Supporting Information

Facile Synthesis of 2-Amino-3-Bromoquinolines by Palladium-Catalyzed Isocyanide Insertion and Cyclization of *gem*-Dibromovinylanilines

Baishan Jiang,*[a] Langxi Hu,[a] and Weijun Gui[a]

[a] Institute of Chemical Biology, Guangzhou Institutes of Biomedicine and Health, Chinese Academy of Sciences. 190 Kaiyuan Avenue, Guangzhou 510530, China. Tel: 86-20-3201-5209; Fax: 86-20-3201-5209; Email: jiang_baishan@gibh.ac.cn

Table of Contents for Supporting Information

1. General Considerations

All reagents were purchased from commercial suppliers and used without further purification. For flash column chromatography, silica gel (200-300 mesh) was applied. Reactions were monitored using thin-layer chromatography (TLC) on commercial silica gel plates (GF 254). Visualization of the developed plates was performed under UV lights (GF 254 nm). ^{1}H and ^{13}C NMR spectra were recorded on a 400 or 500 MHz spectrometer. Chemical shifts (δ) were reported in ppm referenced to an internal tetramethylsilane standard (δ 0.00) or the $CDCl_3$-d1 residual peak (δ 7.26) for ^{1}H NMR. Chemical shifts of ^{13}C NMR were reported relative to $CDCl_3$ (δ 77.0). The following abbreviations were used to describe peak splitting patterns when appropriate: br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constant, J, was reported in Hertz unit (Hz). High resolution mass spectra (HRMS) were obtained on an ESI-LC-MS/MS spectrometer.

2. Preparation of Substrates 1

2-(gem-dibromovinyl)aniline **1** were prepared and characterized in our previous work[1].

3. General Procedures and Characterization Data

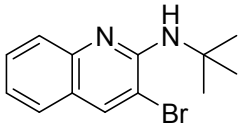
1) Typical synthetic procedure of 2-amino-3-bromoquinolines 2a

A mixture of 2-(gem-dibromovinyl)aniline **1a** (0.2 mmol), $Pd(dppf)Cl_2$ (7.3 mg, 0.01 mmol, 5.0 mol %), Cs_2CO_3 (131 mg, 0.4 mmol), and t-butyl isocyanide (0.034mL, 0.3 mmol) in 1,4-Dioxane (2.0 mL) was stirred under air at 100°C for 3h in sealed tube. After complete consumption of **1a** as monitored by TLC, the reaction mixture was cooled to room temperature, extracted twice with Et_2O, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give the crude product, which was further purified by flash chromatography on silica gel using petroleum ether/ethyl acetate as eluent to afford the desired product **2a**.

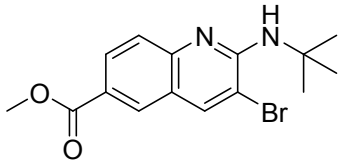
2) Typical synthetic procedure of 3-substituted-2-aminoquinolines

A mixture of 2-(gem-dibromovinyl)aniline **1a** (0.2 mmol), $Pd(dppf)Cl_2$ (5.0 mol %), Cs_2CO_3 (0.4 mmol), and t-butyl isocyanide (0.034mL, 0.3 mmol) in 1,4-Dioxane (2.0 mL) was stirred under air at 100°C for 3h in sealed tube. Upon completion, the reaction mixture was cooled to room temperature and extracted twice with ethyl acetate, dried and concentrated. Then **3**(**4**/**5**) (0.3 mmol), $Pd(dppf)Cl_2$ (5.0 mol %), K_3PO_4 (0.4 mmol), and toluene (2.0 mL) were added to the residue under N_2 and heated at 120°C for further 12h. Upon completion, the reaction mixture was cooled to room temperature and extracted twice with ethyl acetate, dried and concentrated. The residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate as eluent to afford the desired product **6**(**7**/**8**).

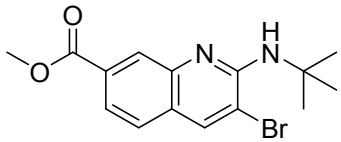
3) Product Characterization



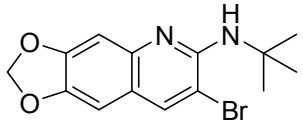
2a: Yellow solid, 48 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.61 (d, *J* = 8.3 Hz, 1H), 7.42 (dd, *J* = 19.4, 7.7 Hz, 2H), 7.11 (d, *J* = 7.4 Hz, 1H), 5.22 (s, 1H), 1.50 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.70, 146.80, 138.34, 132.25, 132.16, 129.46, 128.54, 128.42, 126.71, 126.38, 123.86, 122.41, 108.96, 52.31, 29.03. MS(ESI, m/z): 279.0$[M+H]^+$ HRMS (ESI): Exact mass calcd for $C_{13}H_{15}BrN_2$ $[M+H]^+$ 279.0491, found 279.0495.



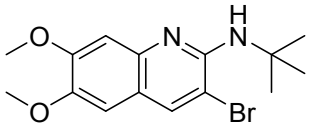
2b: Yellow solid, 55 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.15-8.04 (m, 2H), 7.67 (d, J = 8.7 Hz, 1H), 5.51 (s, 1H), 3.94 (s, 3H), 1.58 (s, 9H). ^{13}C NMR (101 MHz, CDCl3) δ 166.88, 152.86, 149.30, 139.01, 129.48, 129.43, 126.51, 123.91, 122.72, 109.60, 52.55, 51.84, 28.80. MS(ESI, m/z):337.1$[M+H]^+$, HRMS (ESI): Exact mass calcd for $C_{15}H_{18}BrN_2O_2$ $[M+H]^+$ 337.0546, found 337.0552.



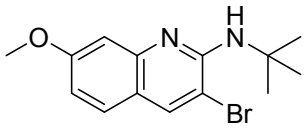
2c: Yellow solid, 58 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.06 (s, 1H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.50 (s, 1H), 5.39 (s, 1H), 3.97 (s, 3H), 1.59 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.12, 152.08, 146.15, 137.85, 131.03, 128.96, 126.37, 126.24, 122.13, 111.25, 52.38, 51.94, 28.80. MS(ESI, m/z): 337.1$[M+H]^+$ HRMS (ESI): Exact mass calcd for $C_{15}H_{18}BrN_2O_2$ $[M+H]^+$ 337.0546, found 337.0554.



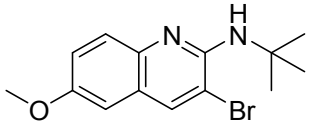
2d: Yellow solid, 55 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.05 (s, 1H), 6.79 (s, 1H), 6.00 (s, 2H), 5.09 (s, 1H), 1.55 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.89, 150.36, 144.55, 137.22, 118.92, 106.14, 104.32, 102.21, 101.16, 51.94, 28.96. MS(ESI, m/z): 323.0 $[M+H]^+$, HRMS (ESI): Exact mass calcd for $C_{14}H_{16}BrN_2O_2$ $[M+H]^+$ 323.0390, found 323.0398.



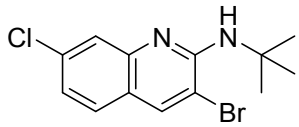
2e: Yellow solid, 53 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.09 (s, 1H), 6.81 (s, 1H), 5.14 (s, 1H), 4.02 (s, 3H), 3.95 (s, 3H), 1.60 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.20, 150.95, 146.57, 143.20, 136.82, 117.86, 106.51, 106.12, 105.03, 55.95, 55.93, 51.94, 29.00. MS (ESI, m/z): 339.1$[M+H]^+$, HRMS (ESI): Exact mass calcd for $C_{15}H_{20}BrN_2O_2$ $[M+H]^+$ 339.0703, found 339.0711.



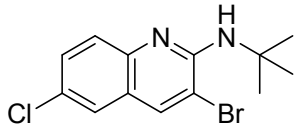
2f: Yellow oil, 51 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.36 (d, J = 8.8 Hz, 1H), 7.05 (s, 1H), 6.85 (d, J = 8.7 Hz, 1H), 5.26 (s, 1H), 3.92 (s, 3H), 1.59 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.98, 151.99, 148.28, 137.82, 127.37, 118.46, 114.41, 105.87, 55.34, 52.08, 28.92. MS(ESI, m/z): 309.1$[M+H]^+$, HRMS (ESI): Exact mass calcd for $C_{14}H_{18}BrN_2O$ $[M+H]^+$ 309.0597, found 309.0603.



2g : Yellow oil, 49 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.61 (d, J = 9.0 Hz, 1H), 7.20 (d, J = 9.0 Hz, 1H), 6.84 (s, 1H), 5.15 (s, 1H), 3.85 (s, 3H), 1.56 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.23, 150.50, 142.39, 137.31, 128.03, 124.06, 120.94, 109.37, 105.67, 55.54, 52.02, 28.98. MS(ESI, m/z): 309.1$[M+H]^+$, HRMS (ESI): Exact mass calcd for $C_{14}H_{18}BrN_2O$ $[M+H]^+$ 309.0597, found 309.0603.

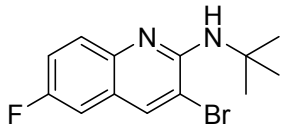


2h: Yellow solid, 54 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.69 (s, 1H), 7.40 (d, J = 8.5 Hz, 1H), 7.14 (d, J = 8.5 Hz, 1H), 5.37 (s, 1H), 1.56 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.18, 147.29, 137.84, 127.31, 125.73, 123.05, 108.95, 52.34, 28.81. MS(ESI, m/z): 313.0 $[M+H]^+$, HRMS (ESI): Exact mass calcd for $C_{13}H_{15}BrClN_2$ $[M+H]^+$ 313.0102, found 313.0108.

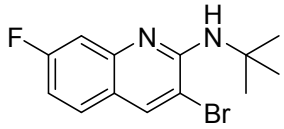


2i: Yellow solid, 52 mg, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.60 (d, J = 8.9 Hz, 1H), 7.44 (d, J = 7.1 Hz, 2H), 5.34 (s, 1H), 1.57 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.62, 145.10, 137.21, 129.98, 128.07, 127.37, 124.98, 124.03, 110.00, 52.25, 28.77. MS(ESI, m/z): 313.0$[M+H]^+$, HRMS (ESI): Exact mass calcd for $C_{13}H_{15}BrClN_2$ $[M+H]^+$ 313.0102, found

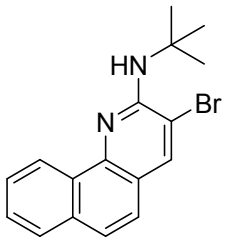
313.0108.



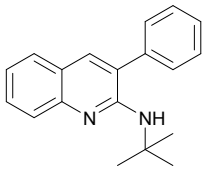
2j: Yellow solid, 49 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.65 (dd, *J* = 8.9, 5.3 Hz, 1H), 7.35 – 7.19 (m, 1H), 7.12 (d, *J* = 8.8 Hz, 1H), 5.27 (s, 1H), 1.57 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.01, 157.08, 151.08, 143.57, 137.49, 137.45, 128.52, 128.45, 123.54, 123.47, 118.91, 118.71, 110.17, 109.79, 109.62, 52.13, 28.80. MS(ESI, m/z): 297.0$[M+H]^+$ HRMS (ESI): Exact mass calcd for $C_{13}H_{14}BrFN_2$ $[M+H]^+$ 297.0397, found 297.0403.



