Asymmetric Conjugate Addition for the Preparation of *syn*-1,3-Dimethyl Arrays: Synthesis and Structure Elucidation of Capensifuranone

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Supporting Information

General Experimental Detail	S2
¹ H NMR for compound 12	S3
¹³ C NMR for compound 12	S4
¹ H NMR for compound (3 <i>S</i>)-3-methylhexanol	S5
¹³ C NMR for compound (3 <i>S</i>)-3-methylhexanol	S6
¹ H NMR for compound 13	S7
¹³ C NMR for compound 13	S8
¹ H NMR for compound 14	S9
¹³ C NMR for compound 14	S10
¹ H NMR for compound 15	S11
¹³ C NMR for compound 15	S12
¹ H NMR for compound 16	S13
¹³ C NMR for compound 16	S14
¹ H NMR for compound 17	S15
¹³ C NMR for compound 17	S16
¹ H NMR for compound 18	S17
¹³ C NMR for compound 18	S18
¹ H NMR for compound 19	S19
¹³ C NMR for compound 19	S20
¹ H NMR for compound 20	S21
¹³ C NMR for compound 20	S22
¹ H NMR for compound 22	S23
¹³ C NMR for compound 22	S24
¹ H NMR for compound 23	S25
¹³ C NMR for compound 23	S26
¹ H NMR for compound 24	S27
¹³ C NMR for compound 24	S28
¹ H NMR for compound 25	S29
¹³ C NMR for compound 25	S30
¹ H NMR for compound 27 (<i>epi</i> -capensifuranone)	S31
¹³ C NMR for compound 27 (<i>epi</i> -capensifuranone)	S32
¹ H NMR for compound 26	S33
¹³ C NMR for compound 26	S34
¹ H NMR for compound 1 (capensifuranone)	S35
¹³ C NMR for compound 1 (capensifuranone)	S36

General Methods. Infrared (FT-IR) spectra were recorded on a 360 FT-IR spectrometer. ^1H NMR and ^{13}C NMR were measured on a 400 MHz spectrometer with CDCl_3 as the solvent. Chemical shifts are reported in ppm on the δ scale using residual chloroform (CHCl_3) as a reference: δ 7.26 ppm for ^1H NMR; δ 77.0 ppm for ^{13}C NMR. Mass spectral data (MS and HRMS) were recorded using chemical ionization (CI). Optical rotations were obtained at 589 nm (sodium D line). Analytical thin-layer chromatography (TLC) was performed on precoated (0.25 mm thick) glass backed silica gel plates. Spots were visualized under UV light and/or staining with ethanolic *p*-anisaldehyde. Flash chromatography was performed using silica gel 30-63 micron (230-400 mesh). All reagents and solvents were used as received, unless noted otherwise. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled under argon from sodium/benzophenone ketyl. Methylene chloride (CH_2Cl_2) was distilled under argon over calcium hydride. Toluene and triethylamine (Et_3N) were distilled from calcium hydride under dry atmosphere. All reactions were conducted in flame- or oven-dried glassware under an atmosphere of argon unless otherwise noted.

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Temp. 29.0 C / 302.1 K

File: res.11.031.1h

VXR400

PULSE SEQUENCE

Relax. delay 0.300 sec

Pulse 45.0 degrees

Acq. time 3.744 sec

Width 4400.0 Hz

32 repetitions

OBSERVE H1, 399.798603 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 4 hr, 37 min, 44 sec

¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 29.0 C / 302.1 K

File: res.II.031.13C

VXR400

PULSE SEQUENCE

Relax. delay 0.600 sec

Pulse 18.1 degrees

Acq. time 1.19 sec

Width 25000.0 Hz

256 repetitions

OBSERVE C13, 100.5295106 MHz

DECOUPLE H1, 399.8012651 MHz

Power 49 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 2.5 Hz

FT size 65536

Total time 2 hr, 3 min, 55 sec

¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: a1n-1-109+145-C13

VXR400

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 27.0 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

576 repetitions

OBSERVE C13, 100.5229488 MHz

DECOUPLE H1, 399.7752075 MHz

Power 45 db

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 2.5 Hz

FT size 65536

Total time 61 hr, 20 min, 20 sec

(3S)-3-methylhexanol

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 29.0 C / 302.1 K
File: res.II.093.1H
VXR400

PULSE SEQUENCE
Relax. delay 0.300 sec
Pulse 45.1 degrees
Acq. time 3.744 sec
Width 4400.0 Hz
32 repetitions
OBSERVE H1, 399.7988560 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 4 hr, 37 min, 44 sec

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Temp. 29.0 C / 302.1 K

File: res.II.117.13C

VXR400

PULSE SEQUENCE

Relax. delay 0.600 sec

Pulse 18.1 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

412 repetitions

OBSERVE C13, 100.5294969 MHz

DECOUPLE H1, 399.8012651 MHz

Power 49 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 2.5 Hz

FT size 65536

Total time 2 hr, 3 min, 55 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: aln-compound18-1H

