

Supporting Information

Iodine Catalyzed Reduction of Quinolines under Mild Reaction

Conditions

Chun-Hua Yang,^a Xixi Chen,^a Huimin Li,^a Wenbo Wei,^a Zhantao Yang,^{*ab} Junbiao Chang^{*b}

^a Henan Province Key Laboratory of New Opto-Electronic Functional Materials, College of Chemistry and Chemical Engineering, Anyang Normal University, 436 Xian'ge Road, Anyang 455000, P. R. China

^b School of Pharmaceutical Sciences, Zhengzhou University, Zhengzhou, Henan 450001, P. R. China

E-mail: zhantaoyang@163.com

changjunbiao@zzu.edu.cn

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1. General Information

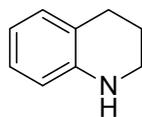
All organic reagents were purchased from Energy Chemical, if not noted otherwise. Dry solvents were obtained by distillation from drying reagents according to procedures described in Purification of Laboratory Chemicals (5th Edition) written by Wilfred L.F. Armarego and Christina L.L. Chai (Elsevier, 2003). Column chromatography was performed with 200-300 mesh silica gel unless otherwise noted. Thin layer chromatography (TLC) was performed on silica gel GF254. ^1H , ^{13}C and ^{11}B NMR spectra were recorded on a Bruker DRX 400 spectrometer at 298 K using deuterated chloroform as solvent and TMS as internal reference. All chemical shifts in nmr experiments are reported as ppm downfield from TMS. HRMS experiments were performed on a Waters LCT PremierxeTM (USA).

2. Reduction of Quinolines and N-Heteroaromatics

2.1 General procedure

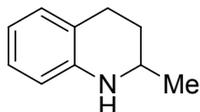
A flask (10 mL) was charged with iodine (0.05 mmol, 20%) and quinoline (0.25 mmol, 1.0 equiv.), exchanged with nitrogen for three times. Then anhydrous CH_2Cl_2 (1 mL) and HBpin (1 mmol, 4 equiv.) were added separately. The reaction mixture was then stirred at room temperature for 24-72 h. The reaction mixture was diluted with CH_2Cl_2 (5 mL) and quenched with water (1 mL). The CH_2Cl_2 phase was separated, and the aqueous solution was extracted with CH_2Cl_2 (5 mL \times 2). The combined organic layers were dried with anhydrous Na_2SO_4 , filtered and concentrated to get a residue which was purified by column chromatography on silica gel (1%-10% petroleum ether/ethyl acetate as eluent; 3% MeOH/ CH_2Cl_2 for isoquinoline) to give the corresponding product.

2.2 Spectral data of products



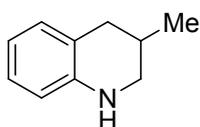
1,2,3,4-tetrahydroquinoline (2a)

Colorless oil, 30mg, 91% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.00 – 6.96 (m, 2H), 6.63 (t, $J = 7.4$ Hz, 1H), 6.49 (d, $J = 7.8$ Hz, 1H), 3.72 (brs, 1H), 3.33 – 3.30 (m, 2H), 2.79 (t, $J = 6.4$ Hz, 2H), 1.99 – 1.93 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.9, 129.6, 126.8, 121.5, 117.0, 114.3, 42.1, 27.1, 22.3. Spectral data is in accordance with the literature.^[1]



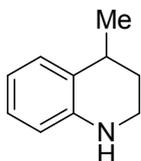
2-methyl-1,2,3,4-tetrahydroquinoline (2b)

Colorless oil, 30 mg, 81% yield. ^1H NMR (400 MHz, CDCl_3) δ 6.99 (t, $J = 6.1$ Hz, 2H), 6.63 (t, $J = 7.3$ Hz, 1H), 6.49 (d, $J = 8.1$ Hz, 1H), 3.71 (brs, 1H), 3.46 – 3.39 (m, 1H), 2.87 – 2.84 (m, 1H), 2.78 – 2.76 (m, 1H), 1.97 – 1.93 (m, 1H), 1.70 – 1.56 (m, 1H), 1.23 (d, $J = 6.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.9, 129.4, 126.8, 121.2, 117.1, 114.1, 47.3, 30.3, 26.7, 22.7. Spectral data is in accordance with the literature.^[2]



3-methyl-1,2,3,4-tetrahydroquinoline (2c)

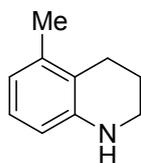
Colorless oil, 31 mg, 84% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.01 – 6.96 (m, 2H), 6.63 (td, $J = 7.4, 0.7$ Hz, 1H), 6.51 (d, $J = 7.9$ Hz, 1H), 3.31 – 3.27 (m, 1H), 2.94 – 2.89 (m, 1H), 2.82 – 2.78 (m, 1H), 2.49 – 2.42 (m, 1H), 2.16 – 1.98 (m, 1H), 1.07 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.4, 129.6, 126.8, 121.2, 117.0, 114.0, 49.0, 35.6, 27.3, 19.2. Spectral data is in accordance with the literature.^[2]



4-methyl-1,2,3,4-tetrahydroquinoline (2d)

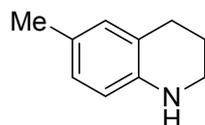
Colorless oil, 28 mg, 76% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.08 (d, $J = 7.5$ Hz, 1H), 7.03 – 6.95 (m, 1H), 6.68 – 6.61 (m, 1H), 6.50 (d, $J = 8.0$ Hz, 1H), 3.87 (brs, 1H), 3.36 – 3.29 (m, 2H), 3.02 – 2.92 (m, 1H), 2.01 – 1.96 (m, 1H), 1.72 – 1.70 (m, 1H),

1.31 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.4, 128.6, 126.9, 126.7, 117.1, 114.3, 39.1, 30.3, 30.0, 22.8. Spectral data is in accordance with the literature.^[2]



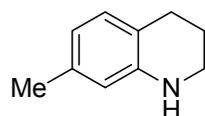
5-methyl-1,2,3,4-tetrahydroquinoline (2e)

Colorless oil, 32 mg, 86% yield. ^1H NMR (400 MHz, CDCl_3) δ 6.95 (t, $J = 7.7$ Hz, 1H), 6.59 (d, $J = 7.4$ Hz, 1H), 6.43 (d, $J = 8.0$ Hz, 1H), 3.64 (brs, 1H), 3.33 – 3.30 (m, 2H), 2.71 (t, $J = 6.6$ Hz, 2H), 2.25 (s, 3H), 2.08 – 2.02 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 145.0, 137.3, 126.3, 120.3, 119.0, 112.5, 41.7, 24.1, 22.6, 19.5. Spectral data is in accordance with the literature.^[3]



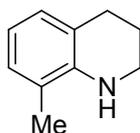
6-methyl-1,2,3,4-tetrahydroquinoline (2f)

Colorless oil, 31 mg, 84% yield. ^1H NMR (400 MHz, CDCl_3) δ 6.85 – 6.84 (m, 2H), 6.48 – 6.45 (m, 1H), 3.46 (brs, 1H), 3.33 – 3.31 (m, 2H), 2.79 (t, $J = 6.4$ Hz, 2H), 2.27 (s, 3H), 2.02 – 1.96 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.4, 130.1, 127.3, 126.3, 121.7, 114.6, 42.3, 27.0, 22.5, 20.5. Spectral data is in accordance with the literature.^[2]



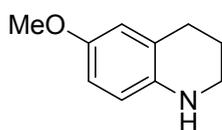
7-methyl-1,2,3,4-tetrahydroquinoline (2g)

