

Rh(I)-Catalyzed Direct Arylation of Azines

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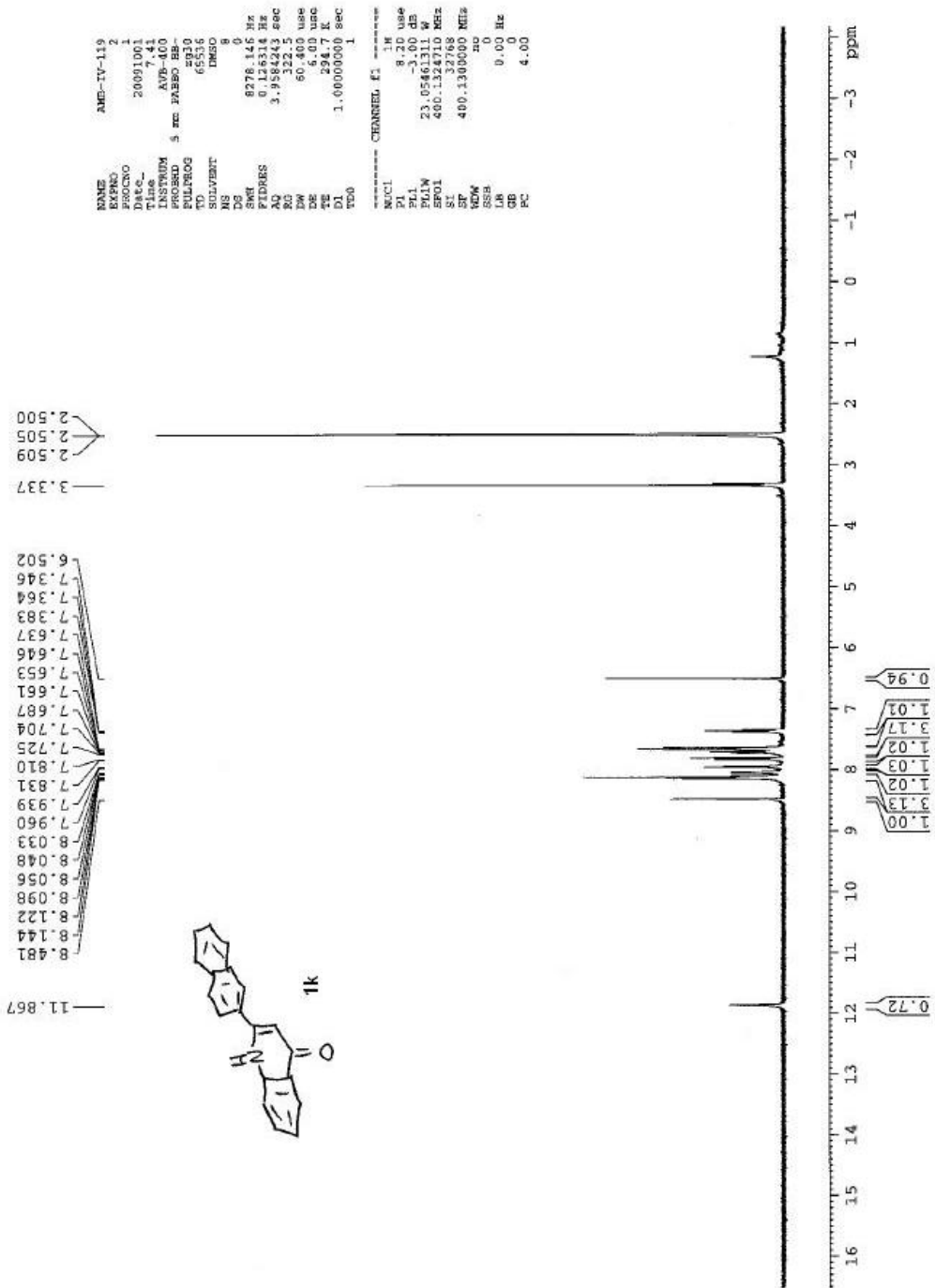
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General Procedures. All reagents were degassed and handled under an inert nitrogen atmosphere using syringe and cannula techniques. Unless otherwise noted, all organic preparations were carried out in flame- or oven-dried glassware under a nitrogen atmosphere and all catalytic arylation reactions were assembled in a nitrogen-filled inert atmosphere box. Flash column chromatography was carried out using hexanes/ethyl acetate or dichloromethane/methanol gradients. ^1H NMR chemical shifts are reported in ppm relative to TMS as an internal standard ($\text{Si}(\text{CH}_3)_4$, 0.00 ppm) in CDCl_3 unless otherwise noted, and coupling constants are reported in Hz. Reported tabular yields are the average of at least two experimental runs; yields reported in the following experimental procedures might vary slightly from those found in the tables. Experimental procedures and full analytical data for compounds **1a – 1f**, **1h – 1j**, **1o – 1x** have been previously reported.⁹

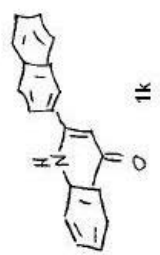
Materials. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. $[\text{RhCl}(\text{CO})_2]_2$ was purchased from commercial suppliers and stored in the glove box. All liquid reagents were thoroughly degassed using three freeze-pump-thaw cycles prior to introduction to the glove box. The 1,4-dioxane and toluene were obtained were dried over alumina under a nitrogen atmosphere prior to introduction to the glove box.

