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Supporting Information

Textile supported silver nanoparticles as highly efficient and recyclable heterogeneous catalyst for nitroaromatics reduction at room temperature

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1 General Procedures and Methods

Proton nuclear magnetic resonance (1H NMR) and carbon NMR (13C NMR) spectra were recorded in CD_3OD and $CDCl_3$ unless otherwise stated. 1H (400 MHz) and 13C (101 MHz) with complete proton decoupling were performed on a 400 MHz Bruker Ultra Shield NMR spectrometer. Chemical shifts were reported as δ in units of parts per million (ppm) downfield from tetramethylsilane (δ 0.00), using the residual solvent signal as an internal standard: CD_3OD (1H NMR, δ 3.31; 13C NMR, δ 49.0), $CDCl_3$ (1H NMR, δ 7.26 singlet; 13C NMR, δ 77.0 triplet). Multiplicities were given as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), ddd (doublet of doublet of doublets), dt (doublet of triplets), dq (doublet of quartets), and br (broad). Coupling constants (J) were recorded in hertz (Hz). The number of proton atoms (n) for a given resonance was indicated by nH. MS was reported in units of mass to charge ratio (m/z). Mass samples were dissolved in MeCN (AR grade). X-Ray Photoelectron Spectroscopy (XPS) was performed on a PerkinElmer, PHI1600 spectrometer. Inductively Coupled Plasma (ICP) was carried out on a Shimadzu ICPE-9800 Series system.

All commercial reagents were purchased from Sigma- Aldrich, Fluka, Alfa Aesar, Merck, TCI, or Acros and were of the highest purity grade available. They were used without further purification unless specified. Reaction solvents were AR grade THF and deionized water.

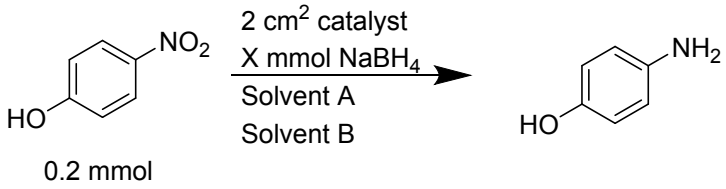
2 Representative procedure for textile supported nanosilver catalyst preparation

Commercially available white cotton textile was washed with deionized water and dried in oven at 60 °C. Silver nitrate (0.7 g) and (3-Aminopropyl) triethoxysilane (APTES) (10ml) were dissolved in deionized water (1L). The dried cotton textile (30g) was bathed in the solution at 60 °C for 10 min. The textile was then washed thoroughly with deionized water and soaked for 10 min in a sodium borohydride (5 mM) solution at room temperature. A yellow color was formed on the textile due to the formation of silver nanoparticles on its surface. The textile was ready to use after rinsing with deionized water to remove any excess reactants and un-bonded silver nanoparticles. It was then dried at room temperature in drying cabinet.

Figure S1, Picture of textile before (white color) and after (yellow color) coating with silver nanoparticles.

3 Reaction optimizations

Table S1 Optimization of TsNS catalyzed 4-nitrophenol reduction.



Entry	Solvent A	Solvent B	X	Time (hours)	Yield (%)[a]
1[b]	2 ml DCM		1	12	trace
2[b]	2 ml MeCN		1	12	~8%
3[b]	2ml THF		1	12	~10%
4	1ml THF	1ml H_2O	1	3	73%
5	1ml THF	1ml H_2O	0.5	3	46%
6	1ml THF	1ml H_2O	2	3	75%
7[b]	1.5 ml THF	0.5 ml H_2O	1	3	50%
8[c]	0.5	1.5	1	3	26%

Nitrophenol, catalyst and $NaBH_4$ were mixed in solvent and stirred at room temperature. [a] isolated yield. [b] $NaBH_4$ is not completely dissolved. [c] nitrophenol is not completely dissolved. Entry 4 is the best condition.

4 Representative procedure for nanotextile catalyzed nitroaromatic reduction

To a 25ml rbf was added a magnetic stirring bar, 2 cm^2 nanosilver textile catalyst, 0.2 mmol nitro compound and 1mmol $NaBH_4$, following this, 1ml THF and 1ml deionized water were added. The mixture was stirred at room temperature (25^{o}C, 100 ^{o}C for certain substrate) until substrate was completely consume as indicated by TLC monitoring. Then the catalyst was taken out and washed thoroughly with deionized water, which was combined with the reaction mixture. Extract with Ether for three times and the organic layers were combined and dried with Na_2SO_4, concentrated and purified by flash chromatography.

5 NMR and Mass data for products

All compounds were purified by flashing silica chromatography with hexane and ethyl acetate (EA) mixture as eluent.

Compound 1: 4-aminophenol

^{1}H NMR (400 MHz, MeOD) δ 6.62 (td, *J* = 9.0, 6.4 Hz, 4H). ^{13}C NMR (101 MHz, MeOD) δ 151.32, 140.22, 118.54, 116.74. LRMS (ESI) m/z 110.0 ($M + H^+$). Eluent: Hexane/ EA = 5/1.

Compound 2: 2-methyl-1H-indol-5-amine

^{1}H NMR (400 MHz, MeOD) δ 7.05 (d, *J* = 8.4 Hz, 1H), 6.83 (d, *J* = 2.0 Hz, 1H), 6.57 (dd, *J* = 8.4, 2.1 Hz, 1H), 5.92 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, MeOD) δ 139.20, 137.04, 133.32, 131.34, 112.81, 111.55, 107.03, 99.49, 13.49. LRMS (ESI) m/z 147.2 ($M + H^+$). Eluent: Hexane/ EA = 1/1.

Compound 3: indolin-5-amine

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.61 – 6.56 (m, 1H), 6.52 (d, *J* = 8.1 Hz, 1H), 6.42 (dd, *J* = 8.1, 2.3 Hz, 1H), 3.49 (t, *J* = 8.3 Hz, 2H), 3.16 (br, 3H), 2.95 (t, *J* = 8.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.11, 139.15, 131.27, 114.27, 113.15, 110.76, 47.57, 30.47. LRMS (ESI) m/z 135.0 ($M + H^+$). Eluent: Hexane/ EA = 1/1.

Compound 4: aniline

^{1}H NMR (400 MHz, MeOD) δ 7.24 – 7.14 (m, 2H), 7.00 – 6.93 (m, 2H), 6.85 (tt, *J* = 7.5, 1.1 Hz, 1H).^{13}C NMR (101 MHz, MeOD) δ 152.69, 129.61, 121.97, 115.14. LRMS (ESI) m/z 93.9 ($M + H^+$). Eluent: Hexane/ EA = 10/1.