Colorless oil, 29 mg, 78% yield. ^1H NMR (400 MHz, CDCl_3) δ 6.91 (d, $J = 7.6$ Hz, 1H), 6.51 (d, $J = 7.5$ Hz, 1H), 6.36 (s, 1H), 3.71 (brs, 1H), 3.35 – 3.32 (m, 2H), 2.79 (t, $J = 6.4$ Hz, 2H), 2.29 (s, 3H), 2.02 – 1.96 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.7, 136.4, 129.4, 118.6, 117.9, 114.8, 42.1, 26.7, 22.5, 21.2. Spectral data is in accordance with the literature.^[2]



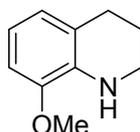
8-methyl-1,2,3,4-tetrahydroquinoline (2h)

Colorless oil, 33 mg, 89% yield. ^1H NMR (400 MHz, CDCl_3) δ 6.89 – 6.84 (m, 2H), 6.56 (t, $J = 7.4$ Hz, 1H), 3.66 (brs, 1H), 3.39 – 3.36 (m, 2H), 2.79 (t, $J = 6.3$ Hz, 2H), 2.08 (s, 3H), 1.98 – 1.92 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.8, 128.0, 127.5, 121.3, 121.0, 116.5, 42.5, 27.4, 22.3, 17.3. Spectral data is in accordance with the literature.^[2]



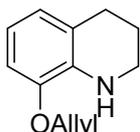
6-methoxy-1,2,3,4-tetrahydroquinoline (2i)

Colorless oil, 35 mg, 85% yield. ^1H NMR (400 MHz, CDCl_3) δ 6.62 – 6.57 (m, 2H), 6.47 (d, $J = 8.5$ Hz, 1H), 3.74 (s, 3H), 3.28 – 3.25 (m, 2H), 2.77 (t, $J = 6.5$ Hz, 2H), 1.97 – 1.91 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 151.8, 138.9, 122.9, 115.6, 114.9, 112.9, 55.8, 42.3, 27.2, 22.4. Spectral data is in accordance with the literature.^[2]



8-methoxy-1,2,3,4-tetrahydroquinoline (2j)

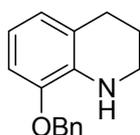
Colorless oil, 38 mg, 93% yield. ^1H NMR (400 MHz, CDCl_3) δ 6.66 – 6.57 (m, 3H), 3.85 (s, 3H), 3.37 – 3.34 (m, 2H), 2.80 (t, $J = 6.4$ Hz, 2H), 2.01 – 1.95 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.4, 134.6, 121.8, 121.5, 115.8, 107.5, 55.5, 41.6, 26.8, 22.2. Spectral data is in accordance with the literature.^[4]



8-(allyloxy)-1,2,3,4-tetrahydroquinoline (2k)

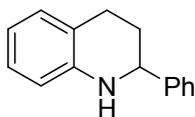
Colorless oil, 42 mg, 89% yield. ^1H NMR (400 MHz, CDCl_3) δ 6.68 (t, $J = 6.9$ Hz,

2H), 6.62 – 6.58 (m, 1H), 6.14 – 6.10 (m, 1H), 5.48 – 5.31 (m, 2H), 4.59 (d, $J = 5.3$ Hz, 2H), 4.24 (brs, 1H), 3.40 – 3.38 (m, 2H), 2.84 (t, $J = 6.4$ Hz, 2H), 2.04 – 1.98 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 145.2, 134.8, 133.8, 122.0, 121.6, 117.4, 115.6, 108.9, 69.1, 41.5, 26.8, 22.2. HRMS–ESI (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{15}\text{NO}$, 190.1232; found: 190.1254.



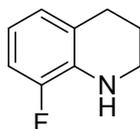
8-(benzyloxy)-1,2,3,4-tetrahydroquinoline (2l)

Colorless oil, 55 mg, 92% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.38 (m, 5H), 6.74 – 6.68 (m, 2H), 6.62 – 6.57 (m, 1H), 5.09 (s, 2H), 4.34 (brs, 1H), 3.42 – 3.30 (m, 2H), 2.88 – 2.78 (m, 2H), 2.04 – 1.95 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 145.5, 137.4, 134.9, 128.6, 128.0, 127.8, 122.1, 121.6, 115.7, 108.9, 70.4, 41.6, 26.8, 22.2. HRMS–ESI (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{17}\text{NO}$, 240.1388; found: 240.1396.



2-phenyl-1,2,3,4-tetrahydroquinoline (2m)

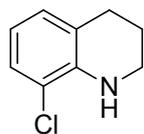
Colorless oil, 44 mg, 84% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.27 (m, 5H), 7.05 (t, $J = 7.4$ Hz, 2H), 6.69 (t, $J = 7.4$ Hz, 1H), 6.58 (d, $J = 7.7$ Hz, 1H), 4.49 – 4.46 (m, 1H), 4.07 (brs, 1H), 2.97 – 2.93 (m, 1H), 2.81 – 2.76 (m, 1H), 2.20 – 2.13 (m, 1H), 2.08 – 1.99 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.9, 144.8, 129.4, 128.7, 127.6, 127.0, 126.7, 121.0, 117.3, 114.1, 56.4, 31.1, 26.5. Spectral data is in accordance with the literature.^[2]



8-fluoro-1,2,3,4-tetrahydroquinoline (2n)

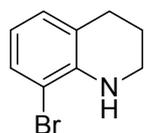
Yellow oil, 33 mg, 87% yield. ^1H NMR (400 MHz, CDCl_3) δ 6.83 – 6.74 (m, 2H), 6.54 – 6.49 (m, 1H), 4.01 (brs, 1H), 3.37 – 3.34 (m, 2H), 2.80 (t, $J = 6.4$ Hz, 2H), 2.00 – 1.94 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.2, 149.9, 133.4, 133.2, 124.6,

124.6, 123.7, 115.7, 115.6, 112.4, 112.2, 41.4, 26.7, 21.9. Spectral data is in accordance with the literature.^[5]



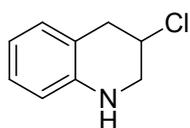
8-chloro-1,2,3,4-tetrahydroquinoline (2o)

Yellow oil, 38 mg, 90% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.07 (d, *J* = 7.9 Hz, 1H), 6.86 (d, *J* = 7.4 Hz, 1H), 6.51 (t, *J* = 7.7 Hz, 1H), 4.41 (brs, 1H), 3.41-3.38 (m, 2H), 2.78 (t, *J* = 6.3 Hz, 2H), 1.97 – 1.91 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 140.8, 127.8, 126.9, 122.7, 118.2, 116.4, 41.9, 27.3, 21.8. Spectral data is in accordance with the literature.^[2]



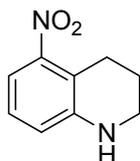
8-bromo-1,2,3,4-tetrahydroquinoline (2p)

Colorless oil, 45 mg, 85% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.22 (d, *J* = 8.5 Hz, 1H), 6.87 (d, *J* = 7.4 Hz, 1H), 6.44 (t, *J* = 7.7 Hz, 1H), 4.41 (brs, 1H), 3.39 – 3.36 (m, 2H), 2.76 (t, *J* = 6.3 Hz, 2H), 1.94 – 1.88 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 141.8, 130.1, 128.5, 122.9, 117.0, 108.8, 42.1, 27.5, 21.8. Spectral data is in accordance with the literature.^[6]



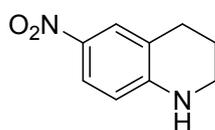
3-chloro-1,2,3,4-tetrahydroquinoline (2q)

Yellow oil, 34 mg, 81% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.07 (dd, *J* = 11.3, 3.9 Hz, 1H), 7.00 (d, *J* = 7.2 Hz, 1H), 6.72 (dd, *J* = 10.7, 4.1 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 4.47 – 4.42 (m, 1H), 3.72 (brs, 1H), 3.65 – 3.61 (m, 1H), 3.41 (dd, *J* = 11.8, 7.5 Hz, 1H), 3.32 (dd, *J* = 16.3, 4.4 Hz, 1H), 3.09 (dd, *J* = 16.3, 7.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 142.9, 129.7, 127.6, 118.2, 118.1, 114.5, 52.6, 48.9, 37.2. HRMS–ESI (m/z): [M+H]⁺ calcd for C₉H₁₀ClN, 168.0580; found: 168.0592.



