Supporting Information

Brønsted Acid Mediated Cyclization of Enaminones. Rapid and Efficient Access to the Tetracyclic Framework of the *Strychnos* Alkaloids

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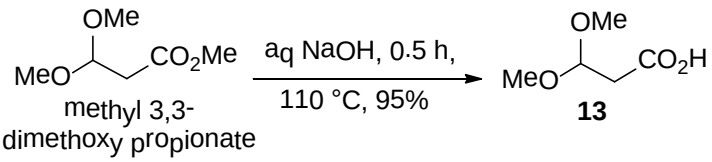
General Experimental Considerations:

All reactions were carried out under an argon atmosphere with dry solvents using anhydrous conditions unless otherwise stated. Tetrahydrofuran (THF) and diethyl ether were freshly distilled from Na/benzophenone ketyl prior to use. Dichloromethane and acetonitrile were distilled from calcium hydride prior to use. Methanol was distilled over magnesium sulfate prior to use. Benzene and toluene were distilled over Na prior to use. Reagents were purchased at the highest commercial quality and used without further purification unless otherwise stated. Thin layer chromatography (TLC) was performed using Dynamic Adsorbents Inc. UV active silica gel, 200 μm, plastic backed; Dynamic Adsorbents Inc. TLC plates were visualized by exposure to short wavelength UV light (254 nm). Indoles were visualized with a saturated solution of ceric ammonium sulfate in 50% sulfuric acid.[1] Elemental analyses were performed on a Carlo Erba model EA-1110 carbon, hydrogen, and nitrogen analyzer. All samples submitted for CHN analyses were first dried under high vacuum for a minimum of six hours using a drying pistol with isopropyl alcohol or benzene as the solvent with potassium hydroxide pellets in the drying bulb. Melting points were taken on a Stuart melting point apparatus SMP3 manufactured by Barloworld Scientific US Ltd. Proton (^{1}H NMR) and carbon high resolution nuclear magnetic resonance spectra (^{13}C NMR) were obtained on a Bruker 300-MHz or a GE 500-MHz NMR spectrometer. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublet of doublet, td = triplet of doublet, m = multiplet), integration, and coupling constants (Hz). ^{13}C NMR data are reported in parts per million (ppm) on the δ scale. The low resolution mass spectra (LRMS) were obtained as electron

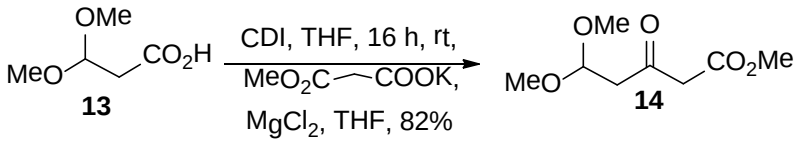
impact (EI, 70eV) mass spectrometer, which were recorded on a Hewlett-Packard 5985B gas chromatography-mass spectrometer, while high resolution mass spectra (HRMS) were recorded on a VG Autospec (Manchester England) mass spectrometer. HRMS recorded by electrospray ionization (ESI) methods were performed at the Laboratory for Biological Mass Spectrometery at Texas A&M University on a API QStar Pulsar model, manufactured by MDS Sciex. Optical rotations were measured on a JASCO Model DIP-370 digital polarimeter. Infra-red spectra were recorded on a Thermo Nicolet Nexus 870 FT-IR or a Perkin Elmer 1600 series FT-IR spectrometer. Flash and gravity chromatography was performed using silica gel P60A, 40-63 μm purchased from Silicycle. All reactions were carried out under an argon atmosphere with dry solvents using anhydrous conditions unless otherwise stated.

Experimental Procedures and Analytical Data:



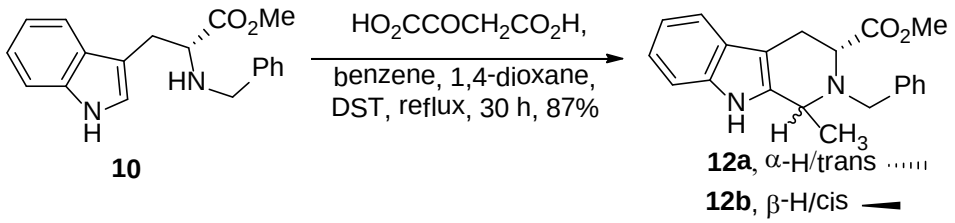
Hydrolysis of Methyl 3,3-dimethoxypropionate to 3,3-dimethoxypropionic Acid (13).[2] A mixture of methyl 3,3-dimethoxypropionate (14.2 g, 95.8 mmol) and 3.5 M aqueous NaOH (4.6 g of NaOH dissolved in 33 mL of H_2O) was stirred at 110 °C for 0.5 h. After 0.5 h, analysis by TLC on (silica gel, EtOAc/hexanes = 1:1) indicated the disappearance of starting material and a new spot at lower R_f had appeared. The clear solution which resulted was allowed to come to rt, cooled and neutralized by careful addition of cold aqueous 12 M HCl. After neutralization the solution was acidified to a

pH of 3 - 4 by addition of more aqueous 12 M HCl at rt. The acid **13** was extracted with EtOAc and CH_2Cl_2 (after each extraction the aqueous phase was acidified with 12 M HCl), and the combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure to yield 12.2 g (95%) of the title acid **13** as a colorless oil. IR (NaCl) ν_{max} 3090, 2942, 1716, 1076 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.85 (1H, t, *J* = 5.8 Hz), 3.40 (6H, s), 2.72 (2H, d, *J* = 5.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.2, 100.9, 53.5, 38.6. The data for this compound matched in all respects with that reported in the literature.[3]



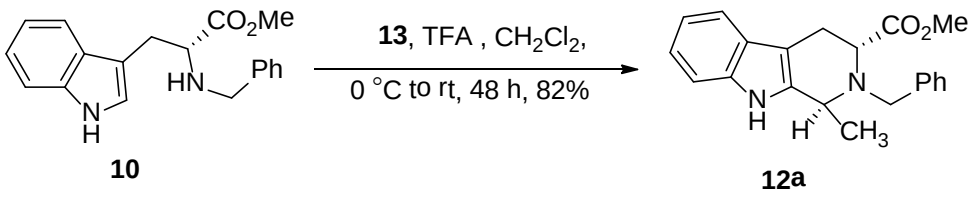
Condensation of carboxylic acid 13 to give Methyl 5,5-dimethoxy-3-oxo-4-pentanoate (**14**). To the carboxylic acid **13** (8.1 g, 60.2 mmol) in THF (323 mL) was added 10.8 g (66.3 mmol) of 1,1'-carbonyldiimidazole and the solution was stirred overnight at rt under argon. In a second flask potassium methyl malonate (18.7 g, 120 mmol), powdered anhydrous magnesium chloride (11.5 g, 120 mmol) and a catalytic amount of 4-(dimethylamino) pyridine (660 mg, 5.4 mmol) were vigorously stirred in a mixture of THF (323 mL) and acetonitrile (176 mL). After stirring for 2 h, the above amide in THF was added dropwise to the malonate solution. The solution which resulted was allowed to stir at rt with the help of an overhead stirrer for 12 h. The suspension which resulted was concentrated under reduced pressure. The residue was dissolved in cold aqueous 1 N HCl (500 mL) and the aqueous layer was extracted with ether (500 mL x 3). The combined organic extracts were washed with a saturated aqueous $NaHCO_3$ solution (500 mL), brine (250 mL) and dried ($MgSO_4$). The solvent was removed under

reduced pressure. The residue was subjected to flash silica gel chromatography to furnish **14** (9.7 g, 82%) as a yellow oil. IR (NaCl) ν_{max} 2955, 1749, 1720, 1438, 1121, 1069 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.78 (1H, t, *J* = 5.5 Hz), 3.75 (3H, s), 3.53 (2H, s), 3.38 (6H, s), 2.86 (2H, d, *J* = 5.5 Hz) (Proton NMR contains 8.5% of enol); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.6, 167.3, 101.3, 53.9, 52.3, 49.8, 46.6; HRESIMS *m/z* 197.0994 [M + Li]$^+$ (calcd for $C_8H_{14}O_5Li$, 197.1001).



Indoles 12a & 12b: **Thermal Conditions**

To a solution of optically active N_b-benzyl-D-tryptophan methyl ester **10** (500 mg, 1.6 mmol) in dry benzene (7 mL) was added a solution of oxalacetic acid (257 mg, 2.0 mmol) in dry 1,4-dioxane (6 mL). After refluxing the above solution for 24 h with the continuous removal of water via a Dean-Stark trap, the solvent was removed under reduced pressure to provide an orange residue, which was purified by flash silica gel column chromatography to provide **12a** & **12b** (470 mg, 87% yield). The spectral data for these two β-carbolines **12a** and **12b** was identical to the published values.[4]

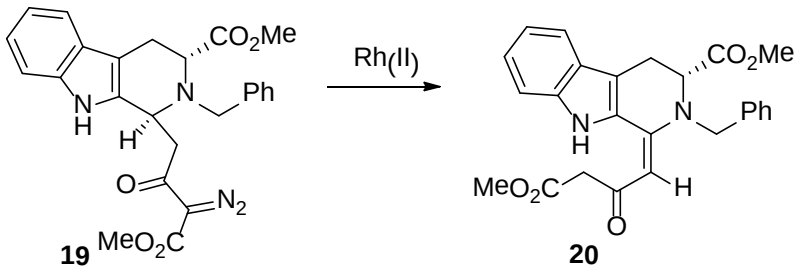


Indole 12a: **Protic Conditions**

Condensation of 10 to provide (1*S*,3*R*)-Methyl-2-benzyl-1-methyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole-3-carboxylate (12a)

To a round bottom flask which contained a solution of optically active N_b-benzyl-D-tryptophan methyl ester **10** (200 mg, 0.7 mmol) in dry CH_2Cl_2 (5 mL) was added 3,3-dimethoxy propionic acid **13** (174 mg, 1.3 mmol) and TFA (96 μL, 1.3 mmol) at 0 °C with stirring. The reaction mixture which resulted was stirred at rt for 48 h and then cooled in an ice bath and brought to pH 8 with a cold aqueous solution of saturated $NaHCO_3$. The aqueous layer was separated and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were washed with brine (2 x 50 mL) and dried (Na_2SO_4). Removal of the solvent under reduced pressure afforded an oil which was purified by flash silica gel column chromatography (EtOAc : hexanes) to give **12a** (177 mg, 82% yield). R_f 0.72 (silica gel, EtOAc/hexanes, 3 : 5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (1H, s), 7.53 (1H, d, *J* = 8.7 Hz), 7.44 (2H, d, *J* = 8.1 Hz), 7.38-7.26 (4H, m), 7.19 (1H, td, *J* = 7.1, 1.4 Hz), 7.14 (1H, td, *J* = 7.1, 1.2 Hz), 4.23 (1H, q, *J* = 6.6 Hz), 4.04 (1H, t, *J* = 6.2 Hz), 3.90 (2H, dd, *J* = 23.0, 14.4 Hz), 3.73 (3H, s), 3.10 (2H, ddd, *J* = 16.0, 10.9, 1.1 Hz), 1.48 (3H, d, *J* = 6.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ173.5 (C), 139.9 (C), 136.1 (2 x C), 128.3 (2 x CH), 128.2 (2 x CH), 127.0 (C), 126.9 (CH), 121.5 (CH), 119.4 (CH), 118.0 (CH), 110.6 (CH), 106.4 (C), 56.9 (CH), 53.9 (CH_2), 51.6 (CH_3), 50.9 (CH), 22.3 (CH_2), 21.1 (CH_3); EIMS *m/z* 334 [M^+] (56), 319 (53), 275 (52), 243 (61), 183 (27), 170 (44), 157 (54), 130 (17), 115 (13), 91 (100); HRESIMS *m/z* 335.1759 $(M + H)^+$ (calcd for $C_{21}H_{23}N_2O_2$, 335.1761). The spectral data for this compound matched in all respects with that reported in the literature.[4]

Table 1



(*R*,*E*)-Methyl-2-benzyl-1-(4-methoxy-2,4-dioxobutylidene)-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole-3-carboxylate (**20**)

Procedure described for Entry 1: To a solution of **19** (207 mg, 0.45 mmol) in dry benzene (6 mL) under nitrogen, rhodium(II) acetate (20 mg, 0.045 mmol) was added. The mixture was allowed to stir at rt for 4.0 h. The solution was then filtered through a pad of celite and washed with ether. The filtrate was concentrated under reduced pressure and the residue was subjected to flash silica gel column chromatography (EtOAc : hexanes) to furnished **20** (130 mg, 67% yield) as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.8 (1H, s), 7.58 (1H, d, *J* = 8.1 Hz), 7.50 (1H, d, *J* = 8.4 Hz), 7.43-7.40 (2H, m), 7.37-7.33 (3H, m), 7.31 (1H, ddd, *J* = 8.3, 7.0, 1.0 Hz), 7.14 (1H, ddd, 1H, *J* = 7.8, 7.3, 0.5 Hz), 5.55 (1H, s), 5.13 (1H, d, *J* = 16.3 Hz), 4.41-4.38 (2H, m), 3.68 (3H, s), 3.65-3.62 (4H, m), 3.50 (2H, dd, *J* = 16.2, 14.4 Hz), 3.39 (1H, dd, *J* = 16.4, 6.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.6 (C), 172.0 (C), 169.6 (C), 152.9 (C), 137.1 (C), 136.3 (C), 129.6 (CH), 129.5 (CH), 128.4 (CH), 128.2 (C), 127.4 (2 x CH), 125.5 (CH), 125.2 (C), 120.5 (CH), 119.8 (CH), 113.6 (CH), 112.6 (C), 95.2 (CH), 63.0 (CH), 57.3 (CH_2), 53.4 (CH_3), 52.6 (CH_3), 51.1 (CH_2), 24.34 (CH_2).

Entry 2: Procedure same as entry 1 except the reaction was performed at 40 °C for 1.5 h. (130 mg, 67% yield).

Entry 3: Procedure same as entry 1 except the reaction was performed at 75 °C for 2.0 h. (145 mg, 75% yield).

Entry 4: Procedure same as entry 1 except CuOTf was used as the catalyst and the reaction performed in CH_2Cl_2 as the solvent at rt for 1 h (100 mg, 51% yield).

Entry 5: Procedure same as entry 1 except CuOTf was used as the catalyst and the reaction performed in CH_2Cl_2 as the solvent ,under reflux for 1 h (92 mg, 47% yield).

Entry 6: Procedure same as entry 1 except CuOTf was used as the catalyst and the reaction performed in benzene as the solvent, at rt for 2 h (100 mg, 51% yield).

Entry 7: To a solution of diazo compound **19** (50 mg, 0.11 mmol) in dry CH_2Cl_2 (4 mL) was added dropwise tetrafluoroboric acid diethylether complex (70 mg, 0.44 mmol) under an atmosphere of argon at 0 °C (ice bath). The reaction mixture was stirred at rt for more than 24 h. During this period regular analysis by TLC indicated presence of starting material **19** and an increase in baseline formation. After 33 h TLC analysis indicated presence of only baseline impurities. The reaction mixture was neutralized with an ice cold aqueous solution of saturated $NaHCO_3$. The two layers were separated, the organic layer was washed with brine, dried (Na_2SO_4) and the solvent concentrated under reduced pressure to give a brown residue. The same result was observed with 8 eq of HBF_4•OEt_2. Reaction was stopped after 24 h.

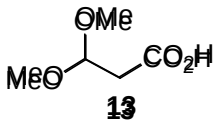
Entry 8: Procedure same as entry 7, except the reaction was performed under refluxing condition for 4 h. Only baseline impurities were observed.

Entry 9: Under a balloon of argon, diazo compound **19** (50 mg, 0.11 mmol) was dissolved in CCl_4 (2 mL) and the vial was placed in between two UV lamps. The mixture was irradiated with UV light (shortwave $\lambda \geq 254$ nm) for 12 h at rt. After 12 h analysis by TLC (silica gel, EtOAc/hexanes, 2 : 3) indicated presence of starting material **19** and baseline impurities.

