Copper- Coordination Polymers Controlled Cu@N-rGO or CuO@C Nanoparticles Formation: Reusable Green Catalyst for A-3 Coupling and Nitroarene Reduction

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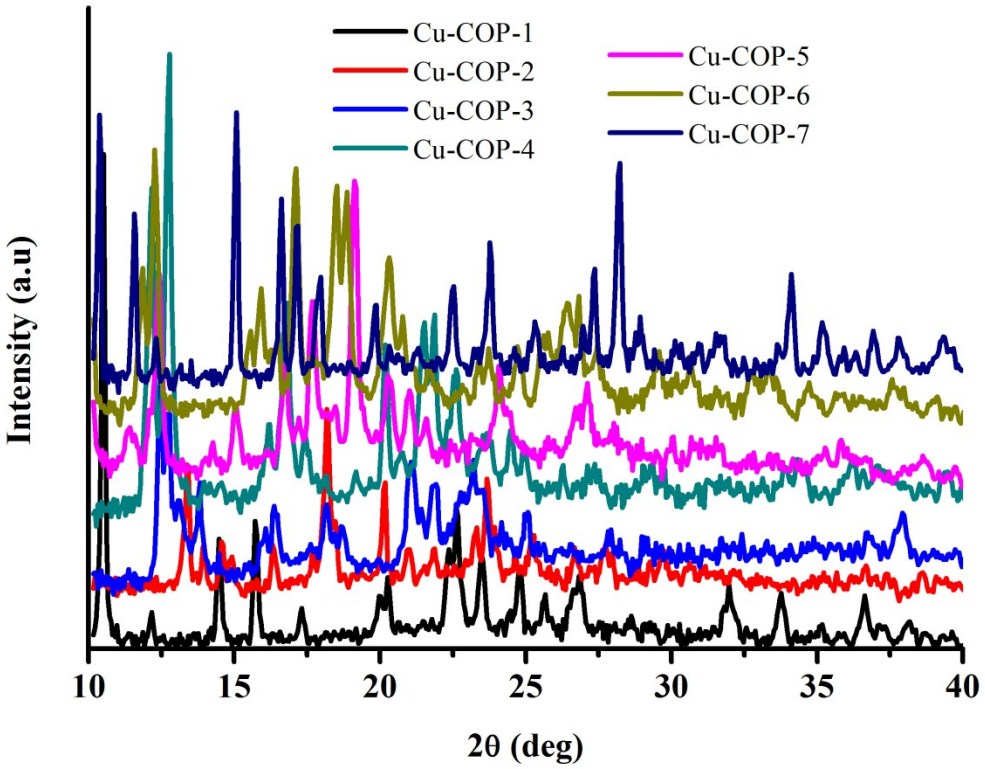


Figure S1. PXRD pattern of Cu-COPs.

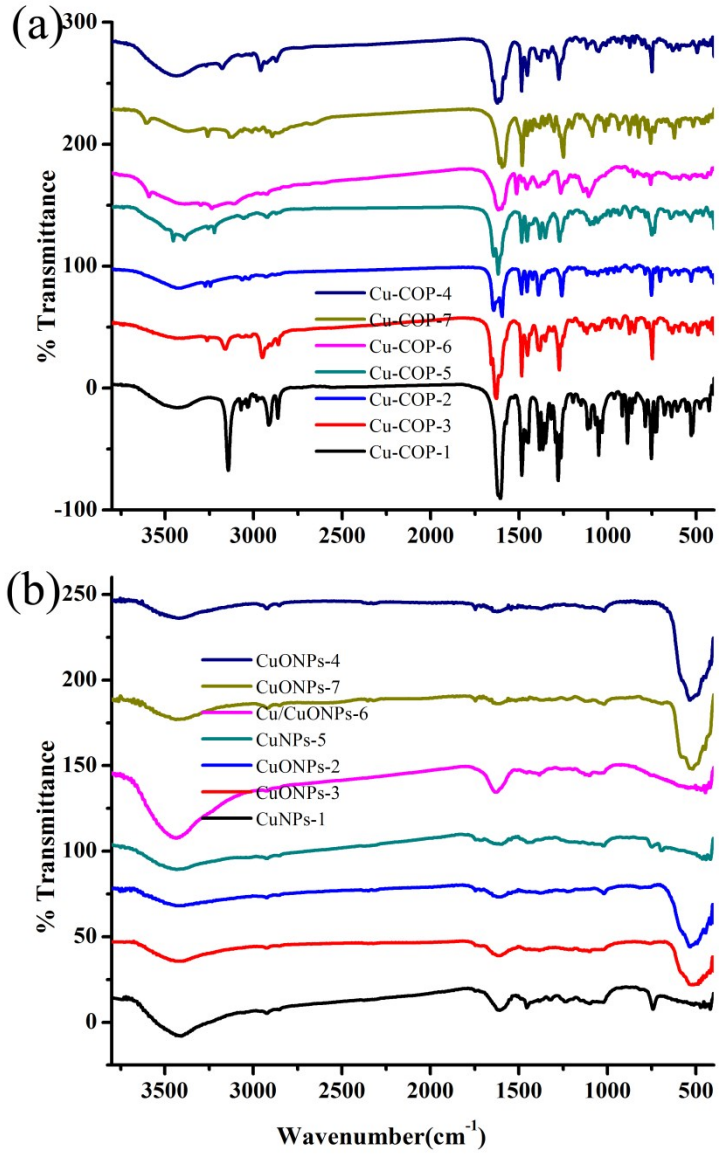


Figure S2. FTIR spectra of (a) Cu-COPs and (b) Cu-COPs after calcination.

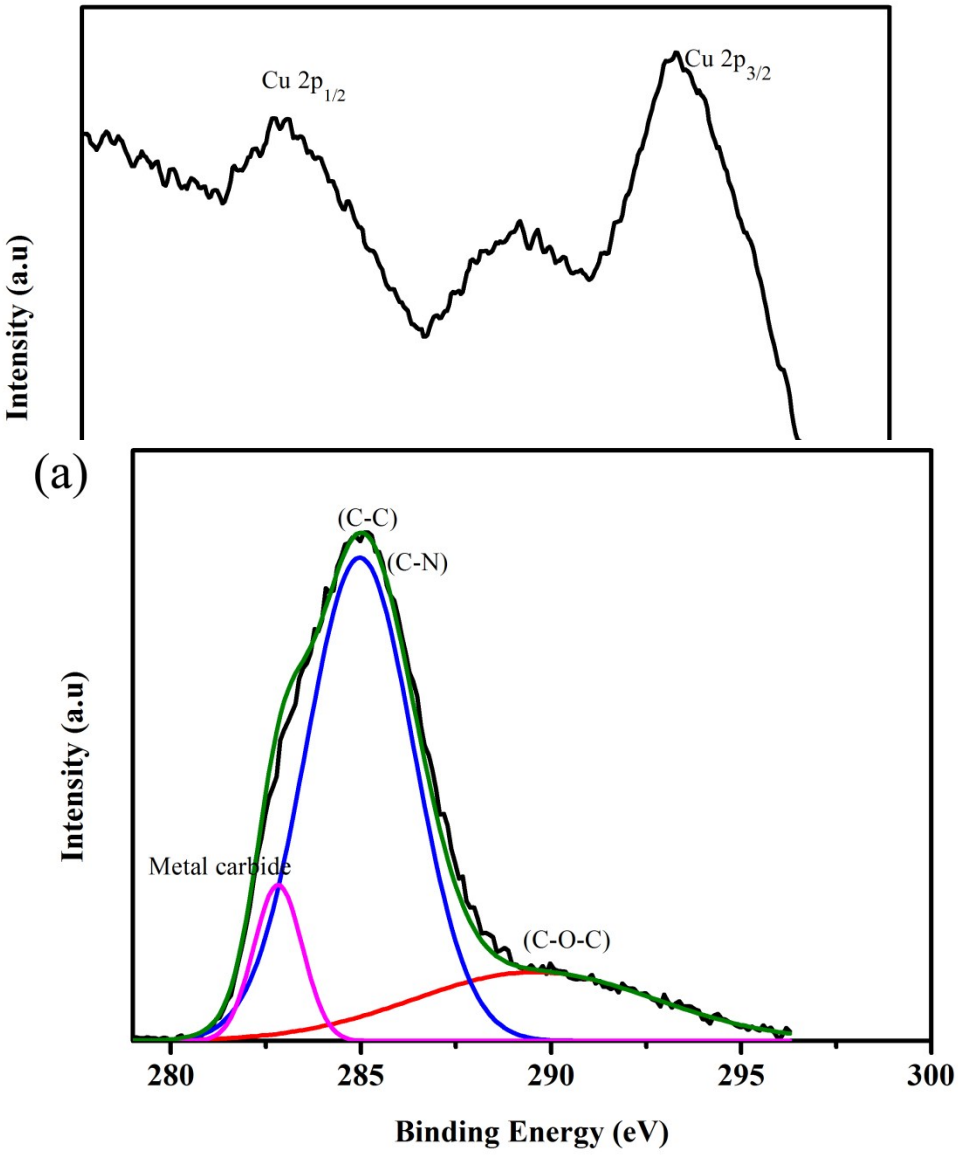


Figure S3. XPS spectra of CuNPs-1 for Cu.

Figure S4. XPS spectra of (a) CuNPs-1 and (b) CuNPs-5 for C.

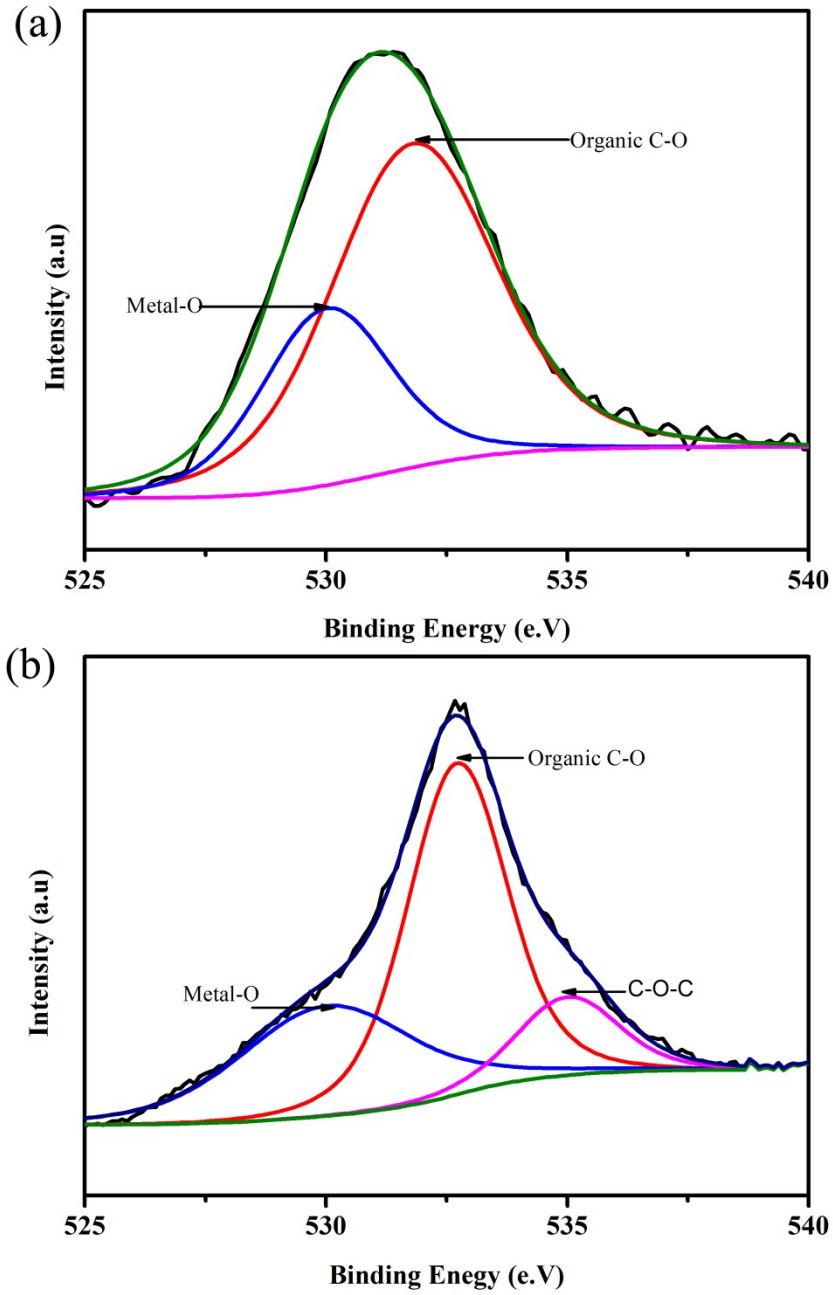


Figure S5. XPS spectra of (a) CuNPs-1 and (b) CuNPs-5 for O.

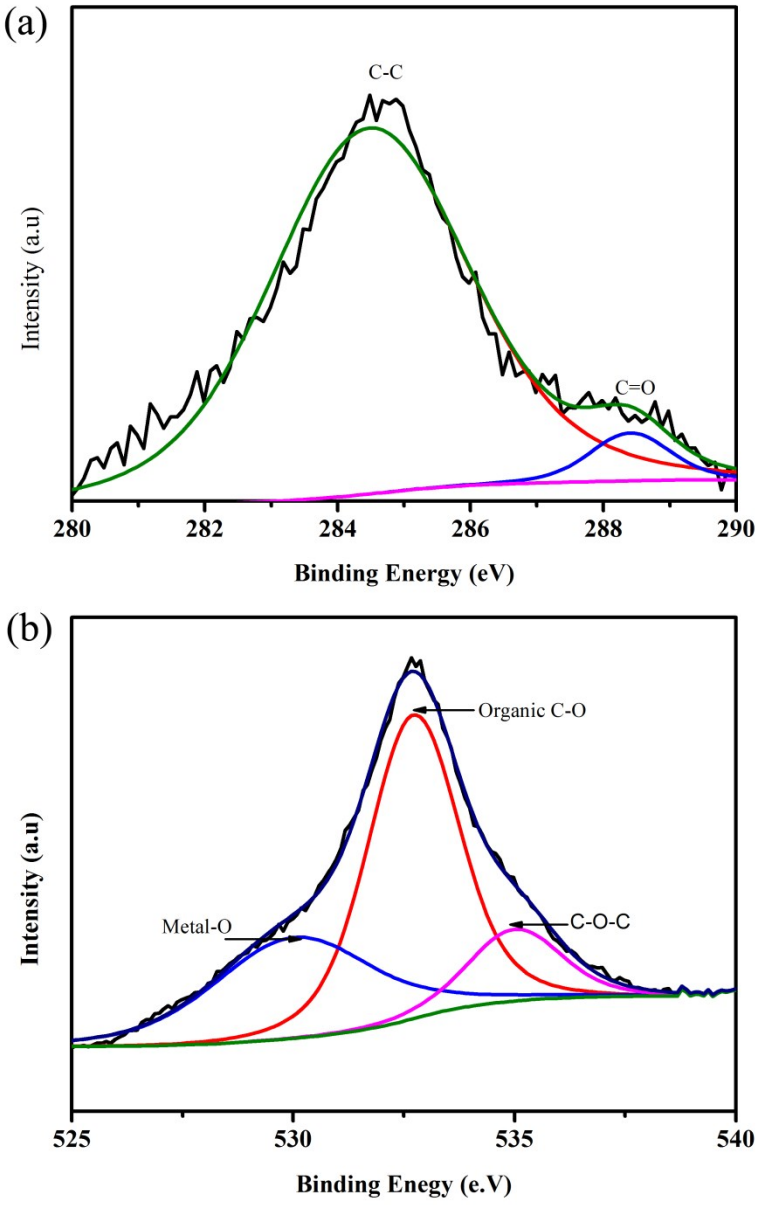


Figure S6. XPS spectra of CuONPs-2 (a) C and (b) O.

