Supporting Information

Asymmetric Synthesis of Stable α-Aminoboronic Esters Catalyzed by N-Heterocylic Carbene and Copper (I) Chloride

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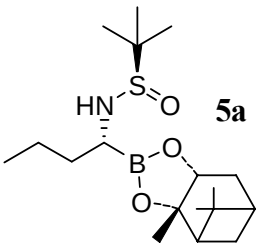
General Information

Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Benzene was treated with sodium. CuCl was purified by standard techniques. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Brucker 400 instruments. Chemical shifts are given in δ relative to tetramethylsilane (TMS), the coupling constants are given in Hz. High-resolution mass spectra were recorded on an Ion Spec Fourier Transform. High-resolution mass spectra were recorded on a Shimadzu Liquid Chromatograph Mass Spectrometer (LCMS-IT-TOF).

Synthetic procedures for 5a-j

A representative procedure with ligand precursor **3** for product **5a** is described below:

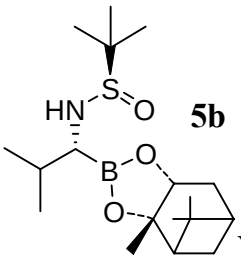


5a

Under argon, ligand precursor **3** (0.2 mmol) was mixed with CuCl (0.2 mmol), NaOBu-*t* (0.2 mmol) in 10 mL benzene. The mixture was stirred at room temperature for 4 h, during which time, the reaction solution turned from colorless to green then to light black color. To this, was then added N-*t*-butylsulfinyl butaldimine (2.0 mmol) in 5 mL benzene and bis(pinanediolato)diboron (2.0 mmol) in 5 mL benzene. The reaction was stirred at room temperature for 48 h. Then the solution was diluted with 30 mL ethyl acetate and quenched with saturated K_2CO_3 solution. After separation and washing the aqueous layer with ethyl acetate (2 × 30 mL), the combined organic solution was dried over anhydrous Na_2SO_4, and then concentrated. Purification using flash column chromatography (CH_2Cl_2/MeOH as eluent) gave **5a**. Yield: 92%. IR (neat): 2939, 2871, 1491, 1380, 1363, 1077, 1021 cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 4.76 (d, J = 6.8 Hz, 1H), 4.34 (dd, J_1 = 2.0 Hz, J_2 = 8.8 Hz, 1H), 2.82(m, 1H), 2.30(m, 1H), 2.16(m, 1H), 1.97(m, 1H), 1.87(m, 1H), 1.71(m, 1H), 1.56(m, 2H), 1.34(m, 2H), 1.32(s, 3H), 1.25(s, 3H), 1.13(m, 1H), 1.08(s, 9H), 0.87(t, J = 7.2 Hz, 3H), 0.82(s, 3H).^{13}C-NMR (100 MHz, DMSO-d_6) δ 85.9,

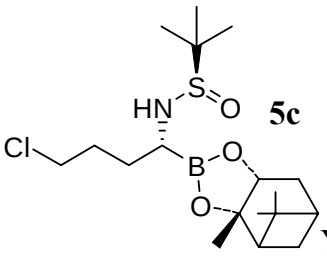
77.4, 55.7, 51.2, 38.3, 35.5, 35.5, 28.8, 27.3, 26.4, 24.1, 23.1, 20.1, 14.5.HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{35}BNO_3S$ 356.2352, found 356.2359.

Following the procedure described above, the following compounds were obtained:



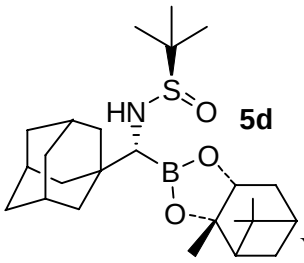
5b Yield: 88%.

IR (neat): 2924, 2871, 1463, 1390, 1376, 1066, 1046 cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 4.73(d, J = 6.4 Hz, 1H), 4.34(m, 1H), 2.66(t, J = 6.4 Hz, 1H), 2.32(m, 1H), 2.16(m, 1H), 1.98(m, 1H), 1.87(m, 2H), 1.70(m, 1H), 1.32(s, 3H), 1.25(s, 3H), 1.18(m, 1H), 1.09(s, 9H), 0.92(d, J = 7.2 Hz, 6H), 0.82(s, 3H). ^{13}C-NMR (100 MHz, DMSO-d_6) δ 86.0, 77.4, 55.9, 51.2, 38.3, 35.5, 31.2, 28.9, 27.3, 26.5, 24.2, 23.0, 20.8, 20.0. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{35}BNO_3S$ 356.2352, found 356.2361.



5c Yield: 86%.

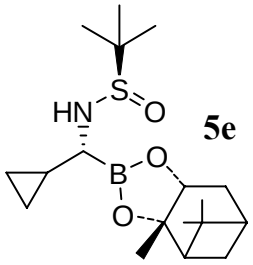
IR (neat): 2925, 2870, 1464, 1376, 1078, 1041, 1029 cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 4.90 (d, J = 6.4 Hz, 1H), 4.36 (dd, J_1 = 2.0 Hz, J_2 = 6.8 Hz, 1H), 3.63 (t, J = 6.4 Hz, 2H), 2.85 (t, J = 7.2 Hz, 1H), 2.32 (m, 1H), 2.17 (m, 1H), 1.98 (t, J = 5.6 Hz, 1H), 1.88 (m, 1H), 1.81(m, 2H), 1.72 (m, 2H), 1.70 (m, 1H), 1.33 (s, 3H), 1.26 (s, 3H), 1.13 (m, 1H), 1.09 (s, 9H), 0.82 (s, 3H).^{13}C-NMR (100 MHz, DMSO-d_6) δ 86.0, 77.5, 55.8, 51.2, 45.9, 38.3, 35.4, 30.6, 30.5, 30.1, 28.8, 27.3, 26.4, 24.1, 23.1. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{34}BClNO_3S$ 390.1963, found 390.1957.



5d

Yield: 80%.

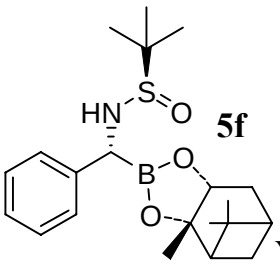
IR (neat): 2911, 2865, 1460, 1376, 1079, 1040 1020 cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 4.38 (m, 1H), 4.36 (m, 1H), 2.46 (d, J = 8.4 Hz, 1H), 2.33 (m, 1H), 2.18 (m, 1H), 1.99 (t, J = 5.6 Hz, 1H), 1.94 (m, 3H), 1.88 (m, 1H), 1.69 (m, 7H), 1.57 (m, 3H), 1.49 (m, 3H), 1.33 (s, 3H), 1.26 (s, 3H), 1.18 (m, 1H), 1.09 (s, 9H), 0.82 (s, 3H).^{13}C-NMR (100 MHz, DMSO-d_6) δ 86.0, 77.3, 56.2, 51.2, 38.3, 37.1, 35.7, 35.6, 28.9, 28.4, 27.3, 26.6, 24.2, 23.0. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{25}H_{43}BNO_3S$ 448.2978, found 448.2967.



5e

Yield: 78%.

IR (neat): 3076, 2922, 2869, 1377, 1364, 1055, 1029 cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 0.19 (m, 1H), 0.26 (m, 1H), 0.44 (m, 1H), 0.82 (s, 3H), 0.96 (m, 1H), 1.09 (s, 9H), 1.18 (d, J = 10.8 Hz, 1H), 1.26 (s, 3H), 1.33 (s, 3H), 1.72 (m, 1H), 1.87 (m. 1H), 1.98 (t, J = 5.2 Hz, 1H), 2.16 (m, 1H), 2.24 (dd, J_1 = 6.4 Hz, J_2 = 9.2 Hz, 1H), 2.32 (m, 1H), 4.36 (dd, J_1 = 2 Hz, J_2 = 8.8 Hz, 1H), 4.74 (d, J = 6 Hz, 1H). ^{13}C-NMR (100 MHz, DMSO-d_6) δ 3.4, 5.5, 14.4, 23.0, 24.1, 26.3, 27.3, 28.8, 35.5, 38.3, 51.2, 55.7, 77.4, 85.9. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{33}BNO_3S$ 354.2196, found 354.2189.

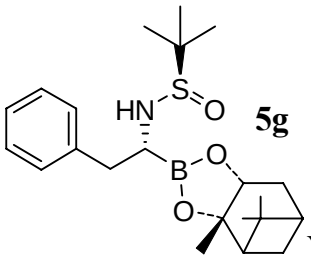


5f

Yield: 86%.

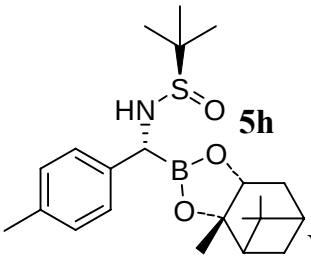
IR (neat): 2920, 2867, 1473, 1394, 1375, 1040, 767, 698 cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.28 (m, 4H), 7.18 (m, 1H), 5.47 (d, J = 5.6 Hz, 1H), 4.34 (m, 1H), 4.13 (d, J = 5.6 Hz, 1H), 2.29 (m, 1H), 2.02 (m, 1H), 1.93 (m, 1H), 1.78 (m, 1H), 1.59(m, 1H),

1.26(s, 3H), 1.21(s, 3H), 1.13(s, 9H), 0.86(m, 1H), 0.78(s, 3H). ^{13}C-NMR (100 MHz, DMSO-d_6) δ 141.7, 128.6, 127.7, 126.8, 86.2, 77.7, 56.2, 51.2, 38.3, 35.3, 28.6, 27.2, 26.0, 24.1, 23.1. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{21}H_{33}BNO_3S$ 390.2186, found 390.2177.



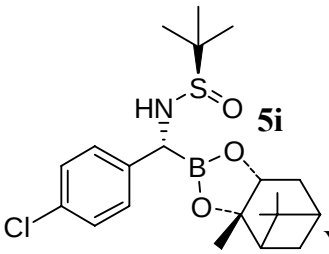
5g Yield: 89%.

IR (neat): 2922, 2870, 1462, 1375, 1079, 1041, 752, 699 cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.24 (m, 5H), 4.88 (d, J = 6.0 Hz, 1H), 4.23 (m, 1H), 3.12 (m, 1H), 2.96 (m, 1H), 2.85 (m, 1H), 2.25 (m, 1H), 1.93 (m, 1H), 1.88 (m, 1H), 1.78 (m, 1H), 1.64 (m, 1H), 1.24 (s, 3H), 1.21 (s, 3H), 1.08 (s, 9H), 0.80 (m, 1H), 0.77 (s, 3H). ^{13}C-NMR (100 MHz, DMSO-d_6) δ 139.2, 129.6, 128.6, 126.7, 86.0, 77.5, 55.7, 51.1, 38.2, 35.2, 28.6, 27.3, 26.1, 24.1, 23.0. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{22}H_{35}BNO_3S$ 404.2352, found 404.2369.

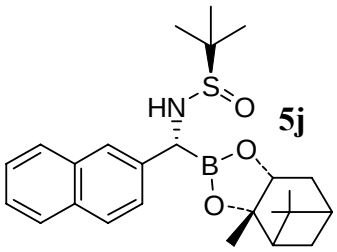


5h Yield: 88%.

IR (neat): 2924, 2867, 1465, 1393, 1061, 820, 725 cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.23 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 7.6 Hz, 2H), 5.34 (d, J = 5.6 Hz, 1H), 4.33 (dd, J_1 = 1.6 Hz, J_2 = 8.8 Hz, 1H), 4.07 (d, J = 6.0 Hz, 1H), 2.27 (m, 1H), 2.27 (s, 3H), 2.03 (m, 1H), 1.93 (m, 1H), 1.79 (m, 1H), 1.64 (m, 1H), 1.25 (s, 3H), 1.21 (s, 3H), 1.12 (s, 9H), 0.89 (m, 1H), 0.79 (s, 3H) ^{13}C-NMR (100 MHz, DMSO-d_6) δ 138.6, 135.8, 129.2, 127.8, 86.2, 77.7, 56.1, 51.3, 38.3, 35.4, 28.7, 27.2, 26.1, 24.1, 23.1, 21.1. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{22}H_{35}BNO_3S$ 404.2352, found 404.2371.



Yield: 90%.
IR (neat): 2924, 2867, 1465, 1393, 1061, 820, 725 cm^{-1} ^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.38 (m, 4H), 4.23 (m, 1H), 4.17 (m, 1H), 4.14 (m, 1H), 2.28 (m, 1H), 2.18 (m, 1H), 1.93 (m, 1H), 1.86 (m, 1H), 1.70 (m, 1H), 1.30 (s, 3H), 1.25 (s, 3H), 1.14 (s, 9H), 1.13 (m, 1H), 0.81(s, 3H). ^{13}C-NMR (100 MHz, DMSO-d_6) δ 139.5, 131.9, 130.0, 128.6, 83.4, 76.1, 55.7, 51.8, 47.7, 38.4, 36.0, 29.0, 27.4, 26.4, 24.1, 23.1. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{21}H_{32}BClNO_3S$ 424.1806, found 424.1813.



Yield: 85%.
IR (neat): 2927, 2875, 1395, 1075, 820, 758 cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.88 (m, 4H), 7.51 (m, 3H), 4.32 (d, J = 8.4 Hz, 1H), 4.32 (m, 1H), 4.22 (d, J = 8.4 Hz, 1H), 2.28 (m, 1H), 2.18 (m, 1H), 1.93 (m, 1H), 1.87 (m, 1H), 1.67 (m, 1H), 1.30 (s, 3H), 1.25 (s, 3H), 1.17 (s, 9H), 1.13 (m, 1H), 0.81 (s, 3H). ^{13}C-NMR (100 MHz, DMSO-d_6) δ 138.0, 133.3, 132.7, 128.2, 128.0, 128.0, 126.8, 126.6, 126.5, 126.2, 83.3, 76.1, 55.7, 51.8, 48.7, 48.5, 38.4, 36.0, 29.0, 27.4, 26.4, 24.1, 23.2. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{25}H_{35}BNO_3S$ 440.2352, found 440.2365.

