Nickel-Catalyzed Cyclization of 2-Iodoanilines with Aroylalkynes: An Efficient Route for Quinoline Derivatives

Korivi Rajendra Prasad, Chien-Hong Cheng*

Department of Chemistry, National Tsing Hua University, Hsinchu, 30013, Taiwan

chcheng@mx.nthu.edu.tw

Supporting Information

Table of Contents

1. Preparation of starting materials	S2
2. General procedure of synthesis	S2
3. Spectral data of the compounds	S3-S6
4. NOE data for the selected compounds	S7
5. X-ray structure, crystal data and structure refinement	S8
6. ^1H and ^{13}C NMR spectra of selected compounds	S10-S37

Preparation of Starting Materials:

The starting materials for the present catalytic reaction are prepared using reported procedures. The *o*-iodoanilines^{1, 2} **1b**, **1c**, **1d** and **1e** are prepared from iodination of corresponding aniline derivatives using I₂ and base in water. The other starting material benzoylalkynes are obtained in excellent yields (~ 85%) from the lithiation of alkyne and followed by the addition of benzoylchloride in THF at -78 °C or the other procedures³ can be used. Both the crude mixtures there after are subjected to chromatography to get pure products.

General Procedure for the Preparation of Quinolines:

A round bottom side-arm flask (25 mL) containing NiBr₂(dppe) (3.1 mg, 0.0050 mmol), 2-iodoaniline **1** (0.10 mmol), alkyne **2** (0.20 mmol) and zinc powder (13 mg, 0.20 mmol) was subjected to the Schlenk-line procedures of evacuation and purging of nitrogen for 3 cycles. Freshly distilled acetonitrile (3.0 mL) was added to the reaction system and the reaction mixture was stirred at 80 °C for 12 h. Then the reaction mixture was cooled to room temperature and diluted with dichloromethane. The mixture thus obtained was filtered through a silica gel pad and washed thoroughly with dichloromethane. The filtrate was concentrated in a rotary evaporator and the residue was separated on a silica gel column using a mixture of hexanes and ethyl acetate as eluent to afford the desired pure product **4**. Compounds **4a-l** were synthesized according to this procedure and the spectral data of these compounds are as follows. The spectral data of products **4a**,⁴ **4d**,⁵ **4e**,⁶ **4f**,⁷ **4m**⁸ and **4n**⁹ were reported in the literature.

2,4-Diphenylquinoline (4a): white solid; mp = 102 °C; R_f = 0.57 (10% ethyl acetate in hexanes); ^1H NMR δ 7.44-7.48 (m, 2H), 7.50-7.57 (m, 7H), 7.72 (t, J = 7.5 Hz, 1H), 7.81 (s, 1H), 7.90 (d, J = 3.0 Hz, 1H), 8.18 (d, J = 8.0 Hz, 2H) and 8.24 (d, J = 9.0 Hz, 1H); ^{13}C NMR δ 119.4, 125.6, 125.8, 126.3, 127.6, 128.4, 128.6, 128.8, 129.3, 129.5, 129.6, 130.1, 138.4, 139.7, 148.8, 149.2 and 156.9; HRMS (EI⁺) 281.1195 (cal for $\text{C}_{21}\text{H}_{15}\text{N}$ 281.1204); IR 1357, 1489, 1590 and 3053 cm^{-1} .

4-Butyl-2-phenylquinoline (4b): viscus liquid; R_f = 0.60 (10% ethyl acetate in hexanes); ^1H NMR δ 0.98 (t, J = 7.0 Hz, 3H), 1.46-1.50 (m, 2H), 1.75-1.80 (m, 2H), 3.12 (t, J = 7.8 Hz, 2H), 7.44 (t, J = 6.8 Hz, 1H), 7.49-7.53 (m, 3H), 7.67-7.70 (m, 2H), 8.03 (d, J = 8.5 Hz, 1H), 8.13 (d, J = 8.5 Hz, 2H) and 8.18 (d, J = 8.0 Hz, 1H); ^{13}C NMR δ 13.9, 22.8, 32.3, 32.3, 118.8, 123.4, 126.0, 126.6, 127.6, 128.5, 128.8, 129.2, 130.4, 139.9, 148.4, 149.4 and 157.1; HRMS (EI⁺) 261.1512 (cal for $\text{C}_{19}\text{H}_{19}\text{N}$ 261.1517); IR 1353, 1447, 1551, 1597 and 2957 cm^{-1} .