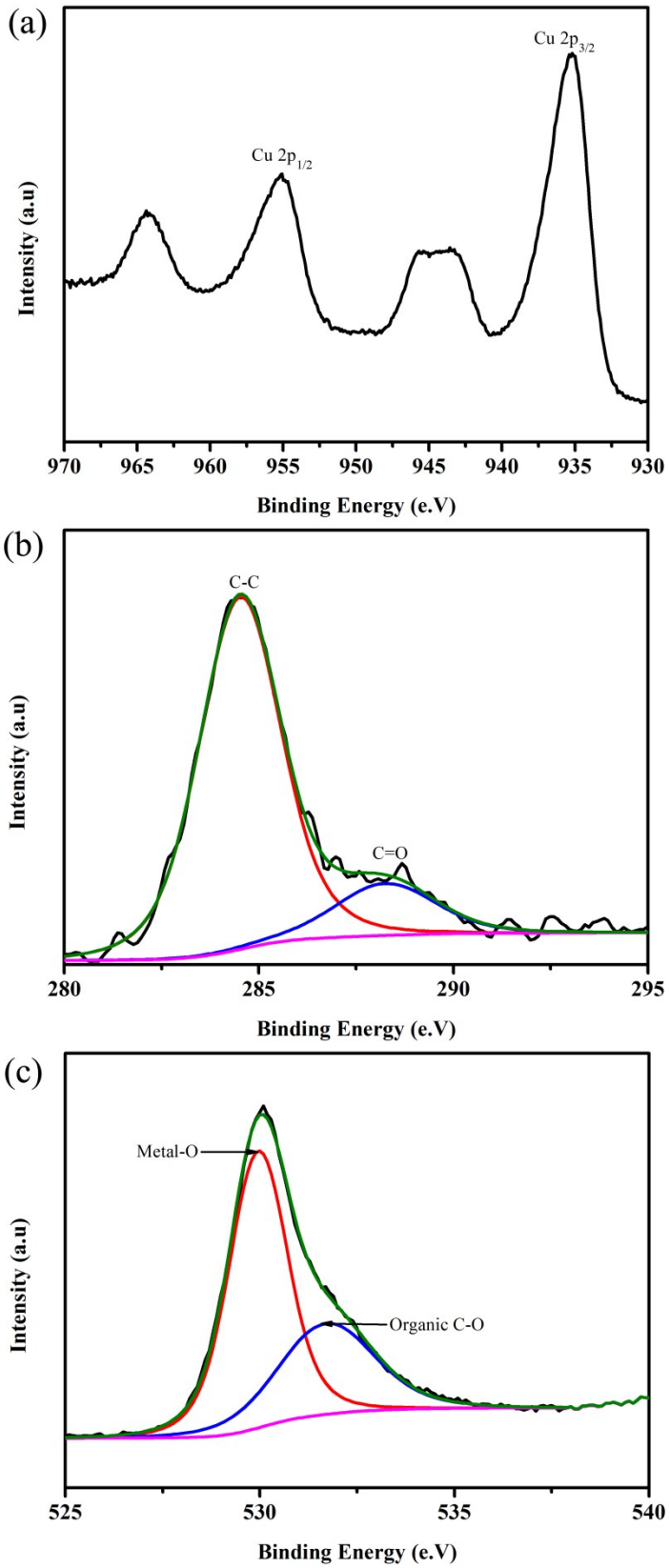


Figure S7. XPS spectra of CuONPs-3 (a) Cu, (b) C and (c) O.

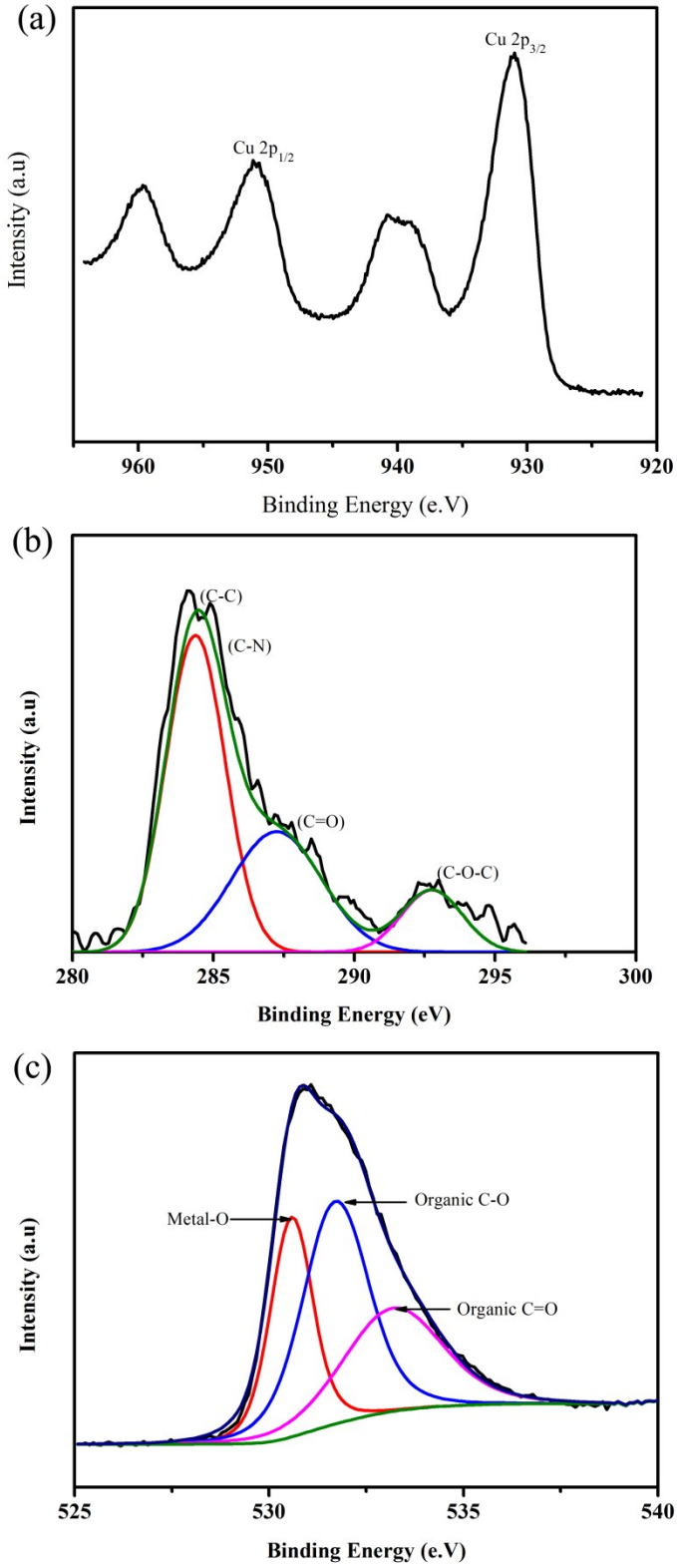


Figure S8. XPS spectra of CuONPs-4 (a) Cu, (b) C and (c) O.

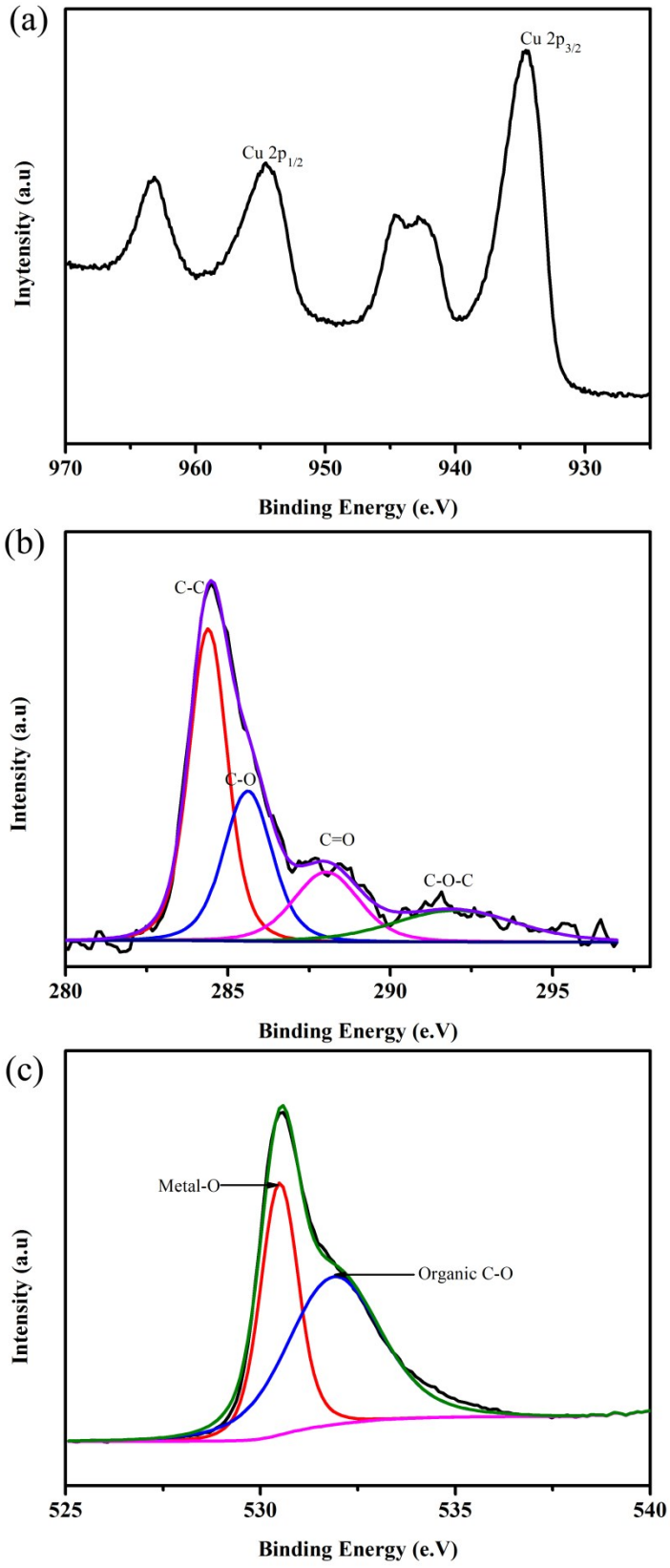


Figure S9. XPS spectra of CuONPs-7 (a) Cu, (b) C and (c) O.

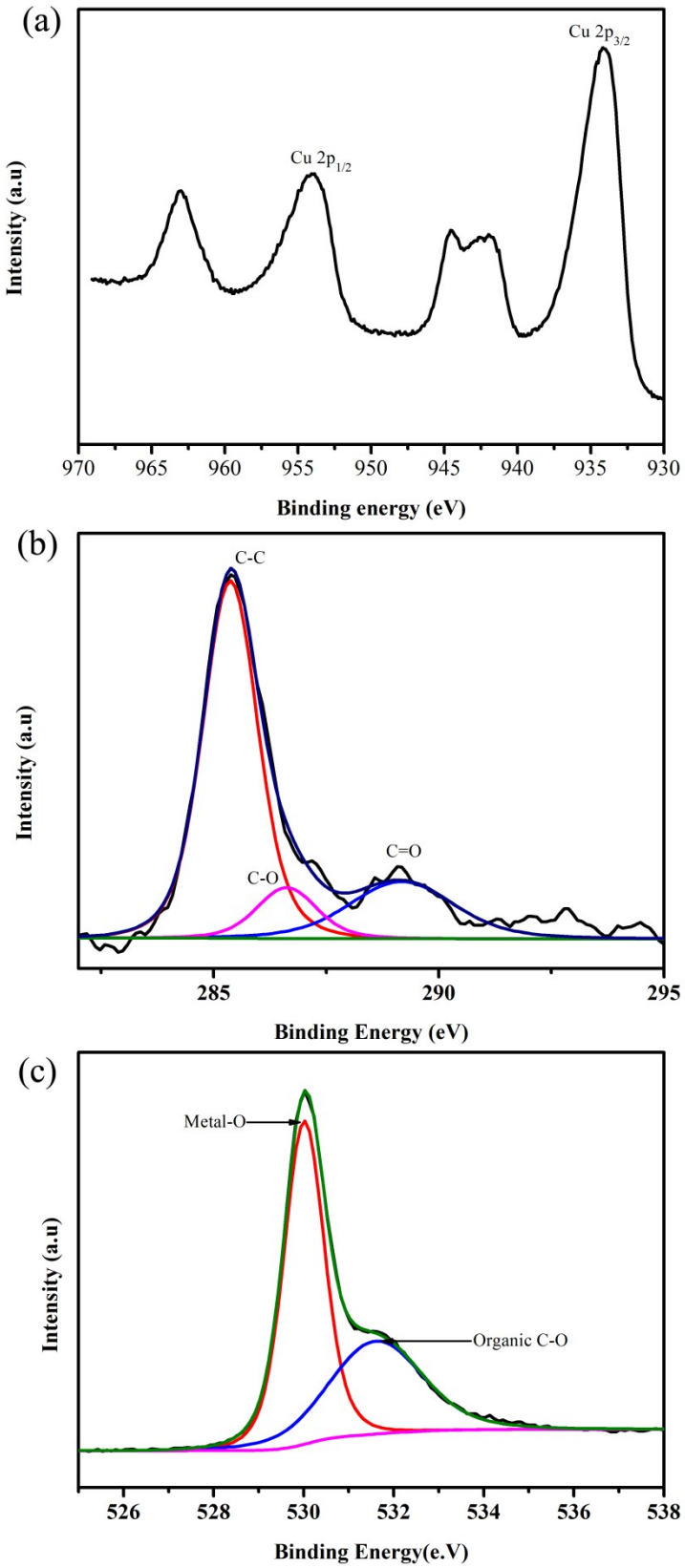


Figure S10. XPS spectra of CuONPs-6 (a) Cu, (b) C and (c) O.