Compound 5: 2-(2-aminophenyl) ethanol

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (t, *J* = 8.2 Hz, 2H), 6.85 – 6.61 (m, 2H), 3.90 (t, *J* = 6.1 Hz, 2H), 2.96 (br, 3H), 2.80 (t, *J* = 6.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.81, 130.60, 127.69, 124.40, 119.37, 116.39, 63.32, 34.75. LRMS (ESI) m/z 138.1 ($M + H^+$). Eluent: Hexane/ EA = 1/1.

Compound 6: 3-aminophenol

^{1}H NMR (400 MHz, MeOD) δ 7.70 (ddd, *J* = 8.2, 2.2, 0.9 Hz, 1H), 7.62 (t, *J* = 2.3 Hz, 1H), 7.42 (t, *J* = 8.2 Hz, 1H), 7.18 (ddd, *J* = 8.2, 2.4, 0.9 Hz, 1H). ^{13}C NMR (101 MHz, MeOD) δ 159.81, 150.65, 131.26, 122.92, 115.09, 110.87. LRMS (ESI) m/z 110.0 ($M + H^+$). Eluent: Hexane/ EA = 3/1.

Compound 7: 1-aminonaphthalen-2-ol

^{1}H NMR (400 MHz, MeOD) δ 7.86 (dd, *J* = 8.5, 0.7 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.36 (ddd, *J* = 8.4, 6.8, 1.3 Hz, 1H), 7.23 (ddd, *J* = 8.8, 5.5, 2.1 Hz, 2H), 7.08 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (101 MHz, MeOD) δ 141.79, 130.50, 129.16, 128.04, 126.61, 125.79, 123.68, 121.58, 120.14, 118.31. LRMS (ESI) m/z 182.3 ($M + Na^+$). Eluent: Hexane/ EA = 1/1.

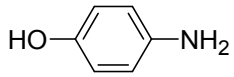
Compound 8: 3-chloroaniline

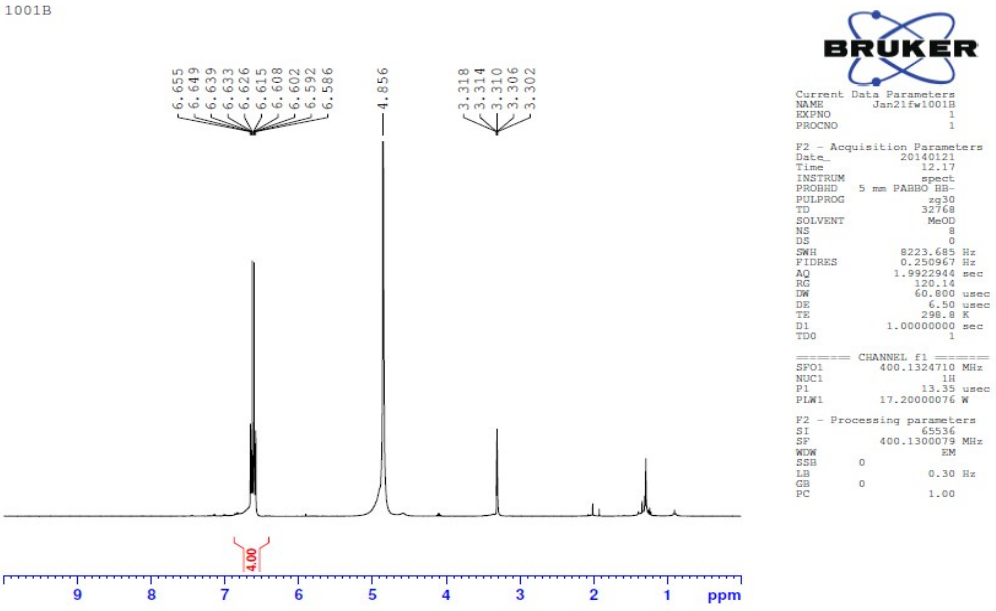
^{1}H NMR (400 MHz, MeOD) δ 7.14 (t, *J* = 8.0 Hz, 1H), 6.96 (t, *J* = 2.1 Hz, 1H), 6.84 – 6.77 (m, 2H). ^{13}C NMR (101 MHz, MeOD) δ 154.53, 135.54, 130.83, 121.12, 114.46, 112.90. LRMS (ESI) m/z 127.9 ($M + H^+$). Eluent: Hexane/ EA = 10/1.

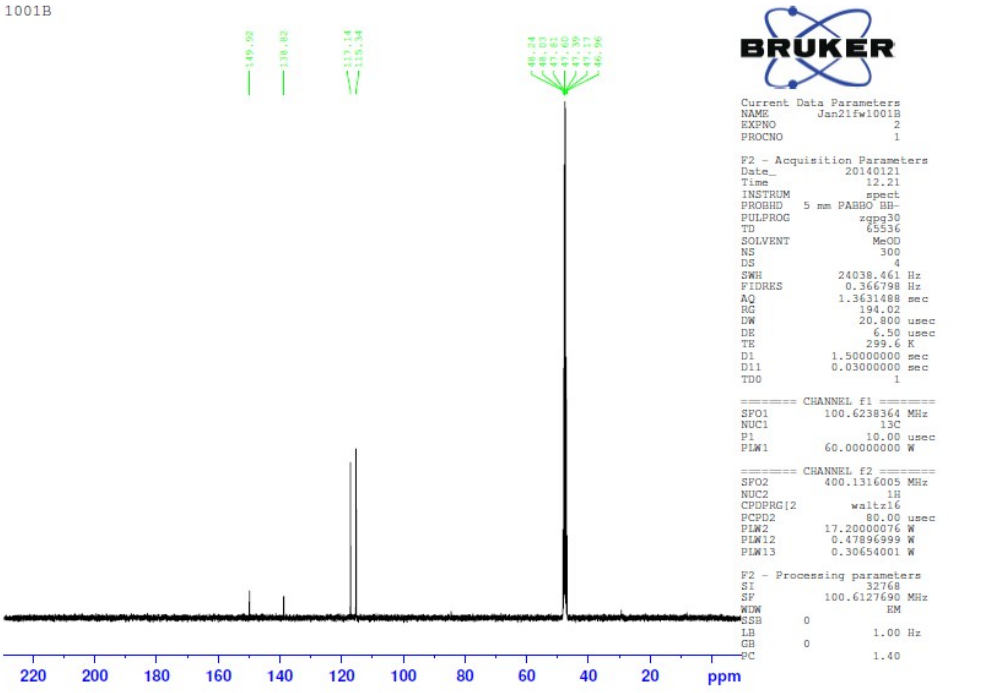
Compound 9: 4-methoxybenzene-1,2-diamine

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.63 (d, *J* = 8.4 Hz, 1H), 6.31 (d, *J* = 2.7 Hz, 1H), 6.25 (dd, *J* = 8.3, 2.7 Hz, 1H), 3.72 (s, 3H), 3.29 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.60, 137.09, 127.36, 118.34, 104.10, 102.96, 55.54. LRMS (ESI) m/z 139.0 ($M + H^+$). Eluent: Hexane/ EA = 3/1.