AVS-400 ZBO Proton starting parameters. 6/11/03 RN



150.33
141.09
134.03
133.03
132.33
131.97
129.15
129.12
128.18
127.99
127.63
127.49
125.40
125.24
125.01
123.76
119.21
108.23

AVB-400 ZBO Carbon Starting Parameters 6/11/03 MW



NAME AMB-IV-152
 EXPNO 2
 PROCNO 1
 Date_ 20091011
 Time 14:49
 INSTRUM AVB-400
 PROBHD 5 mm FATHO BB-
 PULPROG zgpg30
 TD 65536
 SFO1 100.6228298 MHz
 SOLVENT water
 NS 1333
 DS 0
 SWH 23960.814 Hz
 FIDRES 0.365918 Hz
 AQ 1.3664756 sec
 RG 327.5
 DE 20.00 usec
 TE 296.2 K
 DI 1.5000000 sec
 D11 0.0300000 sec
 D12 1
 D13

----- CHANNEL F1 -----
 NUC1 13C
 P1 8.50 usec
 PL 0.00 dB
 FL 47.7726200 dB
 SFO1 100.6228298 MHz

----- CHANNEL F2 -----
 CPDPRG2 waltz16
 NUC2 1H
 P2 70.00 usec
 PL2 -3.00 dB
 SFO2 400.1464018 MHz
 FL2 16.00 dB

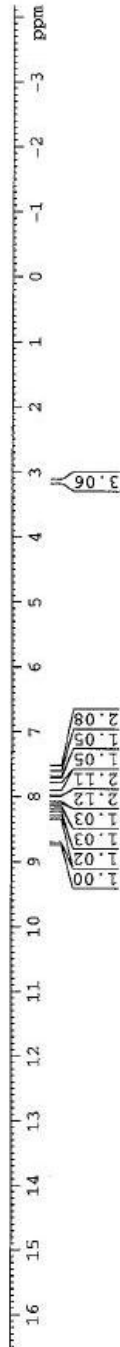
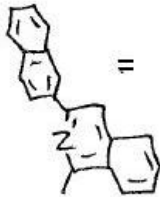
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AVB-400 ZBO Proton starting parameters. 6/11/03 RN

8.720
8.328
8.323
8.306
8.302
8.211
8.190
8.117
8.047
8.041
8.022
8.000
7.954
7.934
7.921
7.915
7.758
7.755
7.740
7.737
7.720
7.717
7.655
7.652
7.637
7.634
7.631
7.617
7.614
7.580
7.567
7.562
7.560
7.552
7.543
7.536
7.524
7.303
3.137

```

NAME      AVB-VI-015
EXPNO     1
PROCNO    1
INSTRUM   AVB-400
PROBHD    5 mm PALBO BBI
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         8
DS         0
SWH        8278.106 Hz
AQ         0.06644 sec
RG         3.958243
RC         645.1
DW         60.400 usec
DE         5.00 usec
TE         300.2 K
TD0        1.00000000 sec
===== CHANNEL f1 =====
NUC1       1H
P1         9.20 usec
PL1        0.00 dB
PL12       19.00 dB
PL13       19.00 dB
PL14       19.00 dB
PL15       19.00 dB
PL16       19.00 dB
PL17       19.00 dB
PL18       19.00 dB
PL19       19.00 dB
PL20       19.00 dB
SFO1       23.0966311 MHz
SFO2       400.1324710 MHz
SFO3       400.1324710 MHz
SFO4       400.1324710 MHz
SFO5       400.1324710 MHz
SFO6       400.1324710 MHz
SFO7       400.1324710 MHz
SFO8       400.1324710 MHz
SFO9       400.1324710 MHz
SFO10      400.1324710 MHz
SFO11      400.1324710 MHz
SFO12      400.1324710 MHz
SFO13      400.1324710 MHz
SFO14      400.1324710 MHz
SFO15      400.1324710 MHz
SFO16      400.1324710 MHz
SFO17      400.1324710 MHz
SFO18      400.1324710 MHz
SFO19      400.1324710 MHz
SFO20      400.1324710 MHz
=====
  
```



NAME: AMD-VI-015
 DATE: 20090929
 TIME: 8:30
 INSTRUM: AVB-400
 PULPROG: 5 mm PABBO DR-
 CPDPRG2: zgpg30
 SOLVENT: CDCl3
 NS: 352
 DS: 0
 SWH: 23980.814 Hz
 FIDRES: 0.355918 Hz
 AQ: 0.3250000 sec
 RG: 1.366384 sec
 DW: 20.8530 usec
 DE: 6.00 usec
 TE: 295.1 K
 D1: 1.50000000 sec
 D2: 0.93000000 sec
 T20: 1

