Supplementary information

2-(2-Nitrophenyl) propyl: A rapidly released photolabile COOH-protecting group for solid-phase peptide synthesis

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1. GENERAL INFOMATION

Room temperature (r.t) refers to ambient temperature. Solid-phase synthesis was carried out manually in polypropylene syringe containing a polyethylene frit. All reagents were commercially available used without further purification. 1, 2-Dichloroethane was dried by 4Å molecular sieves. DMF and NMP were distilled from P_2O_5. Other commercial available solvents were used directly without any treatment.

Visualization of TLC was performed using UV light; Flash column chromatography was performed on silica gel (200-300 mesh). The ^1H NMR and ^{13}C NMR were recorded by JEOL FT-NMR spectrometer at 400 and 150 MHz respectively.

High resolution mass spectrometry (HRMS) measurements were recorded using ESI-TOF by Agilent 1260-G6230A spectrometer.

Analytical high pressure liquid chromatography (HPLC) was carried out on an Agilent instrument (Agilent 1100), automatic injector, photodiode array detector and system controller (Empower login), performed with Venusil ASB C18 column (5 mm, 150 mm×4.6 mm, Bonna-Agela Technologies, Tianjin, China). UV measurements were recorded at 220 nm.

Abbreviations: Boc, *tert*-butyloxy carbonyl; Cbz, benzyloxycarbonyl; DCC,dicyclohexylcarbodiimide; DCM, dichloromethane; DMAP, 4-(*N*, *N*-dimethylamino) pyridine; DMF, *N, N*-dimethylformamide; DMSO, dimethylsulfoxide; ESI-TOF, electrospray ionization-time of flight technique; NMP, *N*-methyl-2-pyrrolidone; EtOAc, ethyl acetate; Et_2O, diethyl ether; Fmoc, 9-fluorenylmethoxycarbonyl; NMM, 4-methylmorpholine; Npp, 2-(2-nitrophenyl) propyl; HOBt, 1-hydroxy benzotriazole; HPLC, high-pressure liquid chromatography; NMR,

nuclear magnetic resonance; PPTS, pyridinium *p*-toluene sulfonate; TIS, tris-isopropylsilane; TBTU,*O*-(Benzotriazol-1-yl)-*N,N,N′,N′*-tetramethyluroniumtetrafluoroborate; *t*Bu, *tert*-butyl; TFA, trifluoroacetic acid.

2. EXPERIMENTAL SECTION

2.1 General procedure for synthesis of Npp-OH (2)

To a solution of 1-ethyl-2-nitrobenzene (15.1 g, 100 mmol) and paraformaldehyde (3.0 g, 100 mmol) in DMSO (60 mL) was added 4 mL of Triton B (40% in MeOH). The solution turned red immediately, and the mixture was heated to 60°C until the reaction was completed. The mixture was concentrated under vacuum, then 200 mL of dilute hydrochloride acid was added, the dark-red oil was separated, and the aqueous layers were extracted with ethyl acetate (3 × 100 mL). The organic portion was washed with saturated brine (3 × 100 mL), combined with the dark-red oil, dried over $MgSO_4$. The solvent was removed under vacuum, and the crude product was purified by flash column chromatography (hexane: EtOAc = 3:1) to give 16.12 g (89 mmol, 89.0%) of 2- (2-nitrophenyl) propanol as a dark-red oil.

2.2 General esterification procedure

A solution of the Fmoc-L-amino acid or other carboxylic acid (10 mmol), DMAP (1 mmol), and the Npp-OH (10 mmol) in 50 mL of DCM was cooled with stirring in an ice bath. DCC (11 mmol) was added in small portions, and the reaction mixture was stirred at 0°C for 30 min and then at r.t for 2 h. The solution was filtered, the filtrate was concentrated to dryness under vacuum, and the residue was purified by flash column chromatography.

2.3 General TFA deprotection procedure

The tBu-protected Npp-ester (5 mmol) was dissolved in 80% TFA in DCM (20 mL) and stirred until the reaction was completed (30-60 min). The volatile components were removed under reduced pressure. The residue was purified by flash column chromatography to give the product as yellow oil or amorphous yellow solid.

2.4 General procedure for anchoring threonine derivatives

To a solution of Fmoc-L-Thr (OH)-COONpp (4.65 g, 9.233 mmol, 3.81 equiv.) in dry 1,2-dichloroethane (20 mL) was added 2.002g of DHP resin (1.21 mmol/g, 2.002 g, 2.42 mmol, 1 equiv.), PPTS (1.21g, 4.84 mmol,2 equiv.) and 4Å molecular sieves. The solution was heated at 80 °C for 20 h, and then the resin was filtered. The resin was then washed with DMF (3 × 1 min), CH_2Cl_2 (3 × 1 min), DMF (3 × 1 min) and MeOH (3 × 1 min). The mass of the resulting dry resin **(4)** was 2.760 g (62% loading). The loading was calculated to be 1.51 mmol.

2.5 General procedures for solid-phase reactions

The peptide was synthesized by using of 1.002 g of resin **(4)** (0.55 mmol) as starting material as followed (a): Fmoc deprotection: 20% piperidine in DMF (10 mL) 15 min; washings: DMF (3 × 1 min), CH_2Cl_2 (3 × 1 min), and DMF (3 × 1 min); (b): Peptide coupling conditions: HOBt (3 equiv.), TBTU (3 equiv.), Fmoc-amino acid (3 equiv.) and NMM (4 equiv.) in DMF (15 mL), 2 h; washings: DMF (3 × 1 min); the coupling reaction was monitored by the Kaiser test.

2.6 Removal of the Npp group

After the last Leu was loaded and the Fmoc group was removed, the resin-bound linear peptide**(5)** was transferred to a quartz bottle and suspended in 50 mL of DMF-MeOH (2:1,*v/v*).The Argon gas was bubbled for 10min to remove the oxygen dissolved in the solvent. The mixture was then irradiated with the high pressure Hg lamp (λ_{max}=365 nm, 250 W，power density=2.95 W/cm^2, irradiation area was calculated to be 4.9 cm^2) with constant Argon bubbling. A reflux condenser was necessary because of the heat effect during the UV irradiation. After 15min, the lamp was tuned off and the dark yellow solvent was replaced by fresh solvent mixtures of DMF-MeOH (2:1, *v/v*, 50 mL), followed continuous irradiation until the solvent was not getting yellow any more. This procedure usually needs 30min in total. Finally the resin **(6)** was collected by filtration, washed with DMF (3 × 1 min), CH_2Cl_2 (3 × 1 min) and DMF (3 × 1 min). A microcleavage procedure was performed after irradiating for 15min and 30min respectively as described in **2.7**.

2.7 General procedure for Microcleavage

Dry resin (5 mg) was treated with TFA/TIS/H_2O (95:2.5:2.5) for 1 h at r.t. The cleavage mixture was filtered and evaporated under vacuum, precipitated with Et_2O, centrifuged to give the pellet, which was dissolved in eluent system for HPLC analysis at 220 nm. (Figure 1)

2.8 Preparation of phakellistatin 13

The resin-bound linear peptide **(6)** was transferred into a reaction vessel and suspended in 15mL NMP, then TBTU (3 equiv.), HOBt (3 equiv.) and NMM (4 equiv.) were added sequentially, the vessel was capped and shaken at r.t until the Kaiser test was negative. Then the solvent was removed by filtration, and the beads were washed sequentially by DMF (3 × 1 min) and MeOH (3 × 1 min).

A heterogeneous mixtures of TFA/H_2O/TIS (95:2.5:2.5 v/v/v) (10mL) were prepared and added to the reaction vessel. The vessel was capped, agitated for 60 min, and then filtered into 100 mL recovery flask. The beads were then sequentially washed and filtered into the flask with CH_2Cl_2 (10 mL) and CH_3OH (5 mL×2). The resulting solution was concentrated in vacuum, after the iced ether was added, a white precipitate appeared soon, and the mixture was kept at 0℃ for 30min. The precipitate was collected by centrifugation to give the crude product (315 mg) as a light yellow powder. The crude product was purified by flash column chromatography (CH_2Cl_2: MeOH=9:1, Rf: 0.82) and lyophilized to give the pure cyclic peptide (7) (106 mg, 33.7%) as a white fluffy solid. The cyclic peptide (7) was analysed by HPLC at 220 nm with 70% CH_3OH-H_2O (0.1% TFA) as eluent system (Figure 2). The structure was identified by HRMS (ESI-TOF): calculated for $C_{42}H_{54}N_8O_8$ $[M+Na]^+$: 821.3957, Found $[M+Na]^+$: 821.3962.

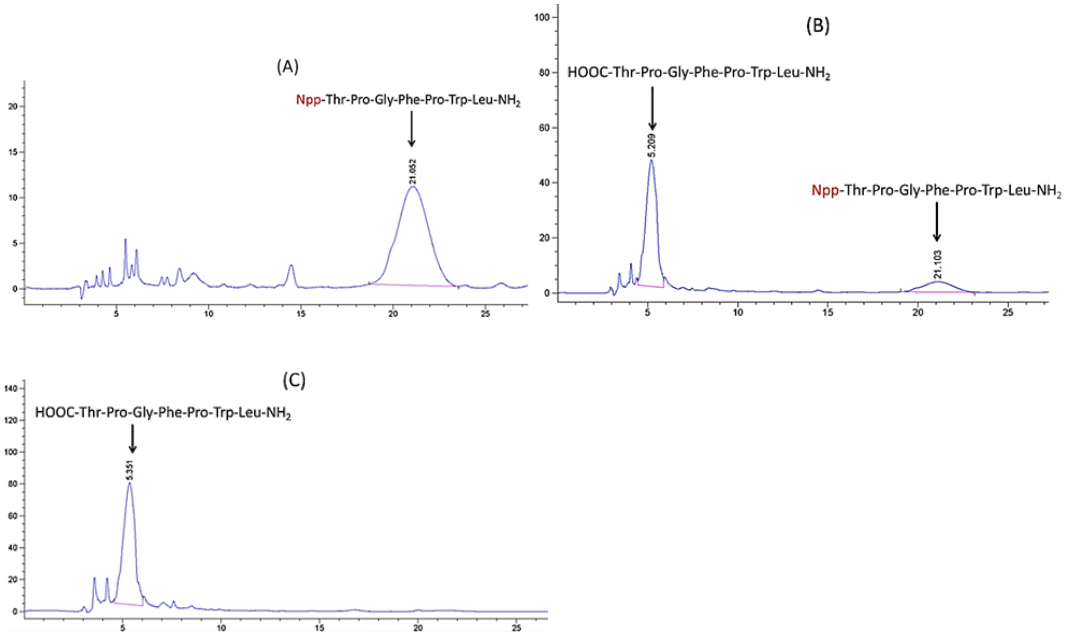


Figure 1.HPLC chromatograms before and after irradiation at different times with 40% CH_3CN-H_2O (0.1%TFA) as eluent system. (A): Before UV irradiation. (B): 15min after UV irradiation. (C): 30min after UV irradiation.

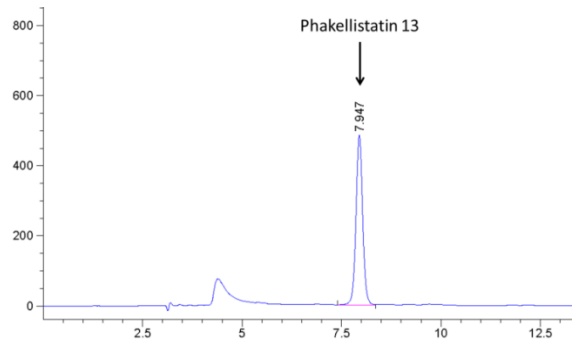
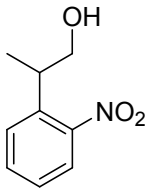


Figure 2.HPLC chromatograms of phakellistatin 13 with 70% CH_3OH-H_2O (0.1%TFA) as eluent system.

