Supporting Information

(Experimental Procedure and NMR Spectral Data)

Practical Total Syntheses of Acromelic Acids A and B

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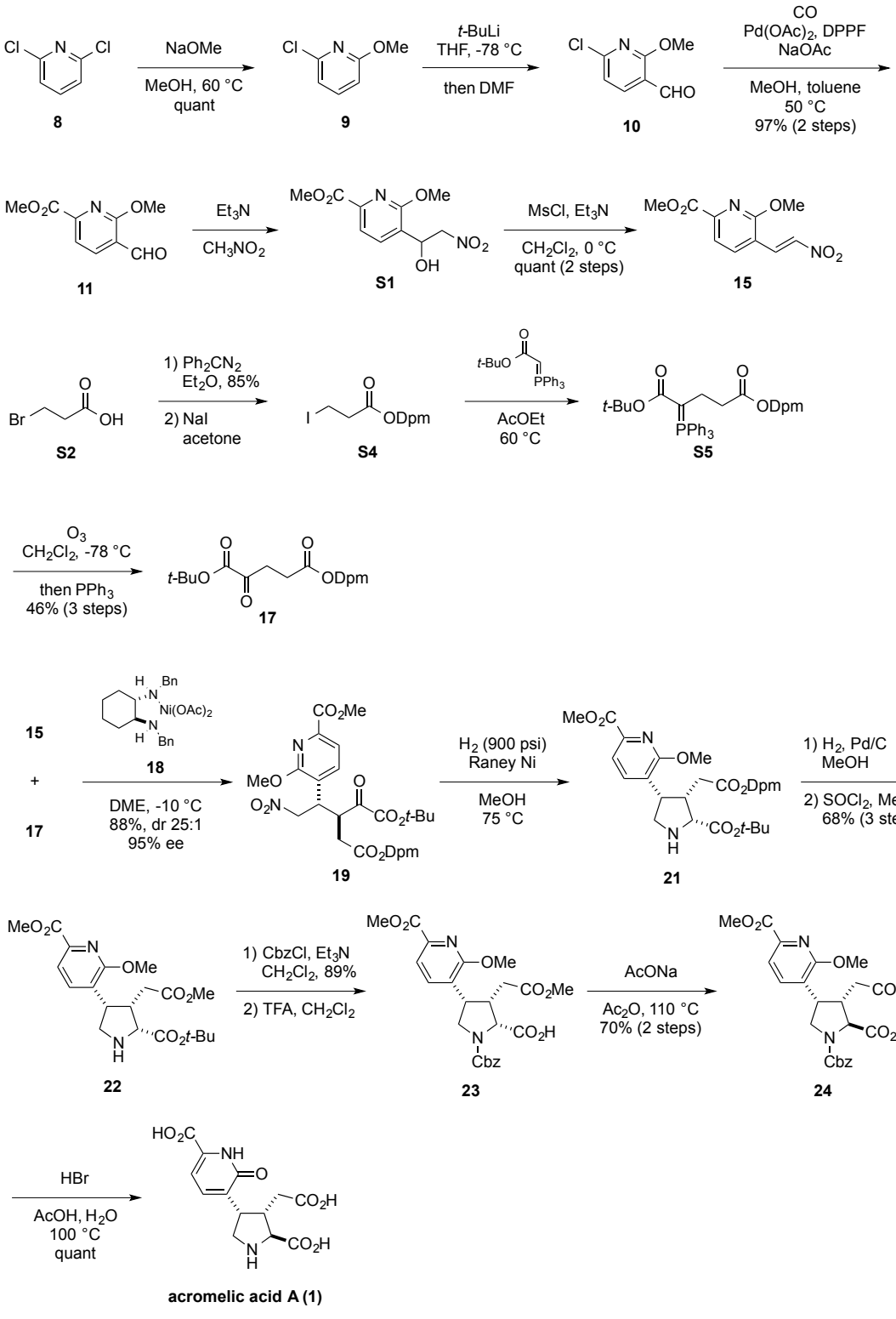
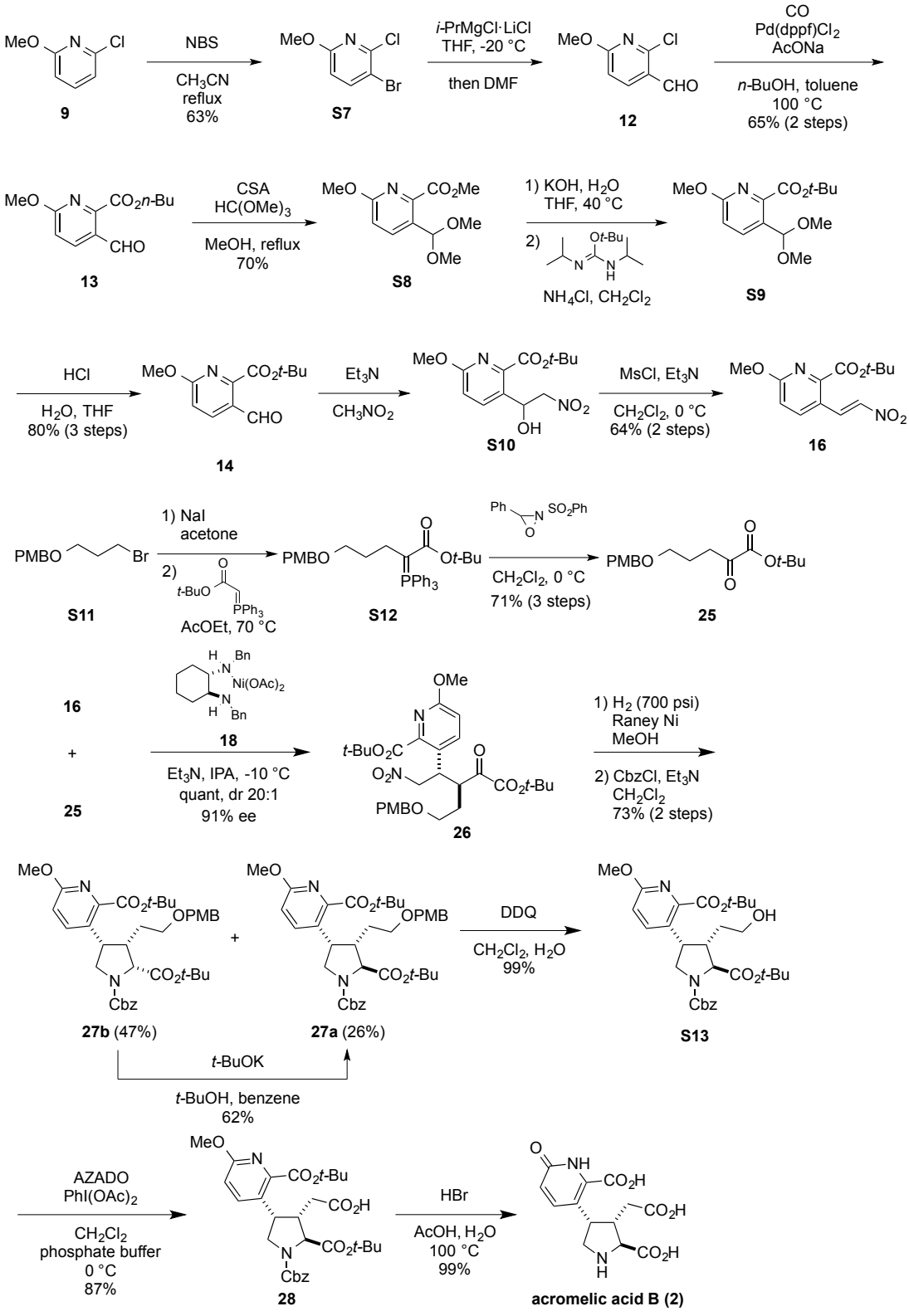

NaOMe
MeOH, 60 °C
quant
t-BuLi
THF, -78 °C
then DMF
CO
Pd(OAc)2, DPPF
NaOAc
MeOH, toluene
50 °C
97% (2 steps)
Et3N
CH3NO2
MsCl, Et3N
CH2Cl2, 0 °C
quant (2 steps)
1) Ph2CN2
Et2O, 85%
2) NaI
acetone
AcOEt
60 °C
O3
CH2Cl2, -78 °C
then PPh3
46% (3 steps)
DME, -10 °C
88%, dr 25:1
95% ee
H2 (900 psi)
Raney Ni
MeOH
75 °C
1) H2, Pd/C
MeOH
2) SOCl2, MeOH
68% (3 steps)
1) CbzCl, Et3N
CH2Cl2, 89%
2) TFA, CH2Cl2
AcONa
Ac2O, 110 °C
70% (2 steps)
HBr
AcOH, H2O
100 °C
quant
8
9
10
11
S1
15
S2
S4
S5
17
18
19
21
22
23
24
acromelic acid A (1)


MeO
N
Cl
9
NBS
CH3CN
reflux
63%
S7
i-PrMgCl·LiCl
THF, -20 °C
then DMF
12
CO
Pd(dppf)Cl2
AcONa
n-BuOH, toluene
100 °C
65% (2 steps)
CO2n-Bu
CHO
13
CSA
HC(OMe)3
MeOH, reflux
70%
CO2Me
OMe
S8
1) KOH, H2O
THF, 40 °C
2)
Ot-Bu
NH4Cl, CH2Cl2
CO2t-Bu
S9
HCl
H2O, THF
80% (3 steps)
14
Et3N
CH3NO2
NO2
OH
S10
MsCl, Et3N
CH2Cl2, 0 °C
64% (2 steps)
16
PMBO
1) NaI
acetone
2)
t-BuO
PPh3
AcOEt, 70 °C
S11
S12
Ph
SO2Ph
CH2Cl2, 0 °C
71% (3 steps)
25
Bn
Ni(OAc)2
18
Et3N, IPA, -10 °C
quant, dr 20:1
91% ee
OMe
t-BuO2C
O2N
CO2t-Bu
26
1) H2 (700 psi)
Raney Ni
MeOH
2) CbzCl, Et3N
CH2Cl2
73% (2 steps)
OPMB
Cbz
27b (47%)
27a (26%)
DDQ
CH2Cl2, H2O
99%
S13
t-BuOK
t-BuOH, benzene
62%
AZADO
PhI(OAc)2
CH2Cl2
phosphate buffer
0 °C
87%
CO2H
28
HBr
AcOH, H2O
100 °C
99%
NH
acromelic acid B (2)

Analysis instruments

Nuclear magnetic resonance [^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz)] spectra were determined on JEOL ECA-500 instrument. Chemical shifts for ^{1}H NMR were reported in parts per million downfields from tetramethylsilane (δ) as the internal standard and coupling constants were in hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Chemical shifts for ^{13}C NMR were reported in ppm relative to the centerline of a triplet at 77.0 ppm for deuteriochloroform.

Melting points (Mp), determined on a Yanaco Micro Melting Point Apparatus MP-S3, are uncorrected.

High-resolution mass spectra (HRMS) were obtained on a BRUKER DALTONICS micrOTOF (ESI).

Infrared (IR) spectra were recorded on a SHIMADZU IRPrestige-21.

Optical rotations were measured on a JASCO P-1030 Polarimeter at RT using the sodium D line.

Analytical thin layer chromatography (TLC) was performed on Merck precoated analytical plates, 0.25 mm thick, silica gel 60 F254.

Column chromatography separations were performed on KANTO CHEMICAL Silica Gel 60 (spherical) 40 - 50 μm, Silica Gel 60 (spherical) 63 - 210 μm or Silica Gel 60 N (spherical, neutral) 63 – 210μm.

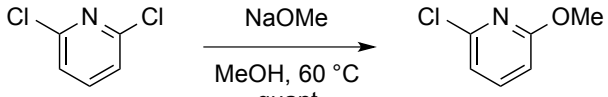
Chiral HPLC was performed on SPD-M20A, CTO-20A and LC-20AD using 0.46 cm ϕ × 25 cm ChiralPak AD-H, ChiralCel OD-H from Daicel.

Reagents and solvents were commercial grades and were used as supplied with the following exceptions.

1) Dichloromethane, diethyl ether, *n*-hexane, tetrahydrofuran and toluene: dried over molecular sieves 4A.

2) Methanol and acetonitrile: dried over molecular sieves 3 A.

2-Chloro-6-methoxypyridine (9)



8 **9**

To a stirred solution of 2,6-dichloropyridine (**8**) (68.9 g, 466 mmol) in MeOH (500 mL) was added NaOMe (100 g, 1.86 mol, 4.0 equiv) and the mixture was stirred at 60 °C for 24 h. After cooling to room temperature, the mixture was quenched with 2 M aqueous HCl, and extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to afford **9** (66.9 g, quant) as a colorless oil.

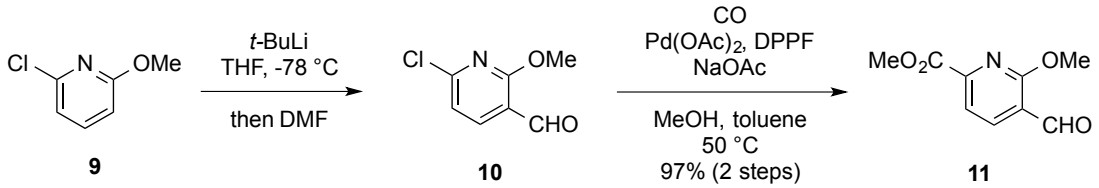
IR (film, cm^{-1}) 1599, 1585, 1560, 1468, 1410, 1302, 1265, 1152, 1024, 876, 789.

^1H NMR ($CDCl_3$, 500 MHz) δ 7.51 (t, *J* = 7.37 Hz, 1H), 6.90 (d, *J* = 7.37 Hz, 1H), 6.65 (d, *J* = 7.37 Hz, 1H), 3.94 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.9, 148.4, 140.5, 116.2, 109.1, 54.0.

HRMS (ESI-TOF) calcd for C_6H_7ClNO $(M+H)^+$ 144.0211, found 144.0211.

Methyl 5-formyl-6-methoxypicolinate (11)



9 **10** **11**

To a stirred solution of **9** (20.8 g, 145 mmol) in THF (400 mL) was added *t*-BuLi in heptane (ca.1.6 M, 100 mL, 160 mmol, 1.1 equiv) at -78 °C under Ar atmosphere. After stirring at the same temperature for 1 h, DMF (33.8 mL, 435 mmol, 3.0 equiv) was added dropwise. After being stirred at the same temperature for 30 min, the reaction mixture was warmed to room temperature over 30 min. After stirring, the reaction was quenched with 2 M aqueous HCl, and extracted with AcOEt. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was used in the next step without further purification.

To a suspention of **10** (crude, 145 mmol) and NaOAc (17.8 g, 218 mmol, 1.5 equiv) in MeOH / toluene (300 mL / 150 mL) were added $Pd(OAc)_2$ (651 mg, 2.90 mmol, 0.02 equiv) and DPPF (2.41 g, 4.35 mmol, 0.03 equiv) under Ar atmosphere. The reaction mixture was stirred at 50 °C under CO atmosphere for 23 h. After stirring, the reaction was quenched with 1 M aqueous HCl, and extracted with AcOEt. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (*n*-Hexane / AcOEt = 2:1) to afford **11** (27.5 g, 97%) as a colorless solid.

Mp. 87 - 88 °C.

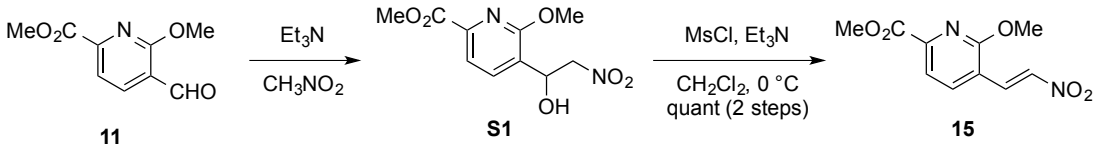
IR (film, cm^{-1}) 1726, 1694, 1591, 1456, 1381, 1254, 1134.

^1H NMR ($CDCl_3$, 500 MHz) δ 10.4 (s, 1H), 8.22 (d, *J* = 7.94 Hz, 1H), 7.79 (d, *J* = 7.94 Hz, 1H), 4.17 (s, 3H), 4.00 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 188.6, 164.7, 164.0, 149.8, 138.6, 121.2, 118.5, 54.3, 53.0.

HRMS (ESI-TOF) calcd for $C_9H_9NO_4Na$ $(M+Na)^+$ 218.0424, found 218.0428.

(*E*)-Methyl 6-methoxy-5-(2-nitrovinyl)picolinate (15)



To a stirred solution of **11** (616 mg, 3.16 mmol) in CH_3NO_2 (10 mL) was added Et_3N (319 mg, 3.16 mmol, 1.0 equiv) at room temperature. After stirring for 1.5 h, the solvent was removed under reduced pressure to afford crude **S1** as a yellow solid.

To the residue dissolved in CH_2Cl_2 (10 mL) were added Et_3N (319 mg, 3.16 mmol, 1.0 equiv) and MsCl (996 mg, 4.74 mmol, 2.0 equiv) at 0 °C. After being stirred for 3 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography ($CHCl_3$ / AcOEt = 9:1) to afford **15** (750 mg, quant) as a pale yellow solid.

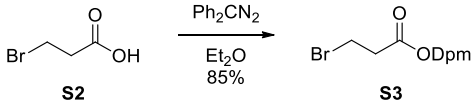
IR (film, cm^{-1}) 1726, 1632, 1516, 1342, 1271.

^1H NMR ($CDCl_3$, 500 MHz) δ 8.02 (d, J = 13.8 Hz, 1H), 7.98 (d, J = 13.8 Hz, 1H), 7.87 (d, J = 7.45 Hz, 1H), 7.79 (d, J = 7.45 Hz, 1H), 4.19 (s, 3H), 3.99 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.8, 161.9, 147.3, 141.9, 140.9, 132.7, 118.8, 117.6, 54.6, 53.0.

HRMS (ESI-TOF) calcd for $C_{10}H_{10}N_2O_5Na$ $(M+Na)^+$ 261.0482, found 261.0494.

Benzhydryl 3-bromopropanoate (S3)



To a stirred solution of **S2** (818 mg, 5.35 mmol) in Et_2O (20 mL) was added diphenyldiazomethane in Et_2O at 0 °C, and the reaction mixture was stirred at room temperature for 21 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography (*n*-Hexane / AcOEt = 8:1) to afford **S3** (1.38 g, 85%) as a colorless oil.

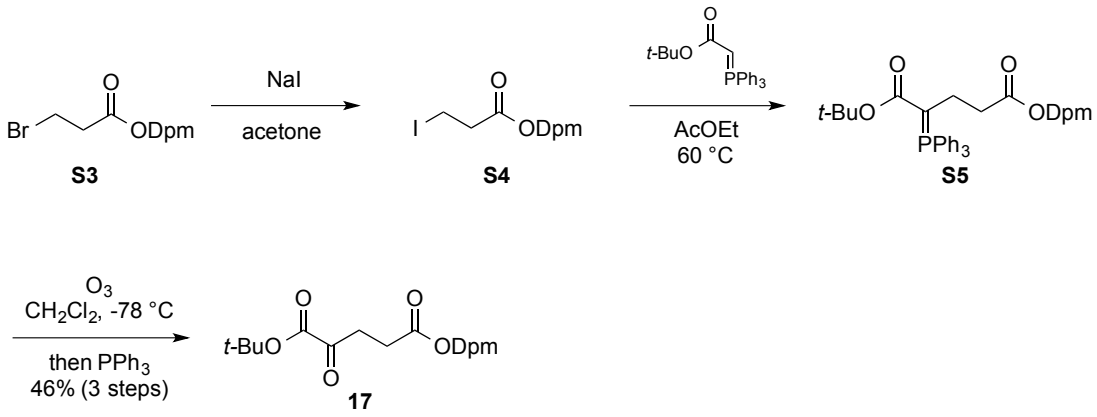
IR (film, cm^{-1}) 1742, 1497, 1450, 1366, 1287, 1267, 1233, 1132.

^1H NMR ($CDCl_3$, 500 MHz) δ 7.25-7.36 (m, 10H), 6.92 (s, 1H), 3.60 (t, *J* = 7.15 Hz, 2H), 3.03 (t, *J* = 7.15 Hz, 2H) .

^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.6, 139.7, 128.5, 128.0, 127.1, 77.6, 38.0, 25.6.

HRMS (ESI-TOF) calcd for $C_{16}H_{15}BrO_2Na$ $(M+Na)^+$ 341.0148, found 341.0162.

5-Benzhydryl 1-*tert*-butyl 2-oxopentanedioate (17)



To a stirred solution of **S3** (18.2 g, 57.0 mmol) in acetone (60 mL) was added NaI (10.26 g, 68.4 mmol, 1.2 equiv), and the mixture was stirred at room temperature for 11 h. Then, the reaction mixture was filtered, and the solvent was removed under reduced pressure. The residue was diluted with $CHCl_3$ and washed with saturated aqueous $Na_2S_2O_3$. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was used in the next step without further purification.

To a solution of crude **S4** in AcOEt (120 mL) was added *tert*-butyl 2-(triphenylphosphoranylidene)acetate (48.3 g, 128 mmol, 2.5 equiv) and the mixture was stirred at 60 °C for 48 h. Then, the reaction mixture was filtered and the organic solvent was concentrated under reduced pressure. The crude residue was used in the next step without further purification.

To a stirred solution of **S5** in CH_2Cl_2 (500 mL) was introduced ozone gas at -78 °C. The reaction was checked by TLC, and Ar gas was introduced to purge of remained ozone gas as soon as **S5** disappeared. The reaction mixture was treated with PPh_3 (11.5 g, 43.9 mmol, 1.2 equiv) and warmed to room temperature. After being stirred for 1.5 h, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography (*n*-Hexane / AcOEt = 4:1) to afford **17** (9.71 g, 46% from **S3**) as a colorless oil.

IR (film, cm^{-1}) 1738, 1722, 1371, 1163, 1080, 1030, 853, 835, 745, 700.