2k: Yellow solid, 50 mg, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.44 (s, 1H), 7.31 (d, *J* = 10.8 Hz, 1H), 6.96 (s, 1H), 5.36 (s, 1H), 1.57 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.57, 152.11, 147.78, 137.90, 128.09, 128.01, 120.46, 112.01, 111.81, 110.74, 110.58, 107.93, 107.91, 52.27, 28.78. MS(ESI, m/z): 297.0$[M+H]^+$ HRMS (ESI): Exact mass calcd for $C_{13}H_{14}BrFN_2$ $[M+H]^+$ 297.0397, found 297.0403.

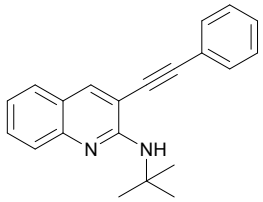


2l: Yellow solid, 56 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (d, *J* = 7.6 Hz, 1H), 8.09 (s, 1H), 7.84 (d, *J* = 7.2 Hz, 1H), 7.64 (t, *J* = 6.3 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 1H), 7.44 (d, *J* = 8.6 Hz, 1H), 5.37 (s, 1H), 1.71 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.73, 144.50, 138.50, 134.16, 130.73, 127.66, 127.53, 126.11, 124.65, 124.36, 123.18, 120.12, 107.60, 52.16, 28.82. MS(ESI, m/z): 329.1$[M+H]^+$ HRMS (ESI): Exact mass calcd for $C_{17}H_{17}BrN_2$ $[M+H]^+$ 329.0648, found 329.0656.

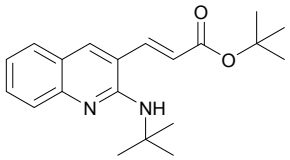


6: Yellow oil, 36.8 mg, 66% yield. 1H NMR (400 MHz, CDCl3) δ 7.66 (d, J = 8.4 Hz, 1H), 7.52 (s, 1H), 7.39 (m, 7H), 7.11 (t, J = 7.4 Hz, 1H), 4.66 (s, 1H), 1.43 (s, 9H); 13C NMR (101 MHz, DMSO) δ 153.30, 146.55, 137.11, 135.30, 132.99, 132.79, 128.89, 128.65, 128.53, 128.40, 128.35, 128.28, 127.80, 127.12, 125.70, 125.44, 122.46, 121.42, 50.92, 28.51. MS(ESI, m/z):

277.1[M+H]+, HRMS (ESI): Exact mass calcd for C19H21N2 [M+H]+ 277.1699, found 277.1705.



7: Yellow oil, 30.6 mg, 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.70 (s, 1H), 7.57 (d, *J* = 4.4 Hz, 2H), 7.53 (t, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 4.5 Hz, 3H), 7.20 (t, *J* = 7.3 Hz, 1H), 5.56 (s, 1H), 1.64 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.70, 147.46, 139.11, 131.50, 129.83, 128.70, 128.52, 128.39, 127.10, 126.76, 122.84, 122.15, 122.08, 107.56, 95.85, 85.21, 51.82, 29.13. MS(ESI, m/z): 301.2 $[M+H]^+$ HRMS (ESI): Exact mass calcd for $C_{21}H_{20}N_2$ $[M+H]^+$ 301.1699, found 301.1705



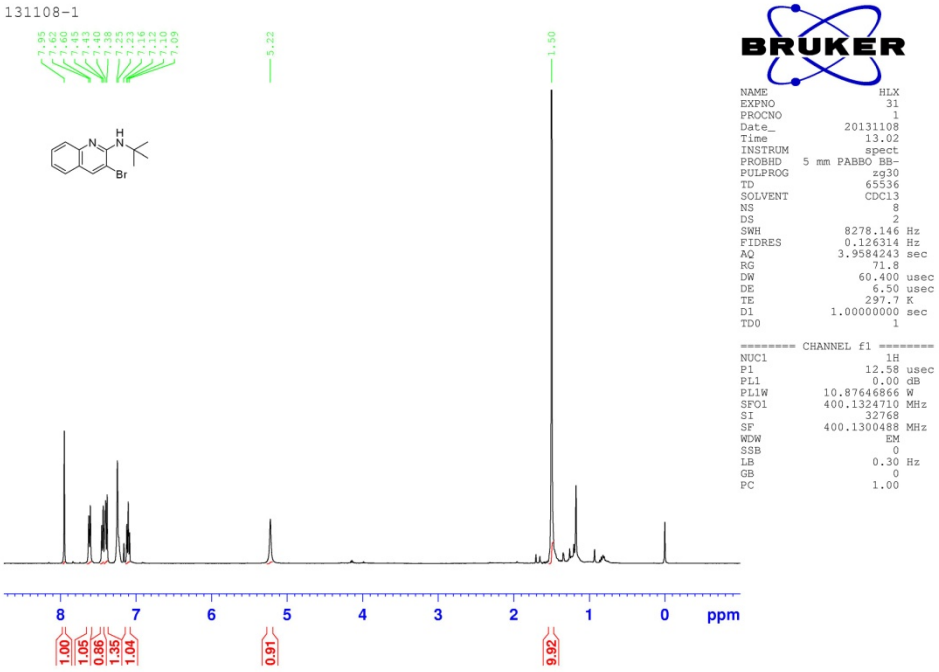
8: Yellow oil, 27.9 mg, 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.59 (m, 4H), 7.18 (t, *J* = 7.3 Hz, 1H), 6.40 (d, *J* = 15.5 Hz, 1H), 4.60 (s, 1H), 1.59 (s, 9H), 1.56 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.76, 153.71, 148.58, 138.46, 135.38, 130.01, 127.68, 126.78, 124.00, 122.86, 122.36, 119.55, 80.93, 52.29, 29.40, 28.32. MS(ESI, m/z): 327.1[M+H]$^+$, HRMS (ESI): Exact mass calcd for $C_{20}H_{27}N_2O_2$ $[M+H]^+$ 327.2067, found 327.2071.

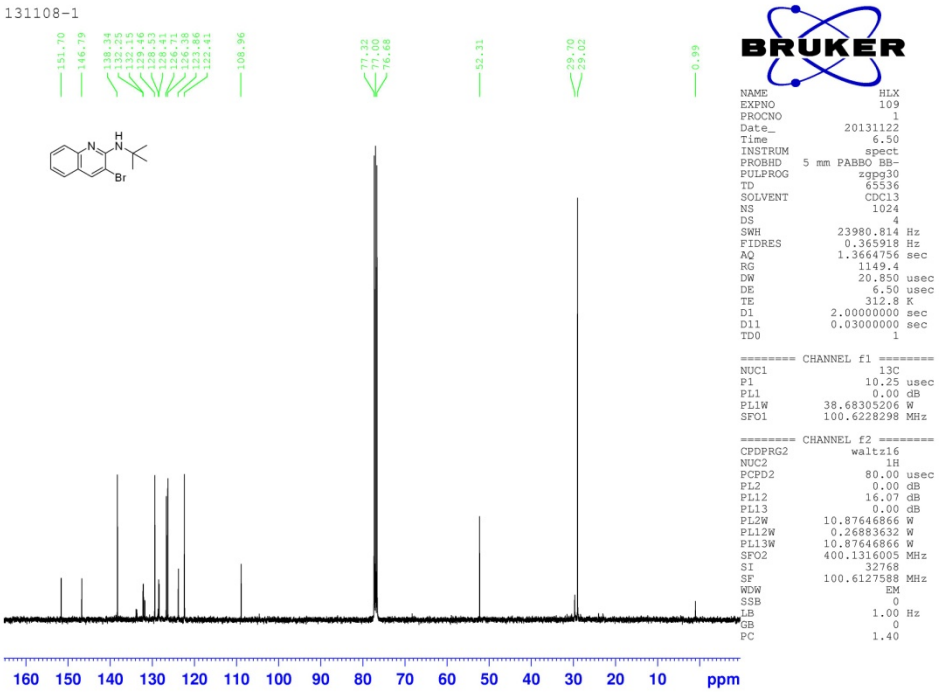
4. References

Baishan Jiang, Kemei Tao, Wang Shen, Jiancun Zhang, *Tetrahedron Letters*, 2010, *Volume 51, Issue 48, 6342-6344.*

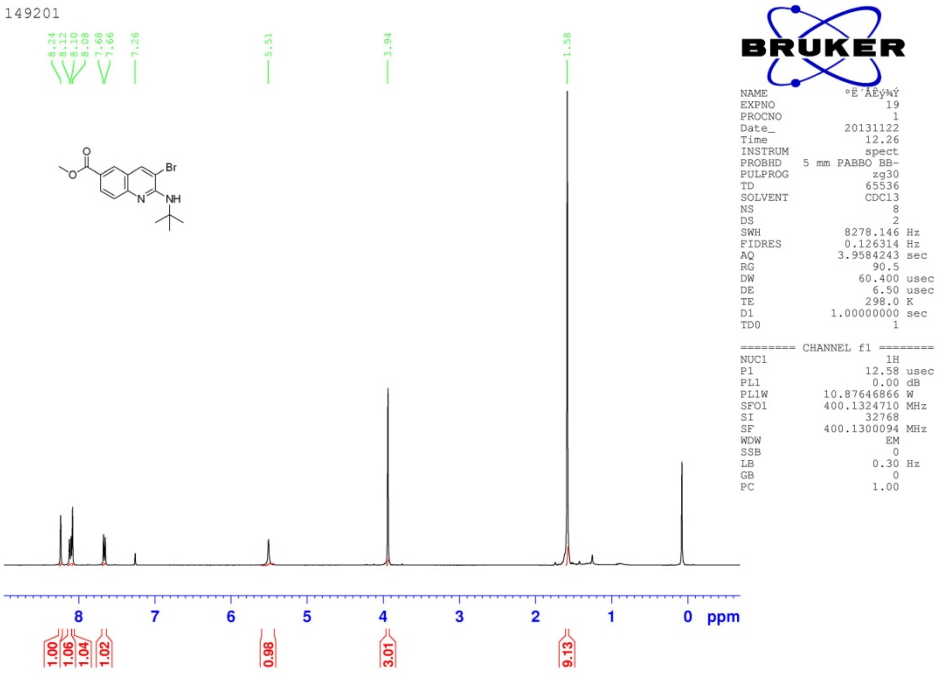
5. ^{1}H and ^{13}C NMR Spectra of Compounds

