Inverse-Electron-Demand Hetero-Diels-Alder Reaction of β,γ -Unsaturated α -Ketophos-phonates Catalyzed by Prolinal Dithioacetals

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Supporting Information

General experimental procedure for the synthesis of the catalysts:

To a solution of (*S*)-*N*-Boc-prolinal (199 mg, 1 mmol) and the thiol (2.2 mol) in CH₂Cl₂ (5 mL) was added indium(III) chloride (44.2 mg, 0.2 mmol) at room temperature. The reaction mixture was then refluxed at 40-45 °C for 1 h. Afterwards trifluoroacetic acid (0.25 mL) was added on the above reaction mixture and stirring was continued for another 3 h. Then the reaction mixture was cooled down to room temperature and it was made alkaline (pH $\approx$ 9) by adding 1 M aqueous NaOH solution. The mixture was extracted with CH₂Cl₂ (3 x 10 mL), washed with brine (2 x 10 mL) and dried over Na₂SO₄. Evaporation of the organic solvent provided the crude product which was purified by column chromatography over silica gel with ethyl acetate/hexane (50:50) as an eluent to furnish the desired product. The product was characterized by their corresponding spectroscopic ¹H and ¹³C NMR data.

(S)-2-[Bis(4-methylphenylthio)methyl]pyrrolidine (13):

Yellowish gummy liquid, yield 93%; ^1H NMR (500 MHz, CDCl_3): δ 7.39-7.27 (m, 4H), 7.11-7.09 (m, 4H), 4.38 (d, $J = 5.0$ Hz, 1H), 3.44-3.40 (m, 1H), 3.11-3.07 (m, 1H), 2.90-2.86 (m, 1H), 2.34 (s, 6H), 2.26 (br s, 1H), 1.99-1.73 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3): δ 138.0, 137.9, 133.4, 133.3, 131.2, 131.1, 130.0, 129.9, 66.3, 61.9, 47.0, 29.8, 25.9, 21.4.

(S)-2-[Bis(2,6-dimethylphenylthio)methyl]pyrrolidine (14):

Yellowish gummy liquid, yield 91%; ^1H NMR (500 MHz, CDCl_3): δ 7.14-7.05 (m, 6H), 4.10 (d, $J = 4.0$ Hz, 1H), 3.33-3.29 (m, 1H), 3.19-3.15 (m, 1H), 2.89-2.84 (m, 1H), 2.44 (s, 6H), 2.35 (s, 6H), 2.02-1.75 (m, 5H). ^{13}C NMR (125 MHz, CDCl_3): δ 138.0, 137.9, 133.4, 133.3, 131.2, 131.1, 130.0, 129.9, 66.3, 61.9, 47.0, 29.8, 25.9, 21.4.

General Procedure for Catalytic Enantioselective Inverse Electron-Demand Hetero-Diels-Alder Reaction:

To a stirred solution of aldehyde (58 mg, 1.0 mmol), catalyst (0.025 mmol) and silica (100 mg) in CH_2Cl_2 (1.0 mL) was added β,γ -unsaturated- α -ketophosphonate (0.25 mmol) at room temperature and the reaction mixture was allowed to stir for the time as specified in Table 2 (monitored by TLC). Afterwards the reaction mixture was directly purified by column chromatography over silica gel with EtOAc/hexane (60:40) as the eluent to provide the Diels–Alder adduct.

In the cases that the enantiomers of this adduct can not be separated directly by using HPLC columns, it was further oxidized by adding 2 equivalent of PCC in CH_2Cl_2 (1.0 mL) at room temperature and stirred for 24 h (monitored by TLC). Such a reaction mixture was purified by column chromatography over silica gel with EtOAc/hexane

(50:50) as the eluent to furnish the pure oxidized product. Either the Diels-Alder adducts or the oxidation products were characterized by their corresponding spectroscopic ^1H NMR and ^{13}C NMR data.

Diethyl *trans*-(4,5-dimethyl-6-oxo-5,6-dihydro-4*H*-pyran-2-yl)phosphonate:
Colorless oil; ^1H NMR (500 MHz, CDCl_3): δ 6.19 (dd, $J = 3.5, 10.0$ Hz, 1H), 4.20-4.13 (m, 4H), 2.44-2.42 (m, 1H), 2.37-2.33 (m, 1H), 1.36 (t, $J = 7.0$ Hz, 3H), 1.35 (t, $J = 7.0$ Hz, 3H), 1.30 (d, $J = 8.0$ Hz, 3H), 1.20 (d, $J = 7.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 170.4 (d), 142.8 (d, $J_{\text{cp}} = 231.62$ Hz), 125.5 (d, $J = 18.25$ Hz), 63.4 (t), 40.3 (d), 33.3 (d, $J = 12.37$ Hz), 19.2, 16.5 (q), 13.9.