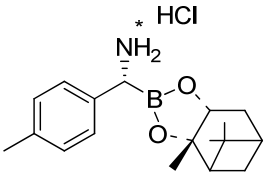
The procedure for synthesis of **5b'** is the same as the above of products (**5a-j**). (S)-N-t-butylsulfinyl butaldimine was used.

Determination of diastereomer ratio

The crude sulfinyl protected α-amino boronic esters were dissolved in dioxane (0.2 M) in an oven-dried vial equipped with a Teflon coated stir bar under nitrogen. Freshly distilled MeOH (10 equiv) was added to the solution, followed by the drop-wise addition of 2.2 M HCl in dioxane (1 equiv). The reaction mixture was stirred at 0 ^{o}Cfor 1.5 h to 2

h before it was directly concentrated under reduced pressure. Diastereomer ratio (dr) was determined from the ^{1}HNMR of the crude amine hydrochloride salt.

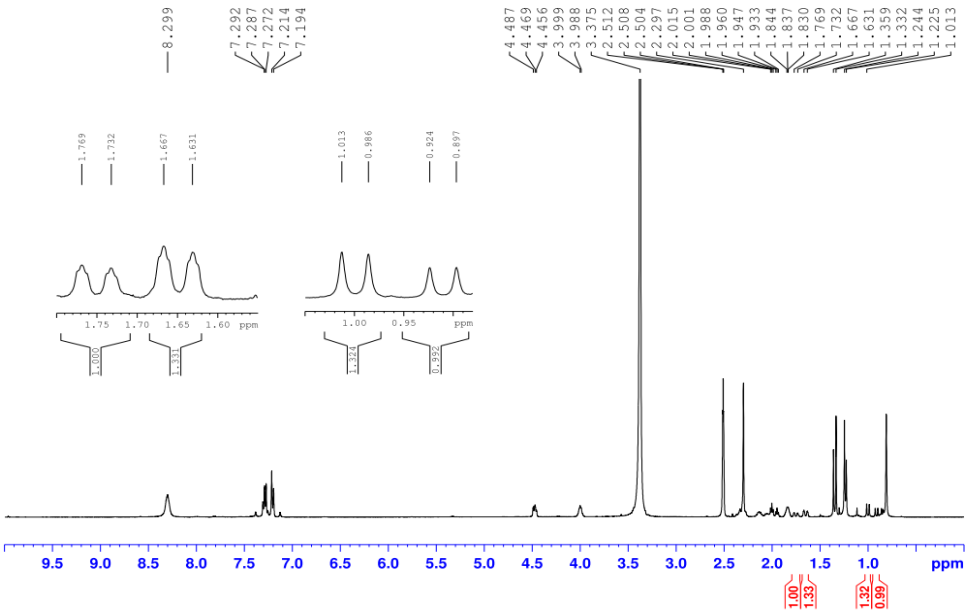
Selected examples



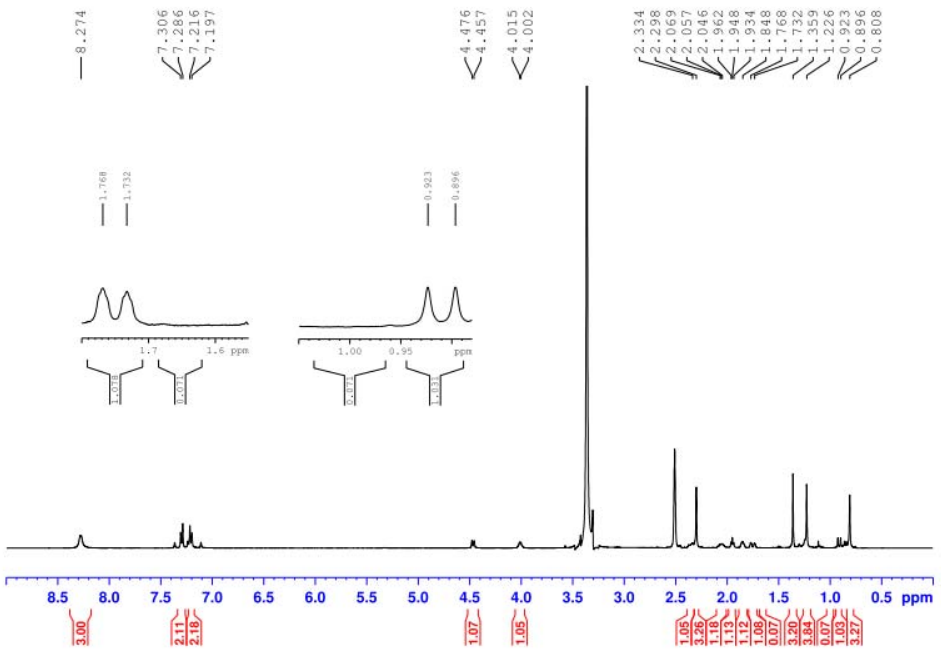
(hydrolysis from **5h**)

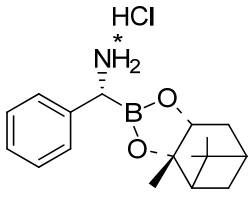
^{1}H-NMR (400 MHz, DMSO-d_6) δ 0.81(s, 3H), 0.91(d, J = 10.8, 1H), 1.23(s, 3H), 1.36(s, 3H), 1.75(m, 1H), 1.85(m, 1H), 1.95(t, J = 5.6 Hz, 1H), 2.06(m, 1H), 2.30(s, 3H), 2.33(m, 1H), 4.01(d, J = 5.2 Hz, 1H), 4.48(d, J = 7.6 Hz, 1H), 7.21(d, J = 7.6 Hz, 2H), 7.30(d, J = 8 Hz, 2H), 8.27(s, 3H).

Sample with racemic N-tert-butanesulfinyl amine



Sample using (R)-N-tert-butanesulfinyl amine dr > 99:1

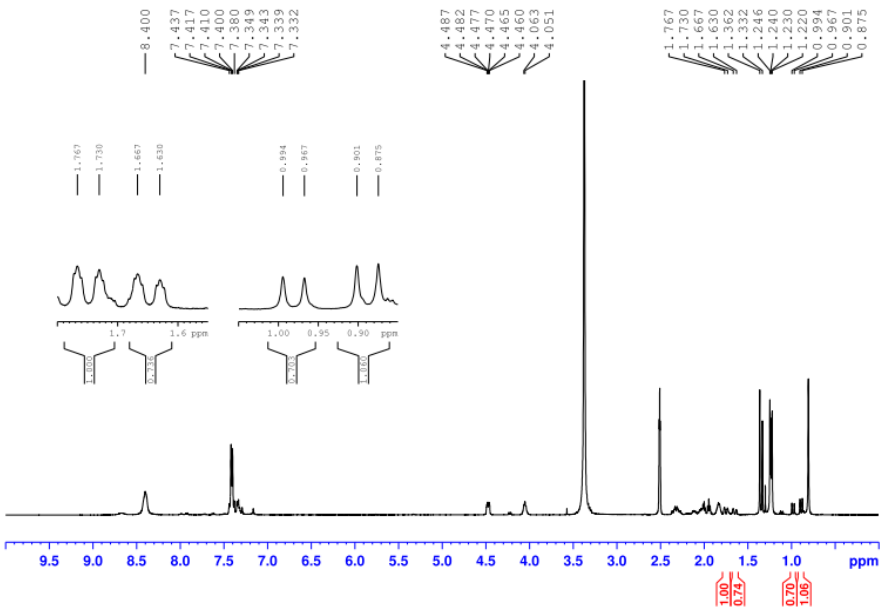




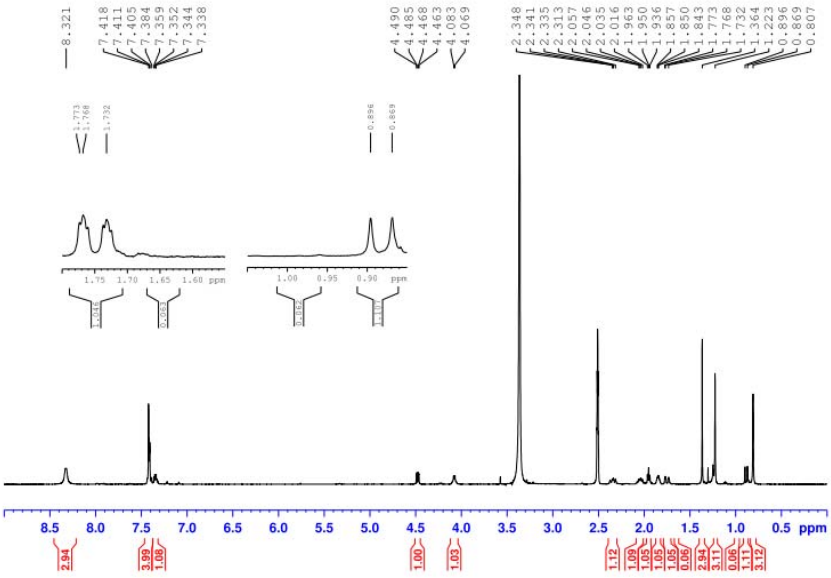
(hydrolysis from **5f**)

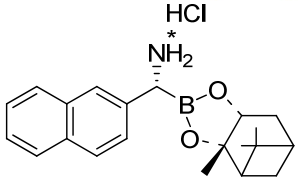
^{1}H-NMR (400 MHz, DMSO-d_6) δ 0.81 (s, 3H), 0.88 (d, J = 10.8 Hz, 1H), 1.22 (s, 3H), 1.36 (s, 3H), 1.77 (m, 1H), 1.85(m, 1H), 1.95 (t, J = 5.2 Hz, 1H), 2.01-2.06 (m, 1H), 2.31-2.35 (m, 1H), 4.08 (d, J = 5.6 Hz, 1H), 4.48 (dd, J_1 = 2.0 Hz, J_2 = 8.8 Hz, 1H), 7.34-7.36 (m, 1H), 7.38-7.42 (m, 4H), 8.32 (s, 3H).

Sample with racemic N-tert-butanesulfinyl amine



Sample using (R)-N-tert-butanesulfinyl amine dr > 99:1

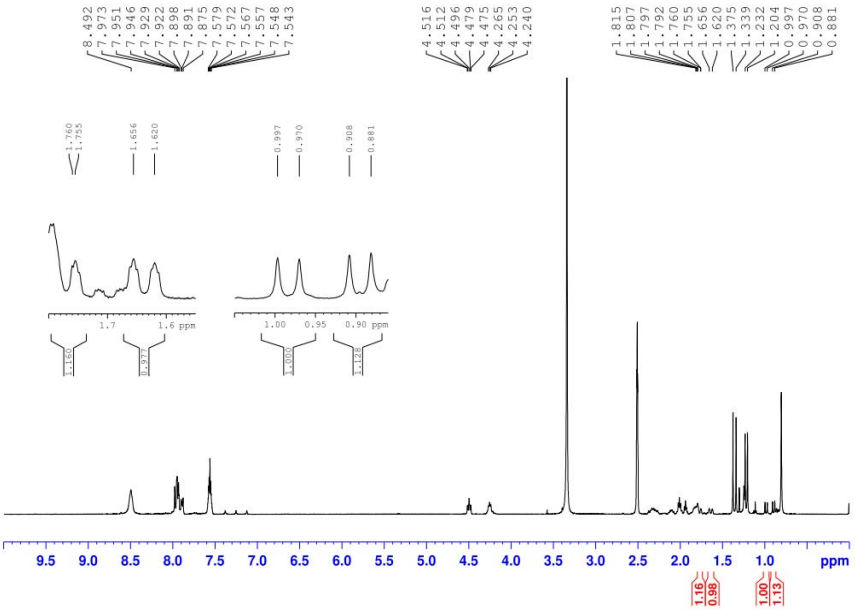




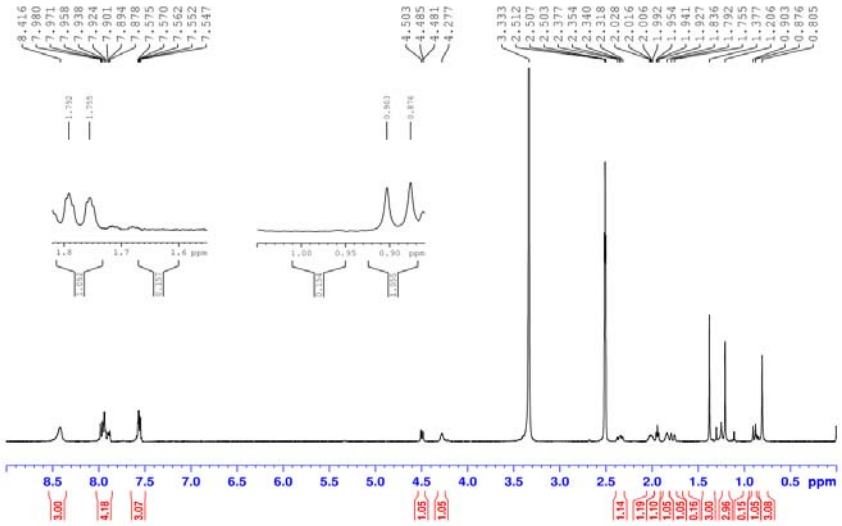
(hydrolysis from **5j**)

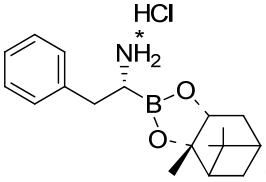
^{1}H-NMR (400 MHz, DMSO-d_6) δ 0.81(s, 3H), 0.89(d, *J* = 10.8 Hz, 1H), 1.21(s, 3H), 1.38(s, 3H), 1.77(m, 1H), 1.84(m, 1H), 1.94(t, *J* = 5.2 Hz, 1H), 1.99-2.03(m, 1H), 2.32-2.38(m, 1H), 4.28(s, 1H), 4.48(m, 1H), 7.55-7.58(m, 3H), 7.88-7.98(m, 4H), 8.42(s, 3H).