2-(Naphthalen-2-yl)-4-phenylquinoline (4c): yellow solid; mp = 110 °C; R_f = 0.58 (10% ethyl acetate in hexanes); ^1H NMR δ 7.49 (dt, J = 5.9 and 0.9 Hz, 1H), 7.51-7.53 (m, 3H), 7.55-7.60 (m, 4H), 7.75 (dt, J = 6.4 and 1.1 Hz, 1H), 7.86-7.90 (m, 1H), 7.92 (d, J = 7.0 Hz, 1H), 7.96-8.00 (m, 3H), 8.30 (d, J = 7.0 Hz, 1H), 8.39 (dd, J = 7.1 and 1.4 Hz, 1H) and 8.64 (s, 1H); ^{13}C NMR δ 119.5, 125.1, 125.7, 125.8, 126.3, 126.4, 126.7, 127.2, 127.7, 128.5, 128.6, 128.6, 128.8, 129.6, 129.7, 130.0, 133.5, 133.9, 136.8, 138.4, 148.8, 149.4 and 156.6; HRMS (EI⁺) 331.1346 (cal for $\text{C}_{25}\text{H}_{17}\text{N}$ 331.1361); IR 1361, 1488, 1548, 1592 and 2926 cm^{-1} .

6-Methyl-2,4-diphenylquinoline (4d): white solid; mp = 111 °C; R_f = 0.53 (10% ethyl acetate in hexanes); ^1H NMR δ 2.46 (s, 3H), 7.44 (t, J = 7.0 Hz, 1H), 7.51 (t, J = 7.3

Hz, 3H), 7.54-7.57 (m, 5H), 7.64 (s, 1H), 7.77 (s, 1H) and 8.13-8.17 (m, 3H); ^{13}C NMR δ 21.8, 119.4, 124.4, 125.7, 127.5, 128.3, 128.6, 128.8, 129.2, 129.5, 129.8, 131.8, 136.3, 138.6, 139.7, 147.3, 148.5 and 156.0; HRMS (EI^+) 295.1369 (cal for $\text{C}_{22}\text{H}_{17}\text{N}$ 295.1361); IR 1358, 1489, 1545, 1588 and 2912 cm^{-1} .

4-Butyl-6-methyl-2-phenylquinoline (4e): white solid; mp = $86\text{ }^{\circ}\text{C}$; R_f = 0.48 (10% ethyl acetate in hexanes); ^1H NMR δ 0.99 (t, J = 7.5 Hz, 3H), 1.46-1.51 (m, 2H), 1.75-1.81 (m, 2H), 2.56 (s, 3H), 3.08 (t, J = 7.8 Hz, 2H), 7.42 (t, J = 7.3 Hz, 1H), 7.48-7.53 (m, 3H), 7.65 (s, 1H), 7.76 (s, 1H), 8.05 (d, J = 8.5 Hz, 1H) and 8.11 (d, J = 8.0 Hz, 2H); ^{13}C NMR δ 14.0, 22.0, 22.8, 32.2(2C), 118.7, 122.4, 126.5, 127.5, 128.7, 128.9, 130.2, 131.4, 135.7, 140.1, 147.0, 148.5 and 156.2; HRMS (EI^+) 275.1650 (cal for $\text{C}_{20}\text{H}_{21}\text{N}$ 275.1674); IR 1354, 1447, 1553, 1596 and 2924 cm^{-1} .

6-Chloro-2,4-diphenylquinoline (4f): yellow solid; mp = $121\text{ }^{\circ}\text{C}$; R_f = 0.60 (10% ethyl acetate in hexanes); ^1H NMR δ 7.47 (t, J = 6.8 Hz, 1H), 7.51-7.53 (m, 5H), 7.55-7.57 (m, 2H), 7.66 (dd, J = 7.5 and 1.9 Hz, 1H), 7.83 (s, 1H), 7.86 (d, J = 1.9 Hz, 1H) and 8.17-8.20 (m, 3H); ^{13}C NMR δ 120.1, 124.5, 126.5, 127.6, 128.7, 128.8, 128.9, 129.4, 129.7, 130.5, 131.6, 132.3, 137.7, 139.0, 147.0, 148.6 and 157.0; HRMS (EI^+) 315.0815 (cal for $\text{C}_{21}\text{H}_{14}\text{ClN}$ 315.0815); IR 1153, 1359, 1484, 1589 and 2924 cm^{-1} .

4-Butyl-6-chloro-2-phenylquinoline (4g): yellow solid; mp = $87\text{ }^{\circ}\text{C}$; R_f = 0.58 (10% ethyl acetate in hexanes); ^1H NMR δ 0.99 (t, J = 7.3 Hz, 3H), 1.45-1.50 (m, 2H), 1.74-1.80 (m, 2H), 3.06 (t, J = 7.8 Hz, 2H), 7.45 (dt, J = 8.0 and 2.0 Hz, 1H), 7.51 (t, J = 7.0 Hz, 2H), 7.62 (dd, J = 8.8 and 2.0 Hz, 1H), 7.71 (s, 1H), 7.97 (d, J = 2.0 Hz, 1H), 8.09-8.13 (m, 3H); ^{13}C NMR δ 13.9, 22.8, 32.1, 32.2, 119.4, 122.5, 127.3, 127.6, 128.9,

129.5, 130.1, 131.8, 131.9, 139.3, 146.7, 148.8 and 157.2; HRMS (EI^+) 295.1142 (cal for $\text{C}_{19}\text{H}_{18}\text{ClN}$ 295.1128); IR 1116, 1166, 1306, 1466, 1598 and 2963 cm^{-1} .