Diethyl *trans*-(5-ethyl-4-methyl-6-oxo-5,6-dihydro-4*H*-pyran-2-yl)phosphonate:
colorless oil; ^1H NMR (500 MHz, CDCl_3): δ 6.25 (dd, $J = 5.0, 10.0$ Hz, 1H), 4.21-4.11 (m, 4H), 2.58-2.54 (m, 1H), 2.37-2.33 (m, 1H), 1.77-1.65 (m, 2H), 1.34 (t, $J = 7.0$ Hz, 3H), 1.32 (t, $J = 7.0$ Hz, 3H), 1.15 (d, $J = 7.0$ Hz, 3H), 0.99 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 169.3 (d), 142.6 (d, $J_{\text{cp}} = 231.37$ Hz), 124.8 (d, $J = 21.11$ Hz), 63.4 (t), 47.1 (d), 31.1 (d), 22.2, 19.3 (d), 16.5 (q), 11.1.

Diethyl *trans*-(5-butyl-4-methyl-6-oxo-5,6-dihydro-4*H*-pyran-2-yl)phosphonate:
colorless oil; ^1H NMR (500 MHz, CDCl_3): δ 6.26 (dd, $J = 4.0, 10.0$ Hz, 1H), 4.19-4.10 (m, 4H), 2.57-2.50 (m, 1H), 2.39-2.33 (m, 1H), 1.65-1.58 (m, 2H), 1.38-1.28 (m, 10 H), 1.15 (d, $J = 7.0$ Hz, 3H), 0.89 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 169.5

(d), 142.6 (d, $J_{cp} = 231.75$ Hz), 124.6 (d = 18.12 Hz), 63.4 (t), 45.8, 31.6 (d), 29.1, 28.9, 22.7, 19.5, 16.5 (q), 14.0.

Diethyl *trans*-(4-methyl-6-oxo-5-pentyl-5,6-dihydro-4*H*-pyran-2-yl)phosphonate:

colorless oil; ^1H NMR (500 MHz, CDCl_3): δ 6.26 ($J = 5.0, 10.0$ Hz, 1H), 4.20-4.08 (m, 4H), 2.57-2.50 (m, 1H), 2.49-2.37 (m, 1H), 1.66-1.57 (m, 2H), 1.39-1.23 (m, 12 H), 1.15 (d, $J = 6.5$ Hz, 3H), 0.87 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 169.5 (d), 142.6 (d, $J_{cp} = 231.25$ Hz), 124.6 (d, $J = 18.62$ Hz), 63.45 (t), 45.9, 31.8, 31.7 (d), 29.4, 26.4, 22.6, 19.4 (d), 16.4 (q), 14.1.

Diethyl *trans*-(4-ethyl-5-methyl-6-oxo-5,6-dihydro-4*H*-pyran-2-yl)phosphonate:

colorless oil; ^1H NMR (500 MHz, CDCl_3): δ 6.25 (dd, $J = 4.0, 10.0$ Hz, 1H), 4.19-4.09 (m, 4H), 2.52-2.46 (m, 1H), 2.30-2.26 (m, 1H), 1.65-1.60 (m, 1H), 1.46-1.40 (m, 1H), 1.33 (t, $J = 7.0$ Hz, 3H), 1.30 (t, $J = 7.00$ Hz, 3H), 1.26 (d, $J = 7.00$ Hz, 3H), 0.93 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 170.7 (d), 143.3 (d, $J_{cp} = 231.25$ Hz), 123.2, (d, $J = 16.87$ Hz), 63.4 (d), 39.7 (d), 37.9 (d), 25.6, 16.5 (t), 14.6, 10.3.

Diethyl *trans*-(4,5-diethyl-6-oxo-5,6-dihydro-4*H*-pyran-2-yl)phosphonate:

colorless oil; ^1H NMR (500 MHz, CDCl_3): δ 6.31 (dd, $J = 5.5, 10.5$ Hz), 4.22-4.12 (m, 4H), 2.50-2.37 (m, 2H), 1.71-1.65 (m, 2H), 1.56-1.47 (m, 2H), 1.37-1.33 (m, 6H), 1.02-0.88 (m,

6H); ^{13}C NMR (125 MHz, CDCl_3): δ 169.6 (d), 143.0 (d, $J_{\text{cp}} = 230.75$ Hz), 122.8 (d, $J = 18.5$ Hz), 63.49 (d), 45.1 (d), 38.13 (d), 26.7 (d), 23.3, 16.5 (t), 11.4, 10.9.

Diethyl (5-benzyl-6-hydroxy-4-methyl-5,6-dihydro-4H-pyran-2-yl)phosphonate: colorless gummy liquid; ^1H NMR (500 MHz, CDCl_3): δ (mixture of two diastereomers) 7.29-7.18 (m, 5H), 5.77 (d, $J = 11.5$ Hz, 1H), 5.08 (s, 0.8H), 5.07 (s, 0.2H), 4.35 (br s, 1H), 4.14-4.06 (m, 4H), 2.87-2.59 (m, 2H), 2.37-2.28 (m, 0.8H), 2.17 -2.13 (m, 0.2H), 1.95-1.90 (m, 0.2H), 1.74-1.70 (0.8H), 1.30 (2t, $J = 7.00$ Hz, 6H), 1.15 (d, $J = 7.00$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ (major diastereomer) 140.3 (d, $J_{\text{cp}} = 229.25$ Hz), 139.7, 129.3, 128.6, 126.4, 122.4 (d, $J = 21.00$ Hz), 92.5 (d), 62.8 (q), 45 (d), 35.2, 28.3 (d), 19.3 (d), 16.5 (q).