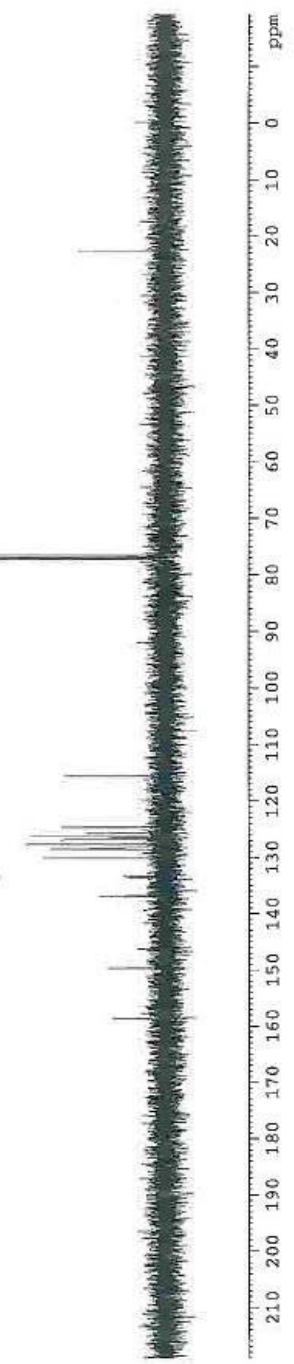
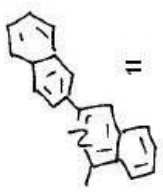
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 NUCL1: 13C
 P1: 8.50 usec
 PL1: 0.00 dB
 FWH: 47.77286188 MHz
 SFO1: 100.6228238 MHz

===== CHANNEL #2 =====
 CPDPRG2: waltz16
 PCPD02: 70.00 usec
 PL2: -3.00 dB
 PL12: 16.00 dB

22.78

158.75
 149.82
 137.11
 136.85
 133.43
 130.13
 128.75
 128.38
 127.71
 127.68
 126.90
 126.70
 126.20
 126.18
 125.73
 124.80
 123.57

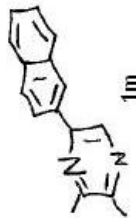
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AVB-400 Z80 Proton starting parameters. 6/11/03 RN

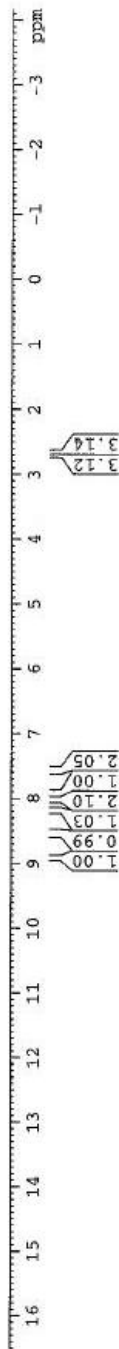
8.900
8.521
8.180
8.159
8.008
7.989
7.917
7.573
7.563
7.302

2.701
2.651



NAME AVB-VI-012
EXPNO 1
PROCNO 1
Date_ 20090929
Time 15.44
INSTRUM AVB-400
PROBHD 5 mm PABBO BB-CP
PULPROG zgpg30
TD 65536
SOLVENT CINO3
NS 8
DS 0
SKE 6278.145 Hz
AQ 0.154443 sec
RG 5160.6
DM 60.400 usec
DE 6.00 usec
TE 295.3 K
DQ 1.0000000 sec
TD0 1

----- CHANNEL f1 -----
NUC1 1H
P1 8.20 usec
PL 0.00 dB
PC1W 23.05461311 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300000 MHz
WDW EM
SS 256
GB 0
EC 4.00



151.90
150.59
149.31
138.54
134.16
133.72
133.50
128.71
127.75
126.71
126.46
126.13
124.14

22.34
21.84

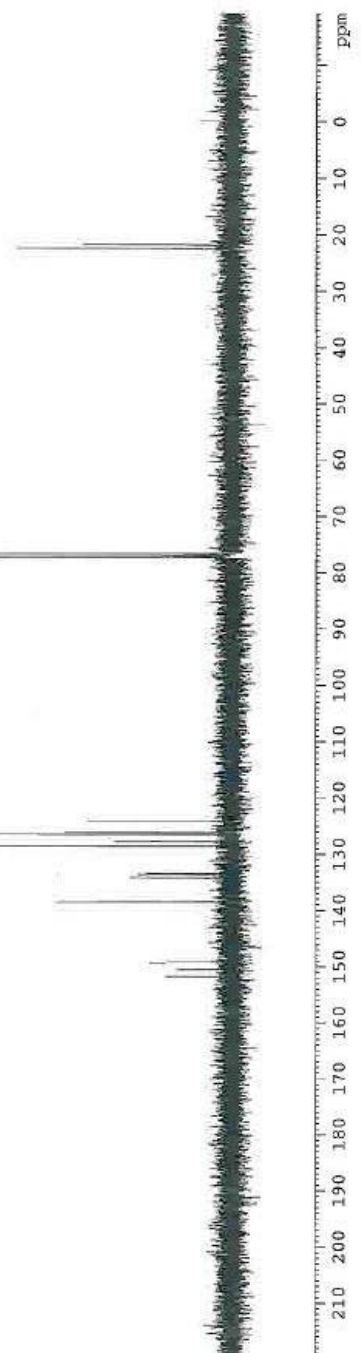
AVB-400 Z80 Carbon Starting parameters 6/11/03 RN