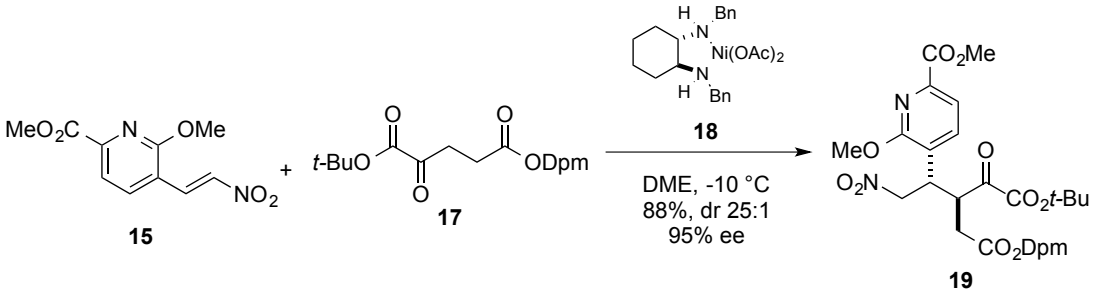
^1H NMR ($CDCl_3$, 500 MHz) δ 7.20-7.35 (m, 10H), 6.87 (s, 1H), 3.12 (t, J = 6.85 Hz, 2H), 2.75 (t, J = 6.85 Hz, 2H), 1.52 (s, 9H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 193.3, 171.1, 159.7, 139.8, 128.4, 127.9, 127.0, 84.0, 77.3, 77.2, 33.9, 27.7.

HRMS (ESI-TOF) calcd for $C_{22}H_{24}O_5Na$ $(M+Na)^+$ 391.1516, found 391.1535.

(*S*)-5-Benzhydryl 1-*tert*-butyl

3-((*S*)-1-(2-methoxy-6-(methoxycarbonyl)pyridin-3-yl)-2-nitroethyl)-2-oxopentanedioate (19)



To a stirred solution of **15** (5.40 g, 22.7 mmol) in DME (230 mL) were added α-ketoester **17** (8.77 g, 23.8 mmol, 1.05 equiv) and Ni-diamine complex **18** (576 mg, 1.14 mmol, 0.05 equiv) at -10 °C, and the mixture was stirred at the same temperature for 48 h. The mixture was diluted with *n*-Hexane and filtered through SiO_2 pad. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography (*n*-Hexane / AcOEt = 2:1) to afford **19** (12.1 g, 88%) as a colorless oil. The ee was determined by chiral HPLC analysis.

$[\alpha]^{25}_D$ +4.4 (*c* 1.0, $CHCl_3$, 95% ee).

IR (film, cm^{-1}) 1724, 1584, 1555, 1460, 1371, 1267, 1167, 1022, 982, 760, 702.

^1H NMR ($CDCl_3$, 500 MHz) δ 7.61 (d, *J* = 7.37 Hz, 1H), 7.45 (d, *J* = 7.37 Hz, 1H), 7.20-7.38 (m, 10H), 6.82 (s, 1H), 4.92 (dd, *J* = 13.0, 9.07 Hz, 1H), 4.78 (dd, *J* = 13.0, 4.53 Hz, 1H), 4.31-4.25 (m, 1H), 4.02 (s, 3H), 4.01-3.95 (m, 1H), 3.93 (s, 3H), 2.95 (dd, *J* = 17.0, 9.64 Hz, 1H), 2.73 (dd, *J* = 17.0, 4.53 Hz, 1H), 1.43 (s, 9H).

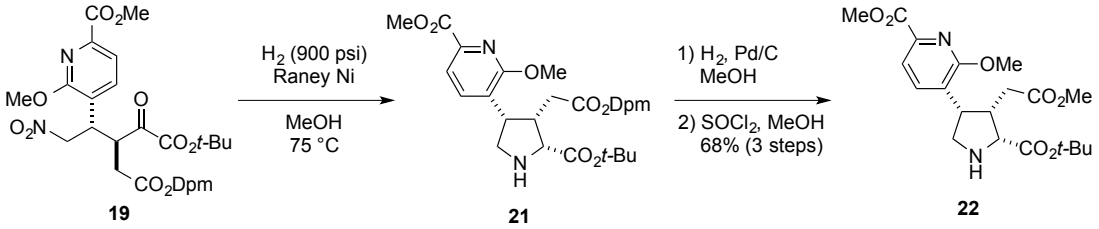
^{13}C NMR ($CDCl_3$, 125 MHz) δ 193.8, 170.0, 165.0, 161.0, 159.3, 145.3, 140.0, 139.4, 139.3, 128.5, 128.4, 128.1, 128.0, 127.2, 126.9, 122.5, 118.7, 84.4, 77.9, 75.1, 53.8, 52.6, 42.9, 41.6, 35.0, 27.5.

HRMS (ESI-TOF) calcd for $C_{32}H_{35}N_2O_{10}$ $(M+H)^+$ 607.2286, found 607.2312.

HPLC (DAICEL CHIRALCEL OD-H, *n*-Hexane / IPA = 9:1, 1.0 mL/min, 254 nm, τ_{major} 25.1 min, τ_{minor} 29.2 min).

Methyl

5-((3*S*,4*S*,5*R*)-5-(*tert*-butoxycarbonyl)-4-(2-methoxy-2-oxoethyl)pyrrolidin-3-yl)-6-methoxypicolinate (22)



Compound **19** (2.33 g, 3.84 mmol) was hydrogenated by Raney nickel (6.0 g, purchased from Aldrich, washed with water and MeOH) in MeOH (80 mL) under hydrogen atmosphere (900 psi) at 75 °C for 2 h. The mixture was cooled to room temperature and filtered through a pad of celite. The catalyst and the celite were washed with AcOEt. The combined organic solvent was concentrated under reduced pressure to afford yellow oil. The residue was used in the next step without further purification.

The residue was hydrogenated by Pd/C (10% dry, 1.0 g) in MeOH (40 mL) under hydrogen atmosphere (balloon) for 1.5 h. The mixture was filtered through a pad of celite and the organic solvent was concentrated under reduced pressure. The residue was used in the next step without further purification.

To the residue dissolved in MeOH (40 mL) was added $SOCl_2$ (0.28 mL, 3.84 mmol, 1.0 equiv) at 0 °C, and the mixture was stirred at room temperature for 20 h. The reaction mixture was diluted with toluene and the solvent was removed under reduced pressure. The residue was purified by column chromatography ($CHCl_3$ / MeOH = 96:4) to afford **22** (1.07 g, 68% from **19**) as a yellow oil.

$[\alpha]^{25}_D$ -89.5 (*c* 0.97, $CHCl_3$).

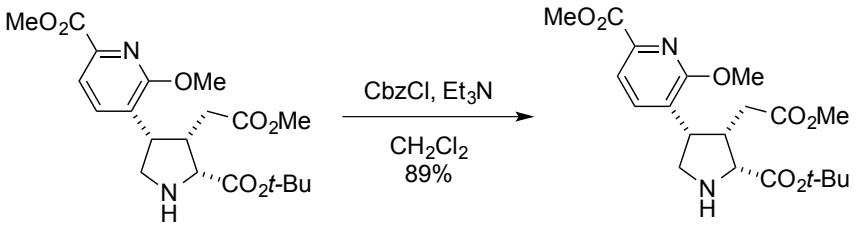
IR (film, cm^{-1}) 1740, 1462, 1263, 1211, 1159.

^1H NMR ($CDCl_3$, 500 MHz) δ 7.68 (br s, 2H), 4.69-4.63 (m, 1H), 4.15-4.08 (m, 2H), 4.07 (s, 3H), 3.96 (s, 3H), 3.89-3.82 (m, 1H), 3.74-3.66 (m, 1H), 3.34 (s, 3H), 2.36 (dd, *J* = 8.00, 17.8 Hz, 1H), 2.18 (dd, *J* = 5.75, 17.8 Hz, 1H), 1.46 (s, 9H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.8, 165.8, 165.3, 161.6, 144.7, 137.3, 122.3, 118.4, 85.6, 63.3, 54.1, 52.7, 51.7, 46.1, 40.6, 38.9, 30.5, 27.9.

HRMS (ESI-TOF) calcd for $C_{20}H_{29}N_2O_7$ $(M+H)^+$ 409.1969, found 409.1968.

(2*R*,3*S*,4*S*)-1-Benzyl 2-*tert*-butyl 3-(2-methoxy-2-oxoethyl)
-4-(2-methoxy-6-(methoxycarbonyl)pyridin-3-yl)pyrrolidine-1,2-dicarboxylate (S6)



22 **S6**

To a stirred solution of **22** (540 mg, 1.22 mmol) in CH_2Cl_2 (5 mL) were added Et_3N (0.51 mL, 3.66 mmol, 3.0 equiv) and CbzCl (0.26 mL, 1.83 mmol, 1.5 equiv) at 0 °C and the mixture was stirred at room temperature for 5 h. After stirring, the reaction was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (*n*-Hexane / AcOEt = 2:1) to afford **S6** (589 mg, 89%) as a colorless amorphous solid.

This compound exists as a mixture of rotamers in $CDCl_3$ at 25 °C.

$[\alpha]^{25}_D$ -63.2 (*c* 0.90, $CHCl_3$).

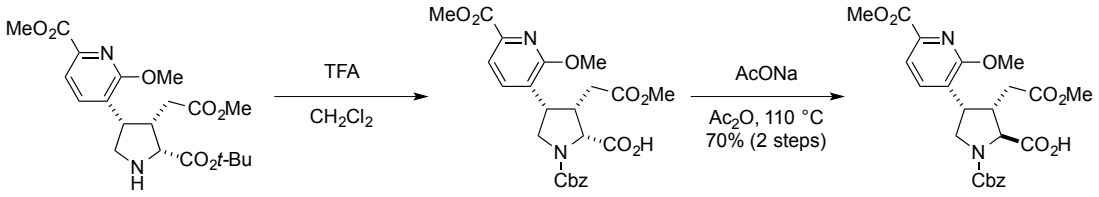
IR (film, cm^{-1}) 1742, 1721, 1709, 1460, 1412, 1368, 1287, 1265, 1213, 1155.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.86 (d, *J* = 7.37 Hz, 0.55H), 7.79 (d, *J* = 7.37 Hz, 0.45H), 7.70-7.66 (m, 1H), 7.40-7.25 (m, 5H), 5.26-5.10 (m, 2H), 4.55 (d, *J* = 8.50 Hz, 0.45H), 4.51 (d, *J* = 8.50 Hz, 0.55H), 4.03 (s, 3H), 3.97-3.86 (m, 3H), 3.95 (s, 3H), 3.55 (s, 1.65H), 3.52 (s, 1.35H), 3.59-3.49 (m, 1H), 2.35 (dd, *J* = 18.0, 6.24 Hz, 0.55H), 2.24 (dd, *J* = 17.6, 6.80 Hz, 0.45H), 2.18 (dd, *J* = 17.6, 8.50 Hz, 0.45H), 2.09 (dd, *J* = 18.0, 8.50 Hz, 0.55H), 1.37 (s, 4H), 1.21 (s, 5H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 117.6, 171.5, 169.1, 168.9, 165.4, 161.4, 154.5, 154.4, 143.7, 143.6, 138.5, 138.1, 136.3, 136.1, 128.4, 128.3, 127.9, 127.8, 125.8, 125.5, 118.5, 118.4, 82.1, 82.0, 67.2, 67.1, 62.3, 61.5, 53.7, 52.5, 51.4, 50.5, 49.5, 40.5, 39.2, 39.0, 37.8, 31.2, 31.1, 27.7, 27.5.

HRMS (ESI-TOF) calcd for $C_{28}H_{35}N_2O_9$ $(M+H)^+$ 543.2337, found 543.2350.

(2*S*,3*S*,4*S*)-1-((Benzyloxy)carbonyl)-3-(2-methoxy-2-oxoethyl)-4-(2-methoxy-6-(methoxycarbonyl)pyridin-3-yl)pyrrolidine-2-carboxylic acid (24)



S6 **23** **24**

To a stirred solution of **S6** (589 mg, 1.09 mmol) in CH_2Cl_2 (7.5 mL) was added TFA (2.5 mL). After stirring at room temperature for 19 h, the mixture was concentrated under reduced pressure. The residue was used in the next step without further purification.

To a suspension of crude **23** and AcONa (894 mg, 10.9 mmol, 10 equiv) in Ac_2O (5.5 mL) was stirred at 110 °C for 25 h. After completion of the reaction, the mixture was concentrated under reduced pressure and the residue was diluted with water. After being stirred for 1 h, the mixture was extracted with $CHCl_3$. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography ($CHCl_3$ / MeOH = 98:2) to afford **24** (370 mg, 70% from **S6**) as a colorless amorphous solid.

This compound exists as a mixture of rotamers in $CDCl_3$ at 25 °C.

$[\alpha]^{25}_D$ -55.3 (*c* 0.87, $CHCl_3$).

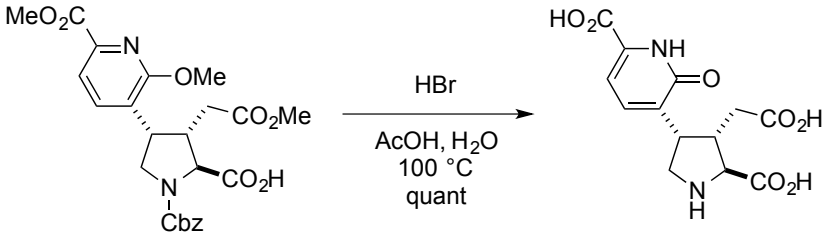
IR (film, cm^{-1}) 1738, 1591, 1462, 1433, 1362, 1267, 1207, 1171, 1132.

^1H NMR ($CDCl_3$, 500 MHz) δ 10.08 (br s, 1H), 7.68 (d, *J* = 7.37 Hz, 0.45H), 7.64 (d, *J* = 7.37 Hz, 0.55H), 7.45-7.25 (m, 6H), 5.28-5.13 (m, 2H), 4.26 (d, *J* = 5.10 Hz, 0.55H), 4.22 (d, *J* = 5.10 Hz, 0.45H), 3.80-4.05 (m, 3H), 3.99 (s, 3H), 3.96 (s, 3H), 3.59 (s, 1.35H), 3.58 (s, 1.65H), 3.44-3.36 (m, 1H), 2.35-2.20 (m, 1H), 2.05-1.95 (m, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 176.0, 175.1, 171.6, 171.5, 165.4, 161.4, 155.1, 154.3, 144.1, 136.6, 135.9, 128.5, 128.4, 128.2, 128.0, 127.7, 125.1, 125.0, 118.8, 118.6, 67.7, 67.6, 63.5, 63.0, 53.9, 52.6, 51.8, 49.0, 48.9, 42.8, 41.6, 39.2, 38.4, 33.1.

HRMS (ESI-TOF) calcd for $C_{24}H_{25}N_2O_9$ $(M-H)^-$ 485.1555, found 485.1554.

Acromelic acid A (1)



24 **acromelic acid A (1)**

To a stirred solution of **24** (271 mg, 557 μmol) in H_2O (1.5 mL) was added HBr in AcOH (5 M, 6.0 mL) and the mixture was stirred at 100 °C for 12 h. The mixture was concentrated under reduced pressure. Purification of **1** was carried out according to the reported procedure.[1] The residue was charged onto a column containing Dowex-50 WX8 hydrogen form (200-400 mesh). After elution with H_2O (25 mL) and 3% aqueous NH_3 (25 mL), the collected fractions were concentrated under reduced pressure. The resulting ammonium was charged onto a column containing Amberlite IRC-50 hydrogen form. After elution with H_2O, the collected fractions were concentrated under reduced pressure to give free amino acid **1** (172 mg, quant) as a colorless solid.

Mp. >310 °C (decomp.).

$[\alpha]^{25}_D$ 30.0 (*c* 1.11, H_2O) (lit.[1] $[\alpha]_D$ 27.8 (*c* 0.35, H_2O)).

IR (film, cm^{-1}) 3422, 1618, 1381, 787.

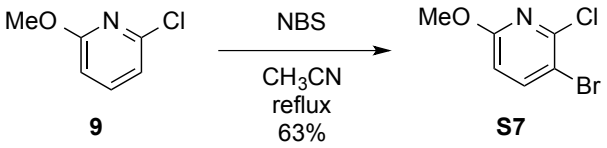
^1H NMR (D_2O, 500 MHz) δ 7.52 (d, *J* = 7.37 Hz, 1H), 6.94 (d, *J* = 7.37 Hz, 1H), 4.12 (d, *J* = 7.37 Hz, 1H), 3.84-3.68 (m, 3H), 3.20-3.12 (m, 1H), 2.61 (dd, *J* = 16.7, 5.10 Hz, 1H), 2.15 (dd, *J* = 16.7, 10.2 Hz, 1H).

^{13}C NMR (D_2O, 125 MHz) δ 176.7, 173.6, 166.3, 163.1, 142.7, 139.5, 129.8, 108.9, 65.8, 47.5, 42.5, 42.4, 35.7.

HRMS (ESI-TOF) calcd for $C_{13}H_{13}N_2O_7$ $(M-H)^-$ 309.0717, found 309.0715.

[1] K. Konno, K. Hashimoto, Y. Ohfune, H. Shirahama, T. Matsumoto, *J. Am. Chem. Soc.* **1988**, *110*, 4807-4815.

3-Bromo-2-chloro-6-methoxypyridine (S7)



9 **S7**

To a stirred solution of **9** (7.00 g, 48.8 mmol) in CH_3CN (25 mL) was added NBS (13.0 g, 73.1 mmol, 1.5 equiv) and the mixture was refluxed for 24 h. After cooling to room temperature, the reaction was quenched with saturated aqueous $Na_2S_2O_3$ and extracted with AcOEt. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (*n*-Hexane / AcOEt = 98:2) to afford **S7** (6.83 g, 63%) as a colorless solid.

Mp. 64 - 65 °C.

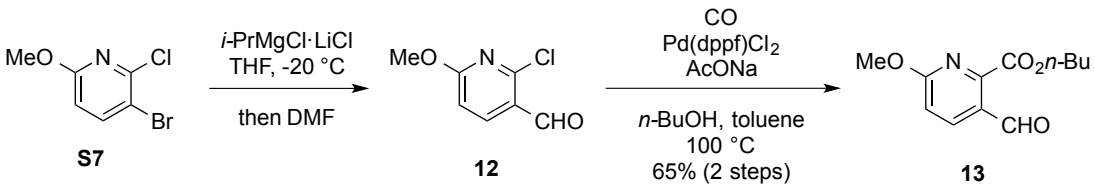
IR (film, cm^{-1}) 1584, 1551, 1466, 1408, 1344, 1306, 1256, 1155, 1121, 1022, 1009.

^1H NMR ($CDCl_3$, 500 MHz) δ 7.72 (d, J = 8.50 Hz, 1H), 6.58 (d, J = 8.50 Hz, 1H), 3.92 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.4, 147.3, 143.8, 110.9, 110.1, 54.3.

HRMS (ESI-TOF) calcd for $C_6H_6BrClNO$ $(M+H)^+$ 221.9316, found 221.9314.

Butyl 3-formyl-6-methoxypicolinate (13)



To a stirred solution of **S7** (6.83 g, 30.7 mmol) in THF (120 mL) was added *i*PrMgCl·LiCl in THF solution (ca.1.0 M, 32.2 mL, 32.2 mmol, 1.05 equiv) at -20 °C under Ar atmosphere. After stirring at the same temperature for 2 h, DMF (7.2 mL, 92.1 mmol, 3.0 equiv) was added dropwise. After being stirred at the same temperature for 30 min, the reaction mixture was warmed to room temperature. The reaction was quenched with saturated aqueous NH_4Cl and extracted with AcOEt. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was used in the next step without further purification.

To a suspention of the crude **12** and AcONa (3.78 g, 46.1 mmol, 1.5 equiv) in *n*BuOH / toluene (60 mL / 60 mL) was added $Pd(dppf)Cl_2$ (1.12 g, 1.54 mmol, 0.05 equiv) under Ar atmosphere. The reaction mixture was stirred at 100 °C under CO atmosphere for 18 h. The reaction was quenched with saturated aqueous NH_4Cl, and the mixture was filtered through a pad of celite. The filtrate was extracted with AcOEt. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (*n*-Hexane / AcOEt = 2:1) to afford **13** (4.75 g, 65% from **S7**) as a yellow oil.

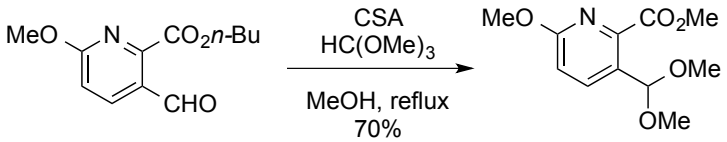
IR (film, cm^{-1}) 2963, 2876, 1721, 1692, 1595, 1481, 1337, 1277, 1261, 1219, 1138, 1072, 1022.

^1H NMR ($CDCl_3$, 500 MHz) δ 10.39 (s, 1H), 8.18 (d, J = 8.50 Hz, 1H), 6.94 (d, J = 8.50 Hz, 1H), 4.44 (t, J = 6.80 Hz, 2H), 4.06 (s, 3H), 1.83-1.76 (m, 2H), 1.54-1.45 (m, 2H), 0.99 (t, J = 7.37 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 189.1, 166.1, 165.2, 150.7, 138.6, 125.9, 114.1, 66.3, 54.5, 30.5, 19.2, 13.7.

HRMS (ESI-TOF) calcd for $C_{12}H_{15}NO_4Na$ $(M+Na)^+$ 260.0893, found 260.0891.

Methyl 3-(dimethoxymethyl)-6-methoxypicolinate (S8)



13 **S8**

To a stirred solution of **13** (4.75 g, 20.0 mmol) in MeOH (100 mL) were added $CH(OMe)_3$ (11 mL, 100 mmol, 5 equiv) and CSA (465 mg, 2.00 mmol, 0.1 equiv), and the resulting mixture was refluxed for 24 h. After cooling to room temperature, the organic solvent was removed under reduced pressure. The residue was diluted with saturated aqueous $NaHCO_3$ and extracted with AcOEt. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (*n*-Hexane / AcOEt = 9:1) to afford **S8** (3.40 g, 70%) as a yellow oil.

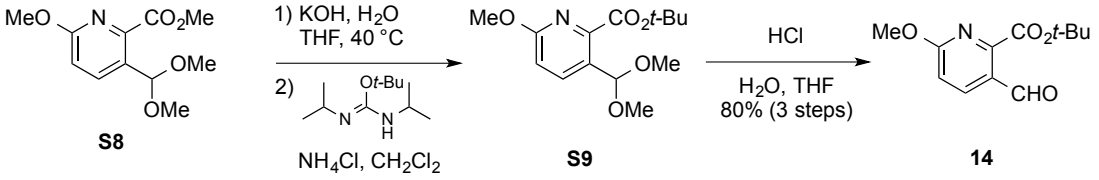
IR (ATR, cm^{-1}) 2951, 2832, 1730, 1597, 1479, 1321, 1250, 1217, 1109, 1070, 1051, 1026, 974, 831.

^1H NMR ($CDCl_3$, 500 MHz) δ 7.90 (d, *J* = 8.50 Hz, 1H), 6.86 (d, *J* = 8.50 Hz, 1H), 5.85 (s, 1H), 3.97 (s, 3H), 3.96 (s, 3H), 3.34 (s, 6H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.9, 163.3, 145.5, 138.3, 127.1, 113.0, 100.0, 53.8, 53.6, 52.6.