6 NMR Spectra

Compound 1 





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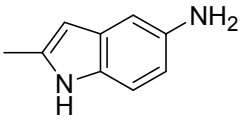
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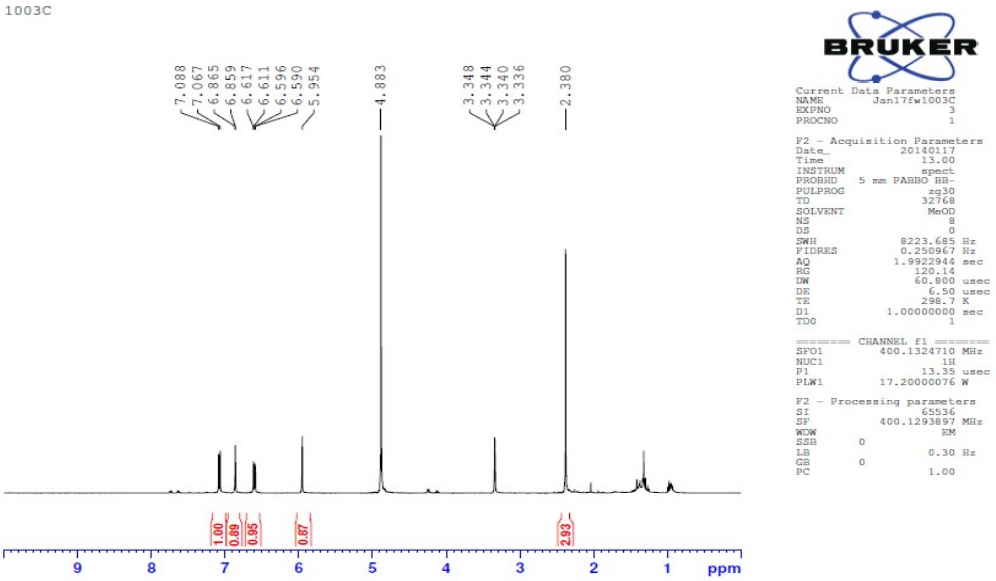
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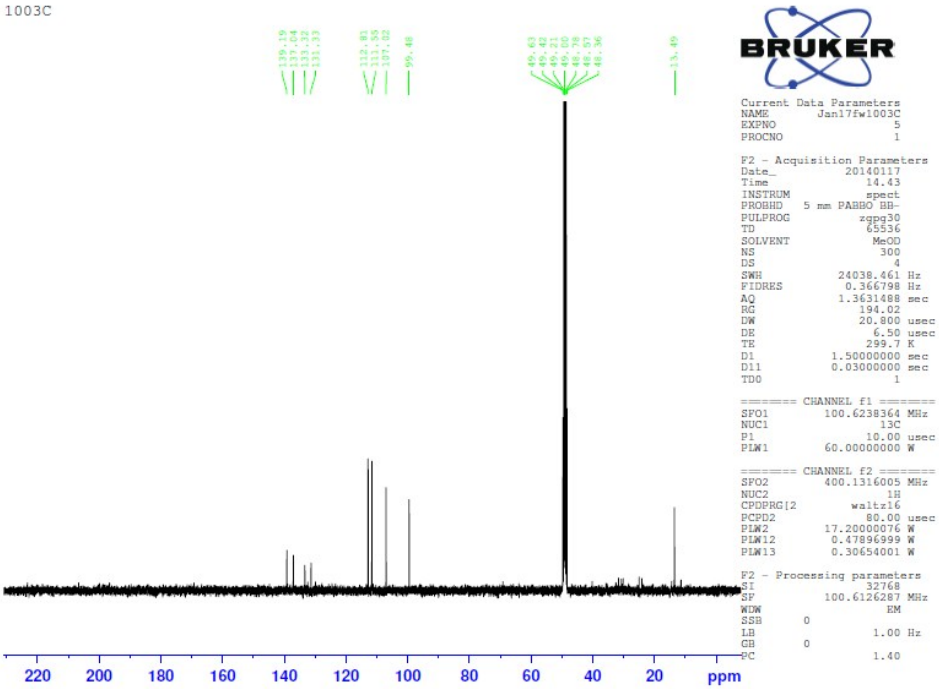
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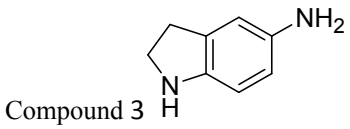