NAME: AVB-VI-012
 PROCNO: 1
 Date: 20090930
 Time: 12.49
 INSTRUM: AVB-400
 PULPROG: 5 mm PABBO BBO
 TD: 65516
 SOLVENT: CDCl3
 NS: 352
 DS: 0
 SWH: 23900.831 Hz
 FWHM: 0.364938 Hz
 AQ: 1.3864756 sec
 RG: 16384
 DW: 20.850 usec
 DE: 6.00 usec
 RE: 1.000000 K
 D1: 1.5000000 sec
 D11: 0.0300000 sec
 T20: 1

===== CHANNEL #1 =====
 NU1: 1
 EL1: 8.50 usec
 FL1: -2.00 dB
 PC1M: 47.77286148 W
 SFO1: 100.6228238 MHz

===== CHANNEL #2 =====
 CH2P16: waltz16
 NU2: 1H
 EL2: 70.00 usec
 FL2: -2.00 dB
 PC2: 16.00 dB



24.26

135.52
 134.56
 133.37
 129.23
 128.34
 128.10
 127.69
 126.85
 126.08
 125.36
 118.07

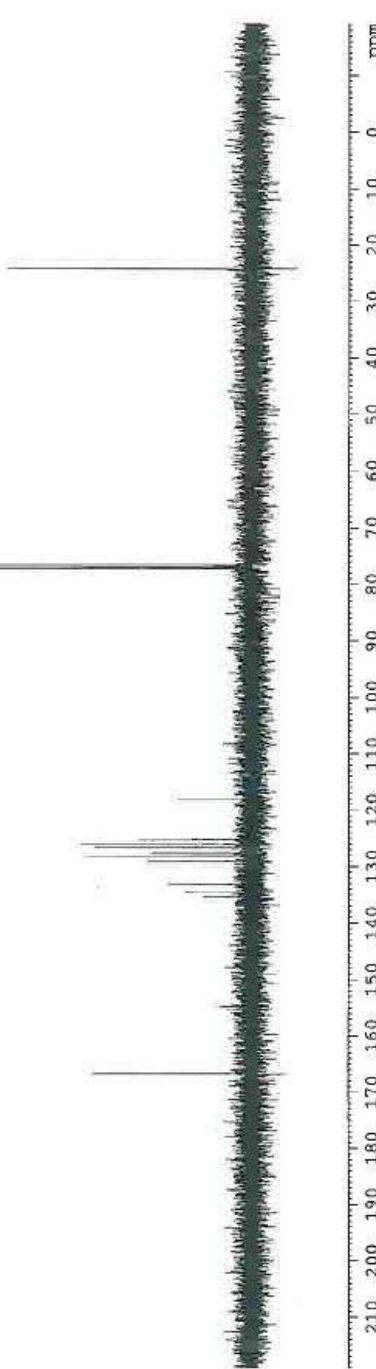
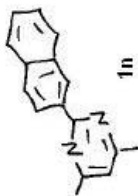
166.85

NAME AME-VI-013
 EXPNO 4
 PROCNO 1
 Time 20090927
 Date_ 11-24
 INSTRUM AVS-400
 PROBRD 5 mm PABBO BB-
 PULPROG zgpg30
 UNPROG hsqc
 SOLVENT CDCl3
 NS 140
 DS 0
 SWH 23940.914 Hz
 FIDRES 0.365938 Hz
 AQ 1.3664736 sec
 RG 327.500
 DW 20.890 usec
 DE 6.00 usec
 TE 295.5 K
 D1 1.50000000 sec
 D11 0.03000000 sec
 TDO 1

===== CHANNEL F1 =====
 NUCL 13C
 P1 8.50 usec
 PL1 2.00 dB
 FWH 47.7284100 dB
 SFO1 100.628338 MHz

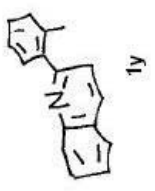
===== CHANNEL F2 =====
 CDEPRG2 waltz16
 NUCL2 1H
 P2 70.00 usec
 PL2 -3.00 dB
 SFO2 400.146401 MHz

AVS-400 2BD Carbon Starting parameters 6/11/03 RN



147.94
136.09
136.03
130.90
129.73
129.66
129.64
128.53
127.54
126.76
126.43
126.05
122.41

NTV-400 280 Carbon Starting parameters 6/11/03 RN

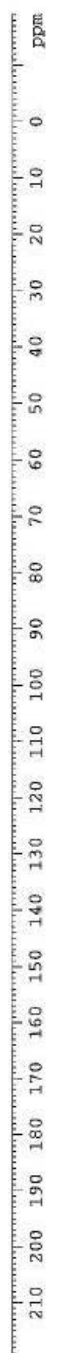


NAME AMB-VI-010
 PROCNO 1
 Date_ 20090330
 Time 14.54
 INSTRUM NTV-400
 REACTIO 5 mm PABOND
 PULPROG P0010
 TD 65336
 SOLVENT CUC13
 NS 352
 DS 0
 RE 23920.81 Hz
 FIDRES 0.365918 Hz
 AQ 1.3664756 sec
 RG 16384
 EW 20.850 usec
 DE 8.00 usec
 FI 25.00 usec
 DI 1.50000000 sec
 DLI 0.03000000 sec
 CH0 1