Sample with racemic N-tert-butanesulfinyl amine



Sample using (R)-N-tert-butanesulfinyl amine dr > 99:1



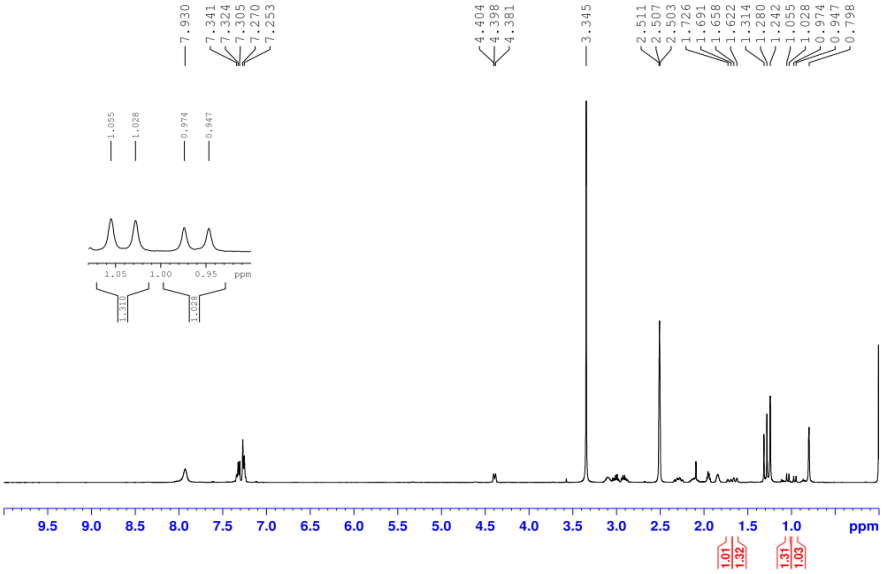


(hydrolysis from **5g**)

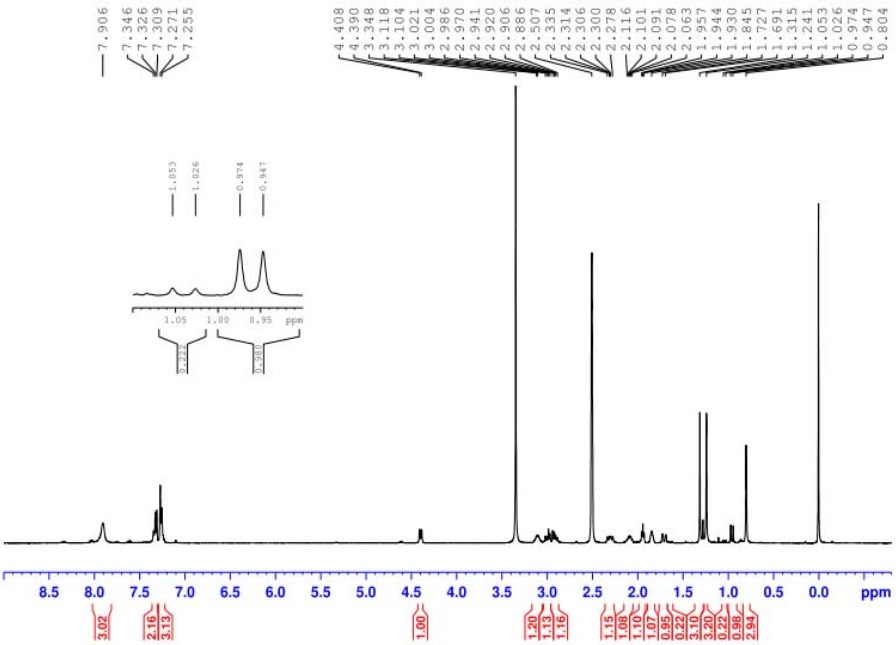
^{1}H-NMR (400 MHz, DMSO-d_6) δ 0.80(s, 3H), 0.96(d, J = 10.8 Hz, 1H), 1.24(s, 3H), 1.32(s, 3H), 1.71(m, 1H), 1.85(m, 1H), 1.94(t, J = 5.2 Hz, 1H), 2.06-2.12(m, 1H), 2.28-

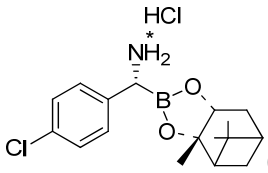
2.51(m, 1H), 2.89-3.02(m, 2H), 3.11(d, *J* = 5.6 Hz, 1H), 4.40(d, *J* = 7.2 Hz, 1H), 7.26-7.35(m, 5H), 7.91(s, 3H).

Sample with racemic N-tert-butanesulfinyl amine



Sample using (R)-N-tert-butanesulfinyl amine dr > 99:1



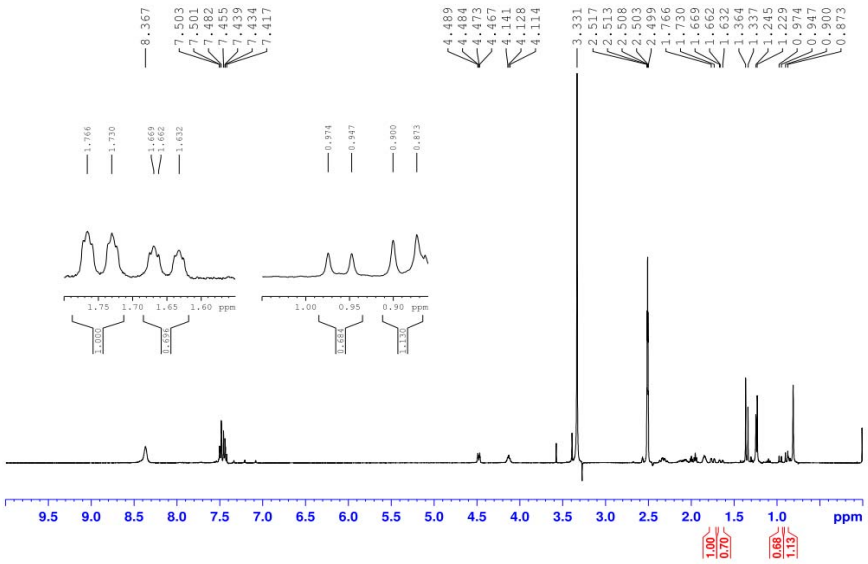


(hydrolysis from **5i**)

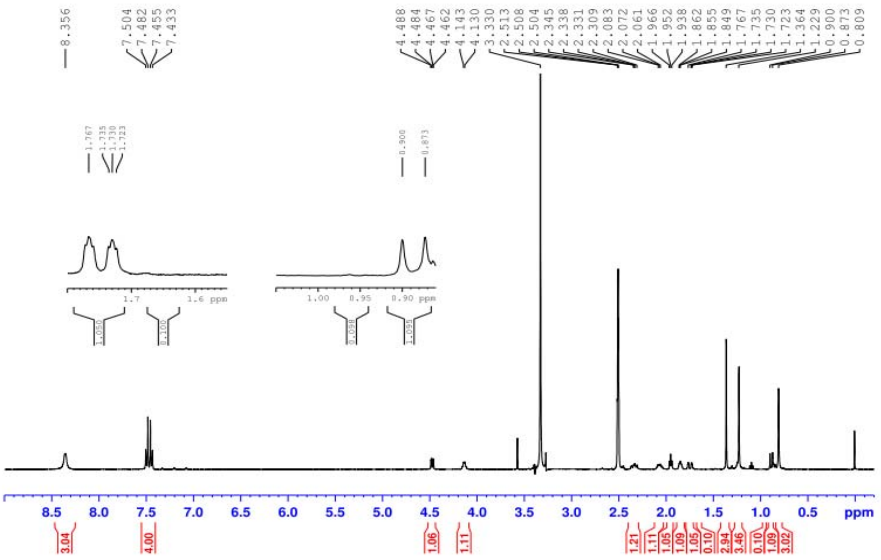
^{1}H-NMR (400 MHz, DMSO-d_6) δ 0.81(s, 3H), 0.89(d, *J* = 10.8 Hz, 1H), 1.23(s, 3H), 1.36(s, 3H), 1.72-1.77(m, 1H), 1.86(m, 1H), 1.95(t, *J* = 5.6 Hz, 1H), 2.07(m, 1H), 2.31-

2.35(m, 1H), 4.14(d, J = 5.2 Hz, 1H), 4.47(dd, J_1 = 2.0 Hz, J_2 = 8.8 Hz, 1H), 7.44(d, J = 8.8 Hz, 2H), 7.49(d, J = 8.8 Hz, 2H), 8.36(s, 3H).

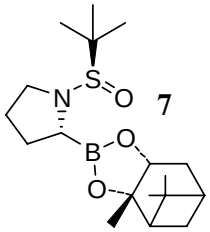
Sample with racemic N-tert-butanesulfinyl amine



Sample using (R)-N-tert-butanesulfinyl amine dr > 99:1



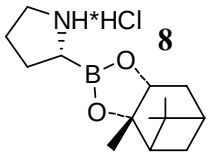
Synthesis of 7 and 8



7

Under argon, to a solution of compound **5c** (2.0 mmol) in 10 mL DMF was added NaOBu-*t* (2.1 mmol). The mixture was stirred at room temperature for 6 h. Then it was quenched with 30 ml ethyl acetate and 30 mL water. The aqueous layer was further extracted with ethyl acetate (2 × 30 mL). The combined organic layer was dried over Na_2SO_4, and then concentrated. Purification using water inactivated silica gel (CH_2Cl_2/MeOH as eluent) gave **7**. Yield: 83%.

IR (neat):2922, 2868, 1462, 1375, 1075, 1050, 1026 cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 4.36 (dd, J_1 = 2.0 Hz, J_2 = 6.8 Hz, 1H), 3.62 (m, 2H), 2.84 (m, 1H), 2.32 (m, 1H), 2.17 (m, 1H), 1.98 (t, J = 5.6 Hz, 1H), 1.88 (m, 1H), 1.81 (m, 2H), 1.72 (m, 2H), 1.70 (m, 1H), 1.33 (s, 3H), 1.26 (s, 3H), 1.13 (m, 1H), 1.09 (s, 9H), 0.82 (s, 3H).^{13}C-NMR (100 MHz, DMSO-d_6) δ 86.0, 77.5, 55.8, 51.2, 45.9, 38.3, 35.4, 30.6, 30.5, 30.1, 28.8, 27.3, 26.4, 24.1, 23.1.HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{33}BNO_3S$ 354.2196, found 354.2190.

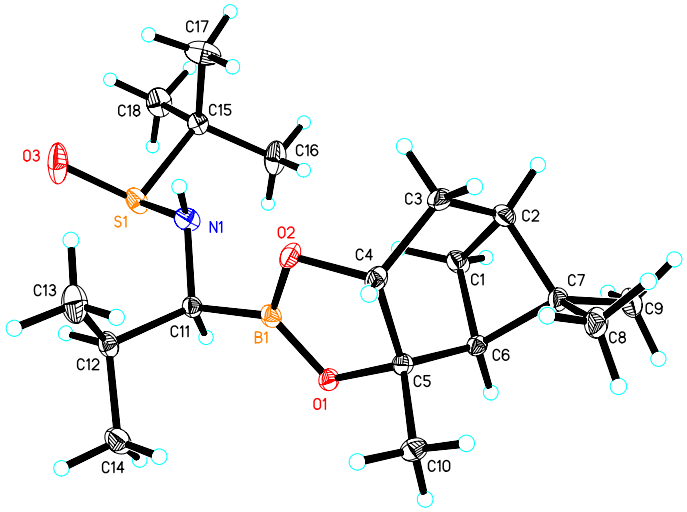


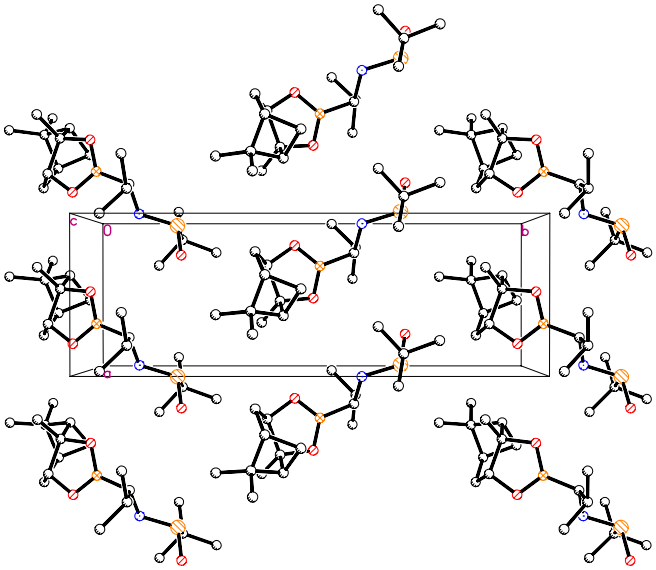
8

Compound **7** (1 mmol) was diluted with 1,4-dioxane (4.7 mL) under a stream of nitrogen. Methanol (9.97 mmol) was added at room temperature followed by the addition of 4.0M HCl (solution in 1,4-dioxane) (0.994 mmol). The resulting mixture was stirred at room temperature for 0.5h before it was concentrated to dryness.The resulting solid was triturated with a 2:1 mixture of hexanes: Et_2O to obtain the desired product as a white solid **8**. Yield: 90%.^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.43 (d, J = 9 Hz, 1H) 3.42 (m, 2H), 3.22 (m, 1H), 2.38-1.83 (m, 10H), 1.45 (s, 3H), 1.30 (s, 3H), 1.13 (m, 1H), 0.83 (s, 3H).

