Supporting Information

Concise Synthesis of Indole-Fused 1,4-Diazepines through Copper(I)-Catalyzed Domino Three-Component Coupling-Cyclization-*N*-Arylation under Microwave Irradiation

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General Methods. Exact mass (HRMS) spectra were recorded on JMS-HX/HX 110A mass spectrometer. ^1H NMR spectra were recorded using a JEOL AL-500 spectrometer at 500 MHz frequency. Chemical shifts are reported in δ (ppm) relative to Me_4Si (in CDCl_3) as internal standard. ^{13}C NMR spectra were recorded using a JEOL AL-500 and referenced to the residual CHCl_3 signal. Microwave reaction was conducted in a sealed glass vessel (capacity 10 mL) using CEM Discover microwave reactor with a run time of no more than 10 min. The temperature was monitored using IR sensor mounted under the reaction vessel. For column chromatography, Wakosil C-300 was employed.

General Procedure for Synthesis of Indole-Fused 1,4-Diazepine through Three-Component Indole Formation–*N*-Arylation: A mixture of 2-ethynylaniline **1a** (25 mg, 0.13 mmol), paraformaldehyde (7.7 mg, 0.26 mmol), secondary amine **2a** (35 mg, 0.14 mmol), and CuI (0.61 mg, 0.0032 mmol) in dioxane (1 mL) was stirred for 20 min at 170 °C under the microwave irradiation (200 W). After the three-component coupling-cyclization reaction was completed on TLC, NaOMe (41.4 mg, 0.77 mmol) was added at room temperature and the mixture was stirred for 20 min at 170 °C under microwave irradiation (200 W). The reaction mixture was concentrated under reduced pressure and purified by column chromatography over silica gel with hexane/EtOAc (3 : 1) as the eluent to give **3a** (33 mg, 88%) as a pale yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 0.96 (t, J = 7.3 Hz, 3H, CH_3), 1.36-1.43 (m, 2H, CH_2CH_3), 1.52-1.65 (br, 2H, NCH_2CH_2), 2.39-2.70 (br, 2H, NCH_2), 3.20-4.05 (br, 4H, $2 \times \text{Ar-CH}_2$), 6.56 (s, 1H, 3-H), 7.16-7.23 (m, 2H, Ar), 7.30 (t, J = 7.4 Hz, 1H, Ar), 7.43 (dd, J = 7.4, 1.3 Hz, 1H, Ar), 7.48 (ddd, J = 7.4, 7.4, 1.3 Hz, 1H, Ar), 7.61-7.69 (m, 3H, Ar); ^{13}C NMR (125 MHz, CDCl_3) δ 14.1, 20.7, 30.2, 48.5, 54.9, 55.9, 102.2, 110.3, 120.6, 120.8, 122.2, 122.8, 126.0, 128.67, 128.70, 130.6, 131.2, 135.8, 136.1, 138.6; MS (FAB) m/z (%): 291 (MH^+ , 100); HRMS (FAB) calcd for $\text{C}_{20}\text{H}_{23}\text{N}_2$ (MH^+): 291.1861; found: 291.1869.

DFIL L-147-1.a1s
 COMNT singlepulse
 DATIM 25-02-2008 18:43:41
 OBNUC 1H
 EXMOD singlepulse.ex2
 OBFRO 500.16 MHz
 OBSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 52428
 FREOU 7507.39 Hz
 SCANS 8
 ACQTM 6.9835 sec
 PD 5.0000 sec
 PM1 6.06 usec
 IRNUC 1H
 CTEMP 26.6 c
 SLVNT CDCl3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 36

single pulse decoupled gated NOE

C:\Documents and Settings\yusukebe0108\デスクトップ\7\#NMR\1-147-carbon-1.als

DFILE L-147-carbon-1.als
 COMNT single pulse decoupled gated
 DATIM 25-02-2008 19:33:00
 OBNUC 13C
 EXMOD single pulse dec
 OFREQ 125.77 MHz
 OBSET 7.87 KHz
 OFPIN 4.21 Hz
 POINT 26214
 FREQU 31446.06 Hz
 SCANS 1024
 ACQTM 0.8336 sec
 PD 2.0000 sec
 PUL 3.83 usec
 IRNUC 1H
 CTEMP 27.0 c
 SLYNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 60

