Supplementary Material (ESI) for Chemical Communications

Supporting Information

Negishi Cross-Coupling of Secondary Alkylzinc Halides with Aryl/Heteroaryl Halides using *Pd-PEPPSI-IPent*

Selçuk Çalimsiz and Michael G. Organ*

Chemistry Department, York University

4700 Keele Street, Toronto, M3J 1P3 (Canada)

Fax: (+1) 416-736-5936

organ@yorku.ca

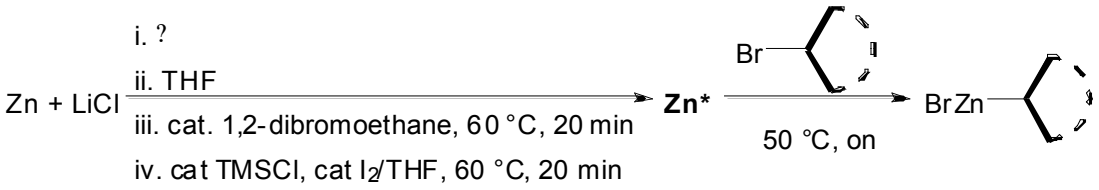
Table of Contents

General Experimental

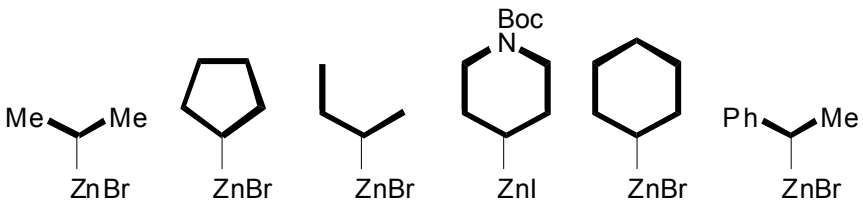
Pd-PEPPSI-IPent[1] and *tert*-Butyl 4-Iodopiperidine-1-carboxylate[2] were prepared according to the literature. Zinc dust (<10 micron) and LiCl were purchased from Aldrich and stored & weighed out in an argon-filled glovebox. All other reagents were purchased from Sigma-Aldrich or Alfa-Aesar and were used without further purification. THF was distilled over sodium metal and toluene was distilled over calcium hydride prior to use. All reaction vials (screw-cap threaded, caps attached, 17 x 60 mm) were purchased from Fisher Scientific. Thin layer chromatography (TLC) was performed on Dynamic 84111 w/h F-254 glass plates and spots were visualized using UV light (254nm) and potassium permanganate or phosphomolybdic acid stains. Flash column chromatography was performed using a Biotage Isolera Four Flash Purification System with 10 gram pre-packed silica cartridges. NMR spectra were recorded on Bruker 300 AVANCE and Bruker 400 AVANCE spectrometers. The chemical shifts for ^{1}H NMR spectra are given in parts per million (ppm) referenced to the residual proton signal of the deuterated solvent; coupling constants are expressed in Hertz (Hz). ^{13}C NMR spectra were referenced to the carbon signals of the deuterated solvent. The following abbreviations are used to describe peak multiplicities: s = singlet, bs = broad singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, q = quartet, quint = quintet, and tt = triplet of triplets, qt = quartet of triplets, qd = quartet of doublets. For ^{13}C JMOD NMR spectra, quartenary carbons, carbonyls, and carbons with an even number of protons attached produce a positive (+) signal. Peaks with a negative (-) signal arise from carbons attached to an odd number of protons. Gas chromatography analysis was performed on Varian Series GC/MS/MS 4000 System. Melting points were determined using a Fisher-Johns melting point apparatus and are uncorrected. All experiments were conducted under an atmosphere of dry argon.

Synthetic Procedures:

Preparation of Secondary Alkylzinc Halides.[3]

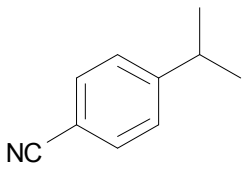


In glove box, a dry 100 mL round-bottom flask equipped with a magnetic stir bar was charged with LiCl (4.24 g, 100 mmol) and zinc dust (6.55 g, 100 mmol). It was sealed with a rubber septum, moved outside the glove box and then heated with a heat gun for 15 min with occasional stirring under high vacuum and backfilled with argon after cooling to rt. After repeating this process once more, freshly distilled THF (50 mL) and 1,2-dibromoethane (214 μL, 2.5 mmol) were added via syringe and the reaction mixture was heated at 60 °C for 20 min. After cooling to rt, trimethylsilyl chloride (63 μL, 0.5 mmol) and a solution of iodine (63 mg, 0.25 mmol) in THF (0.5 mL) were added via syringe. The reaction mixture was heated at 60 °C for 20 min and then cooled to room temperature. The corresponding alkyl halides (50 mmol) were added and the reactions stirred at 50 °C for 16h at which time they were allowed to stand for 6h at rt and the supernatant solution was carefully transferred to a dry vessel via cannula. The concentration of the organozinc solution was determined by iodometric titration using Knochel's procedure.[4] The solutions thus prepared are shown below with their measured titer.



General Procedure for Pd-Catalyzed Negishi Coupling of Aryl Bromides with Secondary Alkylzinc Halides.

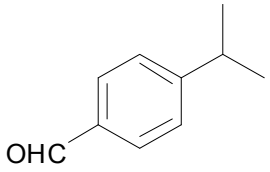
An oven-dried vial (3 mL screw-cap threaded) equipped with a stir bar was charged with *Pd-PEPPSI-IPr* (3.4 mg, 1 mol %) or *Pd-PEPPSI-IPent* (Table 1: 4 mg, 1 mol %, Table 2: 8 mg, 2 mol %,). The vial was sealed with a Teflon-lined screw cap and purged with argon (3X). If liquid, the aryl bromide (0.5 mmol) was added via syringe along with enough toluene to bring the total reaction volume to 2 mL. Alternatively, if the aryl bromide was a solid at room temperature, it was introduced into the reaction vial prior to purging with argon. The solution was cooled to 0 °C in an ice bath and a THF solution of alkyl zinc halide (0.6 mmol) was added slowly via syringe over 2 min. The ice bath was removed after the addition and the reaction was stirred at rt for 3h. The reaction mixture was then quenched by addition of hydrochloric acid (1N), extracted with ethyl acetate (3X), and the organic phase washed with brine (1X). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was purified by flash chromatography using the Biotage Isolera Flash Purification System with 10g pre-packed silica cartridges to afford the product mixture. The ratio of the branched to the linear cross coupled product was determined readily by ^{1}H NMR spectroscopic analysis.



(Table 1, Entry a) 4-Isopropylbenzonitrile: Following the general procedure with *Pd-PEPPSI-IPent*, 66.5 mg (92%) of cross-coupled isomeric products were obtained that were isolated by flash

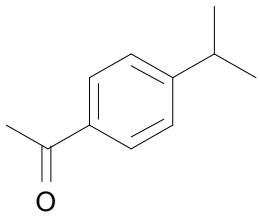
chromatography (0-6% EtOAc/Hexane, rf = 0.27 with 6% EtOAc/Hexane) as a colourless oil. The ratio of the branched to the linear cross-coupled product was determined to be 27:1. Spectral data of the major product were in accordance with those reported in the literature.[5]

Similarly, following the general procedure with *Pd-PEPPSI-IPr*, 61.4 mg (85%) of cross-coupled isomeric products were obtained. The ratio of the branched to the linear cross-coupled product was determined to be 3:1.



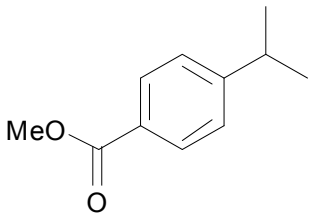
(Table 1, Entry b) 4-Isopropylbenzaldehyde: Following the general procedure with *Pd-PEPPSI-IPent*, 57.8 mg (78%) of cross-coupled isomeric products were obtained that were isolated by flash chromatography (0-6% EtOAc/Hexane, rf = 0.29 with 6% EtOAc/Hexane) as a colourless oil. The ratio of the branched to the linear cross-coupled product was determined to be 39:1. Spectral data were in accordance with those reported in the literature.[5]

Similarly, following the general procedure with *Pd-PEPPSI-IPr*, 47.1 mg (64%) of cross-coupled isomeric products were obtained. The ratio of the branched to the linear cross-coupled product was determined to be 6:1.



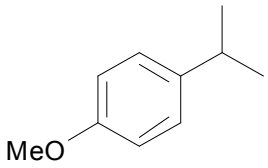
(Table 1, Entry c) *p*-Isopropylacetophenone. Following the general procedure with *Pd-PEPPSI-IPent*, 79.3 mg (98%) of cross-coupled isomeric products were obtained that were isolated by flash chromatography (0-6% EtOAc/Hexane, rf = 0.28 with 6% EtOAc/Hexane) as a colourless oil. The ratio of the branched to the linear cross-coupled product was determined to be 30:1.

Similarly, following the general procedure with *Pd-PEPPSI-IPr*, 81 mg (99%) of cross-coupled isomeric products were obtained. The ratio of the branched to the linear cross-coupled product was determined to be 6:1.



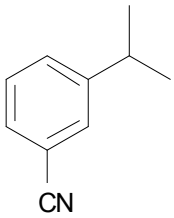
(Table 1, Entry d) Methyl 4-isopropylbenzoate. Following the general procedure with *Pd-PEPPSI-IPent*, 92.7 mg (99%) of cross-coupled isomeric products were obtained that were isolated by flash chromatography (0-6% EtOAc/Hexane, rf = 0.35 with 6% EtOAc/Hexane) as a yellow oil. The ratio of the branched to the linear cross-coupled product was determined to be 40:1. Spectral data were in accordance with those reported in the literature.[5]

Similarly, following the general procedure with *Pd-PEPPSI-IPr*, 74.1 mg (83%) of cross-coupled isomeric products were obtained. The ratio of the branched to the linear cross-coupled product was determined to be 5:1.



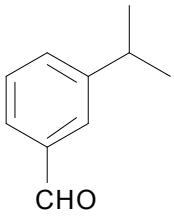
(Table 1, Entry e) 4-Isopropylanisole. Following the general procedure with *Pd-PEPPSI-IPent*, 92.7 mg (99%) of cross-coupled isomeric products were obtained that were isolated by flash chromatography (0-6% EtOAc/Hexane, rf = 0.35 with 6% EtOAc/Hexane) as a yellow oil. The ratio of the branched to the linear cross-coupled product was determined to be 33:1. Spectral data were in accordance with those reported in the literature.[5]

Similarly, following the general procedure with *Pd-PEPPSI-IPr*, 66.7 mg (89%) of cross-coupled isomeric products were obtained. The ratio of the branched to the linear cross-coupled product was determined to be 2.5:1.



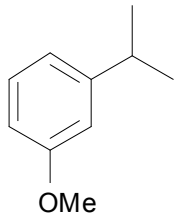
(Table 1, Entry f) 3-Isopropylbenzonitrile. Following the general procedure with *Pd-PEPPSI-IPent*, 60.5 mg (84%) of cross-coupled isomeric products were obtained that were isolated by flash chromatography (0-6% EtOAc/Hexane, rf = 0.33 with 6% EtOAc/Hexane) as a colourless oil. The ratio of the branched to the linear cross-coupled product was determined to be 11:1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.49-7.47 (m, 2H), 7.41-7.38 (m, 1H), 2.96 (q, *J* = 7.1 Hz, 1H), 1.27 (d, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 131.1, 130.0, 129.4, 128.9, 119.0, 112.1, 33.7, 24.0; HRMS (EI) [M] calcd. for $C_{10}H_{11}N$ 145.0891; found 145.0893.

Similarly, following the general procedure with *Pd-PEPPSI-IPr*, 55.4 mg (77%) of cross-coupled isomeric products were obtained. The ratio of the branched to the linear cross-coupled product was determined to be 1:1.4.



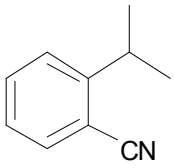
(Table 1, Entry g) 3-Isopropylbenzaldehyde. Following the general procedure with *Pd-PEPPSI-IPent*, 52 mg (71%) of cross-coupled isomeric products were obtained that were isolated by flash chromatography (0-6% EtOAc/Hexane, rf = 0.28 with 6% EtOAc/Hexane) as a yellow oil. The ratio of the branched to the linear cross-coupled product was determined to be 22:1. Spectral data were in accordance with those reported in the literature.[6]

Similarly, following the general procedure with *Pd-PEPPSI-IPr*, 57.4 mg (78%) of cross-coupled isomeric products were obtained. The ratio of the branched to the linear cross-coupled product was determined to be 1.6:1.



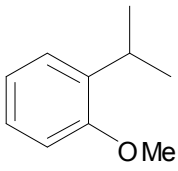
(Table 1, Entry h) 3-Isopropylanisole. Following the general procedure with *Pd-PEPPSI-IPent*, 42.5 mg (57%) of cross-coupled isomeric products were obtained that were isolated by flash chromatography (0-6% EtOAc/Hexane, rf = 0.38 with 6% EtOAc/Hexane) as a yellow oil. The ratio of the branched to the linear cross-coupled product was determined to be 34:1. Spectral data were in accordance with those reported in the literature.[7]

Similarly, following the general procedure with *Pd-PEPPSI-IPr*, 23 mg (78%) of cross-coupled isomeric products were obtained. The ratio of the branched to the linear cross-coupled product was determined to be 3.5:1.



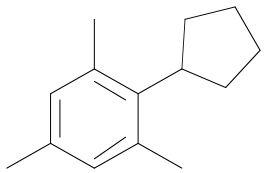
(Table 1, Entry i) 2-Isopropylbenzonitrile. Following the general procedure with *Pd-PEPPSI-IPent*, 58.2 mg (80%) of cross-coupled isomeric products were obtained that were isolated by flash chromatography (0-6% EtOAc/Hexane, rf = 0.21 with 6% EtOAc/Hexane) as a colourless oil. The ratio of the branched to the linear cross-coupled product was determined to be 2.4:1. Spectral data were in accordance with those reported in the literature.[5]

Similarly, following the general procedure with *Pd-PEPPSI-IPr*, 74.5 mg (99%) of cross-coupled isomeric products were obtained. The ratio of the branched to the linear cross-coupled product was determined to be 1:8.

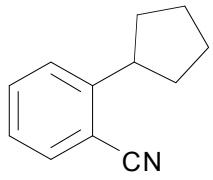


(Table 1, Entry j) 2-Isopropylanisole. Following the general procedure with *Pd-PEPPSI-IPent*, 34.6 mg (46%) of cross-coupled isomeric products were obtained that were isolated by flash chromatography (0-6% EtOAc/Hexane, rf = 0.65 with 6% EtOAc/Hexane) as a colourless oil. The ratio of the branched to the linear cross-coupled product was determined to be 2:1. Spectral data were in accordance with those reported in the literature.[5]

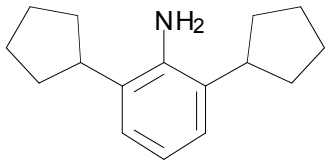
Similarly, following the general procedure with *Pd-PEPPSI-IPr*, 74.5 mg (99%) of cross-coupled isomeric products were obtained. The ratio of the branched to the linear cross-coupled product was determined to be 1:9.



(Table 2, Entry 1) 2-Cyclopentyl-1,3,5-trimethylbenzene. Following the general procedure with *Pd-PEPPSI-IPent*, 74 mg (80%) of product was obtained that was isolated by flash chromatography (Hexane, rf =0.52) as a colourless oil. Spectral data were in accordance with those reported in the literature.[5]

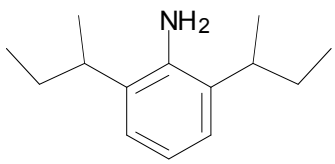


(Table 2, Entry 2) 2-Cyclopentylbenzonitrile. Following the general procedure with *Pd-PEPPSI-IPent*, 60 mg (70%) of product was obtained that was isolated by flash chromatography (20% EtOAc/Hexane, rf = 0.53) as a yellow oil. Spectral data were in accordance with those reported in the literature.[8]

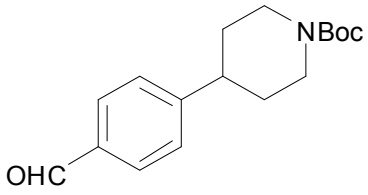


(Table 2, Entry 3) 2,6-Dicyclopentylaniline. Following the general procedure with 3.4 equiv. of cyclopentylzinc bromide and *Pd-*

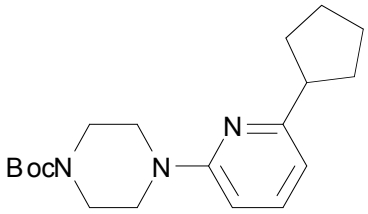
PEPPSI-IPent, 94 mg (82%) of product was obtained that was isolated by flash chromatography (10% EtOAc/Hexane, rf = 0.36) as a pale-orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 7.6 Hz, 2H), 6.79 (t, *J* = 7.6 Hz, 1H), 3.82 (bs, 2H), 3.04 (p, *J* = 7.8 Hz, 2H), 2.11-2.05 (m, 4H), 1.85-1.83 (m, 4H), 1.82-1.63 (m, 8H); ^{13}C NMR JMOD (100 MHz, $CDCl_3$) δ 141.1 (+), 130.1 (+), 123.3 (-), 118.2 (-), 40.1 (-), 32.3 (+), 25.1 (+); HRMS (EI) [M] calcd. for $C_{16}H_{23}N$ 229.1830; found 229.1824.