References:

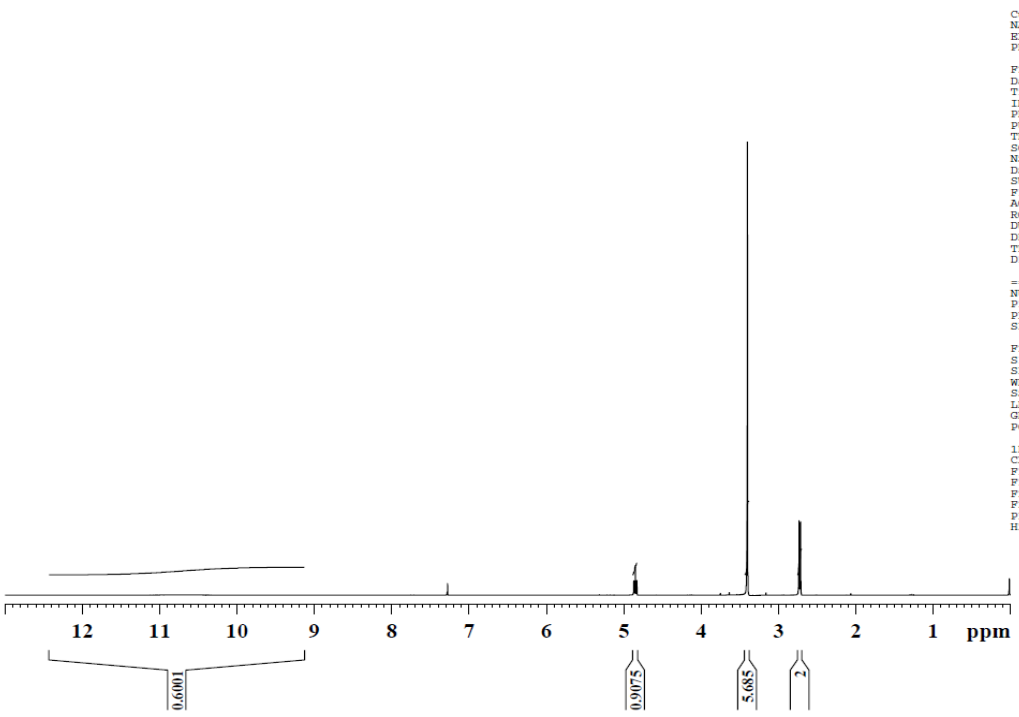
1) Li, J. J.; Limberakis, C.; Pflum, D. A. *Modern Organic Synthesis in the Laboratory*, Oxford University Press, Inc: New York, NY, 2007, Chapter 1, pp 17-20.
2) Compound **13** was synthesized following a procedure by: Zaragoza, F.; Stephensen, H.; Peschke, B.; Rimvall, K. *J. Med. Chem*. **2005**, *48*, 306-311.
3) Valade, A.-G.; Dugat, D.; Jeminet, G.; Royer, J.; Husson, H.-P. *Eur. J. Org. Chem*. **2001**, 2041-2053.
4) Sandrin, J.; Hollinshead, S. P.; Cook, J. M. *J. Org. Chem*. **1989**, *54*, 5636-5640.

Copies of ^{1}H and ^{13}C NMR spectra:



13

Proton Spectrum : 3,3–dimethoxy propionic acid

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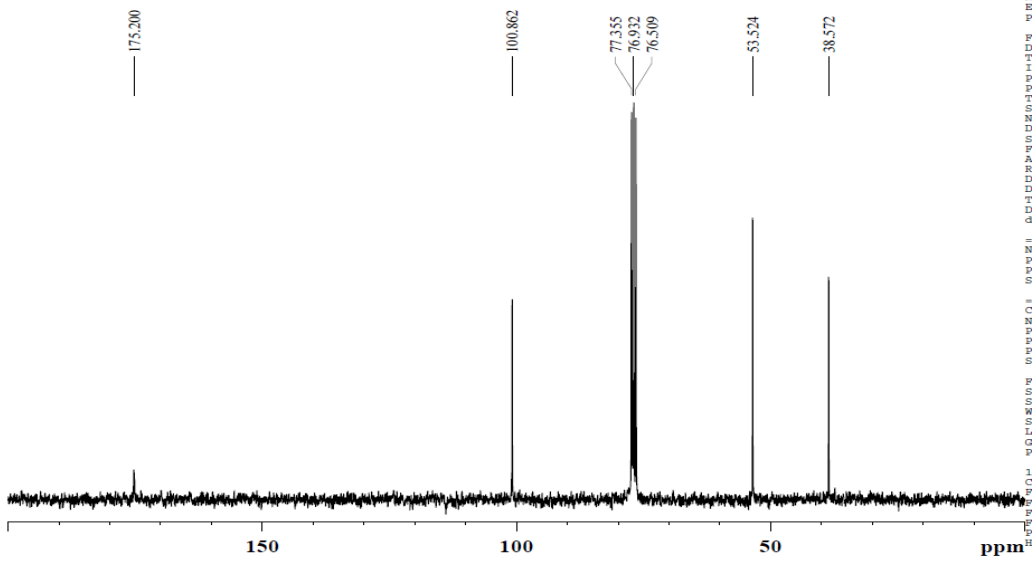
Carbon Spectrum

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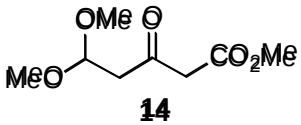

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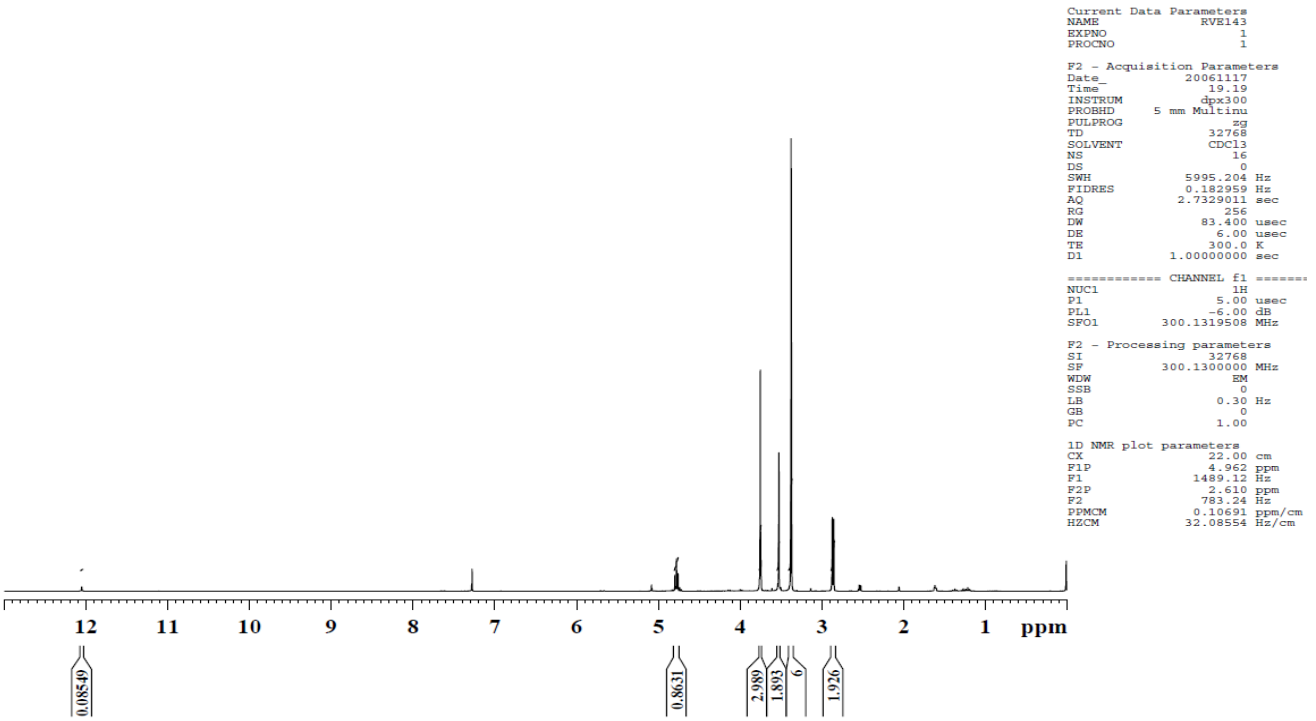
Proton Spectrum : Methyl-5,5-dimethoxy-3-oxopentanoate



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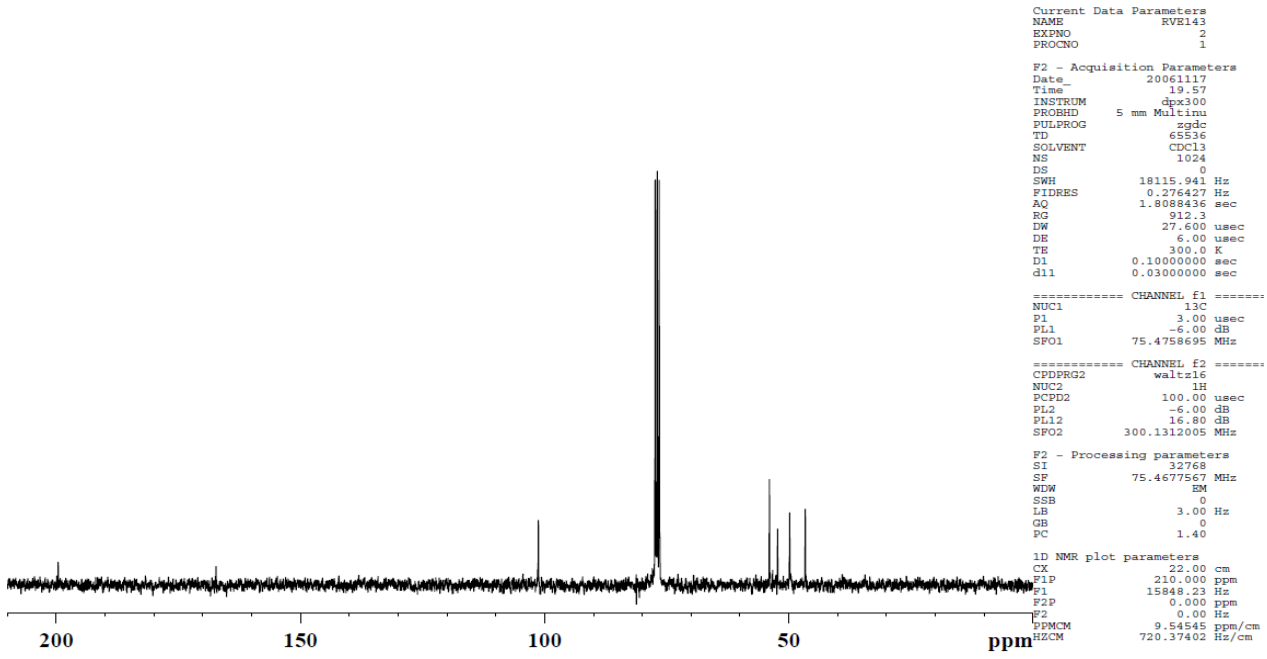

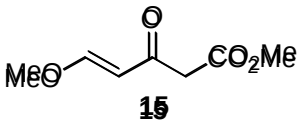

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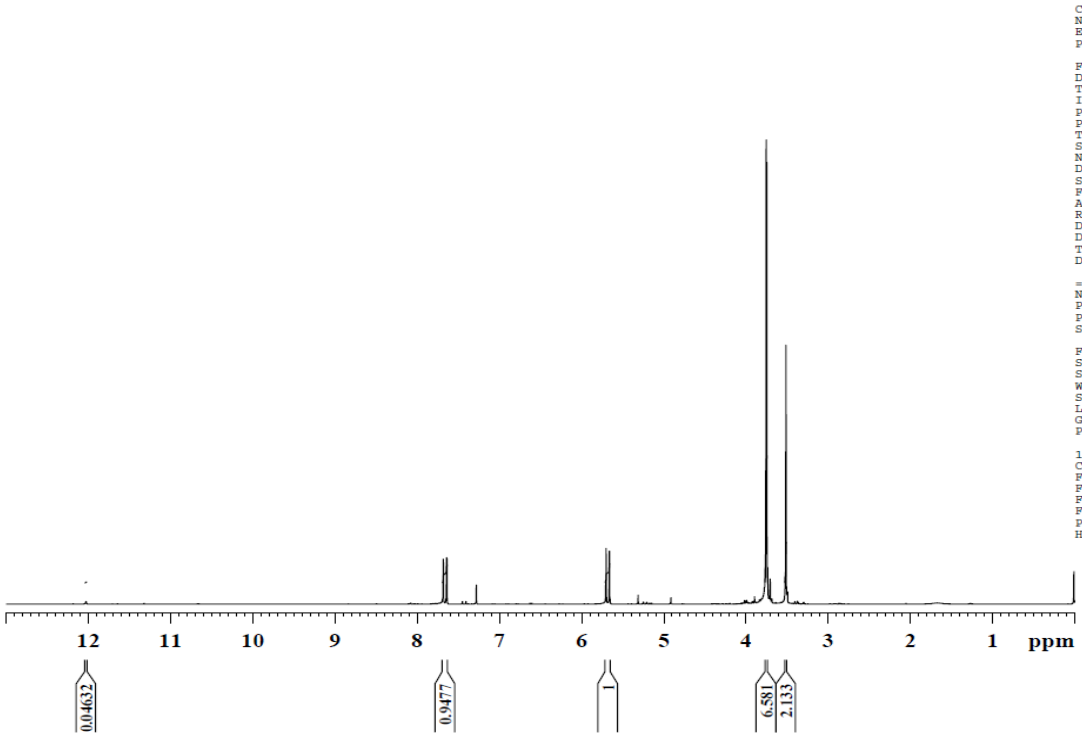
Proton Spectrum

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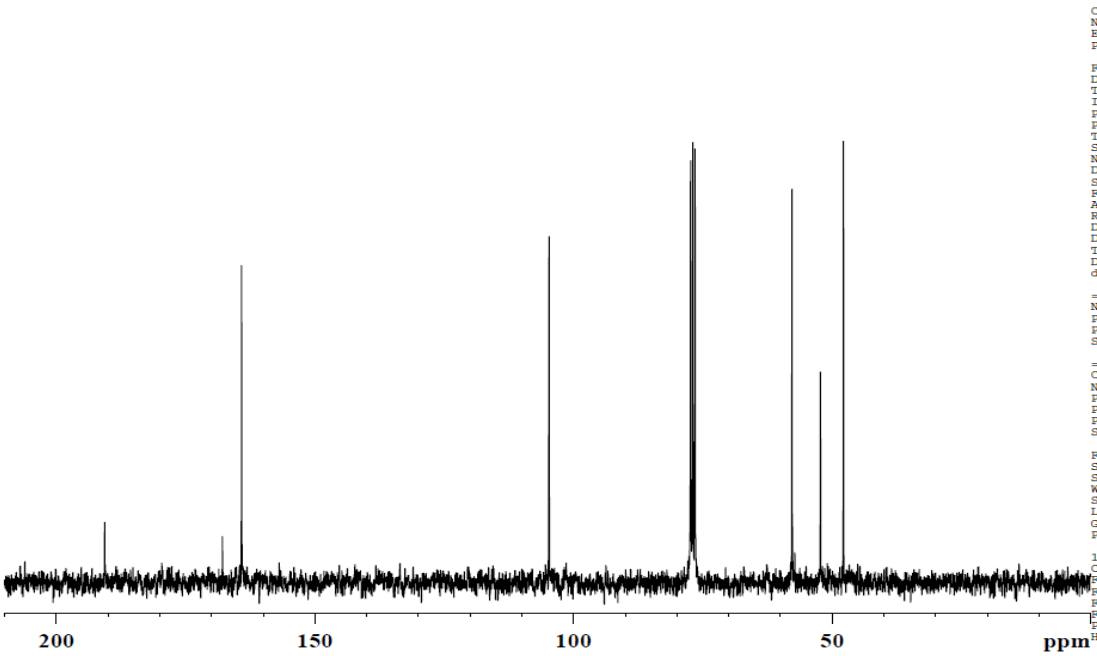