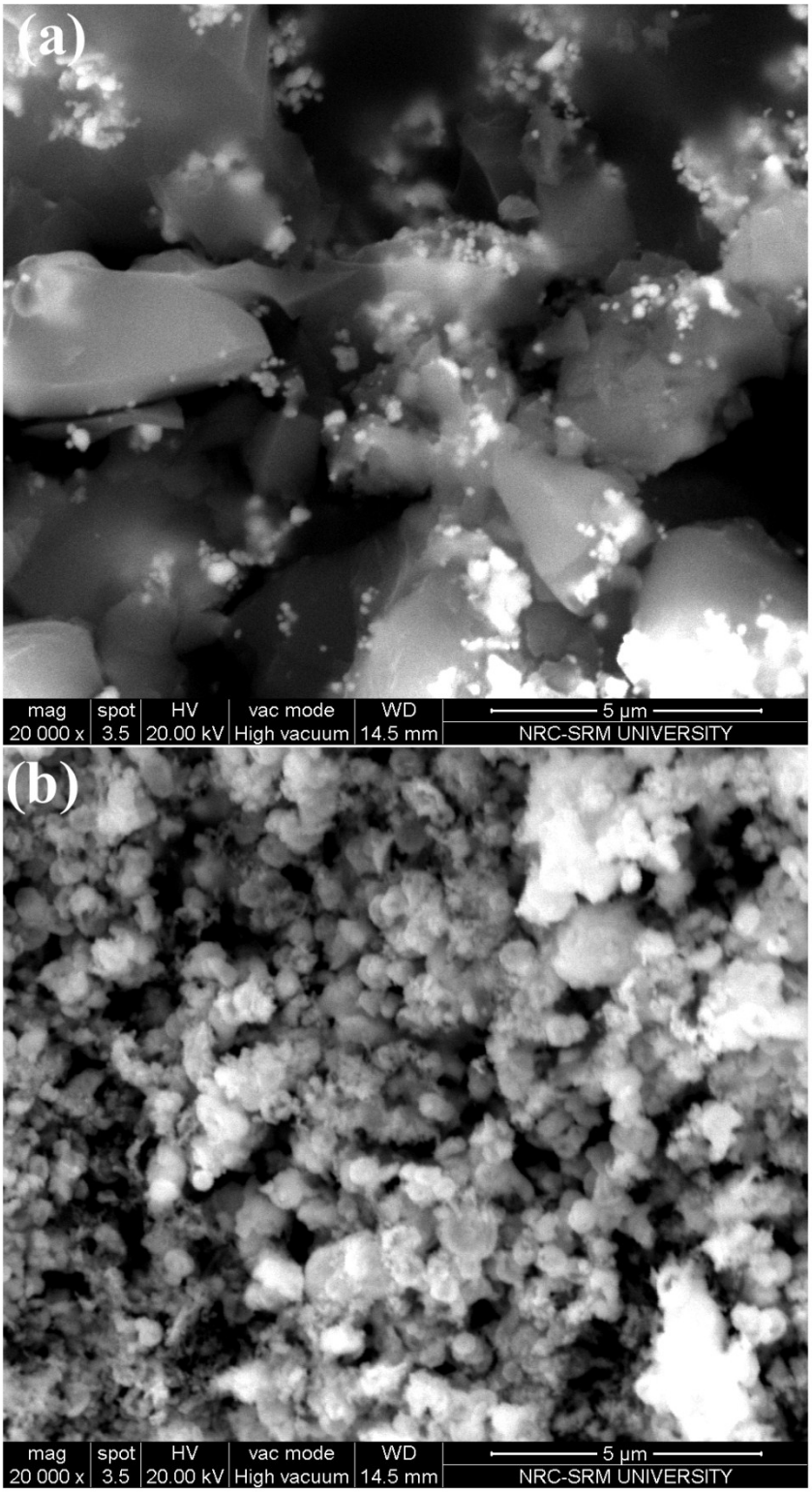


Figure S11. FE-SEM images of (a) CuNPs-1 and (b) CuONPs-4.

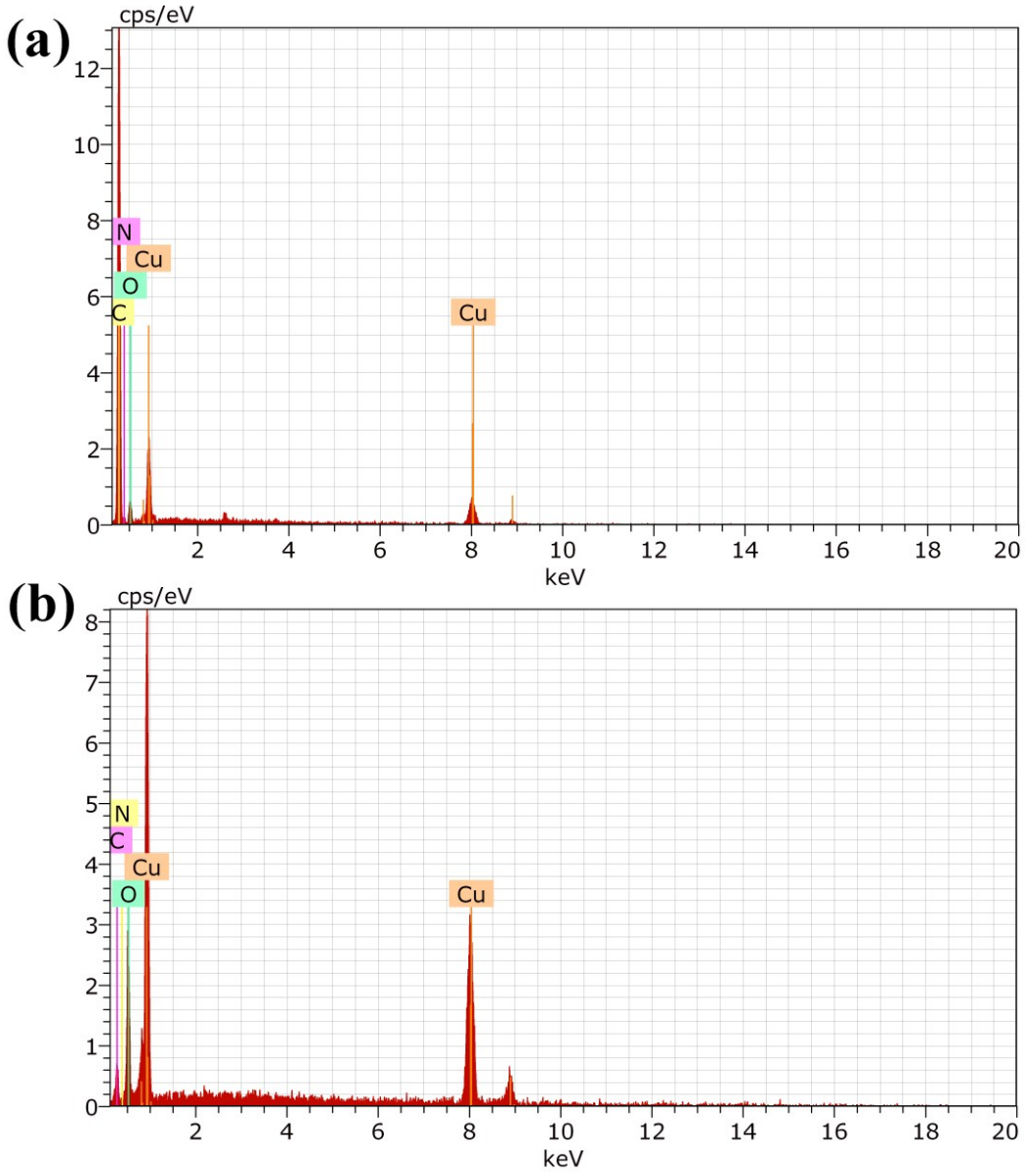


Figure S12. EDAX spectra of (a) CuNPs-1 and (b) CuONPs-4.

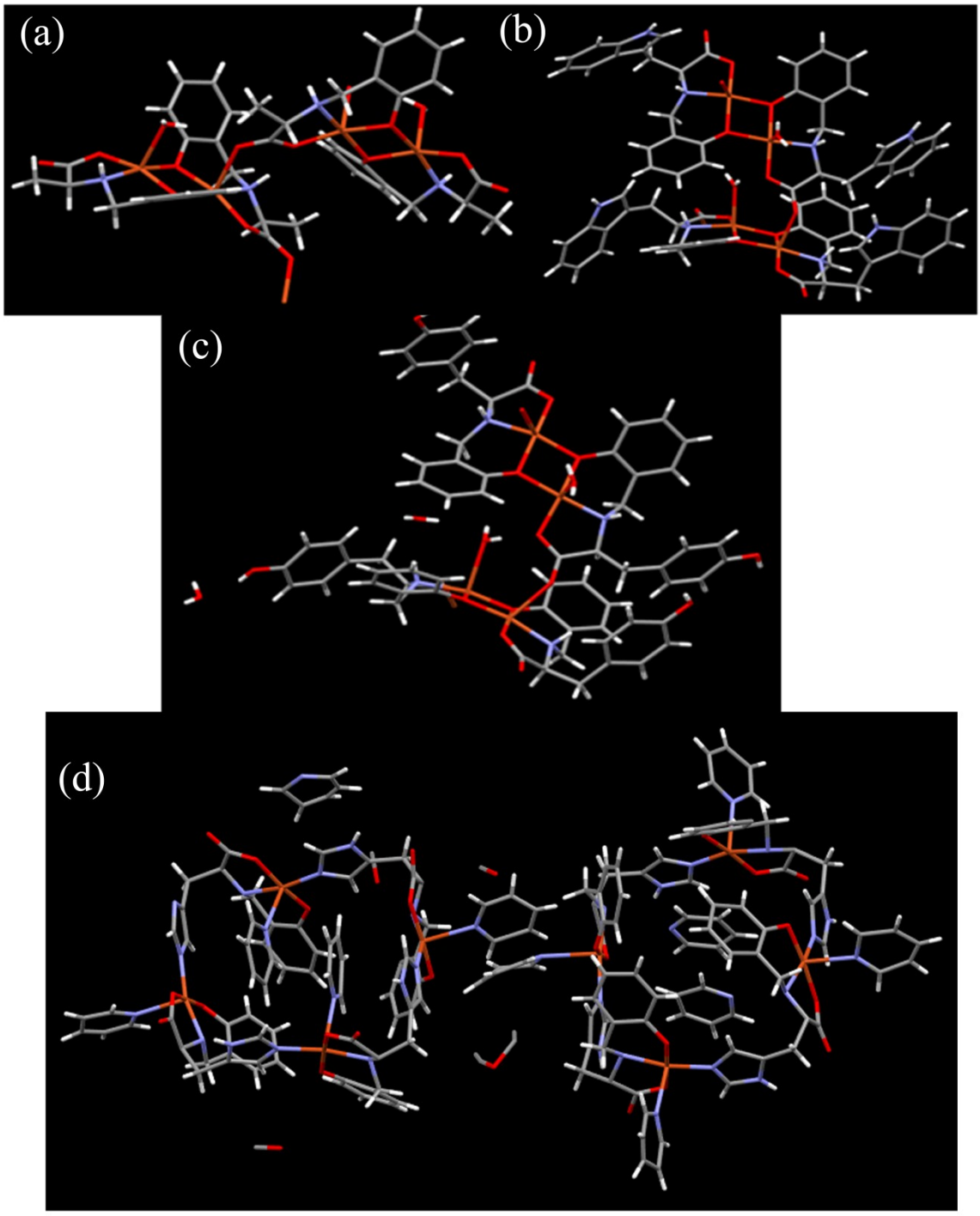


Figure S13. Molecular packing of (a) Cu-COP-1 (CCDC No. 133087), (b) Cu-COP-5 (CCDC No. 209715), (c) Cu-COP-6 (CCDC No. 209714) and (d) Cu-COP-7 (CCDC No. 197602) in solid state.

Table S1. Atomic weight percentage of Cu/CuONPs obtained from XPS analysis.

CuNPs-1	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %

C1s	286.62	4.20	78104.71	81.57
N1s	401.30	4.11	13099.65	8.07
O1s	533.98	4.54	22406.13	9.17
Cu2p	935.73	6.09	17999.53	1.18

CuNPs-5	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %
C1s	289.08	7.27	556227.95	73.63
N1s	402.08	7.72	37517.10	2.76
O1s	537.08	8.01	486249.09	21.97
Cu2p	938.08	9.33	314433.41	1.64

CuONPs-2	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %
C1s	939.76	5.87	2823127.13	23.51
N1s	401.16	0.54	1121.04	0.72
O1s	536.81	4.69	1048264.88	54.32
Cu2p	939.76	5.87	2823127.13	23.51

CuONPs-3	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %
C1s	287.23	2.51	15598.50	15.86
N1s	401.67	0.76	1829.15	1.10
O1s	531.96	2.13	108172.39	43.05
Cu2p	935.26	3.28	626315.17	39.99

CuONPs-4	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %
C1s	286.40	3.15	12199.88	11.73
N1s	400.99	0.30	687.03	0.39
O1s	531.18	3.08	121812.44	45.85
Cu2p	934.90	3.78	695901.47	42.02

CuONPs-7	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %
C1s	286.22	3.33	109236.79	13.34
N1s	400.86	0.46	986.68	0.82
O1s	531.35	3.33	989035.13	47.28
Cu2p	935.01	4.05	3383743.20	39.38

Cu/CuONPs-6	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %
C1s	285.98	2.77	149377.78	14.66
N1s	401.42	0.51	1012.24	0.91
O1s	531.09	2.99	1222401.21	46.96
Cu2p	934.46	3.94	4105417.78	38.38