HRMS (ESI-TOF) calcd for $C_{11}H_{15}NO_5Na$ $(M+Na)^+$ 264.0842, found 264.0842.

***tert*-Butyl 3-formyl-6-methoxypicolinate (14)**



To a stirred solution of **S8** (500 mg, 2.07 mmol) in THF (4 mL) was added aqueous KOH (1 M, 4.15 mL, 4.15 mmol, 2.0 equiv). After stirring at 40 °C for 3 h, the mixture was concentrated under reduced pressure. The residue was used in the next step without further purification.

To a stirred suspension of crude residue in CH_2Cl_2 (5 mL) were added NH_4Cl (277 mg, 5.18 mmol, 2.5 equiv) and *N,N'*-diisopropyl-*O*-*tert*-butylisourea (1.63 mL, 7.25 mmol, 3.5 equiv), and the mixture was stirred at room temperature for 15 h. The reaction mixture was filtered and the organic solvent was removed under reduced pressure. The residue was used in the next step without further purification.

To a stirred solution of the crude **S9** in THF (2 mL) was added aqueous HCl (1 M, 2 mL). After stirring for 1.5 h, the reaction mixture was diluted with water and extracted with AcOEt. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (*n*-Hexane / AcOEt = 4:1) to afford **14** (391 mg, 80% from **S8**) as a colorless oil.

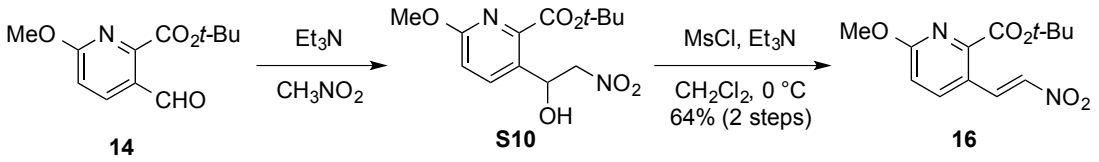
IR (film, cm^{-1}) 2982, 1736, 1595, 1481, 1335, 1279, 1223, 1167, 1138, 1072, 1020, 845.

^1H NMR ($CDCl_3$, 500 MHz) δ 10.35 (s, 1H), 8.14 (d, J = 8.50 Hz, 1H), 6.91 (d, J = 8.50 Hz, 1H), 4.06 (s, 3H), 1.65 (s, 9H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 189.1, 166.1, 164.2, 152.3, 138.5, 125.1, 113.6, 83.9, 54.4, 28.1.

HRMS (ESI-TOF) calcd for $C_{12}H_{15}NO_4Na$ $(M+Na)^+$ 260.0893, found 260.0881.

(*E*)-*tert*-Butyl 6-methoxy-3-(2-nitrovinyl)picolinate (16)



To a stirred solution of **14** (1.48 g, 6.22 mmol) in CH_3NO_2 (30 mL) was added Et_3N (1.72 mL, 12.4 mmol, 2.0 equiv) at room temperature. After stirring for 20 h, the solvent was removed under reduced pressure to afford crude **S10** as a yellow solid.

To the residue dissolved in CH_2Cl_2 (30 mL) were added Et_3N (1.29 mL, 9.33 mmol, 1.5 equiv) and MsCl (963 μL, 12.4 mmol, 2.0 equiv) at 0 °C. After being stirred for 3 h, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography ($CHCl_3$ / AcOEt = 9:1) to afford **16** (1.12 g, 64% from **14**) as a pale yellow solid.

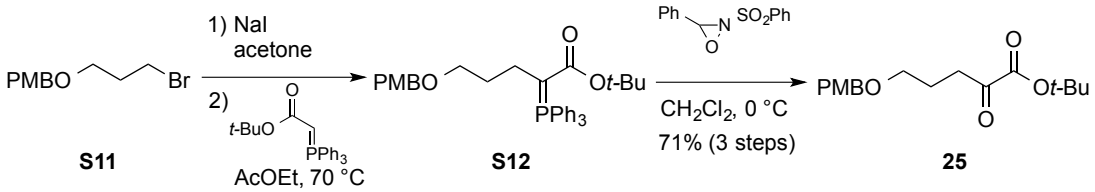
IR (film, cm^{-1}) 3115, 2978, 2943, 1734, 1630, 1595, 1560, 1508, 1481, 1425, 1395, 1370, 1331, 1275, 1260, 1171, 1144, 1074, 1020, 966, 957, 833, 596.

^1H NMR ($CDCl_3$, 500 MHz) δ 8.59 (d, J = 13.6 Hz, 1H), 7.76 (d, J = 8.50 Hz, 1H), 7.42 (d, J = 13.6 Hz, 1H), 6.91 (d, J = 8.50 Hz, 1H), 4.04 (s, 3H), 1.66 (s, 9H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.2, 164.1, 149.1, 137.7, 137.4, 135.5, 118.9, 114.2, 84.0, 54.2, 28.1.

HRMS (ESI-TOF) calcd for $C_{13}H_{16}N_2O_5Na$ $(M+Na)^+$ 303.0954, found 303.0958.

***tert*-Butyl 5-((4-methoxybenzyl)oxy)-2-oxopentanoate (25)**



To a stirred solution of **S11**[2] (18.3 g, 70.5 mmol) in acetone (70 mL) was added NaI (12.7 g, 84.6 mmol, 1.2 equiv). After stirring at room temperature for 6 h, the reaction mixture was quenched with water and extracted with $CHCl_3$. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was used in the next step without further purification.

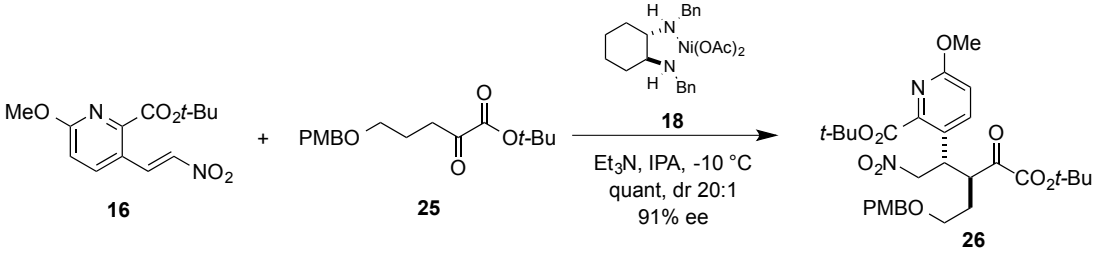
To a stirred solution of the residue in AcOEt (200 mL) was added *tert*-butyl 2-(triphenylphosphoranylidene) acetate (53.0 g, 141 mmol, 2.0 equiv) and stirred at 70 °C for 16 h. The mixture was filtered and the organic layer was concentrated under reduced pressure. The residue was used in the next step without further purification.

To a stirred solution of the crude **S12** in CH_2Cl_2 (140 mL) was added Davis reagent [3] (36.8 g, 141 mmol, 2.0 equiv) at -78 °C. The resulting mixture was warmed to 0 °C and stirred for 8 h. The reaction was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (*n*-Hexane / AcOEt = 9:1) to afford **25** (15.3 g, 71% from **S11**) as a colorless oil.

IR (film, cm^{-1}) 2981, 2937, 2864, 1744, 1713, 1614, 1511, 1372, 1302, 1242, 1173, 1105, 1034, 833, 756, 579.
^1H NMR ($CDCl_3$, 500 MHz) δ 7.23 (d, J = 8.50 Hz, 2H), 6.87 (d, J = 8.50 Hz, 2H), 4.40 (s, 2H), 3.80 (s, 3H), 3.47 (t, J = 6.24 Hz, 2H), 2.87 (t, J = 7.09 Hz, 2H), 1.97-1.90 (m, 2H), 1.52 (s, 9H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ 195.2, 160.5, 159.1, 130.3, 129.2, 113.7, 83.7, 72.4, 68.5, 55.2, 36.1, 27.7, 23.6.
HRMS (ESI-TOF) calcd for $C_{17}H_{24}O_5Na$ $(M+Na)^+$ 331.1516, found 331.1506.

[2] A. Dahan, M. Portnoy, *J. Org. Chem.*, **2001**, *66*, 6480-6482.
[3] In the case of ozone gas, PMB ether was decomposed.

***tert*-Butyl 3-((2*S*,3*S*)-5-(*tert*-butoxy)-3-(2-((4-methoxybenzyl)oxy)ethyl)-1-nitro-4,5-dioxopentan-2-yl)-6-methoxypicolinate (26)**



To a stirred solution of **16** (400 mg, 1.43 mmol) in IPA (0.4 mL) were added Ni-diamine complex **18** (36.2 mg, 71.4 μmol, 0.05 equiv), α-ketoester **25** (880 mg, 2.85 mmol, 2.0 equiv) in IPA (1.1 mL) and Et_3N (49 μL, 357 μmol, 0.25 equiv) at -10 °C, and the mixture was stirred at the same temperature for 14 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography (*n*-Hexane / AcOEt = 7:3) to afford **26** (887 mg, quant) as a colorless oil. The ee was determined by chiral HPLC analysis.

$[\alpha]^{25}_D$ -33.0 (*c* 1.01, $CHCl_3$, 91% ee).

IR (film, cm^{-1}) 2980, 2938, 2868, 1719, 1601, 1555, 1512, 1481, 1370, 1329, 1283, 1250, 1171, 1148, 1098, 1030, 847, 826.

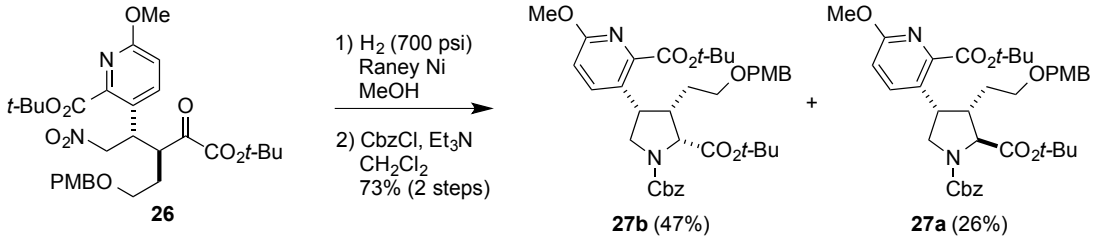
^1H NMR ($CDCl_3$, 500 MHz) δ 7.57 (d, *J* = 8.50 Hz, 1H), 7.17 (d, *J* = 8.50 Hz, 2H), 6.85 (d, *J* = 8.50 Hz, 2H), 6.74 (d, *J* = 8.50 Hz, 1H), 4.87 (dd, *J* = 13.0, 5.10 Hz, 1H), 4.81 (dd, *J* = 13.0, 6.80 Hz, 1H), 4.47-4.38 (m, 1H), 4.30 (d, *J* = 11.9 Hz, 1H), 4.26 (d, *J* = 11.9 Hz, 1H), 4.09 (dt, *J* = 9.6, 4.0 Hz, 1H), 3.92 (s, 3H), 3.79 (s, 3H), 3.49-3.41 (m, 2H), 2.18-2.00 (m, 2H), 1.64 (s, 9H), 1.36 (s, 9H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 195.0, 165.3, 162.4, 159.8, 159.2, 147.3, 139.2, 129.7, 129.3, 125.3, 113.7, 113.0, 83.7, 82.7, 77.6, 72.3, 67.3, 55.3, 53.5, 46.0, 39.9, 31.1, 28.1, 27.6.

HRMS (ESI-TOF) calcd for $C_{30}H_{40}N_2O_{10}Na$ $(M+Na)^+$ 611.2575, found 611.2570.

HPLC (DAICEL CHIRALPAK AD-H, *n*-Hexane / IPA = 19:1, 1.0 mL/min, 254 nm, τ_{minor} 14.1 min, τ_{major} 15.8 min).

1-Benzyl 2-(*tert*-butyl) (3*S*,4*S*)-4-(2-(*tert*-butoxycarbonyl)-6-methoxypyridin-3-yl) -3-(2-((4-methoxybenzyl)oxy)ethyl)pyrrolidine-1,2-dicarboxylate (27b)



Compound **26** (7.77 g, 13.2 mmol) was hydrogenated using Raney nickel (23 g, purchased from Aldrich, washed with water and MeOH) in MeOH (65 mL) under hydrogen atmosphere (700 psi) for 1.5 h. The mixture was filtered through a pad of celite. The separated solid was washed with MeOH. The combined organic solvent was concentrated under reduced pressure to afford pale yellow oil. The residue was used in the next step without further purification.

To a solution of the residue in CH_2Cl_2 (70 mL) were added Et_3N (3.66 mL, 26.4 mmol, 2.0 equiv) and CbzCl (2.81 mL, 19.8 mmol, 1.5 equiv) at 0 °C. After stirring at the same temperature for 30 min, the mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (*n*-Hexane / AcOEt = 3:1) to afford **27a** (2.30 g, 26% from **26**) as a colorless oil and **27b** (4.19 g, 47% from **26**) as a colorless oil.

This compound exists as a mixture of rotamers in $CDCl_3$ at 25 °C.

$[\alpha]^{20}_D$ -31.0 (*c* 1.18, $CHCl_3$).

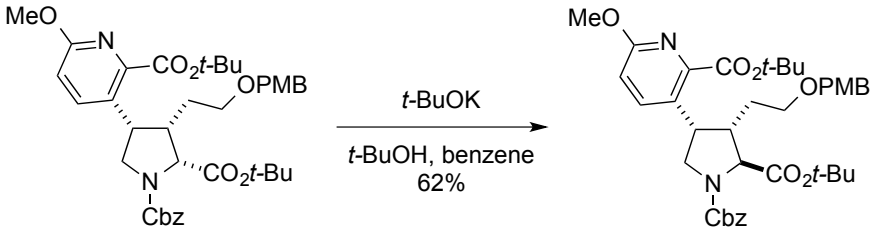
IR (film, cm^{-1}) 3002, 2977, 2941, 2904, 1740, 1721, 1709, 1698, 1601, 1513, 1480, 1412, 1368, 1329, 1281, 1248, 1169, 1144, 1032, 847, 824, 755, 698.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.89 (t, *J* = 8.50 Hz, 1H), 7.40-7.27 (m, 5H), 7.21-7.08 (m, 2H), 6.85-6.72 (m, 3H), 5.22-5.08 (m, 2H), 4.49 (d, *J* = 9.1 Hz, 0.45H), 4.44 (d, *J* = 9.1 Hz, 0.55H), 4.36-4.20 (m, 2H), 4.14-3.89 (m, 2H), 3.93 (s, 3H), 3.83-3.70 (m,1H), 3.78 (s, 3H), 3.40-3.00 (m, 3H), 1.66-1.54 (m, 11H), 1.44 (s, 4H), 1.29 (s, 5H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.5, 170.4, 166.2, 162.0, 159.1, 154.8, 154.4, 148.1, 147.9, 140.2, 140.1, 137.9, 136.5, 136.3, 130.5, 129.2, 128.9, 128.5, 128.4, 128.0, 127.9, 126.4, 126.1, 113.7, 113.6, 112.6, 112.5, 82.6, 82.5, 82.2, 82.1,72.5, 72.4, 68.3, 68.2, 67.2, 67.1, 63.4, 62.9, 55.2, 53.5, 52.4, 51.8, 41.9, 40.9, 40.8, 39.9, 28.2, 28.0, 27.8, 27.7, 27.6.

HRMS (ESI-TOF) calcd for $C_{38}H_{48}N_2O_9Na$ $(M+Na)^+$ 699.3252, found 699.3246.

1-Benzyl 2-(*tert*-butyl) (2*S*,3*S*,4*S*)-4-(2-(*tert*-butoxycarbonyl)-6-methoxypyridin-3-yl) -3-(2-((4-methoxybenzyl)oxy)ethyl)pyrrolidine-1,2-dicarboxylate (27a)



27b **27a**

To a stirred solution of **27b** (60 mg, 88.4 μmol) in *t*BuOH / benzene (810 μL / 90 μL) was added *t*BuOK (14.9 mg, 133 μmol, 1.5 equiv) at 0 °C and the mixture was stirred at room temperature for 6 h. The mixture was quenched with saturated aqueous NH_4Cl and extracted with AcOEt. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (*n*-Hexane / AcOEt = 3:1) to afford **27a** (37 mg, 62%) as a colorless oil.

This compound exists as a mixture of rotamers in $CDCl_3$ at 25 °C.

$[\alpha]^{20}_D$ -17.2 (*c* 1.03, $CHCl_3$).

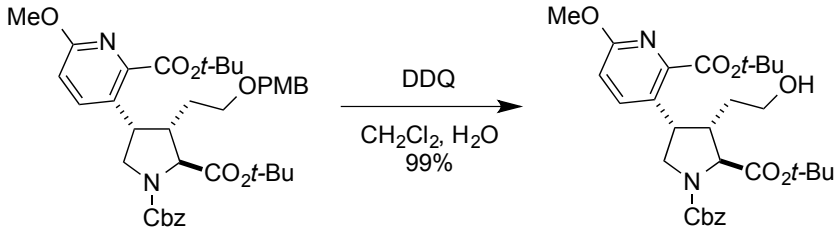
IR (film, cm^{-1}) 2978, 2938, 2870, 1736, 1709, 1599, 1512, 1481, 1414, 1368, 1356, 1331, 1281, 1248, 1157, 1032, 824, 698.

^1H NMR ($CDCl_3$, 500 MHz) δ 7.44-7.28 (m, 6H), 7.21-7.13 (m, 2H), 6.86-6.70 (m, 3H), 5.22-5.07 (m, 2H), 4.36-4.33 (m, 2H), 4.26-4.21 (m, 1H), 4.11-4.04 (m, 1H), 3.96-3.85 (m, 4H), 3.80-3.62 (m, 4H), 3.48-3.19 (m, 2H), 2.80-2.70 (m, 1H), 1.70-1.33 (m, 20H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 171.2, 165.9, 162.0, 159.1, 154.8, 154.5, 148.2, 148.1, 138.5, 136.6, 136.4, 130.3, 129.2, 129.1, 128.5, 128.4, 128.0, 127.9, 127.8, 127.7, 124.9, 113.7, 112.4, 82.5, 82.4, 81.7, 81.6, 72.7, 68.3, 68.0, 67.1, 64.8, 64.4, 55.2, 53.5, 50.0, 45.0, 43.6, 40.4, 39.5, 29.1, 29.0, 28.1, 28.0, 27.8.

HRMS (ESI-TOF) calcd for $C_{38}H_{48}N_2O_9Na$ $(M+Na)^+$ 699.3252, found 699.3263.

1-Benzyl 2-(*tert*-butyl) (2*S*,3*S*,4*S*)-4-(2-(*tert*-butoxycarbonyl)-6-methoxypyridin-3-yl) -3-(2-hydroxyethyl)pyrrolidine-1,2-dicarboxylate (S13)



27a **S13**

To a stirred solution of **27a** (100 mg, 147 μmol) in CH_2Cl_2 / H_2O (700 μL / 35 μL) was added DDQ (50 mg, 221 μmol, 1.5 equiv). After stirring at room temperature for 1 h, the mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (*n*-Hexane / AcOEt = 1:1 and *n*-Hexane / Et_2O = 1:2) to afford **S13** (89.9 mg, 99%) as a colorless oil.

This compound exists as a mixture of rotamers in $CDCl_3$ at 25 °C.

$[\alpha]^{25}_D$ -34.0 (*c* 1.45, $CHCl_3$).

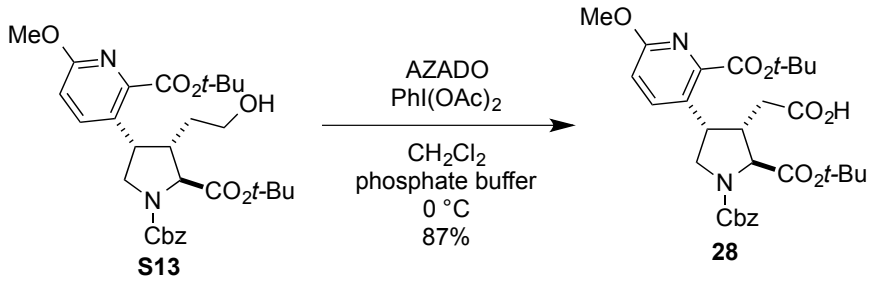
IR (film, cm^{-1}) 2978, 2936, 1740, 1719, 1701, 1690, 1655, 1597, 1560, 1481, 1458, 1420, 1368, 1331, 1283, 1157, 1028, 847, 698.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.43-7.28 (m, 6H), 6.77 (d, *J* = 8.50 Hz, 0.55H), 6.74 (d, *J* = 8.50 Hz, 0.45H), 5.21-5.11 (m, 2H), 4.18 (d, J = 5.10 Hz, 0.45H), 4.16 (d, *J* = 5.10 Hz, 0.55H), 4.09-4.01 (m, 1H), 3.93 (s, 3H), 3.92-3.86 (m, 1H), 3.80-3.67 (m, 1H), 3.64-3.54 (m, 2H), 2.81-2.72 (m, 1H), 1.70-1.35 (m, 2H), 1.59 (s, 9H), 1.49 (s, 4H), 1.39 (s, 5H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 171.5, 171.4, 166.2, 162.1, 154.7, 154.4, 148.1, 148.0, 138.3, 136.5, 136.3, 128.5, 128.4, 128.0, 127.9, 125.5, 125.4, 112.7, 82.8, 82.7, 82.0, 67.3, 67.2, 64.8, 64.4, 60.9, 60.8, 53.5, 50.6, 44.9, 43.8, 40.5, 39.6, 32.1, 28.1, 27.9, 27.8.

HRMS (ESI-TOF) calcd for $C_{30}H_{41}N_2O_8$ $(M+H)^+$ 557.2857, found 557.2858.

2-((2*R*,3*S*,4*S*)-1-((Benzyloxy)carbonyl)-2-(*tert*-butoxycarbonyl)-4-(2-(*tert*-butoxycarbonyl)-6-methoxypyridin-3-yl)pyrrolidin-3-yl)acetic acid (28)



To a stirred solution of **S13** (250 mg, 449 μmol) in CH_2Cl_2 / phosphate buffer (pH 7.6) (1.35 mL / 1.35 mL) were added AZADO (13.7 mg, 89.8 μmol, 0.2 equiv) and $PhI(OAc)_2$ (434 mg, 1.34 mmol, 3.0 equiv) at 0 °C. After stirring at the same temperature for 8 h, the mixture was added to saturated aqueous $Na_2S_2O_3$ at 0 °C. After being stirred at room temperature for 1 h, the mixture was extracted with AcOEt. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (*n*-Hexane / AcOEt = 1:1) to afford **28** (222 mg, 87%) as a colorless amorphous solid.