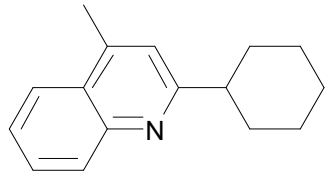
(Table 2, Entry 4) 2,6-Di-sec-butylaniline. Following the general procedure with 3.4 equiv. of 2-butylzinc bromide and *Pd-PEPPSI-IPent*, 78 mg (76%) of product was obtained that was isolated by flash chromatography (5% Et_2O/Pentane, rf = 0.31) as a pale-orange oil. Spectral data were in accordance with those reported in the literature.[9] The ratio of the branched to the linear cross-coupled product was determined to be 16:1 by GC and ^{1}H NMR spectral analysis.



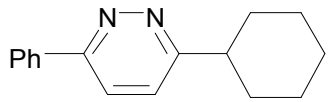
(Table 2, Entry 5)1-Piperidinecarboxylic acid, 4-(4-formylphenyl)-, 1,1-dimethylethyl ester. Following the general procedure with *Pd-PEPPSI-IPent* (reaction was quenched with saturated NH_4Cl solution instead of 1 N HCl), 58 mg (40%) of product was obtained that was isolated by flash chromatography (20% EtOAc/Hexane, rf = 0.31) as a colourless oil. Spectral data were in accordance with those reported in the literature.[2] The ratio of the desired to isomerized product was determined to be 6:1.



(Table 2, Entry 6) tert-butyl 4-(6-cyclopentylpyridin-2-yl)piperazine-1-carboxylate. Following the general procedure with *Pd-PEPPSI-IPent* (reaction was quenched with 1M Na_3EDTA solution instead of 1N HCl), 149 mg (90%) of product was obtained that was isolated by flash chromatography (10% EtOAc/Hexane, rf = 0.27) as a white solid. Mp: 51-53 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (t, *J* = 7.8 Hz, 1H), 6.54 (d, *J* = 7.8 Hz, 1H), 6.44 (d, *J* = 7.8 Hz, 1H), 3.54 (bs, 8H), 3.07-3.02 (m, 1H), 2.01-1.96 (m, 2H), 1.65-1.64 (m, 6H), 1.49 (s, 9H);^{13}C NMR (400 MHz, $CDCl_3$) δ 164.1 (+), 158.8 (+), 154.8 (+), 137.6 (-), 111.5 (-), 104.0 (-), 79.7 (+), 47.1 (-), 45.1 (+), 33.2 (+), 28.4 (-), 25.8 (+); HRMS (ESI) [M+H] calcd. for $C_{11}H_{29}N_3O_2$ 332.2338; found 332.2341.

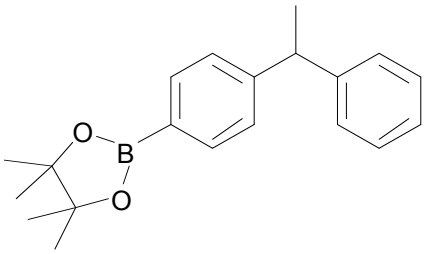


(Table 2, Entry 7) 2-Cyclohexyl-4-methylquinoline. Following the general procedure with *Pd-PEPPSI-IPent* (reaction was quenched with 1N Na_3EDTA solution instead of 1 N HCl), 103.2 mg (92%) of product was obtained that was isolated by flash chromatography (10% EtOAc/Hexane, rf = 0.38) as a yellow oil. Spectral data were in accordance with those reported in the literature.[10]

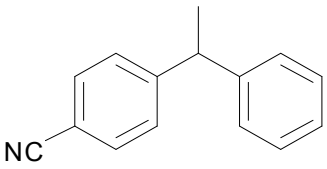


(Table 2, Entry 8) 3-cyclohexyl-6-phenylpyridazine. Following the general procedure with *Pd-PEPPSI-IPent* (reaction was quenched with 1M Na_3EDTA solution instead of 1N HCl), 102 mg (94%) of product was obtained that was isolated by flash chromatography (15% EtOAc/Hexane, rf = 0.21) as a white solid. Mp: 125-127 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, *J* = 6.7 Hz, 2H), 7.79 (d, *J* = 8.9 Hz, 1H), 7.54-7.45 (m, 3H), 7.39 (d, *J* = 8.9 Hz, 1H), 3.00 (tt, *J* = 12.1, 3.3 Hz, 1H), 2.04 (d, *J* = 12.1 Hz, 2H), 1.92

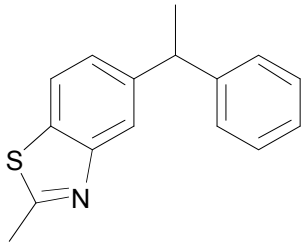
(d, *J* = 12.9 Hz, 2H), 1.81 (d, *J* = 12.9 Hz, 1H), 1.65 (qd, *J* = 12.6, 2.9 Hz, 2H), 1.46 (qt, *J* = 12.6, 3.2 Hz, 2H), 1.33 (qt, *J* = 12.9, 3.2 Hz, 1H); ^{13}C NMR JMOD (100 MHz, $CDCl_3$) δ 165.9 (+), 157.2 (+), 136.4 (+), 129.6 (-), 128.8 (-), 126.7 (-), 125.2 (-), 123.9 (-), 44.4 (-), 32.6 (+), 26.3 (+), 25.8 (+); HRMS (ES) [M+] calcd. for $C_{16}H_{18}N_2$ 239.1548; found 239.1532.



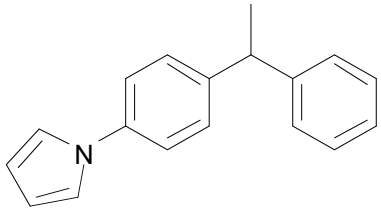
(Table 2, Entry 9) 4,4,5,5-tetramethyl-2-(4-(1-phenylethyl)phenyl)-1,3,2-dioxaborolane. Following the general procedure with *Pd-PEPPSI-IPent* (reaction was quenched with saturated NH_4Cl solution instead of 1N HCl) 94 mg (61%) of product was obtained that was isolated by flash chromatography (hexane-10% EtOAc/Hexane, rf = 0.21 with 10% EtOAc/Hexane) as a white solid. Mp: 36-38 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.7 Hz, 2H), 7.33-7.19 (m, 7H), 4.21 (q, *J* = 7.1 Hz, 1H), 1.68 (d, *J* = 7.1 Hz, 3H), 1.37 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 145.9, 134.8, 128.2, 127.5, 127.0, 125.9, 83.5, 44.8, 24.7, 21.5; HRMS (EI) [M+] calcd. for $C_{20}H_{25}BO_2$ 309.2026; found 309.2013.



(Table 2, Entry 10) 4-(1-Phenylethyl)benzonitrile. Following the general procedure with *Pd-PEPPSI-IPent*, (reaction was quenched with saturated NH_4Cl solution instead of 1N HCl) 98.4 mg (95%) of product was obtained that was isolated by flash chromatography (0-20% EtOAc/Hexane, rf = 0.68 with 20% EtOAc/Hexane) as a white solid. Mp: 46-48 °C. Spectral data were in accordance with those reported in the literature.[11]



(Table 2, Entry 11) 2-methyl-5-(1-phenylethyl)benzo[d]thiazole. Following the general procedure with *Pd-PEPPSI-IPent* (reaction was quenched with saturated NH_4Cl solution instead of 1N HCl) 103 mg (82%) of product was obtained that was isolated by flash chromatography (hexane-20% EtOAc/Hexane, rf = 0.35 with 20% EtOAc/Hexane) as a white solid. Mp: 54-56; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.33-7.29 (m, 4H), 7.23-7.20 (m, 2H), 4.32 (q, *J* = 7.1 Hz, 1H), 2.83 (s, 3H), 1.74 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 153.6, 146.0, 144.7, 133.0, 128.3, 127.5, 126.0, 125.0, 121.0, 120.8, 44.5, 21.8, 20.0; HRMS (EI) [M] calcd. for $C_{16}H_{15}NS$ 253.0925; found 253.0925.



(Table 2, Entry 12) 1-(4-(1-phenylethyl)phenyl)-1H-pyrrole. Following general procedure with *Pd-PEPPSI-IPent* (reaction was quenched with saturated NH_4Cl solution instead of 1N HCl) 103 mg (83%) of product was obtained that was isolated by flash chromatography (heptane-10% EtOAc/Heptane, rf = 0.40 with 10% EtOAc/Heptane) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.29 (m, 9H), 7.13 (t, *J* = 2.3 Hz, 2H), 6.42 (t, *J* = 1.9 Hz, 2H), 4.26 (q, *J* = 7.2 Hz, 1H), 1.75 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 143.8, 138.8, 128.5, 128.4, 127.5, 126.1, 120.5, 119.2, 110.1, 44.1, 21.8; HRMS (EI) [M] calcd. for $C_{18}H_{17}N$ 247.1361; found 247.1367.

References:

1. M. G. Organ, S. Calimsiz, M. Sayah, K. H. Hoi, A. J. Lough, *Angew. Chem. Int. Ed.*, 2009, **48**, 2383.

2. E. G. Corley, K. Conrad, J. A. Murry, C. Savarin, J. Holko and G. Boice, *J. Org. Chem.*, 2004, **69**, 5120.

3. A. Krasovskiy, V. Malakhov, A. Gavryushin and P. Knochel, *Angew. Chem. Int. Ed.*, 2006, **45**, 6040.

4. A. Krasovskiy and P. Knochel, *Synthesis*, 2006, 890.

5. C. Han and S. L. Buchwald, *J. Am. Chem. Soc.*, 2009, **131**, 7532.

6. A. Sulpizio, M. Mella and A. Albini, *Terrahedron* 1989*,* **45***,* 7545.

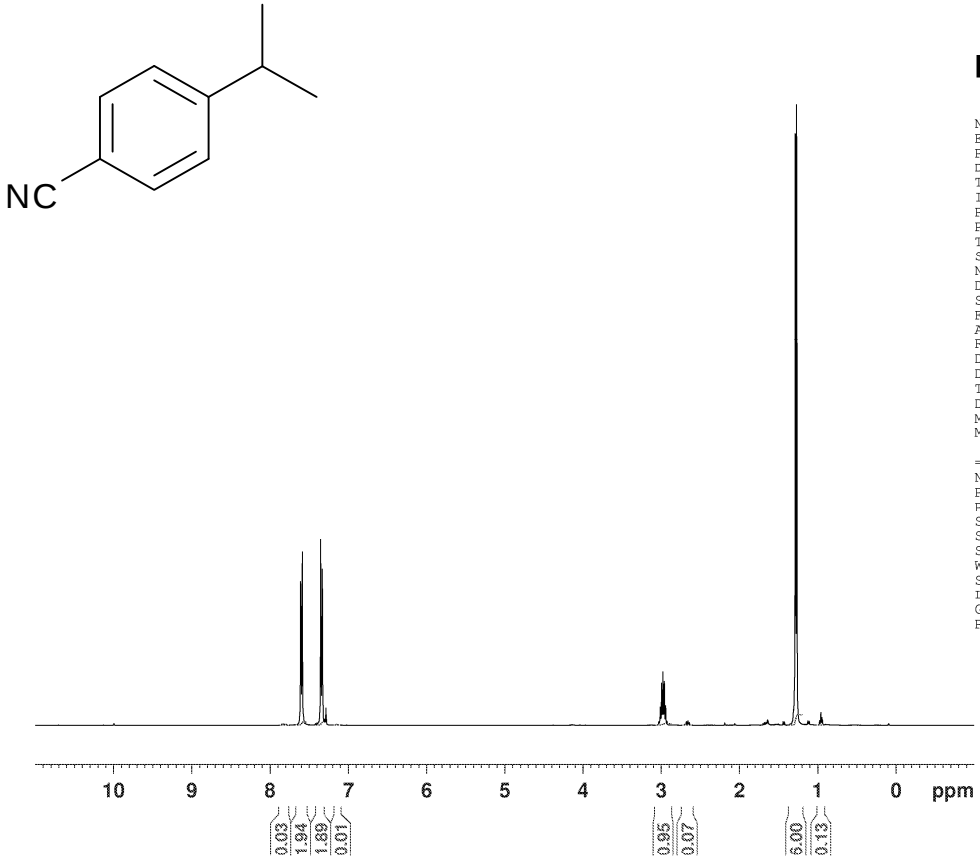
7. L. F. Tietze, C. A. Vock, I. K. Krimmelbein and L. Nacke, *Synthesis*, 2009, 2040.

8. C. –Q. Tan, X. Zheng; Z. Ma and Y. Gu, *Syn. Comm*., 1999, **29**, 123.

9. B. R. Steele, S. Georgakopoulos, M. Micha-Screttas and C. G. Screttas, *Eur. J. Org. Chem.*, 2007, **19**, 3091.

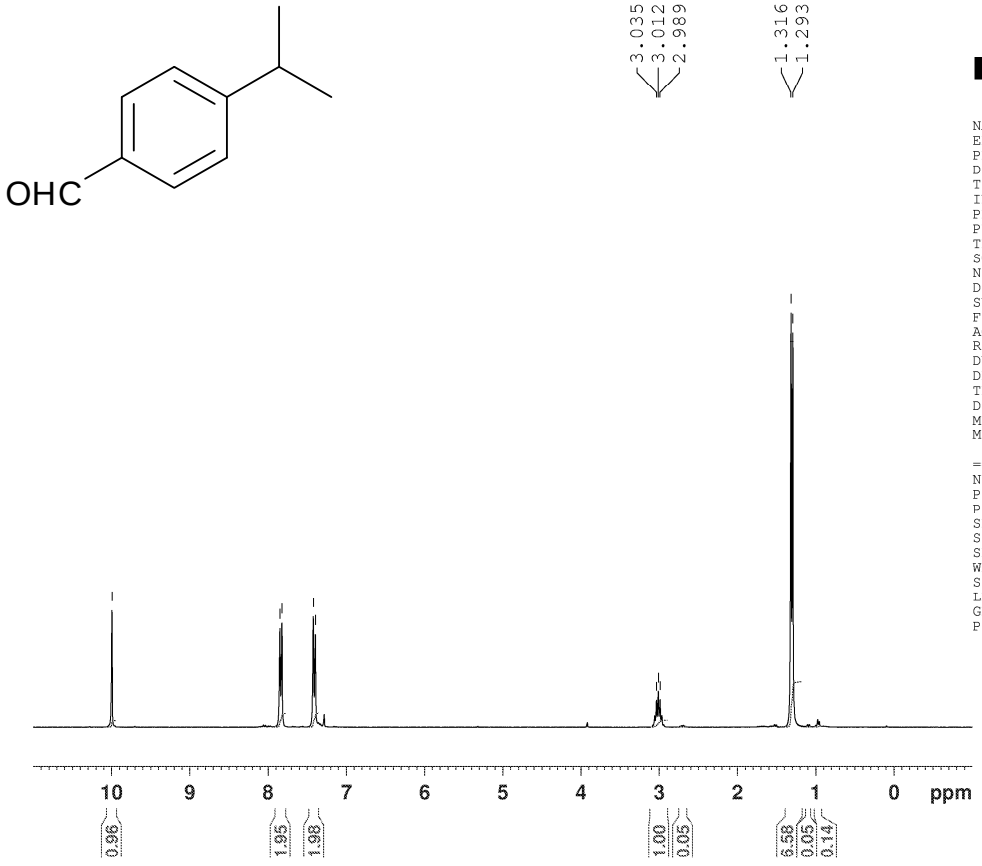
10. H. Togo, S. Matsubayashi, O. Yamazaki and M. Yokoyama, *J. Org. Chem.*, 2000, **65***,* 2816.