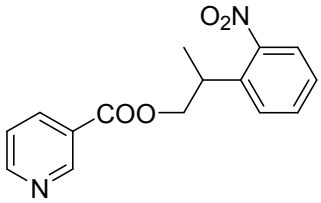
3. CHARACTERIZATION DATA OF THE PRODUCTS



^{1}H NMR (400 MHz, DMSO-d_6): δ 7.77 (dd, 1H, Ar-H), δ 7.63 (m, 2H, Ar-H), δ 7.43 (m, 1H), δ 4.77 (t, 1H, OH), δ 3.51 (m, 2H, CH_2), δ 3.19 (m, 1H, CH), δ 1.22 (d, 3H, CH_3)

^{13}C NMR (150 MHz, DMSO-d_6): δ 150.52, 138.11, 132.58, 128.48, 127.16, 123.37, 65.87, 36.22, 17.65.

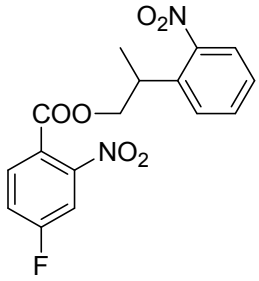
HRMS (ESI-TOF) calculated for $C_9H_{11}NO_3$ $[M+Na]^+$:204.0631, Found: $[M+Na]^+$: 204.0627.



^{1}H NMR (400 MHz, DMSO-d_6): δ 8.9 (d, 1H, Py-H), δ 8.80-8.79 (dd, 1H, Py-H), δ 8.18-8.15 (m, 1H, Py-H), δ 7.85-7.80 (m, 2H, Ar-H) δ 7.71 (dd, 1H, Ar-H), δ 7.55 (m, 1H, Py-H), δ 7.49 (m, 1H, Ar-H), δ 4.56-4.45 (m, 2H, CH_2), δ 3.64 (m, 1H, CH), δ 1.39 (d, 3H, CH_3)

^{13}C NMR (150 MHz, DMSO-d_6): δ 164.36,153.74,150.23,149.81,136.70,136.37,132.94,128.57,127.94,125.35,123.90,123.60,68.85, 32.79, 17.53.

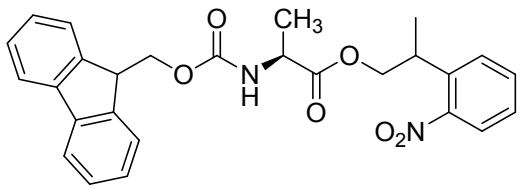
HRMS (ESI-TOF) calculated for $C_{15}H_{14}N_2O_4$ $[M+1]^+$:287.1026, Found: $[M+1]^+$:287.1028.



^{1}H NMR (400 MHz, DMSO-d_6): δ 8.45 (dd, 1H, Ar-H), δ 8.20 (m, 1H, Ar), δ 7.85-7.65 (m, 4H, Ar), δ 7.50 (m, 1H, Ar), δ 4.52 (m, 2H, CH_2), δ 3.64 (m, 1H, CH), δ 1.37 (d, 3H, CH_3).

^{13}C NMR (150 MHz, DMSO-d_6): δ 162.97, 158.76, 156.09, 150.22, 136.70, 136.58, 132.96, 128.57, 128.00, 127.10, 126.44, 123.65, 119.59, 69.31, 32.81, 17.57.

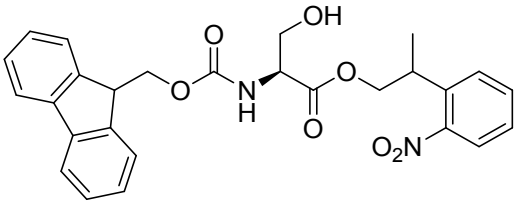
HRMS (ESI-TOF) calculated for $C_{16}H_{13}FN_2O_6$ $[M+Na]^+$:371.0650, Found: $[M+Na]^+$:371.0651.



^{1}H NMR (400 MHz, DMSO-d_6): δ 7.89 (d, 2H, Ar), δ 7.82 (d, 1H, NH), δ 7.76 (m, 1H, Ar), δ 7.66 (m, 4H, Ar), δ 7.48-7.40 (m, 3H, Ar), δ 7.33 (t, 2H, Ar), δ 4.32 (m, 1H, CH), δ 4.27 (d, 2H, CH_2), δ 4.22-4.15 (m, 2H, CH_2), δ 3.98 (m, 1H, CH), δ 3.46 (m, 1H, CH), δ 1.27 (dd, 3H, CH_3), δ 1.11 (dd, 3H, CH_3).

^{13}C NMR (150 MHz, DMSO-d_6): δ 173.13, 156.31, 150.60, 144.30, 141.27, 136.92, 133.45, 129.08, 128.37, 128.17, 127.61, 125.74, 124.22, 120.65, 68.21, 66.15, 49.90, 47.10, 33.43, 18.06, 17.18.

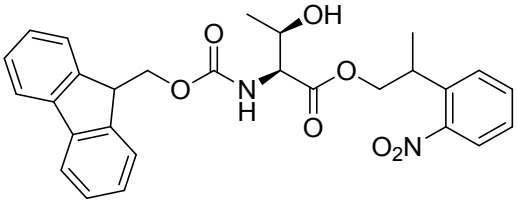
HRMS (ESI-TOF) calculated for $C_{27}H_{26}N_2O_6$ $[M+1]^+$:475.1864, $[M+Na]^+$:497.1863, Found:$[M+1]^+$:475.1861, $[M+Na]^+$:497.1862.



^{1}H NMR (400 MHz, DMSO-d_6): δ 7.89 (d, 2H, Ar), δ 7.83 (d, 1H, NH), δ 7.74-7.62 (m, 5H, Ar), δ 7.49-7.40 (m, 3H, Ar), δ 7.33 (t, 2H, Ar), δ 4.91 (m, 1H, OH), δ 4.31-4.19 (m, 5H, CH_3, CH_2), δ 4.07 (m, 1H, CH), δ 3.55 (m, 2H, CH_2), δ 3.46 (m, 1H, CH), δ 1.27 (d, 3H, CH_3).

^{13}C NMR (150 MHz, DMSO-d_6): δ 170.56, 156.11, 149.96, 143.84, 140.79, 136.42, 132.97, 128.74, 127.89, 127.69, 127.12, 125.30, 123.83, 120.16, 68.07, 65.83, 61.13, 56.78, 46.61, 32.89, 17.67.

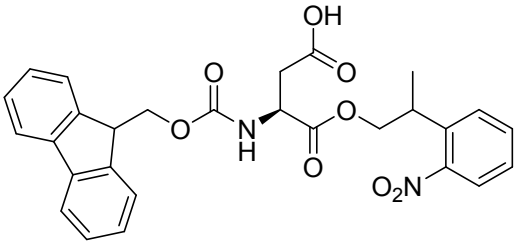
HRMS (ESI-TOF) calculated for $C_{27}H_{26}N_2O_7$ $[M+1]^+$:491.1813, $[M+Na]^+$:513.1632, Found:$[M+1]^+$:491.1815, $[M+Na]^+$: 513.1635.



^{1}H NMR (400 MHz, DMSO-d_6): δ 7.90 (d, 2H, Ar), δ 7.83 (m, 1H, NH), δ 7.74 (d, 2H, Ar), δ 7.70-7.64 (m, 2H, Ar), δ 7.49-7.40 (m, 3H, Ar), δ 7.33 (m, 3H, Ar), δ 4.76 (m, 1H, OH), δ 4.32-4.21 (m, 5H, CH, CH_2, CH_2), δ 4.04-3.97 (m, 2H, CH, CH), δ 3.47 (m, 1H, CH), δ 1.29 (d, 3H, CH_3), δ 1.02 (dd, 3H, CH_3).

^{13}C NMR (150 MHz, DMSO-d_6): δ 170.68, 156.36, 149.97, 143.75, 140.72, 136.37, 132.96, 128.67,127.87,127.68,127.08,125.31,123.80,120.14,68.18,66.35,65.85,60.21,46.59,32.79,19.97,17.55.

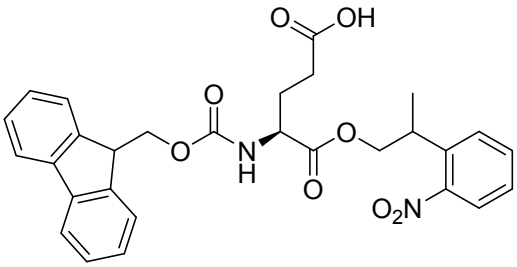
HRMS (ESI-TOF) calculated for $C_{28}H_{28}N_2O_7$ $[M+1]^+$:505.1969, $[M+Na]^+$:527.1789, Found:$[M+1]^+$:505.1971, $[M+Na]^+$:527.1789.



^{1}H NMR (400 MHz, DMSO-d_6): δ 12.49(s, 1H, COOH), δ 7.89 (d, 2H, Ar), δ 7.82 (d, 1H, NH), δ 7.76 (m, 1H, Ar), δ 7.71-7.61 (m, 4H, Ar), δ 7.48-7.40 (m, 3H, Ar), δ 7.33 (t, 2H, Ar), δ 4.33 (m, 1H, CH), δ 4.26-4.18 (m, 5H, CH, CH_2, CH_2), δ 3.45 (m, 1H, CH), δ 2.62-2.51 (m, 2H, CH_2), δ 1.25 (dd, 3H, CH_3).

^{13}C NMR (150 MHz, DMSO-d_6): δ 171.42, 171.01, 155.85, 149.91, 143.79, 140.76, 136.34, 132.95,128.72, 127.90, 127.69, 127.12, 125.25, 123.81, 120.16, 68.31, 65.83, 50.50, 46.58, 35.65, 32.87, 38.81, 17.63.

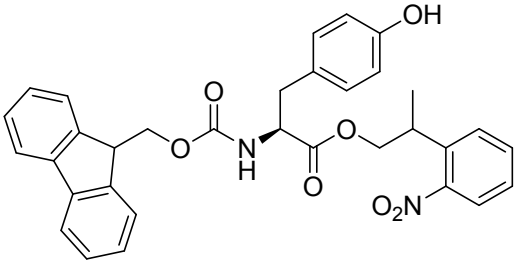
HRMS (ESI-TOF) calculated for $C_{28}H_{26}N_2O_8$ $[M+1]^+$:519.1762, $[M+Na]^+$:541.1581, Found:$[M+1]^+$:519.1763, $[M+Na]^+$:541.1584.



^{1}H NMR (400 MHz, DMSO-d_6): δ 12.41 (s, 1H, COOH), δ 7.90 (d, 2H, Ar), δ 7.83-7.77 (m, 2H, NH, Ar), δ 7.72-7.61 (m, 4H, Ar), δ 7.47-7.40 (m, 3H, Ar), δ 7.32(t, 2H, Ar), δ 4.33-4.18 (m, 5H, CH, CH_2, CH_2), δ 4.01 (m, 1H, CH), δ 3.47 (m, 1H, CH), δ 2.26-2.16 (m, 2H, CH_2), δ 1.88-1.65 (m, 2H, CH_2), δ 1.27 (dd, 3H, CH_3).

^{13}C NMR (150 MHz, DMSO-d_6): δ 173.59, 171.84, 156.07, 149.93, 143.77, 140.72, 136.30, 132.94, 128.70, 127.87, 127.66, 127.08, 125.23, 123.82, 120.14, 68.03, 65.70, 53.04, 46.57, 32.88, 29.87, 25.79, 17.65.

HRMS (ESI-TOF) calculated for $C_{29}H_{28}N_2O_8$ $[M+1]^+$: 533.1918, Found: $[M+1]^+$: 533.1917.