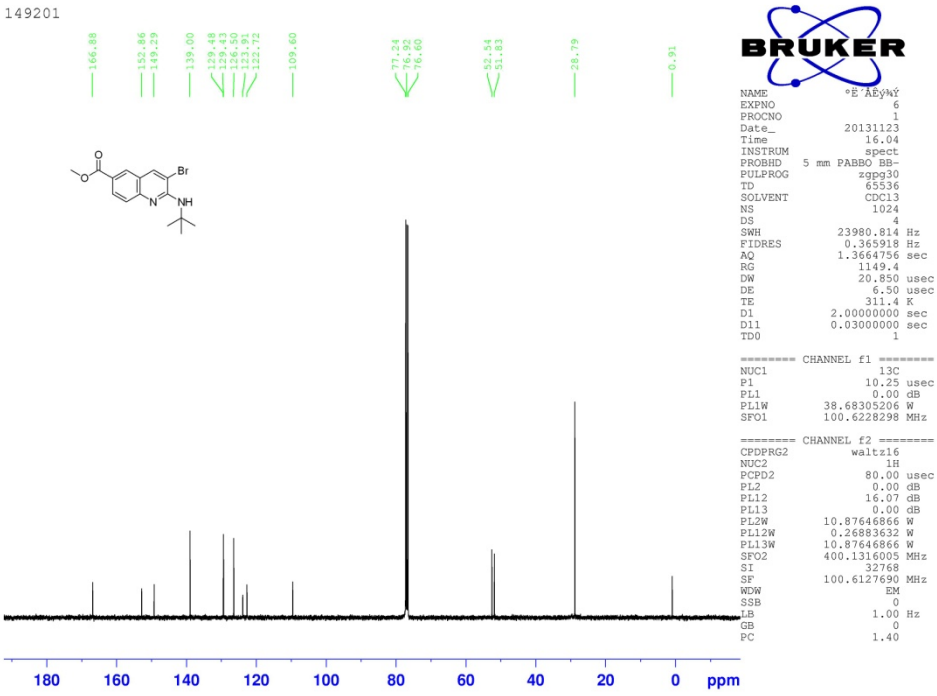
2a



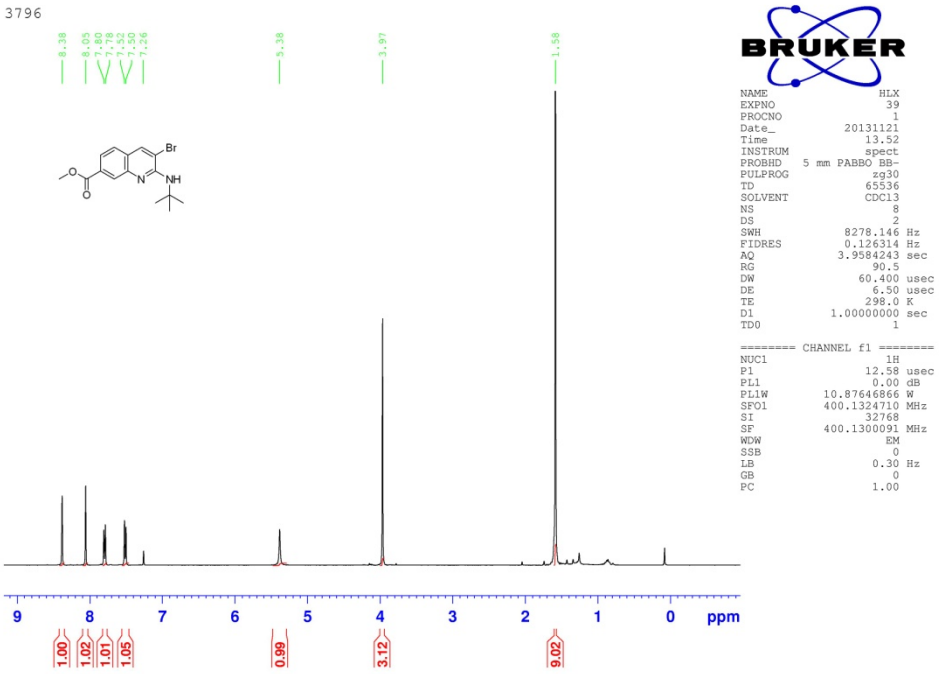


2b

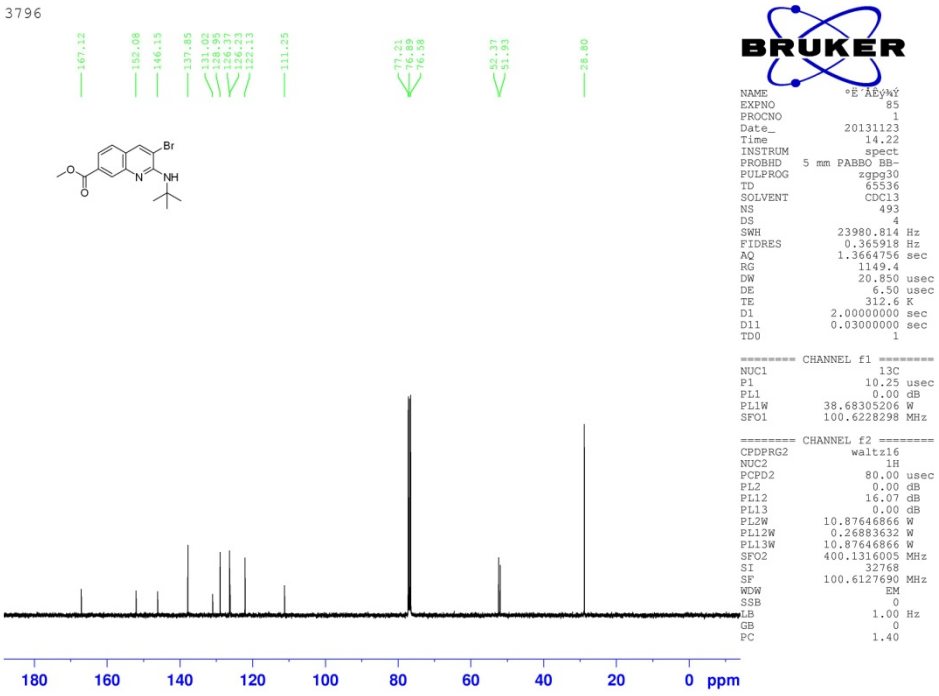

149201
8.24
8.12
8.10
8.08
7.68
7.66
7.26
5.51
3.94
1.58
Br
NH
8
7
6
5
4
3
2
1
0
ppm
1.00
1.06
1.04
1.02
0.98
3.01
9.13


149201
166.88
152.86
149.29
139.00
129.48
129.43
126.50
123.91
122.72
109.60
77.24
76.92
76.60
52.54
51.83
28.79
0.91
Br
NH
180
160
140
120
100
80
60
40
20
0
ppm

2c

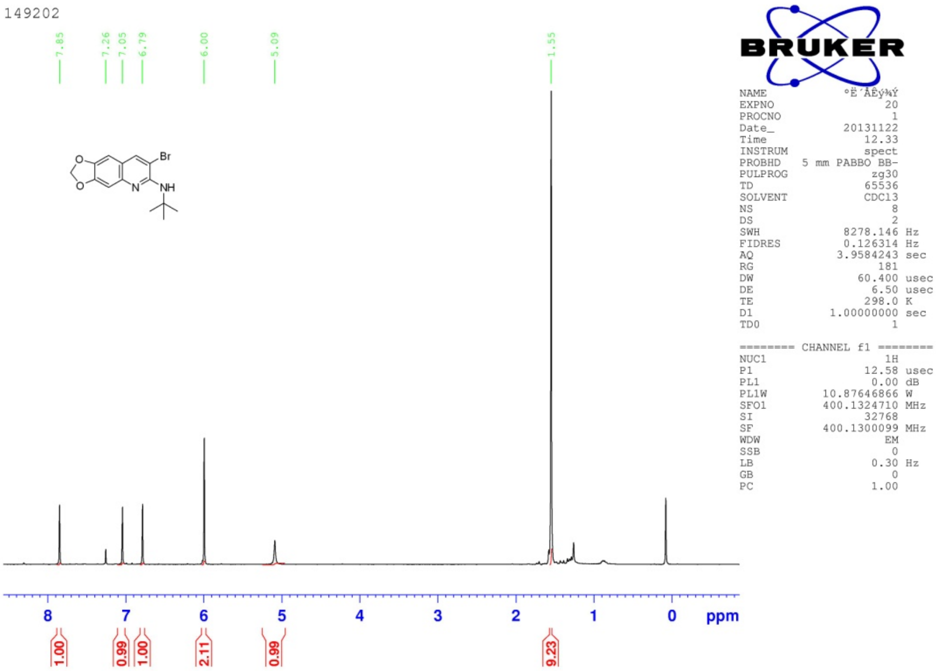


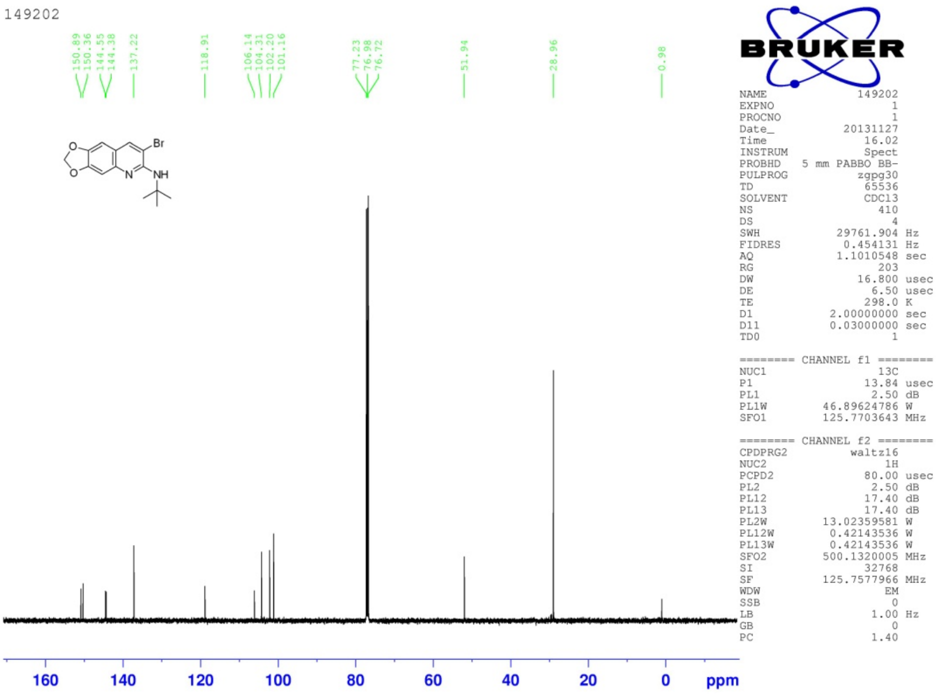

```
NAME                  HLX
EXPNO                  39
PROCNO                  1
Date_            20131121
Time                13.52
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ               3.9584243 sec
RG                   90.5
DW                60.400 usec
DE                 6.50 usec
TE                 298.0 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 12.58 usec
PL1                 0.00 dB
PL1W         10.87646866 W
SFO1         400.1324710 MHz
SI                  32768
SF           400.1300091 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                 1.00
```