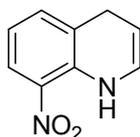
5-nitro-1,2,3,4-tetrahydroquinoline (2r)

Yellow solid, 37 mg, 82% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.12 (d, $J = 8.0$ Hz, 1H), 7.03 (t, $J = 8.0$ Hz, 1H), 6.65 (d, $J = 8.0$ Hz, 1H), 4.22 (brs, 1H), 3.35 – 3.32 (m, 2H), 2.93 (t, $J = 6.4$ Hz, 2H), 1.95 – 1.89 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.5, 146.1, 126.7, 118.0, 115.2, 112.3, 41.0, 24.0, 21.2. Spectral data is in accordance with the literature.^[7]



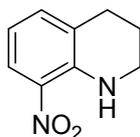
6-nitro-1,2,3,4-tetrahydroquinoline (2s)

Yellow solid, 35 mg, 78% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.90 – 7.88 (m, 2H), 6.38 – 6.36 (m, 1H), 4.76 (brs, 1H), 3.44 – 3.41 (m, 2H), 2.80 (t, $J = 6.3$ Hz, 2H), 1.99 – 1.93 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.5, 137.4, 126.0, 124.4, 120.0, 112.3, 41.9, 27.0, 21.0. Spectral data is in accordance with the literature.^[8]



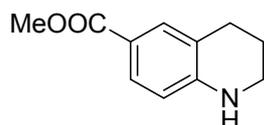
8-nitro-1,4-dihydroquinoline (2t)

Yellow solid, 33 mg, 75% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.07 (brs, 1H), 7.73 (d, $J = 8.7$ Hz, 1H), 6.78 (d, $J = 6.7$ Hz, 1H), 6.35 – 6.31 (m, 1H), 6.20 (d, $J = 10.1$ Hz, 1H), 5.64 – 5.62 (m, 1H), 4.48 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.6, 132.0, 130.1, 125.3, 125.1, 123.1, 122.1, 115.1, 43.5. HRMS–ESI (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_9\text{H}_8\text{N}_2\text{O}_2$, 177.0664; found: 177.0683.



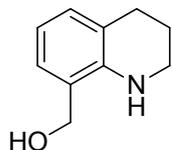
8-nitro-1,2,3,4-tetrahydroquinoline (2u)

Yellow solid, 38 mg, 84% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.32 (brs, 1H), 7.96 (d, $J = 8.6$ Hz, 1H), 7.11 (d, $J = 6.9$ Hz, 1H), 6.48 (dd, $J = 8.6, 7.1$ Hz, 1H), 3.54 – 3.51 (m, 2H), 2.83 (t, $J = 6.2$ Hz, 2H), 1.99 – 1.93 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.4, 135.0, 130.9, 125.0, 124.7, 114.4, 41.5, 27.9, 20.2. Spectral data is in accordance with the literature.^[7]



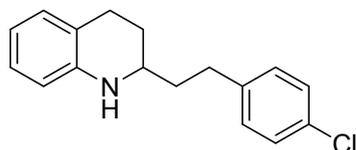
methyl 1,2,3,4-tetrahydroquinoline-6-carboxylate (2v)

White solid, 42 mg, 88% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.65 – 7.64 (m, 2H), 6.40 – 6.38 (m, 1H), 4.41 (brs, 1H), 3.84 (s, 3H), 3.35 – 3.32 (m, 2H), 2.76 (t, $J = 6.3$ Hz, 2H), 1.95 – 1.89 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.6, 148.9, 131.3, 129.2, 119.9, 117.3, 112.7, 51.5, 41.7, 27.0, 21.4. Spectral data is in accordance with the literature.^[5]



(1,2,3,4-tetrahydroquinolin-8-yl)methanol (2w)

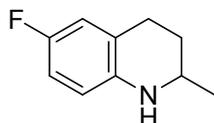
Colorless oil, 35 mg, 85% yield. ^1H NMR (400 MHz, CDCl_3) δ 6.96 (d, $J = 7.4$ Hz, 1H), 6.90 (d, $J = 7.2$ Hz, 1H), 6.57 (t, $J = 7.4$ Hz, 1H), 4.61 (s, 2H), 3.39 – 3.36 (m, 2H), 2.81 (t, $J = 6.2$ Hz, 2H), 1.98 – 1.92 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.2, 129.9, 127.1, 123.6, 122.1, 116.0, 64.7, 42.1, 27.5, 21.9. Spectral data is in accordance with the literature.^[9]



2-(4-chlorophenethyl)-1,2,3,4-tetrahydroquinoline (2x)

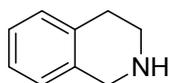
Colorless oil, 59 mg, 87% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.29 – 7.27 (m, 2H), 7.16 (d, $J = 8.3$ Hz, 2H), 6.99 (t, $J = 7.6$ Hz, 2H), 6.63 (t, $J = 7.3$ Hz, 1H), 6.49 (d, $J = 7.8$ Hz, 1H), 3.77 (brs, 1H), 3.32 – 3.30 (m, 1H), 2.79 – 2.71 (m, 4H), 2.03 – 1.99 (m,

1H), 1.86 – 1.79 (m, 2H), 1.71 – 1.67 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 144.5, 140.4, 131.8, 129.8, 129.4, 128.7, 126.9, 121.4, 117.3, 114.3, 51.1, 38.3, 31.6, 28.0, 26.3. HRMS–ESI (m/z): [M+H]⁺ calcd for C₁₇H₁₈CIN, 272.1206; found: 272.1224.



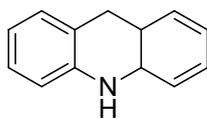
6-fluoro-2-methyl-1,2,3,4-tetrahydroquinoline (2y)

Colorless oil, 18 mg, 44% yield. ¹H NMR (400 MHz, CDCl₃) δ 6.73 – 6.66 (m, 2H), 6.44 – 6.40 (m, 1H), 3.44 – 3.30 (m, 1H), 2.89 – 2.78 (m, 1H), 2.75 – 2.64 (m, 1H), 1.98 – 1.86 (m, 1H), 1.63 – 1.51 (m, 1H), 1.22 (d, *J* = 6.3 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 156.6, 154.3, 140.8, 122.5, 122.4, 115.4, 115.2, 114.7, 114.6, 113.2, 113.0, 47.2, 29.8, 26.6, 22.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -128.27. Spectral data is in accordance with the literature.^[10]



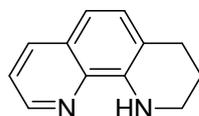
1,2,3,4-tetrahydroisoquinoline (4a)

Colorless oil, 29 mg, 88% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.16 – 7.09 (m, 3H), 7.03 – 6.97 (m, 1H), 4.02 (s, 2H), 3.15 (t, *J* = 6.0 Hz, 2H), 2.81 (t, *J* = 5.9 Hz, 2H), 1.99 (brs, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 136.0, 134.8, 129.3, 126.2, 126.0, 125.7, 48.3, 43.9, 29.2. Spectral data is in accordance with the literature.^[11]