6-(Trifluoromethyl)-2,4-diphenylquinoline (4h): white solid; mp = $138\text{ }^{\circ}\text{C}$; R_f = 0.57 (10% ethyl acetate in hexanes); ^1H NMR δ 7.49-7.60 (m, 8H), 7.90 (d, J = 10.0 Hz, 2H), 8.21 (d, J = 7.5 Hz, 3H) and 8.35 (d, J = 9.0 Hz, 1H); ^{13}C NMR δ 120.4, 123.7, 123.7, 124.9, 125.3, 127.7, 128.9, 129.0, 129.5, 130.0, 131.2, 137.4, 138.8, 149.8, 150.2 and 158.8; HRMS (EI^+) 349.1064 (cal for $\text{C}_{22}\text{H}_{14}\text{F}_3\text{N}$ 349.1078); IR 1117, 1312, 1467, 1592 and 2924 cm^{-1} .

4-Butyl-6-(trifluoromethyl)-2-phenylquinoline (4i): white solid; mp = $92\text{ }^{\circ}\text{C}$; R_f = 0.65 (10% ethyl acetate in hexanes); ^1H NMR δ 1.00 (t, J = 7.2 Hz, 3H), 1.48-1.52 (m, 2H), 1.77-1.82 (m, 2H), 3.14 (t, J = 7.8 Hz, 2H), 7.48 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.8 Hz, 2H), 7.78 (s, 1H), 7.86 (dd, J = 8.4 and 2.0 Hz, 1H), 8.15-8.17 (m, 2H), 8.26 (d, J = 8.4 Hz, 1H) and 8.31 (s, 1H); ^{13}C NMR δ 13.9, 22.7, 32.0, 32.2, 119.6, 121.4, 121.4, 124.9, 125.7, 127.7, 128.9, 129.8, 131.5, 139.2, 149.5, 150.3 and 159.0; HRMS (EI^+) 329.1375 (cal for $\text{C}_{20}\text{H}_{18}\text{F}_3\text{N}$ 329.1391); IR 1116, 1166, 1306, 1598 and 2963 cm^{-1} .

6-chloro-4-ethyl-2-methylquinoline(4j): white solid; mp = $74\text{ }^{\circ}\text{C}$; R_f = 0.58 (20% ethyl acetate in hexanes); ^1H NMR δ 1.36 (t, J = 7.3 Hz, 3H), 2.66 (s, 3H), 3.00 (q, J = 7.5 Hz, 2H), 7.13 (s, 1H), 7.57 (dd, J = 9.0 and 2.0 Hz, 1H) and 7.91-7.94 (m, 2H); ^{13}C NMR δ 13.9, 24.8, 25.3, 121.4, 122.3, 126.5, 129.7, 130.9, 131.2, 146.3, 149.0 and 159.2; HRMS (EI^+) 205.0659 (cal for $\text{C}_{12}\text{H}_{12}\text{ClN}$ 205.0658); IR 1091, 1383, 1603 and 2925 cm^{-1} .

2-(Benzo[d][1,3]dioxol-6-yl)-4-(trimethylsilyl)quinoline (4k): white solid; R_f = 0.47 (10% ethyl acetate in hexanes); ^1H NMR δ 0.51 (s, 9H), 6.03 (s, 2H), 6.94 (d, J =

8.0 Hz, 1H), 7.50 (dt, $J = 7.5$ and 1.0 Hz, 1H), 7.63 (dd, $J = 8.3$ and 1.8 Hz, 1H), 7.66-7.70 (m, 2H), 7.90 (s, 1H), 8.01 (d, $J = 8.5$ Hz, 1H) and 8.15 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR δ -0.2, 101.3, 108.0, 108.5, 121.8, 125.1, 125.7, 127.6, 129.0, 130.4, 130.6, 134.3, 147.4, 148.3, 148.7, 149.4 and 155.3; HRMS (EI^+) 321.1173 (cal for $\text{C}_{19}\text{H}_{19}\text{NO}_2\text{Si}$ 321.1185); IR 1041, 1252, 1445, 1489 and 2922 cm^{-1} .

4-(Trimethylsilyl)-2-phenylquinoline (4l): viscous liquid; $R_f = 0.60$ (10% ethyl acetate in hexanes); ^1H NMR δ 0.52 (s, 9H), 7.45-7.47 (m, 1H), 7.51-7.55 (m, 3H), 7.69-7.73 (t, $J = 7.8$ Hz, 1H), 7.99 (s, 1H), 8.05 (d, $J = 8.5$ Hz, 1H), 8.13 (d, $J = 7.0$ Hz, 2H) and 8.27 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR δ -0.2, 125.6, 126.0, 127.6, 127.8, 128.9, 129.2, 129.4, 130.5, 130.6 and 155.9; HRMS (EI^+) 277.1299 (cal for $\text{C}_{18}\text{H}_{19}\text{NSi}$ 277.1287).