11. M. Amatorea and C. Gosmini, *Chem. Comm.*, 2008, **40**, 5019.



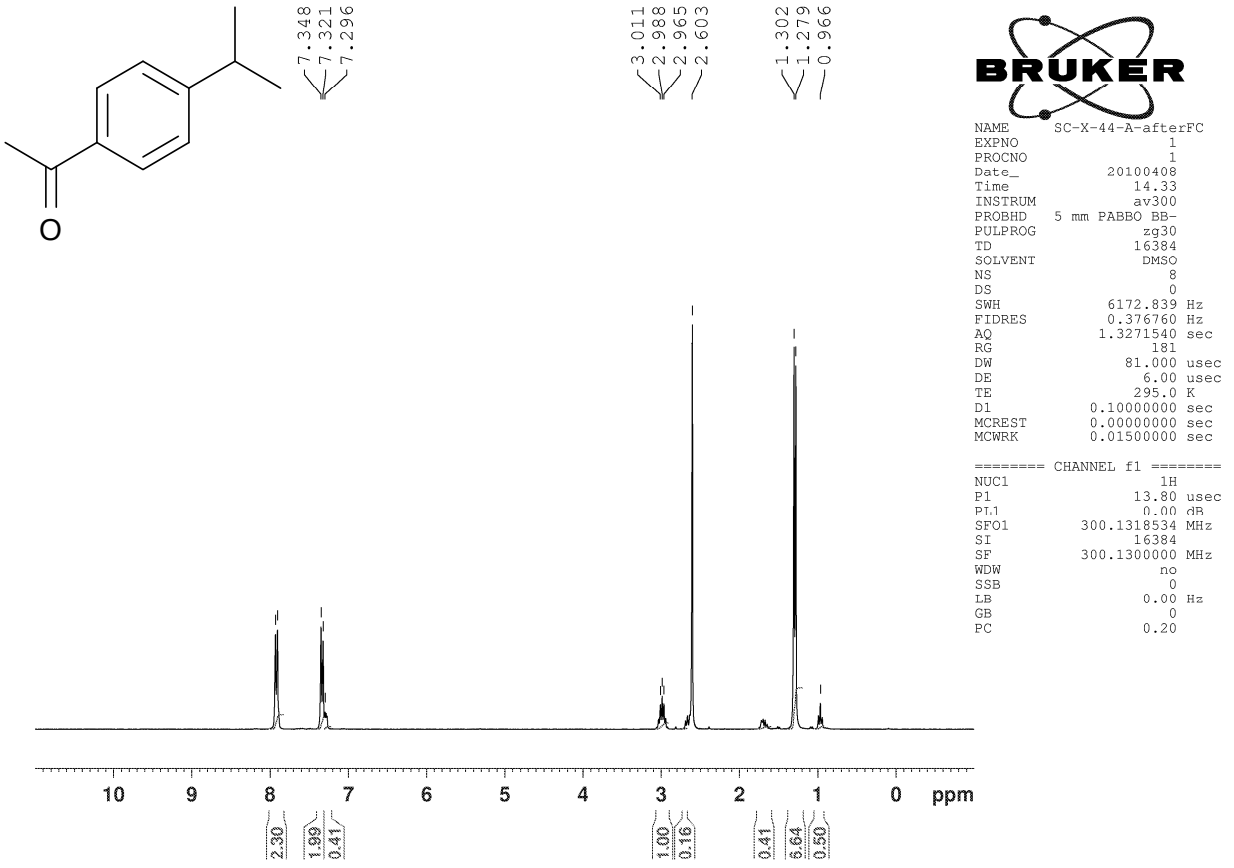

```
NAME        SC-X-31-A-afterFC
EXPNO                       1
PROCNO                      1
Date_                20100323
Time                    18.07
INSTRUM                 av400
PROBHD   5 mm PABBO BB-
PULPROG                  zg30
TD                      16384
SOLVENT                   D2O
NS                          8
DS                          0
SWH                  8278.146 Hz
FIDRES               0.505258 Hz
AQ                   0.9896436 sec
RG                       143.7
DW                     60.400 usec
DE                      6.00 usec
TE                      295.0 K
D1                 0.10000000 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

======== CHANNEL f1 ========
NUC1                        1H
P1                       9.80 usec
PL1                      0.00 dB
SFO1               400.1324710 MHz
SI                         8192
SF                 400.1300000 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```

400 MHz ^{1}H NMR spectrum of **Table 1 Entry a**



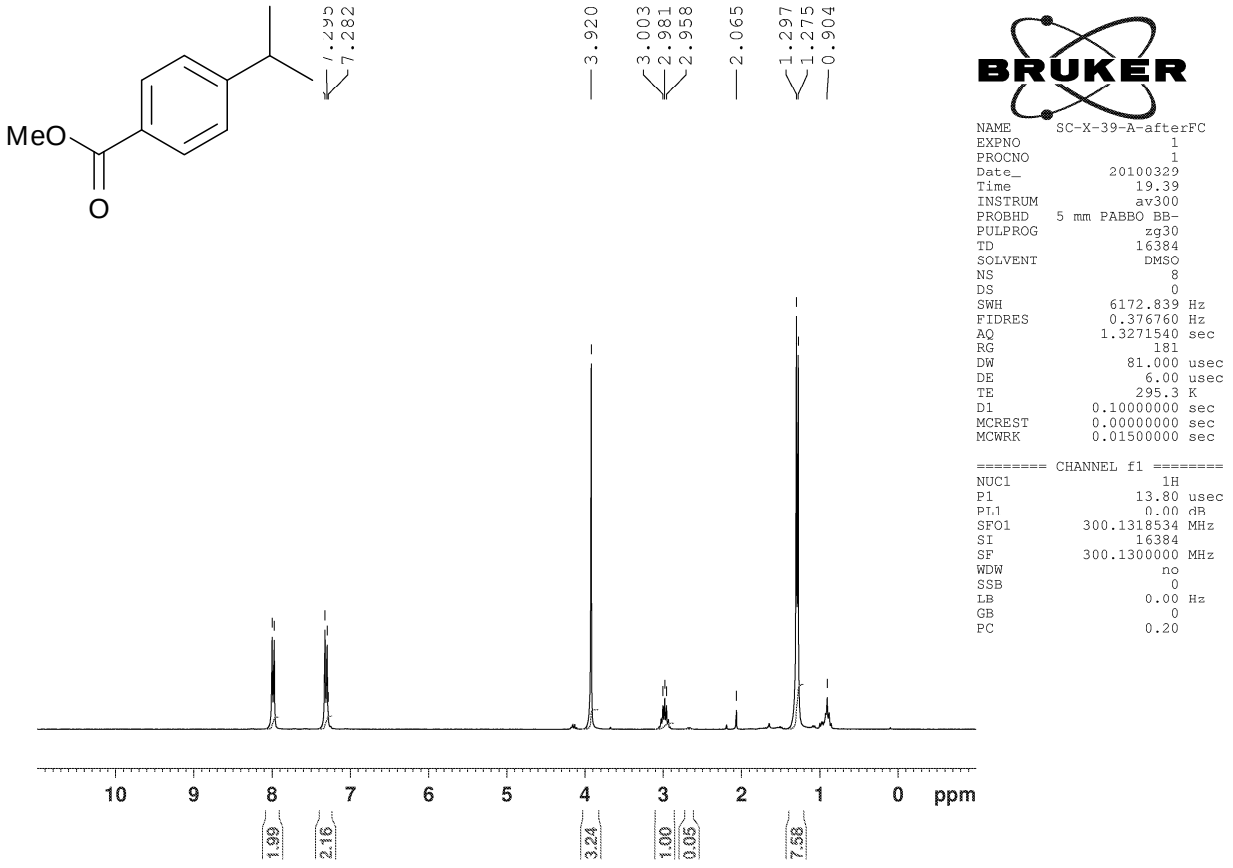

```
NAME      SC-X-40-A-afterFC
EXPNO                    1
PROCNO                   1
Date_             20100330
Time                 17.01
INSTRUM              av300
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   16384
SOLVENT               DMSO
NS                       8
DS                       0
SWH               6172.839 Hz
FIDRES            0.376760 Hz
AQ                1.3271540 sec
RG                   287.4
DW                  81.000 usec
DE                   6.00 usec
TE                   295.2 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   13.80 usec
PL1                   0.00 dB
SFO1          300.1318534 MHz
SI                   16384
SF            300.1300000 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    0.20
```

300 MHz ^{1}H NMR spectrum of **Table 1 Entry b**




```
NAME      SC-X-44-A-afterFC
EXPNO                    1
PROCNO                   1
Date_             20100408
Time                 14.33
INSTRUM              av300
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   16384
SOLVENT               DMSO
NS                       8
DS                       0
SWH               6172.839 Hz
FIDRES            0.376760 Hz
AQ                1.3271540 sec
RG                     181
DW                  81.000 usec
DE                   6.00 usec
TE                   295.0 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   13.80 usec
PL1                   0.00 dB
SFO1          300.1318534 MHz
SI                   16384
SF            300.1300000 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    0.20
```

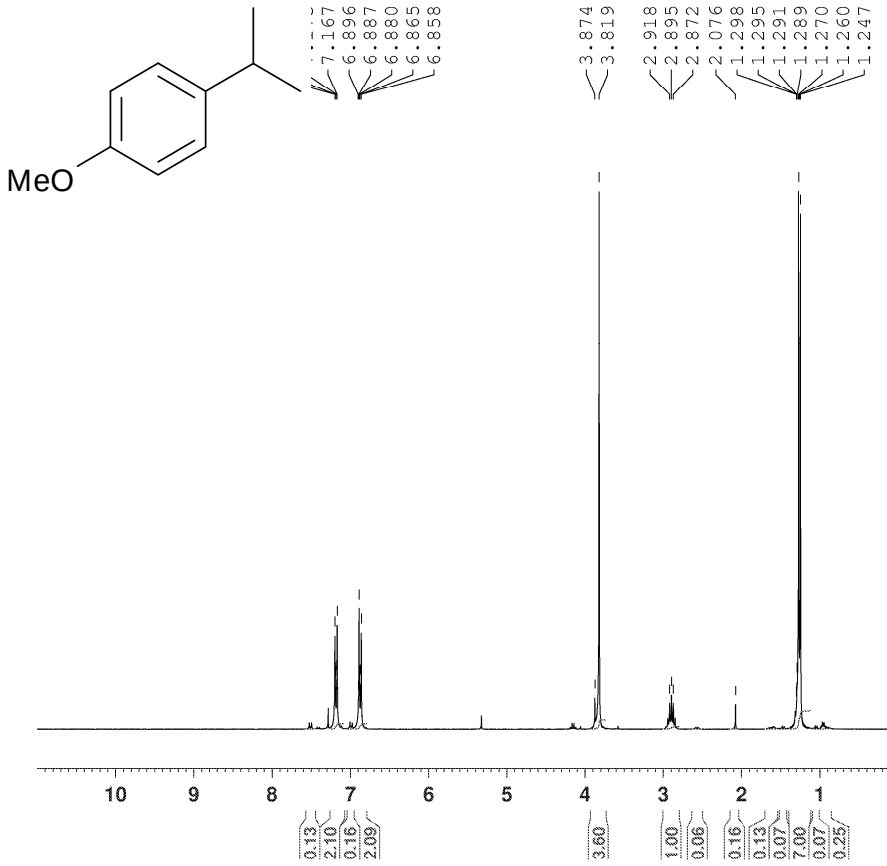
300 MHz ^{1}H NMR spectrum of **Table 1 Entry c**



BRUKER

NAME	SC-X-39-A-afterFC
EXPNO	1
PROCNO	1
Date_	20100329
Time	19.39
INSTRUM	av300
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	16384
SOLVENT	DMSO
NS	8
DS	0
SWH	6172.839 Hz
FIDRES	0.376760 Hz
AQ	1.3271540 sec
RG	181
DW	81.000 usec
DE	6.00 usec
TE	295.3 K
D1	0.10000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec
======== CHANNEL f1 ========	
NUC1	1H
P1	13.80 usec
PL1	0.00 dB
SFO1	300.1318534 MHz
SI	16384
SF	300.1300000 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	0.20

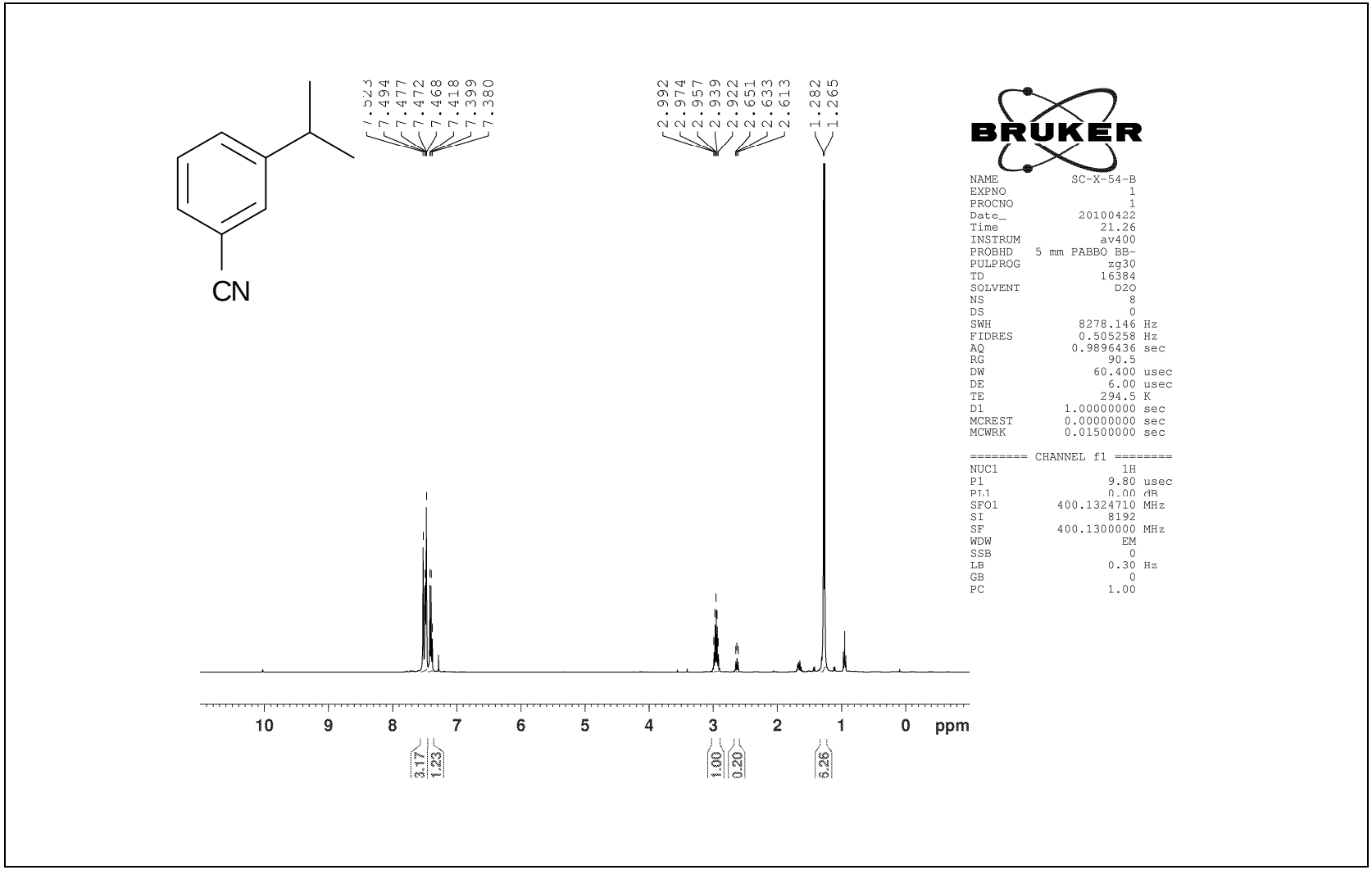
300 MHz ^{1}H NMR spectrum of **Table 1 Entry d**



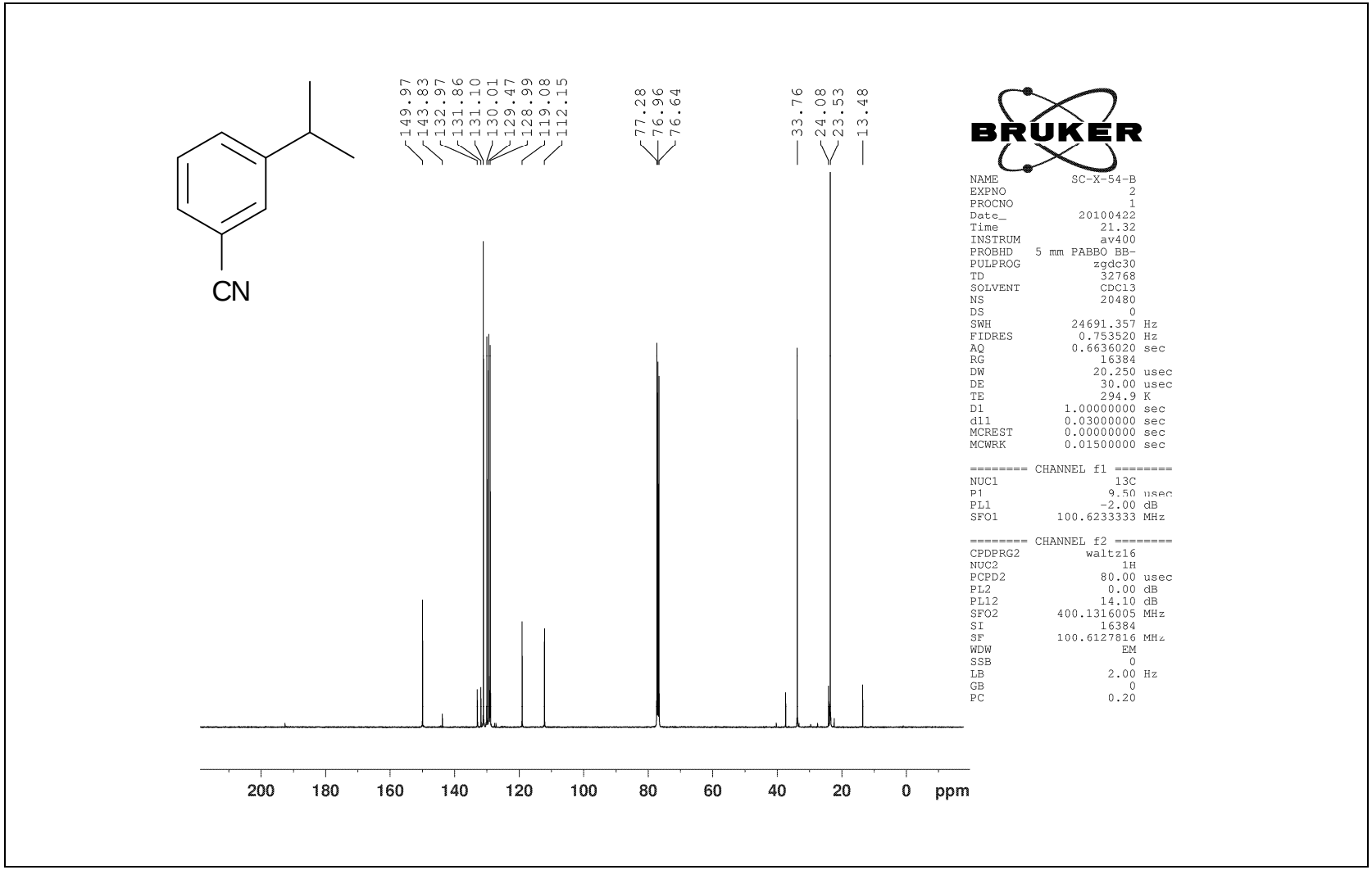
BRUKER