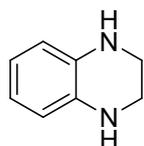
4a,9,9a,10-tetrahydroacridine (4b)

White solid, 40 mg, 87% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.15 – 7.10 (m, 4H), 6.90 (t, *J* = 7.4 Hz, 2H), 6.69 (d, *J* = 7.8 Hz, 2H), 5.97 (brs, 1H), 4.09 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 140.2, 128.7, 127.1, 120.7, 120.1, 113.6, 31.5. Spectral data is in accordance with the literature.^[5]



1,2,3,4-tetrahydro-1,10-phenanthroline (4c)

Yellow oil, 38 mg, 83% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.73 – 8.72 (m, 1H), 8.03 – 8.01 (m, 1H), 7.30 (dd, $J = 8.2, 4.2$ Hz, 1H), 7.19 (d, $J = 8.2$ Hz, 1H), 7.01 (d, $J = 8.2$ Hz, 1H), 6.01 (brs, 1H), 3.56 – 3.53 (m, 2H), 2.95 (t, $J = 6.3$ Hz, 2H), 2.12 – 2.06 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.9, 140.7, 137.5, 135.8, 129.1, 127.4, 120.5, 116.5, 113.1, 41.3, 27.0, 21.8. Spectral data is in accordance with the literature.^[5]



1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydroquinoxaline (4d)

White solid, 27 mg, 81% yield. ^1H NMR (400 MHz, CDCl_3) δ 6.64 (dd, $J = 5.7, 3.4$ Hz, 2H), 6.53 (dd, $J = 5.7, 3.4$ Hz, 2H), 3.63 (brs, 2H), 3.42 (s, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 133.7, 118.6, 114.7, 41.3. Spectral data is in accordance with the literature.^[1]

3. Mechanism studies

NMR experiments were carried out to study the interaction between I_2 , quinoline **1a** and or HBpin. The NMR results indicated that a complex of quinoline and I_2 was formed ^[12] (Figure S1, S2). There was an interaction between I_2 and HBpin (Figure S3, S4).

Interaction between quinoline and I_2 in CD_3Cl

The following Figure S1 refers to the ^1H NMR spectrum of quinoline and I_2 in CD_3Cl .

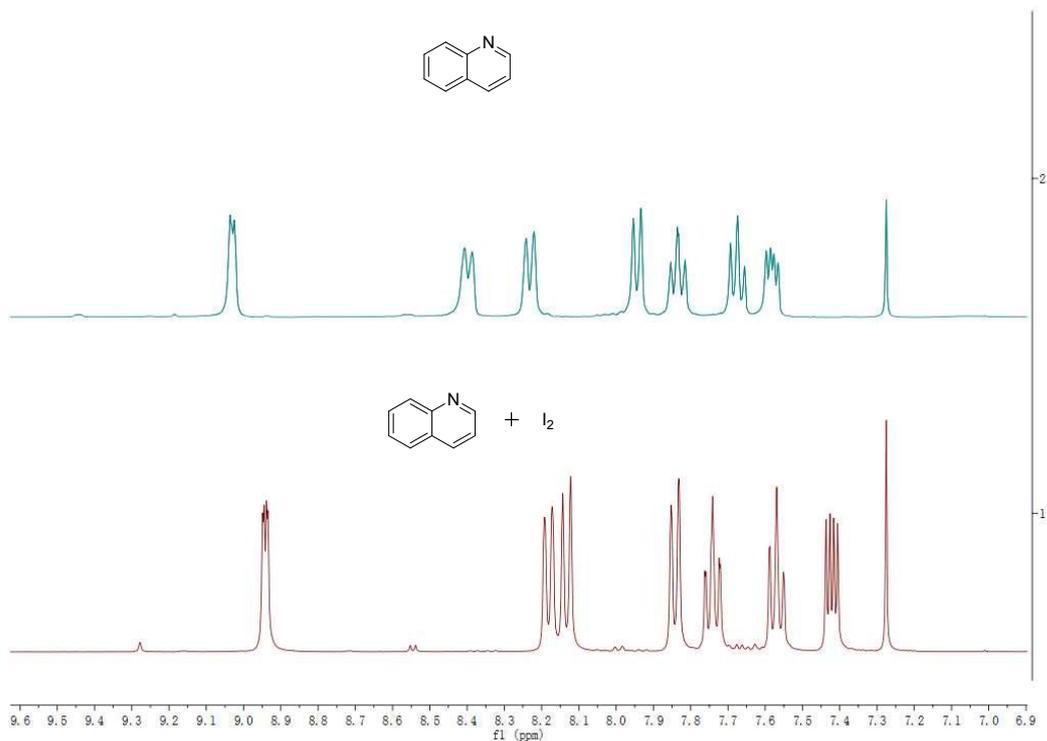


Figure S1. The ^1H NMR spectrum of a mixture of quinoline and I_2 in CD_3Cl .

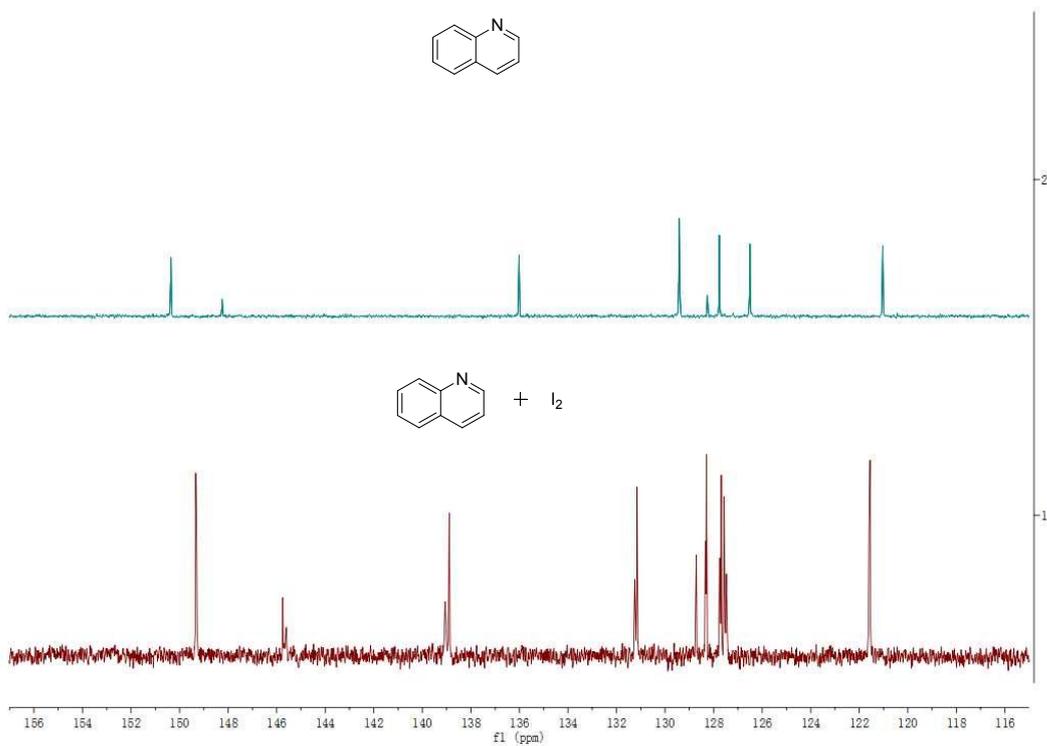


Figure S2. The ^{13}C NMR spectrum of a mixture of quinoline and I_2 in CD_3Cl .