2-(Benzo[d][1,3]dioxol-6-yl)quinoline (4m): white solid; mp = $85\text{ }^\circ\text{C}$; $R_f = 0.33$ (10% ethyl acetate in hexanes); ^1H NMR δ 6.02 (s, 2H), 6.93 (d, $J = 8.0$ Hz, 1H), 7.48 (t, $J = 7.0$ Hz, 1H), 7.64 (dd, $J = 8.0$ and 1.5 Hz, 1H), 7.69 (dt, $J = 8.0$ and 1.0 Hz, 1H), 7.72 (d, $J = 1.5$ Hz, 1H), 7.76-7.79 (m, 2H), 8.11 (d, $J = 8.5$ Hz, 1H) and 8.15 (d, $J = 8.5$ Hz, 1H); ^{13}C NMR δ 101.4, 107.9, 108.5, 118.6, 121.8, 126.1, 127.0, 127.4, 129.5, 129.7, 134.1, 136.7, 148.2, 148.4, 148.8 and 156.7; HRMS (EI^+) 249.0782 (cal for $\text{C}_{16}\text{H}_{11}\text{NO}_2$ 249.0790); IR 1051, 1260, 1497, 1596 and 2923 cm^{-1} .

2-Phenylquinoline (4n): white solid; mp = $72\text{ }^\circ\text{C}$; $R_f = 0.50$ (10% ethyl acetate in hexanes); ^1H NMR δ 7.44-7.47 (t, $J = 7.5$ Hz, 1H), 7.50-7.53 (m, 3H), 7.70-7.73 (dt, $J = 1.5$ and 7.3 Hz, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.86 (d, $J = 8.5$ Hz, 1H), 8.15 (d, $J = 7.5$ Hz, 2H) and 8.20 (t, $J = 9.5$ Hz, 1H); ^{13}C NMR δ 119.0, 126.3, 127.2, 127.4, 127.6, 128.8, 129.3, 129.7, 129.8, 136.8, 139.7, 148.2 and 157.4; HRMS (EI^+) 205.0899 (cal for $\text{C}_{15}\text{H}_{11}\text{N}$ 205.0891); IR 1492, 1598, 1728 and 2929 cm^{-1} .

NOE Experiments. The regiochemistry of most products **4** were established based on the ^1H NMR NOE experiments. The results of the NOE experiments are summarized below.

Figure 1, X-ray Structure for 4-Butyl-6-(trifluoromethyl)-2-phenylquinoline (4i).

Table 1. Crystal data and structure refinement for sp16m (compound 4i).

Identification code	sp16m	
Empirical formula	C ₂₀ H ₁₈ F ₃ N	
Formula weight	329.35	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.8344(15) Å	α = 90°.
	b = 18.814(3) Å	β = 96.537(3)°.
	c = 8.0715(11) Å	γ = 90°.
Volume	1634.6(4) Å ³	
Z	4	
Density (calculated)	1.338 Mg/m ³	

Absorption coefficient	0.102 mm ⁻¹
F(000)	688
Crystal size	0.3 x 0.1 x 0.1 mm ³
Theta range for data collection	1.89 to 25.39°
Index ranges	-13 ≤ h ≤ 12, -22 ≤ k ≤ 20, -9 ≤ l ≤ 9
Reflections collected	9725
Independent reflections	3011 [R(int) = 0.0465]
Completeness to theta = 25.39°	100.0 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3011 / 0 / 218
Goodness-of-fit on F ²	0.928
Final R indices [I>3sigma(I)]	R1 = 0.0634, wR2 = 0.2292
R indices (all data)	R1 = 0.1189, wR2 = 0.2196
Extinction coefficient	0.025(4)
Largest diff. peak and hole	0.545 and -0.410 e.Å ⁻³

References

1. Xiao, W. -J.; Alper, H. *J. Org. Chem.* **1999**, *64*, 9646.
2. Dains, F. B.; Vaughan, T. H.; Janney, W. M. *J. Am. Chem. Soc.* **1918**, *40*, 932.
3. (a) L. Chen, L.; Li, C-J. *Org. Lett.*, **2004**, *6*, 3151. (b) Lee, P. H.; Lee, S. W.; Seomoon, D. *Org. Lett.* **2003**, *5*, 4963.
4. Ahmet, M. T.; Miller, J. R.; Osborne, A. G.; Warmesley, J. F. *Acta Crystallographica Section C*, **1995**, *51*, 2105.
5. Nishio, T.; Omote, Y. *J. Chem. Soc. Perkin. Trans 1*, **1983**, *8*, 1773.
6. Yadav, J. S.; Reddy, B. V. S.; Rao, R. S.; Kumar, V. N. *Synthesis*, **2003**, *10*, 1610.
7. Kobayashi, K.; Morikawa, O.; Konishi, H. *Tetrahedron*, **2004**, *60*, 11639.
8. Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478.
9. Fakhfakh, M. A.; Fournet, A.; Prina, E.; Mouscadet, J-F.; Franck, X.; Hocquemiller, R.; Figadere, B. *Bioorg. Med. Chem.* **2003**, *11*, 5013.

