture was transferred to a separate funnel using 20.0 mL ethyl acetate and 5.0 mL water. The organic layer was separated and the aqueous layer extracted with 10.0 mL ethyl acetate. The combined organic extracts were successively washed with aqueous sodium hydroxide (0.10 M),
water, brine, dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (PE/DCM, 5:1 to 3:1) to give the desired product 3t (14.5 mg, 55%) as a colorless syrup and byproduct 6 (9.0 mg, 34%) as a colorless oil.

1-(tert-butyl)-2-phenyl-1,2-dihydroisoquinoline (6). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.30–7.27 (m, 2H), 7.20 (td, $J = 7.5, 1.5$ Hz, 1H), 7.14–7.06 (m, 4H), 7.00 (d, $J = 7.5$ Hz, 1H), 6.91 (t, $J = 7.3$ Hz, 1H), 6.73 (dd, $J = 7.0, 1.5$ Hz, 1H), 5.93 (d, $J = 7.5$ Hz, 1H), 4.83 (s, 1H), 0.95 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 147.9, 133.1, 130.6, 129.2, 128.9, 128.0, 127.2, 125.3, 123.3, 120.5, 117.1, 108.7, 68.2, 40.5, 27.8; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for C$_{19}$H$_{22}$N 264.1747, found 264.1748.

10. References


(6) (a) T. Qin, J. Cornella, C. Li, L. R. Malins, J. T. Edwards, S. Kawamura, B. D. Maxwell, M. D.


11. **1H NMR and 13C NMR Spectra**

![1H NMR and 13C NMR Spectra](image)

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 1n
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 1n

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 1o
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 1o

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 1q
\[ \text{\( ^{13} \text{C NMR spectrum (CDCl}_3, 126 \text{ MHz) of 1q} \)} \]

\[ \text{\( ^{1} \text{H NMR spectrum (CDCl}_3, 600 \text{ MHz) of 2a} \)} \]

[Chemical structures and spectra images are shown.]
$\text{C NMR spectrum (CDCl}_3, 151 \text{ MHz) of 2a}$

$\text{H NMR spectrum (CDCl}_3, 600 \text{ MHz) of 2b}$
\[ \text{C NMR spectrum (CDCl}_3, \text{ 151 MHz) of 2b} \]

\[ \text{H NMR spectrum (CDCl}_3, \text{ 600 MHz) of 2c} \]
$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of 2e

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 2e
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 2e

$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of 2f
$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of 2f

$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of 2g
$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of 2g

$^{1}$H NMR spectrum (CDCl$_3$, 600 MHz) of 2h
$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of 2h

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 2k
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 2k

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 2n
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 2n

$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of 2o
$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of 2o

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 2p
$^{13}\text{C NMR spectrum (CDCl}_3, 126 \text{ MHz)}$ of $2\text{p}$

$^1\text{H NMR spectrum (CDCl}_3, 500 \text{ MHz)}$ of $2\text{t}$
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of $2t$

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of $2u$
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 2u

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 3a
\[ \text{C NMR spectrum (CDCl}_3, 126 \text{ MHz) of 3a} \]

\[ \text{H NMR spectrum (CDCl}_3, 500 \text{ MHz) of 3b} \]
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 3b

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 3c
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 3e

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 3d
\[ \text{\( ^{13} \)C NMR spectrum (CDCl}_3, 126 \text{ MHz}) \text{ of 3d} \]

\[ \text{\( ^{1} \)H NMR spectrum (CDCl}_3, 500 \text{ MHz}) \text{ of 3e} \]
\[ \text{C NMR spectrum (CDCl}_3, 126 \text{ MHz) of 3e} \]

\[ \text{H NMR spectrum (CDCl}_3, 500 \text{ MHz) of 3f} \]
13C NMR spectrum (CDCl3, 126 MHz) of 3f

1H NMR spectrum (CDCl3, 500 MHz) of 3g
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 3g

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 3h
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 3h

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 3i
$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 3j

$^1$C NMR spectrum (CDCl$_3$, 126 MHz) of 3i
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 3j

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 3k
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 3k

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 3l
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 3m

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 3n
$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 3o

$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 3n
$\text{H NMR spectrum (CDCl}_3, 500 \text{ MHz) of 3p}$

$\text{C NMR spectrum (CDCl}_3, 126 \text{ MHz) of 3o}$
$^1$C NMR spectrum (CDCl$_3$, 126 MHz) of 3p

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 3q
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 3q

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 3r
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 3r

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 3s'}
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 3s'

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 3s''
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 3s$''$

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 3t
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 3t

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 3u
$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 3v
$13^C$ NMR spectrum (CDCl$_3$, 126 MHz) of 3v

$^1H$ NMR spectrum (CDCl$_3$, 500 MHz) of 3w
$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 4b

$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 3w
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 4b

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 4c
$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 4c

$^1$C NMR spectrum (CDCl$_3$, 126 MHz) of 4c
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 4d

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 4e
\[ \text{\textsuperscript{13}C NMR spectrum (CDCl\textsubscript{3}, 126 MHz) of 4f} \]

\[ \text{\textsuperscript{1}H NMR spectrum (CDCl\textsubscript{3}, 500 MHz) of 4g} \]
13C NMR spectrum (CDCl3, 126 MHz) of 4g.

1H NMR spectrum (CDCl3, 500 MHz) of 4h.
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 4i

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 4j
\[ \text{S92} \]

\[ \text{13C NMR spectrum (CDCl}_3, 126 \text{ MHz) of 4j} \]

\[ \text{1H NMR spectrum (CDCl}_3, 500 \text{ MHz) of 4k} \]

\[ \text{N} \quad \text{O} \quad \text{Br} \]

\[ \text{N} \quad \text{O} \]
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 4k

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 4l
$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 4m

$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 4l

NMR spectra of compounds 4m and 4l.
**1^3C NMR spectrum (CDCl₃, 126 MHz) of 4m**

**1^H NMR spectrum (CDCl₃, 500 MHz) of 4n**
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 4n

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 4o
$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 4p

$^13$C NMR spectrum (CDCl$_3$, 126 MHz) of 4o
\[ \text{C NMR spectrum (CDCl}_3, 126 \text{ MHz) of 4p} \]

\[ \text{H NMR spectrum (CDCl}_3, 500 \text{ MHz) of 4q} \]
$^{13}$C NMR spectrum ($\text{CDCl}_3, 126 \text{ MHz}$) of 4q
\text{^1}H \text{ NMR spectrum (CDCl}_3, \ 500 \text{ MHz) of 4s}
S101
$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 4u

$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 4t
\textbf{\textsuperscript{13}C NMR spectrum (CDCl$_3$, 126 MHz) of 4u}

\textbf{\textsuperscript{1}H NMR spectrum (CDCl$_3$, 500 MHz) of 4v}
$\text{\textsuperscript{13}C NMR spectrum (CDCl}_3$, 126 MHz) of $4v$

$\text{\textsuperscript{1}H NMR spectrum (CDCl}_3$, 500 MHz) of $4w$
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 4w

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 3x
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 3x

$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 5
$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of 6

$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 5
$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of 6