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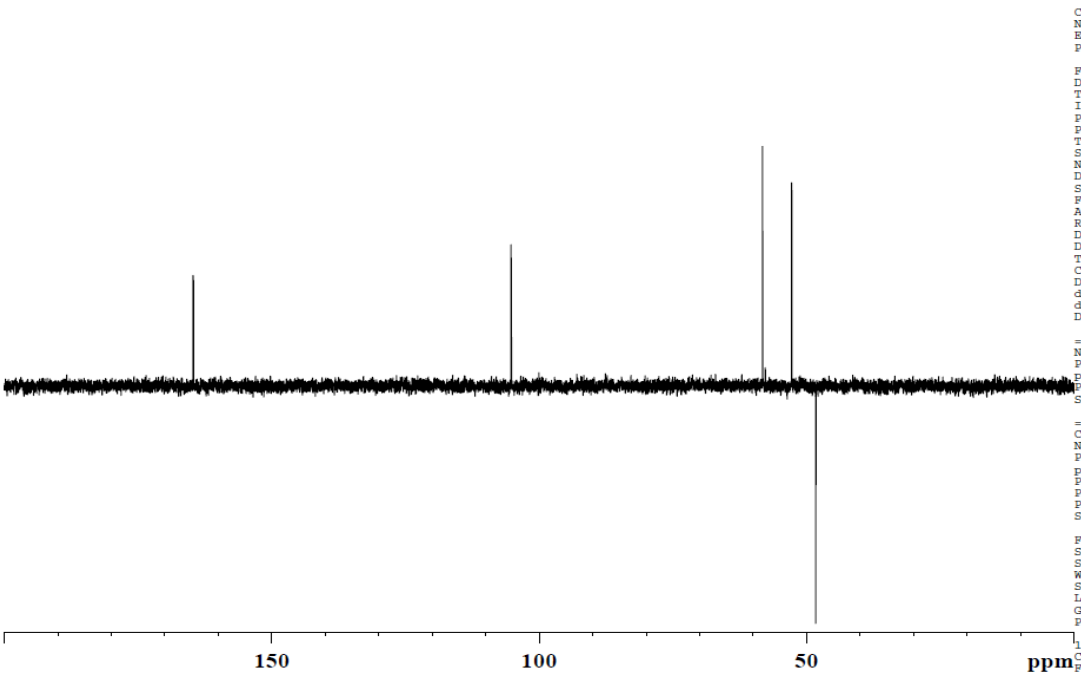


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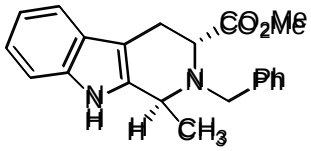
PL2                 -6.00 dB
PL12                16.60 dB
SFO2          300.1312005 MHz

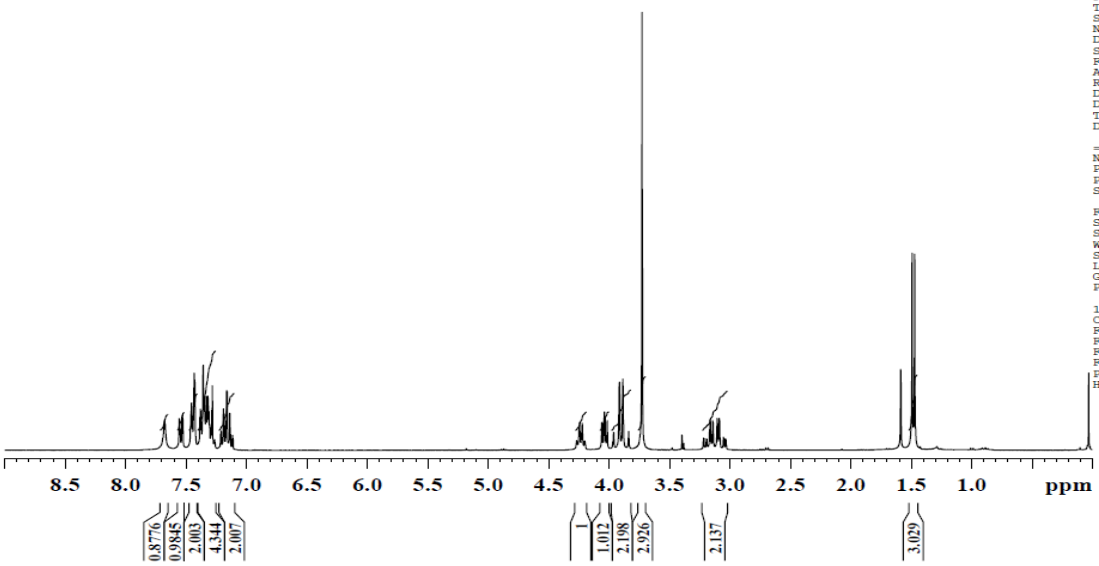
F2 - Processing parameters
SI                   32768
SF             75.4677190 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40

1D NMR plot parameters
CX                   20.00 cm
F1P                200.000 ppm
F1               15093.54 Hz
F2P                  0.000 ppm
F2                   0.00 Hz
PPMCM            10.00000 ppm/cm
HZCM            754.67719 Hz/cm
```



12a

Proton Spectrum




```
Current Data Parameters
NAME                  RVE355
EXPNO                      1
PROCNO                     1

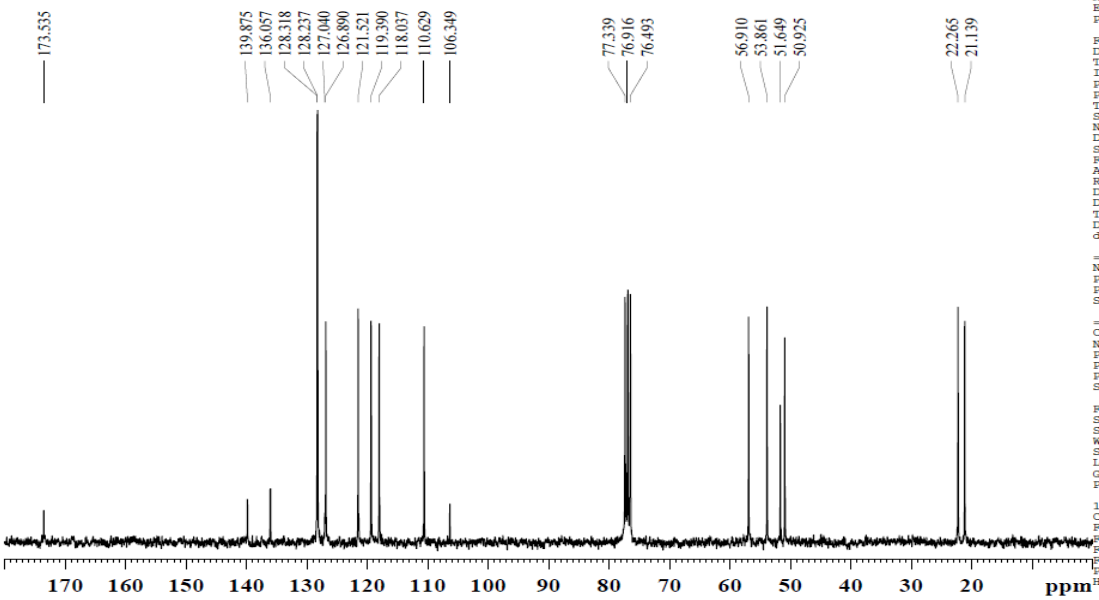
F2 - Acquisition Parameters
Date_              20090706
Time                  21.27
INSTRUM             dpx300
PROBHD     5 mm Multinu
PULPROG                zg
TD                     32768
SOLVENT              CDCl3
NS                        16
DS                         0
SWH                5995.204 Hz
FIDRES             0.182959 Hz
AQ                 2.7329011 sec
RG                     287.4
DW                    83.400 usec
DE                     6.00 usec
TE                    300.0 K
D1                 1.00000000 sec

============ CHANNEL f1 =======
NUC1                       1H
P1                       5.00 usec
PL1                     -6.00 dB
SFO1              300.1319508 MHz

F2 - Processing parameters
SI                     32768
SF                300.1300000 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00

1D NMR plot parameters
CX                     22.00 cm
F1P                    7.770 ppm
F1                  2331.94 Hz
F2P                    7.020 ppm
F2                  2106.89 Hz
PPMCM               0.03408 ppm/cm
HZCM               10.22975 Hz/cm
```

Carbon Spectrum




```
Current Data Parameters
NAME                  RVE355
EXPNO                      7
PROCNO                     1

F2 - Acquisition Parameters
Date_              20090707
Time                   1.04
INSTRUM             dpx300
PROBHD     5 mm Multinu
PULPROG             zgdc
TD                     65536
SOLVENT              CDCl3
NS                      3072
DS                         0
SWH               18115.941 Hz
FIDRES             0.276427 Hz
AQ                 1.8088436 sec
RG                    1824.6
DW                    27.600 usec
DE                     6.00 usec
TE                    300.0 K
D1                 0.10000000 sec
d11                0.03000000 sec

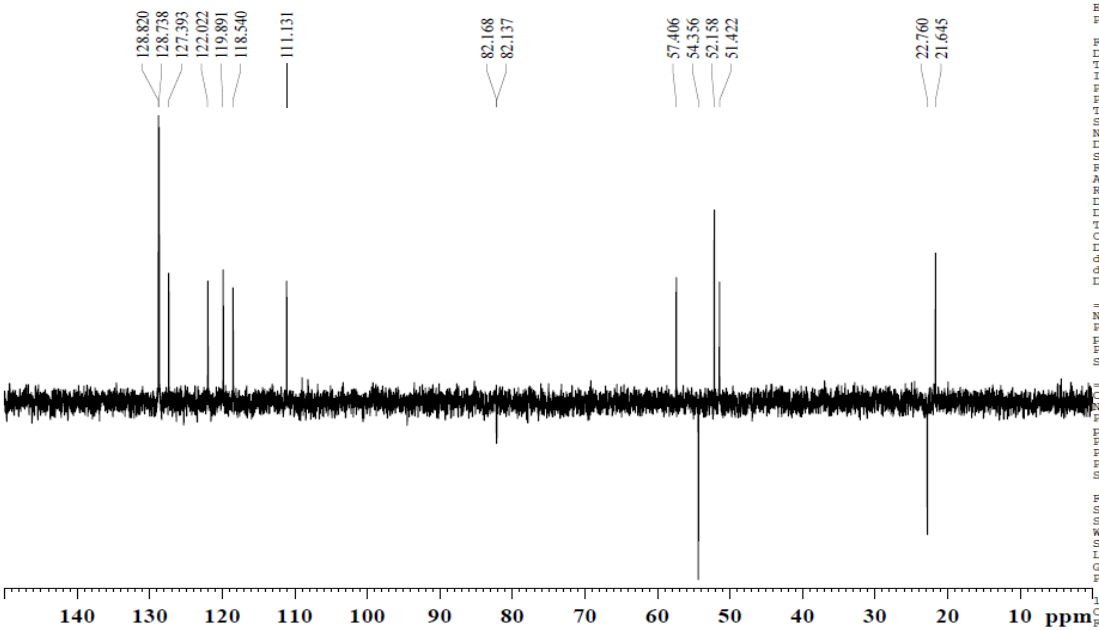
============ CHANNEL f1 =======
NUC1                      13C
P1                       6.80 usec
PL1                     -6.00 dB
SFO1              75.4758695 MHz

============ CHANNEL f2 =======
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  100.00 usec
PL2                     -6.00 dB
PL12                    16.60 dB
SFO2              300.1312005 MHz

F2 - Processing parameters
SI                     32768
SF                75.4677567 MHz
WDW                       EM
SSB                        0
LB                      3.00 Hz
GB                         0
PC                      1.40

1D NMR plot parameters
CX                     22.00 cm
F1P                  180.000 ppm
F1                  13584.20 Hz
F2P                    0.000 ppm
F2                     0.00 Hz
PPMCM               8.18182 ppm/cm
HZCM              617.46350 Hz/cm
```

C−13 DEPT 135




```
Current Data Parameters
NAME                  RVE355
EXPNO                      3
PROCNO                     1

F2 - Acquisition Parameters
Date_               20090706
Time                   22.51
INSTRUM                dpx300
PROBHD      5 mm Multinu
PULPROG             dept135
TD                     65536
SOLVENT                CDCl3
NS                       128
DS                         4
SWH                17361.111 Hz
FIDRES             0.264910 Hz
AQ                 1.8874868 sec
RG                      8192
DW                    28.800 usec
DE                     6.00 usec
TE                    300.0 K
CNST2             145.0000000
D1                  3.00000000 sec
d2                  0.00344828 sec
d12                 0.00002000 sec
DELTA            6366.18261719 sec

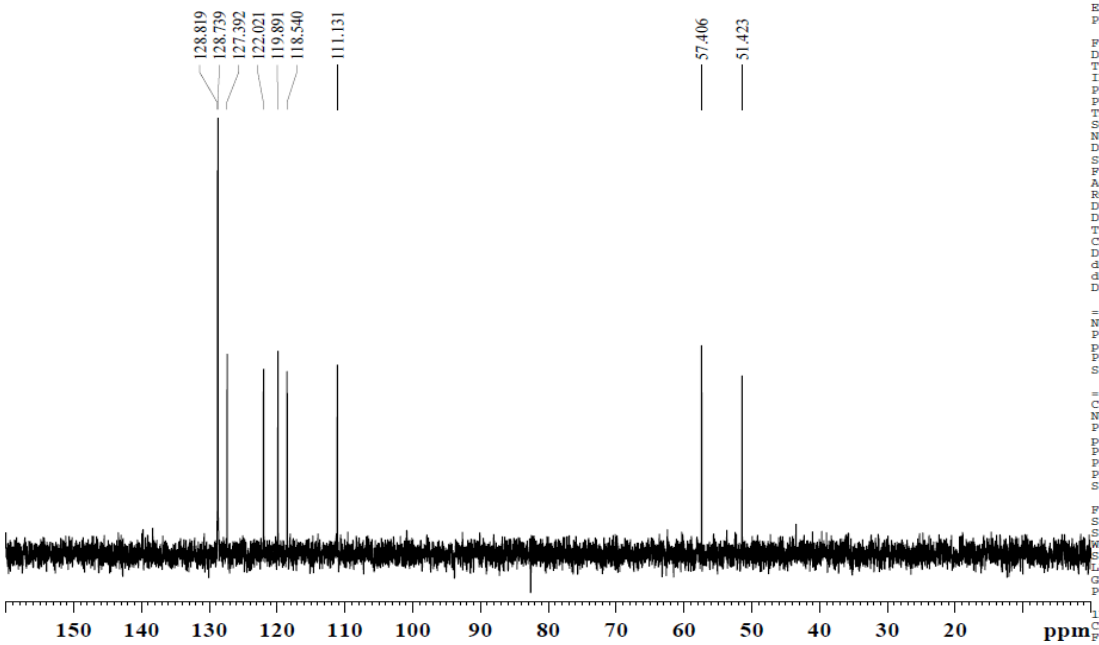
============ CHANNEL f1 =======
NUC1                      13C
P1                       6.63 usec
p2                      13.26 usec
PL1                     -6.00 dB
SFO1               75.4756431 MHz

============ CHANNEL f2 =======
CPDPRG2                waltz16
NUC2                       1H
P3                       9.45 usec
p4                      18.90 usec
PCPD2                  100.00 usec
PL2                     -6.00 dB
PL12                    16.60 dB
SFO2              300.1312005 MHz

F2 - Processing parameters
SI                       32768
SF                 75.4677190 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40

1D NMR plot parameters
CX                       20.00 cm
F1P                     59.842 ppm
F1                    4516.17 Hz
F2P                     48.226 ppm
F2                    3639.48 Hz
PPMCM                 0.58083 ppm/cm
HZCM                 43.83422 Hz/cm
```

C13 DEPT 90




```
Current Data Parameters
NAME                  RVE355
EXPNO                      4
PROCNO                     1

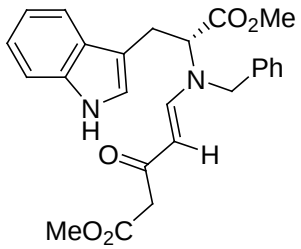
F2 - Acquisition Parameters
Date_               20090706
Time                   23.01
INSTRUM                dpx300
PROBHD      5 mm Multinu
PULPROG             dept90
TD                     65536
SOLVENT                CDCl3
NS                       128
DS                         4
SWH                23809.523 Hz
FIDRES             0.363304 Hz
AQ                 1.3763061 sec
RG                    7298.2
DW                    21.000 usec
DE                     6.00 usec
TE                    300.0 K
CNST2             145.0000000
D1                  3.00000000 sec
d2                  0.00344828 sec
d12                 0.00002000 sec
DELTA            6366.18261719 sec

============ CHANNEL f1 =======
NUC1                      13C
P1                       6.63 usec
p2                      13.26 usec
PL1                     -6.00 dB
SFO1               75.4772501 MHz

============ CHANNEL f2 =======
CPDPRG2                waltz16
NUC2                       1H
P3                       9.45 usec
p4                      18.90 usec
PCPD2                  100.00 usec
PL2                     -6.00 dB
PL12                    16.60 dB
SFO2              300.1312005 MHz

F2 - Processing parameters
SI                       32768
SF                 75.4677190 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40