—1.657

4a

exp2 szpu1

SAMPLE DEC. 8 VT

date Jun 21 2005 dfrq 488.832

solvent CDC13 dn H1

title /export/home/~dpr 38

opis /nmt5484.dor 0

1/GAME/genes84.00- dam yyy

10- ftd 11298

ACQUISITION dmf 11298

sfrq 125.888 dres 1.0

tn C13 homo 1.0

at 0.508 1b PROCESSING 2.50

np 365287 not used

fb 16 proc ft

be 55 fn not used

tpwr 2.000 math

d1 3783.1 warr

cor 1024 wbp

ct 1024 wbp

atlock Y wnt

gain not used

FLAGS n

11 in y

10 in y

10 in y

10 in y

10 in y

10 in y

10 in y

10 in y

10 in y

10 in y

10 in y

10 in y

10 in y

10 in y

10 in y

10 in y

10 in y

10 in y

10 in y

10 in y

10 in y

10 in y

10 in y

156.903
149.168
148.796
139.658
138.381
130.106
129.556
129.512
129.326
128.829
128.580
128.384
127.578
126.319
125.760
125.627
119.364

77.257
77.000
76.752

0.163
0.167
0.137
0.120
0.035
0.016
7.704
7.691
7.674
7.533
7.522
7.511
7.508
7.484
7.453
7.440
7.240

3.130
3.115
3.080

1.800
1.785
1.780
1.754
1.504
1.480
1.475
1.450
0.884
0.880
0.866
0.816
0.802

521
exp4 szpu1
SAMPLE
date Jul 28 2005
event 1013
1113 export/data-
oper/vmrty5/data-
1/GAME/gen0728-00-
1H.fid
ACQUISITION
freq 489.833
in n1
mc 2.112
nu 31272
sw 800.8
fb not used
bs 4
tpwr 55
pw 5.5
sfs 1.203
tcf 800.4
nt 32
ct 32
atlock y
gain not used
FLAGS
11 n
11 n
dp y
hs nm
DISPLAY
sp -250.1
wp 5247.9
vc 82
vc 82
mc 250
h2mm 7.01
ts 484.32
rfi 4883.3
rfp 5818.8
tn 100.000
nm
ph

S21
expt szpu1

SAMPLE DEC. & VT
date Jul 26 2005 dfrq 499.632
solvent CDCl3 dn H1
f1/2 129.175
oper/vmr/vs/data~ dof 38
1/GANE/gane0725.00~ dm YYY
1C-fid dm W
ACQUISITION 11299
sfreq 125.698 dseq 1.0
fn G13 dres n
at 9.508 homo
nu 3769.1 lb PROCESSING 3.00
sv 36529.7 not used wfile
bs 16 proc ft
tpwr 5.0 math not used f
pv 2.000 warr
d1 3769.1 warr
t1 1024 warr
ct 0 warr
alock Y wnt
gain not used
FLAOS
11 n
1n n
dp n
hs y
DISPLAY -0.3
wp 27650.0
vs 116
sc 0
wc 250
hzmm 115.02
f1 1228.5
rfp 9677.5
th 7
ins 100.000
nm ph

157.089
149.399
148.397
139.890
130.390
129.175
128.767
128.474
127.578
126.549
125.946
123.409
118.779

77.248
77.000
76.743

32.329
32.285

22.829

13.941

Current Data Parameters
NAME 518
EXTNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050728
Time 15.48
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 7183.908 Hz
FIDRES 0.219235 Hz
AQ 2.2807028 sec
RG 128
RW 69.600 usec
DE 6.50 usec
TE 0.0 K
D1 1.00000000 sec
MCRESF 0.00000000 sec
MCMRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 10.00 usec
PL1 3.00 dB
SFO1 599.602980 MHz
F2 - Processing parameters
SI 32768
SF 599.600341 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 0.50

1D NMR plot parameters
CX 20.00 cm
CY 6.00 cm
F1P 9.500 ppm
F1 5696.20 Hz
F2P -0.500 ppm
F2 -299.80 Hz
PFGM 0.50000 ppm/cm
HZCM 299.80002 Hz/cm

ppm
8.63975
8.40399
8.38974
7.99557
7.98072
7.97036
7.92214
7.90818
7.74670
7.59890
7.58761
7.58568
7.57450
7.57286
7.56104
7.54895
7.52943
7.52269
7.51766
7.51258
7.50701
7.48430
7.24009

Current Data Parameters
 NAME 518
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters

Date_ 20050728
 Time 15.52
 INSTRUM spect
 PROBRD 5 mm QNP 1H/1
 PULPROG zgpg
 TD 32768
 SOLVENT Acetone
 NS 564
 DS 0
 SWH 45045.047 Hz
 FIDRES 1.374666 Hz
 AQ 0.363778 sec
 RG 1024
 DW 11.100 usec
 DE 5.50 usec
 TE 0.0 K
 D1 4.00000000 sec
 d11 0.03000000 sec
 DELTA 3.90000010 sec
 MCREST 0.00000000 sec
 MCNEX 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 8.00 usec
 PL1 -2.00 dB
 SFO1 150.787623 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 92.00 usec
 PL2 128.00 dB
 PL12 10.00 dB
 PL13 18.00 dB
 SFO2 599.6029980 MHz

F2 - Processing parameters
 SI 65536
 SF 150.7695464 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 0.50

1D NMR plot parameters
 CX 20.00 cm
 CY 10.00 cm
 P1P 200.000 ppm
 P1 30151.91 Hz
 P2P 0.000 ppm
 F2 0.00 Hz
 FPMCM 10.0000 ppm/cm
 HZCM 1507.65343 Hz/cm

8.174
8.172
8.157
8.147
8.128
7.765
7.639
7.568
7.552
7.544
7.521
7.507
7.482
7.439
7.240

— 2.463

exp1 s2pul

SAMPLE
date Aug 15 2005
solvent CDCl3
file /export/home/~
operator/vmare/s/data-
1/GABE/gab0315.00~
IN-71d

DEC. & VT
dfrq 499.832
dm 38
dpr 8
dot mm
dam c
dwt 11289

ACQUISITION
sfrq 499.833
scn 1
ec 2.182
no 38276
sw 8008.8
fb not used
bs 4
ipwr 55
pw 1.000
ct 800.4
nt 32
ct 32
atock y
gain not used

PROCESSING
wtfile f1
proc f1
fn 32768
meth f
wrt f
wrt wrt

FLAGS
11 n
1n n
dp y
hs nm

DISPLAY
sp -259.1
wp 5247.9
vc 0
wc 250
hzm 2.40
is 163.52
rf1 1043.5
rfp 0
cn 1
fns 100.000
nm ph

5.5

```

exp2 szpu1
SAMPLE
date Aug 15 2005 dfrq 400.132
solvent Aug CDCl3 dn H1
file /export/home/~dpuv 38
Operator/vars/data~ dof 0
1/GAME/gam815.00~ dm yyy
IC-710 dm w
ACQUISITION 112.88
dfrq 129.888
in C13 dres 1.0
at 8.508 homd n
np 37888
sv 38521.7 1b PROCESSING 3.00
fb not used write ft
bs 26 proc not used
cpur 35 1b
d1 2.000 math
tof 3781.1 weff
nt 2848 wexp
ct 752 wds
atlock y wnt
gain not used
FLMOS n
11 in n
in dp y
hs hs mh
DISPLAY
sp -0.9
vd 27850.8
vs 80
sc 0
wc 250
hz 4.81
ls 118.21
f1 12290.2
f2 8877.2
t1 10
t2 10
fne 100.000
ph

```

155.800
 148.476
 147.314
 139.695
 138.585
 136.271
 131.785
 129.789
 129.521
 128.148
 128.784
 128.554
 126.279
 127.472
 125.600
 124.367
 119.426

77.248
 77.000
 76.743

28.677
 21.000

8.118
8.102
8.062
8.045
7.763
7.650
7.525
7.510
7.496
7.481
7.437
7.422
7.408
7.240

$\begin{cases} 3.087 \\ 3.082 \\ 3.066 \end{cases}$

—2.555

1.810
1.795
1.779
1.764
1.748
1.628
1.508
1.491
1.476
1.462
1.001
0.888
0.871

[illegible]

```

536
exp2 szpu1
SAMPLE DEC. 4 VT
date Sep 2 2005 dfreq 489.832
solvent CDC13 dn N1
file /export/home/~dpar 38
opara/vnmrsg/data/~dpar 0
1/NAME/pname 1C-fid 397
1C-fid 11295
ACQUISITION 125.818 dseq
ln C13 dres 1.0
at 0.588 homo
np 37089 1b PROCESSING 3.00
7b not used wifile
ba 16 proc ft
tpr 55 ft not used f
pw 5.0 math
d1 2.080 warr
LOF 3788.1 wexp
rt 2046 wexp
wz 1881 wexp
gain not used
flags n
11 n
1n n
dp y
he nm
DISPLAY -0.3
wp 27650.0
ve 153
sc 0
wc 250
12 118.21
1 118.21
rf1 12286.5
rfp 9877.5
th 3
tne 100.000
nm ph

```

Current Data Parameters
NAME f19
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050627
Time 12.56
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 7183.908 Hz
FIDRES 0.219215 Hz
AQ 2.2807028 sec
RG 428
IN 69.400 usec
DE 6.50 usec
TE 298.2 K
D1 1.0000000 sec
MCHEST 0.0000000 sec
PCPRGK 0.0150000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 10.10 usec
PL1 0.00 dB
SFO1 599.6029980 MHz

F2 - Processing parameters
SI 32768
SF 599.6000297 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 0.50