The NMR results indicated that a complex of quinoline and I_2 was formed (Figure S1,

S2).

Interaction between HBpin and I₂ in CD₃Cl

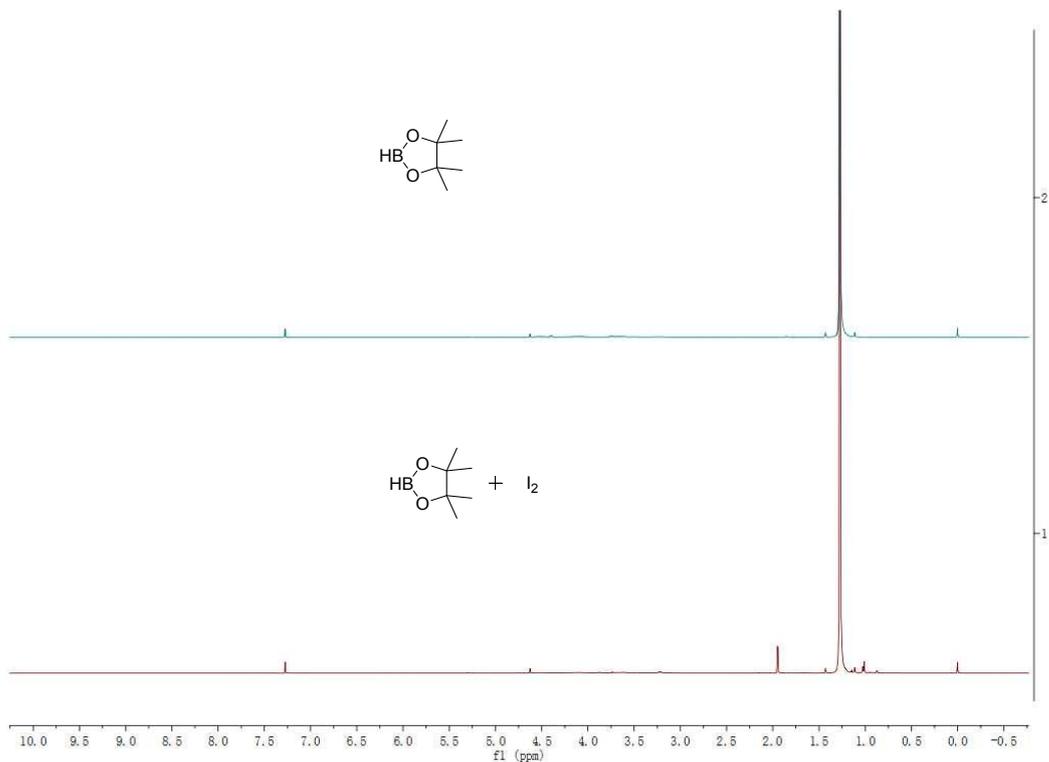


Figure S3. The ¹H NMR spectrum of a mixture of HBpin and I₂ in CD₃Cl.

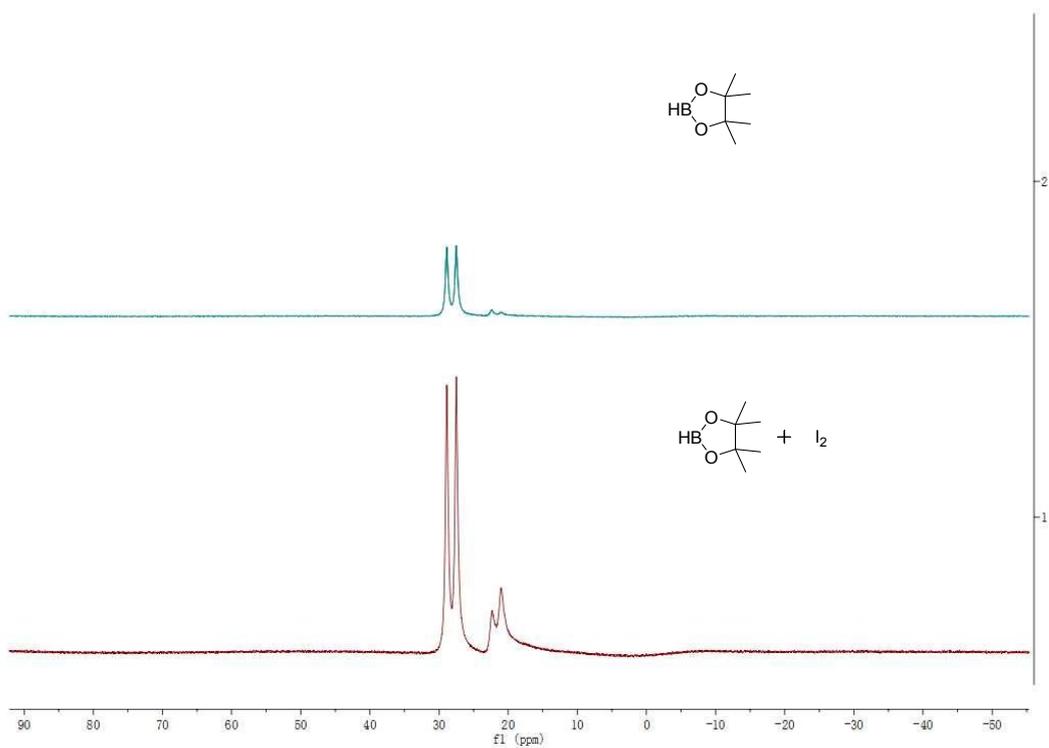
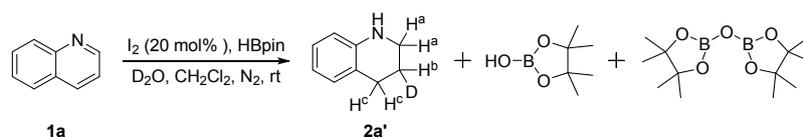


Figure S4. The ¹¹B NMR spectrum of a mixture of HBpin and I₂ in CD₃Cl.

There was an interaction between I₂ and HBpin (Figure S3, S4).

Deuterium-labeled experiments

In order to understand the hydrogen in the transformations, deuterium-labeled experiments were carried out with **1a**. When the reaction system of **1a** was added D₂O, deuterated product **2a'** was obtained. This result clearly demonstrated that D₂O is also H-donor for the hydrogenation reaction via DOBpin^[13]. This result is consistent with the NMR experiments.



Scheme S1. Deuterium-labeled experiments.

A flask (10 mL) was charged with iodine (0.2 mmol, 20%) and quinoline (1 mmol, 1.0 equiv.), exchanged with nitrogen for three times. Then anhydrous CH₂Cl₂ (4 mL) and HBpin (4 mmol, 4 equiv.) were added separately. After 10 minutes' stirring, D₂O (0.05 mL) was added. The reaction mixture was then stirred at room temperature for 3 h. The reaction mixture was quenched with water (1 mL). The CH₂Cl₂ phase was separated, and the aqueous solution was extracted with CH₂Cl₂ (5 mL × 2). The combined organic layers were dried with anhydrous Na₂SO₄, filtered and concentrated to get a residue which was then analyzed by NMR spectroscopy. ¹H NMR (400 MHz, CDCl₃) δ 6.94 (t, *J* = 7.8 Hz, 2H), 6.59 (t, *J* = 7.3 Hz, 1H), 6.47 (d, *J* = 7.8 Hz, 1H), 3.28 (d, *J* = 5.5 Hz), 2.74 (d, *J* = 6.3 Hz), 1.95 – 1.87 (m, H^b). ¹¹B NMR (128 MHz, CDCl₃) δ 22.27, 21.12.