***** CHANNEL F1 *****
 FPC1 8.50 usec
 PL1 -1.00 dB
 FL1W 47.77266148 W
 SFO1 100.622828 MHz

***** CHANNEL F2 *****
 CDFPC2 waltz16
 MDC2 1K
 ECFE2 70.00 usec
 PL2 -2.00 dB
 PL12 16.00 dB

20.39

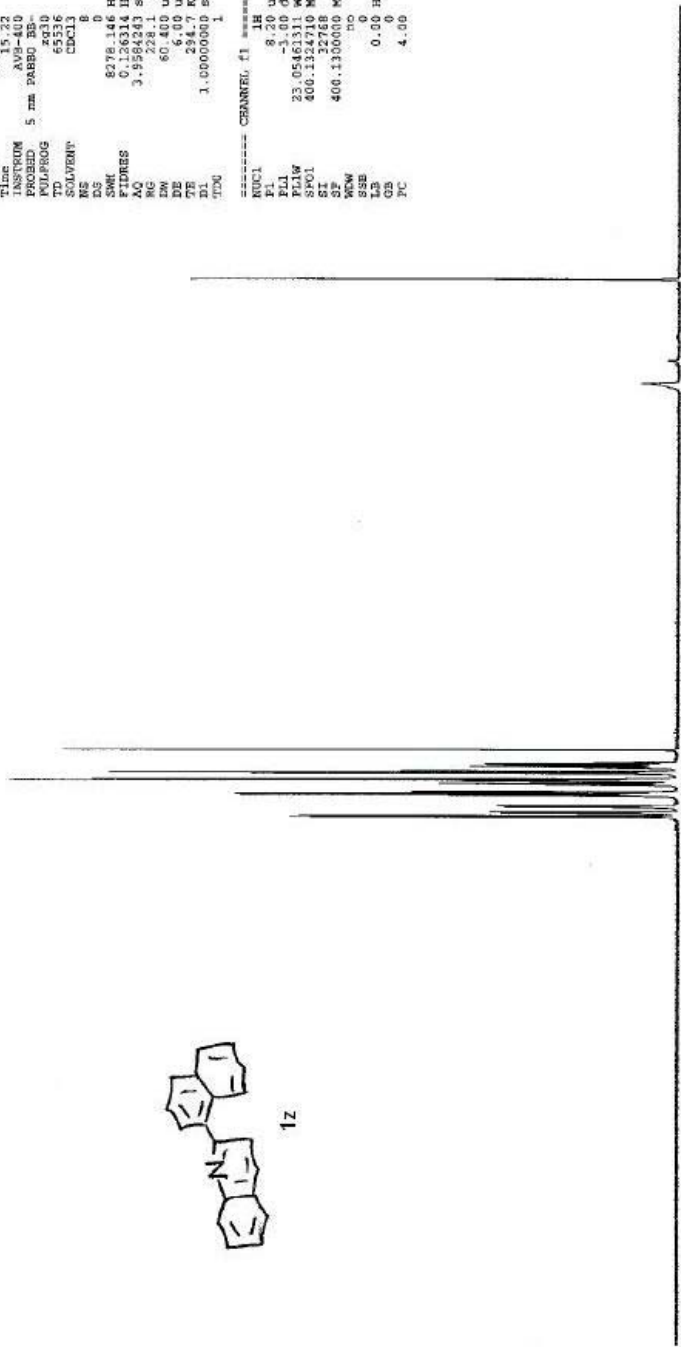
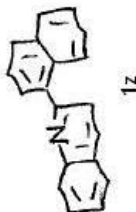


AVB-400 Z80 Proton starting parameters. 6/11/03 RN

8.349
8.328
8.287
8.266
8.191
8.171
8.015
7.994
7.977
7.956
7.850
7.847
7.833
7.829
7.826
7.812
7.808
7.782
7.773
7.766
7.752
7.673
7.670
7.656
7.653
7.650
7.636
7.633
7.585
7.571
7.568
7.551
7.547
7.541
7.537
7.520
7.503
7.303

```

NAME      AME-VI-018
EXPNO    1
PROCNO   1
Date_    20090929
Time     15.22
INSTRUM  AVB-400
PROBHD   5 mm PABBO BB-
PULPROG  zgpg30
TD       65536
SOLVENT  CDCl3
NS       8
DS       0
SWH      8278.146 Hz
FIDRES   0.000243 Hz
AQ        3.1958243 sec
RG        228.1
EW        60.400 usec
DE        6.00 usec
TE        284.7 K
TD0       1.00000000 sec
===== CHANNEL f1 =====
NUC1      1H
P1        8.20 usec
PL1       0.00 dB
PL12      23.0546331 dB
SFO1      400.1324710 MHz
SI        32768
SF        400.1300010 MHz
RGW       DO
LS        0.00 Hz
GB        0
PC        4.00
  