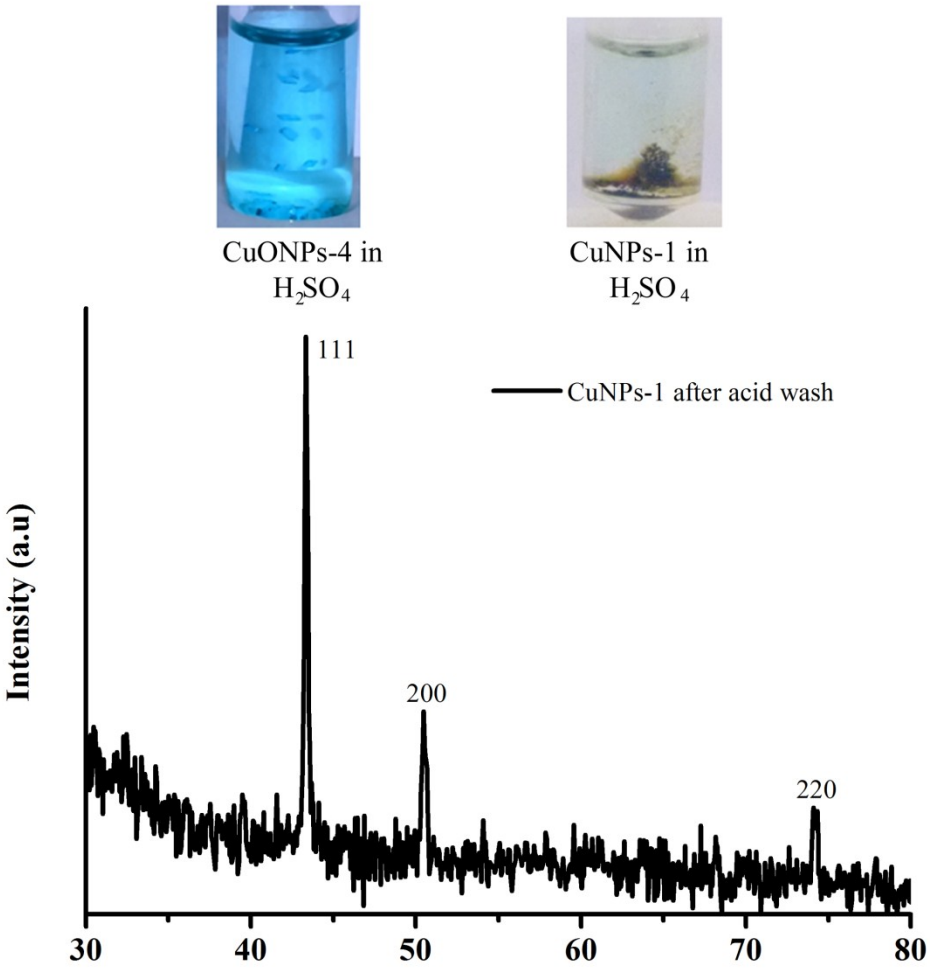
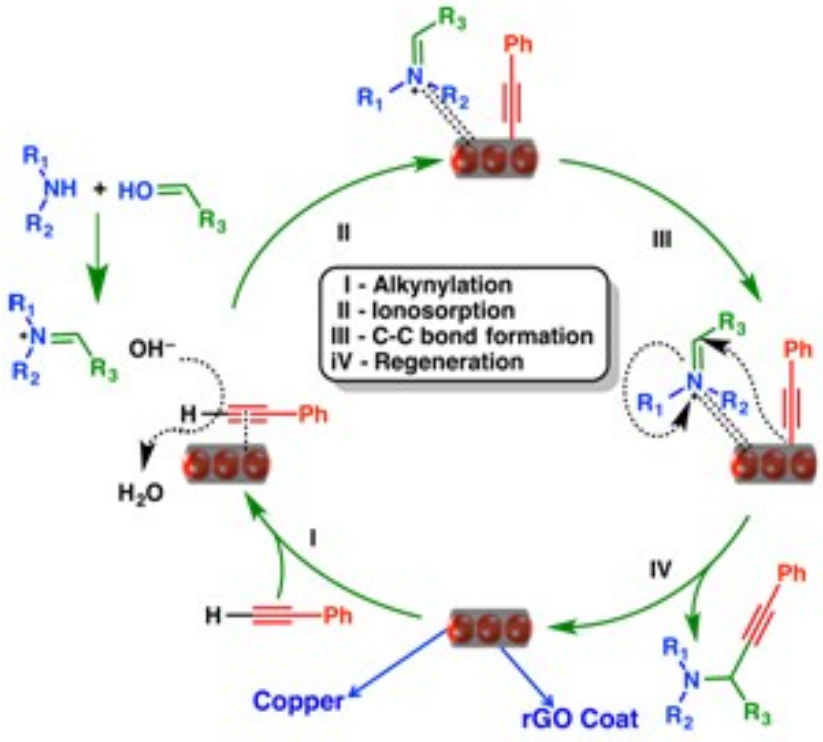
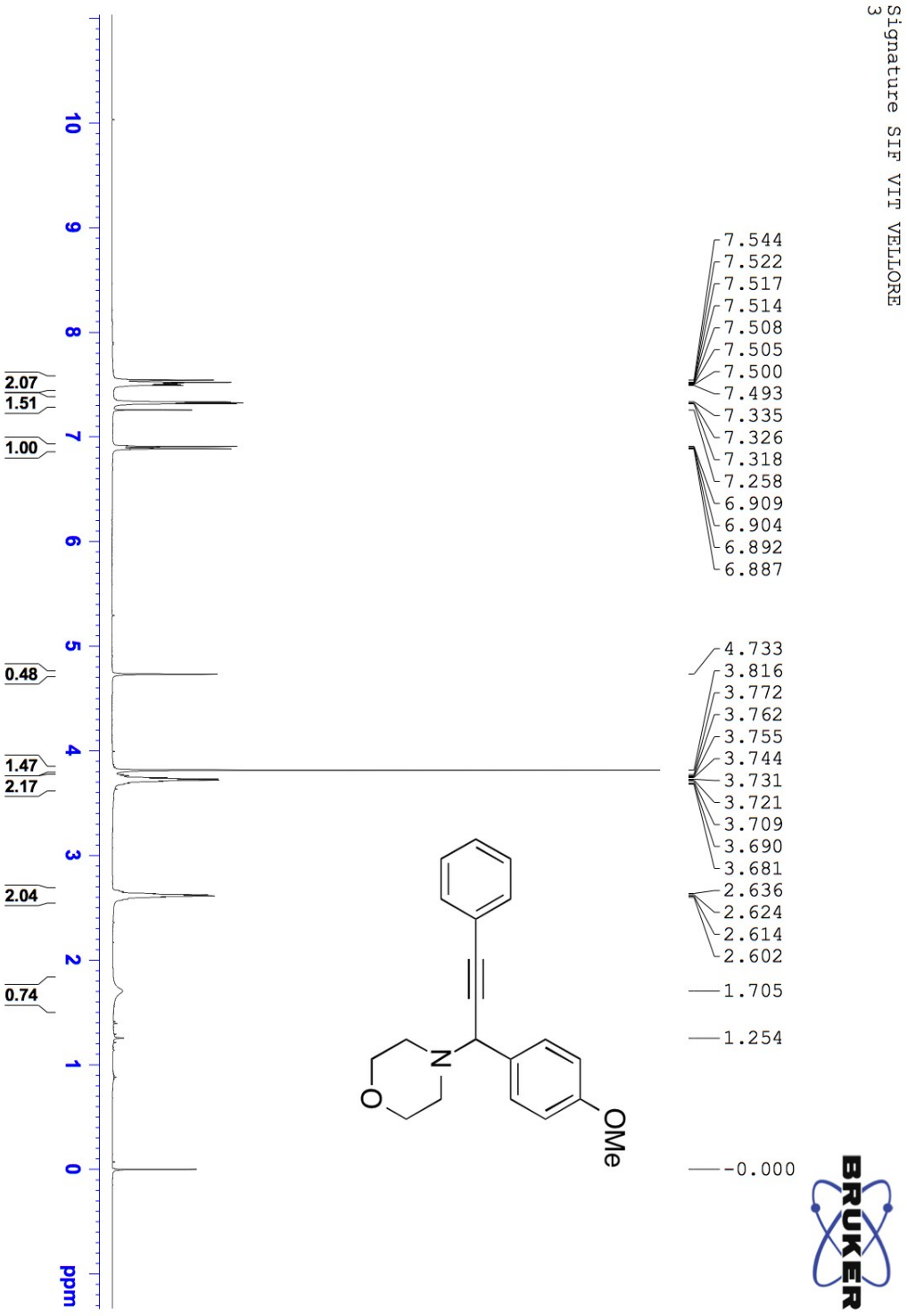


Figure S14. Digital images of CuONPs-4 and CuNPs-1 and PXRD pattern of CuNPs-1 after immersing in concentrated H_2SO_4 (10 M).



Scheme S1. The first step in A3 coupling is deprotonation of acetylene. Chelation of acetylene with N-rGO encapsulated CuNPs-1 might increase the labile nature of C-H bond in acetylene, thus weak base in the reaction medium could deprotonate the proton. The resulting iminium ion might get ionosorped on the surface of N-rGO encapsulated CuNPs-1. Further, electron transfer and C-C bond formation results in the formation of product and the regeneration of catalyst.

Figure S15. [1]H-NMR spectra of propargylamines obtained using CuNPs-1 catalyst.