1D NMR plot parameters
CX                       20.00 cm
F1P                    150.000 ppm
F1                   11320.16 Hz
F2P                      0.000 ppm
F2                       0.00 Hz
PPMCM                 7.50000 ppm/cm
HZCM                566.00781 Hz/cm
```



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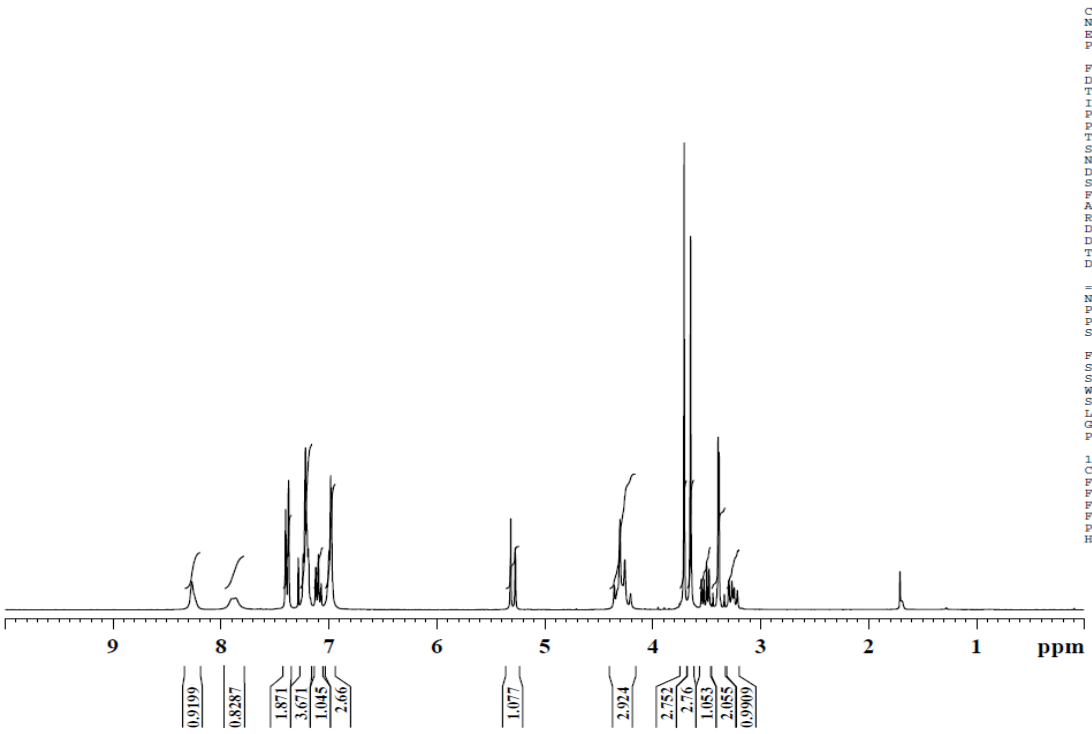
Proton Spectrum




```
Current Data Parameters
NAME                  RVE309
EXPNO                      1
PROCNO                     1

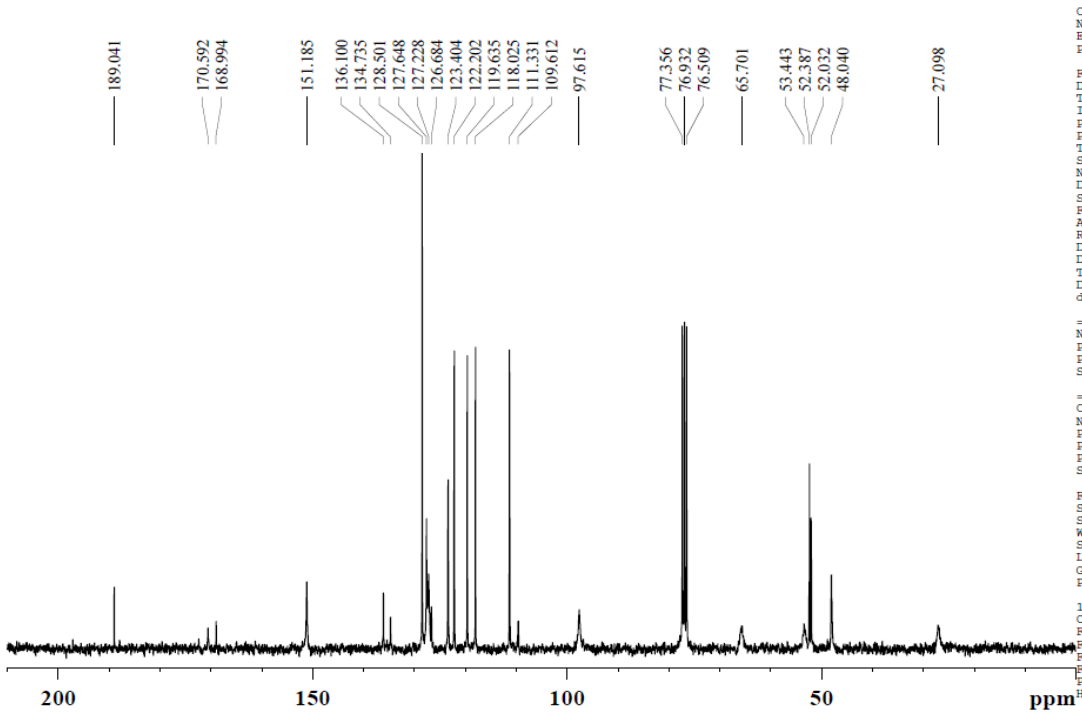
F2 - Acquisition Parameters
Date_              20090409
Time                  17.48
INSTRUM               dpx300
PROBHD     5 mm Multinu
PULPROG                 zg
TD                     32768
SOLVENT               CDCl3
NS                        16
DS                         0
SWH                5995.204 Hz
FIDRES            0.182959 Hz
AQ                2.7329011 sec
RG                     203.2
DW                  83.400 usec
DE                   6.00 usec
TE                   300.0 K
D1                1.00000000 sec

============ CHANNEL f1 =======
NUC1                      1H
P1                   5.00 usec
PL1                  -6.00 dB
SFO1          300.1319508 MHz

F2 - Processing parameters
SI                     32768
SF            300.1300000 MHz
WDW                       EM
SSB                        0
LB                    0.30 Hz
GB                         0
PC                      1.00

1D NMR plot parameters
CX                    22.00 cm
F1P                  10.000 ppm
F1                  3001.30 Hz
F2P                   0.000 ppm
F2                    0.00 Hz
PPMCM              0.45455 ppm/cm
HZCM             136.42273 Hz/cm
```

Carbon Spectrum




```
Current Data Parameters
NAME                  RVE409
EXPNO                      2
PROCNO                     1

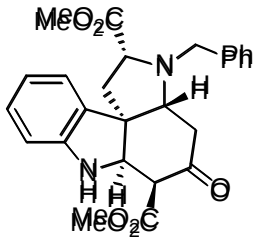
F2 - Acquisition Parameters
Date_              20090410
Time                   1.08
INSTRUM              dpx300
PROBHD     5 mm Multinu
PULPROG                zgdc
TD                    65536
SOLVENT               CDCl3
NS                     3072
DS                        0
SWH               18115.941 Hz
FIDRES            0.276427 Hz
AQ                1.8088436 sec
RG                     3251
DW                   27.600 usec
DE                    6.00 usec
TE                   300.0 K
D1              0.10000000 sec
d11             0.03000000 sec

============ CHANNEL f1 =======
NUC1                     13C
P1                      6.80 usec
PL1                    -6.00 dB
SFO1            75.4758695 MHz

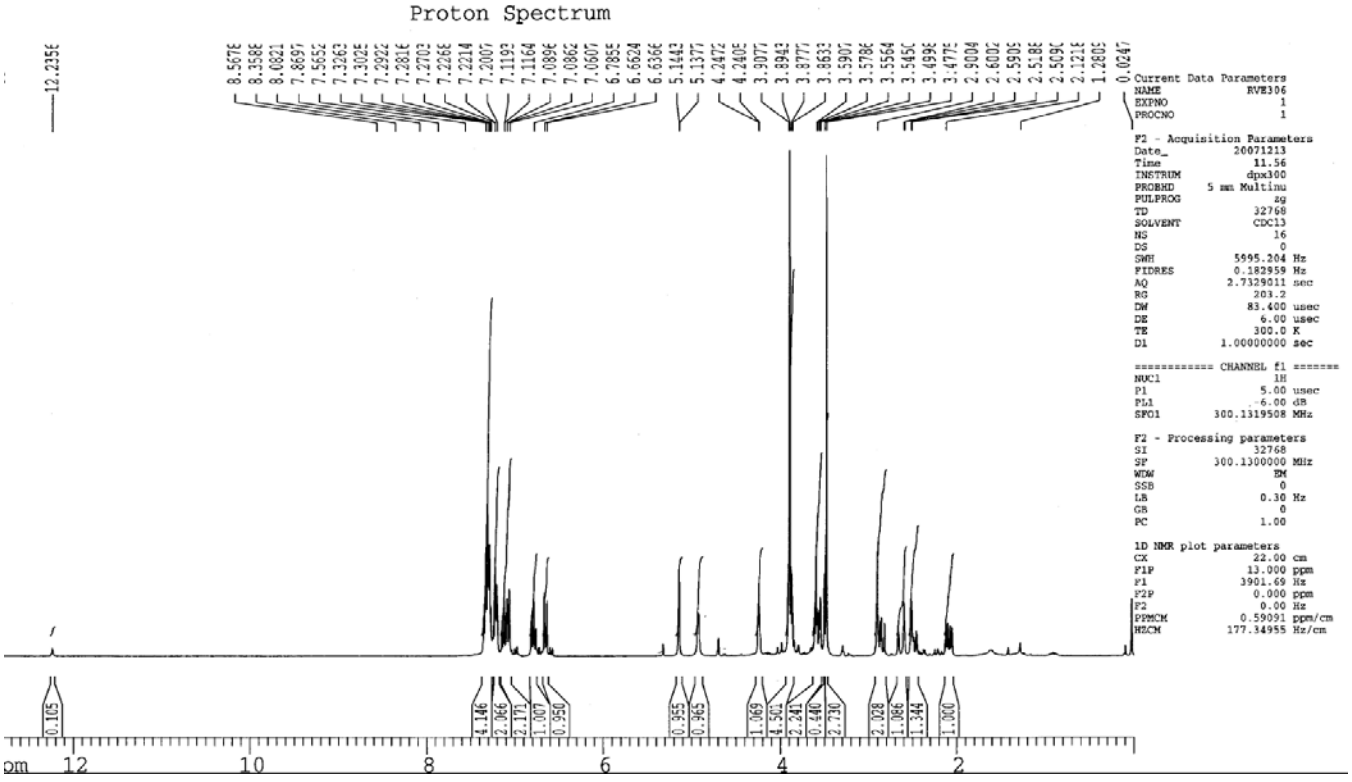
============ CHANNEL f2 =======
CPDPRG2              waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                    -6.00 dB
PL12                   16.60 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                       32768
SF              75.4677567 MHz
WDW                         EM
SSB                          0
LB                        3.00 Hz
GB                           0
PC                        1.40

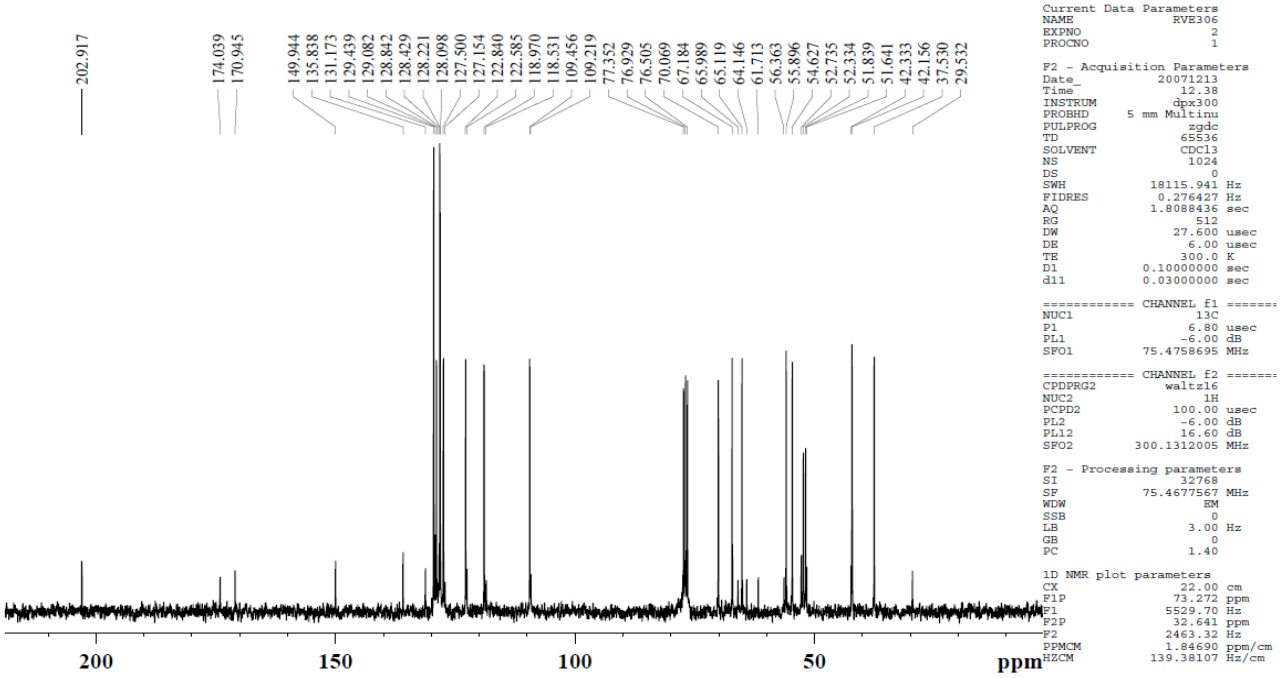
1D NMR plot parameters
CX                       22.00 cm
F1P                   68.976 ppm
F1                  5205.47 Hz
F2P                   21.626 ppm
F2                  1632.04 Hz
PPMCM                2.15229 ppm/cm
HZCM               162.42838 Hz/cm
```


MeO2C
N
Ph
H
N
H
H
O
MeO2C

17


Proton Spectrum
Current Data Parameters
NAME RVE306
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071213
Time 11.56
INSTRUM dpx300
PROBHD 5 mm Multinu
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 203.2
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
CHANNEL f1
NUC1 1H
P1 5.00 usec
PL1 -6.00 dB
SFO1 300.1319508 MHz
F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.00 cm
F1P 13.000 ppm
F1 3901.69 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.59091 ppm/cm
HZCM 177.34955 Hz/cm
ppm
12
10
8
6
4
2

Carbon Spectrum




```
Current Data Parameters
NAME                  RVE306
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20071213
Time                  12.38
INSTRUM               dpx300
PROBHD     5 mm Multinu
PULPROG               zgdc
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       0
SWH              18115.941 Hz
FIDRES           0.276427 Hz
AQ               1.8088436 sec
RG                     512
DW                27.600 usec
DE                 6.00 usec
TE                300.0 K
D1             0.10000000 sec
d11            0.03000000 sec

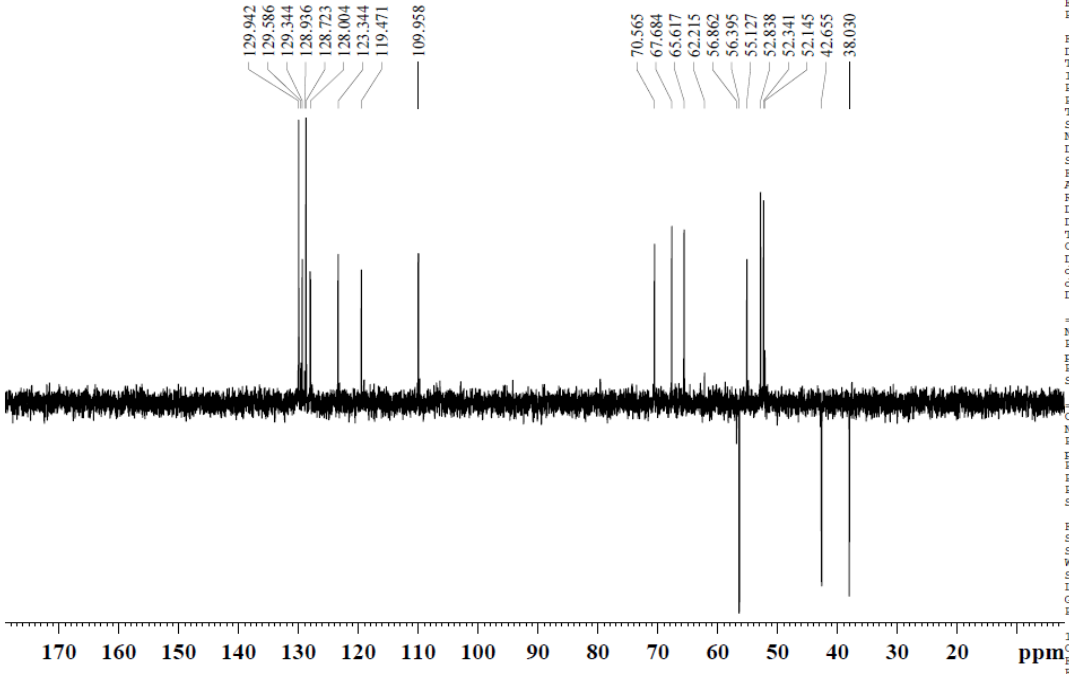
============ CHANNEL f1 =======
NUC1                  13C
P1                 6.80 usec
PL1               -6.00 dB
SFO1          75.4758695 MHz