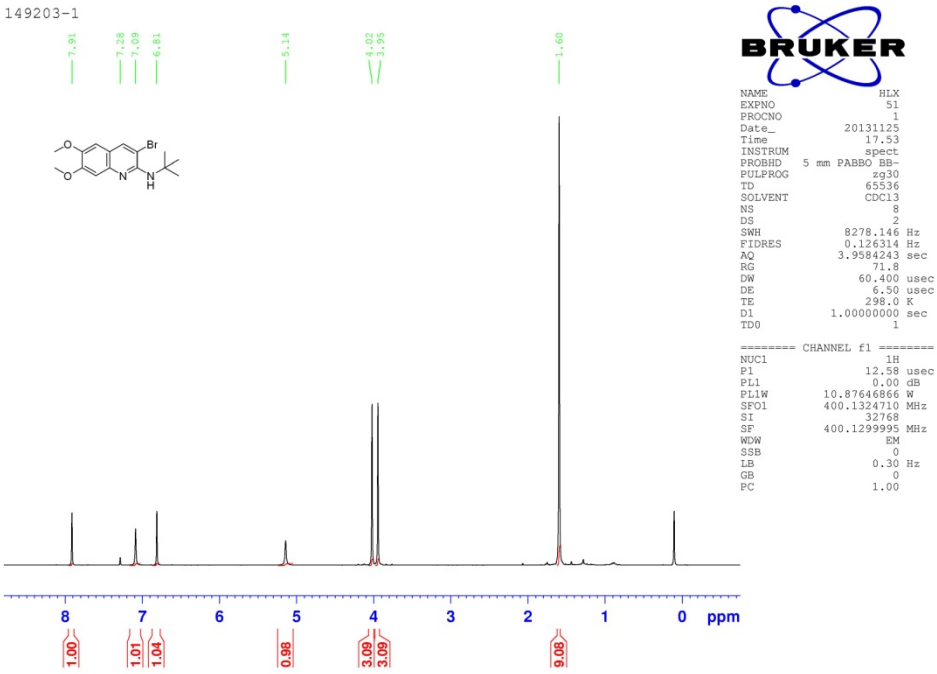

```
NAME                  °È´ÁÉý¾Ý
EXPNO                  85
PROCNO                  1
Date_            20131123
Time                14.22
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    493
DS                      4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ               1.3664756 sec
RG                 1149.4
DW                20.850 usec
DE                 6.50 usec
TE                 312.6 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                 10.25 usec
PL1                 0.00 dB
PL1W         38.68305206 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               16.07 dB
PL13                0.00 dB
PL2W         10.87646866 W
PL12W         0.26883632 W
PL13W        10.87646866 W
SFO2         400.1316005 MHz
SI                  32768
SF           100.6127690 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                 1.40
```

2d

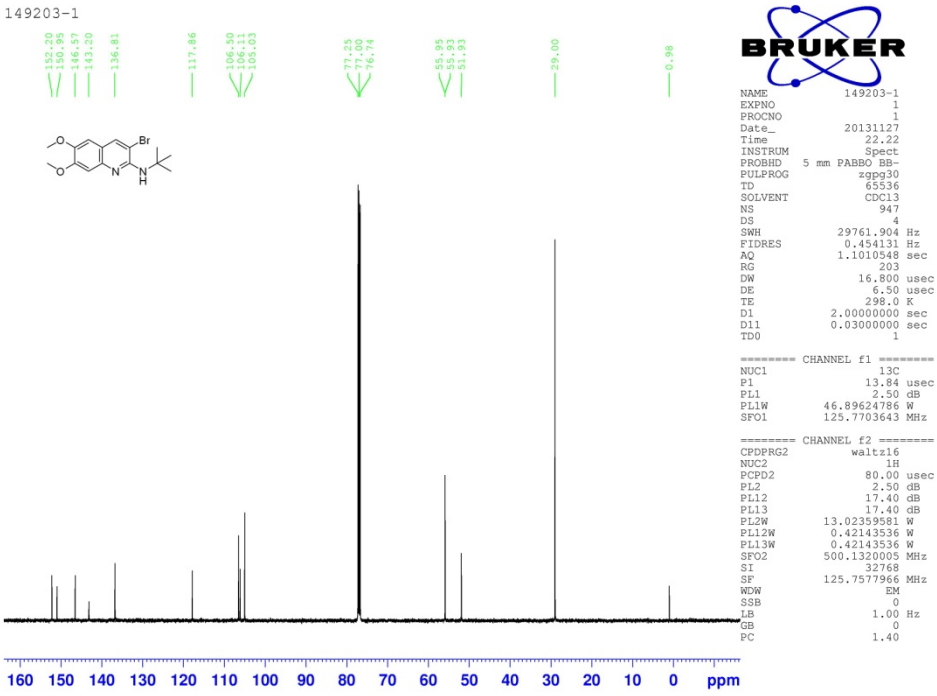

149202
7.85
7.26
7.05
6.79
6.00
5.09
1.55
Br
O
O
N
NH
BRUKER
NAME
EXPNO 20
PROCNO 1
Date_ 20131122
Time 12.33
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 181
DW 60.400 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.58 usec
PL1 0.00 dB
PL1W 10.87646866 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300099 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8
7
6
5
4
3
2
1
0
ppm
1.00
0.99
1.00
2.11
0.99
9.23


149202
150.89
150.36
144.55
144.38
137.22
118.91
106.14
104.31
102.20
101.16
77.23
76.98
76.72
51.94
28.96
0.98
Br
O
O
N
NH
BRUKER
NAME 149202
EXPNO 1
PROCNO 1
Date_ 20131127
Time 16.02
INSTRUM Spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 410
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 203
DW 16.800 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 13.84 usec
PL1 2.50 dB
PL1W 46.89624786 W
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 2.50 dB
PL12 17.40 dB
PL13 17.40 dB
PL2W 13.02359581 W
PL12W 0.42143536 W
PL13W 0.42143536 W
SFO2 500.1320005 MHz
SI 32768
SF 125.7577966 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
160
140
120
100
80
60
40
20
0
ppm

2e

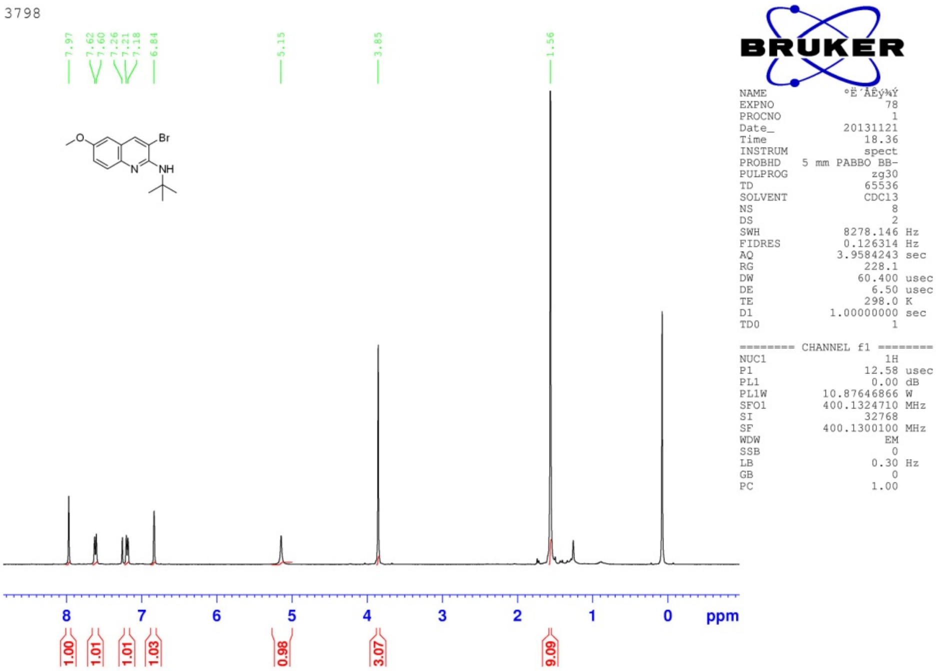


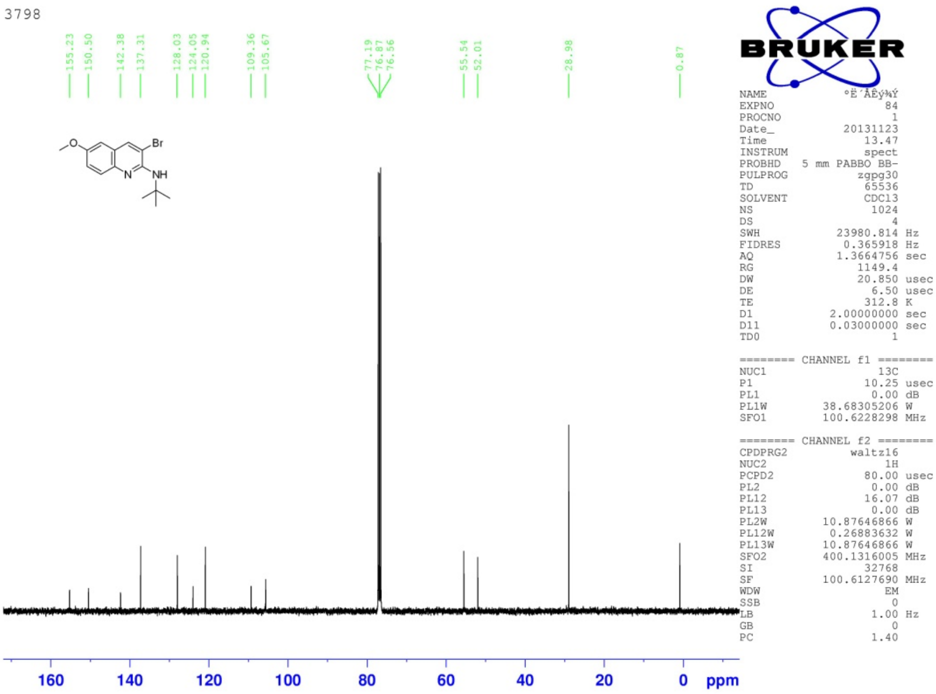

```
NAME                 HLX
EXPNO                 51
PROCNO                 1
Date_           20131125
Time               17.53
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8278.146 Hz
FIDRES             0.126314 Hz
AQ              3.9584243 sec
RG                  71.8
DW                 60.400 usec
DE                  6.50 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.58 usec
PL1                0.00 dB
PL1W         10.87646866 W
SFO1         400.1324710 MHz
SI                 32768
SF           400.1299995 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```



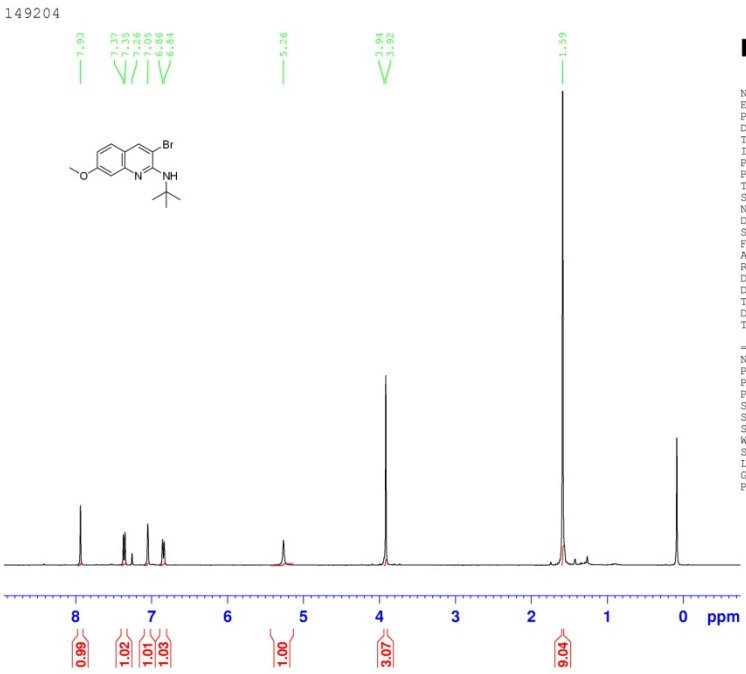