C:\Documents and Settings\ryusukebe0108\Desktop\PMR\1-133-1.a1s

DF11E L-133-1.a1s
 COMNT single_pulse
 DATIM 16-02-2008 12:38:21
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFREQ 500.16 MHz
 OBSSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 52428
 FRECU 7507.39 Hz
 SCANS 8
 ACQTM 6.9835 sec
 PD 5.0000 sec
 PM1 6.06 usec
 IIRNUC 1H
 CTEMP 26.5 c
 SLYNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 46

DFILE 3b-151-carbon-1.als
 COMNT single pulse decoupled satd
 DATIM 28-02-2008 17:43:59
 151C
 EXMOD single_pulse_dec
 OBFRQ 125.77 MHz
 OBSEI 7.87 KHz
 OBFIN 4.21 Hz
 POINT 28214
 FREQU 31446.06 Hz
 SCANS 1024
 ACQTM 0.8336 sec
 PD 2.0000 sec
 PM1 3.83 usec
 1H
 IRENUC 27.8 c
 CTMP CDCL3
 SLVNT 77.00 ppm
 EXREF 1.20 Hz
 BF 60
 RGAIN

C:\Documents and Settings\yusukebe0108\デスクトップ\NMR\PL-175-1.als

DFILE L-175-1.als
 COMNT single-pulse
 DATIM 06-03-2008 10:27:28
 EBMOD 1H
 OBFRQ 500.16 MHz
 OBSSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 52428
 FREQU 7507.39 Hz
 SCANS 8
 ACQTM 6.9835 sec
 PD 5.0000 sec
 PM1 6.05 usec
 IRNUC 1H
 CTEMP 26.0 c
 SLEVT CDCL3
 EAREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 38

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DPF1LE L-175-carbon-1.als
COMNT single pulse decoupled gate
DATIM 06-03-2008 11:16:50
13C
OBNUC 13C
EXMOD single pulse dec
OBFRO 125.77 MHz
OBSRT 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 1024
AQCTM 0.8336 sec
PD 2.0000 sec
PWI 3.83 usec
IRNUC 1H
CTEMP 26.7 c
SLYNT CDCl3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 58

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C:\Documents and Settings\yusukebe0108\デスクトップ\NMR\PL-136-1.a1s

DFILE L-136-1.a1s
 COMNT single_pulse
 DATIM 19-02-2008 22:42:30
 1H
 single_pulse.ex2
 EXMOD 500.16 MHz
 OBFRQ 2.41 KHz
 OBSET 6.01 Hz
 OBFIN 52428
 POINT 7507.39 Hz
 FREQU 8
 SCANS 6.9835 sec
 ACQTM 5.0000 sec
 PD 6.06 usec
 PM1
 1RNOC 1H
 CTMPC 26.3 c
 SLYNT CDCl3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 42