1D NMR plot parameters
CA 20.00 cm
CT 8.00 cm
F1P 9.500 ppm
F1 5696.20 Hz
F2P -0.500 ppm
F2 -299.80 Hz
PPMCM 0.50000 ppm/cm
HZCM 299.80002 Hz/cm

Current Data Parameters
NAME
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050627
Time 11:56

INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg
TD 32768
SOLVENT H2O-D2O
NS 1024
DS 0
SWH 45045.047 Hz
FIDRES 1.314666 Hz
AQ 0.363748 sec
RG 2048
DM 11.100 usec
DE 6.50 usec
TE 299.1 K
D1 3.00000000 sec
d11 0.03000000 sec
DELTA 2.90000010 sec
MCREST 0.00000000 sec
MCNEX 0.01500000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 6.00 usec
PL1 -2.00 dB
SFO1 150.7874323 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 92.00 usec
PL2 120.00 dB
PL12 11.30 dB
PL13 14.00 dB
SFO2 599.6025980 MHz

F2 - Processing parameters
SI 65536
SF 150.7695470 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 0.50

1D NMR plot parameters
CX 26.00 cm
CY 4.50 cm
F1P 200.000 ppm
F1 30151.91 Hz
F2P 0.000 ppm
F2 0.00 Hz
PCKM 10.00000 ppm/cm
HZCM 1507.6543 Hz/cm

Current Data Parameters
NAME 540
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050905
Time 20.27
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 7183.908 Hz
FIDRES 0.21925 Hz
AQ 2.2807028 sec
RG 32
RW 69.500 usec
RE 6.50 usec
TE 301.2 K
D1 1.00000000 sec
WALTZ16 0.00000000 sec
WALTZ17 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 10.30 usec
PL1 1.00 dB
SFO1 599.6023580 MHz

F2 - Processing parameters
SI 32768
SF 599.6000297 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 0.50

1D NMR plot parameters
CX 20.00 cm
CY 6.00 cm
PIP 9.590 ppm
PL 5696.20 Hz
F2P -0.500 ppm
F2 -299.80 Hz
PFGM 0.50000 ppm/cm
H2O 299.80002 Hz/cm

158.988
150.305
149.528
139.180
131.540
129.773
128.880
127.667
125.652
124.865
121.401
121.375
119.610

77.207
76.995
76.783

32.233
32.024

22.701

13.868

Current Data Parameters
NAME: 540
EXPNO: 2
PROCNO: 1
F2 - Acquisition Parameters
Date_ : 20120505
Time : 20.32
INSTRUM : spect
PROBHD : 5 mm QNP 1H/1
PULPROG : zgpg30
TD : 32768
SOLVENT : CDCl3
NS : 147
DS : 0
SWH : 43545.047 Hz
FIDRES : 1.13466 Hz
AQ : 0.137144 sec
RG : 1024
RW : 11.100 Hz
DE : 6.50 Hz
TE : 301.3 K
DT : 3.100000 sec
G1 : 0.150000 sec
G2 : 0.150000 sec
DELTA : 2.400000 sec
PCPRG2 : 0.000000 sec
PCPRG3 : 0.0150000 sec
PCPRG4 : 0.0150000 sec
===== CHANNEL f1 =====
NUC1 : 13C
P1 : 9.00 usec
PL1 : -2.00 dB
SFO1 : 100.719323 MHz
===== CHANNEL f2 =====
NUC2 : 1H
P2 : 12.00 usec
PL2 : -2.00 dB
SFO2 : 400.146400 MHz
F2 - Processing parameters
SI : 32768
SF : 150.769470 MHz
WDW : EM
SSB : 0
LB : 3.00 Hz
GB : 0
PC : 0.50
F2 NMR F2dc parameters
C2 : 25.00 cm
PC2 : 14.46 cm
PL2 : 200.000 dB
PL12 : 30153.91 Hz
F2F : 0.000 Hz
F2PC2 : 8.00000 Hz/cm
H2C2 : 1208.1557 Hz/cm

input output

7.834
 7.817
 7.573
 7.560
 7.555
 7.551
 —7.248
 —7.131

$\begin{array}{r} 3.917 \\ 3.901 \\ 2.986 \\ 2.972 \\ -2.672 \end{array}$

$\left\{ \begin{array}{l} 1.367 \\ 1.353 \\ 1.322 \end{array} \right.$

[illegible]

[illegible]

534
exp2 szpu1

SAMPLE DEC. & VT
date Aug 11, 2005 dfrq 489.832
solvent h₂O nu1 34
file /export/home/~
opera/vmrsvs/data/~
1/GAME/game0810.00~
1C.fid dam yyy
1C.fid dam v
ACQUISITION 125.689 11293
sfrq 125.689 dseq 1.0
a₁ 0.000 d₁ 0.000
nd 37088 homo n
sw 38529.7 lb PROCESSING 3.00
fb not used wifile
bs 16 proc ft
tpwr 5.0 fn not used f
pw 2.000 math
a₂ 37088 wexp
nt 8000 wbs
ct 752 wnt
atlock y
gain not used
flags n
11 n
11 n
d1 y
h1 y
hs nm