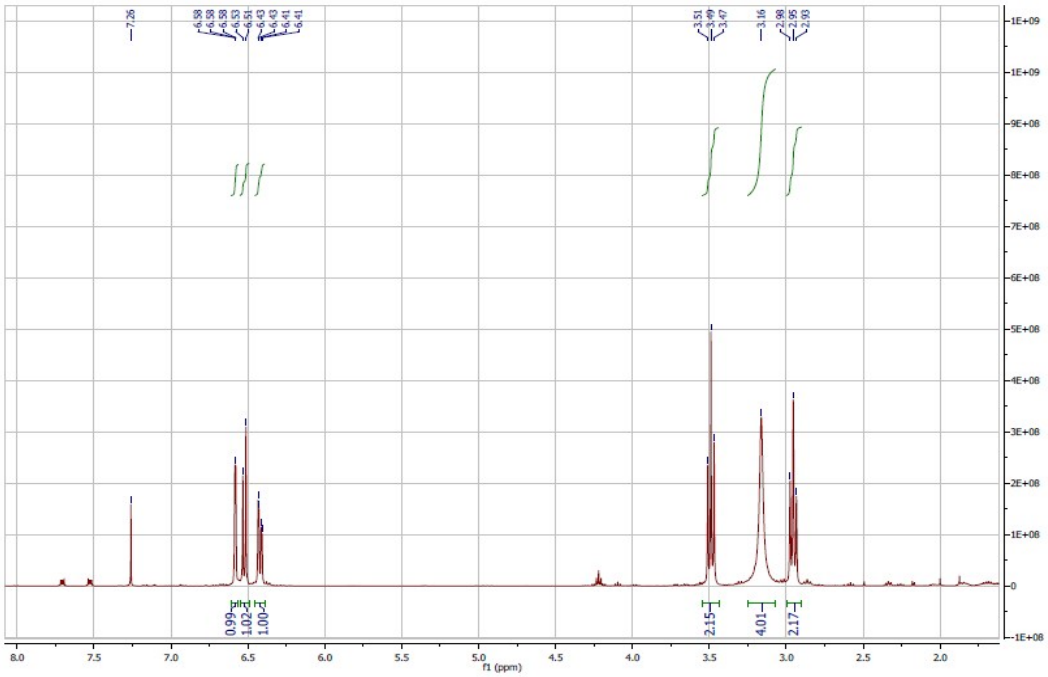

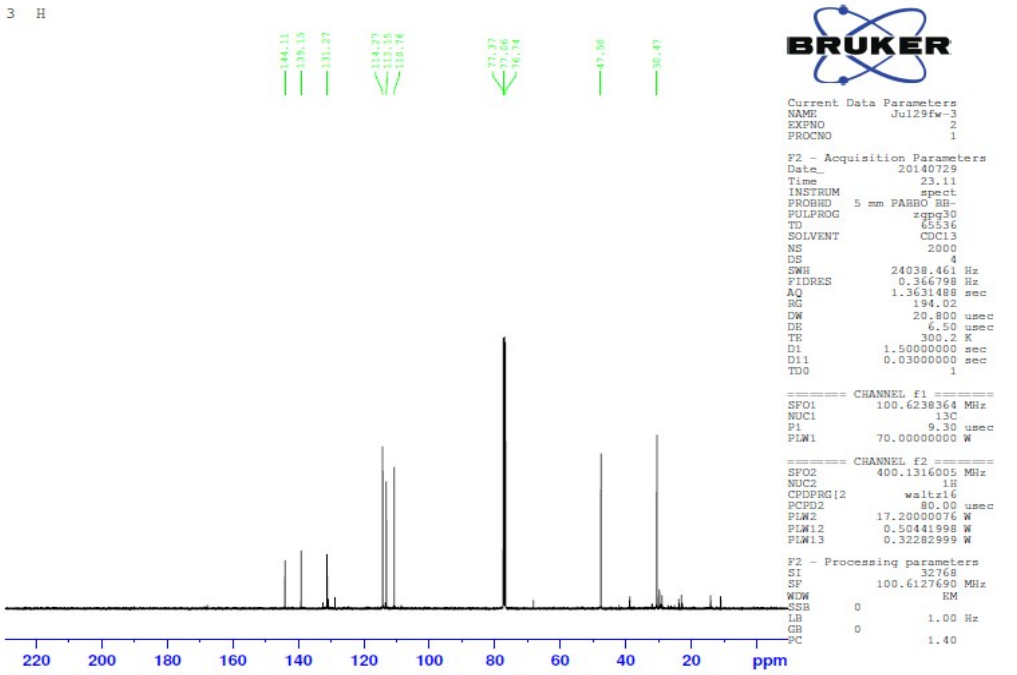

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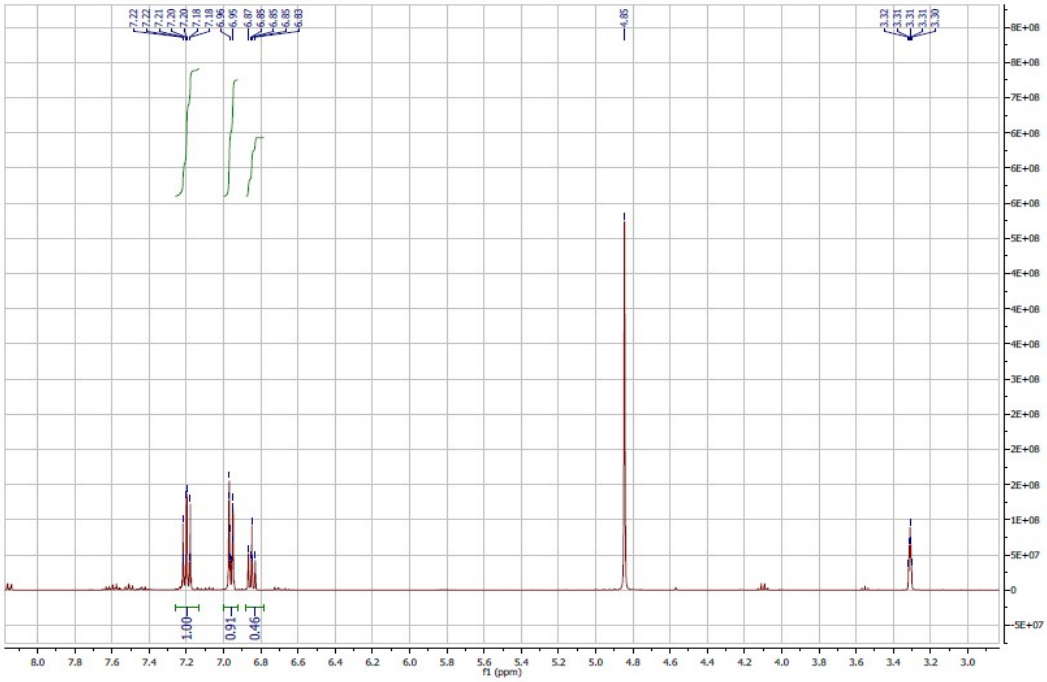