============ CHANNEL f2 =======
CPDPRG2           waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2               -6.00 dB
PL12              16.60 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF               75.4677567 MHz
WDW                      EM
SSB                       0
LB                 3.00 Hz
GB                        0
PC                     1.40

1D NMR plot parameters
CX                   22.00 cm
F1P                  73.272 ppm
F1                 5529.70 Hz
F2P                  32.641 ppm
F2                 2463.32 Hz
PPMCM              1.84690 ppm/cm
HZCM             139.38107 Hz/cm
```

C−13 DEPT 135




```
Current Data Parameters
NAME                  RVE306
EXPNO                      3
PROCNO                     1

F2 - Acquisition Parameters
Date_              20071213
Time                  12.55
INSTRUM               dpx300
PROBHD     5 mm Multinu
PULPROG             dept135
TD                   65536
SOLVENT              CDCl3
NS                     256
DS                       4
SWH              17361.111 Hz
FIDRES           0.264910 Hz
AQ               1.8874868 sec
RG                    8192
DW                28.800 usec
DE                 6.00 usec
TE                300.0 K
CNST2          145.0000000
D1               1.00000000 sec
d2               0.00344828 sec
d12              0.00002000 sec
DELTA         6366.18261719 sec

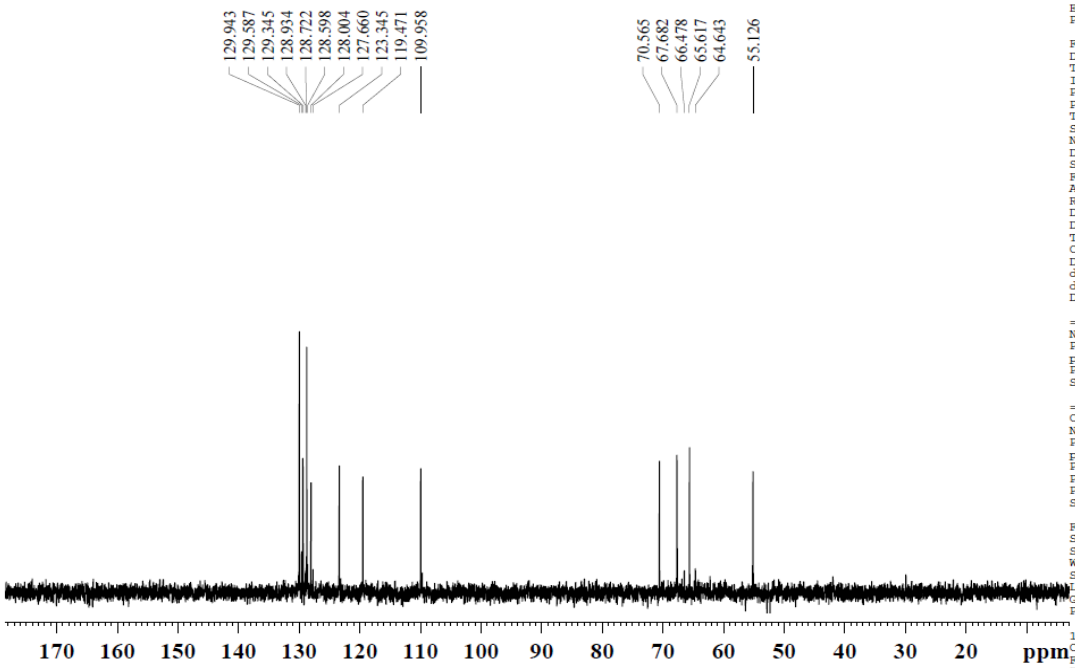
============ CHANNEL f1 =======
NUC1                  13C
P1                 6.80 usec
p2                13.60 usec
PL1               -6.00 dB
SFO1          75.4756431 MHz

============ CHANNEL f2 =======
CPDPRG2           waltz16
NUC2                  1H
P3                 9.45 usec
p4                18.90 usec
PCPD2            100.00 usec
PL2               -6.00 dB
PL12              16.60 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF               75.4677190 MHz
WDW                      EM
SSB                       0
LB                 1.00 Hz
GB                        0
PC                     1.40

1D NMR plot parameters
CX                   20.00 cm
F1P                 133.890 ppm
F1                10104.37 Hz
F2P                 104.306 ppm
F2                 7871.74 Hz
PPMCM              1.47920 ppm/cm
HZCM             111.63165 Hz/cm
```

C13 DEPT 90




```
Current Data Parameters
NAME                  RVE306
EXPNO                      4
PROCNO                     1

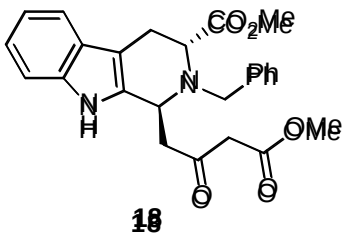
F2 - Acquisition Parameters
Date_              20071213
Time                  13.09
INSTRUM               dpx300
PROBHD     5 mm Multinu
PULPROG              dept90
TD                    65536
SOLVENT               CDCl3
NS                      256
DS                        4
SWH               23809.523 Hz
FIDRES             0.363304 Hz
AQ                 1.3763061 sec
RG                    7298.2
DW                    21.000 usec
DE                     6.00 usec
TE                    300.0 K
CNST2            145.0000000
D1                 1.00000000 sec
d2                 0.00344828 sec
d12                0.00002000 sec
DELTA           6366.18261719 sec

============ CHANNEL f1 =======
NUC1                      13C
P1                       6.80 usec
p2                      13.60 usec
PL1                     -6.00 dB
SFO1              75.4772501 MHz

============ CHANNEL f2 =======
CPDPRG2              waltz16
NUC2                      1H
P3                       9.45 usec
p4                      18.90 usec
PCPD2                  100.00 usec
PL2                     -6.00 dB
PL12                    16.60 dB
SFO2             300.1312005 MHz

F2 - Processing parameters
SI                        32768
SF                75.4677190 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40

1D NMR plot parameters
CX                     20.00 cm
F1P                   133.480 ppm
F1                  10073.43 Hz
F2P                   105.816 ppm
F2                   7985.71 Hz
PPMCM                1.38319 ppm/cm
HZCM               104.38629 Hz/cm
```



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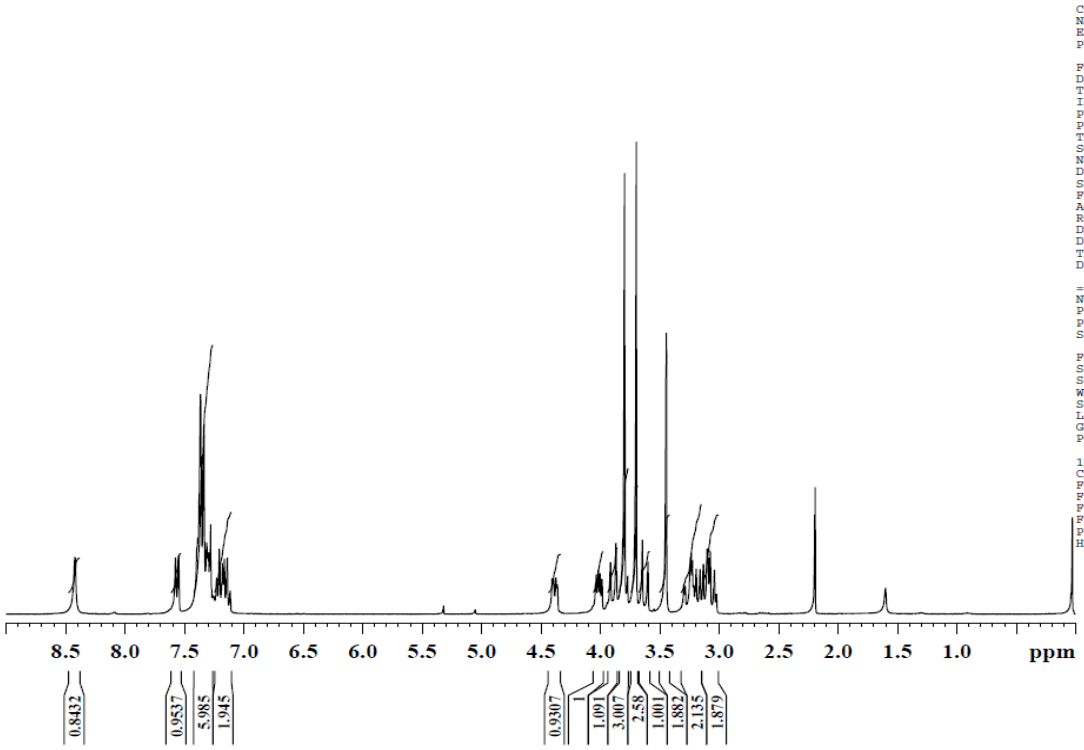
Proton Spectrum




```
Current Data Parameters
NAME                  RVE449
EXPNO                      2
PROCNO                     1

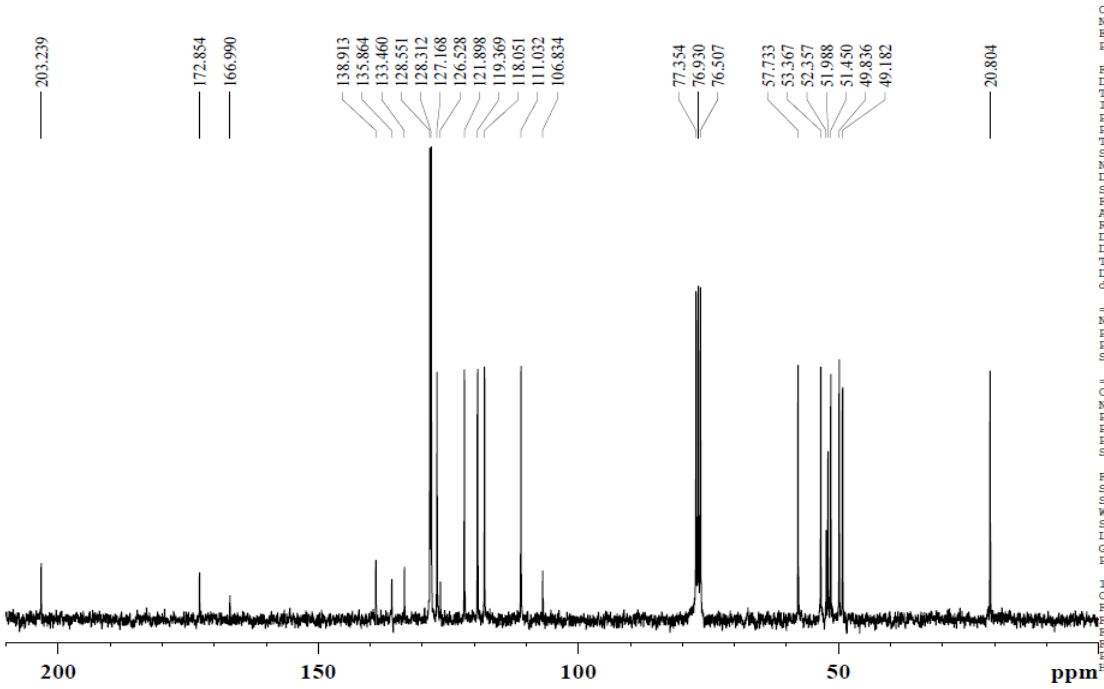
F2 - Acquisition Parameters
Date_              20090629
Time                  15.38
INSTRUM             dpx300
PROBHD      5 mm Multinu
PULPROG                zg
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              5995.204 Hz
FIDRES           0.182959 Hz
AQ               2.7329011 sec
RG                    256
DW                 83.400 usec
DE                  6.00 usec
TE                 300.0 K
D1              1.00000000 sec

============ CHANNEL f1 =======
NUC1                   1H
P1                   5.00 usec
PL1                 -6.00 dB
SFO1         300.1319508 MHz

F2 - Processing parameters
SI                  32768
SF           300.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.00 cm
F1P                 7.681 ppm
F1                2305.15 Hz
F2P                 7.000 ppm
F2                2100.86 Hz
PPMCM             0.03094 ppm/cm
HZCM              9.28577 Hz/cm
```

Carbon Spectrum




```
Current Data Parameters
NAME                  RVE449
EXPNO                      6
PROCNO                     1

F2 - Acquisition Parameters
Date_              20090629
Time                  19.03
INSTRUM               dpx300
PROBHD     5 mm Multinu
PULPROG               zgdc
TD                   65536
SOLVENT              CDCl3
NS                    3072
DS                       0
SWH              18115.941 Hz
FIDRES           0.276427 Hz
AQ               1.8088436 sec
RG                    1024
DW                27.600 usec
DE                 6.00 usec
TE                 300.0 K
D1              0.10000000 sec
d11             0.03000000 sec

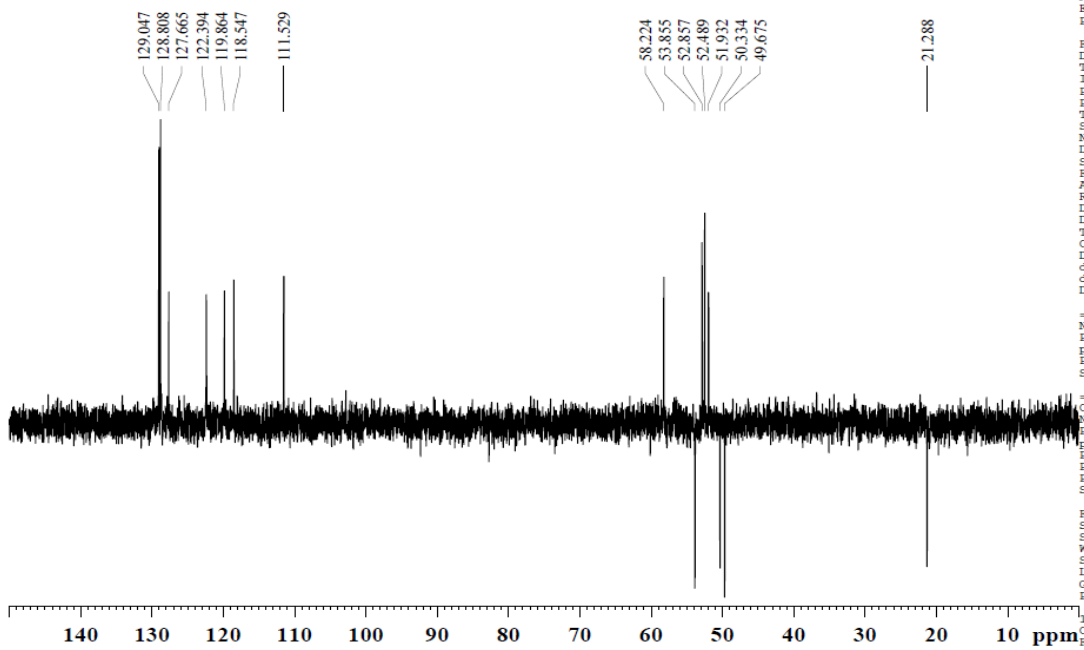
============ CHANNEL f1 =======
NUC1                  13C
P1                   6.80 usec
PL1                 -6.00 dB
SFO1          75.4758695 MHz

============ CHANNEL f2 =======
CPDPRG2             waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -6.00 dB
PL12                16.60 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF            75.4677567 MHz
WDW                      EM
SSB                       0
LB                 3.00 Hz
GB                        0
PC                     1.40

1D NMR plot parameters
CX                   22.00 cm
F1P                210.000 ppm
F1                 15848.23 Hz
F2P                  0.000 ppm
F2                   0.00 Hz
PPMCM              9.54545 ppm/cm
HZCM             720.37402 Hz/cm
```

C−13 DEPT 135




```
Current Data Parameters
NAME                  RVE449
EXPNO                      4
PROCNO                     1