```



16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 ppm

0.99
1.00
2.99
1.03
1.98
1.97
2.01

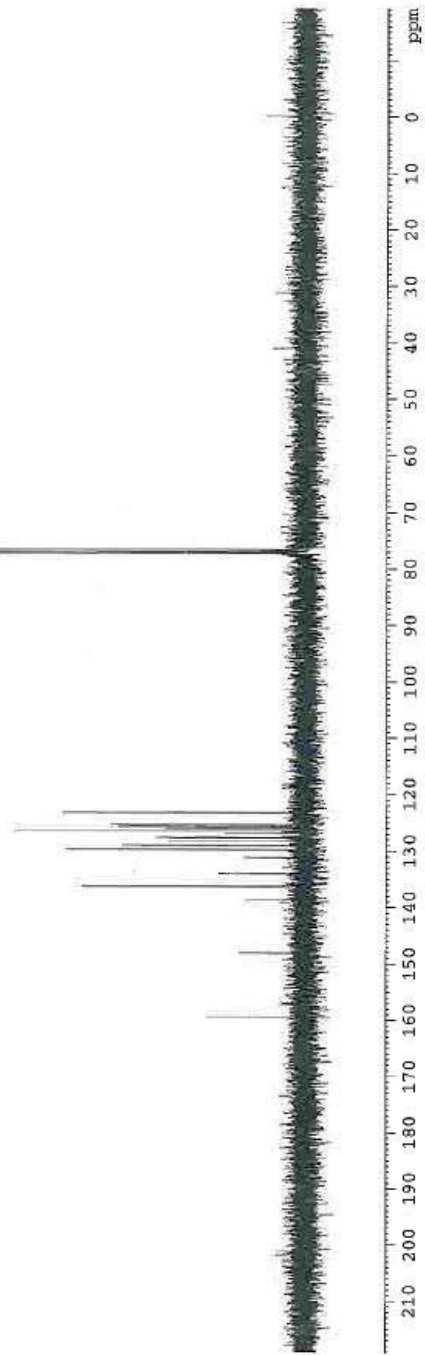
159.48
148.16
138.78
136.30
134.04
131.30
129.81
129.78
129.15
128.44
127.78
127.62
127.04
126.63
126.00
125.73
125.43
123.11

NAME AMB-VI-008
EXPNO 2
PROCNO 1
Date_ 20090922
Time 12.52
INSTRUM AVX-400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
DS 320
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
SWH 6.60 usec
WDW EM
TE 295.6 K
D1 1.5000000 sec
D11 0.0300000 sec
TD0 1

***** CHANNEL F1 *****
NUC1 13C 13C
P1 8.50 usec
PL1 -2.00 dB
SFO1 47.7726148 MHz
SFO2 100.6228278 MHz

***** CHANNEL F2 *****
CEFFG2 waltz16
NUC2 13C 13C
P2 70.00 usec
PL2 -3.00 dB
SFO2 125.7611370 MHz

AVX-400 2BD Carbon Stating parameters 6/11/03 RK

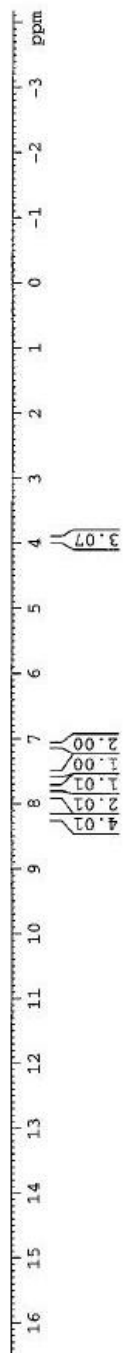
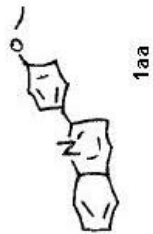