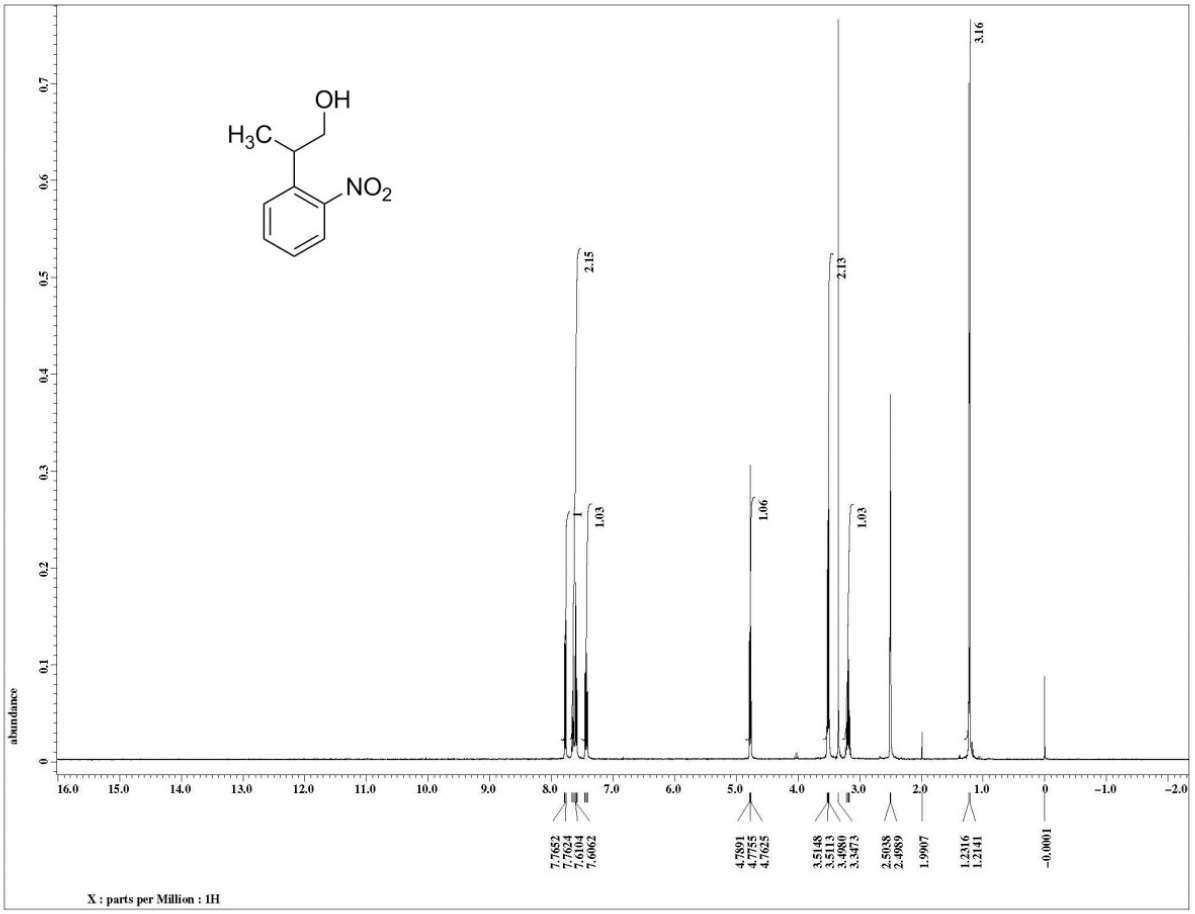


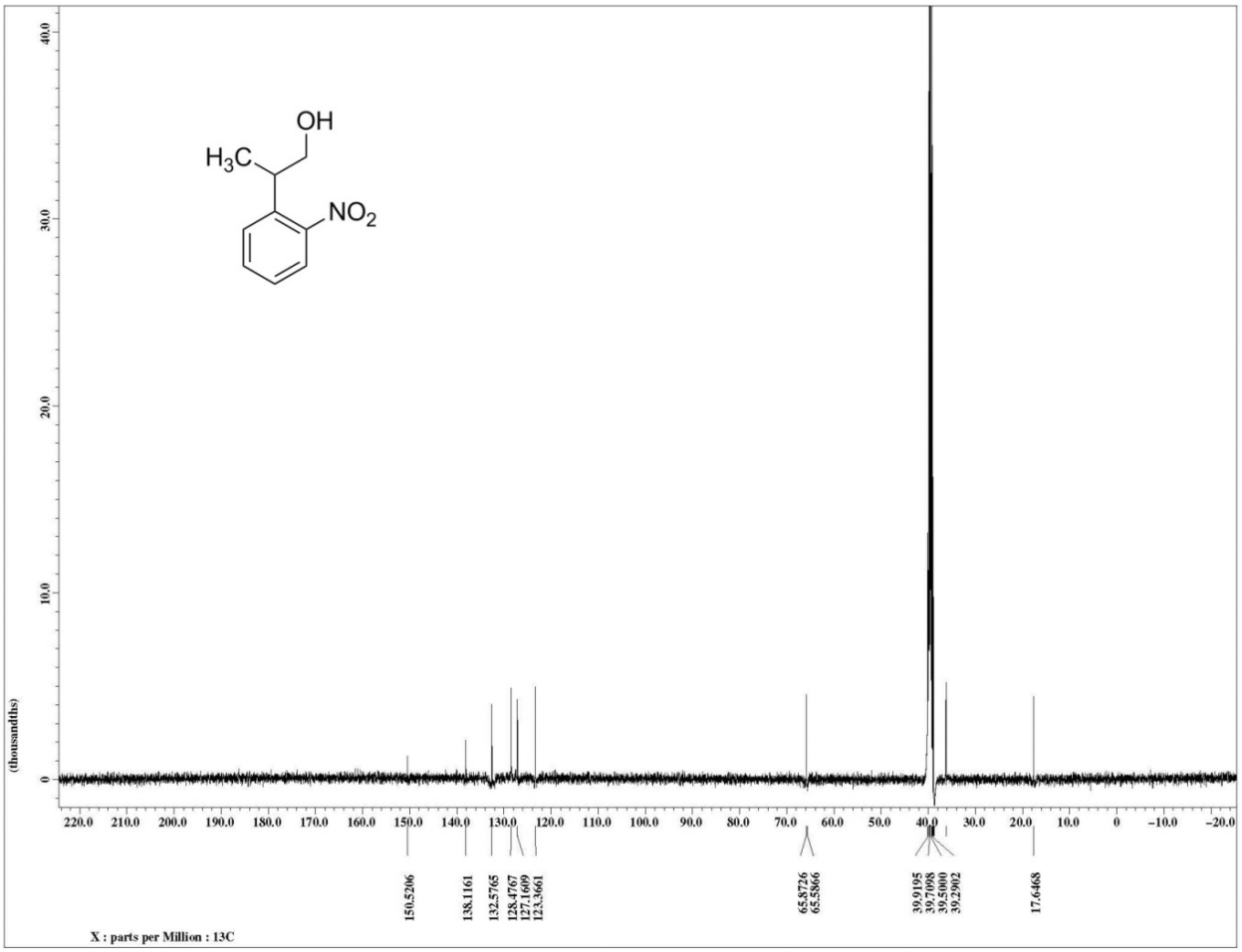
^{1}H NMR (400 MHz, DMSO-d_6): δ 9.25 (s, 1H, OH in phenol-), δ 7.88 (d, 2H, Ar), δ 7.85-7.78 (m, 2H, Ar, NH), δ 7.70-7.76 (m, 4H, Ar), δ 7.49-7.26 (m, 5H, Ar), δ 7.00-6.93 (m, 2H, phenol-Ar), δ 6.66-6.63 (m, 2H, phenol-Ar), δ 4.30-4.14 (m, 5H, CH, CH_2, CH_2), δ 4.12-4.05 (m, 1H, CH), δ 3.48 (m, 1H, OH), δ 2.78-2.55 (m, 2H, CH_2), δ 1.26 (dd, 3H, CH_3).

^{13}C NMR (150 MHz, DMSO-d_6): δ 170.81,156.07, 150.15, 143.75, 140.74, 136.39, 132.96, 130.02, 128.72, 128.61, 127.89, 127.68, 127.52, 127.45, 127.10, 125.31, 123.82, 123.73, 120.14, 115.09, 68.28, 65.74, 55.98, 46.59, 32.77, 17.53.

HRMS (ESI-TOF) calculated for $C_{33}H_{30}N_2O_7$[M+1]$^+$:567.2126, $[M+Na]^+$:589.1945, Found:$[M+1]^+$:567.2126, $[M+Na]^+$:589.1949.

