2012

Tsuji–Trost *N*-Allylation with Allylic Acetates by Using a Cellulose–Palladium Catalyst

Buchi Reddy Vaddula

Amit Saha

Rajender S. Varma

John Leazer

Eur. J. Org. Chem. **2012** · © WILEY-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2012 · ISSN 1434–193X

SUPPORTING INFORMATION

DOI: 10.1002/ejoc.201201241
Title: Tsuji–Trost *N*-Allylation with Allylic Acetates by Using a Cellulose–Palladium Catalyst
Author(s): Buchi Reddy Vaddula, Amit Saha, Rajender S. Varma,* John Leazer*

Contents

1. General Information

The reagents were obtained commercially and used without further purification. Cellulose fiber, medium, was obtained from Sigma-Aldrich. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 300 MHz NMR spectrometer using TMS as the internal standard. Chemical shifts are given in parts per million (δ) and coupling constants (*J*) in Hz. MS data was obtained on Hewlett Packard HP 5973 quadrupole Mass Selective Detector with interface for 6890 series GC. Thin-layer chromatography (TLC) was performed on silica gel 60 F254 precoated glass plates.

2. Experimental Procedures

2.1. Procedure for the catalyst preparation

1 gm of cellulose fiber was dispersed well in 20 mL of water. $PdCl_2$ (150 mg) was added in small quantities to the suspension. It was stirred at room temperature for 1 h. $NaBH_4$ (2.5 equiv.) was added in small quantities to the aqueous suspension and was stirred for 15 h at room temperature. The catalyst was centrifuged followed by washing with acetone and was dried under vacuum to obtain black colored powder catalyst.

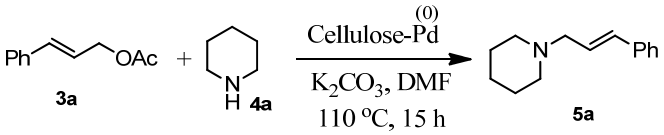
2.2. General procedure for the synthesis of allyl amines

A mixture of allyl acetate (1.0 mmol), nucleophile (1.2 mmol), cellulose-Pd (50 mg) and potassium carbonate (2.0 mmol) in anhydrous DMF (3 mL) is heated at 110 ^oC under N_2 atmosphere for 15 hours. Upon completion of the reaction as indicated by TLC, the reaction mixture is diluted with water and centrifuged/filtered to separate the catalyst. The decanted liquid is extracted with ethyl acetate (3 x 10 mL). The ethyl acetate layer is dried over anhydrous sodium sulfate and evaporated to get the crude product. The crude product is purified by passing through silica gel column eluting with ethyl acetate-hexane.

2.3 Recovery and reuse of Cellulose-Pd catalyst

After completion of the reaction, the catalyst was separated from the reaction mixture by filteration. The catalyst was washed with acetone, dried under vacuum, and recycled for 5 consecutive reactions without any significant loss in efficiency (Table S1).

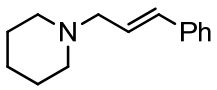
Table S1. Reuse of the cellulose-Pd catalyst.



Cycle	Yield (%)
1	87
2	85
3	85
4	83
5	82

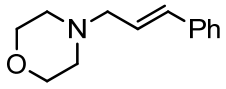
^{1}H & ^{13}C NMR spectra

1-Cinnamylpiperidine (5a)[1]



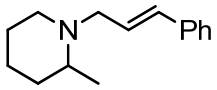
Yield : 87%. ^{1}H NMR (300 MHz, $CDCl_3$) δ1.45 (br s, 2H), 1.61-1.68 (m, 4H), 2.49 (m, 4H), 3.18 (dd, *J* = 6.9 Hz and 6Hz, 2H), 6.32 (dt, *J* = 15.0 and 6.9 Hz, 1H), 6.53 (d, *J* = 15.0 Hz, 1H), 7.20-7.26 (m, 1H), 7.35-7.28 (m, 2H), 7.37-7.41 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ
24.2, 25.7, 54.4, 61.6, 126.3, 126.6, 127.4, 128.5, 133.0, 137.0. MS (EI) calcd for $C_{14}H_{19}N$ (M^+) 201.1517, found 201.1.

4-Cinnamylmorpholine (5b)[1]



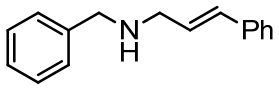
Yield : 90%. ^{1}H NMR (300 MHz, $CDCl_3$) δ2.53 (t, *J* = 6.0 Hz, 4H), 3.18 (dd, *J* = 7.2 and 1.2 Hz, 2H), 3.76 (t, *J* = 6.0 Hz, 4H), 6.28 (dt, *J* = 15.9 and 7.5 Hz, 1H), 6.55 (d, *J* = 15.9 Hz, 1H), 7.22-7.28 (m, 1H), 7.30-7.36 (m, 2H), 7.37-7.41 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ
53.7, 61.5, 67.0, 126.0, 126.3, 127.6, 128.6, 133.5, 136.8. MS (EI) calcd for $C_{13}H_{17}NO$ (M^+) 203.1310, found 203.1.

1-Cinnamyl-2-methylpiperidine (5c)



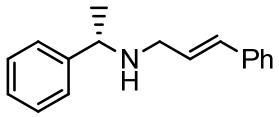
Yield : 95%. ^{1}H NMR (300 MHz, $CDCl_3$) δ1.23 (d, *J* = 6.0 Hz, 3H), 1.28-1.56 (m, 2H), 1.65-1.73 (m, 4H), 2.29-2.38 (m, 1H), 2.49-2.57 (m, 1H), 3.03 (dt, *J* = 12.0 and 6.0 Hz, 1H), 3.27 (dd, *J* = 12.0 and 6.0 Hz, 1H), 3.64 (ddd, *J* = 14.1, 6.0 and 1.5 Hz, 1H), 6.35 (dt, *J* = 15.0 and 5.85 Hz, 1H), 6.55 (d, *J* = 15.0 Hz, 1H), 7.22-7.28 (m, 1H), 7.30-7.36 (m, 2H), 7.38-7.42 (m, 2H). ^{13}C NMR (**75** MHz, $CDCl_3$)
δ18.5, 23.5, 25.2, 33.7, 51.9, 56.0, 56.2, 124.6, 126.4, 127.6, 128.6,134.1, 136.7. MS (EI) calcd for $C_{15}H_{21}N$ (M^+) 215.1674, found 215.1.

