

Supporting Information

Molecular iodine catalyzed aerobic photo-oxidative C-C bond formation between tertiary amines and carbon nucleophiles

Tomoya Nobuta, Akitoshi Fujiya, Tomoaki Yamaguchi, Norihiro Tada, Tsuyoshi Miura, Akichika Itoh*

Gifu Pharmaceutical University, 1-25-4 Daigaku-nishi, Gifu 501-1196, Japan

E-mail: itoaha@gifu-pu.ac.jp

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1. General Information.

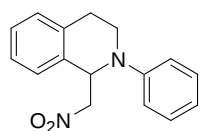
All dry solvents were obtained from Kanto Kagaku Co., Ltd. Other chemicals used were of reagent grade and were obtained from Tokyo Kasei Kogyo Co., Ltd., Wako Pure Chemical Industries, Ltd., Kishida Chemical Co., Ltd., and Nacalai Tesque. ^1H NMR and ^{13}C NMR spectra were obtained on a JEOL ECA 500 (500 MHz for ^1H NMR and 125 MHz for ^{13}C NMR). Chemical shifts (δ) are reported in parts per million (ppm) downfield from internal Me_4Si . Preparative thin-layer chromatography (TLC) was carried out on precoated plates of silica gel (MERCK, silica gel F-254).

2. General Procedure

Preparation of 2-aryl-1,2,3,4-tetrahydroisoquinolines¹: Copper(I) iodide (200 mg, 1.0 mmol) and potassium phosphate (4.25 g, 20.0 mmol) were put into a two-neck flask. The two-neck flask was evacuated and back filled with nitrogen. 2-Propanol (10.0 mL), ethylene glycol (1.11 mL, 20.0 mmol), 1,2,3,4-tetrahydro-isoquinoline (2.0 mL, 15.0 mmol) and iodobenzene (1.12 mL, 10.0 mmol) were added successively at room temperature. The reaction mixture was heated at 90 °C and kept for 24 h and then allowed to cool to room temperature. Diethyl ether (20 mL) and water (20 mL) were then added to the reaction mixture. The organic layer was extracted with diethyl ether (2 × 20 mL). The combined organic phases were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation and purified by column chromatography on silica gel using hexane/ethyl acetate as eluent.

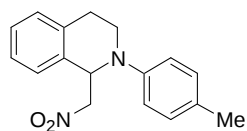
Synthesis of 1-(Nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3aa) (Table 2, Entry 1): a solution of 2-phenyl-1,2,3,4-tetrahydroisoquinoline (**1a**, 0.3 mmol), I_2 (0.015 mmol), MeNO_2 (**2a**, 1.5 mmol) and AcOH (1.5 mmol) in MeCN (3 mL) in a pyrex test tube, purged with an O_2 balloon, was stirred and irradiated externally with 22W fluorescent lamps for 12 h. The reaction mixture was washed with aq. $\text{Na}_2\text{S}_2\text{O}_3$, dried over magnesium sulfate, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel (hexane : ethylacetate = 10 : 1) provided 1-(Nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (**3aa**) (67.9 mg, 84%).

1-(Nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3aa)² (Table 2, Entry 1)



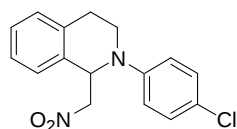
^1H -NMR (500 MHz, CDCl_3): δ = 7.27-7.11 (m, 6H), 6.96 (d, J = 8.6 Hz, 2H), 6.83 (t, J = 7.4 Hz, 1 H), 5.53 (t, J = 7.4 Hz, 1 H), 4.84 (dd, J = 12.1, 8.0 Hz, 1 H), 4.53 (dd, J = 11.5, 6.3, 1H), 3.66-3.56 (m, 2H), 3.09-3.03 (m, 1H), 2.76 (dt, J = 16.0, 5.0 Hz, 1H).

1-(Nitromethyl)-2-p-tolyl-1,2,3,4-tetrahydroisoquinoline (3ba)³ (Table 2, Entry 2)



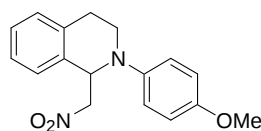
^1H -NMR (500 MHz, CDCl_3): δ = 7.24-7.05 (m, 6H), 6.88 (d, J = 8.6 Hz, 2H), 5.47 (t, J = 7.4 Hz, 1 H), 4.81 (dd, J = 12.1, 8.1 Hz, 1 H), 4.52 (dd, J = 12.1, 6.3, 1H), 3.64-3.52 (m, 2H), 3.06-3.00 (m, 1H), 2.75-2.69 (m, 1H), 2.24 (s, 3H).

2-(4-Chlorophenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (3ca)⁴ (Table 2, Entry 3)



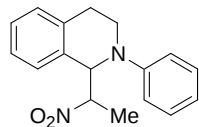
^1H -NMR (500 MHz, CDCl_3): δ = 7.25-7.10 (m, 6H), 6.87 (d, J = 9.2 Hz, 2H), 5.46 (t, J = 7.5 Hz, 1 H), 4.81 (dd, J = 12.0, 8.0 Hz, 1 H), 4.54 (dd, J = 12.0, 6.3, 1H), 3.63-3.54 (m, 2H), 3.06-3.00 (m, 1H), 2.75 (dt, J = 16.1, 4.6 Hz, 1H).