F2 - Acquisition Parameters
Date_              20090629
Time                  17.09
INSTRUM               dpx300
PROBHD     5 mm Multinu
PULPROG           dept135
TD                   65536
SOLVENT              CDCl3
NS                     128
DS                       4
SWH              17361.111 Hz
FIDRES           0.264910 Hz
AQ               1.8874868 sec
RG                    8192
DW                28.800 usec
DE                 6.00 usec
TE                 300.0 K
CNST2            145.0000000
D1               3.00000000 sec
d2               0.00344828 sec
d12              0.00002000 sec
DELTA         6366.18261719 sec

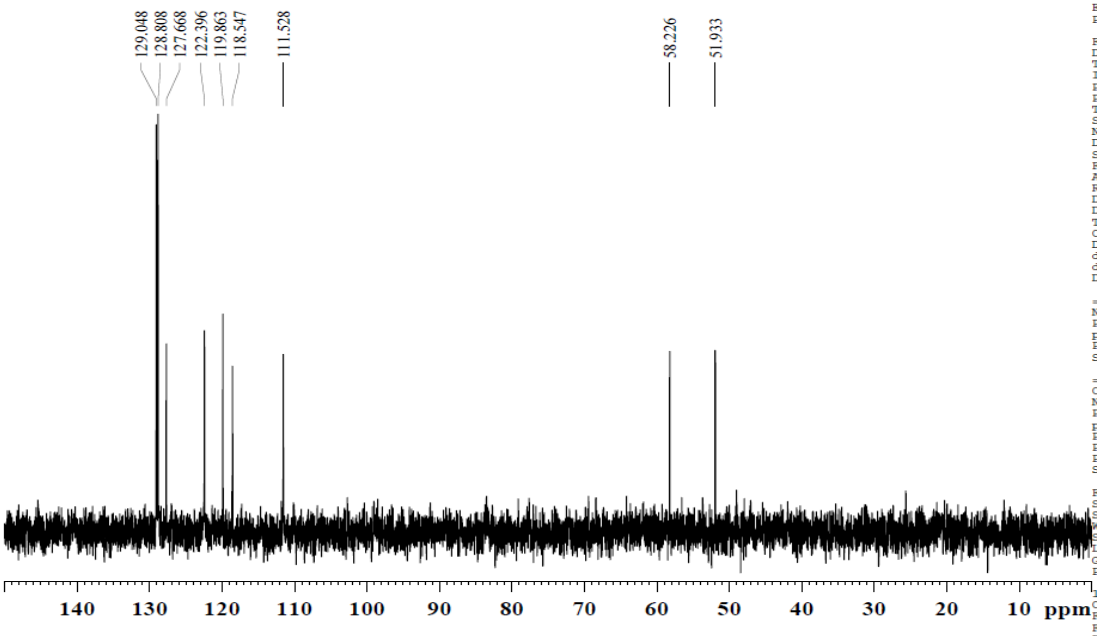
============ CHANNEL f1 =======
NUC1                  13C
P1                   6.63 usec
p2                  13.26 usec
PL1                 -6.00 dB
SFO1          75.4756431 MHz

============ CHANNEL f2 =======
CPDPRG2             waltz16
NUC2                   1H
P3                    9.45 usec
p4                   18.90 usec
PCPD2              100.00 usec
PL2                 -6.00 dB
PL12                16.60 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF            75.4677190 MHz
WDW                      EM
SSB                       0
LB                 1.00 Hz
GB                        0
PC                     1.40

1D NMR plot parameters
CX                   20.00 cm
F1P                61.860 ppm
F1                 4668.42 Hz
F2P                  45.133 ppm
F2                 3406.08 Hz
PPMCM              0.83634 ppm/cm
HZCM              63.11686 Hz/cm
```

C13 DEPT 90

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Current Data Parameters
NAME                  RVE449
EXPNO                      5
PROCNO                     1

F2 - Acquisition Parameters
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Time                  17.18
INSTRUM               dpx300
PROBHD     5 mm Multinu
PULPROG             dept90
TD                   65536
SOLVENT              CDCl3
NS                     128
DS                       4
SWH              23809.523 Hz
FIDRES           0.363304 Hz
AQ               1.3763061 sec
RG                    6502
DW                  21.000 usec
DE                   6.00 usec
TE                  300.0 K
CNST2           145.0000000
D1                3.00000000 sec
d2                0.00344828 sec
d12               0.00002000 sec
DELTA          6366.18261719 sec

============ CHANNEL f1 =======
NUC1                    13C
P1                     6.63 usec
p2                    13.26 usec
PL1                   -6.00 dB
SFO1             75.4772501 MHz

============ CHANNEL f2 =======
CPDPRG2              waltz16
NUC2                    1H
P3                     9.45 usec
p4                    18.90 usec
PCPD2                100.00 usec
PL2                   -6.00 dB
PL12                  16.60 dB
SFO2            300.1312005 MHz

F2 - Processing parameters
SI                     32768
SF               75.4677190 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40

1D NMR plot parameters
CX                     20.00 cm
F1P                   132.665 ppm
F1                  10011.89 Hz
F2P                   106.899 ppm
F2                   8067.42 Hz
PPMCM                 1.28828 ppm/cm
HZCM                 97.22371 Hz/cm
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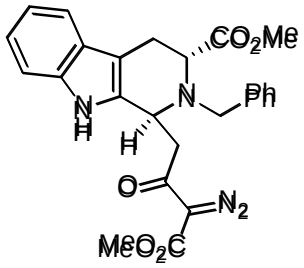

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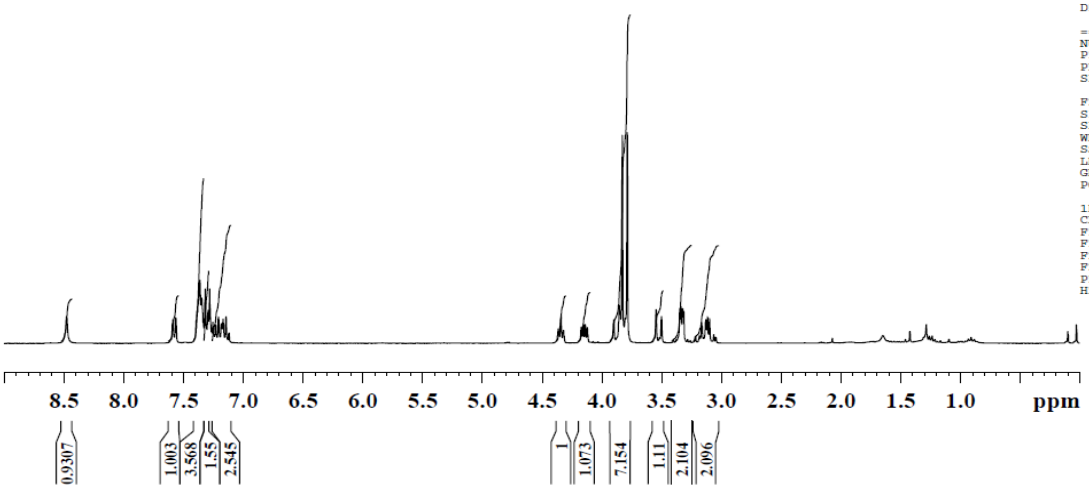
Proton Spectrum

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Current Data Parameters
NAME                  RVE328
EXPNO                      1
PROCNO                     1

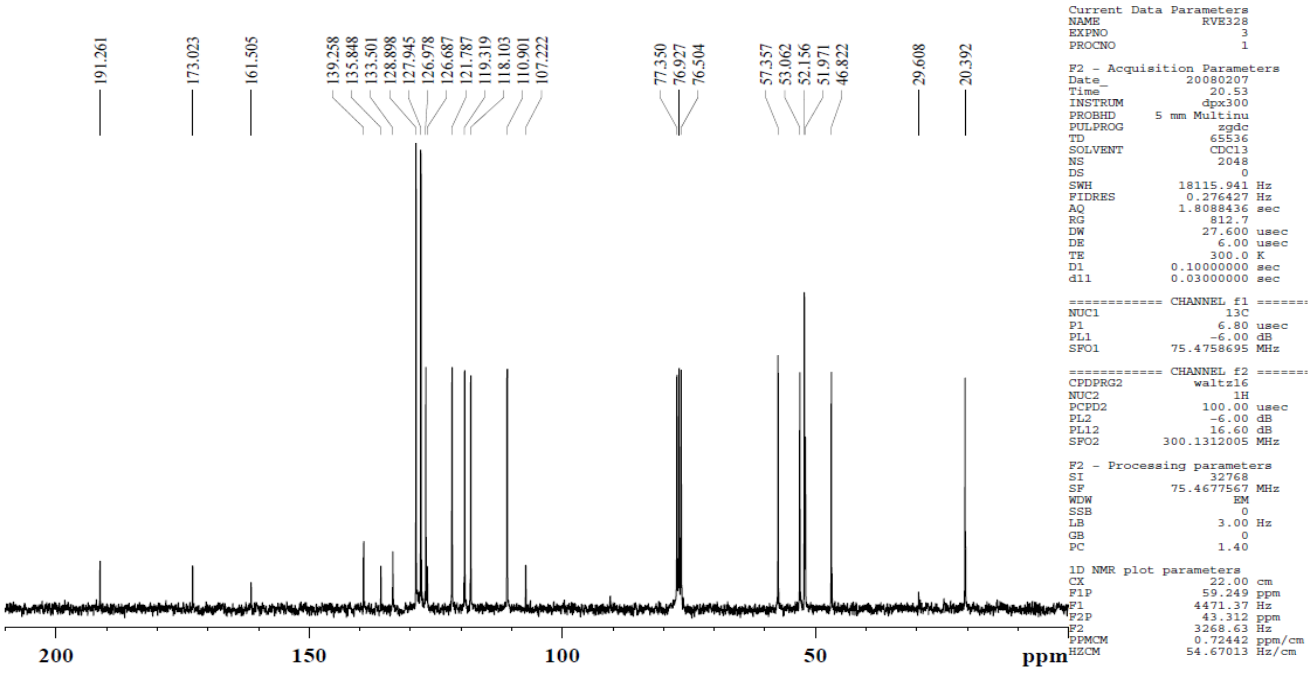
F2 - Acquisition Parameters
Date_              20080207
Time                  19.40
INSTRUM               dpx300
PROBHD      5 mm Multinu
PULPROG                   zg
TD                     32768
SOLVENT               CDCl3
NS                        16
DS                         0
SWH                5995.204 Hz
FIDRES            0.182959 Hz
AQ                2.7329011 sec
RG                     228.1
DW                    83.400 usec
DE                     6.00 usec
TE                    300.0 K
D1                1.00000000 sec

============ CHANNEL f1 =======
NUC1                      1H
P1                     5.00 usec
PL1                   -6.00 dB
SFO1          300.1319508 MHz

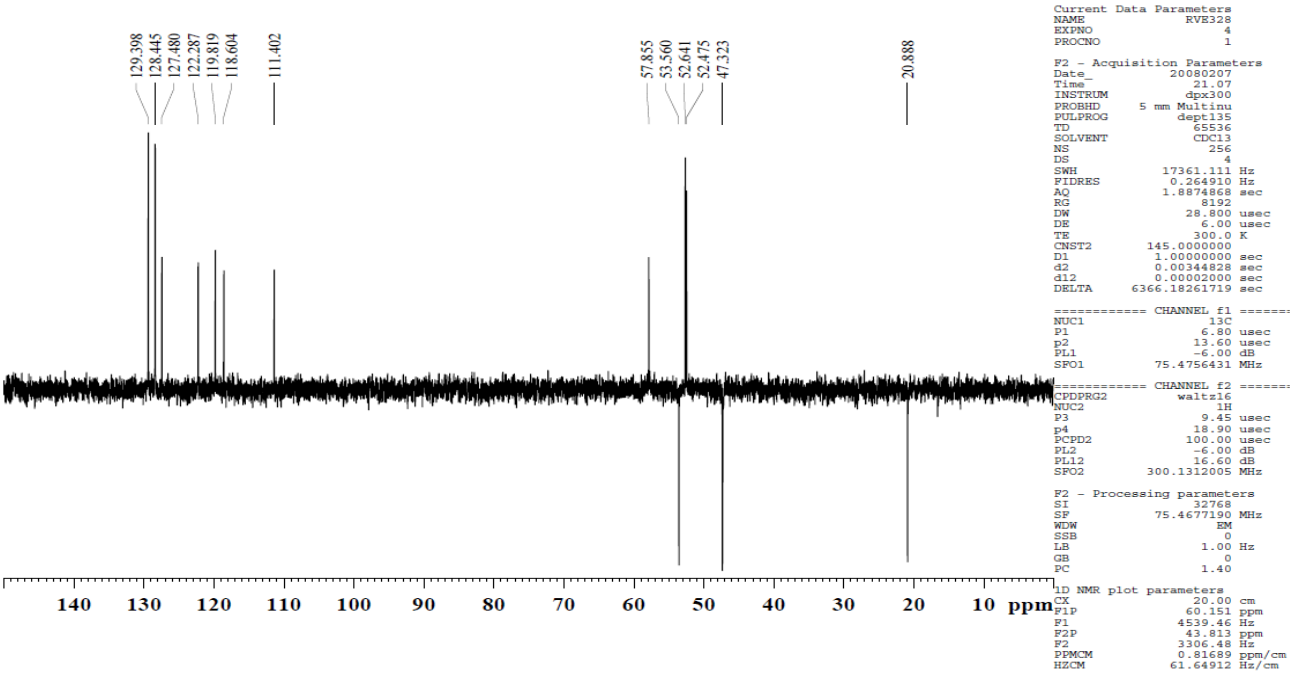
F2 - Processing parameters
SI                     32768
SF            300.1300000 MHz
WDW                       EM
SSB                        0
LB                    0.30 Hz
GB                         0
PC                     1.00

1D NMR plot parameters
CX                    22.00 cm
F1P                   7.740 ppm
F1                 2323.08 Hz
F2P                   6.866 ppm
F2                 2060.80 Hz
PPMCM             0.03972 ppm/cm
HZCM             11.92196 Hz/cm
```