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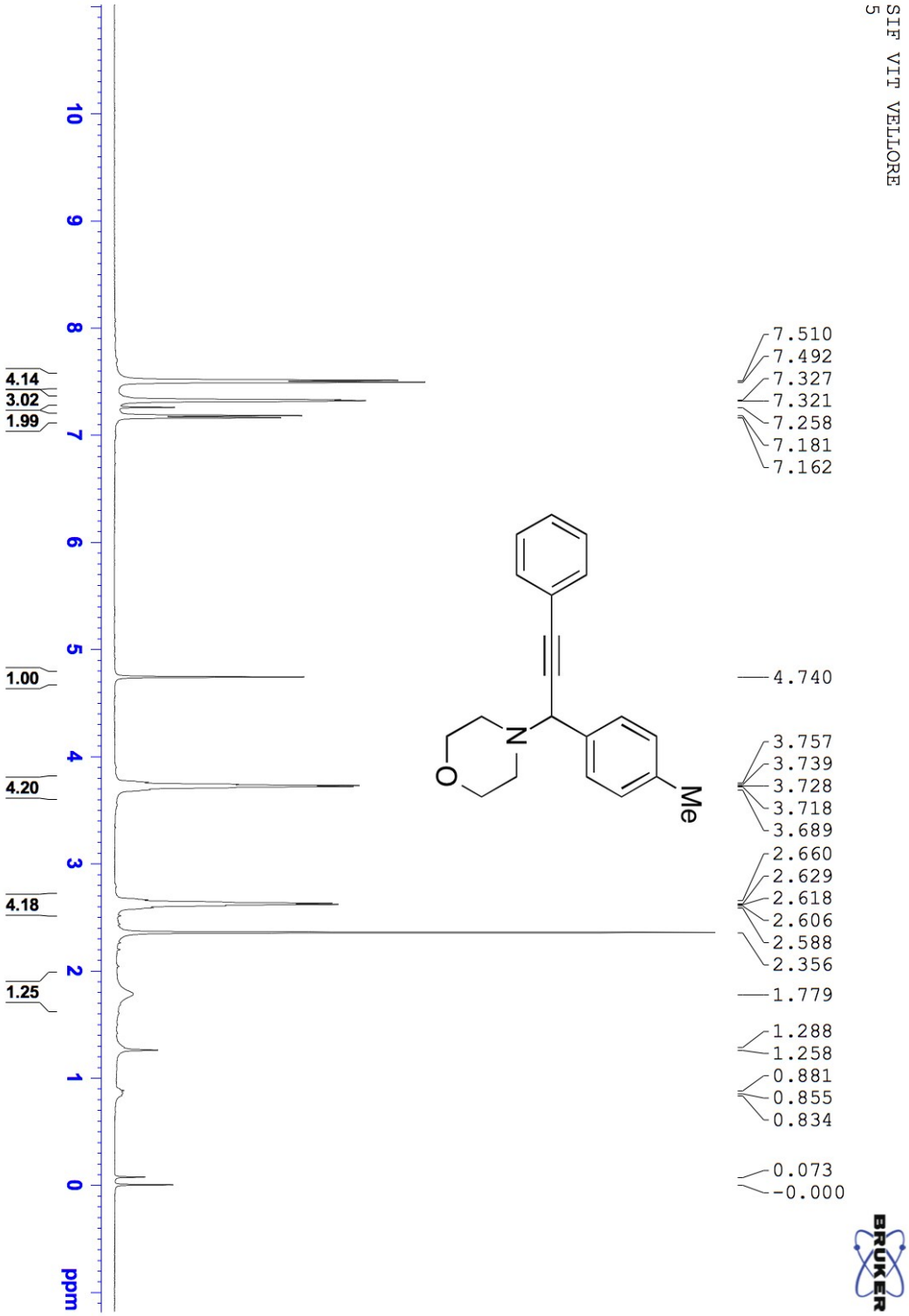
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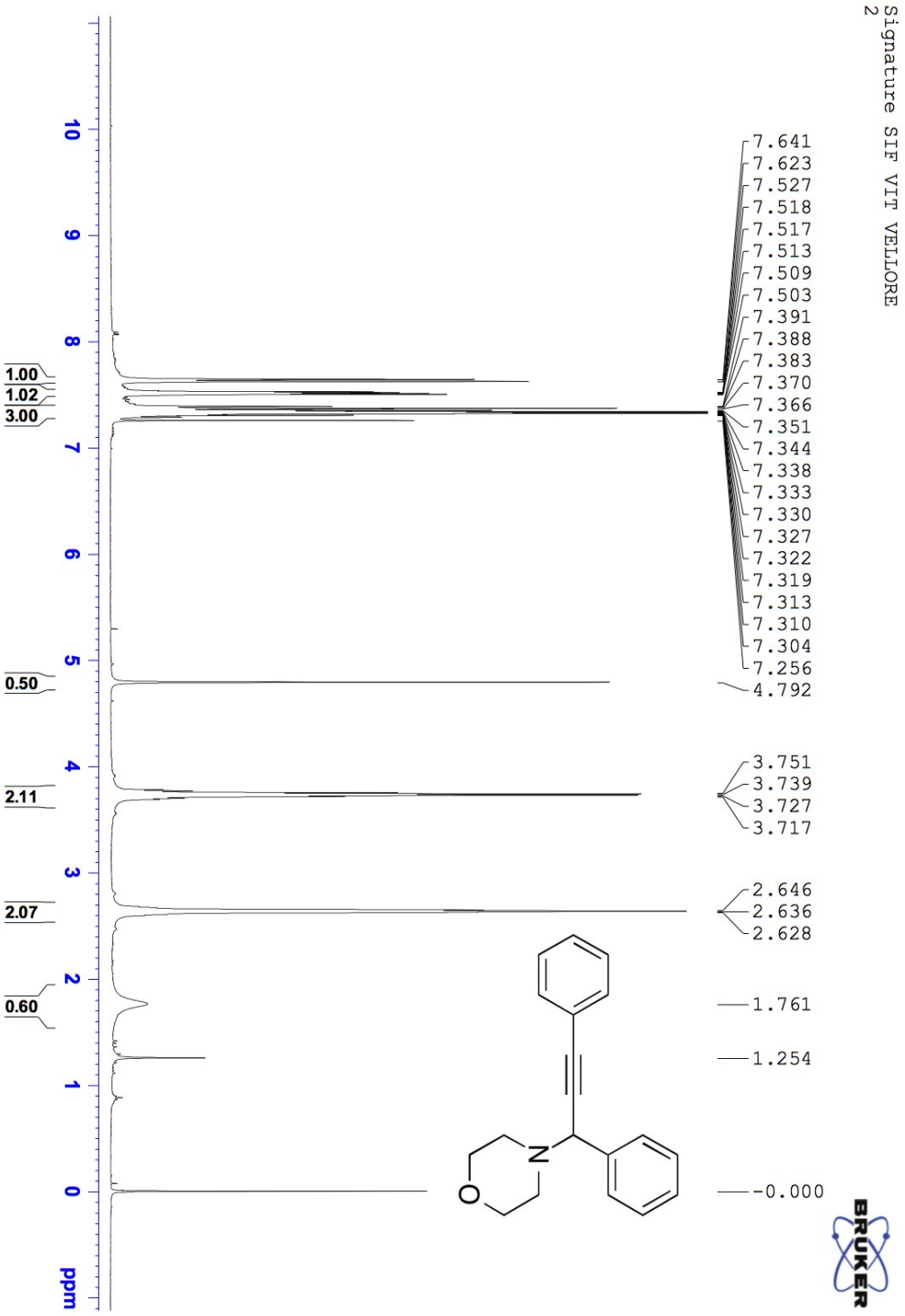
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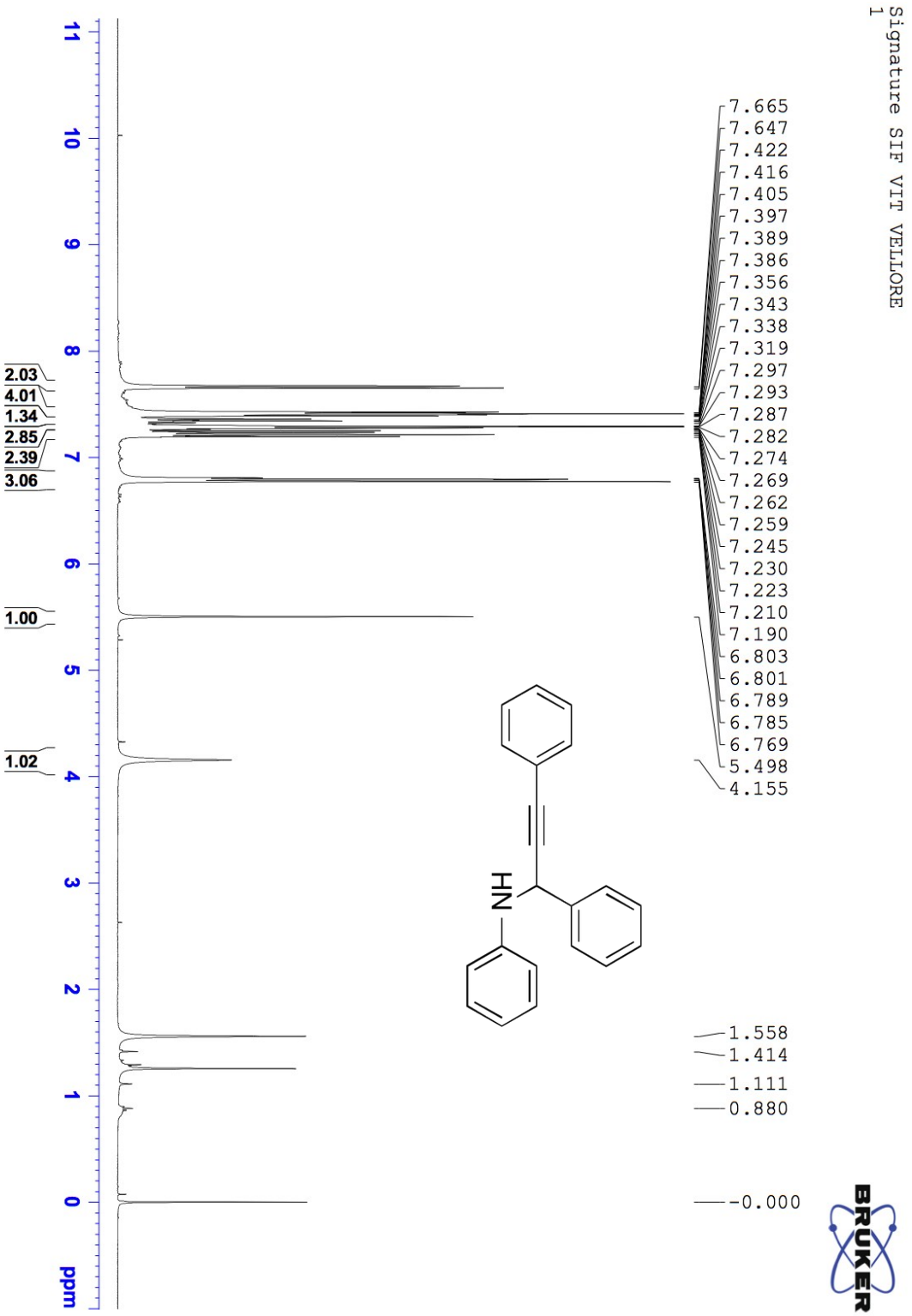
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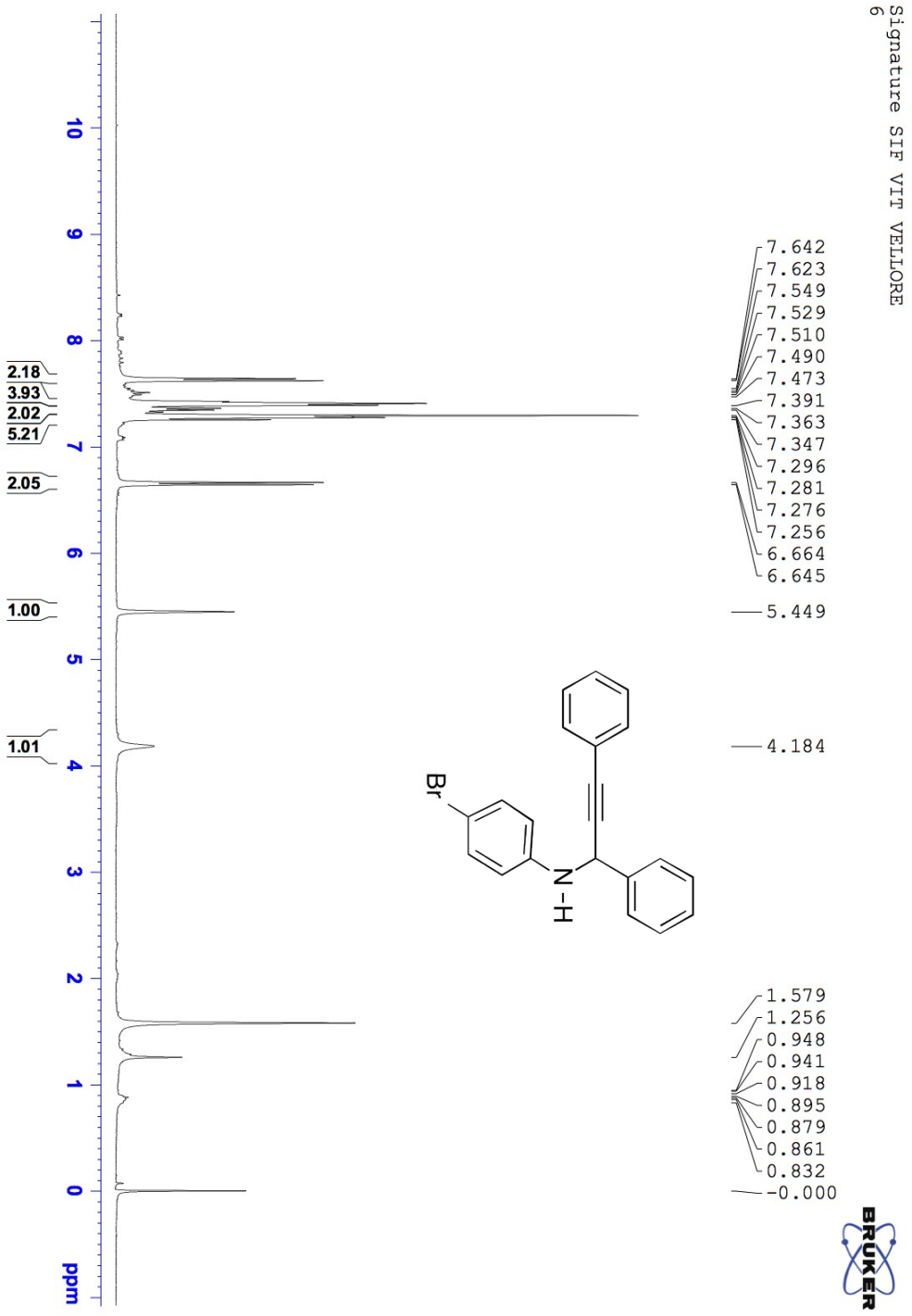
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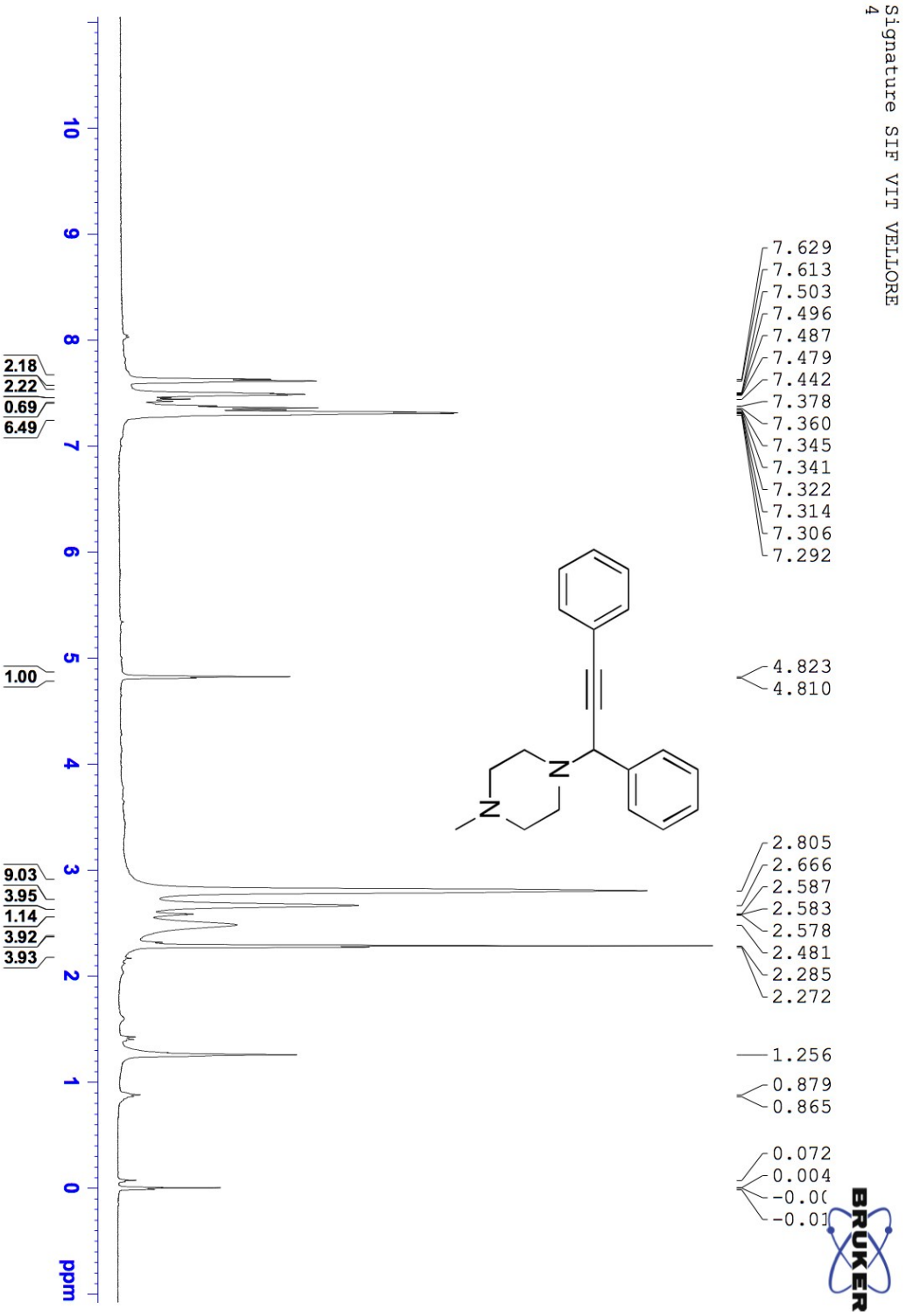
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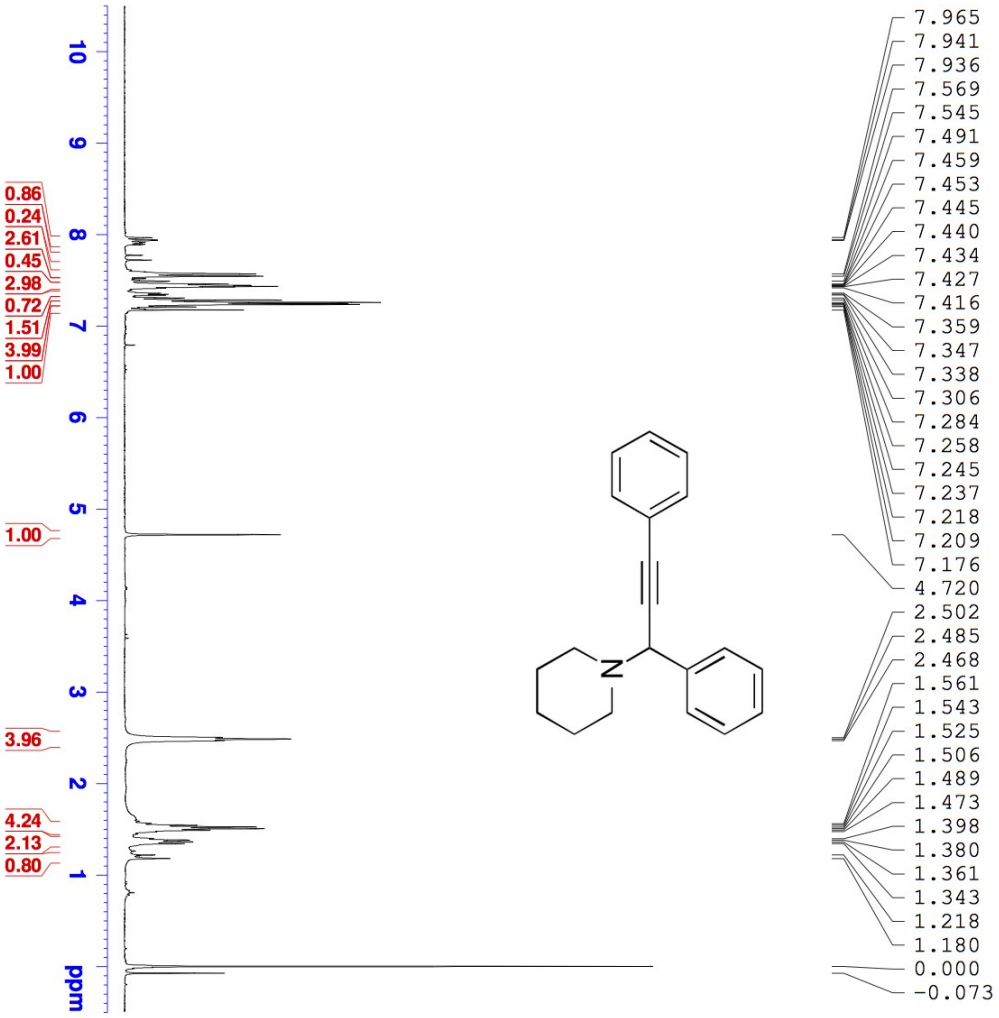
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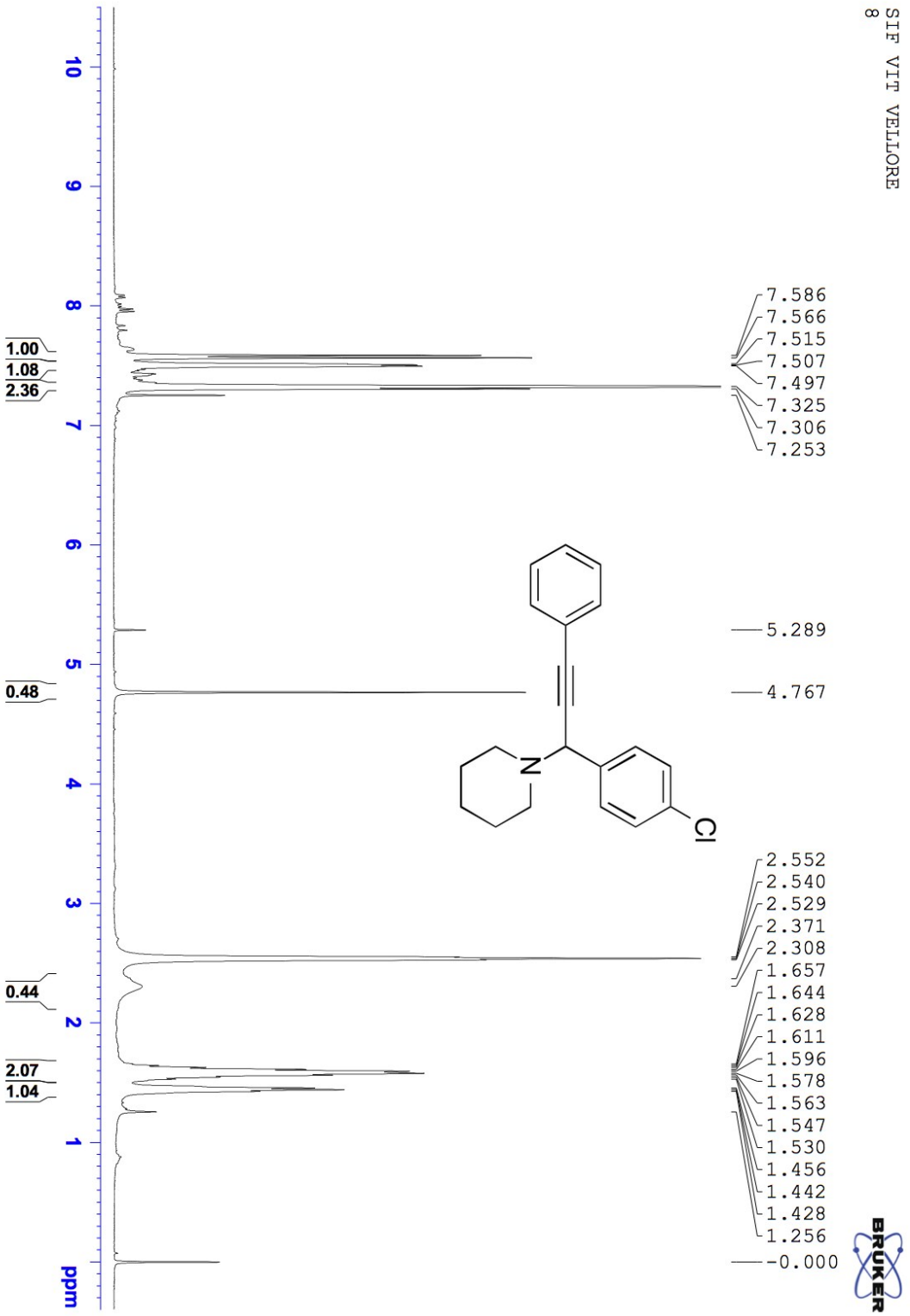
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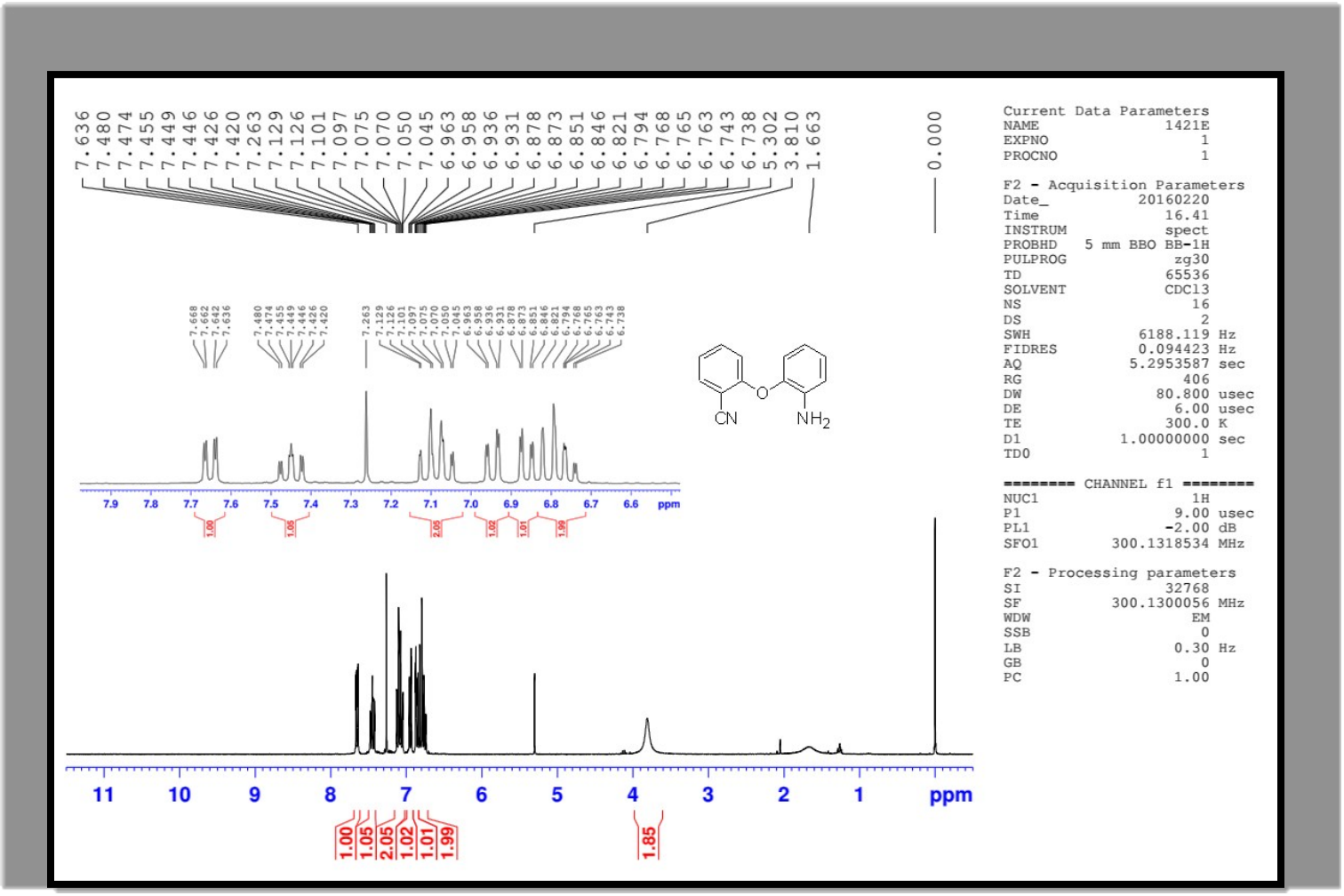
Figure S16. ^{1}H-NMR spectra of products obtained using CuONPs-4 catalyst in the nitroarene reduction.