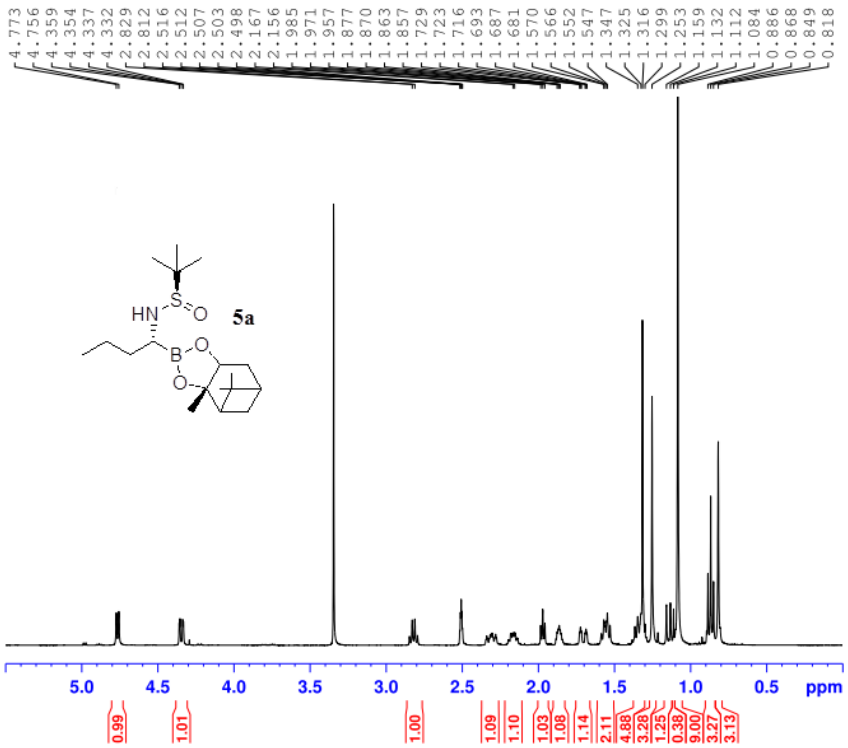
X-ray crystal structure of 5b’

The **5b’** crystal structure has been deposited at the Cambridge Crystallographic Data Centre and was assigned the deposition number： CCDC 901852





^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra



BRUKER

```
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EXPNO                  1
PROCNO                 1
Date_           20120314
Time               15.22
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT             DMSO
NS                    16
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                  80.6
DW                60.800 usec
DE                 6.50 usec
TE                293.9 K
D1              1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                12.86 usec
PL1               -4.00 dB
PL1W        20.19063568 W
SFO1        400.1324710 MHz
SI                 32768
SF          400.1300000 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                 1.00
```

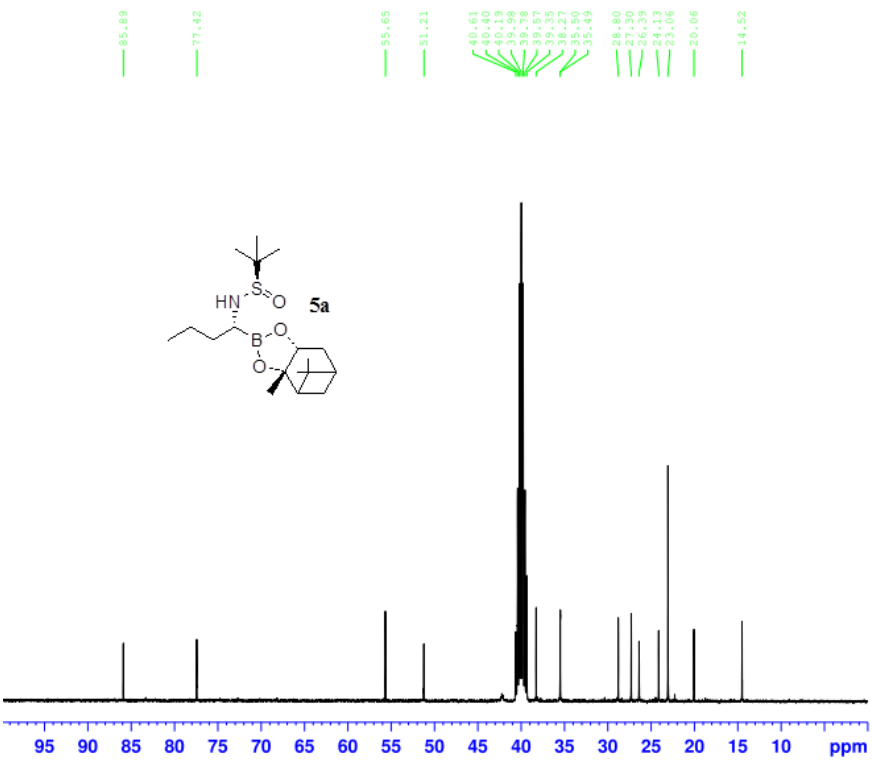

BRUKER

```
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EXPNO                  1
PROCNO                 1
Date_           20120314
Time               18.41
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT             DMSO
NS                  1696
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                   645
DW                20.800 usec
DE                 6.50 usec
TE                297.3 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                10.10 usec
PL1               -3.00 dB
PL1W        64.15196228 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2               -4.00 dB
PL12              11.88 dB
PL13              12.00 dB
PL2W        20.19063568 W
PL12W        0.52137470 W
PL13W        0.50716585 W
SFO2        400.1316005 MHz
SI                 32768
SF          100.6127690 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                 1.40
```

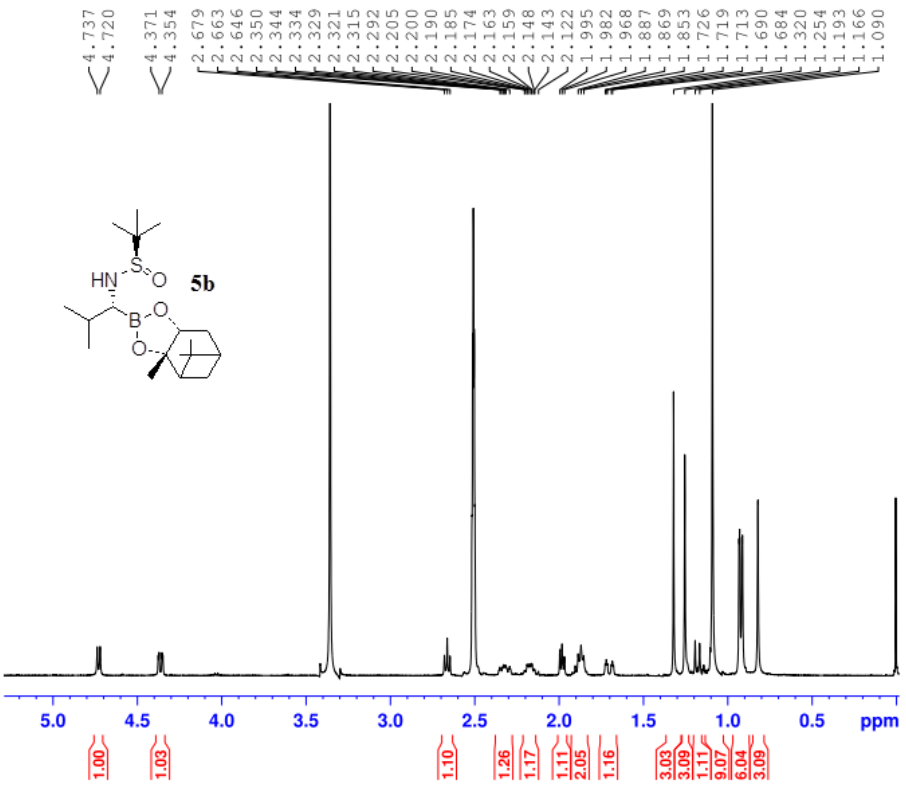

BRUKER

```
NAME          zt-12-01-04-H
EXPNO                     1
PROCNO                    1
Date_              20120104
Time                 21.21
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       80
DS                        2
SWH               8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                      287
DW                 60.800 usec
DE                  6.50 usec
TE                  290.5 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.86 usec
PL1                  -4.00 dB
PL1W           20.19063568 W
SFO1           400.1324710 MHz
SI                    32768
SF             400.1300000 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00
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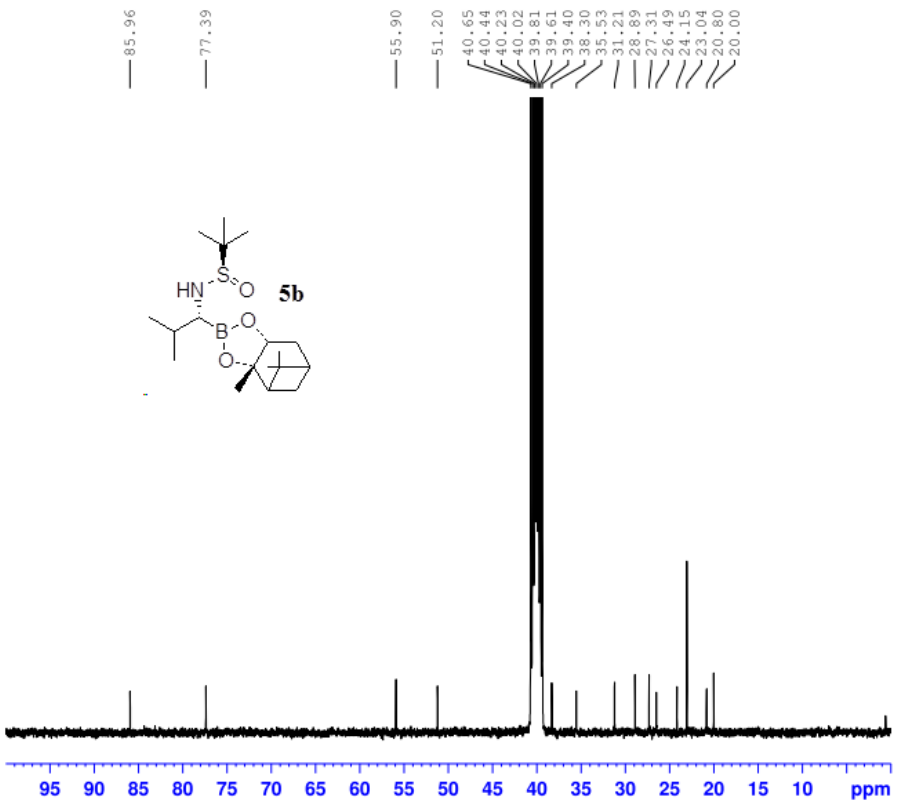

BRUKER

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NAME          zt-12-01-04-c13cpd
EXPNO                         1
PROCNO                        1
Date_                  20120105
Time                      6.02
INSTRUM                  spect
PROBHD        5 mm PABBO BB-
PULPROG                zgpg30
TD                        65536
SOLVENT                   DMSO
NS                        8192
DS                           4
SWH                24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631988 sec
RG                       362
DW                  20.800 usec
DE                   6.50 usec
TE                   295.1 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     13C
P1                   10.10 usec
PL1                  -3.00 dB
PL1W           64.15196228 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                80.00 usec
PL2                  -4.00 dB
PL12                 11.88 dB
PL13                 12.00 dB
PL2W           20.19063568 W
PL12W           0.52137470 W
PL13W           0.50716585 W
SFO2           400.1316005 MHz
SI                    32768
SF             100.6127690 MHz
WDW                     EM
SSB                      0
LB                  1.00 Hz
GB                       0
PC                    1.40
```
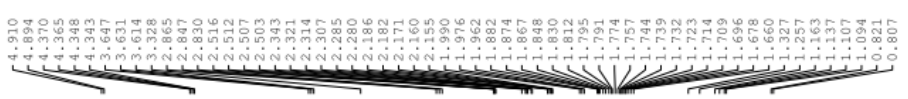
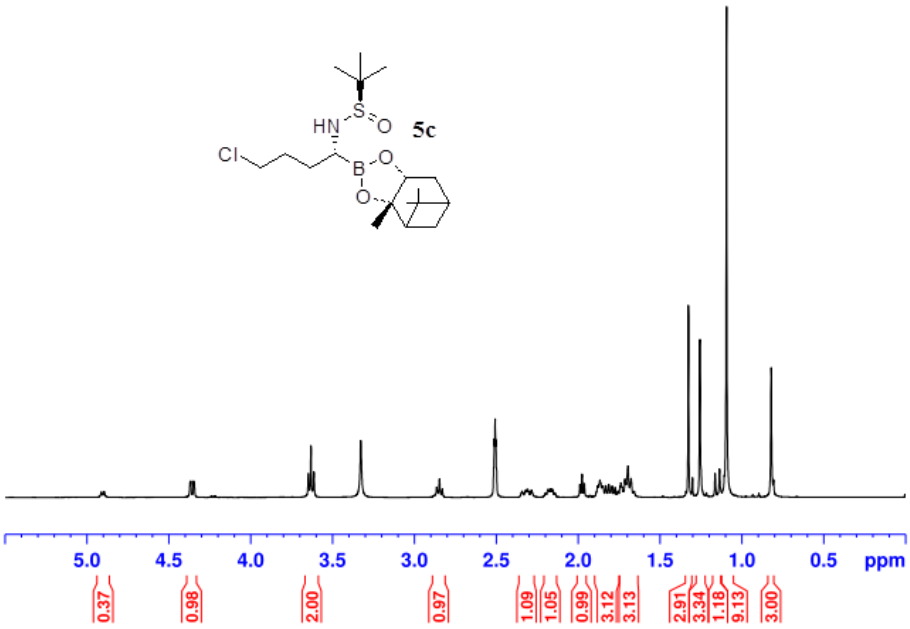
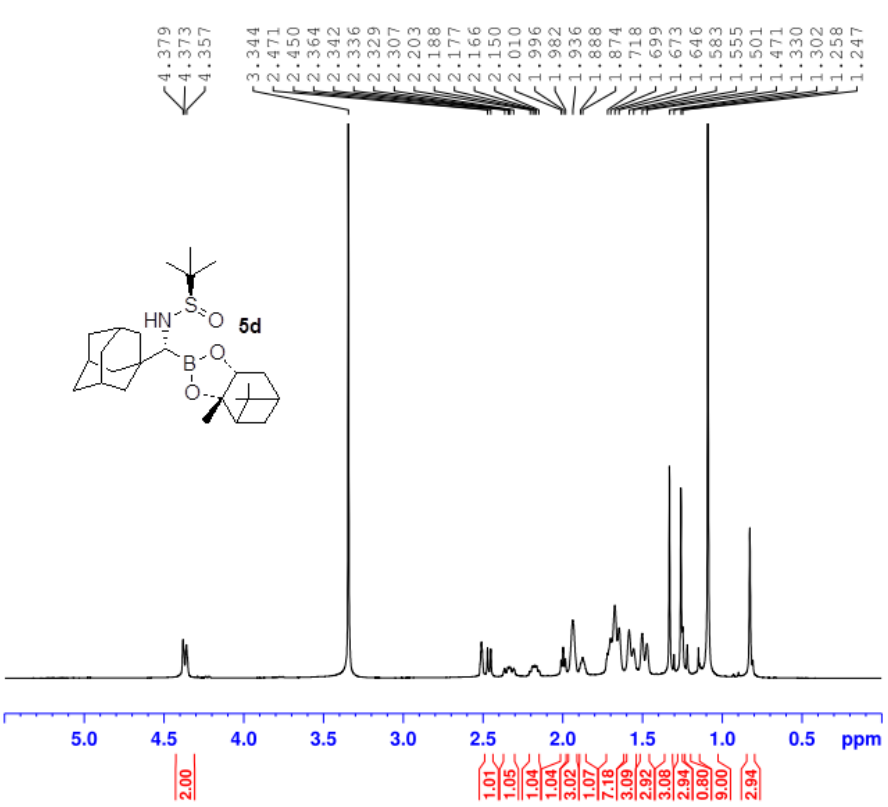