(*E*)-*N*-Benzyl-3-phenylprop-2-en-1-amine (5d)[2]



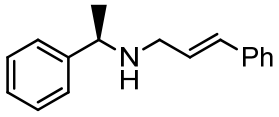
Yield : 85%. ^{1}H NMR (300 MHz, $CDCl_3$) δ3.48 (dd, *J* = 6.30 and 1.35 Hz, 2H), 3.88 (s, 2H), 6.35 (dt, *J* = 15.0 and 7.20 Hz, 1H), 6.57 (d, *J* = 15 Hz, 1H), 7.22-7.42 (m, 10H). ^{13}C NMR (**75** MHz, $CDCl_3$)
δ51.0, 53.1, 126.3, 127.1, 127.4, 128.0, 128.3, 128.5, 128.6, 131.8, 137.1, 139.8.
MS (EI) calcd for $C_{16}H_{17}N$ (M^+) 223.1361, found 223.1.

(*S*,*E*)-3-Phenyl-*N*-(1-phenylethyl)prop-2-en-1-amine (5e)[3]



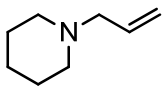
Yield : 89%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.43 (d, J = 6.0 Hz, 3H), 3.30 (dt, J = 6.30 and 1.2 Hz, 2H), 3.89 (dd, J = 12.0 and 6.0 Hz, 1H), 6.31 (dt, J = 15.0 and 6.6 Hz, 1H), 6.50 (d, J = 15 Hz, 1H), 7.21-7.41 (m, 10H). ^{13}C NMR (**75** MHz, $CDCl_3$) δ 24.23, 49.67, 57.60, 126.25, 126.66, 126.98, 127.30, 128.50, 128.52, 128.61, 131.19, 137.21, 145.44. MS (EI) calcd for $C_{17}H_{19}N$ (M^+) 237.1517, found 237.1.

(*R*,*E*)-3-Phenyl-N-(1-phenylethyl)prop-2-en-1-amine (5f) [4]



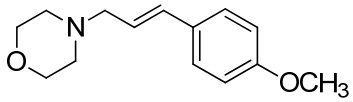
Yield : 90%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.43 (d, J = 6.0 Hz, 3H), 3.31 (dt, J = 6.30 and 1.2 Hz, 2H), 3.89 (dd, J = 12.0 and 6.0 Hz, 1H), 6.31 (dt, J = 15.0 and 6.6 Hz, 1H), 6.50 (d, J = 15 Hz, 1H), 7.20-7.42 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.23, 49.67, 57.60, 126.25, 126.66, 126.98, 127.30, 128.50, 128.52, 128.61, 131.19, 137.21, 145.44. MS (EI) calcd for $C_{17}H_{19}N$ (M^+) 237.1517, found 237.1.

1-Allylpiperidine (5g)[5]



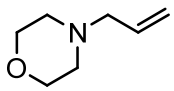
Yield : 96%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.32-1.60 (m, 6H), 2.17-2.40 (m, 4H), 2.85-3.01 (m, 2H), 5.03-5.15 (m, 2H), 5.80-5.92 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.4, 26.0, 54.3, 62.7, 117.7, 135.5. MS (EI) calcd for $C_8H_{15}N$ (M^+) 125.1204, found 125.1.

(*E*)-4-(3-(4-Methoxyphenyl)allyl)morpholine (5h)[6]



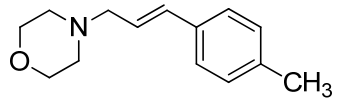
Yield : 86%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.48 (s, 4H), 3.12 (d, J = 6.5 Hz, 2H), 3.75 (dd, J = 4.6 and 4.5 Hz, 4H), 3.79 (s, 3H), 6.12 (dt, J = 16.0 and 6.5 Hz, 1H), 6.48 (d, J = 16.0 Hz, 1H), 6.82–6.83 (m, 2H), 7.28–7.33 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.5, 55.2, 61.4, 67.0, 114.0, 123.5, 127.4, 129.5, 132.7, 159.1. MS (EI) calcd for $C_{14}H_{19}NO_2$ (M^+) 233.1416, found 233.1.

4-Allylmorpholine (5i)[5]



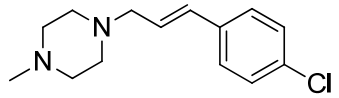
Yield : 93%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.21-2.45 (m, 4H), 2.88-3.03 (m, 2H), 3.55-3.72 (m, 4H), 5.06-5.22 (m, 2H), 5.65-5.82 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.5, 62.1, 67.0, 118.4, 134.5. MS (EI): m/z calcd for $C_7H_{13}NO$ [M^+]: 127.0997; found: 127.1.

(*E*)-4-(3-(*p*-Tolyl)allyl)morpholine (5j)[6]



Yield : 88%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.33 (s, 3H), 2.42–2.56 (m, 4H), 3.10 (dd, *J* = 6.6 and 1.2 Hz, 2H), 3.68-3.73 (m, 4H), 6.18 (dt, *J* = 16.0 and 6.5 Hz, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (75 Hz, $CDCl_3$): δ = 21.4, 53.7, 61.5, 67.2, 124.9, 126.4, 129.3, 133.4, 134.1, 137.5. MS (EI): m/z calcd for $C_{14}H_{19}NO$ [M^+]: 217.1467; found: 217.1.