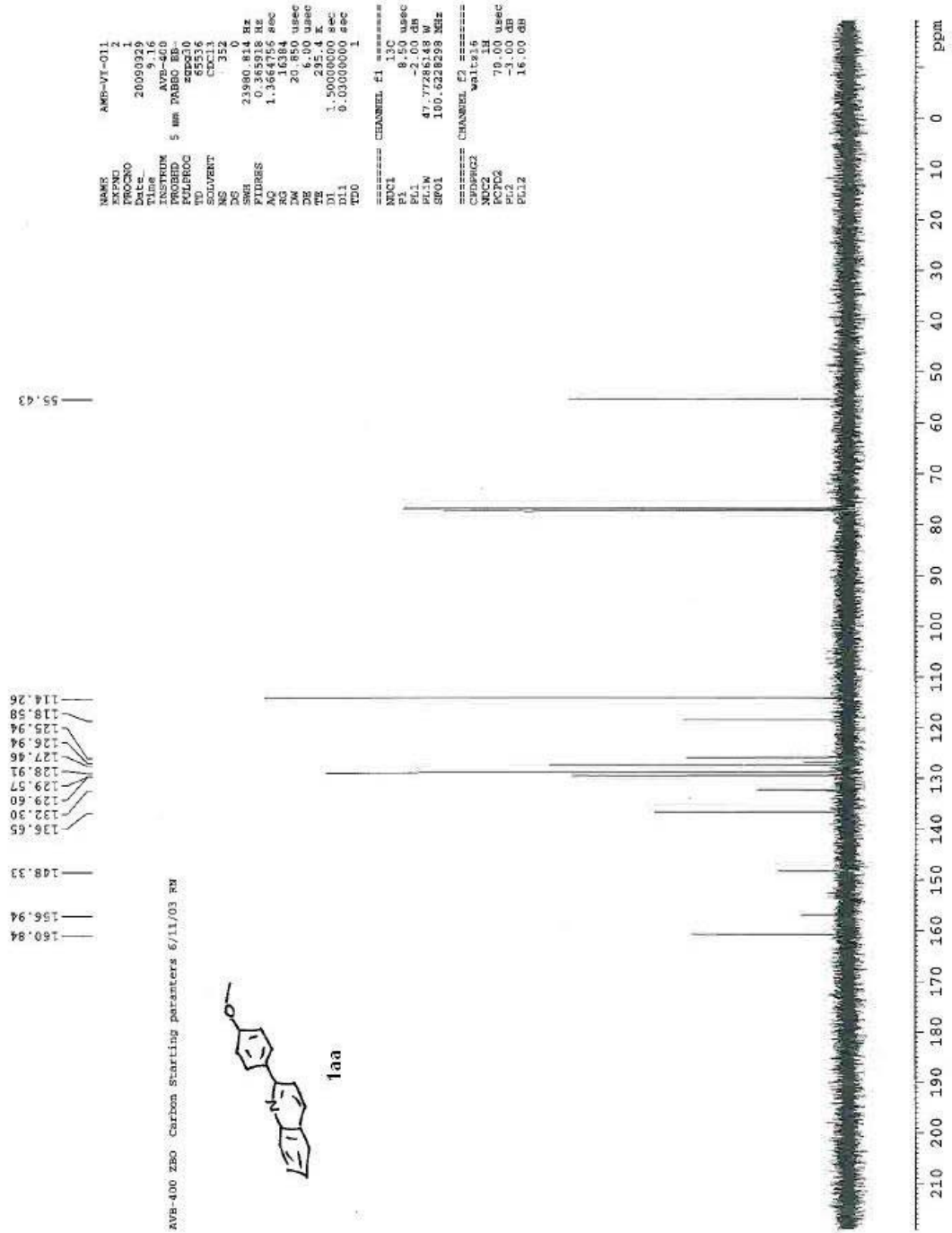
AVS-400 250 Proton starting parameters. 6/11/03 RN

8.229
8.208
8.201
8.196
8.184
8.179
7.889
7.867
7.855
7.835
7.775
7.771
7.758
7.754
7.750
7.737
7.733
7.559
7.542
7.539
7.524
7.522
7.303
7.107
7.102
7.090
7.085
3.932

```

NAME      AMB-VI-011
PROCNO    1
Date_     20090929
Time      9.10
INSTRUM   AVS-400
PROBHD    5 mm PABBO BBO
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         8
DS         0
DE         8270.146 Hz
AQ         0.72511 sec
RG         3.9588243 sec
RG2        228.1
RG3        60.400 usec
DE2        5.00 usec
DE3        284.7 K
TD0        1.00000000 sec
===== CHANNEL F1 =====
NUC1       1H
P1         8.00 usec
PL1        0.00 dB
PL12       2.00 dB
PL1W       23.05661311 W
SFO1       400.1324710 MHz
SI         32788
SF         400.1300000 MHz
WDW        EM
SSB        0
LB         0.00 Hz
GB         0
PC         4.00
  
```





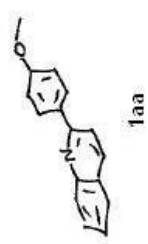
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NAME      AMB-VI-011
EXPNO     2
PROCNO    2009027
Date_     9.16
Time      AVB-460
INSTRUM   5 mm PABBO BB-
PROBHD    zgpg30
PULPROG   zgpg30
TD        65536
SFO       125.76
NUC1       13C
NS        332
DS         0
SWH        23980.814 Hz
FIDRES     0.365918 Hz
AQ         1.3664795 sec
RG         655.36
AQ        20.850 usec
DE         6.00 usec
TE         295.4 K
D1         1.50000000 sec
d11        0.03000000 sec
TD0        1