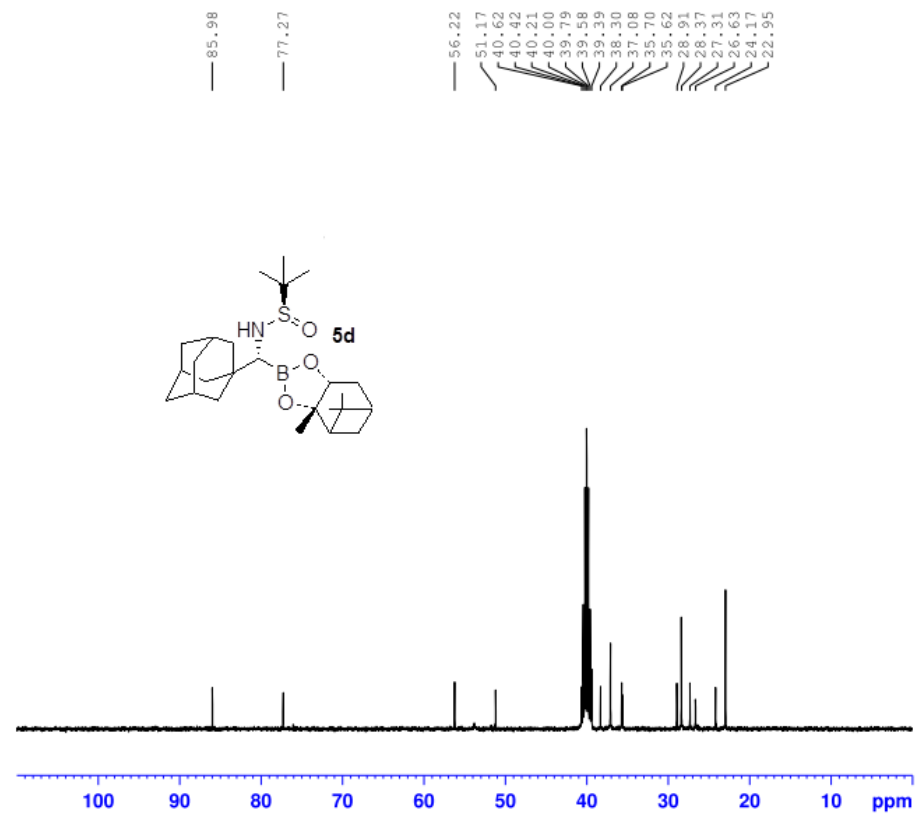

```
NAME          wenkun120309-2-H
EXPNO                        3
PROCNO                       1
Date_                 20120409
Time                     13.54
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                  DMSO
NS                         64
DS                          2
SWH                  8223.685 Hz
FIDRES               0.125483 Hz
AQ                   3.9846387 sec
RG                        71.8
DW                      60.800 usec
DE                       6.50 usec
TE                      298.1 K
D1                 1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        1H
P1                       12.86 usec
PL1                      -4.00 dB
PL1W                20.19063568 W
SFO1                400.1324710 MHz
SI                        32768
SF                  400.1300000 MHz
WDW                          EM
SSB                           0
LB                        0.30 Hz
GB                            0
PC                         1.00
```


```
NAME          wenkun120309-2-C
EXPNO                        3
PROCNO                       1
Date_                 20120409
Time                     15.01
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                  DMSO
NS                       1071
DS                          4
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                   1.3631988 sec
RG                       1030
DW                      20.800 usec
DE                       6.50 usec
TE                      300.1 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                       10.10 usec
PL1                      -3.00 dB
PL1W                64.15196228 W
SFO1               100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                    80.00 usec
PL2                      -4.00 dB
PL12                     11.88 dB
PL13                     12.00 dB
PL2W                20.19063568 W
PL12W                0.52137470 W
PL13W                0.50716585 W
SFO2               400.1316005 MHz
SI                        32768
SF                 100.6127690 MHz
WDW                          EM
SSB                           0
LB                        1.00 Hz
GB                            0
PC                         1.40
```



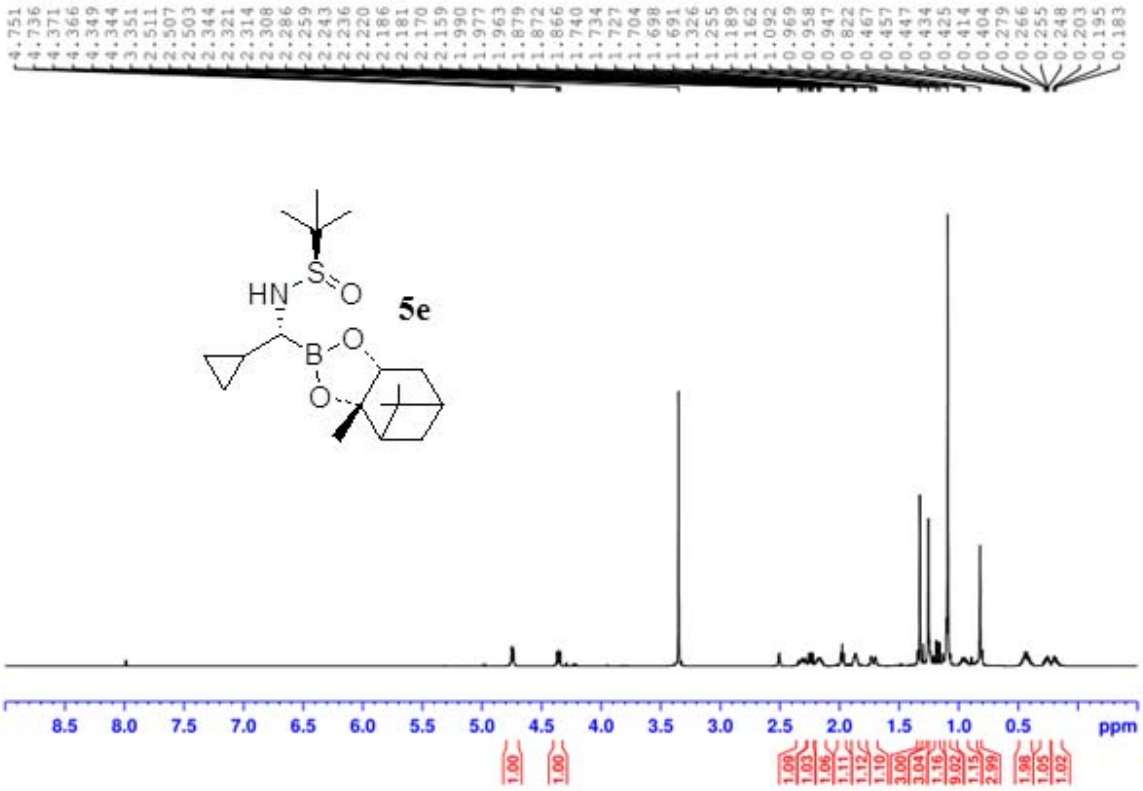
BRUKER

```
NAME        wenkun120511-2-H
EXPNO                      4
PROCNO                     1
Date_               20120511
Time                   12.06
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                       64
DW                   60.800 usec
DE                    6.50 usec
TE                   298.2 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                   12.86 usec
PL1                  -4.00 dB
PL1W            20.19063568 W
SFO1           400.1324710 MHz
SI                    32768
SF             400.1300000 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```



BRUKER