```
NAME              149203-1
EXPNO                  1
PROCNO                 1
Date_           20131127
Time               22.22
INSTRUM            Spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   947
DS                     4
SWH            29761.904 Hz
FIDRES             0.454131 Hz
AQ              1.1010548 sec
RG                   203
DW                 16.800 usec
DE                  6.50 usec
TE                298.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 13.84 usec
PL1                2.50 dB
PL1W         46.89624786 W
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                2.50 dB
PL12               17.40 dB
PL13               17.40 dB
PL2W         13.02359581 W
PL12W         0.42143536 W
PL13W         0.42143536 W
SFO2         500.1320005 MHz
SI                 32768
SF           125.7577966 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```

2f

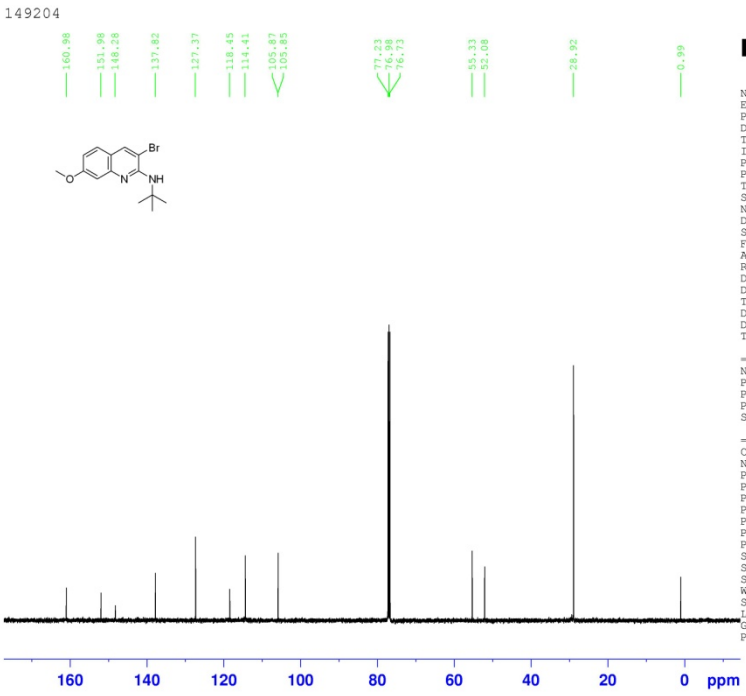

3798
7.97
7.62
7.60
7.26
7.21
7.18
6.84
5.15
3.85
1.56
Br
NH
N
O
BRUKER
NAME
EXPNO 78
PROCNO 1
Date_ 20131121
Time 18.36
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 228.1
DW 60.400 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.58 usec
PL1 0.00 dB
PL1W 10.87646866 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300100 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.01
1.03
0.98
3.07
9.09


3798
155.23
150.50
142.38
137.31
128.03
124.05
120.94
109.36
105.67
77.19
76.87
76.56
55.54
52.01
28.98
0.87
Br
NH
N
O
BRUKER
NAME
EXPNO 84
PROCNO 1
Date_ 20131123
Time 13.47
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 1149.4
DW 20.850 usec
DE 6.50 usec
TE 312.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.25 usec
PL1 0.00 dB
PL1W 38.68305206 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 16.07 dB
PL13 0.00 dB
PL2W 10.87646866 W
PL12W 0.26883632 W
PL13W 10.87646866 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
160
140
120
100
80
60
40
20
0
ppm

2g

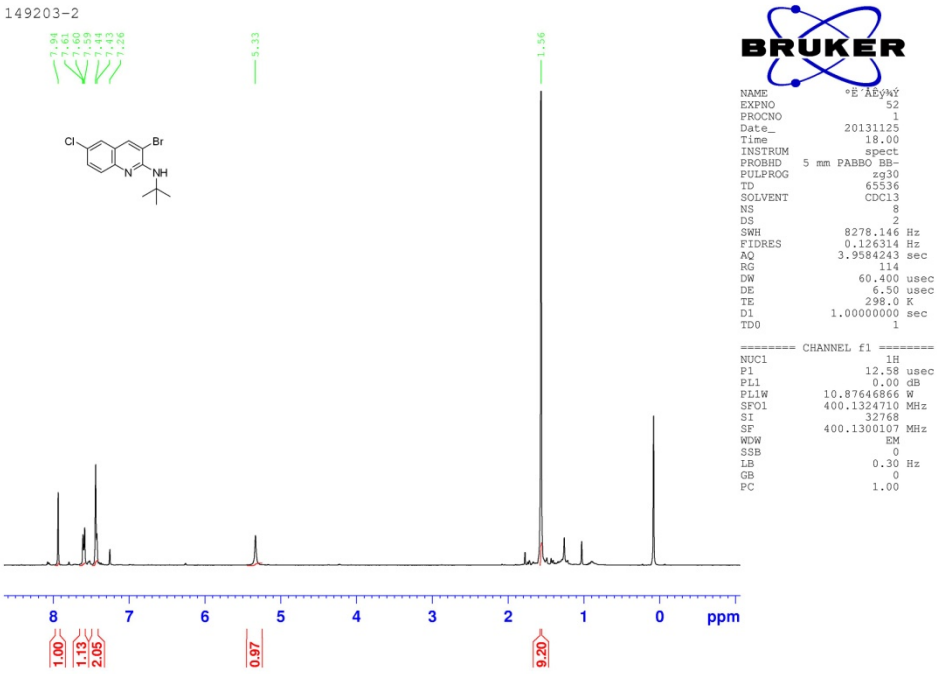



```
NAME                 HLX
EXPNO                 47
PROCNO                 1
Date_           20131126
Time                15.21
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                  90.5
DW                60.400 usec
DE                 6.50 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.58 usec
PL1                0.00 dB
PL1W         10.87646866 W
SFO1         400.1324710 MHz
SI                 32768
SF           400.1300101 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

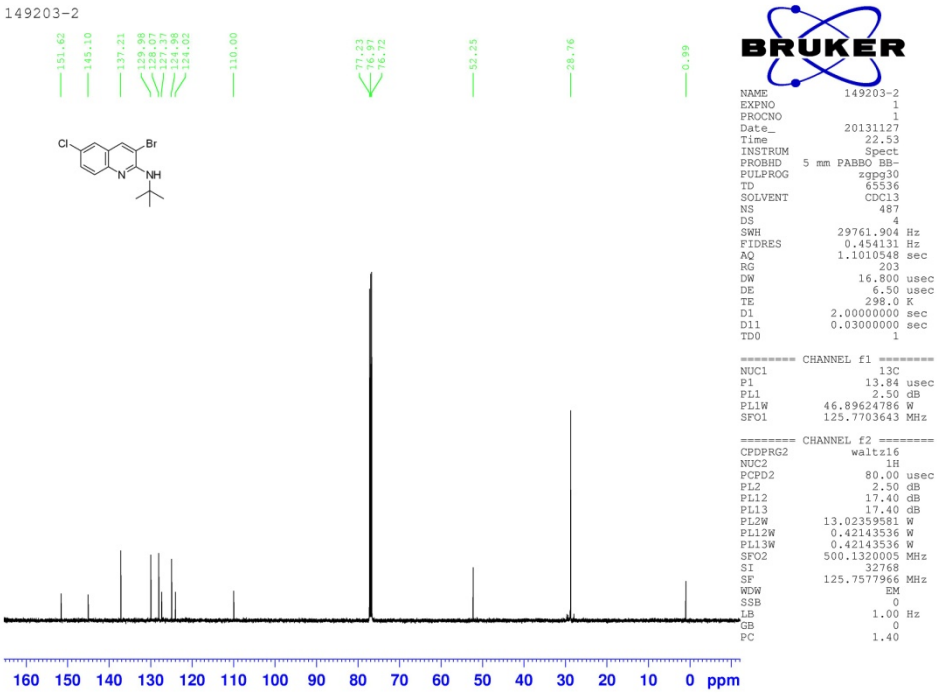



```
NAME                149204
EXPNO                    1
PROCNO                   1
Date_             20131128
Time                 22.45
INSTRUM              Spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     393
DS                       4
SWH              29761.904 Hz
FIDRES           0.454131 Hz
AQ               1.1010548 sec
RG                     203
DW                 16.800 usec
DE                  6.50 usec
TE                 298.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                  13.84 usec
PL1                 2.50 dB
PL1W          46.89624786 W
SFO1          125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                 2.50 dB
PL12               17.40 dB
PL13               17.40 dB
PL2W          13.02359581 W
PL12W          0.42143536 W
PL13W          0.42143536 W
SFO2          500.1320005 MHz
SI                 32768
SF            125.7577966 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

2h

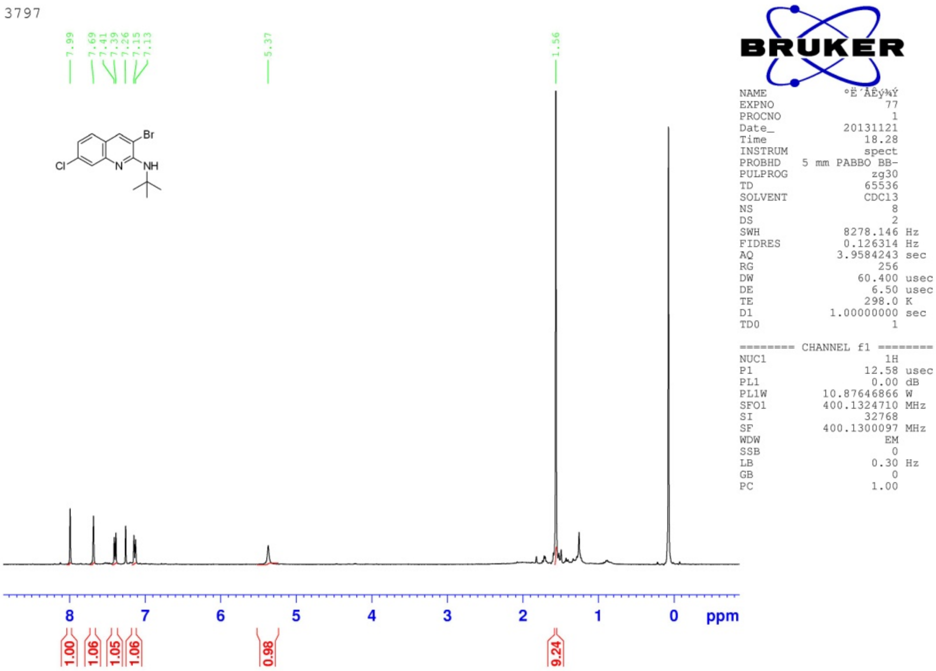


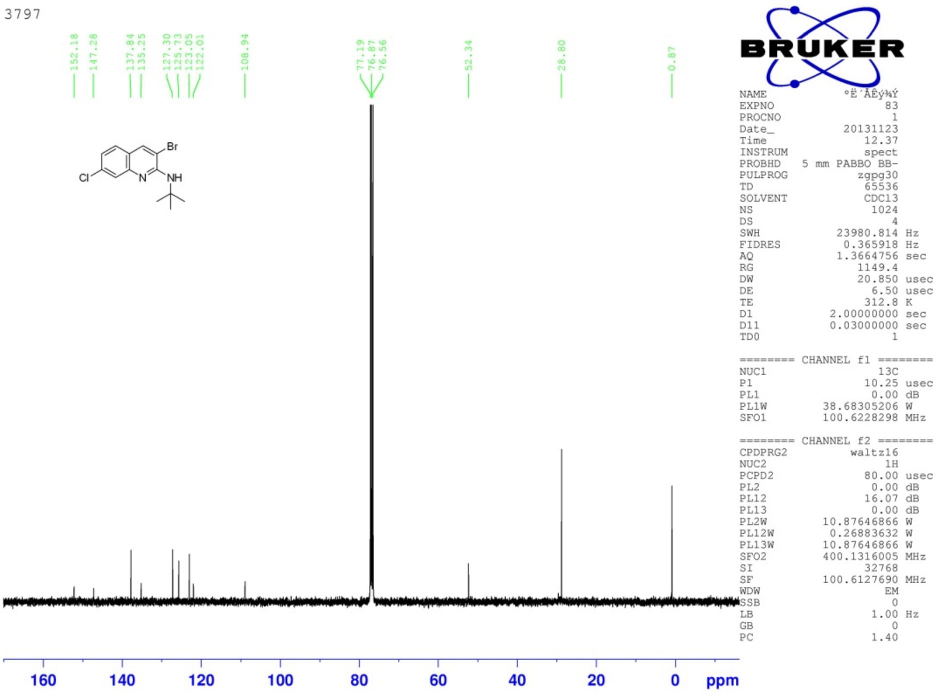

```
NAME                °É´ÁÉý¾Ý
EXPNO                    52
PROCNO                    1
Date_              20131125
Time                  18.00
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        2
SWH                8278.146 Hz
FIDRES                0.126314 Hz
AQ                 3.9584243 sec
RG                      114
DW                   60.400 usec
DE                    6.50 usec
TE                   298.0 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                    12.58 usec
PL1                    0.00 dB
PL1W             10.87646866 W
SFO1             400.1324710 MHz
SI                        32768
SF               400.1300107 MHz
WDW                       EM
SSB                        0
LB                     0.30 Hz
GB                         0
PC                     1.00
```