```
NAME        SC-X-33-A-afterFC
EXPNO                       1
PROCNO                      1
Date_                20100324
Time                    18.20
INSTRUM                av300
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                     16384
SOLVENT                 DMSO
NS                         8
DS                         0
SWH                 6172.839 Hz
FIDRES              0.376760 Hz
AQ                  1.3271540 sec
RG                      228.1
DW                     81.000 usec
DE                      6.00 usec
TE                      295.5 K
D1                 0.10000000 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                     13.80 usec
PL1                     0.00 dB
SFO1            300.1318534 MHz
SI                     16384
SF              300.1300000 MHz
WDW                       no
SSB                        0
LB                      0.00 Hz
GB                         0
PC                      0.20
```

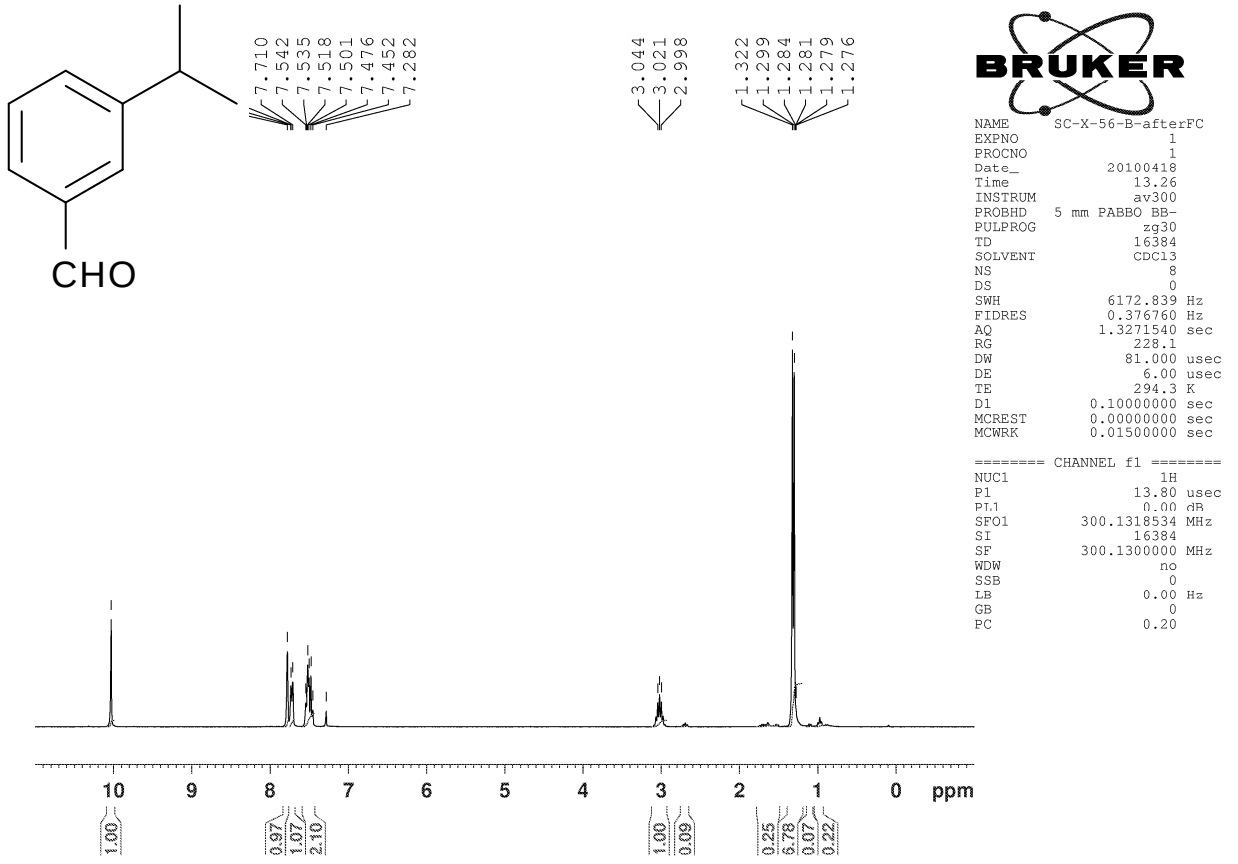
300 MHz ^{1}H NMR spectrum of **Table 1 Entry e**



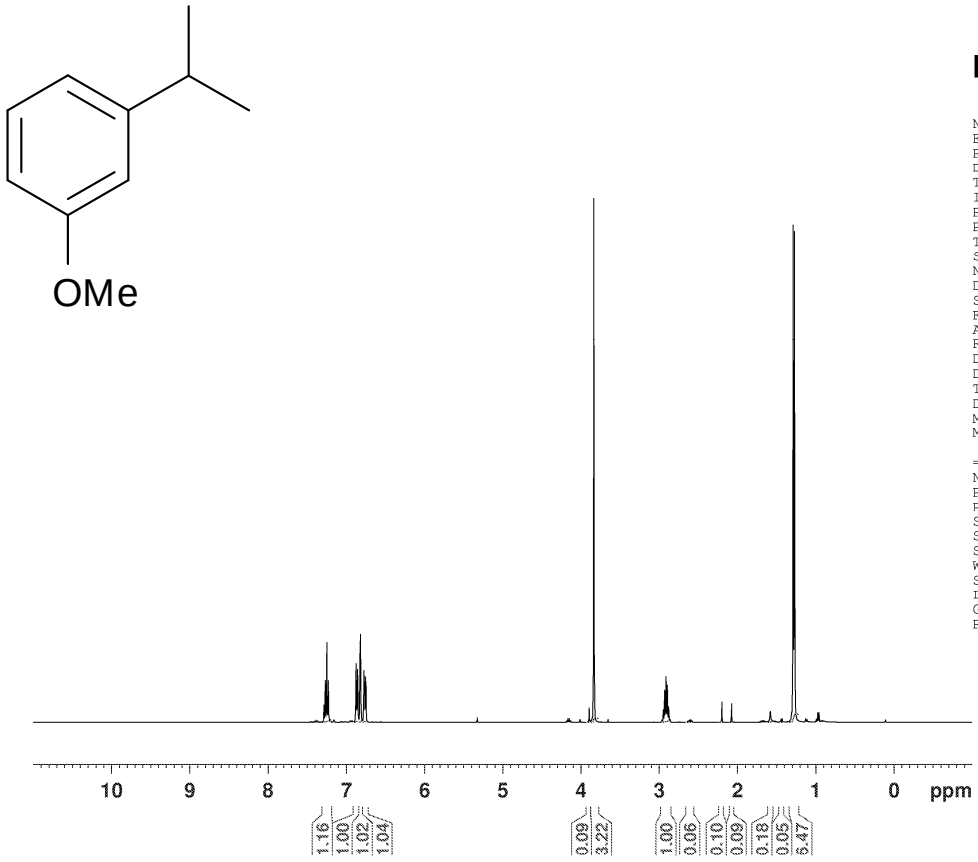
400 MHz ^{1}H NMR spectrum of **Table 1 Entry f**



100 MHz ^{13}C NMR spectrum of **Table 1 Entry f**



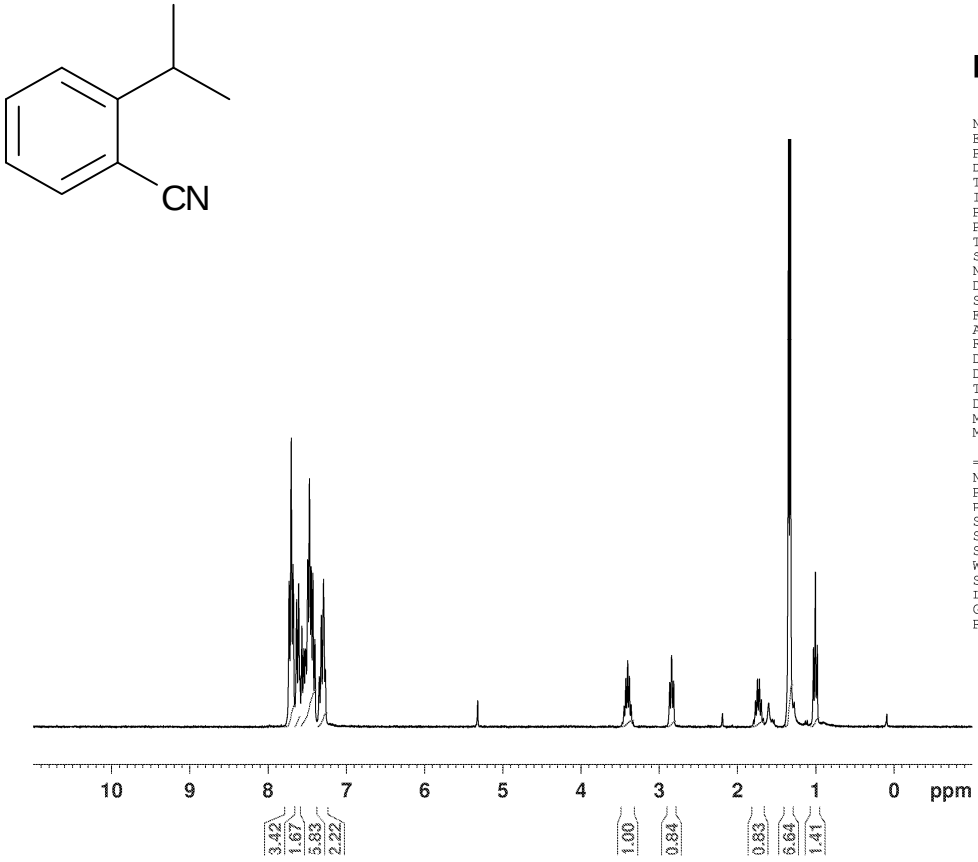
300 MHz ^{1}H NMR spectrum of **Table 1 Entry g**



BRUKER

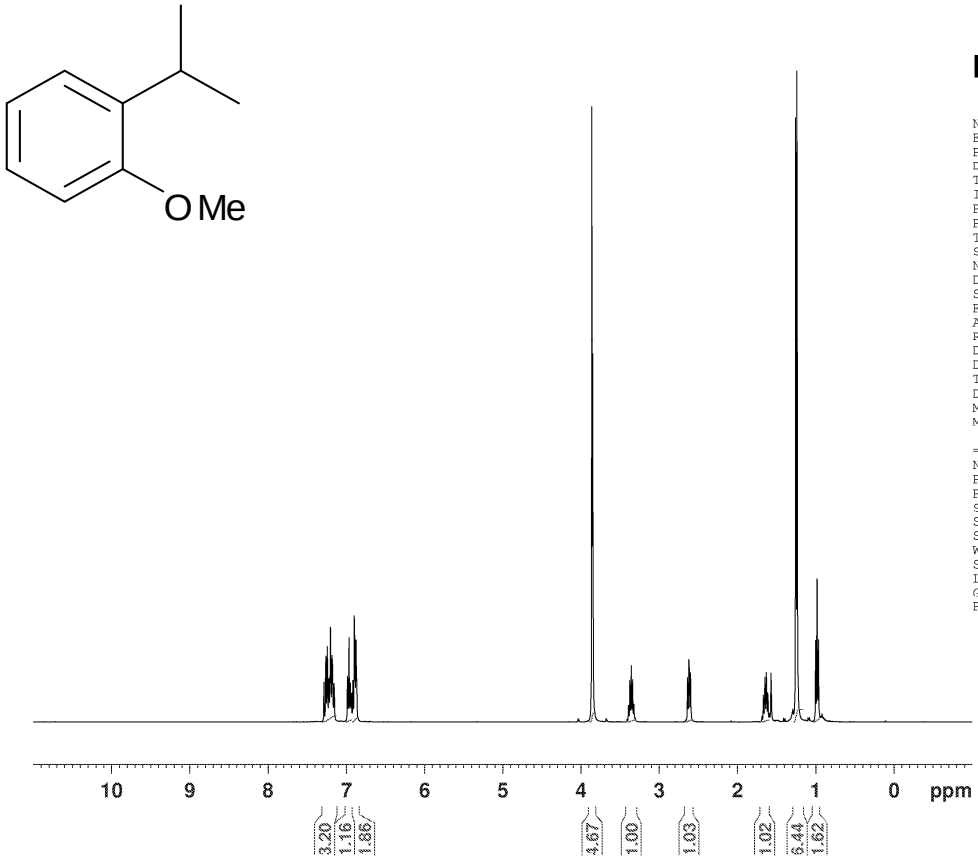
```
NAME      SC-X-55-B-afterFC
EXPNO                    1
PROCNO                   1
Date_             20100415
Time                 14.35
INSTRUM              av400
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   16384
SOLVENT                D2O
NS                       8
DS                       0
SWH               8278.146 Hz
FIDRES            0.505258 Hz
AQ              0.9896436 sec
RG                   203.2
DW                 60.400 usec
DE                  6.00 usec
TE                  298.0 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   9.80 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz
SI                      8192
SF            400.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

400 MHz ^{1}H NMR spectrum of **Table 1 Entry h**




```
NAME      SC-X-38-A-afterFC
EXPNO                    1
PROCNO                   1
Date_             20100330
Time                 16.52
INSTRUM              av300
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   16384
SOLVENT                DMSO
NS                       8
DS                       0
SWH               6172.839 Hz
FIDRES            0.376760 Hz
AQ                1.3271540 sec
RG                     362
DW                  81.000 usec
DE                   6.00 usec
TE                   295.2 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   13.80 usec
PL1                   0.00 dB
SFO1          300.1318534 MHz
SI                   16384
SF            300.1300000 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    0.20
```