===== CHANNEL F1 =====
NUC1      13C
P1         9.50 usec
PL1        2.00 dB
SFO1      125.76 MHz
===== CHANNEL F2 =====
NAME      wait3.5
P2         70.00 usec
PL2        -3.00 dB
SFO2      125.76 MHz

```

AVB-400 Z80 Carbon Starting parameters 6/11/03 RM



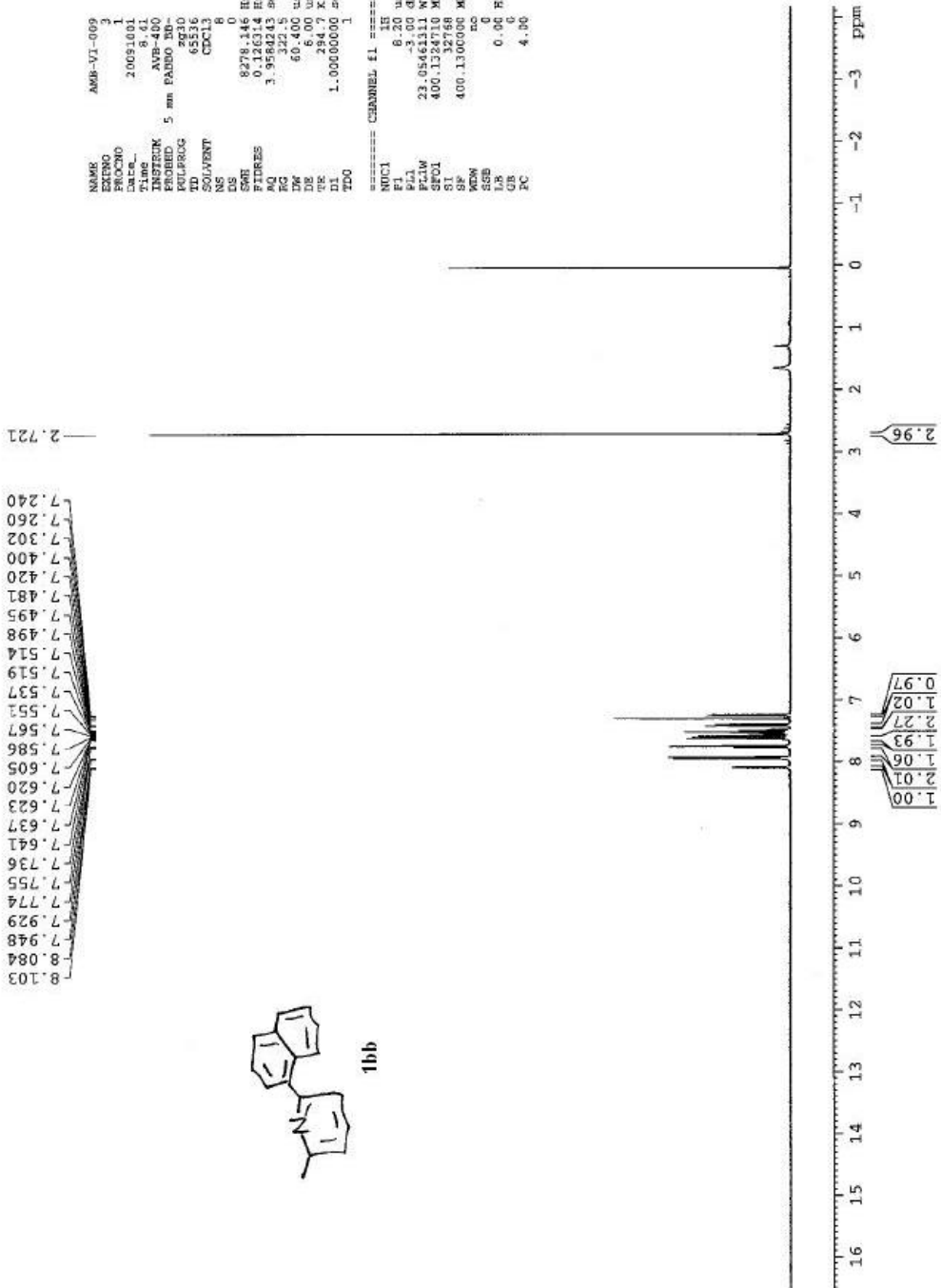
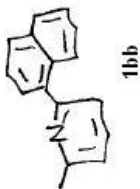
AVB-400 ZBO Proton starting parameters. 6/11/03 RN

8.103
8.084
7.948
7.929
7.774
7.755
7.736
7.641
7.637
7.623
7.620
7.605
7.586
7.567
7.551
7.537
7.519
7.514
7.498
7.481
7.420
7.400
7.302
7.260
7.240

```

NAME      AMB-VI-009
EXPNO     3
PROCNO    1
F2        20091001
Time      8.41
INSTRUM   AVB-400
PROBHD    5 mm PABBO HD-
PULPROG   zg30
SFO1      400.1324118 MHz
SFO2
SFO3
SOLVENT   CDCl3
NS         8
DS         0
SMR       8278.146 Hz
FIDRES    0.126314 Hz
AQ         3.959273 sec
RG         627.5
DE         60.400 usec
DE         6.00 usec
TE        294.7 K
D1         1.00000000 sec
ZDO        1

===== CHANNEL f1 =====
NUC1      15
F1        8.20 usec
P1        3.00 dB
PL1       23.054200 MHz
P2        400.1324118 MHz
SFO1      400.1324118 MHz
SFO2
SFO3
SF        32768
WDW       nc
SSB       0
GB        0.00 Hz
UR        0.00
PC        4.00
  
```



121.59
122.09
125.07
125.78
125.82
126.39
127.36
127.32
128.32
128.72
131.33
134.00
136.58
138.83
158.26
158.66

24.80

NAME AMB-VI-009
EXPNO 1
PROCNO 1
Date_ 20090930
Time 15.46
INSTOR AVB-600
PULPROG zgpg30
TD 65536
SOLVENT CCl4
NS 352
DS 2
SWH 23960.81 Hz
FIDRES 0.362918 Hz
AQ 1.3664756 sec
RG 16384
DM 20.850 usec
DE 8.00 usec
TE 300.2 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 12.00 usec
PL1 -2.00 dB
PL1W 47.77285148 W
SFO1 100.628238 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 -3.00 dB
PL12 16.00 dB

AVB-400 280 Carbon Starting parameters 6/11/03 BX