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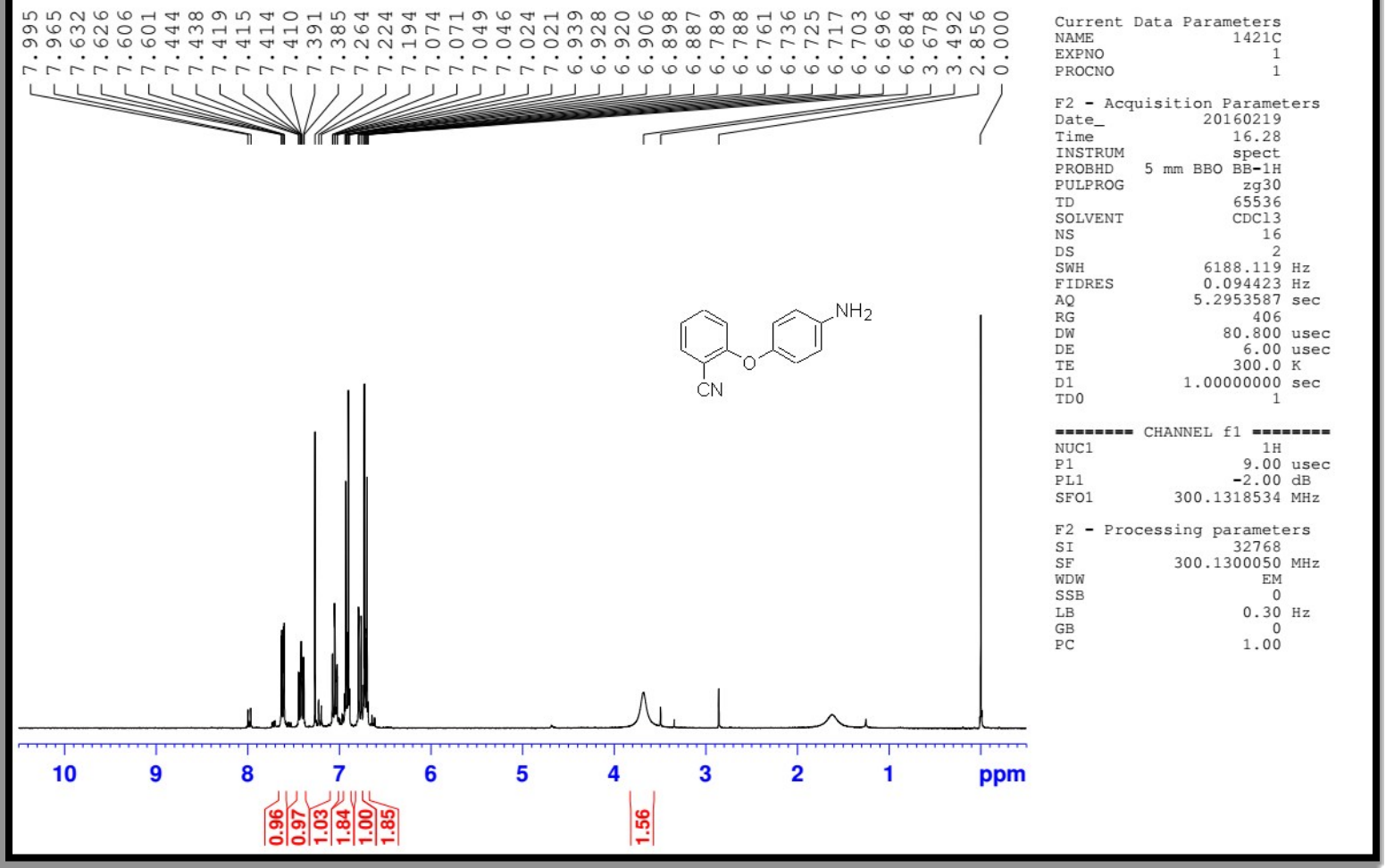
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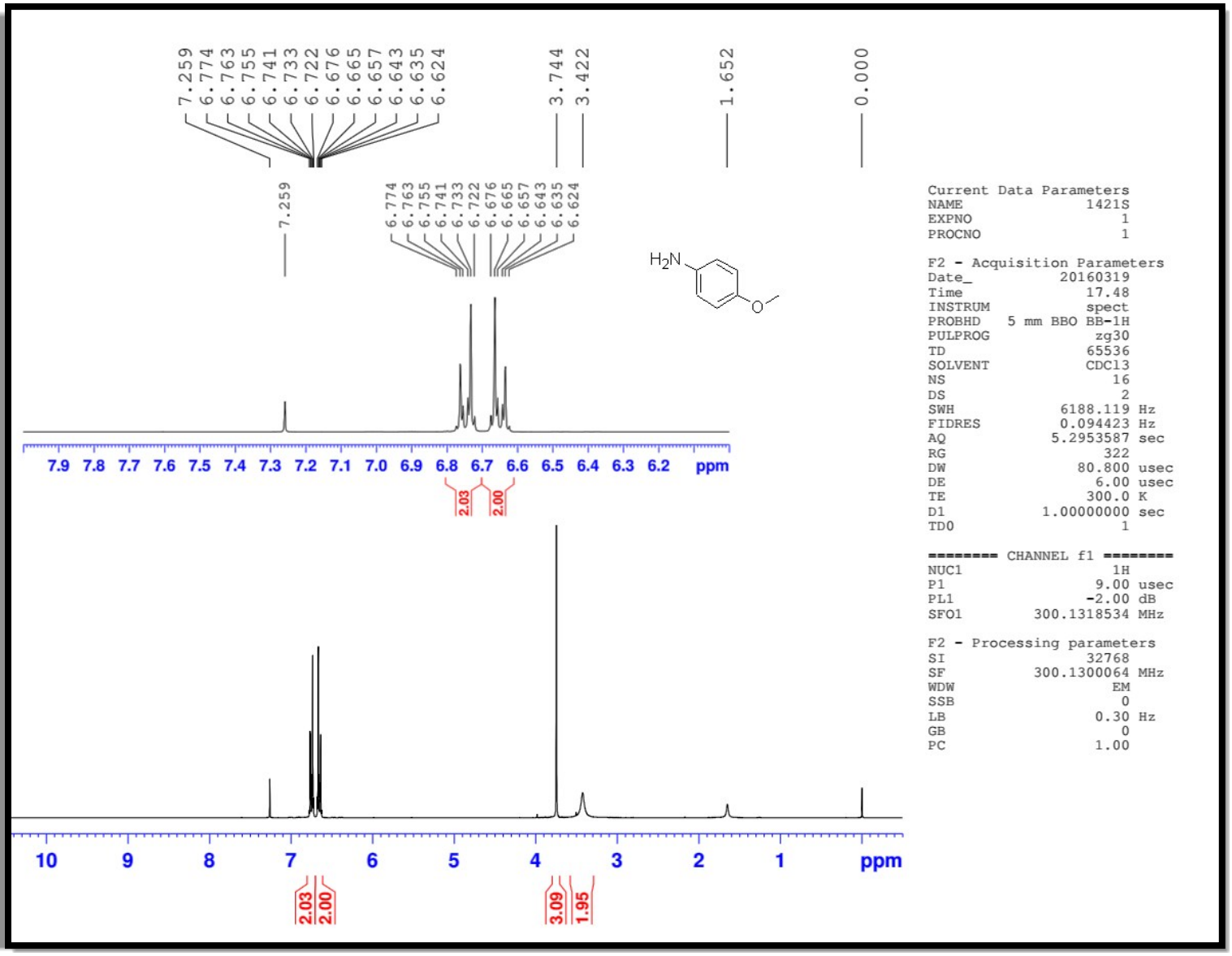