DISPLAY
sp -1257.9
wp 28906.5
vs 93
sc 0
pc 25.0
h₂o 115.82
h₂o 118.21
f₁ 1226.5
f₂ 9677.5
th 6
ins 100.000
nm ph

155.280
149.346
148.743
148.334
147.412

134.328
130.603
130.399
128.980
127.578
125.698
125.077
121.839

108.489
108.010
101.340

77.257
77.000
76.743

-0.215

544-52

8.278
8.262
8.141
8.127
8.059
8.042
7.989
7.727
7.725
7.710
7.696
7.694
7.552
7.550
7.541
7.536
7.527
7.511
7.474
7.460
7.455
7.446
7.240

exp1 s2put

SAMPLE
date Oct 18 2005 dfq 439.832
solvent CDC13 dn
file ACQUISITION exp dper
sfrq 439.839 da
tn H1 dam
at 2.181 dmf
np 38258 deeq
bw 3808.9 dres
fz 1.0
b4 not used home PROCESSING
tpwr 55 wtf1e
pw 5.5 proc
d1 1.000 fn
tof 880.4 meth
ct 32 waf
atlock y wexp
gain not used wfe
flags not used wft

11 n
1n n
du y
hs nm

DISPLAY
sp -550.1
wp 324.3
wc 290
wc 250
h2mm 4.21
ls 394.43
f1 463.3
f1p 583.3
t1 10
ins 9.000
nm

ph

exp2 szpu1

SAMPLE		DEC. & VT	
date	Oct 24 2005	dfreq	493.832
solvent	CDCl3	nmr	13C
file	/export/home/~gmpf	oper	xxx
1/GAME/gam1024.00~	da	1/GAME/gam1024.00~	da
1C.fid	dam	11283	W
ACQUISITION			
sfreq	125.638	dsig	1.0
nu1	37088	nmr	13C
nu2	37088	nmr	13C
nd	37088	nmr	13C
sv	36528.7	1b	PROCESSING
fd	not used	vtfile	3.00
be	not used	proc	ft
ipwr	16	in	not used
nu	37088	match	f
dt	2.000	nt	4576
tof	3758.1	warf	4576
nt	10000	ws	4576
ct	4576	ws	4576
alock	not used	mnt	4576
glin	not used	mnt	4576
FLAGS			
11	n		
in	y		
dp	m		
he	y		
DISPLAY			
sp	-1257.8		
vp	2809.48		
vc	148		
sc	0		
wc	250		
h2nm	115.63		
is	118.21		
rf1	1225.5		
rfp	3677.7		
th			
ins	100.000		
nm	ph		

155.648

138.621
130.514
129.370
129.201
128.864
127.791
127.631
126.052
125.573

77.257
77.000
76.752

-0.207

542
exptl szpu1

date	Aug 28 2005	dfreq	DEC. 4 VT	489.832
solvent	CDCl3	dn	H1	
file	/export/home/~	dpwr	38	
Operator	vmarsys/data~	dot	0	
1/NAME	pane029.10~	dm	nm	
	489.832	dmf	11298	

ACQUISITION

strq	489.833	deed	1.0
tn	H1	dfes	n
at	2.182	homo	PROCESSING
np	3276	wtfile	
sb	not used	proc	
fb	not used	fn	32768
be	4	math	f
tpwr	55	uoft	
pw	1.000	uoft	
stf	5000	uoft	
nt	32	uoft	
ct	32	uoft	
alock	Y	uoft	
gain	not used		

FLAGS

11	n
in	n
dp	Y
hs	nm

DISPLAY

BP	250.1
WC	5257.1
VS	5257.1
SC	101
WC	250
WC	1.13
WC	242.35
WC	442.35
WC	3846.8
WC	100.000

ph

```

542
exp2 szpul
SAMPLE DEC. & VT
date Aug 29 2005 dfreq 499.832
solvent CDCl3 dn H1
f1le /export/home/~dper 36
c1pna watsy/dec-107 38
1/ganf/gane829.00~ dm YYY
1c.fid dm v
ACQUISITION dmf 11293
efreq 125.898 dseq 1.0
ln 0.513 dres n
nt 37088 homp n
sw 36529.7 lb PROCESSING 3.00
fb not used wfile
bs 16 ft
lpwr 15 fn not used f
nt 5.0 match
tof 3769.1 weff
nt 2048 wexp
ct 794 wds
atock n wnt
gain not used
FLOAS
11 n
1n n
dp y
hs nm
DISPLAY
sp -0.3
wp 27659.0
vs 124
sc 0
wc 250
hzmm 119.20
119.41
f1 12265.4
rfp 9877.5
th 7
ins 100.000
nm ph

```

```

156.681
148.831
148.388
148.166
136.688
134.124
129.645
129.521
127.401
126.993
126.052
121.750
118.610
108.463
107.922
101.349
77.257
77.000
76.752

```