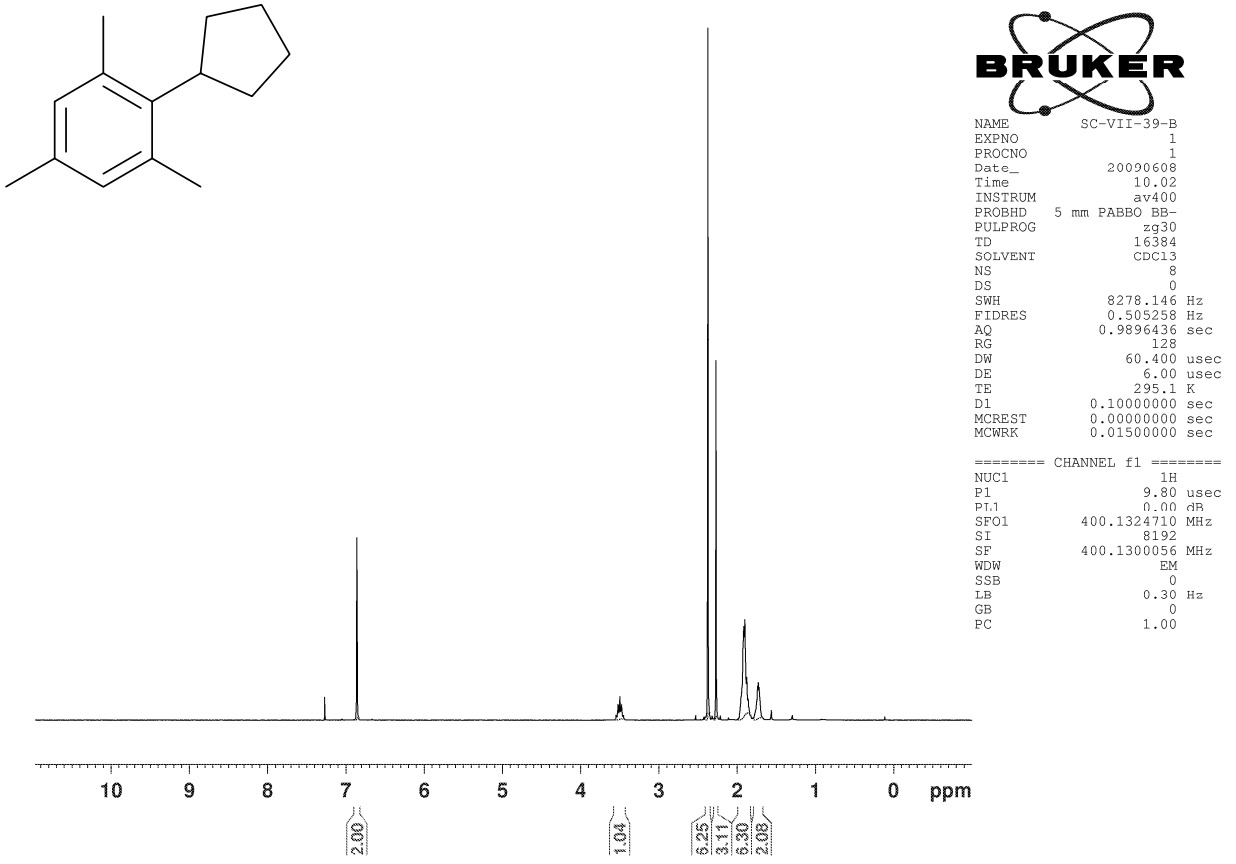
300 MHz ^{1}H NMR spectrum of **Table 1 Entry i**



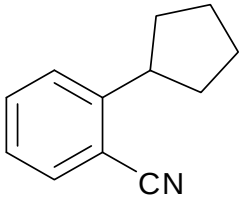
BRUKER

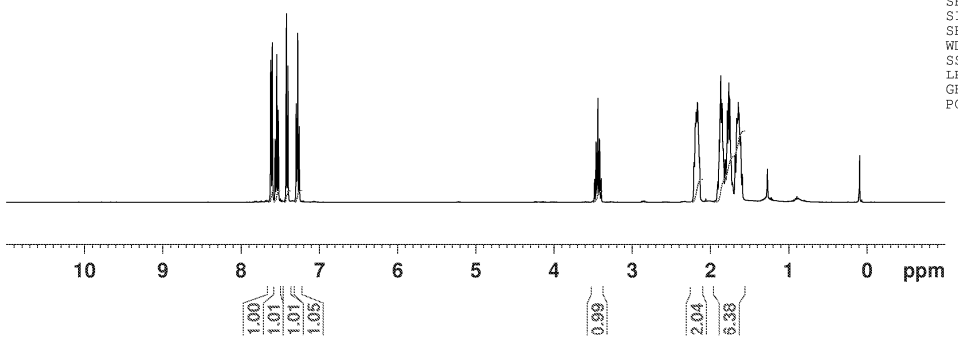
NAME	SC-X-42-B-afterFC-F1
EXPNO	1
PROCNO	1
Date_	20100406
Time	10.06
INSTRUM	av400
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	16384
SOLVENT	D2O
NS	8
DS	0
SWH	8278.146 Hz
FIDRES	0.505258 Hz
AQ	0.9896436 sec
RG	228.1
DW	60.400 usec
DE	6.00 usec
TE	295.9 K
D1	0.10000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec
======== CHANNEL f1 ========	
NUC1	1H
P1	9.80 usec
PL1	0.00 dB
SFO1	400.1324710 MHz
SI	8192
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GR	0
PC	1.00

400 MHz ^{1}H NMR spectrum of **Table 1 Entry j**



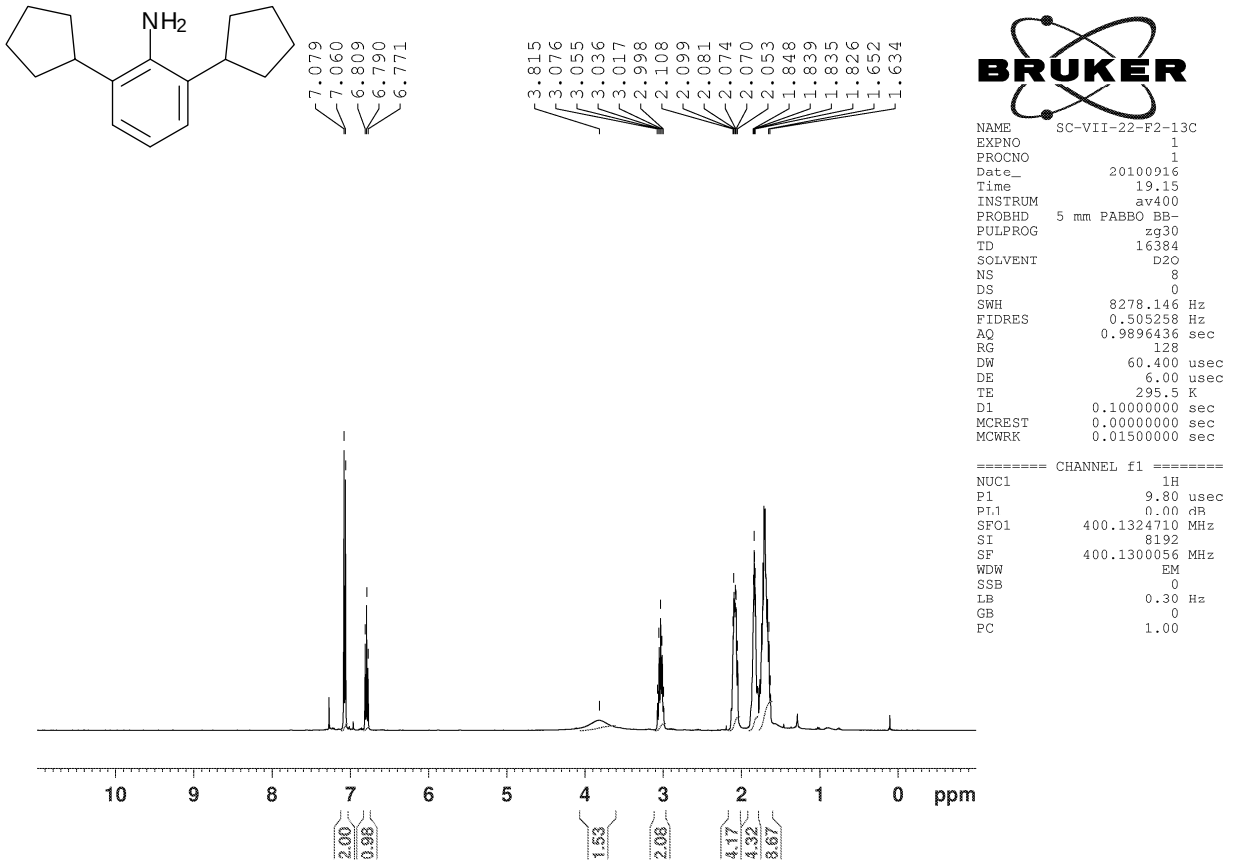
400 MHz ^{1}H NMR spectrum of **Table 2 Entry 1**



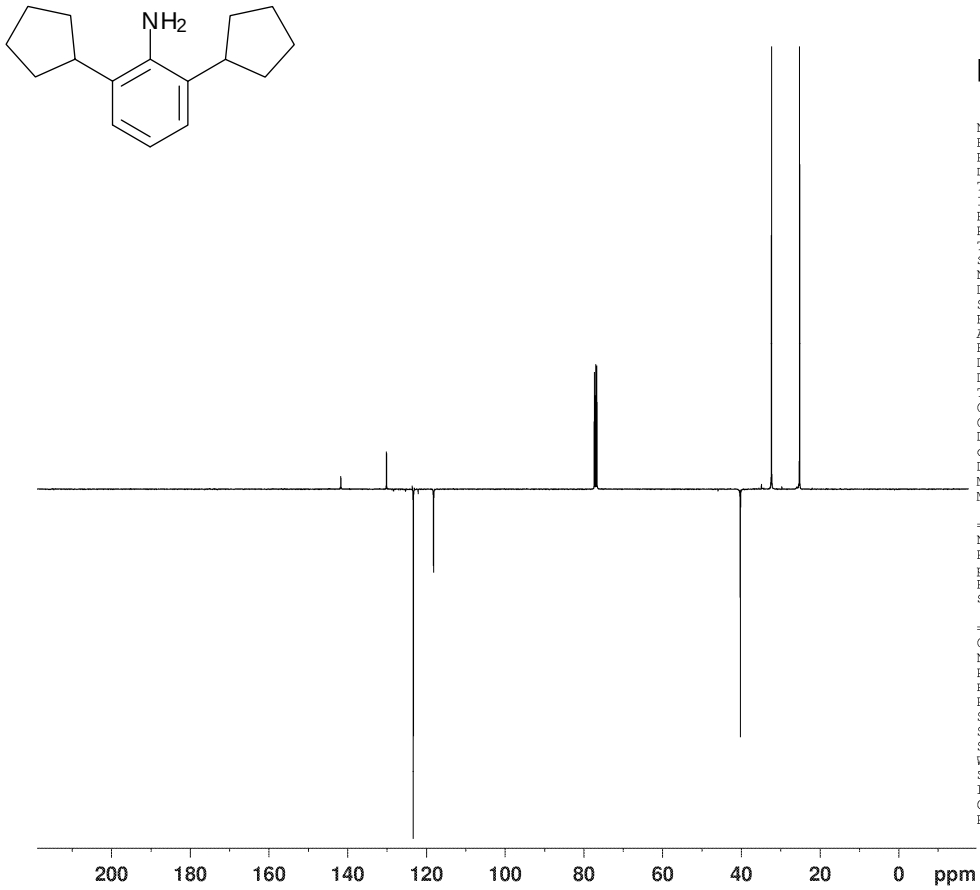



```
NAME          SC-9-23-again
EXPNO                     1
PROCNO                    1
Date_              20091201
Time                  10.21
INSTRUM               av400
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    16384
SOLVENT                 D2O
NS                        8
DS                        0
SWH                8278.146 Hz
FIDRES             0.505258 Hz
AQ                 0.9896436 sec
RG                      90.5
DW                    60.400 usec
DE                     6.00 usec
TE                    294.6 K
D1                 0.10000000 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                      9.80 usec
PL1                     0.00 dB
SFO1            400.1324710 MHz
SI                       8192
SF              400.1300000 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

400 MHz ^{1}H NMR spectrum of **Table 2 Entry 2**

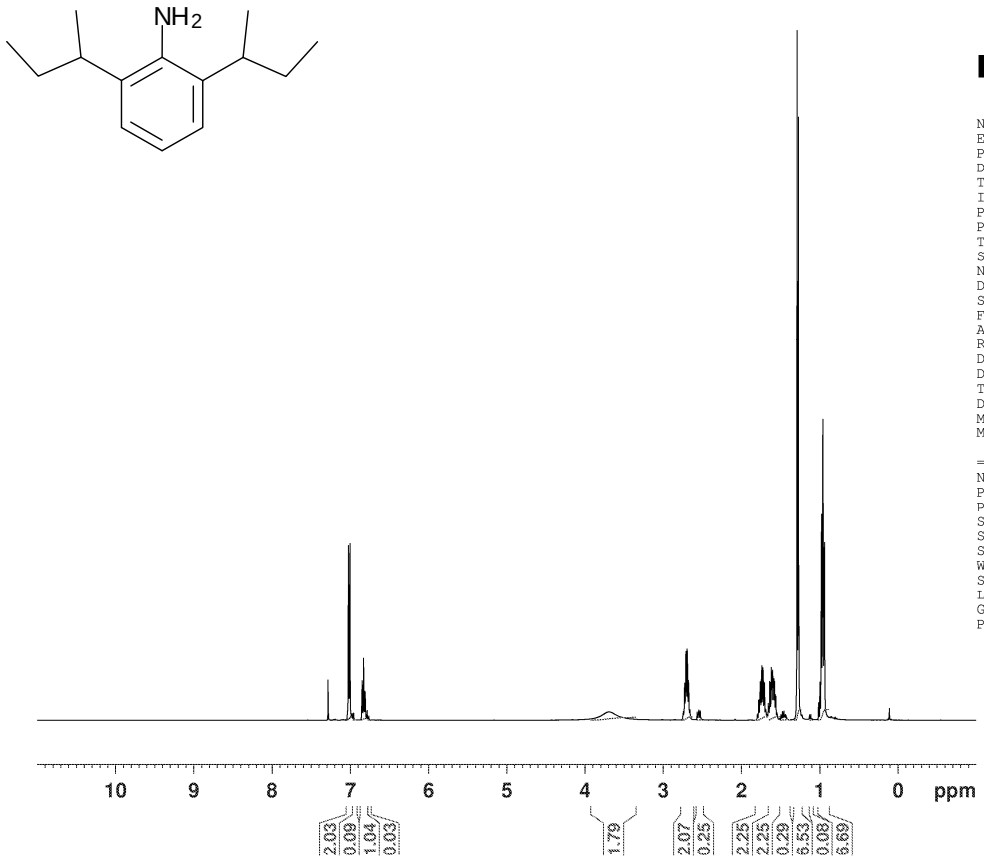


400 MHz ^{1}H NMR spectrum of **Table 2 Entry 3**



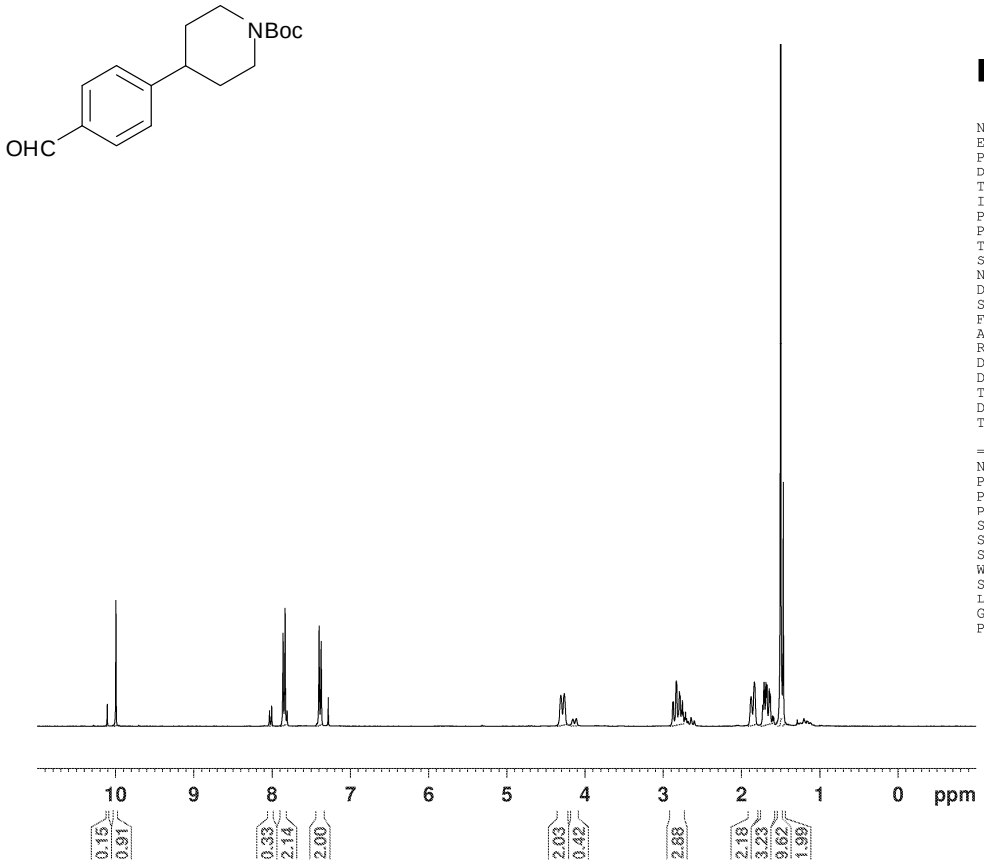