Diethyl (6-hydroxy-4-methyl-5-phenyl-5,6-dihydro-4H-pyran-2-yl)phosphonate ester: colorless gummy liquid; ^1H NMR (500 MHz, CDCl_3): δ (mixture of two diastereomers) 7.37-7.18 (m, 5H), 5.95 (d, $J = 11.00$ Hz, 0.8H), 5.89 (d, $J = 11.00$ Hz, 0.2 H), 5.47 (s, 0.8 H), 5.33 (d, $J = 8.00$ Hz, 0.2H), 4.23-4.08 (m, 4H), 2.95-2.90 (m, 0.8H), 2.80-2.70 (m, 0.2H), 2.68 (dd, $J = 4.00, 12.00$ Hz, 0.8H), 2.54-2.51 (m, 0.2 H), 1.40-1.32 (m, 6H), 0.97 (d, $J = 7.0$ Hz, 0.2H), 0.96 (d, $J = 7.00$, 0.8H); ^{13}C NMR (125 MHz, CDCl_3): δ (major diastereomer) 140.6 (d, $J_{\text{cp}} = 230.37$ Hz), 138.9, 129.7, 128.7, 127.5, 122.9 (d, $J = 21.00$ Hz), 94.5 (d), 62.9(t), 50.8, 27.6 (d), 18.6, 16.6 (q).

Diethyl (6-hydroxy-5-isopropyl-4-methyl-5,6-dihydro-4H-pyran-2-yl)phosphonate:

colorless gummy liquid; ^1H NMR (500 MHz, CDCl_3): δ (mixture of two diastereomers) 5.89 (dd, $J = 4.00, 11.50$ Hz, 0.4 H), 5.81 (dd, $J = 2.5, 11.5$ Hz, 0.6 H), 5.49 (br s, 0.6H), 5.30 (d, $J = 4.50$ Hz, 0.4 H), 4.19-4.08 (m, 4H), 2.53-2.18 (m, 2H), 2.08-1.97 (m, 1H), 1.37-1.33 (m, 6H), 1.20 (d, $J = 7.5$ Hz, 1.2 H), 1.04 (d, $J = 1.8$ Hz, 1.8 H), 1.00-0.96 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3): δ (major diastereomer) 139.7 (d, $J_{\text{cp}} = 229.37$ Hz), 123.8 (d, $J = 21.00$ Hz), 93.2 (d), 62.7 (t), 47.4 (d), 29.4, 26.5, 20.7, 18.5, 16.6 (q).

Diethyl (6-hydroxy-4-methyl-5-octyl-5,6-dihydro-4H-pyran-2-yl)phosphonate:

colorless gummy liquid; ^1H NMR (500 MHz, CDCl_3): δ (mixture of two diastereomers) 5.78 (d, $J = 3.5$ Hz, 0.2H), 5.74 (dd, $J = 2.5, 12.00$ Hz, 0.8H), 5.40 (br s, 0.8H), 5.14 (d, $J = 5.5$ Hz, 0.2H), 4.16-4.08 (m, 4H), 2.22-2.05 (m, 1H), 1.41-1.25 (m, 21H), 1.15 (d, $J = 7.5$ Hz, 0.6H), 1.07 (d, $J = 7.5$ Hz, 2.4H), 0.88-0.85 (m, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ (major diastereomer) 139.9 (d, $J_{\text{cp}} = 229.37$ Hz), 123.1 (d, $J = 20.87$ Hz), 93.2 (d), 62.8 (t), 42.9 (d), 32.1, 30.1, 29.7, 29.5, 28.9, 28.3, 27.1, 22.9, 19.1, 16.5 (q), 14.3.

Diethyl (6-hydroxy-5-methyl-4-phenyl-5,6-dihydro-4H-pyran-2-yl)phosphonate:

Colorless viscous liquid; (Anomeric mixture 78:22); ^1H NMR (500 MHz, CDCl_3) Major isomer: δ 7.35-7.32 (m, 2H), 7.28-7.25 (m, 1H), 7.2 -7.18 (m, 2H), 5.88 (dd, $J_1 = 11.0$ Hz, $J_2 = 5.2$ Hz, 1H), 5.41 (d, $J = 1.0$ Hz, 1H), 4.22-4.15 (m, 4H), 3.35-3.32 (m, 1H), 2.00-1.93 (m, 1H), 1.41-1.35 (m, 6H), 0.92 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 142.2, 128.8 (d), 128.6, 128.3, 127.2 (d), 119.7 (d, $J_{\text{cp}} = 21.0$ Hz), 95.4 (d), 63.1, 41.4 (d), 38.4, 16.7 (d), 14.9. Minor isomer; ^1H NMR (500 MHz, CDCl_3) δ 7.35-7.32 (m, 2H), 7.28-7.25 (m, 1H), 7.21-7.18 (m, 2H), 5.78 (dd, $J_1 = 11.0$ Hz, $J_2 = 5.2$ Hz, 1H), 5.08 (d, $J = 7.5$ Hz, 1H), 4.22-4.15 (m, 4H), 3.21-3.19 (m, 1H), 2.00-1.93 (m, 1H), 1.41-1.35 (m, 6H), 0.99 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 139.5, 128.8 (d), 128.6, 128.3, 127.2 (d), 119.1 (d, $J_{\text{cp}} = 21.0$ Hz), 99.6 (d), 63.1, 41.4 (d), 38.4, 16.7 (d), 15.1.

STANDARD PROTON PARAMETERS
VIII-SS-125p

Archive directory: /home/samanta/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul

Solvent: CDCl₃
Ambient temperature
File: VIII-SS-125p
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7995.2 Hz
8 repetitions
OBSERVE H1, 499.6752742 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 23 sec

13

STANDARD CARBON PARAMETERS
VIII-SS-125c

Archive directory: /home/samanta/vnmrsys/data
Sample directory:

Pulse Sequence: s2pu1

Solvent: CDCl₃
Ambient temperature
User: 1-14-87
File: VIII-SS-125c
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
1344 repetitions
OBSERVE C13, 125.6434176 MHz
DECOUPLE H1, 499.6777727 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 1 hr, 16 min, 58 sec

13

STANDARD PROTON PARAMETERS
VIII-SS 143p

Archive directory: /home/samanta/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pu1

Solvent: CDCl3
Ambient temperature
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7995.2 Hz
8 repetitions
OBSERVE H1, 499.6752742 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 23 sec

14

STANDARD CARBON PARAMETERS
VIII-SS-143c

Archive directory: /home/samanta/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul

Solvent: CDC13
Ambient temperature
User: 1-14-87
File: VIII-SS-143c
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
2816 repetitions
OBSERVE C13, 125.6434176 MHz
DECOUPLE H1, 499.677727 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 1 hr, 55 min, 28 sec

14

STANDARD PROTON PARAMETERS
VIII-SS-151p

Archive directory: /home/samanta/vnmrsys/data
Sample directory:

Pulse Sequence: s2pu1

Solvent: CDCl₃
Ambient temperature
File: VIII-SS-151p
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7995.2 Hz
8 repetitions
OBSERVE H1, 499.6752742 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 23 sec

STANDARD CARBON PARAMETERS
VIII-SS-151c

Archive directory: /home/samanta/vnmrsys/data
Sample directory:

Pulse Sequence: s2pu1

Solvent: CDCl₃
Ambient temperature
User: 1-14-87
File: VIII-SS-151c
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
3000 repetitions
OBSERVE C13, 125.6434176 MHz
DECOUPLE H1, 499.677727 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 1 hr, 55 min, 28 sec

15a

STANDARD PROTON PARAMETERS

Archive directory: /home/samanta/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: relayh

Solvent: CDCl₃
Ambient temperature
INOVA-500 "Inova500"

Relax. delay 1.000 sec
COSY 90-90
Acq. time 0.126 sec
Width 4054.9 HZ
2D Width 4054.9 HZ
4 repetitions
128 increments
OBSERVE H1, 499.6752813 MHz
DATA PROCESSING
Sine bell 0.063 sec
F1 DATA PROCESSING
Sine bell 0.032 sec
FT size 1024 x 1024
Total time 9 min, 52 sec

STANDARD PROTON PARAMETERS

Archive directory: /home/samanta/vnmr/sys/data
Sample directory:
File: PROTON

Pulse Sequence: noesy

Solvent: CDC13
Ambient temperature
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Mixing 0.600 sec
Acq. time 0.126 sec
Width 4054.9 Hz
2D Width 4054.9 Hz
16 repetitions
2 x 168 increments
OBSERVE H1, 499.6752813 MHz
DATA PROCESSING
F1 DATA PROCESSING
Line broadening 0.3 Hz
FT size 1024 x 1024
Total time 2 hr, 37 min, 49 sec

15a

NOESY (positive)

STANDARD PROTON PARAMETERS

Archive directory: /home/samanta/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: noesy

Solvent: CDC13
Ambient temperature
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Mixing 0.600 sec
Acq. time 0.126 sec
Width 4054.9 Hz
2D Width 4054.9 Hz
16 repetitions
2 x 168 increments
OBSERVE H1, 499.6752813 MHz
DATA PROCESSING
F1 DATA PROCESSING
Line broadening 0.3 Hz
FT size 1024 x 1024
Total time 2 hr, 37 min, 49 sec