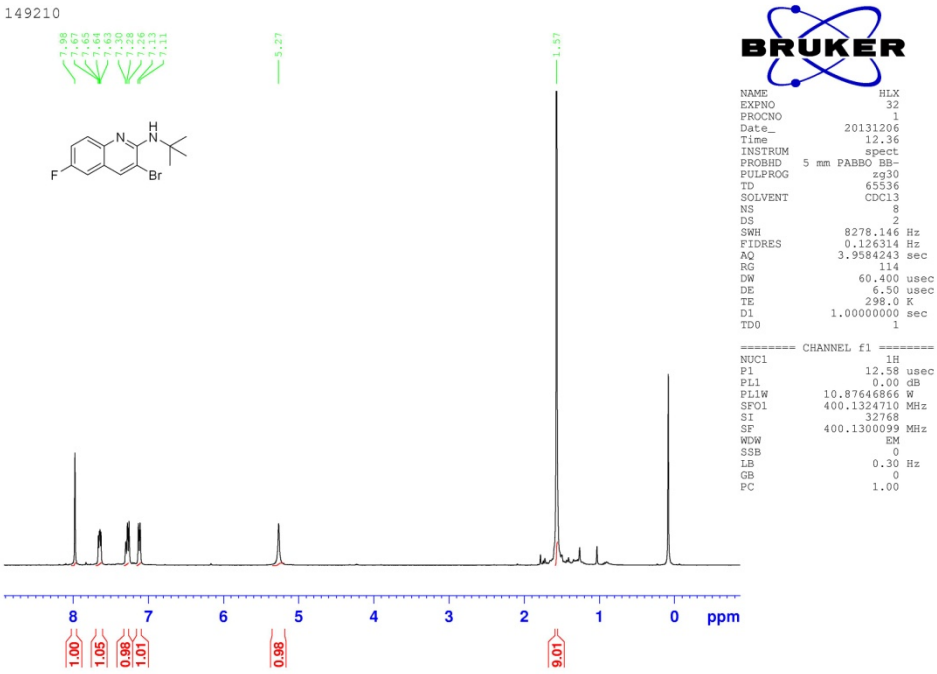

```
NAME                149203-2
EXPNO                      1
PROCNO                     1
Date_              20131127
Time                  22.53
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       487
DS                         4
SWH               29761.904 Hz
FIDRES                0.454131 Hz
AQ                 1.1010548 sec
RG                      203
DW                   16.800 usec
DE                    6.50 usec
TE                   298.0 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     13C
P1                    13.84 usec
PL1                    2.50 dB
PL1W             46.89624786 W
SFO1             125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                      1H
PCPD2                 80.00 usec
PL2                    2.50 dB
PL12                  17.40 dB
PL13                  17.40 dB
PL2W             13.02359581 W
PL12W             0.42143536 W
PL13W             0.42143536 W
SFO2             500.1320005 MHz
SI                        32768
SF               125.7577966 MHz
WDW                       EM
SSB                        0
LB                     1.00 Hz
GB                         0
PC                     1.40
```

2i

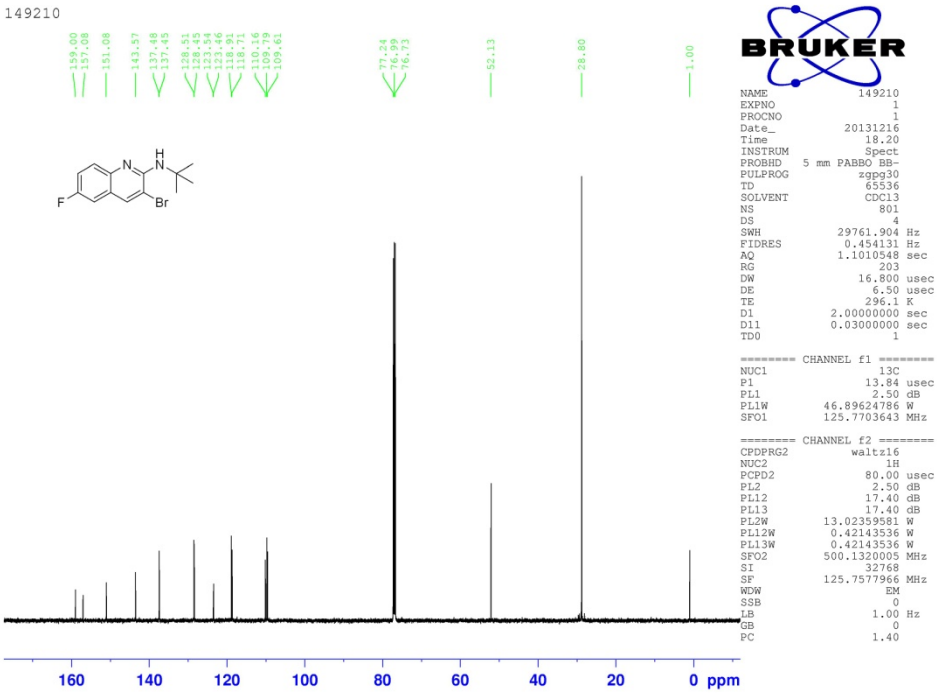

3797
7.99
7.69
7.41
7.39
7.26
7.15
7.13
5.37
1.56
Br
Cl
N
NH
BRUKER
NAME
EXPNO 77
PROCNO 1
Date_ 20131121
Time 18.28
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 256
DW 60.400 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.58 usec
PL1 0.00 dB
PL1W 10.87646866 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300097 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8 7 6 5 4 3 2 1 0 ppm
1.00
1.06
1.05
1.06
0.98
9.24


3797
152.18
147.28
137.84
135.25
127.30
125.73
123.05
122.01
108.94
77.19
76.87
76.56
52.34
28.80
0.87
Br
Cl
N
NH
BRUKER
NAME
EXPNO 83
PROCNO 1
Date_ 20131123
Time 12.37
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 1149.4
DW 20.850 usec
DE 6.50 usec
TE 312.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.25 usec
PL1 0.00 dB
PL1W 38.68305206 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 16.07 dB
PL13 0.00 dB
PL2W 10.87646866 W
PL12W 0.26883632 W
PL13W 10.87646866 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
160 140 120 100 80 60 40 20 0 ppm

2j

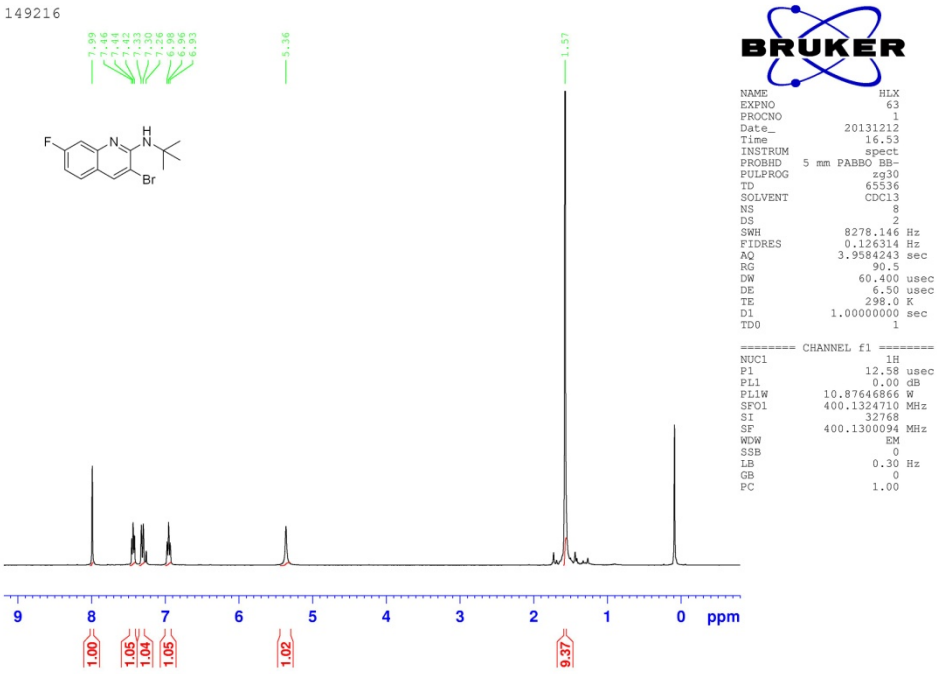



```
NAME                  HLX
EXPNO                  32
PROCNO                  1
Date_            20131206
Time                12.36
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                      8
DS                      2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                    114
DW                60.400 usec
DE                 6.50 usec
TE                298.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 12.58 usec
PL1                 0.00 dB
PL1W         10.87646866 W
SFO1         400.1324710 MHz
SI                  32768
SF           400.1300099 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                 1.00
```