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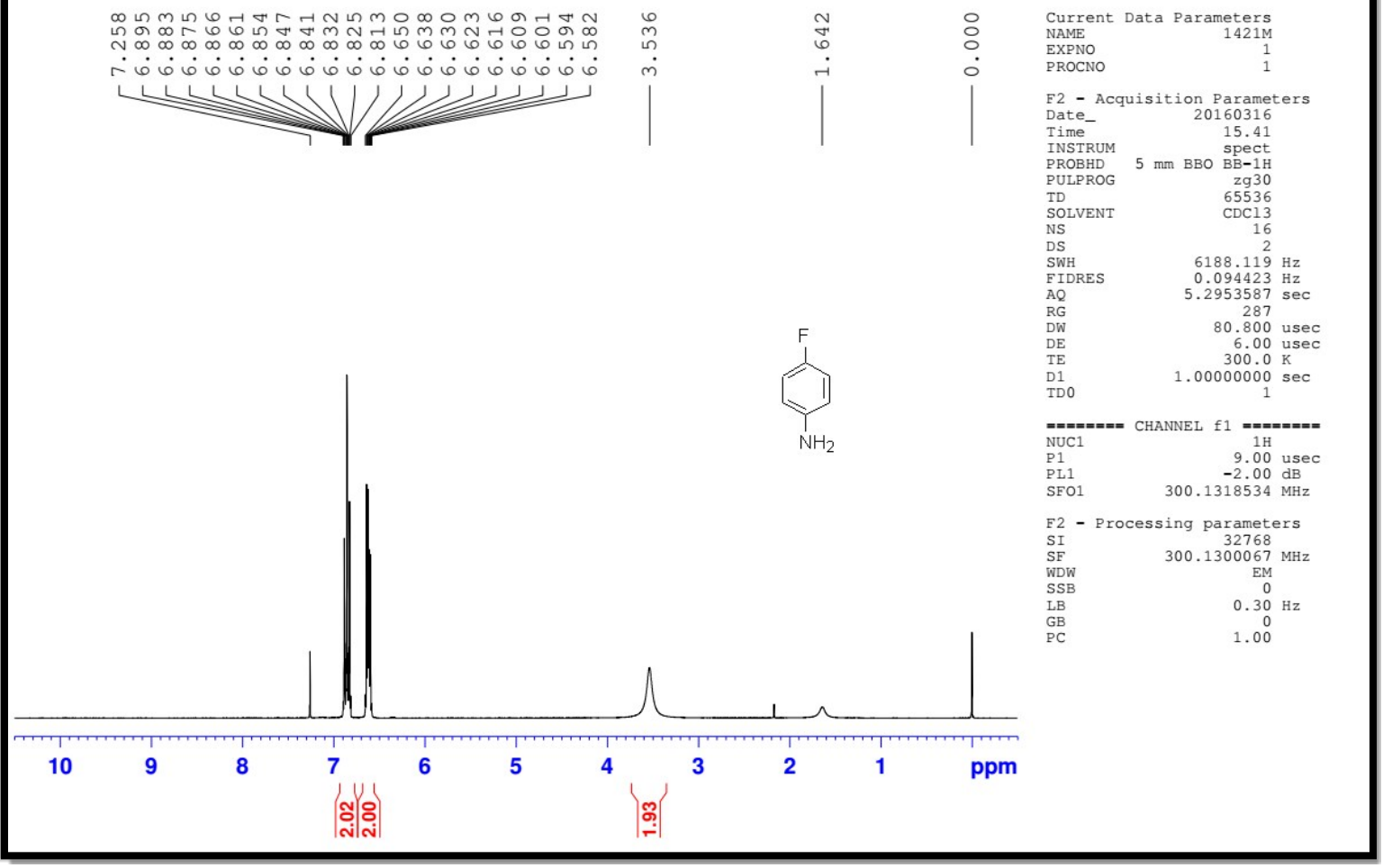
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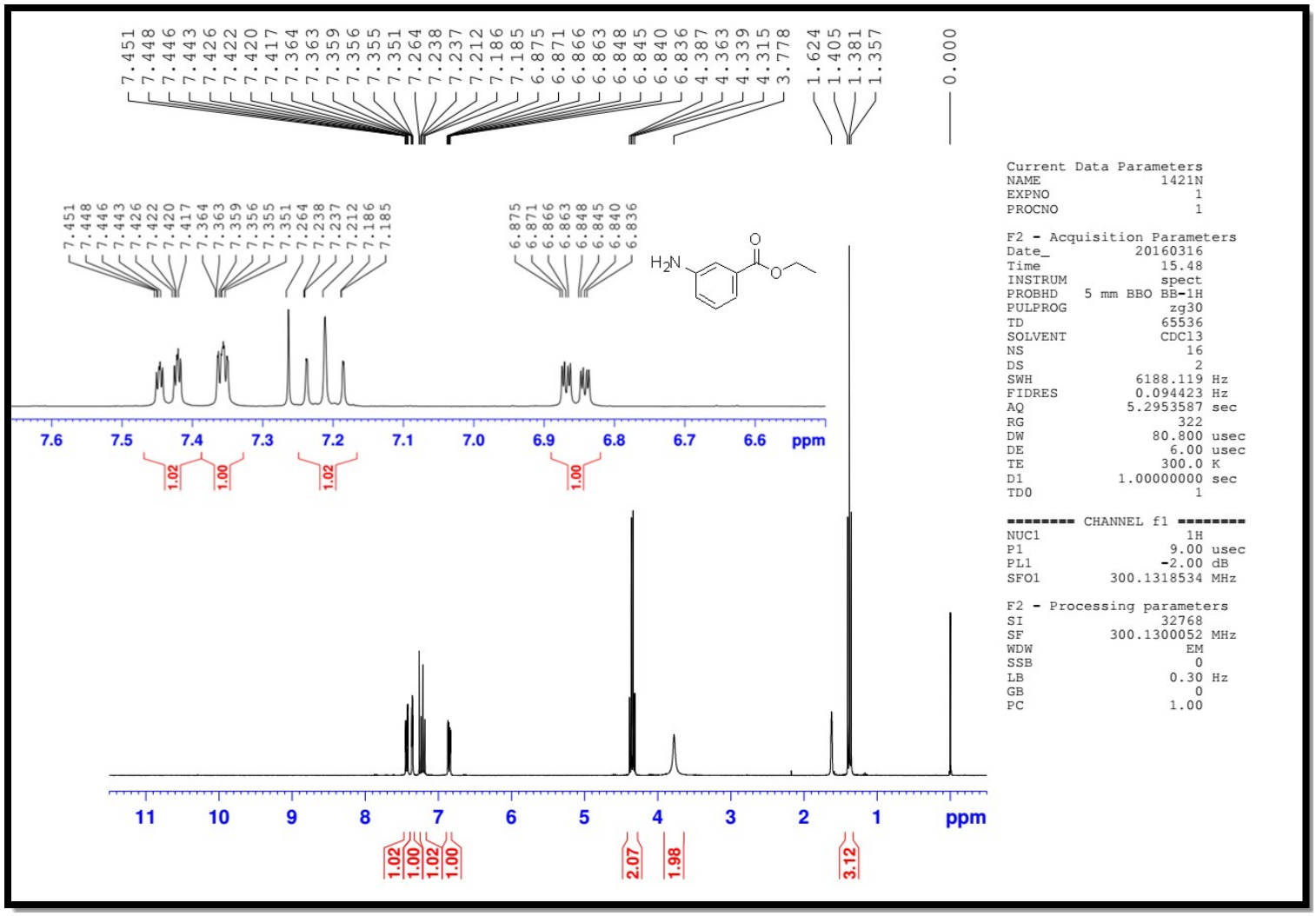
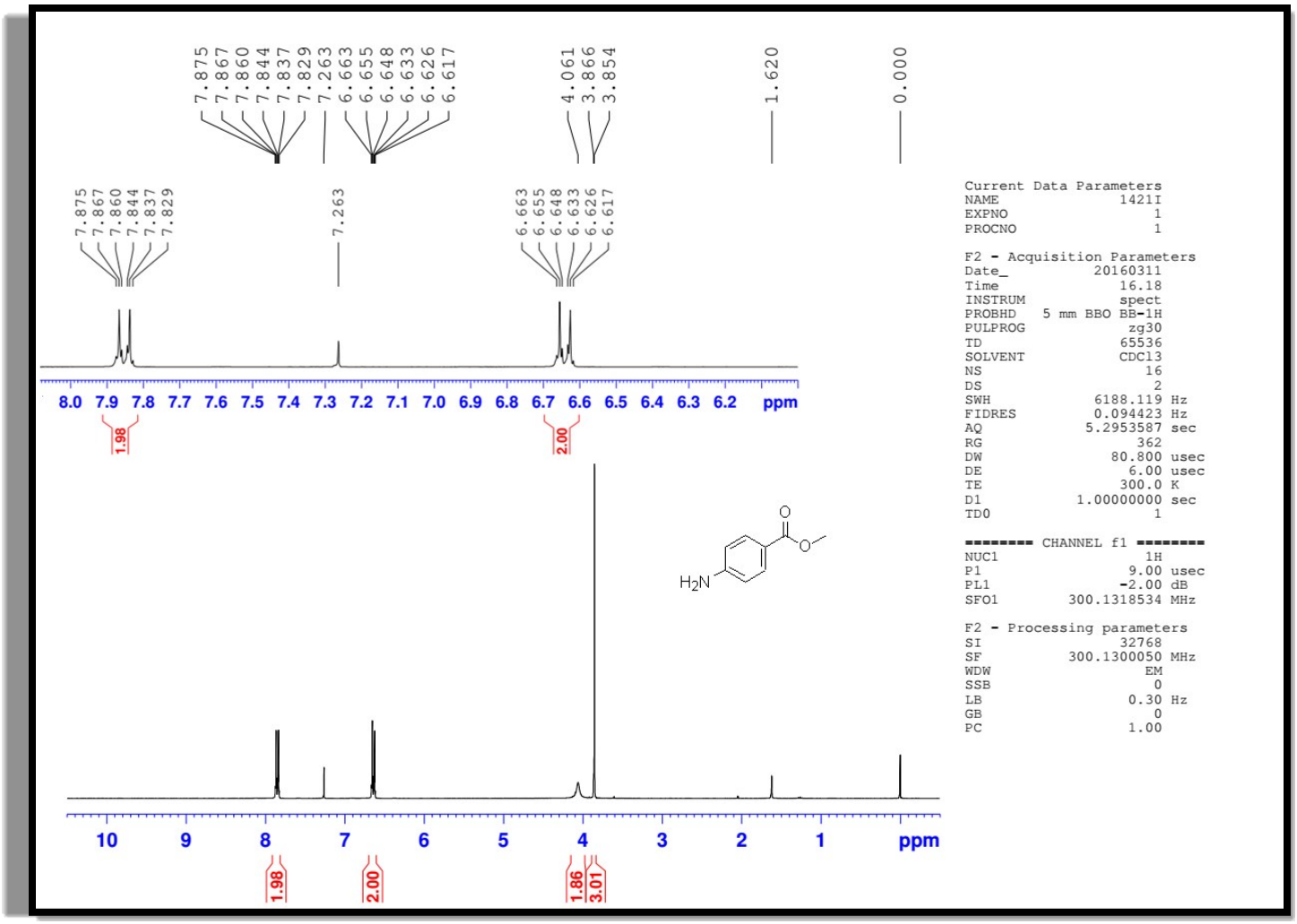
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 32768
SF 300.1300067 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

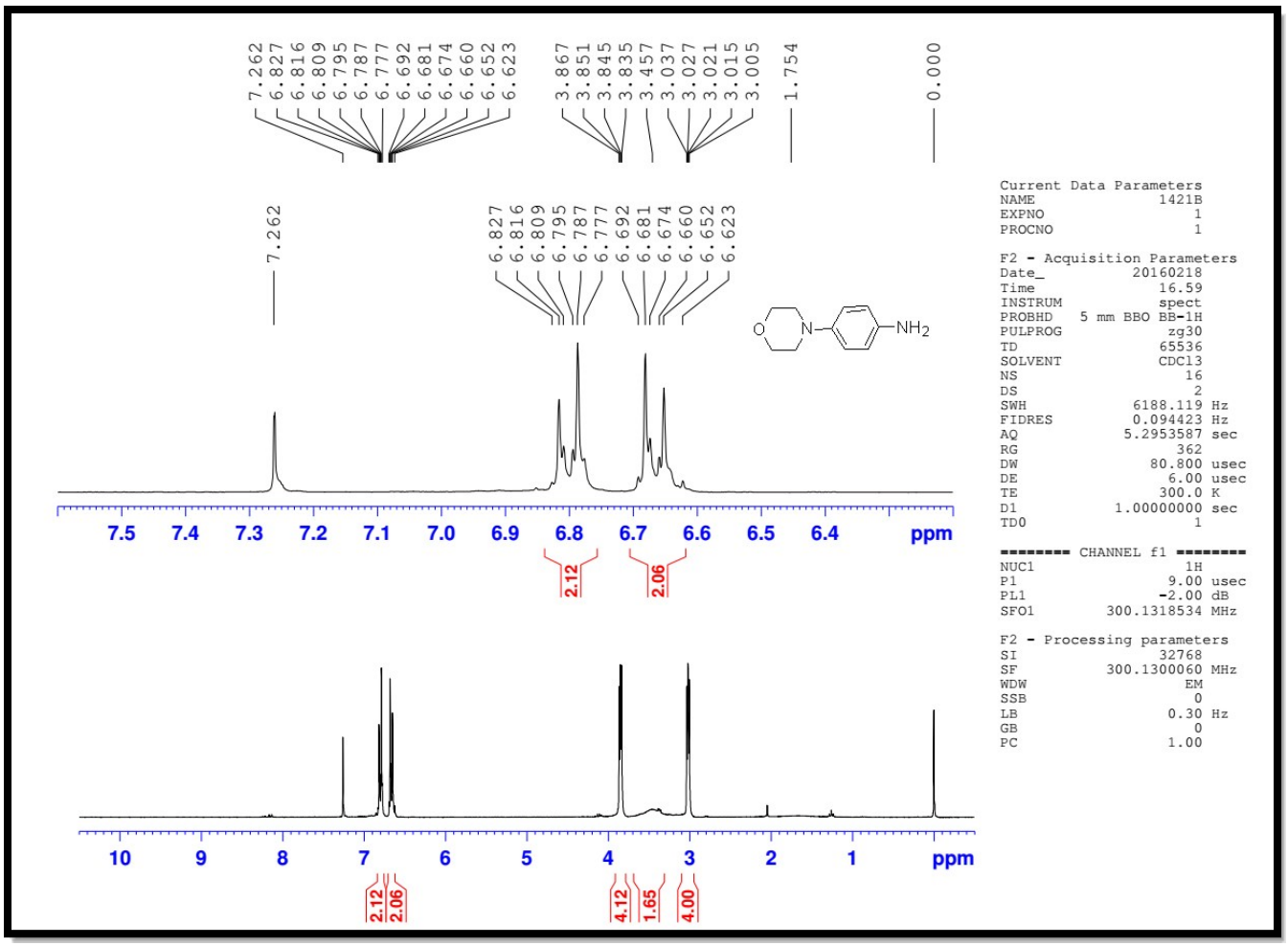
Entry-4


7.451
7.448
7.446
7.443
7.426
7.422
7.420
7.417
7.364
7.363
7.359
7.356
7.355
7.351
7.264
7.238
7.237
7.212
7.186
7.185
6.875
6.871
6.866
6.863
6.848
6.845
6.840
6.836
4.387
4.363
4.339
4.315
3.778
1.624
1.405
1.381
1.357
0.000
H2N
O
O
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
ppm
1.02
1.00
1.02
1.00
11
10
9
8
7
6
5
4
3
2
1
ppm
1.02
1.00
1.02
1.00
2.07
1.98
3.12
Current Data Parameters
NAME 1421N
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160316
Time 15.48
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 322
DW 80.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 32768
SF 300.1300052 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

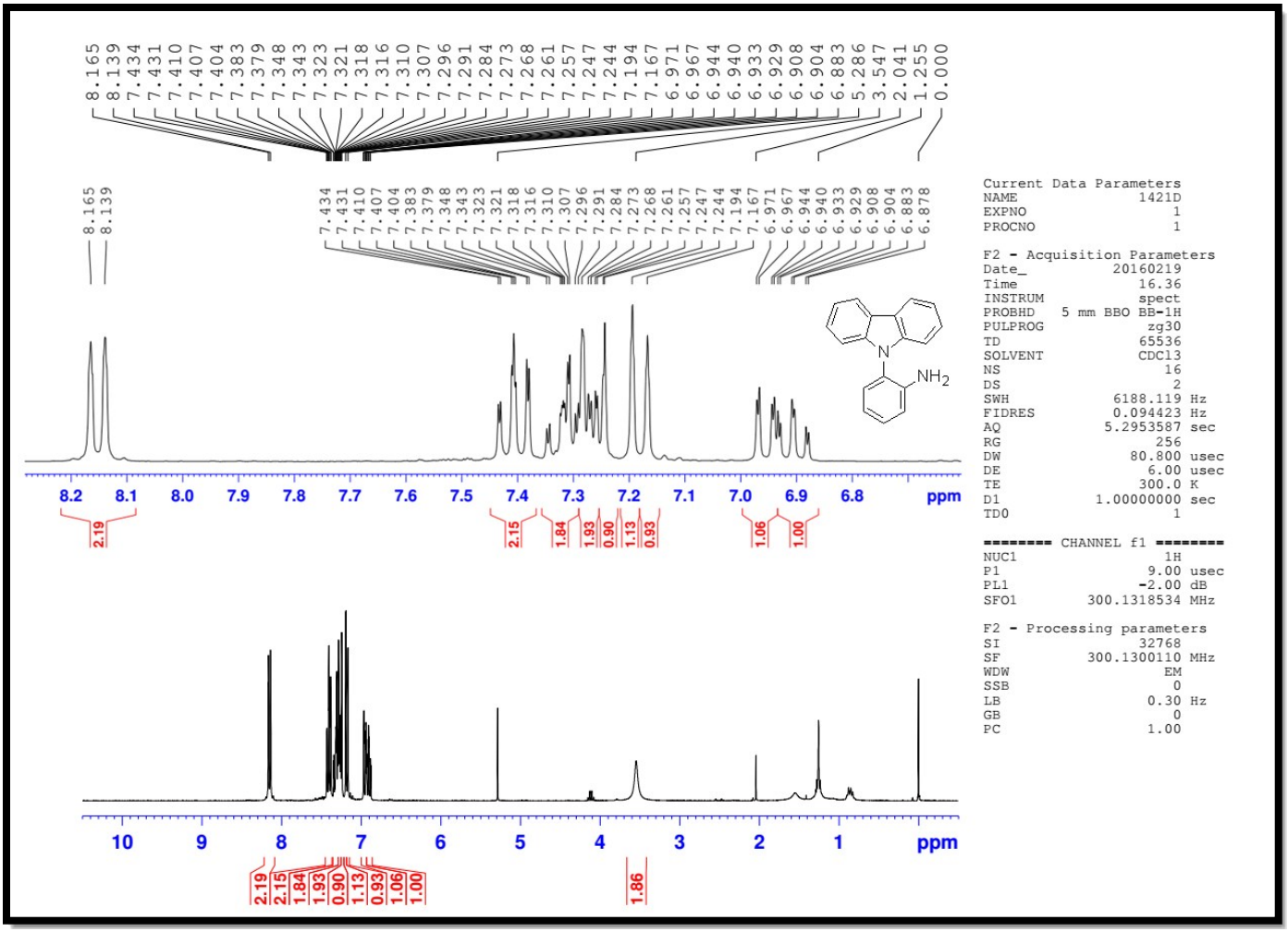
Entry-5


7.875
7.867
7.860
7.844
7.837
7.829
7.263
6.663
6.655
6.648
6.633
6.626
6.617
4.061
3.866
3.854
1.620
0.000
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 ppm
1.98
2.00
10 9 8 7 6 5 4 3 2 1 ppm
1.98
2.00
1.86
3.01
H2N
O
O
Current Data Parameters
NAME 1421I
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160311
Time 16.18
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 362
DW 80.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 32768
SF 300.1300050 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