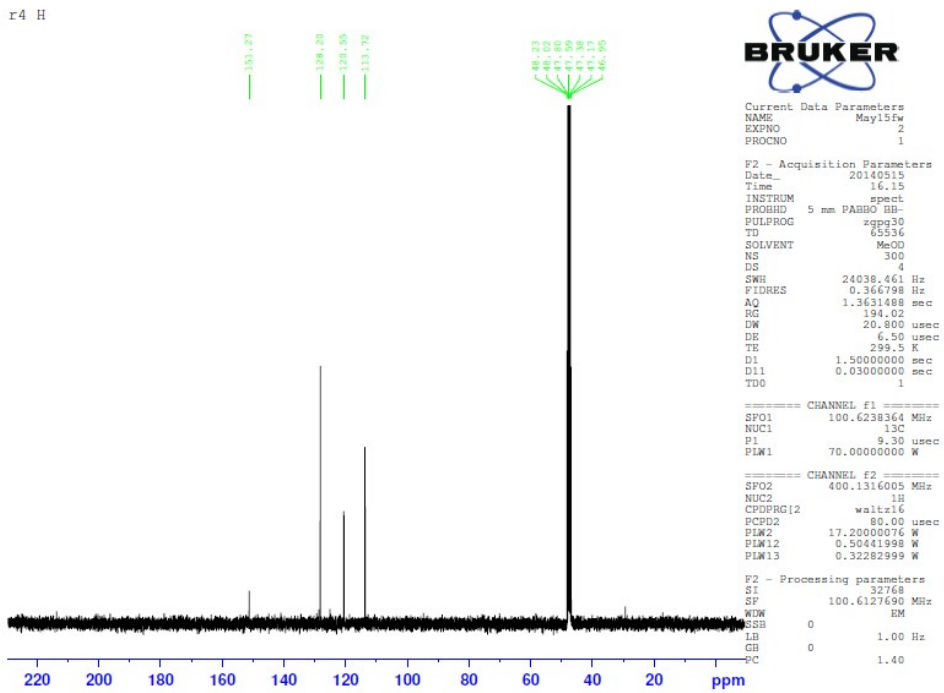
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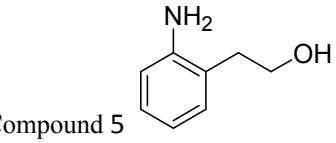
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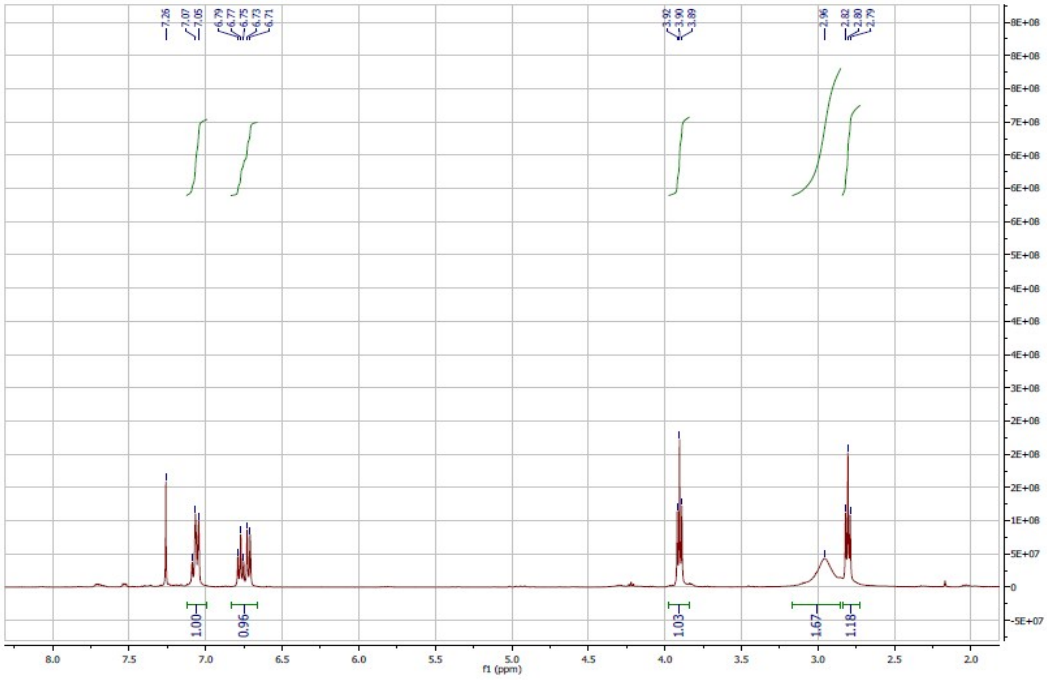
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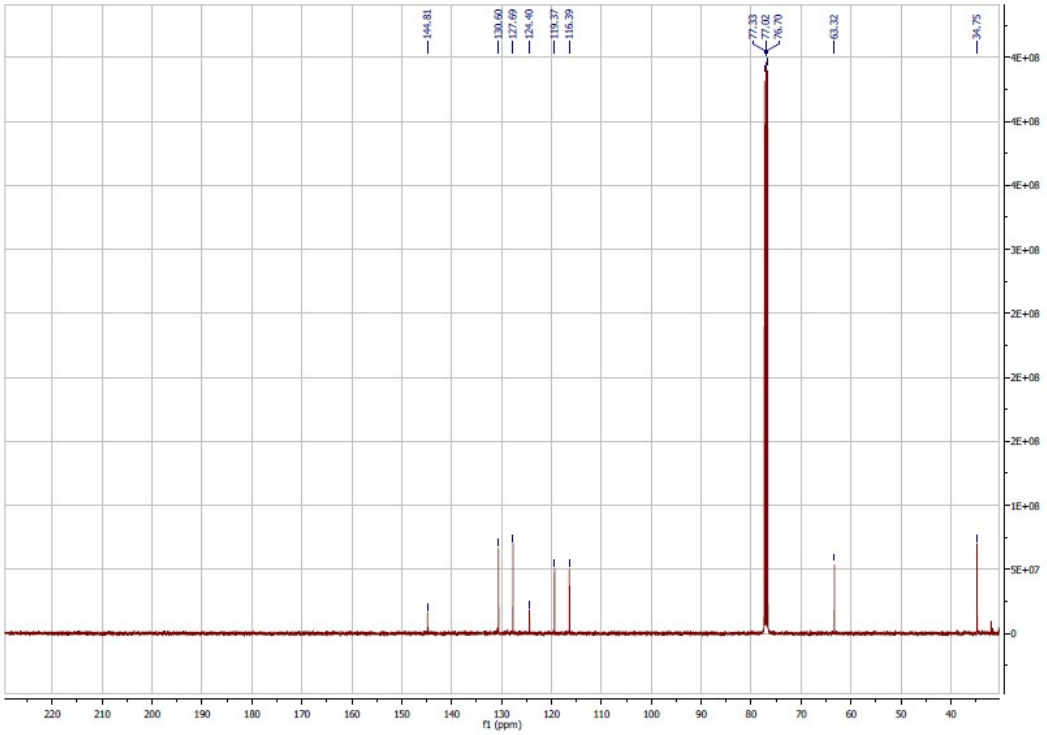
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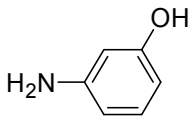