This compound exists as a mixture of rotamers in $CDCl_3$ at 25 °C.

$[\alpha]^{25}_D$ -39.6 (*c* 1.05, $CHCl_3$).

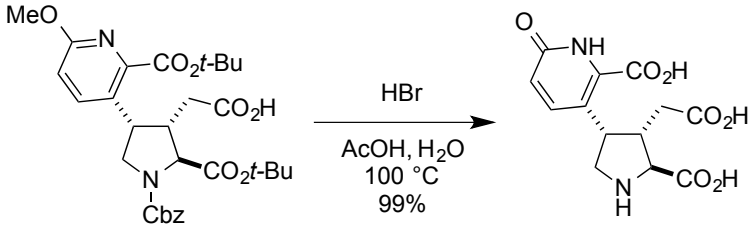
IR (film, cm^{-1}) 2980, 2941, 2906, 1710, 1599, 1560, 1481, 1413, 1367, 1332, 1282, 1253, 1228, 1161, 1093, 1030, 844, 736, 698.

^1H NMR ($CDCl_3$, 500 MHz) δ 7.42-7.28 (m, 6H), 6.77 (d, *J* = 8.50 Hz, 0.55H), 6.74 (d, *J* = 8.50 Hz, 0.45H), 5.22-5.08 (m, 2H), 4.20-4.11 (m, 2H), 3.96-3.89 (m, 1H), 3.92 (s, 3H), 3.80-3.67 (m, 1H), 3.21-3.11 (m, 1H), 2.27-2.16 (m, 2H), 1.57 (s, 9H), 1.47 (s, 4H), 1.37 (s, 5H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 176.4, 176.3, 170.4, 165.6, 162.2, 154.6, 154.4, 148.1, 138.0, 136.4, 136.2, 128.4, 128.3, 128.0, 127.9, 127.8, 124.6, 124.5, 112.8, 82.7, 82.6, 82.0, 81.9, 67.3, 64.9, 64.6, 53.5, 50.1, 49.9, 43.6, 42.6, 39.9, 39.0, 33.8, 28.0, 27.9, 27.7.

HRMS (ESI-TOF) calcd for $C_{30}H_{38}N_2O_9Na$ $(M+Na)^+$ 593.2470, found 593.2486.

Acromelic acid B (2)



28 **acromelic acid B (2)**

To a stirred solution of **28** (195 mg, 342 μmol) in H_2O (1.7 mL) was added 30% HBr in AcOH (3.4 mL) and the mixture was stirred at 100 °C for 36 h. The solvent was removed under reduced pressure. The residue was charged onto a column containing Dowex-50 WX8 hydrogen form (200-400 mesh). After elution with H_2O and 3% aqueous NH_3, the collected fractions were concentrated under reduced pressure. The resulting ammonium salt was charged onto a column containing Amberlite IRC-50 hydrogen form. After elution with H_2O, the collected fractions were concentrated under reduced pressure to give free amino acid **2** (105 mg, 99%) as a colorless amorphous solid.

$[\alpha]^{20}_D$ -68.8 (*c* 0.98, H_2O) (lit.[4] $[\alpha]^{27}_D$ -74.0 (*c* 0.1, H_2O)).

IR (film, cm^{-1}) 3300-2700, 1655, 1597, 1419, 1363, 1251, 1167, 1060, 842, 801, 673.

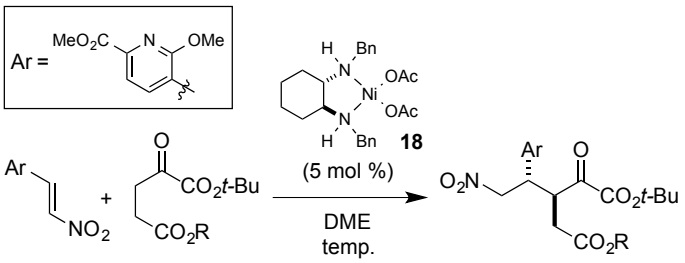
^{1}H NMR (D_2O, 500 MHz) δ 7.68 (d, *J* = 9.16 Hz, 1H), 6.70 (d, *J* = 9.16 Hz, 1H), 4.65 (dt, *J* = 11.5, 8.0 Hz, 1H), 4.08 (d, *J* = 5.7 Hz, 1H), 3.80 (dd, *J* = 11.5, 8.0 Hz, 1H), 3.65 (t, *J* = 11.5 Hz, 1H), 3.27-3.20 (m, 1H), 2.52 (dd, *J* = 16.6, 6.3 Hz, 1H), 2.35 (dd, *J* = 16.6, 8.6 Hz, 1H).

^{13}C NMR (D_2O, 125 MHz) δ 175.7, 173.0, 166.5, 163.1, 143.3, 141.2, 120.4, 115.3, 65.5, 47.3, 42.3, 38.6, 34.7.

HRMS (ESI-TOF) calcd for $C_{13}H_{15}N_2O_7$ $(M+H)^+$ 311.0874, found 311.0877.

[4] S. Takano, S. Tomita, Y. Iwabuchi, K. Ogasawara, *Heterocycles* **1989**, *29*, 1473-1476.

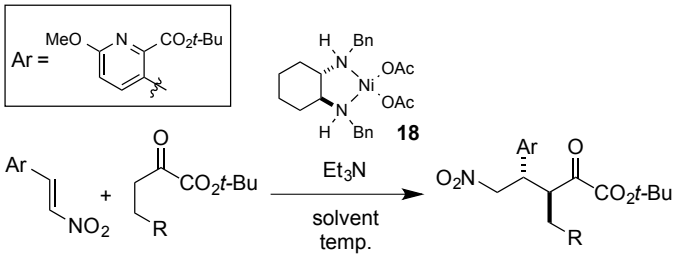
Table S-1. Optimization of the asymmetric reaction for Acromelic acid A (1).



entry	R	temp. (°C)	yield (%)[a]	dr[b]	ee (%)[c]
1	Me-	rt	71	2:1	93
2	Bn-	rt	72	6:1	not determined
3	*t*-Bu-	rt	quant	10:1	79
4	*t*-Bu-	0	75	27:1	94
5	Dpm-	0	93	10:1	92
6	Dpm-	-10	88	25:1	95
7	Dpm-	-20	N.R.	-	-

[a]Yields as a mixture of diastereomers. [b]Determined by ^{1}H NMR.
[c]Determined by HPLC.

Table S-2. Optimization of the asymmetric reaction for Acromelic acid B (2).



entry	R	solvent	**18** (mol %)	Et_3N (mol %)	temp. (°C)	dr[a]
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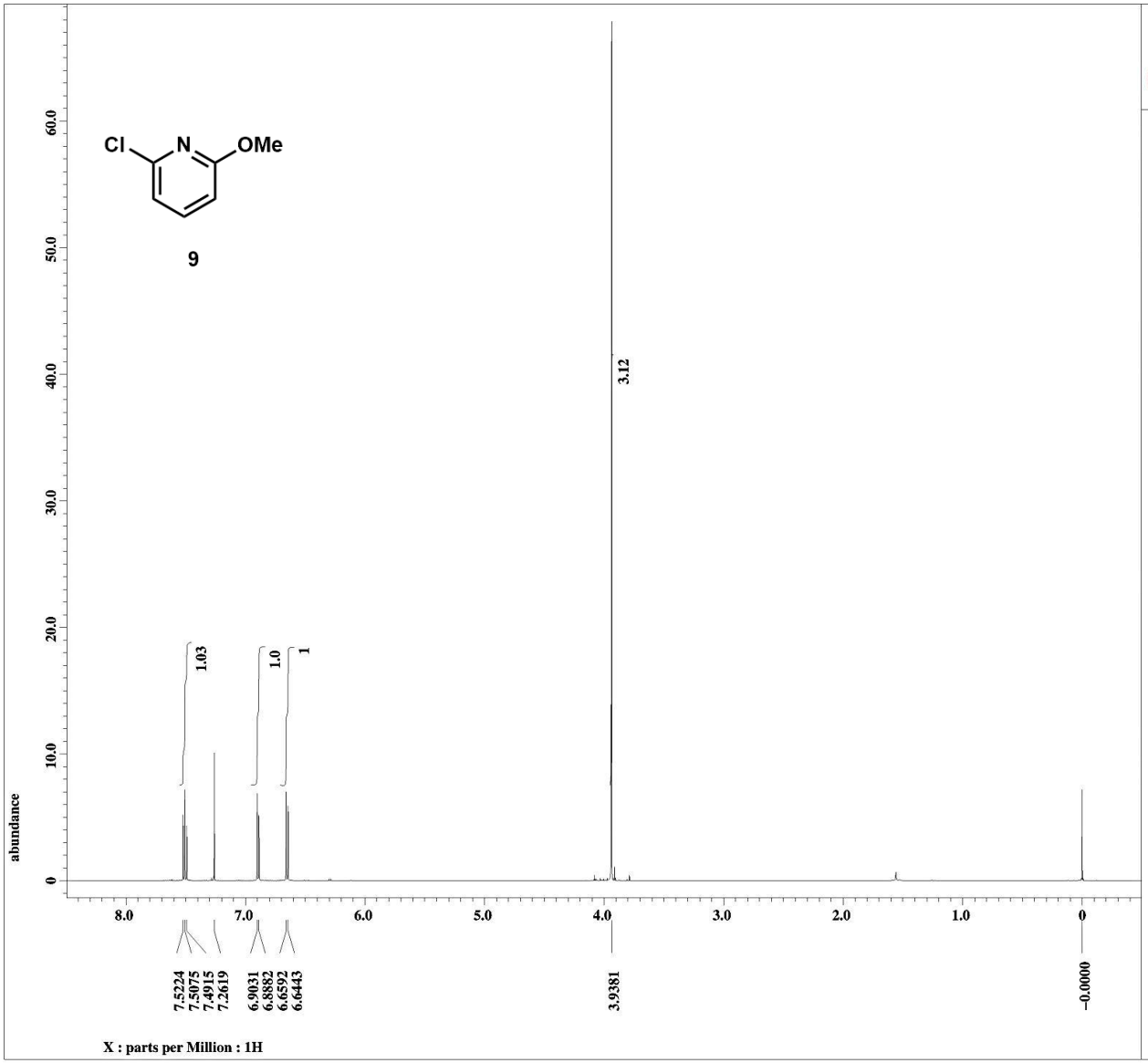
2	-CO_2Dpm	DME	20	25	-10 °C	1.3:1
3	-CO_2Dpm	DME	100	0	0 °C	1.2:1
4	-CO_2Dpm	IPA	20	25	0 °C	1.3:1
5	-CH_2OBn	IPA	20	25	rt	3:1
6	-CH_2OBn	IPA	20	25	0 °C	4:1
7	-CH_2OPMB	IPA	20	25	0 °C	12:1
8	-CH_2OPMB	IPA	5	25	-10 °C	20:1

[a]Determined by ^{1}H NMR.

NMR Spectral Data

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Revision_time     =  8-DEC-2013 15:03:57
Current_time      =  8-DEC-2013 15:07:17

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Spectrometer      = DELTA2_NMR

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X_resolution      = 0.5668198[Hz]
X_sweep           = 9.28677563[kHz]
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Irr_freq          = 495.13191398[MHz]
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Tri_freq          = 495.13191398[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

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X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 3.68[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 44
Relaxation_delay  = 5[s]
Repetition_time   = 6.76422912[s]
Temp_get          = 24.5[dC]
```

abundance
0 0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09 0.1 0.11 0.12 0.13 0.14 0.15 0.16 0.17 0.18 0.19 0.2
Cl
N
OMe
9
X : parts per Million : 13C
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
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148.4005
140.4916
116.2095
109.0761
77.2489
77.0000
76.7415
53.9530
JEOL
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Revision_time = 6-DEC-2013 15:56:50
Current_time = 6-DEC-2013 15:57:52
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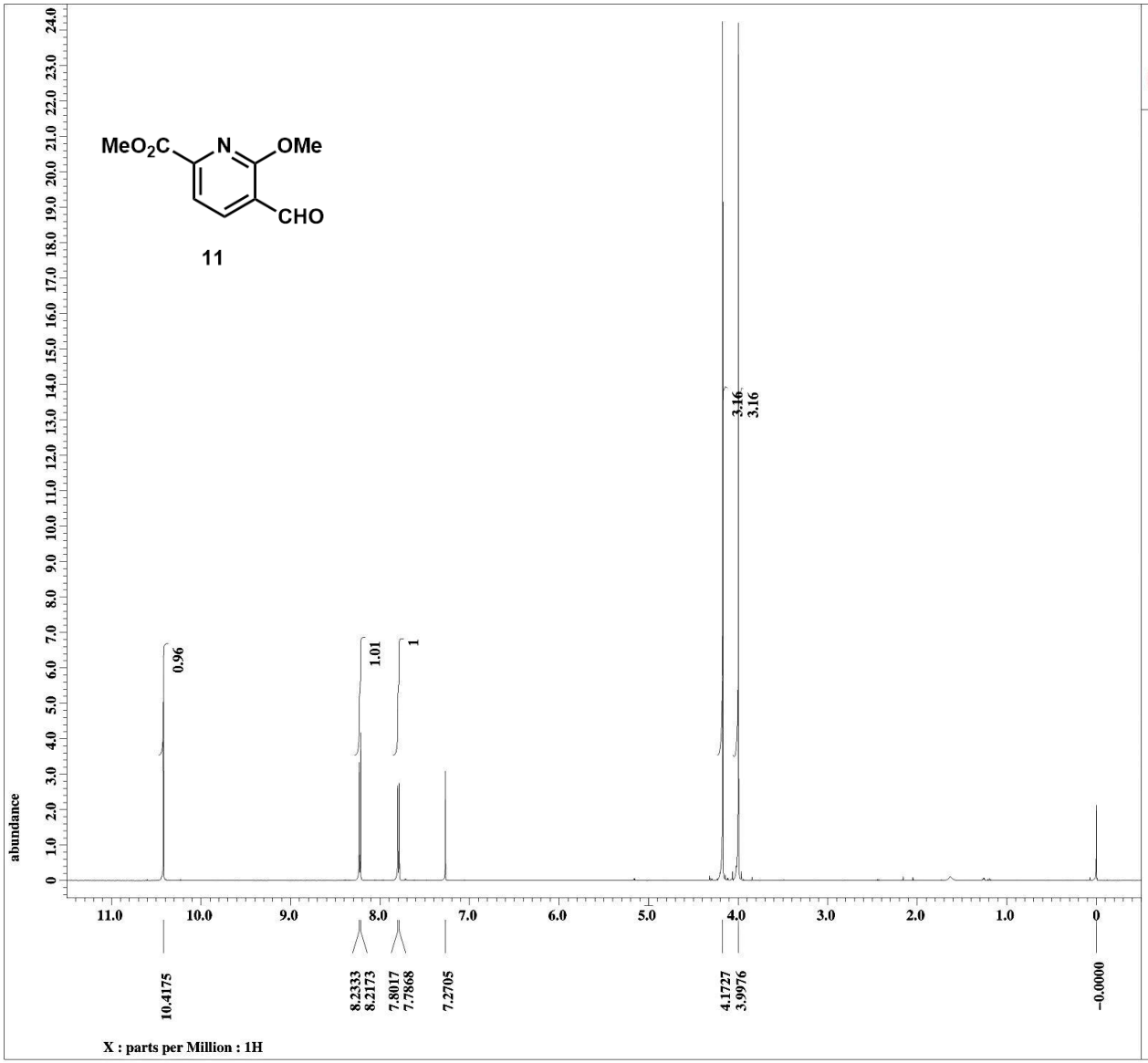


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Revision_time     =  6-DEC-2013 16:13:02
Current_time      =  6-DEC-2013 16:14:58

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Spectrometer      = DELTA2_NMR

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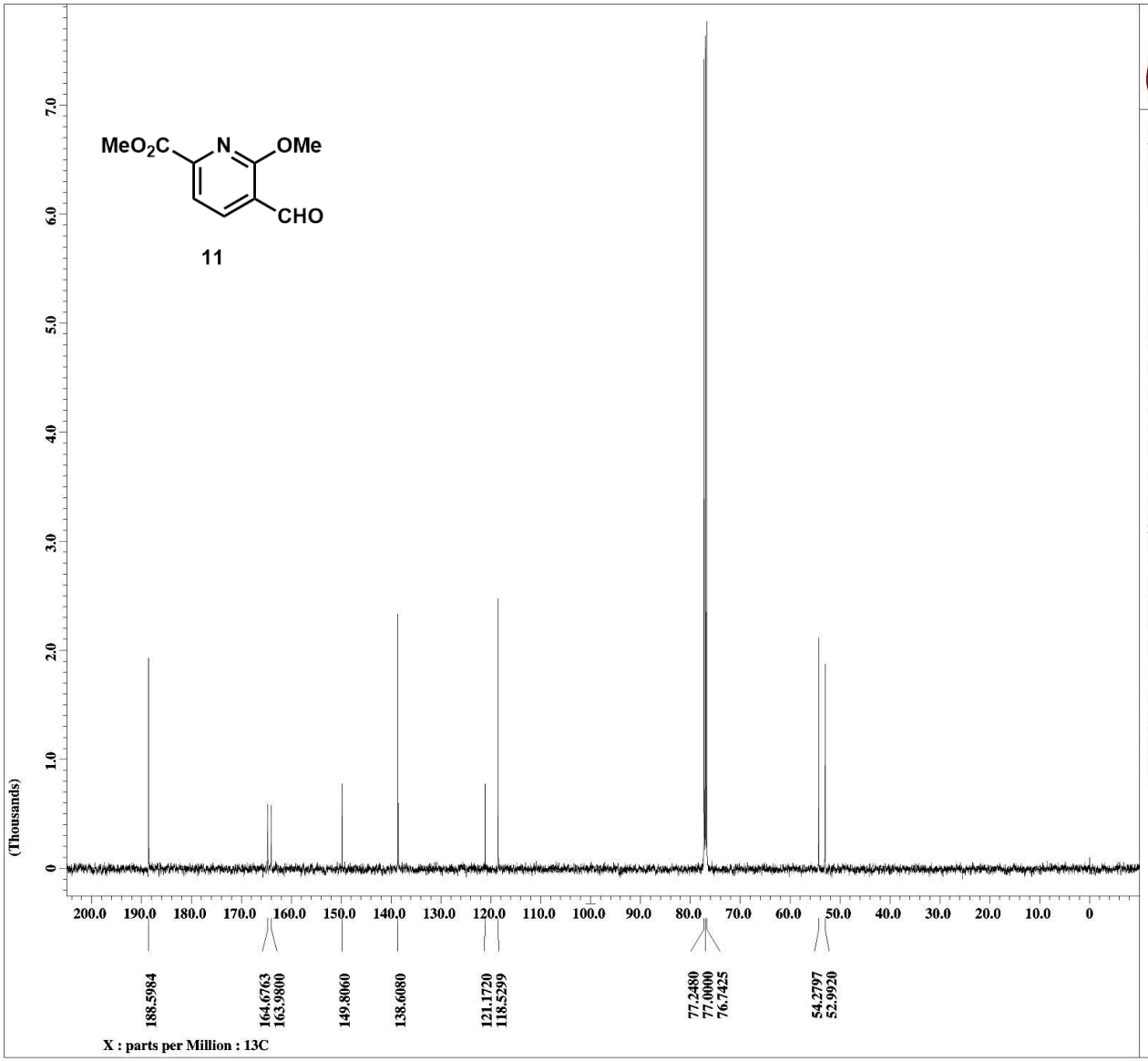


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Current_time      =  8-DEC-2013 21:33:49

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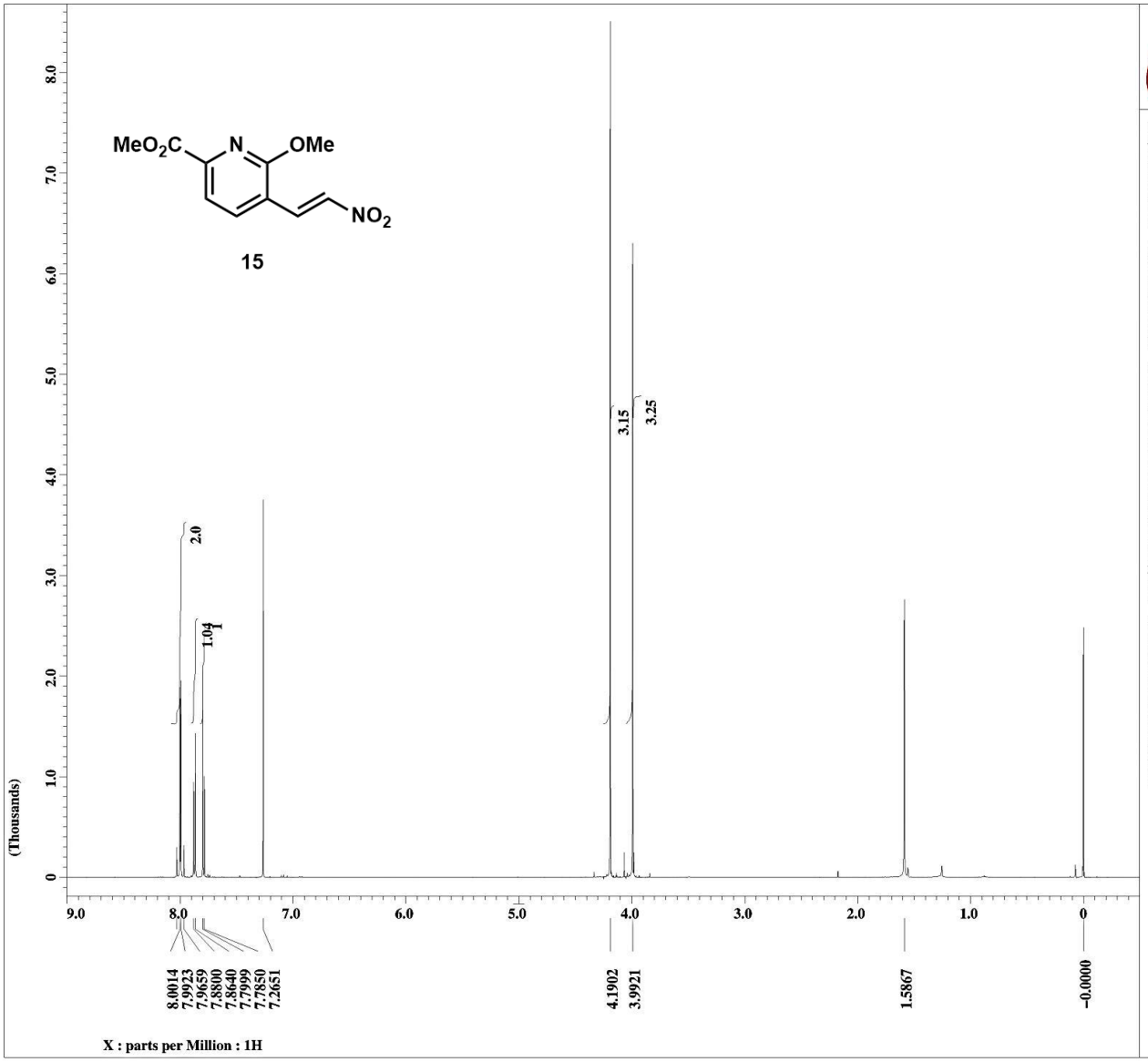


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Scans             = 8
Total_scans       = 8

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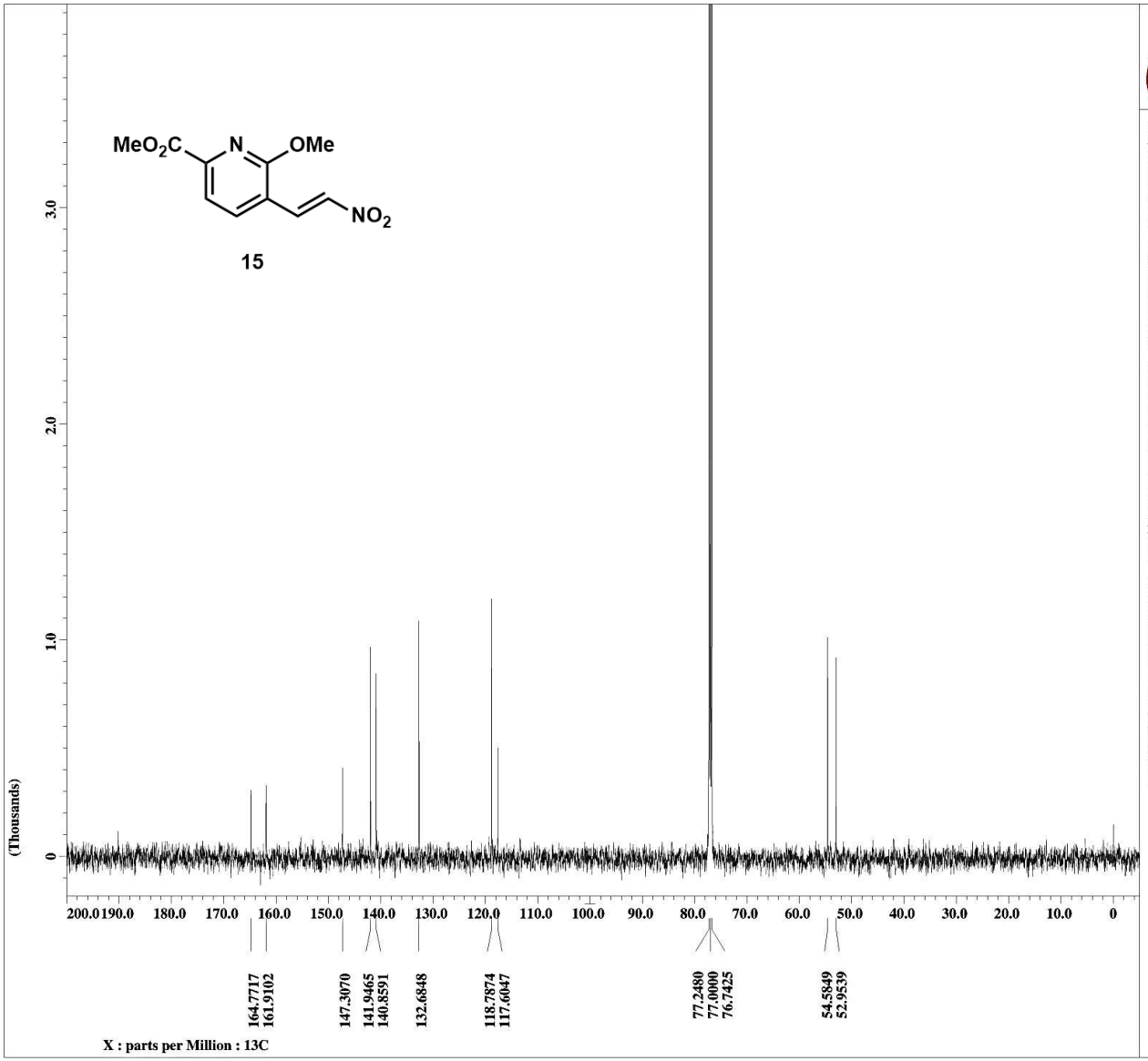

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Spectrometer      = DELTA2_NMR

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X_points          = 32768
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X_sweep           = 39.3081761[kHz]
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Irr_freq          = 500.15991521[MHz]
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X_atn             = 5.4[dB]
X_pulse           = 3.16666667[us]
Irr_atn_dec       = 21.8[dB]
Irr_atn_noe       = 21.8[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 58
Relaxation_delay  = 2[s]
Repetition_time   = 2.83361792[s]
Temp_get          = 22.8[dC]
```
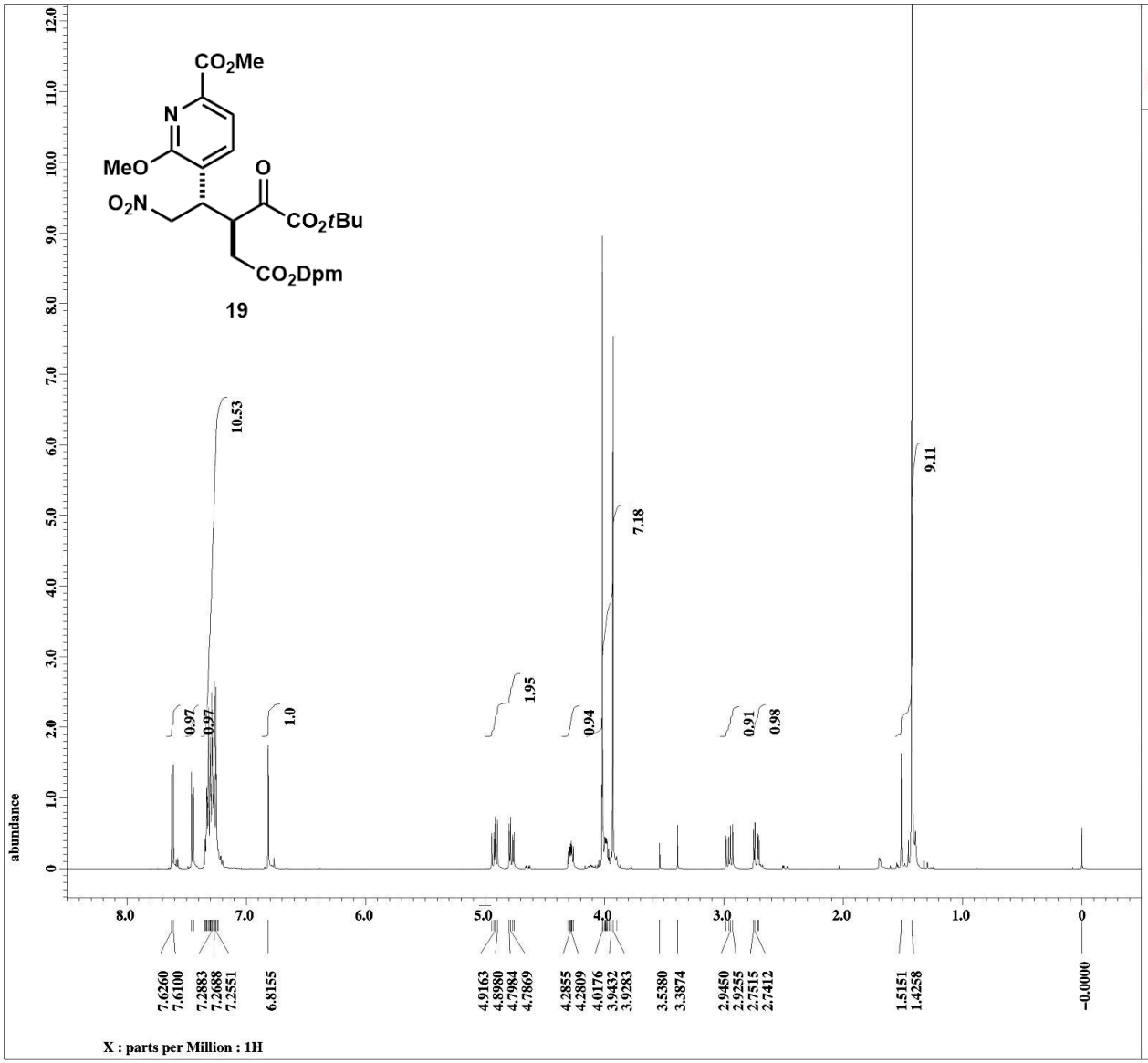

```
Filename                = HOo-120919-2-H-4.jdf
Author                  = delta
Experiment              = single_pulse.ex2
Sample_id               = 1
Solvent                 = CHLOROFORM-D
Creation_time           = 19-SEP-2012 16:22:17
Revision_time           = 6-DEC-2013 16:49:51
Current_time            = 6-DEC-2013 16:50:51

Comment                 = single_pulse
Data_format             = 1D COMPLEX
Dim_size                = 13107
Dim_title               = 1H
Dim_units               = [ppm]
Dimensions              = X
Site                    = ECA 500
Spectrometer            = DELTA2_NMR

Field_strength          = 11.62926421[T] (500[M
X_acq_duration          = 1.76422912[s]
X_domain                = 1H
X_freq                  = 495.13191398[MHz]
X_offset                = 5[ppm]
X_points                = 16384
X_prescans              = 1
X_resolution            = 0.5668198[Hz]
X_sweep                 = 9.28677563[KHz]
Irr_domain              = 1H
Irr_freq                = 495.13191398[MHz]
Irr_offset              = 5[ppm]
Tri_domain              = 1H
Tri_freq                = 495.13191398[MHz]
Tri_offset              = 5[ppm]
Clipped                 = FALSE
Mod_return              = 1
Scans                   = 8
Total_scans             = 8

X_90_width              = 8.7[us]
X_acq_time              = 1.76422912[s]
X_angle                 = 45[deg]
X_atn                   = 4[dB]
X_pulse                 = 4.35[us]
Irr_mode                = Off
Tri_mode                = Off
Dante_presat            = FALSE
Initial_wait            = 1[s]
Recvr_gain              = 44
Relaxation_delay        = 5[s]
Repetition_time         = 6.76422912[s]
Temp_get                = 24.7[dC]
```