```
NAME       SC-VII-22-F2-13C
EXPNO                    2
PROCNO                   1
Date_             20100916
Time                 19.23
INSTRUM              av400
PROBHD    5 mm PABBO BB-
PULPROG                jmod
TD                    32768
SOLVENT               CDCl3
NS                     7168
DS                        0
SWH              24691.357 Hz
FIDRES            0.753520 Hz
AQ                0.6636020 sec
RG                    16384
DW                  20.250 usec
DE                  30.00 usec
TE                  295.7 K
CNST2           145.0000000
CNST11            1.0000000
D1                5.00000000 sec
d20               0.00689655 sec
DELTA             0.00001210 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                    9.50 usec
p2                   19.00 usec
PL1                  -2.00 dB
SFO1           100.6233333 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 14.10 dB
SFO2           400.1316005 MHz
SI                    16384
SF             100.6127755 MHz
WDW                      EM
SSB                       0
LB                    2.00 Hz
GB                        0
PC                    0.20
```

100 MHz ^{13}C NMR spectrum of **Table 2 Entry 3**



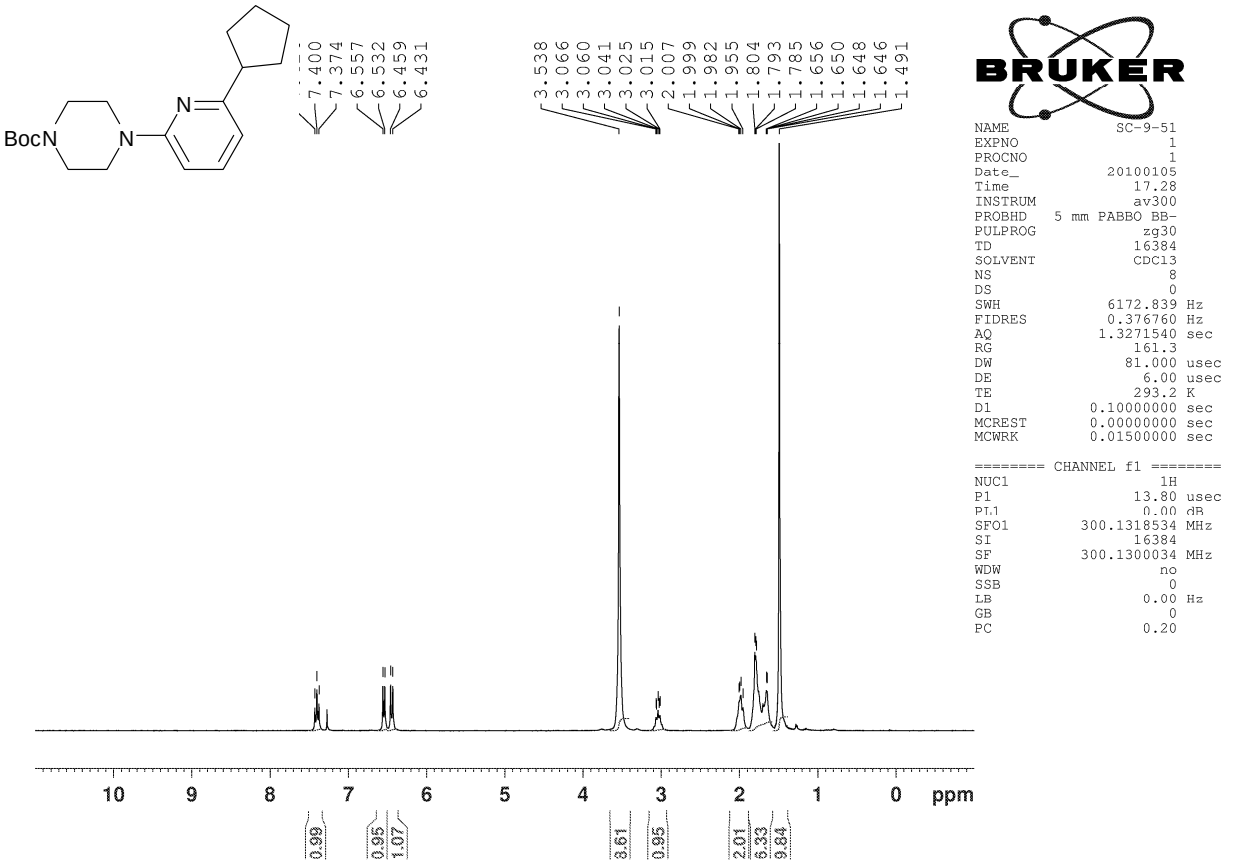

```
NAME          SC-VII-38-F3
EXPNO                    1
PROCNO                   1
Date_             20090605
Time                 9.47
INSTRUM             av400
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   16384
SOLVENT               MeOD
NS                       8
DS                       0
SWH               8278.146 Hz
FIDRES            0.505258 Hz
AQ               0.9896436 sec
RG                    90.5
DW                  60.400 usec
DE                   6.00 usec
TE                  295.0 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   9.80 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz
SI                    8192
SF            400.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

400 MHz ^{1}H NMR spectrum of **Table 2 Entry 4**



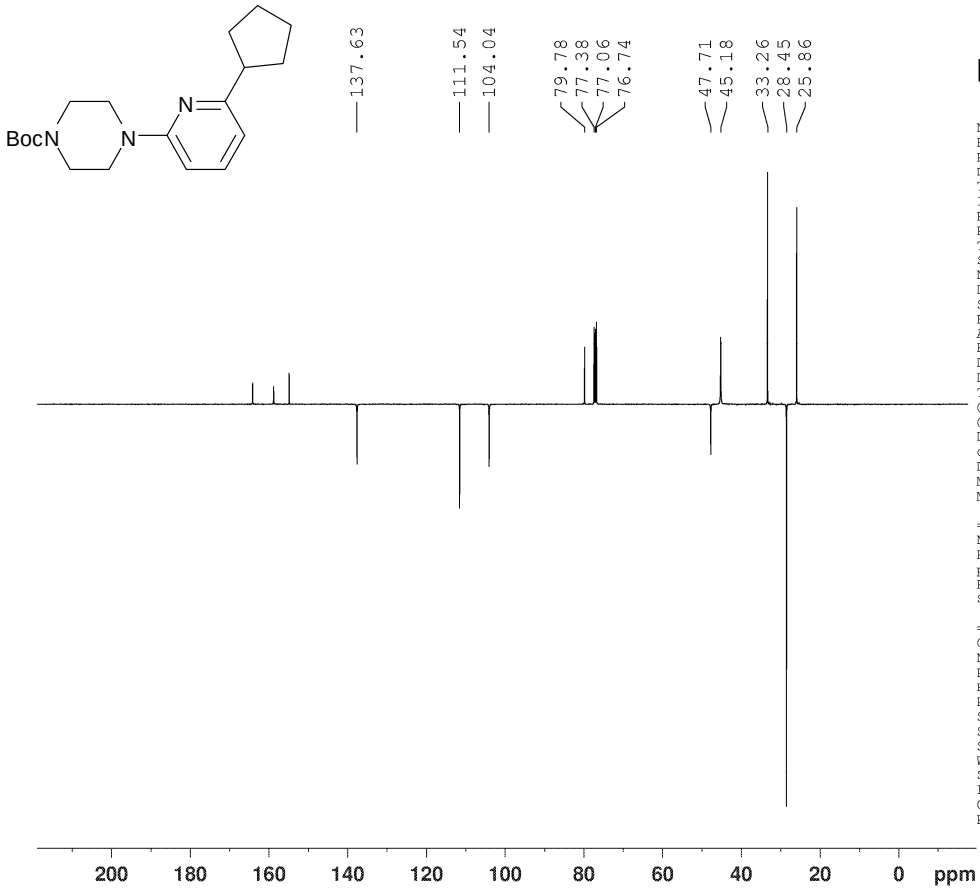

```
NAME              SC-XI-54-A
EXPNO                      1
PROCNO                     1
Date_               20100818
Time                   13.33
INSTRUM                av300
PROBHD   5 mm PABBO BB-
PULPROG                 zg30
TD                     16384
SOLVENT                CDCl3
NS                         8
DS                         0
SWH                 6172.839 Hz
FIDRES              0.376760 Hz
AQ                  1.3271540 sec
RG                       181
DW                    81.000 usec
DE                     6.00 usec
TE                     293.7 K
D1                0.10000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     13.80 usec
PL1                     0.00 dB
PL1W            10.90158749 W
SFO1           300.1318534 MHz
SI                     16384
SF             300.1300000 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      0.20
```

400 MHz ^{1}H NMR spectrum of **Table 2 Entry 5**



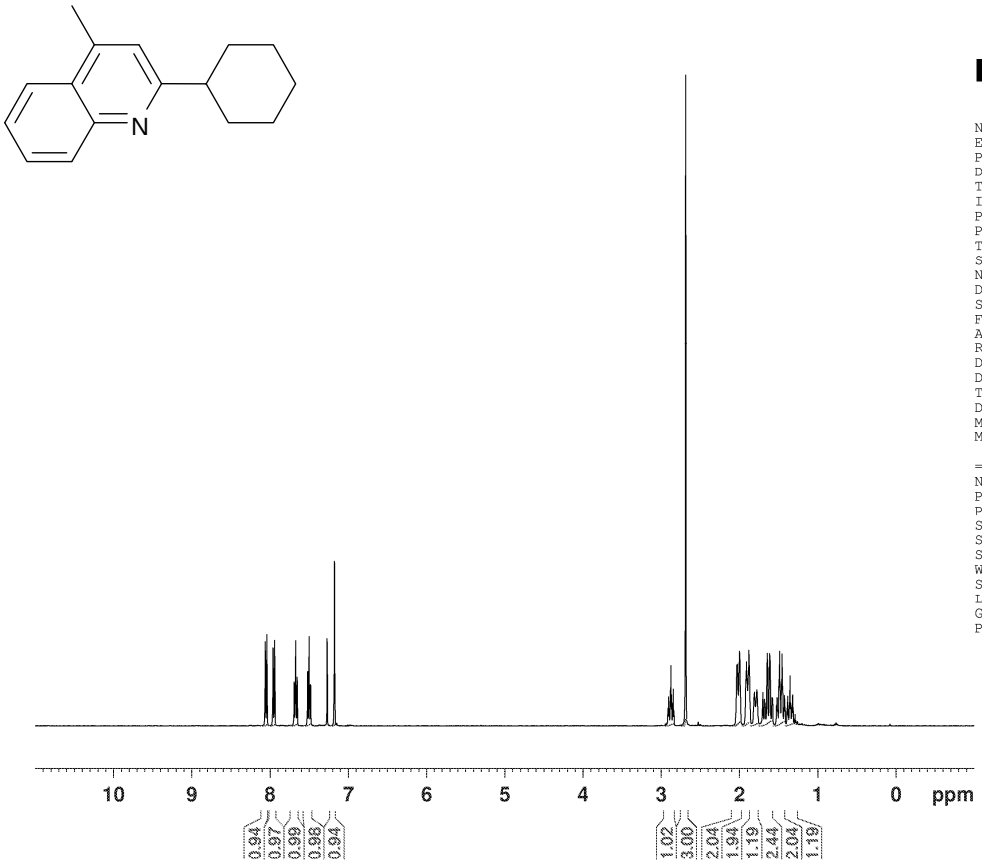

```
NAME                SC-9-51
EXPNO                     1
PROCNO                    1
Date_              20100105
Time                  17.28
INSTRUM               av300
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                        8
DS                        0
SWH                6172.839 Hz
FIDRES             0.376760 Hz
AQ                 1.3271540 sec
RG                    161.3
DW                   81.000 usec
DE                    6.00 usec
TE                    293.2 K
D1                0.10000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     13.80 usec
PL1                    0.00 dB
SFO1            300.1318534 MHz
SI                    16384
SF              300.1300034 MHz
WDW                      no
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     0.20
```

300 MHz ^{1}H NMR spectrum of **Table 2 Entry 6**



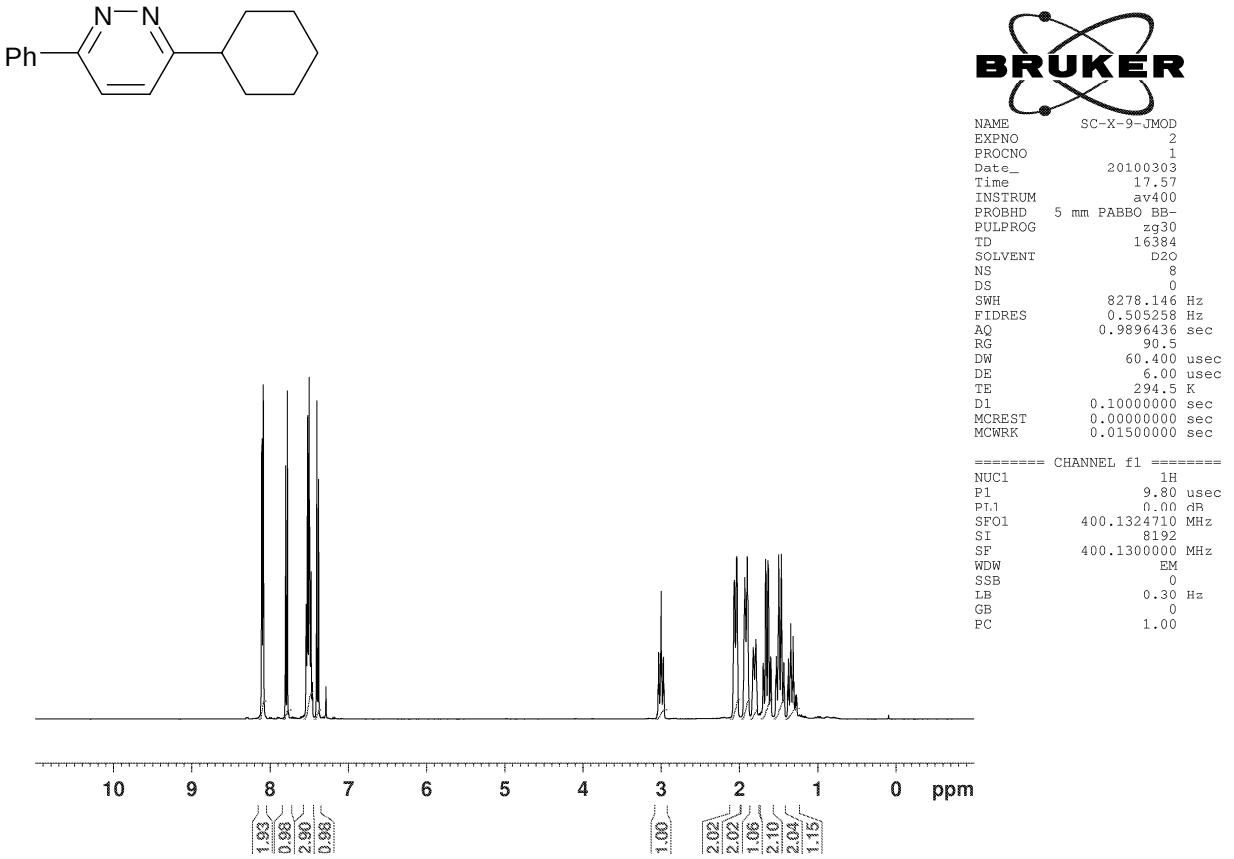

```
NAME          SC-9-49-c13JMOD
EXPNO                       1
PROCNO                      1
Date_              20101103
Time                   18.17
INSTRUM                av400
PROBHD   5 mm PABBO BB-
PULPROG                 jmod
TD                     32768
SOLVENT                CDCl3
NS                      7168
DS                         0
SWH               24691.357 Hz
FIDRES             0.753520 Hz
AQ                 0.6636020 sec
RG                     16384
DW                   20.250 usec
DE                   30.00 usec
TE                    294.4 K
CNST2            145.0000000
CNST11             1.0000000
D1                 5.00000000 sec
d20                0.00689655 sec
DELTA              0.00001210 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                       9.50 usec
p2                      19.00 usec
PL1                     -2.00 dB
SFO1             100.6233333 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                      0.00 dB
PL12                    14.10 dB
SFO2             400.1316005 MHz
SI                     16384
SF               100.6127690 MHz
WDW                       EM
SSB                        0
LB                       2.00 Hz
GB                         0
PC                      0.20
```