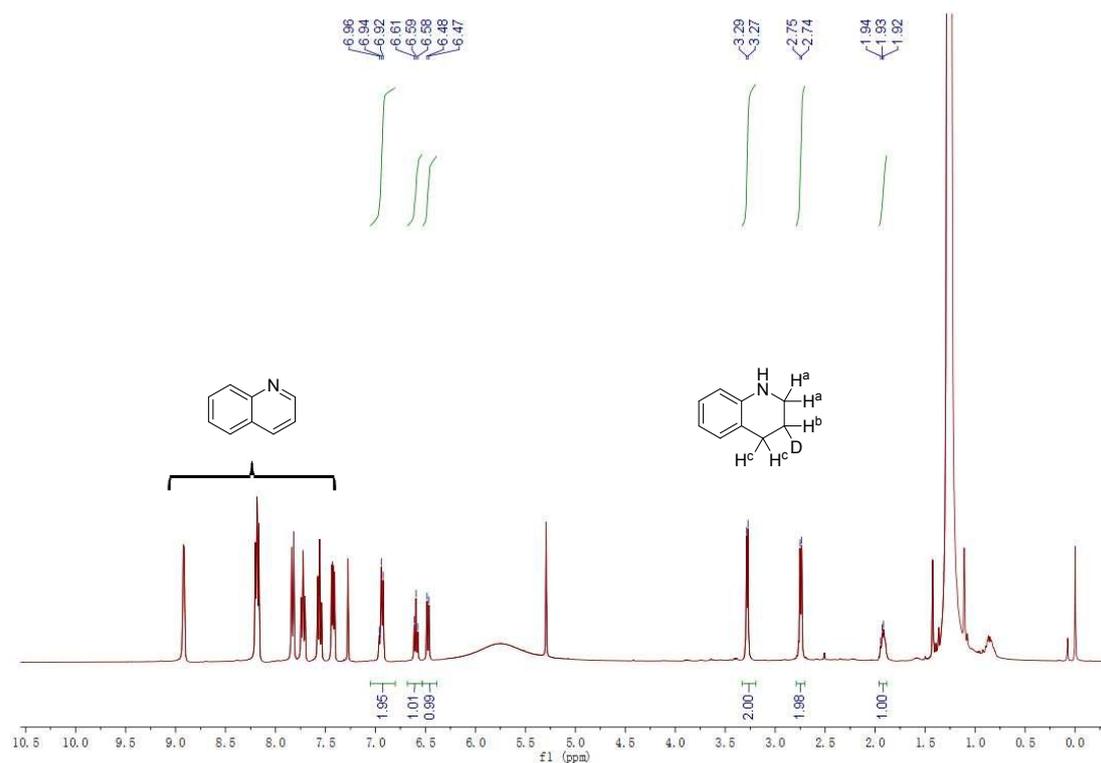


Figure S5. ^1H NMR spectrum for the reduction of quinoline by adding D_2O to the reaction system.

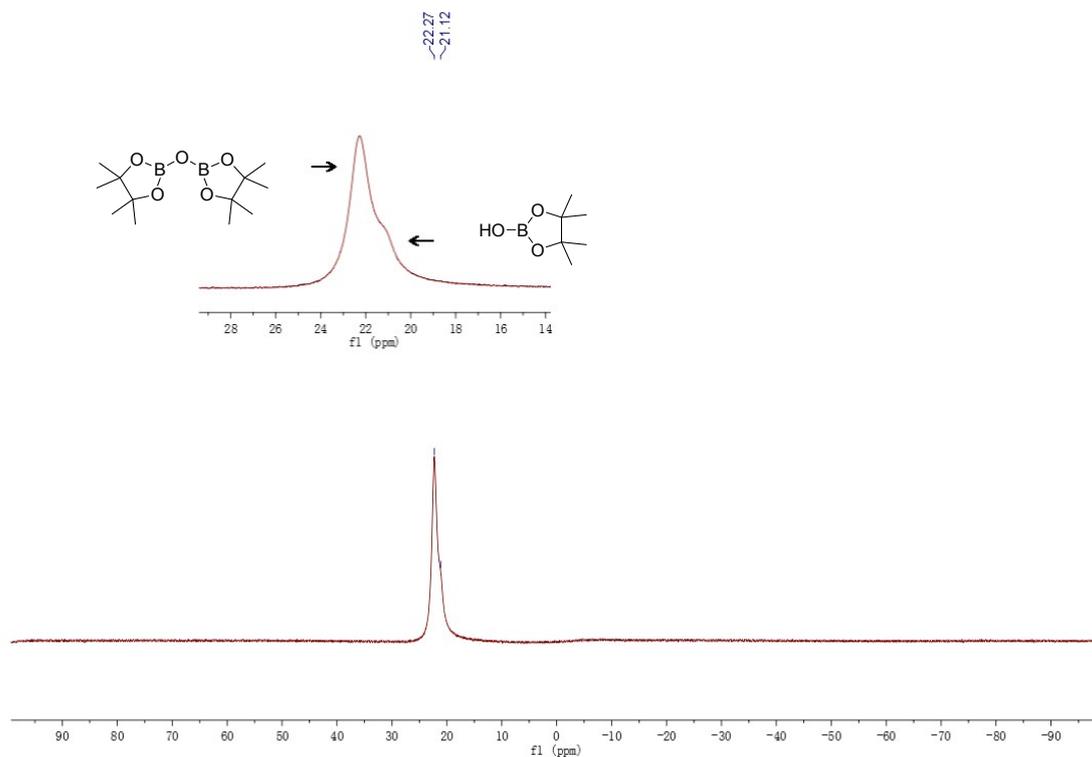


Figure S6. ^{11}B NMR spectrum for the reduction of quinoline by adding D_2O to the reaction system.

The NMR experiments of the reaction mixture before and after quenched were carried out. ^1H NMR experiment of the reaction mixture before quenched was processed directly after 8 hours' stirring (Figure S7). The figure showed that there are signals of the intermediate **H** and the reduction product.