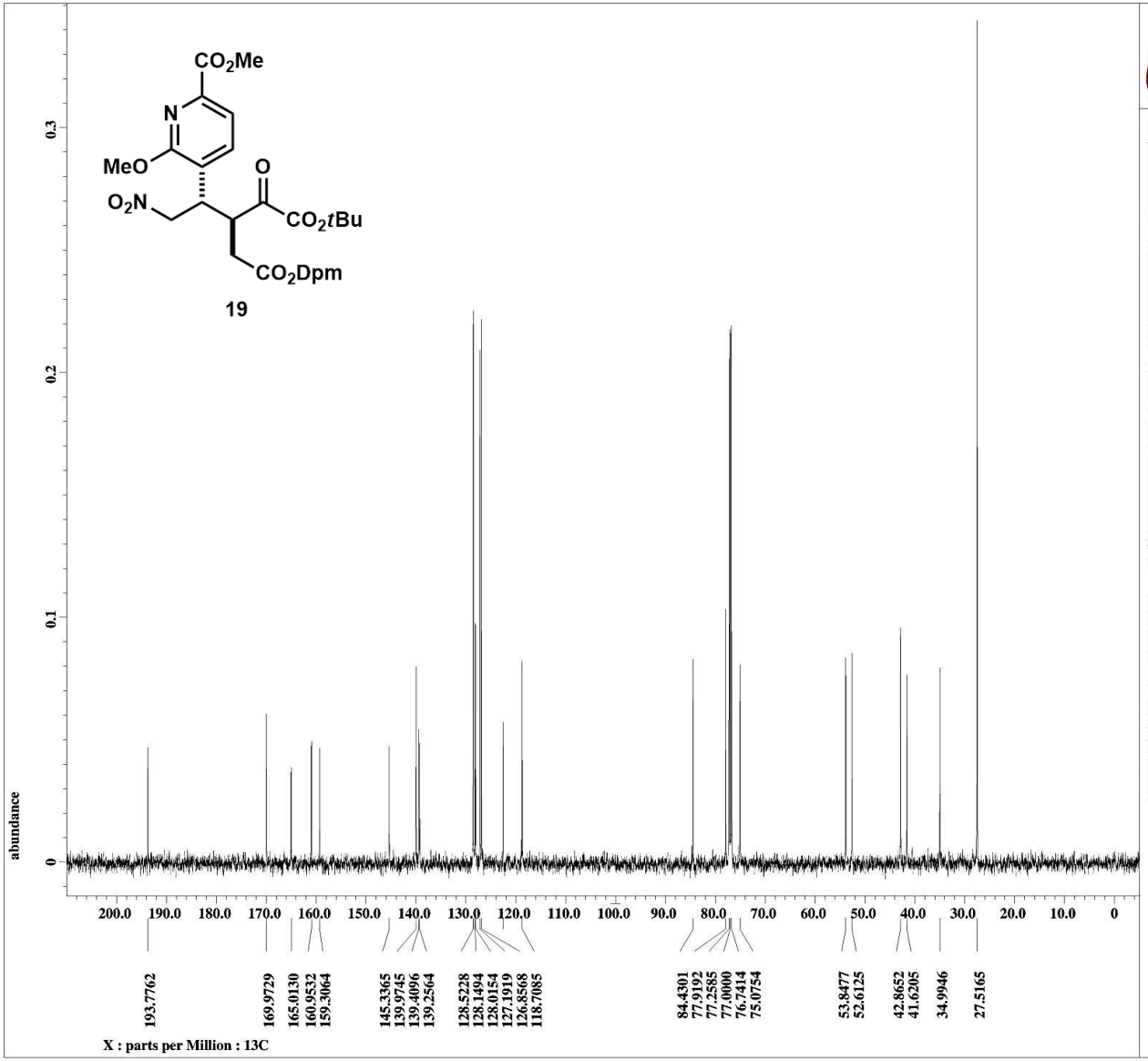
abundance
X : parts per Million : 13C
169.5612
139.7256
128.5229
128.0441
127.1058
77.2490
77.0000
76.7415
37.9820
25.5920
Br
O
ODpm
S3
Filename = HOo-120919-2-C-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 19-SEP-2012 16:42:43
Revision_time = 6-DEC-2013 16:51:38
Current_time = 6-DEC-2013 16:52:53
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.62926421[T] (500[M
X_acq_duration = 0.8388608[s]
X_domain = 13C
X_freq = 124.50100059[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.1920929[Hz]
X_sweep = 39.0625[kHz]
Irr_domain = 1H
Irr_freq = 495.13191398[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 400
Total_scans = 400
X_90_width = 17.2[us]
X_acq_time = 0.8388608[s]
X_angle = 30[deg]
X_atn = 6[dB]
X_pulse = 5.73333333[us]
Irr_atn_dec = 25.42[dB]
Irr_atn_noe = 25.42[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 2.8388608[s]
Temp_get = 25[dC]

abundance
X : parts per Million : 1H
tBuO
ODpm
17
7.3266
7.3175
7.2717
7.2625
7.2282
6.8676
3.1367
3.1230
3.1092
2.7669
2.7532
2.7406
1.5168
0.0000
10.13
1
2.06
2.04
9.05
Filename = HOo-120630-1-H-5.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 1-JUL-2012 02:57:00
Revision_time = 6-DEC-2013 16:57:13
Current_time = 6-DEC-2013 16:57:39
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.62926421[T] (500[M
X_acq_duration = 1.76422912[s]
X_domain = 1H
X_freq = 495.13191398[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.5668198[Hz]
X_sweep = 9.28677563[kHz]
Irr_domain = 1H
Irr_freq = 495.13191398[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 495.13191398[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 7.8[us]
X_acq_time = 1.76422912[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 3.9[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 24
Relaxation_delay = 5[s]
Repetition_time = 6.76422912[s]
Temp_get = 21.8[dC]

abundance
X : parts per Million : 13C
193.3262
171.0645
159.7181
139.8405
128.4176
127.8526
126.9622
84.0280
77.3160
77.2585
77.0000
76.7511
33.9222
27.6506
tBuO
ODpm
17
Filename = HOo-120630-1-C-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 1-JUL-2012 03:23:11
Revision_time = 6-DEC-2013 16:58:28
Current_time = 6-DEC-2013 17:00:45
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.62926421[T] (500[M
X_acq_duration = 0.8388608[s]
X_domain = 13C
X_freq = 124.50100559[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.1920929[Hz]
X_sweep = 39.0625[kHz]
Irr_domain = 1H
Irr_freq = 495.13191398[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 500
Total_scans = 500
X_90_width = 16.7[us]
X_acq_time = 0.8388608[s]
X_angle = 30[deg]
X_atn = 6.2[dB]
X_pulse = 5.56666667[us]
Irr_atn_dec = 25.42[dB]
Irr_atn_noe = 25.42[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recyc_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 2.8388608[s]
Temp_get = 22.1[dC]

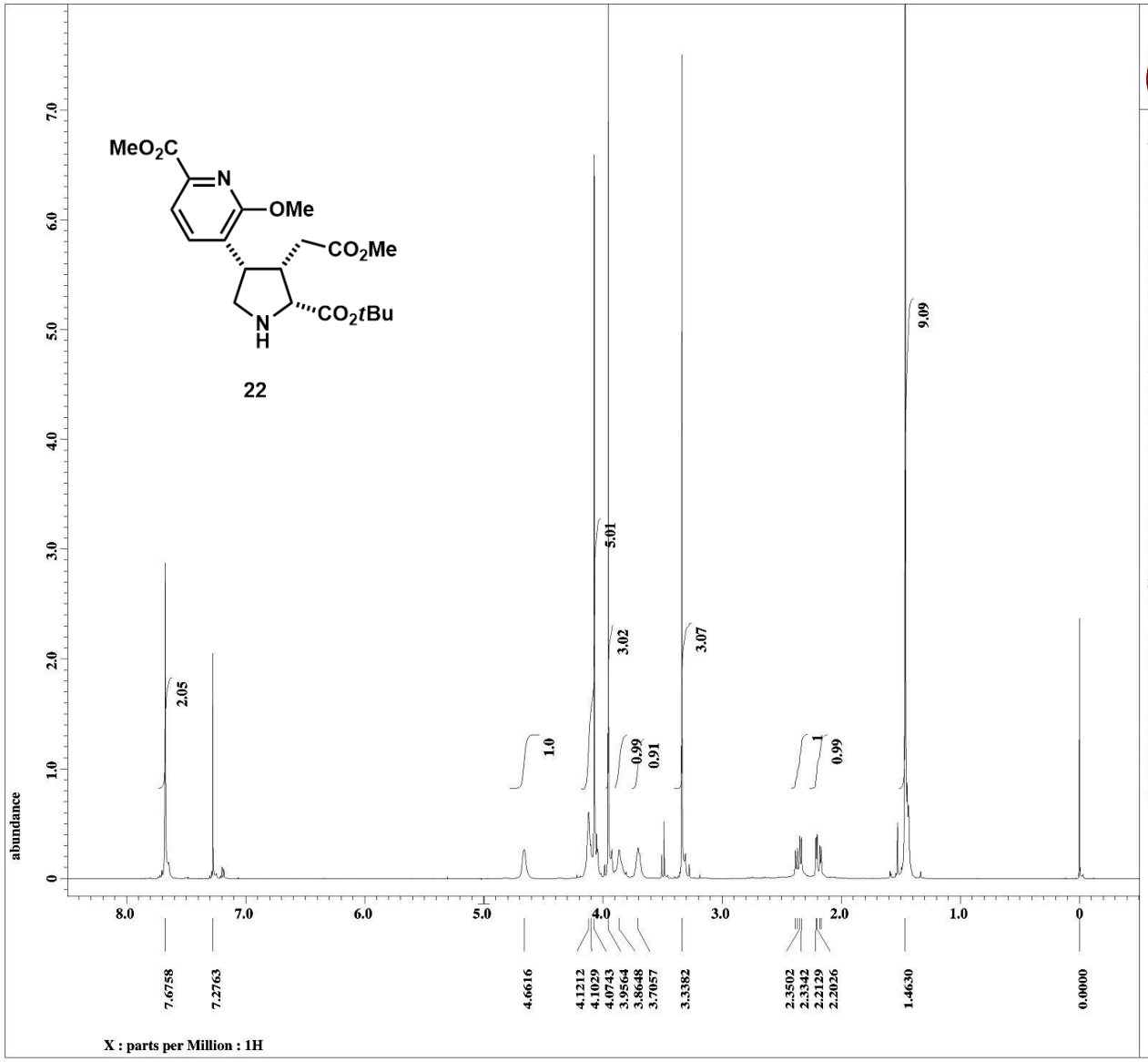


```
Filename          = HOo-120706-1-H-4.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     =  6-JUL-2012 16:52:12
Revision_time     =  6-DEC-2013 17:12:07
Current_time      =  6-DEC-2013 17:13:18

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_strength    = 11.62926421[T] (500[M
X_acq_duration    = 1.76422912[s]
X_domain          = 1H
X_freq            = 495.13191398[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.5668198[Hz]
X_sweep           = 9.28677563[kHz]
Irr_domain        = 1H
Irr_freq          = 495.13191398[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 495.13191398[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 7.8[us]
X_acq_time        = 1.76422912[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 3.9[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 5[s]
Repetition_time   = 6.76422912[s]
Temp_get          = 23.3[dC]
```



JEOL

```
Filename          = HOo-120706-1-C-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     =  6-JUL-2012 17:17:54
Revision_time     =  6-DEC-2013 17:18:53
Current_time      =  6-DEC-2013 17:20:44

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_strength    = 11.62926421[T] (500[M
X_acq_duration    = 0.8388608[s]
X_domain          = 13C
X_freq            = 124.5010059[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.1920929[Hz]
X_sweep           = 39.0625[kHz]
Irr_domain        = 1H
Irr_freq          = 495.13191398[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 500
Total_scans       = 500

X_90_width        = 16.7[us]
X_acq_time        = 0.8388608[s]
X_angle           = 30[deg]
X_atn             = 6.2[dB]
X_pulse           = 5.56666667[us]
Irr_atn_dec       = 25.42[dB]
Irr_atn_noe       = 25.42[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 50
Relaxation_delay  = 2[s]
Repetition_time   = 2.8388608[s]
Temp_get          = 23.6[dC]
```