4. COPIES OF ^{1}H- &^{13}C-NMR SPECTRUM OF THE PRODUCTS:




OH
H3C
NO2
(thousandths)
40.0
30.0
20.0
10.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0
150.5206
138.1161
132.5765
128.4767
127.1609
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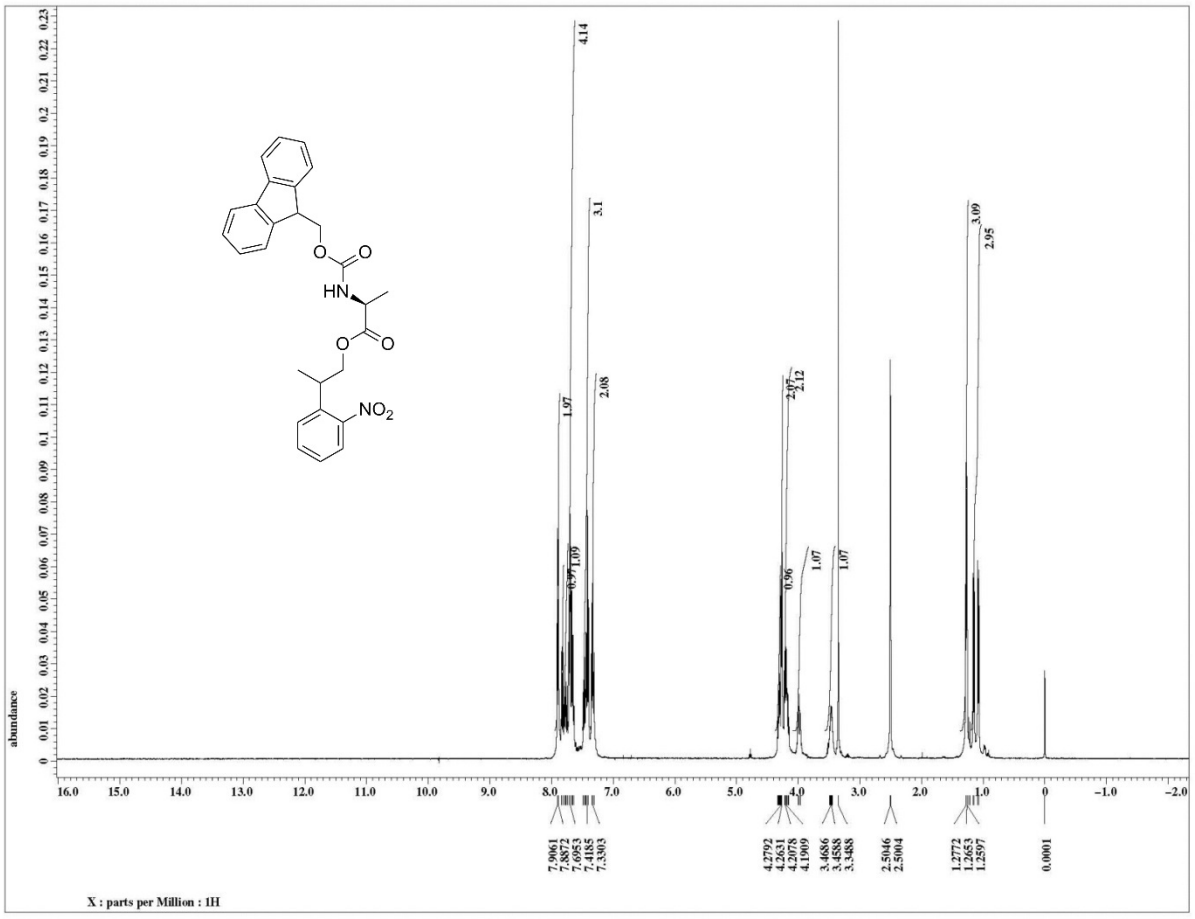
39.2902
17.6468
X : parts per Million : 13C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3.09
2.95
2.08
2.07
2.12
1.97
1.09
1.07
1.07
0.96
O
HN
O
O
O
NO2
7.9061
7.8872
7.6953
7.4185
7.3303
4.2792
4.2631
4.2078
4.1969
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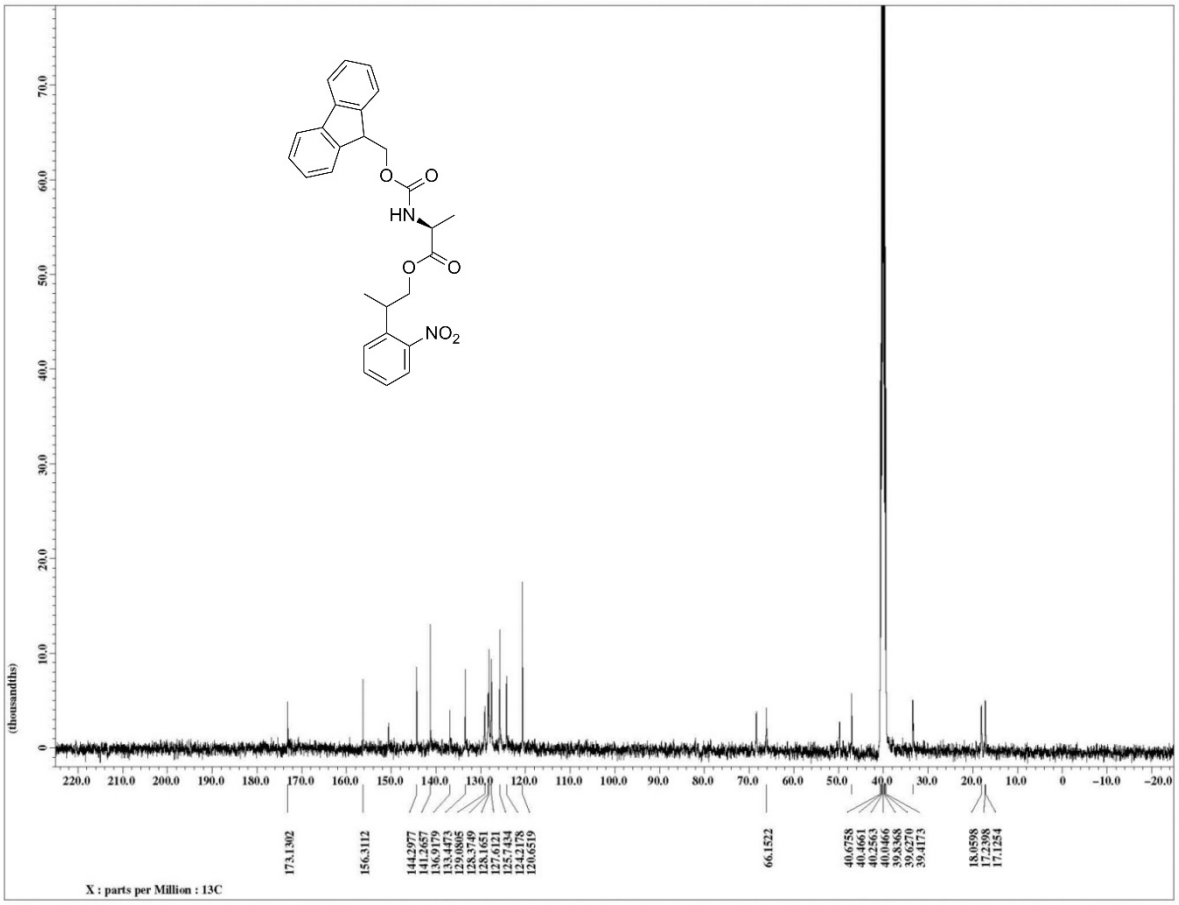
0.0001
X : parts per Million : 1H