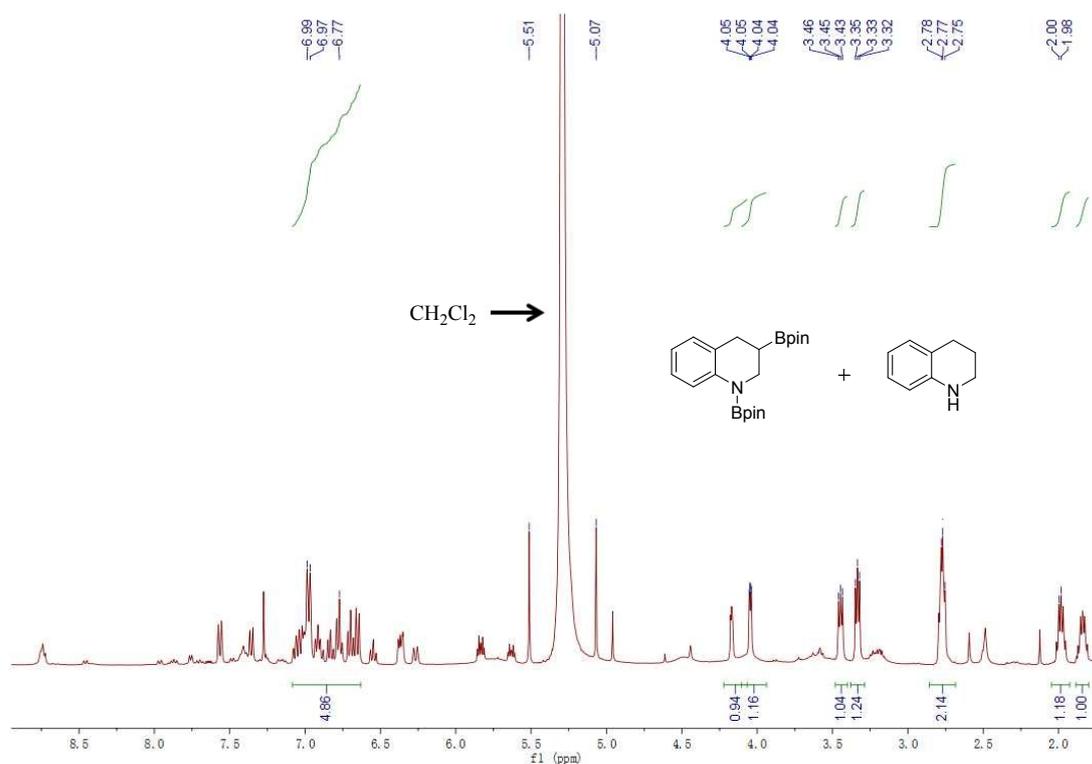


Figure S7. ^1H NMR spectrum of the reaction mixture before quenched

^{11}B NMR experiment of the reaction mixture before quenched was carried out (Figure S8). There were two signals except the signal of HBPin. This result suggested that there were another two forms of boron. We proposed that one form of boron (23.55 ppm, broad peak) was the combined signal of C-Bpin and N-Bpin. The other (20.98 ppm, broad peak) was the combined signal of HOBpin and $\text{O}(\text{Bpin})_2$.

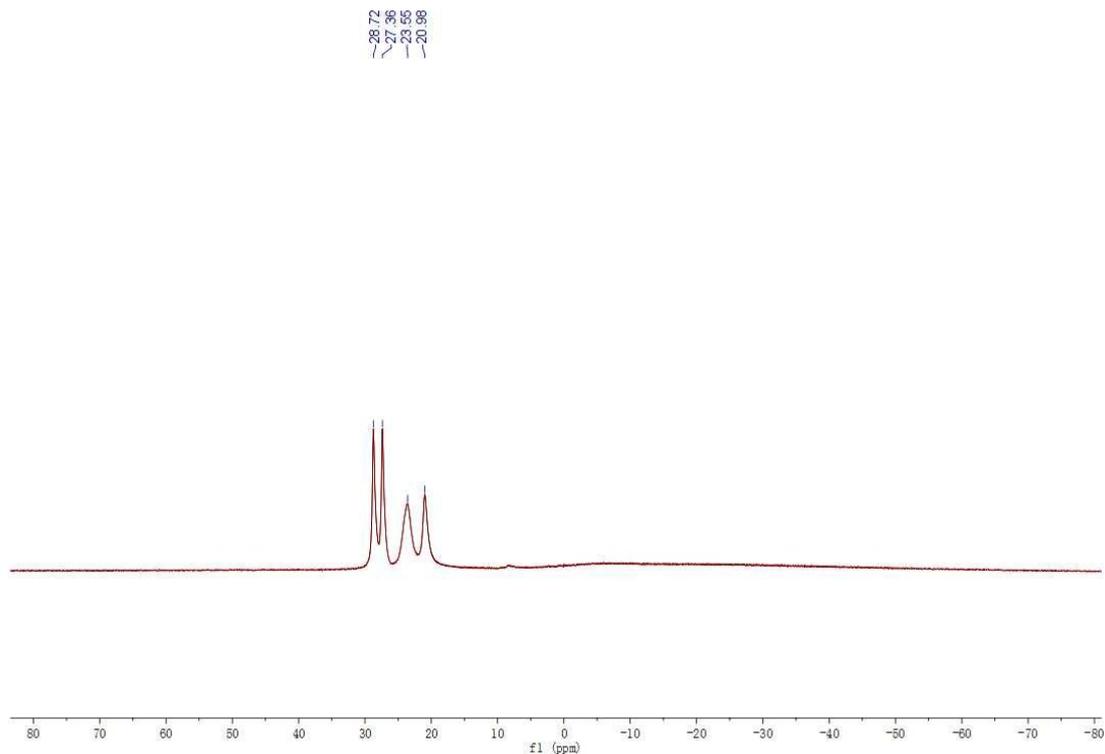


Figure S8. ^{11}B NMR spectrum of the reaction mixture before quenched ^1H NMR experiments of the reaction mixture after quenched was processed directly after adding water to the reaction system after 8 hours' stirring (Figure S9). The signals of the intermediate **H** were disappeared, which converted to the reduction product. ^{11}B NMR spectrum of the reaction mixture after quenched was the same as figure S6.

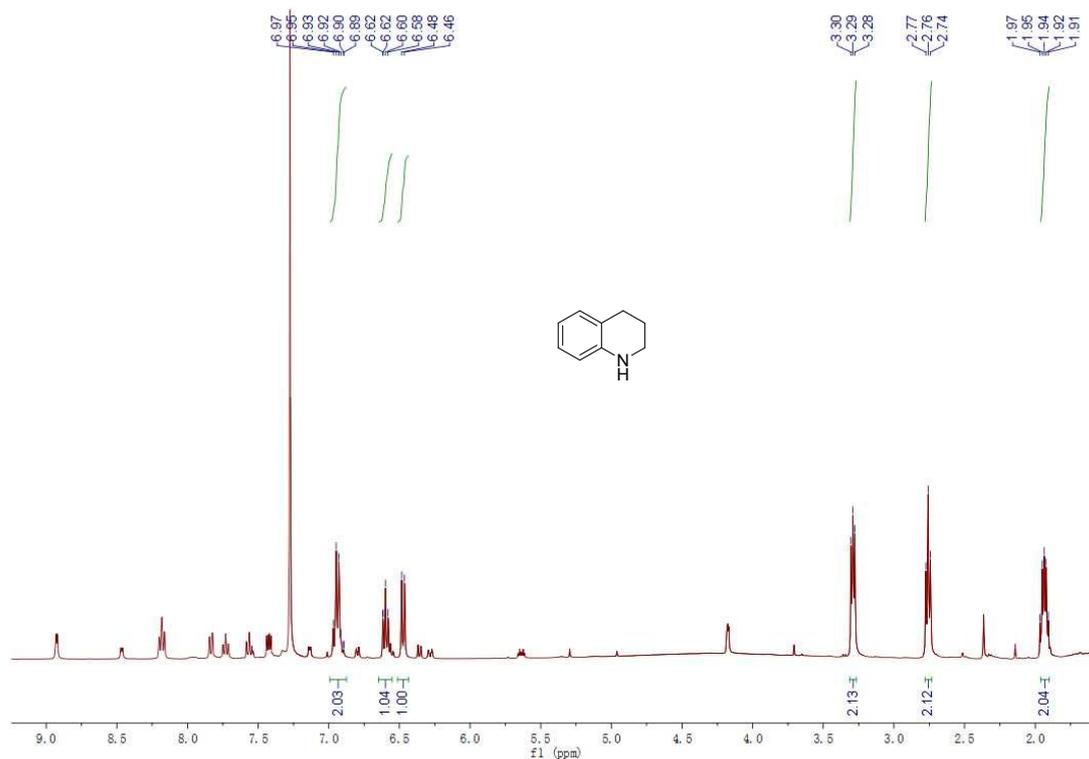
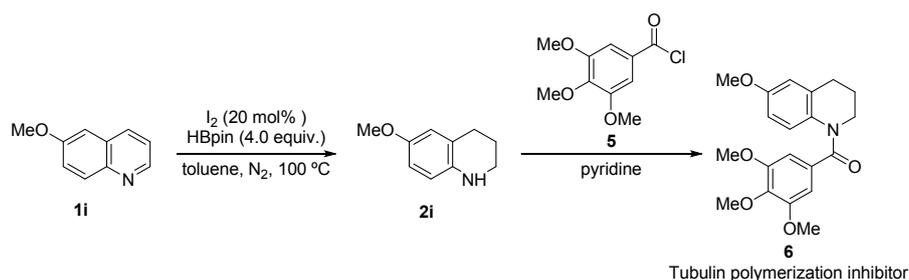


Figure S9. ^1H NMR spectrum of the reaction mixture after quenched

The results of NMR experiments indicated that the intermediate **H** was sensitive to water and was difficult to separate.