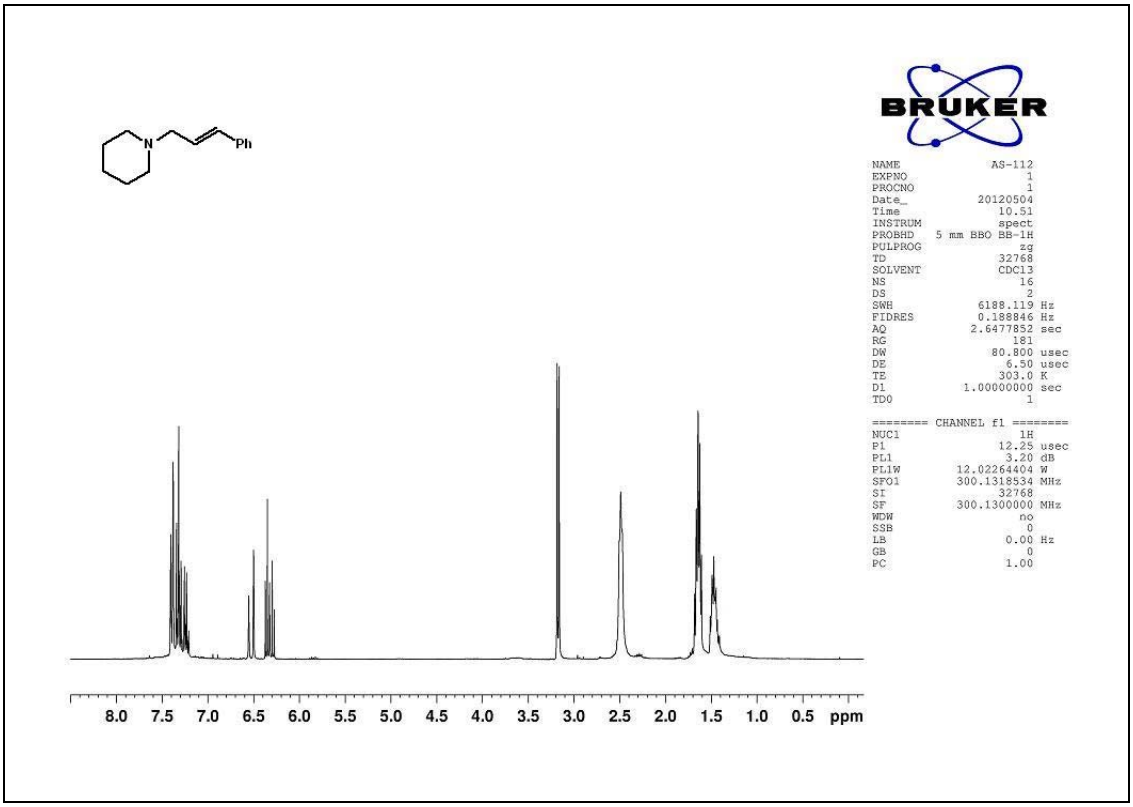
(*E*)-1-(3-(4-chlorophenyl)allyl)-4-methylpiperazine (5k)[7]

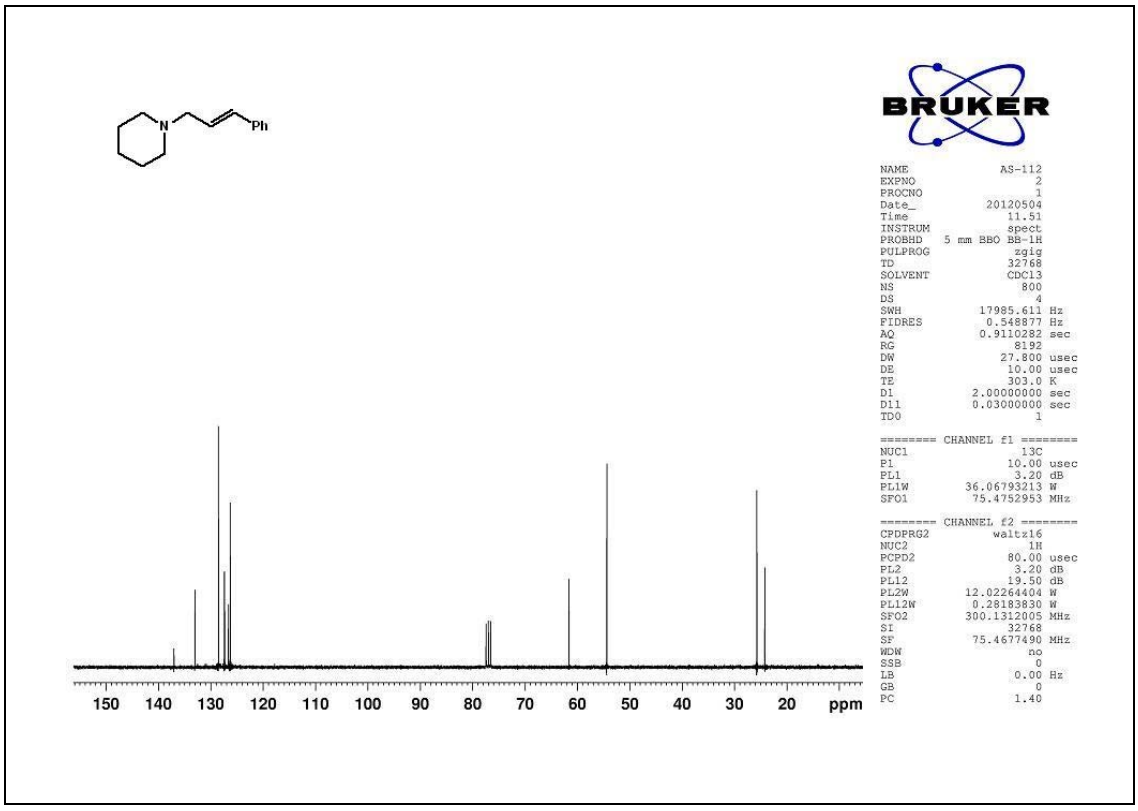


Yield : 92%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.23 (s, 3H), 2.44 (br s, 8H), 3.11 (d, *J* = 6.5 Hz, 2H), 6.14-6.23 (m, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 7.14-7.25 (m, 4H); ^{13}C NMR (75 Hz, $CDCl_3$): δ 46.2, 53.3, 55.2, 60.9, 127.4, 127.6, 128.8, 131.8, 133.2, 135.4; MS (EI): m/z calcd for $C_{14}H_{19}ClN_2$ [M^+]: 250.1237; Found: 250.1.