(thousandths)
X : parts per Million : 13C
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128.1651
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124.2178
120.0519
66.1522
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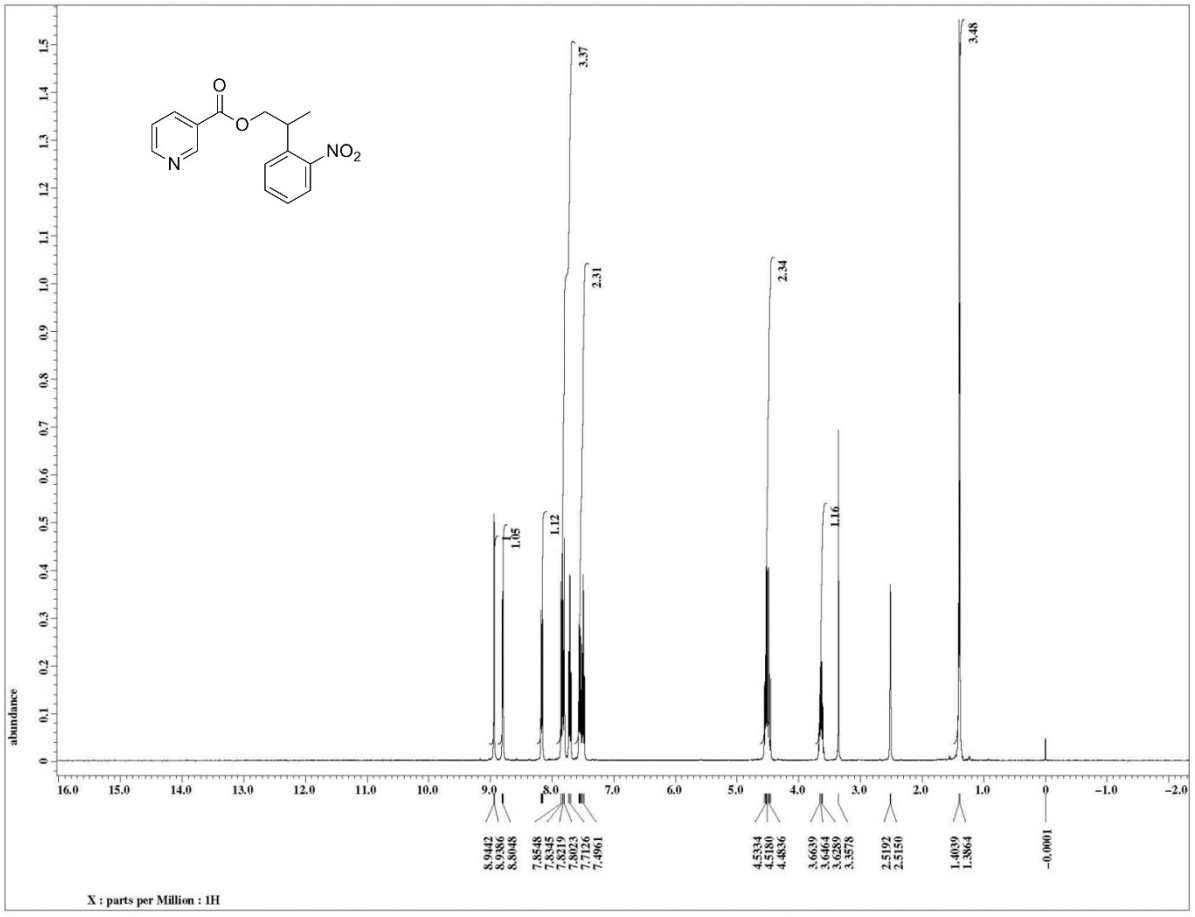
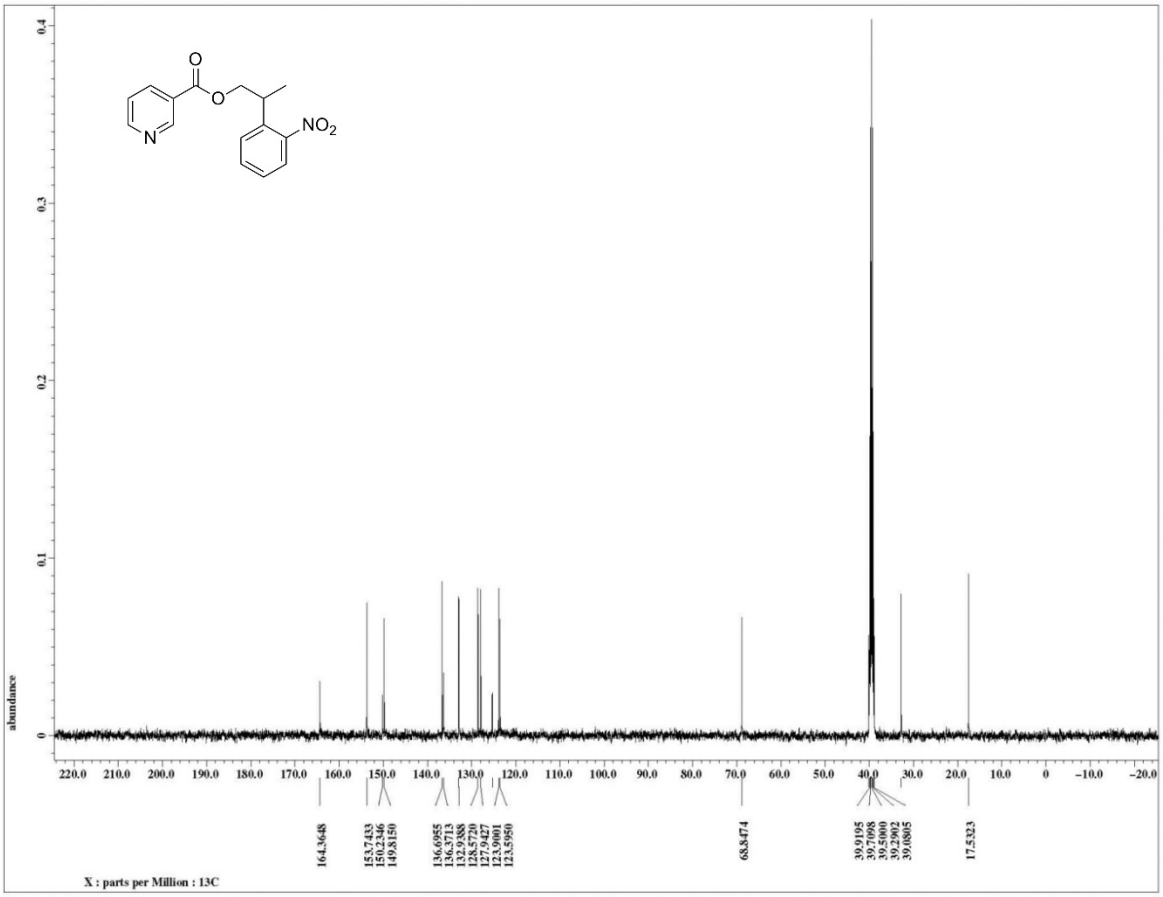
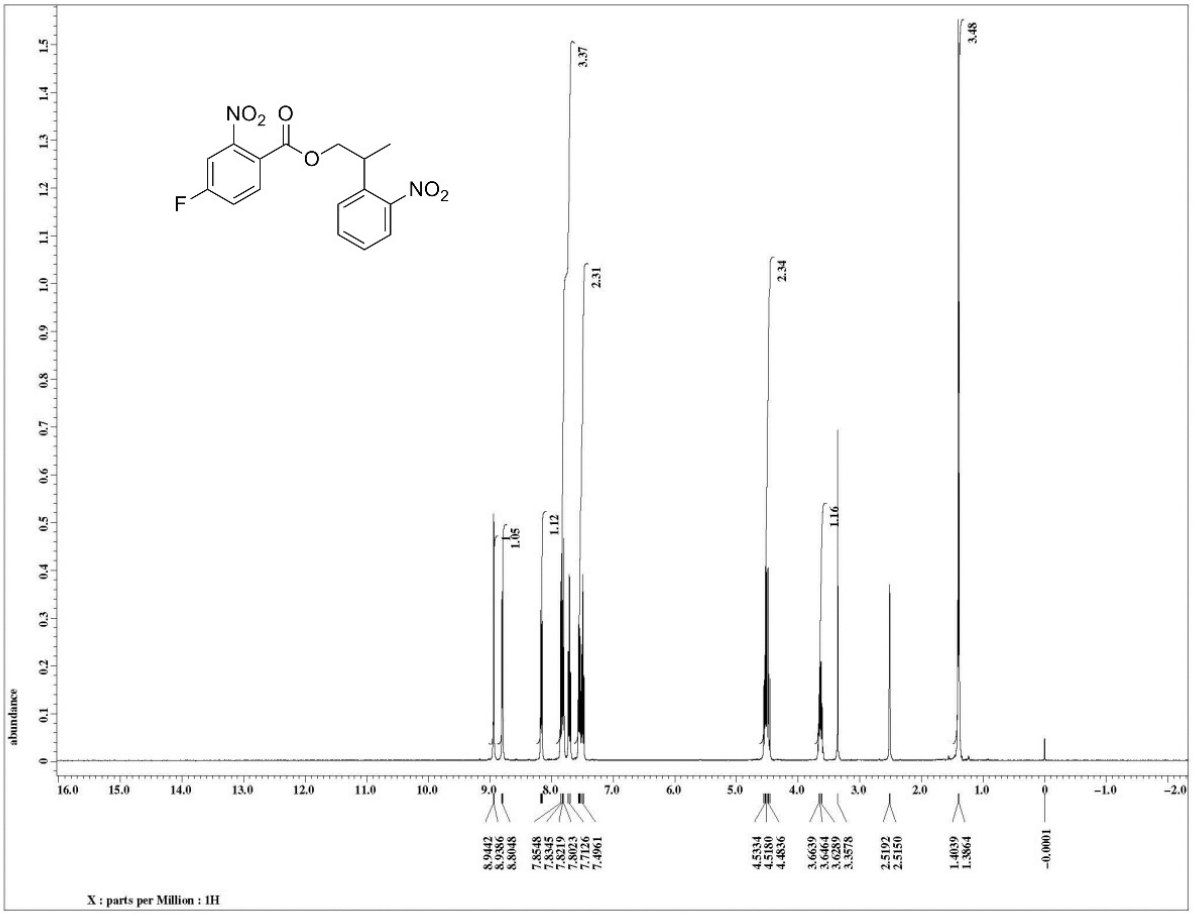
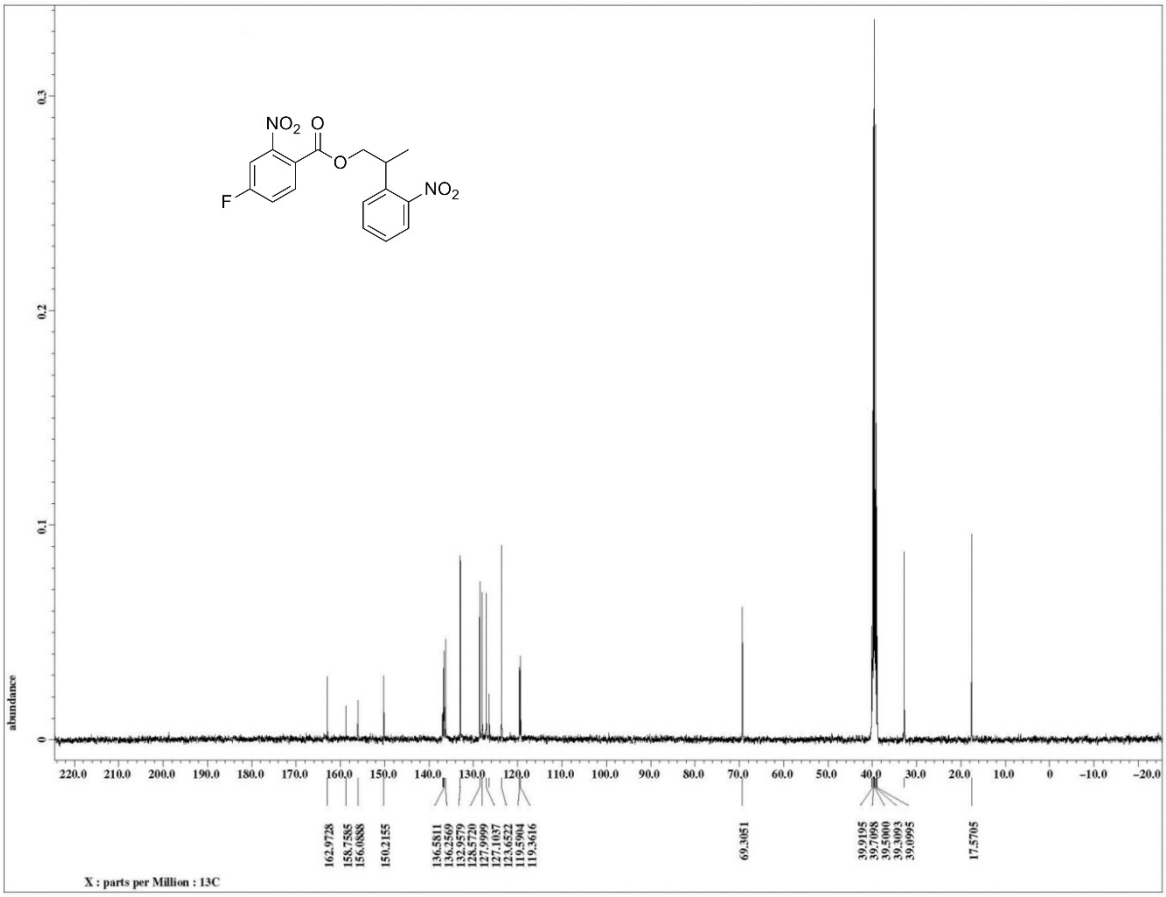
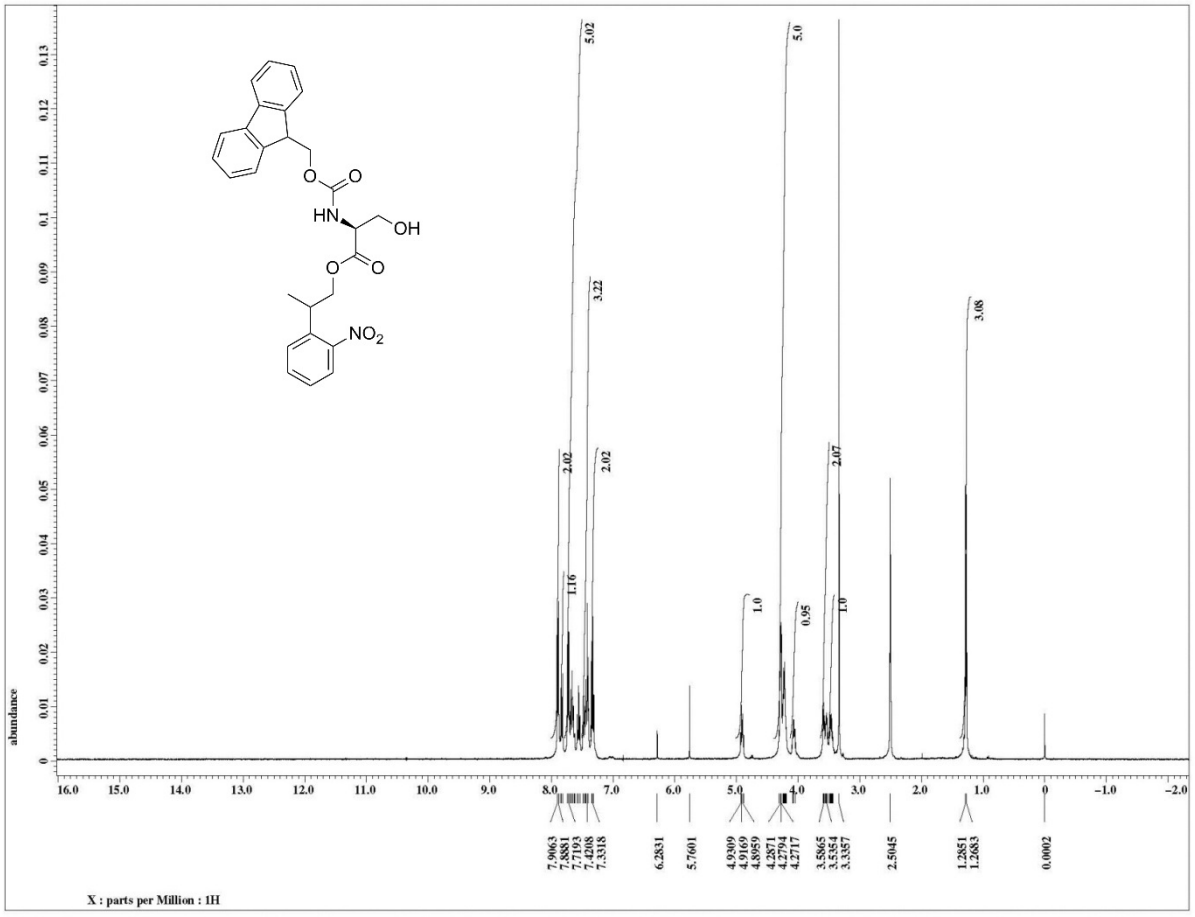
40.0466
39.8368
39.6270
39.4173
18.0598
17.2398
17.1254

