Synthesis and Reactivity of Mixed Alkynylalanes by Direct Triethylamine-Catalyzed Alumination of Terminal Alkynes.

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Compounds **6a**, **6b** and **7a-e** have already been reported elsewhere:

6a, **6b** : Blanchet, J.; Bonin, M.; Micouin, L.; Husson, H.-P. *J. Org. Chem*, **2000**, *65*, 6423

7a, **7d** : Ahn, J. H.; Joung, M. J.; Yoon, N. M., *J. Org. Chem*, **1995**, *60*, 6173

7b : Yamaguchi, M.; Hayashi, A.; Minami, T. *J. Org. Chem*, **1991**, *56*, 4091

7c : Uma, R.; Davies, M. K.; Crévisy, C.; Grée, R. *Eur. J. Org. Chem*. **2001**, 3141

7e : Liang, C. K. *Bull. Soc. Chim. Fr.* **1933**, *53*, 33.

2-[ferrocenylmethyl-(6-chloro-1-phenethyl-hex-2-ynyl)-amino]-2-phenylethanol 6c oil, $[\alpha]_D = +20$ ($c = 1.00$, CHCl_3) ; ^1H NMR (400 MHz, CDCl_3) δ 1.71 (q, $J = 7.6$ Hz, 2H), 1.94 (quint, $J = 6.4$ Hz, 2H), 2.43 (t, $J = 6.4$ Hz, 2H), 2.50 (t, $J = 7.9$ Hz, 2H), 3.61 (m, 4H), 3.76-3.87 (m, 2H), 4.02- 4.16 (m, 11H), 7.00 (d, $J = 7.4$ Hz, 2H), 7.14- 7.36 (m, 8H) ; ^{13}C NMR (75 MHz, CDCl_3) δ 16.3, 31.5, 32.9, 36.7, 43.8, 45.8, 51.9, 61.7, 65.4, 68.0, 68.7, 70.0, 81.4, 83.8, 86.3, 125.9, 127.6, 128.4, 128.5, 128.8, 139.4, 141.8 ; IR (cm^{-1}) 3513, 3072, 2359, 1679, 1494; MS (CI) 555 (MH^+).

6-Hept-1-ynyl-1-(2-hydroxy-1-phenyl-ethyl)-piperidine-2-carbonitrile 9a oil, $[\alpha]_D = -87$ ($c = 0.96$, CH_2Cl_2) ; ^1H NMR (400 MHz, CDCl_3) δ 0.93 (t, $J = 7.2$ Hz, 3H), 1.33- 1.51 (m,

5H), 1.57- 1.68 (m, 4H), 1.83- 1.86 (m, 2H), 1.93- 2.00 (m, 2H), 2.29 (td, $J = 7.1, 2.1$ Hz, 1H), 3.57 (dd, $J = 4.9, 2.1$ Hz, 1H), 3.88 (ddd, $J = 11.0, 6.9, 3.4$ Hz, 1H), 3.99 (dd, $J = 5.0, 3.4$ Hz, 1H), 4.07 (dt, $J = 11.3, 5.6$ Hz, 1H), 4.17 (m, 1H), 7.25- 7.50 (m, 5H) ; ^{13}C NMR (75 MHz, CDCl_3) δ 14.2, 17.0, 18.9, 22.3, 28.2, 29.2, 31.3, 46.1, 47.4, 63.9, 67.0, 75.8, 89.3, 118.4, 128.4, 128.5, 129.2, 139.2 ; IR (cm^{-1}) 3478, 2931, 2360, 2342, 1622, 1492, 1254 ; HRMS for $\text{C}_{21}\text{H}_{28}\text{N}_2\text{ONa}$ calcd. 347.2099; found 347.2097.

