Supporting Information

Palladium-Catalyzed Alkylation of Vinyl Oxiranes with substituted allenes.

Direct Access to Bifunctionalized Allylic Alcohols.

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General procedure for the preparation of substituted allenes (5b- 5j).

A three-necked, round bottom flask equipped with a nitrogen inlet, was charged with 3.0 mL of dry CH_2Cl_2 . The phosphorane (1 mmol) was added to this solution and cooled to 0 °C. Triethylamine (1 mmol) in 1.0 mL of CH_2Cl_2 was then added dropwise to this solution at 0 °C. After 10 min, a solution of the acid chloride (1 mmol) in 1 mL of CH_2Cl_2 was added, and the reaction mixture was stirred at 0 °C for 1h and then allowed to warm to room temperature. The yellow-tinted mixture was evaporated carefully on a rotary evaporator at reduced pressure using a water bath maintained at 22 °C. To the semi- solid residue, 5 mL of pentane was added, and the slurry was let stand for 2 h. The precipitate was filtered and the filter cake was washed with another 5 mL of pentane. The combined filtrate was concentrated at reduced pressure and the semi-solid solution was filtered again. The filtrate was evaporated and the crude material was purified by silica gel column chromatography using 4: 1 hexanes: Et_2O as the eluant.

General Procedure for the Palladium-Catalyzed alkylation of vinyl oxirane 1 with substituted allenes 5.

$\text{Pd}_2(\text{dba})_3$ (0.058 g, 10 mol % to **1a/b**) was weighed into a Schlenk tube under a stream of nitrogen, 3 mL of dry THF was added, and the solution was degassed for ½ h. Dppp (0.04 g, 20 mol % to **1a/b**) was added and stirring was continued for another 15min. then vinyl oxirane (40 μL , 0.5 mmol) and the allenes **5** (0.5 mmol) were added, and the mixture was stirred under N_2 at 60 °C for 24 h. After the reaction was complete, the orange/yellow solution was then concentrated by rotary evaporation, and the residue

was purified by silica gel column chromatography using a mixture of 2:1 hexanes: ethyl acetate as the eluant to afford **6**. Further purification was effected using preparative TLC. Isomers of compound **6c**, and **7a** were separated using a Waters 600 HPLC instrument equipped with Nova Pak silica analytical and preparative columns.

54

13C with proton decoupling

56

57

¹³C with proton decoupling

59

In CD₂Cl₂

S12

S13

S15

13C with proton decoupling

S17

¹³C with proton decoupling

619

520

S21

¹³C with proton decoupling

S23

524

S25

¹³C with proton decoupling

¹H COSY

Current Data Parameters

NAME
EXPNO
PROCNO

Date_

Time

INSTRUM

PROBHD

PULPROG

TD

SOLVENT

NS

DS

SWH

FIDRES

AQ

RG

DM

DE

TE

DO

D1

D13

D16

TAC

TMR

NUC1

NUC2

P1

P2

P3

P4

P5

P6

P7

P8

P9

P10

P11

P12

P13

P14

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P341

1H 13C HMQC

NAME Current Date Parameters
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters

Date_ 20031124
Time 15.12
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 1024
SOLVENT CDCl3
NS 8
DS 2
SWH 2170.139 Hz
FIDRES 0.218256 Hz
AQ 0.227913004 sec
RG 64
DM 230.400 usec
DE 6.00 usec
TE 300.2 K
DMS12 145.000000 sec
d0 0.00000000 sec
d1 1.00000000 sec
d2 0.00000000 sec
d3 0.00000000 sec
d12 0.00000000 sec
d13 0.00000000 sec
d16 0.00000000 sec
SFO 0.00242628 sec
SFO2 0.00000000 sec
SFO3 0.00000000 sec
NUC1 13C
NUC2 1H
NOREST 1.00000000 sec
NMRK 1.00000000 sec

***** CHANNEL f1 *****

NUC1 13C
P1 10.50 usec
PL1 21.00 dB
PL2 19.00 dB
PL3 19.00 dB
SFO1 300.1314023 MHz