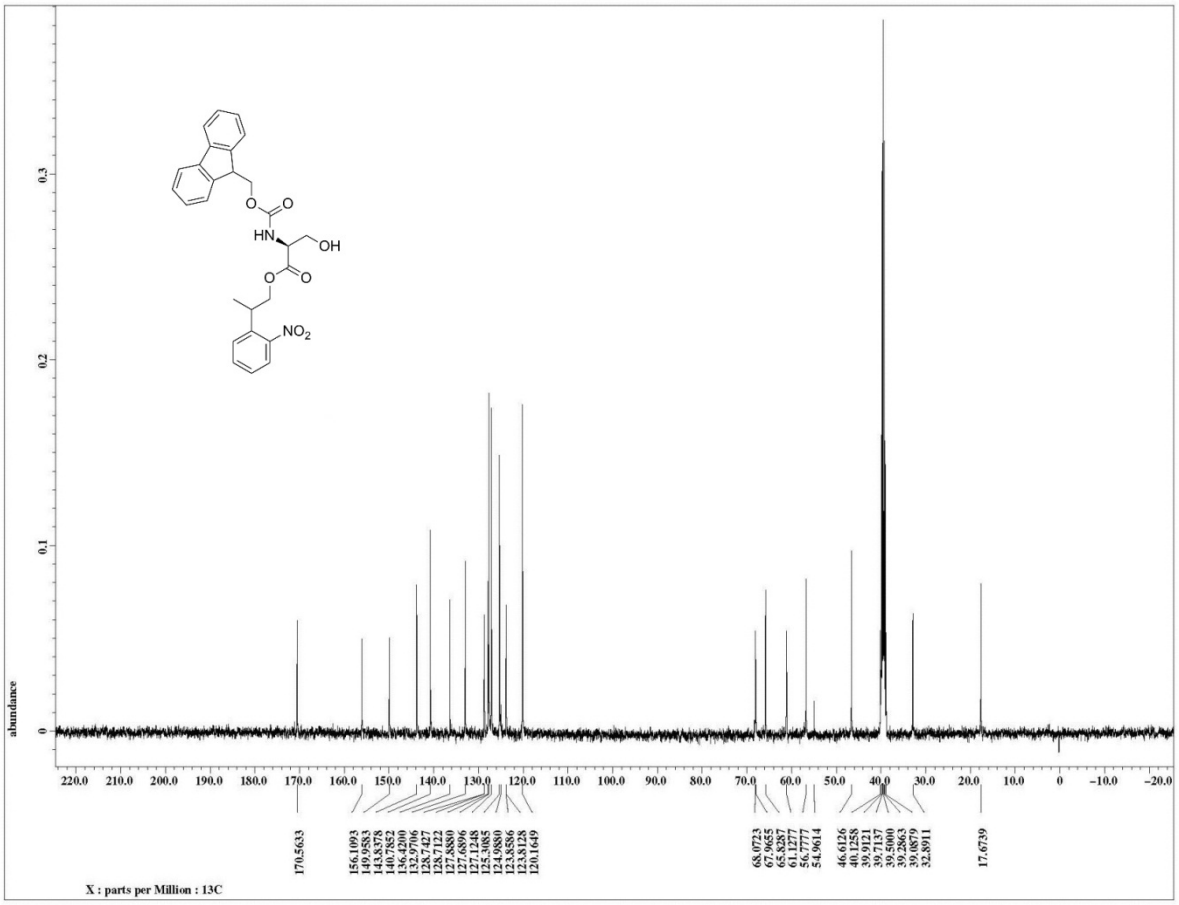

O
O
N
NO2
3.48
3.37
2.34
2.31
1.16
1.12
1.05
abundance
16.0 15.0 14.0 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 −1.0 −2.0
8.9442
8.9386
8.8048
7.8548
7.8345
7.8213
7.8023
7.7126
7.4961
4.5334
4.5180
4.4836
3.6639
3.6464
3.6289
3.3578
2.5192
2.5150
1.4039
1.3864
−0.0001
X : parts per Million : 1H

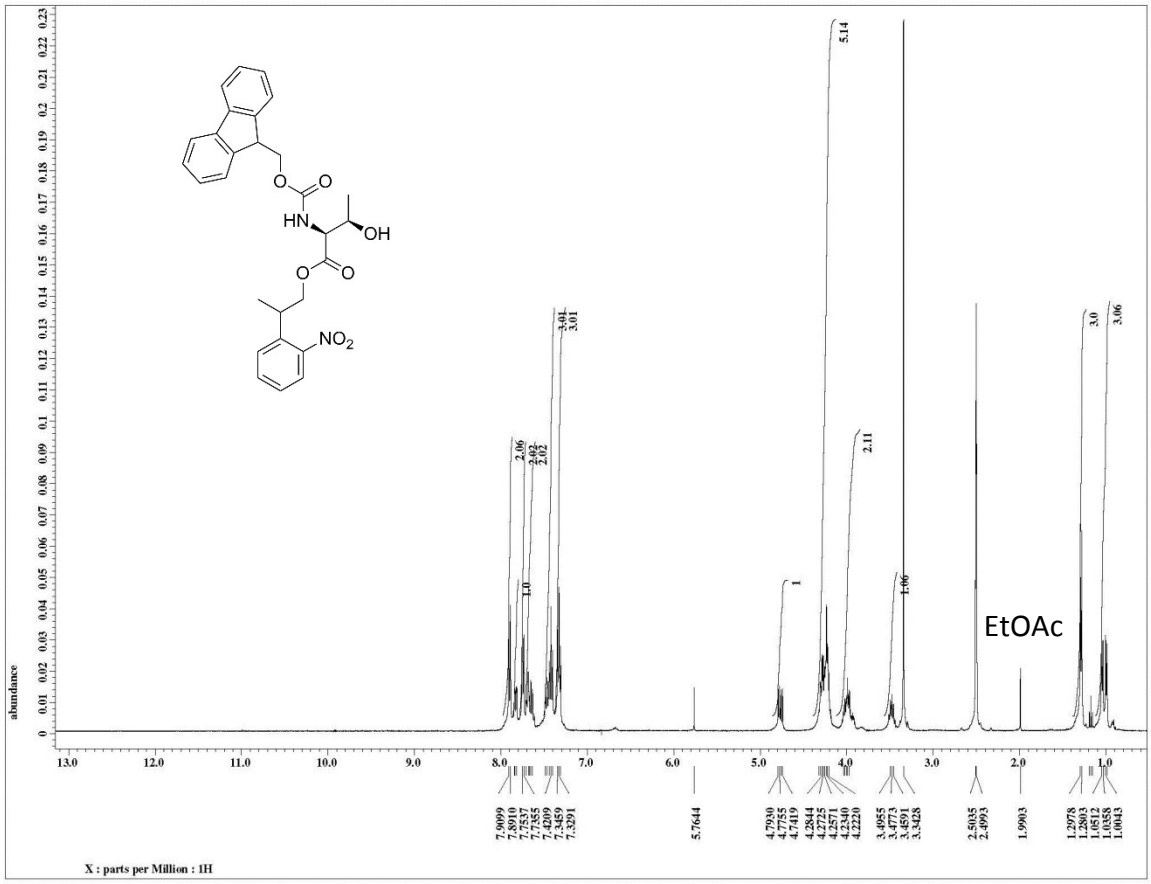

O
O
N
NO2
abundance
0.4
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0
164.3648
153.7433
150.2346
149.8150
136.6955
134.7513
132.9388
128.5720
127.9427
123.9001
123.5950
68.8474
39.9195
39.7098
39.5000
39.2902
39.0805
17.5323
X : parts per Million : 13C

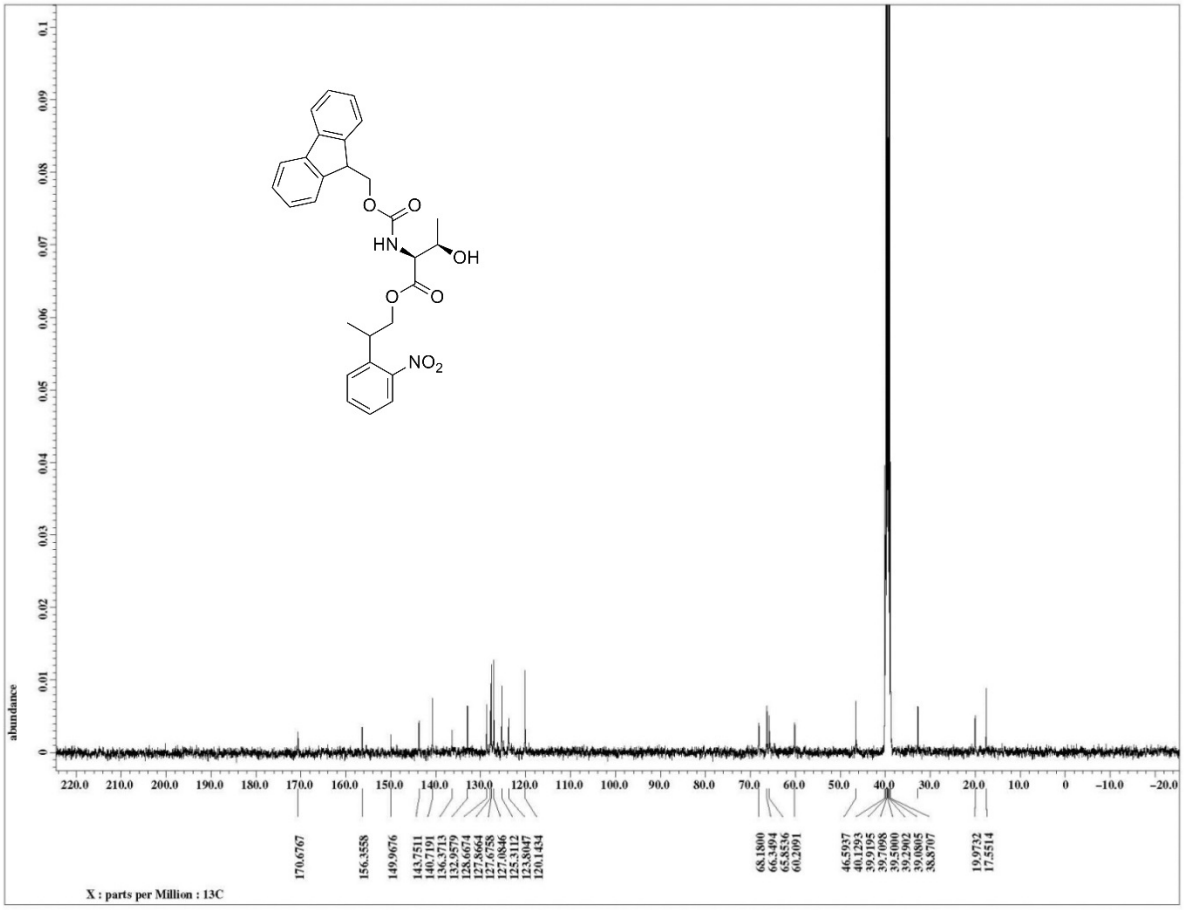

NO2
O
O
F
NO2
abundance
3.48
3.37
2.34
2.31
1.16
1.12
1.05
16.0
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
−1.0
−2.0
8.9442
8.9386
8.8048
7.8548
7.8345
7.8319
7.8023
7.7126
7.4961
4.5334
4.5180
4.4836
3.6639
3.6464
3.6289
3.3578
2.5192
2.5150
1.4039
1.3864
−0.0001
X : parts per Million : 1H

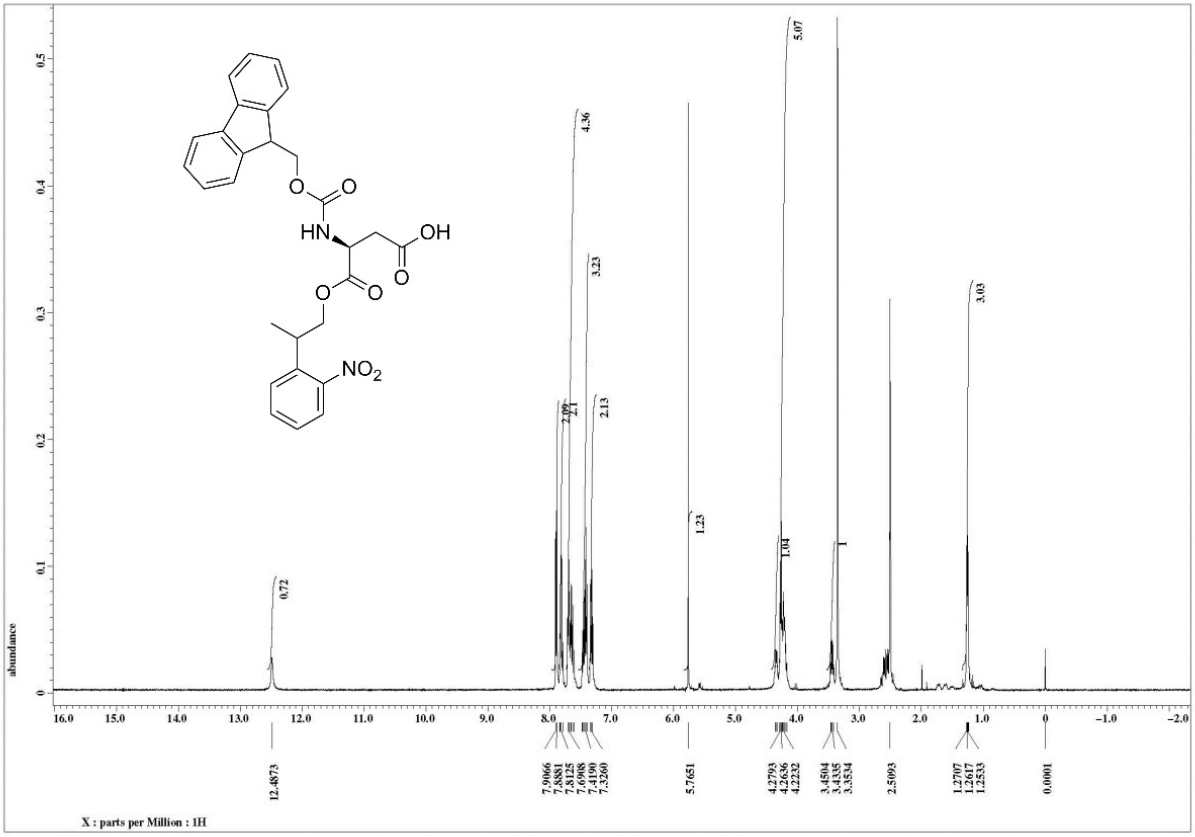

NO2
O
O
F
NO2
abundance
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
162.9728
158.7585
156.0888
150.2155
136.5811
136.2569
132.9579
128.5720
127.9999
127.1037
123.6522
119.5904
119.3616
69.3051
39.9195
39.7098
39.5000
39.3093
39.0995
17.5705
X : parts per Million : 13C