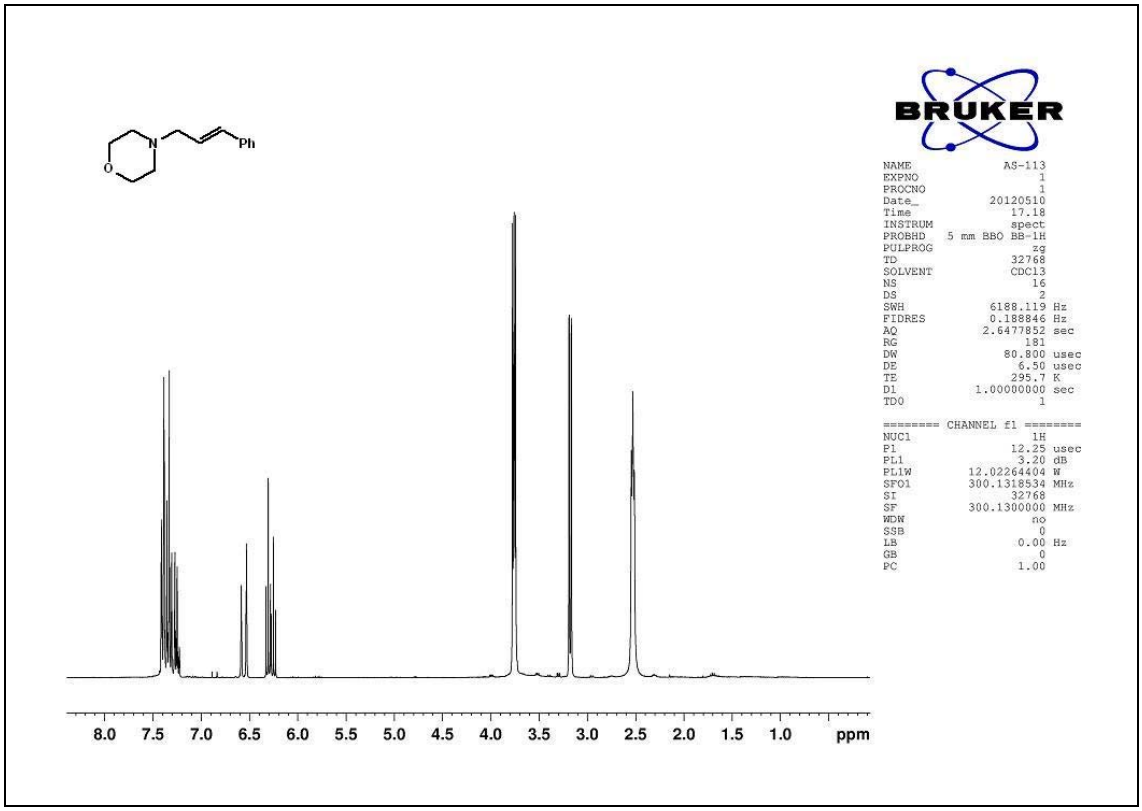
^{1}H & ^{13}C NMR spectra of the representative compounds

1-Cinnamylpiperidine (5a)



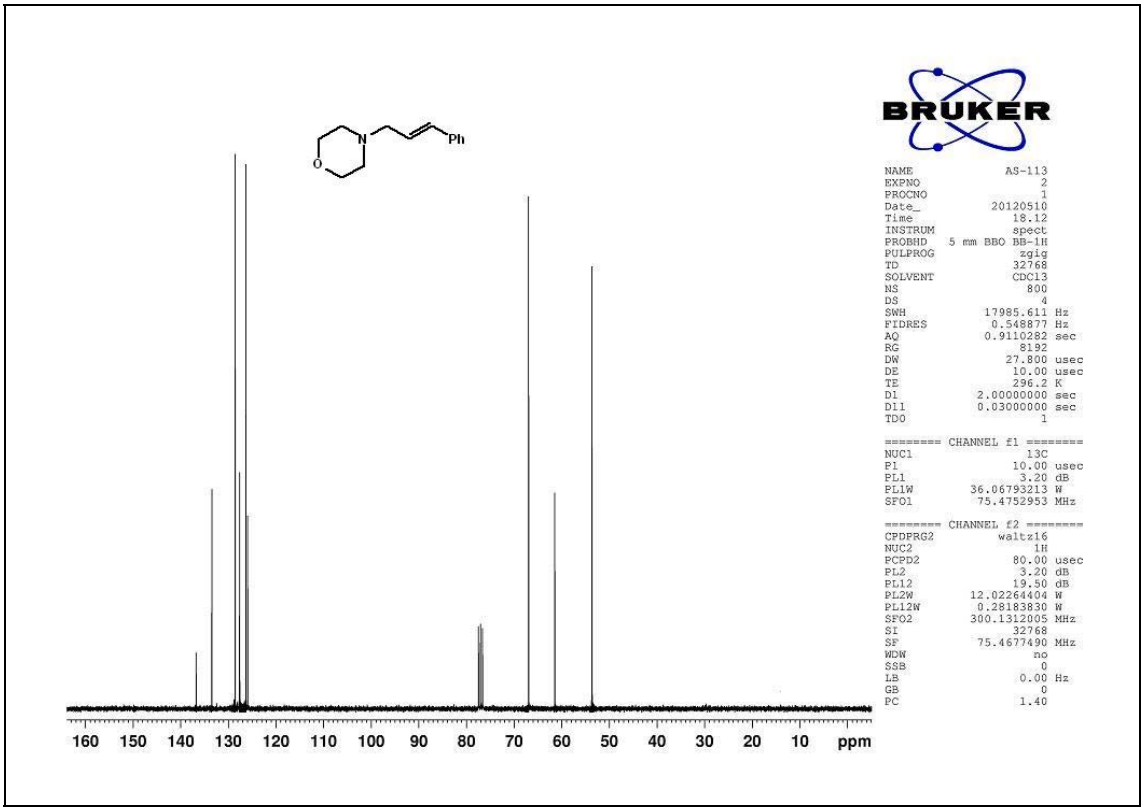


4-Cinnamylmorpholine (5b)