6-(5-Chloro-pent-1-ynyl)-1-(2-hydroxy-1-phenyl-ethyl)-piperidine-2-carbonitrile 9b oil, $[\alpha]_{\text{D}} = -85$ ($c = 0.87$, CH_2Cl_2) ; ^1H NMR (400 MHz, CDCl_3) δ 1.53 (t, $J = 5.9$ Hz, 1H), 1.70 (m, 2H), 1.80- 2.09 (m, 6H), 2.50 (td, $J = 6.5, 1.4$ Hz, 2H), 3.57 (m, 1H), 3.73 (t, $J = 6.4$, 2H), 3.86 (m, 1H), 3.96 (m, 1H), 4.05 (dt, $J = 11.2, 5.0$ Hz, 1H), 4.18 (m, 1H), 7.25- 7.50 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 16.5, 17.1, 29.1, 31.1, 31.2, 44.2, 46.1, 47.4, 63.9, 67.1, 87.0, 118.2, 128.5, 129.2, 139.1 ; IR (cm^{-1}) 3418, 2840, 2364, 2343, 1743, 1622, 1495, 1265 ; HRMS for $\text{C}_{19}\text{H}_{23}\text{N}_2\text{OClNa}$ calcd. 353.1396; found 353.1397.

6-Deca-1,9-diynyl-1-(2-hydroxy-1-phenyl-ethyl)-piperidine-2-carbonitrile 9c oil, $[\alpha]_{\text{D}} = -80$ ($c = 1.05$, CH_2Cl_2) ; ^1H NMR (400 MHz, CDCl_3) δ 1.40-1.70 (m, 13H), 1.82-1.87 (m, 2H), 1.92- 2.03 (m, 2H), 1.94 (t, $J = 2.6$ Hz, 1H), 2.21 (td, $J = 7.0, 2.6$ Hz, 1H), 2.30 (td, $J = 7.0, 2.1$ Hz, 1H), 3.57 (dd, $J = 4.9, 2.1$ Hz, 1H), 3.86 (ddd, $J = 11.3, 3.6, 3.4$ Hz, 1H), 3.97 (dd, $J = 5.0, 3.4$ Hz, 1H), 4.05 (dt, $J = 11.4, 5.4$ Hz, 1H), 4.16 (m, 1H), 7.25- 7.50 (m, 5H) ; ^{13}C NMR (75 MHz, CDCl_3) δ 17.0, 18.4, 18.8, 28.3, 28.5, 29.2, 31.2, 46.1, 47.4, 63.1, 67.0, 68.3, 76.0, 84.8, 89.0, 118.5, 128.4, 128.5, 129.1, 139.2 ; IR (cm^{-1}) 3478, 3290, 2934, 2858, 2361, 2226, 2115, 1749, 1653, 1494; HRMS for $\text{C}_{24}\text{H}_{30}\text{N}_2\text{ONa}$ calcd. 385.2256; found 385.2256.

S3

S4

S5

S6

S7

Current Data Parameters
NAME CF-65a
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020424
Time 16.18
PROBHD 5 mm BBI 1H-
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 1
DS 0
SWH 5995.204 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 64
DW 83.400 usec
DE 6.50 usec
TE 300.0 K
D1 0.50000000 sec

----- CHANNEL f1 -----
NUC1 1H
P1 7.50 usec
PL1 0.00 dB
SFO1 400.1317800 MHz

F2 - Processing parameters
SI 32768
SF 400.1300060 MHz
WDW na
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 7.659 ppm
F1 3064.41 Hz
F2P 1.507 ppm
F2 602.80 Hz
PPMCM 0.30760 ppm/cm
HZCM 123.08035 Hz/cm

6c

S8

S9

Current Data Parameters
 NAME 1m-226-1-1
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20020912
 Time 13.55
 PROBHD 5 mm BBI 1H-
 PULPROG zg30
 TD 16384
 SOLVENT CDCl3
 NS 1
 DS 0
 SWH 5995.204 Hz
 FIDRES 0.365918 Hz
 AQ 1.3664756 sec
 RG 16
 DW 83.400 usec
 DE 6.50 usec
 TE 300.0 K
 D1 0.50000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 7.50 usec
 PL1 0.00 dB
 SFO1 400.1317800 MHz

F2 - Processing parameters
 SI 32768
 SF 400.1300060 MHz
 WDW no
 SSB 0
 LB 0.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 F1P 7.802 ppm
 F1 3121.86 Hz
 F2P 0.531 ppm
 F2 212.64 Hz
 PPMCM 0.36353 ppm/cm
 HZCM 145.46103 Hz/cm