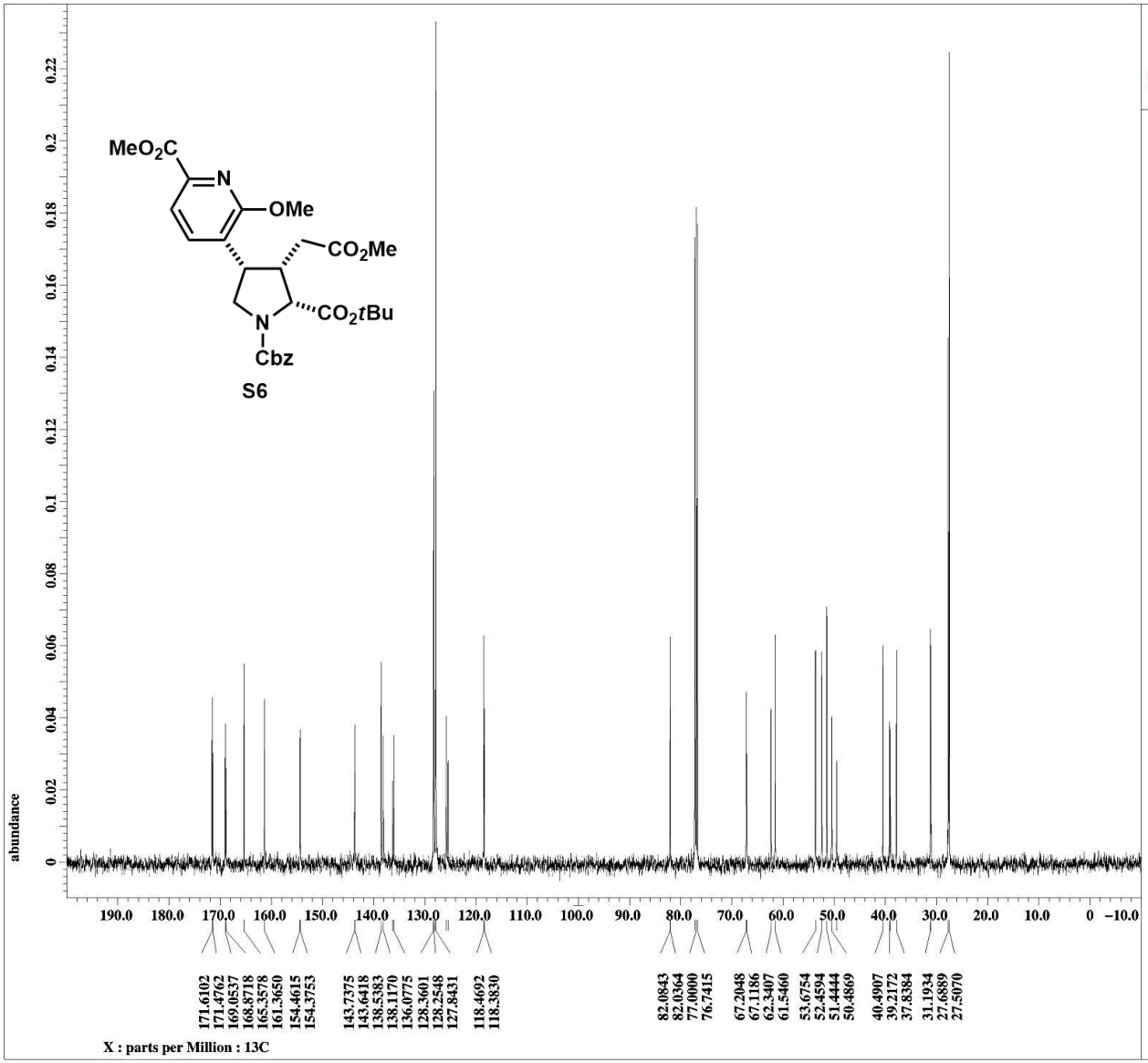


JEOL

```
Filename          = HOo-121203-2-H-4.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     =  3-DEC-2012 15:58:59
Revision_time     =  6-DEC-2013 17:35:19
Current_time      =  6-DEC-2013 17:35:39

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_strength    = 11.62926421[T] (500[M
X_acq_duration    = 1.76422912[s]
X_domain          = 1H
X_freq            = 495.13191398[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.5668198[Hz]
X_sweep           = 9.28677563[kHz]
Irr_domain        = 1H
Irr_freq          = 495.13191398[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 495.13191398[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 8.7[us]
X_acq_time        = 1.76422912[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 4.35[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 40
Relaxation_delay  = 5[s]
Repetition_time   = 6.76422912[s]
Temp_get          = 20.5[dC]
```

abundance
X : parts per Million : 13C
170.7628
165.7886
165.2524
161.6187
144.6854
137.2696
122.3470
118.3543
85.5648
77.2585
77.0000
76.7415
63.3269
54.0967
52.6700
51.7317
46.0633
40.6008
38.9395
30.4657
27.8900
MeO2C
OMe
CO2Me
CO2tBu
22
Filename = HOo-121203-2-C-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 3-DEC-2012 16:47:00
Revision_time = 6-DEC-2013 17:40:32
Current_time = 6-DEC-2013 17:41:56
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.62926421[T] (500[M
X_acq_duration = 0.8388608[s]
X_domain = 13C
X_freq = 124.50100559[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.1920929[Hz]
X_sweep = 39.0625[kHz]
Irr_domain = 1H
Irr_freq = 495.13191398[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 1000
Total_scans = 1000
X_90_width = 17.2[us]
X_acq_time = 0.8388608[s]
X_angle = 30[deg]
X_atn = 6[dB]
X_pulse = 5.73333333[us]
Irr_atn_dec = 25.42[dB]
Irr_atn_noe = 25.42[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 52
Relaxation_delay = 2[s]
Repetition_time = 2.8388608[s]
Temp_get = 20.8[dC]

abundance
X : parts per Million : 1H
MeO2C
OMe
CO2Me
CO2tBu
N
Cbz
S6
7.8670
7.8509
7.6998
7.6838
7.3438
7.3346
7.2992
5.2294
5.1584
5.1492
4.5402
4.5219
4.5047
4.0251
3.9484
3.9255
3.8934
3.5660
3.5465
3.5214
2.3411
2.3285
2.2026
2.1167
2.0984
1.3737
1.3508
1.2112
1.1894
−0.0000
0.98
1.0
5.72
2.05
1
9.05
4.05
2.1
3.83
5.21
Filename = HOo-121205-4-H-4.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 5-DEC-2012 15:50:21
Revision_time = 8-DEC-2013 15:44:48
Current_time = 8-DEC-2013 15:45:38
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.62926421[T] (500[M
X_acq_duration = 1.76422912[s]
X_domain = 1H
X_freq = 495.13191398[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.5668198[Hz]
X_sweep = 9.28677563[kHz]
Irr_domain = 1H
Irr_freq = 495.13191398[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 495.13191398[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 8.7[us]
X_acq_time = 1.76422912[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 4.35[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 24
Relaxation_delay = 5[s]
Repetition_time = 6.76422912[s]
Temp_get = 20.5[dC]



```
Filename          = HOo-121205-4-C-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     =  5-DEC-2012 16:15:12
Revision_time     =  6-DEC-2013 18:00:54
Current_time      =  6-DEC-2013 18:03:42

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_strength    = 11.62926421[T] (500[M
X_acq_duration    = 0.8388608[s]
X_domain          = 13C
X_freq            = 124.5010059[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.1920929[Hz]
X_sweep           = 39.0625[kHz]
Irr_domain        = 1H
Irr_freq          = 495.13191398[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 502.0
Total_scans       = 502.0

X_90_width        = 17.2[us]
X_acq_time        = 0.8388608[s]
X_angle           = 30[deg]
X_atn             = 6[dB]
X_pulse           = 5.73333333[us]
Irr_atn_dec       = 25.42[dB]
Irr_atn_noe       = 25.42[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 46
Relaxation_delay  = 2[s]
Repetition_time   = 2.8388608[s]
Temp_get          = 20.6[dC]
```

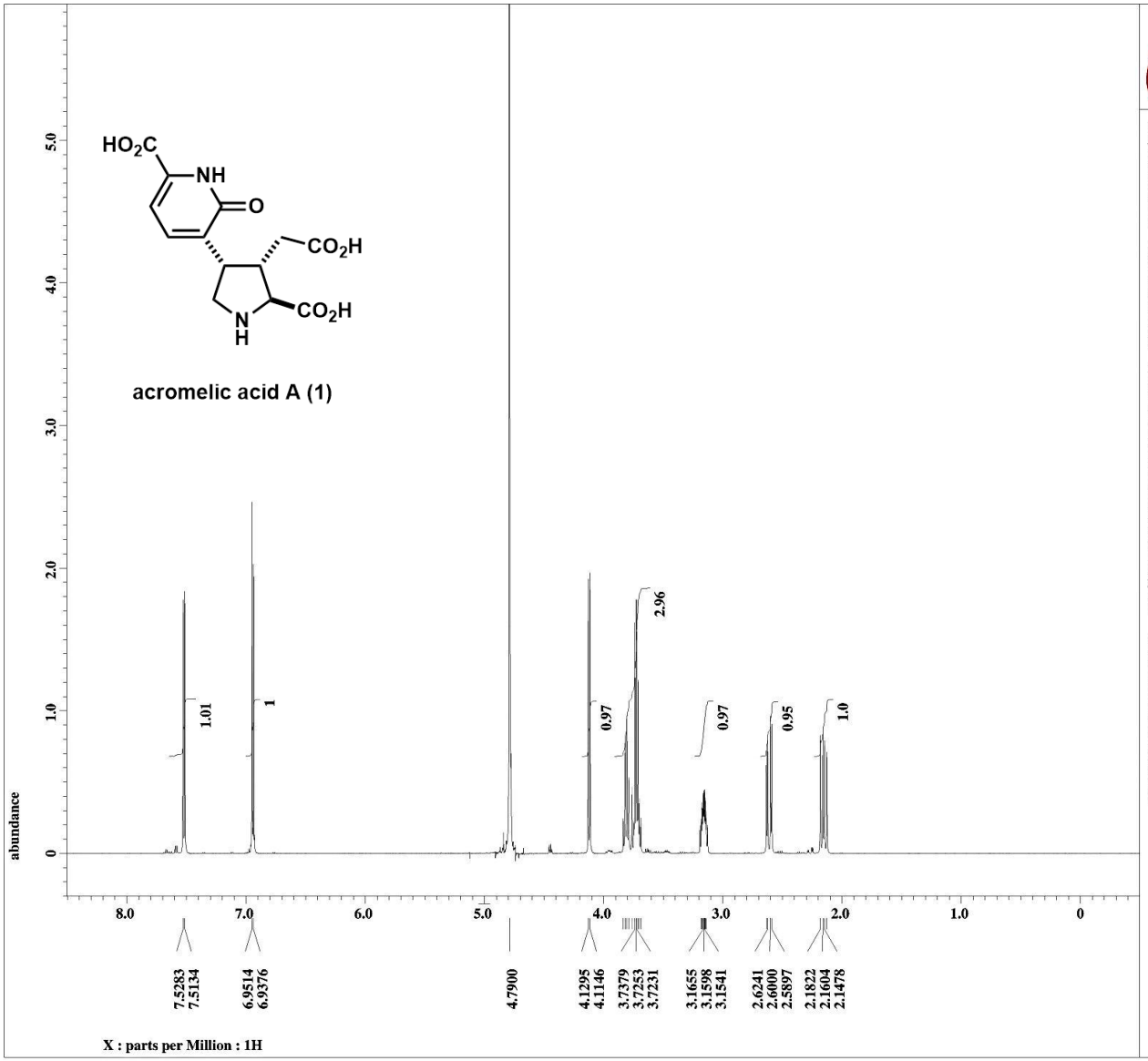
Filename = HOo-121211-2-H-4.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 11-DEC-2012 18:00:31
Revision_time = 6-DEC-2013 18:15:28
Current_time = 6-DEC-2013 18:15:48

Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR

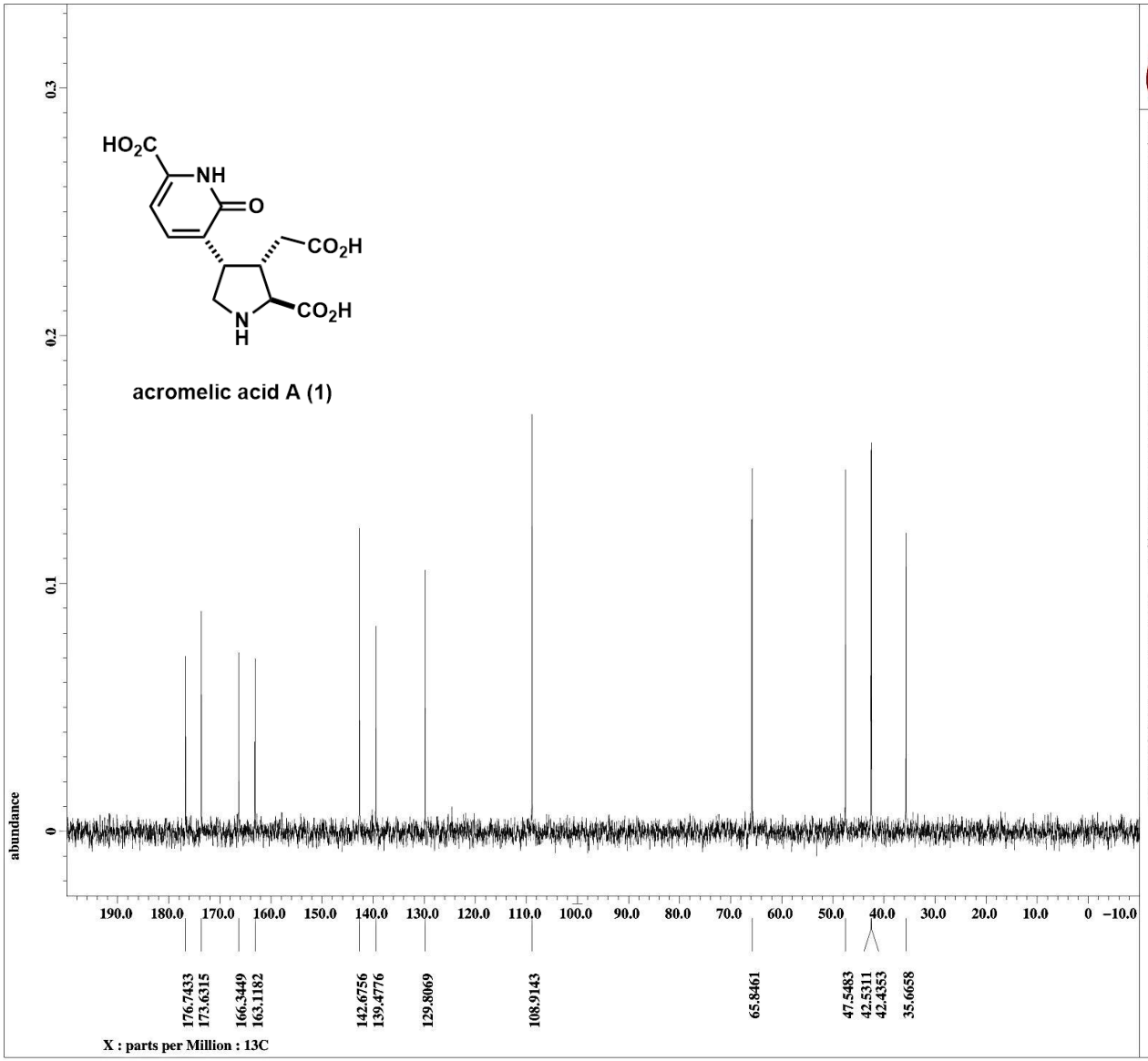
Field_strength = 11.62926421[T] (500[M
X_acq_duration = 1.76422912[s]
X_domain = 1H
X_freq = 495.13191398[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.5668198[Hz]
X_sweep = 9.28677563[kHz]
Irr_domain = 1H
Irr_freq = 495.13191398[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 495.13191398[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8

X_90_width = 8.7[us]
X_acq_time = 1.76422912[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 4.35[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 28
Relaxation_delay = 5[s]
Repetition_time = 6.76422912[s]
Temp_get = 20.6[dC]

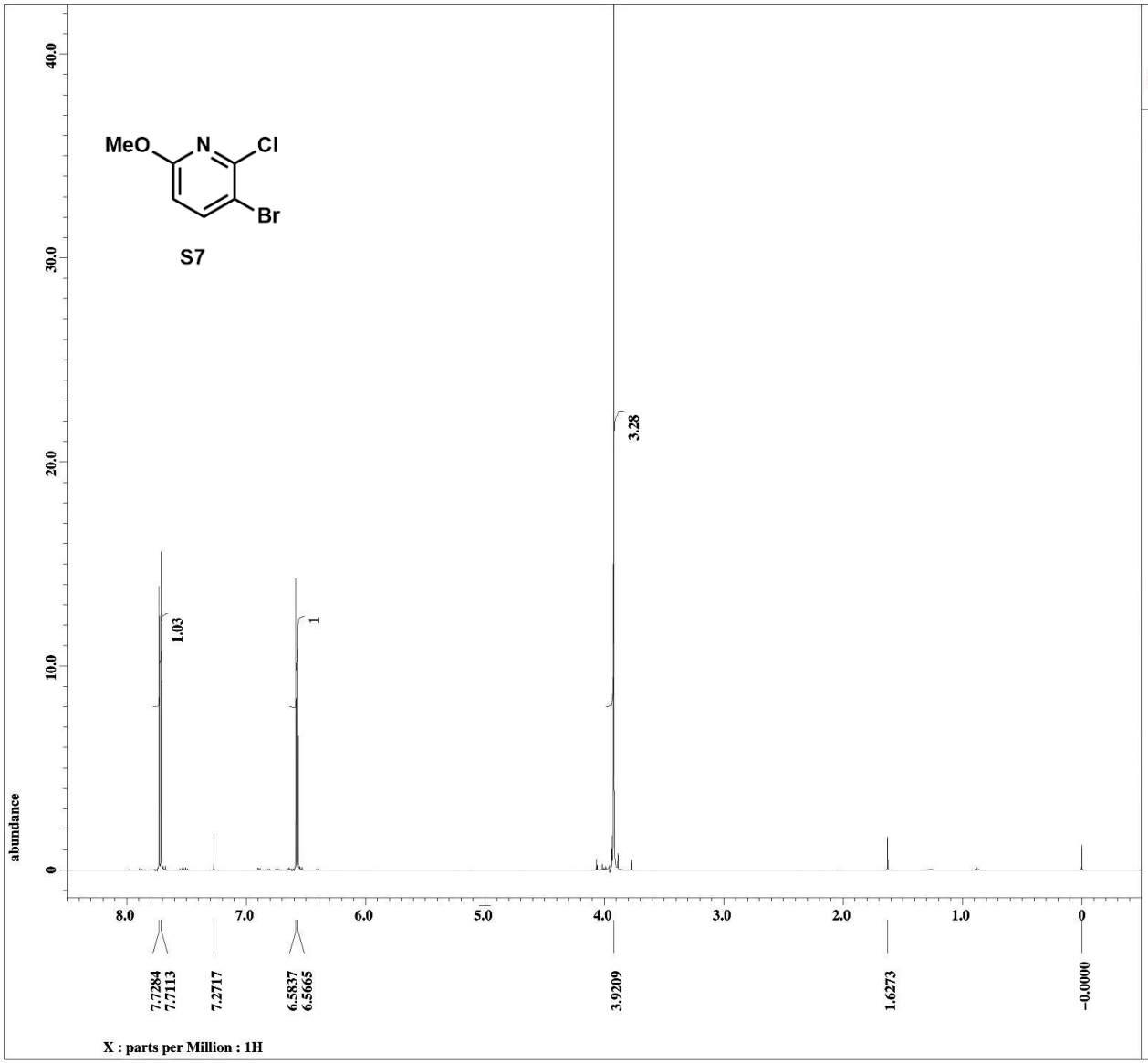
abundance
X : parts per Million : 13C
24
MeO2C
OMe
CO2Me
CO2H
N
Cbz
175.0764
171.6389
171.4857
165.3769
161.4033
155.0647
154.2891
144.1205
136.6425
135.9435
128.5037
128.3984
128.0346
118.7947
118.6415
77.2585
77.0000
76.7415
67.7314
67.5591
63.4706
63.0110
53.8956
52.6413
51.8083
48.8592
42.7599
41.6205
39.2172
38.3650
33.0701
Filename = HOo-121211-2-C-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 11-DEC-2012 18:24:40
Revision_time = 6-DEC-2013 18:19:40
Current_time = 6-DEC-2013 18:25:01
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.62926421[T] (500[M
X_acq_duration = 0.8388608[s]
X_domain = 13C
X_freq = 124.50100559[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.1920929[Hz]
X_sweep = 39.0625[kHz]
Irr_domain = 1H
Irr_freq = 495.13191398[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 500
Total_scans = 500
X_90_width = 17.2[us]
X_acq_time = 0.8388608[s]
X_angle = 30[deg]
X_atn = 6[dB]
X_pulse = 5.73333333[us]
Irr_atn_dec = 25.42[dB]
Irr_atn_noe = 25.42[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recyc_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 2.8388608[s]
Temp_get = 20.5[dC]




```
Filename          = HOo-130117-1-H-4.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = 1
Solvent           = D2O
Creation_time     = 17-JAN-2013 23:01:26
Revision_time     =  6-DEC-2013 18:35:28
Current_time      =  6-DEC-2013 18:36:23

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_strength    = 11.62926421[T] (500[M
X_acq_duration    = 1.76422912[s]
X_domain          = 1H
X_freq            = 495.13191398[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.5668198[Hz]
X_sweep           = 9.28677563[kHz]
Irr_domain        = 1H
Irr_freq          = 495.13191398[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 495.13191398[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 12.9[us]
X_acq_time        = 1.76422912[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.45[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 44
Relaxation_delay  = 5[s]
Repetition_time   = 6.76422912[s]
Temp_get          = 460.0[dC]
```




```
Filename          = HOo-130117-1-C-2.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = 1
Solvent           = D2O
Creation_time     = 17-JAN-2013 23:49:22
Revision_time     =  6-DEC-2013 18:37:53
Current_time      =  6-DEC-2013 18:39:25

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_strength    = 11.62926421[T] (500[M
X_acq_duration    = 0.8388608[s]
X_domain          = 13C
X_freq            = 124.5010059[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.1920929[Hz]
X_sweep           = 39.0625[kHz]
Irr_domain        = 1H
Irr_freq          = 495.13191398[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 1000
Total_scans       = 1000

X_90_width        = 10.6[us]
X_acq_time        = 0.8388608[s]
X_angle           = 30[deg]
X_atn             = 8[dB]
X_pulse           = 3.53333333[us]
Irr_atn_dec       = 21.06[dB]
Irr_atn_noe       = 21.06[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 56
Relaxation_delay  = 2[s]
Repetition_time   = 2.8388608[s]
Temp_get          = 460.0[dC]
```