BRUKER

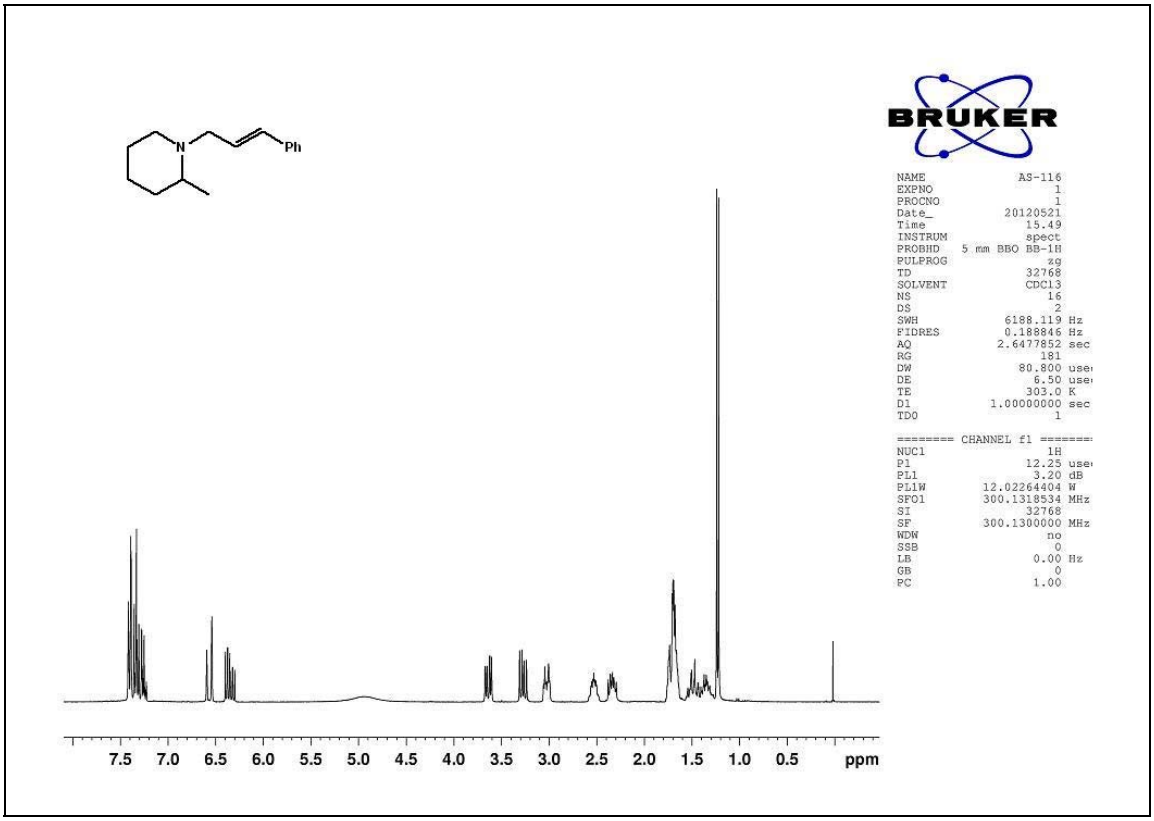
NAME	AS-113
EXPNO	1
PROCNO	1
Date_	20120510
Time	17.18
INSTRUM	spect
PROBHD	5 mm BBO BB-1H
PULPROG	zg
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	6188.119 Hz
FIDRES	0.188846 Hz
AQ	2.6477852 sec
RG	181
DW	80.800 usec
DE	6.50 usec
TE	295.7 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	12.25 usec
PL1	3.20 dB
PL1W	12.02264404 W
SFO1	300.1318534 MHz
SI	32768
SF	300.1300000 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