S10

S11

S13

Current Data Parameters
NAME 1m-243-f2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20021129
Time 16.16
PROBHD 5 mm BBI 1H-
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 1
DS 0
SWH 5995.204 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 32
DW 83.400 usec
DE 6.50 usec
TE 300.0 K
D1 0.50000000 sec

----- CHANNEL f1 -----
NUC1 1H
P1 7.50 usec
PL1 0.00 dB
SFO1 400.1317800 MHz

F2 - Processing parameters
SI 32768
SF 400.1300060 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 8.089 ppm
F1 3236.45 Hz
F2P 0.647 ppm
F2 258.70 Hz
PPMCM 0.37210 ppm/cm
HZCM 148.88753 Hz/cm

S14

S15

Current Data Parameters
NAME 1m-224-1-f1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020906
Time 15.10
PROBHD 5 mm BBI 1H-
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 1
DS 0
SWH 5995.204 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 12.7
DW 83.400 usec
DE 6.50 usec
TE 300.0 K
D1 0.5000000 sec

----- CHANNEL f1 -----
NUC1 1H
P1 7.50 usec
PL1 0.00 dB
SF01 400.1317800 MHz

F2 - Processing parameters
SI 32768
SF 400.1300060 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 4.981 ppm
F1 1993.04 Hz
F2P 0.567 ppm
F2 226.78 Hz
PPMCM 0.22071 ppm/cm
HZCM 88.31258 Hz/cm

S16

S17

Current Data Parameters
NAME 1m-251-1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20021218
Time 11.05
PROBHD 5 mm BBI 1H-
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 1
DS 0
SWH 5995.204 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16
DM 83.400 usec
DE 6.50 usec
TE 300.0 K
D1 0.50000000 sec

----- CHANNEL f1 -----
NUC1 1H
P1 7.50 usec
PL1 0.00 dB
SFO1 400.1317800 MHz

F2 - Processing parameters
SI 32768
SF 400.1300060 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 4.665 ppm
F1 1866.69 Hz
F2P 0.432 ppm
F2 172.68 Hz
PPMCM 0.21168 ppm/cm
HZCM 84.70045 Hz/cm

S19

Current Data Parameters
NAME 1m-264-F1
EXPNO 5
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030918
Time 14.16
PROBHD 5 mm BB1 1H-
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 1
DS 0
SWH 5995.204 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 64
DW 83.400 usec
DE 6.50 usec
TE 300.0 K
D1 0.50000000 sec

----- CHANNEL f1 -----
NUC1 1H
P1 7.50 usec
PL1 0.00 dB
SFO1 400.1317800 MHz

F2 - Processing parameters
SI 32768
SF 400.130060 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 7.638 ppm
F1 3056.10 Hz
F2P 0.730 ppm
F2 291.99 Hz
PPMCM 0.34540 ppm/cm
HZCM 138.20503 Hz/cm

S20

9b

S21

Current Data Parameters
NAME 1m-277-1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20031015
Time 14.29
PROBHD 5 mm BBI 1H-
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 1
DS 0
SWH 5995.204 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 50.8
DW 83.400 usec
DE 6.50 usec
TE 300.0 K
D1 0.50000000 sec

----- CHANNEL f1 -----
NUC1 1H
P1 7.50 usec
PL1 0.00 dB
SF01 400.1317800 MHz

F2 - Processing parameters
SI 32768
SF 400.1300060 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 7.634 ppm
F1 3054.78 Hz
F2P 1.408 ppm
F2 563.55 Hz
PPMCM 0.31130 ppm/cm
HZCM 124.56156 Hz/cm

9b

S22

S23

Current Data Parameters
NAME 1m-275-f2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20031010
Time 15.31
PROBHD 5 mm BBI 1H-
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 1
DS 0
SWH 5995.204 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 64
DW 83.400 usec
DE 6.50 usec
TE 300.0 K
D1 0.5000000 sec

----- CHANNEL f1 -----
NUC1 1H
P1 7.50 usec
PL1 0.00 dB
SF01 400.1317800 MHz

F2 - Processing parameters
SI 32768
SF 400.1300060 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 7.725 ppm
F1 3090.88 Hz
F2P 1.308 ppm
F2 523.39 Hz
PPMCM 0.32083 ppm/cm
H2CM 128.37413 Hz/cm

S24