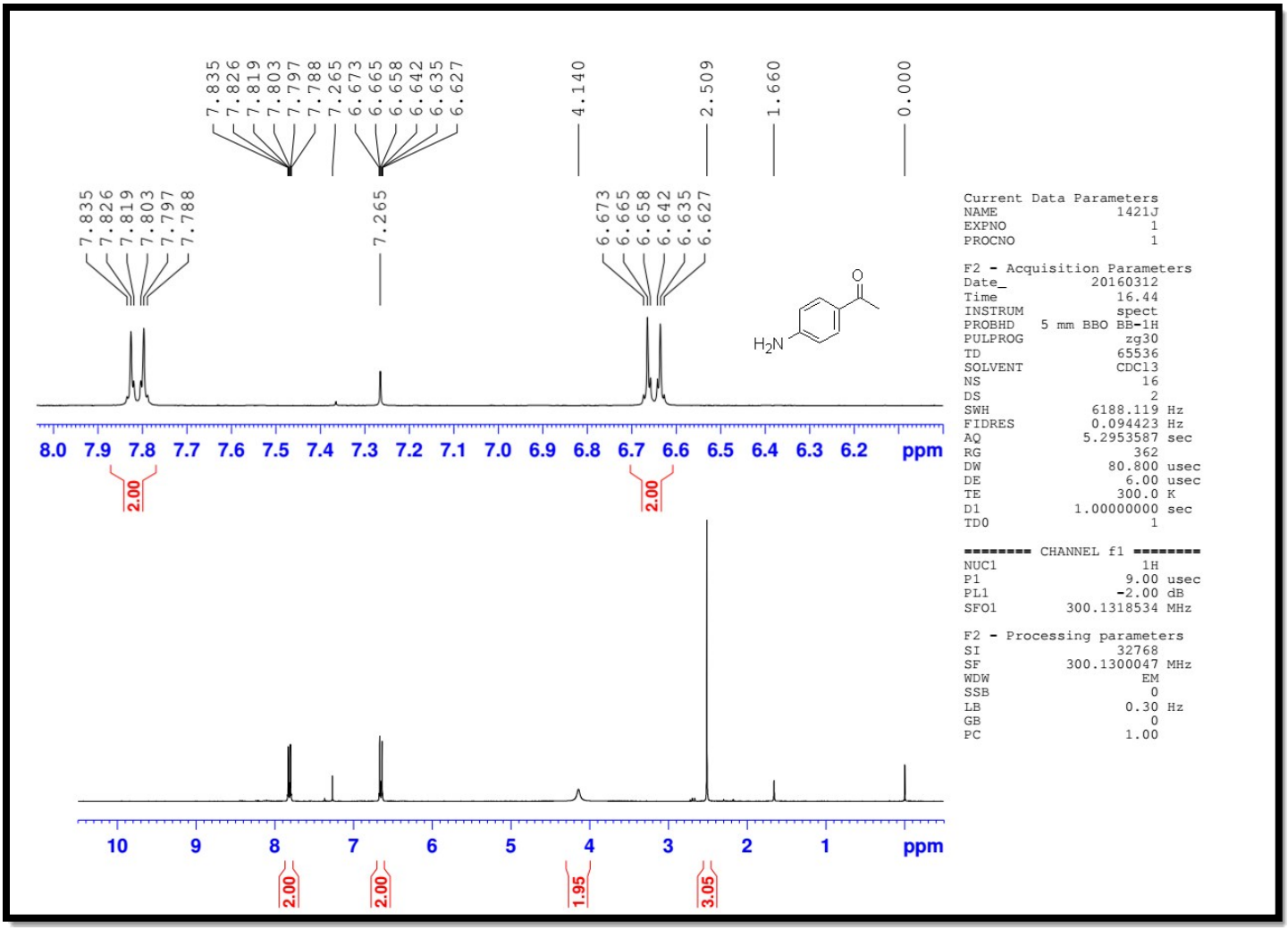
Entry-6


7.262
6.827
6.816
6.809
6.795
6.787
6.777
6.692
6.681
6.674
6.660
6.652
6.623
3.867
3.851
3.845
3.835
3.457
3.037
3.027
3.021
3.015
3.005
1.754
0.000
NH2
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 ppm
2.12
2.06
10 9 8 7 6 5 4 3 2 1 ppm
2.12
2.06
4.12
1.65
4.00
Current Data Parameters
NAME 1421B
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160218
Time 16.59
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 362
DW 80.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 32768
SF 300.1300060 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

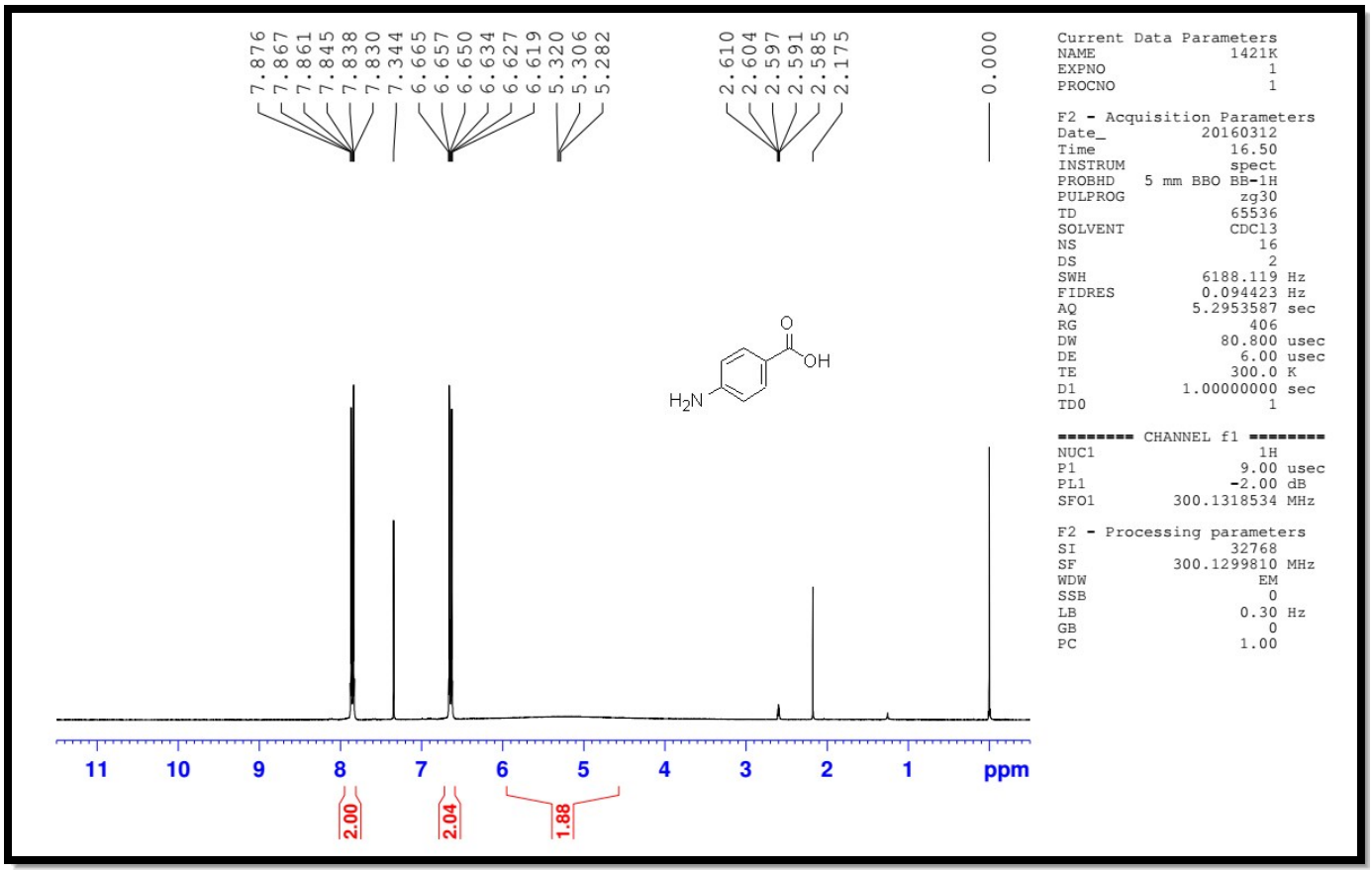
Entry-7


8.165
8.139
7.434
7.431
7.410
7.407
7.404
7.383
7.379
7.348
7.343
7.323
7.321
7.318
7.316
7.310
7.307
7.296
7.291
7.284
7.273
7.268
7.261
7.257
7.247
7.244
7.194
7.167
6.971
6.967
6.944
6.940
6.933
6.929
6.908
6.904
6.883
5.286
3.547
2.041
1.255
0.000
NH2
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 ppm
2.19 2.15 1.84 1.93 0.90 1.13 0.93 1.06 1.00
10 9 8 7 6 5 4 3 2 1 ppm
2.19 2.15 1.84 1.93 0.90 1.13 0.93 1.06 1.00 1.86
Current Data Parameters
NAME 1421D
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160219
Time 16.36
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 256
DW 80.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 32768
SF 300.1300110 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

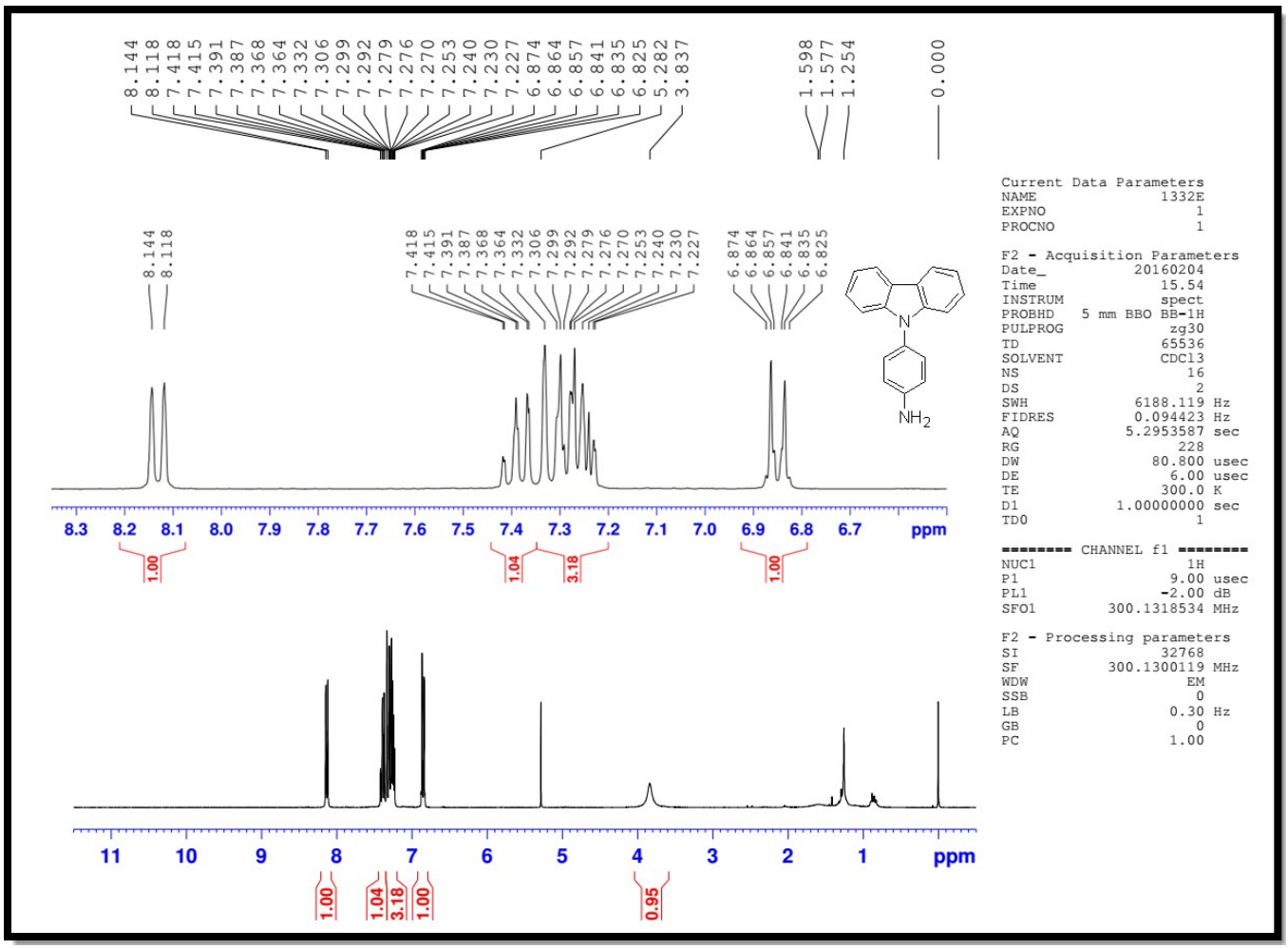
Entry-8


7.835
7.826
7.819
7.803
7.797
7.788
7.265
6.673
6.665
6.658
6.642
6.635
6.627
4.140
2.509
1.660
0.000
O
H2N
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 ppm
2.00
2.00
10 9 8 7 6 5 4 3 2 1 ppm
2.00
2.00
1.95
3.05
Current Data Parameters
NAME 1421J
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160312
Time 16.44
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 362
DW 80.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 32768
SF 300.1300047 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Entry-9


7.876
7.867
7.861
7.845
7.838
7.830
7.344
6.665
6.657
6.650
6.634
6.627
6.619
5.320
5.306
5.282
2.610
2.604
2.597
2.591
2.585
2.175
0.000
O
OH
H2N
11
10
9
8
7
6
5
4
3
2
1
ppm
2.00
2.04
1.88
Current Data Parameters
NAME 1421K
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160312
Time 16.50
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 406
DW 80.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 32768
SF 300.1299810 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Entry-10


8.144
8.118
7.418
7.415
7.391
7.387
7.368
7.364
7.332
7.306
7.299
7.292
7.279
7.276
7.270
7.253
7.240
7.230
7.227
6.874
6.864
6.857
6.841
6.835
6.825
5.282
3.837
1.598
1.577
1.254
0.000
NH2
8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 ppm
1.00
1.04
3.18
1.00
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
1.04
3.18
1.00
0.95
Current Data Parameters
NAME 1332E
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160204
Time 15.54
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 228
DW 80.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 9.00 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 32768
SF 300.1300119 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Entry-11