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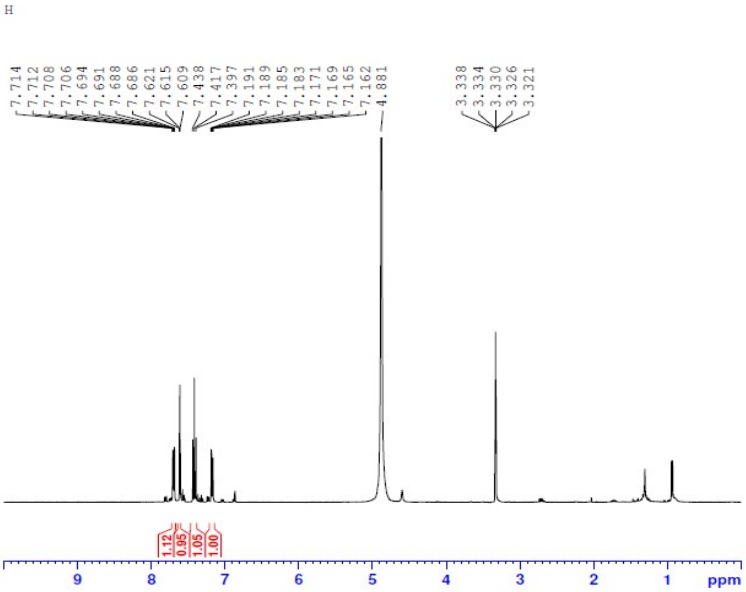
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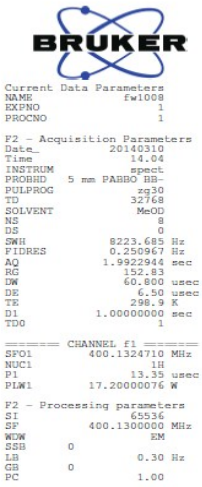
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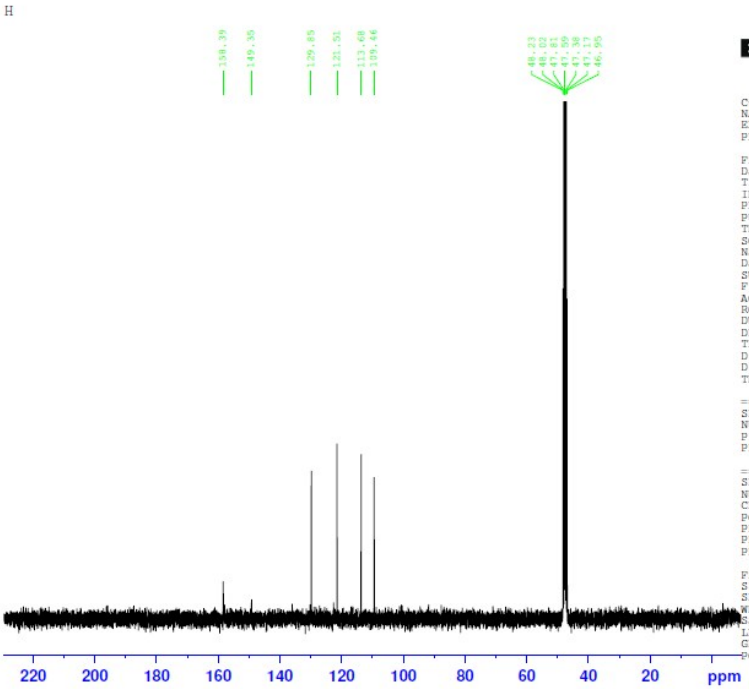
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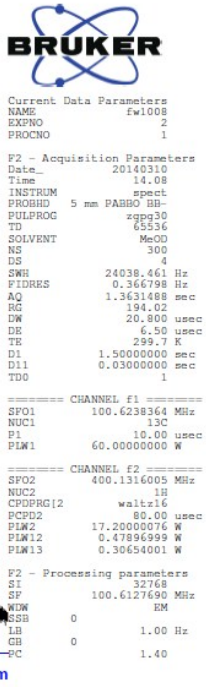
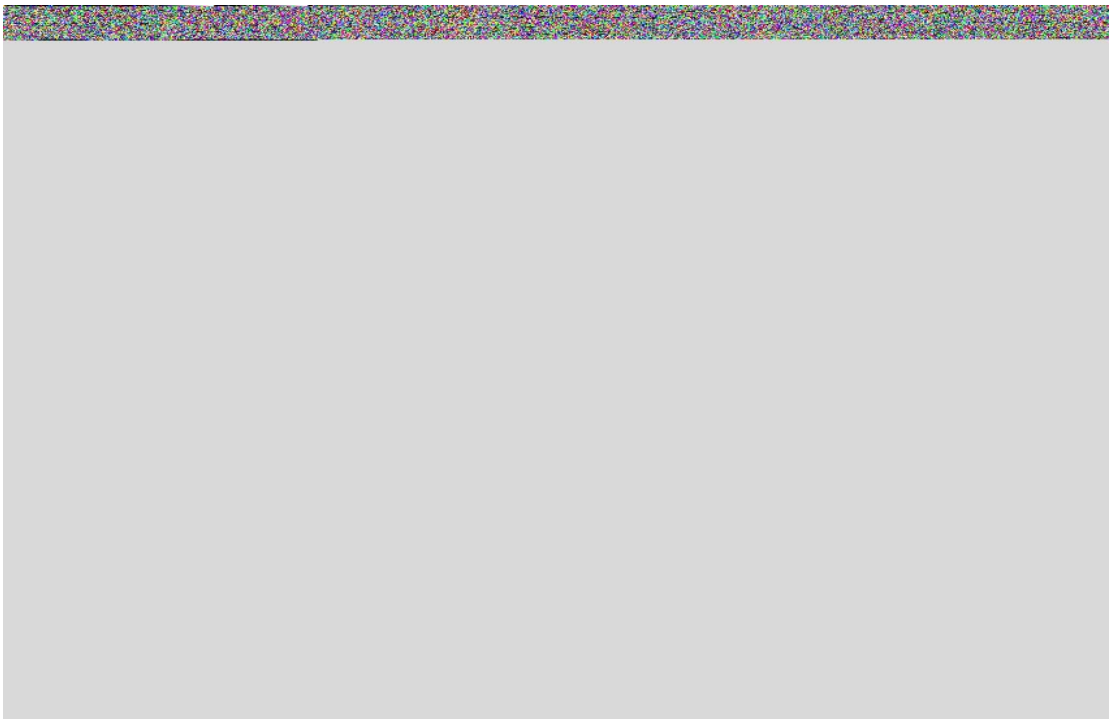
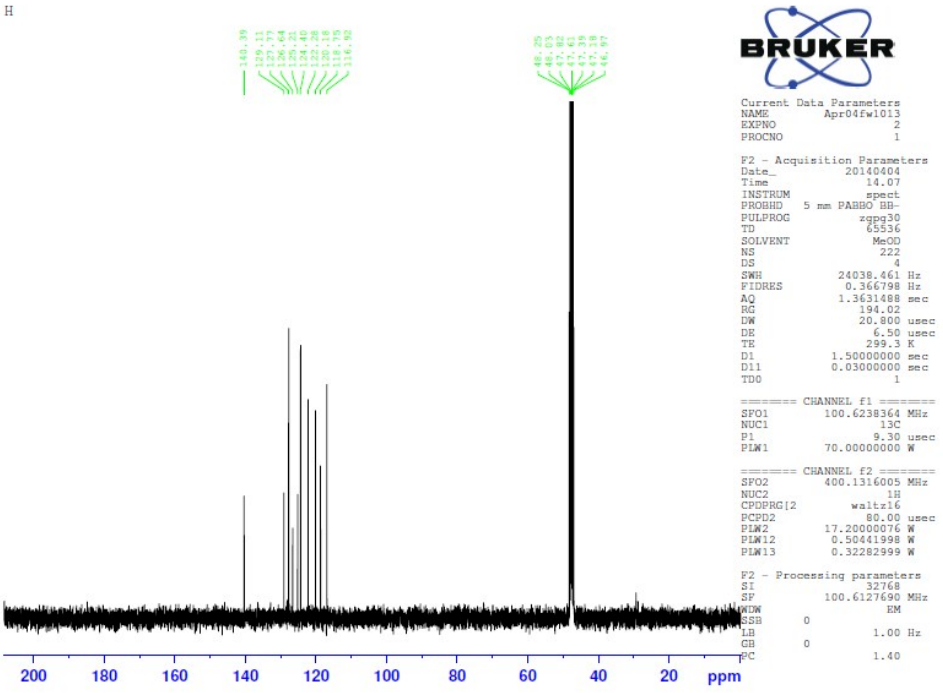
20
ppm