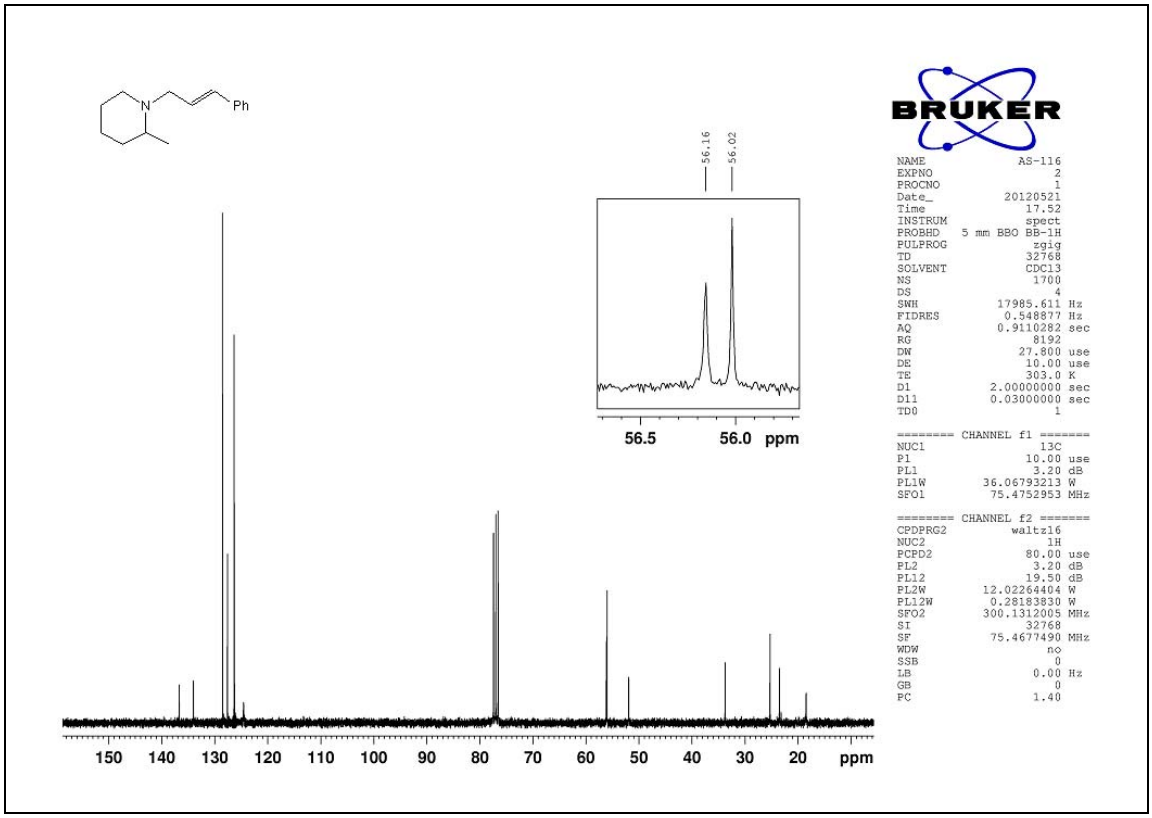


BRUKER

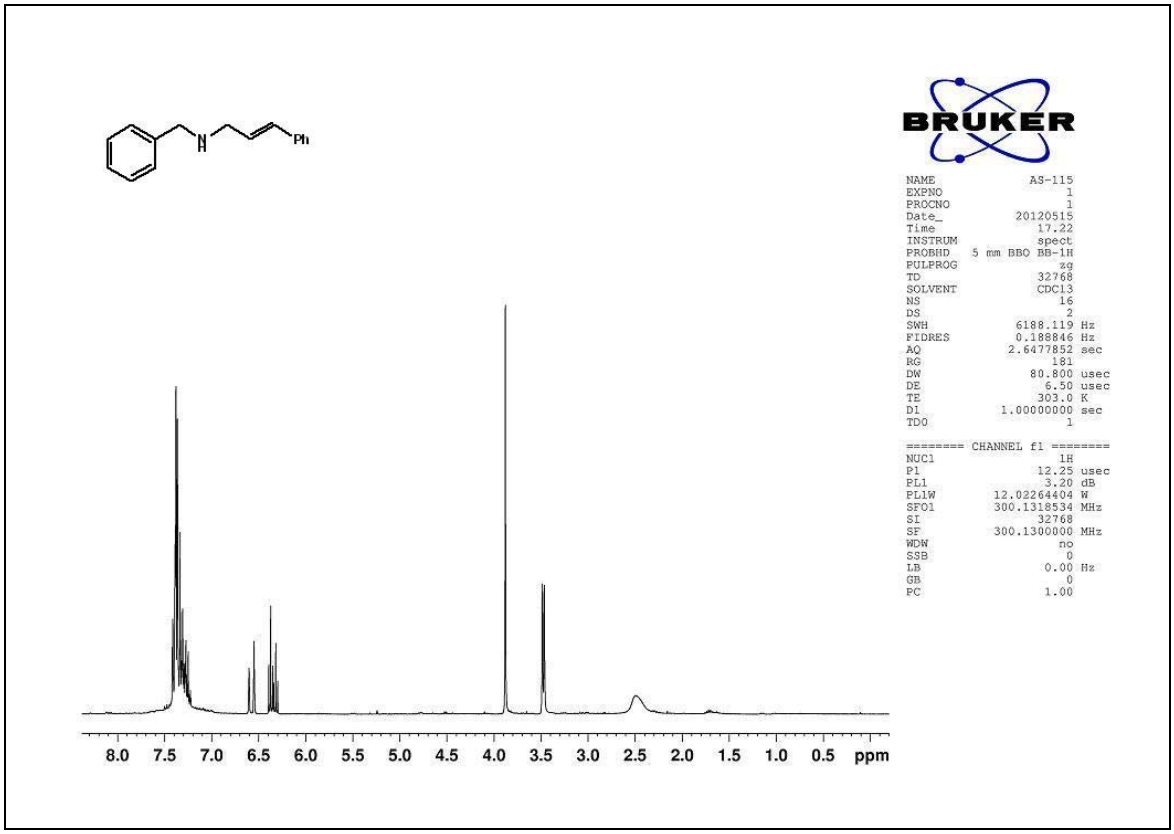
NAME	AS-113
EXPNO	2
PROCNO	1
Date_	20120510
Time	18.12
INSTRUM	spect
PROBHD	5 mm BBO BB-1H
PULPROG	zgig
TD	32768
SOLVENT	CDCl3
NS	800
DS	4
SWH	17985.611 Hz
FIDRES	0.548877 Hz
AQ	0.9110282 sec
RG	8192
DW	27.800 usec
DE	10.00 usec
TE	296.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.00 usec
PL1	3.20 dB
PL1W	36.06793213 W
SFO1	75.4752953 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	3.20 dB
PL12	19.50 dB
PL2W	12.02264404 W
PL12W	0.28183830 W
SFO2	300.1312005 MHz
SI	32768
SF	75.4677490 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.40