2-(4-Methoxyphenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (3da)² (Table 2, Entry 4)



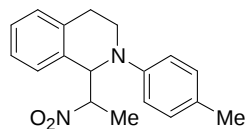
¹H-NMR (500 MHz, CDCl₃): δ = 7.24-7.11 (m, 4H), 6.90 (dt, *J* = 6.3, 4.0 Hz, 2H), 6.82-6.78 (m, 2H), 5.37 (dd, *J* = 8.6, 5.8 Hz, 1 H), 4.80 (dd, *J* = 12.0, 8.6 Hz, 1 H), 4.54 (dd, *J* = 12.0, 5.8, 1H), 3.73 (s, 3H), 3.59-3.50 (m, 2H), 3.02-2.96 (m, 1H), 2.67 (dt, *J* = 16.6, 4.0 Hz, 1H).

1-(Nitroethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3ab)² (Table 2, Entry 5)



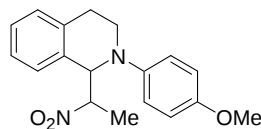
¹H-NMR (500 MHz, CDCl₃): δ = 7.28-7.08 (m, 6H), 7.01-6.97 (m, 2H), 6.83-6.79 (m, 1H), 5.25-5.21 (m, 1H), 5.06-4.84 (m, 1H), 3.84-3.52 (m, 2H), 3.06-2.83 (m, 2H), [1.68 (d, *J* = 6.9 Hz), 1.52 (d, *J* = 6.3 Hz), 3H].

1-(Nitroethyl)-2-p-tolyl-1,2,3,4-tetrahydroisoquinoline (3bb)³ (Table 2, Entry 6)



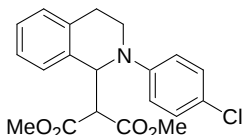
¹H-NMR (500 MHz, CDCl₃): δ = 7.24-6.99 (m, 6H), 6.89-6.87 (m, 2H), 5.18-5.14 (m, 1H), 5.04-4.83 (m, 1H), 3.82-3.49 (m, 2H), 3.04-2.79 (m, 2H), [2.25 (s), 2.22 (s), 3H], [1.67 (d, *J* = 6.9 Hz), 1.51 (d, *J* = 6.9 Hz), 3H].

2-(4-Methoxyphenyl)-1-(nitroethyl)-1,2,3,4-tetrahydroisoquinoline (3db)² (Table 2, Entry 7)



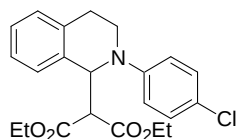
¹H-NMR (500 MHz, CDCl₃): δ = 7.25-7.01 (m, 4H), 6.92-6.90 (m, 2H), 6.83-6.76 (m, 2H), 5.07-4.83 (m, 2H), 3.80-3.44 (m, 5H), 3.00-2.74 (m, 2H), [1.67 (d, *J* = 6.9 Hz), 1.52 (d, *J* = 5.7), 3H].

2-(2-(4-Chlorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-malonic acid dimethyl ester (3cc)⁵ (Table 2, Entry 8)



¹H-NMR (500 MHz, CDCl₃): δ = 7.21-7.10 (m, 6H), 6.89 (d, *J* = 9.1 Hz, 2H), 5.64 (d, *J* = 8.7 Hz, 1 H), 3.91 (d, *J* = 9.2 Hz, 1 H), 3.69-3.51 (m, 8H), 3.07-3.01 (m, 1H), 2.92-2.86 (m, 1H).

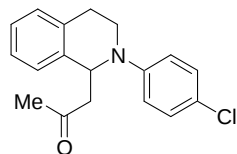
2-(2-(4-Chlorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-malonic acid diethyl ester (3cd) (Table 2, Entry 9)



¹H-NMR (500 MHz, CDCl₃): δ = 7.24 (d, *J* = 6.9 Hz, 1H), 7.20-7.09 (m, 5H), 6.89 (d, *J* = 9.2 Hz, 2 H), 5.65 (d, *J* = 9.2 Hz, 1 H), 4.18-3.94 (m, 4H), 3.86 (d, *J* = 9.2 Hz, 1 H), 3.70-3.65 (m, 1H), 3.57-3.52 (m, 1H), 3.07-2.87 (m, 2H), 1.16 (t, *J* = 7.4 Hz, 3 H), 1.09 (t, *J* = 7.4 Hz, 3 H)).

¹³C-NMR (125 MHz, CDCl₃): δ = 167.9, 167.1, 147.5, 135.8, 134.7, 129.0, 127.8, 127.2, 126.3, 123.2, 116.1, 61.8, 59.6, 58.0, 42.7, 26.2, 14.0. HRMS (ESI⁺) *m/z* calcd for C₂₂H₂₅ClNO₄ [M+H]⁺: 402.14721, found 402.14531.

1-(2-(4-Chlorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (3ce)⁶ (Table 2, Entry 10)



¹H-NMR (500 MHz, CDCl₃): δ = 7.18-7.12 (m, 6H), 6.84 (d, *J* = 9.1 Hz, 2H), 5.33 (t, *J* = 6.3 Hz, 1H), 3.61-3.48 (m, 2H), 3.06-3.00 (m, 2H), 2.84-2.79 (m, 2H), 2.08 (s, 3H).

3. References

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