BRUKER
Current Data Parameters
NAME fw1008
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140310
Time 14.08
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 300
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 194.02
DW 20.800 usec
DE 6.50 usec
TE 299.7 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======= CHANNEL f1 =======
SFO1 100.6238364 MHz
NUC1 13C
P1 10.00 usec
PLW1 60.00000000 W
======= CHANNEL f2 =======
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 17.200000076 W
PLW12 0.47896999 W
PLW13 0.30654001 W
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

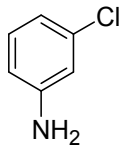
Compound **7**



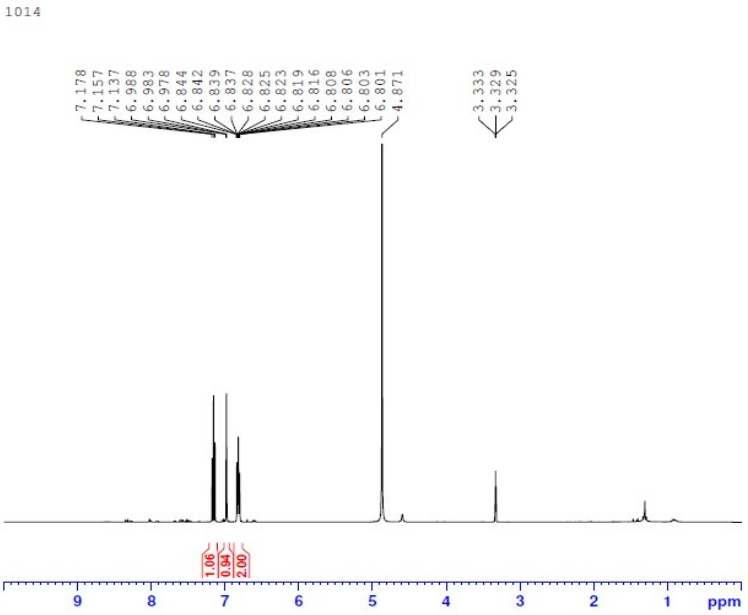


BRUKER

```
Current Data Parameters
NAME          Apr04fw1013
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_              20140404
Time                 14.07
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT             MeOD
NS                   222
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631488 sec
RG                 194.02
DW                20.800 usec
DE                 6.50 usec
TE                299.3 K
D1           1.50000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6238364 MHz
NUC1               13C
P1                9.30 usec
PLW1        70.00000000 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2               1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2        17.20000076 W
PLW12        0.50441998 W
PLW13        0.32282999 W

F2 - Processing parameters
SI                 32768
SF          100.6127690 MHz
WDW                  EM
SSB          0
LB                1.00 Hz
GB           0
PC                1.40
```

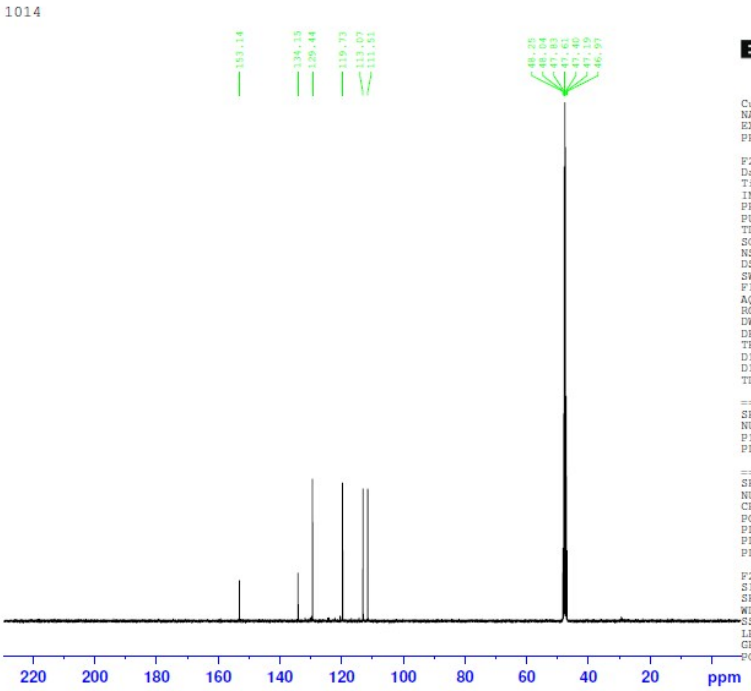


Compound 8



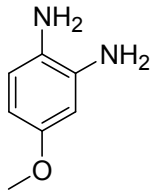
BRUKER

```
Current Data Parameters
NAME                  Apr08fw
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20140408
Time                   22.09
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    32768
SOLVENT                MeOD
NS                        8
DS                        0
SWH                8223.685 Hz
FIDRES             0.250967 Hz
AQ                 1.9922944 sec
RG                    107.13
DW                  60.800 usec
DE                   6.50 usec
TE                  299.3 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 =======
SFO1             400.1324710 MHz
NUC1                       1H
P1                      13.70 usec
PLW1              17.20000076 W

F2 - Processing parameters
SI                        65536
SF               400.1300000 MHz
WDW                          EM
SSB                  0
LB                       0.30 Hz
GB                   0
PC                       1.00
```