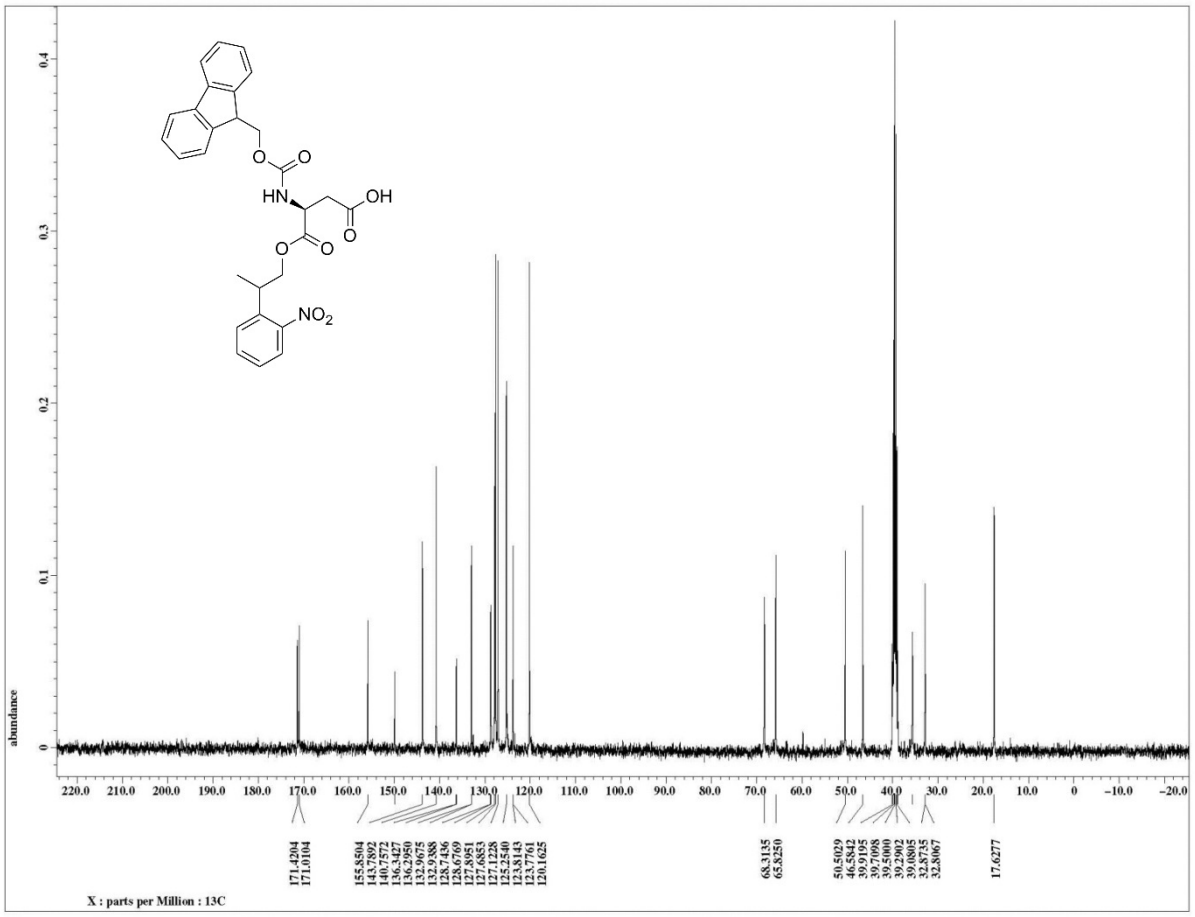

abundance
X : parts per Million : 1H
5.02
5.0
3.22
3.08
2.02
2.02
2.07
1.16
1.0
0.95
1.0
O
O
HN
OH
O
O
NO2
7.9063
7.8881
7.7193
7.7008
7.3318
6.2831
5.7601
4.9309
4.9169
4.8985
4.2871
4.2794
4.2717
3.5865
3.5354
3.3357
2.5045
1.2851
1.2683
0.0002

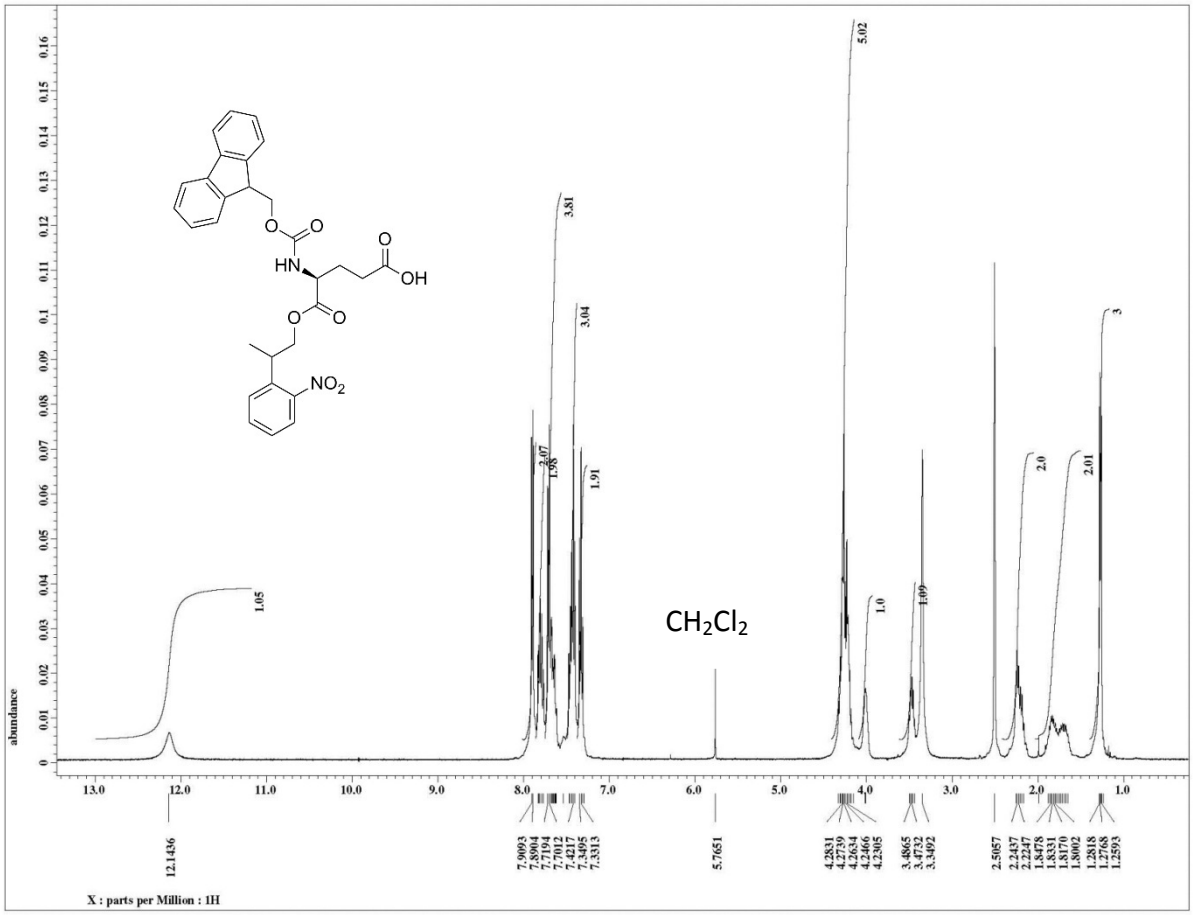

abundance
0
0.1
0.2
0.3
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
170.5633
156.1093
149.9583
143.5778
140.7852
136.4200
132.9706
128.7427
128.7122
127.8880
127.6696
127.1248
125.3085
124.9880
123.8586
123.8128
120.1649
68.0723
67.9655
65.8287
61.1277
56.7777
54.9614
46.6126
40.1255
39.9121
39.7137
39.5000
39.2863
39.0879
32.8911
17.6739
X : parts per Million : 13C

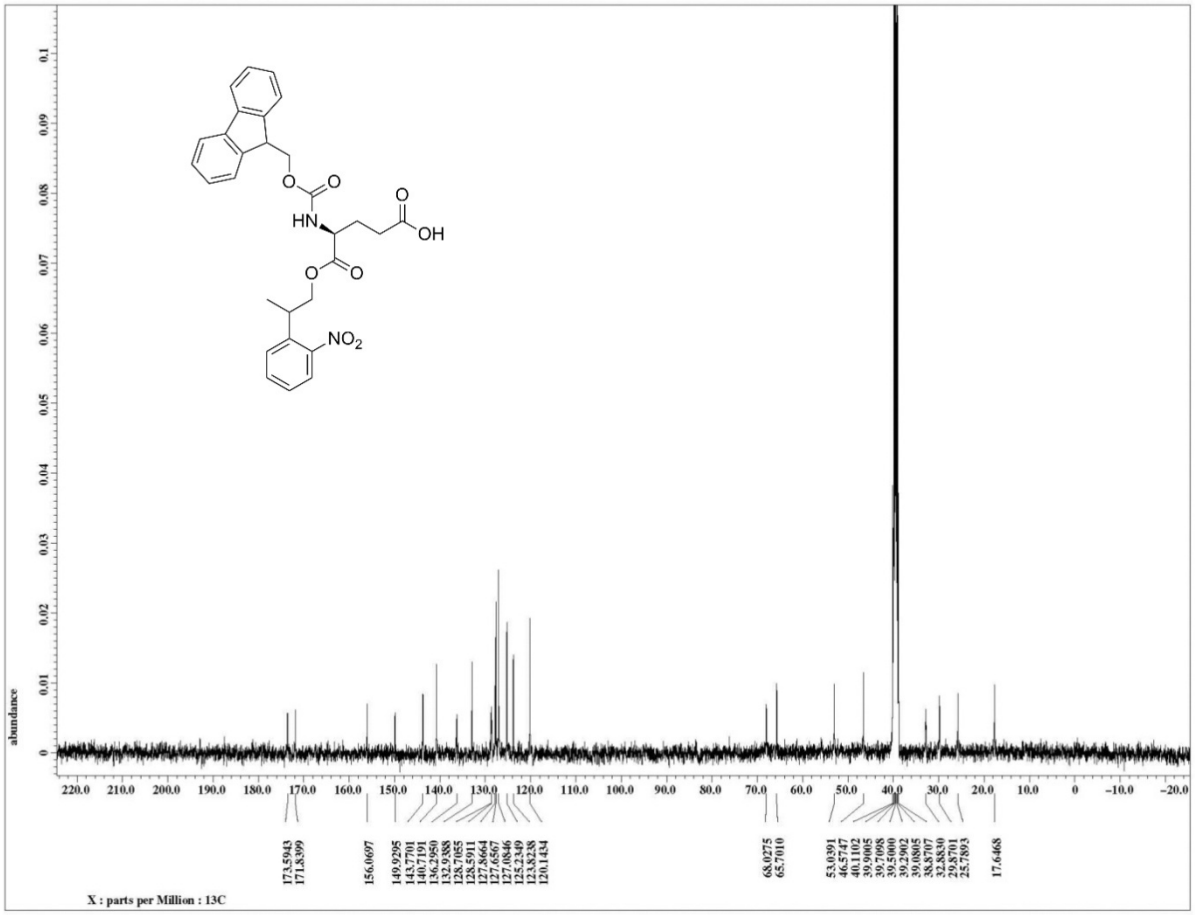

abundance
X : parts per Million : 1H
EtOAc
5.14
2.11
3.01
3.06
2.06
2.02
1.06
1.0
1
3.0
7.9099
7.8910
7.7537
7.7355
7.4209
7.3459
7.3291
5.7644
4.7930
4.7755
4.7419
4.2844
4.2725
4.2571
4.2340
4.2220
3.4955
3.4773
3.4591
3.3428
2.5035
2.4993
1.9903
1.2978
1.2803
1.0457
1.0358
1.0043