VXR400

PULSER SEQUENCE

Relax. delay 2.000 sec

Pulse 90.0 degrees

Acq. time 3.744 sec

Width 4400.0 Hz

16 repetitions

OBSERVE H1, 399.7662749 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 1 min, 32 sec

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: aln-compound18-13C

VXR400

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 27.0 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

1070 repetitions

OBSERVE C13, 100.5213256 MHz

DECOUPLE H1, 399.7686931 MHz

Power 45 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 2.5 Hz

FT size 65536

Total time 61 hr, 20 min, 20 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

File: aln-1-195

VXR400

PULSE SEQUENCE

Relax. delay 2.000 sec

Pulse 90.0 degrees

Acq. time 3.744 sec

Width 4400.0 Hz

16 repetitions

OBSERVE H1, 399.7793049 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 1 min, 32 sec

¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: rjm5-062103bcarbon
I400

PULSE SEQUENCE

Relax. delay 3.000 sec

Pulse 90.0 degrees

Acq. time 0.655 sec

Width 25000.0 Hz

152 repetitions

OBSERVE C13, 100.6097651 MHz

DECOUPLE H1, 400.1200527 MHz

Power 43 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 32768

Total time 10 hr, 10 min, 42 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: aln-1-135-1

VXR400

PULSE SEQUENCE

Relax. delay 2.000 sec

Pulse 90.0 degrees

Acq. time 3.744 sec

Width 4400.0 Hz

16 repetitions

OBSERVE H1, 399.7793051 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 1 min, 32 sec

¹³C OBSERVE

Pulse Sequence: szpul

Solvent: CDCl₃

Ambient temperature

File: rjm5-062103dcarbon
1400

PULSE SEQUENCE

Relax. delay 3.000 sec

Pulse 90.0 degrees

Acq. time 0.655 sec

Width 25000.0 Hz

75 repetitions

OBSERVE C13, 100.6097666 MHz

DECOUPLE H1, 400.1200527 MHz

Power 43 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 32768

Total time 10 hr, 10 min, 42 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: rjms-062403a

VXR400

PULSE SEQUENCE

Relax. delay 2.000 sec

Pulse 90.0 degrees

Acq. time 3.744 sec

Width 4400.0 Hz

16 repetitions

OBSERVE H1, 399.7662756 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 1 min, 32 sec

13C OBSERVE

Pulse Sequence: szpul

Solvent: CDCl3

Ambient temperature

File: rjm5-062403acarbon

VXR400

PULSE SEQUENCE

Relax. delay 3.000 sec

Pulse 90.0 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

118 repetitions

OBSERVE C13, 100.5213107 MHz

DECOUPLE H1, 399.7685931 MHz

Power 45 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 2.5 Hz

FT size 65536

Total time 11 hr, 41 min, 22 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Temp. 29.0 C / 302.1 K

File: res.IT.139.1H

VXR400

PULSE SEQUENCE

Relax. delay 0.300 sec

Pulse 44.9 degrees

Acq. time 3.744 sec

Width 4400.0 Hz

24 repetitions

OBSERVE H1, 399.7988469 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 4 hr, 37 min, 44 sec

¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 29.0 C / 302.1 K

File: res.11.139.13C

VXR400

PULSE SEQUENCE

Relax. delay 0.600 sec

Pulse 17.5 degrees

Acq. time 1.19 sec

Width 25000.0 Hz

64 repetitions

OBSERVE C13, 100.5295007 MHz

DECOUPLE H1, 399.8012651 MHz

Power 49 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 2.5 Hz

FT size 65536

Total time 2 hr, 3 min, 55 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

User: 1-12-87

File: rjm5-062103a

I400

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 2.003 sec

Width 5000.0 Hz

16 repetitions

OBSERVE H1, 400.1180603 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 0 min, 48 sec

13C OBSERVE

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

File: rjm5-062103acarbon
I400

PULSE SEQUENCE

Relax. delay 3.000 sec

Pulse 90.0 degrees

Acq. time 0.655 sec

Width 25000.0 Hz

96 repetitions

OBSERVE C13, 100.6097681 MHz

DECOUPLE H1, 400.1200527 MHz

Power 43 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 32768

Total time 10 hr, 10 min, 42 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: aln-2-131

VXR400

PULSE SEQUENCE

Relax. delay 2.000 sec

Pulse 90.0 degrees

Acq. time 3.744 sec

Width 4400.0 Hz

16 repetitions

OBSERVE H1, 399.7662755 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 1 min, 32 sec