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D1FILE L-136-carbon-1.a1s
COMNT single pulse decoupled satd
DATIM 19-02-2008 23:34:39
OBNUC 13C
EXMOD single-pulse-dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQ0 31446.06 Hz
SCANS 1024
AQCTM 0.8336 sec
PD 2.0000 sec
PM1 3.83 usec
IRNUC 1H
CTEMP 26.8 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 60

```

DFILE L-180-1.a1s
 COMNT single_pulse
 DATIM 11-03-2008 09:39:11
 OBNUC 1H
 EXMOD single_pulse.ex2
 OFFRQ 500.16 MHz
 OBSRT 2.41 kHz
 OFPIN 6.01 Hz
 POINT 52428
 FREOU 7507.39 Hz
 SCANS 8
 ACQTIM 6.9835 sec
 PD 5.0000 sec
 PWT 6.06 usec
 IRENUC 1H
 CTEMP 26.4 c
 SLVNT CDCl3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 44

DF1E L-182-20080318-1.a1s
 COMNT single_pulse
 DATIM 18-03-2008 12:01:28
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 500.16 MHz
 OBSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 52428
 FREQUT 7507.39 Hz
 SCANS 8
 ACQTM 6.9835 sec
 PD 5.0000 sec
 PM1 6.05 usec
 IRLNOC 1H
 CTEMP 26.1 c
 STVNT CDCl3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 40

DFILE L-182-carbon-20080318-1.a1s
 COMNT single pulse decoupled gate
 DATIM 18-03-2008 12:50:41
 OBNUC ¹³C
 EXMOD single pulse dec
 OBFRQ 125.77 MHz
 OBSLT 7.87 KHz
 OBFIN 4.21 Hz
 POINT 26214
 FREQU 31446.06 Hz
 SCANS 1024
 ACQTM 0.8336 sec
 PD 2.0000 sec
 PUL1 3.83 usec
 IRRUC 1H
 CTEMP 26.2 c
 SLYMT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 58

C:\Documents and Settings\yusukebe0108\Desktop\7#NMR#L-184-1.als

DFIL L-184-1.als
 COM single pulse
 DATIM 01-04-2008 08:25:60
 ORNUC 1H
 EXMOD single pulse, ex2
 ORFQA 500.16 MHz
 ORSET 2.41 KHz
 ORFIN 6.01 Hz
 POINT 52428
 FREQ 7507.39 Hz
 SCANS 8
 ACQTM 6.9836 sec
 PD 5.0000 sec
 PWT 6.06 usec
 IRNUC 1H
 CTEMP 24.5 C
 SLYNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 38

DFILE L-184-carbon-1.als
 COMNT single pulse decoupled sat
 DATIM 01-04-2008 09:15:15
 13C
 EXMOD single-pulse-dec
 OBFREQ 125.77 MHz
 OBSET 7.87 KHz
 OBFIN 4.21 Hz
 POINT 26214
 FREQ 31446.06 Hz
 SCANS 1024
 ACQTM 0.8336 sec
 PD 2.0000 sec
 PM1 3.83 usec
 1H
 IRRUC 24.8 c
 CTEMP
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 56

DPFILE L-183-new-2.als
 COMINT single_pulse
 DATIM 12-03-2008 16:42:40
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRO 500.16 MHz
 OBSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 52428
 FREQU 7507.39 Hz
 SCANS 8
 ACQTM 6.9835 sec
 PD 5.0000 sec
 PUL 6.05 usec
 IPRNUC 1H
 CTEMP 25.9 c
 SLYNT CDCl3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 40

C:\Documents and Settings\yusukebe0108\デスクトップ\FMNR#L-185-20080322-1.als

DFILE L-185-20080322-1.als
 COMNT single_pulse
 DATIM 22-03-2008 15:02:11
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 500.16 MHz
 OBSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 52428
 FREQ 7507.39 Hz
 SCANS 8
 ACQTM 6.9835 sec
 PD 5.0000 sec
 PM1 6.05 usec
 IENUC 1H
 CTEMP 25.6 c
 SLYMT CDCl₃
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 44

C:\Documents and Settings\yusukebe0108\Desktop\FNMR\PL-185-carbon-20080322-1.als

DFILE L-185-carbon-20080322-1.als
 COMNT single pulse decoupled satd
 DATIM 22-03-2008 15:51:28
 OBNOC 13C
 EXMOD single pulse dec
 OBFREQ 125.77 MHz
 OBSLET 7.87 KHz
 OBFIN 4.21 Hz
 POINT 26214
 FREQD 31446.06 Hz
 SCANS 1024
 ACQTM 0.8836 sec
 PD 2.0000 sec
 PUL 3.83 usec
 IENUC 1H
 CTEMP 26.1 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 58

DPFILE L-189-1.a1s
 COMNT single_pulse
 DATIM 14-03-2008 18:25:21
 OBNUC 1H
 EBMOD single_pulse.ex2
 OBFRO 500.16 MHz
 OBFSE 2.41 KHz
 OBFIN 6.01 Hz
 POINT 52428
 FREQU 7507.39 Hz
 SCANS 8
 ACQTM 6.9836 sec
 PD 5.0000 sec
 PWT 6.06 usec
 IENUC 1H
 CTEMP 26.0 c
 SLVNT CDCL3
 EREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 38

C:\Documents and Settings\yusukebe0108\デスクトップ\7\#NMR\7L-189-carbon-1.a1s

DFILE L-189-carbon-1.a1s
 COMNT single pulse decoupled gate
 DATIM 14-03-2008 19:18:22
 ORNUC 13C
 EXMOD single pulse dec
 ORFREQ 125.77 MHz
 ORSET 7.87 KHz
 ORFIN 4.21 Hz
 POINT 32768
 FREQU 31446.54 Hz
 SCANS 1024
 ACQTM 1.0420 sec
 PD 2.0000 sec
 PM1 3.83 usec
 IRNUC 1H
 CTEMP 26.2 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 RF 1.20 Hz
 RGAIN 68