A New Coupling Reaction of Secondary Amines, Aldehydes and Alkynes Catalyzed by an Iridium Complex

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Experimental Section

All starting materials were commercially available and used without any purification. GLC analysis was performed with a flame ionization detector using a 0.2 mm x 25 m capillary column (OV-1). ^1H - and ^{13}C -NMR were measured at 270 or 400 MHz and 67.5 MHz, respectively, in CDCl_3 with Me_4Si as the internal standard.

General Procedure: To a 1,4-dioxane solution (2.0 mL) of dichlorobis(1,5-cyclooctadiene)diiridium $[\text{IrCl}(\text{cod})]_2$ (0.025 mmol) were added **1a** (0.5 mmol), **2a** (0.25 mmol) and **3a** (0.5 mmol). Then, the reaction mixture was stirred at 50 °C for 3 h. The reaction was quenched with wet ether, and the GC and GC-MS analyses were performed. The yields of products were estimated from the peak areas based on the internal standard technique using GC. The product was isolated by column chromatography (230-400 mesh silica gel, *n*-hexane : ethyl acetate = 10-20:1), and the isolated yields of the products were slightly lower than the GC yields.

The product **4** was not isolated as a pure form. The NMR spectra of the product consisted of a stereoisomeric mixture of **4**, and a small amount of **5** has been measured (typically, see the NMR spectra of the product **4a-b**, Table 2, Run 4). Therefore, signals on ^{13}C -NMR could not be assigned completely.

Spectral data for compound **4a**: ^1H NMR δ =5.18 (t, J = 7.3 Hz, 1H), 2.82 (s, 2H), 2.21 (t, J = 7.3 Hz, 4H), 2.00-1.91 (m, 4H), 1.37-1.20 (m, 18H), 0.82 (t, J = 7.3 Hz, 12H); ^{13}C NMR δ =138.0, 127.4, 53.5, 52.8, 35.7, 32.0, 30.6-29.5, 29.7, 28.3, 23.4, 22.8, 20.8, 14.2, 13.9; HRMS (EI, M^+) calcd for $\text{C}_{20}\text{H}_{41}\text{N}_1$: 295.3239, found: 295.3246.

Spectral data for compound **4b**: ^1H NMR δ =5.26 (t, J = 7.3 Hz, 1H), 2.90 (s, 2H), 2.27 (t, J = 7.3 Hz, 4H), 2.10-2.02 (m, 4H), 1.47-1.27 (m, 12H), 0.93 (t, J = 7.3 Hz, 3H), 0.89-0.83 (m, 9H); ^{13}C NMR δ =137.4, 129.2, 55.7, 52.6, 35.5, 31.8, 29.2, 28.2, 22.7, 20.8, 20.2, 14.7, 14.1, 12.0.

Spectral data for compound **4c**: ^1H NMR δ =5.25 (t, J = 7.3 Hz, 1H), 2.88 (s, 2H), 2.30 (t, J =

7.3 Hz, 4H), 2.05-2.02 (m, 4H), 1.40-1.27 (m, 30H), 0.88 (t, $J = 7.3$ Hz, 12H); ^{13}C NMR δ =137.9, 127.7, 53.8, 52.8, 35.7, 31.9, 31.7, 29.9, 29.2, 28.3, 27.3, 27.1, 27.0, 22.8, 22.6, 14.1.

Spectral data for compound **4a-b** (The product in Table 2, Run 4): ^1H NMR δ =7.31-7.16 (m, 5H), 5.34 (t, $J = 7.3$ Hz, 1H), 3.38 (s, 2H), 2.80 (s, 2H), 2.35-2.02 (m, 6H), 1.47-1.27 (m, 10H), 0.96-0.84 (m, 9H).

Spectral data for compound **5a-b**: ^1H NMR δ =7.31-7.16 (m, 5H), 6.43 (s, 1H), 3.11 (s, 2H), 2.35-2.02 (m, 6H), 1.47-1.27 (m, 12H), 0.96-0.84 (m, 9H).

Spectral data for compound **4d**: ^1H NMR δ =5.17 (t, $J = 7.3$ Hz, 1H), 2.68 (s, 2H), 2.18 (br, 4H), 2.18-1.88 (m, 4H), 1.45-1.43 (m, 4H), 1.35-1.21 (m, 12H), 0.82 (t, $J = 7.3$ Hz, 3H), 0.81 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR δ =136.9, 127.5, 66.0, 54.6, 31.9-22.5, 14.2, 13.9.

Spectral data for compound **4e**: ^1H NMR δ =5.27 (t, $J = 7.3$ Hz, 1H), 2.86 (s, 2H), 2.07-1.25 (m, 23H), 0.91-0.86 (m, 9H).

Spectral data for compound **4f**: ^1H NMR δ =5.24 (t, $J = 7.3$ Hz, 1H), 2.75 (s, 2H), 2.07-1.25 (m, 23H), 0.91-0.81 (m, 9H); ^{13}C NMR δ =141.3, 127.9, 65.7, 62.1, 54.1, 33.2-19.7, 14.1, 13.9.

Spectral data for compound **4g**: ^1H NMR δ =5.20 (t, $J = 7.3$ Hz, 1H), 3.66-3.59 (m, 4H), 2.73 (s, 2H), 2.28-2.27 (m, 4H), 1.99-1.89 (m, 4H), 1.33-1.21 (m, 10H), 0.82 (t, $J = 7.3$ Hz, 3H), 0.81 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR δ =136.0, 128.6, 67.1, 65.6, 53.6, 31.7-22.4, 14.0, 13.8.

Spectral data for compound **4h**: ^1H NMR δ =7.09-7.00 (m, 4H), 5.34 (t, $J = 7.3$ Hz, 1H), 3.53 (s, 2H), 2.98 (s, 2H), 2.85 (t, $J = 5.7$ Hz, 2H), 2.62 (t, $J = 5.7$ Hz, 2H), 2.11-2.03 (m, 4H), 1.41-1.26 (m, 10H), 0.93 (t, $J = 7.3$ Hz, 3H), 0.88 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR δ =136.6-125.3, 64.9, 56.4, 50.3, 31.9-22.5, 14.2, 14.0.

4a (with small amount of 5a)

YY158.217.182.214nmr¥水田¥6.2.octyne¥H1.als

YY158.217.182.214nmr¥水田¥6.2.octyne¥C.als

4b (with small amount of 5b)

C:\Documents and Settings\YDELL Note\Desktop\NMR\水田\0202diisopropylamine\0202diisopropylamine-1.als

C:\Documents and Settings\YDELL Note\Desktop\NMR\水田\0202diisopropylamine\0204diisopropylamineC-1.als

4a-b (with small amount of 5a-b)

4f (with small amount of 5f)

3-pipecoline H

4f + 5f

DFILE C:\WINDOWS\AP\2,
COMN 3-pipecoline H
DATIM Thu Jun 16 16:53:31
OBNUGH
EXMORON
OBFRO 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 16384
FREQU 7993.6 Hz
SCANS 64
ACQIM 2.050 sec
PD 4.950 sec
PW1 5.8 us
IRNUGH
CTEMP 21.7 c
SLVNTDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 11

3-pipecoline C

4g (with small amount of 5g)