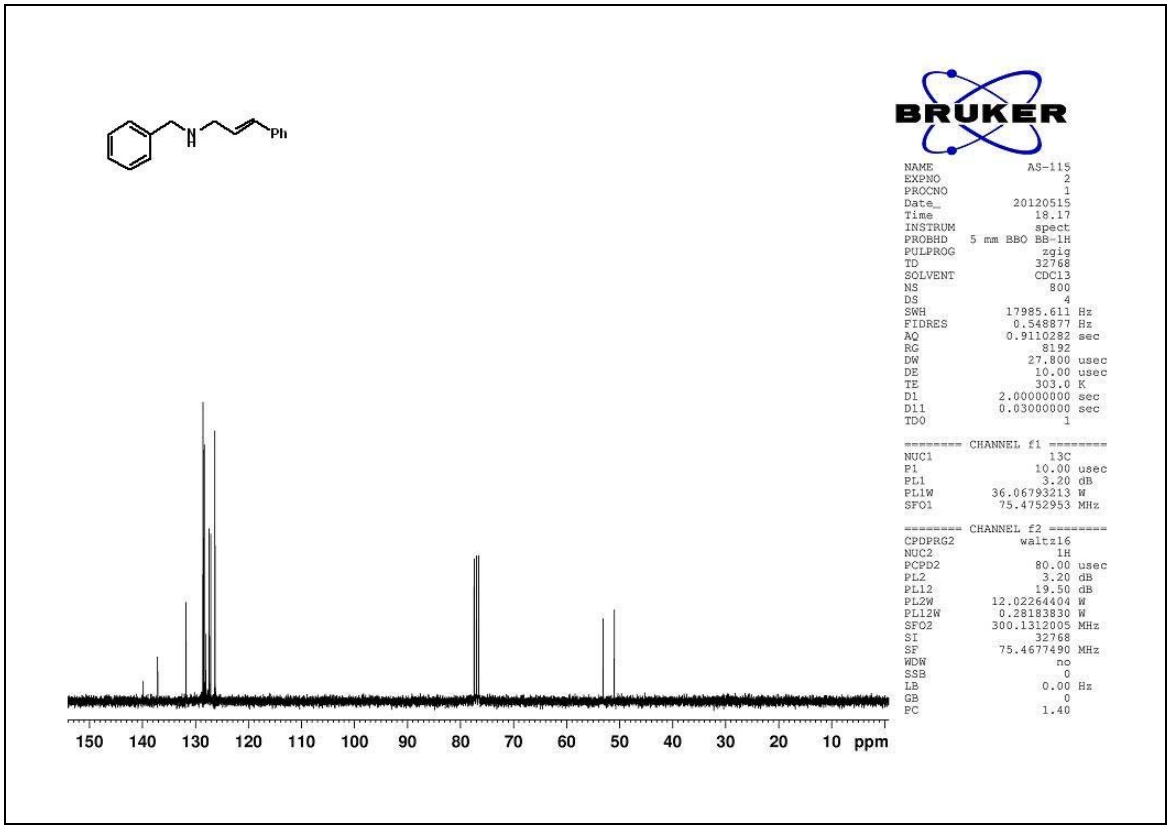
1-Cinnamyl-2-methylpiperidine (5c)



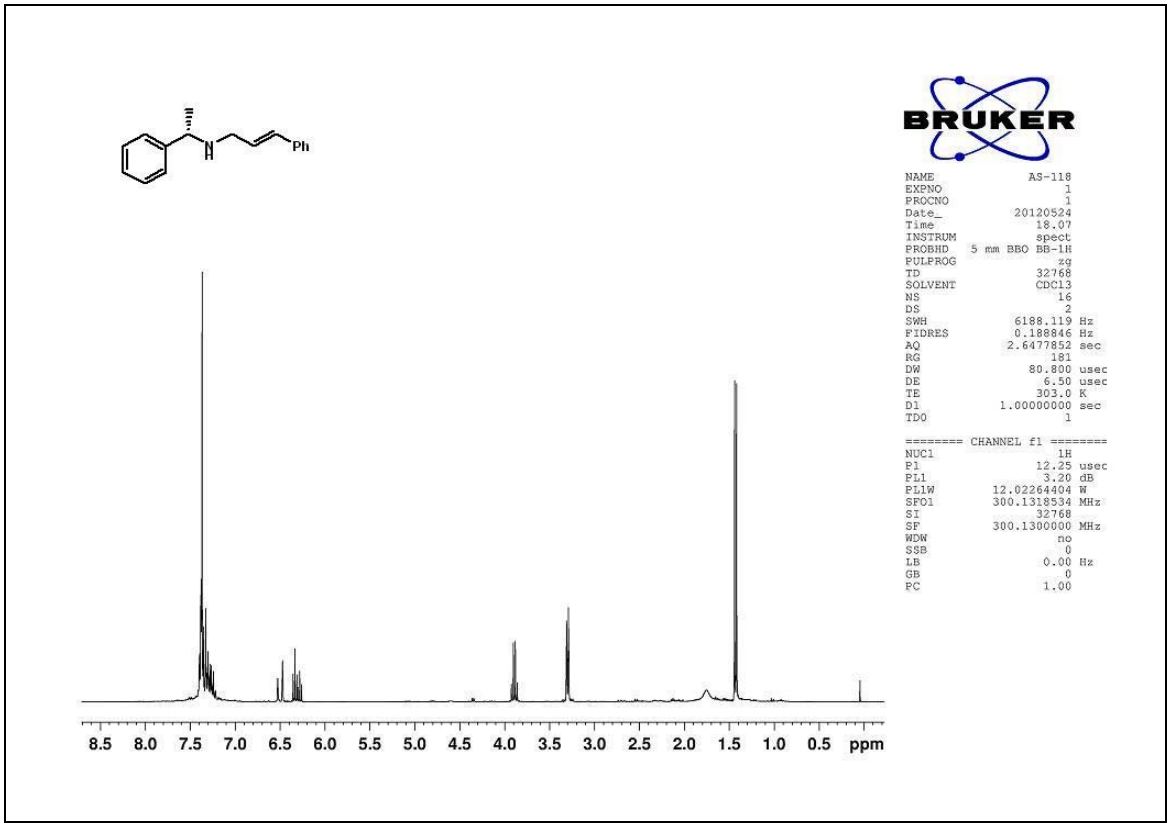


(*E*)-*N*-Benzyl-3-phenylprop-2-en-1-amine (5d)