JEOL

```
Filename          = HOo-130219-5-H-4.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     = 19-FEB-2013 15:21:12
Revision_time     =  6-DEC-2013 20:16:48
Current_time      =  6-DEC-2013 20:17:21

Comment           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_strength    = 11.62926421[T] (500[M
X_acq_duration    = 1.76422912[s]
X_domain          = 1H
X_freq            = 495.13191398[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.5668198[Hz]
X_sweep           = 9.28677563[kHz]
Irr_domain        = 1H
Irr_freq          = 495.13191398[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 495.13191398[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 7.36[us]
X_acq_time        = 1.76422912[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 3.68[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 32
Relaxation_delay  = 5[s]
Repetition_time   = 6.76422912[s]
Temp_get          = 21.8[dC]
```

abundance
0
0.1
0.2
0.3
MeO
N
Cl
Br
S7
X : parts per Million : 13C
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
162.4087
147.2706
143.8428
110.9049
110.1006
77.2489
77.0000
76.7415
54.3073
Filename = HOo-130219-5-C-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 19-FEB-2013 15:35:59
Revision_time = 6-DEC-2013 20:18:47
Current_time = 6-DEC-2013 20:19:58
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.62926421[T] (500[M
X_acq_duration = 0.8388608[s]
X_domain = 13C
X_freq = 124.50100559[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.1920929[Hz]
X_sweep = 39.0625[kHz]
Irr_domain = 1H
Irr_freq = 495.13191398[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 300
Total_scans = 300
X_90_width = 15.6[us]
X_acq_time = 0.8388608[s]
X_angle = 30[deg]
X_atn = 6[dB]
X_pulse = 5.2[us]
Irr_atn_dec = 25.94[dB]
Irr_atn_noe = 25.94[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 46
Relaxation_delay = 2[s]
Repetition_time = 2.8388608[s]
Temp_get = 22.1[dC]

```
Filename                = HOo-130809-1-4.jdf
Author                  = delta
Experiment              = single_pulse.ex2
Sample_id               = S#381530
Solvent                 = CHLOROFORM-D
Creation_time           =  9-AUG-2013 10:28:31
Revision_time           =  8-DEC-2013 15:23:50
Current_time            =  8-DEC-2013 15:24:02

Comment                 = single_pulse
Data_format             = 1D COMPLEX
Dim_size                = 13107
Dim_title               = 1H
Dim_units               = [ppm]
Dimensions              = X
Site                    = ECA 500
Spectrometer            = DELTA2_NMR

Field_strength          = 11.62926421[T] (500[M
X_acq_duration          = 1.76422912[s]
X_domain                = 1H
X_freq                  = 495.13191398[MHz]
X_offset                = 5[ppm]
X_points                = 16384
X_prescans              = 1
X_resolution            = 0.5668198[Hz]
X_sweep                 = 9.28677563[kHz]
Irr_domain              = 1H
Irr_freq                = 495.13191398[MHz]
Irr_offset              = 5[ppm]
Tri_domain              = 1H
Tri_freq                = 495.13191398[MHz]
Tri_offset              = 5[ppm]
Clipped                 = FALSE
Mod_return              = 1
Scans                   = 8
Total_scans             = 8

X_90_width              = 7.36[us]
X_acq_time              = 1.76422912[s]
X_angle                 = 45[deg]
X_atn                   = 4[dB]
X_pulse                 = 3.68[us]
Irr_mode                = Off
Tri_mode                = Off
Dante_presat            = FALSE
Initial_wait            = 1[s]
Recvr_gain              = 44
Relaxation_delay        = 5[s]
Repetition_time         = 6.76422912[s]
Temp_get                = 28.2[dC]
```

abundance
0 0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09 0.1 0.11 0.12 0.13 0.14 0.15 0.16
MeO
N
CO2nBu
CHO
13
X : parts per Million : 13C
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
189.1420
166.0663
165.1567
150.7368
138.6149
125.8706
114.1030
77.2585
77.0000
76.7415
66.2952
54.4605
30.5423
19.1576
13.6712
Filename = HOo-130808-1-C-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = SM390801
Solvent = CHLOROFORM-D
Creation_time = 8-AUG-2013 11:12:03
Revision_time = 6-DEC-2013 20:32:46
Current_time = 6-DEC-2013 20:34:53
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.62926421[T] (500[M
X_acq_duration = 0.8388608[s]
X_domain = 13C
X_freq = 124.50100559[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.1920929[Hz]
X_sweep = 39.0625[kHz]
Irr_domain = 1H
Irr_freq = 495.13191398[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 600
Total_scans = 600
X_90_width = 15.6[us]
X_acq_time = 0.8388608[s]
X_angle = 30[deg]
X_atn = 6[dB]
X_pulse = 5.2[us]
Irr_atn_dec = 25.434[dB]
Irr_atn_noe = 25.434[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recyc_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 2.8388608[s]
Temp_get = 27.8[dC]

abundance
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0 21.0 22.0 23.0 24.0 25.0 26.0 27.0
X : parts per Million : 1H
7.9059
7.8887
7.2660
6.8664
6.8493
5.8493
3.9724
3.9552
3.3405
1.6090
−0.0000
1.0
1.0
0.99
6.18
6.24
MeO
N
CO2Me
OMe
OMe
S8
Filename = HOo-130919-5-4.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = s#861986
Solvent = CHLOROFORM-D
Creation_time = 19-SEP-2013 23:47:40
Revision_time = 6-DEC-2013 20:38:57
Current_time = 6-DEC-2013 20:40:05
Comment = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.62926421[T] (500[M
X_acq_duration = 1.76422912[s]
X_domain = 1H
X_freq = 495.13191398[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.5668198[Hz]
X_sweep = 9.28677563[kHz]
Irr_domain = 1H
Irr_freq = 495.13191398[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 495.13191398[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 7.36[us]
X_acq_time = 1.76422912[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 3.68[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 40
Relaxation_delay = 5[s]
Repetition_time = 6.76422912[s]
Temp_get = 25.5[dC]

abundance
0
0.1
0.2
0.3
MeO
N
CO2Me
OMe
OMe
S8
X : parts per Million : 13C
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
166.9089
163.2800
145.4514
138.3468
127.0771
113.0210
99.9512
77.2585
77.0000
76.7415
53.8094
53.6084
52.5551
Filename = HOo-130919-5-C-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = s#863439
Solvent = CHLOROFORM-D
Creation_time = 20-SEP-2013 00:36:19
Revision_time = 6-DEC-2013 20:42:09
Current_time = 6-DEC-2013 20:43:42
Comment = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.62926421[T] (500[M
X_acq_duration = 0.8388608[s]
X_domain = 13C
X_freq = 124.50100559[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.1920929[Hz]
X_sweep = 39.0625[kHz]
Irr_domain = 1H
Irr_freq = 495.13191398[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 1000
Total_scans = 1000
X_90_width = 15.6[us]
X_acq_time = 0.8388608[s]
X_angle = 30[deg]
X_atn = 6[dB]
X_pulse = 5.2[us]
Irr_atn_dec = 25.434[dB]
Irr_atn_noe = 25.434[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 56
Relaxation_delay = 2[s]
Repetition_time = 2.8388608[s]
Temp_get = 25.7[dC]

abundance
0
10.0
20.0
30.0
MeO
N
CO2tBu
CHO
14
X : parts per Million : 1H
10.3500
8.1509
8.1337
7.2671
6.9156
6.8985
4.0628
1.6531
-0.0000
0.95
1
1.01
3.07
9.29
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
Filename = AA-130628-4-4.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = AA-130628-4
Solvent = CHLOROFORM-D
Creation_time = 28-JUN-2013 14:43:47
Revision_time = 6-DEC-2013 20:47:27
Current_time = 6-DEC-2013 20:50:49
Comment = AA-561 1H date
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.62926421[T] (500[M
X_acq_duration = 1.76422912[s]
X_domain = 1H
X_freq = 495.13191398[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.5668198[Hz]
X_sweep = 9.28677563[kHz]
Irr_domain = 1H
Irr_freq = 495.13191398[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 495.13191398[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 7.36[us]
X_acq_time = 1.76422912[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 3.68[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 40
Relaxation_delay = 5[s]
Repetition_time = 6.76422912[s]
Temp_get = 24.4[dC]

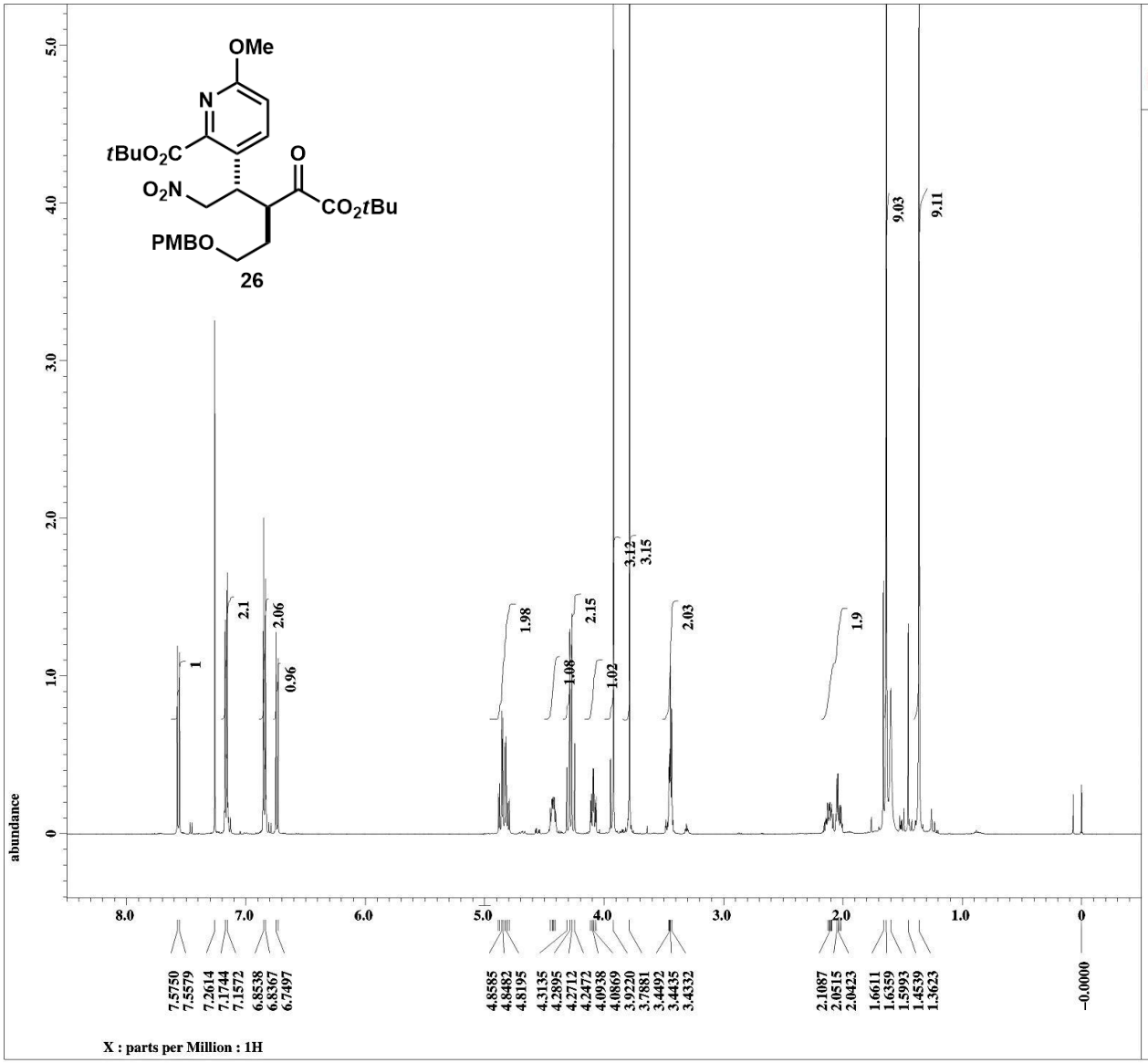
abundance
0
0.1
0.2
0.3
MeO
N
CO2tBu
CHO
14
X : parts per Million : 13C
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
189.0750
166.1238
164.2471
152.2688
138.5000
125.1238
113.5764
83.9132
77.2586
77.0000
76.7415
54.4127
28.1198
Filename = AA-130628-6-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = AA-130628-6
Solvent = CHLOROFORM-D
Creation_time = 28-JUN-2013 15:46:48
Revision_time = 6-DEC-2013 20:57:33
Current_time = 6-DEC-2013 21:00:31
Comment = AA-561 13C date
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.62926421[T] (500[M
X_acq_duration = 0.8388608[s]
X_domain = 13C
X_freq = 124.50100559[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.1920929[Hz]
X_sweep = 39.0625[kHz]
Irr_domain = 1H
Irr_freq = 495.13191398[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 1000
Total_scans = 1000
X_90_width = 15.6[us]
X_acq_time = 0.8388608[s]
X_angle = 30[deg]
X_atn = 6[dB]
X_pulse = 5.2[us]
Irr_atn_dec = 25.434[dB]
Irr_atn_noe = 25.434[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 54
Relaxation_delay = 2[s]
Repetition_time = 2.8388608[s]
Temp_get = 24.2[dC]

abundance
0
10.0
20.0
30.0
40.0
MeO
N
CO2tBu
NO2
16
X : parts per Million : 1H
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.6054
8.5779
0.92
7.7685
7.7502
1
7.4342
7.4068
7.2660
0.97
6.9168
6.9008
0.97
4.0411
3.01
1.6622
1.5981
9.03
−0.0000
Filename = AA-130703-5-4.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = AA-130703-5
Solvent = CHLOROFORM-D
Creation_time = 3-JUL-2013 23:28:40
Revision_time = 6-DEC-2013 21:04:38
Current_time = 6-DEC-2013 21:06:18
Comment = nitroolefin tritu wit
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.62926421[T] (500[M
X_acq_duration = 1.76422912[s]
X_domain = 1H
X_freq = 495.13191398[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.5668198[Hz]
X_sweep = 9.28677563[kHz]
Irr_domain = 1H
Irr_freq = 495.13191398[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 495.13191398[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 7.36[us]
X_acq_time = 1.76422912[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 3.68[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 44
Relaxation_delay = 5[s]
Repetition_time = 6.76422912[s]
Temp_get = 24[dC]

abundance
0 0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09 0.1 0.11 0.12 0.13 0.14 0.15 0.16 0.17
MeO
N
CO2tBu
NO2
16
X : parts per Million : 13C
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
165.1663
164.1034
149.0708
137.7340
137.3893
135.4743
118.8617
114.2179
83.9706
77.2585
77.0000
76.7510
54.2403
28.1294
Filename = AA-130703-6-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = AA-130703-6
Solvent = CHLOROFORM-D
Creation_time = 4-JUL-2013 00:17:53
Revision_time = 6-DEC-2013 21:07:32
Current_time = 6-DEC-2013 21:09:46
Comment = nitroolefin tritu wit
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.62926421[T] (500[M
X_acq_duration = 0.8388608[s]
X_domain = 13C
X_freq = 124.50100559[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.1920929[Hz]
X_sweep = 39.0625[kHz]
Irr_domain = 1H
Irr_freq = 495.13191398[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 1000
Total_scans = 1000
X_90_width = 15.6[us]
X_acq_time = 0.8388608[s]
X_angle = 30[deg]
X_atn = 6[dB]
X_pulse = 5.2[us]
Irr_atn_dec = 25.434[dB]
Irr_atn_noe = 25.434[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 2.8388608[s]
Temp_get = 24.4[dC]

```
Filename                = AA-130703-2-4.jdf
Author                  = delta
Experiment              = single_pulse.ex2
Sample_id               = AA-130703-2
Solvent                 = CHLOROFORM-D
Creation_time           =  3-JUL-2013 14:50:37
Revision_time           =  6-DEC-2013 21:17:00
Current_time            =  6-DEC-2013 21:19:21

Comment                 = a-ketoester
Data_format             = 1D COMPLEX
Dim_size                = 13107
Dim_title               = 1H
Dim_units               = [ppm]
Dimensions              = X
Site                    = ECA 500
Spectrometer            = DELTA2_NMR

Field_strength          = 11.62926421[T] (500[M
X_acq_duration          = 1.76422912[s]
X_domain                = 1H
X_freq                  = 495.13191398[MHz]
X_offset                = 5[ppm]
X_points                = 16384
X_prescans              = 1
X_resolution            = 0.5668198[Hz]
X_sweep                 = 9.28677563[kHz]
Irr_domain              = 1H
Irr_freq                = 495.13191398[MHz]
Irr_offset              = 5[ppm]
Tri_domain              = 1H
Tri_freq                = 495.13191398[MHz]
Tri_offset              = 5[ppm]
Clipped                 = FALSE
Mod_return              = 1
Scans                   = 8
Total_scans             = 8

X_90_width              = 7.36[us]
X_acq_time              = 1.76422912[s]
X_angle                 = 45[deg]
X_atn                   = 4[dB]
X_pulse                 = 3.68[us]
Irr_mode                = Off
Tri_mode                = Off
Dante_presat            = FALSE
Initial_wait            = 1[s]
Recvr_gain              = 38
Relaxation_delay        = 5[s]
Repetition_time         = 6.76422912[s]
Temp_get                = 24[dC]
```

(Thousands)
0
10.0
20.0
30.0
40.0
50.0
PMBO
O
O
OtBu
25
X : parts per Million : 13C
195.1703
160.4698
159.1059
130.2906
129.1841
113.7035
83.6577
77.2480
77.0000
76.7424
72.4216
68.5204
55.1763
36.0710
27.7059
23.6140
Filename = AA-130910-2-7.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = AA-130910-2
Solvent = CHLOROFORM-D
Creation_time = 10-SEP-2013 16:17:19
Revision_time = 6-DEC-2013 21:26:52
Current_time = 6-DEC-2013 21:29:57
Comment = a-ketoester 13C
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA500
Spectrometer = DELTA2_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.83361792[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
X_sweep = 39.3081761[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Mod_return = 1
Scans = 538
Total_scans = 538
X_90_width = 10.2[us]
X_acq_time = 0.83361792[s]
X_angle = 30[deg]
X_atn = 6.3[dB]
X_pulse = 3.4[us]
Irr_atn_dec = 22.1[dB]
Irr_atn_noe = 22.1[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 60
Relaxation_delay = 2[s]
Repetition_time = 2.83361792[s]
Temp_get = 25.3[dC]



JEOL

```
Filename          = AA-130904-2-4.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = AA-130904-2
Solvent           = CHLOROFORM-D
Creation_time     =  4-SEP-2013 16:29:32
Revision_time     =  6-DEC-2013 21:46:08
Current_time      =  6-DEC-2013 21:47:28

Comment           = AA-582p-TLC
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_strength    = 11.62926421[T] (500[M
X_acq_duration    = 1.76422912[s]
X_domain          = 1H
X_freq            = 495.13191398[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.5668198[Hz]
X_sweep           = 9.28677563[kHz]
Irr_domain        = 1H
Irr_freq          = 495.13191398[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 495.13191398[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 7.36[us]
X_acq_time        = 1.76422912[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 3.68[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 40
Relaxation_delay  = 5[s]
Repetition_time   = 6.76422912[s]
Temp_get          = 27.8[dC]
```