100 MHz ^{13}C NMR spectrum of **Table 2 Entry 6**

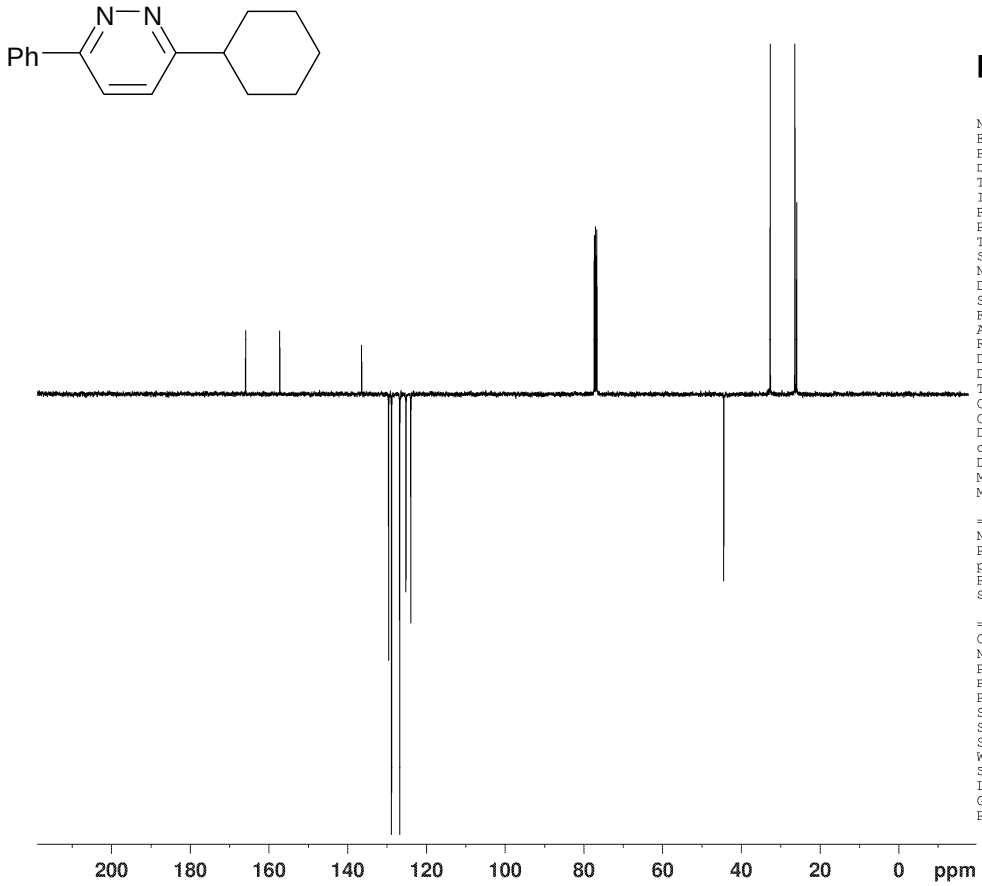



```
NAME        SC-X-10-afterFC
EXPNO                     1
PROCNO                    1
Date_              20100225
Time                  10.12
INSTRUM               av400
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                        8
DS                        0
SWH                8278.146 Hz
FIDRES             0.505258 Hz
AQ                 0.9896436 sec
RG                     406.4
DW                    60.400 usec
DE                     6.00 usec
TE                     293.9 K
D1               0.10000000 sec
MCREST           0.00000000 sec
MCWRK            0.01500000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                      9.80 usec
PL1                     0.00 dB
SFO1           400.1324710 MHz
SI                       8192
SF             400.1300066 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

400 MHz ^{1}H NMR spectrum of **Table 2 Entry 7**

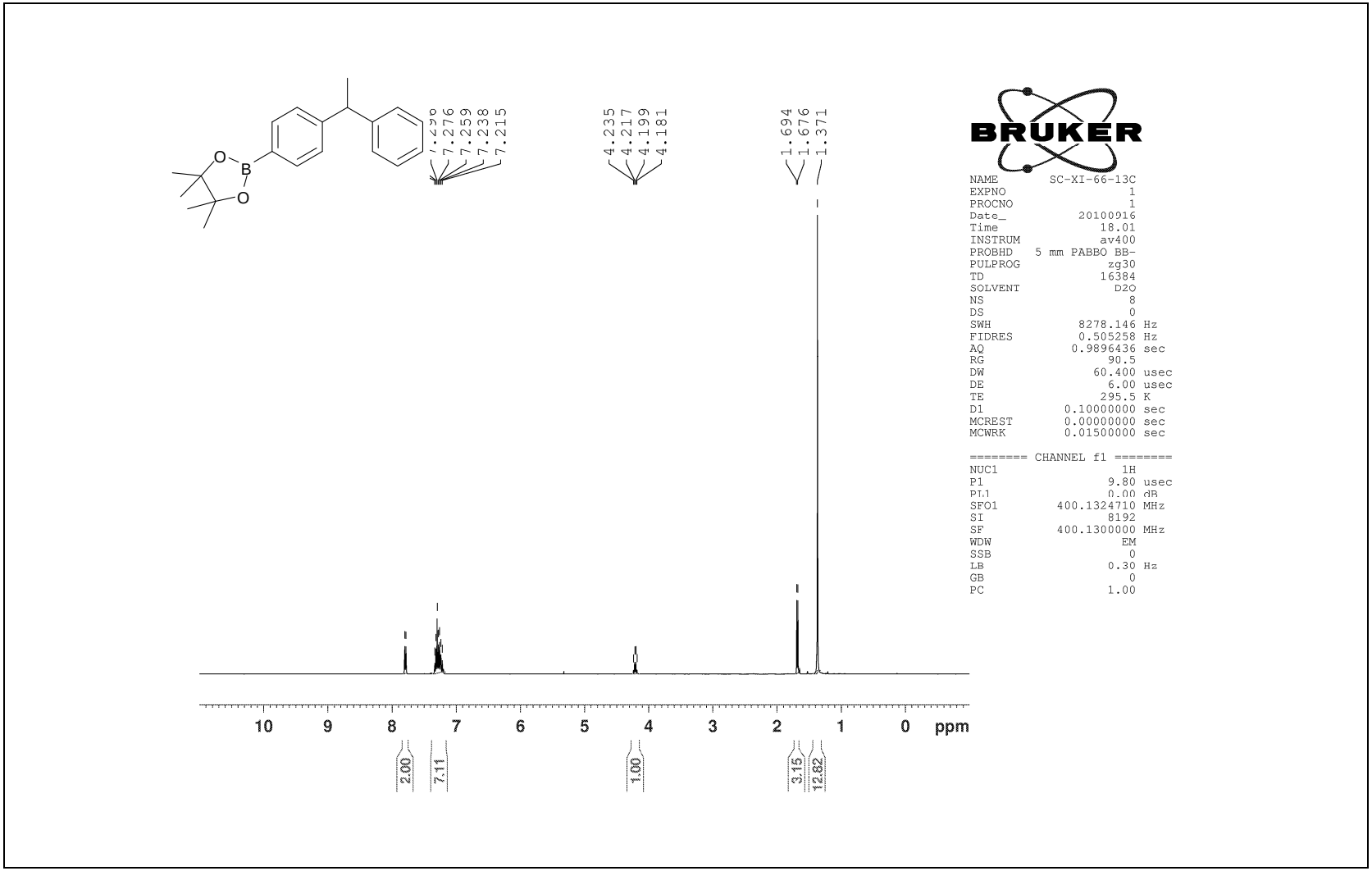


400 MHz ^{1}H NMR spectrum of **Table 2 Entry 8**

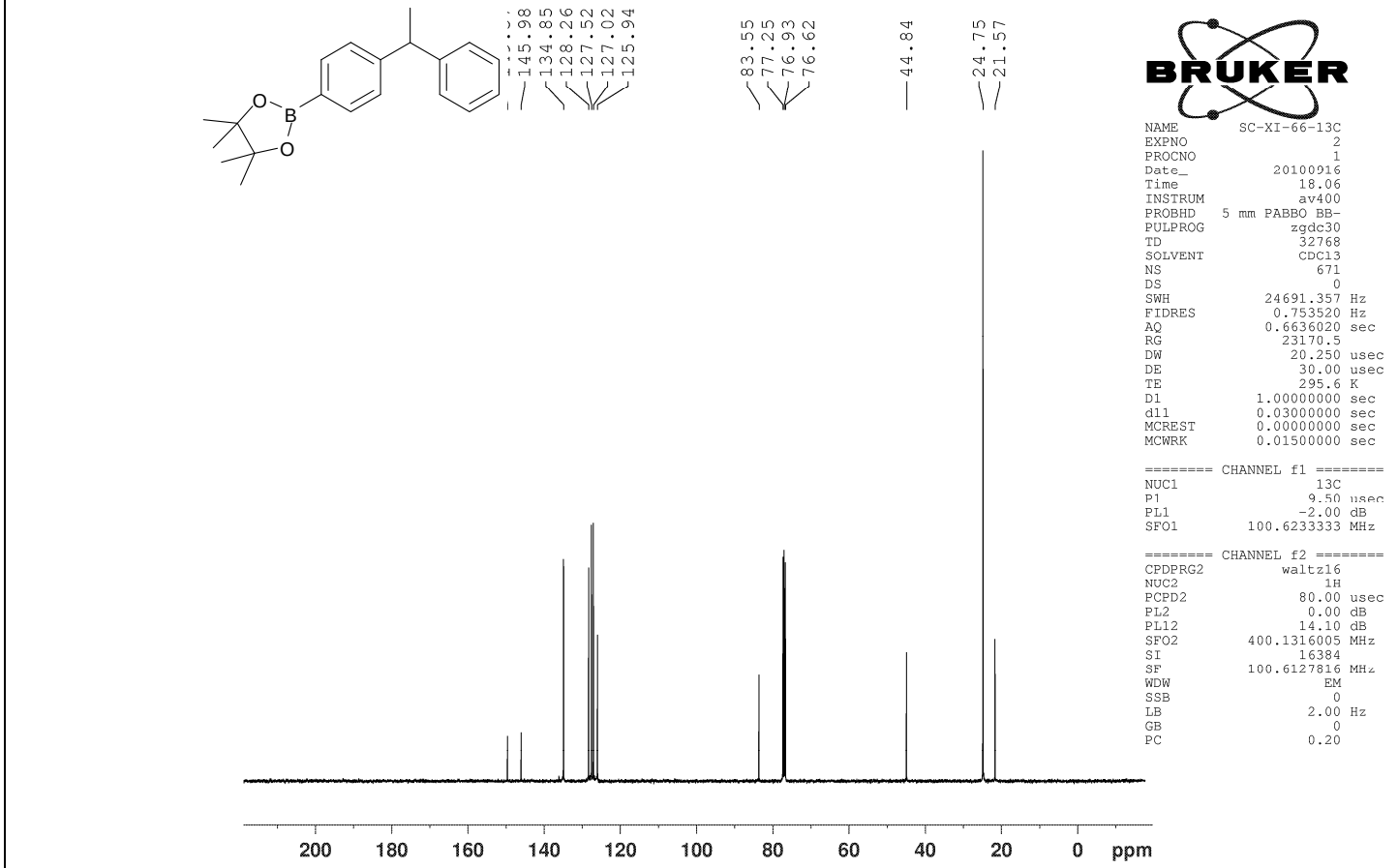