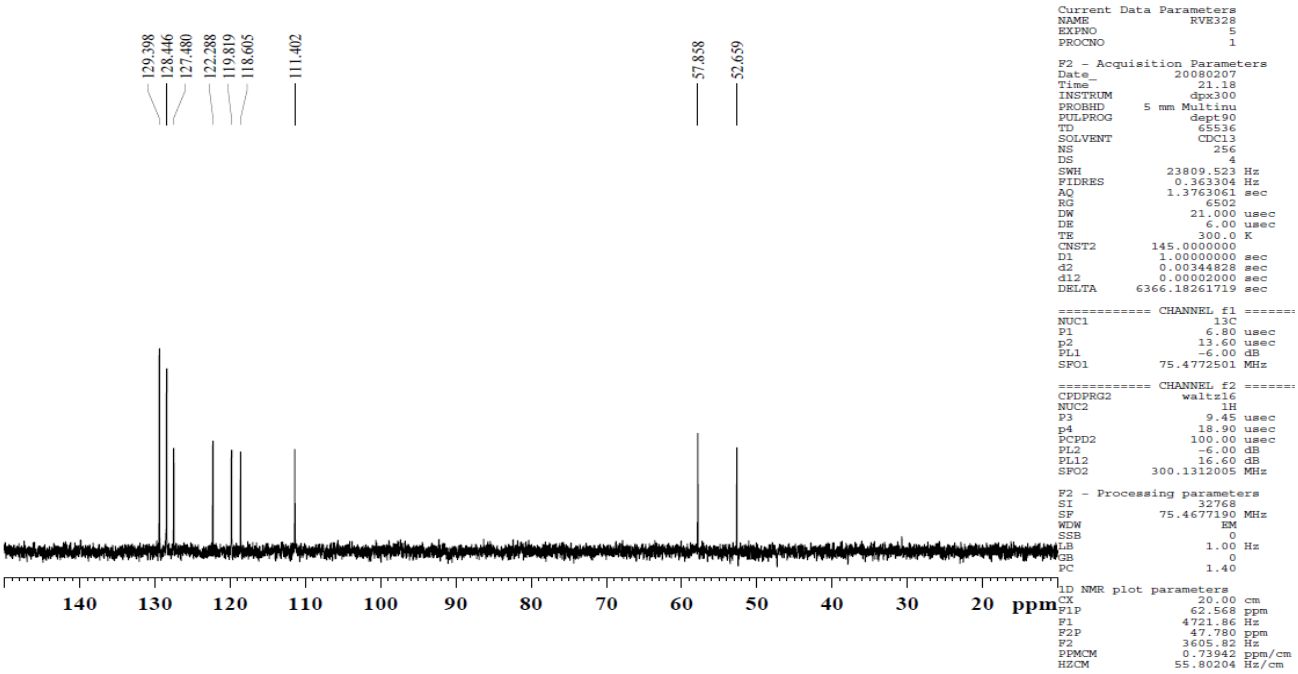
Carbon Spectrum

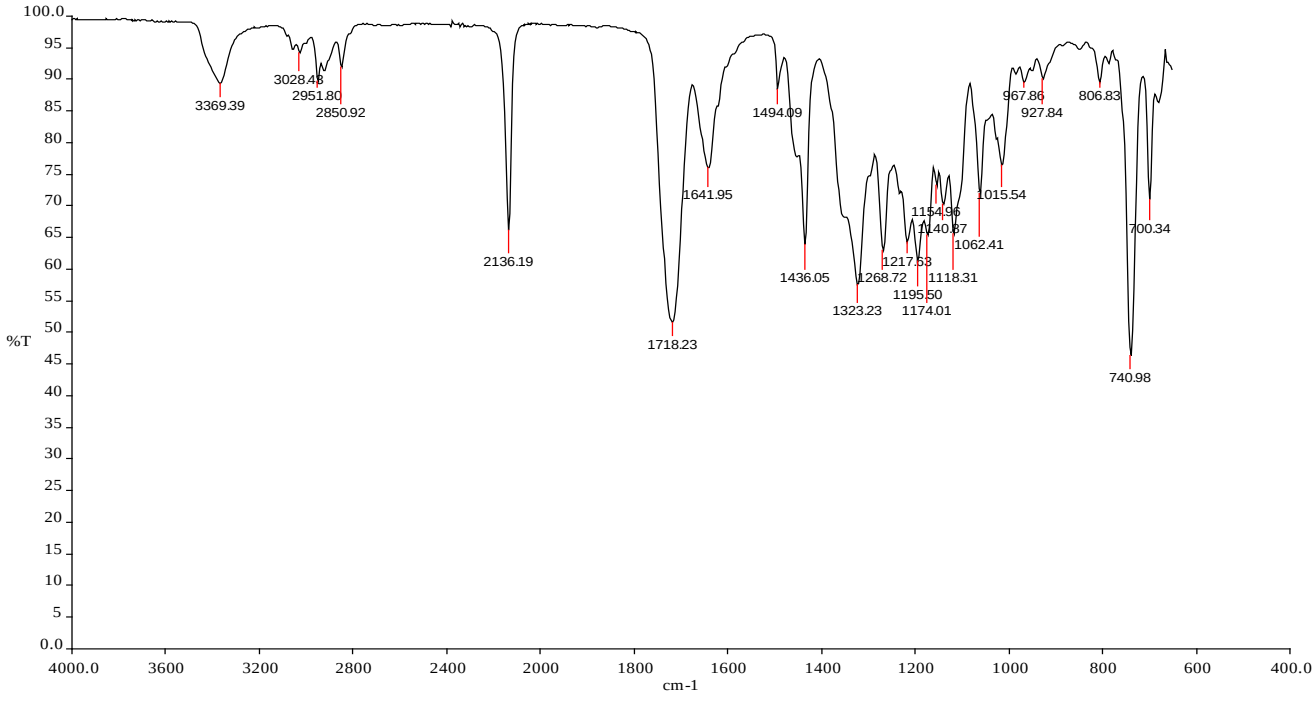


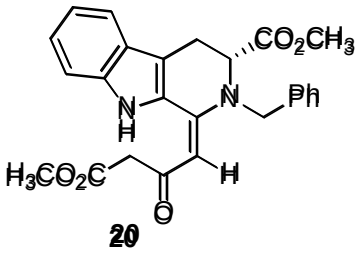
C−13 DEPT 135



C13 DEPT 90


129.398
128.446
127.480
122.288
119.819
118.605
111.402
57.858
52.659
140 130 120 110 100 90 80 70 60 50 40 30 20 ppm
Current Data Parameters
NAME RVE328
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080207
Time 21.18
INSTRUM dpx300
PROBHD 5 mm Multinu
PULPROG dept90
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 23809.523 Hz
FIDRES 0.363304 Hz
AQ 1.3763061 sec
RG 6502
DW 21.000 usec
DE 6.00 usec
TE 300.0 K
CNST2 145.0000000
D1 1.00000000 sec
d2 0.00344828 sec
d12 0.00002000 sec
DELTA 6366.18261719 sec
CHANNEL f1
NUC1 13C
P1 6.80 usec
p2 13.60 usec
PL1 -6.00 dB
SFO1 75.4772501 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
P3 9.45 usec
p4 18.90 usec
PCPD2 100.00 usec
PL2 -6.00 dB
PL12 16.60 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677190 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 62.568 ppm
F1 4721.86 Hz
F2P 47.780 ppm
F2 3605.82 Hz
PPMCM 0.73942 ppm/cm
HZCM 55.80204 Hz/cm


%T
100.0 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0.0
4000.0 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600 400.0
cm-1
3369.39
3028.48
2951.80
2850.92
2136.19
1718.23
1641.95
1494.09
1436.05
1323.23
1268.72
1217.53
1195.50
1174.01
1154.96
1140.87
1118.31
1062.41
1015.54
967.86
927.84
806.83
740.98
700.34



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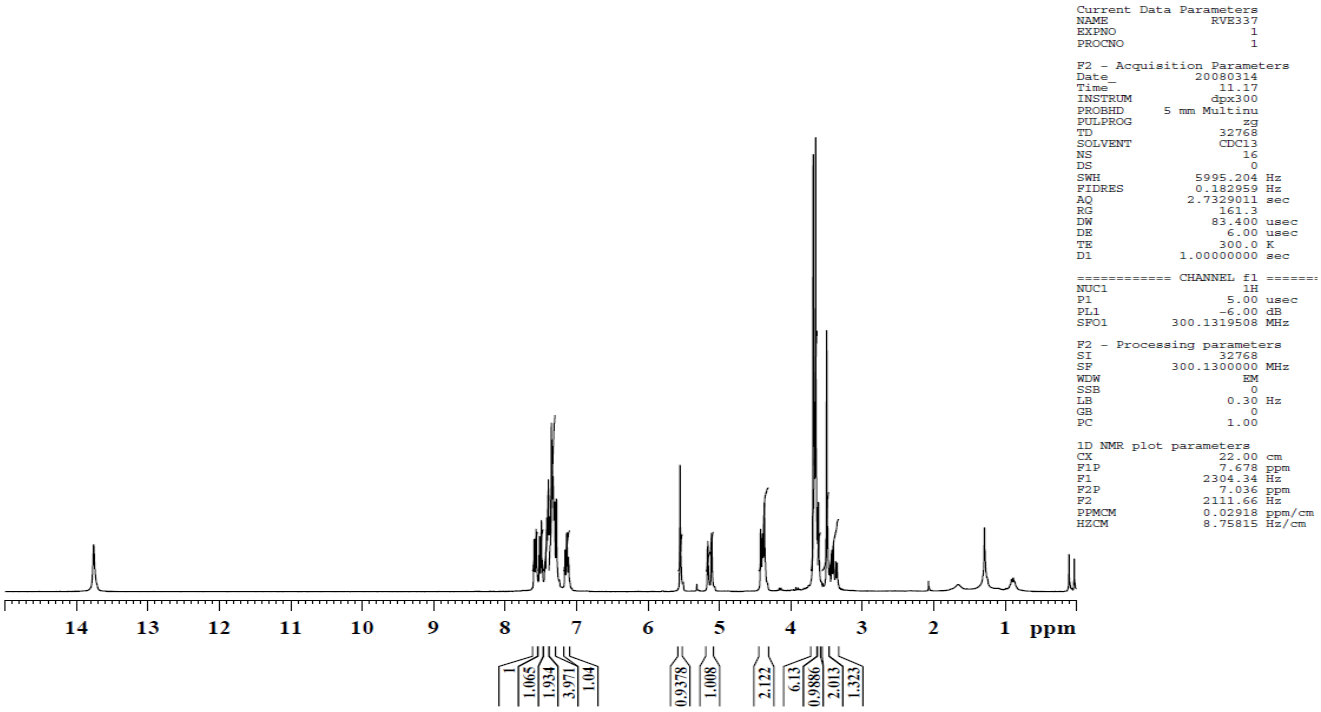
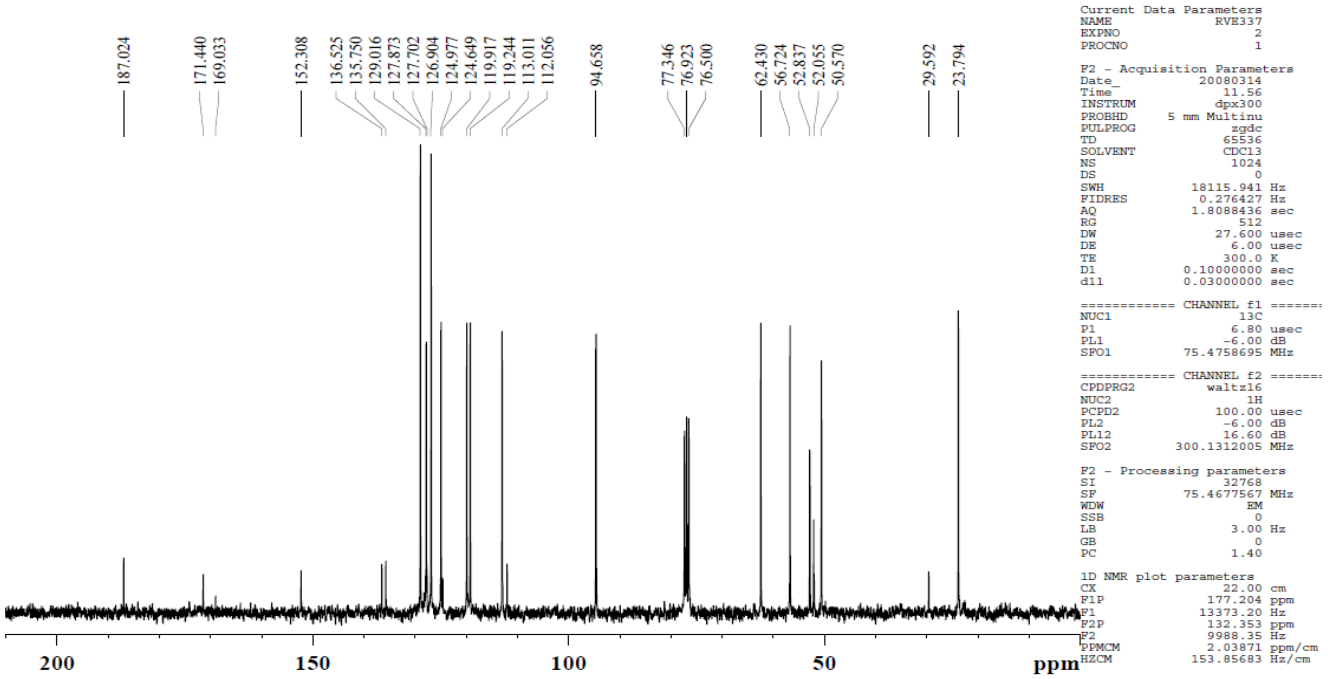
Compound 20 (300 MHz)

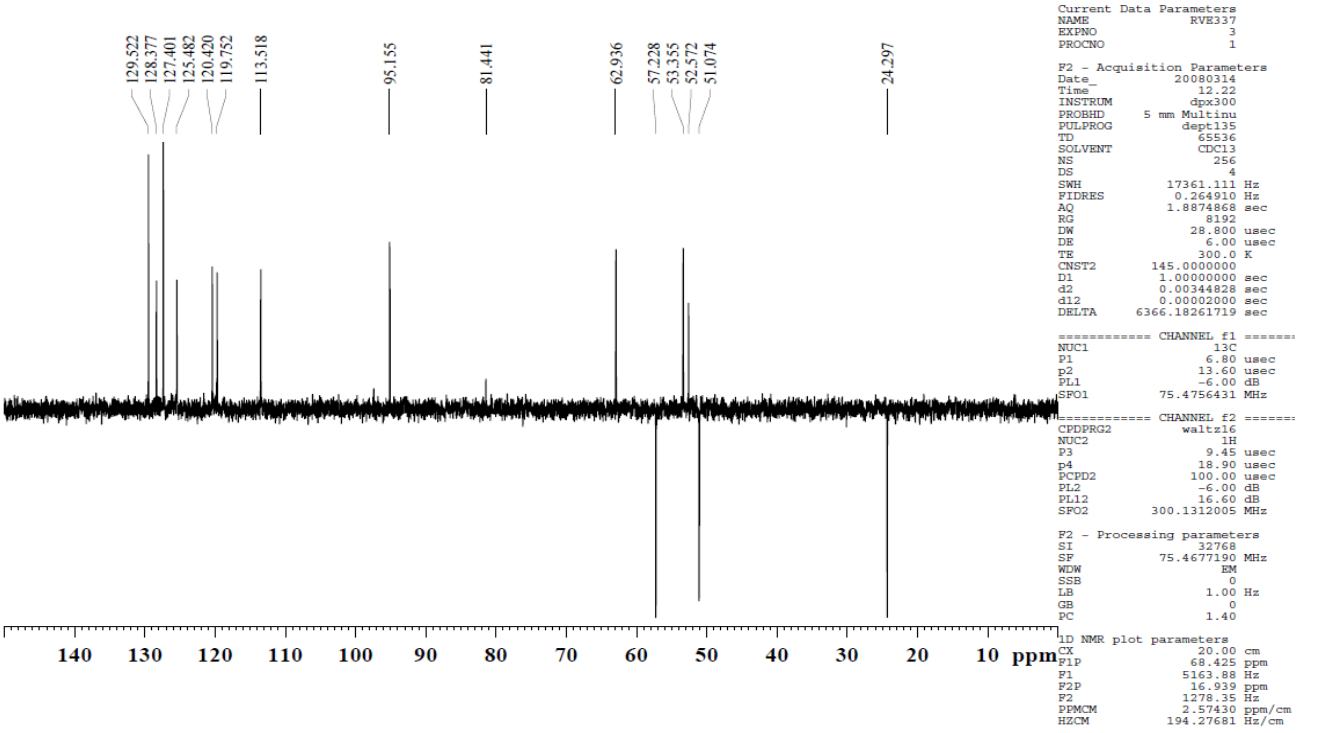
Proton Spectrum



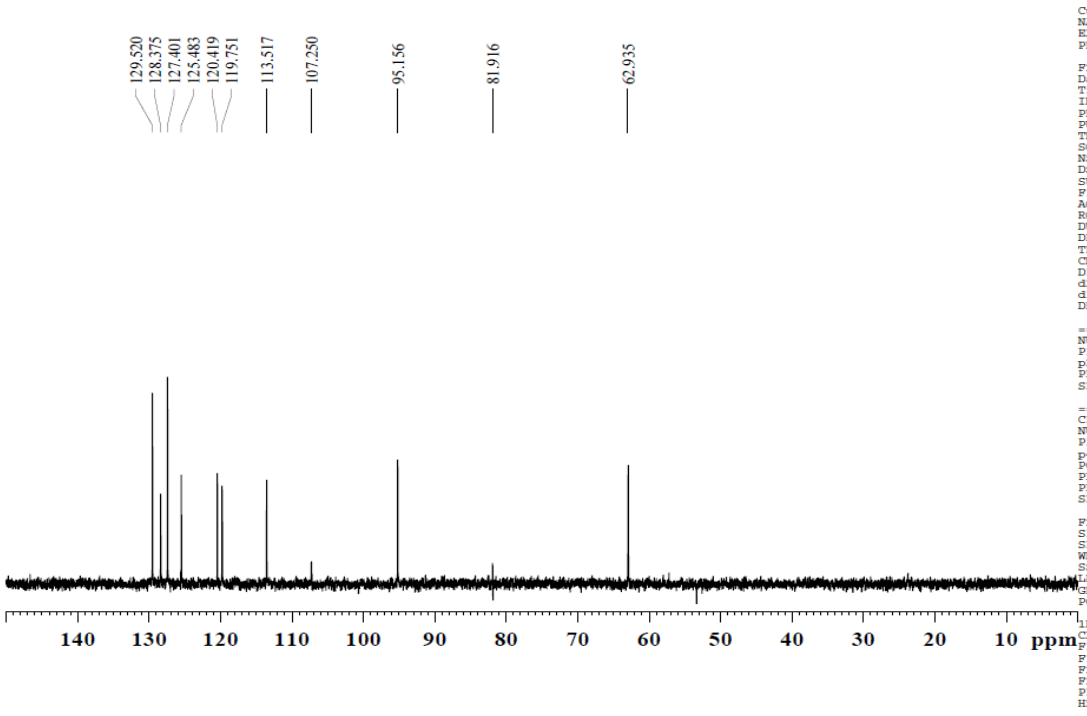
Carbon Spectrum



C−13 DEPT 135



C13 DEPT 90

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Current Data Parameters
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EXPNO                      4
PROCNO                     1