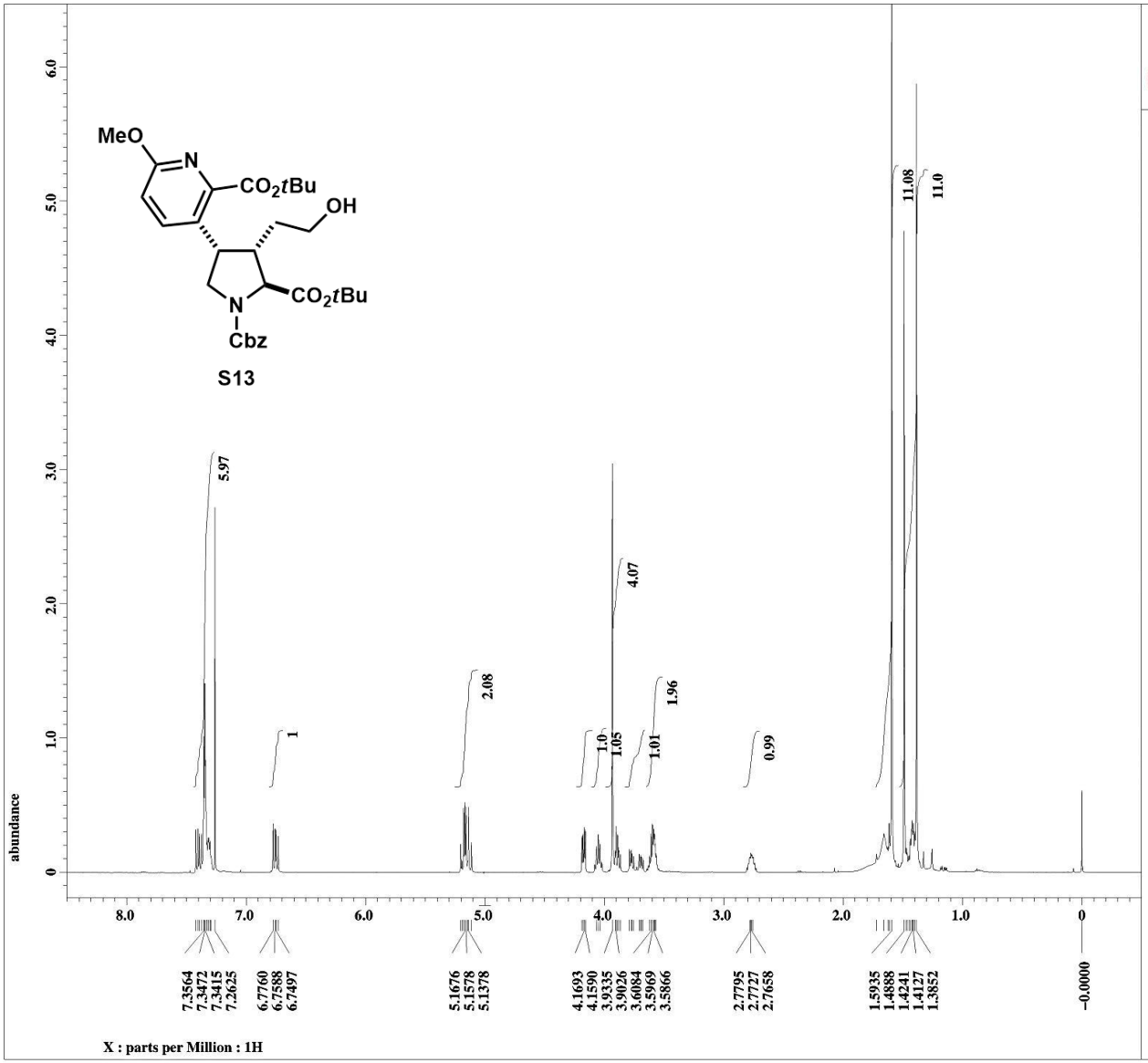
abundance
X : parts per Million : 13C
195.0210
165.3482
162.4183
159.8426
159.2011
147.3473
139.1798
129.7389
129.2697
125.3057
113.7391
113.0114
83.6546
82.7067
77.5745
77.2585
77.0000
76.7415
72.3274
67.2814
55.2553
53.5413
46.0154
39.8587
31.0689
28.0719
27.5645
OMe
N
O
tBuO2C
O2N
PMBO
CO2tBu
26
Filename = AA-130904-3-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = AA-130904-3
Solvent = CHLOROFORM-D
Creation_time = 4-SEP-2013 18:29:03
Revision_time = 6-DEC-2013 21:50:29
Current_time = 6-DEC-2013 21:55:01
Comment = AA-582p-TLC 13C
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.62926421[T] (500[M
X_acq_duration = 0.8388608[s]
X_domain = 13C
X_freq = 124.50100059[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.1920929[Hz]
X_sweep = 39.0625[kHz]
Irr_domain = 1H
Irr_freq = 495.13191398[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 2300
Total_scans = 2300
X_90_width = 15.6[us]
X_acq_time = 0.8388608[s]
X_angle = 30[deg]
X_atn = 6[dB]
X_pulse = 5.2[us]
Irr_atn_dec = 25.434[dB]
Irr_atn_noe = 25.434[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 52
Relaxation_delay = 2[s]
Repetition_time = 2.8388608[s]
Temp_get = 28.3[dC]

abundance
X : parts per Million : 1H
MeO
N
CO2tBu
OPMB
N
Cbz
CO2tBu
27b
7.9105
7.8933
7.8784
7.3507
7.3404
7.2602
7.1583
6.8389
6.8218
6.7531
5.1893
5.1389
5.1332
4.3490
4.3261
4.2804
4.2700
3.9358
3.9289
3.7870
3.7824
3.3428
3.2890
3.2752
1.6050
1.5970
1.5890
1.4379
1.2948
−0.0000
0.94
5.07
1.98
2.97
2.0
0.92
1.96
5.08
3.96
3.02
11.29
9.14
Filename = AA-130806-3-4.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = AA-130806-3
Solvent = CHLOROFORM-D
Creation_time = 6-AUG-2013 15:42:03
Revision_time = 8-DEC-2013 15:36:42
Current_time = 8-DEC-2013 15:37:51
Comment = frac6 P-TLC
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.62926421[T] (500[M
X_acq_duration = 1.76422912[s]
X_domain = 1H
X_freq = 495.13191398[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.5668198[Hz]
X_sweep = 9.28677563[kHz]
Irr_domain = 1H
Irr_freq = 495.13191398[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 495.13191398[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 7.36[us]
X_acq_time = 1.76422912[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 3.68[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 38
Relaxation_delay = 5[s]
Repetition_time = 6.76422912[s]
Temp_get = 27.2[dC]

(Thousands)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
MeO
N
CO2tBu
OPMB
N
Cbz
CO2tBu
27b
X : parts per Million : 13C
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.5137
170.3993
166.1833
162.0151
159.1059
154.4416
148.0891
147.9365
140.1818
140.0578
136.5191
129.2319
128.4020
127.9251
113.7035
112.6066
112.5302
82.1602
82.0648
77.2575
72.3739
68.2057
67.2423
62.9119
55.2431
53.4785
52.4483
41.9276
40.9356
39.8577
28.1638
27.9825
27.8299
Filename = AA-130806-4-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = AA-130806-4
Solvent = CHLOROFORM-D
Creation_time = 6-AUG-2013 19:02:16
Revision_time = 6-DEC-2013 23:24:51
Current_time = 6-DEC-2013 23:26:44
Comment = cis 13C date
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA500
Spectrometer = DELTA2_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.83361792[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
X_sweep = 39.3081761[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Mod_return = 1
Scans = 2200
Total_scans = 2200
X_90_width = 10.2[us]
X_acq_time = 0.83361792[s]
X_angle = 30[deg]
X_atn = 6.3[dB]
X_pulse = 3.4[us]
Irr_atn_dec = 22.1[dB]
Irr_atn_noe = 22.1[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 58
Relaxation_delay = 2[s]
Repetition_time = 2.83361792[s]
Temp_get = 25.2[dC]

abundance
0
1.0
2.0
MeO
N
CO2tBu
OPMB
N
Cbz
CO2tBu
27a
X : parts per Million : 1H
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.3484
7.3415
7.2591
7.1767
6.8447
6.8149
6.7977
5.96
2.04
3.06
5.1699
5.1492
5.1069
2
4.3468
4.2472
4.0789
3.9300
3.7858
3.7721
2.02
1.11
0.98
4.07
4.09
3.4424
3.4218
3.3931
2.16
2.7635
2.7589
2.7509
0.99
1.6222
1.6153
1.5764
1.4836
1.3829
20.44
0.0000
JEOL
Filename = AA-130717-2-4.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = AA-130717-2
Solvent = CHLOROFORM-D
Creation_time = 17-JUL-2013 11:20:49
Revision_time = 6-DEC-2013 23:43:27
Current_time = 6-DEC-2013 23:44:49
Comment = AA-57 trans date
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.62926421[T] (500[M
X_acq_duration = 1.76422912[s]
X_domain = 1H
X_freq = 495.13191398[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.5668198[Hz]
X_sweep = 9.28677563[kHz]
Irr_domain = 1H
Irr_freq = 495.13191398[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 495.13191398[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 7.36[us]
X_acq_time = 1.76422912[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 3.68[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 30
Relaxation_delay = 5[s]
Repetition_time = 6.76422912[s]
Temp_get = 25.1[dC]

MeO
N
CO2tBu
OPMB
N
Cbz
CO2tBu
27a
abundance
X : parts per Million : 13C
171.2368
165.8748
162.0353
159.0862
154.4806
148.1803
148.1324
138.5191
136.5563
136.4222
129.1835
129.1261
128.3793
127.9005
113.7008
112.4178
81.6822
81.5960
77.2585
77.0000
76.7510
68.2580
67.1186
64.3802
55.2169
53.4839
49.9699
44.9622
43.6312
40.3949
39.4949
28.0911
27.9762
27.8421
Filename = AA-130717-3-6.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = AA-130717-3
Solvent = CHLOROFORM-D
Creation_time = 17-JUL-2013 12:05:05
Revision_time = 6-DEC-2013 10:39:29
Current_time = 6-DEC-2013 10:45:47
Comment = AA-57 trans date
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.62926421[T] (500[M
X_acq_duration = 0.8388608[s]
X_domain = 13C
X_freq = 124.5010059[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.1920929[Hz]
X_sweep = 39.0625[kHz]
Irr_domain = 1H
Irr_freq = 495.13191398[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 901
Total_scans = 901
X_90_width = 15.6[us]
X_acq_time = 0.8388608[s]
X_angle = 30[deg]
X_atn = 6[dB]
X_pulse = 5.2[us]
Irr_atn_dec = 25.434[dB]
Irr_atn_noe = 25.434[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 54
Relaxation_delay = 2[s]
Repetition_time = 2.8388608[s]
Temp_get = 25.4[dC]

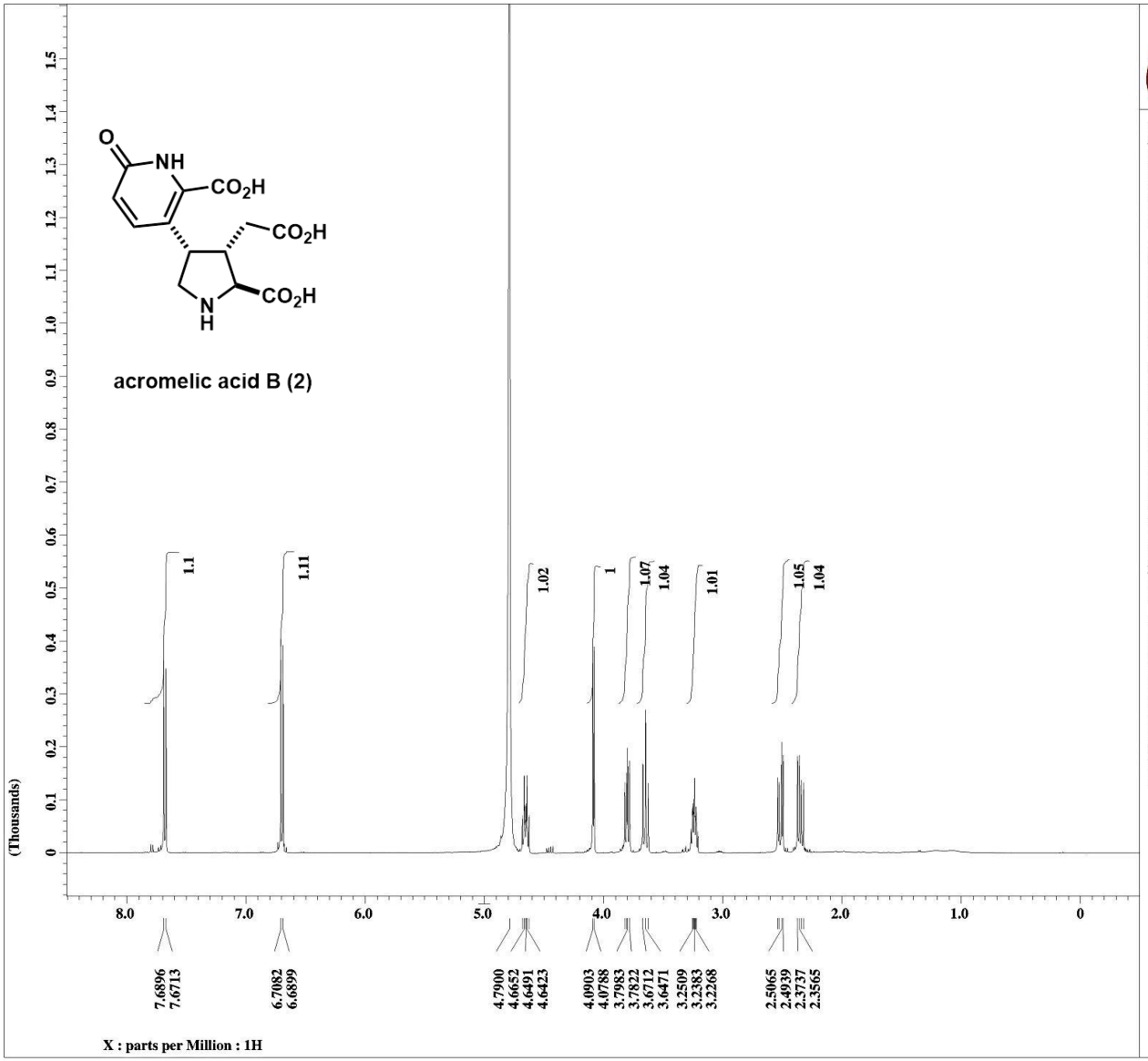



```
Filename          = AA-130725-4-4.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = AA-130725-4
Solvent           = CHLOROFORM-D
Creation_time     = 25-JUL-2013 18:50:16
Revision_time     =  6-DEC-2013 11:21:22
Current_time      =  6-DEC-2013 11:22:09

Comment           = -OH p-TLC Et2O/Hex
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR

Field_strength    = 11.62926421[T] (500[M
X_acq_duration    = 1.76422912[s]
X_domain          = 1H
X_freq            = 495.13191398[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.5668198[Hz]
X_sweep           = 9.28677563[kHz]
Irr_domain        = 1H
Irr_freq          = 495.13191398[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 495.13191398[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 7.36[us]
X_acq_time        = 1.76422912[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 3.68[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 38
Relaxation_delay  = 5[s]
Repetition_time   = 6.76422912[s]
Temp_get          = 25.8[dC]
```

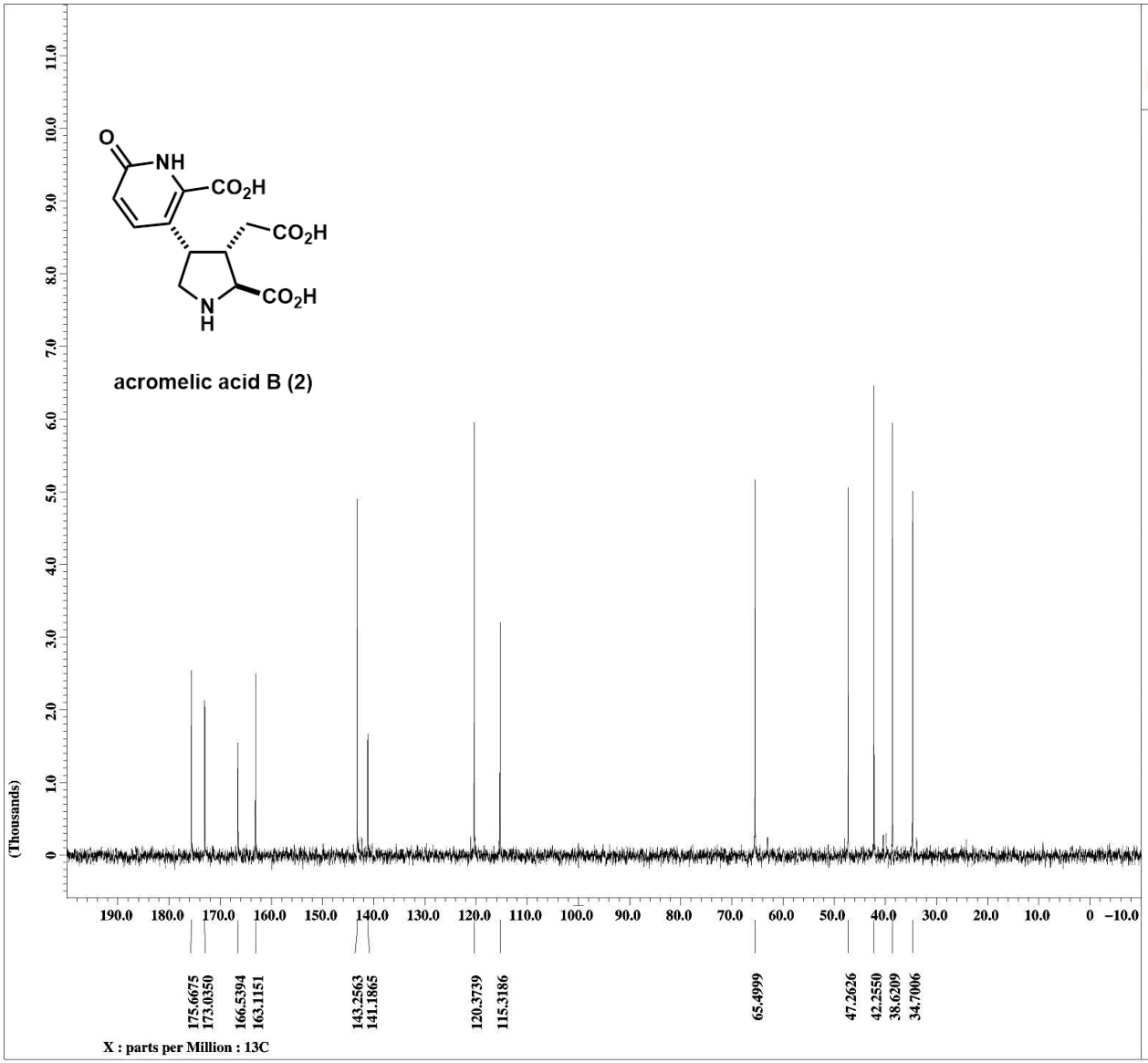
(Thousands)
X : parts per Million : 13C
171.5153
171.4390
166.1738
162.0819
154.6801
154.3749
148.0605
148.0128
138.3219
136.5192
136.2902
128.4593
128.4307
127.8870
112.7115
82.6944
82.0267
77.2576
77.0000
76.7425
67.2518
67.1946
64.4285
60.8516
53.5262
50.6170
44.9036
43.7780
40.5350
39.6002
32.0840
28.1066
27.9444
27.8109
MeO
N
CO2tBu
OH
N
Cbz
CO2tBu
S13
Filename = AA-130725-6-3.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = AA-130725-6
Solvent = CHLOROFORM-D
Creation_time = 26-JUL-2013 08:04:36
Revision_time = 6-DEC-2013 11:31:36
Current_time = 6-DEC-2013 11:35:54
Comment = -OH date 13C
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA500
Spectrometer = DELTA2_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 0.83361792[s]
X_domain = 13C
X_freq = 125.76529768[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.19959034[Hz]
X_sweep = 39.3081761[kHz]
Irr_domain = 1H
Irr_freq = 500.15991521[MHz]
Irr_offset = 5.0[ppm]
Mod_return = 1
Scans = 12000
Total_scans = 12000
X_90_width = 10.5[us]
X_acq_time = 0.83361792[s]
X_angle = 30[deg]
X_atn = 6.3[dB]
X_pulse = 3.5[us]
Irr_atn_dec = 21.79[dB]
Irr_atn_noe = 21.79[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 60
Relaxation_delay = 2[s]
Repetition_time = 2.83361792[s]
Temp_get = 23.3[dC]

```
Filename                = AA-130731-4-4.jdf
Author                  = delta
Experiment              = single_pulse.ex2
Sample_id               = AA-130731-4
Solvent                 = CHLOROFORM-D
Creation_time           = 31-JUL-2013 15:37:31
Revision_time           = 6-DEC-2013 12:58:20
Current_time            = 6-DEC-2013 12:59:32

Comment                 = AA-579pure
Data_format             = 1D COMPLEX
Dim_size                = 131072
Dim_title               = 1H
Dim_units               = [ppm]
Dimensions              = X
Site                    = ECA 500
Spectrometer            = DELTA2_NMR

Field_strength          = 11.62926421[T] (500[M
X_acq_duration          = 1.76422912[s]
X_domain                = 1H
X_freq                  = 495.13191398[MHz]
X_offset                = 5[ppm]
X_points                = 16384
X_prescans              = 1
X_resolution            = 0.56681981[Hz]
X_sweep                 = 9.28677563[kHz]
Irr_domain              = 1H
Irr_freq                = 495.13191398[MHz]
Irr_offset              = 5[ppm]
Tri_domain              = 1H
Tri_freq                = 495.13191398[MHz]
Tri_offset              = 5[ppm]
Clipped                 = FALSE
Mod_return              = 1
Scans                   = 8
Total_scans             = 8

X_90_width              = 7.36[us]
X_acq_time              = 1.76422912[s]
X_angle                 = 45[deg]
X_atn                   = 4[dB]
X_pulse                 = 3.68[us]
Irr_mode                = Off
Tri_mode                = Off
Dante_presat            = FALSE
Initial_wait            = 1[s]
Recvr_gain              = 26
Relaxation_delay        = 5[s]
Repetition_time         = 6.76422912[s]
Temp_get                = 27.2[dC]
```

abundance
0
0.1
0.2
0.3
MeO
N
CO2tBu
CO2H
N
Cbz
CO2tBu
28
X : parts per Million : 13C
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
176.4360
176.3115
170.4133
165.6258
162.2363
154.6242
154.4423
148.1324
138.0308
136.4030
136.2020
128.4367
128.0249
127.8430
124.4631
112.7816
81.9119
77.2585
77.0000
76.7510
67.3197
64.9451
64.5908
53.5030
50.0752
49.8837
43.6408
39.9353
39.0065
33.8264
28.0240
27.7272
JEOL
Filename = AA-130731-5-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = AA-130731-5
Solvent = CHLOROFORM-D
Creation_time = 31-JUL-2013 16:53:28
Revision_time = 6-DEC-2013 13:14:09
Current_time = 6-DEC-2013 13:21:15
Comment = AA-579pure 13C
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 500
Spectrometer = DELTA2_NMR
Field_strength = 11.62926421[T] (500[M
X_acq_duration = 0.8388608[s]
X_domain = 13C
X_freq = 124.50100591[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.1920929[Hz]
X_sweep = 39.0625[kHz]
Irr_domain = 1H
Irr_freq = 495.13191398[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 867
Total_scans = 867
X_90_width = 15.6[us]
X_acq_time = 0.8388608[s]
X_angle = 30[deg]
X_atn = 6[dB]
X_pulse = 5.2[us]
Irr_atn_dec = 25.434[dB]
Irr_atn_noe = 25.434[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 2.8388608[s]
Temp_get = 27.4[dC]




```
Filename          = AA-130722-2-4.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = AA-130722-2
Solvent           = D2O
Creation_time     = 22-JUL-2013 22:09:13
Revision_time     =  6-DEC-2013 14:12:04
Current_time      =  6-DEC-2013 14:13:03

Comment           = Acr B (IRC50)
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA500
Spectrometer      = DELTA2_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 1.74587904[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5.0[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.57277737[Hz]
X_sweep           = 9.38438438[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Tri_domain        = 1H
Tri_freq          = 500.15991521[MHz]
Tri_offset        = 5.0[ppm]
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 11.7[us]
X_acq_time        = 1.74587904[s]
X_angle           = 45[deg]
X_atn             = 3.5[dB]
X_pulse           = 5.85[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 40
Relaxation_delay  = 5[s]
Repetition_time   = 6.74587904[s]
Temp_get          = 23.1[dC]
```




```
Filename          = AA-130724-2-2.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = AA-130724-2
Solvent           = D2O
Creation_time     = 24-JUL-2013 10:39:20
Revision_time     =  6-DEC-2013 15:16:32
Current_time      =  6-DEC-2013 15:24:35

Comment           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA500
Spectrometer      = DELTA2_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Mod_return        = 1
Scans             = 1000
Total_scans       = 1000

X_90_width        = 10.5[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 6.3[dB]
X_pulse           = 3.5[us]
Irr_atn_dec       = 21.79[dB]
Irr_atn_noe       = 21.79[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 60
Relaxation_delay  = 2[s]
Repetition_time   = 2.83361792[s]
Temp_get          = 23.7[dC]
```