```
NAME              SC-X-9-JMOD
EXPNO                       1
PROCNO                      1
Date_              20100303
Time                   18.04
INSTRUM                av400
PROBHD   5 mm PABBO BB-
PULPROG                 jmod
TD                     32768
SOLVENT                CDCl3
NS                       251
DS                         0
SWH                24691.357 Hz
FIDRES              0.753520 Hz
AQ                  0.6636020 sec
RG                     16384
DW                    20.250 usec
DE                    30.00 usec
TE                    294.8 K
CNST2             145.0000000
CNST11              1.0000000
D1                  5.00000000 sec
d20                 0.00689655 sec
DELTA               0.00001210 sec
MCREST              0.00000000 sec
MCWRK               0.01500000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                       9.50 usec
p2                      19.00 usec
PL1                     -2.00 dB
SFO1              100.6233333 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                      0.00 dB
PL12                    14.10 dB
SFO2              400.1316005 MHz
SI                     16384
SF                100.6127755 MHz
WDW                       EM
SSB                        0
LB                      2.00 Hz
GB                         0
PC                      1.00
```

100 MHz ^{13}C NMR spectrum of **Table 2 Entry 8**



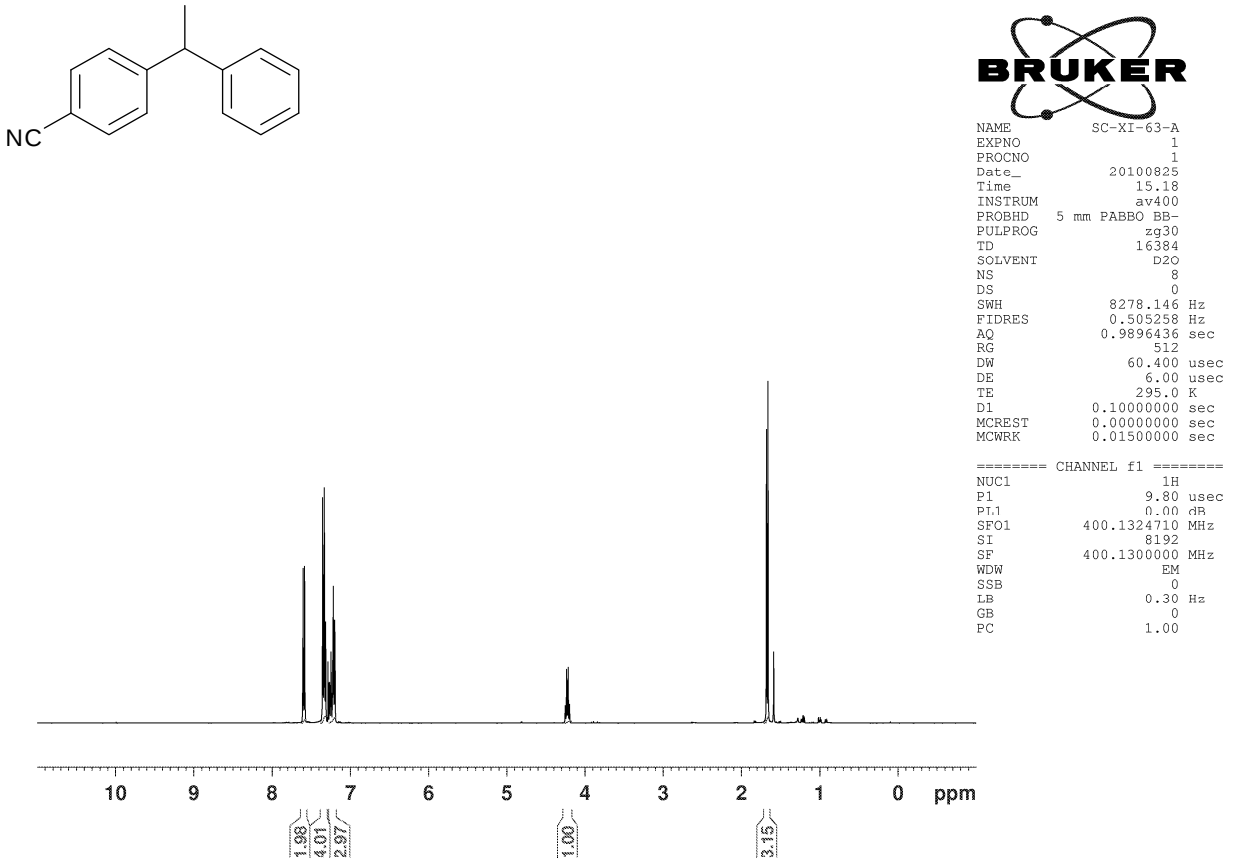
400 MHz ^{1}H NMR spectrum of **Table 2 Entry 9**



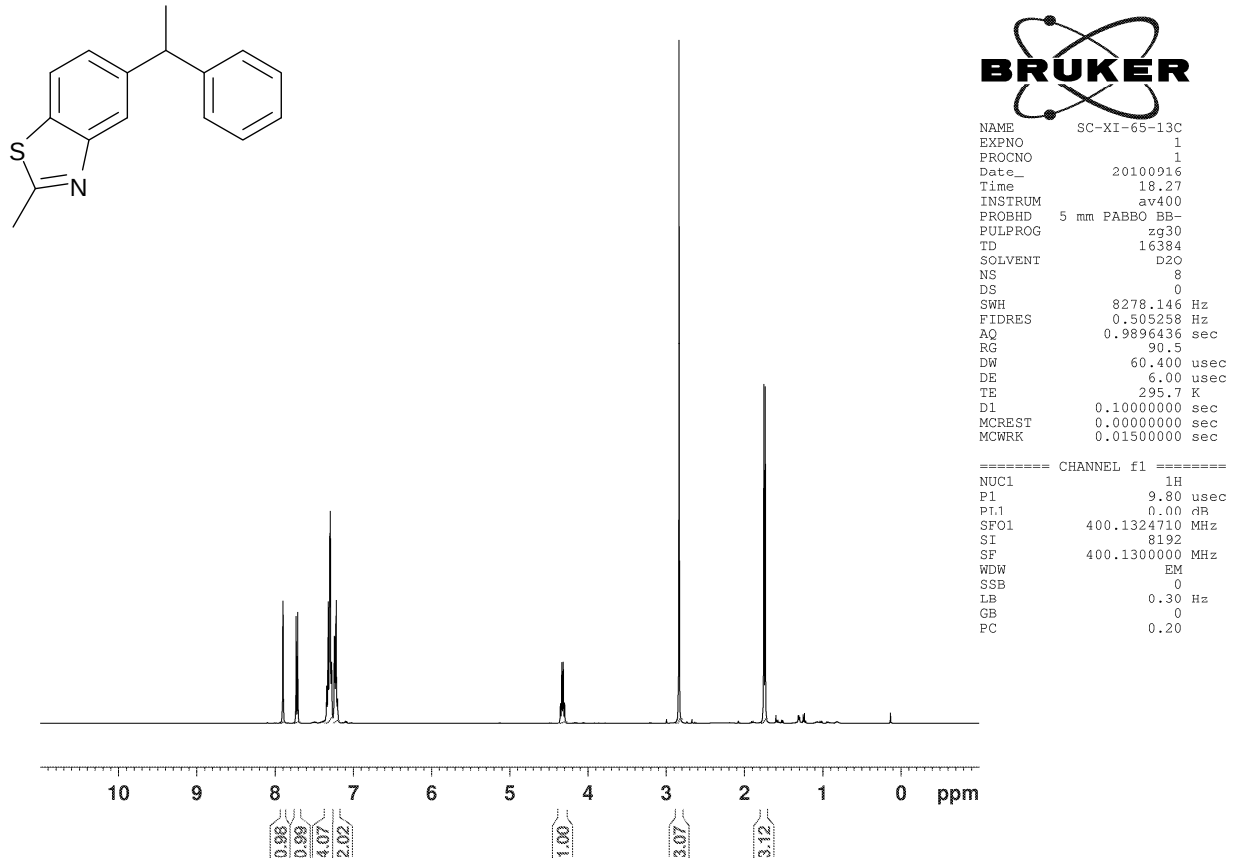
BRUKER

NAME	SC-XI-66-13C
EXPNO	2
PROCNO	1
Date_	20100916
Time	18.06
INSTRUM	av400
PROBHD	5 mm PABBO BB-
PULPROG	zgdc30
TD	32768
SOLVENT	CDCl3
NS	671
DS	0
SWH	24691.357 Hz
FIDRES	0.753520 Hz
AQ	0.6636020 sec
RG	23170.5
DW	20.250 usec
DE	30.00 usec
TE	295.6 K
D1	1.00000000 sec
d11	0.03000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
SFO1	100.6233333 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	14.10 dB
SFO2	400.1316005 MHz
SI	16384
SF	100.6127816 MHz
WDW	EM
SSB	0
LB	2.00 Hz
GB	0
PC	0.20

100 MHz ^{13}C NMR spectrum of **Table 2 Entry 9**

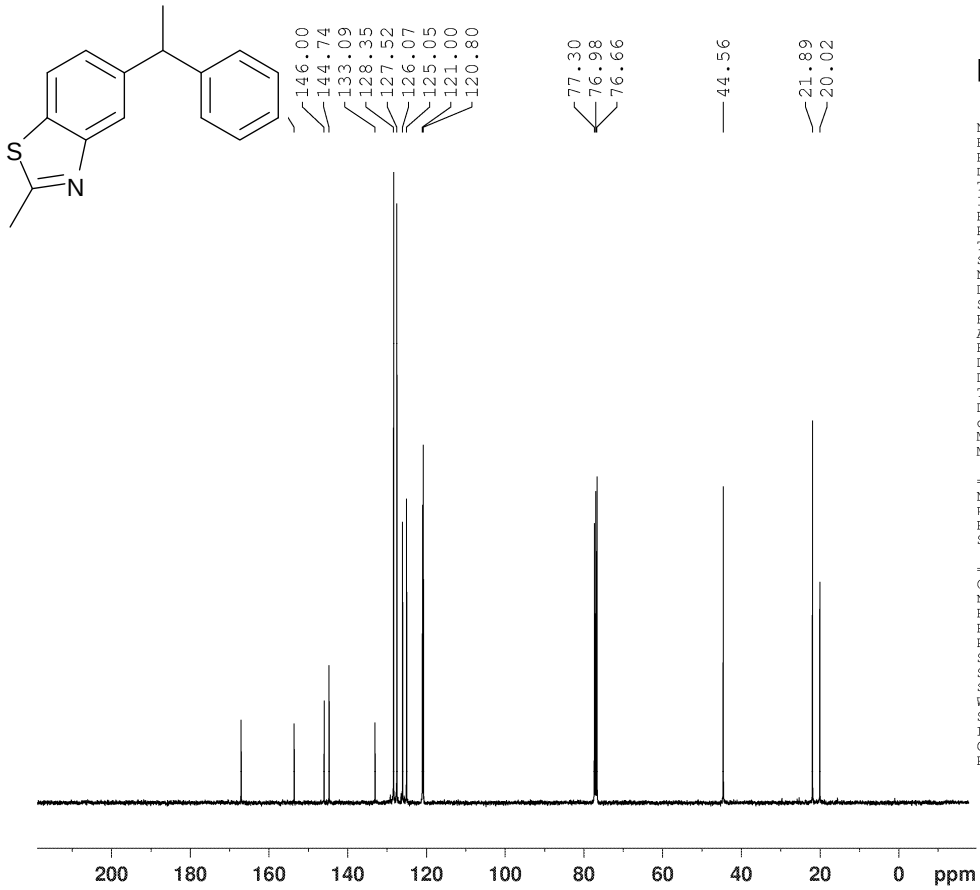


400 MHz ^{1}H NMR spectrum of **Table 2 Entry 10**



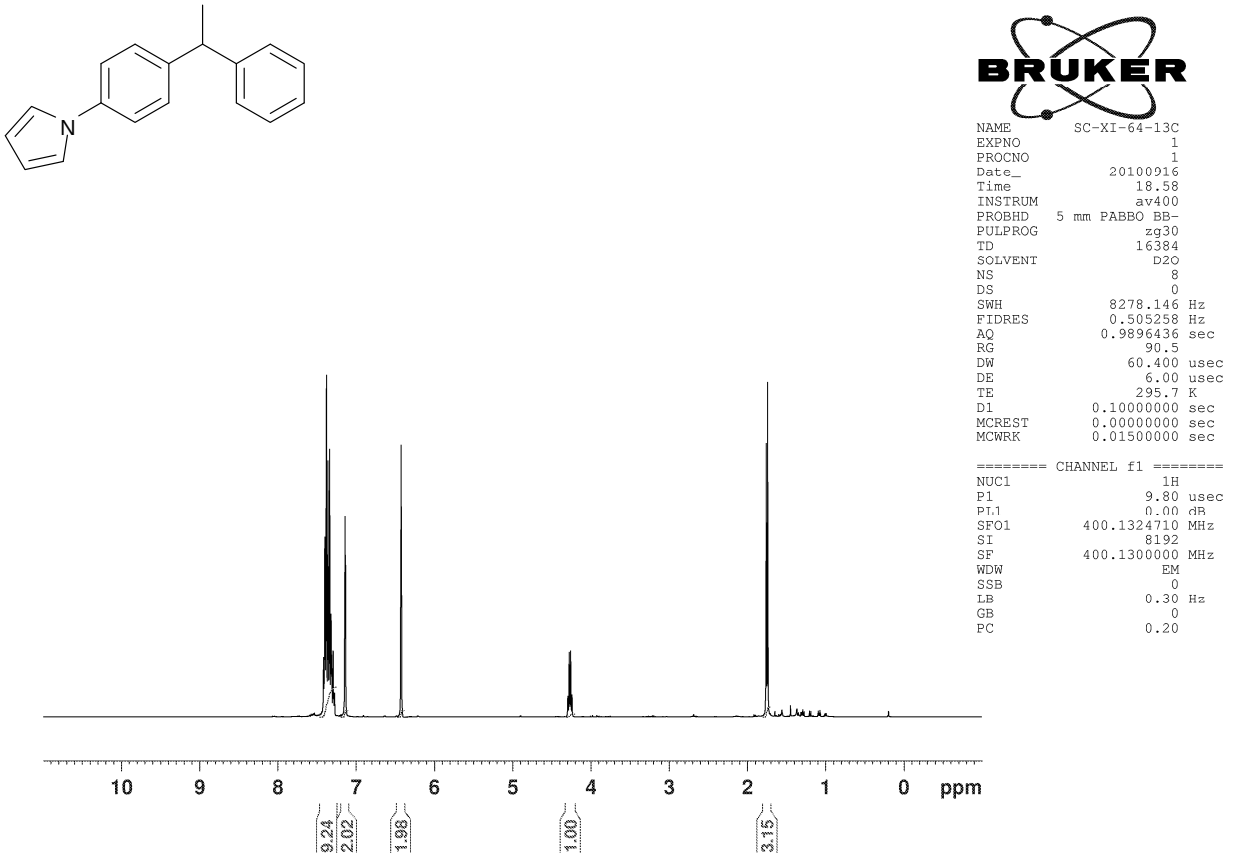

```
NAME          SC-XI-65-13C
EXPNO                    1
PROCNO                   1
Date_             20100916
Time                 18.27
INSTRUM              av400
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   16384
SOLVENT                D2O
NS                       8
DS                       0
SWH               8278.146 Hz
FIDRES            0.505258 Hz
AQ              0.9896436 sec
RG                    90.5
DW                  60.400 usec
DE                   6.00 usec
TE                   295.7 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    9.80 usec
PL1                   0.00 dB
SFO1          400.1324710 MHz
SI                     8192
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                    0.20
```

400 MHz ^{1}H NMR spectrum of **Table 2 Entry 11**

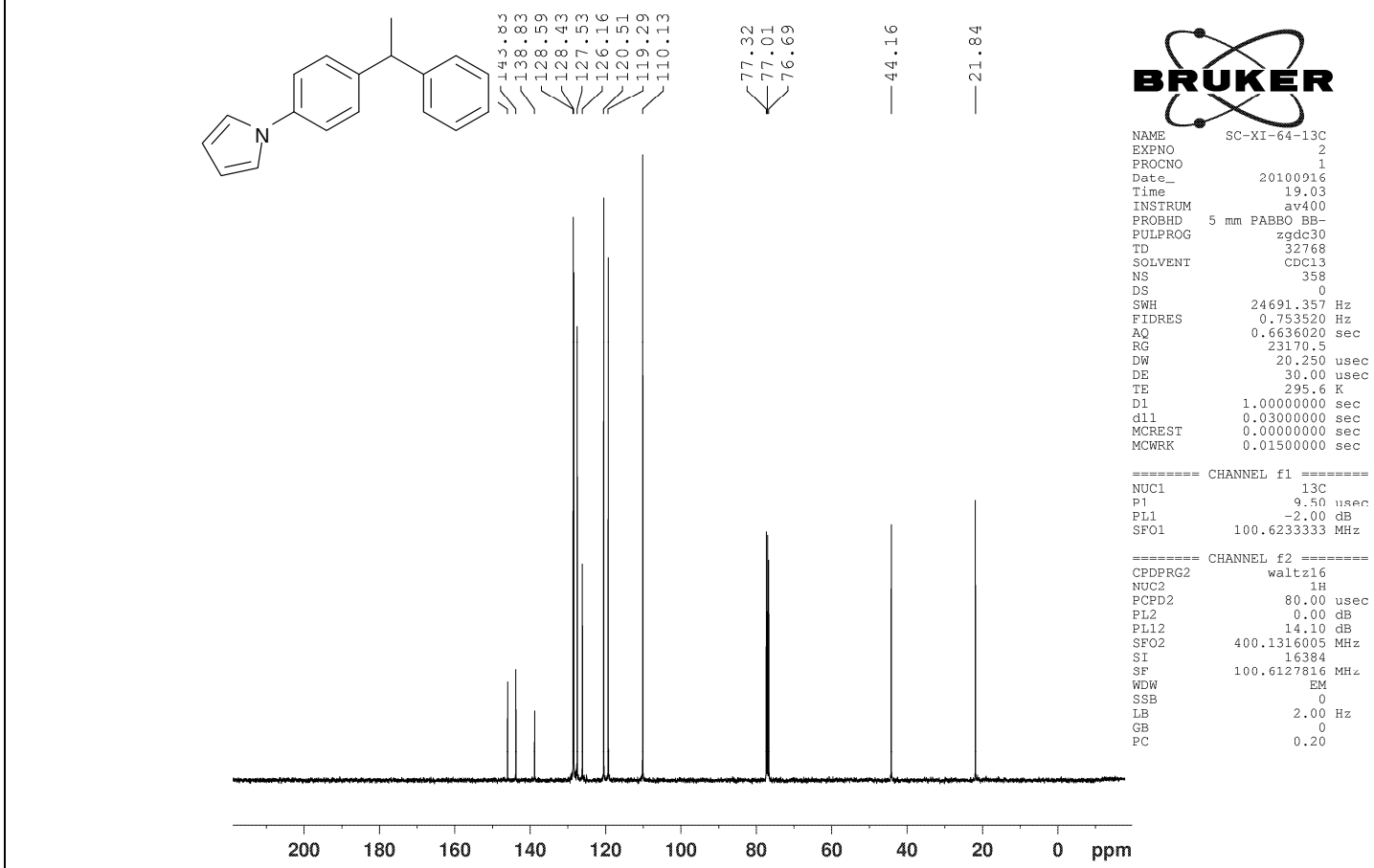



```
NAME            SC-XI-65-13C
EXPNO                      2
PROCNO                     1
Date_               20100916
Time                   18.32
INSTRUM                av400
PROBHD   5 mm PABBO BB-
PULPROG                zgdc30
TD                      32768
SOLVENT                 CDCl3
NS                        868
DS                          0
SWH                24691.357 Hz
FIDRES              0.753520 Hz
AQ                  0.6636020 sec
RG                      16384
DW                     20.250 usec
DE                     30.00 usec
TE                     295.9 K
D1                 1.00000000 sec
d11                0.03000000 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                       9.50 usec
PL1                     -2.00 dB
SFO1             100.6233333 MHz

======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                      1H
PCPD2                  80.00 usec
PL2                     0.00 dB
PL12                   14.10 dB
SFO2             400.1316005 MHz
SI                      16384
SF               100.6127816 MHz
WDW                        EM
SSB                         0
LB                      2.00 Hz
GB                          0
PC                      0.20
```

100 MHz ^{13}C NMR spectrum of **Table 2 Entry 11**



400 MHz ^{1}H NMR spectrum of **Table 2 Entry 12**



100 MHz ^{13}C NMR spectrum of **Table 2 Entry 12**