```
NAME        wenkun120511-2-C
EXPNO                      4
PROCNO                     1
Date_               20120511
Time                   12.36
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT                DMSO
NS                      258
DS                        4
SWH               24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631988 sec
RG                      575
DW                   20.800 usec
DE                    6.50 usec
TE                   300.2 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                   10.10 usec
PL1                  -3.00 dB
PL1W            64.15196228 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                80.00 usec
PL2                  -4.00 dB
PL12                 11.88 dB
PL13                 12.00 dB
PL2W            20.19063568 W
PL12W            0.52137470 W
PL13W            0.50716585 W
SFO2           400.1316005 MHz
SI                    32768
SF             100.6127690 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```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2.503
2.344
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2.308
2.286
2.259
2.243
2.236
2.220
2.186
2.181
2.170
2.159
1.990
1.977
1.963
1.879
1.872
1.866
1.740
1.734
1.727
1.704
1.698
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1.326
1.255
1.189
1.162
1.092
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0.958
0.947
0.822
0.467
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0.447
0.434
0.425
0.414
0.404
0.279
0.266
0.255
0.248
0.203
0.195
0.183
HN
S
O
B
O
O
5e
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
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1.09
1.03
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9.02
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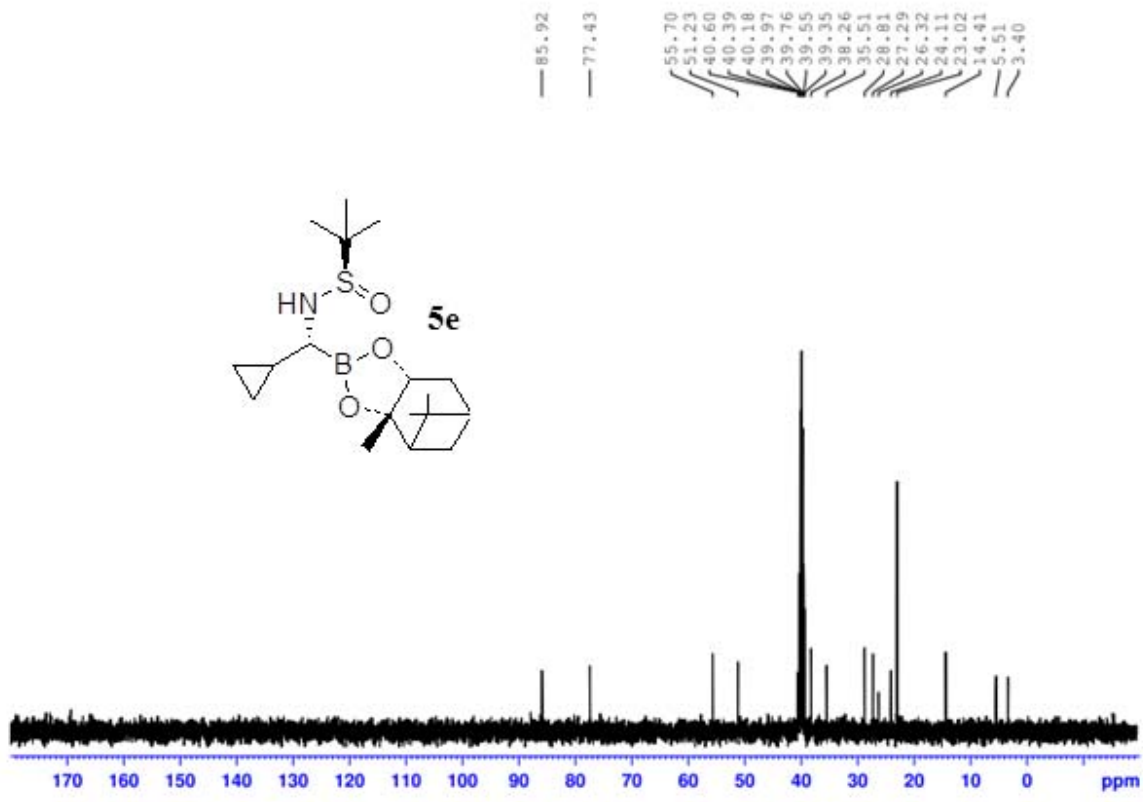
1.05
1.02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40.18
39.97
39.76
39.55
39.35
38.26
35.51
28.81
27.29
26.32
24.11
23.02
14.41
5.51
3.40
HN
S
O
B
O
O
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120
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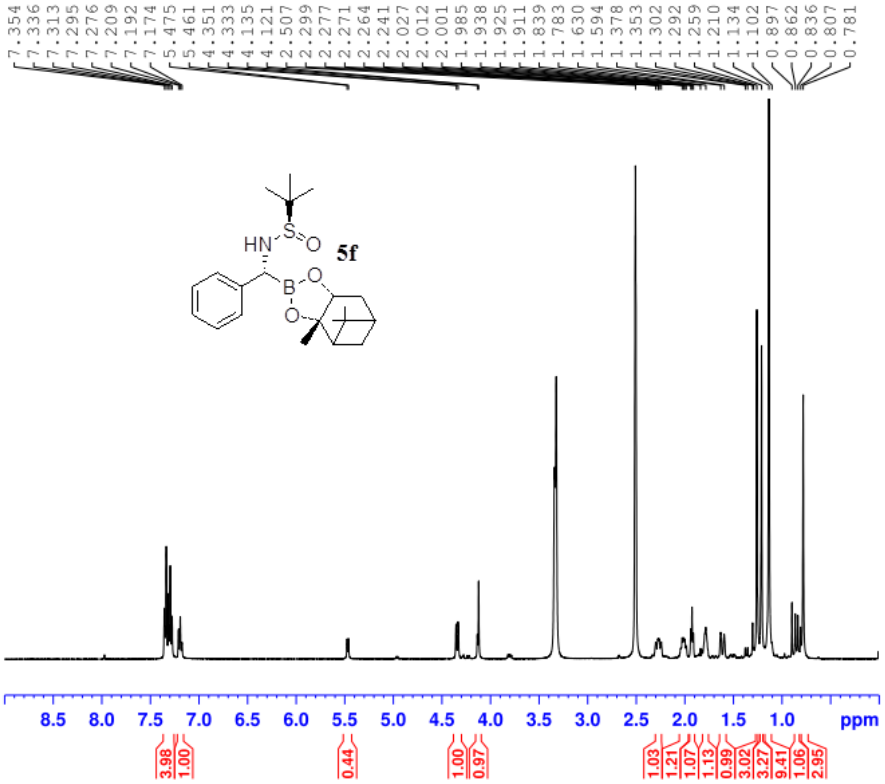
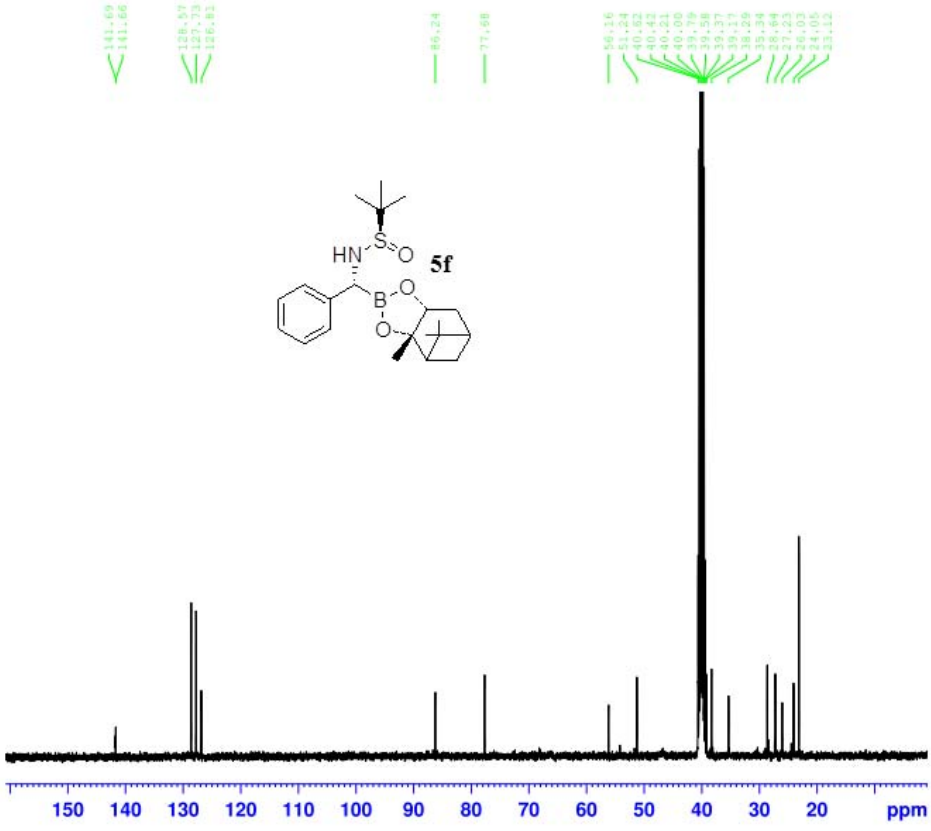
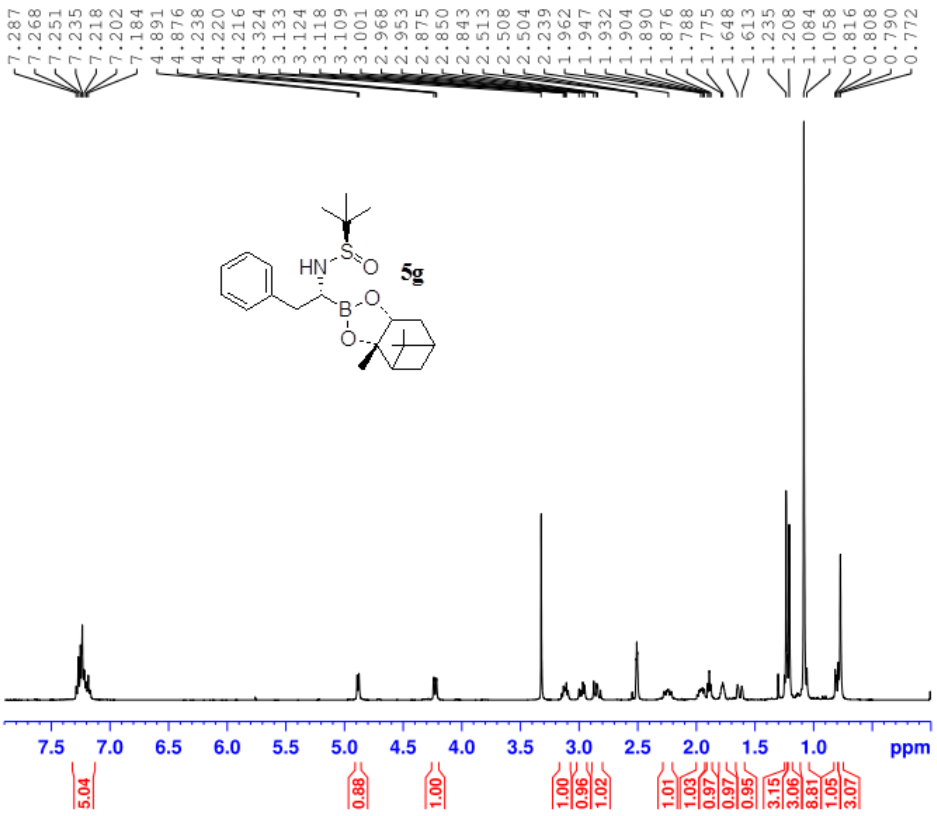



```
NAME        wenkun120310-H
EXPNO                    3
PROCNO                   1
Date_             20120410
Time                 16.29
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT               DMSO
NS                      16
DS                       2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                     128
DW                60.800 usec
DE                 6.50 usec
TE                298.1 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                  12.86 usec
PL1                 -4.00 dB
PL1W          20.19063568 W
SFO1          400.1324710 MHz
SI                   32768
SF            400.1300000 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00
```




```
NAME        wenkun120310-C
EXPNO                    3
PROCNO                   1
Date_             20120410
Time                 17.52
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT               DMSO
NS                    1382
DS                       4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                     362
DW                20.800 usec
DE                 6.50 usec
TE                300.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                  10.10 usec
PL1                 -3.00 dB
PL1W          64.15196228 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               80.00 usec
PL2                 -4.00 dB
PL12                11.88 dB
PL13                12.00 dB
PL2W          20.19063568 W
PL12W          0.52137470 W
PL13W          0.50716585 W
SFO2         400.1316005 MHz
SI                   32768
SF           100.6127690 MHz
WDW                     EM
SSB                      0
LB                  1.00 Hz
GB                       0
PC                    1.40
```



```
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EXPNO                      1
PROCNO                     1
Date_               20120423
Time                   16.55
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                 DMSO
NS                        32
DS                         2
SWH                 8223.685 Hz
FIDRES              0.125483 Hz
AQ                  3.9846387 sec
RG                       101
DW                    60.800 usec
DE                     6.50 usec
TE                    298.3 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     12.86 usec
PL1                    -4.00 dB
PL1W              20.19063568 W
SFO1              400.1324710 MHz
SI                       32768
SF                400.1300000 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```
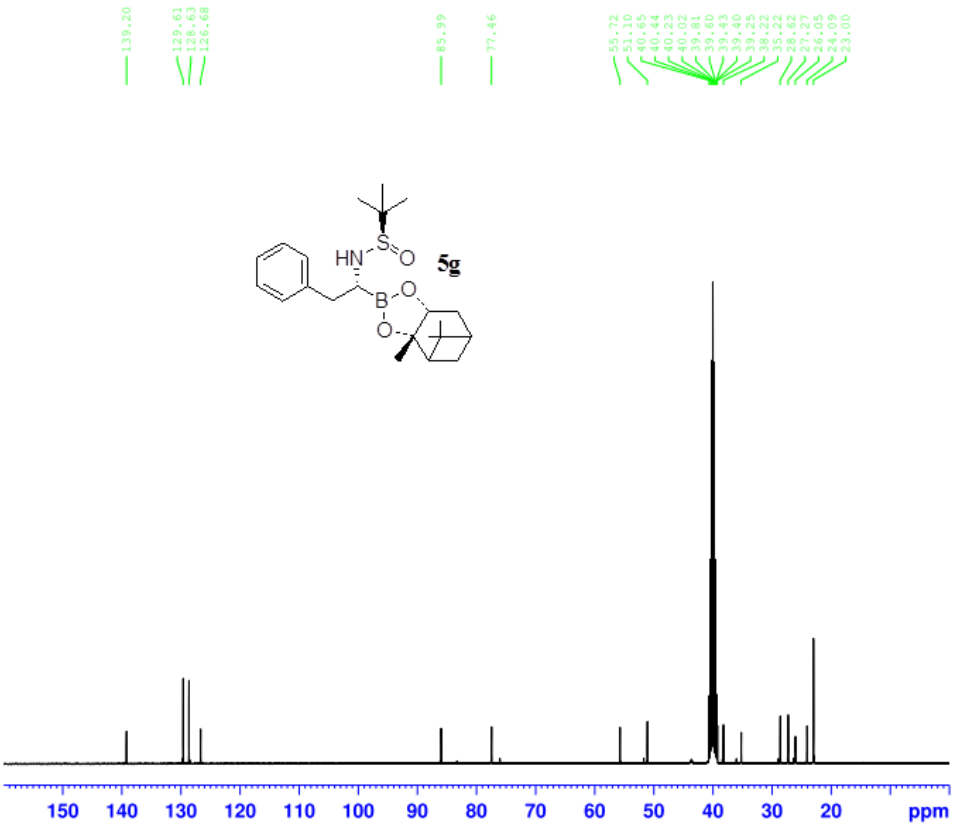
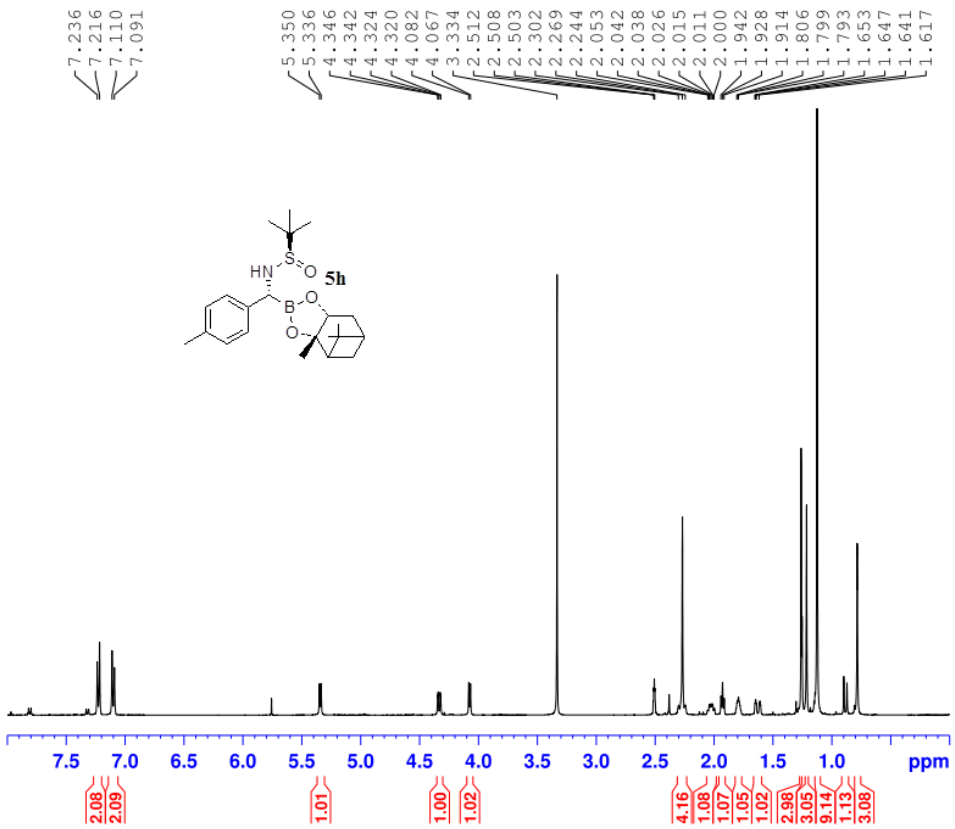
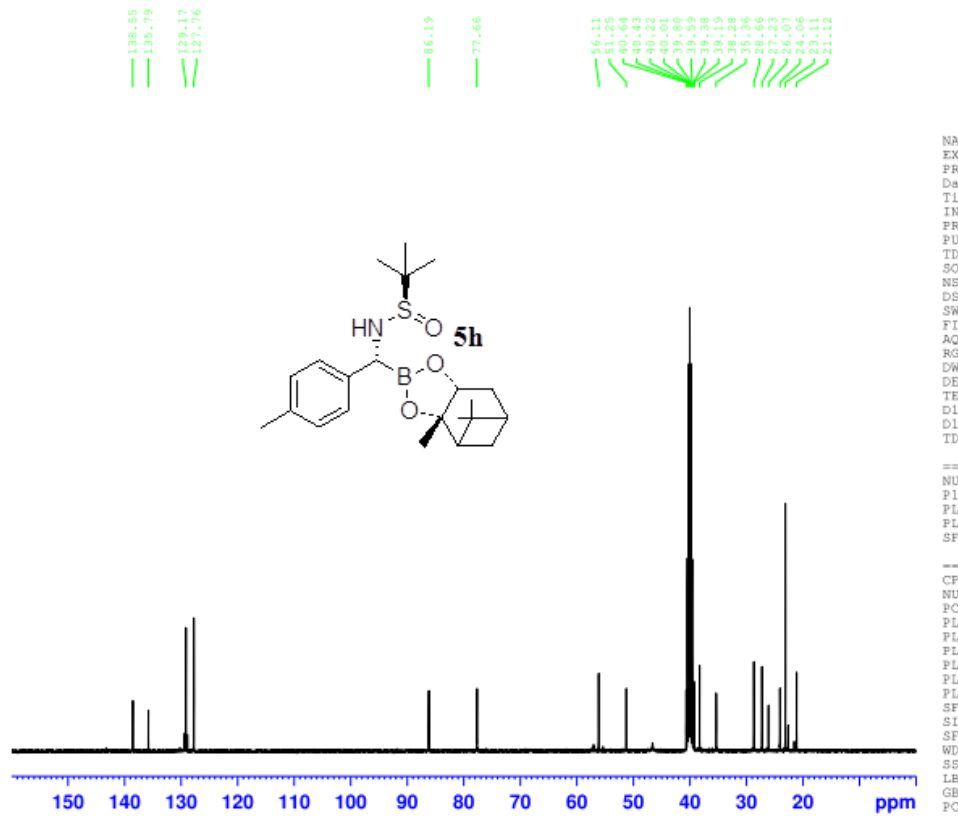



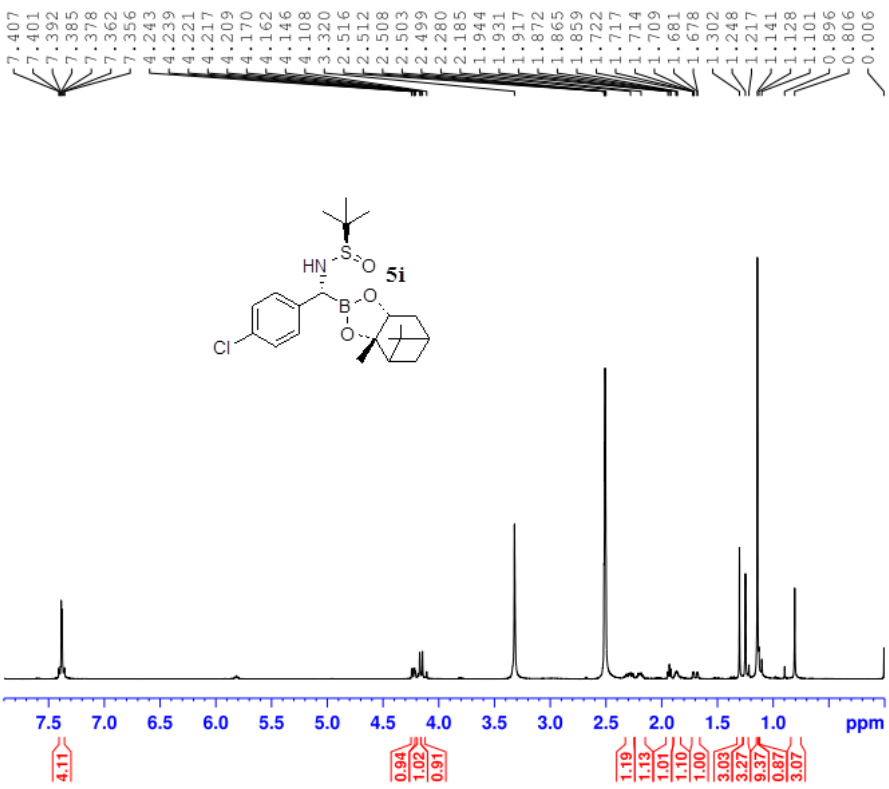
```
NAME        wenkun120423-4-C
EXPNO                      1
PROCNO                     1
Date_               20120424
Time                    2.49
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG              zgpg30
TD                     65536
SOLVENT                 DMSO
NS                      10240
DS                         4
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                      1290
DW                    20.800 usec
DE                     6.50 usec
TE                    300.1 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      13C
P1                     10.10 usec
PL1                    -3.00 dB
PL1W              64.15196228 W
SFO1              100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                      1H
PCPD2                  80.00 usec
PL2                    -4.00 dB
PL12                   11.88 dB
PL13                   12.00 dB
PL2W              20.19063568 W
PL12W              0.52137470 W
PL13W              0.50716585 W
SFO2              400.1316005 MHz
SI                       32768
SF                100.6127690 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```