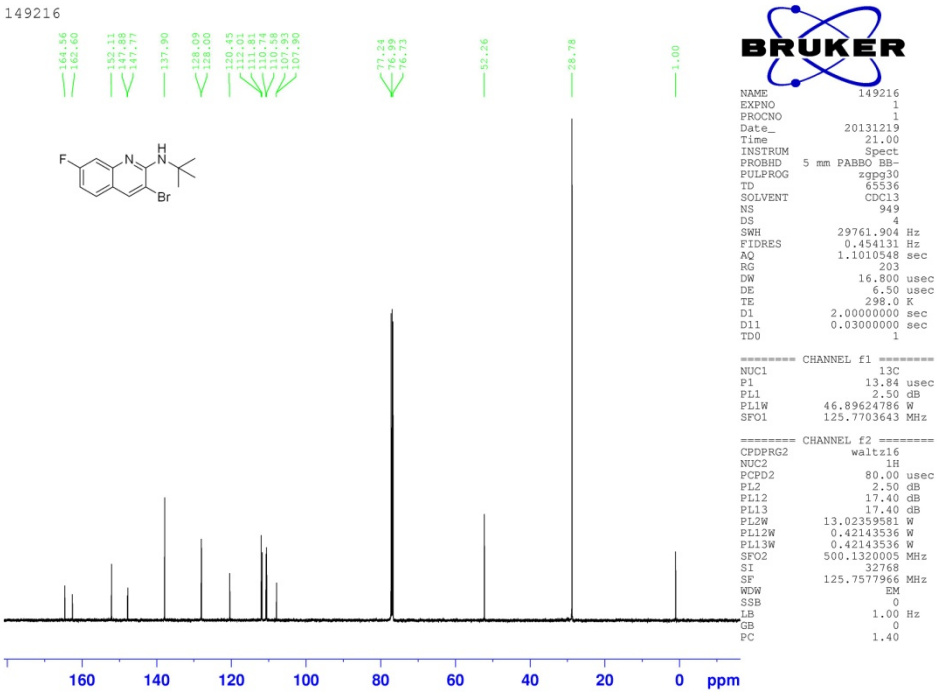



```
NAME                 149210
EXPNO                     1
PROCNO                    1
Date_            20131216
Time                18.20
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    801
DS                      4
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ              1.1010548 sec
RG                    203
DW                16.800 usec
DE                 6.50 usec
TE                296.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                 13.84 usec
PL1                 2.50 dB
PL1W         46.89624786 W
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                 2.50 dB
PL12               17.40 dB
PL13               17.40 dB
PL2W         13.02359581 W
PL12W         0.42143536 W
PL13W         0.42143536 W
SFO2         500.1320005 MHz
SI                  32768
SF           125.7577966 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                 1.40
```

2k

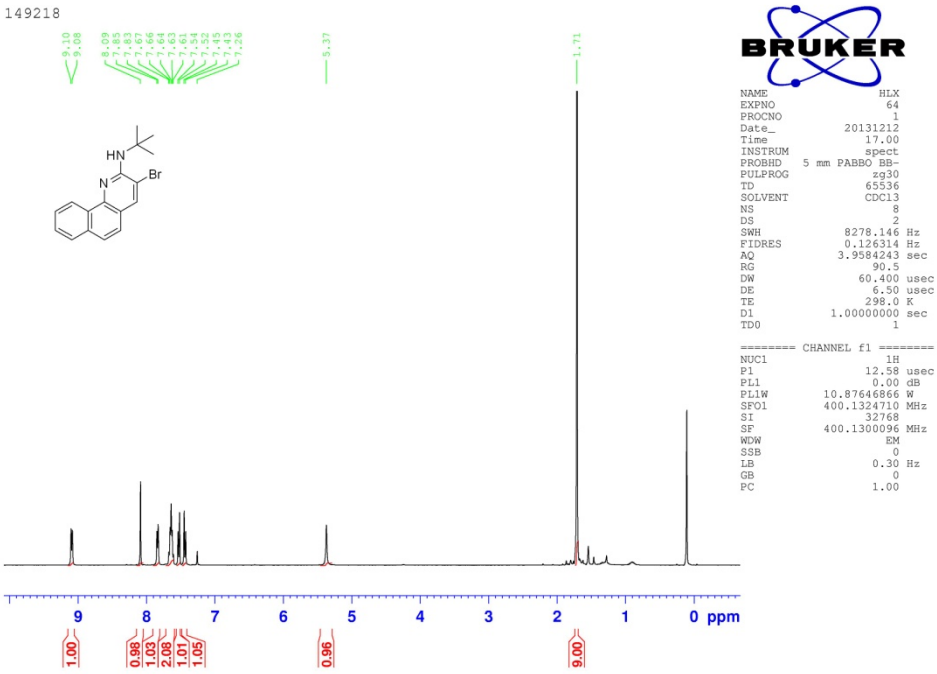



```
NAME                 HLX
EXPNO                 63
PROCNO                 1
Date_           20131212
Time                16.53
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH           8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                  90.5
DW             60.400 usec
DE              6.50 usec
TE                298.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                12.58 usec
PL1                0.00 dB
PL1W        10.87646866 W
SFO1       400.1324710 MHz
SI                 32768
SF         400.1300094 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                 1.00
```

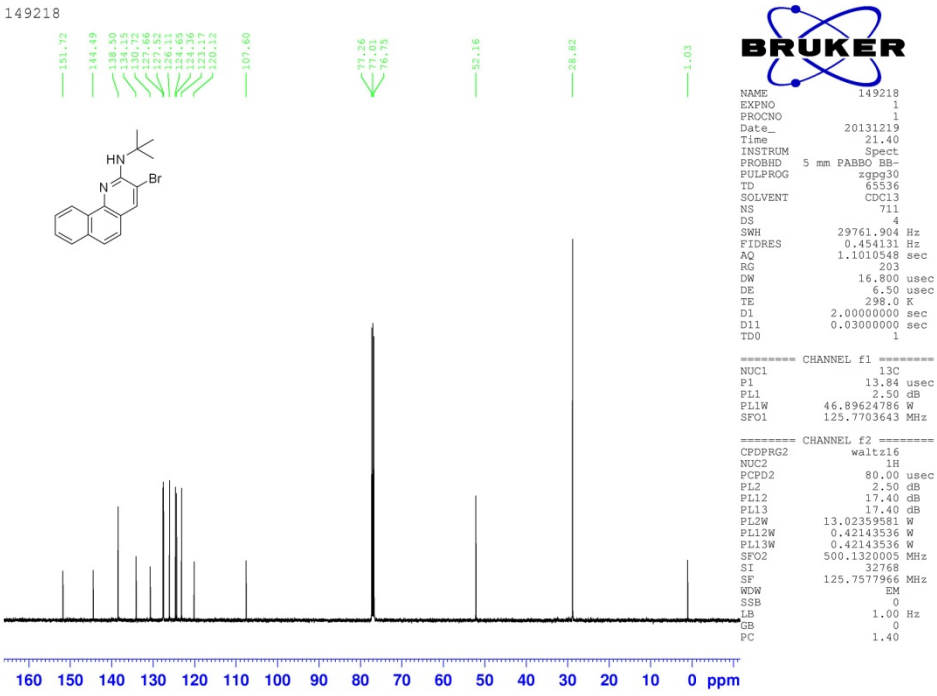



```
NAME                149216
EXPNO                    1
PROCNO                   1
Date_           20131219
Time                21.00
INSTRUM             Spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   949
DS                     4
SWH          29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG                   203
DW             16.800 usec
DE              6.50 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                13.84 usec
PL1                2.50 dB
PL1W        46.89624786 W
SFO1       125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2                2.50 dB
PL12              17.40 dB
PL13              17.40 dB
PL2W        13.02359581 W
PL12W        0.42143536 W
PL13W        0.42143536 W
SFO2       500.1320005 MHz
SI                 32768
SF         125.7577966 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                 1.40
```

2l

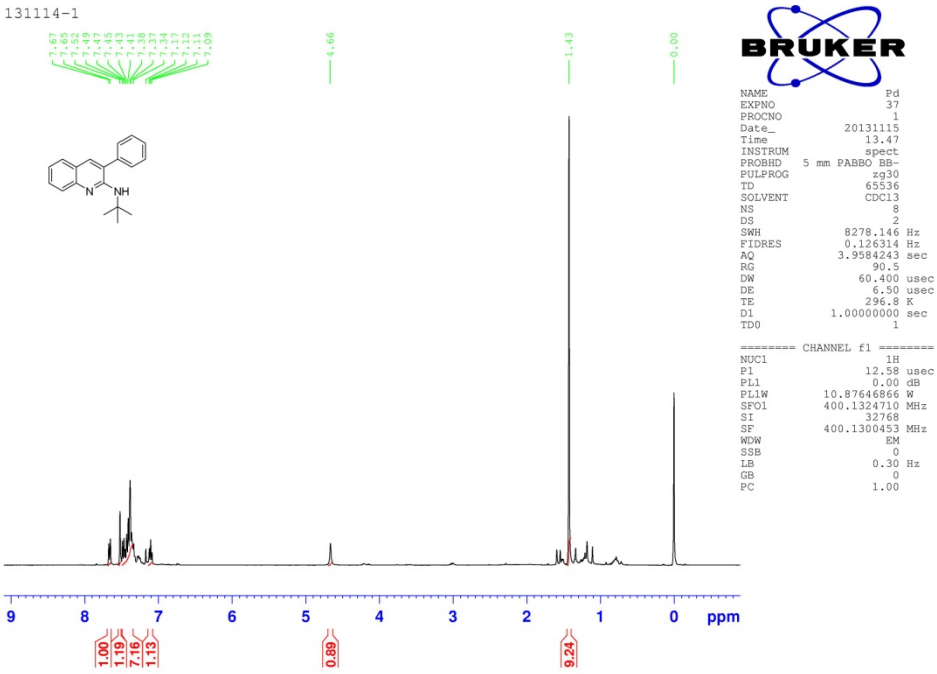


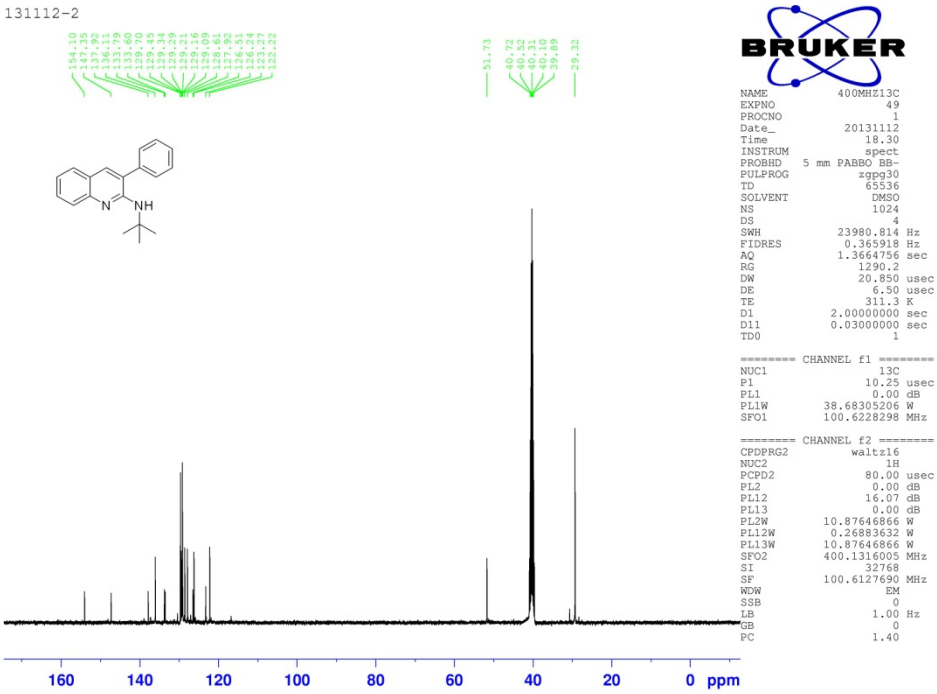

```
NAME                 HLX
EXPNO                 64
PROCNO                 1
Date_           20131212
Time                17.00
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH           8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                  90.5
DW             60.400 usec
DE              6.50 usec
TE              298.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                12.58 usec
PL1               0.00 dB
PL1W        10.87646866 W
SFO1       400.1324710 MHz
SI                 32768
SF         400.1300096 MHz
WDW                   EM
SSB                    0
LB              0.30 Hz
GB                     0
PC                  1.00
```