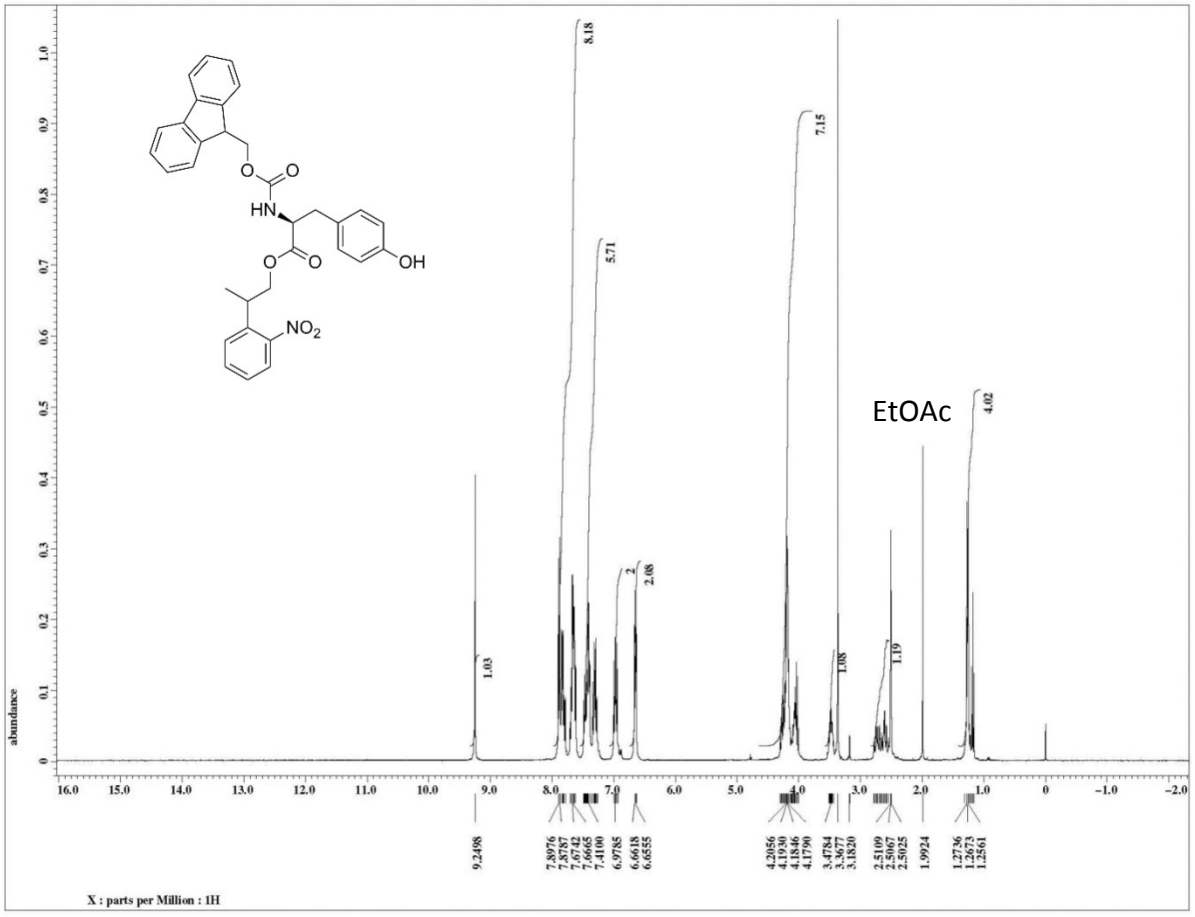

abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
170.6767
156.3558
149.9676
143.7511
140.7191
136.3713
132.9579
128.6674
127.8664
127.7578
127.0846
125.3112
123.8047
120.1434
68.1860
66.3494
65.4556
60.2091
46.5937
40.1293
39.7195
39.5908
39.5000
39.2902
39.0805
38.8707
19.9732
17.5514
X : parts per Million : 13C
HN
OH
O
O
O
O
NO2

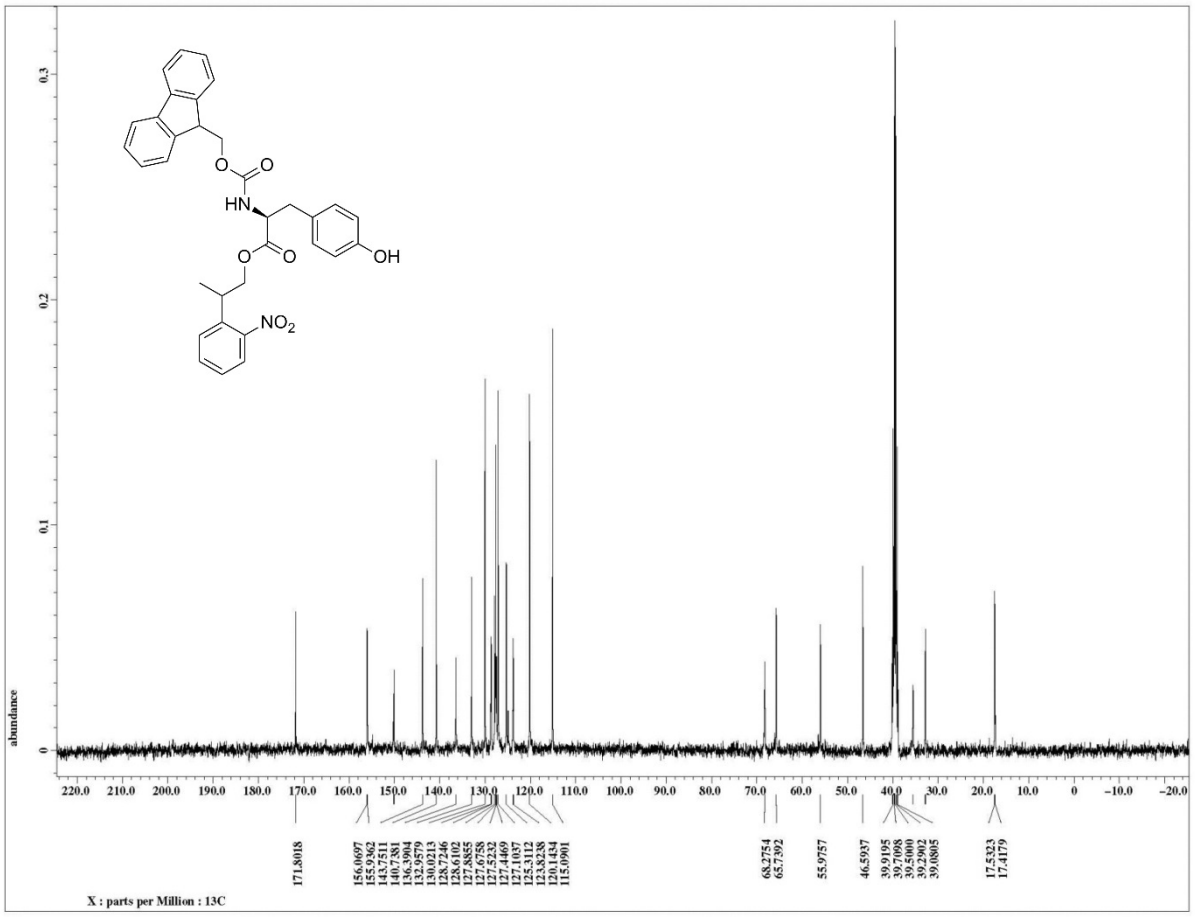

abundance
X : parts per Million : 1H
HN
OH
O
NO2
0.72
4.36
3.23
2.13
1.23
1.04
5.07
3.03
12.4873
7.9066
7.8881
7.8125
7.6908
7.4190
7.3560
5.7651
4.2793
4.2636
4.2232
3.4504
3.4335
3.3534
2.5093
1.2707
1.2617
1.2533
0.0001


abundance
0
0.1
0.2
0.3
0.4
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
171.4204
171.0104
155.8504
143.7892
140.7572
136.3427
136.2950
131.9675
132.9388
128.7436
128.6769
127.8951
127.6853
127.1228
127.0540
123.8144
123.7761
120.1625
68.3135
65.8250
50.5029
46.5842
39.9195
39.7098
39.5000
39.2902
39.0805
33.8735
32.8067
17.6277
X : parts per Million : 13C
HN
OH
O
O
O
O
O
O
NO2


abundance
X : parts per Million : 1H
CH2Cl2
HN
OH
NO2
5.02
3.81
3.04
3.07
1.98
1.91
1.05
1.0
1.09
2.0
2.01
12.1436
7.9093
7.8904
7.7914
7.7012
7.4217
7.3495
7.3313
5.7651
4.2831
4.2730
4.2634
4.2466
4.2305
3.4865
3.4732
3.3492
2.5057
2.2437
2.2247
1.8478
1.8331
1.8171
1.8002
1.2818
1.2768
1.2593


abundance
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
173.5943
171.8399
156.0697
149.9295
143.7701
140.7191
140.2585
132.9388
128.7055
128.5911
127.8664
127.6567
127.0846
125.2549
123.8238
120.1434
68.0275
65.7010
53.0391
46.5747
41.1102
39.9405
39.7098
39.5000
39.2902
39.0805
38.8707
32.8830
21.8701
25.7893
17.6468
X : parts per Million : 13C
O
O
HN
O
OH
O
O
NO2


abundance
X : parts per Million : 1H
EtOAc
8.18
7.15
5.71
4.02
2.08
2
1.03
1.08
1.19
9.2498
7.8976
7.8787
7.6742
7.6645
7.4100
6.9785
6.6618
6.6555
4.2056
4.1930
4.1846
4.1790
3.4784
3.3677
3.1820
2.5109
2.5067
2.5025
1.9924
1.2736
1.2673
1.2561


abundance
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
171.8018
156.0697
155.9362
143.7511
140.7381
138.4004
132.9579
130.0213
128.7246
128.6102
127.8855
127.6758
127.5432
127.1469
127.1037
125.3112
123.8238
120.1434
115.0901
68.2754
65.7392
55.9757
46.5937
39.9195
39.7098
39.5000
39.2902
39.0805
17.5323
17.4179
X : parts per Million : 13C
O
O
HN
O
O
OH
NO2