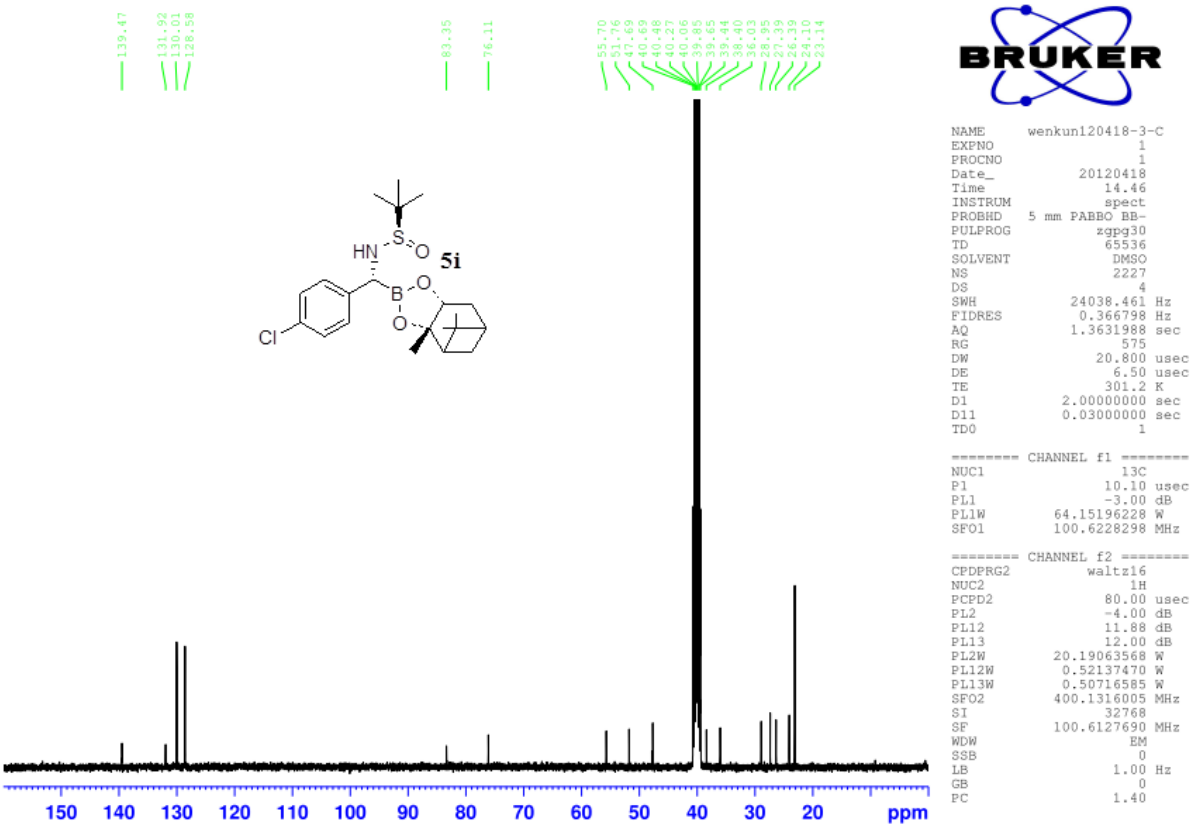


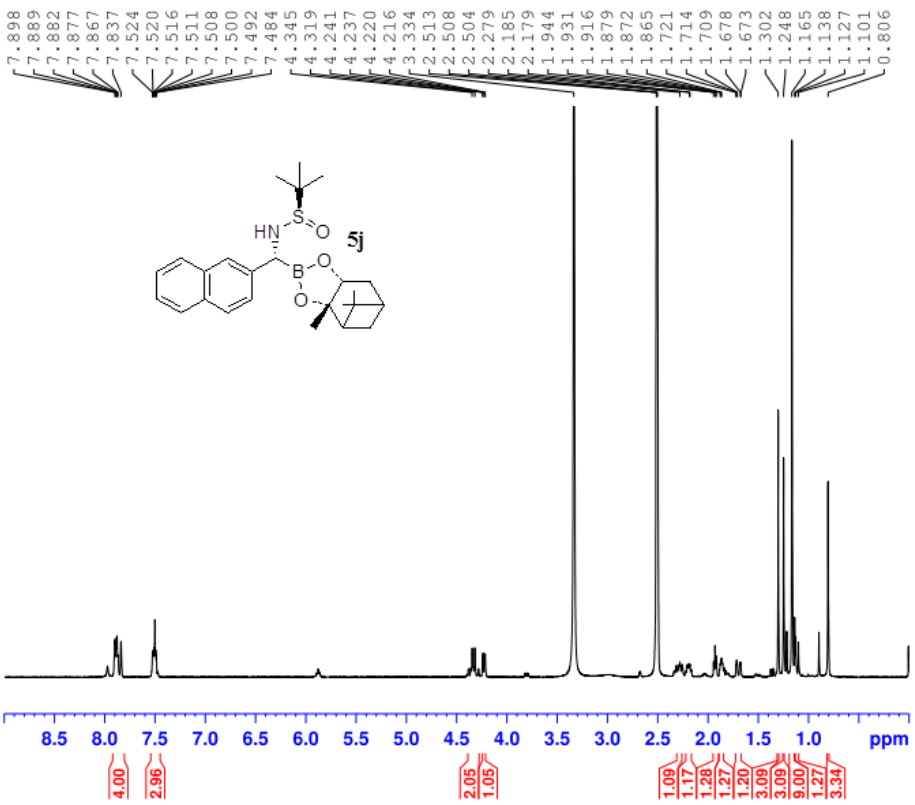

```
NAME          wenkun120428-1-H
EXPNO                       4
PROCNO                      1
Date_                20120428
Time                    12.36
INSTRUM                 spect
PROBHD       5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                 DMSO
NS                        16
DS                         2
SWH                 8223.685 Hz
FIDRES              0.125483 Hz
AQ                  3.9846387 sec
RG                       71.8
DW                     60.800 usec
DE                      6.50 usec
TE                     298.5 K
D1                  1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      12.86 usec
PL1                     -4.00 dB
PL1W               20.19063568 W
SFO1              400.1324710 MHz
SI                       32768
SF                400.1300000 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```




```
NAME          wenkun120428-1-C
EXPNO                       4
PROCNO                      1
Date_                20120428
Time                    12.51
INSTRUM                 spect
PROBHD       5 mm PABBO BB-
PULPROG              zgpg30
TD                     65536
SOLVENT                 DMSO
NS                        926
DS                          4
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                        812
DW                     20.800 usec
DE                      6.50 usec
TE                     299.8 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                      10.10 usec
PL1                     -3.00 dB
PL1W               64.15196228 W
SFO1              100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                     -4.00 dB
PL12                    11.88 dB
PL13                    12.00 dB
PL2W               20.19063568 W
PL12W               0.52137470 W
PL13W               0.50716585 W
SFO2              400.1316005 MHz
SI                       32768
SF                100.6127690 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```