F2 - Acquisition Parameters
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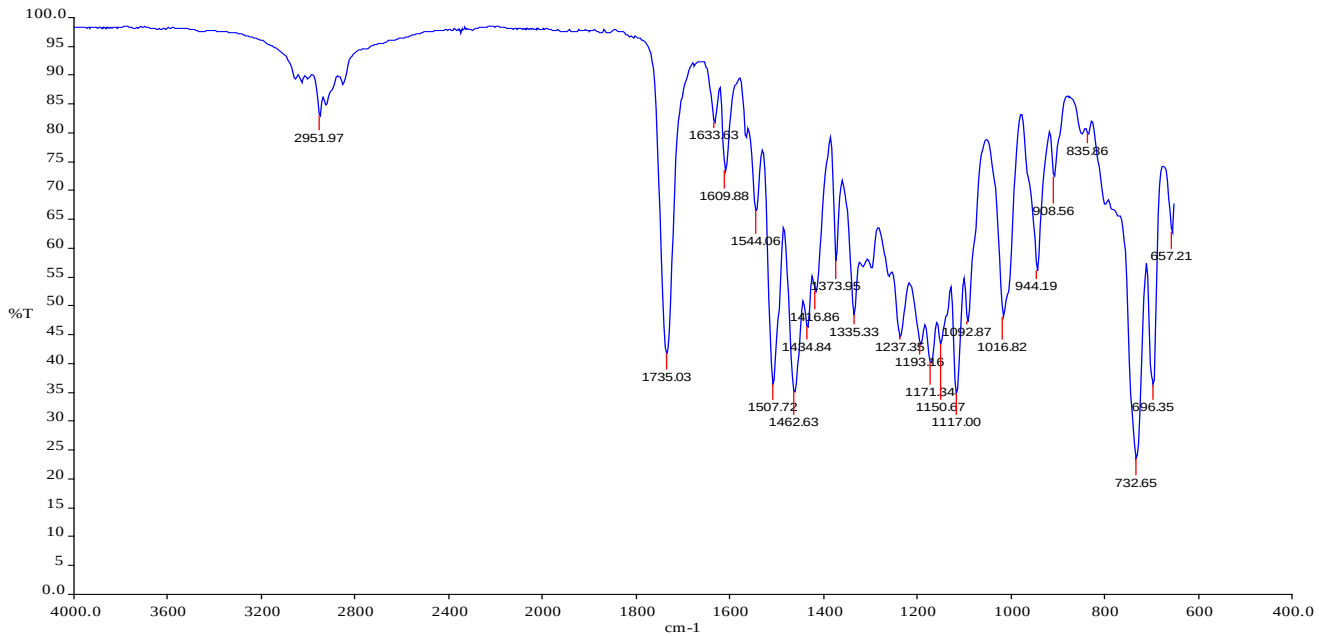
Time                   12.33
INSTRUM                dpx300
PROBHD      5 mm Multinu
PULPROG              dept90
TD                    65536
SOLVENT               CDC13
NS                      256
DS                        4
SWH                23809.523 Hz
FIDRES             0.363304 Hz
AQ                 1.3763061 sec
RG                     6502
DW                   21.000 usec
DE                    6.00 usec
TE                   300.0 K
CNST2             145.0000000
D1                  1.00000000 sec
d2                  0.00344828 sec
d12                 0.00002000 sec
DELTA            6366.18261719 sec

============ CHANNEL f1 =======
NUC1                      13C
P1                       6.80 usec
p2                      13.60 usec
PL1                     -6.00 dB
SFO1               75.4772501 MHz

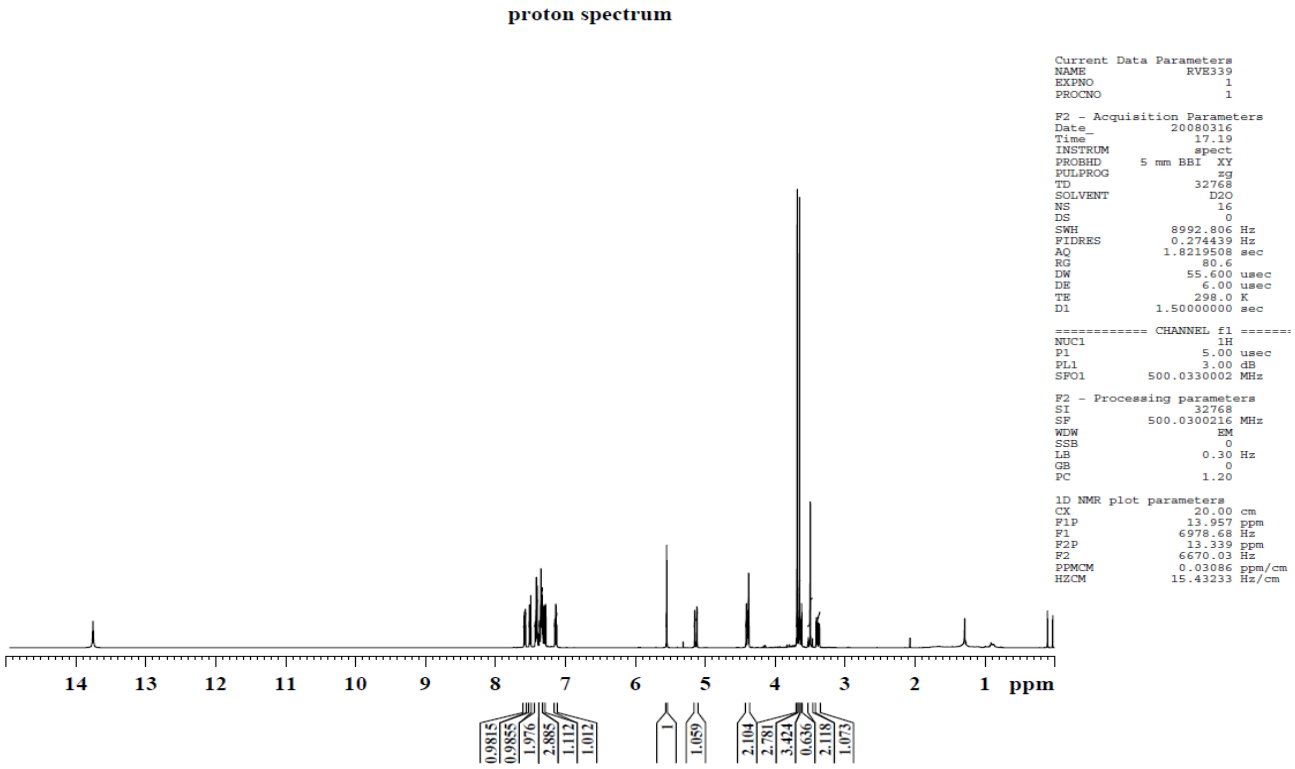
============ CHANNEL f2 =======
CPDPRG2                waltz16
NUC2                       1H
P3                       9.45 usec
p4                      18.90 usec
PCPD2                  100.00 usec
PL2                     -6.00 dB
PL12                    16.60 dB
SFO2              300.1312005 MHz

F2 - Processing parameters
SI                        32768
SF                 75.4677190 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40

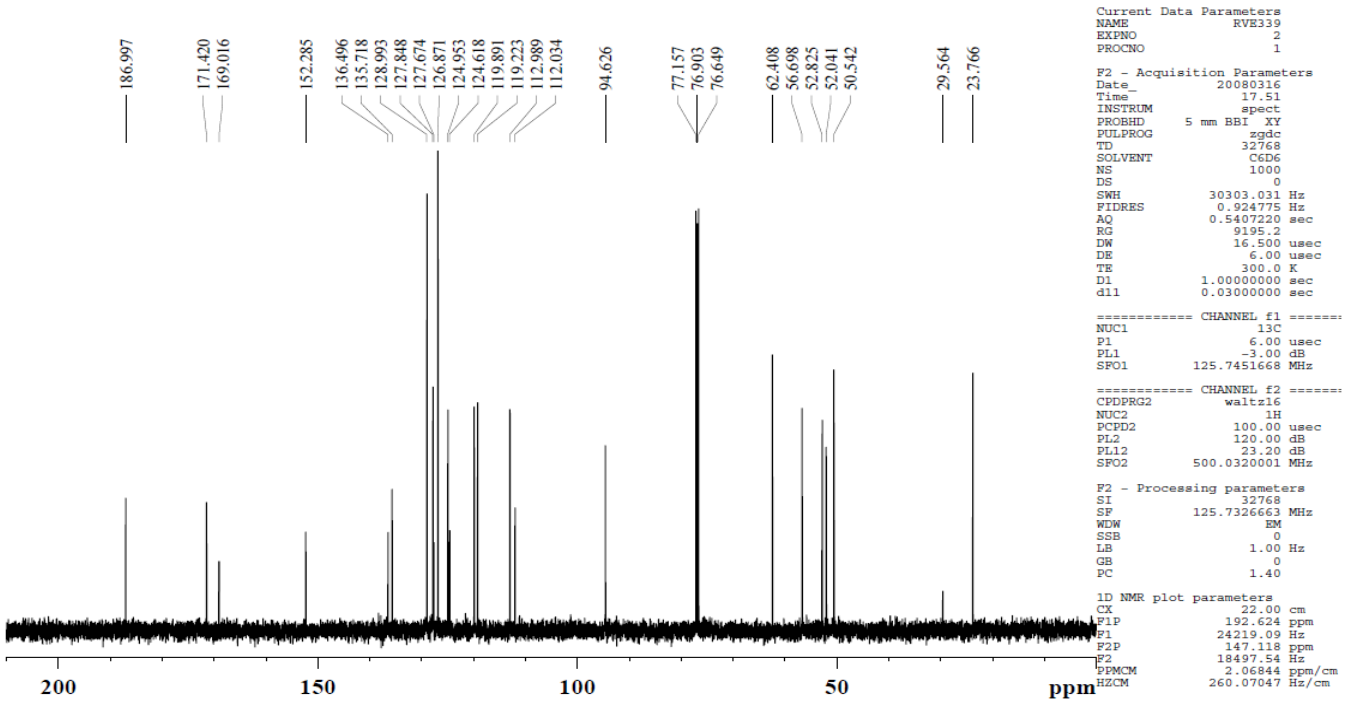
1D NMR plot parameters
CX                        20.00 cm
F1P                      110.254 ppm
F1                      8320.62 Hz
F2P                      46.895 ppm
F2                      3539.04 Hz
PPMCM                    3.16797 ppm/cm
HZCM                   239.07912 Hz/cm
```



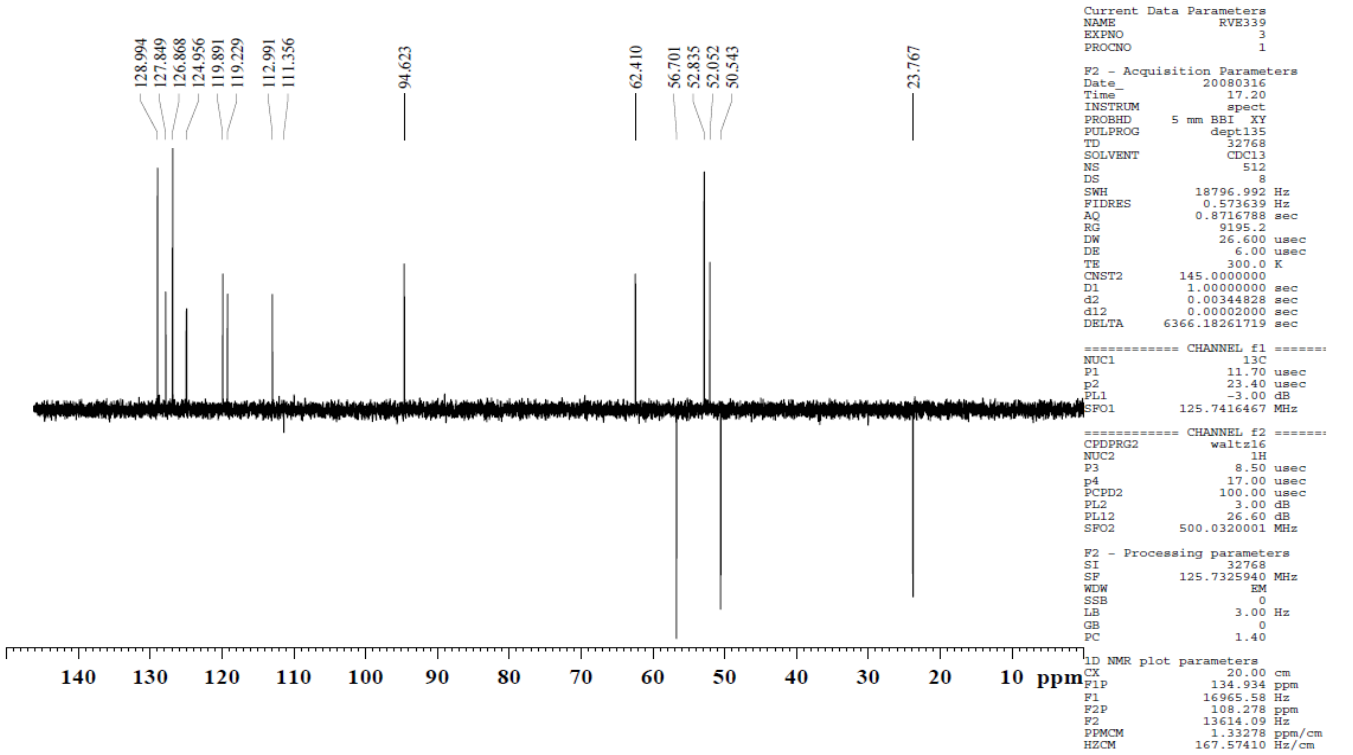
Compound 20 (500 MHz)



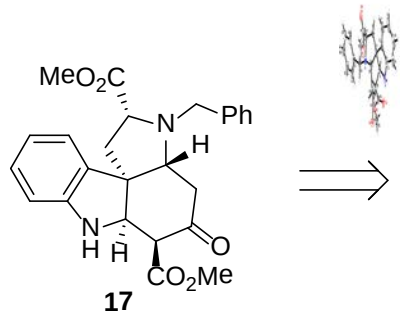
carbon spectrum



C−13 DEPT−135

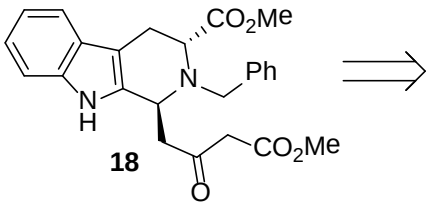


X-ray Structural Analysis and Methods for 17 and 18



17

Figure S1: Displacement ellipsoid plot of (2*R*,3a*R*,6*S*,6a*R*,11b*R*)-Dimethyl 3-benzyl-5-oxo-2,3,3a,4,5,6,6a,7-octahydro-1*H*-pyrrolo[2,3-*d*]carbazole-2,6-dicarboxylate (**17**).



18

Figure S2: Displacement ellipsoid plot of (1*S*,3*R*)-Methyl-2-benzyl-1-(4-(methoxy-2,4-dioxobutyl)-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole-3-carboxylate (**18**)**.**

X-ray Crystal methods for 17 and 18

Single-crystal X-ray diffraction data on compounds **17** and **18** were collected at room temperature (approximately 23 °C) using MoKα radiation and a Bruker APEX 2 CCD area detector. Crystals were prepared for data collection by coating with high viscosity microscope oil (Paratone-N, Hampton Research). The oil-coated crystal was mounted on a Micro Mesh mount (MiteGen Inc.) and transferred immediately to the diffractometer. Corrections were applied for Lorentz, polarization, and absorption effects. All structures were solved by direct methods and refined by

full-matrix least squares on F^2 values using the programs found in the SHELXTL suite (Bruker, SHELXTL v6.10, 2000, Bruker AXS Inc., Madison, WI). Parameters refined included atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms on carbons were included using a riding model [coordinate shifts of C applied to H atoms] with C-H distance set at 0.96 Å.

The crystal of **17**, was monoclinic in space group $P2_1$ with unit cell dimensions a = 10.9243(19) Å, b = 7.6452(13) Å, c = 13.624(2) Å, and β = 92.005(3)°. Data were 97.9% complete to 25.00°θ (approximately 0.82 Å) with an average redundancy of 3.62.

The crystal of **18**, was monoclinic in space group $P2_1$ with unit cell dimensions a = 7.9956(8) Å, b = 12.2939(13) Å, c = 11.3263(11) Å, and β = 91.511(2)°. Data were 100% complete to 28.28°θ (approximately 0.75 Å) with an average redundancy of 4.07.