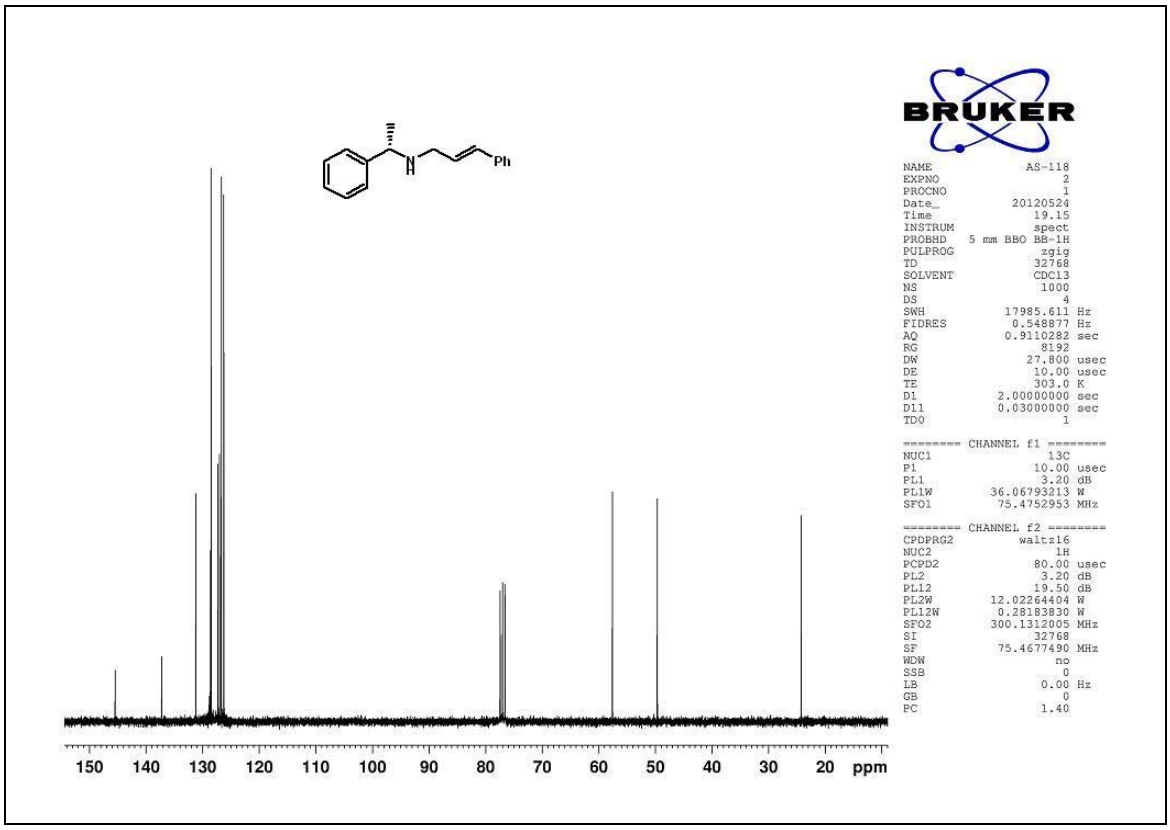


(*S*,*E*)-3-Phenyl-*N*-(1-phenylethyl)prop-2-en-1-amine (5e)




```
NAME                AS-118
EXPNO                    1
PROCNO                   1
Date_             20120524
Time                 18.07
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG                 zg
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6188.119 Hz
FIDRES            0.188846 Hz
AQ                2.6477852 sec
RG                     181
DW                  80.800 usec
DE                   6.50 usec
TE                  303.0 K
D1                1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.25 usec
PL1                   3.20 dB
PL1W            12.02264404 W
SFO1            300.1318534 MHz
SI                   32768
SF              300.1300000 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```




```
NAME                AS-118
EXPNO                    2
PROCNO                   1
Date_             20120524
Time                 19.15
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG                 zgig
TD                   32768
SOLVENT              CDCl3
NS                    1000
DS                       4
SWH              17985.611 Hz
FIDRES            0.548877 Hz
AQ                0.9110282 sec
RG                    8192
DW                  27.800 usec
DE                   10.00 usec
TE                  303.0 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   10.00 usec
PL1                   3.20 dB
PL1W            36.06793213 W
SFO1             75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   3.20 dB
PL12                 19.50 dB
PL2W            12.02264404 W
PL12W            0.28183830 W
SFO2            300.1312005 MHz
SI                   32768
SF               75.4677490 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.40
```

References

[1] O.-Y. Lee, K.-L. Law, C.-Y. Ho, D. Yang, *J. Org. Chem.* **2008**, 73, 8829-8837.
[2] J. Blid, P. Brandt, P. Somfai, *J. Org. Chem.* **2004**, 69, 3043-3049.
[3] S. G. Davies, M. E. C. Polywka, D. R. Fenwick, R. Frank, WO Patent WO/1995/018134, **1995**.
[4] S. Chandrasekhar, M. V. Reddy, L. Chandraiah, *Synth. Commun.* **1999**, 29, 3981-3987.
[5] X. Zhao, D. Liu, H. Guo, Y. Liu, W. Zhang, *J. Am. Chem. Soc.* **2011**, 133, 19354-19357.
[6] N. Nishina, Y. Yamamoto, *Synlett* **2007**, 1767-1770.
[7] L. Adak, K. Chattopadhyay, B. C. Ranu, *J. Org. Chem.* **2009**, 74, 3982-3985.