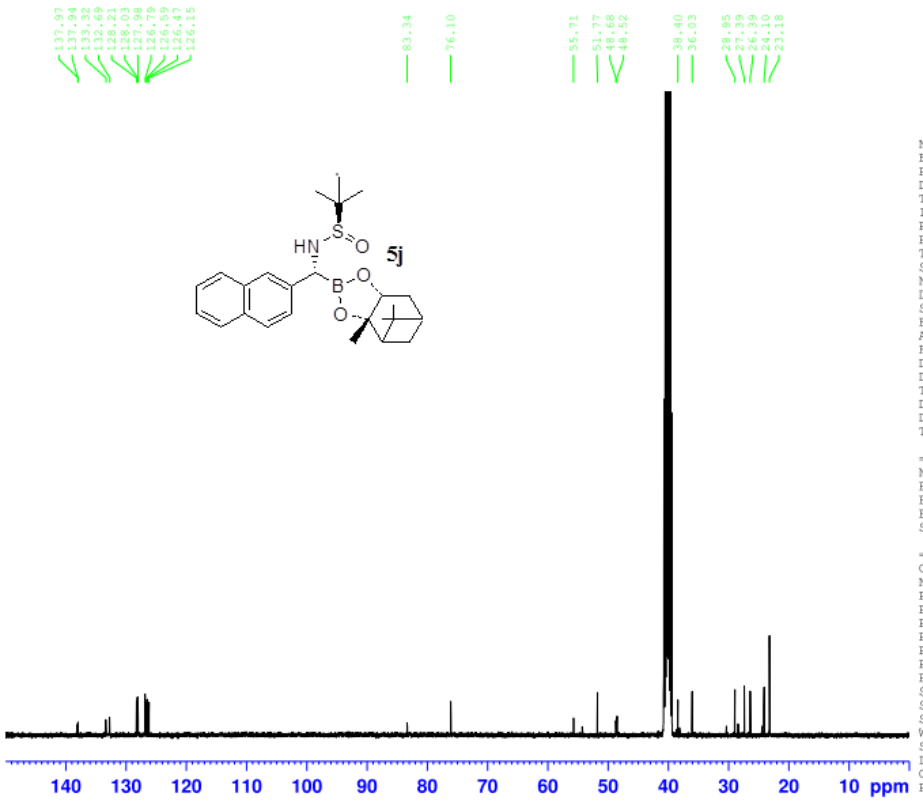

7.407
7.401
7.392
7.385
7.378
7.362
7.356
4.243
4.239
4.221
4.217
4.209
4.170
4.162
4.146
4.108
3.320
2.516
2.512
2.508
2.503
2.499
2.280
2.185
1.944
1.931
1.917
1.872
1.865
1.859
1.722
1.717
1.714
1.709
1.681
1.678
1.302
1.248
1.217
1.141
1.128
1.101
0.896
0.806
0.006
BRUKER
5i
HN
S
O
B
O
O
Cl
NAME wenkun120418-3-H
EXPNO 1
PROCNO 1
Date_ 20120418
Time 13.47
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 32
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 228
DW 60.800 usec
DE 6.50 usec
TE 298.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.86 usec
PL1 -4.00 dB
PL1W 20.19063568 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
4.11
0.94
1.02
0.91
1.19
1.13
1.01
1.10
1.00
3.03
3.27
9.37
0.87
3.07


139.47
131.92
130.01
128.58
83.35
76.11
55.70
51.76
47.69
40.69
40.48
40.27
40.06
39.85
39.65
39.44
38.40
36.03
28.95
27.39
26.39
24.10
23.14
BRUKER
5i
HN
S
O
B
O
O
Cl
NAME wenkun120418-3-C
EXPNO 1
PROCNO 1
Date_ 20120418
Time 14.46
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 2227
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 575
DW 20.800 usec
DE 6.50 usec
TE 301.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.10 usec
PL1 -3.00 dB
PL1W 64.15196228 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 11.88 dB
PL13 12.00 dB
PL2W 20.19063568 W
PL12W 0.52137470 W
PL13W 0.50716585 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm



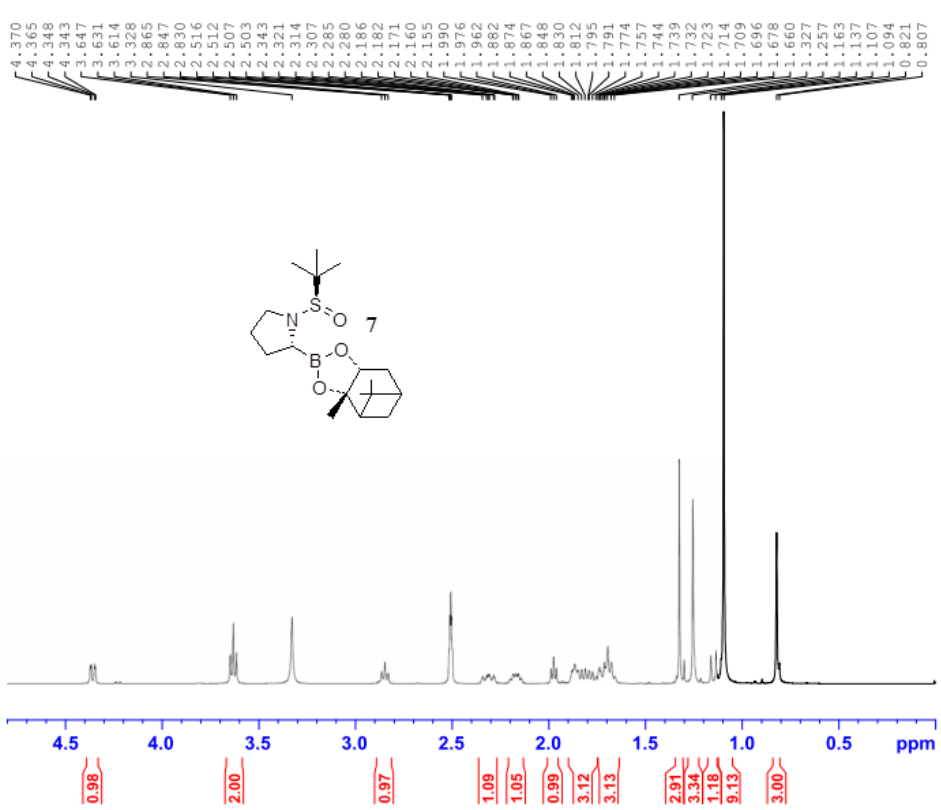
BRUKER

```
NAME          wenkun120419-1-H
EXPNO                        1
PROCNO                       1
Date_                 20120419
Time                     16.38
INSTRUM                  spect
PROBHD   5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                  DMSO
NS                         32
DS                          2
SWH                  8223.685 Hz
FIDRES               0.125483 Hz
AQ                   3.9846387 sec
RG                         144
DW                      60.800 usec
DE                       6.50 usec
TE                      298.5 K
D1                   1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        1H
P1                       12.86 usec
PL1                      -4.00 dB
PL1W                20.19063568 W
SFO1               400.1324710 MHz
SI                       32768
SF                 400.1300000 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```

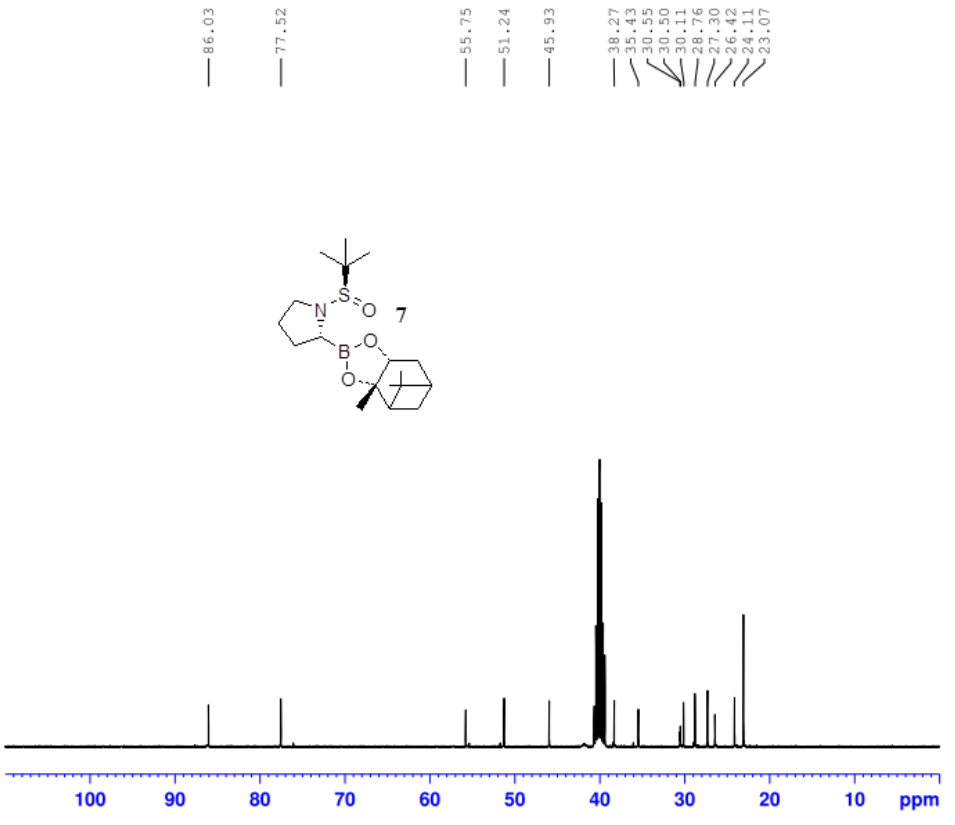


BRUKER

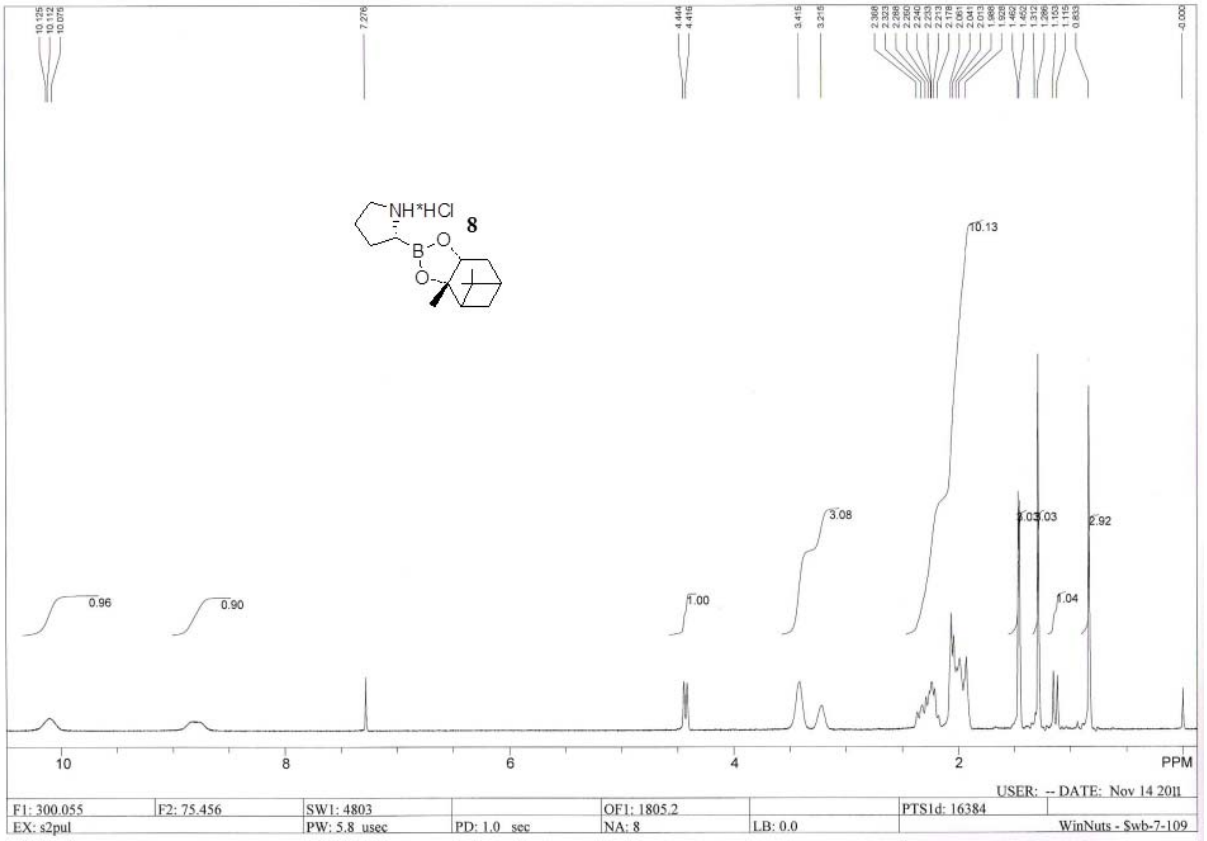
```
NAME          wenkun120419-1-C
EXPNO                        1
PROCNO                       1
Date_                 20120419
Time                     18.26
INSTRUM                  spect
PROBHD   5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                  DMSO
NS                       10240
DS                           4
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                   1.3631988 sec
RG                        40.3
DW                      20.800 usec
DE                       6.50 usec
TE                      301.7 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                       10.10 usec
PL1                      -3.00 dB
PL1W                64.15196228 W
SFO1               100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                    80.00 usec
PL2                      -4.00 dB
PL12                     11.88 dB
PL13                     12.00 dB
PL2W                20.19063568 W
PL12W                0.52137470 W
PL13W                0.50716585 W
SFO2               400.1316005 MHz
SI                       32768
SF                 100.6127690 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```




```
NAME        wenkun120309-2-H'
EXPNO                       3
PROCNO                      1
Date_                20120509
Time                    14.54
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                 DMSO
NS                        64
DS                         2
SWH                 8223.685 Hz
FIDRES              0.125483 Hz
AQ                  3.9846387 sec
RG                       71.8
DW                     60.800 usec
DE                      6.50 usec
TE                     298.1 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     12.86 usec
PL1                    -4.00 dB
PL1W            20.19063568 W
SFO1            400.1324710 MHz
SI                      32768
SF              400.1300000 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```




```
NAME        wenkun120309-2-C'
EXPNO                       3
PROCNO                      1
Date_                20120509
Time                    16.01
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                     65536
SOLVENT                 DMSO
NS                      1071
DS                         4
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                      1030
DW                     20.800 usec
DE                      6.50 usec
TE                     300.1 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      13C
P1                     10.10 usec
PL1                    -3.00 dB
PL1W            64.15196228 W
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                      1H
PCPD2                  80.00 usec
PL2                    -4.00 dB
PL12                   11.88 dB
PL13                   12.00 dB
PL2W            20.19063568 W
PL12W            0.52137470 W
PL13W            0.50716585 W
SFO2            400.1316005 MHz
SI                      32768
SF              100.6127690 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```


NH*HCl
8
10.13
3.08
3.03
3.03
2.92
1.04
1.00
0.96
0.90
10
8
6
4
2
PPM
USER: -- DATE: Nov 14 2011
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1805.2
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
WinNuts - $wb-7-109