¹³C OBSERVE

Pulse Sequence: s2pu1

Solvent: CDCl₃

Ambient temperature

File: rjms-062203acarbon
I400

PULSE SEQUENCE

Relax. delay 3.000 sec

Pulse 90.0 degrees

Acq. time 0.655 sec

Width 25000.0 Hz

41 repetitions

OBSERVE C13, 100.6097651 MHz

DECOUPLE H1, 400.120527 MHz

Power 43 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 32768

Total time 10 hr, 10 min, 42 sec

20

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 File: aln-compound11-1H
 VXR400

PULSE SEQUENCE
 Relax. delay 2.000 sec
 Pulse 90.0 degrees
 Acq. time 3.744 sec
 Width 4400.0 Hz
 16 repetitions
 OBSERVE H1, 399.7662755 MHz
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 65536
 Total time 1 min, 32 sec

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: aln-compound11-13C

VXR400

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 27.0 degrees

Acq. time 1.19 sec

Width 25000.0 Hz

131 repetitions

OBSERVE C13, 100.5213095 MHz

DECOUPLE H1, 399.7686931 MHz

Power 45 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 2.5 Hz

FT size 65536

Total time 61 hr, 20 min, 20 sec

13C OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: aln-2-diol1
VXR400

PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 90.0 degrees
Acq. time 3.744 sec
Width 4400.0 Hz
16 repetitions
OBSERVE H1, 399.7662756 MHz
DATA PROCESSING
Line broadening 2.5 Hz
FT size 65536
Total time 1 min, 32 sec

¹³C OBSERVE

Pulse Sequence: szpul

Solvent: CDCl₃

Ambient temperature

File: aln-compound12-13C

VXR400

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 27.0 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

1054 repetitions

OBSERVE C13, 100.5213111 MHz

DECOUPLE H1, 399.7685931 MHz

Power 45 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 2.5 Hz

FT size 65536

Total time 6 hr, 8 min, 2 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

File: aln-compound13-1H

VXR400

PULSE SEQUENCE

Relax. delay 2.000 sec

Pulse 90.0 degrees

Acq. time 3.744 sec

Width 4400.0 Hz

16 repetitions

OBSERVE H1, 399.7662755 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 1 min, 32 sec

¹³C OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
File: aln-compound13-13C
VXR400

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 27.0 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
1434 repetitions
OBSERVE C13, 100.521308 MHz
DECOUPLE H1, 399.7686931 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.5 Hz
FT size 65536
Total time 613 hr, 23 min, 23 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: aln-compound14-1H-1

VXR400

PULSE SEQUENCE

Relax. delay 2.000 sec

Pulse 90.0 degrees

Acq. time 3.744 sec

Width 4400.0 Hz

16 repetitions

OBSERVE H1, 399.7662751 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 1 min, 32 sec

¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: aln-compound14-13C

VXR400

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 9.0 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

1392 repetitions

OBSERVE C13, 100.5213103 MHz

DECOUPLE H1, 399.7686931 MHz

Power 45 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 2.5 Hz

FT size 65536

Total time 61 hr, 20 min, 20 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

File: aln-compound15-1H

VXR400

PULSE SEQUENCE

Relax. delay 2.000 sec

Pulse 90.0 degrees

Acq. time 3.744 sec

Width 4400.0 Hz

16 repetitions

OBSERVE H1, 399.7662758 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 1 min, 32 sec

¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: aln-compound15-13C

VXR400

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 25.7 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

1274 repetitions

OBSERVE C13, 100.5213077 MHz

DECOUPLE H1, 399.7686931 MHz

Power 49 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 2.5 Hz

FT size 65536

Total time 613 hr, 23 min, 23 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: aln-compound24-1H

VXR400

PULSE SEQUENCE

Relax. delay 2.000 sec

Pulse 90.0 degrees

Acq. time 3.744 sec

Width 4400.0 Hz

16 repetitions

OBSERVE H1, 399.7662757 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 1 min, 32 sec

¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: aln-compound24-13C

GEM300

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 27.0 degrees

Acq. time 1.815 sec

Width 18761.7 Hz

12560 repetitions

OBSERVE C13, 75.4519990 MHz

DECOUPLE H1, 300.0688577 MHz

Power 35 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 131072

Total time 78440 hr, 46 min, 24 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

File: aln-compound25

VXR400

PULSE SEQUENCE

Relax. delay 2.000 sec

Pulse 90.0 degrees

Acq. time 3.744 sec

Width 4400.0 Hz

16 repetitions

OBSERVE H1, 399.7662762 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 1 min, 32 sec

Capensifuranone (1)

¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: aln-compound25-13C

VXR400

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 25.7 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

16306 repetitions

OBSERVE C13, 100.5213054 MHz

DECOUPLE H1, 399.7686931 MHz

Power 49 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 2.5 Hz

FT size 65536

Total time 613 hr, 23 min, 23 sec

Capensifuranone (1)