***** CHANNEL f2 *****

CPDPRG2 gpgp
NUC2 1H
P2 5.00 usec
PL2 19.00 dB
PL3 19.00 dB
SFO2 75.4777964 MHz

***** GRADIENT CHANNEL *****

GP1A1 100.00 usec
GP1A2 100.00 usec
GP1A3 100.00 usec
GP1 0.00 %
GP2 0.00 %
GP3 0.00 %
GP4 0.00 %
GP5 0.00 %
GP6 0.00 %
GP7 0.00 %
GP8 0.00 %
GP9 0.00 %
GP10 0.00 %
GP11 0.00 %
GP12 0.00 %
GP13 0.00 %
GP14 0.00 %
GP15 0.00 %
GP16 0.00 %
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GP91 0.00 %
GP92 0.00 %
GP93 0.00 %
GP94 0.00 %
GP95 0.00 %
GP96 0.00 %
GP97 0.00 %
GP98 0.00 %
GP99 0.00 %
GP100 0.00 %

F1 - Acquisition Parameters

NUC1 13C
P1 10.50 usec
PL1 21.00 dB
PL2 19.00 dB
PL3 19.00 dB
SFO1 300.1314023 MHz

F2 - Processing Parameters

SI 300.1300000 MHz
SF 300.1300000 MHz
WDW 0
SSB 0
LB 0.00 Hz
GB 0
RC 1.00

F1 - Processing Parameters

SI 300.1300000 MHz
SF 300.1300000 MHz
WDW 0
SSB 0
LB 0.00 Hz
GB 0
RC 1.00

F2 - Processing Parameters

SI 300.1300000 MHz
SF 300.1300000 MHz
WDW 0
SSB 0
LB 0.00 Hz
GB 0
RC 1.00

F1 - Processing Parameters

SI 300.1300000 MHz
SF 300.1300000 MHz
WDW 0
SSB 0
LB 0.00 Hz
GB 0
RC 1.00

F2 - Processing Parameters

SI 300.1300000 MHz
SF 300.1300000 MHz
WDW 0
SSB 0
LB 0.00 Hz
GB 0
RC 1.00

530

1H COSY

Current Data Parameters
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 PROCNO 1

F2 - Acquisition Parameters

Date_ 20031124
 Time 18.03
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 PULPROG cosy45pqr
 TO 1024
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 SOLVENT CDCl3
 DS 0
 SWH 2216.312 Hz
 FIDRES 2.164367 Hz
 AQ 0.2310644 sec
 RG 71.6
 DN 225.600 usec
 DE 6.00 usec
 TE 300.0 K
 DO 0.00000300 sec
 D1 1.00000000 sec
 d13 0.00000400 sec
 d16 0.00010000 sec
 d17 0.00045126 sec
 ACQRES 1.00000000 sec
 NCORE 1
 NMRK 1.00000000 sec

CHANNEL f1

NUC1 1H
 P0 5.25 usec
 P1 10.50 usec
 PL1 -3.00 dB
 SFO1 300.1314023 MHz

GRADIENT CHANNEL

CONV1 sine, 100
 GAMMA2 sine, 100
 GPX1 0.00 %
 GPX2 0.00 %
 GPY1 0.00 %
 GPY2 0.00 %
 GPZ1 10.00 %
 GPZ2 10.00 %
 P16 1000.00 usec

F1 - Acquisition Parameters

NUC1 1H
 P0 5.25 usec
 P1 10.50 usec
 PL1 -3.00 dB
 SFO1 300.1314023 MHz

F2 - Processing Parameters

SI 1024
 SF 300.1300000 MHz
 WDW SINE
 SSB 0
 LB 0.00 Hz
 GB 0
 PC 1.00

F1 - Processing Parameters

SI 1024
 SF 300.1300000 MHz
 WDW SINE
 SSB 0
 LB 0.00 Hz
 GB 0

2D NMR plot parameters

CX2 15.00 cm
 CX1 15.00 cm
 F2AQ 8.110 ppm
 F2P0 2452.02 Hz
 F2P1 8.110 ppm
 F2P2 333.10 Hz
 F2P3 8.199 ppm
 F2P4 2450.68 Hz
 F2P5 1.016 ppm
 F2P6 304.97 Hz
 F2P7 0.47067 ppm/cm
 F2P8 141.26105 Hz/cm
 F2P9 0.47884 ppm/cm
 F2P10 143.71395 Hz/cm