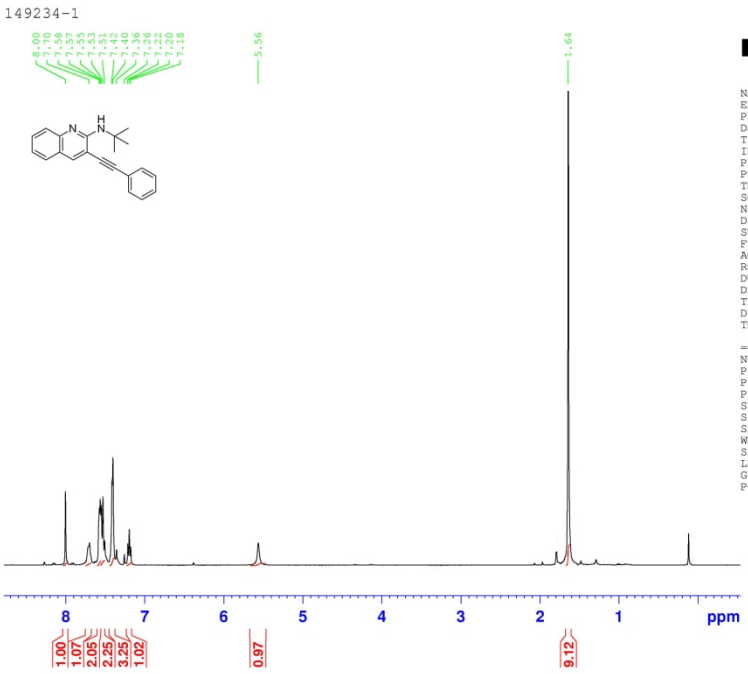

```
NAME                149218
EXPNO                    1
PROCNO                   1
Date_             20131219
Time                 21.40
INSTRUM              Spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     711
DS                       4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG                     203
DW             16.800 usec
DE              6.50 usec
TE              298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                13.84 usec
PL1               2.50 dB
PL1W        46.89624786 W
SFO1       125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                   1H
PCPD2            80.00 usec
PL2               2.50 dB
PL12             17.40 dB
PL13             17.40 dB
PL2W        13.02359581 W
PL12W        0.42143536 W
PL13W        0.42143536 W
SFO2       500.1320005 MHz
SI                 32768
SF         125.7577966 MHz
WDW                   EM
SSB                    0
LB              1.00 Hz
GB                     0
PC                  1.40
```

6

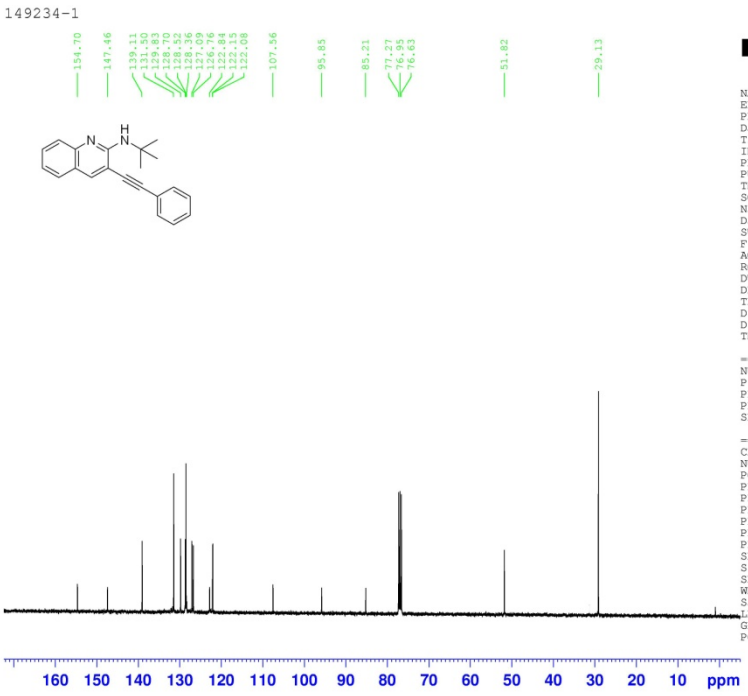

131114-1
7.67
7.65
7.52
7.49
7.47
7.45
7.43
7.41
7.39
7.34
7.17
7.12
7.11
7.09
4.66
1.43
0.00
NH
9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.19
7.16
1.13
0.89
9.24
BRUKER
NAME Pd
EXPNO 37
PROCNO 1
Date_ 20131115
Time 13.47
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 90.5
DW 60.400 usec
DE 6.50 usec
TE 296.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.58 usec
PL1 0.00 dB
PL1W 10.87646866 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300453 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


131112-2
154.10
147.39
137.82
136.11
133.79
133.60
129.70
129.45
129.34
129.29
129.21
129.16
129.09
128.61
127.92
127.31
126.24
123.27
122.22
51.73
40.72
40.52
40.31
40.10
39.89
29.32
NH
160 140 120 100 80 60 40 20 0 ppm
BRUKER
NAME 400MHZ13C
EXPNO 49
PROCNO 1
Date_ 20131112
Time 18.30
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 1290.2
DW 20.850 usec
DE 6.50 usec
TE 311.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.25 usec
PL1 0.00 dB
PL1W 38.68305206 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 16.07 dB
PL13 0.00 dB
PL2W 10.87646866 W
PL12W 0.26883632 W
PL13W 10.87646866 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

7

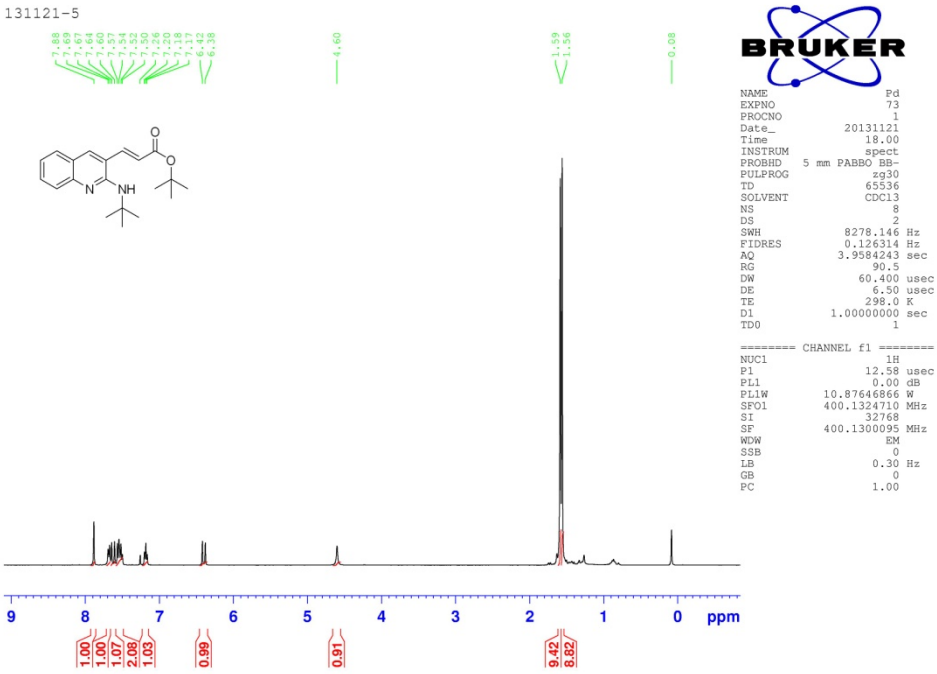



```
NAME                lyue
EXPNO                 24
PROCNO                 1
Date_           20140115
Time                14.14
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                  71.8
DW                60.400 usec
DE                 6.50 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.58 usec
PL1                0.00 dB
PL1W         10.87646866 W
SFO1         400.1324710 MHz
SI                 32768
SF           400.1300096 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



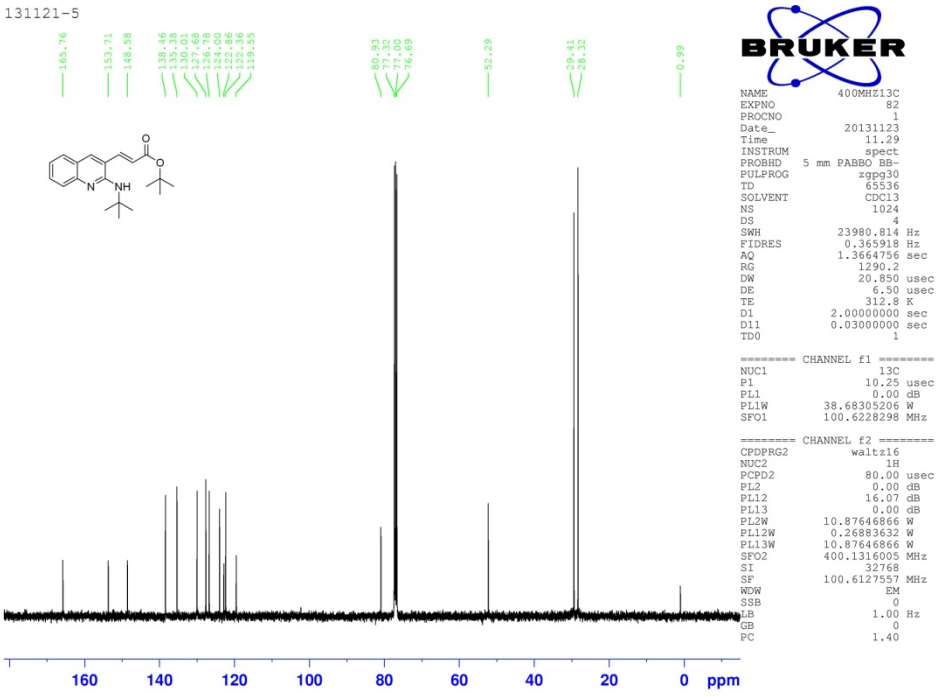

```
NAME                lyue
EXPNO                 48
PROCNO                 1
Date_           20140120
Time                19.16
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ              1.3664756 sec
RG                1149.4
DW                20.850 usec
DE                 6.50 usec
TE                311.4 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 10.25 usec
PL1                0.00 dB
PL1W         38.68305206 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                0.00 dB
PL12              16.07 dB
PL13               0.00 dB
PL2W         10.87646866 W
PL12W         0.26883632 W
PL13W        10.87646866 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127666 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

8



BRUKER

NAME	Pd
EXPNO	73
PROCNO	1
Date_	20131121
Time	18.00
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	90.5
DW	60.400 usec
DE	6.50 usec
TE	298.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	12.58 usec
PL1	0.00 dB
PL1W	10.87646866 W
SFO1	400.1324710 MHz
SI	32768
SF	400.1300095 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



BRUKER

NAME	400MHZ13C
EXPNO	82
PROCNO	1
Date_	20131123
Time	11.29
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	4
SWH	23980.814 Hz
FIDRES	0.365918 Hz
AQ	1.3664756 sec
RG	1290.2
DW	20.850 usec
DE	6.50 usec
TE	312.8 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.25 usec
PL1	0.00 dB
PL1W	38.68305206 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	16.07 dB
PL13	0.00 dB
PL2W	10.87646866 W
PL12W	0.26883632 W
PL13W	10.87646866 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127557 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40