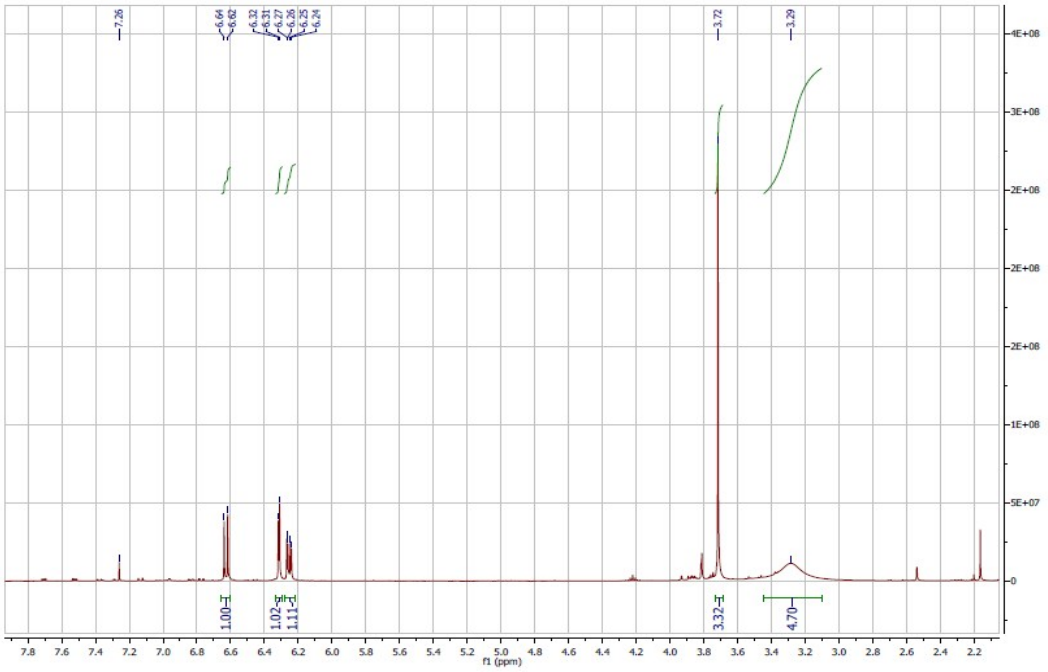


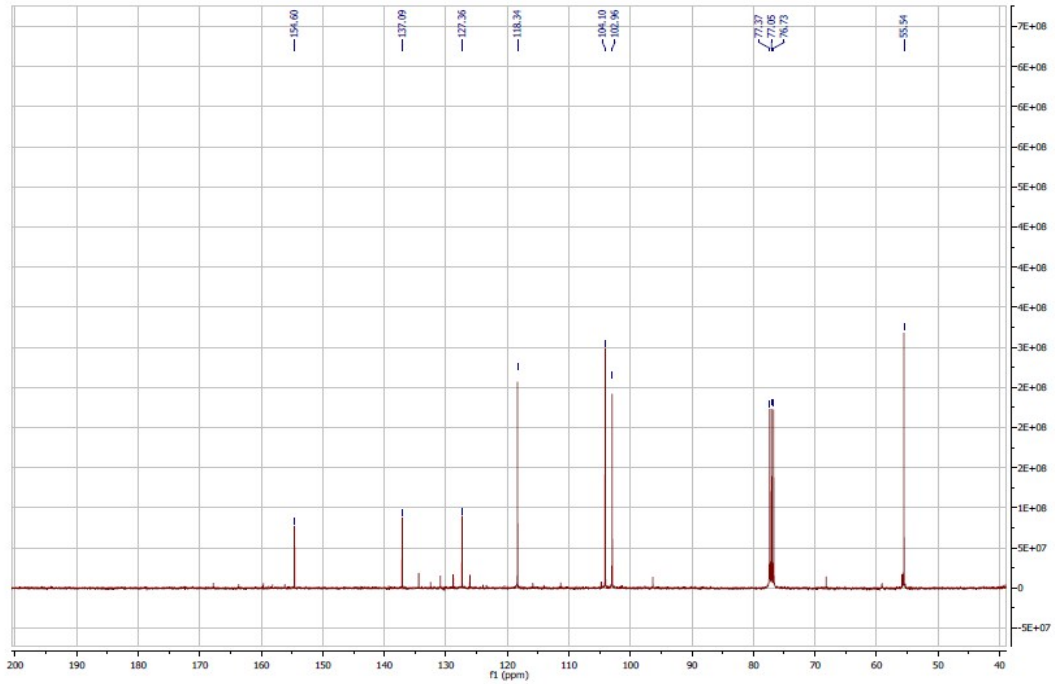
BRUKER

```
Current Data Parameters
NAME                  Apr08fw
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_               20140408
Time                   23.00
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT                MeOD
NS                     1024
DS                        4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                    194.02
DW                  20.800 usec
DE                   6.50 usec
TE                  300.2 K
D1                 1.50000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 =======
SFO1             100.6238364 MHz
NUC1                       13C
P1                       9.30 usec
PLW1              70.00000000 W

======== CHANNEL f2 =======
SFO2             400.1316005 MHz
NUC2                       1H
CPDPRG[2                waltz16
PCPD2                   80.00 usec
PLW2              17.20000076 W
PLW12              0.50441998 W
PLW13              0.32282999 W

F2 - Processing parameters
SI                        32768
SF               100.6127690 MHz
WDW                          EM
SSB                  0
LB                       1.00 Hz
GB                   0
PC                       1.40
```


NH2
NH2
O

Compound 9


7.26
6.64
6.62
6.32
6.31
6.27
6.26
6.25
6.24
3.72
3.29
1.00
1.02
1.11
3.32
4.70
f1 (ppm)


154.60
137.09
127.36
118.34
104.10
102.96
77.27
77.05
76.73
55.54
f1 (ppm)