4. Applications of synthesized 1,2,3,4-tetrahydroquinoline derivatives.

4.1 Synthesis of tubulin polymerization inhibitor (**6**)

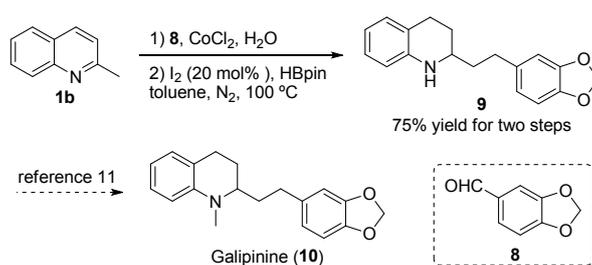


Scheme S3. The synthesis of tubulin polymerization inhibitor.

A solution of 6-methoxy-1,2,3,4-tetrahydroquinoline **2i** (81.5 mg, 0.5 mmol) and 3,4,5-trimethoxybenzoyl chloride **5** (173.0 mg, 0.75 mmol) in pyridine (1.5 mL) was stirred at room temperature for 24 h. After the reaction, the crude reaction mixture was purified by flash chromatography on silica (eluent: hexane / ethyl acetate = 3:1)

to afford 160 mg (90%) of **6** as oil. ¹H NMR (400 MHz, CDCl₃) δ 6.66 (d, *J* = 2.6 Hz, 2H), 6.55 (s, 2H), 6.45 (dd, *J* = 8.6, 2.1 Hz, 1H), 3.84 (t, *J* = 6.5 Hz, 2H), 3.80 (s, 3H), 3.70 (s, 3H), 3.66 (s, 6H), 2.77 (t, *J* = 6.6 Hz, 2H), 1.99 (p, *J* = 6.5 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 169.3, 156.5, 152.7, 139.5, 132.9, 132.5, 131.2, 126.2, 113.1, 111.4, 106.2, 60.8, 56.0, 55.3, 44.5, 27.1, 24.1. Spectral data is in accordance with the literature.^[10]

4.2 Synthesis of Galipinine (10)



Scheme S4. The synthesis of galipinine

To a sealed tube equipped with a magnetic stirrer bar, CoCl₂ (1.3 mg, 2.0 mol%), 2-methylquinoline (0.5 mmol), aldehyde (1.0 mmol), and H₂O (0.3 mL) were added. The resulting mixture was placed into a preheated oil bath at 120 °C with vigorous stirring. After 24 h, the reaction mixture was removed from the oil bath, allowed to cool to rt. and poured into H₂O (10 mL). The mixture was then extracted with EtOAc (3 × 20 mL), washed with brine (40 mL), dried over Na₂SO₄, filtered, and the solvent removed under reduced pressure. The crude product was then purified by flash chromatography on silica (eluent: hexane / ethyl acetate = 95:5) then gave the pure alkenylation product. White solid, 127 mg, 92% yield. Then the pure alkenylation product was converted to tetrahydroquinoline derivative **9** through the general procedure. Colorless oil, 105 mg, 81%. ¹H NMR (400 MHz, CDCl₃) δ 6.99 (t, *J* = 7.5 Hz, 2H), 6.79 – 6.62 (m, 4H), 6.49 (d, *J* = 7.8 Hz, 1H), 5.95 (s, 2H), 3.77 (brs, 1H), 3.31 – 3.29 (m, 1H), 2.84 – 2.74 (m, 2H), 2.71 – 2.67 (m, 2H), 2.03 – 1.99 (m, 1H), 1.84 – 1.78 (m, 2H), 1.72 – 1.66 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 147.8, 145.8, 144.6, 135.8, 129.4, 126.9, 121.4, 121.1, 117.2, 114.3, 108.9, 108.3, 100.9, 51.1, 38.6, 32.0, 28.1, 26.3. Spectral data is in accordance with the literature.^[11]

2-(2-(benzo[d][1,3]dioxol-5-yl)ethyl)-1,2,3,4-tetrahydroquinoline (**9**) could be converted into galipinine according to the literature result.^[11]

5. References

- [1] Z. Y. Liu, Z. H. Wen, X. C. Wang, *Angew. Chem. Int. Ed.* **2017**, *56*, 5817-5820.
- [2] J. Yi - Gang, W. Kai, L. Teng, W. Lei, Z. Wei - Hua, *Advanced Synthesis & Catalysis* **2017**, *359*, 933-940.
- [3] G. B. Russell, G. J. Sutherland, R. D. Topsom, J. Vaughan, *J. Org. Chem.* **1962**, *27*, 4375-4377.
- [4] A. V. Iosub, S. S. Stahl, *Org. Lett.* **2015**, *17*, 4404-4407.
- [5] Q. Xuan, Q. Song, *Org. Lett.* **2016**, *18*, 4250-4253.
- [6] F. Ding, Y. Zhang, R. Zhao, Y. Jiang, R. L.-Y. Bao, K. Lin, L. Shi, *Chem. Commun.* **2017**, *53*, 9262-9264.
- [7] R. He, P. Cui, D. Pi, Y. Sun, H. Zhou, *Tetrahedron Lett.* **2017**, *58*, 3571-3573.
- [8] G. Compain, A. Martin-Mingot, G. Frapper, C. Bachmann, M.-P. Jouannetaud, S. Thibaudeau, *Chem. Commun.* **2012**, *48*, 5877-5879.
- [9] M. Uchida, M. Chihiro, S. Morita, T. Kanbe, H. Yamashita, K. Yamasaki, Y. Yabuuchi, K. Nakagawa, *Chem. Pharm. Bull.* **1989**, *37*, 2109-2116.
- [10] F. Chen, A.-E. Surkus, L. He, M.-M. Pohl, J. Radnik, C. Topf, K. Junge, M. Beller, *J. Am. Chem. Soc.* **2015**, *137*, 11718-11724.
- [11] A. Rosa, C. A. J. R., S. Anke, J. Kathrin, J. Ralf, B. Matthias, *Angew. Chem. Int. Ed.* **2017**, *56*, 3216-3220.
- [12] B. A. A.-A. Ahmed, A. A. E. Mohamed, M. M. Rafat, *Bull. Chem. Soc. Jpn.* **1994**, *67*, 603-606.
- [13] a) G. Villa, G. Povie, P. Renaud, *J. Am. Chem. Soc.* **2011**, *133*, 5913-5920; b) D. Pozzi, E. M. Scanlan, P. Renaud, *J. Am. Chem. Soc.* **2005**, *127*, 14204-14205; c) D. A. Spiegel, K. B. Wiberg, L. N. Schacherer, M. R. Medeiros, J. L. Wood, *J. Am. Chem. Soc.* **2005**, *127*, 12513-12515.

6. Copies of NMR Spectra