15a NOESY (negative)

STANDARD PROTON PARAMETERS
I-JLK-6p

Archive directory: /home/samanta/vnmrsys/data
Sample directory:

Pulse Sequence: s2pu1

Solvent: CDC13
Ambient temperature
File: I-JLK-6p
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7995.2 Hz
8 repetitions
OBSERVE H1, 499.6752742 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 23 sec

STANDARD CARBON PARAMETERS
I-JLK-6c

Archive directory: /home/samanta/vnmrsys/data
Sample directory:

Pulse Sequence: s2pu1

Solvent: CDC13
Ambient temperature
User: 1-14-87
File: I-JLK-6c
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
3000 repetitions
OBSERVE C13, 125.6434176 MHz
DECOUPLE H1, 499.6777727 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 1 hr, 55 min, 28 sec

STANDARD PROTON PARAMETERS
VIII-SS-150p

Archive directory: /home/samanta/vnmrsys/data
Sample directory:

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

File: VIII-SS-150p

INOVA-500 "Inova500"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.892 sec

Width 7995.2 Hz

8 repetitions

OBSERVE H1, 499.6752742 MHz

DATA PROCESSING

FT size 32768

Total time 0 min, 23 sec

STANDARD CARBON PARAMETERS
VIII-SS-150c

Archive directory: /home/samanta/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul

Solvent: CDC13
Ambient temperature
User: 1-14-87
File: VIII-SS-150c
INOV-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
1856 repetitions
OBSERVE C13, 125.6434176 MHz
DECOUPLE H1, 499.6777727 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 1 hr, 16 min, 58 sec

STANDARD PROTON PARAMETERS
IX-SS-26p

Archive directory: /home/samanta/vnmrsys/data
Sample directory:

Pulse Sequence: s2pu1

Solvent: CDCl₃
Ambient temperature
File: IX-SS-26p
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7995.2 Hz
8 repetitions
OBSERVE H1, 499.6752742 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 23 sec

15d

STANDARD CARBON PARAMETERS
IX-SS-26c

Archive directory: /home/samanta/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul

Solvent: CDCl₃
Ambient temperature
User: 1-14-87
File: IX-SS-26c
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
3456 repetitions
OBSERVE C13, 125.6434176 MHz
DECOUPLE H1, 499.6777727 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 2 hr, 14 min, 42 sec

STANDARD PROTON PARAMETERS
I-Jlk-8p

Archive directory: /home/samanta/vnmrSYS/data
Sample directory:

Pulse Sequence: s2pu1

Solvent: CDC13
Ambient temperature

File: I-JLK-8p
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7995.2 Hz
8 repetitions
OBSERVE H1, 499.6752742 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 23 sec

STANDARD CARBON PARAMETERS
I-JLK 8c

Archive directory: /home/samanta/vnmrsys/data
Sample directory:

Pulse Sequence: s2pu1

Solvent: CDC13
Ambient temperature
User: 1-14-87
File: VIII-JLK-8c
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
3136 repetitions
OBSERVE C13, 125.6434176 MHz
DECOUPLE H1, 499.677727 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 2 hr, 3 min, 9 sec

5e

STANDARD PROTON PARAMETERS
IX-SS-14p

Archive directory: /home/samanta/vnmrsys/data
Sample directory:

Pulse Sequence: s2pu1

Solvent: CDCl3
Ambient temperature
File: IX-SS-14p
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7995.2 Hz
30 repetitions
OBSERVE H1, 499.6752742 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 27 sec

STANDARD CARBON PARAMETERS
IX-SS-14c

Archive directory: /home/samanta/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul

Solvent: CDCl₃
Ambient temperature
User: 1-14-87
File: IX-SS-14
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
22000 repetitions
OBSERVE C13, 125.6434176 MHz
DECOUPLE H1, 499.6777727 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 14 hr, 6 min, 46 sec

5f

STANDARD PROTON PARAMETERS
VIII-SS-119phenyl

Archive directory: /home/samanta/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: VIII-SS-119phenyl

INOVA-500 "Inova500"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.882 sec

Width 7995.2 Hz

8 repetitions

OBSERVE H1, 499.6752742 MHz

DATA PROCESSING

FT size 32768

Total time 0 min, 23 sec

5g

STANDARD CARBON PARAMETERS
VIII-SS-140c

Archive directory: /home/samanta/vnmrSYS/data
Sample directory:

Pulse Sequence: s2pu1

Solvent: CDC13
Ambient temperature
User: 1-14-87
File: VIII-SS-140c
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
3712 repetitions
OBSERVE C13, 125.6434176 MHz
DECOUPLE H1, 499.6777727 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 2 hr, 33 min, 57 sec

STANDARD PROTON PARAMETERS
VIII-SS-141p

Archive directory: /home/samanta/vnmrsys/data
Sample directory:

Pulse Sequence: s2pu1

Solvent: CDCl₃
Ambient temperature
File: VIII-SS-141p
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7995.2 Hz
8 repetitions
OBSERVE H1, 499.6752742 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 23 sec

5h

STANDARD CARBON PARAMETERS
VIII-SS-141c

Archive directory: /home/samanta/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul

Solvent: CDC13
Ambient temperature
User: 1-14-87
File: VIII-SS-141c
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
2500 repetitions
OBSERVE C13, 125.6434176 MHz
DECOUPLE H1, 499.6777727 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 1 hr, 36 min, 13 sec

5h

STANDARD PROTON PARAMETERS
IX-SS-38p

Archive directory: /home/samanta/vnmrsys/data
Sample directory:

Pulse Sequence: s2pu1

Solvent: CDC13

Ambient temperature

File: IX-SS-38p

INOVA-500 "Inova500"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.892 sec

Width 7995.2 Hz

8 repetitions

OBSERVE H1, 499.6752742 MHz

DATA PROCESSING

FT size 32768

Total time 0 min, 23 sec

STANDARD CARBON PARAMETERS
IX-SS-38c

Archive directory: /home/samanta/vnmrsys/data
Sample directory:

Pulse Sequence: s2pu1

Solvent: CDC13
Ambient temperature
User: 1-14-87
File: IX-SS-38c
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
3500 repetitions
OBSERVE C13, 125.6434176 MHz
DECOUPLE H1, 499.6777727 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 2 hr, 14 min, 42 sec

STANDARD PROTON PARAMETERS
IX-SS 41p

Archive directory: /home/samanta/vnmrsys/data
Sample directory:

Pulse Sequence: s2pu1

Solvent: CDCl3
Ambient temperature
File: IX-SS-41p
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7995.2 Hz
8 repetitions
OBSERVE H1, 499.6752742 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 23 sec

STANDARD CARBON PARAMETERS
IX-SS-41c

Archive directory: /home/samanta/vnmrsys/data
Sample directory:

Pulse Sequence: s2pu1

Solvent: CDC13
Ambient temperature
User: 1-14-87
File: IX-SS-41c
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
4000 repetitions
OBSERVE C13, 125.6434176 MHz
DECOUPLE H1, 499.6777727 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 2 hr, 33 min, 57 sec

STANDARD PROTON PARAMETERS

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:

Pulse Sequence: s2pu1

Solvent: CDCl3
Ambient temperature
File: III-TM-55p1
INOVA-500 "Inova500"

Relax. delay 1.000 sec
Pulse 67.5 degrees
Acq. time 1.892 sec
Width 7996.0 Hz
8 repetitions
OBSERVE H1, 499.6752742 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 23 sec

5k

¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDC13

Ambient temperature

Mercury-300BB "Varian300"

Pulse 73.6 degrees

Acq. time 1.815 sec

Width 18761.7 Hz

3000 repetitions

OBSERVE C13, 75.3709880 MHz

DECOUPLE H1, 299.7467965 MHz

Power 33 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 131072

Total time 0 min, 0 sec

5k

Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
 Data: C:\EZStart\Projects\Default\Data\viii-ss-83d
 User: System
 Acquired: 3/7/2007 9:52:05 AM
 Printed: 4/11/2007 10:35:14 AM

15a

Racemic

SPD-10AVvp
 Ch1-220nm
 Results

Retention Time	Area	Area %	Height	Height %
18.692	19796940	49.92	711872	51.34
19.550	19863617	50.08	674794	48.66
Totals	39660557	100.00	1386666	100.00

Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
 Data: C:\EZStart\Projects\Default\Data\viii-ss-139d
 User: System
 Acquired: 2/23/2007 12:09:42 PM
 Printed: 4/11/2007 10:36:32 AM

SPD-10AVvp
 Ch1-220nm
 Results

Retention Time	Area	Area %	Height	Height %
19.392	27301856	92.67	888521	92.34
20.308	2158461	7.33	73744	7.66
Totals	29460317	100.00	962265	100.00

Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
Data: C:\EZStart\Projects\Default\Data\I-JLK-6B
User: System
Acquired: 2/12/2007 1:42:18 PM
Printed: 4/11/2007 10:37:13 AM

15b

Racemic

SPD-10AVvp
Ch1-220nm
Results

Retention Time	Area	Area %	Height	Height %
8.875	25208566	48.41	1385426	51.29
9.967	25070162	48.14	1192320	44.14
10.733	1143113	2.20	81785	3.03
10.875	651476	1.25	41531	1.54
Totals	52073317	100.00	2701062	100.00

Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
 Data: C:\EZStart\Projects\Default\Data\viii-ss-148
 User: System
 Acquired: 3/2/2007 9:37:16 AM
 Printed: 4/11/2007 10:37:54 AM

15b

SPD-10AVvp
 Ch1-220nm
 Results

Retention Time	Area	Area %	Height	Height %
9.033	14252053	90.75	794463	91.17
10.292	1451969	9.25	76906	8.83
Totals	15704022	100.00	871369	100.00

Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
 Data: C:\EZStart\Projects\Default\Data\I-JLK-4b
 User: System
 Acquired: 2/6/2007 1:24:18 PM
 Printed: 4/11/2007 10:38:30 AM

SPD-10AVvp
 Ch1-220nm
 Results

Retention Time	Area	Area %	Height	Height %
8.958	10404041	50.29	651836	45.65
9.633	10282462	49.71	776017	54.35
Totals	20686503	100.00	1427853	100.00

Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
Data: C:\EZStart\Projects\Default\Data\ix-ss-15a
User: System
Acquired: 3/9/2007 10:25:43 AM
Printed: 4/11/2007 10:39:13 AM

SPD-10AVvp Ch1-220nm Results

Retention Time	Area	Area %	Height	Height %
10.867	39343	0.41	13553	2.91
11.217	8733126	90.90	409981	88.14
12.233	835145	8.69	41592	8.94
Totals	9607614	100.00	465126	100.00

Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
 Data: C:\EZStart\Projects\Default\Data\IX-SS-26A
 User: System
 Acquired: 3/15/2007 9:18:34 AM
 Printed: 4/11/2007 10:39:53 AM

SPD-10AVvp
Ch1-220nm
Results

Retention Time	Area	Area %	Height	Height %
11.750	21028386	50.26	1221205	53.83
12.175	20810140	49.74	1047265	46.17
Totals	41838526	100.00	2268470	100.00

Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
 Data: C:\EZStart\Projects\Default\Data\IX-SS-30
 User: System
 Acquired: 3/15/2007 10:10:08 AM
 Printed: 4/11/2007 10:40:28 AM

SPD-10AVvp
 Ch1-220nm
 Results

Retention Time	Area	Area %	Height	Height %
11.700	8223749	94.35	454720	90.70
12.042	492739	5.65	46602	9.30
Totals	8716488	100.00	501322	100.00

Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met

Data: C:\EZStart\Projects\Default\Data\I-JLK-8g

User: System

Acquired: 2/27/2007 4:55:07 PM

Printed: 4/11/2007 10:41:07 AM

SPD-10AVvp

Ch1-220nm

Results

Retention Time	Area	Area %	Height	Height %
6.450	13923804	38.72	779490	42.40
8.408	3914981	10.89	188137	10.23
8.942	13988825	38.90	610815	33.22
10.825	2280796	6.34	131439	7.15
10.875	1852941	5.15	128560	6.99
Totals	35961347	100.00	1838441	100.00

Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
 Data: C:\EZStart\Projects\Default\Data\viii-ss-147
 User: System
 Acquired: 3/1/2007 10:02:51 AM
 Printed: 4/11/2007 10:41:59 AM

SPD-10AVvp
 Ch1-220nm
 Results

Retention Time	Area	Area %	Height	Height %
6.808	25865466	66.34	1189539	68.60
8.492	518045	1.33	41502	2.39
8.933	10093224	25.89	389446	22.46
9.442	2013600	5.16	93586	5.40
11.458	501511	1.29	19856	1.15
Totals	38991846	100.00	1733929	100.00

Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
 Data: C:\EZStart\Projects\Default\Data\I-JLK-11A
 User: System
 Acquired: 3/7/2007 12:39:15 PM
 Printed: 4/11/2007 10:42:40 AM

**SPD-10AVvp
 Ch1-220nm
 Results**

Retention Time	Area	Area %	Height	Height %
8.967	4161426	30.16	210659	34.22
9.867	3031881	21.97	137885	22.40
10.317	2670322	19.35	130380	21.18
10.875	756	0.01	215	0.03
13.283	3935508	28.52	136479	22.17
Totals	13799893	100.00	615618	100.00

Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
 Data: C:\EZStart\Projects\Default\Data\ix-ss-14c
 User: System
 Acquired: 3/8/2007 1:42:19 PM
 Printed: 4/11/2007 10:43:18 AM

SPD-10AVvp
 Ch1-220nm
 Results

Retention Time	Area	Area %	Height	Height %
7.517	30970	0.56	3157	1.28
8.083	3003742	54.64	137394	55.80
8.858	2191273	39.86	90799	36.88
9.217	91674	1.67	7972	3.24
11.817	179854	3.27	6893	2.80

Totals	5497513	100.00	246215	100.00
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Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
Data: C:\EZStart\Projects\Default\Data\viii-ss-120
User: System
Acquired: 2/13/2007 1:24:34 PM
Printed: 4/11/2007 10:43:50 AM

Racemic

SPD-10AVvp
Ch1-220nm
Results

Retention Time	Area	Area %	Height	Height %
6.967	21239799	33.07	1643331	44.88
8.550	23799205	37.06	1226816	33.50
8.842	969331	1.51	138195	3.77
12.050	9081849	14.14	342393	9.35
13.467	9136143	14.22	311053	8.49
Totals	64226327	100.00	3661788	100.00

Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
 Data: C:\EZStart\Projects\Default\Data\VIII-SS-140
 User: System
 Acquired: 2/24/2007 10:36:18 AM
 Printed: 4/11/2007 10:44:26 AM

SPD-10AVvp
 Ch1-220nm
 Results

Retention Time	Area	Area %	Height	Height %
7.033	12372927	56.16	989452	70.19
8.733	3025364	13.73	165575	11.75
8.983	499393	2.27	33374	2.37
12.392	5157146	23.41	187772	13.32
13.858	977724	4.44	33526	2.38
Totals	22032554	100.00	1409699	100.00

Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
 Data: C:\EZStart\Projects\Default\Data\wHHHD
 User: System
 Acquired: 2/13/2007 1:45:56 PM
 Printed: 4/11/2007 11:09:45 AM

Racemic

SPD-10AVvp
 Ch1-220nm
 Results

Retention Time	Area	Area %	Height	Height %
6.300	11556325	39.48	790942	41.93
7.242	11650663	39.80	764468	40.53
8.358	3097389	10.58	180992	9.60
9.792	2966062	10.13	149717	7.94
Totals	29270439	100.00	1886119	100.00

Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
 Data: C:\EZStart\Projects\Default\Data\viii-ss-144
 User: System
 Acquired: 3/1/2007 5:03:47 PM
 Printed: 4/11/2007 11:10:22 AM

SPD-10AVvp
 Ch1-220nm
 Results

Retention Time	Area	Area %	Height	Height %
6.358	4607703	74.83	282593	75.96
7.325	140763	2.29	10822	2.91
8.417	1382824	22.46	76919	20.67
9.942	26337	0.43	1718	0.46
Totals	6157627	100.00	372052	100.00

Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
Data: C:\EZStart\Projects\Default\Data\IX-SS-38A
User: System
Acquired: 3/20/2007 9:52:54 AM
Printed: 4/11/2007 11:10:58 AM

SPD-10AVvp
Ch1-220nm
Results

Retention Time	Area	Area %	Height	Height %
13.450	33463301	50.31	1706485	50.05
14.033	33048745	49.69	1703196	49.95
Totals	66512046	100.00	3409681	100.00

Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
 Data: C:\EZStart\Projects\Default\Data\IX-SS-42A
 User: System
 Acquired: 3/21/2007 10:15:42 AM
 Printed: 4/11/2007 11:11:50 AM

15i

SPD-10AVvp
 Ch1-220nm
 Results

Retention Time	Area	Area %	Height	Height %
10.867	3903	0.13	1549	0.79
11.175	2600032	89.69	176106	89.92
11.708	294913	10.17	18201	9.29
Totals	2898848	100.00	195856	100.00

Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
 Data: C:\EZStart\Projects\Default\Data\IX-SS-41A
 User: System
 Acquired: 3/21/2007 1:01:01 PM
 Printed: 4/11/2007 11:12:28 AM

15 j

Racemic

SPD-10AVvp
 Ch1-220nm
 Results

Retention Time	Area	Area %	Height	Height %
9.467	1841619	14.23	117836	15.93
9.992	5504792	42.54	306844	41.48
10.550	5449086	42.11	280535	37.92
10.875	143310	1.11	34586	4.68
Totals	12938807	100.00	739801	100.00

Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
Data: C:\EZStart\Projects\Default\Data\ix-ss-43
User: System
Acquired: 3/22/2007 10:09:01 AM
Printed: 4/11/2007 11:13:30 AM

15 j

SPD-10AVvp
Ch1-220nm
Results

Retention Time	Area	Area %	Height	Height %
9.758	490788	3.58	25958	2.27
10.333	722414	5.27	40834	3.57
10.867	5306716	38.72	538163	47.09
10.875	7185344	52.43	537830	47.06
Totals	13705262	100.00	1142785	100.00

Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
 Data: C:\EZStart\Projects\Default\Data\IX-SS-19
 User: System
 Acquired: 3/12/2007 9:01:10 AM
 Printed: 5/28/2007 12:01:13 PM

SPD-10AVvp
 Ch1-220nm
 Results

Retention Time	Area	Area %	Height	Height %
5.083	17762148	35.55	1798620	39.81
5.633	18231785	36.49	1667248	36.90
6.150	1383531	2.77	101053	2.24
6.625	1292165	2.59	98797	2.19
7.075	5628483	11.26	452813	10.02
8.475	5669029	11.35	399800	8.85
Totals	49967141	100.00	4518331	100.00

Area % Report

Method Name: C:\EZStart\Projects\Default\Methods\AS.met
Data: C:\EZStart\Projects\Default\Data\IX-SS-21A
User: System
Acquired: 3/13/2007 9:38:43 AM
Printed: 5/28/2007 12:00:02 PM

5k

(Chiral, 19% ee)

SPD-10AVvp**Ch1-220nm****Results**

Retention Time	Area	Area %	Height	Height %
5.208	3858050	59.62	378822	61.25
5.792	2612546	40.38	239708	38.75
Totals	6470596	100.00	618530	100.00